# THE SYNTHESIS OF NOVEL AND STERICALLY DEMANDING TETRA-*ORTHO*-SUBSTITUTED ARYL NAPHTHALENES

by

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A DISSERTATION

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# DISSERTATION ABSTRACT

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Title: The Synthesis of Novel and Sterically Demanding Tetra-*ortho*-substituted Aryl Naphthalenes

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Tetra-*ortho*-substituted aryl naphthalenes (TOANs) are a motif of great importance, being present in biologically active natural products, chiral ligands, and building blocks relevant to materials science. The synthesis of sterically demanding and enantioenriched TOANs continues to be a challenge for current synthetic methods.

Herein, we describe the highly effective synthesis of a variety of sterically demanding and enantioenriched TOANs through a rearrangement-based method. Our method utilizes a cyclopropyl carbinol moiety as the key rearrangement precursor. We have demonstrated that carbon-carbon coupling through a simple nucleophilic attack on a cyclopropyl indanone allows for very large aryl substrates to be added and rearranged. We discuss in detail the following: 1) the initial substrate-scope and proof-of-concept studies, 2) our progress in building the most sterically demanding TOANs to date, and 3) the asymmetric synthesis of TOANs through chiral transfer.

This dissertation includes previously published and unpublished co-authored material.

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**Glass, A. C.**; Morris, B. B.; Zakharov, L. N.; Liu, S.-Y. Synthesis of Substituted Naphthalenes via a Catalytic Ring-Expansion Rearrangement. *Org. Lett.* **2008**, *10*, 4855-4857.

Arkoosh, M. R.; Clemons, E.; Kagley, A. N.; Stafford, C.; **Glass, A. C.**; Jacobson, K.; Reno, P.; Myers, M. S.; Casillas, E.; Loge, F.; Johnson, L. L.; Collier, T. K. Survey of Pathogens in Juvenile Salmon *Oncorhynchus* Spp. Migrating through Pacific Northwest Estuaries. *J. Aquat. Anim. Health*. **2004**, *16*, 186-196.

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To my wife Natalie, you never stop caring, and to my parents and brother for teaching me responsibility and patience

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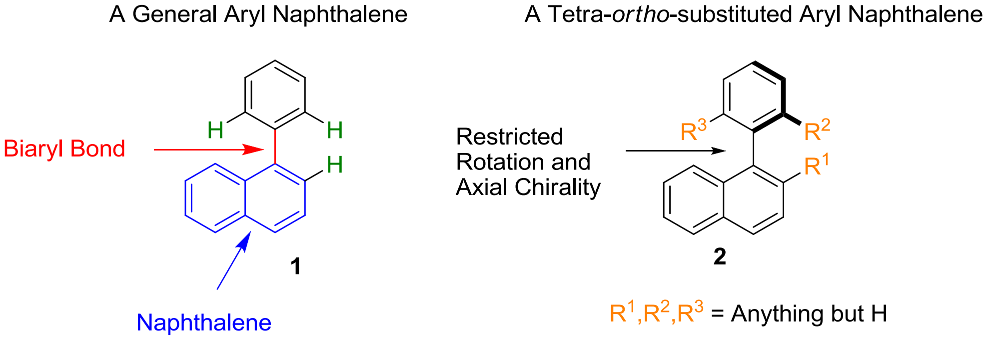
# CHAPTER I

# INTRODUCTION: TETRA-*ORTHO*-SUBSTITUTED ARYL NAPHTHALENES (TOANS)

## General Introduction

Tetra-ortho-substituted aryl naphthalenes (TOANs) are biaryl compounds of great importance, being present in a variety of chemical applications.[1] Many biologically active natural products[2] contain the tetra-*ortho*-substituted aryl naphthalene moiety, having shown potential as: anticancer,[3] antifungal,[4] antibacterial,[5] and birth control agents,[6] among others.[7] Continued identification of novel natural products containing this structure are being discovered.[8] These compounds have also played a predominant role in the development and continued success of asymmetric transformations due to their unique axial chirality (i.e. BINAP and BINOL).[9] In most cases these aryl naphthalenes act as transition metal ligands, where they can confer enantioselectivity during the catalytic cycle.[10] This motif also has shown to be effective in materials applications, e.g., there have been reports describing their use in optoelectronics,[11] molecular switches,[12] and ligands in metal organic frameworks (MOF).[13]

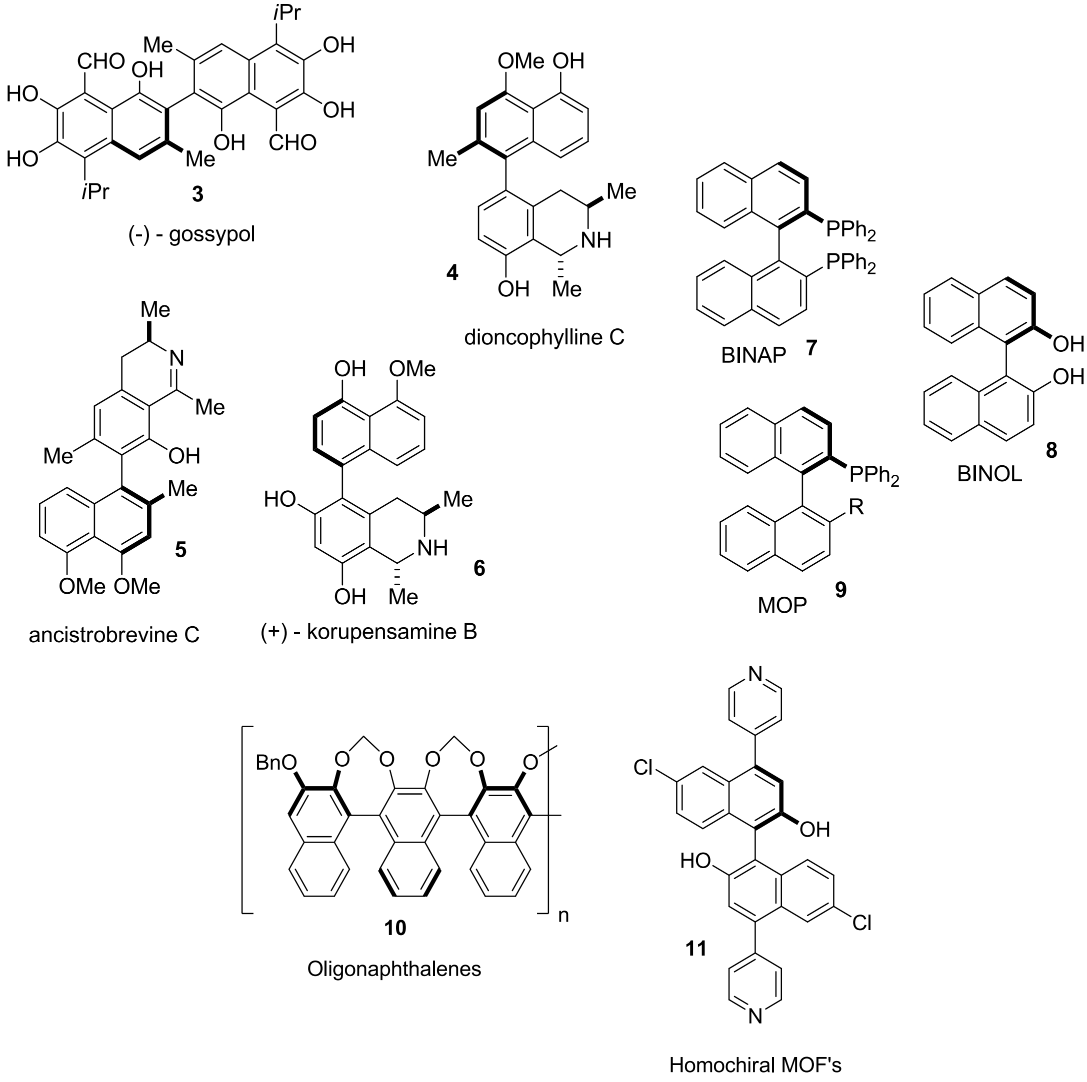
Because of their widespread use in the chemical field, many modern methods for the synthesis of tetra-*ortho*-substituted aryl naphthalenes have been reported in the last decade.[14] Most common are the metal-mediated cross-coupling reactions (direct arylation,[15] catalytic cross-coupling,[16] and oxidative coupling).[17] A major shortcoming of the metal-mediated cross-coupling reactions is the difficulty in establishing large groups in the $R^1$, $R^2$, and $R^3$ positions (Scheme 1).[18] Because of this, alternative



**Scheme 1.** A general example of an aryl naphthalene **1** and a tetra-*ortho*-substituted aryl naphthalene **2**.

approaches have been pursued; these methods include: rearrangement-based synthesis,[19] [2+2+2] cycloannulations,[20] and Diels-Alder reactions.[21] A general tetra-*ortho*-substituted aryl naphthalene is outlined in Scheme 1. Because of the restricted rotation inherent in a TOAN, these compounds are chiral when R1 ≠ R2, known as axial chirality (Scheme 1). Herein, we will describe a short history of TOAN synthesis followed by a review of synthetic methods from the last decade, focusing on the ability of each method to provide a regioselective and enantioselective synthesis of tetra-*ortho*-substituted aryl naphthalenes. Methods focusing solely on biaryls without an example of tetra-*ortho*-substituted aryl naphthalenes will not be discussed.

*TOAN Chemical Applications:* There are a multitude of biologically active natural products that contain the TOAN motif which have many beneficial pharmacological properties. Selected examples are shown in Scheme 2 (Top left corner). Gossypol[22] **3** has shown antimalarial, proapoptotic, and antioxidant properties, while ancistrobrevine **5** and korupensamine[23] **6** have shown anti-HIV potential. Dioncophylline[24] **4** has demonstrated to be an effective insecticide.



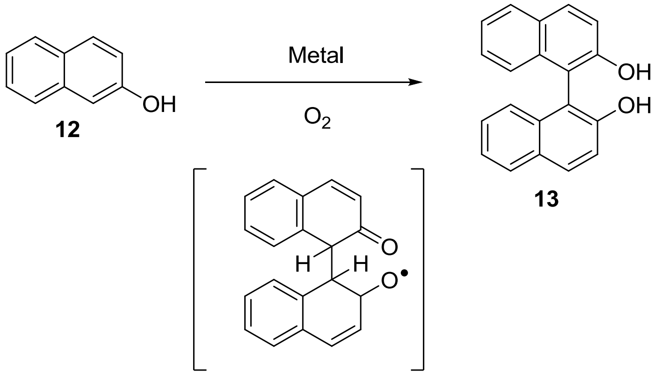
**Scheme 2.** Selected examples of TOANs.

Chiral ligands are another important area where TOANs have been shown to be quite useful (Scheme 2, top right corner). Two of the most well known chiral ligands are BINAP **7** and BINOL **8**. BINAP was a major component of Noyori's Nobel Prize winning asymmetric hydrogenation, and both have demonstrated their prowess in a variety of asymmetric transformations.[25] In a review by Lemaire it was even stated that

“BINAP appears to be both the most used and the most useful ligand for asymmetric catalysis.”[25d] In addition, monodentate phosphine (MOP) **9** has shown to be quite effective as a ligand in metal-catalyzed asymmetric transformations; where bisphosphines have been shown to be ineffective.[26]

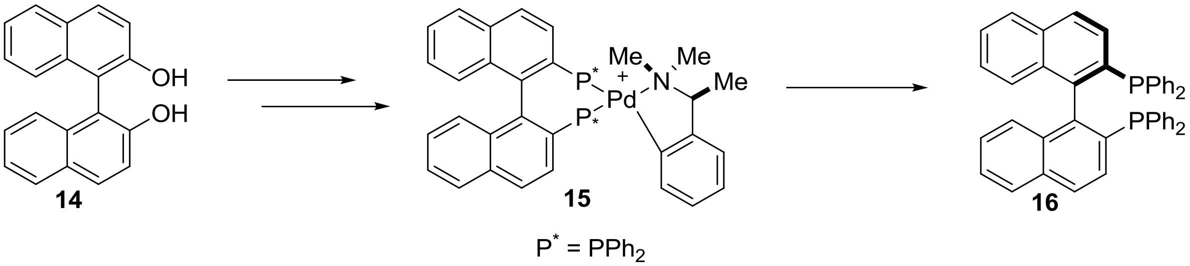
There are also examples of TOANs in materials science, especially in the area of optoelectronics. TOANs have also shown potential as ligands in homochiral metal organic frameworks. Oligonaphthalene **10** (Scheme 2, bottom) demonstrate unique asymmetric optical properties that can be easily tuned[27] and HMOFs **11** have shown usage as chiral chemoselectors.[28]

A History of TOAN Synthesis: Before the 21st century the synthesis of tetra-*ortho*-substituted aryl naphthalenes was rare and only a few examples were reported.[29] Some of the first examples of TOANs are the bisnaphthalene ligands that were used in asymmetric hydrogenations in the 1980’s. In 1873 BINOL was prepared in its racemic form by von Richter.[30] Since this pioneering work, the oxidative coupling process to provide BINOL has been extensively studied from 2-naphthol using copper complexes,[31] $TiCl_4$,[32] and iron[33] among other metals and methods (Scheme 3).[34] Once racemic methods were



**Scheme 3.** A general mechanism of oxidative coupling.

established, effort focused on the asymmetric synthesis of BINOL. One of the earliest examples is through phosphoric acids and Cinchonine salt separation.[35] Enantioenriched BINOL has since been made through a variety of methods, and substitutions off of the hydroxyl moiety have been accomplished.[36] Once enantioenriched, BINOL served as a versatile precursor to a variety of enantioenriched tetra-*ortho*-substituted aryl naphthalenes.[37] Most notably, Noyori pioneered the asymmetric isolation of BINAP **16** from BINOL **14** through a palladium catalyzed fractional recrystallization **15** (Scheme 4).[38] BINAP can now be obtained through a simple cross-coupling approach from the enantioenriched bistriflate.[39]

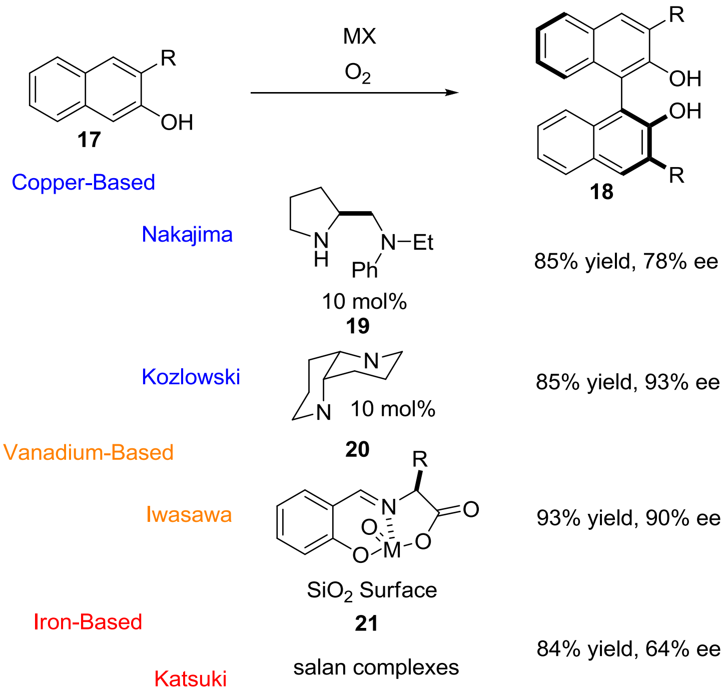


**Scheme 4.** Noyori’s fractional crystallization approach to asymmetric TOAN BINAP.

These initial syntheses of tetra-*ortho*-substituted aryl naphthalenes and their further functionalization played a key role in understanding axial chirality originating from the restricted rotation around the biaryl bond. From these humble beginnings many routes have become available for the generation of these unique motifs.

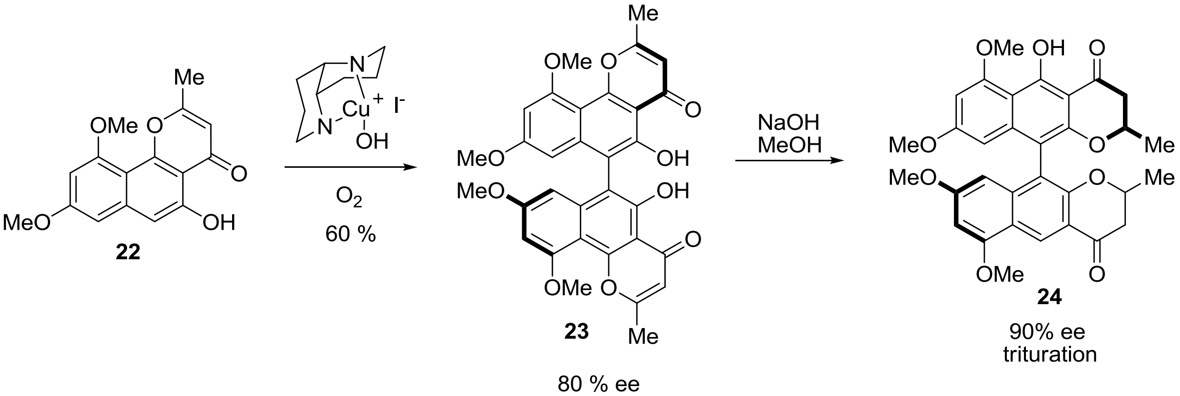
*TOAN Synthesis: Oxidative Coupling:* Since the discovery of the Ullmann reaction over a century ago, oxidative coupling has been one of predominant methods for the synthesis of biaryls.[40] In the last decade there has been a resurgence in optimizing this methodology to obtain synthetically challenging enantioenriched TOANs, especially with a focus on natural products.  Oxidative coupling has shown to be very effective at generating highly enantioenriched TOANs directly from naphthols.  The salient feature of oxidative coupling is the mild reaction conditions that are employed via a one-electron phenolic oxidation process, differentiating them from other cross-coupling processes as they are extremely tolerant of many functional groups.[41]  Unfortunately, regioselectivity can be a problem with oxidative coupling as there is a lack of pre-functionalization which acts as a chemioselector in other methods.[42]  Many unwanted side products are described, especially when the chemical positions on the naphthols are electronically similar.[43]

As previously discussed, there are many metals that can facilitate this coupling (Scheme 5), with the first examples focusing on copper catalysis.  Seminal work in this area was done by Wynberg,[44] Brussee,[45] Yamamoto,[46] and Kocovsky[47] who used chiral



**Scheme 5.** Multiple routes to asymmetric TOAN bisnaphthol substrates through oxidative coupling.

copper(II) amine oxidants to generate chiral BINOL derivatives. Additional work was performed by Nakajima[48] who pioneered the catalytic asymmetric coupling of naphthol with chiral amine ligand **19**. The Kozlowski group made further modifications and has shown excellent yields and enantioselectivities using copper with chiral amine ligand **20** and oxygen as the stoichiometric oxidant.[49] More recently, vanadium-based catalysts have shown to be quite effective at facilitating this coupling.[50] The Iwasawa group has shown that they can provide TOAN **18** in 93% yield and 90% ee on a silica surface **21** from vanadium.[51] Iron-catalyzed coupling has also been demonstrated by the Katsuki group, although the observed enantioselectivity is lower.[52] The iron-mediated coupling was catalyzed by salan complexes. There have also been many examples of natural product total synthesis utilizing the oxidative coupling method.[53] An elegant synthesis of nigerone **24** was performed by the Kozlowski group in >90% ee using asymmetric oxidative coupling as the key synthetic step to obtain precursor **23** in 80% ee. Base mediated rearrangement followed by trituration yielded nigerone in 90% ee (Scheme 6).[54]

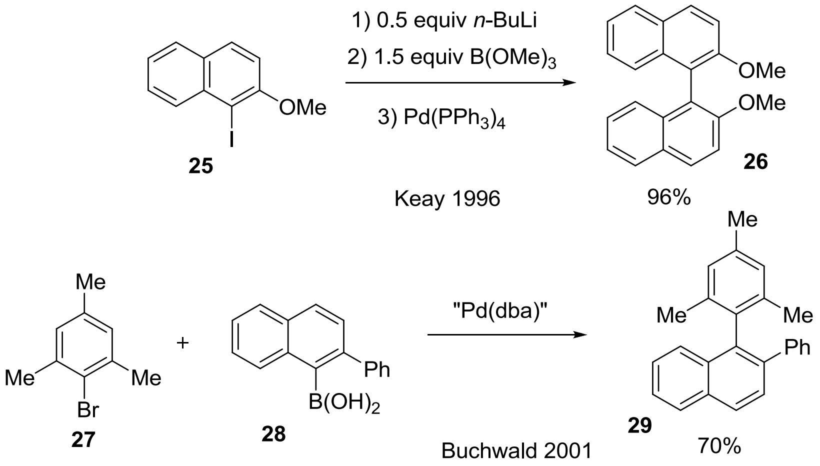


**Scheme 6.** Kozlowski's synthesis of nigerone through asymmetric oxidative coupling.

In all, oxidative coupling is an effective procedure for the coupling of naphthols. However, this method is severely restricted in that regard, being limited solely to a naphthol-based precursor. Large sterically demanding TOANs have not been demonstrated *via* this method.

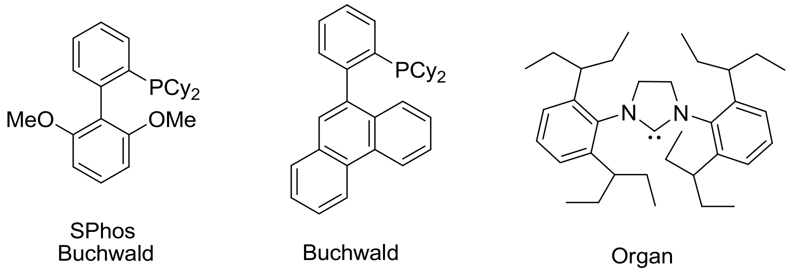
*TOAN Synthesis: Catalytic Cross-Coupling:* Catalytic cross-coupling (Suzuki, Kumada, Stille, etc.) is arguably the most effective and prominent method for the generation of biaryl bond and perhaps even the most effective method for generating a carbon-carbon bond.[55] Unfortunately, Tetra-*ortho*-substituted biaryls have historically been problematic for cross-coupling methods.[56] This is arguably due to difficulties during the reductive elimination step preventing the formation of the critical biaryl bond.[57] Due to the widespread use of catalytic cross-coupling, from academia to industry, there has been a tremendous effort in the last decade to provide routes to these sterically-encumbered compounds through catalytic cross-coupling.[58] Because of the amount of research ongoing in this area we will focus primarily on methods that have shown 1) steric bulk around the *ortho* biaryl bond and those 2) achieving high enantioselectivity.

Seminal work for the synthesis of the first TOAN was accomplished by the Miyano group through a Kumada coupling in 1986.[59] The Keay group was able to introduce Suzkuki coupling for the synthesis of bismethoxy TOAN **26**.[60] Buchwald was then able to generate a host of TOANs through Suzuki couplings and a monophonsphine naphthalene ligand,[61] Buchwald was able to generate TOAN **29** in good yield. Although beyond the scope of this review, it should be noted that Fu pioneered non-naphthalene tetra-*ortho*-substituted biaryls through both Negishi and Stille couplings at the turn of the 21st century.[62]



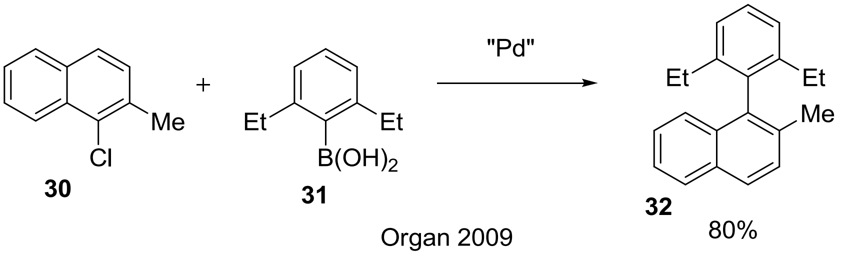
**Scheme 7.** TOAN synthesis through Suzuki catalytic cross-coupling.

Continued work led to further success in the generation of even larger TOANs. Work by Buchwald and Fu demonstrated that large sterically crowded ligands were especially successful in generating TOANs (Scheme 8). It has been reported that the basicity and cone angle of the ligand has a great deal to do with catalytic activity of



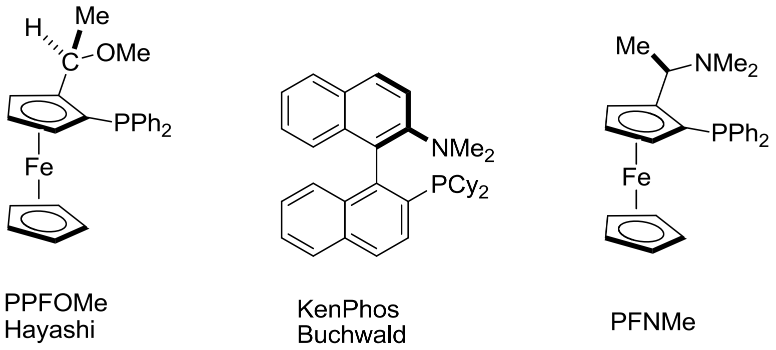
**Scheme 8.** Selected cross-coupling ligands that have shown effectiveness with TOANs.

the metal center, which in turn led to even more active ligands.[63] More recently the groups of Mayer,[64] Organ,[65] and Rahimi[66] have done some elegant work in the preparation of even larger TOANs in good yield utilizing bulky NHC ligands. Organ has to date, generated the largest TOAN (Scheme 9, **32**) with cross-coupling methodology to the author's knowledge.



**Scheme 9.** Organ's synthesis of the largest TOAN through catalytic cross-coupling, *circa* 2009.

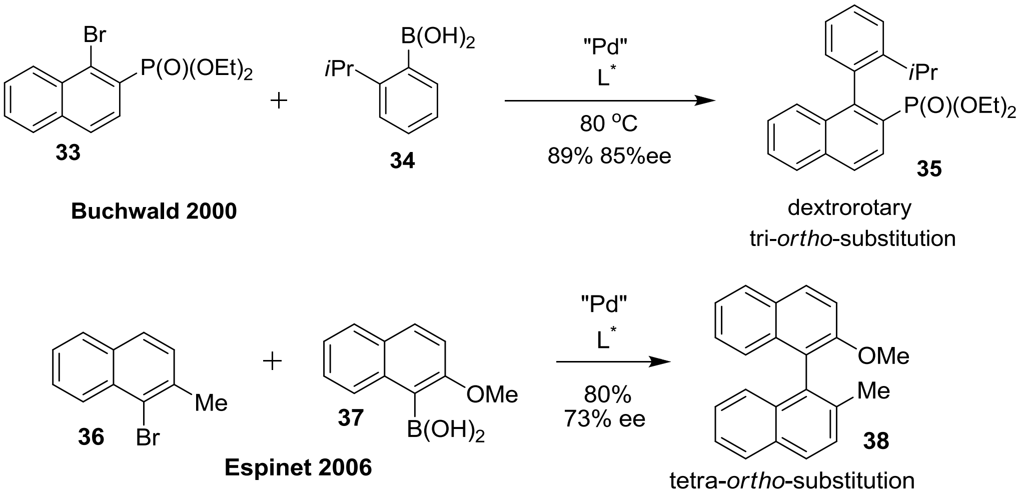
The asymmetric synthesis of TOANs has also been challenging for catalytic cross-coupling, although in the last decade there have been many examples of excellent chiral control of tri-*ortho*-substituted aryl naphthalenes. The use of chiral ligands has allowed the catalytic cycle to proceed enantioselectively (Scheme 10).



**Scheme 10.** Selected ligands for use in asymmetric cross-coupling.

Although many groups have reported success with tri-*ortho*-substituted or smaller biaryls, there have been only a couple of successful TOAN asymmetric syntheses. The first asymmetric TOAN synthesis was by Hayashi in 1988 utilizing a nickel-based

Kumada coupling with a chiral ferrocene ligand.[67] Hayashi continued asymmetric couplings with a successful Kumada coupling to generate tri-*ortho*-substituted biaryls with palladium.[68] Buchwald (Scheme 11, **35**) then introduced work on the asymmetric synthesis of tri-*ortho*-substituted biaryls in 2000 with axially chiral monophosphine ligands using Suzuki coupling.[69] Buchwald has improved on his first successful asymmetric synthesis of tri-*ortho*-substituted aryl naphthalenes by developing the chiral KenPhos (Scheme 10) ligands achieving ee's from 74 to 92% in a number of biaryl naphthalenes bearing phosphonates and other functional groups.[70] Since Buchwald's seminal work was published in 2000 many ligands have been used to mediate these reactions. For example, Espinet has shown chiral ferrocene phosphine ligands (PFNMe, Scheme 10) to be capable of generating chiral TOANs with moderate ee (Scheme 11,



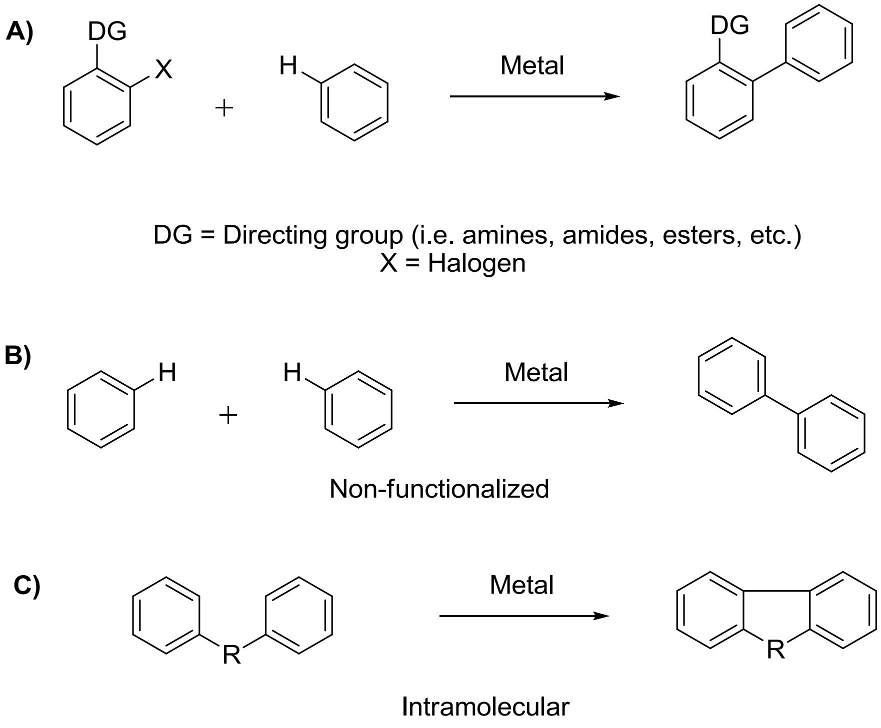
**Scheme 11.** Buchwald's successful asymmetric cross-coupling of tri-*ortho* biaryls and Espinet's asymmetric TOAN synthesis.

**38**),[71] Recently, Lassaletta prepared chiral tri-*ortho*-substituted naphthalenes *via* bis-hydrazone ligands.[72]

Catalytic cross-coupling has shown to be quite effective in the synthesis of a variety of natural products and useful compounds containing TOANs. One of the seminal asymmetric natural product works *via* cross-coupling was the synthesis of Vancomycin by Niccalou,[73] although not a TOAN, it did demonstrate that cross-coupling could be used for these types of applications.

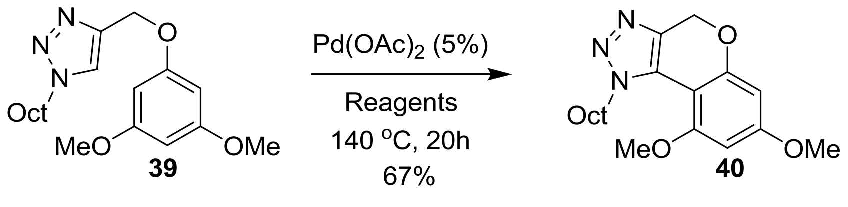
Catalytic cross-coupling is unquestionably the predominant method for the creation of a biaryl bond; however, difficulties with sterics and chiral synthesis still plague this method, adding to the urgency of successful alternative examples of TOAN synthesis.

*TOAN Synthesis: Direct Arylation:* Direct arylation (DA) is the formation of a biaryl bond directly from a C-H bond. Direct arylation has the benefit of being free of organometallics (i.e. B, Sn, Mg, Zn, etc.) and aryl halides, in some cases. Similar to other coupling methods DA uses transition metal catalysts (i.e. Pd, Rh, Ru) to facilitate the formation of the biaryl bond. The reduced pre-functionalization gives DA a smaller environmental footprint and atom economy. Encouragingly for the method, pharmaceutical companies view the synthesis of biaryls *via* DA as the preferred method of the future.[74] DA is a relatively recent breakthrough, with the first reports emerging about 20 years ago.[75] Scheme 12 outlines the types of DA reactions. A majority of successful examples continue to pre-functionalize one aryl group to achieve the coupling. Without pre-functionalization of one aryl group, regioselectivity can become quite a problem.[76] Furthermore, a directing group is commonly used to avoid further regioselectivity issues.[77] Current efforts are focused on the direct coupling between two C-H bonds without utilizing pre-functionalization or directing groups. To the author's knowledge there are no examples of TOAN synthesis via intermolecular direct arylation to date, although there was one example of a tetra-ortho substituted biaryl synthesized by an intramolecular direct arylation (Scheme 13, **40**).[78] Although in its infancy, direct arylation could provide an environmentally benign way to generate TOANs in the future.



DG = Directing group (i.e. amines, amides, esters, etc.)
X = Halogen

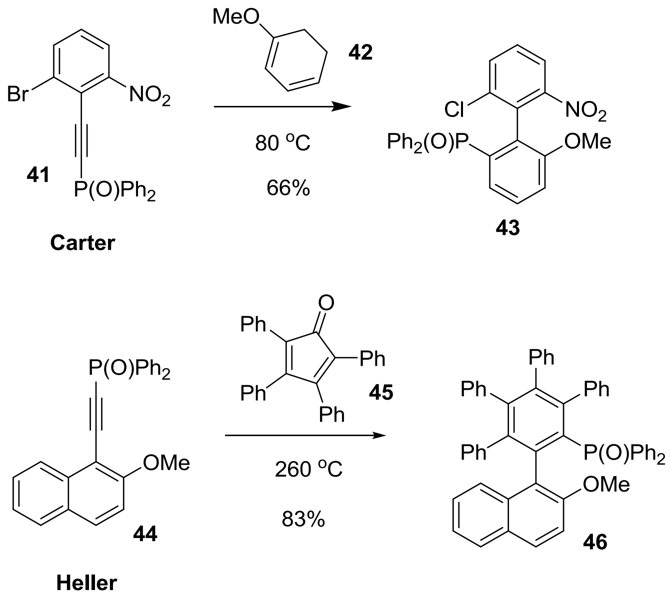
**Scheme 12.** Types of direct arylation: A) DA with an aryl halide and a directing group, B) Non-functionalized DA, C) Intramolecular DA.



**Scheme 13.** Biaryl synthesis *via* intramolecular direct arylation.

<u>*TOAN Synthesis: Alternative Approaches:*</u> Although the lion's share of TOAN synthesis is performed *via* the cross-coupling methods, alternative approaches have been gaining prominence throughout the last decade. This is arguably due to current difficulties with sterics and enantioselectivity as outlined previously. The major alternative routes to TOANs are: Diels-Alder, [2+2+2] cycloaddition, and rearrangement-based synthesis. Each of these methods has shown to be very effective at generating sterically demanding and enantioenriched TOANs. Combined with cross-coupling these methods enhance our current access to these highly desired motifs.

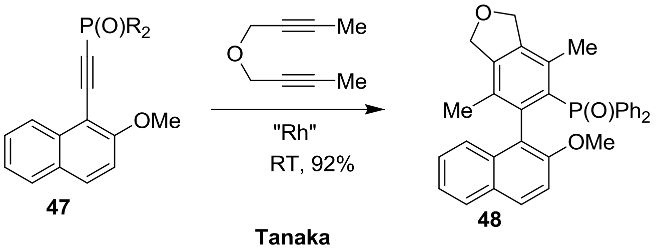
*Alternative Approaches: Diels-Alder:* Diels-Alder [4+2] cycloadditions have been used to generate tetra-*ortho*-substituted biaryls and aryl naphthalenes with high yields and functional group tolerance (Scheme 14). Throughout the last ten years Carter's elegant work has pioneered the "Diels-Alder based approach to biaryls" along with successful examples of natural product synthesis.[79] His work focuses on a tandem cycloaddition-



**Scheme 14.** Carter and Heller's approach to TOANs *via* Diels-Alder cycloadditions.

cycloelimination approach with electron deficient benzylic alkynes and electron rich cyclohexadienes.[80] Carter has also demonstrated a total synthesis of the anti-HIV agent Siamenol.[81] Carter's general method uses alkynyl benzene **41** which undergoes a [4+2] cycloaddition with cyclohexadiene **42** to yield tetra-*ortho*-substituted biaryl **43.** Interestingly, Carter has not reported on the synthesis of TOANs *via* his method. Heller has utilized the Diels-Alder method to demonstrate the synthesis of TOAN **46**, (among others), however, the reaction does require elevated temperatures.[82] Other work, in contrast to Carter's proposed mechanism (cycloaddition then cycloelimination), has described this transformation *via* quantum mechanical calculations that demonstrate the method proceeding *via* a stepwise diradical intermediate.[83] In all, [4+2] cycloadditions are an extremely promising route for highly functionalized, sterically demanding TOANs.

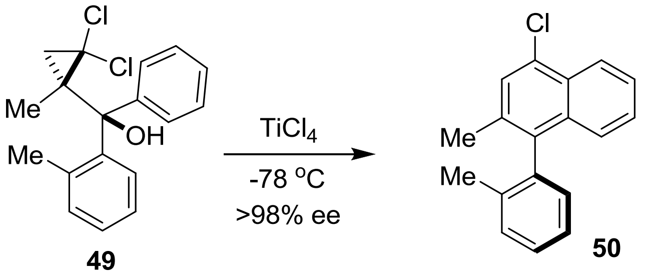
*Alternative Approaches: [2+2+2]:* Tanaka has provided a route to asymmetric TOANs through a rhodium-catalyzed [2+2+2] cycloadditon through naphthylic alkynes **47** and diynes to generate TOAN **48** (Scheme 15).[84] His method shows excellent yields, and can be made to be highly enantioselective by adding BINAP to the rhodium. The enantioselectivities range from 91 to 99% ee.[85] The catalyst loading of rhodium has



**Scheme 15.** Tanaka's [2+2+2] annulation approach to TOANs.

been reported to be 5% and the method has been shown to be adept at generating biaryl chiral monophosphonates, a precursor to the highly desired chiral monophosphine ligand motif.[86]

*Alternative Approaches: Rearrangement-Based:* Rearrangement-based methods focus on the ring expansion rearrangement of strained cycloalkanes, usually cyclopropanes (Scheme 16) and cyclobutanes. Typically, the strained ring can be activated towards breakage through a cyclopropyl carbinol moiety that is activated by Lewis acid catalysis. Tanabe's seminal work introduced this type of chemistry, along with the first example of chirality transfer of a rearrangement-based method to generate enantioenriched aryl naphthalenes **50** from enantioenriched cyclopropyl carbinol **49**.[87] Tanabe's method focused on tri-*ortho*-substituted aryl naphthalenes, and no examples of TOANs were reported.



**Tanabe:** Tri-*ortho*-substitution with chiral transfer

**Scheme 16.** Tanabe's Rearrangement-based method for TOAN synthesis.

## Conclusions

TOANs are an extremely useful motif in all areas of chemistry. This usefulness has led to many methods for the synthesis of these compounds; however, the synthesis of these compounds is only recently beginning to see successes. Oxidative coupling has shown a great deal of promise with naphthols, but beyond these substrates the method is rather limited. Catalytic cross-coupling still suffers from difficulties in the generation of TOANs with large sterically demanding groups in the *ortho* position. Reports of successful cross-coupling approaches to TOANs are few. Direct arylation has shown very limited successful TOAN synthesis to date. While work continues on coupling-based strategies, there is still much progress to be made. Current alternative approaches have been successful, but the substrate scopes are limited and the difficulty in generating complex precursors turns many researchers off to these methods. Furthermore, each method has its own sets of limitations. In all, novel routes towards regioselective, highly enantioenriched, and sterically demanding TOANs are urgently needed.

## Summary of Dissertation

Due to the lack of a TOAN synthetic method capable of addressing regioselectivity, high yields, sterically demanding substituents and asymmetric transformations into one facile synthesis; our group aimed to provide a method that was capable of providing TOANs with all of the aforementioned characteristics. Towards this end, we have established a rearrangement-based method for the synthesis of a variety of TOANs incorporating all the desired elements previously discussed. Herein, we will discuss our initial development and proof of concept studies, substrate scope development, asymmetric synthesis, the stereochemical model of our transformations, and mechanistic postulations.

Chapter II will introduce the design aspects of our rearrangement-based method, focusing on proof of concept studies, rearrangement optimization, initial substrate scope, and our first example of TOAN synthesis. Mechanistic postulations will also be briefly mentioned. This chapter was published in Organic Letters in 2008.[88]

Chapter III will first address lingering regioselectivity issues unresolved from Chapter II. We will then go into a TOAN-focused substrate scope with examples of unprecedented steric bulk around the *ortho* position, culminating in a TOAN with three isopropyl groups in the *ortho* position. We then will discuss purification issues and finally, briefly introduce asymmetric synthesis. This work was published in Chemical Communications in 2011.[89]

Chapter IV focuses heavily on asymmetric TOAN synthesis and a stereochemical model for the chiral transfer. We also discuss our successful incorporation of *t*-butyl and adamantyl groups into the *ortho* position. Another major aspect of this chapter is the transition from a TMS-cyclopropyl-based rearrangement into the simple cyclopropyl-based rearrangement. The material presented in Chapter IV will be the subject of a manuscript to be submitted.[90]

Chapter V will describe preliminary work on the mechanism of rearrangement. Discussion will include the intermediate of a ring-open species en route to aryl naphthalenes, and the implications of these findings. We will also conclude the dissertation with some final concluding remarks.

# **Bridge to Chapter II**

Chapter II introduces our rearrangement-based method, discussing the rationale behind our experimental design. Once these initial method development studies are addressed, the synthesis of the rearrangement precursor is outlined through a simple cyclopropanation of indenone. This is followed by subsequent nucleophilic addition of aryl lithiates or aryl magnesium salts. A limited precursor substrate scope is outlined in Table 1. We then will describe the substrate scope of the rearrangement, both of the parent cyclopropane-based indanone and the more sterically constricted α-methyl precursor. We include our first example of a TOAN in this chapter, along with our difficulties related to the regioselectivity of the rearrangement. We conclude this chapter with a mechanistic postulation, and summary of work to date, followed by the experimental data for this work. This work was published in *Organic Letters* in **2008** on pages 4855-4857.

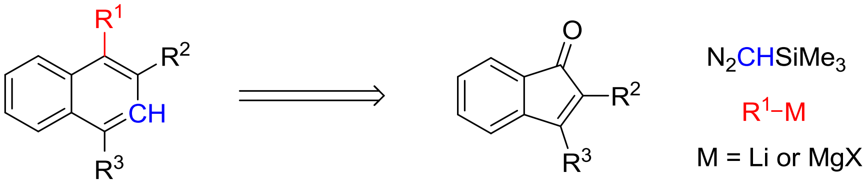
# CHAPTER II

# SYNTHESIS OF SUBSTITUTED NAPHTHALENES VIA A CATALYTIC RING-EXPANSION REARRANGEMENT

This work was published in volume 10 of the journal *Organic Letters* in October 2008. Benjamin B. Morris was involved in starting material preparation, Dr. Lev N. Zakharov performed crystal structure analysis, and Prof. Shih-Yuan Liu was the P.I. I was the primary contributor for the manuscript. This Chapter includes Co-Authored material.

## Results and Discussion

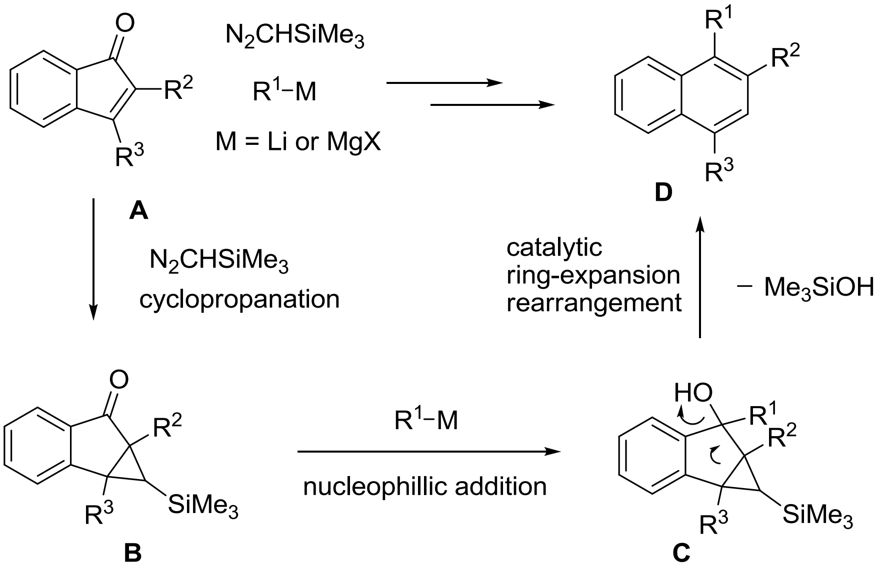
In this chapter we present a new methodology for the preparation of substituted naphthalenes starting from readily available indenones, organolithium/Grignard reagents, and trimethysilyldiazomethane *via* a catalytic rearrangement process (Scheme 1).



**Scheme 1.** Synthesis of naphthalenes from indenones.

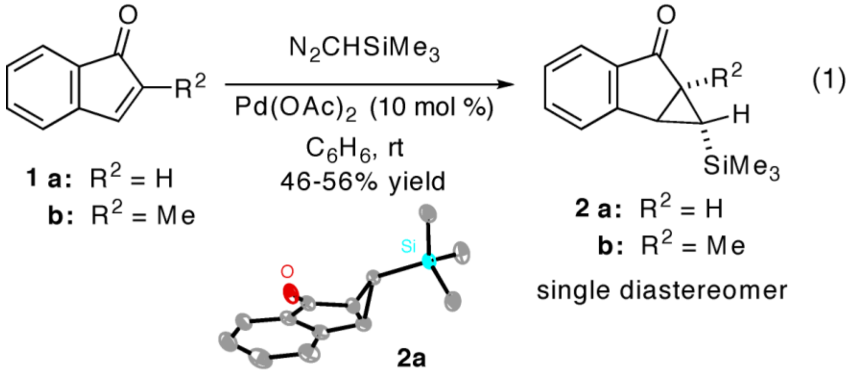
We have been engaged in developing synthetic methods that rearrange easily accessible precursors into valuable target structures. In particular, we sought to provide alternative routes toward naphthalene biaryls that might address some of the limitations of conventional cross-coupling technologies.

We envisioned that cyclopropyl carbinol intermediate **C** (Scheme 2) could be poised to undergo a ring-expansion rearrangement to furnish naphthalenes **D** in a regioselective fashion. Intermediate **C** can be prepared from indenones **A** via a straightforward two-step process, i.e., cyclopropanation followed by nucleophilic addition. The salient feature of this methodology is that the pivotal C–C coupling between $R^1$ and the naphthalene core is accomplished through a simple addition of a nucleophile to a carbonyl.



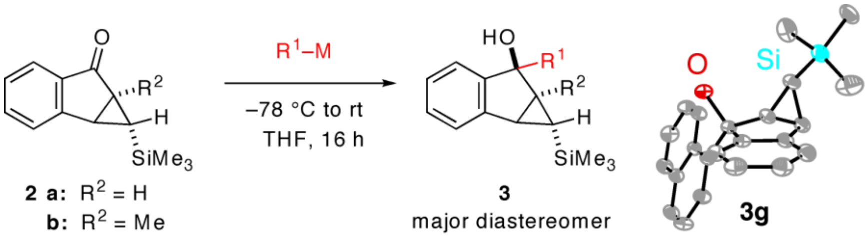
**Scheme 2.** Rearrangement-based synthesis.

Treatment of indenones **1** with commercially available trimethylsilyldiazomethane in the presence of a catalytic amount of $Pd(OAc)_2$ furnishes silylcyclopropanated adducts **2**. The exo diastereomer has been isolated as the major product, the structure of which has been determined by single crystal X-ray crystallography (scheme 3).



**Scheme 3.** Cyclopropanation of indanone **1**.

Table 1 illustrates that addition of nucleophiles to ketones **2** can be readily accomplished with organolithiums (entry 1) as well as with functionalized Grignard reagents (entries 2-5). More hindered ortho-substituted nucleophiles also serve as suitable coupling partners (entries 6-7). Entries 8-11 of Table 1 show that the nucleophilic attack at the more sterically demanding electrophile **2b** is feasible as well, even with a 2,6-disubstituted aryl nucleophile (entry 11). With the exception of two examples (entries 8 and 10), only one diastereomer has been observed for the nucleophilic addition. We have structurally characterized the adduct between ketone **2a** and 1-naphthylmagnesium bromide, i.e., **3g**, via X-ray crystallography. The relative stereochemistry of the structure is consistent with an approach of the nucleophile opposite the blocking silylcyclopropane group.



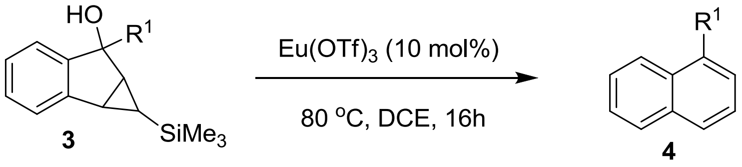
| entry | $R^2$ | $R^1$–M | product | yield (%)[a] | dr[b] |
|---|---|---|---|---|---|
| 1 | H | Ph–Li | **3a** | 73 | >95:5 |
| 2 | H | 4-$MeO_2CC_6H_4$–MgX | **3b** | 50 | >95:5 |
| 3 | H | 4-$MeOC_6H_4$–MgBr | **3c** | 52 | >95:5 |
| 4 | H | 4-$ClC_6H_4$–MgBr | **3d** | 58 | >95:5 |
| 5 | H | 4-$FC_6H_4$–MgBr | **3e** | 56 | >95:5 |
| 6 | H | 2-$MeC_6H_4$–Li | **3f** | 67 | >95:5 |
| 7 | H | 1-naphthyl–MgBr | **3g** | 62 | >95:5 |
| 8 | Me | Ph–Li | **3h** | 70 | 74:26 |
| 9 | Me | 2-$MeC_6H_4$–Li | **3i** | 81 | >95:5 |
| 10 | Me | 2-$MeOC_6H_4$–MgBr | **3j** | 44 | 76:24 |
| 11 | Me | 2,6-$(MeO)_2C_6H_3$–Li | **3k** | 53 | >95:5 |

[a] Isolated yield. [b] Determined by $^1H$ NMR.

**Table 1.** Catalytic Ring Expansion Rearrangement

We chose to optimize the synthesis of naphthalenes via the proposed ring expansion rearrangement using substrate **3a**. A survey of Lewis acids and solvents reveals that the optimal reaction conditions involve 10 mol % $Eu(OTf)_3$ in 1,2-dichloroethane as solvent (See experimental for details). The presence of the silicon group is crucial. A control experiment performed with a substrate bearing H in place of $SiMe_3$ under the optimized reaction conditions produced very little of the desired naphthalene product.

Cyclopropyl carbinols **3** from Table 1 were subjected to the optimized reaction conditions. Table 2 shows that our catalytic ring-expansion rearrangement is compatible with functionalized (entries 2-5), and hindered (entries 6-7) $R^1$ groups. We have also prepared a disubstituted naphthalene **4l** in a regioselective fashion from the corresponding precursor **3l** derived from a *β*-substituted indenone (table 2).



| entry | $R^1$ | product | yield(%)[a] |
|---|---|---|---|
| 1 | Ph | 4a | 84 |
| 2 | $4\text{-MeO}_2\text{CC}_6\text{H}_4$ | 4b | 42 |
| 3 | $4\text{-MeOC}_6\text{H}_4$ | 4c | 46 |
| 4 | $4\text{-ClC}_6\text{H}_4$ | 4d | 56 |
| 5 | $4\text{-FC}_6\text{H}_4$ | 4e | 58 |
| 6 | $2\text{-MeC}_6\text{H}_4$ | 4f | 62 |
| 7 | 1-naphthyl | 4g | 67 |

[a] Isolated yield

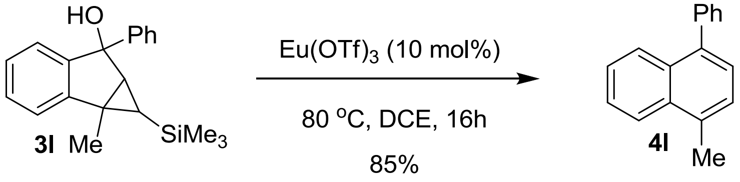
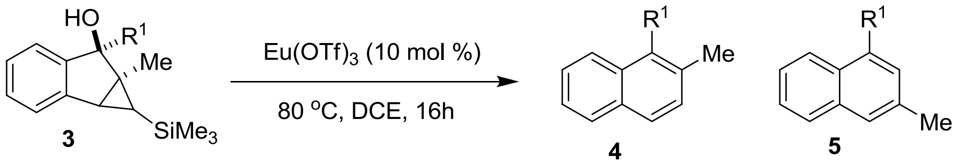
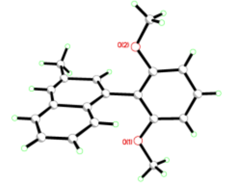


**Table 2.** Nucleophilic Addition to **2**

Interestingly, we discovered that precursors **3h-3k**, which are derived from an *α*-substituted indenone, produce a mixture of naphthalene products **4** and **5** under our optimized conditions (Table 3). The desired 1,2-disubstituted regioisomer **4** is formed in high selectivity for substrates **3h** and **3i**, furnishing di- and triortho-substituted biaryl naphthalenes **4** in good yield (entries 1-2). A diminished regioselectivity is observed for substrate **3j**, which contains the *o*-methoxyphenyl substituent (entry 3). Noteworthy is the preparation of a tetra-*ortho*-substituted biaryl **4k** from precursor **3k**, although the



| entry | $R^1$ | product | yield (%)[a] | 4:5[b] |
|---|---|---|---|---|
| 1 | Ph | h | 70 | 93:7 |
| 2 | 2-MeC$_6$H$_4$ | i | 70 | 93:7 |
| 3 | 2-MeOC$_6$H$_4$ | j | 85 | 83:17 |
| 4 | 1,6-(MeO)$_2$C$_6$H$_4$ | k | 77 | 64:36 |

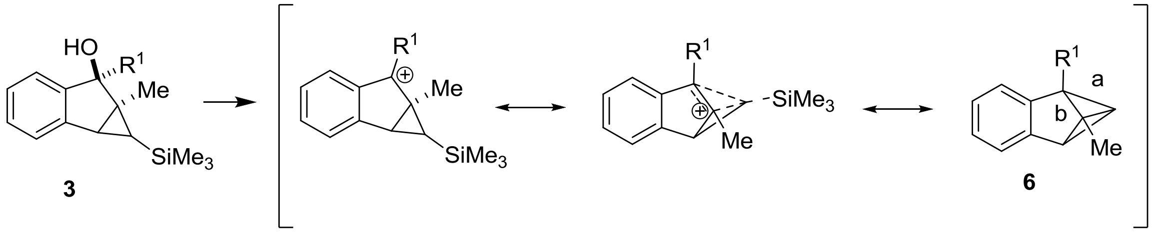

**5k**

[a] Isolated yield of a mixture of **4** and **5**. [b] Determined by $^1$H NMR.

**Table 3.** Catalytic Ring Expansion of Hindered Precursors

regioselectivity of the rearrangement is only moderate (entry 4). We have determined the structure of the rearrangement byproduct **5k** via X-ray crystallography, thus unambiguously establishing the connectivity of the 1,3-disubstituted naphthalene regioisomer **5**.

The presence of isomer **5** may provide some insight into the possible mechanism of the rearrangement process. The current mechanistic hypothesis for its formation involves a benzobenzvalene intermediate **6** (Scheme 4). Breaking bond a in **6** produces the 1,2-disubstituted naphthalene **4** whereas breaking bond b yields the 1,3-disubstituted isomer **5**.



**Scheme 4.** Possible intermediate for the rearrangement.

In summary, we have developed a new method for the synthesis of substituted naphthalenes based on a catalytic ring-expansion rearrangement process. Starting from readily available indenones, biaryl naphthalenes, including hindered triortho-substituted ones, can be accessed in a few steps. Our method provides an alternative to cross-coupling procedures for the synthesis of biaryl naphthalenes, and it distinguishes itself from coupling protocols by achieving the crucial C–C bond-forming step through a simple nucleophilic addition to a carbonyl. Our experimental observations are consistent with a rearrangement mechanism involving a benzvalene-like intermediate. Current efforts are geared toward obtaining a better understanding of the reaction mechanism and improving the substrate scope and reaction efficiency.

## Experimental

### *General*

All oxygen- and moisture-sensitive manipulations were carried out under an inert atmosphere using either standard Schlenk techniques or a glove box.

THF, $Et_2O$, $CH_2Cl_2$, and pentane were purified by passing through a neutral alumina column under argon. Anhydrous benzene, dichloroethane, and hexane were purchased from Aldrich and used as received. All other reagents were purchased (Aldrich or TCI) and used as received. Indenone, 2-methyl-1-indenone, and *o*-tolyllithium were prepared according known procedures.[91]

Thin layer chromatography and preparatory chromatography were performed on Silicycle glass backed plates with UV indicator. Column chromatography was performed on Silicycle silica gel P60.

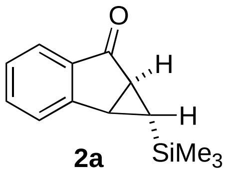
$^1H$ NMR spectra were recorded on a Varian Unity/Inova 300 or Varian Unity/Inova 600 spectrometer. $^{13}C$ NMR spectra were recorded on a Varian Unity/Inova 300 or Varian Unity/Inova 500 spectrometer. All spectra were referenced to their respective solvents: $CDCl_3$ 7.27 ppm and $CD_2Cl_2$ 5.30 ppm. Gas chromatography was performed on an Agilent 6850 Series II GC with an auto loader using ChemStation.

IR spectra were recorded on a Nicolet Magna 550 FT-IR instrument with OMNIC software.

High-resolution mass spectroscopy data were obtained at the Mass Spectroscopy Facilities and Services Core of the Environmental Health Sciences Center at Oregon State

University. Financial support for this facility has been furnished in part by the National Institute of Environmental Health Sciences, NIH (P30 ES00210).

### *Synthesis of Silylcyclopropyl Indanones 2*

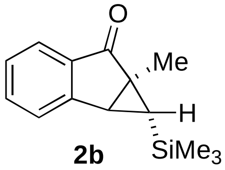


**2a**

**Compound 2a.** To a nitrogen flushed and dried flask, 1-indenone (360 mg, 2.77 mmol) and palladium acetate (62.0 mg, 0.277 mmol) were added. The flask was repurged with $N_2$. Anhydrous benzene (30 mL) was added followed by dropwise addition of $TMSCHN_2$ (3.45 mL, 7.00 mmol, 2.0 M in diethyl ether). The evolution of $N_2$ gas is apparent and the solution turns black. The reaction mixture was allowed to stir at room temperature for 16 h. At the conclusion of the reaction, the reaction mixture was filtered through a plug of Celite, and the solvent removed under reduced pressure. The crude material was subjected to column chromatography (Hex:$Et_2O$ = 10:1), and **2a** was isolated as a red oil (340 mg, 56 % yield). Single crystals were grown via slow evaporation from a solution of **2a** in $CH_2Cl_2$.

$^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 0.05 (s, 9H), 0.95 (t, J = 5.1 Hz, 1H), 2.41 (t, J = 5.1 Hz, 1H), 2.76 (t, J = 4.2 Hz, 1H), 7.25 (t, J = 7.5 Hz, 1H), 7.34-7.41 (m, 2H), 7.60 (d, J = 7.2 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ –2.6, 25.4, 30.7, 41.4, 124.0, 124.8, 126.6, 133.2, 155.6, 155.7, 203.1. IR ($CH_2Cl_2$): 1708 s, (Carbonyl). HRMS (EI) calcd for $C_{13}H_{16}OSi$ (M+) 216.09705, found 216.09623.

**Compound 2b.** The procedure for the preparation of **2a** has been used for the synthesis of **2b** employing 2-methyl-1-indenone (500 mg, 3.44 mmol), palladium acetate (77.0 mg, 0.344 mmol), 35 mL benzene, and TMSCHN$_2$ (4.3 mL, 8.6 mmol, 2.0 M in diethyl ether). Cyclopropane **2b** was isolated as a pale yellow solid (367 mg, 46 % yield).

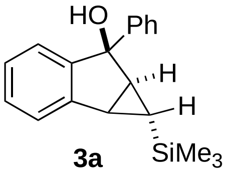


**2b**

$^1$H NMR (300 MHz, CDCl$_3$): δ 0.13 (s, 9H), 0.85 (d, J = 4.8 Hz, 1H), 1.58 (s, 3H), 2.65 (d, J = 4.8 Hz, 1H), 7.21-7.45 (m, 3H), 7.64 (d, J = 8.1 Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ –0.7, 11.7, 31.6, 36.8, 46.3, 123.6, 125.2, 126.3, 133.1, 133.3, 156.2, 205.3. IR (CH$_2$Cl$_2$): 1707 s, (Carbonyl). HRMS (EI) calcd for $C_{14}H_{18}OSi$ (M+) 230.11270, found 230.11236

***Synthesis of Silylcyclopropyl Carbinols 3 (Table 1)***

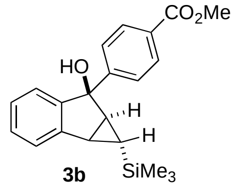
**Compound 3a (Entry 1).** An oven-dried flask was charged with 50 mL anhydrous THF and phenyllithium (7.11 mL, 12.8 mmol, 1.8 M in di-*n*-butyl ether) and cooled to –78 °C. Compound **2a** (1.32 g, 6.11 mmol) in 10.0 mL THF was added to the reaction mixture over 5 minutes at this temperature. The reaction was brought to room temperature after 1 hour and left stirring for 16 more hours. At the conclusion of the reaction, 25 mL of NH$_4$Cl (saturated, aqueous) was added followed by 50 mL ether. The organic phase was washed three times with brine and dried over MgSO$_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). Compound **3a** was isolated as a pale yellow oil (1.32 g, 73% yield).



**3a**

$^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 0.08 (s, 9H), 0.15 (t, J = 4.5 Hz, 1H), 2.10 (t, J = 5.4 Hz, 1H), 2.21 (s, 1H), 2.56 (t, J = 5.4 Hz, 1H), 7.08-7.38 (m, 7H), 7.49 (d, J = 8.4 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ –2.2, 22.7, 27.1, 33.1, 85.0, 123.1, 125.1, 125.8, 126.6, 126.8, 127.7, 128.2, 146.2, 147.2, 147.4. IR ($CH_2Cl_2$): 3592 s, (alcohol). HRMS (EI) calcd for $C_{19}H_{22}OSi$ (M+) 294.14400, found 294.14391.

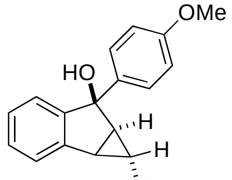
**Compound 3b (Entry 2).** A round-bottomed flask was charged with *p*-Iodomethylbenzoate (353 mg, 1.35 mmol) in 10.0 mL anhydrous THF. The mixture was cooled to –10 $^{o}$C, and isopropylmagnesium bromide (1.76 mL, 1.76 mmol, 1.0 M in THF) was added dropwise. After 2 hours the reaction mixture was cooled to –78 $^{o}$C, and a solution of **2a** (175 mg, 0.810 mmol, in 4.0 mL THF) was added dropwise. After one hour, the mixture was allowed to warm up to room temperature. After 16 hours of stirring at room temperature, the reaction was quenched with 10 mL $NH_4Cl$ (saturated, aqueous) followed by addition of 15 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was then removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 6:1). The product was isolated as a clear colorless liquid (145 mg, 50% yield).



**3b**

$^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 0.08 (s, 9H), 0.17 (t, J = 4.5 Hz, 1H), 2.06 (t, J = 5.4 Hz, 1H), 2.46 (s, 1H), 2.57 (t, J = 5.1 Hz, 1H), 3.91 (s, 3H), 7.04 (d, J = 7.2 Hz, 1H), 7.09 (t, J = 6.9, Hz, 1H), 7.20 (t, J = 6.3 Hz, 1H) 7.31 (d, J = 6.9 Hz, 1H), 7.54 (d, J = 8.1 Hz, 2H), 8.00 (d, J = 8.7 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ –2.3, 22.5, 27.0, 32.8, 52.0, 84.9, 123.2, 125.1, 125.7, 126.7, 127.9, 128.4, 129.5, 145.8, 147.0, 152.3, 167.0. IR ($CH_2Cl_2$): 3593 s, (alcohol), 3503 b (alcohol), 1718 s (carbonyl). HRMS (EI) calcd for $C_{21}H_{23}O_3Si$ (M+) 335.14674, found 335.14560.

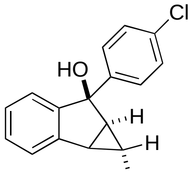
**Compound 3c (Entry 3).** The procedure for the preparation of **3a** has been applied for the synthesis of **3c**, using **2a** (158 mg, 0.730 mmol) in 5.0 mL THF and 4-methoxyphenylmagnesium bromide (2.19 mL, 1.09 mmol, 0.5 M in THF). Compound **3c** was isolated as a light yellow solid (123 mg, 52% yield).



**3c**

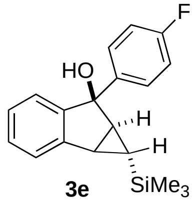
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.09 (s, 9H), 0.15 (t, J = 4.5 Hz, 1H), 2.09 (t, J = 6 Hz, 1H), 2.30 (s, 1H), 2.55 (t, J = 5.4 Hz, 1H), 3.82 (s, 3H), 6.90 (d, J = 8.7 Hz, 2H), 7.10-7.23 (m, 3H), 7.32 (d, J = 6.9 Hz, 1H), 7.15 (d, J = 6.9 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ –2.2, 22.7, 26.9, 33.1, 55.2, 84.8, 113.4, 123.0, 125.8, 126.3, 126.5, 127.6, 139.8, 146.3, 147.0, 158.3. IR ($CH_2Cl_2$): 3589 s, (alcohol). HRMS (EI) calcd for $C_{20}H_{24}O_2Si$ (M+) 324.15456, found 324.15392.

**Compound 3d (Entry 4).** The procedure for the preparation of **3a** has been applied for the synthesis of **3d**, using **2a** (153 mg, 0.708 mmol) in 5.0 mL THF and 4-chlorophenylmagnesium bromide (1.07 mL, 1.07 mmol, 1.0 M in THF). Compound **3d** was isolated as a pale yellow oil (135 mg, 58% yield).



**3d**

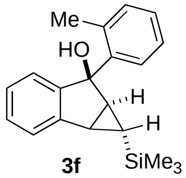
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.06 (s, 9H), 0.14 (t, J = 4.5 Hz, 1H), 2.05 (t, J = 5.4 Hz, 1H), 2.28 (s, 1H), 2.56 (t, J = 5.1 Hz, 1H), 7.06 (d, J = 7.2 Hz, 1H), 7.14 (t, J = 6 Hz, 1H), 7.21 (t, J = 5.7 Hz, 1H), 7.31 (d, J = 4.5 Hz, 3H), 7.42 (d, J = 9 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$): d –2.2, 22.7, 27.0, 33.0, 84.7, 123.2, 125.7, 126.7, 127.9, 128.2, 132.5, 145.9, 147.0. Two additional aromatic carbon atoms have overlapping $^{13}$C signals with those shown. IR ($CH_2Cl_2$): 3592 s, (alcohol). HRMS (EI) calcd for $C_{19}H_{21}OSiCl$ (M+) 328.10503, found 328.10382.



**3e**

**Compound 3e (Entry 5).** The procedure for the preparation of **3a** has been applied for the synthesis of **3e**, using **2a** (151 mg, 0.700 mmol) in 5.0 mL THF and 4-fluorophenylmagnesium bromide (1.39 mL, 1.39 mmol, 1.0 M in THF). Compound **3e** was isolated as a pale yellow oil (123 mg, 56% yield).

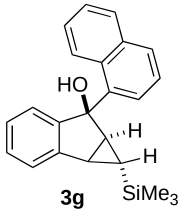
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.09 (s, 9H), 0.14 (t, J = 4.5 Hz, 1H), 2.06 (t, J = 5.7 Hz, 1H), 2.25 (s, 1H), 2.56 (t, J = 4.8 Hz, 1H), 6.99-7.33 (m, 6H), 7.41-7.46 (m, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ –2.2, 22.8, 26.9, 33.1, 84.7, 114.8 (d, $^2J_{CF}$ = 21.1 Hz), 123.1, 125.7, 126.6, 126.8 (d, $^3J_{CF}$ = 8.0 Hz), 127.8, 143.2 (d, $^4J_{CF}$ = 3.1 Hz), 146.0, 147.0, 161.7 (d, $^1J_{CF}$ = 243 Hz). IR ($CH_2Cl_2$): 3590 s, (alcohol). HRMS (EI) calcd for $C_{19}H_{21}OSiF$ (M+) 312.13458, found 312.13381.



**3f**

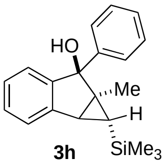
**Compound 3f (Entry 6).** The procedure for the preparation of **3a** has been applied for the synthesis of **3f**, using **2a** (144 mg, 0.667 mmol) in 2.5 mL THF and *o*-tolyllithium (136 mg, 1.39 mmol) in 2.5 mL THF. Compound **3f** was isolated as a pale yellow oil (137 mg, 67% yield).

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.11 (s, 9H), 0.29 (t, J = 4.5 Hz, 1H), 2.18 (t, J = 5.4 Hz, 1H), 2.21 (s, 1H), 2.51 (t, J = 5.1 Hz, 1H), 2.60 (s, 3H), 7.12-7.37 (m, 8H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ –2.2, 21.5, 23.2, 28.1, 32.1, 86.1, 123.4, 125.0, 125.2, 126.5, 126.9, 127.3, 127.9, 132.4, 136.4, 144.0, 145.6, 147.7. IR ($CH_2Cl_2$): 3582 s, (alcohol), 3462 b (alcohol). HRMS (EI) calcd for $C_{20}H_{24}OSi$ (M+) 308.15965, found 308.15902.



3g

**Compound 3g (Entry 7).** The procedure for the preparation of **3a** has been applied for the synthesis of **3g**, using **2a** (146 mg, 0.68 mmol) in 10.0 mL THF and 1-naphthylmagnesium bromide (5.36 mL, 0.68 mmol, 0.25 M in THF). Compound **3g** was isolated as a white solid (144 mg, 62% yield). Single crystals suitable for X-ray crystallography were grown via slow evaporation from a solution of **3g** in $CH_2Cl_2$. IR ($CH_2Cl_2$): 3582 s (alcohol). HRMS (EI) calcd for $C_{23}H_{24}OSi$ (M+) 344.15965, found 344.15879

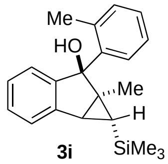


3h

**Compound 3h (Entry 8).** The procedure for the preparation of **3a** has been applied for the synthesis of **3h**, using **2b** (190 mg, 0.826 mmol) in 10.0 mL THF and phenyllithium (0.600 mL, 1.08 mmol, 1.8 M in di-*n*-butyl ether). Compound **3h** was isolated as a pale yellow oil (179 mg, 70% yield). $^1$H NMR indicates a 74:26 ratio of diastereomers.

$^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 0.14 (s, 9H), 0.060 (d, J = 4.5 Hz, 1H), 1.01 (s, 3H), 2.22 (s, 1H), 2.39 (d, J = 4.2 Hz, 1H), 7.02 (d, J = 7.2 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 7.19-7.47 (m, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ –0.3, 15.6, 30.2, 33.9, 37.7, 88.6, 122.1, 126.5, 126.6, 127.9, 144.8, 146.9, 148.9. Three additional aromatic carbon atoms have overlapping $^{13}$C signals with those shown. (IR ($CH_2Cl_2$): 3566 b, (alcohol), 3481 b, (alcohol). HRMS (EI) calcd for $C_{20}H_{24}OSi$ (M+) 308.15965, found 308.16027.

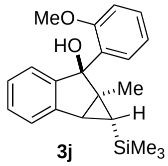
**Compound 3i (Entry 9).** The procedure for the preparation of **3a** has been applied for the synthesis of **3i**, using **2b** (150 mg, 0.650 mmol) in 5.0 mL THF and *o*-tolyllithium (96 mg, 0.98 mmol) in 3.0 mL THF. Compound **3i** was isolated as a pale yellow oil (170 mg, 81% yield).



**3i**

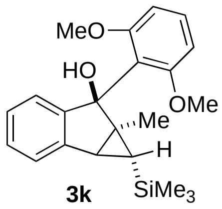
$^1$H NMR (300 MHz, $CDCl_3$): δ –0.01 (apparent s, 10H), 1.65 (s, 3H), 2.072 (s, 1H), 2.27 (d, J = 4.8 Hz, 1H), 2.77 (s, 3H), 6.91 (d, J = 8.1 Hz, 1H), 7.06 (t, J = 7.2 Hz, 1H), 7.18-7.35 (m, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ –0.6, 14.3, 23.2, 31.0, 34.3, 40.2, 89.6, 122.7, 124.2, 125.6, 126.6, 126.8, 128.0, 129.8, 132.6, 137.0, 140.6, 148.0, 148.4. IR ($CH_2Cl_2$): 3580 s, (alcohol), 3450 b (alcohol). HRMS (EI) calcd for $C_{21}H_{26}OSi$ (M+) 322.17530, found 322.17464.

**Compound 3j (Entry 10).** The procedure for the preparation of **3a** has been applied for the synthesis of **3j**, using **2b** (350 mg, 1.52 mmol) in 10.0 mL THF and 2-methoxyphenylmagnesium bromide (3.00 mL, 3.00 mmol, 1.0 M in THF). Compound **3j** was isolated as a white solid (224 mg, 44% yield). $^1$H NMR indicates a 76:24 ratio of diastereomers.



**3j**

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.14 (s, 9H), 0.53 (d, J = 5.4 Hz, 1H), 1.03 (s, 3H), 2.17 (d, J = 5.1 Hz, 1H), 4.04 (s, 3H), 5.66 (s, 1H), 6.39 (dd, J = 5.7, 1.8 Hz, 1H) 6.77-6.89 (m, 1H) 7.02 (d, J = 8.4 Hz, 1H) 7.17-7.32 (m, 5H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ –0.2, 15.6, 29.9, 35.0, 37.9, 55.4, 90.5, 110.9, 121.4, 122.1, 125.9, 127.3, 127.6, 128.2, 129.9, 132.9, 145.7, 149.1, 157.3. IR ($CH_2Cl_2$): 3601 s, (alcohol), 3515 b (alcohol). HRMS (EI) calcd for $C_{21}H_{26}O_2Si$ (M+) 338.17021, found 338.16921.



**3k**

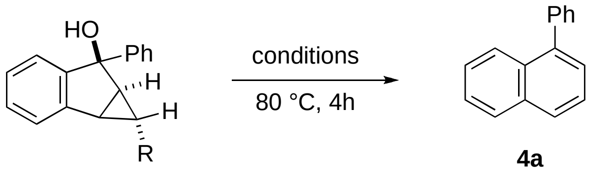
**Compound 3k (Entry 11).** Under an inert atmosphere, a round bottomed flask was charged with 1,3-dimethoxybenzene (750 mg, 5.28mmol) in 15.0 mL anhydrous ether. *n*-BuLi (1.93 mL, 4.88 mmol, 2.53M solution in hexanes) was added dropwise at room temperature. The reaction mixture was stirred for 16 h after which the solvents were removed under reduced pressure. 15 mL THF was added to the precipitate and the resulting solution was cooled to –78 $^{o}$C. Compound **2b** (344 mg, 1.50 mmol) in 5 mL THF was added dropwise. After one hour stirring at –78 °C, the reaction was allowed to warm to room temperature and stirred for 16 more hours. Then, the reaction was quenched with 10 mL $NH_4Cl$ (saturated, aqueous), and 15 mL ether were added. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was then removed under reduced pressure and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). The product was isolated as a white solid (290 mg, 53% yield).

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.13 (s, 9H), 0.55 (d, J = 5.1 Hz, 1H), 1.10 (s, 3H), 2.27 (d, J = 5.4 Hz, 1H), 3.09 (s, 3H), 4.01 (s, 3H), 6.45 (s, 1H), 6.51 (d, J = 8.1 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 7.00-7.08 (m, 3H), 7.16-7.24 (m, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 0.1, 16.3, 27.6, 35.9, 37.2, 56.2, 57.0, 89.5, 105.8, 107.8, 121.6, 122.3, 124.6, 125.4, 126.6, 128.5, 149.2, 149.7, 158.4, 158.7. IR ($CH_2Cl_2$): 3494 s, (alcohol). HRMS (EI) calcd for $C_{22}H_{28}O_3Si$ (M+) 368.18078, found 368.18122.

### *Ring-Expansion Rearrangement Optimization Survey*

A survey of Lewis acids (Table 4, entries 1-8) reveals that $Eu(OTf)_3$ promotes the transformation most efficiently, giving the desired naphthalene product **4a** in 69% yield.

A screen for the optimal solvent shows that 1,2-dichloroethane (entry 8) outperforms etheral (entry 9), aromatic (entries 10-11), and saturated hydrocarbon (entry 12) solvents. Gratifyingly, we have determined that the ring expansion rearrangement can be carried out in the presence of catalytic amounts of the Lewis acid (entry 13). However, a lowering of the catalyst loading from 10 mol% to 1 mol% results in a decrease in yield of **4a** (entry 13 vs. entry 14). Control experiments with $BF_3$•$Et_2O$ (entry 15) and $SnCl_4$ (entry 16) as catalysts demonstrate that these Lewis acids are inferior to $Eu(OTf)_3$ under



**4a**

**3a:** R = $SiMe_3$
**H:** R = H

| entry | conditions | yield (%)[a] |
|---|---|---|
| 1 | **3a**, $FeCl_3$ (1 equiv), DCE | 39 |
| 2 | **3a**, $RuCl_3$ (1 equiv), DCE | 17 |
| 3 | **3a**, $TiCl_4$ (1 equiv), DCE | 6 |
| 4 | **3a**, $ZrCl_4$ (1 equiv), DCE | 4 |
| 5 | **3a**, $BF_3$ • $Et_2O$ (1 equiv), DCE | 52 |
| 6 | **3a**, $AlCl_3$ (1 equiv), DCE | 12 |
| 7 | **3a**, $SnCl_4$ (1 equiv), DCE | 44 |
| 8 | **3a**, $Eu(OTf)_3$ (1 equiv), DCE | 69 |
| 9 | **3a**, $Eu(OTf)_3$ (1 equiv), THF | 36 |
| 10 | **3a**, $Eu(OTf)_3$ (1 equiv), Toluene | 38 |
| 11 | **3a**, $Eu(OTf)_3$ (1 equiv), $C_6H_6$ | 30 |
| 12 | **3a**, $Eu(OTf)_3$ (1 equiv), *n*-Hexane | 8 |
| **13** | **3a, $Eu(OTf)_3$ (10 mol%), DCE** | **81** |
| 14 | **3a**, $Eu(OTf)_3$ (1 mol%), DCE | 50 |
| 15 | **3a**, $BF_3$ • $Et_2O$ (10 mol%), DCE | 42 |
| 16 | **3a**, $SnCl_4$ (10 mol%), DCE | 7 |
| 17 | **H**, $Eu(OTf)_3$ (10 mol%), DCE | 4 |

[a] Determined by GC analysis versus a calibrated internal standard. DCE: 1,2-dichloroethane.

**Table 4.** Ring-Expansion Rearrangement: Optimization Studies

the optimized reaction conditions. The presence of the silicon group is crucial. A control experiment performed with substrate **H** (H in place of $SiMe_3$) under the optimized reaction conditions produced only very little desired rearrangement product (entry 17).

***General Procedure for the Optimization Survey:***

In a nitrogen glovebox, a vial was charged with compound **3a**, Lewis acid, hexadecane, and the solvent. The reaction vial was immersed into an oil bath at 80 $^{o}$C for 4 hours. At the conclusion of the reaction, the mixture was filtered through a silica gel plug with copious washing using ether. An aliquot of the resulting solution was subjected to GC yield analysis. All GC yields (Table S1) have been corrected for response factors.

**Entry 1:** The general procedure was followed, using **3a** (17 mg, 0.057 mmol), $FeCl_3$ (10 mg, 0.064 mmol), and DCE (1.0 mL). GC analysis indicated the formation of **4a** in 39% yield.

**Entry 2:** The general procedure was followed, using **3a** (16 mg, 0.053 mmol), $RuCl_3$ (12 mg, 0.058 mmol), and DCE (1.0 mL). GC analysis indicated the formation of **4a** in 17% yield.

**Entry 3:** The general procedure was followed, using **3a** (16 mg, 0.053 mmol), $TiCl_4$ (11 mg, 0.058 mmol), and DCE (1.0 mL). GC analysis indicated the formation of **4a** in 6% yield.

**Entry 4:** The general procedure was followed, using **3a** (16 mg, 0.053 mmol), $ZrCl_4$ (13 mg, 0.058 mmol), and DCE (1.0 mL). GC analysis indicated the formation of **4a** in 4% yield.

**Entry 5:** The general procedure was followed, using **3a** (17 mg, 0.057 mmol), $BF_3$•$Et_2O$ (9.0 mg, 0.063 mmol), and DCE (1.0 mL). GC analysis indicated the formation of **4a** in 52% yield.

**Entry 6:** The general procedure was followed, using **3a** (16 mg, 0.0530 mmol), $AlCl_3$ (8.0 mg, 0.058 mmol), and DCE (1.0 mL). GC analysis indicated the formation of **4a** in 12% yield.

**Entry 7:** The general procedure was followed, using **3a** (17 mg, 0.057 mmol), $SnCl_4$ (11 mg, 0.063 mmol), and DCE (1.0 mL). GC analysis indicated the formation of **4a** in 44% yield.

**Entry 8:** The general procedure was followed, using **3a** (16 mg, 0.053 mmol), $Eu(OTf)_3$ (41 mg, 0.058 mmol), and DCE (1.0 mL). GC analysis indicated the formation of **4a** in 69% yield.

**Entry 9:** The general procedure was followed, using **3a** (13 mg, 0.044 mmol), $Eu(OTf)_3$ (28 mg, 0.047 mmol), and THF (1.0 mL). GC analysis indicated the formation of **4a** in 36% yield.

**Entry 10:** The general procedure was followed, using **3a** (13 mg, 0.044 mmol), $Eu(OTf)_3$ (28 mg, 0.047 mmol), and toluene (1.0 mL). GC analysis indicated the formation of **4a** in 38% yield.

**Entry 11:** The general procedure was followed, using **3a** (26 mg, 0.087 mmol), $Eu(OTf)_3$ (56 mg, 0.093 mmol), and benzene (1.0 mL). GC analysis indicated the formation of **4a** in 30% yield.

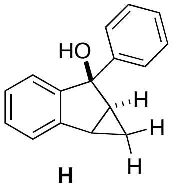
**Entry 12:** The general procedure was followed, using **3a** (12 mg, 0.041 mmol), Eu(OTf)$_3$ (26 mg, 0.044 mmol), and n-hexane (1.0 mL). GC analysis indicated the formation of **4a** in 8% yield.

**Entry 13:** The general procedure was followed, using **3a** (15 mg, 0.051 mmol), Eu(OTf)$_3$ (3 mg, 0.005 mmol), and DCE (1.0 mL). GC analysis indicated the formation of **4a** in 81% yield.

**Entry 14:** The general procedure was followed, using **3a** (14 mg, 0.048 mmol), Eu(OTf)$_3$ (0.33 mg, 0.00055 mmol), and DCE (1.0 mL). GC analysis indicated the formation of **4a** in 50% yield.

**Entry 15:** The general procedure was followed, using **3a** (26 mg, 0.088 mmol), BF$_3$•Et$_2$O (1.2 mg, 0.0090 mmol), and DCE (1.0 mL). GC analysis indicated the formation of **4a** in 7% yield.

**Entry 16:** The general procedure was followed, using **3a** (28 mg, 0.095 mmol), SnCl$_4$ (2.5 mg, 0.0095 mmol), and DCE (1.0 mL). GC analysis indicated the formation of **4a** in 7% yield.



**H**

**Synthesis of Compound H.** Under nitrogen, a vial was charged with **2a** (500 mg, 2.3 mmol) and THF (20 mL). The solution was cooled to 0 $^{o}$C, and tetrabutylammonium fluoride (2.9 mL, 2.9 mmol, 1.0 M THF) was added dropwise. The reaction was allowed to warm to room temperature and stirred overnight. The solvent was then removed under vacuum and the crude mixture was purified via column chromatography (Hex:Ether = 3:1) to give the silicon-free cyclopropyl indanone (218 mg, 66% yield). This material was dissolved in THF (5.0 mL) and transferred dropwise to a solution of PhLi (1.09 mL, 1.97 mmol, 1.8 M in Di-n-butyl ether) in 10.0 mL THF at –78 $^{o}$C. After 16 hours of stirring at room temperature, the reaction was quenched with 10 mL $NH_4Cl$ (saturated, aqueous) followed by addition of 15 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was then removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). The product was isolated as a light yellow oil (260 mg, 78% yield).

$^{1}$H NMR (300 MHz, $CDCl_3$): δ 0.72-0.76 (m, 1H), 1.13-1.18 (m, 1H), 2.11-2.18 (m, 1H), 2.27 (s, 1H), 2.62-2.68 (m, 1H), 7.06-7.46 (m, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 18.8, 23.5, 28.9, 85.1, 123.6, 125.1, 125.5, 126.9, 128.0, 128.2, 145.8, 146.1, 147.6. One aromatic carbon atom has an overlapping $^{13}$C signal.

**Entry 17:** The general procedure was followed, using **H** (8.0 mg, 0.036 mmol), $Eu(OTf)_3$ (1.7 mg, 0.0028 mmol), and DCE (1.0 mL). GC analysis indicated the formation of **4a** in 4% yield.

### *Catalytic Ring-Expansion Rearrangement of 3 (Table 2)*

**General Procedure:** In a nitrogen glovebox, a vial was charged with **3a**, 1,2-dichloroethane, and Eu(OTf)$_3$. The vessel was sealed and stirred at 80 $^{o}$C for 16 h. The reaction was cooled to room temperature, and the mixture was filtered through a silica gel plug with copious ether washings. The solvents were removed under reduced pressure, and the crude material was subjected to either preparatory thin-layer OR column chromatography using hexanes as the eluent.

**Compound 4a [605-02-7] (Entry 1).** The general procedure has been applied using **3a** (178 mg, 0.61 mmol), 1,2-dichloroethane (5.0 mL), and Eu(OTf)$_3$ (36 mg, 0.060 mmol). The product was isolated as an oil (104 mg, 84% yield). $^1$H NMR (300 MHz, CDCl$_3$): δ 7.46-7.60 (m, 9H), 7.90-7.97 (m, 3H).

**Compound 4b [229467-26-9] (Entry 2).** The general procedure has been applied using **3b** (139 mg, 0.412 mmol), 1,2-dichloroethane (5.0 mL), and Eu(OTf)$_3$ (24 mg, 0.040 mmol). The product was isolated as an off-white solid (45 mg, 42% yield). $^1$H NMR (600 MHz, CDCl$_3$): δ 3.99 (s, 3H), 7.44-7.56 (m, 4H), 7.60 (d, J = 7.8 Hz, 2H), 7.90 (d, J = 8.4 Hz, 1H), 7.92 (dd, J = 9, 7.8 Hz, 2H), 8.19 (d, J = 7.8 Hz, 2H).

**Compound 4c [27331-33-5] (Entry 3).** The general procedure has been applied using **3c** (206 mg, 0.640 mmol), 1,2-dichloroethane (5.0 mL), and Eu(OTf)$_3$ (38 mg, 0.063 mmol). The product was isolated as a white solid (69 mg, 46% yield). $^1$H NMR (300 MHz, CDCl$_3$): δ 3.91 (s, 3H), 7.05 (d, J = 8.7 Hz, 2H), 7.40-7.55 (m, 6H), 7.84-7.92 (m, 3H).

**Compound 4d [24382-97-6] (Entry 4).** The general procedure has been applied using **3d** (210 mg, 0.640 mmol), 1,2-dichloroethane (5.0 mL), and Eu(OTf)$_3$ (38 mg, 0.063

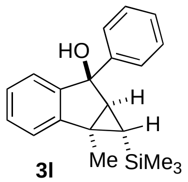
mmol). The product was isolated as an oil (85 mg, 56% yield). $^1$H NMR (600 MHz, $CDCl_3$): δ 7.42-7.58 (m, 8H), 7.88-7.97 (m, 3H).

**Compound 4e [572-52-1] (Entry 5).** The general procedure has been applied using **3e** (200 mg, 0.640 mmol), 1,2-dichloroethane (5.0 mL), and $Eu(OTf)_3$ (38 mg, 0.063 mmol). The product was isolated as an oil (82 mg, 58% yield). $^1$H NMR (300 MHz, $CDCl_3$): δ 7.19-7.28 (m, 3H), 7.42-7.58 (m, 5H), 7.87-7.96 (m, 3H).

**Compound 4f [14476-01-8] (Entry 6).** The general procedure has been applied using **3f** (210 mg, 0.680 mmol), 1,2-dichloroethane (5.0 mL), and $Eu(OTf)_3$ (42 mg, 0.070 mmol). The product was isolated off-white solid (92 mg, 62% yield). $^1$H NMR (300 MHz, $CDCl_3$): δ 2.06 (s, 3H), 7.28-7.59 (m, 9H), 7.93 (dd, J = 3.3, 8.4 Hz, 2H).

**Compound 4g [604-53-5] (Entry 7).** The general procedure has been applied using **3g** (120 mg, 0.350 mmol), 1,2-dichloroethane (5.0 mL), and $Eu(OTf)_3$ (20 mg, 0.033 mmol). The product was isolated as a light yellow solid (60 mg, 67% yield). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.32-7.36 (m, 3H), 7.44-7.66 (m, 8H), 8.00 (d, J = 7.2 Hz, 3H).

***Synthesis of 4l (eq 2)***



**3l**

**Compound 3l.** To a nitrogen flushed and dried flask, 3-methyl-1-indenone (756 mg, 5.25 mmol) and palladium acetate (173 mg, 0.780 mmol) were added. The flask was repurged with $N_2$. Anhydrous benzene (50 mL) was added followed by dropwise addition of $TMSCHN_2$ (7.80 mL, 15.6 mmol, 2.0 M in diethyl ether). The evolution of $N_2$ gas is apparent and the solution turns black. The reaction mixture was allowed to stir at 45 °C for 16 h. At the conclusion of the reaction, the reaction mixture was filtered through a plug of Celite, and the solvent removed under reduced pressure. The crude material was subjected to column chromatography (Hex:$Et_2O$ = 10:1). The isolated material was contaminated with unreacted 3-methyl-1-indenone. This mixture (500 mg in 10 mL THF) was added to phenyllithium (1.61 mL, 2.90 mmol, 1.8 M in di-*n*-butyl ether) at –78 $^{o}$C. The reaction was brought to room temperature after 1 hour and left stirring for 16 more hours. At the conclusion of the reaction, 10 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 50 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:$CH_2Cl_2$ = 1:1). Compound **3l** was isolated as a pale yellow oil (295 mg, 18% yield).

$^1$H NMR (300 MHz, $CDCl_3$): d  0.13 (apparent s, 10H), 1.70 (s, 3H), 1.94 (d, J = 5.4Hz, 1H), 2.17 (s, 1H), 7.05-7.46 (m, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ –0.6, 15.1, 27.1, 33.9, 40.5, 85.0, 121.4, 125.1, 125.6, 126.7, 127.7, 128.2, 146.0, 147.2, 151.0. One aromatic carbon atom has an overlapping $^{13}$C signal. IR ($CH_2Cl_2$): 3587 s (alcohol), 3473 b, (alcohol).  HRMS (EI) calcd for $C_{20}H_{24}OSi$ (M+) 308.15965, found 308.15917.

**Compound 4l [13280-69-8].** The general procedure for the synthesis of compound **4a** has been applied using **3l** (253 mg, 0.821 mmol), 1,2-dichloroethane (5.0 mL), and $Eu(OTf)_3$ (52 mg, 0.087 mmol). The product was isolated as an oil (152 mg, 85% yield). ). $^1$H NMR (300 MHz, $CDCl_3$): δ 2.78 (s, 3H), 7.36-7.59 (m, 9H), 7.945 (d, J = 8.4 Hz, 1H),8.091(d,J=7.8Hz,1H).

***Catalytic Ring-Expansion Rearrangement of Hindered Precursors (Table 3)***

**Compound 4h [29304-63-0] (Entry 1).** The general procedure for the synthesis of **4a** has been applied using **3h** (240 mg, 0.780 mmol), 1,2-dichloroethane (5.0 mL), and Eu(OTf)$_3$ (47 mg, 0.078 mmol). The product was isolated as an oil (120 mg, 70% yield). $^1$H NMR indicated a 93:7 ratio of regioisomers **4h:5h**. NMR of the major isomer: $^1$H NMR (300 MHz, CDCl$_3$) δ 2.36 (s, 3H), 7.37-7.63 (m, 9H), 7.92 (dd, J = 8.4, 8.7 Hz, 2H).

**Compound 4i [93870-58-7] (Entry 2).** The general procedure for the synthesis of **4a** has been applied using **3i** (225 mg, 0.700 mmol), 1,2-dichloroethane (5.0 mL), and Eu(OTf)$_3$ (47 mg, 0.078 mmol). The product was isolated as an oil (113 mg, 70% yield). $^1$H NMR indicated a 93:7 ratio of regioisomers **4i:5i**. NMR of the major isomer: $^1$H NMR (300 MHz, CDCl$_3$) δ 2.04 (s, 3H), 2.28 (s, 3H), 7.23 (d, J = 6.9Hz, 1H), 7.35-7.54 (m, 7H), 7.92 (dd, J = 8.4, 9.3 Hz, 2H).

**Compound 4j [910784-96-2] (Entry 3).** The general procedure for the synthesis of **4a** has been applied using **3j** (183 mg, 0.540 mmol), 1,2-dichloroethane (5.0 mL), and Eu(OTf)$_3$ (33 mg, 0.055 mmol). The product was isolated as an oil (110 mg, 82% yield). $^1$H NMR indicated a 83:17 ratio of regioisomers **4j:5j**. NMR of the major isomer: $^1$H NMR (300 MHx, CDCl$_3$) δ 2.31 (s, 3H), 3.74 (s, 3H), 7.12-7.22 (m, 3H), 7.39-7.52 (m, 5H), 7.89 (dd, J = 8.4, 5.1 Hz, 2H).

**Compound 4k (Entry 4).** The general procedure for the synthesis of **4a** has been applied using **3k** (243 mg, 0.660 mmol), 1,2-dichloroethane (5.0 mL), and Eu(OTf)$_3$ (40 mg, 0.067 mmol). The product was isolated as an oil (139 mg, 76% yield). $^1$H NMR indicated a 64:36 ratio of regioisomers **4k:5k**.

Characterization for 4k: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.28 (s, 3H), 3.68 (s, 6H), 6.78 (d, J = 8.1 Hz, 2H), 7.30-7.52 (m, 5H), 7.86 (dd, J = 4.2, 8.4 Hz, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 20.7, 55.9, 104.5, 124.8, 125.9, 126.4, 127.5, 128.2, 128.9, 129.5, 131.2, 132.3, 132.4, 133.2, 134.8, 158.6. IR (CH$_2$Cl$_2$): 3051, 3002, 1248. HRMS (EI) calcd for $C_{19}H_{18}O_2$ (M+) 278.13068, found 278.13055.

## Bridge to Chapter III

In Chapter II we discussed the introduction of our rearrangement-based method and demonstrated an initial substrate scope with one example of tetra-*ortho*-substitution. Unfortunately, we observed poor regioselectivity with tri and tetra-*ortho*-substituted naphthalenes. Chapter III begins by addressing this key shortcoming through another GC-based optimization, followed by a thorough exploration of tetra-*ortho*-substituted aryl naphthalenes, culminating in a tri-isopropyl-substituted TOAN. We focus on both the addition of sterically congested aryl nucleophiles to an $\alpha$-methyl and isopropyl indanone followed by subsequent rearrangement *via* our improved optimized conditions. We were also able to demonstrate semi-one pot synthesis of our desired naphthalenes. We end the chapter with our initial results on an asymmetric transformation. The material described in Chapter III was published in *Chemical Communications* in 2011 on page 286-288.

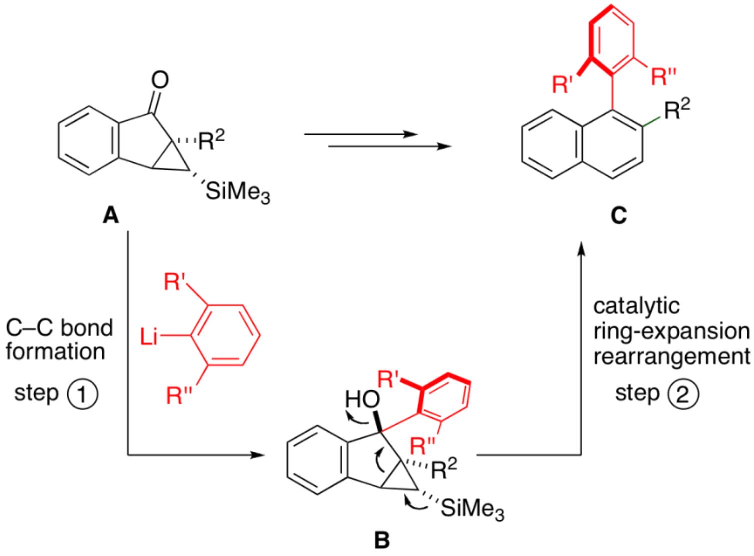
# CHAPTER III

# PUSHING THE LIMITS OF STERIC DEMAND AROUND A BIARYL AXIS: SYNTHESIS OF TETRA-*ORTHO*-SUBSTITUTED BIARYL NAPHTHALENES

This work was published in volume 47 of the journal *Chemical Communications* in August 2010. Sam Klonoski was involved in starting material preparation, Dr. Lev N. Zakharov performed crystal structure analysis, and Prof. Shih-Yuan Liu was the P.I. I was the primary contributor for the manuscript. This Chapter includes Co-Authored material.

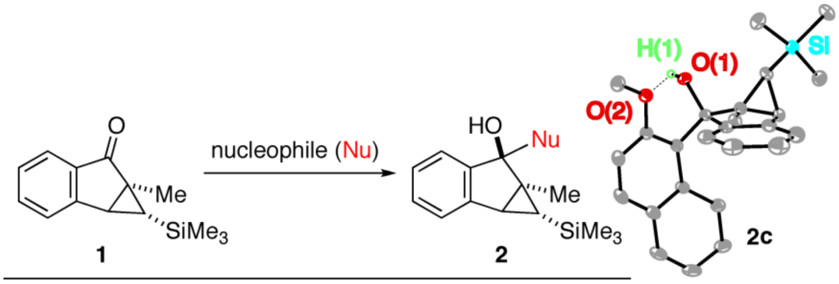
## Results and Discussion

Despite the significant advances that have been made to date, novel strategies for the generation of tetra-*ortho*-substituted biaryls are still highly desired. We have been pursuing a rearrangement-based approach for the synthesis of substituted biaryl naphthalenes. Scheme 1 illustrates our strategy in which the addition of an arene nucleophile to the starting material **A** is followed by a ring-expansion rearrangement to furnish the desired biaryl naphthalene **C** via a cyclopropyl carbinol intermediate **B**. The distinguishing feature of our approach is that the key C–C bond-forming step is accomplished through a simple addition of a nucleophile to a carbonyl. Given the strong thermodynamic driving force for this nucleophilic addition,[92] we envision that our method could serve as a potential method for the construction of tetra-*ortho*-substituted biaryl naphthalenes. In this chapter, we demonstrate that a range of tetra-*ortho*-substituted biaryl naphthalenes can be produced via our method, including a very hindered tetra-*ortho*-substituted biaryl naphthalene bearing three isopropyl groups in the *ortho* positions.

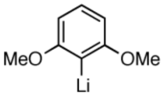
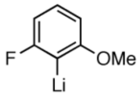
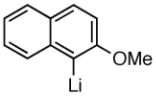
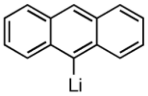
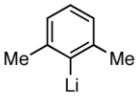
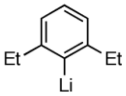
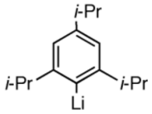
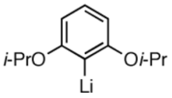


**Scheme 1.** Ring-expansion rearrangement strategy for the synthesis of tetra-*ortho*-substituted aryl naphthalenes.

We first investigated the feasibility of the nucleophilic addition to starting material **A** (Step 1 in Scheme 1). We chose cyclopropyl carbonyl compound **1** (Table 1) as a representative electrophile for our survey. As can be seen from Table 1, the isolated yields of the addition products **2** are relatively independent of the electronic nature (entries 1-5) as well as the steric demand (entry 1 vs. entry 8, and entries 5-7) of the nucleophiles. A consistent yield of ~70% yield was observed. Somewhat surprisingly, the highest isolated yield (81%) for the generation of **2** resulted from the addition of the largest nucleophile, 2,4,6-triisopropylphenyllithium (entry 7).This nucleophilic addition reaction is highly diastereoselective. Only one single diastereomer was observed for each of the products **2** (as analyzed by $^1$H NMR). We have structurally characterized the adduct between **2** and 2-methoxy-1-naphthyllithium, i.e., **2c**, via single crystal X-ray crystallography. The relative stereochemistry of the structure is consistent with an approach of the nucleophile opposite the blocking silylcyclopropane group (see Table 1). Interestingly, compound **2c** adopts a conformation in the solid state where the carbinol proton H(1) engages in hydrogen bonding with the oxygen O(2) of the methoxynaphthalene (O(2)–H(1) = 1.83(2) Å, sum of van der Waals radii = 2.72 Å).



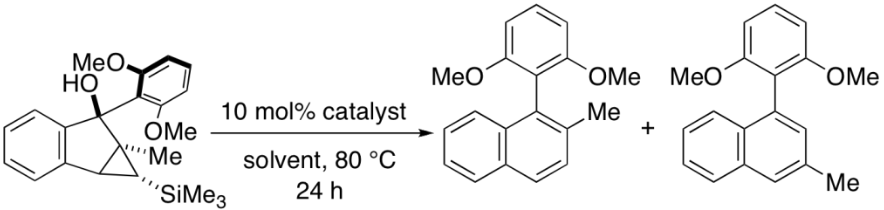
**1** **2** **2c**

| entry | Li–Nu | product | yield %$^a$ |
|---|---|---|---|
| 1 |  | **2a** | 70 |
| 2 |  | **2b** | 71 |
| 3 |  | **2c** | 67 |
| 4 |  | **2d** | 70 |
| 5 |  | **2e** | 68 |
| 6 |  | **2f** | 67 |
| 7 |  | **2g** | 81 |
| 8 |  | **2h** | 68 |

[a] Isolated yield, average of two runs.

**Table 1.** Nucleophilic Addition to **1**

Having established the synthesis of an array of rearrangement precursors **2**, we turned our attention to the catalytic ring-expansion rearrangement. We determined that the rearrangement of cyclopropyl carbinol **2a** in the presence of a catalytic amount of Lewis acid furnished the desired tetra-ortho-substituted biaryl **3a**, however as a 73:27 mixture with its undesired tri-ortho-substituted isomer **4a** (Table 2, entry 1).11 We discovered that the choice of solvent has a dramatic influence on regioselectivity. When the reaction is performed in toluene instead of 1,2-dichloroethane, the ratio of **3a** to **4a** improves to 93:7 (Table 2, entry 2). Other solvents that we screened did not improve the yield and/or the regioselectivity significantly (Table 2, entries 3-8). Interestingly, a reversal of regioselectivity was observed when acetonitrile was used as the solvent (Table 2, entry 8). We also screened a number of Lewis acids (Table 2, entries 9-12) and found europium triflate (entry 2) to be the most efficient catalyst under our conditions.



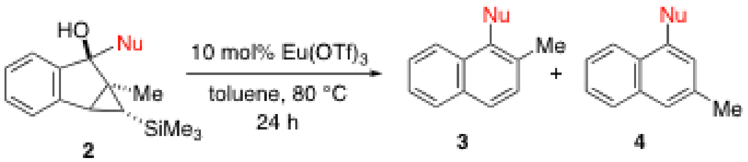
**2a** **3a** **4a**

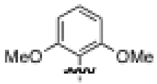
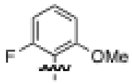
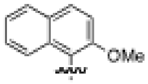
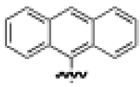
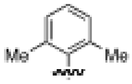
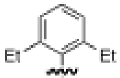
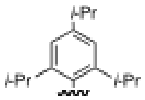
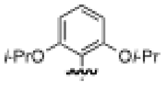
| entry | catalyst | solvent | yield %[a] | **3a** : **4a**[b] |
|---|---|---|---|---|
| 1 | $Eu(OTf)_3$ | 1,2-dichloroethane | 68 | 73:27 |
| **2** | **$Eu(OTf)_3$** | **toluene** | **78** | **93:7** |
| 3 | $Eu(OTf)_3$ | THF | 54 | 92:8 |
| 4 | $Eu(OTf)_3$ | DMF | 29 | 76:24 |
| 5 | $Eu(OTf)_3$ | *t*-BuOH | 42 | 82:18 |
| 6 | $Eu(OTf)_3$ | PhCl | 53 | 96:4 |
| 7 | $Eu(OTf)_3$ | 1,3-dichlorobenzene | 52 | 93:7 |
| 8 | $Eu(OTf)_3$ | MeCN | 15 | 25:75 |
| 9 | $Sm(OTf)_3$ | toluene | 76 | 85:15 |
| 10 | $Er(OTf)_3$ | toluene | 79 | 81:19 |
| 11 | $SnCl_4$ | toluene | 31 | 40:60 |
| 12 | $BF_3 \cdot Et_2O$ | toluene | 29 | 35:65 |

[a] GC yield (**3a** + **4a**) vs. a calibrated internal standard, average of two runs.
[b] Determined by GC.

**Table 2.** Optimization Survey for the Regioselective Synthesis of **3a**

With an optimized rearrangement protocol established, we subjected the various rearrangement precursors **2** from Table 1 to these conditions to test the scope of our method. We were pleased to see that a variety of substrates rearranged to furnish the desired biaryl naphthalenes in moderate to good yields (Table 3). With the exception of entry 1 (Nu = 2,6-dimethoxyphenyl), which gave a 93:7 mixture of regioisomers, all other substrates that we tested gave the tetra-ortho-substituted isomer exclusively. Noteworthy is the rearrangement of **2g**, which produced a tetra-ortho-substituted biaryl bearing two *ortho*-isopropyl groups in 86% yield.

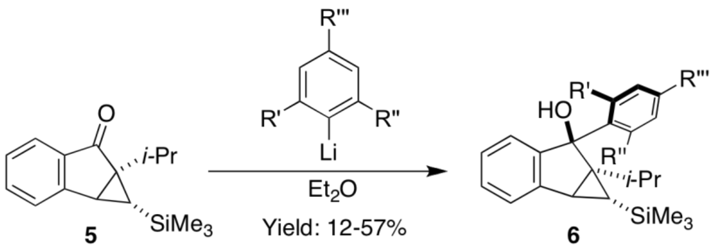


| entry | precursor | Nu | yield %[a] | **3** : **4**[b] |
|---|---|---|---|---|
| 1 | **2a** |  | 71 | 93:7 |
| 2 | **2b** |  | 43 | >95:5 |
| 3 | **2c** |  | 63 | >95:5 |
| 4 | **2d** |  | 55 | >95:5 |
| 5 | **2e** |  | 79 | >95:5 |
| 6 | **2f** |  | 78 | >95:5 |
| 7 | **2g** |  | 86 | >95:5 |
| 8 | **2h** |  | 79 | >95:5 |

[a] Isolated yield, average of two runs. [b] Determined by $^{1}$H NMR.

**Table 3.** Rearrangement of **2** Under Optimized Conditions

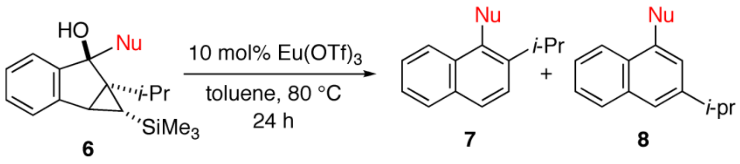
Encouraged by these results, we sought to push the limits of steric demand around the biaryl axis by replacing the α-methyl group in **1** with an isopropyl group. The corresponding precursor **5** (Scheme 2) can be synthesized in a few steps from commercially available indanone. Scheme 2 shows that a series of bis-*ortho*-substituted phenyllithium nucleophiles add to the carbonyl electrophile **5** in modest yield.

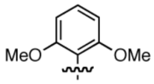
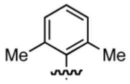
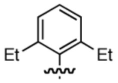
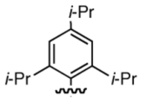


**6a** (R',R'' = OMe; R''' = H); **6b** (R',R'' = Me; R''' = H);
**6c** (R',R'' = Et; R''' = H); **6d** (R',R'',R''' = *i*-Pr)

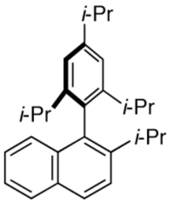
**Scheme 2.** Nucleophilic addition to **5**.

We were very pleased to observe that intermediates **6a**-**6d** underwent catalytic ring opening rearrangement under our optimized conditions to yield hindered tetra-*ortho*-substituted biaryl naphthalenes. As can be seen from Table 4, the isolated yields are independent of the steric demand around the biaryl axis. "Nucleophiles" (Nu in Table 4) containing methoxy, methyl, ethyl, and isopropyl groups in the 2,6-positions rearrange to produce the desired biaryl in reasonable yield (entries 1-4). We were also very pleased to see that the undesired regioisomer **8** is not observed under our reaction conditions. Noteworthy is the synthesis of **7d**, which is a tetra-*ortho*-substituted biaryl containing three *ortho*-isopropyl substituents. To the best of our knowledge, it is the most sterically encumbered biaryl naphthalene that has been synthesized to date. We have structurally characterized **7d** via single crystal X-ray diffraction (see Table 4, bottom), thus unambiguously establishing its identity.

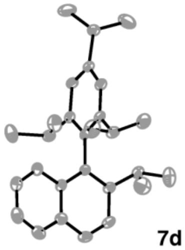


| entry | precursor | Nu | yield %[a] | **7** : **8**[b] |
|---|---|---|---|---|
| 1 | **6a** |  | 63 | >95:5 |
| 2 | **6b** |  | 73 | >95:5 |
| 3 | **6c** |  | 73 | >95:5 |
| 4 | **6d** |  | 76 | >95:5 |

[a] Isolated yield, average of two runs. [b] Determined by $^1$H NMR.



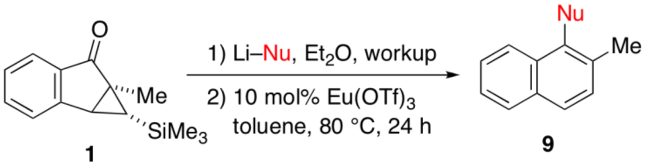
**7d**

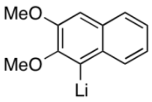
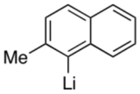


**7d**

**Table 4.** Rearrangement of **6** Under Optimized Conditions

In order to improve the utility of our synthetic method, we attempted the rearrangement without isolating the cyclopropyl carbinol intermediate (Compound B in Scheme 1). When **1** was treated with organolithium reagents followed by catalytic ring expansion rearrangement, we observed the formation of the desired biaryl naphthalenes **9** in up to 65% yield over two steps (Table 5). The undesired tri-*ortho*-substituted biaryl was not observed under these conditions.



| entry | Li–Nu | product | yield %[a] |
|---|---|---|---|
| 1 |  | **9a** | 61 |
| 2 |  | **9b** | 65 |

[a] Isolated yield, average of two runs.

**Table 5.** Aryl-Naphthalene Synthesis Without Isolation of Intermediate

We have initiated preliminary studies toward an asymmetric version of this process. To this end, we successfully isolated optically pure **1** via semi-preparatory chiral HPLC. Treatment of optically pure **1** with 2-methoxynaphthyllithium and subsequent catalytic rearrangement with Eu(OTf)$_3$ furnished the desired tetra-ortho-substituted biaryl naphthalene **3c** in 54% isolated yield (over two steps) in 52% ee. Current efforts are geared toward optimizing the efficiency of this asymmetric process and developing a better understanding its mechanism.

## Experimental

### *General*

All oxygen and moisture-sensitive manipulations were carried out under an inert atmosphere using either standard Schlenk techniques or a glove box.

THF, $Et_2O$, toluene, and pentane were purified by passing through a neutral alumina column under argon. Anhydrous benzene, 1,2-dichloroethane, acetonitrile, and hexane were purchased from Aldrich and used as received. All other reagents were purchased (Aldrich, TCI, Alfa Aesar, or Acros) and used as received. 2-methyl-1-indenone and 2-isopropyl-1-indenone were prepared according to known procedures.[93]

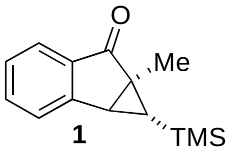
Thin layer chromatography and preparatory chromatography were performed on Silicycle glass backed plates with UV indicator. Column chromatography was performed on Silicycle silica gel P60.

$^{1}H$ NMR spectra were recorded on a Varian Unity/Inova 300 or Varian Unity/Inova 600 spectrometer. $^{13}C$ NMR spectra were recorded on a Varian Unity/Inova 300 or Varian Unity/Inova 500 spectrometer. All spectra were referenced to their respective solvents: $CDCl_3$ 7.27 ppm, and $CD_2Cl_2$ 5.32 ppm. Gas chromatography was performed on an Agilent 6850 Series II GC with an auto loader using ChemStation.

IR spectra were recorded on a Nicolet Magna 550 FT-IR instrument with OMNIC software.

High-resolution mass spectroscopy data were obtained at the Mass Spectroscopy Facilities and Services Core of the Environmental Health Sciences Center at Oregon State University. Financial support for this facility has been furnished in part by the National Institute of Environmental Health Sciences, NIH (P30 ES00210).

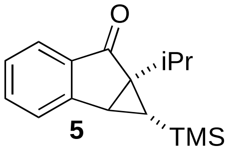
### *Synthesis of Silylcyclopropyl Indanones 1 and 5*



**1**

**Compound 1 [1072849-07-0].** 2-methyl-1-indenone (1.90 g, 13.1 mmol) and palladium acetate (289 mg, 1.31 mmol) were added to an oven-dried flask under nitrogen. Anhydrous benzene (100 mL) was added followed by dropwise addition of $TMSCHN_2$ (20.0 mL, 39.0 mmol, 2.0 M in diethyl ether). The evolution of $N_2$ gas is apparent and the solution turned black. The reaction mixture was allowed to stir at room temperature for 16 h. At the conclusion of the reaction, the reaction mixture was filtered through a plug of Celite, and the solvent removed under reduced pressure. The crude material was subjected to column chromatography (Hex:$Et_2O$ = 9:1), and **1** was isolated as a light yellow solid (2.50 g, 84 % yield).

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.13 (s, 9H), 0.85 (d, J = 4.8 Hz, 1H), 1.58 (s, 3H), 2.65 (d, J = 4.8 Hz, 1H), 7.21-7.45 (m, 3H), 7.64 (d, J = 8.1 Hz, 1H).

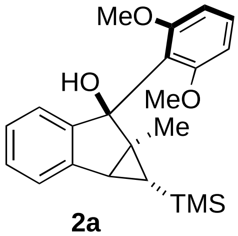


**5**

**Compound 5.** The procedure for the preparation of **1** has been used for the synthesis of **5** employing 2-isopropyl-1-indenone (762 mg, 4.40 mmol), palladium acetate (98 mg, 0.44 mmol), 44.0 mL benzene, and $TMSCHN_2$ (6.50 mL, 13.1 mmol, 2.0 M in diethyl ether). The reaction was run at 50 $^o$C for 3h. Compound **5** was isolated as a pale yellow solid (872 mg, 76 % yield).

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.14 (s, 9H), 0.82 (d, J = 5.1 Hz, 1H), 1.14 (d, J = 6.6 Hz, 3H), 1.51 (d, J = 6.6 Hz, 3H), 1.78 (septet, J = 7.2 Hz, 1H), 2.51 (d, J = 4.8 Hz, 1H), 7.18-7.43 (m, 3H), 7.60 (d, J = 7.8 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ –0.3, 20.3, 20.5, 29.4, 30.9, 47.1, 47.5, 123.3, 124.8, 126.1, 133.2, 134.6, 156.3, 204.4. IR (Neat): 1715 s, (carbonyl).

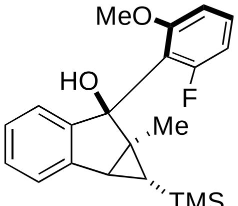
***Nucleophillic Addition to 1 (Table 1):***



**2a**

**Compound 2a (Entry 1) [1072849-18-3].** An oven-dried flask was charged with 50.0 mL anhydrous $Et_2O$ and *m*-dimethoxybenzene (750 mg, 5.42 mmol). *n*-BuLi (2.0 mL, 5.0 mmol, 2.5 M in hexanes) was added dropwise, and the reaction was allowed to stir for 24h. The ether was removed under reduced pressure to yield a white solid. Anhydrous THF was added (15.0 mL) and the reaction was cooled to –78 $^{o}$C. Indanone **1** (500 mg, 2.17 mmol) in THF (5.0 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred for 24h. At the conclusion of the reaction, 10 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 100 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). Compound **2a** was isolated as a white solid (596 mg, 75% yield). A second run had a yield of 64%.

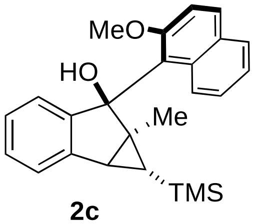
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.13 (s, 9H), 0.55 (d, J = 5.1 Hz, 1H), 1.10 (s, 3H), 2.27 (d, J = 5.4 Hz, 1H), 3.09 (s, 3H), 4.01 (s, 3H), 6.45 (s, 1H), 6.51 (d, J = 8.1 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 7.00-7.08 (m, 3H), 7.16-7.24 (m, 2H).



**2b**

**Compound 2b (Entry 2).** An oven-dried flask was charged with 2.0 mL anhydrous THF and *m*-fluoroanisole (219 mg, 1.74 mmol). The reaction was cooled to –78 $^{o}$C, and *n*-BuLi (0.66 mL, 1.7 mmol, 2.5 M in hexanes) was added dropwise. The reaction was allowed to stir for 2 hours at –78 °C. Subsequently, indanone **1** (200 mg, 0.870 mmol) in THF (2.4 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred for 24h. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). Compound **2b** was isolated as a light yellow oil (229 mg, 73% yield). A second run had a yield of 68%.

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.12 (s, 9H), 0.52 (d, J = 5.1 Hz, 1H), 1.13 (s, 3H), 2.31 (d, J = 4.8 Hz, 1H), 4.06 (s, 3H), 6.15 (s, 1H), 6.59 (dd, J = 8.1,1.8 Hz, 1H) 6.84 (d, J = 8.7 Hz, 1H) 7.07-7.28 (m, 5H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ -0.3, 15.7, 28.2, 35.2, 36.8, 56.8, 88.3, 107.7, 110.0, 110.3, 121.9, 125.3, 125.6, 127.2, 128.5, 128.7, 147.7 (d, $^1J_{CF}$ = 82 Hz), 158.4, 161.7. IR (Neat): 3501 s, (alcohol).

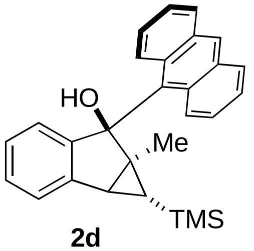


**2c**

**Compound 2c (Entry 3).** An oven-dried flask was charged with 2.0 mL anhydrous $Et_2O$ and 1-bromo-2-methoxynaphthalene (412 mg, 1.74 mmol). *n*-BuLi (0.66 mL, 1.7 mmol, 2.5 M in hexanes) was added dropwise at room temperature, and the reaction was allowed to stir for 15 minutes. The reaction was cooled to –78 °C, and indanone **1** (200 mg, 0.870 mmol) in $Et_2O$ (2.4 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred for 24h. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). Compound **2c** was isolated as a white solid (236 mg, 70% yield). A second run had a yield of 63%. Crystals suitable for diffraction were obtained by slow evaporation of the solvent of a concentrated solution of **2c** in dichloromethane at –20 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.17 (s, 9H), 1.03 (d, J = 5.4 Hz, 1H), 1.12 (s, 3H), 2.48 (d, J = 5.1 Hz, 1H), 4.16 (s, 3H), 6.72 (s, 1H), 6.81 (d, J = 7.2 Hz, 1H) 6.97-7.41 (m, 7H) 7.72 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.7 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ –0.3, 16.6, 28.3, 36.1, 38.7, 57.3, 89.8, 114.1, 122.7, 123.2, 125.2, 126.0, 126.2, 126.4, 126.5, 127.5, 128.1, 129.9, 130.1, 132.4, 147.4, 149.9, 155.2. IR (Neat): 3487 s, (alcohol).

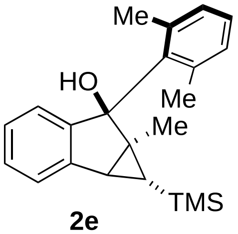
**Compound 2d (Entry 4).** An oven-dried flask was charged with 2.0 mL anhydrous $Et_2O$ and 9-bromoanthracene (447 mg, 1.74 mmol). *n*-BuLi (0.66 mL, 1.7 mmol, 2.5 M in hexanes) was added dropwise at room temperature, and the reaction was allowed to stir for 15 minutes. The reaction was cooled to –78 °C, and indanone **1** (200 mg, 0.870 mmol) in $Et_2O$ (2.4 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred for 24h. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over



**2d**

$MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). Compound **2d** was isolated as an off-white solid (246 mg, 69% yield). A second run had a yield of 71%.

$^1$H NMR (300 MHz, $CDCl_3$): δ –0.17 (s, 9H), 1.04 (d, J = 5.3 Hz, 1H), 1.90 (s, 3H), 2.40 (d, J = 4.8 Hz, 1H), 2.42 (s, 1H), 6.99-7.51 (m, 10H), 7.99 (d, J = 27 Hz, 2H), 9.85 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ –0.5, 16.9, 26.8, 34.8, 42.7, 89.9, 123.8, 124.2, 126.0, 128.4, 129.3, 130.0, 130.4, 136.1, 144.2, 151.2, the remaining 10 carbon signals appear as broad peaks. IR (Neat): 3543 s, (alcohol).

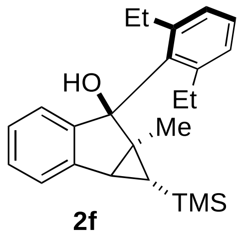


**2e**

**Compound 2e (Entry 5).** An oven-dried flask was charged with 2.0 mL anhydrous $Et_2O$ and 1-bromo-2,6-dimethylbenzene (321 mg, 1.74 mmol). *n*-BuLi (0.66 mL, 1.7 mmol, 2.5 M in hexanes) was added dropwise at room temperature, and the reaction was allowed to stir for 15 minutes. The reaction was cooled to –78 $^o$C, and indanone **1** (200 mg, 0.870 mmol) in $Et_2O$ (2.35 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred for 24h. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). Compound **2e** was isolated as an oil (208 mg, 71% yield). A second run had a yield of 64%.

$^1$H NMR (300 MHz, $CDCl_3$): δ –0.01 (s, 9H), 0.56 (d, J = 5.1 Hz, 1H), 1.65 (s, 3H), 1.68 (s, 3H), 1.91 (s, 1H), 2.88 (s, 3H), 6.91-7.31 (m, 7H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ –

0.4, 16.0, 16.1, 25.7, 26.3, 26.6, 42.5, 88.8, 123.5, 125.5, 125.8, 126.2, 128.1, 130.8, 131.5, 135.3, 139.4, 139.7, 144.9, 150.2. IR (Neat): 3535 s, (alcohol).

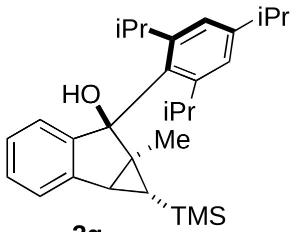


**2f**

**Compound 2f (Entry 6).** An oven-dried flask was charged with 2.0 mL anhydrous $Et_2O$ and 1-bromo-2,6-diethylbenzene (241 mg, 1.13 mmol). The reaction was cooled to –78 °C, and *t*-BuLi (1.3 mL, 2.3 mmol, 1.7 M in pentane) was added dropwise. The reaction was allowed to stir for 2 hours at –78 °C. Subsequently, the reaction was warmed to ambient temperature for 30 minutes before it was cooled to –78 °C again. Indanone **1** (200 mg, 0.870 mmol) in $Et_2O$ (2.4 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred for 24h. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 9:1). Compound **2f** was isolated as a clear oil (224 mg, 71% yield). A second run had a yield of 63%.

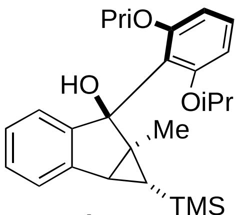
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.02 (s, 9H), 0.42 (d, J = 4.5 Hz, 1H), 0.91 (t, J = 7.5 Hz, 3H), 1.36 (t, J = 7.2 Hz, 3H), 1.62 (s, 3H), 1.81 (s, 1H), 1.82-1.90 (m, 2H), 2.24 (d, J = 4.8 Hz, 1H), 2.84-2.91 (m, 1H), 3.60-3.67 (m, 1H), 7.04-7.32 (m, 7H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ –0.4, 15.4, 17.8, 19.2, 26.6, 29.0, 30.4, 33.9, 41.4, 86.6, 123.3, 124.5, 125.7, 126.5, 127.9, 128.8, 130.1, 138.6, 142.0, 144.4, 146.4, 151.0. IR (Neat): 3591 s, (alcohol).

**Compound 2g (Entry 7).** An oven-dried flask was charged with 2.0 mL anhydrous $Et_2O$ and 1-bromo-2,4,6-triisopropylbenzene (320 mg, 1.13 mmol). The reaction was cooled to –78 °C and *t*-BuLi (1.3 mL, 2.3 mmol, 1.7 M in pentane) was added dropwise. The reaction was allowed to stir for 2 hours at –78 °C. Subsequently, the reaction was warmed to ambient temperature for 30 minutes before it was cooled to –78 °C again. Indanone **1** (200 mg, 0.870 mmol) in $Et_2O$ (2.4 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred for 24h. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 9:1). Compound **2g** was isolated as a white solid (302 mg, 80% yield). A second run had a yield of 81%.



**2g**

$^1H$ NMR (300 MHz, $CDCl_3$): δ 0.05 (s, 9H), 0.54 (d, J = 4.8 Hz, 1H), 0.89-0.92 (m, 6H), 1.26 (d, J = 6.9 Hz, 3H), 1.30 (d, J = 6.9 Hz, 6H), 1.40 (d, J = 3.3 Hz, 3H), 1.67 (s, 3H), 1.80 (s, 1H), 2.09 (septet, J = 6.3 Hz, 1H), 2.21 (d, J = 4.8 Hz, 1H), 2.91 (septet, J = 7.2 Hz, 1H), 4.38 (septet, J = 6.9 Hz, 1H), 6.95-7.29 (m, 6H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ –0.3, 15.6, 23.7, 23.8, 24.0, 24.1 26.0, 26.5, 26.9, 30.6, 30.8, 33.5, 34.3, 40.7, 88.4, 123.0, 124.0, 124.5, 125.5, 127.7, 135.7, 141.2, 143.9, 146.2, 146.7, 151.2, 151.6. IR (Neat): 3425 s, (alcohol).



**2h**

**Compound 2h (Entry 8).** An oven-dried flask was charged with 10.0 mL anhydrous $Et_2O$ and *m*-diisopropylbenzene (337 mg, 1.74 mmol). *n*-BuLi (2.0 mL, 5.0 mmol, 2.5 M in hexanes) was added dropwise at room temperature, and the reaction was allowed to stir for 24h. The ether was removed under reduced pressure to yield a white solid. Anhydrous THF was added (2.0 mL) and the reaction was cooled to –78 $^{o}$C. Subsequently, indanone **1** in THF (2.4 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred for 24h. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). Compound **2h** was isolated as a white solid (254 mg, 69% yield). A second run had a yield of 66%.

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.14 (s, 9H), 0.55 (d, J = 6.0 Hz, 3H), 0.61 (d, J = 5.7 Hz 1H), 0.99 (d, J = 6.3 Hz, 3H), 1.13 (s, 3H), 1.47-1.53 (m, 6H), 4.26 (septet, J = 6.0 Hz, 1H), 4.79 (septet, J = 6.3 Hz, 1H), 6.41 (d, J = 8.1 Hz, 1H), 6.64 (d, J = 8.1 Hz, 1H) 6.98-7.18 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ –0.3, 16.2, 19.9, 21.3, 22.0, 22.3, 27.1, 36.1, 37.3, 67.8, 72.3, 89.0, 105.7, 106.6, 121.7, 122.0, 124.7, 125.0, 126.0, 127.8, 148.9, 149.9, 155.8, 156.8. IR (Neat): 3466 s, (alcohol).

### ***Optimization Survey for the Regioselective Synthesis of 3a (Table 2):***

*General Procedure*: In a glovebox, a vial was charged with compound **2a**, Lewis acid, and the solvent. The reaction vial was immersed into an oil bath at 80 °C for 24 hours. At the conclusion of the reaction, hexadecane as an internal GC standard was added via syringe (25.0 μL, 19.2 mg), and the mixture was filtered through a silica plug with copious ether washing. An aliquot of the resulting solution was subjected to GC analysis. All GC yields (Table 2) have been corrected for response factors. Because the yields that are reported in Table 2 are the average of two runs, the yields that are reported below for a specific experiment may differ from the values presented in the table.

**Entry 1:** The general procedure was followed, using **2a** (20 mg, 0.054 mmol), 1,2-dichloroethane (0.50 mL), and Eu(OTf)$_3$ (3.2 mg, 0.0054 mmol). GC analysis indicated the formation of the biaryl naphthalenes (**3a** + **4a**) in 70% yield in 73:27 (**3a:4a**) ratio.

**Entry 2:** The general procedure was followed, using **2a** (20 mg, 0.054 mmol), Eu(OTf)$_3$ (3.2 mg, 0.0054 mmol), and toluene (0.50 mL). GC analysis indicated the formation of the biaryl naphthalenes (**3a** + **4a**) in 81% yield in 92:8 (**3a:4a**) ratio.

**Entry 3:** The general procedure was followed, using **2a** (20 mg, 0.054 mmol), Eu(OTf)$_3$ (3.2 mg, 0.0054 mmol), and THF (0.50 mL). GC analysis indicated the formation of the biaryl naphthalenes (**3a** + **4a**) in 53% yield in 91:9 (**3a:4a**) ratio.

**Entry 4:** The general procedure was followed, using **2a** (20 mg, 0.054 mmol), Eu(OTf)$_3$ (3.2 mg, 0.0054 mmol), and DMF (0.50 mL). GC analysis indicated the formation of the biaryl naphthalenes (**3a** + **4a**) in 30% yield in 79:21 (**3a:4a**) ratio.

**Entry 5:** The general procedure was followed, using **2a** (20 mg, 0.054 mmol), Eu(OTf)$_3$ (3.2 mg, 0.0054 mmol), and *t*-BuOH (0.50 mL). GC analysis indicated the formation of the biaryl naphthalenes (**3a** + **4a**) in 41% yield in 81:19 (**3a:4a**) ratio.

**Entry 6:** The general procedure was followed, using **2a** (20 mg, 0.054 mmol), Eu(OTf)$_3$ (3.2 mg, 0.0054 mmol), and chlorobenzene (0.50 mL). GC analysis indicated the formation of the biaryl naphthalenes (**3a** + **4a**) in 47% yield in 95:5 (**3a:4a**) ratio.

**Entry 7:** The general procedure was followed, using **2a** (20 mg, 0.054 mmol), Eu(OTf)$_3$ (3.2 mg, 0.0054 mmol), and 1,3-dichlorobenzene (0.50 mL). GC analysis indicated the formation of the biaryl naphthalenes (**3a** + **4a**) in 48% yield in 93:7 (**3a:4a**) ratio.

**Entry 8:** The general procedure was followed, using **2a** (20 mg, 0.054 mmol), Eu(OTf)$_3$ (3.2 mg, 0.0054 mmol), and MeCN (0.50 mL). GC analysis indicated the formation of the biaryl naphthalenes (**3a** + **4a**) in 15% yield in 27:73 (**3a:4a**) ratio.

**Entry 9:** The general procedure was followed, using **2a** (20 mg, 0.054 mmol), Sm(OTf)$_3$ (3.2 mg, 0.0054 mmol), and toluene (0.50 mL). GC analysis indicated the formation of the biaryl naphthalenes (**3a** + **4a**) in 78% yield in 80:20 (**3a:4a**) ratio.

**Entry 10:** The general procedure was followed, using **2a** (20 mg, 0.054 mmol), Er(OTf)$_3$ (3.2 mg, 0.0054 mmol), and toluene (0.50 mL). GC analysis indicated the formation of the biaryl naphthalenes (**3a** + **4a**) in 80% yield in 82:18 (**3a:4a**) ratio.

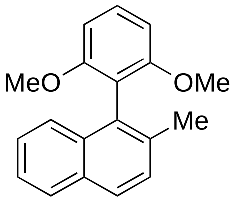
**Entry 11:** The general procedure was followed, using **2a** (20 mg, 0.054 mmol), $SnCl_4$ (1.4 mg, 0.0054 mmol), and toluene (0.50 mL). GC analysis indicated the formation of the biaryl naphthalenes (**3a** + **4a**) in 31% yield in 40:60 (**3a:4a**) ratio.

**Entry 12:** The general procedure was followed, using **2a** (20 mg, 0.054 mmol), $BF_3 \cdot Et_2O$ (0.8 mg, 0.0054 mmol), and toluene (0.50 mL). GC analysis indicated the formation of the biaryl naphthalenes (**3a** + **4a**) in 30% yield in 39:61 (**3a:4a**) ratio.

### *Rearrangement of 2 under Optimized Conditions (Table 3):*

**General Procedure:** In a glovebox, a vial was charged with **3**, toluene, and 10% $Eu(OTf)_3$. The vessel was sealed and stirred at 80 °C for 24 h. The reaction was cooled to ambient temperature, and the mixture was filtered through a silica plug with copious ether washings. The solvents were removed under reduced pressure, and the crude material was subjected to preparatory thin-layer chromatography using 9:1 hexanes:ether as the eluent.

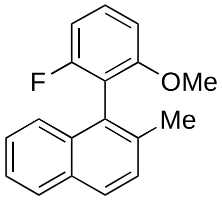
**Compound 3a [1072849-22-9] (Entry 1).** The general procedure was applied using **2a** (191 mg, 0.520 mmol), toluene (5.3 mL), and $Eu(OTf)_3$ (32 mg, 0.053 mmol). The biaryl product was isolated as mixture of **3a** and **4a** (106 mg, 74% yield, in 93:7 (**3a:4a**) ratio). A second run had a yield of 68%.



**3a**

$^{1}$H NMR (300 MHz, CDCl$_3$): δ 2.24 (s, 3H), 3.67 (s, 6H), 6.76 (m, 2H), 7.28-7.49 (m, 5H), 7.85 (m, 2H).

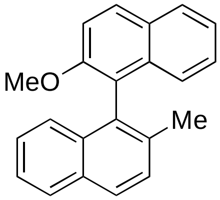
**Compound 3b (Entry 2).** The general procedure was applied using **2b** (181 mg, 0.516 mmol), toluene (5.2 mL), and Eu(OTf)$_3$ (31 mg, 0.052 mmol). The product **3b** was isolated as a white solid (56 mg, 41% yield, >95:5 regioselectivity). A second run had a yield of 44%.



**3b**

$^{1}$H NMR (300 MHz, CDCl$_3$): δ 2.28 (s, 3H), 3.70 (s, 3H), 6.89 (d, J = 9.0 Hz, 2H), 7.37-7.49 (m, 5H), 7.86 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 20.3, 56.0, 106.6 106.7, 108.2 (d, $J_{CF}$ = 23 Hz), 124.7, 125.2, 125.9, 127.9, 128.0, 128.4, 129.3, 129.5, 131.9, 132.6, 134.9, 158.8 (d, $J_{CF}$ = 30 Hz), 162.3.

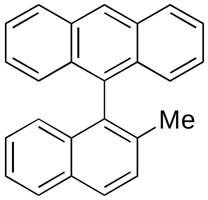
**Compound 3c [106909-87-9] (Entry 3).** The general procedure was applied using **2c** (233 mg, 0.600 mmol), toluene (5.2 mL), and Eu(OTf)$_3$ (36 mg, 0.059 mmol). The product **3c** was isolated as a fluffy white solid (110 mg, 61% yield, >95:5 regioselectivity). A second run had a yield of 64%.



**3c**

$^{1}$H NMR (300 MHz, CDCl$_3$): δ 2.13 (s, 3H), 3.79 (s, 3H), 7.03 (d, J = 9.0 Hz, 1H), 7.15-7.56 (m, 7H), 7.91 (m, 3H), 8.02 (d, J = 9 Hz, 1H).

**Compound 3d [191791-93-2] (Entry 4).** The general procedure was applied using **2d** (250 mg, 0.610 mmol), toluene (6.1 mL), and Eu(OTf)$_3$ (37 mg, 0.061 mmol). The product **3d** was isolated as an off-color solid

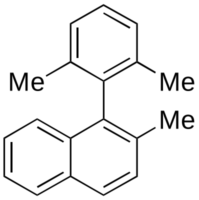


**3d**

(107 mg, 55% yield, >95:5 regioselectivity). A Second run had a yield of 55%.

$^1$H NMR (300 MHz, CDCl$_3$): δ 2.01 (s, 3H), 6.90 (d, J = 8.4 Hz, 1H), 7.12-7.62 (m, 9H), 8.00 (dd, J = 3, 12 Hz, 1H), 8.14 (d, J = 9 Hz, 1H), 8.63 (s, 1H).

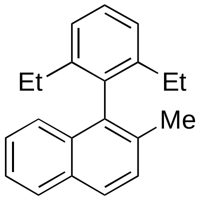
**Compound 3e [814254-89-2] (Entry 5).** The general procedure was applied using **2e** (171 mg, 0.508 mmol), toluene (5.1 mL), and Eu(OTf)$_3$ (30 mg, 0.051 mmol). The product **3e** was isolated as an off-color oil (96 mg, 77% yield, >95:5 regioselectivity). A second run had a yield of 81%.



**3e**

$^1$H NMR (300 MHz, CDCl$_3$): δ 1.87 (s, 6H), 2.16 (s, 3H), 7.18-7.50 (m, 7H), 7.81-7.91 (m, 2H).

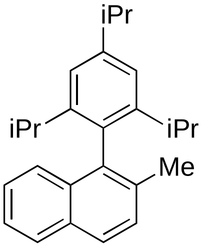
**Compound 3f [1157867-56-5] (Entry 6).** The general procedure was applied using **2f** (250 mg, 0.690 mmol), toluene (6.9 mL), and Eu(OTf)$_3$ (41 mg, 0.069 mmol). The product **3f** was isolated as a light yellow oil (141 mg, 75% yield, >95:5 regioselectivity). A second run had a yield of 80%.



**3f**

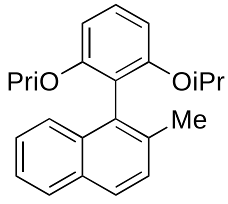
$^1$H NMR (300 MHz, CDCl$_3$): δ 1.06 (m, 6H), 2.17 (m, 7H), 7.25-7.53 (m, 7H), 7.86-7.94 (m, 2H).

**Compound 3g (Entry 7).** The general was applied using **2g** (279 mg, 0.642 mmol), toluene (6.5 mL), and Eu(OTf)$_3$ (39 mg, 0.064 mmol). The product **3g** was isolated as an off-color solid (192 mg, 87% yield, >95:5 regioselectivity). A second run had a yield of 85%.



**3g**

$^{1}$H NMR (300 MHz, CDCl$_3$): δ 1.01 (d, J = 6.9 Hz, 6H), 1.20 (d, J = 6.6 Hz, 6H), 1.50 (d, J = 6.9 Hz, 6H), 2.30 (s, 3H), 2.40 (septet, J = 6.6 Hz, 2H), 3.14 (septet, J = 6.9 Hz, 1H), 7.28 (s, 2H), 7.41-7.56 (m, 4H), 7.90 (d, J = 8.7 Hz, 1H), 7.95 (d, J = 7.8 Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 20.8, 24.1, 24.7, 30.5, 34.2, 121.0, 122.0, 124.3, 124.7, 125.4, 126.5, 126.7, 127.7, 128.4, 131.9 133.0, 133.9, 136.0, 136.5, 146.8, 148.1.

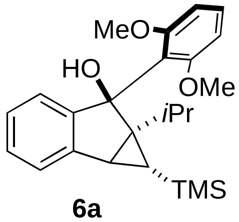


**3h**

**Compound 3h (Entry 8).** The general procedure was applied using **2h** (152 mg, 0.360 mmol), toluene (3.6 mL), and Eu(OTf)$_3$ (22 mg, 0.036 mmol). The product **3h** was isolated as a light yellow oil (97 mg, 81% yield, >95:5 regioselectivity). A second run had a yield of 77%.

$^{1}$H NMR (300 MHz, CDCl$_3$): δ 0.92 (d, J = 6.0 Hz, 6H), 1.03 (d, J = 6.3 Hz, 6H), 2.26 (s, 3H), 4.26 (septet, J = 6.3 Hz, 2H), 6.73 (d, J = 8.1 Hz, 2H), 7.27-7.44 (m, 5H), 7.77 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 20.4, 21.9, 22.0, 70.7, 107.9, 120.0, 124.0, 124.9, 126.1, 126.5, 127.5, 128.3, 128.5, 131.6, 131.7, 133.0, 134.3, 157.0.

***Nucleophillic Addition to 5 (Scheme 2)***

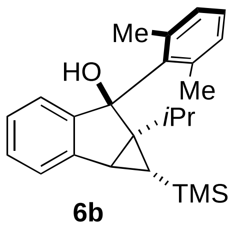


**6a**

**Compound 6a.** An oven-dried flask was charged with 10.0 mL anhydrous Et$_2$O and *m*-dimethoxybenzene (267 mg, 1.93 mmol). *n*-BuLi (0.73 mL, 1.8 mmol, 2.5 M in hexanes) was added dropwise at room temperature, and the reaction was allowed to stir for 24h. The ether was then removed under reduced pressure to yield a white solid. Anhydrous THF was added

(4.0 mL) and the reaction mixture was cooled to –78 °C. Indanone **5** (250 mg, 0.967 mmol) in THF (1.0 mL) was added dropwise at –78 °C. The reaction was allowed to warm to ambient temperature and stirred for 24h. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). Compound **6a** was isolated as a clear oil (46 mg, 12% yield). A second run had a yield of 15%.

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.14 (s, 9H), 0.47 (d, J = 5.4 Hz, 1H), 0.72 (d, J = 6.9 Hz, 3H), 1.02 (d, J = 7.2 Hz, 3H), 1.70 (septet, J = 6.9 Hz, 1H), 2.38 (d, J = 5.4 Hz, 1H), 3.04 (s, 3H), 4.02 (s, 3H), 6.41 (d, J = 9.6 Hz, 1H), 6.60 (s, 1H), 6.69 (d, J = 9.3 Hz, 1H), 6.85-7.28 (m, 5H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 0.5, 20.0, 20.2, 30.1, 31.3, 34.8, 48.6, 55.0, 56.8, 89.0, 105.7, 106.8, 120.3, 122.7, 123.7, 124.8, 126.1, 128.4, 150.1, 150.6, 158.1, 158.7. IR (Neat) 3495 m, (alcohol).

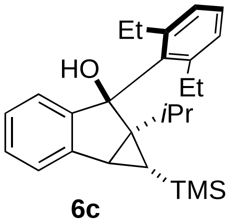


**6b**

**Compound 6b.** An oven-dried flask was charged with 3.0 mL anhydrous $Et_2O$ and 1-bromo-2,6-dimethylbenzene (279 mg, 1.51 mmol). The reaction mixture was cooled to –78 °C, and *t*-BuLi (1.8 mL, 3.0 mmol, 1.7 M in hexanes) was added dropwise. The reaction was allowed to stir for 2 hours at –78 °C. Subsequently, the reaction was allowed to warm to ambient temperature for 30 minutes. The reaction mixture was cooled to –78 °C before indanone **5** (300 mg, 1.16 mmol) in $Et_2O$ (3.0 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred for 24h. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 6:1). Compound **6b** was isolated as a viscous oil (249 mg, 59% yield). A second run had a yield of 54%.

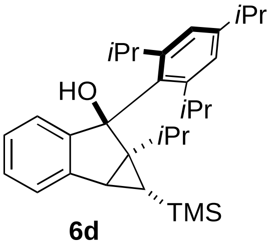
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.09 (s, 9H), 0.62 (d, J = 5.7 Hz, 1H), 0.98 (d, J = 7.5 Hz, 3H), 1.11 (d, J = 7.2 Hz, 3H), 1.77 (s, 3H), 1.77 (s, 1H), 2.40 (d, J = 5.7 Hz, 1H), 2.94 (s, 3H), 3.10 (septet, J = 7.2 Hz, 1H), 6.95-7.32 (m, 7H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 0.6, 21.0, 23.4, 25.3, 26.6, 26.8, 27.6, 32.0, 53.7, 90.9, 122.9, 125.2, 125.4, 126.3, 128.0, 131.1, 131.7, 135.4, 139.7, 139.9, 145.3, 150.2. IR (Neat) 3534 m, (alcohol). HRMS (EI) calcd for $C_{24}H_{32}OSi$ (M+) 364.2223 found 364.2213

**Compound 6c.** An oven-dried flask was charged with 3.0 mL anhydrous $Et_2O$ and 1-bromo-2,6-diethylbenzene (321 mg, 1.51 mmol). The reaction was cooled to –78 $^{o}$C. *t*-BuLi (1.8 mL, 3.0 mmol, 1.7 M in pentane) was added dropwise at –78°C, and the reaction was allowed to stir for 2 hours. Subsequently, the reaction was allowed to warm to ambient temperature for 30 minutes. The reaction mixture was cooled to –78 $^{o}$C before indanone **5** (300 mg, 1.16 mmol) in $Et_2O$ (3.0 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred for 24h At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 9:1). Compound **6c** was isolated as an off color oil (226 mg, 50% yield). A second run had a yield of 46%.



**6c**

$^1$H NMR (300 MHz, CDCl$_3$): δ 0.10 (s, 9H), 0.50 (d, J = 5.4 Hz, 1H), 0.93 (t, J = 7.5 Hz, 3H), 1.01 (d, J = 7.2 Hz, 3H), 1.14 (d, J = 6.9, 3H), 1.41 (t, J = 6.9 Hz, 3H), 1.72 (s, 1H), 1.94 (m, 2H), 2.40 (d, J = 6 Hz, 1H), 2.74 (m, 2H), 3.91 (m, 1H), 7.07-7.32 (m, 7H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 0.6, 18.0, 19.3, 20.8, 23.1, 27.5, 29.6, 32.2, 32.4, 90.8, 122.8, 124.1, 125.5, 127.1, 127.9, 129.2, 130.6, 138.8, 142.1, 144.5, 146.7, 151.2. IR (Neat) 3594 m, (alcohol). HRMS (EI) calcd for $C_{26}H_{36}OSi$ (M+) 392.2536 found 392.2525.



**6d**

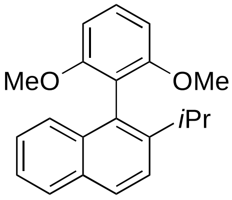
**Compound 6d.** An oven-dried flask was charged with 3.0 mL anhydrous Et$_2$O and 1-bromo-2,4,6-triisopropylbenzene (427 mg, 1.51 mmol). The reaction mixture was cooled to –78 °C, and *t*-BuLi (1.8 mL, 3.0 mmol, 1.7 M in pentane) was added dropwise. The reaction was allowed to stir for 2 hours. Subsequently, the reaction was allowed to warm to ambient temperature for 30 minutes. The reaction mixture was cooled to –78 °C before indanone **5** (300 mg, 1.16 mmol) in Et$_2$O (2.8 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred for 24h. At the conclusion of the reaction, 5 mL of NH$_4$Cl (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over MgSO$_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 9:1). Compound **6d** was isolated as a white solid (76 mg, 14% yield). A second run had a yield of 12%.

$^1$H NMR (300 MHz, CDCl$_3$): δ 0.12 (s, 9H), 0.57 (d, J = 5.7 Hz, 1H), 0.84 (d, J = 6.3 Hz, 3H), 0.99 (d, J = 7.2 Hz, 6H), 1.09 (d, J = 6.9 Hz, 3H), 1.19-1.37 (m, 12H), 1.61 (s, 1H), 2.17 (septet, J = 6.9 Hz, 1H), 2.37 (d, J = 5.7 Hz, 1H), 2.90 (septet, J = 6.9 Hz, 1H), 3.11 (m, 1H), 4.41 (septet, J = 6.6 Hz, 1H), 6.96-7.28 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ

0.8, 21.3, 23.7, 23.8, 24.1, 24.3, 24.9 ( 2 peaks), 26.7, 27.9, 31.1, 31.6, 31.8, 33.4, 52.7, 85.3, 91.0, 122.6, 123.2, 124.1, 125.4, 127.7, 135.6, 144.0, 146.1, 146.8, 151.3, 151.8 IR (Neat) 3302 s, (alcohol).

***Rearrangement of 6 under Optimized Conditions (Table 4):***

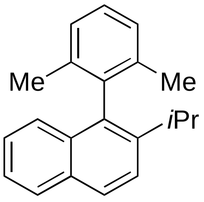
**General Procedure:** In a glovebox, a vial was charged with **6**, toluene, and 10% Eu(OTf)$_3$. The vessel was sealed and stirred at 80 °C for 24 h. The reaction was cooled to ambient temperature, and trifluoroacetic acid was added. The reaction mixture was stirred for one hour before it was filtered through a silica plug with copious ether washings. The solvents were removed under reduced pressure, and the crude material was subjected to preparatory thin-layer chromatography using 9:1 hexanes:ether as the eluent.



**7a**

**Compound 7a (Entry 1).** The general procedure was applied using **6a** (40 mg, 0.010 mmol), toluene (1.0 mL), and Eu(OTf)$_3$ (6.0 mg, 0.0010 mmol). The product **7b** was isolated as an oil (20 mg, 65% yield, >95:5 regioselectivity). A second run had a yield of 60%.

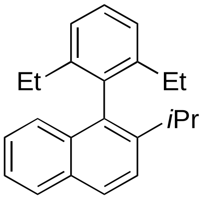
$^1$H NMR (300 MHz, CDCl$_3$): δ 1.20 (d, J = 7.2 Hz, 6H), 2.83 (septet, J = 6.9 Hz, 1H), 3.64 (s, 6H), 6.75 (d, J = 8.4 Hz, 2H), 7.28-7.46 (m, 4H), 7.58 (d, J = 9 Hz, 1H), 7.83-7.91 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 23.5, 31.1, 55.7, 103.9, 116.2, 123.6, 124.6, 125.3, 125.5, 125.9, 127.8, 128.2, 129.0, 131.9, 132.8, 144.5, 158.5.



**7b**

**Compound 7b (Entry 2).** The general procedure was applied using **6b** (169 mg, 0.464 mmol), toluene (5.0 mL), and Eu(OTf)$_3$ (30 mg, 0.046 mmol). The product **7b** was isolated as an off-color oil (89 mg, 70% yield, >95:5 regioselectivity). A second run had a yield of 75%.

$^1$H NMR (300 MHz, CDCl$_3$): δ 1.24 (d, J = 6.9 Hz, 6H), 1.91 (s, 6H), 2.78 (septet, J = 6.9 Hz, 1H), 7.18-7.48 (m, 6H), 7.62 (d, J = 8.7 Hz, 1H), 7.88-7.94 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 20.3, 23.7, 30.5, 124.0, 125.0, 125.5, 126.0, 127.1, 127.4, 127.7, 127.9, 131.9, 132.2, 134.8, 137.2, 138.3, 143.0. HRMS (EI) calcd for $C_{21}H_{22}$ (M+) 274.1722 found 274.1724.

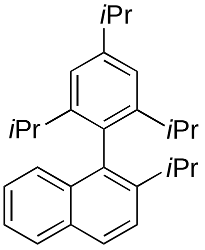


**7c**

**Compound 7c (Entry 3).** The general procedure was applied using **6c** (218 mg, 0.555 mmol), toluene (5.6 mL), and Eu(OTf)$_3$ (33 mg, 0.056 mmol). The product **7c** was isolated as a light yellow oil (122 mg, 73% yield, >95:5 regioselectivity). A second run had a yield of 72%.

$^1$H NMR (300 MHz, CDCl$_3$): δ 1.02 (t, J = 7.5 Hz, 6H), 1.24 (d, J = 7.2 Hz, 6H), 2.12-2.36 (m, 4H), 2.79 (septet, J = 6.9 Hz, 1H), 7.24-7.51 (m, 6H), 7.64 (d, J = 8.7 Hz, 1H), 7.89-7.96 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 14.6, 23.6, 26.1, 30.4, 123.9, 124.9, 125.1, 125.4, 125.5, 126.5, 127.5, 127.7, 132.0, 132.7, 134.4, 137.1, 142.7, 143.2. HRMS (EI) calcd for $C_{23}H_{26}$ (M+) 302.2035 found 302.2038.

**Compound 7d (Entry 4).** The general procedure was applied using **6d** (50 mg, 0.011 mmol), toluene (1.1 mL), and Eu(OTf)$_3$ (6.5 mg, 0.0011 mmol). The product **7d** was isolated as an off-color oil (29 mg, 73% yield, >95:5 regioselectivity). A second run had a yield of 78%. Crystals suitable for diffraction were obtained by slow evaporation of the solvent of a concentrated solution of **7d** in dichloromethane at –20 °C.

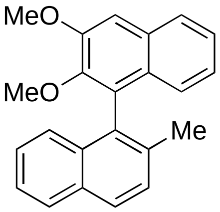


**7d**

$^1$H NMR (300 MHz, CDCl$_3$): δ 0.83 (d, J = 6.6 Hz, 6H), 1.12 (d, J = 6.9 Hz, 6H), 1.22 (d, J = 6.6 Hz, 6H), 1.39 (d, J = 6.6 Hz, 6H), 2.35 (hep, J = 6.6 Hz, 2H), 2.87 (hep, J = 7.2 Hz, 1H), 3.03 (hep, J = 6.9 Hz, 1H), 7.14-7.29 (m, 4H), 7.39 (t, J = 6.9 Hz, 1H), 7.57 (d, J = 9 Hz, 1H), 7.82-7.90 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 23.8, 23.9, 24.1, 25.3, 30.1, 30.3 30.4, 34.1, 120.9, 123.7, 124.9, 125.0, 127.4, 127.5, 127.7, 132.0, 132.7, 133.5, 134.6, 143.8, 147.3, 147.9. HRMS (EI) calcd for $C_{28}H_{36}$ (M+) 372.2817 found 372.2809.

***Biaryl Naphthalene Synthesis without Isolation of Intermediates (Table 5):***

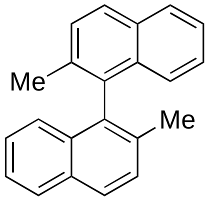
**Compound 9a (Entry 1).** An oven-dried flask was charged with 2.0 mL anhydrous Et$_2$O and 1-bromo-2,3-dimethoxynaphthalene (232 mg, 0.868 mmol). *n*-BuLi (0.330 mL, 0.868 mmol, 2.5 M in hexanes) was added dropwise at room temperature, and the reaction was allowed to stir for 15 minutes. The reaction was then cooled to –78 °C, and indanone **1** (200 mg, 0.870 mmol) in Et$_2$O (2.4 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred for 24h. At the conclusion of the reaction, 5 mL of NH$_4$Cl (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed



**9a**

three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to a silica plug (Hex:Ether = 3:1). This crude material (221 mg, 0.530 mmol) was subjected to the optimized rearrangement procedure (Table 3) using toluene (5.3 mL), and $Eu(OTf)_3$ (32 mg, 0.053 mmol). The product **9a** was isolated as a white solid (176 mg, 62% yield from indanone **1**). A second run had a yield of 60%.

$^1$H NMR (300 MHz, $CDCl_3$): δ 2.17 (s, 3H), 3.51 (s, 3H), 4.09 (s, 3H), 6.96-7.54 (m, 8H), 7.83 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 8.4 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 20.4, 55.6, 60.3, 106.8, 124.1, 124.7, 125.3, 125.5, 125.9, 126.6, 127.6, 127.8, 128.4, 128.6, 128.8, 131.3, 131.8, 131.9, 133.2, 134.9, 146.9, 152.3, one aromatic carbon is not observed.



**9b**

**Compound 9b [32854-84-7] (Entry 2).** An oven-dried flask was charged with 2.0 mL anhydrous $Et_2O$ and 1-bromo-2-methylnaphthalene (384 mg, 1.74 mmol). *n*-BuLi (0.660 mL, 1.65 mmol, 2.5 M in hexanes) was added dropwise, and the reaction was allowed to stir for 15 minutes. The reaction was then cooled to –78 °C, and indanone **1** (200 mg, 0.870 mmol) in $Et_2O$ (2.4 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred for 24h. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to a silica plug (Hex:Ether = 3:1). The crude material (278 mg, 0.746 mmol) was subjected to the optimized rearrangement procedure (Table 3) with toluene

(7.5 mL), and $Eu(OTf)_3$ (45 mg, 0.075 mmol). The product **9b** was isolated as a light yellow solid (164 mg, 67% yield from indanone **1**). A second run had a yield of 62%.

$^1$H NMR (300 MHz, $CDCl_3$): δ 2.09 (s, 6H), 7.14 (d, J = 8.4 Hz, 2H), 7.25 (m, 2H), 7.41-7.57 (m, 4H), 7.94 (m, 4H).

## Bridge to Chapter IV

In Chapter III we focused on tetra-*ortho*-substitution, and briefly highlighted the success with regard to two-step naphthalene synthesis without the need for intermediate purification.  We also touched on the moderately successful chiral transfer *via* our method.  Unfortunately we did identify a limit to our method's ability to generate sterically demanding naphthalenes through the difficulties observed from the nucleophilic addition step.  Furthermore our chiral transfer occurred with modest enantiomeric excess. In Chapter IV we address the steric problem by demonstrating successful rearrangement without the need for a TMS cyclopropyl group, allowing us to employ larger groups in the *ortho* position.  We were then able to introduce *t*-butyl and adamantyl groups into our naphthalenes structure, further pushing the steric-limits of our method.  Once a solution was found for the steric problem, we focused our attention on the asymmetric synthesis. To our delight we witnessed excellent chiral transfer after some solvent modifications, and have developed an effective stereochemical model for this transformation.  Chapter IV is a *manuscript in preparation*.

# CHAPTER IV

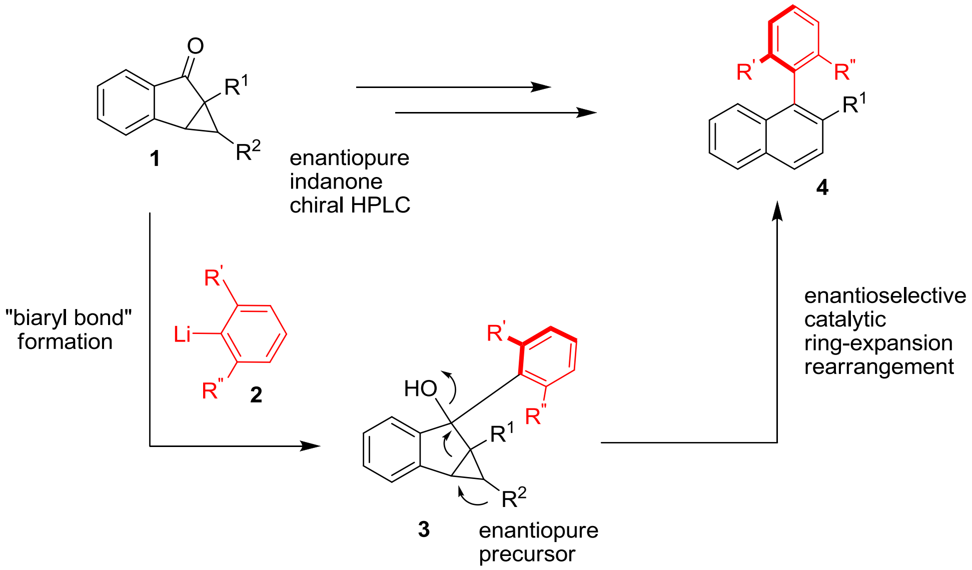
# THE ASYMMETRIC SYNTHESIS OF TETRA-*ORTHO*-SUBSTITUTED ARYL NAPHTHALENES *VIA* A CATALYTIC REARRANGEMENT PROCESS

This work is a *Manuscript in Preparation* that has co-authors. Brian S. Young was involved in the modeling of **14a** and **20**, Dr. Lev N. Zakharov performed crystal structure analysis, and Prof. Shih-Yuan Liu was the P.I. I was the primary contributor for the manuscript. This Chapter includes Co-Authored material.

## Introduction

Due to the limitations regarding the synthesis of tetra-*ortho*-substituted and asymmetric biaryls via metal-mediated coupling, novel strategies for the generation of these motifs are desired. These alternative approaches consist of annulation-based strategies (e.g. Diels-Alder and [2+2+2]) and rearrangement-based approaches. Our group has been focused on a rearrangement-based method for the asymmetric synthesis of tetra-*ortho*-substituted aryl naphthalenes.

Scheme 1 illustrates our general strategy for the generation of aryl naphthalenes. Substituted indanone **1** can be transformed into rearrangement precursor **3** through a simple diastereoselective nucleophilic addition of aryl nucleophile **2**. This cyclopropyl carbinol 3 can then undergo catalytic ring-expansion rearrangement via Lewis acid catalysis to generate tetra-ortho-substituted aryl naphthalene **4**. We envision that when R’ ≠ R” the desired naphthalene can potentially be generated enantioselectively from the enantiopure indanone. Semi-preparatory HPLC is used to separate the two indanone enantiomers.

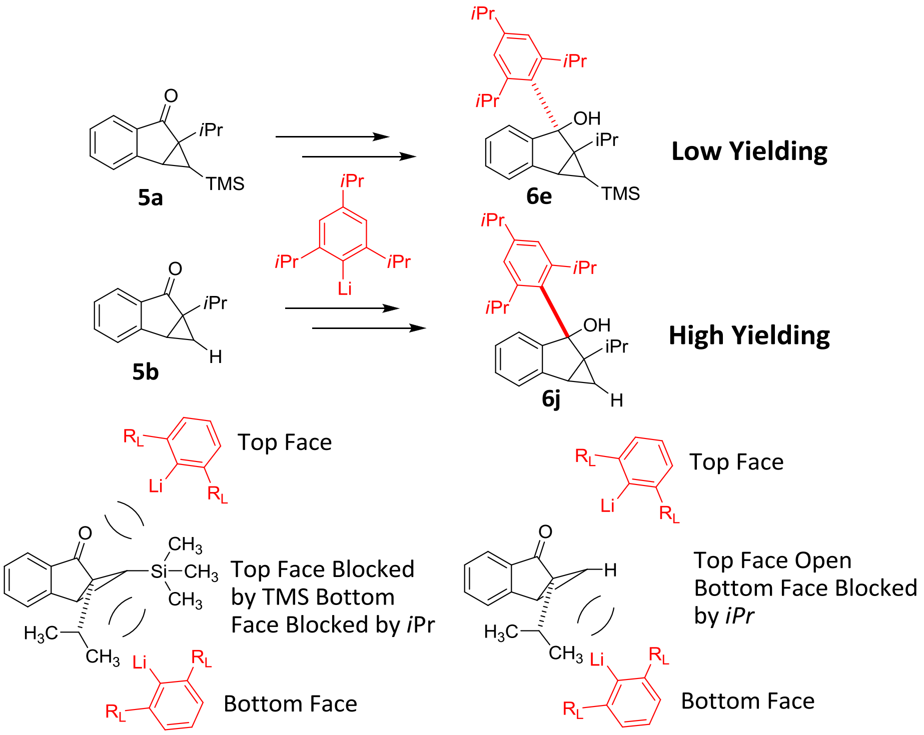


**Scheme 1**. Asymmetric route to TOAN **4**.

In previous chapters we have described that our rearrangement-based method works well for the synthesis of very sterically-demanding tetra-*ortho*-substituted aryl naphthalenes, and preliminary evidence has demonstrated the synthesis of an aryl naphthalene. Herein we will describe the greatly expanded scope of rearrangement to include *t*-butyl and adamantyl groups in the *ortho* position. We also discuss our success with rearrangements from precursors lacking TMS, further abbreviated as non-TMS-based rearrangement. Finally, we have achieved excellent control over the asymmetric synthesis of tetra-*ortho*-substituted aryl naphthalenes, we developed a stereochemical model, and have further functionalized these highly enantioenriched compounds.

## Results and Discussion

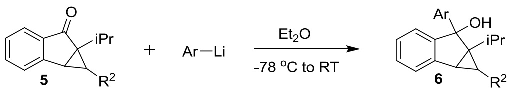
In Chapter III, our method focused around the ring expansion rearrangement of TMS cyclopropyl carbinol **6e** (Scheme 2). While the TMS group allows for the facile rearrangement of **6e** into an aryl naphthalene, it decreases the yield of the nucleophilic addition of the highly sterically demanding tri-isopropyl-*ortho* substituted aryl nucleophile, presumably through steric repulsion of the nucleophile with the TMS cyclopropane group. In order to further expand the synthesis of sterically-encumbered aryl naphthalenes, we needed to get around the addition problem. We began to envision the rearrangement occurring without the TMS group. Prior work had shown that the TMS was necessary for rearrangement under originally published reaction conditions. We felt however, that this issue warranted further exploration. We began by generating the highly sterically congested rearrangement precursor **6j** (Scheme 2**).** Our original

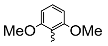
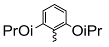
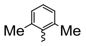
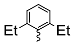
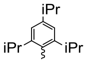
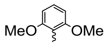
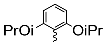
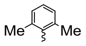
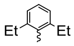
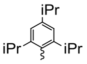


**Scheme 2**. Top face versus bottom face addition and yield

synthesis of this precursor when $R^2$ = TMS was very low yielding (Table 1a, entry 5), however the same synthesis when $R^2$ = H (entry 10) generated the precursor in much higher yield. This compound was then subjected to rearrangement under our optimized conditions, albeit with a higher reaction temperature. We were delighted to observe the quantitative rearrangement of naphthalene **7j** (Table 1b, entry 10). Further studies identified the substrate scope of the non-TMS-based rearrangement method, while allowing for a direct comparison against the TMS-based rearrangement. Consistently we

**a)**

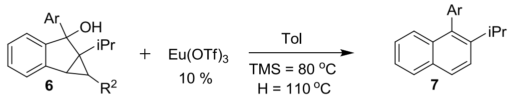


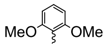
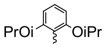
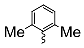
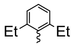
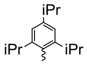
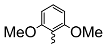
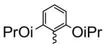
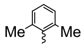
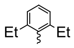
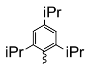
| Entry | $R^2$ | Ar | **6** | Yield % |
|---|---|---|---|---|
| 1 | TMS |  | a | 14 * |
| 2 | TMS |  | b | 41 |
| 3 | TMS |  | c | 57 |
| 4 | TMS |  | d | 48 |
| 5 | TMS |  | e | 13 |
| 6 | H |  | f | 60 |
| 7 | H |  | g | 51 |
| 8 | H |  | h | 63 |
| 9 | H |  | i | 72 |
| 10 | H |  | j | 62 |

* Solvent = THF

All entries are the average of two runs

**b)**



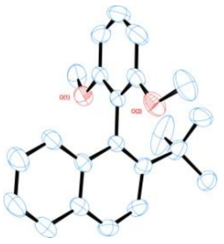
| Entry | **6** | $R^2$ | Ar | **7** | Yield % |
|---|---|---|---|---|---|
| 1 | a | TMS |  | a | 63 |
| 2 | b | TMS |  | b | 82 |
| 3 | c | TMS |  | c | 73 |
| 4 | d | TMS |  | d | 73 |
| 5 | e | TMS |  | e | 76 |
| 6 | f | H |  | f | 59 |
| 7 | g | H |  | g | 87 |
| 8 | h | H |  | h | 57 |
| 9 | i | H |  | i | 93 |
| 10 | j | H |  | j | 100 |

All entries are the average of two runs

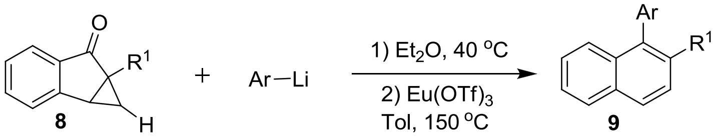
**Table 1**. **a)** Yield Comparison of TMS and Non-TMS Precursor Synthesis. **b)** Yield Comparison of TMS and Non-TMS Naphthalene Synthesis

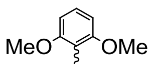
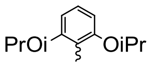
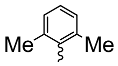
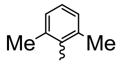
observed improved yields of the addition reaction, especially in the cases of highly congested *ortho*-substitution (entries 7, 8, 9, and 10 versus entries 2, 3, 4 and 5; Table 1a). Rearrangement yields were also improved, except in the cases of low steric congestion (entries 6 and 8 versus entries 1 and 3; Table 1b). From these results it seems that the non- TMS cyclopropyl substrate undergoes facile rearrangement in the presence of sterically demanding groups, but demonstrates diminished yields when smaller groups are placed in the *ortho* position.

Due to the success of the TMS-based cyclopropane rearrangement, we pursued a further increase in steric-demand around the biaryl axis to generate novel tetra-*ortho*-substituted aryl naphthalenes. Table 2 illustrates our success with *t*-butyl and adamantyl-based substitutions at the $R^1$ position. As previously discussed (Chapter III), our method works well using a semi-one pot synthesis of the naphthalene. It should be noted that these are the first examples, to the author's knowledge, of tetra-*ortho*-substituted aryl naphthalenes with either a *t*-butyl or adamantyl substitution in the *ortho* position, we were also able to obtain a crystal structure of *t*-butyl naphthalene **9a**, unambiguously determining its identity.



**9a**



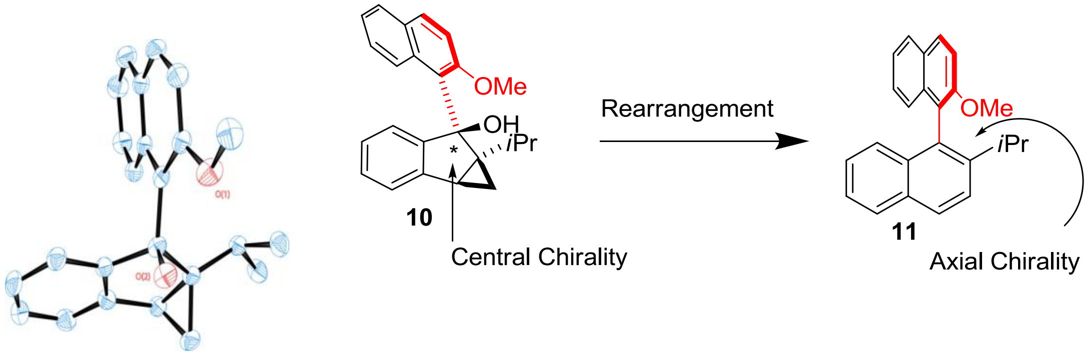
| Entry | $R^1$ | Ar | **9** | Yield % |
|---|---|---|---|---|
| 1 | tBu |  | a | 17 |
| 2 | tBu |  | b | 27 |
| 3 | tBu |  | c | 20 |
| 4 | Adamantane |  | d | 25 |

All entries are the average of two runs

**Table 2**. TOANs Bearing an *Ortho*-*t*-butyl Group

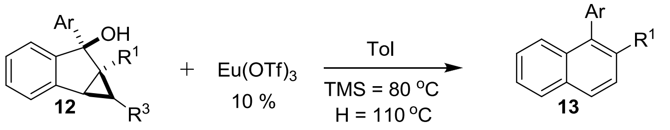
## Asymmetric Synthesis of TOANs

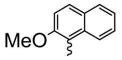
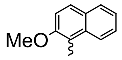
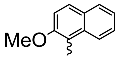
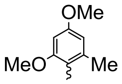
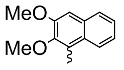
We next investigated the central to axial chirality transfer of the rearrangement. Central to axial chirality transfer has been reported from the Tanabe group,[94] and is described briefly with regard to our method in Scheme 3. One can visualize possible chiral transfer from rearrangement precursor **10** if the pseudo biaryl bond is locked in a single conformation. This will lead to the formation of a single enantiomer of naphthalene **11** as long as rotation is restricted, and if **10** is optically pure. In a previous study (Chapter III) we had observed mediocre enantioselectivity for the rearrangement of **10** when the solvent was DCE (~50% ee). The enantiopure precursor was obtained from semi-preparatory chiral HPLC of the cyclopropyl indanone followed by selective addition of the aryl nucleophile. Fortuitously, further investigation indicated that performing the rearrangement in toluene led to a marked increase in enantioselectivity of the rearrangement of **10** (Table **3**, entry 1). Once excellent enantioselectivity was established, a series of substrates were screened. Increasing the steric-demand by



**Scheme 3**. Proposed central to axial chirality transfer. Notice the methoxy naphthalene locked in a single orientation.

introducing an isopropyl group at the $R^1$ position led to increased enantioselectivity (entry 2). Direct comparison of the TMS-based precursor (entry 2) and the non-TMS-based precursor (entry 3) demonstrated no loss in the chiral transfer. Aryl groups other than the 2-methoxy naphthyl group (entries 4 and 5) also gave excellent enantioselectivities. It is important to note that each of the rearrangement-precursors have the aryl group oriented anti to the cyclopropane, correspondingly bottom-face attack. It seems that this configuration leads to excellent enantioselectivity when this precursor conformation is subjected to rearrangement. We also investigated the chiral transfer when the aryl groups add syn to the cyclopropane (top-face). Syn addition occurs preferentially when the nucleophile is relatively large or if $R^1$ = *t*Bu. Interestingly, the chiral transfer was degraded for the syn configuration (Table **4**, entries 1, 2, and 3). We believe that this is due to increased rotation around the pseudo biaryl bond, which

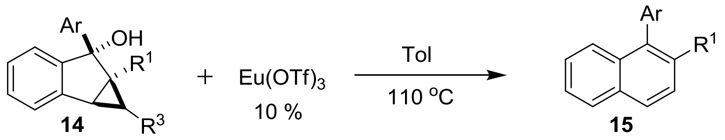


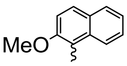
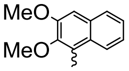
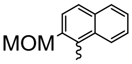
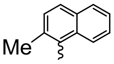
| Entry | **12** | $R^1$ | $R^3$ | Ar | Yield (%) | **13** | ee (%) |
|---|---|---|---|---|---|---|---|
| 1 | a | Me | TMS |  | 57 | a | 92 |
| 2 | b | *i*Pr | TMS |  | 70* | b | >95 |
| 3 | c | *i*Pr | H |  | 47 | c | >95 |
| 4 | d | *i*Pr | H |  | 73 | d | >95 |
| 5 | e | *i*Pr | H |  | 63 | e | >95 |

All entries are the average of two runs. * = One Run

**Table 3**. Asymmetric Rearrangement of Anti-precursor **12**

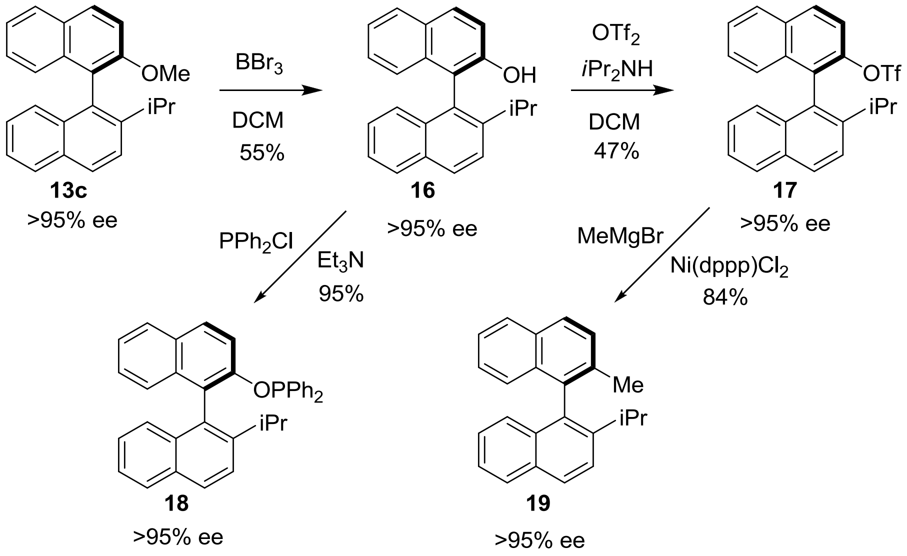
will be discussed in detail later. Continued study also revealed that coordinating groups present in the *ortho* position are necessary to facilitate chiral transfer. A methyl naphthalene (entry 4) in the aryl position showed no chirality transfer. While disappointing, this result did provide insight into the possible mechanism of chiral transfer. We were able to remove the methyl protecting group in **13c** to generate naphthol **16** (Scheme 4). This deprotection occurred without loss of optical purity and the OH could be further functionalized to yield phosphinite **18** in very high ee. We further functionalized this hydroxyl naphthalene to produce a triflate **17** in the *ortho* position without loss of enantiomeric excess. Triflates are known precursors for cross-coupling reactions, thus, triflate **18** was subjected to a Negishi coupling to yield methyl substituted **19** in high enantiomeric excess.



| Entry | **14** | $R^1$ | $R^3$ | Ar | Yield (%) | **15** | ee (%) |
|---|---|---|---|---|---|---|---|
| 1 | a | *t*Bu | H |  | 71 | a | 69 |
| 2 | b | *i*Pr | H |  | 59 | b | 68 |
| 3 | c | *i*Pr | H |  | 65 | c | 74 |
| 4 | d | *i*Pr | H |  | 72 | d | 0 |

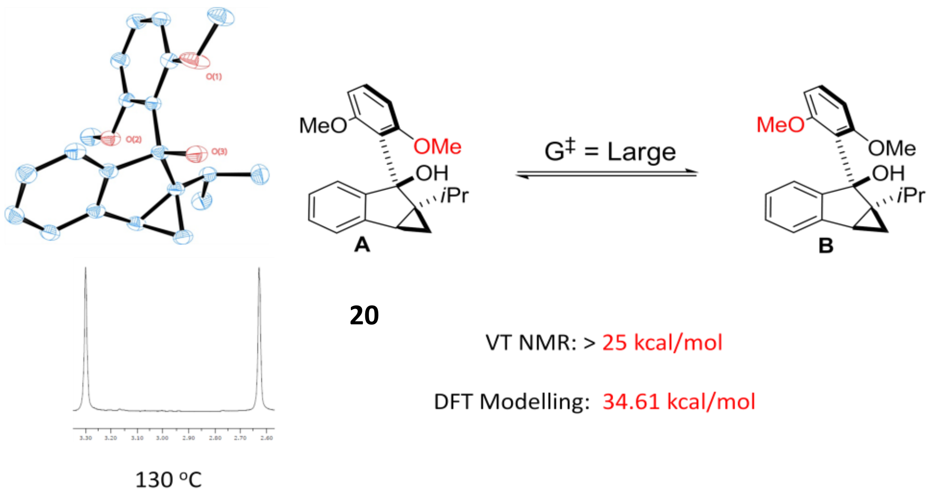
All entries are the average of two runs

**Table 4**. Asymmetric Rearrangement of Syn-precursor **14**



**Scheme 4**. Further functionalization of enantioenriched **13b** without chiral degradation.

In response to the loss of chiral transfer of syn precursors (Table 4, entries 1, 2 and 3) a temperature dependent NMR study was performed in order to quantify the barrier of rotation around the pseudo biaryl axis of syn precursor **14a** and anti precursor **20** (Figures 1 and 2). We determined that anti precursor **20** has a high barrier of rotation around the pseudo biaryl axis ($\Delta G^{\ddagger}$ = >**25** kcal/mol) from VT NMR. Because of the the high rotational barrier we were not able to arrive at an exact value for the barrier to rotation, and modelling studies[95] were performed in order to determine a rotation barrier of 34.61 kcal/mol for anti precursor **20** (Figure 1). The high barrier indicates that the precursor is locked in a single conformation throughout the rearrangement. Studies on syn precursor **14a** showed a much smaller barrier of rotation (Figure 2, $\Delta G^{\ddagger}$ = 13.68 kcal/mol by coalescence measurements, 14.40 kcal/mol *via* DNMR3,[96] and 13.77 kcal/mol *via* modeling). When rotation is restricted (anti precursor) these compounds are locked into place during the rearrangement, allowing for excellent chiral transfer. When the



VT NMR: > 25 kcal/mol

DFT Modelling: 34.61 kcal/mol

**Figure 1**. VT NMR and DFT modeling studies of anti precursor **20**.

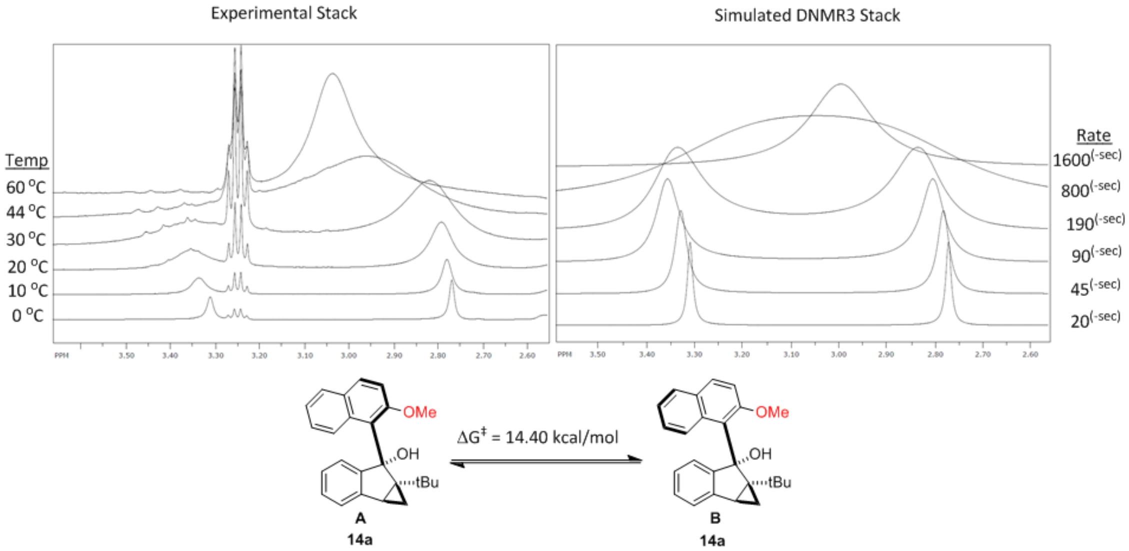
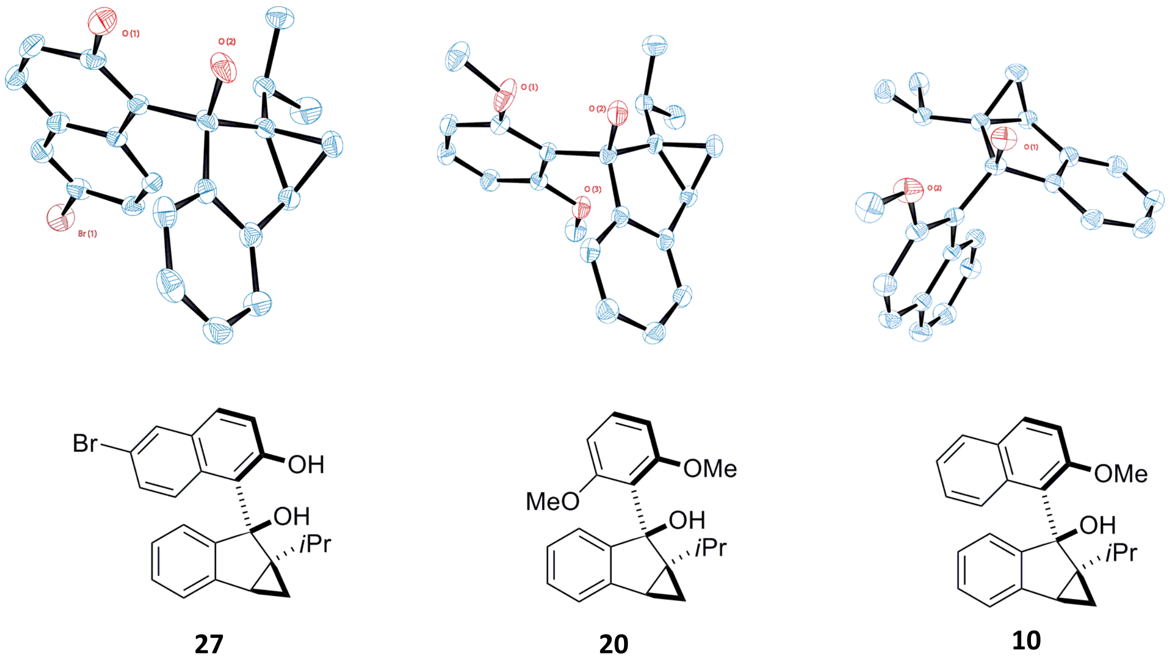


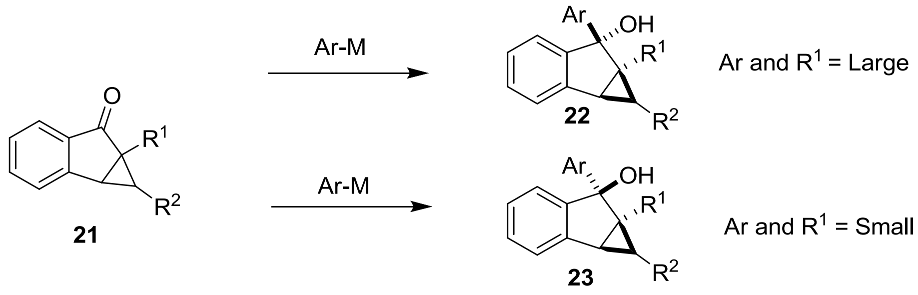
**Figure 2**. The two singlets represent the two methoxy peaks from conformers **A** and **B** from rearrangement precursor **14 a**. The quartet in the experimental residual ether. Simulated rotational rates were calculated from DNMR3.

rotation is not as restricted (syn precursor) chiral information is lost, indicating restricted rotation around the pseudo biaryl bond is of critical importance to maintain the asymmetric transfer. These cyclopropyl carbinols favor a conformation with the coordinating moiety of the *ortho* position aligned with the hydroxyl group, as observed from crystal structures of representative precursors **27**, **20**, and **10** (Scheme 5).



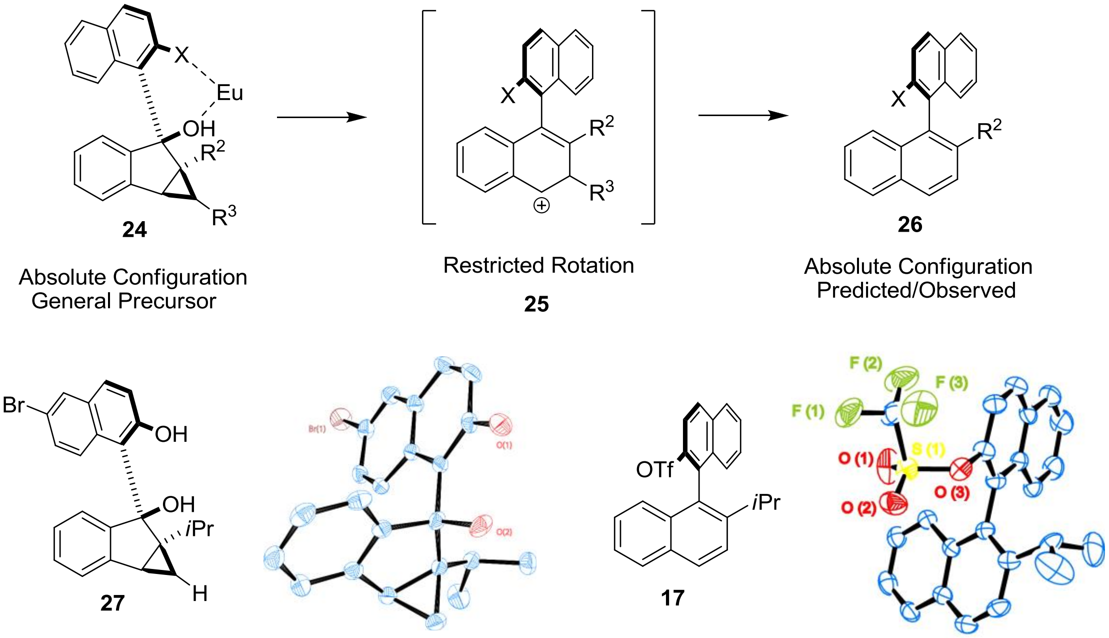
**Scheme 5**. Representative examples of anti-precursors.

Chirality transfer from a central to axially chiral center has been shown to provide stereochemical control. Herein we have utilized this approach to provide efficient chirality transfer to produce axially chiral aryl naphthalenes. As mentioned in previous reports we have observed good diasteroselectivity for the generation of our rearrangement precursors. As our study of these compounds continued we began to see selectivity for either diastereomer depending upon the nature of Ar, $R^2$ and $R^1$. When $R^1$ and Ar were large, while $R^2$ was small, top-face attack (Syn) was preferred, leading to rearrangement precursor **22** (Scheme 6). If R$^1$ and Ar were small the nucleophile preferred bottom-face attack (Anti) leading to rearrangement precursor **23**.



**Scheme 6**. Direction of attack on indanone **21**.

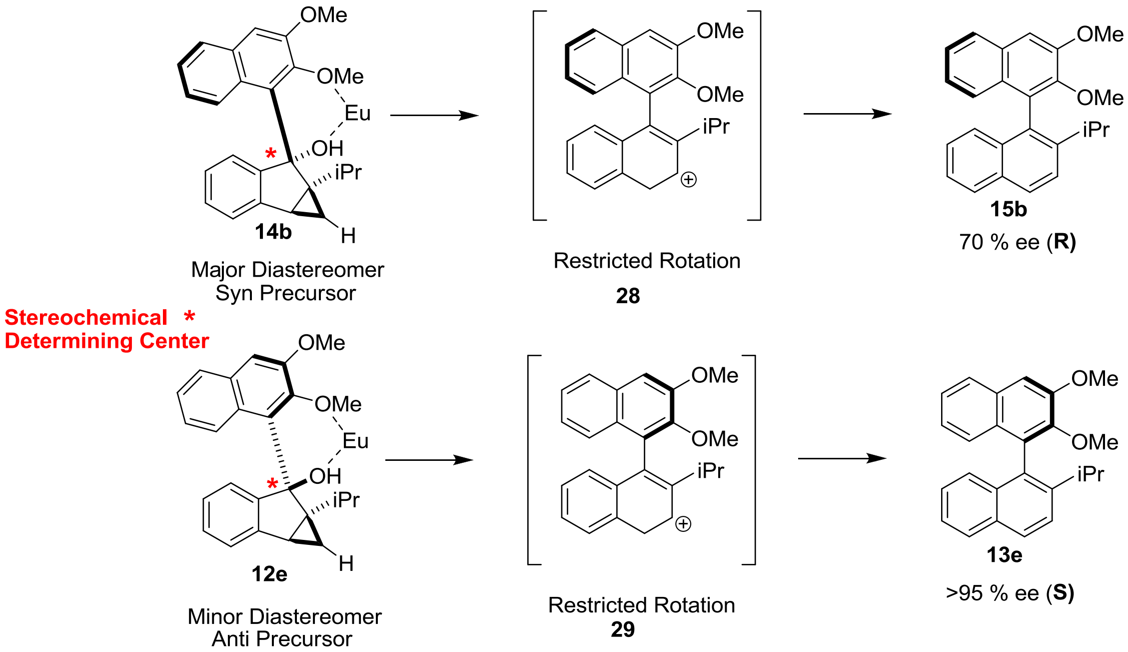
Scheme 7 outlines our proposed stereochemical model for central-to-axial chirality transfer. When rotation is restricted, the coordinating group **X** on general precursor **24** is aligned with the OH group, and quite possibly the Europium could enforce the restricted rotation. The absolute configuration of general anti-precursors was deduced from a



**Scheme 7**. Proposed stereochemical model of rearrangement.

crystal structure of precursor **27**. If rotation is restricted as we predict we would expect to generate the general naphthalene **26** with the depicted absolute configuration. Indeed our prediction was consistent with the abosulute configuration of naphthalene **17** (determined by single crystal x-ray analysis).

Further evidence for this stereochemical model was obtained from the direct comparison of the rearrangement of diastereomers **14b** and **12e** (Scheme 8). Although the cyclopropyl centers were of the same absolute stereochemistry, our model predicts that only the stereocenter containing the pseudo-biaryl bond acts in dictating the stereochemical outcome of the aryl naphthalene. From this comparison we were able to experimentally observe the generation of the two enantiomers from **14b** and **12e** respectively. Furthermore, the anti precursor **12e** continued to show high enantiomeric transfer while the syn configuration **14b** saw attenuated transfer.



**Scheme 8**. Comparison of the rearrangement of diastereomers **14b** and **12e.**

## Conclusion

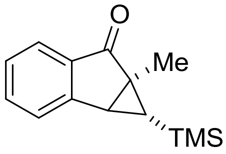
In conclusion, we have established a rearrangement-based method for the synthesis of aryl naphthalenes with challenging steric demand in the *ortho* position (i.e. *t*-butyl and adamantyl groups). We have shown the synthesis of asymmetric tetra-*ortho*-substituted aryl naphthalenes in ee's up to >95%. We have shown through VT NMR and molecular modeling studies that restricted rotation is of key importance for the successful chiral transfer of our rearrangement. Through crystal structure analysis, coupled with polarimetry studies we have established a working stereochemical model to predict the absolute stereochemical structure of our aryl naphthalenes. We have further functionalized our enantiopure aryl naphthalenes to generate chiral triflate precursors without loss of optical purity. In all, we have described a novel synthesis to the aryl naphthalene motif, being: 1)regioselective, 2)enantioselective, 3) and having the ability to generate the "holy grail" of biaryl synthesis, highly sterically demanding tetra-*ortho*-substituted aryl naphthalenes.

## Experimental

### *General*

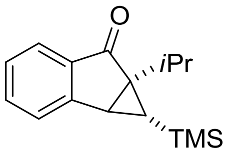
All oxygen and moisture-sensitive manipulations were carried out under an inert atmosphere using either standard Schlenk techniques or a glove box. THF, $Et_2O$, toluene, and pentane were purified by passing through a neutral alumina column under argon. Anhydrous benzene, 1,2-dichloroethane, and hexane were purchased from Aldrich and used as received. All other reagents were purchased (Aldrich, TCI, Alfa Aesar, or Acros) and used as received. 2-methyl-1-indenone, 2-isopropyl-1-indenone, 2-*t*-butylindenone, 2-adamantylindenone, and the sulfur ylide were prepared according to known procedures.[97] Thin layer chromatography and preparatory chromatography were performed on Silicycle glass backed plates with UV indicator. Column chromatography was performed on Silicycle silica gel P60. $^1$H NMR spectra were recorded on a Varian Unity/Inova 300 or Varian Unity/Inova 600 spectrometer. $^{13}$C NMR spectra were recorded on a Varian Unity/Inova 300 or Varian Unity/Inova 500 spectrometer. All spectra were referenced to their respective solvents: $CDCl_3$ 7.27 ppm and $CD_2Cl_2$ 5.30 ppm. Gas chromatography was performed on an Agilent 6850 Series II GC with an auto loader using ChemStation. High-resolution mass spectroscopy data were obtained at the Mass Spectroscopy Facilities and Services Core of the Environmental Health Sciences Center at Oregon State University. Financial support for this facility has been furnished in part by the National Institute of Environmental Health Sciences, NIH (P30 ES00210). Chiral Chromatography was performed on an Agilent 1100 HPLC equipped with either a Chiralcel OD-H or OT(+) chiral column. Polarimetry was performed on a Rudolph Research Analytical Autopol IV at either 365 or 583 nm at room temperature. Variable Temperature NMR was performed on a Varian Unity/Inova 500 spectrometer. DNMR3 in SpinWorks 3 was used to simulate rates. $\Delta G^{\ddagger}$ was determined from the Eyring equation.

*General Synthesis of Silylcyclopropyl Indanones*



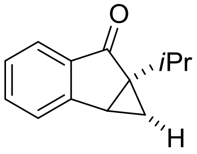
**Compound A [1072849-07-0].** To a nitrogen flushed and dried flask, 2-methyl-1-indenone (1.90 g, 13.1 mmol) and palladium acetate (289 mg, 1.31 mmol) were added. The flask was repurged with $N_2$. Anhydrous benzene (100 mL) was added followed by dropwise addition of $TMSCHN_2$ (20.0 mL, 39.0 mmol, 2.0 M in diethyl ether). The evolution of $N_2$ gas is apparent and the solution turns black. The reaction mixture was allowed to stir at room temperature for 16 h. At the conclusion of the reaction, the reaction mixture was filtered through a plug of Celite, and the solvent removed under reduced pressure. The crude material was subjected to column chromatography (Hex:Et2O = 9:1), and **A** was isolated as a light yellow solid (2.50 g, 84 % yield).

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.13 (s, 9H), 0.85 (d, J = 4.8 Hz, 1H), 1.58 (s, 3H), 2.65 (d, J = 4.8 Hz, 1H), 7.21-7.45 (m, 3H), 7.64 (d, J = 8.1 Hz, 1H).



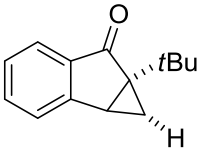
**Compound 5a [1263064-75-0].** The procedure for the preparation of **5a** has been used forthe synthesis of **A** employing 2-isopropyl-1-indenone (762 mg, 4.40 mmol), palladium acetate (98 mg, 0.44 mmol), 44.0 mL benzene, and $TMSCHN_2$ (6.50 mL, 13.1 mmol, 2.0 M in diethyl ether). The reaction was run at 50 $^o$C for 3h. Cyclopropane **5a** was isolated as a pale yellow solid (872 mg, 76 % yield).

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.14 (s, 9H), 0.82 (d, J = 5.1 Hz, 1H), 1.14 (d, J = 6.6 Hz, 3H), 1.51 (d, J = 6.6 Hz, 3H), 1.78 (septet, J = 7.2 Hz, 1H), 2.51 (d, J = 4.8 Hz, 1H), 7.18-7.43 (m, 3H), 7.60 (d, J = 7.8 Hz, 1H)



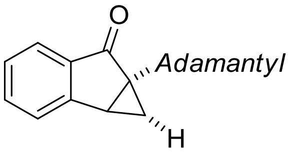
**Compound 5b.** To a nitrogen flushed and dried flask, 2-isopropyl-1-indenone (800 mg, 4.7 mmol) was added. Anhydrous THF (15 mL) was added followed by dropwise addition of sulfur ylide (7.0 mL, 4.7 mmol, 0.7 M in THF). The solution turns a crimson red. The reaction mixture was allowed to stir at room temperature for 0.5 h. At the conclusion of the reaction, the reaction mixture was filtered through a plug of silica, and the solvent removed under reduced pressure. The crude material was subjected to column chromatography (Hex:$Et_2O$ = 9:1), and **5b** was isolated as a light yellow oil (0.865 g, 100 % yield).

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.06 (d, J = 7 Hz, 3H), 1.13 (d, J = 7.1 Hz, 1H), 1.29 (m, 1H), 1.52 (m, 1H), 2.28 (hep, J = 7.1 Hz, 1H), 2.72 (dd, J = 3.8, J = 3.4 Hz, 1H), 7.24 (td, J = 7.1, J = 1.4 Hz, 1H), 7.42 (m, 2H), 7.63 (d, J = 7.4 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 19.5, 20.2, 25.6, 26.7, 36.5, 42.5, 123.9, 124.5, 126.5, 133.4, 134.6, 154.6, 204.4. HRMS (EI) calcd for $C_{13}H_{14}O$ (M+) 186.10447 found 186.10439.



**Compound 8a.** The procedure for the preparation of **8a** has been used for the synthesis of **5b** employing 2-*t*-butyl-1-indenone (1.3 g, 7.0 mmol), 23 mL THF, and sulfur ylide (8.7 mL, 7.0 mmol, 0.8 M in THF). Cyclopropane **8a** was isolated as a pale yellow oil (1.23 g, 89 % yield).

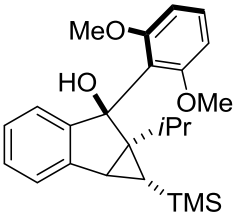
$^1$H NMR (300 MHz, $CDCl_3$): δ 1.06 (s, 9H), 2.48 (dd, J = 7.4, J = 7.4 Hz, 1H), 3.00 (dd, J = 19, J = 4 Hz, 1H), 3.19 (dd, J = 19, J = 8 Hz, 1H), 7.33 (t, J = 7 Hz, 1H), 7.45 (d, J = 8 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.71 (d, J = 8 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 27.5, 29.4, 29.8, 33.7, 56.6, 123.3, 126.1, 127.0, 134.3, 153.2, 207.8. HRMS (EI) calcd for $C_{14}H_{16}O$ (M+) 200.12012 found 200.12002.



**Compound 8b.** The procedure for the preparation of **8b** has been used for the synthesis of **8a** employing 2-adamantyl-1-indenone (1.24 g, 4.7 mmol), 15.0 mL THF, and sulfur ylide (4.7 mL, 4.7 mmol, 1.0 M in THF). Cyclopropane **8b** was isolated as a reddish solid (1.02 g, 78 % yield).

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.53-1.78 (m, 10H), 1.85-2.01 (m, 5H), 2.10-2.18 (m, 1H), 2.33-2.40 (m, 1H), 3.07-3.13 (m, 1H), 7.31 (m, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.53 (m, 1H) 7.71 (d, J = 7.8 Hz, 1H; $^{13}$C NMR (75 MHz, $CDCl_3$): δ 28.1 (broad), 20.3, 36.5 (broad), 37.1, 39.2, 41.5, 75.5, 124.9, 125.9, 127.8, 134.2, 135.4, 149.6, 200.2. HRMS (EI) calcd for $C_{20}H_{22}O$ (M+) 278.16707 found 278.16761.

***Nucleophilic Addition to 6 (Table 1a)***

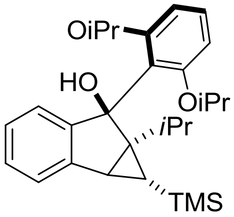


**Compound 6a (Entry 1) [1263064-86-3].** An oven-dried flask was charged with 10.0 mL anhydrous $Et_2O$ and *m*-dimethoxybenzene (267 mg, 1.93 mmol), *n*-BuLi (0.73 mL, 1.8 mmol, 2.5 M in hexanes) was added dropwise and the reaction was allowed to stir overnight. The ether was removed under reduced pressure to yield a white solid. Anhydrous THF was added (4.0 mL) and the reaction was cooled to -78 $^o$C. Indanone **5a** (250 mg, 0.967 mmol) in THF (1.0 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column

chromatography (Hex:Ether = 3:1). Compound **6a** was isolated as a clear oil (46 mg, 12% yield).

A second run had a yield of 15%

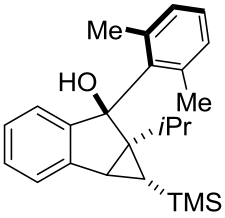
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.14 (s, 9H), 0.47 (d, J = 5.4 Hz, 1H), 0.72 (d, J = 6.9 Hz, 3H), 1.02 (d, J = 7.2 Hz, 3H), 1.70 (septet, J = 6.9 Hz, 1H), 2.38 (d, J = 5.4 Hz, 1H), 3.04 (s, 3H), 4.02 (s, 3H), 6.41 (d, J = 9.6 Hz, 1H), 6.60 (s, 1H), 6.69 (d, J = 9.3 Hz, 1H), 6.85-7.28 (m, 5H)



**Compound 6b (Entry 2).** An oven-dried flask was charged with 1.5 mLanhydrous $Et_2O$ and *m*-diisopropoxybenzene (73 mg, 0.38 mmol), *n*-BuLi (0.22 mL, 0.35 mmol, 1.6 M in hexanes) was added dropwise and the reaction was allowed to stir overnight. The reaction was cooled to -78 $^oC$. Indanone **5a** (75 mg, 0.29 mmol) in $Et_2O$ (1.0 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). Compound **6b** was isolated as a tan solid (54 mg, 41% yield).

A second run had a yield of 40%

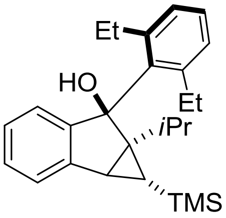
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.03 (s, 9H), 0.73 (d, J = 6.0 Hz, 3H), 0.84 (d, J = 6.0 Hz, 3H), 1.10 (d, J = 7.5 Hz, 3H), 1.19 (d, J = 7.5 Hz, 3H), 1.39 (d, J = 6.0 Hz, 1H), 1.49 (d, J = 6.5 Hz, 3H), 1.57 (d, J = 7.0 Hz, 3H), 2.28 (d, J = 5.8 Hz, 1H), 2.41 (hep, J = 5.8 Hz, 1H), 4.22 (hep, J = 5.8 Hz, 1H), 4.84 (hep, J = 5.8 Hz, 1H), 6.42 (d, J = 7.5 Hz, 1H), 6.63 (d, J = 8.5 Hz, 1H), 6.95-7.22 (m, 5H). HRMS (EI) calcd for $C_{25}H_{33}O_3$ (M+) 381.24298 found 381.24300.



**Compound 6c (Entry 3) [1263064-87-4].** An oven-dried flask was charged with 3.0 mL anhydrous $Et_2O$ and 1-bromo-2,6-dimethylbenzene (279 mg, 1.51 mmol), the reaction was cooled to -78 $^oC$ and *t*-BuLi (1.8 mL, 3.0 mmol, 1.7 M in hexanes) was added dropwise and the reaction was allowed to stir for 2 hours. The reaction was warmed to ambient temperature for 30 minutes and reecooled to -78 $^oC$. Indanone **5a** (300 mg, 1.16 mmol) in $Et_2O$ (3.0 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 6:1). Compound **6c** was isolated as a viscous oil (249 mg, 59% yield).

A second run had a yield of 54%

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.09 (s, 9H), 0.62 (d, J = 5.7 Hz, 1H), 0.98 (d, J = 7.5 Hz, 3H), 1.11 (d, J = 7.2 Hz, 3H), 1.77 (s, 3H), 1.77 (s, 1H), 2.40 (d, J = 5.7 Hz, 1H), 2.94 (s, 3H), 3.10 (septet, J = 7.2 Hz, 1H), 6.95-7.32 (m, 7H)

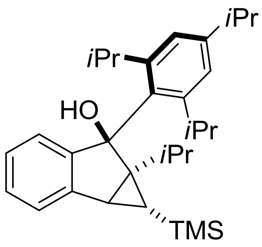


**Compound 6d (Entry 4) [1263064-88-5].** An oven-dried flask was charged with 3.0 mL anhydrous $Et_2O$ and 1-bromo-2,6-diethylbenzene (321 mg, 1.51 mmol), the reaction was cooled to -78 $^oC$ and *t*-BuLi (1.8 mL, 3.0 mmol, 1.7 M in pentane) was added dropwise and the reaction was allowed to

stir for 2 hours. The reaction was warmed to ambient temperature for 30 minutes and re-cooled to -78 °C. Indanone **5a** (300 mg, 1.16 mmol) in $Et_2O$ (3.0 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 9:1). Compound **6d** was isolated as an off color oil (226 mg, 50% yield, compound > 90% pure).

A second run had a yield of 46%

$^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 0.10 (s, 9H), 0.50 (d, J = 5.4 Hz, 1H), 0.93 (t, J = 7.5 Hz, 3H), 1.01 (d, J = 7.2 Hz, 3H), 1.14 (d, J = 6.9, 3H), 1.41 (t, J = 6.9 Hz, 3H), 1.72 (s, 1H), 1.94 (m, 2H), 2.40 (d, J = 6 Hz, 1H), 2.74 (m, 2H), 3.91 (m, 1H), 7.07-7.32 (m, 7H)

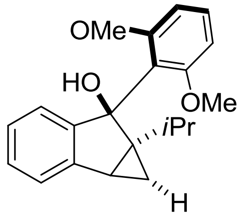


**Compound 6e (Entry 5) [1263064-89-6].** An oven-dried flask was charged with 3.0 mL anhydrous $Et_2O$ and 1-bromo-2,4,6-triisopropylbenzene (427 mg, 1.51 mmol), the reaction was cooled to -78 °C and *t*-BuLi (1.8 mL, 3.0 mmol, 1.7 M in pentane) was added dropwise and the reaction was allowed to stir for 2 hours. The reaction was warmed to ambient temperature for 30 minutes and re-cooled to -78 °C. Indanone **5a** (300 mg, 1.16 mmol) in $Et_2O$ (2.8 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography

(Hex:Ether = 9:1) two times. Compound **6e** was isolated as a white solid (76 mg, 14% yield).

A second run had a yield of 12%

$^1$H NMR (300 MHz, CDCl$_3$): δ 0.12 (s, 9H), 0.57 (d, J = 5.7 Hz, 1H), 0.84 (d, J = 6.3 Hz, 3H), 0.99 (d, J = 7.2 Hz, 6H), 1.09 (d, J = 6.9 Hz, 3H), 1.19-1.37 (m, 12H), 1.61 (s, 1H), 2.17 (septet, J = 6.9 Hz, 1H), 2.37 (d, J = 5.7 Hz, 1H), 2.90 (septet, J = 6.9 Hz, 1H), 3.11 (m, 1H), 4.41 (septet, J = 6.6 Hz, 1H), 6.96-7.28 (m, 6H)

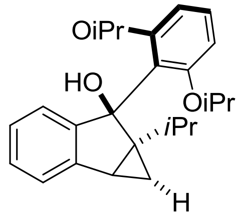


**Compound 6f (Entry 6).** An oven-dried flask was charged with 3.0 mL anhydrous Et$_2$O and *m*-dimethoxybenzene (103 mg, 0.80 mmol), *n*-BuLi (0.47 mL, 0.75 mmol, 1.6 M in hexanes) was added dropwise and the reaction was allowed to stir overnight. The reaction was cooled to -78 °C. Indanone **5b** (100 mg, 0.54 mmol) in THF (2.0 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 5 mL of NH$_4$Cl (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over MgSO$_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 9:1). Compound **6f** was isolated as a clear oil (106 mg, 61% yield).

A second run had a yield of 58%

$^1$H NMR (300 MHz, CDCl$_3$): δ 0.67 (d, J = 6.9 Hz, 3H), 0.97 (d, J = 6.9 Hz, 3H), 1.00-1.10 (m, 2H), 1.86 (hep, J = 6.9 Hz, 1H), 2.47 (dd, J = 3.7 Hz (both), 1H), 3.15 (s, 3H), 4.02 (s, 3H), 6.49 (d, J = 8.6 Hz, 1H), 6.74 (d, J = 8.6 Hz, 1H) 6.82-7.28 (m, 6H). $^{13}$C

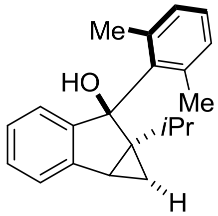
NMR (75 MHz, $CDCl_3$): δ 19.3, 19.4, 21.5, 22.6, 26.4, 30.8, 43.0, 55.3, 57.1, 90.4, 98.4, 110.6, 122.6, 123.4, 125.8, 126.4, 127.5, 140.9, 146.7, 150.3, 158.7, 159.5. HRMS (EI) calcd for $C_{21}H_{25}O_3$ (M+) 325.18038 found 325.18150.



**Compound 6g (Entry 7).** An oven-dried flask was charged with 3.0 mL anhydrous $Et_2O$ and *m*-diisopropoxybenzene (161 mg, 0.80 mmol), *n*-BuLi (0.47 mL, 0.75 mmol, 1.6 M in hexanes) was added dropwise and the reaction was allowed to stir overnight. The reaction was cooled to -78 °C. Indanone **5b** (100 mg, 0.54 mmol) in $Et_2O$ (2.0 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 9:1). Compound **6g** was isolated as a clear oil (105 mg, 52% yield).

A second run had a yield of 49%

Proton and Carbon NMR complex due to a mix of diastereomers 80:20.

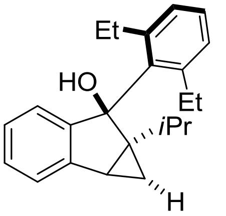


**Compound 6h (Entry 8).** An oven-dried flask was charged with 3.0 mL anhydrous $Et_2O$ and 1-bromo-2,6-dimethylbenzene (128 mg, 0.70 mmol), the reaction was cooled to -78 °C and *t*-BuLi (0.87 mL, 1.4 mmol, 1.6 M in pentane) was added dropwise and the reaction was allowed to stir for 2 hours. The reaction was warmed to ambient temperature for 30 minutes and re-cooled to -78 °C. Indanone **5b** (100 mg, 0.54 mmol) in $Et_2O$ (2.0 mL) was added dropwise. The reaction

was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 9:1) two times. Compound **6h** was isolated as an oil (102 mg, 66% yield).

A second run had a yield of 59%

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.82 (t, 6H), 0.93 (m, 2H), 1.39 (s, 1H), 1.71 (s, 3H, Broad), 2.50 (dd, J = 5.1 Hz, J = 2.92 Hz, 1H), 2.89 (s, 3H), 3.30 (hep, J = 6.6 Hz, 1H), 6.89-7.36 (m, 7H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 17.8, 20.4, 22.2, 22.5, 26.5, 27.5, 46.2, 88.6, 123.8, 124.4, 125.9, 126.3, 128.1, 131.3 (Broad, Multiple Peaks), 139.5, 142.5, 150.5. One aliphatic peak and six aromatic peaks are not visible. HRMS (EI) calcd for $C_{21}H_{25}O$ (M+) 293.19055 found 293.19071.

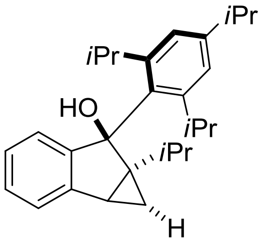


**Compound 6i (Entry 9).** An oven-dried flask was charged with 3.0 mL anhydrous $Et_2O$ and 1-bromo-2,6-diethylbenzene (111 mg, 0.54 mmol), the reaction was cooled to -78 $^oC$ and *t*-BuLi (0.66 mL, 1.1 mmol, 1.6 M in pentane) was added dropwise and the reaction was allowed to stir for 2 hours. The reaction was warmed to ambient temperature for 30 minutes and re-cooled to -78 $^oC$. Indanone **5b** (75 mg, 0.40 mmol) in $Et_2O$ (2.0 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent

was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 9:1). Compound **6i** was isolated as a white solid (96 mg, 73% yield). Crystals suitable for diffraction were generated from the slow evaporation of dichloromethane at room temperature.

A second run had a yield of 71%

$^1$H NMR (300 MHz, CDCl$_3$): δ 0.80 (t, J = 7.0 Hz, 6H), 0.89 (t, J = 7.4 Hz, 3H), 0.97 (dd, J = 5.6 Hz, J = 2.5 Hz, 1H), 1.11 (dd, J = 3.1 Hz, J = 2.1 Hz, 1H), 1.40 (t, J = 7.4 Hz, 3H), 1.62 (s, 1H), 1.78-2.00 (m, 2H), 2.52 (dd, J = 5.1 Hz, J = 3.0 Hz, 1H), 2.63-2.79 (m, 1H), 3.27 (hep, J = 6.6 Hz, 1H), 3.71-3.87 (m, 1H), 7.02-7.37 (m, 7H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 17.5, 18.0, 19.0, 20.3, 22.1, 22.7, 27.4, 29.4, 31.6, 45.6, 88.4, 123.4, 123.6, 126.0, 126.6, 128.0, 129.0, 130.4, 138.8, 142.0, 142.1, 146.9, 151.4. HRMS (EI) calcd for $C_{23}H_{28}O$ (M+) 320.21402 found 320.21341.



**Compound 6j (Entry 10).** An oven-dried flask was charged with 3.0 mL anhydrous Et$_2$O and 1-bromo-2,4,6-triisopropylbenzene (198 mg, 0.70 mmol), the reaction was cooled to -78 °C and *t*-BuLi (0.88 mL, 1.4 mmol, 1.6 M in pentane) was added dropwise and the reaction was allowed to stir for 2 hours. The reaction was warmed to ambient temperature for 30 minutes and re-cooled to -78 °C. Indanone **5b** (75 mg, 0.40 mmol) in Et$_2$O (2.0 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 5 mL of NH$_4$Cl (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over MgSO$_4$. The solvent

was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 9:1). Compound **6j** was isolated as a white solid (100 mg, 64% yield).

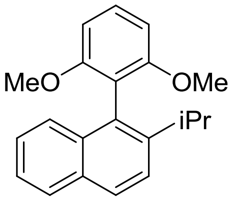
A second run had a yield of 60%

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.79-1.55 (m, 25H), 2.22 (hep, J = 6.2 Hz, 1H), 2.46-2.52 (m, 1H), 2.87 (hep, J = 6.2 Hz, 1H), 3.24 (hep, J = 6.8 Hz, 1H), 4.39 (hep, J = 6.9 Hz, 1H), 6.89-7.33 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 19.0, 20.3, 23.0, 23.3, 23.7, 23.9, 24.8, 26.5, 27.6, 31.0, 31.7, 33.5, 44.2, 89.0, 122.8, 123.1, 123.5, 125.8, 127.7, 135.0, 141.9, 146.2, 146.6, 151.5, 151.7. One aliphatic peak and one aromatic peak are not visible. HRMS (EI) calcd for $C_{28}H_{38}O$ (M+) 390.29227 found 390.29264.

***Rearrangement of 6 (Table 1b):***

**General Procedure:** In a nitrogen glovebox, a vial was charged with **3**, toluene, and 10% $Eu(OTf)_3$. The vessel was sealed and stirred at 80 °C (entries 1-5) or 110 °C (entries 6-10) for 24 h. The reaction was cooled to ambient temperature, and the mixture was filtered through a silica plug with copious ether washings. The solvents were removed under reduced pressure, and the crude material was subjected to preparatory thin-layer chromatography using 9:1 hexanes:ether as the eluent.

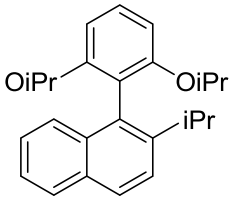
**Compound 7a (Entry 1) [1263064-90-9].** The general procedure has been applied using **6a** (40 mg, 0.010 mmol), toluene (1.0 mL), and $Eu(OTf)_3$ (6.0 mg, 0.0010 mmol). The product **7a** was isolated as an oil (20 mg, 65% yield)



A second run had a yield of 60%

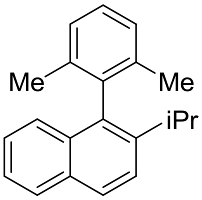
$^1$H NMR (300 MHz, $CDCl_3$): δ 1.20 (d, J = 7.2 Hz, 6H), 2.83 (septet, J = 6.9 Hz, 1H), 3.64 (s, 6H), 6.75 (d, J = 8.4 Hz, 2H), 7.28-7.46 (m, 4H), 7.58 (d, J = 9 Hz, 1H), 7.83-7.91 (m, 2H)

**Compound 7b (Entry 2).** The general procedure has been applied using **6b** (50 mg, 0.10 mmol), toluene (1.0 mL), and $Eu(OTf)_3$ (6 mg, 0.010 mmol). The product **7b** was isolated as a light yellow oil (33 mg, 83% yield).



A second run had a yield of 81%

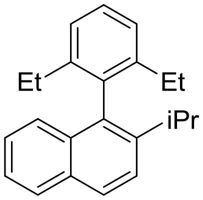
$^1$H NMR (300 MHz, $CDCl_3$): δ 0.88 (d, J = 6.0 Hz, 6H), 1.04 (d, J = 6.1 Hz, 6H), 1.21 (d, J = 6.9 Hz, 6H), 2.90 (hep, J = 7.0 Hz, 1H), 4.33 (hep, J = 5.9 Hz, 2H), 6.68 (d, J = 8.6 Hz, 2H), 7.18-7.42 (m, 4H), 7.54 (d, J = 8.6 Hz, 1H), 7.78-7.90 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 21.7, 21.9, 23.6, 31.0, 69.8, 106.5, 123.4, 124.0, 124.7, 126.4, 127.1, 127.3, 128.3, 130.0, 131.8, 133.0, 144.4, 157.2. HRMS (EI) calcd for $C_{25}H_{31}O_2$ (M+) 363.23241 found 363.23070.



**Compound 7c (Entry 3) [1263064-91-0].** The general procedure has been applied using **6c** (169 mg, 0.494 mmol), toluene (5.0 mL), and Eu(OTf)$_3$ (30 mg, 0.049 mmol). The product **7c** was isolated as an off-color oil (89 mg, 70% yield).

A second run had a yield of 75%

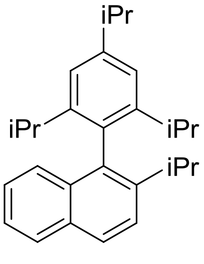
$^1$H NMR (300 MHz, CDCl$_3$): δ 1.24 (d, J = 6.9 Hz, 6H), 1.91 (s, 6H), 2.78 (septet, J = 6.9 Hz, 1H), 7.18-7.48 (m, 6H), 7.62 (d, J = 8.7 Hz, 1H), 7.88-7.94 (m, 2H)



**Compound 7d (Entry 4) [1263064-92-1].** The general procedure has been applied using **6d** (218 mg, 0.555 mmol), toluene (5.6 mL), and Eu(OTf)$_3$ (33 mg, 0.056 mmol). The product **7d** was isolated as a light yellow oil (122 mg, 73% yield).

A second run had a yield of 72%

$^1$H NMR (300 MHz, CDCl$_3$): δ 1.02 (t, J = 7.5 Hz, 6H), 1.24 (d, J = 7.2 Hz, 6H), 2.12-2.36 (m, 4H), 2.79 (septet, J = 6.9 Hz, 1H), 7.24-7.51 (m, 6H), 7.64 (d, J = 8.7 Hz, 1H), 7.89-7.96 (m, 2H)

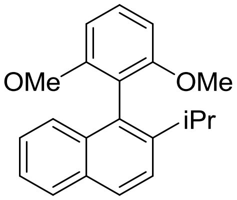


**Compound 7e (Entry 5) [1263064-93-2].** The general procedure has been applied using **6e** (50 mg, 0.011 mmol), toluene (1.1 mL), and Eu(OTf)$_3$ (6.5 mg, 0.0011 mmol). The product **7e** was isolated as an off-color oil (29 mg, 73% yield).

A second run had a yield of 78%

$^{1}$H NMR (300 MHz, $CDCl_3$): δ 0.83 (d, J = 6.6 Hz, 6H), 1.12 (d, J = 6.9 Hz, 6H), 1.22 (d, J = 6.6 Hz, 6H), 1.39 (d, J = 6.6 Hz, 6H), 2.35 (hep, J = 6.6 Hz, 2H), 2.87 (hep, J = 7.2 Hz, 1H), 3.03 (hep, J = 6.9 Hz, 1H), 7.14-7.29 (m, 4H), 7.39 (t, J = 6.9 Hz, 1H), 7.57 (d, J = 9 Hz, 1H), 7.82-7.90 (m, 2H)

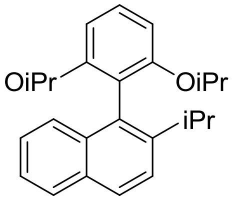
**Compound 7f (Entry 6).** The general procedure has been applied using **6f** (52 mg, 0.16 mmol), toluene (1.6 mL), and $Eu(OTf)_3$ (10 mg, 0.016 mmol). The product **7f** was isolated as an off-color oil (29 mg, 60% yield).



A second run had a yield of 58%

Same characterization data as **7a**

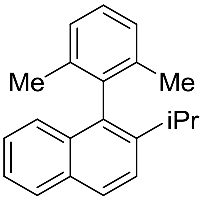
**Compound 7g (Entry 7).** The general procedure has been applied using **6g** (52 mg, 0.14 mmol), toluene (1.5 mL), and $Eu(OTf)_3$ (8.2 mg, 0.014 mmol). The product **7g** was isolated as an off-color oil (45 mg, 90% yield).



A second run had a yield of 83%

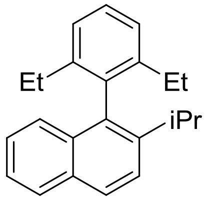
Same characterization data as **7b**

**Compound 7h (Entry 8).** The general procedure has been applied using **6h** (102 mg, 0.35 mmol), toluene (3.5 mL), and $Eu(OTf)_3$ (21 mg, 0.035 mmol). The product **7h** was isolated as an off-color oil (50 mg, 53% yield).



A second run had a yield of 60%

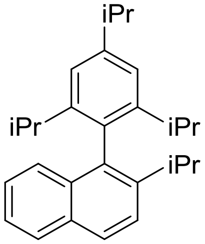
Same characterization data as **7c**



**Compound 7i (Entry 9).** The general procedure has been applied using **6i** (78 mg, 0.24 mmol), toluene (2.4 mL), and Eu(OTf)$_3$ (15 mg, 0.024 mmol). The product **7i** was isolated as an off-color oil (70 mg, 95% yield).

A second run had a yield of 91%

Same characterization data as **7d**

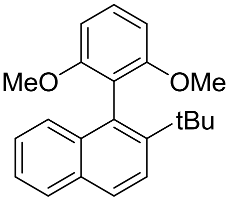


**Compound 7j (Entry 10).** The general procedure has been applied using **6j** (95 mg, 0.24 mmol), toluene (2.4 mL), and Eu(OTf)$_3$ (15 mg, 0.024 mmol). The product **7j** was isolated as an off-color oil (91 mg, 100% yield).

A second run had a yield of 100%

Same characterization data as **7e**

***t-Butyl and Adamantyl Naphthalene Generation (Table 2):***

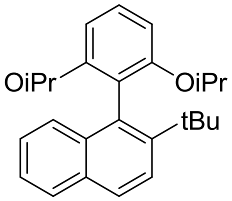


**Compound 9a (Entry 1).** An oven-dried flask was charged with 10.0 mL anhydrous Et$_2$O and *m*-dimethoxybenzene (97 mg, 0.75 mmol), *n*-BuLi (0.44 mL, 0.70 mmol, 1.6 M in hexanes) was added dropwise and the reaction was allowed to stir overnight. The ether was removed under reduced pressure to yield a white solid. Anhydrous Et$_2$O was added (4.0 mL) and the reaction was cooled

to -78 °C. Indanone **8a** (100 mg, 0.50 mmol) in THF (2.0 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to a plug. The crude carbinol (103 mg, 0.30 mmol) was then subjected to rearrangement conditions using toluene (3.0 mL), $Eu(OTf)_3$ (18 mg, 0.030 mmol), and heated to 110 °C for 24 hours. The product **9a** was isolated as an oil (25 mg, 16% from indanone). Crystals suitable for diffraction were obtained from low temperature evaporation from hexane.

A second run had a yield of 17%

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.37 (s, 9H), 3.75 (s, 6H), 6.80 (d, J = 8.3 Hz, 2H), 7.22-7.63 (m, 4H), 7.83-8.00 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 31.7, 55.4, 103.6, 119.1, 124.7, 125.4, 125.6, 126.2, 127.2, 127.4, 129.0, 129.4, 131.7, 133.7, 145.3, 158.5. HRMS (EI) calcd for $C_{22}H_{24}O_2$ (M+) 320.17763 found 320.17789.

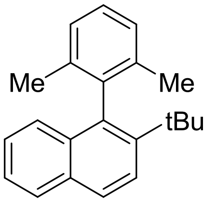


**Compound 9b (Entry 2).** An oven-dried flask was charged with 10.0 mL anhydrous $Et_2O$ and *m*-diisopropoxybenzene (153 mg, 0.75 mmol), *n*-BuLi (0.44 mL, 0.70 mmol, 1.6 M in hexanes) was added dropwise and the reaction was allowed to stir overnight. The ether was removed under reduced pressure to yield a white solid. Anhydrous $Et_2O$ was added (4.0 mL) and the reaction was cooled to -78 °C. Indanone **8a** (100 mg, 0.50 mmol) in $Et_2O$ (2.0 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred

overnight. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to a plug. The crude carbinol (115 mg, 0.29 mmol) was then subjected to rearrangement conditions using toluene (3.0 mL), $Eu(OTf)_3$ (18 mg, 0.030 mmol), and heated to 110 °C for 24 hours. The product **9b** was isolated as an oil (57 mg, 30% from indanone).

A second run had a yield of 23%

$^1$H NMR (300 MHz, $CDCl_3$): δ 0.83 (d, J = 6.1 Hz, 6H), 1.07 (d, J = 6.1 Hz, 6H), 1.28 (s, 9H), 4.35 (hep, J = 6.1 Hz, 2H), 6.61 (d, J = 8.5 Hz, 2H), 7.11-7.38 (m, 4H), 7.68-7.80 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 21.7, 22.1, 22.2, 32.0, 32.1, 37.2, 69.5, 105.4, 121.5, 124.2, 126.1, 126.3, 126.4, 126.9, 128.3, 129.8, 131.6, 133.9, 145.2, 157.3. One aromatic peak and one aliphatic peak not observed. HRMS (EI) calcd for $C_{26}H_{33}O_2$ (M+) 377.24806 found 377.24706.

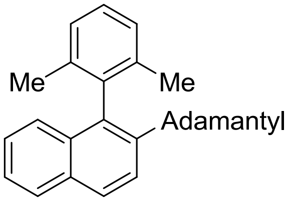


**Compound 9c (Entry 3).** An oven-dried flask was charged with 3.0 mL anhydrous $Et_2O$ and 1-bromo-2,6-dimethylbenzene (120 mg, 0.65 mmol), *t*-BuLi (0.81 mL, 1.3 mmol, 1.6 M in hexanes) was added dropwise at -78 °C and the reaction was allowed to stir for two hours. The reaction was warmed to room temperature for 10 minutes and re-cooled to -78 °C. Indanone **8a** (100 mg, 0.50 mmol) in $Et_2O$ (2.0 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and then brought to 40 °C overnight. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether.

The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to a plug. The crude carbinol (50 mg, 0.13 mmol) was then subjected to rearrangement conditions using toluene (1.3 mL), $Eu(OTf)_3$ (8 mg, 0.013 mmol), and heated to 150 $^{o}$C for 24 hours. The product **9c** was isolated as an oil (23 mg, 16% from indanone).

A second run had a yield of 24%

$^{1}$H NMR (300 MHz, $CDCl_3$): δ 1.22 (s, 9H), 1.88 (s, 6H), 6.90-7.46 (m, 6H), 7.70-7.86 (m, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 20.6, 21.4, 32.4, 33.1, 124.9, 125.1, 125.3, 124.4, 125.8, 126.0, 127.0, 127.1, 127.4, 127.5, 128.3, 129.5, 136.6, 137.4. HRMS (EI) calcd for $C_{22}H_{25}$ (M+) 289.19563 found 289.19606.



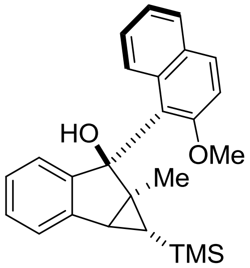
**Compound 9d (Entry 1).** An oven-dried flask was charged with 1.0 mL anhydrous $Et_2O$ and 1-bromo-2,6-dimethylbenzene (50 mg, 0.27 mmol), *t*-BuLi (0.15 mL, 2.5 mmol, 1.6 M in hexanes) was added dropwise at -78 $^{o}$C and the reaction was allowed to stir for two hours. The reaction was warmed to room temperature for 10 minutes and re-cooled to -78 $^{o}$C. Indanone **8b** (50 mg, 0.18 mmol) in $Et_2O$ (0.5 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and then brought to 40 $^{o}$C overnight. At the conclusion of the reaction, 5 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 20 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to a plug. The crude carbinol (69 mg, 0.18 mmol) was then subjected to rearrangement conditions using toluene (1.8 mL), $Eu(OTf)_3$ (11 mg, 0.018 mmol), and

heated to 150 °C for 24 hours. The product **9d** was isolated as an oil (17 mg, 26% from indanone).

A second run had a yield of 23%

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.45-2.48 (m, 21H), 6.91-7.45 (m, 7H), 7.73-7.91 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 21.4, 29.1 (Broad), 36.7 (Broad), 43.0, 43.2 (Broad), 43.5, 122.4, 124.9, 125.2 (Broad), 125.3, 125.4, 125.9, 126.7, 126.9, 127.0 (Broad), 127.3, 128.2, 129.5, 136.4, 137.4. Many peaks not observed due to broad overlap. HRMS (EI) calcd for $C_{28}H_{30}$ (M+) 366.23475 found 366.23314.

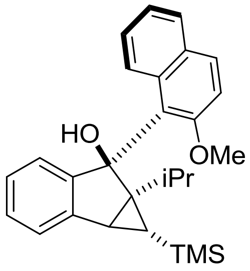
***Asymmetric Precursor:***



**Compound 30a [1263064-77-2].** An oven-dried flask was charged with 0.50 mL anhydrous $Et_2O$ and 1-bromo-2-methoxynaphthalene (27 mg, 0.11 mmol), n-BuLi was added dropwise (0.07 mL, 0.10 mmol, 1.6 M in hexanes) was added dropwise and the reaction was allowed to stir for 5 minutes. The reaction was cooled to -78 °C. Enantiopure indanone **A** (24 mg, 0.10 mmol) in $Et_2O$ (0.50 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 1 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 10 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). Compound **30a** was isolated as a clear solid (20 mg, 50% yield).

The same reaction was run on the opposite enantiomer of indanone to give a 60% yield.

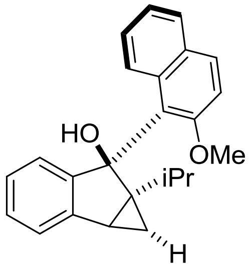
$^1$H NMR (300 MHz, CDCl$_3$): δ 0.17 (s, 9H), 1.03 (d, J = 5.4 Hz, 1H), 1.12 (s, 3H), 2.48 (d, J = 5.1 Hz, 1H), 4.16 (s, 3H), 6.72 (s, 1H), 6.81 (d, J = 7.2 Hz, 1H) 6.97-7.41 (m, 7H) 7.72 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.7 Hz, 1H)



**Compound 30b.** An oven-dried flask was charged with 0.25 mL anhydrous Et$_2$O and 1-bromo-2-methoxynaphthalene (15 mg, 0.07 mmol), n-BuLi was added dropwise (0.04 mL, 0.06 mmol, 1.6 M in hexanes) was added dropwise and the reaction was allowed to stir for 5 minutes. The reaction was cooled to -78 $^o$C. Enantiopure indanone **5a** (15 mg, 0.06 mmol) in Et$_2$O (0.25 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 1 mL of NH$_4$Cl (saturated, aqueous) was added followed by 10 mL ether. The organic phase was washed three times with brine and dried over MgSO$_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). Compound **30b** was isolated as a clear solid (7 mg, 27% yield).

The same reaction was run on the opposite enantiomer of indanone to give a 24% yield.

The precursor could not be purified effectively and crude material was taken forward.

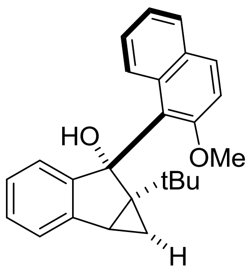


**Compound 10.** An oven-dried flask was charged with 0.50 mL anhydrous Et$_2$O and 1-bromo-2-methoxynaphthalene (31 mg, 0.13 mmol), n-BuLi was added dropwise (0.07 mL, 0.12 mmol, 1.6 M in hexanes) was added dropwise and the reaction was allowed to stir for 5

minutes. The reaction was cooled to -78 $^{o}$C. Enantiopure indanone **5b** (22 mg, 0.12 mmol) in $Et_2O$ (0.50 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 1 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 10 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). Compound **10** was isolated as a clear solid (21 mg, 51% yield). Crystals suitable for diffraction were obtained from slow evaporation of hexane at -20 $^{o}$C

The same reaction was run on the opposite enantiomer of indanone to give a 46% yield.

$^{1}$H NMR (300 MHz, $CDCl_3$): δ 0.60 (d, J = 7.6 Hz, 3H), 0.97 (d, J = 6.6 Hz, 3H), 1.22-1.30 (m, 1H), 1.52 (t, J = 4.4 Hz, 1H), 1.59 (s, 1H), 1.89 (hep, J = 6.7 Hz, 1H), 2.77 (dd, J = 4.4 Hz, J = 3.6 Hz, 1H), 4.16 (s, 3H), 6.74 (d, J = 7.3 Hz, 1H), 6.89-7.44 (m, 6H), 7.67 (dd, J = 12.2 Hz, J = 7.8 Hz, 2H), 7.82 (d, J = 8.8 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 18.9, 20.2, 21.5, 26.2, 30.9, 45.3, 58.5, 90.5, 115.8, 122.8, 123.7, 125.4, 125.6, 125.7, 126.4 (Broad), 127.4, 128.2, 130.4, 145.3, 151.5, 155.4. Three aromatic peaks not observed. HRMS (EI) calcd for $C_{24}H_{24}O$ (M+) 344.17763 found 344.17710.

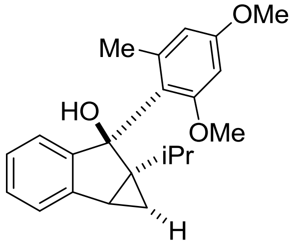


**Compound 30c.** An oven-dried flask was charged with 0.50 mL anhydrous $Et_2O$ and 1-bromo-2-methoxynaphthalene (31 mg, 0.13 mmol), n-BuLi was added dropwise (0.07 mL, 0.12 mmol, 1.6 M in hexanes) was added dropwise and the reaction was allowed to stir for 5 minutes. The reaction was cooled to -78 $^{o}$C. Enantiopure indanone **8a** (24 mg, 0.12 mmol) in $Et_2O$ (0.50 mL) was added dropwise. The reaction was allowed to warm to

ambient temperature and stirred overnight. At the conclusion of the reaction, 1 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 10 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). Compound **30c** was isolated as a clear solid (19 mg, 45% yield).

The same reaction was run on the opposite enantiomer of indanone to give a 60% yield.

$^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.04 ($\sigma$, 1H, Broad) 1.16 (s, 9H), 1.83 (s, 1H, Broad), 2.63 (s, 1H, Broad), 3.26 (s, 1H), 4.19 (s, 3H, Broad), 6.84-7.95 (m, 10H, Broad); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ 21.8 (b), 28.8 (b), 30.2 (b), 30.9, 34.0 (b), 48.3, 56.5 (b), 113.8 (b), 122.8, 123.0, 124.7 (b), 125.7 (b), 128.1 (b), 128.7, 130.7, 131.0 (b), 142.7. Six aromatic peaks not observed due to broadening. HRMS (EI) calcd for $C_{25}H_{26}O_2$ (M+) 358.19328 found 358.19319.

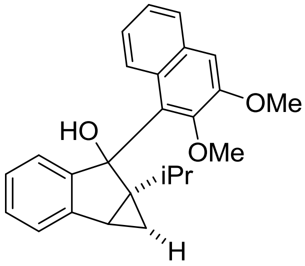


**Compound 30d.** An oven-dried flask was charged with 0.50 mL anhydrous $Et_2O$ and 2-bromo-3,5-dimethoxytoluene (36 mg, 0.15 mmol), n-BuLi was added dropwise (0.09 mL, 0.13 mmol, 1.6 M in hexanes) was added dropwise and the reaction was allowed to stir for 5 minutes. The reaction was cooled to -78 $^{o}$C. Enantiopure indanone **5b** (25 mg, 0.13 mmol) in $Et_2O$ (0.50 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 1 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 10 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under

reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). Compound **30d** was isolated as an oil (6.9 mg, 15% yield).

The same reaction was run on the opposite enantiomer of indanone to give a 15% yield.

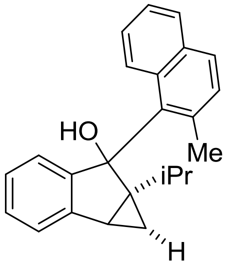
$^1$H NMR (300 MHz, CDCl$_3$): δ 0.67 (d, J = 7.6 Hz, 3H), 0.96 (d, J = 6.5 Hz, 3H), 1.09 (dd, J = 3.3 Hz, J = 4.9 Hz, 1H), 1.21-1.31 (m, 1H), 1.52 (s, 3H), 1.84 (hep, J = 7.1 Hz, 1H), 2.52 (dd, J = 4.4 Hz, J = 3.8 Hz, 1H), 3.80 (s, 3H), 3.98 (s, 3H), 6.27 (d, J = 2.7 Hz, 1H), 6.49 (d, J = 2.7 Hz, 1H), 6.89-7.31 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 19.3, 21.5, 22.6, 26.4, 30.8, 43.0, 53.8, 55.4, 57.0, 90.4, 98.4, 110.6, 122.5, 123.4, 125.7, 126.4, 127.4, 140.9, 146.7, 150.3, 158.7, 159.5.



**Compound 30e.** An oven-dried flask was charged with 0.50 mL anhydrous Et$_2$O and 1-bromo-2,3-dimethoxynaphthalene (36 mg, 0.14 mmol), n-BuLi was added dropwise (0.08 mL, 0.12 mmol, 1.6 M in hexanes) was added dropwise and the reaction was allowed to stir for 5 minutes. The reaction was cooled to -78 $^o$C. Enantiopure indanone **5b** (23 mg, 0.12 mmol) in Et$_2$O (0.50 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 1 mL of NH$_4$Cl (saturated, aqueous) was added followed by 10 mL ether. The organic phase was washed three times with brine and dried over MgSO$_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). Compound **30e** was isolated as a white solid (20 mg, 44% yield). The opposite diastereomer was also isolated as a white solid (5 mg, 11% yield, Crude).

The same reaction was run on the opposite enantiomer of indanone to give a 44% yield of the major diastereomer and 11% for the minor diastereomer (Crude).

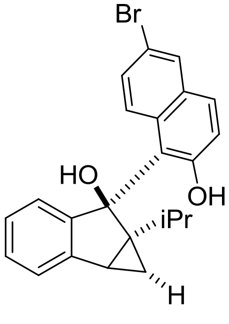
The Crude material was carried forward for both diastereomers. HRMS (EI) calcd for $C_{25}H_{26}O$ (M+) 374.18820 found 374.18863.



**Compound 30f.** An oven-dried flask was charged with 0.50 mL anhydrous $Et_2O$ and 1-bromo-2-methylnaphthalene (30 mg, 0.14 mmol), n-BuLi was added dropwise (0.08 mL, 0.12 mmol, 1.6 M in hexanes) was added dropwise and the reaction was allowed to stir for 5 minutes. The reaction was cooled to -78 $^{o}$C. Enantiopure indanone **5b** (23 mg, 0.12 mmol) in $Et_2O$ (0.50 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 1 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 10 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). Compound **30f** was isolated as a crude oil (11.5 mg)

The same reaction was run on the opposite enantiomer of indanone to yield 11 mg.

The precursor could not be purified effectively and crude material was taken forward.

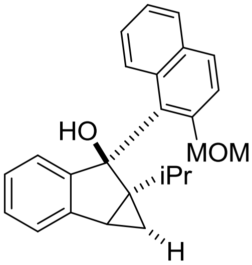


**Compound 27.** An oven-dried flask was charged with 0.50 mL anhydrous $Et_2O$ and 1,6-dibromo-2-hydroxynaphthalene (54 mg, 0.17 mmol), n-BuLi was added dropwise (0.22 mL, 0.34 mmol, 1.6 M in hexanes) was added dropwise and the reaction was allowed to stir for 5 minutes. The reaction

was cooled to -78 $^oC$. Enantiopure indanone **5b** (30 mg, 0.16 mmol) in $Et_2O$ (0.50 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 1 mL of $NH_4Cl$ (saturated, aqueous) was added followed by 10 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). Compound **27** was isolated as a red solid (21 mg, 32% yield ). Crystals suitable for diffraction were obtained from slow evaporation of hexane at -20 $^oC$.

The same reaction was run on the opposite enantiomer of indanone to give a 30% yield.

$^1H$ NMR (300 MHz, $CDCl_3$): δ 0.63 (d, J = 8.5 Hz, 3H), 0.99 (d, J = 7.0 Hz, 3H), 1.02-1.07 (m, 1H), 1.40 (dd, J = 2.9 Hz, J = 5.2 Hz, 1H), 1.94 (hep, J = 6.5 Hz, 1H), 2.92 (dd, J = 4.9 Hz, J = 3.3 Hz, 1H), 6.92-7.40 (m, 7H), 7.61 (d, J = 10.5 Hz, 1H), 7.79 (d, J = 2.3 Hz, 1H), 11.26 (s, 1H); $^{13}C$ NMR (150 MHz, $CDCl_3$): δ 18.2, 21.2, 21.4, 25.7, 31.3, 46.2, 93.5, 115.4, 115.8, 122.3, 123.4, 125.4, 126.0, 127.3, 128.7, 128.8, 129.7, 130.4, 130.6, 131.1, 145.3, 148.5, 156.0.



**Compound 30g.** An oven-dried flask was charged with 0.50 mL anhydrous $Et_2O$ and 1-bromo-2-methoxymethylnaphthalene (52 mg, 0.21 mmol), n-BuLi was added dropwise (0.08 mL, 0.12 mmol, 2.5 M in hexanes) was added dropwise and the reaction was allowed to stir for 5 minutes. The reaction was cooled to -78 $^oC$. Enantiopure indanone **5b** (32 mg, 0.17 mmol) in $Et_2O$ (0.50 mL) was added dropwise. The reaction was allowed to warm to ambient temperature and stirred overnight. At the conclusion of the reaction, 1

mL of $NH_4Cl$ (saturated, aqueous) was added followed by 10 mL ether. The organic phase was washed three times with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (Hex:Ether = 3:1). Compound **30g** was isolated as a fluffy yellowish solid (28 mg, 45% yield Crude ).

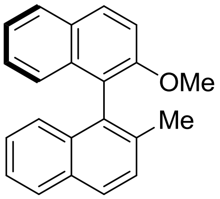
The same reaction was run on the opposite enantiomer of indanone to give a 25% yield.

The precursor could not be purified effectively and crude material was taken forward.

***Anti-Precursor Asymmetric Rearrangement (Table 3):***

**General Procedure:** In a nitrogen glovebox, a vial was charged with rearrangement precursor, toluene, and 10% $Eu(OTf)_3$. The vessel was sealed and stirred at 80 $^{o}$C (entries 1-2) or 110 $^{o}$C (entries 3-10) for 24 h. The reaction was cooled to ambient temperature, and the mixture was filtered through a silica plug with copious ether washings. The solvents were removed under reduced pressure, and the crude material was subjected to preparatory thin-layer chromatography using 9:1 hexanes:ether as the eluent.

**Compound 13a (Entry 1) [106909-87-9].** The general procedure has been applied using **30a** (22 mg, 0.06 mmol), toluene (0.6 mL), and $Eu(OTf)_3$ (3.3 mg, 0.006 mmol). The product **13a** was isolated as an oil (9.1 mg, 55% yield and 90% ee)

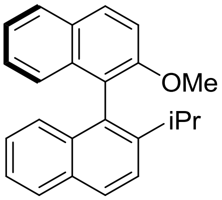


A run of the opposite enantiomer had a yield of 59% and 93% ee.

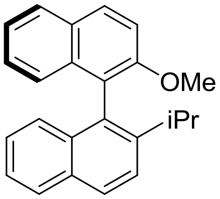
$^1$H NMR (300 MHz, $CDCl_3$): δ 2.13 (s, 3H), 3.79 (s, 3H), 7.03 (d, J = 9.0 Hz, 1H), 7.15-7.56 (m, 7H), 7.91 (m, 3H), 8.02 (d, J = 9 Hz, 1H).

HPLC Chiralpak OT (+) 99.8:0.2 Hexane:IPA mL/min. $t_1$ = 14.5 and $t_2$ = 18.2. $[\alpha]_D$ = (-) 14.0 in $CHCl_3$ at c = 0.10.

**Compound 13b (Entry 2).** The general procedure has been applied using **30b** (6.5 mg, 0.016 mmol), toluene (0.16 mL), and $Eu(OTf)_3$ (0.94 mg, 0.0016 mmol). The product **13b** was isolated as an oil (3.0 mg, 70% yield from crude precursor **30b** and >95% ee). The same characterization data was observed for **13c**.



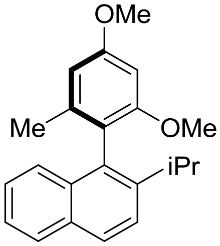
**Compound 13c (Entry 3).** The general procedure has been applied using **10** (23 mg, 0.07 mmol), toluene (0.70 mL), and $Eu(OTf)_3$ (4.0 mg, 0.007 mmol). The product **13c** was isolated as an oil (9.8 mg, 45% yield and >95% ee)



A run of the opposite enantiomer had a yield of 48% and >95% ee.

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.06 (d, J = 6.9 Hz, 3H), 1.19 (d, J = 6.9 Hz, 3H), 2.66 (hep, J = 6.7 Hz, 1H), 3.78 (s, 3H), 7.00-7.44 (m, 6H), 7.48 (d, J = 9.3 Hz, 1H), 7.66 (d, J = 8.9 Hz, 1H), 7.82-8.10 (m, 4H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 23.6, 23.7, 31.0, 56.3, 113.4, 123.5, 123.8, 124.8, 125.4, 125.8, 126.3, 126.4, 127.8, 127.8, 128.1, 129.0, 129.2, 129.2, 130.1, 132.1, 133.1, 134.3, 145.1, 154.7. HRMS (EI) calcd for $C_{24}H_{22}O$ (M+) 326.16707 found 326.16768. HPLC Chiralpak OT (+) Hexane 1 mL/min. $t_1$ = 7.3 and $t_2$ = 7.8. $[\alpha]_{365}$ = (+) 169.7 in EtOH at c = 0.33

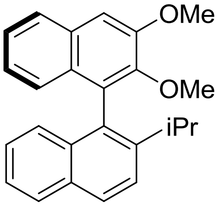
**Compound 13d (Entry 4).** The general procedure has been applied using **30d** (7 mg, 0.02 mmol), toluene (0.2 mL), and Eu(OTf)$_3$ (1.2 mg, 0.002 mmol). The product **13d** was isolated as white oil (5 mg, 76% yield and >95% ee).



A run of the opposite enantiomer had a yield of 70% and > 95% ee.

$^1$H NMR (300 MHz, CDCl$_3$): δ 1.14-1.31 (m, 6H), 1.83 (s, 3H), 2.80 (hep, J = 7.3 Hz, 1H), 3.61 (s, 3H), 3.92 (s, 3H), 6.52 (d, J = 13.1 Hz, 2H), 7.24-7.47 (m, 3H), 7.57 (d, J = 8.7 Hz, 1H), 7.81-7.94 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 20.3, 23.4, 23.7, 30.8, 55.3, 55.4, 96.0, 106.1, 120.0, 123.7, 124.6, 125.7, 127.6, 127.8, 131.8, 132.2, 132.8, 139.3, 144.4, 158.7, 159.7. One aromatic carbon is not observed. HRMS (EI) calcd for $C_{22}H_{24}O_2$ (M+) 320.17763 found 320.17814. HPLC Chiralpak OT (+) Hexane 1 mL/min. $t_1$ = 9.8 and $t_2$ = 10.4.

**Compound 13e (Entry 5).** The general procedure has been applied using **30e** (5 mg, 0.013 mmol), toluene (0.13 mL), and Eu(OTf)$_3$ (0.8 mg, 0.0013 mmol). The product **13e** was isolated as an oil (3 mg, 64% yield and >95% ee).

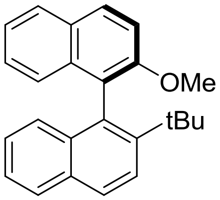


A run of the opposite enantiomer had a yield of 62% and >95% ee.

$^1$H NMR (300 MHz, CDCl$_3$): δ 2.17 (s, 3H), 3.51 (s, 3H), 4.09 (s, 3H), 6.96-7.54 (m, 8H), 7.83 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 8.4 Hz, 2H)

HPLC Chiralpak OT (+) Hexane 1 mL/min. $t_1$ = 12.7 and $t_2$ = 14.3. $[\alpha]_{365}$ = (+) 120.0 in EtOH at c = 0.07

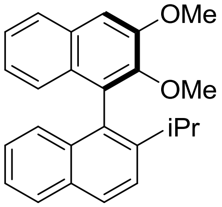
***Syn-Precursor Asymmetric Rearrangement (Table 4):***



**Compound 15a (Entry 1).** The general procedure has been applied using **30c** (22 mg, 0.06 mmol), toluene (0.6 mL), and Eu(OTf)$_3$ (3.6 mg, 0.006 mmol). The product **15a** was isolated as an oil (13.7 mg, 69% yield and 65% ee).

A run of the opposite enantiomer had a yield of 72% and 72% ee.

$^1$H NMR (300 MHz, CDCl$_3$): δ 1.12 (s, 9H), 3.79 (s, 3H), 6.88-7.45 (m, 7H), 7.81-8.03 (m, 5H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 30.9, 32.1, 55.9, 113.0, 123.3, 124.4, 125.0, 125.7, 126.1, 126.2, 126.2, 126.7, 127.3, 127.5, 127.7, 128.7, 129.2, 130.5, 131.9, 133.9, 135.1, 146.0, 154.6. HRMS (EI) calcd for $C_{25}H_{24}O$ (M+) 340.18272 found 340.18213. HPLC Chiralpak OT (+) 98:2 Hexane:IPA 1 mL/min. $t_1$ = 7.5 and $t_2$ = 12.7.

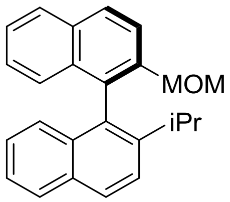


**Compound 15b (Entry 2).** The general procedure has been applied using **30e, opposite diastereomer** (18 mg, 0.05 mmol), toluene (0.5 mL), and Eu(OTf)$_3$ (3.0 mg, 0.005 mmol). The product **15b** was isolated as an oil (10 mg, 59% yield and 68% ee).

A run of the opposite enantiomer had a yield of 58% and 67% ee.

$^1$H NMR (300 MHz, CDCl$_3$): δ 1.05 (d, J = 6.9 Hz, 3H), 1.28 (d, J = 6.9 Hz, 3H), 2.74 (hep, J = 7.2 Hz, 1H), 3.52 (s, 3H), 4.11 (s, 3H), 6.97-7.44 (m, 7H), 7.67 (d, J = 7.7 Hz, 1H), 7.81-7.93 (m, 2H), 8.00 (d, J = 8.8 Hz, 1H). HRMS (EI) calcd for $C_{25}H_{24}O_2$ (M+) 356.17763 found 356.17793. HPLC Chiralpak OT (+) Hexane 1 mL/min. $t_1$ = 12.7 and $t_2$ = 14.3. $[\alpha]_{365}$ = (-) 105.4 in EtOH at c = 0.27

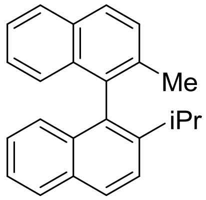
**Compound 15c (Entry 3).** The general procedure has been applied using **30f** (23 mg, 0.06 mmol), toluene (0.6 mL), and Eu(OTf)$_3$ (3.8 mg, 0.006 mmol). The product **15d** was isolated as an oil (14 mg, 64% yield and 74% ee).



A run of the opposite enantiomer had a yield of 65% and 74% ee.

$^1$H NMR (300 MHz, CDCl$_3$): δ 1.02 (d, J = 6.9 Hz, 3H), 1.19 (d, J = 6.9 Hz, 3H), 2.59 (hep, J = 6.9 Hz, 1H), 3.22 (s, 3H), 4.09 (d, J = 12.6 Hz, 1H), 4.21 (d, J = 12.2 Hz, 1H), 7.00 (d, J = 8.6 Hz, 1H), 7.08-7.29 (m, 4H), 7.38-7.49 (m, 2H), 7.65 (d, J = 8.6 Hz, 1H), 7.80-8.04 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 23.5, 24.0, 30.8, 58.5, 72.3, 123.9, 125.1, 125.1, 125.7, 125.9, 126.1, 126.2, 126.5, 127.8, 127.9, 127.9, 128.4, 131.9, 132.0, 132.7, 133.0, 133.1, 134.4, 135.0, 144.9. HPLC Chiralpak OT (+) Hexanes 1 mL/min. $t_1$ = 15.2 and $t_2$ = 21.1.

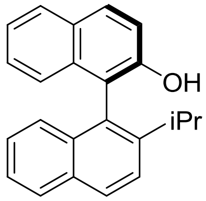
**Compound 15d (Entry 4).** The general procedure has been applied using **30f** (11.5 mg, 0.035 mmol), toluene (0.35 mL), and Eu(OTf)$_3$ (2.1 mg, 0.0035 mmol). The product **15d** was isolated as an off-color oil (8.0 mg, 74% yield and 0% ee).



A run of the opposite enantiomer had a yield of 70% and 0% ee

$^1$H NMR (300 MHz, CDCl$_3$): δ 1.05 (d, J = 6.9 Hz, 3H), 1.28 (d, J = 6.9 Hz, 3H), 2.74 (hep, J = 7.2 Hz, 1H), 3.52 (s, 3H), 4.11 (s, 3H), 6.97-7.44 (m, 7H), 7.67 (d, J = 7.7 Hz, 1H), 7.81-7.93 (m, 2H), 8.00 (d, J = 8.8 Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 20.4, 23.6, 23.9, 30.8, 124.0, 124.9, 125.0, 125.8, 126.0, 126.1, 126.1, 127.3, 127.6, 127.8, 128.1, 128.6, 132.0, 132.2, 132.6, 133.4, 134.6, 135.0, 144.5. One aromatic carbon is not observed. HPLC Chiralpak OT (+) Hexane 1 mL/min. $t_1 = 5.1$ and $t_2 = 5.5$.

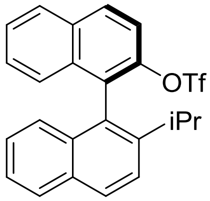
***Further Functionalization of Enantiopure Naphthalenes (Scheme 4)***



**Compound 16.** To a dried flask was added naphthalene **13c** (44 mg, 0.13 mmol) and DCM (1.5 mL). $BBr_3$ (148 μL, 0.15 mmol, 1M in DCM) was added dropwise. The solution was allowed to stir for 12 hours and then quenched with 1 mL $NaHCO_3$ (Aqueous, Saturated). $Et_2O$ (15 mL) was then added. The organic phase was washed 2 more times with water, and dried over $MgSO_4$. The desired compound **16** was isolated as a white solid (24 mg, 57% yield, and >95% ee)

A run of the opposite enantiomer had a yield of 53% and >95% ee.

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.10 (d, J = 6.9 Hz, 3H), 1.22 (d, J = 6.9 Hz, 3H), 2.77 (hep, J = 6.9 Hz, 1H), 4.78 (s, 1H), 7.02 (d, J = 7.0 Hz, 1H), 7.15-7.51 (m, 6H), 7.71 (d, J = 9.2 Hz, 1H), 7.87-7.97 (m, 3H), 8.05 (d, J = 9.0 Hz, 1H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 23.7, 24.1, 31.0, 117.3, 117.4, 123.4, 124.2, 124.8, 125.7, 125.9, 126.6, 126.8, 127.0, 128.0, 128.1, 129.0, 129.7, 132.6, 133.1, 134.0, 147.7, 151.0, 144.5. HPLC Chiralpak OT (+) 98.5:1.5 Hexane:IPA 1 mL/min. $t_1 = 9.3$ and $t_2 = 11.2$. $[\alpha]_D$ = (+) 11.1 in EtOH at c = 0.73

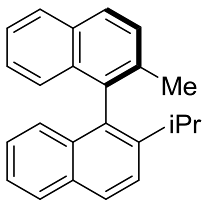


**Compound 17.** To a dried flask was added naphthalene **16** (22 mg, 0.07 mmol) and DCM (0.13 mL). The solution was then cooled to 0 °C. $i$Pr$_2$NH (11 μL, 0.07 mmol) was added dropwise, followed by dropwise

addition of $Tf_2O$ (26 μL, 0.14 mmol). The solution was allowed to warm to room temperature overnight and then quenched with 1 mL $NaHCO_3$ (Aqueous, Saturated). $Et_2O$ (15 mL) was then added. The organic phase was washed 2 more times with water, and dried over $MgSO_4$. The desired compound **17** was isolated as an oil (14 mg, 47% yield, and >95% ee). Crystals suitable for diffraction were isolated from the cold evaporation of hexanes.

A run of the opposite enantiomer had a yield of 47% and >95% ee.

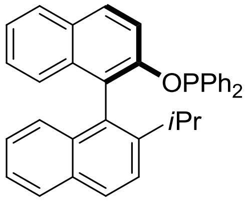
$^1$H NMR (300 MHz, $CDCl_3$): δ 1.03 (d, J = 6.7 Hz, 3H), 1.30 (d, J = 6.9 Hz, 3H), 2.62 (hep, J = 7.2 Hz, 1H), 7.00 (d, J = 8.6 Hz, 1H), 7.21-7.71 (m, 7H), 7.91 (d, J = 8.0 Hz, 1H), 7.98-8.15 (m, 2H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 23.0, 24.3, 31.3, 119.1, 119.4, 123.7, 125.2, 126.1, 126.3, 126.7, 127.0, 127.5, 127.8, 128.2, 129.5, 129.6, 130.2, 132.0, 132.4, 132.7, 134.0, 145.0, 145.6. HPLC Chiralpak OT (+) Hexane 1 mL/min. $t_1$ = 7.3 and $t_2$ = 8.7.



**Compound 19.** To a dried flask was added naphthalene **17** (8 mg, 0.02 mmol), diethyl ether (0.40 mL) and $Ni(dppp)Cl_2$ (1.4 mg, 0.003 mmol). The reaction solution was cooled to 0 $^o$C. MeMgBr (24 μL, 3M in diethyl ether) was added dropwise. The reaction was allowed to warm to room temperature and was stirred for 48h. Upon completion, the reaction mixture was washed with $NH_4Cl$ (5 mL, saturated, aqueous) and 10 mL of diethyl ether. The organic material was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The desired compound **19** was isolated as an oil (4.6 mg, 82% yield, and >95% ee)

A run of the opposite enantiomer had a yield of 86% and >95% ee.

Characterization data was identical to compound **15d**.



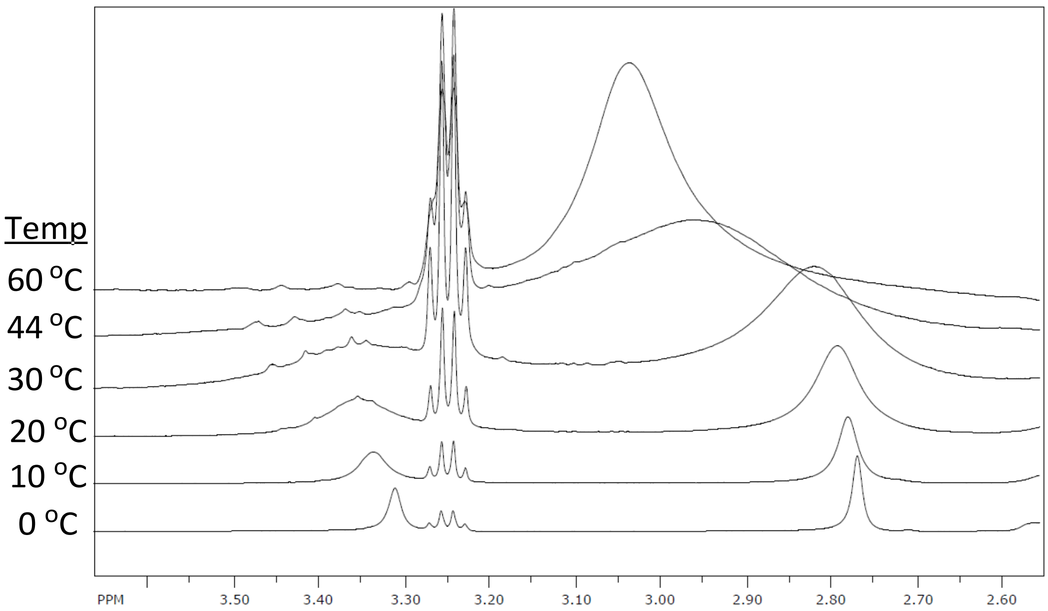
**Compound 18.** To a dried flask was added naphthalene **16** (10 mg, 0.03 mmol), diethyl ether (0.5 mL), triethyl amine (11 μL, 0.08 mmol), and DMAP (1.0 mg, 0.008 mmol). The reaction vessel was cooled to 0 $^{o}$C and ClPPh$_2$ (14 μL, 0.08 mmol) was added dropwise. The reaction was allowed to warm to room temperature and stir overnight. The desired compound **18** was isolated as a greenish solid (15 mg, 94 % yield, and >95% ee).

A run of the opposite enantiomer had a 95% yield and the same ee.

$^{1}$H NMR (300 MHz, CDCl$_3$): δ 0.99 (t, J = 7.4 Hz, 6H), 2.66 (hep, J = 6.9 Hz, 1H), 6.76 (t, J = 7.6 Hz, 2H), 6.91 (d, J = 6.8 Hz, 2H), 6.98-7.34 (m, 12H), 7.46 (d, J = 9.1 Hz, 1H), 7.53 (d, J = 8.3 Hz, 1H), 7.75-7.92 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 23.6, 24.0, 31.1, 119.2, 119.3, 123.9, 124.4, 124.5, 125.0, 126.0, 126.6 (broad), 126.7, 127.8, 127.9, 128.0, 128.1, 128.1, 128.3, 129.2, 129.4, 129.9, 130.0, 130.0, 130.1, 132.3, 133.4, 134.4. Many aromatic peaks not observed due to complexity in the aromatic region; $^{31}$P (202 MHz, CDCl$_3$): δ 110.7 (s). HPLC Chiralpak OT (+) 98:2 Hexane:IPA 1 mL/min. $t_1$ = 9.4 and $t_2$ = 10.4.

***Variable Temperature NMR Data:*** Syn precursor **14a** was subjected to variable temperature NMR in order to calculate the barrier of rotation along the pseudo biaryl axis. Experimental results are described in figure 1 from 0 to 60 degrees centigrade with a coalescence temperature of 44 degrees centigrade. From this value a barrier of rotation can be calculated from the equation: ($\Delta G^{\ddagger} = a T\,[9.972 + \log (T_c / \Delta v)]$) Where $a = 4.575 \times 10^{-3}$ for kcal/mol; $T_c$ is the coalescence temperature in Kelvin; $\Delta v$ = peak separation in Hz; and T being the temperature in Kelvin where $\Delta v$ is measured.

From our data we determined $\Delta G^{\ddagger}$ = 12.55 kcal/mol from coalescence.


Experimental Stack

In order to increase the accuracy of the value of the rotation barrier we utilized SpinWorks 3 and DNMR3 in order to simulate the rates of rotation. These values can be observed in Figure 2. From this data we were able to use the Eyring equation to determine the value of the barrier of rotation at each data point.

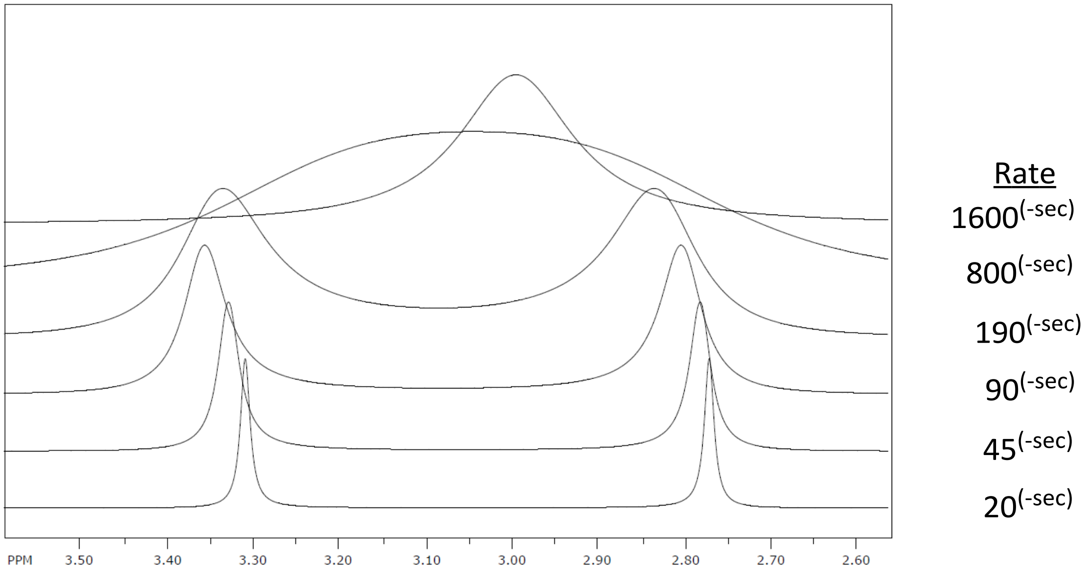
The average value when each rate was imported in the Eyring Equation is:

$\Delta G^{\ddagger}$ = 14.40 kcal/mol from DNMR3 simulation.

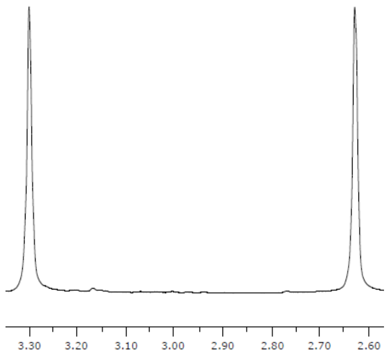
The final piece of data was a DFT modeling study using b3ylp/6-31g* basis set.

$\Delta G^{\ddagger} = 13.77$ kcal/mol from modeling.

Simulated DNMR3 Stack



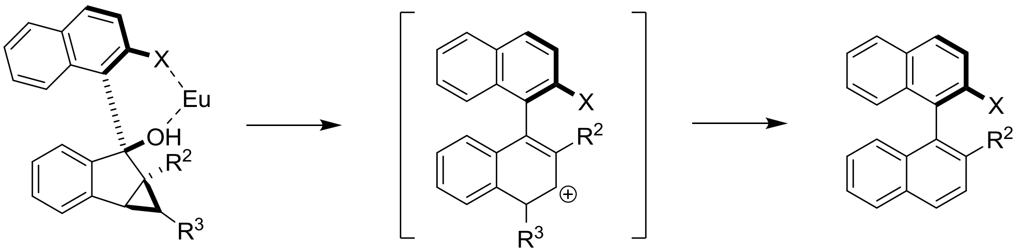
The barrier of rotation was then calculated for anti-precursor **18**. Due to the large energy barrier VT NMR was not useful in determining this barrier, even at 130 degrees centigrade broadening was not observed for the two methoxy peaks. Due to this modeling was used to estimate this value.



No broadening observed at 130 °C

***Stereochemical Model Data:***

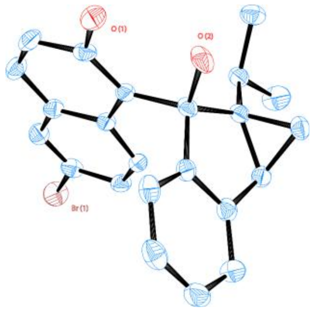
We were able to determine the absolute configuration of precursor **27** from single xray crystallography. From this data we were able to deduce the absolute configuration of indanone **5a**. Once the absolute configuration was determined we could predict the stereochemical outcome from the general transformation outlined below, from general precursor **24** to general naphthalene **26**. This prediction was tested from the absolute configuration of naphthalene **17** which matched the absolute configuration of the general prediction. Naphthalene **17** was generated from indanone **5a**.

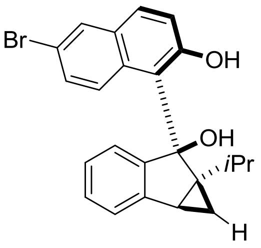


Absolute Configuration
General Precursor **24**

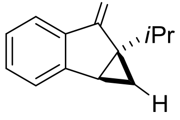
Restricted Rotation

Absolute Configuration
General Naphthalene **26**



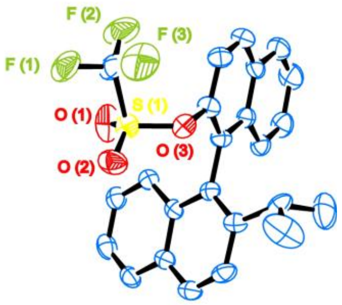


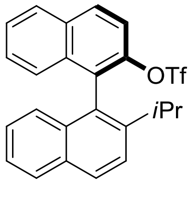
**27**



Absolute Configuration
Indanone

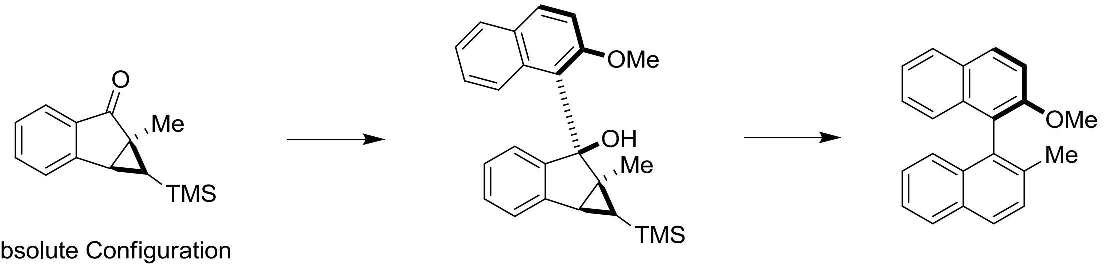
**5a**





**17**

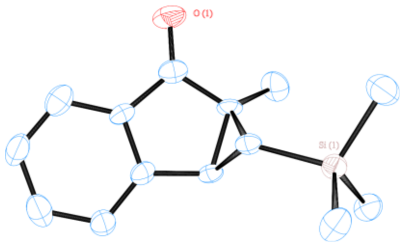
We were able to further test this stereochemical model from methyl indanone **A**. The absolute configuration was determined from crystallography. The absolute configuration of precursor **30a** could be deduced due to the stereochemical control of the nucleophilic addition. Finally, the absolute configuration of naphthalene **13a** was determined from literature reported polarimetry values (See manuscript). This configuration matched the general stereochemical prediction.



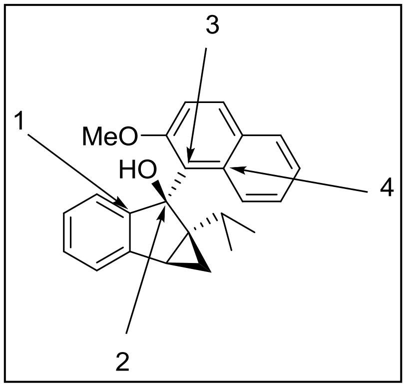
Absolute Configuration
Indanone
**A**

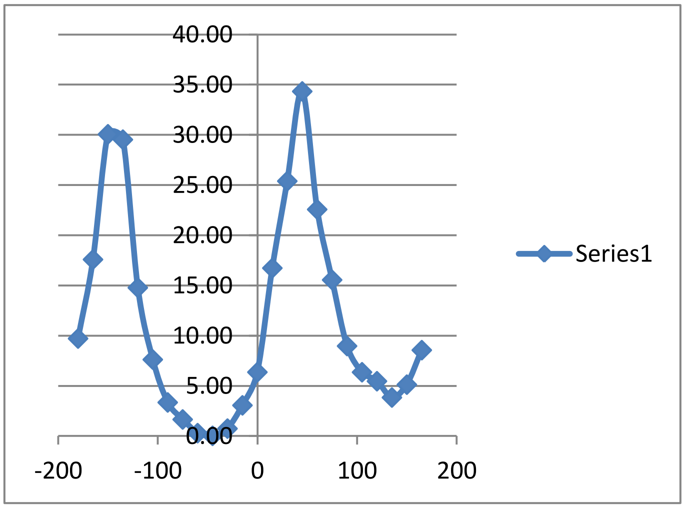
Absolute Configuration
General Precursor **30a**

Absolute Configuration
General Naphthalene **13a**



## *DFT Modeling Data, Basis Set = b3ylp/6-31g*$^*$

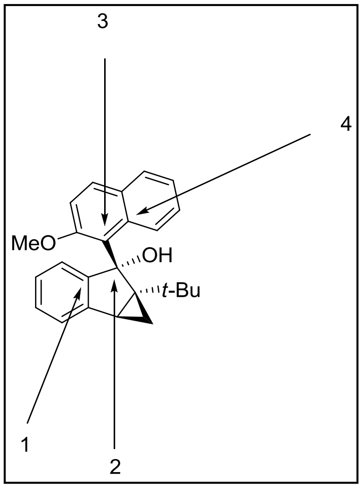


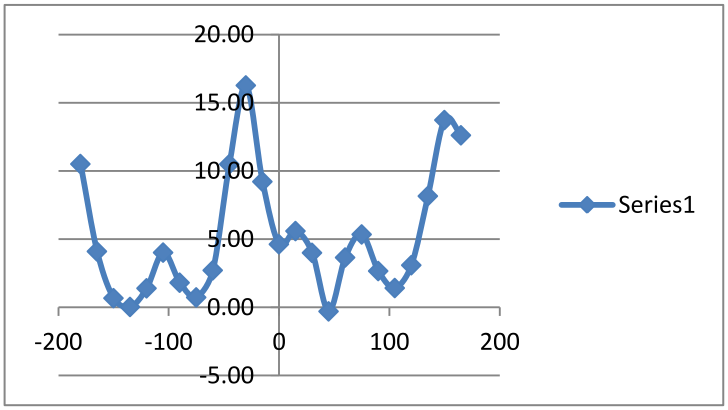


| conformation | au | kcal/mol | kcal/mol | zpe | zpe kcal | imaginary |
|---|---|---|---|---|---|---|
| min1(-42.55) | -1079.40767320 | -677338.57 | 0.00 | | | 0 |
| min2(114.71) | -1079.40490561 | -677336.83 | 1.74 | | | 0 |
| high_qst2(-132) | -1079.35251473 | -677303.96 | **34.61** | | | |
| high2_qst2 | | 0.00 | ######## | | | |
| -180 | -1079.39216119 | -677328.84 | 9.73 | | | 0 |
| -165 | -1079.37961388 | -677320.96 | 17.61 | | | 0 |

| | | | | |
|---|---|---|---|---|
| -150 | -1079.35973545 | -677308.49 | 30.08 | 1 |
| -135 | -1079.36059091 | -677309.02 | 29.54 | 0 |
| -120 | -1079.38409316 | -677323.77 | 14.80 | 0 |
| -105 | -1079.39550250 | -677330.93 | 7.64 | 0 |
| -90 | -1079.40230314 | -677335.20 | 3.37 | 0 |
| -75 | -1079.40500569 | -677336.90 | 1.67 | 0 |
| -60 | -1079.40717533 | -677338.26 | 0.31 | 0 |
| -45 | -1079.40760420 | -677338.53 | 0.04 | 0 |
| -30 | -1079.40645438 | -677337.80 | 0.76 | 0 |
| -15 | -1079.40276379 | -677335.49 | 3.08 | 0 |
| 0 | -1079.39750097 | -677332.19 | 6.38 | 0 |
| 15 | -1079.38098072 | -677321.82 | 16.75 | 0 |
| 30 | -1079.36717758 | -677313.16 | 25.41 | 0 |
| 45 | -1079.35293272 | -677304.22 | 34.35 | 0 |
| 60 | -1079.37166877 | -677315.98 | 22.59 | 0 |

|  |  |  |  |  |
|---|---|---|---|---|
| 75 | -1079.38285771 | -677323.00 | 15.57 | 0 |
| 90 | -1079.39335268 | -677329.58 | 8.99 | 0 |
| 105 | -1079.39750819 | -677332.19 | 6.38 | 0 |
| 120 | -1079.39893401 | -677333.09 | 5.48 | 0 |
| 135 | -1079.40151975 | -677334.71 | 3.86 | 0 |
| 150 | -1079.39947789 | -677333.43 | 5.14 | 0 |
| 165 | -1079.39400098 | -677329.99 | 8.58 | 0 |





| conformation | au | kcal/mol | kcal/mol | zpe | zpe kcal | imagninary |
|---|---|---|---|---|---|---|
| min1(-137) | -1118.70541381 | -701998.27 | 0.00 |  |  | 0 |
| min2(104) | -1118.70315963 | -701996.86 | 1.41 |  |  | 0 |
| high_qst2(151.9) | -1118.68346799 | -701984.50 | **13.77** |  |  | 1 |

| | | | | |
|---|---|---|---|---|
| -180 | -1118.68866751 | -701987.77 | 10.51 | 1 |
| -165 | -1118.69887515 | -701994.17 | 4.10 | 0 |
| -150 | -1118.70434052 | -701997.60 | 0.67 | 0 |
| -135 | -1118.70536457 | -701998.24 | 0.03 | 0 |
| -120 | -1118.70318661 | -701996.88 | 1.40 | 1 |
| -105 | -1118.69901385 | -701994.26 | 4.02 | 1 |
| -90 | -1118.70252966 | -701996.47 | 1.81 | 1 |
| -75 | -1118.70424991 | -701997.54 | 0.73 | 0 |
| -60 | -1118.70108834 | -701995.56 | 2.71 | 0 |
| -45 | -1118.68868863 | -701987.78 | 10.50 | 0 |
| -30 | -1118.67948711 | -701982.01 | 16.27 | 1 |
| -15 | -1118.69072648 | -701989.06 | 9.22 | 0 |
| 0 | -1118.69804088 | -701993.65 | 4.63 | 0 |
| 15 | -1118.69650076 | -701992.68 | 5.59 | 0 |
| 30 | -1118.69903986 | -701994.28 | 4.00 | 0 |
| 45 | -1118.70588299 | -701998.57 | -0.29 | 0 |
| 60 | -1118.69959303 | -701994.62 | 3.65 | 0 |
| 75 | -1118.69689546 | -701992.93 | 5.35 | 1 |
| 90 | -1118.70116783 | -701995.61 | 2.66 | 0 |
| 105 | -1118.70315345 | -701996.86 | 1.42 | 0 |
| 120 | -1118.70048829 | -701995.18 | 3.09 | 0 |
| 135 | -1118.69241393 | -701990.12 | 8.16 | 0 |
| 150 | -1118.68353359 | -701984.54 | 13.73 | 1 |
| 165 | -1118.68531250 | -701985.66 | 12.61 | 1 |

## **Bridge to Chapter V**

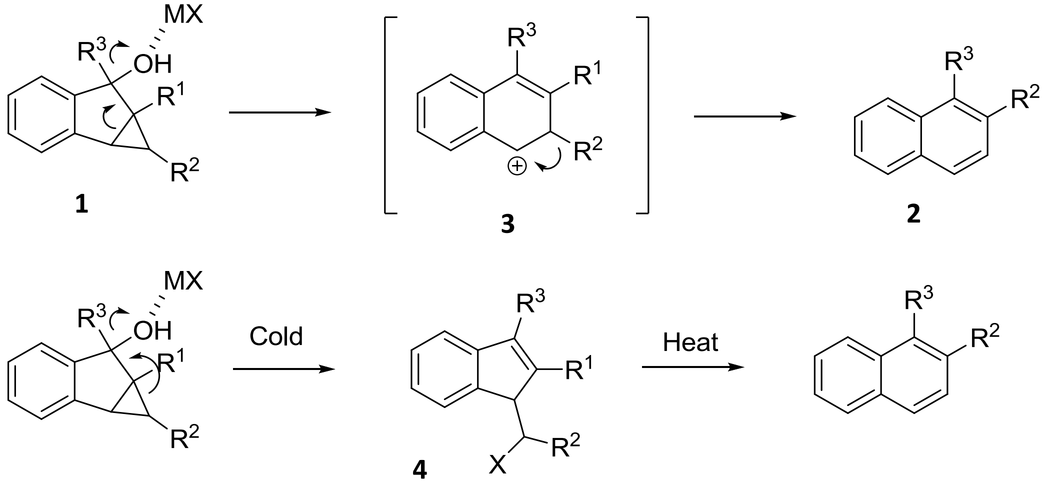
In chapter IV we discussed the successful synthesis of unprecedented sterically congested aryl naphthalenes containing *t*-butyl and adamantyl groups in the *ortho* positions. We also presented an efficient chiral transfer reaction to facilitate the synthesis of asymmetric aryl naphthalenes, and finally demonstrated the ability to perform our rearrangement with non-TMS-based precursors; expanding the scope of the method. In chapter V we will present work that has not yet been published, with a focus on mechanistic details and alternative routes to aryl naphthalenes from indanone. It is important to mention that this work is preliminary; however we feel that it does warrant discussion due to its critical nature in the understanding of our rearrangement-based method.

# CHAPTER V

# ARYL NAPHTHALENES THROUGH A REARRANGEMENT PROCESS FROM INDENE-BASED PRECURSORS

## Results and Discussion

Our rearrangement-based synthesis has shown to be well suited for the generation of highly sterically encumbered and chiral aryl naphthalenes. However, we have yet to determine the mechanistic route of our rearrangement. Although the evidence is preliminary, we believe a discussion on the mechanism of the rearrangement is warranted to further facilitate increased substrate scope and applicability. As previously discussed (Chapter II), our rearrangement-based method proceeds through cyclopropyl carbinol **1**, and once exposed to Lewis acid and heat yields the desired aryl naphthalene **2** (Scheme 1). In addition to the benzvalene mechanism discussed in Chapter II we believe the rearrangement could also occur through intermediate **3**. Furthermore, through our studies

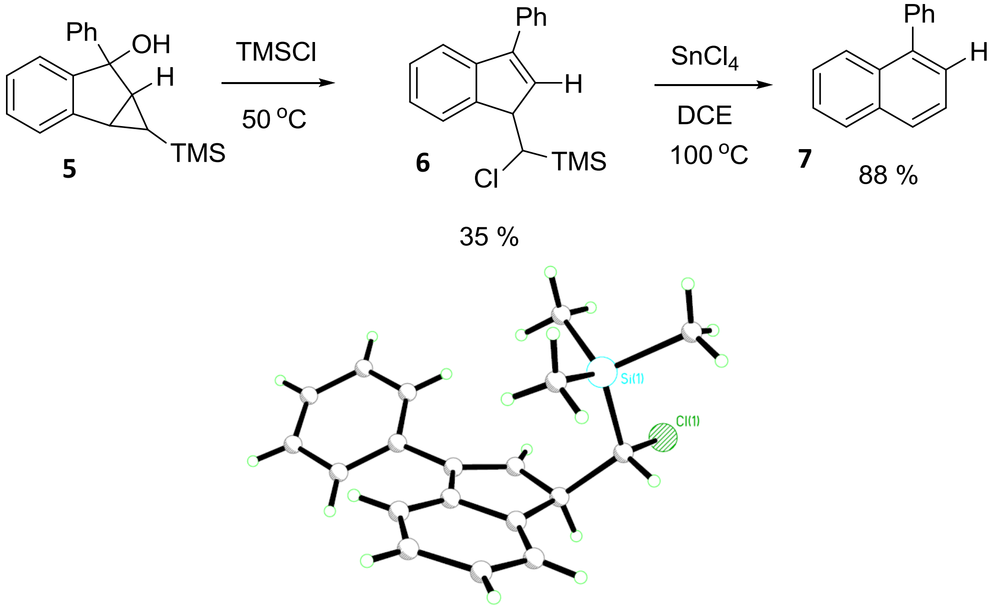


**Scheme 1**: (Top) traditional view of the mechanism of rearrangement. (Bottom) Rearrangement *via* ring-opened **4**.

we have consistently observed ring-opened species **4**, possibly opening up another mechanistic route.

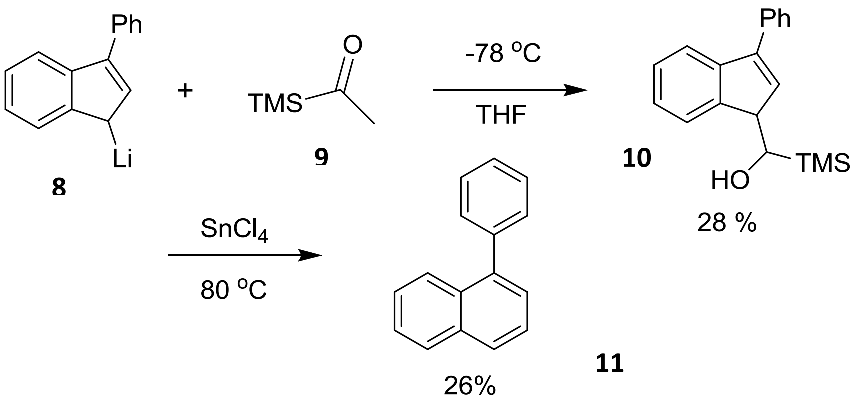
Intermediate **4** was first isolated from cold temperatures at -78 $^{o}$C with $SnCl_4$, however we have since observed and isolated this intermediate from a variety of reaction conditions. We have also observed this intermediate rearranging into desired aryl naphthalene **2** when in the presence of a Lewis acid and heat (Scheme 1).

As an illustrative example, Scheme 2 demonstrates the successful synthesis and isolation of the ring-opened intermediate **6**, of which a low resolution crystal structure was obtained. Intermediate **6** rearranges in the presence of $SnCl_4$ into aryl naphthalene **7**.



**Scheme 2**: Isolation and rearrangement of ring-opened intermediate **6**.

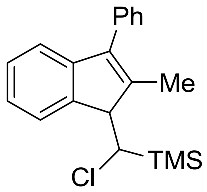
Further study led us towards a more direct synthesis of derivatives **4** *via* the more available indenenyl anion. Specifically we focused on the synthesis of intermediate **10**, which was easily obtained from the nucleophilic addition of phenyl indene **8** onto 1-trimethylsilylethanone **9**. We were delighted to witness the rearrangement of the alcohol intermediate into phenyl naphthalene **11**, although in only moderate yield.



**Scheme 3**: Isolation and rearrangement of alcohol intermediate **10**.

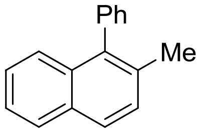
While in its infancy, we believe that this indene-based synthesis, once optimized, could be a direct route to a host of aryl naphthalenes. Furthermore, the mechanism of rearrangement of our original method seems to be slightly more complicated than originally thought, involving multiple possibilities. Continued work on elucidating the mechanism of our original method, would be useful.

# Experimental

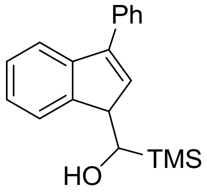


**Compound 6.** To a dried flask was added precursor **5** (387 mg, 1.3 mmol) and DCM (3 mL). TMSCl (1.3 mmol) was dissolved in DCM (3 mL) and the reaction was allowed to heat to 50 °C for 2 hours. The reaction was then quenched with water (10 mL) and extracted with ether (30 mL). The organic layer was dried over $MgSO_4$ and purified *via* preparatory thin-layer chromatography. The desired compound was isolated (142 mg, 35% yield). Crystals suitable for diffraction were isolated for the non-methyl version of the above compound through slow evaporation of DCM.

$^1$H NMR (300 MHz, $CDCl_3$): δ -0.8 (s, 9H), 2.22 (s, 3H), 4.01 (d, 1H), 4.20 (d, 1H), 7.20-7.58 (m, 9H).



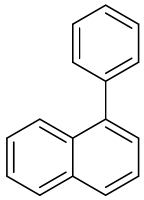
**Compound 7.** To a dried bomb was added **6** (139 mg, 0.45 mmol) and DCE (4 mL). $SnCl_4$ (127 mg, 0.49 mmol) was added dropwise and the reaction was allowed to stir overnight at 125 °C. The reaction was purified *via* preparatory thin-layer chromatography. The desired naphthalene **7** was isolated as an oil (80 mg, 88% yield).



**Compound 10.** To a dried flask was added compound **9** (0.79 mmol) and THF (3 mL). The reaction was cooled to -78 °C and **8** (0.79 mmol) was added dropwise. The reaction was allowed to stir for 3 hours and then quenched with $NH_4Cl$ (10 mL, aqueous, saturated) followed by extraction with ethyl ether (20 mL). The organic layer was then dried over $MgSO_4$. The

crude mixture was then purified *via* preparatory thin-layer chromatography. The desired compound **10** was isolated as a mix of diastereomers (70:30, 64 mg, 28 % yield).

Characterization data is not reported due to the complexity of the spectra from the mix of diastereomers.



**Compound 11.** To a dried flask was added **10** (64 mg, 0.22 mmol) and DCE (1.5 mL). $SnCl_4$ (57 mg, 0.22 mmol) was dissolved in DCE (1 mL) and added dropwise at room temperature. The reaction mixture was warmed to 80 $^oC$ and stirred overnight. The reaction was quenched by running the mixture through a plug of silica. The crude material was purified through preparatory thin-layer chromatography. The desired material **11** was isolated as an oil (10.5 mg, 26 % yield).

## Concluding Remarks

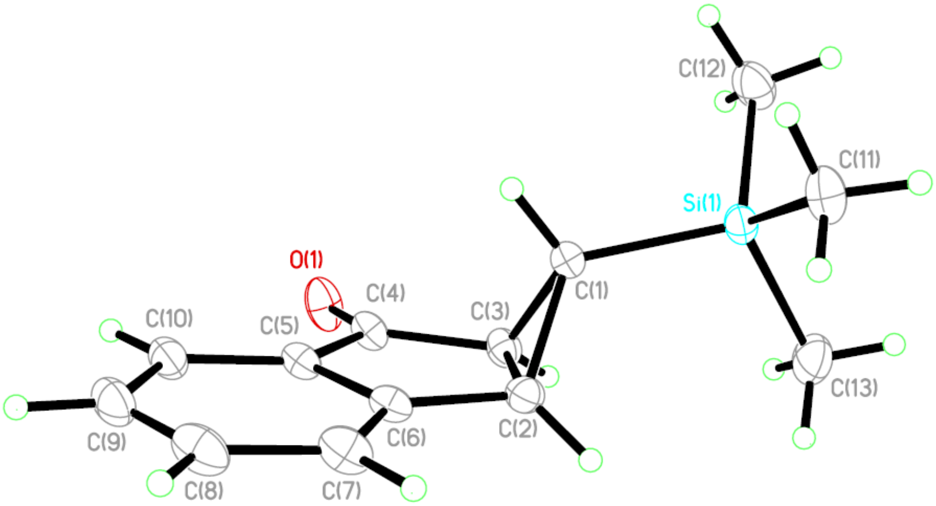
In this dissertation we have outlined a novel and regioselective rearrangement-based method for the synthesis of asymmetric and sterically-encumbered tetra-*ortho*-substituted aryl naphthalenes. We have demonstrated that our method is capable of generating naphthalenes containing large sterically demanding groups around the *ortho* position, adding to the repertoire of current TOAN synthetic methods. We have been able to incorporate large groups, such as: *i*Pr, *t*Bu, and adamantyl groups among others, with excellent yields and selectivity. Our method has utilized TMS and non-TMS-based precursors to facilitate rearrangement. Furthermore, we have discussed our success regarding the asymmetric synthesis of TOANs through central to axial chirality transfer.

We have determined that the restricted rotation of the pseudo biaryl bond in the rearrangement precursor is of critical to importance. We have observed excellent transfer for highly constricted precursors, while observing mediocre transfer for those precursors lacking substantial pseudo-biaryl restriction. We also quantified these values through modeling and VT NMR studies. Additionally, we were able to introduce an effective stereochemical model for the prediction of absolute stereochemistry through crystal structures and polarimetry values. Finally we were able to demonstrate successful cross-coupling from the chiral biaryl triflate species in order to provide further functionalization for enantioenriched biaryls. We also were able to synthesize a biaryl phosphinite. In conclusion, we feel that our rearrangement-based synthesis is a useful contribution to the current modern synthetic routes towards tetra-*ortho*-substituted aryl naphthalenes.

# APPENDIX

# CRYSTAL STRUCTURE DATA

## *Crystallographic Data for 2a (liu 15) Chapter II*



Crystal data and structure refinement for liu15.

| | | |
|---|---|---|
| Identification code | liu15 | |
| Empirical formula | C13 H16 O Si | |
| Formula weight | 216.35 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 9.5789(12) Å | α= 90°. |
| | b = 12.6743(16) Å | β= 108.965(2)°. |

| | | |
|---|---|---|
| | c = 10.9538(14) Å | $\gamma$ = 90°. |
| Volume | 1257.7(3) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.143 $Mg/m^3$ | |
| Absorption coefficient | 0.160 $mm^{-1}$ | |
| F(000) | 464 | |
| Crystal size | 0.35 x 0.24 x 0.08 $mm^3$ | |
| Theta range for data collection | 2.25 to 27.00°. | |
| Index ranges | -12<=h<=12, -16<=k<=16, -13<=l<=13 | |
| Reflections collected | 13877 | |
| Independent reflections | 2744 [R(int) = 0.0262] | |
| Completeness to theta = 27.00° | 100.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9873 and 0.9462 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2744 / 0 / 200 | |
| Goodness-of-fit on $F^2$ | 1.033 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0357, wR2 = 0.0926 | |
| R indices (all data) | R1 = 0.0437, wR2 = 0.1004 | |
| Largest diff. peak and hole | 0.351 and -0.188 e.$Å^{-3}$ | |

Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for liu15. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|

|  |  |  |  |  |
|---|---|---|---|---|
| Si(1) | 667(1) | 1771(1) | 2196(1) | 28(1) |
| O(1) | 2416(1) | -1250(1) | 5365(1) | 42(1) |
| C(1) | 1733(2) | 1245(1) | 3830(1) | 26(1) |
| C(2) | 3408(2) | 1215(1) | 4257(1) | 29(1) |
| C(3) | 2563(2) | 196(1) | 3958(1) | 28(1) |
| C(4) | 2843(2) | -373(1) | 5213(1) | 29(1) |
| C(5) | 3804(1) | 326(1) | 6242(1) | 28(1) |
| C(6) | 4163(1) | 1224(1) | 5680(1) | 29(1) |
| C(7) | 5104(2) | 1968(1) | 6451(2) | 37(1) |
| C(8) | 5669(2) | 1795(1) | 7770(2) | 42(1) |
| C(9) | 5302(2) | 897(1) | 8321(2) | 40(1) |
| C(10) | 4356(2) | 146(1) | 7563(1) | 34(1) |
| C(11) | 773(2) | 3233(1) | 2267(2) | 42(1) |
| C(12) | -1285(2) | 1335(2) | 1752(2) | 45(1) |
| C(13) | 1516(2) | 1268(2) | 1004(2) | 48(1) |

Bond lengths [Å] and angles [°] for liu15.

|  |  |
|---|---|
| Si(1)-C(11) | 1.8564(17) |
| Si(1)-C(12) | 1.8564(17) |
| Si(1)-C(13) | 1.8611(18) |
| Si(1)-C(1) | 1.8719(14) |
| O(1)-C(4) | 1.2141(17) |
| C(1)-C(2) | 1.5188(19) |

| | |
|---|---|
| C(1)-C(3) | 1.5328(18) |
| C(1)-H(1) | 0.996(16) |
| C(2)-C(6) | 1.490(2) |
| C(2)-C(3) | 1.5034(19) |
| C(2)-H(2) | 0.959(18) |
| C(3)-C(4) | 1.4972(19) |
| C(3)-H(3) | 0.930(16) |
| C(4)-C(5) | 1.4925(18) |
| C(5)-C(6) | 1.389(2) |
| C(5)-C(10) | 1.388(2) |
| C(6)-C(7) | 1.386(2) |
| C(7)-C(8) | 1.386(3) |
| C(7)-H(7) | 0.957(18) |
| C(8)-C(9) | 1.386(3) |
| C(8)-H(8) | 0.943(19) |
| C(9)-C(10) | 1.389(2) |
| C(9)-H(9) | 0.937(18) |
| C(10)-H(10) | 0.990(18) |
| C(11)-H(11A) | 0.92(3) |
| C(11)-H(11B) | 0.93(2) |
| C(11)-H(11C) | 0.96(2) |
| C(12)-H(12A) | 0.88(2) |
| C(12)-H(12B) | 0.98(3) |
| C(12)-H(12C) | 0.99(3) |
| C(13)-H(13A) | 0.96(3) |

| | |
|---|---|
| C(13)-H(13B) | 0.91(3) |
| C(13)-H(13C) | 0.96(2) |
| C(11)-Si(1)-C(12) | 110.19(9) |
| C(11)-Si(1)-C(13) | 109.93(9) |
| C(12)-Si(1)-C(13) | 110.32(10) |
| C(11)-Si(1)-C(1) | 108.04(7) |
| C(12)-Si(1)-C(1) | 109.54(8) |
| C(13)-Si(1)-C(1) | 108.78(8) |
| C(2)-C(1)-C(3) | 59.03(9) |
| C(2)-C(1)-Si(1) | 119.80(10) |
| C(3)-C(1)-Si(1) | 120.13(10) |
| C(2)-C(1)-H(1) | 113.4(9) |
| C(3)-C(1)-H(1) | 114.5(9) |
| Si(1)-C(1)-H(1) | 117.2(9) |
| C(6)-C(2)-C(3) | 106.15(12) |
| C(6)-C(2)-C(1) | 115.30(12) |
| C(3)-C(2)-C(1) | 60.95(9) |
| C(6)-C(2)-H(2) | 120.9(10) |
| C(3)-C(2)-H(2) | 120.1(10) |
| C(1)-C(2)-H(2) | 118.4(10) |
| C(4)-C(3)-C(2) | 106.88(11) |
| C(4)-C(3)-C(1) | 115.78(12) |
| C(2)-C(3)-C(1) | 60.02(9) |
| C(4)-C(3)-H(3) | 118.2(10) |
| C(2)-C(3)-H(3) | 123.0(10) |

| | |
|---|---|
| C(1)-C(3)-H(3) | 119.6(10) |
| O(1)-C(4)-C(5) | 126.35(13) |
| O(1)-C(4)-C(3) | 126.74(13) |
| C(5)-C(4)-C(3) | 106.87(12) |
| C(6)-C(5)-C(10) | 122.08(13) |
| C(6)-C(5)-C(4) | 109.41(12) |
| C(10)-C(5)-C(4) | 128.45(13) |
| C(7)-C(6)-C(5) | 119.56(14) |
| C(7)-C(6)-C(2) | 129.85(14) |
| C(5)-C(6)-C(2) | 110.59(12) |
| C(6)-C(7)-C(8) | 118.92(15) |
| C(6)-C(7)-H(7) | 119.5(11) |
| C(8)-C(7)-H(7) | 121.5(11) |
| C(9)-C(8)-C(7) | 121.07(15) |
| C(9)-C(8)-H(8) | 119.7(11) |
| C(7)-C(8)-H(8) | 119.3(11) |
| C(8)-C(9)-C(10) | 120.70(15) |
| C(8)-C(9)-H(9) | 120.0(11) |
| C(10)-C(9)-H(9) | 119.2(11) |
| C(5)-C(10)-C(9) | 117.67(15) |
| C(5)-C(10)-H(10) | 122.1(10) |
| C(9)-C(10)-H(10) | 120.2(10) |
| Si(1)-C(11)-H(11A) | 112.1(14) |
| Si(1)-C(11)-H(11B) | 110.4(13) |
| H(11A)-C(11)-H(11B) | 106(2) |

| | |
|---|---|
| Si(1)-C(11)-H(11C) | 109.0(12) |
| H(11A)-C(11)-H(11C) | 109(2) |
| H(11B)-C(11)-H(11C) | 110.5(18) |
| Si(1)-C(12)-H(12A) | 112.1(15) |
| Si(1)-C(12)-H(12B) | 108.1(15) |
| H(12A)-C(12)-H(12B) | 104(2) |
| Si(1)-C(12)-H(12C) | 114.1(14) |
| H(12A)-C(12)-H(12C) | 108(2) |
| H(12B)-C(12)-H(12C) | 111(2) |
| Si(1)-C(13)-H(13A) | 111.3(17) |
| Si(1)-C(13)-H(13B) | 108.8(16) |
| H(13A)-C(13)-H(13B) | 109(2) |
| Si(1)-C(13)-H(13C) | 111.4(13) |
| H(13A)-C(13)-H(13C) | 107(2) |
| H(13B)-C(13)-H(13C) | 109.0(19) |

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters ($Å^2$x $10^3$)for liu15. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|

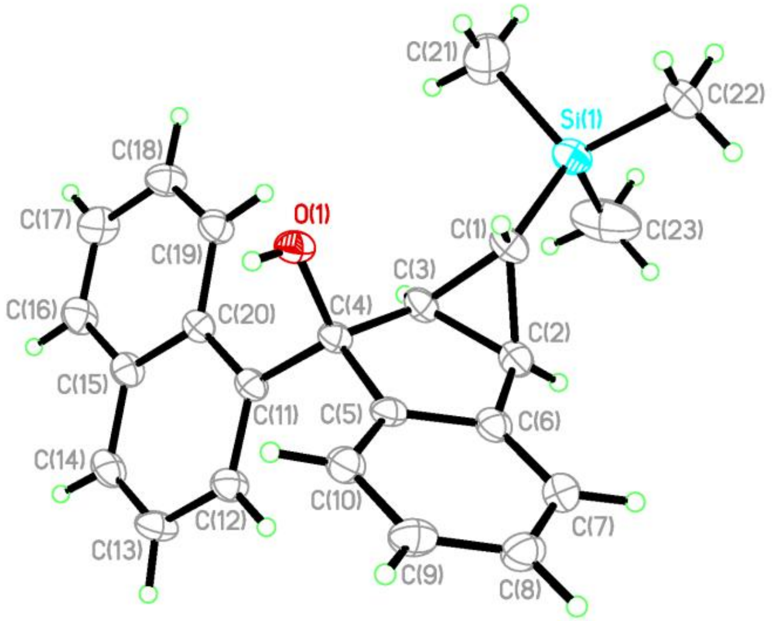
| | | | | | | |
|---|---|---|---|---|---|---|
| Si(1) | 28(1) | 29(1) | 24(1) | 4(1) | 5(1) | 1(1) |
| O(1) | 49(1) | 28(1) | 38(1) | 6(1) | -2(1) | -7(1) |
| C(1) | 25(1) | 28(1) | 25(1) | 3(1) | 7(1) | 3(1) |
| C(2) | 26(1) | 28(1) | 32(1) | 3(1) | 10(1) | 2(1) |
| C(3) | 30(1) | 26(1) | 26(1) | -1(1) | 5(1) | 4(1) |
| C(4) | 27(1) | 25(1) | 31(1) | 1(1) | 3(1) | 3(1) |
| C(5) | 23(1) | 26(1) | 30(1) | -2(1) | 4(1) | 4(1) |
| C(6) | 23(1) | 27(1) | 34(1) | -1(1) | 7(1) | 4(1) |
| C(7) | 31(1) | 29(1) | 48(1) | -3(1) | 7(1) | -3(1) |
| C(8) | 32(1) | 39(1) | 47(1) | -15(1) | 1(1) | -2(1) |
| C(9) | 33(1) | 49(1) | 29(1) | -7(1) | 0(1) | 5(1) |
| C(10) | 29(1) | 37(1) | 30(1) | 1(1) | 4(1) | 4(1) |
| C(11) | 49(1) | 34(1) | 36(1) | 7(1) | 5(1) | 0(1) |
| C(12) | 32(1) | 49(1) | 46(1) | 8(1) | 1(1) | -4(1) |
| C(13) | 59(1) | 56(1) | 31(1) | 4(1) | 18(1) | 7(1) |

Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for liu15.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 1337(18) | 1397(12) | 4548(16) | 32(4) |
| H(2) | 3891(18) | 1483(13) | 3680(16) | 34(4) |
| H(3) | 2477(17) | -202(13) | 3224(16) | 33(4) |

| | | | | |
|---|---|---|---|---|
| H(7) | 5384(19) | 2572(14) | 6059(17) | 41(5) |
| H(8) | 6300(20) | 2303(14) | 8300(18) | 44(5) |
| H(9) | 5743(19) | 770(13) | 9207(18) | 42(5) |
| H(10) | 4111(18) | -498(14) | 7963(16) | 38(4) |
| H(11A) | 1730(30) | 3470(18) | 2520(20) | 76(7) |
| H(11B) | 320(20) | 3521(16) | 1450(20) | 62(6) |
| H(11C) | 310(20) | 3481(16) | 2860(20) | 55(6) |
| H(12A) | -1860(30) | 1667(17) | 1060(20) | 70(7) |
| H(12B) | -1670(30) | 1557(19) | 2440(30) | 86(8) |
| H(12C) | -1430(30) | 570(20) | 1590(20) | 81(7) |
| H(13A) | 2540(30) | 1460(20) | 1240(30) | 98(9) |
| H(13B) | 1030(30) | 1551(18) | 220(30) | 79(7) |
| H(13C) | 1460(20) | 511(18) | 940(20) | 62(6) |

### *Crystallographic Data for 3g (liu30) Chapter II*



Crystal data and structure refinement for liu30.

| | | |
|---|---|---|
| Identification code | liu30 | |
| Empirical formula | C23 H24 O Si | |
| Formula weight | 344.51 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 13.397(2) Å | α= 90°. |
| | b = 8.4240(14) Å | β= 104.160(3)°. |

| | | |
|---|---|---|
| | c = 17.434(3) Å | γ = 90°. |
| Volume | 1907.8(5) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.199 Mg/m$^3$ | |
| Absorption coefficient | 0.130 mm$^{-1}$ | |
| F(000) | 736 | |
| Crystal size | 0.14 x 0.08 x 0.06 mm$^3$ | |
| Theta range for data collection | 1.57 to 25.00°. | |
| Index ranges | -15<=h<=15, -10<=k<=10, -20<=l<=20 | |
| Reflections collected | 17217 | |
| Independent reflections | 3347 [R(int) = 0.1062] | |
| Completeness to theta = 25.00° | 100.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9922 and 0.9820 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 3347 / 0 / 286 | |
| Goodness-of-fit on F$^2$ | 0.994 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0558, wR2 = 0.0967 | |
| R indices (all data) | R1 = 0.1119, wR2 = 0.1182 | |
| Largest diff. peak and hole | 0.187 and -0.220 e.Å$^{-3}$ | |

Atomic coordinates ( x 10$^4$) and equivalent isotropic displacement parameters (Å$^2$x 10$^3$) for liu30. U(eq) is defined as one third of the trace of the orthogonalized U$^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Si(1) | 4534(1) | 6802(1) | 1088(1) | 51(1) |
| O(1) | 1300(2) | 8516(2) | 477(1) | 40(1) |
| C(1) | 3340(3) | 7290(4) | 338(2) | 41(1) |
| C(2) | 3309(3) | 8134(4) | -443(2) | 39(1) |
| C(3) | 2972(2) | 8985(4) | 204(2) | 36(1) |
| C(4) | 1815(2) | 9307(3) | -62(2) | 32(1) |
| C(5) | 1514(2) | 8499(3) | -868(2) | 33(1) |
| C(6) | 2363(2) | 7869(3) | -1086(2) | 36(1) |
| C(7) | 2243(3) | 7078(4) | -1801(2) | 46(1) |
| C(8) | 1269(3) | 6925(4) | -2296(2) | 47(1) |
| C(9) | 425(3) | 7519(4) | -2073(2) | 45(1) |
| C(10) | 537(3) | 8304(4) | -1359(2) | 38(1) |
| C(11) | 1589(2) | 11085(3) | -72(2) | 33(1) |
| C(12) | 1206(2) | 11876(4) | -773(2) | 40(1) |
| C(13) | 995(3) | 13512(4) | -796(2) | 45(1) |
| C(14) | 1164(2) | 14353(4) | -119(2) | 44(1) |
| C(15) | 1573(2) | 13627(3) | 627(2) | 37(1) |
| C(16) | 1755(3) | 14515(4) | 1334(2) | 46(1) |
| C(17) | 2151(3) | 13819(4) | 2042(2) | 51(1) |
| C(18) | 2384(3) | 12192(4) | 2080(2) | 46(1) |
| C(19) | 2209(2) | 11292(4) | 1409(2) | 40(1) |
| C(20) | 1795(2) | 11976(3) | 653(2) | 34(1) |
| C(21) | 4345(3) | 7260(5) | 2079(2) | 79(1) |

|  |  |  |  |  |
|---|---|---|---|---|
| C(22) | 4780(3) | 4646(4) | 1047(2) | 82(1) |
| C(23) | 5612(3) | 7997(5) | 903(2) | 104(2) |

Bond lengths [Å] and angles [°] for liu30.

|  |  |
|---|---|
| Si(1)-C(21) | 1.847(3) |
| Si(1)-C(1) | 1.848(3) |
| Si(1)-C(22) | 1.850(4) |
| Si(1)-C(23) | 1.852(4) |
| O(1)-C(4) | 1.455(3) |
| O(1)-H(1O) | 0.77(4) |
| C(1)-C(3) | 1.510(4) |
| C(1)-C(2) | 1.527(4) |
| C(1)-H(1) | 0.91(2) |
| C(2)-C(6) | 1.490(4) |
| C(2)-C(3) | 1.496(4) |
| C(2)-H(2) | 0.98(3) |
| C(3)-C(4) | 1.530(4) |
| C(3)-H(3) | 0.98(2) |
| C(4)-C(5) | 1.525(4) |
| C(4)-C(11) | 1.527(4) |
| C(5)-C(10) | 1.387(4) |
| C(5)-C(6) | 1.389(4) |
| C(6)-C(7) | 1.387(4) |

| | |
|---|---|
| C(7)-C(8) | 1.383(4) |
| C(7)-H(7) | 0.99(3) |
| C(8)-C(9) | 1.377(5) |
| C(8)-H(8) | 0.99(3) |
| C(9)-C(10) | 1.385(4) |
| C(9)-H(9) | 0.89(3) |
| C(10)-H(10) | 0.94(3) |
| C(11)-C(12) | 1.376(4) |
| C(11)-C(20) | 1.437(4) |
| C(12)-C(13) | 1.405(4) |
| C(12)-H(12) | 0.93(2) |
| C(13)-C(14) | 1.347(4) |
| C(13)-H(13) | 0.93(2) |
| C(14)-C(15) | 1.419(4) |
| C(14)-H(14) | 0.94(3) |
| C(15)-C(16) | 1.411(4) |
| C(15)-C(20) | 1.422(4) |
| C(16)-C(17) | 1.353(4) |
| C(16)-H(16) | 0.94(3) |
| C(17)-C(18) | 1.404(4) |
| C(17)-H(17) | 0.90(3) |
| C(18)-C(19) | 1.365(4) |
| C(18)-H(18) | 0.96(3) |
| C(19)-C(20) | 1.421(4) |
| C(19)-H(19) | 0.93(2) |

| | |
|---|---|
| C(21)-H(21A) | 0.9800 |
| C(21)-H(21B) | 0.9800 |
| C(21)-H(21C) | 0.9800 |
| C(22)-H(22A) | 0.9800 |
| C(22)-H(22B) | 0.9800 |
| C(22)-H(22C) | 0.9800 |
| C(23)-H(23A) | 0.9800 |
| C(23)-H(23B) | 0.9800 |
| C(23)-H(23C) | 0.9800 |
| C(21)-Si(1)-C(1) | 108.78(16) |
| C(21)-Si(1)-C(22) | 107.93(17) |
| C(1)-Si(1)-C(22) | 108.84(16) |
| C(21)-Si(1)-C(23) | 109.9(2) |
| C(1)-Si(1)-C(23) | 109.40(16) |
| C(22)-Si(1)-C(23) | 111.9(2) |
| C(4)-O(1)-H(1O) | 112(3) |
| C(3)-C(1)-C(2) | 59.01(19) |
| C(3)-C(1)-Si(1) | 120.9(2) |
| C(2)-C(1)-Si(1) | 124.4(2) |
| C(3)-C(1)-H(1) | 111.9(16) |
| C(2)-C(1)-H(1) | 112.3(15) |
| Si(1)-C(1)-H(1) | 116.0(15) |
| C(6)-C(2)-C(3) | 106.3(3) |
| C(6)-C(2)-C(1) | 115.7(3) |
| C(3)-C(2)-C(1) | 59.93(19) |

| | |
|---|---|
| C(6)-C(2)-H(2) | 121.8(16) |
| C(3)-C(2)-H(2) | 119.8(16) |
| C(1)-C(2)-H(2) | 117.3(16) |
| C(2)-C(3)-C(1) | 61.1(2) |
| C(2)-C(3)-C(4) | 109.1(2) |
| C(1)-C(3)-C(4) | 118.9(3) |
| C(2)-C(3)-H(3) | 120.6(15) |
| C(1)-C(3)-H(3) | 116.9(15) |
| C(4)-C(3)-H(3) | 117.7(15) |
| O(1)-C(4)-C(5) | 109.3(2) |
| O(1)-C(4)-C(11) | 109.4(2) |
| C(5)-C(4)-C(11) | 114.8(2) |
| O(1)-C(4)-C(3) | 109.2(2) |
| C(5)-C(4)-C(3) | 102.7(2) |
| C(11)-C(4)-C(3) | 111.2(2) |
| C(10)-C(5)-C(6) | 119.9(3) |
| C(10)-C(5)-C(4) | 128.2(3) |
| C(6)-C(5)-C(4) | 111.9(3) |
| C(7)-C(6)-C(5) | 120.4(3) |
| C(7)-C(6)-C(2) | 129.7(3) |
| C(5)-C(6)-C(2) | 109.9(3) |
| C(8)-C(7)-C(6) | 119.3(3) |
| C(8)-C(7)-H(7) | 121.7(16) |
| C(6)-C(7)-H(7) | 118.9(16) |
| C(9)-C(8)-C(7) | 120.3(3) |

| | |
|---|---|
| C(9)-C(8)-H(8) | 122.5(16) |
| C(7)-C(8)-H(8) | 117.2(16) |
| C(8)-C(9)-C(10) | 120.8(4) |
| C(8)-C(9)-H(9) | 120.3(19) |
| C(10)-C(9)-H(9) | 118.8(19) |
| C(9)-C(10)-C(5) | 119.3(3) |
| C(9)-C(10)-H(10) | 123.5(17) |
| C(5)-C(10)-H(10) | 117.2(17) |
| C(12)-C(11)-C(20) | 118.5(3) |
| C(12)-C(11)-C(4) | 121.0(3) |
| C(20)-C(11)-C(4) | 120.4(2) |
| C(11)-C(12)-C(13) | 121.9(3) |
| C(11)-C(12)-H(12) | 118.3(15) |
| C(13)-C(12)-H(12) | 119.8(15) |
| C(14)-C(13)-C(12) | 120.1(3) |
| C(14)-C(13)-H(13) | 123.1(15) |
| C(12)-C(13)-H(13) | 116.7(15) |
| C(13)-C(14)-C(15) | 121.4(3) |
| C(13)-C(14)-H(14) | 120.7(15) |
| C(15)-C(14)-H(14) | 118.0(15) |
| C(16)-C(15)-C(14) | 121.2(3) |
| C(16)-C(15)-C(20) | 120.1(3) |
| C(14)-C(15)-C(20) | 118.8(3) |
| C(17)-C(16)-C(15) | 120.8(3) |
| C(17)-C(16)-H(16) | 123.3(17) |

| | |
|---|---|
| C(15)-C(16)-H(16) | 115.7(17) |
| C(16)-C(17)-C(18) | 120.0(3) |
| C(16)-C(17)-H(17) | 123.2(18) |
| C(18)-C(17)-H(17) | 116.9(18) |
| C(19)-C(18)-C(17) | 120.8(3) |
| C(19)-C(18)-H(18) | 119.2(18) |
| C(17)-C(18)-H(18) | 120.0(18) |
| C(18)-C(19)-C(20) | 121.1(3) |
| C(18)-C(19)-H(19) | 118.6(15) |
| C(20)-C(19)-H(19) | 120.3(15) |
| C(19)-C(20)-C(15) | 117.2(3) |
| C(19)-C(20)-C(11) | 123.5(3) |
| C(15)-C(20)-C(11) | 119.3(3) |
| Si(1)-C(21)-H(21A) | 109.5 |
| Si(1)-C(21)-H(21B) | 109.5 |
| H(21A)-C(21)-H(21B) | 109.5 |
| Si(1)-C(21)-H(21C) | 109.5 |
| H(21A)-C(21)-H(21C) | 109.5 |
| H(21B)-C(21)-H(21C) | 109.5 |
| Si(1)-C(22)-H(22A) | 109.5 |
| Si(1)-C(22)-H(22B) | 109.5 |
| H(22A)-C(22)-H(22B) | 109.5 |
| Si(1)-C(22)-H(22C) | 109.5 |
| H(22A)-C(22)-H(22C) | 109.5 |
| H(22B)-C(22)-H(22C) | 109.5 |

|  |  |
|---|---|
| Si(1)-C(23)-H(23A) | 109.5 |
| Si(1)-C(23)-H(23B) | 109.5 |
| H(23A)-C(23)-H(23B) | 109.5 |
| Si(1)-C(23)-H(23C) | 109.5 |
| H(23A)-C(23)-H(23C) | 109.5 |
| H(23B)-C(23)-H(23C) | 109.5 |

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters ($Å^2$x $10^3$)for liu30. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Si(1) | 49(1) | 58(1) | 43(1) | 9(1) | 3(1) | 14(1) |
| O(1) | 48(2) | 35(1) | 35(1) | 7(1) | 9(1) | -1(1) |
| C(1) | 43(2) | 31(2) | 47(2) | 5(2) | 4(2) | 0(2) |
| C(2) | 39(2) | 35(2) | 44(2) | 5(2) | 9(2) | 4(2) |
| C(3) | 38(2) | 27(2) | 39(2) | 0(1) | 1(2) | 2(2) |
| C(4) | 37(2) | 26(2) | 33(2) | 4(1) | 7(1) | 1(1) |
| C(5) | 42(2) | 26(2) | 29(2) | 6(1) | 6(1) | 0(1) |
| C(6) | 43(2) | 27(2) | 38(2) | 4(1) | 9(2) | 1(2) |
| C(7) | 55(2) | 41(2) | 43(2) | 2(2) | 14(2) | 10(2) |
| C(8) | 67(3) | 40(2) | 34(2) | -3(2) | 12(2) | 1(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(9) | 54(3) | 44(2) | 33(2) | 0(2) | 1(2) | -7(2) |
| C(10) | 41(2) | 36(2) | 37(2) | 2(2) | 7(2) | 2(2) |
| C(11) | 35(2) | 26(2) | 38(2) | 4(1) | 7(1) | 1(1) |
| C(12) | 51(2) | 31(2) | 34(2) | 0(2) | 6(2) | 2(2) |
| C(13) | 61(2) | 35(2) | 36(2) | 10(2) | 4(2) | 0(2) |
| C(14) | 48(2) | 26(2) | 58(2) | 6(2) | 12(2) | 5(2) |
| C(15) | 42(2) | 24(2) | 46(2) | 1(2) | 10(2) | -2(1) |
| C(16) | 56(2) | 30(2) | 52(2) | -4(2) | 11(2) | 1(2) |
| C(17) | 65(3) | 42(2) | 42(2) | -13(2) | 6(2) | -9(2) |
| C(18) | 57(2) | 41(2) | 37(2) | 1(2) | 5(2) | -6(2) |
| C(19) | 48(2) | 30(2) | 41(2) | 1(2) | 7(2) | 2(2) |
| C(20) | 33(2) | 32(2) | 37(2) | 2(1) | 6(1) | 1(1) |
| C(21) | 76(3) | 101(3) | 52(2) | -17(2) | -2(2) | 17(2) |
| C(22) | 112(4) | 81(3) | 58(3) | 26(2) | 32(2) | 58(3) |
| C(23) | 56(3) | 143(4) | 95(3) | 50(3) | -18(2) | -24(3) |

Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for liu30.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(21A) | 4226 | 8402 | 2119 | 119 |
| H(21B) | 4960 | 6949 | 2483 | 119 |
| H(21C) | 3747 | 6673 | 2160 | 119 |

| | | | | |
|---|---|---|---|---|
| H(22A) | 4196 | 4055 | 1150 | 123 |
| H(22B) | 5407 | 4372 | 1449 | 123 |
| H(22C) | 4868 | 4368 | 522 | 123 |
| H(23A) | 5455 | 9129 | 933 | 156 |
| H(23B) | 5706 | 7751 | 376 | 156 |
| H(23C) | 6244 | 7745 | 1303 | 156 |
| H(1O) | 710(30) | 8560(50) | 330(20) | 96(18) |
| H(1) | 2808(19) | 6600(30) | 298(13) | 23(7) |
| H(2) | 3970(20) | 8400(30) | -557(15) | 45(9) |
| H(3) | 3409(19) | 9810(30) | 517(14) | 34(8) |
| H(7) | 2860(20) | 6670(30) | -1950(15) | 40(8) |
| H(8) | 1210(20) | 6370(30) | -2808(17) | 52(9) |
| H(9) | -200(20) | 7360(30) | -2374(17) | 45(10) |
| H(10) | -20(20) | 8730(30) | -1183(15) | 44(9) |
| H(12) | 1090(18) | 11300(30) | -1242(14) | 29(8) |
| H(13) | 770(18) | 13970(30) | -1293(14) | 26(7) |
| H(14) | 994(19) | 15440(30) | -127(14) | 36(8) |
| H(16) | 1550(20) | 15580(40) | 1278(16) | 51(9) |
| H(17) | 2280(20) | 14350(30) | 2504(16) | 46(9) |
| H(18) | 2670(20) | 11700(30) | 2579(17) | 60(10) |
| H(19) | 2381(18) | 10220(30) | 1454(14) | 28(7) |

Torsion angles [°] for liu30.

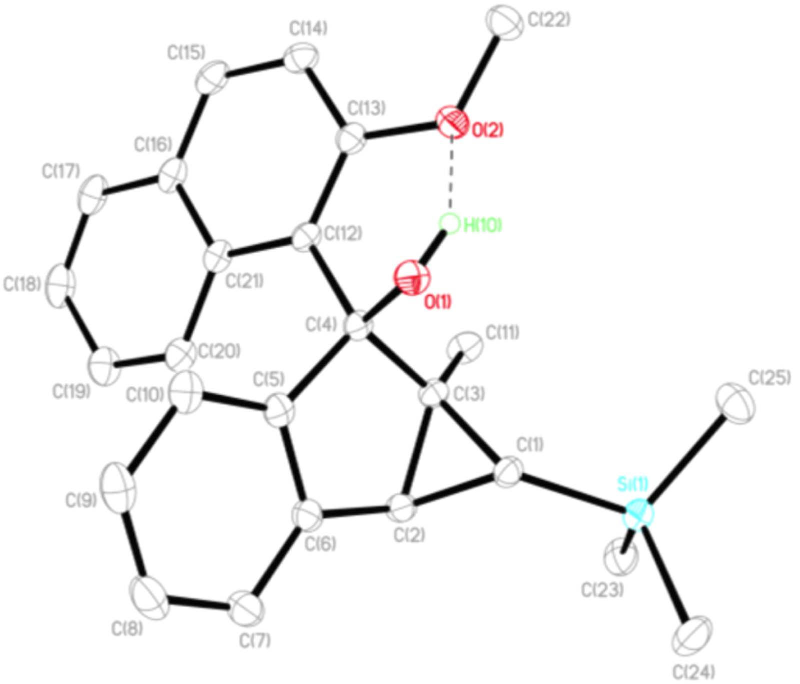
| | |
|---|---|
| C(21)-Si(1)-C(1)-C(3) | 65.8(3) |

| | |
|---|---|
| C(22)-Si(1)-C(1)-C(3) | -176.8(3) |
| C(23)-Si(1)-C(1)-C(3) | -54.2(3) |
| C(21)-Si(1)-C(1)-C(2) | 137.3(3) |
| C(22)-Si(1)-C(1)-C(2) | -105.3(3) |
| C(23)-Si(1)-C(1)-C(2) | 17.3(3) |
| C(3)-C(1)-C(2)-C(6) | -94.7(3) |
| Si(1)-C(1)-C(2)-C(6) | 157.0(2) |
| Si(1)-C(1)-C(2)-C(3) | -108.4(3) |
| C(6)-C(2)-C(3)-C(1) | 110.6(3) |
| C(6)-C(2)-C(3)-C(4) | -2.4(3) |
| C(1)-C(2)-C(3)-C(4) | -113.1(3) |
| Si(1)-C(1)-C(3)-C(2) | 114.1(3) |
| C(2)-C(1)-C(3)-C(4) | 97.1(3) |
| Si(1)-C(1)-C(3)-C(4) | -148.9(2) |
| C(2)-C(3)-C(4)-O(1) | 119.3(3) |
| C(1)-C(3)-C(4)-O(1) | 52.5(3) |
| C(2)-C(3)-C(4)-C(5) | 3.4(3) |
| C(1)-C(3)-C(4)-C(5) | -63.5(3) |
| C(2)-C(3)-C(4)-C(11) | -119.8(3) |
| C(1)-C(3)-C(4)-C(11) | 173.3(3) |
| O(1)-C(4)-C(5)-C(10) | 58.7(4) |
| C(11)-C(4)-C(5)-C(10) | -64.7(4) |
| C(3)-C(4)-C(5)-C(10) | 174.5(3) |
| O(1)-C(4)-C(5)-C(6) | -119.1(3) |
| C(11)-C(4)-C(5)-C(6) | 117.5(3) |

| | |
|---|---|
| C(3)-C(4)-C(5)-C(6) | -3.3(3) |
| C(10)-C(5)-C(6)-C(7) | 1.6(4) |
| C(4)-C(5)-C(6)-C(7) | 179.6(3) |
| C(10)-C(5)-C(6)-C(2) | -176.1(3) |
| C(4)-C(5)-C(6)-C(2) | 1.9(3) |
| C(3)-C(2)-C(6)-C(7) | -177.1(3) |
| C(1)-C(2)-C(6)-C(7) | -113.1(4) |
| C(3)-C(2)-C(6)-C(5) | 0.3(3) |
| C(1)-C(2)-C(6)-C(5) | 64.3(3) |
| C(5)-C(6)-C(7)-C(8) | 0.1(4) |
| C(2)-C(6)-C(7)-C(8) | 177.3(3) |
| C(6)-C(7)-C(8)-C(9) | -1.6(5) |
| C(7)-C(8)-C(9)-C(10) | 1.3(5) |
| C(8)-C(9)-C(10)-C(5) | 0.4(5) |
| C(6)-C(5)-C(10)-C(9) | -1.9(4) |
| C(4)-C(5)-C(10)-C(9) | -179.5(3) |
| O(1)-C(4)-C(11)-C(12) | -127.4(3) |
| C(5)-C(4)-C(11)-C(12) | -4.1(4) |
| C(3)-C(4)-C(11)-C(12) | 111.9(3) |
| O(1)-C(4)-C(11)-C(20) | 54.1(3) |
| C(5)-C(4)-C(11)-C(20) | 177.4(3) |
| C(3)-C(4)-C(11)-C(20) | -66.6(3) |
| C(20)-C(11)-C(12)-C(13) | -1.4(5) |
| C(4)-C(11)-C(12)-C(13) | -179.9(3) |
| C(11)-C(12)-C(13)-C(14) | 0.0(5) |

| | |
|---|---|
| C(12)-C(13)-C(14)-C(15) | 1.0(5) |
| C(13)-C(14)-C(15)-C(16) | 179.6(3) |
| C(13)-C(14)-C(15)-C(20) | -0.6(5) |
| C(14)-C(15)-C(16)-C(17) | -179.5(3) |
| C(20)-C(15)-C(16)-C(17) | 0.7(5) |
| C(15)-C(16)-C(17)-C(18) | -0.2(5) |
| C(16)-C(17)-C(18)-C(19) | -0.5(5) |
| C(17)-C(18)-C(19)-C(20) | 0.6(5) |
| C(18)-C(19)-C(20)-C(15) | -0.1(5) |
| C(18)-C(19)-C(20)-C(11) | -179.6(3) |
| C(16)-C(15)-C(20)-C(19) | -0.5(4) |
| C(14)-C(15)-C(20)-C(19) | 179.6(3) |
| C(16)-C(15)-C(20)-C(11) | 179.0(3) |
| C(14)-C(15)-C(20)-C(11) | -0.9(4) |
| C(12)-C(11)-C(20)-C(19) | -178.7(3) |
| C(4)-C(11)-C(20)-C(19) | -0.2(4) |
| C(12)-C(11)-C(20)-C(15) | 1.8(4) |
| C(4)-C(11)-C(20)-C(15) | -179.7(3) |

### *Crystal Structure Information for Compound 2c, Chapter III*



Crystal data and structure refinement for liu44 **(2c)**.

| | | |
|---|---|---|
| Identification code | liu44 | |
| Empirical formula | C22 H28 O3 Si | |
| Formula weight | 368.53 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | Pna2(1) | |
| Unit cell dimensions | a = 13.5758(18) Å | α= 90°. |
| | b = 8.8613(12) Å | β= 90°. |
| | c = 34.097(5) Å | γ = 90°. |
| Volume | 4101.8(10) Å3 | |

| | |
|---|---|
| Z | 8 |
| Density (calculated) | 1.194 Mg/m3 |
| Absorption coefficient | 0.132 mm-1 |
| F(000) | 1584 |
| Crystal size | 0.27 x 0.24 x 0.18 mm3 |
| Theta range for data collection | 1.19 to 27.00°. |
| Index ranges | -13<=h<=17, -11<=k<=10, -43<=l<=43 |
| Reflections collected | 25158 |
| Independent reflections | 8900 [R(int) = 0.0328] |
| Completeness to theta = 27.00° | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9766 and 0.9652 |
| Refinement method | Full-matrix least-squares on F2 |
| Data / restraints / parameters | 8900 / 1 / 621 |
| Goodness-of-fit on F2 | 1.058 |
| Final R indices [I>2sigma(I)] | R1 = 0.0431, wR2 = 0.1007 |
| R indices (all data) | R1 = 0.0535, wR2 = 0.1114 |
| Absolute structure parameter | 0.00(11) |
| Largest diff. peak and hole | 0.382 and -0.235 e.Å-3 |

Atomic coordinates ( x 104) and equivalent isotropic displacement parameters (Å2x 103) for liu44. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Si(1) | 273(1) | 2337(1) | 161(1) | 34(1) |
| O(1) | 889(1) | 4564(2) | -920(1) | 31(1) |
| O(2) | 1360(1) | 6857(2) | -1324(1) | 39(1) |

| | | | | |
|---|---|---|---|---|
| O(3) | -1641(1) | 6987(2) | -628(1) | 34(1) |
| C(1) | -161(2) | 3179(3 | -310(1) | 25(1) |
| C(2) | -1176(2) | 3900(3) | -380(1) | 25(1) |
| C(3) | -258(2) | 4845(2) | -398(1) | 23(1) |
| C(4) | -54(2) | 5214(2) | -838(1) | 22(1) |
| C(5) | -870(2) | 4359(2) | -1050(1) | 22(1) |
| C(6) | -1534(2) | 3688(2) | -789(1) | 23(1) |
| C(7) | -2347(2) | 2909(3) | -927(1) | 30(1) |
| C(8) | -2472(2) | 2765(3) | -1330(1) | 32(1) |
| C(9) | -1797(2) | 3381(3) | -1589(1) | 32(1) |
| C(10) | -995(2) | 4196(3) | -1451(1) | 27(1) |
| C(11) | -104(2) | 6917(2) | -941(1) | 23(1) |
| C(12) | 599(2) | 7687(3) | -1168(1) | 25(1) |
| C(13) | 520(2) | 9240(3) | -1243(1) | 33(1) |
| C(14) | -274(2) | 10035(3) | -1106(1) | 39(1) |
| C(15) | -1015(2) | 9308(3) | -899(1) | 36(1) |
| C(16) | -925(2) | 7774(3) | -823(1) | 27(1) |
| C(17) | 23(2) | 5984(3) | -90(1) | 28(1) |
| C(18) | 2148(2) | 7593(4) | -1530(1) | 49(1) |
| C(19) | -2405(2) | 7804(4) | -436(1) | 40(1) |
| C(20) | -558(3) | 2742(5) | 583(1) | 64(1) |
| C(21) | 324(4) | 249(4) | 79(1) | 85(1) |
| C(22) | 1537(2) | 3009(4) | 280(1) | 46(1) |
| Si(1') | -7792(1) | 7580(1) | -8877(1) | 34(1) |
| O(1') | -8245(1) | 5372(2) | -7769(1) | 30(1) |
| O(2') | -8689(1) | 3048(2) | -7367(1) | 39(1) |
| O(3') | -5749(1) | 2971(2) | -8108(1) | 35(1) |

|  |  |  |  |  |
|---|---|---|---|---|
| C(1') | -7311(2) | 6744(2) | -8416(1) | 24(1) |
| C(2') | -6279(2) | 6031(2) | -8369(1) | 23(1) |
| C(3') | -7180(2) | 5070(2) | -8323(1) | 22(1) |
| C(4') | -7319(2) | 4713(2) | -7878(1) | 21(1) |
| C(5') | -6463(2) | 5587(2) | -7690(1) | 20(1) |
| C(6') | -5858(2) | 6264(2) | -7971(1) | 23(1) |
| C(7') | -5028(2) | 7070(3) | -7854(1) | 26(1) |
| C(8') | -4835(2) | 7214(3) | -7452(1) | 32(1) |
| C(9') | -5457(2) | 6582(3) | -7176(1) | 31(1) |
| C(10') | -6276(2) | 5756(3) | -7294(1) | 26(1) |
| C(11') | -7256(2) | 3017(2) | -7772(1) | 24(1) |
| C(12') | -7924(2) | 2229(3) | -7536(1) | 29(1) |
| C(13') | -7833(2) | 695(3) | -7460(1) | 39(1) |
| C(14') | -7030(2) | -77(3) | -7608(1) | 44(1) |
| C(15') | -6331(2) | 645(3) | -7824(1) | 39(1) |
| C(16') | -6435(2) | 2180(3) | -7903(1) | 28(1) |
| C(17') | -7497(2) | 3928(3) | -8626(1) | 29(1) |
| C(18') | -9499(2) | 2267(4) | -7195(1) | 45(1) |
| C(19') | -4961(2) | 2189(4) | -8290(1) | 42(1) |
| C(20') | -6965(3) | 7244(5) | -9301(1) | 62(1) |
| C(21') | -7881(4) | 9644(4) | -8788(1) | 83(1) |
| C(22') | -9051(2) | 6852(4) | -8993(1) | 46(1) |

Bond lengths [Å] and angles [°] for liu44.

|  |  |
|---|---|
| Si(1)-C(22) | 1.862(3) |
| Si(1)-C(20) | 1.862(4) |
| Si(1)-C(1) | 1.868(2) |

| | |
|---|---|
| Si(1)-C(21) | 1.873(3) |
| O(1)-C(4) | 1.431(3) |
| O(1)-H(1O) | 0.75(3) |
| O(2)-C(12) | 1.376(3) |
| O(2)-C(18) | 1.436(3) |
| O(3)-C(16) | 1.369(3) |
| O(3)-C(19) | 1.425(3) |
| C(1)-C(3) | 1.513(3) |
| C(1)-C(2) | 1.538(3) |
| C(1)-H(1) | 0.93(3) |
| C(2)-C(6) | 1.488(3) |
| C(2)-C(3) | 1.503(3) |
| C(2)-H(2) | 0.99(2) |
| C(3)-C(17) | 1.506(3) |
| C(3)-C(4) | 1.559(3) |
| C(4)-C(5) | 1.525(3) |
| C(4)-C(11) | 1.550(3) |
| C(5)-C(10) | 1.385(3) |
| C(5)-C(6) | 1.400(3) |
| C(6)-C(7) | 1.385(3) |
| C(7)-C(8) | 1.389(4) |
| C(7)-H(7) | 1.05(3) |
| C(8)-C(9) | 1.386(4) |
| C(8)-H(8) | 0.89(3) |
| C(9)-C(10) | 1.390(4) |
| C(9)-H(9) | 0.99(3) |
| C(10)-H(10) | 0.93(3) |

| | |
|---|---|
| C(11)-C(12) | 1.405(3) |
| C(11)-C(16) | 1.408(3) |
| C(12)-C(13) | 1.405(3) |
| C(13)-C(14) | 1.371(4) |
| C(13)-H(13) | 0.94(3) |
| C(14)-C(15) | 1.386(4) |
| C(14)-H(14) | 0.94(3) |
| C(15)-C(16) | 1.390(3) |
| C(15)-H(15) | 0.92(3) |
| C(17)-H(17A) | 0.95(3) |
| C(17)-H(17B) | 0.95(3) |
| C(17)-H(17C) | 0.95(4) |
| C(18)-H(18A) | 1.02(4) |
| C(18)-H(18B) | 0.98(3) |
| C(18)-H(18C) | 1.00(4) |
| C(19)-H(19A) | 1.03(3) |
| C(19)-H(19B) | 1.04(3) |
| C(19)-H(19C) | 1.00(3) |
| C(20)-H(20A) | 0.9800 |
| C(20)-H(20B) | 0.9800 |
| C(20)-H(20C) | 0.9800 |
| C(21)-H(21A) | 0.9800 |
| C(21)-H(21B) | 0.9800 |
| C(21)-H(21C) | 0.9800 |
| C(22)-H(22A) | 0.9800 |
| C(22)-H(22B) | 0.9800 |
| C(22)-H(22C) | 0.9800 |

| | |
|---|---|
| Si(1')-C(20') | 1.854(4) |
| Si(1')-C(1') | 1.857(2) |
| Si(1')-C(21') | 1.858(3) |
| Si(1')-C(22') | 1.869(3) |
| O(1')-C(4') | 1.435(2) |
| O(1')-H(1O') | 0.82(3) |
| O(2')-C(12') | 1.392(3) |
| O(2')-C(18') | 1.425(3) |
| O(3')-C(16') | 1.358(3) |
| O(3')-C(19') | 1.418(3) |
| C(1')-C(3') | 1.527(3) |
| C(1')-C(2') | 1.545(3) |
| C(1')-H(1') | 0.99(3) |
| C(2')-C(6') | 1.487(3) |
| C(2')-C(3') | 1.499(3) |
| C(2')-H(2') | 0.99(2) |
| C(3')-C(17') | 1.507(3) |
| C(3')-C(4') | 1.561(3) |
| C(4')-C(5') | 1.537(3) |
| C(4')-C(11') | 1.548(3) |
| C(5')-C(10') | 1.381(3) |
| C(5')-C(6') | 1.397(3) |
| C(6')-C(7') | 1.393(3) |
| C(7')-C(8') | 1.403(4) |
| C(7')-H(7') | 0.93(3) |
| C(8')-C(9') | 1.383(4) |
| C(8')-H(8') | 0.97(2) |

| | |
|---|---|
| C(9')-C(10') | 1.391(3) |
| C(9')-H(9') | 0.95(3) |
| C(10')-H(10') | 0.95(2) |
| C(11')-C(12') | 1.400(3) |
| C(11')-C(16') | 1.412(3) |
| C(12')-C(13') | 1.389(4) |
| C(13')-C(14') | 1.382(4) |
| C(13')-H(13') | 0.93(3) |
| C(14')-C(15') | 1.361(4) |
| C(14')-H(14') | 0.96(3) |
| C(15')-C(16') | 1.394(4) |
| C(15')-H(15') | 0.91(3) |
| C(17')-H(17D) | 1.01(3) |
| C(17')-H(17E) | 0.93(3) |
| C(17')-H(17F) | 0.97(3) |
| C(18')-H(18D) | 1.04(4) |
| C(18')-H(18E) | 0.96(4) |
| C(18')-H(18F) | 0.93(3) |
| C(19')-H(19D) | 0.96(3) |
| C(19')-H(19E) | 1.01(4) |
| C(19')-H(19F) | 0.98(4) |
| C(20')-H(20D) | 0.9800 |
| C(20')-H(20E) | 0.9800 |
| C(20')-H(20F) | 0.9800 |
| C(21')-H(21D) | 0.9800 |
| C(21')-H(21E) | 0.9800 |
| C(21')-H(21F) | 0.9800 |

| | |
|---|---|
| C(22')-H(22D) | 0.9800 |
| C(22')-H(22E) | 0.9800 |
| C(22')-H(22F) | 0.9800 |
| C(22)-Si(1)-C(20) | 109.26(16) |
| C(22)-Si(1)-C(1) | 110.47(13) |
| C(20)-Si(1)-C(1) | 113.35(15) |
| C(22)-Si(1)-C(21) | 108.32(18) |
| C(20)-Si(1)-C(21) | 109.2(2) |
| C(1)-Si(1)-C(21) | 106.09(14) |
| C(4)-O(1)-H(1O) | 106(2) |
| C(12)-O(2)-C(18) | 120.4(2) |
| C(16)-O(3)-C(19) | 118.8(2) |
| C(3)-C(1)-C(2) | 59.01(14) |
| C(3)-C(1)-Si(1) | 126.04(16) |
| C(2)-C(1)-Si(1) | 125.48(17) |
| C(3)-C(1)-H(1) | 113.4(15) |
| C(2)-C(1)-H(1) | 113.7(16) |
| Si(1)-C(1)-H(1) | 110.5(16) |
| C(6)-C(2)-C(3) | 107.50(17) |
| C(6)-C(2)-C(1) | 112.53(19) |
| C(3)-C(2)-C(1) | 59.66(14) |
| C(6)-C(2)-H(2) | 119.4(14) |
| C(3)-C(2)-H(2) | 121.5(14) |
| C(1)-C(2)-H(2) | 121.7(14) |
| C(2)-C(3)-C(17) | 123.62(19) |
| C(2)-C(3)-C(1) | 61.33(15) |
| C(17)-C(3)-C(1) | 119.55(19) |

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|---|---|
| C(2)-C(3)-C(4) | 107.81(17) |
| C(17)-C(3)-C(4) | 119.03(19) |
| C(1)-C(3)-C(4) | 112.31(17) |
| O(1)-C(4)-C(5) | 110.91(18) |
| O(1)-C(4)-C(11) | 112.76(17) |
| C(5)-C(4)-C(11) | 110.11(17) |
| O(1)-C(4)-C(3) | 105.28(17) |
| C(5)-C(4)-C(3) | 102.82(16) |
| C(11)-C(4)-C(3) | 114.46(17) |
| C(10)-C(5)-C(6) | 120.4(2) |
| C(10)-C(5)-C(4) | 127.5(2) |
| C(6)-C(5)-C(4) | 112.14(18) |
| C(7)-C(6)-C(5) | 120.5(2) |
| C(7)-C(6)-C(2) | 129.9(2) |
| C(5)-C(6)-C(2) | 109.46(18) |
| C(6)-C(7)-C(8) | 118.7(2) |
| C(6)-C(7)-H(7) | 119.9(16) |
| C(8)-C(7)-H(7) | 121.4(16) |
| C(9)-C(8)-C(7) | 121.0(2) |
| C(9)-C(8)-H(8) | 121.7(18) |
| C(7)-C(8)-H(8) | 117.3(18) |
| C(8)-C(9)-C(10) | 120.4(2) |
| C(8)-C(9)-H(9) | 123.7(17) |
| C(10)-C(9)-H(9) | 116.0(17) |
| C(5)-C(10)-C(9) | 119.0(2) |
| C(5)-C(10)-H(10) | 121.0(16) |
| C(9)-C(10)-H(10) | 120.0(16) |

| | |
|---|---|
| C(12)-C(11)-C(16) | 115.7(2) |
| C(12)-C(11)-C(4) | 124.6(2) |
| C(16)-C(11)-C(4) | 119.7(2) |
| O(2)-C(12)-C(13) | 120.7(2) |
| O(2)-C(12)-C(11) | 117.6(2) |
| C(13)-C(12)-C(11) | 121.7(2) |
| C(14)-C(13)-C(12) | 120.0(2) |
| C(14)-C(13)-H(13) | 123.7(17) |
| C(12)-C(13)-H(13) | 116.1(17) |
| C(13)-C(14)-C(15) | 120.4(2) |
| C(13)-C(14)-H(14) | 120.7(16) |
| C(15)-C(14)-H(14) | 118.8(16) |
| C(14)-C(15)-C(16) | 119.1(2) |
| C(14)-C(15)-H(15) | 122(2) |
| C(16)-C(15)-H(15) | 119(2) |
| O(3)-C(16)-C(15) | 121.8(2) |
| O(3)-C(16)-C(11) | 115.2(2) |
| C(15)-C(16)-C(11) | 123.0(2) |
| C(3)-C(17)-H(17A) | 112.4(17) |
| C(3)-C(17)-H(17B) | 111.0(18) |
| H(17A)-C(17)-H(17B) | 111(2) |
| C(3)-C(17)-H(17C) | 113(2) |
| H(17A)-C(17)-H(17C) | 104(2) |
| H(17B)-C(17)-H(17C) | 105(3) |
| O(2)-C(18)-H(18A) | 101(2) |
| O(2)-C(18)-H(18B) | 109.2(17) |
| H(18A)-C(18)-H(18B) | 110(3) |

| | |
|---|---|
| O(2)-C(18)-H(18C) | 105(2) |
| H(18A)-C(18)-H(18C) | 108(3) |
| H(18B)-C(18)-H(18C) | 122(3) |
| O(3)-C(19)-H(19A) | 108.8(17) |
| O(3)-C(19)-H(19B) | 111.0(14) |
| H(19A)-C(19)-H(19B) | 115(2) |
| O(3)-C(19)-H(19C) | 105.6(17) |
| H(19A)-C(19)-H(19C) | 108(2) |
| H(19B)-C(19)-H(19C) | 109(2) |
| Si(1)-C(20)-H(20A) | 109.5 |
| Si(1)-C(20)-H(20B) | 109.5 |
| H(20A)-C(20)-H(20B) | 109.5 |
| Si(1)-C(20)-H(20C) | 109.5 |
| H(20A)-C(20)-H(20C) | 109.5 |
| H(20B)-C(20)-H(20C) | 109.5 |
| Si(1)-C(21)-H(21A) | 109.5 |
| Si(1)-C(21)-H(21B) | 109.5 |
| H(21A)-C(21)-H(21B) | 109.5 |
| Si(1)-C(21)-H(21C) | 109.5 |
| H(21A)-C(21)-H(21C) | 109.5 |
| H(21B)-C(21)-H(21C) | 109.5 |
| Si(1)-C(22)-H(22A) | 109.5 |
| Si(1)-C(22)-H(22B) | 109.5 |
| H(22A)-C(22)-H(22B) | 109.5 |
| Si(1)-C(22)-H(22C) | 109.5 |
| H(22A)-C(22)-H(22C) | 109.5 |
| H(22B)-C(22)-H(22C) | 109.5 |

| | |
|---|---|
| C(20')-Si(1')-C(1') | 112.50(14) |
| C(20')-Si(1')-C(21') | 108.9(2) |
| C(1')-Si(1')-C(21') | 106.14(13) |
| C(20')-Si(1')-C(22') | 109.46(15) |
| C(1')-Si(1')-C(22') | 111.33(13) |
| C(21')-Si(1')-C(22') | 108.33(18) |
| C(4')-O(1')-H(1O') | 107(2) |
| C(12')-O(2')-C(18') | 119.5(2) |
| C(16')-O(3')-C(19') | 119.3(2) |
| C(3')-C(1')-C(2') | 58.42(14) |
| C(3')-C(1')-Si(1') | 127.10(15) |
| C(2')-C(1')-Si(1') | 124.73(16) |
| C(3')-C(1')-H(1') | 110.5(15) |
| C(2')-C(1')-H(1') | 111.9(16) |
| Si(1')-C(1')-H(1') | 113.3(16) |
| C(6')-C(2')-C(3') | 107.33(18) |
| C(6')-C(2')-C(1') | 112.69(18) |
| C(3')-C(2')-C(1') | 60.18(14) |
| C(6')-C(2')-H(2') | 117.8(14) |
| C(3')-C(2')-H(2') | 122.3(14) |
| C(1')-C(2')-H(2') | 123.1(14) |
| C(2')-C(3')-C(17') | 122.92(19) |
| C(2')-C(3')-C(1') | 61.40(14) |
| C(17')-C(3')-C(1') | 118.55(19) |
| C(2')-C(3')-C(4') | 108.33(17) |
| C(17')-C(3')-C(4') | 119.62(19) |
| C(1')-C(3')-C(4') | 112.54(17) |

| | |
|---|---|
| O(1')-C(4')-C(5') | 110.43(17) |
| O(1')-C(4')-C(11') | 112.49(17) |
| C(5')-C(4')-C(11') | 110.42(17) |
| O(1')-C(4')-C(3') | 106.02(16) |
| C(5')-C(4')-C(3') | 102.28(16) |
| C(11')-C(4')-C(3') | 114.66(17) |
| C(10')-C(5')-C(6') | 121.0(2) |
| C(10')-C(5')-C(4') | 126.99(19) |
| C(6')-C(5')-C(4') | 111.98(18) |
| C(7')-C(6')-C(5') | 120.0(2) |
| C(7')-C(6')-C(2') | 130.1(2) |
| C(5')-C(6')-C(2') | 109.90(18) |
| C(6')-C(7')-C(8') | 118.5(2) |
| C(6')-C(7')-H(7') | 122.0(18) |
| C(8')-C(7')-H(7') | 119.4(18) |
| C(9')-C(8')-C(7') | 121.0(2) |
| C(9')-C(8')-H(8') | 122.9(15) |
| C(7')-C(8')-H(8') | 116.0(15) |
| C(8')-C(9')-C(10') | 120.2(2) |
| C(8')-C(9')-H(9') | 118.4(18) |
| C(10')-C(9')-H(9') | 121.4(18) |
| C(5')-C(10')-C(9') | 119.2(2) |
| C(5')-C(10')-H(10') | 118.8(13) |
| C(9')-C(10')-H(10') | 122.0(13) |
| C(12')-C(11')-C(16') | 115.6(2) |
| C(12')-C(11')-C(4') | 125.7(2) |
| C(16')-C(11')-C(4') | 118.68(19) |

| | |
|---|---|
| C(13')-C(12')-O(2') | 120.0(2) |
| C(13')-C(12')-C(11') | 122.5(2) |
| O(2')-C(12')-C(11') | 117.4(2) |
| C(14')-C(13')-C(12') | 119.1(3) |
| C(14')-C(13')-H(13') | 121.6(17) |
| C(12')-C(13')-H(13') | 119.1(17) |
| C(15')-C(14')-C(13') | 120.9(3) |
| C(15')-C(14')-H(14') | 119.7(19) |
| C(13')-C(14')-H(14') | 119.3(19) |
| C(14')-C(15')-C(16') | 119.6(3) |
| C(14')-C(15')-H(15') | 116.6(19) |
| C(16')-C(15')-H(15') | 123.8(19) |
| O(3')-C(16')-C(15') | 122.3(2) |
| O(3')-C(16')-C(11') | 115.6(2) |
| C(15')-C(16')-C(11') | 122.1(2) |
| C(3')-C(17')-H(17D) | 110.0(15) |
| C(3')-C(17')-H(17E) | 115.1(15) |
| H(17D)-C(17')-H(17E) | 104(2) |
| C(3')-C(17')-H(17F) | 113.2(17) |
| H(17D)-C(17')-H(17F) | 106(2) |
| H(17E)-C(17')-H(17F) | 108(2) |
| O(2')-C(18')-H(18D) | 107.0(19) |
| O(2')-C(18')-H(18E) | 107(2) |
| H(18D)-C(18')-H(18E) | 104(3) |
| O(2')-C(18')-H(18F) | 105.5(18) |
| H(18D)-C(18')-H(18F) | 110(3) |
| H(18E)-C(18')-H(18F) | 123(3) |

| | |
|---|---|
| O(3')-C(19')-H(19D) | 113.0(19) |
| O(3')-C(19')-H(19E) | 105(2) |
| H(19D)-C(19')-H(19E) | 111(3) |
| O(3')-C(19')-H(19F) | 104(2) |
| H(19D)-C(19')-H(19F) | 114(3) |
| H(19E)-C(19')-H(19F) | 109(3) |
| Si(1')-C(20')-H(20D) | 109.5 |
| Si(1')-C(20')-H(20E) | 109.5 |
| H(20D)-C(20')-H(20E) | 109.5 |
| Si(1')-C(20')-H(20F) | 109.5 |
| H(20D)-C(20')-H(20F) | 109.5 |
| H(20E)-C(20')-H(20F) | 109.5 |
| Si(1')-C(21')-H(21D) | 109.5 |
| Si(1')-C(21')-H(21E) | 109.5 |
| H(21D)-C(21')-H(21E) | 109.5 |
| Si(1')-C(21')-H(21F) | 109.5 |
| H(21D)-C(21')-H(21F) | 109.5 |
| H(21E)-C(21')-H(21F) | 109.5 |
| Si(1')-C(22')-H(22D) | 109.5 |
| Si(1')-C(22')-H(22E) | 109.5 |
| H(22D)-C(22')-H(22E) | 109.5 |
| Si(1')-C(22')-H(22F) | 109.5 |
| H(22D)-C(22')-H(22F) | 109.5 |
| H(22E)-C(22')-H(22F) | 109.5 |

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters (Å2x 103)for liu44.  The anisotropic displacement factor exponent takes the form: -2π2[ h2a*2U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Si(1) | 45(1) | 28(1) | 29(1) | 7(1) | -12(1) | -6(1) |
| O(1) | 23(1) | 26(1) | 44(1) | 9(1) | 9(1) | 6(1) |
| O(2) | 36(1) | 34(1) | 47(1) | 11(1) | 19(1) | -1(1) |
| O(3) | 27(1) | 31(1) | 45(1) | 3(1) | 10(1) | 10(1) |
| C(1) | 30(1) | 23(1) | 23(1) | 2(1) | -3(1) | -4(1) |
| C(2) | 26(1) | 25(1) | 24(1) | 2(1) | 4(1) | -6(1) |
| C(3) | 23(1) | 22(1) | 23(1) | 1(1) | 1(1) | 0(1) |
| C(4) | 21(1) | 17(1) | 27(1) | 3(1) | 4(1) | 1(1) |
| C(5) | 22(1) | 17(1) | 26(1) | 2(1) | 2(1) | 5(1) |
| C(6) | 23(1) | 20(1) | 26(1) | 2(1) | -1(1) | 1(1) |
| C(7) | 26(1) | 28(1) | 35(1) | 2(1) | 0(1) | -2(1) |
| C(8) | 28(1) | 28(1) | 41(1) | -5(1) | -11(1) | 1(1) |
| C(9) | 38(1) | 31(1) | 25(1) | -3(1) | -4(1) | 8(1) |
| C(10) | 31(1) | 24(1) | 26(1) | 1(1) | 4(1) | 5(1) |
| C(11) | 27(1) | 20(1) | 22(1) | 0(1) | -3(1) | 2(1) |
| C(12) | 28(1) | 24(1) | 23(1) | 2(1) | -4(1) | -2(1) |
| C(13) | 48(2) | 27(1) | 25(1) | 4(1) | -1(1) | -10(1) |
| C(14) | 68(2) | 16(1) | 31(1) | 3(1) | -6(1) | 1(1) |
| C(15) | 49(2) | 27(1) | 32(1) | -1(1) | -1(1) | 14(1) |
| C(16) | 31(1) | 22(1) | 28(1) | 3(1) | -2(1) | 3(1) |
| C(17) | 31(1) | 24(1) | 29(1) | -3(1) | -1(1) | -4(1) |
| C(18) | 37(2) | 58(2) | 53(2) | 27(2) | 14(2) | -4(2) |
| C(19) | 36(2) | 47(2) | 37(2) | 1(1) | 8(1) | 14(1) |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| C(20) | 55(2) | 105(3) | 32(2) | 20(2) | 2(2) | -16(2) |
| C(21) | 153(4) | 30(2) | 72(2) | 13(2) | -54(2) | -4(2) |
| C(22) | 41(2) | 55(2) | 42(2) | 1(1) | -8(1) | 9(1) |
| Si(1') | 44(1) | 31(1) | 27(1) | 6(1) | -10(1) | -3(1) |
| O(1') | 23(1) | 28(1) | 39(1) | 6(1) | 12(1) | 6(1) |
| O(2') | 40(1) | 32(1) | 45(1) | 6(1) | 19(1) | -8(1) |
| O(3') | 28(1) | 29(1) | 48(1) | 3(1) | 10(1) | 8(1) |
| C(1') | 28(1) | 20(1) | 23(1) | 2(1) | -1(1) | -2(1) |
| C(2') | 24(1) | 24(1) | 22(1) | 2(1) | 1(1) | -2(1) |
| C(3') | 24(1) | 20(1) | 22(1) | 1(1) | 0(1) | -1(1) |
| C(4') | 20(1) | 20(1) | 23(1) | 0(1) | 4(1) | 3(1) |
| C(5') | 21(1) | 14(1) | 26(1) | 0(1) | -1(1) | 1(1) |
| C(6') | 22(1) | 20(1) | 25(1) | 0(1) | 2(1) | 1(1) |
| C(7') | 24(1) | 27(1) | 27(1) | 4(1) | -1(1) | -4(1) |
| C(8') | 32(1) | 26(1) | 38(1) | 6(1) | -12(1) | -6(1) |
| C(9') | 43(2) | 24(1) | 26(1) | 0(1) | -6(1) | -2(1) |
| C(10') | 34(1) | 21(1) | 24(1) | 4(1) | 4(1) | 3(1) |
| C(11') | 28(1) | 19(1) | 25(1) | 0(1) | -2(1) | -3(1) |
| C(12') | 34(1) | 25(1) | 27(1) | 2(1) | 0(1) | -4(1) |
| C(13') | 60(2) | 22(1) | 37(1) | 8(1) | 2(1) | -14(1) |
| C(14') | 70(2) | 21(1) | 40(1) | 2(1) | -5(1) | 2(1) |
| C(15') | 54(2) | 22(1) | 41(1) | 0(1) | -5(1) | 11(1) |
| C(16') | 34(1) | 22(1) | 27(1) | -1(1) | -1(1) | 2(1) |
| C(17') | 31(1) | 29(1) | 26(1) | -5(1) | -1(1) | -4(1) |
| C(18') | 34(2) | 52(2) | 49(2) | 17(2) | 7(1) | -9(1) |
| C(19') | 35(2) | 47(2) | 43(2) | -1(2) | 7(1) | 20(1) |
| C(20') | 50(2) | 101(3) | 37(2) | 23(2) | -2(2) | -11(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(21') | 150(4) | 33(2) | 65(2) | 11(2) | -53(2) | 2(2) |
| C(22') | 40(2) | 59(2) | 40(1) | -4(1) | -9(1) | 6(1) |

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Hydrogen coordinates ( x 104) and isotropic displacement parameters (Å2x 103) for liu44.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(20A) | -589 | 3834 | 626 | 96 |
| H(20B) | -304 | 2245 | 819 | 96 |
| H(20C) | -1220 | 2361 | 525 | 96 |
| H(21A) | 547 | -252 | 319 | 127 |
| H(21B) | 785 | 27 | -135 | 127 |
| H(21C) | -333 | -121 | 9 | 127 |
| H(22A) | 1525 | 4101 | 324 | 69 |
| H(22B) | 1980 | 2777 | 61 | 69 |
| H(22C) | 1773 | 2501 | 517 | 69 |
| H(20D) | -6304 | 7623 | -9240 | 93 |
| H(20E) | -7222 | 7771 | -9532 | 93 |
| H(20F) | -6930 | 6159 | -9355 | 93 |
| H(21D) | -7227 | 10045 | -8726 | 124 |
| H(21E) | -8328 | 9833 | -8568 | 124 |
| H(21F) | -8135 | 10142 | -9024 | 124 |
| H(22D) | -9488 | 7029 | -8769 | 70 |
| H(22E) | -9015 | 5768 | -9047 | 70 |
| H(22F) | -9309 | 7379 | -9224 | 70 |
| H(1O) | 1130(20) | 5080(40) | -1065(9) | 53(10) |

| | | | | |
|---|---|---|---|---|
| H(1O') | -8491(19) | 4810(30) | -7606(9) | 41(8) |
| H(1) | 69(18) | 2610(30) | -523(9) | 19(7) |
| H(1') | -7510(20) | 7300(30) | -8179(9) | 26(7) |
| H(2) | -1662(17) | 4020(30) | -163(7) | 28(6) |
| H(2') | -5814(17) | 5900(30) | -8590(7) | 25(6) |
| H(7) | -2870(20) | 2490(30) | -729(9) | 31(8) |
| H(7') | -4620(20) | 7560(30) | -8033(9) | 34(8) |
| H(8) | -2990(20) | 2260(30) | -1412(8) | 36(8) |
| H(8') | -4230(18) | 7720(30) | -7383(7) | 26(6) |
| H(9) | -1850(20) | 3280(30) | -1877(9) | 51(8) |
| H(9') | -5300(20) | 6710(30) | -6906(9) | 48(8) |
| H(10) | -548(19) | 4620(30) | -1627(8) | 32(7) |
| H(10') | -6712(16) | 5310(20) | -7112(7) | 18(5) |
| H(13) | 1060(20) | 9690(30) | -1373(9) | 45(8) |
| H(13') | -8295(19) | 230(30) | -7300(8) | 35(7) |
| H(14) | -316(19) | 11090(30) | -1141(8) | 41(8) |
| H(14') | -6980(20) | -1150(30) | -7563(9) | 58(9) |
| H(15) | -1540(20) | 9820(40) | -794(8) | 48(8) |
| H(15') | -5800(20) | 90(40) | -7897(8) | 47(8) |
| H(17A) | 720(20) | 6100(30) | -66(8) | 43(8) |
| H(17B) | -290(20) | 6920(40) | -136(8) | 39(7) |
| H(17C) | -180(20) | 5700(40) | 168(11) | 56(9) |
| H(17D) | -7334(18) | 4310(30) | -8898(8) | 34(7) |
| H(17E) | -8170(20) | 3740(30) | -8634(7) | 26(6) |
| H(17F) | -7160(20) | 2960(40) | -8600(9) | 40(7) |
| H(18A) | 2620(30) | 6710(50) | -1577(12) | 82(12) |
| H(18B) | 1900(20) | 7980(30) | -1780(9) | 45(8) |

| | | | | |
|---|---|---|---|---|
| H(18C) | 2460(30) | 8260(40) | -1331(12) | 78(12) |
| H(18D) | -9720(20) | 1450(40) | -7396(11) | 66(10) |
| H(18E) | -9240(20) | 1700(40) | -6978(11) | 61(9) |
| H(18F) | -9990(20) | 2980(30) | -7167(8) | 33(8) |
| H(19A) | -2830(20) | 8330(40) | -645(9) | 49(8) |
| H(19B) | -2119(18) | 8520(30) | -223(8) | 33(7) |
| H(19C) | -2820(20) | 7030(30) | -305(9) | 34(7) |
| H(19D) | -4560(20) | 1650(40) | -8107(9) | 51(9) |
| H(19E) | -5280(30) | 1480(50) | -8486(11) | 74(12) |
| H(19F) | -4610(30) | 2980(50) | -8435(11) | 74(12) |

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Torsion angles [°] for liu44.

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| | |
|---|---|
| C(22)-Si(1)-C(1)-C(3) | -58.7(2) |
| C(20)-Si(1)-C(1)-C(3) | 64.3(3) |
| C(21)-Si(1)-C(1)-C(3) | -175.9(2) |
| C(22)-Si(1)-C(1)-C(2) | -133.4(2) |
| C(20)-Si(1)-C(1)-C(2) | -10.4(3) |
| C(21)-Si(1)-C(1)-C(2) | 109.4(3) |
| C(3)-C(1)-C(2)-C(6) | 97.73(19) |
| Si(1)-C(1)-C(2)-C(6) | -147.78(17) |
| Si(1)-C(1)-C(2)-C(3) | 114.5(2) |
| C(6)-C(2)-C(3)-C(17) | 145.5(2) |
| C(1)-C(2)-C(3)-C(17) | -108.1(2) |
| C(6)-C(2)-C(3)-C(1) | -106.3(2) |
| C(6)-C(2)-C(3)-C(4) | -0.1(2) |
| C(1)-C(2)-C(3)-C(4) | 106.18(19) |
| Si(1)-C(1)-C(3)-C(2) | -113.6(2) |

| | |
|---|---|
| C(2)-C(1)-C(3)-C(17) | 114.5(2) |
| Si(1)-C(1)-C(3)-C(17) | 0.9(3) |
| C(2)-C(1)-C(3)-C(4) | -98.8(2) |
| Si(1)-C(1)-C(3)-C(4) | 147.63(17) |
| C(2)-C(3)-C(4)-O(1) | -118.96(19) |
| C(17)-C(3)-C(4)-O(1) | 93.5(2) |
| C(1)-C(3)-C(4)-O(1) | -53.3(2) |
| C(2)-C(3)-C(4)-C(5) | -2.7(2) |
| C(17)-C(3)-C(4)-C(5) | -150.3(2) |
| C(1)-C(3)-C(4)-C(5) | 62.9(2) |
| C(2)-C(3)-C(4)-C(11) | 116.7(2) |
| C(17)-C(3)-C(4)-C(11) | -30.9(3) |
| C(1)-C(3)-C(4)-C(11) | -177.73(18) |
| O(1)-C(4)-C(5)-C(10) | -62.4(3) |
| C(11)-C(4)-C(5)-C(10) | 63.1(3) |
| C(3)-C(4)-C(5)-C(10) | -174.5(2) |
| O(1)-C(4)-C(5)-C(6) | 117.11(19) |
| C(11)-C(4)-C(5)-C(6) | -117.4(2) |
| C(3)-C(4)-C(5)-C(6) | 5.0(2) |
| C(10)-C(5)-C(6)-C(7) | -2.9(3) |
| C(4)-C(5)-C(6)-C(7) | 177.6(2) |
| C(10)-C(5)-C(6)-C(2) | 174.2(2) |
| C(4)-C(5)-C(6)-C(2) | -5.4(2) |
| C(3)-C(2)-C(6)-C(7) | -180.0(2) |
| C(1)-C(2)-C(6)-C(7) | 116.3(3) |
| C(3)-C(2)-C(6)-C(5) | 3.3(2) |
| C(1)-C(2)-C(6)-C(5) | -60.4(2) |

| | |
|---|---|
| C(5)-C(6)-C(7)-C(8) | 2.1(4) |
| C(2)-C(6)-C(7)-C(8) | -174.3(2) |
| C(6)-C(7)-C(8)-C(9) | 0.2(4) |
| C(7)-C(8)-C(9)-C(10) | -1.9(4) |
| C(6)-C(5)-C(10)-C(9) | 1.2(3) |
| C(4)-C(5)-C(10)-C(9) | -179.3(2) |
| C(8)-C(9)-C(10)-C(5) | 1.2(4) |
| O(1)-C(4)-C(11)-C(12) | 13.3(3) |
| C(5)-C(4)-C(11)-C(12) | -111.1(2) |
| C(3)-C(4)-C(11)-C(12) | 133.6(2) |
| O(1)-C(4)-C(11)-C(16) | -170.4(2) |
| C(5)-C(4)-C(11)-C(16) | 65.2(2) |
| C(3)-C(4)-C(11)-C(16) | -50.0(3) |
| C(18)-O(2)-C(12)-C(13) | 7.2(4) |
| C(18)-O(2)-C(12)-C(11) | -174.6(3) |
| C(16)-C(11)-C(12)-O(2) | -173.3(2) |
| C(4)-C(11)-C(12)-O(2) | 3.1(3) |
| C(16)-C(11)-C(12)-C(13) | 4.9(3) |
| C(4)-C(11)-C(12)-C(13) | -178.6(2) |
| O(2)-C(12)-C(13)-C(14) | 176.0(2) |
| C(11)-C(12)-C(13)-C(14) | -2.1(4) |
| C(12)-C(13)-C(14)-C(15) | -1.6(4) |
| C(13)-C(14)-C(15)-C(16) | 2.1(4) |
| C(19)-O(3)-C(16)-C(15) | -11.8(3) |
| C(19)-O(3)-C(16)-C(11) | 168.6(2) |
| C(14)-C(15)-C(16)-O(3) | -178.6(2) |
| C(14)-C(15)-C(16)-C(11) | 1.0(4) |

| | |
|---|---|
| C(12)-C(11)-C(16)-O(3) | 175.2(2) |
| C(4)-C(11)-C(16)-O(3) | -1.4(3) |
| C(12)-C(11)-C(16)-C(15) | -4.4(3) |
| C(4)-C(11)-C(16)-C(15) | 179.0(2) |
| C(20')-Si(1')-C(1')-C(3') | -66.3(3) |
| C(21')-Si(1')-C(1')-C(3') | 174.7(2) |
| C(22')-Si(1')-C(1')-C(3') | 57.0(2) |
| C(20')-Si(1')-C(1')-C(2') | 7.8(2) |
| C(21')-Si(1')-C(1')-C(2') | -111.3(2) |
| C(22')-Si(1')-C(1')-C(2') | 131.05(19) |
| C(3')-C(1')-C(2')-C(6') | -97.6(2) |
| Si(1')-C(1')-C(2')-C(6') | 146.57(17) |
| Si(1')-C(1')-C(2')-C(3') | -115.8(2) |
| C(6')-C(2')-C(3')-C(17') | -146.1(2) |
| C(1')-C(2')-C(3')-C(17') | 107.2(2) |
| C(6')-C(2')-C(3')-C(1') | 106.67(19) |
| C(6')-C(2')-C(3')-C(4') | 0.5(2) |
| C(1')-C(2')-C(3')-C(4') | -106.22(18) |
| Si(1')-C(1')-C(3')-C(2') | 111.9(2) |
| C(2')-C(1')-C(3')-C(17') | -114.1(2) |
| Si(1')-C(1')-C(3')-C(17') | -2.2(3) |
| C(2')-C(1')-C(3')-C(4') | 99.30(19) |
| Si(1')-C(1')-C(3')-C(4') | -148.78(17) |
| C(2')-C(3')-C(4')-O(1') | 117.70(18) |
| C(17')-C(3')-C(4')-O(1') | -94.4(2) |
| C(1')-C(3')-C(4')-O(1') | 51.8(2) |
| C(2')-C(3')-C(4')-C(5') | 2.0(2) |

| | |
|---|---|
| C(17')-C(3')-C(4')-C(5') | 149.8(2) |
| C(1')-C(3')-C(4')-C(5') | -63.9(2) |
| C(2')-C(3')-C(4')-C(11') | -117.6(2) |
| C(17')-C(3')-C(4')-C(11') | 30.3(3) |
| C(1')-C(3')-C(4')-C(11') | 176.55(17) |
| O(1')-C(4')-C(5')-C(10') | 62.3(3) |
| C(11')-C(4')-C(5')-C(10') | -62.7(3) |
| C(3')-C(4')-C(5')-C(10') | 174.8(2) |
| O(1')-C(4')-C(5')-C(6') | -116.46(19) |
| C(11')-C(4')-C(5')-C(6') | 118.49(19) |
| C(3')-C(4')-C(5')-C(6') | -4.0(2) |
| C(10')-C(5')-C(6')-C(7') | 2.9(3) |
| C(4')-C(5')-C(6')-C(7') | -178.2(2) |
| C(10')-C(5')-C(6')-C(2') | -174.4(2) |
| C(4')-C(5')-C(6')-C(2') | 4.5(2) |
| C(3')-C(2')-C(6')-C(7') | -179.9(2) |
| C(1')-C(2')-C(6')-C(7') | -115.6(3) |
| C(3')-C(2')-C(6')-C(5') | -3.0(2) |
| C(1')-C(2')-C(6')-C(5') | 61.2(2) |
| C(5')-C(6')-C(7')-C(8') | -1.7(4) |
| C(2')-C(6')-C(7')-C(8') | 174.9(2) |
| C(6')-C(7')-C(8')-C(9') | -0.4(4) |
| C(7')-C(8')-C(9')-C(10') | 1.6(4) |
| C(6')-C(5')-C(10')-C(9') | -1.7(3) |
| C(4')-C(5')-C(10')-C(9') | 179.6(2) |
| C(8')-C(9')-C(10')-C(5') | -0.5(4) |
| O(1')-C(4')-C(11')-C(12') | -10.9(3) |

| | |
|---|---|
| C(5')-C(4')-C(11')-C(12') | 113.0(2) |
| C(3')-C(4')-C(11')-C(12') | -132.2(2) |
| O(1')-C(4')-C(11')-C(16') | 172.72(19) |
| C(5')-C(4')-C(11')-C(16') | -63.4(2) |
| C(3')-C(4')-C(11')-C(16') | 51.5(3) |
| C(18')-O(2')-C(12')-C(13') | -14.5(4) |
| C(18')-O(2')-C(12')-C(11') | 166.7(3) |
| C(16')-C(11')-C(12')-C(13') | -5.2(4) |
| C(4')-C(11')-C(12')-C(13') | 178.4(2) |
| C(16')-C(11')-C(12')-O(2') | 173.5(2) |
| C(4')-C(11')-C(12')-O(2') | -2.9(3) |
| O(2')-C(12')-C(13')-C(14') | -175.5(2) |
| C(11')-C(12')-C(13')-C(14') | 3.2(4) |
| C(12')-C(13')-C(14')-C(15') | 0.2(4) |
| C(13')-C(14')-C(15')-C(16') | -1.2(4) |
| C(19')-O(3')-C(16')-C(15') | 7.9(4) |
| C(19')-O(3')-C(16')-C(11') | -172.6(2) |
| C(14')-C(15')-C(16')-O(3') | 178.3(2) |
| C(14')-C(15')-C(16')-C(11') | -1.1(4) |
| C(12')-C(11')-C(16')-O(3') | -175.4(2) |
| C(4')-C(11')-C(16')-O(3') | 1.4(3) |
| C(12')-C(11')-C(16')-C(15') | 4.1(3) |
| C(4')-C(11')-C(16')-C(15') | -179.2(2) |

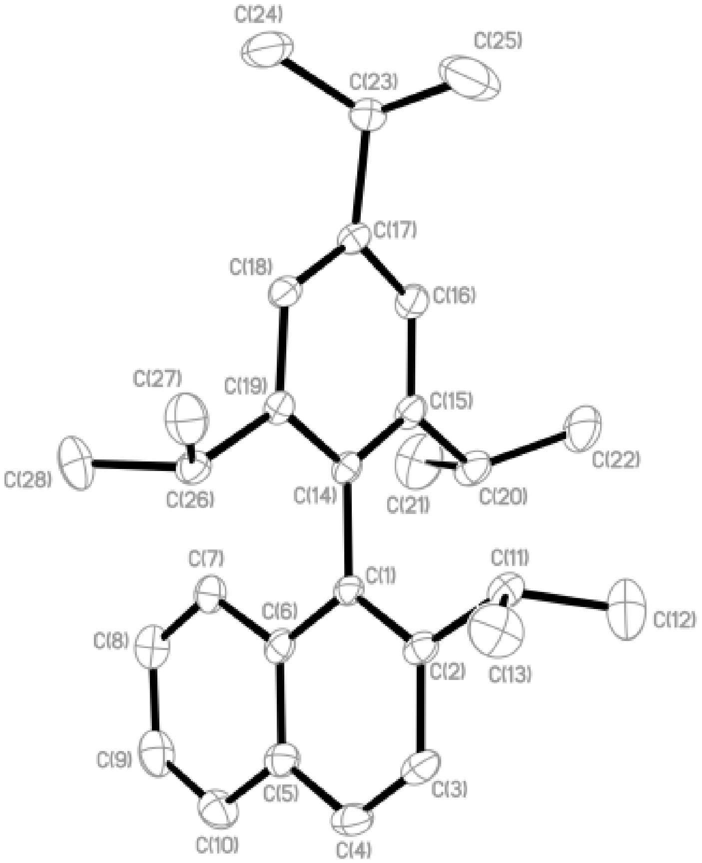
Symmetry transformations used to generate equivalent atoms:

Hydrogen bonds for liu44 [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(1)-H(1O)...O(2) | 0.75(3) | 1.83(3) | 2.537(2) | 156(3) |
| O(1')-H(1O')...O(2') | 0.82(3) | 1.78(3) | 2.546(2) | 155(3) |

Symmetry transformations used to generate equivalent atoms:

### ***Crystal Structure Information for Compound 7d, Chapter III***



Crystal data and structure refinement for liu66 **(7d)**.

| | | |
|---|---|---|
| Identification code | liu66 | |
| Empirical formula | C28 H36 | |
| Formula weight | 372.57 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/n | |
| Unit cell dimensions | a = 16.297(4) Å | a= 90°. |
| | b = 9.649(2) Å | b= 95.118(4)°. |
| | c = 29.806(7) Å | g = 90°. |
| Volume | 4668(2) Å3 | |
| Z | 8 | |
| Density (calculated) | 1.060 Mg/m3 | |
| Absorption coefficient | 0.059 mm-1 | |
| F(000) | 1632 | |
| Crystal size | 0.45 x 0.41 x 0.02 mm3 | |
| Theta range for data collection | 1.37 to 24.00°. | |
| Index ranges | -18<=h<=18, -11<=k<=11, -34<=l<=34 | |
| Reflections collected | 38119 | |
| Independent reflections | 7311 [R(int) = 0.0934] | |
| Completeness to theta = 24.00° | 100.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9988 and 0.9739 | |
| Refinement method | Full-matrix least-squares on F2 | |
| Data / restraints / parameters | 7311 / 0 / 511 | |
| Goodness-of-fit on F2 | 1.004 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0687, wR2 = 0.1617 | |

R indices (all data)  R1 = 0.1209, wR2 = 0.2024

Largest diff. peak and hole  0.343 and -0.218 e.Å-3

Atomic coordinates ( x 104) and equivalent isotropic displacement parameters (Å2x 103) for liu66. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | -1087(2) | 354(3) | 8038(1) | 25(1) |
| C(2) | -752(2) | -653(3) | 8330(1) | 29(1) |
| C(3) | -1290(2) | -1553(3) | 8545(1) | 35(1) |
| C(4) | -2121(2) | -1460(3) | 8467(1) | 39(1) |
| C(5) | -2488(2) | -457(3) | 8165(1) | 34(1) |
| C(6) | -1958(2) | 474(3) | 7952(1) | 29(1) |
| C(7) | -2342(2) | 1496(3) | 7659(1) | 34(1) |
| C(8) | -3180(2) | 1574(4) | 7576(1) | 44(1) |
| C(9) | -3693(2) | 632(4) | 7780(1) | 49(1) |
| C(10) | -3353(2) | -353(4) | 8069(1) | 45(1) |
| C(11) | 169(2) | -853(3) | 8432(1) | 32(1) |
| C(12) | 450(3) | -2228(4) | 8244(2) | 63(1) |
| C(13) | 435(2) | -744(5) | 8936(1) | 55(1) |
| C(14) | -533(2) | 1328(3) | 7809(1) | 26(1) |
| C(15) | -272(2) | 1008(3) | 7383(1) | 30(1) |
| C(16) | 288(2) | 1894(3) | 7198(1) | 34(1) |
| C(17) | 610(2) | 3067(3) | 7419(1) | 31(1) |
| C(18) | 320(2) | 3394(3) | 7830(1) | 31(1) |
| C(19) | -248(2) | 2563(3) | 8027(1) | 26(1) |
| C(20) | -593(2) | -259(3) | 7117(1) | 40(1) |

| | | | | |
|---|---|---|---|---|
| C(21) | -1245(3) | 158(5) | 6740(2) | 72(1) |
| C(22) | 86(3) | -1098(4) | 6924(2) | 63(1) |
| C(23) | 1277(2) | 3905(3) | 7214(1) | 37(1) |
| C(24) | 1286(3) | 5420(4) | 7337(2) | 66(1) |
| C(25) | 2112(3) | 3249(6) | 7337(2) | 95(2) |
| C(26) | -566(2) | 3015(3) | 8470(1) | 32(1) |
| C(27) | 110(2) | 3538(4) | 8816(1) | 45(1) |
| C(28) | -1235(2) | 4124(4) | 8390(1) | 48(1) |
| C(1') | 7237(2) | -1597(3) | -88(1) | 27(1) |
| C(2') | 6573(2) | -2352(3) | -279(1) | 32(1) |
| C(3') | 6724(2) | -3618(3) | -500(1) | 39(1) |
| C(4') | 7490(2) | -4110(3) | -530(1) | 39(1) |
| C(5') | 8187(2) | -3387(3) | -337(1) | 31(1) |
| C(6') | 8060(2) | -2104(3) | -113(1) | 27(1) |
| C(7') | 8766(2) | -1385(3) | 77(1) | 33(1) |
| C(8') | 9543(2) | -1893(4) | 48(1) | 41(1) |
| C(9') | 9658(2) | -3164(4) | -169(1) | 47(1) |
| C(10') | 8998(2) | -3881(4) | -354(1) | 42(1) |
| C(11') | 5686(2) | -1864(4) | -271(1) | 45(1) |
| C(12') | 5169(2) | -2931(4) | -41(2) | 60(1) |
| C(13') | 5302(2) | -1555(4) | -751(2) | 65(1) |
| C(14') | 7144(2) | -226(3) | 146(1) | 27(1) |
| C(15') | 7181(2) | 1020(3) | -104(1) | 30(1) |
| C(16') | 7197(2) | 2274(2) | 130(1) | 39(1) |
| C(18') | 7109(2) | 1123(2) | 828(1) | 39(1) |
| C(19') | 7092(2) | -166(3) | 613(1) | 30(1) |
| C(20') | 7222(2) | 1014(3) | -612(1) | 35(1) |

| | | | | |
|---|---|---|---|---|
| C(21') | 8076(2) | 1464(4) | -733(1) | 53(1) |
| C(22') | 6547(3) | 1909(4) | -857(1) | 54(1) |
| C(17') | 7174(2) | 2351(3) | 592(1) | 40(1) |
| C(23') | 7235(3) | 3753(4) | 829(2) | 76(2) |
| C(25') | 6517(5) | 4477(10) | 860(5) | 79(4) |
| C(17A) | 7174(2) | 2351(3) | 592(1) | 40(1) |
| C(23A) | 7235(3) | 3753(4) | 829(2) | 76(2) |
| C(25A) | 6799(8) | 3965(10) | 1198(4) | 79(4) |
| C(24') | 8022(3) | 4483(4) | 775(2) | 61(1) |
| C(26') | 7019(2) | -1463(3) | 897(1) | 39(1) |
| C(27') | 7715(3) | -1591(4) | 1278(1) | 57(1) |
| C(28') | 6181(2) | -1537(4) | 1095(1) | 52(1) |

Bond lengths [Å] and angles [°] for liu66.

| | |
|---|---|
| C(1)-C(2) | 1.384(4) |
| C(1)-C(6) | 1.425(4) |
| C(1)-C(14) | 1.508(4) |
| C(2)-C(3) | 1.425(4) |
| C(2)-C(11) | 1.517(5) |
| C(3)-C(4) | 1.356(5) |
| C(3)-H(3A) | 0.9500 |
| C(4)-C(5) | 1.417(5) |
| C(4)-H(4A) | 0.9500 |
| C(5)-C(10) | 1.416(5) |
| C(5)-C(6) | 1.432(5) |
| C(6)-C(7) | 1.426(5) |
| C(7)-C(8) | 1.368(5) |

| | |
|---|---|
| C(7)-H(7A) | 0.9500 |
| C(8)-C(9) | 1.409(5) |
| C(8)-H(8A) | 0.9500 |
| C(9)-C(10) | 1.365(5) |
| C(9)-H(9A) | 0.9500 |
| C(10)-H(10A) | 0.9500 |
| C(11)-C(12) | 1.526(5) |
| C(11)-C(13) | 1.530(5) |
| C(11)-H(11A) | 1.0000 |
| C(12)-H(12A) | 0.9800 |
| C(12)-H(12B) | 0.9800 |
| C(12)-H(12C) | 0.9800 |
| C(13)-H(13A) | 0.9800 |
| C(13)-H(13B) | 0.9800 |
| C(13)-H(13C) | 0.9800 |
| C(14)-C(15) | 1.408(4) |
| C(14)-C(19) | 1.416(4) |
| C(15)-C(16) | 1.398(4) |
| C(15)-C(20) | 1.524(4) |
| C(16)-C(17) | 1.389(4) |
| C(16)-H(16A) | 0.9500 |
| C(17)-C(18) | 1.388(4) |
| C(17)-C(23) | 1.526(4) |
| C(18)-C(19) | 1.393(4) |
| C(18)-H(18A) | 0.9500 |
| C(19)-C(26) | 1.525(4) |
| C(20)-C(22) | 1.524(5) |

| | |
|---|---|
| C(20)-C(21) | 1.530(6) |
| C(20)-H(20A) | 1.0000 |
| C(21)-H(21A) | 0.9800 |
| C(21)-H(21B) | 0.9800 |
| C(21)-H(21C) | 0.9800 |
| C(22)-H(22A) | 0.9800 |
| C(22)-H(22B) | 0.9800 |
| C(22)-H(22C) | 0.9800 |
| C(23)-C(24) | 1.506(5) |
| C(23)-C(25) | 1.517(5) |
| C(23)-H(23A) | 1.0000 |
| C(24)-H(24A) | 0.9800 |
| C(24)-H(24B) | 0.9800 |
| C(24)-H(24C) | 0.9800 |
| C(25)-H(25A) | 0.9800 |
| C(25)-H(25B) | 0.9800 |
| C(25)-H(25C) | 0.9800 |
| C(26)-C(27) | 1.526(5) |
| C(26)-C(28) | 1.531(5) |
| C(26)-H(26A) | 1.0000 |
| C(27)-H(27A) | 0.9800 |
| C(27)-H(27B) | 0.9800 |
| C(27)-H(27C) | 0.9800 |
| C(28)-H(28A) | 0.9800 |
| C(28)-H(28B) | 0.9800 |
| C(28)-H(28C) | 0.9800 |
| C(1')-C(2') | 1.384(4) |

| | |
|---|---|
| C(1')-C(6') | 1.437(4) |
| C(1')-C(14') | 1.510(4) |
| C(2')-C(3') | 1.421(4) |
| C(2')-C(11') | 1.522(5) |
| C(3')-C(4') | 1.345(5) |
| C(3')-H(3'A) | 0.9500 |
| C(4')-C(5') | 1.410(5) |
| C(4')-H(4'A) | 0.9500 |
| C(5')-C(10') | 1.411(5) |
| C(5')-C(6') | 1.431(4) |
| C(6')-C(7') | 1.416(4) |
| C(7')-C(8') | 1.367(4) |
| C(7')-H(7'A) | 0.9500 |
| C(8')-C(9') | 1.407(5) |
| C(8')-H(8'A) | 0.9500 |
| C(9')-C(10') | 1.354(5) |
| C(9')-H(9'A) | 0.9500 |
| C(10')-H(10B) | 0.9500 |
| C(11')-C(12') | 1.529(5) |
| C(11')-C(13') | 1.539(6) |
| C(11')-H(11B) | 1.0000 |
| C(12')-H(12D) | 0.9800 |
| C(12')-H(12E) | 0.9800 |
| C(12')-H(12F) | 0.9800 |
| C(13')-H(13D) | 0.9800 |
| C(13')-H(13E) | 0.9800 |
| C(13')-H(13F) | 0.9800 |

| | |
|---|---|
| C(14')-C(19') | 1.402(5) |
| C(14')-C(15') | 1.419(4) |
| C(15')-C(16') | 1.396(4) |
| C(15')-C(20') | 1.520(5) |
| C(16')-C(17') | 1.384(4) |
| C(16')-H(16B) | 0.9500 |
| C(18')-C(17') | 1.387(4) |
| C(18')-C(19') | 1.399(4) |
| C(18')-H(18B) | 0.9500 |
| C(19')-C(26') | 1.521(5) |
| C(20')-C(21') | 1.531(5) |
| C(20')-C(22') | 1.532(5) |
| C(20')-H(20B) | 1.0000 |
| C(21')-H(21D) | 0.9800 |
| C(21')-H(21E) | 0.9800 |
| C(21')-H(21F) | 0.9800 |
| C(22')-H(22D) | 0.9800 |
| C(22')-H(22E) | 0.9800 |
| C(22')-H(22F) | 0.9800 |
| C(17')-C(23') | 1.526(5) |
| C(23')-C(25') | 1.373(9) |
| C(23')-C(24') | 1.484(5) |
| C(23')-H(23B) | 1.0000 |
| C(25')-H(25D) | 0.9800 |
| C(25')-H(25E) | 0.9800 |
| C(25')-H(25F) | 0.9800 |
| C(25A)-H(25G) | 0.9800 |

| | |
|---|---|
| C(25A)-H(25H) | 0.9800 |
| C(25A)-H(25I) | 0.9800 |
| C(24')-H(24D) | 0.9800 |
| C(24')-H(24E) | 0.9800 |
| C(24')-H(24F) | 0.9800 |
| C(26')-C(27') | 1.536(5) |
| C(26')-C(28') | 1.537(5) |
| C(26')-H(26B) | 1.0000 |
| C(27')-H(27D) | 0.9800 |
| C(27')-H(27E) | 0.9800 |
| C(27')-H(27F) | 0.9800 |
| C(28')-H(28D) | 0.9800 |
| C(28')-H(28E) | 0.9800 |
| C(28')-H(28F) | 0.9800 |
| C(2)-C(1)-C(6) | 120.0(3) |
| C(2)-C(1)-C(14) | 120.3(3) |
| C(6)-C(1)-C(14) | 119.7(3) |
| C(1)-C(2)-C(3) | 119.1(3) |
| C(1)-C(2)-C(11) | 122.9(3) |
| C(3)-C(2)-C(11) | 118.0(3) |
| C(4)-C(3)-C(2) | 121.8(3) |
| C(4)-C(3)-H(3A) | 119.1 |
| C(2)-C(3)-H(3A) | 119.1 |
| C(3)-C(4)-C(5) | 120.8(3) |
| C(3)-C(4)-H(4A) | 119.6 |
| C(5)-C(4)-H(4A) | 119.6 |
| C(10)-C(5)-C(4) | 122.2(3) |

| | |
|---|---|
| C(10)-C(5)-C(6) | 119.6(3) |
| C(4)-C(5)-C(6) | 118.2(3) |
| C(1)-C(6)-C(7) | 122.8(3) |
| C(1)-C(6)-C(5) | 120.0(3) |
| C(7)-C(6)-C(5) | 117.2(3) |
| C(8)-C(7)-C(6) | 121.6(3) |
| C(8)-C(7)-H(7A) | 119.2 |
| C(6)-C(7)-H(7A) | 119.2 |
| C(7)-C(8)-C(9) | 120.6(4) |
| C(7)-C(8)-H(8A) | 119.7 |
| C(9)-C(8)-H(8A) | 119.7 |
| C(10)-C(9)-C(8) | 119.8(3) |
| C(10)-C(9)-H(9A) | 120.1 |
| C(8)-C(9)-H(9A) | 120.1 |
| C(9)-C(10)-C(5) | 121.2(4) |
| C(9)-C(10)-H(10A) | 119.4 |
| C(5)-C(10)-H(10A) | 119.4 |
| C(2)-C(11)-C(12) | 111.1(3) |
| C(2)-C(11)-C(13) | 112.1(3) |
| C(12)-C(11)-C(13) | 110.7(3) |
| C(2)-C(11)-H(11A) | 107.6 |
| C(12)-C(11)-H(11A) | 107.6 |
| C(13)-C(11)-H(11A) | 107.6 |
| C(11)-C(12)-H(12A) | 109.5 |
| C(11)-C(12)-H(12B) | 109.5 |
| H(12A)-C(12)-H(12B) | 109.5 |
| C(11)-C(12)-H(12C) | 109.5 |

| | |
|---|---|
| H(12A)-C(12)-H(12C) | 109.5 |
| H(12B)-C(12)-H(12C) | 109.5 |
| C(11)-C(13)-H(13A) | 109.5 |
| C(11)-C(13)-H(13B) | 109.5 |
| H(13A)-C(13)-H(13B) | 109.5 |
| C(11)-C(13)-H(13C) | 109.5 |
| H(13A)-C(13)-H(13C) | 109.5 |
| H(13B)-C(13)-H(13C) | 109.5 |
| C(15)-C(14)-C(19) | 119.0(3) |
| C(15)-C(14)-C(1) | 120.9(3) |
| C(19)-C(14)-C(1) | 120.1(3) |
| C(16)-C(15)-C(14) | 118.7(3) |
| C(16)-C(15)-C(20) | 119.4(3) |
| C(14)-C(15)-C(20) | 121.8(3) |
| C(17)-C(16)-C(15) | 122.9(3) |
| C(17)-C(16)-H(16A) | 118.5 |
| C(15)-C(16)-H(16A) | 118.5 |
| C(18)-C(17)-C(16) | 117.4(3) |
| C(18)-C(17)-C(23) | 123.0(3) |
| C(16)-C(17)-C(23) | 119.6(3) |
| C(17)-C(18)-C(19) | 122.1(3) |
| C(17)-C(18)-H(18A) | 119.0 |
| C(19)-C(18)-H(18A) | 119.0 |
| C(18)-C(19)-C(14) | 119.7(3) |
| C(18)-C(19)-C(26) | 119.3(3) |
| C(14)-C(19)-C(26) | 121.0(3) |
| C(15)-C(20)-C(22) | 113.3(3) |

| | |
|---|---|
| C(15)-C(20)-C(21) | 110.8(3) |
| C(22)-C(20)-C(21) | 110.1(3) |
| C(15)-C(20)-H(20A) | 107.5 |
| C(22)-C(20)-H(20A) | 107.5 |
| C(21)-C(20)-H(20A) | 107.5 |
| C(20)-C(21)-H(21A) | 109.5 |
| C(20)-C(21)-H(21B) | 109.5 |
| H(21A)-C(21)-H(21B) | 109.5 |
| C(20)-C(21)-H(21C) | 109.5 |
| H(21A)-C(21)-H(21C) | 109.5 |
| H(21B)-C(21)-H(21C) | 109.5 |
| C(20)-C(22)-H(22A) | 109.5 |
| C(20)-C(22)-H(22B) | 109.5 |
| H(22A)-C(22)-H(22B) | 109.5 |
| C(20)-C(22)-H(22C) | 109.5 |
| H(22A)-C(22)-H(22C) | 109.5 |
| H(22B)-C(22)-H(22C) | 109.5 |
| C(24)-C(23)-C(25) | 111.0(4) |
| C(24)-C(23)-C(17) | 114.1(3) |
| C(25)-C(23)-C(17) | 109.8(3) |
| C(24)-C(23)-H(23A) | 107.2 |
| C(25)-C(23)-H(23A) | 107.2 |
| C(17)-C(23)-H(23A) | 107.2 |
| C(23)-C(24)-H(24A) | 109.5 |
| C(23)-C(24)-H(24B) | 109.5 |
| H(24A)-C(24)-H(24B) | 109.5 |
| C(23)-C(24)-H(24C) | 109.5 |

| | |
|---|---|
| H(24A)-C(24)-H(24C) | 109.5 |
| H(24B)-C(24)-H(24C) | 109.5 |
| C(23)-C(25)-H(25A) | 109.5 |
| C(23)-C(25)-H(25B) | 109.5 |
| H(25A)-C(25)-H(25B) | 109.5 |
| C(23)-C(25)-H(25C) | 109.5 |
| H(25A)-C(25)-H(25C) | 109.5 |
| H(25B)-C(25)-H(25C) | 109.5 |
| C(19)-C(26)-C(27) | 113.5(3) |
| C(19)-C(26)-C(28) | 110.9(3) |
| C(27)-C(26)-C(28) | 109.6(3) |
| C(19)-C(26)-H(26A) | 107.5 |
| C(27)-C(26)-H(26A) | 107.5 |
| C(28)-C(26)-H(26A) | 107.5 |
| C(26)-C(27)-H(27A) | 109.5 |
| C(26)-C(27)-H(27B) | 109.5 |
| H(27A)-C(27)-H(27B) | 109.5 |
| C(26)-C(27)-H(27C) | 109.5 |
| H(27A)-C(27)-H(27C) | 109.5 |
| H(27B)-C(27)-H(27C) | 109.5 |
| C(26)-C(28)-H(28A) | 109.5 |
| C(26)-C(28)-H(28B) | 109.5 |
| H(28A)-C(28)-H(28B) | 109.5 |
| C(26)-C(28)-H(28C) | 109.5 |
| H(28A)-C(28)-H(28C) | 109.5 |
| H(28B)-C(28)-H(28C) | 109.5 |
| C(2')-C(1')-C(6') | 119.9(3) |

| | |
|---|---|
| C(2')-C(1')-C(14') | 123.0(3) |
| C(6')-C(1')-C(14') | 117.1(3) |
| C(1')-C(2')-C(3') | 118.8(3) |
| C(1')-C(2')-C(11') | 122.6(3) |
| C(3')-C(2')-C(11') | 118.6(3) |
| C(4')-C(3')-C(2') | 122.3(3) |
| C(4')-C(3')-H(3'A) | 118.8 |
| C(2')-C(3')-H(3'A) | 118.8 |
| C(3')-C(4')-C(5') | 121.1(3) |
| C(3')-C(4')-H(4'A) | 119.4 |
| C(5')-C(4')-H(4'A) | 119.4 |
| C(4')-C(5')-C(10') | 122.8(3) |
| C(4')-C(5')-C(6') | 118.3(3) |
| C(10')-C(5')-C(6') | 118.9(3) |
| C(7')-C(6')-C(5') | 117.7(3) |
| C(7')-C(6')-C(1') | 122.8(3) |
| C(5')-C(6')-C(1') | 119.5(3) |
| C(8')-C(7')-C(6') | 121.5(3) |
| C(8')-C(7')-H(7'A) | 119.2 |
| C(6')-C(7')-H(7'A) | 119.2 |
| C(7')-C(8')-C(9') | 120.2(4) |
| C(7')-C(8')-H(8'A) | 119.9 |
| C(9')-C(8')-H(8'A) | 119.9 |
| C(10')-C(9')-C(8') | 120.0(3) |
| C(10')-C(9')-H(9'A) | 120.0 |
| C(8')-C(9')-H(9'A) | 120.0 |
| C(9')-C(10')-C(5') | 121.7(3) |

| | |
|---|---|
| C(9')-C(10')-H(10B) | 119.2 |
| C(5')-C(10')-H(10B) | 119.2 |
| C(2')-C(11')-C(12') | 111.2(3) |
| C(2')-C(11')-C(13') | 110.6(3) |
| C(12')-C(11')-C(13') | 110.6(3) |
| C(2')-C(11')-H(11B) | 108.1 |
| C(12')-C(11')-H(11B) | 108.1 |
| C(13')-C(11')-H(11B) | 108.1 |
| C(11')-C(12')-H(12D) | 109.5 |
| C(11')-C(12')-H(12E) | 109.5 |
| H(12D)-C(12')-H(12E) | 109.5 |
| C(11')-C(12')-H(12F) | 109.5 |
| H(12D)-C(12')-H(12F) | 109.5 |
| H(12E)-C(12')-H(12F) | 109.5 |
| C(11')-C(13')-H(13D) | 109.5 |
| C(11')-C(13')-H(13E) | 109.5 |
| H(13D)-C(13')-H(13E) | 109.5 |
| C(11')-C(13')-H(13F) | 109.5 |
| H(13D)-C(13')-H(13F) | 109.5 |
| H(13E)-C(13')-H(13F) | 109.5 |
| C(19')-C(14')-C(15') | 119.7(3) |
| C(19')-C(14')-C(1') | 120.8(3) |
| C(15')-C(14')-C(1') | 119.3(3) |
| C(16')-C(15')-C(14') | 118.1(3) |
| C(16')-C(15')-C(20') | 120.0(3) |
| C(14')-C(15')-C(20') | 121.9(3) |
| C(17')-C(16')-C(15') | 122.8(3) |

| | |
|---|---|
| C(17')-C(16')-H(16B) | 118.6 |
| C(15')-C(16')-H(16B) | 118.6 |
| C(17')-C(18')-C(19') | 121.7(3) |
| C(17')-C(18')-H(18B) | 119.1 |
| C(19')-C(18')-H(18B) | 119.1 |
| C(18')-C(19')-C(14') | 119.4(3) |
| C(18')-C(19')-C(26') | 118.4(3) |
| C(14')-C(19')-C(26') | 122.1(3) |
| C(15')-C(20')-C(21') | 110.9(3) |
| C(15')-C(20')-C(22') | 112.3(3) |
| C(21')-C(20')-C(22') | 110.8(3) |
| C(15')-C(20')-H(20B) | 107.5 |
| C(21')-C(20')-H(20B) | 107.5 |
| C(22')-C(20')-H(20B) | 107.5 |
| C(20')-C(21')-H(21D) | 109.5 |
| C(20')-C(21')-H(21E) | 109.5 |
| H(21D)-C(21')-H(21E) | 109.5 |
| C(20')-C(21')-H(21F) | 109.5 |
| H(21D)-C(21')-H(21F) | 109.5 |
| H(21E)-C(21')-H(21F) | 109.5 |
| C(20')-C(22')-H(22D) | 109.5 |
| C(20')-C(22')-H(22E) | 109.5 |
| H(22D)-C(22')-H(22E) | 109.5 |
| C(20')-C(22')-H(22F) | 109.5 |
| H(22D)-C(22')-H(22F) | 109.5 |
| H(22E)-C(22')-H(22F) | 109.5 |
| C(16')-C(17')-C(18') | 118.1(3) |

| | |
|---|---|
| C(16')-C(17')-C(23') | 120.2(3) |
| C(18')-C(17')-C(23') | 121.8(3) |
| C(25')-C(23')-C(24') | 121.0(5) |
| C(25')-C(23')-C(17') | 117.4(5) |
| C(24')-C(23')-C(17') | 113.1(3) |
| C(25')-C(23')-H(23B) | 99.8 |
| C(24')-C(23')-H(23B) | 99.8 |
| C(17')-C(23')-H(23B) | 99.8 |
| C(23')-C(25')-H(25D) | 109.5 |
| C(23')-C(25')-H(25E) | 109.5 |
| H(25D)-C(25')-H(25E) | 109.5 |
| C(23')-C(25')-H(25F) | 109.5 |
| H(25D)-C(25')-H(25F) | 109.5 |
| H(25E)-C(25')-H(25F) | 109.5 |
| H(25G)-C(25A)-H(25H) | 109.5 |
| H(25G)-C(25A)-H(25I) | 109.5 |
| H(25H)-C(25A)-H(25I) | 109.5 |
| C(23')-C(24')-H(24D) | 109.5 |
| C(23')-C(24')-H(24E) | 109.5 |
| H(24D)-C(24')-H(24E) | 109.5 |
| C(23')-C(24')-H(24F) | 109.5 |
| H(24D)-C(24')-H(24F) | 109.5 |
| H(24E)-C(24')-H(24F) | 109.5 |
| C(19')-C(26')-C(27') | 112.8(3) |
| C(19')-C(26')-C(28') | 111.6(3) |
| C(27')-C(26')-C(28') | 109.6(3) |
| C(19')-C(26')-H(26B) | 107.5 |

| | |
|---|---|
| C(27')-C(26')-H(26B) | 107.5 |
| C(28')-C(26')-H(26B) | 107.5 |
| C(26')-C(27')-H(27D) | 109.5 |
| C(26')-C(27')-H(27E) | 109.5 |
| H(27D)-C(27')-H(27E) | 109.5 |
| C(26')-C(27')-H(27F) | 109.5 |
| H(27D)-C(27')-H(27F) | 109.5 |
| H(27E)-C(27')-H(27F) | 109.5 |
| C(26')-C(28')-H(28D) | 109.5 |
| C(26')-C(28')-H(28E) | 109.5 |
| H(28D)-C(28')-H(28E) | 109.5 |
| C(26')-C(28')-H(28F) | 109.5 |
| H(28D)-C(28')-H(28F) | 109.5 |
| H(28E)-C(28')-H(28F) | 109.5 |

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters (Å2x 103)for liu66. The anisotropic displacement factor exponent takes the form: -2p2[ h2a*2U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| C(1) | 31(2) | 19(2) | 24(2) | -3(1) | 5(1) | -2(1) |
| C(2) | 38(2) | 23(2) | 25(2) | -3(1) | 2(2) | -4(2) |
| C(3) | 49(2) | 25(2) | 31(2) | 5(2) | 2(2) | -3(2) |
| C(4) | 46(2) | 33(2) | 38(2) | 0(2) | 9(2) | -13(2) |
| C(5) | 40(2) | 29(2) | 32(2) | -5(2) | 4(2) | -5(2) |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| C(6) | 37(2) | 22(2) | 27(2) | -6(1) | 1(2) | -1(2) |
| C(7) | 37(2) | 31(2) | 33(2) | -5(2) | 0(2) | 3(2) |
| C(8) | 47(2) | 42(2) | 42(2) | -5(2) | -3(2) | 8(2) |
| C(9) | 33(2) | 53(2) | 58(3) | -15(2) | -6(2) | 5(2) |
| C(10) | 33(2) | 47(2) | 54(3) | -12(2) | 6(2) | -11(2) |
| C(11) | 36(2) | 27(2) | 33(2) | 5(2) | 0(2) | 1(2) |
| C(12) | 54(3) | 56(3) | 76(3) | -15(2) | -5(2) | 17(2) |
| C(13) | 47(2) | 71(3) | 45(2) | 4(2) | -9(2) | 0(2) |
| C(14) | 28(2) | 22(2) | 26(2) | 5(1) | -1(1) | 4(1) |
| C(15) | 42(2) | 23(2) | 26(2) | 2(1) | 3(2) | 2(2) |
| C(16) | 47(2) | 29(2) | 26(2) | 2(2) | 10(2) | 3(2) |
| C(17) | 35(2) | 24(2) | 35(2) | 7(2) | 6(2) | 1(2) |
| C(18) | 37(2) | 22(2) | 33(2) | -1(1) | 9(2) | -3(2) |
| C(19) | 30(2) | 22(2) | 28(2) | 0(1) | 2(2) | 2(1) |
| C(20) | 60(2) | 28(2) | 33(2) | -5(2) | 11(2) | -5(2) |
| C(21) | 90(4) | 65(3) | 58(3) | -26(2) | -12(3) | -3(3) |
| C(22) | 88(3) | 35(2) | 69(3) | -15(2) | 25(3) | 4(2) |
| C(23) | 39(2) | 34(2) | 40(2) | 3(2) | 12(2) | -2(2) |
| C(24) | 83(3) | 45(2) | 76(3) | -5(2) | 39(3) | -23(2) |
| C(25) | 46(3) | 109(4) | 135(5) | 64(4) | 31(3) | 10(3) |
| C(26) | 39(2) | 25(2) | 31(2) | -4(2) | 9(2) | -6(2) |
| C(27) | 48(2) | 49(2) | 37(2) | -6(2) | 0(2) | 7(2) |
| C(28) | 45(2) | 58(2) | 42(2) | -19(2) | 4(2) | 13(2) |
| C(1') | 34(2) | 19(2) | 27(2) | 1(1) | 3(2) | 2(1) |
| C(2') | 37(2) | 23(2) | 35(2) | -2(2) | 5(2) | -3(2) |
| C(3') | 53(2) | 24(2) | 39(2) | -3(2) | 1(2) | -9(2) |
| C(4') | 61(3) | 23(2) | 35(2) | -4(2) | 8(2) | 2(2) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C(5') | 46(2) | 24(2) | 24(2) | 2(1) | 9(2) | 6(2) | |
| C(6') | 34(2) | 24(2) | 23(2) | 7(1) | 3(2) | 5(1) | |
| C(7') | 34(2) | 30(2) | 33(2) | -1(2) | 0(2) | 4(2) | |
| C(8') | 37(2) | 47(2) | 39(2) | 2(2) | 0(2) | 6(2) | |
| C(9') | 44(2) | 56(3) | 41(2) | 13(2) | 11(2) | 23(2) | |
| C(10') | 57(3) | 31(2) | 38(2) | 1(2) | 12(2) | 17(2) | |
| C(11') | 30(2) | 37(2) | 66(3) | -9(2) | 0(2) | -4(2) | |
| C(12') | 42(2) | 66(3) | 73(3) | -6(2) | 12(2) | -17(2) | |
| C(13') | 42(2) | 54(3) | 95(4) | 11(2) | -16(2) | -2(2) | |
| C(14') | 24(2) | 21(2) | 35(2) | -3(1) | 5(2) | 2(1) | |
| C(15') | 27(2) | 24(2) | 40(2) | -1(2) | 9(2) | -1(1) | |
| C(16') | 39(2) | 22(2) | 58(3) | -2(2) | 16(2) | -2(2) | |
| C(18') | 37(2) | 42(2) | 40(2) | -15(2) | 10(2) | -2(2) | |
| C(19') | 28(2) | 28(2) | 36(2) | -4(2) | 6(2) | 3(1) | |
| C(20') | 39(2) | 28(2) | 39(2) | 2(2) | 6(2) | -2(2) | |
| C(21') | 61(3) | 52(2) | 48(2) | -1(2) | 19(2) | -13(2) | |
| C(22') | 71(3) | 37(2) | 52(3) | 8(2) | -2(2) | 5(2) | |
| C(17') | 35(2) | 29(2) | 57(3) | -16(2) | 19(2) | -5(2) | |
| C(23') | 74(3) | 45(3) | 116(4) | -47(3) | 49(3) | -24(2) | |
| C(25') | 33(5) | 48(6) | 156(12) | -58(7) | | 10(7) | -3(4) |
| C(17A) | | 35(2) | 29(2) | 57(3) | -16(2) | 19(2) | -5(2) |
| C(23A) | | 74(3) | 45(3) | 116(4) | -47(3) | 49(3) | -24(2) |
| C(25A) | | 122(10) | 45(6) | 78(8) | -34(5) | 56(7) | -20(6) |
| C(24') | 62(3) | 43(2) | 78(3) | -20(2) | 6(2) | -16(2) | |
| C(26') | 52(2) | 33(2) | 32(2) | -3(2) | 9(2) | 5(2) | |
| C(27') | 60(3) | 57(3) | 53(3) | 7(2) | 2(2) | 11(2) | |
| C(28') | 60(3) | 44(2) | 56(3) | 3(2) | 18(2) | -3(2) | |

Hydrogen coordinates ( x 104) and isotropic displacement parameters (Å2x 103) for liu66.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3A) | -1060 | -2236 | 8748 | 42 |
| H(4A) | -2461 | -2075 | 8616 | 46 |
| H(7A) | -2007 | 2140 | 7517 | 41 |
| H(8A) | -3418 | 2268 | 7379 | 53 |
| H(9A) | -4274 | 683 | 7717 | 58 |
| H(10A) | -3702 | -980 | 8207 | 53 |
| H(11A) | 451 | -94 | 8277 | 39 |
| H(12A) | 275 | -2278 | 7921 | 94 |
| H(12B) | 203 | -2996 | 8400 | 94 |
| H(12C) | 1051 | -2293 | 8289 | 94 |
| H(13A) | 252 | 145 | 9050 | 83 |
| H(13B) | 1037 | -804 | 8984 | 83 |
| H(13C) | 188 | -1503 | 9096 | 83 |
| H(16A) | 456 | 1683 | 6909 | 40 |
| H(18A) | 515 | 4211 | 7982 | 37 |
| H(20A) | -866 | -875 | 7329 | 48 |
| H(21A) | -1445 | -671 | 6574 | 108 |
| H(21B) | -1002 | 798 | 6533 | 108 |
| H(21C) | -1706 | 613 | 6870 | 108 |
| H(22A) | 505 | -1347 | 7167 | 94 |
| H(22B) | 339 | -544 | 6698 | 94 |

| | | | | |
|---|---|---|---|---|
| H(22C) | -150 | -1944 | 6784 | 94 |
| H(23A) | 1165 | 3844 | 6879 | 44 |
| H(24A) | 1729 | 5888 | 7194 | 99 |
| H(24B) | 1378 | 5518 | 7665 | 99 |
| H(24C) | 756 | 5839 | 7231 | 99 |
| H(25A) | 2538 | 3789 | 7203 | 143 |
| H(25B) | 2112 | 2298 | 7221 | 143 |
| H(25C) | 2227 | 3236 | 7665 | 143 |
| H(26A) | -824 | 2187 | 8602 | 38 |
| H(27A) | 537 | 2827 | 8867 | 68 |
| H(27B) | -126 | 3740 | 9099 | 68 |
| H(27C) | 353 | 4384 | 8703 | 68 |
| H(28A) | -1667 | 3787 | 8166 | 72 |
| H(28B) | -993 | 4972 | 8278 | 72 |
| H(28C) | -1474 | 4321 | 8673 | 72 |
| H(3'A) 6269 | -4136 | -632 | 46 | |
| H(4'A) 7563 | -4957 | -684 | 47 | |
| H(7'A) 8698 | -531 | 227 | 39 | |
| H(8'A) 10006 | -1385 | 175 | 49 | |
| H(9'A) 10198 | -3519 | -186 | 56 | |
| H(10B) | 9084 | -4739 | -499 | 50 |
| H(11B) | 5689 | -985 | -93 | 54 |
| H(12D) | 5423 | -3117 | 263 | 90 |
| H(12E)5142 | -3792 | -216 | 90 | |
| H(12F)4611 | -2568 | -24 | 90 | |
| H(13D) | 5641 | -871 | -892 | 98 |
| H(13E)4744 | -1186 | -737 | 98 | |

| | | | | |
|---|---|---|---|---|
| H(13F) | 5276 | -2411 | -928 | 98 |
| H(16B) | 7225 | 3112 | -36 | 47 |
| H(18B) | 7076 | 1159 | 1145 | 47 |
| H(20B) | 7133 | 38 | -718 | 42 |
| H(21D) | 8498 | 879 | -573 | 79 |
| H(21E) | 8171 | 2434 | -646 | 79 |
| H(21F) | 8105 | 1368 | -1059 | 79 |
| H(22D) | 6007 | 1606 | -774 | 81 |
| H(22E) | 6567 | 1811 | -1183 | 81 |
| H(22F) | 6635 | 2882 | -772 | 81 |
| H(23B) | 7342 | 3437 | 1149 | 91 |
| H(25D) | 6639 | 5351 | 1020 | 118 |
| H(25E) | 6139 | 3924 | 1025 | 118 |
| H(25F) | 6261 | 4673 | 556 | 118 |
| H(23C) | 6874 | 4294 | 604 | 91 |
| H(25G) | 6901 | 4906 | 1314 | 118 |
| H(25H) | 6975 | 3292 | 1434 | 118 |
| H(25I) | 6209 | 3848 | 1110 | 118 |
| H(24D) | 8026 | 5373 | 934 | 92 |
| H(24E) | 8074 | 4646 | 454 | 92 |
| H(24F) | 8484 | 3914 | 901 | 92 |
| H(26B) | 7058 | -2281 | 694 | 46 |
| H(27D) | 8249 | -1542 | 1151 | 85 |
| H(27E) | 7667 | -2479 | 1432 | 85 |
| H(27F) | 7673 | -831 | 1493 | 85 |
| H(28D) | 5738 | -1449 | 851 | 79 |
| H(28E) | 6140 | -780 | 1311 | 79 |

| | | | | |
|---|---|---|---|---|
| H(28F) | 6131 | -2427 | 1248 | 79 |

Torsion angles [°] for liu66.

| | |
|---|---|
| C(6)-C(1)-C(2)-C(3) | -0.5(4) |
| C(14)-C(1)-C(2)-C(3) | 179.5(3) |
| C(6)-C(1)-C(2)-C(11) | 179.2(3) |
| C(14)-C(1)-C(2)-C(11) | -0.8(4) |
| C(1)-C(2)-C(3)-C(4) | 0.8(5) |
| C(11)-C(2)-C(3)-C(4) | -178.9(3) |
| C(2)-C(3)-C(4)-C(5) | 0.2(5) |
| C(3)-C(4)-C(5)-C(10) | 178.6(3) |
| C(3)-C(4)-C(5)-C(6) | -1.4(5) |
| C(2)-C(1)-C(6)-C(7) | 179.4(3) |
| C(14)-C(1)-C(6)-C(7) | -0.6(4) |
| C(2)-C(1)-C(6)-C(5) | -0.7(4) |
| C(14)-C(1)-C(6)-C(5) | 179.3(3) |
| C(10)-C(5)-C(6)-C(1) | -178.3(3) |
| C(4)-C(5)-C(6)-C(1) | 1.6(4) |
| C(10)-C(5)-C(6)-C(7) | 1.5(4) |
| C(4)-C(5)-C(6)-C(7) | -178.5(3) |
| C(1)-C(6)-C(7)-C(8) | 178.8(3) |
| C(5)-C(6)-C(7)-C(8) | -1.1(5) |
| C(6)-C(7)-C(8)-C(9) | -0.2(5) |
| C(7)-C(8)-C(9)-C(10) | 1.0(5) |
| C(8)-C(9)-C(10)-C(5) | -0.5(5) |
| C(4)-C(5)-C(10)-C(9) | 179.3(3) |
| C(6)-C(5)-C(10)-C(9) | -0.8(5) |

| | |
|---|---|
| C(1)-C(2)-C(11)-C(12) | -112.3(4) |
| C(3)-C(2)-C(11)-C(12) | 67.4(4) |
| C(1)-C(2)-C(11)-C(13) | 123.2(3) |
| C(3)-C(2)-C(11)-C(13) | -57.1(4) |
| C(2)-C(1)-C(14)-C(15) | 91.6(4) |
| C(6)-C(1)-C(14)-C(15) | -88.3(4) |
| C(2)-C(1)-C(14)-C(19) | -86.5(4) |
| C(6)-C(1)-C(14)-C(19) | 93.5(4) |
| C(19)-C(14)-C(15)-C(16) | 2.7(5) |
| C(1)-C(14)-C(15)-C(16) | -175.5(3) |
| C(19)-C(14)-C(15)-C(20) | -176.4(3) |
| C(1)-C(14)-C(15)-C(20) | 5.4(5) |
| C(14)-C(15)-C(16)-C(17) | 1.0(5) |
| C(20)-C(15)-C(16)-C(17) | -179.9(3) |
| C(15)-C(16)-C(17)-C(18) | -3.5(5) |
| C(15)-C(16)-C(17)-C(23) | 174.4(3) |
| C(16)-C(17)-C(18)-C(19) | 2.4(5) |
| C(23)-C(17)-C(18)-C(19) | -175.5(3) |
| C(17)-C(18)-C(19)-C(14) | 1.2(5) |
| C(17)-C(18)-C(19)-C(26) | -177.6(3) |
| C(15)-C(14)-C(19)-C(18) | -3.8(4) |
| C(1)-C(14)-C(19)-C(18) | 174.4(3) |
| C(15)-C(14)-C(19)-C(26) | 175.0(3) |
| C(1)-C(14)-C(19)-C(26) | -6.8(4) |
| C(16)-C(15)-C(20)-C(22) | 47.6(4) |
| C(14)-C(15)-C(20)-C(22) | -133.2(3) |
| C(16)-C(15)-C(20)-C(21) | -76.6(4) |

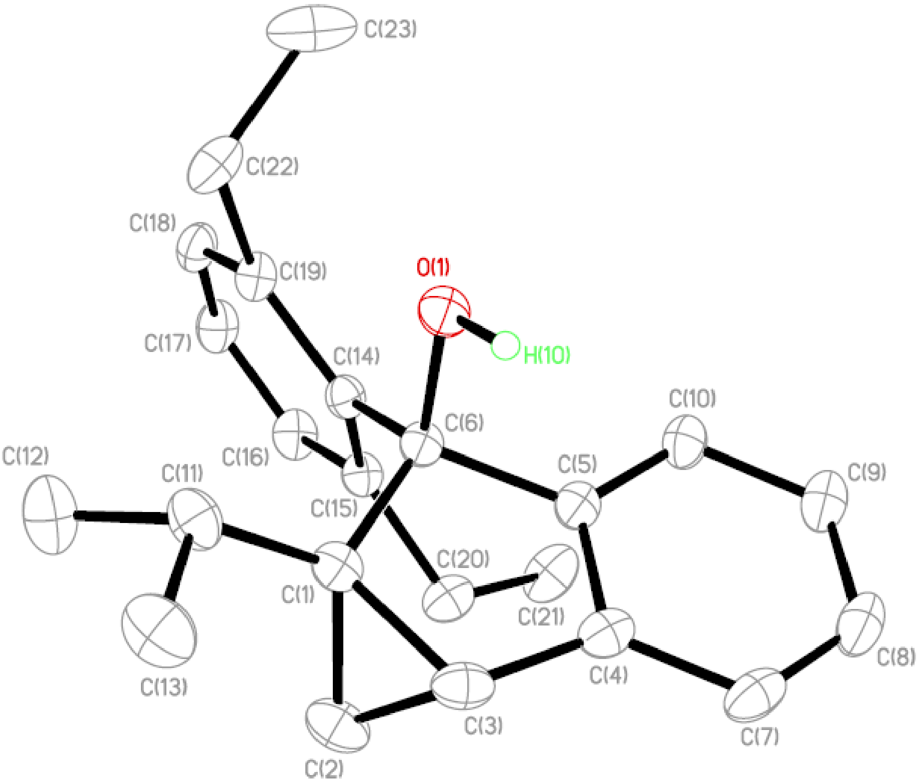
| | |
|---|---|
| C(14)-C(15)-C(20)-C(21) | 102.5(4) |
| C(18)-C(17)-C(23)-C(24) | -30.4(5) |
| C(16)-C(17)-C(23)-C(24) | 151.8(4) |
| C(18)-C(17)-C(23)-C(25) | 94.9(4) |
| C(16)-C(17)-C(23)-C(25) | -83.0(4) |
| C(18)-C(19)-C(26)-C(27) | -44.7(4) |
| C(14)-C(19)-C(26)-C(27) | 136.5(3) |
| C(18)-C(19)-C(26)-C(28) | 79.3(4) |
| C(14)-C(19)-C(26)-C(28) | -99.5(4) |
| C(6')-C(1')-C(2')-C(3') | -0.4(5) |
| C(14')-C(1')-C(2')-C(3') | 178.7(3) |
| C(6')-C(1')-C(2')-C(11') | -179.1(3) |
| C(14')-C(1')-C(2')-C(11') | -0.1(5) |
| C(1')-C(2')-C(3')-C(4') | 0.0(5) |
| C(11')-C(2')-C(3')-C(4') | 178.8(3) |
| C(2')-C(3')-C(4')-C(5') | 0.6(5) |
| C(3')-C(4')-C(5')-C(10') | 178.8(3) |
| C(3')-C(4')-C(5')-C(6') | -0.8(5) |
| C(4')-C(5')-C(6')-C(7') | -179.5(3) |
| C(10')-C(5')-C(6')-C(7') | 0.8(4) |
| C(4')-C(5')-C(6')-C(1') | 0.4(4) |
| C(10')-C(5')-C(6')-C(1') | -179.2(3) |
| C(2')-C(1')-C(6')-C(7') | -179.9(3) |
| C(14')-C(1')-C(6')-C(7') | 1.0(4) |
| C(2')-C(1')-C(6')-C(5') | 0.1(4) |
| C(14')-C(1')-C(6')-C(5') | -178.9(3) |
| C(5')-C(6')-C(7')-C(8') | -0.1(5) |

| | |
|---|---|
| C(1')-C(6')-C(7')-C(8') | 180.0(3) |
| C(6')-C(7')-C(8')-C(9') | -0.7(5) |
| C(7')-C(8')-C(9')-C(10') | 0.7(5) |
| C(8')-C(9')-C(10')-C(5') | 0.1(5) |
| C(4')-C(5')-C(10')-C(9') | 179.5(3) |
| C(6')-C(5')-C(10')-C(9') | -0.8(5) |
| C(1')-C(2')-C(11')-C(12') | -122.0(4) |
| C(3')-C(2')-C(11')-C(12') | 59.3(4) |
| C(1')-C(2')-C(11')-C(13') | 114.7(4) |
| C(3')-C(2')-C(11')-C(13') | -64.0(4) |
| C(2')-C(1')-C(14')-C(19') | 93.1(4) |
| C(6')-C(1')-C(14')-C(19') | -87.9(4) |
| C(2')-C(1')-C(14')-C(15') | -92.4(4) |
| C(6')-C(1')-C(14')-C(15') | 86.6(4) |
| C(19')-C(14')-C(15')-C(16') | 2.4(4) |
| C(1')-C(14')-C(15')-C(16') | -172.1(3) |
| C(19')-C(14')-C(15')-C(20') | -178.9(3) |
| C(1')-C(14')-C(15')-C(20') | 6.5(4) |
| C(14')-C(15')-C(16')-C(17') | -0.4(4) |
| C(20')-C(15')-C(16')-C(17') | -179.0(3) |
| C(17')-C(18')-C(19')-C(14') | 0.1(4) |
| C(17')-C(18')-C(19')-C(26') | -179.9(3) |
| C(15')-C(14')-C(19')-C(18') | -2.3(5) |
| C(1')-C(14')-C(19')-C(18') | 172.1(3) |
| C(15')-C(14')-C(19')-C(26') | 177.7(3) |
| C(1')-C(14')-C(19')-C(26') | -7.8(5) |
| C(16')-C(15')-C(20')-C(21') | 69.5(4) |

| | |
|---|---|
| C(14')-C(15')-C(20')-C(21') | -109.1(4) |
| C(16')-C(15')-C(20')-C(22') | -55.1(4) |
| C(14')-C(15')-C(20')-C(22') | 126.3(3) |
| C(15')-C(16')-C(17')-C(18') | -1.8(5) |
| C(15')-C(16')-C(17')-C(23') | 177.0(3) |
| C(19')-C(18')-C(17')-C(16') | 1.9(5) |
| C(19')-C(18')-C(17')-C(23') | -176.9(3) |
| C(16')-C(17')-C(23')-C(25') | 87.1(8) |
| C(18')-C(17')-C(23')-C(25') | -94.2(8) |
| C(16')-C(17')-C(23')-C(24') | -61.4(6) |
| C(18')-C(17')-C(23')-C(24') | 117.4(4) |
| C(18')-C(19')-C(26')-C(27') | -57.6(4) |
| C(14')-C(19')-C(26')-C(27') | 122.4(3) |
| C(18')-C(19')-C(26')-C(28') | 66.3(4) |
| C(14')-C(19')-C(26')-C(28') | -113.7(4) |

Symmetry transformations used to generate equivalent atoms:

### *Crystallographic Data for 6i (liu 78) Chapter IV*



Crystal data and structure refinement for liu78 **(6i)**.

| | |
|---|---|
| Identification code | liu78 |
| Empirical formula | C23 H28 O |
| Formula weight | 320.45 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Unit cell dimensions | a = 10.227(5) Å α= 90°. |
| | b = 10.182(5) Å β= 105.030(9)°. |
| | c = 18.333(9) Å γ = 90°. |
| Volume | 1843.8(15) Å3 |

| | |
|---|---|
| Z | 4 |
| Density (calculated) | 1.154 Mg/m3 |
| Absorption coefficient | 0.068 mm-1 |
| F(000) | 696 |
| Crystal size | 0.25 x 0.25 x 0.08 mm3 |
| Theta range for data collection | 2.06 to 24.99°. |
| Index ranges | -12<=h<=12, -12<=k<=12, -21<=l<=21 |
| Reflections collected | 16965 |
| Independent reflections | 3235 [R(int) = 0.0845] |
| Completeness to theta = 24.99° | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9946 and 0.9831 |
| Refinement method | Full-matrix least-squares on F2 |
| Data / restraints / parameters | 3235 / 0 / 332 |
| Goodness-of-fit on F2 | 1.034 |
| Final R indices [I>2sigma(I)] | R1 = 0.0561, wR2 = 0.1062 |
| R indices (all data) | R1 = 0.0998, wR2 = 0.1259 |
| Largest diff. peak and hole | 0.152 and -0.172 e.Å-3 |

Atomic coordinates ( x 104) and equivalent isotropic displacement parameters (Å2x 103) for liu78. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 8726(2) | 9181(2) | 9939(1) | 33(1) |
| C(1) | 8956(2) | 8990(2) | 8675(1) | 30(1) |

|  |  |  |  |  |
|---|---|---|---|---|
| C(2) | 8516(3) | 9338(3) | 7850(2) | 43(1) |
| C(3) | 9277(3) | 10351(3) | 8403(1) | 37(1) |
| C(4) | 8406(2) | 11306(2) | 8660(1) | 34(1) |
| C(5) | 7572(2) | 10671(2) | 9036(1) | 29(1) |
| C(6) | 7940(2) | 9225(2) | 9157(1) | 26(1) |
| C(7) | 8334(3) | 12669(3) | 8588(2) | 43(1) |
| C(8) | 7430(3) | 13351(3) | 8885(2) | 46(1) |
| C(9) | 6611(3) | 12720(3) | 9256(2) | 44(1) |
| C(10) | 6675(3) | 11356(2) | 9338(2) | 37(1) |
| C(11) | 10014(3) | 7911(3) | 8907(2) | 39(1) |
| C(12) | 9446(4) | 6582(3) | 8587(2) | 57(1) |
| C(13) | 11323(3) | 8172(4) | 8688(2) | 53(1) |
| C(14) | 6752(2) | 8243(2) | 9037(1) | 27(1) |
| C(15) | 5555(2) | 8417(2) | 8444(1) | 29(1) |
| C(16) | 4533(3) | 7479(3) | 8334(2) | 36(1) |
| C(17) | 4611(3) | 6407(3) | 8791(2) | 38(1) |
| C(18) | 5752(3) | 6241(3) | 9371(2) | 36(1) |
| C(19) | 6839(2) | 7117(2) | 9503(1) | 31(1) |
| C(20) | 5223(3) | 9544(3) | 7881(2) | 37(1) |
| C(21) | 3969(3) | 10316(3) | 7926(2) | 51(1) |
| C(22) | 7995(3) | 6714(3) | 10165(2) | 43(1) |
| C(23) | 7751(4) | 7137(5) | 10914(2) | 67(1) |

Bond lengths [Å] and angles [°] for liu78.

|  |  |
|---|---|
| O(1)-C(6) | 1.451(3) |

|  |  |
|---|---|
| O(1)-H(1O) | 0.93(7) |
| O(1)-H(1OA) | 1.01(7) |
| C(1)-C(2) | 1.503(4) |
| C(1)-C(11) | 1.523(3) |
| C(1)-C(3) | 1.536(4) |
| C(1)-C(6) | 1.549(3) |
| C(2)-C(3) | 1.513(4) |
| C(2)-H(2A) | 1.02(3) |
| C(2)-H(2B) | 1.01(3) |
| C(3)-C(4) | 1.477(4) |
| C(3)-H(3) | 0.99(3) |
| C(4)-C(5) | 1.386(3) |
| C(4)-C(7) | 1.394(4) |
| C(5)-C(10) | 1.377(3) |
| C(5)-C(6) | 1.522(3) |
| C(6)-C(14) | 1.544(3) |
| C(7)-C(8) | 1.376(4) |
| C(7)-H(7) | 0.98(3) |
| C(8)-C(9) | 1.369(4) |
| C(8)-H(8) | 0.93(3) |
| C(9)-C(10) | 1.397(4) |
| C(9)-H(9) | 0.99(3) |
| C(10)-H(10) | 1.00(3) |
| C(11)-C(13) | 1.518(4) |
| C(11)-C(12) | 1.528(4) |

| | |
|---|---|
| C(11)-H(11) | 0.98(2) |
| C(12)-H(12A) | 1.02(3) |
| C(12)-H(12B) | 1.00(3) |
| C(12)-H(12C) | 1.00(3) |
| C(13)-H(13A) | 0.97(3) |
| C(13)-H(13B) | 1.00(3) |
| C(13)-H(13C) | 1.03(3) |
| C(14)-C(19) | 1.419(3) |
| C(14)-C(15) | 1.422(3) |
| C(15)-C(16) | 1.392(3) |
| C(15)-C(20) | 1.521(3) |
| C(16)-C(17) | 1.365(4) |
| C(16)-H(16) | 0.94(2) |
| C(17)-C(18) | 1.371(4) |
| C(17)-H(17) | 1.00(3) |
| C(18)-C(19) | 1.396(3) |
| C(18)-H(18) | 0.97(2) |
| C(19)-C(22) | 1.515(3) |
| C(20)-C(21) | 1.524(4) |
| C(20)-H(20A) | 1.03(3) |
| C(20)-H(20B) | 1.01(2) |
| C(21)-H(21A) | 1.04(3) |
| C(21)-H(21B) | 0.99(3) |
| C(21)-H(21C) | 1.06(3) |
| C(22)-C(23) | 1.520(5) |

| | |
|---|---|
| C(22)-H(22A) | 1.02(3) |
| C(22)-H(22B) | 1.00(2) |
| C(23)-H(23A) | 1.06(4) |
| C(23)-H(23B) | 0.95(4) |
| C(23)-H(23C) | 1.02(3) |
| C(6)-O(1)-H(1O) | 105(5) |
| C(6)-O(1)-H(1OA) | 106(4) |
| H(1O)-O(1)-H(1OA) | 87(5) |
| C(2)-C(1)-C(11) | 117.2(2) |
| C(2)-C(1)-C(3) | 59.69(17) |
| C(11)-C(1)-C(3) | 123.1(2) |
| C(2)-C(1)-C(6) | 117.9(2) |
| C(11)-C(1)-C(6) | 119.0(2) |
| C(3)-C(1)-C(6) | 106.09(19) |
| C(1)-C(2)-C(3) | 61.23(17) |
| C(1)-C(2)-H(2A) | 122.0(14) |
| C(3)-C(2)-H(2A) | 120.5(14) |
| C(1)-C(2)-H(2B) | 114.8(15) |
| C(3)-C(2)-H(2B) | 115.1(15) |
| H(2A)-C(2)-H(2B) | 114(2) |
| C(4)-C(3)-C(2) | 114.5(2) |
| C(4)-C(3)-C(1) | 107.1(2) |
| C(2)-C(3)-C(1) | 59.09(17) |
| C(4)-C(3)-H(3) | 123.0(15) |
| C(2)-C(3)-H(3) | 115.0(14) |

| | |
|---|---|
| C(1)-C(3)-H(3) | 121.6(14) |
| C(5)-C(4)-C(7) | 119.2(3) |
| C(5)-C(4)-C(3) | 110.6(2) |
| C(7)-C(4)-C(3) | 130.3(2) |
| C(10)-C(5)-C(4) | 121.5(2) |
| C(10)-C(5)-C(6) | 126.6(2) |
| C(4)-C(5)-C(6) | 111.3(2) |
| O(1)-C(6)-C(5) | 103.13(17) |
| O(1)-C(6)-C(14) | 109.54(18) |
| C(5)-C(6)-C(14) | 116.76(19) |
| O(1)-C(6)-C(1) | 106.11(18) |
| C(5)-C(6)-C(1) | 104.06(18) |
| C(14)-C(6)-C(1) | 116.01(18) |
| C(8)-C(7)-C(4) | 119.2(3) |
| C(8)-C(7)-H(7) | 123.0(15) |
| C(4)-C(7)-H(7) | 117.8(15) |
| C(9)-C(8)-C(7) | 121.4(3) |
| C(9)-C(8)-H(8) | 120.1(16) |
| C(7)-C(8)-H(8) | 118.6(16) |
| C(8)-C(9)-C(10) | 120.1(3) |
| C(8)-C(9)-H(9) | 122.6(15) |
| C(10)-C(9)-H(9) | 117.3(15) |
| C(5)-C(10)-C(9) | 118.6(3) |
| C(5)-C(10)-H(10) | 121.1(15) |
| C(9)-C(10)-H(10) | 120.3(15) |

| | |
|---|---|
| C(13)-C(11)-C(1) | 114.2(3) |
| C(13)-C(11)-C(12) | 109.1(3) |
| C(1)-C(11)-C(12) | 111.1(2) |
| C(13)-C(11)-H(11) | 107.4(13) |
| C(1)-C(11)-H(11) | 106.5(13) |
| C(12)-C(11)-H(11) | 108.4(13) |
| C(11)-C(12)-H(12A) | 110.3(18) |
| C(11)-C(12)-H(12B) | 110.2(19) |
| H(12A)-C(12)-H(12B) | 108(3) |
| C(11)-C(12)-H(12C) | 112.9(17) |
| H(12A)-C(12)-H(12C) | 108(2) |
| H(12B)-C(12)-H(12C) | 107(3) |
| C(11)-C(13)-H(13A) | 112.4(16) |
| C(11)-C(13)-H(13B) | 111.1(16) |
| H(13A)-C(13)-H(13B) | 108(2) |
| C(11)-C(13)-H(13C) | 110.1(16) |
| H(13A)-C(13)-H(13C) | 107(2) |
| H(13B)-C(13)-H(13C) | 108(2) |
| C(19)-C(14)-C(15) | 117.9(2) |
| C(19)-C(14)-C(6) | 120.9(2) |
| C(15)-C(14)-C(6) | 121.2(2) |
| C(16)-C(15)-C(14) | 119.3(2) |
| C(16)-C(15)-C(20) | 113.1(2) |
| C(14)-C(15)-C(20) | 127.5(2) |
| C(17)-C(16)-C(15) | 122.6(3) |

| | |
|---|---|
| C(17)-C(16)-H(16) | 119.4(14) |
| C(15)-C(16)-H(16) | 118.0(14) |
| C(16)-C(17)-C(18) | 118.5(3) |
| C(16)-C(17)-H(17) | 120.0(14) |
| C(18)-C(17)-H(17) | 121.5(14) |
| C(17)-C(18)-C(19) | 122.3(3) |
| C(17)-C(18)-H(18) | 120.1(15) |
| C(19)-C(18)-H(18) | 117.5(15) |
| C(18)-C(19)-C(14) | 119.3(2) |
| C(18)-C(19)-C(22) | 112.7(2) |
| C(14)-C(19)-C(22) | 127.9(2) |
| C(15)-C(20)-C(21) | 113.3(2) |
| C(15)-C(20)-H(20A) | 109.6(14) |
| C(21)-C(20)-H(20A) | 108.6(14) |
| C(15)-C(20)-H(20B) | 111.0(13) |
| C(21)-C(20)-H(20B) | 109.8(13) |
| H(20A)-C(20)-H(20B) | 104.1(19) |
| C(20)-C(21)-H(21A) | 108.8(16) |
| C(20)-C(21)-H(21B) | 114.9(16) |
| H(21A)-C(21)-H(21B) | 108(2) |
| C(20)-C(21)-H(21C) | 108.1(16) |
| H(21A)-C(21)-H(21C) | 112(2) |
| H(21B)-C(21)-H(21C) | 105(2) |
| C(19)-C(22)-C(23) | 111.7(3) |
| C(19)-C(22)-H(22A) | 108.5(14) |

| | |
|---|---|
| C(23)-C(22)-H(22A) | 110.6(14) |
| C(19)-C(22)-H(22B) | 111.7(13) |
| C(23)-C(22)-H(22B) | 112.3(14) |
| H(22A)-C(22)-H(22B) | 102(2) |
| C(22)-C(23)-H(23A) | 110(2) |
| C(22)-C(23)-H(23B) | 107(2) |
| H(23A)-C(23)-H(23B) | 114(3) |
| C(22)-C(23)-H(23C) | 112.5(17) |
| H(23A)-C(23)-H(23C) | 107(3) |
| H(23B)-C(23)-H(23C) | 107(3) |

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters (Å2x 103)for liu78. The anisotropic displacement factor exponent takes the form: -2π2[ h2a*2U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| O(1) | 31(1) | 36(1) | 28(1) | -3(1) | 0(1) | -2(1) |
| C(1) | 25(1) | 35(2) | 29(1) | -5(1) | 3(1) | -5(1) |
| C(2) | 36(2) | 62(2) | 28(2) | -8(1) | 4(1) | -3(2) |
| C(3) | 32(2) | 48(2) | 29(2) | 3(1) | 6(1) | -8(1) |
| C(4) | 29(1) | 38(2) | 30(1) | 4(1) | -1(1) | -6(1) |
| C(5) | 28(1) | 29(1) | 26(1) | -2(1) | -3(1) | -4(1) |
| C(6) | 24(1) | 27(1) | 24(1) | -2(1) | -1(1) | -2(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(7) | 41(2) | 40(2) | 40(2) | 11(1) | -1(1) | -13(1) |
| C(8) | 51(2) | 28(2) | 52(2) | 4(1) | -1(2) | 0(2) |
| C(9) | 44(2) | 31(2) | 54(2) | -2(1) | 6(2) | 1(1) |
| C(10) | 37(2) | 29(1) | 42(2) | -3(1) | 7(1) | -3(1) |
| C(11) | 32(2) | 44(2) | 41(2) | -9(1) | 9(1) | 1(1) |
| C(12) | 49(2) | 47(2) | 77(3) | -14(2) | 19(2) | 3(2) |
| C(13) | 34(2) | 71(2) | 55(2) | -7(2) | 13(2) | 3(2) |
| C(14) | 26(1) | 26(1) | 29(1) | -4(1) | 7(1) | -2(1) |
| C(15) | 25(1) | 30(1) | 30(1) | -4(1) | 3(1) | -2(1) |
| C(16) | 26(1) | 37(2) | 41(2) | -6(1) | 1(1) | -4(1) |
| C(17) | 31(2) | 31(2) | 51(2) | -6(1) | 10(1) | -7(1) |
| C(18) | 39(2) | 24(1) | 46(2) | 1(1) | 15(1) | -1(1) |
| C(19) | 29(1) | 27(1) | 37(2) | -1(1) | 7(1) | 1(1) |
| C(20) | 29(2) | 41(2) | 36(2) | 7(1) | -1(1) | -3(1) |
| C(21) | 31(2) | 48(2) | 66(2) | 14(2) | 1(2) | 2(2) |
| C(22) | 37(2) | 33(2) | 52(2) | 13(1) | 0(1) | 0(1) |
| C(23) | 55(2) | 102(3) | 38(2) | 24(2) | 3(2) | -17(2) |

Hydrogen coordinates ( x 104) and isotropic displacement parameters (Å2x 103)

for liu78.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1O) | 9360(60) | 9850(80) | 9980(40) | 98(18) |
| H(1OA) | 8230(70) | 9770(70) | 10230(40) | 98(18) |

|  |  |  |  |  |
|---|---|---|---|---|
| H(2A) | 7520(30) | 9480(20) | 7575(14) | 46(7) |
| H(2B) | 9060(30) | 8910(20) | 7527(14) | 53(8) |
| H(3) | 10190(30) | 10570(20) | 8349(13) | 46(7) |
| H(7) | 8940(30) | 13100(20) | 8321(14) | 50(8) |
| H(8) | 7390(30) | 14260(30) | 8831(14) | 52(8) |
| H(9) | 5970(30) | 13200(20) | 9485(14) | 49(8) |
| H(10) | 6090(30) | 10890(20) | 9619(14) | 51(8) |
| H(11) | 10240(20) | 7860(20) | 9461(13) | 28(6) |
| H(12A) | 9300(30) | 6570(30) | 8013(18) | 73(10) |
| H(12B) | 10090(30) | 5870(30) | 8808(18) | 83(11) |
| H(12C) | 8560(30) | 6360(30) | 8702(16) | 72(10) |
| H(13A) | 11770(30) | 8970(30) | 8914(15) | 53(9) |
| H(13B) | 11970(30) | 7430(30) | 8843(15) | 60(9) |
| H(13C) | 11130(30) | 8270(30) | 8114(17) | 64(9) |
| H(16) | 3760(20) | 7600(20) | 7935(13) | 31(7) |
| H(17) | 3850(30) | 5760(30) | 8693(13) | 47(7) |
| H(18) | 5830(20) | 5500(30) | 9706(13) | 41(7) |
| H(20A) | 5080(20) | 9190(20) | 7343(15) | 46(7) |
| H(20B) | 6020(20) | 10160(20) | 7945(12) | 33(6) |
| H(21A) | 3800(30) | 11050(30) | 7524(17) | 70(9) |
| H(21B) | 3130(30) | 9790(30) | 7845(15) | 58(9) |
| H(21C) | 4140(30) | 10690(30) | 8479(18) | 71(10) |
| H(22A) | 8110(20) | 5720(30) | 10150(13) | 52(8) |
| H(22B) | 8890(20) | 7030(20) | 10104(12) | 37(7) |
| H(23A) | 7650(40) | 8170(40) | 10930(20) | 123(17) |

|  |  |  |  |  |
|---|---|---|---|---|
| H(23B) | 8480(40) | 6800(30) | 11300(20) | 98(13) |
| H(23C) | 6880(30) | 6750(30) | 10998(16) | 73(10) |

Torsion angles [°] for liu78.

|  |  |
|---|---|
| C(11)-C(1)-C(2)-C(3) | -114.2(2) |
| C(6)-C(1)-C(2)-C(3) | 93.1(2) |
| C(1)-C(2)-C(3)-C(4) | -95.9(2) |
| C(2)-C(1)-C(3)-C(4) | 108.8(2) |
| C(11)-C(1)-C(3)-C(4) | -146.6(2) |
| C(6)-C(1)-C(3)-C(4) | -4.5(2) |
| C(11)-C(1)-C(3)-C(2) | 104.5(3) |
| C(6)-C(1)-C(3)-C(2) | -113.3(2) |
| C(2)-C(3)-C(4)-C(5) | 61.5(3) |
| C(1)-C(3)-C(4)-C(5) | -1.7(3) |
| C(2)-C(3)-C(4)-C(7) | -119.4(3) |
| C(1)-C(3)-C(4)-C(7) | 177.4(2) |
| C(7)-C(4)-C(5)-C(10) | 0.0(4) |
| C(3)-C(4)-C(5)-C(10) | 179.2(2) |
| C(7)-C(4)-C(5)-C(6) | -171.7(2) |
| C(3)-C(4)-C(5)-C(6) | 7.5(3) |
| C(10)-C(5)-C(6)-O(1) | -70.6(3) |
| C(4)-C(5)-C(6)-O(1) | 100.6(2) |
| C(10)-C(5)-C(6)-C(14) | 49.6(3) |
| C(4)-C(5)-C(6)-C(14) | -139.2(2) |
| C(10)-C(5)-C(6)-C(1) | 178.8(2) |

| | |
|---|---|
| C(4)-C(5)-C(6)-C(1) | -10.0(2) |
| C(2)-C(1)-C(6)-O(1) | -163.8(2) |
| C(11)-C(1)-C(6)-O(1) | 44.0(3) |
| C(3)-C(1)-C(6)-O(1) | -100.0(2) |
| C(2)-C(1)-C(6)-C(5) | -55.4(3) |
| C(11)-C(1)-C(6)-C(5) | 152.4(2) |
| C(3)-C(1)-C(6)-C(5) | 8.4(2) |
| C(2)-C(1)-C(6)-C(14) | 74.3(3) |
| C(11)-C(1)-C(6)-C(14) | -77.9(3) |
| C(3)-C(1)-C(6)-C(14) | 138.07(19) |
| C(5)-C(4)-C(7)-C(8) | -0.5(4) |
| C(3)-C(4)-C(7)-C(8) | -179.5(2) |
| C(4)-C(7)-C(8)-C(9) | 0.7(4) |
| C(7)-C(8)-C(9)-C(10) | -0.4(4) |
| C(4)-C(5)-C(10)-C(9) | 0.3(4) |
| C(6)-C(5)-C(10)-C(9) | 170.7(2) |
| C(8)-C(9)-C(10)-C(5) | -0.1(4) |
| C(2)-C(1)-C(11)-C(13) | 57.1(3) |
| C(3)-C(1)-C(11)-C(13) | -12.9(4) |
| C(6)-C(1)-C(11)-C(13) | -150.5(2) |
| C(2)-C(1)-C(11)-C(12) | -66.8(3) |
| C(3)-C(1)-C(11)-C(12) | -136.7(3) |
| C(6)-C(1)-C(11)-C(12) | 85.6(3) |
| O(1)-C(6)-C(14)-C(19) | -26.6(3) |
| C(5)-C(6)-C(14)-C(19) | -143.3(2) |

|  |  |
|---|---|
| C(1)-C(6)-C(14)-C(19) | 93.5(3) |
| O(1)-C(6)-C(14)-C(15) | 155.4(2) |
| C(5)-C(6)-C(14)-C(15) | 38.7(3) |
| C(1)-C(6)-C(14)-C(15) | -84.6(3) |
| C(19)-C(14)-C(15)-C(16) | -0.9(3) |
| C(6)-C(14)-C(15)-C(16) | 177.2(2) |
| C(19)-C(14)-C(15)-C(20) | 179.3(2) |
| C(6)-C(14)-C(15)-C(20) | -2.6(4) |
| C(14)-C(15)-C(16)-C(17) | 2.1(4) |
| C(20)-C(15)-C(16)-C(17) | -178.1(2) |
| C(15)-C(16)-C(17)-C(18) | -1.1(4) |
| C(16)-C(17)-C(18)-C(19) | -0.9(4) |
| C(17)-C(18)-C(19)-C(14) | 2.0(4) |
| C(17)-C(18)-C(19)-C(22) | -178.9(2) |
| C(15)-C(14)-C(19)-C(18) | -1.0(3) |
| C(6)-C(14)-C(19)-C(18) | -179.1(2) |
| C(15)-C(14)-C(19)-C(22) | 180.0(2) |
| C(6)-C(14)-C(19)-C(22) | 1.9(4) |
| C(16)-C(15)-C(20)-C(21) | 61.4(3) |
| C(14)-C(15)-C(20)-C(21) | -118.8(3) |
| C(18)-C(19)-C(22)-C(23) | -82.2(3) |
| C(14)-C(19)-C(22)-C(23) | 96.8(3) |

Symmetry transformations used to generate equivalent atoms:

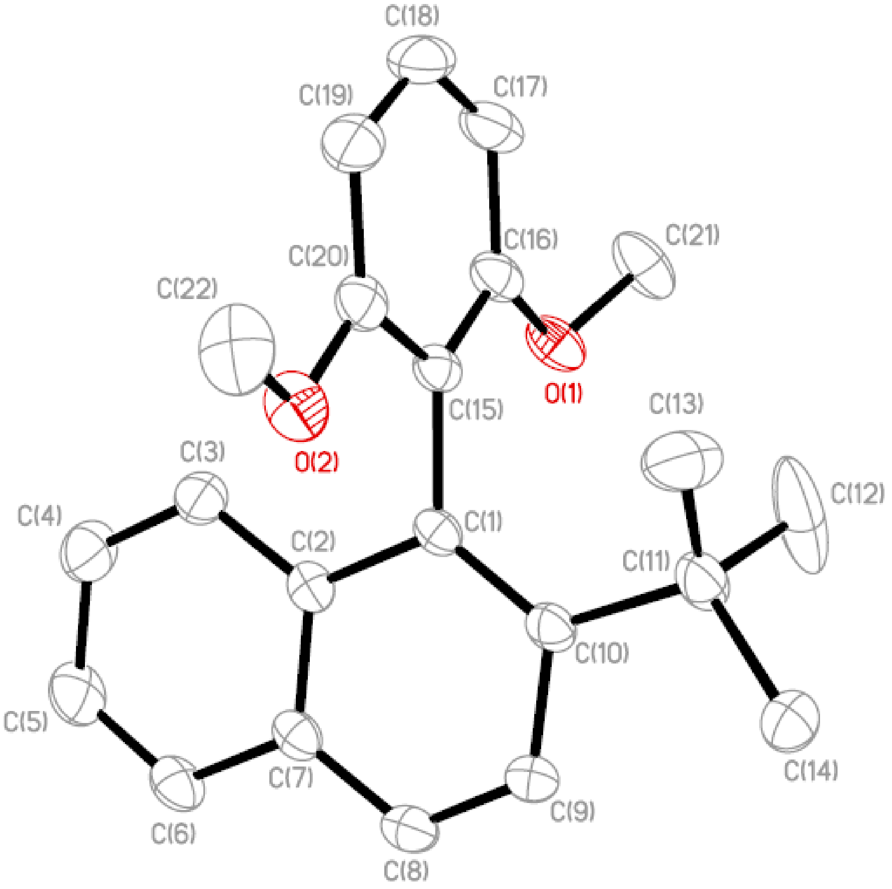
Hydrogen bonds for liu78 [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(1)-H(1O)...O(1)#1 | 0.93(7) | 2.16(6) | 3.053(4) | 160(6) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+2,-z+2

***Crystallographic Data for 9a (liu 103) Chapter IV***



Crystal data and structure refinement for liu103 **(9a)**.

| | |
|---|---|
| Identification code | liu103 |
| Empirical formula | C22 H24 O2 |
| Formula weight | 320.41 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |

| | | |
|---|---|---|
| Unit cell dimensions | a = 14.878(3) Å | α= 90°. |
| | b = 7.8605(14) Å | β= 107.402(3)°. |
| | c = 15.924(3) Å | γ = 90°. |
| Volume | 1777.0(6) Å3 | |
| Z | 4 | |
| Density (calculated) | 1.198 Mg/m3 | |
| Absorption coefficient | 0.075 mm-1 | |
| F(000) | 688 | |
| Crystal size | 0.41 x 0.17 x 0.04 mm3 | |
| Theta range for data collection | 1.43 to 25.00°. | |
| Index ranges | -17<=h<=17, -9<=k<=9, -18<=l<=18 | |
| Reflections collected | 16468 | |
| Independent reflections | 3120 [R(int) = 0.0353] | |
| Completeness to theta = 25.00° | 100.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9970 and 0.9699 | |
| Refinement method | Full-matrix least-squares on F2 | |
| Data / restraints / parameters | 3120 / 0 / 217 | |
| Goodness-of-fit on F2 | 1.029 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0576, wR2 = 0.1420 | |
| R indices (all data) | R1 = 0.0787, wR2 = 0.1581 | |
| Largest diff. peak and hole | 0.489 and -0.401 e.Å-3 | |

Atomic coordinates ( x 104) and equivalent isotropic displacement parameters (Å2x 103) for liu103. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

|  | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 1166(1) | 6390(2) | 1749(1) | 48(1) |
| O(2) | 2878(1) | 1363(2) | 1953(1) | 50(1) |
| C(1) | 2893(2) | 4723(3) | 2346(2) | 31(1) |
| C(2) | 3460(2) | 5297(3) | 1809(2) | 34(1) |
| C(3) | 3173(2) | 5101(3) | 886(2) | 46(1) |
| C(4) | 3727(2) | 5625(4) | 392(2) | 61(1) |
| C(5) | 4604(2) | 6383(4) | 792(2) | 60(1) |
| C(6) | 4902(2) | 6612(3) | 1677(2) | 47(1) |
| C(7) | 4341(2) | 6086(3) | 2205(2) | 36(1) |
| C(8) | 4624(2) | 6342(3) | 3118(2) | 43(1) |
| C(9) | 4074(2) | 5809(3) | 3610(2) | 45(1) |
| C(10) | 3201(2) | 4949(3) | 3248(2) | 36(1) |
| C(11) | 2668(2) | 4347(4) | 3895(2) | 52(1) |
| C(12) | 1883(3) | 5583(7) | 3880(3) | 128(2) |
| C(13) | 2264(3) | 2508(5) | 3684(2) | 88(1) |
| C(14) | 3319(2) | 4247(4) | 4842(2) | 50(1) |
| C(15) | 1998(2) | 3838(3) | 1854(1) | 34(1) |
| C(16) | 1141(2) | 4692(3) | 1547(2) | 41(1) |
| C(17) | 328(2) | 3837(4) | 1071(2) | 56(1) |
| C(18) | 384(2) | 2135(4) | 887(2) | 62(1) |
| C(19) | 1220(2) | 1263(4) | 1163(2) | 55(1) |
| C(20) | 2020(2) | 2114(3) | 1639(2) | 41(1) |
| C(21) | 288(2) | 7195(4) | 1681(2) | 63(1) |

| | | | | |
|---|---|---|---|---|
| C(22) | 2932(2) | -454(3) | 1947(2) | 67(1) |

Bond lengths [Å] and angles [°] for liu103.

| | |
|---|---|
| O(1)-C(16) | 1.371(3) |
| O(1)-C(21) | 1.426(3) |
| O(2)-C(20) | 1.359(3) |
| O(2)-C(22) | 1.430(3) |
| C(1)-C(10) | 1.382(3) |
| C(1)-C(2) | 1.442(3) |
| C(1)-C(15) | 1.499(3) |
| C(2)-C(3) | 1.410(3) |
| C(2)-C(7) | 1.417(3) |
| C(3)-C(4) | 1.362(4) |
| C(3)-H(3A) | 0.9500 |
| C(4)-C(5) | 1.402(4) |
| C(4)-H(4A) | 0.9500 |
| C(5)-C(6) | 1.357(4) |
| C(5)-H(5A) | 0.9500 |
| C(6)-C(7) | 1.412(3) |
| C(6)-H(6A) | 0.9500 |
| C(7)-C(8) | 1.402(3) |
| C(8)-C(9) | 1.356(3) |
| C(8)-H(8A) | 0.9500 |
| C(9)-C(10) | 1.424(3) |
| C(9)-H(9A) | 0.9500 |

| | |
|---|---|
| C(10)-C(11) | 1.549(3) |
| C(11)-C(12) | 1.515(4) |
| C(11)-C(14) | 1.531(3) |
| C(11)-C(13) | 1.563(5) |
| C(12)-H(12A) | 0.9800 |
| C(12)-H(12B) | 0.9800 |
| C(12)-H(12C) | 0.9800 |
| C(13)-H(13A) | 0.9800 |
| C(13)-H(13B) | 0.9800 |
| C(13)-H(13C) | 0.9800 |
| C(14)-H(14A) | 0.9800 |
| C(14)-H(14B) | 0.9800 |
| C(14)-H(14C) | 0.9800 |
| C(15)-C(16) | 1.393(3) |
| C(15)-C(20) | 1.401(3) |
| C(16)-C(17) | 1.394(4) |
| C(17)-C(18) | 1.377(4) |
| C(17)-H(17A) | 0.9500 |
| C(18)-C(19) | 1.372(4) |
| C(18)-H(18A) | 0.9500 |
| C(19)-C(20) | 1.379(4) |
| C(19)-H(19A) | 0.9500 |
| C(21)-H(21A) | 0.9800 |
| C(21)-H(21B) | 0.9800 |
| C(21)-H(21C) | 0.9800 |

| | |
|---|---|
| C(22)-H(22A) | 0.9800 |
| C(22)-H(22B) | 0.9800 |
| C(22)-H(22C) | 0.9800 |

| | |
|---|---|
| C(16)-O(1)-C(21) | 117.0(2) |
| C(20)-O(2)-C(22) | 118.6(2) |
| C(10)-C(1)-C(2) | 120.4(2) |
| C(10)-C(1)-C(15) | 124.7(2) |
| C(2)-C(1)-C(15) | 114.9(2) |
| C(3)-C(2)-C(7) | 117.6(2) |
| C(3)-C(2)-C(1) | 122.4(2) |
| C(7)-C(2)-C(1) | 120.0(2) |
| C(4)-C(3)-C(2) | 121.5(2) |
| C(4)-C(3)-H(3A) | 119.3 |
| C(2)-C(3)-H(3A) | 119.3 |
| C(3)-C(4)-C(5) | 120.5(3) |
| C(3)-C(4)-H(4A) | 119.7 |
| C(5)-C(4)-H(4A) | 119.7 |
| C(6)-C(5)-C(4) | 119.9(2) |
| C(6)-C(5)-H(5A) | 120.0 |
| C(4)-C(5)-H(5A) | 120.0 |
| C(5)-C(6)-C(7) | 120.7(2) |
| C(5)-C(6)-H(6A) | 119.6 |
| C(7)-C(6)-H(6A) | 119.6 |
| C(8)-C(7)-C(6) | 121.9(2) |

| | |
|---|---|
| C(8)-C(7)-C(2) | 118.4(2) |
| C(6)-C(7)-C(2) | 119.8(2) |
| C(9)-C(8)-C(7) | 120.6(2) |
| C(9)-C(8)-H(8A) | 119.7 |
| C(7)-C(8)-H(8A) | 119.7 |
| C(8)-C(9)-C(10) | 123.2(2) |
| C(8)-C(9)-H(9A) | 118.4 |
| C(10)-C(9)-H(9A) | 118.4 |
| C(1)-C(10)-C(9) | 117.4(2) |
| C(1)-C(10)-C(11) | 125.1(2) |
| C(9)-C(10)-C(11) | 117.6(2) |
| C(12)-C(11)-C(14) | 107.8(3) |
| C(12)-C(11)-C(10) | 109.8(2) |
| C(14)-C(11)-C(10) | 111.8(2) |
| C(12)-C(11)-C(13) | 110.2(3) |
| C(14)-C(11)-C(13) | 104.7(2) |
| C(10)-C(11)-C(13) | 112.4(2) |
| C(11)-C(12)-H(12A) | 109.5 |
| C(11)-C(12)-H(12B) | 109.5 |
| H(12A)-C(12)-H(12B) | 109.5 |
| C(11)-C(12)-H(12C) | 109.5 |
| H(12A)-C(12)-H(12C) | 109.5 |
| H(12B)-C(12)-H(12C) | 109.5 |
| C(11)-C(13)-H(13A) | 109.5 |
| C(11)-C(13)-H(13B) | 109.5 |

| | |
|---|---|
| H(13A)-C(13)-H(13B) | 109.5 |
| C(11)-C(13)-H(13C) | 109.5 |
| H(13A)-C(13)-H(13C) | 109.5 |
| H(13B)-C(13)-H(13C) | 109.5 |
| C(11)-C(14)-H(14A) | 109.5 |
| C(11)-C(14)-H(14B) | 109.5 |
| H(14A)-C(14)-H(14B) | 109.5 |
| C(11)-C(14)-H(14C) | 109.5 |
| H(14A)-C(14)-H(14C) | 109.5 |
| H(14B)-C(14)-H(14C) | 109.5 |
| C(16)-C(15)-C(20) | 117.8(2) |
| C(16)-C(15)-C(1) | 122.5(2) |
| C(20)-C(15)-C(1) | 119.6(2) |
| O(1)-C(16)-C(15) | 115.4(2) |
| O(1)-C(16)-C(17) | 123.8(2) |
| C(15)-C(16)-C(17) | 120.9(3) |
| C(18)-C(17)-C(16) | 119.1(3) |
| C(18)-C(17)-H(17A) | 120.5 |
| C(16)-C(17)-H(17A) | 120.5 |
| C(19)-C(18)-C(17) | 121.6(3) |
| C(19)-C(18)-H(18A) | 119.2 |
| C(17)-C(18)-H(18A) | 119.2 |
| C(18)-C(19)-C(20) | 119.0(3) |
| C(18)-C(19)-H(19A) | 120.5 |
| C(20)-C(19)-H(19A) | 120.5 |

| | |
|---|---|
| O(2)-C(20)-C(19) | 123.6(2) |
| O(2)-C(20)-C(15) | 114.8(2) |
| C(19)-C(20)-C(15) | 121.6(3) |
| O(1)-C(21)-H(21A) | 109.5 |
| O(1)-C(21)-H(21B) | 109.5 |
| H(21A)-C(21)-H(21B) | 109.5 |
| O(1)-C(21)-H(21C) | 109.5 |
| H(21A)-C(21)-H(21C) | 109.5 |
| H(21B)-C(21)-H(21C) | 109.5 |
| O(2)-C(22)-H(22A) | 109.5 |
| O(2)-C(22)-H(22B) | 109.5 |
| H(22A)-C(22)-H(22B) | 109.5 |
| O(2)-C(22)-H(22C) | 109.5 |
| H(22A)-C(22)-H(22C) | 109.5 |
| H(22B)-C(22)-H(22C) | 109.5 |

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters (Å2x 103)for liu103. The anisotropic displacement factor exponent takes the form: -2π2[ h2a*2U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| O(1) | 32(1) | 47(1) | 65(1) | 15(1) | 15(1) | 10(1) |
| O(2) | 56(1) | 28(1) | 72(1) | 0(1) | 29(1) | 1(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(1) | 27(1) | 27(1) | 40(1) | 3(1) | 11(1) | 3(1) |
| C(2) | 36(1) | 26(1) | 43(1) | 2(1) | 17(1) | 1(1) |
| C(3) | 50(2) | 45(2) | 45(2) | -3(1) | 19(1) | -15(1) |
| C(4) | 74(2) | 67(2) | 51(2) | -4(1) | 31(2) | -24(2) |
| C(5) | 65(2) | 59(2) | 67(2) | 0(2) | 39(2) | -20(2) |
| C(6) | 43(1) | 39(1) | 64(2) | 0(1) | 25(1) | -9(1) |
| C(7) | 33(1) | 29(1) | 50(2) | 1(1) | 16(1) | 2(1) |
| C(8) | 30(1) | 43(1) | 51(2) | -2(1) | 8(1) | -1(1) |
| C(9) | 30(1) | 61(2) | 39(1) | -2(1) | 6(1) | 2(1) |
| C(10) | 27(1) | 43(1) | 39(1) | 3(1) | 9(1) | 7(1) |
| C(11) | 33(1) | 84(2) | 39(1) | 13(1) | 12(1) | 9(1) |
| C(12) | 94(3) | 229(6) | 87(3) | 83(3) | 67(2) | 105(3) |
| C(13) | 82(2) | 137(3) | 42(2) | 12(2) | 12(2) | -66(2) |
| C(14) | 49(2) | 60(2) | 40(1) | 1(1) | 13(1) | 2(1) |
| C(15) | 33(1) | 37(1) | 33(1) | 6(1) | 12(1) | -4(1) |
| C(16) | 34(1) | 47(2) | 43(1) | 10(1) | 14(1) | -4(1) |
| C(17) | 33(1) | 85(2) | 48(2) | 14(2) | 6(1) | -10(1) |
| C(18) | 57(2) | 78(2) | 51(2) | -8(2) | 14(1) | -37(2) |
| C(19) | 65(2) | 52(2) | 55(2) | -7(1) | 27(2) | -26(2) |
| C(20) | 45(1) | 40(1) | 43(1) | 2(1) | 22(1) | -9(1) |
| C(21) | 39(2) | 71(2) | 84(2) | 31(2) | 27(2) | 23(1) |
| C(22) | 94(2) | 31(2) | 86(2) | 3(1) | 44(2) | 1(2) |

Hydrogen coordinates ( x 104) and isotropic displacement parameters (Å2x 103)

for liu103.

|  | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3A) | 2580 | 4593 | 603 | 55 |
| H(4A) | 3517 | 5475 | -228 | 73 |
| H(5A) | 4989 | 6735 | 444 | 71 |
| H(6A) | 5495 | 7133 | 1945 | 56 |
| H(8A) | 5205 | 6893 | 3395 | 51 |
| H(9A) | 4282 | 6019 | 4225 | 53 |
| H(12A) | 2144 | 6730 | 4014 | 192 |
| H(12B) | 1579 | 5242 | 4321 | 192 |
| H(12C) | 1418 | 5576 | 3295 | 192 |
| H(13A) | 1936 | 2181 | 4109 | 133 |
| H(13B) | 2782 | 1711 | 3723 | 133 |
| H(13C) | 1822 | 2478 | 3088 | 133 |
| H(14A) | 3594 | 5370 | 5026 | 75 |
| H(14B) | 3823 | 3426 | 4873 | 75 |
| H(14C) | 2956 | 3882 | 5232 | 75 |
| H(17A) | -258 | 4419 | 876 | 68 |
| H(18A) | -169 | 1550 | 561 | 75 |
| H(19A) | 1247 | 91 | 1027 | 66 |
| H(21A) | 396 | 8399 | 1840 | 94 |
| H(21B) | -8 | 6639 | 2082 | 94 |
| H(21C) | -127 | 7100 | 1076 | 94 |
| H(22A) | 3590 | -809 | 2190 | 100 |

|  |  |  |  |  |
|---|---|---|---|---|
| H(22B) | 2682 | -869 | 1341 | 100 |
| H(22C) | 2560 | -928 | 2306 | 100 |

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Torsion angles [°] for liu103.

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|  |  |
|---|---|
| C(10)-C(1)-C(2)-C(3) | -179.7(2) |
| C(15)-C(1)-C(2)-C(3) | 2.5(3) |
| C(10)-C(1)-C(2)-C(7) | 0.5(3) |
| C(15)-C(1)-C(2)-C(7) | -177.3(2) |
| C(7)-C(2)-C(3)-C(4) | 1.0(4) |
| C(1)-C(2)-C(3)-C(4) | -178.8(2) |
| C(2)-C(3)-C(4)-C(5) | -0.1(5) |
| C(3)-C(4)-C(5)-C(6) | -0.6(5) |
| C(4)-C(5)-C(6)-C(7) | 0.4(4) |
| C(5)-C(6)-C(7)-C(8) | -178.6(3) |
| C(5)-C(6)-C(7)-C(2) | 0.5(4) |
| C(3)-C(2)-C(7)-C(8) | 178.0(2) |
| C(1)-C(2)-C(7)-C(8) | -2.2(3) |
| C(3)-C(2)-C(7)-C(6) | -1.2(3) |
| C(1)-C(2)-C(7)-C(6) | 178.6(2) |
| C(6)-C(7)-C(8)-C(9) | -179.4(2) |
| C(2)-C(7)-C(8)-C(9) | 1.5(4) |
| C(7)-C(8)-C(9)-C(10) | 1.0(4) |
| C(2)-C(1)-C(10)-C(9) | 1.9(3) |
| C(15)-C(1)-C(10)-C(9) | 179.5(2) |
| C(2)-C(1)-C(10)-C(11) | -178.3(2) |

| | |
|---|---|
| C(15)-C(1)-C(10)-C(11) | -0.7(4) |
| C(8)-C(9)-C(10)-C(1) | -2.8(4) |
| C(8)-C(9)-C(10)-C(11) | 177.5(2) |
| C(1)-C(10)-C(11)-C(12) | -79.3(4) |
| C(9)-C(10)-C(11)-C(12) | 100.4(3) |
| C(1)-C(10)-C(11)-C(14) | 161.1(2) |
| C(9)-C(10)-C(11)-C(14) | -19.2(3) |
| C(1)-C(10)-C(11)-C(13) | 43.7(3) |
| C(9)-C(10)-C(11)-C(13) | -136.6(3) |
| C(10)-C(1)-C(15)-C(16) | 88.5(3) |
| C(2)-C(1)-C(15)-C(16) | -93.8(3) |
| C(10)-C(1)-C(15)-C(20) | -95.8(3) |
| C(2)-C(1)-C(15)-C(20) | 82.0(3) |
| C(21)-O(1)-C(16)-C(15) | -162.2(2) |
| C(21)-O(1)-C(16)-C(17) | 17.6(3) |
| C(20)-C(15)-C(16)-O(1) | -177.8(2) |
| C(1)-C(15)-C(16)-O(1) | -1.9(3) |
| C(20)-C(15)-C(16)-C(17) | 2.5(3) |
| C(1)-C(15)-C(16)-C(17) | 178.3(2) |
| O(1)-C(16)-C(17)-C(18) | 178.6(2) |
| C(15)-C(16)-C(17)-C(18) | -1.7(4) |
| C(16)-C(17)-C(18)-C(19) | 0.2(4) |
| C(17)-C(18)-C(19)-C(20) | 0.3(4) |
| C(22)-O(2)-C(20)-C(19) | -12.9(4) |
| C(22)-O(2)-C(20)-C(15) | 165.7(2) |

| | |
|---|---|
| C(18)-C(19)-C(20)-O(2) | 179.1(2) |
| C(18)-C(19)-C(20)-C(15) | 0.5(4) |
| C(16)-C(15)-C(20)-O(2) | 179.4(2) |
| C(1)-C(15)-C(20)-O(2) | 3.5(3) |
| C(16)-C(15)-C(20)-C(19) | -1.9(3) |
| C(1)-C(15)-C(20)-C(19) | -177.8(2) |

Symmetry transformations used to generate equivalent atoms:

### ***Crystallographic Data for 10 (liu 93a) Chapter IV***

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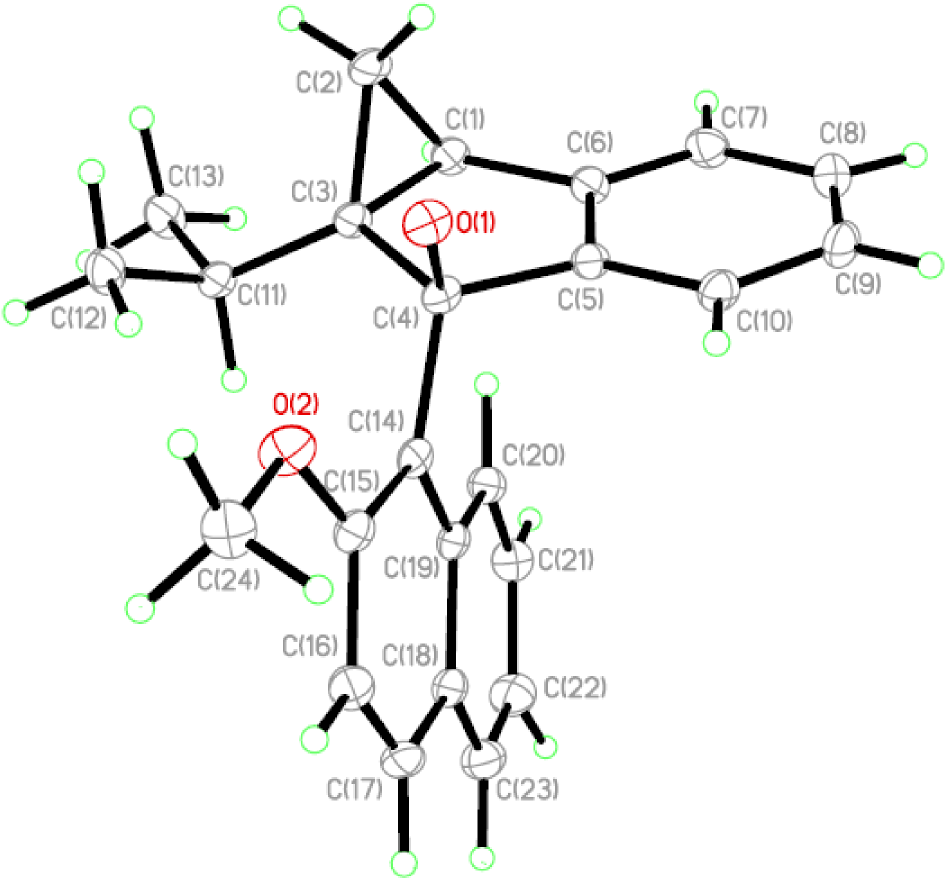

Crystal data and structure refinement for liu93a.

| | | |
|---|---|---|
| Identification code | liu93a | |
| Empirical formula | C24 H23 O2 | |
| Formula weight | 343.42 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 9.427(3) Å | α= 90°. |
| | b = 24.184(8) Å | β= 99.676(6)°. |
| | c = 8.051(3) Å | γ = 90°. |
| Volume | 1809.5(10) Å3 | |
| Z | 4 | |
| Density (calculated) | 1.261 Mg/m3 | |
| Absorption coefficient | 0.079 mm-1 | |
| F(000) | 732 | |
| Crystal size | 0.42 x 0.07 x 0.02 mm3 | |
| Theta range for data collection | 1.68 to 25.00°. | |
| Index ranges | -11<=h<=11, -28<=k<=28, -9<=l<=9 | |
| Reflections collected | 16234 | |
| Independent reflections | 3193 [R(int) = 0.0687] | |
| Completeness to theta = 25.00° | 100.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9984 and 0.9678 | |
| Refinement method | Full-matrix least-squares on F2 | |

Data / restraints / parameters 3193 / 0 / 327

Goodness-of-fit on F2 1.080

Final R indices [I>2sigma(I)] R1 = 0.0603, wR2 = 0.1333

R indices (all data) R1 = 0.0890, wR2 = 0.1478

Largest diff. peak and hole 0.546 and -0.228 e.Å-3

Atomic coordinates ( x 104) and equivalent isotropic displacement parameters (Å2x 103)

for liu93a. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 1367(2) | 6485(1) | 9568(2) | 28(1) |
| O(2) | 3605(2) | 6719(1) | 11675(2) | 34(1) |
| C(1) | 1229(3) | 5469(1) | 6578(3) | 26(1) |
| C(2) | 448(3) | 5437(1) | 8068(4) | 29(1) |
| C(3) | 2003(3) | 5597(1) | 8348(3) | 23(1) |
| C(4) | 2238(3) | 6240(1) | 8459(3) | 21(1) |
| C(5) | 1547(3) | 6437(1) | 6714(3) | 23(1) |
| C(6) | 1005(3) | 6002(1) | 5652(3) | 25(1) |
| C(7) | 326(3) | 6105(1) | 4027(4) | 32(1) |
| C(8) | 125(3) | 6650(1) | 3475(4) | 34(1) |
| C(9) | 592(3) | 7084(1) | 4561(4) | 33(1) |
| C(10) | 1320(3) | 6980(1) | 6169(4) | 28(1) |
| C(11) | 3105(3) | 5216(1) | 9378(3) | 25(1) |
| C(12) | 3097(4) | 5289(1) | 11259(4) | 32(1) |
| C(13) | 2890(3) | 4604(1) | 8897(4) | 34(1) |

| | | | | |
|---|---|---|---|---|
| C(14) | 3850(3) | 6420(1) | 8916(3) | 22(1) |
| C(15) | 4416(3) | 6690(1) | 10407(3) | 25(1) |
| C(16) | 5812(3) | 6926(1) | 10674(4) | 31(1) |
| C(17) | 6673(3) | 6872(1) | 9506(4) | 30(1) |
| C(18) | 6243(3) | 6558(1) | 8042(3) | 27(1) |
| C(19) | 4831(3) | 6320(1) | 7753(3) | 23(1) |
| C(20) | 4513(3) | 5964(1) | 6322(3) | 27(1) |
| C(21) | 5486(3) | 5859(1) | 5290(4) | 32(1) |
| C(22) | 6852(3) | 6111(1) | 5566(4) | 37(1) |
| C(23) | 7215(3) | 6452(1) | 6911(4) | 35(1) |
| C(24) | 4107(4) | 7046(1) | 13142(4) | 35(1) |

Bond lengths [Å] and angles [°] for  liu93a.

| | |
|---|---|
| O(1)-C(4) | 1.439(3) |
| O(2)-C(15) | 1.376(3) |
| O(2)-C(24) | 1.434(3) |
| C(1)-C(6) | 1.486(3) |
| C(1)-C(2) | 1.512(4) |
| C(1)-C(3) | 1.520(4) |
| C(1)-H(1) | 0.99(3) |
| C(2)-C(3) | 1.496(4) |
| C(2)-H(2A) | 1.00(3) |
| C(2)-H(2B) | 0.99(3) |
| C(3)-C(11) | 1.525(3) |
| C(3)-C(4) | 1.570(3) |

| | |
|---|---|
| C(4)-C(5) | 1.523(4) |
| C(4)-C(14) | 1.564(3) |
| C(5)-C(10) | 1.389(3) |
| C(5)-C(6) | 1.396(3) |
| C(6)-C(7) | 1.379(4) |
| C(7)-C(8) | 1.394(4) |
| C(7)-H(7) | 0.97(3) |
| C(8)-C(9) | 1.390(4) |
| C(8)-H(8) | 0.97(3) |
| C(9)-C(10) | 1.383(4) |
| C(9)-H(9) | 0.93(3) |
| C(10)-H(10) | 0.99(3) |
| C(11)-C(12) | 1.525(4) |
| C(11)-C(13) | 1.535(4) |
| C(11)-H(11) | 1.02(3) |
| C(12)-H(12A) | 0.98(4) |
| C(12)-H(12B) | 0.98(3) |
| C(12)-H(12C) | 0.99(3) |
| C(13)-H(13A) | 0.97(3) |
| C(13)-H(13B) | 1.03(4) |
| C(13)-H(13C) | 1.03(3) |
| C(14)-C(15) | 1.392(4) |
| C(14)-C(19) | 1.443(4) |
| C(15)-C(16) | 1.417(4) |
| C(16)-C(17) | 1.349(4) |

| | |
|---|---|
| C(16)-H(16) | 0.96(3) |
| C(17)-C(18) | 1.403(4) |
| C(17)-H(17) | 0.97(3) |
| C(18)-C(23) | 1.419(4) |
| C(18)-C(19) | 1.433(4) |
| C(19)-C(20) | 1.428(4) |
| C(20)-C(21) | 1.362(4) |
| C(20)-H(20) | 1.03(3) |
| C(21)-C(22) | 1.408(4) |
| C(21)-H(21) | 1.04(3) |
| C(22)-C(23) | 1.359(4) |
| C(22)-H(22) | 1.03(3) |
| C(23)-H(23) | 0.99(3) |
| C(24)-H(24A) | 0.99(3) |
| C(24)-H(24B) | 0.98(3) |
| C(24)-H(24C) | 1.06(3) |
| C(15)-O(2)-C(24) | 119.4(2) |
| C(6)-C(1)-C(2) | 113.3(2) |
| C(6)-C(1)-C(3) | 107.4(2) |
| C(2)-C(1)-C(3) | 59.16(17) |
| C(6)-C(1)-H(1) | 118.7(16) |
| C(2)-C(1)-H(1) | 120.4(16) |
| C(3)-C(1)-H(1) | 124.0(16) |
| C(3)-C(2)-C(1) | 60.69(17) |
| C(3)-C(2)-H(2A) | 113.8(16) |

| | |
|---|---|
| C(1)-C(2)-H(2A) | 116.2(16) |
| C(3)-C(2)-H(2B) | 119.8(14) |
| C(1)-C(2)-H(2B) | 117.1(15) |
| H(2A)-C(2)-H(2B) | 117(2) |
| C(2)-C(3)-C(1) | 60.15(17) |
| C(2)-C(3)-C(11) | 119.1(2) |
| C(1)-C(3)-C(11) | 124.2(2) |
| C(2)-C(3)-C(4) | 113.0(2) |
| C(1)-C(3)-C(4) | 107.2(2) |
| C(11)-C(3)-C(4) | 119.3(2) |
| O(1)-C(4)-C(5) | 104.05(18) |
| O(1)-C(4)-C(14) | 111.85(19) |
| C(5)-C(4)-C(14) | 112.2(2) |
| O(1)-C(4)-C(3) | 110.72(19) |
| C(5)-C(4)-C(3) | 102.88(19) |
| C(14)-C(4)-C(3) | 114.33(19) |
| C(10)-C(5)-C(6) | 119.8(2) |
| C(10)-C(5)-C(4) | 127.3(2) |
| C(6)-C(5)-C(4) | 112.6(2) |
| C(7)-C(6)-C(5) | 120.6(2) |
| C(7)-C(6)-C(1) | 129.5(2) |
| C(5)-C(6)-C(1) | 109.9(2) |
| C(6)-C(7)-C(8) | 119.3(3) |
| C(6)-C(7)-H(7) | 121.8(16) |
| C(8)-C(7)-H(7) | 118.9(16) |

| | |
|---|---|
| C(9)-C(8)-C(7) | 120.1(3) |
| C(9)-C(8)-H(8) | 118.4(18) |
| C(7)-C(8)-H(8) | 121.5(18) |
| C(10)-C(9)-C(8) | 120.5(3) |
| C(10)-C(9)-H(9) | 119.1(16) |
| C(8)-C(9)-H(9) | 120.4(16) |
| C(9)-C(10)-C(5) | 119.6(3) |
| C(9)-C(10)-H(10) | 123.6(15) |
| C(5)-C(10)-H(10) | 116.7(15) |
| C(3)-C(11)-C(12) | 110.7(2) |
| C(3)-C(11)-C(13) | 113.3(2) |
| C(12)-C(11)-C(13) | 109.8(2) |
| C(3)-C(11)-H(11) | 106.8(14) |
| C(12)-C(11)-H(11) | 106.8(14) |
| C(13)-C(11)-H(11) | 109.1(14) |
| C(11)-C(12)-H(12A) | 109.6(19) |
| C(11)-C(12)-H(12B) | 113.6(18) |
| H(12A)-C(12)-H(12B) | 107(3) |
| C(11)-C(12)-H(12C) | 112.5(16) |
| H(12A)-C(12)-H(12C) | 110(2) |
| H(12B)-C(12)-H(12C) | 104(2) |
| C(11)-C(13)-H(13A) | 109.4(17) |
| C(11)-C(13)-H(13B) | 110.3(19) |
| H(13A)-C(13)-H(13B) | 109(3) |
| C(11)-C(13)-H(13C) | 111.0(16) |

| | |
|---|---|
| H(13A)-C(13)-H(13C) | 110(2) |
| H(13B)-C(13)-H(13C) | 106(2) |
| C(15)-C(14)-C(19) | 116.4(2) |
| C(15)-C(14)-C(4) | 123.4(2) |
| C(19)-C(14)-C(4) | 120.2(2) |
| O(2)-C(15)-C(14) | 118.9(2) |
| O(2)-C(15)-C(16) | 119.0(2) |
| C(14)-C(15)-C(16) | 122.1(2) |
| C(17)-C(16)-C(15) | 120.5(3) |
| C(17)-C(16)-H(16) | 121.1(18) |
| C(15)-C(16)-H(16) | 118.4(17) |
| C(16)-C(17)-C(18) | 121.1(3) |
| C(16)-C(17)-H(17) | 121.2(16) |
| C(18)-C(17)-H(17) | 117.7(16) |
| C(17)-C(18)-C(23) | 120.6(3) |
| C(17)-C(18)-C(19) | 118.9(2) |
| C(23)-C(18)-C(19) | 120.4(3) |
| C(20)-C(19)-C(18) | 115.8(2) |
| C(20)-C(19)-C(14) | 123.7(2) |
| C(18)-C(19)-C(14) | 120.4(2) |
| C(21)-C(20)-C(19) | 122.2(3) |
| C(21)-C(20)-H(20) | 120.1(15) |
| C(19)-C(20)-H(20) | 117.7(15) |
| C(20)-C(21)-C(22) | 121.0(3) |
| C(20)-C(21)-H(21) | 120.8(17) |

| | |
|---|---|
| C(22)-C(21)-H(21) | 118.3(17) |
| C(23)-C(22)-C(21) | 119.3(3) |
| C(23)-C(22)-H(22) | 118.3(15) |
| C(21)-C(22)-H(22) | 121.9(15) |
| C(22)-C(23)-C(18) | 121.2(3) |
| C(22)-C(23)-H(23) | 123.2(18) |
| C(18)-C(23)-H(23) | 115.7(18) |
| O(2)-C(24)-H(24A) | 104.9(19) |
| O(2)-C(24)-H(24B) | 107.2(19) |
| H(24A)-C(24)-H(24B) | 116(3) |
| O(2)-C(24)-H(24C) | 109.1(16) |
| H(24A)-C(24)-H(24C) | 111(2) |
| H(24B)-C(24)-H(24C) | 109(2) |

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters (Å2x 103) for liu93a. The anisotropic displacement factor exponent takes the form: -2π2[ h2 a*2U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| O(1) | 30(1) | 21(1) | 36(1) | -4(1) | 11(1) | 3(1) |
| O(2) | 42(1) | 29(1) | 31(1) | -11(1) | 9(1) | -9(1) |
| C(1) | 27(1) | 15(1) | 33(2) | -1(1) | 0(1) | -3(1) |
| C(2) | 27(2) | 15(1) | 45(2) | 3(1) | 6(1) | -4(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(3) | 23(1) | 13(1) | 33(2) | 0(1) | 3(1) | -2(1) |
| C(4) | 25(1) | 13(1) | 27(1) | -3(1) | 7(1) | -1(1) |
| C(5) | 21(1) | 18(1) | 30(1) | 1(1) | 5(1) | 1(1) |
| C(6) | 25(1) | 18(1) | 30(2) | -3(1) | 2(1) | 0(1) |
| C(7) | 30(2) | 30(2) | 33(2) | -4(1) | 0(1) | -4(1) |
| C(8) | 34(2) | 35(2) | 31(2) | 8(1) | 2(1) | 0(1) |
| C(9) | 36(2) | 22(2) | 43(2) | 11(1) | 9(1) | 4(1) |
| C(10) | 29(2) | 20(1) | 35(2) | 0(1) | 6(1) | -1(1) |
| C(11) | 26(1) | 13(1) | 35(2) | 2(1) | 1(1) | -3(1) |
| C(12) | 36(2) | 24(2) | 34(2) | 3(1) | -2(1) | -1(1) |
| C(13) | 35(2) | 16(1) | 45(2) | 0(1) | -5(2) | 2(1) |
| C(14) | 28(1) | 9(1) | 29(1) | 1(1) | 3(1) | 0(1) |
| C(15) | 30(1) | 15(1) | 31(2) | 1(1) | 5(1) | -1(1) |
| C(16) | 36(2) | 19(1) | 34(2) | -3(1) | -2(1) | -5(1) |
| C(17) | 27(2) | 21(1) | 41(2) | 3(1) | 0(1) | -7(1) |
| C(18) | 27(1) | 17(1) | 35(2) | 6(1) | 2(1) | 1(1) |
| C(19) | 25(1) | 12(1) | 30(2) | 4(1) | 3(1) | 1(1) |
| C(20) | 26(2) | 21(1) | 33(2) | 1(1) | 4(1) | 2(1) |
| C(21) | 34(2) | 28(2) | 32(2) | -3(1) | 6(1) | 2(1) |
| C(22) | 32(2) | 41(2) | 42(2) | 2(2) | 14(1) | 3(1) |
| C(23) | 28(2) | 31(2) | 47(2) | 5(1) | 8(1) | 0(1) |
| C(24) | 45(2) | 26(2) | 32(2) | -9(1) | 3(2) | -1(1) |

Hydrogen coordinates ( x 104) and isotropic displacement parameters (Å2x 10 3)

for liu93a.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 1390(30) | 5132(12) | 5950(30) | 34(7) |
| H(2A) | 270(30) | 5057(13) | 8480(30) | 40(8) |
| H(2B) | -290(30) | 5720(11) | 8140(30) | 23(7) |
| H(7) | -30(30) | 5806(12) | 3250(30) | 35(8) |
| H(8) | -300(30) | 6737(12) | 2320(40) | 44(9) |
| H(9) | 450(30) | 7448(12) | 4200(30) | 29(7) |
| H(10) | 1650(30) | 7272(11) | 7000(30) | 30(7) |
| H(11) | 4090(30) | 5340(10) | 9170(30) | 24(7) |
| H(12A) | 2140(40) | 5211(14) | 11500(40) | 57(10) |
| H(12B) | 3340(30) | 5662(15) | 11670(40) | 50(9) |
| H(12C) | 3820(30) | 5052(12) | 11960(30) | 37(8) |
| H(13A) | 3670(30) | 4388(12) | 9520(30) | 36(8) |
| H(13B) | 1920(40) | 4463(14) | 9170(40) | 63(10) |
| H(13C) | 2850(30) | 4549(12) | 7620(40) | 40(8) |
| H(16) | 6110(30) | 7139(12) | 11670(40) | 39(8) |
| H(17) | 7620(30) | 7039(11) | 9660(30) | 32(7) |
| H(20) | 3520(30) | 5775(11) | 6110(30) | 28(7) |
| H(21) | 5240(30) | 5585(13) | 4290(40) | 49(9) |
| H(22) | 7530(30) | 6089(11) | 4690(40) | 36(8) |
| H(23) | 8160(30) | 6643(12) | 7170(40) | 44(8) |
| H(24A) | 3360(40) | 7009(13) | 13850(40) | 52(10) |
| H(24B) | 4270(30) | 7421(15) | 12750(40) | 51(9) |

| | | | | |
|---|---|---|---|---|
| H(24C) | 5090(30) | 6881(12) | 13770(40) | 42(8) |

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Torsion angles [°] for liu93a.

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| | |
|---|---|
| C(6)-C(1)-C(2)-C(3) | -97.0(2) |
| C(1)-C(2)-C(3)-C(11) | -115.0(3) |
| C(1)-C(2)-C(3)-C(4) | 97.3(2) |
| C(6)-C(1)-C(3)-C(2) | 107.2(2) |
| C(6)-C(1)-C(3)-C(11) | -146.1(2) |
| C(2)-C(1)-C(3)-C(11) | 106.7(3) |
| C(6)-C(1)-C(3)-C(4) | 0.1(3) |
| C(2)-C(1)-C(3)-C(4) | -107.0(2) |
| C(2)-C(3)-C(4)-O(1) | 47.2(3) |
| C(1)-C(3)-C(4)-O(1) | 111.5(2) |
| C(11)-C(3)-C(4)-O(1) | -100.3(3) |
| C(2)-C(3)-C(4)-C(5) | -63.4(3) |
| C(1)-C(3)-C(4)-C(5) | 0.8(2) |
| C(11)-C(3)-C(4)-C(5) | 149.0(2) |
| C(2)-C(3)-C(4)-C(14) | 174.7(2) |
| C(1)-C(3)-C(4)-C(14) | -121.1(2) |
| C(11)-C(3)-C(4)-C(14) | 27.1(3) |
| O(1)-C(4)-C(5)-C(10) | 57.5(3) |
| C(14)-C(4)-C(5)-C(10) | -63.6(3) |
| C(3)-C(4)-C(5)-C(10) | 173.0(2) |
| O(1)-C(4)-C(5)-C(6) | -117.2(2) |
| C(14)-C(4)-C(5)-C(6) | 121.7(2) |

| | |
|---|---|
| C(3)-C(4)-C(5)-C(6) | -1.6(3) |
| C(10)-C(5)-C(6)-C(7) | 4.2(4) |
| C(4)-C(5)-C(6)-C(7) | 179.2(2) |
| C(10)-C(5)-C(6)-C(1) | -173.3(2) |
| C(4)-C(5)-C(6)-C(1) | 1.8(3) |
| C(2)-C(1)-C(6)-C(7) | -115.1(3) |
| C(3)-C(1)-C(6)-C(7) | -178.3(3) |
| C(2)-C(1)-C(6)-C(5) | 62.1(3) |
| C(3)-C(1)-C(6)-C(5) | -1.2(3) |
| C(5)-C(6)-C(7)-C(8) | -2.9(4) |
| C(1)-C(6)-C(7)-C(8) | 174.0(3) |
| C(6)-C(7)-C(8)-C(9) | -0.7(4) |
| C(7)-C(8)-C(9)-C(10) | 3.2(4) |
| C(8)-C(9)-C(10)-C(5) | -1.9(4) |
| C(6)-C(5)-C(10)-C(9) | -1.7(4) |
| C(4)-C(5)-C(10)-C(9) | -176.0(2) |
| C(2)-C(3)-C(11)-C(12) | -78.7(3) |
| C(1)-C(3)-C(11)-C(12) | -150.6(2) |
| C(4)-C(3)-C(11)-C(12) | 66.9(3) |
| C(2)-C(3)-C(11)-C(13) | 45.3(3) |
| C(1)-C(3)-C(11)-C(13) | -26.6(4) |
| C(4)-C(3)-C(11)-C(13) | -169.2(2) |
| O(1)-C(4)-C(14)-C(15) | 12.2(3) |
| C(5)-C(4)-C(14)-C(15) | 128.7(2) |
| C(3)-C(4)-C(14)-C(15) | -114.6(3) |

| | |
|---|---|
| O(1)-C(4)-C(14)-C(19) | -166.45(19) |
| C(5)-C(4)-C(14)-C(19) | -50.0(3) |
| C(3)-C(4)-C(14)-C(19) | 66.7(3) |
| C(24)-O(2)-C(15)-C(14) | -173.4(2) |
| C(24)-O(2)-C(15)-C(16) | 8.0(3) |
| C(19)-C(14)-C(15)-O(2) | -169.7(2) |
| C(4)-C(14)-C(15)-O(2) | 11.6(4) |
| C(19)-C(14)-C(15)-C(16) | 8.9(3) |
| C(4)-C(14)-C(15)-C(16) | -169.8(2) |
| O(2)-C(15)-C(16)-C(17) | 175.3(2) |
| C(14)-C(15)-C(16)-C(17) | -3.3(4) |
| C(15)-C(16)-C(17)-C(18) | -3.3(4) |
| C(16)-C(17)-C(18)-C(23) | -173.1(3) |
| C(16)-C(17)-C(18)-C(19) | 3.6(4) |
| C(17)-C(18)-C(19)-C(20) | -174.5(2) |
| C(23)-C(18)-C(19)-C(20) | 2.2(3) |
| C(17)-C(18)-C(19)-C(14) | 2.4(3) |
| C(23)-C(18)-C(19)-C(14) | 179.1(2) |
| C(15)-C(14)-C(19)-C(20) | 168.2(2) |
| C(4)-C(14)-C(19)-C(20) | -13.0(3) |
| C(15)-C(14)-C(19)-C(18) | -8.4(3) |
| C(4)-C(14)-C(19)-C(18) | 170.4(2) |
| C(18)-C(19)-C(20)-C(21) | -0.3(4) |
| C(14)-C(19)-C(20)-C(21) | -177.0(2) |
| C(19)-C(20)-C(21)-C(22) | -1.8(4) |

| | |
|---|---|
| C(20)-C(21)-C(22)-C(23) | 1.9(4) |
| C(21)-C(22)-C(23)-C(18) | 0.1(4) |
| C(17)-C(18)-C(23)-C(22) | 174.5(3) |
| C(19)-C(18)-C(23)-C(22) | -2.1(4) |

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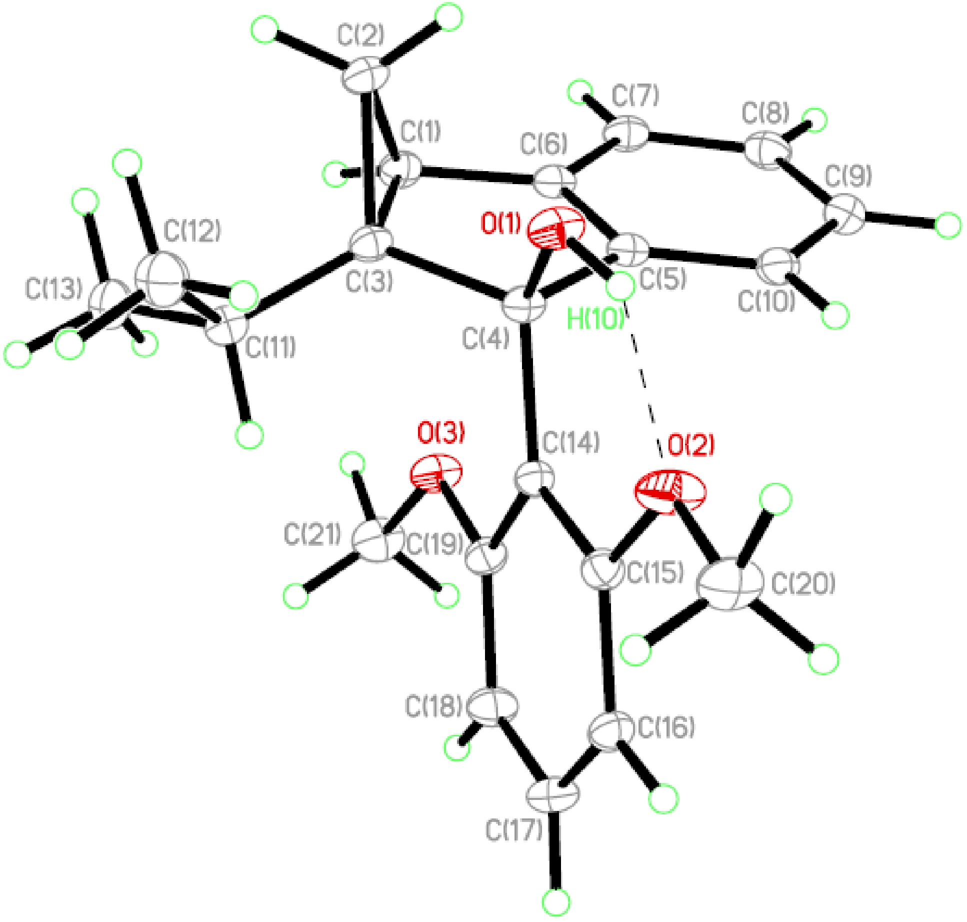
Symmetry transformations used to generate equivalent atoms:

### *Crystallographic Data for 20 (liu 100) Chapter II*



Crystal data and structure refinement for liu100.

| | |
|---|---|
| Identification code | liu100 |
| Empirical formula | C21 H24 O3 |
| Formula weight | 324.40 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | a = 8.3715(11) Å α= 94.572(2)°. |
| | b = 8.9396(11) Å β= 92.290(2)°. |
| | c = 12.4788(16) Å γ = 111.493(2)°. |
| Volume | 863.77(19) Å3 |
| Z | 2 |
| Density (calculated) | 1.247 Mg/m3 |
| Absorption coefficient | 0.082 mm-1 |
| F(000) | 348 |
| Crystal size | 0.29 x 0.11 x 0.07 mm3 |
| Theta range for data collection | 1.64 to 27.00°. |
| Index ranges | -10<=h<=10, -11<=k<=11, -15<=l<=15 |
| Reflections collected | 9676 |
| Independent reflections | 3730 [R(int) = 0.0142] |
| Completeness to theta = 27.00° | 99.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9943 and 0.9766 |
| Refinement method | Full-matrix least-squares on F2 |

Data / restraints / parameters 3730 / 0 / 313

Goodness-of-fit on F2 1.048

Final R indices [I>2sigma(I)] R1 = 0.0385, wR2 = 0.0995

R indices (all data) R1 = 0.0442, wR2 = 0.1047

Largest diff. peak and hole 0.317 and -0.216 e.Å-3

Atomic coordinates ( x 104) and equivalent isotropic displacement parameters (Å2x 103) for liu100. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 8543(1) | 648(1) | 651(1) | 29(1) |
| O(2) | 11438(1) | 3014(1) | 869(1) | 39(1) |
| O(3) | 8839(1) | 999(1) | 4002(1) | 28(1) |
| C(1) | 6153(2) | -1437(1) | 2588(1) | 24(1) |
| C(2) | 5433(2) | -1271(2) | 1487(1) | 27(1) |
| C(3) | 6761(1) | 184(1) | 2134(1) | 22(1) |
| C(4) | 8618(1) | 538(1) | 1785(1) | 21(1) |
| C(5) | 8943(2) | -978(1) | 2032(1) | 22(1) |
| C(6) | 7574(2) | -2051(1) | 2520(1) | 23(1) |
| C(7) | 7656(2) | -3488(1) | 2814(1) | 27(1) |
| C(8) | 9114(2) | -3836(2) | 2612(1) | 30(1) |
| C(9) | 10464(2) | -2768(2) | 2115(1) | 30(1) |
| C(10) | 10385(2) | -1327(1) | 1819(1) | 26(1) |
| C(11) | 6231(2) | 1594(2) | 2492(1) | 26(1) |
| C(12) | 5719(2) | 2283(2) | 1509(1) | 36(1) |

|  |  |  |  |  |
|---|---|---|---|---|
| C(13) | 4808(2) | 1169(2) | 3270(1) | 35(1) |
| C(14) | 10027(1) | 2029(1) | 2425(1) | 21(1) |
| C(15) | 11370(2) | 3208(1) | 1965(1) | 23(1) |
| C(16) | 12616(2) | 4506(1) | 2588(1) | 26(1) |
| C(17) | 12564(2) | 4644(2) | 3691(1) | 30(1) |
| C(18) | 11306(2) | 3498(2) | 4190(1) | 29(1) |
| C(19) | 10077(2) | 2196(1) | 3561(1) | 23(1) |
| C(20) | 12592(2) | 4268(2) | 339(1) | 37(1) |
| C(21) | 8690(2) | 1170(2) | 5136(1) | 36(1) |

Bond lengths [Å] and angles [°] for liu100.

|  |  |
|---|---|
| O(1)-C(4) | 1.4272(13) |
| O(1)-H(1O) | 0.859(19) |
| O(2)-C(15) | 1.3711(14) |
| O(2)-C(20) | 1.4146(15) |
| O(3)-C(19) | 1.3600(14) |
| O(3)-C(21) | 1.4269(15) |
| C(1)-C(6) | 1.4842(17) |
| C(1)-C(3) | 1.5140(16) |
| C(1)-C(2) | 1.5184(17) |
| C(1)-H(1) | 0.958(14) |
| C(2)-C(3) | 1.5100(16) |
| C(2)-H(2A) | 0.989(15) |
| C(2)-H(2B) | 0.981(15) |
| C(3)-C(11) | 1.5246(17) |

| | |
|---|---|
| C(3)-C(4) | 1.5562(16) |
| C(4)-C(5) | 1.5281(16) |
| C(4)-C(14) | 1.5518(15) |
| C(5)-C(10) | 1.3834(17) |
| C(5)-C(6) | 1.3956(16) |
| C(6)-C(7) | 1.3890(17) |
| C(7)-C(8) | 1.3931(18) |
| C(7)-H(7) | 0.953(15) |
| C(8)-C(9) | 1.3907(19) |
| C(8)-H(8) | 0.970(15) |
| C(9)-C(10) | 1.3915(18) |
| C(9)-H(9) | 0.988(16) |
| C(10)-H(10) | 0.973(15) |
| C(11)-C(13) | 1.5248(18) |
| C(11)-C(12) | 1.5292(19) |
| C(11)-H(11) | 0.995(15) |
| C(12)-H(12A) | 0.981(18) |
| C(12)-H(12B) | 0.985(18) |
| C(12)-H(12C) | 1.020(18) |
| C(13)-H(13A) | 0.989(19) |
| C(13)-H(13B) | 0.986(18) |
| C(13)-H(13C) | 0.995(17) |
| C(14)-C(15) | 1.4084(16) |
| C(14)-C(19) | 1.4109(16) |
| C(15)-C(16) | 1.3948(17) |

| | |
|---|---|
| C(16)-C(17) | 1.3759(18) |
| C(16)-H(16) | 0.978(15) |
| C(17)-C(18) | 1.3819(18) |
| C(17)-H(17) | 0.967(17) |
| C(18)-C(19) | 1.3932(17) |
| C(18)-H(18) | 0.959(15) |
| C(20)-H(20A) | 1.00(2) |
| C(20)-H(20B) | 0.990(16) |
| C(20)-H(20C) | 0.98(2) |
| C(21)-H(21A) | 1.008(18) |
| C(21)-H(21B) | 0.994(18) |
| C(21)-H(21C) | 1.003(16) |
| C(4)-O(1)-H(1O) | 109.4(12) |
| C(15)-O(2)-C(20) | 120.01(10) |
| C(19)-O(3)-C(21) | 118.60(10) |
| C(6)-C(1)-C(3) | 106.99(10) |
| C(6)-C(1)-C(2) | 112.55(10) |
| C(3)-C(1)-C(2) | 59.73(7) |
| C(6)-C(1)-H(1) | 120.1(8) |
| C(3)-C(1)-H(1) | 122.5(8) |
| C(2)-C(1)-H(1) | 120.3(9) |
| C(3)-C(2)-C(1) | 59.99(7) |
| C(3)-C(2)-H(2A) | 115.7(8) |
| C(1)-C(2)-H(2A) | 117.3(8) |
| C(3)-C(2)-H(2B) | 117.5(9) |

| | |
|---|---|
| C(1)-C(2)-H(2B) | 116.7(9) |
| H(2A)-C(2)-H(2B) | 117.2(12) |
| C(2)-C(3)-C(1) | 60.28(8) |
| C(2)-C(3)-C(11) | 117.73(10) |
| C(1)-C(3)-C(11) | 125.29(10) |
| C(2)-C(3)-C(4) | 112.91(9) |
| C(1)-C(3)-C(4) | 107.83(9) |
| C(11)-C(3)-C(4) | 119.14(9) |
| O(1)-C(4)-C(5) | 110.57(9) |
| O(1)-C(4)-C(14) | 113.21(9) |
| C(5)-C(4)-C(14) | 108.62(9) |
| O(1)-C(4)-C(3) | 106.35(9) |
| C(5)-C(4)-C(3) | 102.89(9) |
| C(14)-C(4)-C(3) | 114.72(9) |
| C(10)-C(5)-C(6) | 121.19(11) |
| C(10)-C(5)-C(4) | 126.81(10) |
| C(6)-C(5)-C(4) | 112.00(10) |
| C(7)-C(6)-C(5) | 119.93(11) |
| C(7)-C(6)-C(1) | 129.84(11) |
| C(5)-C(6)-C(1) | 110.15(10) |
| C(6)-C(7)-C(8) | 119.06(11) |
| C(6)-C(7)-H(7) | 121.1(9) |
| C(8)-C(7)-H(7) | 119.9(9) |
| C(9)-C(8)-C(7) | 120.61(12) |
| C(9)-C(8)-H(8) | 118.7(9) |

| | |
|---|---|
| C(7)-C(8)-H(8) | 120.7(9) |
| C(8)-C(9)-C(10) | 120.45(12) |
| C(8)-C(9)-H(9) | 121.2(9) |
| C(10)-C(9)-H(9) | 118.4(9) |
| C(5)-C(10)-C(9) | 118.76(11) |
| C(5)-C(10)-H(10) | 120.6(8) |
| C(9)-C(10)-H(10) | 120.6(8) |
| C(13)-C(11)-C(3) | 113.50(10) |
| C(13)-C(11)-C(12) | 110.93(11) |
| C(3)-C(11)-C(12) | 110.13(11) |
| C(13)-C(11)-H(11) | 106.5(8) |
| C(3)-C(11)-H(11) | 107.7(8) |
| C(12)-C(11)-H(11) | 107.8(8) |
| C(11)-C(12)-H(12A) | 110.8(10) |
| C(11)-C(12)-H(12B) | 110.8(10) |
| H(12A)-C(12)-H(12B) | 106.4(14) |
| C(11)-C(12)-H(12C) | 111.2(9) |
| H(12A)-C(12)-H(12C) | 108.2(14) |
| H(12B)-C(12)-H(12C) | 109.2(14) |
| C(11)-C(13)-H(13A) | 113.7(10) |
| C(11)-C(13)-H(13B) | 109.9(10) |
| H(13A)-C(13)-H(13B) | 106.6(14) |
| C(11)-C(13)-H(13C) | 111.8(9) |
| H(13A)-C(13)-H(13C) | 106.5(14) |
| H(13B)-C(13)-H(13C) | 108.1(13) |

| | |
|---|---|
| C(15)-C(14)-C(19) | 115.73(10) |
| C(15)-C(14)-C(4) | 124.96(10) |
| C(19)-C(14)-C(4) | 119.16(10) |
| O(2)-C(15)-C(16) | 120.52(10) |
| O(2)-C(15)-C(14) | 117.33(10) |
| C(16)-C(15)-C(14) | 122.14(11) |
| C(17)-C(16)-C(15) | 119.62(11) |
| C(17)-C(16)-H(16) | 120.3(9) |
| C(15)-C(16)-H(16) | 120.1(9) |
| C(16)-C(17)-C(18) | 120.78(11) |
| C(16)-C(17)-H(17) | 120.4(9) |
| C(18)-C(17)-H(17) | 118.8(9) |
| C(17)-C(18)-C(19) | 119.17(12) |
| C(17)-C(18)-H(18) | 121.7(9) |
| C(19)-C(18)-H(18) | 119.1(9) |
| O(3)-C(19)-C(18) | 122.18(11) |
| O(3)-C(19)-C(14) | 115.38(10) |
| C(18)-C(19)-C(14) | 122.45(11) |
| O(2)-C(20)-H(20A) | 109.8(11) |
| O(2)-C(20)-H(20B) | 106.4(9) |
| H(20A)-C(20)-H(20B) | 109.6(14) |
| O(2)-C(20)-H(20C) | 109.2(11) |
| H(20A)-C(20)-H(20C) | 111.3(16) |
| H(20B)-C(20)-H(20C) | 110.4(14) |
| O(3)-C(21)-H(21A) | 109.8(10) |

| | |
|---|---|
| O(3)-C(21)-H(21B) | 104.1(10) |
| H(21A)-C(21)-H(21B) | 110.7(14) |
| O(3)-C(21)-H(21C) | 112.0(9) |
| H(21A)-C(21)-H(21C) | 111.5(13) |
| H(21B)-C(21)-H(21C) | 108.4(13) |

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters (Å2x 103)for liu100. The anisotropic displacement factor exponent takes the form: -2π2[ h2a*2U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| O(1) | 27(1) | 32(1) | 18(1) | 4(1) | 1(1) | 0(1) |
| O(2) | 42(1) | 32(1) | 25(1) | 0(1) | 12(1) | -10(1) |
| O(3) | 28(1) | 29(1) | 19(1) | 4(1) | 2(1) | 1(1) |
| C(1) | 22(1) | 22(1) | 25(1) | 3(1) | 4(1) | 2(1) |
| C(2) | 21(1) | 25(1) | 28(1) | 1(1) | -1(1) | 2(1) |
| C(3) | 20(1) | 22(1) | 21(1) | 3(1) | 1(1) | 3(1) |
| C(4) | 22(1) | 20(1) | 17(1) | 2(1) | 2(1) | 3(1) |
| C(5) | 23(1) | 19(1) | 19(1) | -1(1) | -1(1) | 4(1) |
| C(6) | 23(1) | 21(1) | 20(1) | 0(1) | 0(1) | 3(1) |
| C(7) | 28(1) | 21(1) | 25(1) | 3(1) | 0(1) | 2(1) |
| C(8) | 35(1) | 21(1) | 31(1) | 1(1) | -4(1) | 9(1) |
| C(9) | 28(1) | 28(1) | 33(1) | -2(1) | 0(1) | 11(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(10) | 24(1) | 24(1) | 24(1) | 0(1) | 2(1) | 4(1) |
| C(11) | 23(1) | 24(1) | 29(1) | 1(1) | 0(1) | 7(1) |
| C(12) | 41(1) | 33(1) | 38(1) | 7(1) | -1(1) | 17(1) |
| C(13) | 29(1) | 40(1) | 37(1) | 2(1) | 7(1) | 14(1) |
| C(14) | 20(1) | 19(1) | 22(1) | 2(1) | 1(1) | 6(1) |
| C(15) | 24(1) | 21(1) | 24(1) | 3(1) | 4(1) | 7(1) |
| C(16) | 21(1) | 21(1) | 33(1) | 3(1) | 2(1) | 3(1) |
| C(17) | 27(1) | 24(1) | 31(1) | -3(1) | -5(1) | 2(1) |
| C(18) | 31(1) | 29(1) | 22(1) | 0(1) | -3(1) | 6(1) |
| C(19) | 22(1) | 22(1) | 23(1) | 4(1) | 1(1) | 6(1) |
| C(20) | 38(1) | 33(1) | 29(1) | 7(1) | 10(1) | -1(1) |
| C(21) | 37(1) | 41(1) | 21(1) | 4(1) | 5(1) | 6(1) |

Hydrogen coordinates ( x 104) and isotropic displacement parameters (Å2x 103) for liu100.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1O) | 9540(20) | 1230(20) | 470(15) | 53(5) |
| H(1) | 5431(19) | -1659(17) | 3178(12) | 27(3) |
| H(2A) | 4248(19) | -1276(17) | 1431(11) | 29(4) |
| H(2B) | 5807(19) | -1754(18) | 860(12) | 31(4) |
| H(7) | 6740(20) | -4231(18) | 3154(12) | 32(4) |
| H(8) | 9208(19) | -4828(18) | 2814(12) | 32(4) |
| H(9) | 11490(20) | -3014(19) | 1955(12) | 38(4) |

|  |  |  |  |  |
|---|---|---|---|---|
| H(10) | 11322(19) | -583(17) | 1464(11) | 28(3) |
| H(11) | 7251(18) | 2458(17) | 2887(11) | 27(3) |
| H(12A) | 5520(20) | 3280(20) | 1725(14) | 48(5) |
| H(12B) | 6650(20) | 2580(20) | 1015(14) | 48(5) |
| H(12C) | 4620(20) | 1470(20) | 1103(13) | 44(4) |
| H(13A) | 3750(20) | 260(20) | 2980(14) | 54(5) |
| H(13B) | 4470(20) | 2110(20) | 3441(14) | 47(5) |
| H(13C) | 5180(20) | 864(19) | 3958(13) | 39(4) |
| H(16) | 13535(19) | 5300(18) | 2243(12) | 33(4) |
| H(17) | 13410(20) | 5550(20) | 4131(13) | 40(4) |
| H(18) | 11258(19) | 3574(18) | 4958(13) | 34(4) |
| H(20A) | 13810(30) | 4450(20) | 593(15) | 62(6) |
| H(20B) | 12390(20) | 3892(19) | -440(13) | 39(4) |
| H(20C) | 12340(20) | 5250(20) | 481(15) | 57(5) |
| H(21A) | 8430(20) | 2170(20) | 5341(14) | 48(5) |
| H(21B) | 7710(20) | 180(20) | 5265(13) | 46(4) |
| H(21C) | 9740(20) | 1190(18) | 5559(13) | 36(4) |

Torsion angles [°] for liu100.

|  |  |
|---|---|
| C(6)-C(1)-C(2)-C(3) | -97.12(11) |
| C(1)-C(2)-C(3)-C(11) | -116.83(12) |
| C(1)-C(2)-C(3)-C(4) | 98.14(11) |
| C(6)-C(1)-C(3)-C(2) | 106.62(11) |
| C(6)-C(1)-C(3)-C(11) | -148.75(11) |
| C(2)-C(1)-C(3)-C(11) | 104.63(13) |

| | |
|---|---|
| C(6)-C(1)-C(3)-C(4) | -0.07(12) |
| C(2)-C(1)-C(3)-C(4) | -106.69(10) |
| C(2)-C(3)-C(4)-O(1) | 53.77(12) |
| C(1)-C(3)-C(4)-O(1) | 118.34(10) |
| C(11)-C(3)-C(4)-O(1) | -90.72(11) |
| C(2)-C(3)-C(4)-C(5) | -62.50(11) |
| C(1)-C(3)-C(4)-C(5) | 2.07(11) |
| C(11)-C(3)-C(4)-C(5) | 153.01(10) |
| C(2)-C(3)-C(4)-C(14) | 179.73(9) |
| C(1)-C(3)-C(4)-C(14) | -115.70(10) |
| C(11)-C(3)-C(4)-C(14) | 35.24(14) |
| O(1)-C(4)-C(5)-C(10) | 63.15(14) |
| C(14)-C(4)-C(5)-C(10) | -61.63(14) |
| C(3)-C(4)-C(5)-C(10) | 176.38(11) |
| O(1)-C(4)-C(5)-C(6) | -116.81(10) |
| C(14)-C(4)-C(5)-C(6) | 118.41(10) |
| C(3)-C(4)-C(5)-C(6) | -3.59(12) |
| C(10)-C(5)-C(6)-C(7) | 0.84(17) |
| C(4)-C(5)-C(6)-C(7) | -179.20(10) |
| C(10)-C(5)-C(6)-C(1) | -176.21(10) |
| C(4)-C(5)-C(6)-C(1) | 3.76(13) |
| C(3)-C(1)-C(6)-C(7) | -178.90(11) |
| C(2)-C(1)-C(6)-C(7) | -115.25(13) |
| C(3)-C(1)-C(6)-C(5) | -2.24(13) |
| C(2)-C(1)-C(6)-C(5) | 61.42(12) |

| | |
|---|---|
| C(5)-C(6)-C(7)-C(8) | -0.11(17) |
| C(1)-C(6)-C(7)-C(8) | 176.28(11) |
| C(6)-C(7)-C(8)-C(9) | -0.57(18) |
| C(7)-C(8)-C(9)-C(10) | 0.53(19) |
| C(6)-C(5)-C(10)-C(9) | -0.87(17) |
| C(4)-C(5)-C(10)-C(9) | 179.17(11) |
| C(8)-C(9)-C(10)-C(5) | 0.19(18) |
| C(2)-C(3)-C(11)-C(13) | 63.94(14) |
| C(1)-C(3)-C(11)-C(13) | -7.76(17) |
| C(4)-C(3)-C(11)-C(13) | -153.25(11) |
| C(2)-C(3)-C(11)-C(12) | -61.11(14) |
| C(1)-C(3)-C(11)-C(12) | -132.81(12) |
| C(4)-C(3)-C(11)-C(12) | 81.69(13) |
| O(1)-C(4)-C(14)-C(15) | -14.05(16) |
| C(5)-C(4)-C(14)-C(15) | 109.16(12) |
| C(3)-C(4)-C(14)-C(15) | -136.36(11) |
| O(1)-C(4)-C(14)-C(19) | 170.55(10) |
| C(5)-C(4)-C(14)-C(19) | -66.24(13) |
| C(3)-C(4)-C(14)-C(19) | 48.23(14) |
| C(20)-O(2)-C(15)-C(16) | -10.77(19) |
| C(20)-O(2)-C(15)-C(14) | 170.76(12) |
| C(19)-C(14)-C(15)-O(2) | 175.15(10) |
| C(4)-C(14)-C(15)-O(2) | -0.39(17) |
| C(19)-C(14)-C(15)-C(16) | -3.29(17) |
| C(4)-C(14)-C(15)-C(16) | -178.83(10) |

| | |
|---|---|
| O(2)-C(15)-C(16)-C(17) | -177.45(12) |
| C(14)-C(15)-C(16)-C(17) | 0.95(18) |
| C(15)-C(16)-C(17)-C(18) | 1.0(2) |
| C(16)-C(17)-C(18)-C(19) | -0.3(2) |
| C(21)-O(3)-C(19)-C(18) | 6.50(18) |
| C(21)-O(3)-C(19)-C(14) | -173.41(11) |
| C(17)-C(18)-C(19)-O(3) | 177.80(11) |
| C(17)-C(18)-C(19)-C(14) | -2.30(19) |
| C(15)-C(14)-C(19)-O(3) | -176.11(10) |
| C(4)-C(14)-C(19)-O(3) | -0.29(15) |
| C(15)-C(14)-C(19)-C(18) | 3.98(17) |
| C(4)-C(14)-C(19)-C(18) | 179.80(11) |

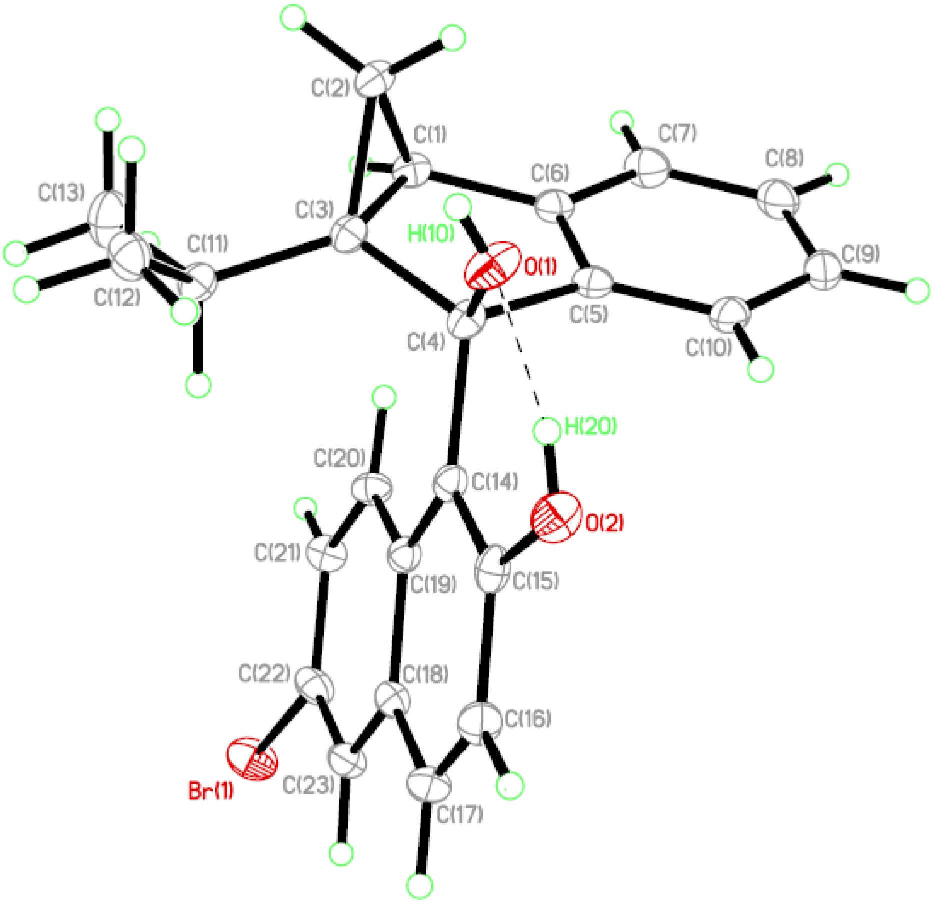
Symmetry transformations used to generate equivalent atoms:

Hydrogen bonds for liu100 [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(1)-H(1O)...O(2) | 0.859(19) | 1.806(19) | 2.5536(12) | 144.3(17) |

Symmetry transformations used to generate equivalent atoms:

## ***Crystallographic Data for 27 (liu 98) Chapter IV***



Crystal data and structure refinement for liu98.

Identification code liu98

Empirical formula C23 H21 Br O2

Formula weight 409.31

Temperature 173(2) K

Wavelength 0.71073 Å

Crystal system Monoclinic

Space group P2(1)

Unit cell dimensions a = 10.6135(12) Å α= 90°.

| | | |
|---|---|---|
| | b = 7.9057(9) Å | β= 108.594(2)°. |
| | c = 11.4416(13) Å | γ = 90°. |
| Volume | 909.92(18) Å3 | |
| Z | 2 | |
| Density (calculated) | 1.494 Mg/m3 | |
| Absorption coefficient | 2.273 mm-1 | |
| F(000) | 420 | |
| Crystal size | 0.19 x 0.13 x 0.08 mm3 | |
| Theta range for data collection | 1.88 to 26.99°. | |
| Index ranges | -13<=h<=13, -10<=k<=10, -14<=l<=14 | |
| Reflections collected | 10130 | |
| Independent reflections | 3932 [R(int) = 0.0222] | |
| Completeness to theta = 26.99° | 100.0 % | |
| Absorption correction | None | |
| Max. and min. transmission | 0.8391 and 0.6719 | |
| Refinement method | Full-matrix least-squares on F2 | |
| Data / restraints / parameters | 3932 / 1 / 243 | |
| Goodness-of-fit on F2 | 1.056 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0296, wR2 = 0.0706 | |
| R indices (all data) | R1 = 0.0325, wR2 = 0.0717 | |
| Absolute structure parameter | 0.024(7) | |
| Largest diff. peak and hole | 0.485 and -0.184 e.Å-3 | |

Atomic coordinates ( x 104) and equivalent isotropic displacement parameters (Å2x 103) for liu98. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

|  | x | y | z | U(eq) |
|---|---|---|---|---|
| Br(1) | 7278(1) | 8848(1) | -2998(1) | 41(1) |
| O(1) | 8980(2) | 5739(3) | 4387(2) | 32(1) |
| O(2) | 10911(2) | 7534(2) | 4487(2) | 31(1) |
| C(1) | 5849(2) | 5271(3) | 2168(2) | 24(1) |
| C(2) | 6447(2) | 3971(4) | 3143(2) | 26(1) |
| C(3) | 7307(2) | 4773(3) | 2471(2) | 22(1) |
| C(4) | 8155(2) | 6281(3) | 3167(2) | 22(1) |
| C(5) | 7115(2) | 7510(3) | 3332(2) | 23(1) |
| C(6) | 5824(2) | 6972(3) | 2702(2) | 25(1) |
| C(7) | 4748(3) | 7929(4) | 2752(3) | 33(1) |
| C(8) | 4979(3) | 9408(3) | 3451(3) | 34(1) |
| C(9) | 6260(3) | 9912(3) | 4098(2) | 32(1) |
| C(10) | 7341(2) | 8958(4) | 4035(2) | 28(1) |
| C(11) | 7867(2) | 3616(3) | 1681(2) | 25(1) |
| C(12) | 8980(3) | 2501(3) | 2497(2) | 31(1) |
| C(13) | 6816(3) | 2520(4) | 770(3) | 42(1) |
| C(14) | 9079(2) | 7197(3) | 2556(2) | 21(1) |
| C(15) | 10346(2) | 7742(3) | 3239(2) | 24(1) |
| C(16) | 11177(2) | 8597(4) | 2697(2) | 29(1) |
| C(17) | 10780(2) | 8965(4) | 1485(2) | 30(1) |
| C(18) | 9481(2) | 8511(3) | 731(2) | 25(1) |
| C(19) | 8624(2) | 7646(3) | 1268(2) | 21(1) |
| C(20) | 7324(2) | 7282(3) | 459(2) | 24(1) |

|  |  |  |  |  |
|---|---|---|---|---|
| C(21) | 6942(2) | 7628(3) | -777(2) | 26(1) |
| C(22) | 7830(3) | 8446(3) | -1272(2) | 28(1) |
| C(23) | 9051(2) | 8910(4) | -546(2) | 29(1) |

Bond lengths [Å] and angles [°] for liu98.

|  |  |
|---|---|
| Br(1)-C(22) | 1.899(2) |
| O(1)-C(4) | 1.456(3) |
| O(1)-H(1O) | 0.63(3) |
| O(2)-C(15) | 1.371(3) |
| O(2)-H(2O) | 0.75(3) |
| C(1)-C(6) | 1.481(3) |
| C(1)-C(2) | 1.501(3) |
| C(1)-C(3) | 1.526(3) |
| C(1)-H(1A) | 1.0000 |
| C(2)-C(3) | 1.508(3) |
| C(2)-H(2A) | 0.9900 |
| C(2)-H(2B) | 0.9900 |
| C(3)-C(11) | 1.533(3) |
| C(3)-C(4) | 1.551(3) |
| C(4)-C(5) | 1.527(3) |
| C(4)-C(14) | 1.553(3) |
| C(5)-C(10) | 1.376(4) |
| C(5)-C(6) | 1.396(3) |
| C(6)-C(7) | 1.386(4) |
| C(7)-C(8) | 1.394(4) |

| | |
|---|---|
| C(7)-H(7A) | 0.9500 |
| C(8)-C(9) | 1.383(4) |
| C(8)-H(8A) | 0.9500 |
| C(9)-C(10) | 1.394(4) |
| C(9)-H(9A) | 0.9500 |
| C(10)-H(10A) | 0.9500 |
| C(11)-C(12) | 1.530(3) |
| C(11)-C(13) | 1.529(4) |
| C(11)-H(11A) | 1.0000 |
| C(12)-H(12A) | 0.9800 |
| C(12)-H(12B) | 0.9800 |
| C(12)-H(12C) | 0.9800 |
| C(13)-H(13A) | 0.9800 |
| C(13)-H(13B) | 0.9800 |
| C(13)-H(13C) | 0.9800 |
| C(14)-C(15) | 1.391(3) |
| C(14)-C(19) | 1.441(3) |
| C(15)-C(16) | 1.403(4) |
| C(16)-C(17) | 1.346(3) |
| C(16)-H(16A) | 0.9500 |
| C(17)-C(18) | 1.419(3) |
| C(17)-H(17A) | 0.9500 |
| C(18)-C(19) | 1.425(3) |
| C(18)-C(23) | 1.420(3) |
| C(19)-C(20) | 1.425(3) |

| | |
|---|---|
| C(20)-C(21) | 1.369(3) |
| C(20)-H(20A) | 0.9500 |
| C(21)-C(22) | 1.402(3) |
| C(21)-H(21A) | 0.9500 |
| C(22)-C(23) | 1.348(3) |
| C(23)-H(23A) | 0.9500 |

| | |
|---|---|
| C(4)-O(1)-H(1O) | 117(3) |
| C(15)-O(2)-H(2O) | 105(2) |
| C(6)-C(1)-C(2) | 111.9(2) |
| C(6)-C(1)-C(3) | 106.9(2) |
| C(2)-C(1)-C(3) | 59.76(15) |
| C(6)-C(1)-H(1A) | 120.9 |
| C(2)-C(1)-H(1A) | 120.9 |
| C(3)-C(1)-H(1A) | 120.9 |
| C(1)-C(2)-C(3) | 60.95(15) |
| C(1)-C(2)-H(2A) | 117.7 |
| C(3)-C(2)-H(2A) | 117.7 |
| C(1)-C(2)-H(2B) | 117.7 |
| C(3)-C(2)-H(2B) | 117.7 |
| H(2A)-C(2)-H(2B) | 114.8 |
| C(2)-C(3)-C(1) | 59.29(15) |
| C(2)-C(3)-C(11) | 117.5(2) |
| C(1)-C(3)-C(11) | 125.1(2) |
| C(2)-C(3)-C(4) | 114.1(2) |

| | |
|---|---|
| C(1)-C(3)-C(4) | 107.38(19) |
| C(11)-C(3)-C(4) | 119.4(2) |
| O(1)-C(4)-C(5) | 107.84(19) |
| O(1)-C(4)-C(3) | 109.81(19) |
| C(5)-C(4)-C(3) | 103.22(19) |
| O(1)-C(4)-C(14) | 107.19(19) |
| C(5)-C(4)-C(14) | 110.11(19) |
| C(3)-C(4)-C(14) | 118.26(19) |
| C(10)-C(5)-C(6) | 121.0(2) |
| C(10)-C(5)-C(4) | 127.2(2) |
| C(6)-C(5)-C(4) | 111.8(2) |
| C(7)-C(6)-C(5) | 119.9(2) |
| C(7)-C(6)-C(1) | 129.5(2) |
| C(5)-C(6)-C(1) | 110.2(2) |
| C(6)-C(7)-C(8) | 119.0(3) |
| C(6)-C(7)-H(7A) | 120.5 |
| C(8)-C(7)-H(7A) | 120.5 |
| C(9)-C(8)-C(7) | 120.8(2) |
| C(9)-C(8)-H(8A) | 119.6 |
| C(7)-C(8)-H(8A) | 119.6 |
| C(8)-C(9)-C(10) | 120.1(2) |
| C(8)-C(9)-H(9A) | 120.0 |
| C(10)-C(9)-H(9A) | 120.0 |
| C(5)-C(10)-C(9) | 119.2(2) |
| C(5)-C(10)-H(10A) | 120.4 |

| | |
|---|---|
| C(9)-C(10)-H(10A) | 120.4 |
| C(12)-C(11)-C(13) | 110.1(2) |
| C(12)-C(11)-C(3) | 110.64(19) |
| C(13)-C(11)-C(3) | 113.8(2) |
| C(12)-C(11)-H(11A) | 107.3 |
| C(13)-C(11)-H(11A) | 107.3 |
| C(3)-C(11)-H(11A) | 107.3 |
| C(11)-C(12)-H(12A) | 109.5 |
| C(11)-C(12)-H(12B) | 109.5 |
| H(12A)-C(12)-H(12B) | 109.5 |
| C(11)-C(12)-H(12C) | 109.5 |
| H(12A)-C(12)-H(12C) | 109.5 |
| H(12B)-C(12)-H(12C) | 109.5 |
| C(11)-C(13)-H(13A) | 109.5 |
| C(11)-C(13)-H(13B) | 109.5 |
| H(13A)-C(13)-H(13B) | 109.5 |
| C(11)-C(13)-H(13C) | 109.5 |
| H(13A)-C(13)-H(13C) | 109.5 |
| H(13B)-C(13)-H(13C) | 109.5 |
| C(15)-C(14)-C(19) | 116.6(2) |
| C(15)-C(14)-C(4) | 121.8(2) |
| C(19)-C(14)-C(4) | 121.42(19) |
| O(2)-C(15)-C(14) | 124.9(2) |
| O(2)-C(15)-C(16) | 112.9(2) |
| C(14)-C(15)-C(16) | 122.2(2) |

| | |
|---|---|
| C(17)-C(16)-C(15) | 121.6(2) |
| C(17)-C(16)-H(16A) | 119.2 |
| C(15)-C(16)-H(16A) | 119.2 |
| C(16)-C(17)-C(18) | 119.8(2) |
| C(16)-C(17)-H(17A) | 120.1 |
| C(18)-C(17)-H(17A) | 120.1 |
| C(17)-C(18)-C(19) | 119.3(2) |
| C(17)-C(18)-C(23) | 120.1(2) |
| C(19)-C(18)-C(23) | 120.7(2) |
| C(18)-C(19)-C(20) | 115.9(2) |
| C(18)-C(19)-C(14) | 120.5(2) |
| C(20)-C(19)-C(14) | 123.7(2) |
| C(21)-C(20)-C(19) | 122.5(2) |
| C(21)-C(20)-H(20A) | 118.8 |
| C(19)-C(20)-H(20A) | 118.8 |
| C(20)-C(21)-C(22) | 119.6(2) |
| C(20)-C(21)-H(21A) | 120.2 |
| C(22)-C(21)-H(21A) | 120.2 |
| C(23)-C(22)-C(21) | 121.0(2) |
| C(23)-C(22)-Br(1) | 120.81(18) |
| C(21)-C(22)-Br(1) | 118.21(19) |
| C(22)-C(23)-C(18) | 120.3(2) |
| C(22)-C(23)-H(23A) | 119.9 |
| C(18)-C(23)-H(23A) | 119.9 |

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters (Å2x 103)for liu98. The anisotropic displacement factor exponent takes the form: -2π2[ h2a*2U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Br(1) | 45(1) | 54(1) | 27(1) | 12(1) | 14(1) | 3(1) |
| O(1) | 38(1) | 26(1) | 23(1) | 9(1) | -6(1) | -6(1) |
| O(2) | 26(1) | 34(1) | 27(1) | -2(1) | 0(1) | -4(1) |
| C(1) | 23(1) | 24(1) | 24(1) | 2(1) | 6(1) | -2(1) |
| C(2) | 28(1) | 20(1) | 28(1) | 1(1) | 7(1) | -4(1) |
| C(3) | 23(1) | 19(1) | 22(1) | 2(1) | 4(1) | 2(1) |
| C(4) | 23(1) | 19(1) | 20(1) | 3(1) | 2(1) | 1(1) |
| C(5) | 25(1) | 24(1) | 21(1) | 5(1) | 10(1) | -1(1) |
| C(6) | 28(1) | 24(1) | 24(1) | 4(1) | 11(1) | -1(1) |
| C(7) | 27(1) | 34(2) | 40(2) | 6(1) | 13(1) | 5(1) |
| C(8) | 39(2) | 28(2) | 44(2) | 7(1) | 24(1) | 10(1) |
| C(9) | 49(2) | 23(1) | 29(1) | 1(1) | 20(1) | 0(1) |
| C(10) | 35(1) | 26(1) | 22(1) | 1(1) | 10(1) | -7(1) |
| C(11) | 26(1) | 22(1) | 25(1) | 2(1) | 6(1) | 1(1) |
| C(12) | 31(1) | 31(1) | 33(1) | 2(1) | 12(1) | 9(1) |
| C(13) | 37(2) | 40(2) | 45(2) | -15(1) | 6(1) | -1(1) |
| C(14) | 19(1) | 17(1) | 25(1) | -2(1) | 6(1) | 1(1) |
| C(15) | 21(1) | 21(1) | 26(1) | -5(1) | 2(1) | 4(1) |
| C(16) | 17(1) | 32(2) | 37(1) | -7(1) | 7(1) | -4(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(17) | 23(1) | 32(1) | 40(1) | -3(2) | 16(1) | -4(1) |
| C(18) | 23(1) | 24(2) | 30(1) | -3(1) | 12(1) | 2(1) |
| C(19) | 20(1) | 19(1) | 26(1) | -1(1) | 8(1) | 2(1) |
| C(20) | 19(1) | 25(1) | 28(1) | 5(1) | 7(1) | 0(1) |
| C(21) | 22(1) | 30(1) | 24(1) | 5(1) | 5(1) | 4(1) |
| C(22) | 33(1) | 32(2) | 22(1) | 7(1) | 14(1) | 8(1) |
| C(23) | 32(1) | 28(1) | 34(1) | 2(2) | 19(1) | 1(2) |

Hydrogen coordinates ( x 104) and isotropic displacement parameters (Å2x 103) for liu98.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 5180 | 4942 | 1365 | 29 |
| H(2A) | 6180 | 2777 | 2951 | 31 |
| H(2B) | 6608 | 4300 | 4014 | 31 |
| H(7A) | 3866 | 7582 | 2315 | 40 |
| H(8A) | 4247 | 10077 | 3485 | 41 |
| H(9A) | 6403 | 10910 | 4585 | 38 |
| H(10A) | 8223 | 9303 | 4472 | 33 |
| H(11A) | 8269 | 4359 | 1187 | 30 |
| H(12A) | 9324 | 1769 | 1977 | 47 |
| H(12B) | 8631 | 1802 | 3031 | 47 |
| H(12C) | 9700 | 3218 | 3007 | 47 |
| H(13A) | 7241 | 1814 | 300 | 63 |

|  |  |  |  |  |
|---|---|---|---|---|
| H(13B) | 6150 | 3249 | 204 | 63 |
| H(13C) | 6384 | 1795 | 1224 | 63 |
| H(16A) | 12042 | 8924 | 3198 | 35 |
| H(17A) | 11367 | 9526 | 1136 | 36 |
| H(20A) | 6698 | 6780 | 789 | 29 |
| H(21A) | 6081 | 7317 | -1297 | 31 |
| H(23A) | 9626 | 9506 | -890 | 35 |
| H(1O) | 8880(30) | 5000(40) | 4550(30) | 18(9) |
| H(2O) | 10440(30) | 6950(30) | 4670(20) | 13(7) |

Torsion angles [°] for liu98.

|  |  |
|---|---|
| C(6)-C(1)-C(2)-C(3) | -97.4(2) |
| C(1)-C(2)-C(3)-C(11) | -116.4(2) |
| C(1)-C(2)-C(3)-C(4) | 96.6(2) |
| C(6)-C(1)-C(3)-C(2) | 106.0(2) |
| C(6)-C(1)-C(3)-C(11) | -150.2(2) |
| C(2)-C(1)-C(3)-C(11) | 103.8(3) |
| C(6)-C(1)-C(3)-C(4) | -2.2(2) |
| C(2)-C(1)-C(3)-C(4) | -108.1(2) |
| C(2)-C(3)-C(4)-O(1) | 56.5(3) |
| C(1)-C(3)-C(4)-O(1) | 120.0(2) |
| C(11)-C(3)-C(4)-O(1) | -89.7(3) |
| C(2)-C(3)-C(4)-C(5) | -58.2(2) |
| C(1)-C(3)-C(4)-C(5) | 5.3(2) |
| C(11)-C(3)-C(4)-C(5) | 155.51(19) |

| | |
|---|---|
| C(2)-C(3)-C(4)-C(14) | 179.94(19) |
| C(1)-C(3)-C(4)-C(14) | -116.6(2) |
| C(11)-C(3)-C(4)-C(14) | 33.7(3) |
| O(1)-C(4)-C(5)-C(10) | 54.5(3) |
| C(3)-C(4)-C(5)-C(10) | 170.7(2) |
| C(14)-C(4)-C(5)-C(10) | -62.1(3) |
| O(1)-C(4)-C(5)-C(6) | -123.1(2) |
| C(3)-C(4)-C(5)-C(6) | -6.9(2) |
| C(14)-C(4)-C(5)-C(6) | 120.2(2) |
| C(10)-C(5)-C(6)-C(7) | 1.9(4) |
| C(4)-C(5)-C(6)-C(7) | 179.7(2) |
| C(10)-C(5)-C(6)-C(1) | -171.9(2) |
| C(4)-C(5)-C(6)-C(1) | 5.9(3) |
| C(2)-C(1)-C(6)-C(7) | -111.7(3) |
| C(3)-C(1)-C(6)-C(7) | -175.2(2) |
| C(2)-C(1)-C(6)-C(5) | 61.4(3) |
| C(3)-C(1)-C(6)-C(5) | -2.2(3) |
| C(5)-C(6)-C(7)-C(8) | -1.0(4) |
| C(1)-C(6)-C(7)-C(8) | 171.4(2) |
| C(6)-C(7)-C(8)-C(9) | -0.6(4) |
| C(7)-C(8)-C(9)-C(10) | 1.3(4) |
| C(6)-C(5)-C(10)-C(9) | -1.1(4) |
| C(4)-C(5)-C(10)-C(9) | -178.6(2) |
| C(8)-C(9)-C(10)-C(5) | -0.5(4) |
| C(2)-C(3)-C(11)-C(12) | -73.1(3) |

| | |
|---|---|
| C(1)-C(3)-C(11)-C(12) | -143.4(2) |
| C(4)-C(3)-C(11)-C(12) | 72.0(3) |
| C(2)-C(3)-C(11)-C(13) | 51.4(3) |
| C(1)-C(3)-C(11)-C(13) | -18.8(4) |
| C(4)-C(3)-C(11)-C(13) | -163.5(2) |
| O(1)-C(4)-C(14)-C(15) | -15.5(3) |
| C(5)-C(4)-C(14)-C(15) | 101.5(2) |
| C(3)-C(4)-C(14)-C(15) | -140.2(2) |
| O(1)-C(4)-C(14)-C(19) | 169.6(2) |
| C(5)-C(4)-C(14)-C(19) | -73.4(3) |
| C(3)-C(4)-C(14)-C(19) | 44.9(3) |
| C(19)-C(14)-C(15)-O(2) | 175.5(2) |
| C(4)-C(14)-C(15)-O(2) | 0.3(3) |
| C(19)-C(14)-C(15)-C(16) | -3.7(3) |
| C(4)-C(14)-C(15)-C(16) | -178.9(2) |
| O(2)-C(15)-C(16)-C(17) | -178.0(3) |
| C(14)-C(15)-C(16)-C(17) | 1.3(4) |
| C(15)-C(16)-C(17)-C(18) | 1.2(4) |
| C(16)-C(17)-C(18)-C(19) | -1.0(4) |
| C(16)-C(17)-C(18)-C(23) | 179.4(3) |
| C(17)-C(18)-C(19)-C(20) | 178.1(2) |
| C(23)-C(18)-C(19)-C(20) | -2.3(3) |
| C(17)-C(18)-C(19)-C(14) | -1.6(3) |
| C(23)-C(18)-C(19)-C(14) | 178.1(2) |
| C(15)-C(14)-C(19)-C(18) | 3.8(3) |

| | |
|---|---|
| C(4)-C(14)-C(19)-C(18) | 179.0(2) |
| C(15)-C(14)-C(19)-C(20) | -175.8(2) |
| C(4)-C(14)-C(19)-C(20) | -0.7(3) |
| C(18)-C(19)-C(20)-C(21) | 4.5(3) |
| C(14)-C(19)-C(20)-C(21) | -175.9(2) |
| C(19)-C(20)-C(21)-C(22) | -3.2(4) |
| C(20)-C(21)-C(22)-C(23) | -0.6(4) |
| C(20)-C(21)-C(22)-Br(1) | 178.33(19) |
| C(21)-C(22)-C(23)-C(18) | 2.7(4) |
| Br(1)-C(22)-C(23)-C(18) | -176.2(2) |
| C(17)-C(18)-C(23)-C(22) | 178.4(3) |
| C(19)-C(18)-C(23)-C(22) | -1.2(4) |

Symmetry transformations used to generate equivalent atoms:

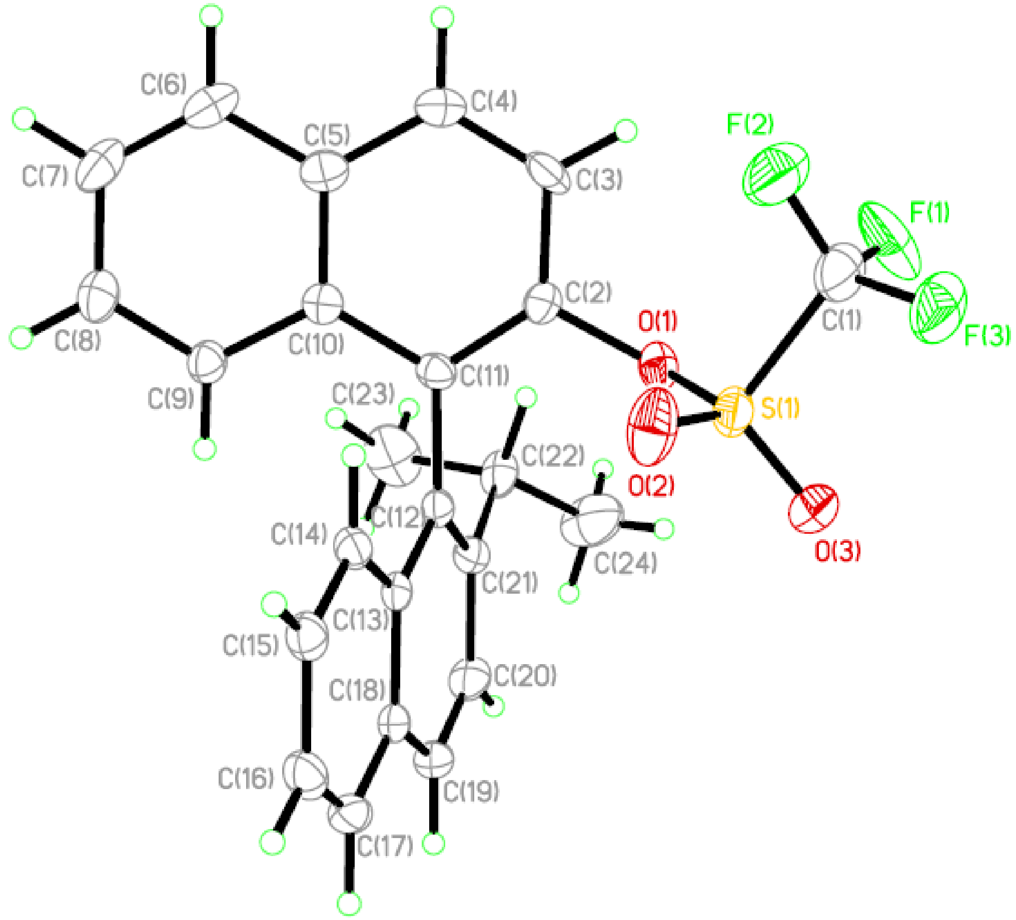
Hydrogen bonds for liu98 [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(1)-H(1O)...O(2)#1 | 0.63(3) | 2.21(3) | 2.828(3) | 164(3) |
| O(2)-H(2O)...O(1) | 0.75(3) | 1.77(3) | 2.465(3) | 154(3) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y-1/2,-z+1

## ***Crystallographic Data for 17 (liu 110) Chapter IV***



Crystal data and structure refinement for liu110.

| | |
|---|---|
| Identification code | liu110 |
| Empirical formula | C24 H19 F3 O3 S |
| Formula weight | 444.45 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Hexagonal |
| Space group | P6(5) |

| | | |
|---|---|---|
| Unit cell dimensions | a = 11.5918(4) Å | α= 90°. |
| | b = 11.5918(4) Å | β= 90°. |
| | c = 55.440(4) Å | γ = 120°. |
| Volume | 6451.4(6) Å3 | |
| Z | 12 | |
| Density (calculated) | 1.373 Mg/m3 | |
| Absorption coefficient | 0.199 mm-1 | |
| F(000) | 2760 | |
| Crystal size | 0.19 x 0.18 x 0.10 mm3 | |
| Theta range for data collection | 2.03 to 25.00°. | |
| Index ranges | -13<=h<=13, -13<=k<=8, -65<=l<=63 | |
| Reflections collected | 35199 | |
| Independent reflections | 7553 [R(int) = 0.0552] | |
| Completeness to theta = 25.00° | 100.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9803 and 0.9631 | |
| Refinement method | Full-matrix least-squares on F2 | |
| Data / restraints / parameters | 7553 / 1 / 559 | |
| Goodness-of-fit on F2 | 1.033 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0569, wR2 = 0.1399 | |
| R indices (all data) | R1 = 0.0700, wR2 = 0.1490 | |
| Absolute structure parameter | 0.03(9) | |
| Largest diff. peak and hole | 0.660 and -0.273 e.Å-3 | |

Atomic coordinates ( x 104) and equivalent isotropic displacement parameters (Å2x 103) for liu110. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| S(1) | 8402(1) | 7494(1) | 1448(1) | 42(1) |
| O(1) | 7894(3) | 8060(3) | 1247(1) | 40(1) |
| O(2) | 7423(4) | 6780(4) | 1623(1) | 67(1) |
| O(3) | 9108(3) | 6960(3) | 1330(1) | 56(1) |
| F(1) | 10450(4) | 9865(4) | 1430(1) | 103(1) |
| F(2) | 9130(4) | 9545(5) | 1725(1) | 108(2) |
| F(3) | 10394(4) | 8700(4) | 1736(1) | 83(1) |
| C(1) | 9671(6) | 9018(7) | 1595(1) | 66(2) |
| C(2) | 6785(4) | 8245(4) | 1295(1) | 35(1) |
| C(3) | 7083(5) | 9492(4) | 1386(1) | 43(1) |
| C(4) | 6074(5) | 9721(5) | 1435(1) | 43(1) |
| C(5) | 4738(5) | 8715(4) | 1392(1) | 38(1) |
| C(6) | 3673(5) | 8927(5) | 1439(1) | 50(1) |
| C(7) | 2404(5) | 7986(6) | 1394(1) | 56(1) |
| C(8) | 2119(5) | 6764(5) | 1291(1) | 46(1) |
| C(9) | 3135(4) | 6529(4) | 1236(1) | 35(1) |
| C(10) | 4469(4) | 7480(4) | 1286(1) | 31(1) |
| C(11) | 5536(4) | 7235(4) | 1240(1) | 30(1) |
| C(12) | 5297(4) | 5948(4) | 1131(1) | 30(1) |
| C(13) | 4656(4) | 4754(4) | 1275(1) | 29(1) |
| C(14) | 4256(4) | 4747(4) | 1516(1) | 31(1) |
| C(15) | 3630(4) | 3593(4) | 1646(1) | 38(1) |

|  |  |  |  |  |
|---|---|---|---|---|
| C(16) | 3368(4) | 2380(5) | 1543(1) | 42(1) |
| C(17) | 3739(4) | 2347(4) | 1310(1) | 40(1) |
| C(18) | 4384(4) | 3526(4) | 1169(1) | 32(1) |
| C(19) | 4772(4) | 3518(4) | 929(1) | 39(1) |
| C(20) | 5375(4) | 4647(5) | 798(1) | 41(1) |
| C(21) | 5636(4) | 5886(4) | 893(1) | 35(1) |
| C(22) | 6203(4) | 7131(5) | 723(1) | 41(1) |
| C(23) | 5065(7) | 7113(7) | 601(1) | 76(2) |
| C(24) | 7246(8) | 7208(7) | 547(1) | 89(2) |
| S(1') | 8503(1) | 9694(1) | 8970(1) | 43(1) |
| O(1') | 7738(3) | 10356(3) | 9080(1) | 40(1) |
| O(2') | 8404(5) | 8673(4) | 9120(1) | 78(1) |
| O(3') | 8255(4) | 9537(5) | 8723(1) | 77(1) |
| F(1') | 10571(3) | 11434(5) | 9215(1) | 111(2) |
| F(2') | 10335(4) | 12141(4) | 8880(1) | 101(1) |
| F(3') | 11002(3) | 10720(4) | 8894(1) | 72(1) |
| C(1') | 10209(5) | 11073(7) | 8998(1) | 62(2) |
| C(2') | 7135(4) | 9942(4) | 9315(1) | 31(1) |
| C(3') | 7900(4) | 10653(4) | 9515(1) | 37(1) |
| C(4') | 7337(4) | 10329(4) | 9735(1) | 37(1) |
| C(5') | 6007(4) | 9282(4) | 9767(1) | 31(1) |
| C(6') | 5407(5) | 8934(5) | 9995(1) | 40(1) |
| C(7') | 4133(5) | 7926(5) | 10021(1) | 44(1) |
| C(8') | 3402(4) | 7233(4) | 9819(1) | 38(1) |
| C(9') | 3924(4) | 7536(4) | 9594(1) | 32(1) |

|  |  |  |  |  |
|---|---|---|---|---|
| C(10') | 5259(4) | 8581(4) | 9559(1) | 27(1) |
| C(11') | 5836(4) | 8941(4) | 9324(1) | 27(1) |
| C(12') | 5041(4) | 8302(4) | 9099(1) | 27(1) |
| C(13') | 4750(4) | 6989(4) | 9035(1) | 29(1) |
| C(14') | 5170(4) | 6231(4) | 9171(1) | 37(1) |
| C(15') | 4847(5) | 4973(5) | 9105(1) | 46(1) |
| C(16') | 4110(5) | 4398(5) | 8897(1) | 45(1) |
| C(17') | 3698(5) | 5089(5) | 8757(1) | 41(1) |
| C(18') | 3992(4) | 6389(4) | 8820(1) | 34(1) |
| C(19') | 3534(4) | 7106(4) | 8685(1) | 33(1) |
| C(20') | 3802(4) | 8348(4) | 8754(1) | 35(1) |
| C(21') | 4555(4) | 8953(4) | 8963(1) | 31(1) |
| C(22') | 4792(4) | 10335(4) | 9033(1) | 38(1) |
| C(23') | 3469(5) | 10276(6) | 9083(1) | 59(1) |
| C(24') | 5540(6) | 11368(5) | 8836(1) | 58(1) |

Bond lengths [Å] and angles [°] for liu110.

|  |  |
|---|---|
| S(1)-O(2) | 1.406(4) |
| S(1)-O(3) | 1.408(3) |
| S(1)-O(1) | 1.548(3) |
| S(1)-C(1) | 1.832(6) |
| O(1)-C(2) | 1.429(5) |
| F(1)-C(1) | 1.317(8) |
| F(2)-C(1) | 1.291(7) |
| F(3)-C(1) | 1.325(6) |

| | |
|---|---|
| C(2)-C(11) | 1.366(6) |
| C(2)-C(3) | 1.402(6) |
| C(3)-C(4) | 1.349(7) |
| C(3)-H(3B) | 0.9500 |
| C(4)-C(5) | 1.418(7) |
| C(4)-H(4A) | 0.9500 |
| C(5)-C(6) | 1.399(6) |
| C(5)-C(10) | 1.429(6) |
| C(6)-C(7) | 1.346(7) |
| C(6)-H(6A) | 0.9500 |
| C(7)-C(8) | 1.406(7) |
| C(7)-H(7A) | 0.9500 |
| C(8)-C(9) | 1.369(6) |
| C(8)-H(8A) | 0.9500 |
| C(9)-C(10) | 1.407(6) |
| C(9)-H(9A) | 0.9500 |
| C(10)-C(11) | 1.424(6) |
| C(11)-C(12) | 1.501(5) |
| C(12)-C(21) | 1.389(6) |
| C(12)-C(13) | 1.441(6) |
| C(13)-C(14) | 1.414(6) |
| C(13)-C(18) | 1.424(6) |
| C(14)-C(15) | 1.366(6) |
| C(14)-H(14A) | 0.9500 |
| C(15)-C(16) | 1.403(6) |

| | |
|---|---|
| C(15)-H(15A) | 0.9500 |
| C(16)-C(17) | 1.373(7) |
| C(16)-H(16A) | 0.9500 |
| C(17)-C(18) | 1.420(6) |
| C(17)-H(17A) | 0.9500 |
| C(18)-C(19) | 1.402(6) |
| C(19)-C(20) | 1.350(6) |
| C(19)-H(19A) | 0.9500 |
| C(20)-C(21) | 1.414(6) |
| C(20)-H(20A) | 0.9500 |
| C(21)-C(22) | 1.568(6) |
| C(22)-C(23) | 1.472(8) |
| C(22)-C(24) | 1.522(7) |
| C(22)-H(22A) | 1.0000 |
| C(23)-H(23A) | 0.9800 |
| C(23)-H(23B) | 0.9800 |
| C(23)-H(23C) | 0.9800 |
| C(24)-H(24A) | 0.9800 |
| C(24)-H(24B) | 0.9800 |
| C(24)-H(24C) | 0.9800 |
| S(1')-O(3') | 1.393(4) |
| S(1')-O(2') | 1.403(4) |
| S(1')-O(1') | 1.558(3) |
| S(1')-C(1') | 1.824(6) |
| O(1')-C(2') | 1.445(5) |

|  |  |
|---|---|
| F(1')-C(1') | 1.273(7) |
| F(2')-C(1') | 1.343(8) |
| F(3')-C(1') | 1.313(6) |
| C(2')-C(11') | 1.366(6) |
| C(2')-C(3') | 1.402(6) |
| C(3')-C(4') | 1.348(6) |
| C(3')-H(3'B) | 0.9500 |
| C(4')-C(5') | 1.417(6) |
| C(4')-H(4'A) | 0.9500 |
| C(5')-C(6') | 1.401(6) |
| C(5')-C(10') | 1.429(6) |
| C(6')-C(7') | 1.357(7) |
| C(6')-H(6'A) | 0.9500 |
| C(7')-C(8') | 1.390(7) |
| C(7')-H(7'A) | 0.9500 |
| C(8')-C(9') | 1.355(6) |
| C(8')-H(8'A) | 0.9500 |
| C(9')-C(10') | 1.423(6) |
| C(9')-H(9'A) | 0.9500 |
| C(10')-C(11') | 1.427(5) |
| C(11')-C(12') | 1.507(5) |
| C(12')-C(21') | 1.373(6) |
| C(12')-C(13') | 1.430(6) |
| C(13')-C(14') | 1.418(6) |
| C(13')-C(18') | 1.434(6) |

| | |
|---|---|
| C(14')-C(15') | 1.362(6) |
| C(14')-H(14B) | 0.9500 |
| C(15')-C(16') | 1.392(7) |
| C(15')-H(15B) | 0.9500 |
| C(16')-C(17') | 1.361(7) |
| C(16')-H(16B) | 0.9500 |
| C(17')-C(18') | 1.412(6) |
| C(17')-H(17B) | 0.9500 |
| C(18')-C(19') | 1.407(6) |
| C(19')-C(20') | 1.367(6) |
| C(19')-H(19B) | 0.9500 |
| C(20')-C(21') | 1.407(6) |
| C(20')-H(20B) | 0.9500 |
| C(21')-C(22') | 1.534(6) |
| C(22')-C(23') | 1.526(7) |
| C(22')-C(24') | 1.529(7) |
| C(22')-H(22B) | 1.0000 |
| C(23')-H(23D) | 0.9800 |
| C(23')-H(23E) | 0.9800 |
| C(23')-H(23F) | 0.9800 |
| C(24')-H(24D) | 0.9800 |
| C(24')-H(24E) | 0.9800 |
| C(24')-H(24F) | 0.9800 |
| O(2)-S(1)-O(3) | 122.4(2) |
| O(2)-S(1)-O(1) | 112.28(19) |

| | |
|---|---|
| O(3)-S(1)-O(1) | 106.4(2) |
| O(2)-S(1)-C(1) | 106.3(3) |
| O(3)-S(1)-C(1) | 105.5(2) |
| O(1)-S(1)-C(1) | 101.8(2) |
| C(2)-O(1)-S(1) | 119.4(3) |
| F(2)-C(1)-F(1) | 110.5(6) |
| F(2)-C(1)-F(3) | 109.2(5) |
| F(1)-C(1)-F(3) | 108.9(5) |
| F(2)-C(1)-S(1) | 111.0(4) |
| F(1)-C(1)-S(1) | 109.2(4) |
| F(3)-C(1)-S(1) | 108.0(4) |
| C(11)-C(2)-C(3) | 125.0(4) |
| C(11)-C(2)-O(1) | 118.5(4) |
| C(3)-C(2)-O(1) | 116.5(4) |
| C(4)-C(3)-C(2) | 119.0(4) |
| C(4)-C(3)-H(3B) | 120.5 |
| C(2)-C(3)-H(3B) | 120.5 |
| C(3)-C(4)-C(5) | 120.1(4) |
| C(3)-C(4)-H(4A) | 119.9 |
| C(5)-C(4)-H(4A) | 119.9 |
| C(6)-C(5)-C(4) | 121.4(4) |
| C(6)-C(5)-C(10) | 118.9(4) |
| C(4)-C(5)-C(10) | 119.6(4) |
| C(7)-C(6)-C(5) | 121.7(5) |
| C(7)-C(6)-H(6A) | 119.2 |

| | |
|---|---|
| C(5)-C(6)-H(6A) | 119.2 |
| C(6)-C(7)-C(8) | 120.2(5) |
| C(6)-C(7)-H(7A) | 119.9 |
| C(8)-C(7)-H(7A) | 119.9 |
| C(9)-C(8)-C(7) | 119.9(5) |
| C(9)-C(8)-H(8A) | 120.0 |
| C(7)-C(8)-H(8A) | 120.0 |
| C(8)-C(9)-C(10) | 121.2(4) |
| C(8)-C(9)-H(9A) | 119.4 |
| C(10)-C(9)-H(9A) | 119.4 |
| C(9)-C(10)-C(11) | 122.2(4) |
| C(9)-C(10)-C(5) | 118.0(4) |
| C(11)-C(10)-C(5) | 119.8(4) |
| C(2)-C(11)-C(10) | 116.3(4) |
| C(2)-C(11)-C(12) | 122.1(4) |
| C(10)-C(11)-C(12) | 121.6(3) |
| C(21)-C(12)-C(13) | 120.0(4) |
| C(21)-C(12)-C(11) | 121.1(4) |
| C(13)-C(12)-C(11) | 118.8(3) |
| C(14)-C(13)-C(18) | 118.6(4) |
| C(14)-C(13)-C(12) | 122.7(4) |
| C(18)-C(13)-C(12) | 118.7(4) |
| C(15)-C(14)-C(13) | 121.2(4) |
| C(15)-C(14)-H(14A) | 119.4 |
| C(13)-C(14)-H(14A) | 119.4 |

| | |
|---|---|
| C(14)-C(15)-C(16) | 120.7(4) |
| C(14)-C(15)-H(15A) | 119.7 |
| C(16)-C(15)-H(15A) | 119.7 |
| C(17)-C(16)-C(15) | 119.9(4) |
| C(17)-C(16)-H(16A) | 120.1 |
| C(15)-C(16)-H(16A) | 120.1 |
| C(16)-C(17)-C(18) | 121.0(4) |
| C(16)-C(17)-H(17A) | 119.5 |
| C(18)-C(17)-H(17A) | 119.5 |
| C(19)-C(18)-C(17) | 122.1(4) |
| C(19)-C(18)-C(13) | 119.2(4) |
| C(17)-C(18)-C(13) | 118.8(4) |
| C(20)-C(19)-C(18) | 121.2(4) |
| C(20)-C(19)-H(19A) | 119.4 |
| C(18)-C(19)-H(19A) | 119.4 |
| C(19)-C(20)-C(21) | 121.8(4) |
| C(19)-C(20)-H(20A) | 119.1 |
| C(21)-C(20)-H(20A) | 119.1 |
| C(12)-C(21)-C(20) | 119.0(4) |
| C(12)-C(21)-C(22) | 121.6(4) |
| C(20)-C(21)-C(22) | 119.2(4) |
| C(23)-C(22)-C(24) | 112.8(5) |
| C(23)-C(22)-C(21) | 107.6(4) |
| C(24)-C(22)-C(21) | 113.3(4) |
| C(23)-C(22)-H(22A) | 107.6 |

| | |
|---|---|
| C(24)-C(22)-H(22A) | 107.6 |
| C(21)-C(22)-H(22A) | 107.6 |
| C(22)-C(23)-H(23A) | 109.5 |
| C(22)-C(23)-H(23B) | 109.5 |
| H(23A)-C(23)-H(23B) | 109.5 |
| C(22)-C(23)-H(23C) | 109.5 |
| H(23A)-C(23)-H(23C) | 109.5 |
| H(23B)-C(23)-H(23C) | 109.5 |
| C(22)-C(24)-H(24A) | 109.5 |
| C(22)-C(24)-H(24B) | 109.5 |
| H(24A)-C(24)-H(24B) | 109.5 |
| C(22)-C(24)-H(24C) | 109.5 |
| H(24A)-C(24)-H(24C) | 109.5 |
| H(24B)-C(24)-H(24C) | 109.5 |
| O(3')-S(1')-O(2') | 123.3(3) |
| O(3')-S(1')-O(1') | 108.5(2) |
| O(2')-S(1')-O(1') | 110.9(2) |
| O(3')-S(1')-C(1') | 105.2(3) |
| O(2')-S(1')-C(1') | 106.5(3) |
| O(1')-S(1')-C(1') | 99.7(2) |
| C(2')-O(1')-S(1') | 119.2(3) |
| F(1')-C(1')-F(3') | 110.4(5) |
| F(1')-C(1')-F(2') | 107.1(6) |
| F(3')-C(1')-F(2') | 107.6(5) |
| F(1')-C(1')-S(1') | 113.8(4) |

| | |
|---|---|
| F(3')-C(1')-S(1') | 108.1(4) |
| F(2')-C(1')-S(1') | 109.7(4) |
| C(11')-C(2')-C(3') | 125.1(4) |
| C(11')-C(2')-O(1') | 117.4(3) |
| C(3')-C(2')-O(1') | 117.4(3) |
| C(4')-C(3')-C(2') | 118.5(4) |
| C(4')-C(3')-H(3'B) | 120.8 |
| C(2')-C(3')-H(3'B) | 120.8 |
| C(3')-C(4')-C(5') | 121.3(4) |
| C(3')-C(4')-H(4'A) | 119.4 |
| C(5')-C(4')-H(4'A) | 119.4 |
| C(6')-C(5')-C(4') | 121.9(4) |
| C(6')-C(5')-C(10') | 119.5(4) |
| C(4')-C(5')-C(10') | 118.5(4) |
| C(7')-C(6')-C(5') | 120.8(4) |
| C(7')-C(6')-H(6'A) | 119.6 |
| C(5')-C(6')-H(6'A) | 119.6 |
| C(6')-C(7')-C(8') | 120.0(4) |
| C(6')-C(7')-H(7'A) | 120.0 |
| C(8')-C(7')-H(7'A) | 120.0 |
| C(9')-C(8')-C(7') | 121.8(4) |
| C(9')-C(8')-H(8'A) | 119.1 |
| C(7')-C(8')-H(8'A) | 119.1 |
| C(8')-C(9')-C(10') | 120.0(4) |
| C(8')-C(9')-H(9'A) | 120.0 |

| | |
|---|---|
| C(10')-C(9')-H(9'A) | 120.0 |
| C(9')-C(10')-C(11') | 121.6(4) |
| C(9')-C(10')-C(5') | 117.8(4) |
| C(11')-C(10')-C(5') | 120.5(4) |
| C(2')-C(11')-C(10') | 116.0(4) |
| C(2')-C(11')-C(12') | 122.0(3) |
| C(10')-C(11')-C(12') | 121.9(3) |
| C(21')-C(12')-C(13') | 120.3(4) |
| C(21')-C(12')-C(11') | 120.2(3) |
| C(13')-C(12')-C(11') | 119.4(3) |
| C(14')-C(13')-C(12') | 123.7(4) |
| C(14')-C(13')-C(18') | 117.3(4) |
| C(12')-C(13')-C(18') | 119.0(4) |
| C(15')-C(14')-C(13') | 121.6(4) |
| C(15')-C(14')-H(14B) | 119.2 |
| C(13')-C(14')-H(14B) | 119.2 |
| C(14')-C(15')-C(16') | 120.7(5) |
| C(14')-C(15')-H(15B) | 119.7 |
| C(16')-C(15')-H(15B) | 119.7 |
| C(17')-C(16')-C(15') | 120.2(4) |
| C(17')-C(16')-H(16B) | 119.9 |
| C(15')-C(16')-H(16B) | 119.9 |
| C(16')-C(17')-C(18') | 121.2(4) |
| C(16')-C(17')-H(17B) | 119.4 |
| C(18')-C(17')-H(17B) | 119.4 |

| | |
|---|---|
| C(19')-C(18')-C(17') | 122.5(4) |
| C(19')-C(18')-C(13') | 118.4(4) |
| C(17')-C(18')-C(13') | 119.0(4) |
| C(20')-C(19')-C(18') | 121.2(4) |
| C(20')-C(19')-H(19B) | 119.4 |
| C(18')-C(19')-H(19B) | 119.4 |
| C(19')-C(20')-C(21') | 120.9(4) |
| C(19')-C(20')-H(20B) | 119.6 |
| C(21')-C(20')-H(20B) | 119.6 |
| C(12')-C(21')-C(20') | 120.1(4) |
| C(12')-C(21')-C(22') | 121.7(4) |
| C(20')-C(21')-C(22') | 118.2(4) |
| C(23')-C(22')-C(24') | 109.3(4) |
| C(23')-C(22')-C(21') | 110.4(4) |
| C(24')-C(22')-C(21') | 111.8(4) |
| C(23')-C(22')-H(22B) | 108.4 |
| C(24')-C(22')-H(22B) | 108.4 |
| C(21')-C(22')-H(22B) | 108.4 |
| C(22')-C(23')-H(23D) | 109.5 |
| C(22')-C(23')-H(23E) | 109.5 |
| H(23D)-C(23')-H(23E) | 109.5 |
| C(22')-C(23')-H(23F) | 109.5 |
| H(23D)-C(23')-H(23F) | 109.5 |
| H(23E)-C(23')-H(23F) | 109.5 |
| C(22')-C(24')-H(24D) | 109.5 |

| | |
|---|---|
| C(22')-C(24')-H(24E) | 109.5 |
| H(24D)-C(24')-H(24E) | 109.5 |
| C(22')-C(24')-H(24F) | 109.5 |
| H(24D)-C(24')-H(24F) | 109.5 |
| H(24E)-C(24')-H(24F) | 109.5 |

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Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters (Å2x 103)for liu110. The anisotropic displacement factor exponent takes the form: -2π2[ h2a*2U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| S(1) | 33(1) | 49(1) | 48(1) | -1(1) | 1(1) | 22(1) |
| O(1) | 30(2) | 47(2) | 38(2) | -1(1) | 2(1) | 16(1) |
| O(2) | 51(2) | 96(3) | 62(2) | 31(2) | 14(2) | 41(2) |
| O(3) | 51(2) | 57(2) | 70(2) | -12(2) | -1(2) | 35(2) |
| F(1) | 59(2) | 70(2) | 124(3) | 1(2) | -26(2) | -11(2) |
| F(2) | 113(3) | 143(4) | 116(3) | -80(3) | -69(3) | 101(3) |
| F(3) | 83(2) | 126(3) | 72(2) | -39(2) | -40(2) | 75(2) |
| C(1) | 64(4) | 90(5) | 62(4) | -30(3) | -28(3) | 52(4) |
| C(2) | 30(2) | 37(2) | 40(2) | -1(2) | 6(2) | 18(2) |
| C(3) | 34(2) | 25(2) | 54(3) | -6(2) | -10(2) | 2(2) |
| C(4) | 52(3) | 33(2) | 46(3) | -5(2) | -2(2) | 22(2) |
| C(5) | 47(3) | 33(2) | 36(2) | 8(2) | 2(2) | 22(2) |
| C(6) | 68(4) | 57(3) | 44(3) | -4(2) | 1(3) | 47(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(7) | 57(3) | 74(4) | 60(3) | -4(3) | 0(3) | 51(3) |
| C(8) | 37(3) | 59(3) | 48(3) | -1(2) | -4(2) | 27(2) |
| C(9) | 32(2) | 40(2) | 37(2) | -2(2) | -4(2) | 20(2) |
| C(10) | 34(2) | 33(2) | 24(2) | 4(2) | 4(2) | 16(2) |
| C(11) | 31(2) | 26(2) | 30(2) | 0(2) | 5(2) | 10(2) |
| C(12) | 23(2) | 32(2) | 34(2) | -5(2) | -4(2) | 14(2) |
| C(13) | 19(2) | 29(2) | 38(2) | -1(2) | -4(2) | 12(2) |
| C(14) | 26(2) | 29(2) | 36(2) | 2(2) | 1(2) | 11(2) |
| C(15) | 30(2) | 40(3) | 41(2) | 1(2) | -4(2) | 17(2) |
| C(16) | 33(2) | 33(2) | 55(3) | 12(2) | -2(2) | 12(2) |
| C(17) | 37(2) | 31(2) | 55(3) | -3(2) | -11(2) | 20(2) |
| C(18) | 21(2) | 30(2) | 46(3) | -6(2) | -7(2) | 14(2) |
| C(19) | 34(2) | 35(2) | 48(3) | -11(2) | -4(2) | 18(2) |
| C(20) | 42(3) | 52(3) | 34(2) | -14(2) | -1(2) | 27(2) |
| C(21) | 29(2) | 34(2) | 40(2) | -6(2) | 2(2) | 14(2) |
| C(22) | 36(2) | 62(3) | 28(2) | -11(2) | 1(2) | 26(2) |
| C(23) | 74(4) | 69(4) | 72(4) | 30(3) | -4(3) | 27(3) |
| C(24) | 92(5) | 72(4) | 109(5) | 21(4) | 58(4) | 45(4) |
| S(1') | 37(1) | 49(1) | 42(1) | -1(1) | 3(1) | 21(1) |
| O(1') | 33(2) | 55(2) | 35(2) | 8(1) | 6(1) | 24(2) |
| O(2') | 90(3) | 70(3) | 102(3) | 37(2) | 45(3) | 61(3) |
| O(3') | 58(2) | 137(4) | 38(2) | -24(2) | -4(2) | 50(3) |
| F(1') | 49(2) | 180(4) | 82(3) | -63(3) | -12(2) | 42(3) |
| F(2') | 82(3) | 64(2) | 150(4) | 12(3) | 47(3) | 31(2) |
| F(3') | 51(2) | 97(3) | 79(2) | -13(2) | 5(2) | 44(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(1') | 36(3) | 89(5) | 62(4) | -11(3) | 3(3) | 32(3) |
| C(2') | 32(2) | 30(2) | 31(2) | 5(2) | 5(2) | 17(2) |
| C(3') | 29(2) | 28(2) | 48(3) | 0(2) | -2(2) | 10(2) |
| C(4') | 34(2) | 34(2) | 36(2) | -10(2) | -8(2) | 11(2) |
| C(5') | 28(2) | 32(2) | 33(2) | -4(2) | -4(2) | 16(2) |
| C(6') | 42(3) | 47(3) | 31(2) | -6(2) | -4(2) | 22(2) |
| C(7') | 36(2) | 63(3) | 29(2) | 6(2) | 8(2) | 22(2) |
| C(8') | 27(2) | 42(3) | 41(2) | 9(2) | 7(2) | 15(2) |
| C(9') | 28(2) | 29(2) | 34(2) | 1(2) | -5(2) | 10(2) |
| C(10') | 30(2) | 28(2) | 28(2) | 3(2) | 2(2) | 19(2) |
| C(11') | 25(2) | 28(2) | 29(2) | 1(2) | -4(2) | 14(2) |
| C(12') | 22(2) | 27(2) | 27(2) | 2(2) | 4(2) | 9(2) |
| C(13') | 23(2) | 32(2) | 32(2) | 3(2) | 9(2) | 13(2) |
| C(14') | 35(2) | 36(2) | 40(2) | 1(2) | 1(2) | 17(2) |
| C(15') | 46(3) | 38(3) | 57(3) | -1(2) | 0(2) | 23(2) |
| C(16') | 51(3) | 32(2) | 52(3) | -8(2) | 9(2) | 20(2) |
| C(17') | 43(3) | 38(3) | 37(2) | -6(2) | 3(2) | 18(2) |
| C(18') | 31(2) | 32(2) | 27(2) | -1(2) | 7(2) | 6(2) |
| C(19') | 33(2) | 34(2) | 21(2) | -3(2) | -2(2) | 9(2) |
| C(20') | 34(2) | 38(2) | 24(2) | 7(2) | 4(2) | 12(2) |
| C(21') | 30(2) | 31(2) | 32(2) | 2(2) | 4(2) | 16(2) |
| C(22') | 42(2) | 40(3) | 35(2) | -9(2) | -13(2) | 24(2) |
| C(23') | 56(3) | 70(4) | 66(3) | -18(3) | -7(3) | 43(3) |
| C(24') | 84(4) | 34(3) | 54(3) | 7(2) | -2(3) | 27(3) |

Hydrogen coordinates ( x 104) and isotropic displacement parameters (Å2x 103) for liu110.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3B) | 7981 | 10166 | 1413 | 51 |
| H(4A) | 6260 | 10557 | 1499 | 52 |
| H(6A) | 3850 | 9757 | 1505 | 59 |
| H(7A) | 1699 | 8148 | 1433 | 67 |
| H(8A) | 1223 | 6103 | 1259 | 56 |
| H(9A) | 2935 | 5708 | 1163 | 42 |
| H(14A) | 4427 | 5559 | 1589 | 38 |
| H(15A) | 3369 | 3612 | 1808 | 45 |
| H(16A) | 2935 | 1582 | 1635 | 50 |
| H(17A) | 3562 | 1523 | 1241 | 48 |
| H(19A) | 4607 | 2702 | 859 | 46 |
| H(20A) | 5630 | 4609 | 636 | 49 |
| H(22A) | 6638 | 7945 | 826 | 50 |
| H(23A) | 5388 | 7885 | 494 | 113 |
| H(23B) | 4467 | 7148 | 722 | 113 |
| H(23C) | 4581 | 6292 | 506 | 113 |
| H(24A) | 7564 | 8005 | 446 | 134 |
| H(24B) | 6851 | 6414 | 444 | 134 |
| H(24C) | 7995 | 7254 | 637 | 134 |
| H(3'B) | 8797 | 11347 | 9496 | 45 |

|  |  |  |  |  |
|---|---|---|---|---|
| H(4'A) | 7840 | 10812 | 9872 | 44 |
| H(6'A) | 5898 | 9410 | 10133 | 48 |
| H(7'A) | 3740 | 7694 | 10176 | 52 |
| H(8'A) | 2513 | 6527 | 9840 | 45 |
| H(9'A) | 3397 | 7051 | 9459 | 38 |
| H(14B) | 5691 | 6610 | 9312 | 45 |
| H(15B) | 5126 | 4482 | 9202 | 55 |
| H(16B) | 3895 | 3522 | 8852 | 55 |
| H(17B) | 3204 | 4690 | 8614 | 49 |
| H(19B) | 3030 | 6721 | 8542 | 40 |
| H(20B) | 3474 | 8808 | 8660 | 41 |
| H(22B) | 5339 | 10626 | 9184 | 45 |
| H(23D) | 3636 | 11162 | 9130 | 88 |
| H(23E) | 3005 | 9646 | 9215 | 88 |
| H(23F) | 2915 | 9982 | 8938 | 88 |
| H(24D) | 6392 | 11411 | 8804 | 87 |
| H(24E) | 5704 | 12243 | 8890 | 87 |
| H(24F) | 5003 | 11112 | 8689 | 87 |

Torsion angles [°] for liu110.

|  |  |
|---|---|
| O(2)-S(1)-O(1)-C(2) | 21.9(4) |
| O(3)-S(1)-O(1)-C(2) | 158.4(3) |
| C(1)-S(1)-O(1)-C(2) | -91.4(4) |
| O(2)-S(1)-C(1)-F(2) | -43.7(5) |
| O(3)-S(1)-C(1)-F(2) | -175.1(5) |

| | |
|---|---|
| O(1)-S(1)-C(1)-F(2) | 74.0(5) |
| O(2)-S(1)-C(1)-F(1) | -165.7(4) |
| O(3)-S(1)-C(1)-F(1) | 62.8(5) |
| O(1)-S(1)-C(1)-F(1) | -48.1(4) |
| O(2)-S(1)-C(1)-F(3) | 76.0(5) |
| O(3)-S(1)-C(1)-F(3) | -55.4(5) |
| O(1)-S(1)-C(1)-F(3) | -166.3(4) |
| S(1)-O(1)-C(2)-C(11) | -92.1(4) |
| S(1)-O(1)-C(2)-C(3) | 90.7(4) |
| C(11)-C(2)-C(3)-C(4) | 3.1(7) |
| O(1)-C(2)-C(3)-C(4) | -179.9(4) |
| C(2)-C(3)-C(4)-C(5) | -0.7(7) |
| C(3)-C(4)-C(5)-C(6) | -179.6(5) |
| C(3)-C(4)-C(5)-C(10) | -2.7(7) |
| C(4)-C(5)-C(6)-C(7) | 178.7(5) |
| C(10)-C(5)-C(6)-C(7) | 1.9(7) |
| C(5)-C(6)-C(7)-C(8) | -1.8(8) |
| C(6)-C(7)-C(8)-C(9) | 0.2(8) |
| C(7)-C(8)-C(9)-C(10) | 1.2(7) |
| C(8)-C(9)-C(10)-C(11) | 177.4(4) |
| C(8)-C(9)-C(10)-C(5) | -1.1(6) |
| C(6)-C(5)-C(10)-C(9) | -0.4(6) |
| C(4)-C(5)-C(10)-C(9) | -177.3(4) |
| C(6)-C(5)-C(10)-C(11) | -179.0(4) |
| C(4)-C(5)-C(10)-C(11) | 4.1(6) |

| | |
|---|---|
| C(3)-C(2)-C(11)-C(10) | -1.7(6) |
| O(1)-C(2)-C(11)-C(10) | -178.6(3) |
| C(3)-C(2)-C(11)-C(12) | 176.8(4) |
| O(1)-C(2)-C(11)-C(12) | -0.1(6) |
| C(9)-C(10)-C(11)-C(2) | 179.6(4) |
| C(5)-C(10)-C(11)-C(2) | -1.9(6) |
| C(9)-C(10)-C(11)-C(12) | 1.0(6) |
| C(5)-C(10)-C(11)-C(12) | 179.5(4) |
| C(2)-C(11)-C(12)-C(21) | -72.0(5) |
| C(10)-C(11)-C(12)-C(21) | 106.5(5) |
| C(2)-C(11)-C(12)-C(13) | 110.5(4) |
| C(10)-C(11)-C(12)-C(13) | -71.0(5) |
| C(21)-C(12)-C(13)-C(14) | -178.4(4) |
| C(11)-C(12)-C(13)-C(14) | -0.8(5) |
| C(21)-C(12)-C(13)-C(18) | 0.1(5) |
| C(11)-C(12)-C(13)-C(18) | 177.6(3) |
| C(18)-C(13)-C(14)-C(15) | 0.4(6) |
| C(12)-C(13)-C(14)-C(15) | 178.9(4) |
| C(13)-C(14)-C(15)-C(16) | 0.1(6) |
| C(14)-C(15)-C(16)-C(17) | -0.2(6) |
| C(15)-C(16)-C(17)-C(18) | -0.2(6) |
| C(16)-C(17)-C(18)-C(19) | -180.0(4) |
| C(16)-C(17)-C(18)-C(13) | 0.7(6) |
| C(14)-C(13)-C(18)-C(19) | 179.9(4) |
| C(12)-C(13)-C(18)-C(19) | 1.4(5) |

| | |
|---|---|
| C(14)-C(13)-C(18)-C(17) | -0.8(5) |
| C(12)-C(13)-C(18)-C(17) | -179.3(3) |
| C(17)-C(18)-C(19)-C(20) | 179.5(4) |
| C(13)-C(18)-C(19)-C(20) | -1.2(6) |
| C(18)-C(19)-C(20)-C(21) | -0.4(7) |
| C(13)-C(12)-C(21)-C(20) | -1.6(6) |
| C(11)-C(12)-C(21)-C(20) | -179.1(4) |
| C(13)-C(12)-C(21)-C(22) | 173.8(4) |
| C(11)-C(12)-C(21)-C(22) | -3.8(6) |
| C(19)-C(20)-C(21)-C(12) | 1.8(7) |
| C(19)-C(20)-C(21)-C(22) | -173.6(4) |
| C(12)-C(21)-C(22)-C(23) | -90.1(5) |
| C(20)-C(21)-C(22)-C(23) | 85.2(5) |
| C(12)-C(21)-C(22)-C(24) | 144.5(5) |
| C(20)-C(21)-C(22)-C(24) | -40.2(6) |
| O(3')-S(1')-O(1')-C(2') | 142.5(3) |
| O(2')-S(1')-O(1')-C(2') | 4.2(4) |
| C(1')-S(1')-O(1')-C(2') | -107.8(4) |
| O(3')-S(1')-C(1')-F(1') | 174.3(5) |
| O(2')-S(1')-C(1')-F(1') | -53.3(6) |
| O(1')-S(1')-C(1')-F(1') | 62.1(5) |
| O(3')-S(1')-C(1')-F(3') | -62.6(5) |
| O(2')-S(1')-C(1')-F(3') | 69.8(5) |
| O(1')-S(1')-C(1')-F(3') | -174.9(4) |
| O(3')-S(1')-C(1')-F(2') | 54.4(5) |

| | |
|---|---|
| O(2')-S(1')-C(1')-F(2') | -173.2(4) |
| O(1')-S(1')-C(1')-F(2') | -57.9(4) |
| S(1')-O(1')-C(2')-C(11') | -92.1(4) |
| S(1')-O(1')-C(2')-C(3') | 91.8(4) |
| C(11')-C(2')-C(3')-C(4') | 0.9(6) |
| O(1')-C(2')-C(3')-C(4') | 176.7(4) |
| C(2')-C(3')-C(4')-C(5') | 1.0(6) |
| C(3')-C(4')-C(5')-C(6') | -179.9(4) |
| C(3')-C(4')-C(5')-C(10') | -1.0(6) |
| C(4')-C(5')-C(6')-C(7') | -179.9(4) |
| C(10')-C(5')-C(6')-C(7') | 1.2(6) |
| C(5')-C(6')-C(7')-C(8') | -0.6(7) |
| C(6')-C(7')-C(8')-C(9') | -0.3(7) |
| C(7')-C(8')-C(9')-C(10') | 0.7(7) |
| C(8')-C(9')-C(10')-C(11') | -179.1(4) |
| C(8')-C(9')-C(10')-C(5') | -0.1(6) |
| C(6')-C(5')-C(10')-C(9') | -0.8(6) |
| C(4')-C(5')-C(10')-C(9') | -179.7(4) |
| C(6')-C(5')-C(10')-C(11') | 178.3(4) |
| C(4')-C(5')-C(10')-C(11') | -0.7(6) |
| C(3')-C(2')-C(11')-C(10') | -2.5(6) |
| O(1')-C(2')-C(11')-C(10') | -178.3(3) |
| C(3')-C(2')-C(11')-C(12') | 174.6(4) |
| O(1')-C(2')-C(11')-C(12') | -1.2(6) |
| C(9')-C(10')-C(11')-C(2') | -178.7(4) |

| | |
|---|---|
| C(5')-C(10')-C(11')-C(2') | 2.3(5) |
| C(9')-C(10')-C(11')-C(12') | 4.2(6) |
| C(5')-C(10')-C(11')-C(12') | -174.8(3) |
| C(2')-C(11')-C(12')-C(21') | -76.3(5) |
| C(10')-C(11')-C(12')-C(21') | 100.7(4) |
| C(2')-C(11')-C(12')-C(13') | 106.3(4) |
| C(10')-C(11')-C(12')-C(13') | -76.8(5) |
| C(21')-C(12')-C(13')-C(14') | -177.5(4) |
| C(11')-C(12')-C(13')-C(14') | -0.1(6) |
| C(21')-C(12')-C(13')-C(18') | 2.5(5) |
| C(11')-C(12')-C(13')-C(18') | 180.0(3) |
| C(12')-C(13')-C(14')-C(15') | 178.7(4) |
| C(18')-C(13')-C(14')-C(15') | -1.4(6) |
| C(13')-C(14')-C(15')-C(16') | 1.4(7) |
| C(14')-C(15')-C(16')-C(17') | -0.4(7) |
| C(15')-C(16')-C(17')-C(18') | -0.6(7) |
| C(16')-C(17')-C(18')-C(19') | -177.4(4) |
| C(16')-C(17')-C(18')-C(13') | 0.6(6) |
| C(14')-C(13')-C(18')-C(19') | 178.5(4) |
| C(12')-C(13')-C(18')-C(19') | -1.6(5) |
| C(14')-C(13')-C(18')-C(17') | 0.4(5) |
| C(12')-C(13')-C(18')-C(17') | -179.7(4) |
| C(17')-C(18')-C(19')-C(20') | 178.1(4) |
| C(13')-C(18')-C(19')-C(20') | 0.1(6) |
| C(18')-C(19')-C(20')-C(21') | 0.6(6) |

| | |
|---|---|
| C(13')-C(12')-C(21')-C(20') | -2.0(6) |
| C(11')-C(12')-C(21')-C(20') | -179.4(3) |
| C(13')-C(12')-C(21')-C(22') | 177.1(4) |
| C(11')-C(12')-C(21')-C(22') | -0.3(6) |
| C(19')-C(20')-C(21')-C(12') | 0.4(6) |
| C(19')-C(20')-C(21')-C(22') | -178.7(4) |
| C(12')-C(21')-C(22')-C(23') | -117.7(4) |
| C(20')-C(21')-C(22')-C(23') | 61.4(5) |
| C(12')-C(21')-C(22')-C(24') | 120.5(4) |
| C(20')-C(21')-C(22')-C(24') | -60.4(5) |

Symmetry transformations used to generate equivalent atoms:

# REFERENCES CITED

**1)** de Koning, C. B.; Rousseau, A. L.; van Otterlo, W. A. L. *Tetrahedron* **2003**, *59*, 7–36.

**2)** Bringmann, G.; Gulder, T.; Gulder, T. A. M.; Breuning, M. *Chem. Rev.*, **2011**, *111*, 563-639.

**3)** Band, V.; Hoffer, A. P.; Band, H.; Rhinehardt, A. E.; Knapp, R. C.; Matlin, S. A.; Anderson, D. J. *Gynecol. Oncol.* **1989**, *32*, 273.

**4)** Gorst-Allman, D. P.; Stern, P. S.; Rabie, C. J. *J. Chem. Soc., Perkin Trans.* **1980**, 2474.

**5)** Y. Auffray; P. Boutibonnes, *Mutat. Res., Genet. Toxicol*., **1986**,*171*, 79–82.

**6)** Wu, F.C. *Baillieres Clin. Obstet. Gynaecol.* **1996**, *10*, 1-23.

**7)** Manfredi, K. P.; Blunt, J. W.; Cardellina, J. H., II; McMahon, J. B.; Pannell, L. L.; Cragg, G. M.; Boyd, M. R. *J. Med. Chem.* **1991**, *34*, 3402.

**8)** Xu M.; Bruhn, T.; Hertlein, B.; Brun, R.; Stich, A.; Wu, J.; Bringmann, G. *Chem. Eur. J.*, **2010**, *16*, 4206-4216.

**9)** a) Noyori, R.; Takaya, H. *Acc. Chem. Res.*, **1990**, *23*, 345-350. b) Brunel, J. M. *Chem. Rev.*, **2005**, *105*, 857-897.

**10)** Ohta, T.; Takaya, H.; Kitamura, M.; Nagai, K.; Noyori, R. *J. Org. Chem.*, **1987**, *52*, 3176-3178.

**11)** Takaishi, K.; Kawamoto, M.; Tsubaki, K. *Org. Lett.*, **2010**, *12*, 1832-1835.

**12)** Feringa, B. L.; Koumura, N.; Van Delden, R. A.; Ter Wiel, M. K. J. *Appl. Phys. A*, **2002**, *75*, 301-308.

**13)** Bao, X.; Snurr, R. Q.; Broadbelt L. J. *Langmuir*, **2009**, *25*, 10730-10736.

**14)** See **1** and **2**.

**15)** McGlacken, G. P.; Bateman, L. M. *Chem. Soc. Rev.*, **2009**, *38*, 2447-2464.

**16)** Martin, R.; Buchwald, S. L. *Acc. Chem. Res.*, **2008**, *41*, 1461-1473.

**17)** Kozlowski, M. C.; Morgan, B. J.; Linton, E. C. *Chem. Soc. Rev.*, **2009**, *38*, 3193-3207.

**18)** Wurtz, S.; Glorius, F. *Acc. Chem. Res.*, **2008**, *41*, 1523-1533.

**19)** a) Nishii, Y.; Wakasugi, K.; Koga, K.; Tanabe, Y. *J. Am. Chem. Soc.*, **2004**, *126*, 5358-5359. b) Lu, J.-M.; Shi, M. *Tetrahedron*, **2007**, *63*, 7545-7549. c) Glass, A. C.; Klonoski, S.; Zakharov, L. N.; Liu, S.-Y. *Chem. Commun.*, **2011**, *47*, 286-288.

**20)** Nishida G.; Suzuki, N.; Noguchi, K.; Tanaka, K. *Org. Lett.*, **2006**, *8*, 3489-3492.

**21)** Perkins, J. R.; Carter, R. G. *J. Am. Chem. Soc.*, **2008**, *130*, 3290-3291.

**22)** a) Razakantoanina, V.; Phung, N. K. P.; Jaureguiberry, G. *Prasitol. Res.*, **2000**, *86*, 665-668. b) Wang, X.; Wang, J.; Wong, S. C. H.; Chow, L. S. N.; Nicholls, J. M.; Wong, Y. C.; Liu, Y.; Kwong, D. L. W.; Sham, J. S. T.; Tsao, S. W. *Life Sciences*, **2000**, *67*, 2663-2671. c) Laughton, M. J.; Halliwell, B.; Evans, P. J.; Robin, J.; Hoult, S. *Biochem. Pharm.*, **1989**, *38*, 2859-2865.

**23)** Hallock, Y. F.; Manfredi, K. P.; Dai, J.-R.; Cardellina, J. H.; Gulakowski, R. J.; McMahon, J. B.; Schaffer, M.; Stahl, M.; Gulden, K.-P.; Bringmann, G.; Francois, G.; Boyd, M. R. *J. Nat. Prod.*, **1997**, *60*, 677-683.

**24)** Bringmann G.; Holenz, J.; Wiesen, B.; Nugroho, B. W.; Proksch, P. *J. Nat. Prod.*, **1997**, *60*, 342-347.

**25)** a) See: **9** and **10**. b) Wang, Z.-J.; Deng, G.-D.; Li, Y.; He, Y.-M.; Tang, W.-J.; Fan, Q.-H. *Org. Lett*., **2007**, *9*, 1243-1246. c) Arai, N.; Suzuki, K.; Sugizaki, S.; Sorimachi, H.; Ohkuma, T.; *Angew. Chem. Int. Ed.*, **2008**, *47*, 1770-1773. d) Berthod, M.; Mignani, G.; Woodward, G.; Lemaire, M. *Chem. Rev.*, **2005**, *105*, 1801-1836.

**26)** Hayashi, T. *Acc. Chem. Res.*, **2000**, *33*, 354-362.

**27)** Takaishi, K.; Kawamoto, M.; Tsubaki, K. *Org. Lett.*, **2010**, *12*, 1832-1835

**28)** Bao, X.; Snurr, R. Q.; Broadbelt, L. J. *Langmuir*, **2009**, *25*, 10730-10736.

**29)** A Scifinder search of TOAN's before 2000 turns up only examples using oxidative coupling which is discussed in detail. After 2000 many examples for the generation of TOAN's are reported.

**30)** Von Richter, V. *Chem. Ber.*, **1873**, *6*, 1252

**31)** a) Taylor, W. I.; Battersby, A.R. *Oxidative Coupling of* Phenols, **1967**, Marcel Dekker, New York, New York. b)Feringa, B.; Wynberg, H. *Tetrahedron Lett.*, **1977**, 4447-4450.

**32)** Doussot, J.; Guy, A.; Ferroud, C. *Tetrahedron Lett.*, **2000**, *41*, 2545-2547.

**33)** Pummerer, R.; Rieche, A.; Prell, E. *Chem. Ber.*, **1926**, *59*, 2159
**34)** See: **9b**.

**35)** Love, B. E. *Current Organic Synthesis*, **2006**, *3*, 169-185.

**36)** See: **9b**

**37)** Yamada, S.-I.; Akimoto, H. *Tetrahedron Letters*, **1968**, 3967-3970.

**38)** Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.*, **1980**, *102*, 7932-7934.

**39)** *Organic Syntheses*, **2004**, *10*, 112

**40)** Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.*, **2002**, *102*, 1359-1469.

**41)** See: **17**.

**42)** See: **17**.

**43)** See: **17**.

**44)** Feringa, B.; Wynberg, H. *Bioorg. Chem.*, **1978**, *7*, 397-408.

**45)** Brussee, J.; Groenendijk, J. L. G.; te Koppele, J. M.; Jansen, A. C. A. *Tetrahedron*, **1985**, *41*, 3313-3319.

**46)** Yamamoto, K.; Fukushima, H.; Nakazaki, M. *Chem. Commun.*, **1984**, 1490-1491.

**47)** Smrcina, M.; Lorenc, M.; Hanus V.; Sedmera, P.; Kocovsky, P.; *J. Org. Chem.*, **1992**, *57*, 1917-1920.

**48)** Nakajima, M; Kanayama, K.; Miyoshi, I.; Hashimoto, S.; *Tetrahedron Lett.*, **1995**, *36*, 9519-9520.

**49)** Li, X.; Hewgley, B.; Mulrooney, C. A.; Yang, J.; Kozlowski, M. C. *J. Org. Chem.*, **2003**, *68*, 5500-5511.

**50)** a) Barhate, N. B.; Chen, C.-T.; *Org. Lett.*, **2002**, *4*, 2529-2532. b) Chu, C.-Y.; Uang, B.-J. *Tetrahedron: Asymmetry*, **2003**, *14*, 53-55.

**51)** Tada, M.; Taniike, T.; Kantam, L. M.; Iwasawa, Y. *Chem. Commun.*, **2004**, 2542-2543.

**52)** Egami, H.; Katsuki, T. *J. Am. Chem. Soc.*, **2009**, *131*, 6082-6083.

**53)** See: **17**.

**54)** DiVirgilio, E. S.; Dugan, E. C.; Mulrooney, C. A.; Kozlowski, *Org. Lett.*, **2007**, *9*, 385-388.

**55)** Denmark, S. E.; Sweis, R. F. *Acc. Chem. Res.* **2002**, *35*, 835–846.

**56)** "…this high degree of steric hindrance presents a serious challenge to many cross-coupling transformations." Shen, S.; Jones, G. O.; Watson, D. A.; Bhayana, B.; Buchwald, S. L. *J. Am. Chem. Soc.*, **2010**, *132*, 11278-11287.

**57)** Phan, N. T. S.; Van Der Sluys, M.; Jones, C. W. *Adv. Synth. Catal.*, **2006**, *348,* 609-679.

**58)** Martin, R.; Buchwald, S. L. *Acc. Chem. Res.*, **2008**, *41*, 1461-1473.

**59)** Miyano, S.; Okada, S.-I.; Suzuki, T.; Handa, S.; Hashimoto, H. *Bull. Chem. Soc. J.* **1986**, *59*, 2044-2046

**60)** Anderson, N. G.; Maddaford, S. P.; Keay, B. A. *J. Org. Chem.*, **1996**, *61*, 9556-9559.

**61)** Yin, J.; Rainka, M. P.; Zhang, X.-X.; Buchwald, S. L. *J. Am. Chem. Soc.*, **2001**, *124*, 1162-1163.

**62)** a) Dai, C.; Fu, G. C. *J. Am. Chem. Soc.*, **2000**, *123*, 2719-2724. b) Littke, A. F.; Schwarz, L.; Fu, G. C. *J. Am. Chem. Soc.*, **2001**, *124*, 6343-6348.

**63)** Fleckenstein, C. A.; Plenio, H. *Chem. Soc. Rev.*, **2010**, *39*, 694-711

**64)** Ackermann, L.; Potukuchi, H. K.; Althammer, A.; Born, R.; Mayer, P.; *Org. Lett.*, 2010, *12*, 1004-1007.

**65)** a) Organ, M. G.; Calimsiz, S.; Sayah, M.; Hoi, K. H.; Lough, A. *Angew. Chem. Int. Ed.*, **2009**, *48*, 2383-2387. b) Calimsiz, S.; Sayah, M.; Mallik, D.; Organ, M. G. **2010**, *49*, 2014-2017.

**66)** Schmidt, A.; Rahimi, A. *Chem. Commun.*, **2010**, *46*, 2995-2997.

**67)** a) Hayashi, T.; Hayashizaki, K.; Kiyoi, T.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8153-8156. b)

**68)** Hayashi, T.; Niizuma, S.; Kamikawa, T.; Suzuki, N.; Uozumi, Y. *J. Am. Chem. Soc.*, **1995**, *117*, 9101-9102.

**69)** Yin, J.; Buchwald, S. L. *J. Am. Chem. Soc.*, **2000**, *122*, 12051-12052

**70)** See: **56**.

**71)** a)Genov, M.; Almorin, A.; Espinet, P. *Chem. Eur. J.* **2006**, *12*, 9346-9352. b) Genov, M.; Almorin, A.; Espinet, P. *Tetrahedron Asymmetry*, **2007**, *18*, 625-627.

**72)** Bermejo, A.; Ros, A.; Fernandez R.; Lassaletta, J. *J. Am. Chem. Soc.*, **2008**, *130*, 15798-15799.

**73)** Nicolau, K. C.; Boddy, C. N. C.; Brase, S.; Winssinger, N. *Angew. Chem. Int. Ed.*, **1999**, *38*, 2097-2152.

**74)** a) See: **15**. b) Alberico, D.; Scott, M. E.; Lautens M. *Chem. Rev.*, **2007**, *107*, 174-238.

**75)** Ames, D. E.; Opalko, A.; *Synthesis*, **1983**, 234-235.

**76)** This area has been heavily reviewed, see: a) Pascual S.; de Mendoza, P.; Echavarren, A. M. *Org. Biomol. Chem.*, **2007**, *5*, 2727-2734. b) Baudoin, O. *Angew. Chem. Int. Ed.* **2007**, *46*, 1373-1375.

**77)** Daugulis, O.; Zaitsev, V. G.; Shabashov, D.; Lazareva, A. *Synlett*, **2006**, 3382.

**78)** Ackermann, L.; Jeyachandran, R.; Potukuchi, K.; Novak, P,; Buttner, L. *Org. Lett.*, **2010**, *12*, 2056-2059.

**79)** a) Ashburn, B. O.; Carter, R. G. *Angew. Chem. Int. Ed.* **2006**, *45*, 6737-6741. b) Perkins, J. R.; Carter, R. G. *J. Am. Chem. Soc.* **2008**, *130*, 3290-3291. c) Ashburn, B. O.; Carter, R. G.; Zakharov, L. N. *J. Am. Chem. Soc.*, **2007**, *129*, 9109-9116.

**80)** Perkins, J. R.; Carter, R. G. *J. Am. Chem. Soc.*, **2008**, *130*, 3290-3291.

**81)** a) b) Naffziger, M. R.; Ashburn, B. O.; Perkins, J. R.; Carter, R. G. *J. Org. Chem.* **2007**, *72*, 9857-9865.

**82)** Hapke, M.; Gutnov, A.; Weding, N.; Spannenberg, A.; Fischer, C.; Benkhauser-Schunk, C.; Heller, B. *Eur. J. Org. Chem.* **2010**, 509-514.

**83)** Kirk, B. H.; Ess, D. H. *Tetrahedron Letters*, **2011**, *52*, 1245-1249.

**84)** Nishida, G.; Suzuki, N.; Noguchi, K.; Tanaka, K. *Org. Lett.*, **2006**, *8*, 3489-3492.

**85)** Nishida, G.; Noguchi, K.; Hirano, M.; Tanaka, K. *Angew. Chem. Int. Ed.*, **2007**, *46*, 3951-3954.

**86)** Hara, H.; Hirano, M.; Tanaka, K. *Org. Lett.*, **2009**, *11*, 1337-1340.

**87)** a)Wakasugi, K.; Nishii, Y.; Tanabe, Y. *Tetrahedron Letters*, **2000**, *41*, 5937-5942. b) Nishii, Y.; Yoshida, T.; Tanabe, Y. *Tetrahedron Letters*, **1997**, *41*, 7195-7198. c) Nishii, Y.; Wakasugi, K.; Koga, K.; Tanabe, Y. *J. Am. Chem. Soc.*, **2004**, *126*, 5358-5359.

**88)** Glass, A. C.; Morris, B. B.; Zakharov, L. N.; Liu, S.-Y. *Org. Lett.*, **2008**, *10*, 4855-4857.

**89)** See: **19c**.

**90)** Glass, A. C.; Young, B.; Zakharov, L. N.; Liu, S.-Y. *Manuscript in Preparation*, **2011**.

**91)** a) Zimmerman, H. E.; Suryanarayan, V. *Eur. J. Org. Chem.*, **2007**, 4091-4102. b) The synthesis of 2-methyl indenone was adapted from a procedure used by Clive et al., see: Clive, D. L. J.; Yu, M.; Sannigrahi, M. *J. Org. Chem.* **2004**, *69*, 4116-4125. c) Capparelli, M. P.; Deschepper, R. E.; Swenton, J. S. *J. Org. Chem*. **1987**, *52*, 4953-4961.

**92)** For example, the enthalpy of the addition of MeMgBr to di-*t*-butyl ketone has been determined to be – 150 kJ mol$^{-1}$, see: T. Holm, *Acta Chem. Scand., Ser. B*, **1976**, *30*, 985-990.

**93)** Malosh, C. F.; Ready, J. M. *J. Am. Chem. Soc.* **2004** *126*, 10240-10241.

**94)** See: **86c**.

**95)** At 130 $^{o}$C we observed no line broadening of the two methoxy peaks of **20**. Modeling was conducted using DFT, with a basis set b3ylp/6-31g* for both **14a** and **20**.

**96)** For a published report using DNMR3, see: K. D. Zimmer, R. Shoemaker and R. R. Ruminski, *Inorganic Chimica Acta*, **2006**, *359*, 1478-1484. For further details on the stereochemical model please see the Supporting Information.

**97)** Reetz, M. T.; Maier, W. F.; Chatziiosifidis, I.; Giannis, A.; Heimbach, H.; Loewe, U. *Chemische Berichte*, **1980**, *113*, 3741-3757.