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Catalytic, Enantioselective, Intramolecular Carbosulfenylation of Olefins. Preparative and Stereochemical Aspects

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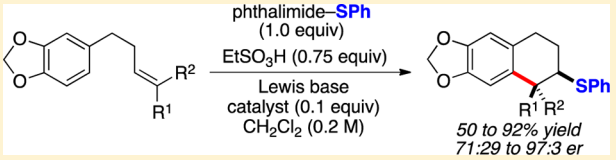
Supporting Information

ABSTRACT: The first catalytic, enantioselective, intramolecular carbosulfenylation of isolated alkenes with aromatic nucleophiles is described. The combination of *N*-phenylsulfenylphthalimide, a chiral selenophosphoramide derived from BINAM, and ethanesulfonic acid as a cocatalytic Brønsted acid induced an efficient and selective cyclofunctionalization of various alkenes (aliphatic and aromatic) tethered to a 3,4-methylenedioxyphenyl ring. Under these conditions, 6-phenylthio-5,6,7,8-tetrahydronaphthalenes are formed diastereospecifically in good yields (50−92%) and high enantioselectivities (71:29−97:3 er). *E*-Alkenes reacted much more rapidly and with much higher selectivity than *Z*-alkenes, whereas electron-rich alkenes reacted more rapidly but with comparable selectivity to electron-neutral alkenes and electron-deficient alkenes. The Brønsted acid played a critical role in effecting reproducible enantioselectivity. A model for the origin of enantioselectivity and the dependence of rate and selectivity on alkene structure is proposed along with a rationale for the site selectivity in reactions with monoactivated arene nucleophiles.



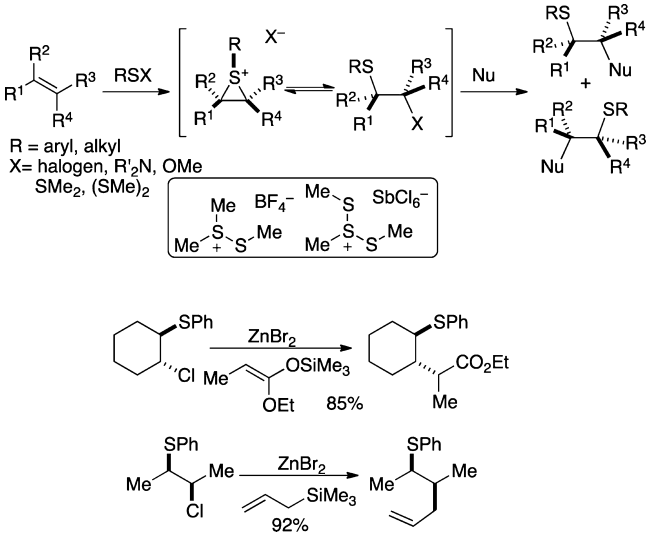
INTRODUCTION AND BACKGROUND

1. Sulfenofunctionalization. The reaction of sulfur(II) electrophiles with alkenes[1] to afford sulfenofunctionalized products has been thoroughly studied since the 1960s primarily in the context of investigating the chemistry of thiiranium ions.[2] These reactive intermediates can be generated by a variety of different sulfenylating reagents such as dimethyl(methylthio)sulfonium tetrafluoroborate,[2d] methyl(bismethylthio)sulfonium hexachloroantimonate, sulfenyl halides,[2e,3] sulfenate esters,[4] sulfenylamides, and disulfides. A wide range of nucleophiles, such as enol ethers, silyl ketene acetals, allylsilanes, aromatic rings, organometallic agents (aluminum, zinc), carboxylic acids, alcohols, amines, nitriles, and thiols have been employed in sulfenofunctionalization reactions following the general process illustrated in Scheme 1.[2d] For many such processes, the chlorosulfenylation product is generated first followed by generation of the thiiranium ion with a Lewis acid in the presence of the pronucleophile.

Alternatively, intramolecular captures (sulfenocyclization reactions) can be effected with sulfenylating agents to form carbocycles and heterocycles (Scheme 2). Warren and coworkers[5] have extensively investigated the preparative and mechanistic features of sulfenyl migration reactions from thiiranium ions generated by neighboring group participation of the sulfur moiety for the synthesis of oxygen- and nitrogen-containing[6] heterocycles. In addition, sulfenium-initiated cyclizations have also been successful with polyolefins[7] and electron-rich arenes.[8]

1.1. Enantioselective Sulfenofunctionalization. Several examples of nucleophilic opening of chiral thiiranium ions are on record. These species are generated by anchimerically assisted ionization of enantiomerically enriched hydroxy sulfides formed from asymmetric dihydroxylation of alkenes.[9] These

Scheme 1



enantiomerically enriched thiiranium ions have been captured by nitriles, sulfonamides, silyl enol ethers, and substituted benzene rings. Intramolecular capture has also been developed.[10] However, only two reports of direct, enantioselective methylsulfenylation reactions have been reported, both employing stoichiometric reagents (Scheme 3).[11]

1.2. Lewis Base Catalysis of Sulfenofunctionalization. As part of a broadly based program to apply the concept of Lewis base activation of Lewis acids[12] to the reactions of main group

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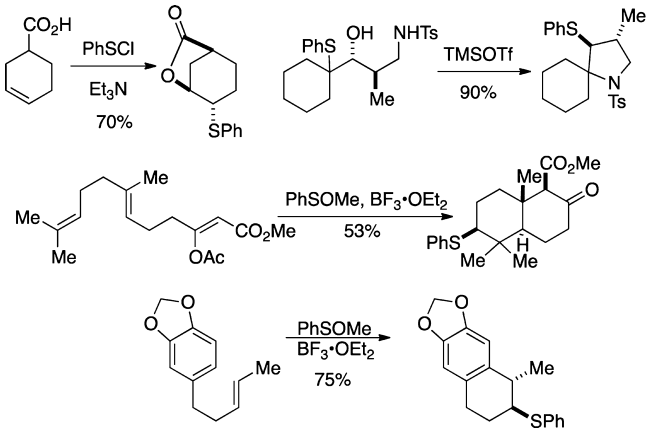
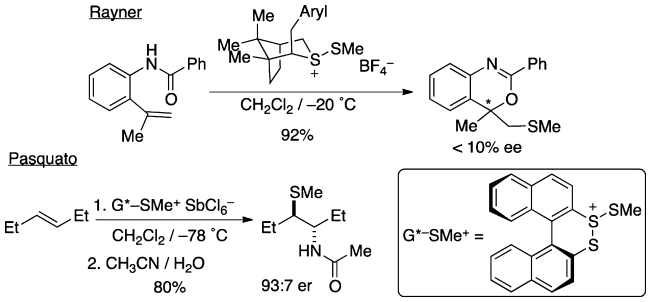
Scheme 2

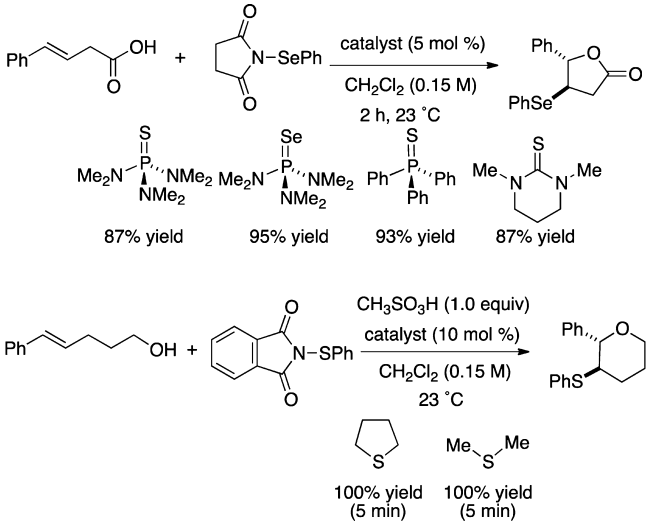


Scheme 3



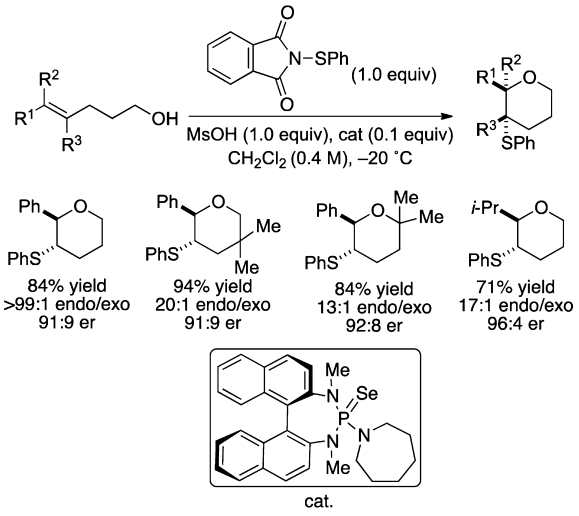
elements, we have investigated the chemistry of selenium(II)[13] and sulfur(II)[14] electrophiles. From extensive preparative and mechanistic studies, we have discovered that the functionalization of isolated alkenes with both *N*-phenylselenosuccinimide and *N*-phenylsulfenophthalimide is susceptible to catalysis by Lewis bases (Scheme 4).

Scheme 4



However, whereas the intermediate seleniranium ions are not configurationally stable, the corresponding thiiranium ions are stable[15a] and can be captured stereospecifically with a variety of heteroatom nucleophiles.[15b] These insights led to the development of the first, catalytic, enantioselective sulfenofunctionalization of isolated alkenes (Scheme 5).[14,16−18]

Scheme 5



In continuation of these studies, we sought to expand the scope of the asymmetric sulfenofunctionalization to include carbocyclizations with aromatic nucleophiles. Although such transformations are known (as mentioned above), no examples of catalytic, enantioselective cyclizations are on record. Thus, we initiated a program to evaluate (1) the diversity of substituent patterns on the alkene tether, (2) the nucleophilicity of the aromatic residue needed for effective cyclization, (3) the reactivity of the thiiranium ions generated under catalytic conditions compared to those generated stoichiometrically, and (4) the dependence of enantioselectivity on the alkene structure. The results of these studies along with some unexpected insights into the role of the Brønsted acid coactivator are described herein.[19]

RESULTS

1. Synthesis of the Alkene Substrates. As the point of entry, we chose to evaluate electron-rich methylenedioxybenzenes to capture the intermediate thiiranium ions given the success of sulfenocarbocyclizations with these species.[8,20] To study the scope of the carbosulfenylation with variously substituted alkenes required a general and flexible synthesis of geometrically defined olefins. Of the many methods to synthesize trans-disubstituted carbon−carbon double bonds, initial attempts focused on the Schlosser modification of the Wittig olefination reaction.[21] Thus, 5-(3-oxopropyl)-1,3-benzodioxolane **1**[22] was combined with the ethylidenetriphenylphosphorane under standard Wittig−Schlosser olefination conditions to afford the alkene **2** in 60% yield as a 96:4 *E*/*Z* mixture (Table 1, entry 1). Initial optimization of the carbosulfenocyclization reaction was carried out with this *E*/*Z* mixture of isomers **2a**. However, the 4% of *Z*-alkene produced when R^2 = Me and the low yielding reaction when R^2 = *i*-butyl and Ph (entries 2 and 3) stimulated the search for an alternative preparation of these substrates.[23]

The next strategy for the preparation of geometrically defined (3,4-methylenedioxyphenyl) alkenes employed the Warren modification of the Horner−Wittig reaction.[24] Thus, addition of methyl ester **3**[25] to a solution of ethyldiphenylphosphine oxide and *n*-BuLi afforded *β*-keto diphenylphosphine oxide **4** (Scheme 6). Both diastereomeric alcohols *anti*- and *syn*-**5** could be selectively prepared by the reduction of **4** under appropriate reaction conditions.[26] Treatment of ketone **4** with

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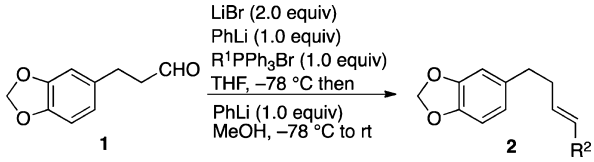
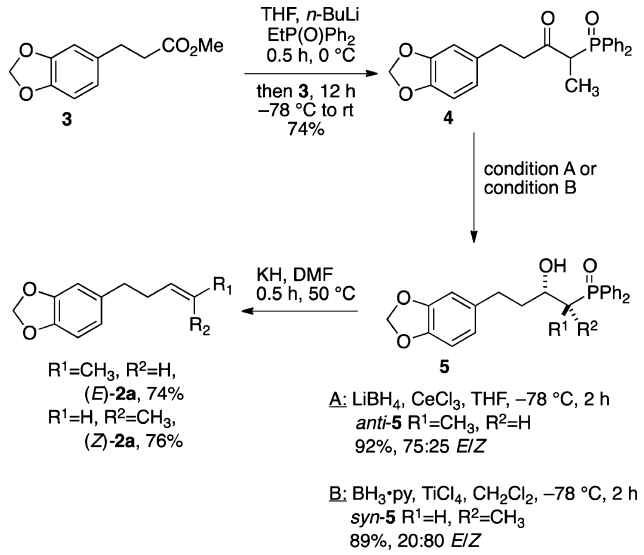
Table 1. Wittig–Schlosser Olefination



entry	R^1	product	R^2	E/Z^a	yield, %^{b}
1	Et	**2a**	Me	96:4	60
2	$PhCH_2$	**2b**	Ph	>99:1	42

^{a}E/Z selectivity was determined by ^{1}H NMR spectroscopic analysis of the purified product. ^{b}Yield of isolated, purified products.

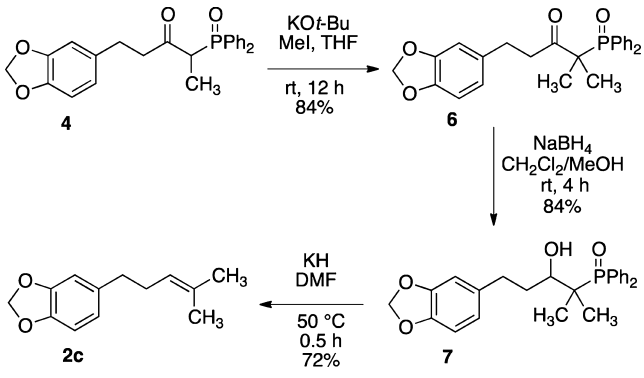
Scheme 6



$LiBH_4$ and $CeCl_3$ afforded a (separable) mixture of β-hydroxy diphenylphosphine oxide diastereoisomers **5** in a 75:25 anti/syn ratio, whereas reduction of **4** with BH_3·py and $TiCl_4$ furnished diastereoisomers **5** in a 20:80 anti/syn ratio. Finally, β-hydroxy phosphine oxides **5** were transformed into the corresponding alkenes **2** in good yields (74–76%, Scheme 6).

To access the trisubstituted alkenes, β-hydroxy phosphine oxide **4** was first alkylated with MeI and KO*t*-Bu and the *gem*-dimethylated product **6** was subsequently reduced with $NaBH_4$ to afford β-hydroxy phosphine oxide **7** (Scheme 7). β-Hydroxy phosphine oxide **7** was converted into trisubstituted alkene **2c** in good yield (72%), upon treatment with KH.

Scheme 7



A third strategy was employed for the synthesis of various (3,4-methylenedioxyphenyl)-derived alkenes through a B-alkyl Suzuki–Miyaura cross-coupling reaction.[27] In view of the ready availability of styrenes and vinyl iodides, this reaction was envisaged to provide access to aliphatic and aromatic substituted (3,4-methylenedioxyphenyl)-derived alkenes (Table 2).

The initial conditions for the cross-coupling reaction between styrene **8a** and (*E*)-(2-iodoethenyl)benzene (**10b**) employed $PdCl_2$(dppf) (5 mol %), Cs_2CO_3 (2.0 equiv), Ph_3As (10 mol %), and H_2O (15.0 equiv) in DMF/THF for 15 h at room temperature (Table 2, entry 1).[28] Three products were isolated from this reaction: cross-coupling product **2b**, alkene hydroboration product **9**, and starting alkene **8a** formed from β-elimination of **9** during the cross-coupling. By extending the reaction time to 24 h, no hydroboration product **9** was observed by ^{1}H NMR spectroscopic analysis and the cross-coupling product **2b** was isolated in 43% yield (Table 1, entry 2). Despite extensive optimization of the reaction conditions (solvent, temperature, base, and ligands), none of the modifications completely suppressed of the formation of the β-elimination product **8a**. Decreasing the amount of H_2O increased the amount of **8a** (entry 3), but increasing the amount of both $PdCl_2$(dppf) and Ph_3As slightly improved the formation of the desired alkene **2b** (entry 4). The absence of the Ph_3PAs slightly favored the formation of alkene **8a** (entry 5). Removing water slowed the cross-coupling reaction and afforded only alkylborane **9** (entry 6). Changing the base to either CsF or NaOMe also caused the cross-coupling reaction to fail (entries 7 and 8). Modification of the palladium source to $Pd(OAc)_2$, as reported by Fu,[29] did not improve the coupling (entry 9).

Although still far from optimal, the conditions in entry 2 were employed in the cross-coupling of (*E*)-1-iodoheptene (**10n**) to afford the target alkene (*E*)-**2n** in 20% yield (Table 3, entry 1). Despite the use of different bases to activate the alkyl-9-BBN derivative, it is clear that other activators for the cross-coupling reactions needed to be evaluated. For example, thallium salts (TlOH, Tl_2CO_3, TlOEt) have been used to enhance the rate of Suzuki–Miyaura cross-coupling reactions between vinylboronic acids and vinyl halides[30,31] as well as between alkylboranes and vinyl halides.[32] When the conditions recommended by Danishefsky [$PdCl_2$(dppf) (20 mol %), Ph_3As (20 mol %), TlOEt (3.0 equiv), H_2O (5.0 equiv), THF, rt] (Table 3, entry 2) were employed, the cross-coupling product (*E*)-**2n** was formed in a gratifying 71% yield.

Reoptimization of certain experimental variables was next conducted. The first series of experiments evaluated the loading of the palladium catalyst. Lowering the palladium loading to 10 mol % afforded an identical yield of 70% (entry 3), but with 5 mol %, the yield of (*E*)-**2n** dropped to 58% (entry 4). The amount of TlOEt was next investigated. Two equivalents of TlOEt afforded a comparable yield of **2c**; however, lowering the amount of the salt to 1.5 equiv afforded (*E*)-**2n** in 66% yield (entries 5 and 6). Moreover, the use of $Pd(PPh_3)_4$ produced (*E*)-**2n** in only 20% yield (entry 7).

From these optimization studies, the best conditions were identified as $PdCl_2$(dppf) (10 mol %), Ph_3As (20 mol %), TlOEt (2.0 equiv), H_2O (5.0 equiv), THF, rt, 12 h. However, in several cases, the use of TlOEt did not afford superior yields compared with the previous protocol using Cs_2CO_3. Considering the high cost and toxicity of TlOEt, aryl-substituted alkenyl iodides **2e**, **2h**, **2j**, and **2s** were cross-coupled using the initial reaction conditions (B: ($PdCl_2$(dppf) (5 mol %), Ph_3As (10 mol %), Cs_2CO_3 (2.0 equiv), H_2O (15.0 equiv),

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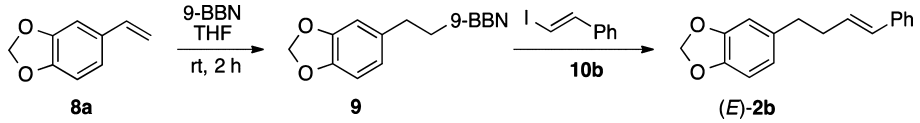
Table 2. Optimization of Suzuki Cross−Coupling Reaction

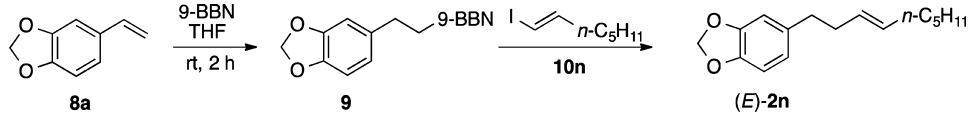


8a 9 (*E*)-**2b**

								ratio, %[a]		
entry	Pd source (mol %)	ligand (mol %)	base (equiv)	H_2O, equiv	solvent	time, h	temp, °C	**8**	**9**	**2b**
1	$PdCl_2$(dppf) (5)	Ph_3As (10)	Cs_2CO_3 (2.0)	15.0	DMF/THF	15	22	25	25	50
2	$PdCl_2$(dppf) (5)	Ph_3As (10)	Cs_2CO_3 (2.0)	15.0	DMF/THF	24	22	35		65[b]
3	$PdCl_2$(dppf) (5)	Ph_3As (10)	Cs_2CO_3 (2.0)	10.0	DMF/THF	24	22	88		12
4	$PdCl_2$(dppf) (15)	Ph_3As (30)	Cs_2CO_3 (2.0)	10.0	DMF/THF	24	22	30		70
5	$PdCl_2$(dppf) (5)		Cs_2CO_3 (2.0)	15.0	DMF/THF	24	22	55		45
6	$PdCl_2$(dppf) (5)	Ph_3As (10)	Cs_2CO_3 (2.0)		DMF/THF	24	22		100	
7	$PdCl_2$(dppf) (3)		NaOMe (2.0)		THF	12	66		100	
8	$PdCl_2$(dppf) (50)		CsF (4.0)	49.0	CH_3CN	24	82		100	
9	$Pd(OAc)_2$ (4)	Cy_3P (8)	K_3PO_4 (2.0)	0.8	THF	12	22	50	50	

[a]Ratio determined by ^{1}H NMR spectroscopic analysis. [b](*E*)-**2b** was isolated in 43% yield.

Table 3. Effect of Thallium Ethoxide in the Suzuki−Miyaura Cross-Coupling of 9[a]



8a 9 (*E*)-**2n**

entry	Pd source (mol %)	$AsPh_3$, mol %	TlOEt, equiv	H_2O, equiv	(*E*)-**2n**, yield, %[b]
1	$PdCl_2$(dppf) (5)	10	*c*	15	20[d]
2	$PdCl_2$(dppf) (20)	20	3.0	5.0	71
3	$PdCl_2$(dppf) (10)	20	3.0	5.0	70
4	$PdCl_2$(dppf) (5)	20	3.0	5.0	58
5	$PdCl_2$(dppf) (10)	20	2.0	5.0	70
6	$PdCl_2$(dppf) (10)	20	1.5	5.0	66
7	$Pd(PPh_3)_4$ (10)		2.0	825.0	20

[a]Reaction carried out in THF at 22 °C for 12 h. [b]Yield of isolated, purified product. [c]Cs_2CO_3 (2.0 equiv) was used instead of TlOEt. [d]Starting alkene **8a** was recovered (37%).

THF/DMF, rt, 12 h). A wide variety of alkyl- and aryl-substituted alkenyl iodides coupled in acceptable yields (60−70%) (Table 4). The electronic character of the aryl substituent of the alkenyl iodides did not affect the yield of reaction, as both electron-deficient and electron-rich aryl residues afforded the *trans*-alkenes in acceptable yields (64−70%) (entries 1−6). However, substitution in the 2-position of the benzene ring afforded the alkene **2i** in lower yield (entry 7). In contrast, alkyl-substituted alkenyl iodides furnished *trans*-alkenes **2k−2p** in good yields (entries 9−14). Finally, **10b** and **10n** coupled with (3-methoxyphenyl)- (**8b**) and (4-methoxyphenyl)alkylboranes (**8c**) in good yields (entries 15−18).

2. Optimization of the Sulfenocarbocyclization. *2.1. Initial Survey of Cyclization Conditions.* A recent disclosure from these laboratories described the development of a catalytic, enantioselective sulfenoetherification of unactivated double bonds using *N*-phenylsulfenylphthalimide **13**, MsOH (to help activate **13**), and a chiral selenophosphoramide as the Lewis base.[14] In view of these studies and the known configurational stability of the intermediate thiiranium species at −20 °C,[15] the initial conditions for the sulfenocarbocyclization of alkene **2a** employed MsOH (1.0 equiv), **13** (1.0 equiv), and Lewis base (10 mol %) in CH_2Cl_2 at −20 °C. The initial success of these reaction conditions led to the following optimization of the Lewis base structure. However, as will become apparent in subsequent sections, the role of MsOH in these reactions was quite different from the sulfenoetherifications and required a significant amount or reoptimization. Moreover, careful investigation of the uncatalyzed reaction revealed a remarkable autocatalytic process that had heretofore gone unnoticed.

2.2. Survey of Chiral Lewis Bases. With a method for effecting the racemic, intramolecular sulfenocarbocyclization in hand, a number of chiral phosphoramides were tested to develop an asymmetric variant of the reaction. The initial survey of Lewis bases was carried out with *E*/*Z* mixtures of the starting material **2a** (Table 5). As was observed in the sulfenoetherification reaction, 1,1′-binaphthalene-2,2′-diamine (BINAM)-derived thio- and selenophosphoramides proved to be efficient and selective chiral Lewis base catalysts.[14] In early studies, various modifications of the BINAM backbone and the internal nitrogen substituents were evaluated. Thio- and selenophosphoramides derived from the parent 2,2′-dimethylamino-1,1′-binaphthyl were the most selective to evaluate the various Lewis base catalysts with initial reactions conditions of MsOH (1.0 equiv), **13** (1.0 equiv), and phosphoramide (*R*)-**15a** (10 mol %). The trans/cis ratio of the diastereomeric products **14a** was determined by ^{1}H NMR spectroscopic analysis of the purified material, and the enantiomeric composition of the products was determined by chiral stationary phase, supercritical fluid chromatographic (CSP-SFC) analysis (Table 5).

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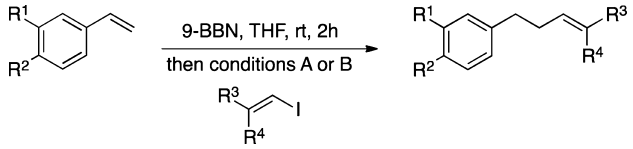
Table 4. Substrate Scope of the B-Alkyl Suzuki–Miyaura Cross-Coupling Reaction[a]



entry	conditions	R^1	R^2	R^3	R^4	iodide	product	yield, %[b]
1	A	−OCH_2O−		C_6H_5	H	**10b**	(*E*)-**2b**	71
2	A	−OCH_2O−		4-$CH_3C_6H_4$	H	**10d**	(*E*)-**2d**	60
3	B	−OCH_2O−		4-NC-C_6H_4	H	**10e**	(*E*)-**2e**	61
4	A	−OCH_2O−		4-$CH_3OC_6H_4$	H	**10f**	(*E*)-**2f**	61
5	A	−OCH_2O−		2-naphthyl	H	**10g**	(*E*)-**2g**	70
6	B	−OCH_2O−		4-$CF_3C_6H_4$	H	**10h**	(*E*)-**2h**	64
7	A	−OCH_2O−		2-$CH_3C_6H_4$	H	**10i**	(*E*)-**2i**	47
8	B	−OCH_2O−		C_6H_5	CH_3	**10j**	(*E*)-**2j**	80
9	A	−OCH_2O−		cyclopropyl	H	**10k**	(*E*)-**2k**	82
10	A	−OCH_2O−		cyclopentyl	H	**10l**	(*E*)-**2l**	62
11	A	−OCH_2O−		cyclohexyl	H	**10m**	(*E*)-**2m**	56
12	A	−OCH_2O−		*n*-C_5H_{11}	H	**10n**	(*E*)-**2n**	70
13	A	−OCH_2O−		$Cl(CH_2)_3$	H	**10o**	(*E*)-**2o**	73
14	A	−OCH_2O−		$(CH_3)_2CHCH_2$	H	**10p**	(*E*)-**2p**	69
15	A	CH_3O	H	C_6H_5	H	**10b**	(*E*)-**11b**	68
16	A	CH_3O	H	*n*-C_5H_{11}	H	**10n**	(*E*)-**11n**	75
17	B	H	CH_3O	C_6H_5	H	**10b**	(*E*)-**12b**	54
18	B	H	CH_3O	*n*-C_5H_{11}	H	**10n**	(*E*)-**12n**	70

[a]Conditions A: $PdCl_2$(dppf) (10 mol %), $AsPh_3$ (20 mol %), TlOEt (2.0 equiv), H_2O (5.0 equiv), THF, 22 °C, 12 h. Conditions B: $PdCl_2$(dppf) (5 mol %), $AsPh_3$ (10 mol %), Cs_2CO_3 (2.0 equiv) H_2O (15.0 equiv), THF/DMF, 22 °C, 24 h. [b]Yield of analytically pure products.

Chiral Lewis base (*R*)-**15a** afforded cyclized products **14a** with high diastereospecificity (trans/cis, 62:38) and reasonable enantioselectivity for the major product, *trans*-**14a** (Table 5 entry 1). However, the minor *cis*-**14a** was produced in racemic form. The corresponding thiophosphoramide catalyst (*R*)-**15b** still afforded excellent diastereospecificity (trans/cis, 96:4), but significantly lower enantioselectivity was obtained for *trans*-**14a**. Nevertheless, (*R*)-**15b** delivered the first nonracemic sample of *cis*-**14a** (entry 2). Altering the external nitrogen substituent to a piperidine (catalyst (*R*)-**16a**) afforded excellent diastereospecificity but did not improve the selectivity of *trans*-**14a** and *cis*-**14a** (entry 3). Once again, the corresponding thiophosphoramide catalyst (*R*)-**16b** provided excellent diastereospecificity; however, the enantiomeric composition of *trans*-**14a** was lower compared with that formed from the selenophosphoramide catalyst (*R*)-**16a** (cf. entries 3 and 4). On the other hand, the enantiomeric ratio of *cis*-**14a** was slightly improved.

In general, thiophosphoramide catalysts (i.e., (*R*)-**15b**, (*R*)-**16b**) afforded lower enantioselectivity for *trans*-**14a** than the corresponding selenophosphoramides (i.e., (*R*)-**15a**, (*R*)-**16**). For these reasons, the thiophosphoramide catalysts were not further evaluated, and the investigation focused on the substituents on the external nitrogen. Increasing the size of the ring to the azepane catalyst (*R*)-**17a** led to excellent diastereospecificity (trans/cis, 96:4) and higher enantioselectivity for *trans*-**14a** but to *cis*-**14a** in racemic form (entry 5). A further increase in the size of the ring to produce the azocane catalyst (*R*)-**18a** still achieved excellent diastereospecificity but slightly reduced enantioselectivity in the formation of *trans*-**14a** (entry 6). As was observed with the previous catalysts, *cis*-**14a** was obtained with moderate enantioselectivity.

The next evaluation of external nitrogen substituents focused on the use of acyclic, branched, secondary amines. For example, diisopropylamino-substituted selenophosphoramide (*R*)-**19a** afforded excellent diastereospecificity and reasonable enantioselectivity for *trans*-**14a** (entry 7). As with the cyclic secondary amine-based catalysts, this catalyst produced *cis*-**14a** with poor enantioselection (entry 7). The corresponding thiophosphoramide catalyst (*R*)-**19b** afforded excellent diastereospecificity but lower enantioselectivity compared to selenophosphoramide catalysts (*R*)-**19a** for *trans*-**14a**. Evaluation of other catalysts prepared from branched secondary amines allowed the identification of the diisobutyl-derived catalyst (*S*)-**20a**, which afforded excellent diastereospecificity and enantioselectivity for *trans*-**14a** (entry 9). Further extension to the diisoamylamine-derived catalyst (*S*)-**21a** afforded results similar to the azepane catalyst (*R*)-**17a** for *trans*-**14a** and a slight improvement for *cis*-**14a** (entry 10).

Continuing the survey of chiral Lewis bases for this cyclization led to the evaluation of selenophosphoramides derived from linear dialkylamines. Catalysts (*R*)-**22a** and (*S*)-**23a** bearing diethylamino and dibutylamino substituents afforded excellent diastereospecificity and enantioselectivities for *trans*-**14a** but lower enantioselectivities than (*S*)-**19a** bearing a diisobutylamino group. The ethyl(butyl)amino-derived catalyst (*S*)-**24a** furnished excellent diastereospecificity and enantiomeric ratio for *trans*-**14a**, as well (entry 13). Finally, phenyl(methyl)-amine-derived catalyst (*R*)-**25a** afforded moderate and poor enantioselectivity for *trans*- and *cis*-**14a**, respectively (entry 14).

In the final phase of optimization, the loading of catalyst (*S*)-**20a** was evaluated. Lowering the catalyst loading to 5 and 7.5 mol % led to decreases in the enantioselection for *trans*-**14a** (entries 15 and 16), whereas increasing the loading to 15 mol % did not improve the enantioselectivity (entry 17). At this point, the reaction conditions in Table 5, entry 9, were deemed sufficient to explore the generality of this transformation with respect to other substrates.

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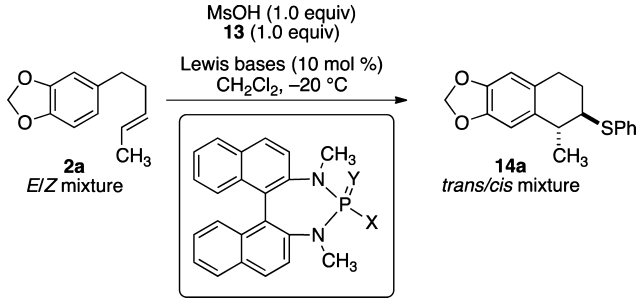
Table 5. Survey of Chiral Lewis Bases to Sulfenocarbocyclization of 2a[a]



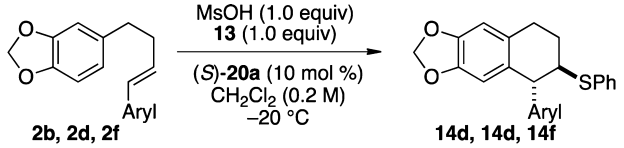
Entry	E/Z[b]	cat	mol %	Y	X	*trans*/*cis*[c]	er,[d] *trans*	er,[d] *cis*
1	62:38	(*R*)-**15a**	10	Se		62:38	19:81	49:51
2	96:4	(*R*)-**15b**	10	S		96:4	44:56	36:64
3	62:38	(*R*)-**16a**	10	Se		62:38	33:67	44:56
4	96:4	(*R*)-**16b**	10	S		96:4	49:51	40:60
5	96:4	(*R*)-**17a**	10	Se		96:4	11:89	49:51
6	94:6	(*S*)-**18a**	10	Se		94:6	86:14	60:40
7	94:6	(*S*)-**19a**	10	Se	N(*i*-Pr)$_2$	94:6	82:18	53:47
8	96:4	(*R*)-**19b**	10	S	N(*i*-Pr)$_2$	96:4	24:76	40:60
9	96:4	(*S*)-**20a**	10	Se	N(*i*-Bu)$_2$	96:4	95:5	52:48
10	95:5	(*S*)-**21a**	10	Se	N(*i*-amyl)$_2$	95:5	88:12	64:36
11	62:38	(*R*)-**22a**	10	Se	N(Et)$_2$	62:38	15:85	47:53
12	95:5	(*S*)-**23a**	10	Se	N(*n*-Bu)$_2$	95:5	92:8	66:34
13	96:4	(*S*)-**24a**	10	Se	N(*n*-Bu)Et	96:4	94:6	58:42
14	62:38	(*R*)-**25a**	10	Se	N(Me)Ph	62:38	31:69	52:48
15	100:0	(*S*)-**20a**	5	Se	N(*i*-Bu)$_2$	100:0	86:14	-
16	100:0	(*S*)-**20a**	7.5	Se	N(*i*-Bu)$_2$	100:0	94:6	-
17	100:0	(*S*)-**20a**	15	Se	N(*i*-Bu)$_2$	100:0	95:5	-

[a]Reaction conditions: **2a** (0.12 mmol), **13** (0.12 mmol), MsOH (0.12 mmol), CH_2Cl_2 (0.2 M), −20 °C. All reactions were completed in 24 h. [b]E/Z ratio of the starting material was determined by ^{1}H NMR spectroscopic analysis. [c]The trans/cis ratios of the cyclization products were determined by ^{1}H NMR spectroscopic analysis. [d]Enantiomeric ratio was determined by CSP-SFC analysis.

2.3. Brønsted Acid Effect. 2.3.1. An Unexpected Complication. With the various reaction parameters established for the catalytic, asymmetric sulfenocarbocyclization of (*E*)-**2a**, an evaluation of the substrate scope was next undertaken. Good enantioselectivities were obtained with *E*-aryl-substituted alkenes, on a 0.1 mmol scale (>89:11 er, Table 6). Effectively, the same enantioselectivity was obtained with electron-rich and electron-neutral aromatic substrates (phenyl (*E*)-**2b**, (entry 1); 4-tolyl (*E*)-**2d**, (entry 2), and 4-methoxyphenyl (*E*)-**2f** (entry 3)). Surprisingly, however, upon scaling the reactions to 1.0 mmol, the enantioselectivity decreased. Clearly, not all the critical reaction parameters had been properly optimized. Because of the early success of the conditions adapted from sulfenoetherification, the amount of the Brønsted acid employed was not evaluated, making it the prime suspect for the lack of reproducibility.

Several modifications relating to the Brønsted acid were explored. First, the rate of the addition of MsOH was reduced from 6.5 to 0.7 μL/s, but lower enantiomeric ratios were still observed on a 1.0 mmol scale. Second, a solution of MsOH in CH_2Cl_2 (0.2 M) was prepared and precooled to −70 °C before slow addition (0.7 μL/s) into the reaction mixture. Unfortunately, MsOH (mp 19 °C) crystallized in the precooled solution. Thus, an alternative Brønsted acid with similar a pK_a value but a lower melting point was sought. Fortunately, ethanesulfonic acid ($EtSO_3H$), which possesses a melting point of −18 °C and a pK_a value of −1.68 in H_2O,[33] is commercially available.

Table 6. Initial Survey of Reaction Scope[a]



entry	aryl	substrate	er[b] on 0.1 mmol scale	er[b] on 1.0 mmol scale
1	C_6H_5	**2b**	92:8	87:13
2	4-$CH_3C_6H_4$	**2d**	93:7	89:11
3	4-$CH_3OC_6H_4$	**2f**	89:11	87:13

[a]All reactions were complete within 24 h. Conversion was determined by ^{1}H NMR spectroscopic analysis. [b]The enantiomeric ratio was determined by CSP-SFC analysis.

2.3.2. Optimization of the Brønsted Acid. Extensive optimization of the loading and delivery (neat vs solution) of the Brønsted acid cocatalyst revealed that 0.75 equiv of $EtSO_3H$ gave reproducible results and restored the original enantioselectivity for the cyclization. Detailed studies on the protonation state of the catalyst, (*S*)-**20a**, the sulfenylating agent, **13**, the structure, and concentration of the catalytically active species revealed the remarkable behavior of $EtSO_3H$ in these reactions

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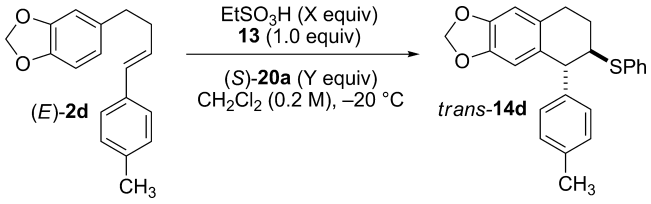
and are the subject of a forthcoming manuscript. For the purposes of the preparative component of this study, the use of 0.75 equiv of $EtSO_3H$ delivered neat solved the problem of reproducibility.

2.3.3. Optimization of the Catalyst Loading. Identification of the appropriate conditions for the cyclization reaction led to a reoptimization of the catalyst loading with alkene (*E*)-**2d**. With 0.75 equiv of $EtSO_3H$ and 10 mol % of catalyst (*S*)-**20a**, cyclization afforded excellent enantioselection (Table 7, entry 1),

Table 7. Effect of Catalyst Loading on the Enantioselectivity[a]

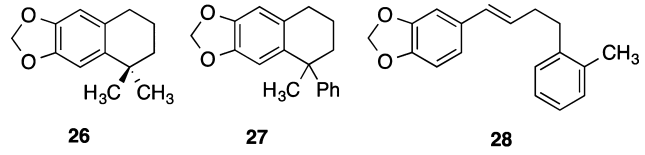


entry	$EtSO_3H$, equiv	(*S*)-**20a**, equiv	conv, %[b]	er[c]
1	0.75	0.10	82	93:7
2	0.75	0.05	60	88:12
3	0.75	0.02	36	83:17
4	0.5	0.10	80	93:7

[a]Reaction conditions: (*E*)-**2d** (0.5 mmol), **13** (0.5 mmol), CH_2Cl_2 (0.2 M) at −20 °C for 10 h. [b]Conversion was determined by ^1H NMR spectroscopic analysis of the crude product. [c]The enantiomeric ratio was determined by CSP-SFC analysis.

slightly higher than with 1.0 equiv of $EtSO_3H$. Lowering the loading of (*S*)-**20a** to 5 and 2 mol % afforded enantiomeric ratios of 88:12 and 83:17, respectively (entries 2 and 3). In addition to the erosion of enantioselection, the rate of the reactions with 5 and 2 mol % of Lewis base (*S*)-**20a** was slower, affording only 60 and 36% conversion to product *trans*-**14d**. The use of 0.5 equiv of $EtSO_3H$ and 10 mol % of (*S*)-**20a** produced identical enantioselection (entry 4), compared to 0.75 equiv of $EtSO_3H$, with 80% conversion after 10 h (entry 4). The best conditions for the sulfenocarbocyclization were defined in regard to the enantioselectivity achieved with 10 mol % of (*S*)-**20a** and the better conversion obtained with the use 0.75 equiv of $EtSO_3H$.

3. Sulfenocarbocyclization with (3,4-Methylenedioxyphenyl)-Derived Alkenes. *3.1. Alkyl Substituents.* At this point, the exploration of the generality of this transformation with other substrates was investigated. Gratifyingly, application of the optimized conditions to a large variety of *E*-alkyl- and aryl-substituted alkenes afforded the cyclized products in moderate to excellent yields (50−92%) with good to excellent enantioselectivities and as single (trans) diastereomers. For example, under these conditions, *E*-methyl-substituted alkene (*E*)-**2a** formed *trans*-**14a** in excellent yield and enantioselectivity (Table 8, entry 1). In contrast, the corresponding isomer (*Z*)-**2a** led to *cis*-**14a** as a nearly racemic mixture (52:48 er, entry 2) but in excellent yield (91%). *E*-Alkenes **2n**−**2p** lacking substitution at the allylic position furnished the cyclized products *trans*-**14n**−*trans*-**14p** in moderate yields but very good enantiomeric ratios (entries 3−5). Cyclopropyl substrate (*E*)-**2k** bearing branching at the allylic position led to a good yield and enantioselectivity (entry 6), whereas common cycloalkyls (five- and six-membered) gave lower yields and enantioselectivities (entries 7 and 8). If the alkene contained a *tert*-butyl substituent, no cyclization occurred.[34] Cyclization of substrates **2c** and (*E*)-**2j** containing geminally disubstituted alkenes allowed formation of quaternary carbon centers albeit with moderate enantiomeric ratios but good yields (entries 9 and 10). Interestingly, byproducts **26** and **27** resulting from the proton-initiated cyclization reaction were formed in 2−8% yield with these trisubstituted alkenes (Figure 1).

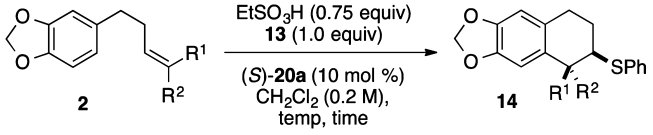


26 **27** **28**

Figure 1. Products of unexpected side reactions.

3.2. Aryl Substituents. The next stage of the investigation focused on the scope of *E*-aryl-substituted alkenes that could participate in the cyclization (Table 9). Substrates (*E*)-**2b**, (*E*)-**2d**, and (*E*)-**2f** bearing no substituents or electron-donating

Table 8. Cyclization with Alkyl-Substituted Alkenes



2 **14**

entry	substrate	R^1	R^2	product	time, days	temp, °C	yield, %[a]	er[b,c]
1	(*E*)-**2a**	H	CH_3	*trans*-**14a**	3	−20	92	97:3
2	(*Z*)-**2a**	CH_3	H	*cis*-**14a**	1	0	91	52:48
3	(*E*)-**2n**	H	*n*-C_5H_{11}	*trans*-**14n**	3	−20	73	96:4
4	(*E*)-**2o**	H	$(CH_2)_3Cl$	*trans*-**14o**	6	20	63	93:7
5	(*E*)-**2p**	H	*i*-Bu	*trans*-**14p**	3	−20	77	96:4
6	(*E*)-**2k**	H	cyclopropyl	*trans*-**14k**	3	−20	88	95:5
7	(*E*)-**2l**	H	cyclopentyl	*trans*-**14l**	3	0	50[d]	82:18
8	(*E*)-**2m**	H	cyclohexyl	*trans*-**14m**	3	0	70[e]	85:15
9	**2c**	CH_3	CH_3	**14c**	1	−20	90[f]	80:20
10	(*E*)-**2j**	CH_3	C_6H_5	*trans*-**14j**	2	−20	82[g]	71:29

[a]Yields of analytically pure products. [b]The enantiomeric ratio was determined by CSP-SFC analysis. [c]The absolute configurations of the products were assigned by comparison of their CD spectra with *trans*-**14d**. [d]Unreacted starting material was recovered (15%). [e]Unreacted starting material was recovered (16%). [f]An 8% yield of **26** was isolated. [g]A 2% yield of **27** was isolated.

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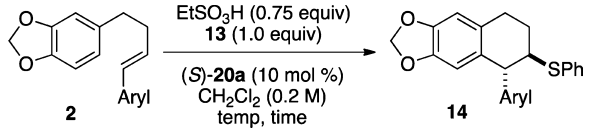
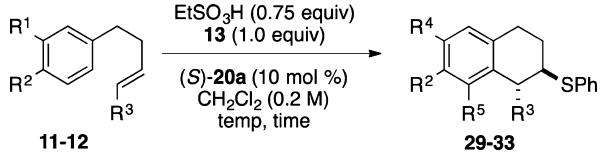
Table 9. Cyclization of Aryl-Substituted Alkenes

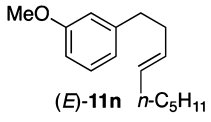
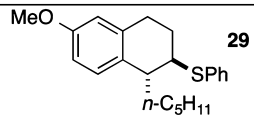
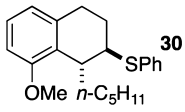
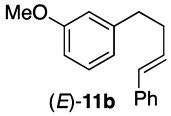
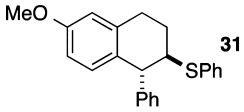
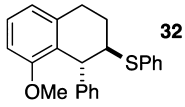
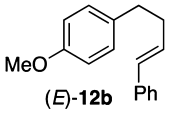
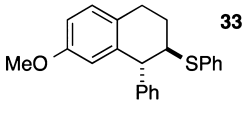


entry	substrate	aryl	product	time, days	temp, °C	yield, %[a]	er[b,c]
1	(*E*)-**2b**	Ph	*trans*-**14b**	2	−20	90	94:6
2	(*E*)-**2d**	4-$CH_3C_6H_4$	*trans*-**14d**	2	−20	86	94:6
3	(*E*)-**2f**	4-$CH_3OC_6H_4$	*trans*-**14f**	1	−20	86	92:8
4	(*E*)-**2i**	2-$CH_3C_6H_4$	*trans*-**14i**	3.5	−20	82[d]	92:8
5	(*E*)-**2g**	2-naphthyl	*trans*-**14g**	2	−20	61[e]	89:11
6	(*E*)-**2e**	4-NC-C_6H_4	*trans*-**14e**	6	20	83	89:11
7	(*E*)-**2h**	4-$CF_3C_6H_4$	*trans*-**14h**	3	20	85	92:8

[a]Yields of analytically pure products. [b]The enantiomeric ratio was determined by CSP-SFC analysis. [c]The absolute configurations of the products were assigned by comparison of their CD spectra with *trans*-**14d**. [d]A 4% yield of **28** was isolated from earlier, unoptimized experiments. [e]Unreacted starting material was recovered (36%).

Table 10. Cyclization with Monomethoxyphenyl-Substituted Substrates



entry	substrate	time, d	temp, °C	products	isomeric ratio	yield, %[a]	er[b,c]
1	 (*E*)-**11n** *n*-C_5H_{11}	3	-20	 **29**  **30**	**29:30** 3:1	60	96:4
						20	91:9
2	 (*E*)-**11b** Ph	3	-20	 **31**  **32**	**31:32** 1:1	45	94:6
						45	90:10
3	 (*E*)-**12b** Ph	1.5	0	 **33**	-	85	84:16

[a]Yields of analytically pure products. [b]The enantiomeric ratio was determined by CSP-SFC analysis. [c]The absolute configurations of the products were assigned by comparison of their CD spectra with *trans*-**14d** .

substituents afforded cyclization products in good yields and enantioselectivities (entries 1−3). However, substrate (*E*)-**2i** bearing a methyl group in the ortho position reacted slowly, but with good enantioselectivity (entry 4). Interestingly, **28**, the product of proton-initiated isomerization of the double bond, was obtained in 4% yield (Figure 1). Substrate (*E*)-**2g** bearing a 2-naphthyl substituent afforded good selectivity but in lower yield (entry 5). Finally, alkenes (*E*)-**2e** and (*E*)-**2h** bearing electron-deficient aromatic groups furnished nearly identical enantioselectivities in very slow reactions (entries 6 and 7).

4. Sulfenocarbocyclization with Methoxyphenyl Derivatives. The final exploration of substrate scope was carried out with less nucleophilic aryl groups. The position of the electron-donating substituent on the aromatic ring had a major impact on the reactivity and site selectivity of the sulfenocarbocyclization. Substrates bearing a methoxy group in the 3-position with respect to the tethered alkene afforded a mixture of cyclized products **29**−**33**, with both *n*-pentyl ((*E*)-**11n**) and phenyl ((*E*)-**11b**) substituents (Table 10). With (*E*)-**11n**, a 3:1 ratio of **30**/**31** was produced in good yields and

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enantioselectivities (entry 1). However, substrate (*E*)-**11b** bearing a phenyl substituent afforded a 1:1 ratio of **31**/**32**, but good enantioselectivity was still achieved for both constitutional isomers (entry 2). For substrate (*E*)-**12b** with the activating group in the 4-position, a good yield of **33** was obtained, albeit with moderate enantioselectivity (entry 3). Interestingly, having the activating group in the 4-position of the phenyl ring did not lead to cyclization with the corresponding *n*-pentyl-substituted alkene (*E*)-**12n**.[35]

5. Stereochemical Assignment. Most of the sulfenocarbocyclization took place with high enantioselectivity. The relative configuration of tetrahydronaphthalenes was confirmed by correlation of the ^{1}H NMR chemical shifts of HC(3) with known products *trans*-**2a** and *cis*-**2a** (Figure 2). All of the trans-products displayed diastereotopic methylene protons on C(3) of the tetrahydronaphthalene that split in two distinct chemical shift around 1.80−1.92 and 2.08−2.18 ppm. On the other hand, in the syn-product, the chemical shift of the methylene protons on C(3) appeared around 2.00 and 2.06 ppm. Furthermore, the absolute configuration of the (−)-*trans*-**14d** was determined to be (1*R*,2*R*) by X-ray crystallographic analysis of the derived sulfone *trans*-**34** (obtained by *m*-CPBA oxidation of the parent sulfide) (Scheme 8).[36]

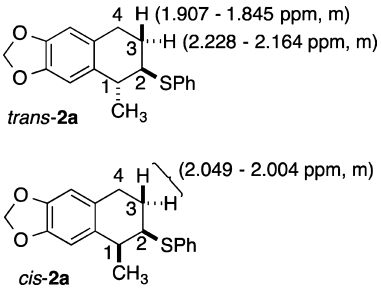
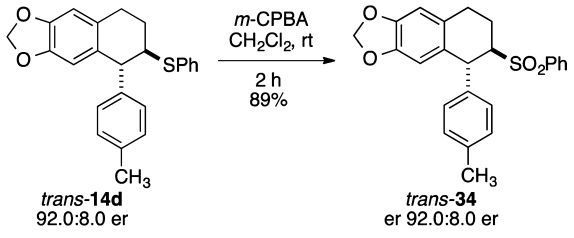


Figure 2. Configurations of *trans*-**2a** and *cis*-**2a**.

The negative Cotton effect in the CD spectra of the products allowed an unambiguous assignment of the absolute configurations of the major enantiomer of the cyclization products by in comparison with *trans*-**14d**.

Scheme 8



DISCUSSION

Our primary objective in this work was to develop a catalytic, asymmetric carbosulfenylation of olefins as a method to prepare enantioenriched 1-alkyl- or 1-aryl-2-thiophenyl-1,2,3,4-tetrahydronaphthalenes. Moreover, given the striking divergence in behavior of these cyclizations compared to the sulfenocycloetherifications reported previously,[14] a second goal focused on a more refined understanding of the role of the Brønsted acid in these reactions.

1. Synthesis of the Alkene Substrates. In a view of the ready availability of (*E*)-2-iodostyrene and other vinyl iodides, a general synthesis of alkyl- and aryl-substituted olefins was undertaken using the B-alkyl Suzuki−Miyaura cross-coupling reaction. Since the first report of cross-coupling between B-alkyl-9-BBN derivatives and aromatic or alkenyl halide in 1989,[37] detailed accounts of the reaction conditions of the B-alkyl Suzuki−Miyaura reaction have been reported.[38] The most commonly used conditions for the Suzuki−Miyaura reaction between alkylborane derivatives and iodoalkenyl or styrenyl iodides employs $PdCl_2$(dppf), Ph_3As, and Cs_2CO_3, with the borane partner prepared by hydroboration of the corresponding olefin. Initial attempts to effect cross-coupling between in situ generated B-alkyl borane **9** and (*E*)-(2-iodoethenyl)benzene (**10**) employed these standard conditions ($PdCl_2$(dppf) (2 mol %), $AsPh_3$ (10 mol %), Cs_2CO_3 (2.0 equiv), and water (15.0 equiv)) and afforded two products, **2b**, and *β*-hydride elimination product **8a**.[39] No further optimization could be achieved by adjusting these reaction parameters. Ultimately, success was achieved by the use of thallium bases as has been described by others previously.[40] Kishi et al. first reported the use of TlOH for the cross-coupling reaction between sp^2 centers. Subsequently, Roush,[31a] Chamberlain,[31b] and Markó[40] employed various thallium salts (TlOEt, in situ generated TlOH, and Tl_2CO_3) to improve the efficiency of Suzuki cross-coupling reactions. Markó commented that a likely reason for the performance of thallium salts is the precipitation of the thallium halide by combination with palladium(II) species (ArylPd(dppf)X). This process would then form a highly reactive, cationic palladium(II) species (ArylPd(dppf)$^+$) that would undergo rapid transmetalation with alkenyl-B(catechol)-OTl$^-$ followed by rapid reductive elimination. After screening the conditions described by Danishefsky et al. (using TlOEt), it was possible to reduce the amount of $PdCl_2$(dppf) to 10 mol % and TlOEt to 2.0 equiv without adversely affecting the yield and the reaction time of the cross-coupling. Under these newly developed conditions, a wide range of (*E*)-(2-iodoethenyl)benzenes and vinyl iodides were coupled. Interestingly, the cross-coupling of electron-poor (*E*)-(2-iodoethenyl)benzene derivatives afforded comparable yields using either activator Cs_2CO_3 or TlOEt. This behavior may result from the greater electrophilicity of the palladium(II) species (Pd(dppf)(styrene)$^+$) with electron-deficient styrenyl moieties.

2. Sulfenocarbocyclization of 3,4-Methylenedioxyphenyl Derivatives. The sulfenocarbocyclization of *E*-alkenes catalyzed by (*S*)-**20a** afforded the cyclized products in good to excellent yields (Tables 8−10). The exclusive formation of *trans*- and *cis*-1,2-disubstituted-1,2,3,4-tetrahydronaphthalenes from *E*- and *Z*-olefins, respectively, is in accordance with the anticipated diastereospecificity characteristic of other seleno-[13] and thiofunctionalizations.[15]

2.1. Effect of the Olefin Configuration on Enantioselectivity and Rate. Both the enantioselectivity and the rate of the reaction were highly dependent on the substitution and configuration of the alkene, whereas the formation of the catalytically active species is independent of the alkene. To enter the catalytic cycle, sulfenylating agent **13** is activated by protonation with $EtSO_3H$ (Figure 3, step a), whereupon the sulfenyl group is transferred to the Lewis base to generate the catalytically active sulfenylating agent **35** (step b). Approach of **35** onto the alkene leads to the formation of thiiranium ion ***i*** (step c), which upon subsequent intra- or intermolecular nucleophilic capture (step d) delivers the

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corresponding enantioenriched thioether (step e). The dramatic difference in reactivity and selectivity among the various alkenes (and in particular between *E*- and *Z*-alkenes)[41] must arise from either the rate of formation of the thiiranium ion ***i*** (step c) or the intramolecular trapping of that ion (step d).

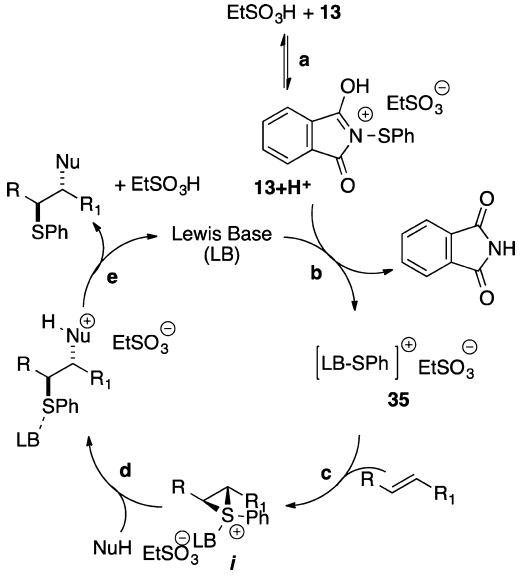

Figure 3. Proposed catalytic cycle for sulfenofunctionalization.

Our interest in a detailed mechanistic understanding of this reaction—especially the structure of the catalytically active species **35**—led to numerous attempts at crystallization of various salts which have been unsuccessful to date. Computational studies to determine the conformation of the putative catalytic species **35** and develop a better understanding of the transition state structure for the formation of thiiranium ion ***i*** are ongoing. However, a single-crystal X-ray diffraction analysis of Lewis base catalyst (*S*)-**17a**[42] could be obtained from which working models can be proposed to explain the origin of the enantioselectivity with related Lewis base (*S*)-**20a**.

The solid-state structure of (*S*)-**17a** revealed the pseudo-equatorial positions of the *N*-methyl groups of the azepine ring relative to the 1,3,2-diazaphosphephine ring. Moreover, the plane defined by the C(1)−N−C(6) atoms of the azepine ring is nearly coincident with the P═Se unit (−8.77°) and thus the ring carbons occupy space near the P═Se unit (Figure 4).

The models employed in the discussion below are derived from the crystallographic coordinates of catalyst (*S*)-**17a** with the following modifications: (1) the azepino group of (*S*)-**17a** is replaced with the diisobutylamino group of catalyst (*S*)-**20a**; (2) all of the atoms of the (*S*)-**17a** backbone are fixed, and the diisobutylamino group was minimized with molecular mechanics; and (3) an *S*-phenyl group was attached to the selenium atom and again minimized with molecular mechanics. Model 1 illustrates the destabilizing steric interaction between the *S*-phenyl group and the diisobutylamino group of the active species **35**, causing the phenylsulfenyl group to point toward the binaphthyl subunit (models 2 and 3). The energy profile for the C−S−Se−P dihedral angle is very flat with two minima at 121 and 83°. For our purposes, this angle is assumed to be close to 120° as seen in $[(Me_2N)_3P{-}Se]_2^{2+}[(BiCl_4)_2]_n^{n-}$, in which the P−Se−Se−P dihedral angle is 112°.[43]

The next step in rationalizing the stereochemical course of the reaction involves the approach of the alkene onto **35**. Several factors influence this approach such that the orbital interactions are maximized and the destabilizing steric interactions are minimized. To maximize orbital overlap between the HOMO of the alkene and the LUMO of the electrophile, the bonding π-electrons of the alkene must approach the sulfur atom in ***i*** along the trajectory of the S−Se σ^*-orbital.[44] Two, limiting transition state geometries are considered for the thiiranium ion formation: the spiro and the planar approaches (Figure 5). By analogy with the epoxidation of alkenes with dioxiranes and peracids,[45] a spiro transition state is favored over the planar transition state due to stabilizing interaction of a sulfur lone pair with π^*-orbital of the alkene in the former.

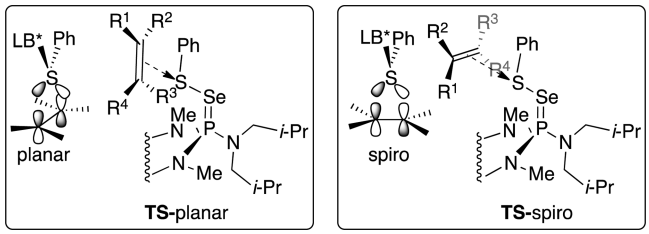

Figure 5. Spiro and planar transition states for the thiiranium ion formation.

Taken together, these two factors allow the formulation of six limiting transition structures **TS-A**−**TS-F** to rationalize the enantioselectivity of the reaction. In the case of *Z*-alkenes, models **TS-A**−**TS-C** explain the lower reactivity as well as the poor enantioselectivity of the thiiranium ion formation (Figure 6). In model **TS-A**, the *Z*-alkene approaches ***i*** on the *Si*−*Re* face,[46] with the alkene substituents facing down (*Si*−*Re* (d)). This arrangement suffers from destabilizing steric interactions between the binaphthyl moiety of **35** and the substituents on the alkene. It is important to note that same argument can be made if

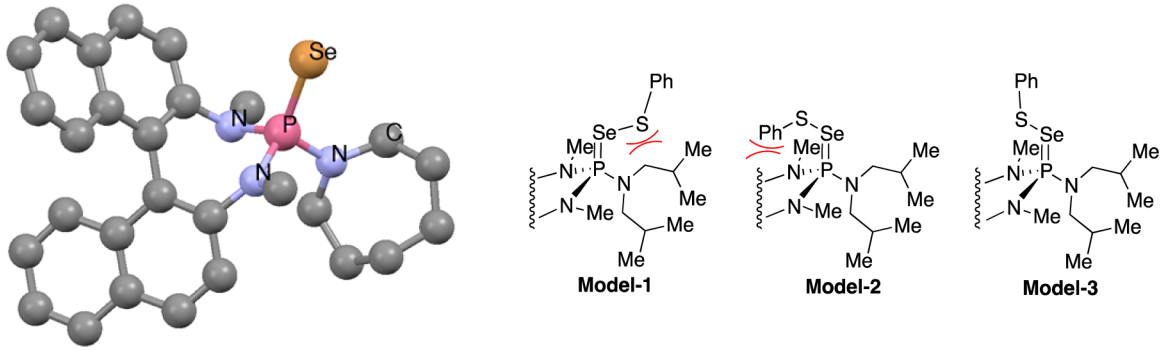

Figure 4. X-ray crystallographic structure of (*S*)-**17a** and proposed models for the geometry of the catalytically active species ***i***.

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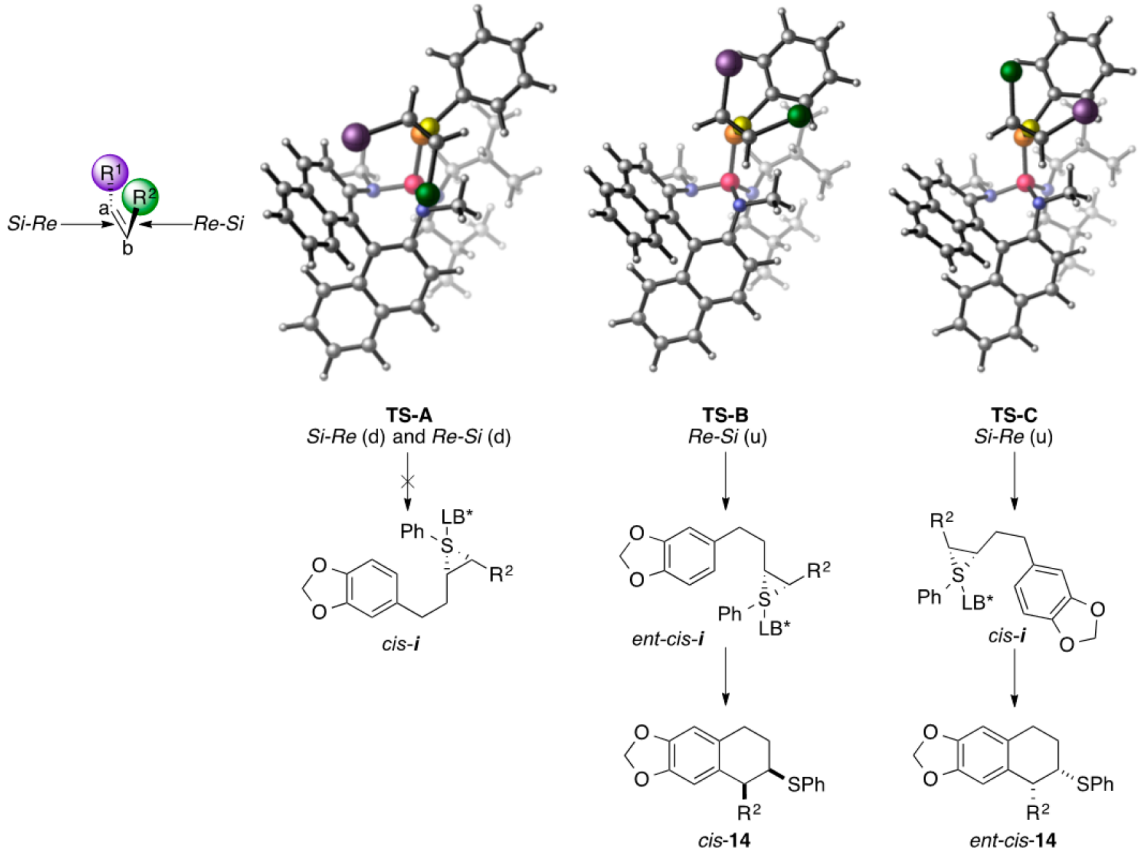

Figure 6. Proposed rationale for the unselective formation of thiiranium ions from *Z*-alkenes.

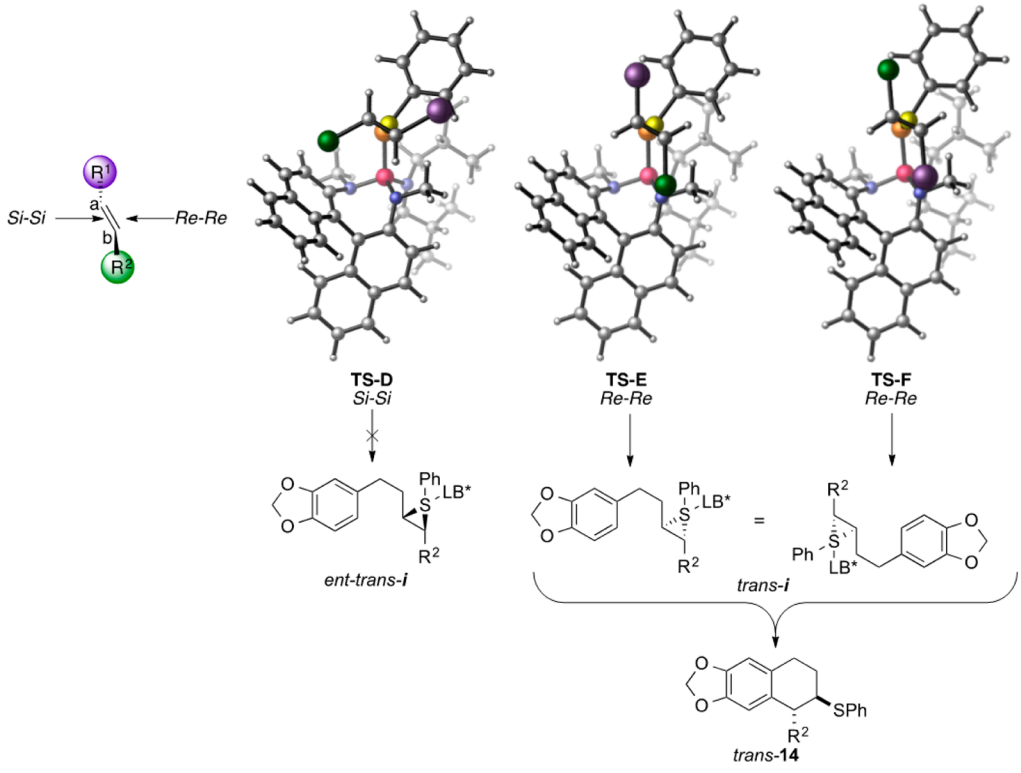

Figure 7. Proposed rationale for the selective formation of thiiranium ions from *E*-alkenes.

the alkene approaches **35** on the *Re*−*Si* face with the substituent of the alkene down (*Re*−*Si* (d), not shown). In models **TS-B** and **TS-C**, the alkene approaches **35** on the *Si*−*Re* and *Re*−*Si* faces, respectively, with the alkene substituents facing up (u). In these transition structures, destabilizing interactions between the *S*-phenyl group and the R^1/R^2 substituents of the alkene would

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reduce the rate of the formation of the thiiranium ion. As none of these arrangements is devoid of nonbonding interactions, the formation of two thiiranium ion enantiomers *cis*-***i*** and *ent-cis*-***i*** will occur at similar rates which, after cyclization, afford tetralin enantiomers *cis*-**14** and *ent-cis*-**14** with equal facility.

In the case of *E*-alkenes, model **TS-D** illustrates the approach of the *Si*−*Si* face of the alkene to the active species **35** in which destabilizing interactions between the R^2 substituent of the alkene and the binaphthyl rings of **35** would disfavor this approach (Figure 7). The same argument is also valid when R^1 and R^2 substituents are interchanged. The two models **TS-E** and **TS-F** depict the approach of the *Re*−*Re* face of the alkene to **35** in which no repulsive steric interactions occur between the R^1 or R^2 substituents of the alkene and the binaphthyl rings of **35**. In addition, the approach of the *Re*−*Re* face of the alkene may prefer **TS-E** because the bulkier substituent (R^1) does not encounter steric repulsions with the *N*-methyl group of the Lewis base. As a consequence of reaction via transition states **TS-E** and **TS-F**, a single thiiranium ion *trans*-***i*** is formed which after ring closure affords tetralin *trans*-**14**. Comparison of models **TS-E** and **TS-F** with models **TS-B** and **TS-C** illustrates why the formation of the thiiranium ion is faster for *E*-alkenes than for *Z*-alkenes.

2.2. Reaction of Alkyl-Substituted Alkenes. Unactivated *E*-alkenes bearing linear, *β*-branched, and alicyclic substituents afforded excellent levels of enantioselectivity and reacted with similar rates. The length of the alkyl chain on the alkene did not influence the rate or enantioselectivity of the reaction, substrates with longer carbon chains ((*E*)-**2n**−(*E*)-**2p**) led to moderate yields, and substrate (*E*)-**2a** bearing a methyl group gave excellent yield. The lower enantioselectivity of the sulfenocarbocyclization observed for alkenes bearing branched substituents (*E*)-**2l** and (*E*)-**2m** implies that neither **TS-E** nor **TS-F** can accommodate larger groups on each end of the alkene. The alkene approach via **TS-D** may become competitive, but more likely an alternative transition structure that can accommodate at least one large group leading to the minor enantiomer can be considered. For example, **TS-G** in which the S−Se bond is rotated at a different minimum may lead to an increase in the formation of the *ent-trans*-**14** (Figure 8).

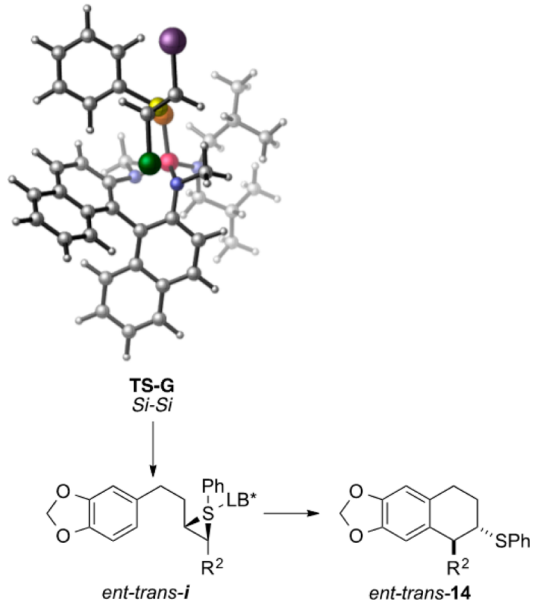
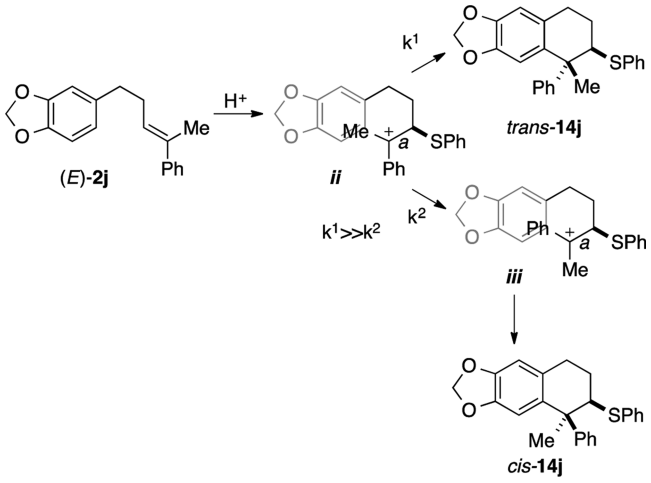


Figure 8. Proposed rationale for thiiranium ion formation from branched *E*-alkenes.

The presence of a chlorine atom on the alkyl chain ((*E*)-**2o**) decreased the rate of the reaction while maintaining a high level of enantioselectivity.[47] The low cyclization rate could be explained by protonation of the chlorine atom or interception of the thiiranium species with the pendant chlorine atom. However, the latter explanation can be ruled out because this would change the relative configuration of the product.[48] Protonation of the chlorine atom, which has been proposed in an acid-catalyzed Friedel−Crafts alkylation,[49] would reduce the concentration of Brønsted acid in the solution. Lowering the concentration of the acid would shift the equilibrium protonation of the sulfenylating agent to the left (step a, Figure 3) and lower the overall rate of the reaction.

The electronic properties of the alkenes also influenced the outcome of cyclization. For example, trisubstituted alkenes were more reactive than disubstituted *E*-alkenes, although the enantioselectivities were lower. These results reflect the influence played by the substituent in cis position of the alkyl chain, bearing the veratryl ring, on the approach of the alkene to **35**. The greater rate of reaction coupled with the lower enantioselectivity is puzzling. Given the additional steric contributions from a cis substituent, these results imply that several competing transition states are lower in energy than those for disubstituted alkenes. This outcome may arise from earlier transition states which result from greater electron density in the trisubstituted alkene. Alternatively, reactions of these substrates may be highly asynchronous or involve discrete carbocations. Although all of the sulfenocarbocyclizations were highly diastereospecific, it is conceivable that the reaction of (*E*)-**2j** proceeded through a stepwise process via formation of a tertiary carbocation ***ii***. However, as only one diastereomer was observed, capture of the carbocation must be faster than rotation of bond *a* ($k^1 \gg k^2$) to form ***iii*** (Scheme 9).

Scheme 9



In addition to the Lewis base catalyzed sulfenocarbocyclization reaction of trisubstituted alkenes, the formation of non-sulfur-containing 1,1-disubstituted-1,2,3,4-tetrahydronaphthalenes **26** and **27** was also observed in certain cases resulting from a proton-initiated intramolecular Friedel−Crafts reaction.

2.3. Reaction of Aryl-Substituted Alkenes. In the case of *E*-alkenes bearing neutral or electron-donating aryl substituents ((*E*)-**2b**, (*E*)-**2d**, (*E*)-**2f**) with Hammett's values $0 > \sigma_p > -0.2$,[50] very good enantioselectivities were achieved. These selectivities were slightly lower than alkenes bearing linear or *β*-branched

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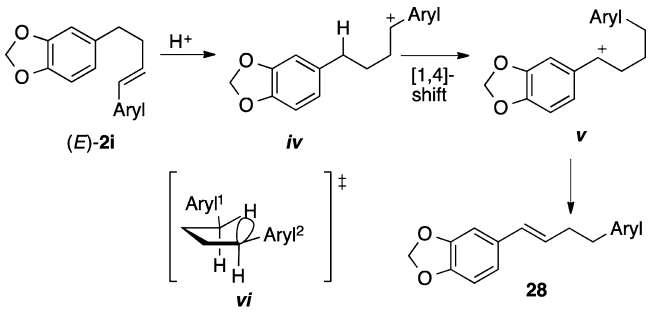
substituents most likely because of different steric demands. Likewise *E*-alkenes bearing electron-donating aryl substituents with Hammett values $\sigma_p < -0.2$ led to a slight decrease of enantioselectivity compared to neutral aryl-substituted alkenes. As was observed with trisubstituted alkenes, increasing the electronic density of the double bond led to faster cyclization. Both of these observations are explained by analogy to the behavior of the trisubstituted alkenes above.

Sterically hindered, aryl-substituted alkenes ((*E*)-**2i** and (*E*)-**2g**)) cyclized with lower enantioselectivities. This outcome was attributed to the congestion around **35** that renders the approach of the alkene difficult (models **TS-E** and **TS-F**). The lower reactivity of alkene (*E*)-**2i** allowed for a competing pathway to appear involving migration of the double bond along the alkyl chain into conjugation with the veratryl group. Protonation of the alkene presumably led to formation of a benzylic carbocation ***iv*** that could undergo a 1,4-hydride shift[51] to produce a more stable benzylic carbocation ***v***, potentially through the bridging transition state structure ***vi***.[52] Subsequent deprotonation afforded *E*-alkene **28** that did not cyclize (Scheme 10).

Scheme 10

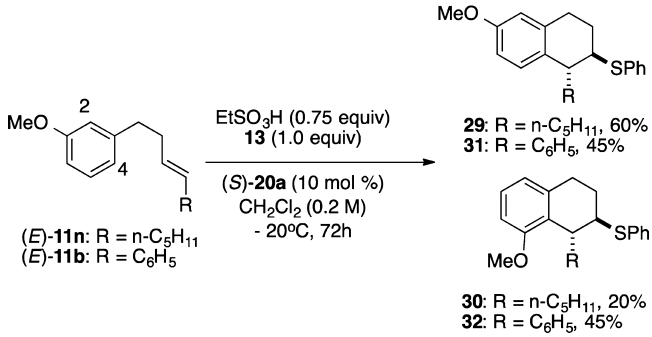


The very slow cyclization (even at room temperature) of *E*-styrenes bearing electron-withdrawing substituents ((*E*)-**2e** and (*E*)-**2h**) could be ascribed to a number of factors. In addition to the electron-deficient nature of the alkene, which would slow the formation of the thiiranium species, the presence of the cyano group in substrate (*E*)-**2e** might serve as a buffer for the Brønsted acid coactivator. Inefficient protonation of the sulfenylating agent **13** (Figure 3, step b) would lead to slow reaction.

Comparison of alkyl-substituted and aryl-substituted alkenes allowed the identification of some trends: (1) increasing the electron density of the alkenes (with electron-rich aryl or trisubstituted alkenes) afforded faster sulfenocarbocyclization but with slightly lower enantioselectivity; (2) small aliphatic rings have identical selectivity as linear alkyl-substituted alkenes; (3) increasing the size of the allylic substituent or the steric bulk of aryl-substituted alkene decreased both the rate and the enantioselectivity of the reaction; and (4) electron-deficient aryl-substituted alkenes reacted slowly without affecting the enantioselectivity.

2.4. Influence of the Nucleophilic Activator on the Aryl Group. The position of the electron-donating substituent on the nucleophilic aryl group influenced the rate of product formation. Substrate (*E*)-**11n** containing a 3-methoxy-substituted aryl ring attached to an alkyl-substituted alkene reacted to afford two constitutional isomers **29** and **30** in a 3:1 ratio (Scheme 11). In previous studies, cationic ring closures with *m*-anisole occurred at both C(2) and C(4) positions.[53] The enantiomeric

Scheme 11



ratio obtained for **29** was identical to that obtained for *trans*-**14n**. For the phenyl-substituted alkene (*E*)-**11b**, the cyclization led to the formation of constitutional isomers **31** and **32** in a 1:1 ratio.

Interestingly, substrate (*E*)-**12n** containing a 4-methoxy-substituted aryl ring bearing the alkyl-substituted alkene did not cyclize. This outcome is ascribed to the decreased electron density on the C(3) and C(5) positions of the 4-methoxy-substituted aryl group ($\sigma_p = -0.115$). However, phenyl-substituted alkene (*E*)-**12b** afforded 1,2,3,4-tetrahydronaphthalene **33**. The formation of products **31**, **32**, and **33** is likely attributed to the presence of the phenyl substituent on the alkene, which through charge stabilization can enhance the electrophilic character of the benzylic carbon of the thiiranium ion.

Cyclizations with the electron-rich veratryl group occurred exclusively at the C(6) position which finds ample precedent in intramolecular cationic cyclization reactions such as *N*-acyliminium ion closures and Friedel–Crafts reactions.[54] To explain the difference in the site selectivity for the sulfenocarbocyclization reaction between the methylenedioxy and the methoxy activating groups, computational studies were performed using density functional theory (B3LYP/6-31G*) with substrates **36** and **37** to simplify calculations (Figure 9).

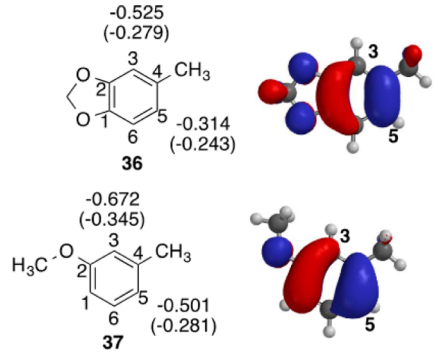


Figure 9. Electrostatic charge (natural charge values) and local energies of HOMO orbitals for models **36** and **37**.

Computational studies of simplified model **36** showed localization of the HOMO orbital at the C(5) position of the aromatic group and not at the C(3) position. In the case of **37**, similar calculations showed HOMO populations at both C(3) and C(5) positions of the nucleophilic ring. Comparison of the electrostatic (and natural) charges between models **36** and **37** showed in both cases that the C(3) position of the aryl group exhibits higher negative charge than the C(5) position, which if the reaction were purely charge-controlled would indicate a

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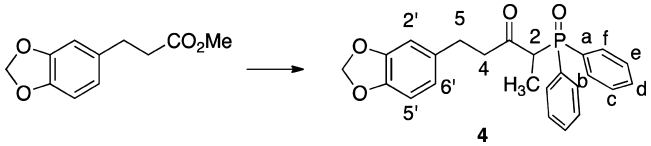
higher nucleophilic character at C(3) for alkene substrates **36** and **37**. However, the experimental results do not align with these charges densities. Calculations of the HOMO orbital occupancies support the experimental data. Thus, the calculations suggest that the sulfenocarbocyclization is under FMO control rather than electrostatic control despite the formation of a charged thiiranium ion intermediate.

CONCLUSION

In conclusion, the first catalytic, asymmetric carbosulfenylation of olefins has been accomplished by using a cocatalytic system of a Brønsted acid ($EtSO_3H$) and a chiral Lewis base (*S*)-**20a**. This method enables efficient access to enantioenriched *trans*-tetrahydronaphthalenes with complete diastereospecificity, generally high enantiomeric ratios, and a broad substrate scope with *E*-olefins. Olefins bearing α-substituted alkyl groups (cyclic or branched) and electron-poor olefins tend to give lower enantioselectivities due to the higher temperature required. *E*-Olefins reacted slowly and with very poor enantioselectivity. Formation of quaternary centers was achieved in moderate enantioselectivity. Further investigations aimed at expanding the scope of the reaction (different ring sizes and heterocycles) along with mechanistic studies on the origins of the enantioselectivity are in progress. Studies on the role of the Brønsted acid and resting state of the catalyst are the subjects of a forthcoming manuscript.

EXPERIMENTAL PROCEDURES

Preparation of Cyclization Substrates. Phosphine Oxide Route.



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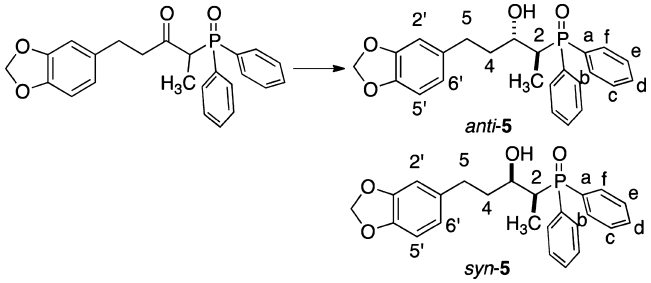
*Preparation of 2-Diphenylphosphinoyl-5(3′,4′-methylenedioxyphenyl)pentan-3-one (**4**).* *n*-BuLi (2.5 M in hexanes, 32.7 mL, 81.8 mmol) was added dropwise to a stirred solution of diphenylethylphosphine oxide (19.0 g, 82.6 mmol) in THF (300 mL) at 0 °C. After 30 min, the red solution was cooled to −70 °C and a solution of methyl-3-(3′,4′-methylenedioxyphenyl)propanoate **3** (8.6 g, 41.3 mmol) in THF (80 mL) was added dropwise over 30 min, with a syringe. After complete addition, the reaction mixture was slowly warmed to room temperature and stirred for 12 h. The reaction was quenched with saturated aq NH_4Cl (90 mL), and the aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with brine (120 mL) then dried over $MgSO_4$, filtered through glass wool, and concentrated in vacuo (20−23 °C, 10 mmHg). The product was first purified by flash column chromatography on silica gel (SiO_2, 25 g, 30 mm Ø, pentane/EtOAc, 4:1) to afford a mixture of **4** and diphenylethylphosphine oxide (14.76 g). Purification of the mixture via recrystallization from pentane/CH_2Cl_2 (85:15 v/v) (200 mL) gave **4** as white solid 8.5 g for the first crop and 3.9 g for the second crop (pentane/CH_2Cl_2 (85:15 v/v) (90 mL)) (74%). Data for **4**: mp 149−151 °C (pentane/CH_2Cl_2 (85:15 v/v)); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82−7.74 (m, 4 H, HC(b) and HC(f)), 7.58−7.55 (m, 2 H, HC(d)), 7.51−7.48 (m, 4 H, HC(c) and HC(e)), 6.67 (d, J = 7.5 Hz, 1 H, HC(5′)), 6.56 (d, J = 1.5 Hz, 1 H, HC(2′)), 6.53 (dd, J = 7.5, 1.5 Hz, 1 H, HC(6′)), 5.91 (s, 2 H, OCH_2O), 3.66 (d, J = 14.0, 7.0 Hz, 1 H, HC(2)), 2.84 (t, J = 7.5 Hz, 2 H, HC(5)), 2.66 (t, J = 7.5 Hz, 2 H, HC(4)), 1.37 (dd, J = 16.0, 7.0 Hz, 3 H, HC(1)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.8 (CO), 147.6 (C(3′)), 145.9 (C(4′)), 134.8 (C(1′)), 132.4 (d, J = 2.8, C(d)), 131.6 (d, J = 9.3, C(b)), 131.5 (d, J = 9.3, C(f)), 131.2 (d, J = 98.6, C(a)), 131.0 (d, J = 98.6, C(a)), 129.0 (d, J = 6.3, C(c)), 128.9 (d, J = 6.3, C(e)), 121.4 (C(6′)), 109.2 (C(2′)), 108.3 (C(5′)), 101.0 (OCH_2O), 50.7 (d, J = 56.8, C(2)), 45.0 (C(5)), 29.4 (C(4)), 11.5 (C(1)); ^{31}P NMR (202 MHz, $CDCl_3$) δ 31.25; IR (KBr) 2922 (s), 2853 (s), 2850 (s), 1737 (m), 1703 (w), 1498 (s), 1485 (w), 1462 (s), 1403 (m), 1376 (s), 1363 (s), 1346 (m), 1325 (m), 1240 (s), 1185 (s), 1119 (s), 1094 (s), 1035 (s), 996 (m), 928 (s); MS (ES^+) 408.1 (20), 407.1 (100); TLC R_f 0.54 (EtOAc/pentane, 4:1). Anal. Calcd for $C_{24}H_{23}O_4P$ (406.41): C, 70.93; H, 5.70; P, 7.62%. Found: C, 70.65; H, 5.67;P, 7.76%.



*Preparation of anti-2-Diphenylphosphinoyl-5-(3′,4′-methylenedioxyphenyl)pentan-3-ol (anti-**5**) and syn-2-Diphenylphosphinoyl-5-(3′,4′-methylenedioxyphenyl)pentan-3-ol (syn-**5**).* Dried $CeCl_3$[55] (788.0 mg, 3.2 mmol) was suspended in THF (30 mL) and stirred for 2 h at room temperature. A solution of ketone **4** (1.0 g, 2.5 mmol) in THF (25 mL) was added, and the reaction mixture was stirred for 12 h and then cooled at −70 °C. $LiBH_4$ (1 M in THF, 7.4 mL) was slowly added, and the reaction mixture was vigorously stirred for 3 h at −70 °C. The reaction was quenched by slow addition of saturated NH_4Cl (20 mL) at 0 °C. The aqueous phase was extracted with Et_2O (3 × 20 mL). A diluted solution of HCl (10% in H_2O, 5 mL) was added into the aqueous phase and extracted again with Et_2O (20 mL). The combined organic layers were washed with brine (60 mL), dried over $MgSO_4$, filtered through glass wool, and then concentrated in vacuo (20−23 °C, 10 mmHg). Purification via flash column chromatography (Teledyne Isco Combiflash R_f 75, Silicycle SiO_2, 25 g, 15−40 μm mesh, gradient: 35 to 50% EtOAc in hexane over 70 min, 30 mL/min) to afford *syn*-**5** as pale white oil (230 mg, 23%) that crystallized upon standing and *anti*-**5** as white solid (690 mg, 69%). Data for *anti*-**5**: mp 118−122 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82−7.73 (m, 4 H, HC(b) and HC(f)), 7.58−7.55 (m, 2 H, HC(d)), 7.52−7.48 (m, 4 H, HC(c) and HC(e)), 6.95 (d, J = 8.0 Hz, 1 H, HC(5′)), 6.64 (d, J = 1.0 Hz, 1 H, HC(2′)), 6.60 (dd, J = 8.0, 1.0 Hz, 1 H, HC(6′)), 5.91 (s, 2 H, OCH_2O), 4.71 (s, 1 H, OH), 3.88 (q, J = 7.5 Hz, 1 H, HC(3)), 2.82−2.76 (m, 1 H, HC(5)), 2.74−2.69 (m, 1 H, HC(2)), 2.61−2.55 (m, 1 H, HC(5)), 1.90−1.83 (m, 1 H, HC(4)), 1.77−1.70 (m, 1H, HC(4)), 1.04 (d, J = 17.5, 7.5 Hz, HC(1)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7 (C(3′)), 145.7 (C(4′)), 136.1 (C(1′)), 132.5 (d, J = 95.5 Hz, C(a)), 132.3 (d, J = 2.6 Hz, C(d)), 132.2 (d, J = 2.6 Hz, C(d)), 132.1 (d, J = 9.0 Hz, C(e)), 131.2 (d, J = 9.0 Hz, C(c)), 130.5 (d, J = 95.5 Hz, C(a)), 129.1 (d, J = 11.4 Hz, C(f)), 128.7 (d, J = 11.4 Hz, C(b)), 121.4 (C(2′)), 109.2 (C(6′)), 108.3 (C(5′)), 100.9 (OCH_2O), 71.6 (C(3)), 38.4 (d, J = 68.8 Hz, C(2)), 37.1 (C(4)), 31.5 (C(5)), 11.9 (C(1)); ^{31}P NMR (202 MHz, $CDCl_3$) δ 41.76; IR (KBr) 3303 (br s), 2926 (m), 2878 (m), 1503 (s), 1487 (s), 1434 (s), 1313 (w), 1243 (s), 1115 (s), 1035 (s), 994 (w), 928 (m); MS (EI^+, 70 eV) 408.1 (15.4), 259.1 (15.7), 230.0 (12.4), 229.0 (11.1), 203.0 (14.9), 202.0 (100.0), 201.0 (72.4), 188.1 (13.5), 135.0 (29.3), 77.1 (33.7), 57.1 (13.9), 51.1 (14.9); HRMS calcd for $C_{24}H_{25}O_4P^+$ 408.1491, found 408.1499; TLC R_f 0.34 (EtOAc/pentane, 7:3) [$KMnO_4$]. Data for *syn*-**5**: mp 56−58 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80−7.74 (m, 4 H, HC(b) and HC(f)), 7.55−7.46 (m, 6 H, HC(c), HC(d), H(e)), 6.66 (d, J = 8.0 Hz, 1 H, HC(5′)), 6.62 (d, J = 1.0 Hz, 1 H, HC(2′)), 6.56 (dd, J = 8.0, 1.0 Hz, 1 H, HC(6′)), 5.91 (d, J = 2.5 Hz, 2 H, OCH_2O), 4.25 (s, 1 H, OH), 4.11−4.06 (m, 1 H, HC(3)), 2.69−2.63 (m, 1 H, HC(5)), 2.54−2.48 (m, 1 H, HC(5)), 2.32 (dq, J = 7.5, 7.5 Hz, 1 H, HC(2)), 2.03−1.96 (m, 1 H, HC(4)), 1.63−1.56 (m, 1 H, HC(4)), 1.21 (dd, J = 17.0, 7.5 Hz, 3 H, HC(1)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7 (C(3′)), 145.8 (C(4′)), 135.6 (C(1′)), 132.2 (d, J = 2.8 Hz, C(d)), 132.0 (d, J = 2.8 Hz, C(d)), 131.9 (d, J = 94.4 Hz, C(a)), 131.4 (d, J = 94.4 Hz, C(a)), 131.0 (d, J = 11.5 Hz, C(b)), 130.9 (d, J = 11.5 Hz, C(f)),

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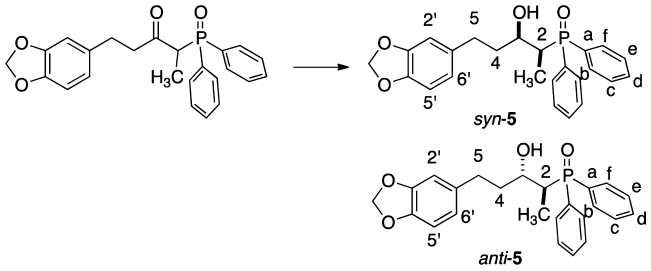
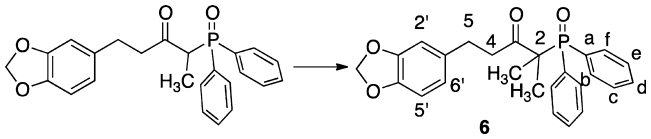
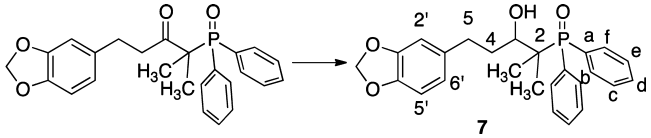
129.1 (d, J = 4.1 Hz, C(c)), 129.0 (d, J = 4.1 Hz, C(e)), 121.3 (C(6′)), 109.0 (C(2′)), 108.3 (C(5′)), 100.9 (OCH_2O), 68.5 (C(3)), 36.8 (d, J = 12.5 Hz, C(4)), 36.1 (d, J = 70.1 Hz, C(2)), 32.1 (C(5)), 5.9 (C(1)); ^{31}P NMR (202 MHz, $CDCl_3$) δ 41.69; IR (KBr) 3425 (br s), 3059 (m), 2926 (s), 2885 (s), 1712 (s), 1608 (m), 1590 (m), 1503 (s), 1486 (s), 1451 (m), 1434 (m), 1361 (m), 1337 (m), 1234 (s), 1160 (s), 1115 (m), 1035 (m), 924 (s); MS (EI^+, 70 eV) 408.2 (16.1), 259.1 (12.3), 231.2 (10.0), 230.1 (13.7), 229.1 (12.2), 203.1 (15.6), 202.0 (100.0), 201.0 (64.0), 191.1 (9.7), 188.1 (20.2), 155.1 (10.8), 135.0 (25.9), 91.1 (11.1), 77.1 (28.6), 71.1 (37.9), 69.1 (12.4), 57.1 (25.7), 55.1 (20.4), 51.0 (12.5); HRMS calcd for $C_{24}H_{25}O_4P^+$ 408.14905, found 408.14850; TLC R_f 0.42 (EtOAc/pentane, 7:3) [$KMnO_4$].



*Preparation of syn-2-Diphenylphosphinoyl-5-(3′,4′-methylenedioxyphenyl)pentan-3-ol (syn-**5**) and anti-2-Diphenylphosphinoyl-5-(3′,4′-methylenedioxyphenyl)pentan-3-ol (anti-**5**).* Titanium tetrachloride (0.7 mL, 6.4 mmol) was added to a solution of ketone **4** (2.0 g, 4.92 mmol) in CH_2Cl_2 (30 mL) at −30 °C. The reaction turned immediately red. After 1 h, the reaction mixture was cooled to −70 °C and BH_3·py (1 M, 8.4 mL, 9.84 mmol) was slowly added and the reaction mixture was stirred for 3 h and then warmed to room temperature. The reaction was quenched with slow addition of dilute HCl (10% in H_2O, 20 mL) at 0 °C. The aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL), and the combined organic layers were washed with brine (80 mL), dried over $MgSO_4$, filtered through glass wool, and then concentrated in vacuo (20−23 °C, 10 mmHg). Purification via flash column chromatography (Teledyne Isco Combiflash R_f 75, Silicycle silica gel, 25 g, 15−40 μm mesh, gradient: 35 to 50% EtOAc in hexane over 70 min, 30 mL/min) to afford *syn*-**5** as pale white oil (1.4 g, 72%) that crystallized upon standing, and *anti*-**5** as white solid (343 mg, 17%). Characterizations were in accordance with the previously described compounds for *anti*-**5** and *syn*-**5**.



*Preparation of 2-Methyl-2-diphenylphosphinoyl-5-(3′,4′-methylenedioxyphenyl)pentan-3-one (**6**).* A solution of KO*t*-Bu (435 mg, 3.9 mmol) in THF (20 mL) was added at 0 °C via syringe, into a solution of ketone **4** (1.5 g, 3.7 mmol) in THF (50 mL). The homogeneous mixture was then vigorously stirred for 1 h followed by slow addition of MeI (460.0 μL, 7.4 mmol). After complete addition, the reaction mixture was warmed to room temperature and stirred for 12 h. The reaction was quenched with dilute HCl (10% in H_2O, 20 mL). The aqueous phase was extracted with Et_2O (3 × 20 mL), and the combined organic layers were washed with brine (60 mL), dried over Na_2SO_4, filtered through glass wool, and then concentrated in vacuo (20−23 °C, 10 mmHg). Purification via by flash column chromatography (SiO_2, 20 g, 25 mm Ø, EtOAc/pentane, 7:3) afforded **6** as white solid (1.36 g, 87%). Recrystallization from hot Et_2O provided 1.31 g of analytically pure **6**. Data for **6**: mp 108−110 °C (Et_2O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84−7.80 (m, 4 H, HC(b) and HC(f)), 7.58−7.54 (m, 2 H, HC(d)), 7.50−7.46 (m, 4 H, HC(c) and HC(e)), 6.67 (d, J = 8.0 Hz, 1 H, HC(5′)), 6.56 (d, J = 1.5 Hz, 1 H, HC(2′)), 6.54 (dd, J = 8.0, 1.5 Hz, 1 H, HC(6′)), 5.90 (s, 2 H, OCH_2O), 2.91 (t, J = 7.5 Hz, 2 H, HC(5)), 2.62 (t, J = 7.5 Hz, 2 H, HC(4)), 1.45 (d, J = 15.0 Hz, 6 H, HC(1)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.3 (CO), 147.6 (C(3′)), 145.9 (C(4′)), 135.0 (C(1′)), 132.4 (d, J = 15.0 Hz, C(b,f)), 132.3 (d, J = 2.8 Hz, C(d)), 130.7 (d, J = 95.5 Hz, C(a)), 128.7 (d, J = 14.6 Hz, C(c,e)), 121.5 (C(2′)), 109.3 (C(6′)), 108.3 (C(5′)), 100.9 (OCH_2O), 53.2 (d, J = 57.5 Hz, C(2)), 42.9 (C(5)), 29.8 (C(4)), 21.4 (C(1)); ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.61; IR (KBr) 3060 (w), 2970 (w), 2922 (w), 1699 (s), 1606 (w), 1592 (w), 1505 (m), 1490 (m), 1482 (m), 1439 (s), 1417 (m), 1370 (m), 1297 (w), 1241 (s), 1177 (s), 1116 (s), 1099 (s), 1039 (s), 996 (m), 928 (s); MS (TOF ES^+) 422.1 (25.0), 421.1 (16.1, M+H^+); HRMS calcd for $C_{25}H_{26}O_4P^+$ 421.1569, found 421.1574; TLC R_f 0.49 (pentane/EtOAc, 3:7). Anal. Calcd for $C_{25}H_{25}O_4P$ (420.44): C, 71.42; H, 5.99; P, 7.37%. Found: C, 71.29; H, 6.02; P, 7.49%.



*Preparation of 2-Methyl-2-diphenylphosphinoyl-5-(3′,4′-methylenedioxyphenyl)pentan-3-ol (**7**).* Sodium borohydride (675 mg, 17.8 mmol) was added portion wise to a solution of ketone **6** (2.50 g, 5.95 mmol) in CH_2Cl_2/MeOH (1:1 v/v, 100 mL) at room temperature and stirred for 4 h. The reaction was quenched with saturated aq NH_4Cl (30 mL) at 0 °C. The aqueous phase was extracted with Et_2O (3 × 55 mL), and the combined organic layers were successively washed with brine (100 mL), dried over $MgSO_4$, filtered through glass wool, and then concentrated in vacuo (20−23 °C, 10 mmHg). The product **7** was obtained as a white solid (2.51 g, 99%). The crude material was used without further purification. Recrystallization of an aliquot (400 mg) from CH_2Cl_2 20%/Et_2O 80% (v/v) (5 mL) gave an analytical sample of **7** (380 mg). Data for **7**: mp 123−125 °C (CH_2Cl_2/Et_2O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03−8.00 (m, 2 H, HC(d)), 7.97−7.94 (m, 2 H, HC(e)), 7.60−7.50 (m, 6 H, HC(d), HC(c) and HC(f)), 6.70 (d, J = 8.0 Hz, 1 H, HC(5′)), 6.66 (d, J = 1.0 Hz, 1 H, HC(2′)), 6.62 (dd, J = 8.0, 1.0 Hz, 1 H, HC(6′)), 5.92 (s, 2 H, OCH_2O), 5.46 (s, 1 H, OH), 3.86 (dt, J = 11.0, 1.5 Hz, 1 H, HC(3)), 2.88 (ddd, J = 14.0, 10.5, 4.5 Hz, 1 H, HC(5)), 2.48 (ddd, J = 14.0, 9.5, 6.5 Hz, 1 H, HC(5)), 1.72−1.64 (m, 1 H, HC(4)), 1.58−1.52 (m, 1 H, HC(4)), 1.26 (d, J = 16.0 Hz, 3 H, HC(1)), 1.08 (d, J = 17.0 Hz, 3 H, HC(1)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6 (C(3′)), 145.7 (C(4′)), 136.5 (C(1′)), 132.4 (d, J = 8.1 Hz, C(c)), 132.3 (d, J = 8.1 Hz, C(e)), 132.2 (d, J = 2.6 Hz, C(d)), 131.1 (d, J = 2.5 Hz, C(d)), 130.4 (d, J = 89.1 Hz, C(a)), 128.8 (d, J = 10.8 Hz, C(b)), 128.7 (d, J = 10.8 Hz, C(f)), 121.4 (C(6′)), 109.2 (C(2′)), 108.3 (C(5′)), 100.9 (OCH_2O), 73.8 (C(3)), 40.5 (d, J = 68.7 Hz, C(2)), 32.5 (C(4,5), 21.4 (C(1)), 16.3 (C(1)); ^{31}P NMR (202 MHz, $CDCl_3$) δ 44.8; IR (KBr) 3306 (bm), 3056 (w), 2966 (m), 2927 (m), 2879 (m), 1609 (w), 1592 (w), 1501 (m), 1488 (s), 1437 (s), 1241 (s), 1168 (s), 1146 (s), 1110 (s), 1093 (s), 1037 (m), 998 (w), 929 (s); MS (TOF ES^+) 457.1 (4.0), 425.2 (3.5), 424.2 (23.2), 423.2 (100, M+2H^+), 403.1 (3.5); HRMS calcd for $C_{25}H_{28}O_4P^+$ 423.1725, found 423.1715; TLC R_f 0.47 (EtOAc/pentane, 7:3) [$KMnO_4$].

*General Procedure **1**.* An oven-dried, 50 mL, two-necked, round-bottomed flask was charged with KH (1.5 equiv) in a glovebox and capped with a septum and a stopper. Outside of the glovebox, a solution of the requisite β-hydroxy diphenylphosphine oxide (1.0 equiv) in DMF (30 mL) at room temperature then the reaction mixture was heated at 50 °C. After 30 min, the homogeneous orange solution was allowed to cool to room temperature, and the reaction was quenched with H_2O (50 mL). The aqueous phase was extracted with pentane (3 × 20 mL). HCl (1 M, 30 mL) was added to the aqueous solution. The aqueous phase was extracted with pentane (2 × 15 mL). The combined organic layers were washed with brine (60 mL), dried over $MgSO_4$, filtered through glass wool, and then concentrated in vacuo (20−23 °C, 10 mmHg). The product olefins were purified by flash column chromatography on silica gel (SiO_2, 15 g, 20 mm Ø, pentane/Et_2O, 98:2) followed by distillation.

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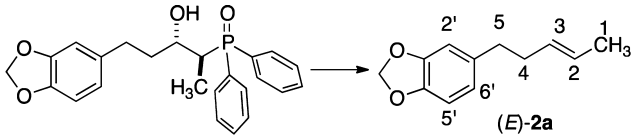
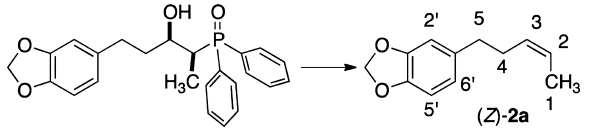
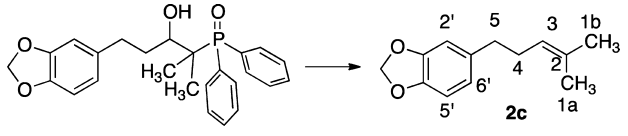


*Preparation of (E)-5-(3′,4′-Methylenedioxyphenyl)pent-2-ene ((E)-**2a**).* Following General Procedure 1, oven-dried 50 mL KH (160 mg, 3.97 mmol) and alcohol *anti*-**5** (1.08 mg, 2.6 mmol) were reacted to give (*E*)-**2a** (372 mg, 74%) as colorless liquid after purification by distillation. Data for (*E*)-**2a**: bp 45 °C at 3.2×10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.75 (d, J = 8.0 Hz, 1 H, HC(5′)), 6.70 (d, J = 1.0 Hz, 1 H, HC(2′)), 6.65 (dd, J = 8.0, 1.0 Hz, 1 H, HC(6′)), 5.94 (s, 2 H, OCH_2O), 5.49−5.47 (m, 2 H, HC(2) and HC(3)), 2.61 (t, J = 7.5 Hz, 2 H, HC(5)), 2.30−2.26 (m, 2 H, HC(4)), 1.67 (d, J = 3.5 Hz, 3 H, HC(1)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6 (C(3′)), 145.7 (C(4′)), 136.3 (C(1′)), 130.6 (C(3)), 125.7 (C(2)), 121.3 (C(6′)), 109.2 (C(2′)), 108.3 (C(5′)), 100.9 (OCH_2O), 36.0 (C(5)), 35.0 (C(4)), 18.1 (C(1)); IR (neat) 3017 (m), 2912 (s), 2857 (s), 2766 (w), 1608 (w), 1503 (w), 1486 (s), 1441 (s), 1358 (m), 1243 (s), 1035 (s), 966 (s), 938 (s), 855 (m), 806 (s); MS (EI$^+$, 70 eV) 191.1 (3.0), 190.1 (22.2), 136.1 (8.3), 135.0 (100.0), 105.0 (4.2), 79.1 (3.5), 77.1 (11.4), 55.1 (2.4), 51.0 (6.4); HRMS calcd for $C_{12}H_{14}O_2^+$ 190.0988, found 190.0994; TLC R_f 0.71 (pentane) [$KMnO_4$]. Anal. Calcd for $C_{12}H_{14}O_2$ (190.24): C, 75.76; H, 7.42%. Found: C, 76.15; H, 7.58%.



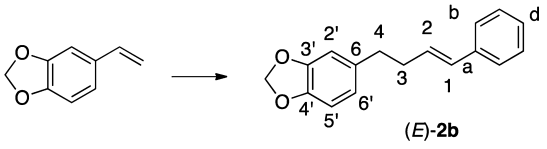
*Preparation of (Z)-5(3′,4′-Methylenedioxyphenyl)pent-2-ene ((Z)-**2a**).* Following General Procedure 1, KH (134 mg, 3.35 mmol) and alcohol *syn*-**5** (913 mg, 2.23 mmol) were reacted to give (*Z*)-**2a** (2 mg, 76%) as colorless liquid after purification by distillation. Data for (*Z*)-**2a**: bp 40 °C at 3.2×10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.75 (d, J = 8.0 Hz, 1 H, HC(5′)), 6.72 (d, J = 1.0 Hz, 1 H, HC(2′)), 6.67 (dd, J = 8.0, 1.0 Hz, 1 H, HC(6′)), 5.94 (s, 2 H, OCH_2O), 5.53−5.41 (m, 2 H, HC(2) and HC(3)), 2.61 (t, J = 7.5 Hz, 2 H, HC(5)), 2.34 (dt, J = 7.5, 7.5 Hz, 2 H, HC(4)), 1.60 (d, J = 6.5 Hz, 3 H, HC(1)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7 (C(3′)), 145.7 (C(4′)), 136.3 (C(1′)), 129.7 (C(3)), 124.8 (C(2)), 121.4 (C(6′)), 109.1 (C(2′)), 108.3 (C(5′)), 100.9 (OCH_2O), 35.7 (C(5)), 29.3 (C(4)), 13.0 (C(1)); IR (neat) 3010 (s), 2926 (s), 2773 (m), 1608 (w), 1503 (s), 1486 (s), 1441 (s), 1358 (m), 1247 (s), 1039 (s), 935 (s), 858 (m), 810 (s); MS (EI$^+$, 70 eV) 191.1 (2.0), 190.1 (14.9), 136.1 (8.2), 135.1 (100.0), 105.0 (4.8), 79.1 (3.7), 78.1 (2.4), 77.1 (14.9), 63.1 (2.3), 51.0 (8.6); HRMS calcd for $C_{12}H_{14}O_2^+$ 190.0994, found 190.0997; TLC R_f 0.71 (pentane) [$KMnO_4$]. Anal. Calcd for $C_{12}H_{14}O_2$ (190.24): C, 75.76; H, 7.42%. Found: C, 75.73; H, 7.39%.



*Preparation of 2-Methyl-5(3′,4′-methylenedioxyphenyl)pent-2-ene (**2c**).* Following General Procedure 1, oven-dried 50 mL KH (108 mg, 2.7 mmol) and alcohol **7** (760 mg, 1.8 mmol) were reacted to give **2c** (293 mg, 72%) as colorless liquid after purification by distillation. Data for **2c**: bp 50 °C at 3.2×10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.75 (d, J = 8.0 Hz, 1 H, HC(5′)), 6.72 (d, J = 1.0 Hz, 1 H, HC(2′)), 6.66 (dd, J = 8.0, 1.0 Hz, 1 H, HC(6′)), 5.94 (s, 2 H, OCH_2O), 5.18 (tq, J = 7.0, 1.5 Hz, 1 H, HC(3)), 2.57 (t, J = 8.0 Hz, 2 H, HC(5)), 2.27 (dt, J = 7.5, 7.5 Hz, 2 H, HC(4)), 1.72 (s, 3 H, HC(1a)), 1.60 (s, 3 H, HC(1b)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6 (C(3′)), 145.7 (C(4′)), 136.5 (C(1′)), 132.4 (C(2)), 123.8 (C(3)), 121.3 (C(6′)), 109.1 (C(2′)), 108.3 (C(5′)), 100.9 (OCH_2O), 36.1 (C(5)), 30.6 (C(4)), 25.9 (C(1a)), 17.9 (C(1b)); IR (neat) 2961 (s), 2912 (s), 2773 (w), 1608 (w), 1503 (s), 1486 (s), 1441 (s), 1379 (m), 1247 (s), 1188 (w), 1094 (w), 1042 (s), 938 (s), 855 (m), 806 (s); MS (EI$^+$, 70 eV) 205.2 (2.6), 204.2 (17.4), 204.1 (17.4), 136.1 (9.1), 135.1 (100.0), 105.0 (3.7), 79.1 (2.8), 77.1 (11.1), 51.0 (5.7); HRMS calcd for $C_{13}H_{16}O_2^+$ 204.1150, found 204.1155; TLC R_f 0.35 (pentane) [$KMnO_4$]. Anal. Calcd for $C_{13}H_{16}O_2$ (204.26): C, 76.44; H, 7.90%. Found: C, 76.41; H, 7.65%.

Preparation of Cyclization Substrates. Suzuki Coupling Route. *Preparation of Cyclization Substrates (please refer to footnote 56 for the safe handling and disposal of thallium and arsenic containing compounds). General Procedure **3**.* To an oven-dried, 20 mL, two-necked, round-bottomed flask charged with the requisite alkene (1.0 equiv) was added dropwise a solution of 9-BBN (solution in THF, 1.5 equiv) at room temperature with stirring. In a separate flask, the requisite vinyl iodide (1.2 equiv) was added at room temperature to a mixture of $PdCl_2$(dppf) (0.1 equiv), $AsPh_3$ (0.2 equiv), and THF. After 2 h, TlOEt (2.0 equiv) and H_2O (5.0 equiv) were sequentially added dropwise to the alkylborane solution. Immediately, the solution turned gray. The reaction mixture was allowed to stir for 2 min, then the alkylborane solution was transferred via cannula into the orange suspension of the vinyl iodide, Pd(dppf)Cl_2, and $AsPh_3$ at room temperature whereupon the reaction mixture turned pale green.[56a] The flask containing the borane solution was rinsed with THF (2 mL) and was transferred via cannula into the reaction solution. The reaction flask was wrapped in aluminum foil to exclude light. After being stirred for 12 h, the contents of the flask were poured into H_2O (30 mL).[56b] The aqueous phase was extracted with Et_2O (3 × 15 mL). Then, the combined organic extracts were stirred with H_2O_2 (30% aq, 4.0 equiv) at room temperature for 20 min whereupon the mixture turned a cloudy yellow. Saturated aq Na_2SO_3 solution (10 mL) was added dropwise to quench any remaining H_2O_2 (a slight warming of the solution was noted), prompting the mixture to become clear and orange. Starch-iodide paper was used to confirm that no H_2O_2 remained. The organic phase was successively washed with H_2O (20 mL), brine (60 mL), then dried over $MgSO_4$, filtered through glass wool,[56c] and concentrated in vacuo (20−23 °C, 10 mmHg). The crude products were purified by flash column chromatography on silica gel[56d] followed by distillation or recrystallization as necessary.

*General Procedure **4**.* To an oven-dried, 20 mL, two-necked, round-bottomed flask charged with the requisite alkene (1.0 equiv) was added dropwise a solution of 9-BBN (solution in THF, 1.5 equiv) at room temperature with stirring. In a separate flask, the requisite vinyl iodide (1.2 equiv) was added at room temperature to a mixture $PdCl_2$(dppf) (0.05 equiv), $AsPh_3$ (0.1 equiv), Cs_2CO_3 (2.0 equiv), and DMF. After 2 h, H_2O (15.0 equiv) and alkylborane solution were sequentially added dropwise to the Pd(dppf)Cl_2 solution. After stirring for 24 h at room temperature, the contents of the flask were poured into H_2O (50 mL). The aqueous phase was extracted with Et_2O (3 × 15 mL). Then, the combined organic layers were stirred with H_2O_2 (30% aq) at room temperature for 20 min to oxidize $AsPh_3$ residues. The organic phase were successively washed with H_2O (20 mL), brine (60 mL), then dried over $MgSO_4$, filtered through glass wool, and concentrated in vacuo (20−23 °C, 10 mmHg). The crude products were purified by flash column chromatography on silica gel.



*Preparation of (E)-4-(3′,4′-Methylenedioxyphenyl)-1-phenylbut-1-ene ((E)-**2b**).* Following General Procedure 3, olefin **8a** (149 mg, 1.0 mmol), 9-BBN (0.345 M in THF, 4.4 mL, 1.5 mmol), TlOEt (142 μL, 2.0 mmol), and H_2O (91 μL, 5.0 mmol) were reacted with $PdCl_2$(dppf) (73.5 mg, 0.1 mmol), $AsPh_3$ (61.2 mg, 0.4 mmol), (*E*)-(2-iodovinyl)benzene **10b** (277.6 mg, 1.2 mmol), and THF (4 mL). The product was purified by flash column chromatography (SiO_2, 30 g, 40 mm Ø, hexane/Et_2O, 98:2) to afford 183 mg of (*E*)-**2b** as orange oil. Purification by distillation afforded 179 mg (71%) of

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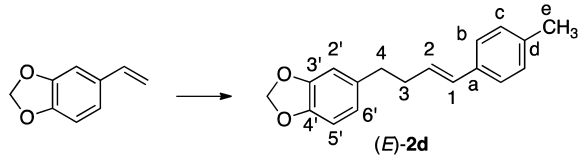
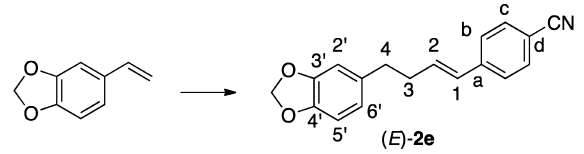
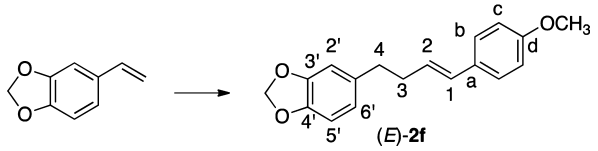
analytically pure (*E*)-**2b** as slightly orange oil. Data for (*E*)-**2b**: bp 120 °C at 3.0 × 10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.29 (m, 4 H, HC(b) and HC(c)), 7.22 (dt, J = 7.0, 1.5 Hz, 1 H, HC(d)), 6.76 (d, J = 8.0 Hz, 1 H, HC(5′)), 6.74 (d, J = 1.0 Hz, 1 H, HC(2′)), 6.68 (dd, J = 8.0, 1.0 Hz, 1 H, HC(6′)), 6.42 (d, J = 16.0 Hz, 1 H, HC(1)), 6.26 (dt, J = 16.0, 6.5 Hz, 1 H, HC(2)), 5.94 (s, 2 H, OCH_2O), 2.73 (t, J = 7.5 Hz, 2 H, HC(4)), 2.50 (dtd, J = 7.5, 7.5, 1.0 Hz, 2 H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8 (C(3′)), 145.9 (C(4′)), 137.9 (C(a)), 135.8 (C(1′)), 130.7 (C(d)), 130.1 (C(1)), 128.7 (C(c)), 127.2 (C(2)), 126.2 (C(b)), 121.4 (C(6′)), 109.1 (C(2′)), 108.4 (C(5′)), 100.9 (OCH_2O), 35.9 (C(4)), 35.3 (C(3)); IR (neat) 3060 (w), 3024 (m), 2931 (m), 2902 (m), 2845 (m), 1607 (w), 1596 (w), 1499 (s), 1487 (s), 1447 (s), 1366 (m), 1242 (s), 1200 (s), 1117 (m), 1101 (m), 1036 (s), 962 (s), 923 (s), 868 (s), 804 (s), 757 (s), 737 (s), 687 (s); MS (EI$^+$, 70 eV) 252.1 (45.0), 136.1 (11.5), 135.1 (100.0), 117.1 (9.0), 115.1 (8.8); HRMS calcd for $C_{17}H_{16}O_2^+$ 252.1150, found 252.1142; TLC R_f 0.49 (hexane/Et_2O, 96:4) [$KMnO_4$].



*Preparation of (E)-4-(3′,4′-Methylenedioxyphenyl)-1-(4-methylphenyl)but-1-ene ((E)-**2d**).* Following General Procedure 3, olefin **8a** (149 mg, 1.0 mmol), 9-BBN (0.345 M in THF, 4.4 mL, 1.5 mmol), TlOEt (142 μL, 2.0 mmol), and H_2O (91 μL, 5.0 mmol) were reacted with $PdCl_2$(dppf) (73.5 mg, 0.10 mmol), $AsPh_3$ (61.6 mg, 0.20 mmol), (*E*)-1-(2-iodovinyl)-4-methylbenzene **10d** (292 mg, 1.2 mmol), and THF (4 mL). Purification by flash column chromatography (SiO_2, 24 g, 40 mm Ø, hexanes/Et_2O, 96:4) afforded (*E*)-**2d** (166 mg, 62%) as white solid. Recrystallization from hot hexane provided 160 mg (60%) of analytically pure (*E*)-**2d**. Data for (*E*)-**2d**: mp 67–68 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, J = 8.0 Hz, 2 H, HC(b)), 7.14 (d, J = 8.0 Hz, 2 H, HC(c)), 6.77 (d, J = 8.0 Hz, 1 H, HC(5′)), 6.75 (d, J = 1.0 Hz, 1 H, HC(2′)), 6.70 (dd, J = 8.0, 1.0 Hz, 1 H, HC(6′)), 6.41 (d, J = 16.0 Hz, 1 H, HC(1)), 6.22 (dt, J = 15.5, 6.5 Hz, 1 H, HC(2)), 5.96 (s, 2 H, OCH_2O), 2.74 (t, J = 8.0 Hz, 2 H, HC(4)), 2.51 (dt, J = 7.5, 7.5 Hz, 2H, HC(3)), 2.36 (s, 3 H, HC(1)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8 (C(3′)), 145.9 (C(4′)), 136.9 (C(d)), 135.9 (C(a)), 135.1 (C(1′)), 130.5 (C(2)), 129.4 (C(b)), 129.0 (C(1)), 126.1 (C(c)), 121.4 (C(6′)), 109.2 (C(2′)), 108.4 (C(5′)), 101.0 (OCH_2O), 35.9 (C(4)), 35.4 (C(3)), 21.4 (C(e)); IR (KBr) 3022 (w), 2929 (m), 2897 (m), 2852 (w), 2783 (w), 1607 (w), 1498 (s), 1486 (s), 1442 (s), 1355 (m), 1243 (s), 1189 (s), 1122 (m), 1100 (s), 1037 (s), 970 (s), 936 (s), 924 (s), 859 (s), 810 (s), 800 (s), 768 (s); MS (TOF ES$^+$) 364.4 (50.0), 341.3 (72.0), 282.3 (100.0), 267.1 (65.0), 175.1 (80.0), 145.1 (91.5); HRMS calcd for $C_{18}H_{19}O_2^+$ 267.1385, found 267.1382; TLC R_f 0.51 (hexane/Et_2O, 96:4) [$KMnO_4$]. Anal. Calcd for $C_{18}H_{18}O_2$ (266.33): C, 81.17; H, 6.81%. Found: C, 81.42; H, 6.68%.



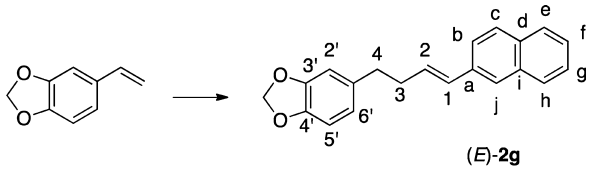
*Preparation of (E)-4-(3′,4′-Methylenedioxyphenyl)-1-(4-cyanophenyl)but-1-ene ((E)-**2e**).* Following General Procedure 4, olefin **8a** (222.0 mg, 1.5 mmol) in THF (2 mL), 9-BBN (0.577 M in THF, 3.9 mL, 2.25 mmol), and H_2O (0.41 mL, 22.5 mmol) were reacted with $PdCl_2$(dppf) (54.8 mg, 74.9 μmol), $AsPh_3$ (45.8 mg, 149.8 μmol), Cs_2CO_3 (976.4 mg, 3.0 mmol), (*E*)-4-(2-iodovinyl)benzonitrile **10e** (458.6 mg, 1.8 mmol), and DMF (4 mL). Purification by flash column chromatography (SiO_2, 27 g, 30 mm Ø, hexanes/Et_2O, 80:20) afforded (*E*)-**2e** (262 mg, 63%) as white solid, along with starting material **8a** (26 mg 12%). Recrystallization of (*E*)-**2e** from hot hexane provided 253 mg (16%) of analytically pure (*E*)-**2e**. Data for (*E*)-**2e**: mp 105–106 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 8.0 Hz, 2 H, HC(c)), 7.41 (d, J = 8.0 Hz, 2H, HC(b)), 6.74 (d, J = 7.5 Hz, 1 H, HC(5′)), 6.72 (s, 1H, HC(2′)), 6.70 (d, J = 7.5, 1.0 Hz, 1 H, HC(6′)), 6.45–6.36 (m, 2 H, HC(1) and HC(2)), 5.95 (s, 2 H, OCH_2O), 2.75 (t, J = 7.5 Hz, 2 H, HC(4)), 2.51 (dt, J = 7.0, 7.0 Hz, 2 H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9 (C(3′)), 146.0 (C(4′)), 142.4 (C(a)), 135.3 (C(1)), 134.3 (C(1′)), 132.6 (C(c)), 129.4 (C(2)), 126.7 (C(b)), 121.4 (C(6′)), 119.3 (CN), 110.4 (C(d)), 109.1 (C(2′)), 108.4 (C(5′)), 101.0 (OCH_2O), 35.4 (C(4)), 35.3 (C(3)); IR (KBr) 3026 (w), 2990 (w), 2909 (w), 2880 (w), 2775 (w), 2223 (m), 1645 (w), 1645 (w), 1603 (s), 1500 (s), 1486 (s), 1452 (m), 1440 (s), 1411 (m), 1351 (m), 1251 (s), 1229 (s), 1185 m), 1100 (m), 1029 (s), 974 (s), 956 (s), 920 (s), 873 (s), 859 (s), 802 (s); MS (TOF ES$^+$) 324 0 (20.0), 323.0 (100.0), 278.1 (10.0); HRMS calcd for $C_{18}H_{16}O_2^+$ 278.1181, found 278.1174; TLC R_f 0.37 (hexane/Et_2O, 80:20) [$KMnO_4$]. Anal. Calcd for $C_{18}H_{15}NO_2$ (277.32): C, 77.96; H, 5.45; N, 5.05%. Found: C, 77.88; H, 5.51; N, 4.98%.



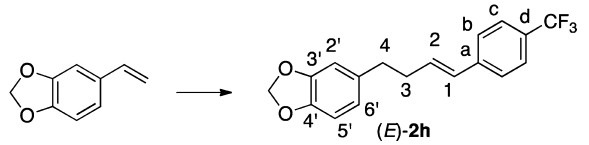
*Preparation of (E)-4-(3′,4′-Methylenedioxyphenyl)-1-(4-methoxyphenyl)but-1-ene ((E)-**2f**).* Following General Procedure 4, olefin **8a** (222.0 mg, 1.5 mmol) in THF (2 mL), 9-BBN (0.577 M in THF, 3.9 mL, 2.25 mmol), and H_2O (0.41 mL, 22.5 mmol) were reacted with $PdCl_2$(dppf) (54.8 mg, 74.9 μmol), $AsPh_3$ (45.8 mg, 149.8 μmol), Cs_2CO_3 (976.4 mg, 3.0 mmol), (*E*)-1-(2-iodovinyl)-4-methoxybenzene **10f** (458.6 mg, 1.8 mmol), and DMF (4 mL). Purification by flash column chromatography (SiO_2, 35 g, 30 mm Ø, hexanes/Et_2O, 95:5) afforded (*E*)-**2e** (180 mg, 43%) as white solid, along with starting material **8a** (22 mg, 10%). Recrystallization of (*E*)-**2e** from hot hexane provided 170 mg (40%) of (*E*)-**2e**. Data for (*E*)-**2f**: mp 92–93 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, J = 9.0 Hz, 2 H, HC(b)), 6.87 (d, J = 8.0 Hz, 2 H, HC(c)), 6.77 (d, J = 8.0 Hz, 1 H, HC(5′)), 6.75 (d, J = 1.0 Hz, 1 H, HC(2′)), 6.69 (dd, J = 8.0, 1.0 Hz, 1 H, HC(6′)), 6.39 (d, J = 16.0 Hz, 1 H, HC(1)), 6.12 (dt, J = 16.0, 7.0 Hz, 1 H, HC(2)), 5.95 (s, 2 H, OCH_2O), 3.83 (s, 3 H, OCH_3), 2.73 (t, J = 7.5 Hz, 2 H, HC(4)), 2.51 (dt, J = 7.5, 7.5 Hz, 2 H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0 (C(d)), 147.8 (C(3′)), 145.8 (C(4′)), 136.0 (C(1′)), 130.8 (C(a)), 130.0 (C(1)), 127.9 (C(2)), 127.3 (C(b)), 121.4 (C(6′)), 114.15 (C(c)), 109.1 (C(2′)), 108.4 (C(5′)), 101.0 (OCH_2O), 55.5 (OCH_3), 36.1 (C(4)), 35.4 (C(3)); IR (KBr) 3014 (m), 2961 (m), 2937 (w), 2913 (w), 2840 (m), 1597 (s), 1569 (s), 1506 (s), 1464 (s), 1410 (s), 1415 (s), 1369 (w), 1300 (s), 1247 (s), 1177 (s), 1112 (s), 1025 (s), 982 (s), 958 (s), 817 (s), 800 (s), 750 (s); MS (EI$^+$, 70 eV) 282.1 (16.9), 267.1 (5.4), 266.1 (27.0), 265.1 (6.2), 235.1 (6.2), 151.0 (6.0), 148.0 (11.2), 147.1 (100.0), 135.0 (23.8), 121.0 (7.8), 115.0 (6.6); HRMS calcd for $C_{18}H_{18}O_3^+$ 282.12560, found 282.12578; TLC R_f 0.29 (hexane/Et_2O, 95:5) [$KMnO_4$]. Anal. Calcd for $C_{18}H_{18}O_3$ (282.12): C, 76.57; H, 6.43%. Found: C, 76.67; H, 6.51%.

Following General Procedure 3, olefin **8a** (149 mg, 2.0 mmol), 9-BBN (0.345 M in THF, 4.4 mL, 1.5 mmol), TlOEt (142 μL, 2.0 mmol), and H_2O (91 μL, 5.0 mmol) were reacted with $PdCl_2$(dppf) (73.5 mg, 0.1 mmol), Ph_3As (61.6 mg, 0.2 mmol), and (*E*)-1-(2-iodovinyl)-4-methoxybenzene **10f** (313.8 mg, 1.2 mmol). Purification by flash column chromatography (SiO_2, 25 g, 40 mm Ø, hexanes/Et_2O, 95:5) afforded (*E*)-**2f** (160 mg, 64%) as pale yellow solid. Recrystallization from hot hexane provided 172 mg (61%) of analytically pure (*E*)-**2f**. Spectroscopic data matched those of the product from the previous procedure.

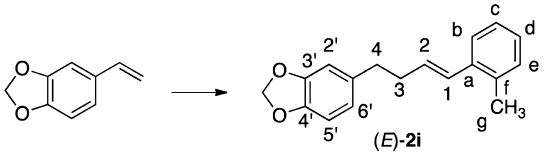
dx.doi.org/10.1021/jo4023765 | J. Org. Chem. XXXX, XXX, XXX–XXX



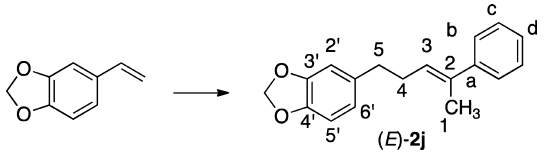
*Preparation of (E)-4-(3′,4′-Methylenedioxyphenyl)-1-(2-naphthalenyl)but-1-ene ((E)-**2g**).* Following General Procedure 3, olefin **8a** (149 mg, 1.0 mmol), 9-BBN (0.345 M in THF, 4.4 mL, 1.5 mmol), TlOEt (142.4 μL, 2.0 mmol), and H_2O (91.0 μL, 5.0 mmol) were reacted with $PdCl_2$(dppf) (73.5 mg, 0.1 mmol), $AsPh_3$ (61.6 mg, 0.2 mmol), (*E*)-2-(2-iodovinyl)naphthalene **10g** (313.8 mg, 1.2 mmol), and THF (4 mL). Purification by flash column chromatography (SiO_2, 26 g, 40 mm Ø, hexanes/Et_2O, 96:4) afforded (*E*)-**2g** (217 mg, 72%) as pale green solid. Recrystallization from hot hexane provided 212 mg (70%) of analytically pure (*E*)-**2g**. Data for (*E*)-**2g**: mp 96−98 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83−7.79 (m, 3 H, HC(c) and H(f) and H(g)), 7.70 (s, 1 H, HC(j)), 7.60 (dd, *J* = 8.5, 1.0 Hz, 1 H, HC(h)), 7.50−7.43 (m, 2 H, HC(b), HC(e)), 6.79 (d, *J* = 8.0 Hz, 1 H, HC(5′)), 6.78 (d, *J* = 1.0 Hz, 1 H, HC(2′)), 6.72 (dd, *J* = 8.0, 1.0 Hz, 1 H, HC(6′)), 6.61 (d, *J* = 16.0 Hz, 1 H, HC(1)), 6.40 (dt, *J* = 16.0, 7.0 Hz, 1 H, HC(2)), 5.97 (s, 2 H, OCH_2O), 2.79 (t, *J* = 8.0 Hz, 2 H, HC(4)), 2.51 (dt, *J* = 8.0, 8.0 Hz, 2 H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8 (C(3′)), 145.9 (C(4′)), 135.8 (C(1′)), 135.4 (C(i)), 133.9 (C(a)), 133.0 (C(d)), 130.8 (C(2)), 130.5 (C(1)), 128.3 (C(c)), 128.1 (C(g)), 127.9 (C(f)), 126.4 (C(e)), 125.8 (C(j)), 125.7 (C(b)), 123.8 (C(h)), 121.5 (C(6′)), 109.1 (C(2′)), 108.4 (C(5′)), 101.0 (OCH_2O), 35.9 (C(4)), 35.5 (C(3)); IR (KBr) 3051 (m), 3018 (w), 2994 (w), 2917 (m), 2856 (m), 2795 w), 1624 (w), 1605 (w), 1496 (s), 1486 (s), 1440 (s), 1359 (s), 1247 (s), 1187 (s), 1122 (s), 1098 (s), 1041 (s), 960 (s), 924 (s), 867 (s), 814 (s), 780 (s), 766 (s), 738 (s); MS (EI^+, 70 eV) 381.3 (6.1), 365.3 (7.1), 340.2 (15.1), 326.2 (17.3), 325.2 (71.8), 303.2 (7.2), 302.2 (24.8), 287.2 (6.3), 279.2 (7.5), 266.1 (15.6), 239.1 (9.7), 231.1 (14.6), 191.1 (17.3), 168.1 (5.9), 167.1 (58.8), 166.1 (5.9), 165.1 (13.2), 152.1 (9.2), 147.1 (7.4), 141.0 (6.0), 136.0 (10.7), 135.0 (100.0), 127.1 (7.5), 121.1 (6.4), 105.1 (8.8); HRMS calcd for $C_{21}H_{18}O_2^+$ 302.1307, found 302.1304; TLC R_f 0.42 (hexane/Et_2O, 96:4) [$KMnO_4$]. Anal. Calcd for $C_{21}H_{18}O_2$ (302.37): C, 83.42; H, 6.00%. Found: C, 83.52; H, 6.24%.



*Preparation of (E)-4-(3′,4′-Methylenedioxyphenyl)-1-(4-trifluorophenyl)but-1-ene ((E)-**2h**).* Following General Procedure 4, olefin **8a** (250 mg, 1.7 mmol) in THF (2 mL), 9-BBN (0.577 M in THF, 4.4 mL, 2.5 mmol), and H_2O (455 μL, 25.2 mmol) were reacted with $PdCl_2$(dppf) (61.7 mg, 84.4 μmol), $AsPh_3$ (51.7 mg, 168.7 μmol), Cs_2CO_3 (1.1 g, 3.4 mmol), (*E*)-1-(2-iodovinyl)-4-(trifluoromethyl)-benzene **10h** (603.5 mg, 2.0 mmol), and DMF (4 mL). Purification by flash column chromatography (SiO_2, 30 g, 30 mm Ø, hexanes/Et_2O, 95:5) afforded (*E*)-**2h** (357 mg, 66%) as pale yellow solid along with **8a** (25 mg, 10%). Recrystallization of (*E*)-**2h** from hot hexane provided 346 mg (64%) of analytically pure (*E*)-**2h**. Data for (*E*)-**2h**: mp 53−54 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2 H, HC(b)), 7.43 (d, *J* = 8.0, 2 H, HC(c)), 6.77 (d, *J* = 8.0 Hz, 1 H, HC(5′)), 6.74 (d, *J* = 1.0 Hz, 1 H, HC(2′)), 6.69 (dd, *J* = 8.0, 1.0 Hz, 1 H, HC(6′)), 6.46 (d, *J* = 16.0 Hz, 1 H, HC(1)), 6.39 (dt, *J* = 15.5, 8.0 Hz, 1 H, HC(2)), 5.96 (s, 2 H, OCH_2O), 2.75 (t, *J* = 8.0 Hz, 2 H, HC(4)), 2.54 (dt, *J* = 7.5, 7.5 Hz, 2 H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9 (C(3′)), 146.0 (C(4′)), 141.4 (C(a)), 135.5 (C(1′)), 132.9 (C(2)), 129.5 (C(1)), 129.0 (q, *J* = 32.6 Hz, C(d)), 126.3 (C(b)), 125.7 (q, *J* = 3.8 Hz, C(c)), 124.4 (d, *J* = 250.0 Hz, CF_3), 121.4 (C(6′)), 109.1 (C(2′)), 108.4 (C(5′)), 101.0 (OCH_2O), 35.6 (C(4)), 35.3 (C(3)); ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.8; IR (KBr) 3010 (w), 2929 (w), 2876 (m), 2779 (w), 1652 (m), 1614 (s), 1500 (s), 1488 (s), 1438 (s), 1413 (s), 1320 (s), 1329 (s), 1168 (s), 1124 (s), 1108 (s), 1063 (s), 1041 (s), 1015 (s), 972 (s), 954 (s), 936 (s), 922 (s), 861 (s), 806 (s); MS (EI^+, 70 eV) 320.1 (32.4), 227.0 (5.9), 191.1 (5.8), 165.0 (6.9), 159.0 (5.8), 152.0 (24.6), 149.0 (12.6), 147.0 (5.0), 137.0 (5.6), 136.0 (61.6), 135.0 (100.0), 131.0 (5.4), 116.0 (7.8), 115.0 (12.1), 105.0 (20.6), 91.0 (7.8), 79.1 (9.1), 78.1 (6.2), 77.1 (51.4); HRMS calcd for $C_{18}H_{15}F_3O_2^+$ 320.1024, found 320.1021; TLC R_f 0.53 (hexane/Et_2O, 95:5) [$KMnO_4$]. Anal. Calcd for $C_{18}H_{15}F_3O_2$ (320.31): C, 67.50; H, 4.72; F, 17.79%. Found: C, 67.59; H, 4.65; F, 17.23%.



*Preparation of (E)-4-(3′,4′-Methylenedioxyphenyl)-1-(2-methylphenyl)but-1-ene ((E)-**2i**).* Following General Procedure 4, olefin **8a** (222 mg, 1.5 mmol) in THF (2 mL), 9-BBN (0.577 M in THF, 3.9 mL, 1.5 mmol), and H_2O (405 μL, 22.5 mmol) were reacted with $PdCl_2$(dppf) (54.8 mg, 74.9 μmol), $AsPh_3$ (45.9 mg, 149.8 μmol), Cs_2CO_3 (976.4 g, 3.0 mmol), (*E*)-1-(2-iodovinyl)-2-methylbenzene **10i** (603.5 mg, 2.0 mmol), and DMF (4 mL). Purification by flash column chromatography (SiO_2, 30 g, 30 mm Ø, hexanes/Et_2O, 98:2) afforded (*E*)-**2i** (194 mg, 49%) as pale yellow solid along with **8a** (19 mg, 9%). Recrystallization of (*E*)-**2i** from hot hexane provided 346 mg (47%) of analytically pure (*E*)-**2i**. Data for (*E*)-**2i**: mp 38−40 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 2 H, HC(b)), 7.18−7.14 (m, 3 H, HC(c), HC(d), HC(e)), 6.77 (d, *J* = 8.0 Hz, 1 H, HC(5′)), 6.75 (d, *J* = 1.0 Hz, 1 H, HC(2′)), 6.70 (dd, *J* = 8.0, 1.0 Hz, 1 H, HC(6′)), 6.60 (d, *J* = 15.5 Hz, 1 H, HC(1)), 6.11 (dt, *J* = 15.5, 7.0 Hz, 1 H, HC(2)), 5.95 (s, 2 H, OCH_2O), 2.75 (t, *J* = 8.0 Hz, 2 H, HC(4)), 2.54 (dt, *J* = 7.0, 7.0 Hz, 2 H, HC(3)), 2.33 (s, 3 H, HC(1)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9 (C(3′)), 146.8 (C(4′)), 137.2 (C(a)), 135.9 (C(f)), 135.2 (C(1′)), 131.4 (C(2)), 130.4 (C(d)), 128.9 (C(1)), 127.1 (C(c)), 126.3 (C(e)), 125.9 (C(b)), 121.5 (C(6′)), 109.2 (C(2′)), 108.4 (C(5′)), 101.0 (OCH_2O), 36.0 (C(4)), 35.5 (C(3)), 19.9 (C(g)); IR (KBr) 3017 (w), 2922 (m), 2891 (m), 2776 (w), 1607 (w), 1502 (s), 1487 (s), 1441 (s), 1362 (w), 1242 (s), 1186 (m), 1096 (w), 1037 (s), 964 (m), 936 (m), 925 (m), 807 (m), 745 (s); MS (EI^+, 70 eV) 267.1 (2.7), 266.1 (13.7), 136.0 (8.2), 135.0 (100.0), 131.1 (12.8), 116.0 (4.2), 115.0 (4.6), 105.0 (2.7), 91.0 (4.1), 77.0 (8.5), 51.0 (3.9); HRMS calcd for $C_{18}H_{18}O_2^+$ 266.13068, found 266.12971; TLC R_f 0.52 (hexane/Et_2O, 96:4) [$KMnO_4$]. Anal. Calcd for $C_{18}H_{18}O_2$ (266.33): C, 81.17; H, 6.81%. Found: C, 80.90; H, 6.73%.



*Preparation of (E)-5-(3′,4′-Methylenedioxyphenyl)-2-phenylpent-2-ene ((E)-**2j**).* Following General Procedure 4, olefin **8a** (500 mg, 3.4 mmol) in THF (2 mL), 9-BBN (0.577 M in THF, 8.8 mL, 5.1 mmol), and H_2O (911 μL, 50.6 mmol) were reacted with $PdCl_2$(dppf) (123.5 mg, 168.7 μmol), $AsPh_3$ (103.3 mg, 337.5 μmol), Cs_2CO_3 (2.2 g, 6.7 mmol), (*E*)-(1-iodoprop-1-en-2-yl)benzene **10j** (988.4 mg, 4.0 mmol), and DMF (8 mL). Purification by flash column chromatography (SiO_2, 30 g, 50 mm Ø, hexane/Et_2O, 98:2) afforded 733 mg of (*E*)-**2j** as pale yellow oil along with **8a** (45 mg, 9%). The product was purified by distillation to afford (*E*)-**2j** (719 mg, 80%) as colorless oil. Data for (*E*)-**2j**: bp 125 °C at 2.7 × 10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2 H, HC(b)), 7.32 (d, *J* = 8.0, 2 H, HC(c)), 7.23 (dt, *J* = 7.0, 1.0 Hz, 1 H, HC(d)), 6.75 (d, *J* = 8.0 Hz, 1 H, HC(5′)), 6.74 (d, *J* = 1.5 Hz, 1 H, HC(2′)), 6.68 (dd, *J* = 8.0, 1.5 Hz, 1 H, HC(6′)), 5.94 (s, 2 H, OCH_2O), 5.80 (dt, *J* = 7.0, 1.5 Hz, 1 H, HC(3)), 2.70 (t, *J* = 8.0 Hz, 2 H, HC(5)), 2.49 (dt, *J* = 7.5, 7.5 Hz, 2 H, HC(4)), 2.00 (s, 3 H, HC(1)); ^{13}C NMR (125 MHz,

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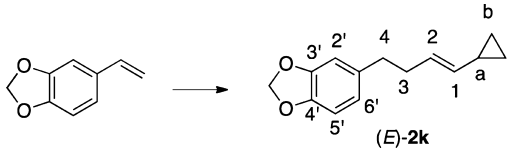
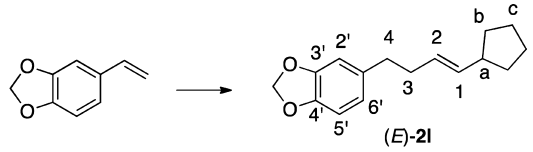
$CDCl_3$) δ 147.8 (C(3′)), 145.8 (C(4′)), 144.1 (C(a)), 136.1 (C(1′)), 135.7 (C(2)), 128.4 (C(c)), 127.5 (C(3)), 126.8 (C(d)), 125.9 (C(b)), 121.4 (C(6′)), 109.2 (C(2′)), 108.3 (C(5′)), 101.0 (OCH_2O), 35.8 (C(5)), 31.2 (C(4)), 16.1 (C(1)); IR (neat) 3056 (w), 3030 (w), 2918 (m), 2889 (m), 1600 (w), 1501 (s), 1487 (s), 1440 (s), 1359 (w), 1242 (s), 1189 (m), 1097 (w), 1038 (s), 935 (s), 854 (m), 807 (m), 755 (s), 694 (s); MS (TOF ES$^+$) 323.0 (96.2), 265.1 (100.0), 145.1 (63.2); HRMS calcd for $C_{18}H_{19}O_2^+$ 267.1385, found 267.1393; TLC R_f 0.49 (hexane/Et_2O, 96:4) [$KMnO_4$]. Anal. Calcd for $C_{18}H_{18}O_2$ (266.33): C, 81.17; H, 6.81%. Found: C, 81.01; H, 6.75%.



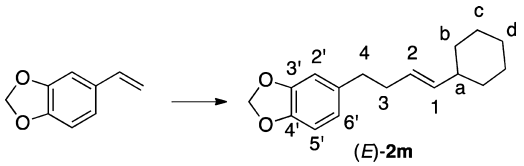
(*E*)-**2k**

*Preparation of (E)-4-(3′,4′-Methylenedioxyphenyl)-1-cyclopropyl-but-2-ene ((E)-**2k**).* Following General Procedure 3, olefin **8a** (296 mg, 2.0 mmol), 9-BBN (0.321 M in THF, 9.4 mL, 3.0 mmol), TlOEt (283.3 μL, 4.0 mmol), and H_2O (180.0 μL, 10.0 mmol) were reacted with $PdCl_2$(dppf) (146.4 mg, 0.2 mmol), $AsPh_3$ (122.5 mg, 0.4 mmol), (*E*)-(2-iodovinyl)cyclopropyl **10k** (465.6 mg, 2.4 mmol), and THF (9 mL). Purification by flash column chromatography (SiO_2, 25 g, 40 mm Ø, hexanes/diethyl ether, 98:2) afforded (*E*)-**2k** (370 mg, 85%) as colorless oil. Distillation provided 355 mg (82%) of analytically pure (*E*)-**2k**. Data for (*E*)-**2k**: bp 65 °C at 3 × 10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.75 (d, J = 8.0 Hz, 1 H, HC(5′)), 6.70 (d, J = 1.0 Hz, 1 H, HC(2′)), 6.65 (dd, J = 8.0, 1.0 Hz, 1 H, HC(6′)), 5.94 (s, 2 H, OCH_2O), 5.56 (dt, J = 15.0, 6.5 Hz, 1 H, HC(2), 5.03 (dd, J = 15.0, 8.5 Hz, 1 H, HC(1)), 2.61 (t, J = 8.0 Hz, 2 H, HC(4)), 2.27 (dt, J = 7.5, 7.5 Hz, 2 H, HC(3)), 1.40−1.33 (m, 1 H, HC(a)), 0.70−0.67 (m, 2 H, HC(b *trans*), 0.35−0.32 (m, 2 H, HC(b *cis*)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6 (C(3′)), 145.7 (C(4′)), 136.3 (C(1′)), 134.7 (C(1)), 127.3 (C(2)), 121.3 (C(6′)), 109.1 (C(2′)), 108.3 (C(5′)), 100.9 (OCH_2O), 36.1 (C(4)), 34.9 (C(3)), 13.7 (C(a)), 6.5 (C(b)); IR (neat) 3078 (w), 3009 (w), 2925 (m), 2772 (w), 1609 (w), 1503 (s), 1487 (s), 1441 (s), 1364 (m), 1242 (s), 1186 (s), 1097 (m), 1037 (s), 962 (s), 935 (s), 855 (s), 808 (s); MS (EI$^+$)216.1 (17.8), 136.0 (9.1), 135.0 (24.1), 81.1 (7.7), 77.1 (14.4), 51.0 (7.6); HRMS calcd for $C_{14}H_{16}O_2^+$ 216.1150, found 216.1152; TLC R_f 0.63 (hexane/Et_2O, 96:4) [$KMnO_4$].



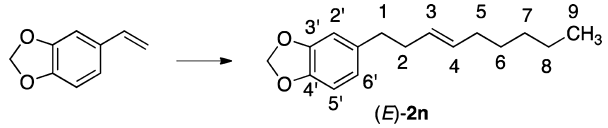
(*E*)-**2l**

*Preparation of (E)-4-(3′,4′-Methylenedioxyphenyl)-1-cyclopentyl-but-2-ene ((E)-**2l**).* Following General Procedure 3, olefin **8a** (296 mg, 2.0 mmol), 9-BBN (0.321 M in THF, 9.4 mL, 3.0 mmol), TlOEt (283.3 μL, 4.0 mmol), and H_2O (180.0 μL, 10.0 mmol) were reacted with $PdCl_2$(dppf) (146.4 mg, 0.2 mmol), $AsPh_3$ (122.5 mg, 0.4 mmol), (*E*)-(2-iodovinyl)cyclopentane **10l** (532.9 mg, 2.4 mmol), and THF (9 mL). Purification by flash column chromatography (SiO_2, 30 g, 40 mm Ø, hexanes/diethyl ether, 98:2) afforded 310 mg (63%) of (*E*)-**2l** as colorless oil. Distillation provided 303 mg (62%) of analytically pure (*E*)-**2l**. Data for (*E*)-**2l**: bp 50 °C at 2.4 × 10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.75 (d, J = 8.0 Hz, 1 H, HC(5′)), 6.70 (d, J = 1.5 Hz, 1 H, HC(2′)), 6.64 (dd, J = 8.0, 1.5 Hz, 1 H, HC(6′)), 5.94 (s, 2 H, OCH_2O), 5.44−5.42 (m, 2 H, HC(1) and HC(2)), 2.61 (t, J = 7.5 Hz, 2 H, HC(4)), 2.43−2.36 (m, 1 H, HC(a)), 2.29−2.25 (m, 2 H, HC(3)), 1.79−1.73 (m, 2 H, HC(b)), 1.69−1.61 (m, 2H, HC(c)), 1.60−1.51 (m, 2 H, HC(c)), 1.30−1.23 (m, 2H, HC(b)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6 (C(3′)), 145.7 (C(4′)), 136.3 (C(1′)), 136.1 (C(1)), 127.4 (C(2)), 121.4 (C(6′)), 109.2 (C(2′)), 108.2 (C(5′)), 100.9 (OCH_2O), 43.5 (C(a)), 36.2 (C(4)), 35.0 (C(3)), 33.4 (C(b)), 25.3 (C(c)); IR (neat) 2949 (m), 2866 (m), 1609 (w), 1503 (s), 1488 (s), 1441 (s), 1362 (m), 1242 (s), 1186 (m), 1121 (m), 1097 (m), 1039 (s), 966 (m), 938 (s), 856 (m), 805 (s); MS (TOF ES$^+$) 339.2 (14.9), 322.0 (100.0), 243.1 (28.6), 187.1 (18.7), 161.1 (15.1), 135.0 (28.6); HRMS calcd for $C_{16}H_{21}O_2^+$ 245.1542, found 245.1544; TLC R_f 0.67 (hexane/Et_2O, 96:4) [$KMnO_4$]. Anal. Calcd for $C_{16}H_{20}O_2$ (244.33): C, 78.65; H, 8.25%. Found: C, 78.91; H, 8.16%.



(*E*)-**2m**

*Preparation of (E)-4-(3′,4′-Methylenedioxyphenyl)-1-cyclohexyl-but-2-ene ((E)-**2m**).* Following General Procedure 3, olefin **8a** (296 mg, 2.00 mmol), 9-BBN (0.345 M in THF, 8.7 mL, 3.00 mmol), TlOEt (283.3 μL, 4.0 mmol), and H_2O (180.0 μL, 10.0 mmol) were reacted with $PdCl_2$(dppf) (146.3 mg, 0.2 mmol), $AsPh_3$ (122.5 mg, 0.4 mmol), (*E*)-(2-iodovinyl)cyclohexane **10m** (567 mg, 2.40 mmol), and THF (9 mL). Purification by flash column chromatography (SiO_2, 25 g, 40 mm Ø, hexanes/diethyl ether, 98:2) afforded 300 mg (58%) of (*E*)-**2m** as colorless oil. Distillation provided 289 mg (56%) of analytically pure (*E*)-**2m**. Data for (*E*)-**2m**: bp 70 °C at 2.4 × 10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 (d, J = 8.0 Hz, 1 H, HC(5′)), 6.70 (d, J = 1.5 Hz, 1 H, HC(2′)), 6.64 (dd, J = 7.5, 1.5 Hz, 1 H, HC(6′)), 5.94 (s, 2 H, OCH_2O), 5.42−5.40 (m, 2 H, HC(1) and HC(2)), 2.60 (t, J = 7.5 Hz, 2 H, HC(4)), 2.28−2.25 (m, 1H, HC(a)), 1.95−1.89 (m, 2 H, HC(3)), 1.75−1.65 (m, 5 H, HC(b) and HC(c) and HC(d)), 1.32−1.21 (m, 2 H, HC(c)), 1.21−1.14 (m, 2 H, HC(d)), 1.10−1.03 (m, 2 H, HC(b)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6 (C(3′)), 145.7 (C(4′)), 137.5 (C(1′)), 136.4 (C(1)), 126.8 (C(2)), 121.4 (C(6′)), 109.2 (C(2′)), 108.2 (C(5′)), 100.9 (OCH_2O), 40.9 (C(a)), 36.0 (C(4)), 35.1 (C(3)), 33.4 (C(b)), 26.5 (C(d)), 26.4 (C(c)); IR (neat) 2921 (m), 2850 m), 1503 (m), 1488 (s), 1442 (m), 1360 (w), 1242 (s), 1186 (m), 1096 (w), 1039 (s), 967 (m), 938 (m), 855 (w), 805 (m); MS (TOF ES$^+$) 338.3 (28.9), 300.2 (27.8), 275.2 (22.2), 271.2 (55.1), 259.2 (77.2), 257.2 (56.4), 175.1 (19.4), 161.1 (28.1), 135.0 (100.0); HRMS calcd for $C_{17}H_{22}O_2^+$ 259.1698, found 259.1706; TLC R_f 0.67 (hexane/Et_2O, 96:4) [$KMnO_4$]. Anal. Calcd for $C_{17}H_{22}O_2$ (258.36): C, 79.03; H, 8.58%. Found: C, 79.24; H, 8.46%.



(*E*)-**2n**

*Preparation of (E)-1-(3′,4′-Methylenedioxyphenyl)non-3-ene ((E)-**2n**).* Following General Procedure 3, olefin **8a** (296 mg, 2.0 mmol), 9-BBN (0.312 M in THF, 9.4 mL, 3.0 mmol), TlOEt (283.3 μL, 4.00 mmol), and H_2O (180.0 μL, 10.0 mmol) were reacted with $PdCl_2$(dppf) (146.4 mg, 0.2 mmol), $AsPh_3$ (122.5 mg, 0.4 mmol), (*E*)-1-iodoheptene **10n** (537.8 mg, 2.4 mmol), and THF (9 mL). Purification by flash column chromatography (SiO_2, 32 g, 40 mm Ø, hexanes/diethyl ether, 97:3) afforded (*E*)-**2n** (360 mg, 73%) as colorless oil. Distillation provided 345 mg (68%) of analytically pure (*E*)-**2n**. Data for (*E*)-**2n**: bp 75 °C at 3 × 10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.75 (d, J = 8.0 Hz, 1 H, HC(5′)), 6.70 (d, J = 1.5 Hz, 1 H, HC(2′)), 6.65 (dd, J = 8.0, 1.5 Hz, 1 H, HC(6′)), 5.94 (s, 2 H, OCH_2O), 5.46−5.44 (m, 2 H, HC(3) and HC(4)), 2.62 (t, J = 8.0 Hz, 2 H, HC(1)), 2.28 (dt, J = 7.0, 7.0 Hz, 2 H, HC(2)), 2.00 (dt, J = 7.0, 7.0 Hz, 2 H, HC(5)), 1.36−1.26 (m, 6 H, HC(6) and HC(7) and HC(8)), 1.92 (t, J = 7.5 Hz, 3 H, HC(9)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7 (C(3′)), 145.7 (C(4′)), 136.3 (C(1′)), 131.5 (C(3)), 129.4 (C(4)), 121.4 (C(6′)), 109.2 (C(2′)), 108.3 (C(5′)), 100.9 (OCH_2O), 36.1 (C(1)), 35.0 (C(2)), 32.8 (C(5)), 31.6 (C(7)), 29.5 (C6)), 22.8 (C(8)), 14.3 (C(9)); IR (neat) 2957 (m), 2922 (m), 2862 (m), 1609(w), 1503 (s), 1488 (s), 1443 (s), 1359 (m), 1243 (s), 1185 (m), 1095 (m), 1040 (s), 966 (m), 938 (s), 856 (m), 804 (s); MS (TOF ES$^+$) 343.3 (58.7), 341.2 (100.0), 245.3 (50.1), 231.1 (28.2), 135.0 (53.0); HRMS calcd for $C_{16}H_{23}O_2^+$ 247.1698, found 247.1697;

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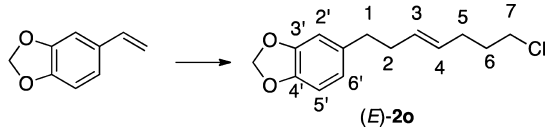
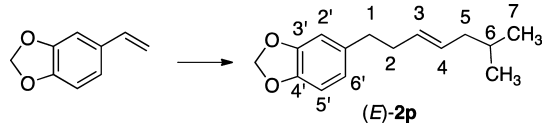
TLC R_f 0.69 (hexane/Et_2O, 96:4) [$KMnO_4$]. Anal. Calcd for $C_{16}H_{22}O_2$ (246.35): C, 78.01; H, 9.00%. Found: C, 78.31; H, 8.98%.



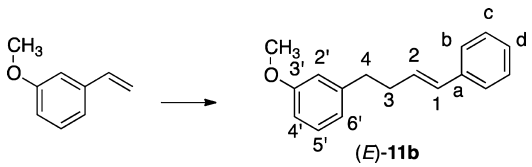
(*E*)-**2o**

*Preparation of (E)-7-(3′,4′-Methylenedioxyphenyl)-1-chlorohept-4-ene ((E)-**2o**).* Following General Procedure 3, olefin **8a** (296 mg, 2.0 mmol), 9-BBN (0.321 M in THF, 9.4 mL, 3.0 mmol), TlOEt (283.3 μL, 4.0 mmol), and H_2O (180.0 μL, 10.0 mmol) were reacted with $PdCl_2$(dppf) (146.4 mg, 0.2 mmol), Ph_3As (122.5 mg, 0.4 mmol), (*E*)-5-chloro-1-iodopent-1-ene **10o** (553.1 mg, 2.4 mmol), and THF (9 mL). Purification by flash column chromatography (SiO_2, 30 g, 40 mm Ø, hexanes/diethyl ether, 98:2) afforded (*E*)-**2o** (378 mg, 75%) as colorless oil. Distillation provided 368 mg (73%) of analytically pure (*E*)-**2o**. Data for (*E*)-**2o**: bp 65 °C at 3.0 × 10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.73 (d, *J* = 8.0 Hz, 1 H, HC(5′)), 6.67 (d, *J* = 1.0 Hz, 1 H, HC(2′)), 6.62 (dd, *J* = 8.0, 1.0 Hz, 1 H, HC(6′)), 5.92 (s, 2 H, OCH_2O), 5.48 (dt, *J* = 14.0, 6.5 Hz, 1 H, HC(3)), 5.36 (dt, *J* = 14.0, 6.5 Hz, 1 H, HC(4)), 3.48 (t, *J* = 6.5 Hz, 2 H, HC(7)), 2.59 (t, *J* = 8.0 Hz, 2 H, HC(1)), 2.27 (dt, *J* = 7.5, 7.5 Hz, 2 H, HC(2)), 2.13 (dt, *J* = 7.0, 7.0 Hz, 2 H, HC(5)), 1.80 (dq, *J* = 7.0, 7.0 Hz, 2 H, HC(6)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7 (C(3′)), 145.8 (C(4′)), 136.0 (C(1′)), 131.1 (C(3)), 129.2 (C(4)), 121.4 (C(6′)), 109.1 (C(2′)), 108.3 (C(5′)), 101.0 (OCH_2O), 44.6 (C(7)), 35.9 (C(1)), 34.9 (C(2)), 32.4 (C(6)), 29.8 (C(5)); IR (neat) 2857 (w), 2930 (m), 2849 (w), 2780 (w), 1607 (w), 1503 (s), 1488 (s), 1441 (s), 1357 (w), 1243 (s), 1187 (m), 1097 (w), 1039 ((s), 969 (m), 937 (s), 858 (s), 808 (s), 723 (m); MS (TOF ES$^+$) 359.1 (55.7), 338.3 (38.9), 309.1 (55.7), 267.1 (39.4), 251.1 (59.4), 239.0 (21.4), 219.0 (100.0), 217.2 (26.3), 149.0 (21.3), 135.0 (30.3); HRMS calcd for $C_{14}H_{16}ClO_2^+$ 251.0839, found 251.0846; TLC R_f 0.50 (hexane/Et_2O, 96:4) [$KMnO_4$]. Anal. Calcd for $C_{14}H_{17}ClO_2$ (252.74): C, 66.53; H, 6.78%. Found: C, 66.45; H, 7.07%.



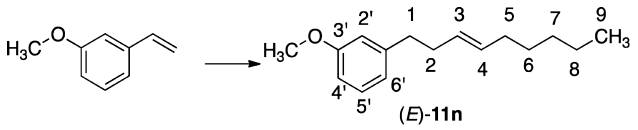
(*E*)-**2p**

*Preparation of (E)-1-(3′,4′-Methylenedioxyphenyl)-6-methylhept-3-ene ((E)-**2p**).* Following General Procedure 3, olefin **8a** (296 mg, 2.00 mmol), 9-BBN (0.321 M in THF, 9.4 mL, 3.0 mmol), TlOEt (283.3 μL, 4.0 mmol), and H_2O (180.0 μL, 10.0 mmol) were reacted with $PdCl_2$(dppf) (146.3 mg, 0.2 mmol), Ph_3As (122.5 mg, 0.4 mmol), (*E*)-1-iodo-4-methyl-1-pentene **10p** (504.1 mg, 2.4 mmol), and THF (9 mL). Purification by flash column chromatography (SiO_2, 28 g, 40 mm Ø, hexanes/diethyl ether, 98:2) afforded (*E*)-**2p** (333 mg, 71%) as colorless oil. Distillation provided 321 mg (69%) of analytically pure (*E*)-**2p**. Data for (*E*)-**2p**: bp 40 °C at 3.0 × 10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.75 (d, *J* = 8.0 Hz, 1 H, HC(5′)), 6.70 (d, *J* = 1.0 Hz, 1 H, HC(2′)), 6.65 (dd, *J* = 8.0, 1.0 Hz, 1 H, HC(6′)), 5.94 (s, 2 H, OCH_2O), 5.44−5.42 (m, 2 H, HC(3) and HC(4)), 2.16 (t, *J* = 8.0 Hz, 2 H, HC(1)), 2.31−2.28 (m, 2 H, HC(2)), 1.90−1.87 (m, 2 H, HC(5)), 1.64−1.55 (m, 1 H, HC(6)), 0.88 (dd, *J* = 6.5, 1.5 Hz, 6 H, HC(7)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6 (C(3′)), 145.7 (C(4′)), 136.3 (C(1′)), 130.5 (C(3)), 130.1 (C(4)), 121.4 (C(6′)), 109.2 (C(2′)), 108.2 (C(5′)), 100.9 (OCH_2O), 42.2 (C(5)), 36.2 (C(1)), 35.0 (C(2)), 28.7 (C(6)), 22.5 (C(7)); IR (neat) 2949 (s), 2929 (m), 2901 (m), 2872 (m), 1608 (w), 1502 (s), 1488 (s), 1442 (s), 1365 (w), 1243 (s), 1187 (m), 1096 (s), 1039 (s), 966 (m), 940 (s); MS (EI$^+$, 70 eV) 233.1 (2.8), 232 (15.4), 136.0 (8.9), 135.0 (100.0), 105.0 (2.5), 77.0 (6.2); HRMS calcd for $C_{15}H_{20}O_2^+$ 232.1463, found 232.1468; TLC R_f 0.67 (hexane/Et_2O, 96:4) [$KMnO_4$].



(*E*)-**11b**

*Preparation of (E)-4-(3′-Methoxyphenyl)-1-phenylbut-1-ene ((E)-**11b**).* Following General Procedure 4, 3-methoxystyrene **8b** (500.0 mg, 3.7 mmol) in THF (4 mL), 9-BBN (0.577 M in THF, 9.7 mL, 5.6 mmol), and H_2O (1.0 mL, 55.9 mmol) were reacted with $PdCl_2$(dppf) (136.3 mg, 0.19 mmol), Ph_3As (114.1 mg, 0.37 mmol), Cs_2CO_3 (2.4 g, 7.45 mmol), (*E*)-(2-iodovinyl)benzene **10b** (1.03 mg, 4.47 mmol), and DMF (6 mL). Purification by flash column chromatography (SiO_2, 32 g, 40 mm Ø, hexanes/diethyl ether, 98:2) afforded (*E*)-**11b** (621 mg, 70%) as colorless oil along with starting material **8b** (70 mg, 14%). Distillation of (*E*)-**11b** provided 607 mg (68%) of analytically pure (*E*)-**11b**. Data for (*E*)-**11b**: bp 100 °C at 2.4 × 10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37−7.21 (m, 6 H, HC(b) and HC(c) and HC(d) and HC(5′)), 6.85 (d, *J* = 8.0, 1 H, HC(6′)), 6.81−6.77 (m, 2 H, HC(2′), HC(4′)), 6.45 (d, *J* = 16.0 Hz, 1 H, HC(1)), 6.29 (dd, *J* = 16.0, 7.0 Hz, 1 H, HC(2)), 3.83 (s, 3 H, OCH_3), 2.80 (t, *J* = 8.0 Hz, 2 H, HC(4)), 2.56 (dt, *J* = 8.0, 8.0 Hz, 2H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1 (C(3′)), 143.7 (C(a)), 138.1 (C(1′)), 130.8 (C(2)), 130.3 (C(1)), 129.6 (C(5′)), 128.7 (C(c)), 127.2 (C(d)), 126.3 (C(b)), 121.2 (C(6′)), 114.6 (C(3′)), 55.4 (OCH_3), 36.2 (C(4)), 34.9 (C(3)); IR (neat) 3022 (m), 2935 (m), 2832 (m), 1596 (s), 1581 (s), 1488 (s), 1452 (s), 1435 (s), 1259 (s), 1150 (s), 1043 (s), 963 (s), 910 (m), 872 (s), 777 (s), 735 (s), 691 (s); MS (TOF ES$^+$) 341.2 (42.5), 323.0 (65.1), 282.3 (28.3), 278.1 (32.1), 239.1 (39.6), 237.1 (90.6), 161.1 (100.0), 131.1 (17.8), 121.1 (13.5); HRMScalcd for $C_{17}H_{19}O^+$ 239.1436, found 239.1438; TLC R_f 0.47 (hexane/Et_2O, 96:4) [$KMnO_4$]. Anal. Calcd for $C_{17}H_{18}O$ (238.32): C, 85.67; H, 7.61%. Found: C, 85.49; H, 7.39%.



(*E*)-**11n**

*Preparation of (E)-1-(3′-Methoxyphenyl)non-3-ene ((E)-**11n**).* Following General Procedure 3, 3-methoxystyrene **8b** (268.8 mg, 2.0 mmol), 9-BBN (0.321 M in THF, 9.4 mL, 3.0 mmol), TlOEt (283.3 μL, 4.0 mmol), and H_2O (180.0 μL, 10.0 mmol) were reacted with $PdCl_2$(dppf) (146.4 mg, 0.2 mmol), Ph_3As (122.5 mg, 0.4 mmol), (*E*)-1-iodoheptene **10n** (538 mg, 2.4 mmol), and THF (9 mL). Purification by flash column chromatography (SiO_2, 30 g, 40 mm Ø, hexanes/diethyl ether, 97:3) afforded (*E*)-**11n** (365 mg (77%) as colorless oil. Distillation provided 357 mg (75%) of analytically pure (*E*)-**11n**. Data for (*E*)-**11n**: bp 60 °C at 2.6 × 10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H, HC(5′)), 6.81−6.74 (m, 3 H, HC(2′) and HC(4′) and HC(6′)), 5.47−5.45 (m, 2 H, HC(3) and HC(4)), 3.82 (s, 3 H, OCH_3), 2.67 (t, *J* = 7.5 Hz, 2 H, HC(1)), 2.34−2.30 (m, 2 H, HC(2)), 2.01−1.97 (m, 2 H, HC(5)), 1.38−1.24 (m, 6 H, HC(6) and HC(7) and HC(8)), 0.90 (t, *J* = 7.0 Hz, 3 H, HC(9)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9 (C(3′)), 144.0 (C(1′)), 131.4 (C(4′)), 129.4 (C(3′)), 129.3 (C(5′)), 121.1 (C(6′)), 114.6 (C(2′)), 111.3 (C(4′)), 55.3 (OCH_3), 36.4 (C(1)), 34.3 (C(2)), 32.6 (C(5)), 31.5 (C(7)), 29.4 (C(6)), 22.6 (C(8)), 14.1 (C(9)); IR (neat) 2957 (m), 2924 (s), 2853 (m), 1602 (s), 1585 (s), 1488 (s), 1467 (m), 1454 (s), 1435 (m), 1259 (s), 1164 (m), 1151 (s), 1045 (s), 968 (s), 869 (s), 775 (s), 694 (s); MS (TOF ES$^+$) 231.2 (5.5), 122.0 (8.8), 121.0 (100.0), 91.0 (3.2), 78.1 (4.6), 77.1 (3.9); HRMS calcd for $C_{16}H_{24}O^+$ 232.1827, found 232.1821; TLC R_f 0.67 (hexane/Et_2O, 96:4) [$KMnO_4$].

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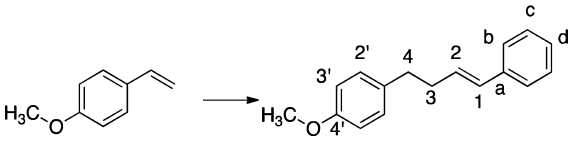
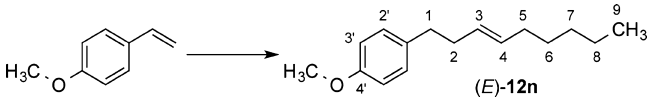
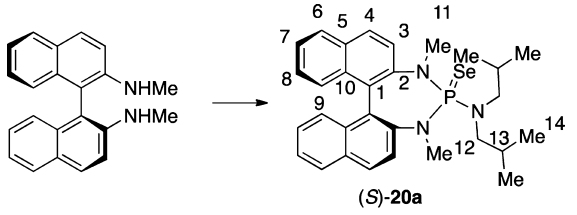


*Preparation of (E)-4-(4′-Methoxyphenyl)-1-phenylbut-1-ene ((E)-**12b**).* Following General Procedure 4, 4-methoxystyrene **8c** (500.0 mg, 3.72 mmol) in THF (4 mL), 9-BBN (0.577 M in THF, 9.7 mL, 5.6 mmol), and H_2O (1.0 mL, 55.9 mmol) were reacted with $PdCl_2$(dppf) (136.3 mg, 0.19 mmol), Ph_3As (114.1 mg, 0.37 mmol), Cs_2CO_3 (2.42 g, 7.45 mmol), (*E*)-(2-iodovinyl)benzene **10b** (1.03 mg, 4.47 mmol), and DMF (6 mL). Purification by flash column chromatography (SiO_2, 32 g, 40 mm Ø, hexanes/Et_2O, 97:3) afforded (*E*)-**12b** (506 mg, 57%) as white solid along with starting material **8c** (60 mg, 12%). Recrystallization from hot hexane provided 480 mg (54%) of analytically pure (*E*)-**12b**. Data for (*E*)-**12b**: mp 75−77 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 7.5 Hz, 2 H, HC(b)), 7.33 (t, J = 8.0, 2 H, HC(c)), 7.23 (d, J = 7.5 Hz, 1 H, HC(d)), 7.17 (d, J = 8.5 Hz, 1 H, HC(2′)), 6.89 (d, J = 8.5 Hz, 1 H, HC(3′)), 6.45 (d, J = 15.5 Hz, 1 H, HC(1)), 6.29 (dt, J = 15.5, 7.0 Hz, 1H, HC(2)), 3.83 (s, 3 H, OCH_3), 2.79 (t, J = 8.0 Hz, 2 H, HC(4)), 2.54 (dt, J = 8.0, 8.0 Hz, 2 H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1 (C(4′)), 138.0 (C(a)), 134.1 (C(1′)), 130.5 (C(2)), 130.3 (C(1)), 129.6 (C(2′)), 128.7 (C(c)), 127.2 (C(d)), 126.2 (C(b)), 114.0 (C(3′)), 55.5 (OCH_3), 35.4 (C(4)), 35.2 (C(3)); IR (KBr) 3030 (w), 3009 (w), 2935 (m), 2909 (w), 2836 (w), 1650 (w), 1609 (m), 1598 (w), 1507 (w), 1507 (s), 1465 (m), 1445 (m), 1441 (m), 1299 (m), 1237 (s), 1179 (s), 1151 (s), 1033(s), 985 (s), 977 (s), 828 (s), 809 (s), 740 (s); MS (EI$^+$, 70 eV) 238.2 (7.6), 136.1 (9.0), 135.1 (100.0), 122.1 (8.2), 121.1 (95.5), 77.1 (8.8); HRMS calcd for $C_{17}H_{18}O^+$ 238.1358, found 238.1354; TLC R_f 0.47 (hexane/Et_2O, 96:4) [$KMnO_4$]. Anal. Calcd for $C_{17}H_{18}O$ (238.32): C, 85.67; H, 7.61%. Found: C, 85.77; H, 7.66%.



(*E*)-**12n**

*Preparation of (E)-1-(4′-Methoxyphenyl)non-3-ene ((E)-**12n**).* Following General Procedure 3, olefin **45** (276 mg, 2.0 mmol), 9-BBN (0.345 M in THF, 8.7 mL, 3.0 mmol), TlOEt (283.3 μL, 4.0 mmol), and H_2O (180.0 μL, 10.0 mmol) were reacted with $PdCl_2$(dppf) (146.3 mg, 0.2 mmol), Ph_3As (122.5 mg, 0.4 mmol), (*E*)-1-iodoheptene **10n** (537.8 mg, 2.4 mmol), and THF (9 mL). Purification by flash column chromatography (SiO_2, 28 g, 40 mm Ø, hexanes/diethyl ether, 98:2) afforded (*E*)-**12n** (331 mg, 70%) as colorless oil. Data for (*E*)-**12n**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, J = 8.5 Hz, 2 H, HC(3′)), 6.83 (d, J = 8.5 Hz, 2 H, HC(2′)), 5.47−5.37 (m, 2 H, HC(3) and HC(4)), 3.79 (s, 3 H, OCH_3), 2.61 (t, J = 8.0 Hz, 2 H, HC(1)), 2.31−2.22 (m, 2 H, HC(2)), 2.00−1.92 (m, 2 H, HC(5)), 1.38−1.19 (m, 6 H, HC(6) and HC(7) and HC(8)), 0.89 (t, J = 7.0 Hz, 3 H, HC(9)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6 (C(4′)), 134.3 (C(1′)), 131.1 (C(3)), 129.3 (C(2′)), 129.3 (C(4)), 113.6 (C(3′)), 55.22 (OCH_3), 35.2 (C(1)), 34.7 (C(2)), 32.5 (C(5)), 31.4 (C(7)), 29.2 (C6)), 22.6 (C(8)), 14.1 (C(9)); IR (neat) 2954 (s), 2919 (s), 2850 (m), 1611 (w), 1510 (s), 1462 (w), 1438 (w), 1299 (w), 1243 (s), 1174 (m), 1039 (m), 966 (w), 820 (w); MS (EI$^+$, 70 eV) 233.2 (3.5), 232.2 (24.5), 122.1 (12.7), 121.0 (100.0), 91.1 (14.1), 86.0 (3.0), 84.9 (4.6), 84.0 (5.1), 82.9 (7.1), 78.0 (12.8), 77.0 (12.9); HRMS calcd for $C_{16}H_{24}O^+$ 232.1827, found 232.1826; TLC R_f 0.68 (hexane/Et_2O, 96:4) [$KMnO_4$].



(*S*)-**20a**

*Preparation of (S)-4-(Diisobutylamino)-3,5-dimethyl-4,5-dihydro-3H-dinaphtho[2,1-d:1′,2′-f][1,3,2]diazaphosphepine-4-selenide ((S)-**20a**).* To a flame-dried, 100 mL Schlenk flask equipped with a magnetic stir bar and septum were added *N*,*N*′-dimethyl-1,1′-binaphthalene-2,2′-diamine (**37**) (2.00 g, 6.40 mmol), Et_3N (2.23 mL, 16.0 mmol, 2.50 equiv), and THF (64.0 mL) via syringe. The homogeneous mixture was cooled to 0 °C. PCl_3 (1.68 mL, 19.2 mmol, 3.00 equiv) was added dropwise via syringe whereupon a colorless precipitate formed immediately. The reaction mixture was stirred at 0 °C for 1.5 h, then was allowed to warm to room temperature and was stirred for another 3 h. The volatiles were removed under high vacuum (room temperature, 0.5 mmHg), and Et_2O (20.0 mL) was added via syringe, then the mixture was stirred for 5 min. The supernatant was cannula filtered into a tared, flame-dried, argon filled, 200 mL Schlenk flask equipped with a rubber septum. The remaining precipitate in the reaction flask was washed with Et_2O (20 mL) and was filtered into the receiver Schlenk flask. The volatiles were removed under high vacuum (room temperature, 0.5 mmHg) to afford a light yellow solid. The solid was redissolved with Et_2O (20 mL), and the volatiles were again removed under high vacuum (room temperature, 1.0 mmHg) to afford a white solid. The solid was then dried for 3 h at reduced pressure (45 °C, 0.50 mmHg) to give a white foam (2.34 g). CH_2Cl_2 (60.0 mL) was added via syringe, and the mixture was cooled to 0 °C. Et_3N (0.74 mL, 5.30 mmol, 1.2 equiv) and diisobutylamine (1.23 mL, 7.10 mmol, 1.1 equiv) were added via syringe, and the reaction mixture was allowed to warm to room temperature and then stirred for 14 h. Powdered selenium (1.46 g, 18.6 mmol, 2.9 equiv) was added, and the mixture was stirred for 50 h and then filtered through a pad of Celite (12 g, 70 mm Ø). The pad was washed with EtOAc (100 mL), and the filtrate was concentrated in vacuo (40 °C, 10 mmHg). Purification via flash column chromatography (SiO_2, 55 g, 50 mm Ø, hexane/Et_2O 4:1) afforded (*S*)-**20a** (2.55 g, 73%) as slightly orange solid. Recrystallization from hot pentane provided (2.35 g, 67%). Data for (*S*)-**20a**: mp 118−120 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 9.0 Hz, 1 H, HC(4)), 7.92 (d, J = 9.0 Hz, 1 H, HC(4′)), 7.90 (d, J = 8.5 Hz, 1 H, HC(6)), 7.86 (d, J = 8.0 Hz, 1 H, HC(6′)), 7.67 (d, J = 9.0 Hz, 1 H, HC(3′)), 7.66 (dd, J = 9.0, 1.0 Hz, 1 H, HC(3)), 7.43 (dt, J = 7.5, 1.0 Hz, 1 H, HC(7)), 7.36 (t, J = 7.5 Hz, 1 H, HC(7′)), 7.28 (d, J = 8.0 Hz, 1 H, HC(8)), 7.24 (dt, J = 8.5, 1.0 Hz, 1 H, HC(9)), 7.12 (dt, J = 8.0, 1.0 Hz, 1 H, HC(8′)), 7.04 (d, J = 9.0 Hz, 1 H, HC(9′)), 3.21 (d, J = 13.5 Hz, 3 H, HC(11′)), 3.18−3.11 (m, 2 H, HC(12)), 2.96 (d, J = 13.5 Hz, 3 H, H_3C(11)), 2.81 (dt, J = 14.0, 6.0 Hz, 2 H, HC(12′)), 1.96−1.87 (m, 2 H, HC(13, 13′)), 0.86 (d, J = 6.5 Hz, 6 H, HC(14′)), 0.84 (d, J = 6.5 Hz, 6 H, HC(14)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.4 (d, J = 5.0 Hz, C(2′)), 142.3 (C(2)), 132.7 (C(10)), 132.5 (C(10′)), 131.5 (C(5′)), 131.3 (C(5)), 129.5 (C(4)), 128.7 (C(4′)), 128.3 (C(9)), 128.2 (C(6′), 128.0 (C(6)), 127.5 (C(1,1′)), 127.3 (C(9′)), 126.3 (C(8)), 125.9 (C(8′)), 125.5 (C(7)), 124.9 (C(7′)), 124.6 (C(3′)), 122.6 (C(3)), 55.1 (C(12, 12′)), 39.3 (d, J = 11.3 Hz, C(11′)), 36.1 (d, J = 5.0 Hz, C(11)), 27.2 (C(13, 13′)), 21.0 (C(14′)), 20.9 (C(14′)); ^{31}P NMR (202 MHz, $CDCl_3$) δ 95.39; IR (KBr) 3052 (w), 2954 (s), 2864 (s), 2801 (w), 1618 (w), 1590 (m), 1503 (s), 1465 (s), 1386 (m), 1365 (m), 1327 (s), 1271 (s), 1261 (s), 1157 (m), 1115 (s), 1087 (s), 1007 (s), 955 (m), 935 (s), 876 (m), 810 (s), 747 (s); MS (EI$^+$, 70 eV) 422.1 (5.6), 421.1 (18.7), 419.1 (9.5), 342.1 (23.5), 341.1 (100.0), 312.1 (6.4), 282.2 (5.2), 281.1 (18.4), 215.1 (6.3), 128.1 (15.5), 57.1 (7.6); HRMS calcd for $C_{30}H_{36}N_3PSe^+$ 549.1812, found 549.1809; TLC R_f 0.61 (hexanes/Et_2O, 4:1) [CAM]; $[\alpha]_D^{24}$ +187.5 (c = 1.67, EtOH); SFC (*S*)-**37**, t_R 12.8 min (99.8%); (*R*)-**37**, t_R 15.6 min (0.8%) (Chiralpak OJ, 5% MeOH in CO_2, 2 mL/min, 220 nm, 40 °C).[57] Anal. Calcd for $C_{30}H_{36}N_3PSe$ (549.56): C, 65.68; H, 6.61%; N, 7.66; P, 5.65; Se, 14.39%. Found: C, 65.75; H, 6.69%; N, 7.42; P, 5.52; Se, 14.46%.

*Sulfenocarbocyclizations with (S)-**20a**. General Procedure **8**.* An oven-dried, 10 mL, two-necked, round-bottomed flask under nitrogen was charged with *N*-phenylthiophthalimide **13** (256 mg, 1.00 mmol, 1.0 equiv), **20a** (54.9 mg, 0.10 mmol, 0.1 equiv), and olefin (1.00 mmol) in CH_2Cl_2. The flask was placed into isopropyl alcohol bath and cooled at the requisite temperature via cryocool. A solution of

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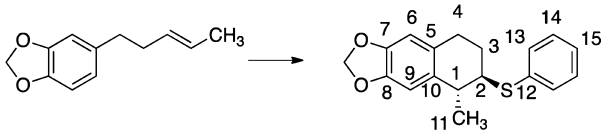
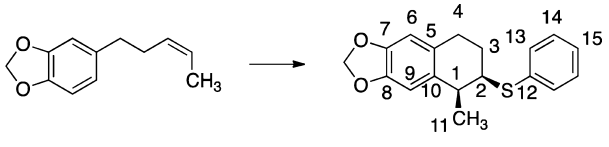
$EtSO_3H$ (1 M in CH_2Cl_2) was added over 20 s, and the mixture was allowed to stir for the specified time. The reaction was quenched while cold by addition of Et_3N (1.6 mL). The resultant mixture was poured into H_2O (20 mL), and the aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered through glass wool, and then concentrated in vacuo (20−23 °C, 10 mmHg). The thioether products were purified by flash column chromatography followed by distillation or recrystallization.



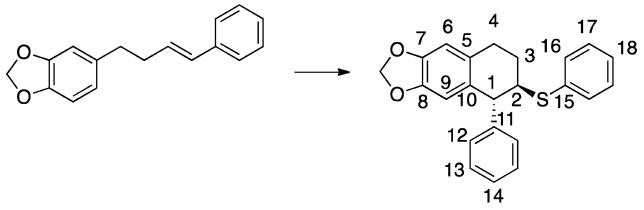
trans-**14a**

*Preparation of (5R,6R)-5-Methyl-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-d]-1,3-dioxole (trans-**14a**).* Following General Procedure 8, (*E*)-**2a** (190 mg, 1.0 mmol), **13** (256 mg, 1.0 mmol), (*S*)-**20a** (54.8 mg, 0.1 mmol), and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at −20 °C for 72 h. Purification by flash column chromatography (SiO_2, 32 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**14a** (277 mg, 93%) as a white solid. Recrystallization from hot pentane provided 273 mg (92%) of analytically pure *trans*-**14a**. Data for *trans*-**14a**: mp 46−48 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, J = 8.0, 1.0 Hz, 2 H, HC(13)), 7.34 (t, J = 8.0 Hz, 2 H, HC(14)), 7.27 (tt, J = 8.5, 1.5 Hz, 1 H, HC(15)), 6.64 (s, 1 H, HC(6)), 6.58 (s, 1 H, HC(9)), 5.91 (s, 2 H, OCH_2O), 3.43−3.40 (m, 1 H, HC(2)), 2.97−2.91 (m, 2 H, HC(1) and HC(4)), 2.66 (ddd, J = 16.5, 5.5, 5.5 Hz, 1 H, HC(4)), 2.23−2.16 (m, 1 H, HC (3)), 1.91−1.85 (m, 1 H, HC(3)), 1.42 (d, J = 7.0 Hz, 3 H, HC(11)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.0 (C(7)), 145.9 (C(8)), 135.4 (C(12)), 132.6 (C(5)), 131.9 (C(13)), 129.0 (C(14)), 128.2 (C(10)), 126.9 (C(15)), 108.8 (C(9)), 108.6 (C(6)), 100.7 (OCH_2O), 49.9 (C(2)), 38.3 (C(1)), 26.6 (C(4)), 24.8 (C(3)), 24.1 (C(11)); IR (KBr) 3052 (w), 2961 (m), 2926 (m), 2885 (m), 2766 (w), 1580 (m), 1500 (s), 1479 (s), 1438 (m), 1379 (m), 1233 (s), 1184 (m), 1087 (w), 1035 (s), 938 (s), 858 (m), 740 (s); MS (EI$^+$, 70 eV) 299.1 (14.2), 298.1 (69.8), 190.1 (13.2), 189.1 (100.0), 188.1 (75.1), 174.0 (18.0), 173.0 (43.8), 162.1 (26.5), 159.1 (34.4), 131.1 (22.0), 116.1 (12.2), 115.0 (26.2), 103.1 (7.3), 91.1 (10.9), 85.0 (31.7), 83.0 (48.7), 65.1 (8.1); HRMS calcd for $C_{18}H_{18}O_2S^+$ 298.1028, found 298.1032; TLC R_f 0.44 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ −18.7 (c = 0.53, EtOH); SFC (5*S*,6*S*)-**14a**, t_R 11.7 min (3%); (5*R*,6*R*)-**14a**, t_R 15.2 min (97%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{18}H_{18}O_2S$ (298.40): C, 72.45; H, 6.08%. Found: C, 72.59; H, 5.90%.



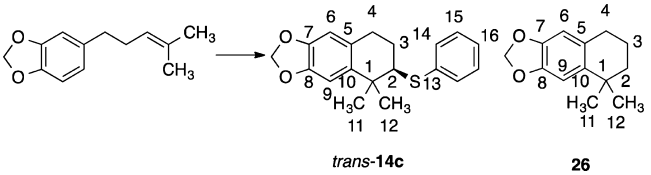
syn-**14a**

*Preparation of trans-5-Methyl-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-d]-1,3-dioxole (cis-**14a**).* Following General Procedure 8, (*Z*)-**2a** (190 mg, 1.0 mmol), **13** (256.0 mg, 1.0 mmol), (*S*)-**20a** (54.8 mg, 0.1 mmol), and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at 0 °C for 72 h. Purification by flash column chromatography (SiO_2, 32 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded of *cis*-**14a** (275 mg, 92%) as a white solid. Recrystallization from hot pentane provided 271 mg (91%) of analytically pure *cis*-**14a**. Data for *cis*-**14a**: mp 76−78 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, J = 7.5 Hz, 2 H, HC(13)), 7.33 (t, J = 7.5 Hz, 2 H, HC(14)), 7.26 (t, J = 7.6 Hz, 1 H, HC(15)), 6.58 (s, 1 H, HC(6)), 6.56 (s, 1 H, HC(9)), 5.90 (s, 2 H, OCH_2O), 3.69−3.65 (m, 1 H, HC(2)), 3.10−3.04 (m, 1 H, HC(1)), 2.89 (ddd, J = 17.0, 5.5, 5.5 Hz, 1 H, HC(4)), 2.80 (ddd, J = 17.0, 8.5, 8.5 Hz, 1 H, HC(4)), 2.05−2.00 (m, 2 H, HC (3)), 1.33 (d, J = 7.0 Hz, 3 H, HC(11)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1 (C(7)), 145.9 (C(8)), 135.5 (C(12)), 134.6 (C(5)), 131.5 (C(13)), 129.1 (C(14)), 127.8 (C(10)), 126.8 (C(15)), 108.5 (C(9)), 108.5 (C(6)), 100.8 (OCH_2O), 48.9 (C(2)), 36.9 (C(1)), 29.3 (C(4)), 24.9 (C(3)), 18.9 (C(11)); IR (KBr) 2961 (m), 2898 (m), 1580 (w), 1500 (s), 1479 (s), 1434 (w), 1375 (w), 1247 (s), 1219 (s), 1087 (w), 1039 (s), 941 (m), 928 (m), 893 (w), 862 (m), 737 (m), 688 (m); MS (EI$^+$, 70 eV) 299.1 (14.4), 298.1 (68.5), 231.2 (35.6), 189.1 (100.0), 188.1 (24.8), 174.1 (11.2), 173.1 (26.7), 162.1 (34.9), 159.1 (37.9), 135.1 (20.7), 131.1 (31.6), 128.1 (10.8), 116.1 (15.2), 115.1 (30.0), 107.1 (12.6), 103.1 (12.1), 91.1 (27.6), 78.1 (12.6), 77.1 (18.8), 65.1 (14.6), 57.1 (23.6), 55.1 (12.0), 51.1 (11.6); HRMS calcd for $C_{18}H_{18}O_2S^+$ 298.1028, found 298.1034; TLC R_f 0.42 (hexanes/Et_2O, 96:4) [$KMnO_4$]; SFC *cis*-**14a**, t_{R1} 12.6 min (52%); *cis*-**14a**, t_{R2} 14.1 min (48%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{18}H_{18}O_2S$ (298.40); Calcd: C, 72.45; H, 6.08%. Found: C, 72.43; H, 6.03%.



trans-**14b**

*Preparation of ((5R,6R)-5-Phenyl-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-d]-1,3-dioxole (trans-**14b**).* Following General Procedure 8, (*E*)-**2b** (252.3 mg, 1.0 mmol), **13** (256 mg, 1.0 mmol), (*S*)-**20a** (54.9 mg, 0.1 mmol), and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at −20 °C for 48 h. Purification by flash column chromatography (SiO_2, 30 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**14b** (328 mg, 91%) as a pale yellow solid. Recrystallization form hot pentane provided 324 mg (90%) of analytically pure *trans*-**14b**. Data for *trans*-**14b**: mp 54−56 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 7.5 Hz, 2 H, HC(16)), 7.34−7.22 (m, 6 H, HC(13) and HC(14) and HC(17) and HC(18)), 7.07 (d, J = 7.5 Hz, 2 H, HC(12)), 6.66 (s, 1 H, HC(6)), 6.32 (s, 1 H, C(9)), 5.90 (d, J = 2.5 Hz, 2 H, OCH_2O), 4.13 (d, J = 5.0 Hz, 1 H, HC(1)), 3.68−3.65 (m, 1 H, HC(2)), 3.00 (ddd, J = 16.0, 8.0, 5.5 Hz, 1 H, HC(4)), 2.81 (ddd, J = 17.0, 6.0, 6.0 Hz, 1 H, HC(4)), 2.20−2.14 (m, 1 H, HC(3)), 2.19−2.12 (m, 1 H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4 (C(7)), 146.2 (C(8)), 145.5 (C(11)), 135.1 (C(15)), 132.4 (C(16)), 129.5 (C(5)), 129.4 (C(10)), 129.1 (C(12)), 129.0 (C(13)), 128.5 (C(17)), 127.2 (C(18)), 126.7 (C(14)), 110.4 (C(9)), 108.3 (C(6)), 100.8 (OCH_2O), 51.5 (C(2)), 50.4 (C(1)), 26.8 (C(4)), 24.9 (C(3)); IR (KBr) 3052 (w), 3017 (w), 2919 (m), 2885 (m), 1580 (w), 1500 (m), 1479 (s), 1448 (m), 1434 (m), 1382 (w), 1236 (s), 1170 (w), 1039 (s), 938 (m), 869 (m), 740 (m), 699 (m); MS (EI$^+$, 70 eV) 361.1 (18.7), 360.0 (71.7), 252.1 (16.6), 251.1 (91.6), 250.0 (100.0), 224.0 (20.2), 223.0 (29.6), 205.1 (19.0), 194.0 (15.6), 193.1 (10.4), 191.1 (19.0), 189.0 (13.2), 178.0 (13.9), 173.0 (13.6), 166.1 (17.0), 165.0 (35.2), 160.0 (9.5), 159.0 (15.7), 152.0 (8.4), 143.0 (7.3), 135.0 (18.3), 115.0 (28.6), 109.0 (11.8); HRMS calcd for $C_{23}H_{20}O_2S^+$ 360.1164, found 360.1178; TLC R_f 0.40 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ −33.0 (c = 0.65, EtOH); SFC (5*R*,6*R*)-**14b**, t_R 14.0 min (94%); (5*S*,6*S*)-**14b**, t_R 17.2 min (6%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C).



trans-**14c** **26**

*Preparation of (6R)-5,5-Dimethyl-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-d]-1,3-dioxole ((R)-**14c**) and 5,5-Dimethyl-5,6,7,-8-tetrahydronaphtho[2,3-d]-1,3-dioxole (**26**).* Following General Procedure 8, a 10 mL Schlenk flask was charged with **4c** (204.3 mg,

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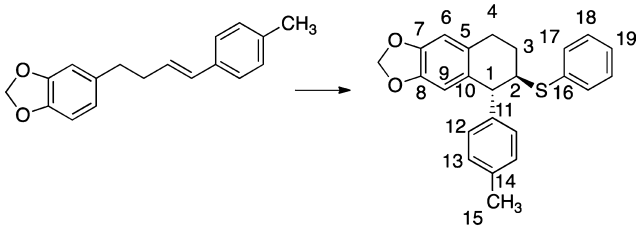
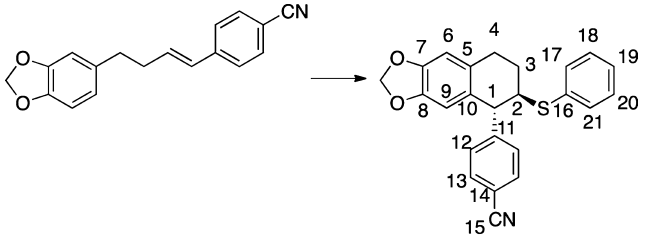
1.0 mmol), **13** (256.0 mg, 1.0 mmol), (*S*)-**20a** (54.9 mg, 0.1 mmol), and CH_2Cl_2 (4.5 mL) and reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.5 mL, 0.5 mmol) at −20 °C for 24 h. Purification by flash column chromatography (SiO_2, 32 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded (*R*)-**14c** (284 mg, 91%) as a white solid along with **26** (20 mg, 10%) as colorless oil. Distillation provided 281 mg (90%) of analytically pure (*R*)-**14c**. Data for (*R*)-**14c**: bp 130 °C at 2.2×10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (t, J = 8.0, 1.5 Hz, 2 H, HC(14)), 7.33 (t, J = 7.5 Hz, 2 H, HC(15)), 7.25 (t, J = 7.0 Hz, 1 H, HC(16)), 6.85 (s, 1 H, HC(6)), 6.51 (s, 1 H, C(9)), 5.91 (s, 2 H, OCH_2O), 3.43 (dd, J = 10.5, 3.0 Hz, 1 H, HC(2)), 2.86 (ddd, J = 16.5, 5.5, 5.0 Hz, 1 H, HC(4)), 2.71 (ddd J = 16.0, 10.0, 1.0 Hz, 1 H, HC(4)), 2.21−2.15 (m, 1 H, HC(3)), 2.06−1.98 (m, 1 H, HC(3)), 1.56 (s, 3 H, HC(12)), 1.40 (m, 3 H, HC(11)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3 (C(7)), 145.7 (C(8)), 138.1 (C(12)), 136.6 (C(5)), 131.6 (C(14)), 129.1 (C(15)), 128.0 (C(10)), 126.7 (C(16)), 108.3 (C(9)), 106.6 (C(6)), 100.8 (OCH_2O), 57.8 (C(2)), 38.9 (C(1)), 30.8 (C(11)), 29.5 (C(4)), 27.7 (C(12)), 26.6 (C(3)); IR (neat) 3066 (m), 2961 (s), 2891 (s), 2766 (m), 1625 (w), 1580 (s), 1503 (s), 1434 (s), 1368 (s), 1333 (s), 1302 (s), 1240 (s), 1191 (s), 1160 (s), 1115 (s), 1087 (s), 1049 (s), 1021 (s), 938 (s), 914 (s), 893 (s); MS (EI$^+$, 70 eV) 313.0 (10.0), 312.0 (46.5), 204.1 (13.6), 203.1(100.0), 202.1 (13.7), 188.0 (21.3), 187.0 (29.6), 176.0 (20.6), 173.0 (23.1), 161.0 (10.4), 145.1 (10.2), 131.0 (10.4), 129.0 (9.5), 128.0 (8.3), 115.0 (11.2), 103.0 (6.5), 77.1 (6.6); HRMS calcd for $C_{19}H_{20}O_2S^+$ 312.1184, found 312.1190; TLC R_f 0.42 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ −10.72 (c = 0.63, EtOH); SFC (5*S*)-**14c**, t_R 14.7 min (20%); (6*R*)-**14c**, t_R 16.5 min (80%) (Chiralpak AD, 1−5% MeOH over 40 min in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{19}H_{20}O_2S$ (312.12): C, 73.04; H, 6.45%. Found: C, 73.24; H, 6.57%. Data for **26**:[54k] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 (s, 1 H, HC(6)), 6.53 (s, 1 H, C(9)), 5.90 (s, 2 H, OCH_2O), 2.69 (t, J = 6.5 Hz, 2 H, HC(4)), 1.82−1.77 (m, 2 H, HC(3)), 1.66−1.64 (m, 2 H, HC(2)), 1.27 (s, 6 H, HC(11) and HC(12)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9 (C(7)), 145.2 (C(8)), 139.0 (C(5)), 129.3 (C(10)), 108.6 (C(9)), 106.6 (C(6)), 100.6 (OCH_2O), 39.4 (C(2)), 34.1 (C(1)), 32.1 (C(11) and C(12)), 31.0 (C(4)), 20.0 (C(3)); IR (neat) 2947 (s), 2926 (s), 2766 (w), 1621 (w), 1500 (s), 1483 (s), 1371 (s), 1333 (w), 1233 (s), 1191 (m), 1108 (m), 1039 (s), 1011 (w), 931 (m), 865 (m), 844 (m), 740 (w); MS (EI$^+$, 70 eV) 204.1 (29.0), 190.1 (12.5), 189.1 (100.0), 160.1 (29.6), 176.0 (20.6), 173.0 (23.1), 160.1 (5.7), 159.1 (23.2), 131.1 (15.0), 115.0 (9.3), 91.1 (6.8), 84.0 (6.8); HRMS calcd for $C_{13}H_{16}O_2^+$ 204.1150, found 204.1154; TLC R_f 0.52 (hexanes/Et_2O, 96:4) [$KMnO_4$].



trans-**14d**

*Preparation of ((5R,6R)-5-(4-Methylphenyl)-6-(phenylthio)-5,6,7,-8-tetrahydronaphtho[2,3-d]-1,3-dioxole (trans-**14d**).* Following General Procedure 8, 10 mL of (*E*)-**2d** (266.3 mg, 1.0 mmol), **13** (256 mg, 1.0 mmol), (*S*)-**20a** (54.9 mg, 0.1 mmol, 0.1 equiv), and CH_2Cl_2 (4.25 mL) was reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at −20 °C for 48 h. Purification by flash column chromatography (SiO_2, 30 g, 30 mm Ø, hexane/Et_2O, 96:4) afford *trans*-**14d** (327 mg, 87%) as a white solid. Recrystallization from hot pentane provided 322 mg (86%) of analytically pure *trans*-**14d**. Data for *trans*-**14d**: mp 72−74 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 7.0 Hz, 2 H, HC(17), 7.32 (t, J = 7.5 Hz, 2 H, HC(18)), 7.27 (t, J = 7.5 Hz, 1 H, HC(19)), 7.11 (d, J = 7.5 Hz, 2 H, HC(13)), 6.96 (d, J = 7.5 Hz, 2 H, HC(12)), 6.65 (s, 1 H, HC(6)), 6.33 (s, 1 H, C(9)), 5.89 (s, 2 H, OCH_2O), 4.09 (d, J = 4.5 Hz, 1 H, HC(1)), 3.67−3.64 (m, 1 H, HC(2)), 2.99 (ddd, J = 16.0, 8.0, 5.5 Hz, 1 H, HC(4)), 2.80 (ddd, 1H, J = 16.0, 6.0, 6.0 Hz, 1 H, HC(4)), 2.35 (s, 3 H, HC(15)), 2.20−2.14 (m, 1 H, HC(3)), 1.87−1.81 (m, 1 H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4 (C(7)), 146.1 (C(8)), 142.5 (C(14)), 136.2 (C(11)), 135.1 (C(16)), 132.3 (C(17)), 129.8 (C(5)), 129.4 (C(10)), 129.2 (C(13)), 129.0 (C(18)), 128.9 (C(12)), 127.0 (C(19)), 110.3 (C(9)), 108.2 (C(6)), 100.8 (OCH_2O), 51.4 (C(2)), 50.0 (C(1)), 26.8 (C(4)), 24.9 (C(3)), 21.2 (C(15)); IR (KBr) 3003 (w), 2919 (m), 2885 (m), 1580 (w), 1500 (s), 1479 (s), 1434 (m), 1382 (w), 1236 (s), 1174 (w), 1035 (s), 938 (m), 869 (w), 806 (w), 740 (m), 692 (m); MS (EI$^+$, 70 eV) 375.1 (21.2), 374.1 (75.9), 326.2 (26.2), 266.1 (19.0), 265.1 (100.0), 264.1 (90.0), 249.0 (9.3), 237.0 (9.8), 224.0 (9.8), 223.0 (58.2), 191.1 (10.8), 189.0 (11.0), 179.0 (9.8), 178.0 (10.7), 173.0 (17.7), 165.0 (21.8), 159.0 (96.4), 159.0 (15.7), 143.0 (11.4), 135.0 (14.0), 115.0 (23.2), 109.0 (10.9), 105.1 (66.4); HRMS calcd for $C_{24}H_{22}O_2S^+$ 374.1341, found 374.1336; TLC R_f 0.35 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ −28.4 (c = 0.59, EtOH); SFC (5*S*,6*S*)-**14d**, t_R 12.7 min (6%); (5*R*,6*R*)-**14d**, t_R 14.1 min (94%) (Chiralpak AD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{24}H_{22}O_2S$ (374.50): C, 76.97; H, 5.92%. Found: C, 76.79; H, 6.03%.



trans-**14e**

*Preparation of ((5R,6R)-5-(4-Cyanophenyl)-6-(phenylthio)-5,6,7,-8-tetrahydronaphtho[2,3-d]-1,3-dioxole (trans-**14e**).* Following General Procedure 8, (*E*)-**2e** (277.3 mg, 1.0 mmol, 1.0 equiv), **13** (256 mg, 1.0 mmol), (*S*)-**20a** (54.9 mg, 0.1 mmol), and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at room temperature for 96 h. Purification by flash column chromatography (SiO_2, 30 g, 30 mm Ø, hexane/Et_2O, 80:20) afford *trans*-**14e** (324 mg, 84%) as a white solid. Recrystallization from hot pentane provided 320 mg (83%) of analytically pure *trans*-**14e**. Data for *trans*-**14e**: mp 64−66 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 8.0 Hz, 2 H, HC(13)), 7.37−7.35 (m, 2 H, HC(17) and HC(23)), 7.41−7.25 (m, 3 H, HC(18) and HC(19) and HC(20)), 7.13 (d, J = 8.0 Hz, 2 H, HC(12)), 6.63 (s, 1 H, HC(6)), 6.17 (s, 1 H, C(9)), 5.88 (s, 2 H, OCH_2O), 4.11 (d, J = 5.5 Hz, 1 H, HC(1)), 3.52−3.49 (m, 1 H, HC(2)), 2.97 (ddd, J = 17.0, 14.0, 6.0 Hz, 1 H, HC(4)), 2.79 (ddd, 1H, J = 17.0, 6.5, 6.5 Hz, 1 H, HC(4)), 2.13−2.07 (m, 1 H, HC(3)), 1.88−1.82 (m, 1 H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0 (C(7)), 146.9 (C(8)), 146.5 (C(16)), 134.5 (C(17,21)), 132.9 (C(13)), 132.4 (C(12), 129.7 (C(10)), 129.3 (C(18,20)), 128.4 (C(5)), 127.7 (C(19)), 119.1 (C(15)), 110.7 (C(14)), 110.0 (C(9)), 108.6 (C(6)), 101.1 (OCH_2O), 51.8 (C(2)), 50.9 (C(1)), 27.3 (C(4)), 25.8 (C(3)); IR (KBr) 3059 (w), 2968 (w), 2926 (w), 2885 (w), 2216 (m), 1604 (w), 1580 (w), 1500 (s), 1476 (s), 1434 (m), 1382 (m), 1236 (s), 1035 (s), 938 (m), 820 (m), 740 (m); MS (EI$^+$, 70 eV) 385.2 (22.9), 381.3 (18.4), 340.3 (17.6), 326.2 (24.7), 325.2 (100), 276.2 (30.4), 275.1 (33.4), 269.2 (14.2), 239.2 (14.6), 231.2 (34.4), 191.2 (48.8), 190.1 (16.6), 175.1 (12.8), 160.1 (14.1), 141.1 (12.4), 135.1 (29.8), 121.0 (12.8), 115.1 (22.3), 107.1 (18.8), 91.1 (22.0), 77.1 (19.2), 69.1 (14.0), 57.1 (48.1), 55.1 (22.0); HRMS calcd for $C_{24}H_{19}NO_2S^+$ 385.1137, found 385.1129; TLC R_f 0.38 (hexanes/Et_2O, 80:20) [$KMnO_4$]; $[\alpha]_D^{25}$ −19.9 (c = 0.58, EtOH); SFC (5*S*,6*S*)-**14e**, t_R 23.9 min (89%); (5*R*,6*R*)-**14e**, t_R 27.6 min (11%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{24}H_{19}NO_2S$ (385.48): C, 74.78; H, 4.97%; N, 3.63%. Found: C, 74.50; H, 4.69%; N, 3.60%.

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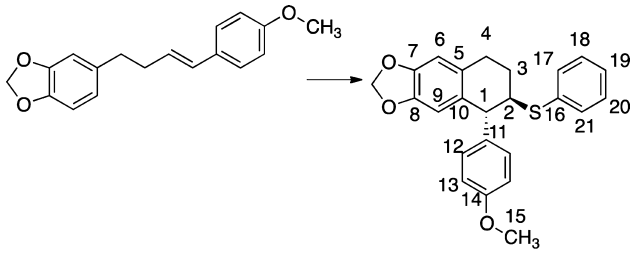
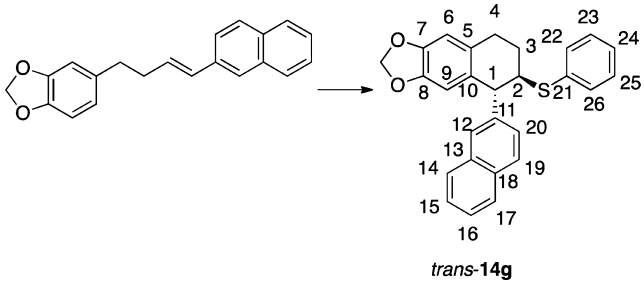


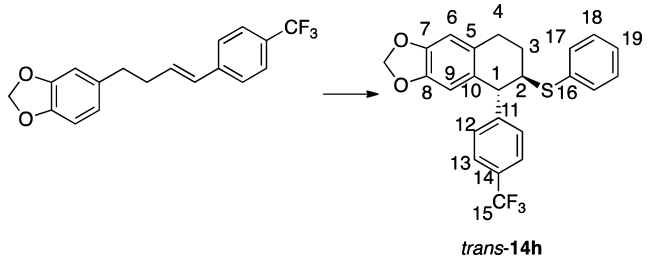
trans-**14f**

*Preparation of ((5R,6R)-5-(4-Methoxyphenyl)-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-d]-1,3-dioxole (trans-**14f**).* Following General Procedure 8, a 10 mL Schlenk flask was charged with (*E*)-**2f** (282.3 mg, 1.0 mmol), **13** (256.0 mg, 1.0 mmol), (*S*)-**20a** (54.9 mg, 0.1 mmol), and CH_2Cl_2 (4.25 mL) and reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at −20 °C for 24 h. Purification by flash column chromatography (SiO_2, 32 g, 30 mm Ø, hexane/Et_2O, 90:10) afforded *trans*-**14f** (340 mg, 87%) as a white solid. Recrystallization from hot pentane provided 336 mg (86%) of analytically pure *trans*-**14f**. Data for *trans*-**14f**: mp 104−106 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42−7.41 (m, 2 H, HC(17) and HC(21)), 7.33−7.28 (m, 2 H, HC(18) and HC(20)), 7.26 (tt, *J* = 7.0, 2.0 Hz, 1 H, HC(19)), 6.97 (d, *J* = 7.5 Hz, 2 H, HC(13)), 6.84 (d, *J* = 7.5 Hz, 2 H, HC(12)), 6.64 (s, 1 H, HC(6)), 6.32 (s, 1 H, C(9)), 5.86 (s, 2 H, OCH_2O), 4.06 (d, *J* = 5.0 Hz, 1 H, HC(1)), 3.81 (s, 3 H, HC(15)), 3.63−3.60 (m, 1 H, HC(2)), 2.98 (ddd, *J* = 16.0, 9.0, 6.0 Hz, 1 H, HC(4)), 2.79 (ddd, *J* = 17.0, 5.5, 5.5 Hz, 1 H, HC(4)), 2.19−2.13 (m, 1 H, HC(3)), 1.88−1.81 (m, 1 H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.4 (C(14)), 146.4 (C(7)), 146.2 (C(8)), 137.7 (C(11)), 135.3 (C(16)), 132.4 (C(17,20)), 130.1 (C(13)), 130.0 (C(5)), 129.4 (C(10)), 129.1 (C(18,20)), 127.2 (C(19)), 113.9 (C(12)), 110.4 (C(9)), 108.3 (C(6)), 100.9 (OCH_2O), 55.5 (C(15)), 51.7 (C(2)), 49.7 (C(1)), 27.0 (C(4)), 25.0 (C(3)); IR (KBr) 2919 (m), 2829 (m), 1608 (m), 1580 (m), 1507 (s), 1479 (s), 1434 (m), 1389 (w), 1299 (w), 1240 (s), 1039 (m), 941 (w), 869 (w), 817 (m), 740 (m); MS (EI$^+$, 70 eV) 390.2 (17.0), 381.5 (16.5), 340.3 (20.3), 326.2 (26.2), 325.2 (100.0), 295.4 (12.0), 281.2 (23.0), 280.2 (20.2), 269.3 (15.0), 231.2 (43.9), 223.1 (16.0), 191.2 (58.7), 175.2 (14.2), 159.1 (14.1), 149.2 (16.1), 143.1 (11.5), 141.1 (20.0), 135.1 (40.6), 133.1 (12.1), 128.1 (14.8), 127.1 (13.6), 121.1 (32.2), 115.1 (28.0), 57.0 (60.0); HRMS calcd for $C_{24}H_{22}O_3S^+$ 390.1290, found 390.1297; TLC R_f 0.36 (hexanes/Et_2O, 90:10) [$KMnO_4$]; $[\alpha]_D^{25}$ −25.9 (*c* = 0.54, EtOH); SFC (5*R*,6*R*)-**14f**, t_R 23.7 min (92%); (5*S*,6*S*)-**14f**, t_R 42.7 min (8%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{24}H_{22}O_3S$ (390.13): C, 73.82; H, 5.68%. Found: C, 73.89; H, 5.60%.



trans-**14g**

*Preparation of ((5R,6R)-5-(2-Naphthyl)-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-d]-1,3-dioxole (trans-**14g**).* Following General Procedure 8, (*E*)-**2g** (302 mg, 1.0 mmol, 1.0 equiv), **13** (256 mg, 1.0 mmol, 1.0 equiv), (*S*)-**20a** (55 mg, 0.1 mmol, 0.1 equiv), and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at −20 °C for 48 h. Purification by flash column chromatography (SiO_2, 30 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**14g** (254 mg, 62%) as a white solid along with unreacted (*E*)-**2g** (109 mg, 36%). Recrystallization from hot pentane provided 250 mg (61%) of analytically pure *trans*-**14g**. Data for *trans*-**14g**: mp 92−94 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83−7.77 (m, 2 H, H(C-aryl)), 7.50−7.42 (m, 5 H, HC(22) and HC(26) and H(C-aryl)), 7.32−7.20 (m, 5 H, HC(23) and HC(24) and HC(25) and H(C-aryl)), 6.69 (s, 1 H, HC(6)), 6.33 (s, 1 H, C(9)), 5.89 (s, 2 H, OCH_2O), 4.27 (d, *J* = 5.5 Hz, 1 H, HC(1)), 3.78−3.73 (m, 1 H, HC(2)), 3.03 (ddd, *J* = 18.0, 8.0, 6.5 Hz, 1 H, HC(4)), 2.86 (ddd, *J* = 17.0, 6.0, 5.5 Hz, 1 H, HC(4)), 2.25−2.18 (m, 1 H, HC(3)), 1.91−1.85 (m, 1 H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6 (C(7)), 146.3 (C(8)), 142.9 (C(11)), 135.1 (C(21)), 133.5 (C-aryl), 132.6 (C(22,26)), 132.5 (C-aryl), 129.7 (C(5)), 129.5 (C(10)), 129.1 (C(23,25)), 128.4 (C(aryl)), 128.3 (C(aryl)), 128.0 (C(aryl)), 127.8 (C(aryl)), 127.3 (C(aryl), 127.0 (C(24)), 126.3 (C(aryl)), 125.9 (C(aryl)), 110.5 (C(9)), 108.4 (C(6)), 101.0 (OCH_2O), 51.5 (C(2)), 50.8 (C(1)), 27.2 (C(4)), 25.5 (C(3)); IR (KBr) 3045 (w), 2968 (w), 2919 (m), 2885 (m), 1597 (w), 1580 (w), 1500 (s), 1479 (s), 1438 (m), 1382 (w), 1236 (s), 1170 (w), 1115 (m), 1035 (s), 938 (m), 855 (w), 817 (m), 796 (w), 744 (s), 692 (m); MS (EI$^+$, 70 eV) 446.2 (66.5), 325.2 (58.7), 310.4 (12.6), 295.3 (34.6), 279.3 (30.9), 259.3 (18.2), 247.2 (17.8), 239.2 (54.4), 231.2 (100.0), 227.2 (21.0), 215.2 (17.1), 205.2 (15.7), 191.2 (93.0), 175.2 (28.9), 159.1 (24.4), 149.1 (27.1), 143.1 (25.5), 141.1 (33.5), 133.1 (21.2), 128.1 (25.7), 121.1 (32.4), 115.1 (38.3), 109.1 (30.5), 107.1 (44.4), 105.1 (46.2); HRMS calcd for$C_{27}H_{22}O_2S^+$ 410.1341, found 410.1343; TLC R_f 0.36 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ −19.2 (*c* = 0.54, EtOH); SFC (5*S*,6*S*)-**14g**, t_R 23.4 min (11%); (5*R*,6*R*)-**14g**, t_R 23.5 min (89%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{27}H_{22}O_2S$ (410.13): C, 78.99; H, 5.40%. Found: C, 78.98; H, 5.48%.



trans-**14h**

*Preparation of ((5R,6R)-5-(4-Trifluoromethylphenyl)-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-d]-1,3-dioxole (trans-**14h**).* Following General Procedure 8, (*E*)-**2h** (320.3 mg, 1.0 mmol), **13** (256.0 mg, 1.0 mmol), (*S*)-**20a** (54.9 mg, 0.1 mmol), and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at 22 °C for 72 h. Purification by flash column chromatography (SiO_2, 30 g, 32 mm Ø, hexane/Et_2O, 96:4) afford *trans*-**14h** (368 mg, 86%) as a white solid. Recrystallization from hot pentane provided 364 mg (85%) of analytically pure *trans*-**14h**. Data for *trans*-**14h**: mp 98−100 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2 H, HC(13)), 7.39 (t, *J* = 7.0 Hz, 2 H, HC(17), 7.31 (t, *J* = 6.5 Hz, 2 H, HC(18)), 7.23 (t, *J* = 7.5 Hz, 1 H, HC(19)), 7.16 (d, *J* = 8.0 Hz, 2 H, HC(12)), 6.66 (s, 1 H, HC(6)), 6.23 (s, 1 H, C(9)), 5.90 (s, 2 H, OCH_2O), 4.16 (d, *J* = 5.5 Hz, 1 H, HC(1)), 3.60−3.57 (m, 1 H, HC(2)), 3.00 (ddd, *J* = 16.5, 8.0, 6.0 Hz, 1 H, HC(4)), 2.82 (ddd, 1H, *J* = 17.0, 6.0, 6.0 Hz, 1 H, HC(4)), 2.18−2.11 (m, 1 H, HC(3)), 1.90−1.84 (m, 1 H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5 (C(11)), 146.7 (C(7)), 146.3 (C(8)), 134.6 (C(16)), 132.6 (C(18)), 129.6 (C(10)), 129.5 (C(12)), 129.1 (C(17)), 129.0 (q, *J* = 32.0 Hz, (C(14)), 128.8 (C(5)), 127.5 (C(19)), 125.4 (q, *J* = 3.9 Hz, C(13)), 124.3 (q, *J* = 272.0 Hz, C(15)), 110.1 (C(9)), 108.4 (C(6)), 101.0 (OCH_2O), 51.6 (C(2)), 50.6 (C(1)), 27.1 (C(4)), 25.5 (C(3)); IR (KBr) 2927 (w), 2891 (w), 1608 (w), 1580 (w), 1503 (s), 1479 (s), 1437 (m), 1381 (w), 1301 (w), 1238 (s), 1171 (m), 1032 (s), 937 (m), 906 (w), 818 (m); MS (EI$^+$, 70 eV) 429.2 (22.9), 428.2 (84.1), 325.2 (17.9), 319.1 (17.2), 318.1 (100.0), 291.1 (9.2), 289.2 (9.5), 260.1 (9.2), 233.1 (12.0), 223.1 (47.5), 191.1 (10.3), 189.1 (11.4), 165.0 (20.0), 161.1 (11.6), 160.1 (36.1), 159.1 (30.9), 115.1 (16.3); HRMS calcd for $C_{24}H_{19}F_3O_2S^+$ 428.1058, found 428.1050; TLC R_f 0.29 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ −18.5 (*c* = 0.55, EtOH); SFC (5*R*,6*R*)-**14h**, t_R 6.4 min (92%); (5*S*,6*S*)-**14h**, t_R 9.8 min (8%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{24}H_{22}F_3O_2S$ (428.11): C, 67.28; H, 4.47%. Found: C, 67.92; H, 4.35%.

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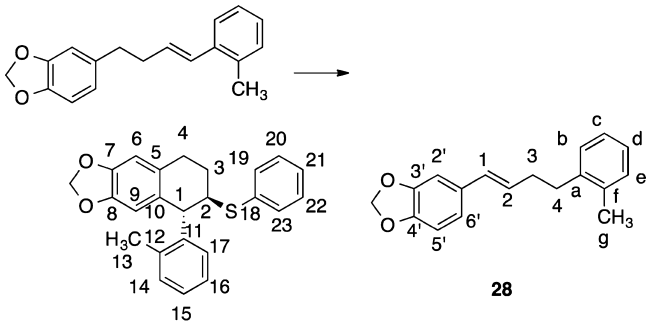
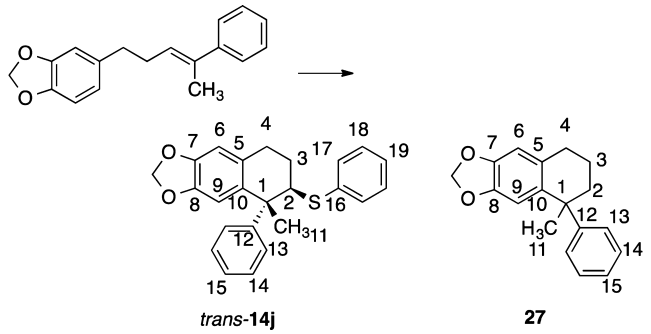


trans-**14i** **28**

*Preparation of ((5R,6R)-5-(2-Methylphenyl)-6-(phenylthio)-5,6,7,-8-tetrahydronaphtho[2,3-d]-1,3-dioxole (trans-**14i**) and (E)-1-(3′,4′-Methylenedioxyphenyl)-4-(2-methylphenyl)but-1-ene (**28**).* Following General Procedure 8, (*E*)-**2i** (266.3 mg, 1.00 mmol), **13** (256.0 mg, 1.0 mmol), (*S*)-**20a** (54.9 mg, 0.1 mmol), and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at −20 °C for 86 h. Purification by flash column chromatography (SiO_2, 95 g, 40 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**14i** (323 mg, 86%) as a white solid. Recrystallization of *trans*-**14i** from hot pentane provided 308 mg (82%) of analytically pure *trans*-**14i**. Isomerized starting material **28** was isolated from earlier unoptimized experiments. Data for *trans*-**14i**: mp 56−58 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45−7.43 (m, 2 H, HC(19) and HC(23)), 7.32−7.25 (m, 3 H, HC(20) and HC(21) and HC(22)), 7.18 (d, J = 6.5 Hz, 1 H, HC(14)), 7.12 (d, J = 7.5 Hz, 1.5 H, HC(15)), 7.08 (dt, J = 7.5, 1.5 Hz, 1 H, HC(16)), 6.76 (d, J = 7.5 Hz, 1 H, HC(17)), 6.66 (s, 1 H, HC(6)), 6.28 (s, 1 H, C(9)), 5.90 (s, 2 H, OCH_2O), 4.36 (d, J = 4.5 Hz, 1 H, HC(1)), 3.58−3.55 (m, 1 H, HC(2)), 3.06 (ddd, J = 16.5, 11.5, 5.5 Hz, 1 H, HC(4)), 2.80 (ddd, J = 16.5, 5.5, 5.5 Hz, 1 H, HC(4)), 2.31 (s, 3 H, HC(13)), 2.18−2.11 (m, 1 H, HC(3)), 1.87−1.80 (m, 1 H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4 (C(7)), 146.3 (C(8)), 143.6 (C(14)), 136.2 (C(18)), 135.1 (C(12)), 133.2 (C(19,23)), 130.5 (C(14)), 130.0 (C(5)), 129.6 (C(17)), 129.5 (C(10)), 129.0 (C(20, 22)), 127.4 (C(21)), 126.5 (C(15)), 126.0 (C(16)), 110.1 (C(9)), 108.2 (C(6)), 100.8 (OCH_2O), 50.4 (C(2)), 46.6 (C(1)), 26.5 (C(4)), 24.5 (C(3)), 19.6 (C(13)); IR (KBr) 3059 (m), 3015 (m), 2924 (s), 2770 (w), 1583 (m), 1504 (s), 1485 (s), 1454 (s), 1385 (s), 1348 (m), 1305 (w), 1283 (w), 1236 (s), 1176 (m), 1088 (w), 1038 (s), 941 (s), 907 (m), 868 (m), 823 (m), 741 (s); MS (EI$^+$, 70 eV) 374.1 (32.2), 325.2 (25.5), 265.1 (41.9), 264.1 (33.9), 239.1 (14.8), 223.1 (28.9), 220.2 (28.9), 206.2 (21.1), 205.2 (71.9), 192.1 (15.5), 191.1 (100.0), 175.1 (16.6), 165.1 (17.3), 149.0 (43.8), 145.1 (16.6), 135.1 (86.3), 131.1 (16.1), 129.1 (17.1), 128.1 (15.4), 121.1 (27.4), 115.1 (28.3), 111.1 (13.1), 109.1 (12.2), 107.1 (36.4), 105.1 (44.9); HRMS calcd for $C_{24}H_{22}O_2S^+$ 374.1341, found 374.1334; TLC R_f 0.37 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ −40.1 (c = 0.43, EtOH); SFC (5*S*,6*S*)-**14i**, t_R 10.2 min (8%); (5*R*,6*R*)-**14i**, t_R 11.5 min (92%) (Chiralpak AD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{24}H_{22}O_2S$ (374.13): C, 76.97; H, 5.92%. Found: C, 77.26; H, 5.77%. Data for **28**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17−7.08 (m, 4 H, HC(b) and HC(c) and HC(d) and HC(e)), 6.70 (d, J = 7.0 Hz, 1 H, HC(5′)), 6.62 (s, 1 H, HC(2′)), 6.59 (d, J = 7.0 Hz, 1 H, C(6′)), 6.44 (d, J = 11.5 Hz, 1 H, HC(1)), 5.90 (s, 2 H, OCH_2O), 5.72 (dt, J = 11.5, 7.0 Hz, 1 H, HC(2)), 2.63 (t, J = 8.0 Hz, 2 H, HC(4)), 2.48 (dt, J = 7.0, 7.0 Hz, 2 H, HC(3)), 2.21 (s, 3 H, HC(g)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6 (C(3′)), 145.7 (C(4′)), 136.7 (C(a)), 136.4 (C(f)), 135.7 (C(1′)), 131.6 (C(2)), 129.9 (C(aryl), 129.1 (C(1)), 128.8 (C(aryl), 127.0 (C(aryl), 125.4 (C(b)), 121.3 (C(6′)), 109.1 (C(2′)), 108.2 (C(5′)), 100.9 (OCH_2O), 35.8 (C(3)), 30.5 (C(4)), 20.0 (C(g)); IR (KBr) 3017 (w), 2919 (m), 1601(w), 1500 (m), 1486 (s), 1441 (m), 1361 (w), 1243 (s), 1184 (w), 1094 (s), 1039 (w), 962 (w), 935 (m), 858 (w), 806 (w), 744 (m); MS (EI$^+$, 70 eV) 266.1 (22.9), 149.0 (5.6), 136.0 (9.0), 135.0 (100.0), 131.1 (10.3), 120.9 (5.8), 118.9 (6.8), 115.0 (5.2); HRMS calcd for $C_{18}H_{18}O_2^+$ 266.1307, found 266.1315; TLC R_f 0.60 (hexanes/Et_2O, 96:4) [$KMnO_4$].



trans-**14j** **27**

*Preparation of ((5R,6R)-5-Methyl-5-phenyl-6-(phenylthio)-5,6,7,-8-tetrahydronaphtho[2,3-d]-1,3-dioxole (trans-**14j**) and 5-Methyl-5-phenyl-5,6,7,8-tetrahydronaphtho[2,3-d]-1,3-dioxole (**27**).* Following General Procedure 8, a 10 mL Schlenk flask was charged with (*E*)-**2j** (266 mg, 1.0 mmol, 1.0 equiv), **13** (256 mg, 1.0 mmol, 1.0 equiv), (*S*)-**20** (55 mg, 0.1 mmol, 0.1 equiv), and CH_2Cl_2 (4.25 mL) reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at −20 °C for 48 h. Purification by flash column chromatography (SiO_2, 30 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**14j** (318 mg, 85%) as a white solid along with **27** (5 mg, 2%) as colorless oil. Recrystallization from hot pentane provided 310 mg of analytically pure *trans*-**14j**. Data for *trans*-**14j**: mp 90−92 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33−7.19 (m, 10 H, HC(13) and HC(14), and HC(15) and HC(17) and HC(18) and HC(19)), 6.59 (s, 1 H, HC(6)), 6.34 (s, 1 H, C(9)), 5.89 (s, 2 H, OCH_2O), 3.68 (dd, J = 9.0, 4.5 Hz, 1 H, HC(2)), 2.97 (ddd, J = 17.0, 5.5, 5.5 Hz, 1 H, HC(4)), 2.86 (ddd, J = 16.0, 8.0, 8.0 Hz, 1 H, HC(4)), 2.13−2.07 (m, 2 H, HC(3)), 1.84 (s, 3 H, HC(11)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6 (C(12)), 146.1(C(7)), 146.0 (C(8)), 137.4 (C(5)), 136.2 (C(16), 132.2 (C(17)), 128.9 (C(14)), 128.7 (C(10)), 128.0 (C(13) and C(18)), 126.8 (C(15), 126.3 (C(19)), 109.2 (C(9)), 107.9 (C(6)), 100.8 (OCH_2O), 60.2 (C(2)), 47.7 (C(1)), 29.3 (C(4)), 26.8 (C(3)), 25.7 (C(11)); IR (KBr) 3045 (w), 2968 (m), 2933 (m), 2885 (m), 1580 (w), 1500 (m), 1483 (s), 1438 (m), 1368 (m), 1330 (w), 1229 (s), 1115 (w), 1035 (s), 935 (m), 858 (m), 752 (m), 737 (m), 699 (s); MS (EI$^+$, 70 eV) 375.1 (16.9), 374.1 (55.4), 266.1 (23.0), 265.1 (100.0), 264.1 (16.3), 249.1 (12.5), 237.1 (14.0), 224.0 (10.7), 223.0 (70.1), 205.1 (12.0), 1919.1 (17.7), 189.0 (12.5), 187.0 (11.0), 178.0 (12.7), 173.0 (107), 165.0 (24.9), 135.0 (13.0), 129.0 (10.5), 120.9 (19.6), 118.9 (22.1), 115.0 (15.7), 110.0 (12.4), 109.0 (13.8), 105.0 (32.6), 101.0 (9.5); HRMS calcd for $C_{24}H_{22}O_2S^+$ 374.1341, found 374.1343; TLC R_f 0.37 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ +72.9 (c = 0.48, EtOH); SFC (5*R*,6*R*)-**14j**, t_R 15.5 min (71%); (5*S*,6*S*)-**14j**, t_R 21.5 min (29%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{24}H_{22}O_2S$ (374.13): C, 76.97; H, 5.92%. Found: C, 76.91; H, 5.85%. Data for **27**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (t, J = 7.5 Hz, 2 H, HC(14)), 7.17 (t, J = 7.5 Hz, 1 H, HC(15)), 7.16 (d, J = 7.5 Hz, 2 H, HC(13)), 6.60 (s, 1 H, HC(6)), 6.46 (s, 1 H, C(9)), 5.89 (d, J = 10.0 Hz, 2 H, OCH_2O), 2.77 (t, J = 6.5 Hz, 2 H, HC(4)), 2.02 (ddd, J = 13.5, 8.5, 3.0 Hz, 1 H, HC(2)), 1.86 (ddd, J = 12.5, 9.0, 3.0 Hz, 1 H, HC(2)), 1.79−1.72 (m, 1 H, HC(3)), 1.70 (s, 3 H, HC(11)), 1.68−1.62 (m, 1 H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.6 (C(12)), 145.9 (C(7)), 145.7 (C(8)), 137.4 (C(5)), 130.4 (C(10)), 127.9 (C(14), 127.5 (C(13)), 125.6 (C(15)), 108.9 (C(9)), 108.3 (C(6)), 100.7 (OCH_2O), 43.1 (C(1)), 41.6 (C(2)), 30.6 (C(4)), 30.1 (C(3)), 15.8 (C(11)); IR (neat) 2926 (m), 1500 (m), 1479 (s), 1441 (w), 1372 (w), 1226 (s), 1163 (w), 1039 (m), 931 (w), 827 (w), 754 (w), 695 (w); MS (EI$^+$, 70 eV) 267.1 (10.8), 266.1 (56.8), 252.0 (17.8), 251.1 (100.0), 189.0 (16.9), 115.1 (7.4), 91.1 (22.7), 86.0 (15.3), 84.0 (24.0); HRMS calcd for $C_{18}H_{18}O_2^+$ 266.1307, found 266.1303; TLC R_f 0.58 (hexanes/Et_2O, 96:4) [$KMnO_4$].

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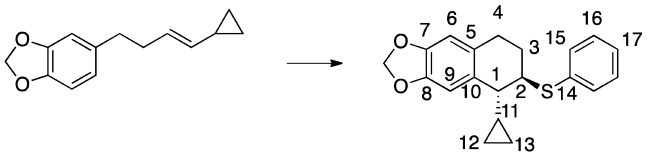
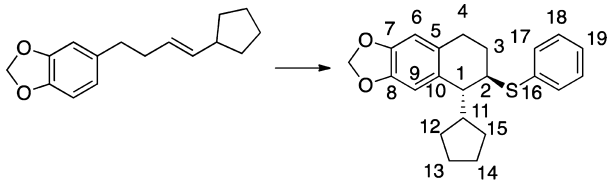


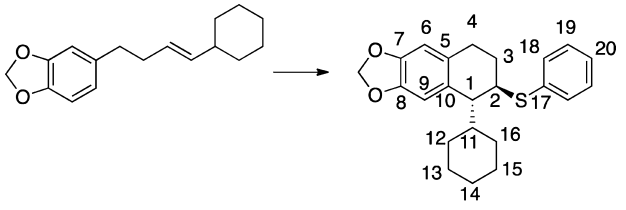
trans-**14k**

*Preparation of ((5R,6R)-5-Cyclopropyl-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-d]-1,3-dioxole (trans-**14k**).* Following General Procedure 8, (*E*)-**2k** (216.3 mg, 1.0 mmol), **13** (256.0 mg, 1.0 mmol), (*S*)-**20a** (54.9 mg, 0.1 mmol), and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at −20 °C for 72 h. Purification by flash column chromatography (SiO_2, 30 g, 25 mm Ø, hexane/Et_2O, 96:4) to afford *trans*-**14k** (292 mg, 90%) as colorless oil. Recrystallization from hot pentane provided 285 mg (88%) of analytically pure *trans*-**14k**. Data for *trans*-**14k**: mp 25 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 7.5, 1.0, 2 H, HC(15)), 7.32 (t, J = 7.5 Hz, 2 H, HC(16)), 7.25 (tt, J = 7.5, 1.0 Hz, 1 H, HC(17)), 6.68 (s, 1 H, HC(6)), 6.61 (s, 1 H, C(9)), 5.92 (s, 2 H, OCH_2O), 3.85 (q, J = 2.0 Hz, 1 H, HC(2)), 3.04 (ddd, J = 17.5, 12.0, 6.0 Hz, 1 H HC(4)), 2.68 (ddd, J = 17.0, 6.0, 1.5 Hz, 1 H, HC(4)), 2.34−2.27 (m, 1 H, HC(3)), 2.03 (d, J = 9.0 Hz, 1 H, HC(1)), 2.02−1.97 (m, 1 H, HC(3)), 0.99−0.92 (m, 1 H, HC(11)), 0.65−0.60 (m, 1 H, HC(12)), 0.56−0.50 (m, 1 H, HC(13)), 0.48−0.44 (m, 1 H, HC(12)), 0.29−0.22 (m, 1 H, HC(13)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4 (C(7)), 145.7 (C(8)), 135.6 (C(14)), 131.7 (C(15)), 139.5 (C(5)), 129.0 (C(16)), 128.1 (C(10)), 126.8 (C(17)), 109.4 (C(9)), 108.7 (C(6)), 100.8 (OCH_2O), 48.3 (C(1,2)), 25.2 (C(4)), 23.2 (C(3)), 19.9 (C(11)), 6.2 (C(12)), 4.0 (C(13)); IR (neat) 3066 (s), 2996 (s), 2919 (s), 2766 (s), 1580 (s), 1503 (s), 1379 (s), 1344 (s), 1271 (s), 1229 (s), 1181 (s), 1125 (m), 1046 (s), 1021 (s), 983 (s), 938 (s), 737 (s); MS (EI$^+$, 70 eV) 324.9 (12.2), 324.0 (54.6), 215.0 (30.2), 214.0 (36.0), 185.0 (13.3), 175.0 (12.7), 174.0 (100.0), 173.0 (39.3), 161.0 (13.1), 160.1 (9.6), 143.0 (9.2), 128.0 (11.1), 116.0 (11.7), 115.0 (33.2), 85.9 (28.5), 83.9 (44.0); HRMS calcd for $C_{20}H_{20}O_2S^+$ 324.1184, found 324.1181; TLC R_f 0.29 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ −23.9 (c = 0.53, EtOH); SFC (5*S*,6*S*)-**14k**, t_R 9.6 min (5%); (5*R*,6*R*)-**14k**, t_R 11.3 min (95%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C).



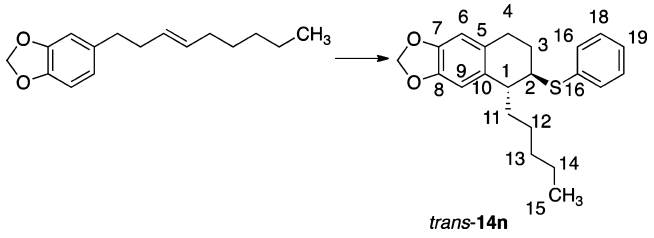
trans-**14l**

*Preparation of ((5R,6R)-5-Cyclopentyl-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-d]-1,3-dioxole (trans-**14l**).* Following General Procedure 8, (*E*)-**2l** (244.4 mg, 1.0 mmol), **13** (256.0 mg, 1.0 mmol), (*S*)-**20a** (54.9 mg, 0.1 mmol), and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at 0 °C for 72 h. Purification by flash column chromatography (SiO_2, 30 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**14l** (183 mg, 52%) as a white solid along with unreacted (*E*)-**2l** (37 mg, 15%). Recrystallization from hot pentane provided 180 mg (50%) of analytically pure *trans*-**14l**. Data for *trans*-**14l**: mp 102−104 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 7.0 Hz, 2 H, HC(17)), 7.29 (t, J = 7.0 Hz, 2 H, HC(18)), 7.22 (tt, J = 7.0, 1.5 Hz, 1 H, HC(19)), 6.58 (s, 1 H, HC(6)), 6.55 (s, 1 H, C(9)), 5.89 (dd, J = 4.5, 1.5 Hz, 2 H, OCH_2O), 3.82−3.80 (m, 1 H, HC(2)), 2.97 (ddd, J = 18.0, 11.0, 7.5 Hz, 1 H, HC(4)), 2.70 (ddd, J = 18.0, 7.0, 2.0 Hz, 1 H, HC(4)), 2.56 (d, J = 9.0 Hz, 1 H, HC(1)), 2.26−2.19 (m, 1 H, HC(3)), 1.91−1.76 (m, 3 H, HC(3) and HC(11) and HC(13)), 1.68−1.62 (m, 3 H, HC(13) and HC(14) and HC(15)), 1.58−1.51 (m, 1 H, HC(12)), 1.48−1.37 (m, 1 H, HC(14)), 1.31−1.17 (m, 3 H, HC(12), and HC(15)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2 (C(7)), 145.1 (C(8)), 136.0 (C(16)), 131.7 (C(17)), 131.1 (C(5)), 129.0 (C(18)), 128.2 (C(10)), 126.8 (C(19)), 110.4 (C(9)), 108.8 (C(6)), 100.7 (OCH_2O), 49.6 (C(1)), 47.7 (C(11)), 46.9 (C(2)), 32.9 (C(15)), 30.9 (C(12)), 25.0 (C(13)), 24.9 (C(14)), 24.4 (C(4)), 22.6 (C(3)); IR (KBr) 2926 (m), 2864 (m), 1500 (s), 1479 (s), 1455 (m), 1434 (w), 1375 (w), 1347 (w), 1229 (s), 1181 (m), 1118 (w), 1035 (s), 935 (m), 851 (w); MS (EI$^+$, 70 eV) 325.1 (10.1), 352.1 (36.8), 284.0 (6.7), 283.0 (43.2), 243.1 (7.9), 242.1 (8.4), 175.0 (20.5), 174.0 (100.0), 173.0 (63.3), 161.0 (16.0), 145.1 (6.7), 144.0 (10.0), 143.0 (8.6), 135.0 (8.3), 119.9 (5.6), 117.0 (9.5), 116.0 (16.0), 115.0 (35.3), 110.0 (12.9), 109.0 (9.4), 103.0 (5.0); HRMS calcd for $C_{22}H_{24}O_2S^+$ 352.1497, found 352.1491; TLC R_f 0.52 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ +11.8 (c = 0.19, EtOH); SFC (5*S*,6*S*)-**14l**, t_R 9.6 min (18%); (5*R*,6*R*)-**14l**, t_R 11.3 min (82%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{22}H_{24}O_2S$ (352.49): C, 74.59; H, 6.86%. Found: C, 74.72; H, 6.50%.



trans-**14m**

*Preparation of ((5R,6R)-5-Cyclohexyl-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-d]-1,3-dioxole (trans-**14m**).* Following General Procedure 8, (*E*)-**2m** (258.4 mg, 1.0 mmol), **13** (256.0 mg, 1.0 mmol), (*S*)-**20a** (54.9 mg, 0.1 mmol), and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at 0 °C for 72 h. Purification by flash column chromatography (SiO_2, 40 g, 50 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**14m** (264 mg, 72%) as a white solid along with unreacted (*E*)-**2m** (41 mg, 16%). Recrystallization from hot pentane provided 257 mg of analytically pure *trans*-**14m**. Data for *trans*-**14m**: mp 90−92 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 8.0, 1.5 Hz, 2 H, HC(18)), 7.32 (t, J = 8.0 Hz, 2 H, HC(19)), 7.22 (dt, 1H, J = 7.0, 1.0 Hz, 1 H, HC(20)), 6.59 (s, 1 H, HC(6)), 6.55 (s, 1 H, C(9)), 5.92 (dd, J = 7.0, 1.5 Hz, 2 H, OCH_2O), 3.82 (dt, J = 7.0, 4.0 Hz, 1 H, HC(2)), 2.91 (ddd, J = 17.0, 10.0, 7.0 Hz, 1 H, HC(4)), 2.70 (ddd, 1H, J = 17.0, 10.0, 4.0 Hz, 1 H, HC(4)), 2.59 (dd, J = 4.0, 2.0 Hz, 1 H, HC(1)), 2.20−2.13 (m, 1 H, HC(3)), 1.89−1.84 (m, 1 H, HC(3)), 1.79−1.71 (m, 3 H, HC(14) and HC(15) and HC(16)), 1.67−1.63 (m, 1 H, HC(12)), 1.62−1.59 (m, 1 H, HC(13)), 1.59−1.43 (m, 1 H, HC(11)), 1.22−1.12 (m, 3 H, HC(13), and HC(14) and HC(15)), 1.08−1.00 (m, 2H, HC(12) and HC(16)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1 (C(7)), 145.2 (C(8)), 136.0 (C(17)), 131.9 (C(18)), 130.1 (C(5)), 129.2 (C(10)), 129.0 (C(19)), 126.9 (C(20)), 110.6 (C(9)), 108.5 (C(6)), 100.7 (OCH_2O), 49.7 (C(1)), 45.5 (C(2)), 44.3 (C(11)), 32.2 (C(12)), 31.1 (C(16)), 27.0 (C(13)), 26.9 (C(15)), 26.6 (C(14)), 2.55 (C(4)), 24.3 (C(3)); IR (KBr) 2919 (s), 2843 (m), 1580 (w), 1500 (m), 1479 (s), 1444 (m), 1375 (w), 1347 (w), 1236 (s), 1036 (s), 935 (m), 865 (m), 737 (m), 688 (m); MS (EI$^+$, 70 eV) 366.1 (31.9), 284.1 (10.2), 283.1 (51.0), 191.1 (8.5), 175.1 (18.5), 174.1 (100.0), 173.0 (53.4), 161.0 (9.8), 144.0 (10.2), 135.0 (10.6), 116.0 (16.2), 115.0 (28.6); HRMS calcd for $C_{23}H_{26}O_2S^+$ 366.1654, found 366.1659; TLC R_f 0.52 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ −1.29 (c = 0.21, EtOH); SFC (5*S*,6*S*)-**14m**, t_R 11.0 min (15%); (5*R*,6*R*)-**14m**, t_R 12.8 min (85%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{22}H_{24}O_2S$ (366.53): C, 75.37; H, 7.15%. Found: C, 75.40; H, 7.11%.



trans-**14n**

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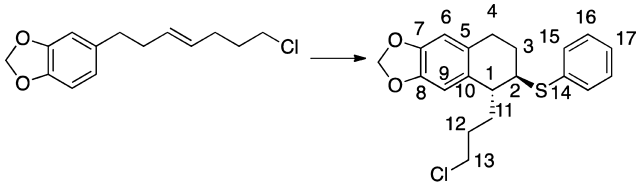
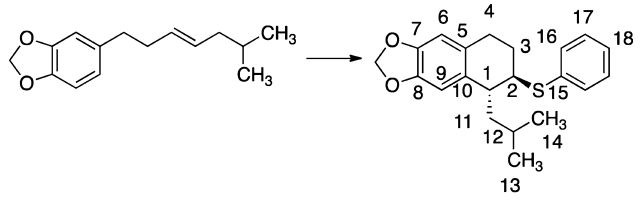
*Preparation of ((5R,6R)-5-Pentyl-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-d]-1,3-dioxole (trans-**14n**).* Following General Procedure 8, (*E*)-**2n** (246.3 mg, 1.0 mmol), **13** (256.0 mg, 1.0 mmol), (*S*)-**20a** (54.9 mg, 0.1 mmol), and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at −20 °C for 72 h. Purification by flash column chromatography (SiO_2, 32 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded of *trans*-**14n** (266 mg, 76%) as colorless oil. Distillation provided 259 mg of analytically pure *trans*-**14n**. Data for *trans*-**14n**: bp 140 °C at 5.5 × 10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, J = 7.5, 1.0 Hz, 2 H, HC(17)), 7.33 (t, J = 7.5 Hz, 2 H, HC(18)), 7.26 (tt, J = 7.0, 1.0 Hz, 1 H, HC(19)), 6.58 (s, 2 H, HC(6) and HC(9)), 5.91 (s, 2 H, OCH_2O), 3.673−3.65 (m, 1 H, HC(2)), 2.97 (ddd, J = 17.0, 10.5, 6.0 Hz, 1 H, HC(4)), 2.80 (dt, J = 8.0, 4.5 Hz, 1 H, HC(1)), 2.64 (ddd, J = 17.0, 6.0, 3.5 Hz, 1 H, HC(4)), 2.15 (dddd, J = 11.0, 6.5, 3.5 Hz, 1 H, HC(3)), 1.91−1.85 (m, 1 H, HC(3)), 1.72−1.59 (m, 2 H, HC (11)), 1.41−1.22 (m, 6 H, HC(12) and HC(13) and HC(14)), 0.90 (t, J = 7.0 Hz, 3 H, HC(15)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.0 (C(7)), 145.8 (C(8)), 135.6 (C(16)), 132.0 (C(17)), 131.8 (C(5)), 129.0 (C(18)), 128.3 (C(10)), 126.9 (C(19)), 109.3 (C(6)), 108.6 (C(9)), 100.7 (OCH_2O), 46.6 (C(2)), 43.6 (C(1)), 38.1 (C(11)), 32.0 (C(13)), 27.1 (C(12)), 25.6 (C(4)), 23.4 (C(3)), 22.7 (C(14)), 14.2 (C(15)); IR (neat) 3052 (m), 2926 (s), 2857 (m), 2766 (m), 2666 (w), 2613 (w), 1621 (w), 1583 (s), 1503 (s), 1483 (s), 1469 (s), 1451 (s), 1441 (s), 1379 (s), 1233 (s), 1118 (s), 1087 (s), 1035 (s), 938 (s), 903 (s), 858 (m); MS (EI$^+$, 70 eV) 299.1 (14.2), 298.1 (69.8), 190.1 (13.2), 189.1 (100.0), 188.1 (75.1), 174.0 (18.0), 173.0 (43.8), 162.1 (26.5), 159.1 (34.4), 131.1 (22.0), 116.1 (12.2), 115.0 (26.2), 103.1 (7.3), 91.1 (10.9), 85.0 (31.7), 83.0 (48.7), 65.1 (8.1); HRMS calcd for $C_{22}H_{26}O_2S^+$ 354.1650, found 354.1654; TLC R_f 0.52 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ +12.8 (c = 0.76, EtOH); SFC (5*S*,6*S*)-**14n**, t_R 9.2 min (4%); (5*R*,6*R*)-**14n**, t_R 10.3 min (96%) (Chiralpak OD, 4% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C).



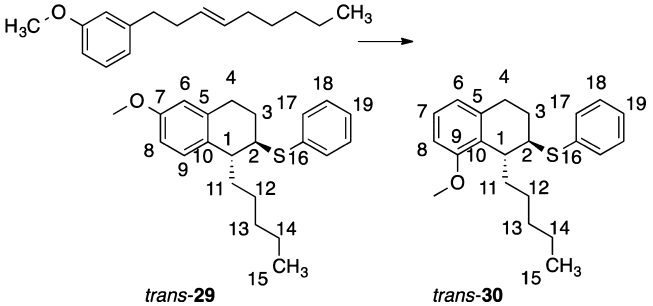
trans-**14o**

*Preparation of ((5R,6R)-5-(3-Chloropropyl)-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-d]-1,3-dioxole (trans-**14o**).* Following General Procedure 8, (*E*)-**2o** (253.7 mg, 1.0 mmol), **13** (256.0 mg, 1.0 mmol), (*S*)-**20** (54.9 mg, 0.1 mmol), and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at room temperature for 6 days. Purification by flash column chromatography (SiO_2, 32 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**14o** (235 mg, 65%) as colorless oil. Distillation provided 227 mg of analytically pure *trans*-**14o**. Data for *trans*-**14o**: bp 135 °C at 3.2 × 10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (t, J = 7.5 Hz, 2 H, HC(15)), 7.34 (t, J = 7.5 Hz, 2 H, HC(16)), 7.28 (t, J = 7.0 Hz, 1 H, HC(17)), 6.58 (s, 2 H, HC(6) and C(9)), 5.92 (d, J = 2.5 Hz, 2 H, OCH_2O), 3.59−3.56 (m, 1 H, HC(2)), 3.55−3.45 (m, 2 H, HC(13)), 2.95 (ddd, J = 16.5, 10.5, 5.0 Hz, 1 H, HC(4)), 2.85−2.82 (m, 1 H, HC (1)), 2.65 (ddd, J = 10.5, 5.5, 5.5 Hz, 1 H, HC(4)), 2.16 (dddd, J = 13.5, 10.0, 5.5, 3.0 Hz, 1 H, HC(3)), 1.92−1.76 (m, 5 H, HC(3) and HC(11) and HC(12)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2 (C(7)), 146.0 (C(8)), 135.1 (C(14)), 132.6 (C(16)), 130.8 (C(5)), 129.1 (C(15)), 128.6 (C(10)), 127.2 (C(17)), 109.1 (C(9)), 108.7 (C(6)), 100.8 (OCH_2O), 46.9 (C(2)), 45.0 (C(13)), 42.9 (C(1)), 34.8 (C(11)), 30.2 (C(12)), 25.9 (C(4)), 24.0 (C(3)); IR (neat) 3044 (m), 2911 (s), 2761 (m), 1581 (s), 1501 (s), 1484 (s), 1466 (s), 1431 (s), 1378 (s), 1290 (s), 1237 (s), 1030 (s), 933 (s), 902 (s), 858 (s), 823 (s); MS (EI$^+$, 70 eV) 360.1 (63.8), 283.2 (13.6), 253.1 (30.6), 252.1 (28.7), 251.1 (92.5), 250.1 (47.2), 188.1 (19.0), 187.2 (13.8), 175.1 (18.4), 174.1 (89.9), 173.1 (100.0), 161.1 (24.9), 145.1 (17.7), 144.1 (14.8), 131.0 (18.2), 129.1 (13.0), 128.1 (13.1), 117.1 (13.1), 116.1 (23.1), 115.1 (58.9), 109.0 (13.0), 103.1 (14.6), 91.1 (10.9), 77.1 (12.8), 65.1 (11.0); HRMS calcd for $C_{20}H_{21}ClO_2S^+$ 360.0951, found 360.0941; TLC R_f 0.21 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ +16.03 (c = 0.51, EtOH); SFC (5*S*,6*S*)-**14o**, t_R 12.1 min (6%); (5*R*,6*R*)-**14o**, t_R 14.6 min (94%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{20}H_{21}ClO_2S$ (360.90): C, 66.56; H, 5.87%. Found: C, 66.61; H, 5.90%.



trans-**14p**

*Preparation of ((5R,6R)-5-(2-Methylpropyl)-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-d]-1,3-dioxole (trans-**14p**).* Following General Procedure 8, a 10 mL Schlenk flask was charged with (*E*)-**2p** (232.3 mg, 1.0 mmol), **13** (256.0 mg, 1.0 mmol), (*S*)-**20a** (54.9 mg, 0.1 mmol), and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at −20 °C for 72 h. Purification by flash column chromatography (SiO_2, 32 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**14p** (269 mg, 79%) as colorless oil. Distillation provided 262 mg (77%) of analytically pure *trans*-**14p**. Data for *trans*-**14p**: bp >135 °C at 1.5 × 10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 8.0, 1.5, 2 H, HC(16)), 7.34 (t, J = 7.0 Hz, 2 H, HC(17)), 7.24 (tt, J = 7.0, 1.5 Hz, 1 H, HC(18)), 6.56 (s, 1 H, HC(6)), 6.51 (s, 1 H, C(9)), 5.88 (s, 2 H, OCH_2O), 3.64−3.62 (m, 1 H, HC(2)), 3.00 (ddd, J = 17.5, 9.5, 6.5 Hz, 1 H, HC(4)), 2.84 (dd, J = 9.0, 4.5 Hz, 1 H, HC(1)), 2.61 (ddd, J = 17.0, 6.0, 1.5 Hz, 1 H, HC(4)), 2.14−2.07 (m, 1 H, HC(3)), 1.90−1.86 (m, 1 H, HC(3)), 1.71−1.63 (m, 1 H, HC(12)), 1.52 (ddd, J = 14.0, 9.5, 5.0 Hz, 1 H, HC(11)), 1.37 (ddd, J = 14.0, 9.0, 5.0 Hz, 1 H, HC(11)), 0.90 (d, J = 6.5 Hz, 3 H, HC(14)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.0 (C(7)), 145.9 (C(8)), 135.5 (C(15)), 132.3 (C(16)), 132.1 (C(5)), 129.0 (C(17)), 128.0 (C(10)), 127.1 (C(18)), 109.4 (C(9)), 108.7 (C(6)), 100.7 (OCH_2O), 48.4 (C(11)), 46.6 (C(2)), 41.2 (C(1)), 25.7 (C(12)), 24.9 (C(4)), 23.6 (C(14)), 22.3 (C(3)), 22.0 (C(13)); IR (neat) 2917 (s), 2850 (s), 1580 (w), 1503 (s), 1483 (s), 1451 (s), 1377 (s), 1240 (s), 1216 (s), 1181 (m), 1122 (w), 1043 (s), 945 (m), 858 (m), 692 (s); MS (EI$^+$, 70 eV) 341.1 (20.6), 340.2 (83.8), 283.1 (19.1), 231.2 (63.9), 230.2 (48.2), 187.1 (12.3), 175.1 (44.3), 174.1 (100.0), 173.1 (75.0), 161.1 (50.0), 159.1 (12.6), 145.1 (15.4), 144.1 (13.8), 135.1 (13.0), 131.0 (19.2), 128.1 (10.2), 117.1 (13.5), 116.1 (23.8), 115.1 (49.3), 109.0 (13.7), 103.1 (14.4), 91.1 (12.9), 77.1 (11.6), 65.1 (10.5), 57.1 (11.2); HRMS calcd for $C_{21}H_{24}O_2S^+$ 340.1497, found 340.1493; TLC R_f 0.47 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ +17.16 (c = 0.61, EtOH); SFC (5*R*,6*S*)-**14p**, t_R 6.4 min (96%); (5*S*,6*S*)-**14p**, t_R 6.9 min (4%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{21}H_{24}O_2S$ (340.48): C, 74.08; H, 7.10%. Found: C, 74.33; H, 7.31%.



trans-**29** *trans*-**30**

*Preparation of (1R,2R)-6-Methoxy-1-pentyl-2-(phenylthio)-1,2,3,4-tetrahydronaphthalene (**29**) and (1R,2R)-8-Methoxy-1-pentyl-2-(phenylthio)-1,2,3,4-tetrahydronaphthalene (**30**).* Following General Procedure 8, (*E*)-**11n** (232.3 mg, 1.0 mmol), **13** (256.0 mg,

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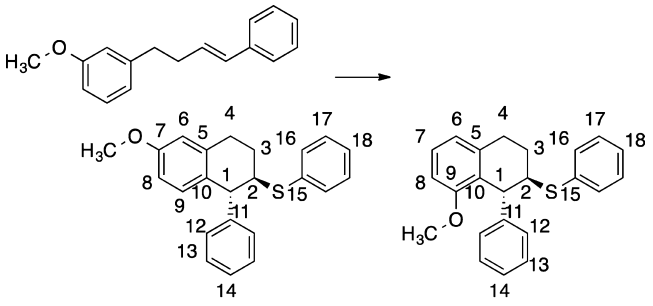
1.0 mmol), (*S*)-**20a** (54.9 mg, 0.1 mmol), and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at −20 °C for 72 h. Purification by flash column chromatography (SiO_2, 32 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded **29** (210 mg, 62%) as colorless oil along with **30** (73 mg, 21%) as a white solid. Distillation provided 204 mg (60%) of analytically pure **29**. Recrystallization of **30** from hot pentane provided 68 mg (20%) of analytically pure **30**. Data for **29**: bp 140 °C at 1.5×10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, J = 7.5, 1.5 Hz, 2 H, HC(17)), 7.33 (tt, J = 7.5, 1.5 Hz, 2 H, HC(18)), 7.27 (tt, J = 7.0, 1.0 Hz, 1 H, HC(19)), 7.04 (d, J = 8.5 Hz, 1 H, HC(9)), 6.76 (dd, J = 8.5, 2.5 Hz, 1 H, HC(8)), 6.66 (d, J = 2.5 Hz, 1 H, HC(6)), 3.81 (s, 3 H, OCH_3), 3.71−3.69 (m, 1 H, HC(2)), 3.06 (ddd, J = 17.0, 11.0, 5.5 Hz, 1 H, HC(4)), 2.89−2.86 (m, 1 H, HC(1)), 2.72 (ddd, J = 17.5, 6.0, 4.0 Hz, 1H, HC(4)), 2.19 (dddd, J = 14.0, 9.0, 6.0, 3.0 Hz, 1 H, HC(3)), 1.94−1.88 (m, 1 H, HC(3)), 1.74−1.62 (m, 2 H, HC(11)), 1.42−1.24 (m, 6 H, H(12) and HC(13), and HC(14)), 0.90 (t, J = 7.0 Hz, 3 H, HC(15)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.7 (C(7)), 136.5 (C(5)), 135.6 (C(16)), 132.0 (C(17)), 131.1 (C(10)), 130.7 (C(9)), 129.0 (C(18)), 126.9 (C(19)), 113.2 (C(6)), 112.4 (C(8)), 55.2 (OCH_3), 46.8 (C(2)), 42.7 (C(1)), 38.0 (C(11)), 32.00 (C(13)), 27.0 (C(12)), 25.8 (C(4)), 23.4 (C(3)), 22.7 (C(14)), 14.2 (C(15)); IR (neat) 3052 (s), 2919 (s), 2843 (s), 1608 (s), 1580 (s), 1500 (s), 1455 (s), 1434 (s), 1375 (m), 1320 (m), 1254 (s), 1233 (s), 1157 (m), 1125 (s), 1087 (m), 1039 (s), 896 (m), 844 (m), 813 (m), 740 (s); MS (EI$^+$, 70 eV) 340.1 (20.5), 269.2 (23.0), 231.1 (100.0), 191.2 (47.8), 161.1 (24.5), 160.1 (36.1), 159.1 (30.2), 147.1 (31.4), 135.1 (48.5), 121.1 (24.7), 115.1 (19.2), 107.1 (26.8), 91.1 (25.00), 77.1 (19.5), 57.1 (37.7), 55.1 (22.8); HRMS calcd for $C_{22}H_{28}OS^+$ 340.1861, found 340.1856; TLC R_f 0.38 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ +14.5 (c = 0.54, EtOH); SFC (1*R*,2*R*)-**29**, t_R 8.8 min (96%); (1*S*,2*S*)-**29**, t_R 13.7 min (4%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{22}H_{28}OS$ (340.19): C, 77.60; H, 8.29%. Found: C, 77.89; H, 8.42%. Data for **30**: mp 72−74 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, J = 7.5 Hz, 2 H, HC(17)), 7.32 (t, J = 7.5 Hz, 2 H, HC(18), 7.25 (t, J = 7.0, 1.0 Hz, 1 H, HC(19)), 7.13 (t, J = 8.0 Hz, 1 H, HC(7)), 6.74 (d, J = 8.5, 1 H, HC(6)), 6.71 (d, J = 8.5 Hz, 1 H, HC(8)), 3.82 (s, 3 H, OCH_3), 3.79 (s, 1 H, HC(2)), 3.22 (d, J = 6.0 Hz, 1 H, HC(1)), 3.10 (ddd, J = 17.5, 11.5, 6.0 Hz, 1 H, HC(4)), 2.72 (dd, J = 17.5, 4.5 Hz, 1 H, HC(4)), 2.20−2.13 (m, 1 H, HC(3)), 1.90−1.87 (m, 1 H, HC(3)), 1.79−1.68 (m, 1 H, HC(11)), 1.50−1.23 (m, 7 H, HC(11) and (HC(12) and HC(13), and HC(14)), 0.91 (t, J = 7.0 Hz, 3 H, HC(15)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6 (C(9)), 136.4 (C(16)), 136.1 (C(5)), 131.8 (C(17)), 128.9 (C(18)), 128.1 (C(10)), 126.70 (C(19)), 126.4 (C(7)), 121.66 (C(6)), 107.7 (C(8)), 55.3 (OCH_3), 45.6 (C(2)), 37.6 (C(1)), 35.6 (C(11)), 31.7 (C(13)), 27.6 (C(12)), 24.9 (C(4)), 22.7 (C(14)), 22.0 (C(3)), 14.2 (C(15)); IR (KBr) 2940 (m), 2912 (s), 2843 (m), 1580 (s), 1465 (s), 1451 (s), 1438 (m), 1337 (m), 1250 (s), 1084 (s), 1066 (s), 765 (m), 737 (m); MS (EI$^+$, 70 eV) 341.1 (12.6), 340.2 (47.4), 269.1 (34.7), 231.2 (42.7), 230.2 (11.9), 174.1 (13.9), 161.1 (50.4), 160.1 (31.8), 159.1 (69.0), 148.0 (12.1), 147.1 (100.0), 145.1 (13.3), 144.0 (17.2), 135.1 (11.6), 129.1 (14.2), 128.1 (14.9), 127.0 (10.3), 121.1 (10.3), 115.1 (24.0), 109.0 (10.8), 91.1 (14.7), 85.9 (52.3), 84.0 (79.4), 58.1 (9.6); HRMS calcd for $C_{22}H_{28}OS^+$ 340.1861, found 340.1865; TLC R_f 0.54 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ +13.6 (c = 0.61, EtOH); SFC (1*R*,2*R*)-**30**, t_R 5.8 min (91%); (1*S*,2*S*)-**30**, t_R 8.9 min (9%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{22}H_{28}OS$ (340.19): C, 77.60; H, 8.29%. Found: C, 77.43; H, 8.22%.



*Preparation of (1R,2R)-6-Methoxy-1-phenyl-2-(phenylthio)-1,2,-3,4-tetrahydronaphthalene (**31**) and (1R,2R)-8-Methoxy-1-phenyl-2-(phenylthio)-1,2,3,4-tetrahydronaphthalene (**32**).* Following General Procedure 8, (*E*)-**11b** (238.3 mg, 1.0 mmol), **13** (256.0 mg, 1.0 mmol), (*S*)-**20a** (54.9 mg, 0.1 mmol), and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at −20 °C for 72 h. Purification by flash column chromatography (SiO_2, 32 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded **31** (160 mg, 46%) as colorless oil along with **32** (161 mg, 46%) as a white solid. Distillation provided 156 mg (45%) of analytically pure **31**. Recrystallization of **32** from hot pentane provided 156 mg (45%) of analytically pure **32**. Data for **31**: bp 135 °C at 1.6×10^{-5} mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, J = 8.5, 1.5 Hz, 2 H, HC(16)), 7.35 (t, J = 9.0 Hz, 2 H HC(17), 7.30−7.22 (m, 4 H, HC(7) and HC(13) and HC(18)), 7.18 (tt, J = 7.0, 1.0 Hz, 1 H, HC(14)), 6.99 (d, J = 7.0 Hz, 2 H, HC(12)), 6.88 (d, J = 7.5 Hz, 1 H, HC(6)), 6.70 (d, J = 8.0 Hz, 1 H, HC(8)), 4.55 (s, 1 H, HC(1)), 3.81−3.79 (m, 1 H, HC(2)), 3.57 (s, 3 H, OCH_3), 3.19 (ddd, J = 17.5, 12.5, 6.0 Hz, 1 H, HC(4)), 2.85 (ddd, J = 17.0, 5.5, 2.0 Hz, 1H, HC(4)), 2.11−2.03 (m, 1 H, HC(3)), 1.83−1.77 (m, 1 H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1 (C(9)), 146.0 (C(11), 137.7 (C(10)), 135.8 (C(15)), 132.1 (C(16)), 129.2 (C(12), 128.3 (C(17)), 128.2 (C(13)), 127.4 (C(7)), 127.1 (C(18)), 126.2 (C(14)), 125.7 (C(5)), 121.3 (C(6)), 108.3 (C(7)), 55.7 (OCH_3), 50.8 (C(2)), 44.0 (C(1)), 25.1 (C(4)), 21.6 (C(3)); IR (neat) 3052 (w), 3017 (w), 2926 (m), 2829 (w), 1583 (s), 1465 (s), 1434 (m), 1337 (w), 1254 (s), 1222 (w), 1091 (s), 1066 (m), 1021 (w), 955 (w), 817 (w), 768 (m), 737 (s), 699 (s); MS (EI$^+$, 70 eV) 346.0 (12.4), 346.0 (43.1), 238.0 (18.9), 237.1 (98.4), 236.0 (29.3), 179.0 (12.1), 178.0 (13.6), 165.0 (13.7), 159.0 (27.4), 145.0 (21.7), 144.0 (11.0); 129.0 (11.8), 121 (16.5), 115.0 (19.4), 109.0 (10.8), 91.0 (100.0), 65.1 (10.3); HRMS calcd for $C_{23}H_{22}OS^+$ 346.1391, found 346.1384; TLC R_f 0.38 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ −84.3 (c = 0.55, EtOH); SFC (1*R*,2*R*)-**31**, t_R 12.3 min (90%); (1*S*,2*S*)-**31**, t_R 13.8 min (10%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Data for **32**: mp 77−79 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 7.5 Hz, 2 H, HC(16)), 7.32−7.19 (m, 6 H, HC(13) and HC(14) and HC(17) and HC(18)), 7.03 (d, J = 7.5 Hz, 1 H, HC(12)), 6.76 (d, J = 8.5 Hz, 1 H, HC(9)), 6.71 (d, J = 2.5 Hz, 1 H, HC(6)), 6.66 (dd, J = 8.5, 2.5 Hz, 1 H, HC(8)), 4.16 (d, J = 5.5 Hz, 1 H, HC(1)), 3.77 (s, 3 H, OCH_3), 3.67 (ddd, J = 8.5, 5.5, 3.0 Hz, 1 H, HC(2)), 3.05 (ddd, J = 16.5, 8.5, 5.5 Hz, 1 H, HC(4)), 2.86 (ddd, J = 17.0, 6.0, 6.0 Hz, 1 H, HC(4)), 2.21−2.15 (m, 1 H, HC(3)), 1.89−1.83 (m, 1 H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2 (C(7)), 145.9 (C(11), 137.5 (C(10)), 135.2 (C(15)), 132.5 (C(16)), 132.1 (C(9), 129.2 (C(5,12)), 129.1 (C(17)), 128.5 (C(13)), 127.2 (C(18)), 125.7 (C(14)), 113.1 (C(6)), 113.0 (C(8)), 55.4 (OCH_3), 51.8 (C(2)), 49.9 (C(1)), 27.3 (C(4)), 25.3 (C(3)); IR (KBr) 3052 (m), 3017 (m), 2926 (s), 2829 (m), 1608 (s), 1583 (s), 1503 (s), 1451 (s), 1434 (s), 1323 (s), 1250 (s), 1236 (s), 1219 (s), 1153 (s), 1122 (s), 1108 (m), 1087 (m), 1035 (s), 928 (m), 893 (m), 858 (m), 820 (m), 792 (s), 696 (s); MS (EI$^+$, 70 eV) 246.3 (15.0), 243.5 (14.5), 237.2 (26.8), 231.12 (100.0), 191.2 (86.0), 175.2 (17.7), 159.1 (17.2), 149.1 (42.0), 145.1 (14.8), 135.1(99.9), 129.1 (13.3), 121.0 (43.0), 115.1 (19.3), 111.1 (12.4), 107.1 (53.5), 105.1 (22.2), 95.1 (20.9), 91.1 (37.8), 81.1 (16.2), 77.1 (23.8), 69.1 (20.8), 67.1 (14.7), 65.1 (11.7), 57.1 (65.4), 55.1 (38.4); HRMS calcd for $C_{23}H_{22}OS^+$ 346.1391, found 346.1383; TLC R_f

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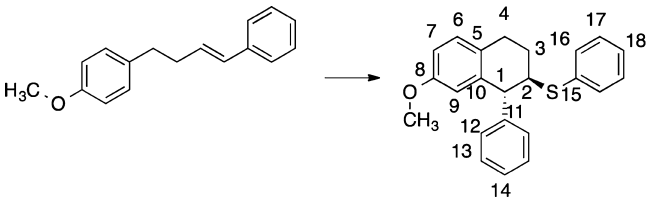
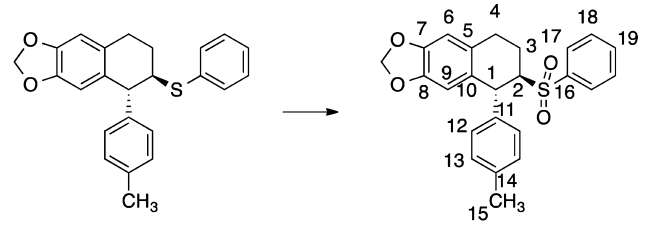
0.32 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ −55.0 (c = 0.48, EtOH); SFC (1*R*,2*R*)-**32**, t_R 13.6 min (94%); (1*S*,2*S*)-**32**, t_R 16.1 min (6%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{23}H_{22}OS$ (346.14): C, 79.73; H, 6.40%. Found: C, 80.01; H, 6.03%.



trans-**33**

*Preparation of (1R,2R)-7-Methoxy-1-phenyl-2-(phenylthio)-1,2,-3,4-tetrahydronaphthalene (**33**).* Following General Procedure 8, (*E*)-**12b** (238.3 mg, 1.0 mmol), **13** (256.0 mg, 1.0 mmol), (*S*)-**20a** (54.9 mg, 0.1 mmol), and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ in CH_2Cl_2 (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at 0 °C for 36 h. Purification by flash column chromatography (SiO_2, 26 g, 30 mm Ø, hexane/Et_2O, 96:4) to afforded **33** (298 mg, 86%) as a white solid. Recrystallization from hot pentane provided 294 mg (85%) of analytically pure **33**. Data for **33**: mp 92−94 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 8.0, 2.0 Hz, 2 H, HC(16)), 7.34−7.21 (m, 6 H, HC(13) and HC(14) and HC(17) and HC(18)), 7.11 (d, J = 8.5 Hz, 1 H, HC(6)), 7.05 (d, J = 6.5 Hz, 2 H, HC(12)), 6.78 (dt, J = 8.5, 2.5 Hz, 1 H, HC(7)), 6.39 (d, J = 2.0 Hz, 1 H, HC(9)), 4.18 (d, J = 5.0 Hz, 1 H, HC(1)), 3.68 (s, 3 H, OCH_3), 3.70−3.66 (m, 1 H, HC(2)), 3.06−3.00 (m, 1 H, HC(4)), 2.84 (ddd, J = 17.0, 6.0, 6.0 Hz, 1 H, HC(4)), 2.23−2.16 (m, 1 H, HC(3)), 1.90−1.86 (m, 1 H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0 (C(8)), 145.5 (C(11), 138.0 (C(15)), 135.2 (C(5)), 132.5 (C(16)), 129.9 (C(6), 129.2 (C(17), 129.1 C(12)), 128.6 (C(10)), 128.5 (C(13)), 127.2 (C(18)), 126.7 (C(14)), 115.5 (C(9)), 113.2 (C(7)), 55.4 (OCH_3), 51.6 (C(2)), 50.8 (C(1)), 26.1 (C(4)), 25.4 (C(3)); IR (KBr) 3045(w), 3017 (w), 2926 (m), 2829 (w), 1608 (m), 1580 (m), 1500 (s), 1451 (m), 1434 (m), 1268 (s), 1250 (s), 1157 (s), 1111 (w), 1035 (m), 876 (w), 813 (m), 740 (s), 696 (s); MS (EI$^+$, 70 eV) 347.0 (14.2), 346.0 (55.5), 238.1 (13.1), 237.1 (78.2), 236.1 (93.2), 235.0 (10.6), 210.0 (11.1), 209.0 (18.1), 179.0 (16.7), 178.0 (15.7), 165.0 (15.3), 159.0 (24.9), 145.0 (28.8), 129.0 (10.2), 121.0 (16.7), 115.0 (15.4), 109.0 (9.3), 91.0 (100.0), 77.0 (9.0), 65.1 (9.7); HRMS calcd for $C_{23}H_{22}OS^+$ 346.1391, found 346.1386; TLC R_f 0.33 (hexanes/Et_2O, 96:4) [$KMnO_4$]; $[\alpha]_D^{25}$ −29.3 (c = 0.53, EtOH); SFC (1*R*,2*R*)-**33**, t_R 12.0 min (84%); (1*S*,2*S*)-**33**, t_R 15.7 min (16%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{23}H_{22}OS$ (346.14): C, 79.73; H, 6.40%. Found: C, 79.66; H, 6.28%.



trans-**34**

*Preparation of ((5R,6R)-5-(4-Methylphenyl)-6-(phenylsulfonyl)-5,6,7,8-tetrahydronaphtho[2,3-d]-1,3-dioxole (trans-**34**).* To a solution of *trans*-**14d** (128.0 mg, 0.34 mmol) in CH_2Cl_2 (6 mL) was added *m*-CPBA (177 mg, 1.02 mmol) at room temperature After being stirred for 2 h, the contents of the flask were poured in H_2O (30 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were successively washed with saturated aq Na_2SO_3 (10 mL), brine (40 mL), then dried over $MgSO_4$ and filtered through glass wool, and then concentrated in vacuo (20−23 °C, 10 mmHg). Purification by flash column chromatography (SiO_2, 15 g, 25 mm Ø, hexane/Et_2O, 1:1) afforded *trans*-**34** (135 mg, 98%) as white solid. Recrystallization from pentane/CH_2Cl_2 (60:10) (v/v) (14 mL) provided 130 mg (94%) of analytically pure *trans*-**34**. Data for *trans*-**34**: mp 138−140 °C (pentane/CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 7.5 Hz, 2 H, HC(17)), 7.62 (t, J = 7.5 Hz, 1 H, HC(19)), 7.49 (t, J = 8.0, 2 H, HC(18)), 6.98 (d, J = 8.0 Hz, 2 H, HC(13)), 6.77 (d, J = 8.0 Hz, 2 H, HC(12)), 6.58 (s, 1 H, HC(6)), 6.31 (s, 1 H, HC(9)), 5.87 (d, J = 2.5 Hz, 2 H, OCH_2O), 4.54 (d, J = 4.5 Hz, 1 H, HC(1)), 3.57−3.54 (m, 1 H, HC(2)), 3.03 (ddd, J = 16.0, 8.0, 5.5, 1 H, HC(4)), 2.81 (ddd, J = 17.0, 6.0, 6.0 Hz, 1 H, HC(4)), 2.28 (s, 3 H, HC(14)), 2.29−2.23 (m, 1 H, HC(3)), 2.19−2.12 (m, 1 H, HC(3)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4 (C(7,8)), 141.6 (C(11)), 138.7 (C(16)), 136.5 (C(14)), 133.5 (C(19)), 129.4 (C(13)), 129.1 (C(10,18)), 128.9 (C(5)), 128.7 (C(17)), 128.5 (C(12)), 109.8 (C(9)), 108.0 (C(6)), 100.9 (OCH_2O), 67.1 (C(2)), 43.6 (C(1)), 26.7 (C(4)), 21.1 (C(15)), 20.5 (C(3)); IR (KBr) 3445 (bm), 2968 (m), 2912 (m), 2878 (m), 1698 (s), 1573 (w), 1503 (m), 1483 (s), 1444 (m), 1302 (s), 1261 (s), 1240 (s), 1143 (s), 1084 (m), 1035 (m), 938 (w), 848 (w), 810 (w), 747 (s). MS (EI$^+$, 70 eV) 325.5 (21.7), 265.1 (21.1), 264.1 (1000), 231.1 (37.6), 191.1 (60.5), 158.0 (21.0), 156.0 (63.3), 141.0 (21.6), 139.0 (64.1), 135.1 (37.3), 115.0 (19.7), 11.0 (35.6), 107.0 (24.4), 105.1 (30.6); HRMS calcd $C_{24}H_{23}O_4S^+$ 407.1317, found 407.1316; TLC R_f 0.37 (hexanes/Et_2O, 50:50) [$KMnO_4$]; $[\alpha]_D^{25}$ −30.3 (c = 0.52, EtOH); SFC (1*R*,2*R*)-**34**, t_R 14.0 min (92%); (1*S*,2*S*)-**34**, t_R 17.7 min (8%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C). Anal. Calcd for $C_{24}H_{22}O_4S$ (406.12): C, 70.91; H, 5.46%. Found: C, 70.85; H, 5.38%.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Optimization experiments, X-ray coordinates for (*S*)-**17a** and *trans*-**34**, and copies of ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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was collected in a double-skinned ziplock, plastic bag and disposed of as thallium and arsenic-contaminated silica gel waste.
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