Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Visible-light-promoted CO_2 Oxidative 1,2-Thiosulfonylation of Styrenes with Sodium Sulfinates and Thiophenols

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1. General Information

All air- and moisture-insensitive reactions were carried out under an ambient atmosphere and monitored by thin-layer chromatography (TLC). Concentration under reduced pressure was performed by rotary evaporation at 40-50 °C at an appropriate pressure. Purified compounds were further dried under high vacuum. Yields refer to purified and spectroscopically pure compounds, unless otherwise stated. All air- and moisture-sensitive manipulations were performed using oven-dried glassware (120 ^{o}C for a minimum of 15 h), including standard Schlenk techniques under an atmosphere of argon. Irradiation of photochemical reactions were carried out using 40 W blue LEDs (450-470 nm, Wuhan GeAo Chemical Ltd.).

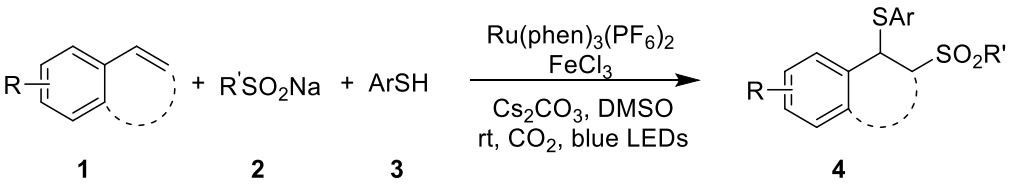
Solvents

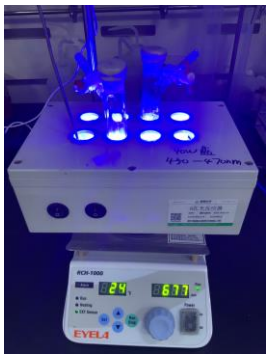
All solvents were purchased from Titan and dried by distillation. All deuterated solvents were purchased from J&K Scientific.

Spectroscopy and Instruments

^{1}H NMR spectra were recorded on Bruker Avance II 400 MHz spectrophotometers. Chemical shifts (δ) were reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. For ^{1}H NMR: $CDCl_3$, 7.26; For ^{13}C NMR: $CDCl_3$, 77.16; ^{13}C NMR spectra were recorded on 101 Hz with complete proton decoupling spectrophotometers. ^{19}F NMR spectra were observed in the ^{1}H-decoupled mode. NMR yield was determined by ^{1}H NMR using 1.1.2.2 - tetrachloroethane as an internal standard before working up the reaction. High-resolution mass spectra were obtained using Shimadzu LCMS-IT-TOF mass spectrometer and DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer. Gas chromatography analysis was performed on a 7820 (Zhongkehuifen China) instrument.

2. General Procedure of Product 4





In a 25 mL Schlenk tube styrenes **1** (0.2 mmol, 1 equiv), sodium sulfinates **2** (0.3 mmol, 1.5 equiv), thiophenols **3** (0.3 mmol, 1.5 equiv), $Ru(phen)_3(PF_6)_2$ (0.004 mmol, 2 mol%), $FeCl_3$ (0.06 mmol, 30 mol%), Cs_2CO_3 (0.4 mmol, 2 equiv) were added. Then it was evacuated by CO_2 cycles for three times. After that DMSO (2 mL) was added into the Schlenk tube under CO_2. The reaction mixture was placed under 40 W blue LEDs at room temperature. After 20 h, the reaction was completed and quenched upon the addition of water (10 mL). The mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried using $MgSO_4$ and then concentrated in vacuo. The crude product was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to give the pure product **4**.

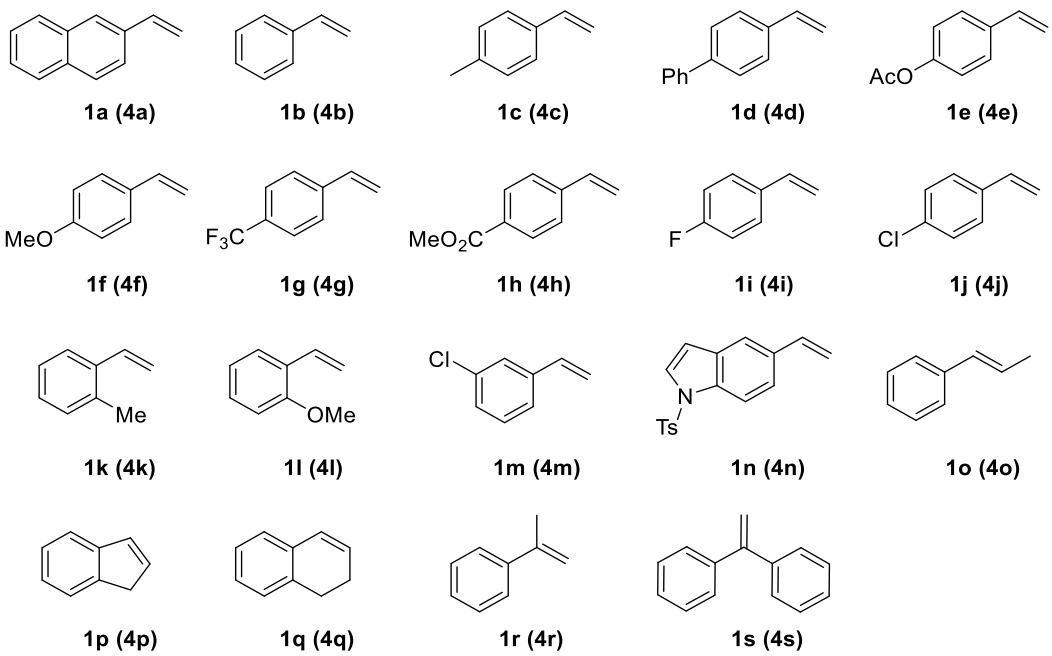
3. General Procedure of Gram-Scale Reaction

In a 350 mL Schlenk tube styrenes **1b** (417 mg, 4 mmol, 1 equiv), sodium sulfinates **2a** (1.0 g, 6.0 mmol, 1.5 equiv), thiophenols **3a** (740 mg, 6 mmol, 1.5 equiv), $Ru(phen)_3(PF_6)_2$ (74 mg, 0.08 mmol, 4 mol%), $FeCl_3$ (195 mg, 1.2 mmol, 30 mol%), Cs_2CO_3 (2.6 g, 8 mmol, 2 equiv) were added. Then it was evacuated by CO_2 cycles for three

times. After that DMSO (40 mL) was added into the Schlenk tube under CO_2. The reaction mixture was placed under 40 W blue LEDs at room temperature. After 20 h, the reaction was completed and quenched upon the addition of water (100 mL). The mixture was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were dried using $MgSO_4$ and then concentrated in vacuo. The crude product was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to give the pure product **4b** (0.76 g, 52%).

4. Substrates 1

All substrates **1** are commercially available. Inside the parentheses are the corresponding product number.



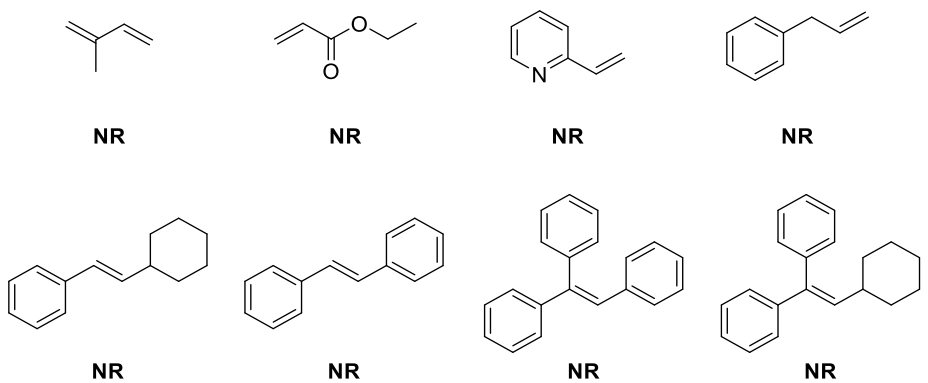
1a (4a) **1b (4b)** **1c (4c)** **1d (4d)** **1e (4e)**

1f (4f) **1g (4g)** **1h (4h)** **1i (4i)** **1j (4j)**

1k (4k) **1l (4l)** **1m (4m)** **1n (4n)** **1o (4o)**

1p (4p) **1q (4q)** **1r (4r)** **1s (4s)**

Substrates **1** below could not afford the corresponding products.



NR **NR** **NR** **NR**

NR **NR** **NR** **NR**

5. Substrates 2

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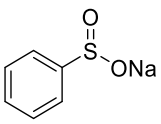
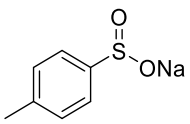
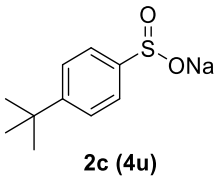


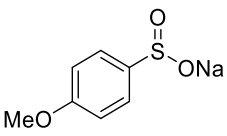
2a (4a)



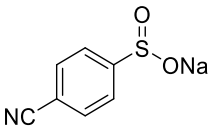
2b (4t)



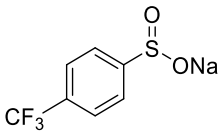
2c (4u)



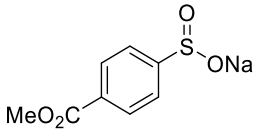
2d (4v)



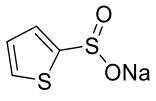
2e (4w)



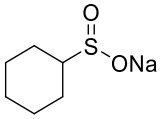
2f (4x)



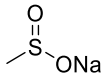
2g (4y)



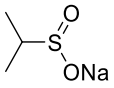
2h (4aa)



2i (4ab)

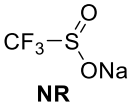


2j (4ac)



2k (4ad)

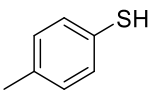
Substrates **2** below could not afford the corresponding products.



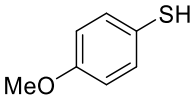
NR

6. Substrates 3

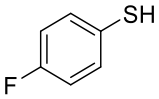
All substrates **3** are commercially available. Inside the parentheses are the corresponding product number.



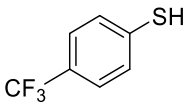
3a (4a)



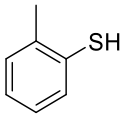
3b (4ae)



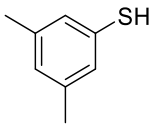
3c (4af)



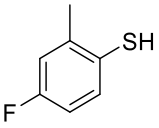
3d (4ag)



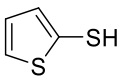
3e (4ah)



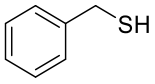
3f (4ai)



3g (4aj)

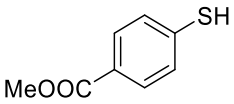


3h (4ak)

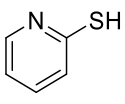


3i (4al)

Substrates **3** below could not afford the corresponding products.



NR



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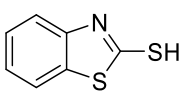
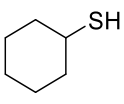


NR



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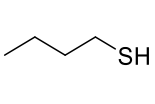
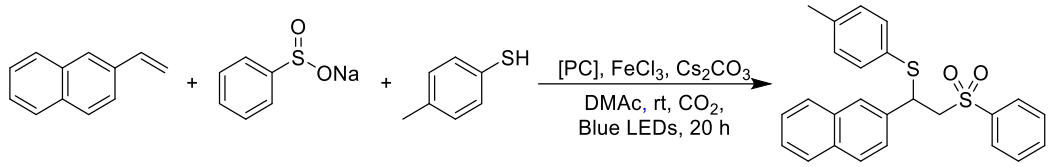


NR

7. Screening of Catalysts

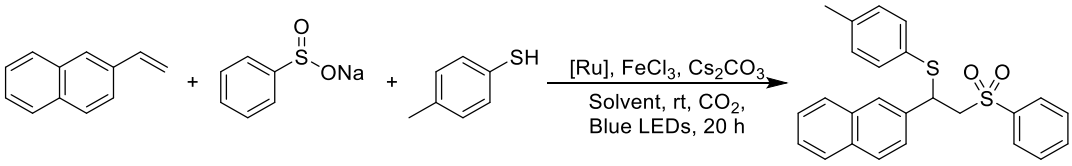


1a **2a** **3a** **4a**

Entry	PC	Yields(%)
1	$Ir[dF(CF_3)bpy)_2(dtbbpy)]PF_6$	41
2	$Ir[(bpy)_2(dtbbpy)]PF_6$	67
3	4CzIPN	31
4	$Ir(ppy)_3$	NR
5	Acid Red 94	trace
6	Solvent Red 43	62
7	$[Ru(phen)_3](PF_6)_2$	81
8	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	44
9	Eosin Y	NR
10	Rhodamine B	NR

Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), **3a** (0.3 mmol, 1.5 equiv), [PC] (2 mol%), $FeCl_3$ (30 mol%), Cs_2CO_3 (0.4 mmol, 2 equiv), DMAc (2 mL), rt, 20 h, CO_2, isolated yield.

8. Screening of Solvents

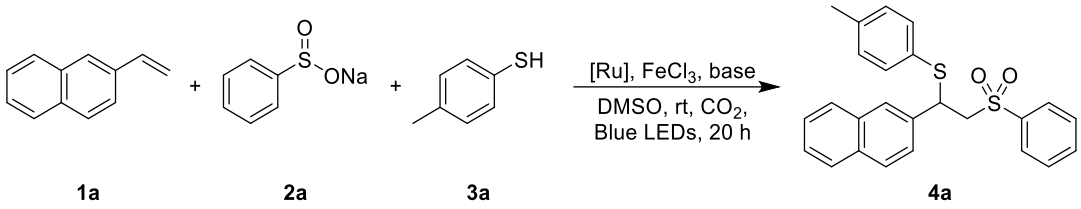


1a **2a** **3a** **4a**

Entry	Solvent	Yields(%)
1	MeCN	35
2	NMP	64
3	DMSO	85
4	DMF	50
5	THF	11
6	DCM	0

Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), **3a** (0.3 mmol, 1.5 equiv), $Ru(phen)_3(PF_6)_2$ (2 mol%), $FeCl_3$ (30 mol%), Cs_2CO_3 (0.4 mmol, 2 equiv), solvent (2 mL), rt, 20 h, CO_2, isolated yield.

9. Screening of Bases

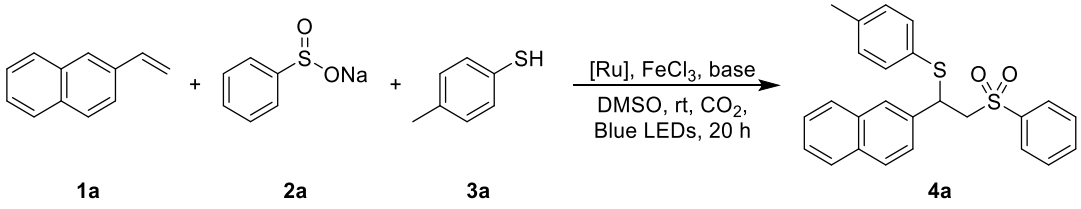


1a **2a** **3a** **4a**

Entry	Base	Yields(%)
1	NaO^tBu	64
2	LiO^tBu	64
3	KO^tBu	42
4	Cs_2CO_3	85
5	DMAP	61
6	HCOOK	70
7	K_2CO_3	50
8	Na_2CO_3	78
9	——	60

Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), **3a** (0.3 mmol, 1.5 equiv), $Ru(phen)_3(PF_6)_2$ (2 mol%), $FeCl_3$ (30 mol%), base (0.4 mmol, 2 equiv), DMSO (2 mL), rt, 20 h, CO_2, isolated yield.

10. Screening of $FeCl_3$ Loading



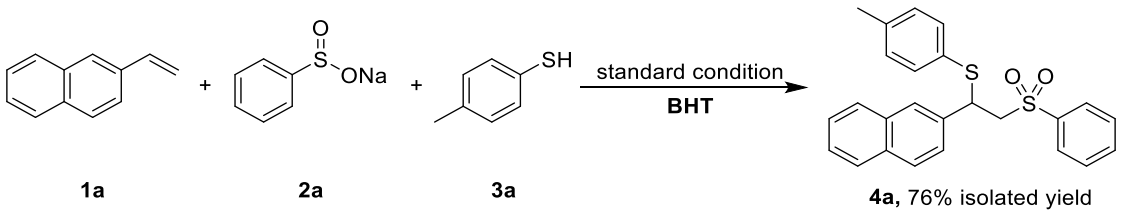
1a **2a** **3a** **4a**

Entry	$FeCl_3$ (mol%)	Yields(%)
1	5	17
2	10	26
3	20	79
4	30	85

Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), **3a** (0.3 mmol, 1.5 equiv), $Ru(phen)_3(PF_6)_2$ (2 mol%), $FeCl_3$, Cs_2CO_3 (0.4 mmol, 2 equiv), DMSO (2 mL), rt, 20 h, CO_2, isolated yield.

11. Investigation of Reaction Mechanism

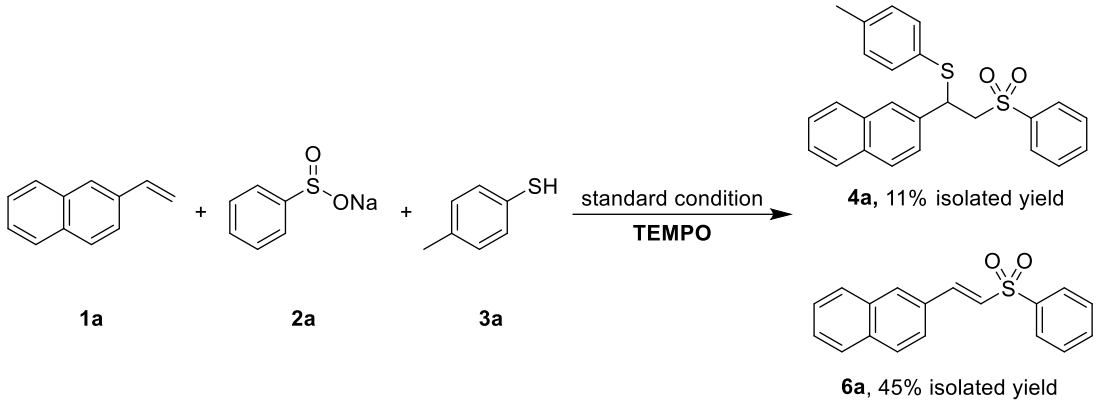
11.1. BHT Trapping Experiment



1a **2a** **3a** **4a,** 76% isolated yield

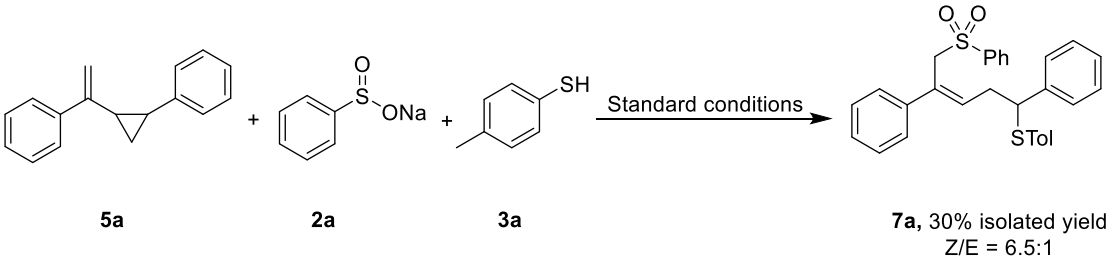
In a 25 mL Schlenk tube **1a** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), **3a** (0.3 mmol, 1.5 equiv), $Ru(phen)_3(PF_6)_2$ (0.004 mmol, 2 mol%), $FeCl_3$ (0.06 mmol, 30 mol%), Cs_2CO_3 (0.4 mmol, 2 equiv) and **BHT** (0.6 mmol, 3 equiv) were added and it was evacuated by CO_2 cycles for three times. Then DMSO (2 mL) was added into the Schlenk tube under CO_2. The reaction was placed under 40 W blue LEDs at room temperature. After 20 h, the reaction was completed and quenched upon the addition of water (10 mL). The mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried using $MgSO_4$ and then concentrated in vacuo. The crude product was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (3/1) as the eluent to give the pure product **4a** (76%) as white solid.

11.2. TEMPO Trapping Experiment



In a 25 mL Schlenk tube **1a** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), **3a** (0.3 mmol, 1.5 equiv), $Ru(phen)_3(PF_6)_2$ (0.004 mmol, 2 mol%), $FeCl_3$ (0.06 mmol, 30 mol%), Cs_2CO_3 (0.4 mmol, 2 equiv) and **TEMPO** (0.6 mmol, 3 equiv) were added and it was evacuated by CO_2 cycles for three times. Then DMSO (2 mL) wsa added into the Schlenk tube under CO_2. The reaction was placed under 40 W blue LEDs at room temperature. After 20 h, the reaction was completed and quenched upon the addition of water (10 mL). The mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried using $MgSO_4$ and then concentrated in vacuo. The crude product was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (3/1) as the eluent to give the pure product **4a** (11%) as white solid and **6a** (45%) as yellow oil.

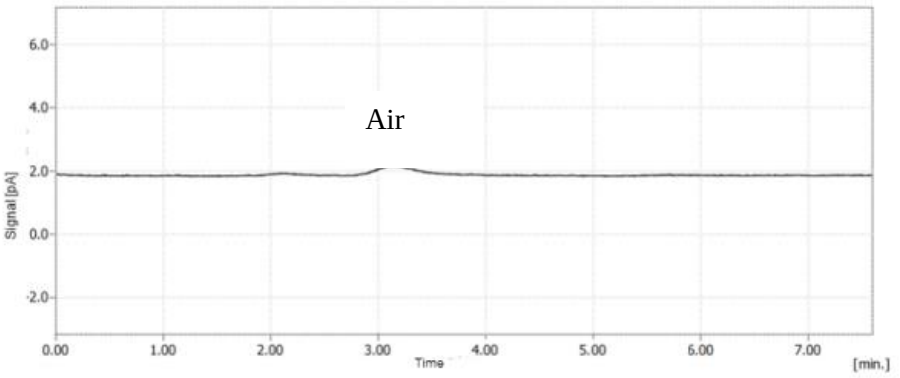
11.3. Radical Clock Experiment



In a 25 mL Schlenk tube **5a** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), **3a** (0.3 mmol, 1.5 equiv), $Ru(phen)_3(PF_6)_2$ (0.004 mmol, 2 mol%), $FeCl_3$ (0.06 mmol, 30 mol%) and Cs_2CO_3 (0.4 mmol, 2 equiv) were added and it was evacuated by CO_2 cycles for three times. Then DMSO (2 mL) was added into the Schlenk tube under CO_2. The reaction was placed under 40 W blue LEDs at room temperature. After 20 h, the reaction was completed and quenched upon the addition of water (10 mL). The mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried using $MgSO_4$ and then concentrated in vacuo. The crude product was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (3/1) as the eluent to give the pure product **7a** (30%) as white solid.

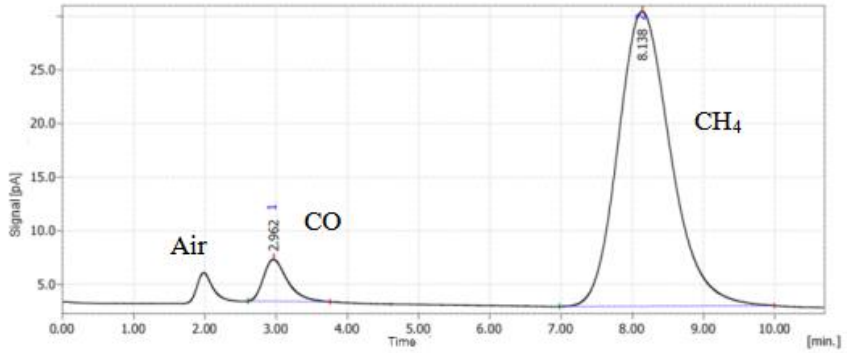
12. Component of Gas Phase

Gas phase component detected by GC. The signal of air means contamination during sampling.
(a) Component of gas phase at the beginning of the reaction.



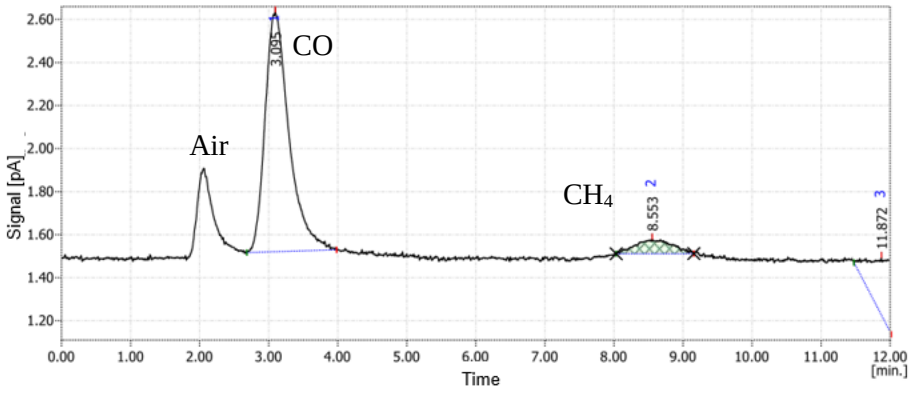
No	Name	Time	Area	Concentration	Area (%)	Concentration (%)
Sum			0.0000	0.0000	100	0.0000

(b) Component of gas phase after the reaction was completed.



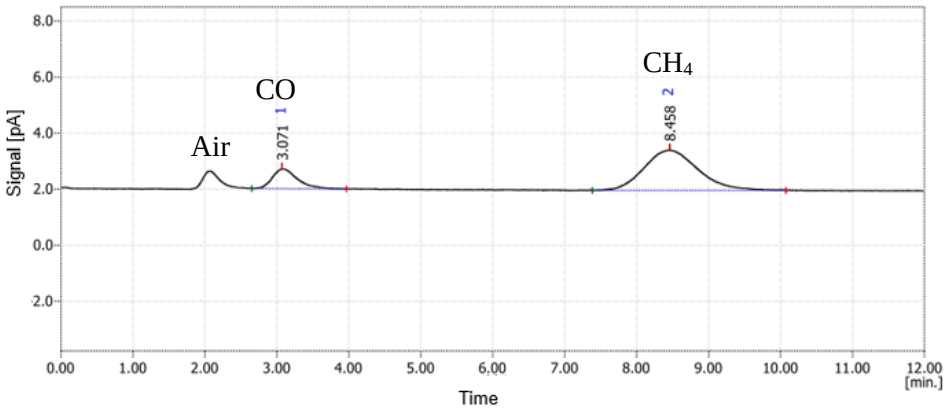
No	Name	Time	Area	Concentration	Area (%)	Concentration (%)
1		2.9617	91.8331	0.0000	6.1303	0.0000
2		8.1384	1406.1980	0.0000	93.8698	0.0000
sum			1498.0310	0.0000	100	0.0000

(c) Component of gas phase after the reaction was completed (MeCN as solvent).



No	Name	Time	Area	Concentration	Area (%)	Concentration (%)
1		3.0950	27.1354	0.0000	91.1194	
2		8.5535	2.6447	0.0000	8.8806	
Sum			29.7801	0.00000	100	0.0000

(d) Component of gas phase after the reaction was completed (NMP as solvent).



No	Name	Time	Area	Concentration	Area (%)	Concentration (%)
1		3.0708	17.0756	0.0000	18.5007	0.0000
2		8.4585	75.2211	0.0000	81.4993	0.0000
Sum			92.2966	0.00000	100	0.0000

Table S1. Concentration of CO and CH_4 changed with reaction time (NMP as solvent).

Time	CO	CH_4	Time	CO	CH_4
0	0	0	**10**	20.2	55.8
1	21.8	6.1	**11**	18.4	64
2	22.2	14.7	**12**	15.9	64.1
3	24.9	21.1	**13**	18	63.4
4	19.9	24.4	**14**	16.3	68.8
5	19.1	31	**15**	17.9	66.5
6	19.9	38.5	**16**	17.9	70.8
7	18.8	45.9	**17**	16.9	70
8	18.3	51.8	**18**	17.5	74.6
9	21.5	53.7	**19**	18.1	75.2

In a 25 mL Schlenk tube **1a** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), **3a** (0.3 mmol, 1.5 equiv), $Ru(phen)_3(PF_6)_2$ (0.004 mmol, 2 mol%), $FeCl_3$ (0.06 mmol, 30 mol%), Cs_2CO_3 (0.4 mmol, 2 equiv) were added and it was evacuated by CO_2 cycles for three times. Then NMP (2 mL) was added into the Schlenk tube under CO_2. After that the Schlenk tube was charged with a CO_2 gas bag. The reaction was placed under 40 W blue LEDs at room temperature. Subsequently, 3 mL gas from the system was extracted by syringe to detect the component every hour. Extra CO_2 was added from the CO_2 gas bag to balance the pressure in the reaction system. Calibrated data of gas concentration were calculated as follows (500 ppm per 1100 peak area):

$$c\,(t+1) = \Delta c\,(t) + c\,(t);$$

$$\Delta c\,(t) = [\,c\,(t+1) \times v - c\,(t) \times (v-3)\,] \div v;\ (t \geq 1)$$

c: Concentration of gas (ppm);

t: reaction time (h);

Δc: The increase in gas concentration per unit time (ppm);

v: Volume of gas (Volume of reaction vessel, mL).

Table S2. Calibrated concentration of CO and CH_4 changed with reaction time (NMP as the solvent).

Time	CO	CH_4	Time	CO	CH_4
0	0.00	0.00	**10**	34.92	78.47
1	21.80	6.10	**11**	34.71	91.08
2	23.92	15.18	**12**	33.66	96.23
3	28.37	22.74	**13**	37.02	100.59
4	25.34	27.71	**14**	36.74	111.00
5	26.11	36.23	**15**	39.63	114.13
6	28.42	46.18	**16**	41.04	123.68
7	28.89	56.62	**17**	41.45	128.47
8	29.87	66.14	**18**	43.39	138.59
9	34.52	72.13	**19**	45.37	145.08

13. Proposed Mechanism for CO_2 Reduction to CO and CH_4

We proposed a plausible mechanism of CO_2 reduction to CO and CH_4.[1] We draw detailedly this process in Figure S1. Firstly, the starting Fe(III) is reduced with three electrons to the Fe(0). The Fe(0) reduces CO_2, with the resultant Fe(I) regenerated through electron transfer from the excited photosensitizer $*Ru(phen)_3^{2+}$. The produced CO binds to Fe(II) and is further reduced with a total of six electrons (transferred from the excited photosensitizer $*Ru(phen)_3^{2+}$) and six protons to generate CH_4. The consume ration of electron and hole is 1.

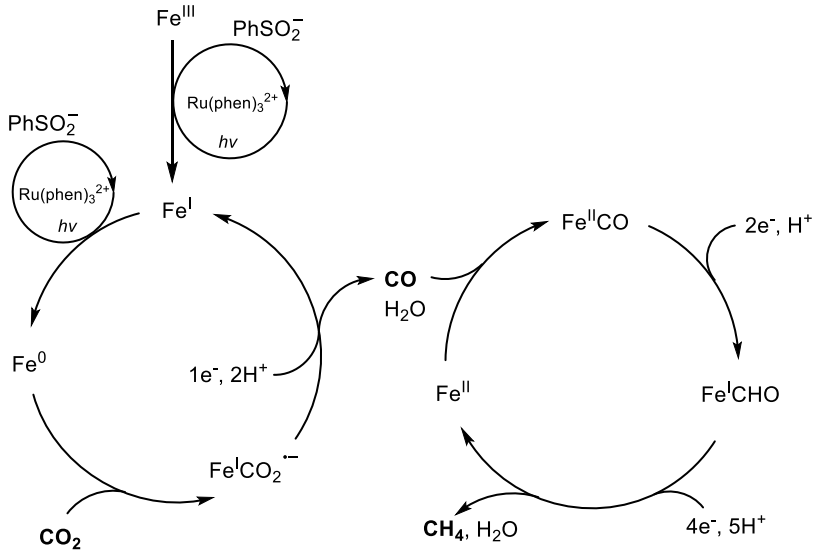


Figure S1. Proposed mechanism for CO_2 reduction to CO and CH_4

14. Stern-Volmer Quenching Experiments

Stern-Volmer fluorescence quenching experiments are run with freshly prepared solution of $5x10^{-5}$ M solution of $Ru(phen)_3(PF_6)_2$ in DMSO added the appropriate amount of a quencher in a screw-top quartz cuvette at room temperature. The solutions are irradiated at 450 nm and fluorescence is measured from 470 nm to 750 nm. Figure S2 shows an obvious linear relationship between the fluorescence intensities and the concentrations of **2a** and $FeCl_3$. All these results suggest that the excited state of the photocatalyst is quenched by $FeCl_3$.

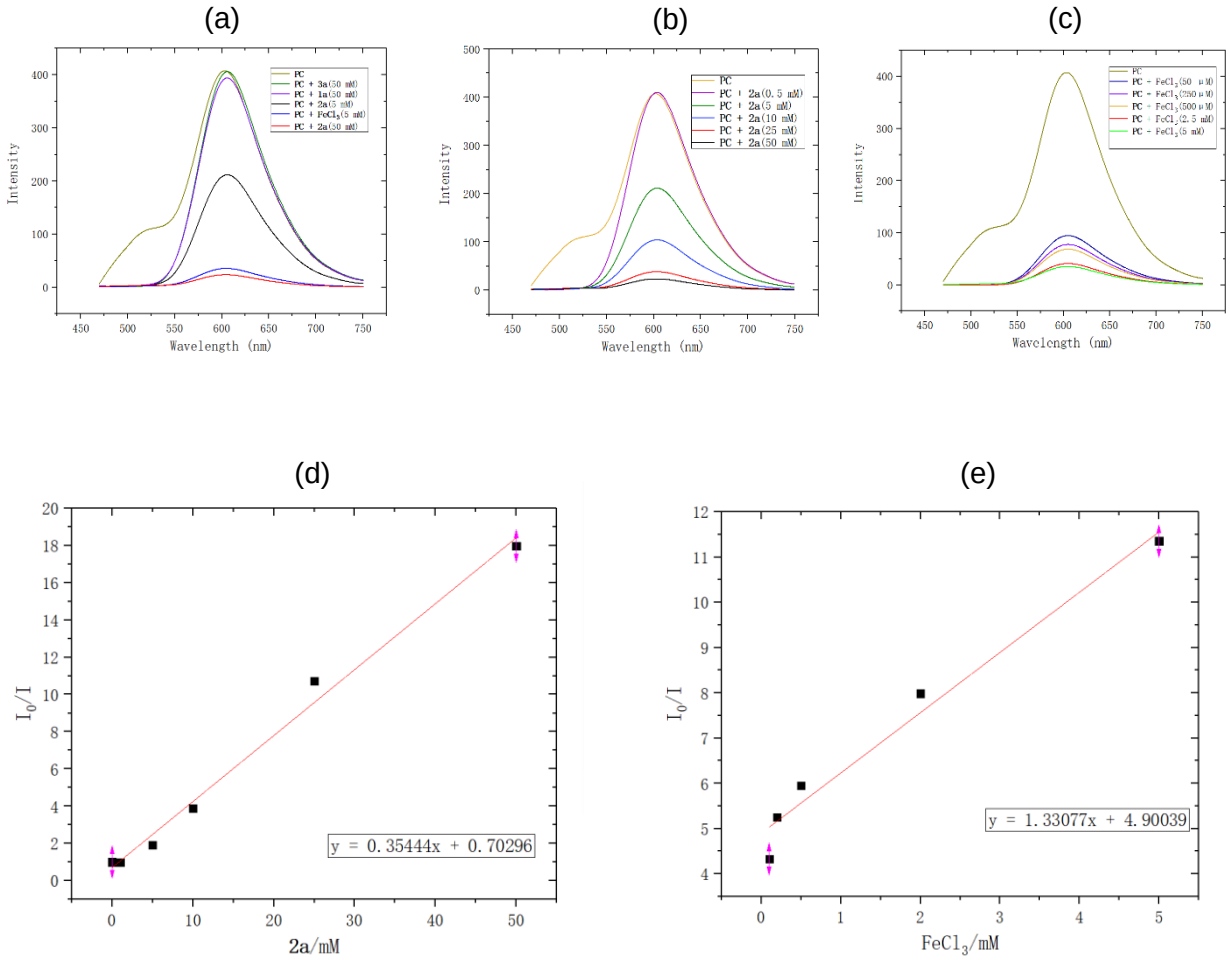


Figure S2. Luminescence quenching study: (a) The emission spectra of a 5x10^{-5} M solution of photocatalyst Ru(phen)$_3$(PF$_6$)$_2$ with reactants in DMSO excited at 450 nm; The solubility of FeCl$_3$ in DMSO is limited, so we used 5mM solution of FeCl$_3$; (b) The emission spectra of a 5x10^{-5} M solution of Ru(phen)$_3$(PF$_6$)$_2$ with various concentrations of **2a** in DMSO excited at 450 nm; (c) The emission spectra of a 5x10^{-5} M solution of Ru(phen)$_3$(PF$_6$)$_2$ with various concentrations of FeCl$_3$ in DMSO excited at 450 nm; (d) The linear relationship between I_0 /I and the increasing concentration of **2a**; (e) The linear relationship between I_0 /I and the increasing concentration of FeCl$_3$.

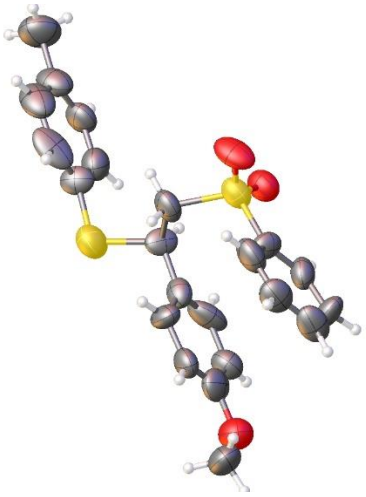
15. Apparent Quantum Yield

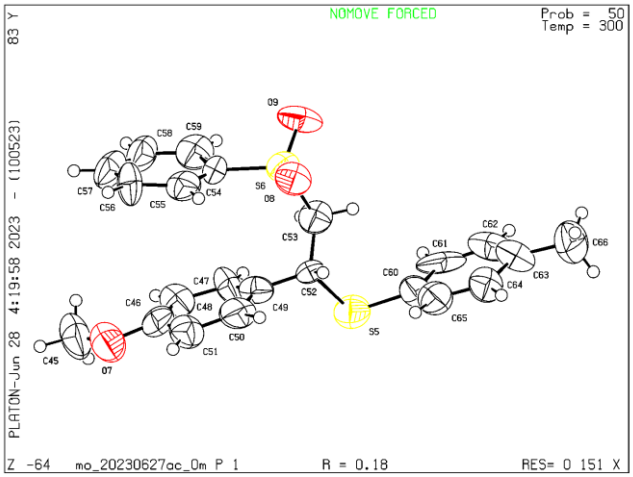
The apparent quantum yield (AQE) was measured using a 40 W blue LED with band pass filter of 450 nm. The AQY was calculated by the following equation:

$$\text{AQY} = \frac{Number\ of\ reacted\ electrons}{Number\ of\ incident\ of\ photos} = \frac{(2*M_{CO}+8*M_{CH_4})*N_A}{I*A*T*(\frac{\lambda}{h}*c)}$$

where M_{CO} and M_{CH4} are the amounts of CO and CH$_4$, respectively. I, A, T and λ are the light density, light irradiation area, irradiation time, and light wavelength, respectively. AQY is 0.14% after 20 h of irradiation.

16. X-ray Crystallographic Data of 4f

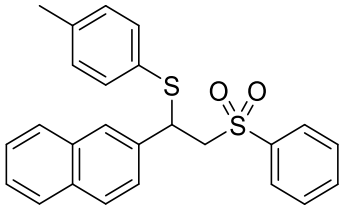




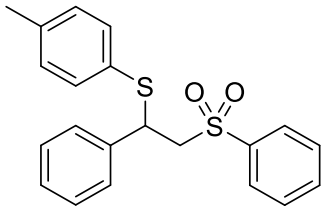
The product **4f** (CCDC number 2277380) was crystallized from ethyl acetate. The atoms are depicted with 50% probability ellipsoids. The crystallographic data are summarized in the following table.

Identification code	**4f**
Empirical formula	$C_{22}H_{22}O_3S_2$
Formula weight	398.10
Temperature/K	300
Crystal system	triclinic
Space group	P1
a/Å	5.750(13)
b/Å	14.69(3)
c/Å	22.89(5)
α/°	91.75(11)
β/°	91.21(12)
γ/°	92.01(11)
Volume/Å3	1931(7)
Z	1
ρcalcg/cm3	1.285
μ/mm-1	0.293
F(000)	747
Crystal size/mm3	0.19 × 0.15 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.446 to 58.042
Index ranges	-7 ⩽ h ⩽ 7, -19 ⩽ k ⩽ 19, -30 ⩽ l ⩽ 30
Reflections collected	166470
Independent reflections	18339 [Rint = 0.7039, Rsigma = 0.4727]
Data/restraints/parameters	18339/3/982
Goodness-of-fit on F2	1.042
Final R indexes [I>=2σ (I)]	R1 = 0.1767, wR2 = 0.2815
Final R indexes [all data]	R1 = 0.4146, wR2 = 0.3937
Largest diff. peak/hole / e Å-3	0.35/-0.39
Flack parameter	0.23(19)

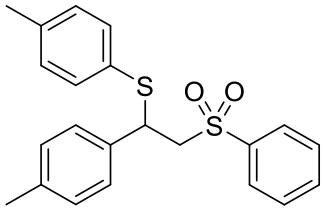
17. Characterisation of Products 4, 6a, and 7a



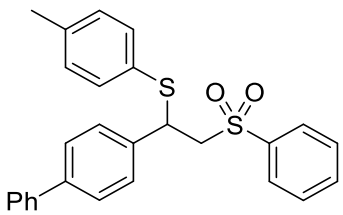
(1-(Naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)(*p*-tolyl)sulfane (4a): The reaction was conducted on 0.2 mmol scale. The product **4a** (71.2 mg, 85% yield) as white solid (mp 140.6-141.0 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.68 (m, 1H), 7.59 (dd, *J* = 13.6, 7.3 Hz, 2H), 7.44 (dd, *J* = 13.8, 6.3 Hz, 5H), 7.24 – 7.16 (m, 4H), 7.11 – 6.94 (m, 4H), 4.74 (dd, *J* = 10.7, 3.8 Hz, 1H), 3.94 (dd, *J* = 14.8, 10.7 Hz, 1H), 3.74 (dd, *J* = 14.7, 3.8 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 139.0, 134.6, 134.0, 133.1, 133.0, 132.9, 130.2, 128.9, 128.7, 128.6, 127.9, 127.9, 127.6 (2C), 126.4, 126.3, 125.3, 60.7, 48.1, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{22}O_2S_2Na$ 441.0959; Found 441.0958.



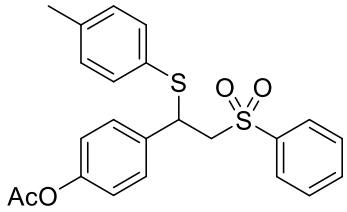
(1-Phenyl-2-(phenylsulfonyl)ethyl)(*p*-tolyl)sulfane (4b): The reaction was conducted on 0.2 mmol scale. The product **4b** (65.5 mg, 89% yield) as white solid (mp 135.2-135.6 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.51 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.15 – 7.01 (m, 7H), 4.59 (dd, *J* = 10.5, 3.7 Hz, 1H), 3.85 (dd, *J* = 14.7, 10.6 Hz, 1H), 3.66 (dd, *J* = 14.7, 3.8 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 138.9, 137.4, 133.9, 133.4, 130.1, 129.0, 128.9, 128.6, 128.1, 128.0, 127.9, 60.6, 47.8, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{20}O_2S_2Na$ 391.0803; Found 391.0796.[2]



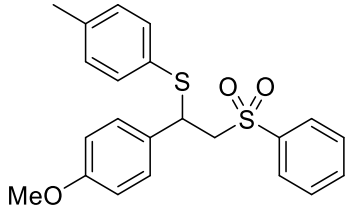
(2-(Phenylsulfonyl)-1-(p-tolyl)ethyl)(*p*-tolyl)sulfane (4c): The reaction was conducted on 0.2 mmol scale. The product **4c** (55.1 mg, 72% yield) as white solid (mp 145.2-146.0 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.44 (m, 3H), 7.29 (dd, *J* = 8.4, 7.4 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.01 – 6.87 (m, 4H), 4.56 (dd, *J* = 10.7, 3.6 Hz, 1H), 3.82 (dd, *J* = 14.7, 10.7 Hz, 1H), 3.62 (dd, *J* = 14.7, 3.7 Hz, 1H), 2.34 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 138.7, 137.8, 134.3, 133.7, 133.2, 130.1, 129.29,129.28, 128.9, 128.0, 127.9, 60.7, 47.4, 21.2 (2C). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{22}O_2S_2Na$ 405.0959; Found 405.0962.



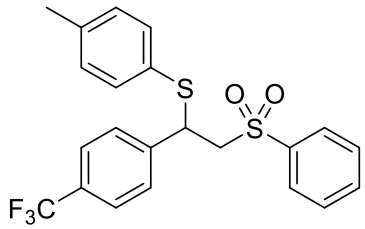
(1-([1,1'-Biphenyl]-4-yl)-2-(phenylsulfonyl)ethyl)(*p*-tolyl)sulfane (4d): The reaction was conducted on 0.2 mmol scale. The product **4d** (73.8 mg, 83% yield) as white solid (mp 116.9-117.7 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.40 (m, 7H) , 7.37 – 7.33 (m, 1H), 7.30 – 7.22 (m, 6H), 7.09 (d, *J* = 8.1 Hz, 4H), 4.63 (dd, *J* = 10.9, 3.6 Hz, 1H), 3.88 (dd, *J* = 14.8, 10.9 Hz, 1H), 3.68 (dd, *J* = 14.8, 3.6 Hz,1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 140.6, 139.4, 139.0, 136.2, 134.0, 133.2, 130.2, 128.95, 128.93, 128.91, 128.5, 128.0, 127.6, 127.2, 127.0, 60.7, 47.6, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{24}O_2S_2Na$ 467.1116; Found 467.1110.



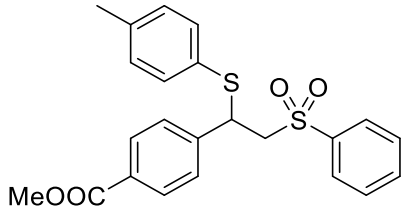
(1-4-(2-(Phenylsulfonyl)-1-(*p*-tolylthio)ethyl)phenyl acetate (4e): The reaction was conducted on 0.2 mmol scale. The product **4e** (52 mg, 61% yield) as white solid (130.5-130.9 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 3H), 7.34 – 7.30 (m, 2H), 7.23 – 7.15 (m, 2H), 7.08 – 7.01 (m, 4H), 6.87 – 6.78 (m, 2H), 4.59 (dd, *J* = 10.6, 3.8 Hz, 1H), 3.79 (dd, *J* = 14.8, 10.5 Hz, 1H), 3.65 (dd, *J* = 14.8, 3.8 Hz, 1H), 2.33 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 150.2, 139.2, 139.0, 135.0, 134.1, 133.6, 130.2, 129.1, 129.0, 128.7, 127.9, 121.7, 60.7, 47.2, 21.3 (2C). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{22}O_4S$ Na 449.0858; Found 449.0856.



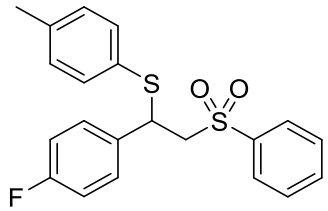
(1-(4-Methoxyphenyl)-2-(phenylsulfonyl)ethyl)(*p*-tolyl)sulfane (4f): The reaction was conducted on 0.2 mmol scale. The product **4f** (51 mg, 64% yield) as white solid (mp 163.7-165.0 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.41 (m, 3H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.63 (d, *J* = 8.7 Hz, 2H), 4.56 (dd, *J* = 10.8, 3.7 Hz, 1H), 3.85 – 3.77 (m, 1H), 3.74 (s, 3H), 3.62 (dd, *J* = 14.7, 3.7 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 139.6, 138.8, 133.8, 133.3, 130.2, 129.33, 129.30, 129.2, 128.9, 128.0, 114.0, 60.8, 55.4, 47.2, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{22}O_3S_2Na$ 421.0908; Found 421.0906.



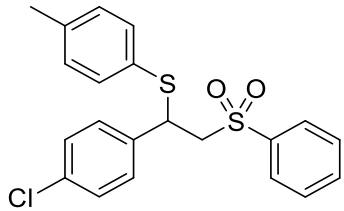
(2-(Phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethyl)(*p*-tolyl)sulfane (4g): The reaction was conducted on 0.2 mmol scale. The product **4g** (34.9 mg, 40% yield) as white solid (mp 135.0-136.7 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 4H), 7.34 – 7.26 (m, 4H), 7.18 – 7.08 (m, 6H), 4.60 (dd, *J* = 10.9, 3.7 Hz, 1H), 3.82 (dd, *J* = 14.7, 10.8 Hz, 1H), 3.69 (dd, *J* = 14.7, 3.7 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 139.4, 139.1, 134.2, 133.5, 130.2, 130.0 (q, J_{C-F} = 32.3 Hz), 129.5, 129.0, 128.4, 128.0, 127.8, 125.4 (q, J_{C-F} = 3.7 Hz), 123.8 (q, J_{C-F} = 270.3 Hz), 60.3, 47.4, 21.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{19}F_3O_2S_2Na$ 459.0677; Found 459.0676.



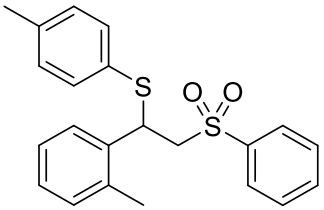
Methyl 4-(2-(Phenylsulfonyl)-1-(*p*-tolylthio)ethyl)benzoate (4h): The reaction was conducted on 0.2 mmol scale. The product **4h** (47.8 mg, 56% yield) as white solid (mp 141.5-142.5 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 2H), 7.55 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.49 (m, 1H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.15 – 6.98 (m, 6H), 4.58 (dd, *J* = 10.4, 3.9 Hz, 1H), 3.90 (s, 3H), 3.81 (dd, *J* = 14.7, 10.5 Hz, 1H), 3.68 (dd, *J* = 14.7, 3.9 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 143.1, 139.4, 139.3, 134.3, 133.6, 130.2, 129.9, 129.8, 129.1, 128.4, 128.12, 128.06, 60.5, 52.3, 47.6, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{22}O_4S_2Na$ 449.0858; Found 449.0846.



(1-(4-Fluorophenyl)-2-(phenylsulfonyl)ethyl)(*p*-tolyl)sulfane (4i): The reaction was conducted on 0.2 mmol scale. The product **4i** (51.8 mg, 67% yield) as white solid (mp 137.2-138.0 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.51 – 7.46 (m, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 7.04 – 6.99 (m, 2H), 6.78 (t, *J* = 8.6 Hz, 2H), 4.57 (dd, *J* = 10.8, 3.7 Hz, 1H), 3.78 (dd, *J* = 14.7, 10.8 Hz, 1H), 3.64 (dd, *J* = 14.7, 3.7 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$ = 246.0 Hz), 139.3, 139.1, 134.1, 133.5, 133.31 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.2, 129.8 (d, $J_{C\text{-}F}$ = 8.3 Hz), 129.0, 128.6, 127.9, 115.5 (d, $J_{C\text{-}F}$ = 21.7Hz), 60.6, 47.0, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{19}FO_2S_2Na$ 409.0708; Found 409.0702.

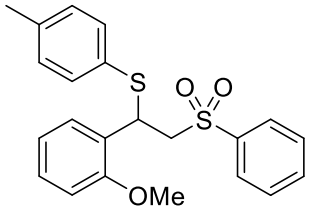


(1-(4-Chlorophenyl)-2-(phenylsulfonyl)ethyl)(*p*-tolyl)sulfane (4j): The reaction was conducted on 0.2 mmol scale. The product **4j** (55.6 mg, 69% yield) as white solid (mp 128.0-128.7 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 3H), 7.36 – 7.30 (m, 2H), 7.21 – 7.15 (m, 2H), 7.12 – 7.01 (m, 4H), 6.97 – 6.90 (m, 2H), 4.52 (dd, *J* = 10.7, 3.7 Hz, 1H), 3.78 (dd, *J* = 14.8, 10.7 Hz, 1H), 3.64 (dd, *J* = 14.8, 3.7 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 139.3, 139.1, 134.2, 133.6, 130.2, 129.8, 129.0, 128.3, 128.1, 127.7, 126.3, 60.2, 47.4, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{19}ClO_2S_2Na$ 425.0413; Found 425.0406.

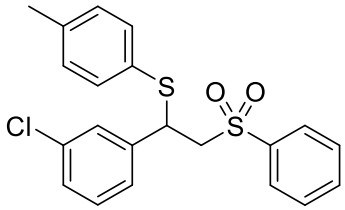


(2-(Phenylsulfonyl)-1-(o-tolyl)ethyl)(*p*-tolyl)sulfane (4k): The reaction was conducted on 0.2 mmol scale. The product **4k** (51.2 mg, 67% yield) as white solid (mp 111.1-112.0 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 3H), 7.26 – 7.18 (m, 4H), 7.10 – 7.00 (m, 4H), 6.87 – 6.75 (m, 2H), 4.82 (dd, *J* = 10.9, 3.7 Hz, 1H), 3.91 (dd, *J* = 14.7, 10.9 Hz, 1H), 3.64 (dd, *J* = 14.8, 3.7 Hz, 1H), 2.39

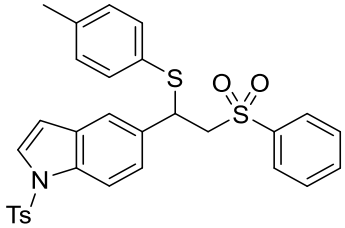
(s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 138.9, 136.3, 134.9, 134.1, 133.3, 130.7, 130.2, 129.1, 128.9, 127.8, 127.7, 126.7, 126.2, 60.1, 43.3, 21.3, 19.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{22}O_2S_2Na$ 405.0959; Found 405.0948.



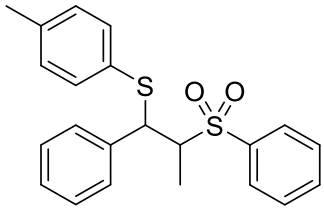
(1-(2-Methoxyphenyl)-2-(phenylsulfonyl)ethyl)(*p*-tolyl)sulfane (4l): The reaction was conducted on 0.2 mmol scale. The product **4l** (44.6 mg, 56% yield) as pale yellow oil was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.50 (m, 2H), 7.49 – 7.41 (m, 1H), 7.34 – 7.25 (m, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.16 – 7.03 (m, 3H), 6.95 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.72 (td, *J* = 7.5, 1.1 Hz, 1H), 6.60 (dd, *J* = 8.3, 1.0 Hz, 1H), 4.87 (dd, *J* = 10.8, 3.8 Hz, 1H), 4.12 (dd, *J* = 14.7, 10.8 Hz, 1H), 3.71 (s, 3H), 3.65 (dd, *J* = 14.7, 3.8 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 139.2, 138.4, 133.6, 133.2, 130.05, 130.00, 129.3, 129.1, 128.6, 128.0, 125.5, 120.6, 110.9, 59.5, 55.4, 44.2, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{22}O_3S_2Na$ 421.0908; Found 421.0907.



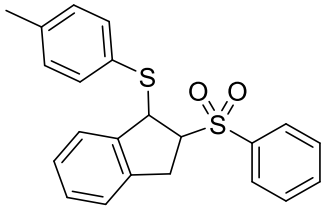
(1-(3-Chlorophenyl)-2-(phenylsulfonyl)ethyl)(*p*-tolyl)sulfane (4m): The reaction was conducted on 0.2 mmol scale. The product **4m** (41.1 mg, 51% yield) as white solid (107.8-109.3 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.46 (m, 3H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.10 – 7.04 (m, 4H), 6.99 – 6.91 (m, 2H), 4.51 (dd, *J* = 10.6, 3.8 Hz, 1H), 3.77 (dd, *J* = 14.8, 10.6 Hz, 1H), 3.64 (dd, *J* = 14.8, 3.8 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 139.3, 139.25, 134.4, 134.3, 133.7, 130.3, 129.8, 129.0, 128.4, 128.2, 128.1, 128.0, 126.4, 60.4, 47.4, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{19}ClO_2S_2Na$ 425.0413; Found 425.0407.



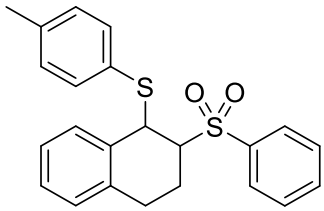
5-(2-(Phenylsulfonyl)-1-(*p*-tolylthio)ethyl)-1-tosyl-1H-indole (4n): The reaction was conducted on 0.2 mmol scale. The product **4n** (57.3 mg, 51% yield) as white solid (mp 167.2-169.0 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.52 (d, *J* = 3.7 Hz, 1H), 7.42 – 7.32 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.13 – 7.00 (m, 5H), 6.90 (t, *J* = 7.9 Hz, 2H), 6.43 (d, *J* = 3.7 Hz, 1H), 4.65 (dd, *J* = 10.9, 3.6 Hz, 1H), 3.85 (dd, *J* = 14.8, 10.9 Hz, 1H), 3.65 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 139.2, 138.9, 135.4, 134.2, 133.8, 132.2, 130.8, 130.2, 130.0, 129.12, 129.07, 128.4, 127.7, 127.1, 126.9, 124.6, 121.0, 113.6, 108.8, 60.9, 47.9, 21.7, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{27}NO_4S_3Na$ 584.1000; Found 584.0994.



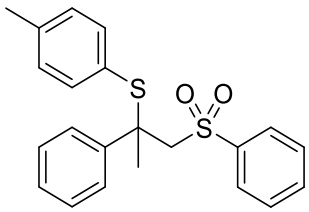
(1-Phenyl-2-(phenylsulfonyl)propyl)(*p*-tolyl)sulfane (4o): The reaction was conducted on 0.2 mmol scale. The product **4o** (50.5 mg, 66% yield) as white solid (85.3-86.3 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.61 – 7.52 (m, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.27 – 7.20 (m, 2H), 7.19 – 7.11 (m, 3H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 4.82 (d, *J* = 5.0 Hz, 1H), 3.58 (qd, *J* = 7.1, 4.9 Hz, 1H), 2.24 (s, 3H), 1.56 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 138.5, 137.6, 133.5, 132.6, 130.1, 129.7, 129.0, 128.9, 128.5, 128.4, 127.6, 66.2, 53.5, 21.2, 10.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{22}O_2S_2Na$ 405.0959; Found 405.0960.



(2-(Phenylsulfonyl)-2,3-dihydro-1H-inden-1-yl)(*p*-tolyl)sulfane (4p): The reaction was conducted on 0.2 mmol scale. The product **4p** (54.8 mg, 70% yield) as white solid (mp 144.3-145.1 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.62 – 7.53 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.36 – 7.28 (m, 1H), 7.22 – 7.12 (m, 2H), 7.12 – 7.04 (m, 3H), 6.99 (d, *J* = 7.9 Hz, 2H), 4.99 (d, *J* = 2.5 Hz, 1H), 3.91 (dt, *J* = 8.7, 2.8 Hz, 1H), 3.43 (dd, *J* = 17.8, 2.9 Hz, 1H), 3.23 (dd, *J* = 17.5, 8.7 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 140.0, 138.4, 137.4, 133.7, 133.4, 129.9, 129.1, 128.9, 128.7, 128.5, 127.5, 125.1, 124.4, 69.2, 53.1, 31.8, 21.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{20}O_2S_2Na$ 403.0803; Found 403.0805.

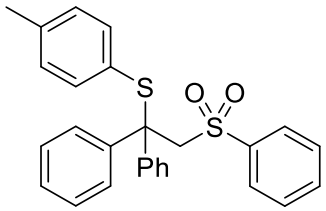


(2-(Phenylsulfonyl)-1,2,3,4-tetrahydronaphthalen-1-yl)(*p*-tolyl)sulfane (4q): The reaction was conducted on 0.2 mmol scale. The product **4q** (54.4mg, 69% yield) as white solid (mp 160.3-161.2 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 3H), 7.48 – 7.40 (m, 2H), 7.37 – 7.31 (m, 1H), 7.18 (dd, *J* = 5.8, 3.3 Hz, 2H), 7.07 (m, 1H), 7.03 (m, 2H), 6.97 (m, 2H), 4.73 (m, 1H), 3.50 (m, 1H), 3.13 (m, 1H), 2.80 (m, 1H), 2.70 – 2.53 (m, 1H), 2.42 – 2.35 (m, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 138.0, 136.5, 133.6, 133.0, 131.8, 130.5, 130.1, 129.9, 129.2, 128.9, 128.6, 127.8, 126.3, 62.5, 45.6, 25.2, 21.3, 18.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{22}O_2S_2Na$ 417.0959; Found 417.0951.

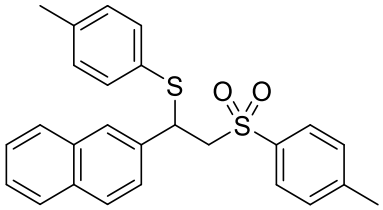


(2-Phenyl-1-(phenylsulfonyl)propan-2-yl)(*p*-tolyl)sulfane (4r): The reaction was conducted on 0.2 mmol scale. The product **4r** (25.2 mg, 33% yield) as white solid (mp 141.0-142.3 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 3H), 7.29 – 7.17 (m, 6H), 7.12 – 7.03 (m, 5H), 4.23 (d, *J* = 14.7 Hz, 1H), 3.67 (d, *J* = 14.6 Hz, 1H), 2.35 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$)

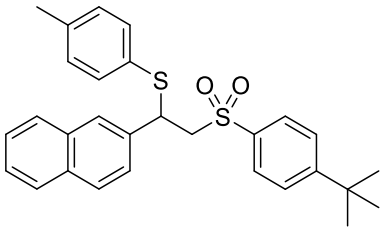
δ 140.6, 140.3, 140.0, 137.6, 133.1, 129.8, 129.0, 128.1, 127.8, 127.5, 127.2, 127.1, 67.0, 51.8, 24.8, 21.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{22}O_2S_2Na$ 405.0959; Found 405.0960.



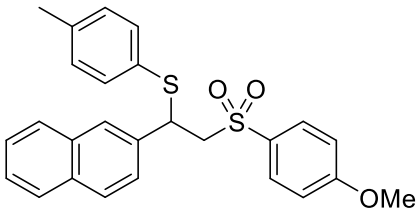
(1,1-Diphenyl-2-(phenylsulfonyl)ethyl)(*p*-tolyl)sulfane (4s): The reaction was conducted on 0.2 mmol scale. The product **4s** (84.5 mg, 95% yield) as white solid (mp 148.0-149.0 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 5H), 7.24 – 7.14 (m, 10H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.80 – 6.73 (m, 2H), 4.33 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 140.8, 140.1, 137.4, 132.7, 129.9, 129.5, 128.8, 127.7, 127.5, 127.3, 126.9, 66.7, 60.8, 21.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{24}O_2S_2Na$ 467.1116; Found 467.1123.



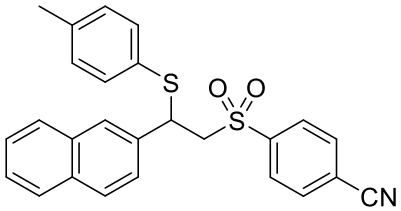
(1-(Naphthalen-2-yl)-2-tosylethyl)(*p*-tolyl)sulfane (4t): The reaction was conducted on 0.2 mmol scale. The product **4t** (56.2 mg, 65% yield) as white solid (mp 131.1-132.2 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.69 (m, 1H), 7.61 – 7.50 (m, 2H), 7.43 (dt, *J* = 6.2, 3.4 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.26 – 7.17 (m, 3H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 4.73 (dd, *J* = 10.9, 3.6 Hz, 1H), 3.93 (dd, *J* = 14.7, 10.9 Hz, 1H), 3.72 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.32 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 138.9, 136.1, 134.5, 134.0, 132.94, 132.89, 130.1, 129.2, 128.9, 128.5, 127.8, 127.5, 127.4, 126.24, 126.22, 125.5, 60.5, 48.1, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{24}O_2S_2Na$ 455.1116; Found 455.1111.



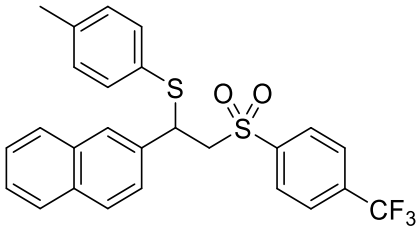
(2-((4-(Tert-butyl)phenyl)sulfonyl)-1-(naphthalen-2-yl)ethyl)(*p*-tolyl)sulfane (4u): The reaction was conducted on 0.2 mmol scale. The product **4u** (53.2 mg, 56% yield) as white solid (mp 151.4-152.0 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 1H), 7.61 (dt, *J* = 8.1, 2.9 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.44 – 7.39 (m, 3H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.15 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.08 (d, *J* = 7.9 Hz, 2H), 7.02 – 6.94 (m, 2H), 4.78 (dd, *J* = 11.1, 3.4 Hz, 1H), 3.95 (dd, *J* = 14.8, 11.1 Hz, 1H), 3.73 (dd, *J* = 14.8, 3.4 Hz, 1H), 2.33 (s, 3H), 1.07 (s, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 138.9, 136.0, 134.5, 134.0, 133.0, 132.8, 130.2, 129.0, 128.4, 127.9, 127.8, 127.7, 127.6, 126.4, 126.3, 125.5, 125.2, 60.5, 48.2, 35.0, 30.9, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{30}O_2S_2$ 497.1585; Found 497.1582.



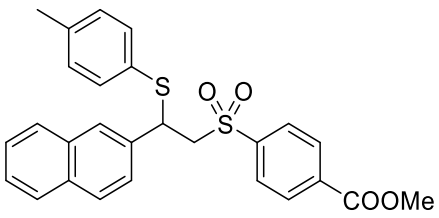
(2-((4-Methoxyphenyl)sulfonyl)-1-(naphthalen-2-yl)ethyl)(*p*-tolyl)sulfane (4v): The reaction was conducted on 0.2 mmol scale. The product **4v** (46.6 mg, 52% yield) as white solid (mp 115.1-116.1 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 1H), 7.66 – 7.54 (m, 2H), 7.48 – 7.39 (m, 2H), 7.36 – 7.30 (m, 3H), 7.26 – 7.19 (m, 3H), 7.07 (d, *J* = 7.9 Hz, 2H), 4.73 (dd, *J* = 10.9, 3.6 Hz, 1H), 3.91 (dd, *J* = 14.7, 10.9 Hz, 1H), 3.72 (dd, *J* = 14.7, 3.6 Hz, 1H), 3.50 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 138.9, 134.6, 134.0, 133.0, 132.9, 130.6, 130.1, 130.0, 129.0, 128.5, 127.9, 127.52, 127.48, 126.3, 126.2, 125.5, 113.7, 60.7, 55.4, 48.2, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{24}O_3S_2Na$ 471.1065; Found 471.1059.



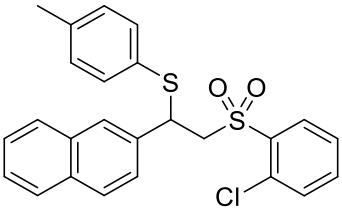
4-((2-(Naphthalen-2-yl)-2-(*p*-tolylthio)ethyl)sulfonyl)benzonitrile (4w): The reaction was conducted on 0.2 mmol scale. The product **4w** (48.8 mg, 55% yield) as white solid (mp 157.7-158.7 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 1H), 7.64 – 7.45 (m, 4H), 7.44 – 7.37 (m, 2H), 7.31 (d, *J* = 1.8 Hz, 1H), 7.25 (d, *J* = 4.3 Hz, 2H), 7.17 – 7.03 (m, 5H), 4.70 (dd, *J* = 11.2, 3.7 Hz, 1H), 3.94 (dd, *J* = 15.0, 11.2 Hz, 1H), 3.76 (dd, *J* = 15.0, 3.7 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 139.4, 134.3, 133.8, 133.0, 132.8, 132.0, 130.4, 128.8, 128.6, 128.3, 127.8, 127.6 (2C), 127.2, 127.0, 125.3, 116.8, 116.4, 61.0, 48.2, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{21}NO_2S_2Na$ 466.0912; Found 441.0958.



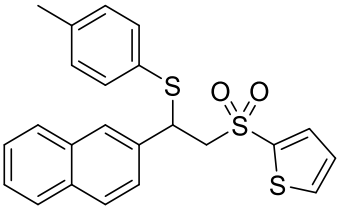
(1-(Naphthalen-2-yl)-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)(*p*-tolyl)sulfane (4x): The reaction was conducted on 0.2 mmol scale. The product **4x** (45.7 mg, 47% yield) as white solid (mp 103.1-104.1 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 1H), 7.59 – 7.56(m, 1H), 7.51 – 7.40 (m, 5H), 7.38 (d, *J* = 1.9 Hz, 1H), 7.25 (d, *J* = 5.8 Hz, 2H), 7.15 – 7.07 (m, 5H), 4.73 (dd, *J* = 11.2, 3.6 Hz, 1H), 3.96 (dd, *J* = 14.9, 11.2 Hz, 1H), 3.77 (dd, *J* = 15.0, 3.6 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 139.3, 134.5 (q, J_{C-F} = 33.8 Hz), 134.1, 133.7, 132.8, 132.7, 130.1, 128.58, 128.55, 128.3, 127.7, 127.5, 127.47, 126.6, 126.58, 125.4 (q, J_{C-F} = 3.8 Hz), 124.8, 122.8 (q, J_{C-F} = 271.0 Hz), 60.7, 48.2, 21.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.43. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{21}F_3O_2S_2Na$ 509.0833; Found 509.0829.



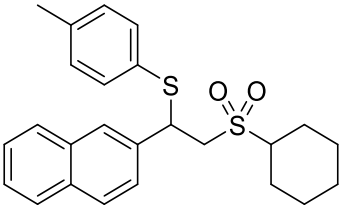
Methyl-4-((2-(naphthalen-2-yl)-2-(*p*-tolylthio)ethyl)sulfonyl)benzoate (4y): The reaction was conducted on 0.2 mmol scale. The product **4y** (35.3 mg, 37% yield) as white solid (mp 144.2-145.5 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.65 (m, 1H), 7.64 – 7.51 (m, 4H), 7.48 – 7.38 (m, 4H), 7.29 (d, *J* = 1.8 Hz, 1H), 7.28 – 7.18 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 4.70 (dd, *J* = 11.0, 3.6 Hz, 1H), 4.00 – 3.91 (m, 1H), 3.85 (s, 3H), 3.75 (dd, *J* = 14.9, 3.6 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 143.0, 139.2, 134.2 (2C), 134.0, 133.0, 132.9, 130.3, 129.6, 128.8, 128.7, 127.9, 127.8, 127.65, 127.60, 126.42, 126.39, 125.4, 60.7, 52.6, 48.1, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{24}O_4S_2Na$ 499.1014; Found 499.1010.



(2-((2-Chlorophenyl)sulfonyl)-1-(naphthalen-2-yl)ethyl)(*p*-tolyl)sulfane (4z): The reaction was conducted on 0.2 mmol scale. The product **4z** (28.1 mg, 31% yield) as white solid (mp 113.8-114.3 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.56 (m, 2H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.45 – 7.39 (m, 4H), 7.35 – 7.20 (m, 3H), 7.16 – 7.04 (m, 3H), 6.92 (td, *J* = 7.7, 1.7 Hz, 1H), 6.68 (td, *J* = 7.7, 1.2 Hz, 1H), 4.74 (dd, *J* = 11.2, 3.6 Hz, 1H), 4.46 (dd, *J* = 14.9, 11.2 Hz, 1H), 3.83 (dd, *J* = 14.9, 3.6 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 136.5, 134.05, 134.01, 133.7, 132.9, 132.7, 132.0, 131.3, 131.0, 130.2, 128.8, 128.5, 127.8, 127.4 (2C), 126.4, 126.3, 126.2, 125.1, 58.3, 48.4, 21.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{21}ClO_2S_2Na$ 475.0569; Found 475.0557.

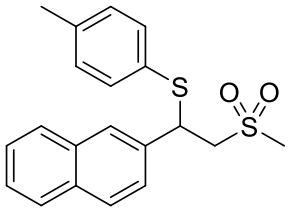


2-((2-(Naphthalen-2-yl)-2-(*p*-tolylthio)ethyl)sulfonyl)thiophene (4aa): The reaction was conducted on 0.2 mmol scale. The product **4aa** (26.3 mg, 31% yield) as white solid (mp 141.0-142.3 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 1H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.50 – 7.41 (m, 3H), 7.35 – 7.27 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 3.8, 1H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.61 (dd, *J* = 5.0, 3.8 Hz, 1H), 4.78 (dd, *J* = 10.5, 3.7 Hz, 1H), 4.03 (dd, *J* = 14.8, 10.5 Hz, 1H), 3.82 (dd, *J* = 14.8, 3.8 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 139.0, 134.9, 134.6, 134.05, 134.02, 133.1, 133.0, 130.2, 129.0, 128.6, 128.0, 127.7, 127.5, 127.4, 126.4 (2C), 125.3, 62.0, 48.3, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{20}O_2S_3Na$ 447.0523; Found 447.0525.

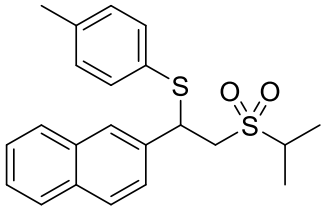


(2-(Cyclohexylsulfonyl)-1-(naphthalen-2-yl)ethyl)(*p*-tolyl)sulfane (4ab): The reaction was conducted on 0.2 mmol scale. The product **4ab** (27.2 mg, 32% yield) as white solid (mp 79.4-81.2 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.74 (m, 4H), 7.54 – 7.46 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 4.84 (dd, *J* = 10.1, 4.0 Hz, 1H), 3.74 (dd, *J* = 14.7, 10.2 Hz, 1H), 3.43 (dd, *J* = 14.7, 3.9 Hz, 1H), 2.31 (s, 3H), 2.01 (m, 1H), 1.91 (dt, *J* = 12.8, 3.2 Hz, 1H), 1.83 – 1.67 (m, 2H), 1.61 (dd, *J* =

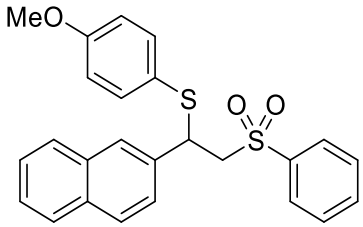
13.6, 3.5 Hz, 1H), 1.50 – 1.42 (m, 1H), 1.32 (m, 3H), 1.00 (m, 1H), 0.73 (m, 1H), 0.54 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 136.1, 133.8, 133.2, 133.1, 130.2, 129.2, 129.0, 128.0, 127.8, 127.4, 126.7, 126.6, 125.3, 61.5, 54.8, 48.0, 25.7, 25.0, 24.9, 24.7, 23.6, 21.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{28}O_2S_2Na$ 447.1429; Found 447.1427. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{28}O_2S_2Na$ 447.1429; Found 447.1427.



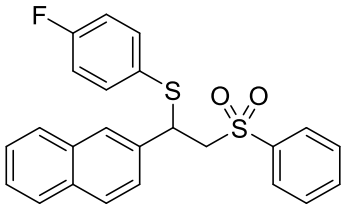
(2-(Methylsulfonyl)-1-(naphthalen-2-yl)ethyl)(*p*-tolyl)sulfane (4ac): The reaction was conducted on 0.2 mmol scale. The product **4ac** (24.2 mg, 34% yield) as white solid (mp 127.8-129.3 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 1H), 7.83 (dd, *J* = 6.2, 3.3 Hz, 1H), 7.79 (dd, *J* = 6.1, 3.4 Hz, 1H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.52 (td, *J* = 6.3, 5.8, 2.7 Hz, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 4.82 (dd, *J* = 10.4, 4.0 Hz, 1H), 3.76 (dd, *J* = 14.9, 10.4 Hz, 1H), 3.62 – 3.47 (m, 1H), 2.32 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 135.5, 134.1, 133.2, 133.2, 130.3, 129.4, 128.8, 128.1, 127.9, 127.6, 126.9, 126.8, 125.1, 60.3, 48.4, 42.4, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{20}O_2S_2Na$ 379.0803; Found 379.0803.



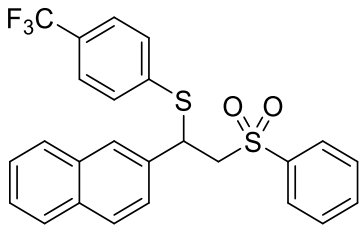
(2-(Isopropylsulfonyl)-1-(naphthalen-2-yl)ethyl)(*p*-tolyl)sulfane (4ad): The reaction was conducted on 0.2 mmol scale. The product **4ad** (39.2 mg, 51% yield) as white solid (mp 98.2-99.1 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.71 (m, 4H), 7.49 (m, 3H), 7.27 (d, *J* = 7.7 Hz, 2H), 7.07 (d, *J* = 7.7 Hz, 2H), 4.86 (dd, *J* = 9.9, 4.1 Hz, 1H), 3.77 (dd, *J* = 14.7, 9.9 Hz, 1H), 3.47 (dd, *J* = 14.7, 4.1 Hz, 1H), 2.49 (m, 1H), 2.30 (s, 3H), 1.13 (dd, *J* = 20.0, 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 136.0, 133.8, 133.2, 133.1, 130.2, 129.1, 129.0, 128.1, 127.8, 127.4, 126.62, 126.55, 125.2, 54.7, 53.6, 47.9, 21.3, 15.7, 14.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{24}O_2S_2Na$ 407.1116; Found 407.1111.



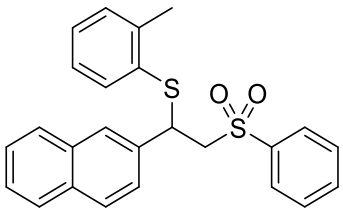
(4-Methoxyphenyl)(1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)sulfane (4ae): The reaction was conducted on 0.2 mmol scale. The product **4ae** (60 mg, 69% yield) as white solid (125.6-126.5 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 1H), 7.58 (t, *J* = 8.0 Hz, 2H), 7.47 – 7.40 (m, 4H), 7.34 (d, *J* = 1.9 Hz, 1H), 7.24 – 7.15 (m, 4H), 7.05 (t, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 4.65 (dd, *J* = 10.6, 3.9 Hz, 1H), 3.94 (dd, *J* = 14.7, 10.6 Hz, 1H), 3.77 (s, 3H), 3.77 – 3.69 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 139.3, 136.6, 134.7, 133.1, 132.9, 132.8, 128.7, 128.6, 128.5, 127.9, 127.8, 127.6, 127.5, 126.3, 126.2 125.3, 122.7, 60.5, 55.4, 48.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{22}O_3S_2Na$ 457.0908; Found 457.0903.



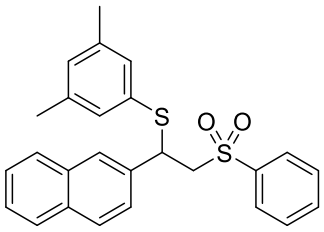
(4-Fluorophenyl)(1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)sulfane (4af): The reaction was conducted on 0.2 mmol scale. The product **4af** (63.4 mg, 75% yield) as white solid (mp 104.1-105.1 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 1H), 7.58 (m, 2H), 7.5 – 7.38 (m, 4H), 7.33 (d, *J* = 1.9 Hz, 1H), 7.24 (m, 3H), 7.18 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.08 (t, *J* = 7.9 Hz, 2H), 6.91 (t, *J* = 8.6 Hz, 2H), 4.72 (dd, *J* = 10.3, 4.1 Hz, 1H), 3.93 (dd, *J* = 14.7, 10.3 Hz, 1H), 3.74 (dd, *J* = 14.7, 4.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (d, J_{C-F} = 248.0), 139.2, 136.5 (d, J_{C-F} = 8.3 Hz), 134.5, 133.3, 132.9 (d, J_{C-F} = 3.6 Hz), 128.74 (2C), 128.68, 127.9 (3C), 127.59, 127.55, 126.46, 126.42, 125.1, 116.4 (d, J_{C-F} = 21.6 Hz), 60.5, 48.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{19}FO_2S_2Na$ 445.0708; Found 445.0708.



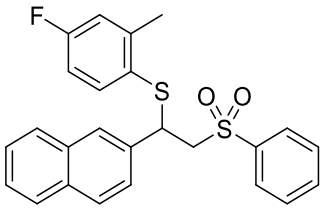
(1-(Naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)(4-(trifluoromethyl)phenyl)sulfane (4ag): The reaction was conducted on 0.2 mmol scale. The product **4ag** (48.2 mg, 75% yield) as white solid (mp 102.1-103.3 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 1H), 7.62 (m, 2H), 7.58 – 7.51 (m, 2H), 7.50 – 7.41 (m, 5H), 7.37 (m, 2H), 7.31 – 7.23 (m, 2H), 7.12 (m, 2H), 4.95 (dd, *J* = 10.1, 4.0 Hz, 1H), 3.96 (dd, *J* = 14.8, 10.1 Hz, 1H), 3.74 (dd, *J* = 14.8, 4.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 138.2, 134.2, 133.3, 133.0, 132.9, 131.6, 129.8 (q, J_{C-F} = 32.4 Hz), 128.9, 128.8, 127.9, 127.6, 127.5, 126.6, 126.5, 126.0 (q, J_{C-F} = 3.6 Hz), 124.9, 123.8 (q, J_{C-F} = 270.7 Hz), 60.7, 46.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.73. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{19}F_3O_2S_2Na$ 495.0677; Found 495.0676.



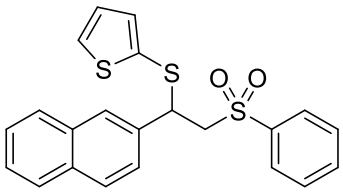
(1-(Naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)(*o*-tolyl)sulfane (4ah): The reaction was conducted on 0.2 mmol scale. The product **4ah** (15.9 mg, 19% yield) as white solid (mp 119.3-120.8 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.69 (m, 1H), 7.60 (m, 2H), 7.51 – 7.42 (m, 5H), 7.38 – 7.31 (m, 1H), 7.24 – 7.16 (m, 4H), 7.13 – 7.05 (m, 3H), 4.74 (dd, *J* = 10.7, 3.6 Hz, 1H), 3.98 (dd, *J* = 14.7, 10.7 Hz, 1H), 3.73 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 139.3, 134.6, 133.9, 133.2, 133.1, 133.0, 132.1, 130.9, 128.73, 128.71, 128.7, 128.0, 127.9, 127.6, 127.5, 126.9, 126.41, 126.38, 125.2, 60.6, 47.0, 20.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{22}O_2S_2Na$ 441.0959; Found 441.0953.



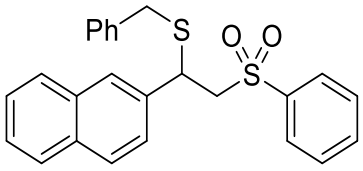
(3,5-Dimethylphenyl)(1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)sulfane (4ai): The reaction was conducted on 0.2 mmol scale. The product **4ai** (26.0 mg, 30% yield) as white solid (mp 122.2-130.7 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (m, 1H), 7.60 (m, 2H), 7.49 – 7.39 (m, 5H), 7.24 – 7.18 (m, 2H), 7.10 – 7.02 (m, 2H), 6.91 (d, *J* = 12.6 Hz, 3H), 4.77 (dd, *J* = 11.3, 3.6 Hz, 1H), 3.96 (dd, *J* = 14.6 Hz, 10.9 Hz, 1H), 3.76 (dd, J = 14.6 Hz, 3.6 Hz 1H), 2.22 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 139.0, 134.5, 133.1, 133.04, 133.02, 132.2, 131.1, 130.4, 128.7, 128.6, 127.92, 127.90, 127.65, 127.60, 126.4, 126.3, 125.3, 60.7, 47.7, 21.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{24}O_2S_2Na$ 455.1116; Found 455.1111.



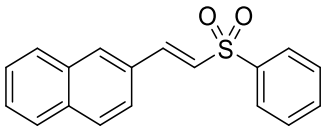
(4-Fluoro-2-methylphenyl)(1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)sulfane (4aj): The reaction was conducted on 0.2 mmol scale. The product **4aj** (19.2 mg, 22% yield) as white solid (mp 105.4-106.4 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.68 (m, 1H), 7.59 (m, 2H), 7.49 – 7.41 (m, 4H), 7.34 (s, 1H), 7.30 – 7.23 (m, 4H), 7.18 (m, 1H), 7.09 (m, 2H), 6.88 (m, 1H), 6.77 (m, 1H), 4.62 (dd, *J* = 10.6, 3.8 Hz, 1H), 4.12 – 3.84 (m, 1H), 3.79 – 3.62 (m, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, $J_{C\text{-}F}$ = 247.9 Hz), 144.8 (d, *J* = 8.4 Hz), 139.2, 137.2 (d, $J_{C\text{-}F}$ = 8.6 Hz), 134.5, 133.1, 132.9, 128.6, 128.55, 127.8, 127.5, 127.3, 126.8 (d, $J_{C\text{-}F}$ = 3.1 Hz), 126.33, 126.32, 124.9, 117.7 (d, $J_{C\text{-}F}$ = 21.6 Hz), 113.9 (d, $J_{C\text{-}F}$ = 21.3 Hz), 60.5, 47.7, 21.0. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{21}FO_2S_2Na$ 459.0865; Found 459.0858.



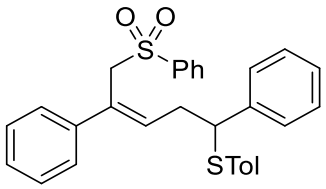
2-((1-(Naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)thio)thiophene (4ak): The reaction was conducted on 0.2 mmol scale. The product **4ak** (48.4 mg, 59% yield) as white solid (mp 91.2-91.9 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 1H), 7.64 – 7.54 (m, 2H), 7.50 – 7.39 (m, 4H), 7.35 – 7.31 (m, 2H), 7.24 – 7.15 (m, 2H), 7.07 (m, 2H), 6.93 – 6.89 (m, 2H), 4.64 (dd, *J* = 10.4, 4.1 Hz, 1H), 3.96 (dd, *J* = 14.7, 10.4 Hz, 1H), 3.81 (dd, *J* = 14.7, 4.1 Hz, 1H). δ 139.3, 136.8, 134.2, 133.2, 133.01, 132.97, 131.8, 130.3, 128.7, 128.6, 127.9 (3C), 127.62, 127.61, 126.5, 126.4, 125.2, 60.3, 50.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{18}O_2S_3Na$ 33.0367; Found 433.0359.



Benzyl(1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)sulfane (4al): The reaction was conducted on 0.2 mmol scale. The product **4al** (30.1 mg, 36% yield) as white solid (mp 107.4-108.1 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.66 (m, 2H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.57 – 7.39 (m, 5H), 7.35 – 7.20 (m, 5H), 7.19 – 7.04 (m, 4H), 4.36 (dd, *J* = 9.6, 4.6 Hz, 1H), 3.81 (dd, *J* = 14.7, 9.6 Hz, 1H), 3.68 (dd, *J* = 14.7, 4.7 Hz, 1H), 3.60 – 3.41 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 137.1, 135.5, 133.1, 132.93, 132.86, 129.0, 128.8, 128.7, 128.6, 127.84, 127.81, 127.7, 127.6, 127.3, 126.4, 126.3, 124.9, 61.2, 43.4, 36.0. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{22}O_2S_2Na$ 441.0959; Found 441.0951.



(*E*)-2-(2-(Phenylsulfonyl)vinyl)naphthalene (6a): The reaction was conducted on 0.2 mmol scale. The product **6a** (26.5 mg, 45% yield) as white solid was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.3 Hz, 2H), 7.93 (s, 1H), 7.89 – 7.79 (m, 4H), 7.69 – 7.48 (m, 6H), 6.98 (d, J = 15.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.57, 140.9, 134.5, 133.4, 133.2, 130.9, 129.9, 129.4, 129.0, 128.7, 127.8, 127.8, 127.7, 127.4, 127.0, 123.5.[3]



(*Z*)-(1,4-Diphenyl-5-(phenylsulfonyl)pent-3-en-1-yl)(*p*-tolyl)sulfane (7a): The reaction was conducted on 0.2 mmol scale. The product **7a** (29.1 mg, 30% yield) as white solid (mp 141.1-143.0 °C) was purified by flash column chromatography (PE/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.63 (m, 2H), 7.54 – 7.46 (m, 1H), 7.36 (m, 2H), 7.30 – 7.27 (m, 1H), 7.26 – 7.21 (m, 4H), 7.19 – 7.12 (m, 4H), 7.09 – 7.02 (m, 4H), 5.95 (t, *J* = 7.4 Hz, 1H), 4.33 – 3.95 (m, 3H), 2.66 (m, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 140.8, 139.2, 137.7, 134.9, 133.6, 133.3, 130.9, 129.8, 129.8, 129.0, 128.6 (2C), 128.4, 128.0, 127.5, 126.6, 57.9, 53.5, 36.1, 21.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{28}O_2S_2Na$ 507.1429; Found 507.1431.

18. Reference

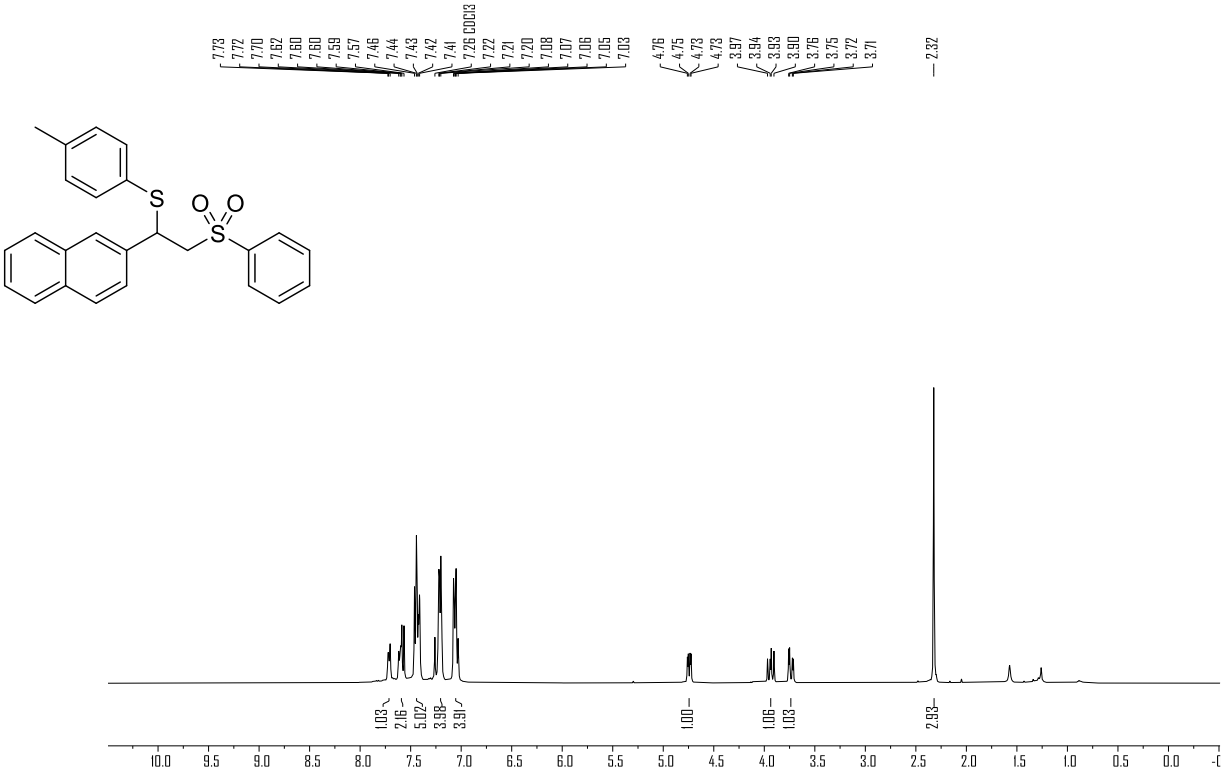
[1] H. Rao, L. C. Schmidt, J. Bonin and M. Robert, Visible-light-driven methane formation from CO_2 with a molecular iron catalyst, *Nature*, 2017, **548**, 74-77.

[2] H.-Y. Li, C.-C. Shan, C.-H. Tung, Z.-H Xu, Dual gold and photoredox catalysis: visible light-mediated intermolecular atom transfer thiosulfonylation of alkenes, *Chem. Sci.*, 2017, **8**, 2610-2615.

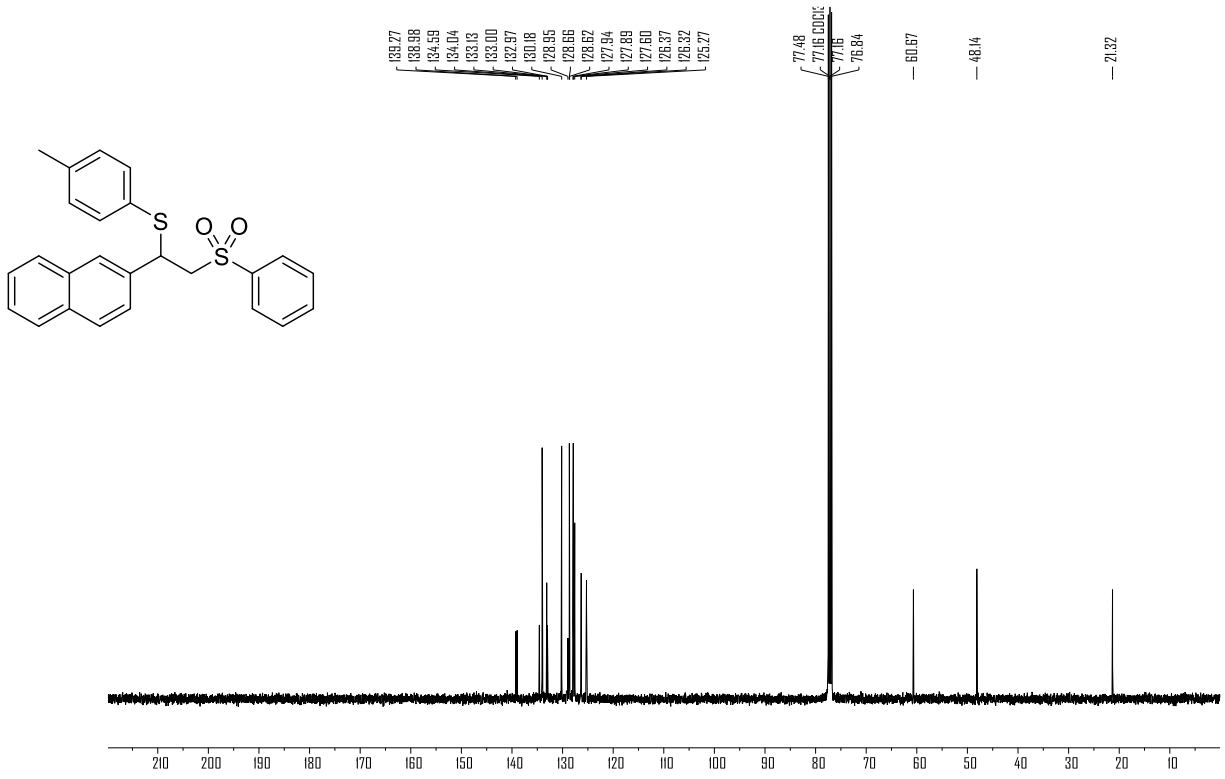
[3] A. U. Meyer, S. Jäger, D. P. Hari, B. König, Visible Light-Mediated Metal-Free Synthesis of Vinyl Sulfones from Aryl Sulfinates, *Adv. Synth. Catal.* 2015, **357**, 2050-2054.

19. NMR Spectra

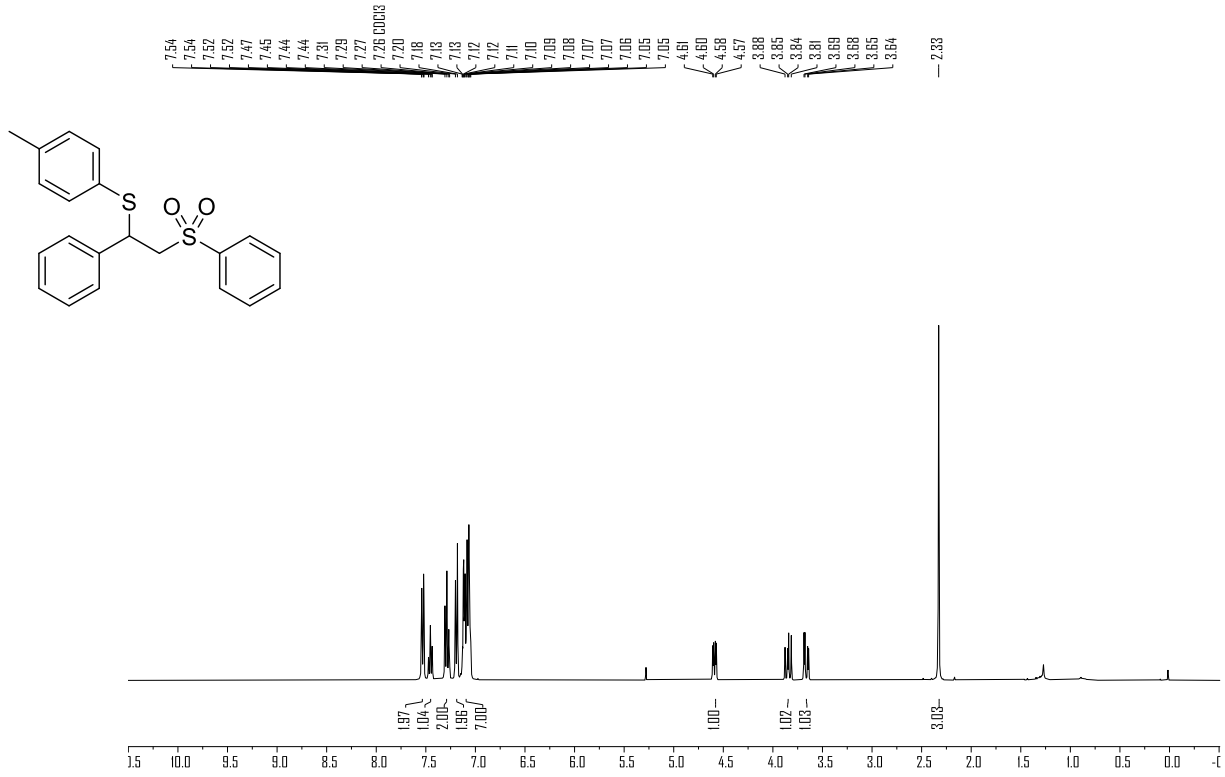
(1-(Nphthalen-2-yl)-2-(phenylsulfonyl)ethyl)(p-tolyl)sulfane (4a): ^{1}H NMR (400 MHz, $CDCl_3$)



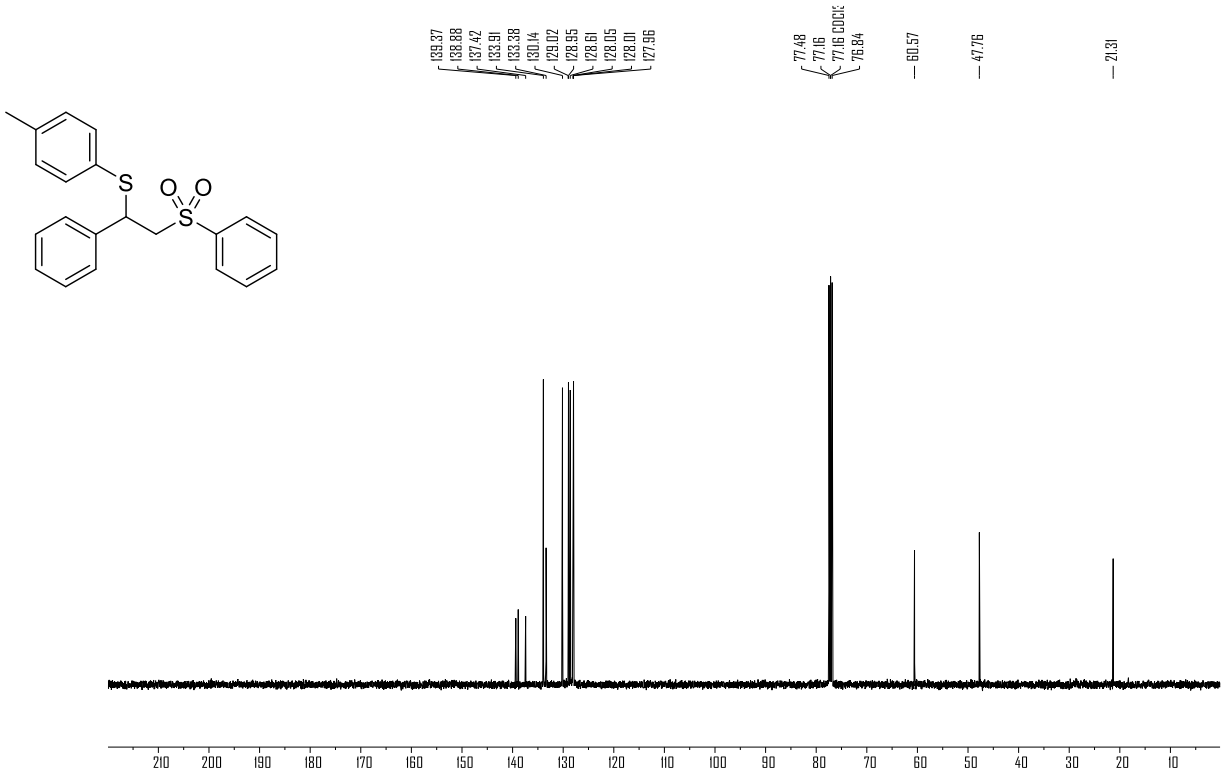
(1-(Nphthalen-2-yl)-2-(phenylsulfonyl)ethyl)(p-tolyl)sulfane (4a): ^{13}C NMR (101 MHz, $CDCl_3$)



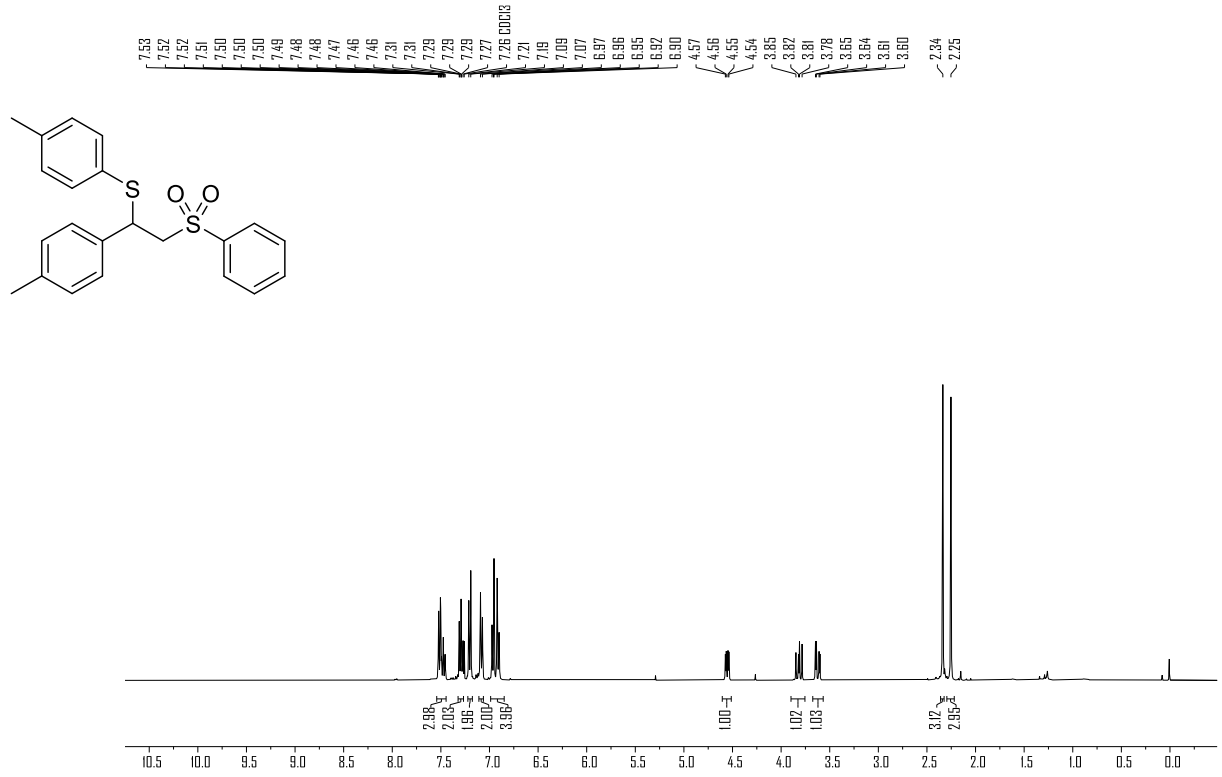
(2-(Phenylsulfonyl)phenyl)(p-tolyl)sulfane (4b): ^{1}H NMR (400 MHz, $CDCl_3$)



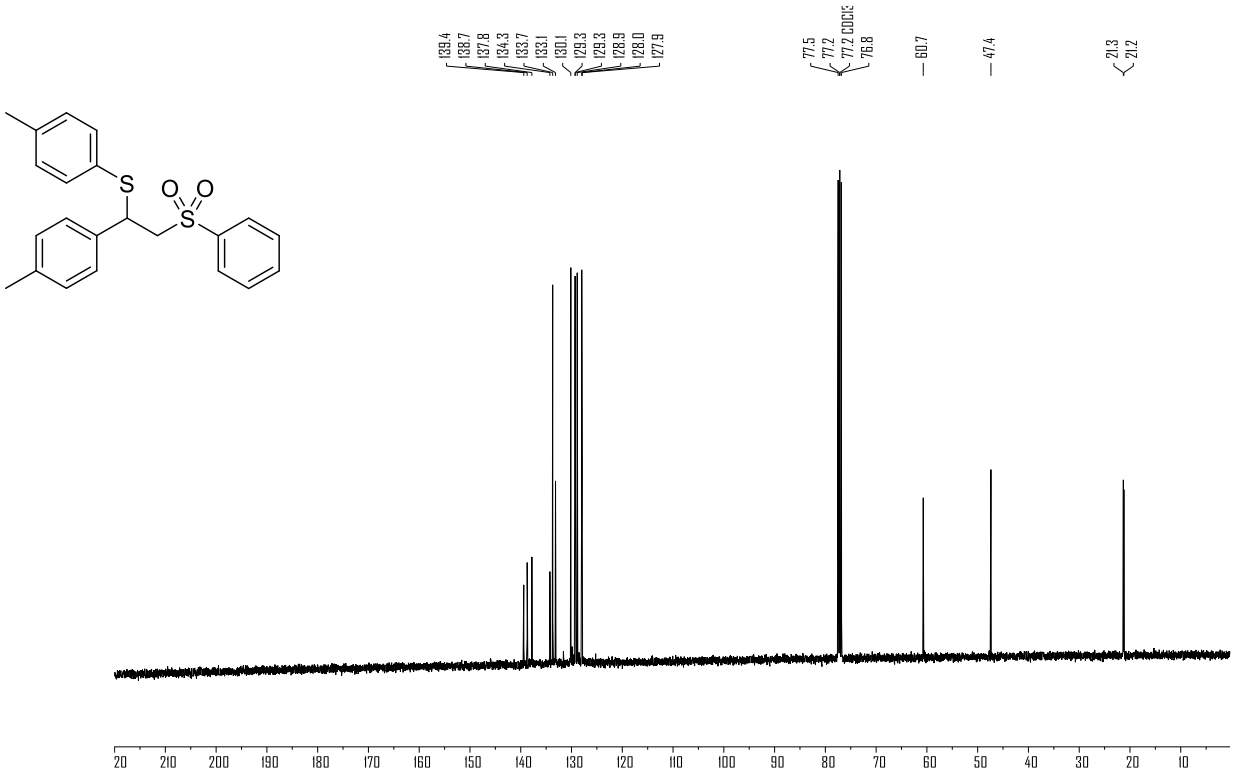
(2-(Phenylsulfonyl)phenyl)(p-tolyl)sulfane (4b): ^{13}C NMR (101 MHz, $CDCl_3$)



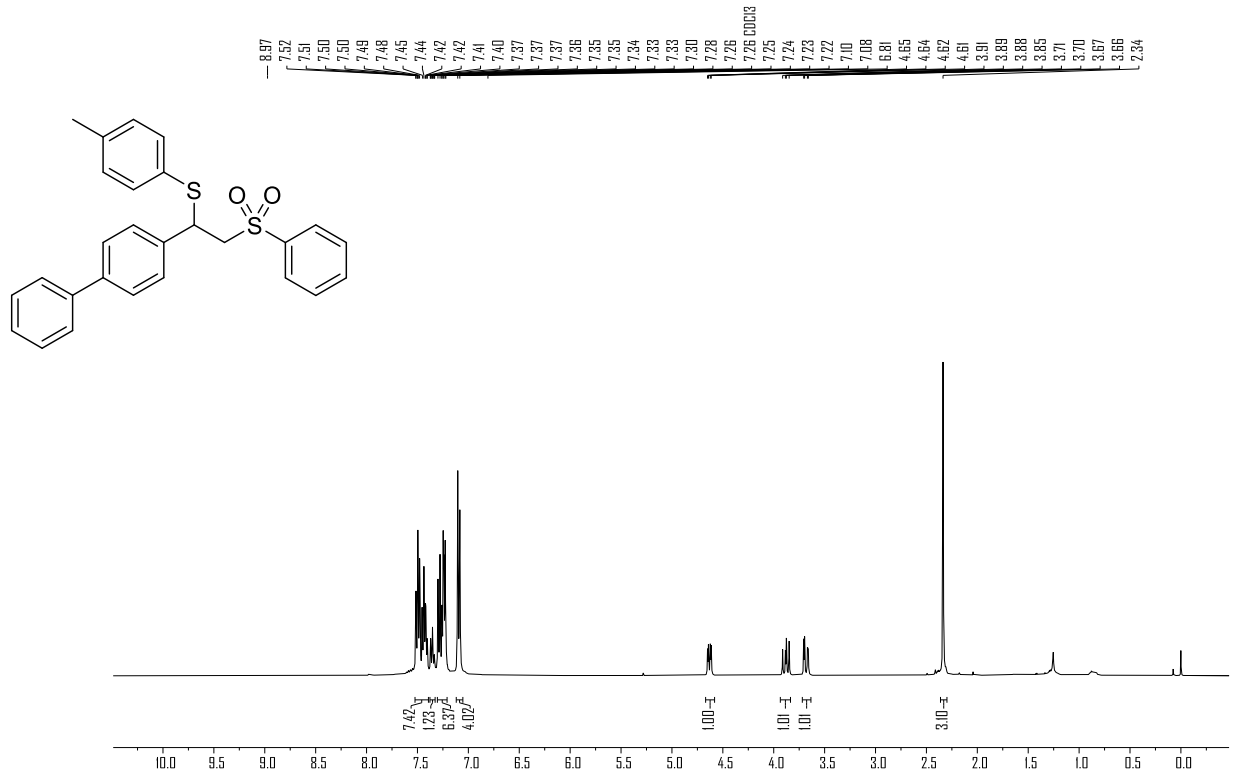
(2-(Phenylsulfonyl)-1-(p-tolyl)ethyl)(p-tolyl)sulfane (4c): ^{1}H NMR (400 MHz, $CDCl_3$)



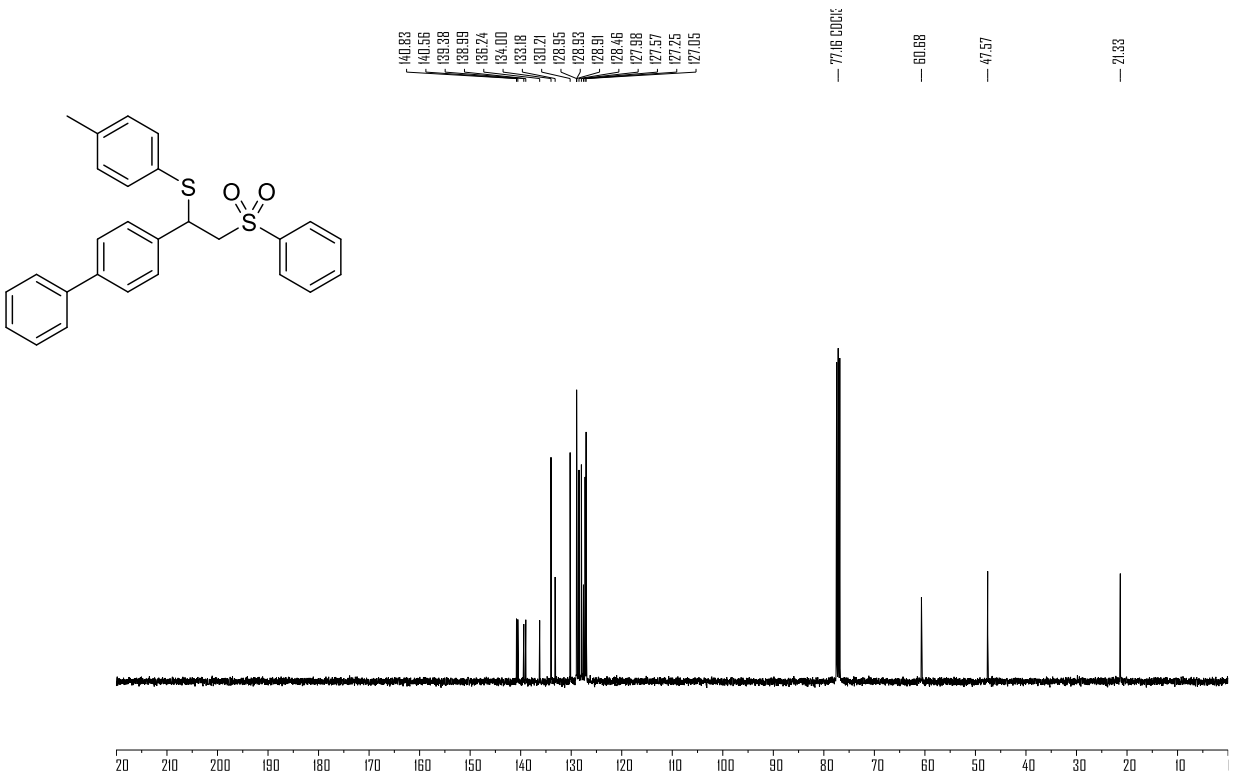
(2-(Phenylsulfonyl)-1-(p-tolyl)ethyl)(p-tolyl)sulfane (4c): ^{13}C NMR (101 MHz, $CDCl_3$)



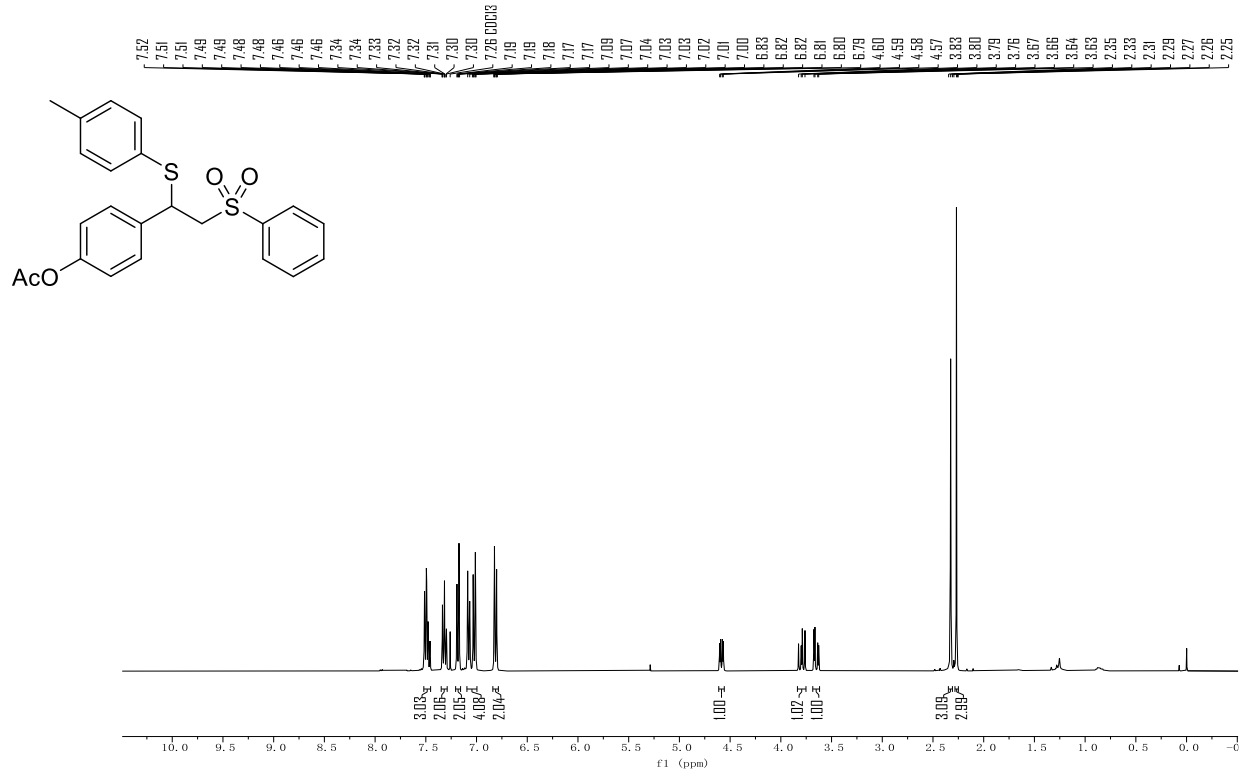
(1-([1,1'-Biphenyl]-4-yl)-2-(phenylsulfonyl)ethyl)(p-tolyl)sulfane (4d): ^{1}H NMR (400 MHz, $CDCl_3$)



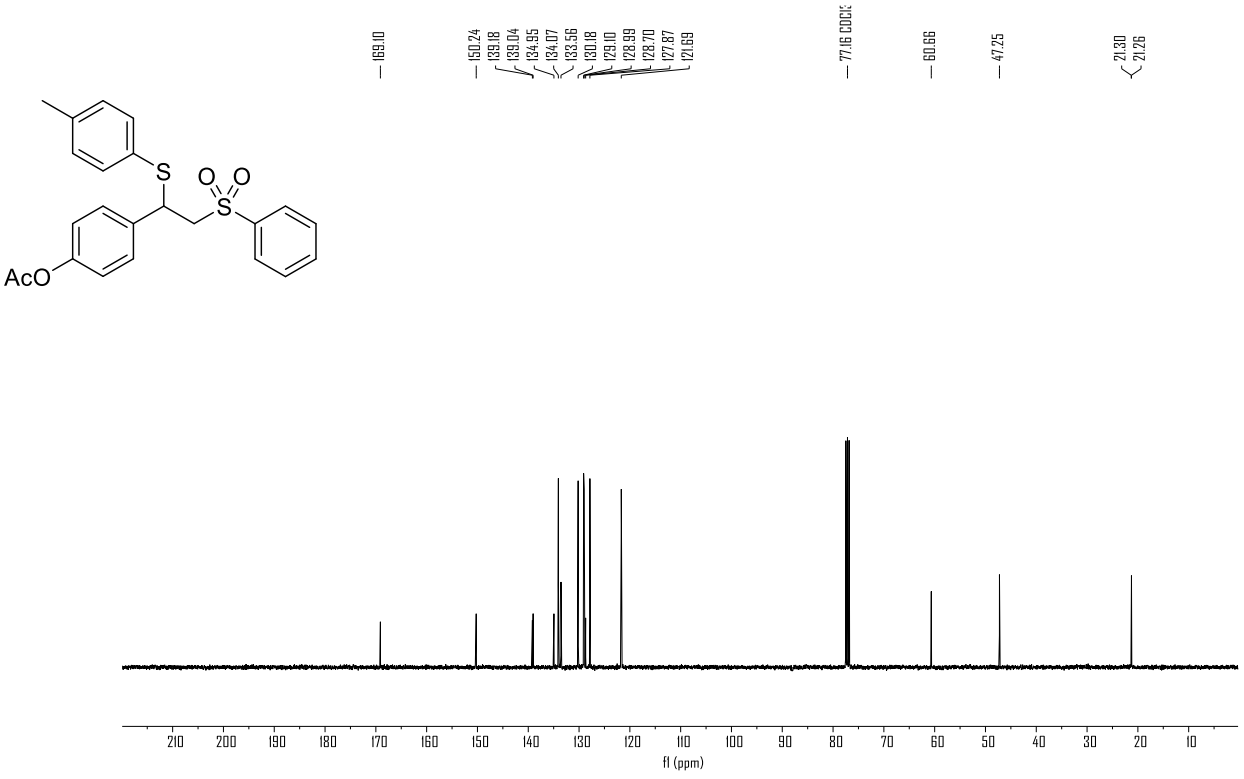
(1-([1,1'-Biphenyl]-4-yl)-2-(phenylsulfonyl)ethyl)(p-tolyl)sulfane (4d): ^{13}C NMR (101 MHz, $CDCl_3$)



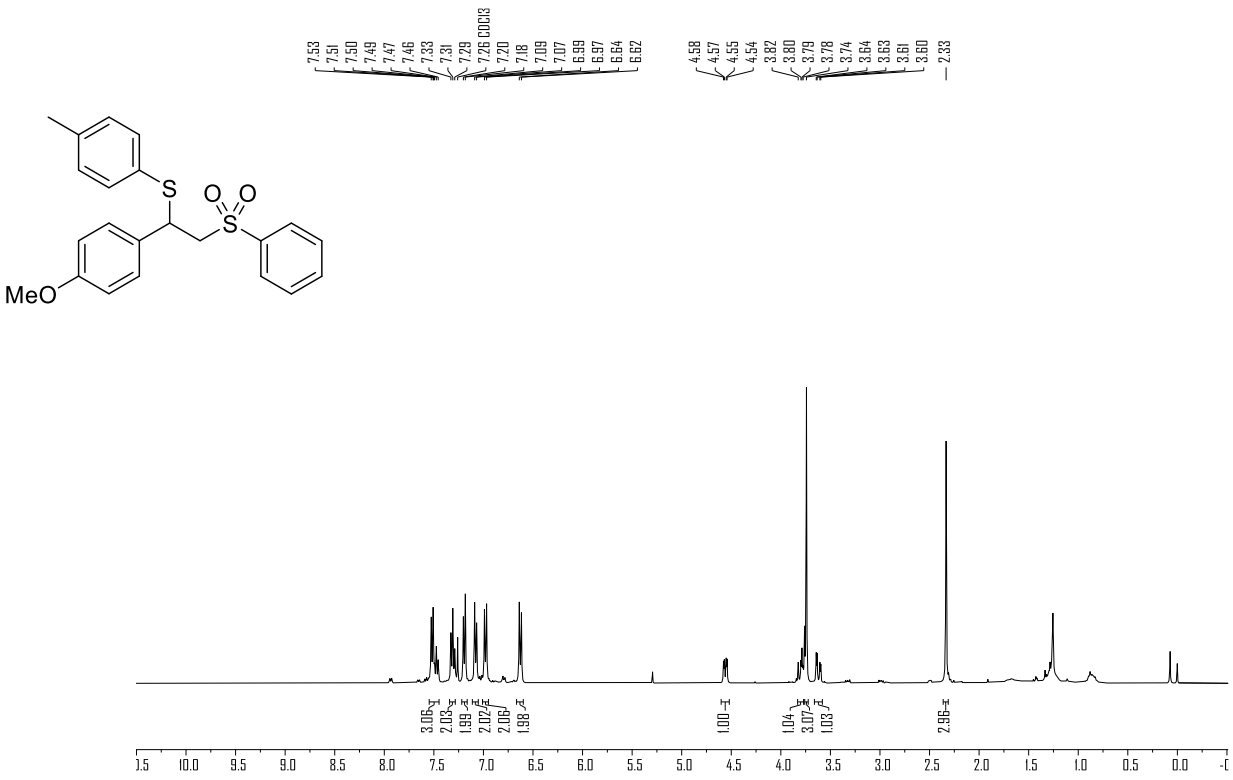
4-(2-(Phenylsulfonyl)-1-(p-tolylthio)ethyl)phenyl acetate (4e): ^{1}H NMR (400 MHz, $CDCl_3$)



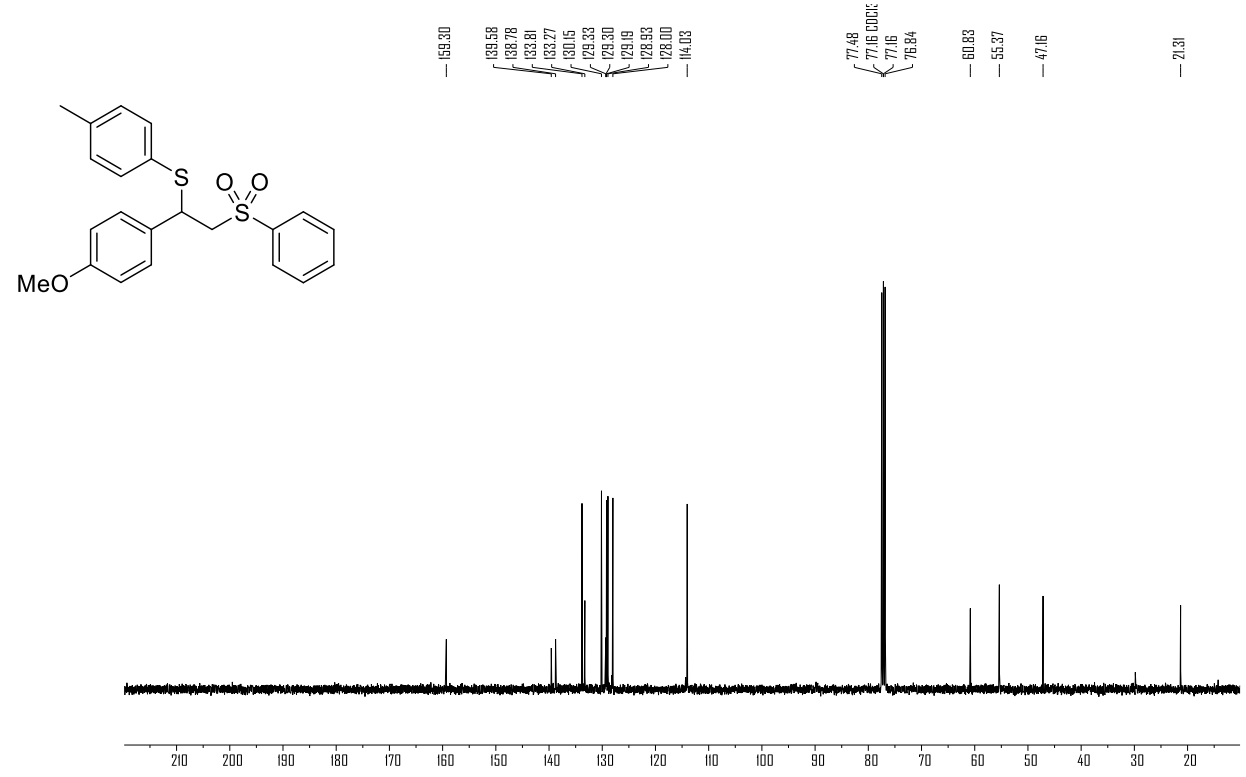
4-(2-(Phenylsulfonyl)-1-(p-tolylthio)ethyl)phenyl acetate (4e): ^{13}C NMR (101 MHz, $CDCl_3$)



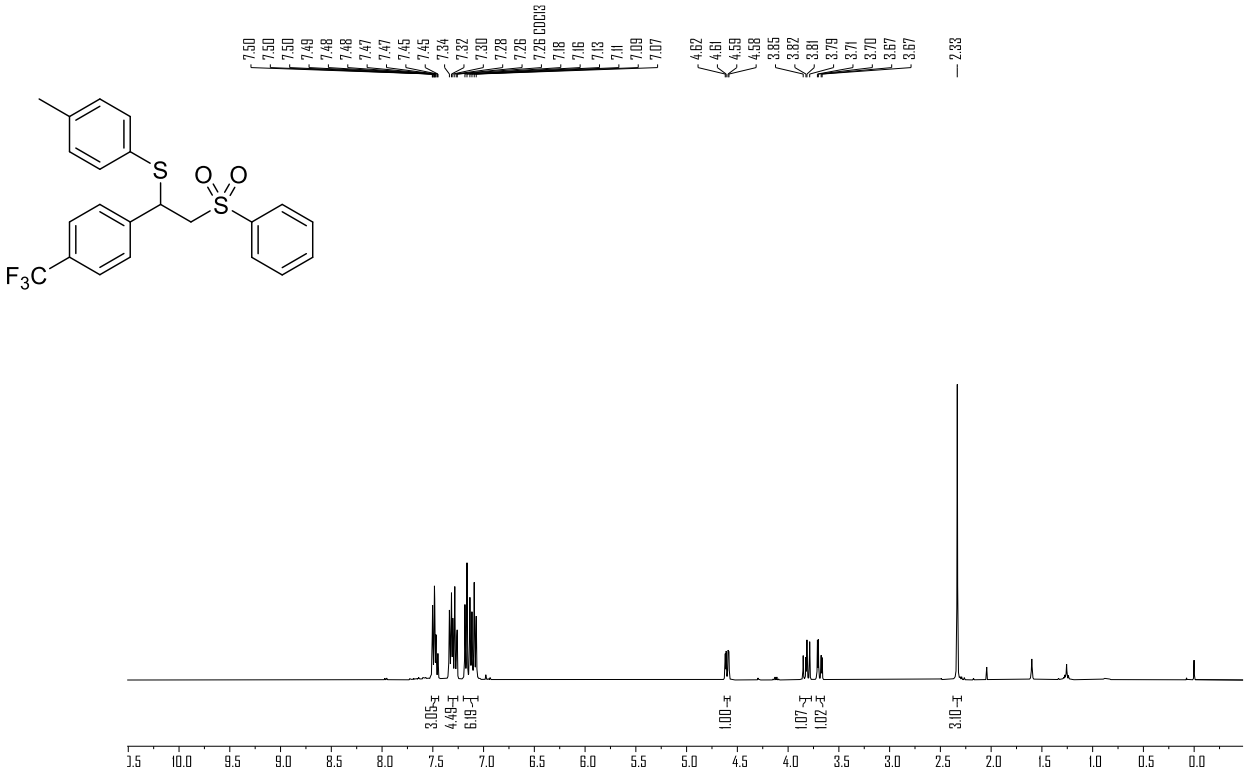
(1-(4-Methoxyphenyl)-2-(phenylsulfonyl)ethyl)(p-tolyl)sulfane (4f): ^{1}H NMR (400 MHz, $CDCl_3$)



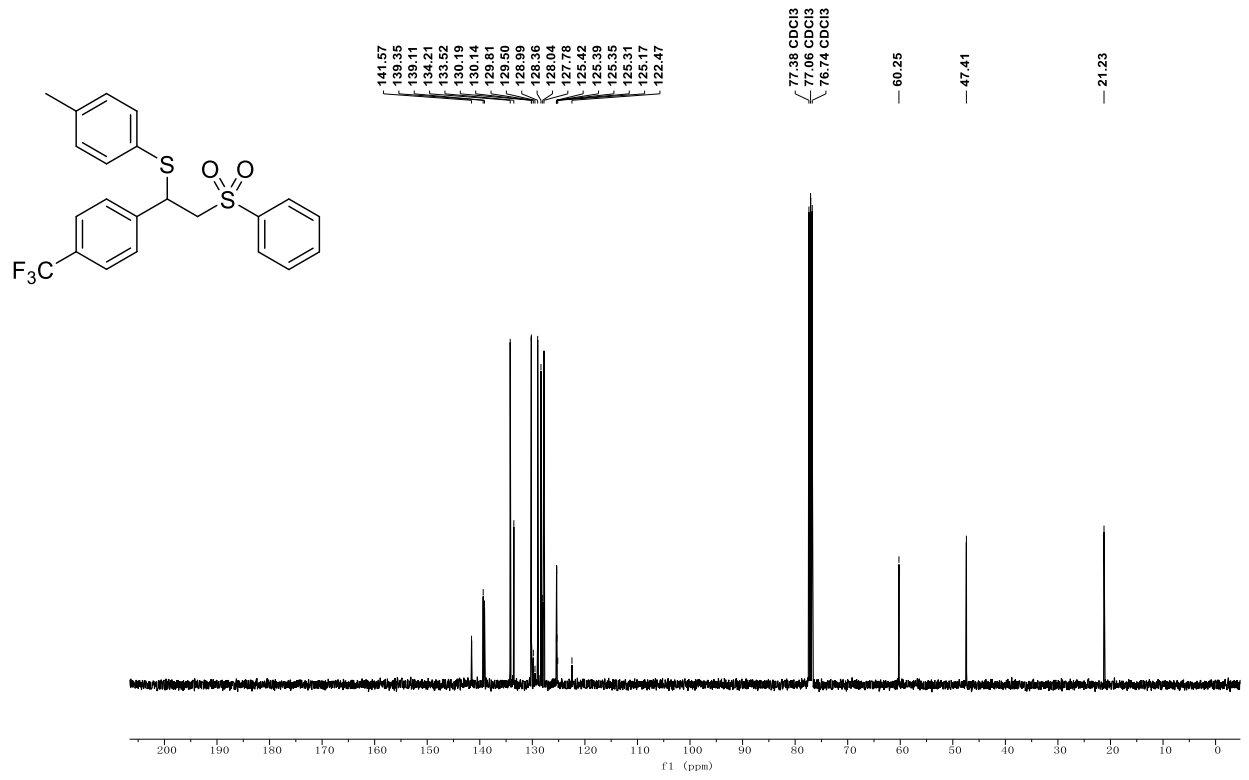
(1-(4-Methoxyphenyl)-2-(phenylsulfonyl)ethyl)(p-tolyl)sulfane (4f): ^{13}C NMR (101 MHz, $CDCl_3$)



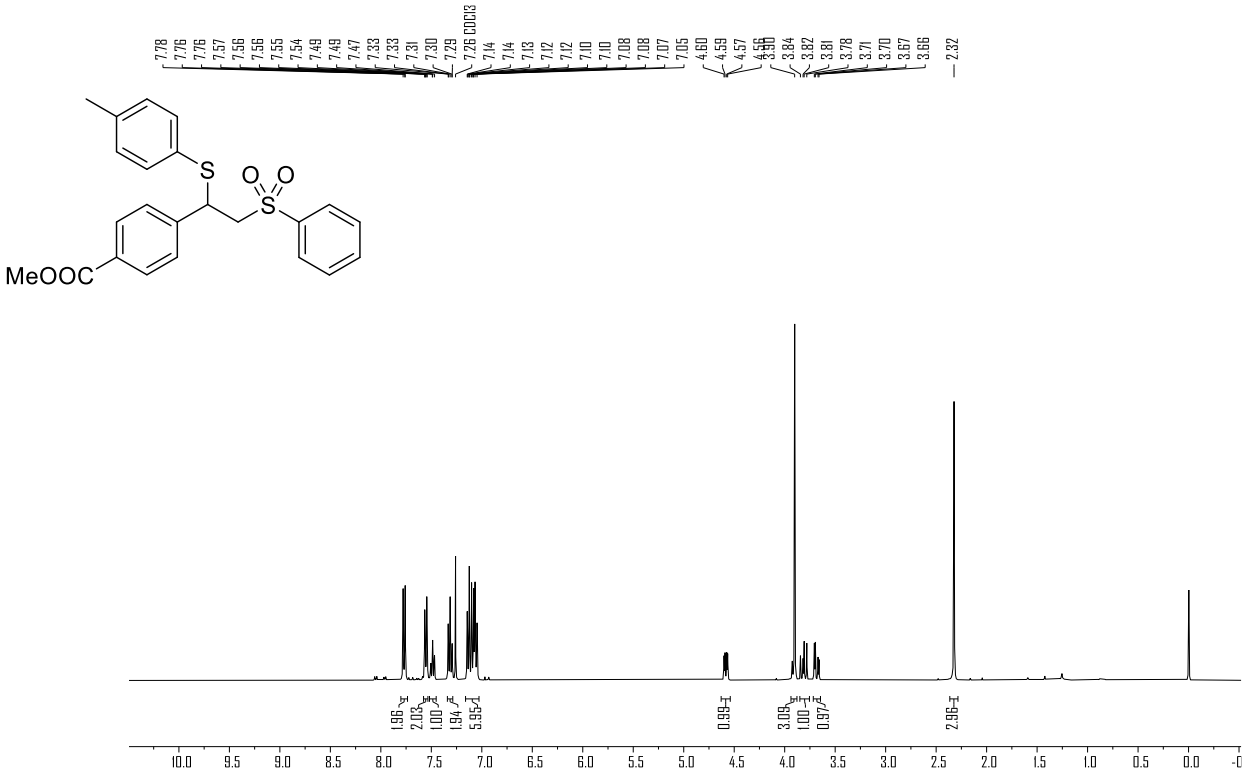
(2-(Phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethyl)(p-tolyl)sulfane (4g): ^{1}H NMR (400 MHz, $CDCl_3$)



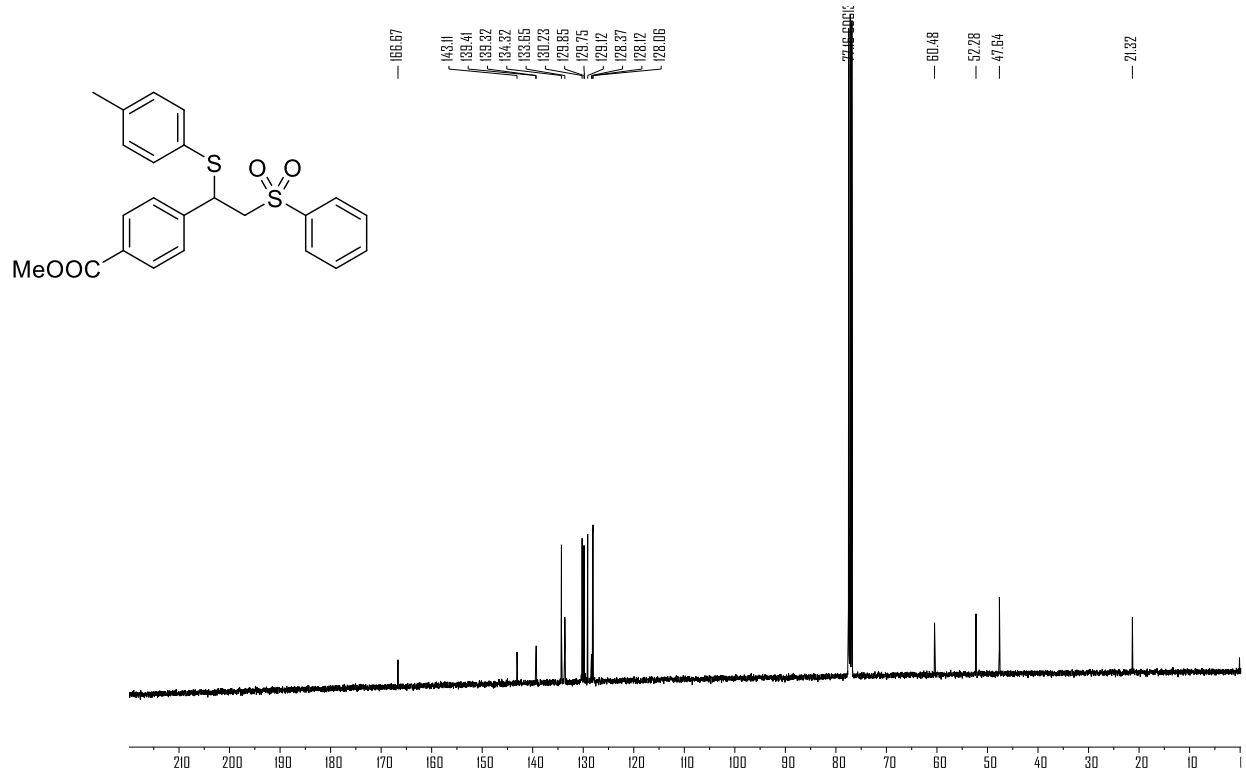
(2-(Phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethyl)(p-tolyl)sulfane (4g): ^{13}C NMR (101 MHz, $CDCl_3$)



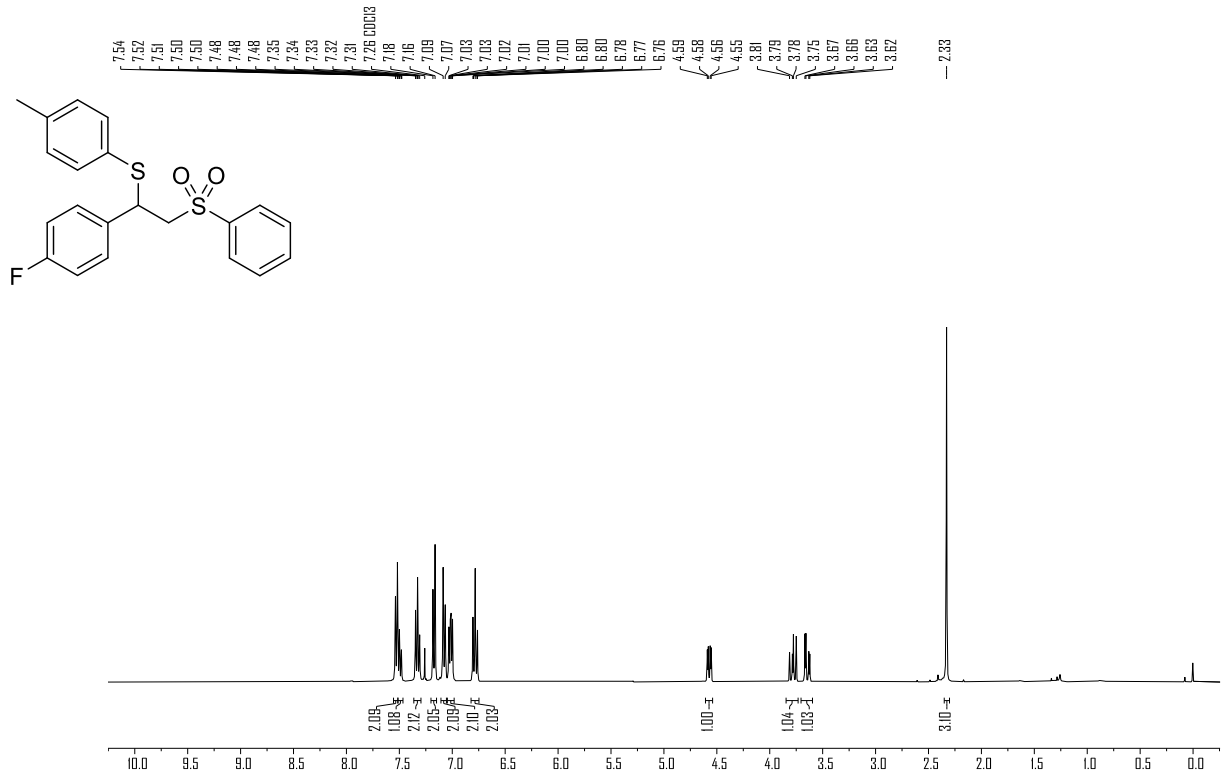
Methyl 4-(2-(Phenylsulfonyl)-1-(p-tolylthio)ethyl)benzoate (4h): ^{1}H NMR (400 MHz, $CDCl_3$)



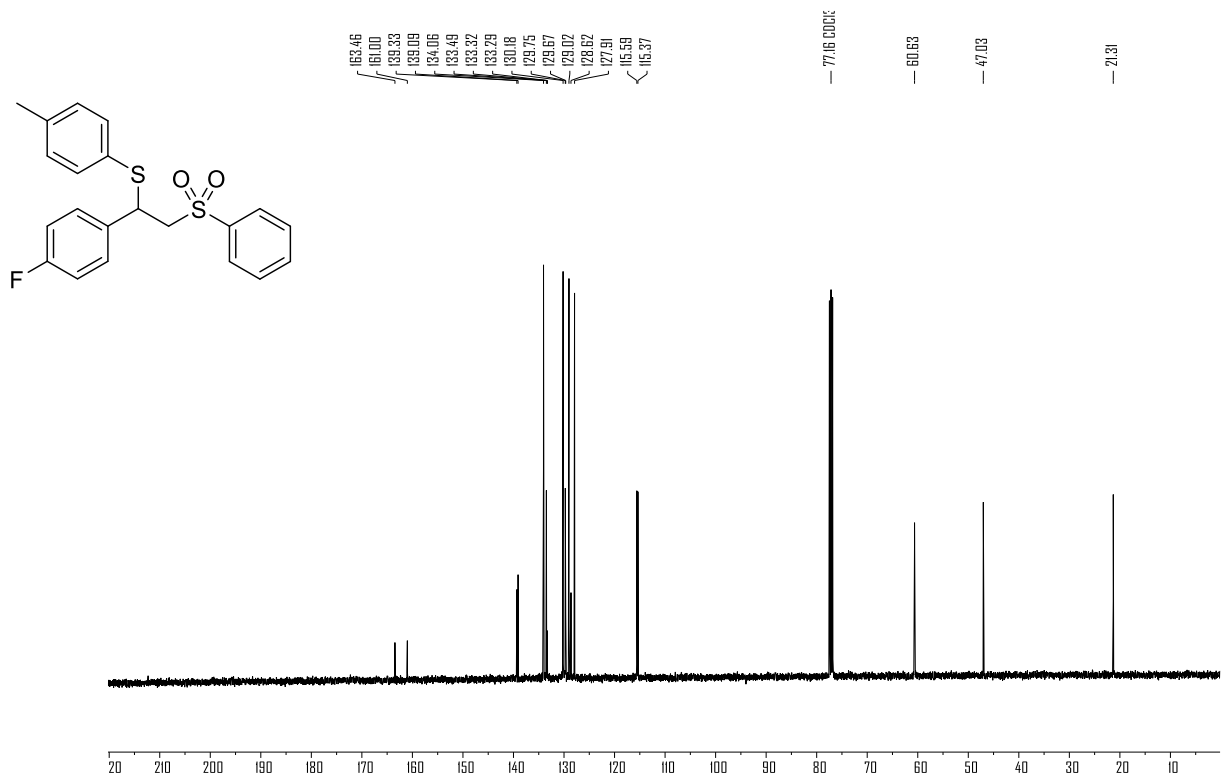
Methyl 4-(2-(Phenylsulfonyl)-1-(p-tolylthio)ethyl)benzoate (4h): ^{13}C NMR (101 MHz, $CDCl_3$)



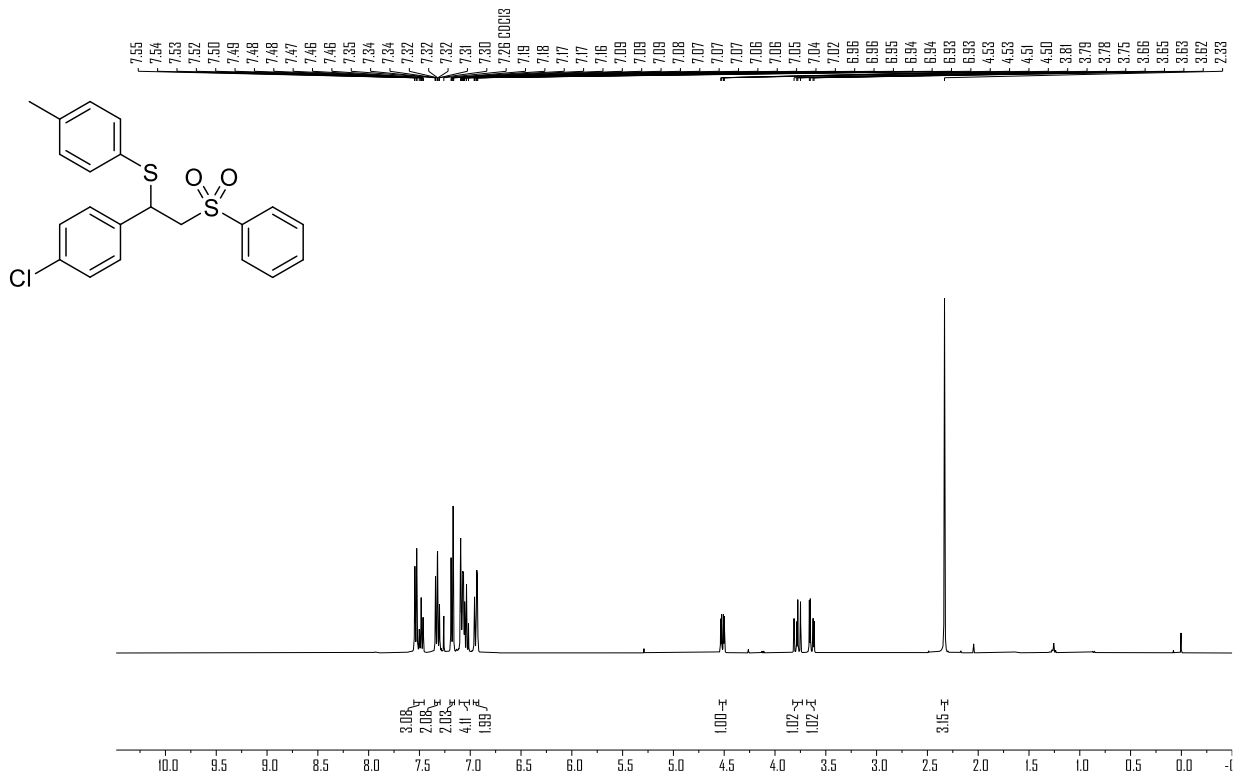
(1-(4-Fluorophenyl)-2-(phenylsulfonyl)ethyl)(p-tolyl)sulfane (4i): ^{1}H NMR (400 MHz, $CDCl_3$)



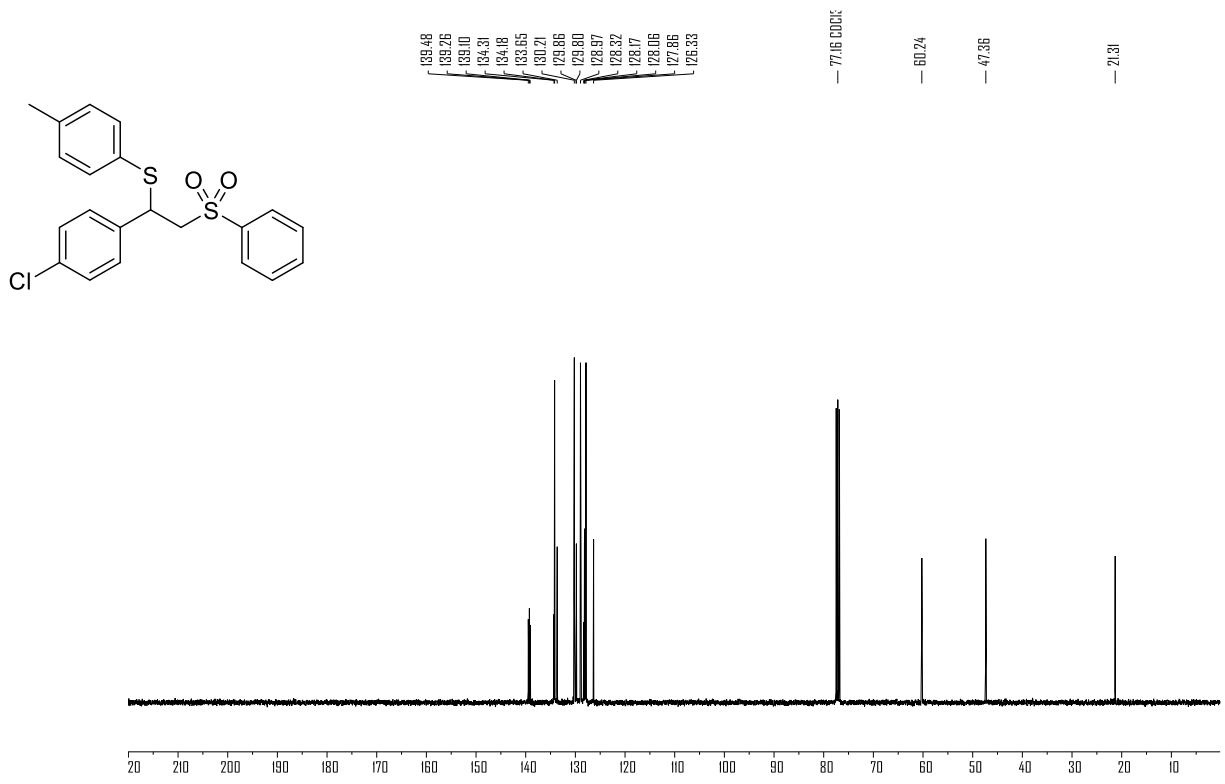
(1-(4-Fluorophenyl)-2-(phenylsulfonyl)ethyl)(p-tolyl)sulfane (4i): ^{13}C NMR (101 MHz, $CDCl_3$)



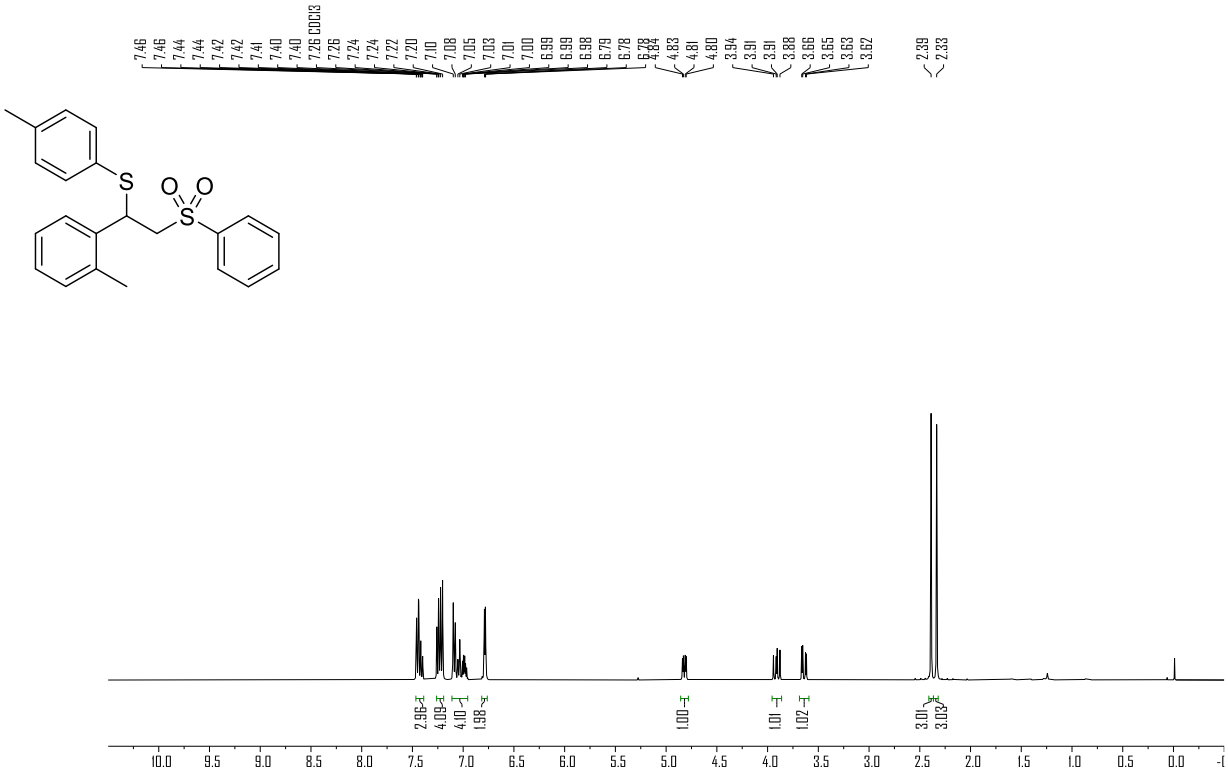
(1-(4-Chlorophenyl)-2-(phenylsulfonyl)ethyl)(p-tolyl)sulfane (4j): ^{1}H NMR (400 MHz, $CDCl_3$)



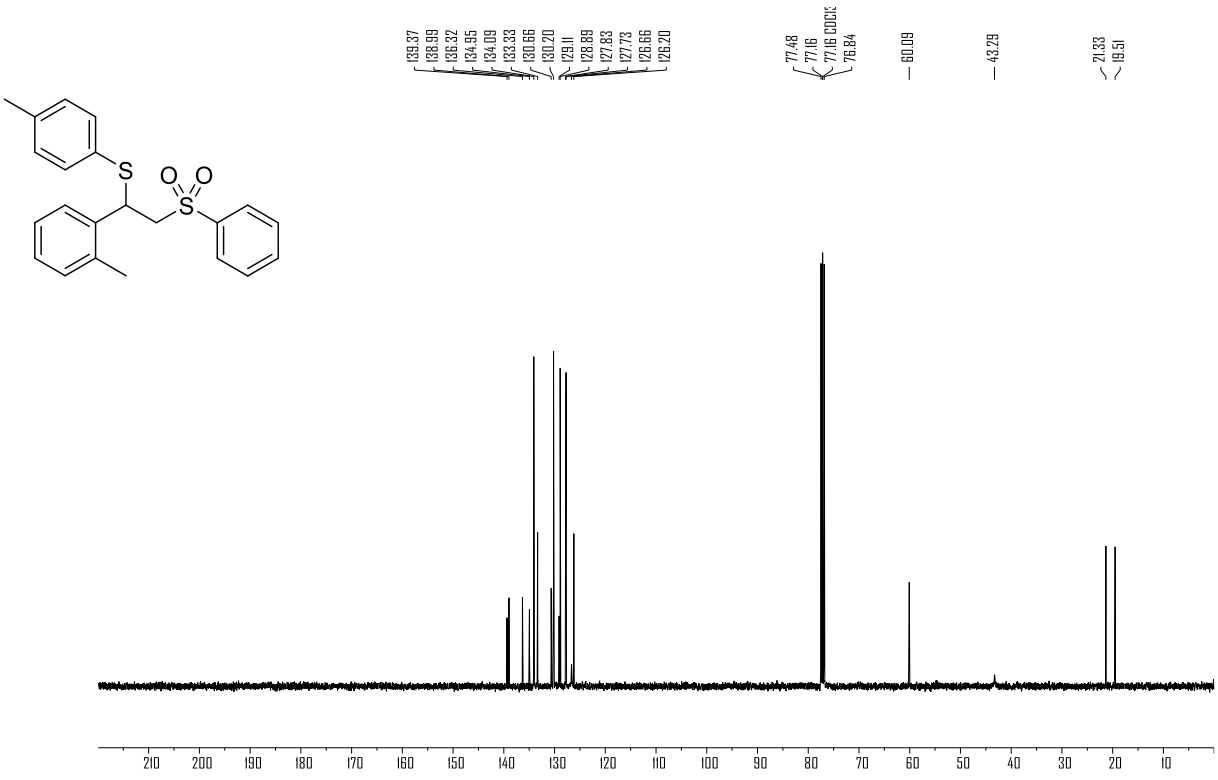
(1-(4-Chlorophenyl)-2-(phenylsulfonyl)ethyl)(p-tolyl)sulfane (4j): ^{13}C NMR (101 MHz, $CDCl_3$)



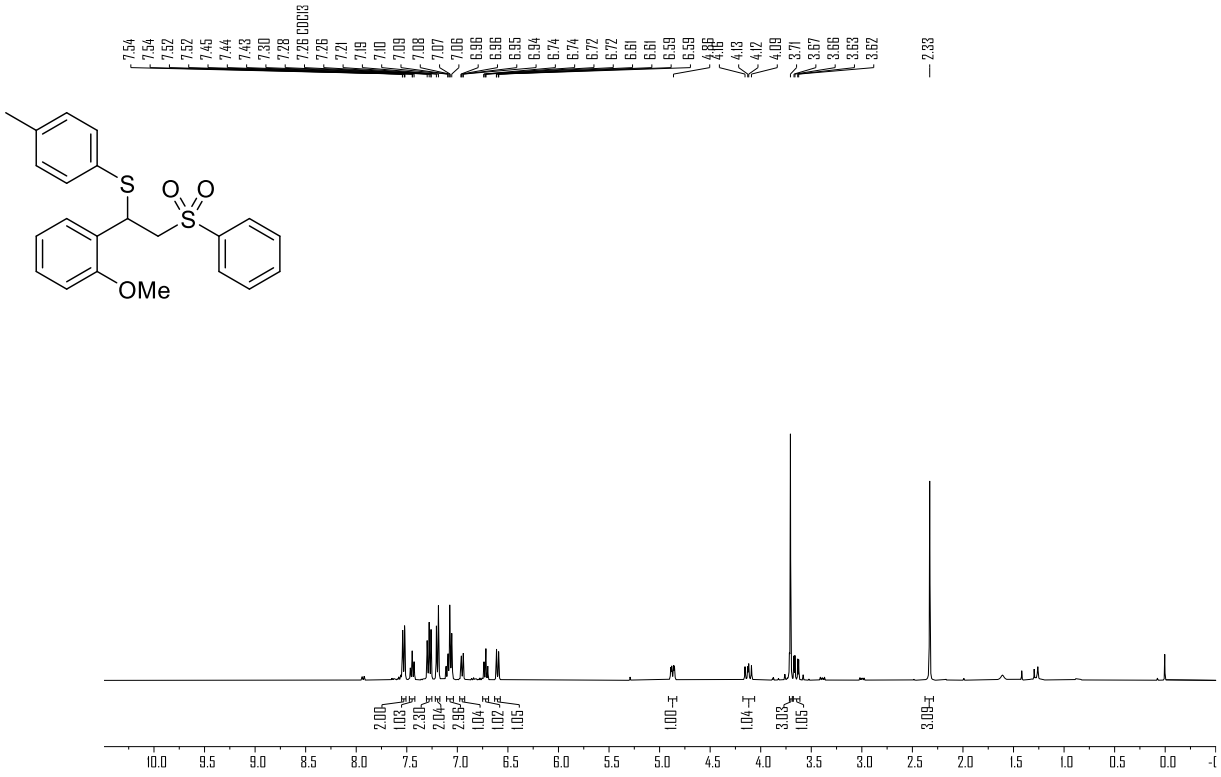
(2-(Phenylsulfonyl)-1-(o-tolyl)ethyl)(p-tolyl)sulfane (4k): ^{1}H NMR (400 MHz, $CDCl_3$)



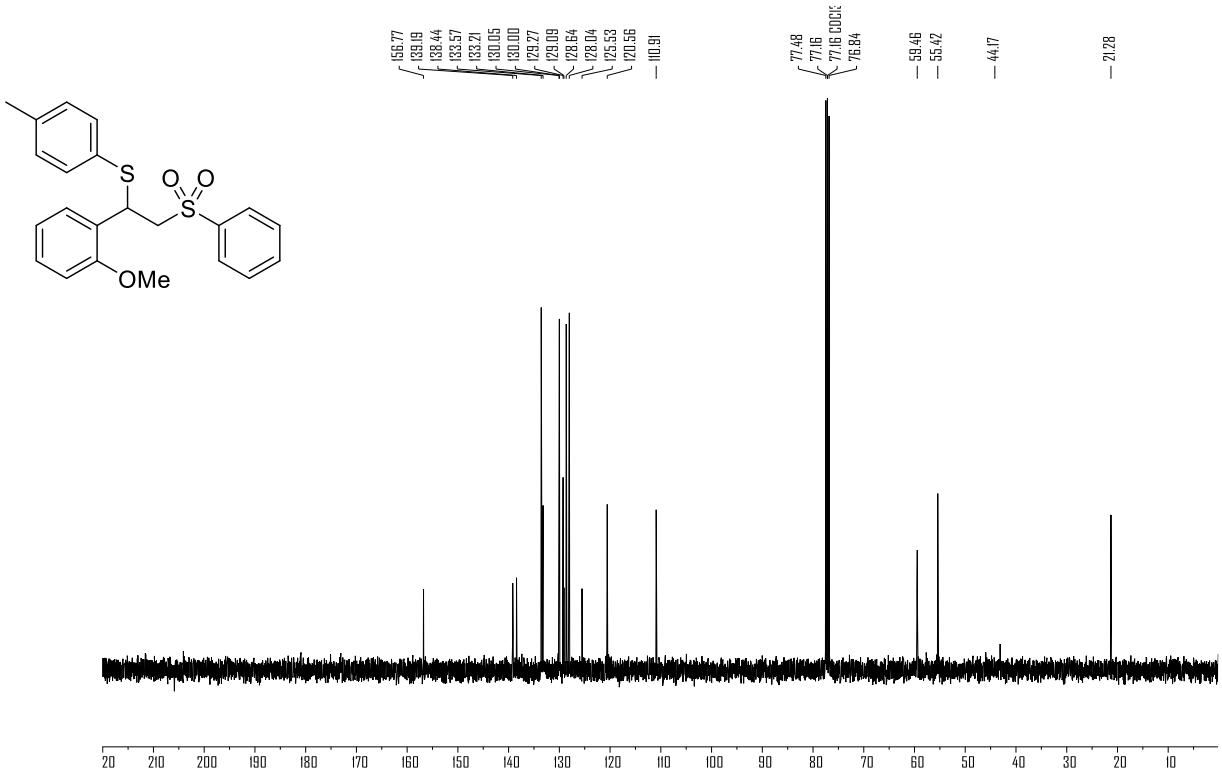
(2-(Phenylsulfonyl)-1-(o-tolyl)ethyl)(p-tolyl)sulfane (4k): ^{13}C NMR (101 MHz, $CDCl_3$)



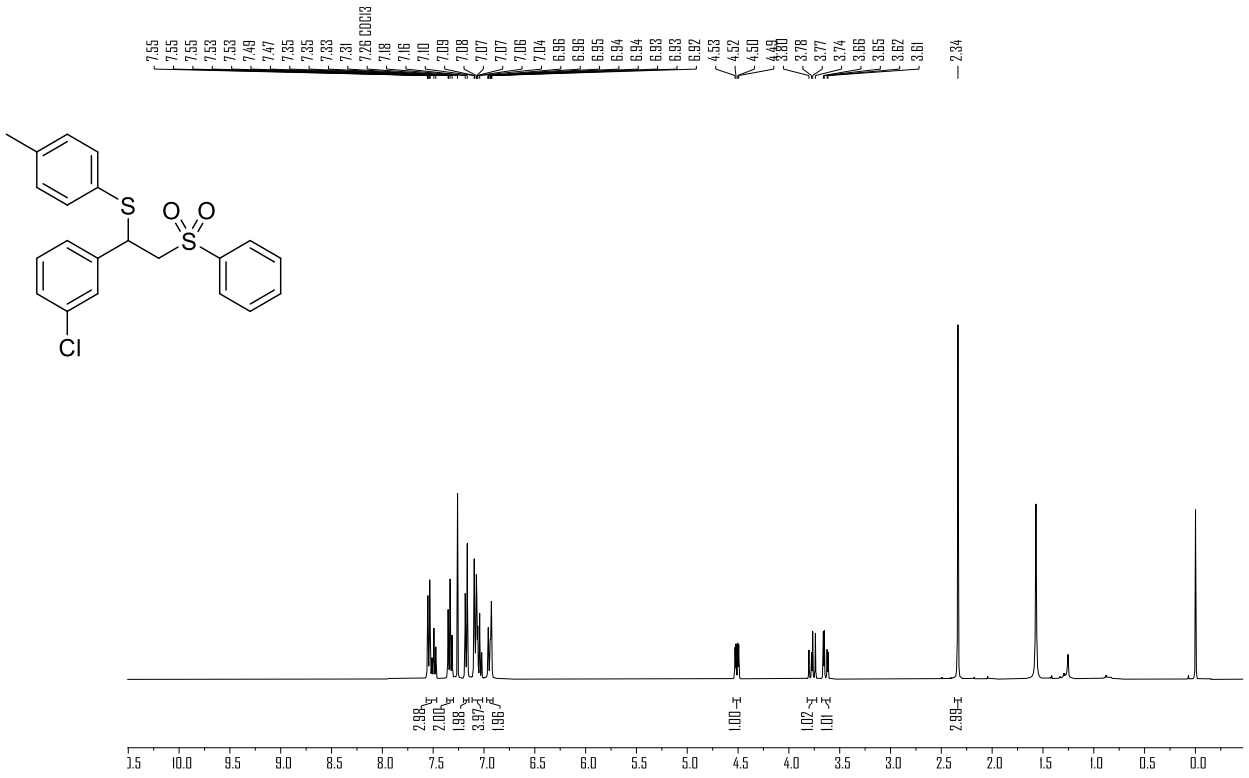
(1-(2-Methoxyphenyl)-2-(phenylsulfonyl)ethyl)(p-tolyl)sulfane (4l): ^{1}H NMR (400 MHz, $CDCl_3$)



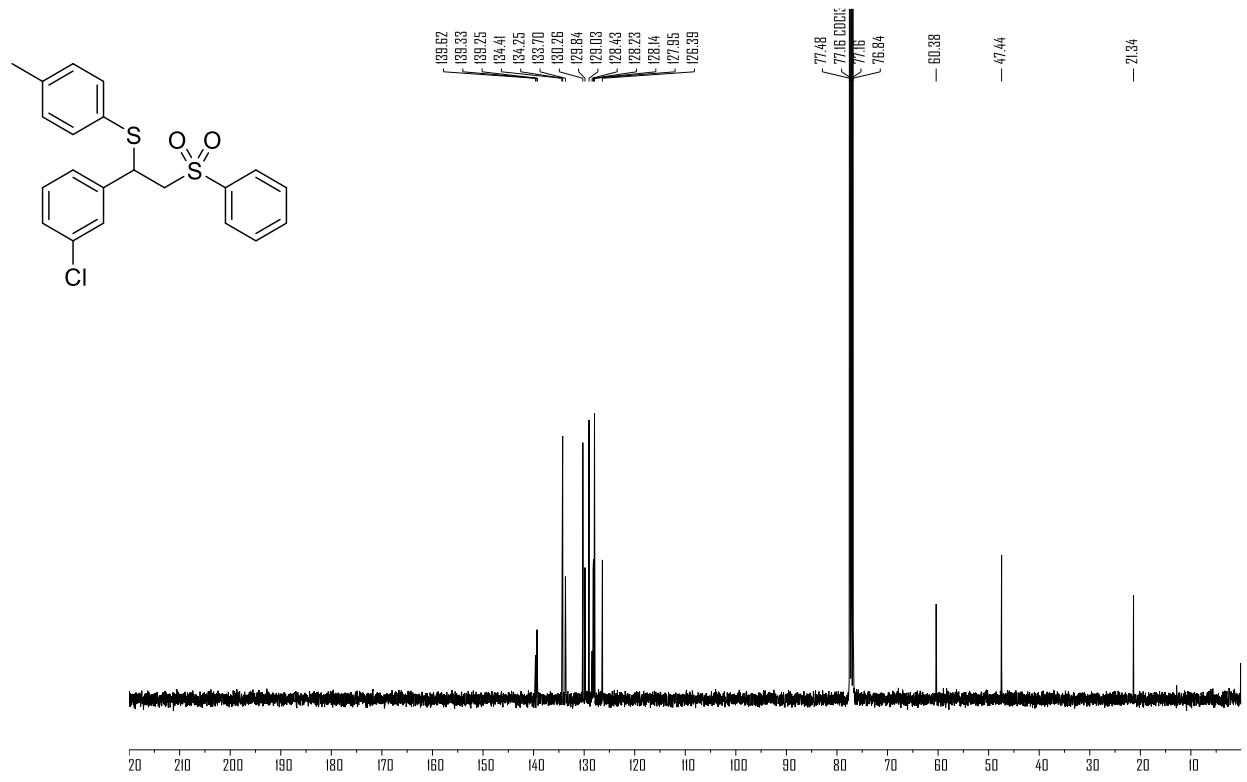
(1-(2-Methoxyphenyl)-2-(phenylsulfonyl)ethyl)(p-tolyl)sulfane (4l): ^{13}C NMR (101 MHz, $CDCl_3$)



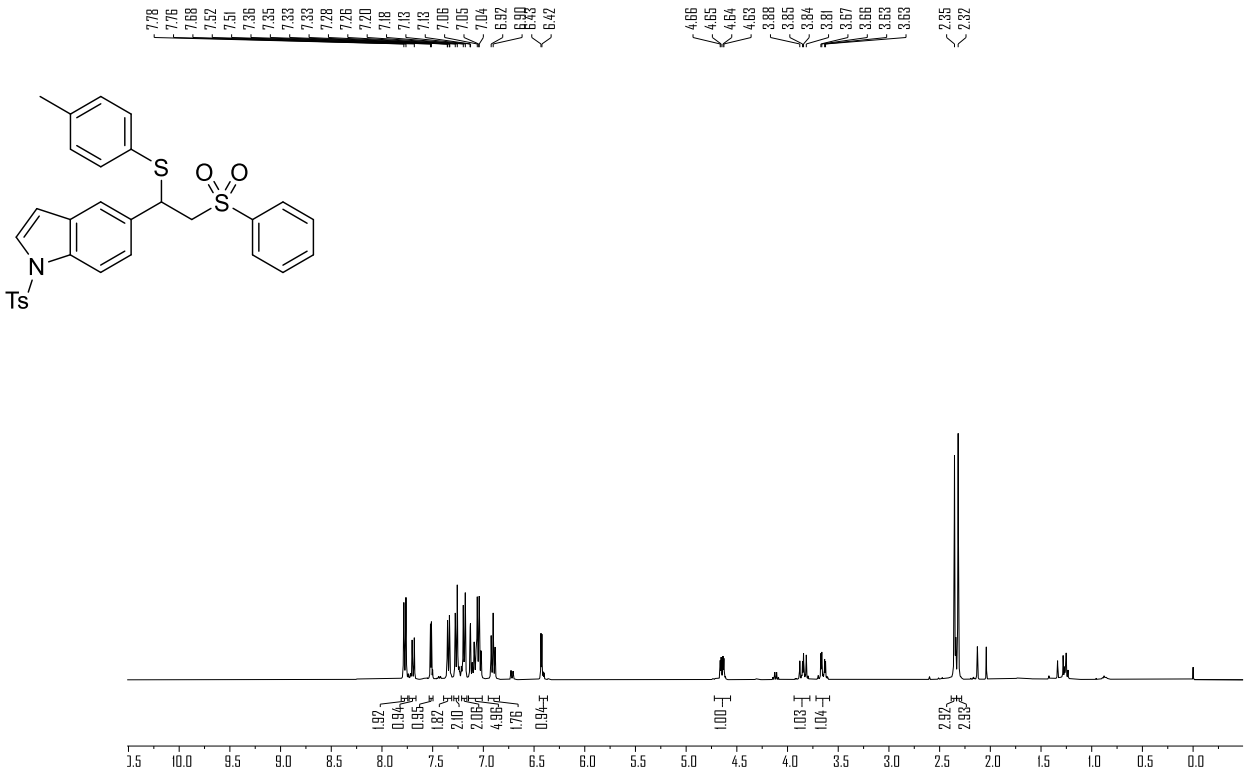
(1-(3-Chlorophenyl)-2-(phenylsulfonyl)ethyl)(p-tolyl)sulfane (4m): ^{1}H NMR (400 MHz, $CDCl_3$)



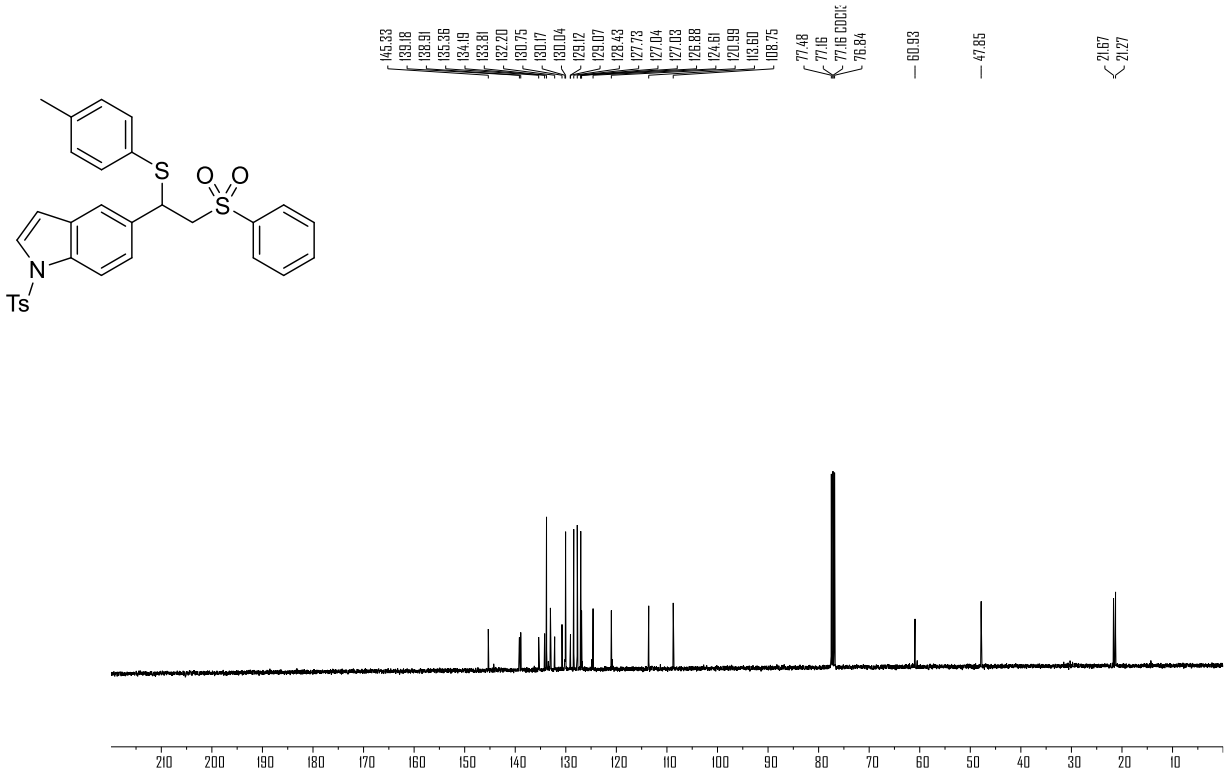
(1-(3-Chlorophenyl)-2-(phenylsulfonyl)ethyl)(p-tolyl)sulfane (4m): ^{13}C NMR (101 MHz, $CDCl_3$)



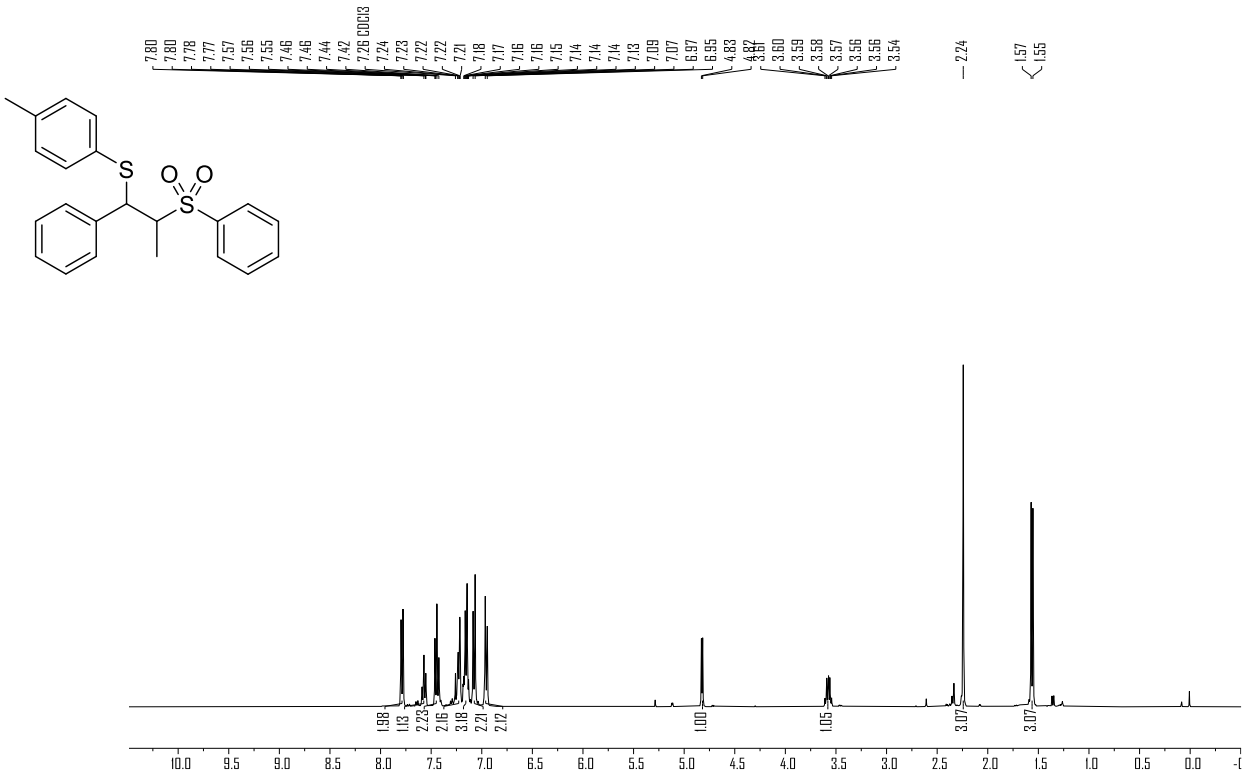
5-(2-(Phenylsulfonyl)-1-(p-tolylthio)ethyl)-1-tosyl-1H-indole (4n): ^{1}H NMR (400 MHz, $CDCl_3$)



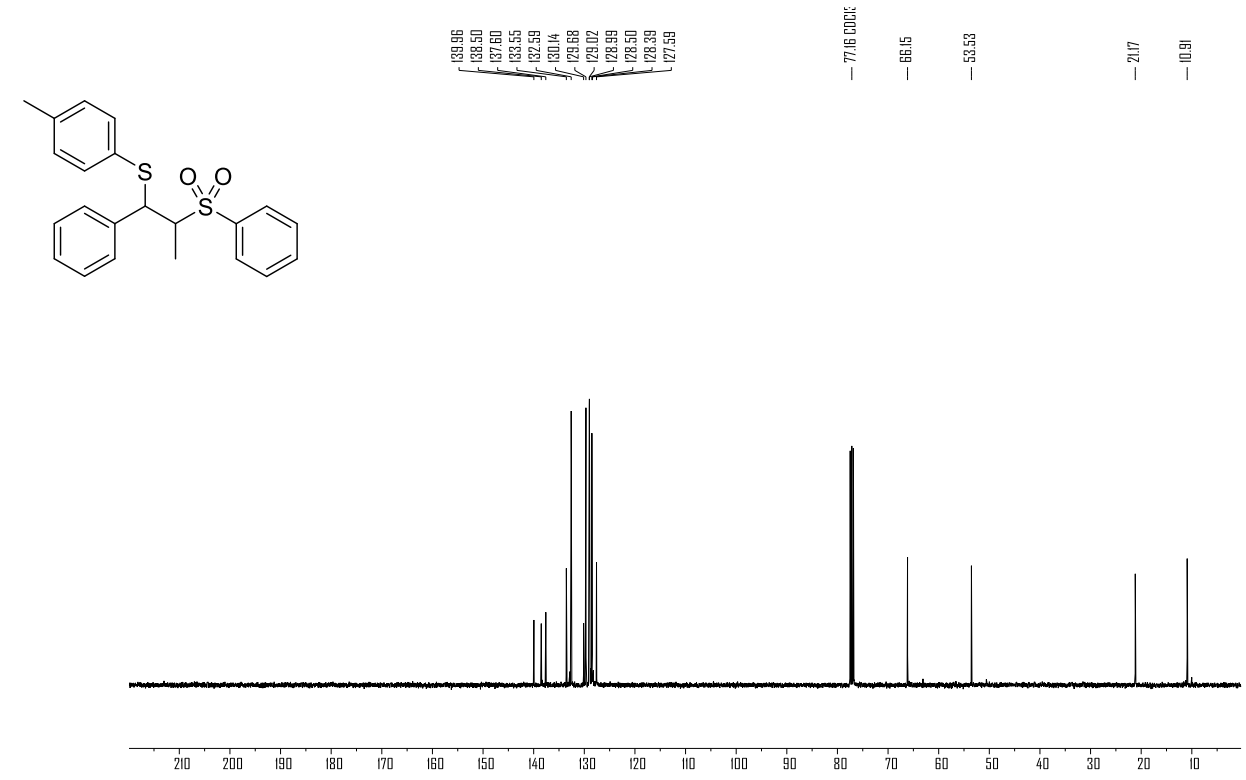
5-(2-(Phenylsulfonyl)-1-(p-tolylthio)ethyl)-1-tosyl-1H-indole (4n): ^{13}C NMR (101 MHz, $CDCl_3$)



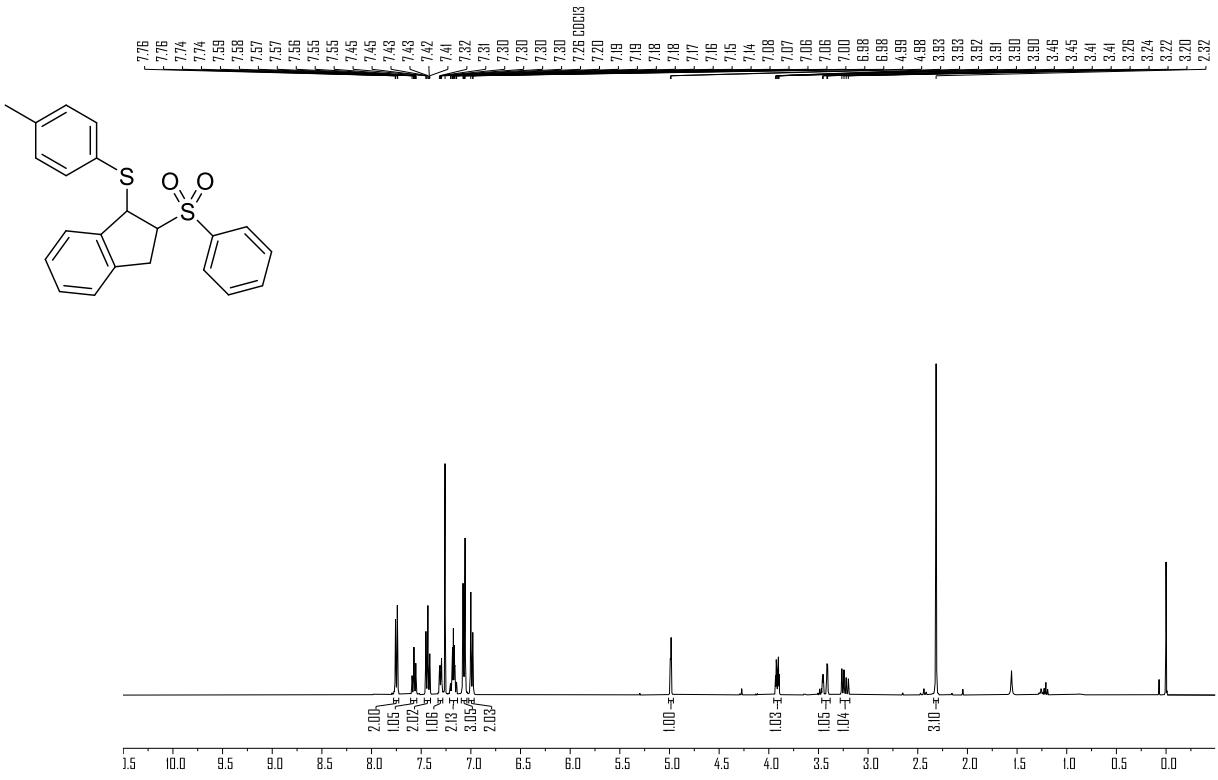
(1-Phenyl-2-(phenylsulfonyl)propyl)(p-tolyl)sulfane (4o): ^{1}H NMR (400 MHz, $CDCl_3$)



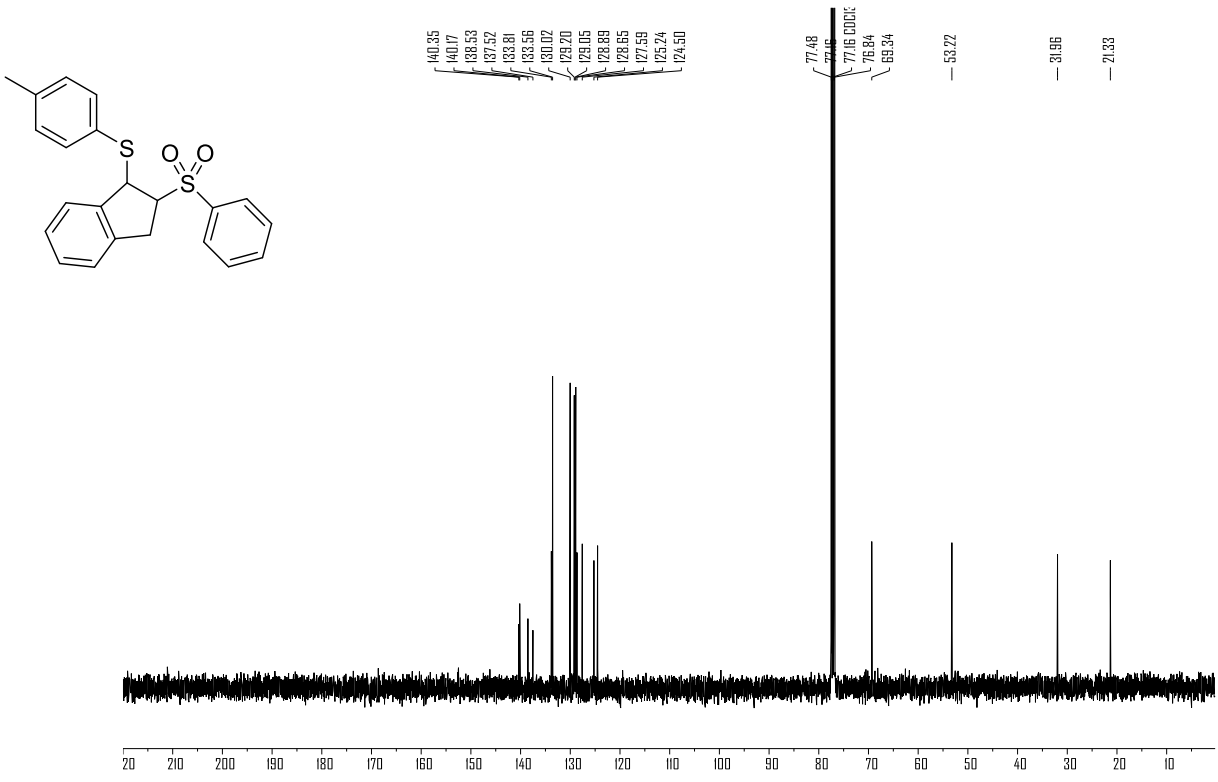
(1-Phenyl-2-(phenylsulfonyl)propyl)(p-tolyl)sulfane (4o): ^{13}C NMR (101 MHz, $CDCl_3$)



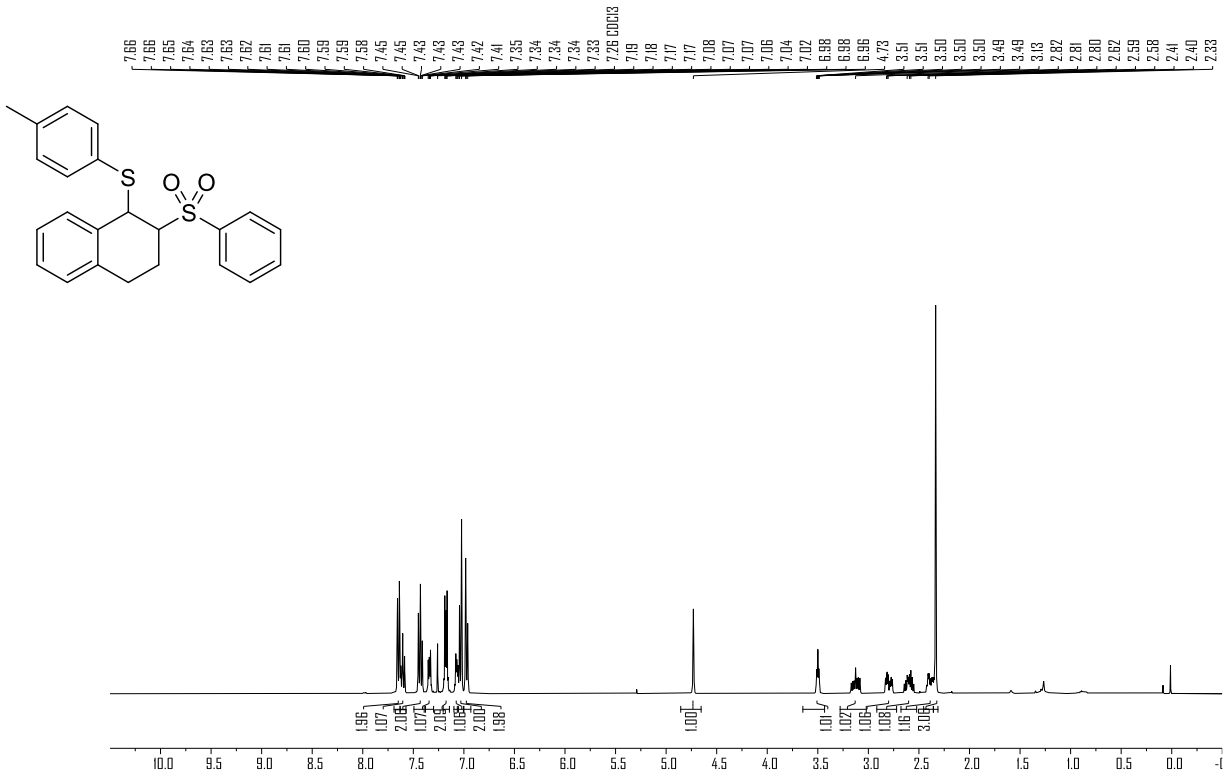
(2-(Phenylsulfonyl)-2,3-dihydro-1H-inden-1-yl)(p-tolyl)sulfane (4p): ^{1}H NMR (400 MHz, $CDCl_3$)



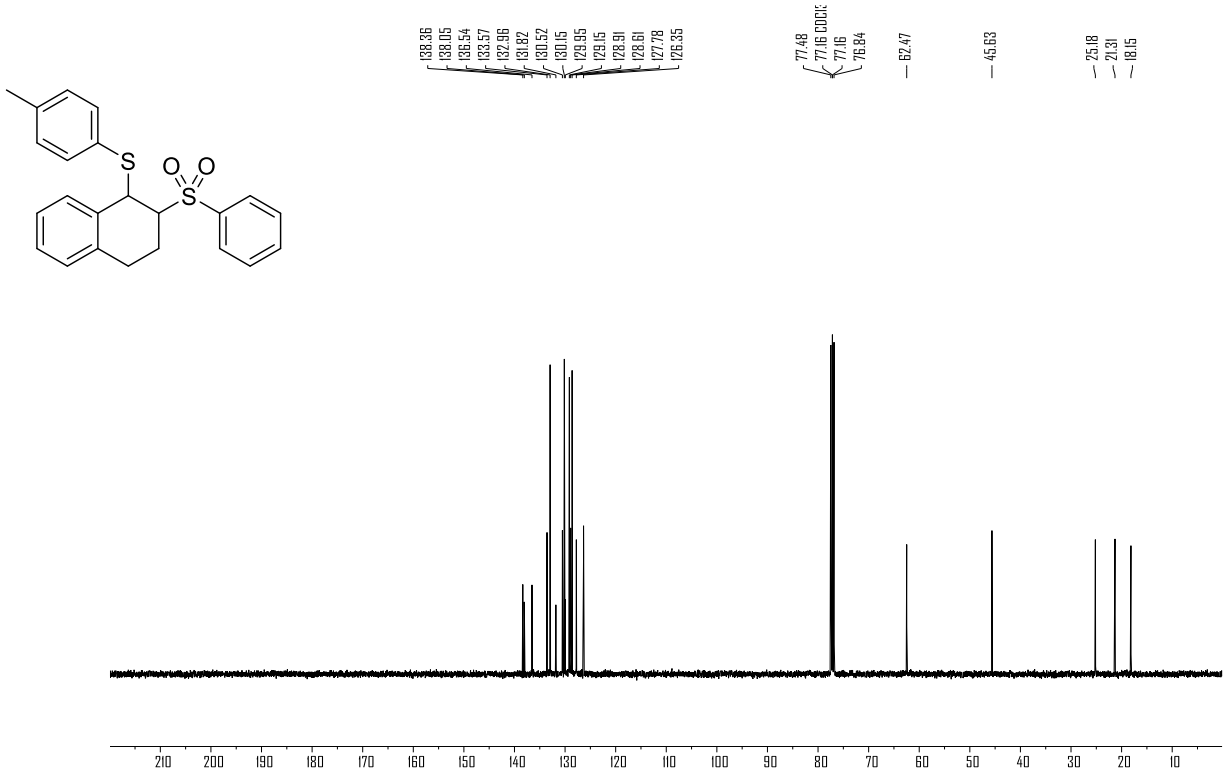
(2-(Phenylsulfonyl)-2,3-dihydro-1H-inden-1-yl)(p-tolyl)sulfane (4p): ^{13}C NMR (101 MHz, $CDCl_3$)



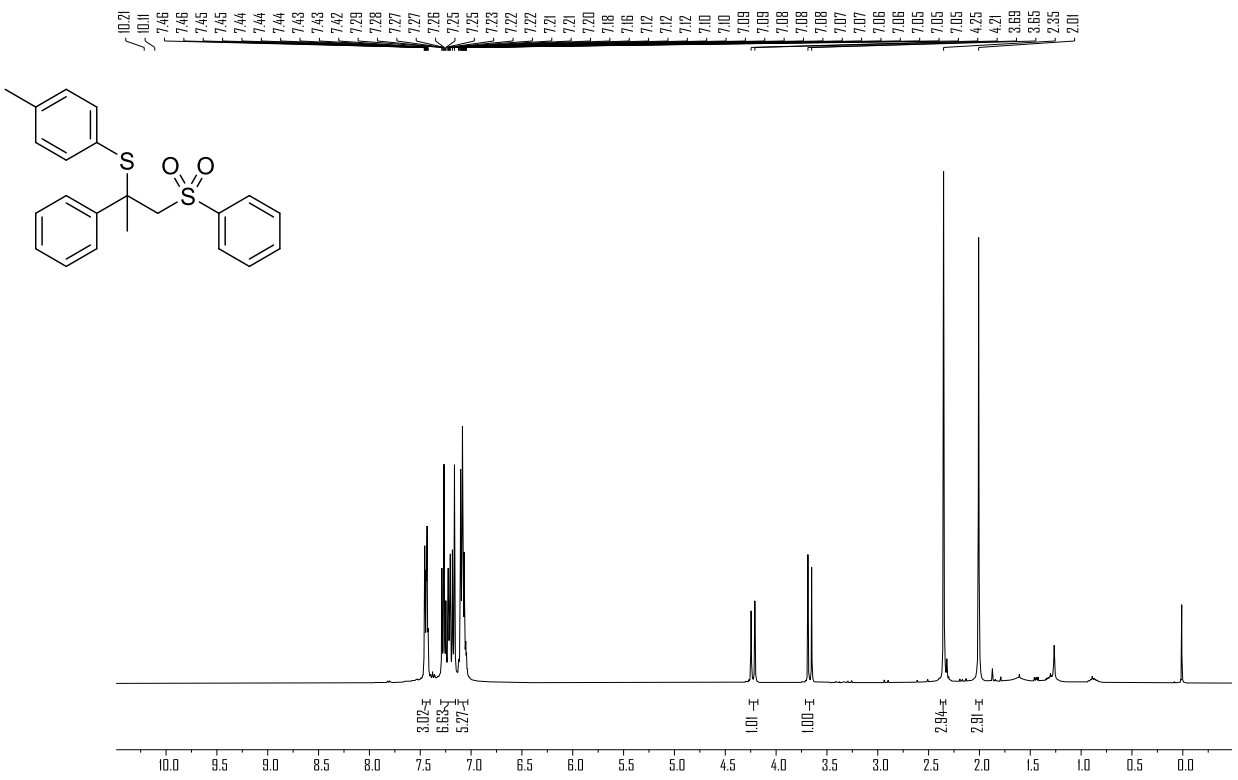
(2-(Phenylsulfonyl)-1,2,3,4-tetrahydronaphthalen-1-yl)(p-tolyl)sulfane (4q): ^{1}H NMR (400 MHz, $CDCl_3$)



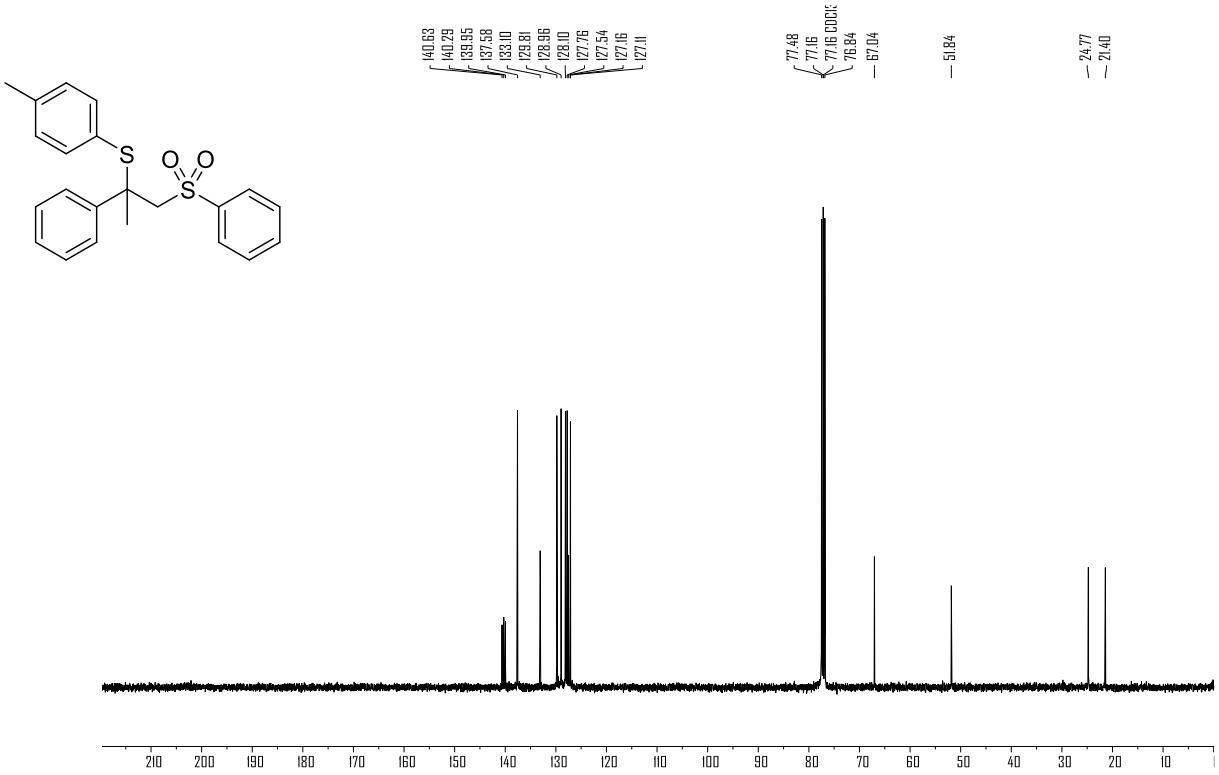
(2-(Phenylsulfonyl)-1,2,3,4-tetrahydronaphthalen-1-yl)(p-tolyl)sulfane (4q): ^{13}C NMR (101 MHz, $CDCl_3$)



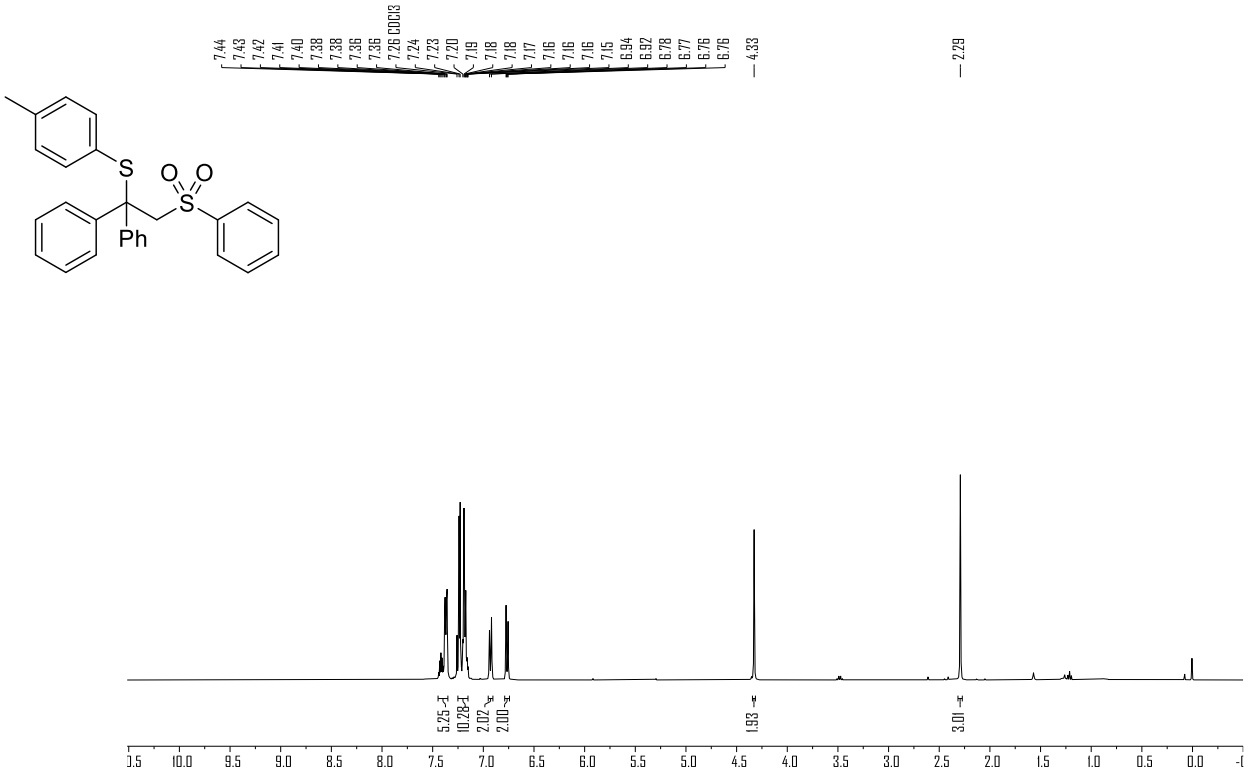
(2-Phenyl-1-(phenylsulfonyl)propan-2-yl)(p-tolyl)sulfane (4r): ^{1}H NMR (400 MHz, $CDCl_3$)



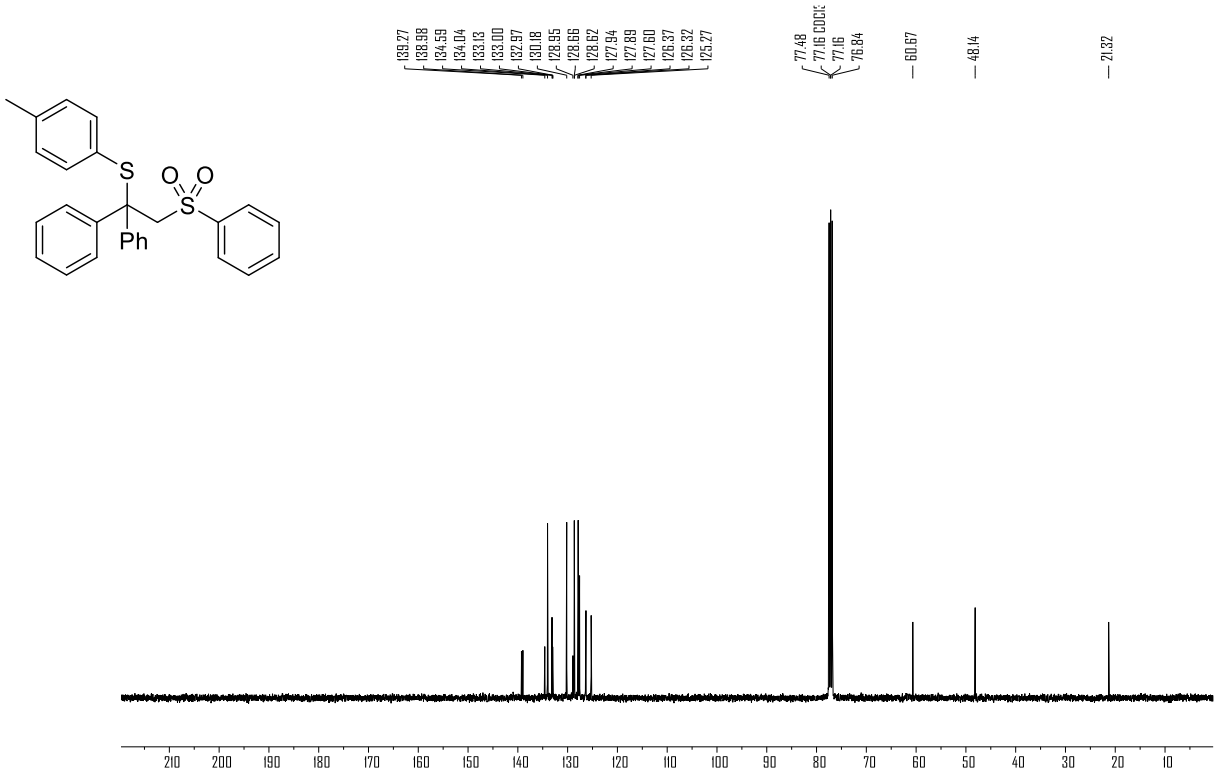
(2-Phenyl-1-(phenylsulfonyl)propan-2-yl)(p-tolyl)sulfane (4r): ^{13}C NMR (101 MHz, $CDCl_3$)



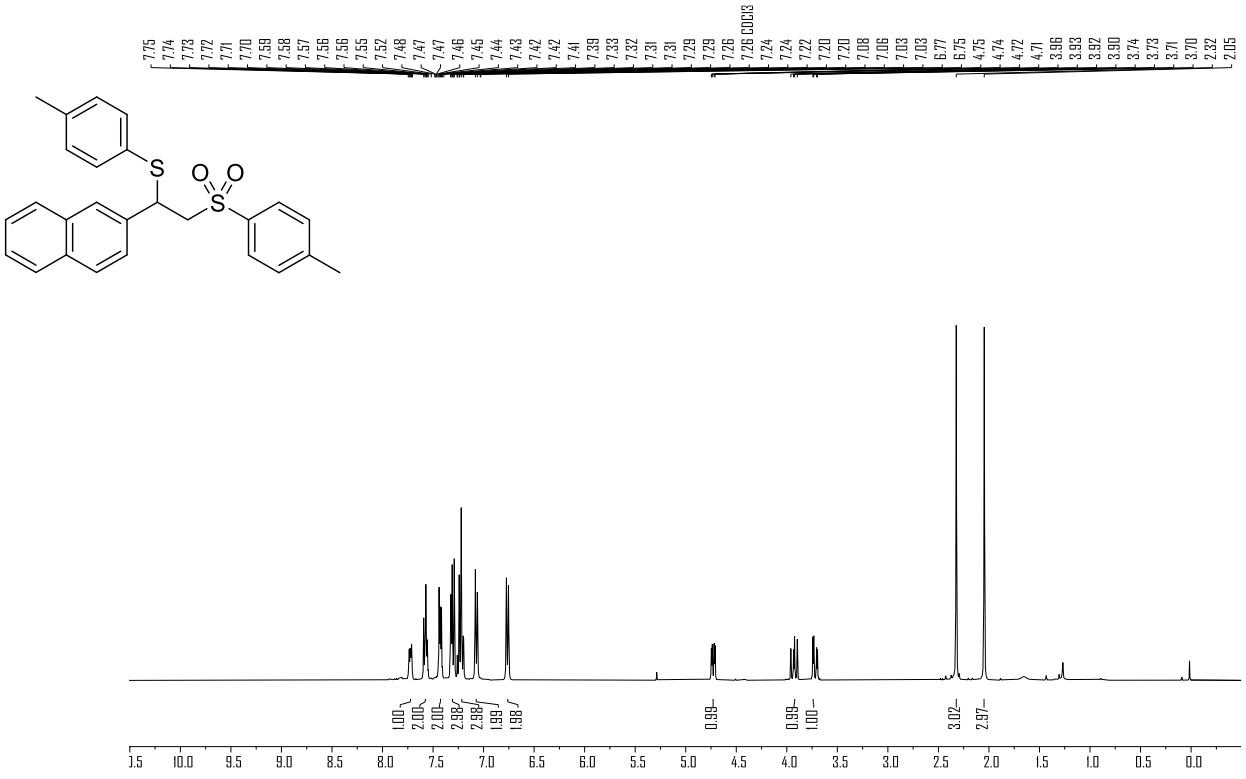
(1,1-Piphenyl-2-(phenylsulfonyl)ethyl)(p-tolyl)sulfane (4s): ^{1}H NMR (400 MHz, $CDCl_3$)



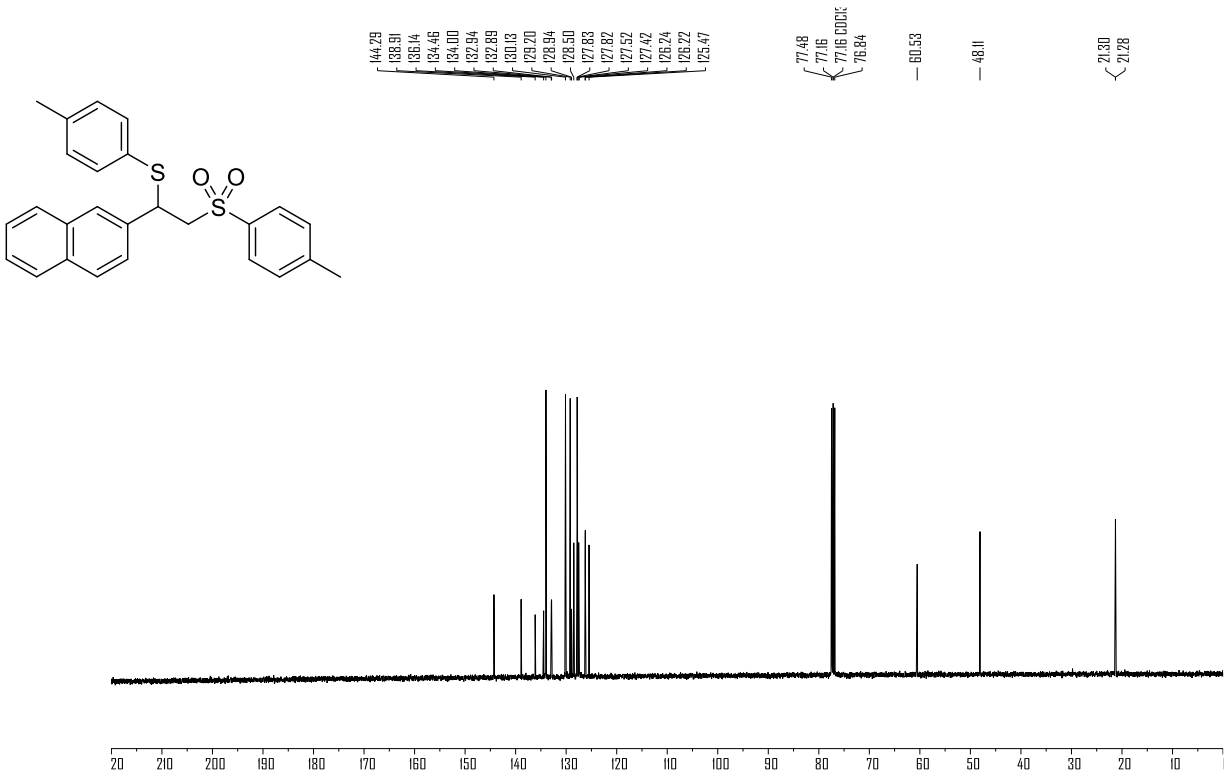
(1,1-Piphenyl-2-(phenylsulfonyl)ethyl)(p-tolyl)sulfane (4s): ^{13}C NMR (101 MHz, $CDCl_3$)



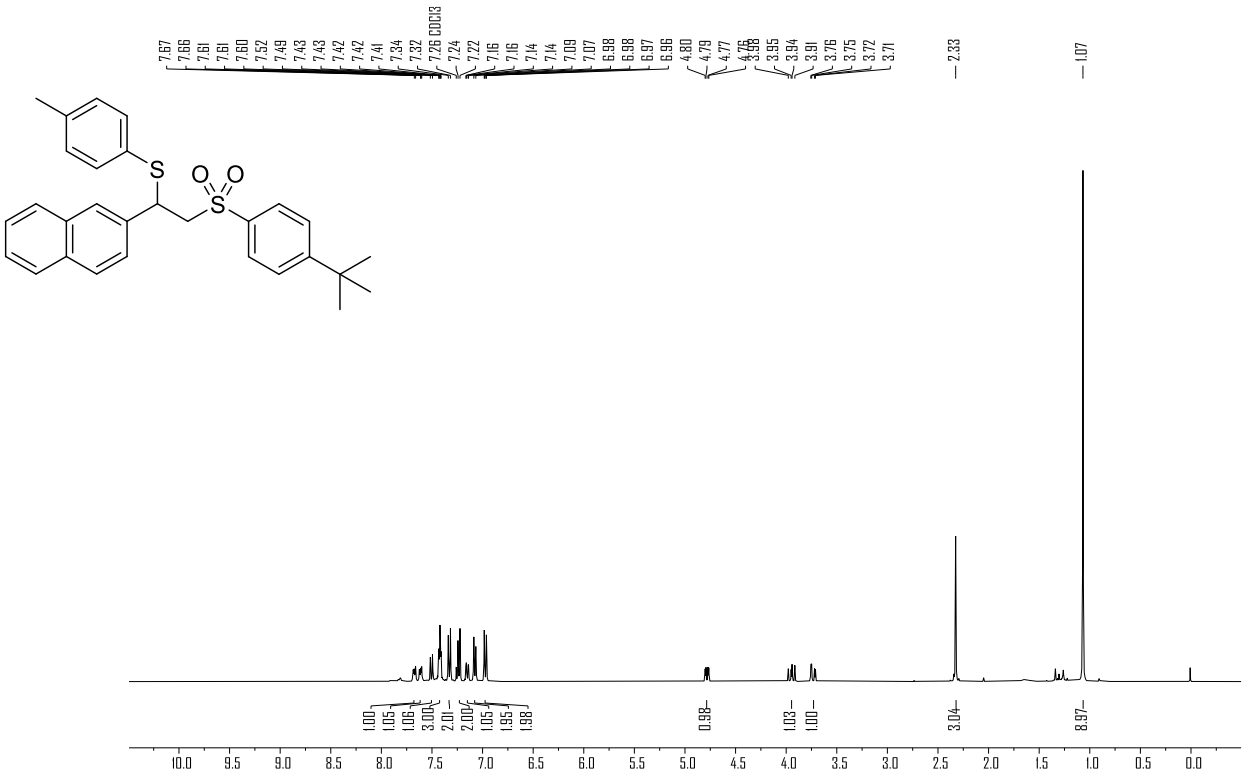
(1-(Naphthalen-2-yl)-2-tosylethyl)(p-tolyl)sulfane (4t): ^{1}H NMR (400 MHz, $CDCl_3$)



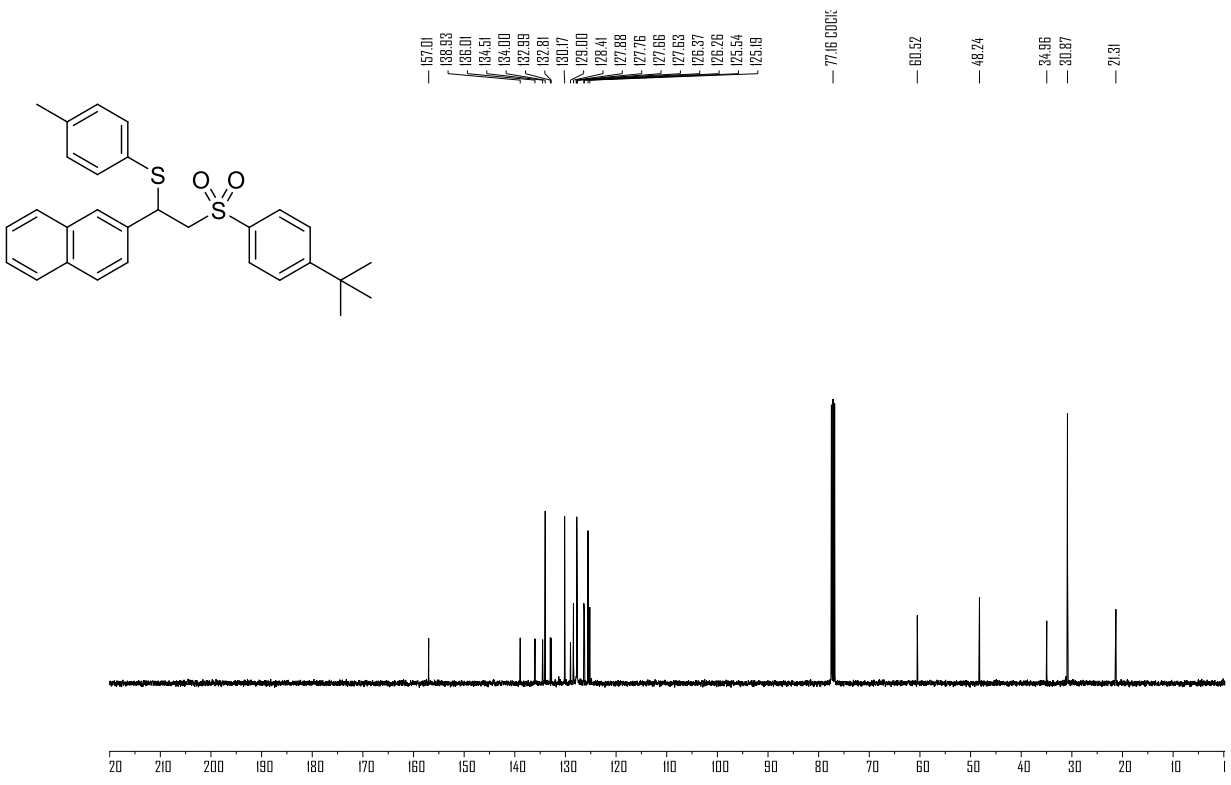
(1-(Naphthalen-2-yl)-2-tosylethyl)(p-tolyl)sulfane (4t): ^{13}C NMR (101 MHz, $CDCl_3$)



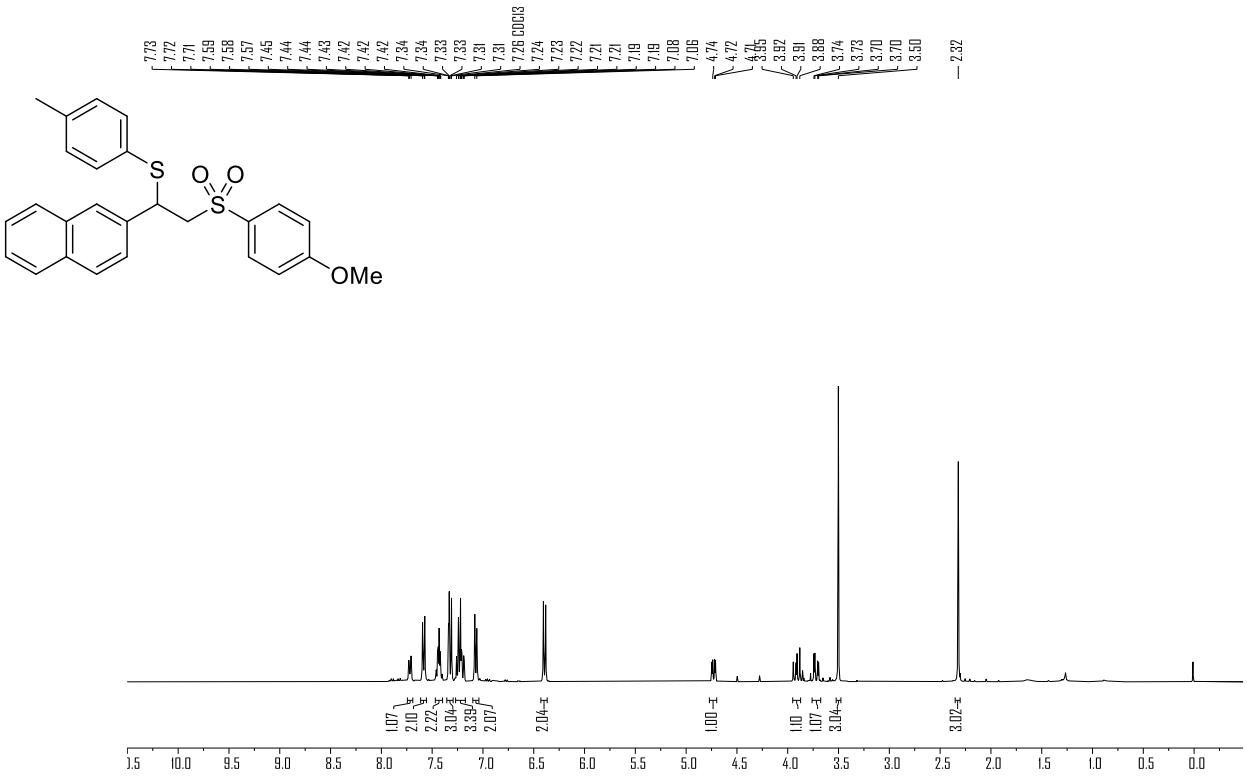
(2-((4-(Tert-butyl)phenyl)sulfonyl)-1-(naphthalen-2-yl)ethyl)(p-tolyl)sulfane (4u): ^{1}H NMR (400 MHz, $CDCl_3$)



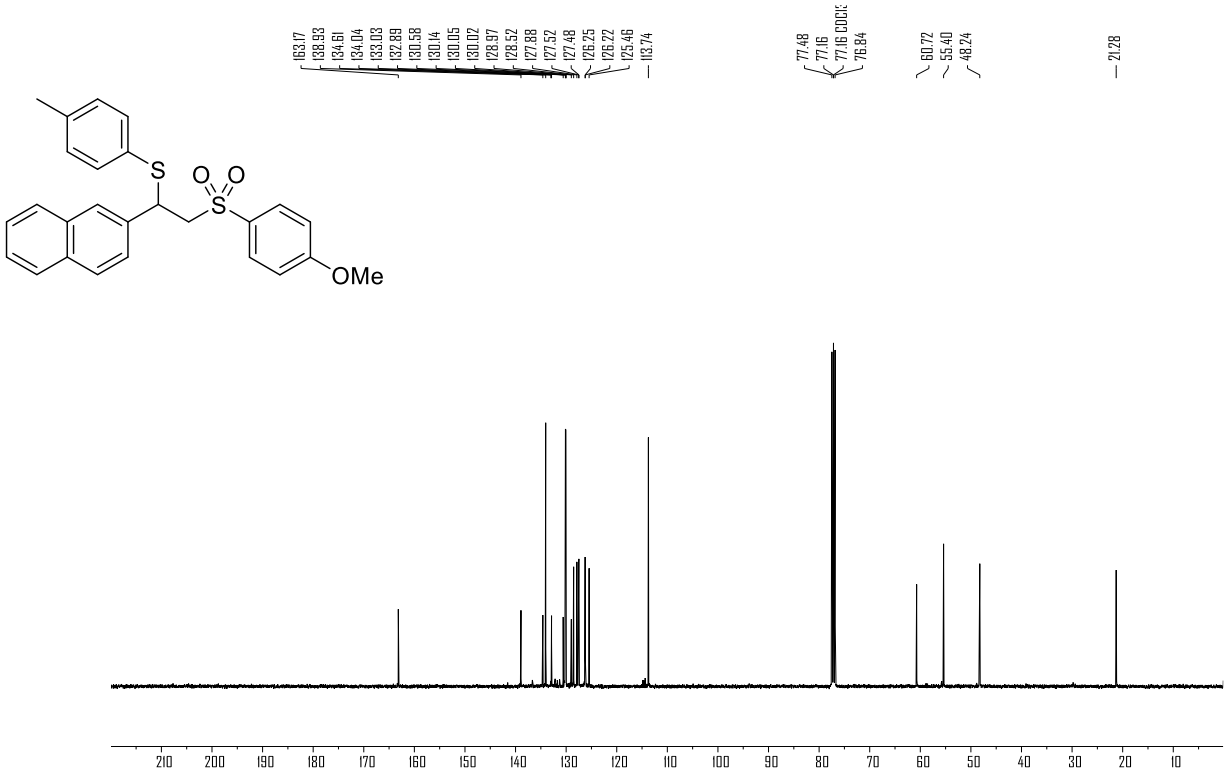
(2-((4-(Tert-butyl)phenyl)sulfonyl)-1-(naphthalen-2-yl)ethyl)(p-tolyl)sulfane (4u): ^{13}C NMR (101 MHz, $CDCl_3$)



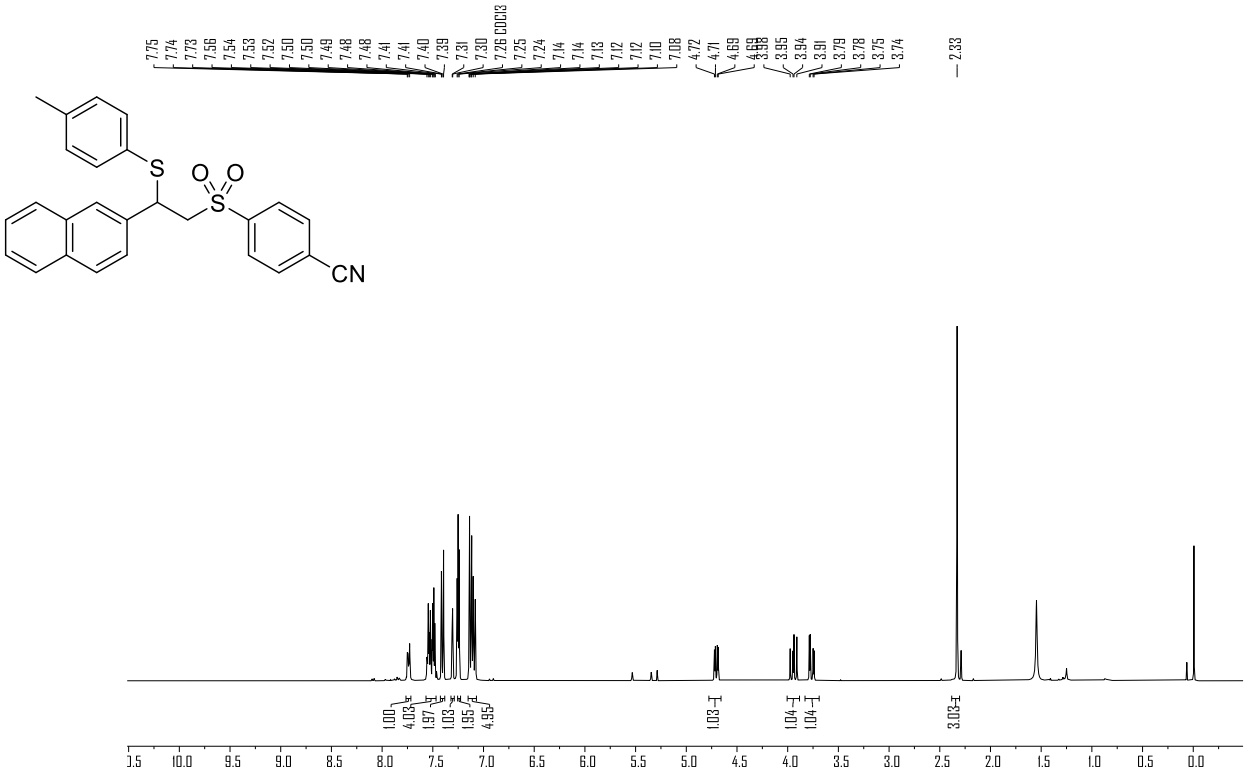
(2-((4-Methoxyphenyl)sulfonyl)-1-(naphthalen-2-yl)ethyl)(p-tolyl)sulfane (4v): ^{1}H NMR (400 MHz, $CDCl_3$)



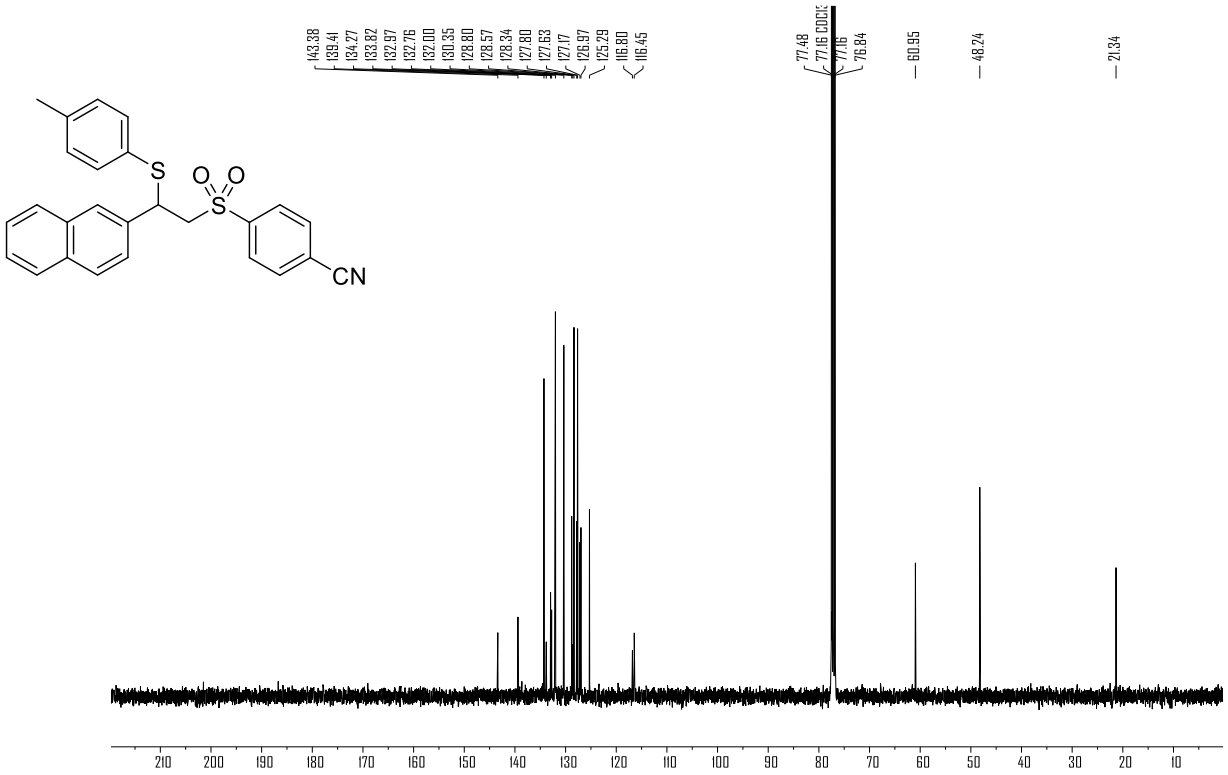
(2-((4-Methoxyphenyl)sulfonyl)-1-(naphthalen-2-yl)ethyl)(p-tolyl)sulfane (4v): ^{13}C NMR (101 MHz, $CDCl_3$)



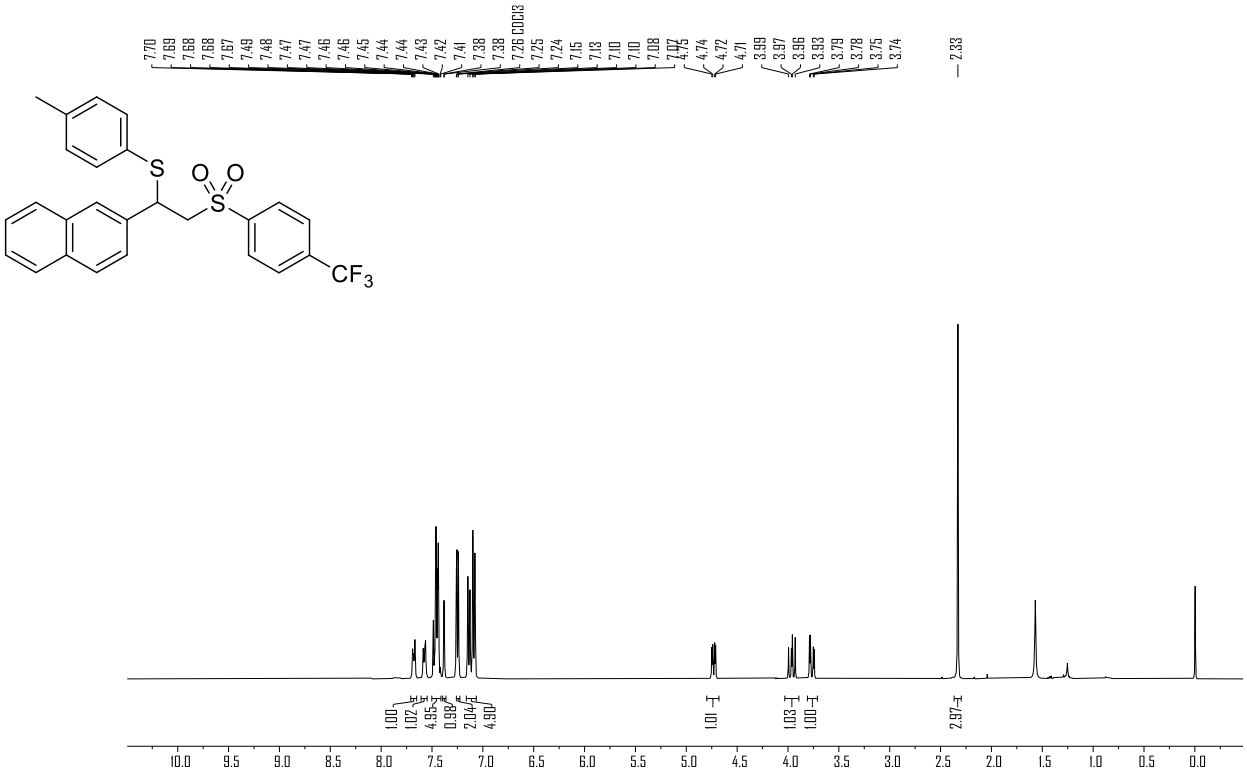
4-((2-(Naphthalen-2-yl)-2-(p-tolylthio)ethyl)sulfonyl)benzonitrile (4w): ^{1}H NMR (400 MHz, $CDCl_3$)



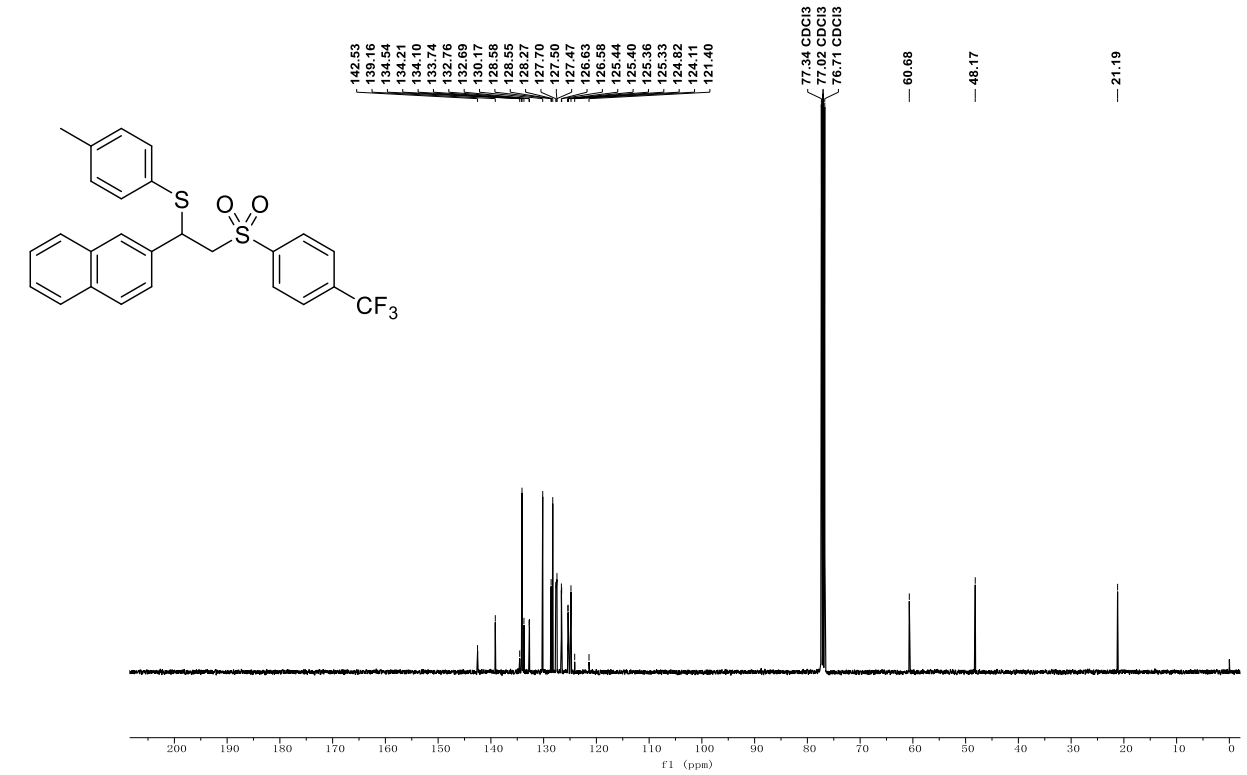
4-((2-(Naphthalen-2-yl)-2-(p-tolylthio)ethyl)sulfonyl)benzonitrile (4w): ^{13}C NMR (101 MHz, $CDCl_3$)



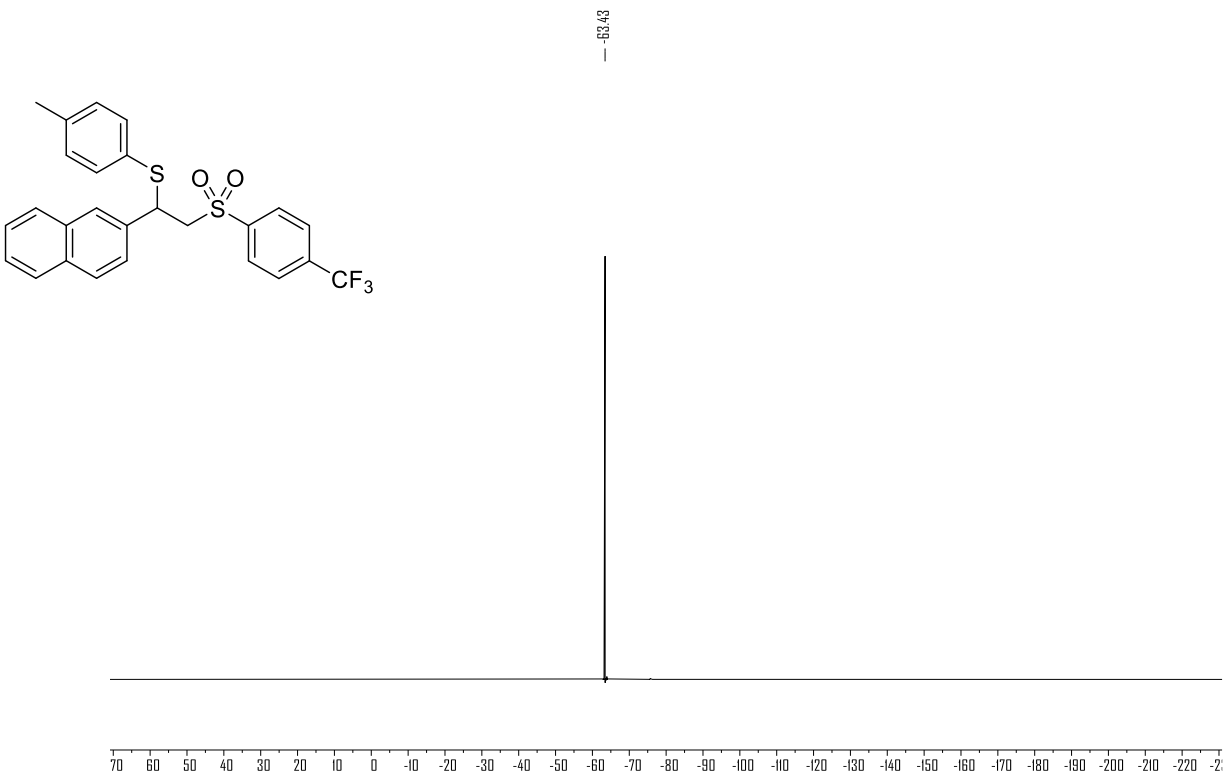
(1-(Naphthalen-2-yl)-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)(p-tolyl)sulfane (4x): ^{1}H NMR (400 MHz, $CDCl_3$)



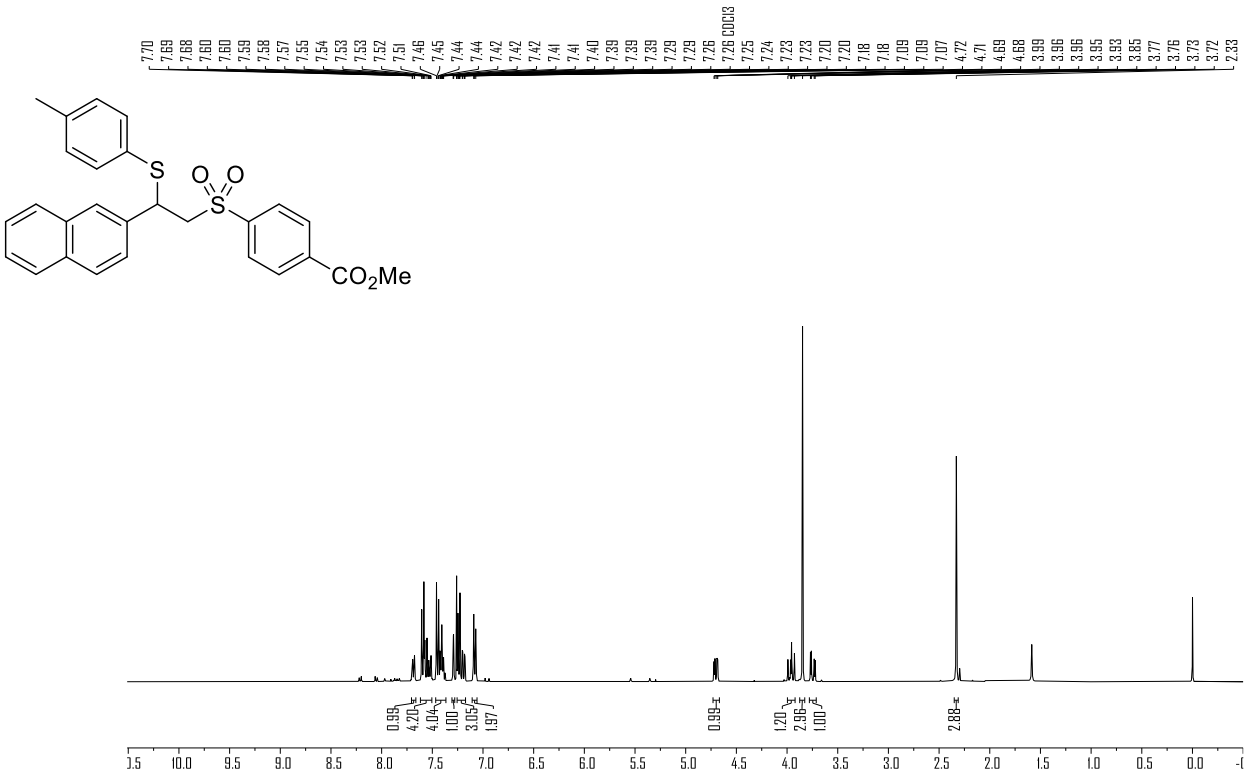
(1-(Naphthalen-2-yl)-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)(p-tolyl)sulfane (4x): ^{13}C NMR (101 MHz, $CDCl_3$)



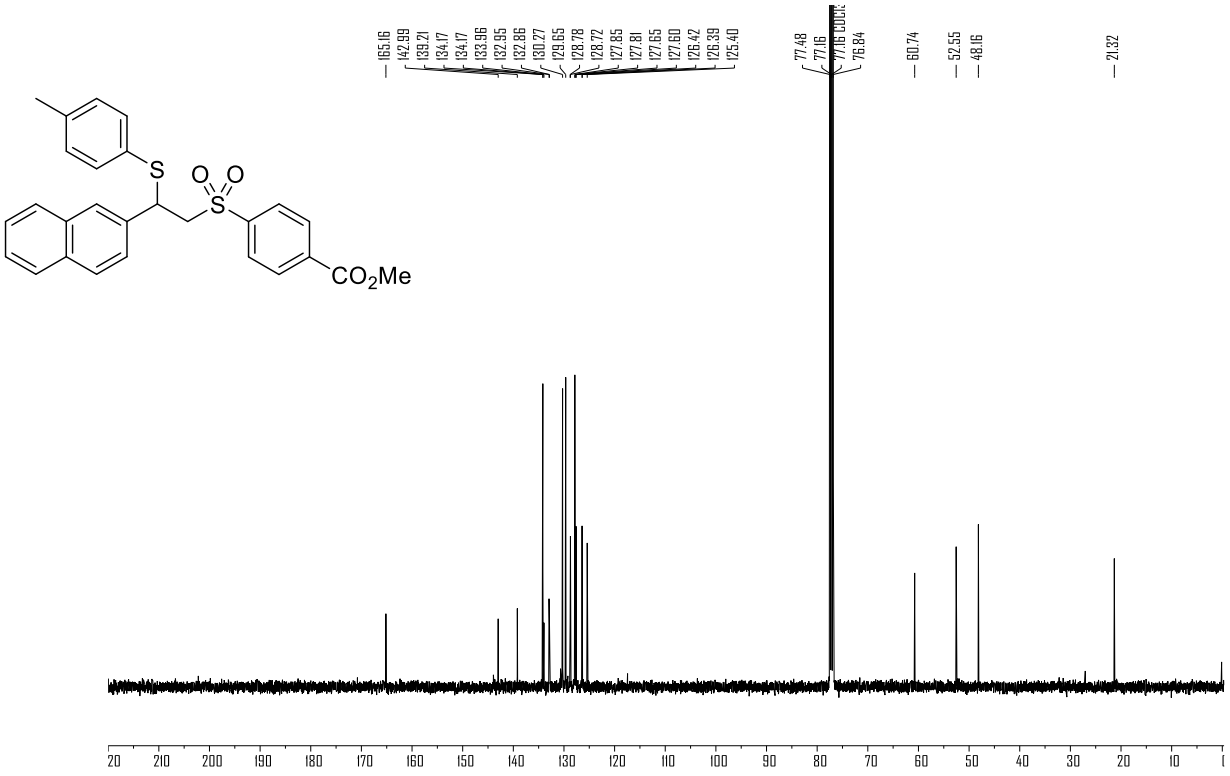
(1-(Naphthalen-2-yl)-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)(p-tolyl)sulfane (4x): ^{19}F NMR (101 MHz, $CDCl_3$)



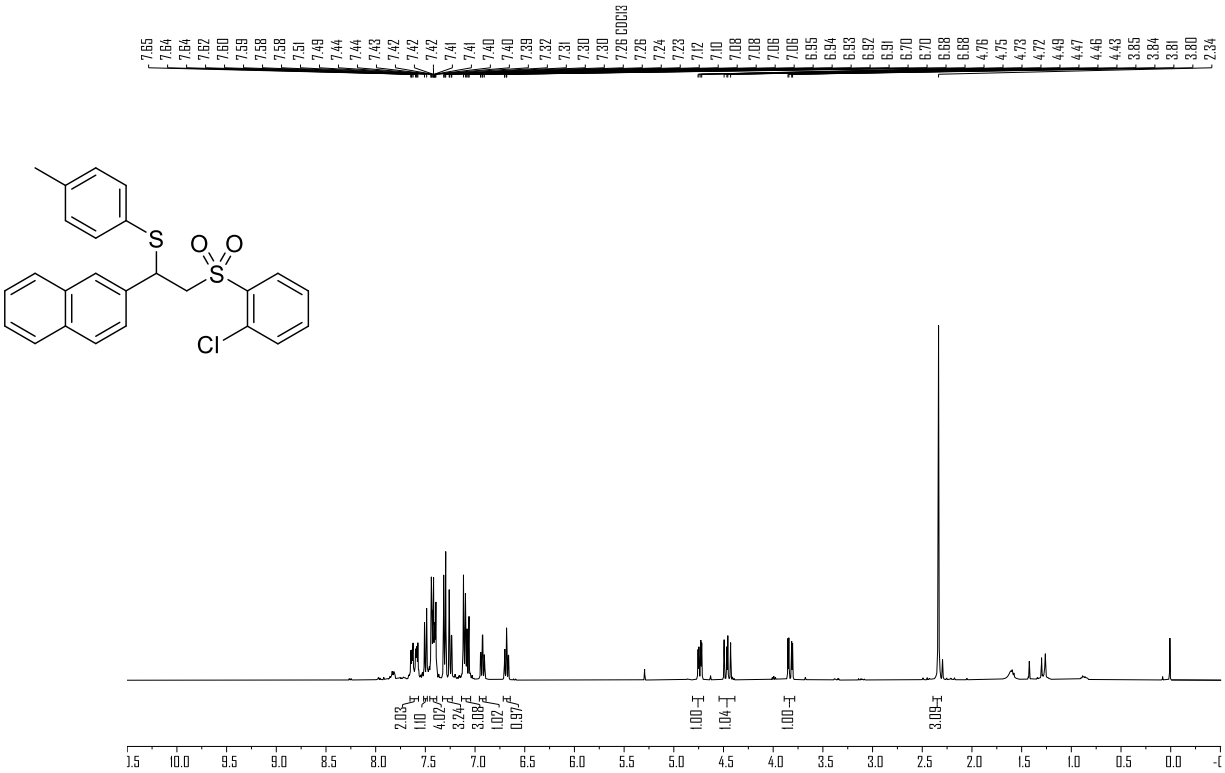
Methyl 4-((2-(naphthalen-2-yl)-2-(p-tolylthio)ethyl)sulfonyl)benzoate (4y): ^1H NMR (400 MHz, $CDCl_3$)



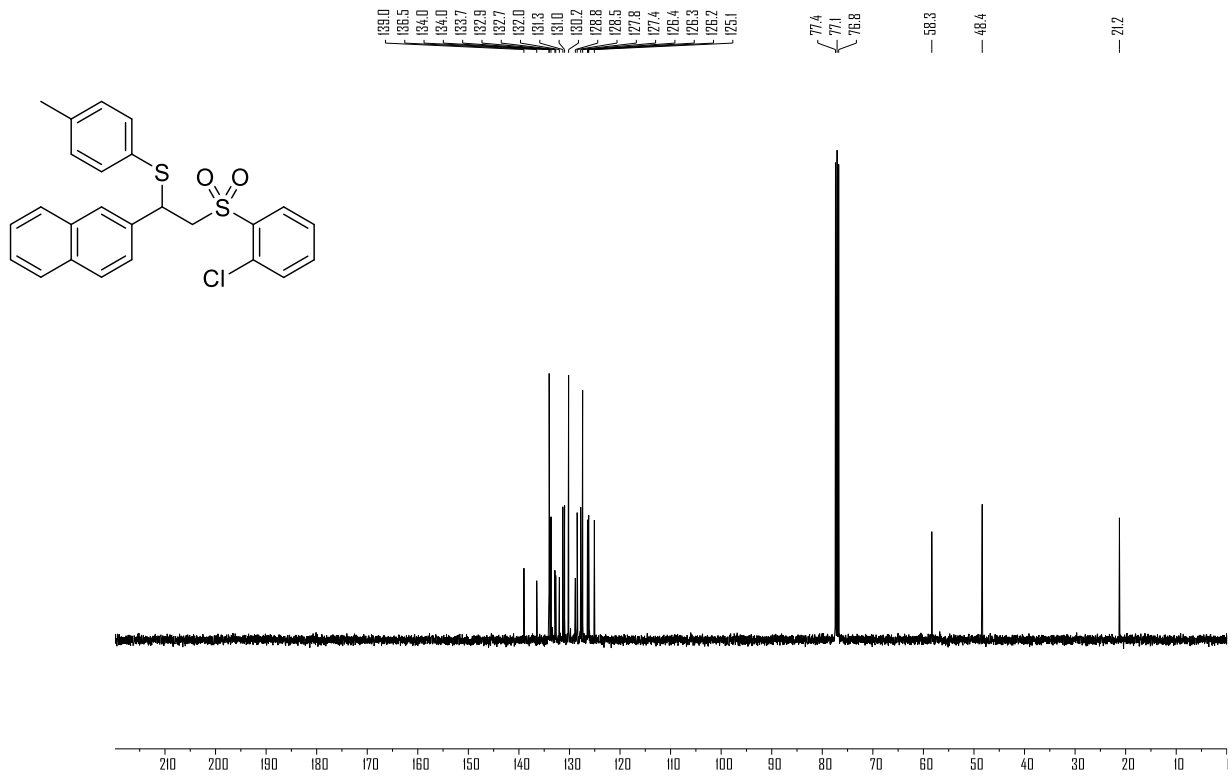
Methyl 4-((2-(naphthalen-2-yl)-2-(p-tolylthio)ethyl)sulfonyl)benzoate (4y): ^{13}C NMR (101 MHz, $CDCl_3$)



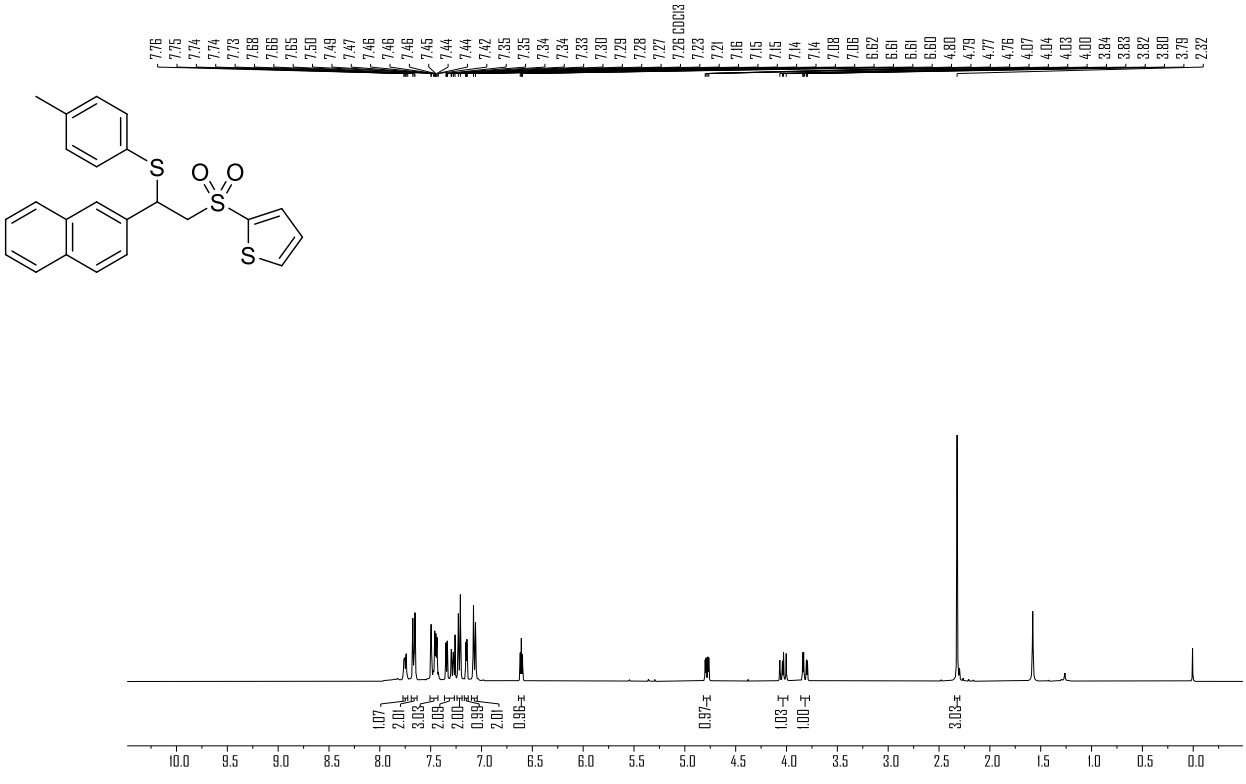
(2-((2-Chlorophenyl)sulfonyl)-1-(naphthalen-2-yl)ethyl)(p-tolyl)sulfane (4z): ^{1}H NMR (400 MHz, $CDCl_3$)



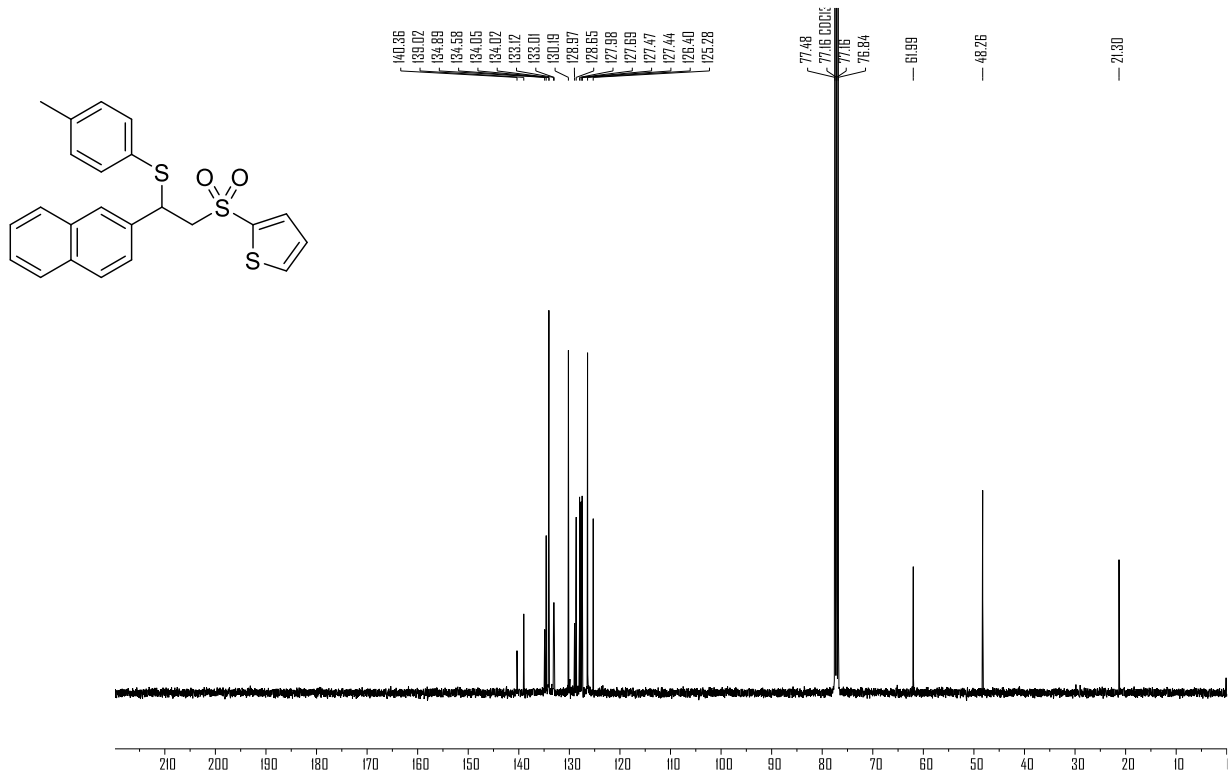
(2-((2-Chlorophenyl)sulfonyl)-1-(naphthalen-2-yl)ethyl)(p-tolyl)sulfane (4z): ^{13}C NMR (101 MHz, $CDCl_3$)



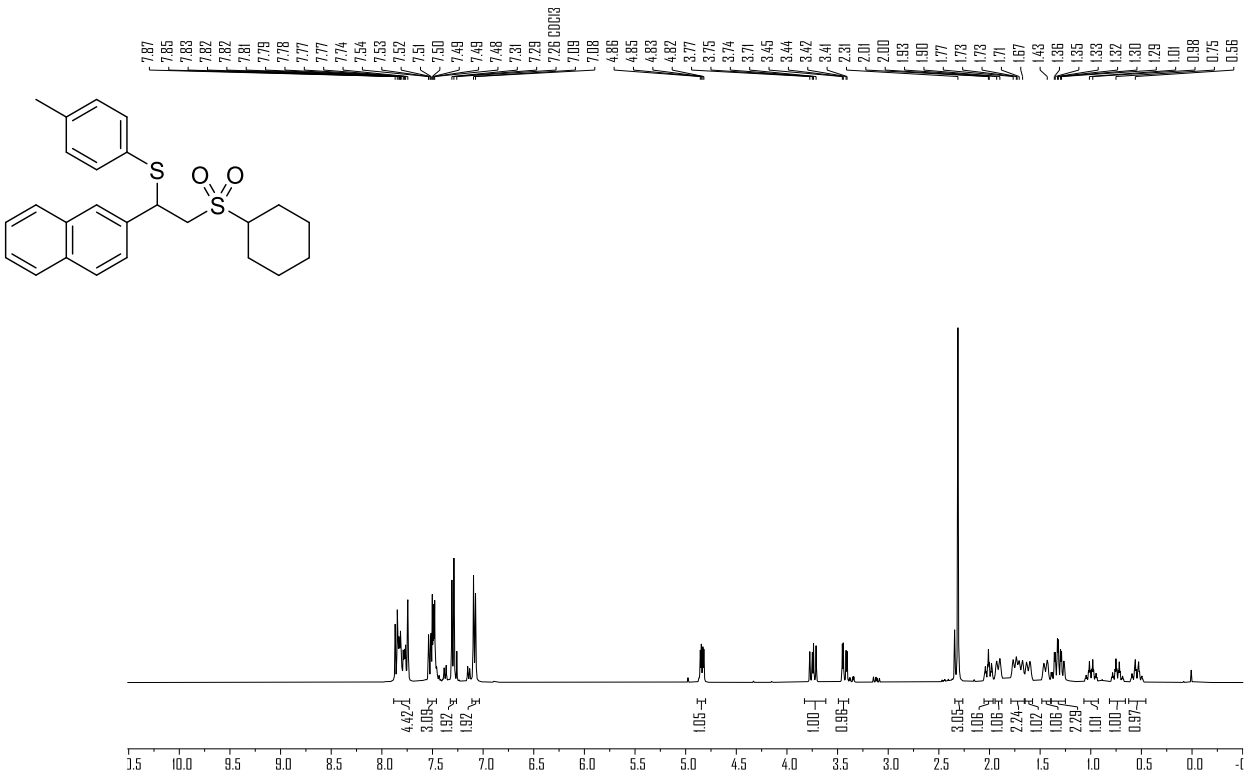
2-((2-(Naphthalen-2-yl)-2-(p-tolylthio)ethyl)sulfonyl)thiophene (4aa): ^{1}H NMR (400 MHz, $CDCl_3$)



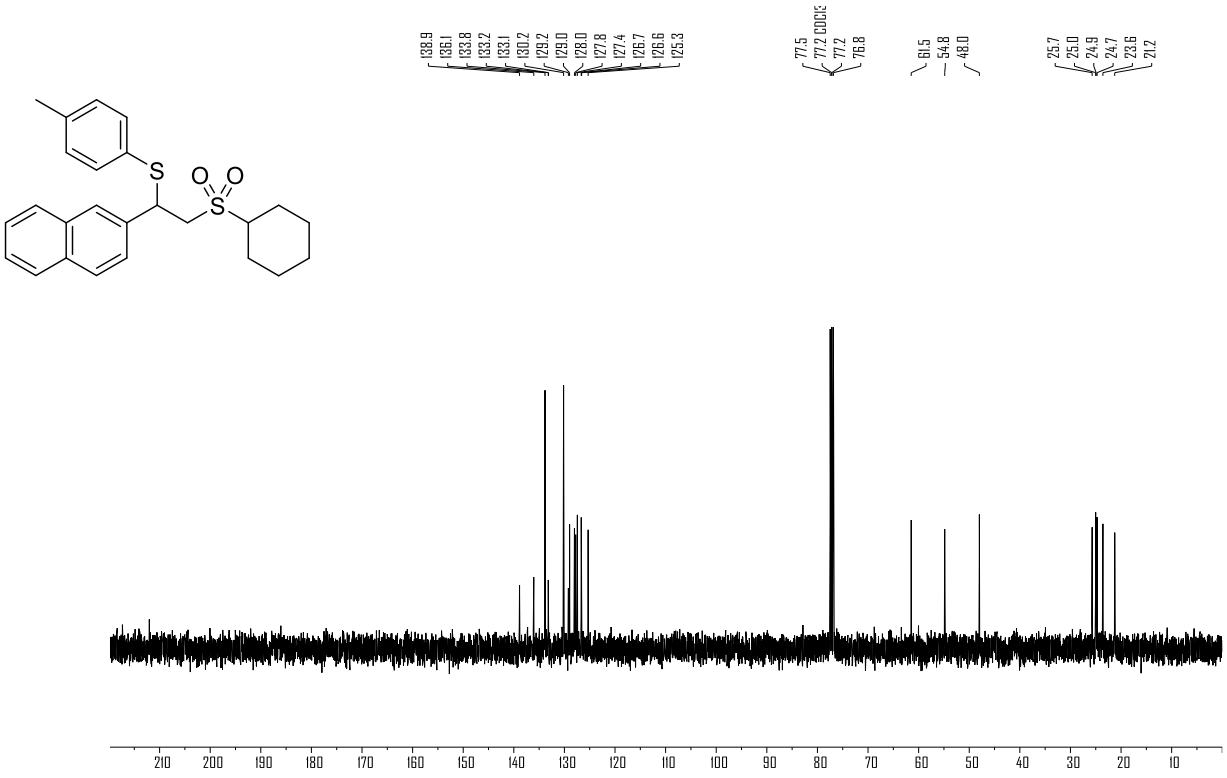
2-((2-(Naphthalen-2-yl)-2-(p-tolylthio)ethyl)sulfonyl)thiophene (4aa): ^{13}C NMR (101 MHz, $CDCl_3$)



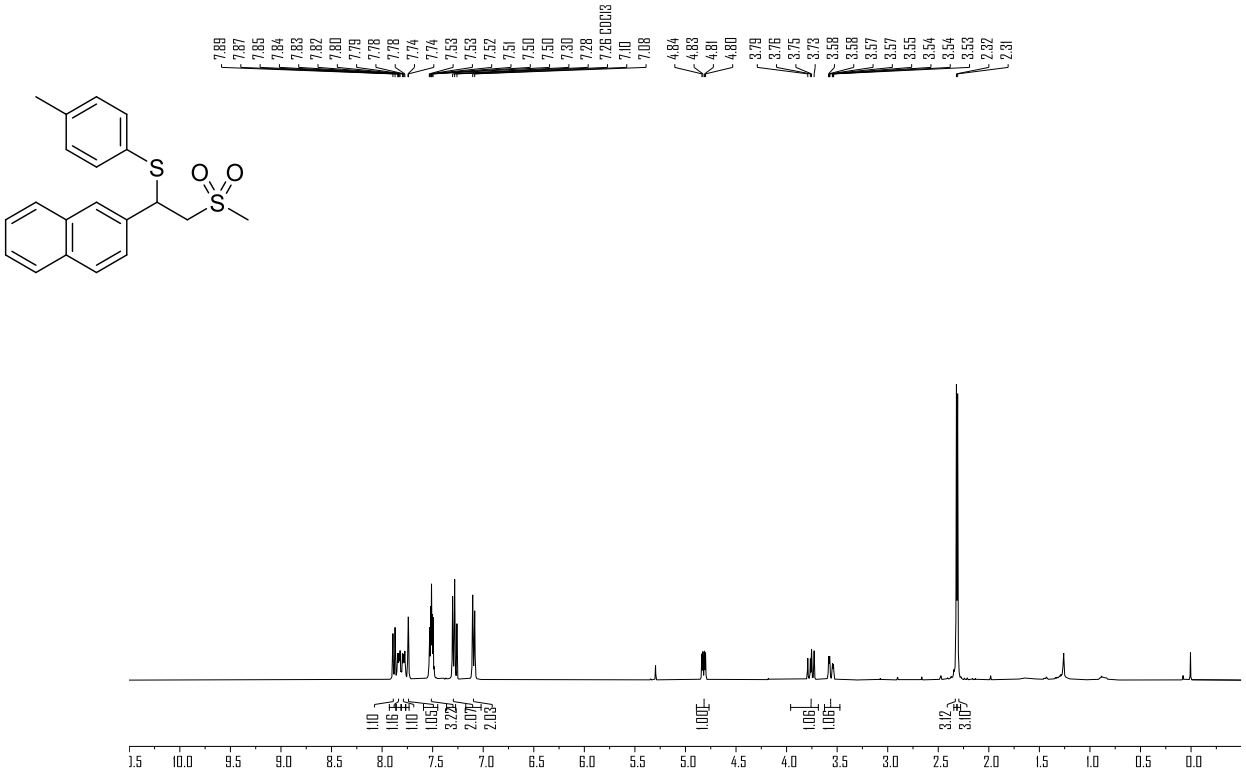
(2-(Cyclohexylsulfonyl)-1-(naphthalen-2-yl)ethyl)(p-tolyl)sulfane (4ab): ^{1}H NMR (400 MHz, $CDCl_3$)



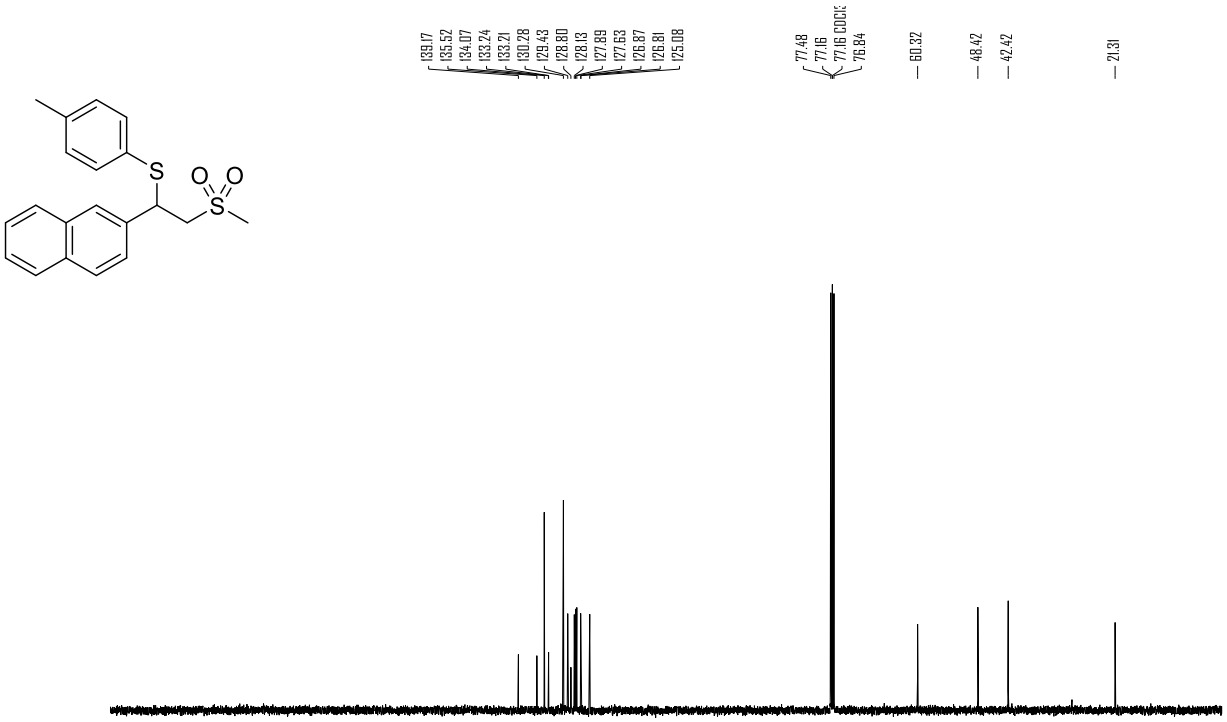
(2-(Cyclohexylsulfonyl)-1-(naphthalen-2-yl)ethyl)(p-tolyl)sulfane (4ab): ^{13}C NMR (101 MHz, $CDCl_3$)



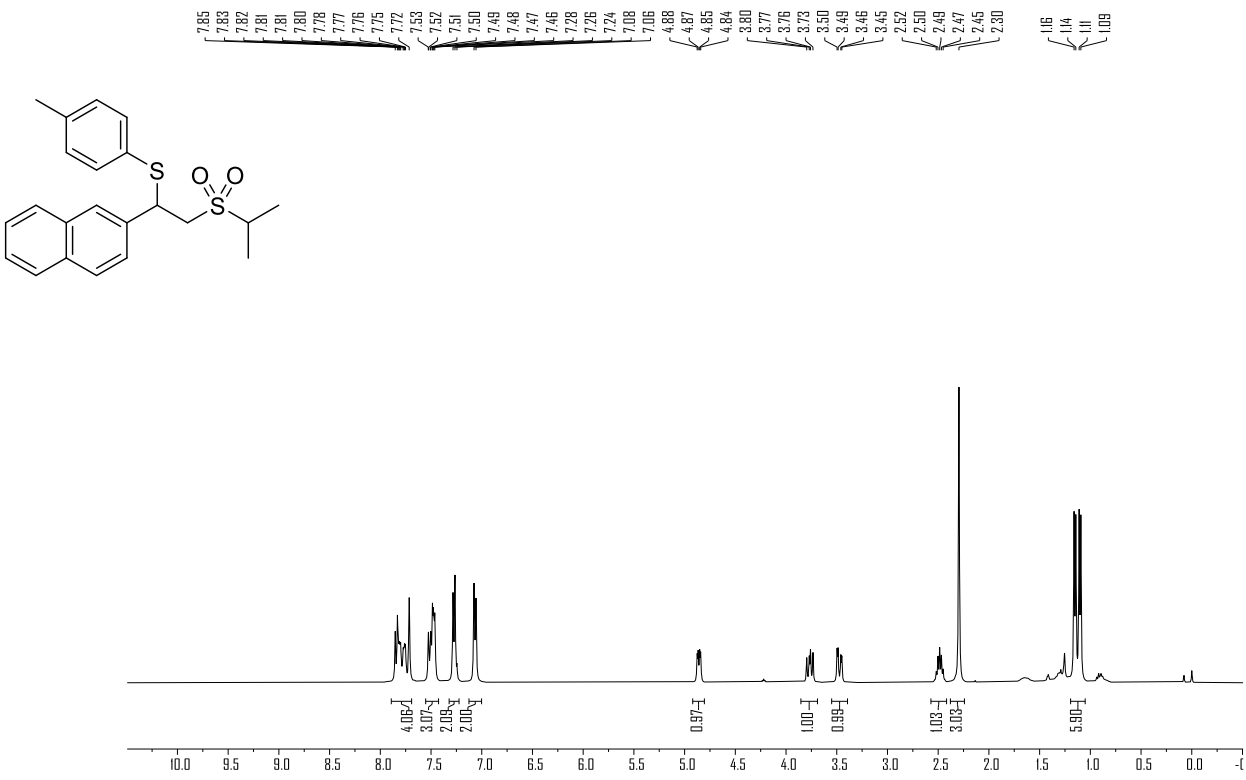
(2-(Methylsulfonyl)-1-(naphthalen-2-yl)ethyl)(p-tolyl)sulfane (4ac): ^{1}H NMR (400 MHz, $CDCl_3$)



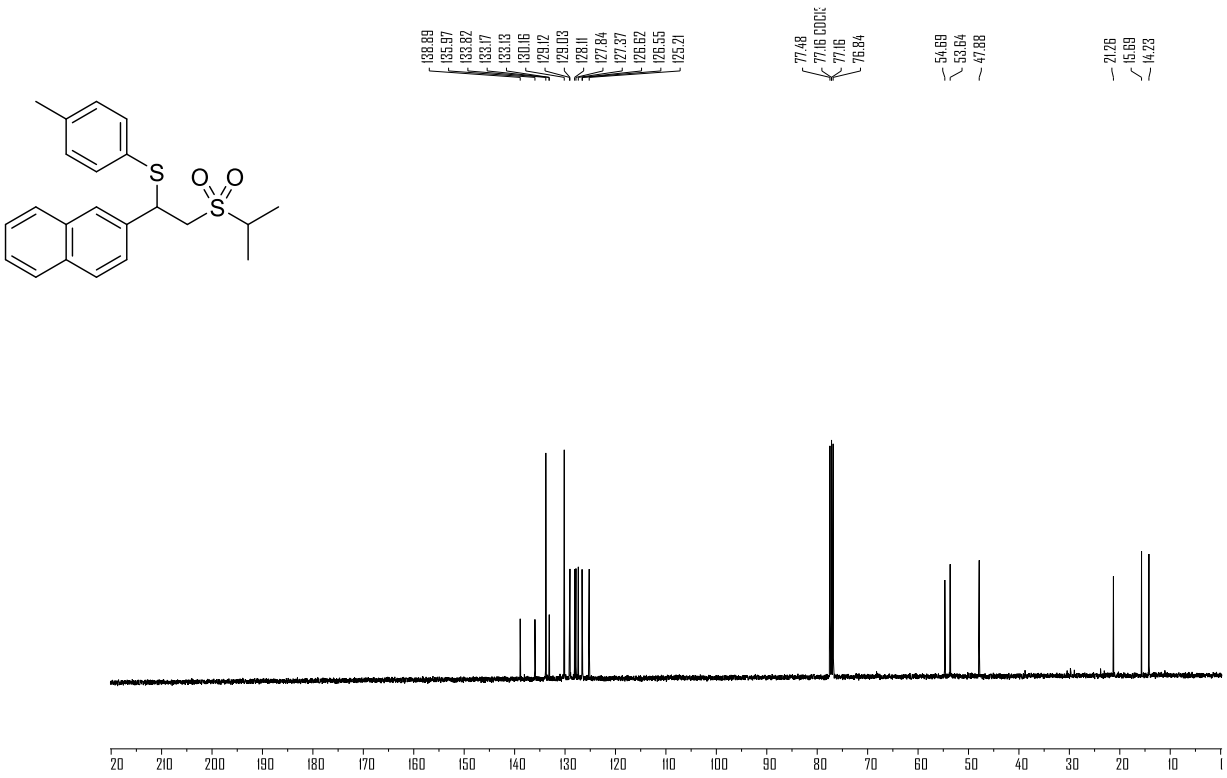
(2-(Methylsulfonyl)-1-(naphthalen-2-yl)ethyl)(p-tolyl)sulfane (4ac): ^{13}C NMR (101 MHz, $CDCl_3$)



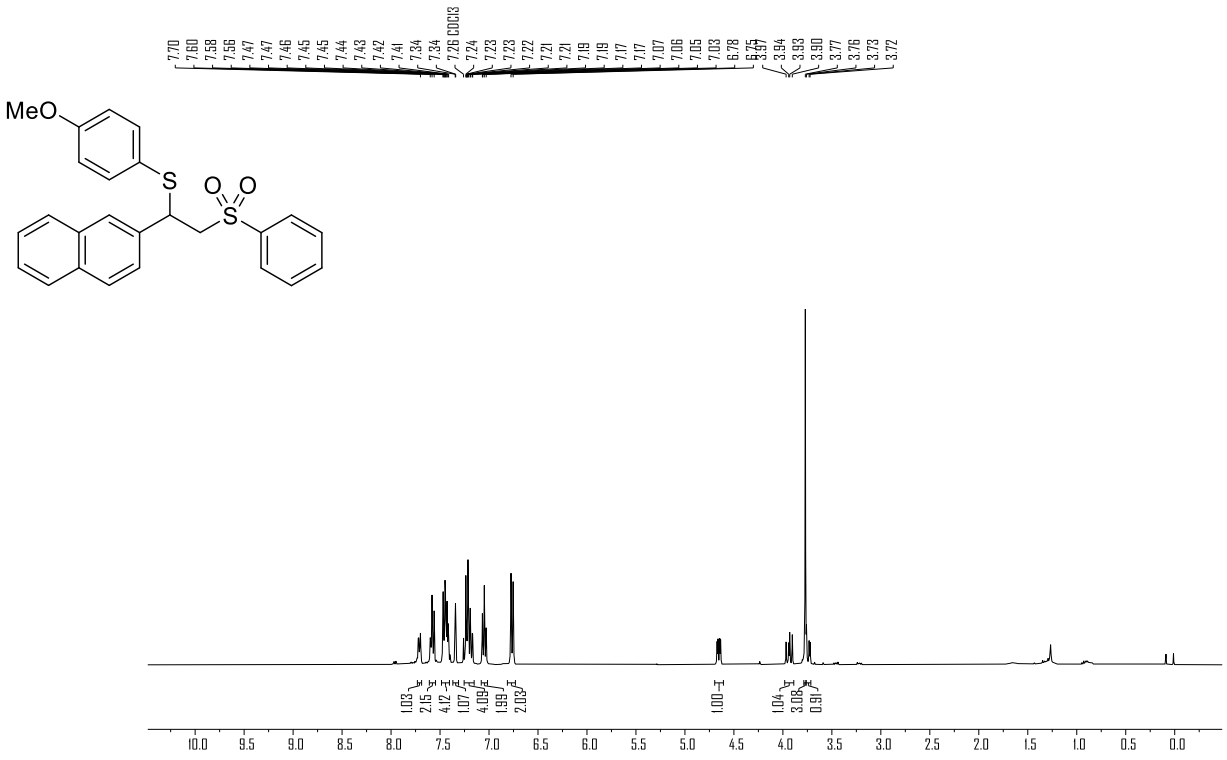
(2-(Isopropylsulfonyl)-1-(naphthalen-2-yl)ethyl)(p-tolyl)sulfane (4ad): ^{1}H NMR (400 MHz, $CDCl_3$)



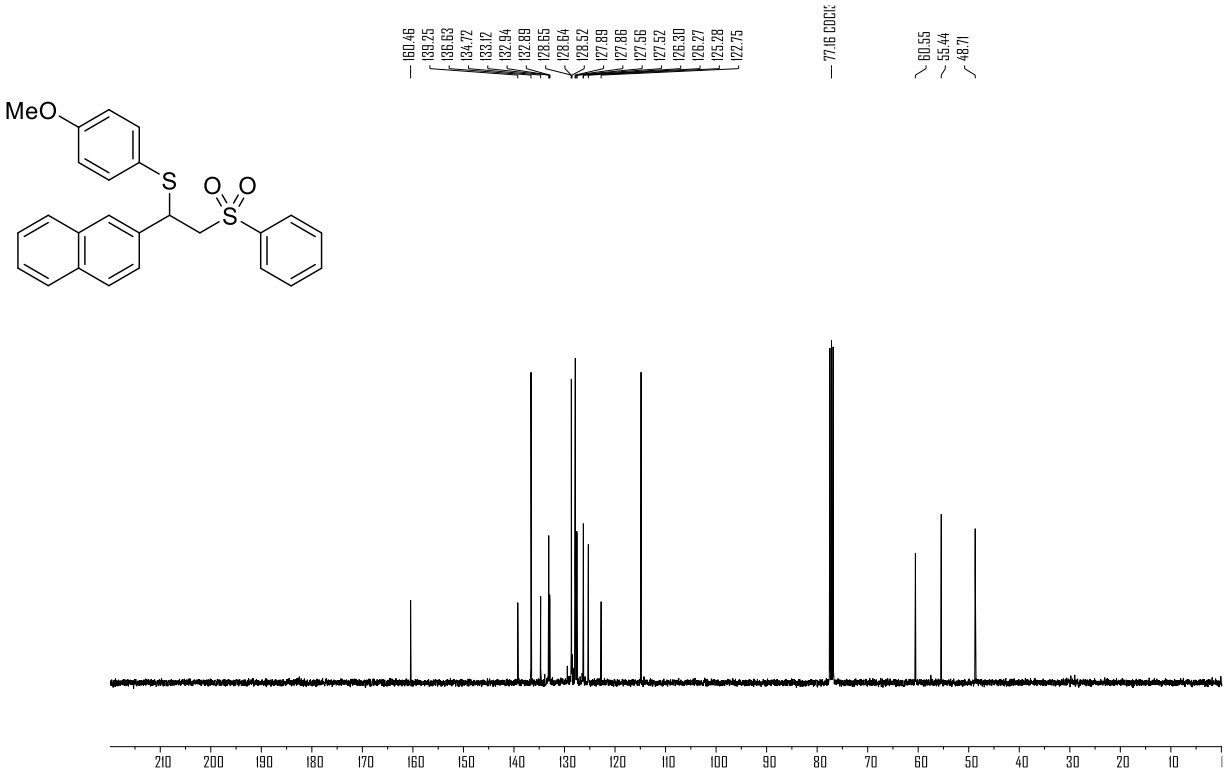
(2-(Isopropylsulfonyl)-1-(naphthalen-2-yl)ethyl)(p-tolyl)sulfane (4ad): ^{13}C NMR (101 MHz, $CDCl_3$)



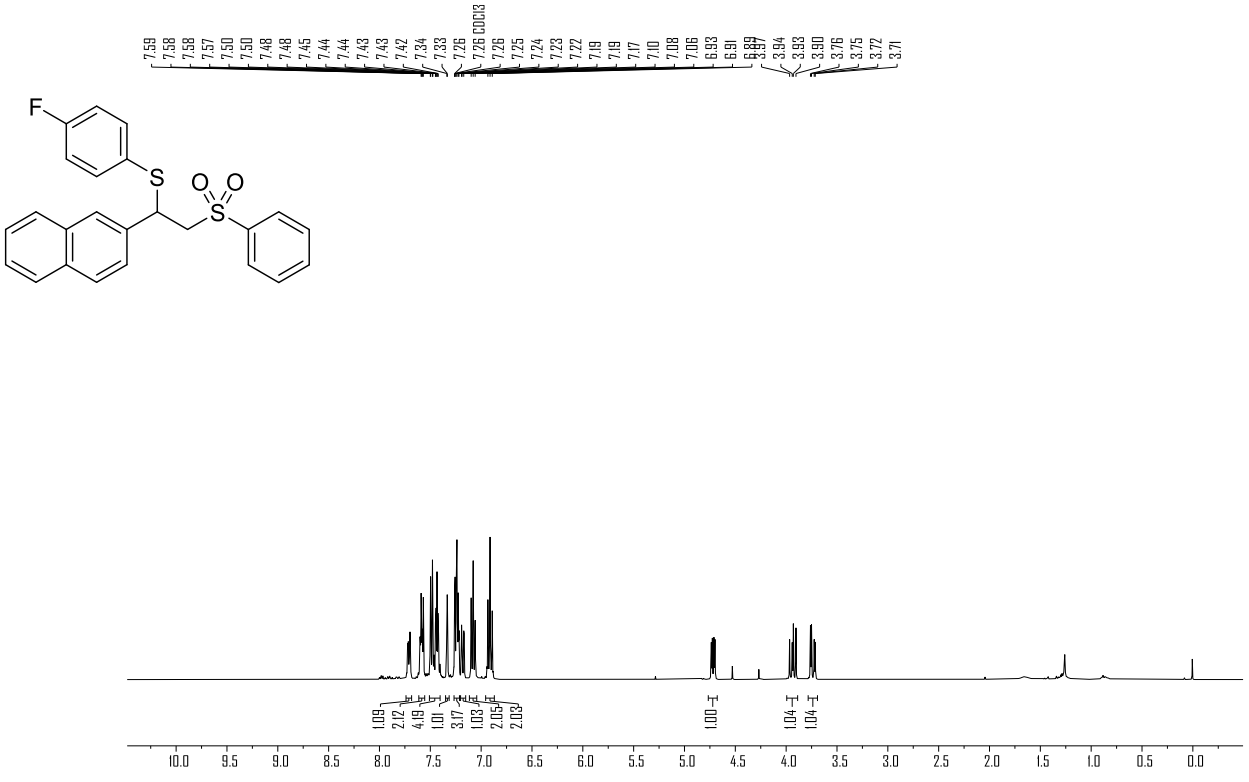
(4-Methoxyphenyl)(1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)sulfane (4ae): ^{1}H NMR (400 MHz, $CDCl_3$)



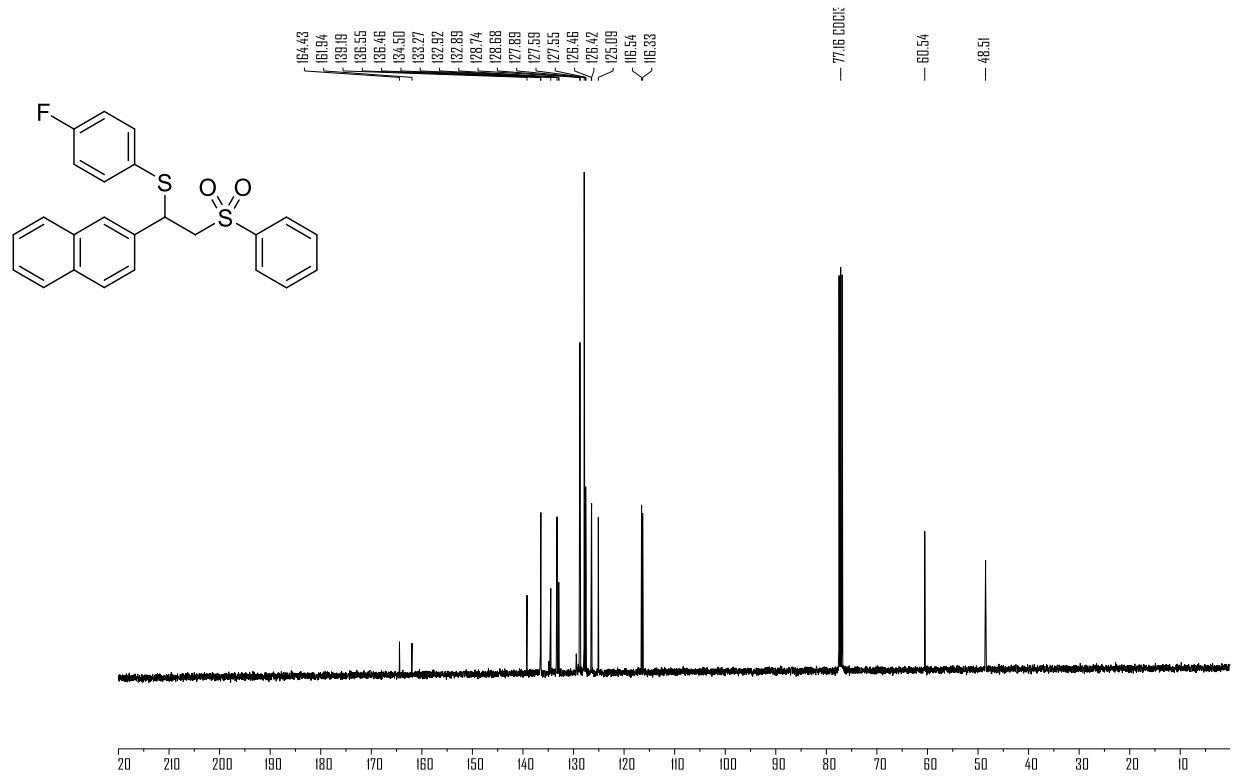
(4-Methoxyphenyl)(1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)sulfane (4ae): ^{13}C NMR (101 MHz, $CDCl_3$)



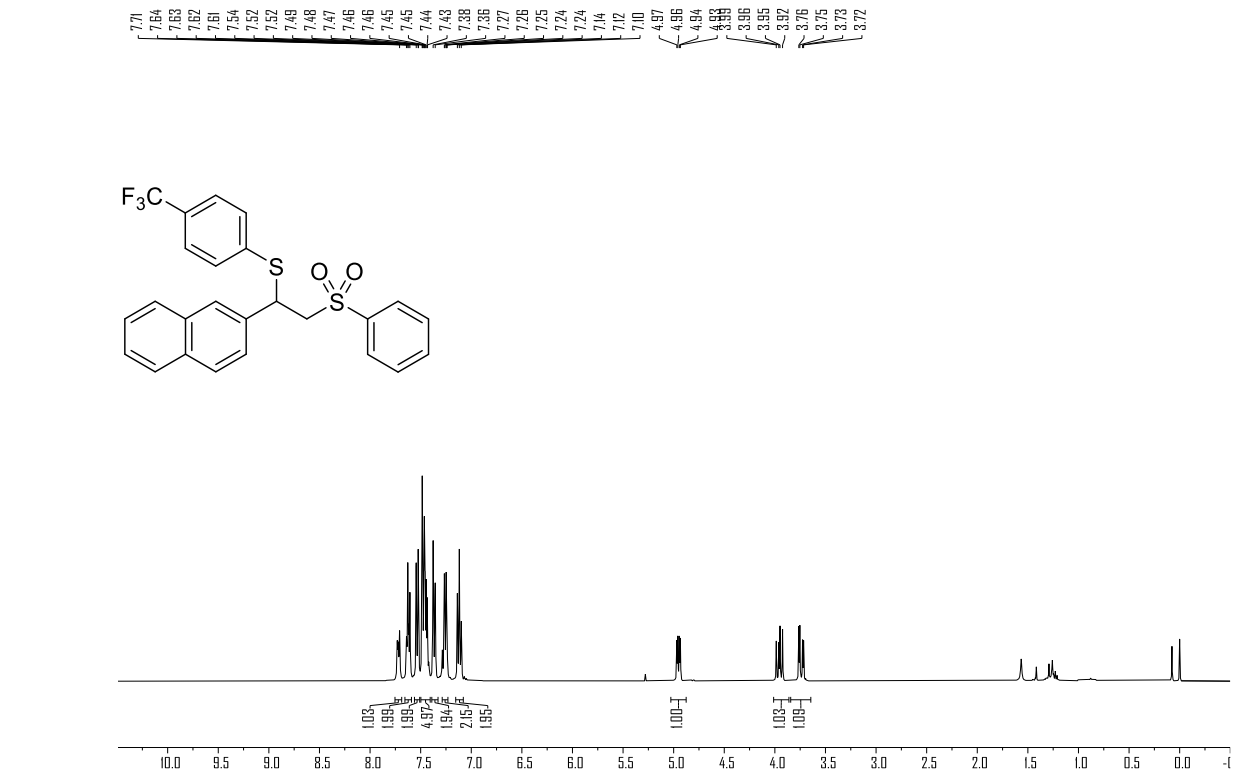
(4-Fluorophenyl)(1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)sulfane (4af): ^{1}H NMR (400 MHz, $CDCl_3$)



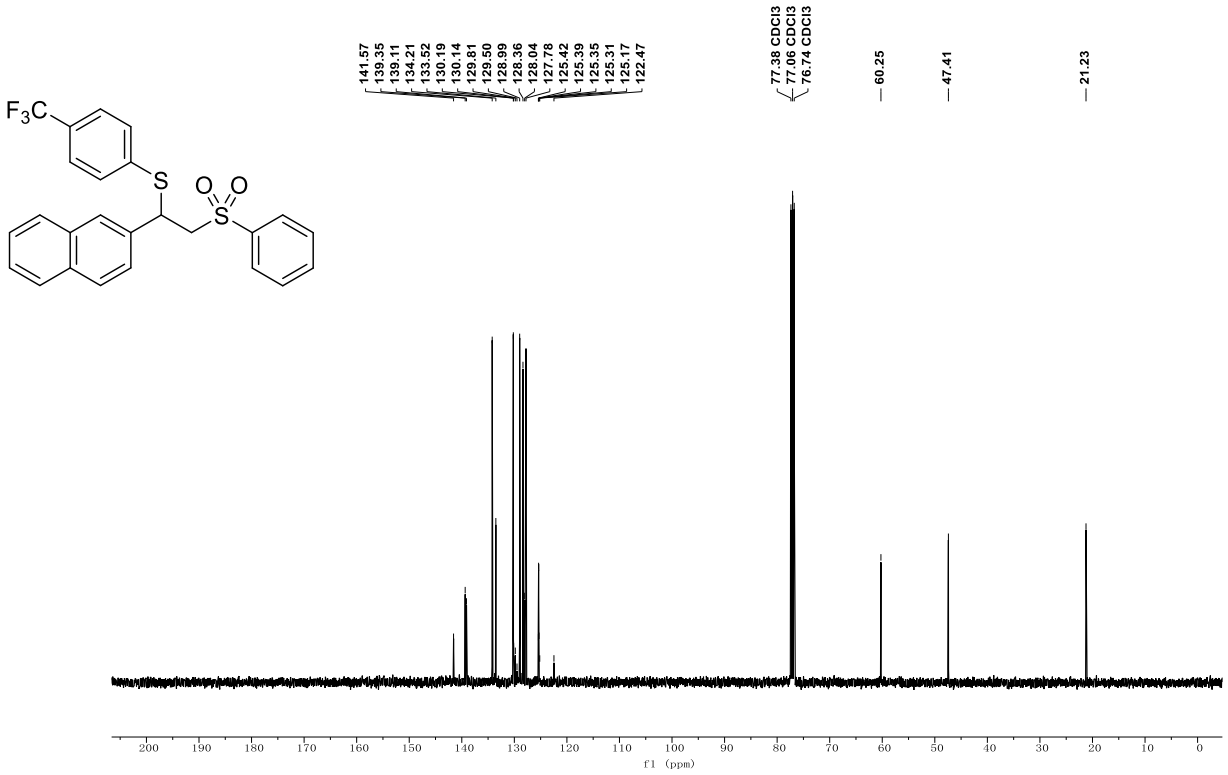
(4-Fluorophenyl)(1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)sulfane (4af): ^{13}C NMR (101 MHz, $CDCl_3$)



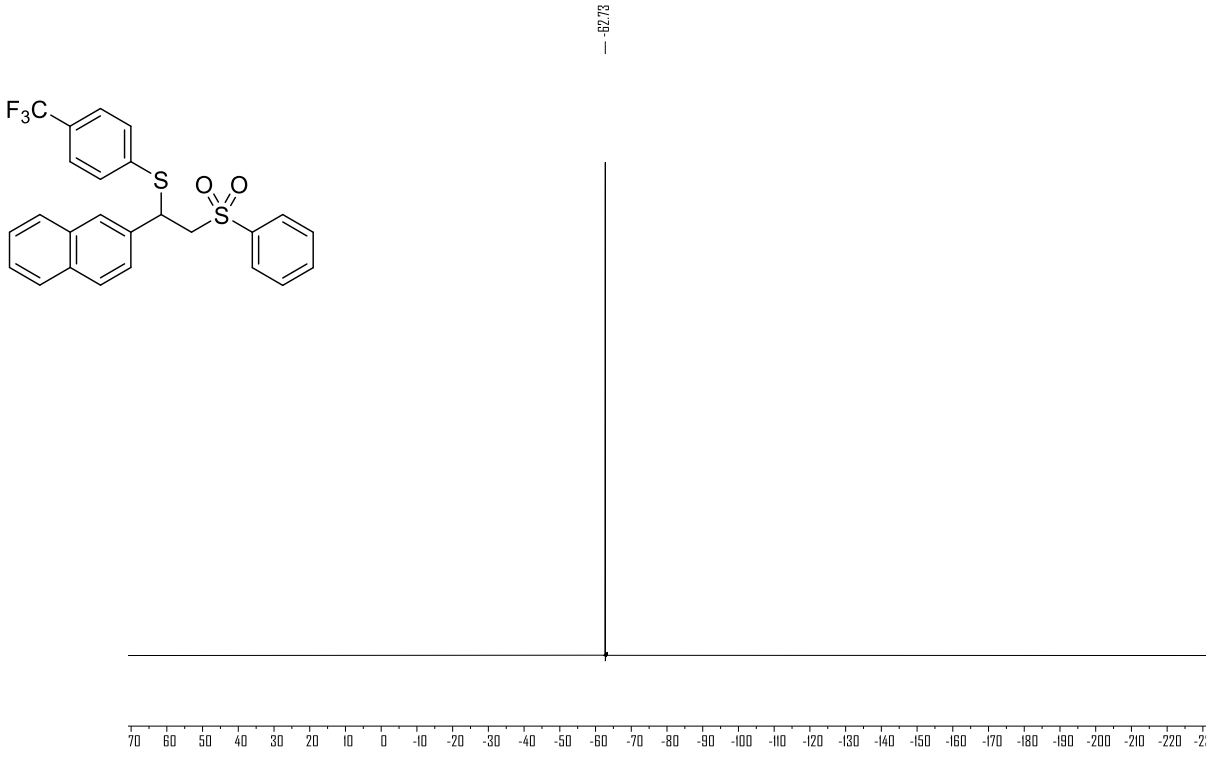
(1-(Naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)(4-(trifluoromethyl)phenyl)sulfane (4ag): ^{1}H NMR (400 MHz, $CDCl_3$)



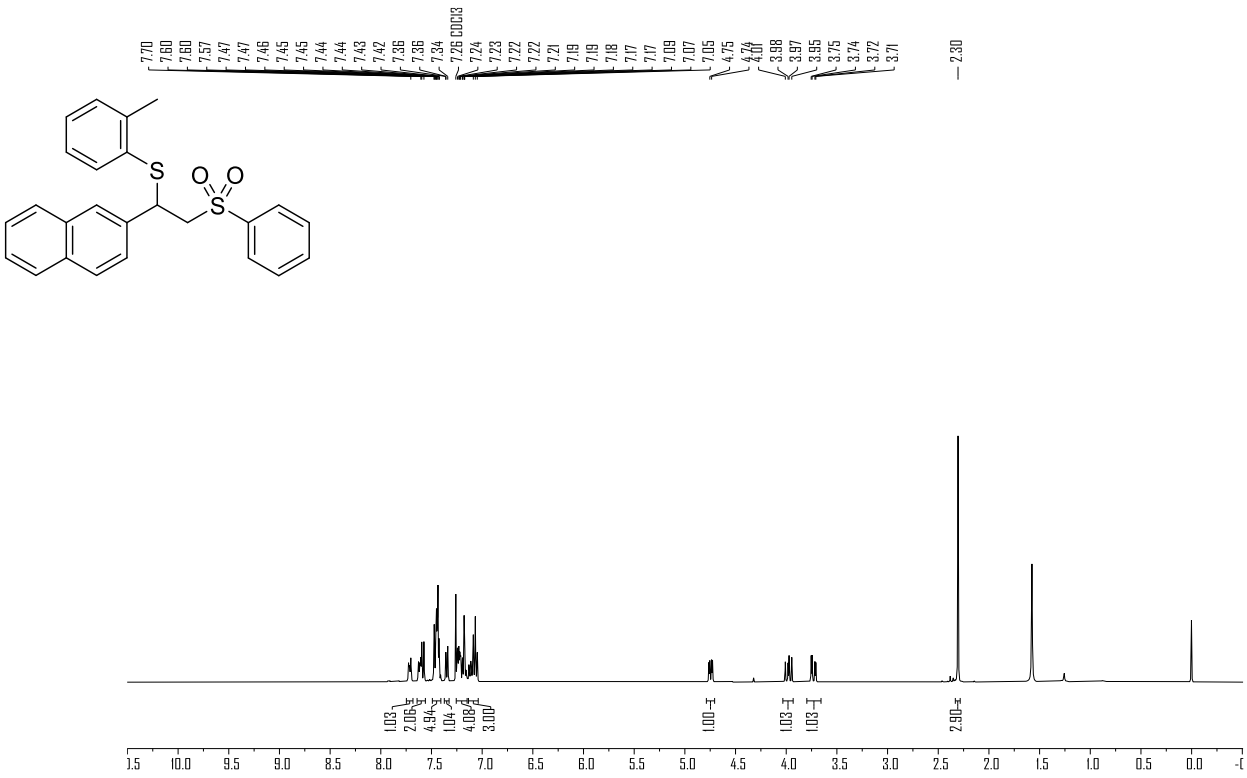
(1-(Naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)(4-(trifluoromethyl)phenyl)sulfane (4ag): ^{13}C NMR (101 MHz, $CDCl_3$)



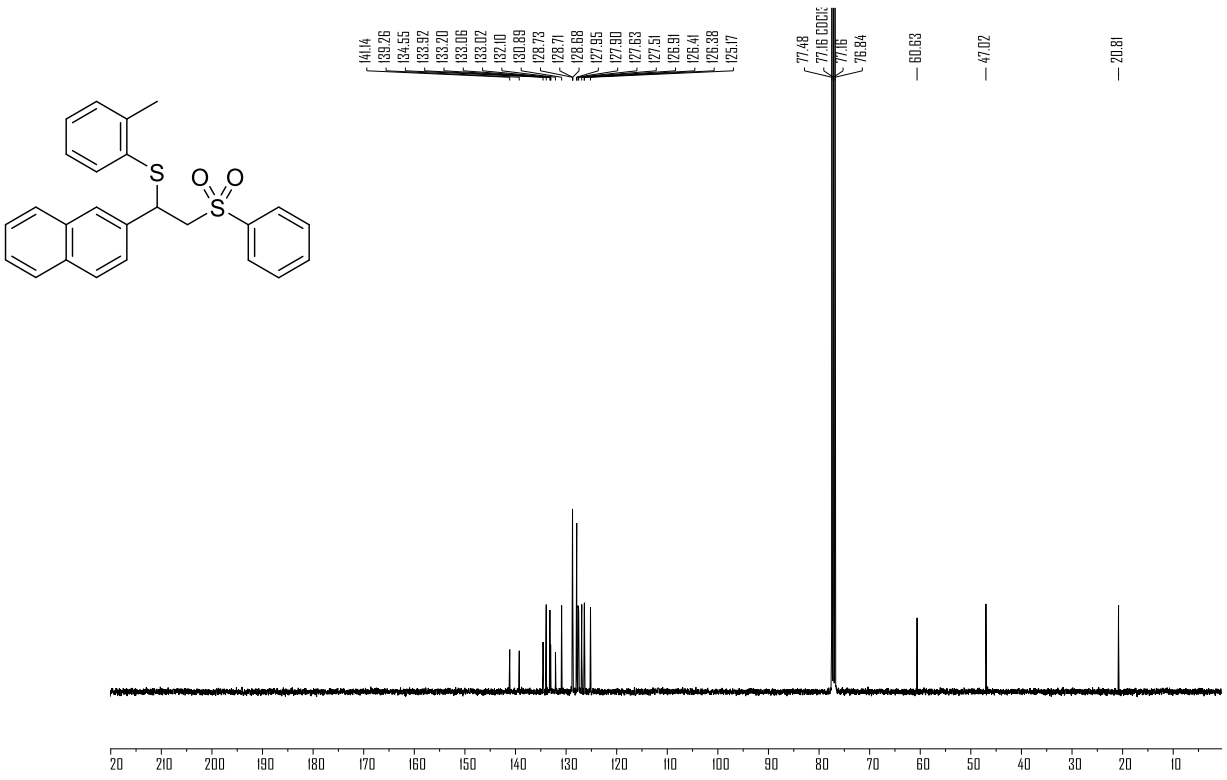
(1-(Naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)(4-(trifluoromethyl)phenyl)sulfane (4ag): ^{19}F NMR (377 MHz, $CDCl_3$)



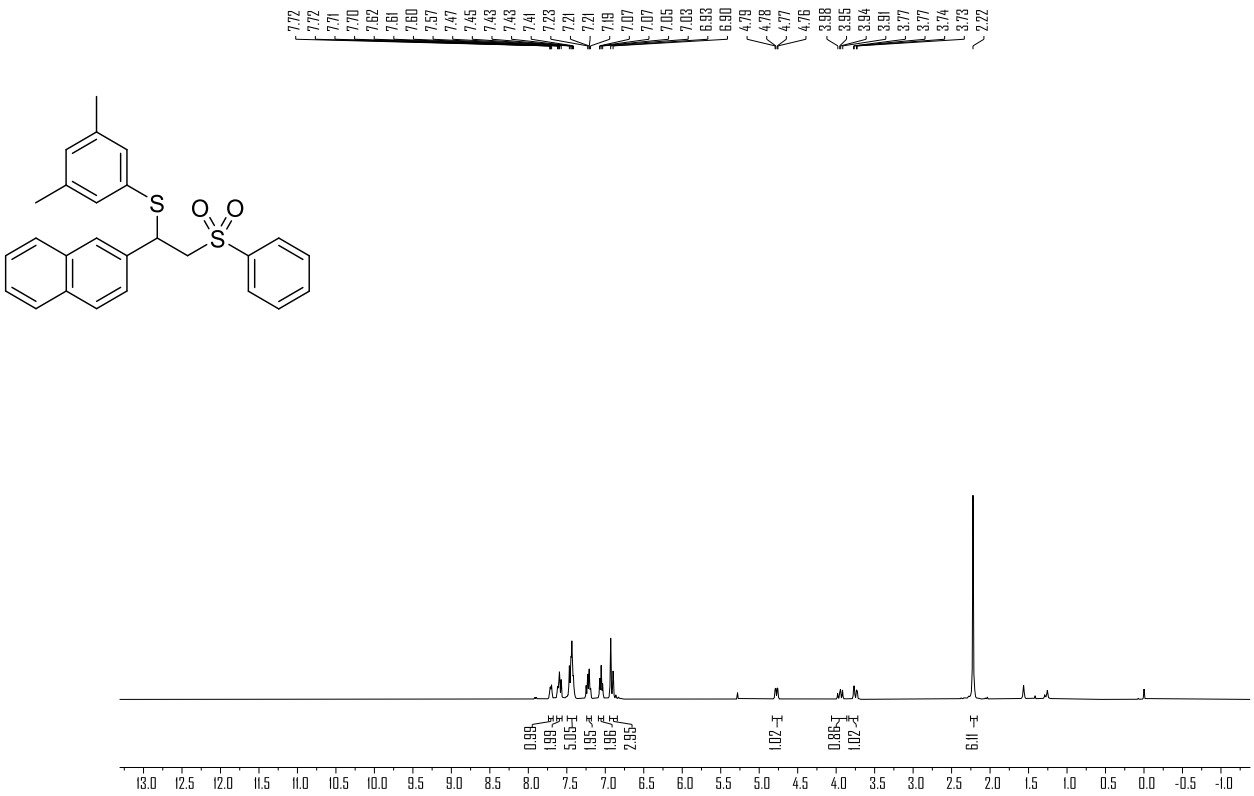
(1-(Naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)(o-tolyl)sulfane (4ah): ^{1}H NMR (400 MHz, $CDCl_3$)



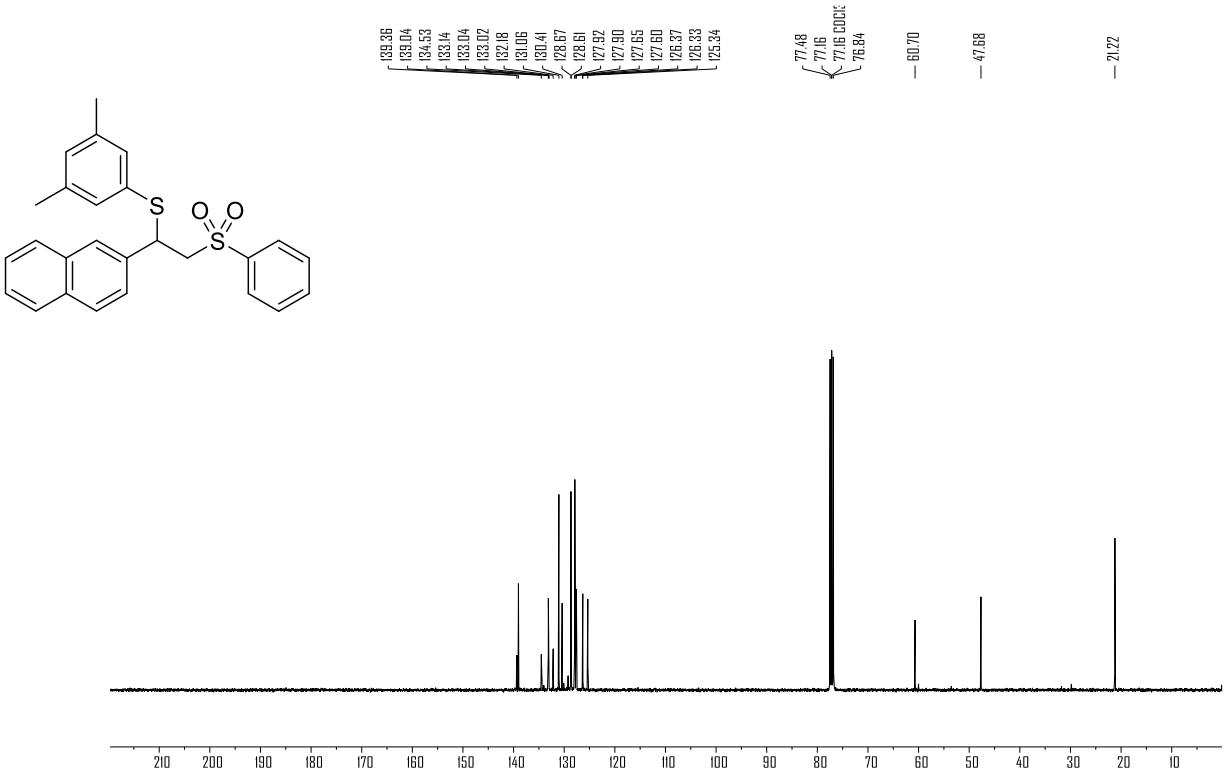
(1-(Naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)(o-tolyl)sulfane (4ah): ^{13}C NMR (101 MHz, $CDCl_3$)



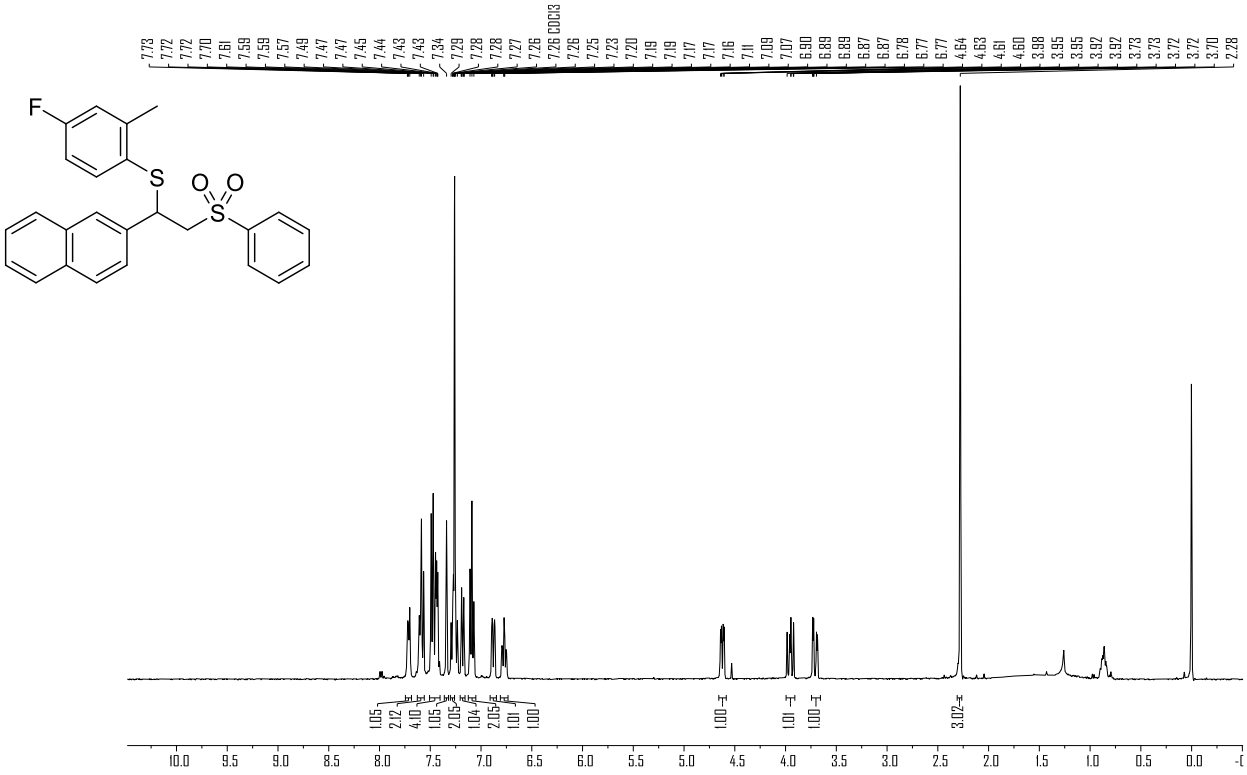
(3,5-Dimethylphenyl)(1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)sulfane (4ai): ^{1}H NMR (400 MHz, $CDCl_3$)



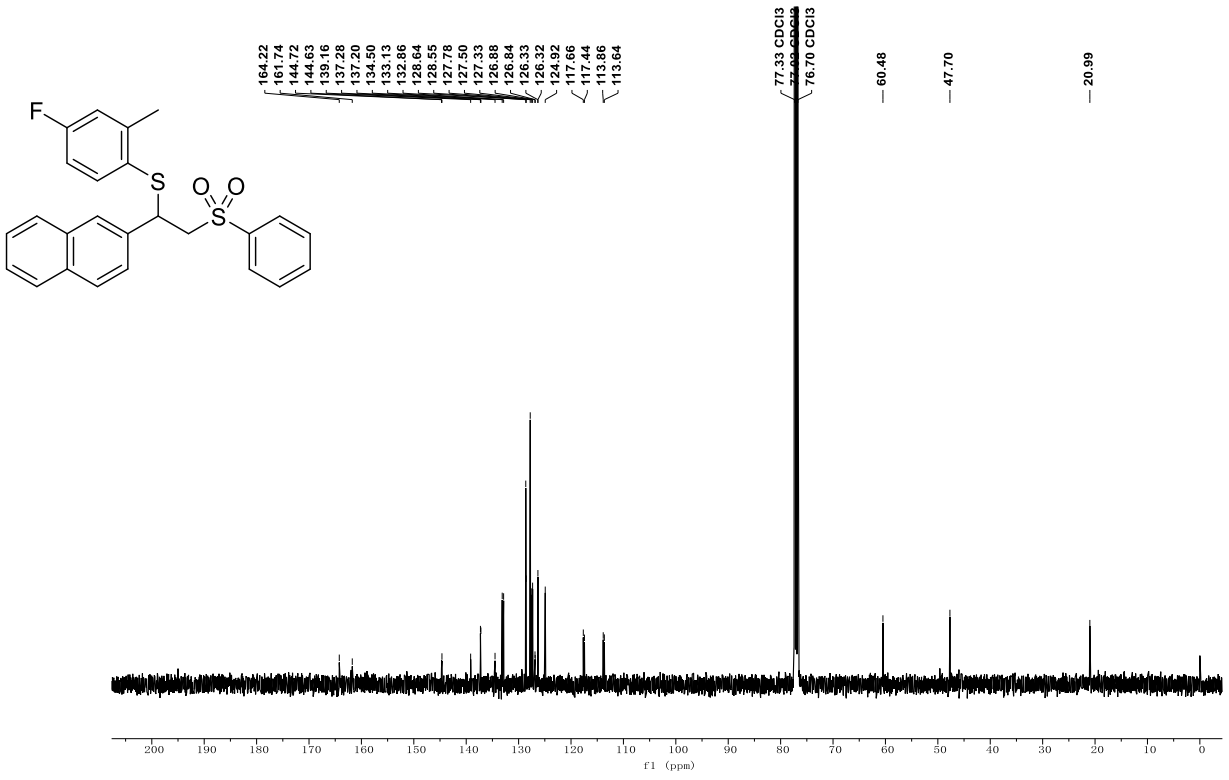
(3,5-Dimethylphenyl)(1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)sulfane (4ai): ^{13}C NMR (101 MHz, $CDCl_3$)



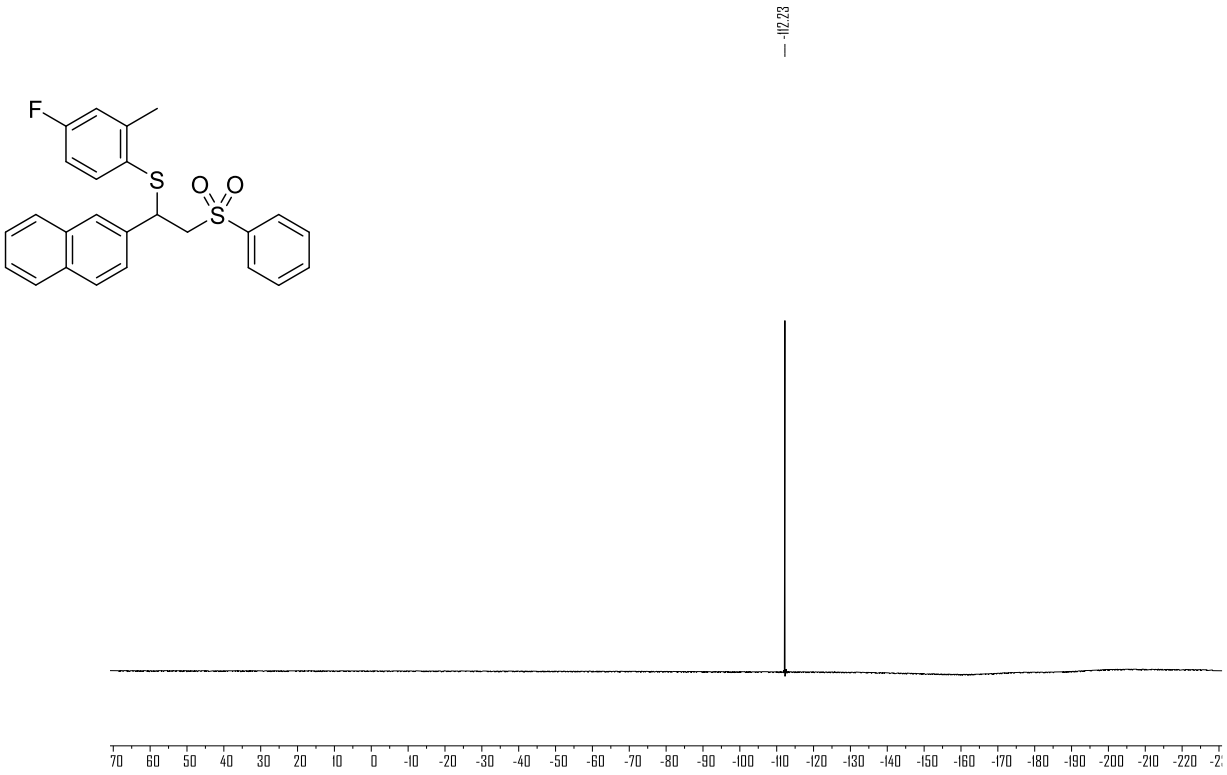
(4-Fuoro-2-methylphenyl)(1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)sulfane (4aj): ^{1}H NMR (400 MHz, $CDCl_3$)



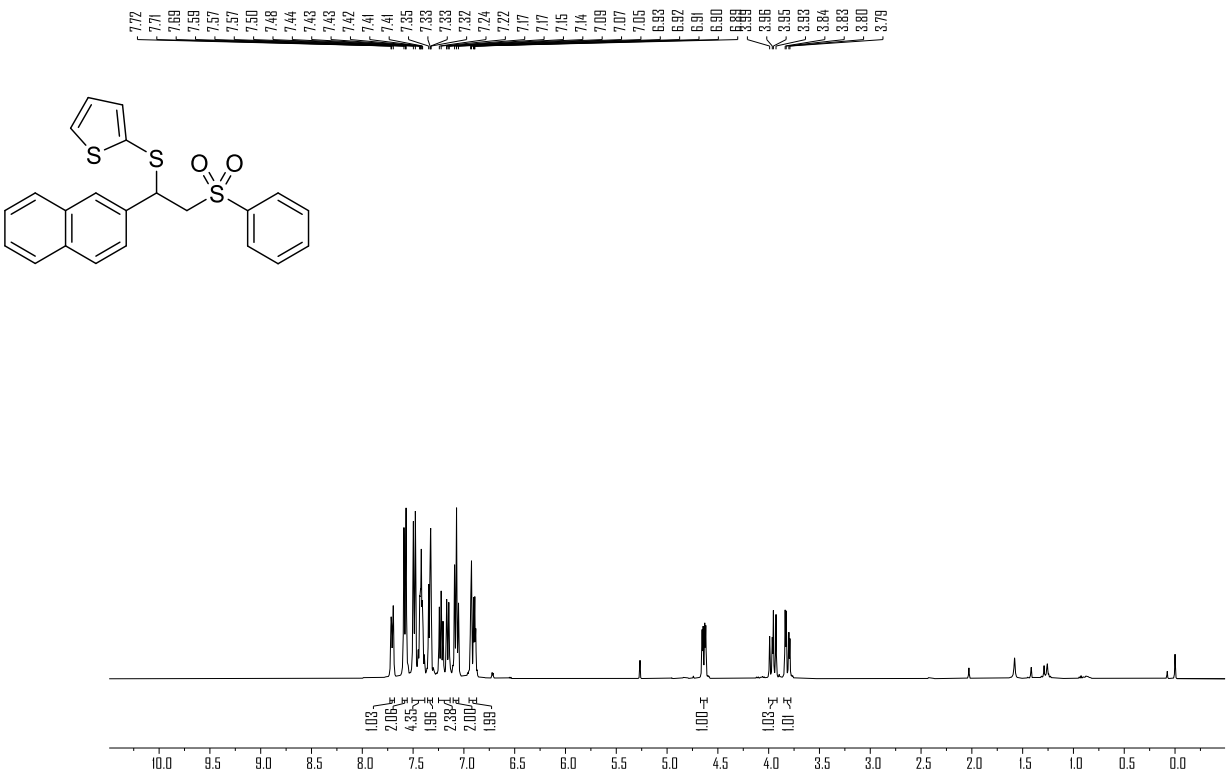
(4-Floro-2-methylphenyl)(1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)sulfane (4aj): ^{13}C NMR (101 MHz, $CDCl_3$)



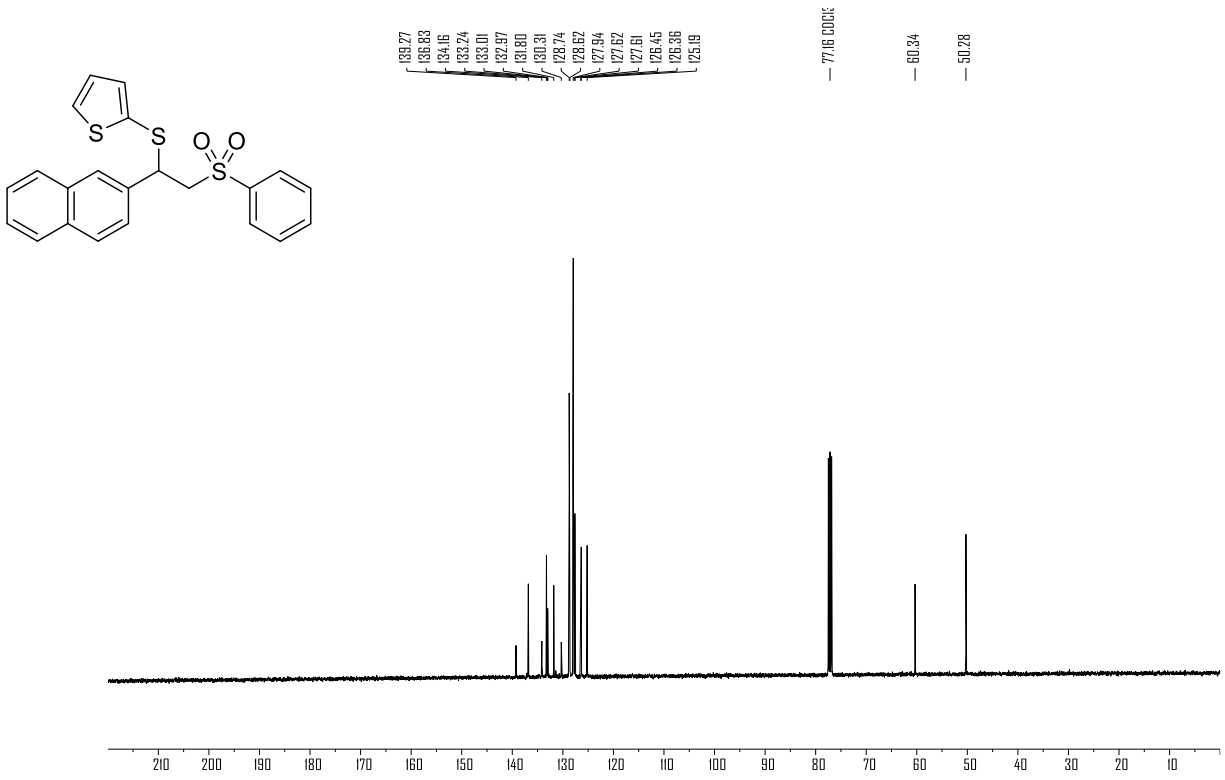
(4-Fuoro-2-methylphenyl)(1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)sulfane (4aj): ^{19}F NMR (101 MHz, $CDCl_3$)



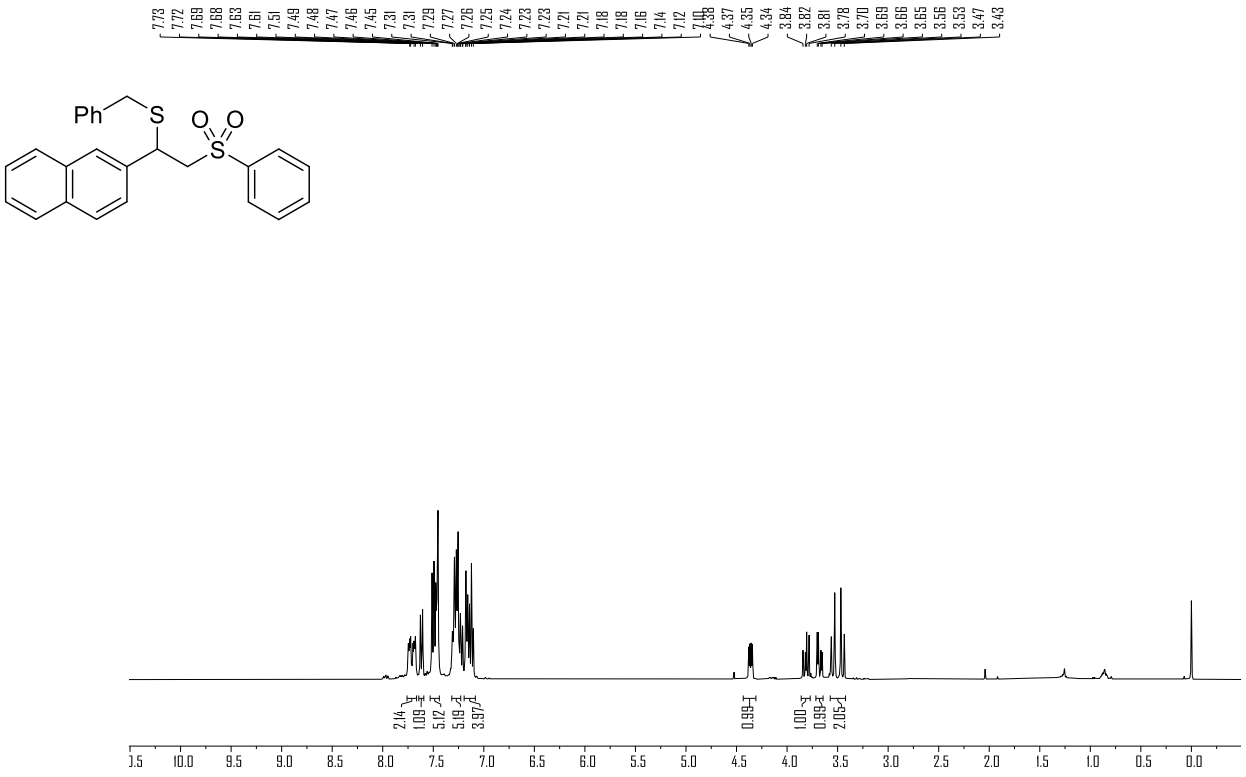
2-((1-(Naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)thio)thiophene (4ak): ^1H NMR (400 MHz, $CDCl_3$)



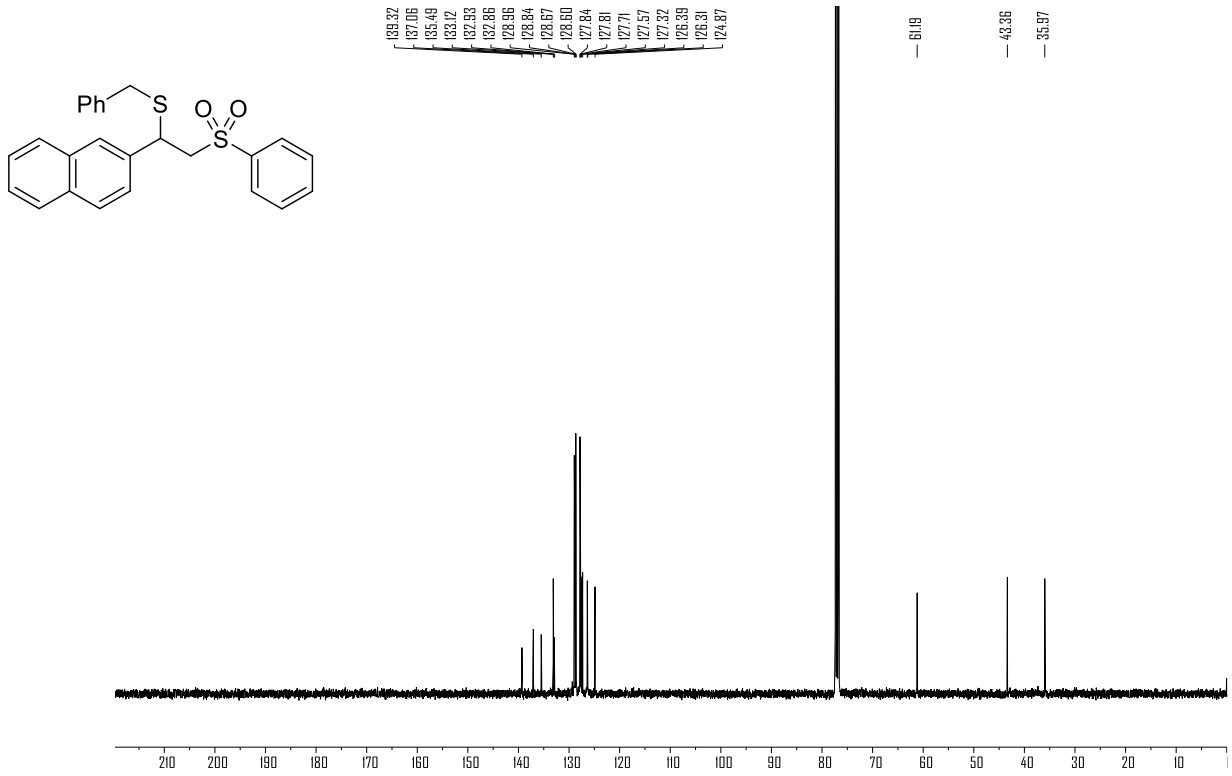
2-((1-(Naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)thio)thiophene (4ak): ^{13}C NMR (101 MHz, $CDCl_3$)



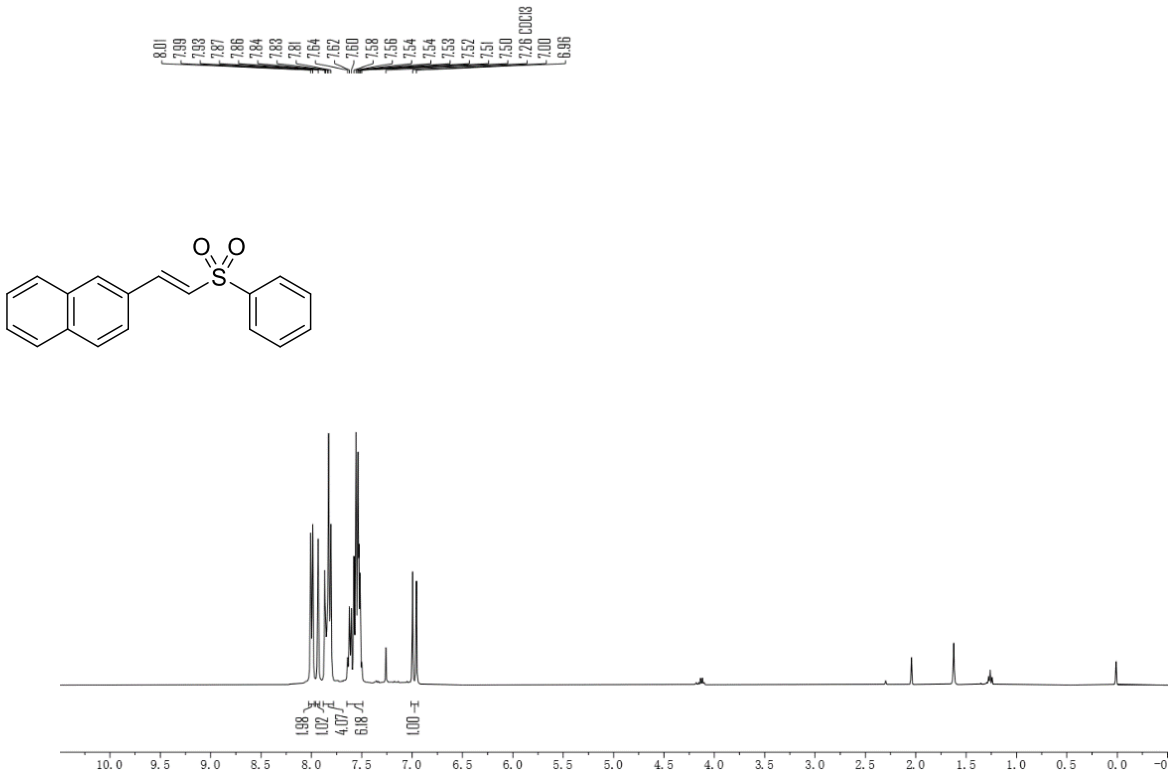
Benzyl(1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)sulfane (4al): ^{1}H NMR (400 MHz, $CDCl_3$)



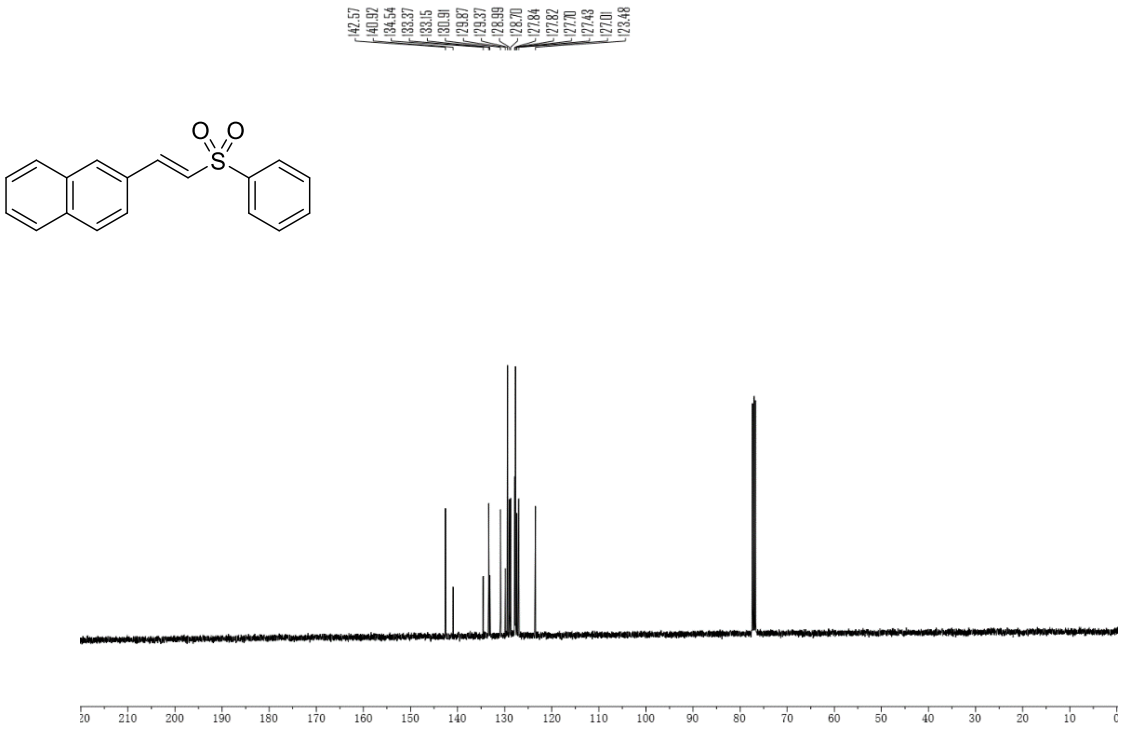
Benzyl(1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)sulfane (4al): ^{13}C NMR (101 MHz, $CDCl_3$)



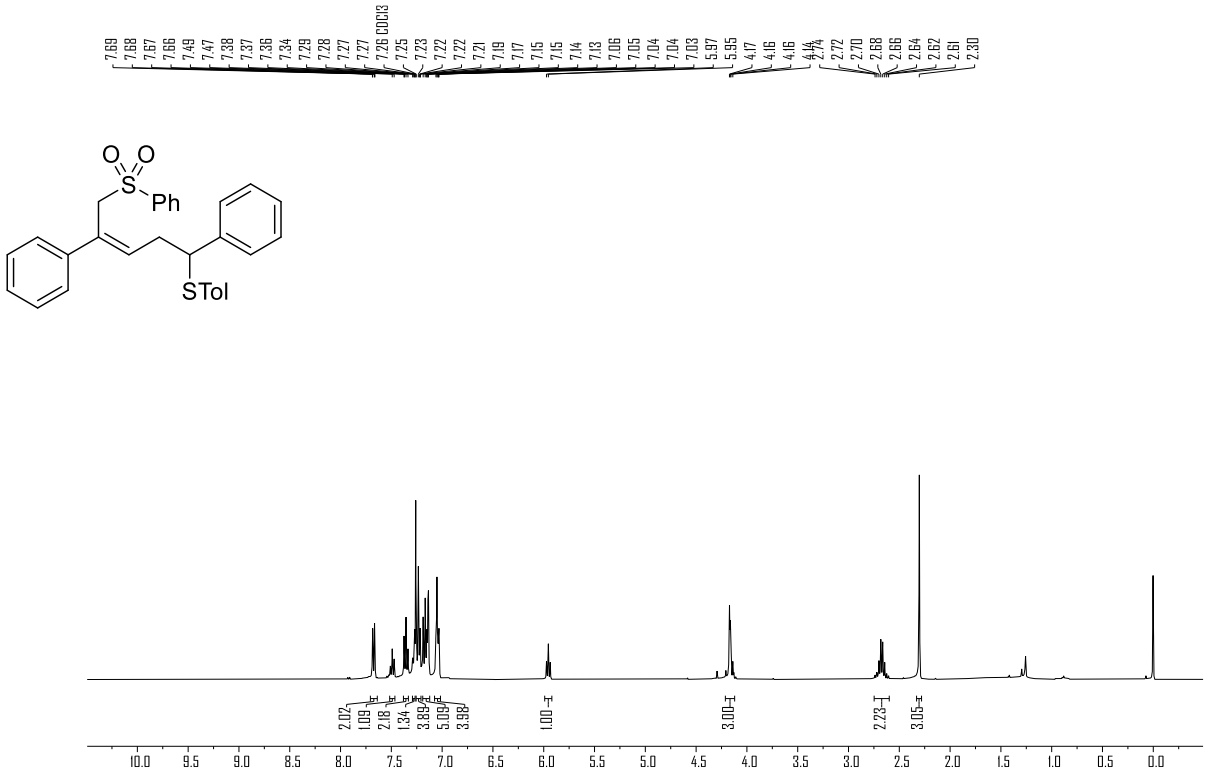
(*E*)-2-(2-(Phenylsulfonyl)vinyl)naphthalene (6a): ^{1}H NMR (400 MHz, $CDCl_3$)



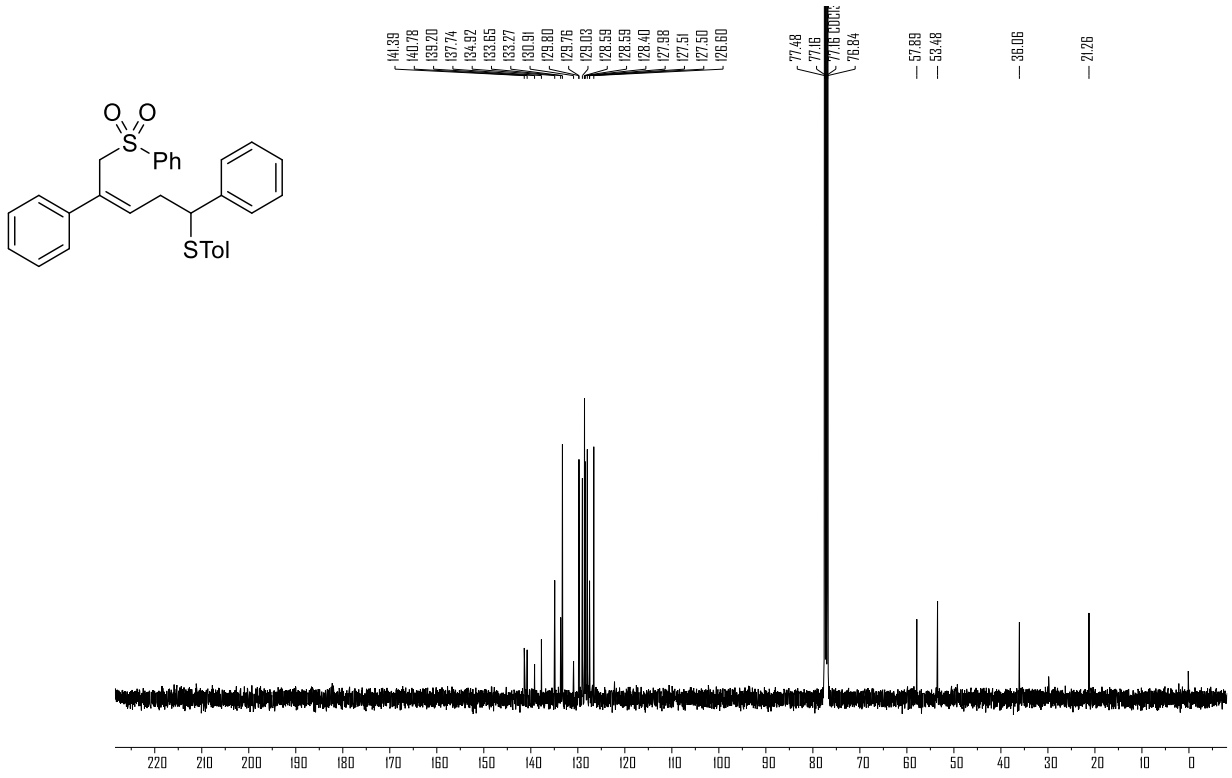
(*E*)-2-(2-(Phenylsulfonyl)vinyl)naphthalene (6a): ^{13}C NMR (101 MHz, $CDCl_3$)



(*Z*)-(1,4-Diphenyl-5-(phenylsulfonyl)pent-3-en-1-yl)(p-tolyl)sulfane (7a): ^{1}H NMR (400 MHz, $CDCl_3$)



(*Z*)-(1,4-Diphenyl-5-(phenylsulfonyl)pent-3-en-1-yl)(p-tolyl)sulfane (7a): ^{13}C NMR (101 MHz, $CDCl_3$)



(*Z*)-(1,4-Diphenyl-5-(phenylsulfonyl)pent-3-en-1-yl)(p-tolyl)sulfane (7a): NOE

There is NOE effect between protons (H8, H4)