

Supporting Information

Rhodium-catalyzed denitrogenative thioacetalization of N-sulfonyl-1,2,3-triazoles with disulfides: an entry to diverse transformation of terminal alkynes

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General experimental procedures

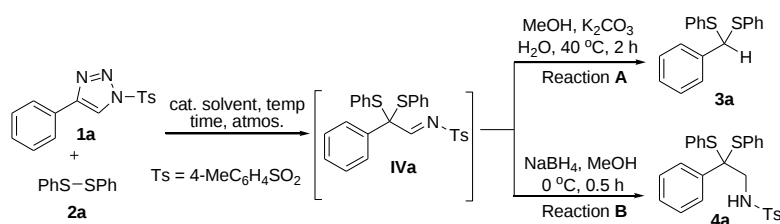
All reactions were carried out under nitrogen atmosphere. Proton and carbon magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) in the solvent of CDCl_3 as the internal standard (^1H NMR: TMS at 0.00 ppm, CHCl_3 at 7.26 ppm; ^{13}C NMR: CDCl_3 at 77.4 ppm) or were recorded using tetramethylsilane (TMS) in the solvent of $\text{DMSO}-d_6$ as the internal standard (^1H NMR: TMS at 0.00 ppm, DMSO at 2.50 ppm; ^{13}C NMR: DMSO at 39.5 ppm).

Preparation of *N*-sulfonyl-1,2,3-triazoles (1a-r). *N*-Sulfonyl-1,2,3-triazoles (**1a-r**) were synthesized according to the known literatures.¹

Optimization of conditions on rhodium-catalyzed thioacetalization

As shown in Table 1, our investigation for optimized conditions began by using model reaction of 4-phenyl-1-tosyl-1*H*-1,2,3-triazole (**1a**) with diphenyl disulfide (**2a**). The reaction was performed by using 2.5 mol% $\text{Rh}_2(\text{Oct})_4$ as the catalyst, toluene as the solvent at 60 °C under nitrogen atmosphere for 6 h (entry 1), and **1a** almost quantitatively transformed into 2-phenyl-2,2-bis(phenylthio)-*N*-tosylethanamine (**IVa**) (determination by TLC). After a work-up, **IVa** was isolated in only 44% yield because of instability of **IVa** during the work-up (*note: structure of IVa was confirmed by ^1H , ^{13}C NMR and mass spectroscopy, see Supporting Information for the details*), so we decided to continue the following two procedures (Reactions **A** and **B**). When **IVa** was hydrolyzed in the presence of aqueous K_2CO_3 at 40 °C for 2 h (Reaction **A**), 1-(phenyl(phenylthio)methylthio)benzene (**3a**) was obtained in 75% yield (entry 1). Reduction of **IVa** with NaBH_4 provided 2-phenyl-2,2-bis(phenylthio)-*N*-tosylethanamine (**4a**) in 81% yield (Reaction **B**) (entry 1). Other rhodium catalysts were tested (entries 2-5), and they were inferior to $\text{Rh}_2(\text{Oct})_4$. No **IVa** was found in the absence of catalyst (entry 6). Effect of solvents was investigated, and toluene was a suitable solvent (compare entries 1, 7-11). Yields decreased when temperature was lowered (entries 12 and 13). Only trace amount of products (**3a** and **4a**) were observed when nitrogen atmosphere was replaced with air (entry 14). Variation of time led to lower yields (entries 15 and 16).

Table 1 Optimization of conditions on rhodium-catalyzed thioacetalization of 4-phenyl-1-tosyl-1*H*-1,2,3-triazole (**1a**) with diphenyl disulfide (**2a**) leading to 2-phenyl-2-bis(phenylthio)-*N*-tosylethanamine (**IVa**), and synthesis of 1-(phenyl(phenylthio)methylthio)benzene (**3a**) and 2-phenyl-2-bis(phenylthio)-*N*-tosylethanamine (**4a**)^a



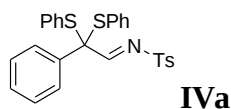
Entry	Cat.	Solvent	Temp (°C)	Time (h)	Yield of 3a/4a (%) ^b
1	Rh ₂ (Oct) ₄	PhMe	60	6	75/81
2	Rh ₂ (OAc) ₄	PhMe	60	6	34/35
3	[RhCp*Cl ₂] ₂	PhMe	60	6	0/0
4	[Rh(COD)Cl] ₂	PhMe	60	6	0/0
5	Rh(PPh ₃) ₃ Cl	PhMe	60	6	0/0
6	-	PhMe	60	6	0/0
7	Rh ₂ (Oct) ₄	benzene	60	6	58/62
8	Rh ₂ (Oct) ₄	<i>o</i> -xylene	60	6	75/79
9	Rh ₂ (Oct) ₄	<i>p</i> -xylene	60	6	10/12
10	Rh ₂ (Oct) ₄	mesitylene	60	6	66/68
11	Rh ₂ (Oct) ₄	DCE	60	6	56/55
12	Rh ₂ (Oct) ₄	PhMe	25	6	0/0
13	Rh ₂ (Oct) ₄	PhMe	40	6	trace/trace
14 ^c	Rh ₂ (Oct) ₄	PhMe	60	6	trace/trace
15	Rh ₂ (Oct) ₄	PhMe	60	3	31/40
16	Rh ₂ (Oct) ₄	PhMe	60	12	59/65

^a Reaction conditions: under nitrogen atmosphere, 4-phenyl-1-tosyl-1*H*-1,2,3-triazole (**1a**) (0.2 mmol), diphenyl disulfide (**2a**) (0.22 mmol), catalyst (0.005 mmol), solvent (2.0 mL), temperature (25–60 °C), time (3–12 h) in a sealed Schlenk tube for reaction of **1a** with **2a**. For Reaction **A**, MeOH (2.0 mL), K₂CO₃ (0.4 mmol), H₂O (0.2 mL) at 40 °C for 2 h; For Reaction **B**, NaBH₄ (0.2 mmol), MeOH (0.5 mL) at 0 °C for 0.5 h. OAc = acetate. Oct = octanoate. Cp* = 1,2,3,4,5-pentamethylcyclopenta-1,3-diene. COD = (1*Z*,5*Z*)-cycloocta-1,5-diene. DCE = 1,2-dichloroethane. ^b Isolated yield. ^c Under air.

General procedure for synthesis of compounds 3 and 4. A 25 mL Schlenk tube was evacuated and refilled with nitrogen atmosphere for three times, and then *N*-sulfonyl-1,2,3-triazole (**1**) (0.2 mmol), disulfide (**2**) (0.22 mmol), Rh₂(Oct)₄ (0.005

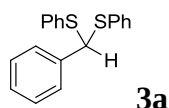
mmol, 4.0 mg), PhMe (2.0 mL) were added to the tube under nitrogen atmosphere. The tube was sealed, and the mixture was stirred at 60 °C till the reaction completed (TLC determination). The following procedures were performed for the resulting solution. For synthesis of **3**, methanol (2.0 mL), water (0.2 mL) and K₂CO₃ (0.4 mmol, 55 mg) were added to the tube with the solution, and the mixture was stirred at 40 °C for 2 h. The solvent in the resulting solution was removed, and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to provide the desired product (**3**); For synthesis of **4**, methanol (2.0 mL) and NaBH₄ (0.2 mmol, 7.6 mg) were added to the tube with the solution under condition of an ice bath, and the mixture was stirred at 0 °C for 0.5 h. The resulting solution was concentrated by a rotary evaporator, and the residue was purified by column chromatography on silica gel using dichloromethane/petroleum ether as the eluent to give the desired product (**4**).

Characterization data of compounds IVa



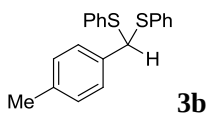
2-Phenyl-2,2-bis(phenylthio)-N-tosylethanamine (IVa). Eluent: petroleum ether/ethyl acetate (10:1). Yield 43 mg (44%). White solid. ¹H NMR (CDCl₃, 400 MHz) δ 2.46 (s, 3H), 7.08-7.12 (m, 4H), 7.23-7.31 (m, 13H), 7.68-7.70 (d, 2H, *J* = 8.68 Hz), 8.68 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz) δ 21.8, 70.3, 128.3, 128.4, 128.5, 128.7, 128.8, 129.4, 129.7, 129.9, 134.8, 136.1, 136.9, 144.8, 170.7. HR-MS (ESI) [M+Na]⁺ *m/z* calcd for C₂₇H₂₃NNaO₂S₃ 512.0789, found 512.0795.

Characterization data of compounds 3a-l and 4a-u

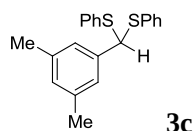


1-(Phenyl(phenylthio)methylthio)benzene (3a).² Eluent: petroleum ether/ethyl acetate (100:1). Yield 53 mg (75%) using **1a** as the substrate; 53 mg (75%) using **1k** as the substrate; 57 mg (81%) using **1p** as the substrate; 58 mg (82%) using **1q** as the

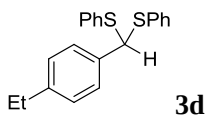
substrate; 62 mg (88%) using **1r** as the substrate. Yellow solid, m.p. 56-57 °C. ¹H NMR (CDCl₃, 400 MHz) δ 5.42 (s, 1H), 7.16-7.39 (m, 15H). ¹³C NMR (CDCl₃, 100 MHz) δ 60.5, 127.9, 128.0, 128.2, 128.6, 129.0, 132.6, 134.6, 139.8. ESIMS [M+Na]⁺ m/z 331.4.



1-((Phenylthio)(p-tolyl)methylthio)benzene (3b).³ Eluent: petroleum ether/ethyl acetate (100:1). Yield 53 mg (82%) using **1b** as the substrate; 45 mg (70%) using **1l** as the substrate. Yellow solid, m.p. 75-76 °C. ¹H NMR (CDCl₃, 400 MHz) δ 2.30 (s, 3H), 5.41 (s, 1H), 7.06-7.07 (d, 2H, *J* = 7.8 Hz), 7.21-7.27 (m, 8H), 7.32-7.35 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz) δ 21.3, 60.2, 127.8, 127.9, 128.9, 129.3, 132.4, 134.9, 136.8, 138.0. ESIMS [M+Na]⁺ m/z 345.3.

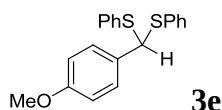


1-(Bis(phenylthio)methyl)-3,5-dimethylbenzene (3c). Eluent: petroleum ether/ethyl acetate (100:1). Yield 44 mg (66%). Yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 2.25 (s, 6H), 5.36 (s, 1H), 6.86 (s, 1H), 6.97 (s, 2H), 7.22-7.26 (m, 6H), 7.33-7.35 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz) δ 21.5, 60.7, 125.8, 127.9, 129.0, 130.0, 132.5, 135.1, 138.3, 139.7. HR-MS (ESI) [M+H]⁺ m/z calcd for C₂₁H₂₀NaS₂ 359.0904, found 359.0911.

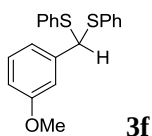


1-((4-Ethylphenyl)(phenylthio)methylthio)benzene (3d). Eluent: petroleum ether/ethyl acetate (100:1). Yield 57 mg (84%) using **1d** as substrate; 46 mg (67%) using **1m** as the substrate. Yellow solid, m.p. 63-64 °C. ¹H NMR (CDCl₃, 400 MHz) δ 1.18-1.22 (t, 3H, *J* = 7.32 Hz), 2.58-2.64 (q, 2H, *J* = 7.64 Hz), 5.42 (s, 1H), 7.08-7.11 (d, 2H, *J* = 8.24 Hz), 7.21-7.25 (m, 6H), 7.28-7.30 (d, 2H, *J* = 7.8 Hz), 7.33-7.35 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz) δ 15.6, 28.7, 60.4, 127.9, 128.0, 128.2, 129.0, 132.5, 135.0, 137.1, 144.4. HR-MS (ESI) [M+H]⁺ m/z calcd for C₂₁H₂₀NaS₂ 359.0904,

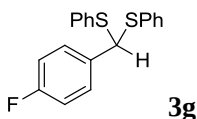
found 359.0908.



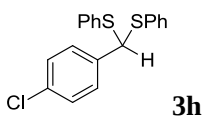
1-((4-Methoxyphenyl)(phenylthio)methylthio)benzene (3e).⁴ Eluent: petroleum ether/ethyl acetate (100:1). Yield 52 mg (77%) using **1e** as the substrate; 61 mg (90%) using **1n** as the substrate. Yellow solid, m.p. 82-83 °C. ¹H NMR (CDCl₃, 400 MHz) δ 3.75 (s, 3H), 5.42 (s, 1H), 6.77-6.79 (d, 2H, *J* = 8.24 Hz), 7.21-7.24 (m, 6H), 7.28-7.34 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz) δ 55.5, 59.9, 114.0, 127.9, 129.0, 129.3, 131.8, 132.6, 134.9, 159.5. ESIMS [M+Na]⁺ *m/z* 361.6.



1-((3-Methoxyphenyl)(phenylthio)methylthio)benzene (3f).⁵ Eluent: petroleum ether/ethyl acetate (100:1). Yield 36 mg (52%). Yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 3.73 (s, 3H), 5.39 (s, 1H), 6.76-6.78 (dd, 1H, *J* = 8.24 Hz, *J* = 2.72 Hz), 6.90-6.95 (m, 2H), 7.15-7.19 (m, 1H), 7.21-7.25 (m, 6H), 7.34-7.36 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz) δ 55.3, 60.5, 113.1, 114.2, 120.3, 127.9, 129.0, 129.6, 132.6, 134.6, 141.3, 159.7. ESIMS [M+Na]⁺ *m/z* 361.2.

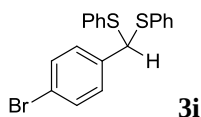


1-((4-Fluorophenyl)(phenylthio)methylthio)benzene (3g).⁶ Eluent: petroleum ether/ethyl acetate (100:1). Yield 54 mg (83%). Yellow solid, m.p. 51-52 °C. ¹H NMR (CDCl₃, 400 MHz) δ 5.40 (s, 1H), 6.90-6.94 (m, 2H), 7.22-7.26 (m, 6H), 7.28-7.34 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz) δ 59.7, 115.5 (d, *J* = 21.9 Hz), 128.1, 129.1, 129.7 (d, *J* = 8.6 Hz), 132.9, 134.3, 135.6 (d, *J* = 2.9 Hz), 162.3. (d, *J* = 246.0 Hz) ESIMS [M+Na]⁺ *m/z* 349.3.

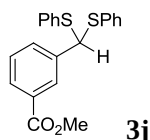


1-((4-Chlorophenyl)(phenylthio)methylthio)benzene (3h).³ Eluent: petroleum ether/ethyl acetate (100:1). Yield 48 mg (70%) using **1h** as the substrate; 51 mg (74%)

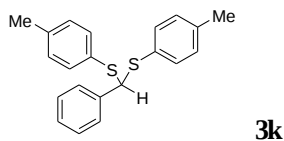
using **1o** as the substrate. Yellow solid, m.p. 99-100 °C. ¹H NMR (CDCl₃, 400 MHz) δ 5.37 (s, 1H), 7.20-7.28 (m, 10H), 7.31-7.34 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz) δ 59.8, 128.2, 128.7, 129.1, 129.4, 132.9, 133.8, 134.1, 138.4. ESIMS [M+Na]⁺ m/z 365.2.



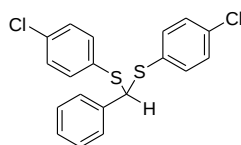
1-((4-Bromophenyl)(phenylthio)methylthio)benzene (3i).⁷ Eluent: petroleum ether/ethyl acetate (100:1). Yield 41 mg (53%). Yellow solid, m.p. 106-107 °C. ¹H NMR (CDCl₃, 400 MHz) δ 5.36 (s, 1H), 7.19-7.26 (m, 8H), 7.31-7.38 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz) δ 60.0, 122.1, 128.3, 129.2, 129.8, 131.8, 133.0, 134.2, 139.0. ESIMS [M+Na]⁺ m/z 409.2, 411.1.



Methyl 3-(bis(phenylthio)methyl)benzoate (3j). Eluent: petroleum ether/ethyl acetate (100: 1). Yield 30 mg (41%). Yellow solid, m.p. 63-64 °C. ¹H NMR (CDCl₃, 400 MHz) δ 3.89 (s, 3H), 5.46 (s, 1H), 7.22-7.25 (m, 6H), 7.30-7.35 (m, 5H), 7.53-7.55 (d, 1H, *J* = 7.80 Hz), 7.90-7.92 (d, 1H, *J* = 7.76 Hz), 8.02 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz) δ 52.3, 60.2, 128.2, 128.7, 129.0, 129.2, 129.3, 130.5, 132.4, 132.9, 134.1, 140.3, 166.7. HR-MS (ESI) [M+H]⁺ m/z calcd for C₂₁H₁₈NaO₂S₂ 389.0646, found 389.0639.

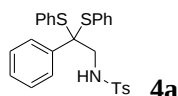


1-((p-Tolylthio)(phenyl)methylthio)-4-methylbenzene (3k).⁸ Eluent: petroleum ether/ethyl acetate (100:1). Yield 54 mg (81%) using **1a** as substrate; 59 mg (89%) using **1k** as the substrate. Yellow solid, m.p. 83-84 °C. ¹H NMR (CDCl₃, 400 MHz) δ 2.29 (s, 6H), 5.31 (s, 1H), 7.02-7.04 (d, 4H, *J* = 7.76 Hz), 7.20-7.26 (m, 7H), 7.31-7.33 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 21.3, 61.4, 128.0, 128.5, 129.7, 130.9, 133.3, 138.1, 140.1. ESIMS [M+Na]⁺ m/z 359.3.



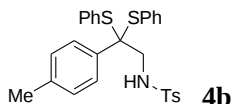
3l

1-((4-Chlorophenylthio)(phenyl)methylthio)-4-chlorobenzene (3l).³ Eluent: petroleum ether/ethyl acetate (100:1). Yield 54 mg (71%). Yellow solid, m.p. 65-66 °C. ¹H NMR (CDCl₃, 400 MHz) δ 5.33 (s, 1H), 7.18-7.31 (m, 13H). ¹³C NMR (CDCl₃, 100 MHz) δ 60.9, 127.9, 128.5, 128.7, 129.2, 132.6, 134.3, 134.4, 139.0. ESIMS [M+Na]⁺ m/z 399.1.



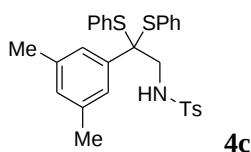
4a

2-Phenyl-2-bis(phenylthio)-N-tosylethanamine (4a). Eluent: dichloromethane/petroleum ether (2:1). Yield 79 mg (81%). White solid, m.p. 190-191 °C. ¹H NMR (CDCl₃, 400 MHz) δ 2.46 (s, 3H), 3.38-3.40 (d, 2H, *J* = 5.48 Hz), 5.16-5.19 (t, 1H, *J* = 5.48 Hz), 7.06-7.07 (m, 8H), 7.15-7.17 (m, 3H), 7.22-7.32 (m, 6H), 7.67-7.69 (d, 2H, *J* = 8.24 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 21.8, 46.8, 67.0, 127.4, 128.2, 128.4, 128.8, 129.8, 130.0, 136.7, 138.7, 143.7. HR-MS (ESI) [M+H]⁺ m/z calcd for C₂₇H₂₅NNaO₂S₃ 514.0945, found 514.0928.



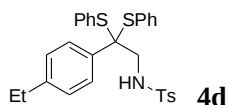
4b

2,2-Bis(phenylthio)-2-p-tolyl-N-tosylethanamine (4b). Eluent: dichloromethane/petroleum ether (2:1). Yield 83 mg (82%). White solid, m.p. 183-184 °C. ¹H NMR (CDCl₃, 400 MHz) δ 2.29 (s, 3H), 2.45 (s, 3H), 3.36-3.37 (d, 2H, *J* = 5.52 Hz), 5.14-5.16 (t, 1H, *J* = 5.52 Hz), 6.95-6.97 (d, 2H, *J* = 8.24 Hz), 7.07-7.09 (m, 8H), 7.18-7.20 (d, 2H, *J* = 8.28 Hz), 7.23-7.29 (m, 4H), 7.66-7.68 (d, 2H, *J* = 8.24 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 21.3, 21.8, 47.0, 66.9, 127.3, 128.3, 128.8, 129.7, 130.0, 135.6, 136.6, 138.0, 143.6. HR-MS (ESI) [M+H]⁺ m/z calcd for C₂₈H₂₇NNaO₂S₃ 528.1102, found 528.1111.

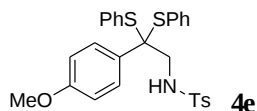


4c

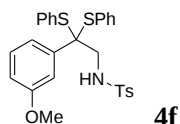
2-(3,5-Dimethylphenyl)-2,2-bis(phenylthio)-*N*-tosylethanamine (4c). Eluent: dichloromethane/petroleum ether (2:1). Yield 81 mg (78%). White solid, m.p. 178-179 °C. ¹H NMR (CDCl₃, 400 MHz) δ 2.15 (s, 6H), 2.44 (s, 3H), 3.37-3.39 (d, 2H, *J* = 5.04 Hz), 5.08-5.11 (t, 1H, *J* = 5.28 Hz), 6.80 (s, 1H), 6.84 (s, 2H), 7.09-7.12 (m, 8H), 7.25-7.29 (m, 4H), 7.65-7.67 (d, 2H, *J* = 8.24 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 21.5, 21.8, 46.9, 67.0, 125.9, 127.3, 128.8, 129.68, 129.74, 129.9, 130.0, 136.7, 137.6, 138.2, 143.6. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₂₉H₂₉NNaO₂S₃ 542.1258, found 542.1267.



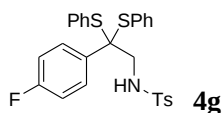
2-(4-Ethylphenyl)-2,2-bis(phenylthio)-*N*-tosylethanamine (4d). Eluent: dichloromethane/petroleum ether (2:1). Yield 89 mg (86%). White solid, m.p. 165-166 °C. ¹H NMR (CDCl₃, 400 MHz) δ 1.18-1.21 (t, 3H, *J* = 7.8 Hz), 2.46 (s, 3H), 2.56-2.61 (q, 2H, *J* = 7.64 Hz), 3.38-3.39 (d, 2H, *J* = 5.48 Hz), 5.14-5.17 (t, 1H, *J* = 5.52 Hz), 6.97-6.99 (d, 2H, *J* = 8.24 Hz), 7.05-7.08 (m, 8H), 7.21-7.30 (m, 6H), 7.67-7.69 (d, 2H, *J* = 8.24 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 15.8, 21.8, 28.6, 46.9, 66.9, 127.3, 127.6, 128.3, 128.8, 129.7, 129.9, 130.0, 135.7, 136.57, 136.63, 143.6, 144.4. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₂₉H₂₉NNaO₂S₃ 542.1258, found 542.1269.



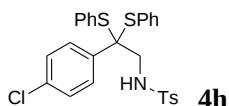
2-(4-Methoxyphenyl)-2,2-bis(phenylthio)-*N*-tosylethanamine (4e). Eluent: dichloromethane/petroleum ether (2:1). Yield 96 mg (92%). White solid, m.p. 175-176 °C. ¹H NMR (CDCl₃, 400 MHz) δ 2.46 (s, 3H), 3.35-3.37 (d, 2H, *J* = 5.48 Hz), 3.77 (s, 3H), 5.17-5.19 (t, 1H, *J* = 5.52 Hz), 6.68-6.70 (d, 2H, *J* = 9.16 Hz), 7.08-7.11 (m, 8H), 7.24-7.30 (m, 6H), 7.67-7.69 (d, 2H, *J* = 8.24 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 21.8, 47.0, 55.5, 66.7, 113.4, 127.3, 128.8, 129.7, 129.8, 129.9, 130.0, 130.6, 136.6, 143.7, 159.2. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₂₈H₂₇NNaO₃S₃ 544.1051, found 544.1039.



2-(3-Methoxyphenyl)-2-bis(phenylthio)-N-tosylethanamine (4f). Eluent: dichloromethane/petroleum ether. Yield 68 mg (65%). White solid, m.p. 181-182 °C. ¹H NMR (CDCl₃, 400 MHz) δ 2.45 (s, 3H), 3.37-3.38 (d, 2H, *J* = 5.48 Hz), 3.68 (s, 3H), 5.17-5.19 (t, 1H, *J* = 5.50 Hz), 6.72-6.74 (dd, 1H, *J* = 7.80 Hz, *J* = 2.28 Hz), 6.88-6.92 (m, 2H), 7.05-7.12 (m, 9H), 7.24-7.29 (m, 4H), 7.66-7.68 (d, 2H, *J* = 8.24 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 46.8, 55.4, 66.8, 113.9, 114.2, 120.4, 127.2, 128.8, 129.0, 129.66, 129.72, 129.9, 136.5, 140.0, 143.6, 159.3. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₂₈H₂₇NNaO₃S₃ 544.1051, found 544.1064.

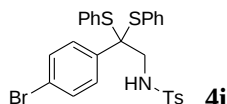


2-(4-Fluorophenyl)-2-bis(phenylthio)-N-tosylethanamine (4g). Eluent: dichloromethane/petroleum ether (2:1). Yield 97 mg (95%). White solid, m.p. 191-192 °C. ¹H NMR (CDCl₃, 400 MHz) δ 2.46 (s, 3H), 3.36-3.38 (d, 2H, *J* = 5.52 Hz), 5.21-5.24 (t, 1H, *J* = 5.48 Hz), 6.82-6.87 (dd, 2H, *J* = 8.72 Hz, *J* = 8.72 Hz), 7.06-7.01 (m, 8H), 7.25-7.33 (m, 6H), 7.68-7.70 (d, 2H, *J* = 8.24 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 46.8, 66.2, 114.9 (d, *J* = 21.9 Hz), 127.2, 128.9, 129.4, 129.8, 129.9, 130.3 (d, *J* = 8.6 Hz), 134.5 (d, *J* = 3.8 Hz), 136.4, 136.6, 143.7, 162.0. (d, *J* = 247.9 Hz). HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₂₇H₂₄FNNaO₂S₃ 532.0851, found 532.0843.

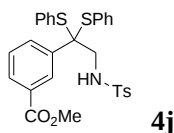


2-(4-Chlorophenyl)-2-bis(phenylthio)-N-tosylethanamine (4h). Eluent: dichloromethane/petroleum ether (2:1). Yield 89 mg (85%). White solid, m.p. 195-196 °C. ¹H NMR (CDCl₃, 400 MHz) δ 2.46 (s, 3H), 3.35-3.36 (d, 2H, *J* = 5.52 Hz), 5.23-5.26 (t, 1H, *J* = 5.26 Hz), 7.08-7.13 (m, 10H), 7.25-7.29 (m, 6H), 7.67-7.69 (d, 2H, *J* = 8.24 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 46.7, 66.2, 127.2, 128.1, 128.9, 129.2, 129.7, 129.9, 133.8, 136.3, 136.5, 137.3, 143.7. HR-MS (ESI) [M+H]⁺

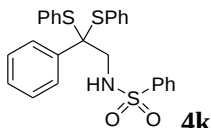
m/z calcd for $C_{27}H_{24}ClNNaO_2S_3$ 548.0555, found 548.0565.



2-(4-Bromophenyl)-2,2-bis(phenylthio)-N-tosylethanamine (4i). Eluent: dichloromethane/petroleum ether (2:1). Yield 78 mg (68%). White solid, m.p. 189-190 °C. 1H NMR ($CDCl_3$, 400 MHz) δ 2.46 (s, 3H), 3.34-3.36 (d, 2H, J = 5.48 Hz), 5.22-5.25 (t, 1H, J = 5.50 Hz), 7.07-7.12 (m, 8H), 7.18-7.20 (d, 2H, J = 8.72 Hz), 7.25-7.30 (m, 6H), 7.66-7.68 (d, 2H, J = 8.24 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.8, 46.7, 66.4, 122.1, 127.3, 129.0, 129.3, 130.0, 130.1, 131.1, 136.4, 136.6, 138.0, 143.8. HR-MS (ESI) $[M+H]^+$ m/z calcd for $C_{27}H_{24}BrNNaO_2S_3$ 592.0050, 594.0030, found 592.0061, 594.0042.

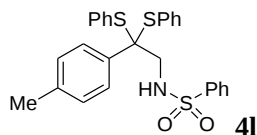


Methyl 3-(1,1-bis(phenylthio)-2-(tosylamino)ethyl)benzoate (4j). Eluent: dichloromethane/petroleum ether (2:1). Yield 58 mg (53%). White solid, m.p. 174-175 °C. 1H NMR ($CDCl_3$, 400 MHz) δ 2.46 (s, 3H), 3.43-3.44 (d, 2H, J = 5.52 Hz), 3.90 (s, 3H), 5.30-5.33 (t, 1H, J = 5.50 Hz), 7.04-7.09 (m, 8H), 7.18-7.31 (m, 5H), 7.39-7.41 (d, 1H, J = 7.8 Hz), 7.70-7.73 (d, 2H, J = 8.24 Hz), 7.84-7.86 (d, 1H, J = 7.8 Hz), 8.12 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 46.7, 52.3, 66.7, 127.2, 128.1, 128.9, 129.1, 129.2, 129.6, 129.85, 129.91, 130.1, 132.6, 136.4, 136.6, 139.4, 143.7, 166.6. HR-MS (ESI) $[M+H]^+$ m/z calcd for $C_{29}H_{27}NNaO_4S_3$ 572.1000, found 572.1009.

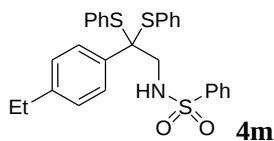


2-Phenyl-2,2-bis(phenylthio)-N-benzenesulfonyl ethanamine (4k). Eluent: dichloromethane/petroleum ether (2:1). Yield 73 mg (76%). White solid, m.p. 183-184 °C. 1H NMR ($CDCl_3$, 400 MHz) δ 3.40-3.41 (d, 2H, J = 5.52 Hz), 5.26-5.29 (t, 1H, J = 5.50 Hz), 7.07-7.08 (m, 8H), 7.15-7.17 (m, 3H), 7.22-7.27 (m, 2H),

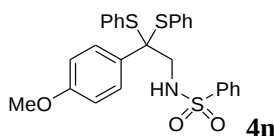
7.30-7.32 (m, 2H), 7.48-7.52 (m, 2H), 7.59-7.61 (m, 1H), 7.80-7.82 (d, 2H, $J = 8.24$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 46.6, 66.7, 127.2, 128.1, 128.3, 128.8, 129.3, 129.5, 129.8, 132.9, 136.6, 138.5, 139.4. HR-MS (ESI) $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{26}\text{H}_{23}\text{NNaO}_2\text{S}_3$ 500.0789, found 500.0799.



2,2-Bis(phenylthio)-2-*p*-tolylethyl-*N*-benzenesulfonylethanamine (4l). Eluent: dichloromethane/petroleum ether (2:1). Yield 73 mg (74%). White solid, m.p. 165-166 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 2.28 (s, 3H), 3.37-3.39 (d, 2H, $J = 5.52$ Hz), 5.22-5.25 (t, 1H, $J = 5.50$ Hz), 6.95-6.97 (d, 2H, $J = 8.24$ Hz), 7.05-7.09 (m, 8H), 7.17-7.20 (d, 2H, $J = 8.72$ Hz), 7.22-7.26 (m, 2H), 7.46-7.50 (m, 2H), 7.57-7.59 (m, 1H), 7.78-7.80 (d, 2H, $J = 8.72$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 21.2, 46.8, 66.7, 127.1, 128.1, 128.8, 129.3, 129.66, 129.71, 132.8, 135.5, 136.5, 137.9, 139.4. HR-MS (ESI) $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{27}\text{H}_{25}\text{NNaO}_2\text{S}_3$ 514.0945, found 514.0956.

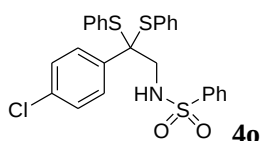


2-(4-Ethylphenyl)-2,2-bis(phenylthio)-*N*-benzenesulfonylethanamine (4m). Eluent: dichloromethane/petroleum ether (2:1). Yield 85 mg (84%). White solid, m.p. 159-160 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 1.17-1.21 (t, 3H, $J = 7.56$ Hz), 2.55-2.61 (q, 2H, $J = 7.48$ Hz), 3.39-3.40 (d, 2H, $J = 5.04$ Hz), 5.22-5.25 (t, 1H, $J = 5.28$ Hz), 6.97-6.99 (d, 2H, $J = 7.80$ Hz), 7.05-7.08 (m, 8H), 7.20-7.24 (m, 4H), 7.47-7.51 (m, 2H), 7.58-7.62 (m, 1H), 7.79-7.81 (d, 2H, $J = 7.32$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 15.7, 28.5, 46.8, 66.7, 127.1, 127.6, 128.2, 128.7, 129.3, 129.66, 129.71, 132.8, 135.5, 136.6, 139.4, 144.4. HR-MS (ESI) $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{28}\text{H}_{27}\text{NNaO}_2\text{S}_3$ 528.1102, found 528.1114.



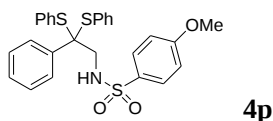
2-(4-Methoxyphenyl)-2,2-bis(phenylthio)-*N*-benzenesulfonylethanamine (4n).

Eluent: dichloromethane/petroleum ether (2:1). Yield 93 mg (92%). White solid, m.p. 153-154 °C. ¹H NMR (CDCl₃, 400 MHz) δ 3.37-3.38 (d, 2H, *J* = 5.48 Hz), 3.77 (s, 3H), 5.22-5.25 (t, 1H, *J* = 5.26 Hz), 6.68-6.70 (d, 2H, *J* = 9.16 Hz), 7.08-7.11 (m, 7H), 7.23-7.28 (m, 5H), 7.49-7.53 (m, 2H), 7.59-7.63 (m, 1H), 7.80-7.82 (d, 2H, *J* = 7.76 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 46.9, 55.4, 66.6, 113.3, 127.1, 128.8, 129.3, 129.6, 129.7, 130.5, 132.8, 136.5, 139.5, 159.1. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₂₇H₂₅NNaO₃S₃ 530.0894, found 530.0905.



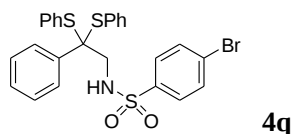
2-(4-Chlorophenyl)-2,2-bis(phenylthio)-N-benzenesulfonyl ethanamine (4o).

Eluent: dichloromethane/petroleum ether (2:1). Yield 87 mg (85%). White solid, m.p. 172-173 °C. ¹H NMR (CDCl₃, 400 MHz) δ 3.36-3.38 (d, 2H, *J* = 5.52 Hz), 5.25-5.28 (t, 1H, *J* = 5.50 Hz), 7.07-7.14 (m, 10H), 7.24-7.30 (m, 4H), 7.49-7.53 (m, 2H), 7.60-7.64 (m, 1H), 7.80-7.82 (d, 2H, *J* = 7.32 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 46.6, 66.1, 127.1, 128.2, 128.9, 129.2, 129.3, 129.7, 130.0, 132.9, 133.8, 136.5, 137.3, 139.4. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₂₆H₂₂ClNNaO₂S₃ 534.0399, found 534.0375.

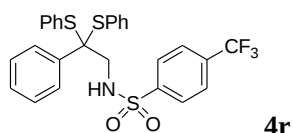


4-Methoxy-N-(2-phenyl-2-bis(phenylthio)ethyl)benzenesulfonamide (4p).

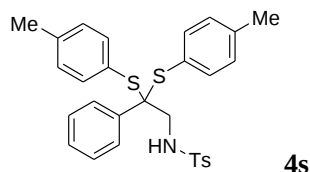
Eluent: dichloromethane/petroleum ether (2:1). Yield 83 mg (82%). White solid, m.p. 194-195 °C. ¹H NMR (CDCl₃, 400 MHz) δ 3.38-3.40 (d, 2H, *J* = 5.48 Hz), 3.88 (s, 3H), 5.18-5.21 (t, 1H, *J* = 5.50 Hz), 6.94-6.96 (d, 2H, *J* = 9.2 Hz), 7.07-7.11 (m, 8H), 7.14-7.18 (m, 3H), 7.23-7.27 (m, 2H), 7.31-7.33 (m, 2H), 7.72-7.74 (m, 2H, *J* = 8.72 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 46.6, 55.8, 66.8, 114.4, 128.0, 128.3, 128.8, 129.3, 129.6, 129.7, 131.0, 136.5, 138.6, 163.1. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₂₇H₂₅NNaO₃S₃ 530.0894, found 530.0909.



4-Bromo-*N*-(2-phenyl-2,2-bis(phenylthio)ethyl)benzenesulfonamide (4q). Eluent: dichloromethane/petroleum ether (2:1). Yield 95 mg (85%). White solid, m.p. 210-211 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 3.57-3.58 (d, 2H, J = 5.24 Hz), 5.46-5.49 (t, 1H, J = 5.04 Hz), 7.23-7.29 (m, 8H), 7.34-7.36 (m, 3H), 7.42-7.49 (m, 4H), 7.76-7.82 (m, 4H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 46.6, 66.8, 127.8, 128.1, 128.2, 128.7, 128.8, 129.5, 129.7, 132.5, 136.3, 138.4, 138.5. HR-MS (ESI) $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{26}\text{H}_{22}\text{BrNO}_2\text{S}_3$ 577.9894, 579.9873, found 577.9909, 579.9889.

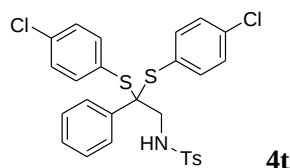


***N*-(2-Phenyl-2,2-bis(phenylthio)ethyl)-4-(trifluoromethyl)benzenesulfonamide (4r).** Eluent: dichloromethane/petroleum ether (2:1). Yield 97 mg (89%). White solid, m.p. 200-201 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 3.42-3.44 (d, 2H, J = 5.48 Hz), 5.42-5.44 (t, 1H, J = 5.04 Hz), 7.06-7.07 (m, 8H), 7.15-7.18 (m, 3H), 7.21-7.26 (m, 2H), 7.29-7.31 (m, 2H), 7.70-7.72 (d, 2H, J = 8.28 Hz), 7.88-7.90 (d, 2H, J = 8.28 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 46.7, 66.8, 123.4 (q, J = 270.8 Hz), 126.4 (q, J = 3.8 Hz), 127.6, 128.2, 128.8, 129.5, 129.8, 134.4 (q, J = 33.4 Hz), 136.2, 138.5, 142.9. HR-MS (ESI) $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{27}\text{H}_{22}\text{F}_3\text{NNaO}_2\text{S}_3$ 568.0662, found 568.0671.

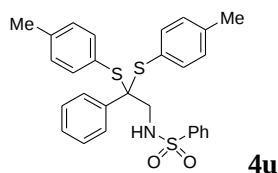


2,2-Bis(*p*-tolylthio)-2-phenyl-*N*-tosylethanamine (4s). Eluent: dichloromethane/petroleum ether (2:1). Yield 85 mg (82%). White solid, m.p. 177-178 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 2.26 (s, 6H), 2.47 (s, 3H), 3.33-3.35 (d, 2H, J = 5.52 Hz), 5.18-5.21 (t, 1H, J = 5.50 Hz), 6.85-6.88 (d, 4H, J = 8.24 Hz), 6.93-6.95 (d, 4H, J = 8.24 Hz), 7.16-7.19 (m, 3H), 7.29-7.34 (m, 4H), 7.69-7.71 (d, 2H, J = 8.28 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 21.4, 21.7, 46.4, 66.4, 126.0, 127.3,

127.9, 128.0, 128.4, 129.5, 129.8, 136.5, 136.6, 138.8, 140.0, 143.5. HR-MS (ESI) $[M+H]^+$ m/z calcd for $C_{29}H_{29}NNaO_2S_3$ 542.1258, found 542.1275.

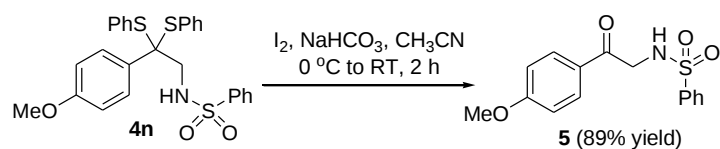


2,2-Bis(4-chlorophenylthio)-2-phenyl-N-tosylethanamine (4t). Eluent: dichloromethane/petroleum ether (2:1). Yield 87 mg (78%). White solid, m.p. 194-195 °C. 1H NMR ($CDCl_3$, 400 MHz) δ 2.49 (s, 3H), 3.31-3.32 (d, 2H, J = 5.48 Hz), 5.12-5.14 (t, 1H, J = 5.50 Hz), 6.96-6.98 (d, 4H, J = 8.72 Hz), 7.02-7.04 (d, 4H, J = 8.72 Hz), 7.19-7.21 (m, 3H), 7.26-7.32 (m, 4H), 7.67-7.69 (d, 2H, J = 8.24 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 46.4, 67.0, 127.2, 127.9, 128.2, 128.3, 128.4, 129.0, 129.9, 136.2, 136.3, 137.5, 138.1, 143.9. HR-MS (ESI) $[M+H]^+$ m/z calcd for $C_{27}H_{23}Cl_2NNaO_2S_3$ 582.0166, found 582.0185.



2,2-Bis(p-tolylthio)-2-phenyl-N-benzenesulfonyl-ethanamine (4u). Eluent: dichloromethane/petroleum ether (2:1). Yield 97 mg (96%). White solid, m.p. 151-152 °C. 1H NMR ($CDCl_3$, 400 MHz) δ 2.24 (s, 6H), 3.36-3.38 (d, 2H, J = 5.52 Hz), 5.25-5.28 (t, 1H, J = 5.50 Hz), 6.85-6.87 (d, 4H, J = 8.28 Hz), 6.93-6.95 (d, 4H, J = 7.80 Hz), 7.15-7.18 (m, 3H), 7.31-7.33 (m, 2H), 7.48-7.51 (m, 2H), 7.59-7.60 (m, 1H), 7.80-7.82 (d, 2H, J = 7.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 46.4, 66.4, 126.0, 127.2, 127.9, 128.0, 128.4, 129.3, 129.6, 132.8, 136.6, 138.8, 139.5, 140.0. HR-MS (ESI) $[M+H]^+$ m/z calcd for $C_{28}H_{27}NNaO_2S_3$ 528.1102, found 528.1089.

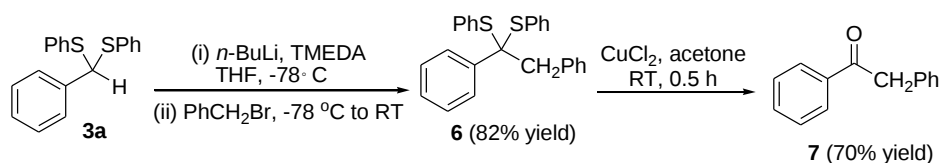
Synthesis of compound 5



Synthesis of compound 5.

2-(4-Methoxyphenyl)-2,2-bis(phenylthio)-*N*-benzenesulfonyl ethanamine (**4n**) (0.11 mmol, 55 mg) in CH₃CN (2.0 mL) was added to NaHCO₃ saturated aqueous solution (2 mL), the mixture was cooled to 0 °C, and I₂ (0.275 mmol, 70 mg) was added. After about 2 h, the resulting solution was quenched with a saturated aqueous Na₂S₂O₃ solution (1 mL). The solution was extracted with ethyl acetate (3×5 mL), and the combined organic phase was dried over anhydrous Na₂SO₄. The filtrate was concentrated by a rotary evaporator, and the residue was purified by a column chromatography on silica gel to provide the desired product (**5**) in 89% yield (29 mg). 1-(4-Methoxyphenyl)-2-(benzenesulfonylamino)ethanone (**5**). Eluent: dichloromethane/petroleum ether (2:1). White solid, m.p. 154-155 °C. ¹H NMR (CDCl₃, 400 MHz) δ 3.86 (s, 3H), 4.41-4.43 (d, 2H, *J* = 4.56 Hz), 5.75-5.77 (t, 1H, *J* = 4.12 Hz), 6.91-6.93 (d, 2H, *J* = 9.2 Hz), 7.47-7.56 (m, 3H), 7.81-7.84 (m, 2H, *J* = 8.72 Hz), 7.89-7.91 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) 48.3, 55.7, 114.3, 126.8, 127.2, 129.3, 130.3, 132.9, 139.2, 164.6, 190.8. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₁₅H₁₅NNaO₄S 328.0619, found 328.0612.

Synthesis of compounds 6 and 7

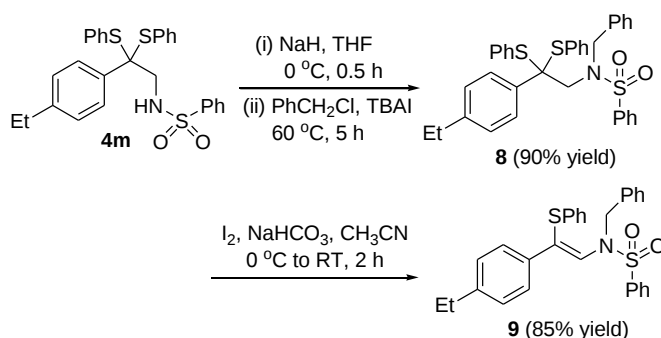


Synthesis of compound 6. 1-(Phenyl(phenylthio)methylthio)benzene (**3a**) (0.32 mmol, 100 mg) in anhydrous THF (4.0 mL), and TMEDA (0.4 mmol, 46.4 mg) were added to a flask, the mixture was cooled to -78 °C, and *n*-BuLi (0.4 mmol, 1.6 M in hexane) was added dropwise to the flask under N₂ atmosphere. The solution was stirred at room temperature for 0.5 h and cooled to -78 °C, then benzyl bromide (0.4 mmol, 69 mg) was added. The mixture was stirred at room temperature overnight, and then quenched with water. The resulting solution was filtrated through a pad of silica gel, and the filtrate was concentrated. The residue was purified by column chromatography on silica gel to provide the desired product (**6**) in 82% yield (104 mg). 1,2-Diphenyl-1,1-bis(phenylthio)ethane (**6**).⁹ Eluent: petroleum ether/ethyl acetate (100:1). Yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 3.58 (s, 2H), 6.88-6.90 (d,

2H, $J = 7.32$ Hz), 7.11-7.30 (m, 16H), 7.59-7.61 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) 47.1, 70.3, 126.7, 127.5, 127.6, 128.0, 128.1, 128.4, 128.8, 130.9, 133.1, 134.7, 136.0, 140.8. ESIMS $[\text{M}+\text{Na}]^+$ m/z 421.1.

Syntheisis of compound 7. 1,2-Diphenyl-1,1-bis(phenylthio)ethane (**6**) (0.23 mmol, 90 mg), CuCl_2 (0.58 mmol, 78 mg) and acetone (4.0 mL) were added to a flask, and the mixture was stirred for 0.5 h. The resulting solution was filtered, the filtrate was evaporated, and the residue was purified by column chromatography on silica gel to provide the desired product (**6**) in 70% yield (31 mg). 1,2-Diphenylethanone (**7**).¹⁰ Eluent: petroleum ether/ethyl acetate (20:1). Yellow solid, m.p. 61-62 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 4.29 (s, 2H), 7.25-7.28 (m, 3H), 7.31-7.35 (m, 2H), 7.44-7.47 (m, 2H), 7.53-7.57 (m, 1H), 8.01-8.03 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 45.6, 127.0, 128.72, 128.76, 128.78, 129.6, 133.3, 134.6, 136.7, 197.7 ESIMS. $[\text{M}+\text{Na}]^+$ m/z 219.2.

Syntheisis of compounds 8 and 9



Syntheisis of compounds 8. 2-(4-Ethylphenyl)-2,2-bis(phenylthio)-*N*-benzenesulfonylamine (**4m**) (1 mmol, 505 mg) was dissolved in anhydrous THF (8 mL), and the solution was cooled to 0 °C. NaH (1.5 mmol, 60 mg) was added to the solution, and the mixture was stirred at room temperature for 0.5 h, then benzyl chloride (1.5 mmol, 190 mg) in THF (2.0 mL) and tetrabutylammonium iodide (TBAI) (0.1 mmol, 37 mg) were added to the mixture at the same temperature. After a 5 h stirring at 60 °C, the resulting solution was quenched with small amount of water at room temperature, and the solution was filtrated through a pad of silica gel. The filtrate was concentrated, and the residue was purified by column

chromatography to provide the desired product (**8**) in 90% yield (535 mg). *N*-Benzyl-*N*-(2-(4-ethylphenyl)-2,2-bis(phenylthio)ethyl)- benzenesulfonamide (**8**). Eluent: dichloromethane/petroleum ether (2:1). Yellow oil. ^1H NMR (CDCl_3 , 300 MHz) δ 1.22-1.27 (t, 3H, $J = 7.56$ Hz), 2.59-2.67 (q, 2H, $J = 7.56$ Hz), 4.10 (s, 2H), 4.20 (s, 2H), 6.74-6.77 (m, 2H), 7.02-7.26 (m, 15H), 7.34-7.39 (m, 2H), 7.49-7.58 (m, 5H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 15.6, 28.4, 51.9, 56.9, 70.7, 127.3, 127.7, 127.8, 127.9, 128.1, 128.2, 128.5, 128.6, 129.3, 132.3, 133.2, 133.6, 135.4, 136.4, 140.8, 144.4. ESIMS $[\text{M}+\text{Na}]^+$ m/z 618.4.

Syntheisis of compounds 9. *N*-Benzyl-*N*-(2-(4-ethylphenyl)-2,2-bis(phenylthio)-ethyl)benzenesulfonamide (**8**) (0.5 mmol, 298 mg) was dissolved in CH_3CN (2.5 mL) and saturated NaHCO_3 aqueous solution (2.5 mL), the solution was cooled to 0 $^\circ\text{C}$, and I_2 (1.25 mmol, 320 mg) was added protionwise to the solution. After 2 h, the mixture was quenched with a saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution (1.0 mL). The solution was extracted with ethyl acetate (3 $\times$ 5 mL), the combined organic phase was dried over anhydrous Na_2SO_4 . The filtrate was concentrated by a rotary evaporator, and the residue was purified by a column chromatography on silica gel to provide the desired product (**9**) in 85% yield (206 mg). *N*-Benzyl-*N*-(2-(4-ethylphenyl)-2-(phenylthio)vinyl)benzenesulfonamide (**9**). Eluent: dichloromethane/petroleum ether (2:1). Yellow solid, m.p. 88-89 $^\circ\text{C}$. ^1H NMR (CDCl_3 , 400 MHz) δ 1.15-1.18 (t, 3H, $J = 7.56$ Hz), 2.51-2.57 (q, 2H, $J = 7.64$ Hz), 4.18 (s, 2H), 6.69 (s, 1H), 6.75-6.77 (d, 2H, $J = 8.28$ Hz), 6.85-6.90 (m, 4H), 7.02-7.10 (m, 5H), 7.16-7.25 (m, 3H), 7.56-7.60 (m, 2H), 7.65-7.69 (m, 1H), 7.84-7.86 (m, 2H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 15.3, 28.6, 51.6, 126.5, 127.2, 127.4, 127.5, 127.7, 128.30, 128.34, 128.8, 129.2, 129.4, 129.7, 130.3, 133.1, 133.4, 135.1, 135.7, 138.9, 144.7. HR-MS (ESI) $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{29}\text{H}_{27}\text{NNaO}_2\text{S}_2$ 508.1381, found 508.1364.

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^1H and ^{13}C NMR spectra of compounds **IVa**, **3**, **4** and **6-10**

