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Nickel-Catalyzed Oxidative Coupling Reaction of Phenyl Benzyl Sulfoxides

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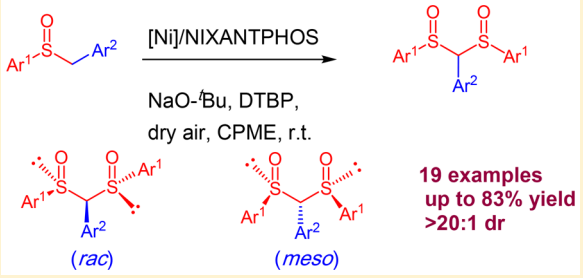
Supporting Information

ABSTRACT: A novel method to produce disulfoxides diastereoselectively from phenyl benzyl sulfoxides is reported. The $Ni(P^nBu_3)_2Cl_2$]/NIXANTPHOS catalyst system successfully promotes an oxidative coupling reaction of aryl benzylic sulfoxides to disulfoxides. An intermediate aldehyde, produced from the elimination of α-hydroxy sulfoxides, is proposed to generate the key sulfenate anion, enabling the formation of the disulfoxide product. A range of disulfoxides was produced in moderate to high yields (30−83%) and diastereoselectivity (*rac*/*meso* ranging from 3:1 to >20:1).



INTRODUCTION

Sulfoxides have attracted considerable interest from researchers in different fields for a variety of applications. They have been found in natural products,[1−3] successfully employed as synthetic intermediates (Figure 1A−C),[4−15] and used in drug discovery and as medications, including armodafinil[16] and nexium[17] (Figure 1D−F). They have been gaining attention as ligands in transition-metal catalysis (Figure 1G−I).[18−29] Particular attention has been paid to the coordination chemistry of bis(sulfoxides), which are useful as ligands for metal-catalyzed transformations[18−31] and for liquid−liquid extractions of lanthanide and actinide ions (Figure 1J).[32]

Sulfoxides are generally prepared by selective oxidation of sulfides,[33−36] nucleophilic displacements on R′S(=O)XR (XR = NR_2 or OR) with Grignard or organolithium complexes,[37] cross-coupling with α-halo sulfoxides[38] or direct C−H functionalization,[39] and arylation of sulfenate anions [RS−O]$^-$ using transition metal catalysts.[40−51] Bis(phenylsulfinyl) methanes are typically accessed by either selective oxidation of bis(phenylsulfides)[11,52−54] or nucleophilic substitution of sulfonate esters.[52,55] In some cases, the oxidative approach leads to low yields.[53]

Oxidative cross-coupling methods have recently undergone rapid development, owing to their potential for green and economic synthesis. This area of intense research activity includes classical couplings, C−H functionalizations,[56] and radical chemistry for chemical, materials, and biological synthesis.[57−62] During the past several years, palladium complexes have dominated the catalytic systems; however, the expense and greater toxicity of palladium have prompted significant interest in developing nickel-catalyzed oxidative coupling reactions for the construction of carbon−carbon and carbon−heteroatom bonds.[63,64] Novel methods for oxidative

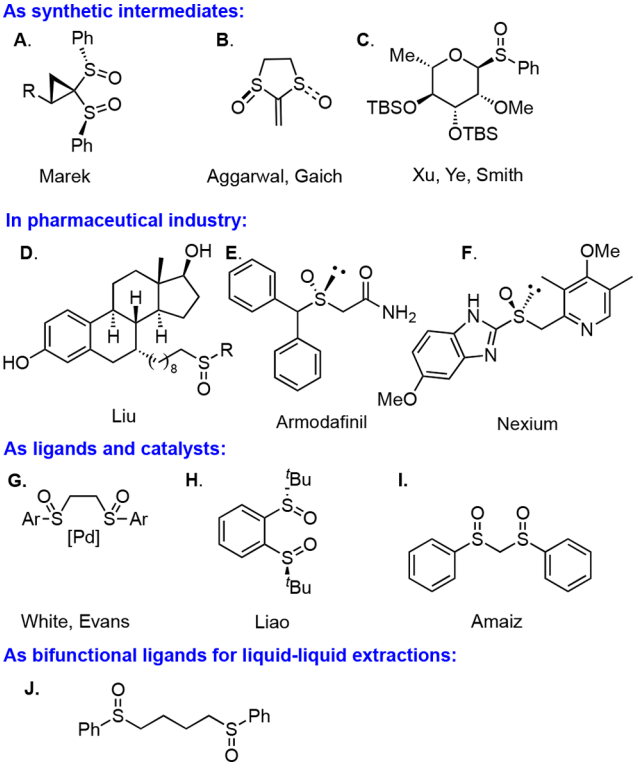


Figure 1. Representative sulfoxides and their uses.

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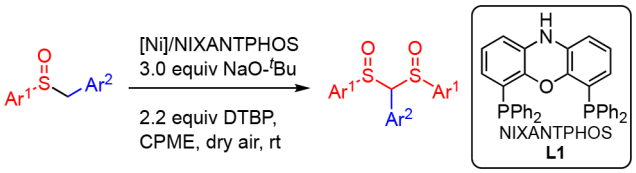
coupling to form C−C, C−N, C−O, C−S, and C−halogen bonds have been reported.[65−67] Despite these advances, diastereoselective oxidative coupling reactions to generate bis(sulfoxides) with formation of the C−S bond remains challenging.

Herein, we present a novel nickel-catalyzed diastereoselective oxidative coupling reaction to produce disulfoxides (Scheme 1). We hypothesize that the reaction proceeds via a sulfenate anion $[ArSO]^-$, which is cross-coupled by the nickel catalyst. Disulfoxides are produced in moderate to good yields with fair to excellent diastereoselectivities.

Scheme 1. Synthetic Approach to Bis(phenylsulfinyl) Methanes Outlined Herein[a]



[a]DTBP: di-*tert*-butyl peroxide; CPME: cyclopentyl methyl ether.

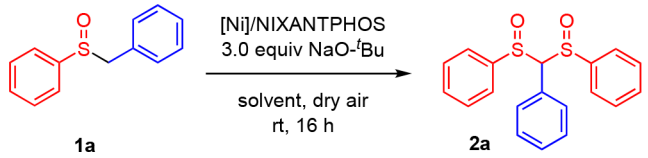
RESULTS AND DISCUSSION

Initial studies began with phenyl benzyl sulfoxide (**1a**), $Ni(COD)_2$ (10 mol %), and van Leeuwen's NIXANTPHOS (**L1**, 10 mol %) as the ligand.[68,69] Given the important role that solvents and bases play in coupling reactions, we first screened a variety of solvents [cyclopentyl methyl ether (CPME), toluene, tetrahydrofuran (THF), dimethoxyethane (DME), 1,4-dioxane, 2-methyltetrahydrofuran (2-Me-THF), dichloromethane (DCM)] with NaO-^{t}Bu as the base. After 16 h at room temperature, only three of the reactions led to products (Table 1, entries 1−3). Among the solvents tested, the coupling of **1a** with NaO-^{t}Bu in CPME afforded the best assay yield (AY, determined by ^{1}H NMR spectroscopy of worked up, unpurified reaction mixtures by integration against a toluene internal standard; 32%, entry 1). Under otherwise identical reaction conditions, substitution of KO-^{t}Bu and LiO-^{t}Bu for NaO-^{t}Bu afforded lower AY (8 and 16%, entries 4 and 5), and no product was obtained using other bases [$LiN(SiMe_3)_2$, $NaN(SiMe_3)_2$, $KN(SiMe_3)_2$, $LiOSiMe_3$, or $KOSiMe_3$].

We next screened several nickel sources (for more details, see Table S1). The yield increased to 48% when $Ni(P^nBu_3)_2Cl_2$ was used in place of $Ni(COD)_2$ (entry 6), but did not improve with $Ni(dppp)Cl_2$ or $Ni(OAc)_2$ (entries 7 and 8). A series of 12 phosphine ligands and 6 nitrogen-based ligands were compared with NIXANTPHOS (**L1**) but only NIXANTPHOS provided the disulfoxide product (see Table S2 for details). Increasing the [Ni]/NIXANTPHOS loading from 10:10 to 20:20 mol % improved the AY to 56% (entry 9). Lastly, different oxidants were examined (see Table S3), and the highest yield was observed when the reaction was conducted in the presence of di-*tert*-butyl peroxide (DTBP, 2.2 equiv) and dry air (entry 10, 68% AY).

Having established suitable conditions, we examined the effect of increasing the reaction scale from 0.1 to 0.5 mmol of sulfoxide **1a** (entry 11, 70% AY) and decreasing the concentration of **1a** (entry 12, 82% AY and 76% isolated yield of **2a** after column chromatography). It is noteworthy that the minor diastereomer, *meso*-**2a** (*anti-anti*), was characterized by X-ray crystallography (see the Supporting Information for details). Note that there are two possible *meso* diastereomers, but only the *anti-anti* is observed throughout this work and not the *syn-syn* diastereomer. The background reactions in the absence of the Ni source and NIXANTPHOS also were tested, and the results indicated that the disulfoxide was only produced when both $Ni(P^nBu_3)_2Cl_2$ and NIXANTPHOS were present (entries 13−15).

Table 1. Optimization of the Oxidative Coupling of Phenyl Benzyl Sulfoxide 1a[a]



entry	nickel source	base	solvent	AY (%)[b,c]	dr[d]
1	$Ni(COD)_2$	NaO-^{t}Bu	CPME	32	6:1
2	$Ni(COD)_2$	NaO-^{t}Bu	Tol	20	6:1
3	$Ni(COD)_2$	NaO-^{t}Bu	THF	12	6:1
4	$Ni(COD)_2$	KO-^{t}Bu	CPME	8	6:1
5	$Ni(COD)_2$	LiO-^{t}Bu	CPME	16	6:1
6	$Ni(P^nBu_3)_2Cl_2$	NaO-^{t}Bu	CPME	48	8.5:1
7	$Ni(dppp)Cl_2$	NaO-^{t}Bu	CPME	25	6:1
8	$Ni(OAc)_2$	NaO-^{t}Bu	CPME	20	5:1
9	$Ni(P^nBu_3)_2Cl_2$	NaO-^{t}Bu	CPME	56[e]	8.5:1
10	$Ni(P^nBu_3)_2Cl_2$	NaO-^{t}Bu	CPME	68[e,f]	8.5:1
11	$Ni(P^nBu_3)_2Cl_2$	NaO-^{t}Bu	CPME	70[e,f,g]	8.5:1
12	$Ni(P^nBu_3)_2Cl_2$	NaO-^{t}Bu	CPME	82[e,f,h]	8.5:1
13	$Ni(P^nBu_3)_2Cl_2$	NaO-^{t}Bu	CPME	0[i]	0
14	without nickel source	NaO-^{t}Bu	CPME	0[i]	0
15	without nickel source	NaO-^{t}Bu	CPME	0	0

[a]Assay yields (AY) of the mixtures of diastereomers were determined with ^{1}H NMR spectroscopy by integration of the worked up but unpurified reaction mixtures using toluene as internal standard. [b]Reactions were conducted on a 0.1 mmol scale of **1a** in 2 mL of solvent. [c]Reactions were conducted with [Ni]/NIXANTPHOS loading 10/10 mol %. [d]Diastereomeric ratios were determined by ^{1}H NMR spectroscopy of crude reaction mixtures. [e]Reactions were conducted with [Ni]/NIXANTPHOS loading 20/20 mol %. [f]Reactions were conducted with di-*tert*-butyl peroxide (DTBP). [g]Reactions were conducted on a 0.5 mmol scale of **1a** in 10 mL of solvent. [h]Reactions were conducted on a 0.5 mmol scale of **1a** in 25 mL of solvent. [i]Reactions were conducted without NIXANTPHOS.

Using the optimized reaction conditions (Table 1, entry 12), the scope of substituted aryl benzyl sulfoxides was explored. The diastereoselectivity (*rac* to *meso*) ranged from 3:1 to 8.7:1 (Table 2). Reactions with substituted phenyl benzyl sulfoxides bearing electron-withdrawing groups, like 4-F (**1b**), 4-CF_3 (**1c**), and 4-Cl (**1d**), gave **2b**, **2c**, and **2d** in 82% (6:1 dr), 70% (4:1 dr), and 83% yields (8.7:1 dr), respectively. Compound *rac*-**2c** was characterized by X-ray crystallography (see the Supporting Information for details). Substituted phenyl benzyl sulfoxides with electron-donating 4-Me (**1e**) and 4-^{t}Bu (**1f**) groups produced products **2e** and **2f** in 61% (4.5:1 dr) and 69% yield (4:1 dr). Sterically hindered 1-naphthyl benzyl sulfoxide provided the corresponding product (**2g**) in 60% yield (3:1 dr). Due to the importance of heterocycles in medicinal chemistry, heterocyclic substrates were examined. 2-(Benzylsulfinyl) thiophene **1h** furnished the coupling product **2h** in 60% yield (4:1 dr). Under the conditions outlined above, 1-(benzylsulfinyl)-4-methoxybenzene led to very low yield

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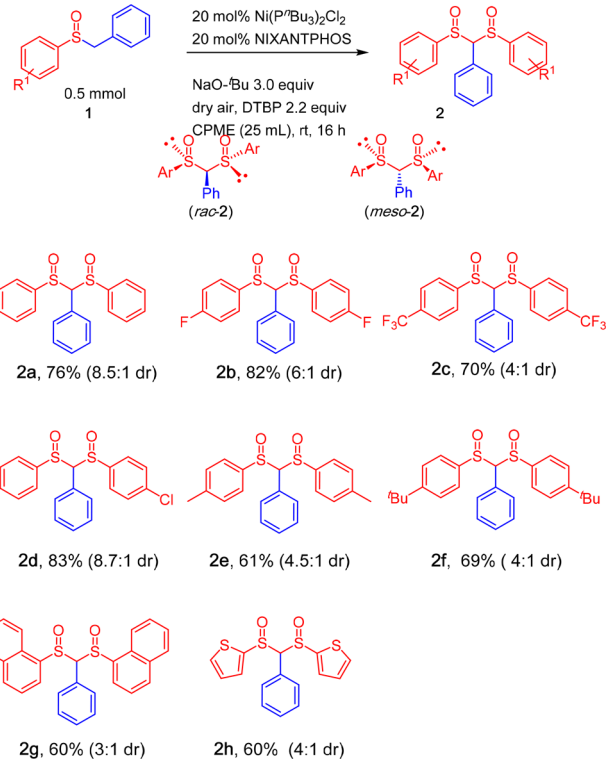
Table 2. Diastereoselective Oxidative Coupling of Various Substituted Phenyl Benzyl Sulfoxides[a,b]

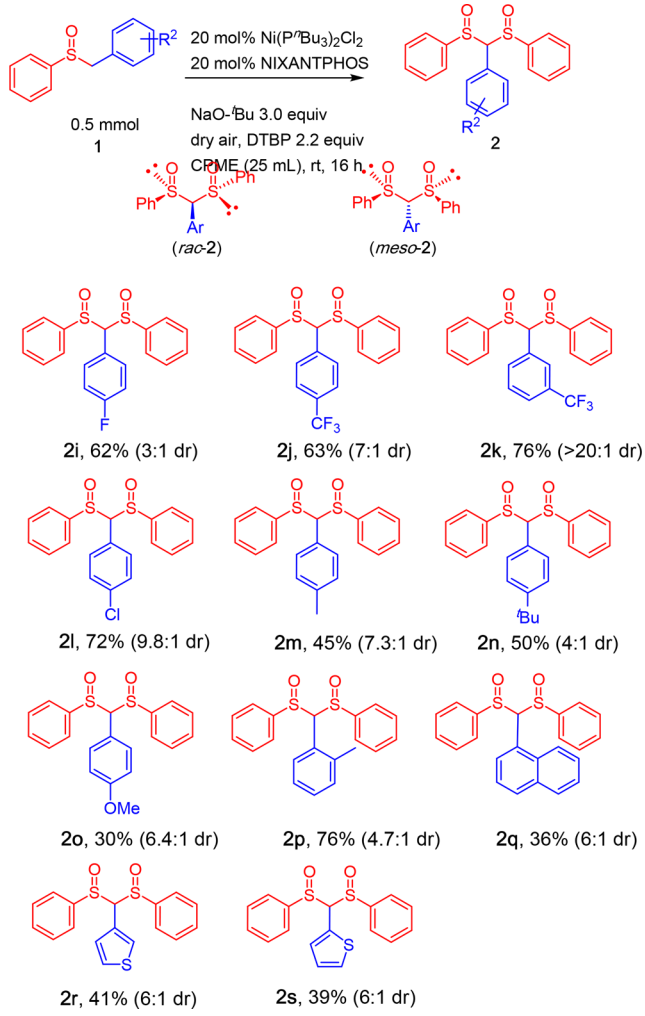


[a]Isolated yields for mixtures of diastereomers after chromatographic purification. [b]Diastereomeric ratios were determined by ^{1}H NMR spectroscopy of the crude reaction mixtures.

(<10%), most likely due to the higher pK_a value of the benzylic hydrogens. We were unsuccessful at increasing the yield through optimization. Attempts to carry out the coupling of *N*-heterocyclic substrates, such as 3-(benzylsulfinyl)pyridine and 3-(benzylsulfinyl)-quinoline, resulted in recovery of starting material and decomposition, respectively.

After demonstrating the scope of substituted aryl benzyl sulfoxides in the coupling reactions, we next turned our attention to the substrate scope with respect to substitution on the benzyl group (Table 3). Overall, substrates with electron-withdrawing groups gave better yields than those with electron-donating groups, and the diastereoselectivity (*rac* to *meso*) ranged from 3:1 to >20:1. Electron-withdrawing 4-F (**1i**), 4-CF_3 (**1j**), 3-CF_3 (**1k**), and 4-Cl (**1l**) groups were well-tolerated, giving **2i**, **2j**, **2k**, and **2l** in 62% (3:1 dr), 63% (7:1 dr), 76% (>20:1 dr), and 72% yields (9.8:1 dr), respectively. Substrates bearing electron-donating groups, such as 4-Me (**1m**), 4-^{t}Bu (**1n**), and 4-OMe (**1o**), furnished the products **2m**–**2o** in 30–50% yield and 4:1–7.3:1 dr. Analogues with sterically hindered groups, such as 2-tolyl (**1p**) and 1-naphthyl (**1q**), yielded the corresponding products in 76% (4.7:1 dr) and 36% yields (6:1 dr), respectively. The heterocyclic substrates, 3-(phenylsulfinylmethyl) thiophene (**1r**) and 2-(phenylsulfinylmethyl) thiophene (**1s**), provided 41% (6:1 dr) and 39% yields (6:1 dr), respectively. No products derived from oxidation of the thiophene sulfur were identified. Increasing the catalyst loading to 40 mol % Ni(P^{n}Bu$_3$)$_2$Cl$_2$ and 40 mol % NIXANTPHOS and increasing the reaction time to 24 h did not increase the yield with heterocyclic substrates. Furthermore, under the same conditions, attempts

Table 3. Diastereoselective Oxidative Coupling of Various Phenyl Substituted Benzyl Sulfoxides[a,b]



[a]Isolated yields for mixtures of diastereomers after chromatographic purification. [b]Diastereomeric ratios were determined by ^{1}H NMR spectroscopy of the crude reaction mixtures.

to couple *N*-heterocyclic substrates, 3-(phenylsulfinyl-methyl)-pyridine, and 3-(phenyl-sulfinylmethyl) quinoline, led to recovery of starting material and decomposition, respectively.

To gain insight into the pathway for this novel nickel-catalyzed diastereoselective oxidative coupling reaction, several experiments were carried out, as shown in Scheme 2. Both benzaldehyde (17% yield by GC) and benzoic acid (22% isolated yield), the product from oxidation of benzaldehyde, were identified as byproducts of the reaction (Scheme 2A). Observation of the isolated byproduct diphenyl disulfide (8%, Scheme 2A) suggests that the sulfenate anion[70] may be an intermediate, because sulfenate anions are known to undergo disproportionation to generate disulfides and benzenesulfinate salts.[70−72] To explore the possibility of a sulfenate anion intermediate, we next employed phenethyl-sulfinylbenzene in the reaction (Scheme 2B). It is known that under basic conditions phenethyl-sulfinylbenzene undergoes elimination to generate styrene and the sulfenate anion.[73] In the reaction, both disulfoxide **2e** (15%) and **2t** (9%) were found, supporting the intermediacy of the sulfenate anion. We were curious if the benzyl group of **1a** could be cleaved in a pathway that did not involve the nickel catalyst. Thus, sulfoxide **1a** was subjected to

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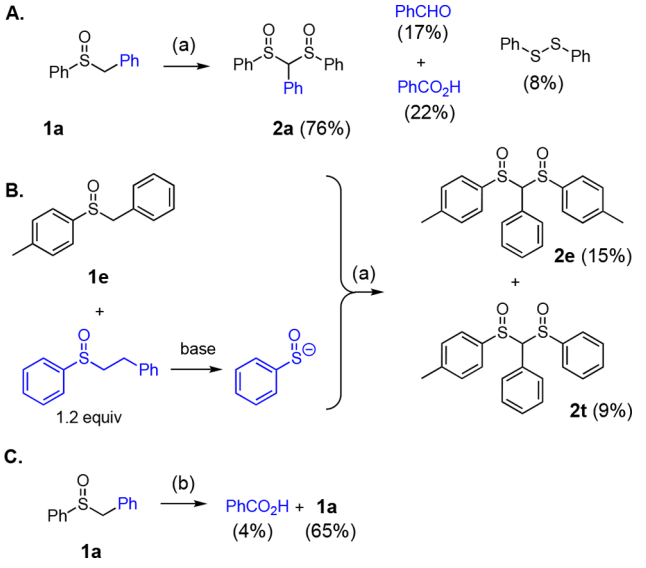
Scheme 2. Experiments to Probe the Reaction Mechanism[a]



[a]Reaction conditions (a): 20 mol % $Ni(P^nBu_3)_2Cl_2$, 20 mol % NIXANTPHOS, 3 equiv NaO-^{t}Bu, 2.2 equiv DTBP, and dry air, in 25 mL CPME at room temperature for 16 h; (b): 3 equiv NaO-^{t}Bu, 2.2 equiv DTBP, and dry air, in 25 mL CPME at room temperature for 16 h.

base (NaO-^{t}Bu), dry air, and DTBP at rt for 16 h. Although conversion was low (Scheme 2C) benzoic acid (4% isolated yield), derived from air oxidation of benzaldehyde, and starting sulfoxide **1a** (65%) were observed when the reaction was conducted without nickel and ligand (Scheme 2C). This result suggests that there is a transition metal free route to cleave the S-benzyl group, likely generating sulfenate anions. Given the low conversion in Scheme 2C, however, under the disulfoxide forming reaction conditions it may be possible that there is a nickel catalyzed oxidation of **1a** under basic conditions that leads to the sulfenate anions and benzaldehyde. Alternatively, there may be an in situ generated intermediate that is more efficient at benzylic oxidation.

On the basis of the results of these experiments, a catalytic cycle is proposed in Figure 2. Deprotonation of the sulfoxide (**A**) by base generates a nucleophile (**B**) that can undergo transmetalation with Ni(II) complex **F** via path a to form a Ni−C bond. Deprotonated sulfoxide **B**, with an electron-rich carbanion, can be oxidized through path b to form an α-hydroxy sulfoxide (**C**). In the presence of base, **C** is deprotonated to expel the sulfenate anion (**D**), and form the aromatic aldehyde (**E**). Oxidation of the liberated benzaldehyde (**E**) to benzoic acid can explain its formation in Scheme 2A. Sulfenate anions are known to undergo transmetalation with transition metals.[40,41,43,50] Attack by the sulfenate anion (**D**) on Ni(II) intermediate **G** provides the transmetalation product (**H**), which undergoes reductive elimination to generate the C−S bond of the disulfoxide (**I**). The resulting Ni(0) intermediate (**J**) can be oxidized to a Ni(II) species, such as **F** or a related Ni(II) compound to close the catalytic cycle.

The oxidation processes in the proposed reaction pathway can be envisioned to occur with either dioxygen or di-*tert*-butyl peroxide. One might imagine that the diastereoselectivity can be set in either the transmetalation or reductive elimination steps. We recently disclosed computational evidence that in the case of the palladium catalyzed enantioselective arylation of sulfenate anions, the palladium sulfenate is O-bound after transmetalation. It was also discovered that the isomerization of the Pd−O−SPh to Pd−S(=O)Ph has a higher barrier than the reductive elimination to form the sulfoxide, Ar−S(=O)Ph.[50] Thus, in the Ni-catalyzed process outlined herein, it is also possible that the diastereoselectivity determining step is isomerization to S-bound sulfenate anion [Ni]−S(=O)Ph.

CONCLUSION

In summary, we have reported a unique oxidative coupling process to generate disulfoxides directly from phenyl benzyl sulfoxides in a diastereoselective fashion. A $[Ni(P^nBu_3)_2]Cl_2$/NIXANTPHOS-based catalyst promotes the reaction, and a variety of disulfoxides were produced in moderate yields and diastereoselectivities. Mechanistic studies indicate the sulfenate anion formation through C−S bond cleavage and a core catalytic cycle involving C−S bond formation. The proposed mechanism highlights the possible reasons for the moderate yields in these reactions. To achieve high yields, the fate of the deprotonated sulfoxide must be equally divided between

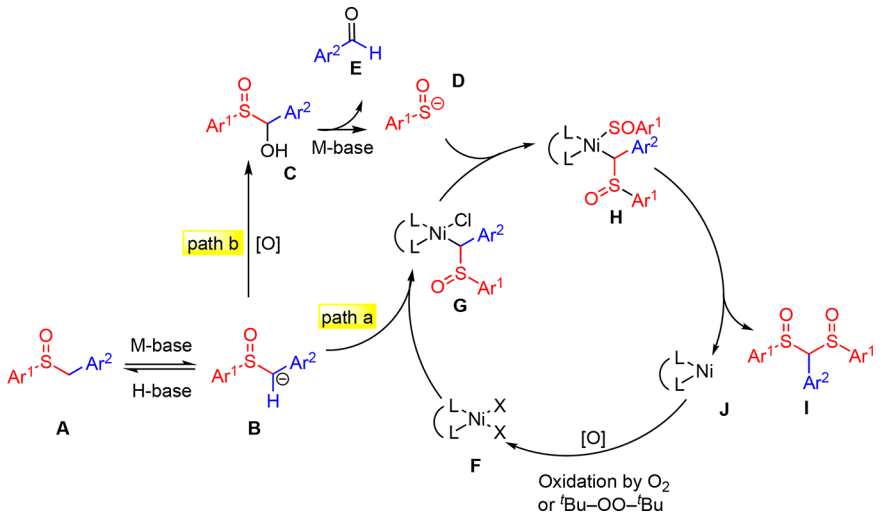


Figure 2. Proposed mechanism highlighting key intermediates in the nickel-catalyzed oxidative coupling process.

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formation of the sulfenate anion and transmetalation to nickel(II). Excess conversion to the sulfenate anion, for example, would result in less deprotonated sulfoxide for the transmetalation and reduce the yield. Additionally, the sensitivity of sulfenate anions to oxidation may also reduce the yields observed in these reactions.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out under dry air. Anhydrous CPME, Toluene, THF, DME, 1,4-dioxane, 2-Me-THF, and DCM were purchased from Sigma-Aldrich and directly used without further purification. Unless otherwise stated, reagents were commercially available and used as purchased without further purification. Chemicals were purchased from Sigma-Aldrich, Acros, Alfa Aesar Matrix Scientific, or Frontier Scientific, and solvents were purchased from Fisher Scientific and Sigma-Aldrich. The progress of the reactions was monitored by thin-layer chromatography using Whatman precoated silica gel 60 F-254 plates and visualized by short-wave ultraviolet light as well as by treatment with I_2. Flash chromatography was performed with silica gel (230−400 mesh, Silicycle). The NMR spectra were obtained using a Brüker 500 MHz Fourier transform NMR spectrometer. Chemical shifts are reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants are reported in hertz. The infrared spectra were taken with KBr plates with a PerkinElmer Spectrum 1600 Series spectrometer. High-resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (model LCT-XE Premier) using electrospray ionization (ESI) in positive or negative mode, depending on the analytes. Melting points were determined on a Mel-Temp melting point apparatus and were uncorrected. Phenyl benzyl sulfoxide and its derivatives were prepared according to the literature procedures.[74,75]

Procedure and Characterization for Formation of Bis-(phenylsulfinyl)-phenylmethane Derivatives by Nickel-Catalyzed Oxidative Coupling Reactions. *General Procedure A.* To an oven-dried vial (20 mL) equipped with a stir bar were added $Ni(P^nBu_3)_2Cl_2$ (53.4 mg, 0.1 mmol) and NIXANTPHOS (55.2 mg, 0.1 mmol) inside a nitrogen filled glovebox, followed by 5.0 mL of dry CPME; meanwhile, NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv) and sulfoxide (**1**, 0.5 mmol, 1.0 equiv) were mixed in the oven-dried flask, followed by 20.0 mL dry CPME. After the catalyst/ligand solution and the starting material/base solution were stirred for 2 h at 24 °C separately, they were mixed in an oven-dried round-bottomed flask (100 mL). The flask was sealed with a rubber septum and sealing tap and moved out of glovebox. Di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv) was added by syringe into the flask. Then, dry air was added through a syringe opened to the air, loaded with cotton and anhydrous $CaCl_2$ on the top. The reaction mixture was stirred at room temperature for 16 h. Afterward, the sealed flask was opened to air, and the reaction mixture was passed through a short pad of silica gel packed in a syringe. The pad was then rinsed with 25 mL of ethyl acetate. The solvent was removed under reduced pressure to yield a brown solid. The residue was purified byflash chromatography on silica gel to give the product.

General Procedure B. To an oven-dried vial (20 mL) equipped with a stir bar were added $Ni(P^nBu_3)_2Cl_2$ (53.4 mg, 0.1 mmol) and NIXANTPHOS (55.2 mg, 0.1 mmol) inside a nitrogen-filled glovebox, followed by 5.0 mL of dry CPME. After the catalyst/ligand solution was stirred for 2 h at 24 °C, it was added to the mixture solution of NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv) and sulfoxide (1, 0.5 mmol, 1.0 equiv) with CPME (20 mL) in an oven-dried round-bottomed flask (100 mL). The flask was sealed with a rubber septum and sealing tap, then moved out of glovebox. Di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv) was added by syringe. Then, dry air was added through a syringe opened to the air, loaded with cotton and anhydrous $CaCl_2$ on top. The reaction mixture was stirred at room temperature for 16 h. The sealed flask was opened to air, and the reaction mixture was passed through a short pad of silica gel packed in a syringe. The pad was then rinsed with 25 mL of ethyl acetate. The solvent was removed under reduced pressure to yield a brown solid. The residue was purified by flash chromatography on silica gel to give the product.

*Bis(phenylsulfinyl)phenylmethane (**2a**).* The reaction was performed following General Procedure A with **1a** (108 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv), and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 5:95) to give the product (64.6 mg, 76% yield, *rac*/*meso* = 8.5:1) as a white solid. Compound *rac*-**2a** was purified by silica gel column (eluted with EtOAc/CH_2Cl_2 = 3:97) to give white solid (55.3 mg, 65% yield). The spectroscopic data of *rac*-**2a** are as follows: R_f = 0.2 (EtOAc/CH_2Cl_2 = 1:9). Mp = 170−171 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46−7.26 (m, 9H), 7.18−7.11 (m, 3H), 6.80 (d, $^3J_{H-H}$ = 7.6 Hz, 2H), 4.30 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 142.2, 140.7, 131.9, 131.4, 130.8, 129.8, 129.2, 129.0, 128.4, 125.0, 124.9, 124.7, 95.4 ppm. IR (thin film): 3057, 2921, 1492, 1418, 1214, 1174, 1118, 1098, 998, 786, 612 cm^{-1}. HRMS calculated for $C_{19}H_{16}O_2S_2Na$ 363.0489, found 363.0477 $[M + Na]^+$.

*Bis(4-fluorophenylsulfinyl)phenylmethane (**2b**).* The reaction was performed following General Procedure B with **1b** (117 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv), and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 5:95) to give the product (77.3 mg, 82% yield, *rac*/*meso* = 6:1) as a yellow solid. The product was dissolved in chloroform and layered with ethanol (ethanol/$CHCl_3$ (20:1)), which was left open to the air at room temperature. After slow evaporation, crystalline *rac*-**2b** (white solid, 65.1 mg, 69% yield) was obtained. The spectroscopic data of *rac*-**2b** are as follows: R_f = 0.3 (EtOAc/CH_2Cl_2 = 1:9). Mp = 150−151 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51−7.46 (m, 4H), 7.38 (m, 1H), 7.27 (m, 2H), 7.16 (m, 4H), 7.08 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 4.25 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 164.9 (d, J_{C-F} = 253.7 Hz), 136.2, 130.8, 129.8, 128.4, 127.5, 127.4, 125.2, 116.7, 116.5, 92.4 ppm [two carbon signals are missing due to overlapping]. IR (thin film): 3060, 2903, 1587, 1489, 1455, 1402, 1294, 1226, 1155, 1083, 1012, 751, 635 cm^{-1}. HRMS calculated for $C_{19}H_{15}F_2O_2S_2$ 377.0482, found 377.0490 $[M + H]^+$.

*Bis[4-(trifluoromethyl)phenylsulfinyl]phenylmethane (**2c**).* The reaction was performed following General Procedure B with **1c** (142 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1 mmol, 3.0 equiv) and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 5:95) to give the product (83.4 mg, 70% yield, *rac*/*meso* = 4:1) as a yellow solid. The product was dissolved in chloroform and layered with ethanol (ethanol/$CHCl_3$ (20:1)), which was left open to the air at room temperature. After slow evaporation, crystalline *rac*-**2c** (yellow solid, 65.0 mg, 56% yield) was obtained. The spectroscopic data of *rac*-**2c** are as follows: R_f = 0.4 (EtOAc/CH_2Cl_2 = 1:9). Mp = 152−153 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.53 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.38−7.30 (m, 5H), 7.20 (t, $^3J_{H-H}$ = 7.8 Hz, 2H), 6.80 (s, 2H), 4.31 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 146.1, 144.8, 133.6 (q, J_{C-F} = 33.2 Hz), 130.4, 130.3, 129.6 (q, J_{C-F} = 270.0 Hz), 128.8, 125.9 (q, J_{C-F} = 7.5 Hz), 125.8 (q, J_{C-F} = 7.5 Hz), 125.6, 125.3 (q, J_{C-F} = 270.0 Hz), 125.0, 124.9, 123.8, 95.1 ppm. IR (thin film): 3018, 2962, 1323, 1260, 1215, 1093, 1061, 1015, 757, 668 cm^{-1}. HRMS calculated for $C_{21}H_{15}F_6O_2S_2$ 477.0418, found 477.0417 $[M + H]^+$.

*Bis(4-clorophenylsulfinyl)phenylmethane (**2d**).* The reaction was performed following General Procedure B with **1d** (145 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv), and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 5:95) to give the product (83.9 mg, 83% yield, *rac*/*meso* = 8.7:1) as a white solid. The product was dissolved in chloroform and layered with ethanol (ethanol/$CHCl_3$ (20:1)), which was left open to the air at room temperature. After slow evaporation, crystalline *rac*-**2d** (white solid, 68.1 mg, 67% yield) was obtained. The spectroscopic data of *rac*-**2d** are as follows: R_f = 0.3 (EtOAc/CH_2Cl_2 = 1:9). Mp = 158−159 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40−

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7.30 (m, 2H), 7.26−7.16 (m, 7H), 7.09 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 6.80 (s, 2H), 4.24 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 140.2, 138.7, 138.0, 137.6, 130.4, 129.9, 129.2, 129.1, 128.4, 125.9, 125.8, 124.1, 95.0 ppm. IR (thin film): 3059, 2912, 1572, 1493, 1452, 1294, 1277, 1171, 1082, 1011, 784, 697 cm^{-1}. HRMS calculated for $C_{19}H_{14}Cl_2O_2S_2Na$ 430.9710, found 430.9732 $[M + Na]^+$.

*Bis(4-methylphenylsulfinyl)phenylmethane (**2e**).* The reaction was performed following General Procedure A with **1e** (115 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv) and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 5:95) to give the product (56.2 mg, 61% yield, *rac*/*meso* = 4.5:1) as a yellow solid. Compound *rac*-**2e** was purified by silica gel column (eluted with EtOAc/CH_2Cl_2 = 3:97) to give yellow solid (42 mg, 46% yield). The spectroscopic data of *rac*-**2e** are as follows: R_f = 0.2 (EtOAc/CH_2Cl_2 = 1:9). Mp = 150−151 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.26 (m, 2H), 7.18 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 7.13 (t, $^3J_{H-H}$ = 8.0 Hz, 2H), 7.09−7.05 (m, 5H), 6.81 (d, $^3J_{H-H}$ = 7.2 Hz, 2H), 4.28 (s, 1H), 2.29 (s. 3H), 2.28 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 142.1, 141.6, 138.5, 137.0, 130.5, 129.5, 129.4, 129.3, 128.0, 124.8, 124.5, 124.4, 94.9, 21.3, 21.2 ppm. IR (thin film): 3019, 1445, 1374, 1260, 1215, 1096, 1046, 755, 668 cm^{-1}. HRMS calculated for $C_{21}H_{21}O_2S_2$ 369.0983, found 369.0980 $[M + H]^+$.

*Bis(4-(tert-butyl)phenylsulfinyl)phenylmethane (**2f**).* The reaction was performed following General Procedure A with **1f** (136 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv), and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 5:95) to give the product (78.2 mg, 69% yield, *rac*/*meso* = 4:1) as a yellow solid. Compound *rac*-**2f** was purified by silica gel column (eluted with EtOAc/CH_2Cl_2 = 3:97) to give yellow solid (60.2 mg, 53% yield). The spectroscopic data of *rac*-**2f** are as follows: R_f = 0.2 (EtOAc/CH_2Cl_2 = 1:9). Mp = 141−142 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.28 (m, 1H), 7.27−7.19 (m, 6H), 7.11 (t, $^3J_{H-H}$ = 7.8 Hz, 2H), 7.05 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 6.80 (d, $^3J_{H-H}$ = 7.3 Hz, 2H), 4.28 (s, 1H), 1.21(s, 9H), 1.20 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 155.2, 154.9, 138.7, 137.1, 130.7, 129.3, 127.9, 125.9, 125.7, 124.9, 124.4, 124.2, 95.0, 34.9, 34.8, 31.1, 31.0 ppm. IR (thin film): 2961, 1474, 1461, 1443, 1416, 1269, 1107, 1070, 1021, 990. 842, 745, 688 cm^{-1}. HRMS calculated for $C_{27}H_{33}O_2S_2$ 453.1922, found 453.1935 $[M + H]^+$.

*Bis(1-naphthylsulfinyl)phenylmethane (**2g**).* The reaction was performed following General Procedure B with **1g** (133 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv), and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 3:97) to give the product (66.0 mg, 60% yield, *rac*/*meso* = 3:1) as a yellow solid. Compound *rac*-**2g** was purified by silica gel column (eluted with EtOAc/CH_2Cl_2 = 2:98) to give white solid (44.8 mg, 41% yield). The spectroscopic data of *rac*-**2g** are as follows: R_f = 0.4 (EtOAc/CH_2Cl_2 = 1:9). Mp = 140−141 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.01 (s, 1H), 7.89−7.67 (m, 5H), 7.46−7.31 (m, 3H), 7.25−7.15 (m, 3H), 7.05 (m, 4H), 6.73 (s, 2H), 4.83 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 138.2, 136.0, 133.5, 132.9, 132.2, 131.0, 130.7, 129.4, 129.2, 128.9, 128.7, 127.7, 127.6, 127.3, 127.1, 126.7, 126.3, 125.5, 125.3, 125.1, 125.0, 124.7, 121.7, 120.3, 88.1 ppm. IR (thin film): 3021, 2984, 2941, 1478, 1465, 1445, 1374, 1248, 1216, 1096, 1046, 939, 847, 757, 668 cm^{-1}. HRMS calculated for $C_{27}H_{21}O_2S_2$ 441.0983, found 441.0992 $[M + H]^+$.

*Bis(2-thienylsulfinyl)phenylmethane (**2h**).* The reaction was performed following General Procedure A with **1h** (111 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv), and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 5:95) to give the product (52.6 mg, 60% yield, *rac*/*meso* = 4:1) as a yellow solid. Compound *rac*-**2h** was purified by silica gel column (eluted with EtOAc/CH_2Cl_2 = 3:97) to give yellow solid (40.2 mg, 46% yield). The spectroscopic data of *rac*-**2h** are as follows: R_f = 0.2 (EtOAc/CH_2Cl_2 = 1:9). Mp = 131−132 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.52 (d, $^4J_{H-H}$ = 4.0 Hz, 1H), 7.46 (d, $^4J_{H-H}$ = 4.0 Hz, 1H), 7.36 (t, $^3J_{H-H}$ = 7.5 Hz, 1H), 7.24 (m, 3H), 7.04 (d, $^3J_{H-H}$ = 7.0 Hz, 2H), 6.97 (s, 2H), 6.87 (s, 1H), 4.75 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 143.1, 141.6, 132.2, 131.9, 130.6, 130.5, 129.9, 129.6, 128.5, 127.2, 127.0, 125.1, 96.3 ppm. IR (thin film): 3080, 2922, 1493, 1452, 1437, 1400, 1338, 1267, 1223, 1159, 1089, 1000, 852, 783, 615 cm^{-1}. HRMS calculated for $C_{15}H_{13}O_2S_4$ 352.9798, found 352.9822 $[M + H]^+$.

*Bis(phenylsulfinyl)(4-fluorophenyl)methane (**2i**).* The reaction was performed following General Procedure B with **1i** (117 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv) and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 5:95) to give the product (55.5 mg, 62% yield, *rac*/*meso* = 3:1) as a yellow solid. Compound *rac*-**2i** was purified by silica gel column (eluted with EtOAc/CH_2Cl_2 = 3:97) to give yellow solid (38.0 mg, 42% yield). The spectroscopic data of *rac*-**2i** are as follows: R_f = 0.2 (EtOAc/CH_2Cl_2 = 1:9). Mp = 124−125 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.38 (m, 1H), 7.34−7.28 (m, 5H), 7.25−7.28 (m, 2H), 7.15 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 6.83 (t, $^3J_{H-H}$ = 8.6 Hz, 2H), 6.77 (m, 2H), 4.27 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 162.5 (J_{C-F} = 233.7 Hz), 141.7, 140.1, 132.2, 132.1, 131.7, 131.2, 128.9, 128.8, 124.5, 124.2, 120.6, 115.4 (d, J_{C-F} = 21.2 Hz), 94.2 ppm [one carbon signal is missing due to overlapping]. IR (thin film): 3018, 1215, 1106, 757, 668 cm^{-1}. HRMS calculated for $C_{19}H_{16}FO_2S_2$ 359.0576, found 359.0590 $[M + H]^+$.

*Bis(phenylsulfinyl)(4-(trifluoromethyl)phenyl)methane (**2j**).* The reaction was performed following General Procedure B with **1j** (142 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv), and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 5:95) to give the product (64.3 mg, 63% yield, *rac*/*meso* = 7:1) as brown a solid. Compound *rac*-**2j** was purified by silica gel column (eluted with EtOAc/CH_2Cl_2 = 3:97) to give brown solid (55.3 mg, 54% yield). The spectroscopic data of *rac*-**2j** are as follows: R_f = 0.3 (EtOAc/CH_2Cl_2 = 1:9). Mp = 141−142 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.40 (m, 1H), 7.38 (d, $^3J_{H-H}$ = 8.2 Hz, 3H), 7.32−7.26 (m, 4H), 7.24 (m, 2H), 7.13 (d, $^3J_{H-H}$ = 8.2 Hz, 2H), 6.91 (d, $^3J_{H-H}$ = 7.7 Hz, 2H), 4.35 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 141.4, 139.9, 132.0, 131.4, 130.5, 129.2, 129.1, 128.9, 127.1 (q, J_{C-F} = 278.9 Hz), 124.8 (q, J_{C-F} = 5.0 Hz), 124.5, 124.1, 94.4 ppm [one carbon signal is missing due to overlapping]. IR (thin film): 3018, 1215, 1050, 757, 669 cm^{-1}. HRMS calculated for $C_{20}H_{16}F_3O_2S_2$ 409.0544, found 409.0522 $[M + H]^+$.

*Bis(phenylsulfinyl)(3-(trifluoromethyl)phenyl)methane (**2k**).* The reaction was performed following General Procedure B with **1k** (142 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv), and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 5:95) to give the product (77.2 mg, 76% yield, *rac*/*meso* > 20:1) as a yellow solid. Compound *rac*-**2k** was purified by silica gel column (eluted with EtOAc/CH_2Cl_2 = 3:97) to give yellow solid (72.1 mg, 71% yield). The spectroscopic data of *rac*-**2k** are as follows: R_f = 0.3 (EtOAc/CH_2Cl_2 = 1:9). Mp = 131−132 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.54 (d, $^3J_{H-H}$ = 7.5 Hz, 1H), 7.42−7.33 (m, 7H), 7.23−7.28 (m, 3H), 7.13 (d, $^3J_{H-H}$ = 7.5 Hz, 2H), 6.73 (s, 1H), 4.36 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 141.4, 139.9, 133.4, 131.9, 131.4, 130.7, 129.1, 128.9, 128.5, 127.1 (q, J_{C-F} = 275.0 Hz), 127.0 (q, J_{C-F} = 7.25 Hz), 126.0, 125.9 (q, J_{C-F} = 7.25 Hz), 124.4, 124.0, 94.5 ppm. IR (thin film): 3018, 1331, 1215, 1135, 1050, 758, 669 cm^{-1}. HRMS calculated for $C_{20}H_{16}F_3O_2S_2$ 409.0544, found 409.0557 $[M + H]^+$.

*Bis(phenylsulfinyl)(4-chlorophenyl)methane (**2l**).* The reaction was performed following General Procedure B with **1l** (145 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv), and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 5:95) to give the product (67.4 mg, 72% yield, *rac*/*meso* = 9.8:1) as a yellow solid. Compound *rac*-**2l** was purified by silica gel column (eluted with EtOAc/CH_2Cl_2 = 3:97) to give yellow

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solid (58.2 mg, 62% yield). The spectroscopic data of *rac*-**2l** are as follows: R_f = 0.2 (EtOAc/CH_2Cl_2 = 1:9). Mp = 138−139 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (m, 2H), 7.32−7.24 (m, 6H), 7.14 (d, $^3J_{H-H}$ = 7.7 Hz, 2H), 7.09 (d, $^3J_{H-H}$ = 7.7 Hz, 2H), 6.73 (d, $^3J_{H-H}$ = 7.5 Hz, 2H), 4.27 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 141.6, 140.3, 135.9, 131.8, 131.5, 131.2, 129.0, 128.8, 128.3, 124.5, 124.2, 123.2, 94.4 ppm. IR (thin film): 3018, 1490, 1444, 1215, 1088, 1050, 755, 690 cm^{-1}. HRMS calculated for $C_{19}H_{16}ClO_2S_2$ 375.0280, found 375.0298 $[M + H]^+$.

*Bis(phenylsulfinyl)(4-methylphenyl)methane (**2m**).* The reaction was performed following General Procedure A with **1m** (115 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv), and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 5:95) to give the product (40.1 mg, 45% yield, *rac*/*meso* = 7.25:1) as a yellow solid. Compound *rac*-**2m** was purified by silica gel column (eluted with EtOAc/CH_2Cl_2 = 3:97) to give yellow solid (35.0 mg, 40% yield). The spectroscopic data of *rac*-**2m** are as follows: R_f = 0.2 (EtOAc/CH_2Cl_2 = 1:9). Mp = 123−124 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44−7.35 (m, 8H), 7.16 (d, $^3J_{H-H}$ = 8.1 Hz, 2H), 6.93 (d, $^3J_{H-H}$ = 7.8 Hz, 2H), 6.67 (d, $^3J_{H-H}$ = 7.2 Hz, 2H), 4.26 (s, 1H), 2.27 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 142.0, 140.5, 139.6, 131.4, 131.0, 130.4, 128.8, 128.8, 128.6, 125.3, 124.5, 124.4, 121.4, 95.1, 21.2 ppm. IR (thin film): 3055, 2922, 2854, 1511, 1476, 1443, 1112, 1076, 1022, 998, 826, 719, 688 cm^{-1}. HRMS calculated for $C_{20}H_{18}O_2S_2Na$ 377.0646, found 377.0638 $[M + Na]^+$.

*Bis(phenylsulfinyl)(4-(tert-butyl)phenyl))methane (**2n**).* The reaction was performed following General Procedure A with **1n** (136 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv), and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 5:95) to give the product (49.7 mg, 50% yield, *rac*/*meso* = 4:1) as a yellow solid. Compound *rac*-**2n** was purified by silica gel column (eluted with EtOAc/CH_2Cl_2 = 3:97,) to give yellow solid (37.1 mg, 37% yield). The spectroscopic data of *rac*-**2n** are as follows: R_f = 0.2 (EtOAc/CH_2Cl_2 = 1:9). Mp = 118−119 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37−7.22 (m, 8H), 7.14 (d, $^3J_{H-H}$ = 7.5 Hz, 4H), 6.72 (d, $^3J_{H-H}$ = 7.5 Hz, 2H), 4.29 (s, 1H), 1.25 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 153.0, 142.1, 140.6, 131.5, 131.1, 130.2, 128.8, 128.6, 125.0, 124.6, 124.6, 121.5, 95.0, 34.6, 31.1 ppm. IR (thin film): 3018, 1215, 1050, 746, 669 cm^{-1}. HRMS calculated for $C_{23}H_{25}O_2S_2$ 397.1296, found 397.1318 $[M + H]^+$.

*Bis(phenylsulfinyl)(4-(methoxyl)phenyl)methane (**2o**).* The reaction was performed following General Procedure A with **1o** (123 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv), and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 7:93) to give the product (27.4 mg, 30% yield, *rac*/*meso* = 6.4:1) as a yellow solid. Compound *rac*-**2o** was purified by silica gel column (eluted with EtOAc/CH_2Cl_2 = 5:95) to give yellow solid (20.0 mg, 22% yield). The spectroscopic data of *rac*-**2o** are as follows: R_f = 0.2 (EtOAc/CH_2Cl_2 = 1:9). Mp = 104−105 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44−7.24 (m, 8H), 7.15 (d, $^3J_{H-H}$ = 7.5 Hz, 2H), 6.71 (d, $^3J_{H-H}$ = 7.5 Hz, 2H), 6.65 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 4.24 (s, 1H), 3.74 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 160.7, 142.1, 140.5, 131.8, 131.4, 131.0, 128.8, 128.6, 124.5, 124.4, 116.3, 113.5, 94.8, 55.1 ppm. IR (thin film): 3018, 1510, 1441, 1254, 1215, 1179, 1086, 1046, 754, 668 cm^{-1}. HRMS calculated for $C_{20}H_{18}O_3S_2Na$ 393.0595, found 393.0599 $[M + Na]^+$.

*Bis(phenylsulfinyl)(2-methylphenyl)methane (**2p**).* The reaction was performed following General Procedure A with **1p** (115 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv) and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 5:95) to give the product (67.0 mg, 76% yield, *rac*/*meso* = 4.73:1) as a yellow solid. Compound *rac*-**2p** was purified by silica gel column (eluted with EtOAc/CH_2Cl_2 = 3:97) to give yellow solid (50.3 mg, 57% yield). The spectroscopic data of *rac*-**2p** are as follows: R_f = 0.2 (EtOAc/CH_2Cl_2 = 1:9). Mp = 150−151 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, $^3J_{H-H}$ = 7.5 Hz, 1H), 7.36−7.31 (m, 4H), 7.26−7.19 (m, 8H), 6.73 (d, $^3J_{H-H}$ = 7.5 Hz, 1H), 4.66 (s, 1H), 0.81 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 141.8, 138.1, 131.6, 131.5, 131.2, 129.9, 129.6, 128.8, 128.7, 125.6, 124.7, 124.5, 123.0, 90.4, 17.8 ppm [one carbon signal is missing due to overlapping]. IR (thin film): 3056, 2924, 2854, 1452, 1437, 1419, 1383, 1274, 1197, 1159, 1132, 1119, 786, 697 cm^{-1}. HRMS calculated for $C_{20}H_{19}O_2S_2$ 355.0826, found 355.0832 $[M + H]^+$.

*Bis(phenylsulfinyl)(1-naphthyl)methane (**2q**).* The reaction was performed following General Procedure B with **1q** (145 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv), and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 3:97) to give the product (34.7 mg, 36% yield, *rac*/*meso* = 6:1) as a yellow solid. Compound *rac*-**2q** was purified by silica gel column (eluted with EtOAc/CH_2Cl_2 = 2:98) to give yellow solid (27.8 mg, 29% yield). The spectroscopic data of *rac*-**2q** are as follows: R_f = 0.2 (EtOAc/CH_2Cl_2 = 1:9). Mp = 130−131 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, $^3J_{H-H}$ = 7.5 Hz, 1H), 7.78 (d, $^3J_{H-H}$ = 8.0 Hz, 1H), 7.58 (t, $^3J_{H-H}$ = 7.5 Hz, 2H), 7.26 (m, 3H), 7.15−7.01 (m, 6H), 6.95 (t, $^3J_{H-H}$ = 7.5 Hz, 2H), 6.83 (t, $^3J_{H-H}$ = 7.5 Hz, 1H), 6.45 (t, $^3J_{H-H}$ = 8.6 Hz, 1H), 5.29 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 141.7, 140.3, 132.9, 131.8, 131.4, 131.1, 130.2, 129.8, 128.7, 128.4, 128.3, 126.2, 125.3, 124.4, 124.3, 120.4, 120.0, 89.0 ppm [one carbon signal is missing due to overlapping]. IR (thin film): 3056, 2966, 2928, 1464, 1418, 1160, 1129, 1070, 998, 804, 780, 688 cm^{-1}. HRMS calculated for $C_{23}H_{18}O_2S_2Na$ 413.0646, found 413.0647 $[M + Na]^+$.

*Bis(phenylsulfinyl)(3-thienyl)methane (**2r**).* The reaction was performed following General Procedure A with **1r** (111 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv), and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 5:95) to give the product (35.6 mg, 41% yield, *rac*/*meso* = 6:1) as a yellow solid. The *rac*-**2r** was purified by silica gel column (eluted with EtOAc/CH_2Cl_2 = 3:97) to give yellow solid (28.5 mg, 33% yield). The spectroscopic data of *rac*-**2r** are as follows: R_f = 0.2 (EtOAc/CH_2Cl_2 = 1:9). Mp = 132−133 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45−7.39 (m, 2H), 7.35−7.26 (m, 7H), 7.21 (s, 1H), 7.20 (t, $^4J_{H-H}$ = 1.7 Hz, 1H), 7.14 (m, 1H), 7.10 (m, 1H), 4.51 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 142.0, 140.4, 131.6, 131.2, 128.9, 128.8, 128.5, 127.3, 125.6, 124.5, 124.3, 123.8, 90.9 ppm. IR (thin film): 3057, 2920, 1474, 1418, 1173, 1069, 1021, 874, 836, 798, 688 cm^{-1}. HRMS calculated for $C_{17}H_{14}O_2S_3Na$ 369.0054. found 369.0063 $[M + Na]^+$.

*Bis(phenylsulfinyl)(2-thienyl)methane (**2s**).* The reaction was performed following General Procedure A with **1s** (111 mg, 0.5 mmol, 1.0 equiv), NaO-^{t}Bu (144 mg, 1.5 mmol, 3.0 equiv), and di-*tert*-butyl peroxide (200 μL, 1.1 mmol, 2.2 equiv). The crude product was isolated by flash chromatography on silica gel (eluted with EtOAc/CH_2Cl_2 = 5:95) to give the product (33.3 mg, 39% yield, *rac*/*meso* = 6:1) as a yellow solid. Compound *rac*-**2s** was purified by silica gel column (eluted with EtOAc/CH_2Cl_2 = 3:97) to give yellow solid (26.8 mg, 31% yield). The spectroscopic data of *rac*-**2s** are as follows: R_f = 0.2 (EtOAc/CH_2Cl_2 = 1:9). Mp = 112−113 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (m, 1H), 7.47 (m, 1H), 7.35 (m, 2H), 7.28−7.21 (m, 4H), 7.04 (d, $^3J_{H-H}$ = 7.0 Hz, 2H), 6.98 (m, 2H), 6.87 (m, 1H), 4.76 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 143.1, 141.6, 132.8, 132.4, 132.0, 130.7, 130.5, 130.0, 129.7, 128.7, 128.6, 127.3, 127.1, 125.2, 96.3 ppm. IR (thin film): 3082, 2922, 2854, 1579, 1493, 1451, 1400, 1338, 1223, 1089, 1000, 918, 852, 783, 615 cm^{-1}. HRMS calculated for $C_{17}H_{15}O_2S_3$ 347.0234, found 347.0227 $[M + H]^+$.

■ ASSOCIATED CONTENT

Supporting Information

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CCDC 1831929−1831930 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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