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Dienolate Annulation Approach for Assembly of Densely Substituted Aromatic Architectures

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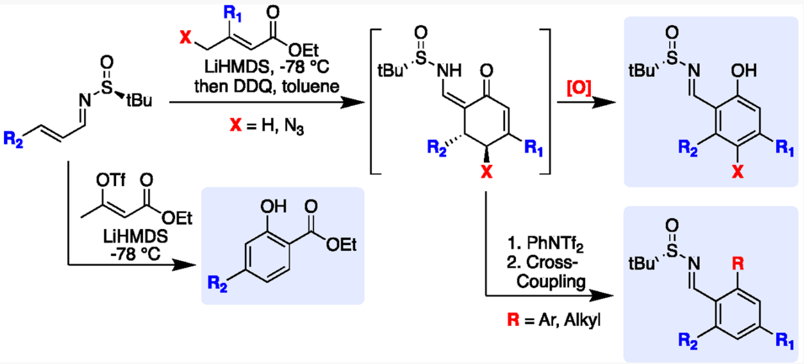
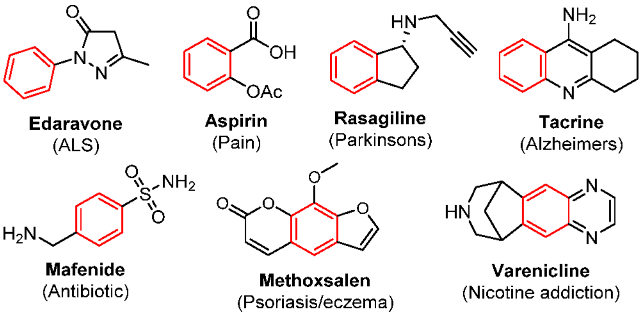


ABSTRACT: The efficient assembly of complex aromatic structures from simple acyclic building blocks is reported. An anion-cascade union of an enoate and a conjugated imine affords cyclohexenone products, which are readily aromatized to phenols. By engaging the intermediate cyclohexenones with Grignard reagents, a facile addition/elimination proceeds yielding chiral cyclohexadienes, which are then aromatized. In a complementary approach, the cyclohexenone products are converted into enol triflates, which provides a gateway to diverse aromatic architectures following cross-couplings and aromatization steps.

■ INTRODUCTION

The benzene ring is without a doubt one of the most significant core structural fragments of countless natural products, pharmaceuticals, and commodity chemicals. For example, detailed analysis of US FDA approved drugs by Taylor and co-workers, highlight that the benzene ring is the most prevalent of all ring systems.[1] In spite of a move toward greater sp^3 carbon content in drug leads, 24 out of 29 (83%) of small molecules approved in 2020 contain aromatic rings, and 17 of the 29 (62%) aromatic rings are benzene rings. Most recently, Stuart and Sherer have expertly analyzed the frequency of arene substitution patterns.[2] The success of this core fragment is highlighted with the seven low molecular weight US FDA approved drugs presented in Scheme 1, which represent diverse arene substitution patterns and disease applications.

Scheme 1. Examples of Small FDA Approved Drugs Containing an Aryl Group Core



Given the significance of the benzene ring as a core structural fragment, and the infinite number of possible substituted benzene architectures that could be made, it is not surprising that since the dawn of organic chemistry a myriad of approaches have been devised for assembling such architectures. Early approaches to arene structures relied on functionalization of readily available aromatic petroleum feedstock sources or aromatic structures available in sufficient quantities from natural sources. As the field of organic chemistry grew and new chemistry principles and reactions were established, alternative approaches for synthesizing simple and complex arene architectures emerged wherein the aromatic core was assembled de novo from acyclic building blocks (Scheme 2).

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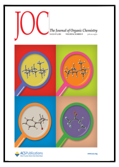

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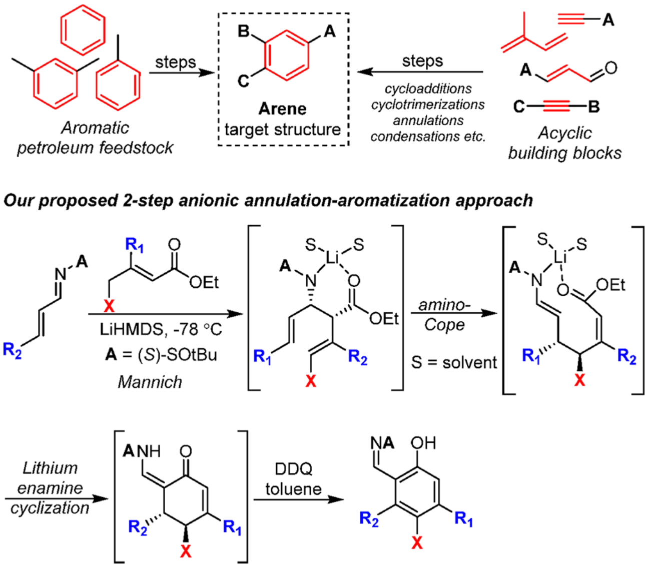
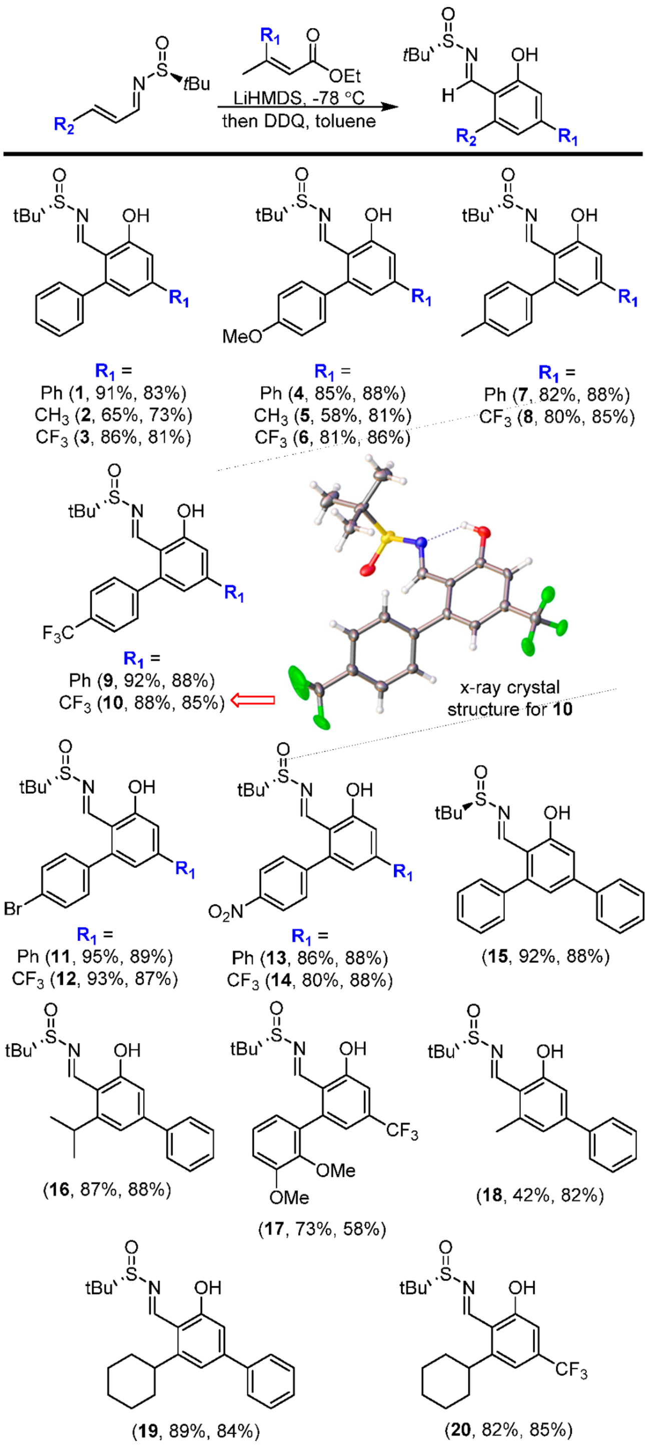
Scheme 2. Classic Approaches for Assembling Arenes and New Phenol Synthesis Proposal



Scheme 3. Dienolate Annulation−Aromatization Route to Bis-*meta*-substituted Phenols (Compound Number, Dienolate Annulation Yield (%), DDQ Aromatization Yield (%))



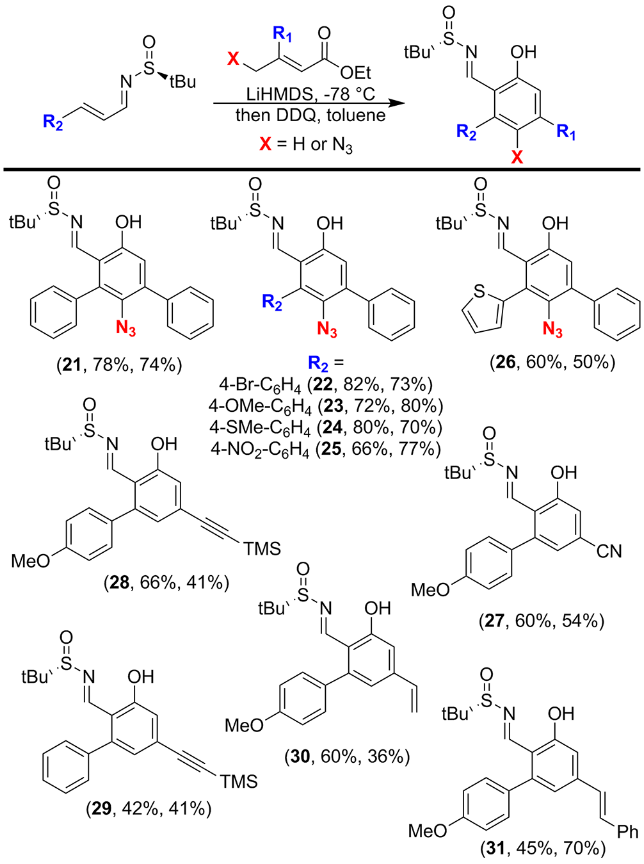
We postulated that densely substituted phenol and arene structures could be assembled in a regiocontrolled fashion from two acyclic building blocks, by utilizing our recently reported anion-accelerated amino-Cope rearrangement.[3,4] The enolate annulation (amino-Cope) product we envisioned could be readily aromatized via a 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) dehydrogenation step to afford a phenol. Furthermore, the intermediate cyclohexenone annulation product seemed primed for accessing other arene products by engaging the ketone moiety via direct additions or enol triflates. This approach represents a useful approach for assembling highly substituted aromatic structures from readily available simple enal and acrylate starting materials.

■ RESULTS AND DISCUSSION

We have validated our proposed approach for assembling complex phenol products in two operations from simple acyclic building blocks. The 20 examples presented in Scheme 3 highlight the synthesis of chiral salicylaldehyde imines with two *meta*-substituents (**R**$_2$ and **R**$_1$) composed of aryl, alkyl, and trifluoromethyl substituents. Two *meta*-substitutions are particularly noteworthy given the natural bias of phenols toward substitutions at *ortho*- and *para*-positions making *meta*-substitutions very challenging, which has inspired innovative approaches in recent years.[5−11] Yields for the asymmetric amino-Cope step range from good to excellent (1st yield in parentheses) with yields for the DDQ driven aromatization step similarly successful (2nd yield in parentheses). Crystal structure analysis for bis-trifluoromethyl substituted product **10** afforded unambiguous confirmation of structure (CCDC 1451255). Given the high prevalence of trifluoromethylated aromatic fragments among US FDA approved drugs, we hope this new approach provides a useful new entry point for synthesis design (Scheme 3: **3**, **6**, **8**, **10**, **12**, **14**, **17**, and **20**).[12,13]

We next turned our attention toward expanding the scope of enoate substituents toward the goal of delivering versatile functional group handles in the phenol products. Given the high occurrence of nitrogen heterocycles and nitrogen-containing substituents in drugs,[14] we were particularly interested in exploring the feasibility of employing dienolates with cyano, azide, and nitro substituents. Impressively, azides were tolerated as a substituent in the γ-position of the enoate, thus delivering phenol products with an azide in the *para* position (Scheme 4: **21**−**26**). A cyano group, which is a uniquely useful functional group, was also shown to be compatible with the amino-Cope cascade (**27**), while a nitro group proved not to be suitable. Alkynes are versatile and

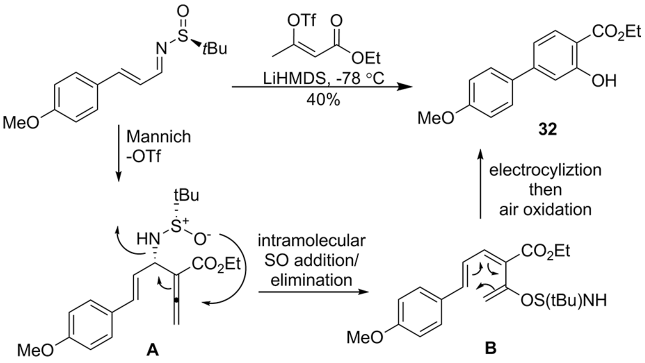
Scheme 4. Dienolate Annulation−Aromatization Assembly of Tetra Substituted Phenols with Useful Functional Groups (Compound Number, Dienolate Annulation Yield (%), DDQ Aromatization Yield (%))



useful functional groups. An enoate substituted with a trimethylsilyl group at the alkyne terminus performed well in the amino-Cope/aromatization cascade (**28** and **29**). We were delighted to learn that double bonds were also reasonably well tolerated, with a vinyl group performing better than a styrenyl group in the amino-Cope step, while the reverse performance was observed in the DDQ aromatization step, which we partially attribute to polymerization of **30**.

Given the versatility of enol/phenolic triflates as a functional group handle, we decided to explore its potential as dienolate substituent (Scheme 5). We were fully aware of the triflate's most likely premature enolate elimination, but we decided to explore it regardless. Treatment of ethyl crotonate containing a 3-enol-triflate substituent with base in the presence of our standard imine resulted in the formation of diaryl-phenol **32** as the major product (40%). The mechanism for this unexpected annulation cascade is not clear at present, but spectroscopic data and isolation of early intermediates suggest a Mannich addition followed by triflate elimination to form an allene (**A**). How the phenol oxygen atom is incorporated is not confirmed yet, but we are most intrigued by the possibility of the oxygen atom originating from the sulfinamide auxiliary via an intramolecular conjugated addition of the nucleophilc oxygen followed by in situ elimination of the C−N bond (**A** to **B**).[15] Intermediate **B** is expected to undergo a facile electrocyclization and air-oxidation to form the product (**32**). Alternatively, it is also possible that the oxygen arises from the triflate via cyclization from the intermediate Mannich to eliminate the auxiliary followed by air oxidation of the resulting cyclohexadiene.

Scheme 5. New Unexpected Triflate Enoate Annulation Cascade



We next set our sights on accessing arene products from the phenol substituent. Two complementary approaches are presented in Scheme 6. Addition of a Grignard reagent to the amino-Cope product followed by immediate elimination afforded chiral cyclohexadiene **33**, whose structure has been unambiguously confirmed with X-ray crystallography (CCDC 2079822). Alternatively, this same diene product can be accessed from enol triflate **34** via traditional cross-coupling approaches such as the Suzuki cross-coupling shown. Aromatization of diene **33** proceeds smoothly to arene **35**.

The Suzuki cross-coupling is one of the most reliable and robust reactions used to forge sp^2−sp^2 bonds and ranks highly among reactions favored by the pharmaceutical industry. Shown in Scheme 7 are four examples highlighting the union of enol triflate **34** with four commercially available aryl-boronic acids followed by DDQ aromatization to afford products **36**−**39**. The first yield in parentheses represents the Suzuki cross-coupling step with the second for the DDQ step. Yields for the Suzuki step are generally excellent, with the aromatization step being very good.

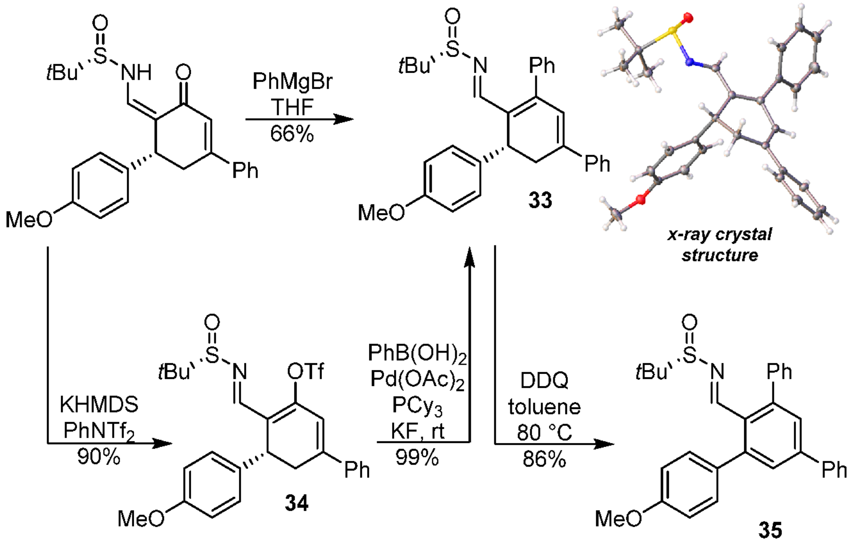
Alternatively, by converting phenol product **1** (Scheme 3) to triflate **40** a complementary route to access 1,3,5-substituted arylsulfinamides can be employed as highlighted for the Stille coupling example (**41**, Scheme 8). Interestingly, when diene triflate **34** is subjected to Negishi coupling reaction conditions in the presence of zinc cyanide, the expected installation of the nitrile group is accompanied by in situ aromatization to afford aryl nitrile **42**.

During the development of these new amino-Cope-enabled routes to aromatic architectures we came across a new Horner−Wadsworth−Emmons (HWE) reagent (Scheme 9, **43**), which the Ding group first made and used in their total synthesis of jatrophalactam.[16] By partnering this type of HWE reagent with our amino-Cope cascade/aromatization approach the sequence for assembling these complex aromatic products can be streamlined into only three steps as highlighted for an azide nucleophile example in Scheme 9.

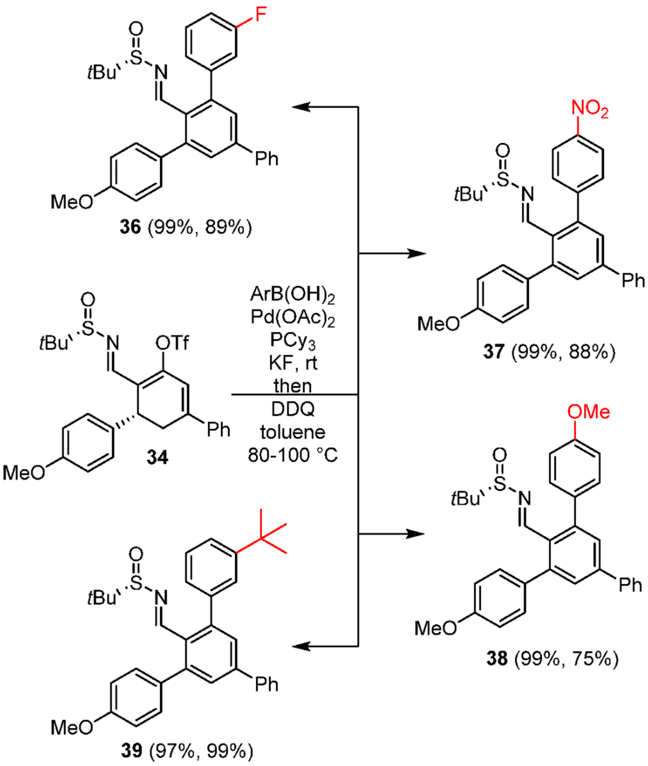
■ CONCLUSIONS

In conclusion, we have demonstrated that simple conjugated imines and enoate nucleophiles can in only two steps be converted into complex phenol products with two *meta*-substituents and a chiral sulfinamide functional group. Furthermore, the amino-Cope intermediates can upon treat-

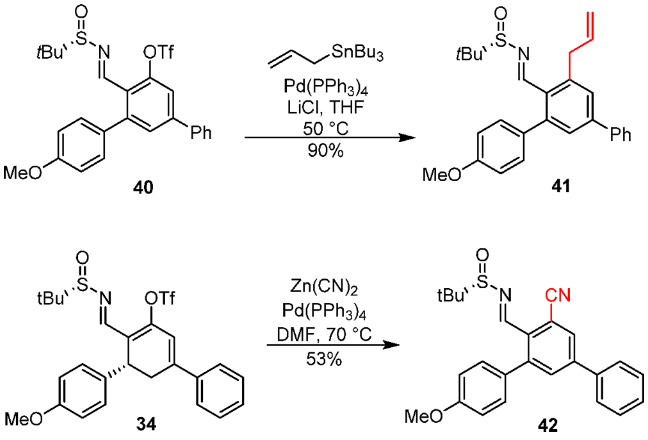
Scheme 6. Beyond Phenols: Synthesis of Arenes by Intercepting Ketone Annulation Intermediate Prior to Aromatization



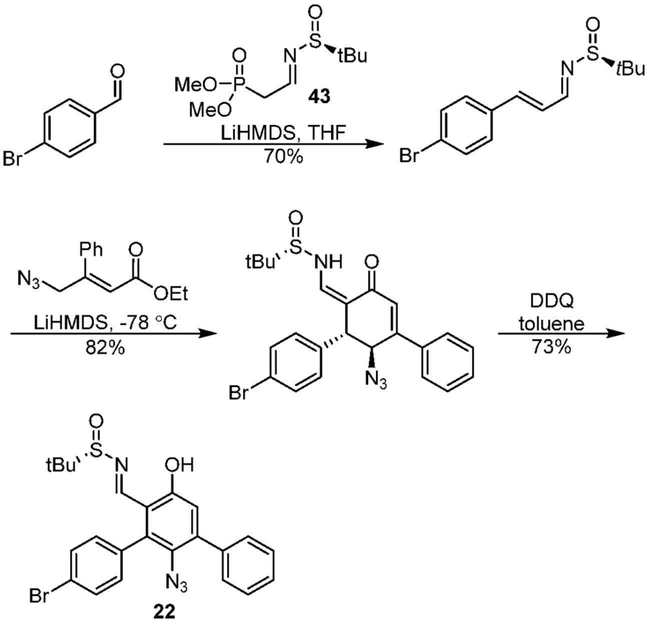
Scheme 7. Triflates as Gateway to Diverse Aryl Products



Scheme 8. Stille and Negishi Route to Aryl Products



Scheme 9. Three-Step Route to Complex Phenols



ment with Grignard reagents be diverted toward formation of aryl products or via their enol-triflate be funneled into complementary Suzuki cross-coupling pathways.

General Experimental. All commercial reagents purchased were used without further purification or manipulation unless otherwise specified. HPLC-grade tetrahydrofuran (THF) and toluene were dried over alumina and degassed with argon before use. Thin layer chromatography (TLC) via EMD 250 mm silica gel 60-F254 plates was used to visualize spots on TLC plates. Flash chromatography purification was performed with SilicaFlash F60 (particle size 40−63 mm). ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were acquired using a Bruker NEO500 and MestReNova software. Spectra were referenced in $CDCl_3$ using internal standards: 7.26 for ^1H NMR and 77.2 for ^{13}C NMR. Signals processed on MestReNova are reported as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), ddd (doublet of doublet of doublets), dt (doublet of triplets), or m (multiplet). Coupling constants are reported in hertz (Hz). Shimadzu prestige FT-IR was used to obtain relevant IR spectra. High-resolution mass spectra HRMS were acquired with an LTQ Orbitrap Velos (60000 resolution) with assistance from the University of Arizona Mass Spectral Facility. **X-ray crystallographic data:** Single crystals were submitted for structure determination. A suitable crystal was selected and mounted on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 100 K during data collection. Using Olex2 [1], the structure was solved with the XT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimization.

General Procedure for Aromatization of Cyclohexenones to Phenols. General Procedure A: Synthesis of Phenols **1**−**20**. The relevant cyclohexanone (60 mg) was taken into dry toluene (final concentration of 0.1 M) and added to a scintillation vial charged with a magnetic stir bar under nitrogen. To this solution was added 1.5 equiv of DDQ, and the mixture was heated (using an oil bath) to 110 °C in a sealed vial for 1.5 h or until disappearance of the starting material as estimated by TLC. After cooling to room temperature, the mixture was diluted with EtOAc and filtered through Celite, and the solvent was removed under reduced pressure. All compounds were purified by silica gel chromatography using a solvent gradient from 5% EtOAc in hexanes.

General Procedure B: Synthesis of Phenols **21**−**31**. To a 4 mL dram equipped with a stir bar was added cyclohexanone (1 equiv) at a final concentration of 0.1 M of dry toluene. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 2 equiv) in minimal toluene was then added dropwise at room temperature. The orange mixture was stirred overnight at room temperature. The crude reaction mixture was then filtered through Celite. The crude product in toluene was subsequently loaded on a flash column and purified (silica gel, 0−20% EtOAc/Hexanes gradient) to afford pure azido-phenols.

General Procedure for Suzuki Coupling of Enol Triflates. General Procedure C: Enol triflate (1.0 equiv, 50 mg, 0.09 mmol) is taken into 0.39 mL of dry THF (final concentration of 0.25 M) and transferred to a flame-dried 4 dram vial charged with a magnetic stir bar and 3-fluorophenylboronic acid (1.5 equiv, 15 mg, 0.11 mmol). Potassium fluoride (KF, 3.0 equiv, 16 mg, 0.28 mmol), tricyclohexylphosphine (PCy_3, 0.06 equiv, 1.4 mg, 0.005 mmol), and palladium acetate ($Pd(OAc)_2$) (0.05 equiv, 1 mg, 0.0045 mmol) are added sequentially, and the solution is purged with argon for 1 min. The reaction mixture is heated (using an oil bath) to 50 °C for 3−6 h or stirred at room temperature overnight. Upon completion the reaction is quenched with ammonium chloride, diluted with EtOAc, and washed with brine. After removing solvent, crude material is purified by column chromatography using a gradient of 5−20% EtOAc in hexanes to give **36a** as a yellow oil (43 mg, 0.089 mmol, 99% yield).

Cope Cyclization Cascade and Synthesis of Phenol 32 (NOTE: when the substituent is triflate phenol 32 is formed; when the substituent is alkyl, aryl, or alkenyl compounds 17a and 27a−31a are formed). General Procedure D: To a flame-dried round-bottomed flask equipped with a stir bar was added imine (1.1 equiv, 125 mg, 0.47 mmol) at a final concentration of 0.1 M in dry THF, and LiHMDS (2.0 equiv, 1 M solution in THF/Ethylbenzene). The reaction was subsequently cooled to −78 °C. Ester (1.0 equiv, 112 mg, 0.43 mmol) in 1 mL dry THF was then added dropwise via syringe pump over 1 h. After the addition, the reaction was stirred for an additional 2 h at −78 °C before warming to 0 °C. After stirring at 0 °C for 15 min, the reaction was quenched with saturated ammonium chloride and warmed to room temperature. After extraction with EtOAc (3 times), washing with brine, and drying with sodium sulfate (Na_2SO_4), the crude product was concentrated *in vacuo.* The crude cyclohexenones were purified by flash chromatography (silica gel, 0−40% EtOAc/Hexanes gradient) to give 47 mg (0.172 mmol, 40% yield) and 46 mg of starting imine (0.173 mmol) for a total of 80% yield of compound **32** based on recovered starting material.

Compounds 1−16, 18−20. All the cyclohexenone cope precursors that were used for the DDQ aromatization step were synthesized according to general procedure D, and the spectral data matched with the reported ones.[3]

Compounds 21−26. All the cyclohexenone cope precursors that were used for the DDQ aromatization step, were synthesized according to general procedure D, and the spectral data matched with the reported ones.[4]

*(S,E)-N-((5′-Hydroxy-[1,1′:3′,1″-terphenyl]-4′-yl)-methylene)-2-methylpropane-2-sulfinamide (**1**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **1** as a colorless solid from General Procedure A (49.5 mg, 0.1312 mmol, 83%): ^1H NMR (500 MHz, $CDCl_3$) δ 11.94 (s, 1H), 8.79 (s, 1H), 7.69−7.66 (m, 2H), 7.50−7.43 (m, 6H), 7.39−7.36 (m, 2H), 7.30−7.27 (m, 1H), 7.18 (d, J = 1.8 Hz, 1H), 1.27 (s, 9H). ^{13}C NMR{^1H} (125 MHz, $CDCl_3$) δ 164.3, 161.3, 146.8, 146.7, 139.4, 138.4, 129.7, 128.8, 128.5, 128.5, 128.2, 127.1, 120.6, 114.8, 114.5, 57.8, 22.2; FT-IR (NaCl film) 3058, 3031, 2977, 2926, 2866, 1618, 1586, 1576, 1092 cm^{-1}; HRMS (ESI$^+$) m/z [M + H]$^+$ calcd for $C_{23}H_{24}NO_2S$, 378.1522; found, 378.1527; $[\alpha]^{23}_D$ = +88.6° (c 1.8, $CHCl_3$).

*(S,E)-N-((3-Hydroxy-5-methyl-[1,1′-biphenyl]-2-yl)-methylene)-2-methylpropane-2-sulfinamide (**2**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **2** as a colorless solid from General Procedure A (43.5 mg, 0.1370 mmol, 73%): ^1H NMR (500 MHz, $CDCl_3$) δ 11.83 (s, 1H), 8.71 (s, 1H), 7.46−7.38 (m, 3H), 7.29 (m, 2H), 6.85 (dt, J = 1.6, 0.7 Hz, 1H), 6.74 (dd, J = 1.7, 0.7 Hz, 1H), 2.39 (s, 3H), 1.23 (s, 9H); ^{13}C NMR{^1H} (125 MHz, $CDCl_3$) δ 164.4, 161.1, 146.2, 145.5, 138.4, 129.7, 128.4, 128.0, 122.9, 116.7, 113.6, 57.6, 22.1, 21.9; FT-IR (NaCl film) 3056, 3030, 2976, 2925, 2866, 1621, 1553, 1334, 1092 cm^{-1}; HRMS (ESI$^+$) m/z [M + Na]$^+$ calcd for $C_{18}H_{21}NNaO_2S$, 338.1185; found, 338.1185; $[\alpha]^{23}_D$ = +69.6° (c 0.8, $CHCl_3$).

*(S,E)-N-((3-Hydroxy-5-(trifluoromethyl)-[1,1′-biphenyl]-2-yl)methylene)-2-methylpropane-2-sulfinamide (**3**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **3** as a white solid from General Procedure A (48.3 mg, 0.1308 mmol, 81%): ^1H NMR (400 MHz, $CDCl_3$) δ 12.02 (s, 1H), 8.79 (s, 1H), 7.51−7.47 (m, 3H), 7.36−7.32 (m, 2H), 7.31 (dq, J = 1.8, 0.6 Hz, 1H), 7.18 (dq, J = 1.8, 0.6 Hz, 1H), 1.29 (s, 9H); ^{13}C NMR{^1H} (100 MHz, $CDCl_3$) δ 164.1, 161.1, 147.2, 137.3, 135.2, 129.7, 128.8, 128.8, 113.6,

58.1, 22.2; ^{19}F NMR{^{1}H} (376 MHz, $CDCl_3$) δ −63.63, FT-IR (NaCl film) 3061, 3033, 2964, 2927, 2869, 1593, 1371, 1175, 1097 cm^{-1}; HRMS (ESI$^+$) m/z [M + H]$^+$ calcd for $C_{18}H_{19}F_3NO_2S$, 370.1083; found, 370.1086 ; $[\alpha]^{23}_D$ = +56.2° (c 1.2, $CHCl_3$).

*(S,E)-N-((5′-Hydroxy-4″-methoxy-[1,1′:3′,1″-terphenyl]-4′-yl)methylene)-2-methylpropane-2-sulfinamide (**4**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **4** as a white solid from General Procedure A (300 mg, 0.7315 mmol, 88% on a 0.836 mmol scale (IC), or 300 mg, 0.7315 mmol, 72% on a 1.016 mmol scale (JRG)): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.90 (s, 1H), 8.83 (s, 1H), 7.66 (d, J = 7.02 Hz, 2H), 7.46 (m, 2H), 7.41 (m, 1H), 7.30 (d, J = 8.6 Hz, 2H), 7.25 (d, J = 1.76 Hz, 1H), 7.16 (d, J = 1.8 Hz, 1H), 7.00 (d, J = 8.72 Hz, 2H), 3.87 (s, 3H), 1.27 (s, 9H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$) δ 164.5, 161.4, 159.7, 146.9, 146.5, 139.5, 130.9, 130.8, 128.8, 128.4, 127.1, 120.6, 115.0, 114.2, 114.1, 57.7, 55.3, 22.2; FT-IR (NaCl film) 3063, 3033, 2964, 2924, 2869, 1593, 1371, 1175, 1092 cm^{-1}; HRMS (ESI$^+$) m/z [M + H]$^+$ calcd for $C_{24}H_{26}NO_3S$, 408.1627; found, 408.1633 $[\alpha]^{23}_D$ = +69.2° (c 2.0, $CHCl_3$).

*(S,E)-N-((5′-Hydroxy-4″-methoxy-[1,1′:3′,1″-terphenyl]-4′-yl)methylene)-2-methylpropane-2-sulfinamide (**5**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **5** as a white solid from General Procedure A (48.3 mg, 0.1399 mmol, 81%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.82 (s, 1H), 8.76 (s, 1H), 7.24 (d, J = 8.81 Hz, 2H), 6.99 (d, J = 8.77 Hz, 2H), 6.84 (d, J = 1.7 Hz, 1H), 6.74 (d, J = 1.7 Hz, 1H), 3.87 (s, 3H), 2.41 (s, 3H), 1.26 (s, 9H); ^{13}C NMR{^{1}H} (100 MHz, $CDCl_3$) δ 164.6, 161.2, 159.5, 146.0, 145.6, 130.9, 130.8, 122.9, 116.3, 114.0, 113.7, 57.6, 55.3, 22.2, 21.9; FT-IR (NaCl film) 3061, 3032, 2964, 2927, 2869, 1593, 1369, 1175, 1093 cm^{-1}; HRMS (ESI$^+$) m/z [M + H]$^+$ calcdfor $C_{19}H_{24}NO_3S$, 346.1471; found, 346.1474.

*(S,E)-N-((3-Hydroxy-4′-methoxy-5-(trifluoromethyl)-[1,1′-biphenyl]-2-yl)methylene)-2-methylpropane-2-sulfinamide (**6**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **6** as a white solid from General Procedure A (51.3 mg, 0.1285 mmol, 86%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.95 (s, 1H), 8.81 (s, 1H), 7.23 (m, 3H), 7.14 (m, 1H), 7.00 (d, J = 1.7 Hz, 2H), 3.86 (s, 3H), 1.26 (s, 9H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$) δ 164.3, 161.1, 160.1, 147.1, 135.2, 130.9, 129.5, 123.2, 117.8, 114.3, 113.1, 58.1, 55.3, 22.2; ^{19}F NMR{^{1}H} (376 MHz, $CDCl_3$) δ −63.68, −63.64; FT-IR (NaCl film) 3061, 3033, 2964, 2927, 2869, 1593, 1371, 1175, 1097 cm^{-1}; HRMS (ESI$^+$) m/z [M + Na]$^+$ calcd for $C_{19}H_{20}F_3NNaO_3S$, 422.1008; found, 422.1013; $[\alpha]^{23}_D$ = +57.6° (c 1.6, $CHCl_3$).

*(S,E)-N-((5′-Hydroxy-4″-methyl-[1,1′:3′,1″-terphenyl]-4′-yl)methylene)-2-methylpropane-2-sulfinamide (**7**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **7** as a white solid from General Procedure A (50.7 mg, 0.1296 mmol, 85%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.93 (s, 1H), 8.82 (s, 1H), 7.67 (m, 2H), 7.46 (m, 2H), 7.41 (m, 1H), 7.27 (dd, J = 5.1, 2.5 Hz, 5H), 7.18 (d, J = 1.8 Hz, 1H), 2.42 (s, 3H), 1.27 (s, 9H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$) δ 164.4, 161.3, 146.8, 139.4, 138.0, 135.4, 129.6 (2C), 129.2, 128.8, 128.4 (2C), 127.1, 120.5, 114.8, 114.3, 57.7, 22.2, 21.1; FT-IR (NaCl film) 3055, 3030, 2976, 2924, 2866, 1617, 1586, 1348, 1091 cm^{-1}; HRMS (ESI$^+$) m/z [M + H]$^+$ calcd for $C_{24}H_{26}NO_2S$, 392.1679; found, 392.1679; $[\alpha]^{23}_D$ = +67.8° (c 3.2, $CHCl_3$).

*(S,E)-N-((3-Hydroxy-4′-methyl-5-(trifluoromethyl)-[1,1′-biphenyl]-2-yl)methylene)-2-methylpropane-2-sulfinamide (**8**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **8** as a white solid from General Procedure A (50.7 mg, 0.1323 mmol, 85%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.97 (s, 1H), 8.80 (s, 1H), 7.29−7.25 (m, 3H), 7.22−7.18 (m, 2H), 7.15 (dd, J = 1.8, 0.7 Hz, 1H), 2.41 (s, 3H), 1.26 (s, 9H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$) δ 164.3, 161.0, 147.3, 138.7, 135.1, 134.2, 129.5, 129.4, 123.1, 117.8, 117.8, 113.3, 58.1, 22.2, 21.1; ^{19}F NMR{^{1}H} (376 MHz, $CDCl_3$) δ −63.64; FT-IR (NaCl film) 3063, 3027, 2977, 2926, 2869, 1661,1593, 1371, 1175, 1097 cm^{-1}; HRMS (ESI$^+$) m/z [M + H]$^+$ 384.1242 calcd for $C_{19}H_{21}F_3NO_2S$, (M + H)$^+$ 384.1239], $[\alpha]^{23}_D$ = +53.2° (c 4.1, $CHCl_3$).

*(S,E)-N-((5′-Hydroxy-4″-(trifluoromethyl)-[1,1′:3′,1″-terphenyl]-4′-yl)methylene)-2-methylpropane-2-sulfinamide (**9**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **9** as a white solid from General Procedure A (52.5 mg, 0.1180 mmol, 88%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.95 (s, 1H), 8.73 (s, 1H), 7.75 (d, J = 7.2 Hz, 2H), 7.66 (d, J = 7.01, Hz, 2H), 7.47 (m, 5H), 7.32 (d, J = 1.8 Hz, 1H), 7.14 (d, J = 1.8 Hz, 1H), 1.27 (s, 9H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$) δ 163.5, 161.5, 147.1, 145.0, 142.1, 139.1, 130.1, 128.9 (2C), 128.7, 127.1, 126.1, 125.5, 120.6,115.4, 114.5, 57.9, 22.2; ^{19}F NMR{^{1}H} (376 MHz, $CDCl_3$) δ −62.53; FT-IR (NaCl film) 3062, 3034, 2961, 2927, 2866, 1593, 1175, 1092 cm^{-1}; HRMS (ESI$^+$) m/z [M + H]$^+$ calcd for $C_{24}H_{23}F_3NO_2S$, 446.1396; found, 446.1400.

*(S,E)-N-((3-Hydroxy-4′,5-bis(trifluoromethyl)-[1,1′-biphenyl]-2-yl)methylene)-2-methylpropane-2-sulfinamide (**10**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **10** as a white solid from General Procedure A (54.4 mg, 0.1244 mmol, 85%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.04 (s, 1H), 8.72 (s, 1H), 7.75 (d, J = 1.8 Hz, 2H), 7.46 (d, J = 1.8 Hz, 2H), 7.33 (d, J = 1.8 Hz, 1H), 7.13 (d, J = 1.8 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$) δ 163.2, 161.2, 145.4, 140.8, 135.4, 130.0, 125.8, 123.8, 126.2, 117.8, 117.6, 114.6, 58.3, 22.2; ^{19}F NMR{^{1}H} (376 MHz, $CDCl_3$) δ −62.70, −63.71; FT-IR (NaCl film) 3062, 3034, 2961, 2927, 2866, 1593, 1175, 1092 cm^{-1}; HRMS (ESI$^+$) m/z [M + Na]$^+$ calcd for $C_{19}H_{17}F_6NNaO_2S$, 460.0776; found, 460.0776.

*(S,E)-N-((4″-Bromo-5′-hydroxy-[1,1′:3′,1″-terphenyl]-4′-yl)methylene)-2-methylpropane-2-sulfinamide (**11**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **11** as a white solid and from General Procedure A (53.2 mg, 0.1165 mmol, 89%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.92 (s, 1H), 8.75 (s, 1H), 7.65 (d, J = 8.2 Hz, 2H)), 7.60 (d, J = 8.4 Hz, 2H)), 7.46 (m, 2H)), 7.42 (m, 1H), 7.29 (d, J = 1.8 Hz, 1H), 7.24 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 1.7 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$) δ 163.8, 161.5, 147.1, 145.4, 139.3, 137.4, 131.85, 131.3, 129.0, 128.7, 127.2, 122.8, 120.5, 115.0, 114.6, 57.9, 22.3; FT-IR (NaCl film) 3062, 3033, 2961, 2927, 2866, 1593, 1175, 1092 cm^{-1}; HRMS (ESI$^+$) m/z [M + H]$^+$ calcd for $C_{23}H_{23}BrNO_2S$, 456.0627; found, 456.0629; $[\alpha]^{23}_D$ = +53.6° (c 2.8, $CHCl_3$).

*(S,E)-N-((4′-Bromo-3-hydroxy-5-(trifluoromethyl)-[1,1′-biphenyl]-2-yl)methylene)-2-methylpropane-2-sulfinamide (**12**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **12** as a white solid from General Procedure A (52.0 mg, 0.1165 mmol, 87%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.98 (s, 1H), 8.73 (s, 1H), 7.60 (d, J = 8.48

Hz, 2H), 7.28 (d, *J* = 1.7 Hz, 1H), 7.19 (d, *J* = 8.40 Hz, 2H), 7.10 (d, *J* = 1.9 Hz, 1H), 1.25 (s, 9H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$) δ 163.4, 161.1, 145.7, 136.0, 135.2, 131.9, 131.1, 123.3, 122.9, 117.5, 114.0, 58.2, 22.1; ^{19}F NMR{^{1}H} (376 MHz, $CDCl_3$) δ −63.63; FT-IR (NaCl film) 3058, 3032, 2962, 2926, 2866, 1615, 1175, 1091 cm^{-1}; HRMS (ESI^{-}) *m*/*z* [M + H]$^{+}$ calcd for $C_{18}H_{16}BrF_3NO_2S$, (M + H)$^{+}$ 446.0031]; [α]$^{23}_{D}$ = +64.8° (*c* 4.8, $CHCl_3$).

*(S,E)-N-((5′-Hydroxy-4″-nitro-[1,1′:3′,1″-terphenyl]-4′-yl)methylene)-2-methylpropane-2-sulfinamide (**13**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **13** as a white solid from General Procedure A (52.5 mg, 0.1244 mmol, 88%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.89 (s, 1H), 8.67 (d, *J* = 0.6 Hz, 1H), 8.32 (d, *J* = 8.77 Hz, 2H), 7.67−7.63 (m, 2H), 7.55 (d, *J* = 8.75 Hz, 2H), 7.47 (m, 2H), 7.42 (m, 1H), 7.34 (dd, *J* = 1.7, 0.6 Hz, 1H), 7.13 (d, *J* = 1.8 Hz, 1H), 1.25 (s, 11H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$) δ 163.0, 161.7, 147.7, 147.3, 145.2, 144.0, 139.0, 130.7, 129.0, 128.8, 127.2, 123.8, 120.4, 115.9, 114.4, 58.0, 22.2; FT-IR (NaCl film) 3060, 3032, 2964, 2977, 2927, 2871, 1617, 1586, 1519, 1347, 1088 cm^{-1}; HRMS (ESI^{+}) *m*/*z* [M + H]$^{+}$ calcd for $C_{23}H_{23}N_2O_4S$, 423.1373; found, 423.1373; [α]$^{23}_{D}$ = +90.3° (*c* 3.3, $CHCl_3$).

*(S,E)-N-((3-Hydroxy-4′-nitro-5-(trifluoromethyl)-[1,1′-biphenyl]-2-yl)methylene)-2-methylpropane-2-sulfinamide (**14**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **14** as a white solid from General Procedure A (52.5 mg, 0.1268 mmol, 88%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.01 (s, 1H), 8.66 (s, 1H), 8.35(d, *J* = 8.85 Hz, 2H), 7.52 (d, *J* = 8.68 Hz, 2H), 7.36 (m, 1H), 7.13 (dd, *J* = 1.7, 0.7 Hz, 1H), 1.25 (s, 9H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$) δ 162.8, 161.3, 148.0, 144.4, 143.7, 135.5, 130.7, 124.0, 122.9, 117.6, 117.5, 115.2, 58.4, 22.2; ^{19}F NMR{^{1}H} (376 MHz, $CDCl_3$) δ −63.69; FT-IR (NaCl film) 3062, 3031, 2964, 2927, 2869, 1577, 1371, 1175, 1097 cm^{-1}; HRMS (ESI^{+}) *m*/*z* [M + H]$^{+}$ calcd for $C_{18}H_{18}F_3N_2O_4S$, 415.0933; found, 415.0931; [α]$^{23}_{D}$ = +98.6° (*c* 1.0, $CHCl_3$).

*(R,E)-N-((5′-Hydroxy-[1,1′:3′,1″-terphenyl]-4′-yl)methylene)-2-methylpropane-2-sulfinamide (**15**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **15** as a white solid from General Procedure A (52.5 mg, 0.1268 mmol, 88%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.94 (s, 1H), 8.79 (s, 1H), 7.68−7.66 (m, 2H), 7.50−7.44 (m, 5H), 7.43−7.40 (m, 1H), 7.39−7.36 (m, 2H), 7.28 (dd, *J* = 1.8, 0.5 Hz, 1H), 7.18 (d, *J* = 1.8 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$) δ 164.3, 161.4, 146.9, 146.7, 139.4, 138.4, 129.7, 128.8, 128.5, 128.5, 128.2, 127.2, 120.6, 114.8, 114.5, 57.8, 22.4; FT-IR (NaCl film) 3058, 3030, 2977, 2962, 2926, 1618, 1585, 1543, 1092 cm^{-1}; HRMS (ESI^{+}) *m*/*z* [M + Na]$^{+}$ calcd for $C_{23}H_{23}NNaO_2S$, 400.1341; found, 400.1341; [α]$^{23}_{D}$ = −58.4° (*c* 3.7, $CHCl_3$).

*(S,E)-N-((3-Hydroxy-5-isopropyl-[1,1′-biphenyl]-4-yl)methylene)-2-methylpropane-2-sulfinamide (**16**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **16** as a white solid from General Procedure A (52.5 mg, 0.1268 mmol, 88%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.99 (s, 1H), 9.22 (s, 1H), 7.63 (m, 2H), 7.46 (m, 2H), 7.40 (m, 1H), 7.15 (d, *J* = 1.8 Hz, 1H), 7.11 (d, *J* = 1.7 Hz, 1H), 3.61 (m, 1H), 1.37 (d, *J* = 6.88 Hz, 3H), 1.35 (d, *J* = 6.88 Hz, 3H), 1.29 (s, 9H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$) δ 161.9, 161.7, 151.9, 147.7, 140.1, 128.8, 128.4, 127.2, 115.6, 114.1, 113.5, 57.9, 28.7, 24.3, 23.9, 22.3; FT-IR (NaCl film) 3059, 3032, 2964, 2928, 2870, 1622, 1575, 1544, 1093 cm^{-1}; HRMS (ESI^{+}) *m*/*z* [M + Na]$^{+}$ calcd for $C_{20}H_{25}NNaO_2S$, 366.1498; found, 366.1498; [α]$^{23}_{D}$ = +84.6° (*c* 3.2, $CHCl_3$).

*(S,E)-N-((3-Hydroxy-2′,3′-dimethoxy-5-(trifluoromethyl)-[1,1′-biphenyl]-2-yl)methylene)-2-methylpropane-2-sulfinamide (**17**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **17** as a white solid and as inseparable topoisomers from General Procedure A **at a maximum temperature of 50 °C** (464 mg, 0.784 mmol, 73%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.01 (s, 1H, *topoisomer 1*), 11.95 (s, 1H, *topoisomer 2*), 8.57 (d, *J* = 5.7 Hz, 2H), 7.28 (d, *J* = 1.7 Hz, 20H), 7.17−7.08 (m, 4H), 7.01 (dt, *J* = 8.3, 1.4 Hz, 2H), 6.81 (ddd, *J* = 9.0, 7.6, 1.5 Hz, 2H), 3.90 (s, 6H), 3.56 (s, 3H, *topoisomer 1*), 3.53 (s, 3H, *topoisomer 2*), 1.25 (s, 9H, *topoisomer 1*), 1.22 (s, 9H, *topoisomer 2*); ^{13}C NMR{^{1}H} (126 MHz, $CDCl_3$) δ 14.0, 22.1, 22.2, 29.6, 55.9, 56.1, 57.8, 58.0, 60.4, 60.6, 76.6, 76.9, 77.1, 77.2, 113.5, 113.7, 113.8, 113.8, 113.9, 118.0, 118.1, 118.1, 118.4, 122.1, 122.6, 122.8, 124.2, 124.2, 124.3, 131.2, 131.3, 134.7, 134.9, 143.1, 143.2, 146.3, 146.5, 152.8, 160.5, 160.5, 164.6 ; ^{19}F NMR{^{1}H} (470 MHz, $CDCl_3$) δ (−63.55 *topoisomer 1*), (−63.54 *topoisomer 2*); FT-IR (NaCl) 2931, 1595, 1626, 1475, 1369, 1261.85, 1202, 1172, 1131, 1095, 977, 750, 685 cm^{-1}; HRMS (ESI^{+}) *m*/*z* [M + H]$^{+}$ calcd for $C_{20}H_{22}F_3NO_4S$, 430.1294; found, 430.1292; [α]$^{23}_{D}$ = +70.8° (*c*1.70, $CHCl_3$).

*(S,E)-N-((3-Hydroxy-5-methyl-[1,1′-biphenyl]-4-yl)methylene)-2-methylpropane-2-sulfinamide (**18**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **18** as a white solid from General Procedure A (48.9 mg, 0.1550 mmol, 82%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.78 (s, 1H), 9.07 (s, 1H), 7.63−7.59 (m, 2H), 7.46−7.42 (m, 2H), 7.41−7.35 (m, 1H), 7.10 (d, *J* = 1.7 Hz, 1H), 7.01 (dd, *J* = 1.8, 0.9 Hz, 1H), 2.61 (s, 3H), 1.28 (s, 9H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$) δ 162.2, 161.5, 147.4, 141.1, 139.5, 128.7, 128.3, 127.0, 120.6, 115.4, 113.6, 57.7, 22.1, 19.4; FT-IR (NaCl film) 3059, 3033, 2962, 2926, 1623, 1557, 1346, 1090 cm^{-1}; HRMS (ESI^{+}) *m*/*z* [M + Na]$^{+}$ calcd for $C_{18}H_{21}NNaO_2S$, 338.1185; found, 338.1187; [α]$^{23}_{D}$ = +67.5° (*c* 2.5, $CHCl_3$).

*(S,E)-N-((3-Cyclohexyl-5-hydroxy-[1,1′-biphenyl]-4-yl)methylene)-2-methylpropane-2-sulfinamide (**19**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **19** as a white solid from General Procedure A (50.1 mg, 0.1306 mmol, 84%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.01 (s, 1H), 9.19 (s, 1H), 7.63 (m, 2H), 7.46 (m, 2H), 7.40 (m, 1H), 7.13 (d, *J* = 1.7 Hz, 1H), 7.09 (d, *J* = 1.7 Hz, 1H), 3.16 (tt, *J* = 11.5, 3.1 Hz, 1H), 1.89 (m, 4H), 1.81 (ddt, *J* = 14.6, 3.0, 1.6 Hz, 1H), 1.55 (m, 5H), 1.29 (s, 9H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$) δ 161.8, 161.6, 151.0, 147.4, 140.1, 128.7, 128.2, 127.1, 116.1, 114.0, 113.3, 57.8, 39.3, 34.7, 34.6, 26.7, 26.7, 26.0, 22.2; FT-IR (NaCl film) 3058, 3032, 2927, 2852, 1621, 1585, 1544, 1090 cm^{-1}; HRMS (ESI^{+}) *m*/*z* [M + H]$^{+}$ calcd for $C_{23}H_{30}NO_2S$, 384.1991; found, 384.1998; [α]$^{23}_{D}$ = +31.1° (*c* 0.7, $CHCl_3$).

*(S,E)-N-(2-Cyclohexyl-6-hydroxy-4-(trifluoromethyl)-benzylidene)-2-methylpropane-2-sulfinamide (**20**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **20** as a white solid and from General Procedure A (50.7 mg, 0.1353 mmol, 85%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.00 (s, 1H), 9.15 (s, 1H), 7.08 (s, 2H), 3.12 (tt, *J* = 11.4, 3.1 Hz, 1H), 1.90−1.74 (m, 6H), 1.53−1.45 (m, 4H), 1.26 (s, 9H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$) δ 161.9, 161.3, 151.8, 135.7, 123.3, 117.1, 113.3, 112.47, 58.2, 39.3, 34.7, 34.4, 26.6, 26.6, 25.9, 22.2; ^{19}F NMR{^{1}H} (376 MHz,

$CDCl_3$) δ −63.78; FT-IR (NaCl film) 3062, 3034, 2930, 2855, 1594, 1557, 1372, 1095 cm^{-1}; HRMS (ESI$^+$) *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{25}F_3NO_2S$, 376.1552; found, 376.1557; $[\alpha]^{23}_D$ = +44.8° (*c* 3.2, $CHCl_3$).

(S,E)-N-((2′-Azido-5′-hydroxy-[1,1′,3′,1″-terphenyl]-4′-yl)-methylene)-2-methylpropane-2-sulfinamide (**21**). Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **21** as a white solid from General Procedure B (70 mg, 0.1672 mmol, 74%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.79 (s, 1H), 8.47 (s, 1H), 7.60−7.43 (m, 8H), 7.39 (dt, *J* = 8.1, 1.6 Hz, 1H), 7.36−7.33 (m, 1H), 7.07 (s, 1H), 1.25 (s, 9H); ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 164.3, 158.4, 143.0, 139.9, 137.6, 134.0, 130.6, 130.5, 129.1 (2C), 129.1, 128.9 (2C), 128.6 (2C), 128.6, 127.8, 119.1, 116.5, 58.1, 22.3 (3C); FT-IR (NaCl film) 3978, 2115, 1830, 1818, 1611, 1585, 1535, 1315, 1093, 977, 823, 734, 700 cm^{-1}; HRMS (ESI+) *m*/*z* 419.1536 [M + H]$^+$ calcd for $C_{23}H_{23}N_4O_2S$, 419.1542; found, 419.1536; $[\alpha]^{23}_D$ = −324.9°(*c* 3.8, $CHCl_3$).

(S,E)-N-((2′-Azido-4″-bromo-5′-hydroxy-[1,1′:3′,1″-terphenyl]-4′-yl)methylene)-2-methylpropane-2-sulfinamide (**22**). Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **22** as an orange oil from General Procedure B (22 mg, 0.0442 mmol, 73%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.82 (s, 1H), 8.48 (s, 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.56−7.42 (m, 5H), 7.28−7.19 (m, 2H), 7.07 (s, 1H), 1.26 (s, 9H); ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 163.8, 158.6, 143.2, 138.5, 137.3, 133.1, 132.2, 132.2, 132.1, 132.1, 129.1 (2C), 128.8 (2C), 128.8, 127.8, 123.5, 119.6, 116.3, 58.2, 22.4 (3C); FT-IR (NaCl film) 4000, 2117, 1583, 1573, 1093, 740, 700 cm^{-1}; HRMS (ESI+) *m*/*z* [M + Na]$^+$ calcd for $C_{23}H_{21}BrN_4NaO_2S$, 519.0466 and 521.04424 (1:1); found, 519.0461 and 521.04362 (1:1); $[\alpha]^{23}_D$ = +19.4°(*c* 1.0).

(S,E)-N-((2′-Azido-5′-hydroxy-4″-methoxy-[1,1′:3′,1″-terphenyl]-4′-yl)methylene)-2-methylpropane-2-sulfinamide (**23**). Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **23** as an orange oil from General Procedure B (8 mg, 0.0178 mmol, 80%): ^{1}H NMR (400 MHz, $CDCl_3$) *Major diastereomer* δ 11.81 (s, 1H), 8.54 (s, 1H), 7.71−7.67 (m, 1H), 7.57−7.46 (m, 4H), 7.33−7.29 (m, 1H), 7.27−7.25 (m, 1H), 7.06−7.03 (m, 3H), 3.90 (s, 3H), 1.26 (s, 9H); ^{1}H NMR (400 MHz, $CDCl_3$) *Minor diastereomer* δ 11.90 (s, 1H), 8.81 (s, 1H), 7.46−7.40 (m, 4H), 7.31−7.27 (m, 1H), 7.23−7.21 (m, 1H), 7.15 (d, *J* = 1.8 Hz, 1H), 7.01−6.96 (m, 3H), 3.87 (s, 3H), 1.27 (s, 9H); ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) *Major diastereomer* δ 164.3, 159.9, 158.3, 146.6, 142.6, 139.6, 137.6, 131.7, 131.6, 131.0, 129.0 (2C), 128.4 (2C), 125.8, 118.7, 116.7, 114.3, 114.1, 57.9, 55.2, 22.2 (3C); ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) *Minor diastereomer* δ 164.5, 161.5, 159.7, 146.9, 130.8, 128.9 (2C), 128.5, 128.4, 128.0, 127.2 (2C), 120.7, 115.0, 114.2, 114.1, 57.8, 55.3, 22.2 (3C). NOTE: all other signals were indistinguishable due to overlap; FT-IR (NaCl film) 2108, 1613, 1581, 1510, 1246, 1178, 1091, 1031, 823, 700 cm^{-1}; HRMS (ESI+) *m*/*z* [M + Na]$^+$ calcdfor $C_{24}H_{24}N_4NaO_3S$, 471.1467; found, 471.1461; $[\alpha]^{23}_D$ = +49.2° (*c* 0.5, $CHCl_3$).

(S,E)-N-((2′-Azido-5′-hydroxy-4″-(methylthio)-[1,1′:3′,1″-terphenyl]-4′-yl)methylene)-2-methylpropane-2-sulfinamide (**24**). Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **24** as an orange oil from General Procedure B (45 mg, 0.0969 mmol, 70%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.79 (s, 1H), 8.50 (s, 1H), 7.53−7.42 (m, 5H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.29−7.20 (m, 2H), 7.03 (s, 1H), 2.54 (s, 3H), 1.24 (s, 9H); ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 164.3, 158.5, 143.0, 140.1, 139.4, 137.5, 131.0, 130.8, 130.3, 129.1 (2C), 128.7 (2C), 128.6, 128.0, 126.3, 126.2, 119.2, 116.5, 58.1, 22.4 (3C), 15.4; FT-IR (NaCl film) 3900, 2976, 2922, 2117, 1608, 1585, 1575, 1394, 1319, 1199, 1089, 731, 700 cm^{-1}; HRMS (ESI+) *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{24}N_4NaO_2S_2$, 487.1238; 487.1233; $[\alpha]^{23}_D$ = +66.4° (*c* 1.0, $CHCl_3$).

(S,E)-N-((2′-Azido-5′-hydroxy-4″-nitro-[1,1′:3′,1″-terphenyl]-4′-yl)methylene)-2-methylpropane-2-sulfinamide (**25**). Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **25** as an orange oil from General Procedure B (53 mg, 0.1143 mmol, 77%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.75 (s, 1H), 8.37 (d, *J* = 8.9 Hz, 2H), 8.34 (s, 1H), 7.58−7.44 (m, 7H), 7.10 (s, 1H), 1.23 (s, 9H); ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 163.1, 158.7, 148.1, 143.4, 141.4, 137.0, 136.8, 131.8, 131.6, 129.0, 129.0 (2C), 128.9 (2C), 127.6, 124.0, 124.0, 120.4, 115.9, 58.3, 22.3 (3C); FT-IR (NaCl film) 4200, 2119, 1597, 1585, 1521, 1348, 1091, 734, 700 cm^{-1}; HRMS (ESI+) *m*/*z* [M + Na]+ calcd for $C_{23}H_{21}N_5NaO_4S$, (M+Na)$^+$ 486.1212]; $[\alpha]^{23}_D$ = +42.3°(*c* 3.5, $CHCl_3$).

(S,E)-N-((2-Azido-5-hydroxy-3-(thiophen-2-yl)-[1,1′-biphenyl]-4-yl)methylene)-2-methylpropane-2-sulfinamide (**26**). Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **26** as an orange oil from General Procedure B (38 mg, 0.0895 mmol, 50%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.76 (s, 1H), 8.62 (s, 1H), 7.56 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.52−7.43 (m, 5H), 7.19 (dd, *J* = 5.1, 3.5 Hz, 1H), 7.13 (dd, *J* = 3.5, 1.2 Hz, 1H), 7.05 (s, 1H), 1.24 (s, 9H); ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 164.1, 158.2, 142.7, 137.5, 133.7, 131.9, 130.9, 129.3, 129.2 (2C), 128.8, 128.7, 128.7 (2C), 127.6, 120.2, 117.6, 58.3, 22.4 (3C); FT-IR (NaCl film) 2960, 2924, 2112, 1608, 1585, 1317, 1274, 1215, 1093, 731, 700 cm^{-1}; HRMS (ESI+) *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{20}N_4NaO_2S_2$, 447.0925; found, 447.0919; $[\alpha]^{23}_D$ = +38.4° (*c* 0.5, $CHCl_3$).

(S,E)-N-((5-Cyano-3-hydroxy-4′-methoxy-[1,1′-biphenyl]-2-yl)methylene)-2-methylpropane-2-sulfinamide (**27b**). Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **27b** as a clear oil from General Procedure A (38 mg, 0.1066 mmol, 54%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.00 (s, 1H), 8.78 (s, 1H), 7.25 (d, *J* = 1.7 Hz, 1H), 7.23−7.18 (m, 2H), 7.16 (d, *J* = 1.6 Hz, 1H), 7.03−6.96 (m, 2H), 3.86 (s, 3H), 1.25 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, $CDCl_3$) δ 22.1, 29.6, 55.2, 58.2, 76.6, 76.9, 77.1, 77.2, 114.3, 116.6, 117.7, 118.7, 119.3, 124.2, 128.5, 130.8, 147.0, 160.2, 160.8, 164.0; FT-IR (NaCl Film) 3010, 2963, 2929, 2867, 2839, 2231, 1608, 1541, 1516, 1459, 1340, 1252, 1236.26, 1179, 1093, 1031, 869, 836, 752, 716, 583 cm^{-1}; HRMS (ESI+) *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{20}N_4NaO_2S_2$, 447.0925; 447.0919; $[\alpha]^{23}_D$ = +186.1 (*c* 2.025, $CHCl_3$).

(S,E)-N-((3-Hydroxy-4′-methoxy-5-((trimethylsilyl)-ethynyl)-[1,1′-biphenyl]-2-yl)methylene)-2-methylpropane-2-sulfinamide (**28b**). Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **28b** as a clear oil from General Procedure A (38 mg, 0.0351 mmol, 41%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.08 (s, 1H), 9.00 (s, 1H), 7.53 (s, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.33 (s, 1H), 7.28−7.21 (m, 3H), 4.12 (s, 3H), 1.51 (s, 9H), 0.52 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, $CDCl_3$) δ 22.1, 55.2, 57.8, 76.6, 76.9, 77.1, 77.2, 97.9, 103.9, 114.0, 115.9, 118.8, 125.0, 128.6, 129.9, 130.8, 146.0, 159.7, 160.7, 164.3; FT-IR (NaCl Film) 2958, 2926, 2150, 1610, 1579, 1515, 1249, 1132, 1093, 841 cm^{-1}; HRMS

(ESI+) *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{29}NO_3SSi$, 428.17102; found, 428.17084; [*α*]$^{23}{}_D$ = +110.3° (*c* 0.37, CHCl$_3$).

*(S,E)-N-((3-Hydroxy-5-((trimethylsilyl)ethynyl)-[1,1′-biphenyl]-2-yl)methylene)-2-methylpropane-2-sulfinamide (**29b**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **29b** as a clear oil from General Procedure A (17 mg, 0.0428 mmol, 41%): ^{1}H NMR (500 MHz, CDCl$_3$) *δ* 11.83 (s, 1H), 8.70 (s, 1H), 7.47−7.37 (m, 3H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 1.6 Hz, 1H), 7.01 (d, *J* = 1.6 Hz, 1H), 1.24 (s, 9H), 0.25 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, CDCl$_3$) *δ* 22.1, 57.8, 76.6, 76.9, 77.2, 98.1, 103.8, 115.8, 119.3, 125.0, 128.3, 128.5, 128.6, 129.6, 137.6, 146.2, 160.7, 164.1; FT-IR (NaCl Film) 2959, 2926, 2150, 1612, 1580, 1344, 1095, 843, 732 cm$^{-1;}$ HRMS (ESI+) *m*/*z* 398.16030 [M + H]$^+$ calcd for $C_{22}H_{27}NO_2SSi$ (M + H)$^+$, 398.16045; found 398.16030; [*α*]$^{23}{}_D$ = +66.4° (*c* 0.27, CHCl$_3$).

*(S,E)-N-((3-Hydroxy-4′-methoxy-5-vinyl-[1,1′-biphenyl]-2-yl)methylene)-2-methylpropane-2-sulfinamide (**30b**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **30b** as a clear oil from General Procedure A (6 mg, 0.0168 mmol, 36%): ^{1}H NMR (500 MHz, CDCl$_3$) *δ* 11.83 (s, 1H), 8.74 (d, *J* = 0.6 Hz, 1H), 7.27−7.21 (m, 4H), 7.02 (d, *J* = 1.7 Hz, 1H), 7.00−6.96 (m, 2H), 6.94 (d, *J* = 1.8 Hz, 1H), 6.70 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.90 (dd, *J* = 17.5, 0.7 Hz, 1H), 5.42 (dd, *J* = 10.7, 0.7 Hz, 1H), 3.85 (s, 3H), 1.24 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, CDCl$_3$) *δ* 22.1, 55.2, 57.7, 76.6, 76.9, 77.1, 77.2, 113.2, 114.0, 115.4, 117.4, 119.8, 130.6, 130.8, 135.8, 143.2, 146.3, 159.6, 161.3, 164.3; FT-IR (NaCl Film) 2959, 2924, 2850, 1616, 1577, 1516, 1249, 1090, 1032, 838, 741; HRMS (ESI+) *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{23}NO_3S$, 358.1471; found, 358.1467; [*α*]$^{23}{}_D$ = +256.8° (*c* 0.095, CHCl$_3$).

*(S)-N-((E)-(3-Hydroxy-4′-methoxy-5-((E)-styryl)-[1,1′-biphenyl]-2-yl)methylene)-2-methylpropane-2-sulfinamide (**31b**).* Product was purified with a gradient of 5−15% EtOAc in hexanes on silica gel, giving **31b** as a clear oil from General Procedure A (17 mg, 0.0392 mmol, 70%): ^{1}H NMR (500 MHz, CDCl$_3$) *δ* 11.87 (s, 1H), 8.75 (s, 1H), 7.56−7.50 (m, 2H), 7.38 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.34−7.22 (m, 4H), 7.14−7.04 (m, 2H), 7.03−6.96 (m, 2H), 3.87 (s, 2H), 1.25 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, CDCl$_3$) *δ* 22.1, 29.6, 55.2, 57.7, 76.6, 76.9, 77.1, 77.2, 113.3, 114.0, 115.2, 120.0, 126.8, 127.3, 128.3, 128.7, 130.7, 130.8, 132.1, 136.5, 143.1, 146.4, 159.6, 161.4, 164.2; FT-IR (NaCl Film) 2957, 2924, 2852, 1635, 1611, 1506, 1248, 1089, 1032, 831, 751, 691 cm^{-1}; HRMS (ESI+) *m*/*z* [M + H] calcd for $C_{26}H_{28}NO_3S$, 434.1784; found, 434.1780; [*α*]$^{23}{}_D$ = +245.5° (*c* 0.585, CHCl$_3$).

*Ethyl 3-Hydroxy-4′-methoxy-[1,1′-biphenyl]-4-carboxylate (**32**).* Conjugated ester precursor of 32 was synthesized using a previously published method;[21] spectral data matched published spectra. Product was purified with a gradient of 0−40% EtOAc in hexanes on silica gel, giving **32** as a yellow solid according to General Procedure D (47 mg, 0.1726 mmol, 40%, 80% brsm): ^{1}H NMR (500 MHz, CDCl$_3$) *δ* 7.71−7.65 (m, 1H), 7.46−7.40 (m, 2H), 7.19−7.12 (m, 1H), 6.96 (dd, *J* = 15.5, 2.3 Hz, 1H), 6.84 (dd, *J* = 8.7, 2.4 Hz, 2H), 4.24 (dtd, *J* = 8.7, 6.8, 1.9 Hz, 2H), 3.80−3.76 (m, 3H), 3.48−3.44 (m, 1H), 2.11 (t, *J* = 1.7 Hz, 4H), 1.29 (tt, *J* = 7.4, 1.8 Hz, 3H); ^{13}C NMR{^{1}H} (126 MHz, CDCl$_3$) *δ* 14.2, 30.8, 55.3, 61.3, 76.6, 76.9, 77.1, 77.2, 78.0, 85.5, 112.2, 114.3, 122.9, 128.7, 129.2, 142.8, 149.1, 160.9, 165.2; FT-IR (NaCl Film) 3288, 3168, 3935, 2840, 1687, 1599, 1573, 1510, 1426, 1373, 1306, 1282, 1255, 1209, 1174, 1143, 1076, 1030, 946, 823, 766, 751, 694, 602 cm^{-1}; HRMS (ESI+) *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{16}O_4$ (M + H)$^+$, 279.0991; found, 279.0988.

*(S)-N-((E)-((R)-4-Methoxy-5′-phenyl-1′,6′-dihydro-[1,1′:3′,1″-terphenyl]-2′-yl)methylene)-2-methylpropane-2-sulfinamide (**33**).* Product was purified with a gradient of 0−40% EtOAc in hexanes on silica gel, giving **33** as an oily solid (74 mg, 0.1576 mmol, 66%) according to the following procedure: Cyclohexenone (1.0 equiv, 100 mg, 0.244 mmol) was taken into dry diethyl ether at a final concentration of 0.5 M and transferred to a flame-dried scintillation vial charged with a magnetic stir bar. A 5 equiv amount of Grignard reagent was added portionwise, and the mixture was immediately heated (using an oil bath) to 45 °C for 3 h. The reaction mixture was cooled and diluted with EtOAc and quenched very slowly with saturated ammonium chloride. The contents of the reaction flask were transferred to a separatory funnel and washed with brine, and the organic layer was dried over sodium sulfate. Volatiles were removed under reduced pressure to give a crude mixture, which was purified by silica gel chromatography with a gradient of 0−5% EtOAc in hexanes to give a yellow oily solid (75 mg, 0.158 mmol, 65% yield) that readily crystallizes. ^{1}H NMR (500 MHz, CDCl$_3$) *δ* 8.39 (s, 1H), 7.49−7.43 (m, 3H), 7.40 (dd, *J* = 8.9, 4.5 Hz, 5H), 7.38−7.24 (m, 5H), 7.20 (d, *J* = 8.2 Hz, 4H), 6.78−6.73 (m, 2H), 6.73−6.69 (m, 1H), 4.58 (d, *J* = 9.7 Hz, 1H), 3.73 (d, *J* = 1.5 Hz, 3H), 3.31 (ddd, *J* = 17.3, 9.6, 2.8 Hz, 1H), 3.01 (d, *J* = 17.3 Hz, 1H), 1.33−1.24 (m, 1H), 0.88 (s, 1H), 0.83 (d, *J* = 1.5 Hz, 9H); ^{13}C NMR{^{1}H} (126 MHz, CDCl$_3$) *δ* 22.1, 22.3, 34.7, 36.9, 55.4, 57.73, 76.9, 77.2, 77.4, 77.4, 114.0, 125.7, 125.9, 128.6, 128.8, 128.9, 128.9, 129.2, 129.2, 130.8, 135.6, 138.7, 140.1, 141.8, 148.9, 158.5, 161.2; FT-IR (NaCl film) 3056, 2955, 2864, 2834, 2241, 1608, 1543, 1509, 1493, 1444, 1364, 1247, 1178, 1080, 1035, 911, 787, 731, 699 cm^{-1}; HRMS (ESI$^+$) *m*/*z* [M + Na]$^+$ calcd for $C_{30}H_{31}NO_2S$, 492.1967; found, 492.1963; [*α*]$^{23}{}_D$ = −23.6° (*c* 0.445, CHCl$_3$).

*(R)-6′-((E)-(((S)-tert-Butylsulfinyl)imino)methyl)-4-methoxy-1′,2′-dihydro-[1,1′:3′,1″-terphenyl]-5′-yl trifluoromethanesulfonate (**34**).* Product was purified with a gradient of 0−40% EtOAc in hexanes on silica gel, giving **34** as a yellow oil (92 mg, 0.1698 mmol, 90%) according to the following procedure: Cyclohexadiene (1.0 equiv, 78 mg, 0.189 mmol) is taken into dry THF (0.76 mL, 0.25 M) and transferred to a flame-dried round-bottom flask charged with a magnetic stir bar, fitted with a septum under dry argon, and cooled to −78 °C. Potassium hexamethyldisilazide (KHMDS, 1.5 equiv, 0.286 mmol, 1 M solution in THF) is added dropwise. Subsequently, bis(trifluoromethanesulfonyl)aniline (PhNTf$_2$) (1.5 equiv, 102 mg, 0.286 mmol) is taken into a minimal amount of THF and added portionwise. The reaction is followed by TLC until starting material is completely consumed (typically about 2 h) after which the reaction is warmed to 0 °C. The reaction is diluted with EtOAc and quenched with saturated ammonium chloride. The mixture is transferred to a separatory funnel and washed with brine. The organic phase is dried over sodium sulfate, solvent is removed, and the crude product is purified by silica gel chromatography using a gradient of 5−15% EtOAc in hexanes to give 92 mg of a yellow oil (0.170 mmol, 90% yield). ^{1}H NMR (500 MHz, CDCl$_3$) *δ* 8.64 (s, 1H), 7.40 (td, *J* = 6.8, 5.7, 3.7 Hz, 2H), 7.38−7.31 (m, 3H), 7.23−7.12 (m, 2H), 6.79−6.68 (m, 2H), 6.53 (d, *J* = 3.0 Hz, 1H), 4.54 (dd, *J* = 10.1, 1.4 Hz, 1H), 3.73 (s, 3H), 3.33 (ddd, *J* = 17.7, 10.2, 3.1 Hz, 1H), 3.01 (dd, *J* = 17.8, 1.5 Hz, 1H), 0.85 (s, 9H); ^{13}C

NMR{^{1}H} (126 MHz, CDCl$_3$) δ 21.9, 30.7, 34.3, 36.9, 55.1, 58.1, 76.6, 76.9, 77.1, 77.2, 114.0, 116.5, 123.5, 125.9, 128.1, 128.8, 129.7, 133.4, 138.1, 146.8, 151.7, 154.9, 158.7; ^{19}F NMR{^{1}H} (470 MHz, CDCl$_3$) δ −72.73; FT-IR (NaCl film) 2924, 2854, 1596, 1538, 1519, 1510, 1346, 1247, 1178, 1079, 856, 756 cm^{-1}; HRMS (ESI$^+$) *m/z* [M + H]$^+$ calcd for $C_{25}H_{31}F_3NO_5S_2$, 542.1277; found, 542.1275; $[\alpha]^{23}_{D}$ = −158.0° (*c* 0.900, CHCl$_3$).

*(S,E)-N-((4-Methoxy-5′-phenyl-[1,1′:3′,1″-terphenyl]-2′-yl)methylene)-2-methylpropane-2-sulfinamide (**35**).* Product was purified with a gradient of 0−40% EtOAc in hexanes on silica gel, giving **35** as a yellow oil as a single diastereomer according to General Procedure C (26 mg, 0.0556 mmol, 86%): ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.55 (s, 1H), 7.70−7.65 (m, 2H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.56 (d, *J* = 1.9 Hz, 1H), 7.48−7.26 (m, 10H), 6.98−6.92 (m, 2H), 3.85 (s, 3H), 0.88 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, CDCl$_3$) δ 22.1, 55.2, 56.8, 76.6, 76.9, 77.1, 77.2, 113.6, 127.2, 127.9, 128.0, 128.7, 128.8, 129.4, 129.5, 130.8, 132.7, 139.5, 141.1, 142.4, 144.2, 144.4, 159.1, 163.1; FT-IR (NaCl Film) 2954, 2920, 1607, 1590, 1511, 1248, 1177, 1083, 835, 763, 699 cm^{-1}; HRMS (ESI$^+$) *m/z* [M + Na]$^+$ calcd for $C_{30}H_{29}NO_2S$ (M + H)$^+$, 468.1991; found, 468.1988; $[\alpha]^{23}_{D}$ = +67.3° (*c* 0.205, CHCl$_3$).

*(S)-N-((E)-((R)-3″-Fluoro-4-methoxy-5′-phenyl-1′,6′-dihydro-[1,1′:3′,1″-terphenyl]-2′-yl)methylene)-2-methylpropane-2-sulfinamide (**36**).* Product was purified with a gradient of 5−20% EtOAc in hexanes on silica gel, giving **36** as a yellow oil as a single diastereomer according to General Procedure C (45 mg, 0.0103 mmol, 99%): ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.35 (s, 1H), 7.46−7.38 (m, 3H), 7.35−7.26 (m, 3H), 7.22−7.14 (m, 3H), 7.14−7.07 (m, 2H), 6.79−6.72 (m, 2H), 6.65 (d, *J* = 2.9 Hz, 1H), 4.58 (d, *J* = 9.6 Hz, 1H), 3.73 (s, 3H), 3.30 (ddd, *J* = 17.5, 9.8, 3.0 Hz, 1H), 3.05−2.98 (m, 1H), 1.56 (s, 3H), 1.32−1.24 (m, 2H), 0.93−0.84 (m, 2H), 0.83 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, CDCl$_3$) δ 14.0, 20.8, 21.8, 29.5, 34.3, 36.5, 55.1, 57.5, 60.2, 76.6, 76.9, 77.2, 113.7, 115.4, 115.6, 115.6, 115.8, 124.8, 124.9, 125.0, 125.6, 128.3, 128.5, 128.5, 130.2, 130.3, 131.0, 135.0, 139.6, 140.6, 140.6, 141.9, 147.2, 147.2, 158.3, 160.3, 161.9, 163.8; ^{19}F NMR{^{1}H} (470 MHz, CDCl$_3$) δ −112.12 (td, *J* = 9.2, 6.0 Hz); FT-IR (NaCl Film) 2925, 2861, 1609, 1582, 1541, 1509, 1247, 1177, 1080, 1036, 762, 737, 693 cm^{-1}; HRMS (ESI$^+$) *m/z* [M + H]$^+$ calcd for $C_{30}H_{30}FNO_2S$, 488.2054; found, 488.2045; $[\alpha]^{23}_{D}$ = −100.9° (*c* 0.105, CHCl$_3$).

*(S)-N-((E)-((R)-4-Methoxy-4″-nitro-5′-phenyl-1′,6′-dihydro-[1,1′:3′,1″-terphenyl]-2′-yl)methylene)-2-methylpropane-2-sulfinamide (**37**).* Product was purified with a gradient of 5−20% EtOAc in hexanes on silica gel, giving **37** as a yellow oil as a single diastereomer according to General Procedure C (47 mg, 0.0913 mmol, 99%): ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.36−8.30 (m, 2H), 8.27 (s, 1H), 7.61−7.55 (m, 2H), 7.46−7.39 (m, 2H), 7.37−7.26 (m, 6H), 7.23−7.16 (m, 2H), 6.80−6.73 (m, 2H), 6.63 (d, *J* = 2.9 Hz, 1H), 4.61 (d, *J* = 9.7 Hz, 1H), 3.74 (s, 3H), 3.34 (ddd, *J* = 17.6, 9.9, 2.9 Hz, 1H), 3.09−3.02 (m, 1H), 0.83 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, CDCl$_3$) δ 22.2, 34.7, 36.9, 42.3, 55.4, 58.0, 76.9, 77.2, 77.4, 77.4, 114.1, 124.0, 124.2, 125.9, 128.4, 128.8, 129.0, 130.1, 132.0, 134.9, 139.5, 142.8, 145.3, 146.3, 147.9, 158.6, 159.7; FT-IR (NaCl Film) 2924, 2854, 1596, 1538, 1519, 1510, 1346, 1247, 1178, 1079, 1035, 856, 756 cm^{-1}; HRMS (ESI$^+$) *m/z* [M + H]$^+$ calcd for $C_{30}H_{30}N_2O_4S$ (M + H)$^+$, 515.1999; found, 515.1996; $[\alpha]^{23}_{D}$ = +7.0° (*c* 0.285, CHCl$_3$).

*(S)-N-((E)-((R)-4,4″-Dimethoxy-5′-phenyl-1′,6′-dihydro-[1,1′:3′,1″-terphenyl]-2′-yl)methylene)-2-methylpropane-2-sulfinamide (**38**).* Product was purified with a gradient of 5−20% EtOAc in hexanes on silica gel, giving **38** as a yellow oil as a single diastereomer according to General Procedure C (46 mg, 0.0920 mmol, 99%): ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.39 (s, 1H), 7.49−7.43 (m, 3H), 7.40 (dd, *J* = 8.9, 4.5 Hz, 5H), 7.38−7.24 (m, 5H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.78−6.73 (m, 2H), 6.73−6.69 (m, 1H), 4.58 (d, *J* = 9.7 Hz, 1H), 3.73 (d, *J* = 1.5 Hz, 3H), 3.31 (ddd, *J* = 17.3, 9.6, 2.8 Hz, 1H), 3.01 (d, *J* = 17.3 Hz, 1H), 0.83 (d, *J* = 1.5 Hz, 9H); ^{13}C NMR{^{1}H} (126 MHz, CDCl$_3$) δ 21.9, 22.0, 34.4, 36.6, 55.1, 57.4, 76.6, 76.9, 77.1, 77.2, 113.7, 125.5, 125.6, 128.4, 128.5, 128.6, 128.7, 128.9, 129.0, 130.5, 135.3, 138.4, 139.9, 141.5, 148.7, 158.3, 160.9; FT-IR (NaCl film) 2954, 2928, 2863, 2835, 1606, 1540, 1508, 1457, 1445, 1418, 1364, 1299, 1248, 1209, 1078, 1032, 910, 833, 765, 734, 694 cm^{-1}; HRMS (ESI$^+$) *m/z* [M + H]$^+$ calcd for $C_{30}H_{31}NO_2S$, 492.1967; found, 492.1963; $[\alpha]^{23}_{D}$ = +23.6° (*c* 0.0.445, CHCl$_3$).

*(S)-N-((E)-((R)-3″-(tert-Butyl)-4-methoxy-5′-phenyl-1′,6′-dihydro-[1,1′:3′,1″-terphenyl]-2′-yl)methylene)-2-methylpropane-2-sulfinamide (**39**).* Product was purified with a gradient of 5−20% EtOAc in hexanes on silica gel, giving **39** as a yellow oil as a single diastereomer according to General Procedure C (48 mg, 0.0913 mmol, 99%): ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.42 (s, 1H), 7.47−7.41 (m, 3H), 7.41−7.36 (m, 2H), 7.36−7.17 (m, 9H), 6.75 (dd, *J* = 9.2, 2.5 Hz, 3H), 4.62−4.56 (m, 1H), 3.73 (s, 3H), 3.32 (ddd, *J* = 17.4, 9.8, 3.0 Hz, 1H), 3.04−2.96 (m, 1H), 1.37 (s, 9H), 0.83 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, CDCl$_3$) δ 22.0, 31.3, 34.5, 34.7, 36.8, 55.1, 57.4, 76.6, 76.9, 77.1, 77.2, 113.6, 125.5, 125.6, 125.6, 125.9, 126.2, 128.2, 128.3, 128.3, 128.4, 130.3, 135.3, 137.8, 139.9, 141.2, 148.9, 151.4, 158.1, 161.0; FT-IR (NaCl film) 2960, 2866, 1538, 1509, 1247, 1082, 801; HRMS (ESI$^+$) *m/z* [M + H]$^+$ calcd for $C_{34}H_{39}NO_4S$, 526.2774; found, 526.2778 $[\alpha]^{23}_{D}$ = +10.5° (*c* 0.115, CHCl$_3$).

*(S,E)-N-((3-Fluoro-4″-methoxy-5′-phenyl-[1,1′:3′,1″-terphenyl]-2′-yl)methylene)-2-methylpropane-2-sulfinamide (**36**).* Product was purified with a gradient of 5−20% EtOAc in hexanes on silica gel, giving **36** as a clear oil according to General Procedure A **between 60 and 80 °C** (27 mg, 0.0556 mmol, 89%): ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.54 (s, 1H), 7.70−7.64 (m, 2H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 1.9 Hz, 1H), 7.51−7.27 (m, 7H), 7.26 (s, 1H), 7.15−6.93 (m, 5H), 3.85 (s, 3H), 0.92 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, CDCl$_3$) δ 22.1, 55.2, 56.9, 60.3, 76.6, 76.9, 77.1, 77.2, 113.7, 113.9, 114.0, 116.5, 116.7, 125.2, 125.2, 127.1, 128.2, 128.5, 128.9, 129.1, 129.2, 129.3, 129.4, 130.8, 132.2, 139.3, 142.5, 142.6, 143.6, 143.6, 144.8, 159.3, 161.3, 162.7, 163.3; ^{19}F NMR{^{1}H} (470 MHz, CDCl$_3$) δ −113.83 (td, *J* = 9.2, 5.8 Hz); FT-IR (NaCl Film) 2956, 2848, 1641, 1609, 1585, 1512, 1249, 1083, 834, 765, 696 cm^{-1}; HRMS (ESI$^+$) *m/z* [M + H]$^+$ calcd for $C_{31}H_{31}NO_2S$ (M + H)$^+$, 486.1897; found, 486.1895; $[\alpha]^{23}_{D}$ = +85.6° (*c* 0.360, CHCl$_3$).

*(S,E)-N-((4-Methoxy-4″-nitro-5′-phenyl-[1,1′:3′,1″-terphenyl]-2′-yl)methylene)-2-methylpropane-2-sulfinamide (**37b**).* Product was purified with a gradient of 5−20% EtOAc in hexanes on silica gel, giving **37b** as a clear oil according to General Procedure A **between 60 and 80 °C** (26 mg, 0.0507 mmol, 86%): ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.55 (s, 1H), 8.39−8.34 (m, 1H), 8.30−8.23 (m, 3H), 8.17−8.11 (m, 2H), 7.83−7.76 (m, 1H), 7.71−7.63 (m, 4H), 7.55−7.42 (m, 8H), 7.42−7.38 (m, 1H), 7.33−7.26 (m, 4H), 7.00−6.93 (m, 3H),

6.88−6.81 (m, 2H), 6.76 (s, 1H), 3.84 (s, 3H), 0.91 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, CDCl$_3$) δ 22.5, 55.7, 57.7, 77.2, 77.4, 77.7, 114.4, 116.0, 123.6, 124.8, 126.6, 127.7, 128.7, 128.8, 129.0, 129.5, 130.1, 130.8, 131.4, 131.9, 139.5, 142.1, 143.6, 146.1, 160.1, 162.9; FT-IR (NaCl Film) 3076, 2957, 2925, 2853, 2360, 2340, 1658, 1591, 1551, 1500, 1514, 1452, 1342, 1291, 1249, 1178, 1110, 1178, 1040; HRMS (ESI$^+$) *m/z* [M + H]$^+$ calcd for $C_{31}H_{31}N_2O_4S$, 513.1842; found, 513.1843; $[\alpha]^{23}_{D}$ = +65.3° (*c* 0.150, CHCl$_3$).

*(S,E)-N-((4,4″-Dimethoxy-5′-phenyl-[1,1′:3′,1″-terphenyl]-2′-yl)methylene)-2-methylpropane-2-sulfinamide (**38b**).* Product was purified with a gradient of 5−20% EtOAc in hexanes on silica gel, giving **38b** as a clear oil according to General Procedure A **between 60 and 80 °C** (22 mg, 0.0442 mmol, 75%): ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.56 (s, 2H), 7.70−7.64 (m, 4H), 7.57 (s, 4H), 7.45 (dd, *J* = 8.3, 6.7 Hz, 4H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.32−7.26 (m, 9H), 6.97−6.91 (m, 8H), 3.84 (s, 11H), 0.91 (s, 17H); ^{13}C NMR{^{1}H} (126 MHz, CDCl$_3$) δ 14.6, 22.6, 55.7, 57.4, 60.8, 77.2, 77.4, 77.6, 77.7, 114.0, 127.6, 128.5, 129.2, 129.3, 130.0, 131.3, 133.6, 140.1, 142.8, 144.6, 159.5, 163.7; FT-IR (NaCl Film) 2955, 2925, 2835, 1608, 1590, 1509, 1246, 1176, 1081, 1031, 833 cm^{-1}; HRMS (ESI$^+$) *m/z* [M + H]$^+$ calcd for $C_{31}H_{31}NO_3S$, 498.2097; found, 498.2100; $[\alpha]^{23}_{D}$ = +58.1° (*c* 0.540, CHCl$_3$).

*(S,E)-N-((3-(tert-Butyl)-4″-methoxy-5′-phenyl-[1,1′:3′,1″-terphenyl]-2′-yl)methylene)-2-methylpropane-2-sulfinamide (**39b**).* Product was purified with a gradient of 5−20% EtOAc in hexanes on silica gel, giving **39b** as a clear oil according to General Procedure A **between 60 and 80 °C** (27 mg, 0.0516 mmol, 75%): ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.55 (s, 1H), 7.71−7.65 (m, 2H), 7.59 (t, *J* = 1.5 Hz, 2H), 7.49−7.42 (m, 2H), 7.42−7.27 (m, 7H), 7.17 (dt, *J* = 7.3, 1.5 Hz, 1H), 6.98−6.92 (m, 2H), 3.85 (s, 3H), 1.34 (s, 9H), 1.29−1.24 (m, 1H), 0.87 (s, 2H), 0.86 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, CDCl$_3$) δ 22.1, 31.3, 34.6, 55.2, 56.8, 76.6, 76.9, 77.1, 77.2, 113.6, 124.2, 126.6, 126.7, 127.2, 127.6, 128.0, 128.7, 128.8, 128.8, 129.5, 130.8, 132.9, 139.6, 140.6, 142.3, 144.1, 144.8, 150.8, 159.1, 163.2; FT-IR (NaCl Film) 2958, 2925, 2865, 1590, 1511, 1248, 1084, 834, 764, 698 cm^{-1}; HRMS (ESI$^+$) *m/z* [M + H]$^+$ calcd for $C_{34}H_{37}NO_2S$, 524.2617; found, 524.2615; $[\alpha]^{23}_{D}$ = +45.0° (*c* 0.280, CHCl$_3$).

*(S,E)-6′-(((tert-Butylsulfinyl)imino)methyl)-4-methoxy-[1,1′:3′,1″-terphenyl]-5′-yl Trifluoromethanesulfonate (**40**).* Product was purified with a gradient of 5−20% EtOAc in hexanes on silica gel, giving **40** as a clear oil (395 mg, 0.7321 mmol, 99%) according to the following procedure: Phenol 4 (1.0 equiv, 300 mg, 0.74 mmol) was taken into dry THF (7.4 mL) to a final concentration of 0.1 M and transferred to a flame-dried scintillation vial. Cesium carbonate (1.5 equiv, 360 mg, 1.1 mmol) and PhNTf$_2$ (1.5 equiv, 393 mg, 1.1 mmol) were added portionwise sequentially. The reaction was stirred overnight, then quenched with saturated ammonium chloride, diluted with EtOAc, and washed with brine. The solvent was removed, and the crude product was purified by silica gel chromatography using a gradient of 0−10% EtOAc in hexanes to give **40** as a colorless oil (395 mg, 0.73 mmol, 99% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.51 (s, 1H), 7.67−7.60 (m, 3H), 7.56−7.42 (m, 4H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.01−6.95 (m, 2H), 3.86 (s, 3H), 1.28 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, CDCl$_3$) δ 22.4, 24.0, 32.1, 55.2, 58.0, 76.6, 76.9, 77.1, 77.2, 114.1, 119.7, 123.9, 127.2, 129.1, 129.1, 129.2, 129.8, 131.1, 138.1, 145.2, 147.3, 148.2, 158.7, 160.2; ^{19}F NMR{^{1}H} (470 MHz, CDCl$_3$) δ −73.12; FT-IR (NaCl Film) 3064, 3035, 3009, 2960, 2936, 2840, 1699, 1608, 1514, 1427, 1244, 1209, 1178, 1140, 1090, 1031, 945, 835, 765, 668, 594 cm^{-1}; HRMS (ESI$^+$) *m/z* [M + H]$^+$ calcd for $C_{25}H_{24}F_3NO_5S$, 540.11208; found, 540.11210; $[\alpha]^{23}_{D}$ = +3.407° (*c* 0.270, CHCl$_3$).

*(S,E)-N-((5′-Allyl-4″-methoxy-[1,1′:3′,1″-terphenyl]-4′-yl)-methylene)-2-methylpropane-2-sulfinamide (**41**).* Product was purified with a gradient of 5−20% EtOAc in hexanes on silica gel, giving **41** as a clear oil (21 mg, 0.0487 mmol, 90%) according to the following procedure: Phenyl triflate (1.0 equiv, 30 mg, 0.055 mmol) was taken into dry THF (0.22 mL) and transferred to a flame-dried scintillation vial charged with a magnetic stir bar, and LiCl (3.7 mg, 0.087 mmol) and allylSnBu$_3$ (1.1 equiv, 20 mg, 0.019 mL, o.061 mmol) were added. Pd(PPh$_3$)$_4$ (0.05 equiv, 3.3 mg, 0.0028 mmol) was added, and the reaction mixture was immediately purged with argon for 1 min. The vial was sealed, and the reaction was heated (using an oil bath) to 50 °C and stirred overnight. The reaction was diluted with EtOAc, washed with brine, and dried over Na$_2$SO$_4$. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.66 (s, 1H), 7.68−7.59 (m, 3H), 7.56−7.45 (m, 5H), 7.44 (d, *J* = 1.6 Hz, 1H), 7.43−7.35 (m, 1H), 7.26−7.22 (m, 2H), 7.02−6.92 (m, 3H), 6.11 (ddt, *J* = 18.0, 9.5, 6.4 Hz, 1H), 5.13−5.05 (m, 2H), 4.00−3.87 (m, 2H), 3.85 (s, 3H), 1.24 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, CDCl$_3$) δ 22.5, 38.8, 55.2, 57.2, 76.6, 76.9, 77.1, 77.2, 113.7, 115.8, 127.2, 127.7, 128.0, 128.4, 128.8, 129.1, 130.9, 132.1, 137.4, 139.8, 141.4, 143.1, 146.0, 159.3, 163.5; FT-IR (NaCl film) 2924, 2586, 2359, 1743, 1725, 1688, 1639, 1607, 1547, 1512, 1461, 1426, 1364, 1293, 1247, 1207, 1177, 1141, 1083, 1031, 882, 834, 808, 764, 697, 668, 634, 597, 580, 508; HRMS (ESI$^+$) *m/z* [M + H]$^+$ calcd for $C_{27}H_{30}NO_2S$, 432.1991; found, 432.1992; $[\alpha]^{23}_{D}$ = +210.7° (*c* 0.075, CHCl$_3$).

*(S,E)-N-((5′-Cyano-4″-methoxy-[1,1′:3′,1″-terphenyl]-4′-yl)methylene)-2-methylpropane-2-sulfinamide (**42**).* Product was purified with a gradient of 20−30% EtOAc in hexanes on silica gel, giving **42** as a red oil (25.6 mg, 0.0615 mmol, 53%) according to the following procedure: enol triflate (62.0 mg, 0.1145 mmol) and Zn(CN)$_2$ (8.5 mg, 0.0724 mmol) were combined in a small vial and dissolved in dry DMF (0.3 mL). The vial was then purged with N$_2$ for 15 min, Pd(PPh$_3$)$_4$ was then added, and the mixture was heated (using an oil bath) to 70 °C for 15 h. The reaction mixture was then allowed to cool, diluted with EtOAc, and quenched with 20% ammonium hydroxide. The aqueous layer was then extracted with EtOAc. The combined organic extracts were then washed with brine, dried over Na$_2$SO$_4$, and then liberated from solvent under reduced pressure to afford a red crude material. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.61 (s, 1H), 8.04 (d, *J* = 1.9 Hz, 1H), 7.66−7.61 (m, 2H), 7.53−7.45 (m, 4H), 7.05−6.98 (m, 3H), 3.86 (s, 3H), 1.35 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, CDCl$_3$) δ 22.3, 55.3, 58.2, 76.6, 76.9, 77.1, 77.2, 112.0, 114.3, 118.6, 127.1, 127.3, 129.0, 129.2, 129.4, 130.7, 130.9, 131.3, 132.8, 133.2, 144.0, 159.4; FT-IR (NaCl Film) 2924, 2853, 2226, 1733, 1540, 1250, 1178, 1083, 1030, 764 cm^{-1}; HRMS (ESI$^+$) *m/z* [M + Na]$^+$ calcd for $C_{25}H_{24}N_2O_2S$, 439.1450; found, 439.1451; $[\alpha]^{23}_{D}$ = +50.8° (*c* 0.315, CHCl$_3$).

*(S)-N-((Z)-((R)-2′,3′-Dimethoxy-3-oxo-5-(trifluoromethyl)-3,6-dihydro-[1,1′-biphenyl]-2(1H)-ylidene)methyl)-2-methylpropane-2-sulfinamide (**17a**).* Product was purified with a gradient of 20−30% EtOAc in hexanes on silica gel, giving **17a** as a yellow oil as a single diastereomer according to General Procedure D (465 mg, 1.08 mmol, 73%): ^{1}H NMR (500 MHz, CDCl$_3$) δ 11.35 (d, *J* = 10.6 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 1H),

6.86 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.78 (dd, *J* = 10.6, 1.3 Hz, 1H), 6.68 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.50 (q, *J* = 1.6 Hz, 1H), 4.47 (ddd, *J* = 8.2, 6.5, 1.3 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 2.80−2.67 (m, 2H), 1.25 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, $CDCl_3$) δ 22.3, 22.3, 22.7, 22.8, 29.5, 35.9, 55.9, 57.6, 61.1, 76.9, 77.2, 77.4, 77.4, 109.9, 111.7, 120.3, 123.9, 124.3, 129.3, 129.4, 135.1, 142.0, 142.3, 147.0, 147.0, 153.1, 186.7; ^{19}F NMR{^{1}H} (470 MHz, $CDCl_3$) δ −70.61; FT-IR (NaCl Film) 2964, 2836, 1635, 1478, 1558, 1266, 1171, 1093, 1008, 757, 789 cm^{-1}; HRMS (ESI$^+$) *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{24}F_3NO_4$, 454.12703; found, 454.1267; $[\alpha]^{23}_{D}$ = +16.8° (*c* 0.075, $CHCl_3$).

*(S)-N-((Z)-((R)-5-Cyano-4′-methoxy-3-oxo-3,6-dihydro-[1,1′-biphenyl]-2(1H)-ylidene)methyl)-2-methylpropane-2-sulfinamide (**27**).* Conjugated ester was synthesized using a a procedure modified from a previously published method;[17] spectral data matched published spectra. Product was purified with a gradient of 20−30% EtOAc in hexanes on silica gel, giving **27** as a yellow oil as a single diastereomer according to General Procedure D (202.6 mg, 0.5652 mmol, 60%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.46 (d, *J* = 9.9 Hz, 1H), 7.13−7.05 (m, 2H), 6.91−6.82 (m, 3H), 6.67 (t, *J* = 1.8 Hz, 1H), 3.98 (ddd, *J* = 8.0, 6.4, 1.2 Hz, 1H), 3.81 (s, 3H), 2.87−2.82 (m, 1H), 2.82−2.73 (m, 2H), 1.25 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, $CDCl_3$) δ 22.0, 34.4, 41.2, 55.2, 57.5, 76.6, 76.9, 77.1, 77.2, 110.1, 114.4, 117.1, 123.8, 128.7, 132.4, 139.9, 149.2, 158.9, 182.7; FT-IR (NaCl Film) 2959, 2925, 2852, 2217, 1636, 1557, 1511, 1249, 1178, 1096, 1033, 833, 758 cm^{-1}; HRMS (ESI$^+$) *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{23}N_2O_3S$, 359.1424; found, 359.1423; $[\alpha]^{23}_{D}$ = +75.0° (*c* 0.435, $CHCl_3$).

*(S)-N-((Z)-((R)-4′-Methoxy-3-oxo-5-((trimethylsilyl)-ethynyl)-3,6-dihydro-[1,1′-biphenyl]-2(1H)-ylidene)methyl)-2-methylpropane-2-sulfinamide (**28**).* Conjugated ester was synthesized using a a procedure modified from a previously published method;[18] spectral data matched published spectra. Product was purified with a gradient of 20−30% EtOAc in hexanes on silica gel, giving **28** as a yellow oil as a single diastereomer according to General Procedure D (178 mg, 0.4143 mmol, 66%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.34 (d, *J* = 10.8 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.56 (d, *J* = 10.7 Hz, 1H), 6.31 (s, 1H), 3.90 (t, *J* = 7.7 Hz, 1H), 3.80 (d, *J* = 1.3 Hz, 3H), 2.77−2.64 (m, 2H), 1.25 (s, 9H), 0.19 (d, *J* = 1.4 Hz, 9H); ^{13}C NMR{^{1}H} (126 MHz, $CDCl_3$) δ 22.1, 37.2, 42.2, 55.1, 57.1, 76.6, 76.9, 77.2, 103.5, 105.5, 111.5, 114.1, 129.0, 133.7, 134.0, 137.8, 145.1, 158.7, 188.5; FT-IR (NaCl Film) 2958, 2140, 1633, 1552, 1512, 1250, 1197, 1179, 1094, 1036, 843, 761 cm^{-1}; HRMS (ESI$^+$) *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{32}NO_3SSi$, 430.1867; found, 430.1863; $[\alpha]^{23}_{D}$ = +12.1° (*c* 1.205, $CHCl_3$).

*(S)-2-Methyl-N-((Z)-((R)-3-oxo-5-((trimethylsilyl)ethynyl)-3,6-dihydro-[1,1′-biphenyl]-2(1H)-ylidene)methyl)propane-2-sulfinamide (**29**).* Conjugated ester was synthesized using a a procedure modified from a previously published method;[18] spectral data matched published spectra. Product was purified with a gradient of 20−30% EtOAc in hexanes on silica gel, giving **29** as a yellow oil as a single diastereomer according to General Procedure D (139 mg, 0.3478 mmol, 41%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.36 (d, *J* = 10.8 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.30−7.23 (m, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.59 (d, *J* = 10.7 Hz, 1H), 6.33 (s, 1H), 3.95 (t, *J* = 7.5 Hz, 1H), 2.80−2.69 (m, 2H), 1.25 (s, 9H), 0.20 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, $CDCl_3$) δ 22.7, 37.6, 43.5, 57.6, 77.2, 77.4, 77.6, 77.7, 104.0, 106.1, 111.5, 127.6, 128.4, 129.2, 134.4, 138.1, 142.4, 145.6, 188.7; FT-IR (NaCl film) 2958, 2140, 1638, 1631, 1493, 1408, 1262, 1198, 1095, 843, 843, 758 cm^{-1}; HRMS (ESI$^+$) *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{29}NaNO_2SSi$, 422.1580; found, 422.1576; $[\alpha]^{23}_{D}$ = +30.9° (*c* 0.265, $CHCl_3$).

*(S)-N-((Z)-((R)-4′-Methoxy-3-oxo-5-vinyl-3,6-dihydro-[1,1′-biphenyl]-2(1H)-ylidene)methyl)-2-methylpropane-2-sulfinamide (**30**).* Conjugated ester was synthesized using a a procedure modified from a previously published method;[19] spectral data matched published spectra. Product was purified with a gradient of 20−30% EtOAc in hexanes on silica gel, giving **30** as a yellow oil as a single diastereomer according to General Procedure D (81 mg, 0.2253 mmol, 60%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.37 (d, *J* = 10.8 Hz, 1H), 7.20−7.11 (m, 2H), 6.91−6.83 (m, 2H), 6.60−6.51 (m, 1H), 6.50 (d, *J* = 10.8 Hz, 1H), 6.06 (s, 1H), 5.62 (d, *J* = 17.5 Hz, 1H), 5.44 (d, *J* = 10.7 Hz, 1H), 3.91 (ddd, *J* = 9.5, 5.9, 1.5 Hz, 1H), 3.81 (s, 3H), 2.82−2.66 (m, 2H), 1.57 (s, 1H), 1.26 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, $CDCl_3$) δ 22.2, 31.6, 42.1, 55.2, 57.0, 76.6, 76.9, 77.1, 77.2, 112.2, 114.1, 120.4, 128.9, 129.1, 134.2, 137.3, 144.0, 152.2, 158.5, 189.9; FT-IR (NaCl film) 2959, 1634, 1511, 1251, 1176, 1084, 777, 764 cm^{-1}; HRMS (ESI$^+$) *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{25}NO_3S$, 360.1628; 360.1624; $[\alpha]^{23}_{D}$ = +36.0° (*c* 0.585, $CHCl_3$).

*(S)-N-((Z)-((R)-4′-Methoxy-3-oxo-5-((E)-styryl)-3,6-dihydro-[1,1′-biphenyl]-2(1H)-ylidene)methyl)-2-methylpropane-2-sulfinamide (**31**).* Conjugated ester was synthesized using a a procedure modified from a previously published method;20 spectral data matched published spectra. Product was purified with a gradient of 20−30% EtOAc in hexanes on silica gel, giving **31** as a yellow oil as a single diastereomer according to General Procedure D (43 mg, 0.0987 mmol, 45%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.43 (d, *J* = 10.7 Hz, 1H), 7.48−7.43 (m, 2H), 7.40−7.26 (m, 3H), 7.24−7.15 (m, 2H), 6.98−6.85 (m, 4H), 6.57 (dd, *J* = 10.8, 1.4 Hz, 1H), 6.18 (s, 1H), 4.00−3.92 (m, 1H), 3.82 (s, 3H), 2.93 (dd, *J* = 16.7, 5.9 Hz, 1H), 2.84 (ddd, *J* = 16.8, 9.4, 1.5 Hz, 1H), 2.04 (s, 1H), 1.27 (s, 9H); ^{13}C NMR{^{1}H} (126 MHz, $CDCl_3$) δ 14.1, 20.9, 22.2, 32.4, 42.2, 55.2, 57.0, 60.3, 76.6, 76.9, 77.1, 77.2, 112.3, 114.1, 127.1, 128.7, 128.8, 129.0, 129.0, 134.3, 135.0, 135.9, 143.9, 152.3, 158.5, 189.6; FT-IR (NaCl Film) 2958, 2927, 1634, 1615, 1541, 1511, 1253, 1197, 1089, 782, 761 cm^{-1}; HRMS (ESI$^+$) *m*/*z* [M + H]$^+$ calcdfor $C_{26}H_{29}NO_3S$, 436.1941; found, 436.1937; $[\alpha]^{23}_{D}$ = −13.6° (*c* 0.150, $CHCl_3$).

*(S)-N-((1Z,2E)-3-(4-Bromophenyl)allylidene)-2-methylpropane-2-sulfinamide (**22SM**).* To a 1-dram vial charged with a magnetic stir bar was added phosphonate (136.3 mg, 0.47 mmol) and THF (0.31 mL). The mixture was cooled to 0 °C with an ice bath, and 1 M LiHMDS (0.35 mmol) was then added and allowed to stir for 30 min at 0 °C. 4-Bromobenzaldehyde (46 mg, 0.23 mmol) in THF (0.31 mL) was added and allowed to stir at 0 °C. After stirring for 2.5 h the reaction mixture was quenched with saturated NH_4Cl. The organic layer was extracted with EtOAc, washed with brine, and dried over Na_2SO_4; solvent was evaporated; and the crude material was purified via flash chromatography (0%−20% EtOAc/Hexanes) to give the desired imine (52 mg, 0.16 mmol, 70%). Spectra matched literature values.[3]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c01211.

Experimental procedures, characterization and spectroscopic data for all new compounds (PDF)

Accession Codes

CCDC 1451255 and 2079822 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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