

Electronic Supplementary Information for

A supramolecular dimer strategy for enhancing the selective generation of sulfides and sulfoxides by visible-light induced photoredox thiol-ene cross-coupling reactions of anthraquinone

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Experimental section

Materials: Unless specifically mentioned, all chemicals are commercially available and were used as received.

Characterization

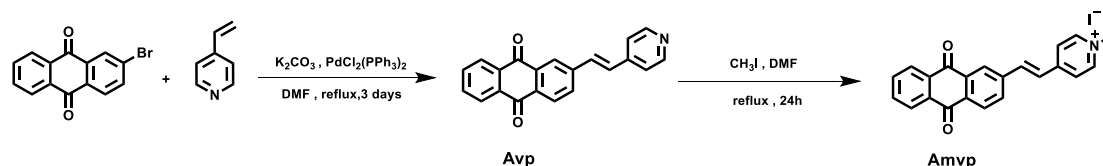
¹H NMR spectra was recorded on a Bruker Advance 400 spectrometer (400 MHz) at 298 K, and the chemical shifts (δ) were expressed in ppm and J values were given in Hz. UV-vis spectra were obtained on a Shimadzu UV-1601PC spectrophotometer in a quartz cell (light path 10 mm) at 298 K. Steady-state fluorescence measurements were carried out using a Hitachi 4500 spectrophotometer. Dynamic light scattering (DLS) and zeta potential are measured on Malvern Zetasizer Nano ZS90. Transmission electron microscopy (TEM) images were obtained on a JEM 2100 operating at 120 kV. Samples for TEM measurements were prepared by dropping the mixture aqueous solution on carbon-coated copper grid (300 mesh) and drying by slow evaporation. Electron paramagnetic resonance (EPR) spectroscopy was recorded with a Bruker EMXplus. The cyclic voltammetry (CV) of Amvp-CB[8] was performed on a CHI660C electrochemical workstation (Shanghai Chenhua, China), and the CV curves were obtained using a typical three electrode battery system, with calomel electrode as the reference electrode, glassy carbon (GC) as the working electrode, and Pt line as the counter electrode. Taking CV scans at a scanning rate of 100 mV s⁻¹. The photocatalytic reaction was performed on WATTCAS Parallel Photocatalytic Reactor (WP-TEC-HSL) with 10W COB LED. Hamamatsu absolute quantum yield measuring instrument Quantaaurus-QY was used to obtain fluorescence quantum yields. The time-resolved fluorescence decay curve and photoluminescence spectra was obtained by the FLS5 Steady-State/Transient Fluorescence Spectrometer.

General procedure for the coupling reaction of styrene and 4-methylbenzenethiol:

Styrene (0.2 mmol, 20.8 mg) and 4-methylbenzenethiol (0.3 mmol, 37.2 mg) were added in the newly produced solution of Amvp-CB[8] (0.5 mol%, 2.0 mL, [Amvp]= 5.0×10^{-4} M, CB[8]= 2.5×10^{-4} M). The reaction was irradiated with purple light (10 W, 395 nm) at room temperature under the ambient air condition for 0.5 h. Then the mixture was extracted with dichloromethane, and the combined organic layer was dried with anhydrous Na₂SO₄. Then the organic solvent was removed in vacuo and purified by flash column chromatography with petroleum ether/ethyl acetate to afford the products.

General procedure for the oxidation reaction of phenethyl(p-tolyl)sulfane:

Styrene (0.2 mmol, 20.8 mg) and 4-methylbenzenethiol (0.3 mmol, 37.2 mg) were added in the newly produced solution of Amvp-CB[8] (0.5 mol%, 2.0 mL, [Amvp]= 5.0×10^{-4} M, CB[8]= 2.5×10^{-4} M). The reaction was irradiated with purple light (10 W, 395 nm) at room temperature under the ambient air condition for 12 h. Then the mixture was extracted with dichloromethane, and the combined organic layer was dried with anhydrous Na₂SO₄. Then the organic solvent was removed in vacuo and purified by flash column chromatography with petroleum ether/ethyl acetate to afford the products.



Scheme S1. Synthetic route of Amvp.

Synthesis of Amvp: The synthesis of Amvp was as shown in Scheme S1. 4-vinyl pyridine (4 mmol) was added into the solution of 2-dibromoanthracene-9,10-dione (1.148 g, 4.0 mmol) in DMF (30.0 mL), then Pd(PPh₃)₂Cl₂ (0.28 g, 0.4 mmol) and potassium carbonate (3.32 g, 24.0 mmol) were added. The mixed solution was refluxed for 3 days. The reaction mixture was then cooled to room temperature. The precipitate was dissolved in CH₂Cl₂ and the solution was washed with water for three times. After the solvent is removed, the product can be obtained by silica gel chromatography (petroleum ether:ethyl acetate = 1:2, v/v) as an orange yellow color solid (1.026 g, 82.5%). Avp (0.2 g, 0.643 mmol) was added in 5 mL of DMF, and CH₃I (0.71 g, 5.0 mmol) was then added. The mixed solution was stirred at 100 °C for 1 days. The resulting precipitate was collected by filtration and washed with CH₃CN several times. The resulting precipitation was collected through filtration and dried under vacuum to obtain Amvp as an orange precipitate (0.244 g, 85%). ¹H NMR (400 MHz, DMSO-d₆) δ 8.98 - 8.94 (m, 2H), 8.54 (d, J = 1.8 Hz, 1H), 8.33 (dd, J = 7.5, 2.2 Hz, 3H), 8.30 - 8.21 (m, 4H), 8.00 - 7.96 (m, 2H), 7.86 (d, J = 16.4 Hz, 1H), 4.30 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 182.80, 182.47, 152.11, 145.92, 141.17, 138.70, 135.25, 135.13, 134.15, 133.87, 133.62, 133.52, 133.34, 128.23, 127.55, 127.34, 127.31, 126.64, 124.64, 47.66.

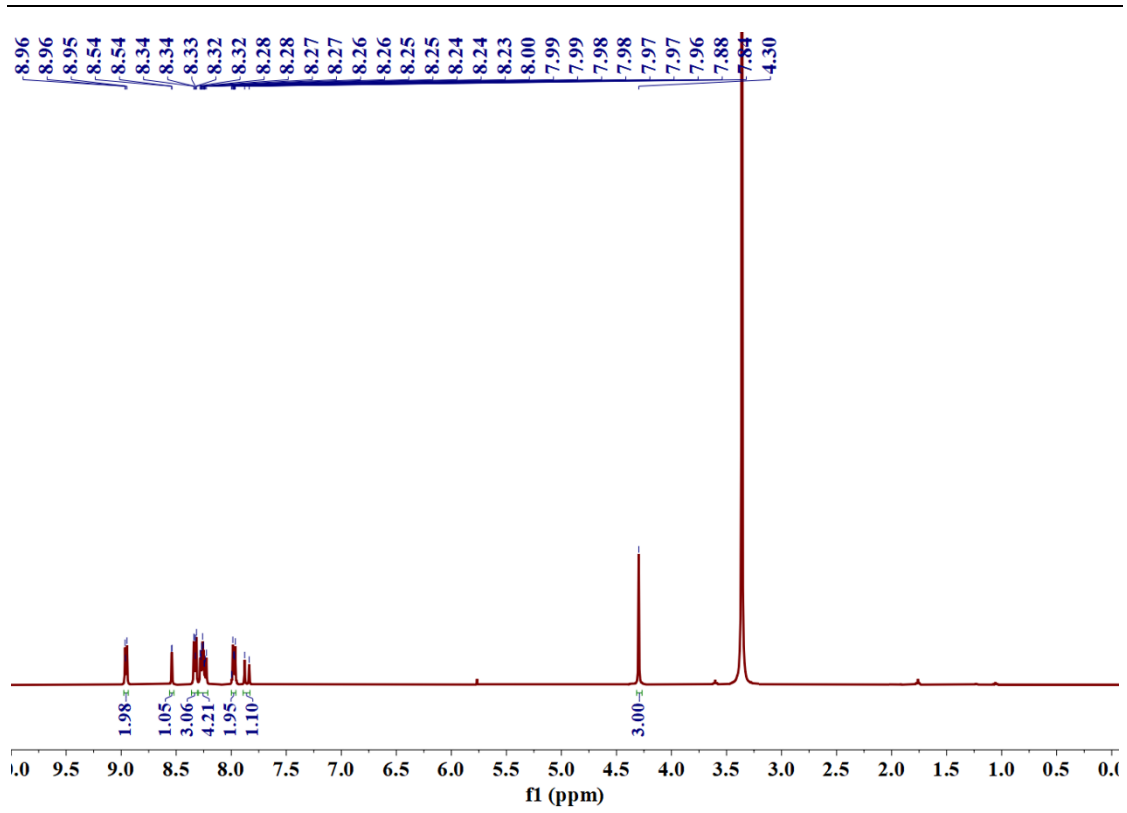


Fig. S1. ^1H NMR spectrum of compound Amvp in $\text{DMSO-}d_6$.

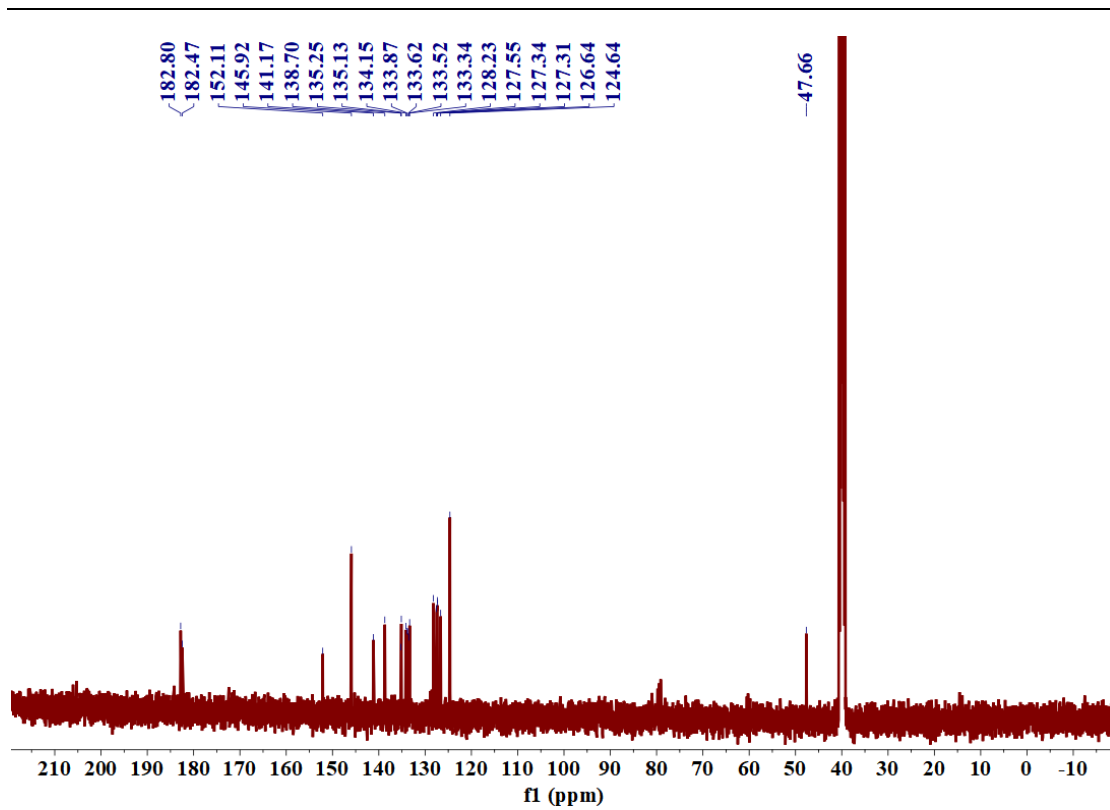


Fig. S2. ^{13}C NMR spectrum of compound Amvp in $\text{DMSO-}d_6$.

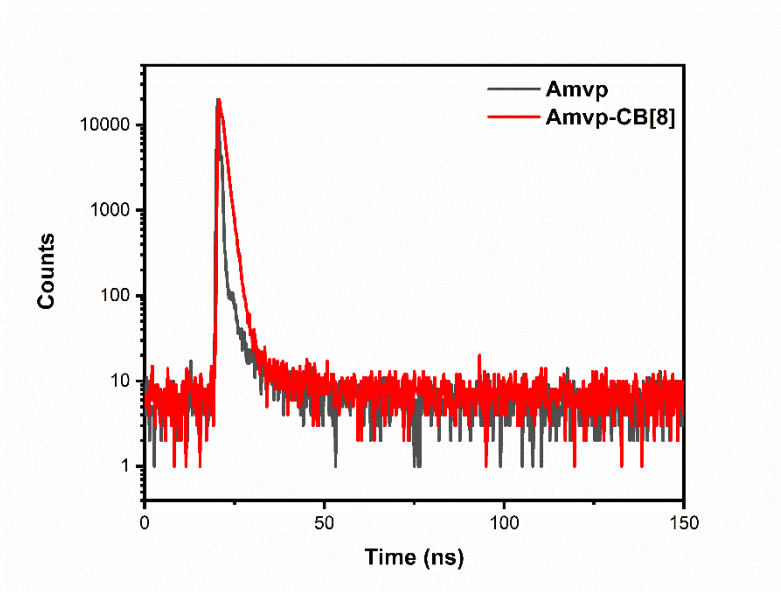


Fig. S3. Fluorescence lifetime maps of Amvp (0.66 ns) and fluorescence lifetime maps of Amvp-CB[8] (1.43 ns). ($[Amvp]=2.0\times 10^{-5}$ M, $[Amvp-CB[8]]=2.0\times 10^{-5}$ M).

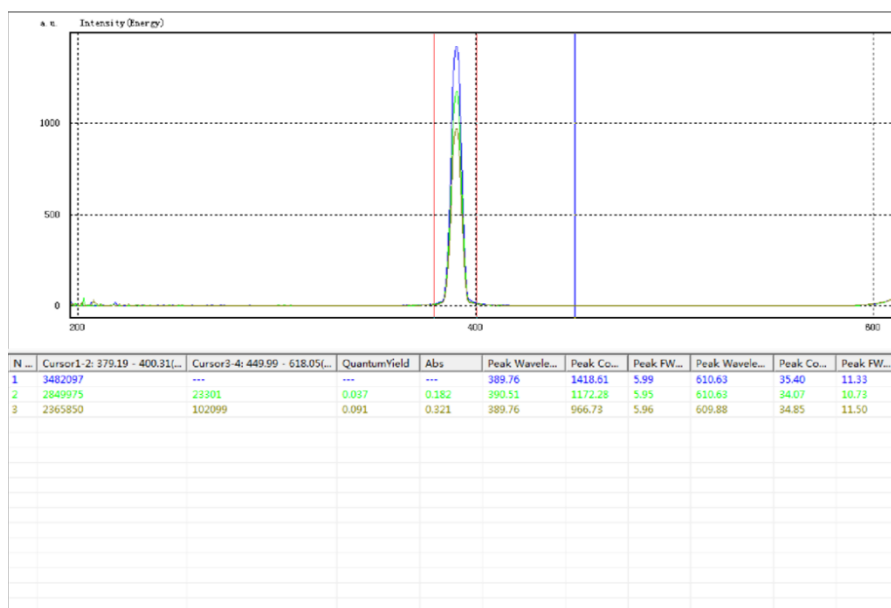


Fig. S4. Fluorescence quantum yields of Amvp and Amvp-CB[8] in H₂O. ([Amvp]= 2.0×10^{-5} M, [Amvp-CB[8]]= 2.0×10^{-5} M).

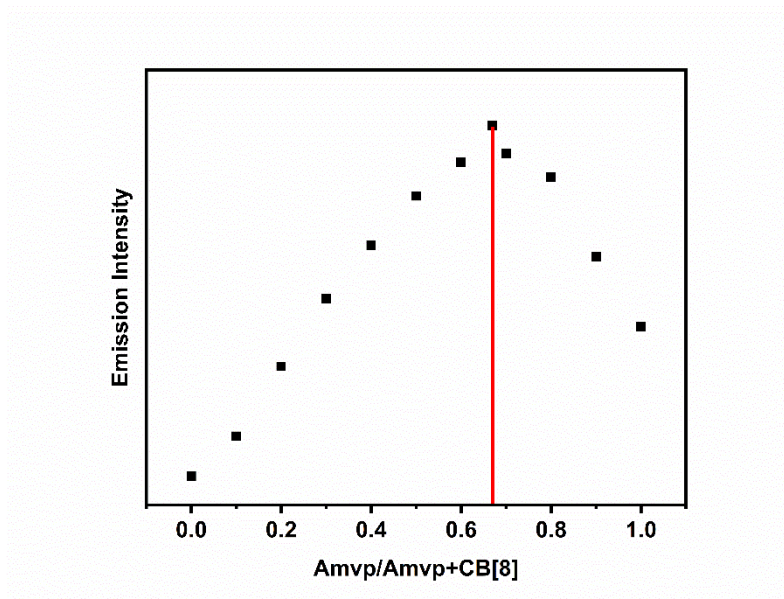


Fig. S5. Job's plot of Amvp and CB[8].

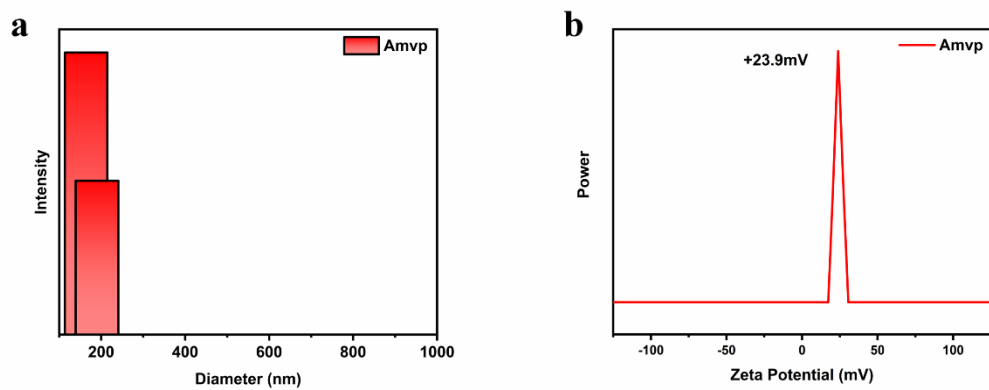


Fig. S6. (a) The particle size distribution of Amvp; (b) Zeta potential of Amvp. ([Amvp]= 2.0×10^{-5} M).

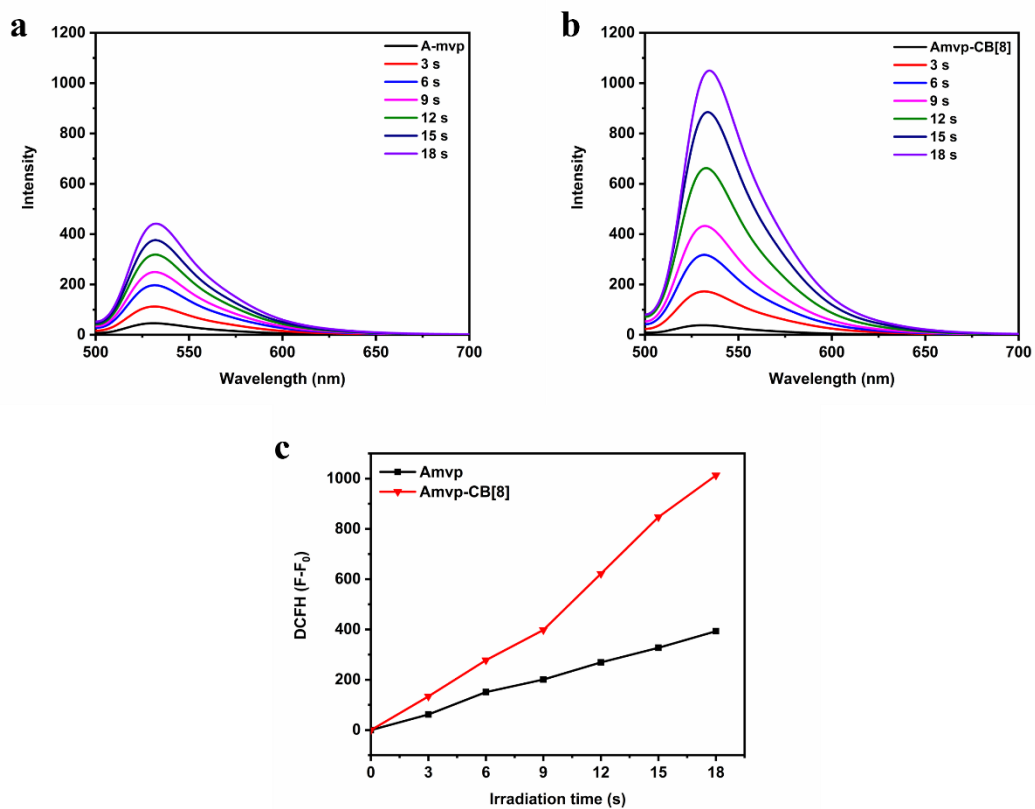


Fig. S7. The fluorescence spectra of DCFH (20 μM) after irradiation (390-400 nm) for different time in the presence of (a) Amvp and (b) Amvp-CB[8]; (c) Plots of $\Delta F(F-F_0)$ of DCFH at fluorescence emission maxima upon light irradiation for different time intervals in the presence of Amvp and Amvp-CB[8]. ($[Amvp]=2.0 \times 10^{-5}$ M, $[Amvp-CB[8]]=2.0 \times 10^{-5}$ M).

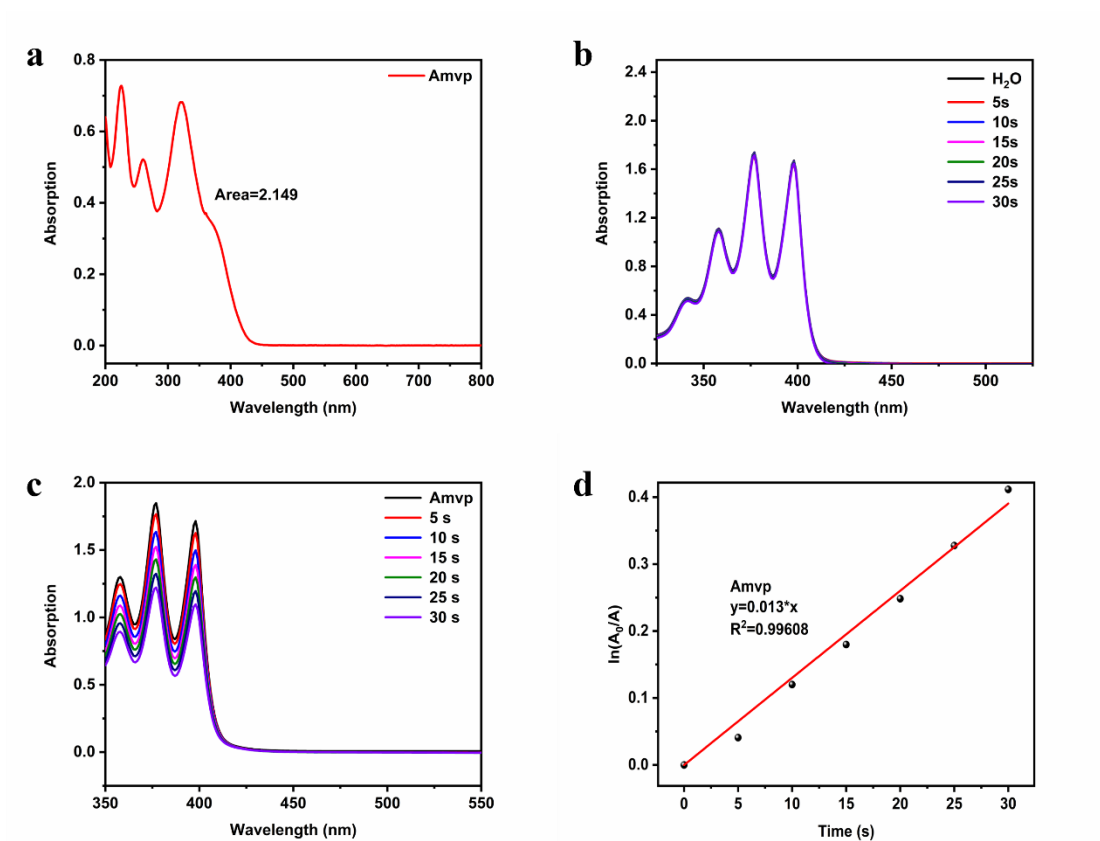


Fig. S8. (a) The UV-vis absorption spectra of Amvp in the aqueous solution; (b) The decomposition rates of ABDA in the presence of H₂O; (c) The absorption spectra of ABDA after irradiation (395 nm, 10 W) for different time in the presence of Amvp; (d) The decomposition rates of ABDA in the presence of Amvp. ($[Amvp]=2.0 \times 10^{-5}$ M).

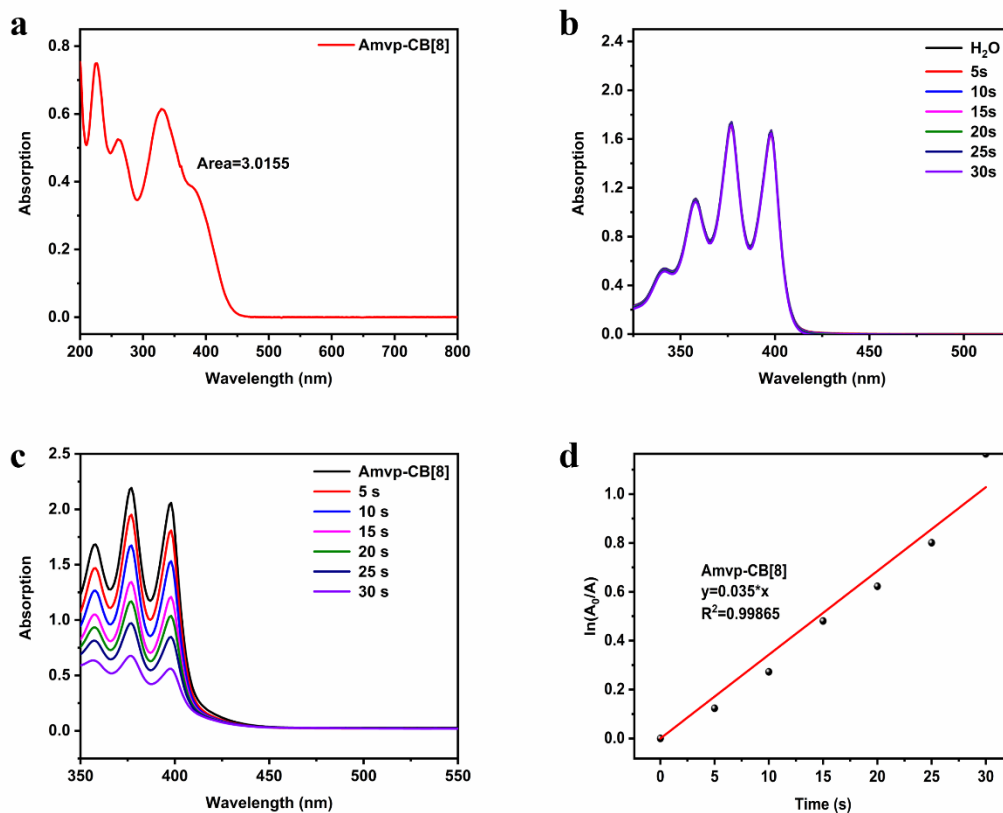


Fig. S9. (a) The UV-vis absorption spectra of Amvp-CB[8] in the aqueous solution; (b) The decomposition rates of ABDA in the presence of H₂O. (c) The absorption spectra of ABDA after irradiation (395 nm, 10 W) for different time in the presence of Amvp-CB[8]; (d) The decomposition rates of ABDA in the presence of Amvp-CB[8]. ([Amvp-CB[8]]=[Amvp-CB[8]]= 2.0×10^{-5} M).

Procedure for $^1\text{O}_2$ Quantum Yield Measurement.

The $^1\text{O}_2$ quantum yield was measured using Rose Bengal (RB) as the reference photosensitizer and calculated using the following S1:

$$\Phi_{probe} = \Phi_{RB} \times (K_{probe} A_{RB} / K_{RB} A_{probe}) \quad (S1)$$

where K_{probe} and K_{RB} are the decomposition rate constants of ABDA in the presence of the probe and RB, respectively. Φ_{RB} is the $^1\text{O}_2$ quantum yield of RB ($\Phi_{RB} = 0.75$ in water). A_{probe} and A_{RB} represent the integration area of absorption bands ranging from 390 to 400 nm of the probe and RB, respectively. The ABDA (5.0×10^{-5} mol) in 3 mL of the probe solution was exposed to purple light irradiation (395 nm) with a power density of 10W. The natural logarithm of the absorbance ratio (A_0/A) of ABDA at 380 nm was plotted against irradiation time and the slope is regarded as the decomposition rate.

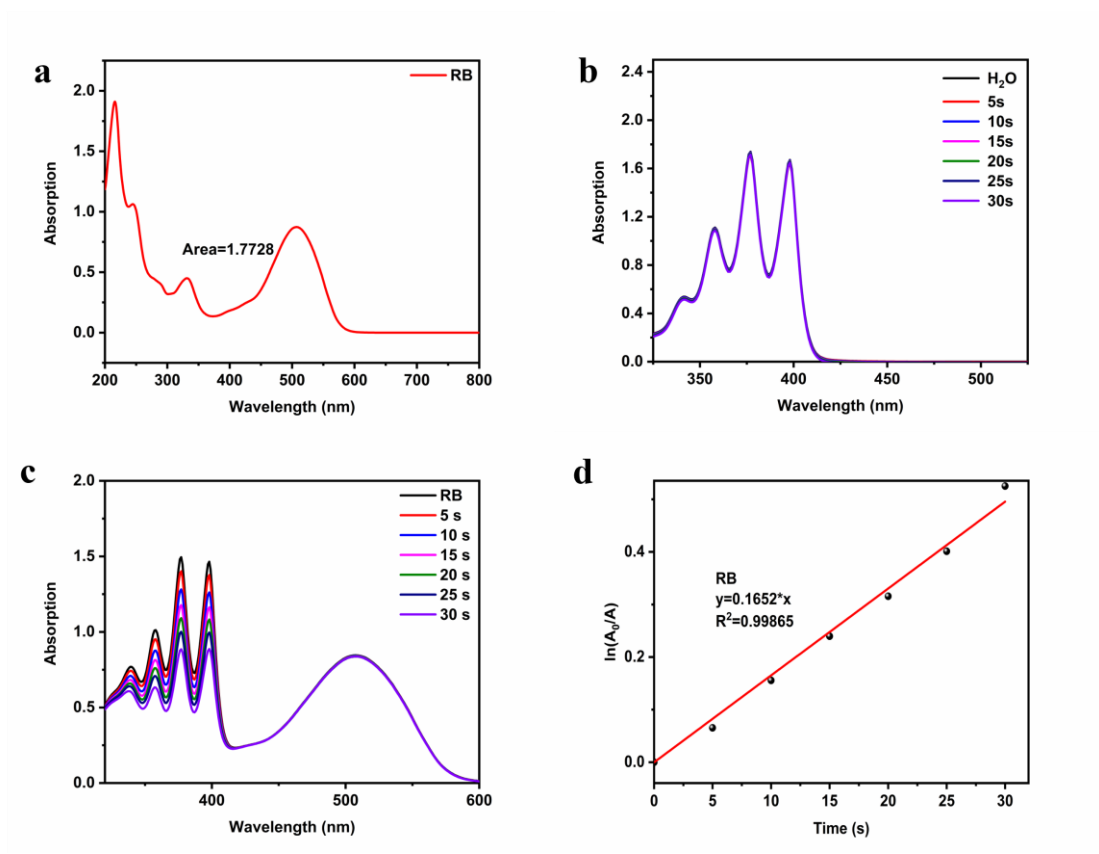


Fig. S10. (a) The UV-vis absorption spectra of RB in the aqueous solution; (b) The decomposition rates of ABDA in the presence of H₂O. (c) The absorption spectra of ABDA after irradiation (395 nm, 10 W) for different time in the presence of RB; (d) The decomposition rates of ABDA in the presence of RB. ($[RB]=2.0 \times 10^{-5}$ M).

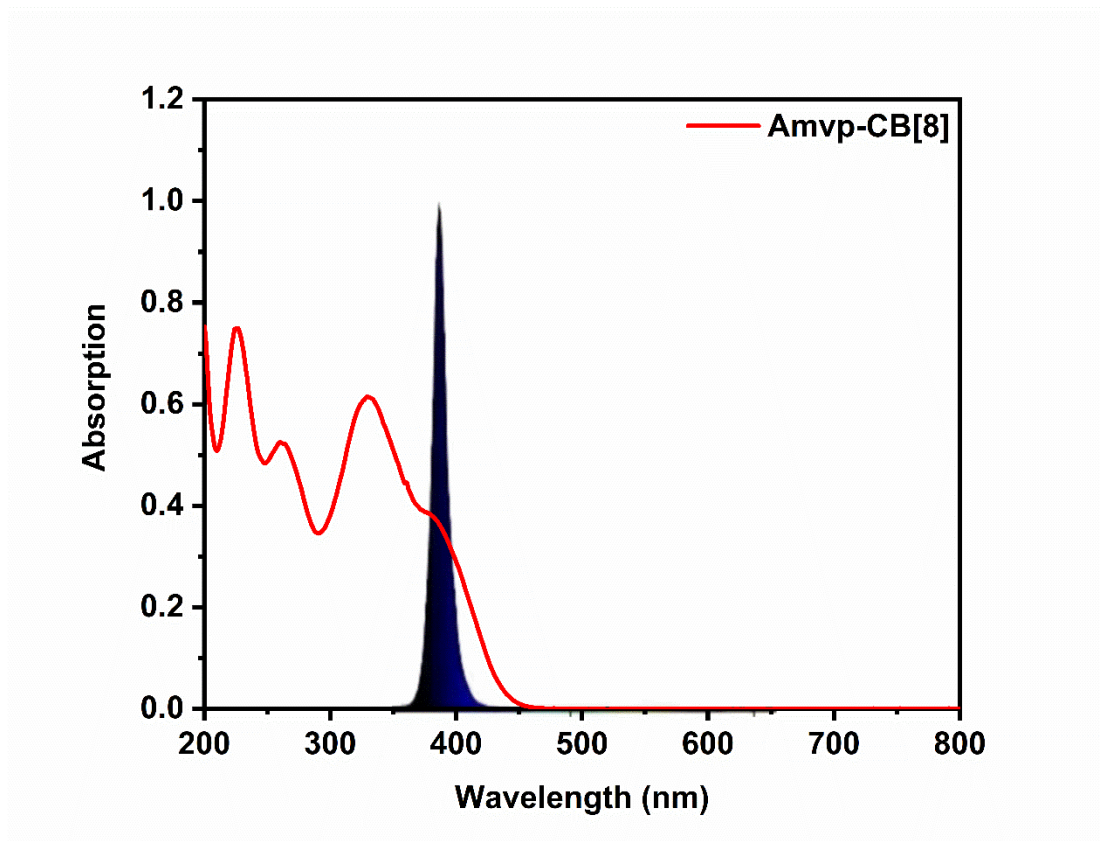


Fig. S11. The UV-vis overlapped absorption spectra of the light source and Amvp-CB[8]. ($[\text{Amvp-CB[8]}]=2.0 \times 10^{-5} \text{ M}$).

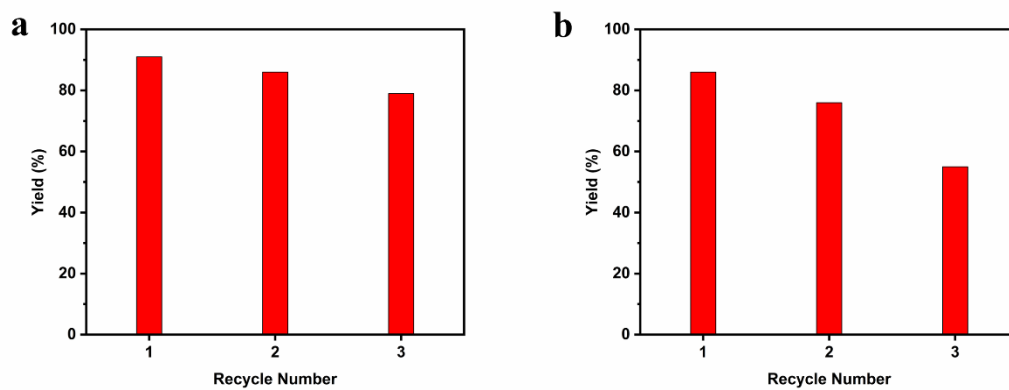


Fig. S12. Photocatalytic activity of Amvp-CB[8] after recycling for photoredox thiol-ene cross-coupling reaction of sulfide (a) and sulfoxide (b).

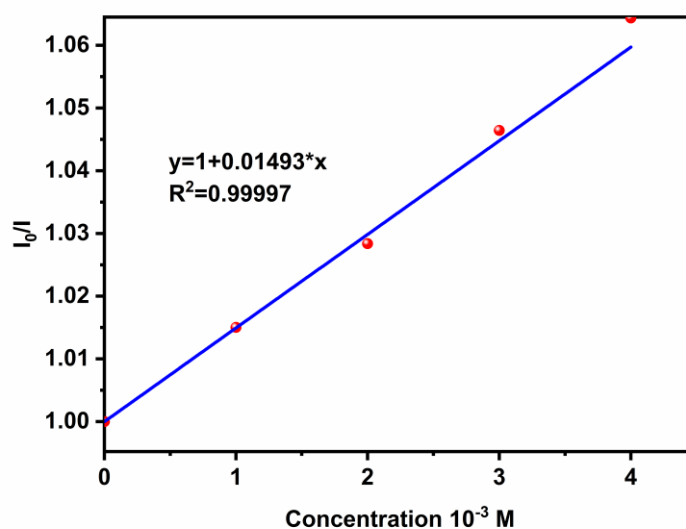


Fig. S13. Stern-Volmer quenching studies of Amvp-CB[8] with styrene Quenching constant, $k_q = 5.05 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for styrene (monitoring emission at $\lambda_{\text{ex}} = 542 \text{ nm}$). ($[\text{Amvp-CB}[8]] = 2.0 \times 10^{-5} \text{ M}$).

According to the Stern-Volmer equations: $I_0/I = 1 + k_{\text{sv}} [Q] = 1 + k_q \tau_0 [Q]$ where τ_0 is the lifetimes of radical anion (1.43 ns), and I_0 and I are the emission intensities in the absence and in the presence of the quencher Q, respectively, k_{sv} is the Stern Volmer constant and k_q is the quenching constant.

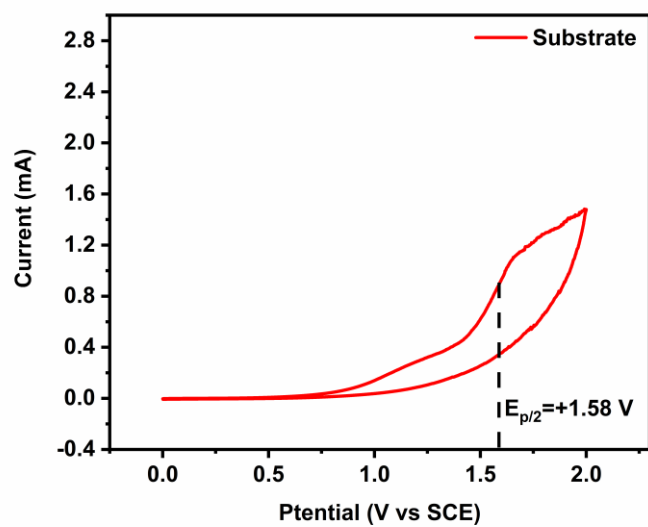
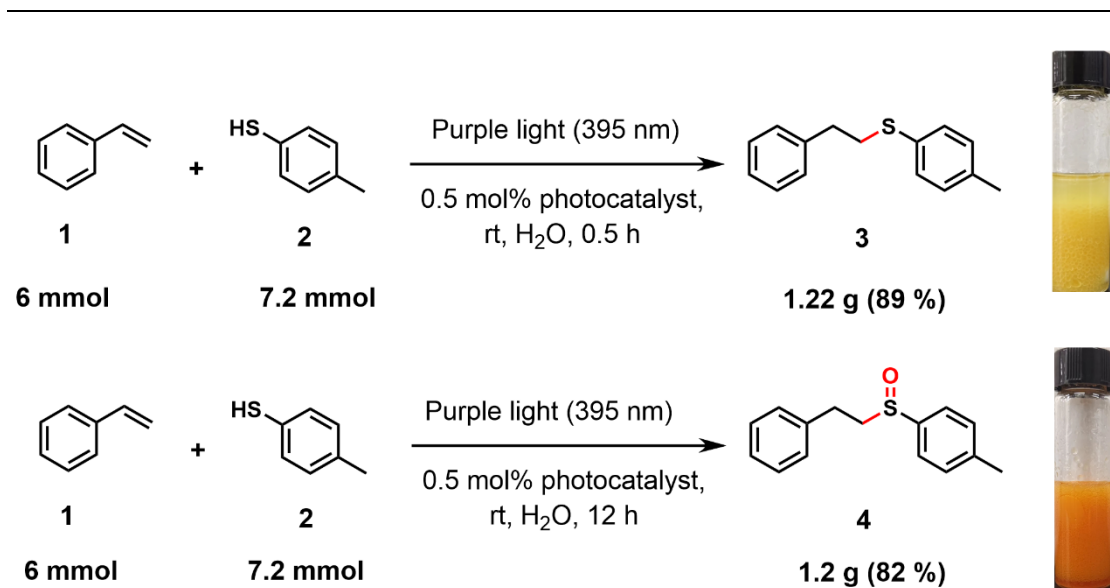


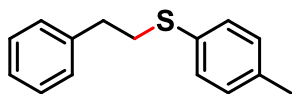
Fig. S14. CV experimental spectrum of 4-methylthiophenol (1.0×10^{-3} M).



Scheme S2. Amplification experiment of the photocatalytic reaction.

^1H NMR and ^{13}C NMR data of 3a-3ab and 4a-4o

3a. phenethyl(p-tolyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give 3a as a colorless oil (41.5 mg, 91% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.31 - 7.25 (m, 4H), 7.23 - 7.19 (m, 1H), 7.19 - 7.15 (m, 2H), 7.10 (d, $J = 7.9$ Hz, 2H), 3.16 - 3.08 (m, 2H), 2.89 (dd, $J = 9.4, 6.4$ Hz, 2H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 140.38, 136.25, 132.50, 130.14, 129.78, 128.57, 128.53, 126.44, 35.86, 35.79, 21.08.

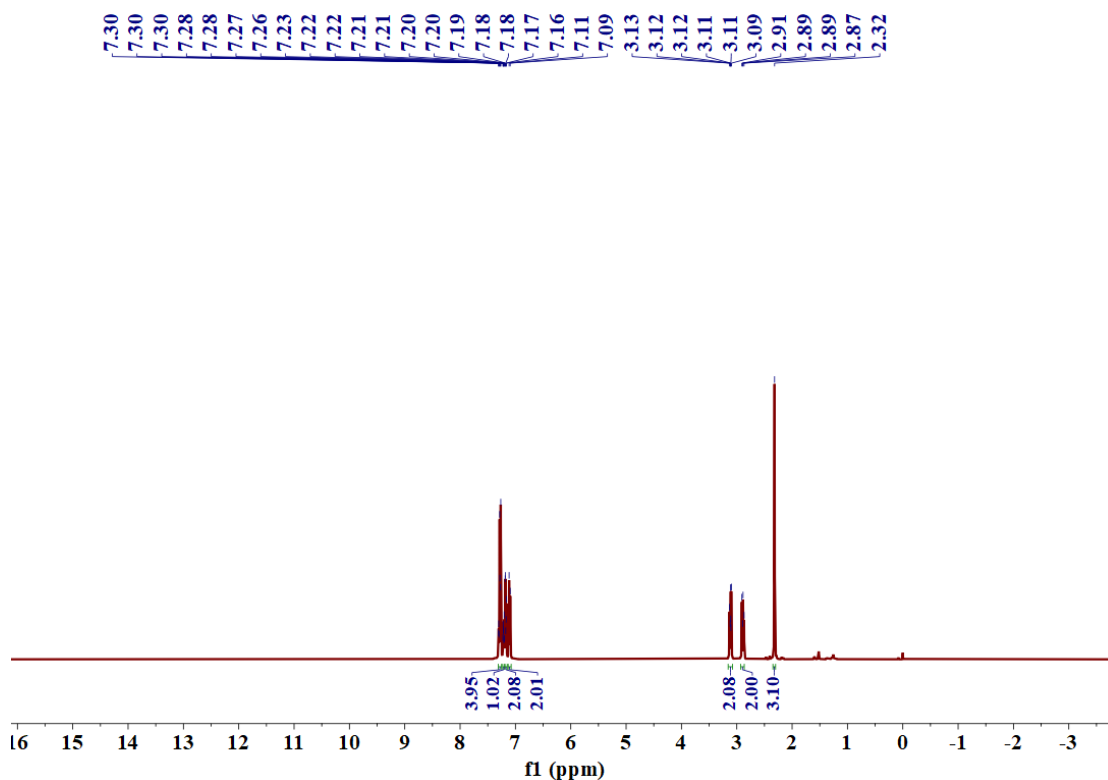


Fig. S15. ^1H NMR spectra of phenethyl(p-tolyl)sulfane in CDCl_3 .

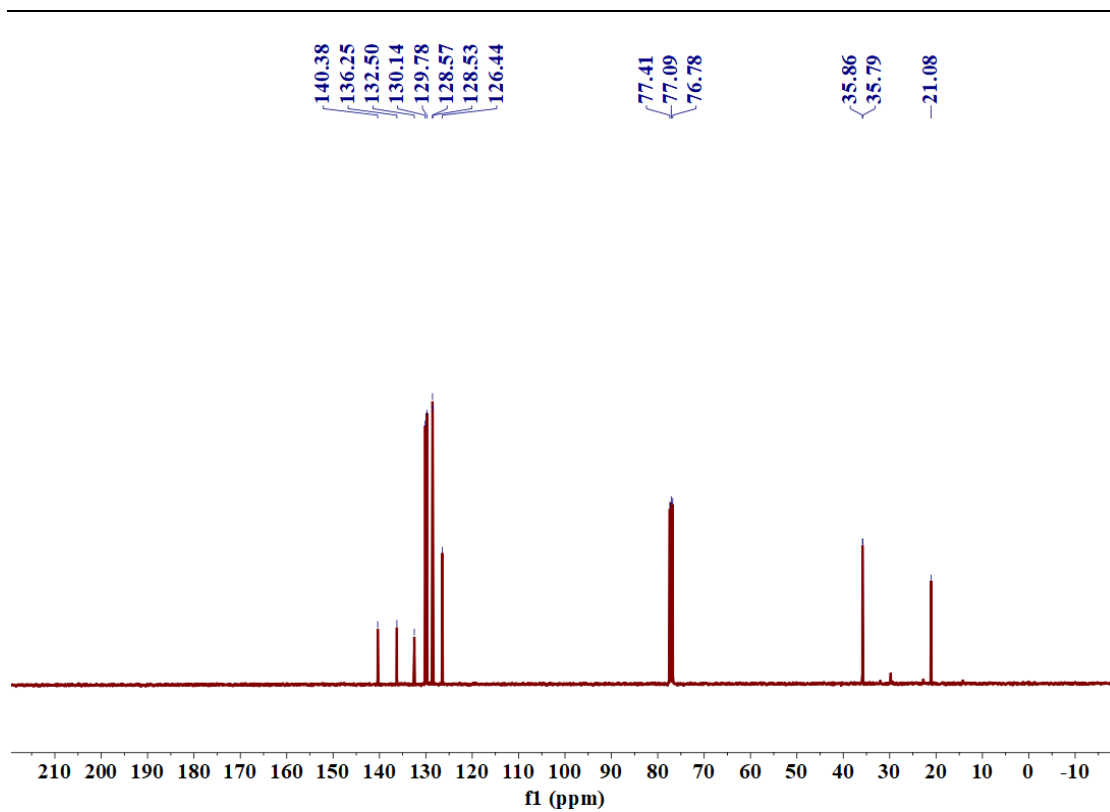
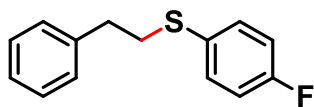


Fig. 16. ^{13}C NMR spectra of phenethyl(p-tolyl)sulfane in CDCl_3 .

3b. (4-fluorophenyl)(phenethyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give 3b as a colorless oil (38.1 mg, 82% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.26 - 7.20 (m, 2H), 7.17 (dd, $J = 8.1, 6.7$ Hz, 2H), 7.13 - 7.07 (m, 1H), 7.07 - 7.02 (m, 2H), 6.87 (t, $J = 8.7$ Hz, 2H), 2.98 (dd, $J = 9.2, 6.4$ Hz, 2H), 2.76 (dd, $J = 9.3, 6.5$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 163.06, 160.61, 140.14, 132.43, 132.35, 131.26, 131.23, 128.62, 128.60, 126.58, 116.24, 116.02, 36.52, 35.79.

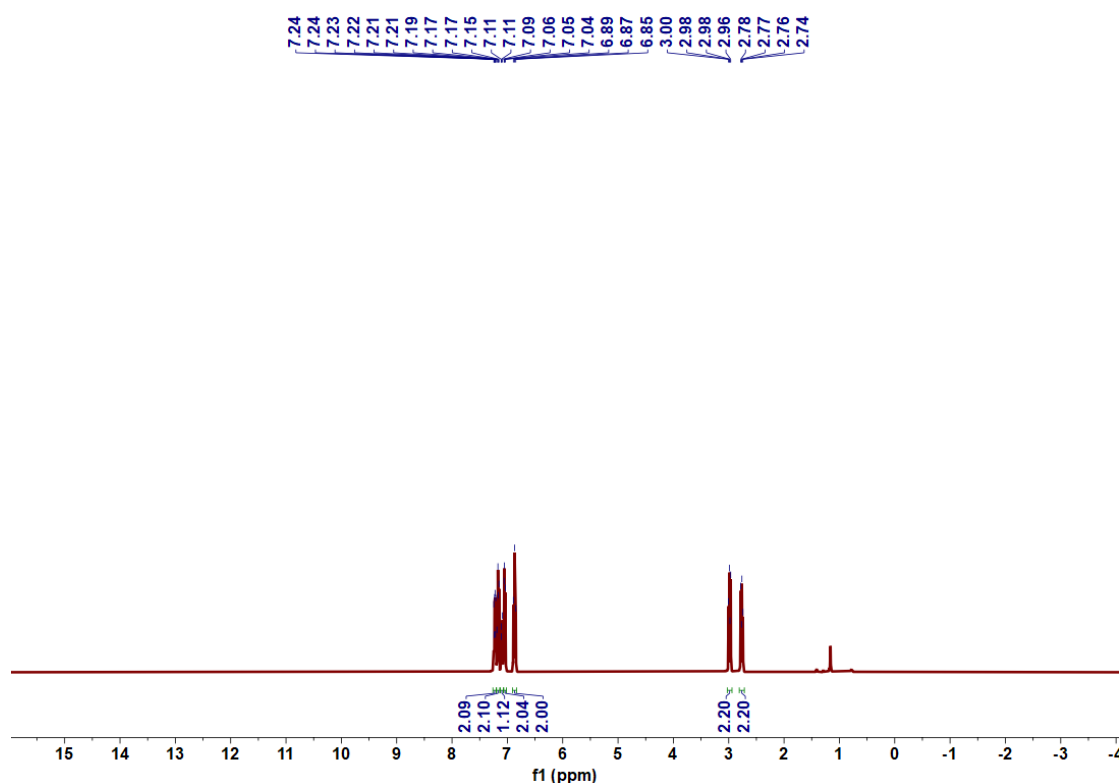


Fig. S17. ^1H NMR spectra of (4-fluorophenyl)(phenethyl)sulfane in CDCl_3 .

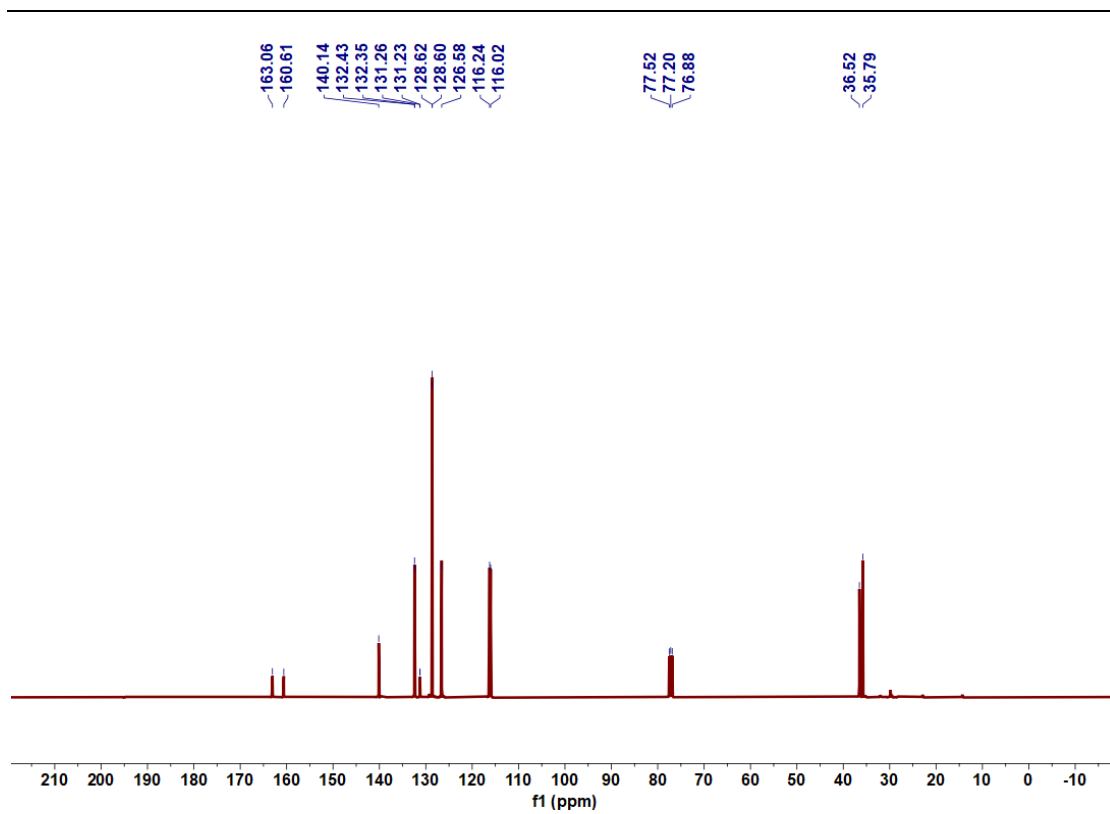
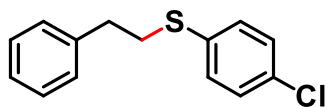


Fig. S18. ^{13}C NMR spectra of (4-fluorophenyl)(phenethyl)sulfane in CDCl_3 .

3c. (4-chlorophenyl)(phenethyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give **3c** as yellow oil (41.2 mg, 83% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.37 - 7.21 (m, 7H), 7.21 - 7.15 (m, 2H), 3.13 (dd, $J = 9.1, 6.6$ Hz, 2H), 2.90 (dd, $J = 9.2, 6.5$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 139.96, 134.93, 131.99, 130.58, 129.09, 128.60, 128.54, 126.60, 35.54, 35.40.

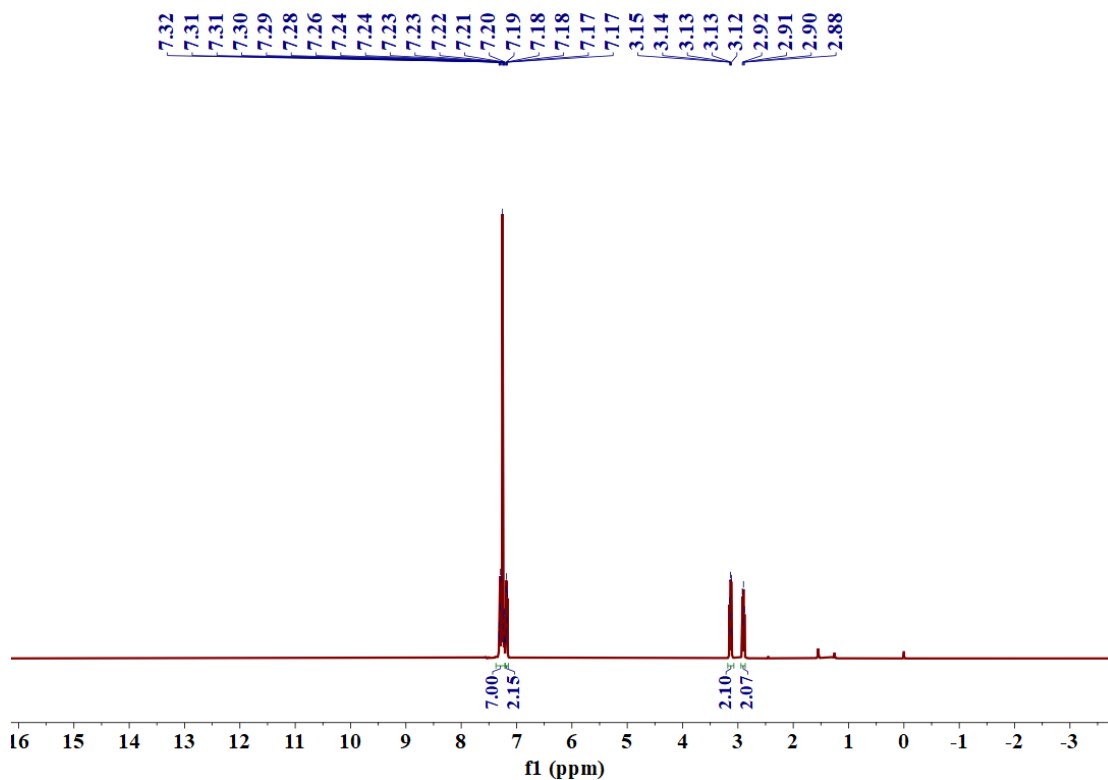


Fig. S19. ^1H NMR spectra of (4-chlorophenyl)(phenethyl)sulfane in CDCl_3 .

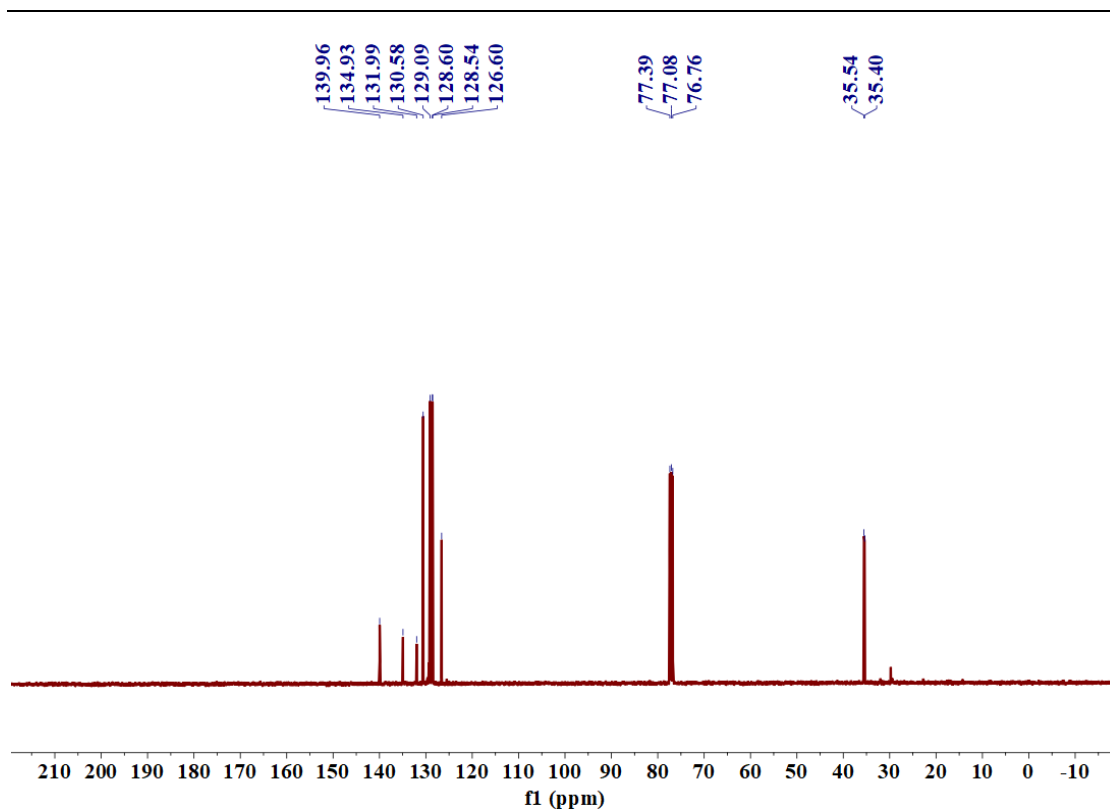
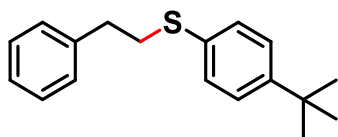


Fig. S20. ^{13}C NMR spectra of (4-chlorophenyl)(phenethyl)sulfane in CDCl_3 .

3d. (4-(tert-butyl)phenyl)(phenethyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give 3d as a colorless oil (50.2 mg, 93% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.35 - 7.27 (m, 6H), 7.25 - 7.16 (m, 3H), 3.18 - 3.12 (m, 2H), 2.92 (dd, $J = 9.4, 6.4$ Hz, 2H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 149.36, 140.37, 132.66, 129.47, 128.54, 128.51, 126.43, 126.02, 35.82, 35.51, 34.49, 31.31.

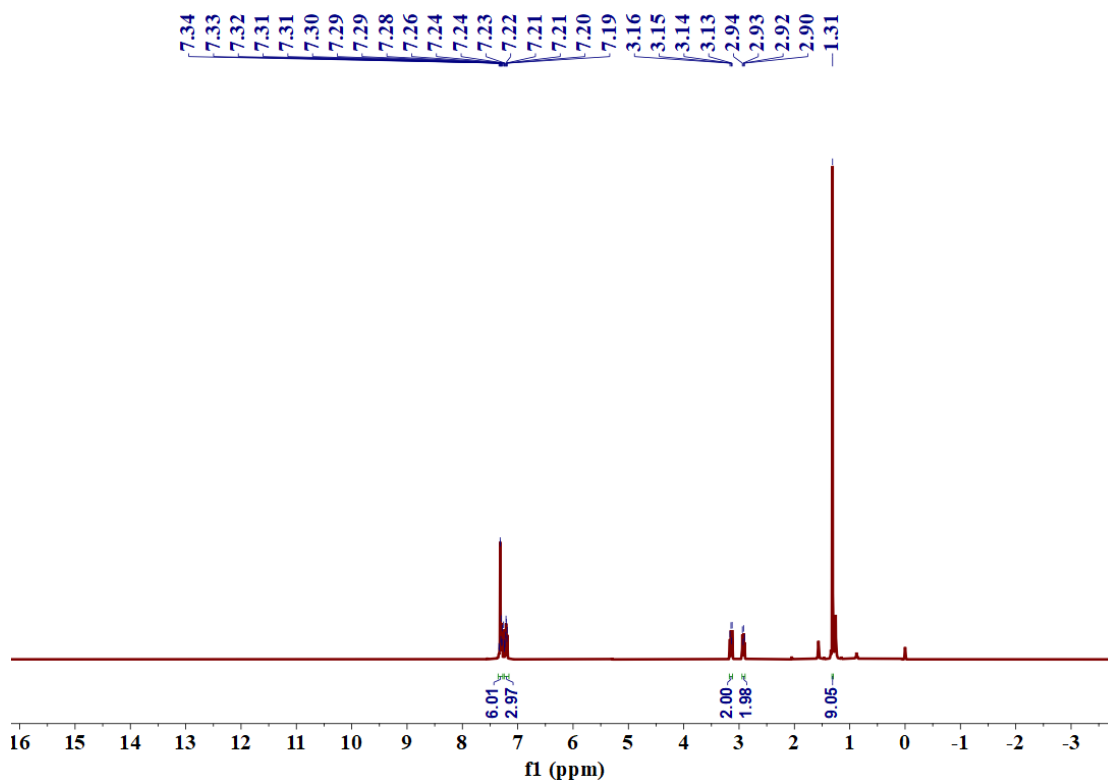


Fig. S21. ^1H NMR spectra of (4-(tert-butyl)phenyl)(phenethyl)sulfane in CDCl_3 .

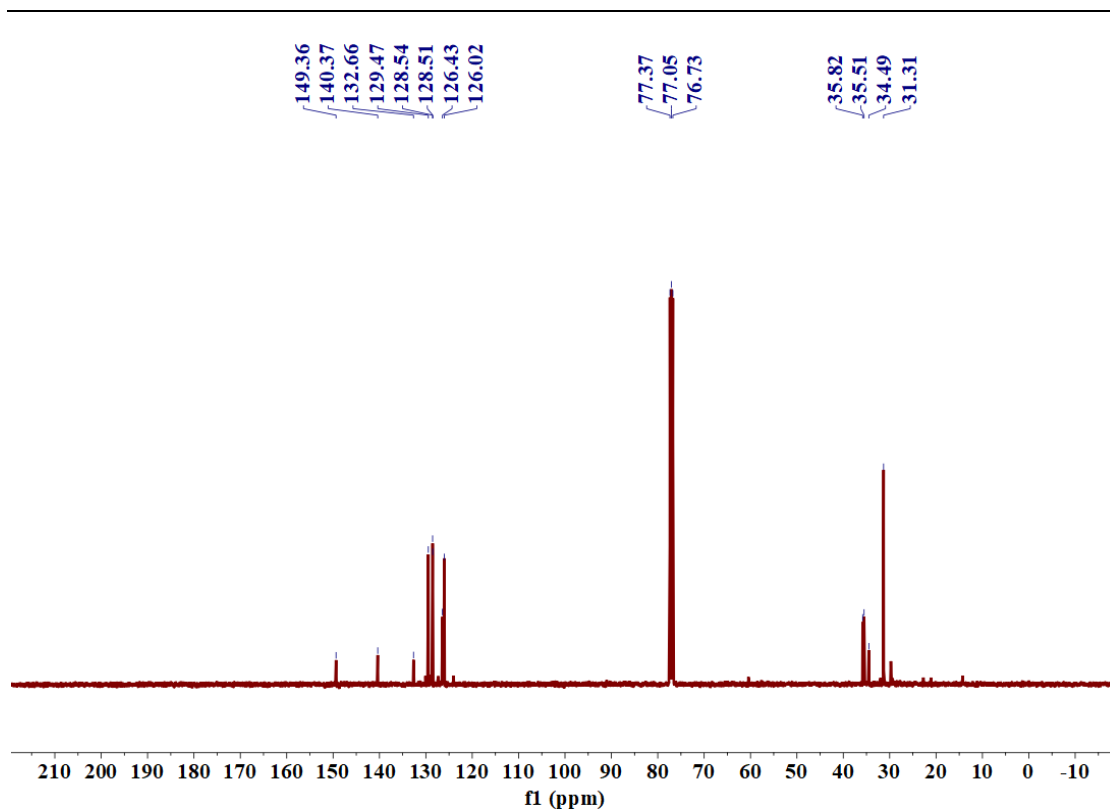
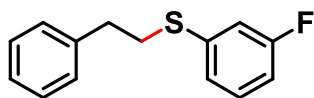


Fig. S22. ^{13}C NMR spectra of (4-(tert-butyl)phenyl)(phenethyl)sulfane in CDCl_3 .

3e. (3-fluorophenyl)(phenethyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give 3e as a colorless oil (36.2 mg, 78% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.30 (dd, $J = 8.0, 6.6$ Hz, 2H), 7.26 - 7.17 (m, 4H), 7.08 (m, 1H), 7.02 (m, 1H), 6.89 - 6.82 (m, 1H), 3.17 (dd, $J = 8.9, 6.7$ Hz, 2H), 2.93 (dd, $J = 9.2, 6.5$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 164.19, 161.73, 139.93, 139.14, 139.06, 130.25, 130.17, 128.63, 128.56, 126.65, 124.10, 124.07, 115.34, 115.11, 112.83, 112.62, 35.43, 34.67.

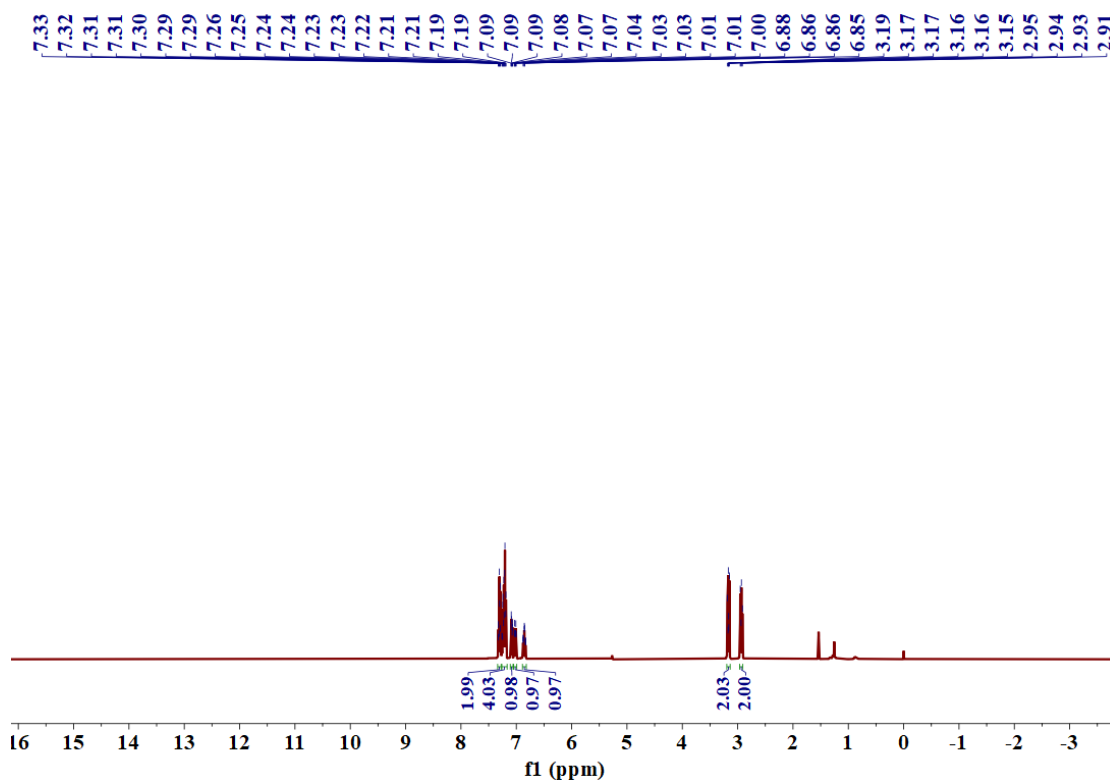


Fig. S23. ^1H NMR spectra of (3-fluorophenyl)(phenethyl)sulfane in CDCl_3 .

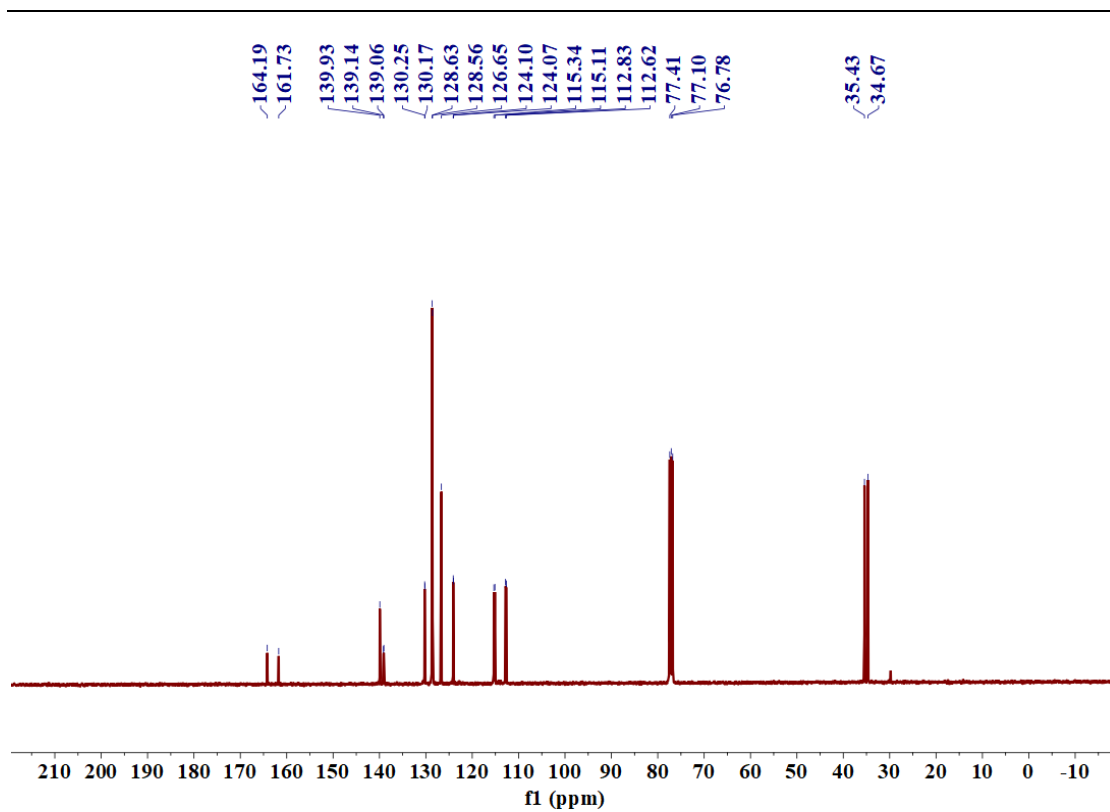
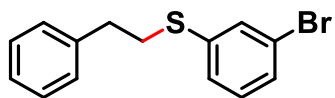


Fig. S24. ^{13}C NMR spectra of (3-fluorophenyl)(phenethyl)sulfane in CDCl_3 .

3f. (3-bromophenyl)(phenethyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give 3f as a colorless oil (44.5 mg, 76% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.46 - 7.43 (m, 1H), 7.33 - 7.26 (m, 3H), 7.25 - 7.17 (m, 4H), 7.13 (t, $J = 7.9$ Hz, 1H), 3.16 (dd, $J = 9.1, 6.5$ Hz, 2H), 2.92 (dd, $J = 9.2, 6.5$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 139.87, 139.09, 131.09, 130.24, 128.86, 128.64, 128.57, 127.23, 126.67, 122.91, 35.43, 34.85.

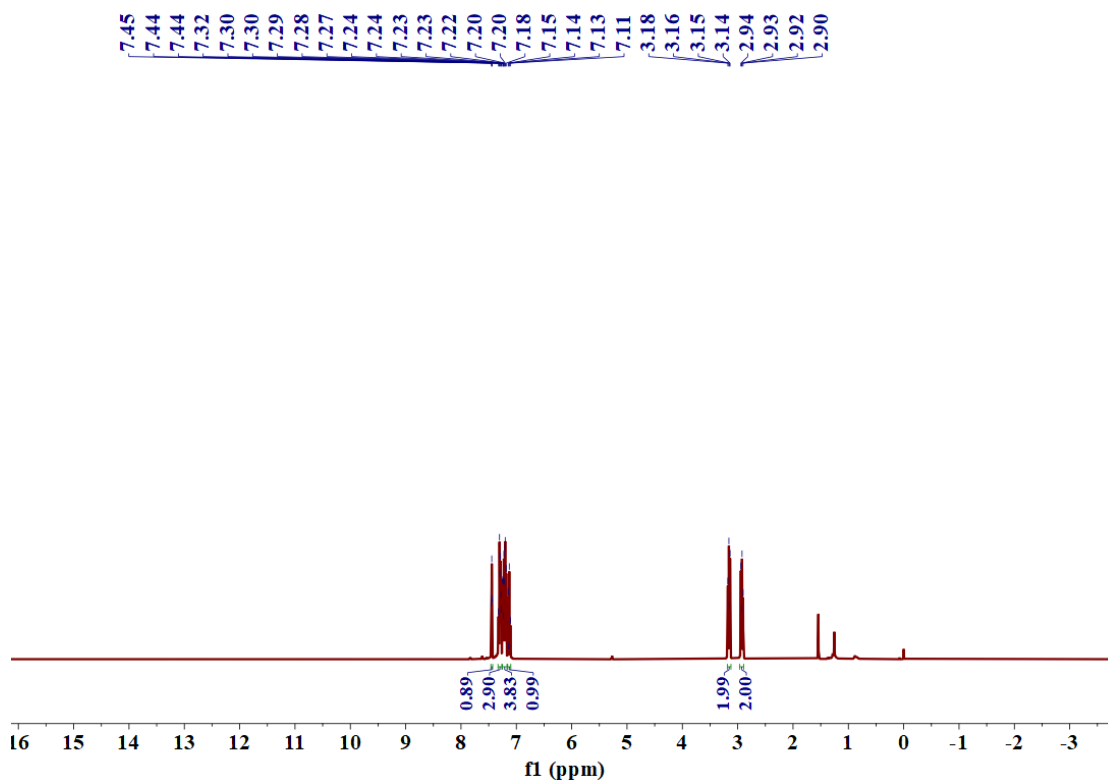


Fig. S25. ^1H NMR spectra of (3-bromophenyl)(phenethyl)sulfane in CDCl_3 .

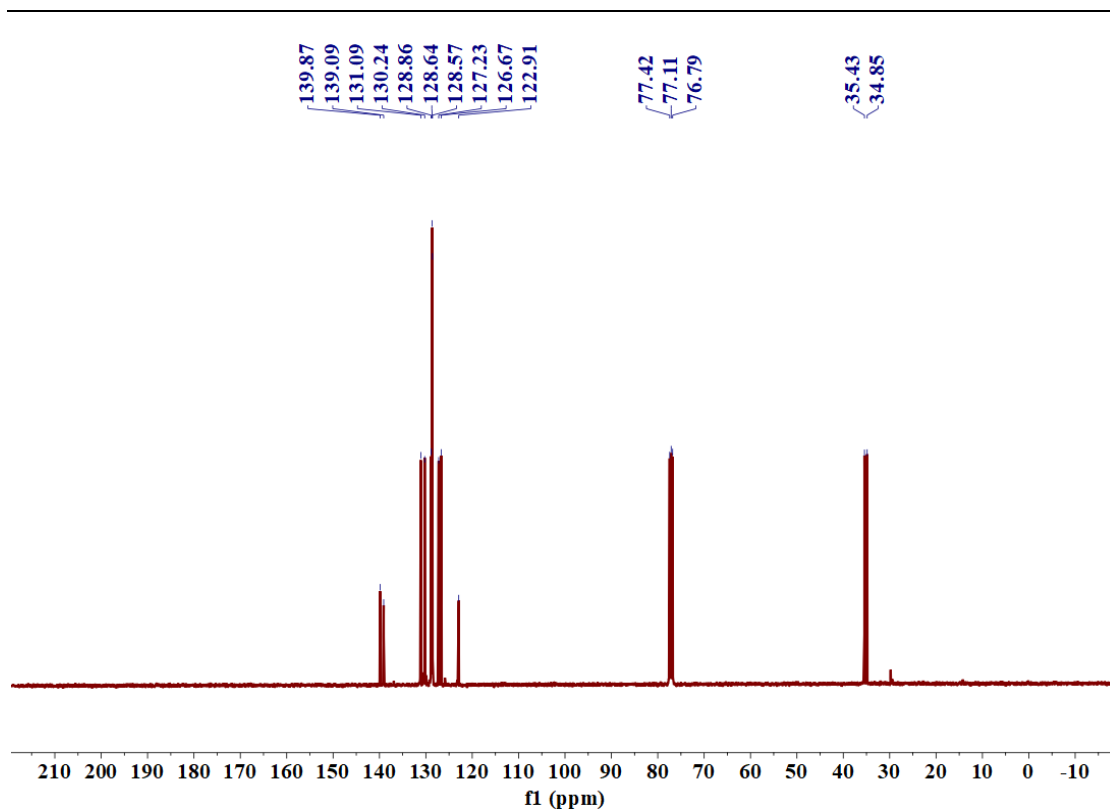
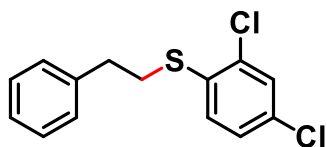


Fig. S26. ^{13}C NMR spectra of (3-bromophenyl)(phenethyl)sulfane in CDCl_3 .

3g. (2,4-dichlorophenyl)(phenethyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give **3g** as a yellow oil (41.9 mg, 74% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.37 (d, $J = 2.2$ Hz, 1H), 7.34 - 7.27 (m, 3H), 7.26 - 7.22 (m, 1H), 7.19 (tt, $J = 5.7, 1.4$ Hz, 2H), 7.12 (dd, $J = 8.4, 2.2$ Hz, 1H), 3.15 (dd, $J = 8.8, 6.7$ Hz, 2H), 2.92 (dd, $J = 9.0, 6.6$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 139.66, 137.01, 132.93, 130.58, 130.11, 129.87, 128.66, 128.56, 128.06, 126.73, 35.39, 35.11.

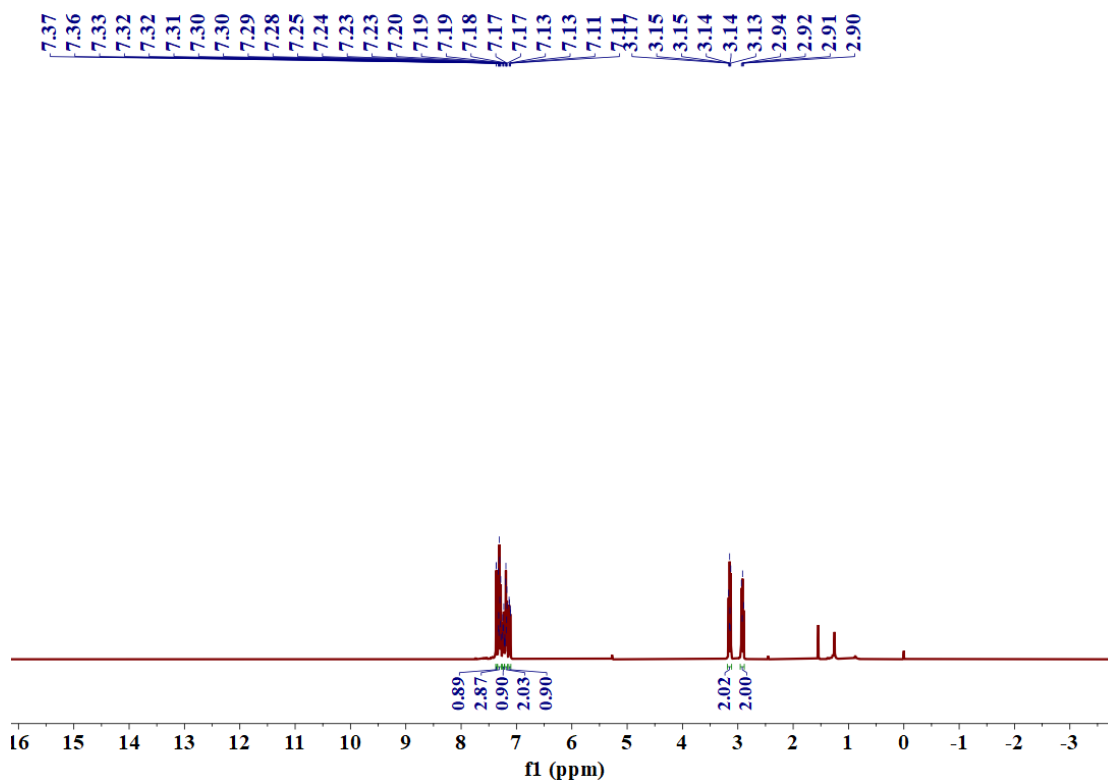


Fig. S27. ^1H NMR spectra of (2,4-dichlorophenyl)(phenethyl)sulfane in CDCl_3 .

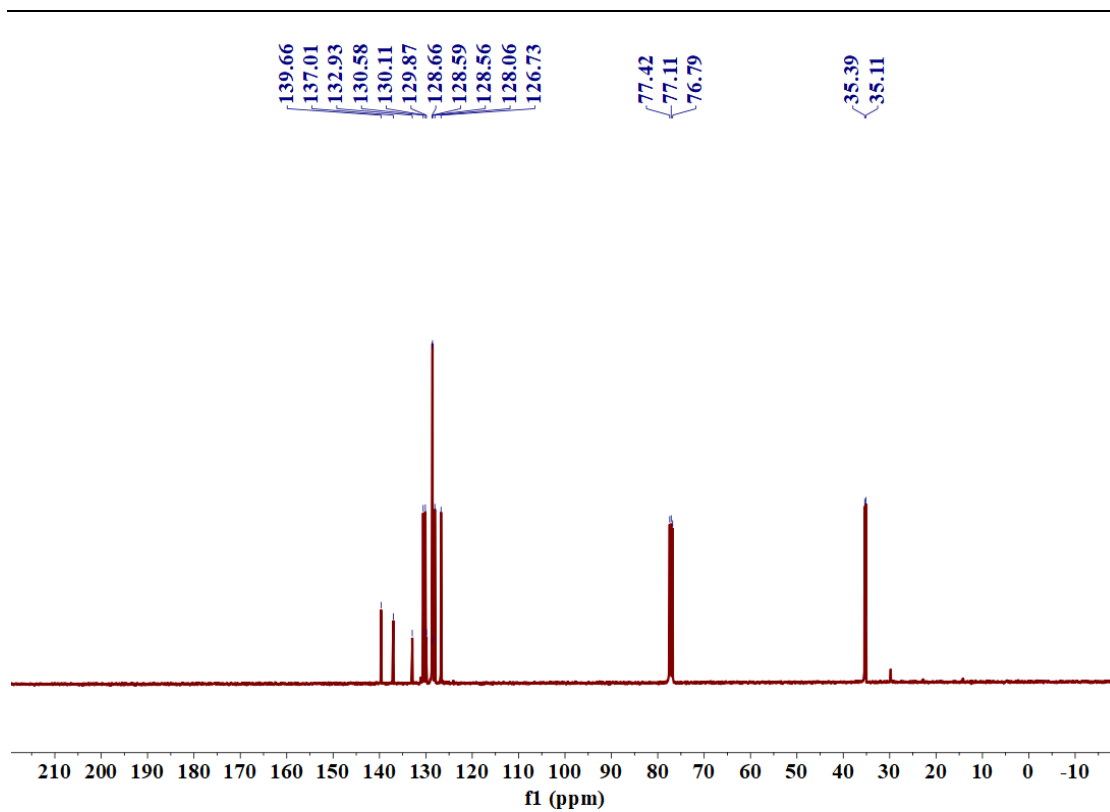
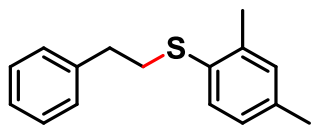


Fig. S28. ^{13}C NMR spectra of (2,4-dichlorophenyl)(phenethyl)sulfane in CDCl_3

3h. (2,4-dimethylphenyl)(phenethyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give 3h as a colorless oil (42.1 mg, 87% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.29 (dd, $J = 8.0, 6.6$ Hz, 2H), 7.25 - 7.16 (m, 4H), 7.01 (d, $J = 2.0$ Hz, 1H), 6.98 (dd, $J = 7.8, 2.0$ Hz, 1H), 3.12 - 3.06 (m, 2H), 2.90 (dd, $J = 9.4, 6.5$ Hz, 2H), 2.35 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 140.48, 138.21, 135.97, 131.82, 131.19, 129.28, 128.54, 127.22, 126.44, 35.68, 35.02, 20.95, 20.48.

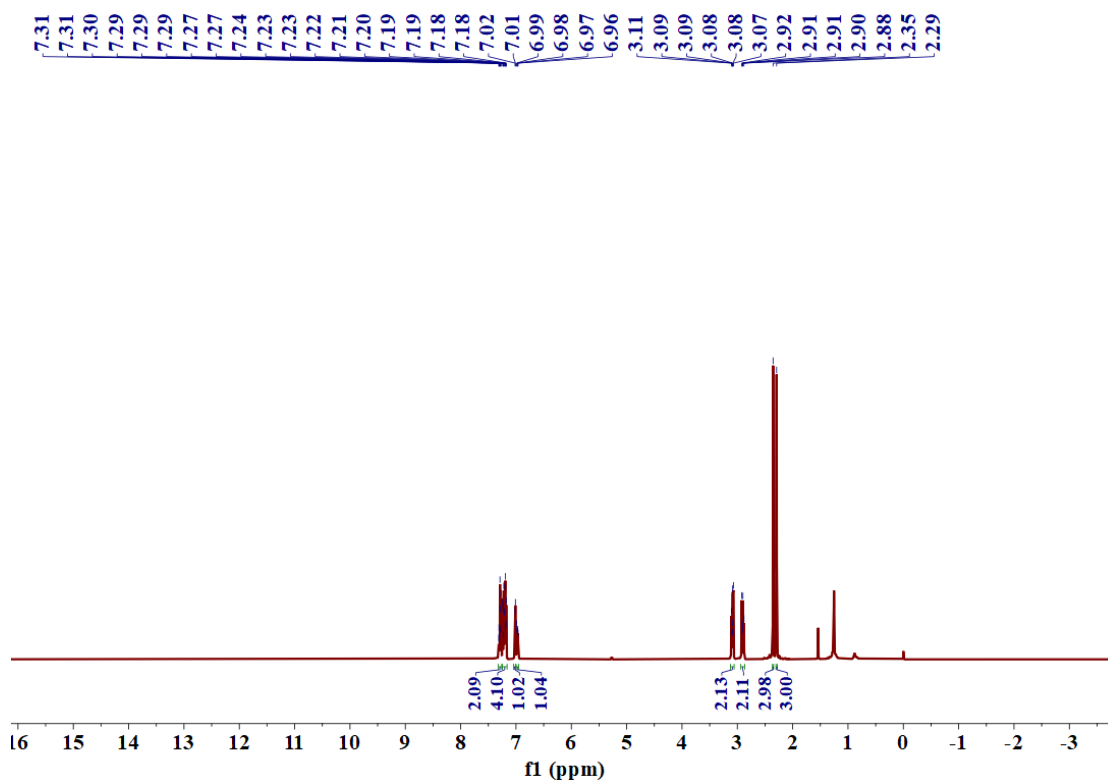


Fig. S29. ^1H NMR spectra of (2,4-dimethylphenyl)(phenethyl)sulfane in CDCl_3

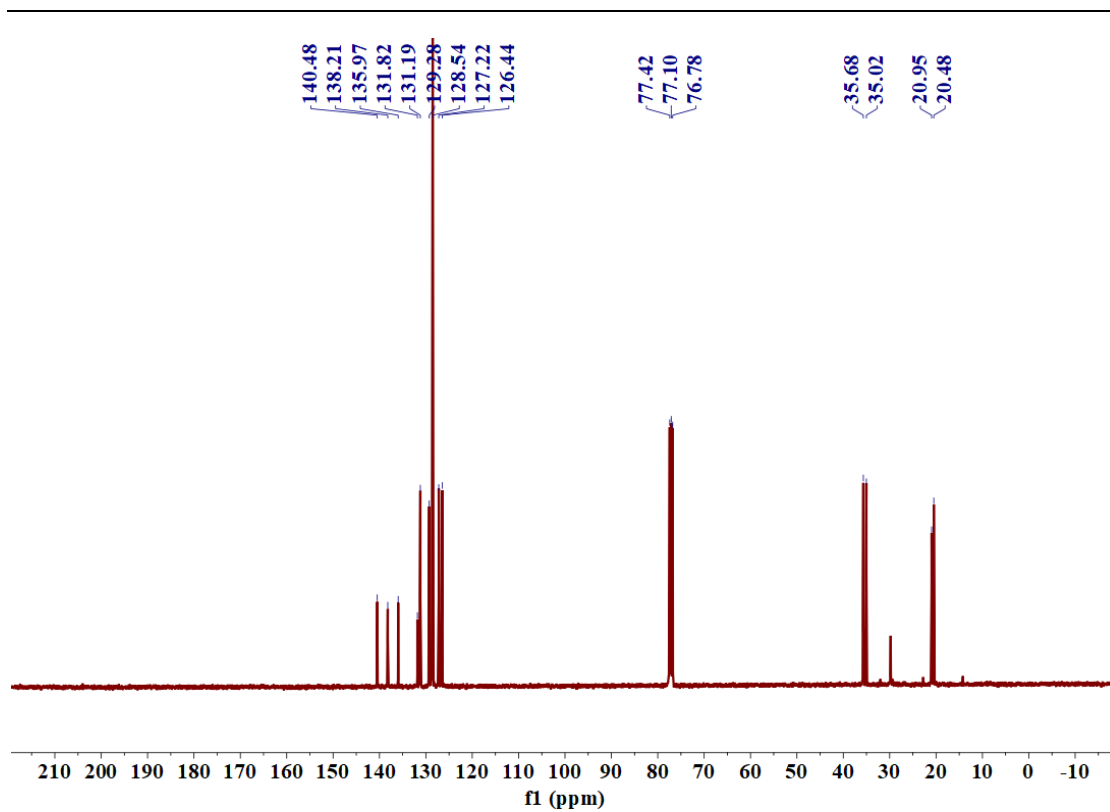
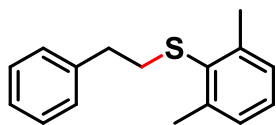


Fig. S30. ^{13}C NMR spectra of (2,4-dimethylphenyl)(phenethyl)sulfane in CDCl_3

3i. (2,6-dimethylphenyl)(phenethyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give 3i as a colorless oil (38.7 mg, 80% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.26 (t, $J = 7.4$ Hz, 2H), 7.19 (q, $J = 7.4, 6.8$ Hz, 1H), 7.15 - 7.06 (m, 5H), 2.92 - 2.86 (m, 2H), 2.84 - 2.78 (m, 2H), 2.52 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 143.11, 140.56, 133.50, 128.48, 128.44, 128.21, 128.14, 126.34, 36.51, 36.41, 22.19.

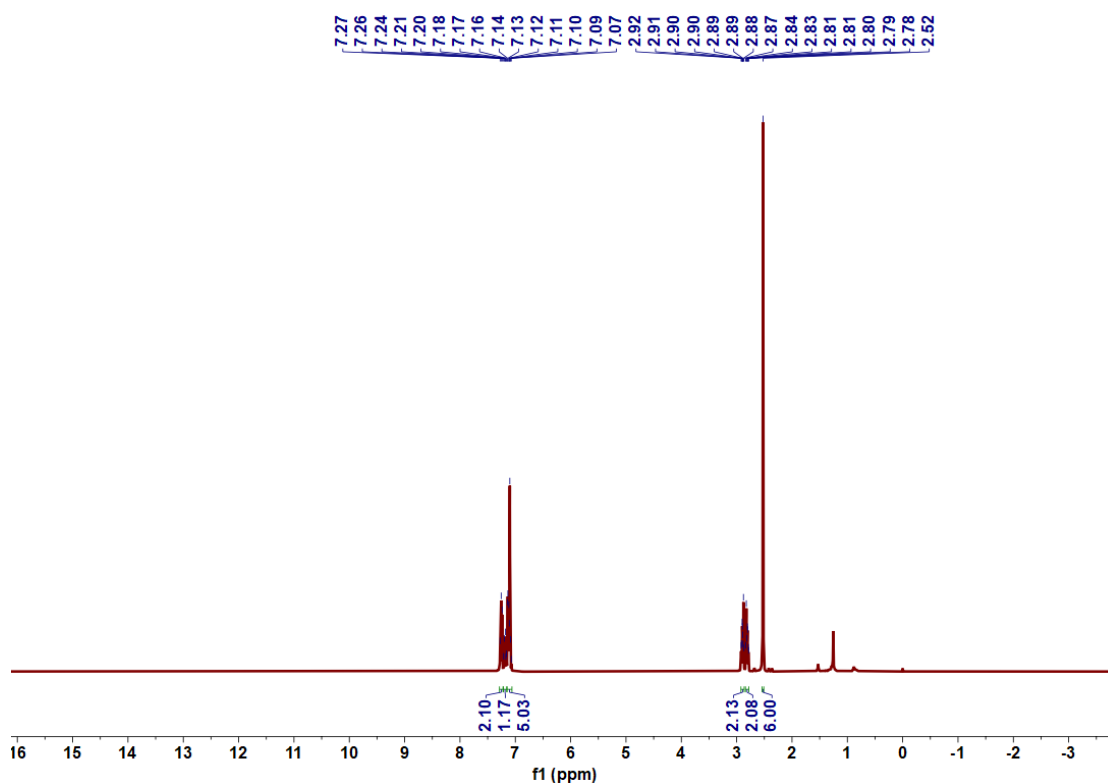


Fig. S31. ^1H NMR spectra of (2,6-dimethylphenyl)(phenethyl)sulfane in CDCl_3 .

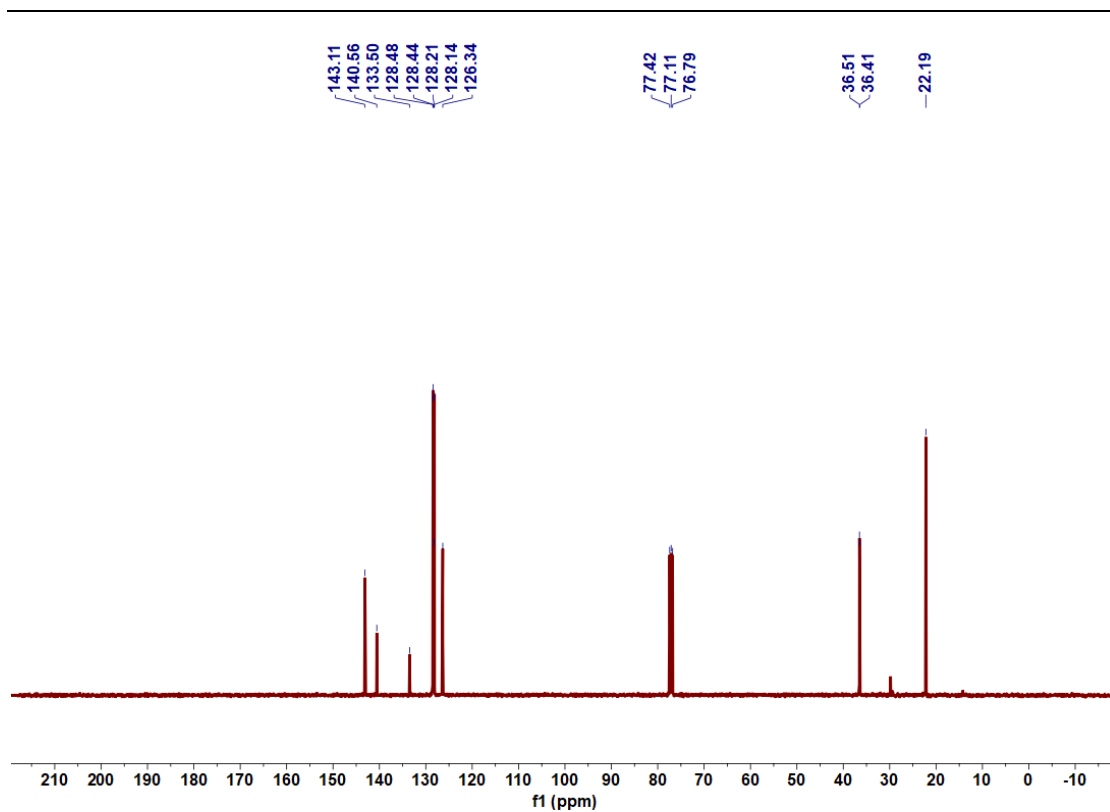
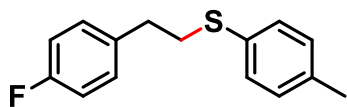


Fig. S32. ^{13}C NMR spectra of (2,6-dimethylphenyl)(phenethyl)sulfane in CDCl_3

3j. (4-fluorophenethyl)(p-tolyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give 3j as a colorless oil (42.3 mg, 86% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.26 (m, 2H), 7.11 (dd, $J = 8.4, 3.6$ Hz, 5H), 6.97 (m, 2H), 3.13 - 3.05 (m, 2H), 2.86 (m, 2H), 2.32 (d, $J = 3.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 162.79, 160.36, 136.38, 135.95, 135.92, 132.25, 131.27, 130.60, 130.26, 130.03, 130.00, 129.93, 129.77, 128.22, 115.36, 115.14, 36.02, 34.89, 21.04.

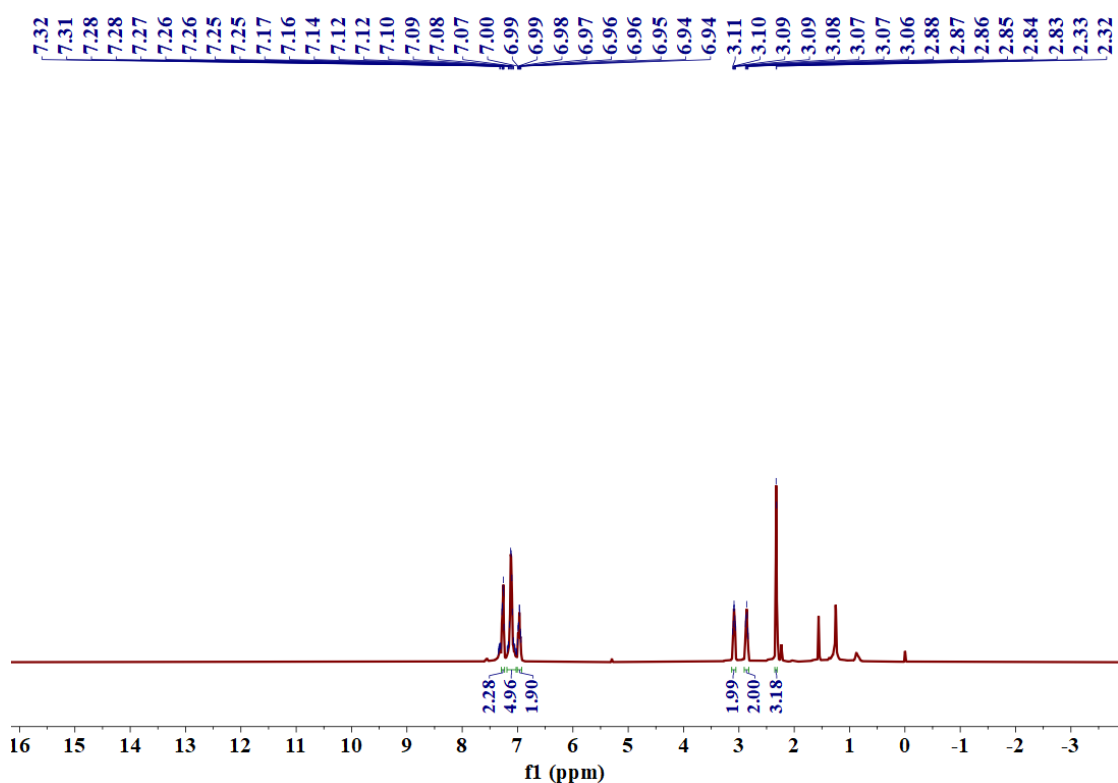


Fig. S33. ^1H NMR spectra of (4-fluorophenethyl)(p-tolyl)sulfane in CDCl_3 .

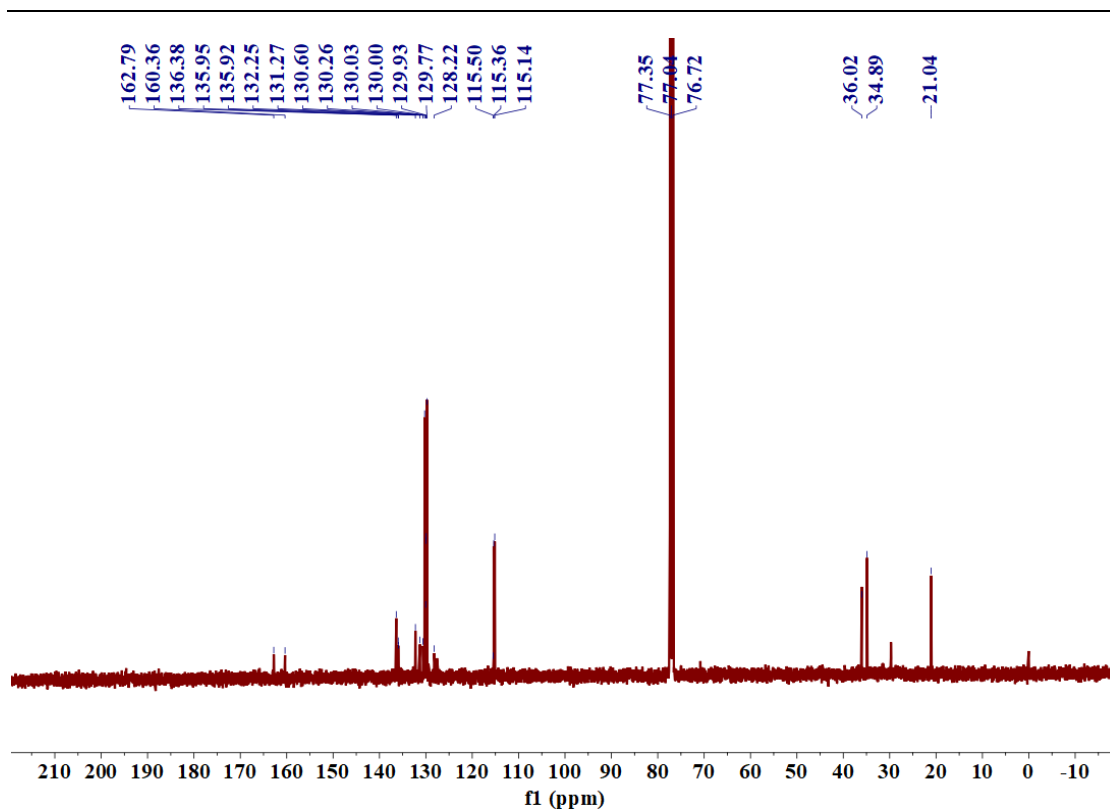
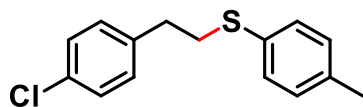


Fig. S34. ^{13}C NMR spectra of (4-fluorophenethyl)(p-tolyl)sulfane in CDCl_3

3k. (4-chlorophenethyl)(p-tolyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give 3k as a colorless oil (46.1 mg, 88% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.30 - 7.23 (m, 4H), 7.14 - 7.07 (m, 4H), 3.09 (dd, J = 8.8, 6.7 Hz, 2H), 2.86 (dd, J = 9.0, 6.5 Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 138.70, 136.46, 132.18, 132.12, 130.34, 129.93, 129.80, 128.59, 35.81, 35.03, 21.06.

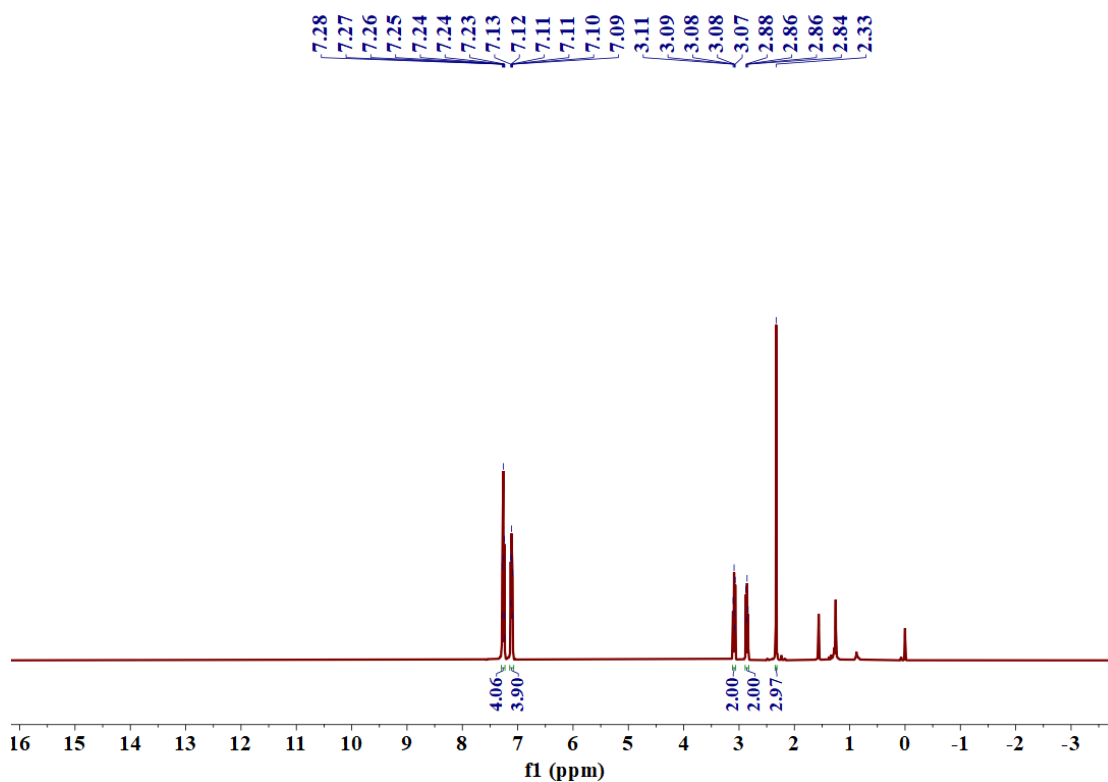


Fig. S35. ^1H NMR spectra of (4-chlorophenethyl)(p-tolyl)sulfane in CDCl_3 .

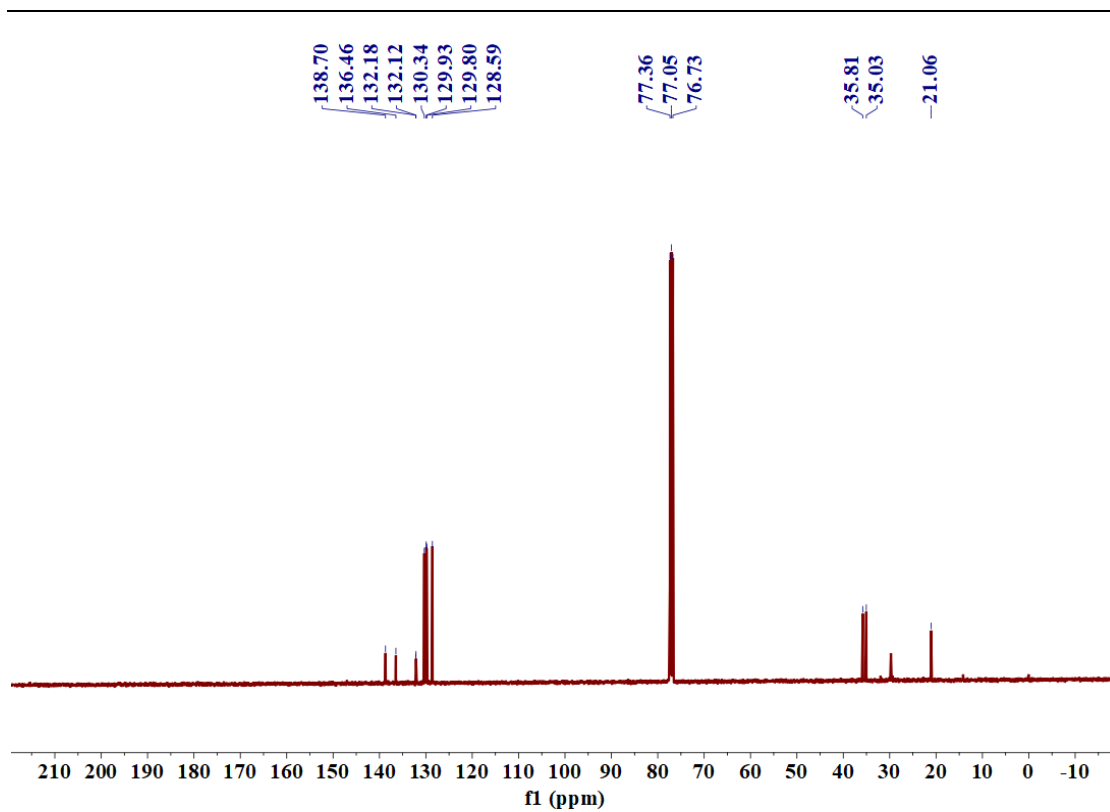
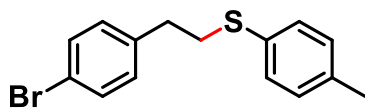


Fig. S36. ^{13}C NMR spectra of (4-chlorophenethyl)(p-tolyl)sulfane in CDCl_3

31. (4-bromophenethyl)(p-tolyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give 31 as a colorless oil (51.5 mg, 84% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.40 (d, $J = 8.1$ Hz, 2H), 7.27 (d, $J = 8.1$ Hz, 2H), 7.13 - 7.10 (m, 2H), 7.06 (t, $J = 8.0$ Hz, 3H), 3.09 (dd, $J = 8.9, 6.6$ Hz, 2H), 2.84 (dd, $J = 9.0, 6.5$ Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 139.21, 136.48, 133.91, 132.08, 131.54, 130.35, 129.81, 128.20, 127.75, 124.05, 120.23, 35.73, 35.09, 21.08.

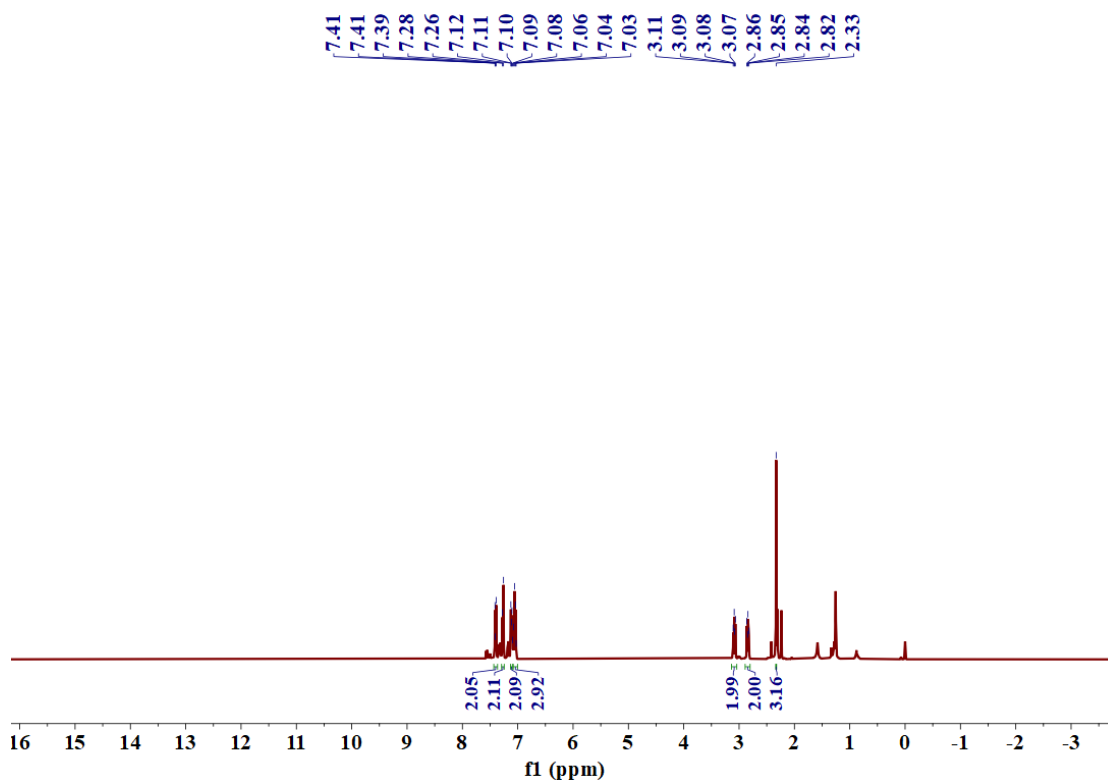


Fig. S37. ^1H NMR spectra of (4-bromophenethyl)(p-tolyl)sulfane in CDCl_3 .

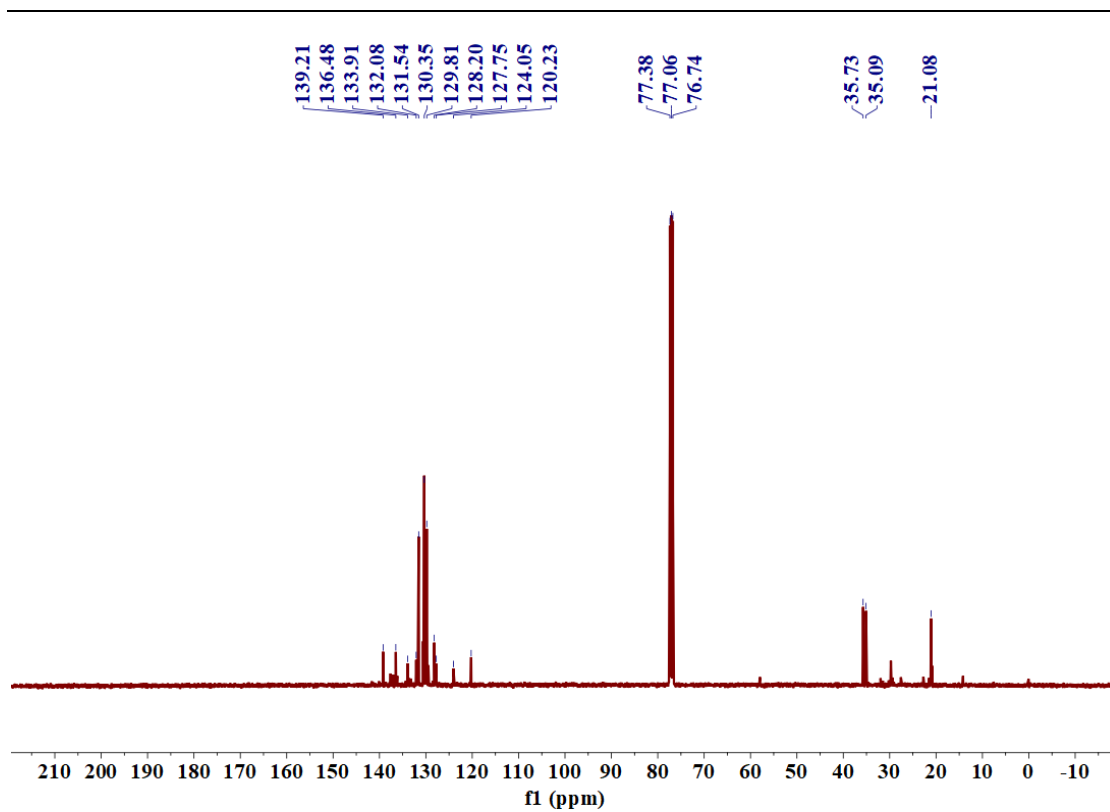
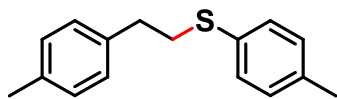


Fig. S38. ^{13}C NMR spectra of (4-bromophenethyl)(p-tolyl)sulfane in CDCl_3

3m. (4-methylphenethyl)(p-tolyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give **3m** as a colorless oil (45.5 mg, 94% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.30 - 7.24 (m, 2H), 7.15 - 7.05 (m, 6H), 3.13 - 3.07 (m, 2H), 2.86 (dd, $J = 9.4, 6.4$ Hz, 2H), 2.32 (d, $J = 2.7$ Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 137.29, 136.15, 135.94, 132.55, 130.05, 129.73, 129.19, 128.41, 35.92, 35.31, 21.07, 21.04.

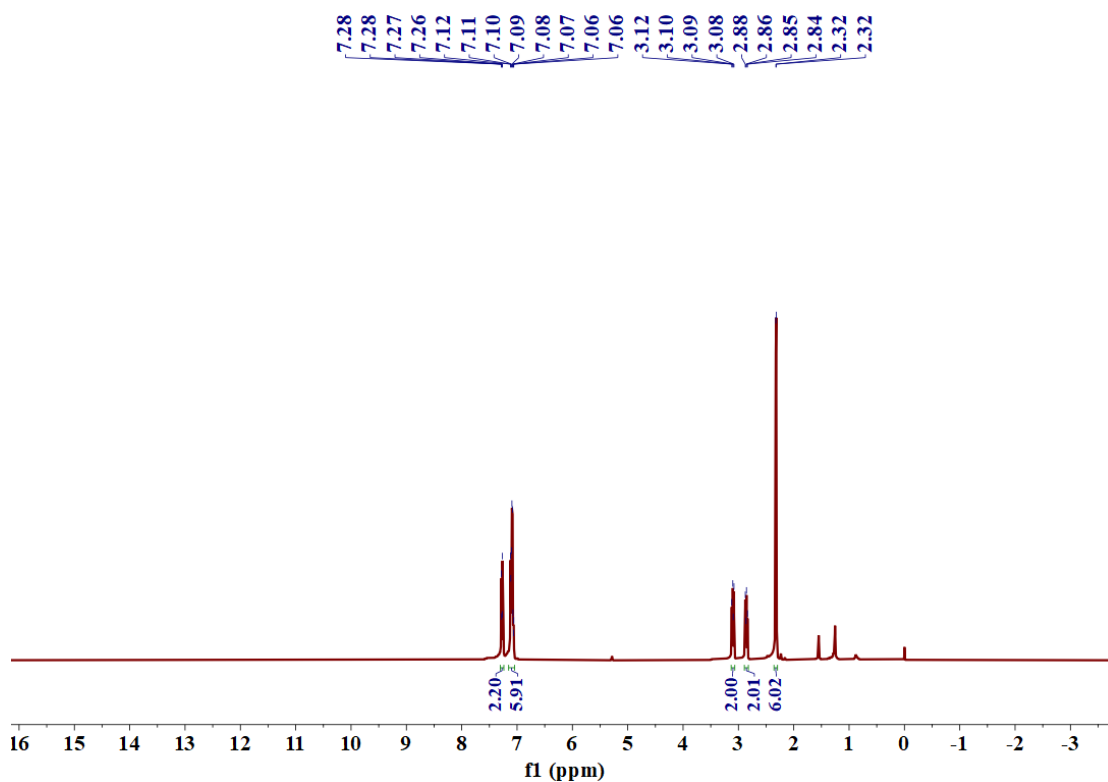


Fig. S39. ^1H NMR spectra of (4-methylphenethyl)(p-tolyl)sulfane in CDCl_3 .

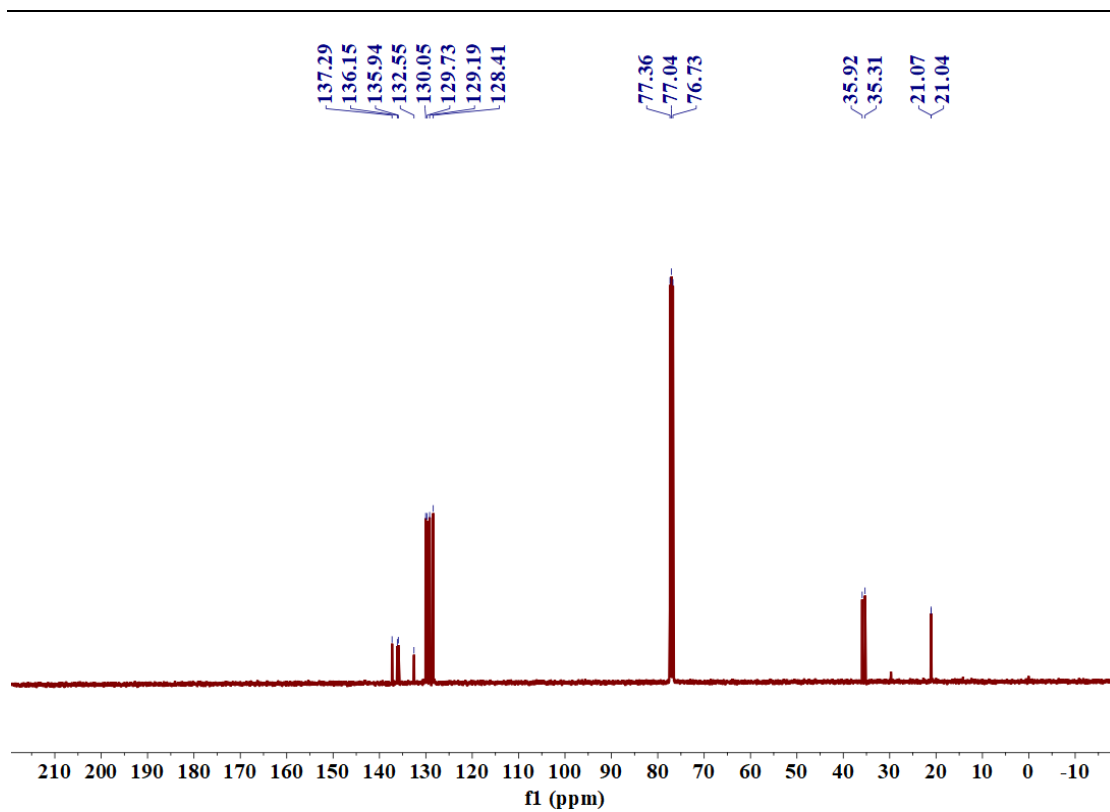
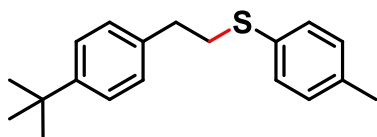


Fig. S40. ^{13}C NMR spectra of (4-methylphenethyl)(p-tolyl)sulfane in CDCl_3

3n. (4-(tert-butyl)phenethyl)(p-tolyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give **3n** as a colorless oil (52.8 mg, 93% yield).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30 (m, 4H), 7.12 (td, $J = 7.9, 2.5$ Hz, 4H), 3.12 (m, 2H), 2.87 (m, 2H), 2.33 (d, $J = 2.7$ Hz, 3H), 1.34 - 1.29 (m, 9H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.24, 137.32, 136.12, 132.60, 129.97, 129.73, 128.18, 125.40, 35.73, 35.27, 34.43, 31.40, 21.05.

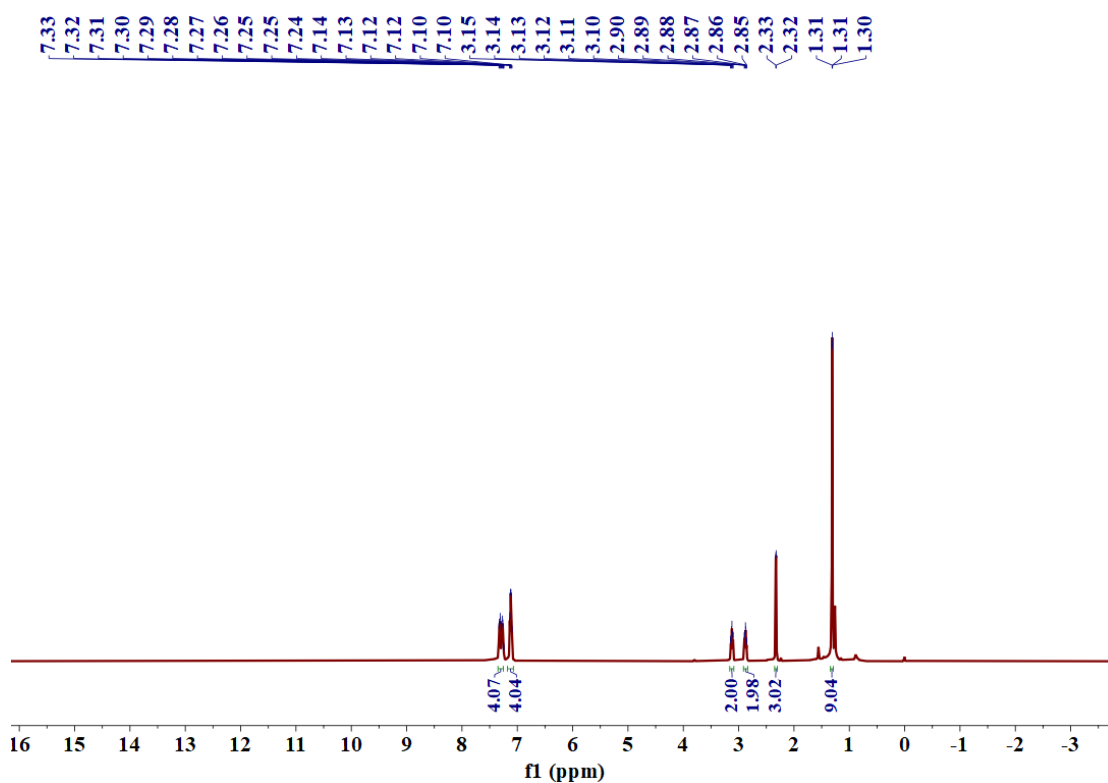


Fig. S41. $^1\text{H NMR}$ spectra of (4-(tert-butyl)phenethyl)(p-tolyl)sulfane in CDCl_3 .

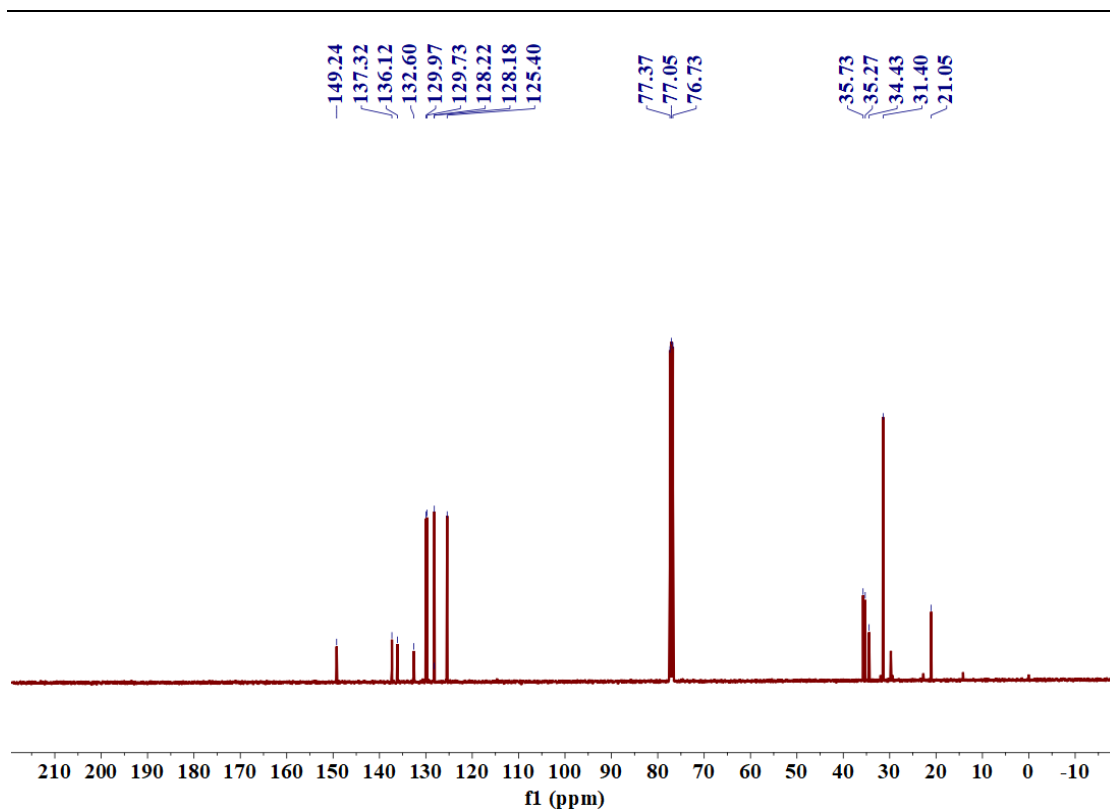
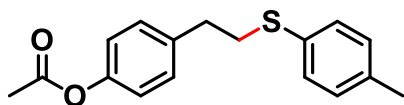


Fig. S42. ^{13}C NMR spectra of (4-(tert-butyl)phenethyl)(p-tolyl)sulfane in CDCl_3

3o. 4-(2-(p-tolylthio)ethyl)phenyl acetate



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=20:1) to give **3o** as a colorless oil (37.7 mg, 66 % yield).

^1H NMR (400 MHz, CDCl_3) δ 7.27 - 7.20 (m, 2H), 7.14 - 7.08 (m, 2H), 7.05 (d, J = 8.0 Hz, 2H), 7.00 - 6.92 (m, 2H), 3.08 - 2.98 (m, 2H), 2.82 (dd, J = 9.3, 6.5 Hz, 2H), 2.26 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.48, 149.31, 137.93, 136.20, 132.59, 130.14, 129.88, 129.57, 121.64, 35.71, 35.20, 21.13, 21.12.

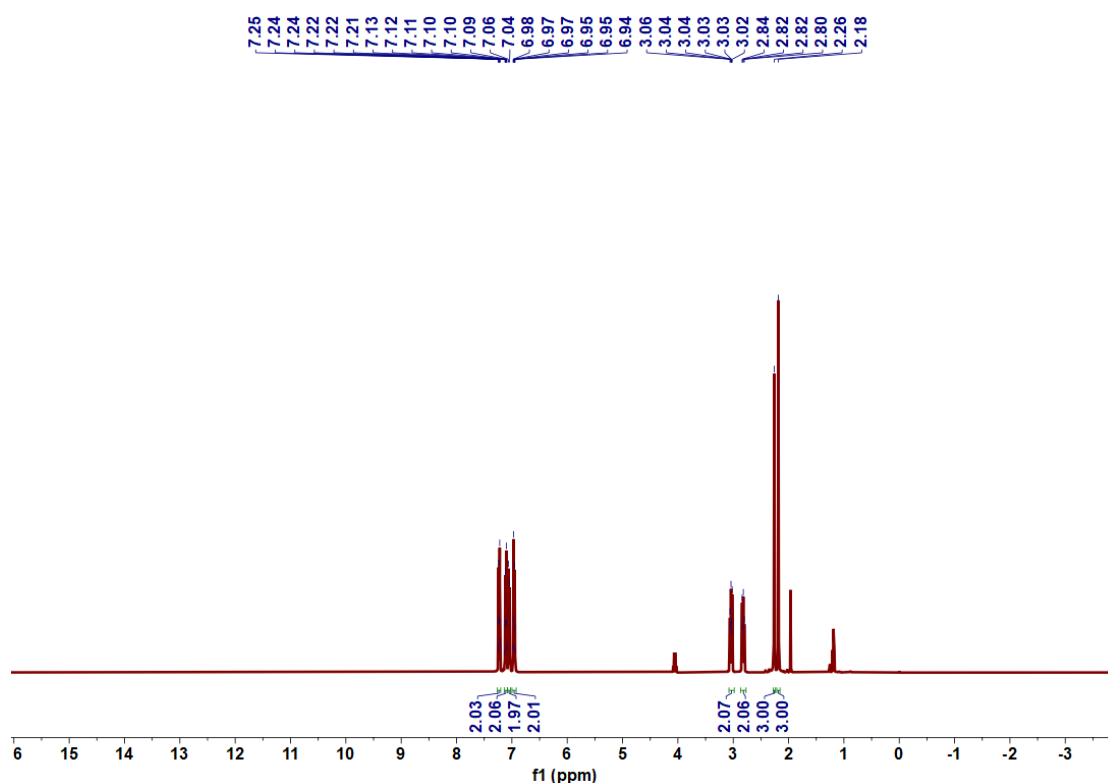


Fig. S43. ^1H NMR spectra of 4-(2-(p-tolylthio)ethyl)phenyl acetate in CDCl_3 .

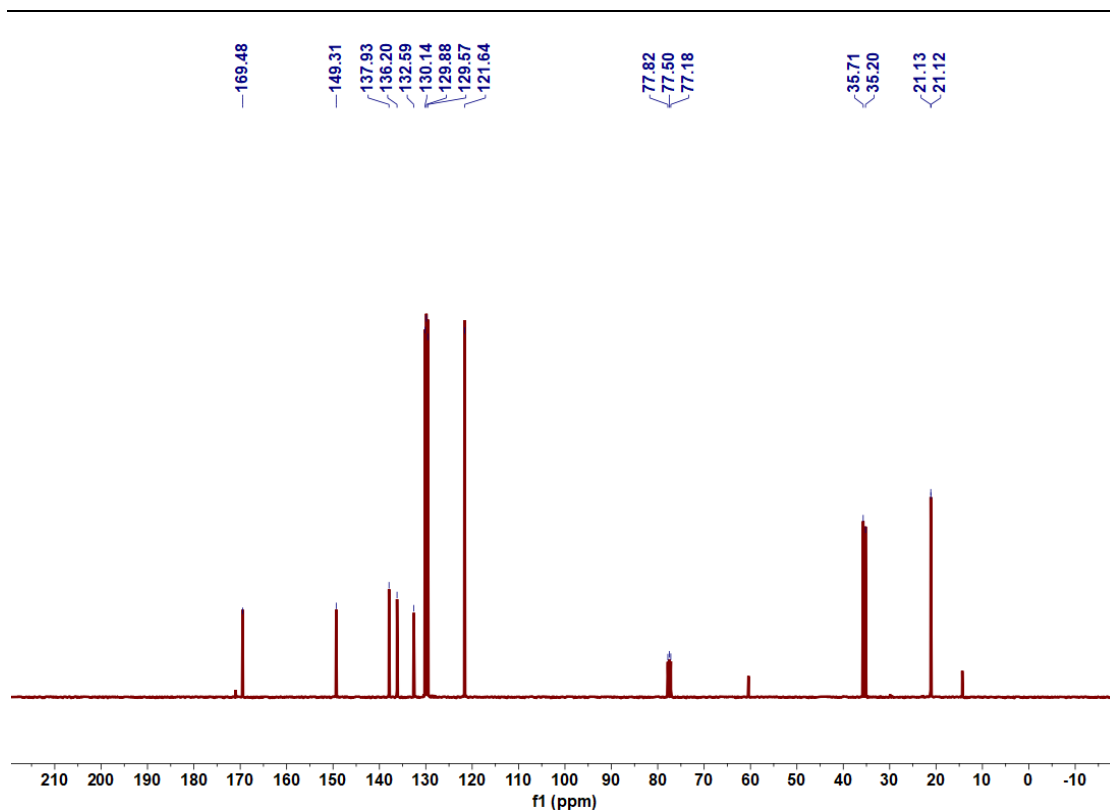
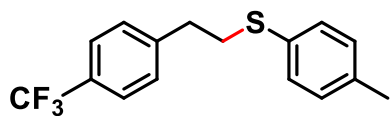


Fig. S44. ^{13}C NMR spectra of 4-(2-(p-tolylthio)ethyl)phenyl acetate in CDCl_3

3p. p-tolyl(4-(trifluoromethyl)phenethyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give **3p** as a colorless oil (43.2 mg, 73% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, $J = 8.0$ Hz, 2H), 7.24 - 7.15 (m, 4H), 7.02 (d, $J = 7.9$ Hz, 2H), 3.03 (dd, $J = 8.8, 6.4$ Hz, 2H), 2.85 (dd, $J = 8.9, 6.5$ Hz, 2H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 144.31, 144.30, 136.60, 131.96, 130.48, 129.85, 128.95, 128.89, 128.57, 125.66, 125.46, 125.42, 125.38, 125.34, 122.95, 35.61, 35.53, 21.06.

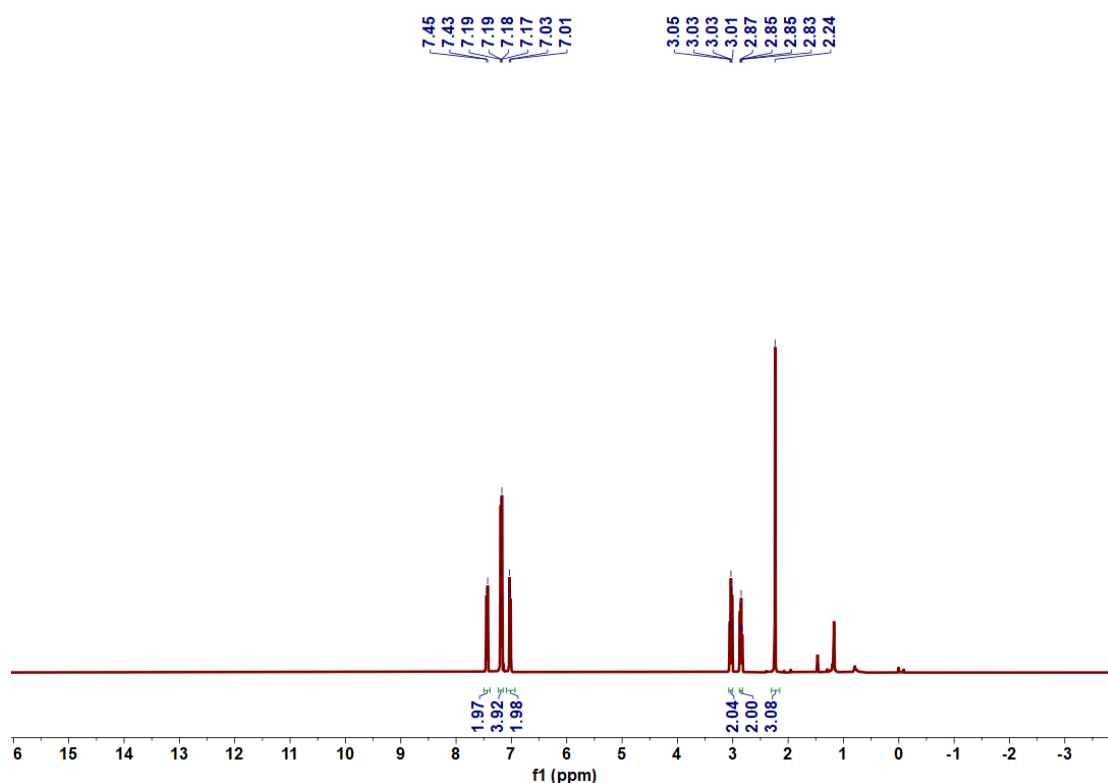


Fig. S45 ^1H NMR spectra of p-tolyl(4-(trifluoromethyl)phenethyl)sulfane in CDCl_3 .

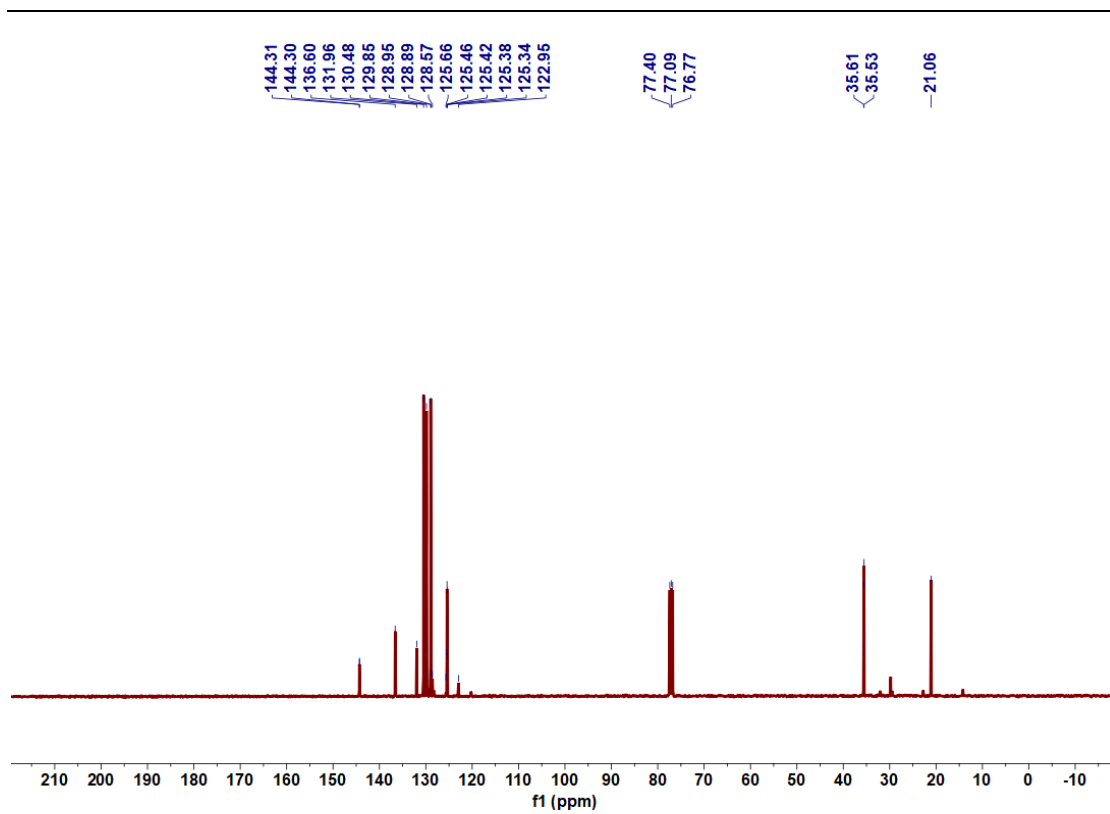
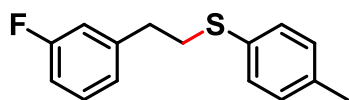


Fig. S46. ^{13}C NMR spectra of p-tolyl(4-(trifluoromethyl)phenethyl)sulfane in CDCl_3

3q. (3-fluorophenethyl)(p-tolyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give 3q as a colorless oil (35.4 mg, 72% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.32 - 7.23 (m, 3H), 7.12 (d, $J = 7.9$ Hz, 2H), 7.00 - 6.82 (m, 3H), 3.11 (dd, $J = 8.9, 6.6$ Hz, 2H), 2.88 (dd, $J = 9.1, 6.5$ Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 164.11, 161.67, 142.83, 142.76, 136.49, 132.09, 130.37, 129.96, 129.88, 129.82, 124.24, 124.21, 115.55, 115.34, 113.42, 113.21, 35.63, 35.46, 35.44, 21.07.

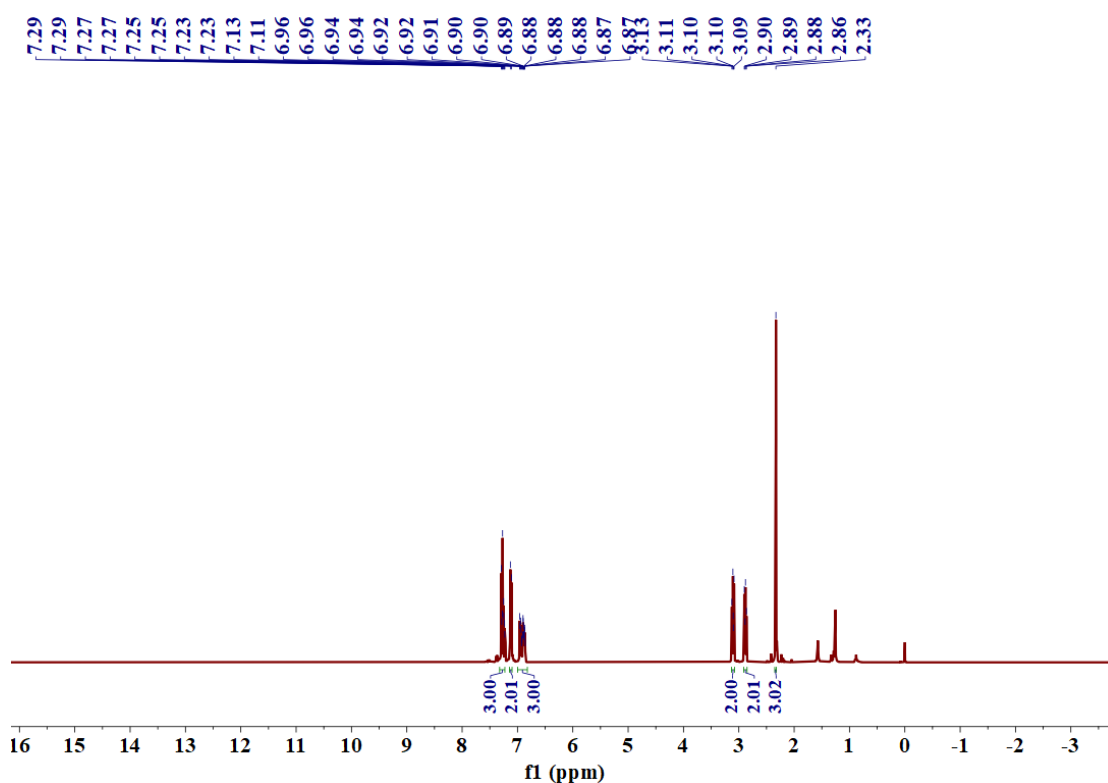


Fig. S47. ^1H NMR spectra of (3-fluorophenethyl)(p-tolyl)sulfane in CDCl_3 .

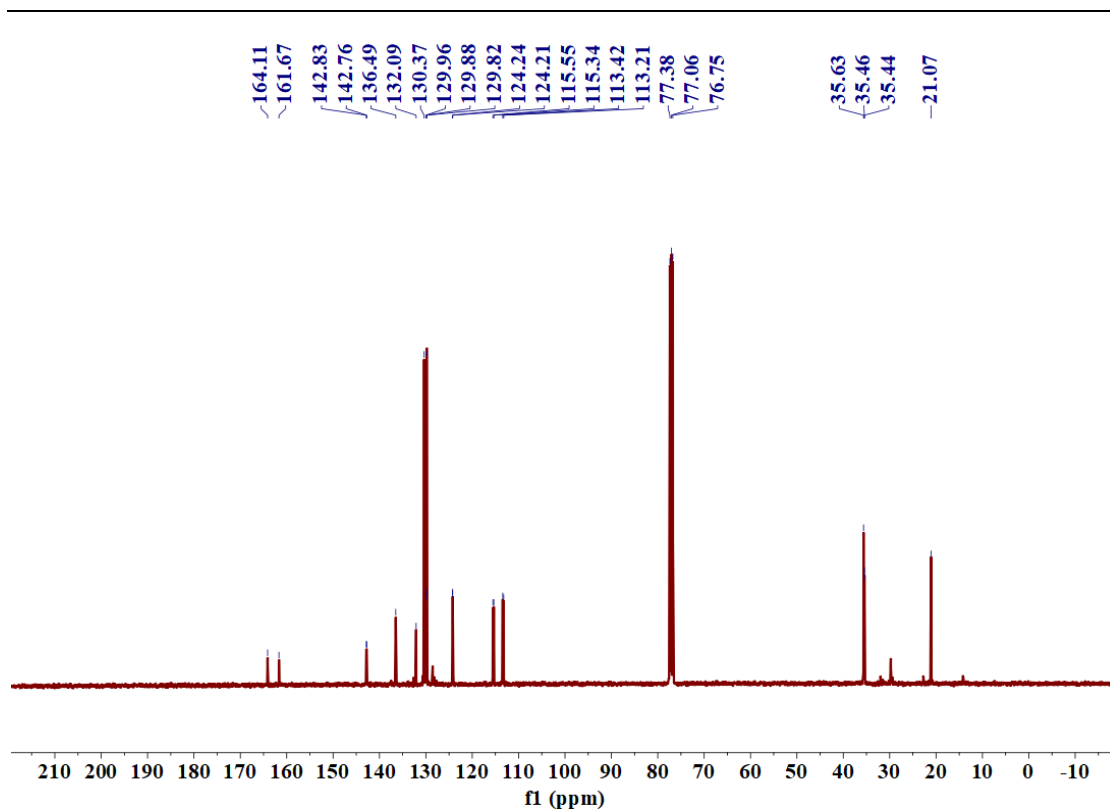
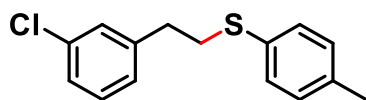


Fig. S48. ¹³C NMR (3-fluorophenethyl)(p-tolyl)sulfane in CDCl₃

3r. (3-chlorophenethyl)(p-tolyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give **3r** as a colorless oil (37.2 mg, 71% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.27 (t, $J = 6.8$ Hz, 2H), 7.22 - 7.15 (m, 3H), 7.12 (d, $J = 7.9$ Hz, 2H), 7.06 (td, $J = 5.5, 4.9, 3.1$ Hz, 1H), 3.10 (dd, $J = 9.2, 6.4$ Hz, 2H), 2.86 (dd, $J = 9.2, 6.5$ Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 142.27, 136.52, 134.21, 132.03, 130.59, 130.42, 130.04, 129.82, 129.77, 129.74, 128.70, 128.53, 128.20, 126.79, 126.61, 35.66, 35.40, 21.08.

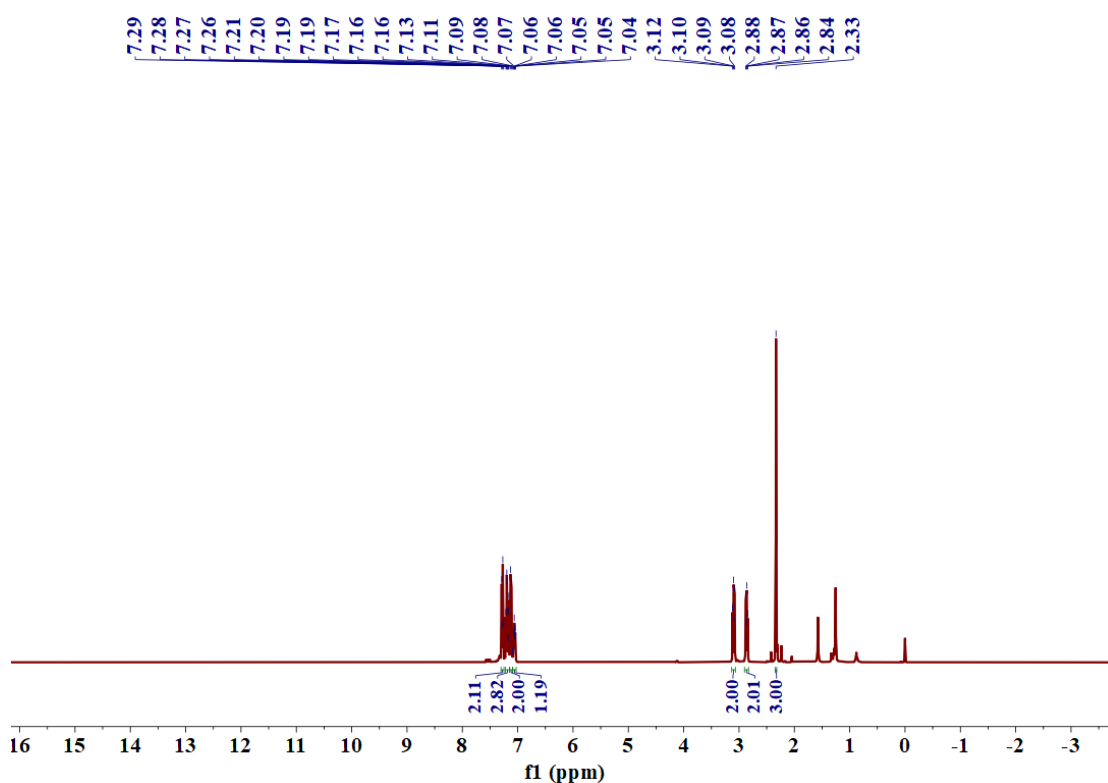


Fig. S49. ^1H NMR spectra of (3-chlorophenethyl)(p-tolyl)sulfane in CDCl_3 .

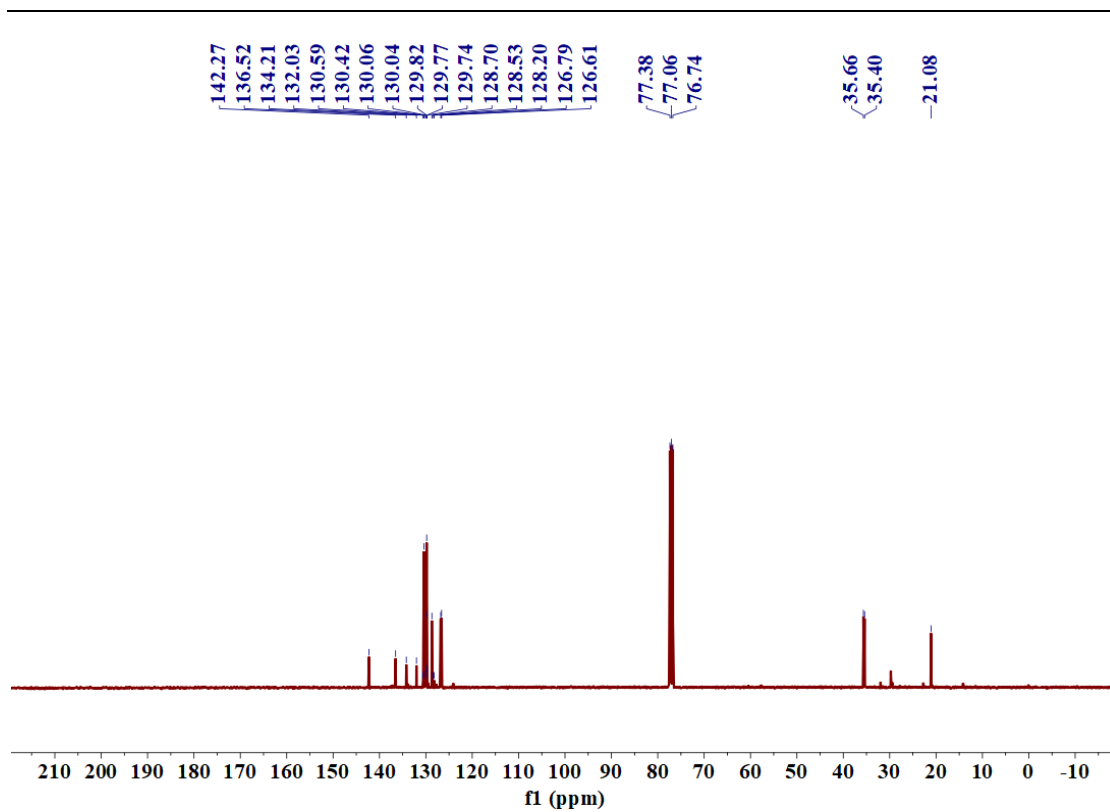
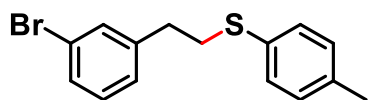


Fig. S50. ^{13}C NMR spectra of (3-chlorophenethyl)(p-tolyl)sulfane in CDCl_3

3s. (3-bromophenethyl)(p-tolyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give **3s** as a colorless oil (42.9 mg, 70% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.37 - 7.24 (m, 4H), 7.18 - 7.06 (m, 4H), 3.08 (dd, J = 9.1, 6.5 Hz, 2H), 2.84 (dd, J = 9.1, 6.5 Hz, 2H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 142.59, 136.51, 132.05, 131.62, 130.44, 130.05, 129.83, 129.53, 127.27, 122.52, 35.69, 35.40, 21.10.

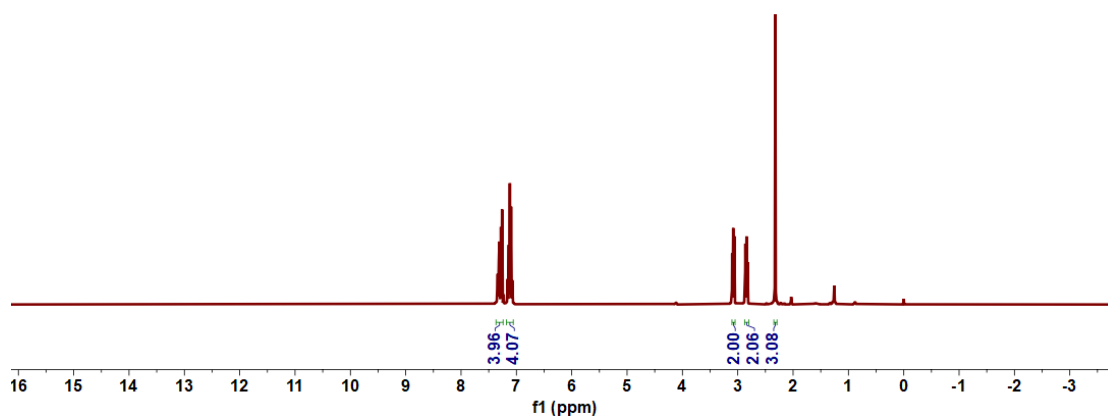


Fig. S51. ^1H NMR spectra of (3-bromophenethyl)(p-tolyl)sulfane in CDCl_3 .

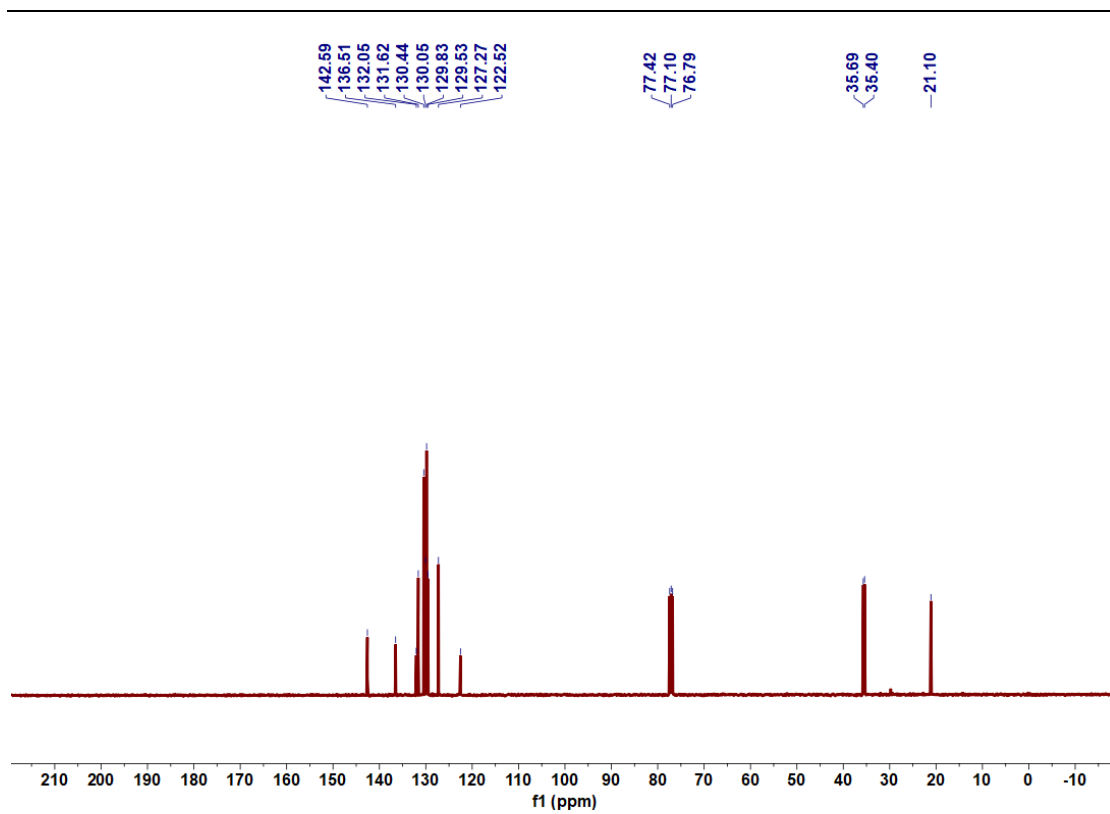
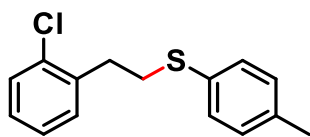


Fig. S52. ^{13}C NMR spectra of (3-bromophenethyl)(p-tolyl)sulfane in CDCl_3

3t. (2-chlorophenethyl)(p-tolyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give **3t** as yellow oil (40.3 mg, 77% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.37 - 7.28 (m, 3H), 7.18 (m, 3H), 7.12 (d, $J = 7.9$ Hz, 2H), 3.16 - 3.09 (m, 2H), 3.05 - 2.98 (m, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 137.84, 136.27, 133.95, 132.21, 130.87, 130.12, 129.74, 129.60, 127.98, 126.87, 33.88, 33.78, 21.06.

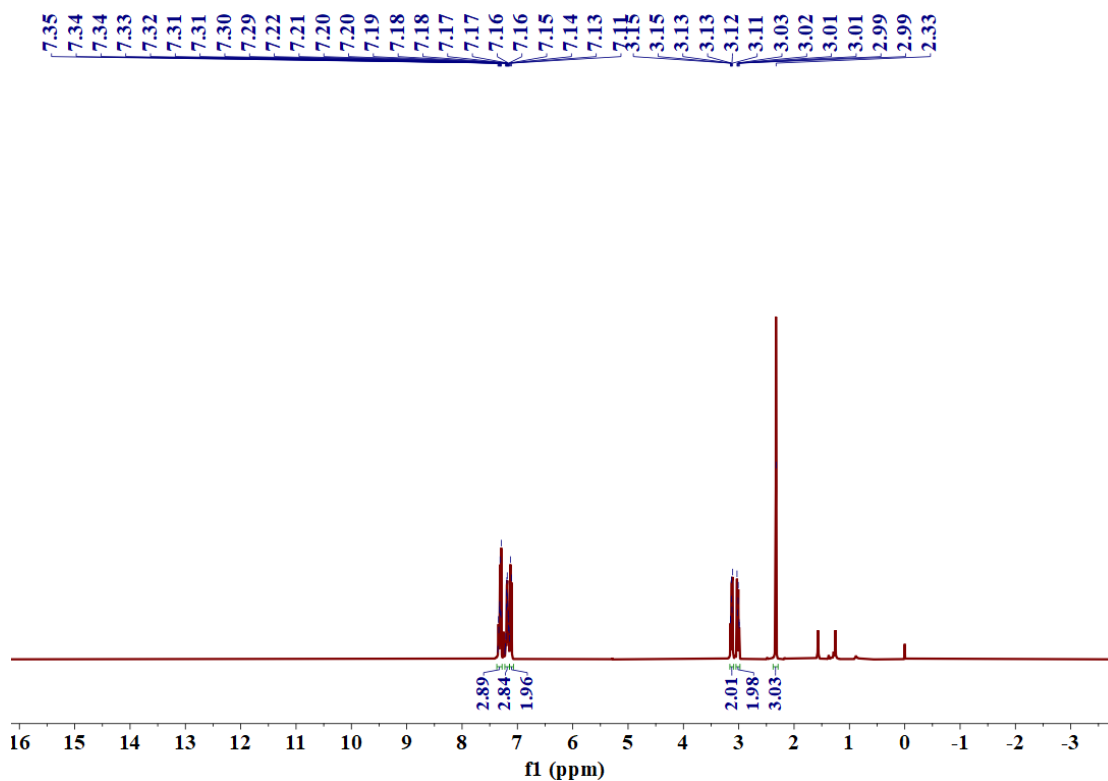


Fig. S53. ^1H NMR spectra of (2-chlorophenethyl)(p-tolyl)sulfane in CDCl_3 .

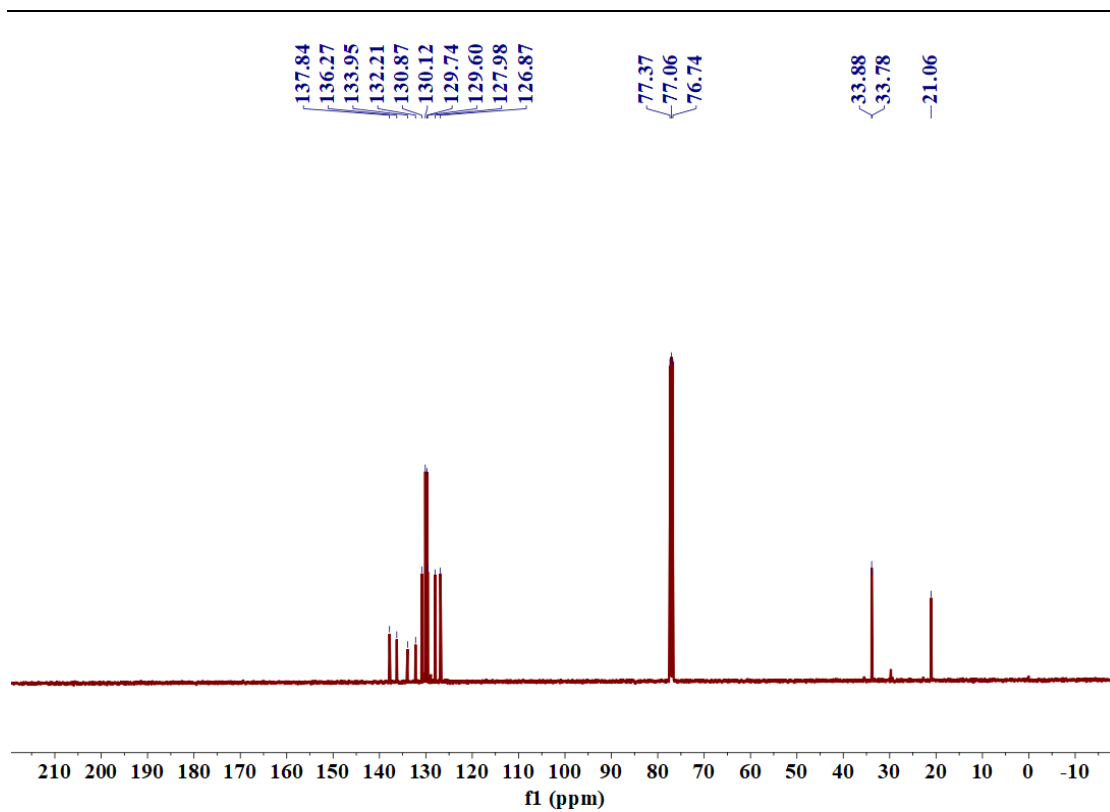
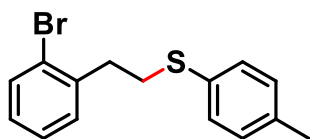


Fig. S54. ^{13}C NMR spectra of (2-chlorophenethyl)(p-tolyl)sulfane e in CDCl_3

3u. (2-bromophenethyl)(p-tolyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give **3u** as yellow oil (45.5 mg, 74% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, $J = 7.9$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.25 - 7.18 (m, 2H), 7.14 - 7.06 (m, 3H), 3.13 (dd, $J = 9.3, 5.5$ Hz, 2H), 3.02 (dd, $J = 10.0, 6.2$ Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 139.55, 136.31, 132.91, 132.15, 130.88, 130.22, 129.74, 128.21, 127.52, 124.33, 36.35, 33.92, 21.07.

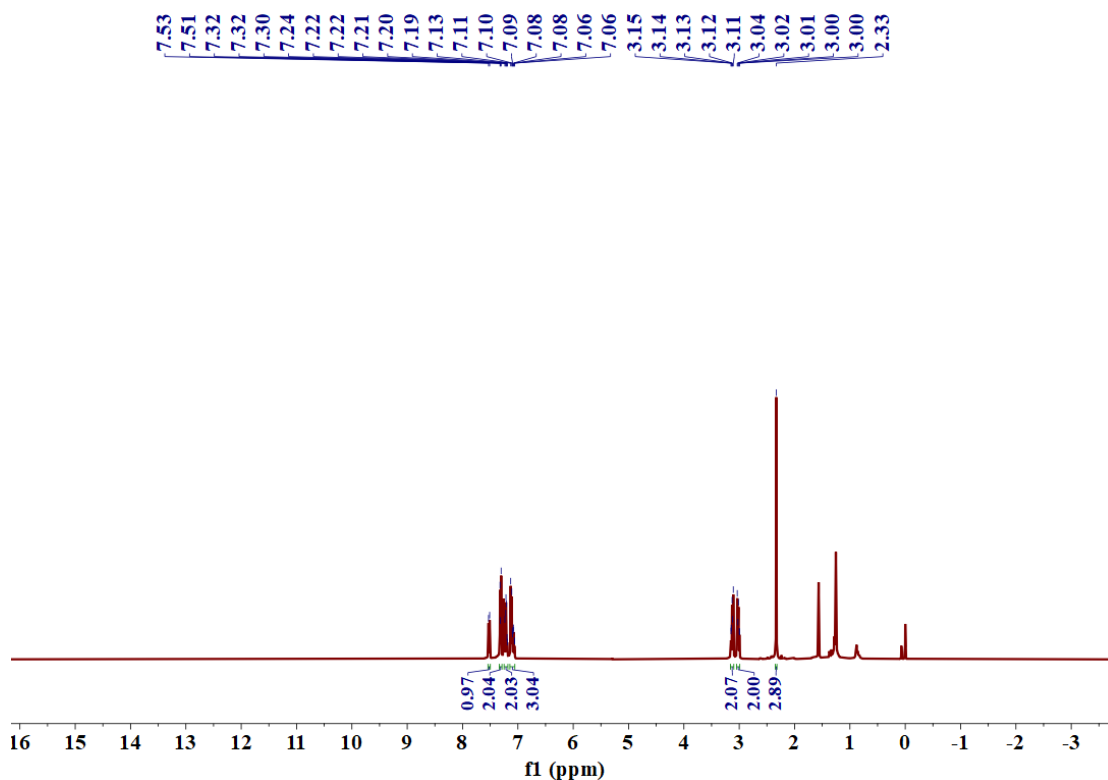


Fig. S55. ^1H NMR spectra of (2-bromophenethyl)(p-tolyl)sulfane in CDCl_3 .

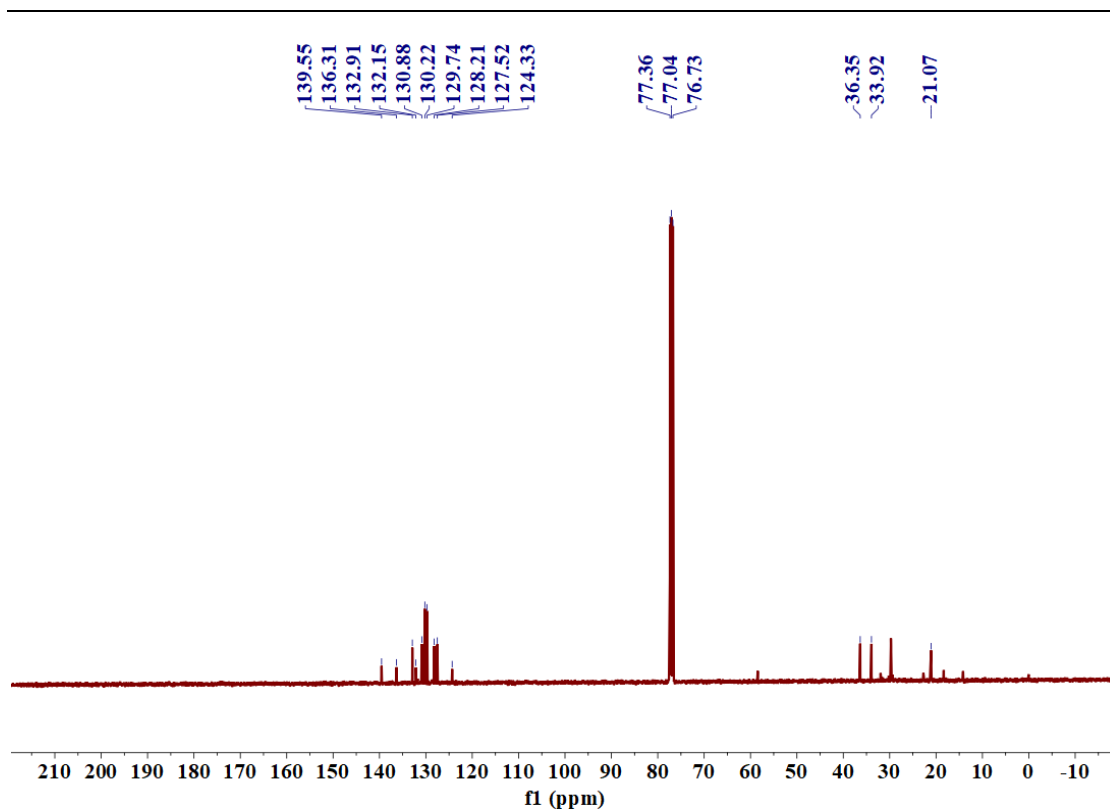
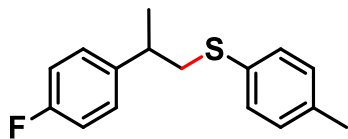


Fig. S56. ¹³C NMR spectra of (2-bromophenethyl)(p-tolyl)sulfane in CDCl₃

3v. (2-(4-fluorophenyl)propyl)(p-tolyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give **3v** as a colorless oil (35.3 mg, 68% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.25 - 7.18 (m, 2H), 7.12 - 7.03 (m, 4H), 6.99 - 6.89 (m, 2H), 3.09 (dd, $J = 12.5, 6.5$ Hz, 1H), 2.94 (m, 2H), 2.28 (s, 3H), 1.32 (d, $J = 6.8$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 162.81, 160.39, 141.31, 141.28, 136.18, 132.94, 130.40, 130.24, 130.21, 130.14, 129.82, 128.55, 128.47, 115.42, 115.21, 42.98, 38.90, 21.27, 21.12.

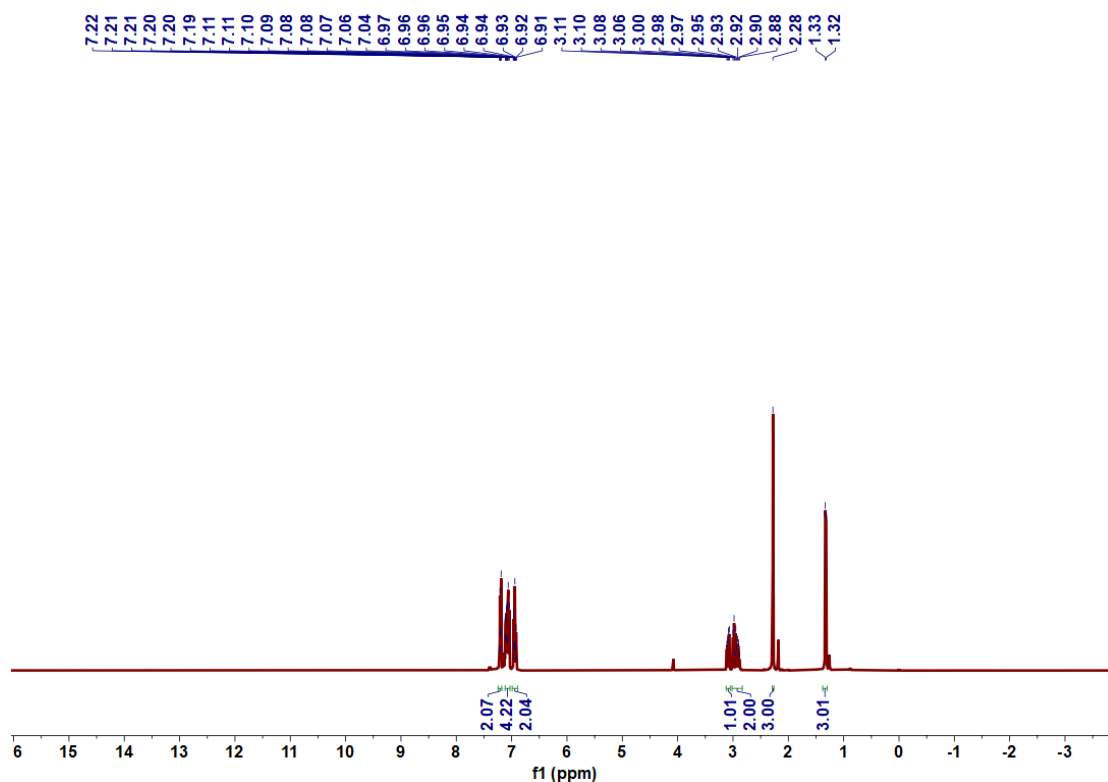


Fig. S57. ^1H NMR spectra of (2-(4-fluorophenyl)propyl)(p-tolyl)sulfane in CDCl_3 .

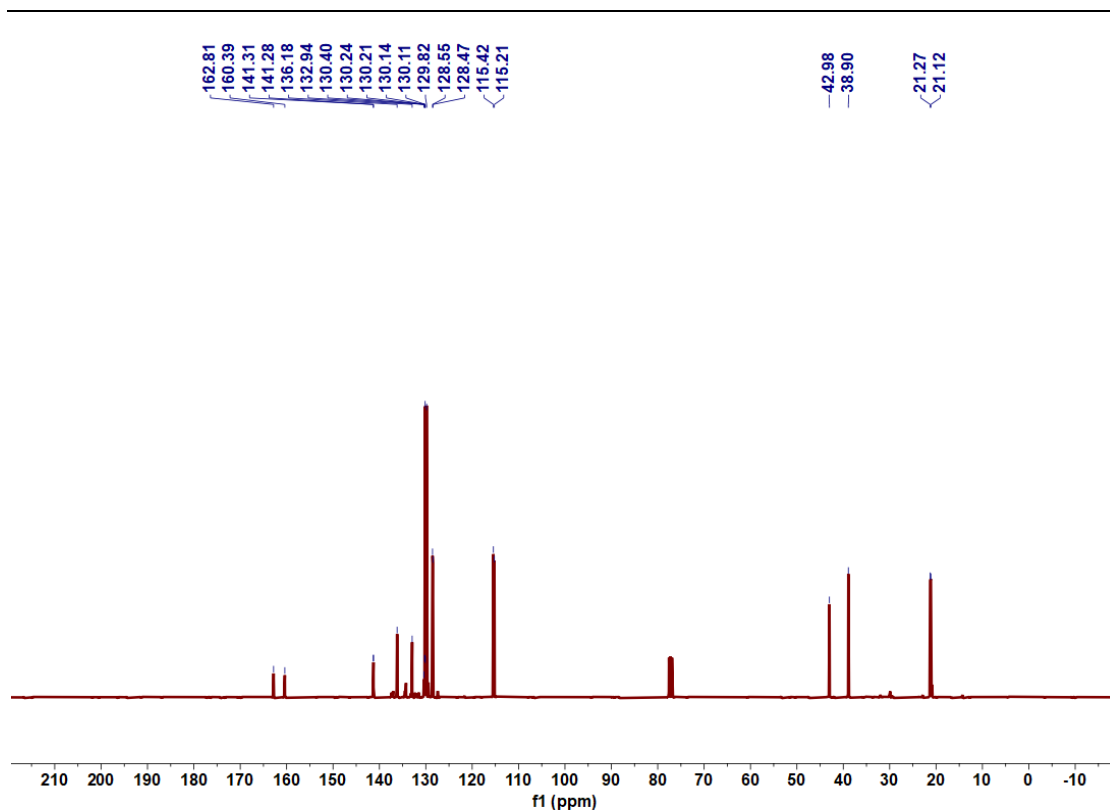
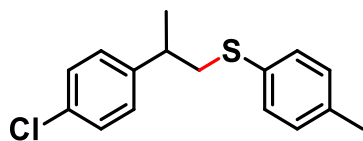


Fig. S58. ^{13}C NMR spectra of (2-(4-fluorophenyl)propyl)(p-tolyl)sulfane in CDCl_3

3w. (2-(4-chlorophenyl)propyl)(p-tolyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give **3w** as a colorless oil (38.1 mg, 69% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.27 - 7.20 (m, 2H), 7.16 - 7.06 (m, 4H), 6.98 (t, $J = 8.7$ Hz, 2H), 3.11 (dd, $J = 12.6, 6.7$ Hz, 1H), 2.97 (m, 2H), 2.32 (s, 3H), 1.35 (d, $J = 6.8$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 162.74, 160.31, 141.20, 141.17, 136.18, 132.76, 130.09, 129.76, 129.72, 128.44, 128.37, 115.34, 115.13, 42.95, 38.81, 21.20, 21.04.

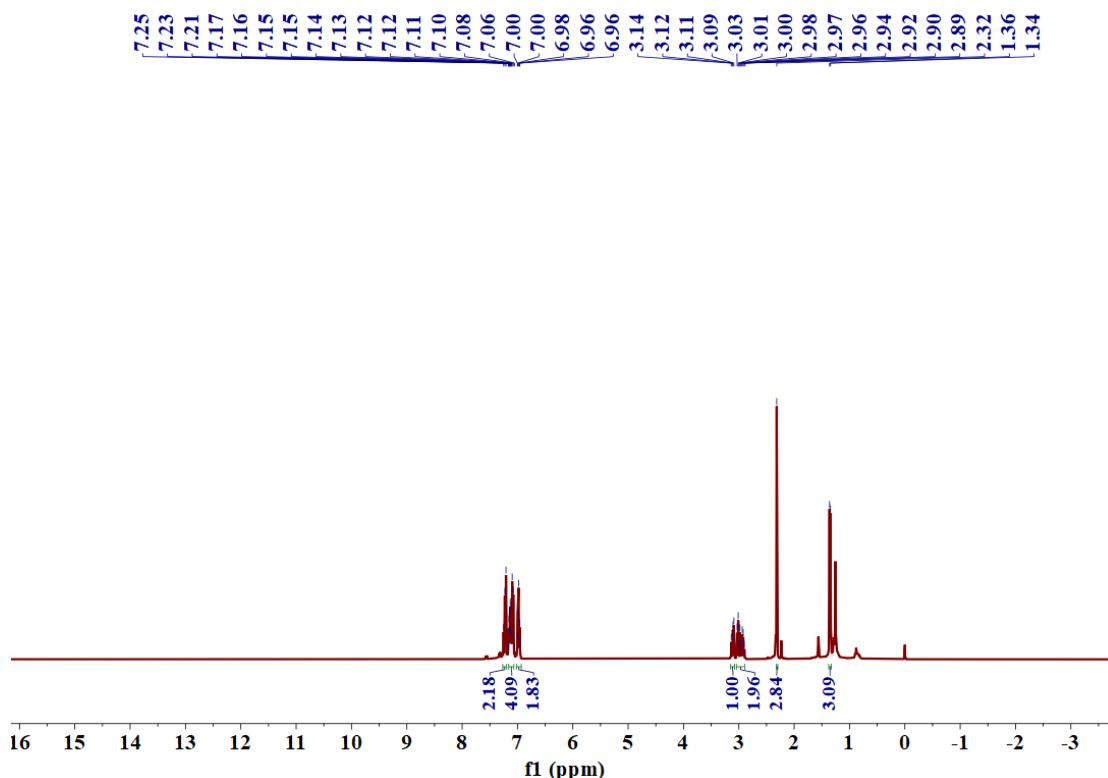


Fig. S59. ^1H NMR spectra of (2-(4-chlorophenyl)propyl)(p-tolyl)sulfane in CDCl_3 .

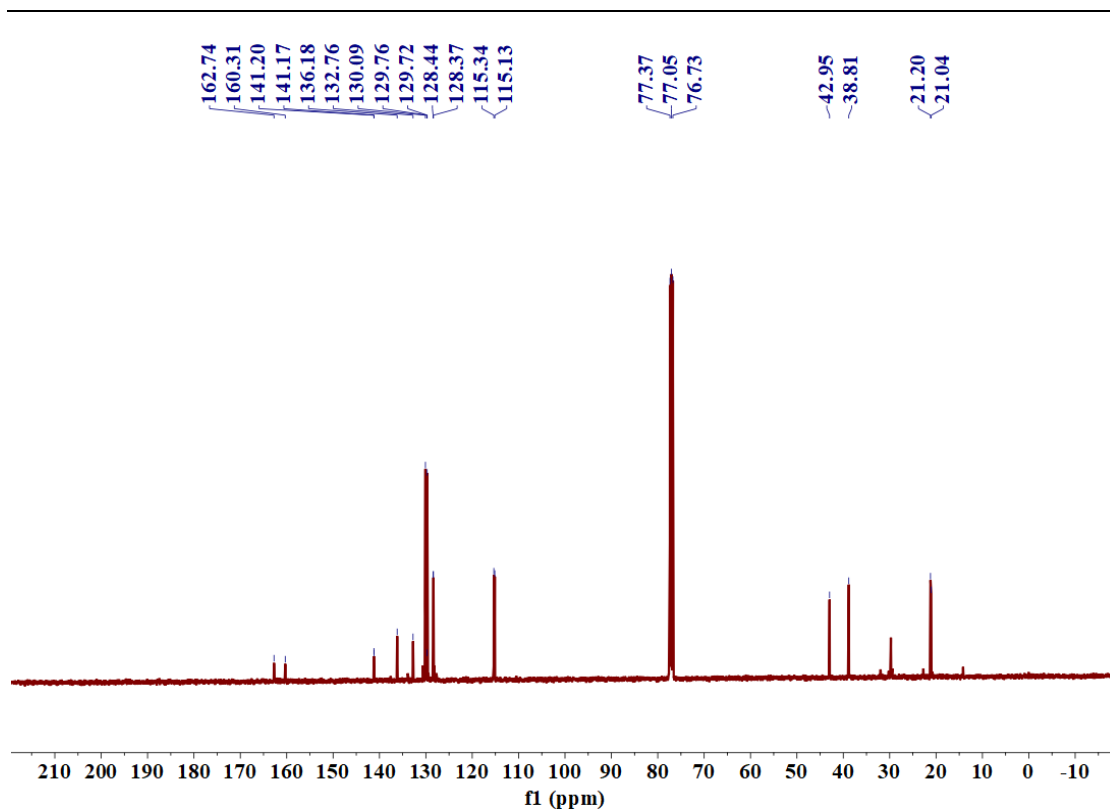
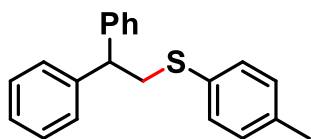


Fig. S60. ^{13}C NMR spectra of (2-(4-chlorophenyl)propyl)(p-tolyl)sulfane in CDCl_3

3x. (2,2-diphenylethyl)(p-tolyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give 3x as a colorless oil (40.7 mg, 67% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.71 - 7.59 (m, 10H), 7.56 (m, 2H), 7.44 (d, $J = 8.0$ Hz, 2H), 4.63 (t, $J = 7.9$ Hz, 1H), 3.96 (d, $J = 7.9$ Hz, 2H), 2.66 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 143.64, 136.47, 133.39, 130.61, 130.23, 129.01, 128.46, 127.10, 51.03, 40.68, 21.51.

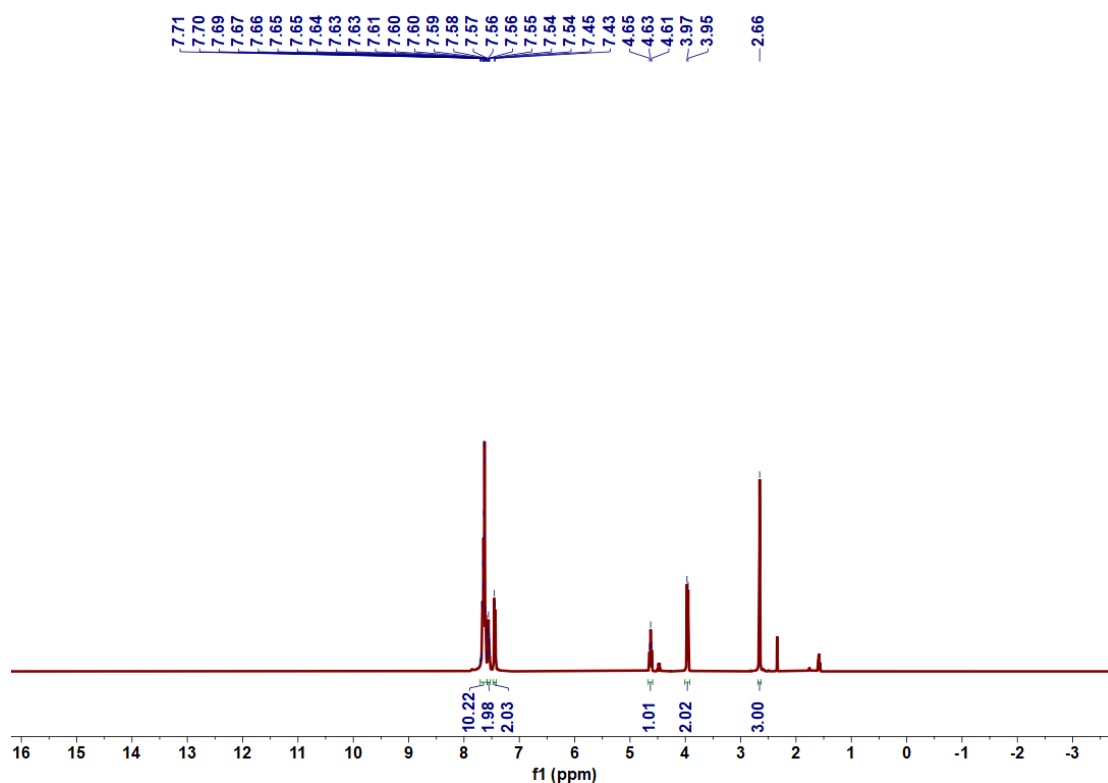


Fig. S61. ^1H NMR spectra of (2,2-diphenylethyl)(p-tolyl)sulfane in CDCl_3 .

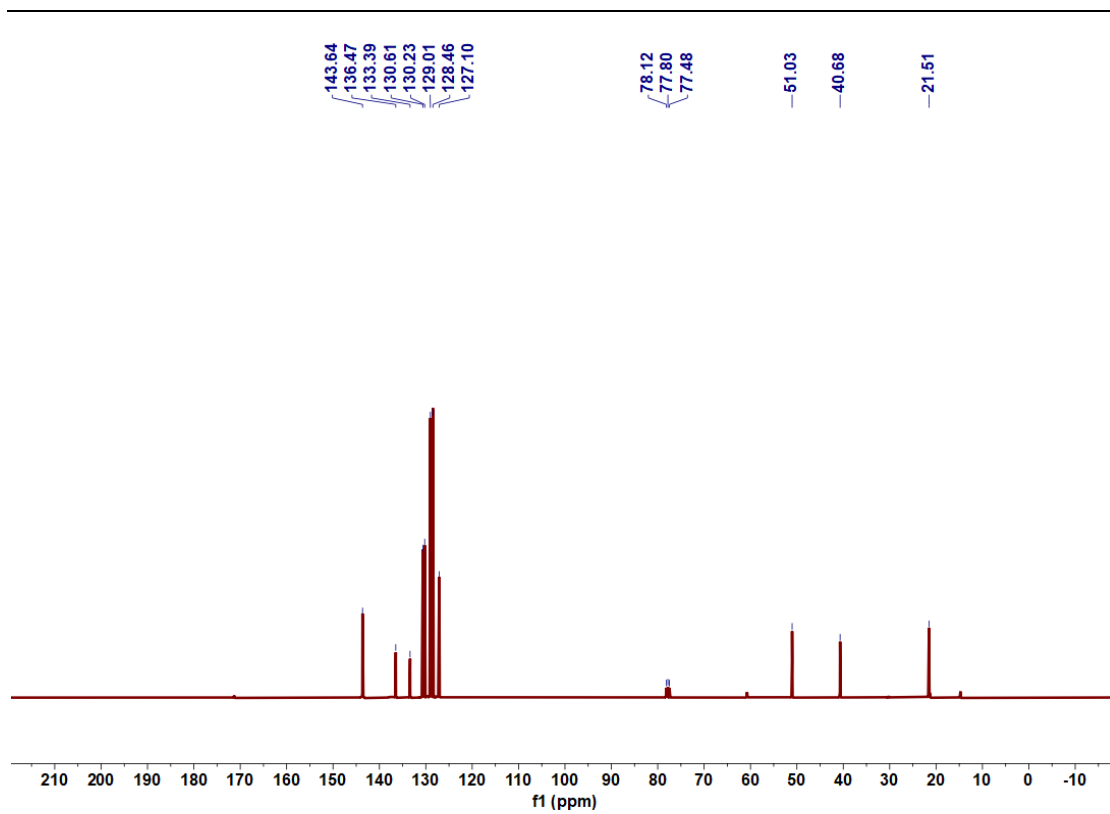
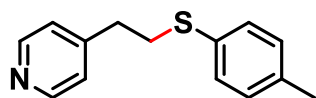


Fig. S62. ^{13}C NMR spectra of (2,2-diphenylethyl)(p-tolyl)sulfane in CDCl_3

3y. 4-(2-(p-tolylthio)ethyl)pyridine



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=5:1) to give 3y as a brown oil (34.8 mg, 76% yield).

^1H NMR (400 MHz, CDCl_3) δ 8.56 - 8.42 (m, 2H), 7.33 - 7.25 (m, 2H), 7.18 - 7.05 (m, 4H), 3.11 (dd, $J = 8.6, 6.8$ Hz, 2H), 2.87 (dd, $J = 8.8, 6.6$ Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 149.83, 149.04, 136.76, 131.68, 130.65, 129.88, 123.96, 34.91, 34.81, 21.09.

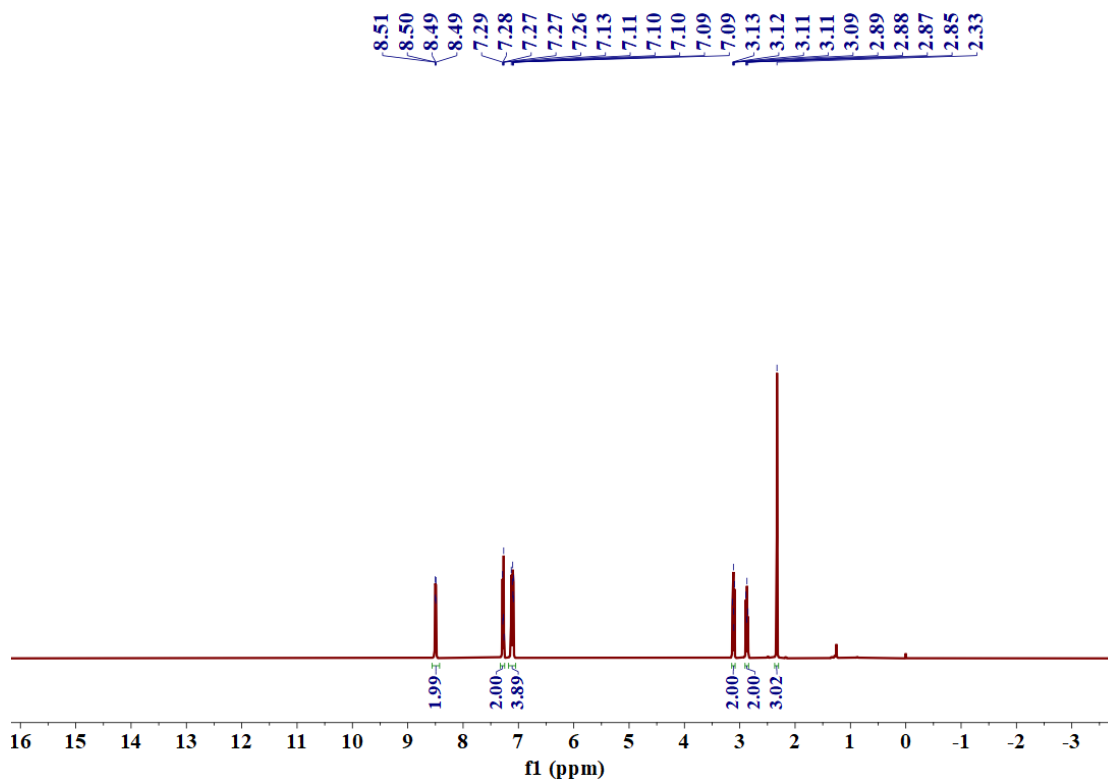


Fig. S63. ^1H NMR spectra of 4-(2-(p-tolylthio)ethyl)pyridine in CDCl_3 .

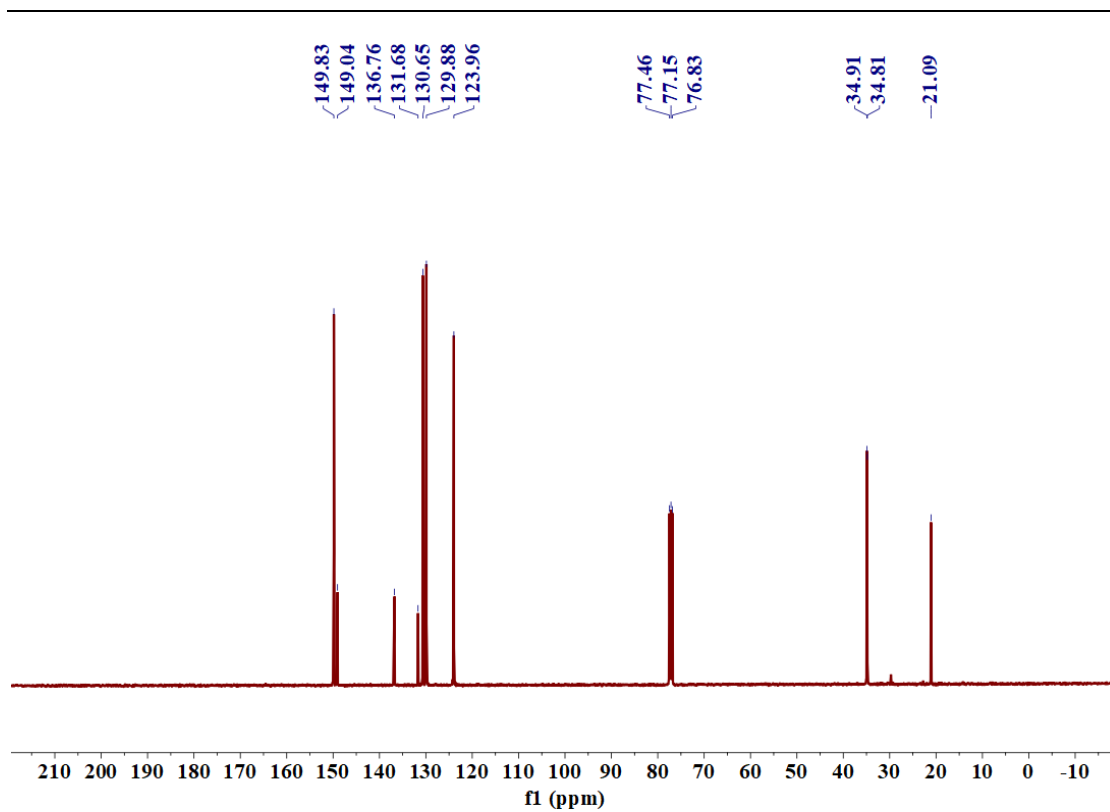
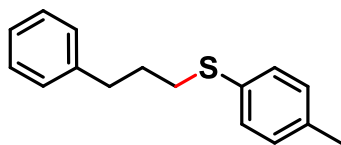


Fig. S64. ^{13}C NMR spectra of 4-(2-(p-tolylthio)ethyl)pyridine in CDCl_3

3z. (3-phenylpropyl)(p-tolyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give **3z** as a colorless oil (28.6 mg, 59% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.28 - 7.19 (m, 4H), 7.18 - 7.11 (m, 3H), 7.05 (d, $J = 7.9$ Hz, 2H), 2.84 (t, $J = 7.2$ Hz, 2H), 2.71 (t, $J = 7.5$ Hz, 2H), 2.28 (s, 3H), 1.91 (p, $J = 7.4$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 141.49, 136.08, 132.82, 130.10, 129.78, 128.62, 128.50, 128.42, 126.06, 34.77, 33.73, 30.84, 21.14.

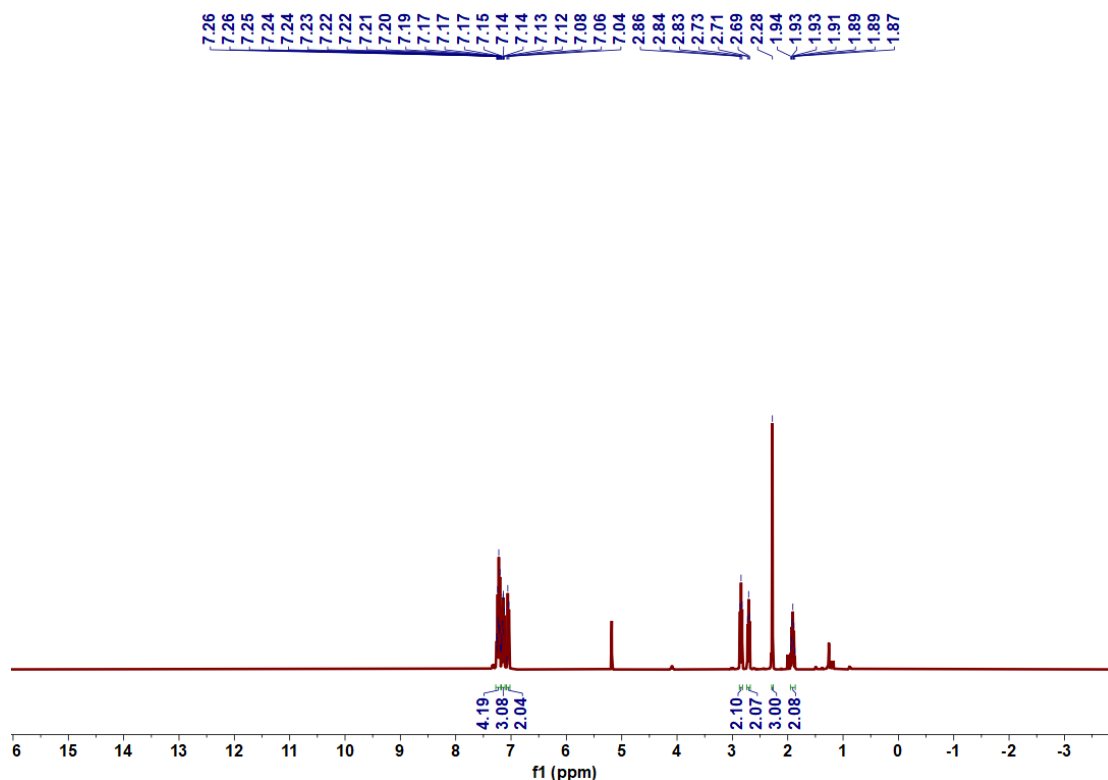


Fig. S65. ^1H NMR spectra of (3-phenylpropyl)(p-tolyl)sulfane in CDCl_3 .

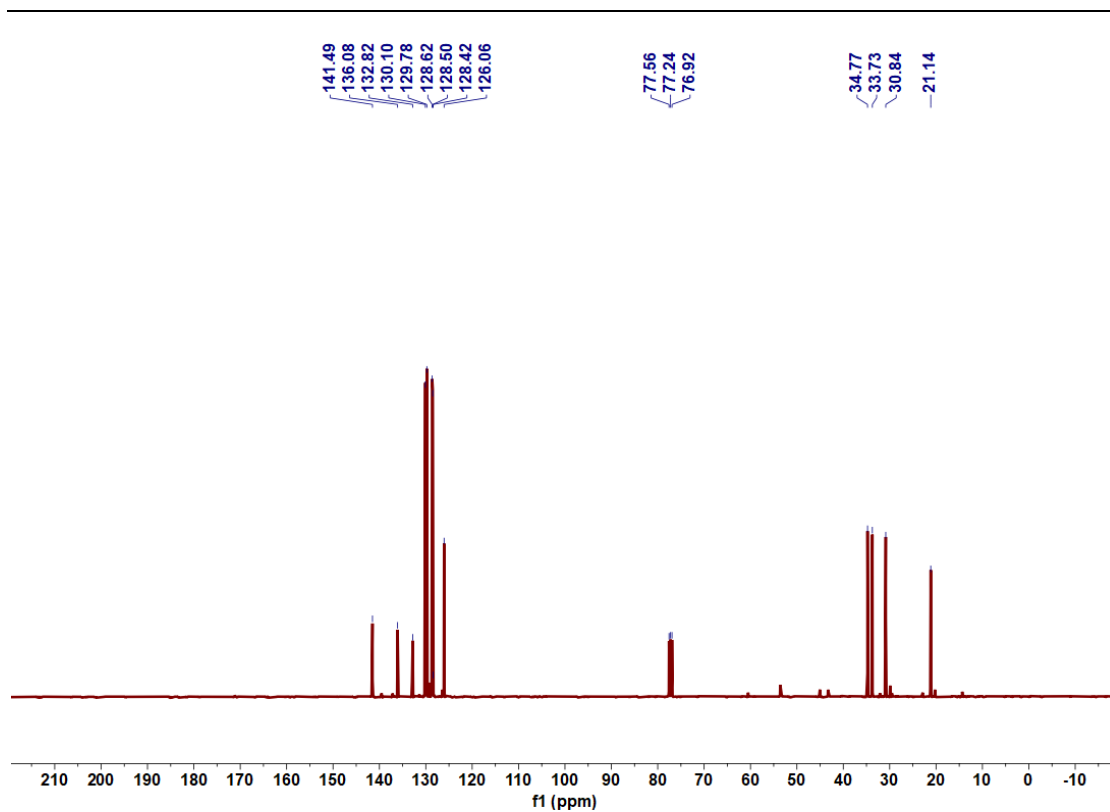
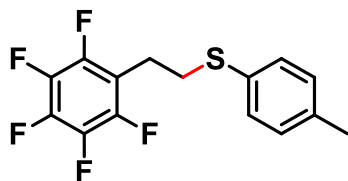


Fig. S66. ^{13}C NMR spectra of (3-phenylpropyl)(p-tolyl)sulfane in CDCl_3

3aa. (2-(perfluorophenyl)ethyl)(p-tolyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give 3aa as a colorless oil (38.1 mg, 60% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.27 (dd, $J = 9.0, 2.7$ Hz, 2H), 7.11 (d, $J = 7.8$ Hz, 2H), 3.09 (dd, $J = 8.1, 5.9$ Hz, 2H), 2.98 (dd, $J = 8.0, 6.0$ Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 139.86, 139.05, 136.90, 131.16, 131.06, 130.56, 130.21, 129.82, 128.84, 128.61, 128.54, 127.20, 126.64, 35.40, 22.84, 21.05.

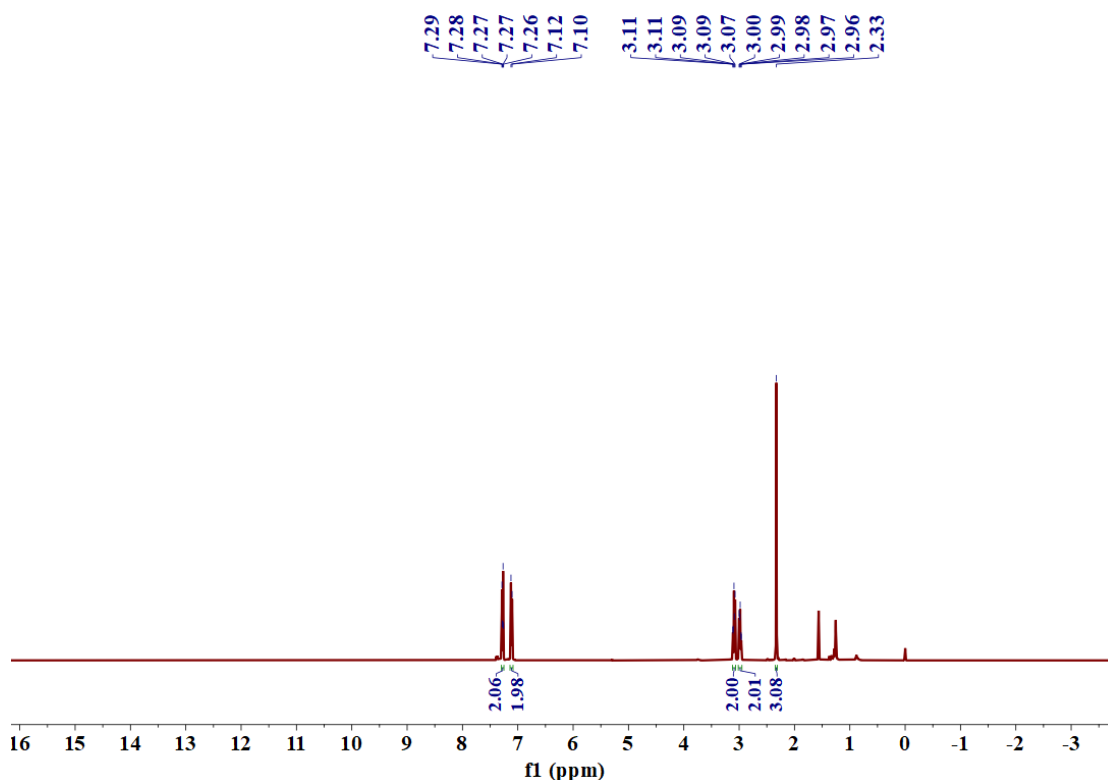


Fig. S67. ^1H NMR spectra of (2-(perfluorophenyl)ethyl)(p-tolyl)sulfane in CDCl_3 .

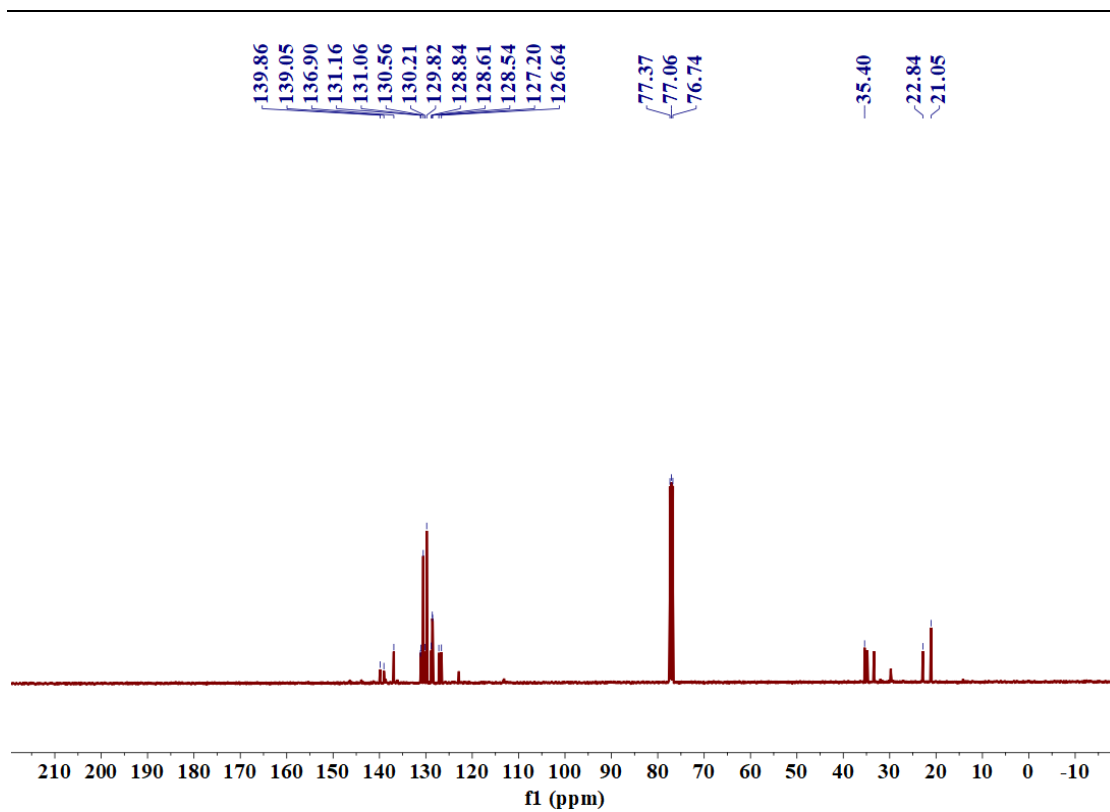
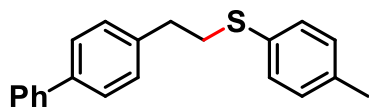


Fig. S68. ^{13}C NMR spectra of (2-(perfluorophenyl)ethyl)(p-tolyl)sulfane in CDCl_3

3ab. (2-([1,1'-biphenyl]-4-yl)ethyl)(p-tolyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=30:1) to give **3ab** as a yellow oil (37.7 mg, 62% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.59 - 7.54 (m, 2H), 7.54 - 7.49 (m, 2H), 7.42 (dd, $J = 8.4, 6.9$ Hz, 2H), 7.35 - 7.27 (m, 3H), 7.25 (dd, $J = 8.7, 2.4$ Hz, 2H), 7.12 (d, $J = 8.0$ Hz, 2H), 3.18 - 3.12 (m, 2H), 2.94 (dd, $J = 9.3, 6.5$ Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 140.97, 139.44, 139.40, 136.30, 132.44, 130.19, 130.14, 129.80, 129.07, 129.01, 128.79, 127.27, 127.19, 127.07, 35.84, 35.42, 21.09.

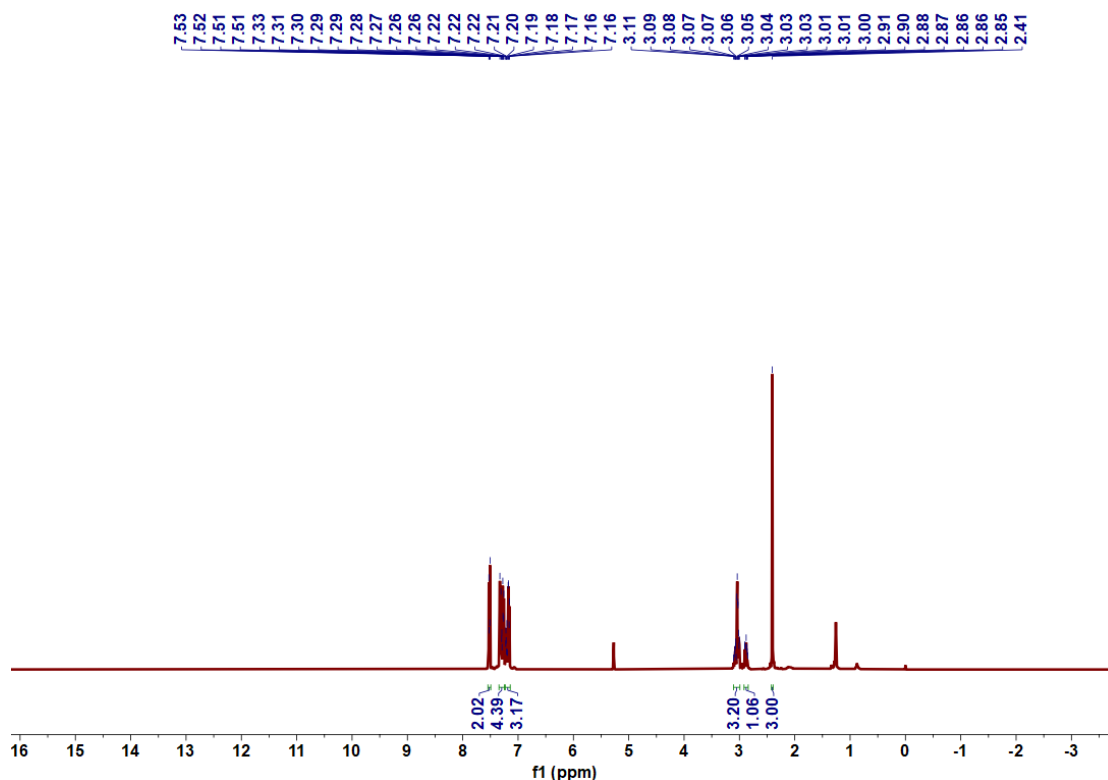


Fig. S69. ^1H NMR spectra of (2-([1,1'-biphenyl]-4-yl)ethyl)(p-tolyl)sulfane in CDCl_3 .

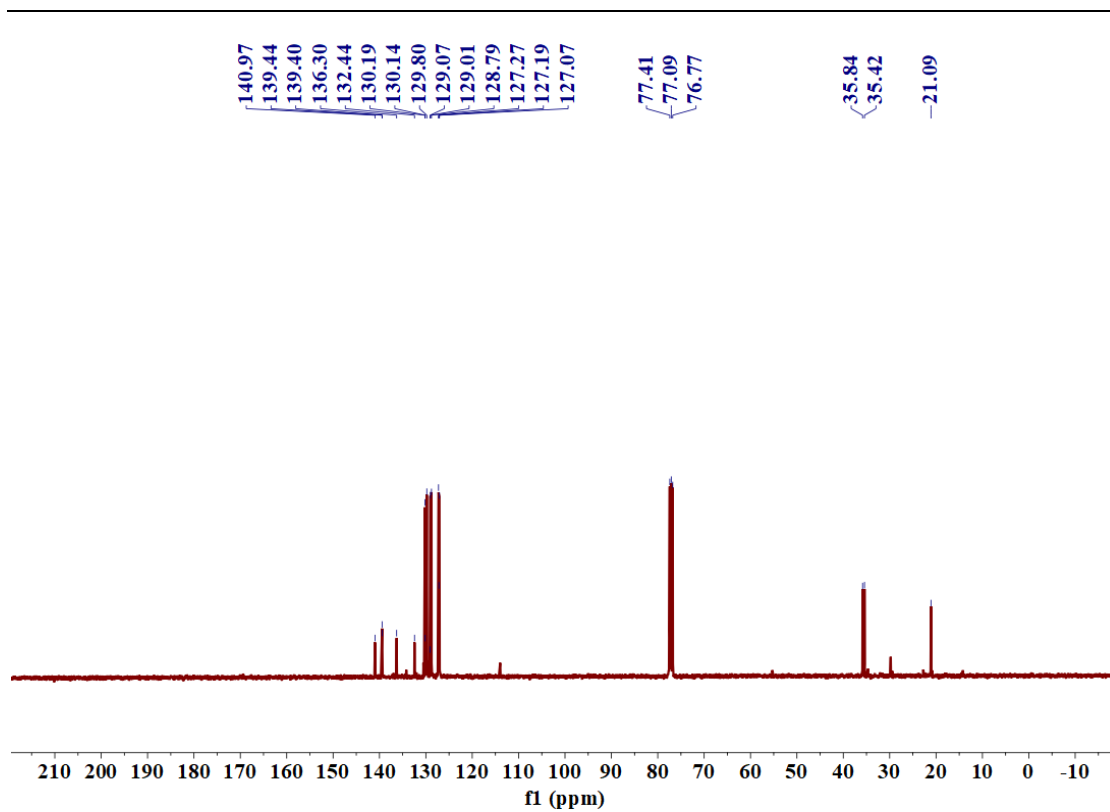
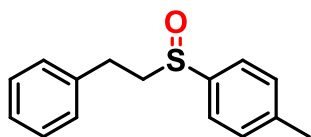


Fig. S70. ¹³C NMR spectra of (2-([1,1'-biphenyl]-4-yl)ethyl)(p-tolyl)sulfane in CDCl₃

4a. 1-methyl-4-(phenethylsulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=10:1) to give 4a as a colorless oil (41.9 mg, 86% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.55 - 7.49 (m, 2H), 7.35 - 7.25 (m, 4H), 7.23 - 7.14 (m, 3H), 3.11 - 2.99 (m, 3H), 2.92 - 2.84 (m, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 141.51, 140.32, 138.84, 129.99, 128.73, 128.55, 126.67, 124.08, 58.33, 28.21, 21.45.

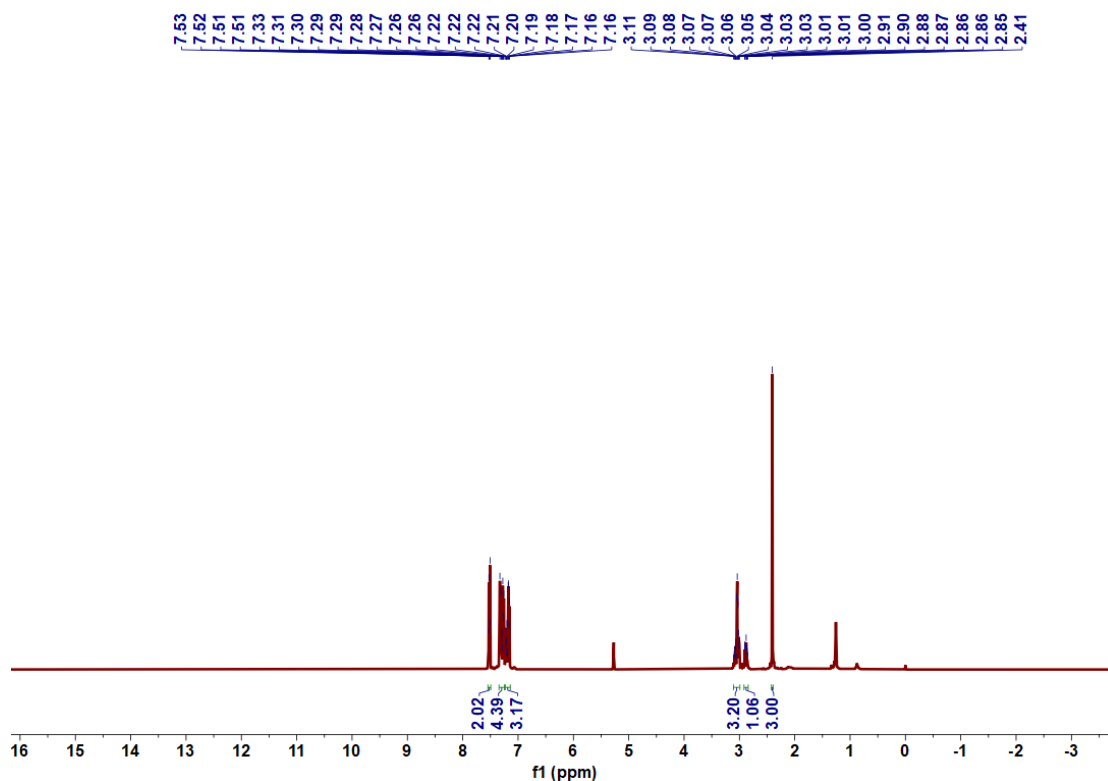


Fig. S71. ^1H NMR spectra of 1-methyl-4-(phenethylsulfinyl)benzene in CDCl_3 .

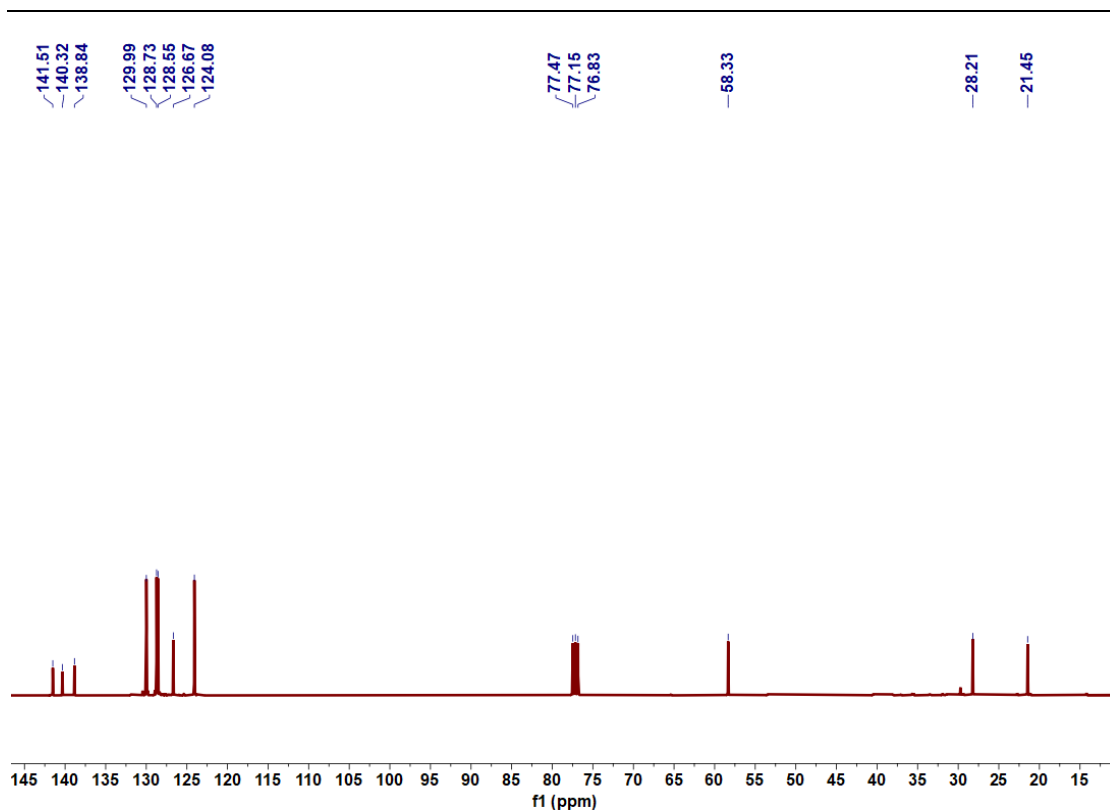
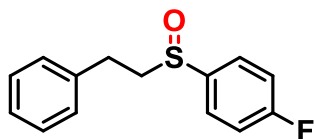


Fig. S72. ^{13}C NMR spectra of 1-methyl-4-(phenethylsulfinyl)benzene in CDCl_3

4b. (2-chlorophenethyl)(p-tolyl)sulfane



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=10:1) to give 4b as a white solid (40.7 mg, 82% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.66 - 7.57 (m, 2H), 7.31 - 7.23 (m, 2H), 7.23 - 7.09 (m, 5H), 3.11 - 2.96 (m, 3H), 2.87 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 165.49, 163.00, 139.08, 139.05, 138.55, 128.77, 128.54, 126.75, 126.38, 126.29, 116.71, 116.49, 58.39, 58.38, 28.11.

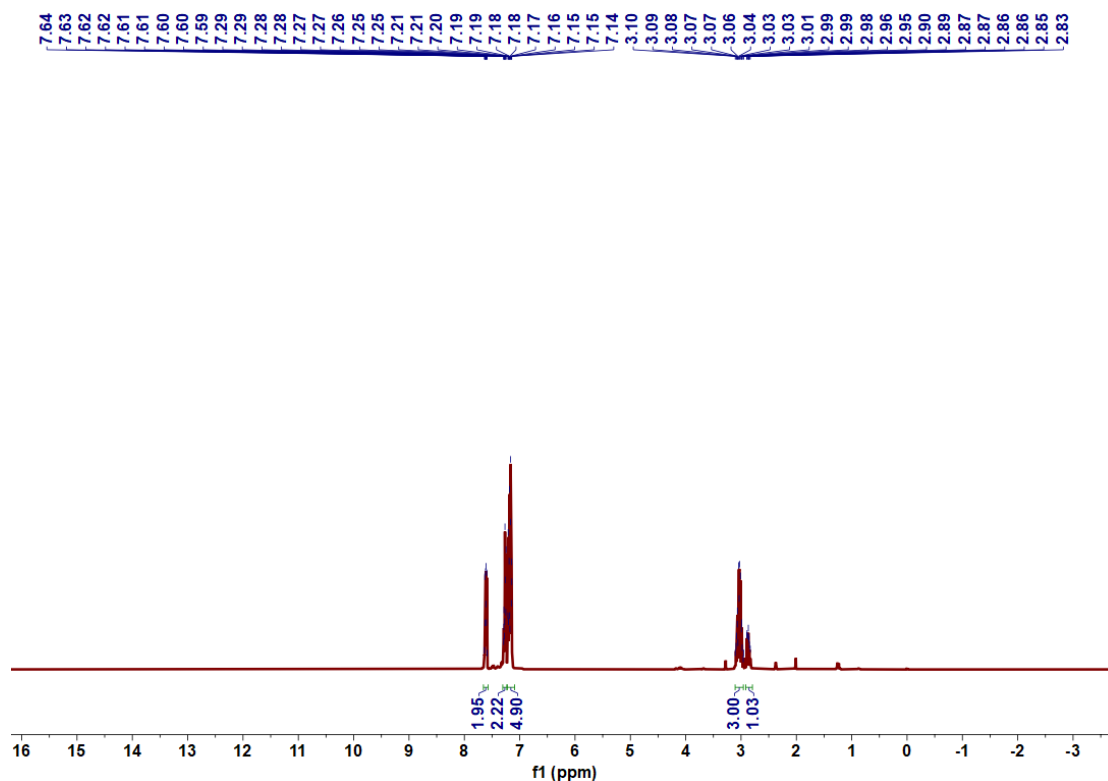


Fig. S73. ^1H NMR spectra of (2-chlorophenethyl)(p-tolyl)sulfane in CDCl_3 .

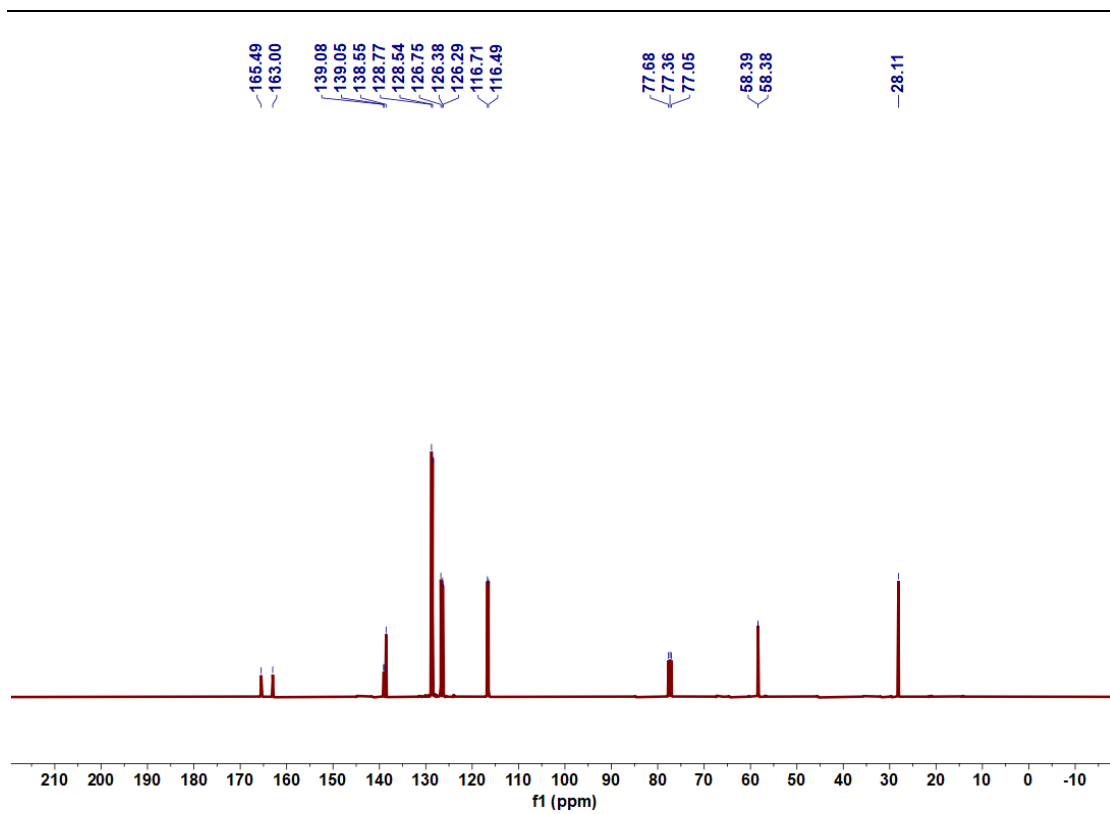
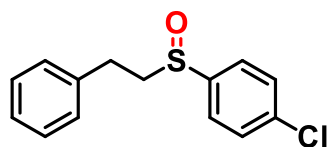


Fig. S74. ¹³C NMR spectra of (2-chlorophenethyl)(p-tolyl)sulfane e in CDCl₃

4c. 1-chloro-4-(phenethylsulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=10:1) to give 4c as a yellow solid (43.8 mg, 83% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.61 - 7.55 (m, 2H), 7.54 - 7.47 (m, 2H), 7.33 - 7.15 (m, 5H), 3.16 - 2.98 (m, 3H), 2.88 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 142.09, 138.46, 137.26, 129.60, 128.81, 128.55, 126.82, 125.47, 58.37, 28.08.

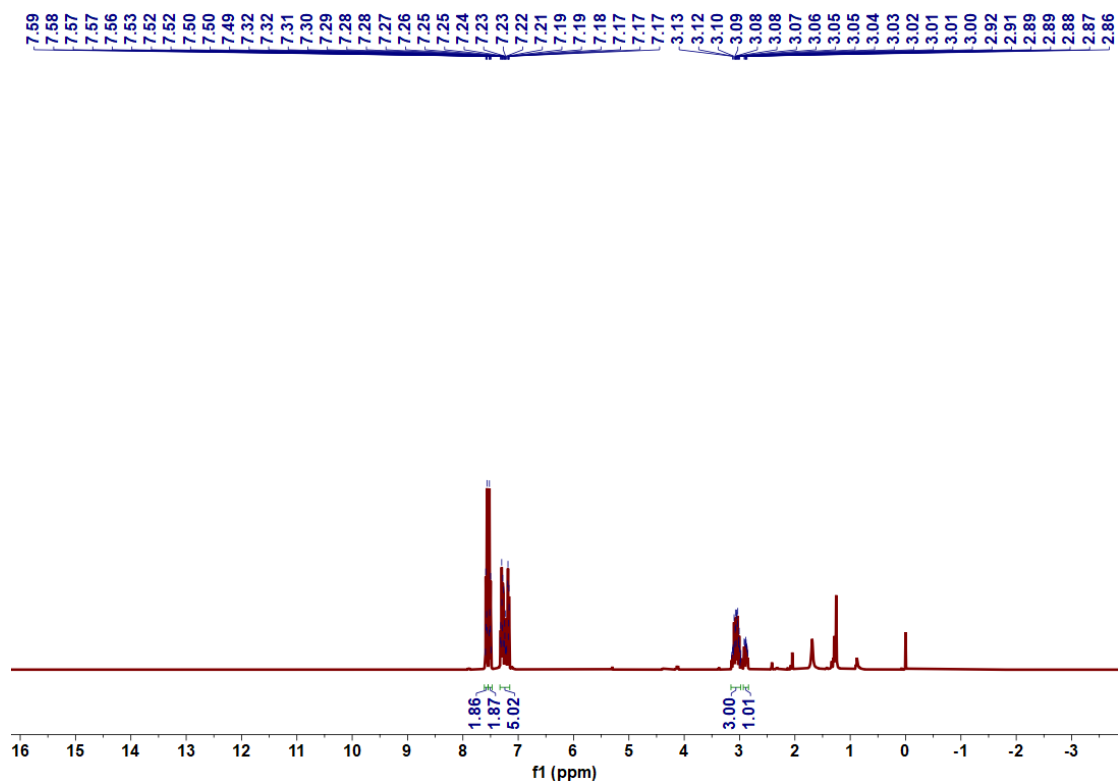


Fig. S75. ^1H NMR spectra of 1-chloro-4-(phenethylsulfinyl)benzene in CDCl_3 .

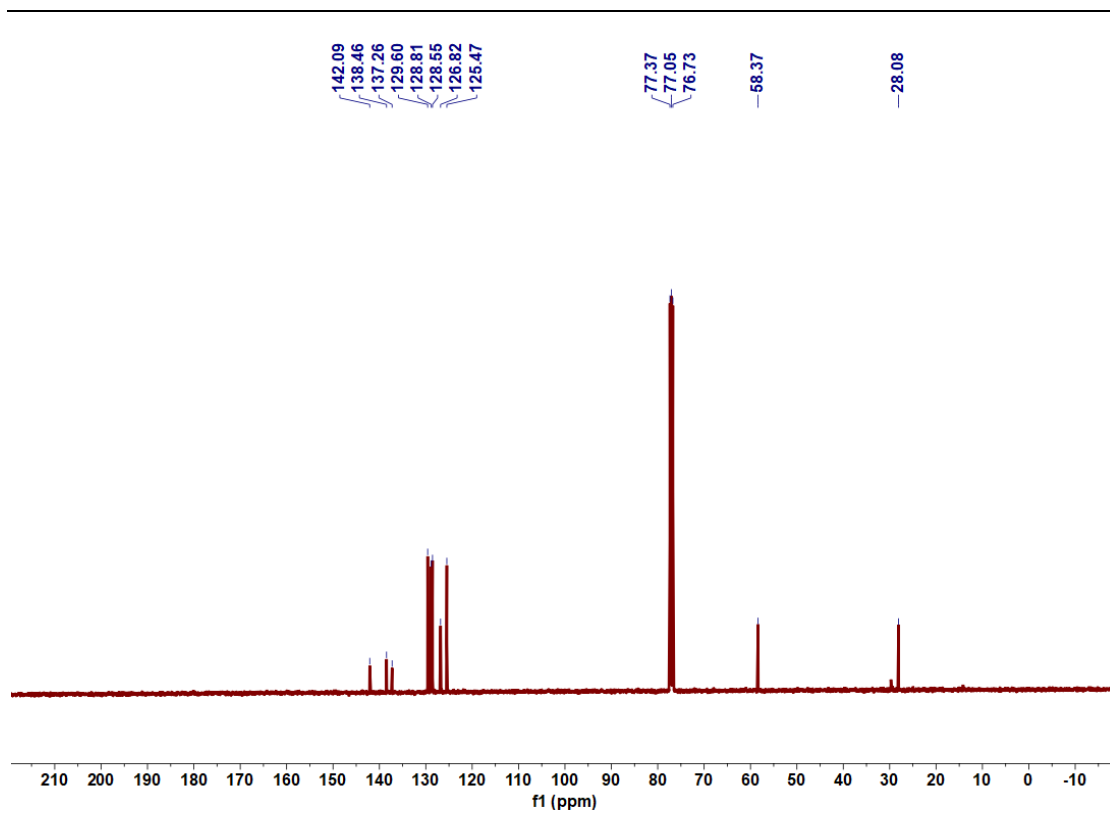
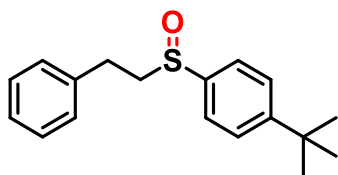


Fig. S76. ^{13}C NMR spectra of 1-chloro-4-(phenethylsulfinyl)benzene in CDCl_3

4d. 1-(tert-butyl)-4-(phenethylsulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=10:1) to give 4d as a white solid (50.3 mg, 88% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.59 - 7.51 (m, 4H), 7.28 (dd, $J = 7.9, 6.4$ Hz, 2H), 7.23 - 7.15 (m, 3H), 3.15 - 3.00 (m, 3H), 2.99 - 2.88 (m, 1H), 1.34 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 154.67, 140.25, 138.87, 128.73, 128.56, 126.67, 126.34, 123.92, 58.33, 35.01, 31.24, 28.36.

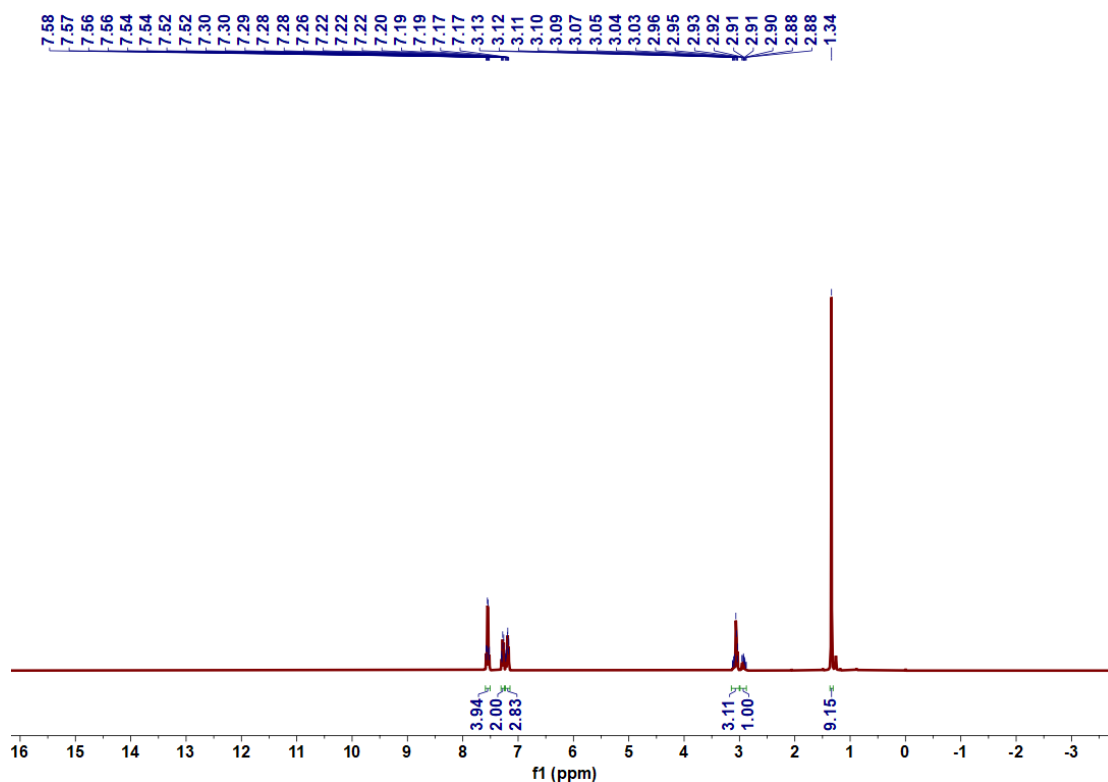


Fig. S77. ^1H NMR spectra of 1-(tert-butyl)-4-(phenethylsulfinyl)benzene in CDCl_3 .

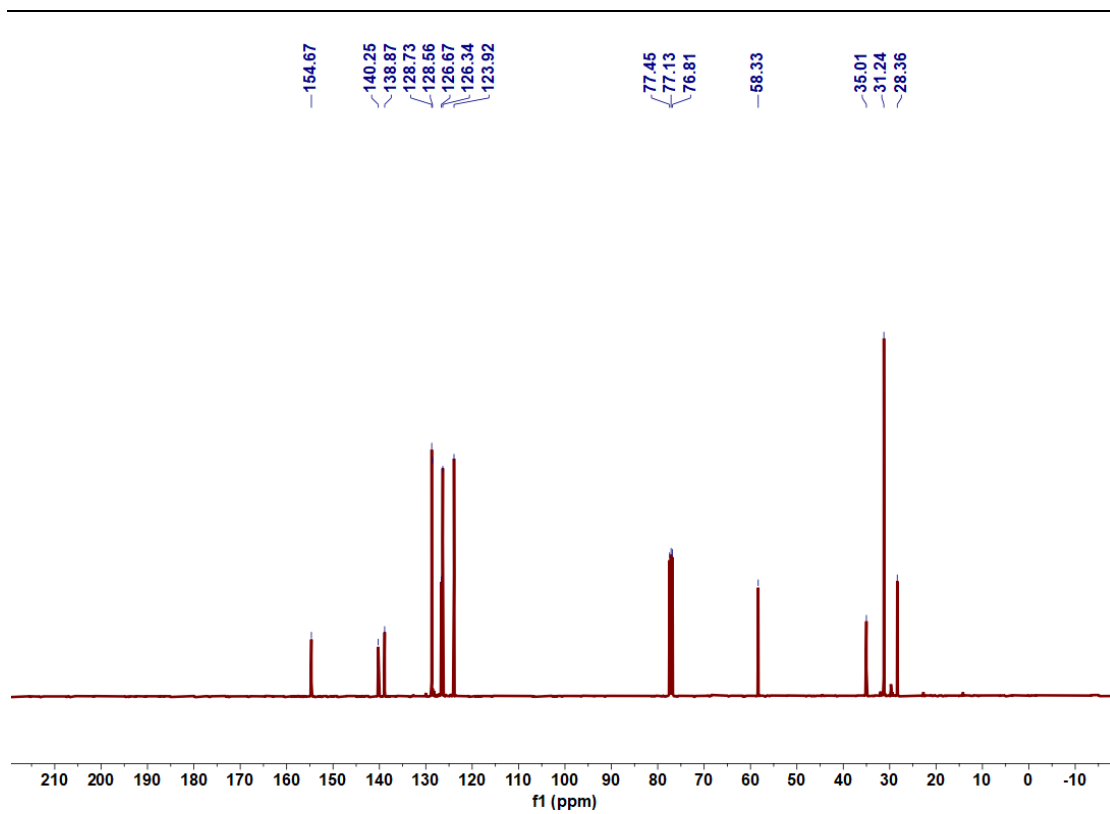
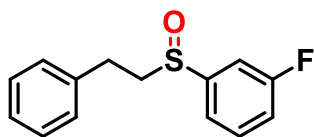


Fig. S78. ^{13}C NMR spectra of 1-(tert-butyl)-4-(phenethylsulfinyl)benzene in CDCl_3

4e. 1-fluoro-3-(phenethylsulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=10:1) to give **4e** as a white solid (38.7 mg, 78% yield).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49 (m, 1H), 7.38 (dd, $J = 17.2, 8.0$ Hz, 2H), 7.33 - 7.03 (m, 6H), 3.08 (m, 3H), 2.95 - 2.81 (m, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 164.35, 161.84, 146.34, 146.28, 138.46, 131.05, 130.97, 128.81, 128.57, 126.82, 119.66, 119.63, 118.26, 118.04, 111.47, 111.24, 58.29, 28.07.

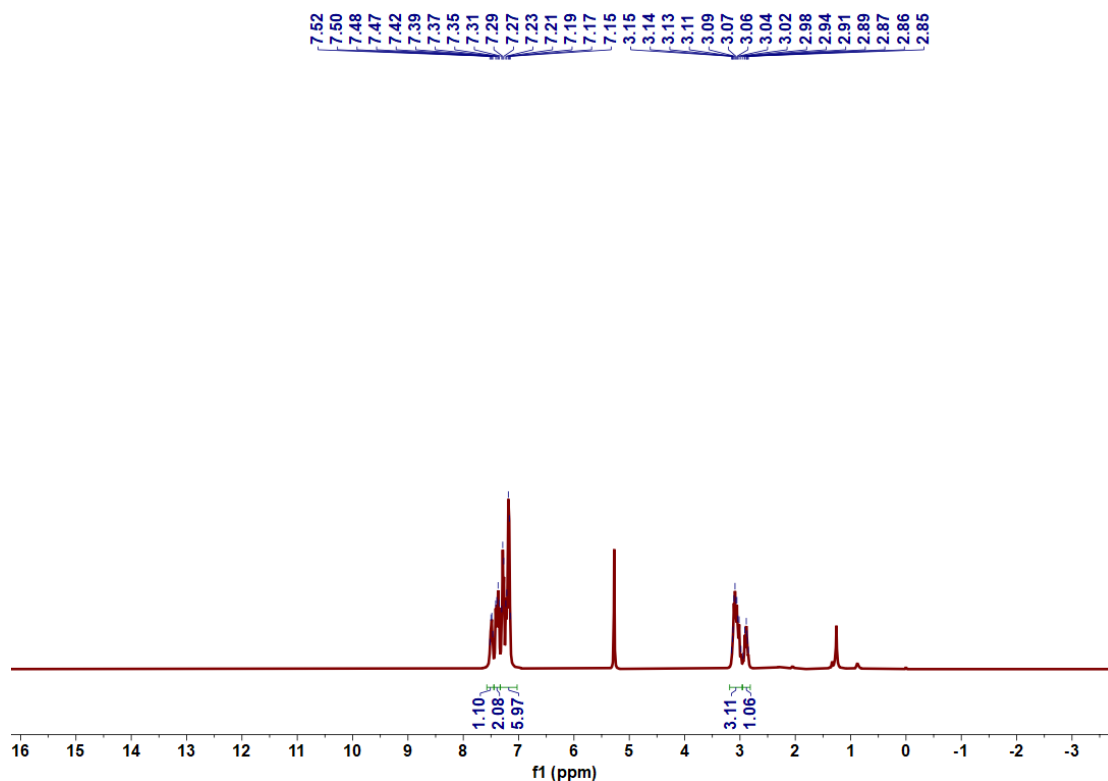


Fig. S79. $^1\text{H NMR}$ spectra of 1-fluoro-3-(phenethylsulfinyl)benzene in CDCl_3 .

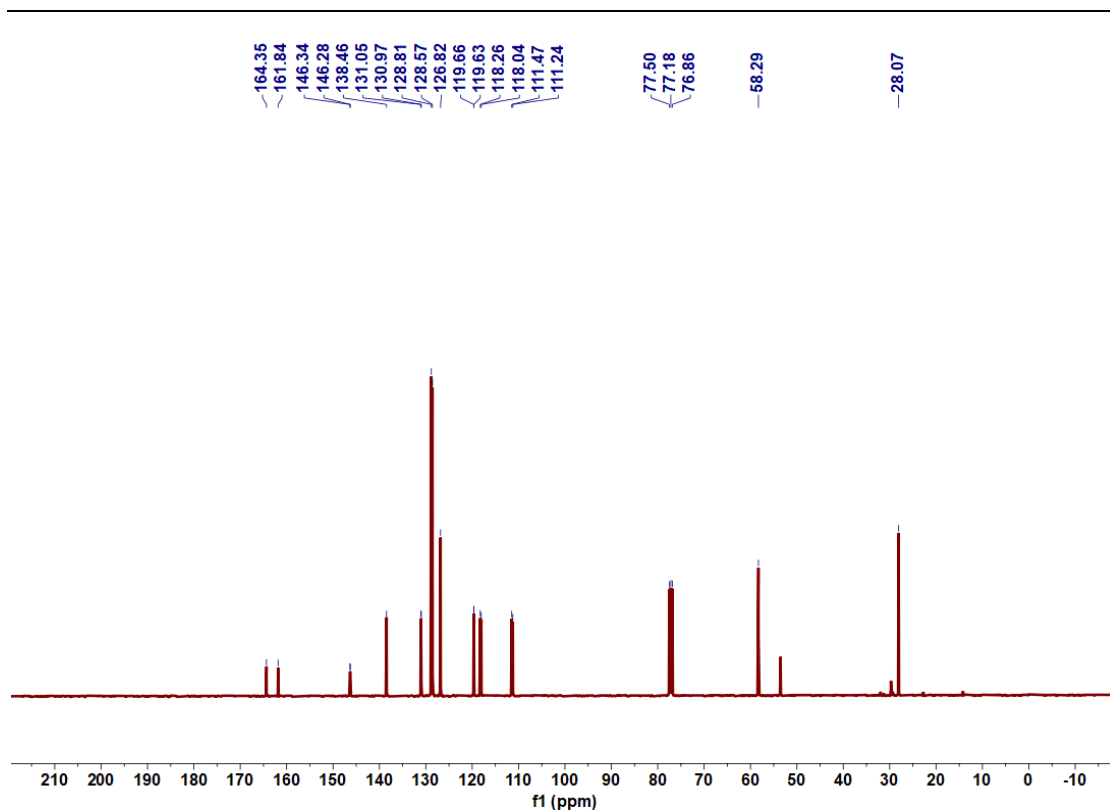
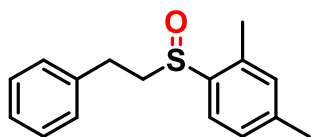


Fig. S80. ^{13}C NMR spectra of 1-fluoro-3-(phenethylsulfinyl)benzene in CDCl_3

4f. 2,4-dimethyl-1-(phenethylsulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=10:1) to give 4f as a colorless oil (43.9 mg, 85% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 8.0$ Hz, 1H), 7.31 - 7.15 (m, 6H), 7.00 (s, 1H), 3.16 - 2.89 (m, 4H), 2.35 (s, 3H), 2.26 (s, 3H)

^{13}C NMR (101 MHz, CDCl_3) δ 141.09, 138.95, 138.53, 134.20, 131.54, 128.71, 128.53, 127.93, 126.64, 124.01, 56.45, 28.44, 21.25, 18.08.

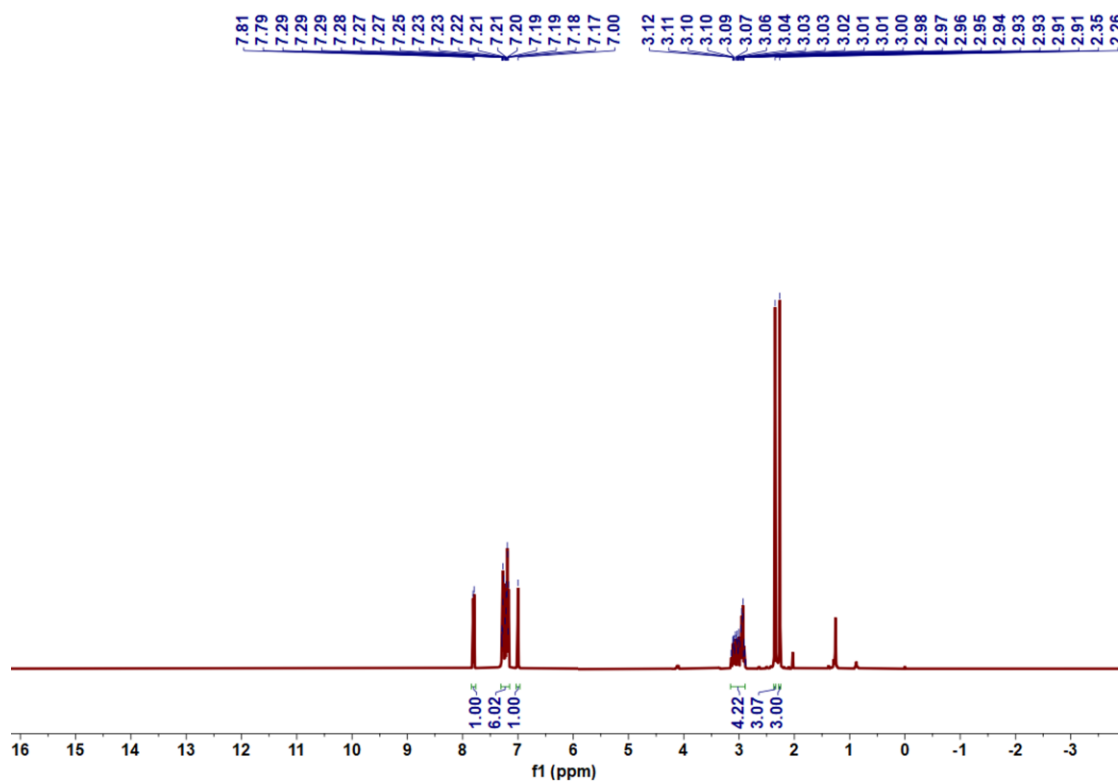


Fig. S81. ^1H NMR spectra of 2,4-dimethyl-1-(phenethylsulfinyl)benzene in CDCl_3 .

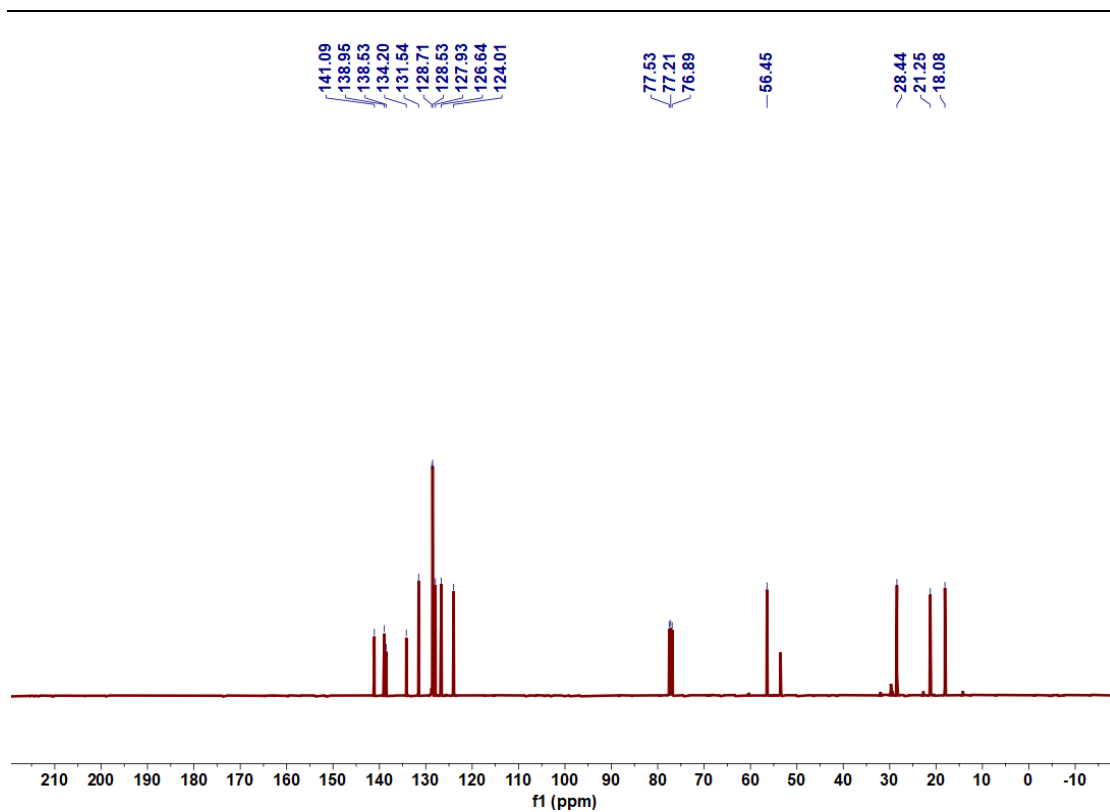
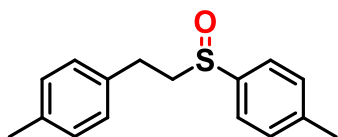


Fig. S82. ^{13}C NMR spectra of 2,4-dimethyl-1-(phenethylsulfinyl)benzene in CDCl_3

4g. 1-methyl-4-((4-methylphenethyl)sulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=10:1) to give 4g as a white solid (44.9 mg, 87% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 7.9$ Hz, 2H), 7.11 - 7.03 (m, 4H), 3.06 - 2.97 (m, 3H), 2.90 - 2.80 (m, 1H), 2.40 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 141.46, 140.32, 136.20, 135.69, 129.97, 129.39, 128.43, 124.07, 58.47, 27.78, 21.43, 21.04.

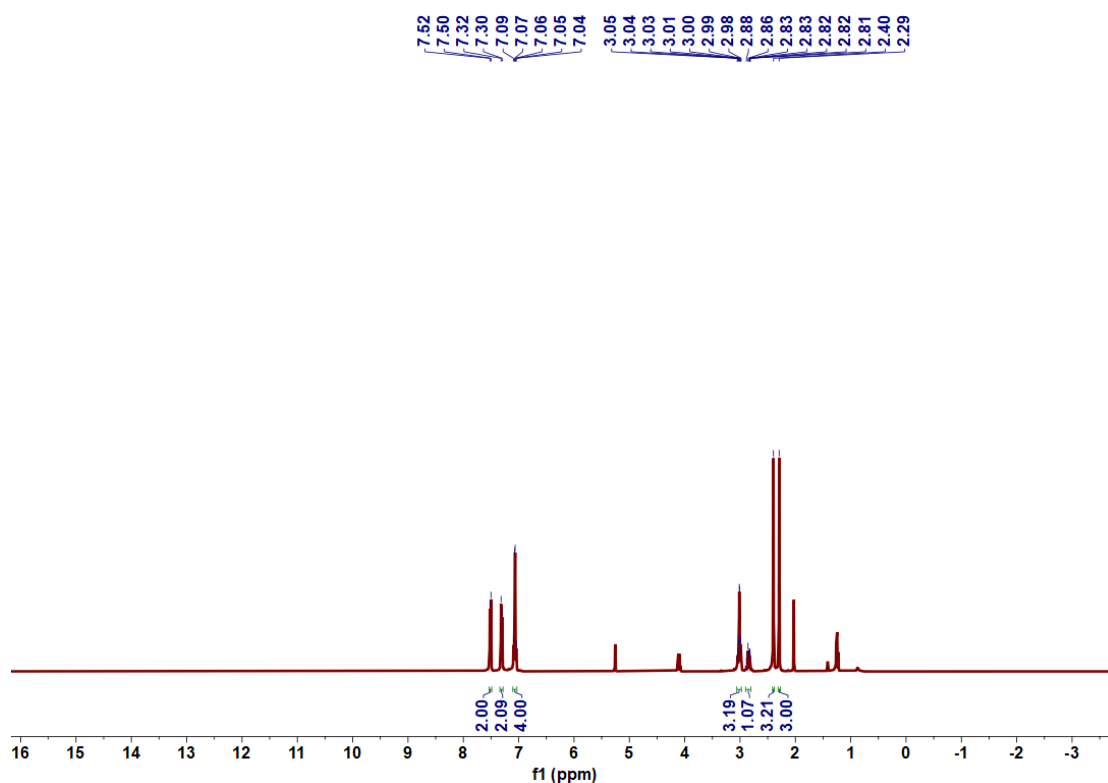


Fig. S83. ^1H NMR spectra of 1-methyl-4-((4-methylphenethyl)sulfinyl)benzene in CDCl_3 .

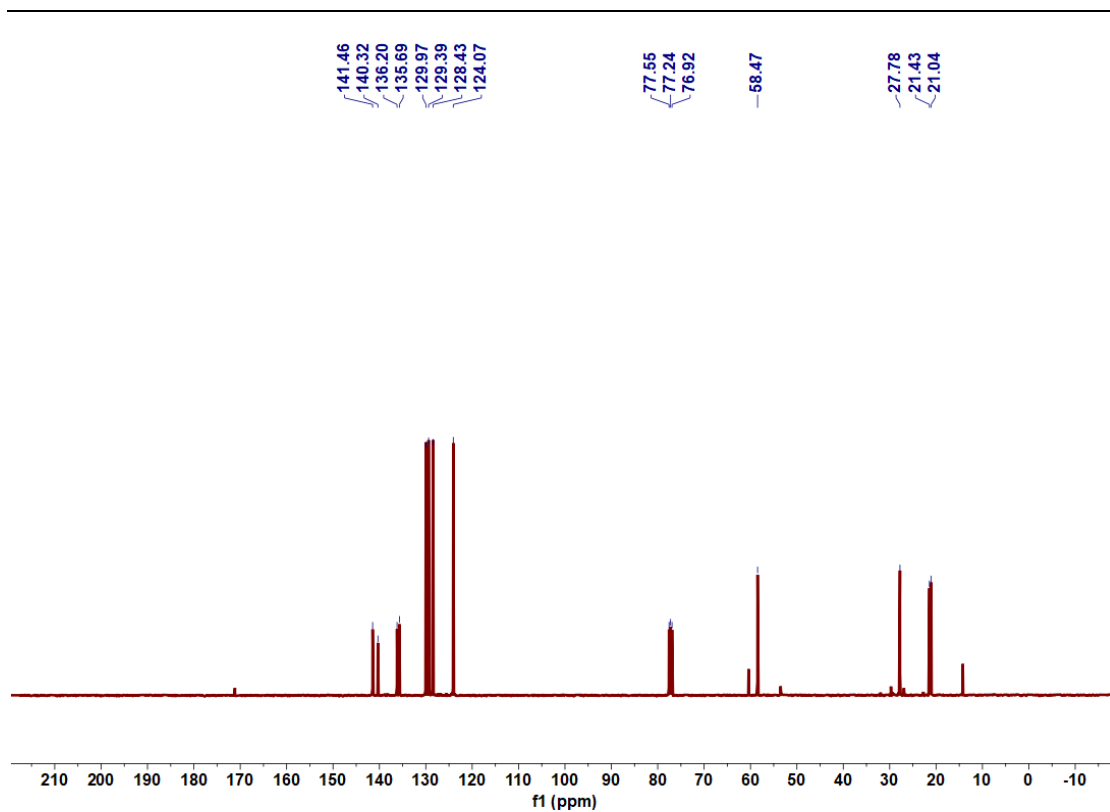
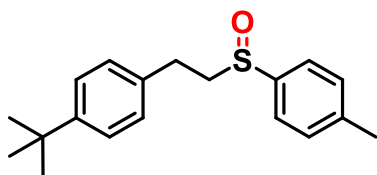


Fig. S84. ^{13}C NMR spectra of 1-methyl-4-((4-methylphenethyl)sulfinyl)benzene in CDCl_3

4h. 1-(tert-butyl)-4-(2-(p-tolylsulfinyl)ethyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=10:1) to give 4h as a white solid (54 mg, 90% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.55 - 7.49 (m, 2H), 7.31 (dd, $J = 8.4, 6.9$ Hz, 4H), 7.14 - 7.08 (m, 2H), 3.08 - 2.99 (m, 3H), 2.92 - 2.84 (m, 1H), 2.41 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 149.56, 141.47, 140.36, 135.75, 129.96, 128.20, 125.62, 124.09, 58.37, 34.44, 31.36, 27.70, 21.45.

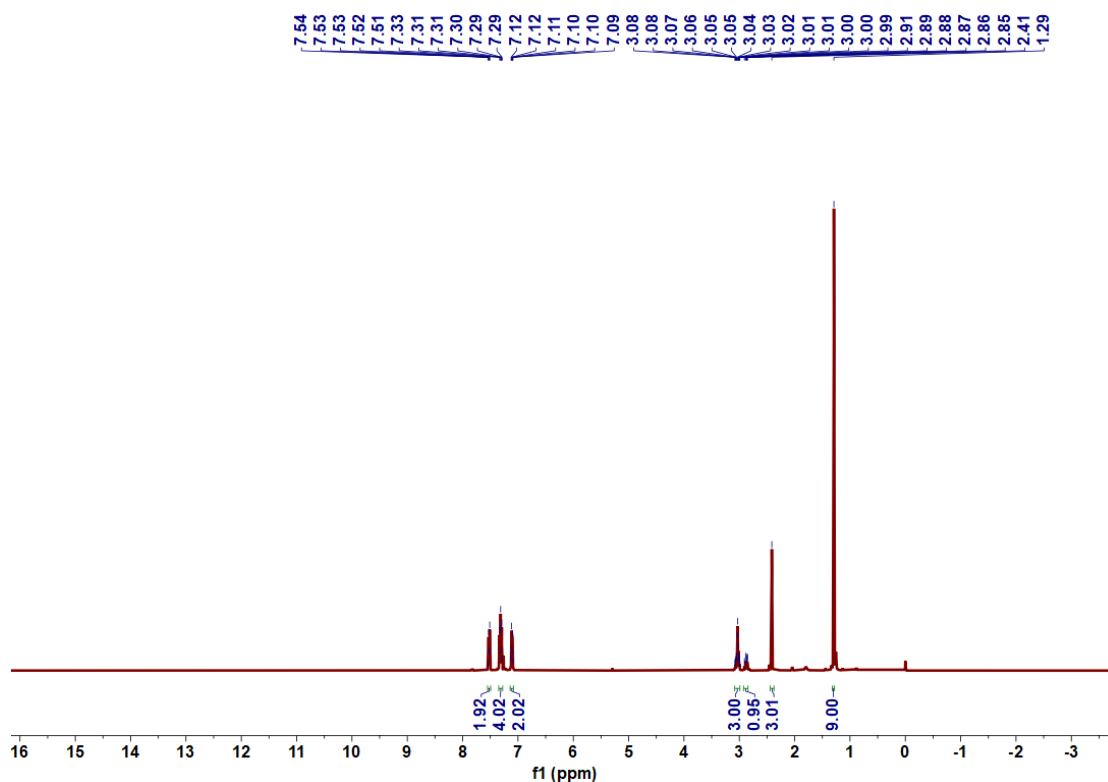


Fig. S85. ^1H NMR spectra of 1-(tert-butyl)-4-(2-(p-tolylsulfinyl)ethyl)benzene in CDCl_3 .

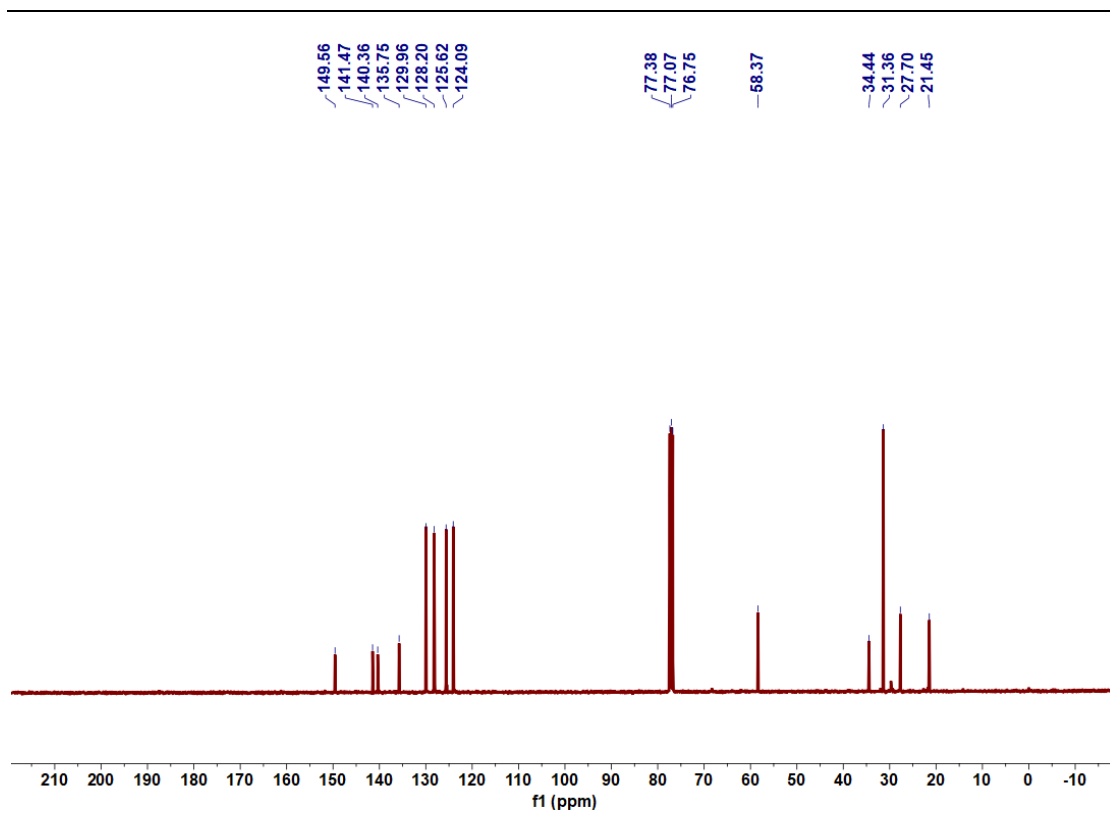
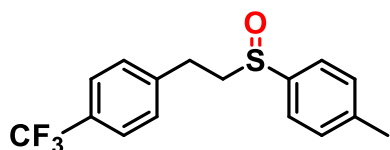


Fig. S86. ^{13}C NMR spectra of 1-(tert-butyl)-4-(2-(p-tolylsulfinyl)ethyl)benzene in CDCl_3

4i 1-methyl-4-((4-(trifluoromethyl)phenethyl)sulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=10:1) to give **4i** as a yellow solid (46.1 mg, 74% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.53 (dd, $J = 8.1, 5.5$ Hz, 4H), 7.31 (dd, $J = 15.8, 8.0$ Hz, 4H), 3.20 - 3.00 (m, 3H), 3.00 - 2.89 (m, 1H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 143.00, 142.98, 141.68, 139.89, 130.02, 128.93, 125.65, 125.61, 125.57, 125.54, 123.99, 57.53, 27.81, 21.37, 21.01.

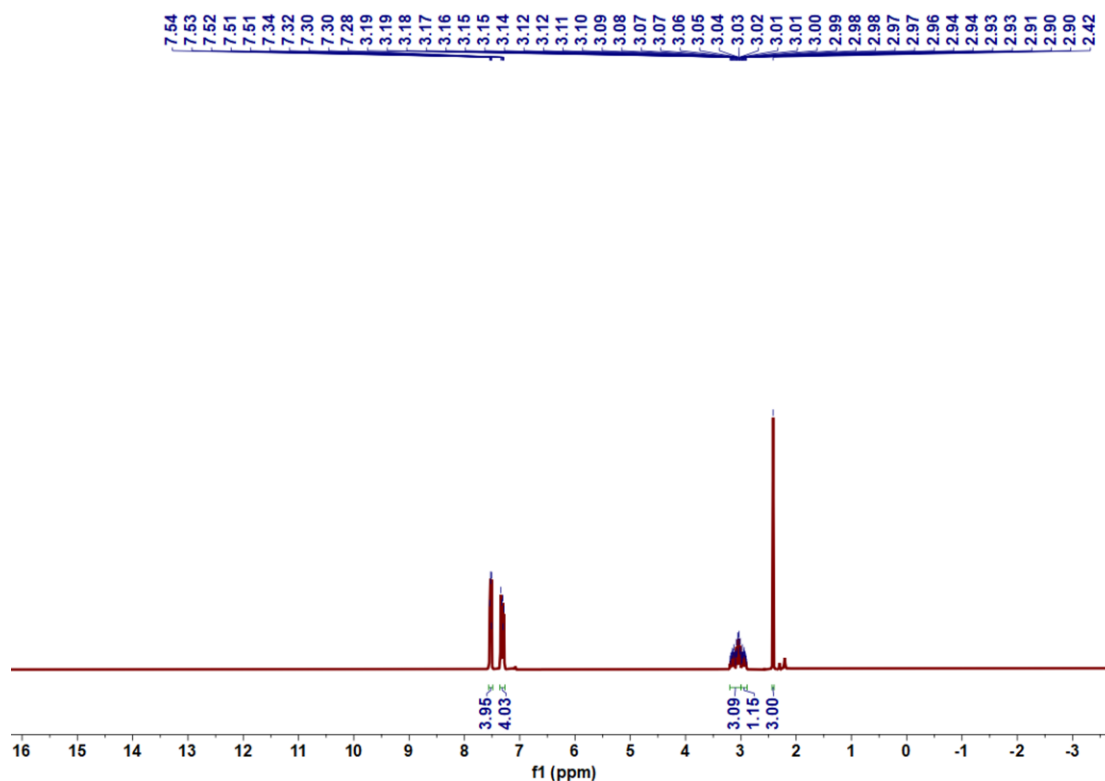


Fig. S87. ^1H NMR spectra of 1-methyl-4-((4-(trifluoromethyl)phenethyl)sulfinyl)benzene in CDCl_3 .

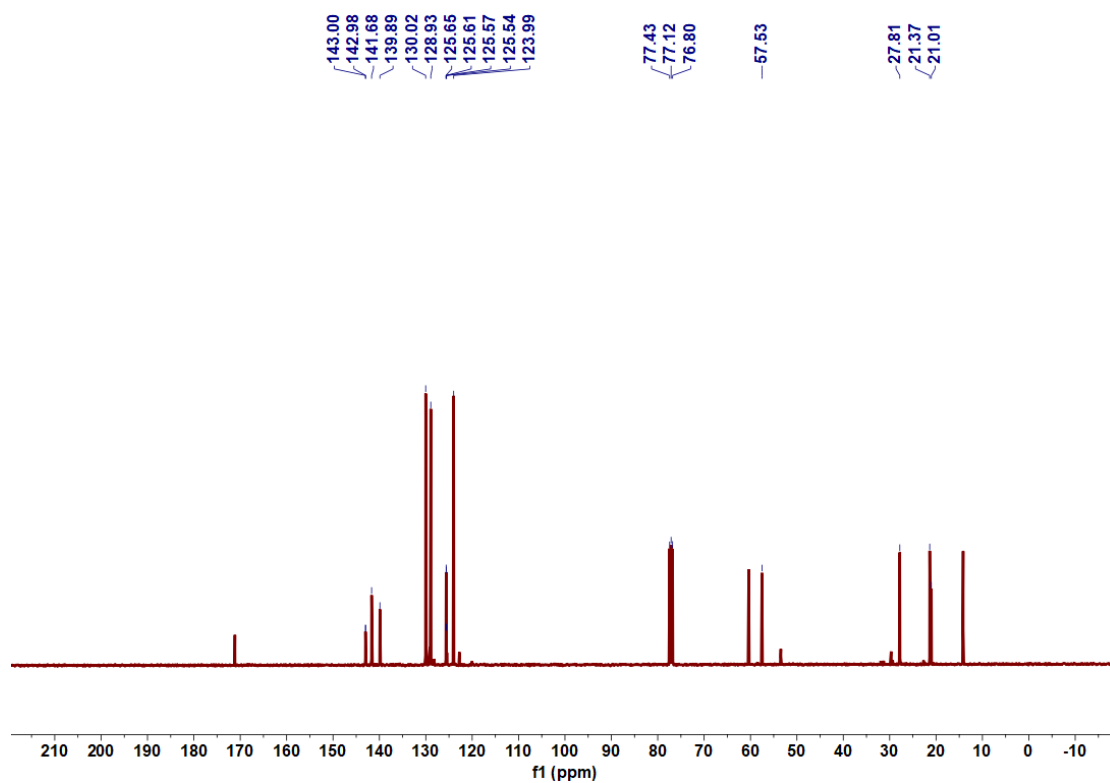
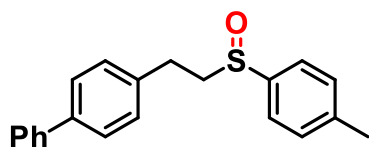


Fig. S88. ^{13}C NMR spectra of 1-methyl-4-((4-(trifluoromethyl)phenethyl)sulfinyl)benzene in CDCl_3 .

4j. 4-(2-(p-tolylsulfinyl)ethyl)-1,1'-biphenyl



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=10:1) to give 4j as a white solid (48.6 mg, 76% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.58 - 7.49 (m, 6H), 7.43 (m, 2H), 7.37 - 7.29 (m, 3H), 7.25 (d, $J = 7.2$ Hz, 2H), 3.08 (m, 3H), 2.93 (t, $J = 8.6$ Hz, 1H), 2.42 (d, $J = 2.6$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 141.57, 140.71, 139.66, 137.89, 130.02, 128.99, 128.78, 127.45, 127.27, 127.01, 124.10, 58.27, 27.85, 21.46.

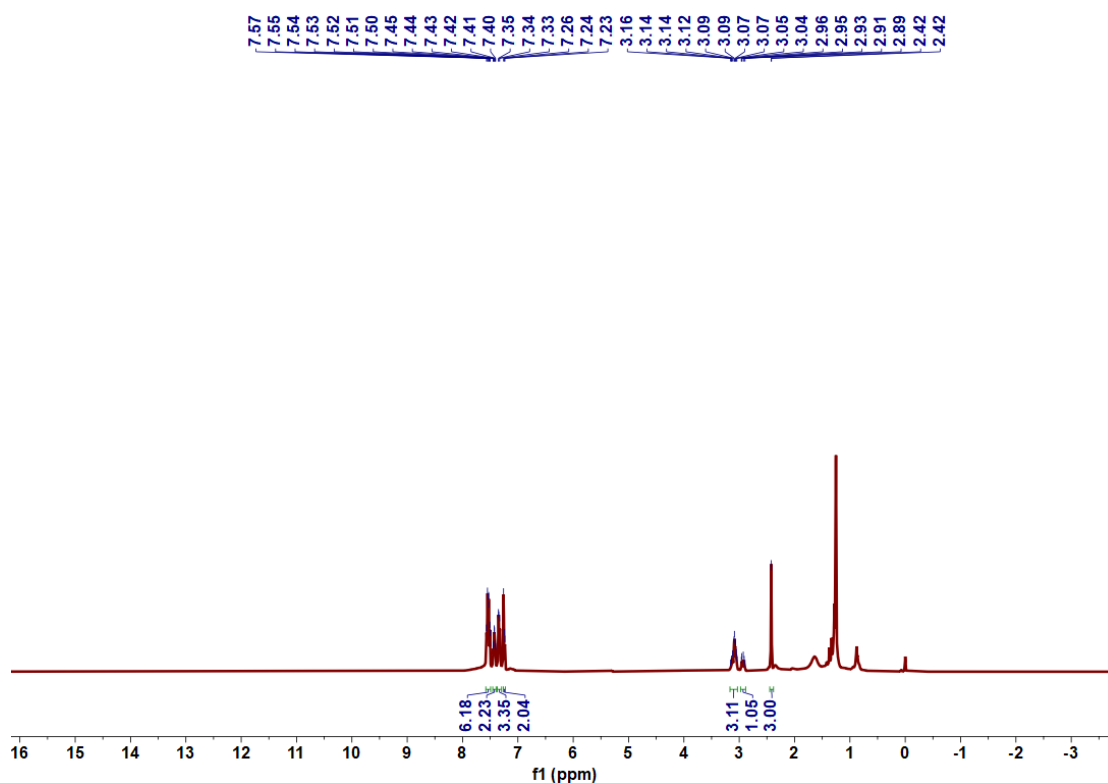


Fig. S89. ^1H NMR spectra of 4-(2-(p-tolylsulfinyl)ethyl)-1,1'-biphenyl in CDCl_3 .

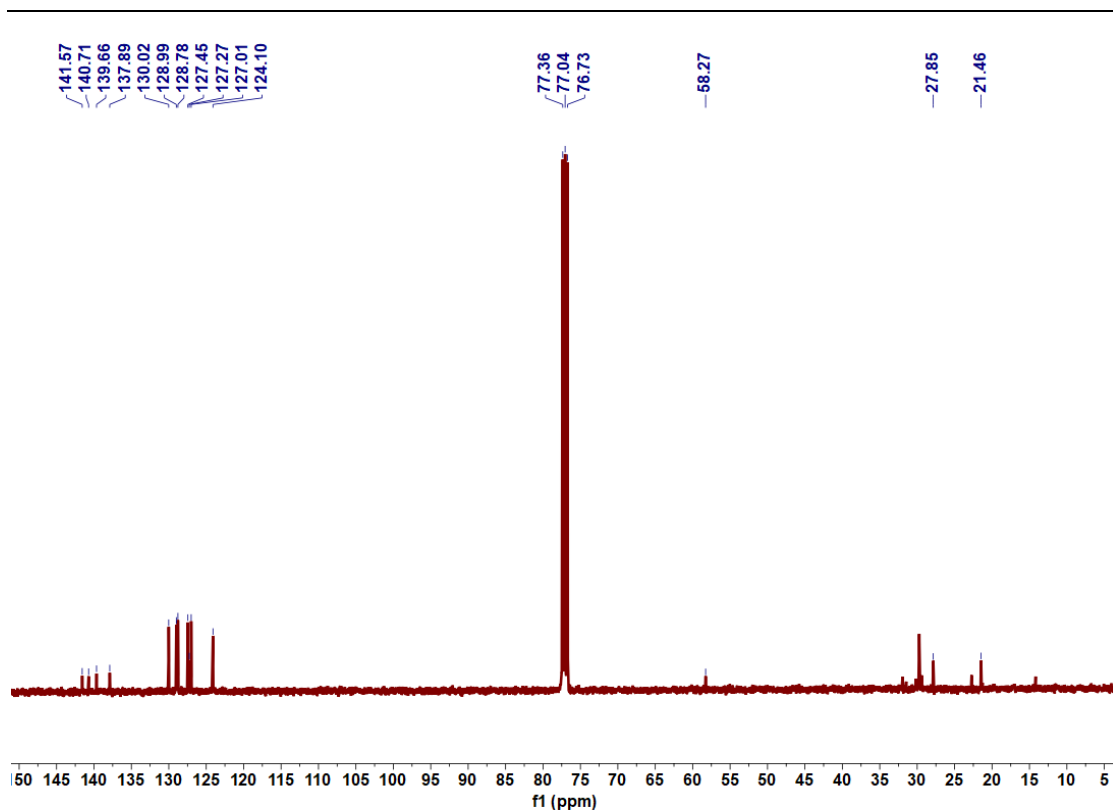
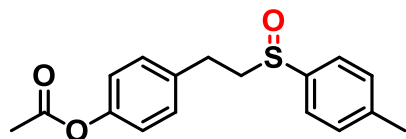


Fig. S90. ^{13}C NMR spectra of 4-(2-(p-tolylsulfinyl)ethyl)-1,1'-biphenyl in CDCl_3 .

4k. 4-(2-(p-tolylsulfinyl)ethyl)phenyl acetate



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=8:1) to give 4k as a colorless oil (43.5 mg, 72% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.99 - 7.93 (m, 2H), 7.55 - 7.50 (m, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.25 (d, $J = 8.2$ Hz, 2H), 3.90 (s, 3H), 3.18 - 3.00 (m, 3H), 2.92 (m, 1H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 166.86, 144.24, 141.69, 139.95, 130.05, 130.03, 128.62, 124.04, 57.61, 52.13, 28.07, 21.45.

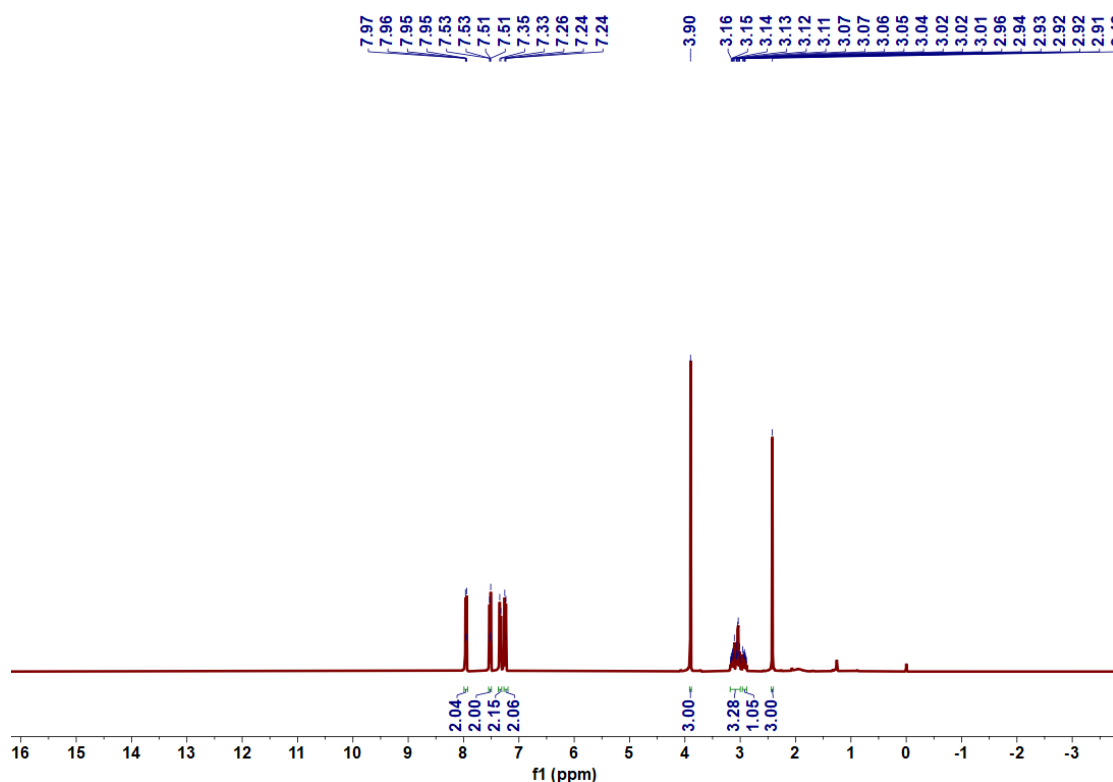


Fig. S91. ^1H NMR spectra of 4-(2-(p-tolylsulfinyl)ethyl)phenyl acetate in CDCl_3 .

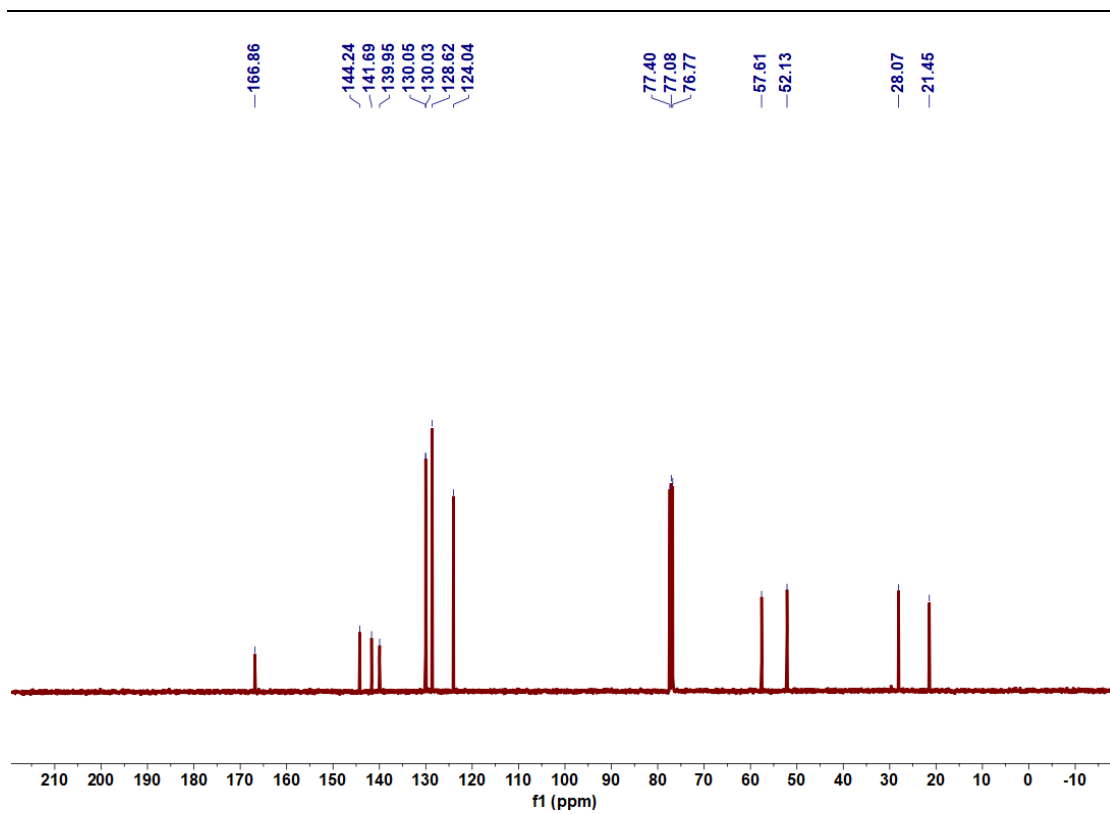
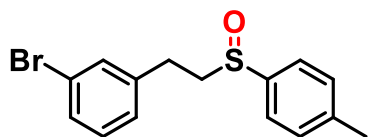


Fig. S92. ^{13}C NMR spectra of 4-(2-(p-tolylsulfinyl)ethyl)phenyl acetate in CDCl_3 .

4l. 1-bromo-3-(2-(p-tolylsulfinyl)ethyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=10:1) to give 4l as a white solid (51 mg, 79% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 7.9$ Hz, 2H), 7.37 - 7.28 (m, 4H), 7.14 (m, 2H), 3.03 (m, 3H), 2.88 - 2.80 (m, 1H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 141.70, 141.15, 139.93, 131.57, 130.29, 130.05, 129.82, 127.27, 124.05, 122.69, 57.74, 27.68, 21.46.

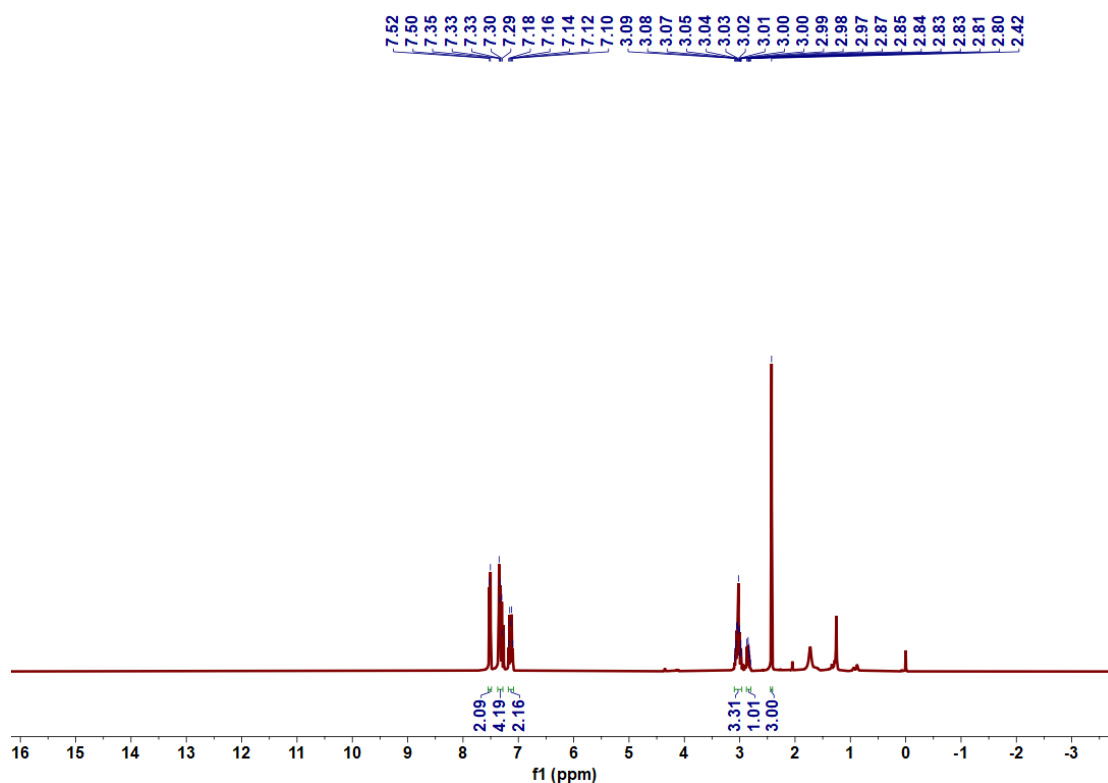


Fig. S93. ^1H NMR spectra of 1-bromo-3-(2-(p-tolylsulfinyl)ethyl)benzene in CDCl_3 .

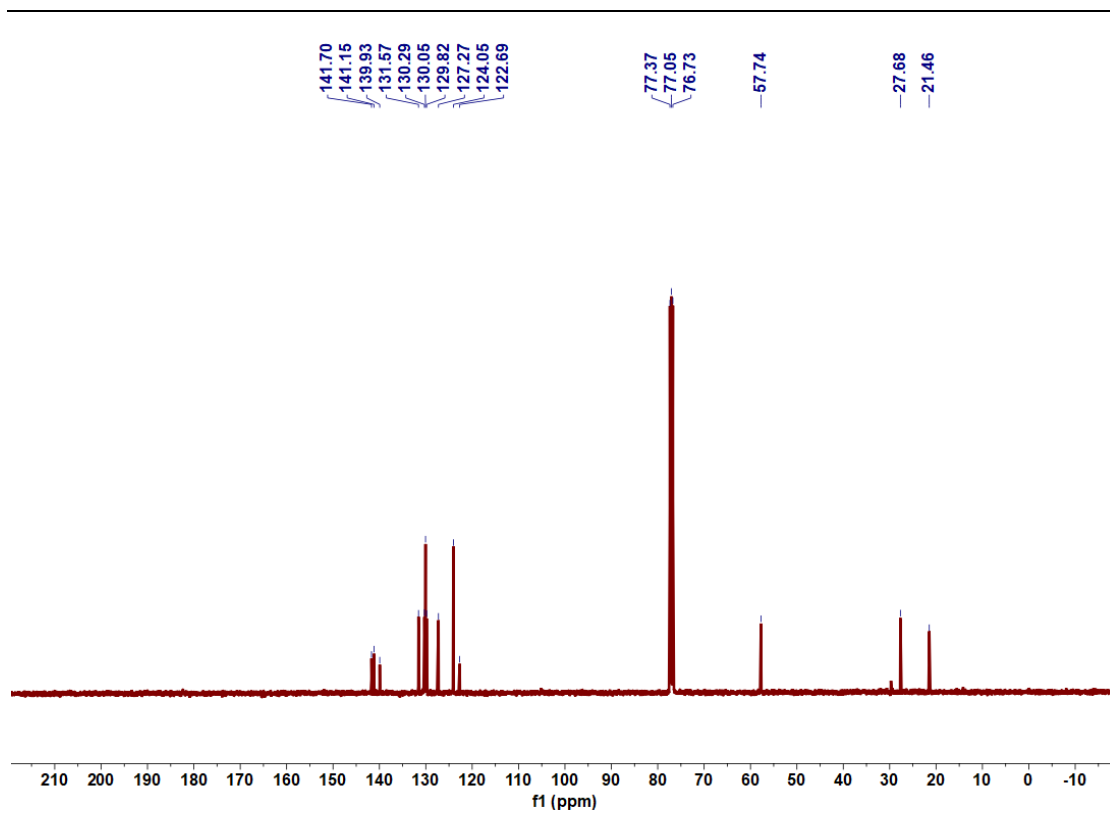
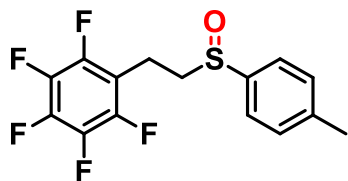


Fig. S94. ^{13}C NMR spectra of 1-bromo-3-(2-(p-tolylsulfinyl)ethyl)benzene in CDCl_3 .

4m. 1,2,3,4,5-pentafluoro-6-(2-(p-tolylsulfinyl)ethyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=10:1) to give 4m as a yellow solid (46.1 mg, 69% yield).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.52 (d, $J = 7.9$ Hz, 2H), 7.34 (d, $J = 7.9$ Hz, 2H), 3.23 - 2.89 (m, 4H), 2.43 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 141.91, 139.38, 130.07, 124.03, 54.38, 21.44, 15.20.

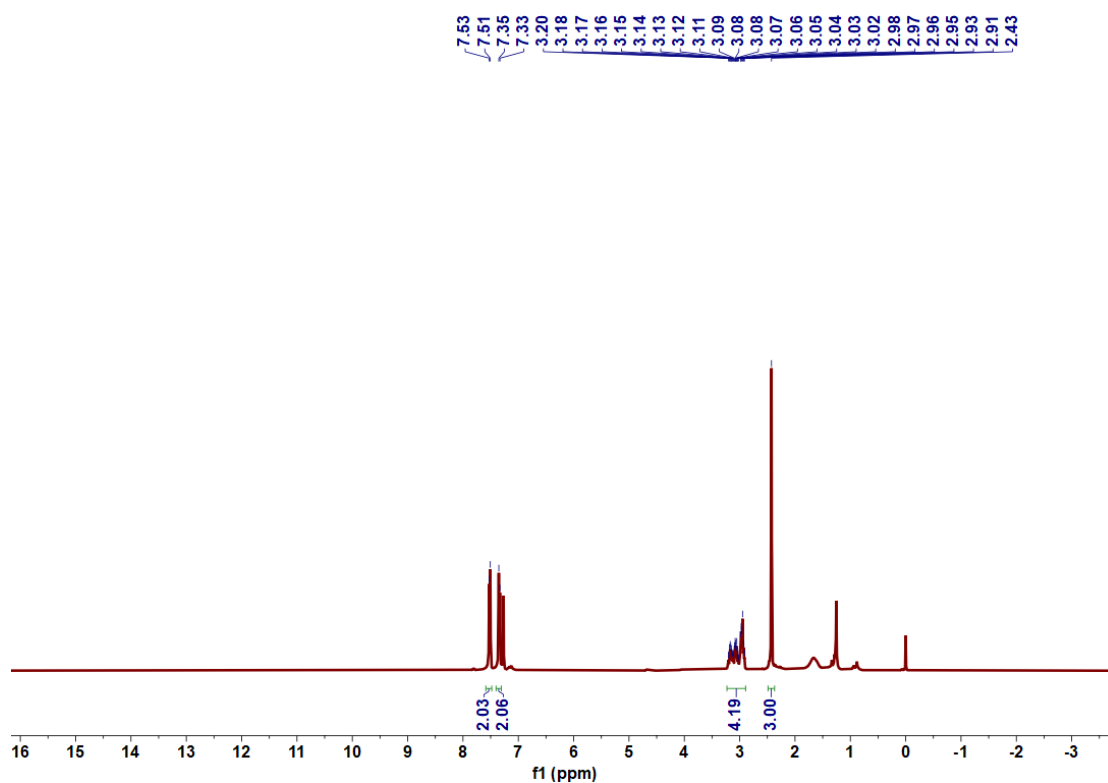


Fig. S95. $^1\text{H NMR}$ spectra of 1,2,3,4,5-pentafluoro-6-(2-(p-tolylsulfinyl)ethyl)benzene in CDCl_3 .

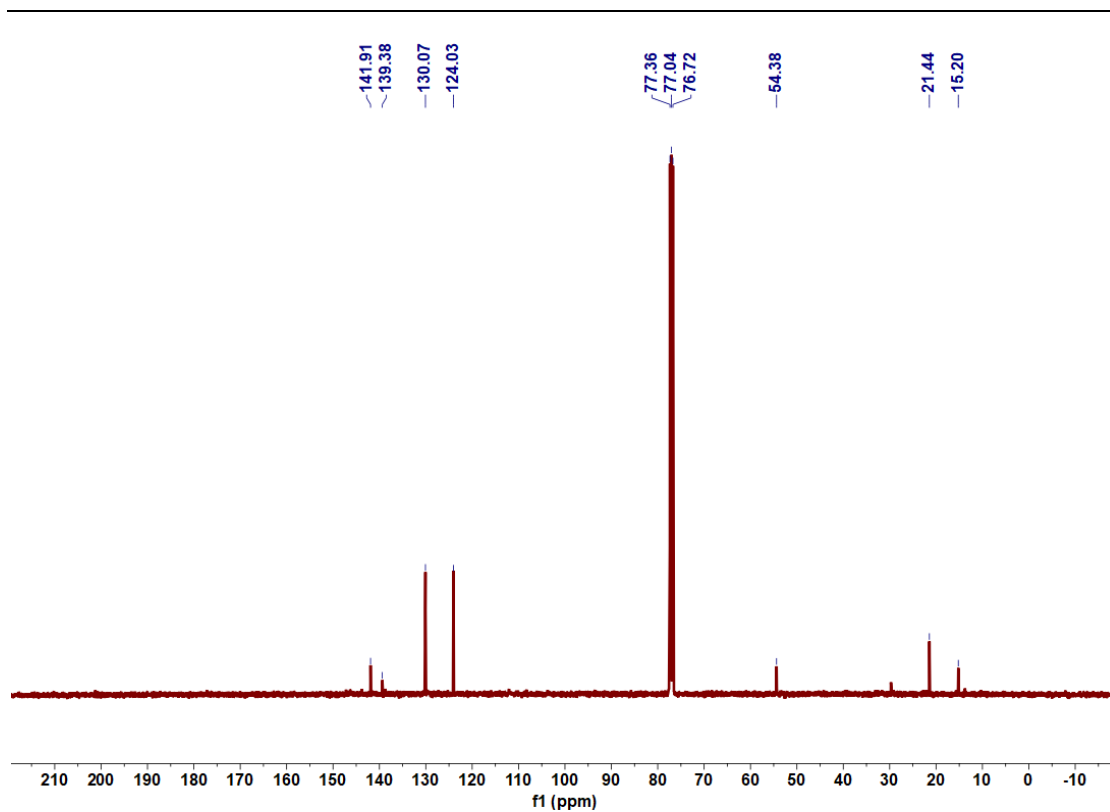
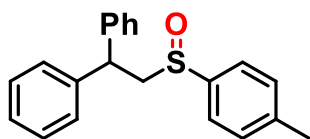


Fig. S96. ^{13}C NMR spectra of 1,2,3,4,5-pentafluoro-6-(2-(p-tolylsulfinyl)ethyl)benzene in CDCl_3 .

4n. (2-(p-tolylsulfinyl)ethane-1,1-diyl)dibenzene



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=10:1) to give **4n** as a white solid (46.7 mg, 73% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.49 (dd, $J = 16.0, 8.0$ Hz, 2H), 7.44 - 7.15 (m, 12H), 4.54 (dd, $J = 10.7, 5.3$ Hz, 1H), 3.67 - 3.32 (m, 3H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 142.42, 142.19, 141.75, 141.48, 141.05, 140.51, 130.26, 130.08, 128.96, 128.79, 128.58, 128.36, 128.27, 127.74, 127.65, 127.48, 127.24, 126.94, 126.68, 125.68, 124.15, 124.11, 64.72, 45.51, 21.52, 21.51.

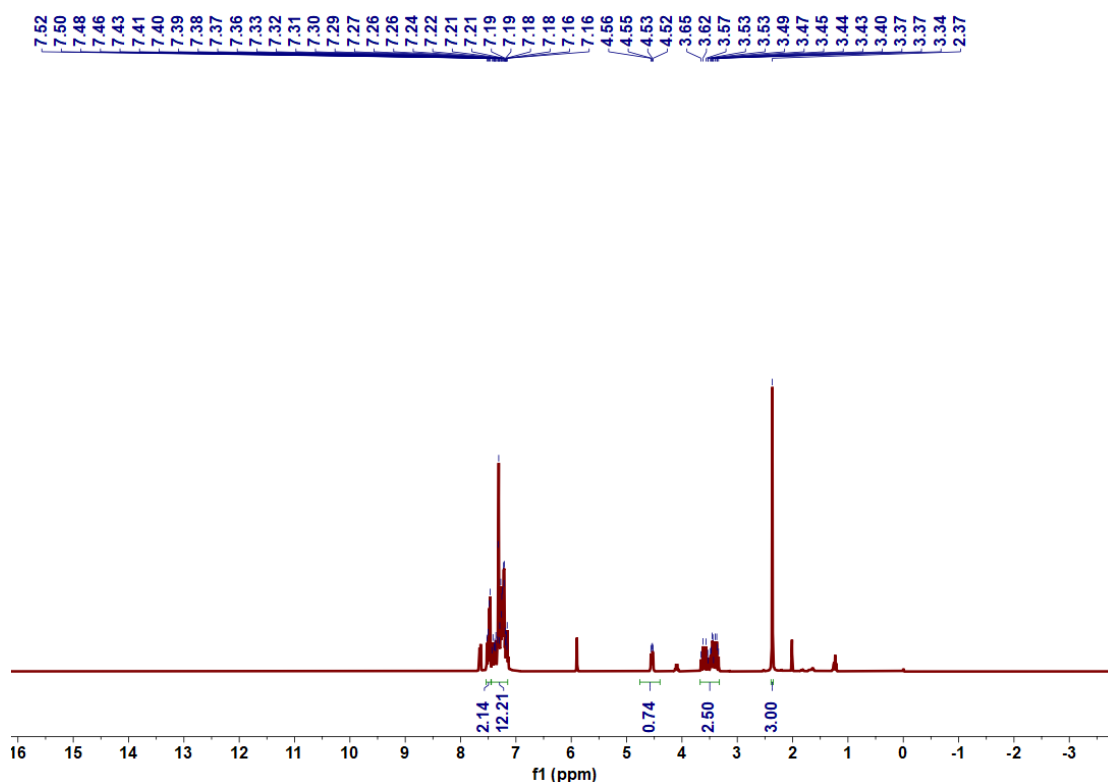


Fig. S97. ^1H NMR spectra of (2-(p-tolylsulfinyl)ethane-1,1-diyl)dibenzene in CDCl_3 .

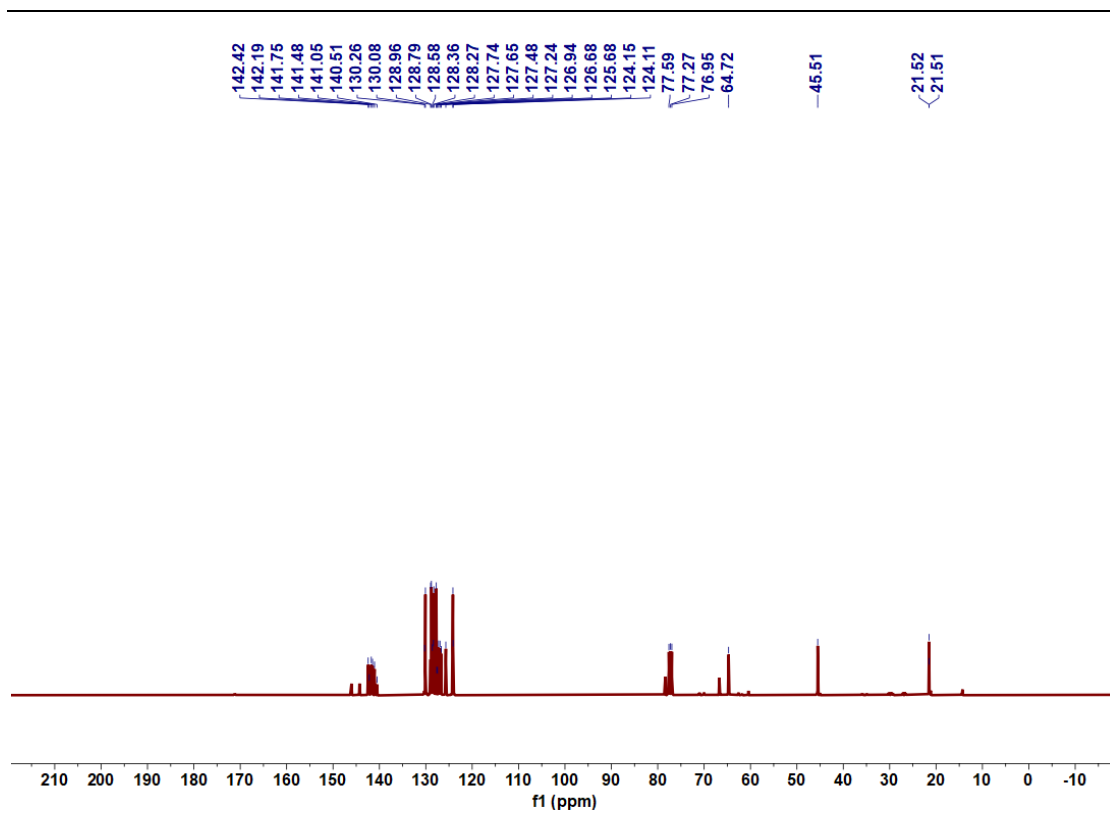
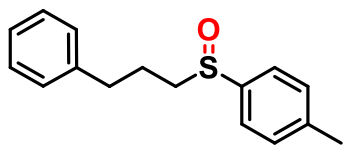


Fig. S98. ^{13}C NMR spectra of (2-(p-tolylsulfinyl)ethane-1,1-diyl)dibenzene in CDCl_3 .

4o. 1-methyl-4-((3-phenylpropyl)sulfinyl)benzene



Following the general procedure, the crude material was purified by rapid column chromatography (petroleum ether/ethyl acetate=10:1) to give 4o as a white solid (36.6 mg, 71% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.48 - 7.42 (m, 2H), 7.30 - 7.19 (m, 4H), 7.19 - 7.05 (m, 3H), 2.74 (t, $J = 7.7$ Hz, 2H), 2.68 (m, 2H), 2.34 (s, 3H), 2.11 - 1.98 (m, 1H), 1.97 - 1.81 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 141.31, 140.52, 140.47, 129.91, 128.50, 128.42, 126.22, 124.02, 56.23, 34.52, 23.62, 21.40.

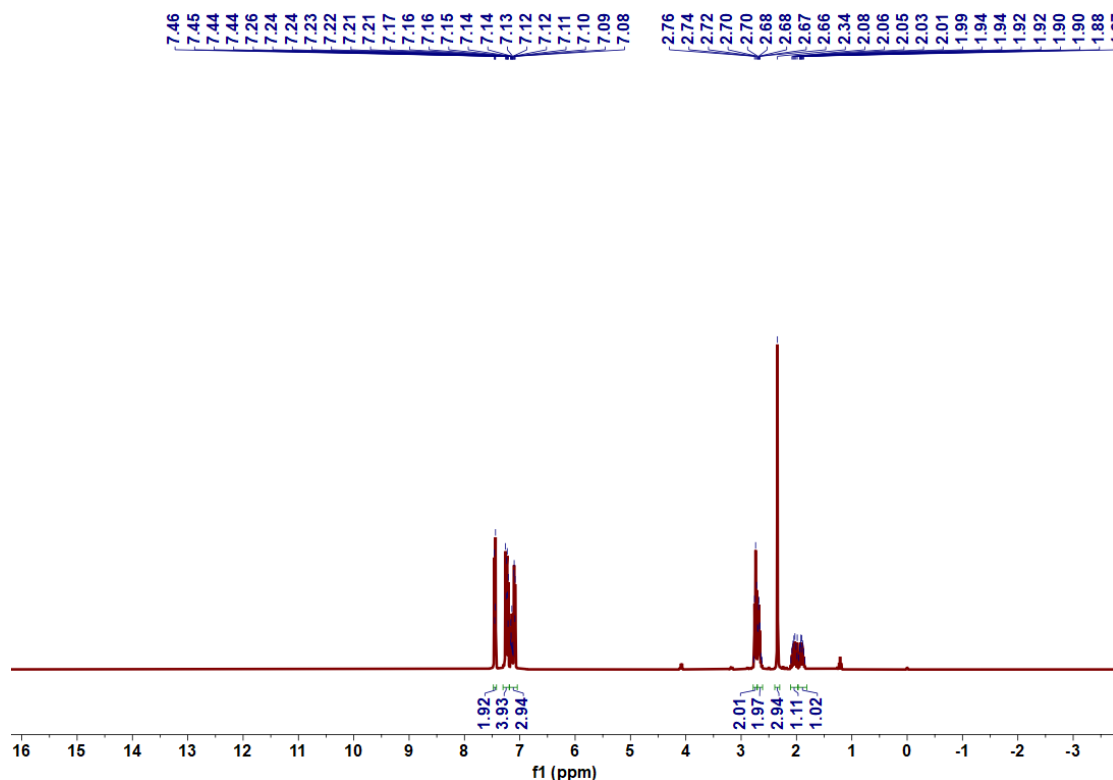


Fig. S99 ^1H NMR spectra of 1-methyl-4-((3-phenylpropyl)sulfinyl)benzene in CDCl_3 .

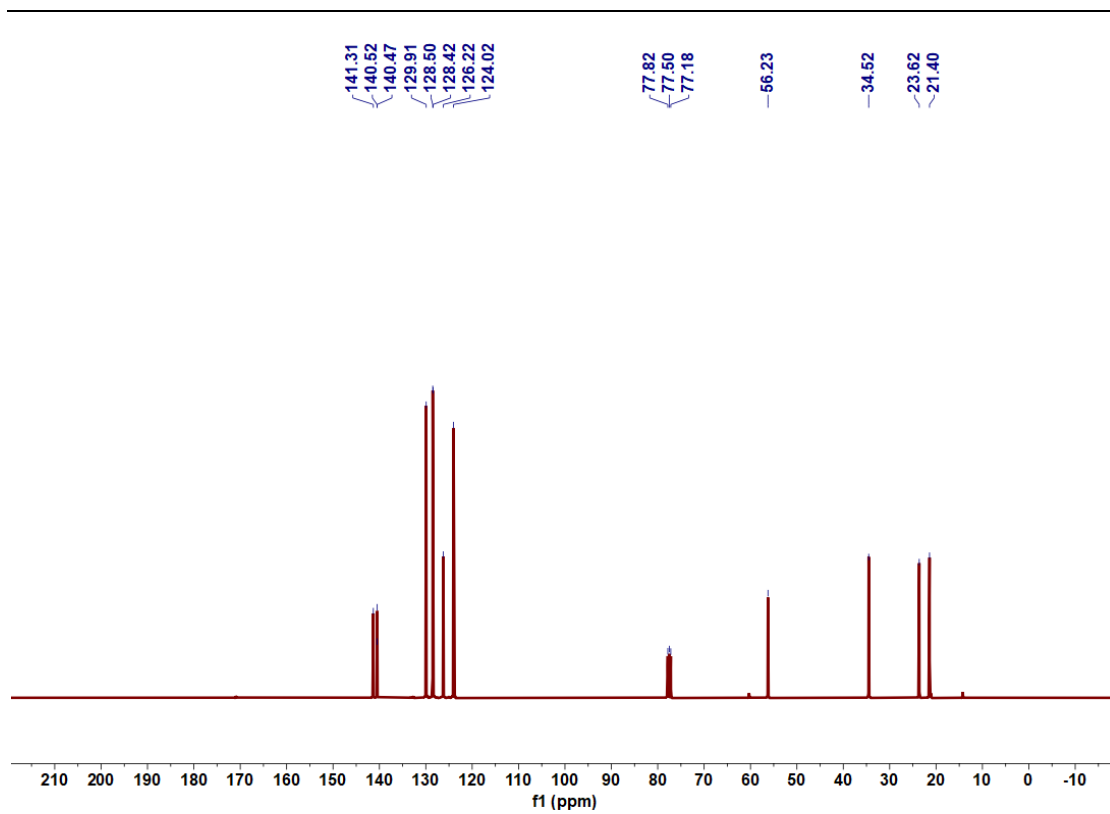


Fig. S100. ^{13}C NMR spectra of 1-methyl-4-((3-phenylpropyl)sulfinyl)benzene in CDCl_3 .