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A Route to Benzylic Arylsulfoxides from β-Ketosulfoxides

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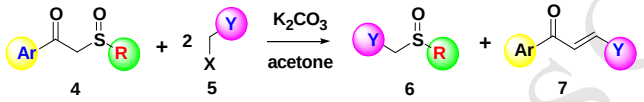

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A Route to Benzylic Arylsulfoxides from β-Ketosulfoxides

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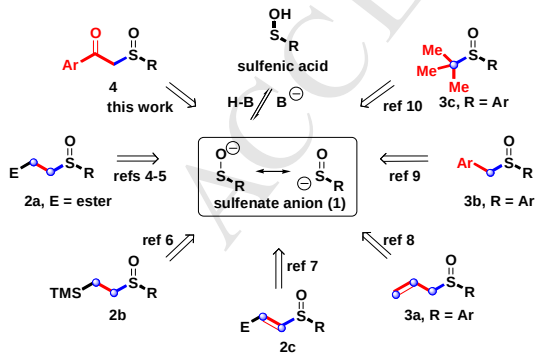
Abstract—The K_2CO_3-mediated benzylation of β-ketosulfoxides **4** with 2.0 equivalents of benzylic halides **5** affords benzylic arylsulfoxides **6** in moderate yields along with trace amounts of chalcones **7**. The products **6** are assumed to form in situ intermediates of sulfenate anions from β-ketosulfoxides which are commonly involved in carbon-sulfur bond formation. A plausible mechanism has been proposed.

1. Introduction

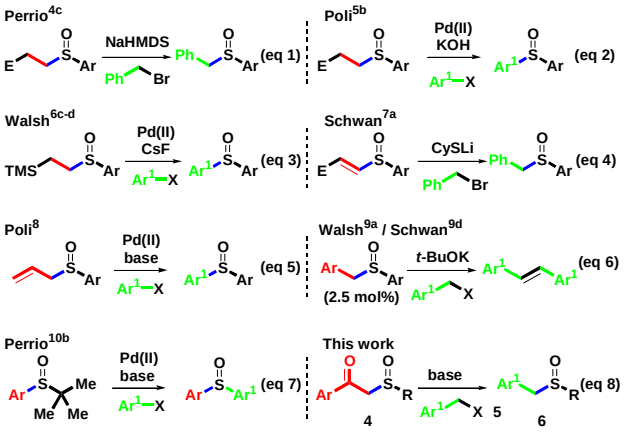
Sulfenate anion (**1**), a conjugated base of a sulfenic acid, is known to act as a highly reactive species in the synthetic [1 -2] and biological arenas.[3] From palladium-catalyzed, base-promoted or fluoride-mediated carbon-sulfur bond cleavage and formation processes, this intermediate sulfenate anion has been generated and trapped in situ from diversified precursors, including 2-carbons chain of β-sulfinyl esters **2a**,[4-5] β-sulfinyl silanes **2b**,[6] and 2-sulfinyl acrylates **2c**;[7] 3-carbon chains of allyl aryl sulfoxides **3a**;[8] and 1-carbon chains of aryl benzyl sulfoxides **3b**[9] and benzyl *t*-butyl sulfoxides **3c**.[10] The complementary routes based on the release of sulfenate anions have became viable alternatives for the enantio- and diastereoselective syntheses of substituted sulfoxides.[4a,11] General synthetic routes to sulfenate anion (**1**) are summarized in Scheme 1.

Scheme 1. Synthetic routes to sulfenate anions (**1**)



Despite a number of successful reports on the synthetic applications of **1**, it is still significant to find new precursors with a high level of chemical control. Due to the importance of such intermediates, the development of a new precursor of **1** with a broad substrate scope is still highly desirable. Herein, we introduce β-ketosulfoxides **4** as a synthon of **1** and demonstrate its ability in the conversion of benzylic halide into benzylic arylsulfoxide. Pioneering works by the groups of Perrio, Poli, Walsh and Schwan have been developed to access difunctionalized sulfoxides via one-pot alterative strategies (Scheme 2).[12] Generally, sulfoxides are generated by the metal complexes catalyzed oxidation of sulfides with oxidants[13] or the nucleophilic substitution of sulfinates with organometallic reagents.[14] As part of our ongoing efforts toward α-substituted β-ketosulfones,[15] the α-benzylation of β-ketosulfoxides is examined.

Scheme 2. Applications of sulfenate anion precursors



2. Results and discussion

To demonstrate the conversion from **4** to **6**, we employed coupling materials, **4a** and **5c**, as the model substrates to

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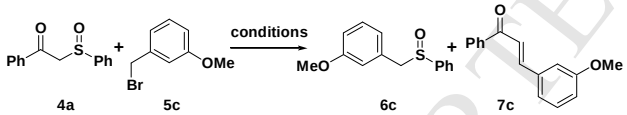
investigate the reaction conditions. Initially, the use of various bases (Cs_2CO_3, K_2CO_3, NaH, *t*-BuOK) was investigated, as shown in Table 1. Entries 1-2 show that poorer yields of **6c** are observed in the presence of Cs_2CO_3 and K_2CO_3 (2.0 equiv) in refluxing THF for 5 h. Among these bases screened, NaH and *t*-BuOK provides an unknown mixture (entries 3-4). After changing the solvents from THF to acetone, the yield of **6c** was enhanced slightly. In entries 5-6, K_2CO_3 produced a higher yield (30%) than Cs_2CO_3 (18%). While controlling K_2CO_3 as the base, the factors of time and equivalents were studied next. When the time was elongated to 20 h, the yield was improved to 50%. However, after an additional 5 h, the yield was decreased to 44% (entries 7-8). By increasing the equivalents of K_2CO_3 (2.0 → 3.3), **6c** was provided in 70% yield, as shown in entry 9. With excess amounts of K_2CO_3 (5.0 equiv), a lower yield (61%) was observed (entry 10). When the solvent was changed to warm DMF, no desired **6c** was isolated. Among entries 1-11, we hypothesized that low conversion to **7c** is due to the Michael reaction of chalcone with acetone. By elevating the temperature, elongating the time and increasing the base equivalents, more amounts of the complex mixture were derived from **7c**. These results show that 3.3 equivalents of K_2CO_3 caused a competition between the debenozylative benzylation of the sulfenate anion (for **6c**) and the benzylative desulfenylation of **4a** (for **7c**). In particular, **4a** auto-decomposed in the absence of **5c** in acetone at reflux for 80 h (entry 12). Overall, we believe that the system consisting of K_2CO_3 (3.3 equiv)/boiling acetone/20 h is an optimal combination for generating **6c**.

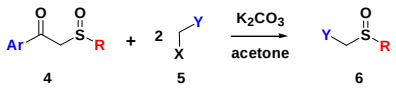
Table 1. Optimization conditions[a]



entry	base (equiv) /solvent	temp (°C)	time (h)	yield (%)[b] 6c	7c
1	Cs_2CO_3 (2.0) / THF	67	5	10	—[c]
2	K_2CO_3 (2.0) / THF	67	5	<5	—[c]
3	NaH (2.0) / THF	67	5	—[d]	
4	*t*-BuOK (2.0) / THF	67	5	—[d]	
5	Cs_2CO_3 (2.0) / acetone	57	5	18	—[c]
6	K_2CO_3 (2.0) / acetone	57	5	30	8
7	K_2CO_3 (2.0) / acetone	57	20	50	20
8	K_2CO_3 (2.0) / acetone	57	25	44	12
9	K_2CO_3 (3.3) / acetone	57	20	70	—[c]
10	K_2CO_3 (5.0) / acetone	25	25	61	10
11	K_2CO_3 (3.3) / DMF	100	5	—[d]	
12	K_2CO_3 (5.0) / acetone	57	80	—[e]	

[a]The reaction was run on **4a** (1.0 mmol), **5c** (2.0 equiv), solvents (10 mL). [b]Isolated yields. [c]No detection. [d]Complex products. [e]Removal of **5c**.

Table 2. Synthesis of **6**[a]

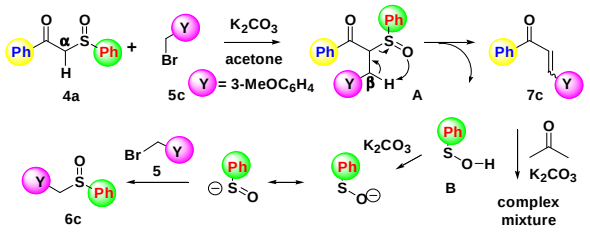


entry	**4**, Ar =, R =	**5**, Y =, X =	**6** (%)[b]
1	**4a**, Ph, Ph	**5a**, Ph, Br	**6a**, 76
2	**4a**, Ph, Ph	**5b**, 2-FC_6H_4, Br	**6b**, 70
3	**4a**, Ph, Ph	**5c**, 3-$MeOC_6H_4$, Br	**6c**, 70
4	**4a**, Ph, Ph	**5d**, 4-FC_6H_4, Br	**6d**, 68
5	**4a**, Ph, Ph	**5e**, 4-$NO_2C_6H_4$, Br	**6e**, 70
6	**4a**, Ph, Ph	**5f**, 4-PhC_6H_4 , Br	**6f**, 73
7	**4a**, Ph, Ph	**5g**, 1-naphthalene, Br	**6g**, 72
8	**4a**, Ph, Ph	**5h**, 2-quinoline, Br	**6h**, 65
9	**4a**, Ph, Ph	**5i**, 9-anthracene, Br	**6i**, 60
10	**4a**, Ph, Ph	**5j**, $CH=CH_2$, Br	**6j**, 65
11	**4b**, Ph, 3-$MeOC_6H_4$	**5a**, Ph, Br	**6k**, 70
12	**4b**, Ph, 3-$MeOC_6H_4$	**5b**, 2-FC_6H_4, Br	**6l**, 72
13	**4b**, Ph, 3-$MeOC_6H_4$	**5c**, 3-$MeOC_6H_4$, Br	**6m**, 73
14	**4b**, Ph, 3-$MeOC_6H_4$	**5e**, 4-$NO_2C_6H_4$, Br	**6n**, 67
15	**4b**, Ph, 3-$MeOC_6H_4$	**5g**, 1-naphthalene, Br	**6o**, 65
16	**4b**, Ph, 3-$MeOC_6H_4$	**5h**, 2-quinoline, Br	**6p**, 60
17	**4c**, Ph, 4-FC_6H_4	**5a**, Ph, Br	**6q**, 68
18	**4c**, Ph, 4-FC_6H_4	**5b**, 2-FC_6H_4, Br	**6r**, 64
19	**4c**, Ph, 4-FC_6H_4	**5c**, 3-$MeOC_6H_4$, Br	**6s**, 67
20	**4c**, Ph, 4-FC_6H_4	**5e**, 4-$NO_2C_6H_4$, Br	**6t**, 63
21	**4c**, Ph, 4-FC_6H_4	**5g**, 1-naphthalene, Br	**6u**, 60
22	**4d**, Ph, $PhCH_2$	**5a**, Ph, Br	**6v**, 76
23	**4d**, Ph, $PhCH_2$	**5b**, 2-FC_6H_4, Br	**6w**, 78
24	**4d**, Ph, $PhCH_2$	**5c**, 3-$MeOC_6H_4$, Br	**6x**, 77
25	**4d**, Ph, $PhCH_2$	**5g**, 1-naphthalene, Br	**6y**, 76
26	**4e**, 4-$MeOC_6H_4$, Ph	**5a**, Ph, Br	**6a**, 71
27	**4f**, 4-$NO_2C_6H_4$, Ph	**5a**, Ph, Br	**6a**, 70
28	**4g**, 4-PhC_6H_4, Ph	**5a**, Ph, Br	**6a**, 73
29	**4h**, 3,4-$CH_2O_2C_6H_3$, Ph	**5a**, Ph, Br	**6a**, 71
30	**4i**, 2-naphthalene, Ph	**5a**, Ph, Br	**6a**, 68
31	**4j**, 3,4-$Cl_2C_6H_3$, Ph	**5a**, Ph, Br	**6a**, 66
32	**4e**, 4-$MeOC_6H_4$, Ph	**5b**, 2-FC_6H_4, Br	**6b**, 70
33	**4f**, 4-$NO_2C_6H_4$, Ph	**5b**, 2-FC_6H_4, Br	**6b**, 62
34	**4e**, 4-$MeOC_6H_4$, Ph	**5c**, 2-$MeOC_6H_4$, Br	**6c**, 62
35	**4f**, 4-$NO_2C_6H_4$, Ph	**5c**, 2-$MeOC_6H_4$, Br	**6c**, 69
36	**4a**, Ph, Ph	**5k**, (*E*)-CH=CHPh, Cl	**6z**, 70
37	**4a**, Ph, Ph	**5l**, 2-pyridine, Cl	**6aa**, 65
38	**4a**, Ph, Ph	**5m**, 3,4-$(MeO)_2$-2-pyridine, Cl	**6ab**, 60
39	**4a**, Ph, Ph	**5n**, 3,5-Me_2-4-MeO-2-pyridine, Cl	**6ac**, 60
40	**4a**, Ph, Ph	**5o**, 2-benzothiazole, Cl	**6ad**, 55

[a]The reaction was run on **4** (1.0 mmol), **5** (2.0 mmol), K_2CO_3 (3.3 mmol), acetone (10 mL), 57 °C, 20 h. [b]Isolated yields.

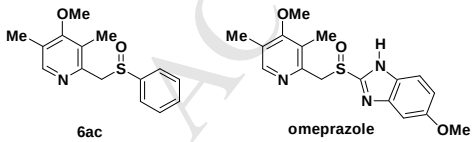
The proposed mechanism is illustrated in Scheme 3. Beginning with **4a**, the K_2CO_3-mediated α-benzylation of **4a** with **5c** generates **A**. Through the thermal-assisted intramolecular [2,3]-sigmatropic rearrangement of **A** (for β-H), **B** is formed along with chalcones **7c**. Following the deprotonation of **B** by K_2CO_3, in situ formed **1** undergoes nucleophilic substitution with **5c** to provide **6c**. Through the involvement of acetone, only minor amounts of **7c** were yielded.

Scheme 3. Proposed mechanism



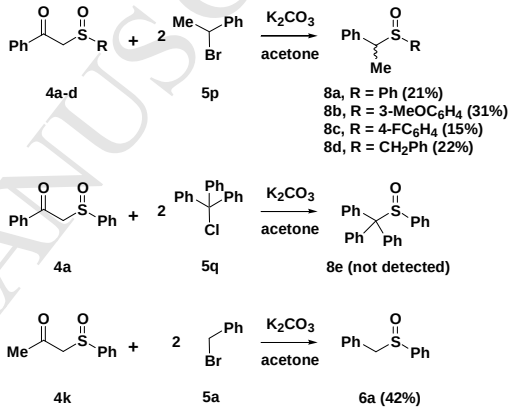
With the optimized conditions for the K_2CO_3-mediated reaction of **4a** and **5c** in boiling acetone, the substrate scope of β-ketosulfoxides **4a-j** (Ar = Ph, 4-$MeOC_6H_4$, 4-$NO_2C_6H_4$, 4-PhC_6H_4, 3,4-$CH_2O_2C_6H_3$, 2-naphthalene, 3,4-$Cl_2C_6H_3$; R = Ph, 3-$MeOC_6H_4$, 4-FC_6H_4, CH_2Ph) and aryl halides **5a-o** (Y = Ph, 2-FC_6H_4, 3-$MeOC_6H_4$, 4-FC_6H_4, 4-$NO_2C_6H_4$, 4-PhC_6H_4, 1-naphthalene, 2-quinoxline, 9-anthracene, vinyl, cinnamyl, 2-pyridine, 3,4-$(MeO)_2$-2-pyridine, 3,5-Me_2-4-MeO-2-pyridine, 2-benzothiazole; X = Br, Cl) was investigated, as shown in Table 2. In this process, a variety of benzylic arylsulfoxides **6a-ad** could be prepared from the reaction of **4** with 2.0 equivalents of benzylic halides **5** in the presence of 3.3 equivalents of K_2CO_3 with a range of 50%~78% yield. For the Ar and R substituents of **4**, the diversified electron-withdrawing or electron-donating aryl groups were well tolerated. When the Y group of **5** was tricyclic anthracene **5i**, heterocyclic quinoline **5h**, pyridine **5l-n** and benzothiazole **5o**, the desired skeleton **6** was formed. For the X group (Br and Cl) of **5**, no obvious yield changes were observed. The structure of **6f** was determined by single-crystal X-ray crystallography.[16]

Scheme 4. Structures of **6ac** and omeprazole

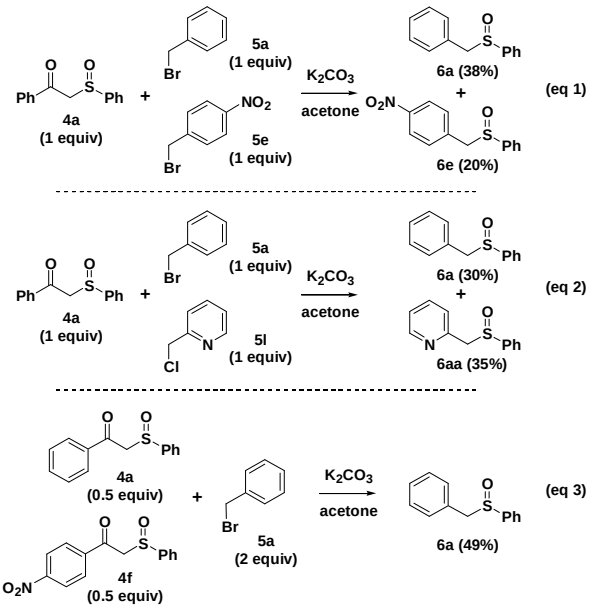


In Scheme 4, **6ac**, a stable surrogate of omeprazole, was synthesized by the one-pot route.[17a] Omeprazole is reported as a proton pump inhibitor used to treat gastroesophageal reflux disease and stomach ulcers.[17-18] Moreover, when 2.0 g of **4a** (8.2 mmol) was treated with the combination, 1.02 g of **6a** was isolated in a 58% yield. This route can be enlarged to a gram scale. Changing the primary bromide **5a** to a secondary bromide **5p**, the one-pot conversion of **4a-d** (R = Ph, 3-$MeOC_6H_4$, 4-FC_6H_4, $PhCH_2$) to **8a-d** was performed with a yield range of 15~31%, as shown in Scheme 5. Compared with the given yields of **6a-ad**, **8a-d** were produced in lower yields. Based on the above results, we envision that the sulfenate anion was not easily released via the alkylation of **4a-d** with secondary **5p** followed by a sequential [2,3]-sigmatropic rearrangement. Compounds **8a-d** were generated as two inseparated diastereoisomers with two chiral centers at carbon and sulfur atoms. Interestingly, **8d**, generated from the benzyl sulfenate anion, provided a ratio of 8:1. Attempts to use a tertiary trityl chloride (**5q**) failed to produce **8e** due to steric hindrance inhibiting the alkylation procedure. To change the aryl group (**4a-j**) to the methyl group (**4k**), **6a** was isolated in a 42% yield.

Scheme 5. Synthesis of **8a-d** and **6a**



Scheme 6. Control experiments



To extend the limitation of this one-pot domino route for cross coupling (Scheme 6), the reaction of **4a** with **5a** and **5e** was examined first. In Eq. 1, **6a** and **6e** were provided in

38% and 20% yields, respectively. Compound **4a** should prefer to alkylate **5e** with better reactivity such that the resulting sulfonate anion could trap **5a** to generate **6a** in a higher yield. We believe that the reactivity is a key factor affecting the product distribution. Compared with **5a** (X = Br) and **5l** (X = Cl), similar yields of **6a** (30%) and **6aa** (33%) were obtained by involving different leaving groups, as shown in Eq. 2. Furthermore, treatment of **4a** (Ar = Ph) and **4f** (Ar = 4-$NO_2C_6H_4$) with **5a** provided **6a** in 49% yield via the exchange of the intermolecular aryl group (Eq. 3). The control experiments could explain the plausible mechanism.

3. Conclusion

In summary, we developed a novel route for preparing various benzylic arylsulfoxides **6** in moderate yields via K_2CO_3-mediated benzylation of β-ketosulfoxides **4** with 2.0 equivalents of benzylic halides **5**. A plausible mechanism was proposed for the synthesis of **6** by the in situ-generated sulfonate anion. The structure of the key product was confirmed by X-ray crystallography. Further investigations regarding the synthetic application of β-ketosulfoxides will be conducted and published.

4. Experimental section

4.1. General. All other reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry nitrogen with magnetic stirring. Products in organic solvents were dried with anhydrous magnesium sulfate before concentration in vacuo. Melting points were determined with a SMP3 melting apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 400/200 and at 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (*J*) are given in Hertz. High resolution mass spectra (HRMS) were measured with a mass spectrometer Finnigan/Thermo Quest MAT 95XL. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD). Elemental analyses were carried out with Heraeus Vario III-NCSH, Heraeus CHN-OS-Rapid Analyzer or Elementar Vario EL III.

4.2. A representative synthetic procedure of skeleton 4 is as follows: K_2CO_3 (304 mg, 2.2 mmol) was added to a solution of thiophenol (1.0 mmol) in acetone (10 mL) at 25 ^{o}C. The reaction mixture was stirred at 25 ^{o}C for 10 min. α-Bromoketone (1.0 mmol) was added to the reaction mixture at 25 ^{o}C. The reaction mixture was stirred at 25 ^{o}C for 8 h. The reaction mixture was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Without further purification, freshly prepared *m*-chloroperoxybenzoic acid (*m*CPBA, 170 mg, 1.0 mmol) was added the resulting crude product in CH_2Cl_2 (10 mL) at 0 ^{o}C. The reaction mixture was stirred at 25 ^{o}C for 30 min. $NaHCO_3$ (1 g) was added to the stirred solution at 25 ^{o}C. The reaction mixture was stirred at 25 ^{o}C for 20 min. Then, water (10 mL) was added to the stirred solution at 25 ^{o}C. The reaction mixture was stirred at 25 ^{o}C for 20 min. The reaction mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 4/1~1/1) afforded **4**.

4.2.1. 2-Benzenesulfinyl-1-phenylethanone (4a). Yield = 70% (171 mg); Colorless solid; mp = 70-82 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{14}H_{13}O_2S$ 245.0636, found 245.0639; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.85 (m, 2H), 7.71-7.66 (m, 2H), 7.59-7.55 (m, 1H), 7.50-7.41 (m, 5H), 4.56 (d, *J* = 14.0 Hz, 1H), 4.29 (d, *J* = 14.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.30, 143.22, 135.92, 134.09, 131.52, 129.28 (2x), 128.73 (2x), 128.71 (2x), 124.20 (2x), 65.95.

4.2.2. 2-(3-Methoxybenzenesulfinyl)-1-phenylethanone (4b). Yield = 73% (200 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{15}H_{15}O_3S$ 275.0742, found 275.0748; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.86 (m, 2H), 7.60-7.56 (m, 1H), 7.46-7.42 (m, 2H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.26-7.25 (m, 1H), 7.19 (dt, *J* = 0.4, 6.8 Hz, 1H), 6.99 (ddd, *J* = 0.8, 2.8, 8.0 Hz, 1H), 4.55 (d, *J* = 14.0 Hz, 1H), 4.28 (d, *J* = 14.0 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.25, 160.37, 144.66, 135.96, 134.09, 130.26, 128.74 (2x), 128.72 (2x), 118.06, 116.21, 108.43, 66.06, 55.50.

4.2.3. 2-(4-Fluorobenzenesulfinyl)-1-phenylethanone (4c). Yield = 75% (197 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{14}H_{12}FO_2S$ 263.0542, found 263.0545; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.78 (m, 2H), 7.66-7.61 (m, 2H), 7.54-7.50 (m, 1H), 7.39-7.35 (m, 2H), 7.13-7.08 (m, 2H), 4.51 (d, *J* = 14.4 Hz, 1H), 4.29 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.16, 164.23 (d, *J* = 250.9 Hz), 138.42 (d, *J* = 3.1 Hz), 135.57, 133.99, 128.57 (2x), 128.46 (2x), 126.50 (d, *J* = 9.1 Hz, 2x), 116.37 (d, *J* = 22.8 Hz, 2x), 65.66; Anal. Calcd for $C_{14}H_{11}FO_2S$: C, 64.11; H, 4.23. Found: C, 64.32; H, 4.45.

4.2.4. 1-Phenyl-2-phenylmethanesulfinylethanone (4d). Yield = 73% (188 mg); Colorless solid; mp = 127-129 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{15}H_{15}O_2S$ 259.0793, found 259.0795; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.88 (m, 2H), 7.63-7.59 (m, 1H), 7.50-7.45 (m, 2H), 7.37-7.30 (m, 5H), 4.28 (d, *J* = 13.2 Hz, 1H), 4.23 (d, *J* = 15.2 Hz, 1H), 4.12 (d, *J* = 15.2 Hz, 1H), 4.11 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.54, 135.89, 134.26, 130.38 (2x), 129.09, 128.84 (2x), 128.83 (2x), 128.59 (2x), 128.51, 57.66, 57.56.

4.2.5. 2-Benzenesulfinyl-1-(4-methoxyphenyl)ethanone (4e). Yield = 75% (206 mg); Colorless solid; mp = 86-88 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{15}H_{15}O_3S$ 275.0742, found 275.0749; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.8 Hz, 2H), 7.63-

7.60 (m, 2H), 7.43-7.40 (m, 3H), 6.82 (d, *J* = 8.8 Hz, 2H), 4.45 (d, *J* = 14.4 Hz, 1H), 4.19 (d, *J* = 14.4 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.41, 164.05, 143.08, 131.22, 130.98 (2x), 129.03 (2x), 128.80, 123.97 (2x), 113.72 (2x), 65.55, 55.30.

4.2.6. 2-Benzenesulfinyl-1-(4-nitrophenyl)ethanone (4f). Yield = 76% (220 mg); Colorless solid; mp = 90-91 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{14}H_{12}NO_4S$ 290.0487, found 290.0485; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25-8.21 (m, 2H), 8.04-8.00 (m, 2H), 7.64-7.60 (m, 2H), 7.50-7.46 (m, 3H), 4.50 (d, *J* = 14.4 Hz, 1H), 4.38 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.17, 150.46, 142.34, 140.30, 131.72, 129.84 (2x), 129.35 (2x), 123.97 (2x), 123.73 (2x), 65.18.

4.2.7. 2-Benzenesulfinyl-1-biphenyl-4-ylethanone (4g). Yield = 77% (246 mg); Colorless solid; mp = 99-100 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{20}H_{17}O_2S$ 321.0949, found 321.0951; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.72-7.69 (m, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.59-7.56 (m, 2H), 7.51-7.37 (m, 6H), 4.57 (d, *J* = 14.0 Hz, 1H), 4.32 (d, *J* = 14.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.76, 146.53, 143.12, 139.18, 134.51, 131.41, 129.26 (2x), 129.19 (2x), 128.84 (2x), 128.37, 127.17 (2x), 127.08 (2x), 124.10 (2x), 65.80.

4.2.8. 2-Benzenesulfinyl-1-benzo[1,3]dioxol-5-yl-ethanone (4h). Yield = 76% (219 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{15}H_{13}O_4S$ 289.0535, found 289.0542; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.63 (m, 2H), 7.49-7.46 (m, 3H), 7.43 (dd, *J* = 2.0, 8.4 Hz, 1H), 7.31 (d, *J* = 2.0 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.01 (s, 2H), 4.45 (d, *J* = 14.4 Hz, 1H), 4.18 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.08, 152.66, 148.28, 143.18, 131.42, 130.81, 129.19 (2x), 125.87, 124.11 (2x), 107.90, 107.87, 102.02, 65.77; Anal. Calcd for $C_{15}H_{12}O_4S$: C, 62.49; H, 4.20. Found: C, 62.67; H, 4.41.

4.2.9. 2-Benzenesulfinyl-1-naphthalen-2-yl-ethanone (4i). Yield = 75% (221 mg); Colorless solid; mp = 96-97 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{18}H_{15}O_2S$ 295.0793, found 295.0796; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.84-7.79 (m, 2H), 7.73-7.64 (m, 4H), 7.52-7.37 (m, 5H), 4.61 (d, *J* = 14.4 Hz, 1H), 4.37 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.94, 142.95, 135.42, 132.91, 131.79, 131.16, 131.00, 129.40, 128.96 (2x), 128.79, 128.31, 127.40, 126.68, 123.91 (2x), 123.16, 65.65; Anal. Calcd for $C_{18}H_{14}O_2S$: C, 73.44; H, 4.79. Found: C, 73.62; H, 4.95.

4.2.10. 2-Benzenesulfinyl-1-(3,4-dichlorophenyl)ethanone (4j). Yield = 70% (218 mg); Colorless solid; mp = 84-87 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{14}H_{11}Cl_2O_2S$ 312.9857, found 312.9855; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 2.0 Hz, 1H), 7.69 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.66-7.63 (m, 2H), 7.52 (s, 1H), 7.51-7.48 (m, 3H), 4.43 (d, *J* = 14.0 Hz, 1H), 4.26 (d, *J* = 14.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.27, 142.64, 138.81, 135.59, 133.47, 131.73, 130.82, 130.59, 129.38 (2x), 127.85, 124.07 (2x), 65.19; Anal. Calcd for $C_{14}H_{10}Cl_2O_2S$: C, 53.69; H, 3.22. Found: C, 53.81; H, 3.17.

4.2.11. 1-Benzenesulfinylpropan-2-one (4k).[19] Yield = 70% (127 mg); Colorless solid; mp = 60-61 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_9H_{11}O_2S$ 183.0480, found 183.0488; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.69-7.56 (m, 5H), 3.86-3.75 (m, 2H), 2.25 (s, 1H).

4.3. A representative synthetic procedure of skeleton 6 is as follows: K_2CO_3 (460 mg, 3.3 mmol) was added to a solution of **4** (1.0 mmol) in acetone (10 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min. Benzylic halide **5** (2.0 mmol) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at 57 °C for 20 h. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 2/1~1/2) afforded **6**.

4.3.1. 1-Benzenesulfinylmethylbenzene (6a). For **4a**, yield = 76% (164 mg); For **4k**, yield = 42% (91 mg); Colorless solid; mp = 129-131 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{13}H_{13}OS$ 217.0687, found 217.0689; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.36 (m, 5H), 7.29-7.22 (m, 3H), 6.98-6.96 (m, 2H), 4.08 (d, *J* = 12.8 Hz, 1H), 3.99 (d, *J* = 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.67, 131.06, 130.26 (2x), 129.75 (2x), 129.00, 128.34 (2x), 128.14, 124.34 (2x), 63.52.

4.3.2. 1-Benzenesulfinylmethyl-2-fluorobenzene (6b). Yield = 70% (164 mg); Colorless solid; mp = 89-91 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{13}H_{12}FOS$ 235.0593, found 235.0598; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.32 (m, 5H), 7.22-7.16 (m, 1H), 7.01-6.95 (m, 2H), 6.91-6.86 (m, 1H), 4.05 (d, *J* = 12.8 Hz, 1H), 4.00 (d, *J* = 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.80 (d, *J* = 246.4 Hz), 142.46, 132.16 (d, *J* = 3.0 Hz), 131.00, 129.96 (d, *J* = 7.5 Hz), 128.59 (2x), 123.93 (2x), 123.77 (d, *J* = 3.8 Hz), 116.62 (d, *J* = 15.2 Hz), 114.96 (d, *J* = 22.0 Hz), 56.20.

4.3.3. 1-Benzenesulfinylmethyl-3-methoxybenzene (6c). Yield = 70% (172 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{14}H_{15}O_2S$ 247.0793, found 247.0796; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.32 (m, 5H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.73 (dd, *J* = 2.4, 8.0 Hz, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 6.41 (t, *J* = 2.0 Hz, 1H), 3.97 (d, *J* = 12.4 Hz, 1H), 3.87 (d, *J* = 12.4 Hz, 1H), 3.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.07, 142.44, 130.77, 130.20, 129.03, 128.48 (2x), 124.02 (2x), 122.29, 114.99, 113.86, 63.19, 54.71.

4.3.4. 1-Benzenesulfinylmethyl-4-fluorobenzene (6d). Yield = 68% (159 mg); Colorless solid; mp = 149-150 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{13}H_{12}FOS$ 235.0593, found 235.0599; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.29 (m, 5H), 6.87 (br s, 2H), 6.85 (br s, 2H), 3.96 (d, *J* = 12.8 Hz, 1H), 3.91 (d, *J* = 12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.46 (d, *J* = 245.6 Hz), 142.16, 131.80 (d, *J* = 8.4 Hz, 2x), 130.97, 128.65 (2x), 124.59 (d, *J* = 3.0 Hz), 124.07 (2x), 115.06 (d, *J* = 21.9 Hz, 2x), 61.85; Anal. Calcd for $C_{13}H_{11}FOS$: C, 66.64; H, 4.73. Found: C, 66.82; H, 4.79.

4.3.5. 1-Benzenesulfinylmethyl-4-nitrobenzene (6e). Yield = 70% (183 mg); Colorless solid; mp = 163-165 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{13}H_{12}NO_3S$ 262.0538, found 262.0541; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.48-7.39 (m, 3H), 7.34-7.31 (m, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 4.18 (d, *J* = 12.8 Hz, 1H), 3.98 (d, *J* = 12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.56, 141.62, 136.11, 131.44, 131.12 (2x), 129.00 (2x), 124.00 (2x), 123.13 (2x), 61.60.

4.3.6. 4-Benzenesulfinylmethylbiphenyl (6f). Yield = 73% (213 mg); Colorless solid; mp = 198-199 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{19}H_{17}OS$ 293.1000, found 293.1005; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.55 (m, 2H), 7.50-7.42 (m, 9H), 7.38-7.33 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 4.12 (d, *J* = 12.8 Hz, 1H), 4.06 (d, *J* = 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.75, 141.03, 140.34, 131.16, 130.75 (2x), 128.86 (2x), 128.77 (2x), 128.03, 127.47, 127.05 (2x), 126.99 (2x), 124.41 (2x), 63.23; Anal. Calcd for $C_{19}H_{16}OS$: C, 78.05; H, 5.52. Found: C, 78.16; H, 5.75. X-Ray diagram: crystal of compound **6f** was grown by slow diffusion of EtOAc into a solution of compound **6f** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the orthorhombic crystal system, space group P c a 21, *a* = 8.1512(5) Å, *b* = 5.4945(4) Å, *c* = 32.278(2) Å, *V* = 1445.65(17) Å^3, *Z* = 4, d_{calcd}= 1.274 g/cm^3, *F*(000) = 556, 2θ range 1.262~26.409°, R indices (all data) R1 = 0.0402, wR2 = 0.1172.

4.3.7. 1-Benzenesulfinylmethylnaphthalene (6g). Yield = 72% (192 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{17}H_{15}OS$ 267.0844, found 267.0843; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.54 (m, 1H), 7.84-7.82 (m, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.52-7.45 (m, 2H), 7.41-7.27 (m, 6H), 6.99 (d, *J* = 7.2 Hz, 1H), 4.67 (d, *J* = 12.8 Hz, 1H), 4.34 (d, *J* = 12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.08, 133.42, 131.72, 131.02, 129.46, 129.00, 128.60 (2x), 128.56, 126.37, 125.77, 125.55, 124.96, 124.08 (2x), 123.17, 61.90.

4.3.8. 2-Benzenesulfinylmethylquinoline (6h). Yield = 65% (174 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{16}H_{14}NOS$ 268.0796, found 268.0802; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.58 (dt, *J* = 1.6, 8.4 Hz, 1H), 7.47-7.39 (m, 3H), 7.35-7.28 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 1H), 4.34 (d, *J* = 12.4 Hz, 1H), 4.27 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.97, 147.57, 142.81, 136.34, 130.92, 129.53, 128.73 (2x), 128.60, 127.29, 126.89, 126.48, 123.86 (2x), 122.35, 65.75.

4.3.9. 9-Benzenesulfinylmethylanthracene (6i). Yield = 60% (190 mg); Colorless solid; mp = 138-139 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{21}H_{17}OS$ 317.1000, found 317.1008; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 8.01-7.97 (m, 4H), 7.45-7.39 (m, 4H), 7.33-7.28 (m, 1H), 7.21-7.16 (m, 4H), 5.33 (d, *J* = 13.2 Hz, 1H), 4.99 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.17 (2x), 131.09 (2x), 131.06, 129.06 (2x), 128.65 (3x), 126.45 (2x), 125.03 (3x), 124.12 (2x), 123.66 (2x), 120.91, 57.47.

4.3.10. (Prop-2-ene-1-sulfinyl)benzene (6j). Yield = 65% (108 mg); Colorless oil; HRMS (ESI, M^++1) calcd for $C_9H_{11}OS$ 167.0531, found 167.0533; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.54 (m, 2H), 7.50-7.45 (m, 3H), 5.66-5.55 (m, 1H), 5.29 (dq, *J* = 1.2, 10.8 Hz, 1H), 5.16 (dq, *J* = 1.2, 16.8 Hz, 1H), 3.53 (dd, *J* = 7.6, 12.8 Hz, 1H), 3.47 (dd, *J* = 7.6, 12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.70, 130.98, 128.90 (2x), 125.07, 124.20 (2x), 123.75, 60.66.

4.3.11. (3-Methoxybenzenesulfinylmethyl)benzene (6k). Yield = 70% (172 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{14}H_{15}O_2S$ 247.0793, found 247.0798; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.11 (m, 4H), 6.90-6.79 (m, 5H), 3.93 (d, *J* = 12.8 Hz, 1H), 3.89 (d, *J* = 12.4 Hz, 1H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.52, 143.58, 129.94 (2x), 129.30, 128.68, 127.90 (2x), 127.71, 117.42, 115.93, 108.04, 62.81, 54.92.

4.3.12. 1-Fluoro-2-(3-methoxybenzenesulfinylmethyl)benzene (6l). Yield = 72% (190 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{14}H_{14}FO_2S$ 265.0699, found 265.0695; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.09 (m, 2H), 6.95-6.88 (m, 2H), 6.85-6.80 (m, 4H), 3.94 (s, 2H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.63 (d, *J* = 247.1 Hz), 159.54, 143.69, 132.01 (d, *J* = 3.0 Hz), 129.73 (d, *J* = 8.3 Hz), 129.34, 123.53 (d, *J* = 3.8 Hz), 117.48, 116.47 (d, *J* = 15.2 Hz), 115.81, 114.72 (d, *J* = 21.2 Hz), 107.78, 55.93, 54.87.

4.3.13. 1-Methoxy-3-(3-methoxybenzenesulfinylmethyl)benzene (6m). Yield = 73% (201 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{15}H_{17}O_3S$ 277.0899, found 277.0897; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.15 (m, 1H), 7.04-7.00 (m, 1H), 6.84-6.83 (m, 1H), 6.82 (br s, 2H), 6.68 (dd, *J* = 2.8, 8.4 Hz, 1H), 6.49 (d, *J* = 7.2 Hz, 1H), 6.80 (t, *J* = 1.6 Hz, 1H), 3.88 (d, *J* = 12.8 Hz, 1H), 3.82 (d, *J* = 12.8 Hz, 1H), 3.56 (s, 3H), 3.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.51, 158.92, 143.77, 130.15, 129.26, 128.84, 122.19, 117.25, 115.86, 114.90, 113.64, 108.03, 62.97, 54.86, 54.54.

4.3.14. 1-(3-Methoxybenzenesulfinylmethyl)-4-nitrobenzene (6n). Yield = 67% (195 mg); Colorless solid; mp = 114-116 °C (recrystallized from hexanes and EtOAc);

HRMS (ESI, M^++1) calcd for $C_{14}H_{14}NO_4S$ 292.0644, found 292.0650; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.8 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.92 (ddd, *J* = 0.8, 2.4, 8.0 Hz, 1H), 6.86-6.84 (m, 1H), 6.84 (br s, 1H), 4.16 (d, *J* = 12.8 Hz, 1H), 3.95 (d, *J* = 12.8 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.01, 147.42, 143.00, 136.19, 131.07 (2x), 129.87, 123.01 (2x), 117.63, 115.90, 108.37, 61.53, 55.28.

4.3.15. 1-(3-Methoxybenzenesulfinylmethyl)naphthalene (6o). Yield = 65% (192 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{18}H_{17}O_2S$ 297.0949, found 297.0951; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.84 (m, 1H), 7.73-7.70 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.41-7.34 (m, 2H), 7.23-7.19 (m, 1H), 7.14-7.10 (m, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.84-6.81 (m, 3H), 4.51 (d, *J* = 12.8 Hz, 1H), 4.27 (d, *J* = 12.8 Hz, 1H), 3.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.42, 144.21, 133.05, 131.43, 129.22, 129.17, 128.59, 128.16, 125.99, 125.42, 125.30, 124.63, 122.86, 117.34, 115.81, 107.82, 61.28, 54.76.

4.3.16. 2-(3-Methoxybenzenesulfinylmethyl)quinoline (6p). Yield = 60% (178 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{17}H_{16}NO_2S$ 298.0902, found 298.0906; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.77 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.70-7.66 (m, 1H), 7.52-7.48 (m, 1H), 7.29 (t, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.07-7.04 (m, 2H), 6.95-6.92 (m, 1H), 4.40 (d, *J* = 12.4 Hz, 1H), 4.33 (d, *J* = 12.4 Hz, 1H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.10, 151.24, 147.86, 144.55, 136.54, 129.89, 129.79, 128.88, 127.48, 127.17, 126.73, 122.64, 117.94, 116.21, 108.07, 66.15, 55.28.

4.3.17. (4-Fluorobenzenesulfinylmethyl)benzene (6q). Yield = 68% (159 mg); Colorless solid; mp = 133-135 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{13}H_{12}FOS$ 235.0593, found 235.0599; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.28 (m, 2H), 7.25-7.19 (m, 3H), 7.09-7.04 (m, 2H), 6.94-6.91 (m, 2H), 4.06 (d, *J* = 12.4 Hz, 1H), 3.95 (d, *J* = 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.21 (d, *J* = 250.2 Hz), 137.86 (d, *J* = 3.1 Hz), 130.18 (2x), 128.55, 128.32 (2x), 128.17, 126.56 (d, *J* = 8.3 Hz, 2x), 115.96 (d, *J* = 22.7 Hz, 2x), 63.30.

4.3.18. 1-Fluoro-2-(4-fluorobenzenesulfinylmethyl)benzene (6r). Yield = 64% (161 mg); Colorless solid; mp = 112-113 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{13}H_{11}F_2OS$ 253.0499, found 253.0506; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.32 (m, 2H), 7.27-7.21 (m, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.05-7.02 (m, 2H), 6.94-6.89 (m, 1H), 4.10 (d, *J* = 12.8 Hz, 1H), 4.01 (d, *J* = 12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.35 (d, *J* = 250.2 Hz), 160.88 (d, *J* = 247.1 Hz), 137.86 (d, *J* = 2.3 Hz), 132.30 (d, *J* = 3.8 Hz), 130.23 (d, *J* = 8.3 Hz), 126.44 (d, *J* = 8.3 Hz, 2x), 123.96 (d, *J* = 3.7 Hz), 116.34 (d, *J* = 15.2 Hz), 116.03 (d, *J* = 22.0 Hz, 2x), 115.16 (d, *J* = 22.0 Hz), 56.21; Anal. Calcd for $C_{13}H_{10}F_2OS$: C, 61.89; H, 4.00. Found: C, 61.96; H, 4.12.

4.3.19. 1-(4-Fluorobenzenesulfinylmethyl)-3-methoxybenzene (6s). Yield = 67% (177 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{14}H_{14}FO_2S$ 265.0699, found 265.0702; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.29 (m, 2H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.07-7.02 (m, 2H), 6.77-6.75 (m, 1H), 6.50 (d, *J* = 7.6 Hz, 1H), 6.45-6.44 (m, 1H), 4.01 (d, *J* = 12.4 Hz, 1H), 3.87 (d, *J* = 12.4 Hz, 1H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.10 (d, *J* = 250.2 Hz), 159.25, 137.94 (d, *J* = 3.0 Hz), 129.99, 129.23, 126.49 (d, *J* = 8.3 Hz, 2x), 122.37, 115.86 (d, *J* = 22.7 Hz, 2x), 115.24, 113.92, 63.36, 54.85; Anal. Calcd for $C_{14}H_{13}FO_2S$: C, 63.62; H, 4.96. Found: C, 63.75; H, 5.10.

4.3.20. 1-(4-Fluorobenzenesulfinylmethyl)-4-nitrobenzene (6t). Yield = 63% (176 mg); Colorless solid; mp = 137-139 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{13}H_{11}FNO_3S$ 280.0444, found 280.0446; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.8 Hz, 2H), 7.35-7.30 (m, 2H), 7.15-7.08 (m, 4H), 4.18 (d, *J* = 12.8 Hz, 1H), 3.98 (d, *J* = 12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.42 (d, *J* = 250.9 Hz), 147.66, 137.08 (d, *J* = 3.0 Hz), 135.82, 131.16 (2x), 126.39 (d, *J* = 9.1 Hz, 2x), 123.26 (2x), 116.43 (d, *J* = 22.7 Hz, 2x), 61.73.

4.3.21. 1-(4-Fluorobenzenesulfinylmethyl)naphthalene (6u). Yield = 60% (170 mg); Colorless oil; HRMS (ESI, M^++1) calcd for $C_{17}H_{14}FOS$ 285.0749, found 285.0754; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.88 (m, 1H), 7.83-7.79 (m, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.49-7.44 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.28-7.23 (m, 2H), 7.01-6.96 (m, 3H), 4.68 (d, *J* = 12.4 Hz, 1H), 4.28 (d, *J* = 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.18 (d, *J* = 250.1 Hz), 138.33 (d, *J* = 3.1 Hz), 133.38, 131.64, 129.44, 129.06, 128.56, 126.41, 126.39 (d, *J* = 9.1 Hz, 2x), 125.82, 125.17, 124.92, 123.08, 115.81 (d, *J* = 26.7 Hz, 2x), 61.75.

4.3.22. (Phenylmethanesulfinylmethyl)benzene (6v). Yield = 76% (175 mg); Colorless solid; mp = 132-134 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{14}H_{15}OS$ 231.0844, found 231.0842; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.28 (m, 6H), 7.27-7.24 (m, 4H), 3.89 (d, *J* = 12.8 Hz, 2H), 3.80 (d, *J* = 12.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 129.82 (2x), 129.75 (4x), 128.49 (4x), 127.88 (2x), 56.81 (2x).

4.3.23. 1-Fluoro-2-(phenylmethanesulfinylmethyl)benzene (6w). Yield = 78% (193 mg); Colorless solid; mp = 73-75 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{14}H_{14}FOS$ 249.0749, found 249.0752; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.19 (m, 7H), 7.07-6.99 (m, 2H), 3.98 (d, *J* = 13.2 Hz, 1H), 3.90 (d, *J* = 13.2 Hz, 1H), 3.81 (d, *J* = 13.2 Hz, 1H), 3.79 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.48 (d, *J* = 245.6 Hz), 131.96 (d, *J* = 3.0 Hz), 129.80, 129.72, 129.65 (2x), 128.34 (2x), 127.79, 124.03 (d, *J* = 3.8 Hz), 117.28 (d, *J* = 15.2 Hz), 115.07 (d, *J* = 21.2 Hz), 57.27, 50.04.

4.3.24. 1-Methoxy-3-(phenylmethanesulfinylmethyl)benzene (6x). Yield = 77% (200 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{15}H_{17}O_2S$ 261.0949, found 261.0954; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.23 (m, 6H), 6.87-6.81 (m, 3H), 3.91 (d, *J* = 13.2 Hz, 1H), 3.87 (d, *J* = 13.2 Hz, 1H), 3.84 (d, *J* = 9.6 Hz, 1H), 3.81 (d, *J* = 9.6 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.57, 131.35, 129.89 (2x), 129.66 (2x), 128.62 (2x), 128.04, 122.05, 115.28, 113.64, 57.07, 57.00, 54.95.

4.3.25. 1-Phenylmethanesulfinylmethylnaphthalene (6y). Yield = 76% (213 mg); Colorless solid; mp =154-156 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{18}H_{17}OS$ 281.1000, found 281.1001; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.80 (m, 3H), 7.53-7.30 (m, 9H), 4.46 (d, *J* = 13.2 Hz, 1H), 4.34 (d, *J* = 13.2 Hz, 1H), 4.05 (d, *J* = 12.8 Hz, 1H), 3.98 (d, *J* = 12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.79, 131.64, 130.04 (2x), 129.18, 129.12, 128.84 (2x), 128.78, 128.61, 128.27, 126.61, 126.55, 126.02, 125.33, 123.28, 58.23, 55.96.

4.3.26. (3-Phenylprop-2-ene-1-sulfinyl)benzene (6z). Yield = 70% (169 mg); Colorless solid; mp = 84-85 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{15}H_{15}OS$ 243.0844, found 243.0846; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.58 (m, 2H), 7.51-7.47 (m, 3H), 7.30-7.21 (m, 5H), 6.41 (d, *J* = 15.6 Hz, 1H), 5.98 (dt, *J* = 7.6, 15.6 Hz, 1H), 3.73-3.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.76, 138.30, 135.94, 131.03, 128.89 (2x), 128.45 (2x), 128.05, 126.38 (2x), 124.24 (2x), 115.90, 60.57.

4.3.27. 2-Benzenesulfinylmethylpyridine (6aa). Yield = 65% (141 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{12}H_{12}NOS$ 218.0640, found 218.0644; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (dd, *J* = 0.8, 8.8 Hz, 1H), 7.54 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.45-7.35 (m, 5H), 7.13 (dd, *J* = 0.8, 8.8 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 4.16 (d, *J* = 12.4 Hz, 1H), 4.10 (d, *J* = 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.37, 149.49, 142.77, 136.41, 131.00, 128.84 (2x), 125.12, 123.89 (2x), 122.75, 65.30.

4.3.28. 2-Benzenesulfinylmethyl-3,4-dimethoxypyridine (6ab). Yield = 60% (166 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{14}H_{16}NO_3S$ 278.0851, found 278.0855; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 5.6 Hz, 1H), 7.52-7.48 (m, 2H), 7.38-7.35 (m, 3H), 6.70 (d, *J* = 5.6 Hz, 1H), 4.37 (d, *J* = 12.4 Hz, 1H), 4.003 (d, *J* = 12.4 Hz, 1H), 3.78 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.46, 145.58 (2x), 144.81, 143.71, 130.87, 128.77 (2x), 123.85 (2x), 107.24, 60.98, 60.44, 55.44.

4.3.29. 2-Benzenesulfinylmethyl-4-methoxy-3,5-dimethylpyridine (6ac). Yield = 60% (165 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{15}H_{18}NO_2S$ 276.1058, found 276.1067; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.42-7.40 (m, 2H), 7.38-7.33 (m, 3H), 4.33 (d, *J* = 12.4 Hz, 1H), 3.98 (d, *J* = 12.8 Hz, 1H), 3.57 (s, 3H), 2.12 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.86, 149.26, 149.15, 143.32, 130.85, 128.67 (2x), 126.82, 125.58, 123.80 (2x), 63.26, 59.52, 12.98, 11.04.

4.3.30. 2-Benzenesulfinylmethylbenzothiazole (6ad). Yield = 55% (150 mg); Colorless solid; mp = 108-110 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{14}H_{12}NOS_2$ 274.0360, found 274.0366; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 1.2, 8.8 Hz, 1H), 7.80 (dd, *J* = 1.2 Hz, 8.8 Hz, 1H), 7.55-7.52 (m, 2H), 7.46-7.35 (m, 4H), 7.35 (dt, *J* = 1.2, 7.2 Hz, 1H), 4.49 (d, *J* = 13.6 Hz, 1H), 4.45 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.57, 152.70, 142.21, 135.57, 131.52, 129.12 (2x), 126.18, 125.41, 123.97 (2x), 122.98, 121.41, 60.70.

4.4. A representative synthetic procedure of skeleton 8 is as follows: K_2CO_3 (460 mg, 3.3 mmol) was added to a solution of **4** (1.0 mmol) in acetone (10 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min. 2-Phenylethyl bromide **5p** (370 mg, 2.0 mmol) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at 57 °C for 20 h. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 2/1~1/2) afforded **8** with two unseparated isomers.

4.4.1. (1-Phenylethane-1-sulfinyl)benzene (8a). Two isomers with a ratio of 3:1; Yield = 21% (48 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{14}H_{15}OS$ 231.0844, found 231.0845; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.20 (m, 6H), 7.11-7.09 (m, 1H), 7.01-6.94 (m, 3H), 4.03 (q, *J* = 7.2 Hz, 1/4H), 3.79 (q, *J* = 7.2 Hz, 3/4H), 1.68 (d, *J* = 7.2 Hz, 3/4H), 1.58 (d, *J* = 7.2 Hz, 9/4H).

4.4.2. 1-Methoxy-3-(1-phenylethane-1-sulfinyl)benzene (8b). Two isomers with a ratio of 2:1; Yield = 31% (81 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{15}H_{17}O_2S$ 261.0949, found 261.0951 ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.19 (m, 4H), 7.02-6.88 (m, 3H), 6.78-6.70 (m, 5/3H), 6.55-6.54 (m, 1/3H), 3.98 (q, *J* = 7.2 Hz, 1/3H), 3.80 (q, *J* = 7.2 Hz, 2/3H), 3.66 (s, 2H), 3.60 (s, 1H), 1.67 (d, *J* = 7.2 Hz, 2H), 1.60 (d, *J* = 7.2 Hz, 1H).

4.4.3. 1-Fluoro-4-(1-phenylethane-1-sulfinyl)benzene (8c). Two isomers with a ratio of 2:1; Yield = 15% (37 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{14}H_{14}FOS$ 249.0749, found 249.0746; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.14 (m, 4H), 7.06-6.92 (m, 5H), 4.01 (q, *J* = 7.2 Hz, 1/3H), 3.75 (q, *J* = 7.2 Hz, 2/3H), 1.68 (d, *J* = 7.2 Hz, 2H), 1.56 (d, *J* = 6.8 Hz, 1H).

4.4.4. (1-Phenylethane-1-sulfinylmethyl)benzene (8d). Two isomers with a ratio of 8:1; Yield = 22% (54 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{15}H_{17}OS$ 245.1000, found 245.1002; For major product: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.24 (m, 8H), 7.19-7.16 (m, 2H), 3.79 (q, *J* = 7.2 Hz, 1H), 3.76 (d, *J* = 12.8 Hz, 1H),

3.59 (d, *J* = 13.2 Hz, 1H), 1.70 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.64, 130.47, 129.84 (2x), 128.93 (2x), 128.48 (2x), 128.18, 127.90 (2x), 127.83, 61.07, 55.12, 15.32.

4.5. A synthetic procedure of compounds 6c and 7c is as follows: (In Table 1, entry 7). K_2CO_3 (460 mg, 3.3 mmol) was added to a solution of **4a** (245 mg, 1.0 mmol) in acetone (10 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min. 3-Methoxybenzylic bromide **5c** (405 mg, 2.0 mmol) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at 57 °C for 20 h. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexane/EtOAc = 2/1~1/2) afforded **6c** (50%) and **7c** (20%).

4.5.1. 3-(3-Methoxyphenyl)-1-phenylpropenone (7c). Yield = 20% (48 mg); Colorless oil; HRMS (ESI, M^++1) calcd for $C_{16}H_{15}O_2$ 239.1072, found 239.1076; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04-8.01 (m, 2H), 7.77 (d, *J* = 16.0 Hz, 1H), 7.61-7.57 (m, 1H), 7.53-7.49 (m, 3H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.24 (br d, *J* = 8.0 Hz, 1H), 7.46 (br t, *J* = 2.0 Hz, 1H), 6.97 (dd, *J* = 2.4, 8.4 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.51, 159.89, 144.72, 138.12, 136.20, 132.76, 129.90, 128.59 (2x), 128.46 (2x), 122.33, 121.05, 116.26, 113.38, 55.30.

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Supplementary Material

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