

Supporting Information

Synthesis of Unsymmetrical Thiosulfonates via Ring-Opening Reaction of Cyclic Sulfonium Salts with Sodium Thiosulfonates

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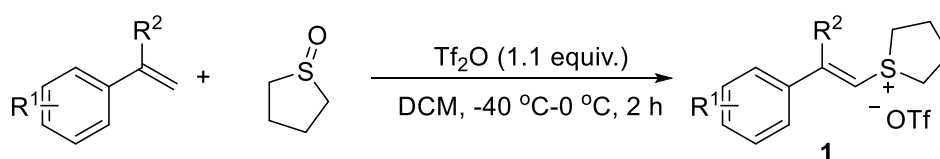
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1. General Information

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers and used without further purification. ^1H , ^{13}C , and ^{19}F NMR spectra were recorded at 400, 101, and 376 MHz, respectively. Chemical shifts were quoted in ppm relative to CDCl_3 ($\delta_{\text{H}} = 7.26$, $\delta_{\text{C}} = 77.0$ ppm). Data are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc. The reactions were monitored by thin-layer chromatography (TLC) using GF_{254} silica gel-coated TLC plates. Mass spectra were performed on a spectrometer operating on ESI-TOF.

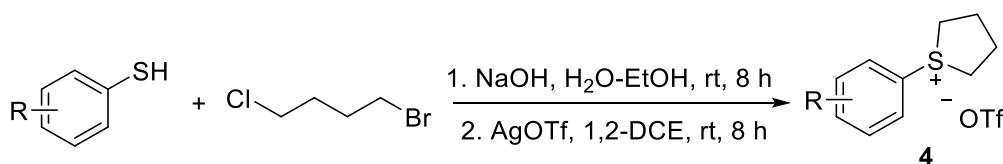
2. Experimental Section

General procedure for compound 1



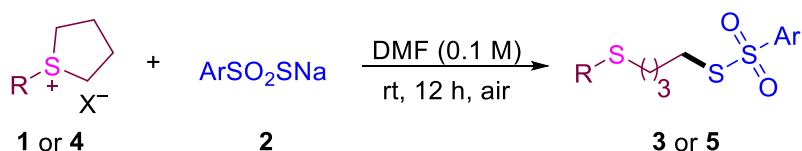
Compound **1** was prepared according to Wen's work.^[1] Under an argon atmosphere, tetramethylene sulfoxide (5.5 mmol, 1.1 equiv.) and anhydrous DCM (20 mL) were added to a 100 mL round bottom flask at $-40\text{ }^{\circ}\text{C}$. The Tf_2O (1.1 equiv., 5.5 mmol) was added dropwise under argon, and then alkene (5.0 mmol, 1.0 equiv.) was added gradually. The reaction mixture was stirred at $-40\text{ }^{\circ}\text{C}$ for 30 min before warming to $0\text{ }^{\circ}\text{C}$. Upon completion monitored by the TLC, the solvent was removed under reduced pressure. The resulted crude product was dissolved in a small amount of anhydrous DCM, which was slowly dropped into anhydrous ether (20 mL) to precipitate out the cyclic sulfonium salts solid. The solid was collected by filtration and washed three times with ether to afford the cyclic sulfonium salts **1**, or the crude product was purified by column chromatography on silica gel (DCM/MeOH, from 50:1 to 20:1) to afford the alkenyl sulfonium salt **1**.

General procedure for the synthesis of compound 4



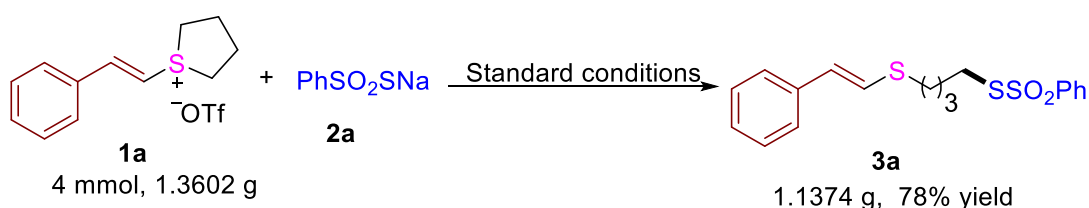
According to the literature,^[2] thiophenol (8.0 mmol) was added into a solution of NaOH (0.32 g, 8.0 mmol) in a mixture solvent of EtOH and H_2O ($v/v = 1:1$, 60 mL) with vigorous stirring. After 10 min, 1-bromo-4-chlorobutane (1.02 mL, 8.8 mmol) was introduced and the mixture was reacted at room temperature for 8 h. The volatile species were removed by rotary evaporator under reduced pressure. The residue was then extracted with Et_2O ($3 \times 20\text{ mL}$) and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness to give (4-chlorobutylsulfanyl)benzene as a yellow oil. Next, AgOTf (1.55 g, 6.0 mmol) was added into a solution of (4-chlorobutylsulfanyl)benzene (1.0 eq, 6.0 mmol) in 1,2-DCE (30 mL) and reacted at room temperature in the darkness for 8 h. The gray precipitates were removed and the solution was treated with Na_2SO_4 and filtered. The filter cake was washed with 1,2-DCE ($3 \times 5\text{ mL}$). The combined filtrates were concentrated under the reduced pressure to give a viscous yellow oil, which was further washed by Et_2O to obtain compound **4**.

General procedure for the synthesis of ring-opening product 3 and 5



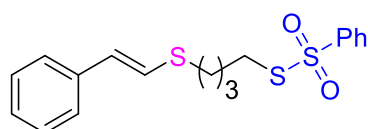
A 10 mL round-bottom flask equipped with a stirring bar was charged with cyclic sulfonium salt **1** or **4** (0.3 mmol, 1 equiv), sodium thiosulfonate **2** (0.6 mmol, 2 equiv), and DMF (3 mL). The reaction mixture was then stirred at room temperature for approximately 12 h, with progress monitored by TLC. Upon completion, 10 mL of H₂O was added to the mixture, followed by extraction with EtOAc three times (10 mL × 3). The organic phase was subsequently dried over anhydrous sodium sulfate and concentrated under vacuum, and the residue was purified via flash column chromatography using a petroleum ether/ethyl acetate eluent mixture (PE/EA 10:1–4:1) to afford the desired products **3** or **5**.

Gram-scale synthesis of **3a**

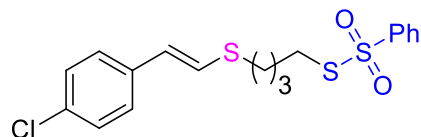


A 100 mL round-bottom flask equipped with a stirring bar was charged with **1a** (4 mmol, 1.3602 g), **2a** (8 mmol, 1.5697 g), and DMF (40 mL). The reaction mixture was then stirred at room temperature for approximately 12 h. Upon completion, 40 mL of H₂O was added to the mixture, followed by extraction with EtOAc three times (40 mL × 3). The organic phase was subsequently dried over anhydrous sodium sulfate and concentrated under vacuum, and the residue was purified via flash column chromatography using a petroleum ether/ethyl acetate eluent mixture (PE/EA 10:1–6:1) to afford 1.1374 g of **3a** in 78% yield.

3. Characterization data of products

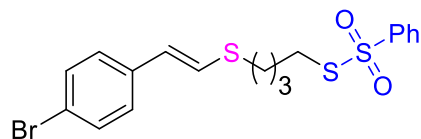


(E)-S-(4-((4-styrylthio)butyl) benzenesulfonothioate (3a): Colorless liquid (89.7 mg, 82%). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 7.7 Hz, 2H), 7.60 - 7.56 (m, 1H), 7.52 - 7.48 (m, 2H), 7.28 - 7.22 (m, 4H), 7.17 - 7.14 (m, 1H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.40 (d, *J* = 15.6 Hz, 1H), 2.99 (t, *J* = 6.9 Hz, 2H), 2.68 (t, *J* = 6.8 Hz, 2H), 1.76 - 1.62 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 144.9, 137.0, 133.8, 129.4, 128.8, 127.7, 127.1, 127.0, 125.6, 124.5, 35.6, 31.9, 28.2, 27.7. HRMS (ESI): *m/z* [M+H]⁺ calcd for C₁₈H₂₁O₂S₃: 365.0698; found: 365.0696.

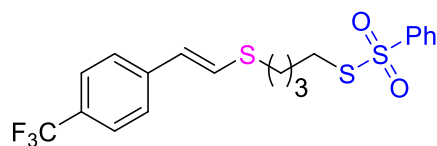


(E)-S-(4-((4-chlorostyryl)thio)butyl) benzenesulfonothioate (3b): Colorless liquid (89.8 mg, 75%). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.61 - 7.58 (m, 1H), 7.53 - 7.50 (m, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 6.60 (d, *J* = 15.6 Hz, 1H), 6.34 (d, *J* = 15.6 Hz, 1H), 3.00 (t, *J* = 6.9 Hz, 2H), 2.70 (t, *J* = 6.8 Hz, 2H), 1.79 - 1.64 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 144.9,

135.5, 133.8, 132.6, 129.5, 128.9, 127.1, 126.8, 126.1, 125.5, 35.6, 31.9, 28.2, 27.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{20}ClO_2S_3$: 399.0308; found: 399.0309.



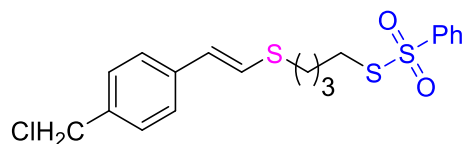
(E)-S-(4-((4-bromostyryl)thio)butyl) benzenesulfonylthioate (3c): Colorless liquid (94.5 mg, 71%). 1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.8 Hz, 2H), 7.60 - 7.6 (m, 1H), 7.52 - 7.48 (m, 2H), 7.35 (d, J = 8.3 Hz, 2H), 7.08 (d, J = 8.3 Hz, 2H), 6.60 (d, J = 15.6 Hz, 1H), 6.31 (d, J = 15.6 Hz, 1H), 2.98 (t, J = 6.9 Hz, 2H), 2.68 (t, J = 6.8 Hz, 2H), 1.77 - 1.62 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 136.0, 133.8, 131.9, 129.5, 127.1, 127.1, 126.1, 125.7, 120.7, 35.6, 31.9, 28.2, 27.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{20}BrO_2S_3$: 442.9803; found: 442.9805.



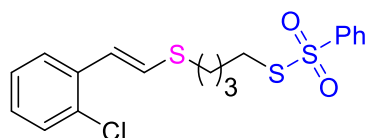
(E)-S-(4-((4-(trifluoromethyl)styryl)thio)butyl) benzenesulfonylthioate (3d): Colorless liquid (90.8 mg, 70%). 1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.9 Hz, 2H), 7.63 - 7.60 (m, 1H), 7.57 - 7.46 (m, 4H), 7.34 (d, J = 8.0 Hz, 2H), 6.78 (d, J = 15.6 Hz, 1H), 6.40 (d, J = 15.6 Hz, 1H), 3.02 (t, J = 6.8 Hz, 2H), 2.75 (t, J = 6.7 Hz, 2H), 1.83 - 1.67 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 140.4, 133.9, 129.5, 128.7 (q, J_{C-F} = 32.6 Hz), 128.2, 127.1, 125.8 (q, J_{C-F} = 3.8 Hz), 125.3, 123.0, 121.5 (q, J_{C-F} = 272.8 Hz), 35.6, 31.8, 28.1, 27.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.39. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{20}F_3O_2S_3$: 433.0572; found: 433.0571.



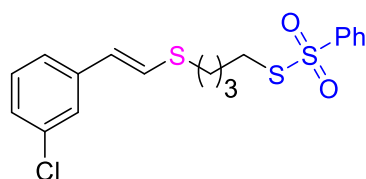
methyl (E)-4-(2-((4-((phenylsulfonyl)thio)butyl)thio)vinyl)benzoate (3e): Colorless liquid (100.1 mg, 79%). 1H NMR (400 MHz, $CDCl_3$) δ 7.91 - 7.86 (m, 4H), 7.59 - 7.55 (m, 1H), 7.51 - 7.47 (m, 2H), 7.26 (d, J = 8.2 Hz, 2H), 6.76 (d, J = 15.6 Hz, 1H), 6.36 (d, J = 15.6 Hz, 1H), 3.84 (s, 3H), 2.98 (t, J = 6.8 Hz, 2H), 2.71 (t, J = 6.7 Hz, 2H), 1.80 - 1.62 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 144.9, 141.4, 133.9, 130.2, 129.5, 128.3, 127.1, 125.6, 125.3, 52.2, 35.6, 31.8, 28.1, 27.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{23}O_4S_3$: 423.0753; found: 423.0757.



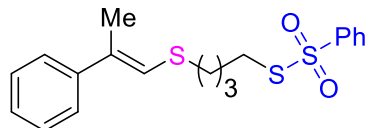
(E)-S-(4-((4-(chloromethyl)styryl)thio)butyl) benzenesulfonylthioate (3f): Colorless liquid (64.4 mg, 52%). 1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.9 Hz, 2H), 7.58 - 7.55 (m, 1H), 7.47 - 7.43 (m, 2H), 7.12 - 7.06 (m, 4H), 6.65 (d, J = 15.6 Hz, 1H), 6.37 (d, J = 15.6 Hz, 1H), 4.21 (s, 2H), 3.55 (t, J = 6.1 Hz, 2H), 2.80 (t, J = 6.8 Hz, 2H), 1.94 - 1.81 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 137.0, 133.6, 132.1, 129.6, 129.3, 127.0, 126.4, 125.9, 125.8, 44.5, 40.4, 31.9, 31.5, 26.7. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{22}ClO_2S_3$: 413.0465; found: 413.0462.



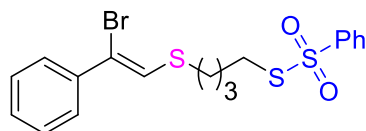
(E)-S-(4-((2-chlorostyryl)thio)butyl) benzenesulfonothioate (3g): Colorless liquid (86.2 mg, 72%). ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, J = 8.0 Hz, 2H), 7.58 - 7.55 (m, 1H), 7.51 - 7.47 (m, 2H), 7.36 (d, J = 7.7 Hz, 1H), 7.27 (d, J = 7.9 Hz, 1H), 7.16 - 7.12 (m, 1H), 7.09 - 7.05 (m, 1H), 6.70 (d, J = 15.6 Hz, 1H), 6.61 (d, J = 15.6 Hz, 1H), 2.98 (t, J = 6.7 Hz, 2H), 2.70 (t, J = 6.6 Hz, 2H), 1.75 - 1.63 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 135.0, 133.8, 132.0, 129.9, 129.4, 128.0, 127.8, 127.0, 127.0, 126.1, 122.7, 35.6, 31.6, 28.0, 27.8. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{20}\text{ClO}_2\text{S}_3$: 399.0308; found: 399.0312.



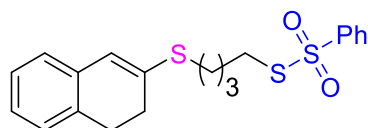
(E)-S-(4-((3-chlorostyryl)thio)butyl) benzenesulfonothioate (3h): Colorless liquid (81.4 mg, 68%). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 7.8 Hz, 2H), 7.60 - 7.56 (m, 1H), 7.52 - 7.48 (m, 2H), 7.22 - 7.14 (m, 2H), 7.11 - 7.07 (m, 2H), 6.62 (d, J = 15.6 Hz, 1H), 6.30 (d, J = 15.6 Hz, 1H), 2.98 (t, J = 6.9 Hz, 2H), 2.68 (t, J = 6.8 Hz, 2H), 1.76 - 1.62 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 138.8, 134.7, 133.8, 130.0, 129.5, 127.1, 126.9, 126.7, 125.7, 125.4, 123.8, 35.6, 31.9, 28.1, 27.8. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{20}\text{ClO}_2\text{S}_3$: 399.0308; found: 399.0305.



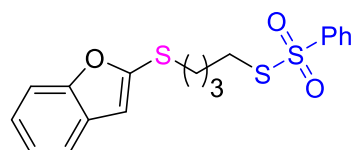
(E)-S-(4-((2-phenylprop-1-en-1-yl)thio)butyl) benzenesulfonothioate (3i): Colorless liquid (70.4 mg, 62%). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 7.8 Hz, 2H), 7.63 - 7.56 (m, 1H), 7.53 - 7.49 (m, 2H), 7.30 - 7.27 (m, 4H), 7.21 (d, J = 6.3 Hz, 1H), 6.17 (s, 1H), 3.00 (t, J = 6.9 Hz, 2H), 2.67 (t, J = 6.8 Hz, 2H), 2.08 (s, 3H), 1.80 - 1.62 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 142.0, 134.3, 133.8, 129.4, 128.5, 127.1, 126.9, 125.2, 123.1, 35.7, 33.5, 29.2, 27.6, 17.8. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{23}\text{O}_2\text{S}_3$: 379.0855; found: 379.0857.



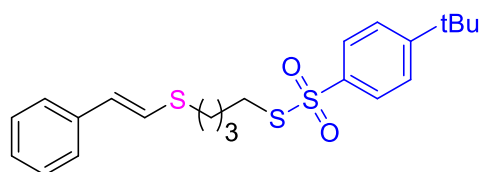
(Z)-S-(4-((2-bromo-2-phenylvinyl)thio)butyl) benzenesulfonothioate (3j): Colorless liquid (70.5 mg, 53%). ^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, J = 8.0 Hz, 2H), 7.57 - 7.53 (m, 1H), 7.49 - 7.45 (m, 2H), 7.40 (d, J = 7.5 Hz, 2H), 7.28 - 7.19 (m, 3H), 6.73 (s, 1H), 2.96 (t, J = 6.7 Hz, 2H), 2.71 (t, J = 6.6 Hz, 2H), 1.74 - 1.61 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 138.6, 133.9, 129.5, 128.5, 128.5, 128.3, 127.0, 126.8, 120.0, 35.6, 33.1, 29.2, 27.5. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{20}\text{BrO}_2\text{S}_3$: 442.9803; found: 442.9808.



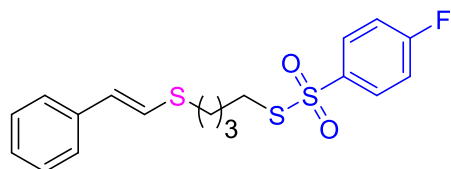
O-phenyl 4-((3,4-dihydronaphthalen-2-ylthio)butyl) benzenesulfonothioate (3k): Colorless liquid (76.2 mg, 65%). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 7.9 Hz, 2H), 7.61 - 7.57 (m, 1H), 7.53 - 7.49 (m, 2H), 7.14 - 7.06 (m, 1H), 7.03 (d, J = 12.9 Hz, 2H), 6.92 (d, J = 7.3 Hz, 1H), 6.13 (s, 1H), 3.00 (t, J = 7.0 Hz, 2H), 2.79 (t, J = 7.9 Hz, 2H), 2.73 (t, J = 6.9 Hz, 2H), 2.33 (t, J = 7.9 Hz, 2H), 1.79 - 1.63 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 136.6, 134.5, 133.8, 133.7, 129.4, 127.4, 127.1, 126.8, 126.3, 125.0, 120.1, 35.6, 30.1, 29.2, 28.5, 28.0, 27.3. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{22}\text{O}_2\text{S}_3$: 391.0855; found: 391.0858.



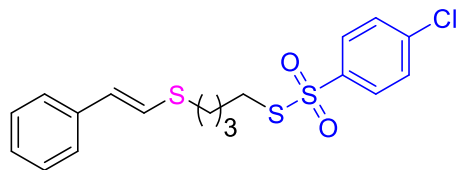
S-(4-(benzofuran-2-ylthio)butyl) benzenesulfonothioate (3l): Colorless liquid (69.3 mg, 61%). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 7.8 Hz, 2H), 7.60 - 7.55 (m, 1H), 7.51 - 7.46 (m, 3H), 7.39 (d, J = 8.1 Hz, 1H), 7.27 - 7.17 (m, 2H), 6.74 (s, 1H), 2.97 (t, J = 7.2 Hz, 2H), 2.82 (t, J = 6.9 Hz, 2H), 1.78 - 1.70 (m, 2H), 1.66 - 1.60 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.5, 149.9, 144.9, 133.8, 129.4, 128.6, 127.1, 124.7, 123.1, 120.6, 111.6, 111.1, 35.6, 33.9, 28.6, 27.5. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{19}\text{O}_3\text{S}_3$: 379.0491; found: 379.0495.



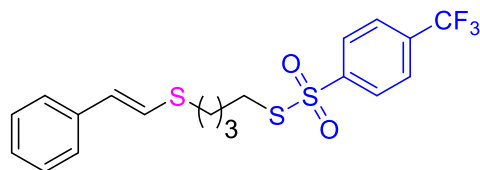
(E)-S-(4-(styrylthio)butyl) 4-(tert-butyl)benzenesulfonothioate (3m): Colorless liquid (71.9 mg, 57%). ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.28 - 7.22 (m, 4H), 7.16 - 7.11 (m, 1H), 6.61 (d, J = 15.6 Hz, 1H), 6.41 (d, J = 15.5 Hz, 1H), 2.99 (t, J = 6.7 Hz, 2H), 2.69 (t, J = 6.6 Hz, 2H), 1.79 - 1.65 (m, 4H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.9, 141.9, 137.0, 128.8, 127.7, 127.1, 127.0, 126.4, 125.6, 124.6, 35.6, 35.4, 32.0, 31.2, 28.2, 27.8. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{29}\text{O}_2\text{S}_3$: 421.1324; found: 421.1327.



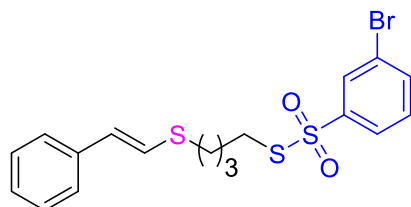
(E)-S-(4-(styrylthio)butyl) 4-fluorobenzenesulfonothioate (3n): Colorless liquid (75.7 mg, 66%). ^1H NMR (400 MHz, CDCl_3) δ 7.94 - 7.91 (m, 2H), 7.31 - 7.25 (m, 4H), 7.21 - 7.17 (m, 3H), 6.62 (d, J = 15.6 Hz, 1H), 6.44 (d, J = 15.5 Hz, 1H), 3.02 (t, J = 7.0 Hz, 2H), 2.73 (t, J = 6.8 Hz, 2H), 1.81 - 1.67 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.7 (d, $J_{\text{C-F}}$ = 257.9 Hz), 141.0, 137.0, 130.0 (d, $J_{\text{C-F}}$ = 9.6 Hz), 128.8, 127.9, 127.2, 125.7, 124.5, 116.7 (d, $J_{\text{C-F}}$ = 22.9 Hz), 35.7, 32.0, 28.2, 27.8. ^{19}F NMR (376 MHz, CDCl_3) δ -102.86. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{20}\text{FO}_2\text{S}_3$: 383.0604; found: 383.0605.



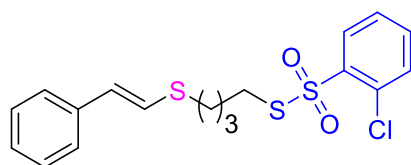
(E)-S-(4-(styrylthio)butyl) 4-chlorobenzenesulfonothioate (3o): Colorless liquid (74.2 mg, 62%). ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 7.32 - 7.24 (m, 4H), 7.21 - 7.15 (m, 1H), 6.62 (d, J = 15.6 Hz, 1H), 6.44 (d, J = 15.6 Hz, 1H), 3.01 (t, J = 7.0 Hz, 2H), 2.72 (t, J = 6.8 Hz, 2H), 1.81 - 1.66 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.3, 140.5, 137.0, 129.8, 128.8, 128.5, 127.9, 127.2, 125.7, 124.4, 35.8, 32.0, 28.2, 27.8. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{20}\text{ClO}_2\text{S}_3$: 399.0308; found: 399.0304.



(E)-S-(4-(styrylthio)butyl) 4-(trifluoromethyl)benzenesulfonothioate (3p): Colorless liquid (85.6 mg, 66%). ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, J = 8.2 Hz, 2H), 7.80 (d, J = 8.2 Hz, 2H), 7.31 - 7.25 (m, 4H), 7.20 - 7.17 (m, 1H), 6.62 (d, J = 15.6 Hz, 1H), 6.44 (d, J = 15.6 Hz, 1H), 3.04 (t, J = 7.0 Hz, 2H), 2.74 (t, J = 6.7 Hz, 2H), 1.83 - 1.68 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.1, 137.0, 135.4 (q, $J_{\text{C-F}}$ = 33.5 Hz), 128.8, 128.0, 127.6, 127.2, 126.7 (q, $J_{\text{C-F}}$ = 3.7 Hz), 125.7, 124.4, 123.2 (q, $J_{\text{C-F}}$ = 273.9 Hz), 35.9, 32.0, 28.2, 27.8. ^{19}F NMR (376 MHz, CDCl_3) δ -63.13. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{20}\text{F}_3\text{O}_2\text{S}_3$: 433.0572; found: 433.0577.

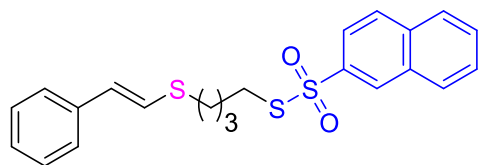


(E)-S-(4-(styrylthio)butyl) 3-bromobenzenesulfonothioate (3q): Colorless liquid (74.5 mg, 56%). ^1H NMR (400 MHz, CDCl_3) δ 8.06 (s, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.43 - 7.39 (m, 1H), 7.32 - 7.26 (m, 4H), 7.22 - 7.17 (m, 1H), 6.64 (d, J = 15.5 Hz, 1H), 6.45 (d, J = 15.6 Hz, 1H), 3.05 (t, J = 7.0 Hz, 2H), 2.75 (t, J = 6.8 Hz, 2H), 1.84 - 1.69 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 146.5, 137.0, 136.9, 131.0, 129.9, 128.8, 127.9, 127.2, 125.7, 125.6, 124.5, 123.4, 35.9, 32.0, 28.2, 27.8. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{20}\text{BrO}_2\text{S}_3$: 442.9803; found: 442.9806.

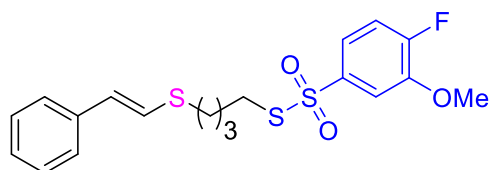


(E)-S-(4-(styrylthio)butyl) 2-chlorobenzenesulfonothioate (3r): Colorless liquid (88.6 mg, 74%). ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, J = 7.8 Hz, 1H), 7.58 - 7.49 (m, 2H), 7.43 - 7.39 (m, 1H), 7.31 - 7.26 (m, 4H), 7.20 - 7.17 (t, J = 6.4 Hz, 1H), 6.61 (d, J = 15.6 Hz, 1H), 6.43 (d, J = 15.6 Hz, 1H), 3.08 (t, J = 6.9 Hz, 2H), 2.70 (t, J = 6.8 Hz, 2H), 1.79 - 1.65 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.7,

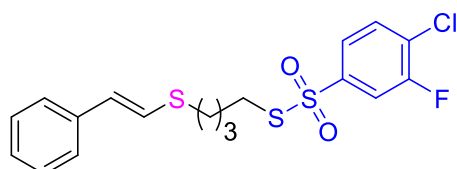
137.0, 134.6, 132.7, 132.6, 130.3, 128.8, 127.8, 127.2, 125.7, 124.5, 36.4, 32.0, 28.2, 28.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{20}ClO_2S_3$: 399.0308; found: 399.0306.



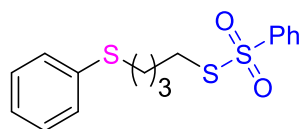
(E)-S-(4-(styrylthio)butyl) naphthalene-2-sulfonylthioate (3s): Colorless liquid (75.9 mg, 61%). 1H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.90 - 7.83 (m, 2H), 7.65 - 7.56 (m, 2H), 7.26 - 7.19 (m, 4H), 7.16 - 7.13 (m, 1H), 6.54 (d, J = 15.6 Hz, 1H), 6.35 (d, J = 15.5 Hz, 1H), 3.00 (t, J = 7.0 Hz, 2H), 2.64 (t, J = 6.8 Hz, 2H), 1.76 - 1.62 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 137.0, 135.3, 132.0, 130.1, 129.7, 129.6, 128.8, 128.6, 128.2, 128.1, 127.7, 127.1, 125.7, 124.5, 122.1, 35.8, 31.9, 28.2, 27.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{23}O_2S_3$: 415.0855; found: 415.0856.



(E)-S-(4-(styrylthio)butyl) 4-fluoro-3-methoxybenzenesulfonylthioate (3t): Colorless liquid (78.0 mg, 63%). 1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.7 Hz, 1H), 7.63 (d, J = 10.1 Hz, 1H), 7.32 - 7.25 (m, 4H), 7.22 - 7.15 (m, 1H), 7.05 - 7.01 (m, 1H), 6.64 (d, J = 15.6 Hz, 1H), 6.45 (d, J = 15.5 Hz, 1H), 3.94 (s, 3H), 3.02 (t, J = 6.9 Hz, 2H), 2.75 (t, J = 6.8 Hz, 2H), 1.84 - 1.66 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5 (d, J_{C-F} = 10.5 Hz), 151.7 (d, J_{C-F} = 254.1 Hz), 137.0, 136.8 (d, J_{C-F} = 5.5 Hz), 128.8, 127.8, 127.2, 125.7, 124.6 (d, J_{C-F} = 3.8 Hz), 124.5, 115.3 (d, J_{C-F} = 21.5 Hz), 112.8, 56.7, 35.7, 32.0, 28.2, 27.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -130.83. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{22}FO_3S_3$: 413.0710; found: 413.0712.

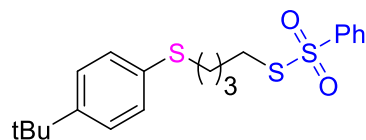


(E)-S-(4-(styrylthio)butyl) 4-chloro-3-fluorobenzenesulfonylthioate (3u): Colorless liquid (66.3 mg, 53%). 1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 6.5 Hz, 1H), 7.86 - 7.75 (m, 1H), 7.31 - 7.25 (m, 5H), 7.20 (d, J = 6.0 Hz, 1H), 6.63 (d, J = 15.5 Hz, 1H), 6.46 (d, J = 15.6 Hz, 1H), 3.05 (t, J = 7.0 Hz, 2H), 2.76 (t, J = 6.7 Hz, 2H), 1.84 - 1.68 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3 (d, J_{C-F} = 260.3 Hz), 141.8, 137.0, 130.1, 128.8, 128.0, 127.7 (d, J_{C-F} = 8.8 Hz), 127.2, 125.7, 122.9 (d, J_{C-F} = 16.6 Hz), 124.4, 117.7 (d, J_{C-F} = 22.7 Hz), 36.0, 32.0, 28.2, 27.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.09. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{19}ClFO_2S_3$: 417.0214; found: 417.0210.

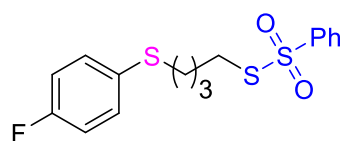


S-(4-(phenylthio)butyl) benzenesulfonylthioate (5a): Colorless liquid (79.2 mg, 78%). 1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 2H), 7.61 - 7.58 (m, 1H), 7.53 - 7.49 (m, 2H), 7.29 - 7.21 (m, 4H),

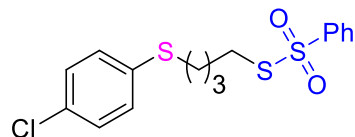
7.17 - 7.15 (m, 1H), 2.97 (t, $J = 7.1$ Hz, 2H), 2.81 (t, $J = 7.0$ Hz, 2H), 1.79 - 1.68 (m, 2H), 1.64 - 1.59 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 136.2, 133.8, 129.5, 129.4, 129.1, 127.1, 126.3, 35.6, 33.1, 27.9, 27.8. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{19}\text{O}_2\text{S}_3$: 339.0542; found: 339.0544.



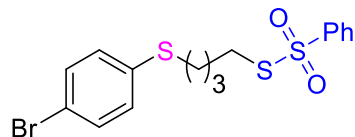
***S*-(4-((4-*tert*-butyl)phenyl)thio)butyl benzenesulfonothioate (5b):** Colorless liquid (86.4 mg, 73%). ^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, $J = 7.6$ Hz, 2H), 7.57 - 7.53 (m, 1H), 7.48 - 7.45 (m, 2H), 7.23 (d, $J = 8.4$ Hz, 2H), 7.16 (d, $J = 8.3$ Hz, 2H), 2.92 (t, $J = 7.2$ Hz, 2H), 2.73 (t, $J = 7.0$ Hz, 2H), 1.73 - 1.62 (m, 2H), 1.59 - 1.53 (m, 2H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.7, 144.9, 133.8, 132.5, 129.8, 129.4, 127.1, 126.1, 35.7, 34.6, 33.5, 31.4, 28.0, 27.7. ^{19}F NMR (376 MHz, CDCl_3) δ -100.85. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{27}\text{O}_2\text{S}_3$: 395.1168; found: 395.1171.



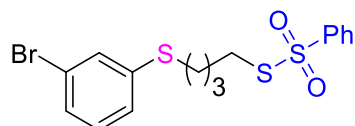
***S*-(4-((4-fluorophenyl)thio)butyl) benzenesulfonothioate (5c):** Colorless liquid (83.4 mg, 78%). ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 7.7$ Hz, 2H), 7.65 - 7.61 (m, 1H), 7.56 - 7.53 (m, 2H), 7.31 - 7.28 (m, 2H), 7.00 - 6.96 (m, 2H), 2.99 (t, $J = 7.2$ Hz, 2H), 2.78 (t, $J = 7.0$ Hz, 2H), 1.79 - 1.71 (m, 2H), 1.63 - 1.58 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.0 (d, $J_{\text{C-F}} = 247.5$ Hz), 144.9, 133.8, 132.6 (d, $J_{\text{C-F}} = 8.0$ Hz), 130.9 (d, $J_{\text{C-F}} = 3.3$ Hz), 129.4, 127.0, 116.2 (d, $J_{\text{C-F}} = 21.9$ Hz), 35.6, 34.5, 27.9, 27.7. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{18}\text{FO}_2\text{S}_3$: 357.0447; found: 357.0452.



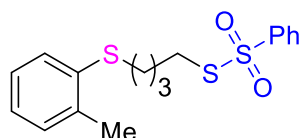
***S*-(4-((4-chlorophenyl)thio)butyl) benzenesulfonothioate (5d):** Colorless liquid (89.5 mg, 80%). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 7.9$ Hz, 2H), 7.64 - 7.60 (m, 1H), 7.55 - 7.52 (m, 2H), 7.24 - 7.19 (m, 4H), 2.99 (t, $J = 7.1$ Hz, 2H), 2.80 (t, $J = 7.0$ Hz, 2H), 1.81 - 1.69 (m, 2H), 1.65 - 1.60 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 134.7, 133.8, 132.3, 130.9, 129.5, 129.2, 127.1, 35.6, 33.4, 27.8, 27.8. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{18}\text{ClO}_2\text{S}_3$: 373.0152; found: 373.0149.



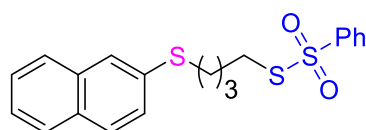
***S*-(4-((4-bromophenyl)thio)butyl) benzenesulfonothioate (5e):** Colorless liquid (95.2 mg, 76%). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 7.8$ Hz, 2H), 7.61 - 7.58 (m, 1H), 7.53 - 7.49 (m, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.11 (d, $J = 8.1$ Hz, 2H), 2.96 (t, $J = 7.1$ Hz, 2H), 2.78 (t, $J = 6.9$ Hz, 2H), 1.77 - 1.68 (m, 2H), 1.63 - 1.57 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 135.4, 133.8, 132.1, 131.0, 129.4, 127.1, 120.1, 35.6, 33.2, 27.7. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{18}\text{BrO}_2\text{S}_3$: 416.9647; found: 416.9647.



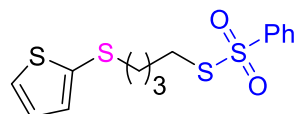
S-(4-((3-bromophenyl)thio)butyl) benzenesulfonothioate (5f): Colorless liquid (92.7 mg, 74%). ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, J = 7.9 Hz, 2H), 7.65 - 6.61 (m, 1H), 7.56 - 7.53 (m, 2H), 7.38 (s, 1H), 7.29 (d, J = 7.7 Hz, 1H), 7.19 - 7.11 (m, 2H), 3.00 (t, J = 7.1 Hz, 2H), 2.83 (t, J = 7.0 Hz, 2H), 1.82 - 1.71 (m, 2H), 1.67 - 1.60 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 138.8, 133.9, 131.4, 130.4, 129.5, 129.2, 127.6, 127.1, 123.0, 35.6, 32.9, 27.8, 27.7. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{18}\text{BrO}_2\text{S}_3$: 416.9647; found: 416.9646.



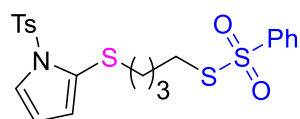
S-(4-(o-tolylthio)butyl) benzenesulfonothioate (5g): Colorless liquid (65.6 mg, 62%). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 7.8 Hz, 2H), 7.62 - 7.58 (m, 1H), 7.54 - 7.50 (m, 2H), 7.16 - 7.05 (m, 4H), 2.99 (t, J = 7.1 Hz, 2H), 2.79 (t, J = 7.0 Hz, 2H), 2.32 (s, 3H), 1.80 - 1.72 (m, 2H), 1.68 - 1.60 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 137.7, 135.5, 133.8, 130.3, 129.4, 128.0, 127.1, 126.5, 125.9, 35.7, 32.2, 27.9, 27.8, 20.5. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{21}\text{O}_2\text{S}_3$: 353.0698; found: 353.0702.



S-(4-(naphthalen-2-ylthio)butyl) benzenesulfonothioate (5h): Colorless liquid (82.8 mg, 71%). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 7.9 Hz, 2H), 7.78 - 7.66 (m, 4H), 7.58 - 7.54 (m, 1H), 7.51 - 7.39 (m, 4H), 7.34 (d, J = 8.6 Hz, 1H), 2.97 (t, J = 7.1 Hz, 2H), 2.90 (t, J = 6.9 Hz, 2H), 1.80 - 1.71 (m, 2H), 1.69 - 1.60 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 133.9, 133.8, 133.6, 131.9, 129.4, 128.6, 127.8, 127.5, 127.2, 127.2, 127.0, 126.7, 125.9, 35.6, 33.0, 27.8, 27.8. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{21}\text{O}_2\text{S}_3$: 389.0698; found: 389.0701.

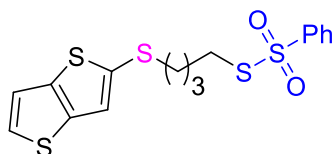


S-(4-(thiophen-2-ylthio)butyl) benzenesulfonothioate (5i): Colorless liquid (52.7 mg, 51%). ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, J = 7.9 Hz, 2H), 7.64 - 7.60 (m, 1H), 7.56 - 7.52 (m, 2H), 7.33 (d, J = 5.3 Hz, 1H), 7.06 (d, J = 3.2 Hz, 1H), 6.99 - 6.93 (m, 1H), 2.98 (t, J = 7.2 Hz, 2H), 2.68 (t, J = 7.0 Hz, 2H), 1.77 - 1.68 (m, 2H), 1.64 - 1.57 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.0, 134.1, 134.0, 133.8, 129.5, 129.5, 127.7, 127.1, 38.1, 35.7, 28.1, 27.4. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{17}\text{O}_2\text{S}_4$: 345.0106; found: 345.0111.

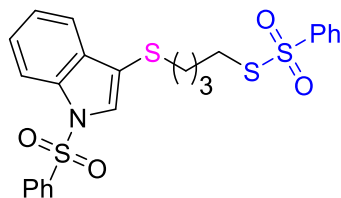


S-(4-((1-tosyl-1H-pyrrol-2-yl)thio)butyl) benzenesulfonothioate (5j): Colorless liquid (109.8 mg, 76%). ^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, J = 7.7 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.58 - 7.43 (m,

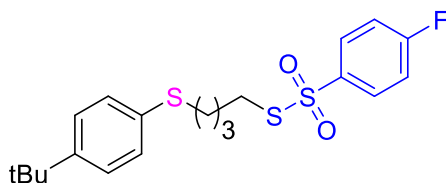
4H), 7.26 - 7.17 (m, 2H), 6.32 - 6.28 (m, 1H), 6.17 - 6.1 (m, 1H), 2.95 - 2.86 (m, 2H), 2.55 (t, $J = 7.1$ Hz, 2H), 2.33 (s, 3H), 1.68 - 1.57 (m, 2H), 1.51 - 1.39 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.2, 144.9, 135.9, 133.8, 129.8, 129.4, 127.9, 127.0, 126.2, 124.1, 122.9, 111.7, 36.6, 35.6, 27.6, 27.6, 21.8. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_4\text{S}_4$: 482.0583; found: 482.0585.



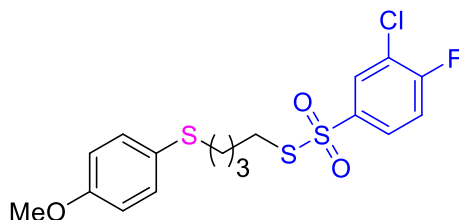
S-(4-(thieno[3,2-b]thiophen-2-ylthio)butyl) benzenesulfonothioate (5k): Colorless liquid (57.7 mg, 48%). ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 7.9$ Hz, 2H), 7.64 - 7.60 (m, 1H), 7.53 (t, $J = 7.6$ Hz, 2H), 7.43 (d, $J = 5.2$ Hz, 1H), 7.29 (s, 1H), 7.19 (d, $J = 5.2$ Hz, 1H), 3.00 (t, $J = 7.1$ Hz, 2H), 2.74 (t, $J = 7.0$ Hz, 2H), 1.81 - 1.70 (m, 2H), 1.66 - 1.61 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 142.1, 138.4, 136.0, 133.8, 129.4, 127.9, 127.0, 126.5, 119.5, 38.3, 35.6, 28.1, 27.4. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{17}\text{O}_2\text{S}_5$: 400.9827; found: 400.9824.



S-(4-((1-(phenylsulfonyl)-1H-indol-3-yl)thio)butyl) benzenesulfonothioate (5l): Colorless liquid (111.8 mg, 72%). ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.2$ Hz, 1H), 7.92 - 7.88 (m, 4H), 7.64 - 7.49 (m, 6H), 7.47 - 7.43 (m, 2H), 7.38 - 7.35 (m, 1H), 7.31 - 7.26 (m, 1H), 2.96 (t, $J = 7.2$ Hz, 2H), 2.67 (t, $J = 7.1$ Hz, 2H), 1.76 - 1.67 (m, 2H), 1.56 - 1.47 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.8, 138.0, 135.3, 134.2, 133.8, 131.4, 129.5, 129.4, 128.4, 127.0, 126.9, 125.6, 123.9, 120.1, 114.5, 113.9, 35.6, 34.0, 28.2, 27.5. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{24}\text{NO}_4\text{S}_4$: 518.6985; found: 518.6989.

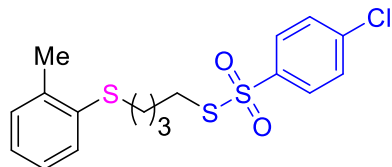


S-(4-((4-(tert-butyl)phenyl)thio)butyl) 4-fluorobenzenesulfonothioate (5m): Colorless liquid (84.2 mg, 68%). ^1H NMR (400 MHz, CDCl_3) δ 7.93 - 7.90 (m, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 7.22 - 7.17 (m, 4H), 2.98 (t, $J = 7.2$ Hz, 2H), 2.80 (t, $J = 6.9$ Hz, 2H), 1.79 - 1.71 (m, 2H), 1.65 - 1.60 (m, 2H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.7 (d, $J_{\text{C-F}} = 257.9$ Hz), 149.7, 141.0, 132.4, 130.0 (d, $J_{\text{C-F}} = 9.7$ Hz), 129.8, 126.2, 116.7 (d, $J_{\text{C-F}} = 22.9$ Hz), 35.7, 34.6, 33.5, 31.4, 28.0, 27.7. ^{19}F NMR (376 MHz, CDCl_3) δ -102.92. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{26}\text{FO}_2\text{S}_3$: 413.1073; found: 413.1075.

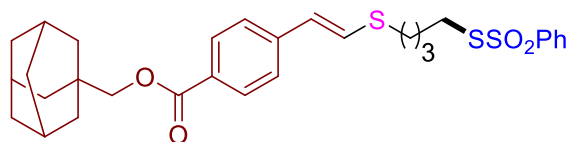


S-(4-((4-methoxyphenyl)thio)butyl) 3-chloro-4-fluorobenzenesulfonothioate (5n): Colorless liquid (88.4 mg, 70%). ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 6.4$ Hz, 1H), 7.79 - 7.72 (m, 1H), 7.28 -

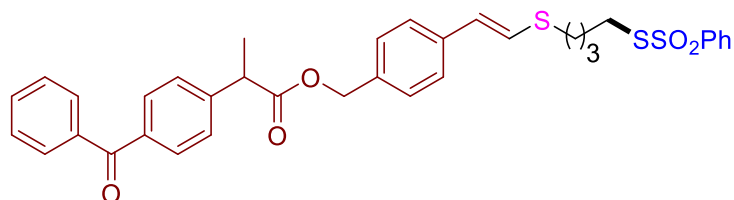
7.21 (m, 3H), 6.77 (d, $J = 8.3$ Hz, 2H), 3.73 (s, 3H), 2.94 (t, $J = 7.3$ Hz, 2H), 2.70 (t, $J = 7.0$ Hz, 2H), 1.75 - 1.67 (m, 2H), 1.57 - 1.51 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.2 (d, $J_{\text{C-F}} = 259.6$ Hz), 159.2, 141.8, 133.6, 130.1, 127.6 (d, $J_{\text{C-F}} = 8.8$ Hz), 126.0, 117.7 (d, $J_{\text{C-F}} = 22.7$ Hz), 122.9 (d, $J_{\text{C-F}} = 19.1$ Hz), 114.8, 55.5, 36.0, 35.3, 28.1, 27.6. ^{19}F NMR (376 MHz, CDCl_3) δ -105.20. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{19}\text{ClFO}_3\text{S}_3$: 421.0163; found: 421.0166



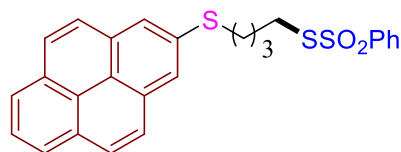
***S*-(4-(*o*-tolylthio)butyl) 4-chlorobenzenesulfonothioate (5o):** Colorless liquid (72.0 mg, 62%). ^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, $J = 8.2$ Hz, 2H), 7.44 (d, $J = 8.3$ Hz, 2H), 7.19 - 6.98 (m, 4H), 2.94 (t, $J = 7.2$ Hz, 2H), 2.76 (t, $J = 6.9$ Hz, 2H), 2.28 (s, 3H), 1.78 - 1.69 (m, 2H), 1.64 - 1.56 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.4, 140.5, 137.8, 135.5, 130.3, 129.7, 128.5, 128.1, 126.6, 126.0, 35.8, 32.3, 27.9, 27.8, 20.5. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{20}\text{ClO}_2\text{S}_3$: 387.0308; found: 387.0310.



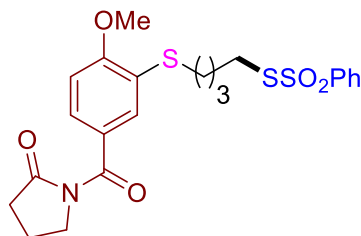
Adamantan-1-ylmethyl (*E*)-4-(2-((4-(phenoxysulfonothioyl)butyl)thio)vinyl)benzoate (3v): Colorless liquid (106.9 mg, 64%). ^1H NMR (400 MHz, CDCl_3) δ 7.98 - 7.93 (m, 4H), 7.65 - 7.61 (m, 1H), 7.57 - 7.53 (m, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 6.82 (d, $J = 15.6$ Hz, 1H), 6.44 (d, $J = 15.6$ Hz, 1H), 3.91 (s, 2H), 3.05 (t, $J = 6.8$ Hz, 2H), 2.77 (t, $J = 6.7$ Hz, 2H), 2.08 - 1.98 (m, 3H), 1.85 - 1.63 (m, 16H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.6, 144.9, 141.3, 133.8, 130.2, 129.5, 128.8, 128.2, 127.1, 125.8, 125.3, 74.5, 39.6, 37.1, 35.6, 33.7, 31.8, 28.2, 28.1, 27.8. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{37}\text{O}_4\text{S}_3$: 557.1848; found: 557.1853.



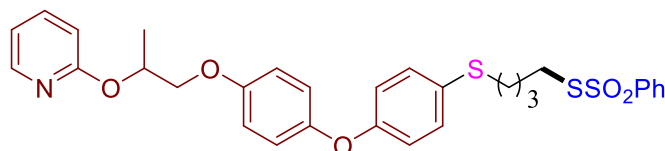
(*E*)-4-(2-((4-(phenylsulfonyl)thio)butyl)thio)vinyl)benzyl 2-(3-benzoylphenyl)propanoate (3w) : Colorless liquid (107.9 mg, 57%). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 7.7$ Hz, 2H), 7.76 - 7.70 (m, 3H), 7.67 - 7.49 (m, 7H), 7.46 - 7.41 (m, 3H), 7.20 - 7.14 (m, 4H), 6.61 (d, $J = 15.6$ Hz, 1H), 6.38 (d, $J = 15.5$ Hz, 1H), 5.05 (s, 2H), 3.82 (q, $J = 7.1$ Hz, 1H), 3.01 (t, $J = 7.0$ Hz, 2H), 2.70 (t, $J = 6.8$ Hz, 2H), 1.78 - 1.66 (m, 4H), 1.53 - 1.52 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.6, 174.0, 144.9, 140.8, 138.1, 137.6, 137.0, 134.5, 133.8, 132.7, 131.7, 130.2, 129.5, 129.4, 129.2, 128.7, 128.6, 128.5, 127.1, 127.0, 125.7, 125.3, 66.5, 45.6, 35.6, 31.9, 28.2, 27.8, 18.5. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{35}\text{H}_{35}\text{O}_5\text{S}_3$: 631.1641; found: 631.1645.



O-phenyl 4-(pyren-2-ylthio)butane-1-sulfonothioate (5p): Colorless liquid (112.4 mg, 81%). ^1H NMR (400 MHz, CDCl_3) δ 8.62 (d, J = 9.2 Hz, 1H), 8.20 - 8.11 (m, 3H), 8.09 - 7.98 (m, 5H), 7.86 (d, J = 7.9 Hz, 2H), 7.52 - 7.49 (m, 1H), 7.45 - 7.41 (m, 2H), 2.98 - 2.92 (m, 4H), 1.81 - 1.71 (m, 2H), 1.64 - 1.58 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 133.7, 131.6, 131.5, 131.1, 130.6, 130.4, 129.7, 129.4, 128.1, 127.7, 127.4, 127.0, 126.4, 125.5, 125.5, 125.3, 125.0, 124.6, 124.6, 35.6, 34.9, 28.2, 27.8. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{23}\text{O}_2\text{S}_3$: 463.0855; found: 463.0890.



O-phenyl 4-((2-methoxy-5-(2-oxopyrrolidine-1-carbonyl)phenyl)thio)butane-1-sulfonothioate (5q): Colorless liquid (93.5 mg, 65%). ^1H NMR (400 MHz, CDCl_3) δ 7.97 - 7.92 (m, 2H), 7.67 - 7.53 (m, 5H), 6.85 (d, J = 9.0 Hz, 1H), 3.98 - 3.92 (m, 5H), 3.06 - 2.79 (m, 4H), 2.61 (t, J = 7.9 Hz, 2H), 2.18 - 2.11 (m, 2H), 1.82 - 1.73 (m, 2H), 1.68 - 1.60 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 174.8, 169.8, 160.7, 145.0, 133.8, 131.6, 129.9, 129.5, 129.4, 128.2, 127.1, 126.8, 124.0, 109.4, 56.2, 47.0, 35.6, 33.6, 31.5, 27.9, 27.7, 17.8. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_5\text{S}_3$: 480.0968; found: 480.0966.

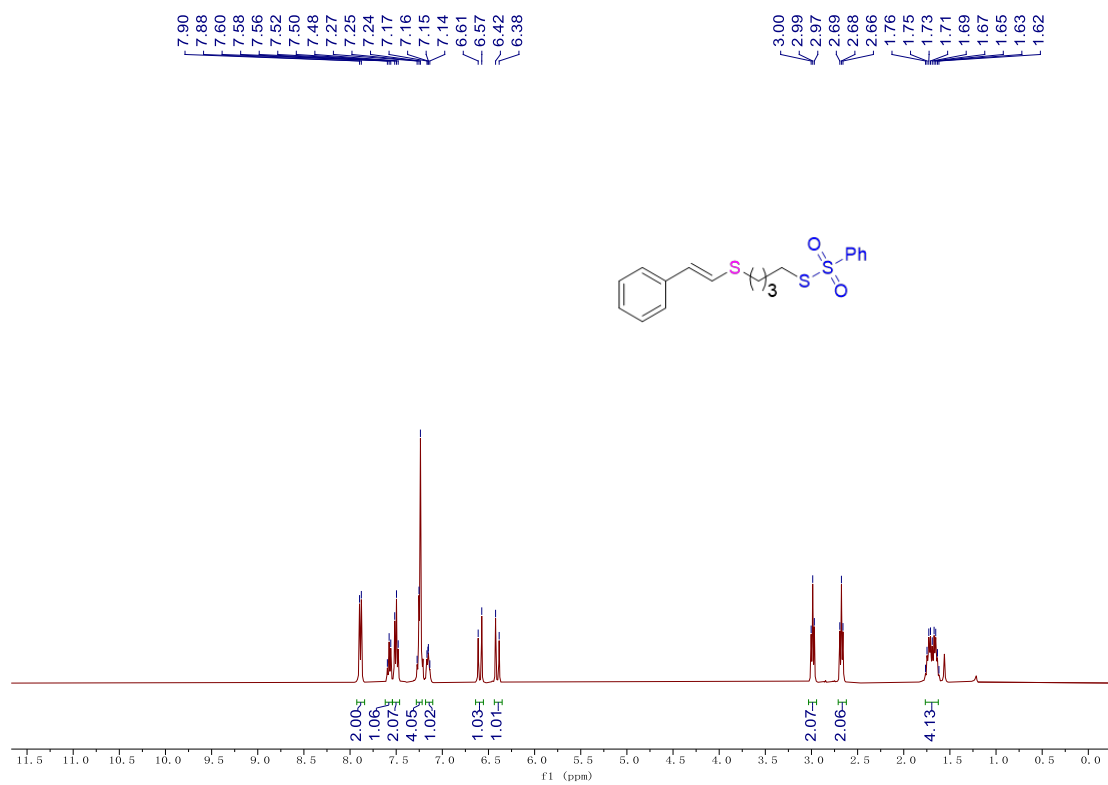


O-phenyl 4-((4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)thio)butane-1-sulfonothioate (5r): Colorless liquid (94.2 mg, 54%). ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, J = 4.5 Hz, 1H), 7.89 - 7.84 (m, 2H), 7.54 (d, J = 7.3 Hz, 1H), 7.51 - 7.45 (m, 3H), 7.25 - 7.18 (m, 2H), 6.91 - 6.83 (m, 4H), 6.82 - 6.73 (m, 3H), 6.67 (d, J = 8.3 Hz, 1H), 5.59 - 5.40 (m, 1H), 4.13 - 4.10 (m, 1H), 4.02 - 3.98 (m, 1H), 2.94 - 2.66 (m, 4H), 1.71 - 1.53 (m, 4H), 1.41 (d, J = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.4, 158.1, 155.7, 150.1, 147.0, 145.0, 138.9, 134.4, 133.9, 132.9, 129.5, 129.4, 128.5, 128.2, 127.2, 121.1, 118.3, 118.3, 117.0, 116.1, 111.9, 71.3, 69.5, 35.8, 34.8, 28.1, 27.8, 17.2. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{32}\text{NO}_5\text{S}_3$: 582.1437; found: 582.1433.

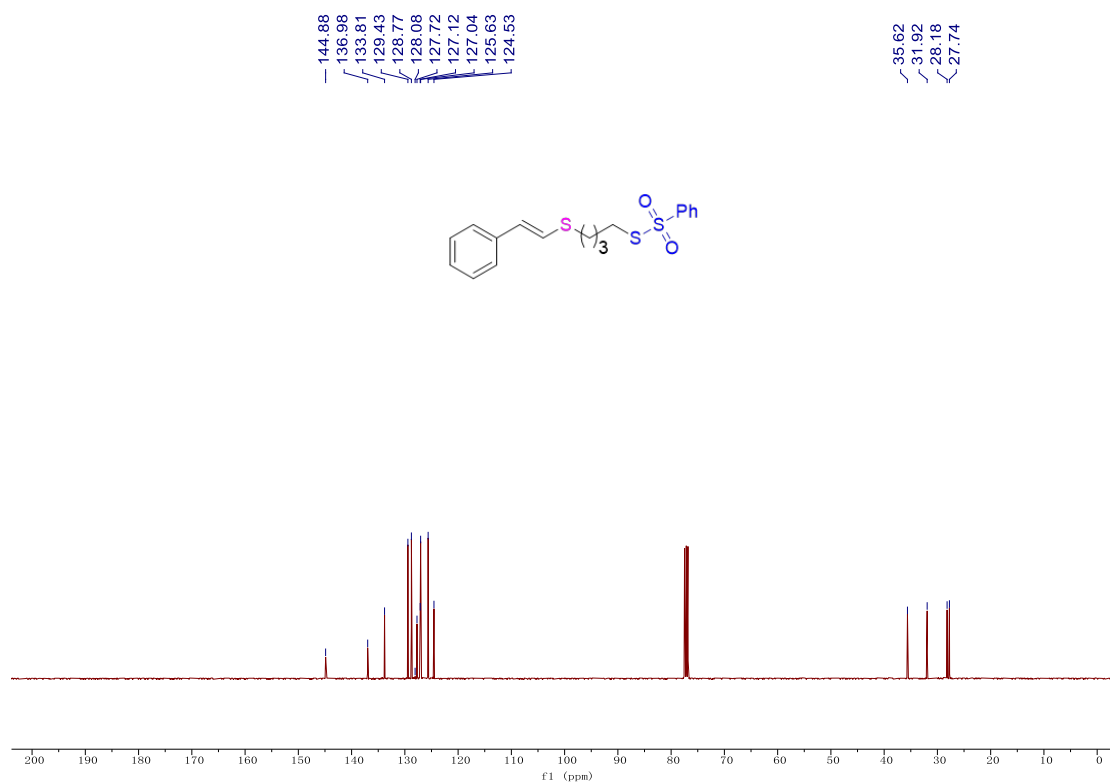
4. References

- [1] Wang, C.; Liu, B.; Shao, Z.; Zhou, J.; Shao, A.; Zou, L.-H.; Wen, J., Synthesis of 1,2-Diamines from Vinyl Sulfonium Salts and Arylamines. *Org. Lett.* **2022**, 24, 6455-6459.
- [2] Wang, S.-M.; Song, H.-X.; Wang, X.-Y.; Liu, N.; Qin, H.-L.; Zhang, C.-P., Palladium-catalyzed Mizoroki–Heck-type reactions of $[\text{Ph}_2\text{SR}_{\text{fn}}][\text{OTf}]$ with alkenes at room temperature. *Chem. Comm.* **2016**, 52, 11893-11896.

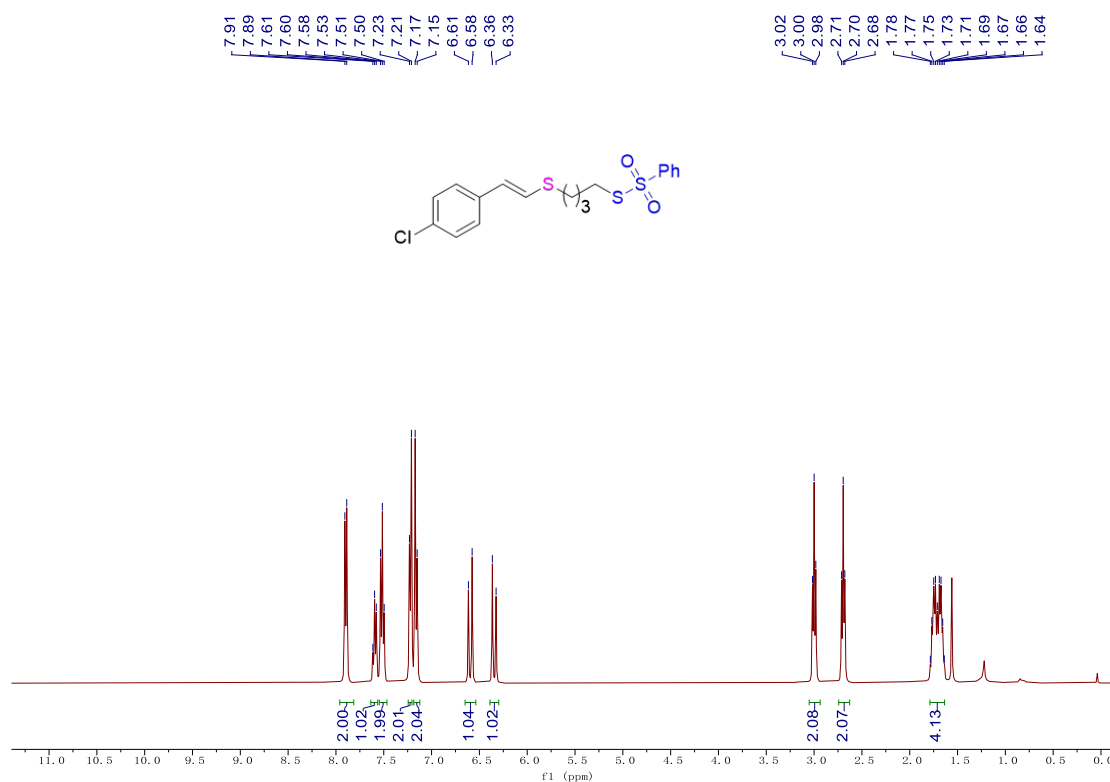
5. NMR spectra of products



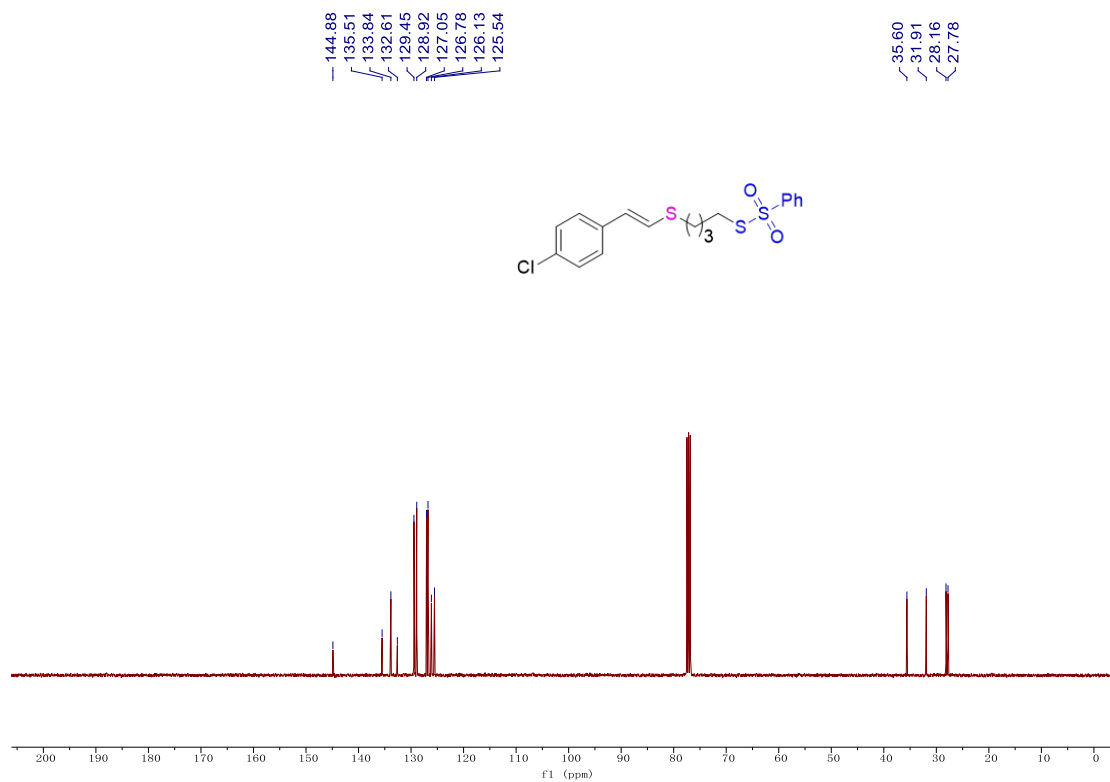
¹H NMR (400 MHz, CDCl₃) spectra of **3a**



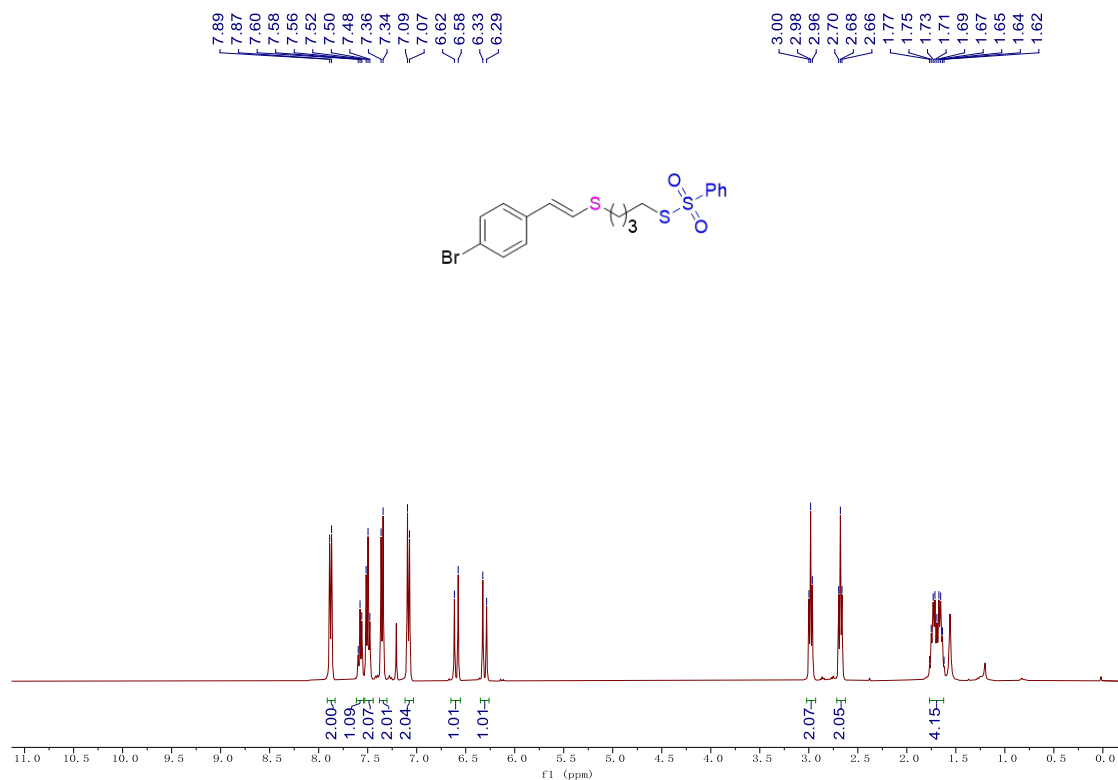
¹³C NMR (101 MHz, CDCl₃) spectra of **3a**



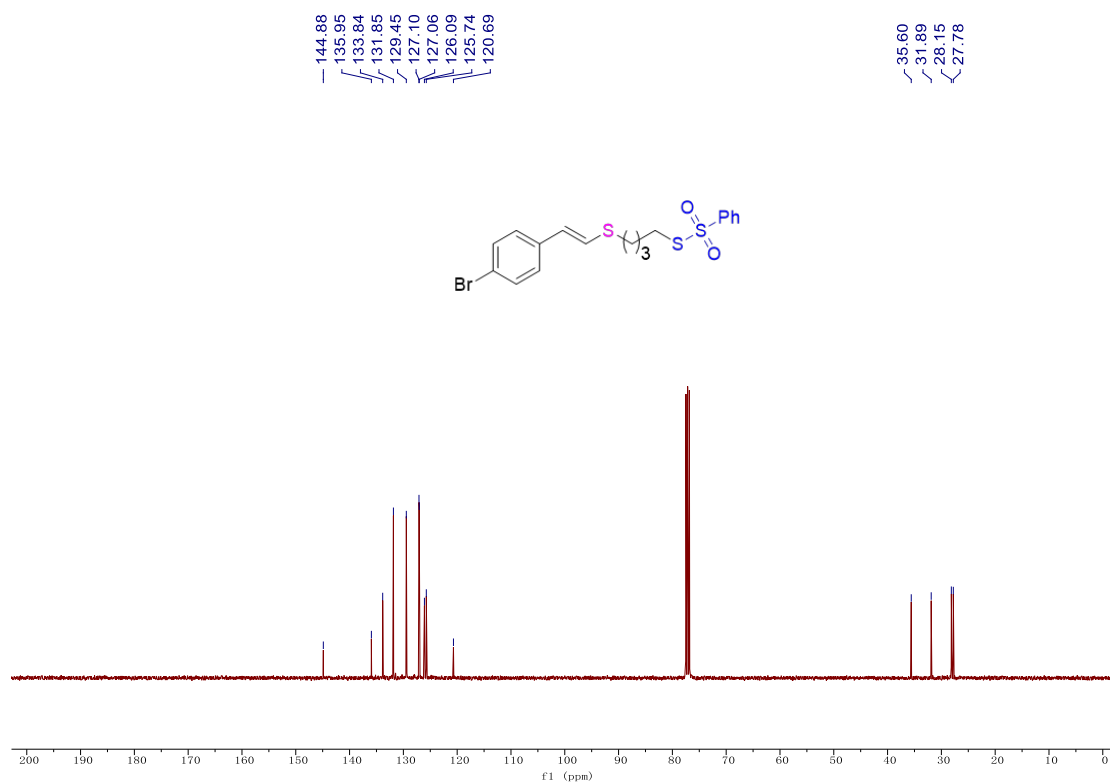
¹H NMR (400 MHz, CDCl₃) spectra of **3b**



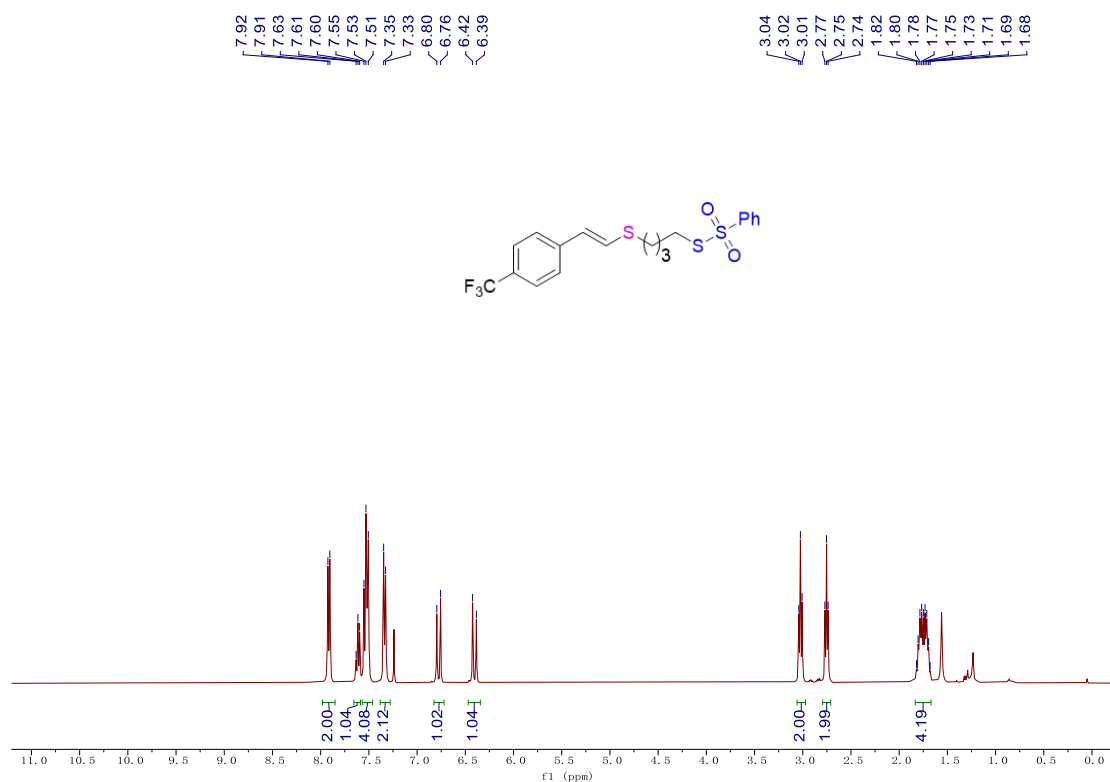
¹³C NMR (101 MHz, CDCl₃) spectra of **3b**



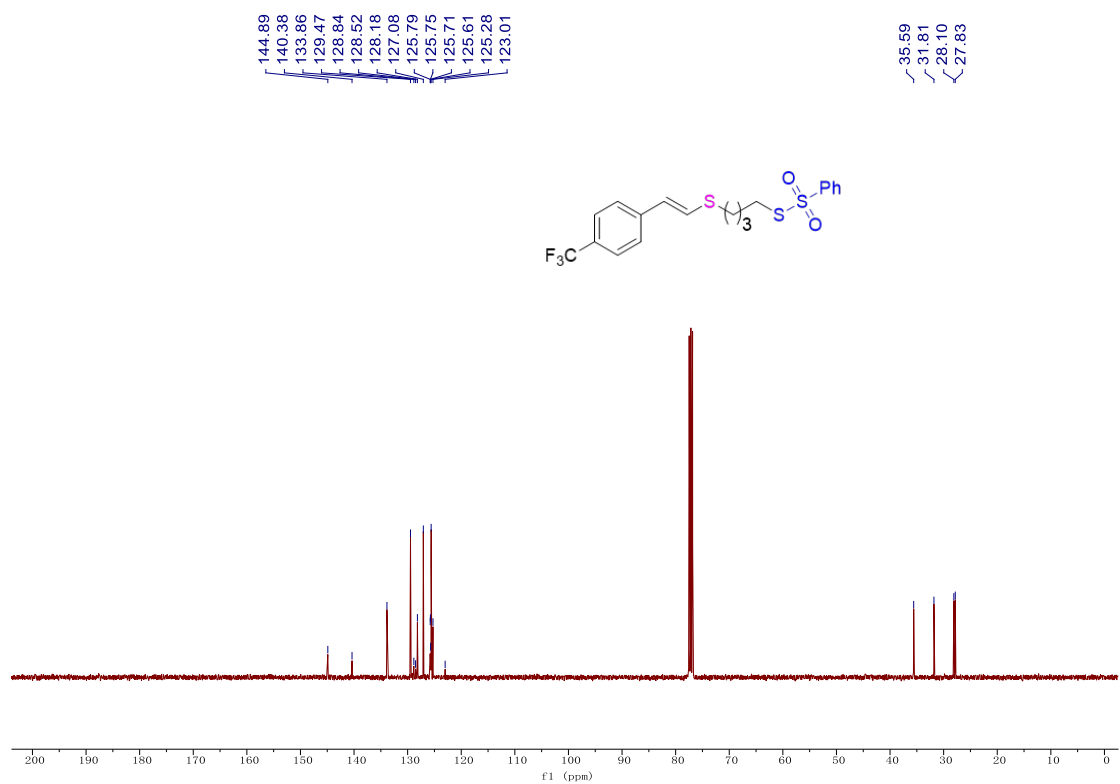
¹H NMR (400 MHz, CDCl₃) spectra of **3c**



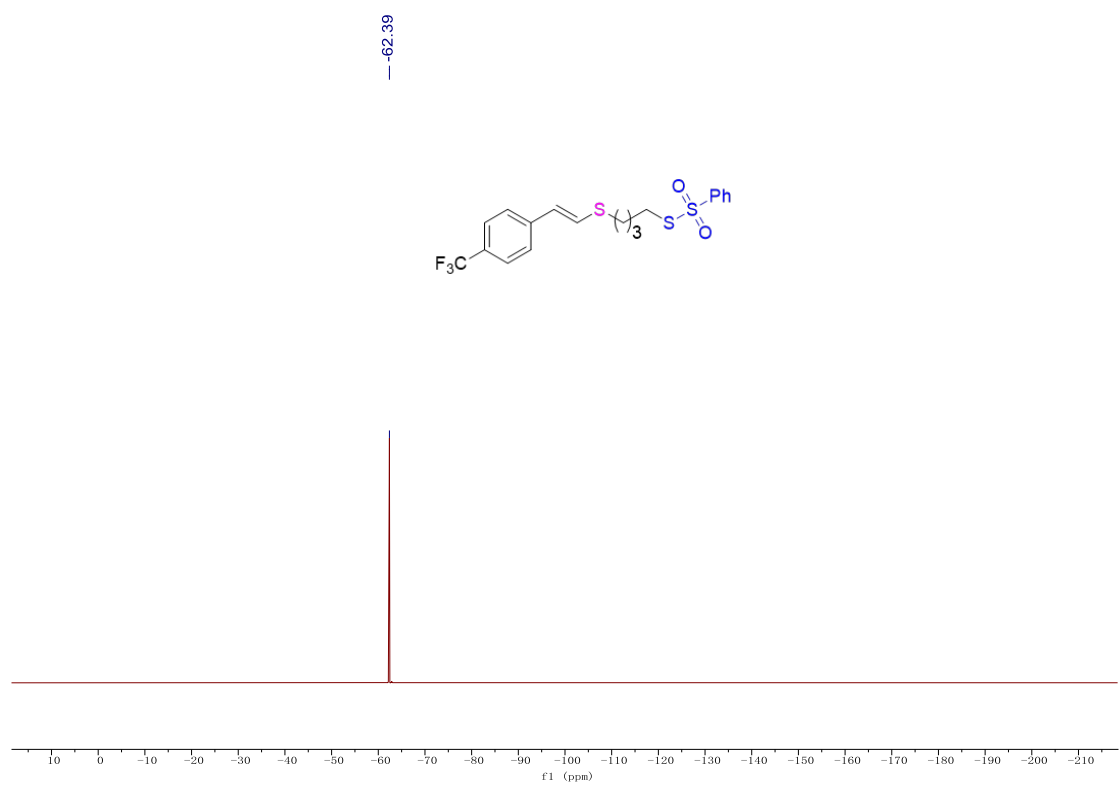
¹³C NMR (101 MHz, CDCl₃) spectra of **3c**



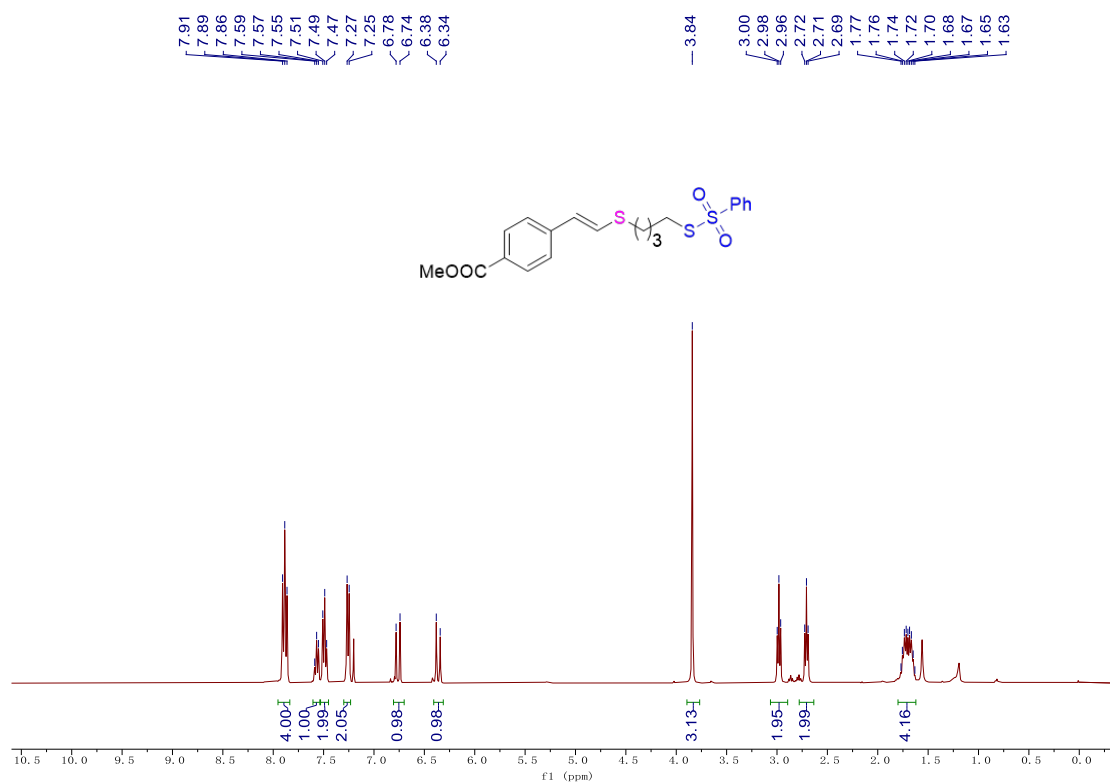
¹H NMR (400 MHz, CDCl₃) spectra of **3d**



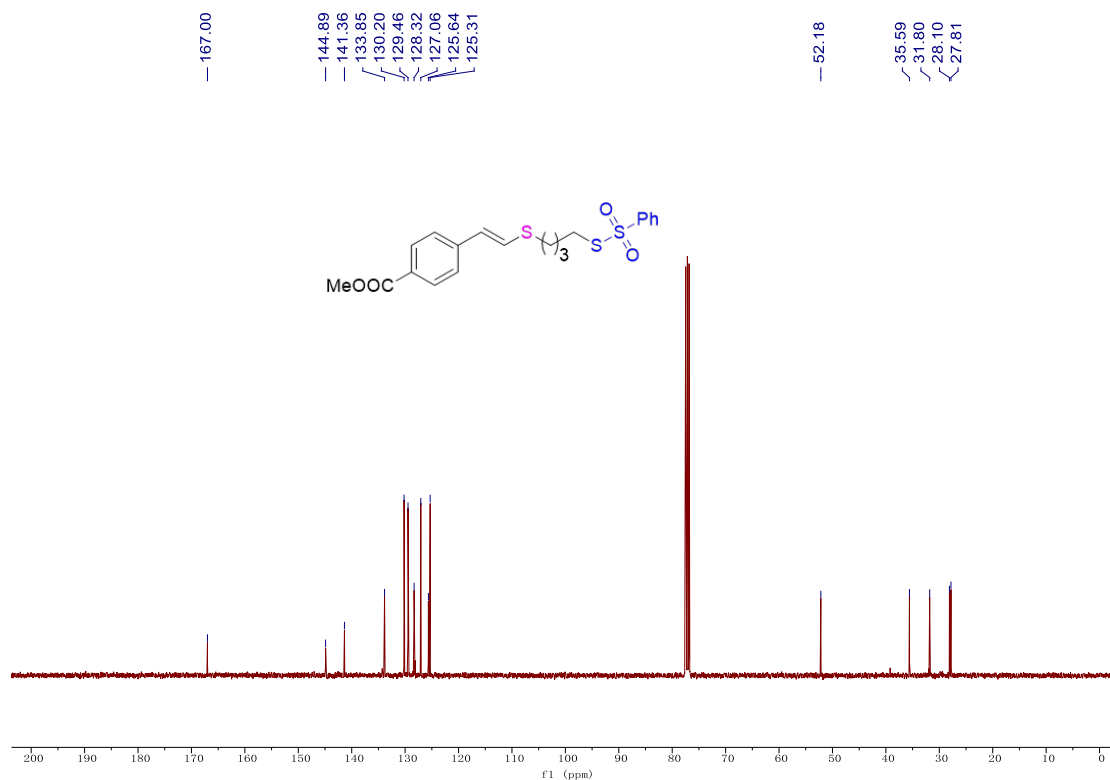
¹³C NMR (101 MHz, CDCl₃) spectra of **3d**



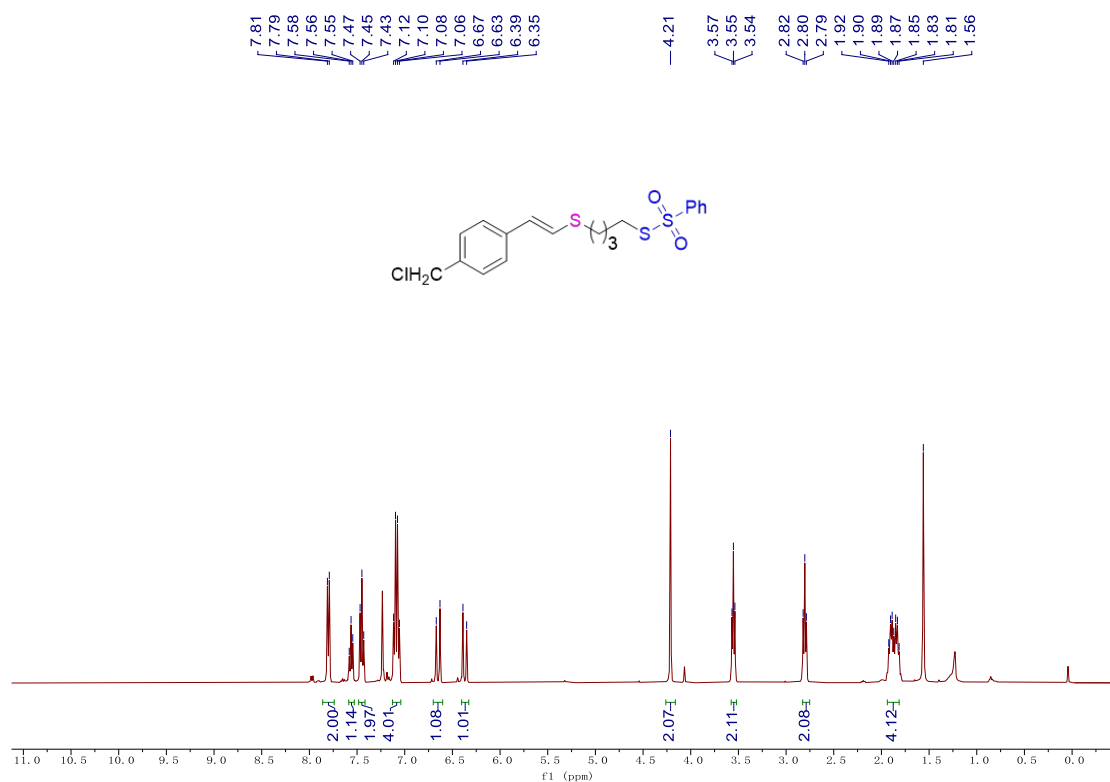
¹⁹F NMR (376 MHz, CDCl₃) spectra of **3d**



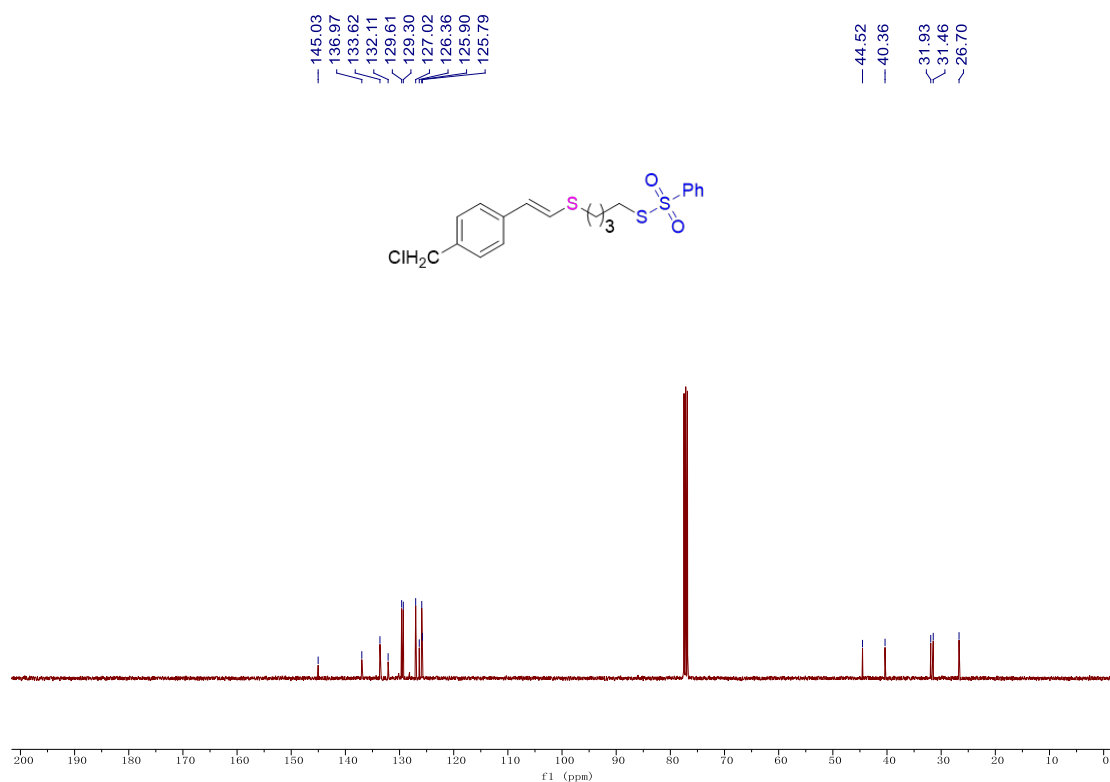
¹H NMR (400 MHz, CDCl₃) spectra of **3e**



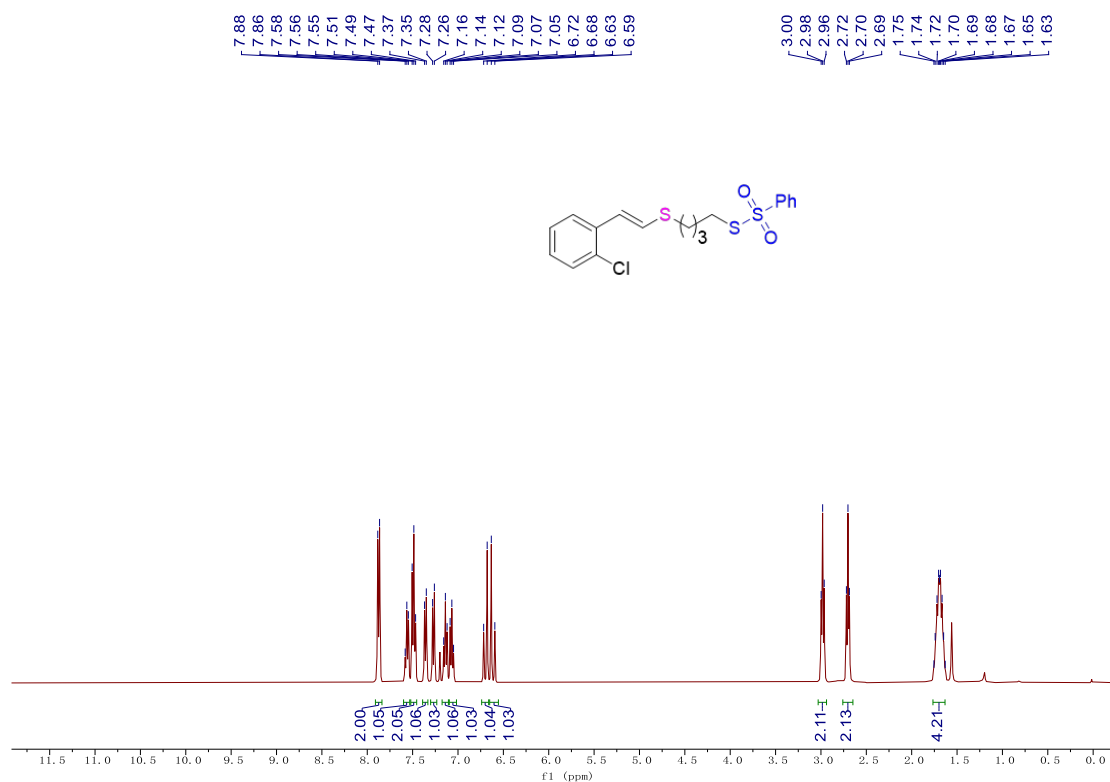
¹³C NMR (101 MHz, CDCl₃) spectra of **3e**



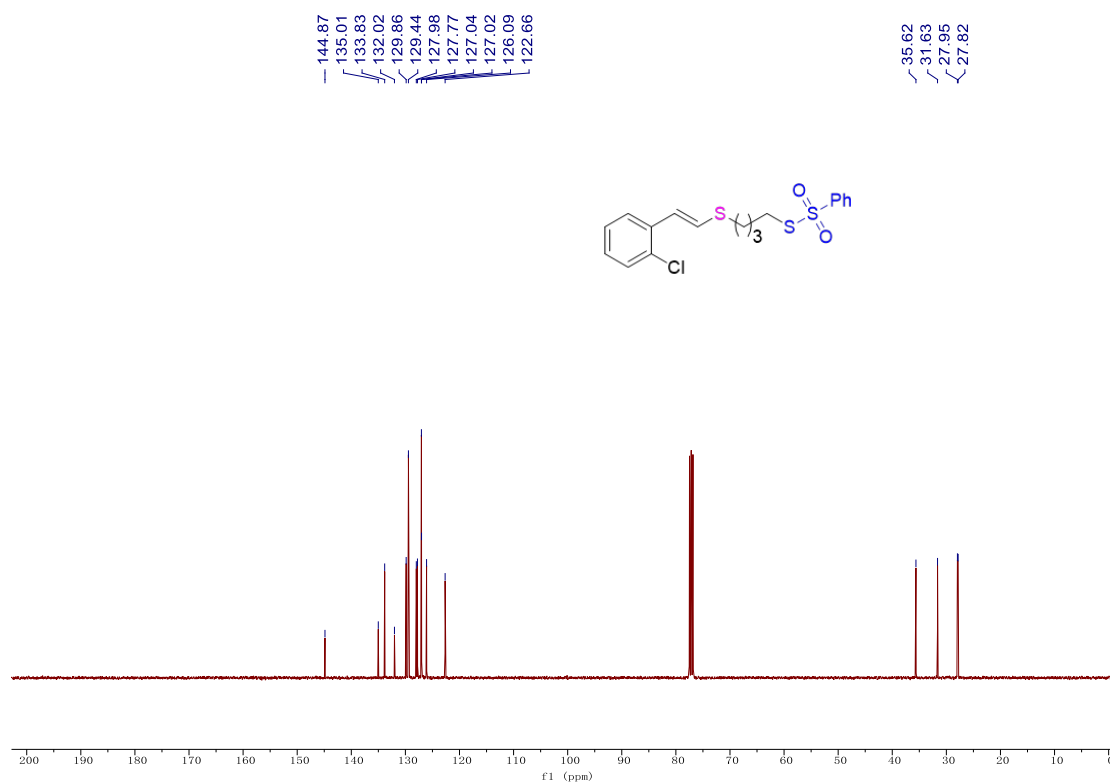
¹H NMR (400 MHz, CDCl₃) spectra of **3f**



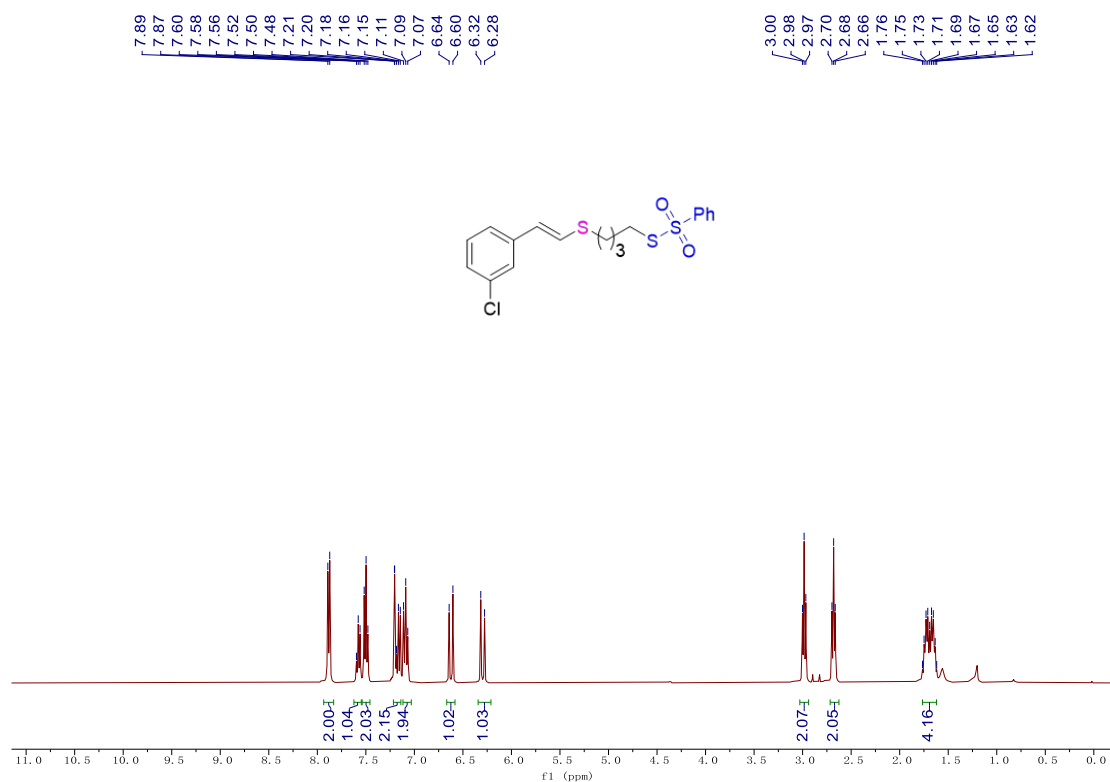
¹³C NMR (101 MHz, CDCl₃) spectra of **3f**



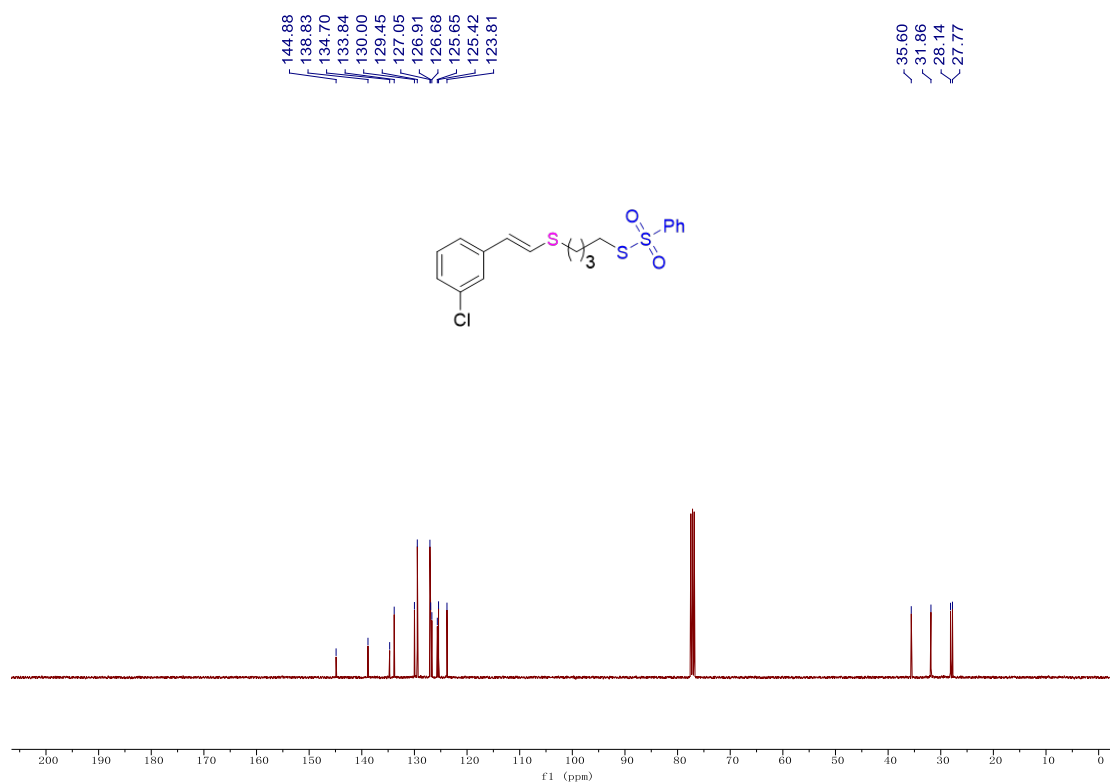
¹H NMR (400 MHz, CDCl₃) spectra of **3g**



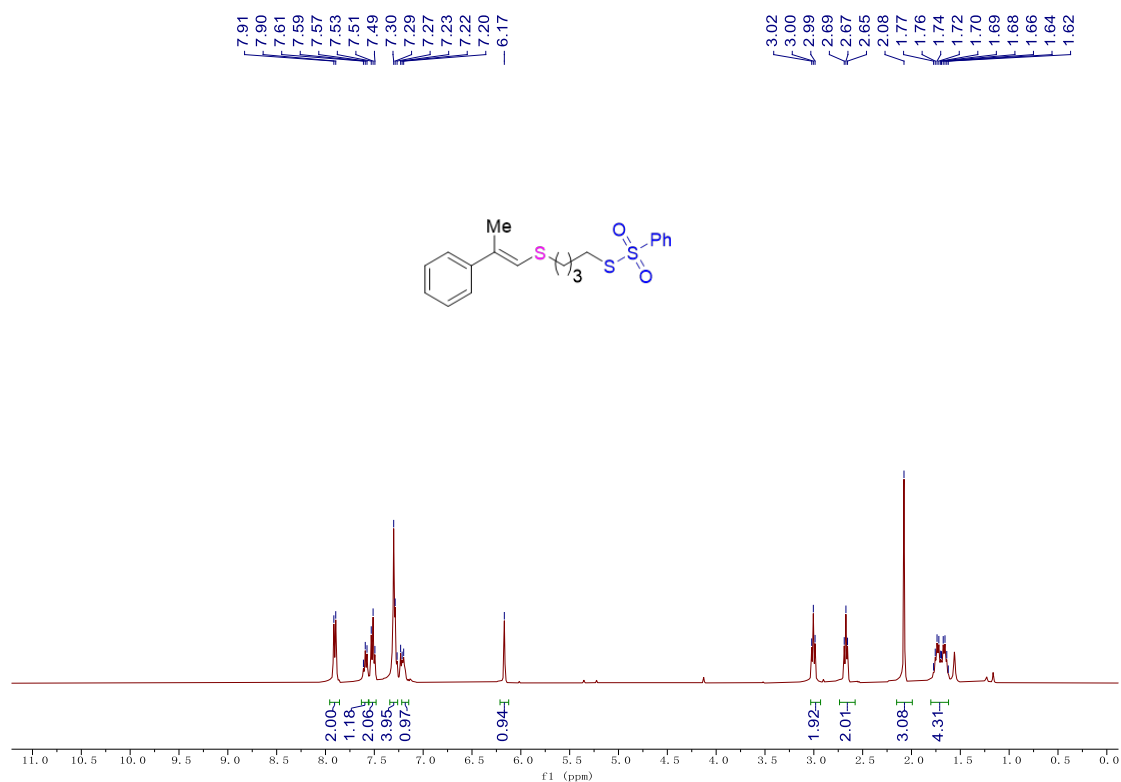
¹³C NMR (101 MHz, CDCl₃) spectra of **3g**



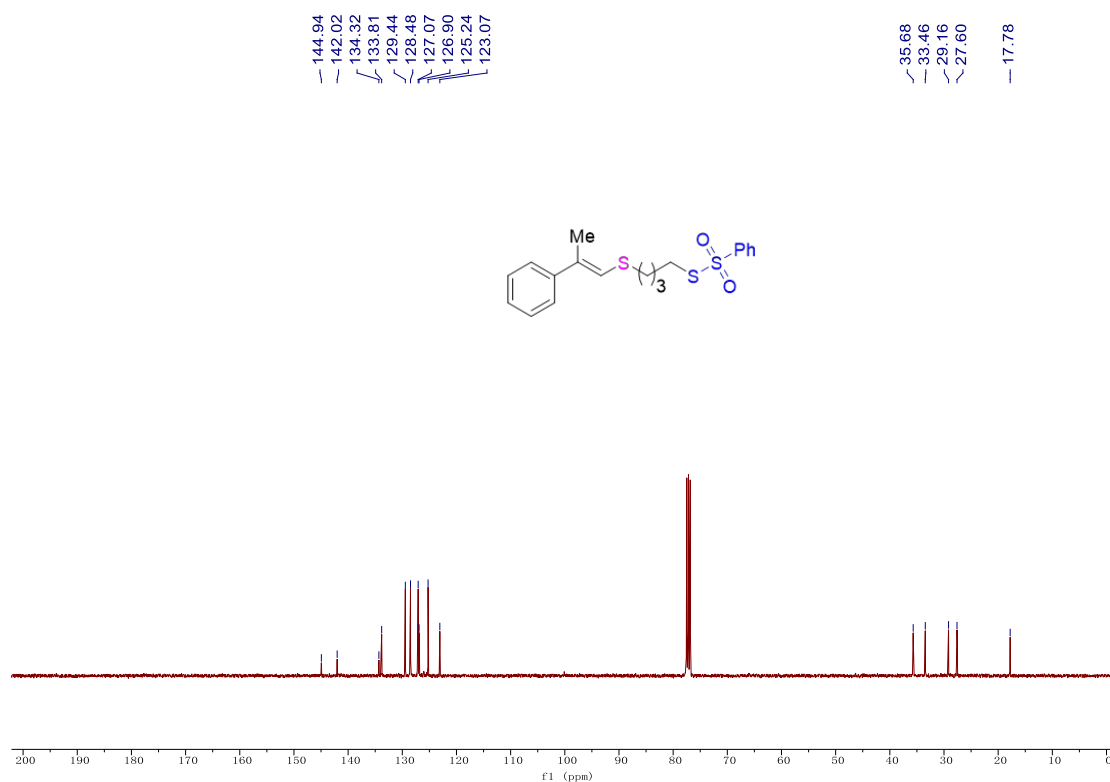
¹H NMR (400 MHz, CDCl₃) spectra of **3h**



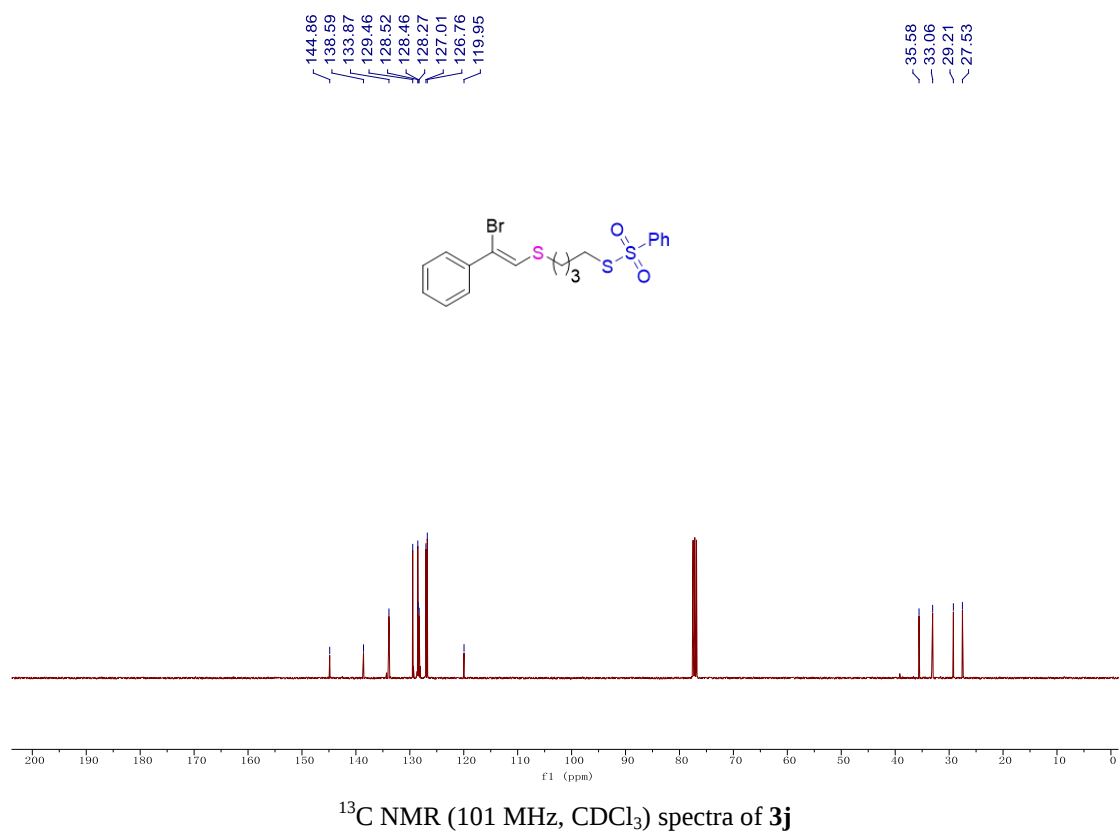
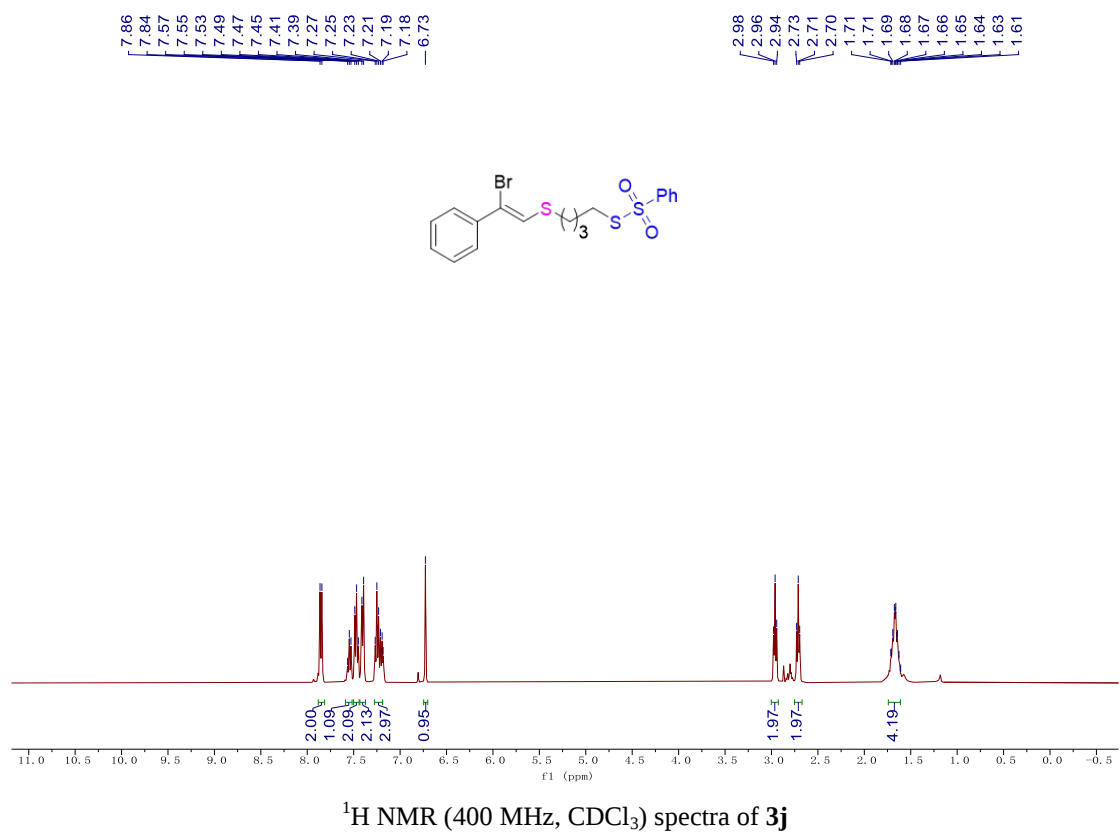
¹³C NMR (101 MHz, CDCl₃) spectra of **3h**

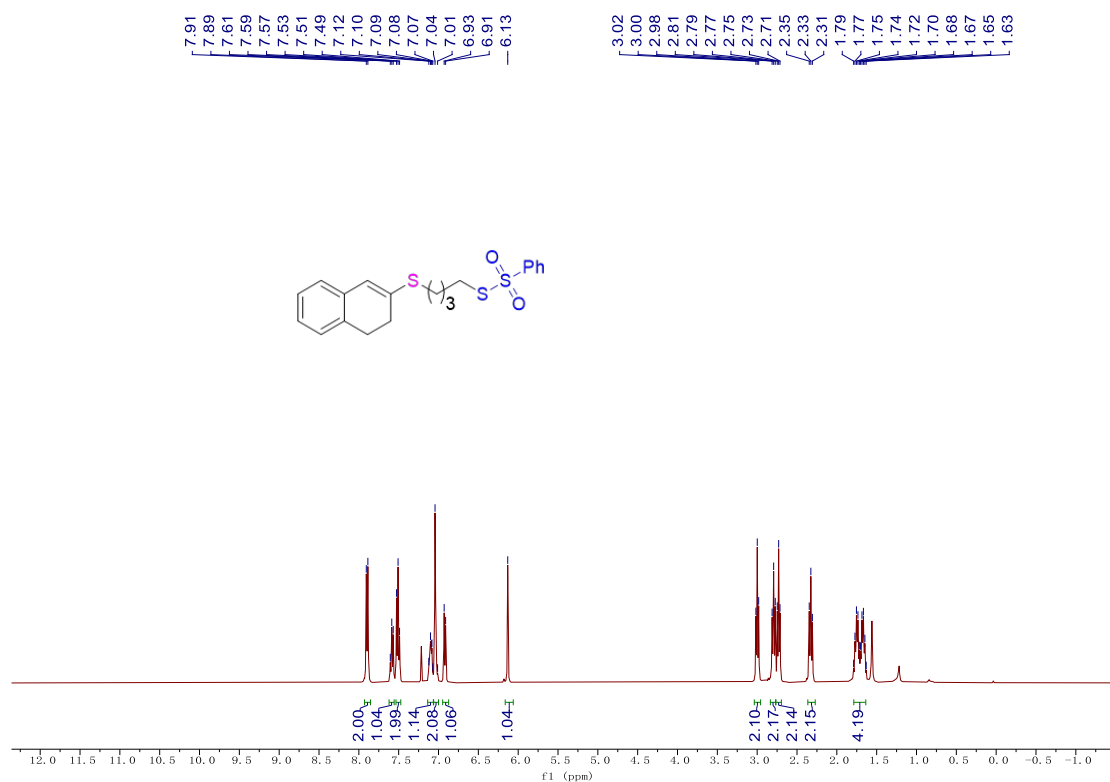


¹H NMR (400 MHz, CDCl₃) spectra of **3i**

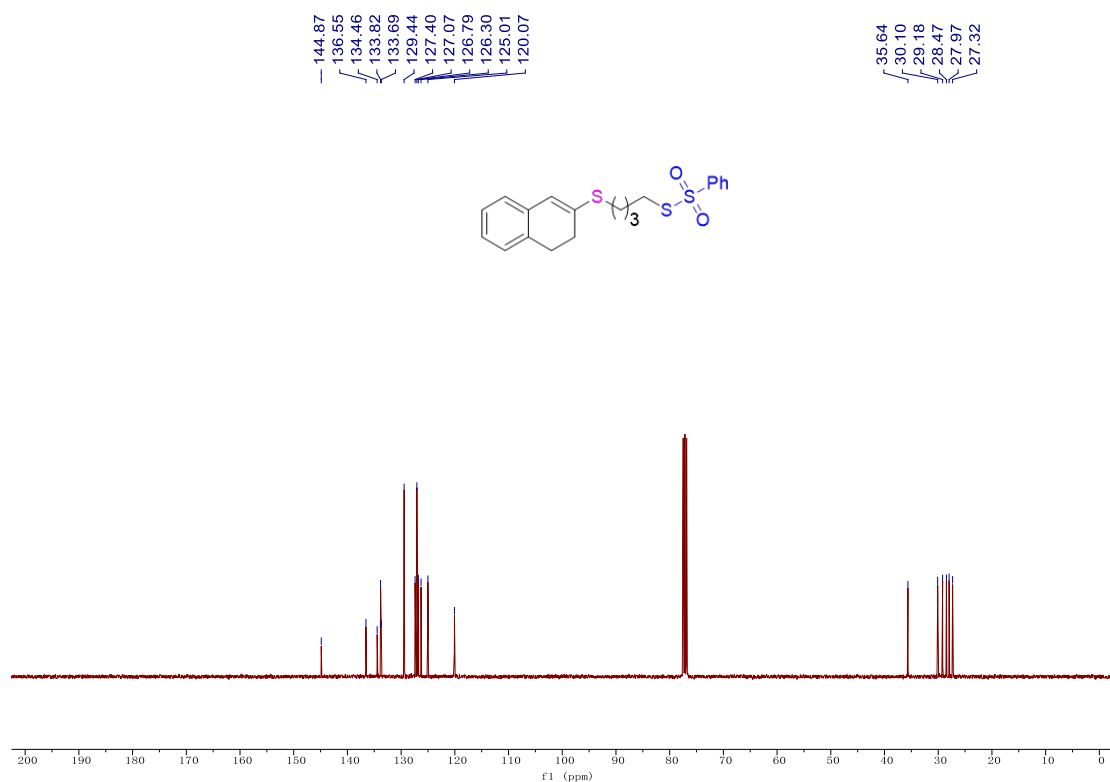


¹³C NMR (101 MHz, CDCl₃) spectra of **3i**

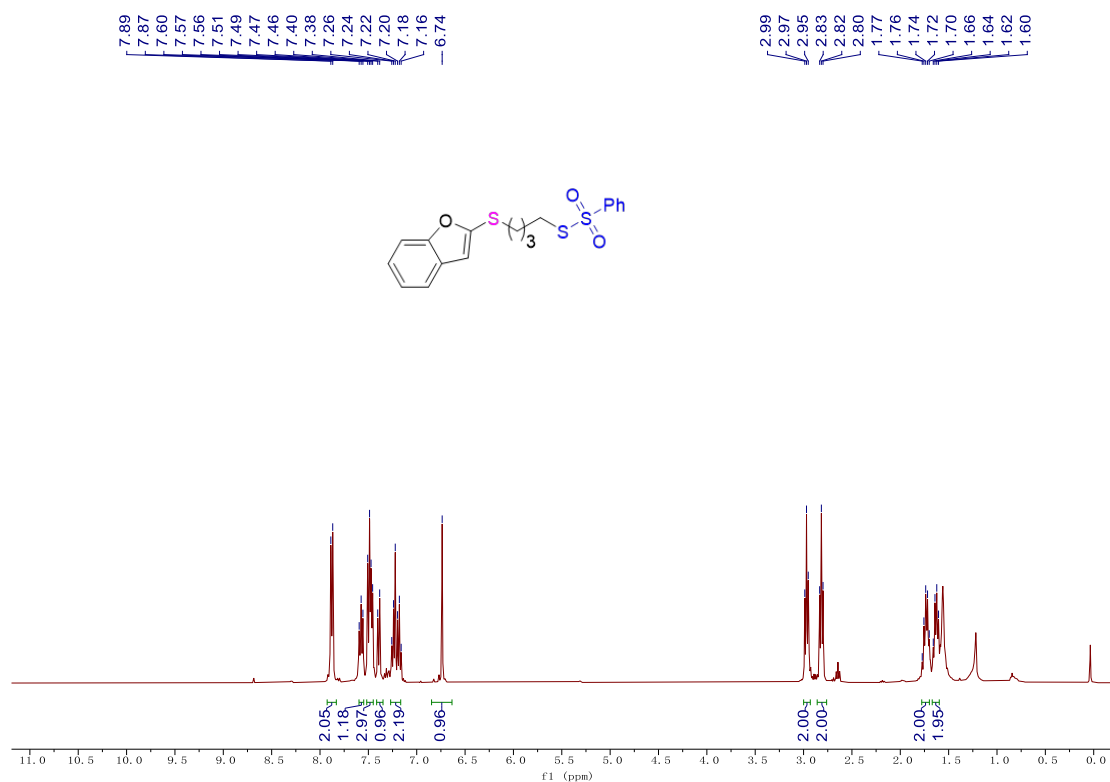




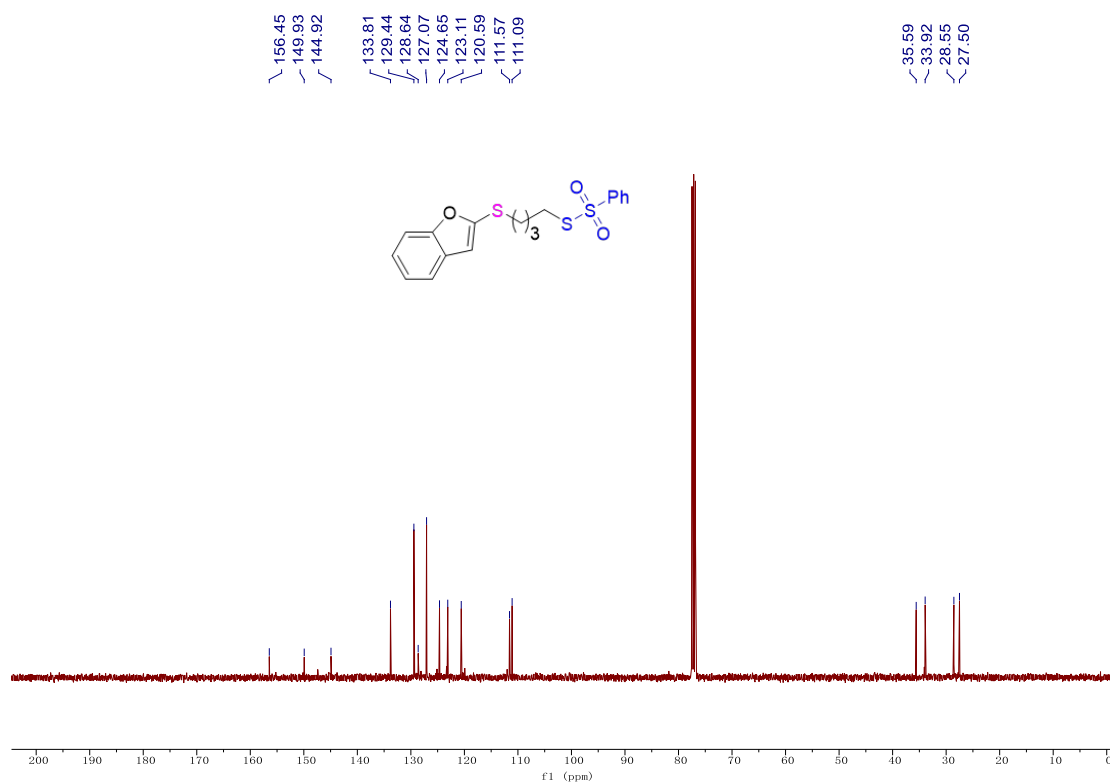
¹H NMR (400 MHz, CDCl₃) spectra of **3k**



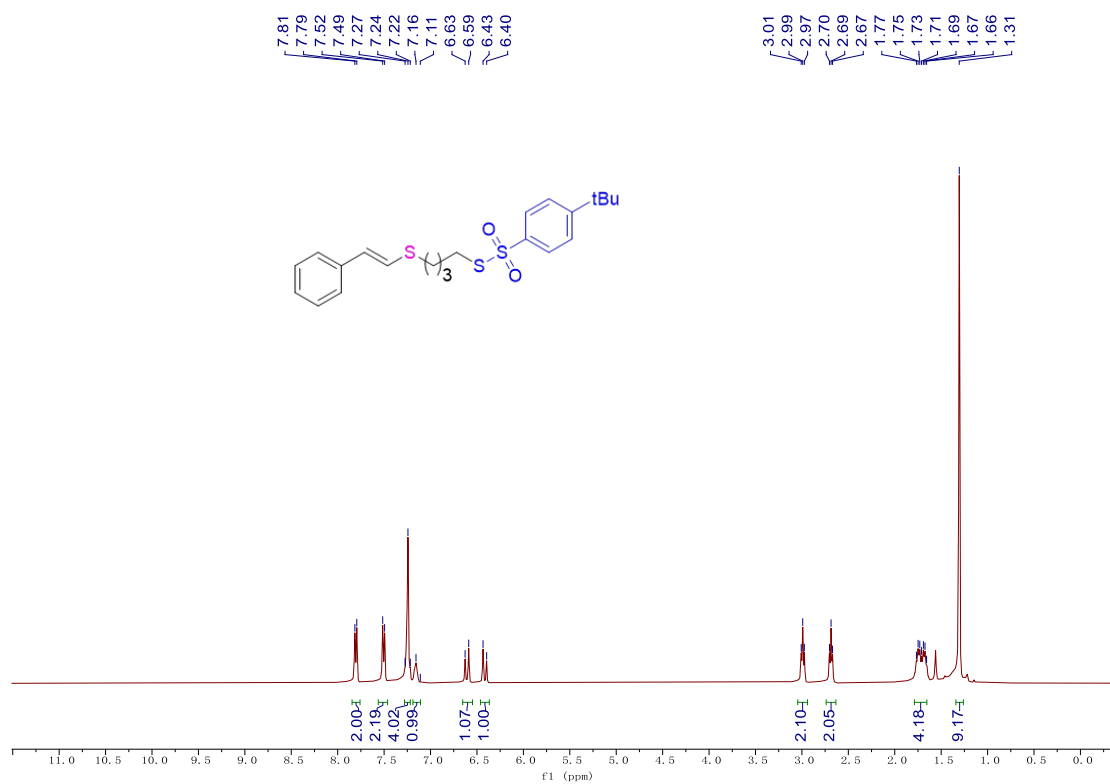
¹³C NMR (101 MHz, CDCl₃) spectra of **3k**



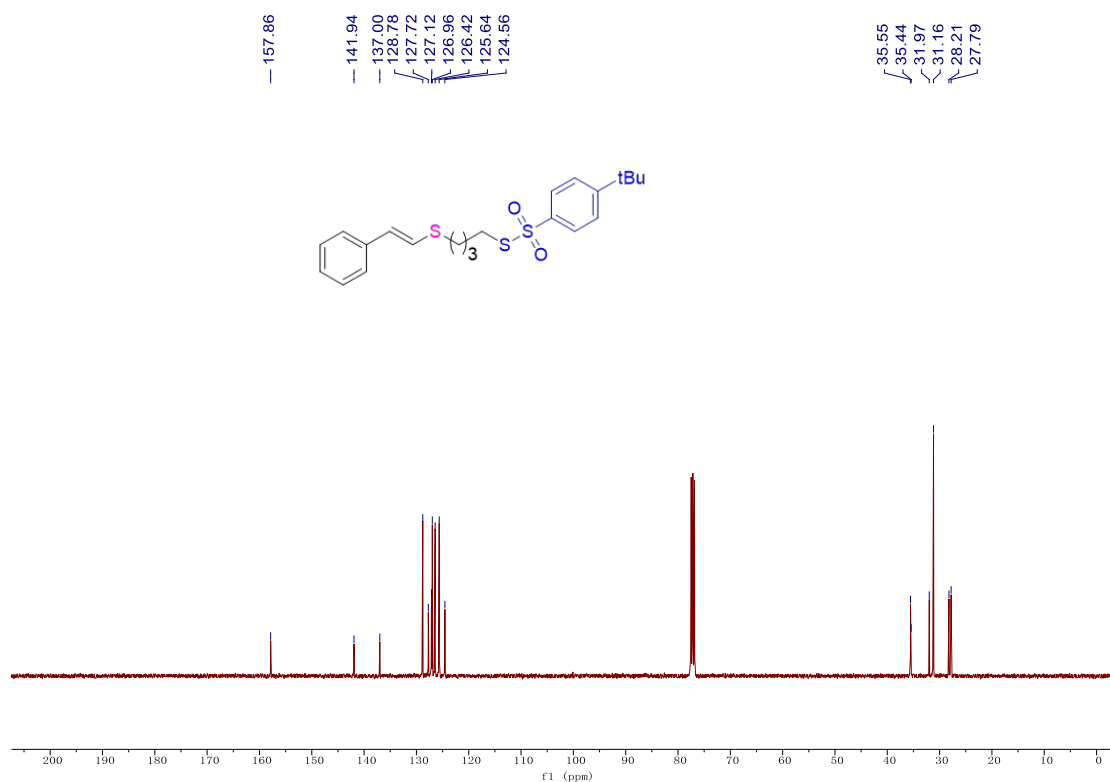
¹H NMR (400 MHz, CDCl₃) spectra of **3l**



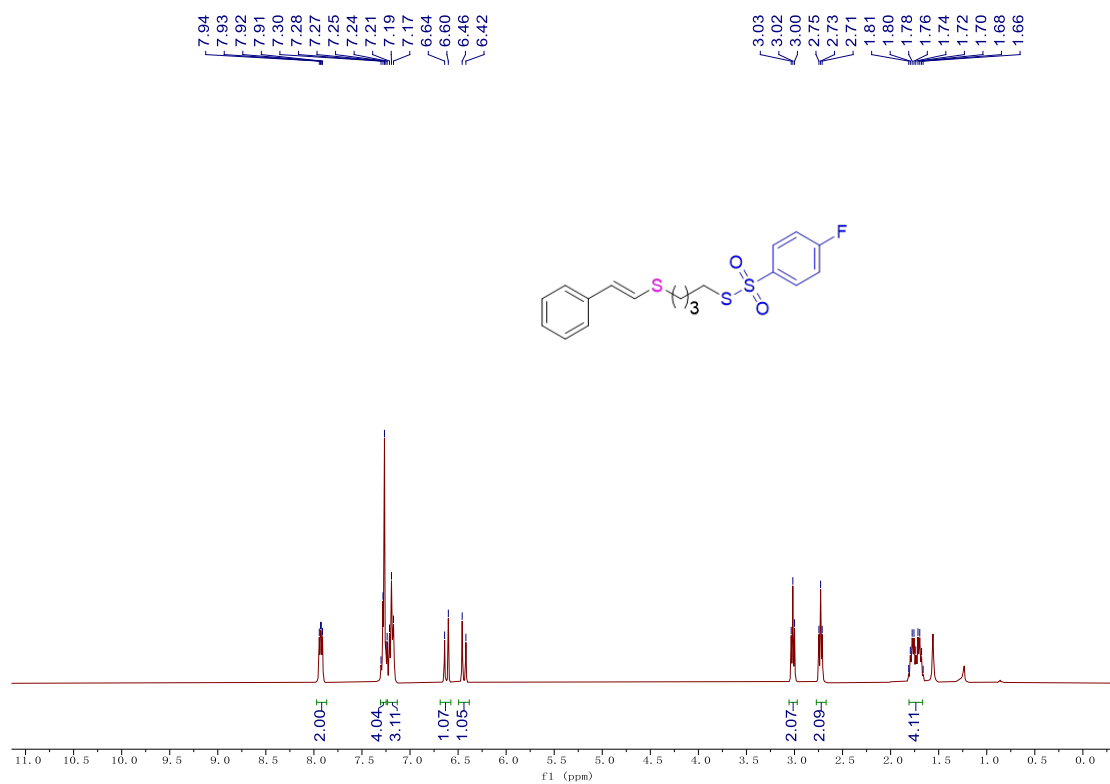
¹³C NMR (101 MHz, CDCl₃) spectra of **3l**



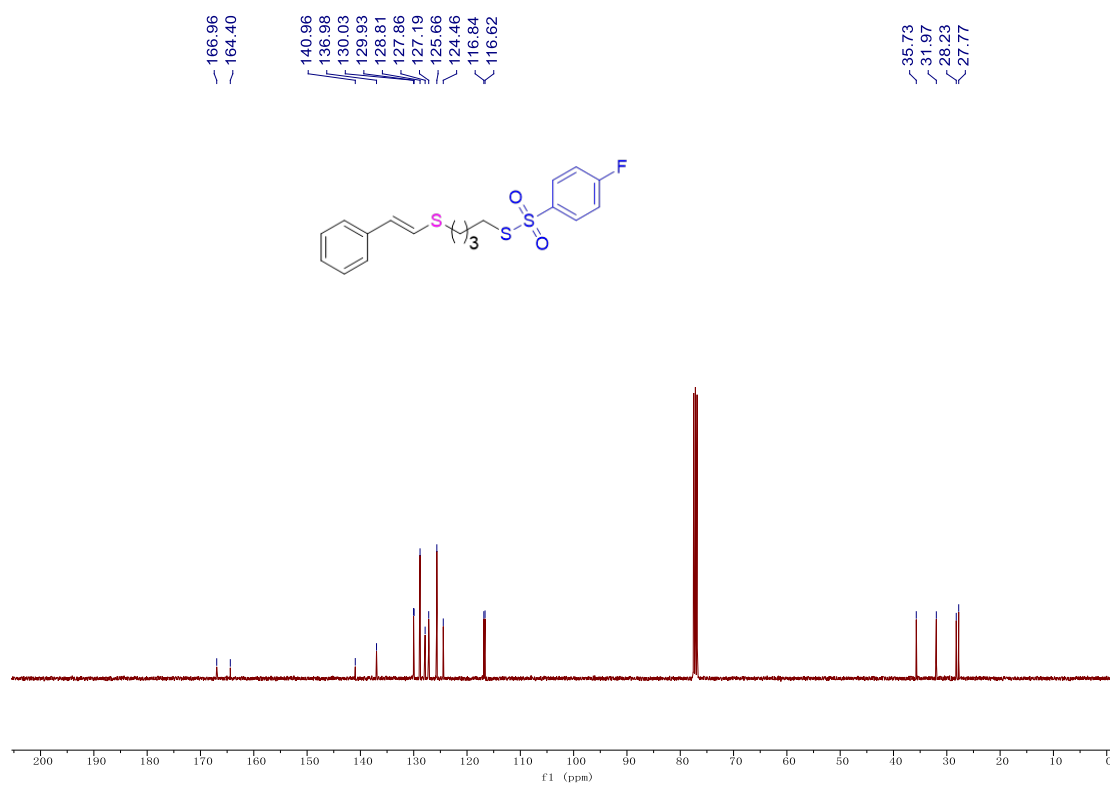
¹H NMR (400 MHz, CDCl₃) spectra of **3m**



¹³C NMR (101 MHz, CDCl₃) spectra of **3m**



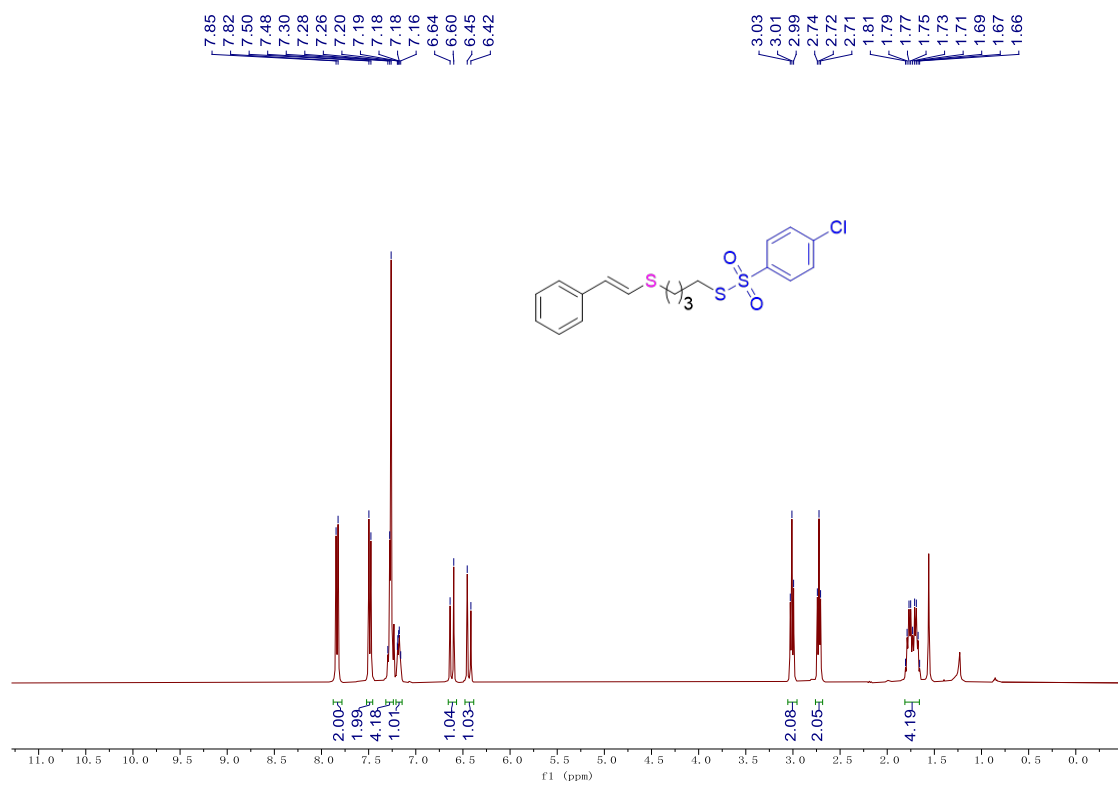
¹H NMR (400 MHz, CDCl₃) spectra of **3n**



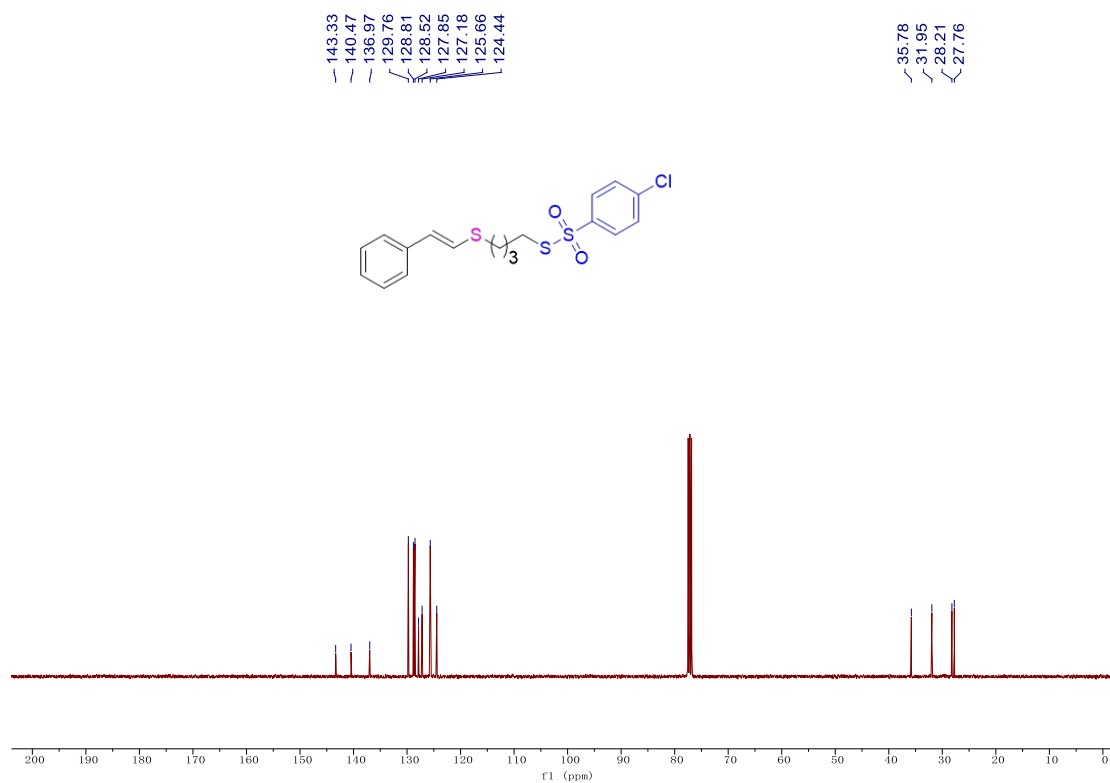
¹³C NMR (101 MHz, CDCl₃) spectra of **3n**



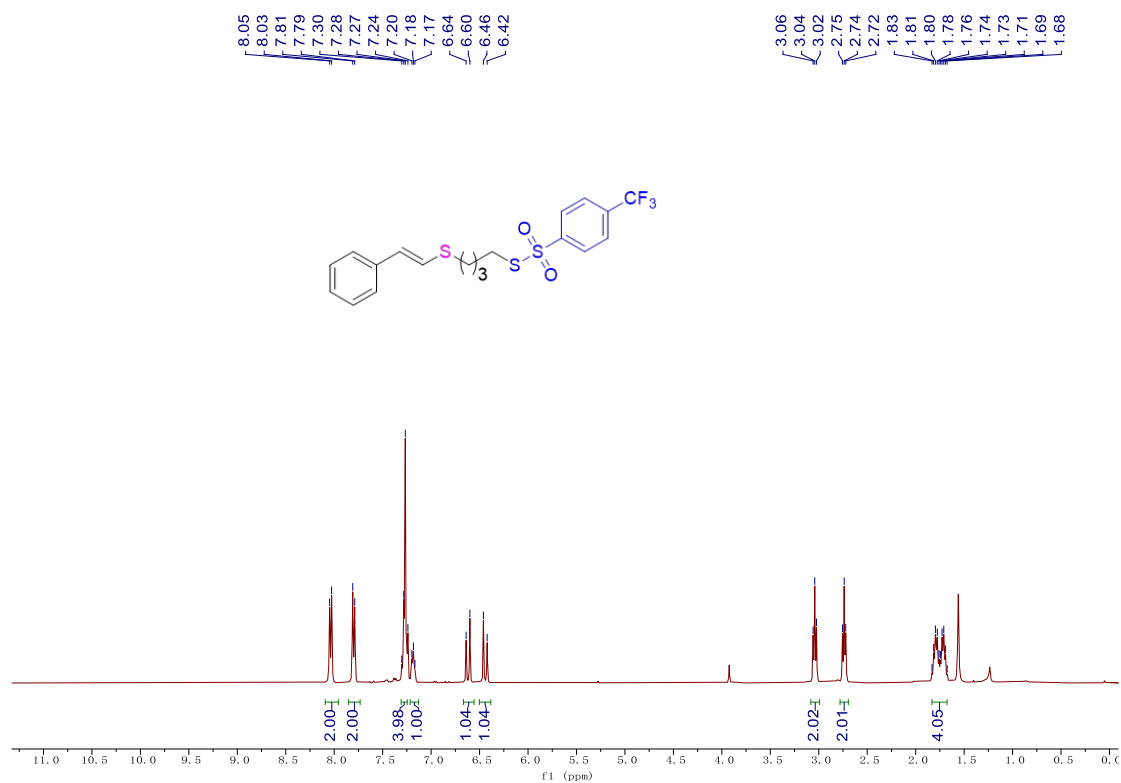
¹⁹F NMR (376 MHz, CDCl₃) spectra of **3n**



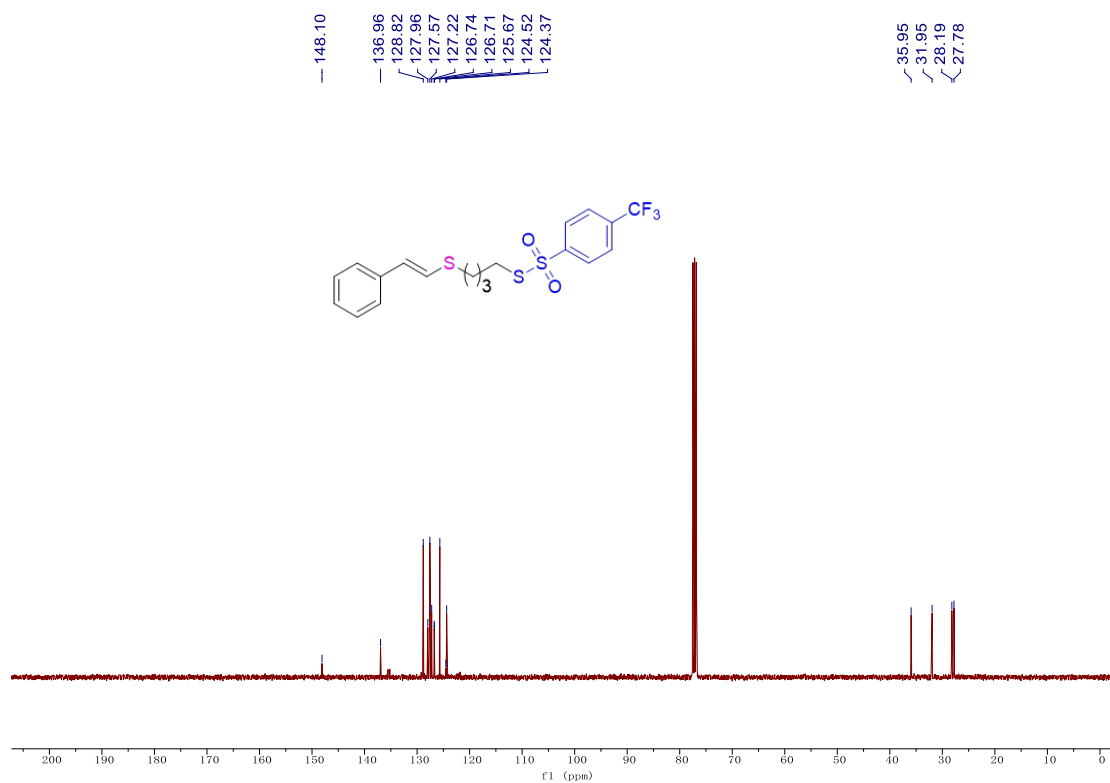
¹H NMR (400 MHz, CDCl₃) spectra of **3o**



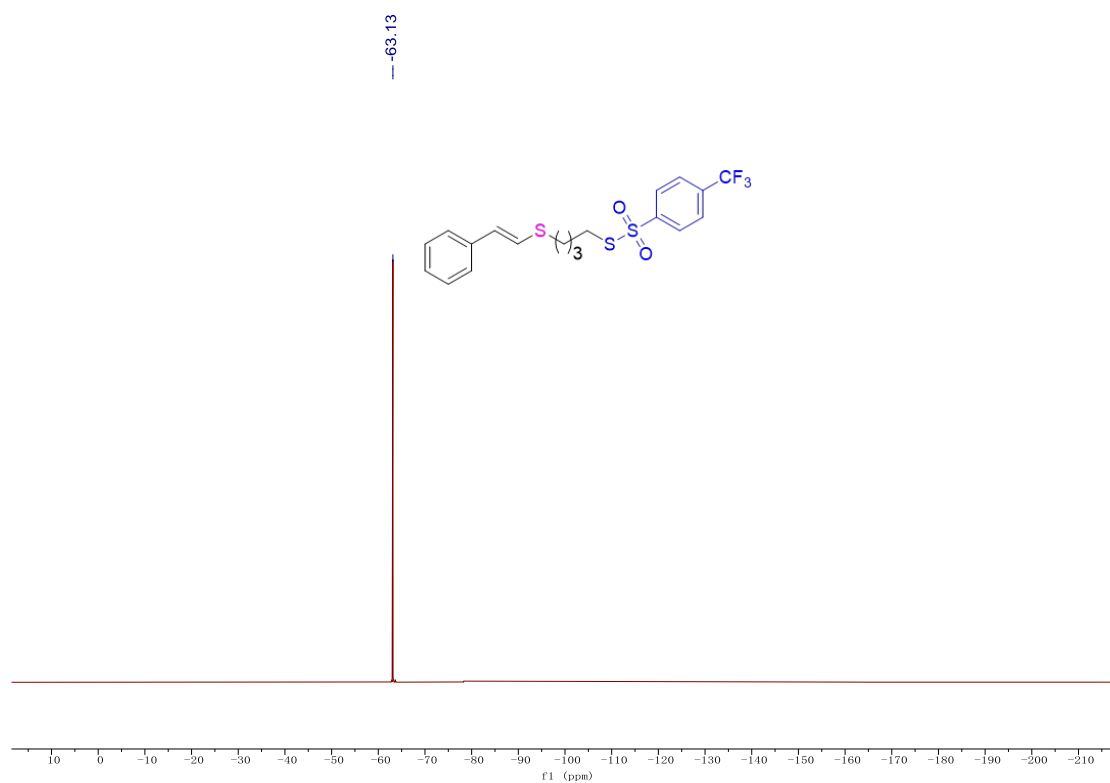
¹³C NMR (101 MHz, CDCl₃) spectra of **3o**



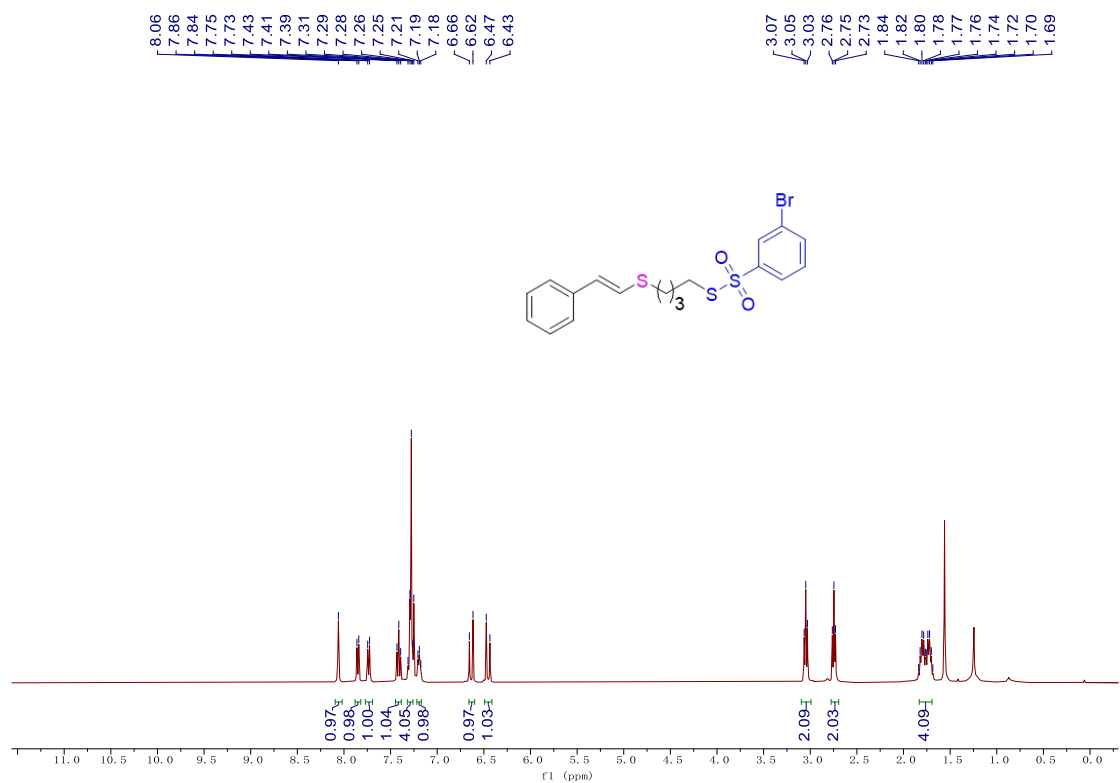
¹H NMR (400 MHz, CDCl₃) spectra of **3p**



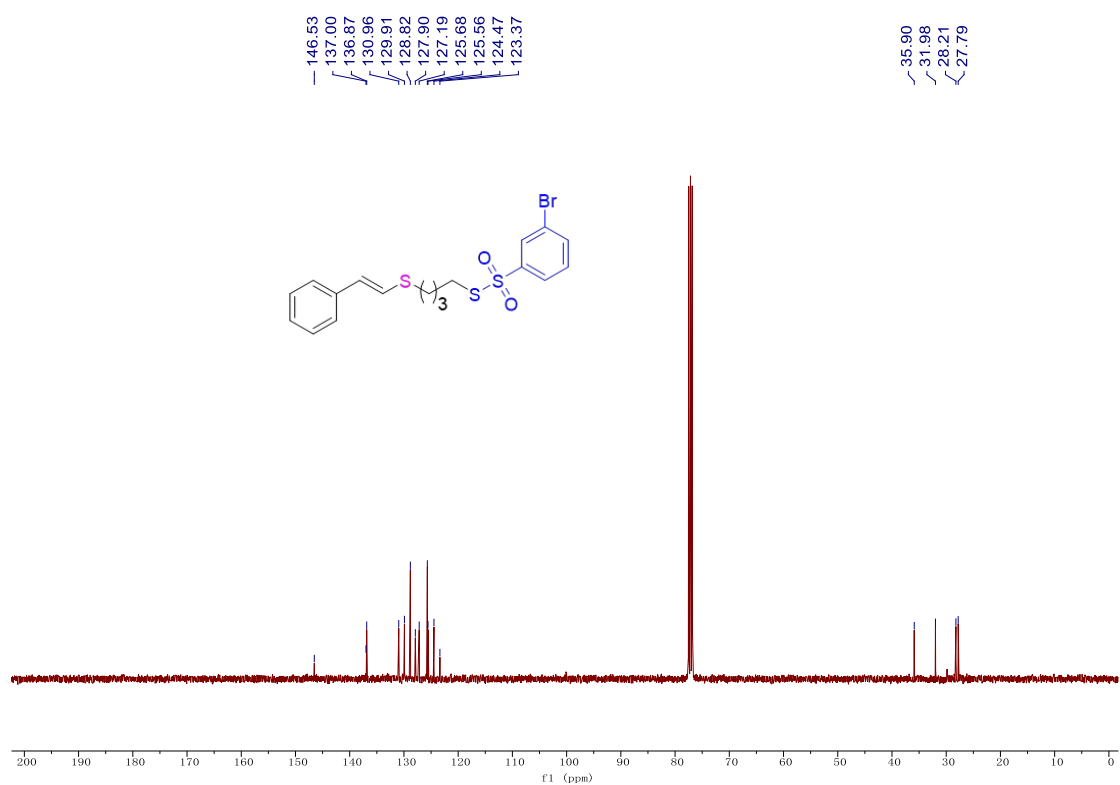
¹³C NMR (101 MHz, CDCl₃) spectra of **3p**



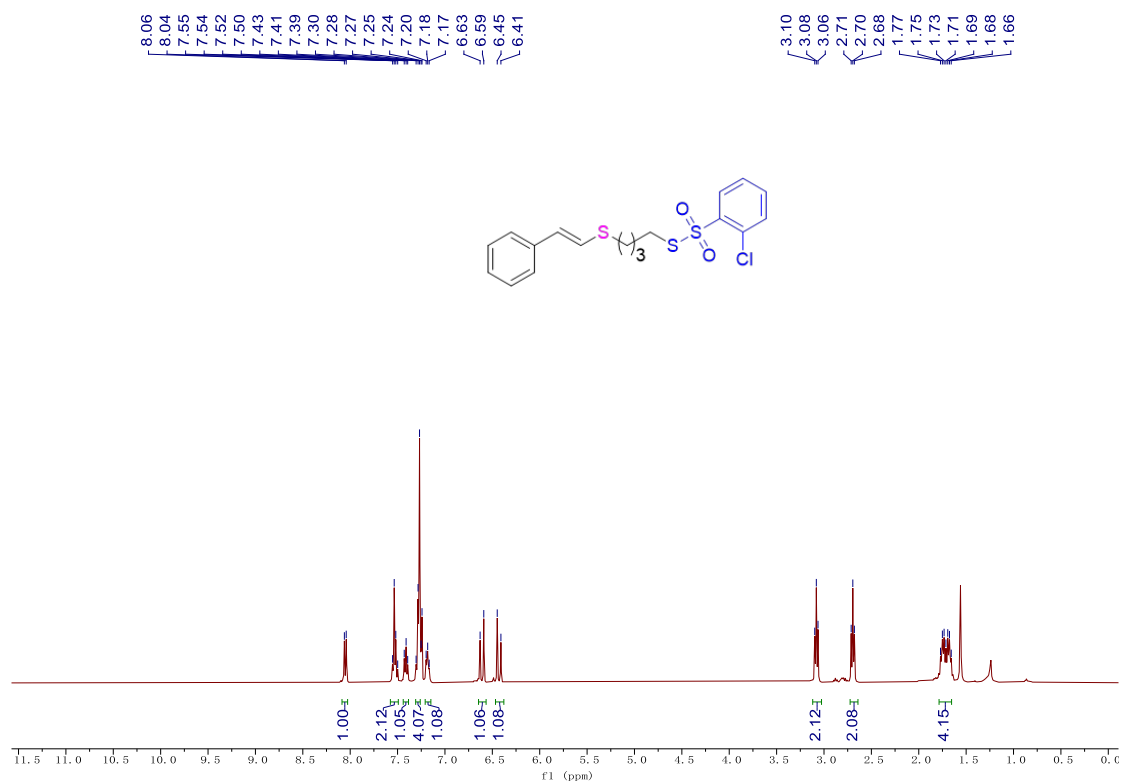
¹⁹F NMR (376 MHz, CDCl₃) spectra of **3p**



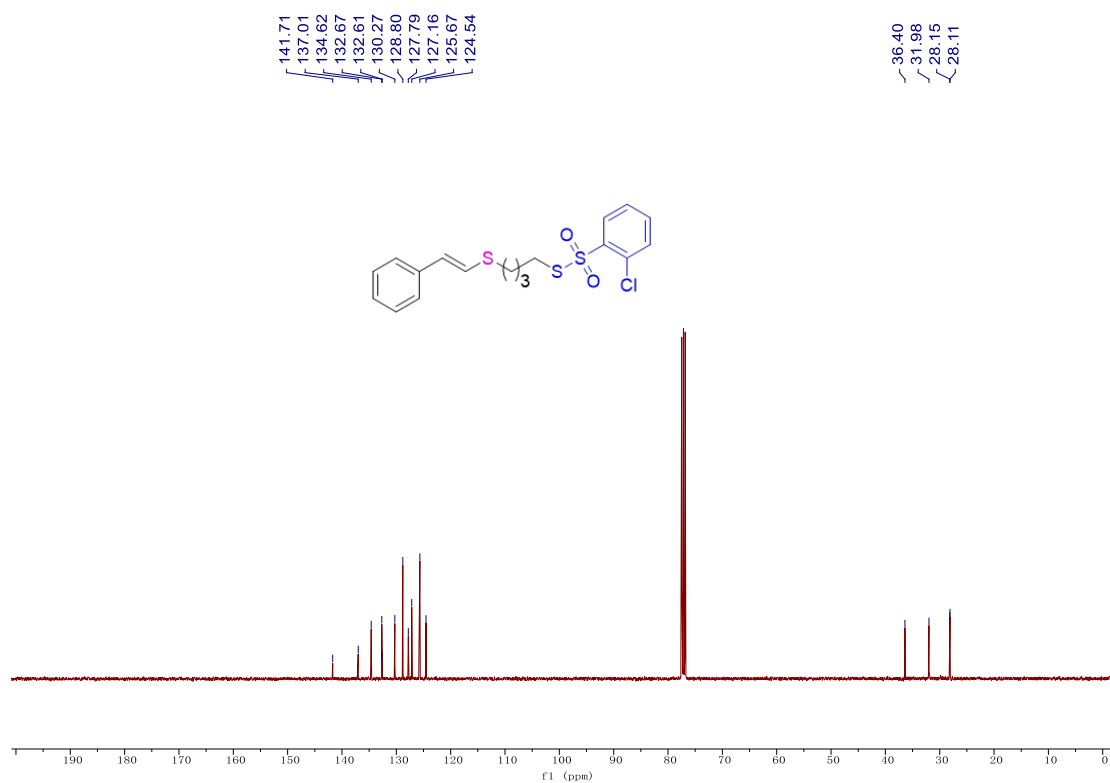
¹H NMR (400 MHz, CDCl₃) spectra of **3q**



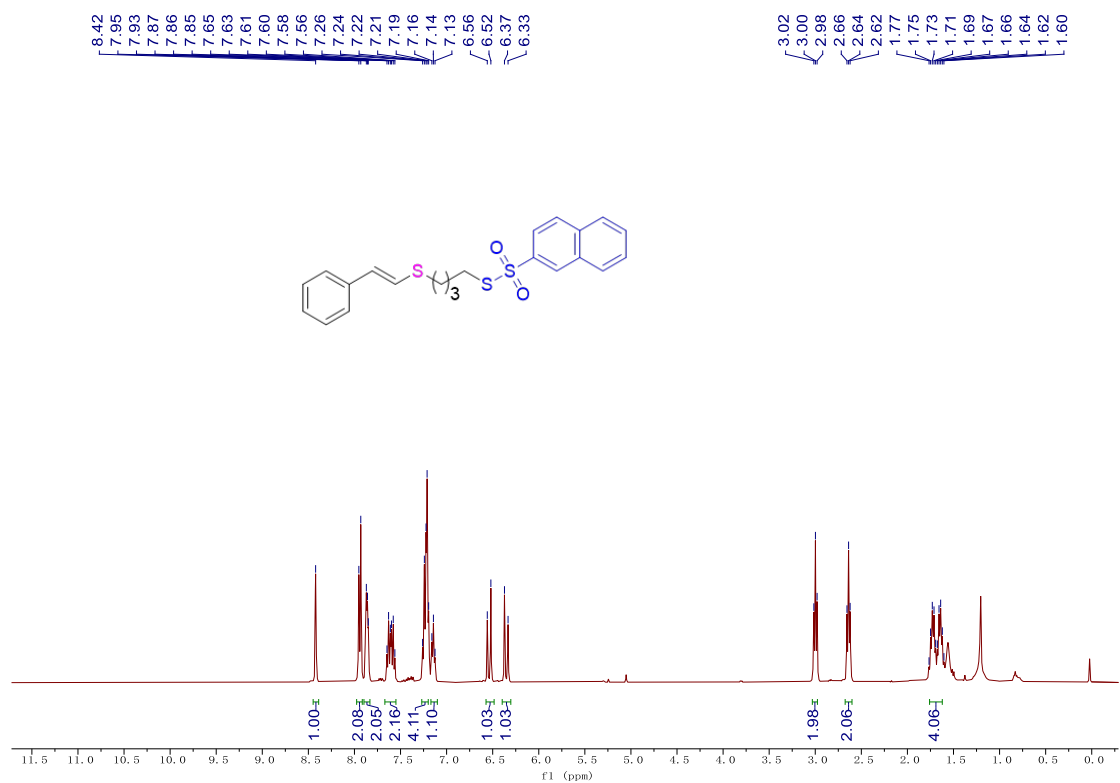
¹³C NMR (101 MHz, CDCl₃) spectra of **3q**



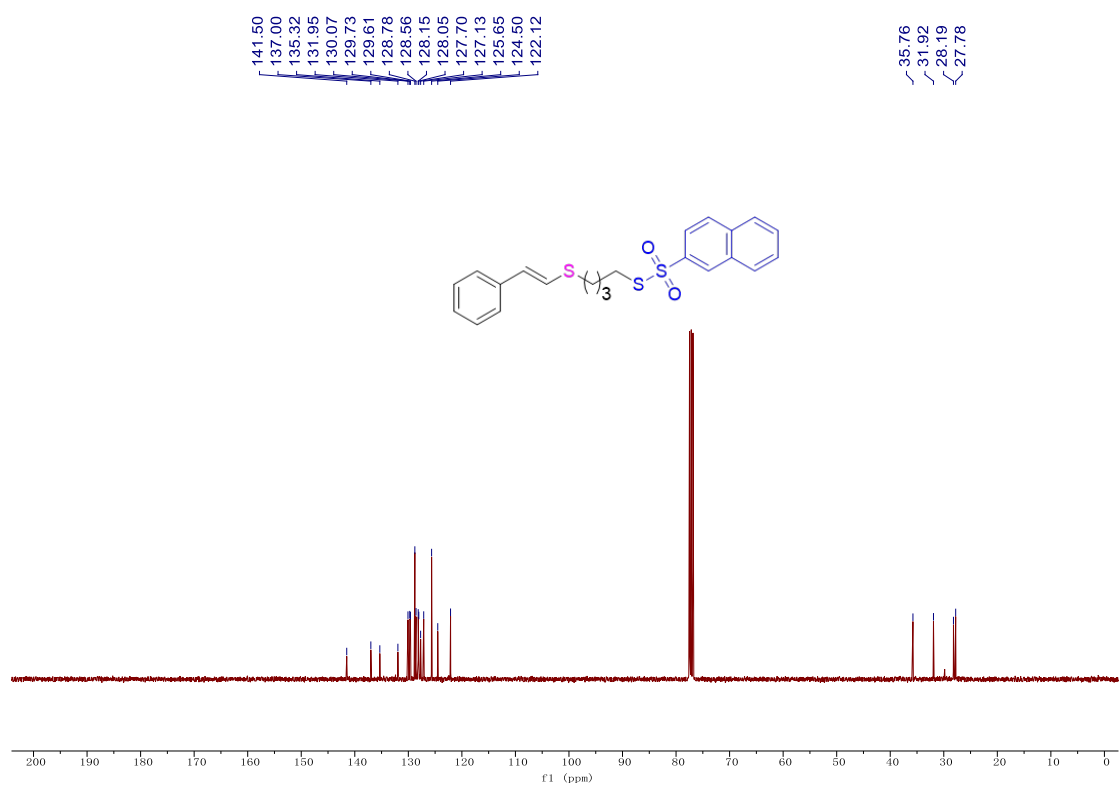
¹H NMR (400 MHz, CDCl₃) spectra of **3r**



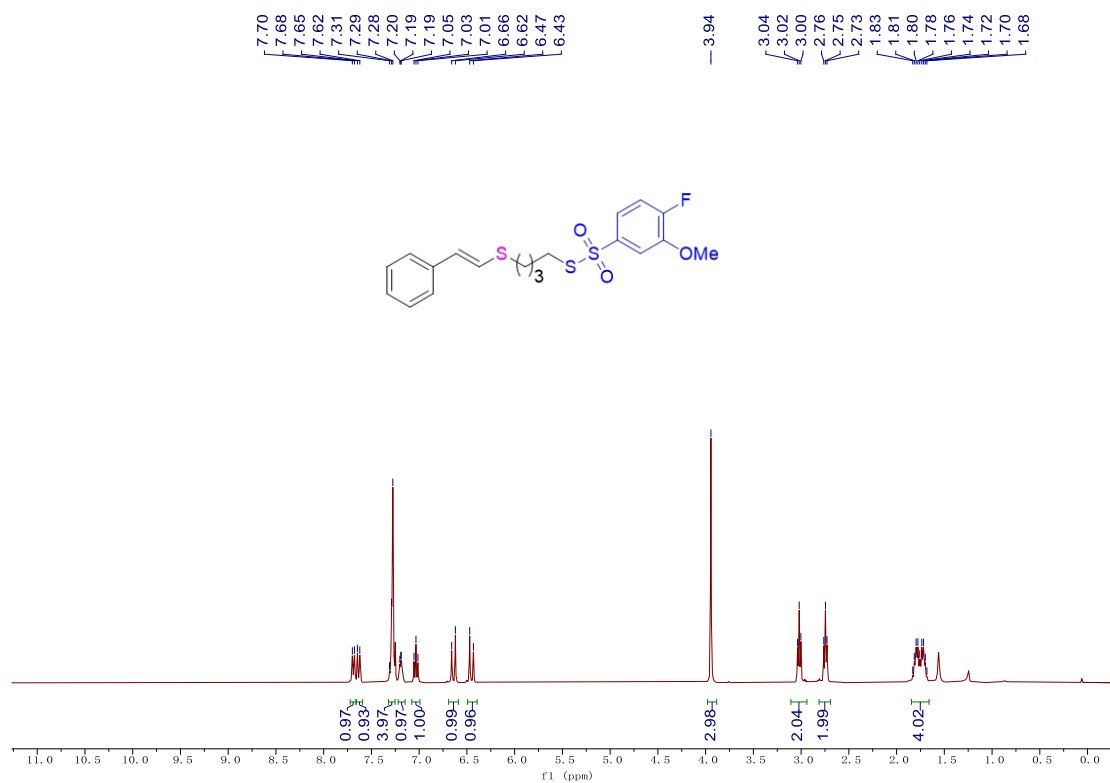
¹³C NMR (101 MHz, CDCl₃) spectra of **3r**



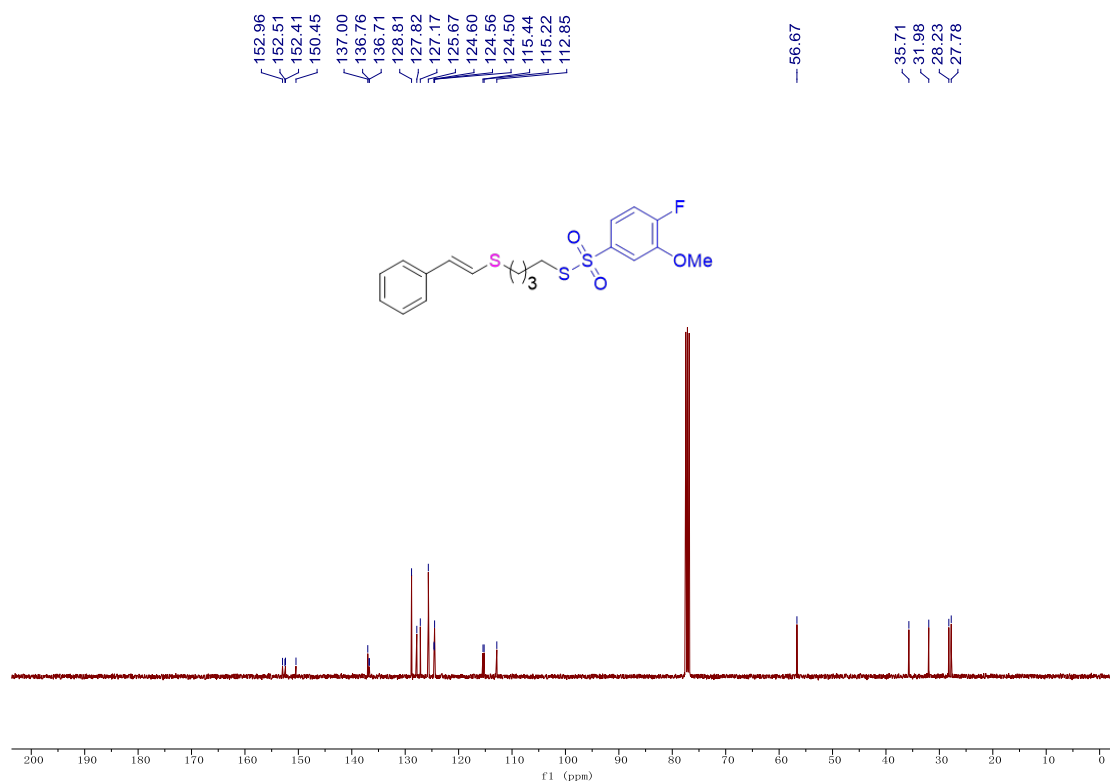
¹H NMR (400 MHz, CDCl₃) spectra of **3s**



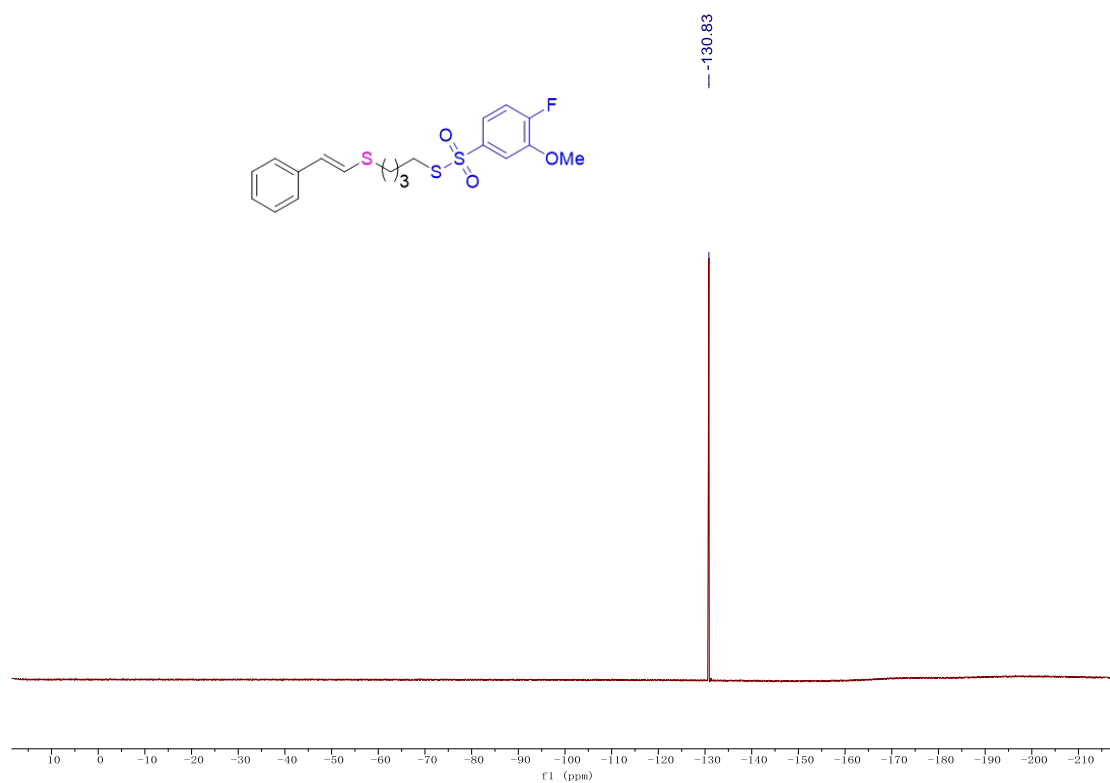
¹³C NMR (101 MHz, CDCl₃) spectra of **3s**



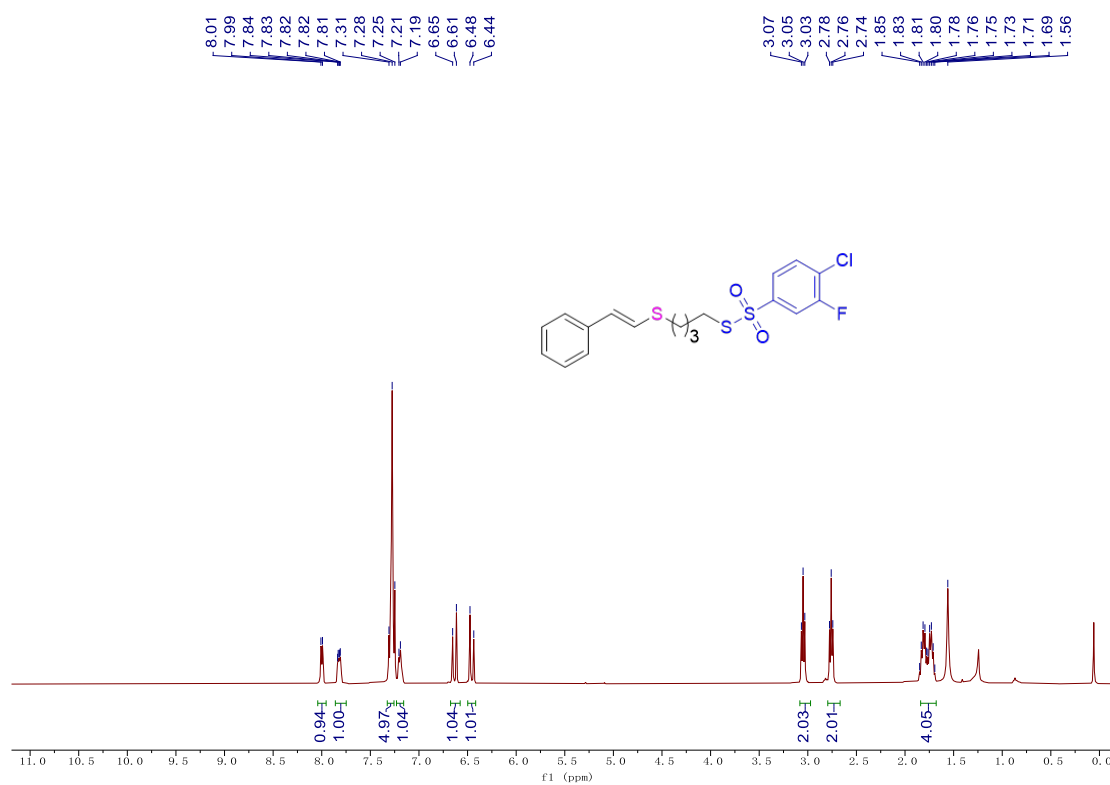
¹H NMR (400 MHz, CDCl₃) spectra of **3t**



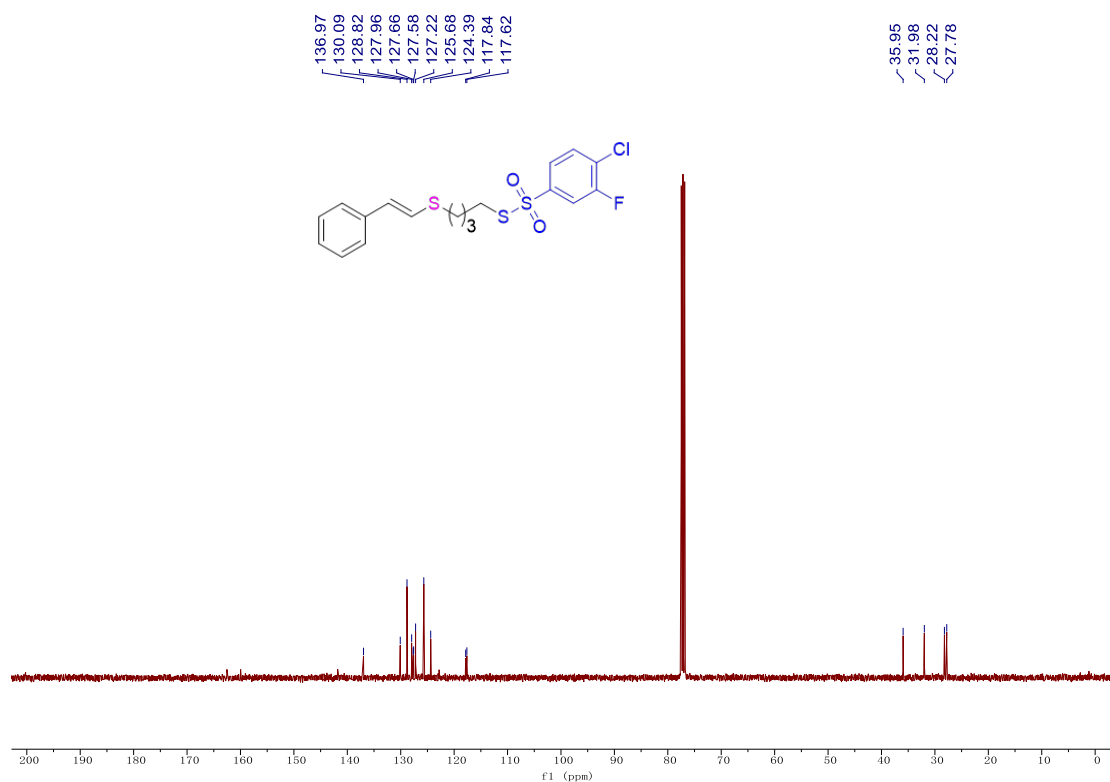
¹³C NMR (101 MHz, CDCl₃) spectra of **3t**



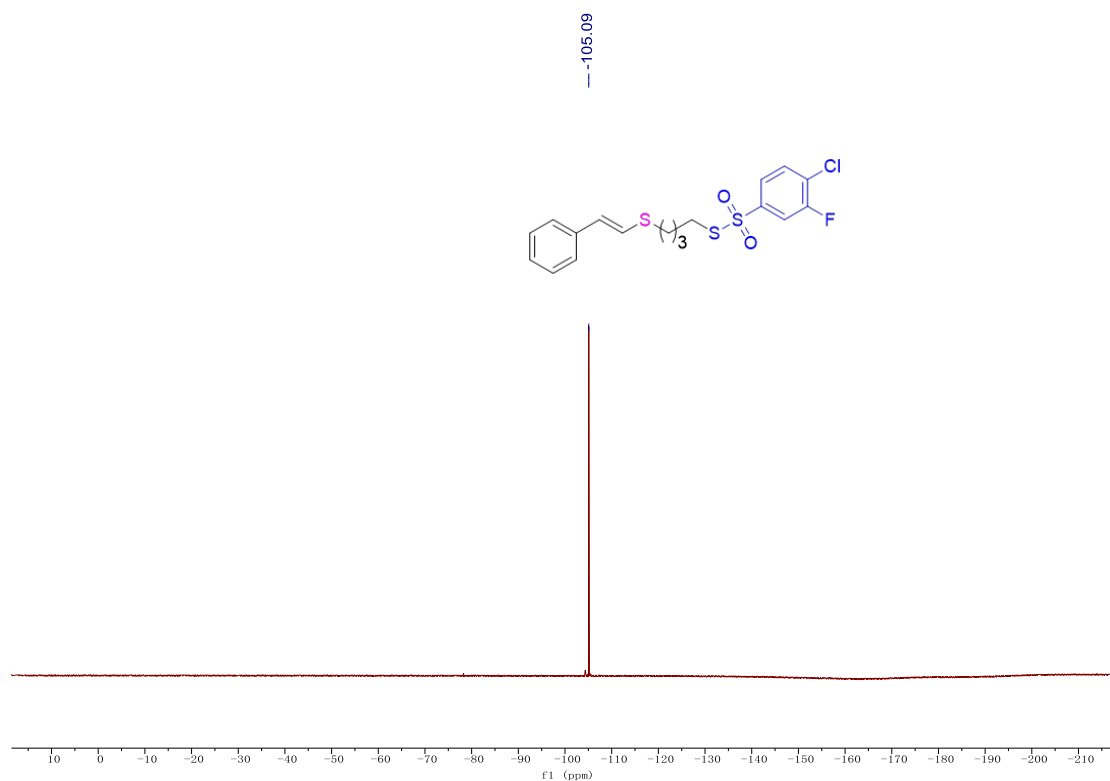
^{19}F NMR (376 MHz, CDCl_3) spectra of **3t**



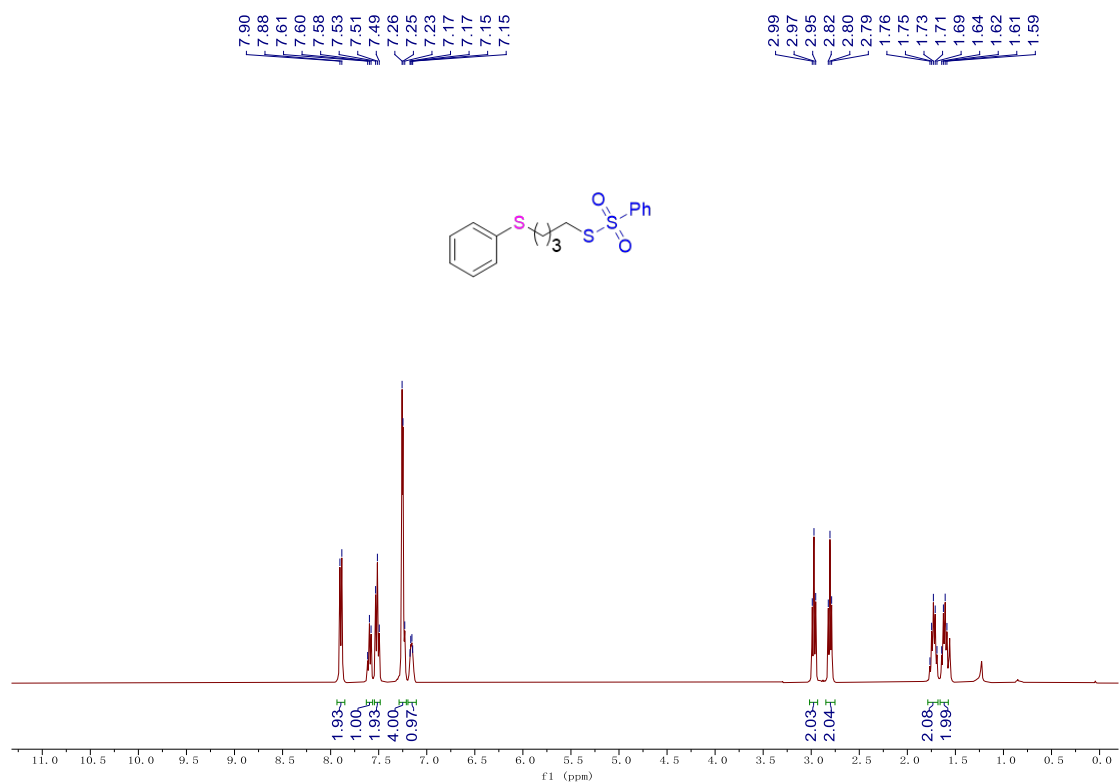
^1H NMR (400 MHz, CDCl_3) spectra of **3u**



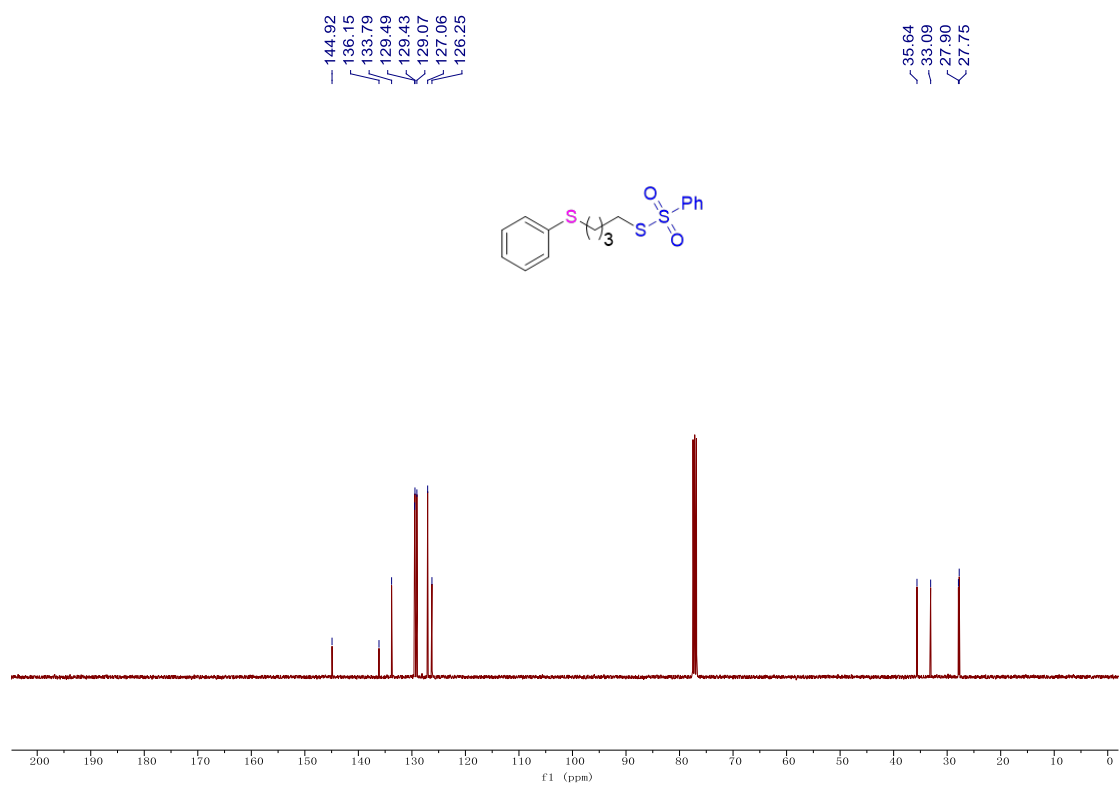
¹³C NMR (101 MHz, CDCl₃) spectra of **3u**



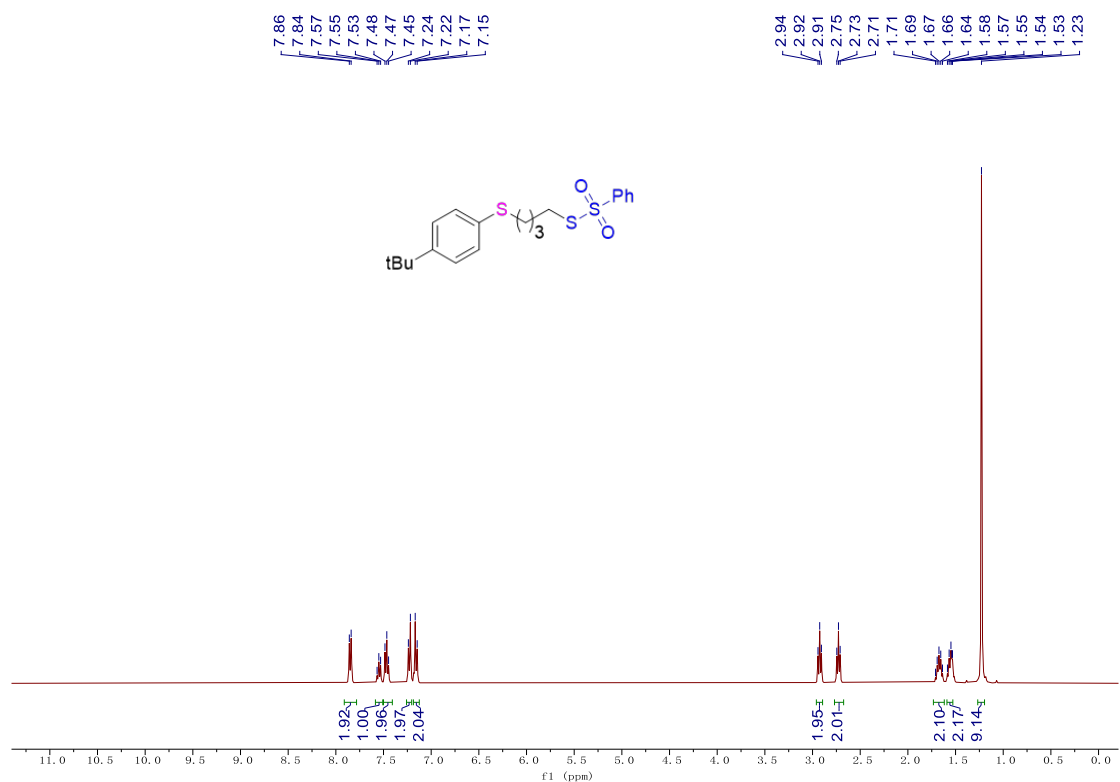
¹⁹F NMR (376 MHz, CDCl₃) spectra of **3u**



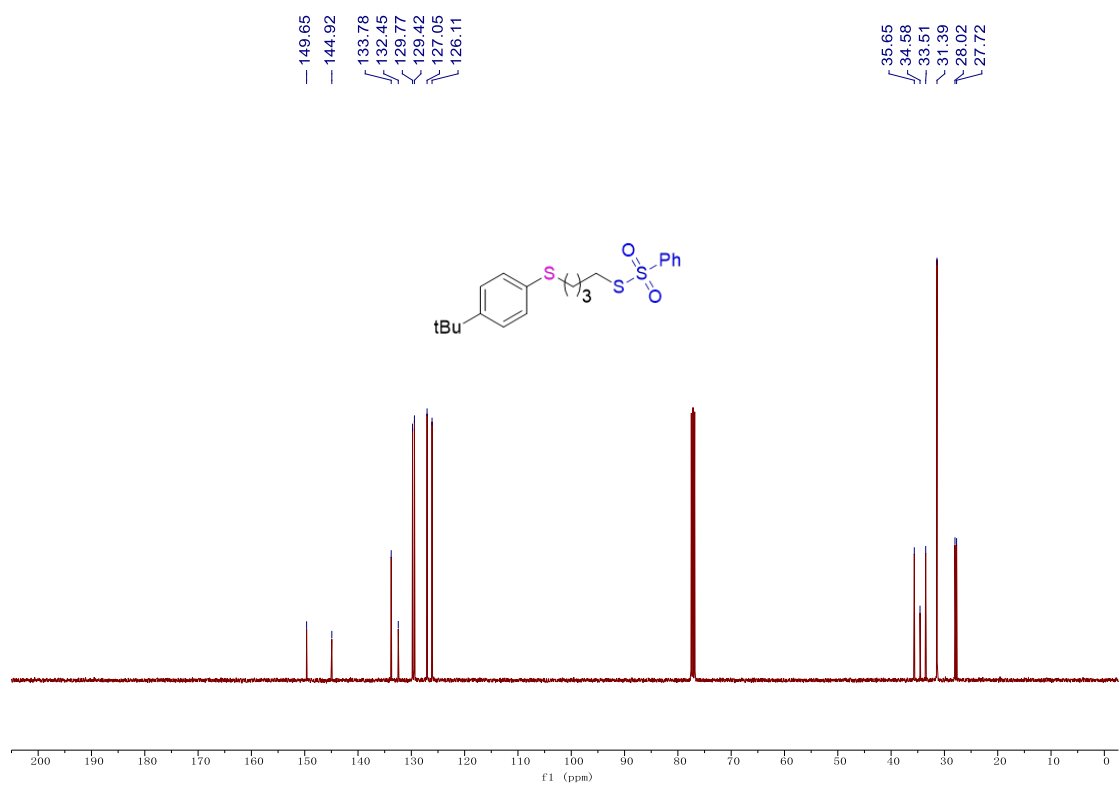
¹H NMR (400 MHz, CDCl₃) spectra of **5a**



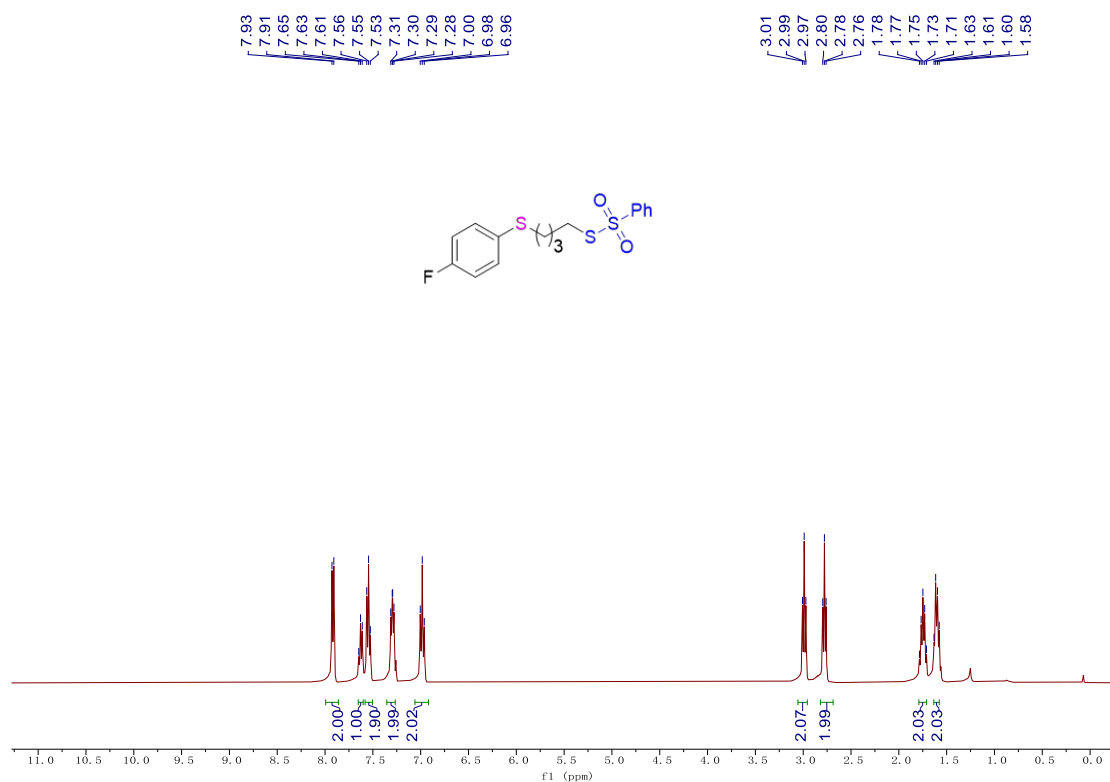
¹³C NMR (101 MHz, CDCl₃) spectra of **5a**



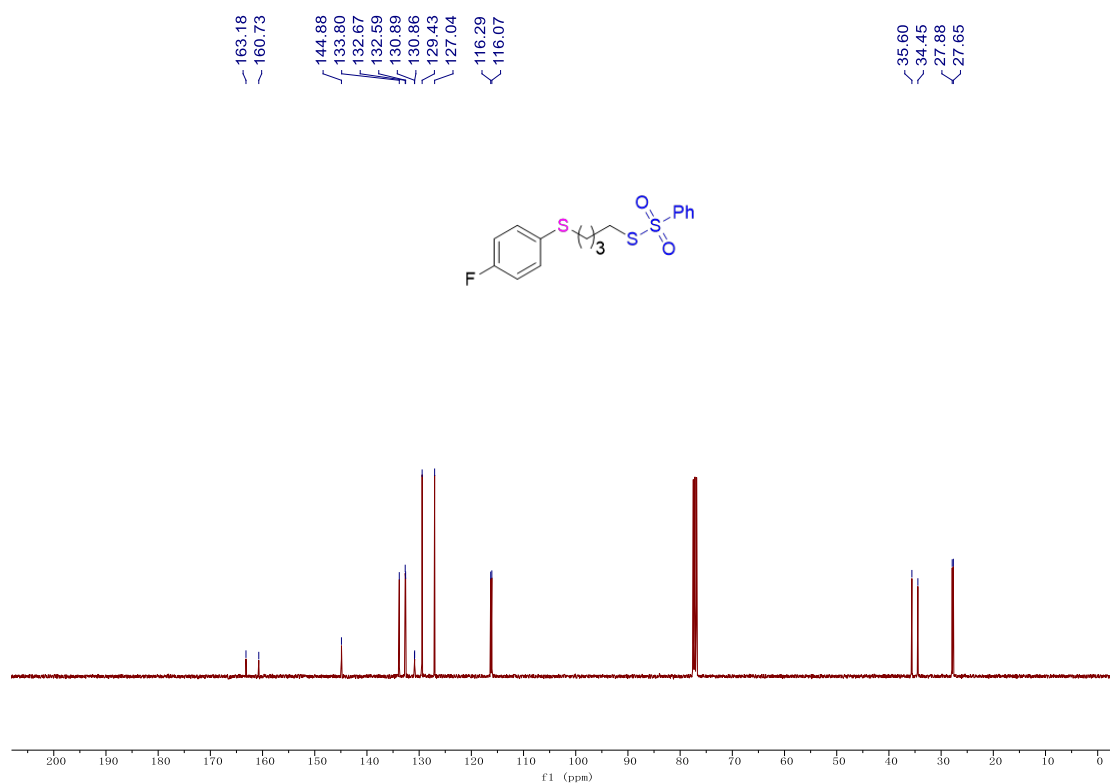
¹H NMR (400 MHz, CDCl₃) spectra of **5b**



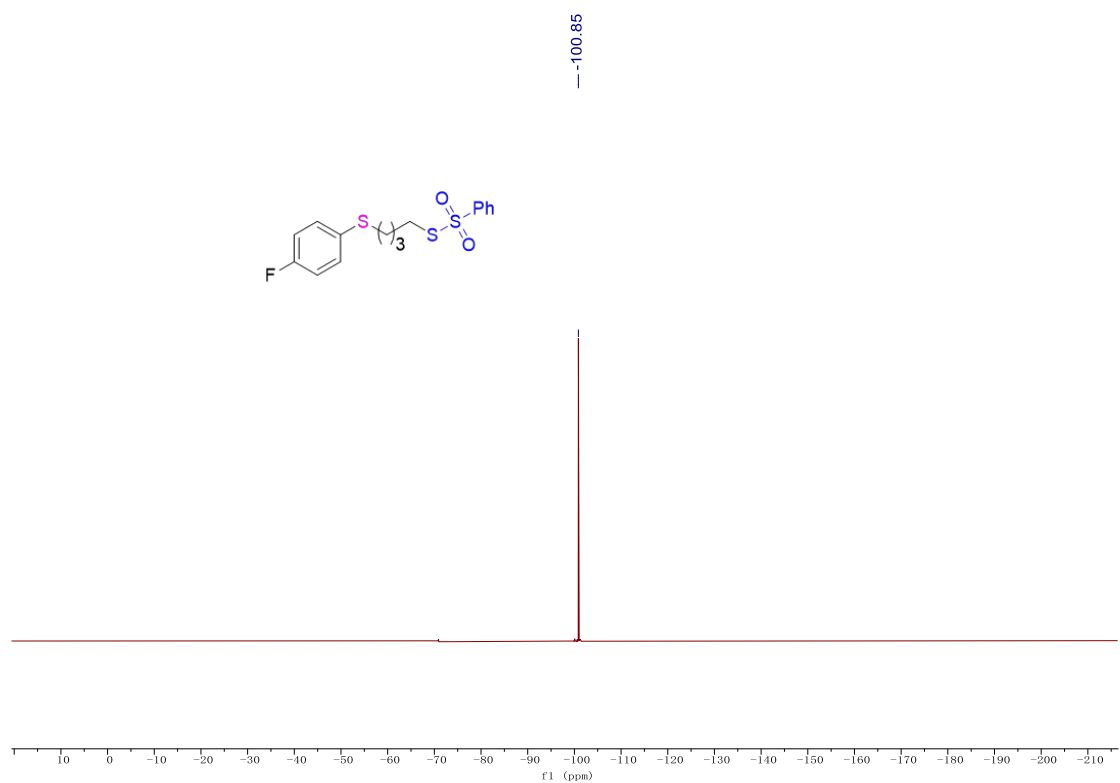
¹³C NMR (101 MHz, CDCl₃) spectra of **5b**



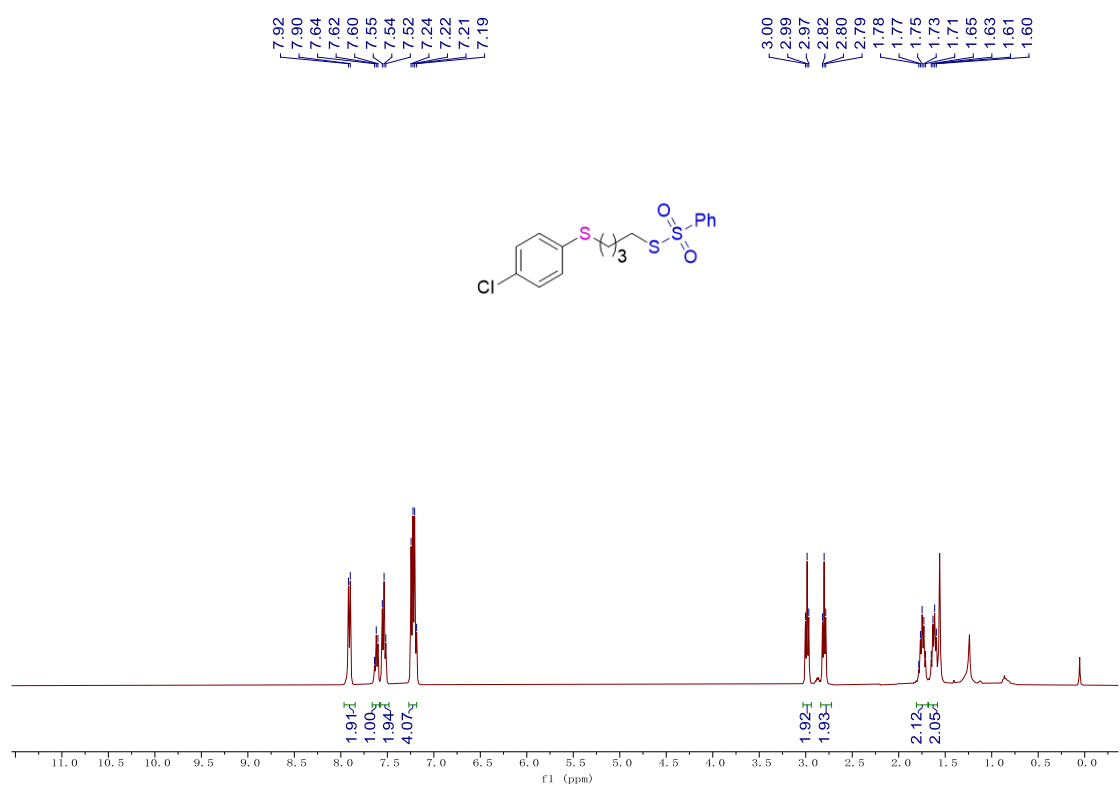
¹H NMR (400 MHz, CDCl₃) spectra of 5c



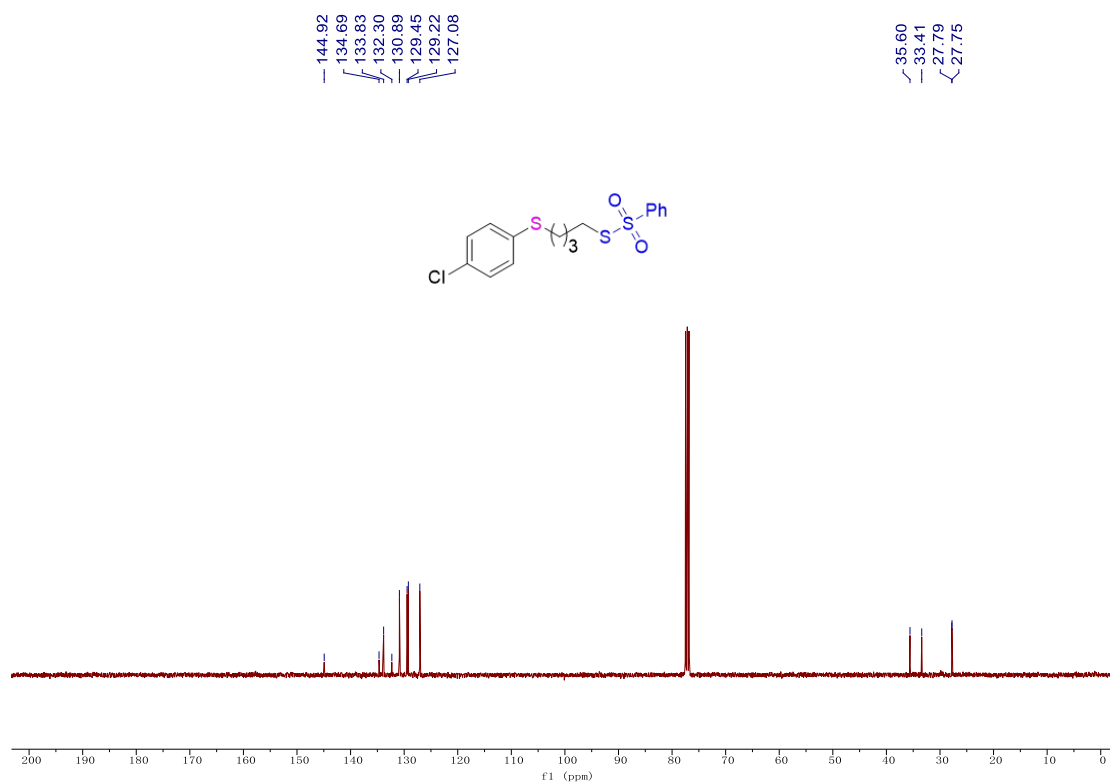
¹³C NMR (101 MHz, CDCl₃) spectra of 5c



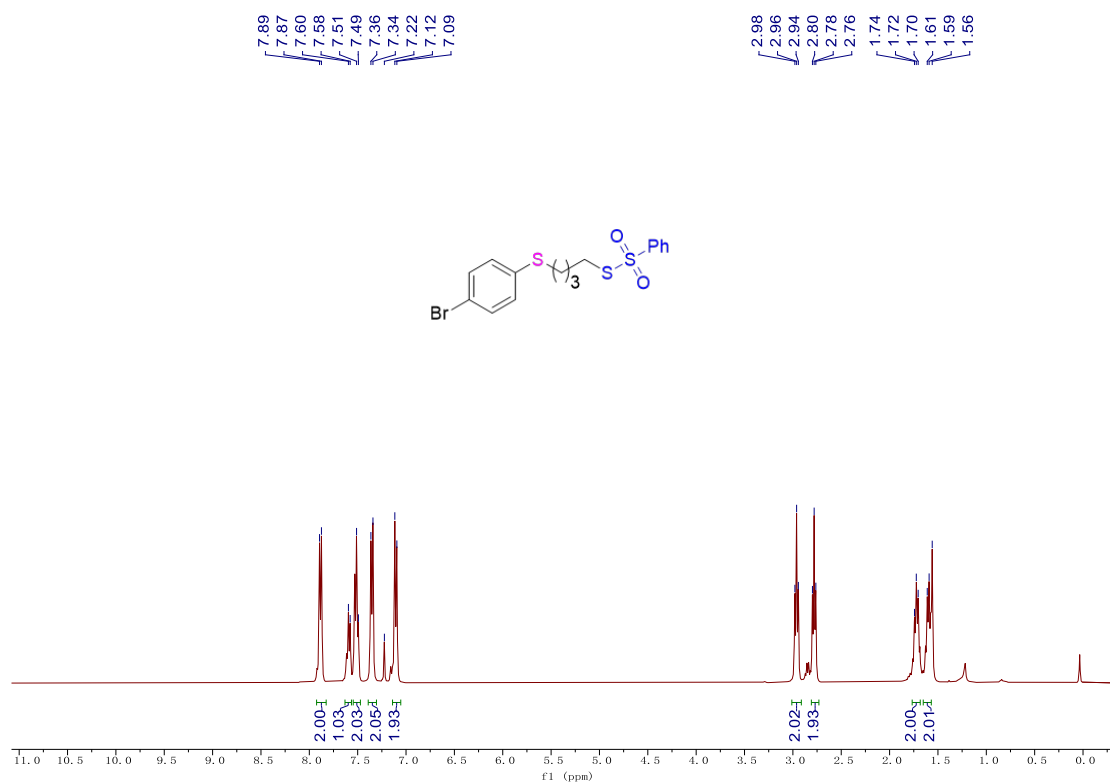
^{19}F NMR (376 MHz, CDCl_3) spectra of **5c**



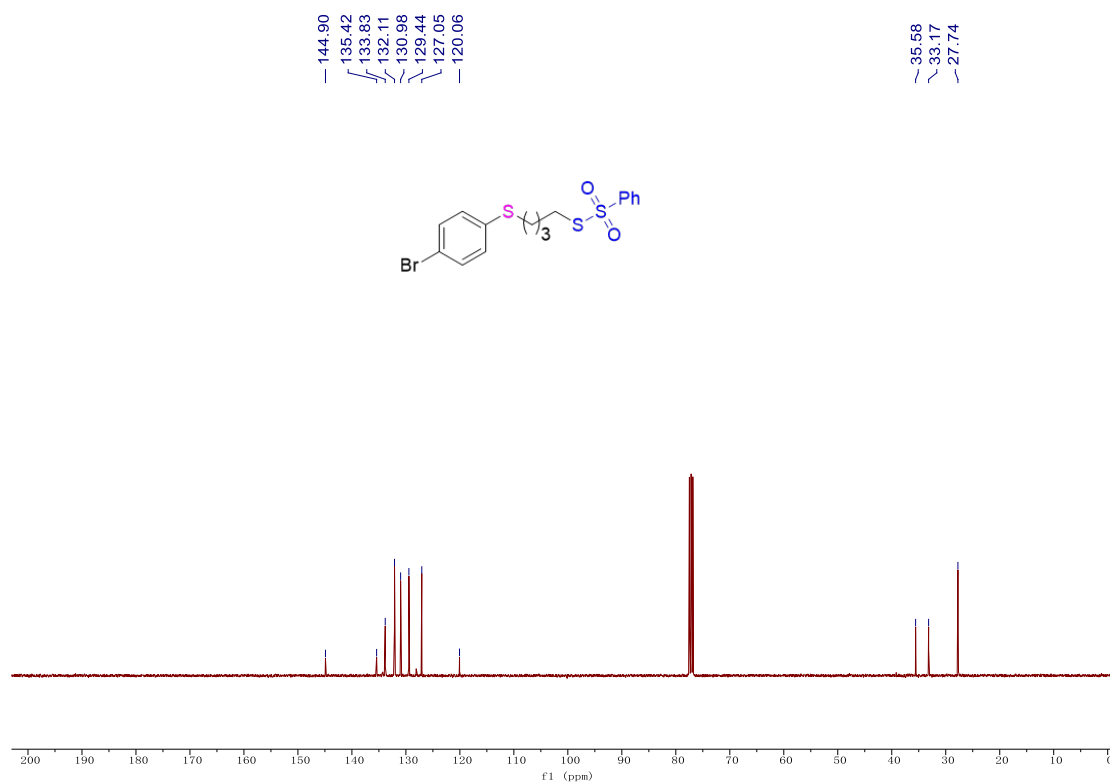
^1H NMR (400 MHz, CDCl_3) spectra of **5d**



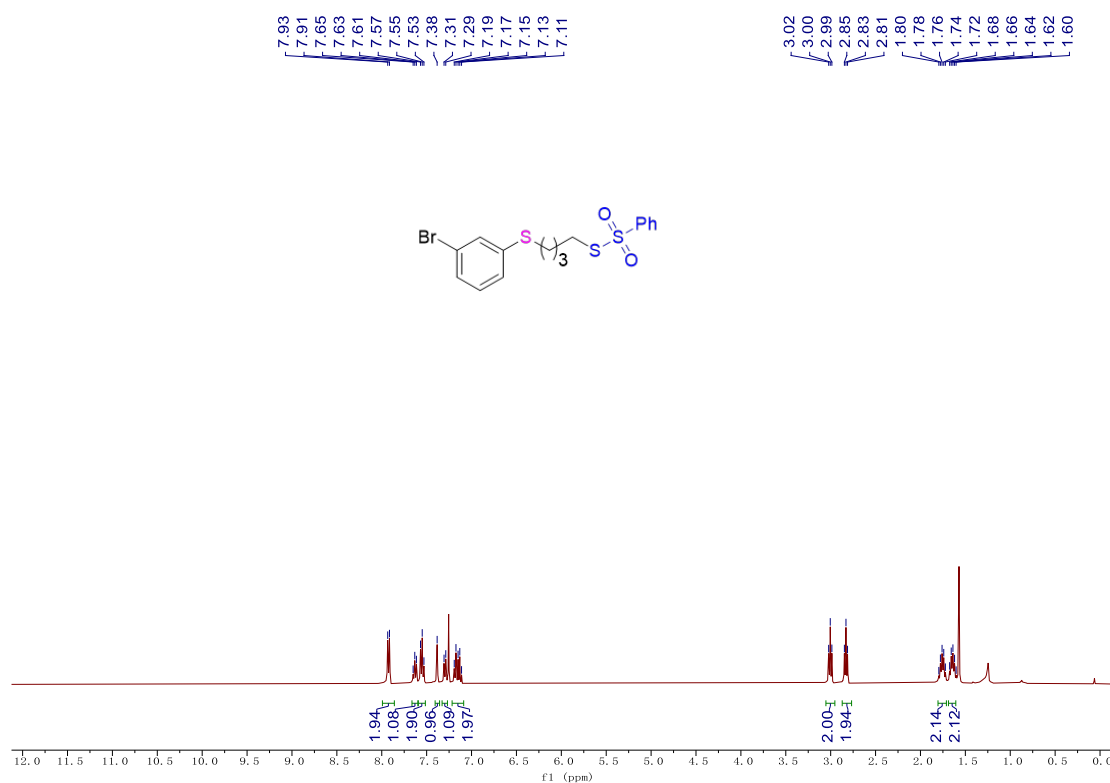
¹³C NMR (101 MHz, CDCl₃) spectra of **5d**



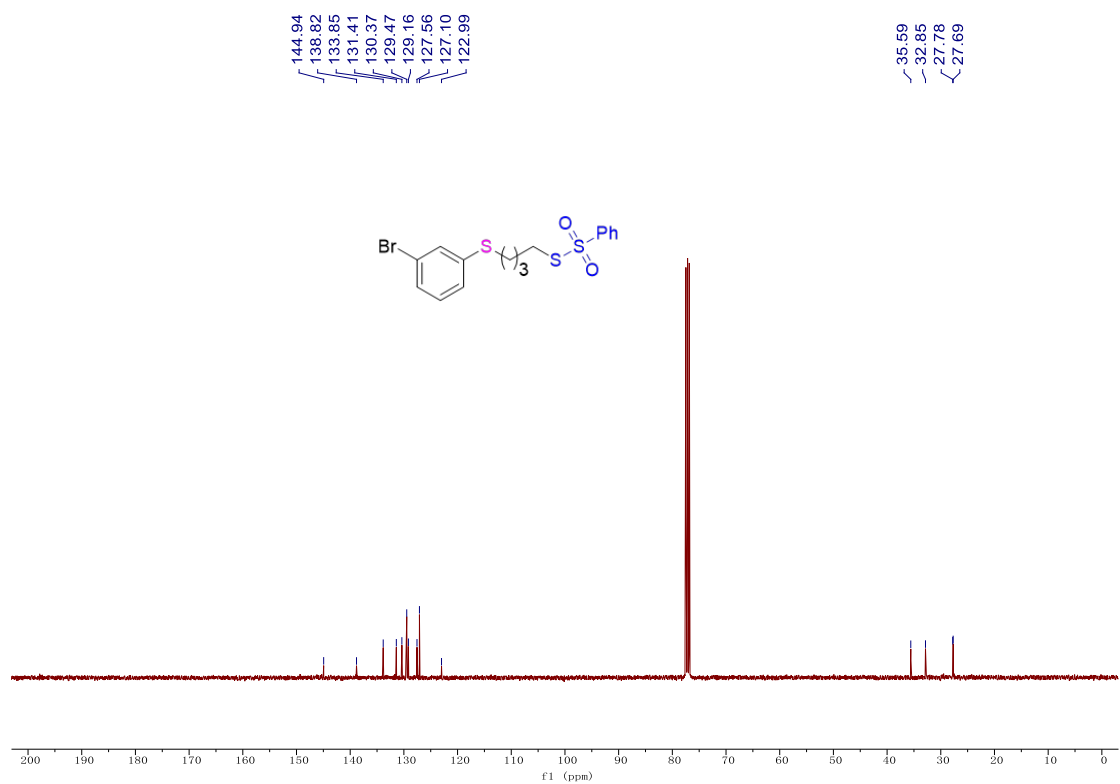
¹H NMR (400 MHz, CDCl₃) spectra of **5e**



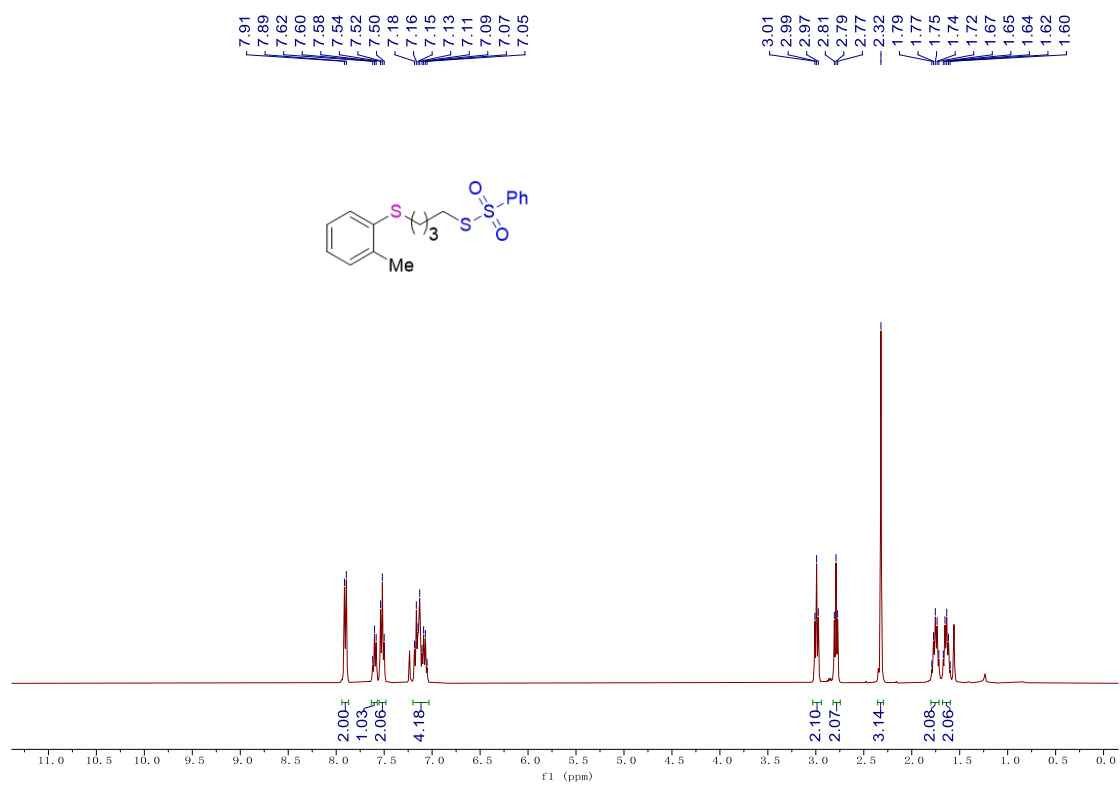
¹³C NMR (101 MHz, CDCl₃) spectra of **5e**



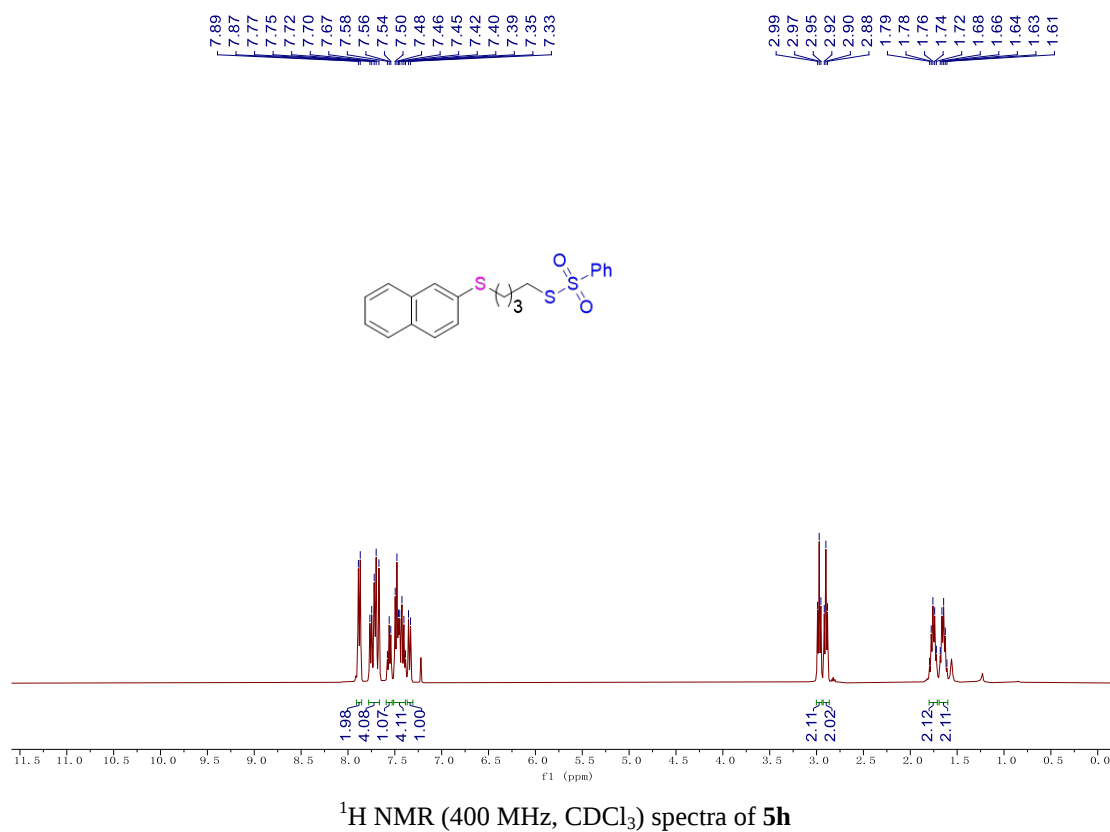
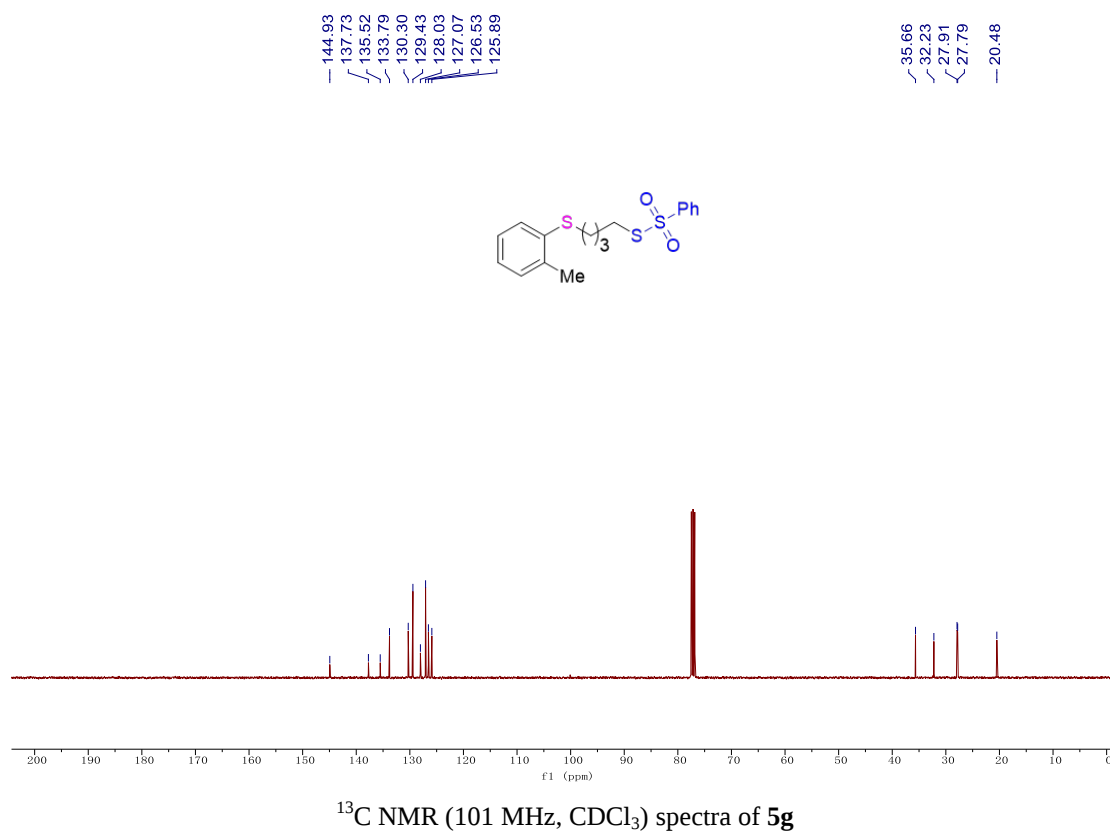
¹H NMR (400 MHz, CDCl₃) spectra of **5f**

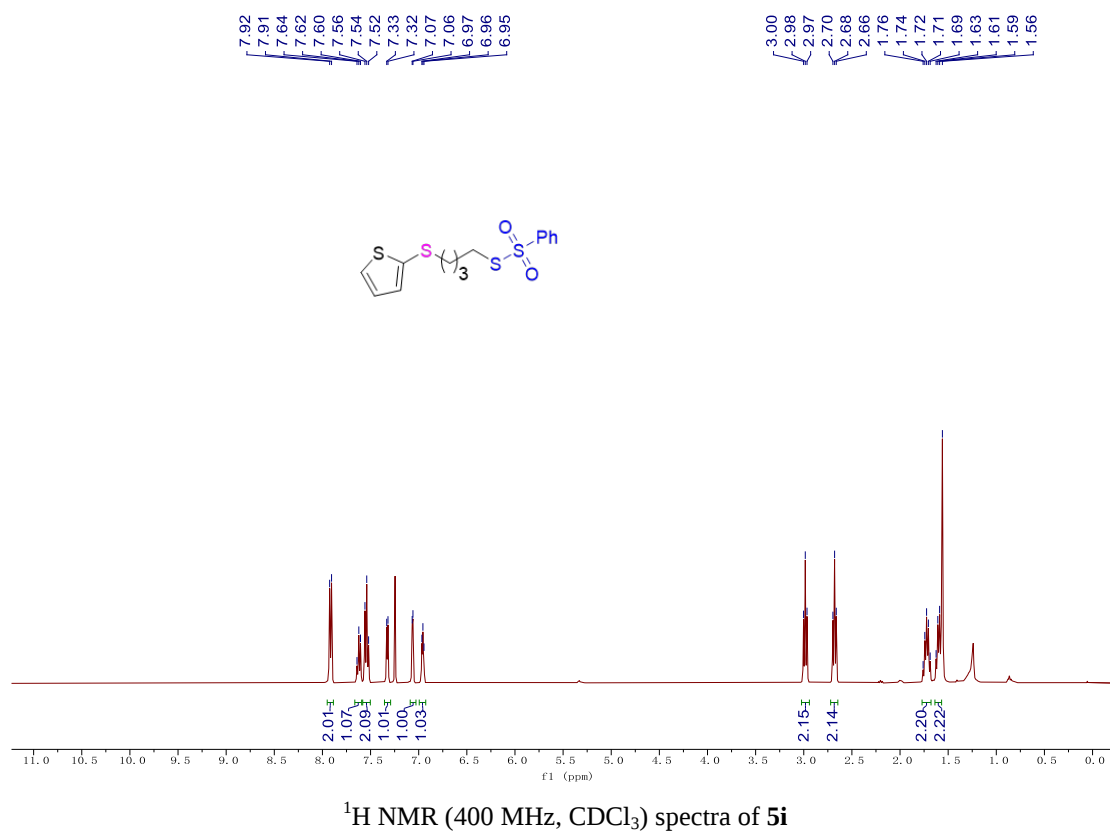
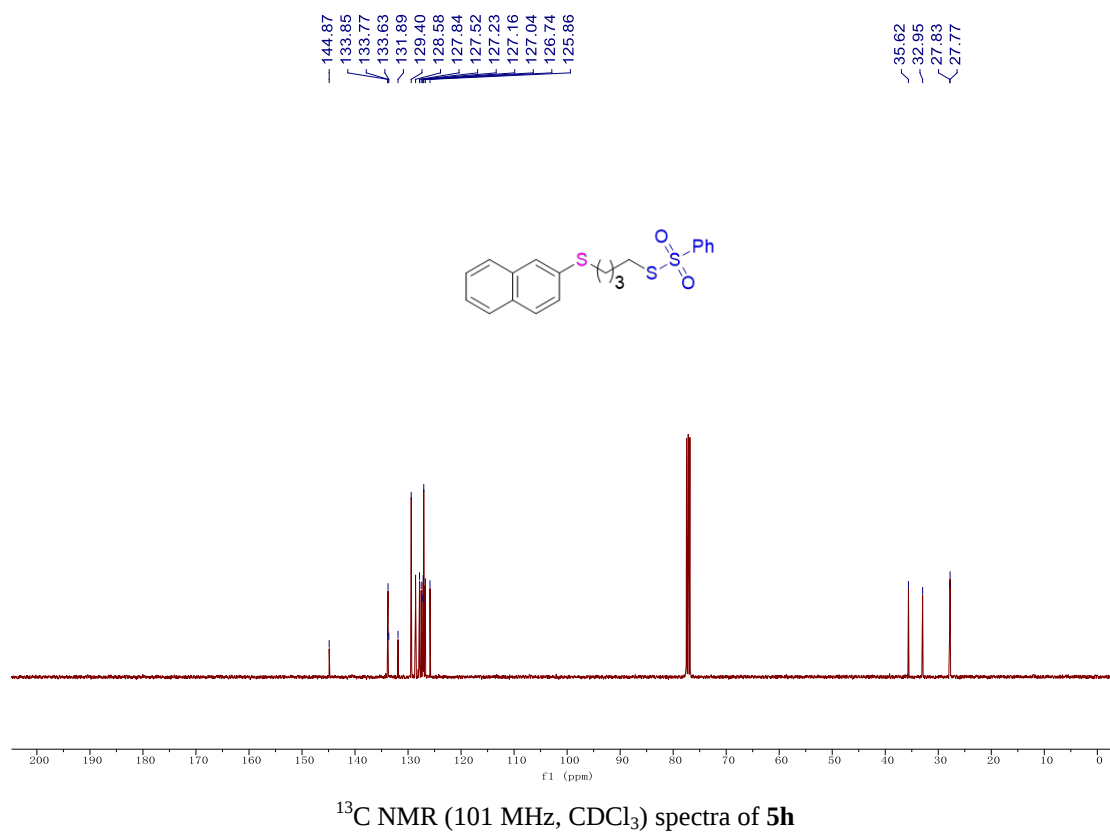


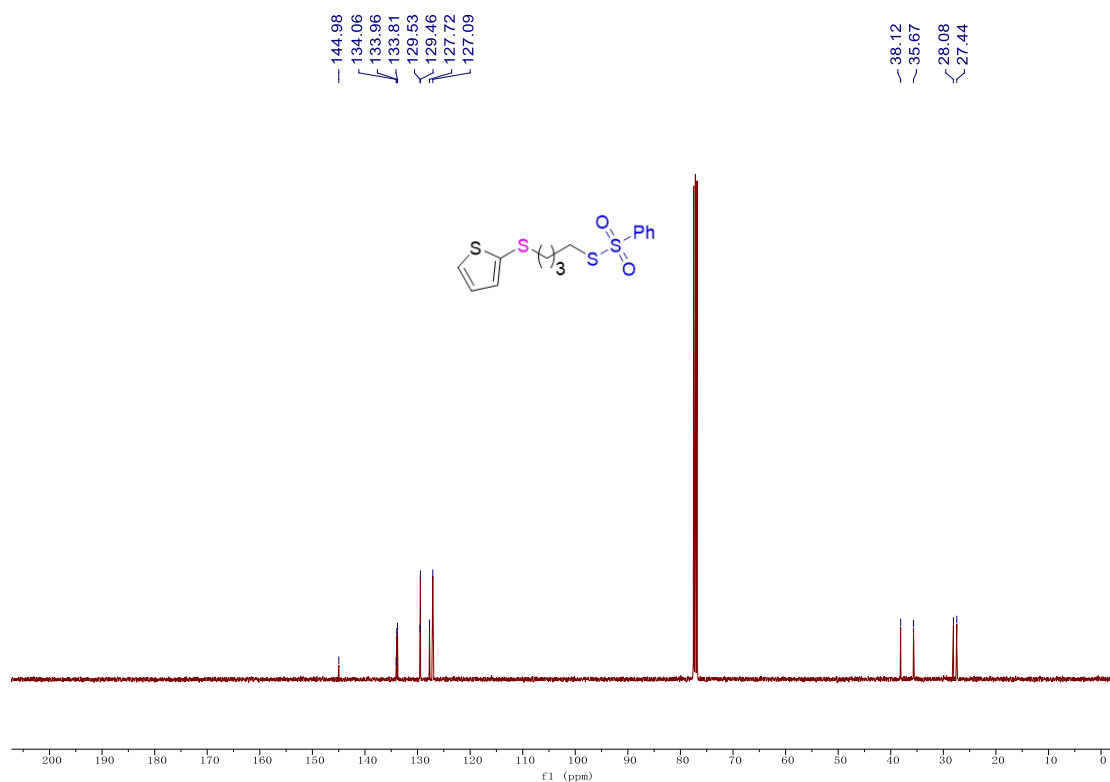
¹³C NMR (101 MHz, CDCl₃) spectra of **5f**



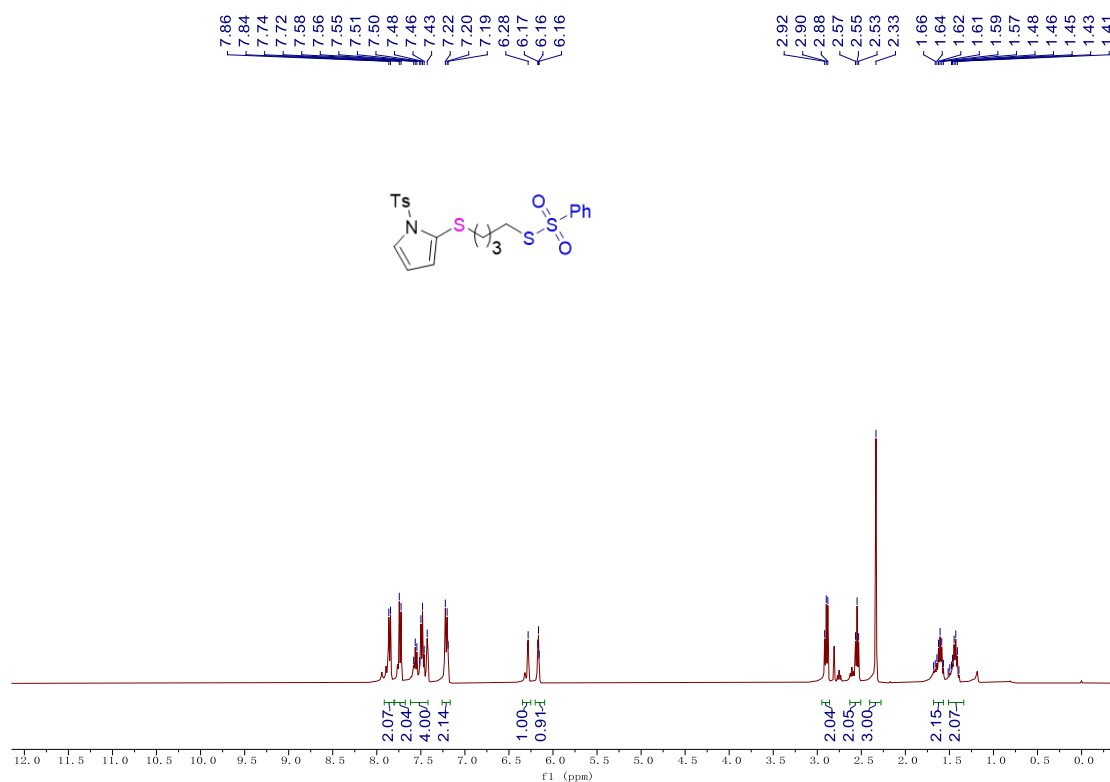
¹H NMR (400 MHz, CDCl₃) spectra of **5g**



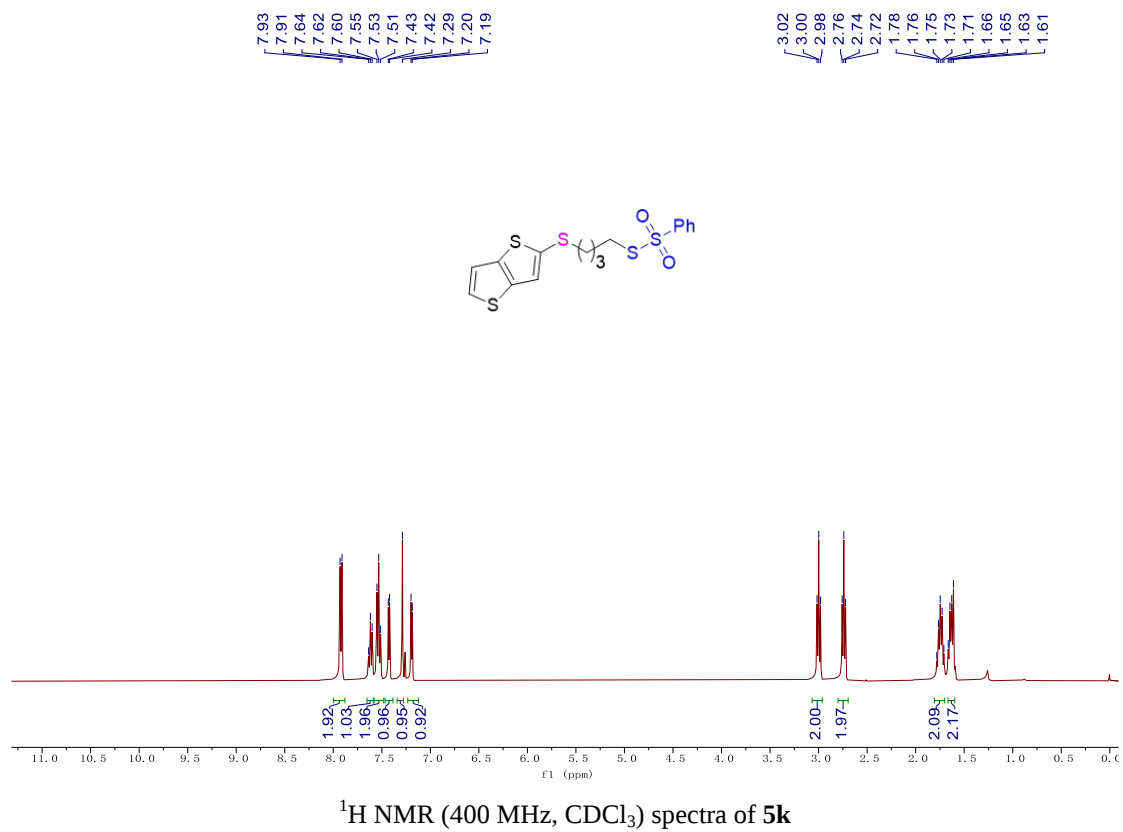
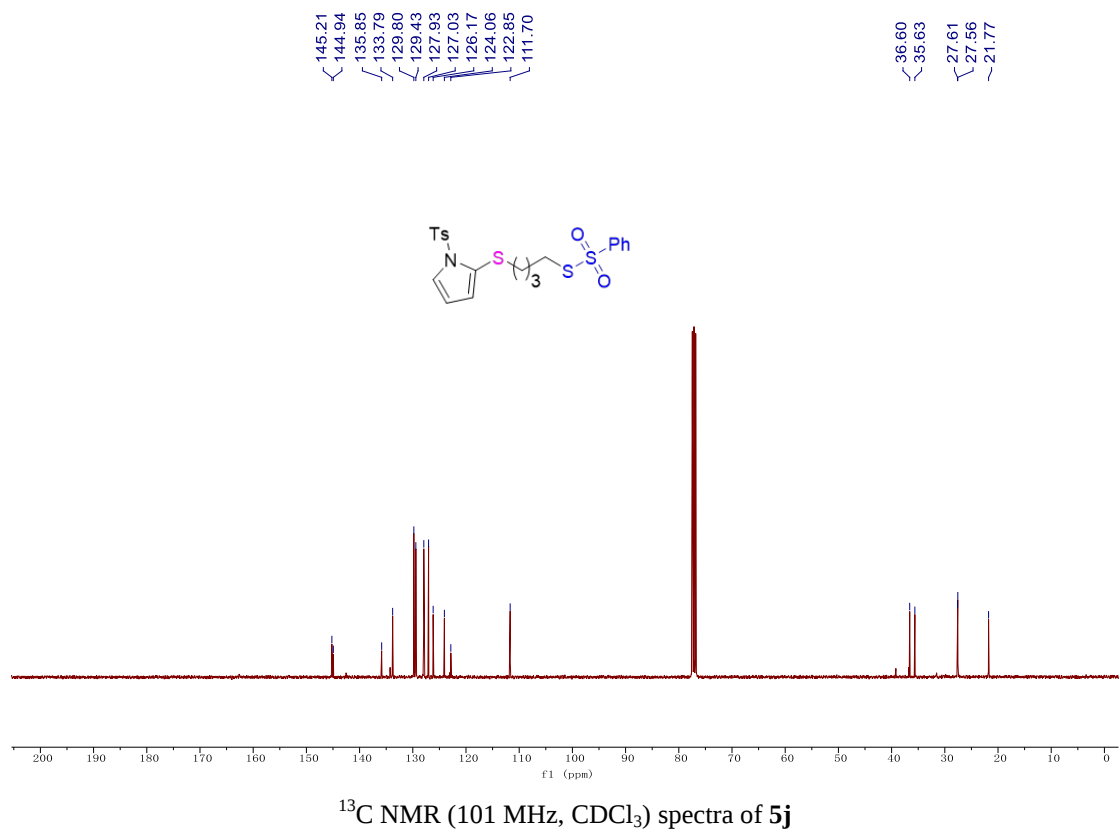


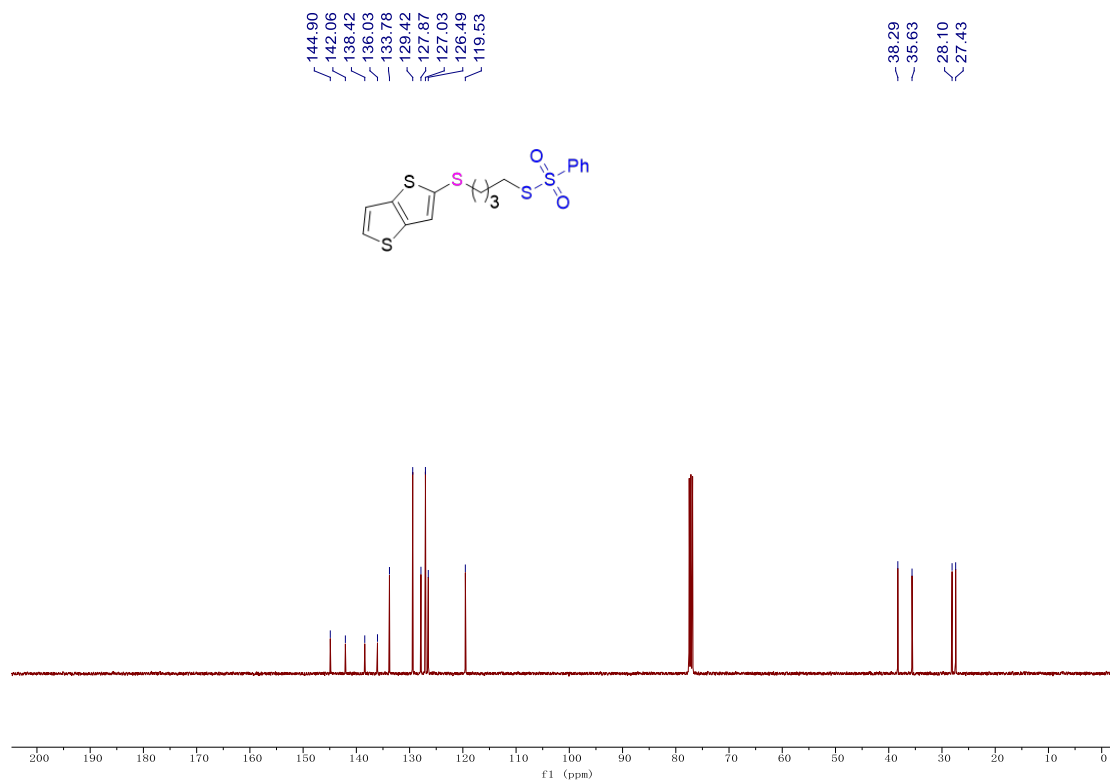


¹³C NMR (101 MHz, CDCl₃) spectra of **5i**

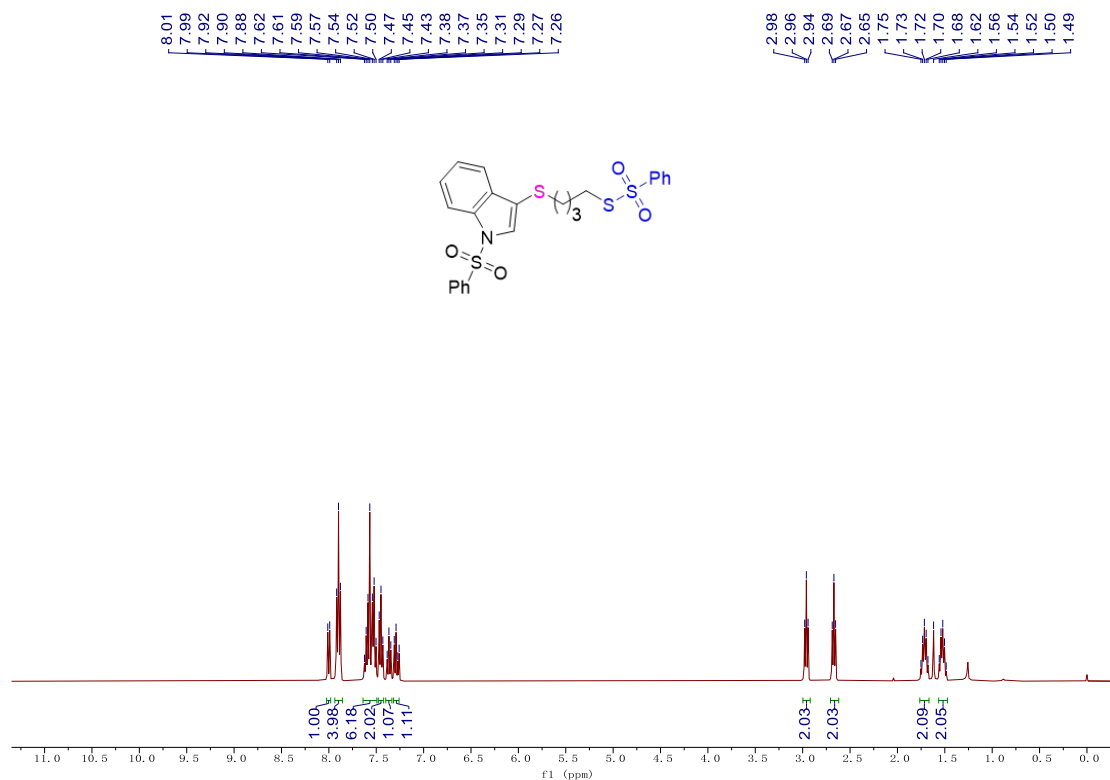


¹H NMR (400 MHz, CDCl₃) spectra of **5j**

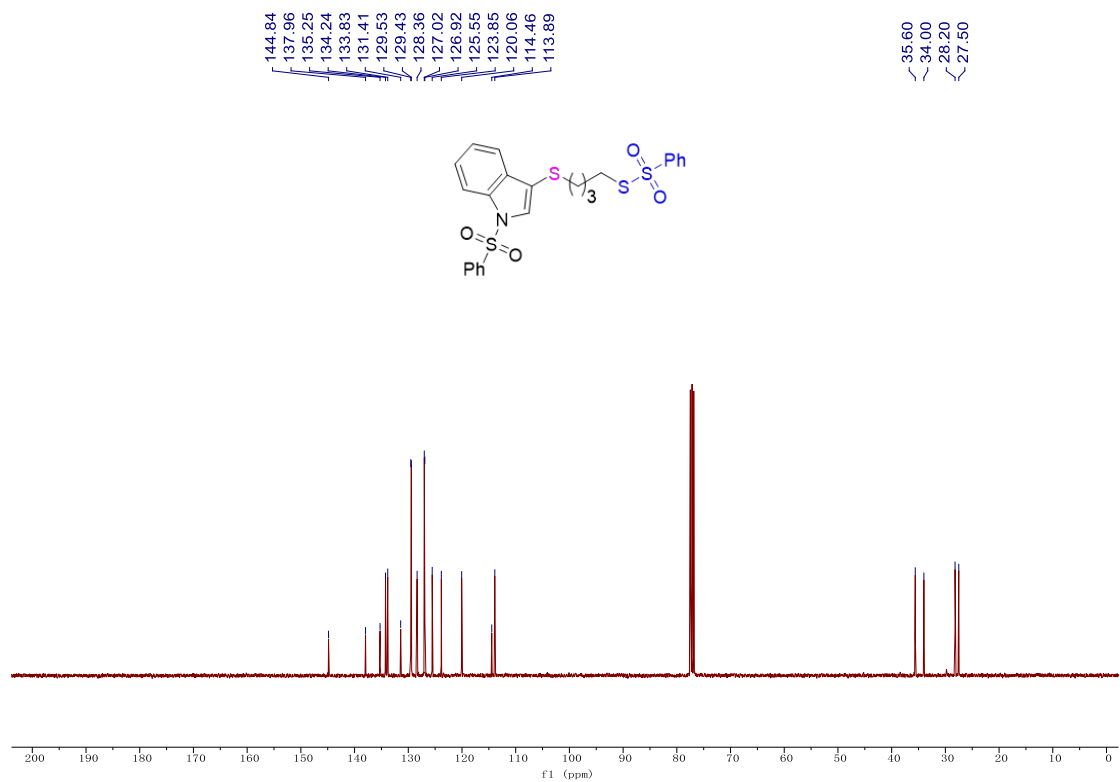




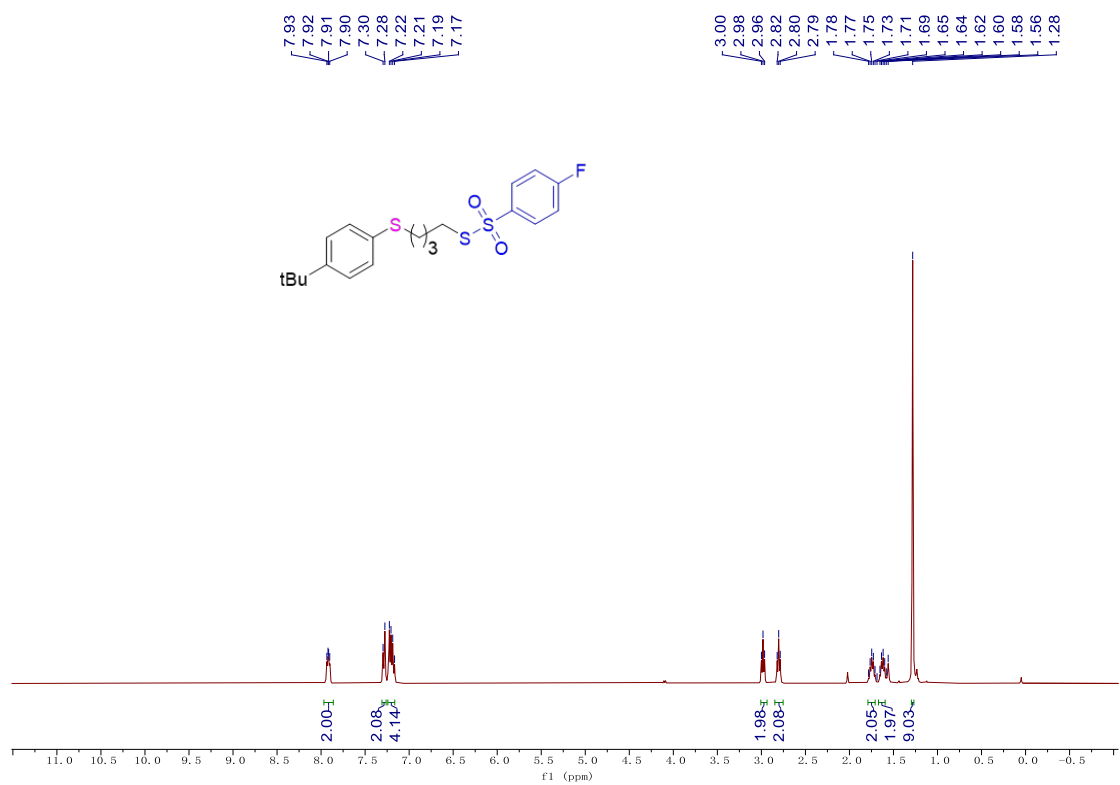
¹³C NMR (101 MHz, CDCl₃) spectra of **5k**



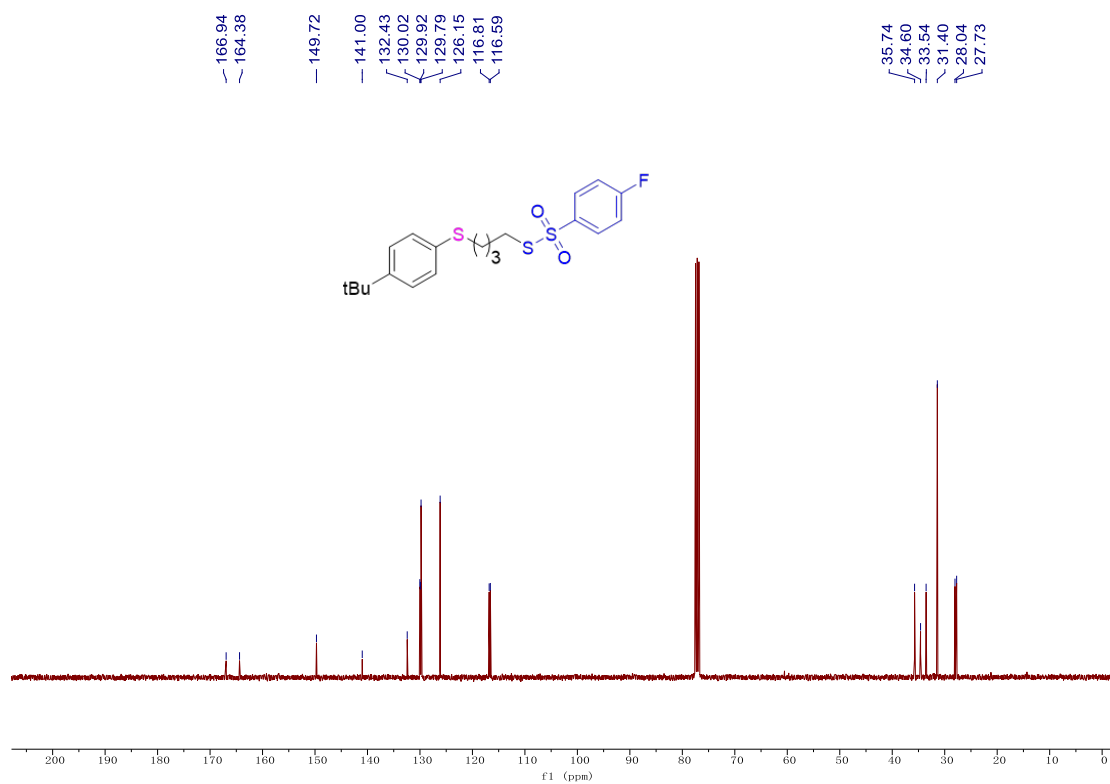
¹H NMR (400 MHz, CDCl₃) spectra of **5l**



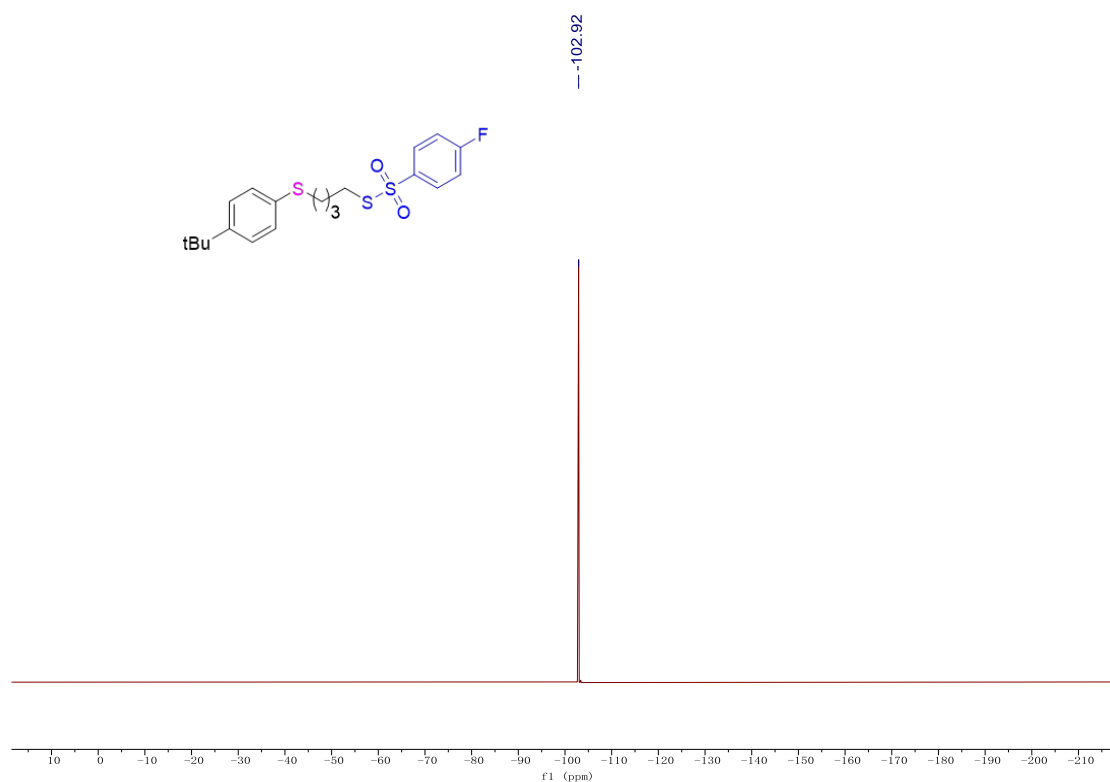
¹³C NMR (101 MHz, CDCl₃) spectra of **5l**



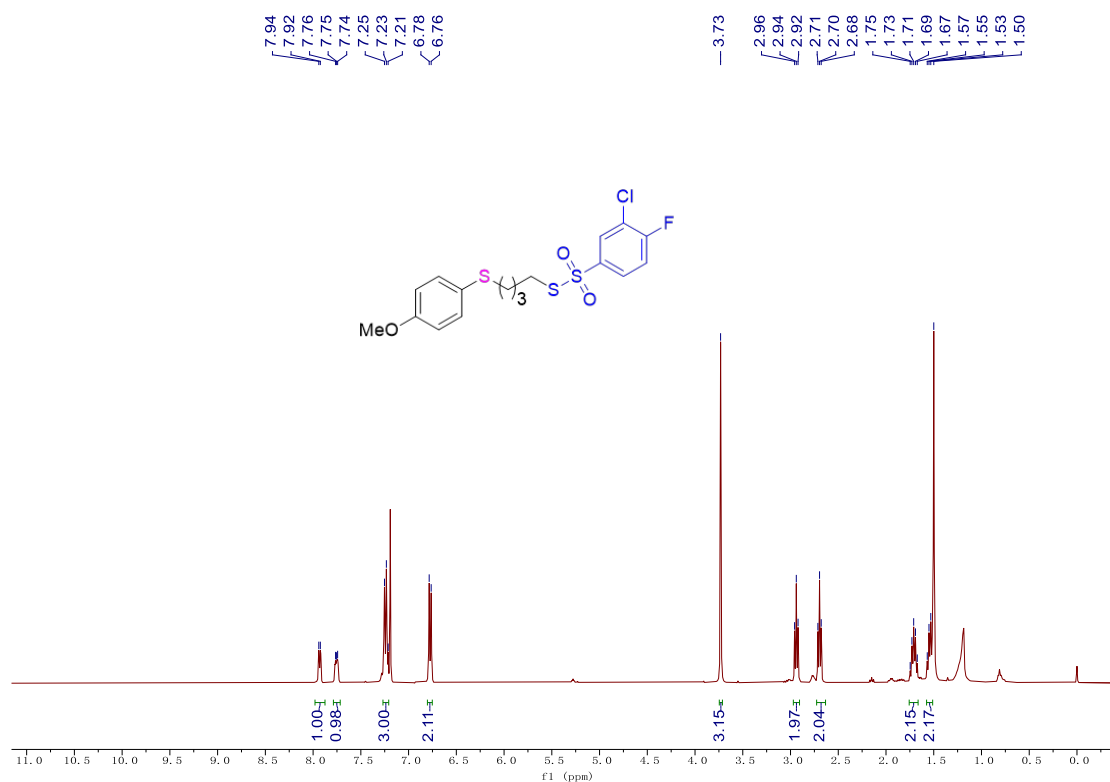
¹H NMR (400 MHz, CDCl₃) spectra of **5m**



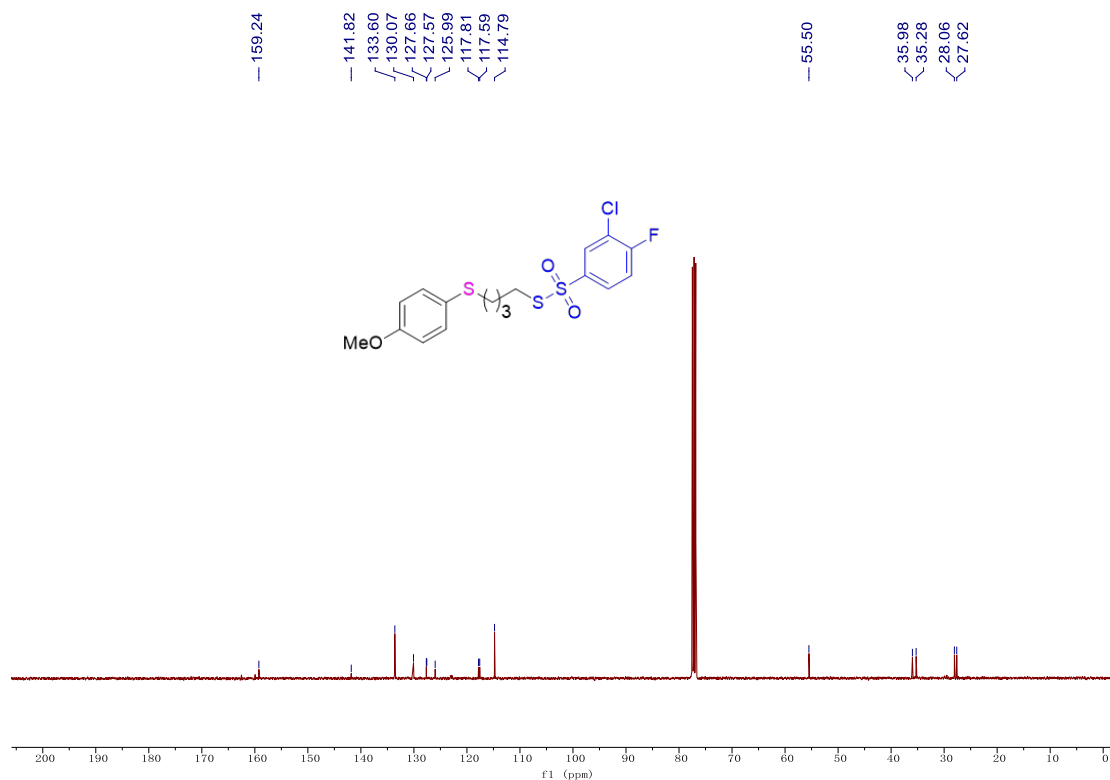
¹³C NMR (101 MHz, CDCl₃) spectra of **5m**



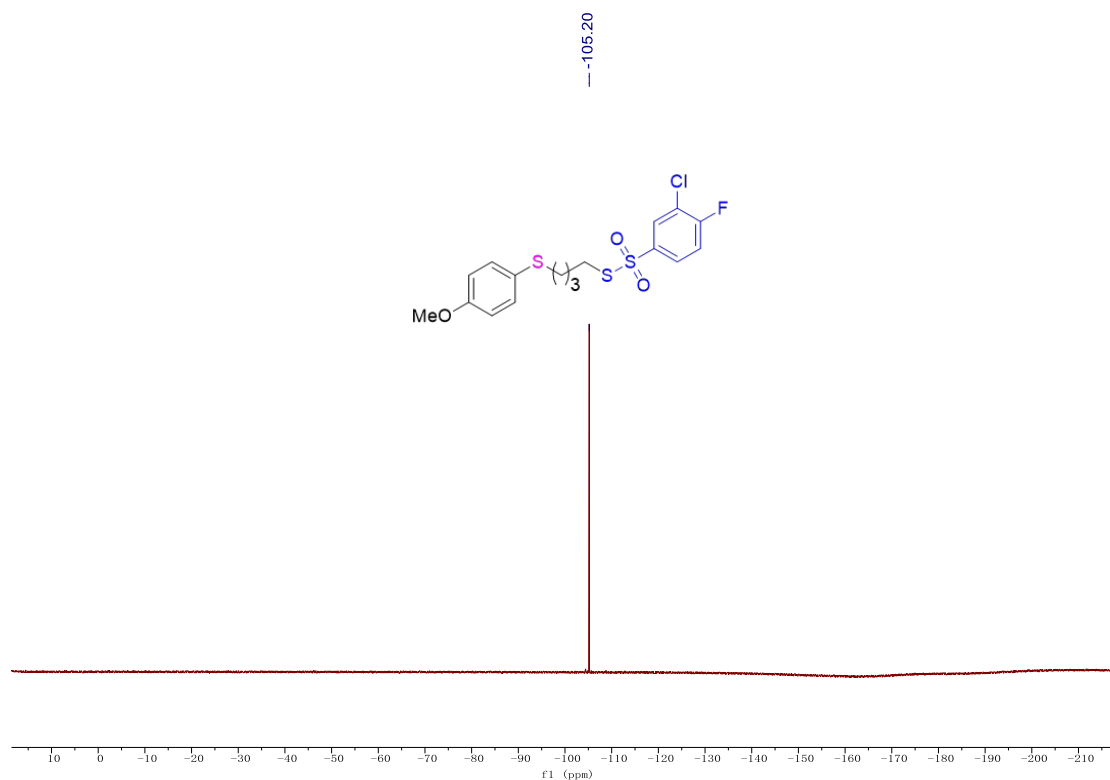
¹⁹F NMR (376 MHz, CDCl₃) spectra of **5m**



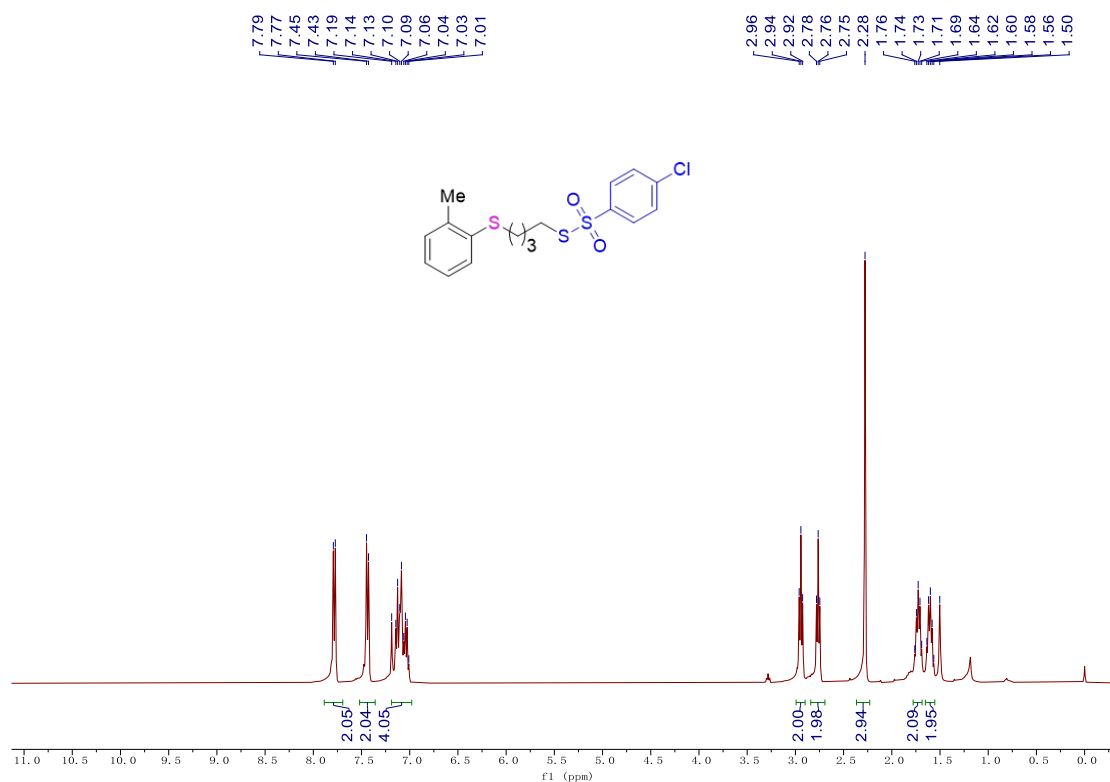
¹H NMR (400 MHz, CDCl₃) spectra of **5n**



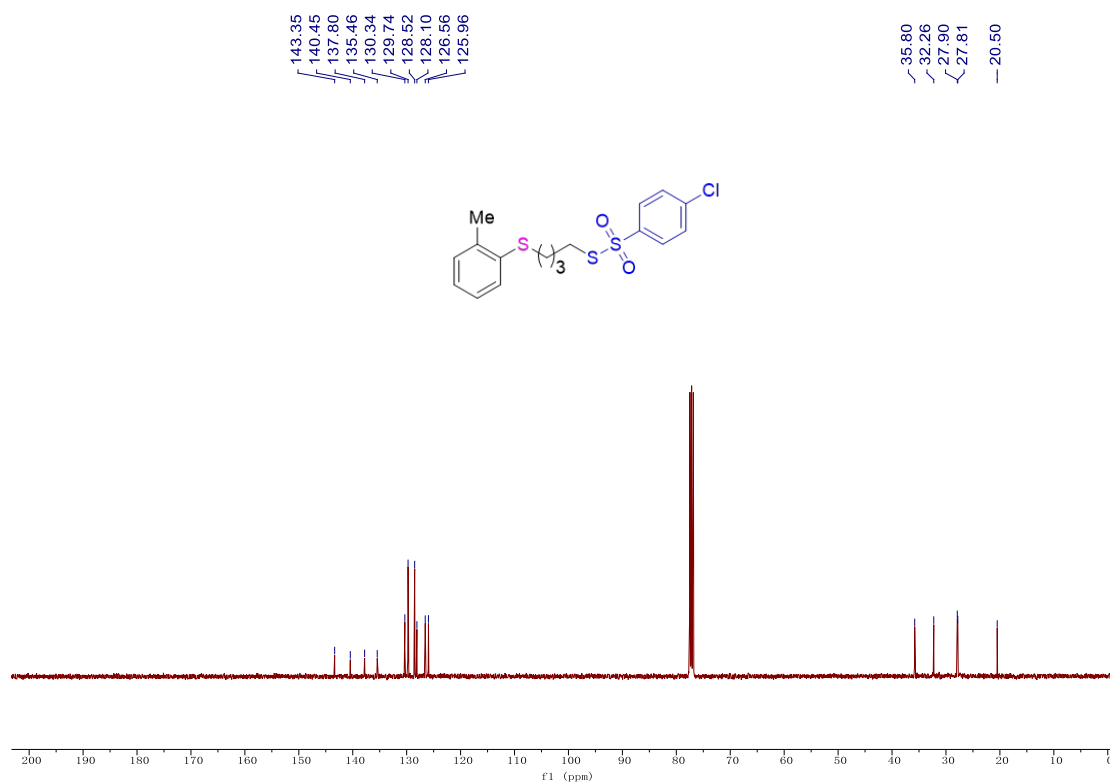
¹³C NMR (101 MHz, CDCl₃) spectra of **5n**



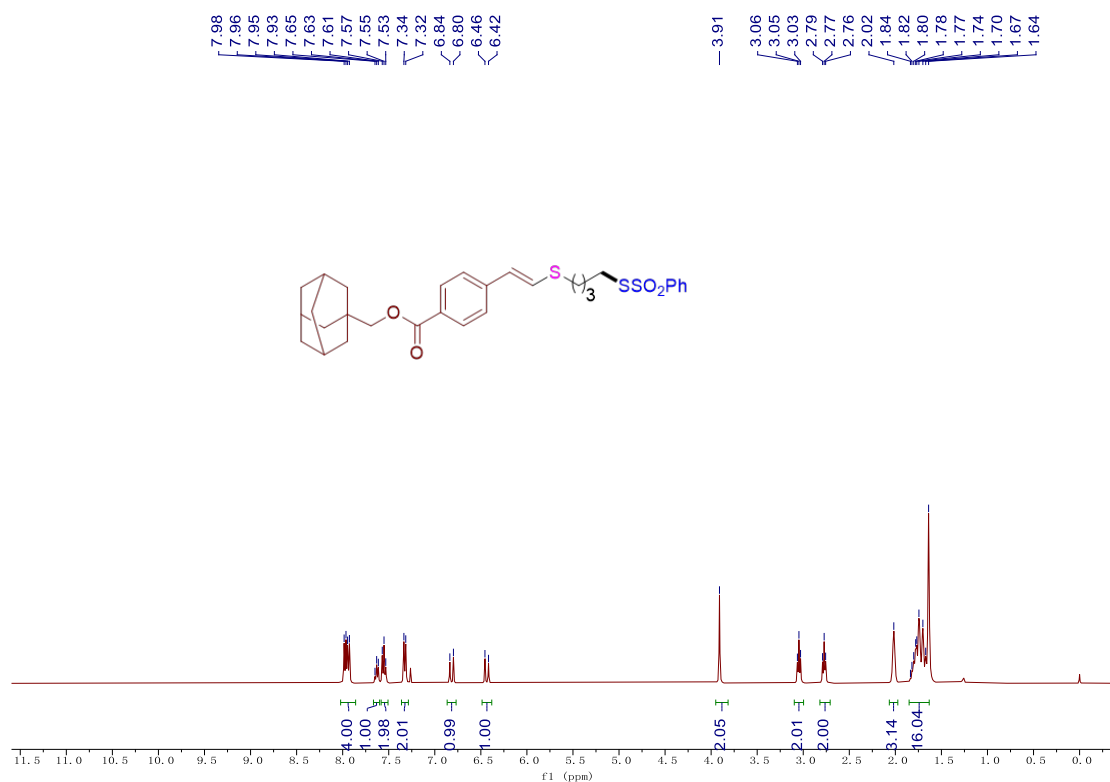
^{19}F NMR (376 MHz, CDCl_3) spectra of **5n**



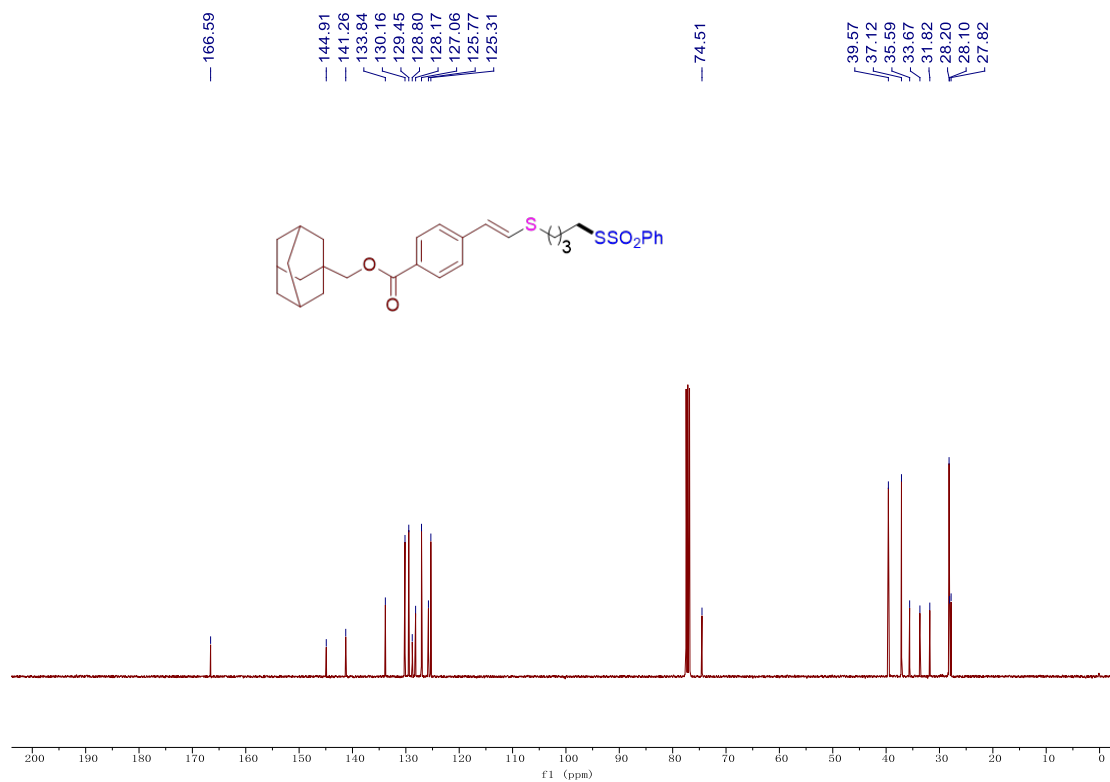
^1H NMR (400 MHz, CDCl_3) spectra of **5o**



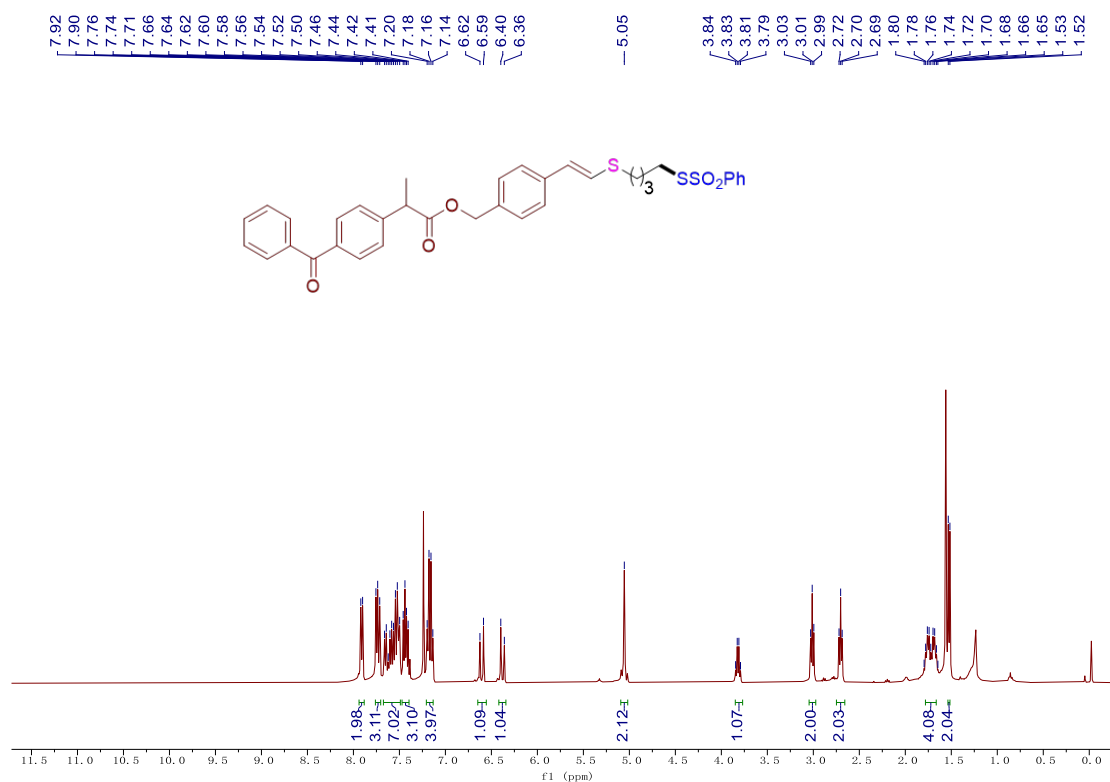
¹³C NMR (101 MHz, CDCl₃) spectra of **5o**



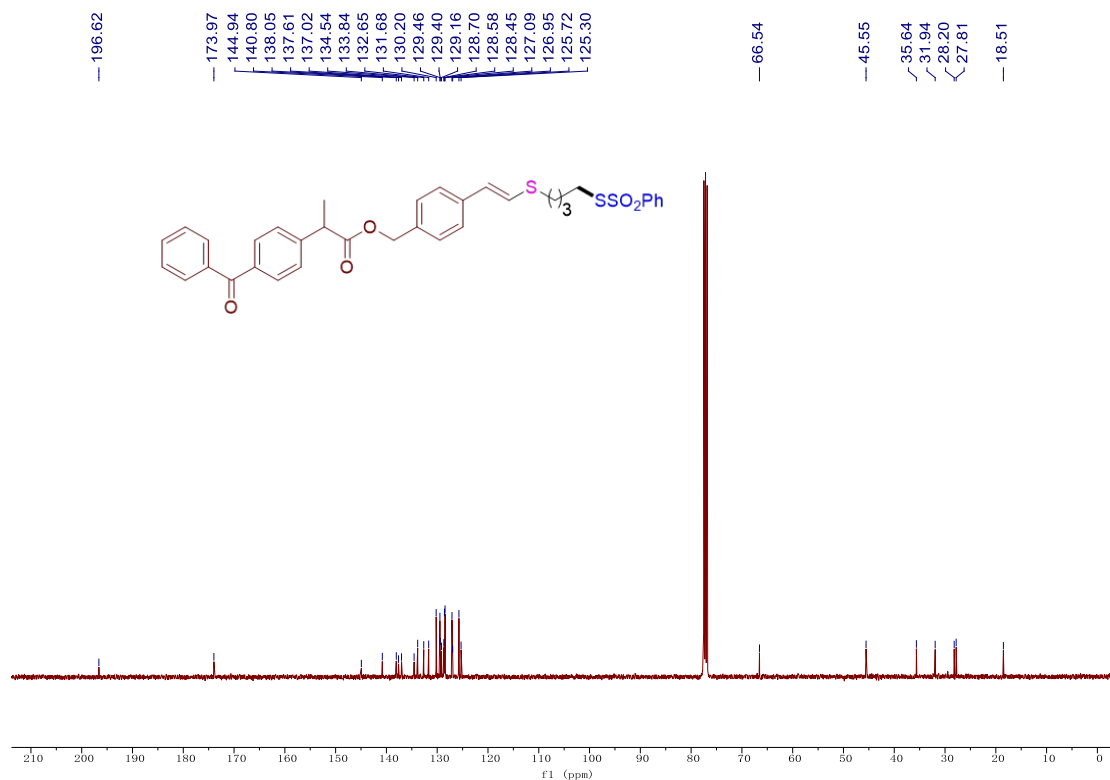
¹H NMR (400 MHz, CDCl₃) spectra of **3v**



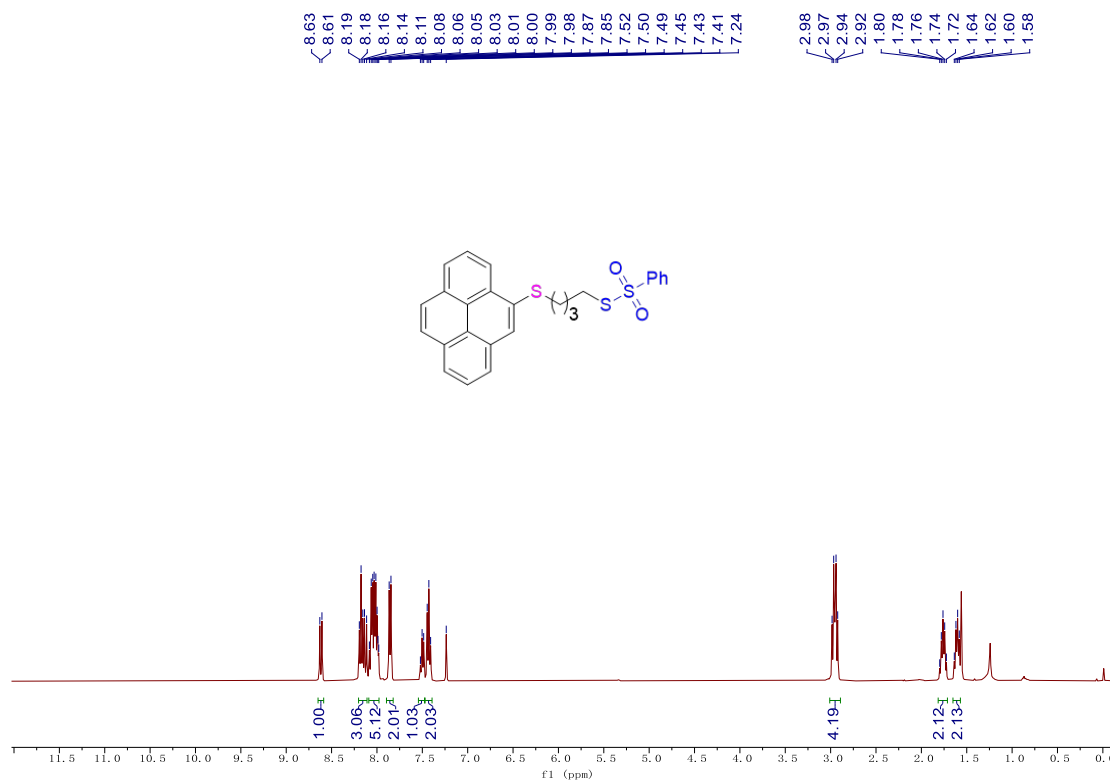
¹³C NMR (101 MHz, CDCl₃) spectra of **3v**



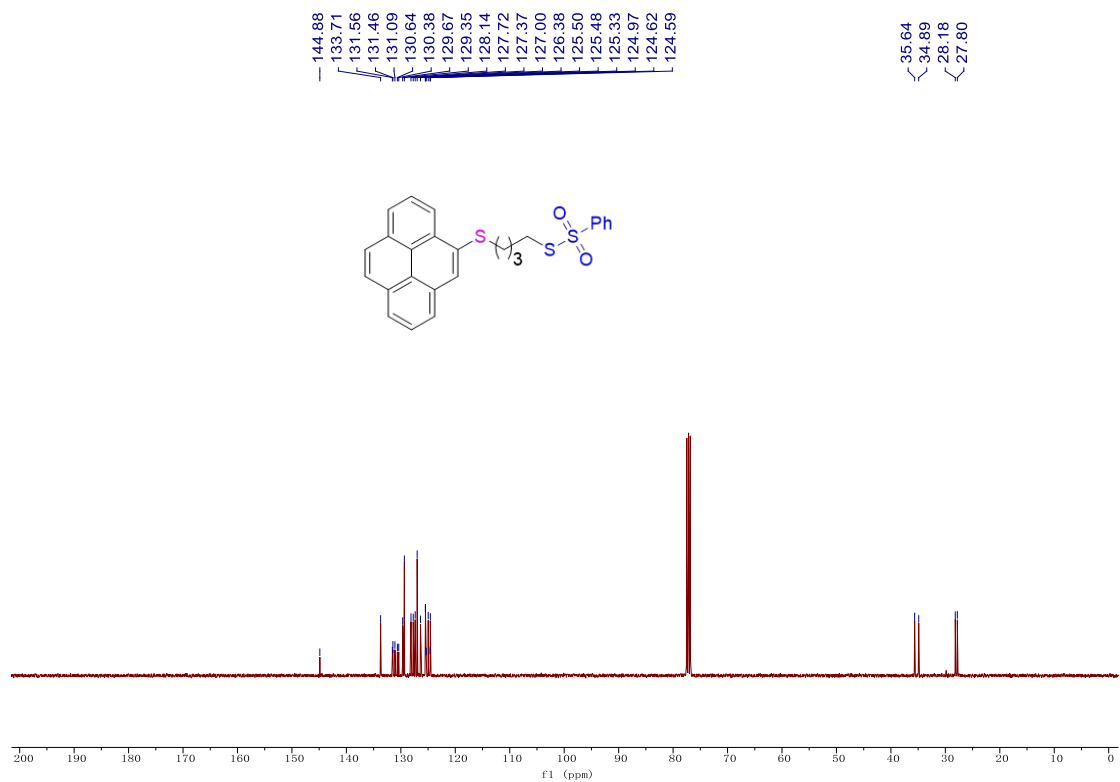
¹H NMR (400 MHz, CDCl₃) spectra of **3w**



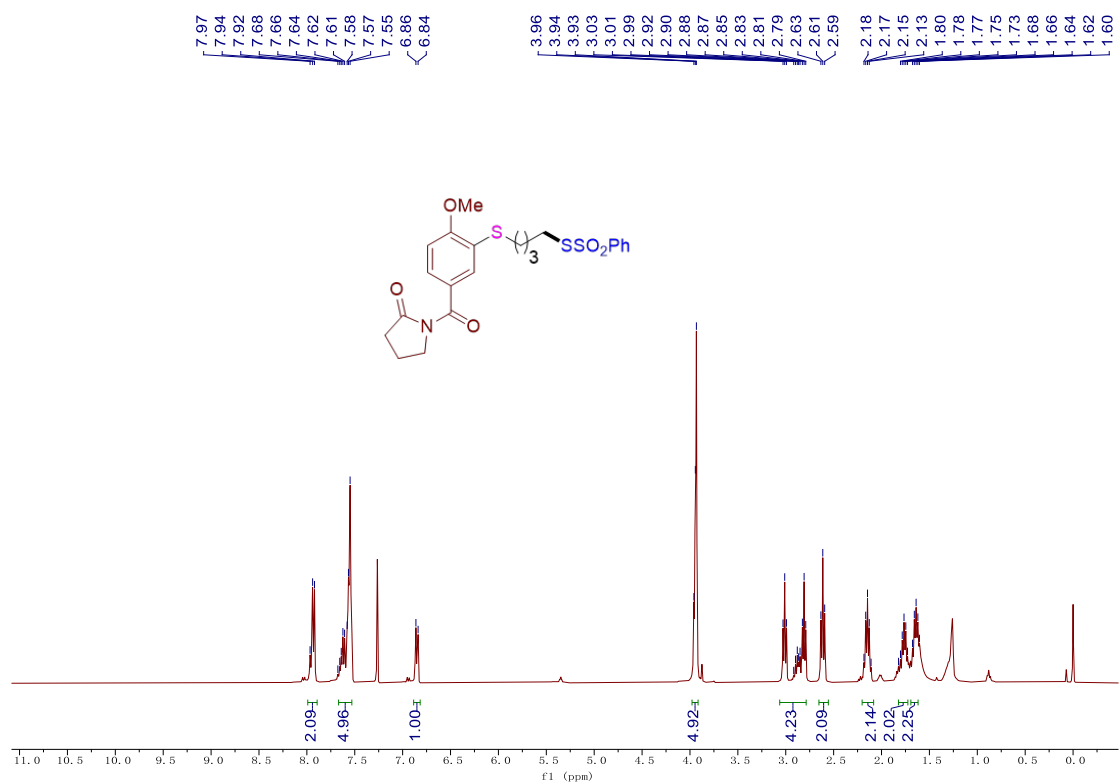
¹³C NMR (101 MHz, CDCl₃) spectra of **3w**



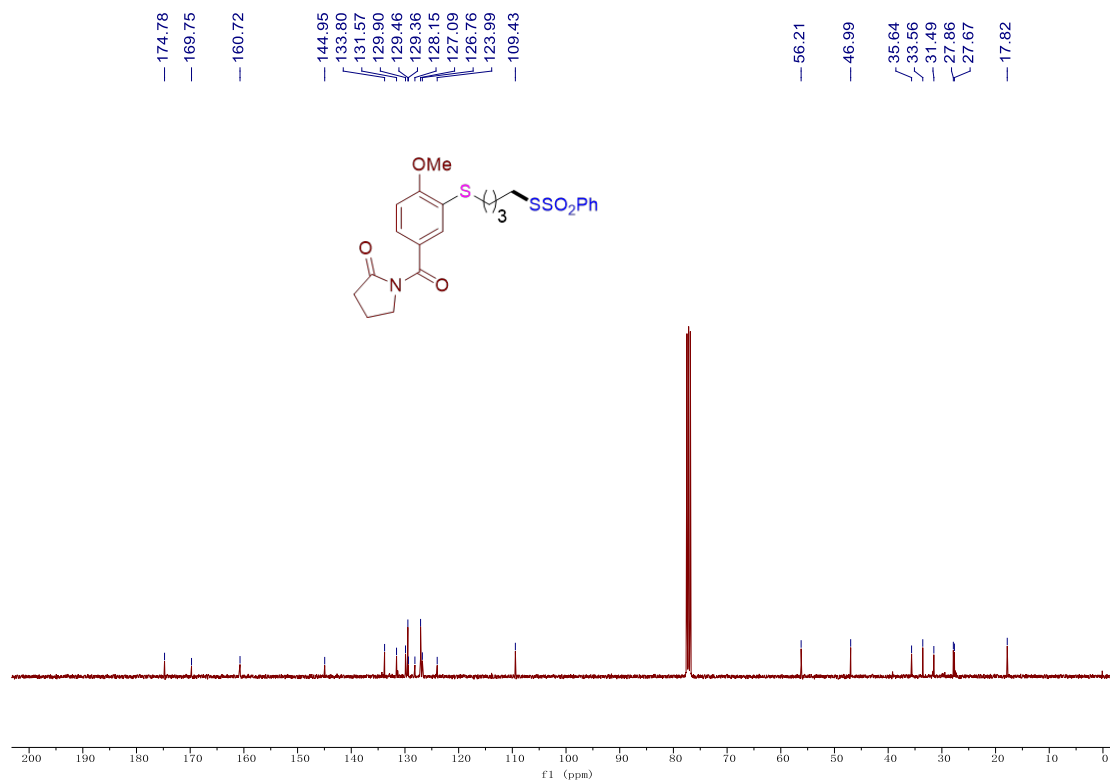
¹H NMR (400 MHz, CDCl₃) spectra of **5p**



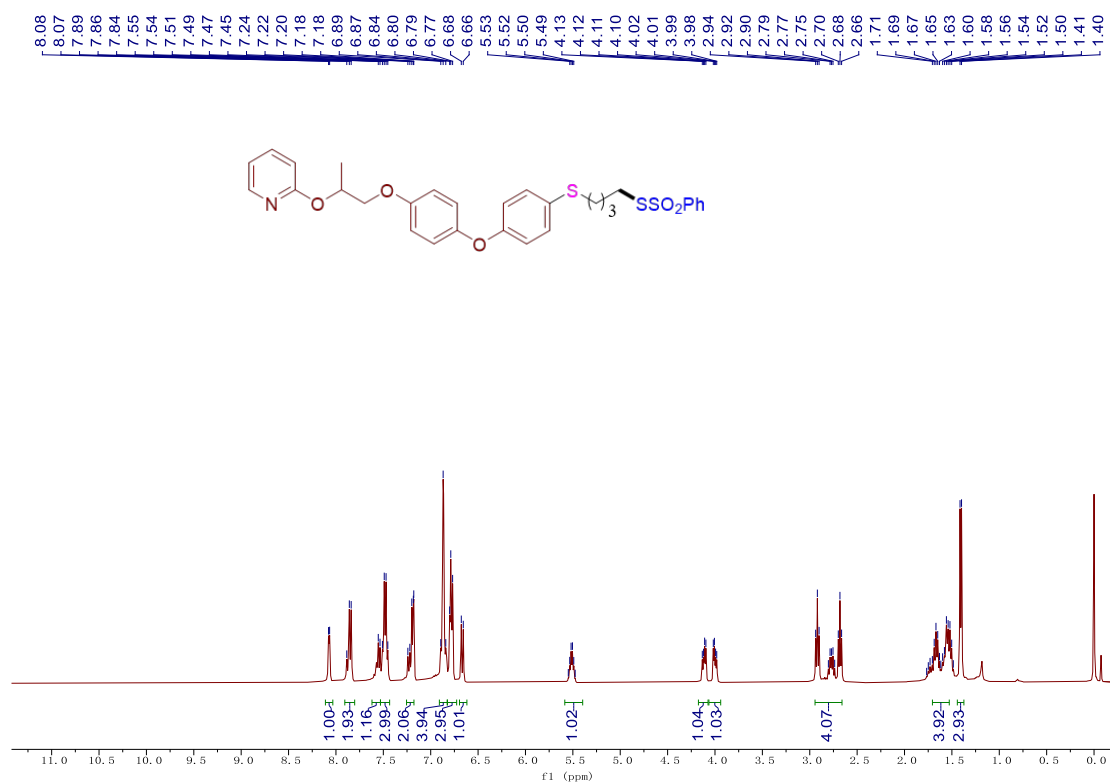
¹³C NMR (101 MHz, CDCl₃) spectra of **5p**



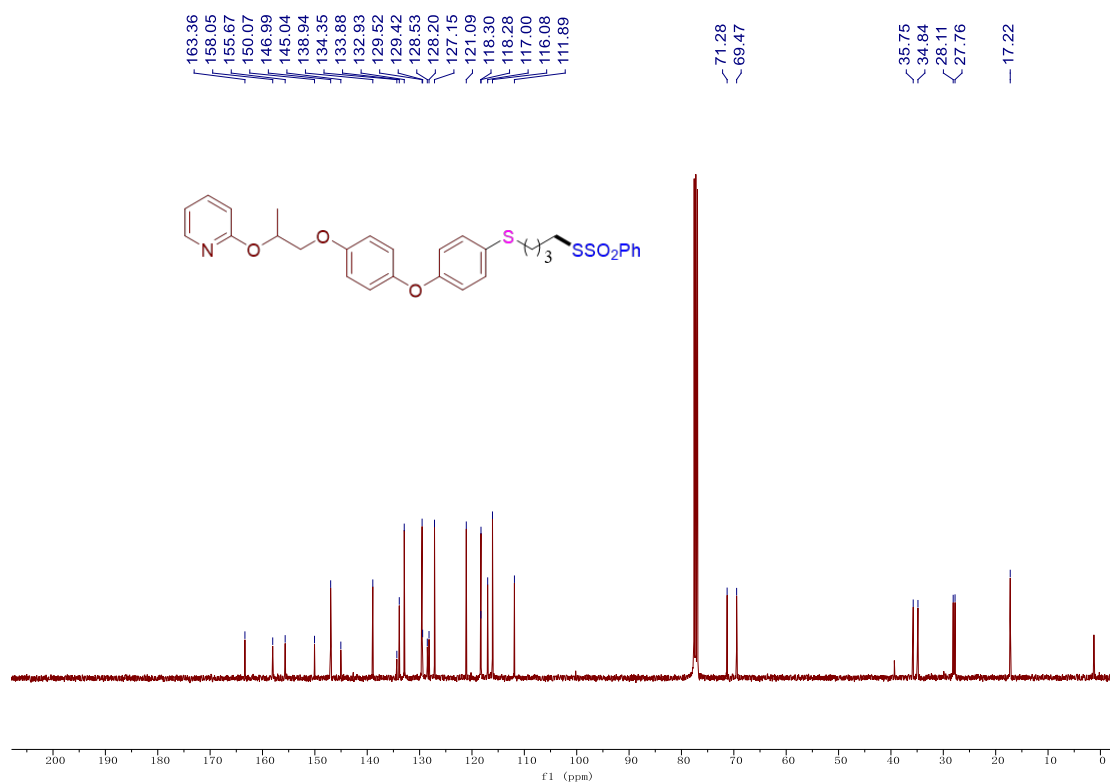
¹H NMR (400 MHz, CDCl₃) spectra of **5q**



¹³C NMR (101 MHz, CDCl₃) spectra of **5q**



¹H NMR (400 MHz, CDCl₃) spectra of **5r**



¹³C NMR (101 MHz, CDCl₃) spectra of 5r