

Supporting Information for

Synthesis of α -sulfenylated carbonyl compounds *via* combining gold-catalyzed rearrangement and photoinduced nickel-catalyzed Giese reaction

Yue-Liu-Ting Fu^a, Yun-Long Han^a, Liang-Qiu Lu^{a,b}, Ying Cheng^{*a,b} and Wen-Jing Xiao^{*a,b}

^a. Engineering Research Center of Photoenergy Utilization for Pollution Control and Carbon Reduction, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, China

^b. Wuhan Institute of Photochemistry and Technology, Wuhan 430083, China

*E-mail: wxiao@ccnu.edu.cn; ycheng@ccnu.edu.cn

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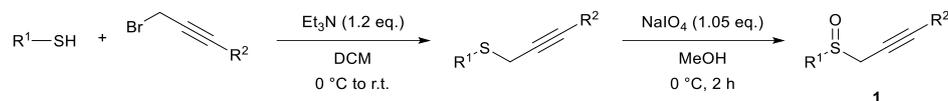
1. General Information

¹H NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) and the spectra are calibrated to the resonance resulting from incomplete deuteration of the solvent (CDCl₃: 7.26 ppm). ¹³C NMR spectra were recorded on the same spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (¹³CDCl₃: 77.0 ppm, t). Data are reported as follows: chemical shift δ /ppm, integration (¹H only), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or combinations thereof; ¹³C signals are singlets unless otherwise stated), coupling constants *J* in Hz, assignment. ¹⁹F NMR spectra were recorded on the same Spectrometer. High Resolution Mass Spectrometry (HRMS) were recorded on Bruker micrOTOF II ESI-TOF using a positive electrospray ionization (ESI⁺). Measured values are reported to 4 decimal places of the calculated value. The calculated values are based on the most abundant isotope.

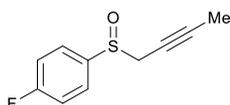
Analytical thin layer chromatography was performed using Qingdao Puke Parting Materials Co. silica gel plates (Silicagel 60 F254). Visualization was by ultraviolet fluorescence ($\lambda = 254$ nm). Flash column chromatography was performed using 200-300 mesh silica gel. All the solvents were treated according to standard methods, and all chemicals were used without purification.

2. General Procedures and Characterization Data

General procedure for the synthesis of propargylic sulfoxides¹

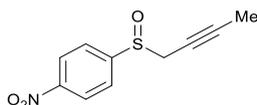


To a solution of propargyl bromide (33 mmol, 1.1 eq.) and Et₃N (5.0 mL, 36 mmol, 1.2 eq.) in CH₂Cl₂ (50 mL), thiophenol or thiol (30 mmol, 1.0 eq.) was added. The mixture was stirred at room temperature for 8 hours, and H₂O (50 mL) was added. The aqueous layer was washed with CH₂Cl₂ (3 x 20 mL), and the combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure to give propargyl sulfide without purification (quantitative yield). Propargyl sulfide was dissolved in 30 mL of methanol. After stirring for 5 minutes at 0 °C, an aqueous solution of NaIO₄ (6.80 g, 31.5 mmol, 1.05 eq.) was added slowly. The reaction mixture was stirred for 2 hours at 0 °C and diluted with CH₂Cl₂ (20 mL). The aqueous layer was washed with CH₂Cl₂ (2 x 20 mL), and the combined organic layers were dried over Na₂SO₄, filtered, and concentrated. The residue was purified by flash chromatography on silica gel eluted with PE/EA (v/v = 2/1) to give **1**.



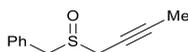
1-(But-2-yn-1-ylsulfinyl)-4-fluorobenzene (**1c**)

White solid, 4.77 g, 81% yield. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.72 – 7.69 (m, 2H), 7.26 – 7.21 (m, 2H), 3.68 – 3.58 (m, 2H), 1.81 (t, *J* = 2.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 164.7 (d, *J* = 251.8 Hz), 138.6 (d, *J* = 3.0 Hz), 126.8 (d, *J* = 8.9 Hz), 116.3 (d, *J* = 22.7 Hz), 84.9, 67.5, 48.7, 3.7. ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm) -107.9. HRMS (ESI) *m/z* for C₁₀H₉FOS [M+H]⁺: calcd 197.0430, found 197.0431.



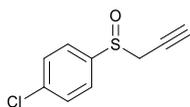
1-(But-2-yn-1-ylsulfinyl)-4-nitrobenzene (**1d**)

White solid, 4.48 g, 67% yield. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.42 – 8.39 (m, 2H), 7.92 – 7.88 (m, 2H), 3.75 – 3.62 (m, 2H), 1.82 (t, *J* = 2.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 150.6, 149.8, 125.6, 123.9, 85.8, 66.8, 48.5, 3.7. HRMS (ESI) *m/z* for C₁₀H₉NO₃S [M+H]⁺: calcd 224.0375, found 224.0380.



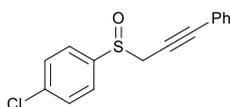
(But-2-yn-1-ylsulfinyl)methylbenzene (**1f**)

White solid, 3.69 g, 64% yield. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.42 – 7.33 (m, 5H), 4.23 (d, *J* = 13.0 Hz, 1H), 4.05 (d, *J* = 13.0 Hz, 1H), 3.42 – 3.28 (m, 2H), 1.95 (t, *J* = 2.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 130.3, 129.1, 128.9, 128.5, 85.0, 67.5, 55.9, 40.6, 3.9. HRMS (ESI) *m/z* for C₁₁H₁₂OS [M+H]⁺: calcd 193.0681, found 193.0681.



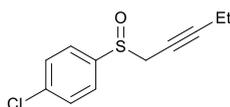
1-Chloro-4-(prop-2-yn-1-ylsulfinyl)benzene (1g)

White solid, 3.99 g, 67% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.67 (d, $J = 8.6$ Hz, 2H), 7.53 (d, $J = 8.6$ Hz, 2H), 3.71 – 3.59 (m, 2H), 2.36 (t, $J = 2.7$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 141.2, 138.1, 129.4, 125.9, 76.8, 72.3, 47.8. HRMS (ESI) m/z for $\text{C}_9\text{H}_7\text{ClOS}$ $[\text{M}+\text{H}]^+$: calcd 198.9978, found 198.9974.



1-Chloro-4-((3-phenylprop-2-yn-1-yl)sulfinyl)benzene (1h)

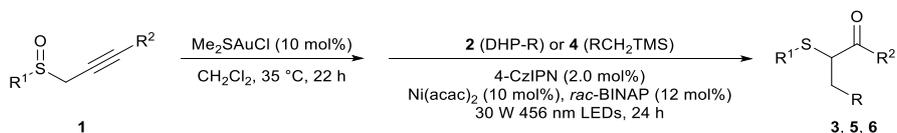
White solid, 6.45 g, 74% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.73 – 7.70 (m, 2H), 7.55 – 7.52 (m, 2H), 7.37 – 7.28 (m, 5H), 3.96 (d, $J = 15.6$ Hz, 1H), 3.81 (d, $J = 15.5$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 141.5, 138.0, 131.7, 129.3, 128.9, 128.4, 126.0, 121.8, 88.5, 77.6, 49.0. HRMS (ESI) m/z for $\text{C}_{15}\text{H}_{11}\text{ClOS}$ $[\text{M}+\text{H}]^+$: calcd 275.0292, found 275.0291.



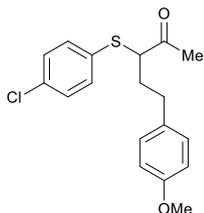
1-Chloro-4-(pent-2-yn-1-ylsulfinyl)benzene (1i)

White solid, 5.58 g, 82% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.65 (d, $J = 6.7$ Hz, 2H), 7.51 (d, $J = 6.6$ Hz, 2H), 3.69 (d, $J = 15.7$ Hz, 1H), 3.55 (d, $J = 15.3$ Hz, 1H), 2.20 – 2.14 (m, 2H), 1.08 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 141.6, 137.8, 129.1, 126.0, 90.8, 67.6, 48.6, 13.5, 12.5. HRMS (ESI) m/z for $\text{C}_{11}\text{H}_{11}\text{ClOS}$ $[\text{M}+\text{H}]^+$: calcd 227.0291, found 227.0297.

General procedure for the synthesis of products

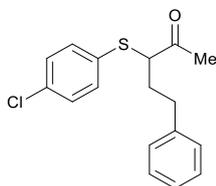


The procedure was conducted in an argon-filled glove box. To a 10 mL vial equipped with a magnetic stir bar were added **1** (0.20 mmol), Me_2SAuCl (5.8 mg, 0.020 mmol, 10 mol%), and CH_2Cl_2 (1.0 mL). The mixture was stirred at 35 °C for 22 h. Then **2** or **4** (0.10 mmol), 4-CzIPN (1.6 mg, 0.0020 mmol, 2.0 mol%), $\text{Ni}(\text{acac})_2$ (2.6 mg, 0.010 mmol, 10 mol%), *rac*-BINAP (7.5 mg, 0.012 mmol, 12 mol%) were added under Ar. The mixture was irradiated with 30 W 456 nm LEDs at room temperature for 24 h. The residue was purified by silica gel chromatography with PE/EA (v/v = 20:1-10:1) as eluent to afford product **3**, **5**, or **6**.



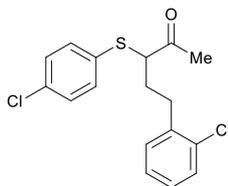
3-((4-Chlorophenyl)thio)-5-(4-methoxyphenyl)pentan-2-one (3a)

Light yellow oil, 26.7 mg, 80% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.29 – 7.23 (m, 4H), 7.07 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 3.79 (s, 3H), 3.52 (t, $J = 7.4$ Hz, 1H), 2.71 – 2.67 (m, 2H), 2.24 (s, 3H), 2.13 – 2.04 (m, 1H), 1.98 – 1.89 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.6, 158.1, 134.5, 134.2, 132.5, 130.8, 129.4, 129.3, 114.0, 56.4, 55.3, 32.1, 31.7, 26.9. HRMS (ESI) m/z for $\text{C}_{18}\text{H}_{19}\text{ClO}_2\text{S}$ $[\text{M}+\text{Na}]^+$: calcd 357.0686, found 357.0684.



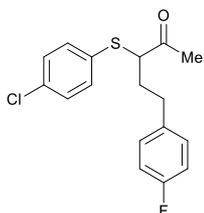
3-((4-Chlorophenyl)thio)-5-phenylpentan-2-one (3b)

Light yellow oil, 26.1 mg, 86% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.31 – 7.26 (m, 6H), 7.25 – 7.14 (m, 3H), 3.53 (t, $J = 7.4$ Hz, 1H), 2.77 – 2.72 (m, 2H), 2.25 (s, 3H), 2.17 – 2.08 (m, 1H), 2.01 – 1.92 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.4, 140.4, 134.5, 134.2, 130.7, 129.3, 128.6, 128.5, 126.3, 56.4, 33.0, 31.4, 26.9. HRMS (ESI) m/z for $\text{C}_{17}\text{H}_{17}\text{ClOS}$ $[\text{M}+\text{H}]^+$: calcd 305.0761, found 305.0767.



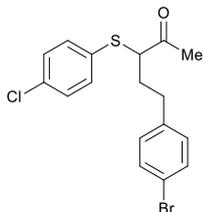
3-((4-Chlorophenyl)thio)-5-(3-methoxyphenyl)pentan-2-one (3c)

Light yellow oil, 28.1 mg, 83% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.36 – 7.34 (m, 1H), 7.30 – 7.27 (m, 3H), 7.26 – 7.25 (m, 1H), 7.20 – 7.14 (m, 3H), 3.57 (t, $J = 7.4$ Hz, 1H), 2.95 – 2.87 (m, 1H), 2.85 – 2.77 (m, 1H), 2.29 (s, 3H), 2.19 – 2.10 (m, 1H), 2.02 – 1.93 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.3, 138.2, 135.5, 134.5, 134.2, 133.9, 130.6, 129.7, 129.3, 127.9, 127.0, 56.8, 31.1, 29.8, 26.8. HRMS (ESI) m/z for $\text{C}_{17}\text{H}_{16}\text{Cl}_2\text{OS}$ $[\text{M}+\text{Na}]^+$: calcd 361.0191, found 361.0188.



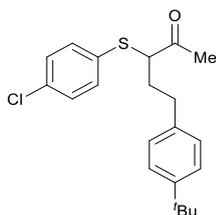
3-((4-Chlorophenyl)thio)-5-(4-fluorophenyl)pentan-2-one (3d)

Light yellow oil, 19.7 mg, 61% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.26 (s, 4H), 7.13 – 7.09 (m, 2H), 7.00 – 6.95 (m, 2H), 3.50 (t, $J = 7.4$ Hz, 1H), 2.78 – 2.66 (m, 2H), 2.26 (s, 3H), 2.14 – 2.04 (m, 1H), 1.99 – 1.89 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.4, 161.5 (d, $J = 242.9$ Hz), 136.1 (d, $J = 3.2$ Hz), 134.6, 134.2, 130.5, 129.8 (d, $J = 7.8$ Hz), 129.3, 115.3 (d, $J = 20.9$ Hz), 56.3, 32.2, 31.5, 27.0. ^{19}F NMR (376 MHz, CDCl_3) δ (ppm) -116.8. HRMS (ESI) m/z for $\text{C}_{17}\text{H}_{16}\text{ClFOS}$ $[\text{M}+\text{Na}]^+$: calcd 345.0487, found 345.0492.



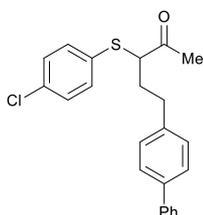
5-(4-Bromophenyl)-3-((4-chlorophenyl)thio)pentan-2-one (3e)

Light yellow oil, 24.5 mg, 64% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.43 – 7.39 (m, 2H), 7.27 – 7.26 (m, 4H), 7.05 – 7.03 (m, 2H), 3.49 (t, $J = 7.4$ Hz, 1H), 2.72 – 2.68 (m, 2H), 2.27 (s, 3H), 2.13 – 2.04 (m, 1H), 1.97 – 1.88 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.3, 139.4, 134.7, 134.3, 131.6, 130.3, 130.2, 129.4, 120.1, 56.2, 32.4, 31.2, 27.1. HRMS (ESI) m/z for $\text{C}_{17}\text{H}_{16}\text{BrClOS}$ $[\text{M}+\text{Na}]^+$: calcd 404.9686, found 404.9683.



5-(4-(tert-Butyl)phenyl)-3-((4-chlorophenyl)thio)pentan-2-one (3f)

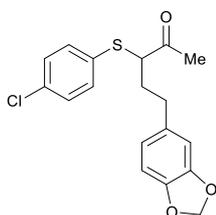
Light yellow oil, 25.7 mg, 72% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.31 (d, $J = 8.3$ Hz, 2H), 7.25 (s, 4H), 7.09 (d, $J = 8.3$ Hz, 2H), 3.55 (t, $J = 7.4$ Hz, 1H), 2.74 – 2.69 (m, 2H), 2.25 (s, 3H), 2.14 – 2.07 (m, 1H), 2.00 – 1.91 (m, 1H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.6, 149.2, 137.4, 134.5, 134.2, 130.8, 129.3, 128.2, 125.5, 56.6, 34.4, 32.5, 31.5, 31.4, 26.9. HRMS (ESI) m/z for $\text{C}_{21}\text{H}_{25}\text{ClOS}$ $[\text{M}+\text{Na}]^+$: calcd 383.1206, found 383.1214.



5-([1,1'-Biphenyl]-4-yl)-3-((4-chlorophenyl)thio)pentan-2-one (3g)

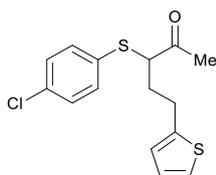
Light yellow oil, 25.1 mg, 66% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.59 – 7.56 (m, 2H), 7.54 – 7.51 (m, 2H), 7.46 – 7.41 (m, 2H), 7.36 – 7.31 (m, 1H), 7.29 – 7.22 (m, 6H), 3.56 (t, $J = 7.4$ Hz, 1H), 2.81 – 2.77 (m, 2H), 2.27 (s, 3H), 2.20 – 2.11 (m, 1H), 2.04 – 1.95 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.4, 140.8, 139.5, 139.3,

134.5, 134.2, 130.6, 129.3, 128.9, 128.7, 127.3, 127.2, 127.0, 56.4, 32.6, 31.4, 27.0. HRMS (ESI) m/z for $C_{23}H_{21}ClOS$ $[M+Na]^+$: calcd 403.0893, found 403.0898.



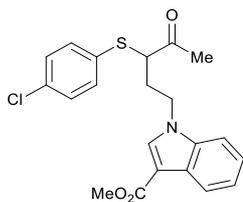
5-(Benzo[d][1,3]dioxol-5-yl)-3-((4-chlorophenyl)thio)pentan-2-one (3h)

White solid, 30.2 mg, 87% yield. 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.26 (s, 4H), 6.73 (d, $J = 7.9$ Hz, 1H), 6.64 (s, 1H), 6.60 (d, $J = 7.9$ Hz, 1H), 5.93 (s, 2H), 3.51 (t, $J = 7.4$ Hz, 1H), 2.66 (t, $J = 7.5$ Hz, 2H), 2.26 (s, 3H), 2.11 – 2.00 (m, 1H), 1.96 – 1.87 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 204.5, 147.8, 146.0, 134.6, 134.3, 134.2, 130.6, 129.3, 121.3, 108.9, 108.3, 100.9, 56.2, 32.7, 31.6, 27.0. HRMS (ESI) m/z for $C_{18}H_{17}ClO_3S$ $[M+Na]^+$: calcd 371.0479, found 371.0479.



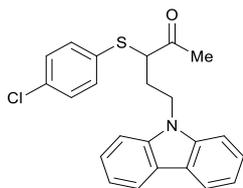
3-((4-Chlorophenyl)thio)-5-(thiophen-2-yl)pentan-2-one (3i)

Light yellow oil, 23.8 mg, 77% yield. 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31 – 7.25 (m, 4H), 7.14 (dd, $J = 5.1$, 1.2 Hz, 1H), 6.94 – 6.92 (m, 1H), 6.79 – 6.78 (m, 1H), 3.57 (t, $J = 7.4$ Hz, 1H), 2.99 (t, $J = 7.3$ Hz, 2H), 2.27 (s, 3H), 2.21 – 2.11 (m, 1H), 2.04 – 1.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 204.1, 143.0, 134.7, 134.5, 130.4, 129.3, 126.9, 124.9, 123.6, 56.0, 31.5, 27.3, 27.0. HRMS (ESI) m/z for $C_{15}H_{15}ClOS_2$ $[M+Na]^+$: calcd 333.0145, found 333.0147.



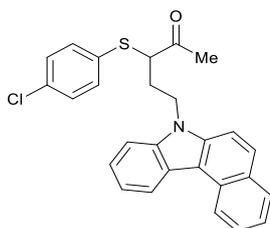
Methyl 1-(3-((4-chlorophenyl)thio)-4-oxopentyl)-1H-indole-3-carboxylate (3j)

Light yellow oil, 27.6 mg, 69% yield. 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.20 – 8.18 (m, 1H), 7.77 (s, 1H), 7.34 – 7.25 (m, 5H), 7.23 – 7.20 (m, 2H), 4.38 – 4.21 (m, 2H), 3.92 (s, 3H), 3.26 (t, $J = 7.3$ Hz, 1H), 2.39 – 2.30 (m, 1H), 2.24 (s, 3H), 2.17 – 2.08 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 203.1, 165.3, 136.3, 135.3, 134.9, 133.9, 129.5, 129.0, 126.6, 123.1, 122.1, 121.9, 109.8, 107.6, 53.2, 51.0, 43.9, 29.7, 27.8. HRMS (ESI) m/z for $C_{21}H_{20}ClNO_3S$ $[M+H]^+$: calcd 402.0925, found 402.0921.



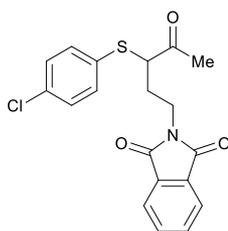
5-(9H-Carbazol-9-yl)-3-((4-chlorophenyl)thio)pentan-2-one (3k)

Light yellow oil, 25.1 mg, 64% yield. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.10 (d, *J* = 7.8 Hz, 2H), 7.48 – 7.43 (m, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.15 (m, 6H), 4.52 – 4.36 (m, 2H), 3.31 (t, *J* = 7.2 Hz, 1H), 2.45 – 2.36 (m, 1H), 2.24 – 2.15 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 203.5, 140.2, 135.1, 134.7, 129.4, 125.9, 123.0, 120.5, 119.3, 108.7, 53.5, 40.2, 28.9, 27.8. HRMS (ESI) *m/z* for C₂₃H₂₀ClNOS [M+H]⁺: calcd 394.1026, found 394.1030.



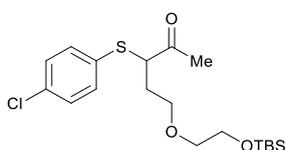
5-(7H-Benzo[c]carbazol-7-yl)-3-((4-chlorophenyl)thio)pentan-2-one (3l)

White solid, 30.4 mg, 69% yield. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.78 (d, *J* = 8.3 Hz, 1H), 8.59 (d, *J* = 7.9 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.9 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.59 (d, *J* = 8.9 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.41 – 7.37 (m, 1H), 7.18 – 7.12 (m, 4H), 4.61 – 4.46 (m, 2H), 3.25 (t, *J* = 7.2 Hz, 1H), 2.46 – 2.38 (m, 1H), 2.26 – 2.17 (m, 1H), 2.14 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 203.4, 139.0, 137.7, 135.0, 134.6, 129.9, 129.5, 129.4, 129.2, 128.9, 127.4, 127.1, 124.3, 123.6, 123.1, 123.0, 122.2, 120.1, 115.1, 110.5, 109.2, 53.4, 40.2, 29.3, 27.8. HRMS (ESI) *m/z* for C₂₇H₂₂ClNOS [M+H]⁺: calcd 444.1183, found 444.1180.



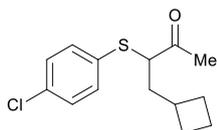
2-(3-((4-Chlorophenyl)thio)-4-oxopentyl)isoindoline-1,3-dione (3m)

White solid, 30.4 mg, 57% yield. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.86 – 7.83 (m, 2H), 7.75 – 7.72 (m, 2H), 7.34 – 7.32 (m, 2H), 7.29 – 7.25 (m, 2H), 3.82 – 3.78 (m, 2H), 3.57 (t, *J* = 7.2 Hz, 1H), 2.37 (s, 3H), 2.21 – 2.12 (m, 1H), 1.98 – 1.90 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 202.9, 168.4, 135.9, 135.4, 134.1, 131.9, 129.3, 128.9, 123.3, 54.1, 35.8, 28.9, 27.6. HRMS (ESI) *m/z* for C₁₉H₁₆ClNO₃S [M+H]⁺: calcd 374.0612, found 374.0613.



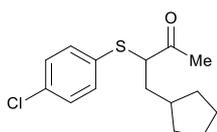
5-(2-((*tert*-Butyldimethylsilyloxy)ethoxy)-3-((4-chlorophenyl)thio)pentan-2-one (3n)

Light yellow oil, 30.1 mg, 75% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.32 – 7.25 (m, 4H), 3.84 (t, $J = 7.4$ Hz, 1H), 3.73 (t, $J = 5.2$ Hz, 2H), 3.67 – 3.61 (m, 1H), 3.55 – 3.51 (m, 1H), 3.50 – 3.46 (m, 2H), 2.28 (s, 3H), 2.14 – 2.05 (m, 1H), 1.91 – 1.83 (m, 1H), 0.90 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.3, 134.5, 134.3, 130.9, 129.3, 72.4, 67.9, 62.6, 54.0, 30.3, 27.5, 25.9, 18.4, -5.3. HRMS (ESI) m/z for $\text{C}_{19}\text{H}_{31}\text{ClO}_3\text{SSi}$ $[\text{M}+\text{H}]^+$: calcd 403.1524, found 403.1521.



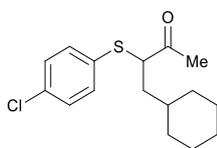
3-((4-Chlorophenyl)thio)-4-cyclobutylbutan-2-one (3o)

Light yellow oil, 16.8 mg, 63% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.29 – 7.24 (m, 4H), 3.51 (t, $J = 7.5$ Hz, 1H), 2.45 – 2.35 (m, 1H), 2.23 (s, 3H), 2.12 – 2.00 (m, 2H), 1.93 – 1.74 (m, 4H), 1.68 – 1.58 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 205.2, 134.1, 133.5, 131.5, 129.2, 55.8, 37.2, 33.7, 28.3, 28.1, 26.2, 18.4. HRMS (ESI) m/z for $\text{C}_{14}\text{H}_{17}\text{ClOS}$ $[\text{M}+\text{H}]^+$: calcd 269.0761, found 269.0760.



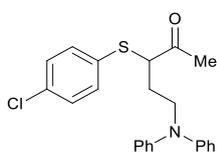
3-((4-Chlorophenyl)thio)-4-cyclopentylbutan-2-one (3p)

Light yellow oil, 18.2 mg, 64% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.30 – 7.24 (m, 4H), 3.63 (t, $J = 7.6$ Hz, 1H), 2.25 (s, 3H), 1.96 – 1.88 (m, 1H), 1.86 – 1.74 (m, 3H), 1.73 – 1.49 (m, 5H), 1.17 – 1.03 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 205.2, 134.1, 133.6, 131.4, 129.2, 57.0, 37.7, 36.4, 32.6, 32.4, 26.1, 25.0, 25.0. HRMS (ESI) m/z for $\text{C}_{15}\text{H}_{19}\text{ClOS}$ $[\text{M}+\text{H}]^+$: calcd 283.0917, found 283.0912.



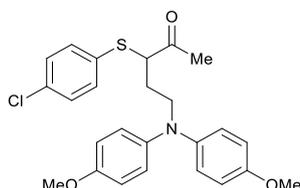
3-((4-Chlorophenyl)thio)-4-cyclohexylbutan-2-one (3q)

Light yellow oil, 18.9 mg, 64% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.29 – 7.24 (m, 4H), 3.71 (t, $J = 7.7$ Hz, 1H), 2.24 (s, 3H), 1.74 – 1.64 (m, 6H), 1.60 – 1.53 (m, 1H), 1.46 – 1.36 (m, 1H), 1.28 – 1.08 (m, 3H), 0.97 – 0.85 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 205.3, 134.2, 133.6, 131.4, 129.3, 55.3, 37.6, 35.3, 33.1, 33.1, 26.4, 26.1, 26.1, 26.1. HRMS (ESI) m/z for $\text{C}_{16}\text{H}_{21}\text{ClOS}$ $[\text{M}+\text{H}]^+$: calcd 297.1074, found 297.1073.



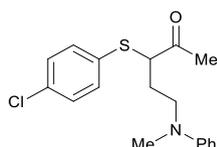
3-((4-Chlorophenyl)thio)-5-(diphenylamino)pentan-2-one (5a)

Light yellow oil, 30.4 mg, 77% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.28 – 7.18 (m, 8H), 6.98 – 6.95 (m, 6H), 3.93 – 3.79 (m, 2H), 3.64 (t, $J = 7.3$ Hz, 1H), 2.20 (s, 3H), 2.17 – 2.12 (m, 1H), 2.04 – 1.93 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 203.9, 147.7, 134.7, 134.5, 130.3, 129.4, 129.3, 121.6, 121.0, 54.7, 49.6, 27.9, 27.3. HRMS (ESI) m/z for $\text{C}_{23}\text{H}_{22}\text{ClNOS}$ $[\text{M}+\text{H}]^+$: calcd 396.1183, found 396.1184.



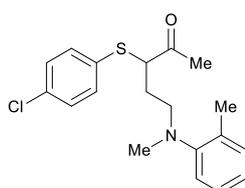
5-(Bis(4-methoxyphenyl)amino)-3-((4-chlorophenyl)thio)pentan-2-one (5b)

Light yellow oil, 35.5 mg, 78% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.25 – 7.19 (m, 4H), 6.87 – 6.78 (m, 8H), 3.78 (s, 6H), 3.76 – 3.67 (m, 3H), 2.22 (s, 3H), 2.16 – 2.07 (m, 1H), 1.96 – 1.87 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.1, 154.6, 142.1, 134.6, 134.3, 130.6, 129.3, 122.3, 114.7, 55.6, 54.9, 50.1, 27.9, 27.2. HRMS (ESI) m/z for $\text{C}_{25}\text{H}_{26}\text{ClNO}_3\text{S}$ $[\text{M}+\text{H}]^+$: calcd 456.1394, found 456.1394.



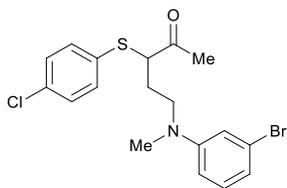
3-((4-Chlorophenyl)thio)-5-(diphenylamino)pentan-2-one (5c)

Light yellow oil, 21.6 mg, 65% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.29 – 7.21 (m, 6H), 6.74 – 6.70 (m, 3H), 3.59 (t, $J = 7.2$ Hz, 1H), 3.50 – 3.38 (m, 2H), 2.88 (s, 3H), 2.22 (s, 3H), 2.17 – 2.08 (m, 1H), 1.95 – 1.86 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.0, 149.1, 134.7, 134.3, 130.5, 129.3, 129.3, 116.9, 112.6, 54.8, 50.2, 38.4, 27.6, 27.1. HRMS (ESI) m/z for $\text{C}_{18}\text{H}_{20}\text{ClNOS}$ $[\text{M}+\text{H}]^+$: calcd 334.1026, found 334.1023.



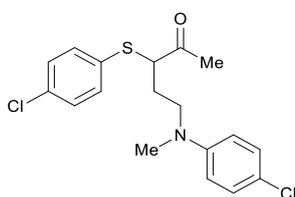
3-((4-Chlorophenyl)thio)-5-(methyl(o-tolyl)amino)pentan-2-one (5d)

Light yellow oil, 20.4 mg, 59% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.25 – 7.14 (m, 6H), 7.04 – 6.98 (m, 2H), 3.71 (t, $J = 7.3$ Hz, 1H), 3.10 – 3.01 (m, 2H), 2.61 (s, 3H), 2.27 (s, 3H), 2.23 (s, 3H), 2.07 – 1.98 (m, 1H), 1.86 – 1.78 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.3, 151.2, 134.7, 134.1, 133.3, 131.2, 131.1, 129.2, 126.5, 123.4, 120.3, 55.0, 52.6, 42.6, 27.9, 27.4, 18.1. HRMS (ESI) m/z for $\text{C}_{19}\text{H}_{22}\text{ClNOS}$ $[\text{M}+\text{H}]^+$: calcd 348.1183, found 348.1181.



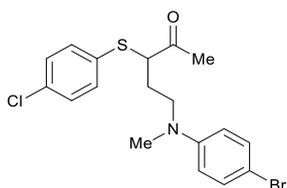
3-((4-Chlorophenyl)thio)-5-(methyl(*o*-tolyl)amino)pentan-2-one (5e)

Light yellow oil, 25.8 mg, 63% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.28 (s, 4H), 7.08 – 7.03 (m, 1H), 6.83 – 6.81 (m, 2H), 6.61 – 6.58 (m, 1H), 3.55 (t, $J = 7.2$ Hz, 1H), 3.47 – 3.37 (m, 2H), 2.87 (s, 3H), 2.25 (s, 3H), 2.14 – 2.05 (m, 1H), 1.93 – 1.84 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 203.8, 150.2, 134.9, 134.5, 130.5, 130.2, 129.4, 123.6, 119.4, 115.1, 110.9, 54.7, 50.0, 38.3, 27.4, 27.2. HRMS (ESI) m/z for $\text{C}_{18}\text{H}_{19}\text{BrClNOS}$ $[\text{M}+\text{H}]^+$: calcd 412.0132, found 412.027.



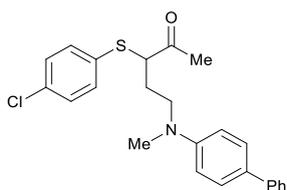
5-((4-Chlorophenyl)(methyl)amino)-3-((4-chlorophenyl)thio)pentan-2-one (5f)

Light yellow oil, 22.3 mg, 61% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.30 – 7.26 (m, 4H), 7.17 – 7.14 (m, 2H), 6.62 – 6.60 (m, 2H), 3.56 (t, $J = 7.2$ Hz, 1H), 3.43 – 3.38 (m, 2H), 2.86 (s, 3H), 2.24 (s, 3H), 2.13 – 2.05 (m, 1H), 1.92 – 1.84 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 203.9, 147.7, 134.8, 134.4, 130.3, 129.4, 129.0, 121.7, 113.7, 54.7, 50.3, 38.5, 27.4, 27.2. HRMS (ESI) m/z for $\text{C}_{18}\text{H}_{19}\text{Cl}_2\text{NOS}$ $[\text{M}+\text{H}]^+$: calcd 368.0637, found 368.0635.



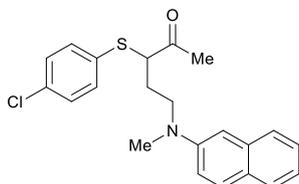
5-((4-Bromophenyl)(methyl)amino)-3-((4-chlorophenyl)thio)pentan-2-one (5g)

Light yellow oil, 24.6 mg, 60% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.23 – 7.19 (m, 6H), 6.51 – 6.47 (m, 2H), 3.48 (t, $J = 7.2$ Hz, 1H), 3.36 – 3.31 (m, 2H), 2.78 (s, 3H), 2.17 (s, 3H), 2.07 – 1.98 (m, 1H), 1.85 – 1.76 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 203.9, 148.1, 134.8, 134.4, 131.9, 130.3, 129.4, 114.1, 108.7, 54.7, 50.2, 38.4, 27.4, 27.2. HRMS (ESI) m/z for $\text{C}_{18}\text{H}_{19}\text{BrClNOS}$ $[\text{M}+\text{H}]^+$: calcd 412.0132, found 412.027.



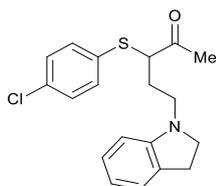
5-((Bis(4-methoxyphenyl)amino)-3-((4-chlorophenyl)thio)pentan-2-one (5h)

Light yellow oil, 27.4 mg, 67% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.54 (d, $J = 7.4$ Hz, 2H), 7.49 (d, $J = 8.8$ Hz, 2H), 7.40 (t, $J = 7.7$ Hz, 2H), 7.30 – 7.24 (m, 5H), 6.77 (d, $J = 8.5$ Hz, 2H), 3.61 (t, $J = 7.2$ Hz, 1H), 3.52 – 3.44 (m, 2H), 2.93 (s, 3H), 2.24 (s, 3H), 2.20 – 2.11 (m, 1H), 1.98 – 1.89 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.0, 148.5, 141.0, 134.8, 134.4, 130.4, 129.4, 128.7, 127.9, 126.3, 126.1, 112.8, 54.8, 50.2, 38.5, 27.6, 27.2. HRMS (ESI) m/z for $\text{C}_{24}\text{H}_{24}\text{ClNOS}$ $[\text{M}+\text{H}]^+$: calcd 410.1339, found 410.1333.



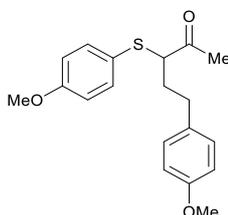
3-((4-Chlorophenyl)thio)-5-(methyl(naphthalen-2-yl)amino)pentan-2-one (5i)

Light yellow oil, 24.9 mg, 65% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.70 – 7.67 (m, 2H), 7.63 (d, $J = 8.3$ Hz, 1H), 7.39 – 7.35 (m, 1H), 7.28 – 7.19 (m, 5H), 7.11 (dd, $J = 9.1, 2.6$ Hz, 1H), 6.91 (d, $J = 2.6$ Hz, 1H), 3.62 (t, $J = 7.2$ Hz, 1H), 3.57 – 3.50 (m, 2H), 2.98 (s, 3H), 2.21 – 2.13 (m, 4H), 1.99 – 1.91 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.0, 147.2, 135.0, 134.7, 134.4, 130.5, 129.4, 129.0, 127.5, 126.9, 126.4, 126.2, 122.3, 116.2, 106.8, 54.8, 50.4, 38.6, 27.8, 27.2. HRMS (ESI) m/z for $\text{C}_{22}\text{H}_{22}\text{ClNOS}$ $[\text{M}+\text{H}]^+$: calcd 384.1183, found 384.1176.



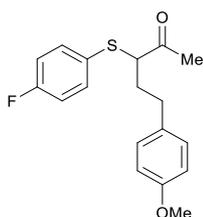
3-((4-Chlorophenyl)thio)-5-(indolin-1-yl)pentan-2-one (5j)

Light yellow oil, 26.2 mg, 76% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.33 – 7.26 (m, 4H), 7.08 – 7.04 (m, 2H), 6.67 (t, $J = 7.3$ Hz, 1H), 6.47 (d, $J = 7.8$ Hz, 1H), 3.77 (t, $J = 7.2$ Hz, 1H), 3.34 – 3.21 (m, 3H), 3.16 – 3.09 (m, 1H), 2.94 (t, $J = 8.3$ Hz, 2H), 2.26 (s, 3H), 2.20 – 2.11 (m, 1H), 1.96 – 1.87 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.2, 152.3, 134.7, 134.5, 130.6, 129.9, 129.3, 127.4, 124.5, 118.0, 107.0, 54.7, 53.5, 47.1, 28.5, 28.4, 27.5. HRMS (ESI) m/z for $\text{C}_{19}\text{H}_{20}\text{ClNOS}$ $[\text{M}+\text{H}]^+$: calcd 346.1026, found 346.1027.



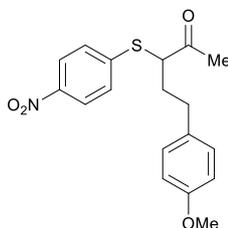
5-(4-Methoxyphenyl)-3-((4-methoxyphenyl)thio)pentan-2-one (6b)

Light yellow oil, 21.2 mg, 64% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.31 – 7.29 (m, 2H), 7.08 (d, $J = 8.6$ Hz, 2H), 6.84 – 6.81 (m, 4H), 3.79 (s, 6H), 3.40 (t, $J = 7.4$ Hz, 1H), 2.71 – 2.66 (m, 2H), 2.26 (s, 3H), 2.10 – 1.98 (m, 1H), 1.96 – 1.85 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.6, 160.3, 158.0, 136.2, 132.8, 129.4, 121.9, 114.7, 113.9, 57.0, 55.3, 55.2, 32.1, 31.4, 27.4. HRMS (ESI) m/z for $\text{C}_{19}\text{H}_{22}\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: calcd 333.1362, found 333.1370.



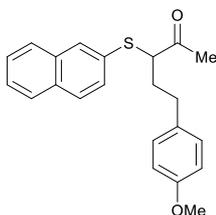
3-((4-Fluorophenyl)thio)-5-(4-methoxyphenyl)pentan-2-one (6c)

Light yellow oil, 16.8 mg, 53% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.36 – 7.31 (m, 2H), 7.09 – 7.05 (m, 2H), 7.02 – 6.96 (m, 2H), 6.85 – 6.81 (m, 2H), 3.79 (s, 3H), 3.46 (t, $J = 7.4$ Hz, 1H), 2.68 (t, $J = 7.5$ Hz, 2H), 2.25 (s, 3H), 2.10 – 2.01 (m, 1H), 1.96 – 1.86 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.5, 163.0 (d, $J = 247.6$ Hz), 158.1, 135.9 (d, $J = 8.3$ Hz), 132.5, 129.4, 126.9 (d, $J = 3.3$ Hz), 116.3 (d, $J = 21.9$ Hz), 113.9, 56.7, 55.2, 32.1, 31.5, 27.1. ^{19}F NMR (376 MHz, CDCl_3) δ (ppm) -112.3. HRMS (ESI) m/z for $\text{C}_{18}\text{H}_{19}\text{FO}_2\text{S}$ $[\text{M}+\text{Na}]^+$: calcd 341.0982, found 341.0981.



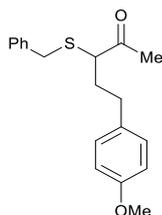
5-(4-Methoxyphenyl)-3-((4-nitrophenyl)thio)pentan-2-one (6d)

Light yellow oil, 17.2 mg, 50% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.11 (d, $J = 8.9$ Hz, 2H), 7.36 (d, $J = 8.9$ Hz, 2H), 7.08 (d, $J = 8.6$ Hz, 2H), 6.85 (d, $J = 8.6$ Hz, 2H), 3.80 (s, 3H), 3.76 (t, $J = 7.5$ Hz, 1H), 2.75 – 2.71 (m, 2H), 2.27 – 2.18 (m, 4H), 2.09 – 2.00 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.6, 158.3, 146.2, 143.7, 131.8, 129.4, 128.9, 124.1, 114.1, 55.3, 55.1, 32.1, 32.0, 26.0. HRMS (ESI) m/z for $\text{C}_{18}\text{H}_{19}\text{NO}_4\text{S}$ $[\text{M}+\text{Na}]^+$: calcd 368.0927, found 368.0923.



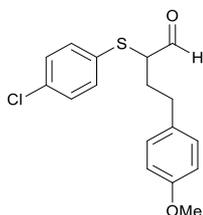
5-(4-Methoxyphenyl)-3-(naphthalen-2-ylthio)pentan-2-one (6e)

Colorless oil, 23.4 mg, 67% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.82 – 7.74 (m, 4H), 7.51 – 7.45 (m, 2H), 7.40 – 7.37 (m, 1H), 7.12 – 7.08 (m, 2H), 6.85 – 6.81 (m, 2H), 3.79 (s, 3H), 3.68 (t, $J = 7.4$ Hz, 1H), 2.76 – 2.72 (m, 2H), 2.27 (s, 3H), 2.21 – 2.11 (m, 1H), 2.07 – 1.99 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 205.1, 158.1, 133.6, 132.6, 132.6, 131.4, 130.1, 129.5, 129.4, 128.7, 127.7, 127.5, 126.6, 126.5, 113.9, 56.4, 55.3, 32.2, 31.9, 27.0. HRMS (ESI) m/z for $\text{C}_{22}\text{H}_{22}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$: calcd 373.1232, found 373.1227.



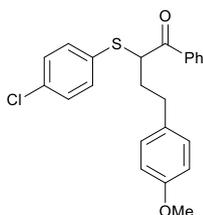
4-(Benzylthio)-6-(4-methoxyphenyl)hexan-3-one (6f)

Light yellow oil, 19.4 mg, 62% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) 7.32 – 7.25 (m, 5H), 6.98 (d, $J = 8.6$ Hz, 2H), 6.79 (d, $J = 8.6$ Hz, 2H), 3.78 (s, 3H), 3.66 – 3.55 (m, 2H), 3.12 (t, $J = 7.5$ Hz, 1H), 2.64 – 2.54 (m, 2H), 2.20 (s, 3H), 2.13 – 2.04 (m, 1H), 1.94 – 1.85 (m, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ (ppm) 204.9, 157.9, 137.4, 132.7, 129.4, 129.1, 128.5, 127.2, 113.9, 55.2, 52.7, 34.8, 32.1, 31.7, 26.2. HRMS (ESI) m/z for $\text{C}_{19}\text{H}_{22}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$: calcd 337.1233, found 337.1238.



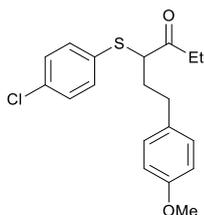
2-((4-Chlorophenyl)thio)-4-(4-methoxyphenyl)butanal (6g)

White solid, 27.8 mg, 87% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) 9.39 (d, $J = 3.6$ Hz, 1H), 7.30 – 7.24 (m, 4H), 7.11 – 7.08 (m, 2H), 6.86 – 6.82 (m, 2H), 3.79 (s, 3H), 3.45 (td, $J = 7.4, 3.7$ Hz, 1H), 2.81 – 2.70 (m, 2H), 2.15 – 2.06 (m, 1H), 1.95 – 1.86 (m, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ (ppm) 194.5, 158.2, 134.7, 134.5, 132.1, 129.7, 129.4, 129.4, 114.0, 56.0, 55.3, 31.7, 29.3. HRMS (ESI) m/z for $\text{C}_{17}\text{H}_{17}\text{ClO}_2\text{S}$ $[\text{M}+\text{H}]^+$: calcd 321.0711, found 321.0716.



2-((4-Chlorophenyl)thio)-4-(4-methoxyphenyl)butanal (6h)

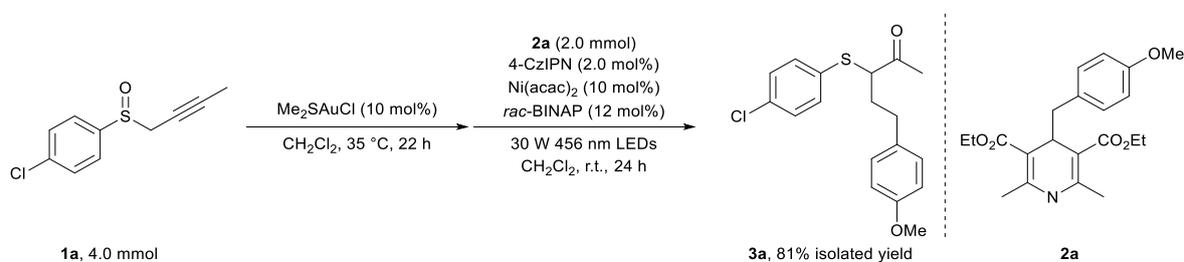
White solid, 33.6 mg, 85% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) 7.85 – 7.82 (m, 2H), 7.59 – 7.54 (m, 1H), 7.46 – 7.42 (m, 2H), 7.24 – 7.19 (m, 4H), 7.07 – 7.04 (m, 2H), 6.83 – 6.80 (m, 2H), 4.36 (t, $J = 7.2$ Hz, 1H), 3.79 (s, 3H), 2.79 – 2.64 (m, 2H), 2.33 – 2.24 (m, 1H), 2.11 – 2.02 (m, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ (ppm) 195.3, 158.0, 136.1, 136.0, 135.2, 133.2, 132.8, 129.7, 129.5, 129.1, 128.6, 128.5, 113.9, 55.3, 49.8, 32.3, 32.2. HRMS (ESI) m/z for $\text{C}_{23}\text{H}_{21}\text{ClO}_2\text{S}$ $[\text{M}+\text{Na}]^+$: calcd 419.0843, found 419.0833.



4-((4-Chlorophenyl)thio)-6-(4-methoxyphenyl)hexan-3-one (**6i**)

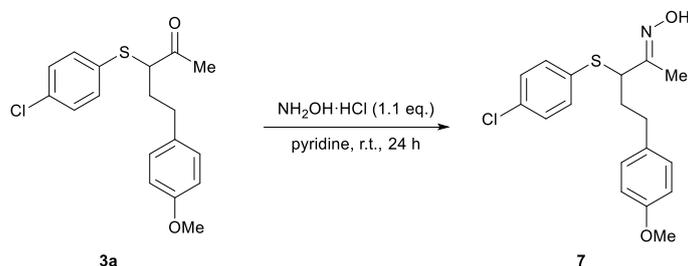
Light yellow oil, 24.0 mg, 69% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.27 – 7.25 (m, 4H), 7.08 – 7.04 (m, 2H), 6.84 – 6.81 (m, 2H), 3.79 (s, 3H), 3.53 (t, $J = 7.4$ Hz, 1H), 2.71 – 2.63 (m, 3H), 2.54 – 2.44 (m, 1H), 2.15 – 2.05 (m, 1H), 1.98 – 1.89 (m, 1H), 1.04 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 207.2, 158.0, 134.4, 134.3, 132.5, 130.8, 129.4, 129.2, 113.9, 55.4, 55.2, 33.0, 32.1, 31.7, 8.0. HRMS (ESI) m/z for $\text{C}_{19}\text{H}_{21}\text{ClO}_2\text{S}$ [$\text{M}+\text{Na}$] $^+$: calcd 371.0842, found 371.0849.

Scale-up synthesis

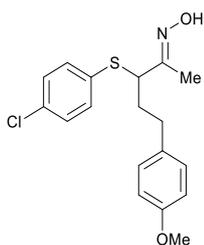


The procedure was conducted in an argon-filled glove box. To a 50 mL vial equipped with a magnetic stir bar were added **1a** (0.85 g, 4.0 mmol), Me_2SAuCl (0.12 g, 0.40 mmol, 10 mol%), and CH_2Cl_2 (20 mL). The mixture was stirred at 35 °C for 22 h. Then **2a** (0.75 g, 2.0 mmol), 4-CzIPN (32 mg, 0.040 mmol, 2.0 mol%), $\text{Ni}(\text{acac})_2$ (52 mg, 0.20 mmol, 10 mol%), *rac*-BINAP (0.15 g, 0.24 mmol, 12 mol%) were added under Ar. The mixture was irradiated with 30 W 456 nm LEDs at room temperature for 24 h. The residue was purified by silica gel chromatography with PE/EA (v/v = 20:1-10:1) as eluent to afford product **3a** (0.54 g, 81% yield).

Transformations of product **3a**²⁻⁵

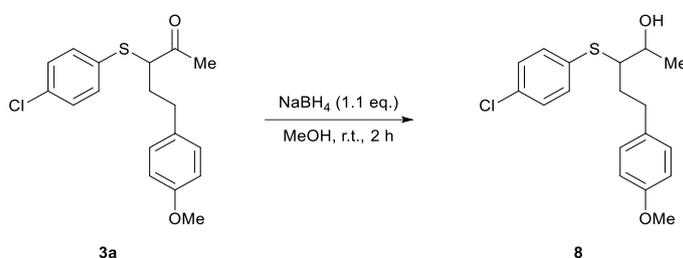


3a (33.5 mg, 0.100 mmol) was dissolved in pyridine (1.0 mL), and hydroxylamine hydrochloride (20.8 mg, 0.300 mmol) was added to the solution. The reaction was stirred at room temperature for 24 h. The pH of the solution was adjusted to 7 with 3 M HCl in an ice-water bath, and the solution was extracted with ethyl acetate (3 x 5 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The crude material was purified by flash chromatography (PE/EA, v/v = 3:1) to provide the compound **7** as light brown solid (24.5 mg, 70% yield).

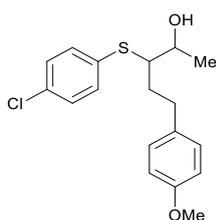


(E)-3-((4-Chlorophenyl)thio)-5-(4-methoxyphenyl)pentan-2-one oxime (7)

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.99 (s, 1H), 7.25 – 7.19 (m, 4H), 7.08 (d, $J = 8.4$ Hz, 2H), 6.82 (d, $J = 8.5$ Hz, 2H), 3.78 (s, 3H), 3.71 (t, $J = 7.6$ Hz, 1H), 2.70 – 2.62 (m, 2H), 1.98 (q, $J = 7.7$ Hz, 2H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 158.0, 157.2, 133.7, 133.6, 132.6, 132.2, 129.4, 129.0, 113.9, 55.2, 52.4, 33.4, 32.4, 10.1. HRMS (ESI) m/z for $\text{C}_{18}\text{H}_{20}\text{ClNO}_2\text{S}$ $[\text{M}+\text{H}]^+$: calcd 350.0976, found 350.0973.

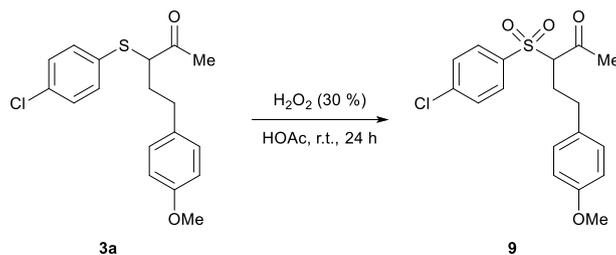


3a (33.5 mg, 0.100 mmol) was dissolved in MeOH (1.0 mL), and NaBH_4 (4.2 mg, 0.11 mmol) was added to the solution. The reaction was stirred at room temperature for 2 h and quenched with dilute HCl carefully. EtOAc was added to this mixture, and the organic phase was separated and dried over anhydrous sodium sulfate. After removal of the solvent, the crude material was purified by flash chromatography (PE/EA, v/v = 10:1) to provide the compound **8** as light yellow oil (27.8 mg, 83% yield, 5:1 dr).

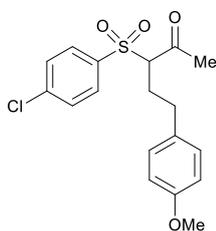


3-((4-Chlorophenyl)thio)-5-(4-methoxyphenyl)pentan-2-ol (8)

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.34 (d, $J = 8.6$ Hz, 2H), 7.24 (d, $J = 8.5$ Hz, 2H), 7.05 (d, $J = 8.6$ Hz, 2H), 6.81 (d, $J = 8.6$ Hz, 2H), 3.78 – 3.73 (m, 4H), 2.95 – 2.86 (m, 2H), 2.76 – 2.64 (m, 1H), 2.48 (br, 1H), 2.04 – 1.96 (m, 1H), 1.76 – 1.67 (m, 1H), 1.23 – 1.16 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 157.9, 133.4, 133.2, 133.2, 133.1, 133.1, 133.0, 133.0, 129.3, 129.1, 129.1, 113.8, 69.1, 68.4, 57.8, 57.6, 55.2, 32.6, 32.4, 32.3, 31.7, 20.0, 19.2. HRMS (ESI) m/z for $\text{C}_{18}\text{H}_{21}\text{ClO}_2\text{S}$ $[\text{M}+\text{H}]^+$: calcd 337.1024, found 337.1029.

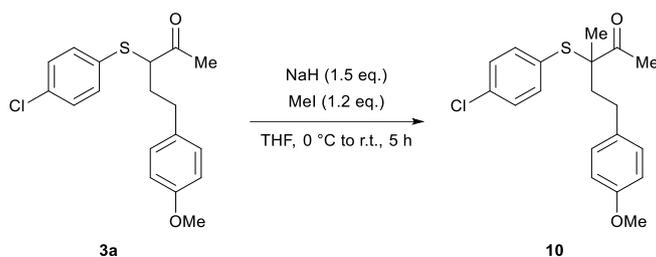


3a (33.5 mg, 0.100 mmol) was dissolved in HOAc (1.0 mL), and H₂O₂ (3 drops, 30% aq.) was added to the solution. The mixture was stirred at 30 °C for 24 h, and H₂O was added. The aqueous layer was washed with CH₂Cl₂ (3 x 3 mL), and the combined organic layers were dried over Na₂SO₄, filtered, and concentrated. The mixture was purified by flash chromatography (PE/EA, v/v = 2:1) to give the compound **9** as light yellow oil (23.4 mg, 74% yield).

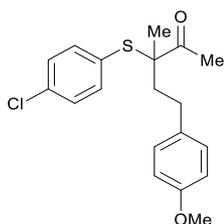


3-((4-Chlorophenyl)sulfonyl)-5-(4-methoxyphenyl)pentan-2-one (**9**)

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.68 – 7.65 (m, 2H), 7.53 – 7.49 (m, 2H), 6.98 – 6.95 (m, 2H), 6.83 – 6.79 (m, 2H), 4.08 – 4.04 (m, 1H), 3.78 (s, 3H), 2.65 – 2.55 (m, 1H), 2.46 – 2.40 (m, 1H), 2.36 (s, 3H), 2.18 – 2.11 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 200.1, 158.4, 141.2, 134.5, 131.0, 130.7, 129.4, 129.4, 114.1, 74.5, 55.2, 32.1, 31.7, 28.6. HRMS (ESI) *m/z* for C₁₈H₁₉ClO₄S [M+Na]⁺: calcd 389.0584, found 389.0579.



An oven dried 10 mL Schlenk tube was charged with 60% dispersion of NaH in mineral oil (6.0 mg, 0.15 mmol), THF (1.0 mL), **3a** (33.5 mg, 0.100 mmol), and methyl iodide (7.5 μL, 0.12 mmol) at 0 °C. The mixture was stirred at r.t. for 5 h, the reaction was diluted with saturated aqueous NH₄Cl. The layers were separated, and the aqueous phase was extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated. The crude mixture was purified by flash chromatography (PE/EA, v/v = 15:1) to provide the compound **10** as light yellow oil (17.8 mg, 51% yield).

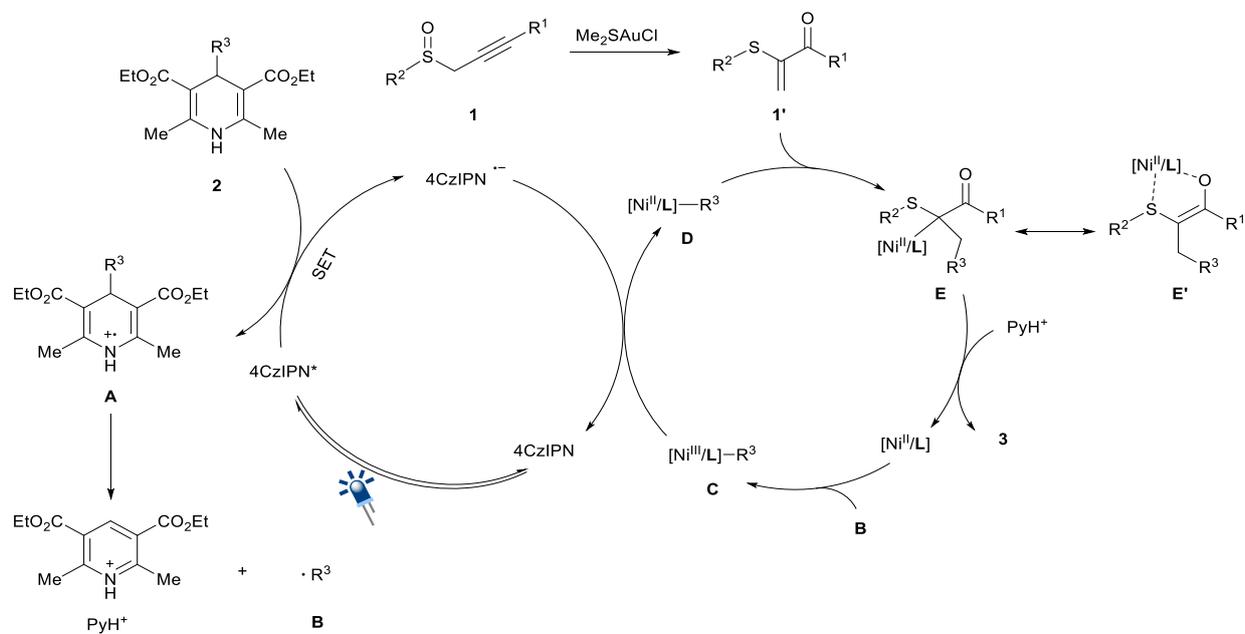


(4-Chlorophenyl)(5-(4-methoxyphenyl)-2-methylpent-1-en-3-yl)sulfane (10)

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.27 (s, 4H), 7.08 – 7.05 (m, 2H), 6.85 – 6.81 (m, 2H), 3.79 (s, 3H), 2.76 – 2.68 (m, 1H), 2.47 – 2.39 (m, 4H), 2.12 – 2.04 (m, 1H), 1.98 – 1.90 (m, 1H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 205.3, 158.0, 137.3, 135.9, 133.1, 129.2, 129.1, 129.1, 113.9, 60.4, 55.3, 38.9, 30.2, 24.8, 20.8. HRMS (ESI) m/z for $\text{C}_{19}\text{H}_{21}\text{ClO}_2\text{S}$ $[\text{M}+\text{Na}]^+$: calcd 371.0842, found 371.0841.

Possible pathway for the generation of 3

A reaction pathway proceeding via a Ni(III) intermediate, formed by addition of the alkyl radical to a Ni(II) species, cannot be ruled out.



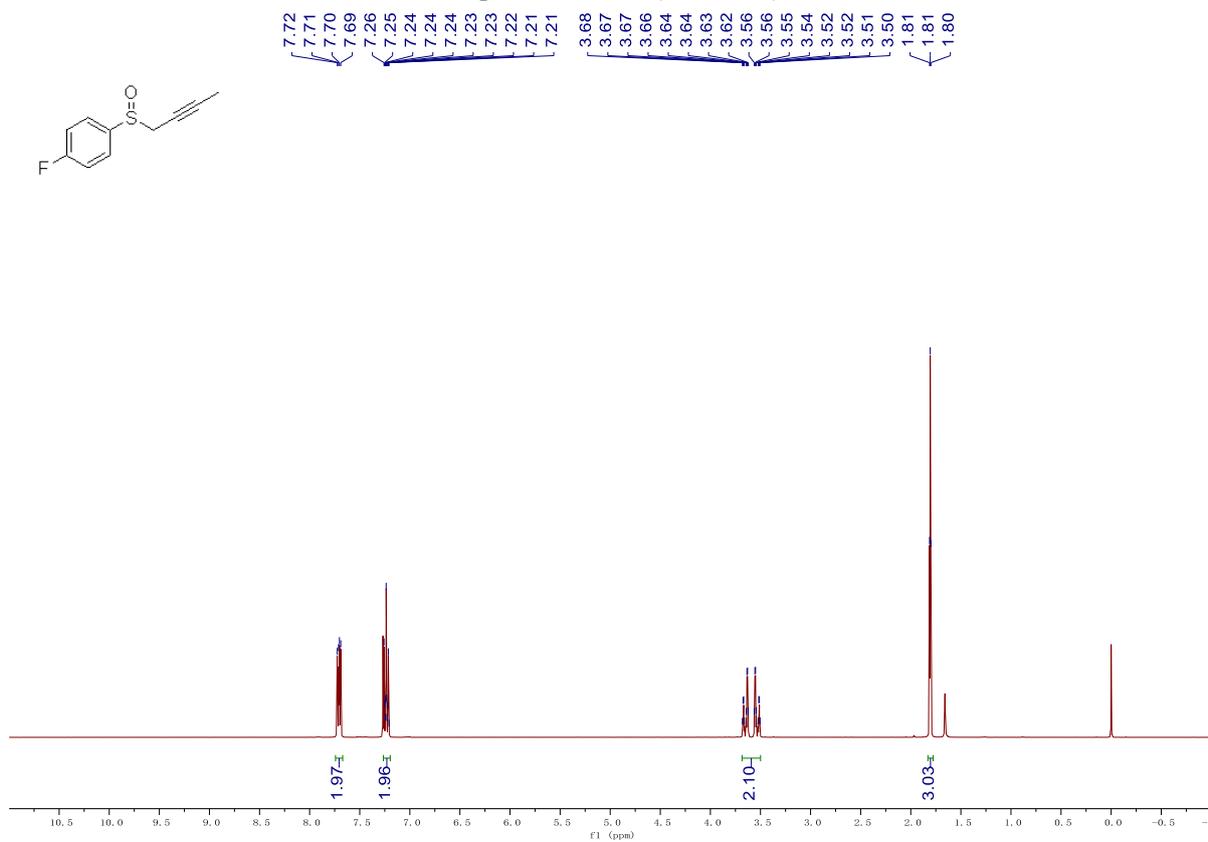
Scheme S1 Proposed mechanism.

3. References

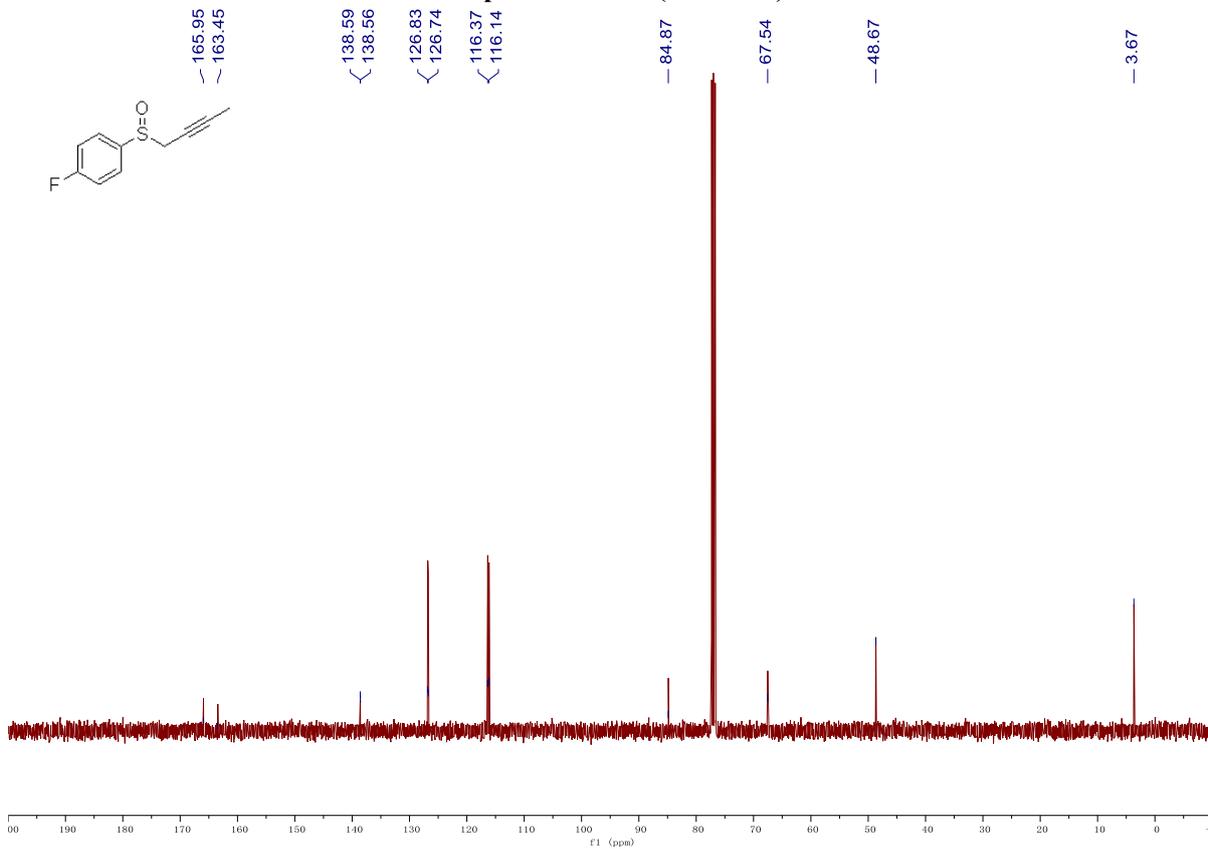
1. M. Šiaučiulis, S. Sapmaz, A. P. Pulis and D. J. Procter, Dual Vicinal Functionalisation of Heterocycles *via* an Interrupted Pummerer Coupling/[3,3]-Sigmatropic Rearrangement Cascade. *Chem. Sci.*, 2018, **9**, 754–759.
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5. G.-B. Zhang, F.-X. Wang, J.-Y. Du, H. Qu, X.-Y. Ma, M.-X. Wei, C.-T. Wang, Q. Li and C.-A. Fan, Toward the Total Synthesis of Palhinine A: Expedient Assembly of Multifunctionalized Isotwistane Ring System with Contiguous Quaternary Stereocenters. *Org. Lett.*, 2012, **14**, 3696–3699.

4. Copies of NMR Spectra

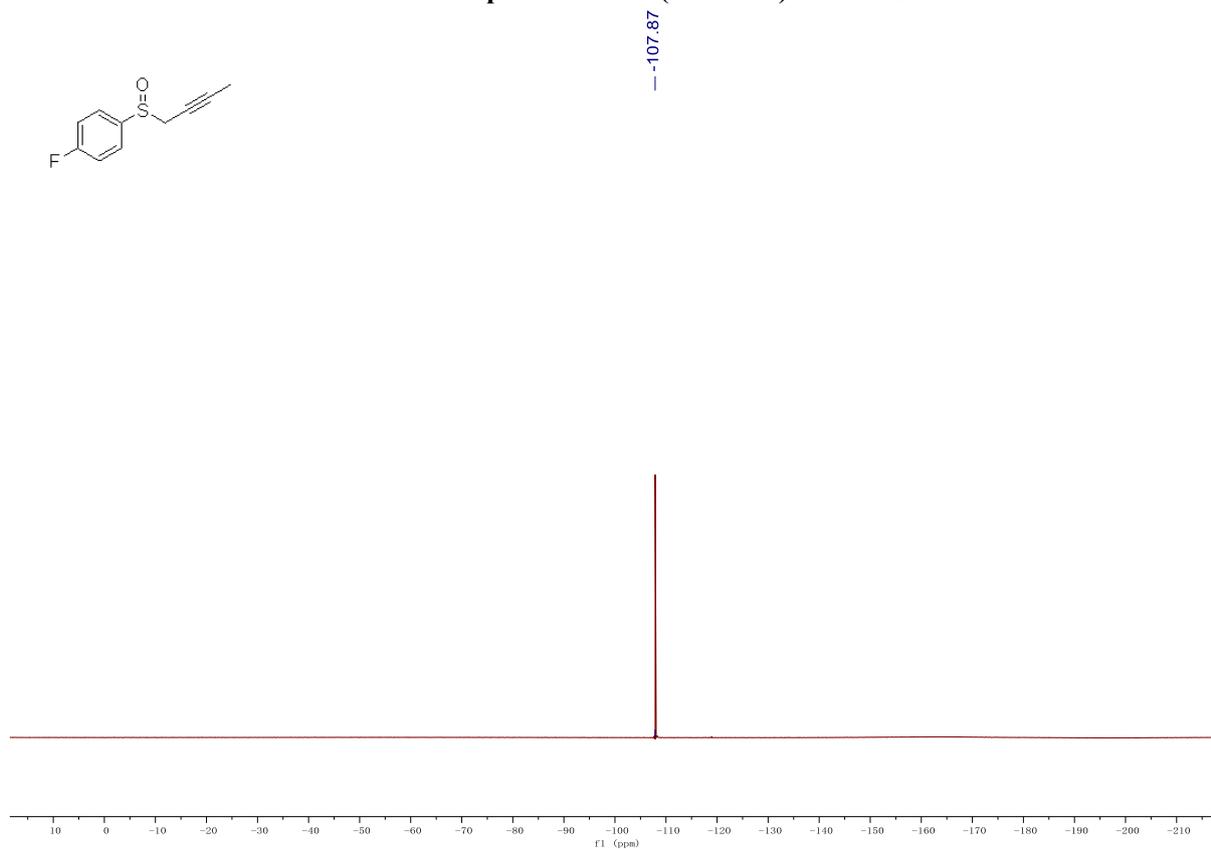
¹H NMR Spectrum of 1c (400 MHz) in CDCl₃



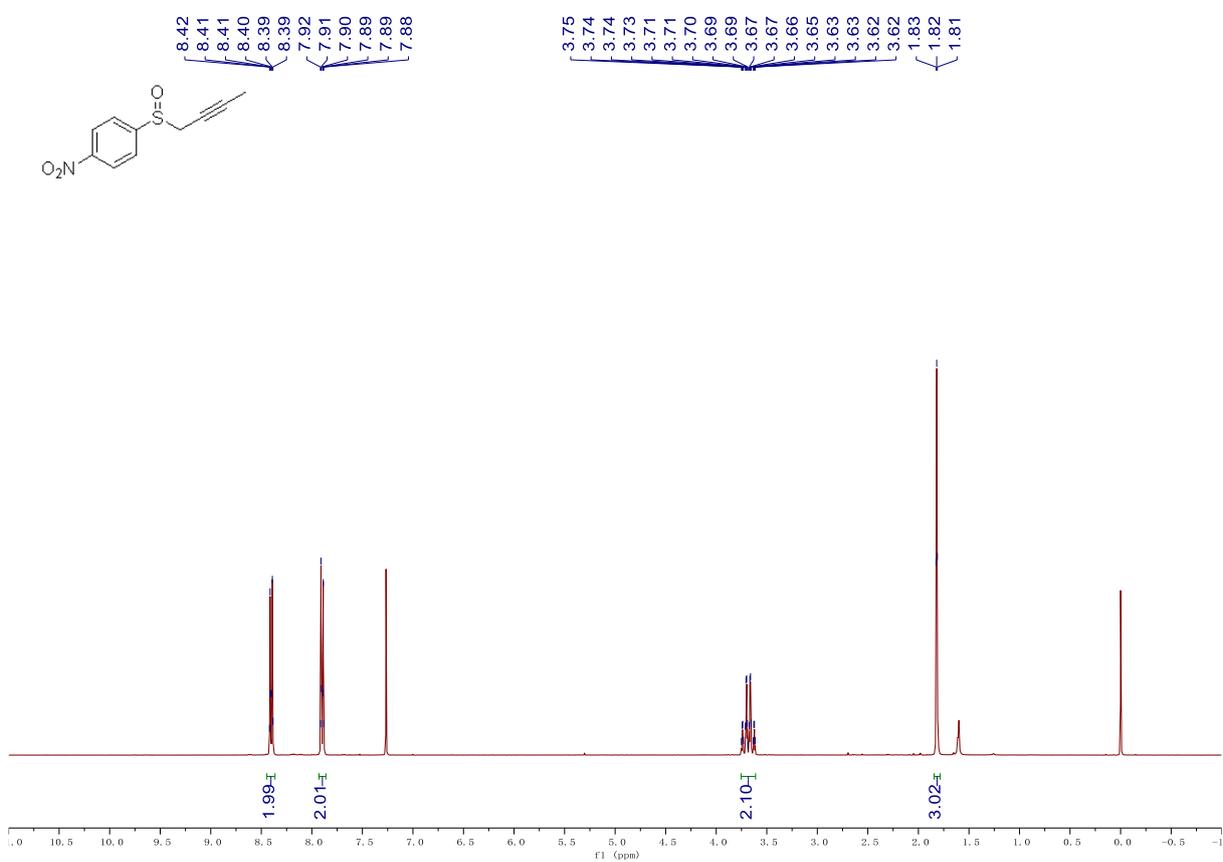
¹³C NMR Spectrum of 1c (100 MHz) in CDCl₃

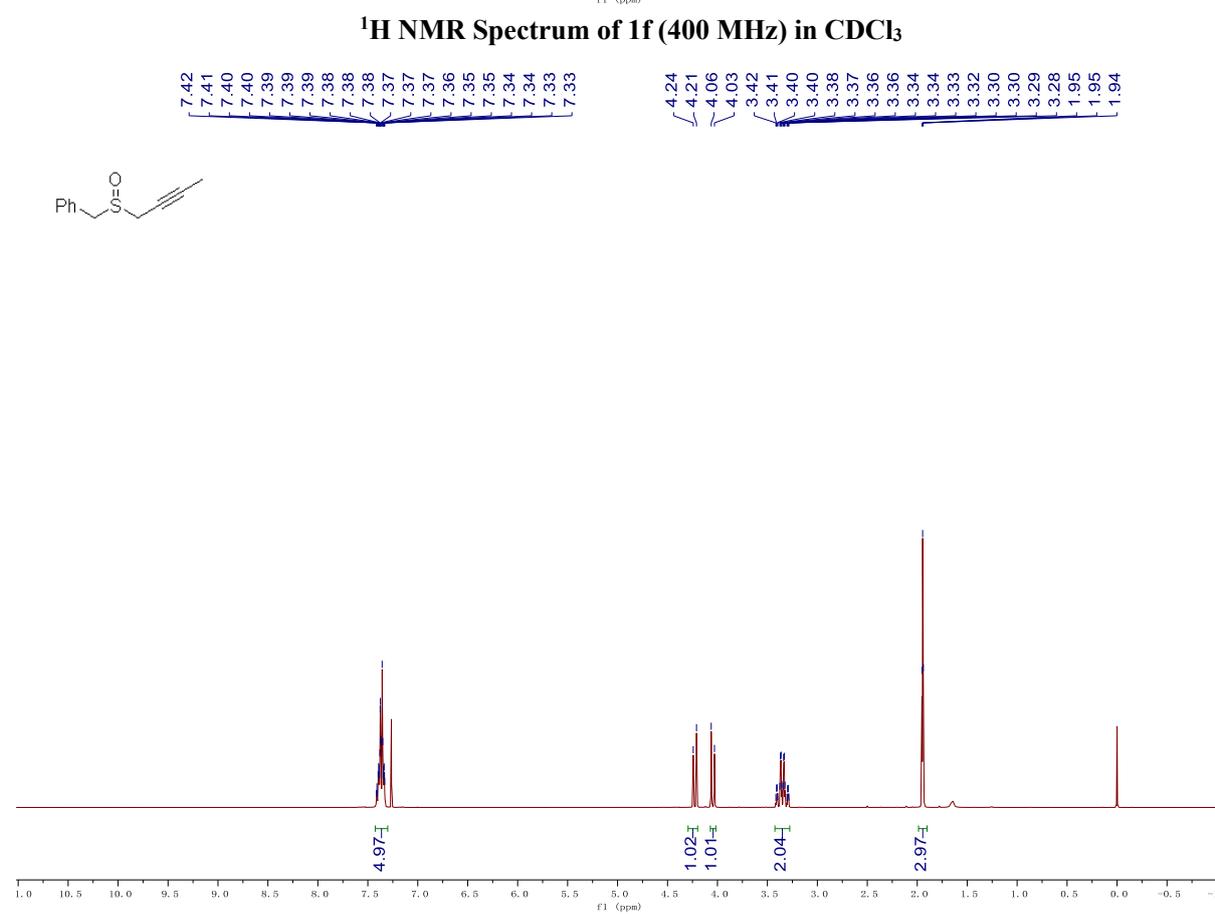
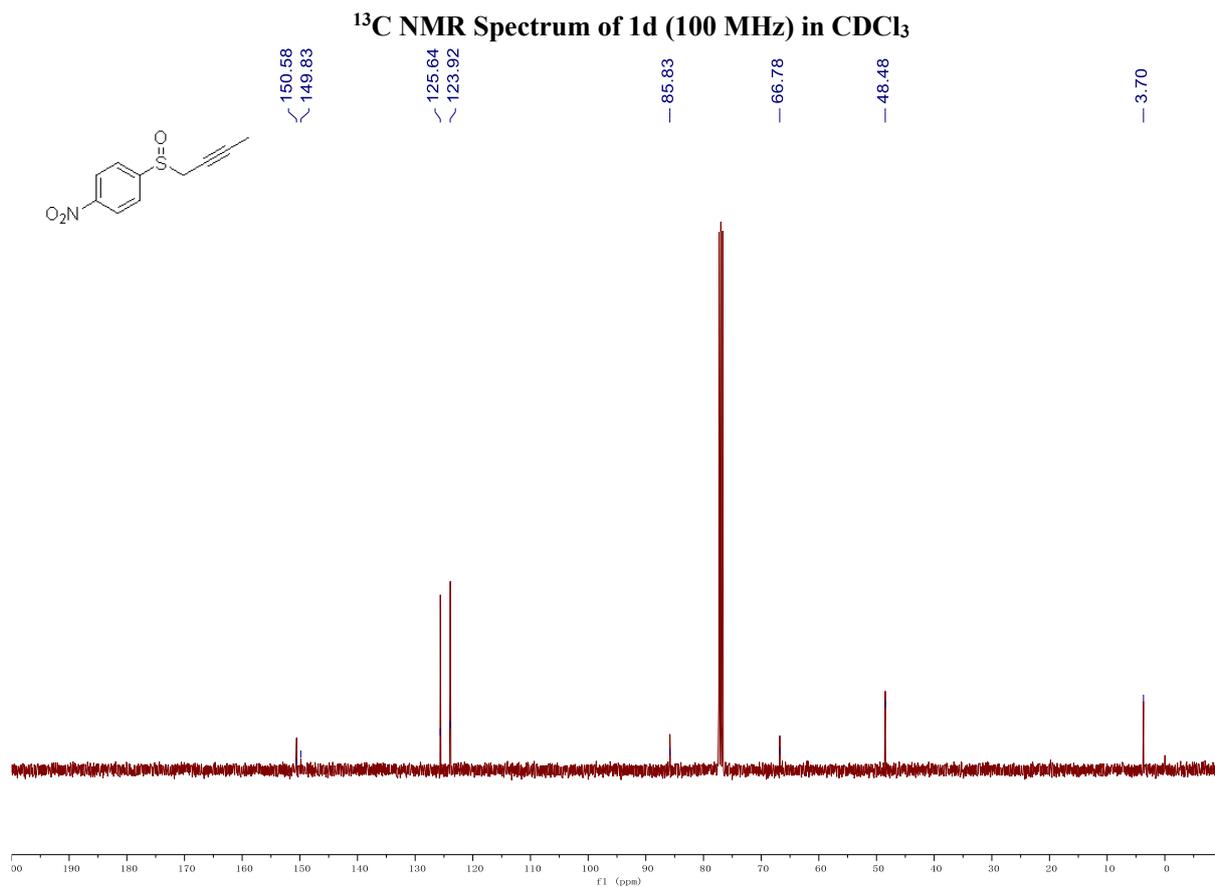


^{19}F NMR Spectrum of 1c (376 MHz) in CDCl_3

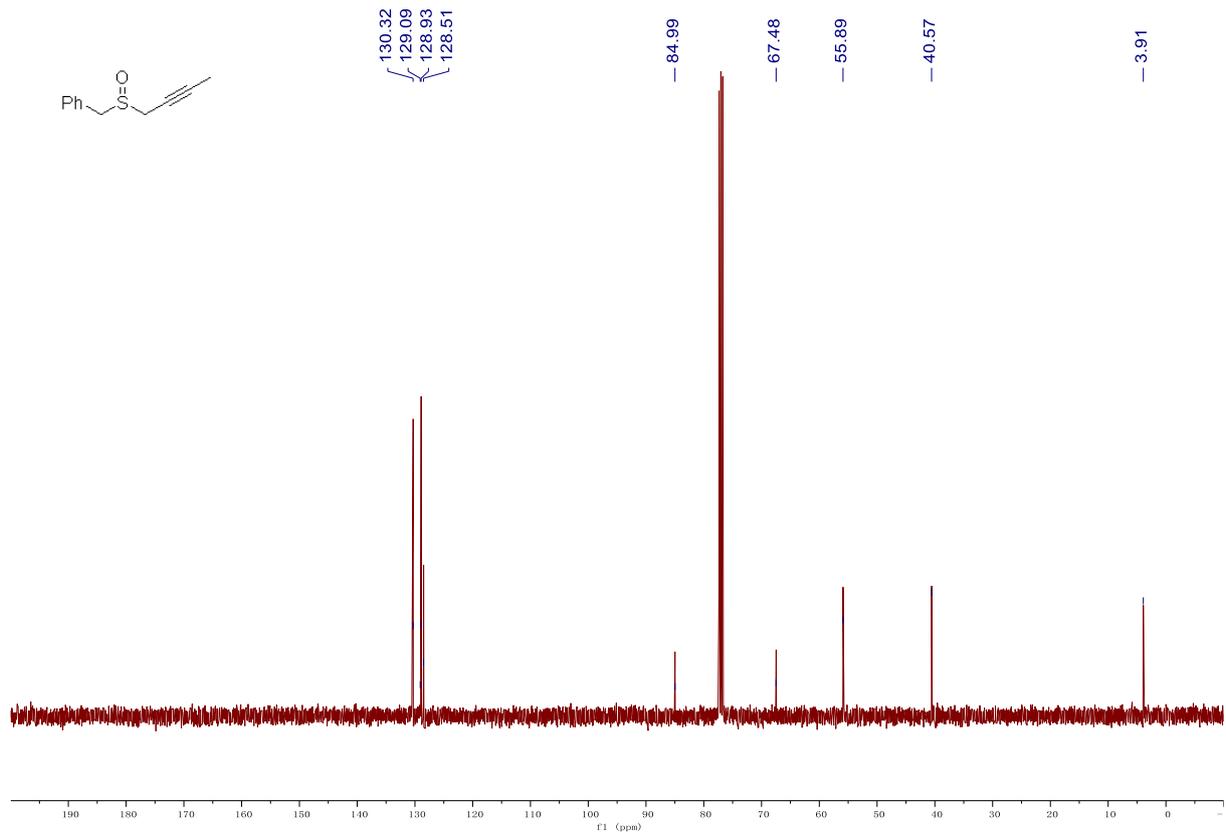


^1H NMR Spectrum of 1d (400 MHz) in CDCl_3

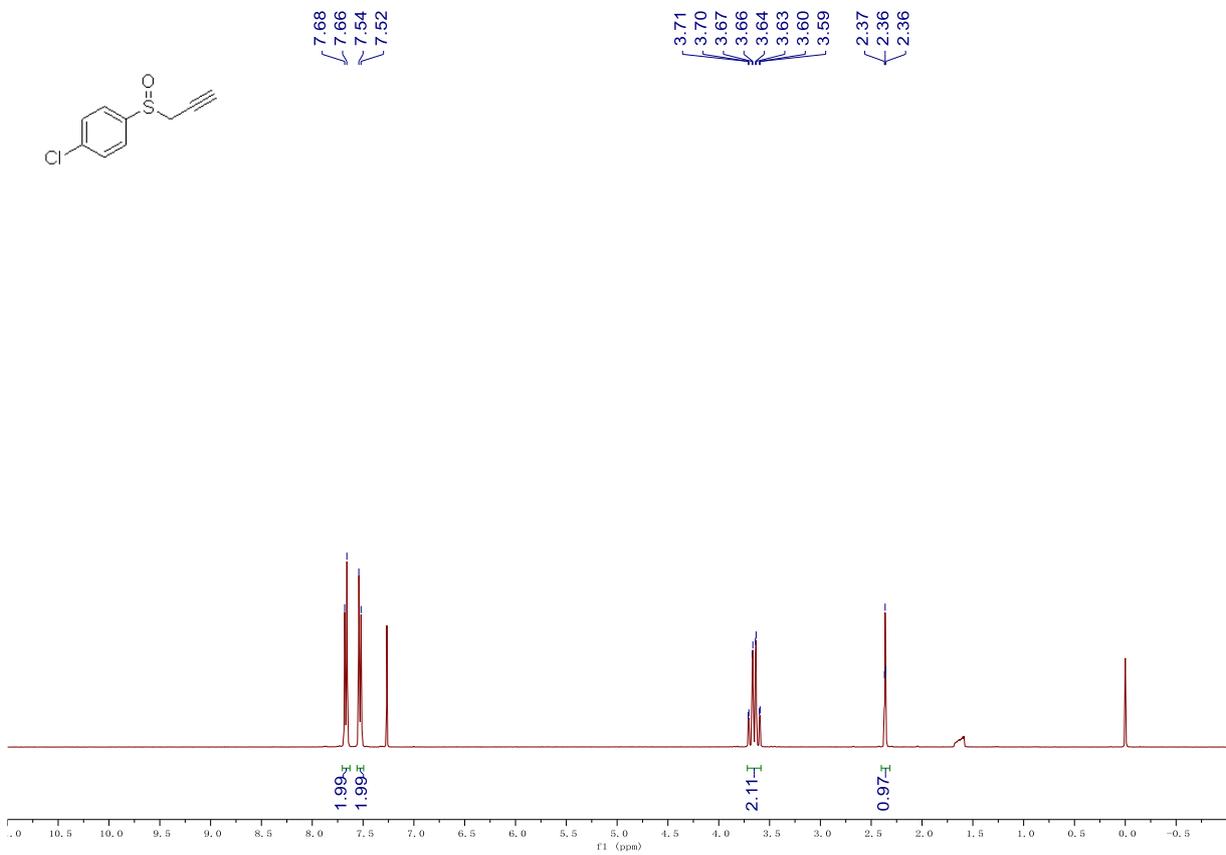




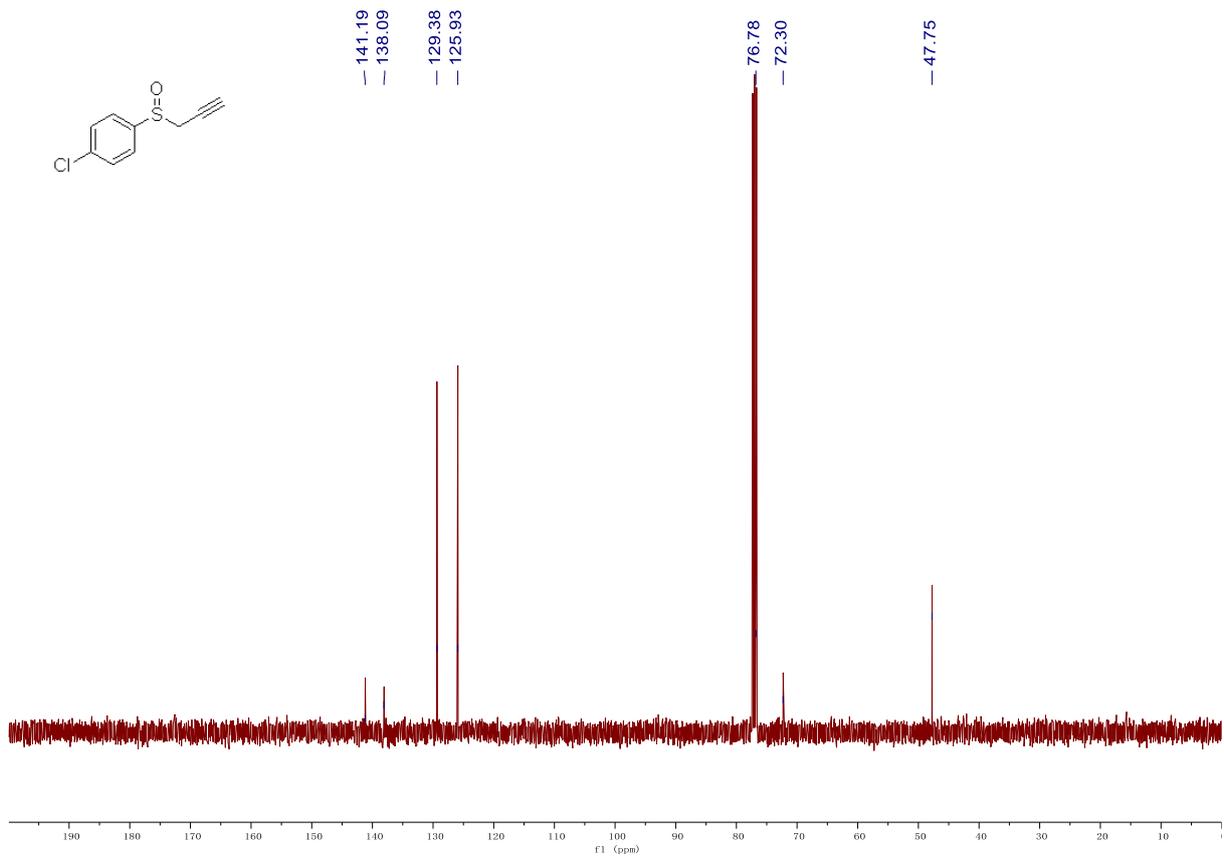
¹³C NMR Spectrum of 1f (100 MHz) in CDCl₃



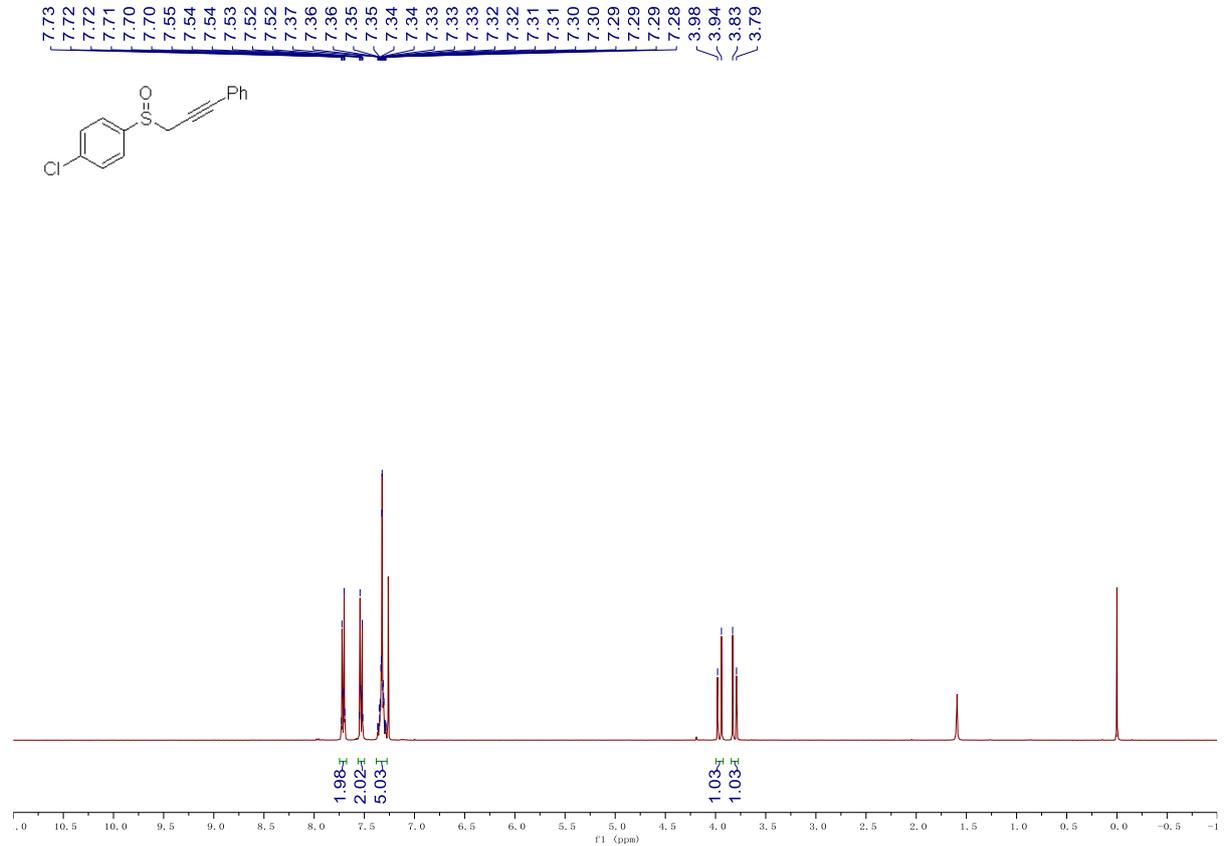
¹H NMR Spectrum of 1g (400 MHz) in CDCl₃



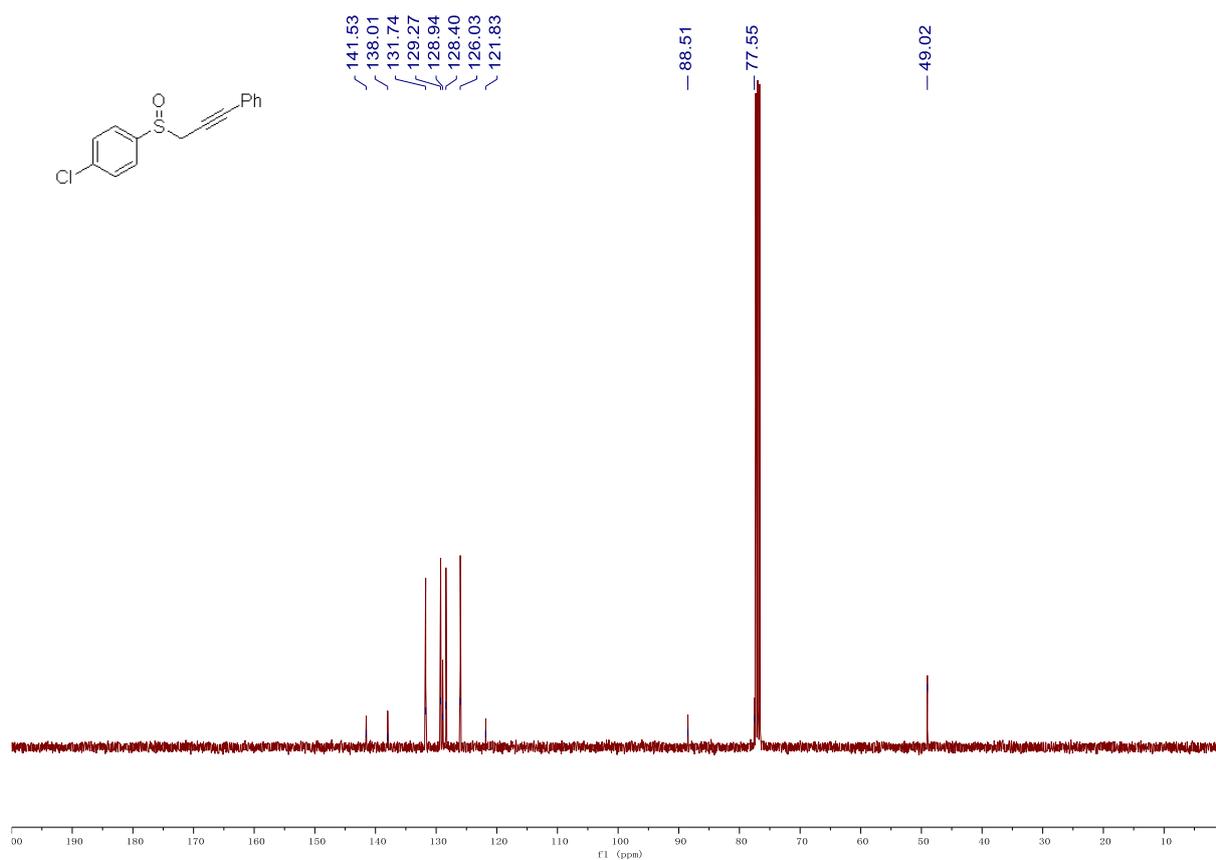
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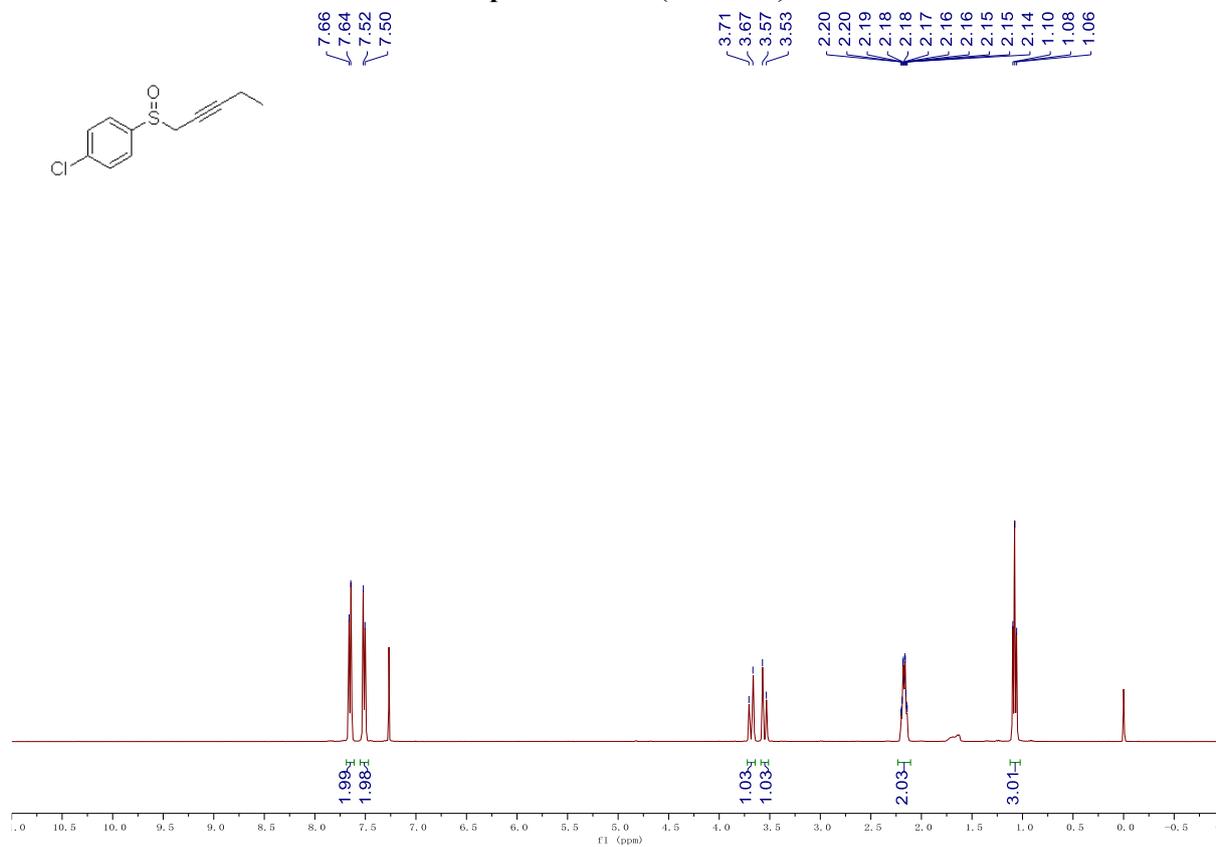
¹H NMR Spectrum of 1h (400 MHz) in CDCl₃



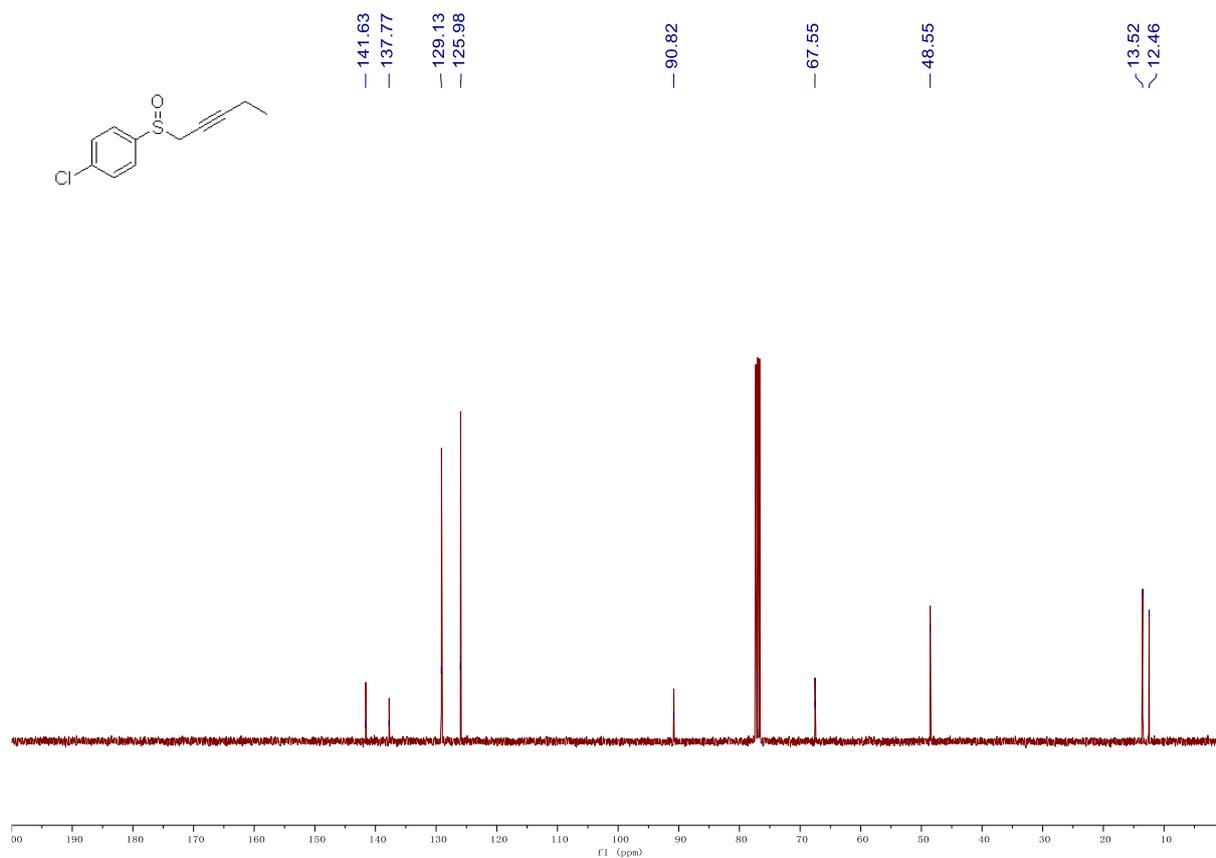
¹³C NMR Spectrum of 1h (100 MHz) in CDCl₃



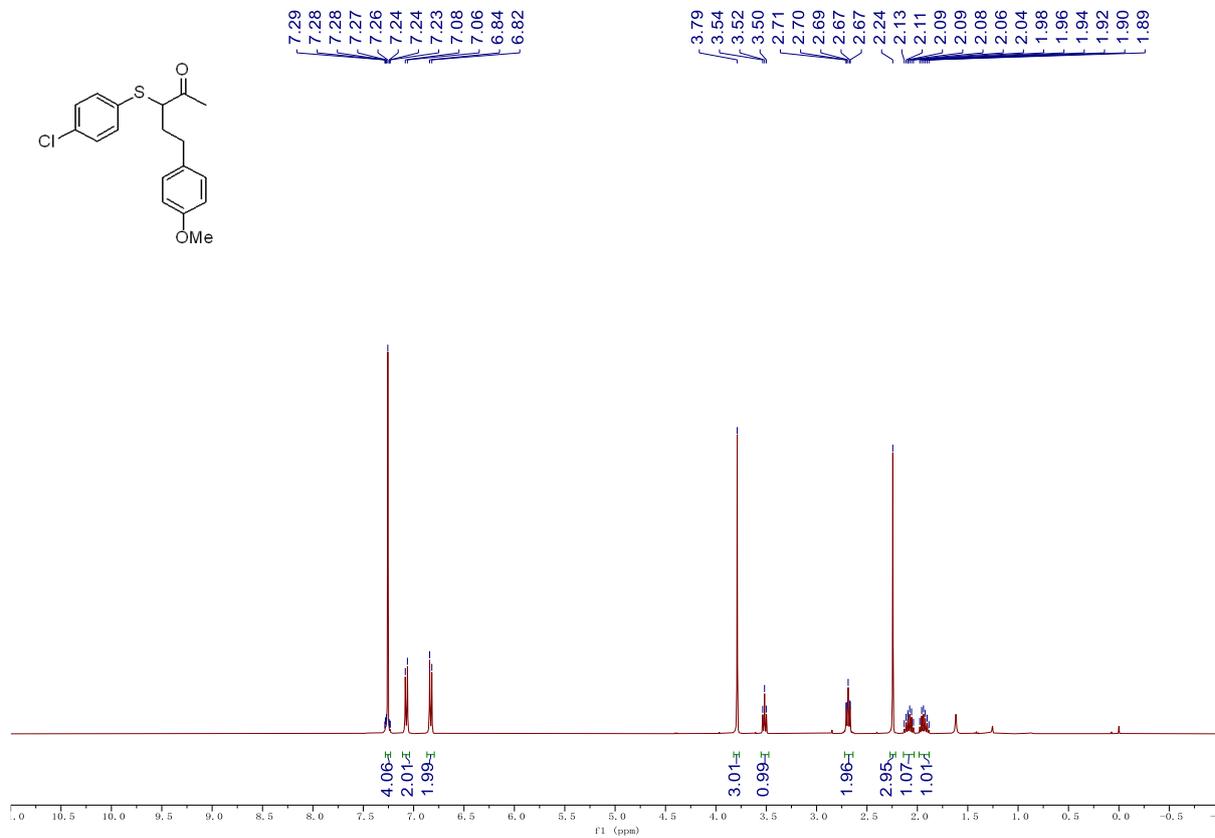
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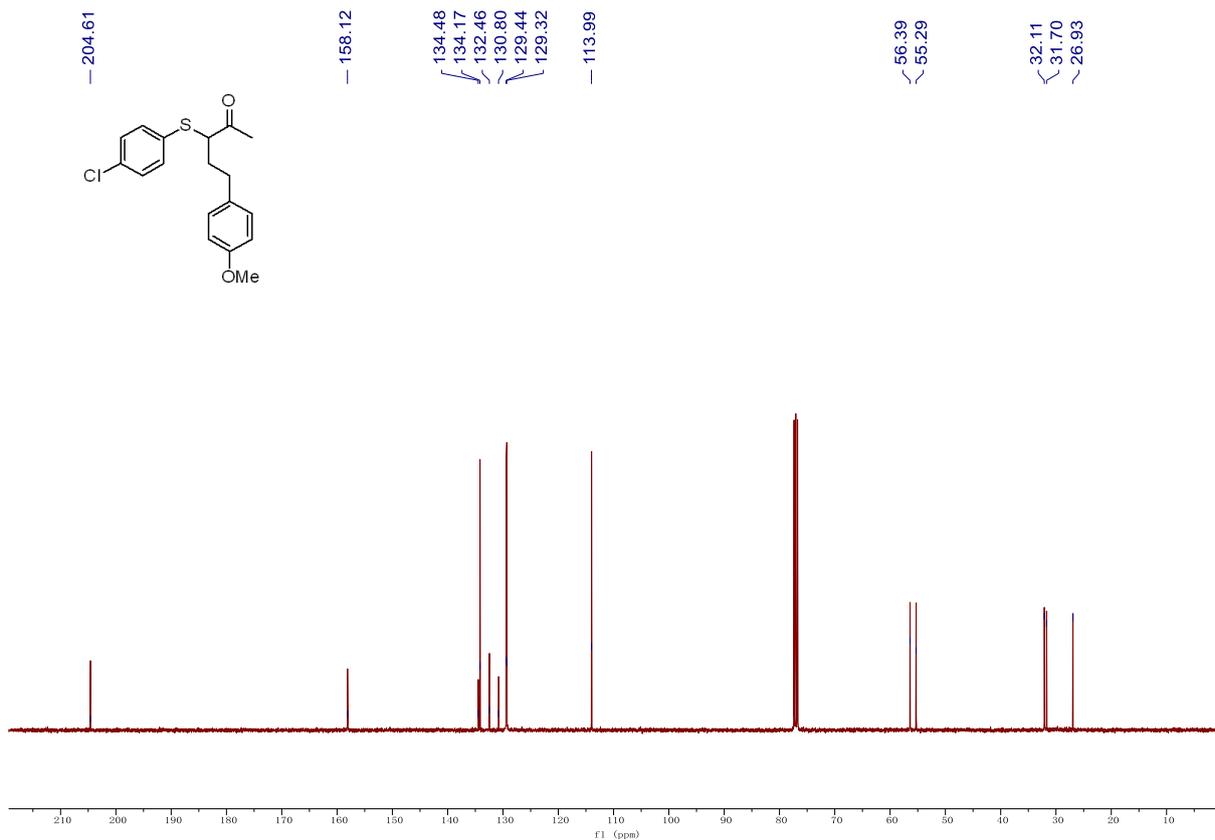
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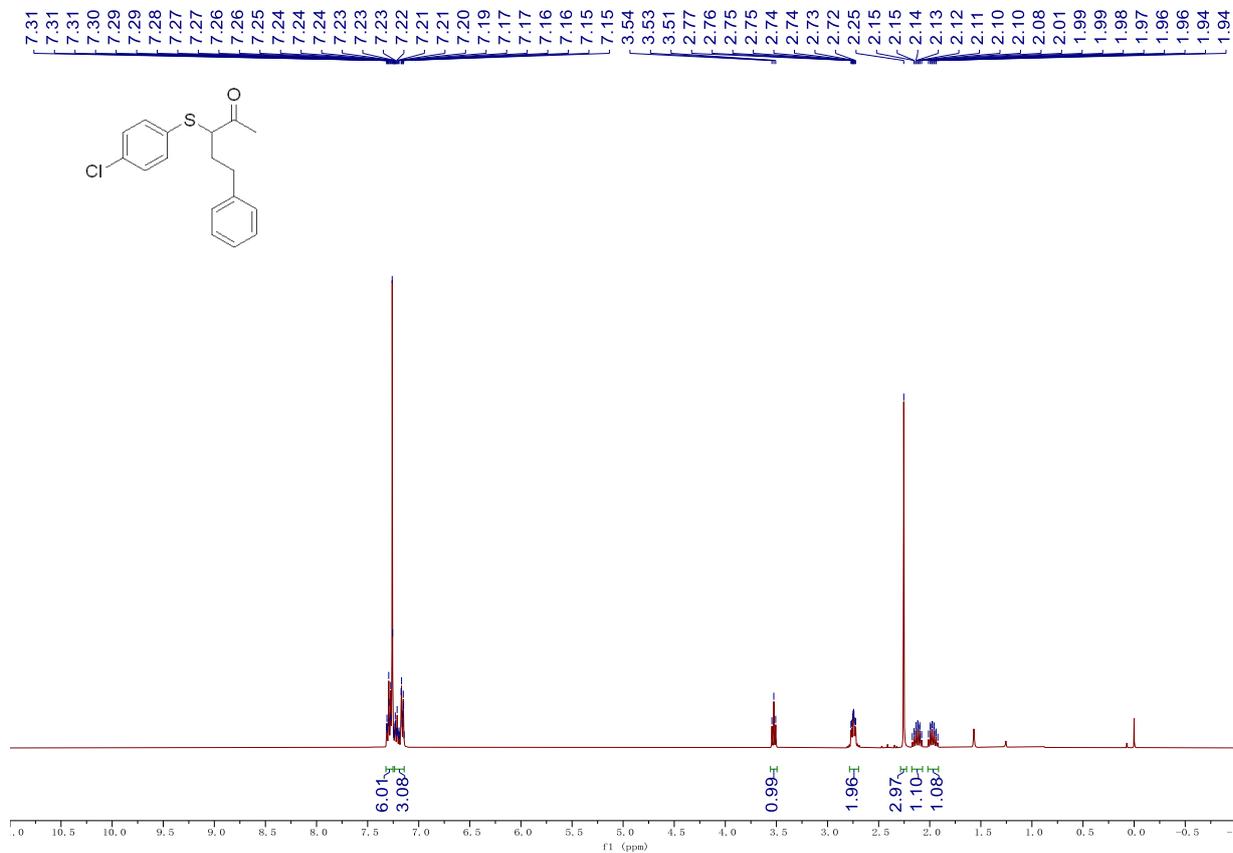
¹H NMR Spectrum of 3a (400 MHz) in CDCl₃



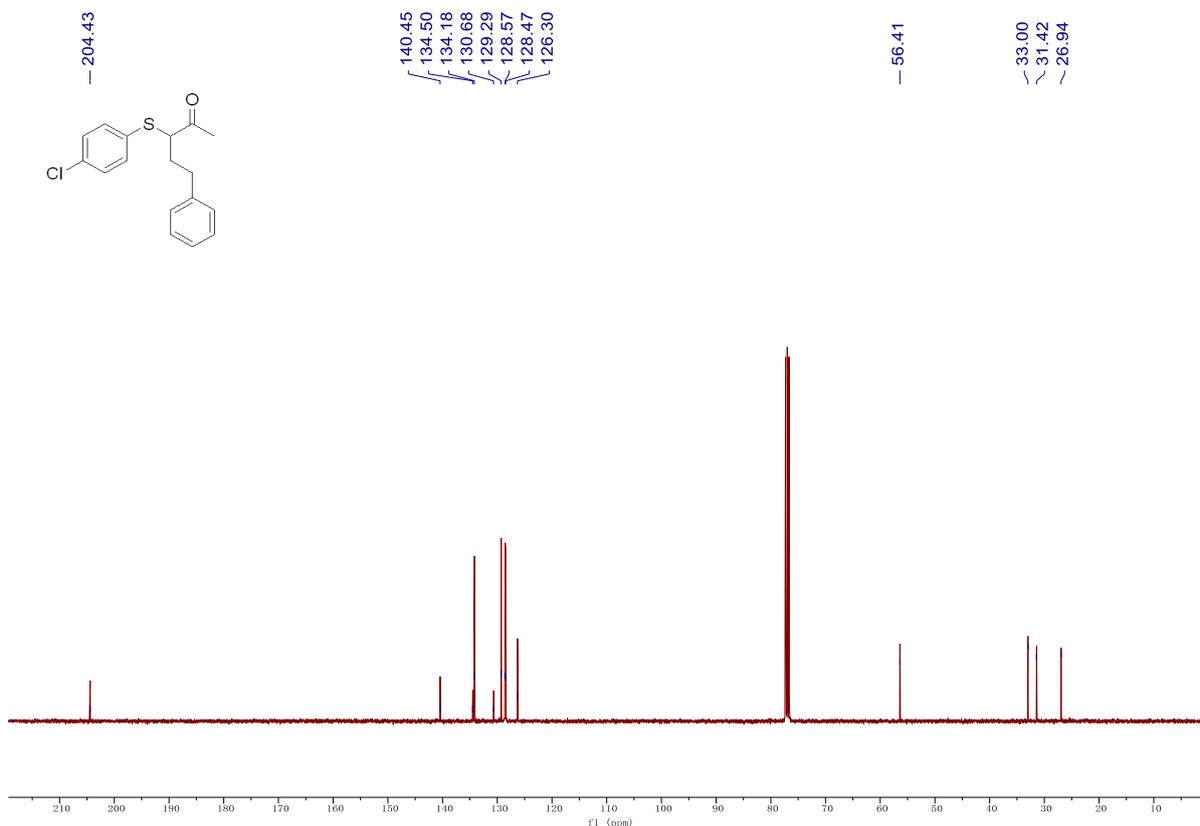
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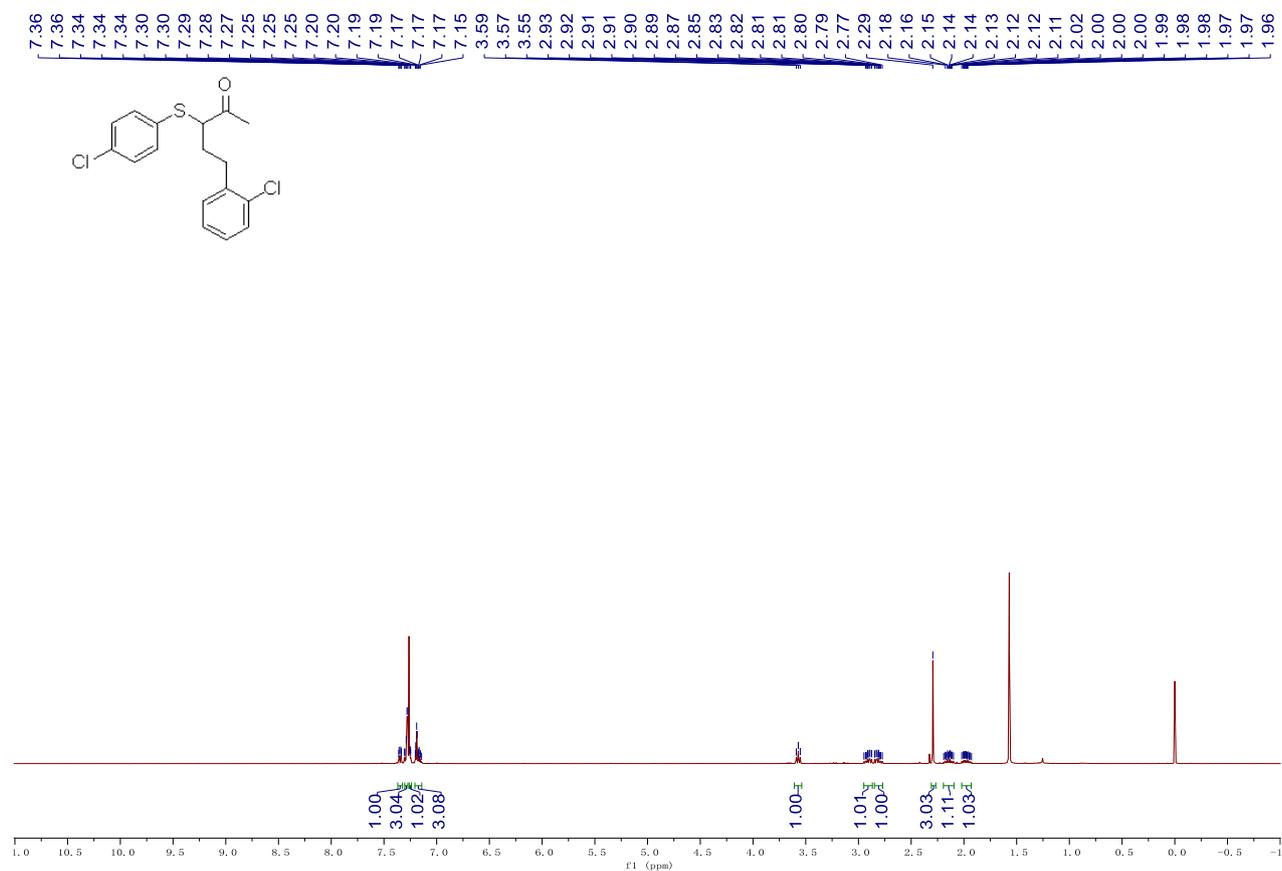
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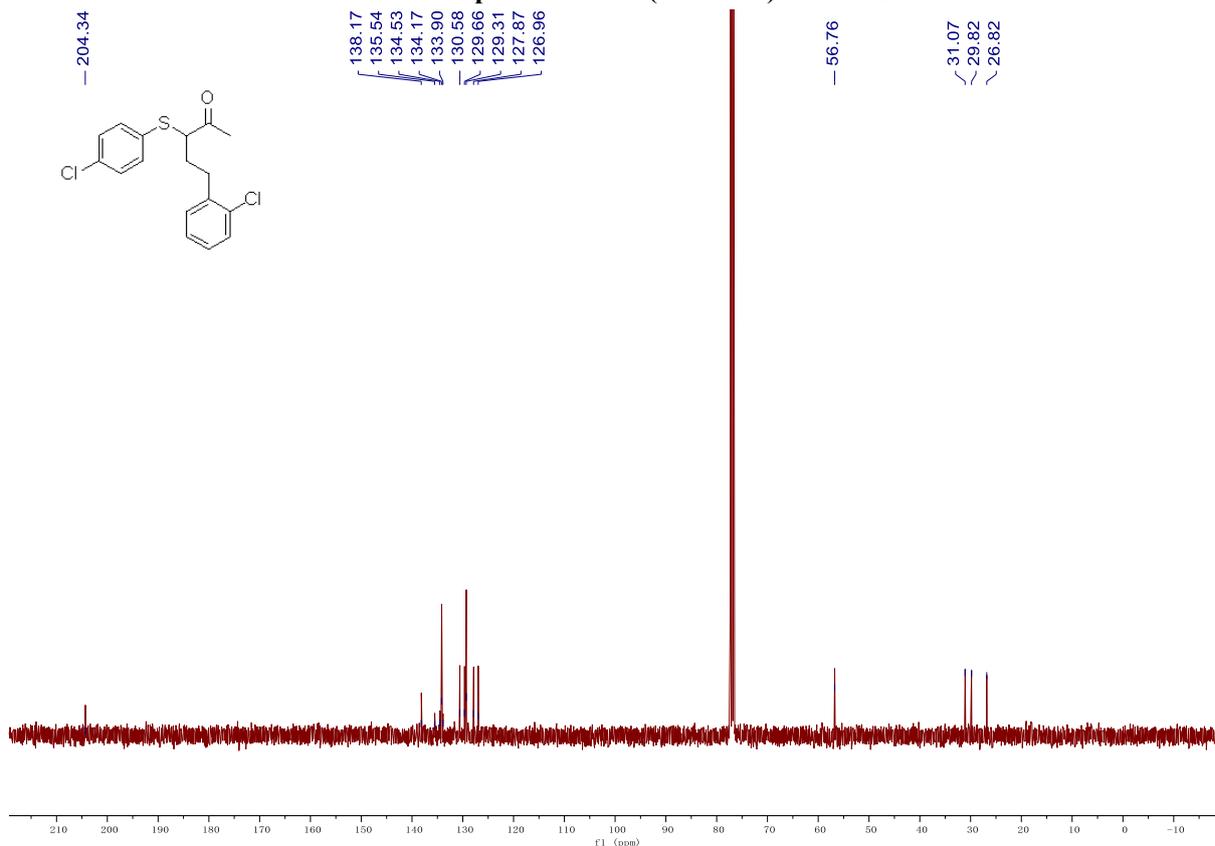
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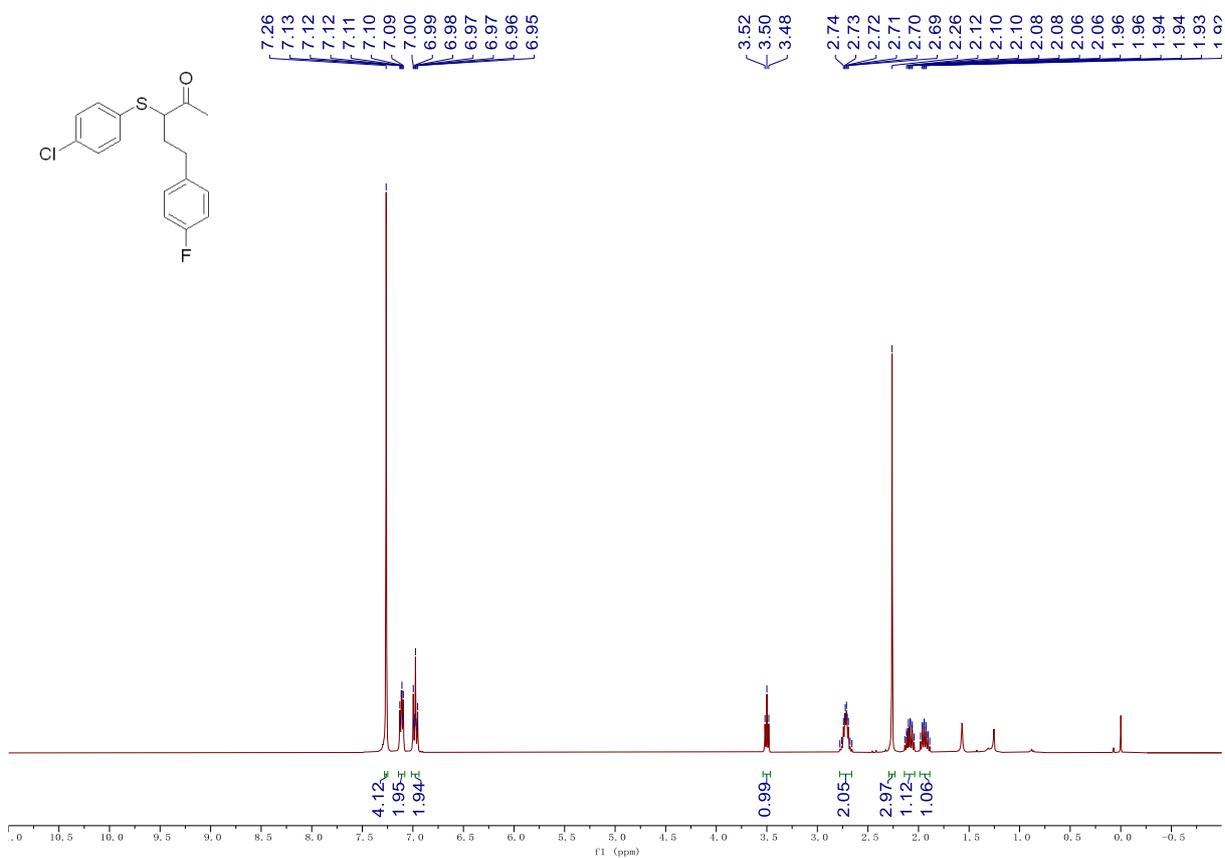
¹H NMR Spectrum of 3c (400 MHz) in CDCl₃



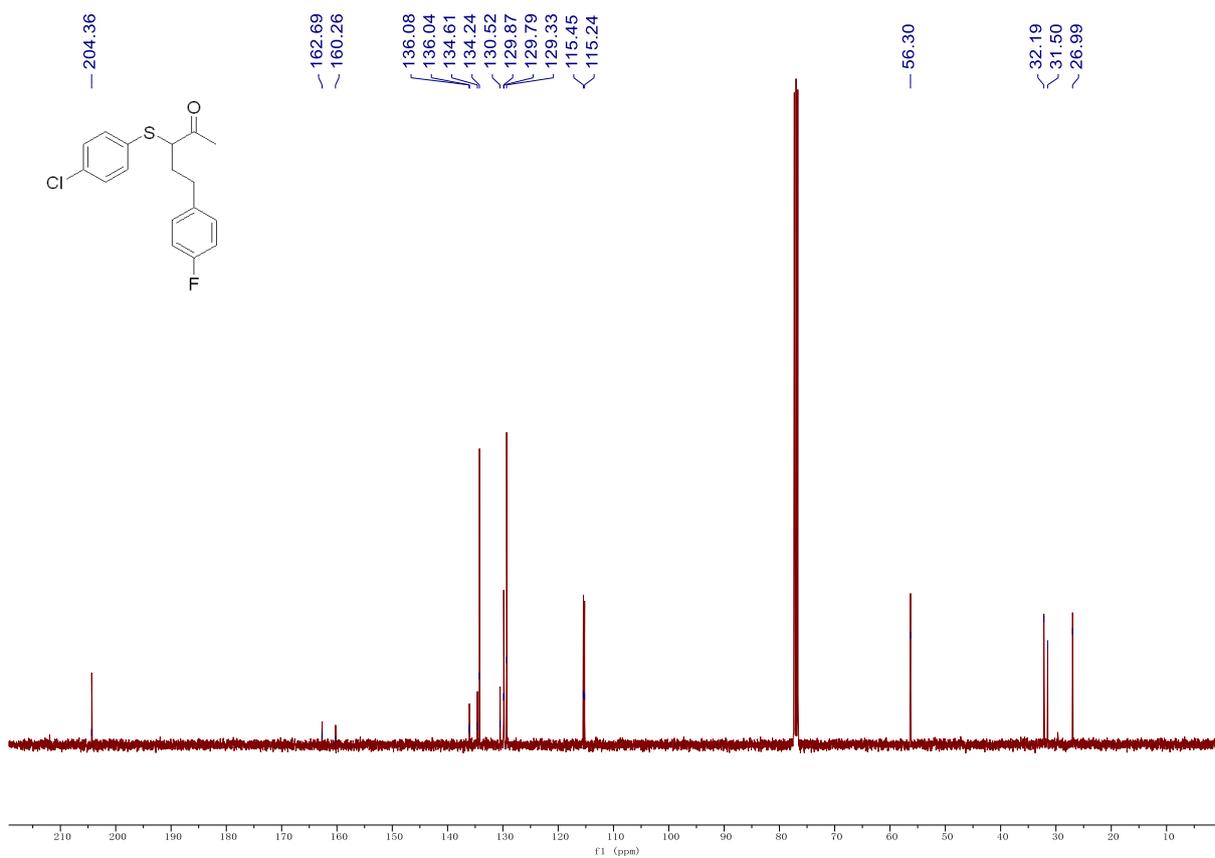
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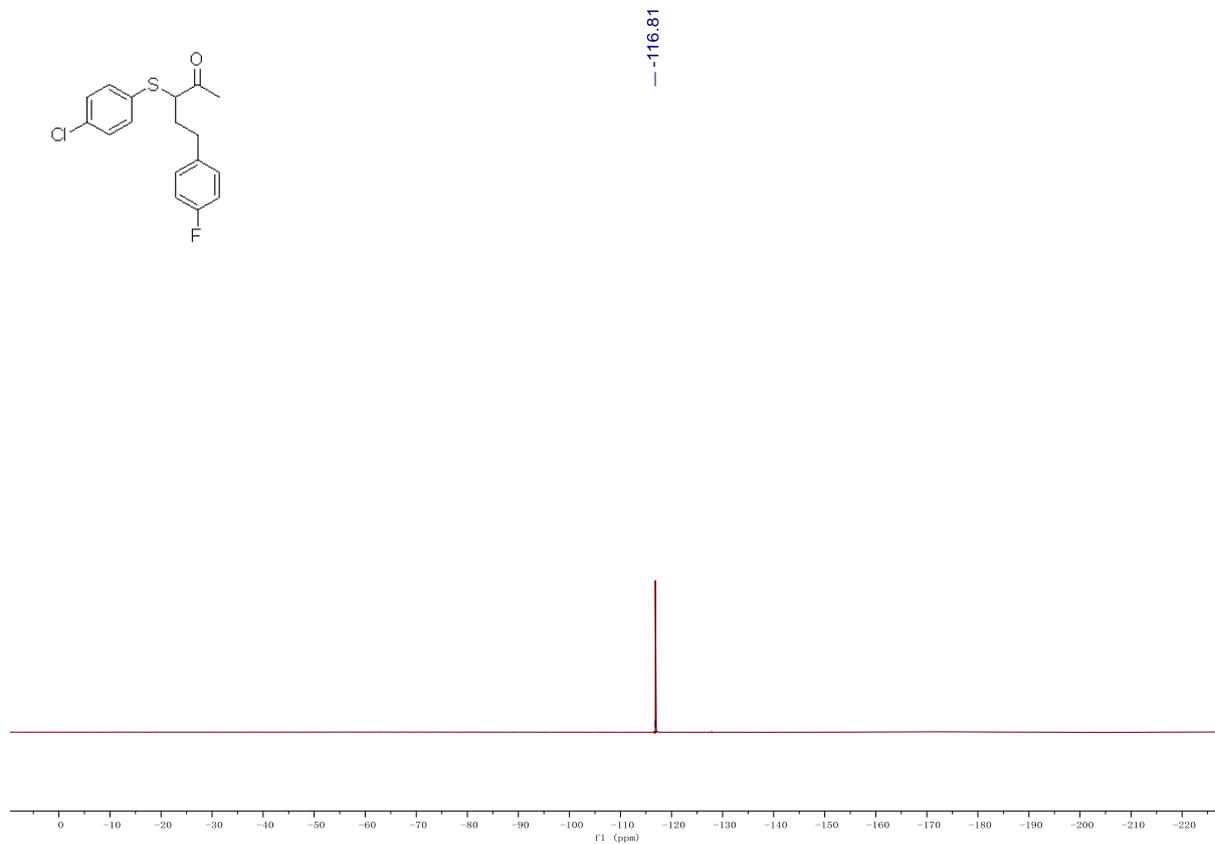
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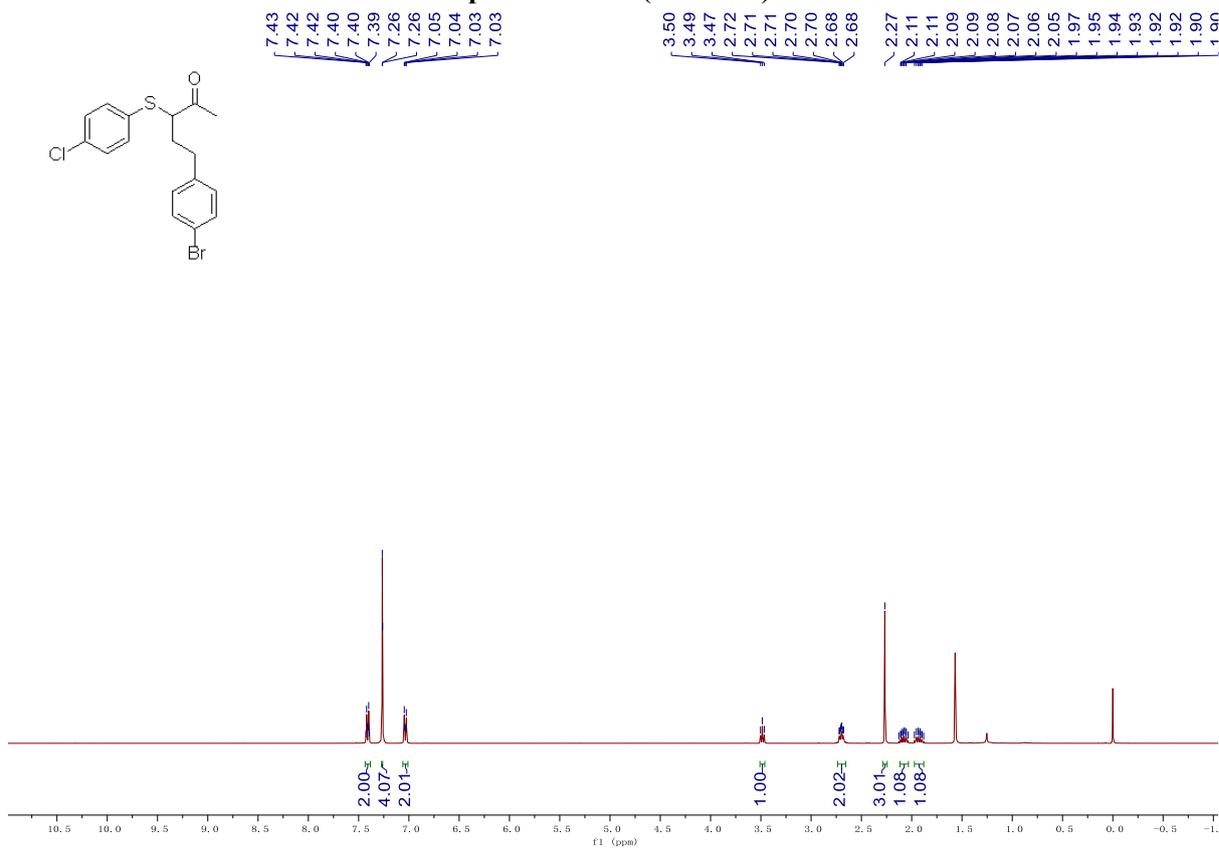
¹³C NMR Spectrum of 3d (100 MHz) in CDCl₃



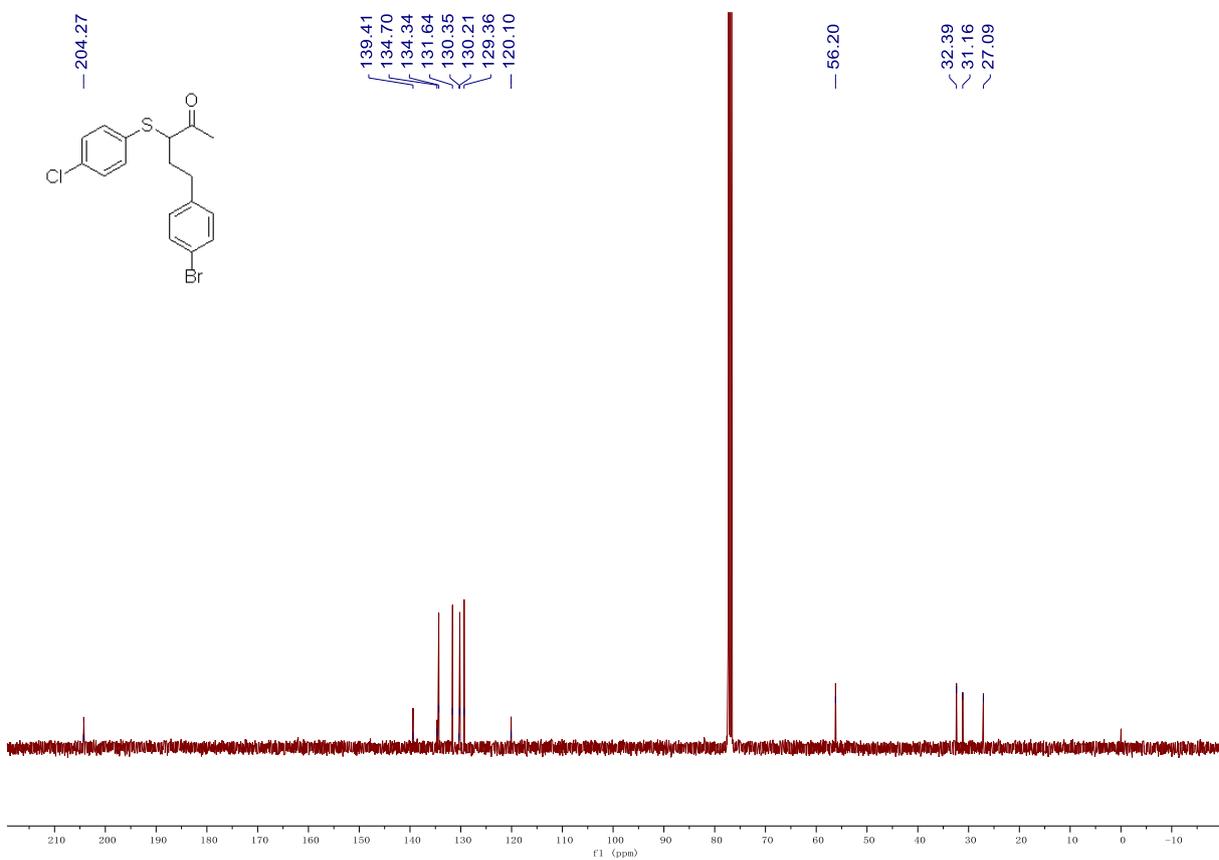
¹⁹F NMR Spectrum of 3d (376 MHz) in CDCl₃



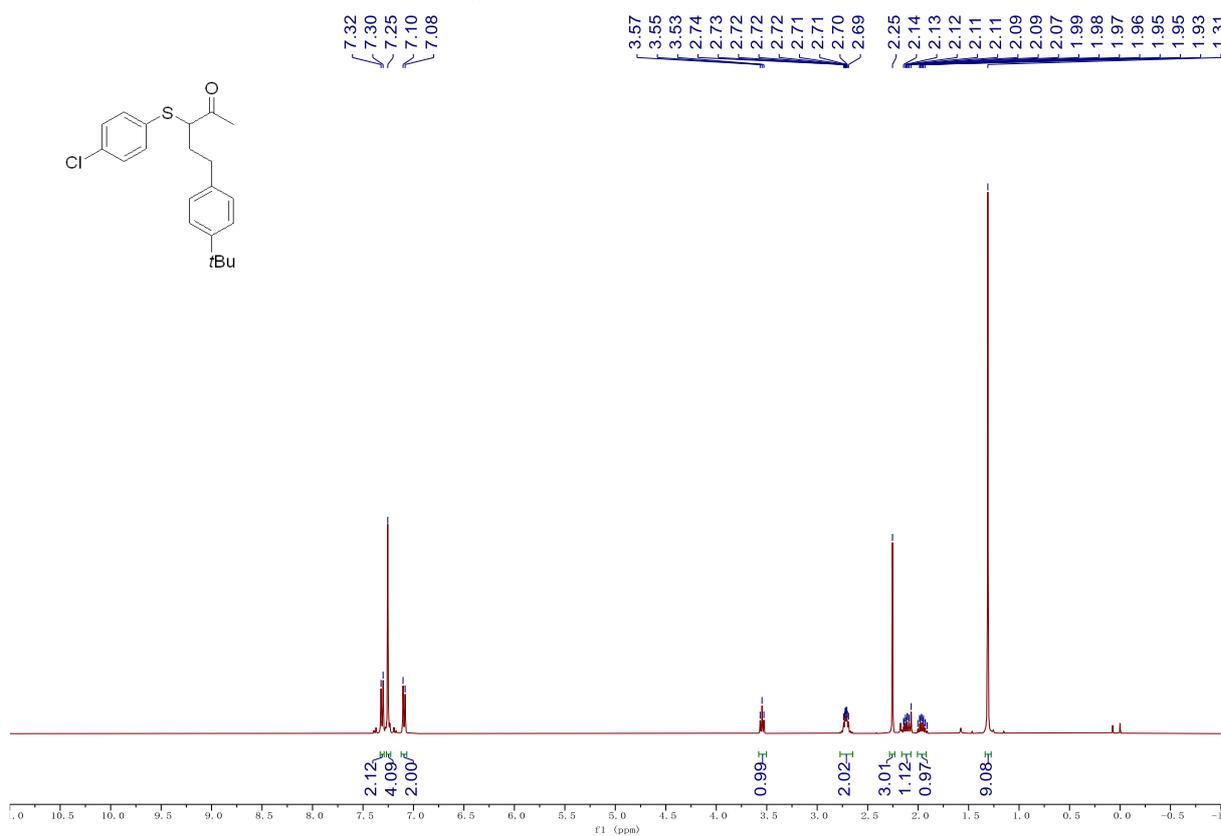
¹H NMR Spectrum of 3e (400 MHz) in CDCl₃



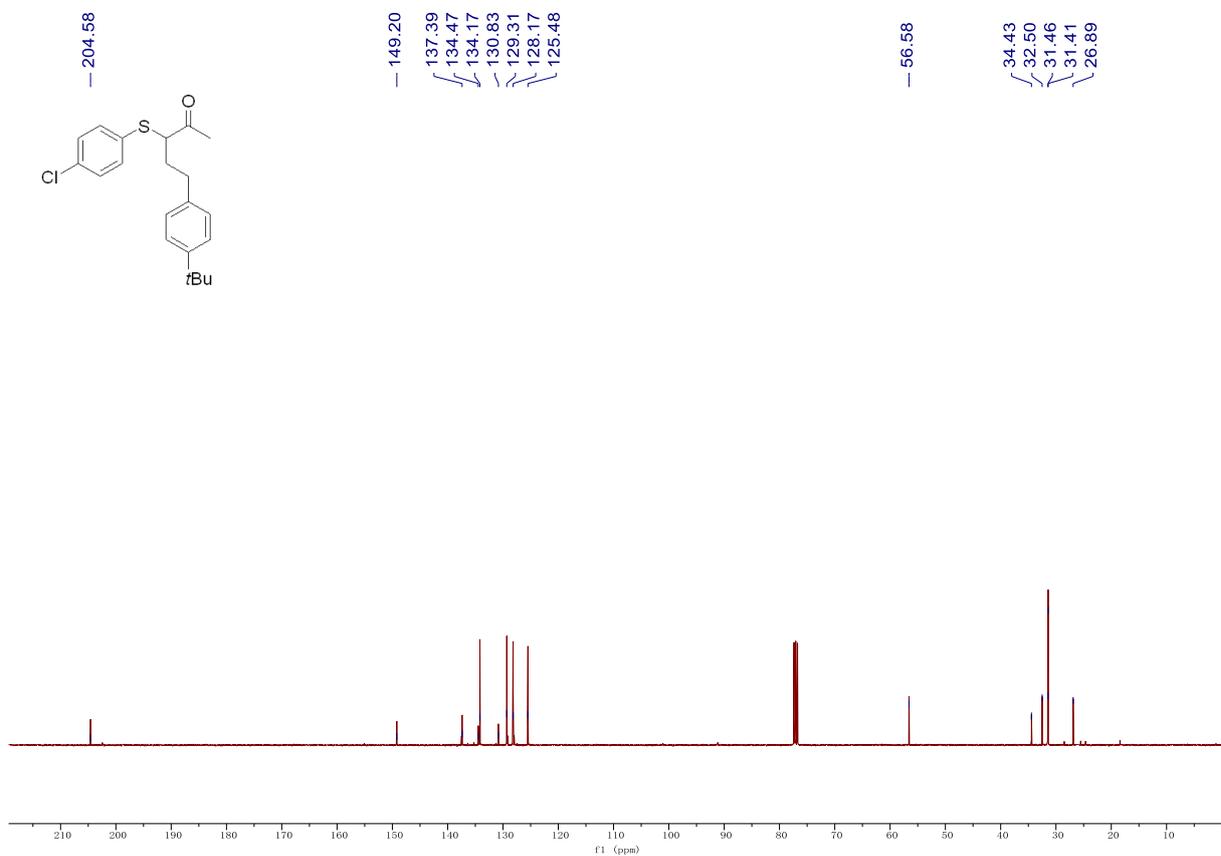
¹³C NMR Spectrum of 3e (100 MHz) in CDCl₃



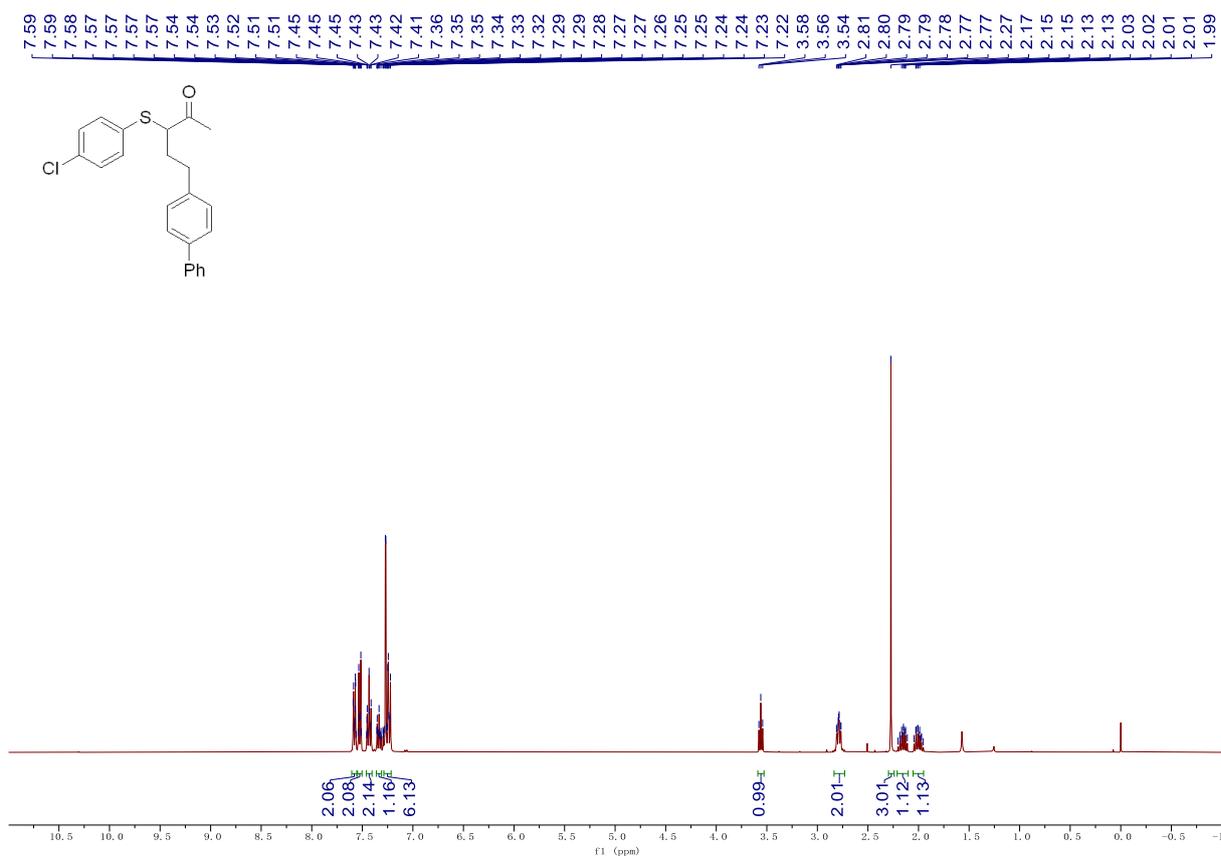
¹H NMR Spectrum of 3f (400 MHz) in CDCl₃



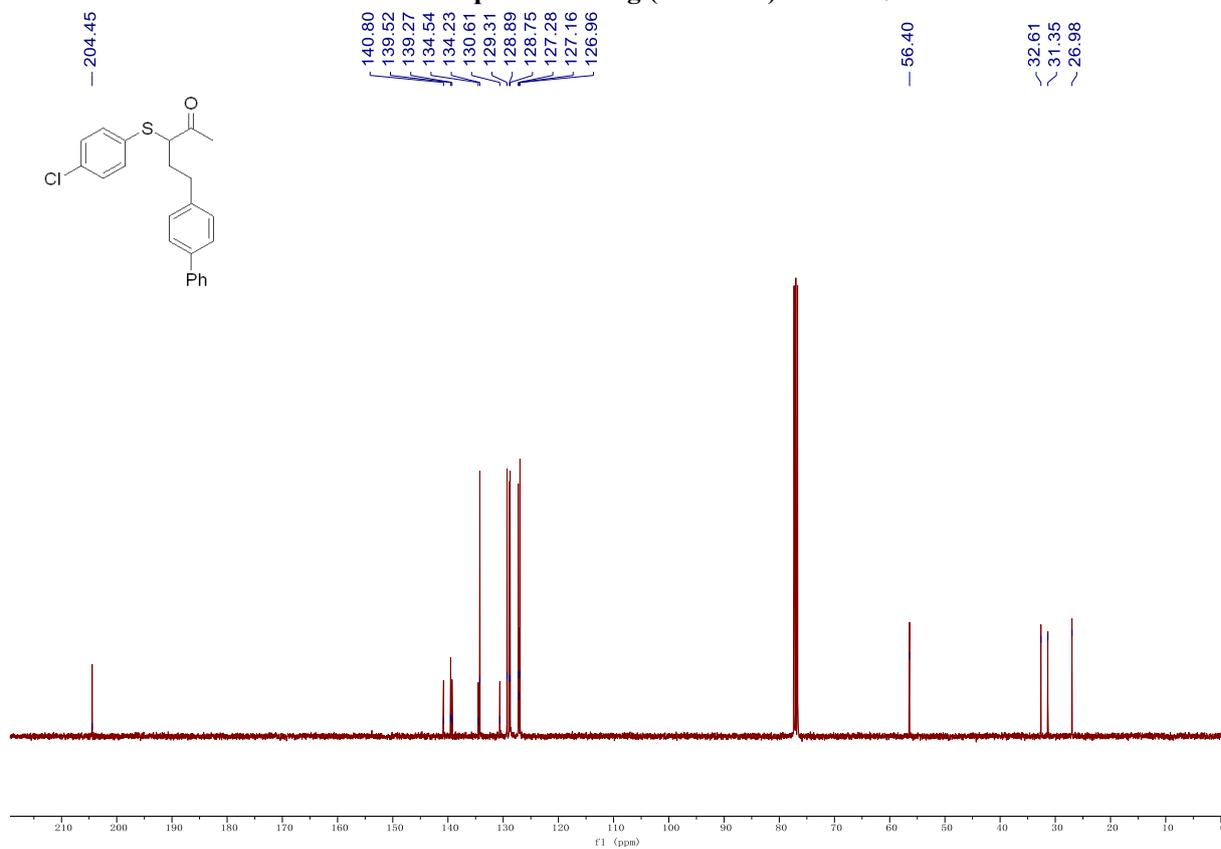
¹³C NMR Spectrum of 3f (100 MHz) in CDCl₃



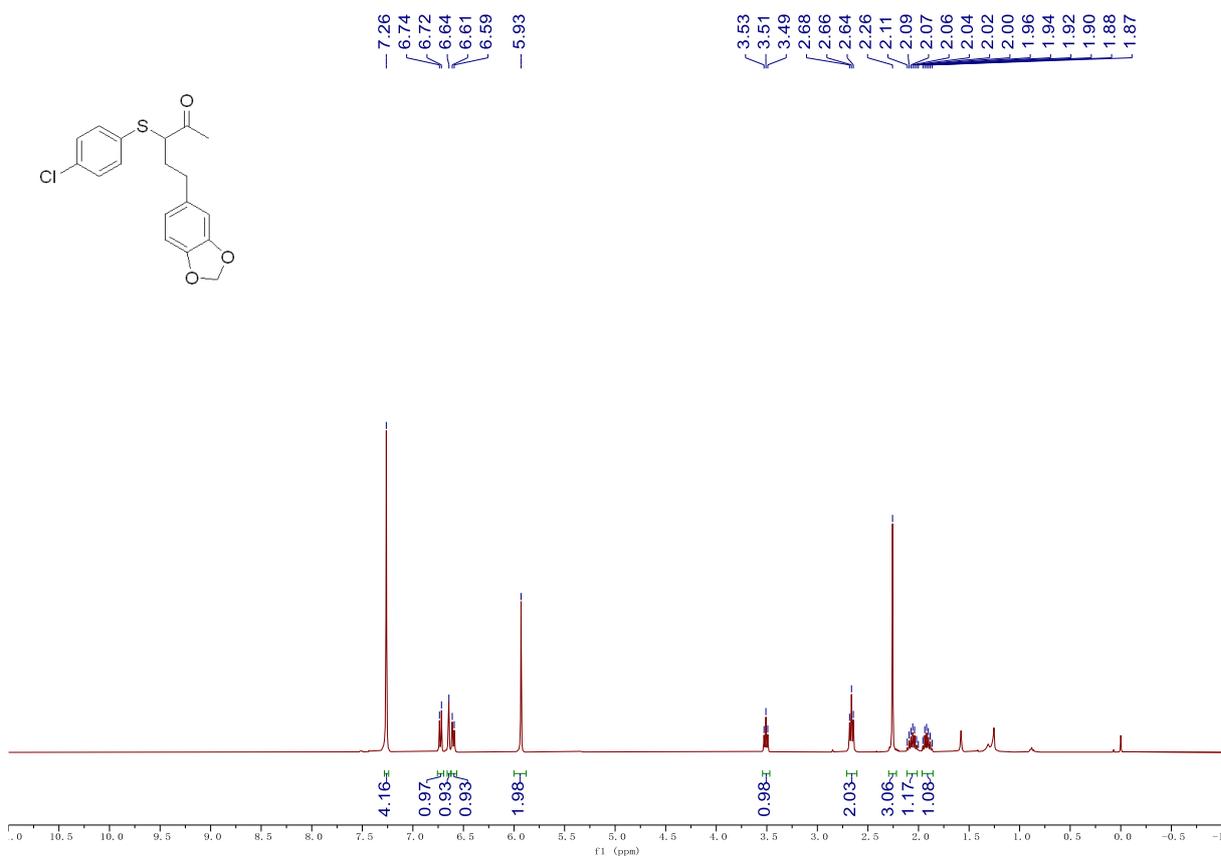
¹H NMR Spectrum of 3g (400 MHz) in CDCl₃



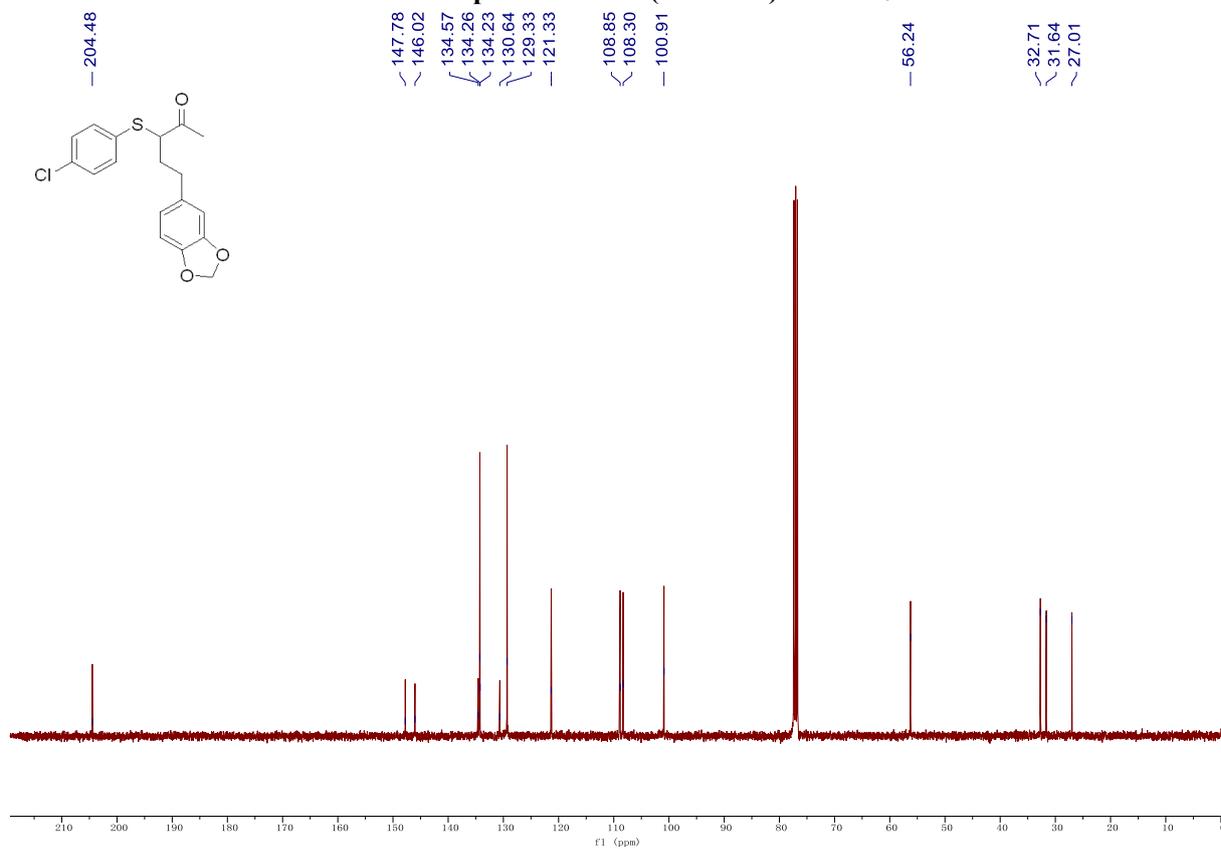
¹³C NMR Spectrum of 3g (100 MHz) in CDCl₃



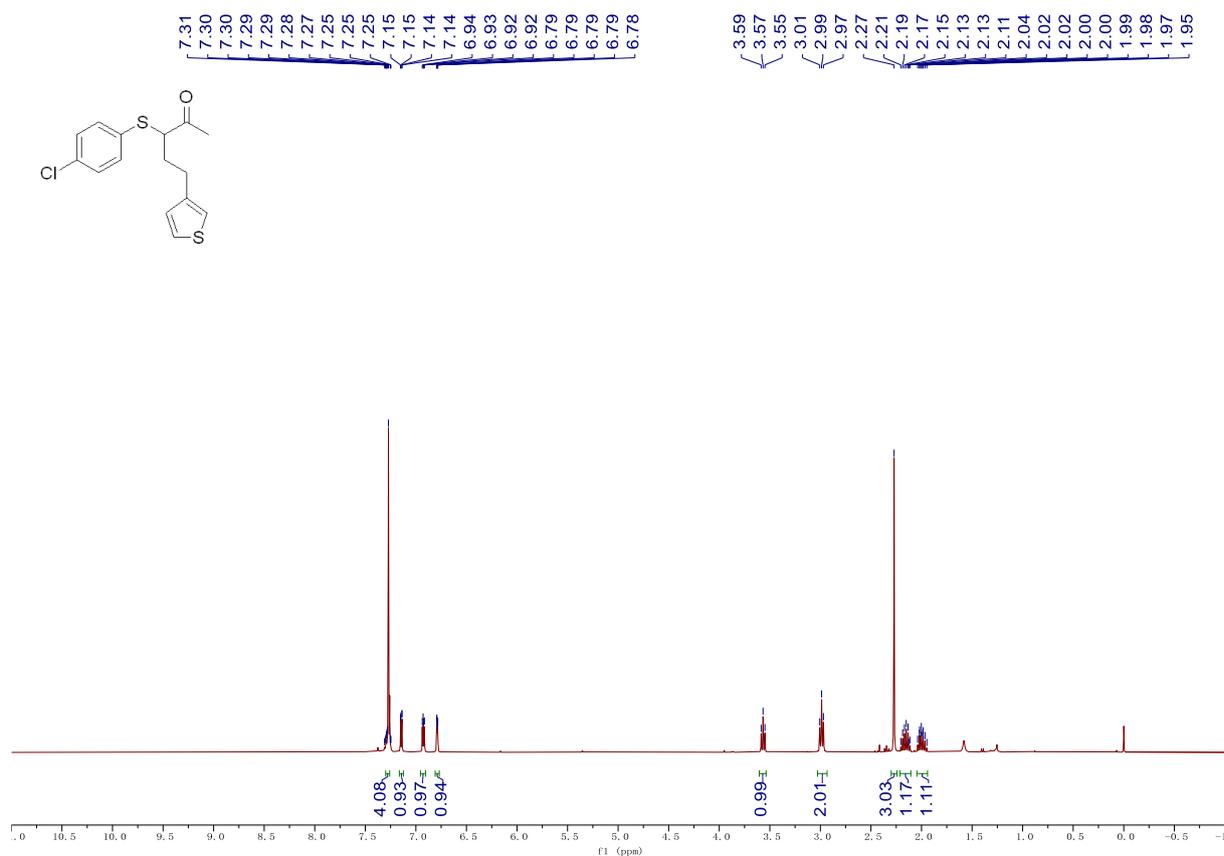
¹H NMR Spectrum of 3h (400 MHz) in CDCl₃



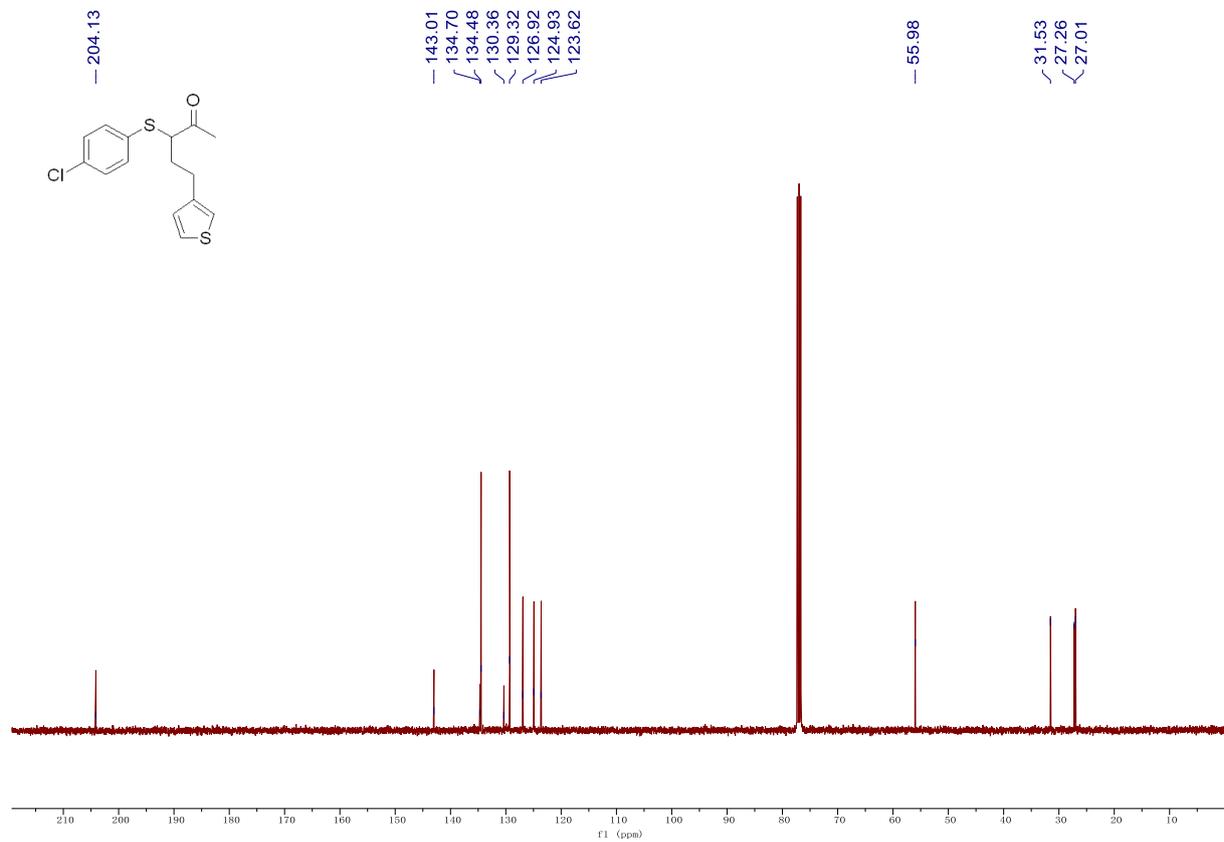
¹³C NMR Spectrum of 3h (100 MHz) in CDCl₃



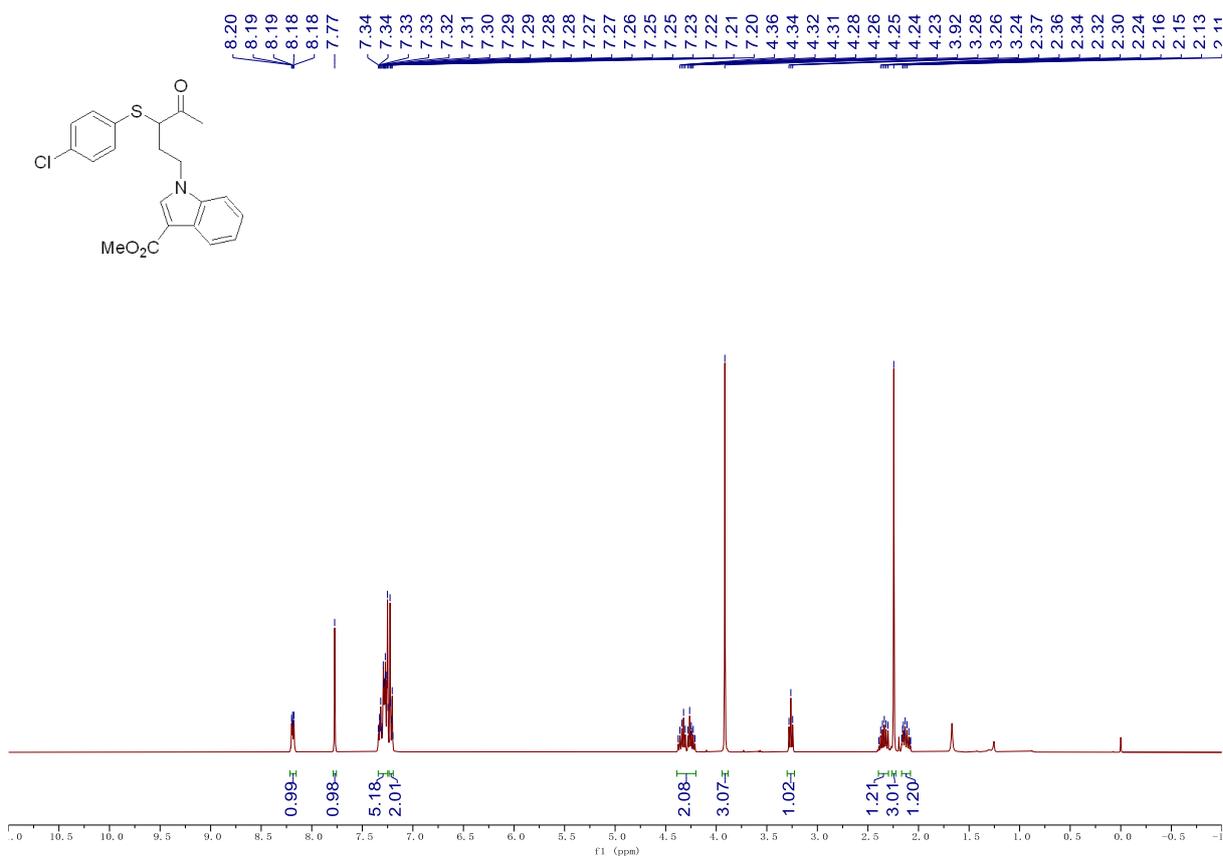
¹H NMR Spectrum of 3i (400 MHz) in CDCl₃



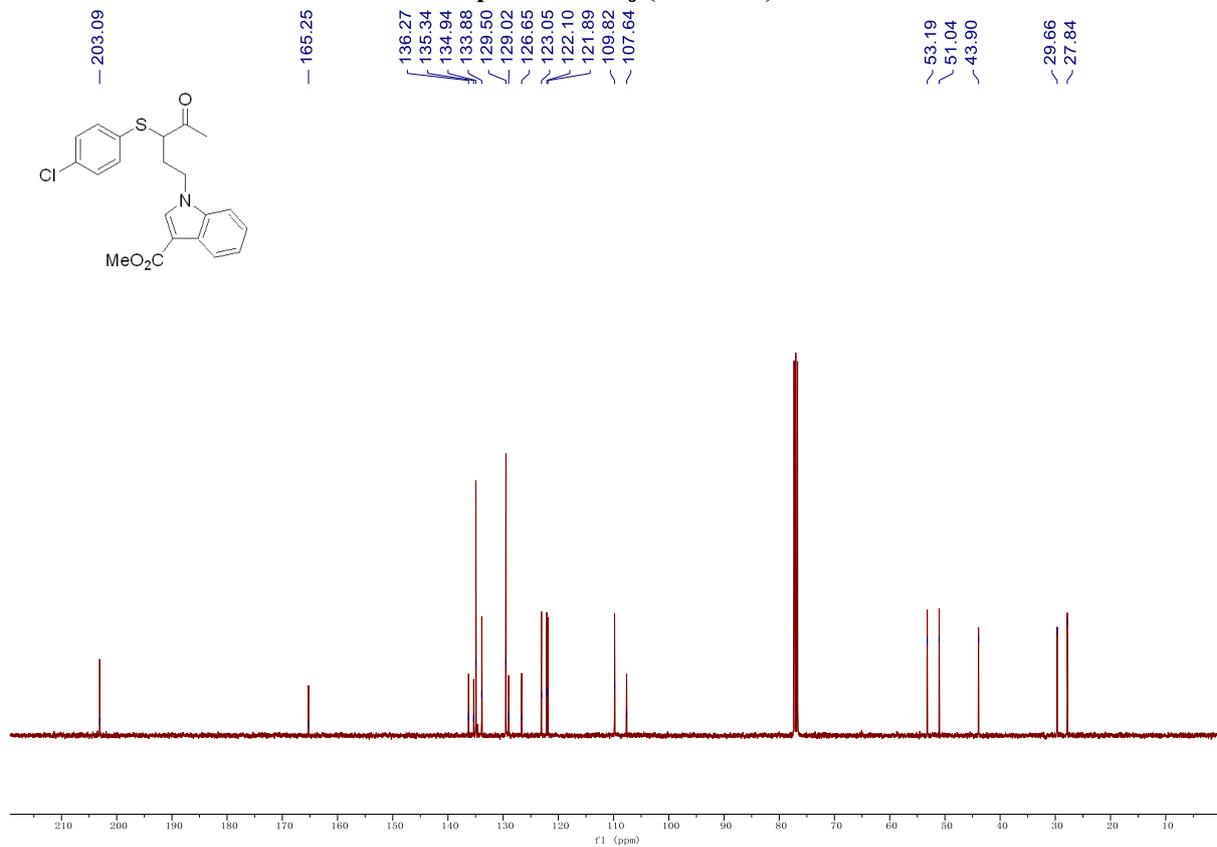
¹³C NMR Spectrum of 3i (100 MHz) in CDCl₃



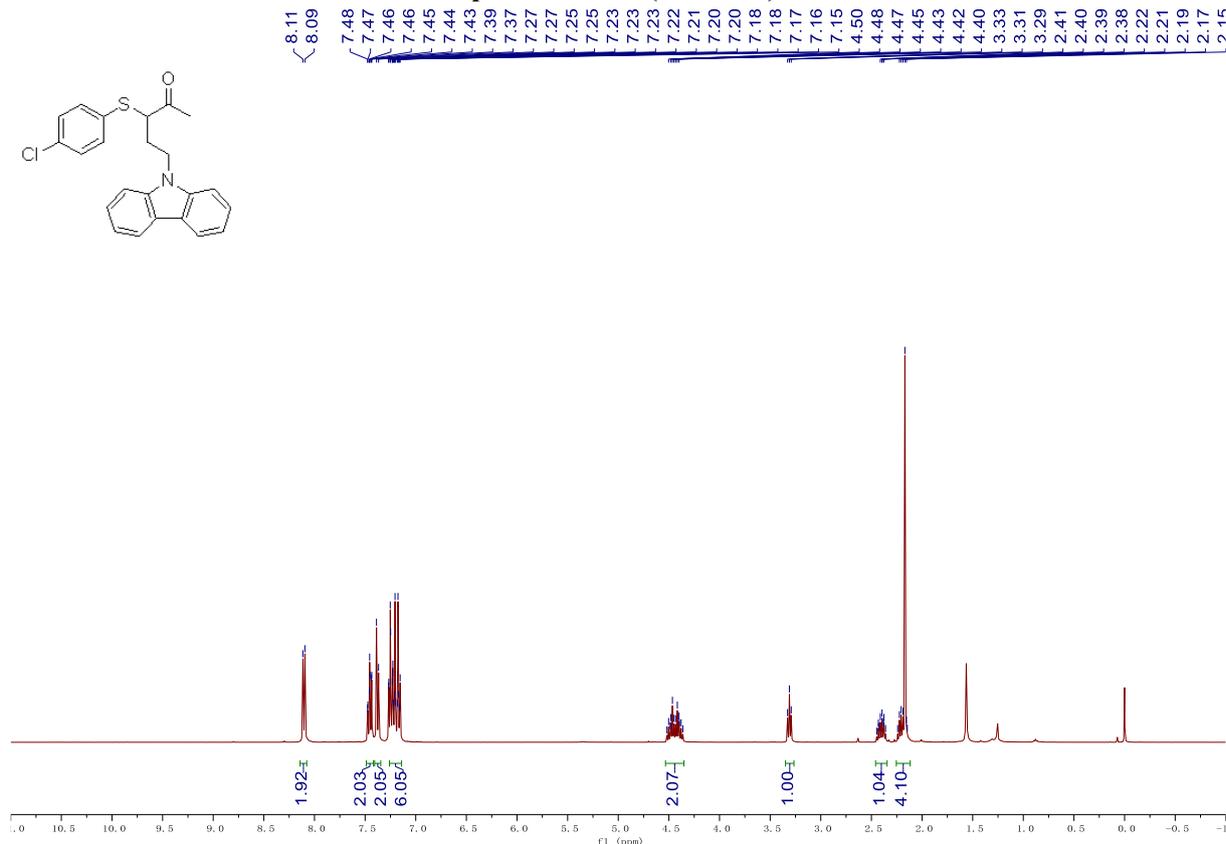
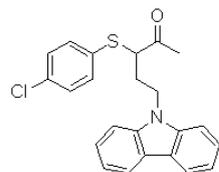
¹H NMR Spectrum of 3j (400 MHz) in CDCl₃



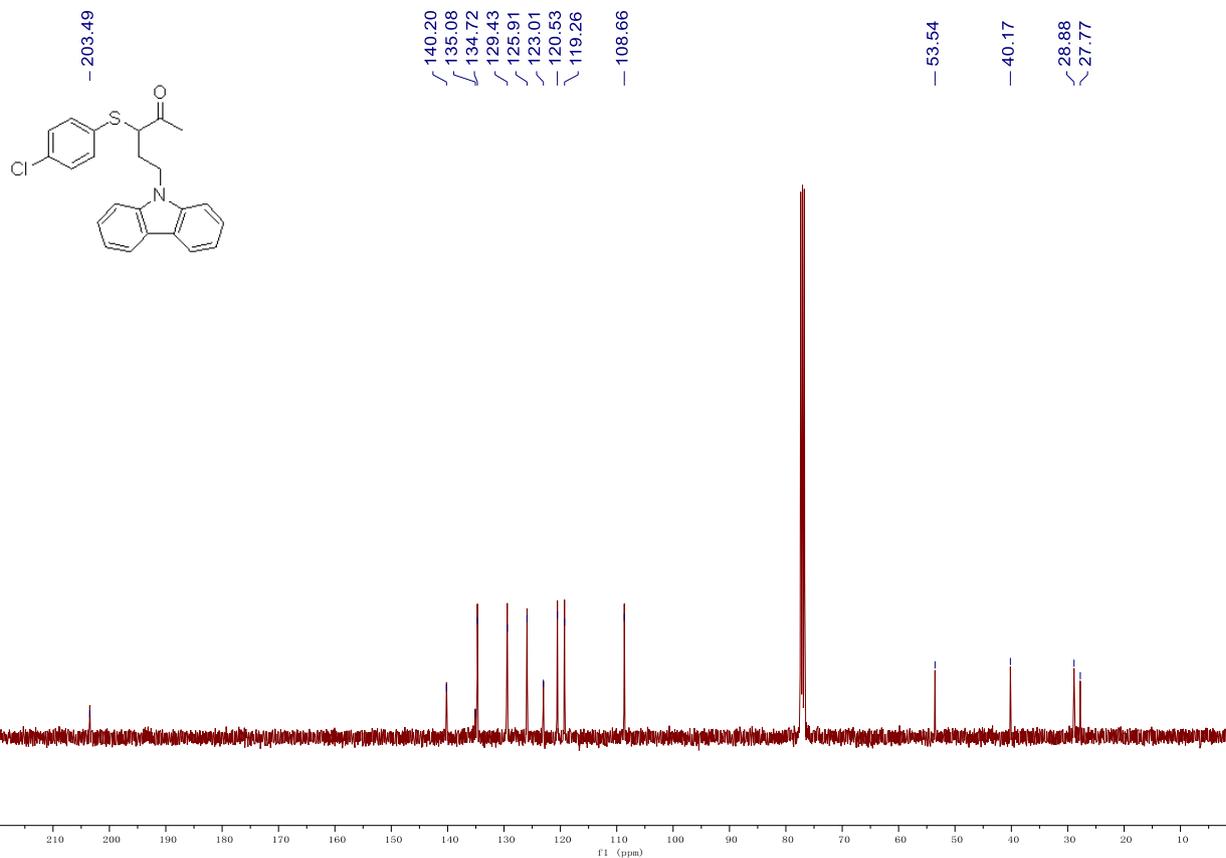
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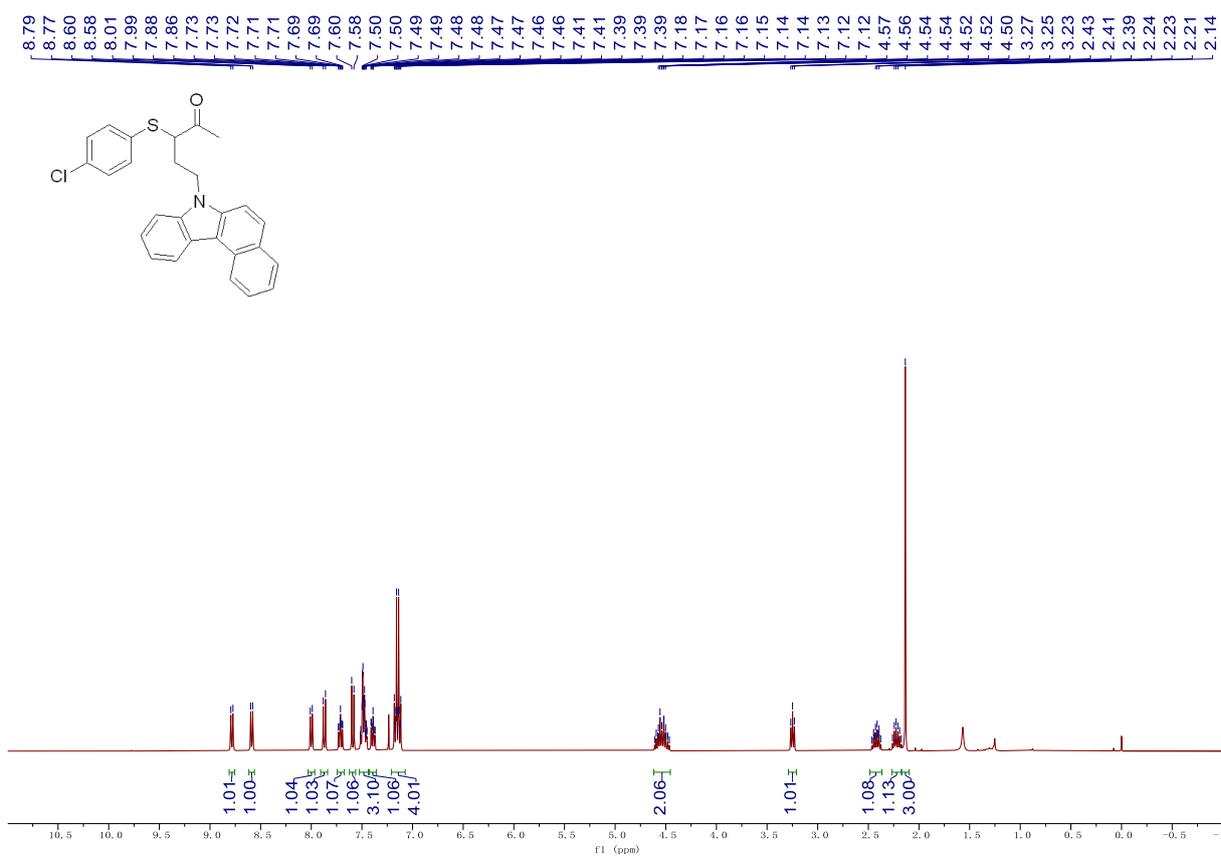
¹H NMR Spectrum of 3k (400 MHz) in CDCl₃



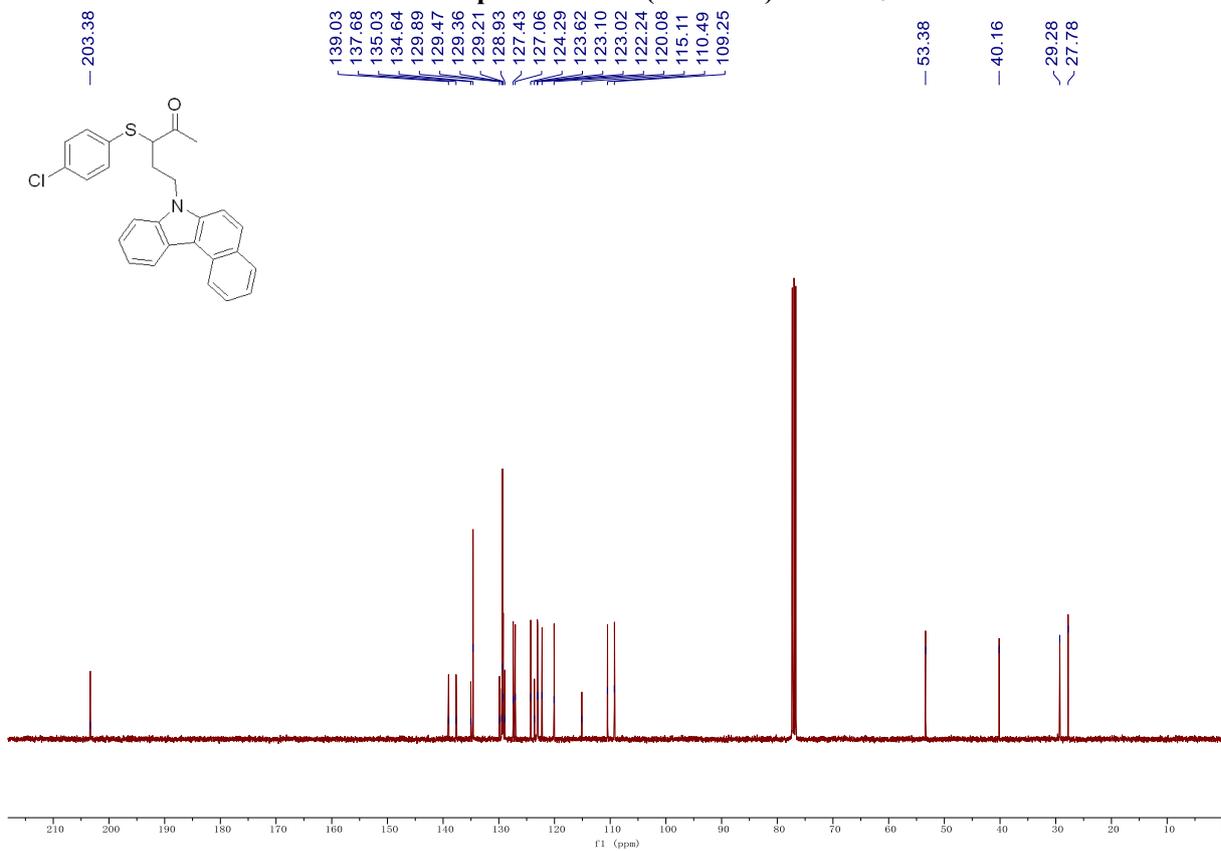
¹³C NMR Spectrum of 3k (100 MHz) in CDCl₃



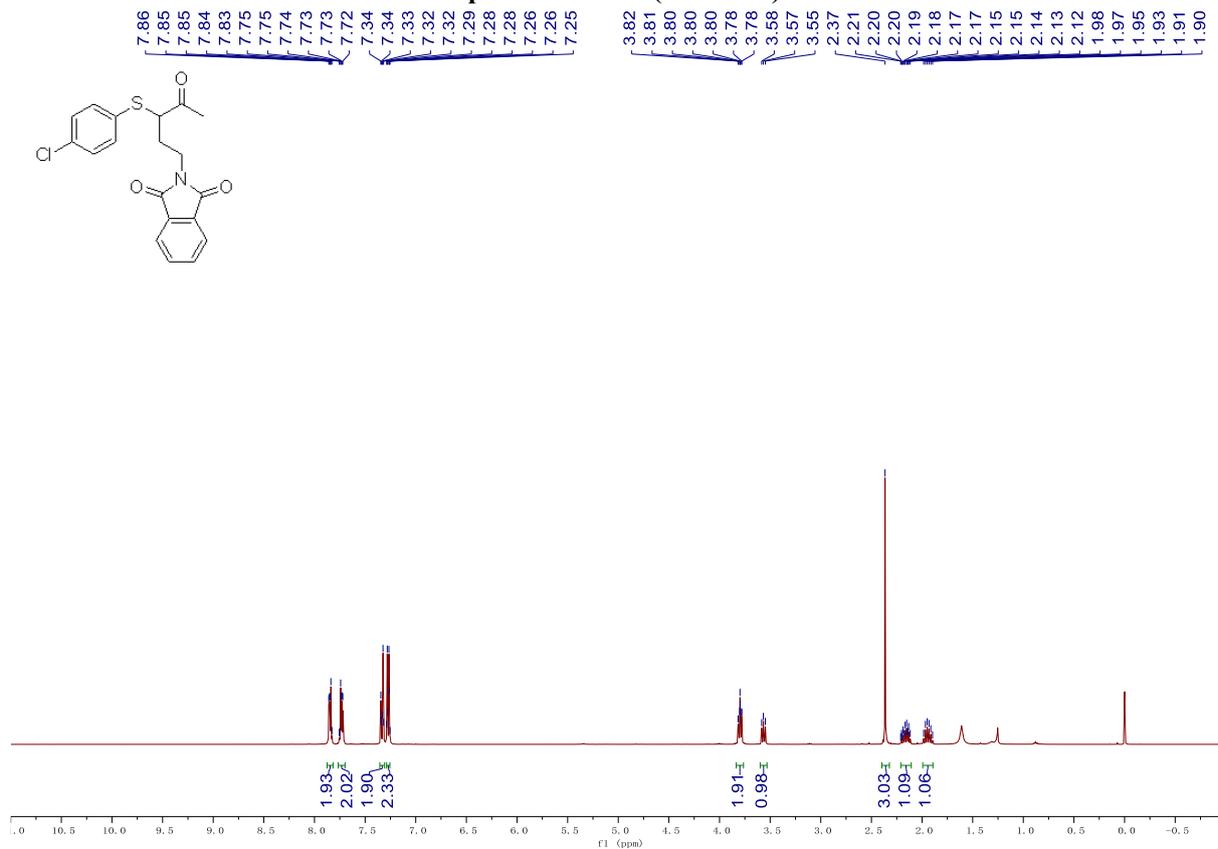
¹H NMR Spectrum of 31 (400 MHz) in CDCl₃



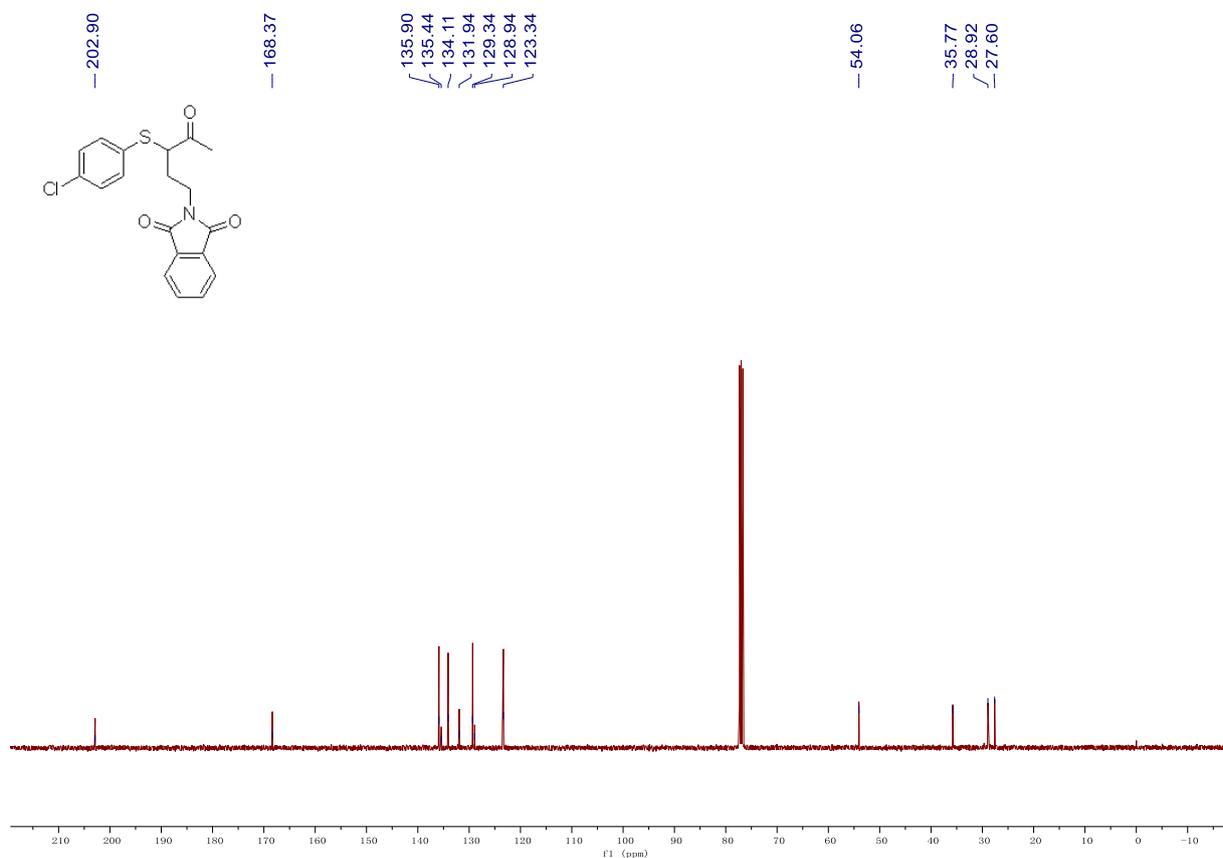
¹³C NMR Spectrum of 31 (100 MHz) in CDCl₃



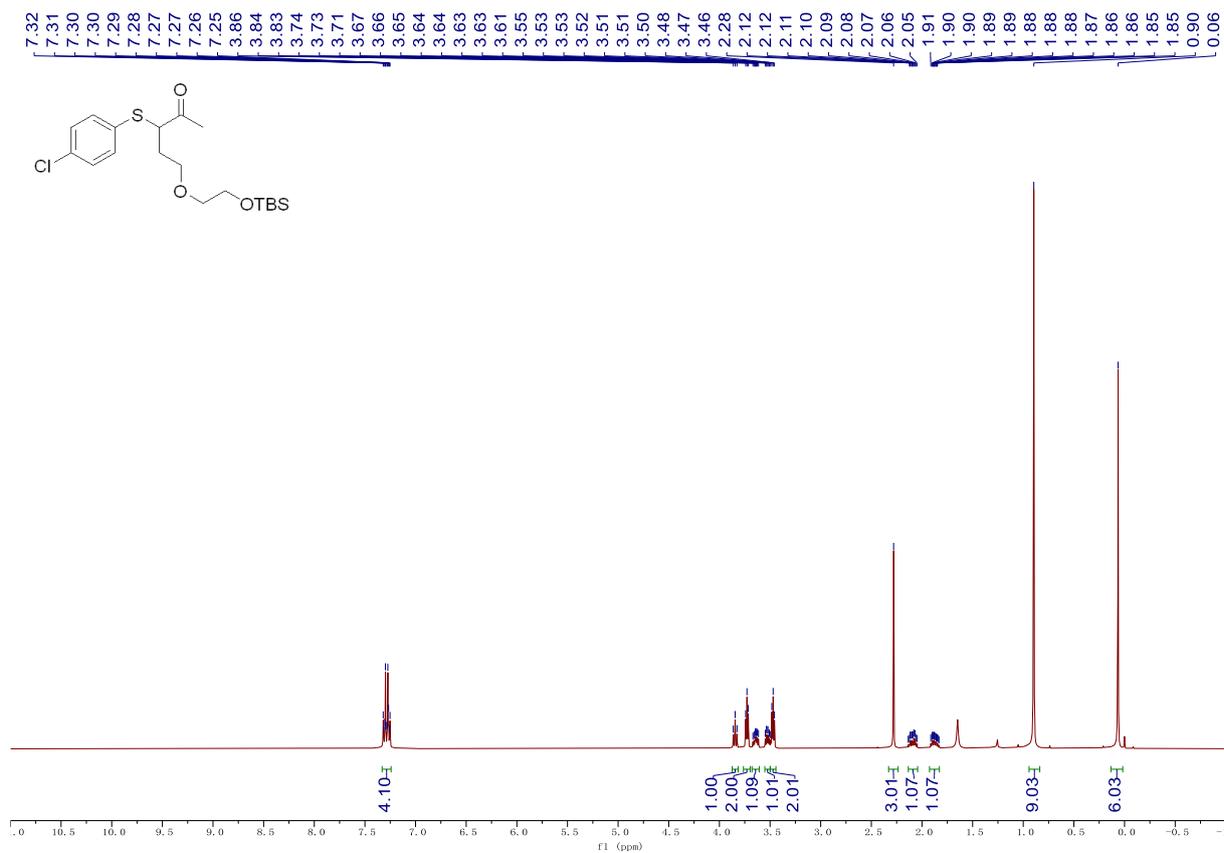
¹H NMR Spectrum of 3m (400 MHz) in CDCl₃



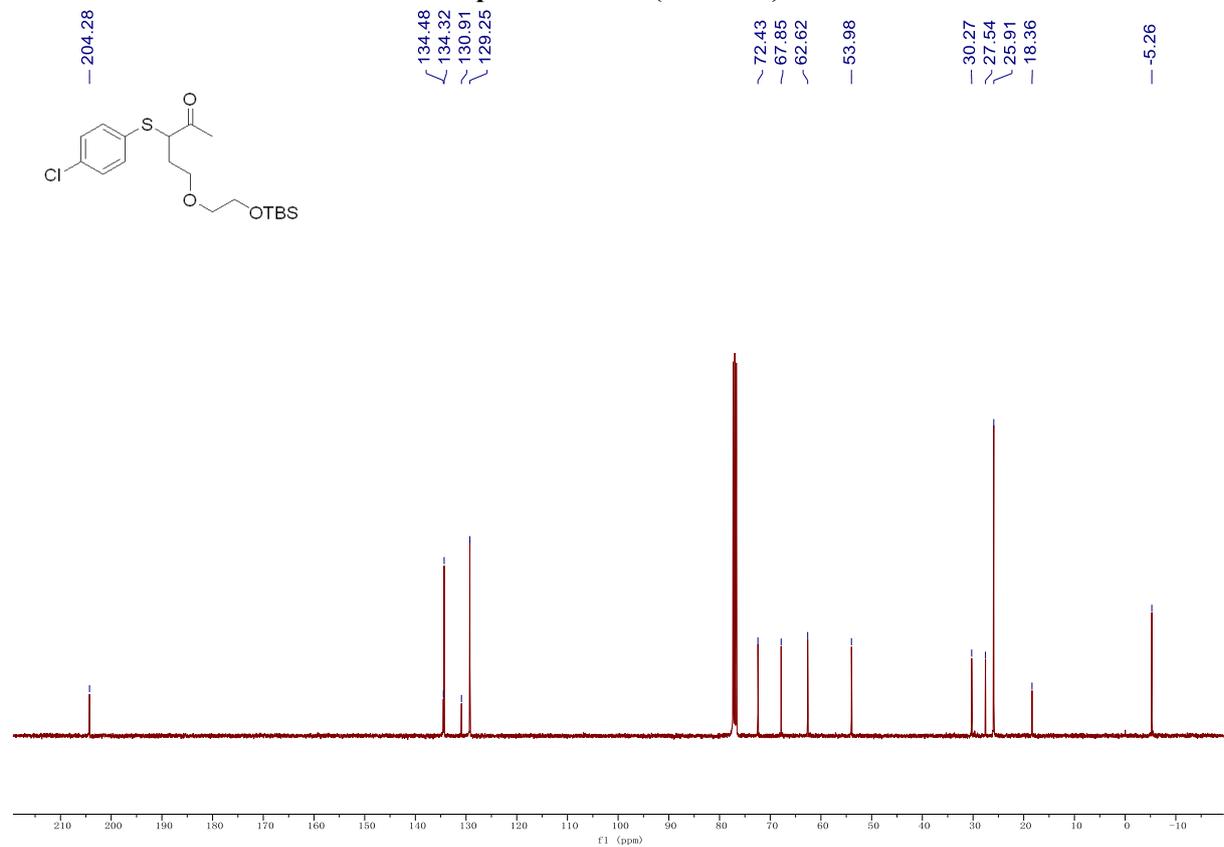
¹³C NMR Spectrum of 3m (100 MHz) in CDCl₃



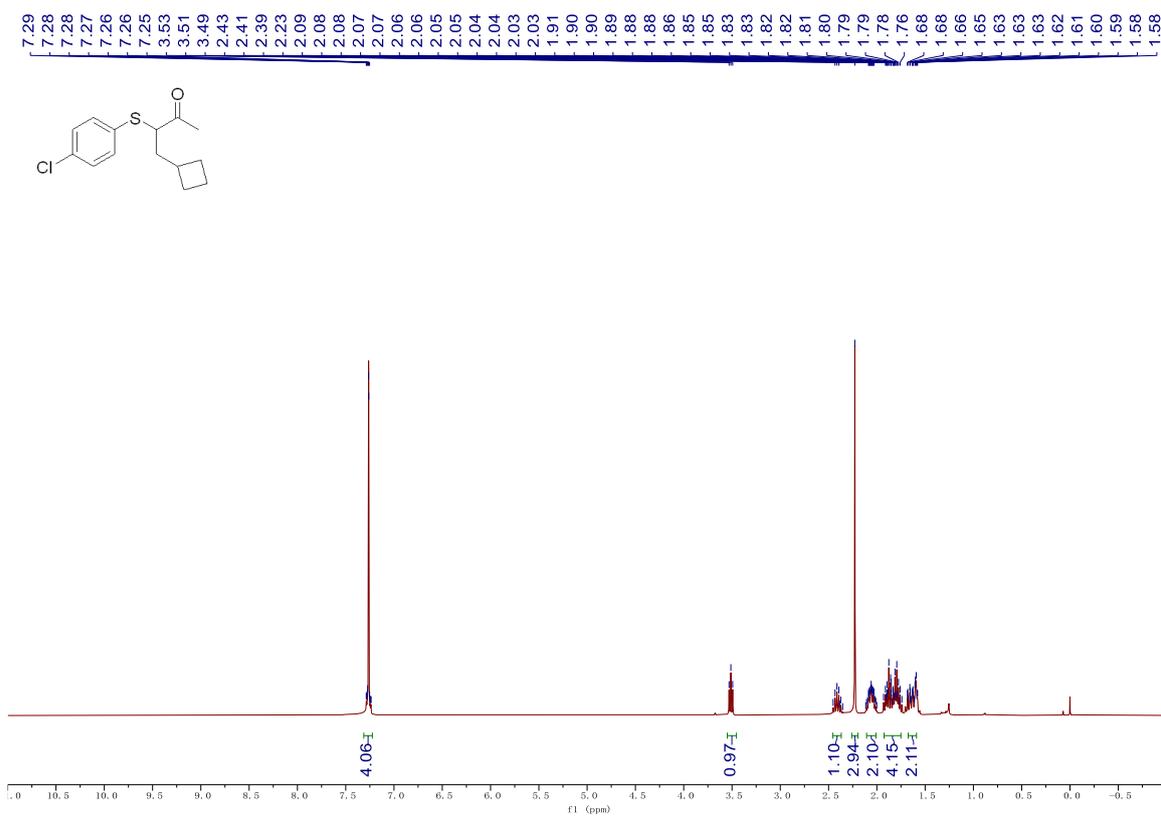
¹H NMR Spectrum of 3n (400 MHz) in CDCl₃



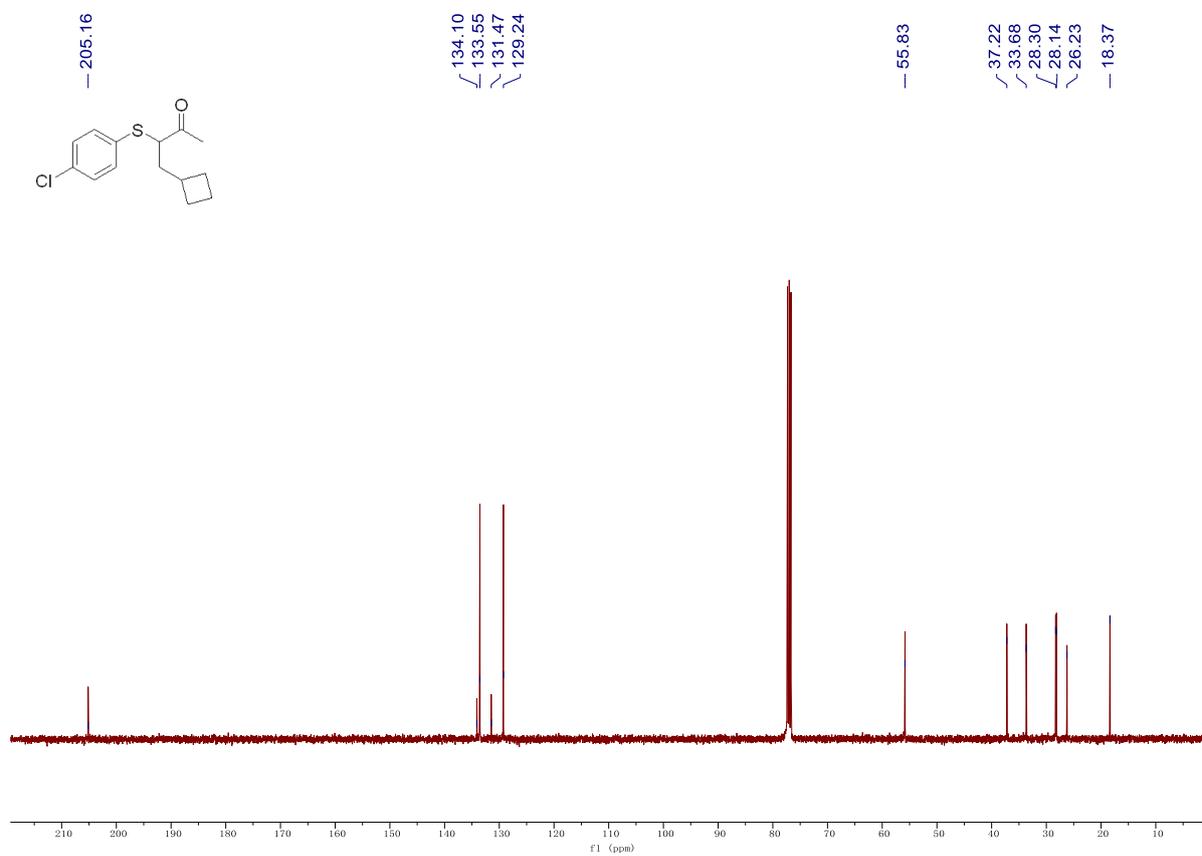
¹³C NMR Spectrum of 3n (100 MHz) in CDCl₃



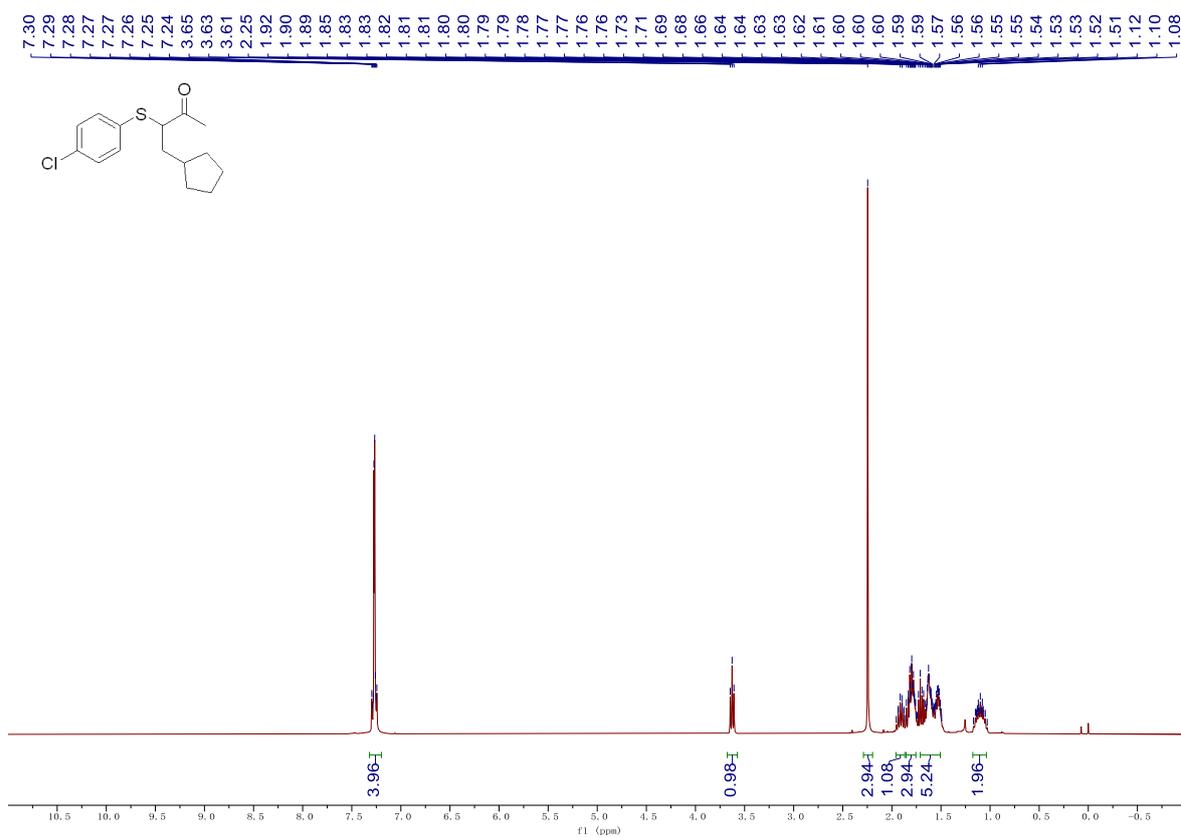
¹H NMR Spectrum of 3o (400 MHz) in CDCl₃



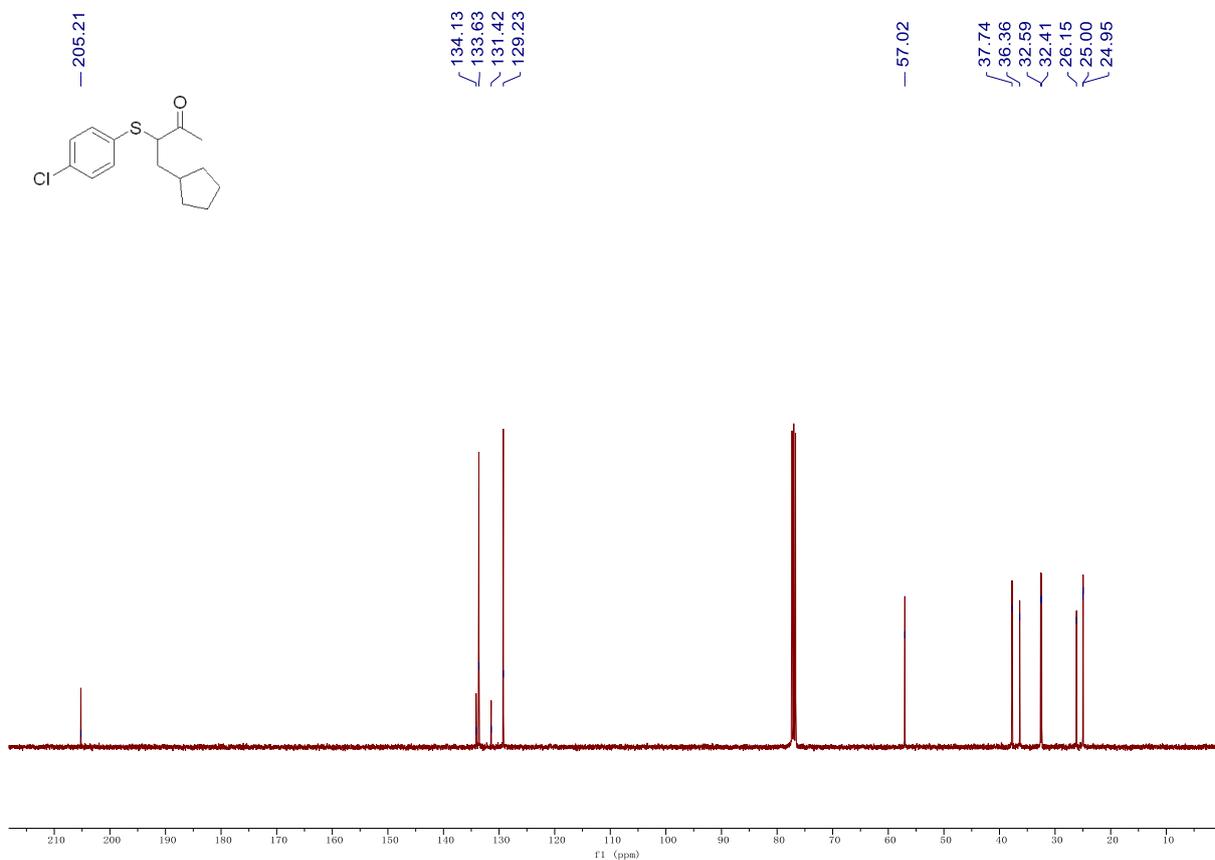
¹³C NMR Spectrum of 3o (100 MHz) in CDCl₃



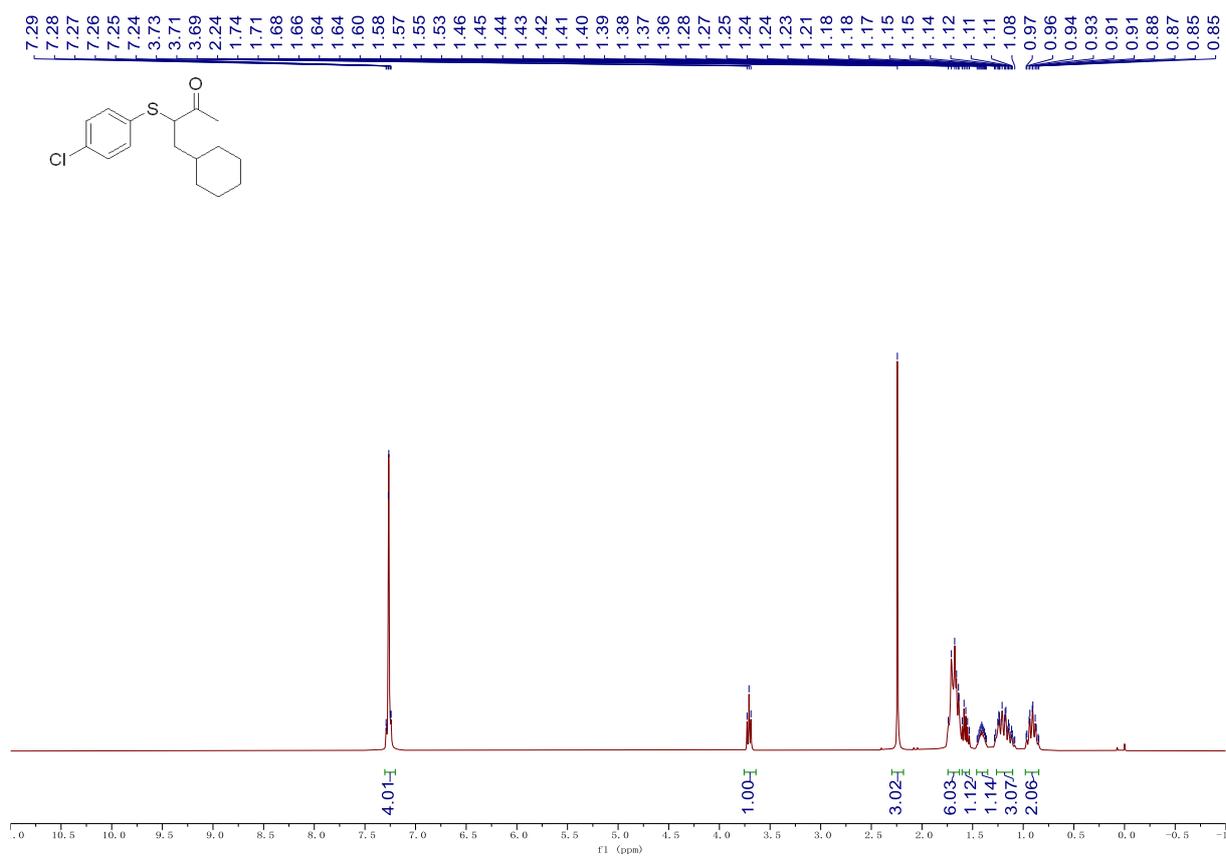
¹H NMR Spectrum of 3p (400 MHz) in CDCl₃



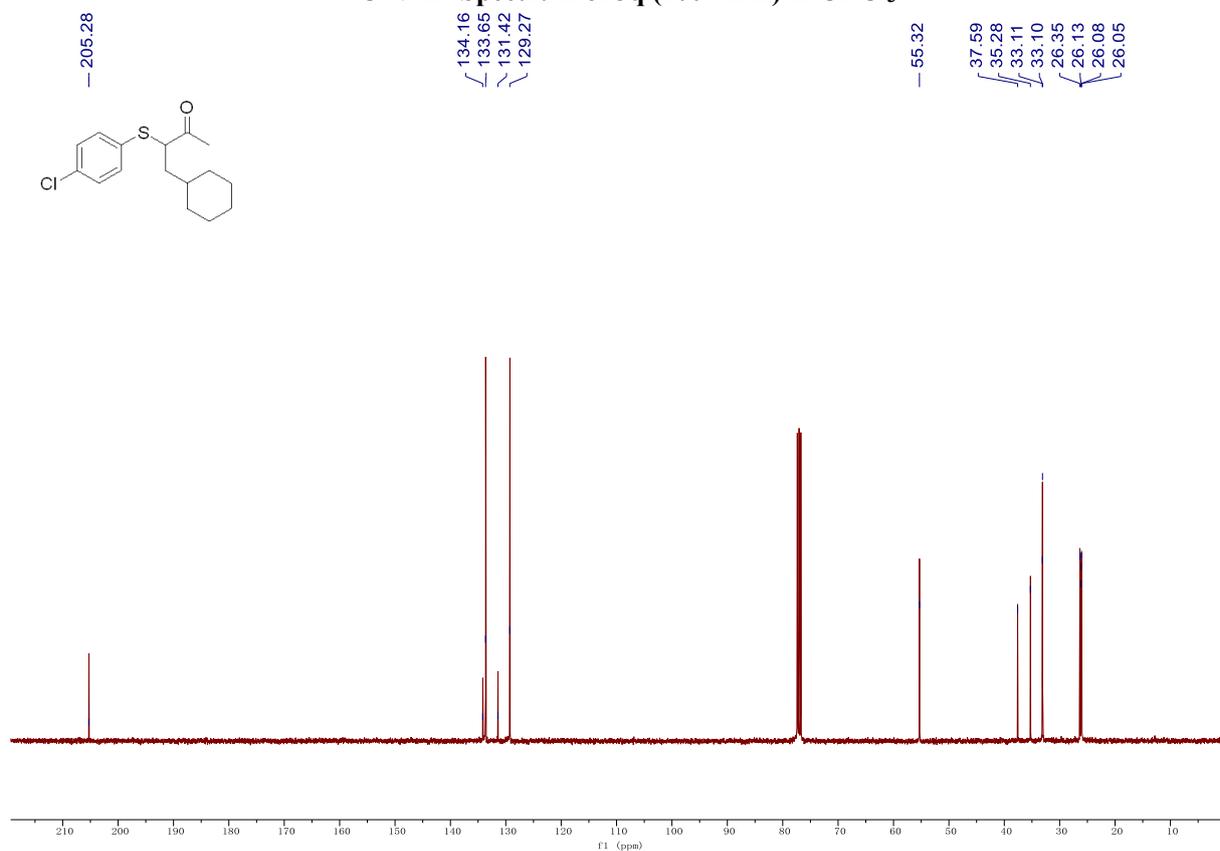
¹³C NMR Spectrum of 3p (100 MHz) in CDCl₃



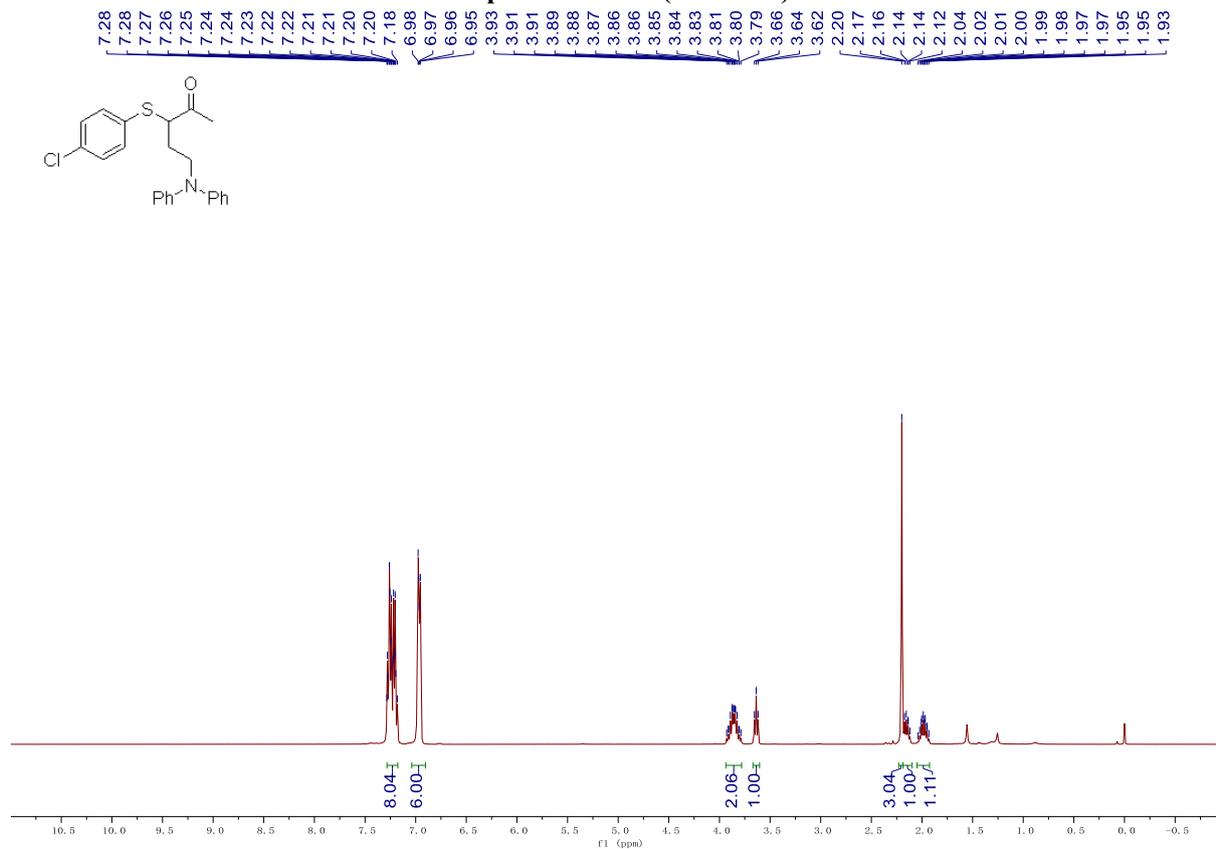
¹H NMR Spectrum of 3q (400 MHz) in CDCl₃



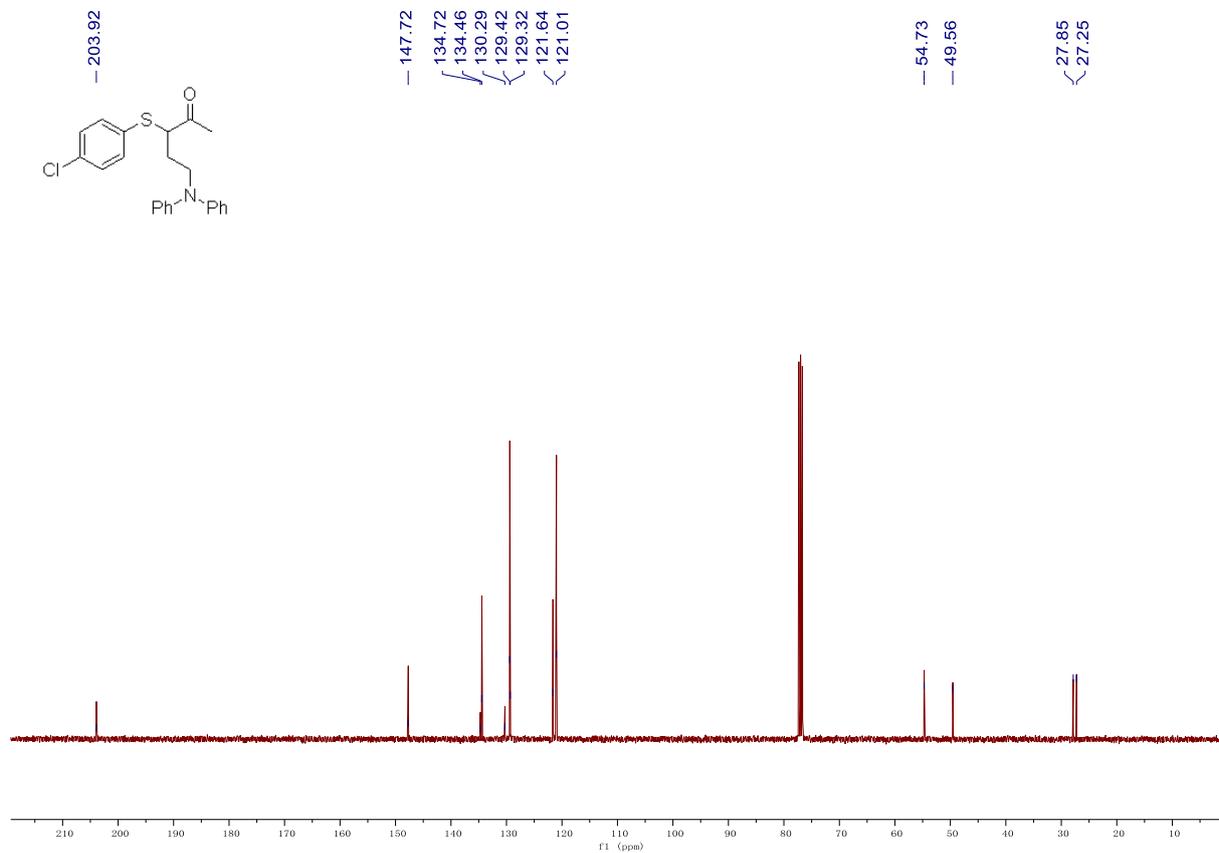
¹³C NMR Spectrum of 3q (100 MHz) in CDCl₃



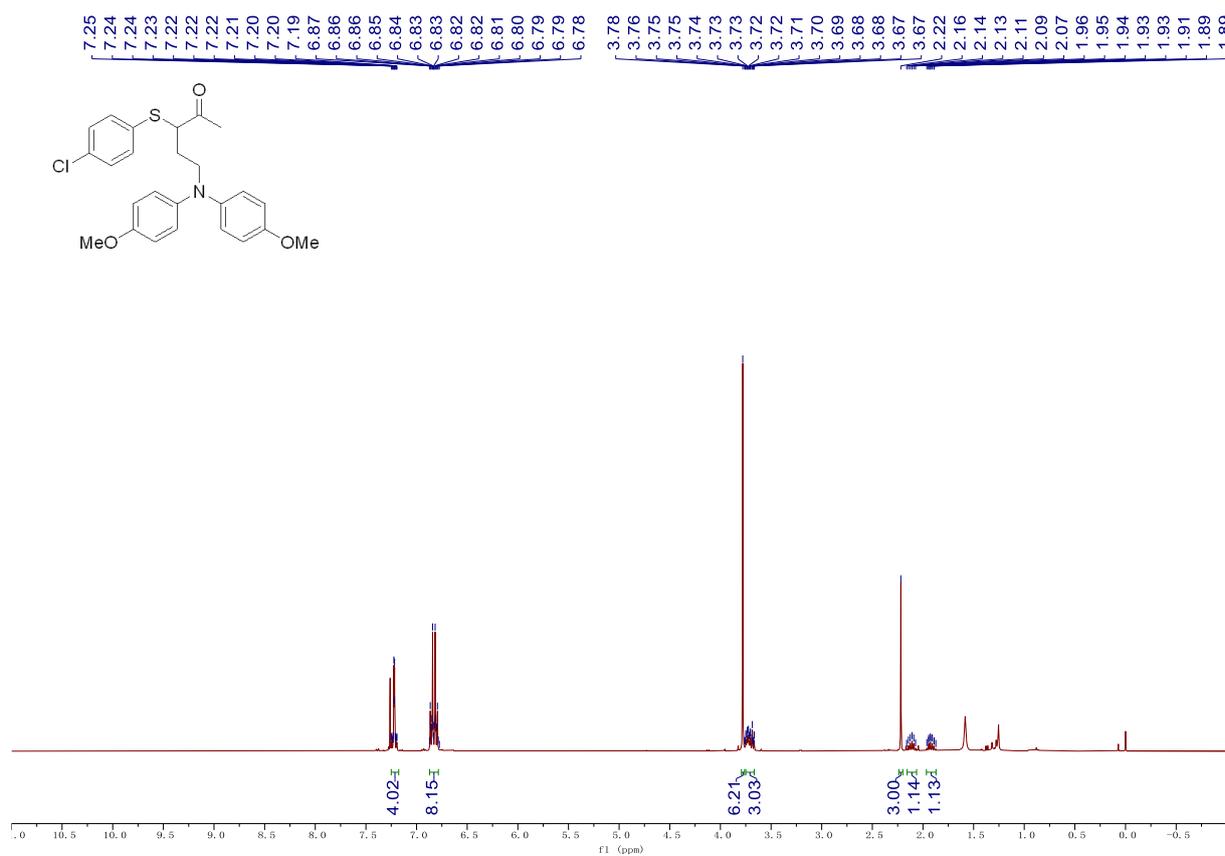
¹H NMR Spectrum of 5a (400 MHz) in CDCl₃



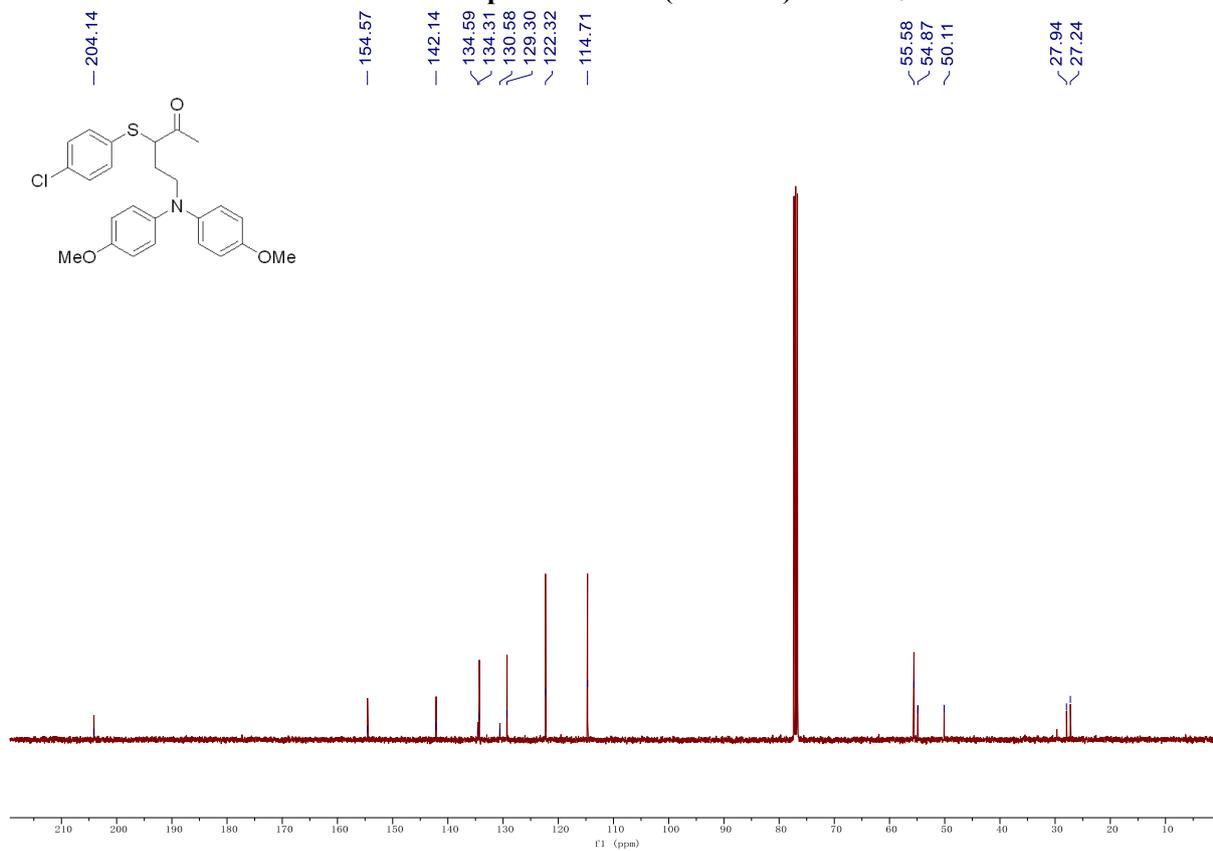
¹³C NMR Spectrum of 5a (100 MHz) in CDCl₃



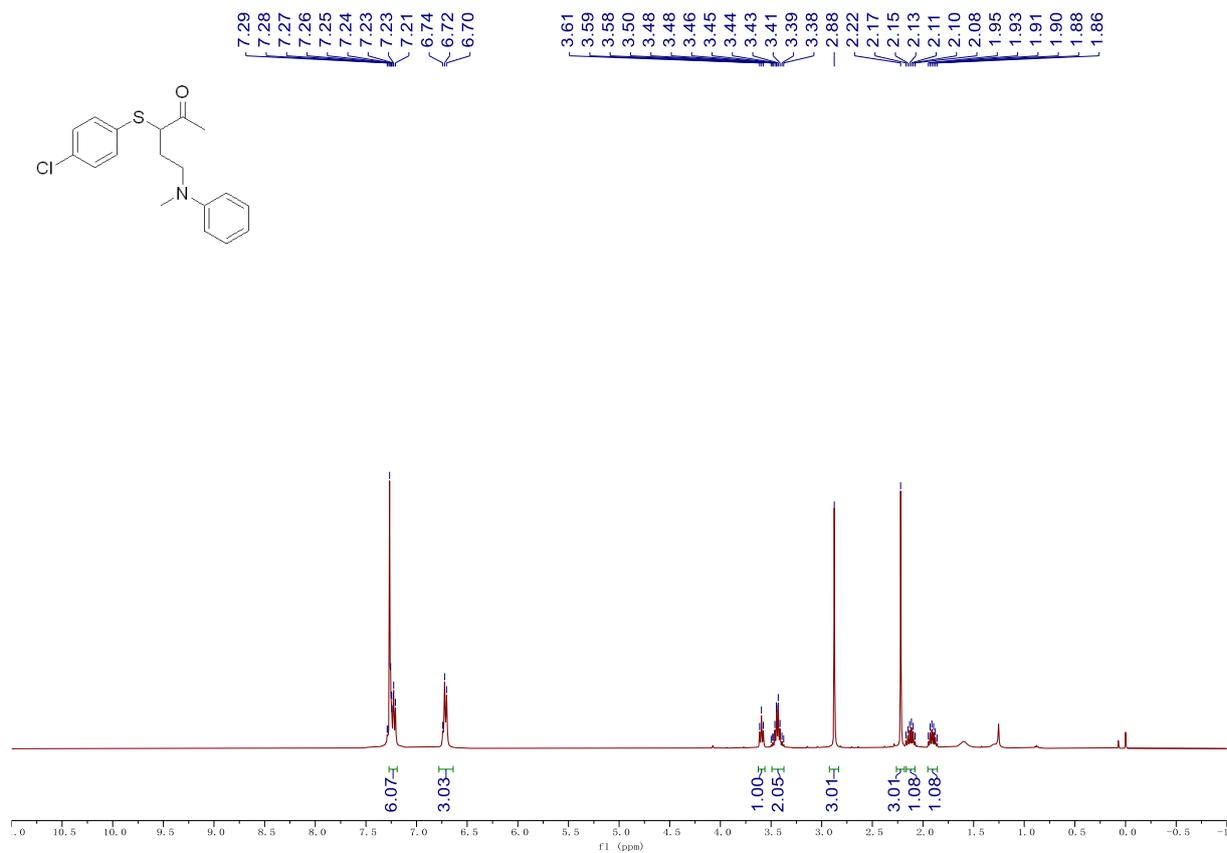
¹H NMR Spectrum of 5b (400 MHz) in CDCl₃



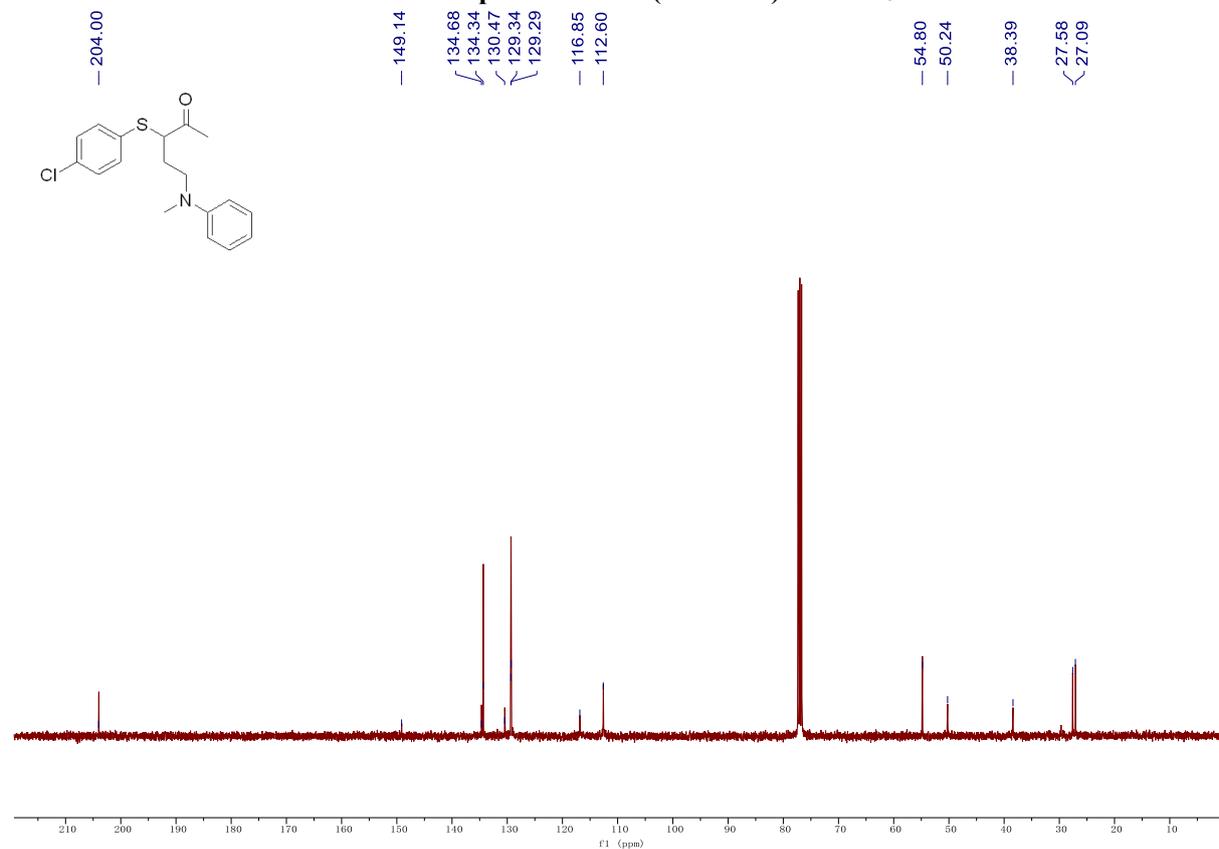
¹³C NMR Spectrum of 5b (100 MHz) in CDCl₃



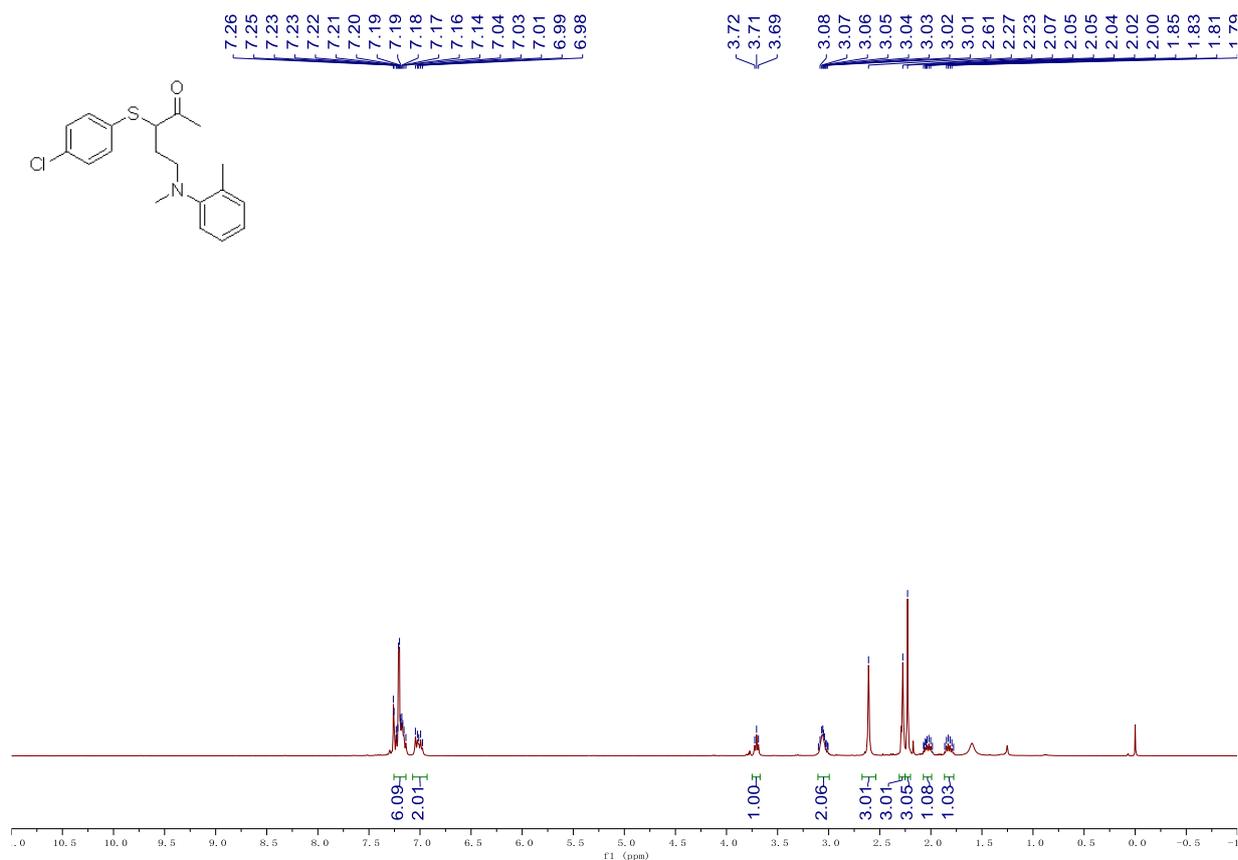
¹H NMR Spectrum of 5c (400 MHz) in CDCl₃



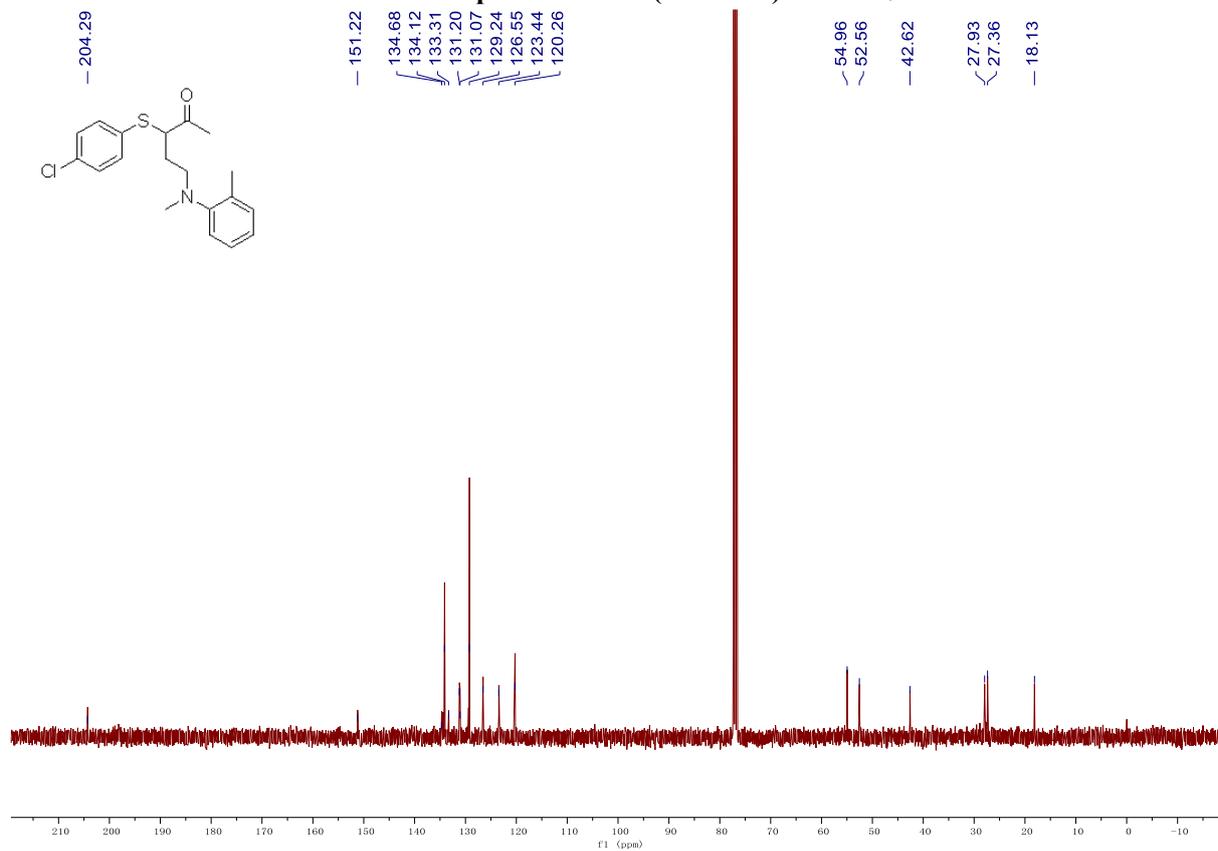
¹³C NMR Spectrum of 5c (100 MHz) in CDCl₃



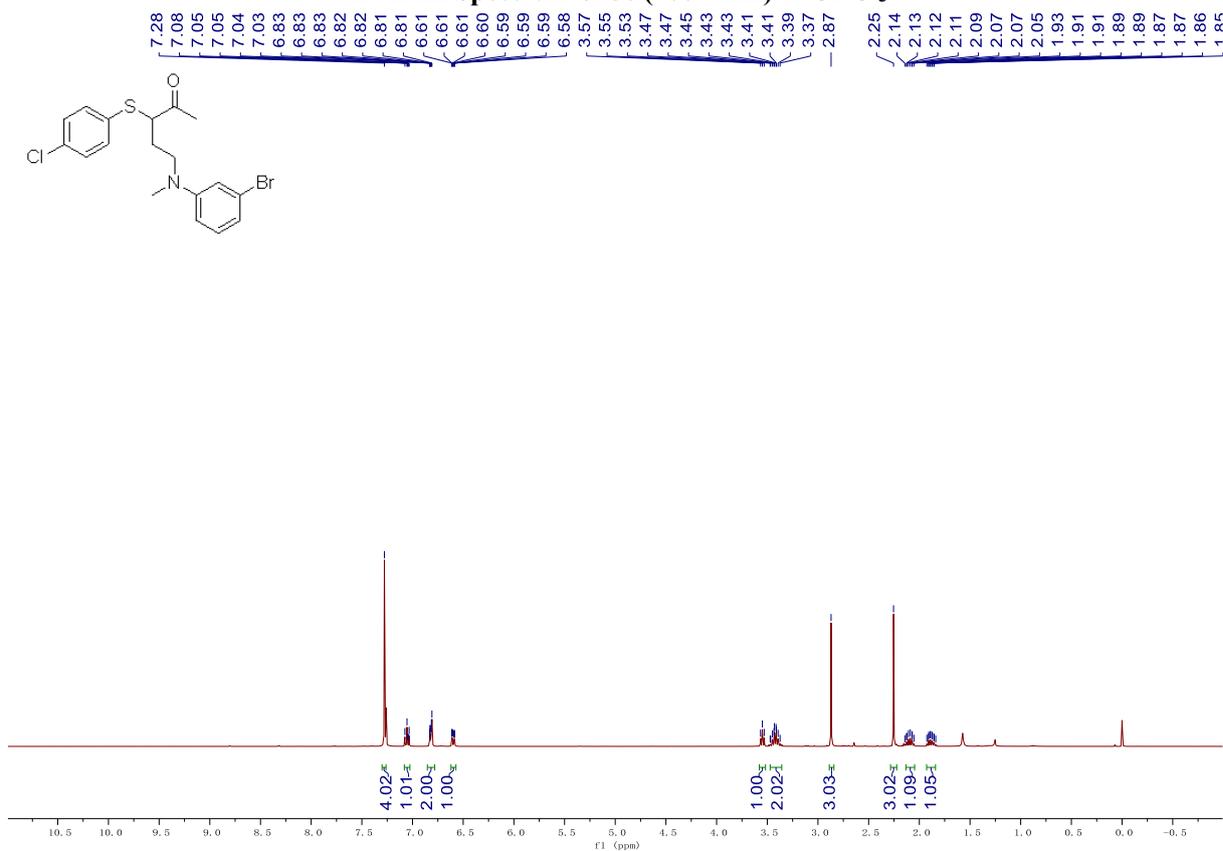
¹H NMR Spectrum of 5d (400 MHz) in CDCl₃



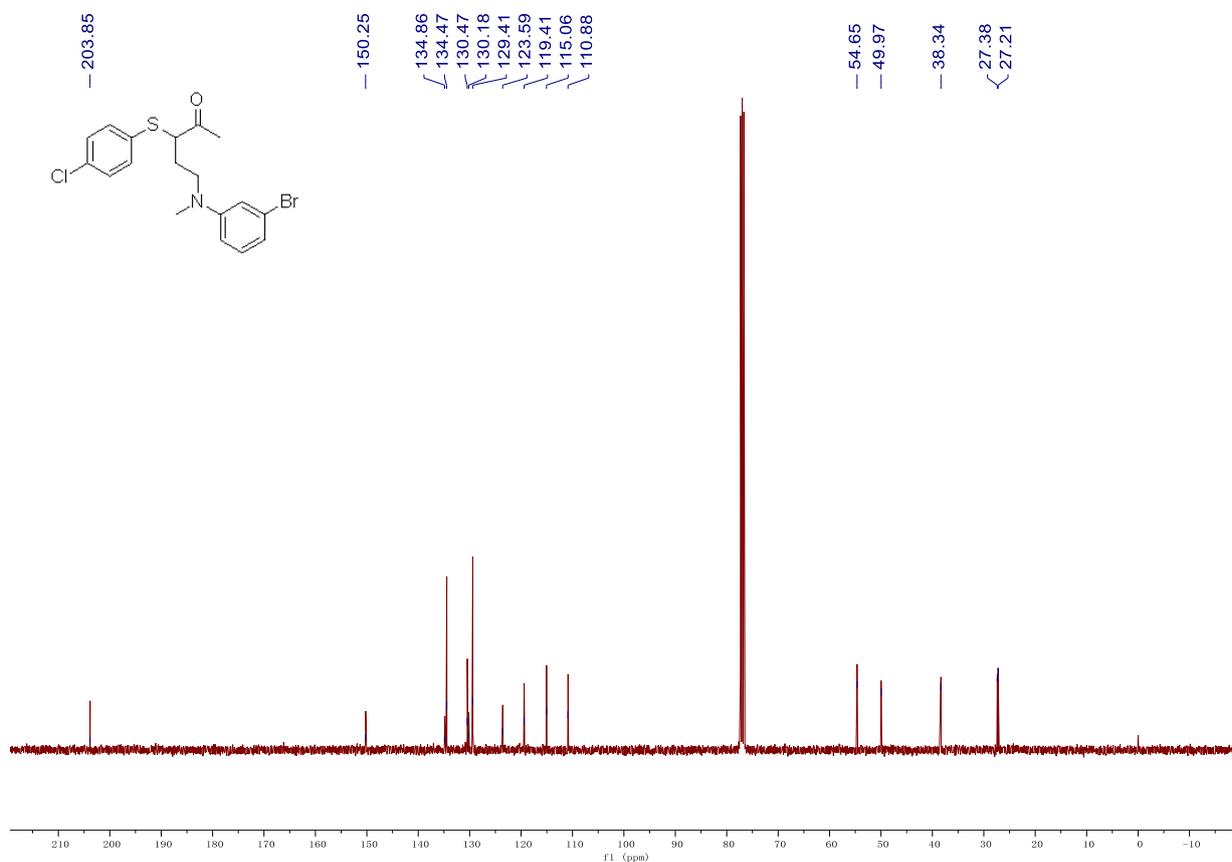
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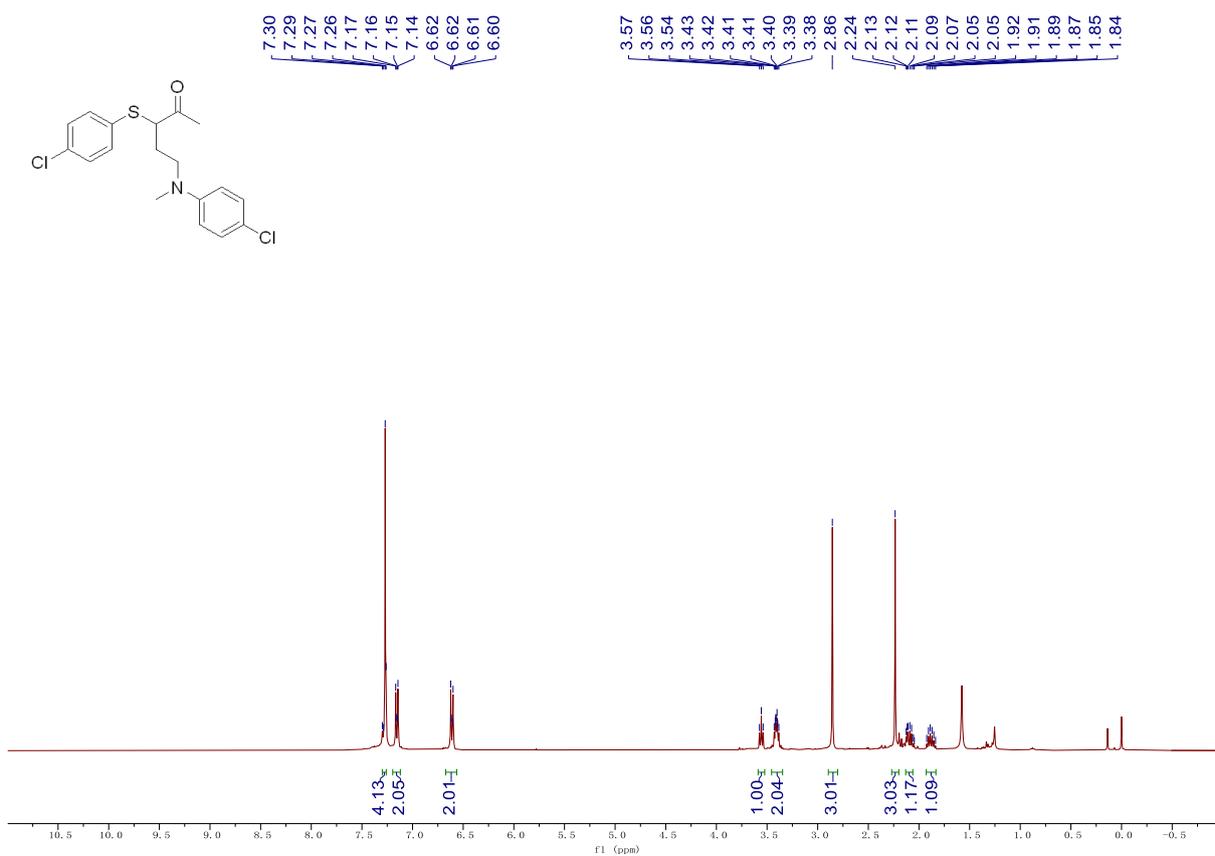
¹H NMR Spectrum of 5e (400 MHz) in CDCl₃



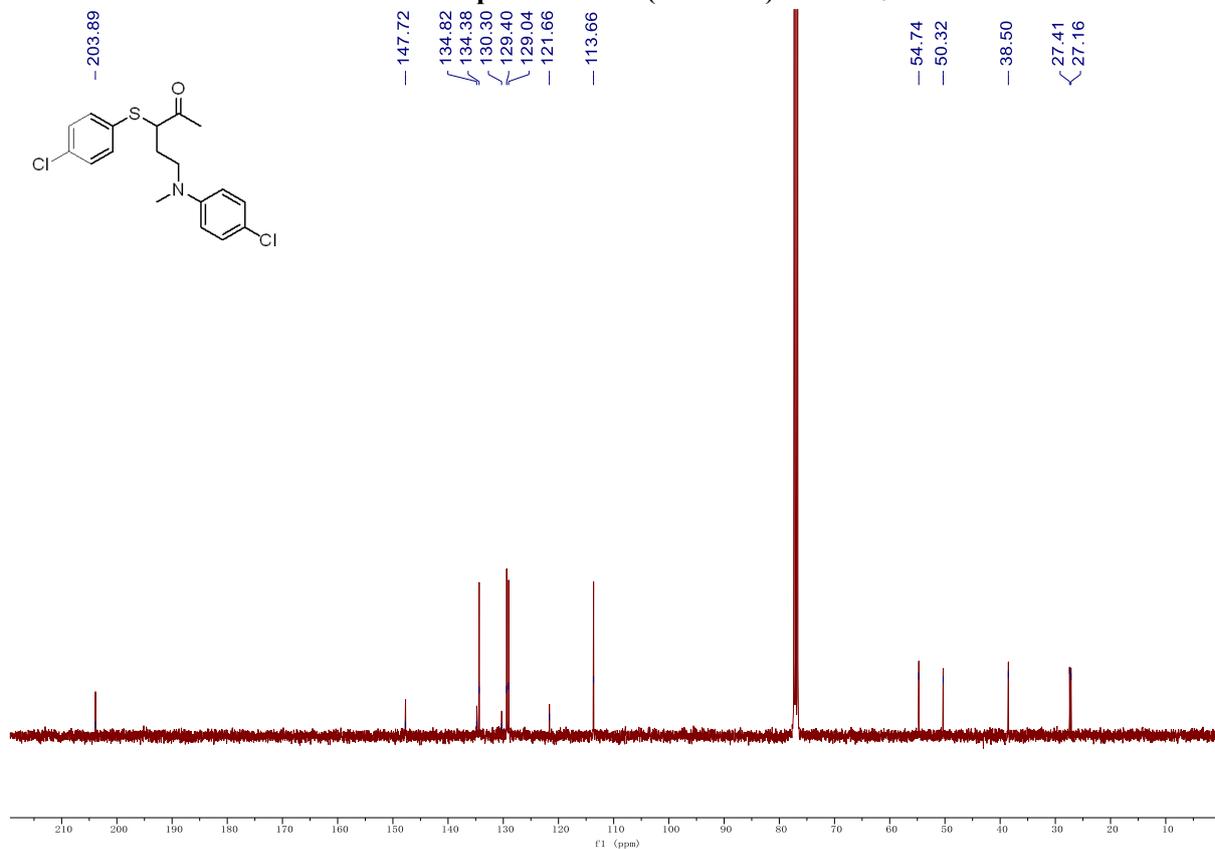
¹³C NMR Spectrum of 5e (100 MHz) in CDCl₃



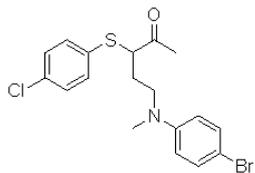
¹H NMR Spectrum of 5f (400 MHz) in CDCl₃



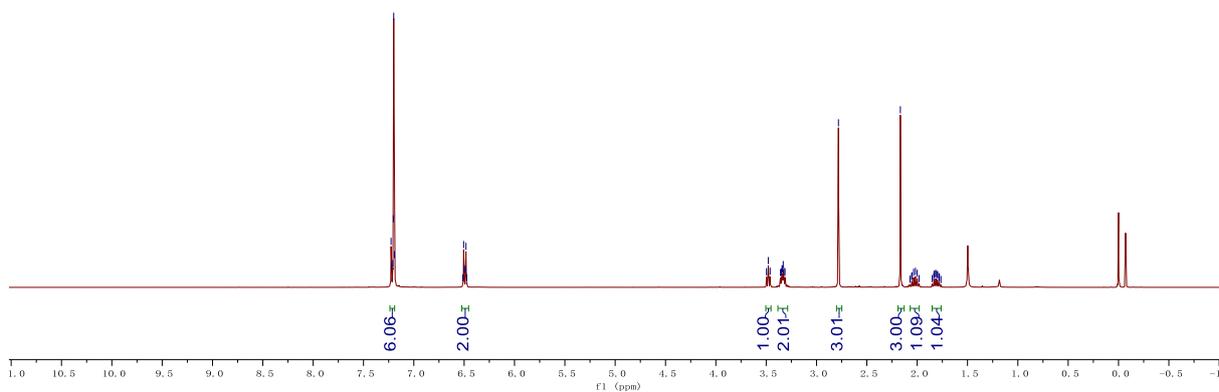
¹³C NMR Spectrum of 5f (100 MHz) in CDCl₃



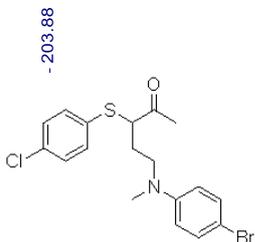
¹H NMR Spectrum of 5g (400 MHz) in CDCl₃



7.23, 7.22, 7.21, 7.20, 7.20, 7.19, 6.51, 6.51, 6.50, 6.49, 6.48, 6.47, 3.50, 3.48, 3.46, 3.36, 3.35, 3.34, 3.34, 3.33, 3.32, 3.31, 2.78, 2.17, 2.07, 2.05, 2.05, 2.04, 2.02, 2.00, 1.98, 1.85, 1.84, 1.83, 1.82, 1.80, 1.80, 1.78, 1.78

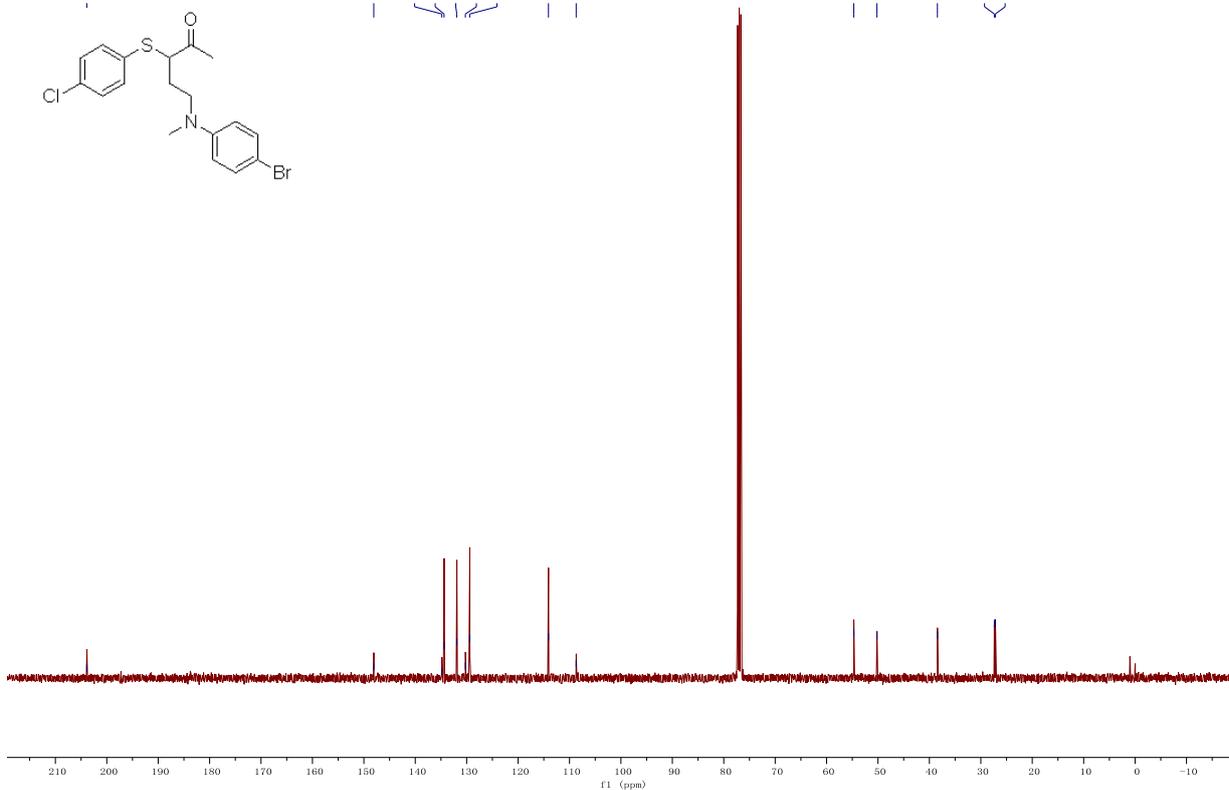


¹³C NMR Spectrum of 5g (100 MHz) in CDCl₃

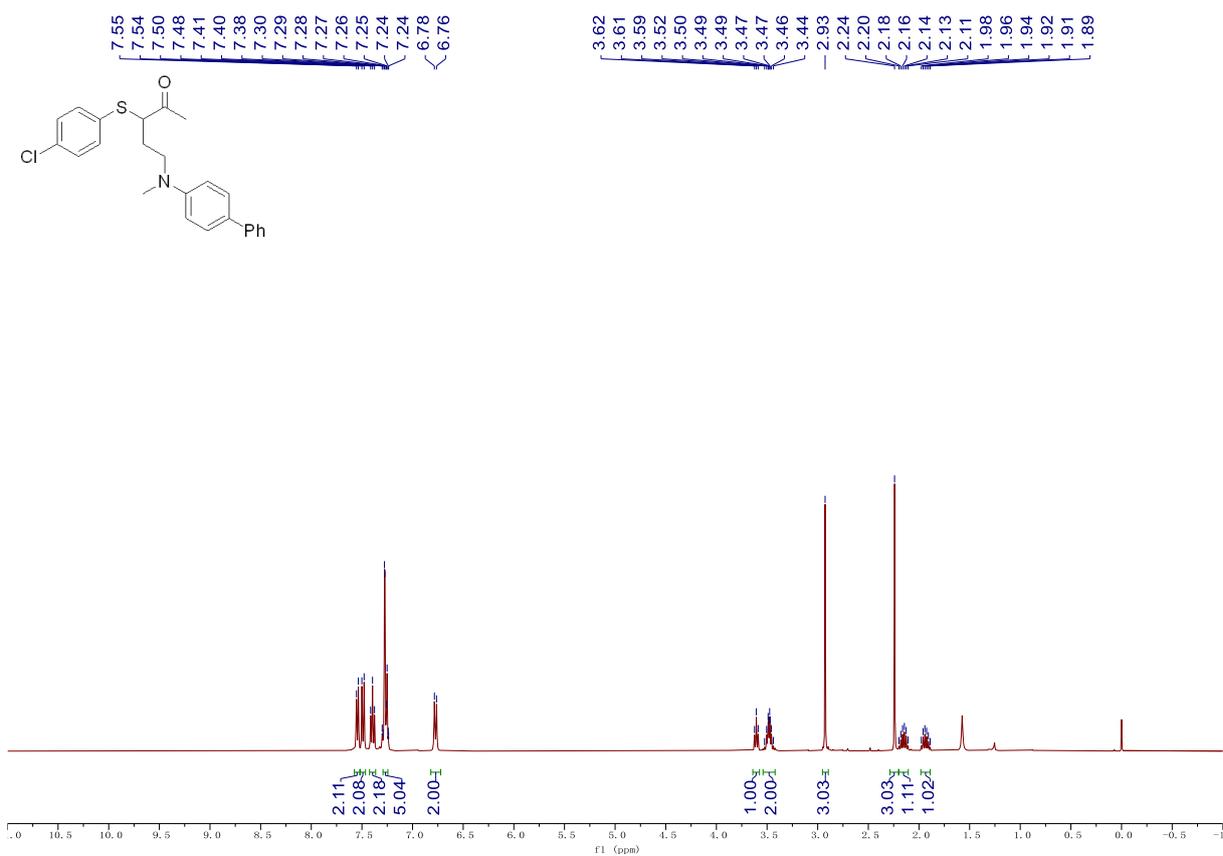


-203.88

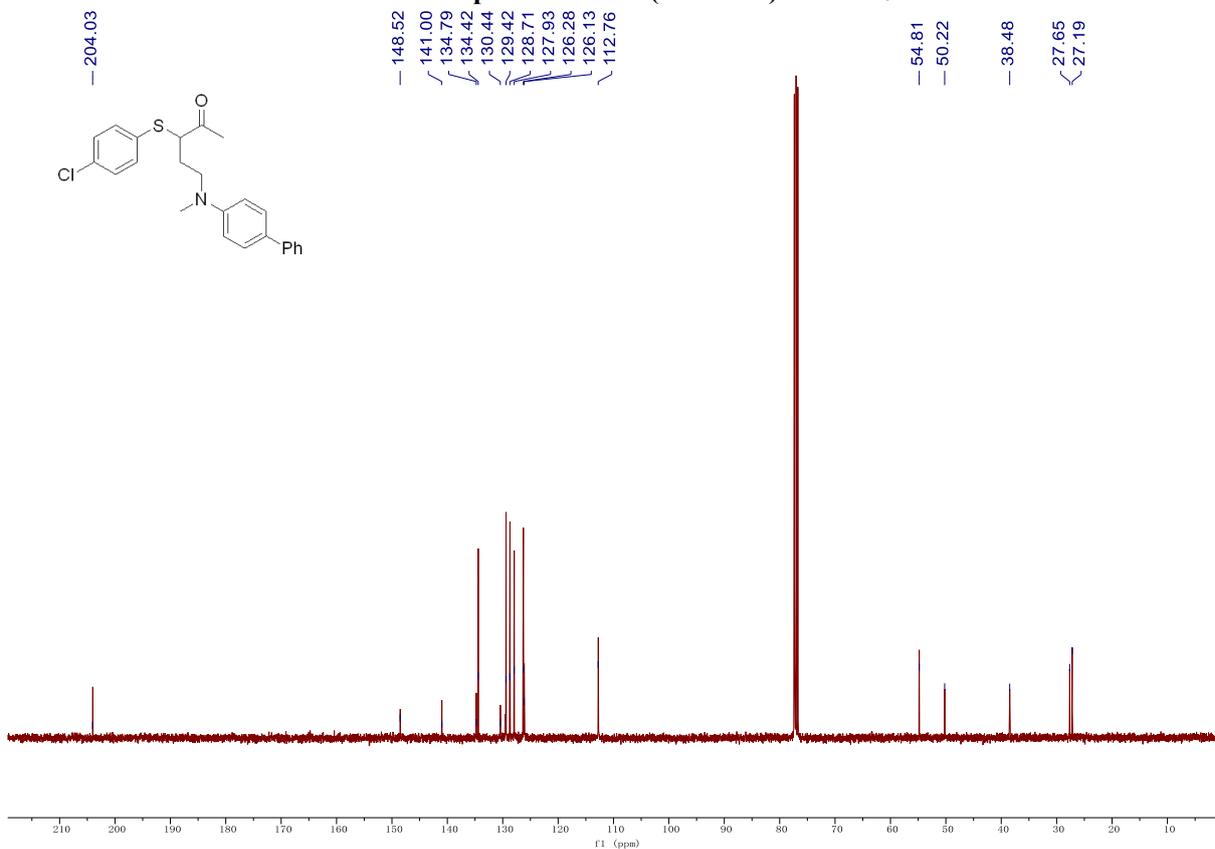
148.07, 134.83, 134.40, 131.93, 130.26, 129.40, 114.09, 108.71, 54.71, 50.21, 38.44, 27.37, 27.17



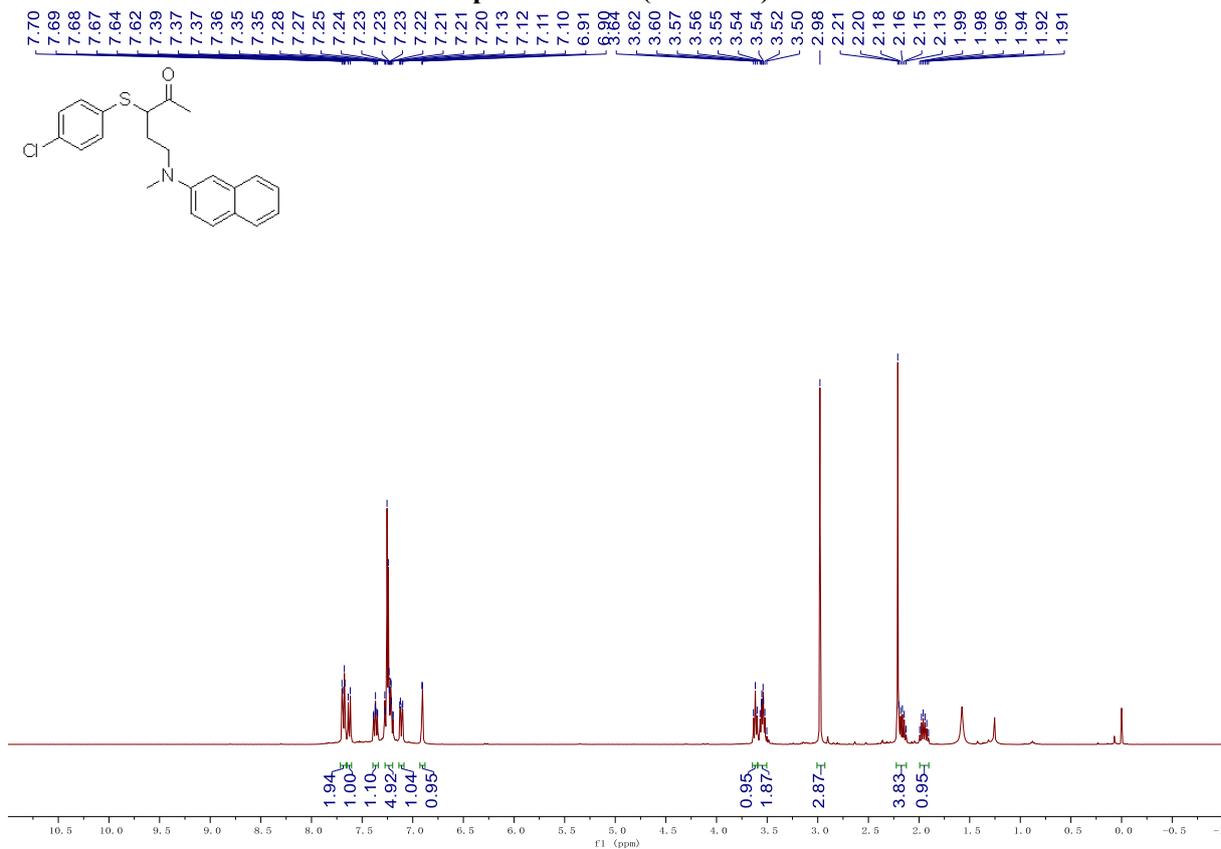
¹H NMR Spectrum of 5h (400 MHz) in CDCl₃



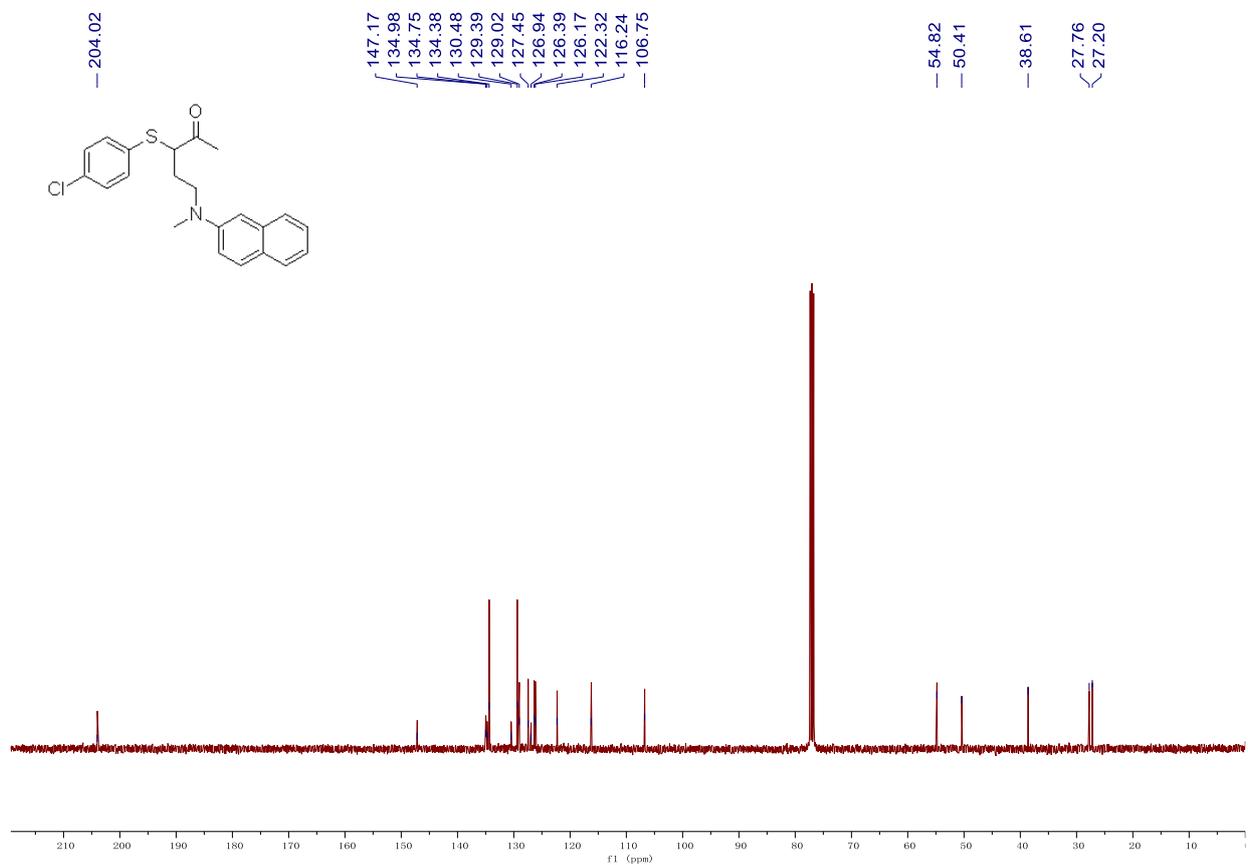
¹³C NMR Spectrum of 5h (100 MHz) in CDCl₃



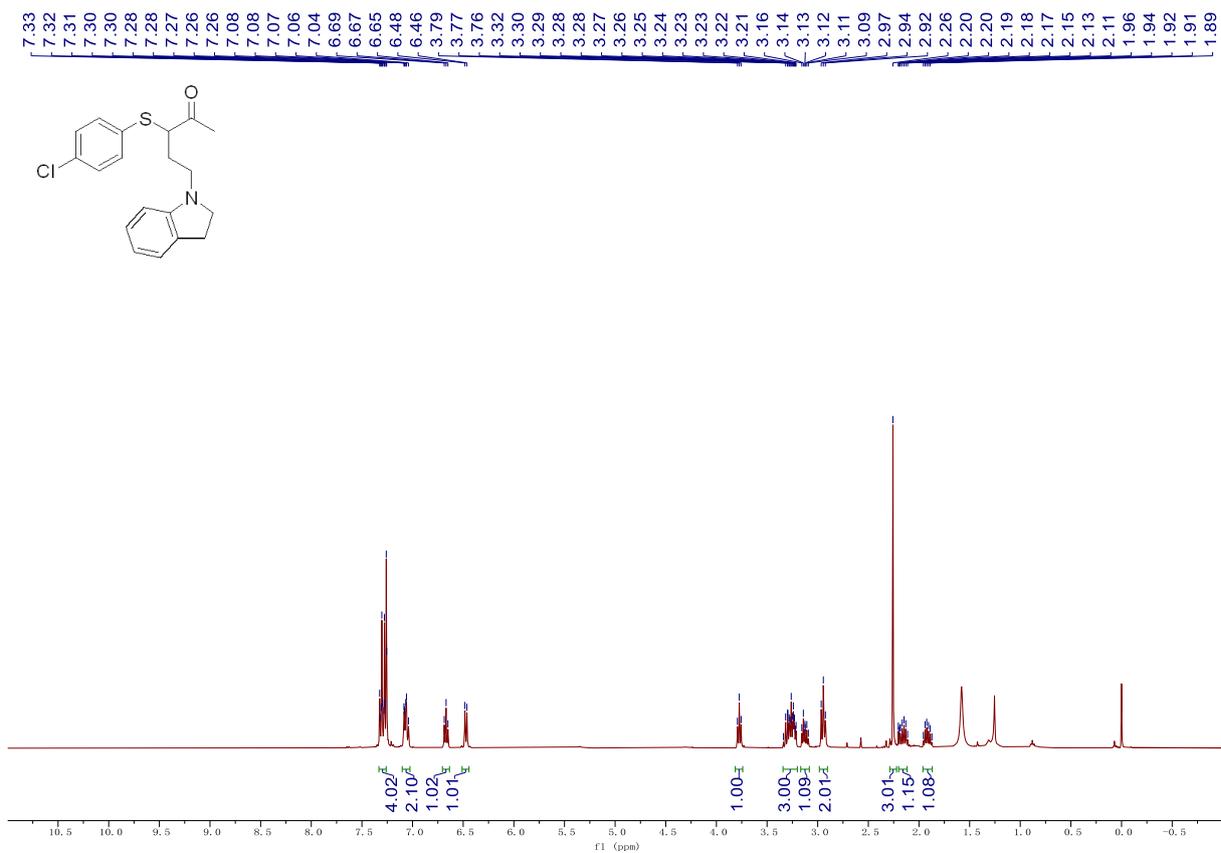
¹H NMR Spectrum of 5i (400 MHz) in CDCl₃



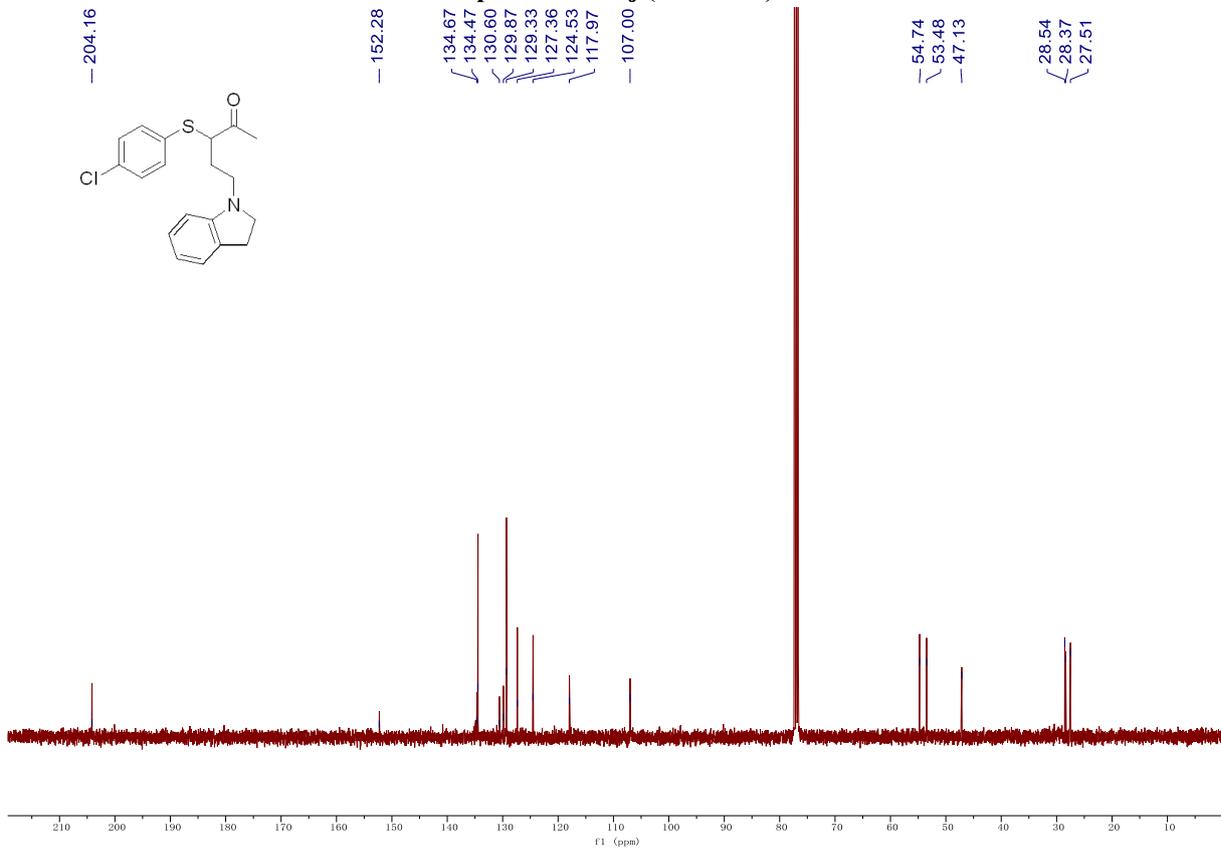
¹³C NMR Spectrum of 5i (100 MHz) in CDCl₃



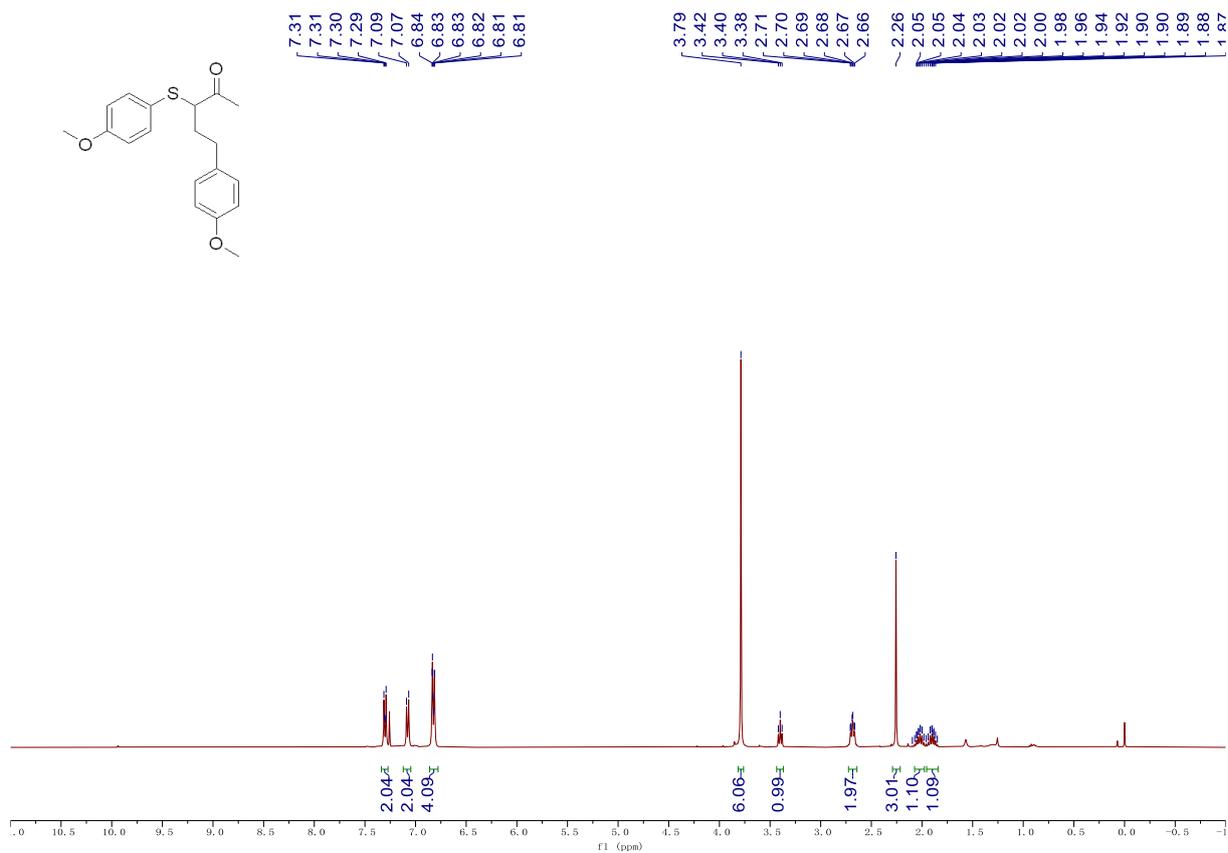
¹H NMR Spectrum of 5j (400 MHz) in CDCl₃



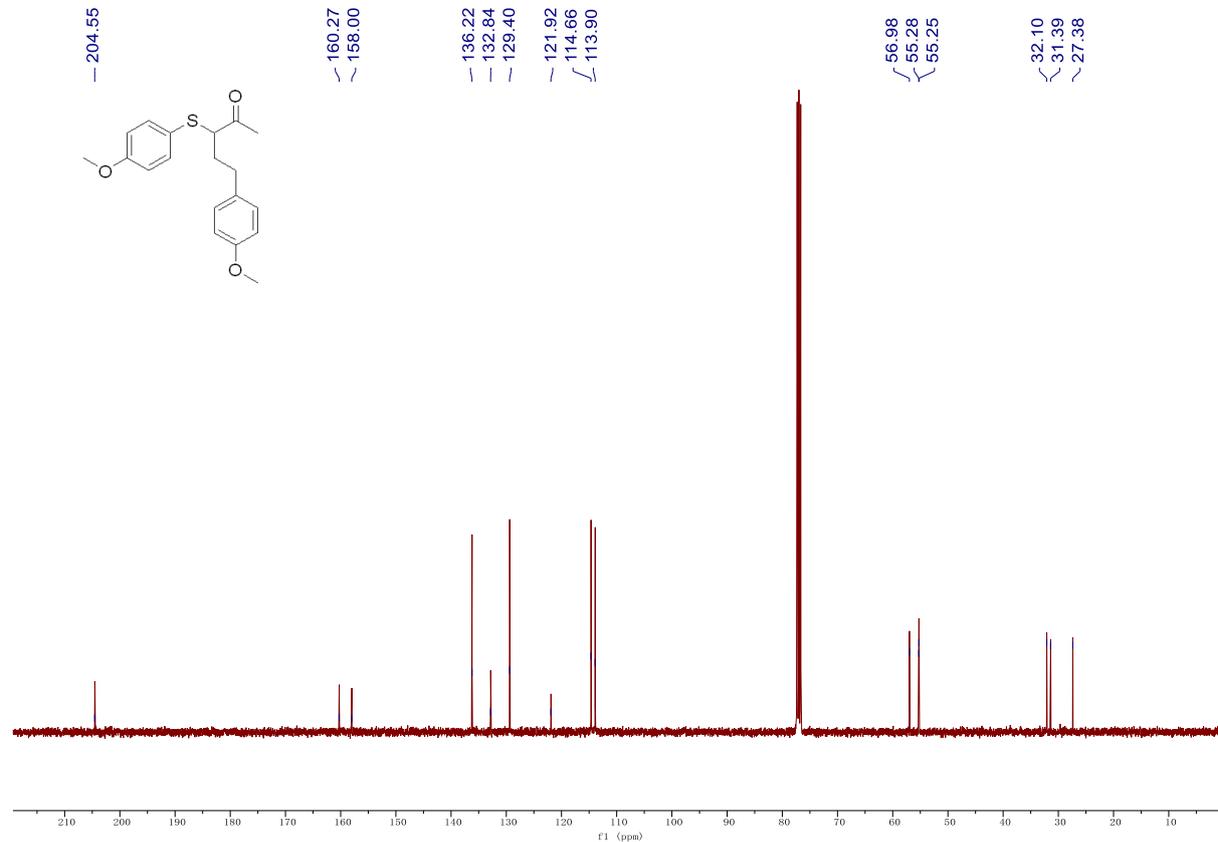
¹³C NMR Spectrum of 5j (100 MHz) in CDCl₃



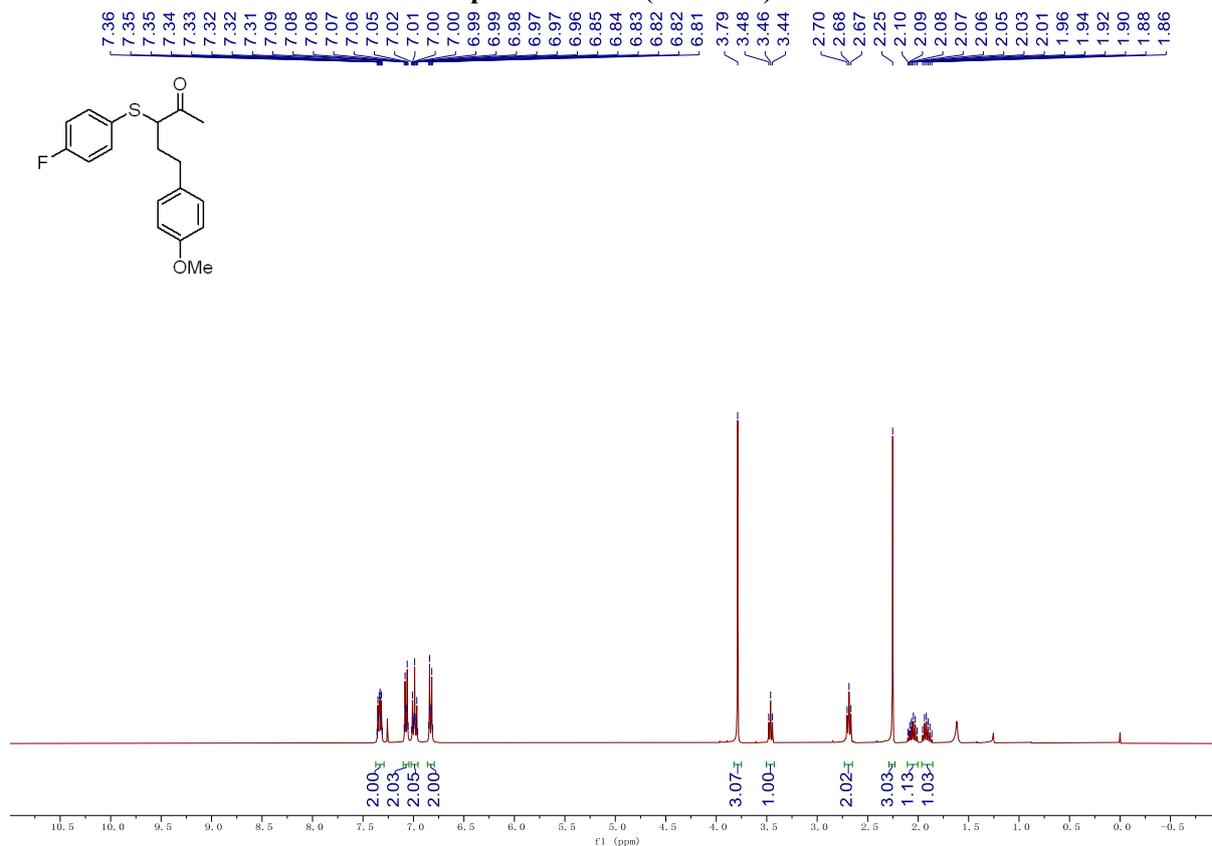
¹H NMR Spectrum of 6b (400 MHz) in CDCl₃



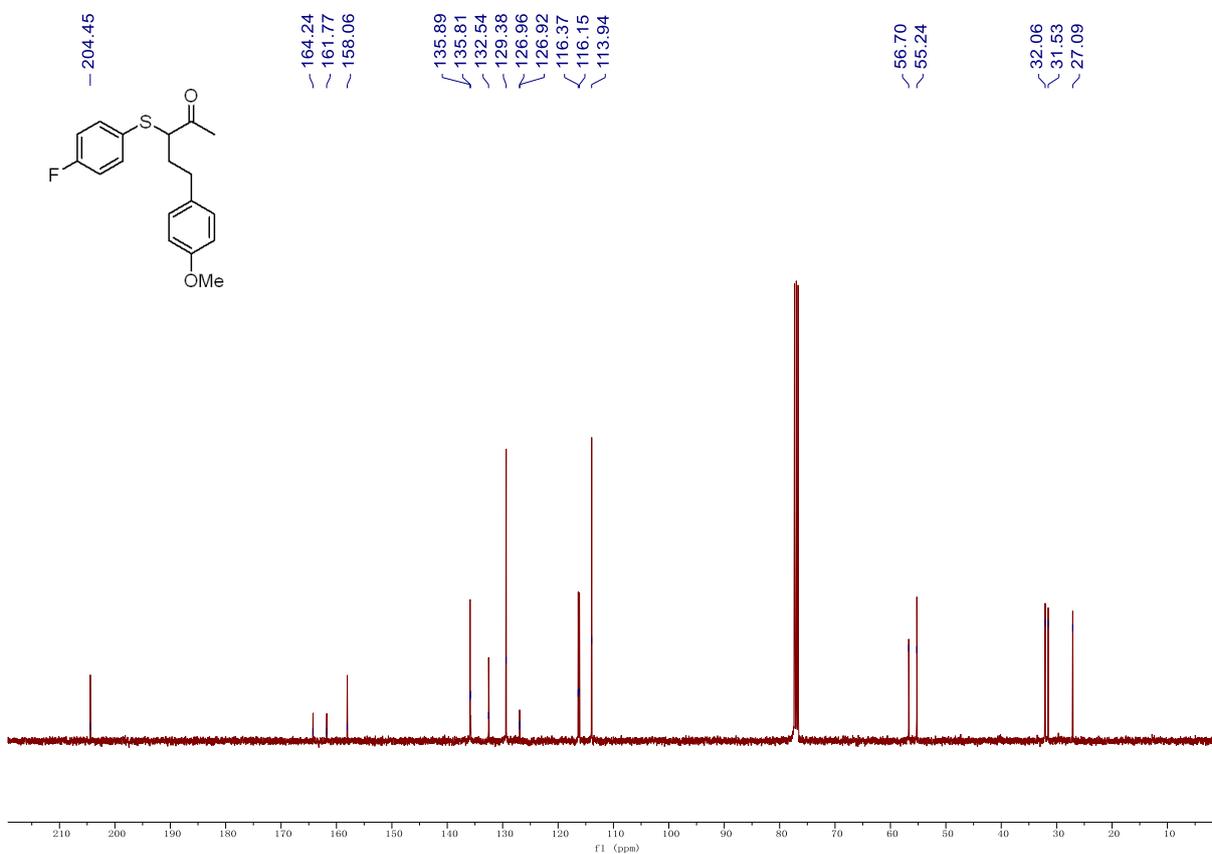
¹³C NMR Spectrum of 6b (100 MHz) in CDCl₃



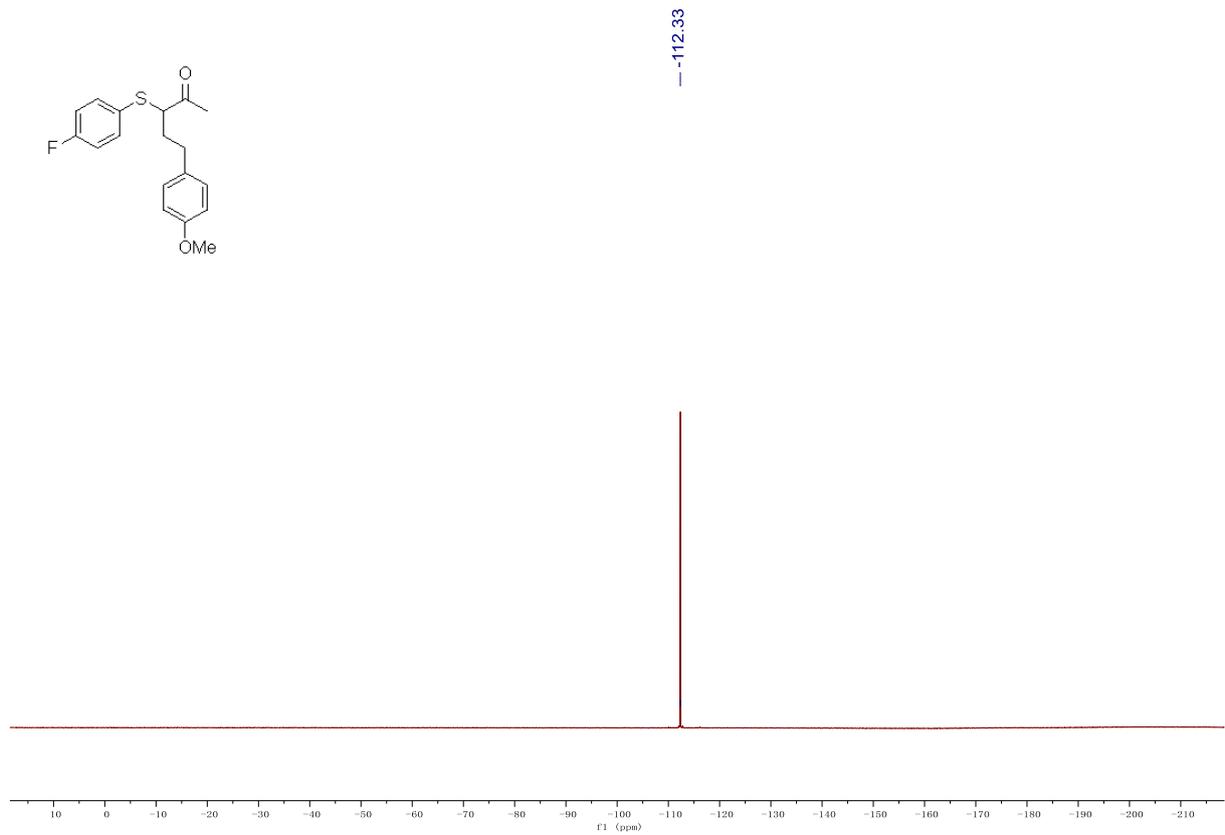
¹H NMR Spectrum of 6c (400 MHz) in CDCl₃



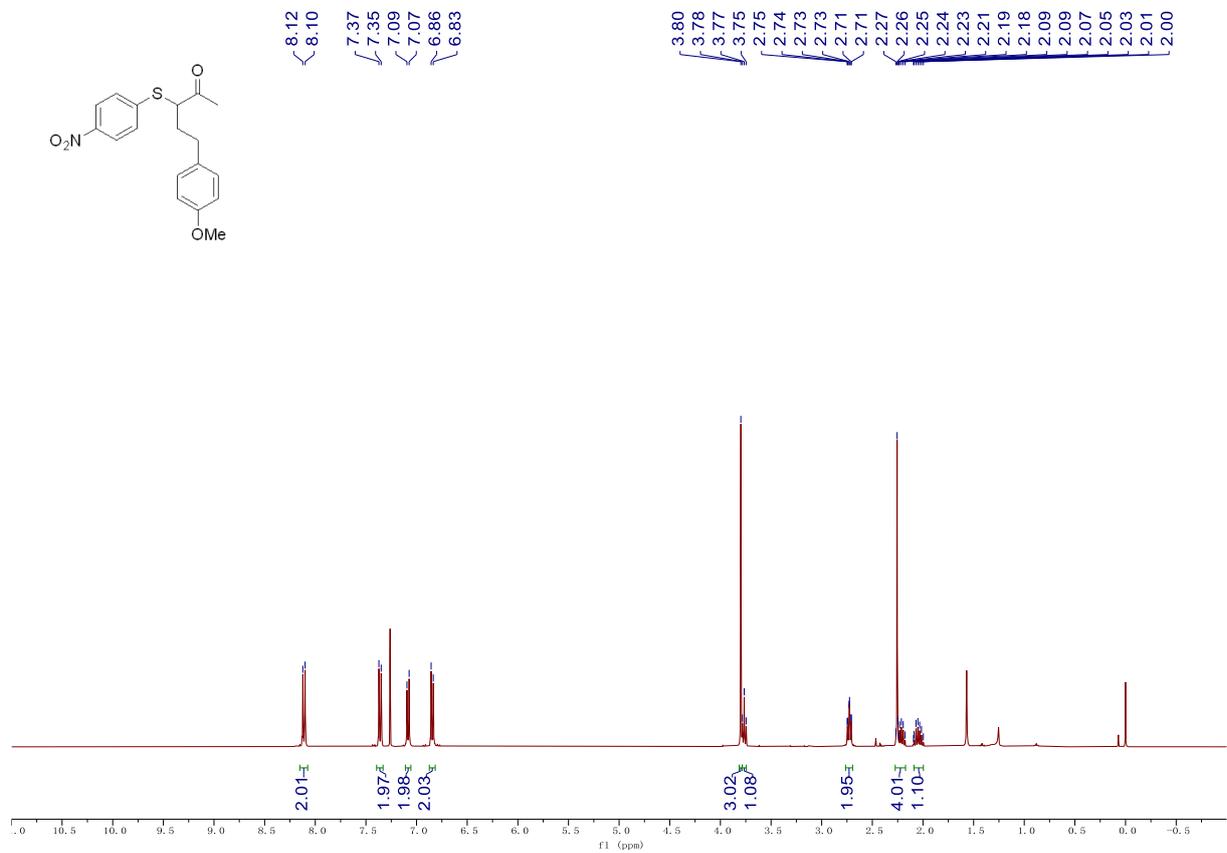
¹³C NMR Spectrum of 6c (100 MHz) in CDCl₃



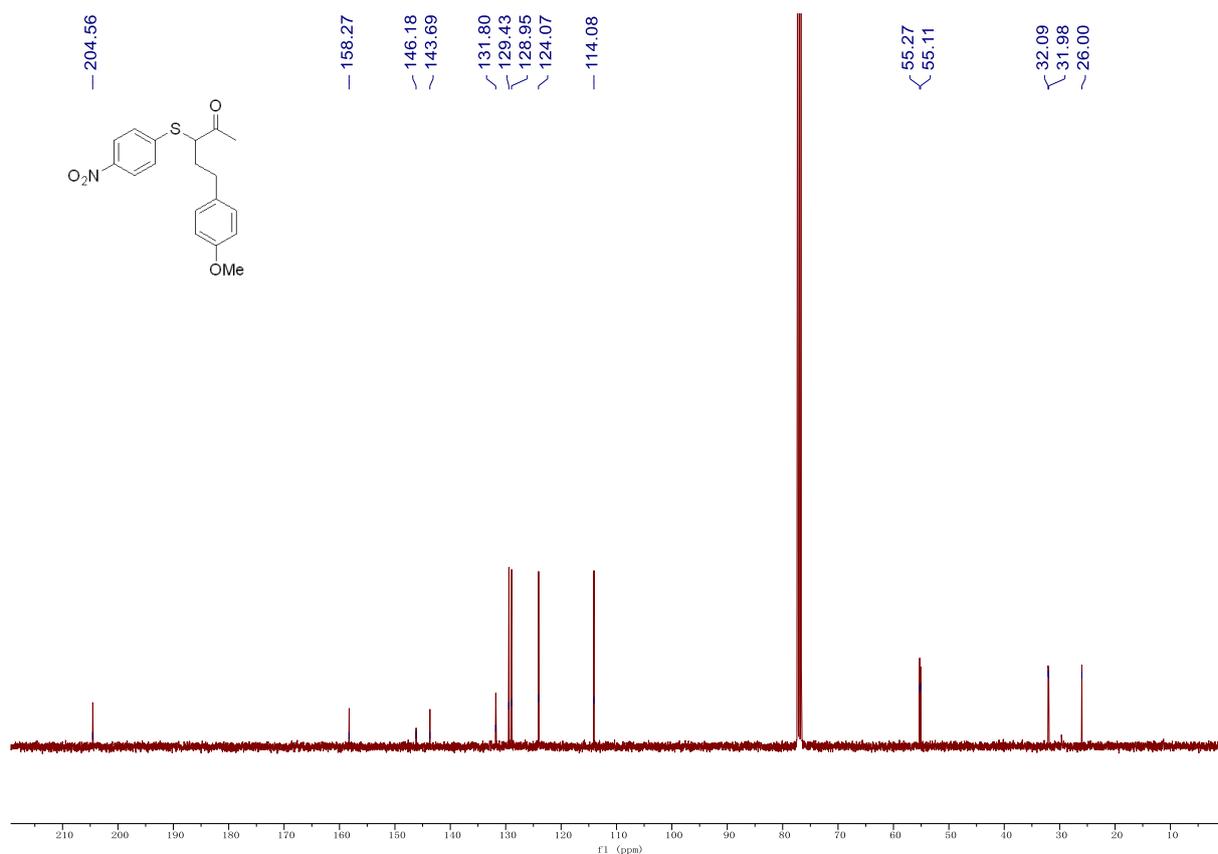
¹⁹F NMR Spectrum of 6c (376 MHz) in CDCl₃



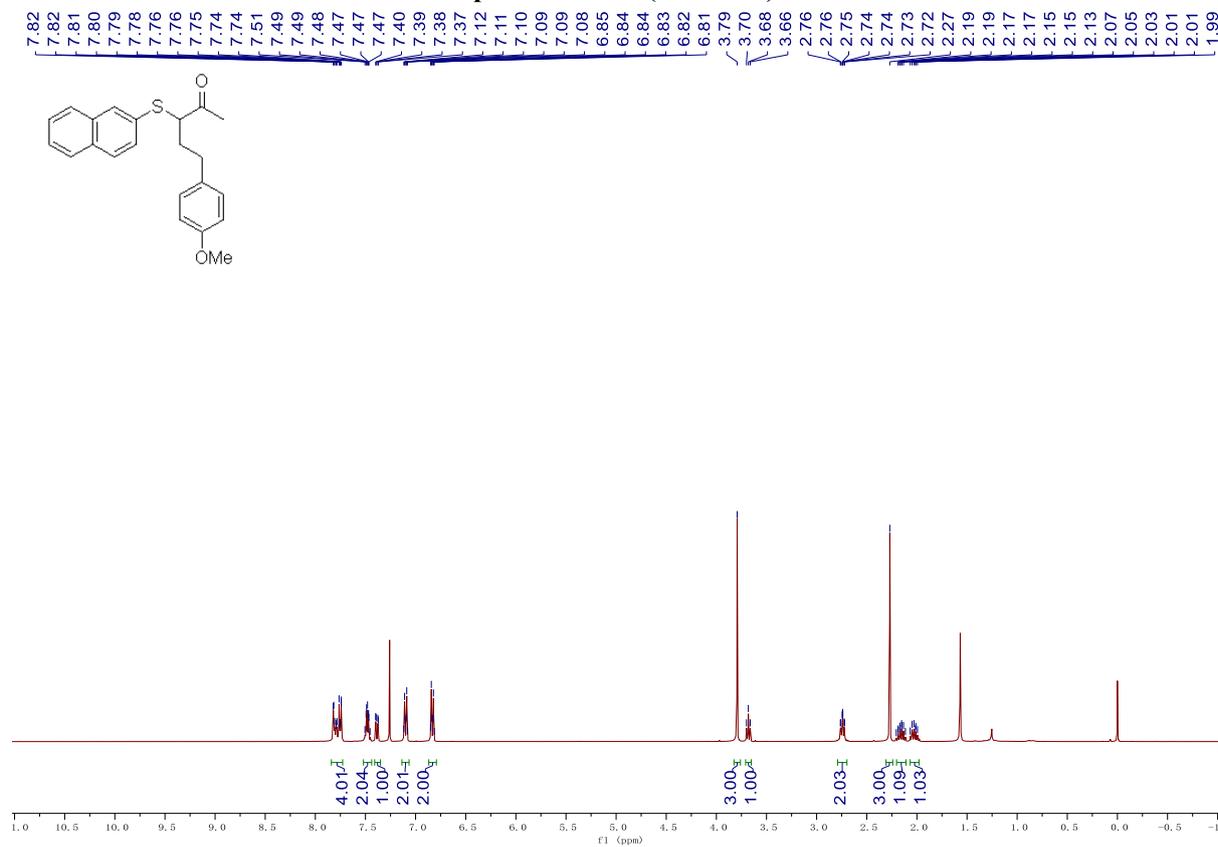
¹H NMR Spectrum of 6d (400 MHz) in CDCl₃

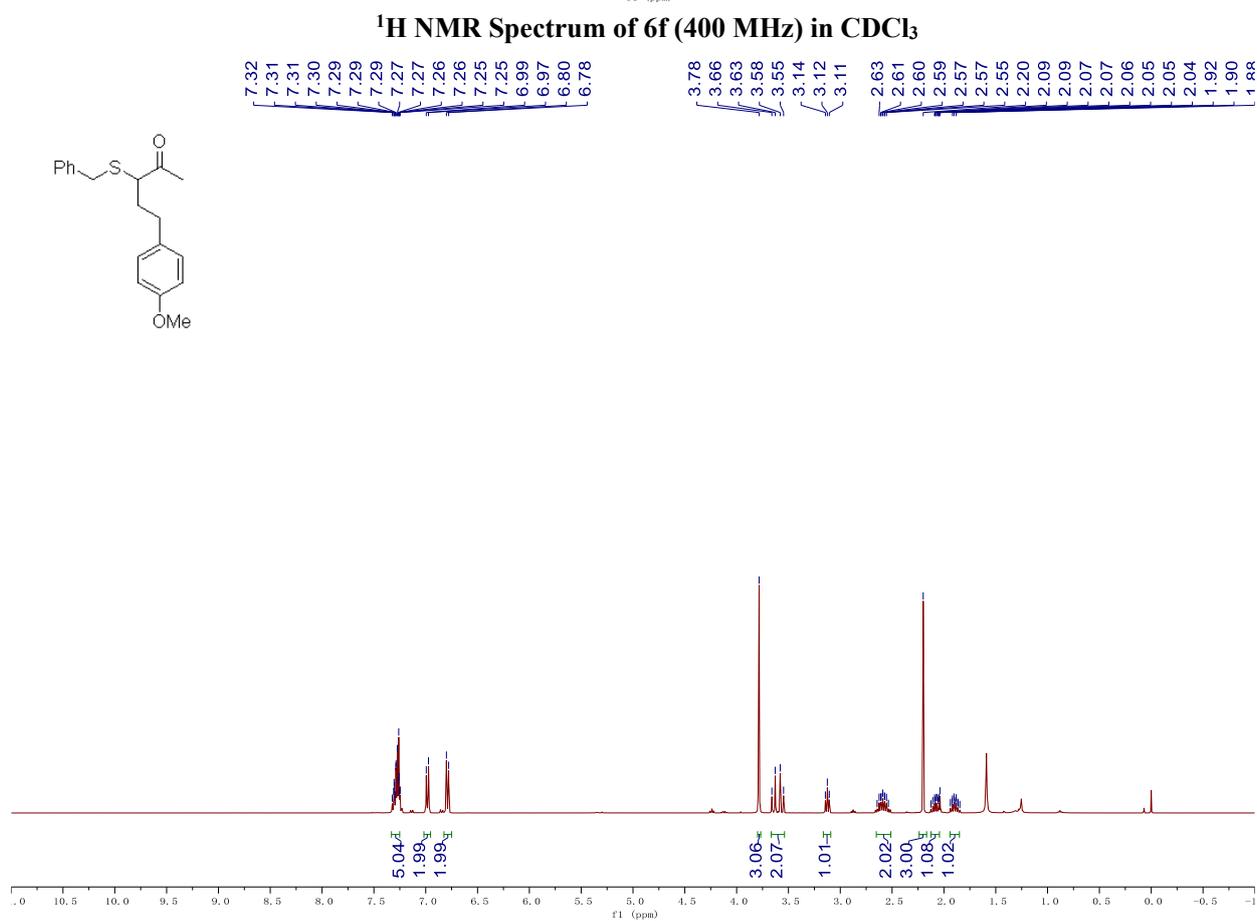
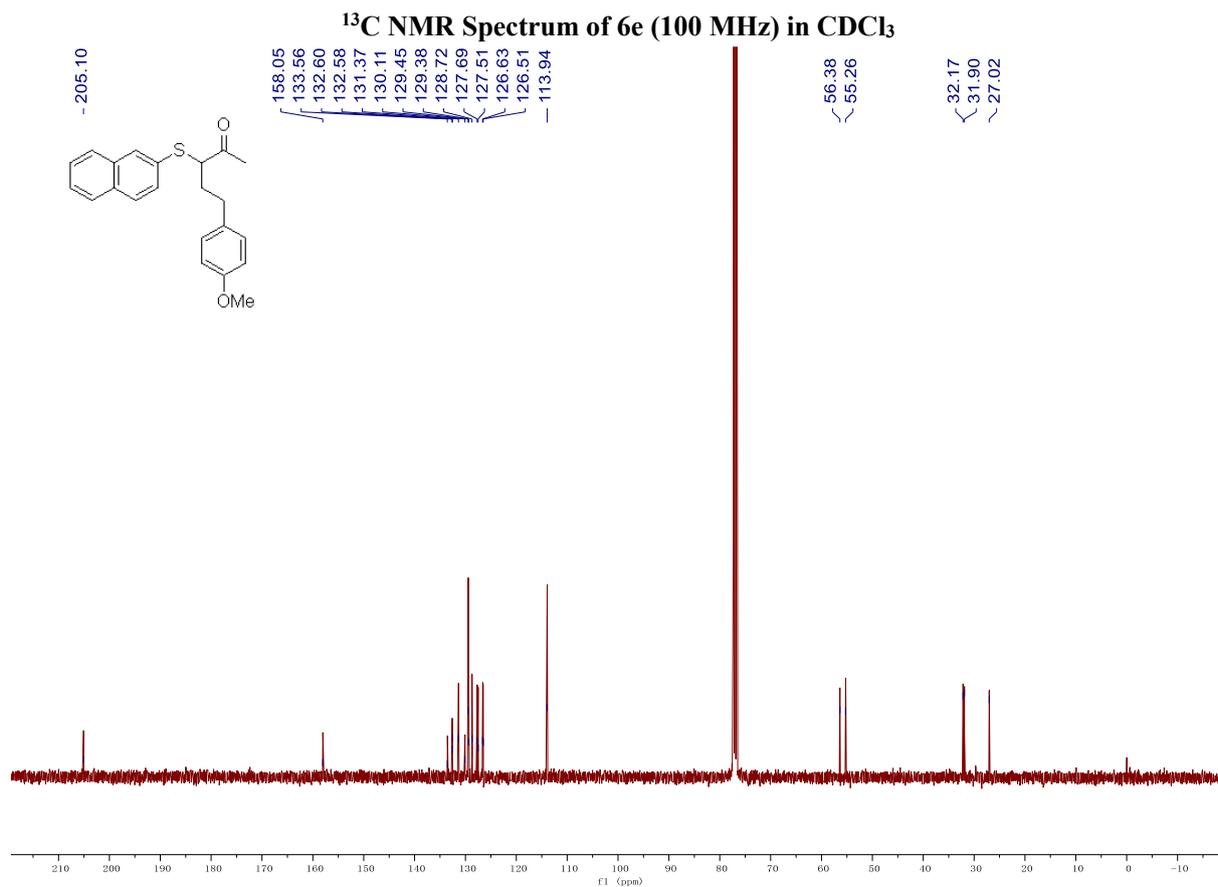


¹³C NMR Spectrum of 6d (100 MHz) in CDCl₃

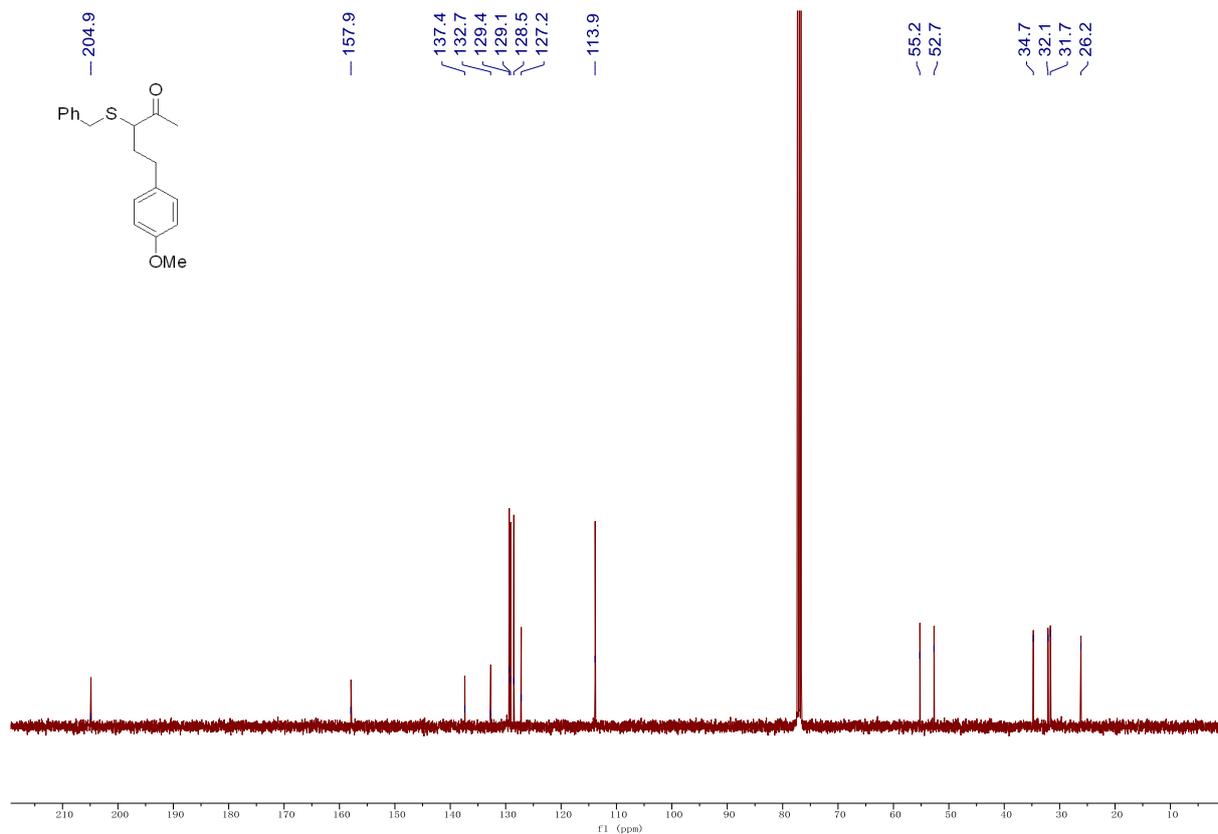


¹H NMR Spectrum of 6e (400 MHz) in CDCl₃

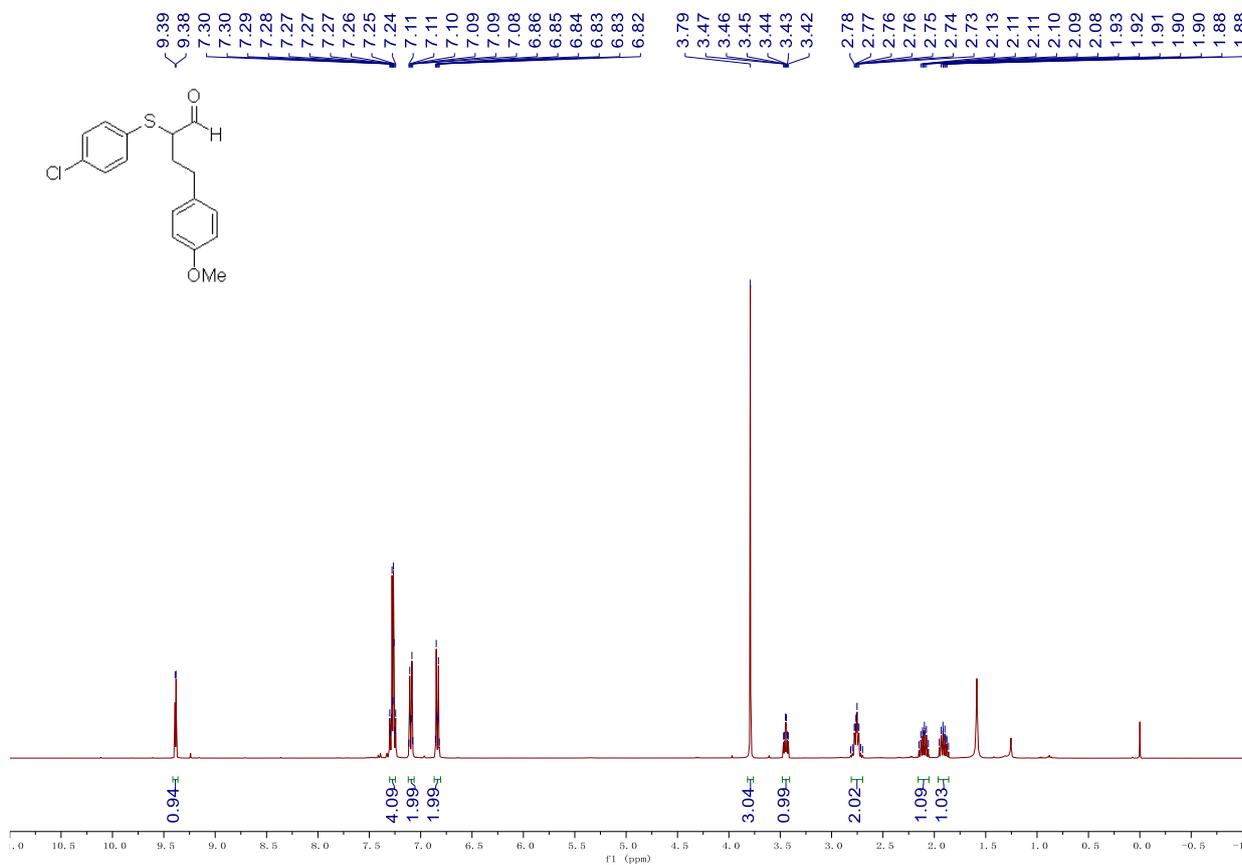




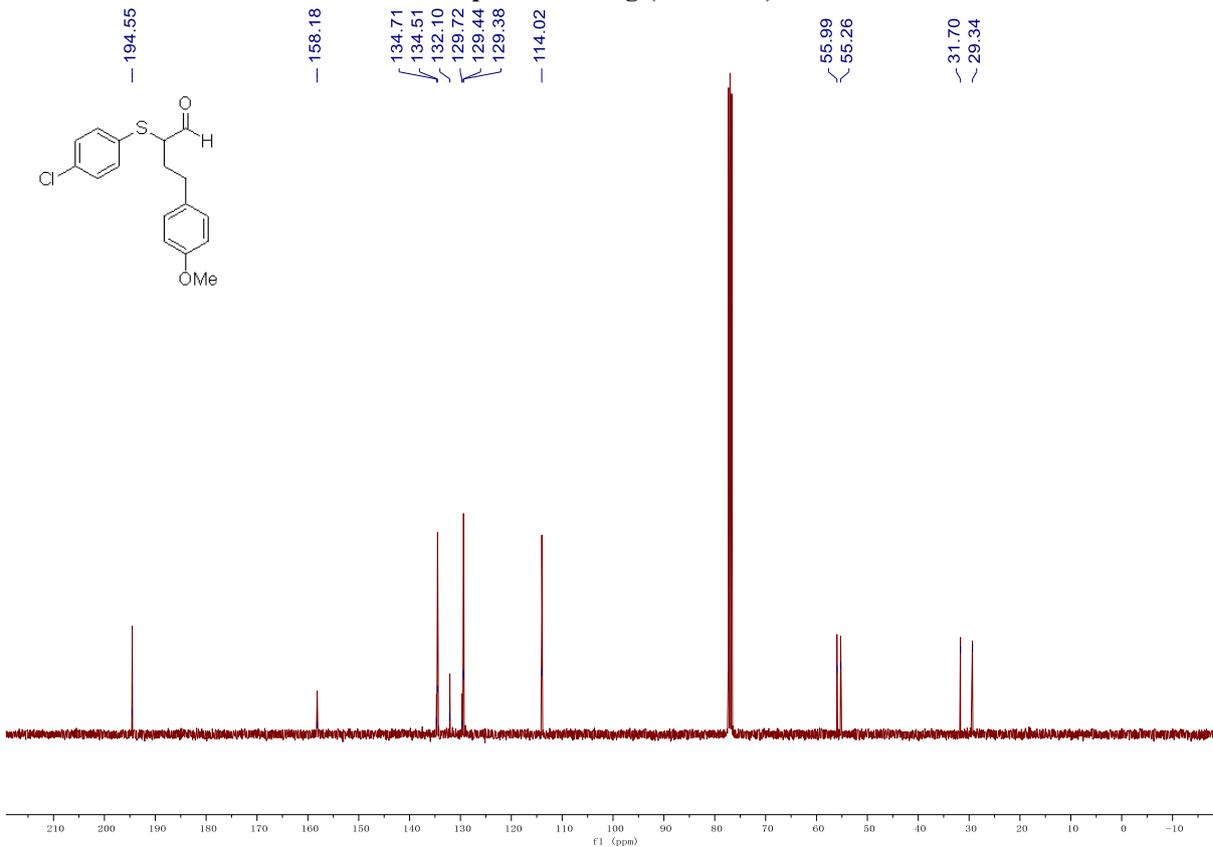
¹³C NMR Spectrum of 6f (100 MHz) in CDCl₃



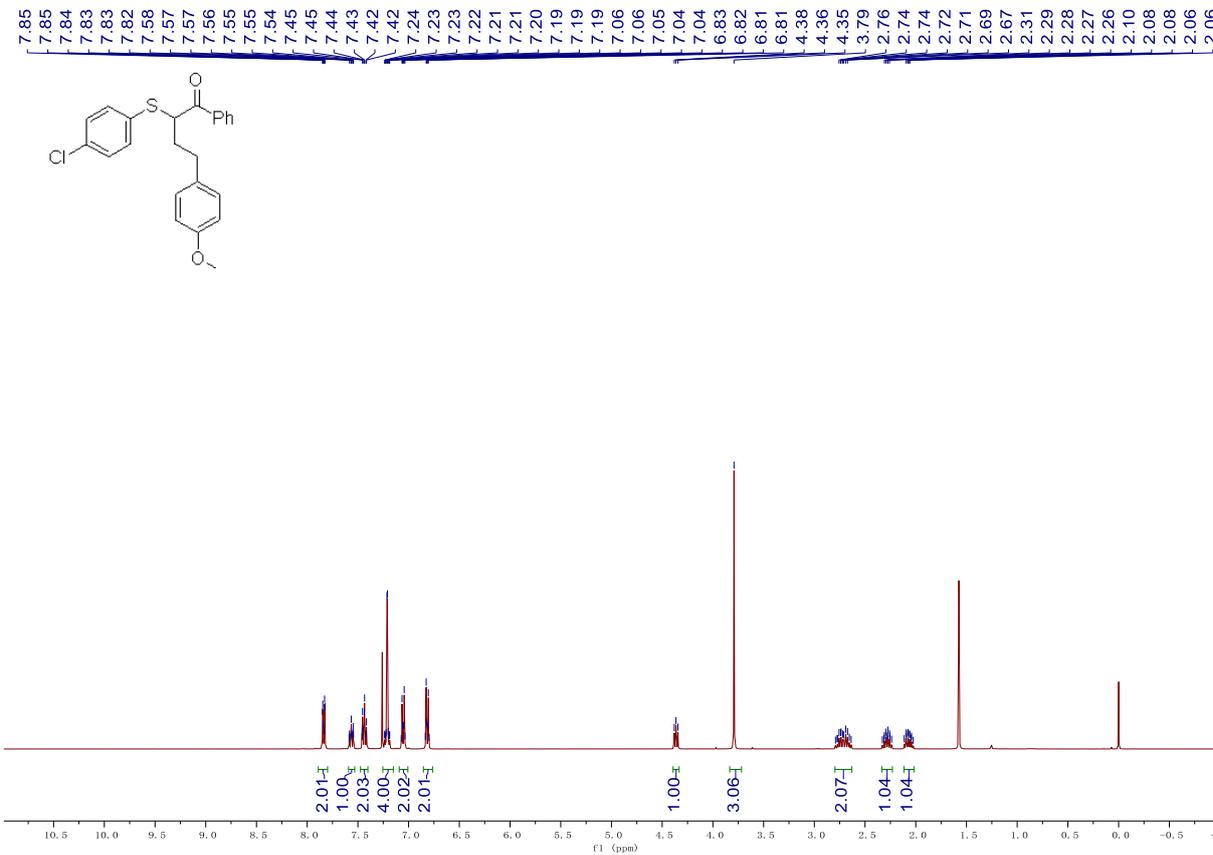
¹H NMR Spectrum of 6g (400 MHz) in CDCl₃



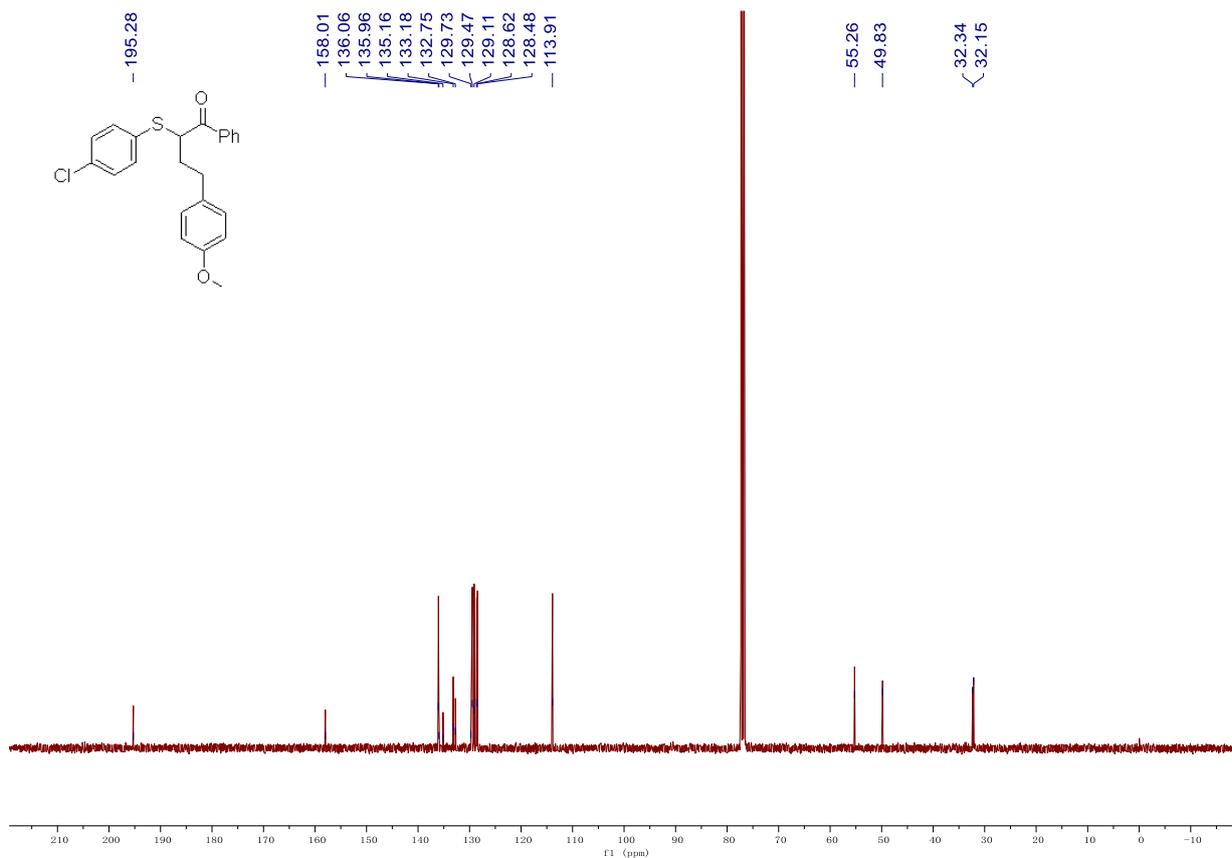
¹³C NMR Spectrum of 6g (100 MHz) in CDCl₃



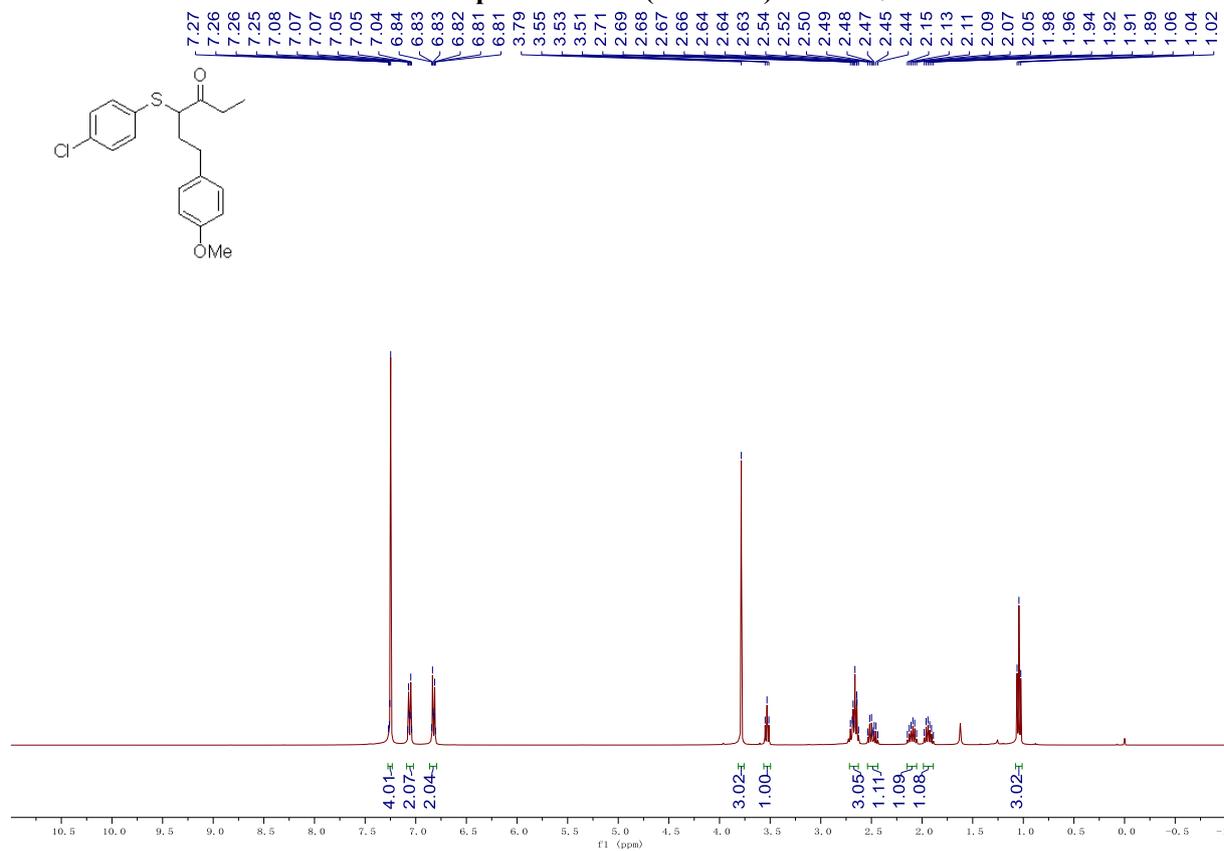
¹H NMR Spectrum of 6h (400 MHz) in CDCl₃

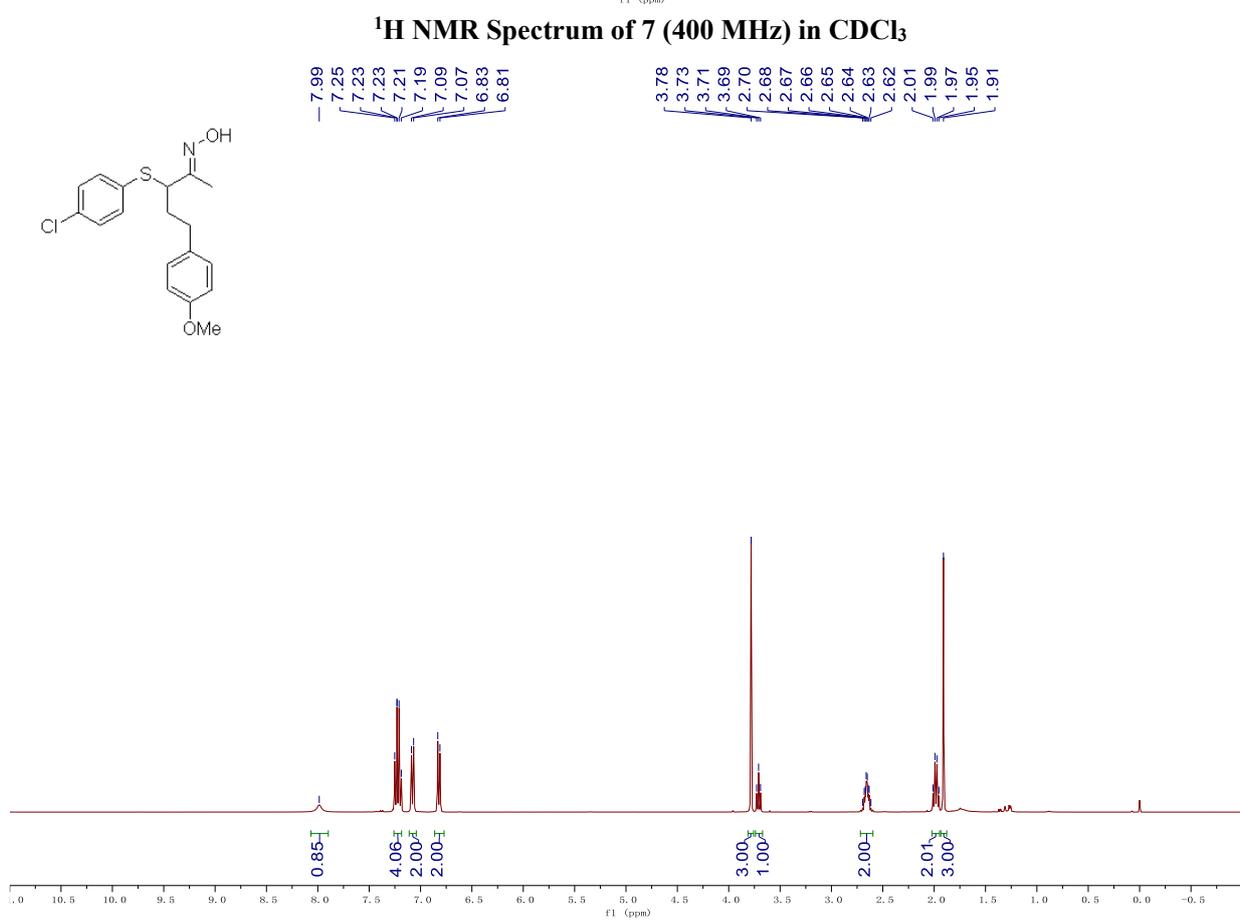
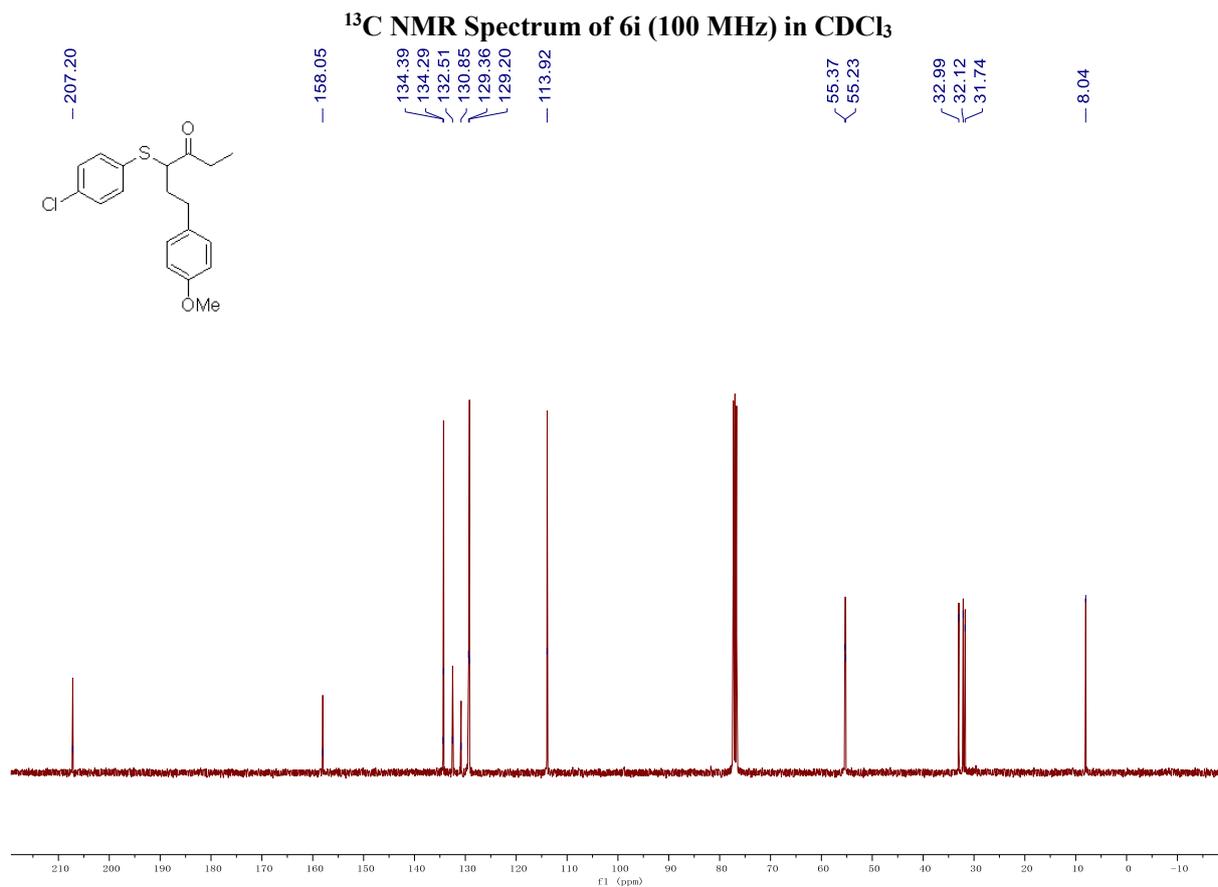


¹³C NMR Spectrum of 6h (100 MHz) in CDCl₃

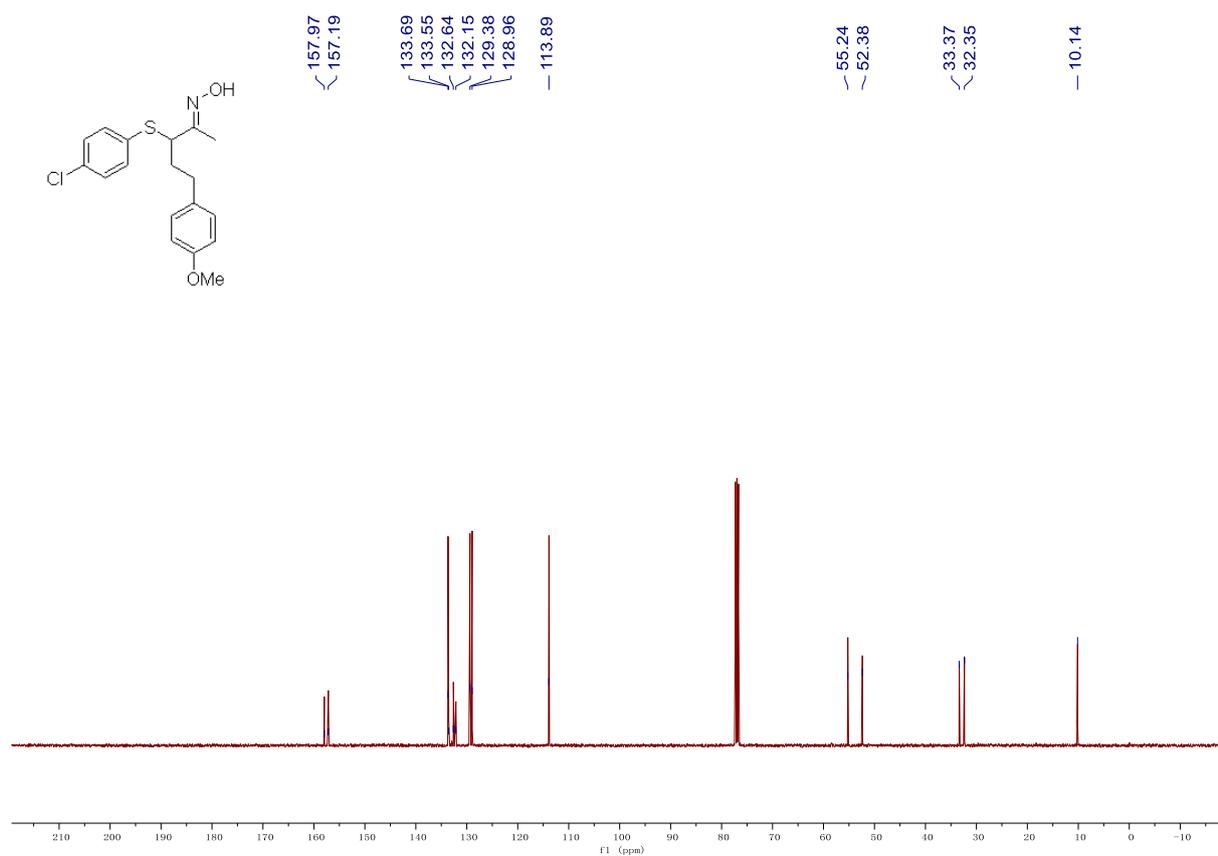


¹H NMR Spectrum of 6i (400 MHz) in CDCl₃

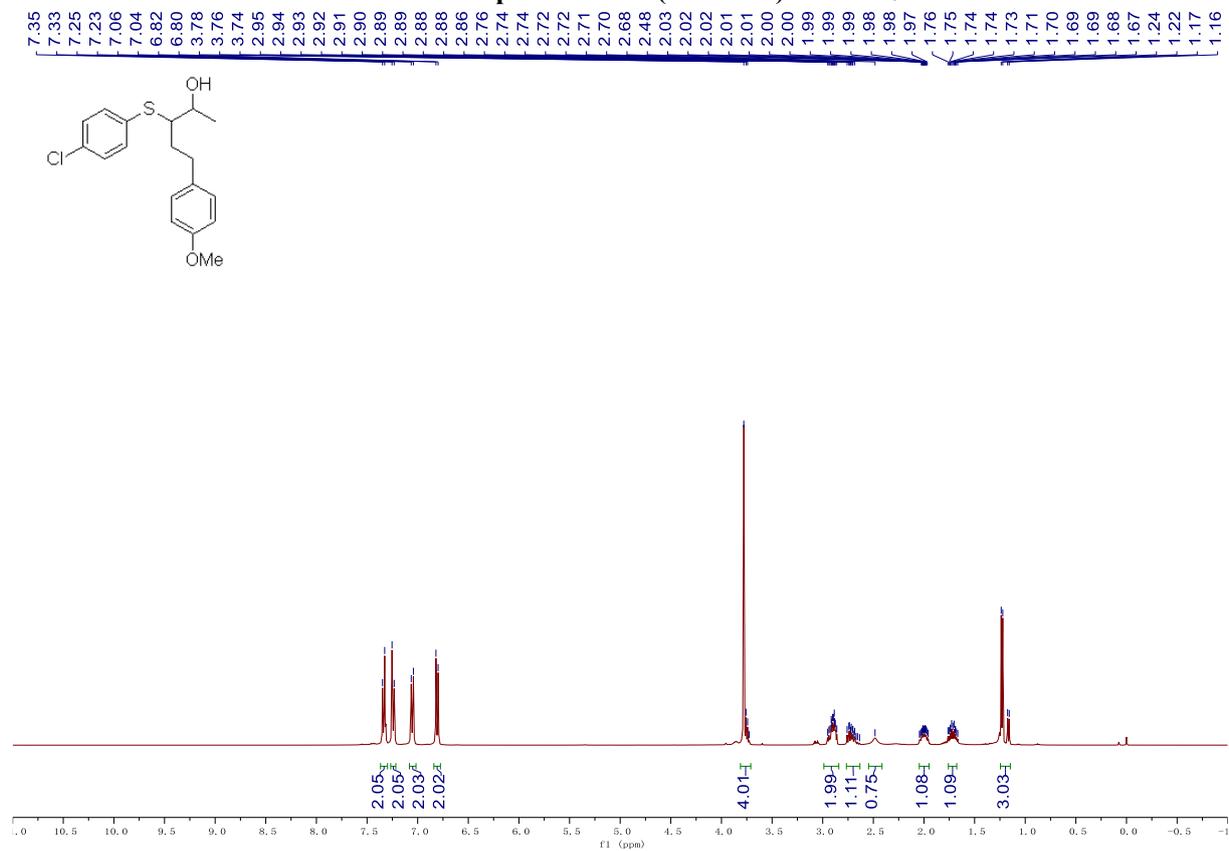




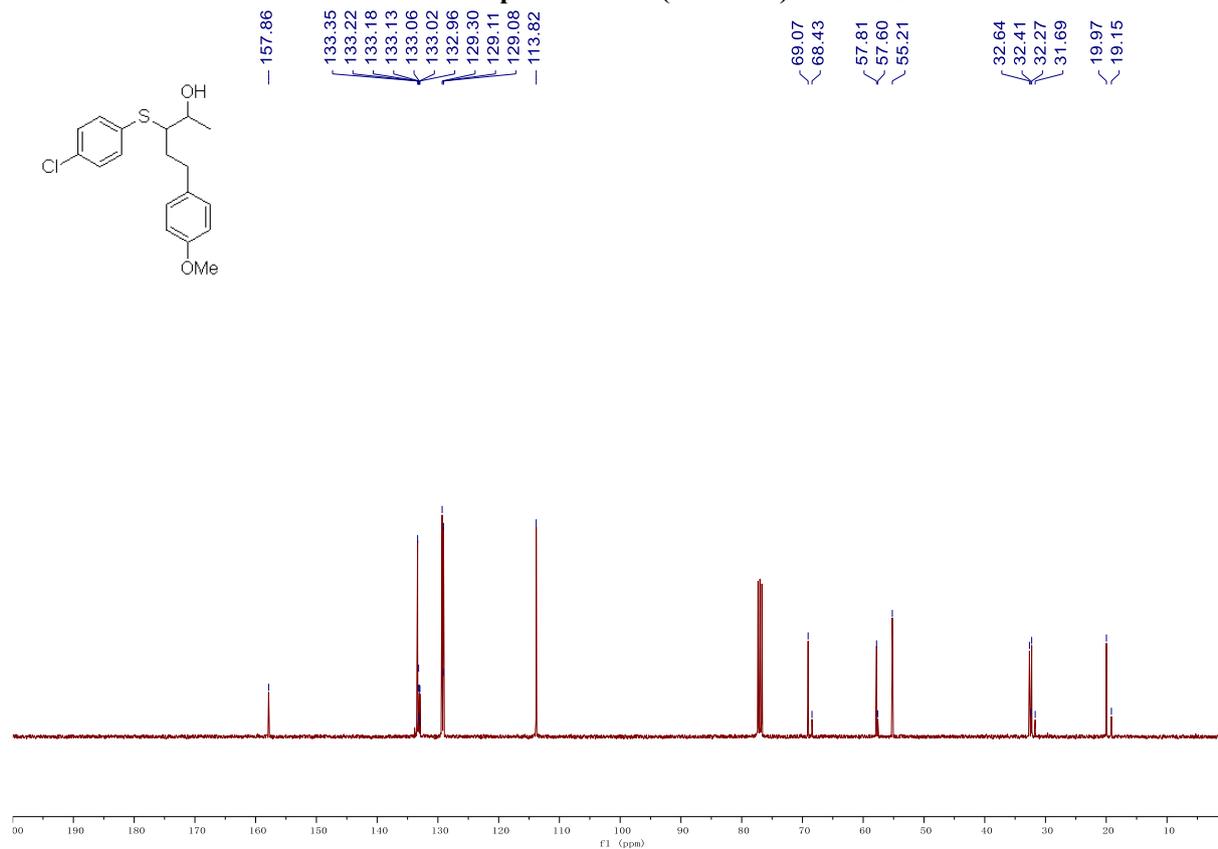
¹³C NMR Spectrum of 7 (100 MHz) in CDCl₃



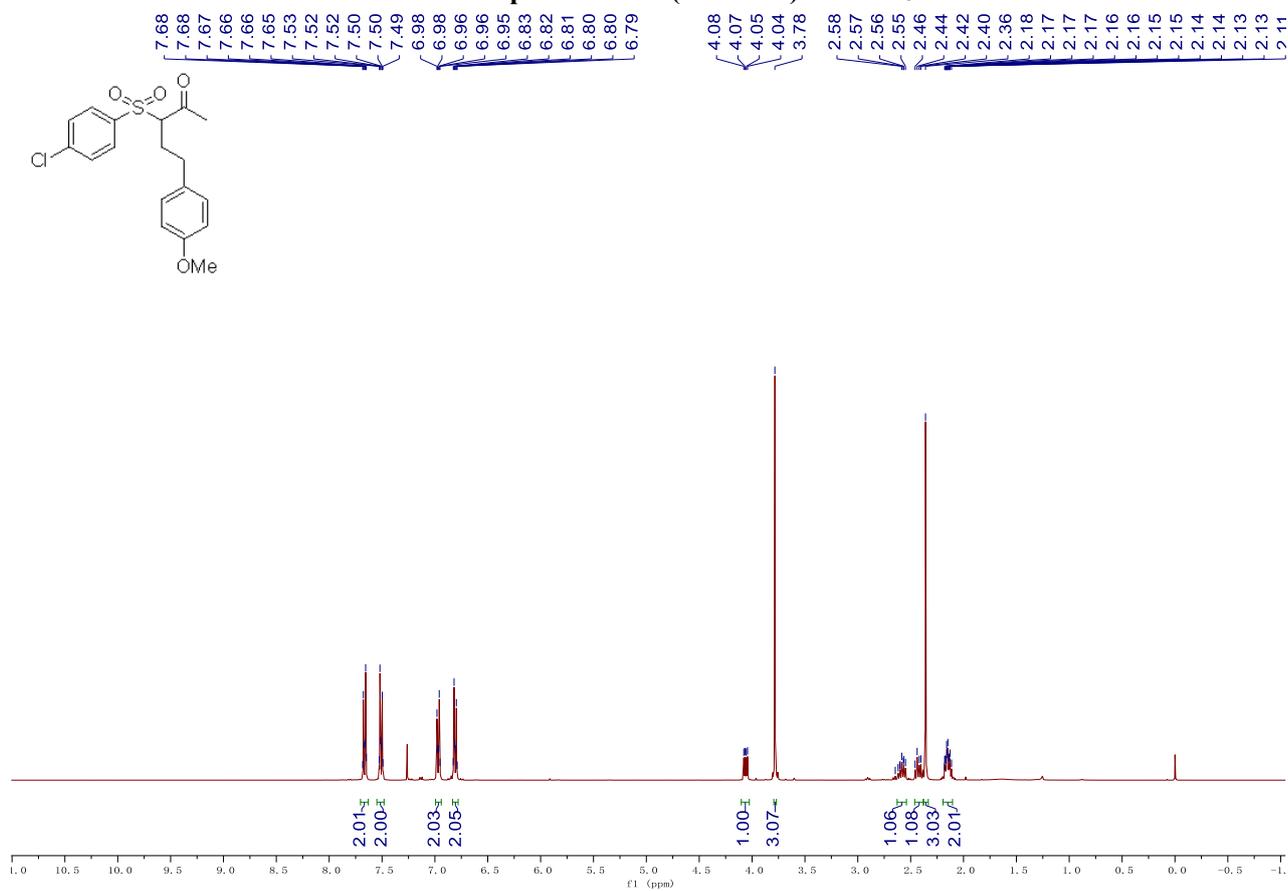
¹H NMR Spectrum of 8 (400 MHz) in CDCl₃



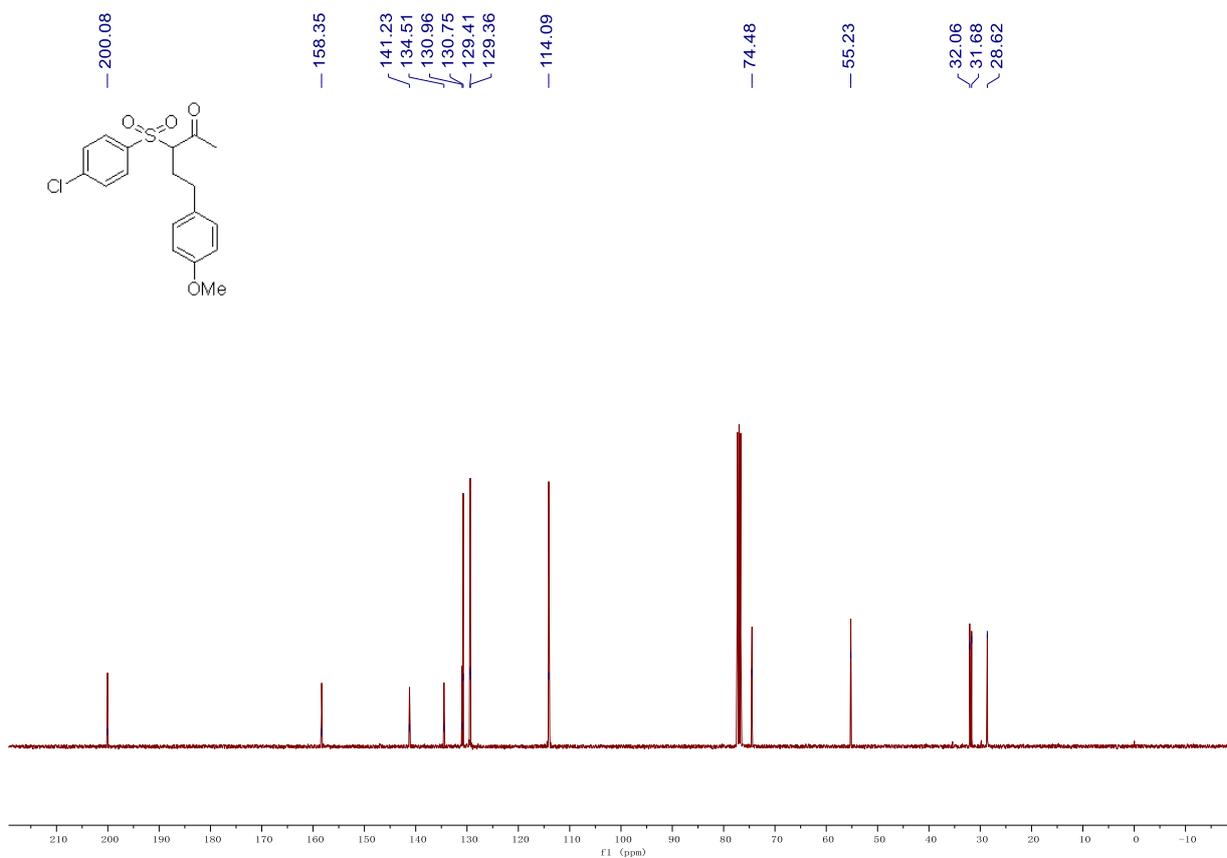
¹³C NMR Spectrum of 8 (100 MHz) in CDCl₃



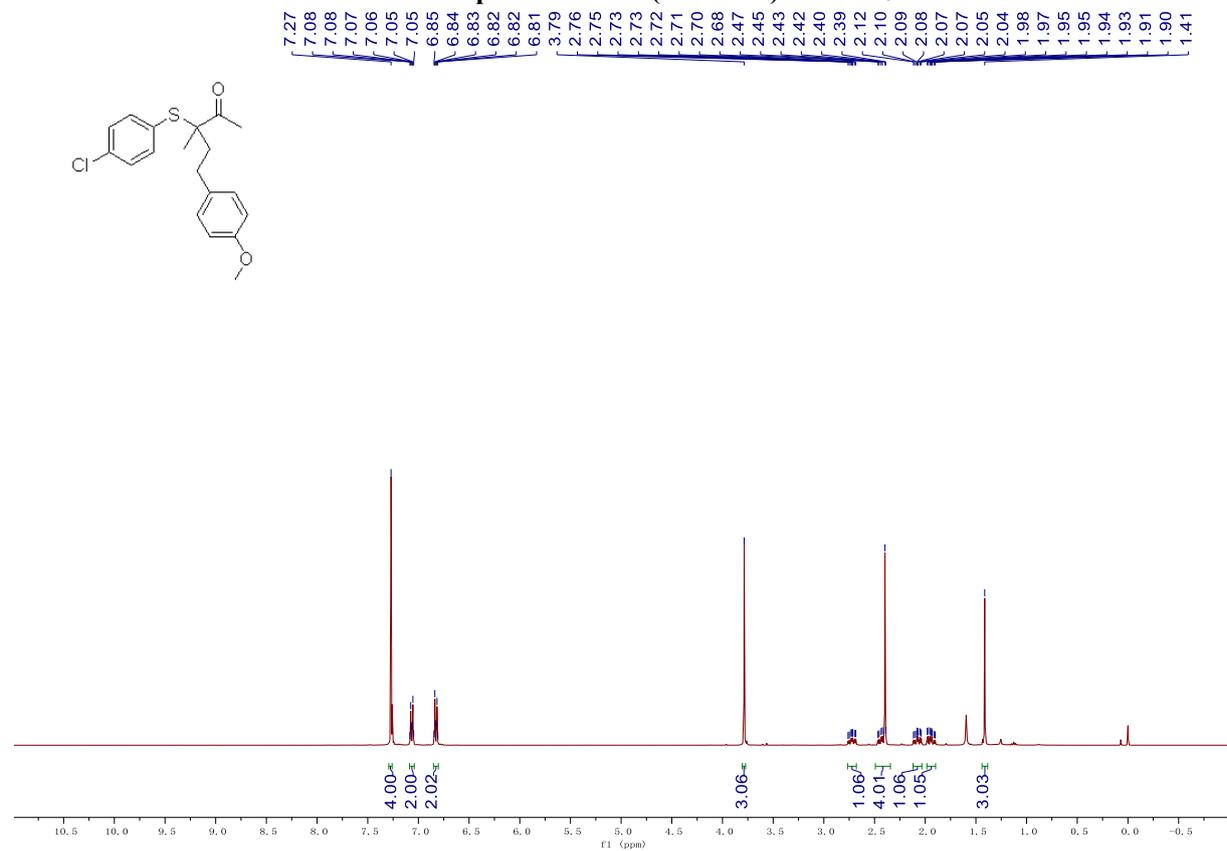
¹H NMR Spectrum of 9 (400 MHz) in CDCl₃



¹³C NMR Spectrum of 9 (100 MHz) in CDCl₃



¹H NMR Spectrum of 10 (400 MHz) in CDCl₃



¹³C NMR Spectrum of 10 (100 MHz) in CDCl₃

