Supporting Information

Palladium-catalyzed a convenient synthesis of thioesters from carboxylic acids and disulfides

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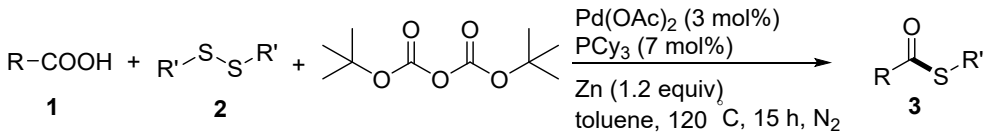
1. General Information

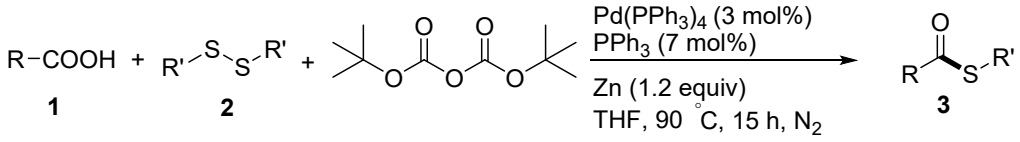
All experiments were carried out using schlenk-flask in N_2. Carboxylic acids were purchased from commercial suppliers and used as received directly unless otherwise noted. All solvents and other commercially available reagents were purchased from Acros or TCI companies and used directly. Reactions were monitored by thin layer chromatography (TLC) (Qingdao Haiyang Chemical Co. Ltd. Silica gel 60 GF254). Products were detected using a UV/Vis lamp (254 nm). Column chromatography was performed on Qingdao Haiyang Chemical Co. Ltd. Gel 60 (200–300 mesh). The ^{1}H and ^{13}C NMR spectras were obtained on a Bruker 400 MHz NMR Fourier transform spectrometer. ^{1}H NMR data were reported as: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR data were reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). The spectra are referenced against the internal solvent ($CDCl_3$, δ ^{1}H= 7.26 ppm, ^{13}C= 77.0 ppm). ^{1}H and ^{13}C spectra were recorded on a Varian Mercury-400 MHz (400 MHz for ^{1}H, 100 MHz for ^{13}C). ESI-MS spectra were recorded on a Bruker Esquire 3000. High resolution mass spectra (HR MS) were obtained on a Waters Micromass Q-Tof MicroTM instrument using the ESI technique.

2. General Procedure of Thioesters 3



Conditions **A**:

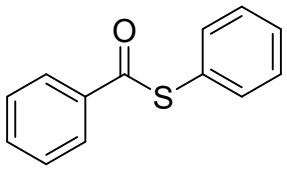
A schlenk flask (10 mL) equipped with a magnetic stir bar was charged with carboxylic acid (**1**, 0.5 mmol), disulfide (**2**, 0.6 mmol), ditertbutyl dicarbonate (0.6 mmol), $Pd(OAc)_2$ (3 mol%), PCy_3 (7 mol%), Zn powder (0.6 mmol). Then the reaction flask was placed under vacuum and refilled with nitrogen for three times, following toluene (3 mL) was injected sequentially. The mixtures were allowed to react at 120 ℃ for 15 h. When the reaction was complete, brine water (30 mL) were added and the aqueous layer was extracted with ethyl acetate (2×20 mL), the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1 to 50:1, v/v) to furnish the desired product **3**.



Conditions **B**:

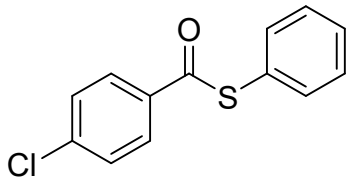
A schlenk flask (10 mL) equipped with a magnetic stir bar was charged with carboxylic acid (**1**, 0.5 mmol), disulfide (**2**, 0.6 mmol), ditertbutyl dicarbonate (0.6 mmol), $Pd(PPh_3)_4$ (3 mol%), PPh_3 (7 mol%), Zn powder (0.6 mmol). Then the reaction flask was placed under vacuum and refilled with nitrogen for three times, following THF (3 mL) was injected sequentially. The mixtures were allowed to react at 120 ℃ for 15 h. When the reaction was complete, brine water (30 mL) were added and the aqueous layer was extracted with ethyl acetate (2×20 mL), the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1 to 50:1, v/v) to furnish the desired product **3**.

3. Characterization of Products **3-6**



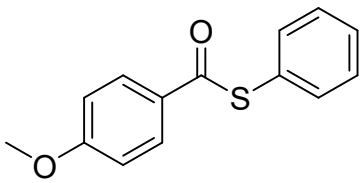
_S_-phenyl benzothioate (3aa)[1,2]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (d, J = 8.0 Hz, 2H), 7.64 (t, J = 8.0 Hz, 1H), 7.48-7.56 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.2, 136.7, 135.1, 133.7, 129.6, 129.3, 128.8, 127.5, 127.4.



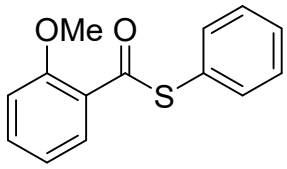
_S_-(phenyl) 4-chlorobenzothioate (3ba)[2,4]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, J = 8.0 Hz, 2H), 7.48-7.56 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.1, 140.1, 135.1, 135.0, 129.8, 129.4, 129.1, 128.9, 127.0.



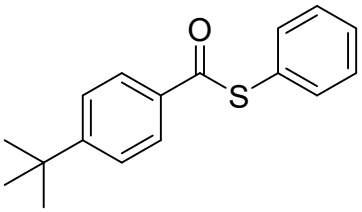
_S_-(phenyl) 4-methoxybenzothioate (3ca)[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (d, J = 8.0 Hz, 2H), 7.54-7.56 (m, 2H), 7.47-7.49 (m, 3H), 6.98 (d, J = 8.0 Hz, 2H); 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.6, 164.0, 135.2, 129.7, 129.4, 129.2, 127.7, 113.9, 55.6.



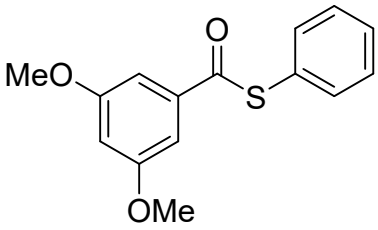
_S_-(phenyl) 2-methoxybenzothioate (3da)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, J = 8.0 Hz, 1H), 7.46-7.58 (m, 6 H), 7.06 (t, J = 8.0 Hz, 2H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.2, 158.2, 135.0, 134.1, 129.9, 129.3, 129.1, 128.8, 126.4, 120.6, 112.1, 55.9.



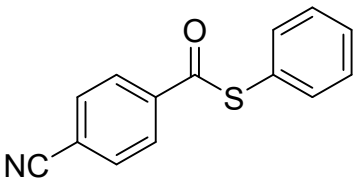
***S*-(phenyl) 4-(tert-butyl)benzothioate (3ea)[3,4]**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, J = 8.0 Hz, 2H), 7.54-7.59 (m, 4H), 7.50-7.51 (m, 3H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.7, 157.6, 135.2, 134.1, 129.5, 129.3, 127.6, 127.5, 125.8, 35.3, 31.1.



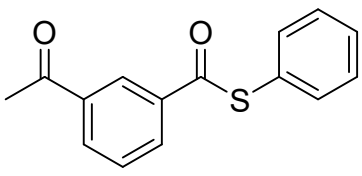
***S*-(phenyl) 3,5-dimethoxybenzothioate (3fa)[4]**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54-7.56 (m, 2H), 7.48-7.49 (m, 3H), 7.20 (d, J = 2.0 Hz, 2H), 6.72 (t, J = 2.0 Hz, 1H), 3.86 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.1, 160.9, 138.6, 135.1, 129.6, 127.4, 106.0, 105.2, 55.6.



***S*-(phenyl) 4-cyanobenzothioate (3ga)[3]**

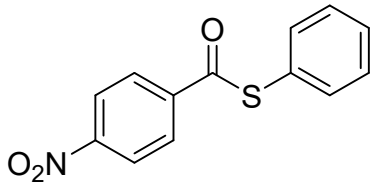
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.51-7.53 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.1, 139.8, 134.9, 132.7, 130.0, 129.5, 127.9, 126.2, 117.8, 116.9.



***S*-(phenyl) 3-acetylbenzothioate (3ha)**

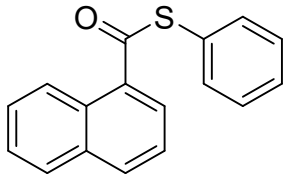
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20 (t, J = 4.0 Hz, 1H), 8.20-8.23 (m, 2H), 7.61 (t, J = 8.0 Hz, 1H), 7.48-7.55 (m, 5H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.9,

189.6, 137.6, 137.1, 135.0, 133.0, 131.6, 130.0, 129.4, 129.3, 127.3, 126.8, 26.7. HRMS(ESI):$[M+H]^+$calcd for $C_{15}H_{13}O_2S$, 257.0636; found: 257.0638.



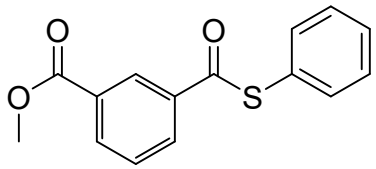
_S_-(phenyl) 4-nitrobenzothioate (3ia)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (d, *J* = 6.8 Hz, 2H), 8.22 (d, *J* = 9.2 Hz, 2H), 7.52-7.56 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.9, 150.7, 141.3, 134.9, 130.1, 129.5, 128.5, 126.2, 124.0. HRMS(ESI):$[M+H]^+$ calcd for $C_{13}H_{10}NO_3S$, 260.0381; found：260.0386



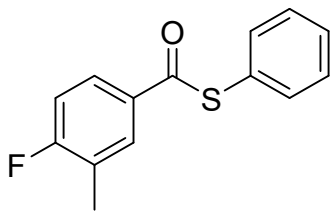
_S_-(phenyl) naphthalene-1-carbothioate (3ja)[1,3]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (d, *J* = 6.4 Hz, 1H), 8.22 (d, *J* = 6.4 Hz, 1H), 8.03 (d, *J* = 6.8 Hz, 1H), 7.89 (d, *J* = 6.4 Hz, 1H), 7.53-7.60 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.3, 135.0, 134.7, 133.9, 133.3, 129.6, 129.4, 128.4, 128.3, 128.1, 128.0, 126.7, 125.3, 124.5.



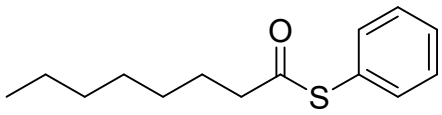
Methyl 3-((phenylthio)carbonyl)benzoate (3ka)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.71 (t, *J* = 2.0 Hz, 1H), 8.31 (d, *J* = 7.6 Hz, 1H), 8.22 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.56-7.57 (m, 2H), 7.49-7.55 (m, 3H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.5, 166.0, 137.0, 135.1, 134.4, 131.5, 130.9, 129.7, 129.4, 129.0, 128.6, 126.9, 52.5. HRMS(ESI):$[M+H]^+$calcd for $C_{15}H_{13}O_3S$, 273.0585; found: 273.0591.



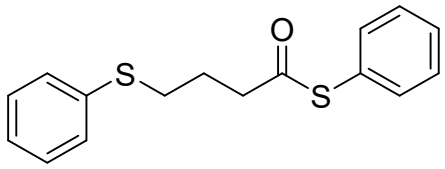
***S*-(phenyl) 4-fluoro-3-methylbenzothioate (3la)**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (t, *J* = 8.0 Hz, 2H), 7.42-7.43 (m, 2H), 7.37-7.38 (m, 3H), 7.01 (t, *J* = 8.0 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.8, 164.7, 162.6($J_{C\text{-}F}$ = 210.0 Hz), 134.1, 131.6, 130.1, 128.5, 128.2, 126.3, 124.8, 124.6, 114.5, 13.56. HRMS(ESI):$[M+H]^+$calcd for $C_{14}H_{12}FOS$, 247.0593; found: 247.0596.



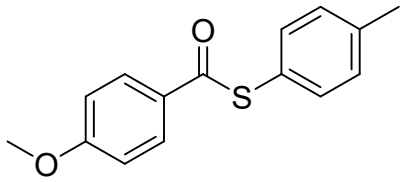
***S*-(phenyl) octanethioate (3ma)[5]**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (s, 5H), 2.69 (t, *J* = 7.6 Hz, 2H), 1.73-1.77 (m, 2H), 1.34-1.37 (m, 8H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.6, 134.5, 129.1, 128.0, 43.8, 31.7, 28.9, 25.6, 22.6, 14.1.



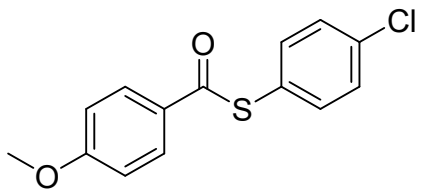
***S*-(phenyl) 4-(phenylthio)butanethioate (3na)**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (s, 5H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 2H), 3.04 (t, *J* = 8.0 Hz, 2H), 2.88 (t, *J* = 8.0 Hz, 2H), 2.02-2.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.9, 135.8, 134.5, 129.6, 129.4, 129.3, 129.0, 127.6, 126.3, 42.1, 32.9, 24.8. HRMS(ESI):$[M+H]^+$calcd for $C_{16}H_{17}OS_2$, 289.0721; found: 289.0725.



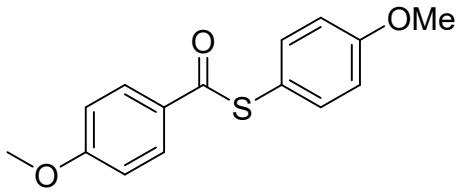
***S*-(p-tolyl) 4-methoxybenzothioate (3cb)[4]**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.1, 164.0, 139.7, 135.2, 130.1, 129.7, 129.5, 124.1, 113.9, 55.6, 21.4.



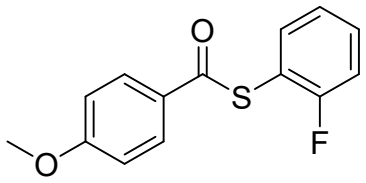
***S*-(4-chlorophenyl) 4-methoxybenzothioate (3cc)[6]**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, *J* = 8.8 Hz, 2H), 7.43-7.48 (m, 4H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.0, 164.2, 136.4, 135.8, 129.4, 126.2, 114.0, 55.6.



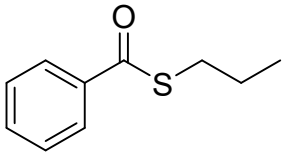
***S*-(4-methoxyphenyl) 4-methoxybenzothioate (3cd)[4]**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 6.97-7.02 (m, 4H), 3.90 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.5, 163.9, 160.7, 136.8, 129.7, 129.5, 118.2, 114.9, 113.9, 55.6, 55.4.



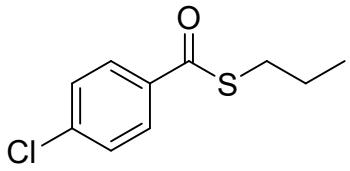
***S*-(2-fluorophenyl) 4-methoxybenzothioate (3ce)**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, *J* = 8.8 Hz, 2H), 7.46-7.55 (m, 2H), 7.24-7.26 (m, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 186.6, 164.2, 161.4($J_{C\text{-}F}$ = 280.0 Hz), 137.3, 132.1, 129.0, 124.7, 116.4, 115.2, 114.0, 55.6.
HRMS(ESI):$[M+H]^+$calcd for $C_{14}H_{12}FO_2S$, 263.0542; found: 263.0549.



***S*-(propyl) 4-benzothioate (3ag)[7]**

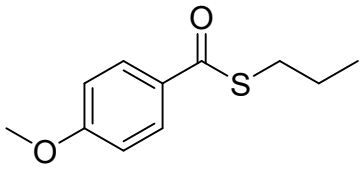
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 3.08 (t, *J* = 8.0 Hz, 2H), 1.71-1.76 (m, 2H), 1.06 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.2, 137.3, 133.2, 128.6, 127.2, 30.9, 23.0, 13.5.



***S*-(propyl) benzothioate (3bg)**

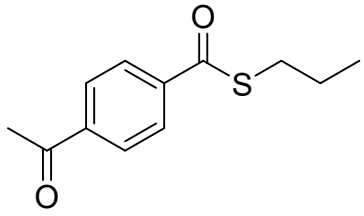
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 3.07 (t, *J* = 8.0 Hz, 2H), 1.70-1.75 (m, 2H), 1.05 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.0, 139.6, 135.6, 128.9, 128.6, 31.1, 22.9, 13.5.

HRMS(ESI):$[M+H]^+$calcd for $C_{10}H_{12}ClOS$, 215.0297; found: 215.0292.



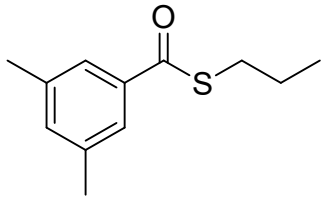
***S*-(propyl) 4-methoxybenzothioate (3cg)[4]**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 3.88 (s, 3H), 3.05 (t, *J* = 8.0 Hz, 2H), 1.69-1.74 (m, 2H), 1.05 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.7, 163.6, 130.2, 129.3, 113.7, 55.5, 30.8, 23.1, 13.5.



***S*-(propyl) 4-acetylbenzothioate (3og)[7]**

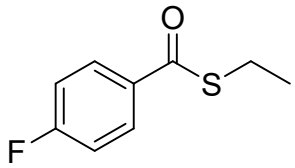
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01-8.07 (m, 4H), 3.10 (t, *J* = 8.0 Hz, 2H), 2.66 (s, 3H), 1.71-1.77 (m, 2H), 1.06 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.4, 191.5, 140.5, 140.31, 128.5, 127.4, 31.2, 26.9, 22.9, 13.5.



***S*-(propyl) 3,5-dimethylbenzothioate (3pg)**

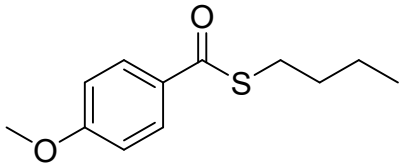
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (s, 2H), 7.21 (s, 1H), 3.06 (t, *J* = 8.0 Hz, 2H), 2.38 (s, 6H), 1.69-1.75 (m, 2H), 1.06 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.4, 138.3, 137.4, 134.9, 124.9, 30.9, 23.0, 21.21, 13.5.

HRMS(ESI):$[M+H]^+$calcd for $C_{12}H_{17}OS$, 209.1000; found: 209.1010.



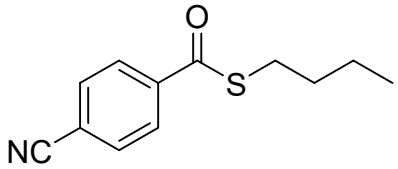
***S*-(ethyl) 4-fluorobenzothioate (3qh)**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02 (dd, *J* = 8.0 Hz, *J'* = 4.0 Hz, 2H), 7.14 (t, J = 8.0 Hz, 2H), 3.11 (q, *J* = 8.0 Hz, 2H), 1.38 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.6, 167.1, 164.6, 133.6, 129.7, 115.8, 23.6, 14.7.
HRMS(ESI):$[M+H]^+$calcd for $C_9H_{10}FOS$, 185.0436; found: 185.0439.



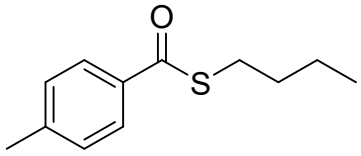
***S*-(butyl) 4-methoxybenzothioate (3ci)[4]**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 3H), 3.07 (t, *J* = 8.0 Hz, 2H), 1.63-1.70 (m, 2H), 1.44-1.51 (m, 2H), 0.96 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.7, 163.6, 130.2, 129.3, 113.7, 55.5, 31.8, 28.6, 22.1, 13.6.



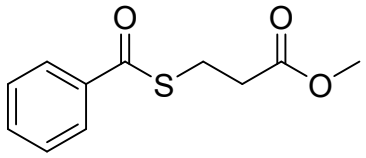
***S*-(butyl) 4-cyanobenzothioate (3gi)**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 3.11 (t, *J* = 8.0 Hz, 2H), 1.64-1.71 (m, 2H), 1.42-1.51 (m, 2H), 0.96 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.8, 140.3, 132.5, 127.6, 117.9, 116.5, 31.4, 29.2, 22.0, 13.6. HRMS(ESI):$[M+H]^+$calcd for $C_{12}H_{14}NOS$, 220.0796; found: 220.0801.



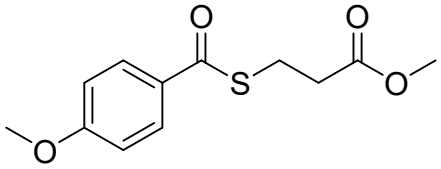
***S*-(butyl) 4-methylbenzothioate (3ri)**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 6.4 Hz, 2H), 7.15 (d, *J* = 6.4 Hz, 2H), 2.99 (t, *J* = 5.6 Hz, 2H), 2.33 (s, 3H), 1.56-1.59 (m, 2H), 1.38-1.40 (m, 2H), 0.87 (t, *J* = 5.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.8, 144.0, 134.8, 129.2, 127.2, 31.7, 28.7, 22.1, 21.7, 13.7. HRMS(ESI):$[M+H]^+$calcd for $C_{12}H_{17}OS$, 209.1000; found: 209.1007.



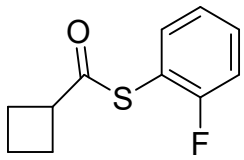
Methyl 3-(benzoylthio)propanoate (3aj)[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 3.72 (s, 3H), 3.33 (t, *J* = 8.0 Hz, 2H), 2.75 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.5, 172.2, 136.8, 133.5, 128.6, 127.2, 51.9, 34.3, 24.0.



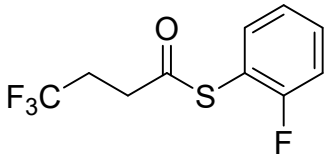
Methyl 3-((4-methoxybenzoyl)thio)propanoate (3cj)[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (d, *J* = 9.2 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 3.69 (s, 3H), 3.28 (t, *J* = 6.8 Hz, 2H), 2.74 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.9, 172.2, 163.8, 129.8, 113.8, 55.5, 51.9, 34.4, 23.9.



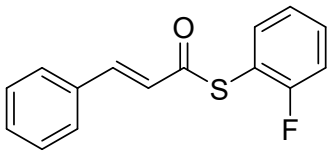
***S*-(2-fluorophenyl) cyclobutanecarbothioate (3se)**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, *J* = 8.8 Hz, 2H), 7.46-7.55 (m, 2H), 7.24-7.26 (m, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.5, 163.4, 160.9($J_{C\text{-}F}$ = 250.0 Hz), 136.8, 131.9, 124.6, 116.3, 115.2, 46.6, 26.1, 18.0.
HRMS(ESI):$[M+H]^+$calcd for $C_{11}H_{12}FOS$, 211.0593; found: 211.0598.



***S*-(2-fluorophenyl) 4,4,4-trifluorobutanethioate (3te)**

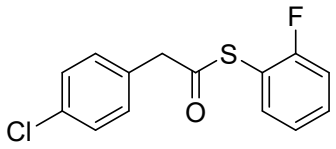
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42-7.50 (m, 2H), 7.19-7.28 (m, 2H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.52-2.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.7, 163.3, 160.8($J_{C\text{-}F}$ = 250.0 Hz), 136.6, 132.6, 127.7, 124.8, 116.2, 114.3, 35.7, 29.4.
HRMS(ESI):$[M+H]^+$calcd for $C_{10}H_9F_4OS$, 253.0310; found: 253.0316.



***S*-(2-fluorophenyl) (E)-3-phenylprop-2-enethioate (3ue)**

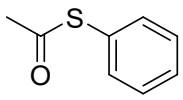
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, J = 16.0 Hz, 1H), 7.59-7.61 (m, 2H), 7.43-7.52 (m, 5H), 7.24-7.27 (m, 2H), 6.86 (d, J = 15.6 Hz, 1H), 7.00 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 186.1, 163.5, 161.1($J_{C\text{-}F}$ = 240.0

Hz), 142.3, 136.8, 133.9, 132.2, 130.9, 129.1, 128.6, 124.7, 123.8, 116.3. HRMS(ESI):[M+H]$^+$calcd for $C_{15}H_{12}FOS$, 259.0593; found: 259.0595.



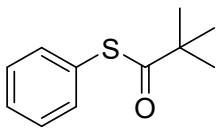
***S*-(2-fluorophenyl) 2-(4-chlorophenyl)ethanethioate (3ve)**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (d, J = 4.0 Hz, 1H), 7.46-7.55 (m, 2H), 7.24-7.28 (m, 3H), 7.06 (t, J = 4.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.1, 163.1, 161.1($J_{C\text{-}F}$ = 200.0 Hz), 136.5, 133.7, 132.3, 131.4, 131.0, 128.9, 124.7, 116.3, 115.0, 49.1. HRMS(ESI):[M+H]$^+$calcd for $C_{14}H_{11}ClFOS$, 281.0203; found: 281.0211.



***S*-(phenyl) ethanethioate (4)[3]**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (m, 5H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.1, 134.5, 129.5, 129.3, 128.0, 30.2.



***S*-(phenyl) 2,2-dimethylpropanethioate (5)[8]**

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (s, 5H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.7, 135.0, 129.1, 129.0, 128.1, 46.9, 27.4.

Reference

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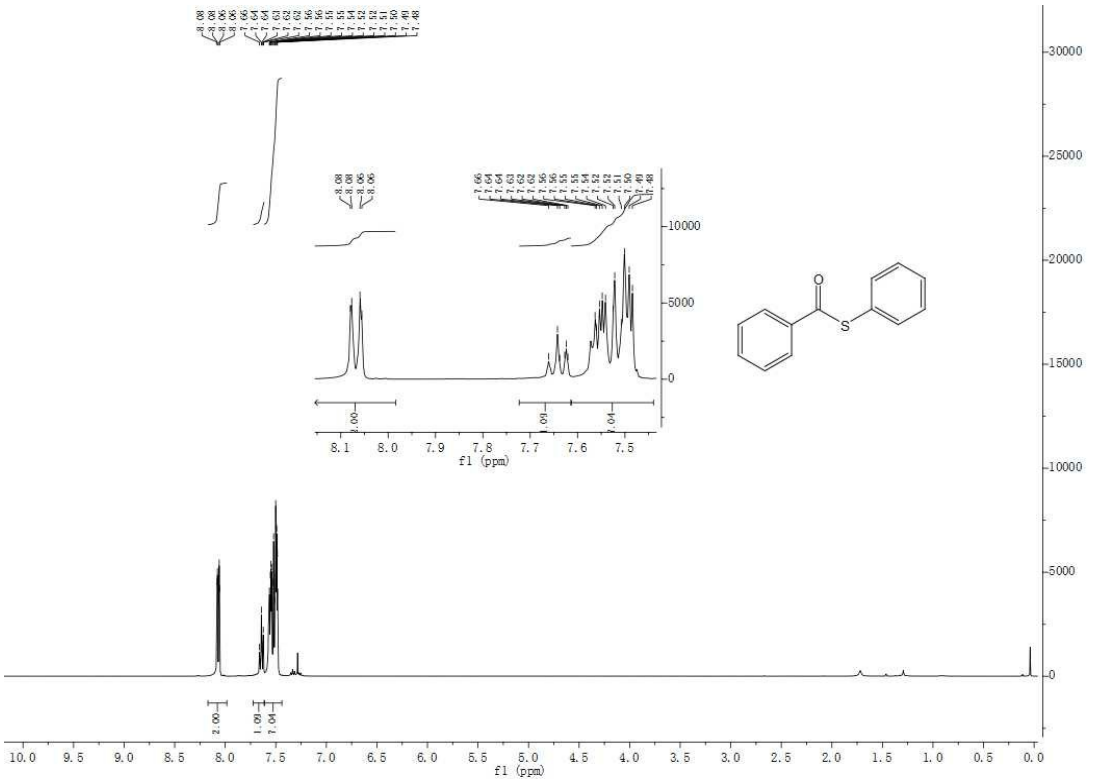
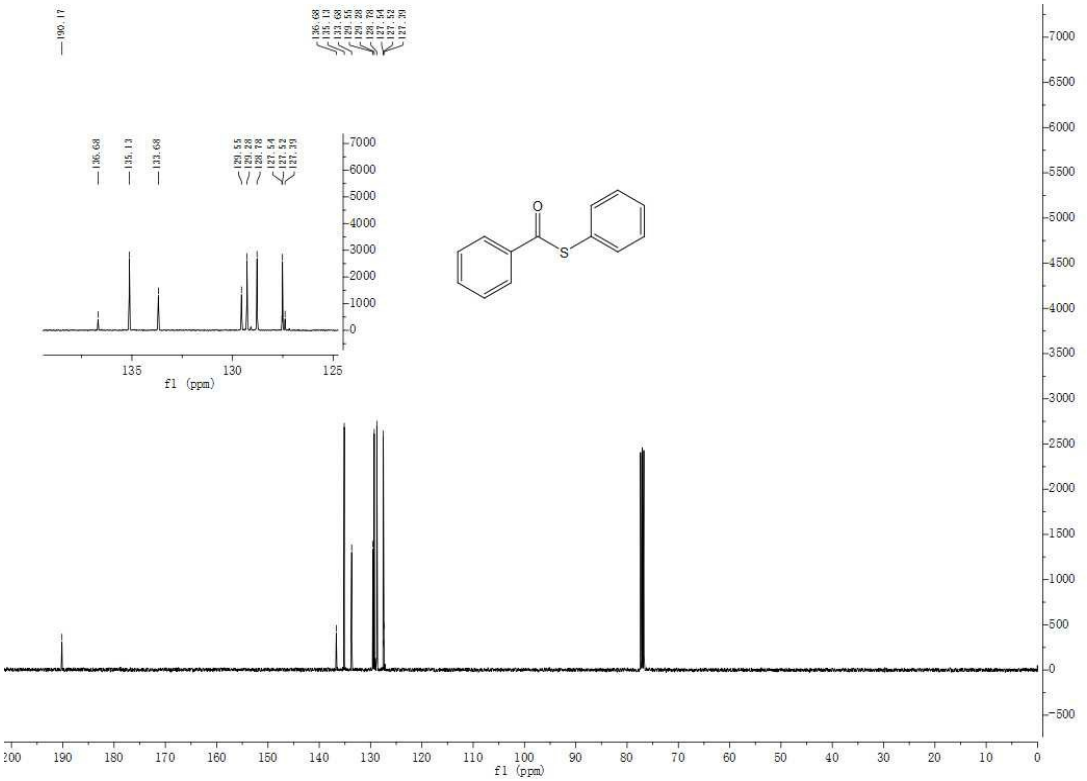
8. F. Bie, H. Cao, C. Liu, X. Liu, Y. Shi, M. Szostak, T. Zhou, Org. Lett., 2021, 23, 20, 8098-8103.

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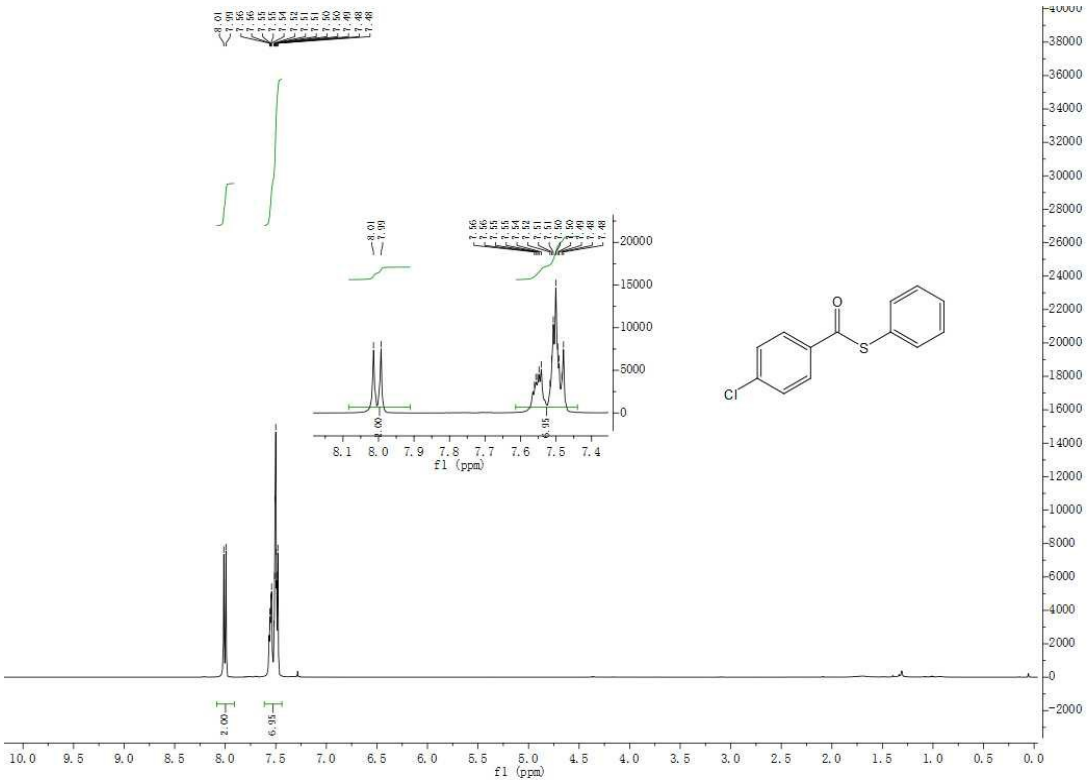
135.13
133.68
129.55
129.28
128.78
127.54
127.52
127.39
O
S
f1 (ppm)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7.99
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7.55
7.54
7.52
7.51
7.50
7.49
7.48
2.00
6.95
O
S
Cl
f1 (ppm)


189.06
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135.11
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129.38
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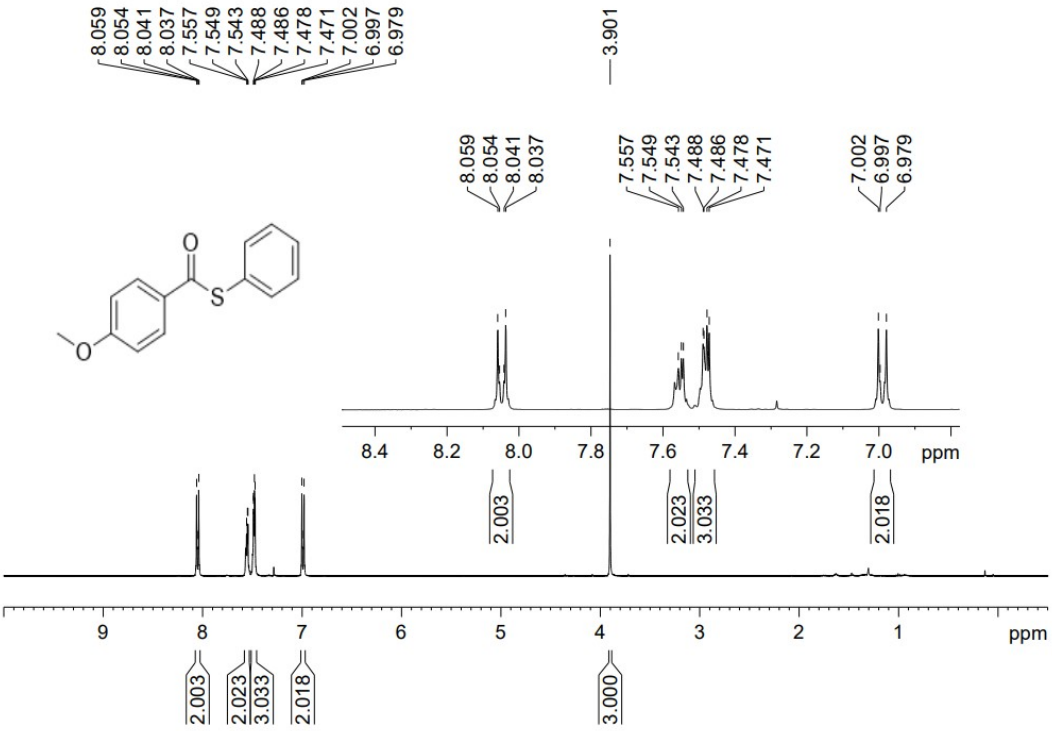
128.88
126.95
O
S
Cl
f1 (ppm)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8.041
8.037
7.557
7.549
7.543
7.488
7.486
7.478
7.471
7.002
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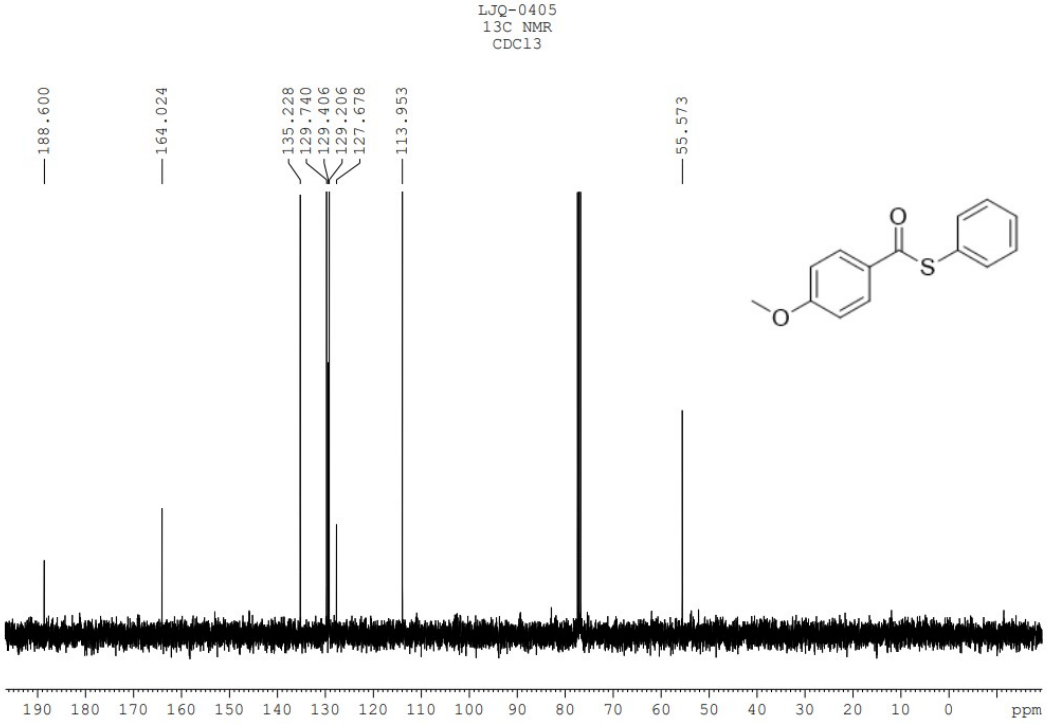
6.979
3.901
O
S
O
ppm
2.003
2.023
3.033
2.018
3.000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CDCl3
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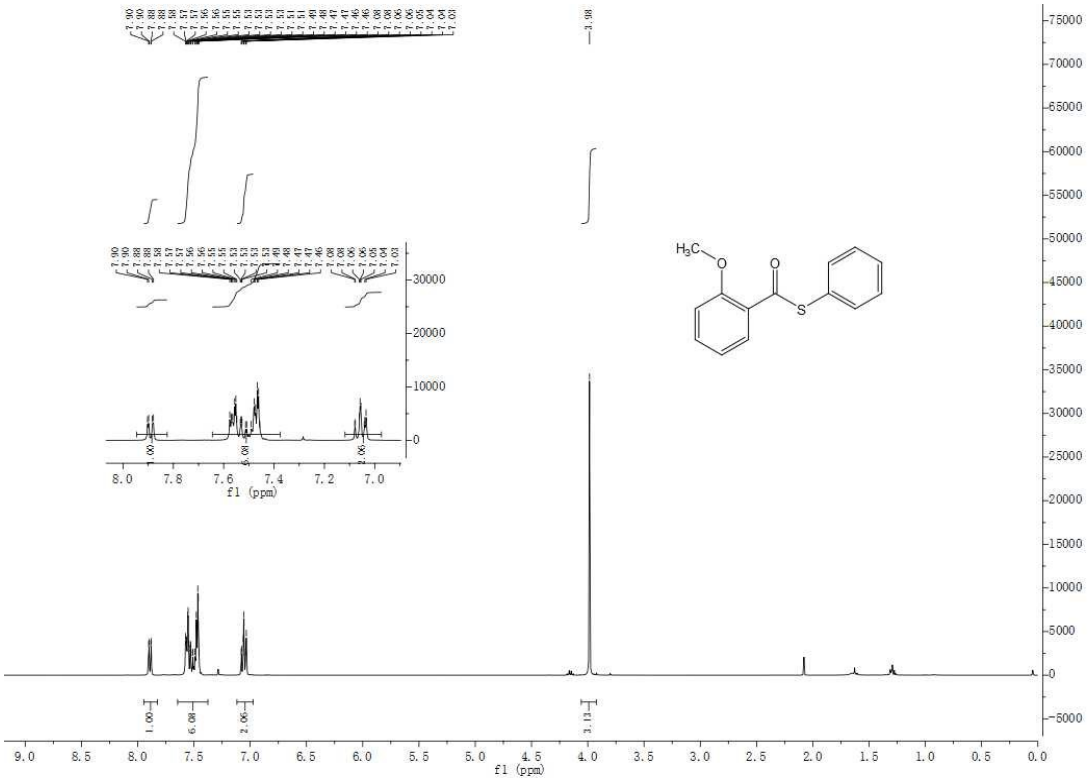
135.228
129.740
129.406
129.206
127.678
113.953
55.573
O
S
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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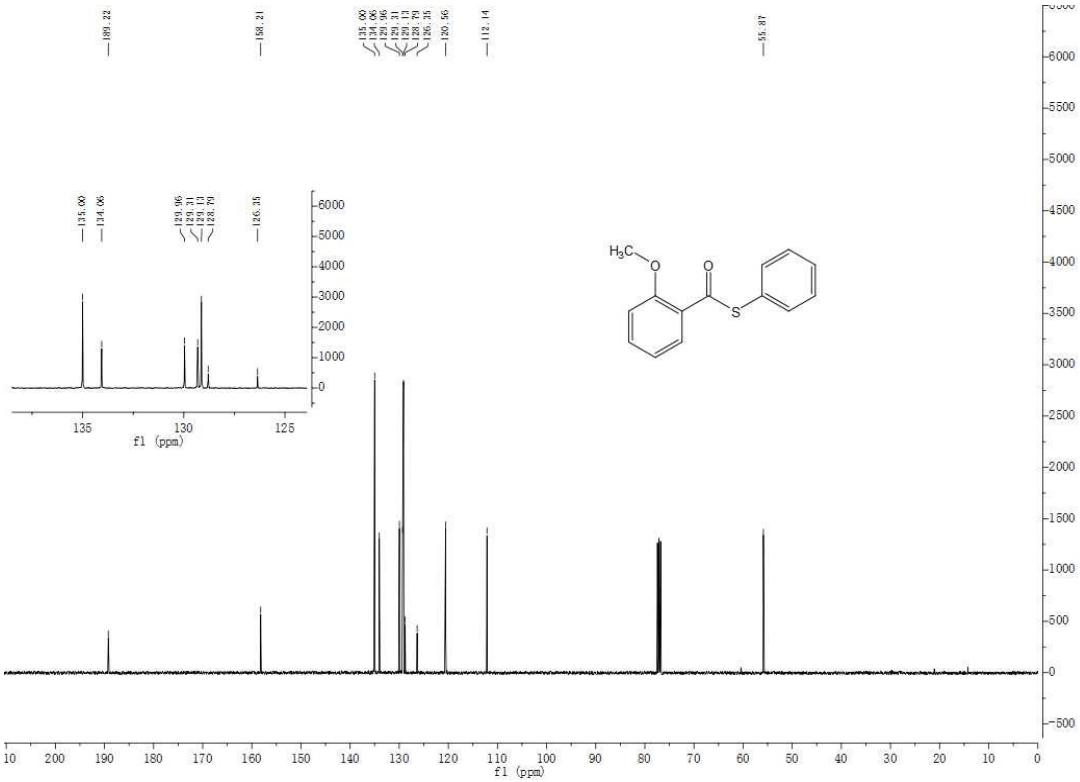
O
O
S
1.00
6.08
2.06
3.13
f1 (ppm)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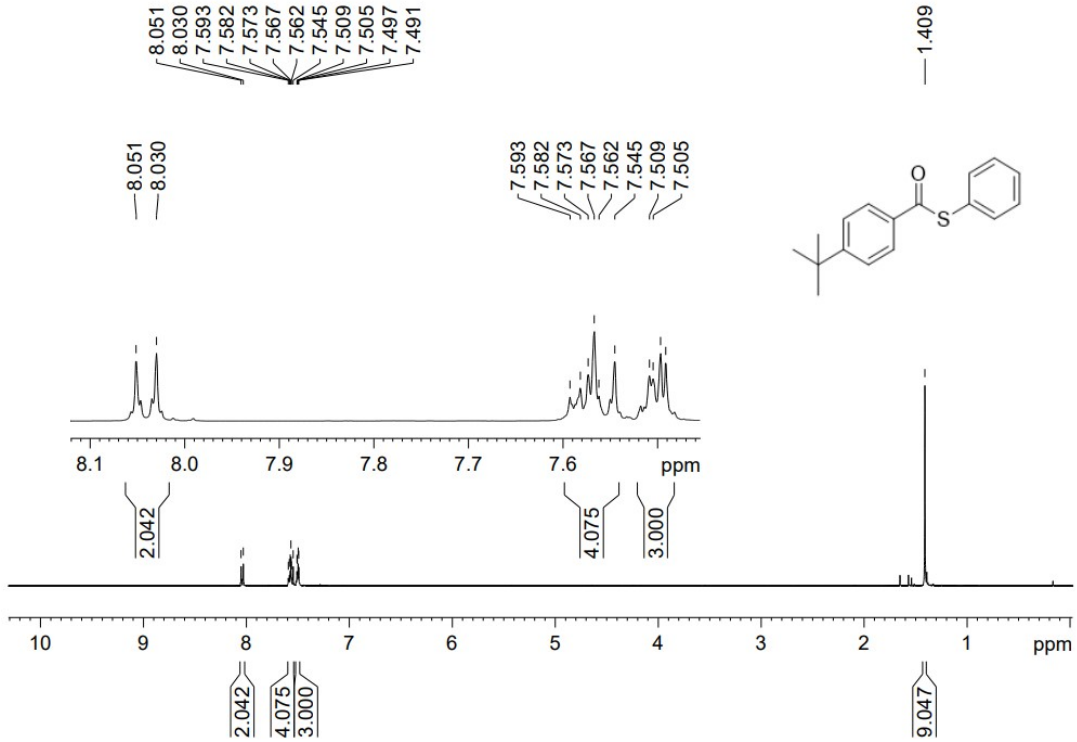
129.13
128.79
126.35
120.56
112.14
55.87
f1 (ppm)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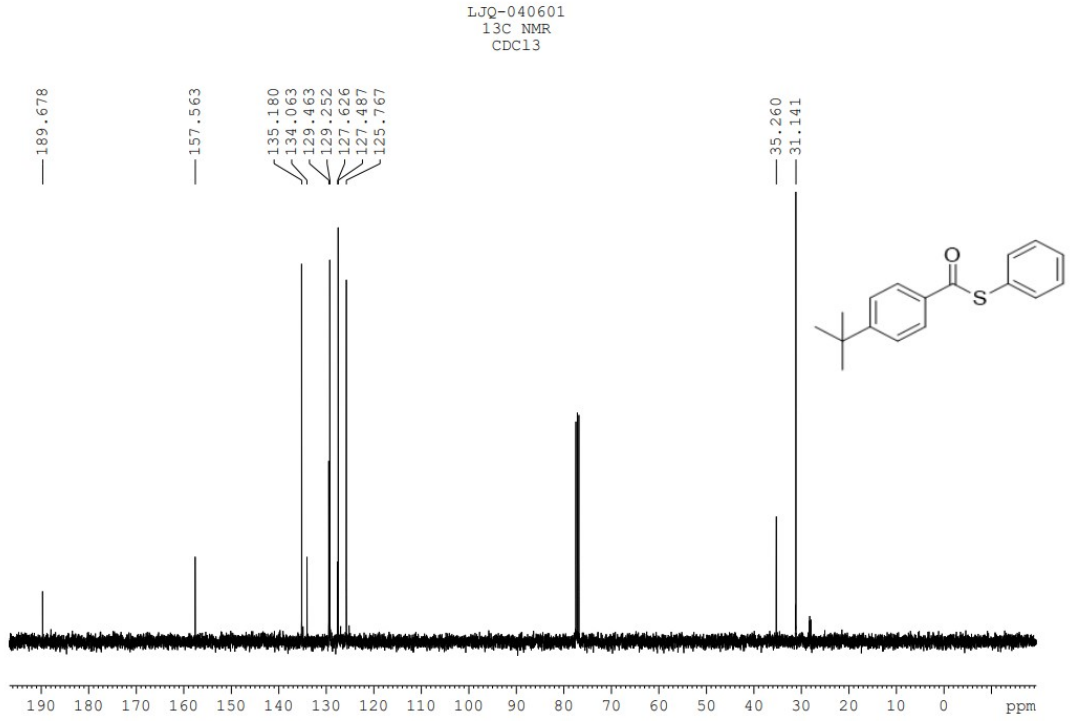
9.047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127.487
125.767
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31.141
O
S
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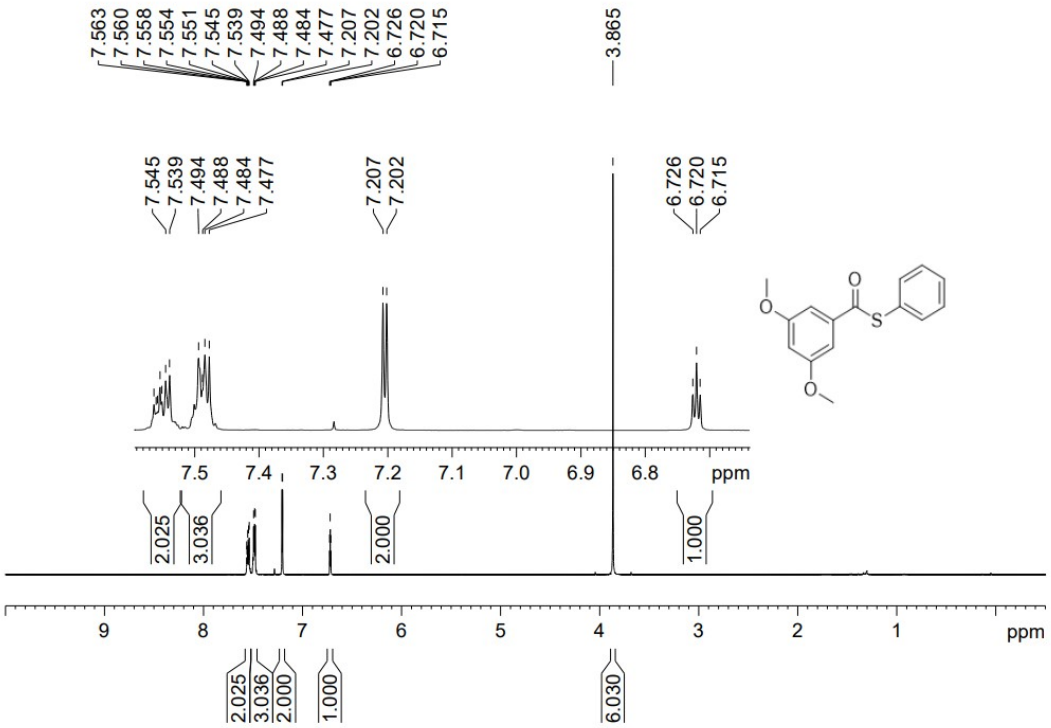
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7.554
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7.494
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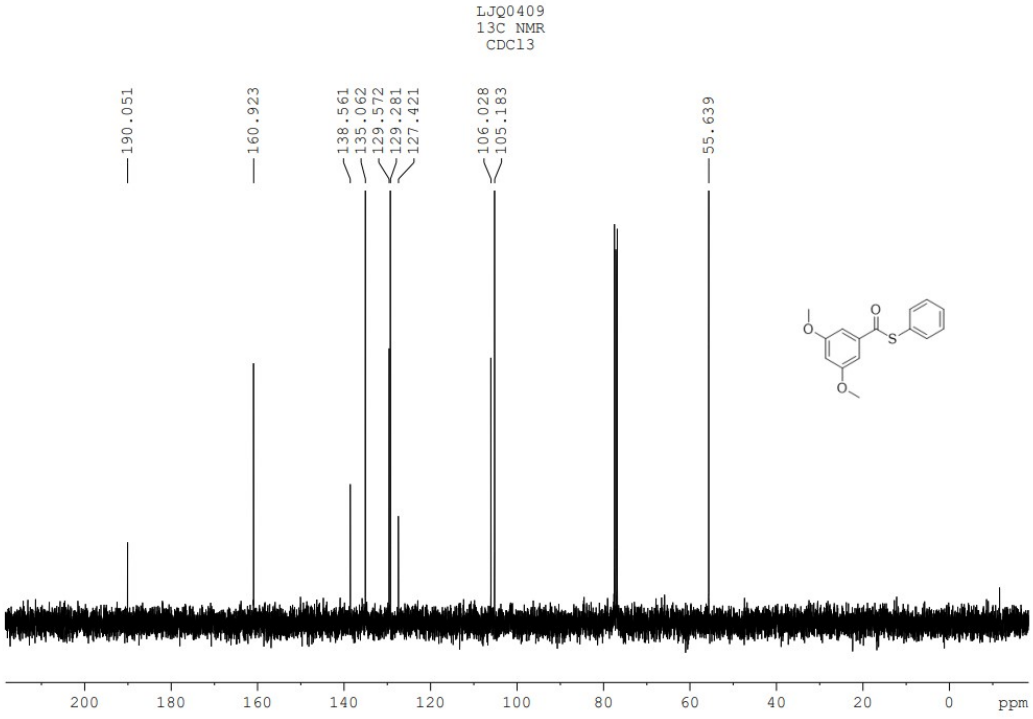
7.207
7.202
6.726
6.720
6.715
3.865
O
S
O
O
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 ppm
2.025
3.036
2.000
1.000
9 8 7 6 5 4 3 2 1 ppm
2.025
3.036
2.000
1.000
6.030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200
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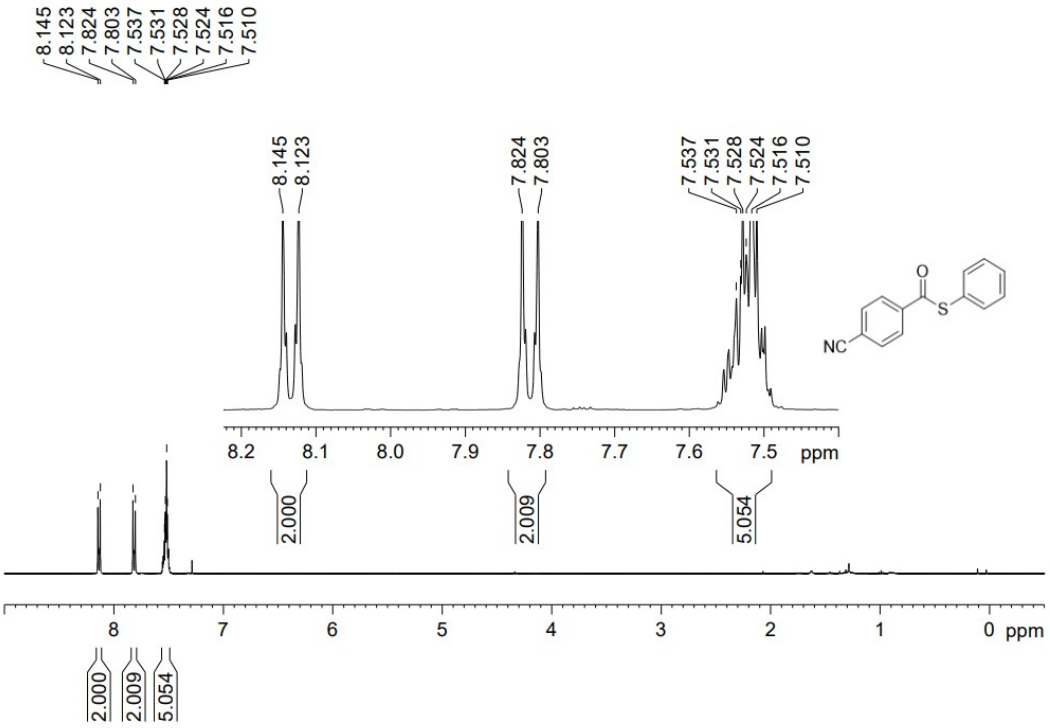
160
140
120
100
80
60
40
20
0
ppm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7.516
7.510
NC
8.2
8.1
8.0
7.9
7.8
7.7
7.6
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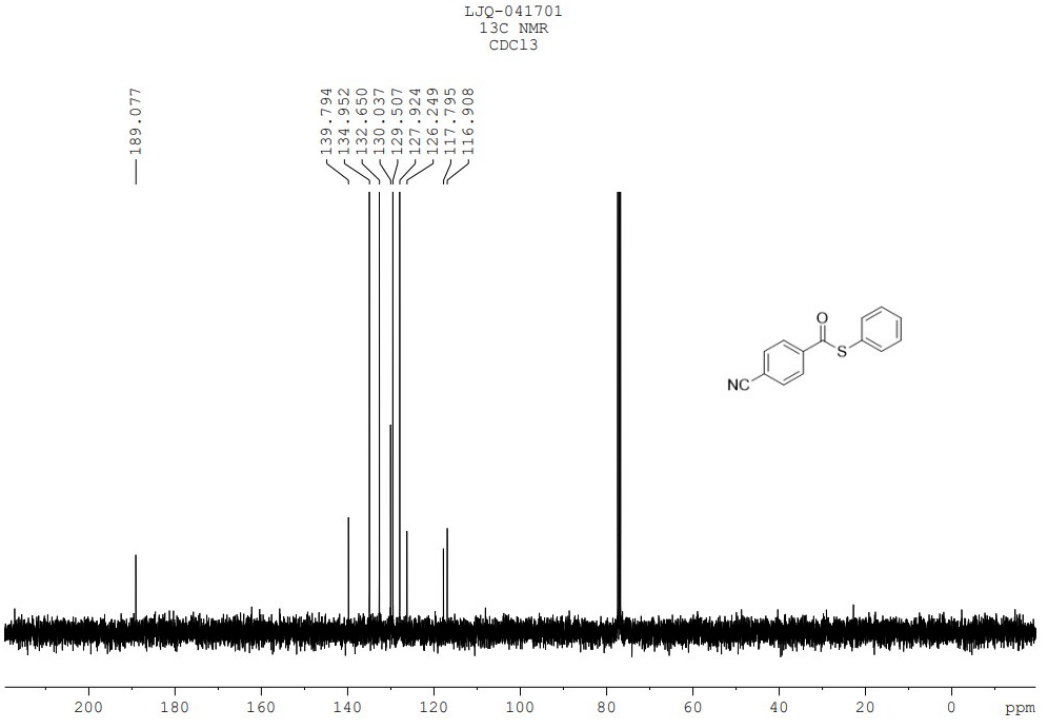
ppm
2.000
2.009
5.054
8
7
6
5
4
3
2
1
0 ppm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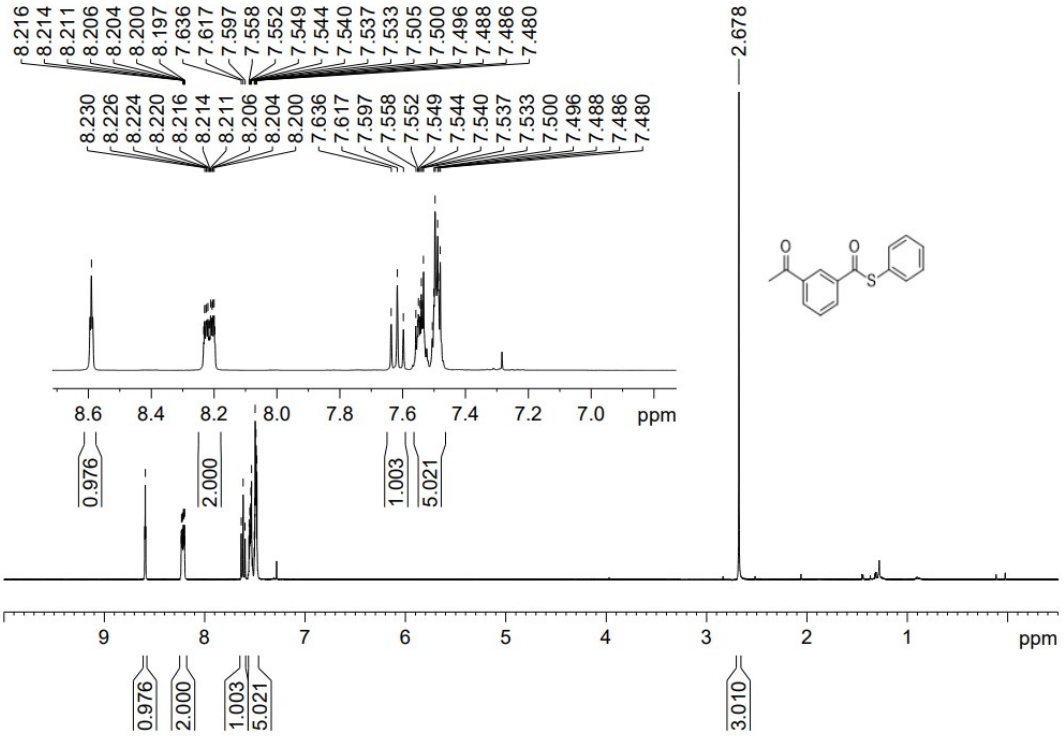
13C NMR
CDCl3
189.077
139.794
134.952
132.650
130.037
129.507
127.924
126.249
117.795
116.908
NC
O
S
200
180
160
140
120
100
80
60
40
20
0
ppm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8.214
8.211
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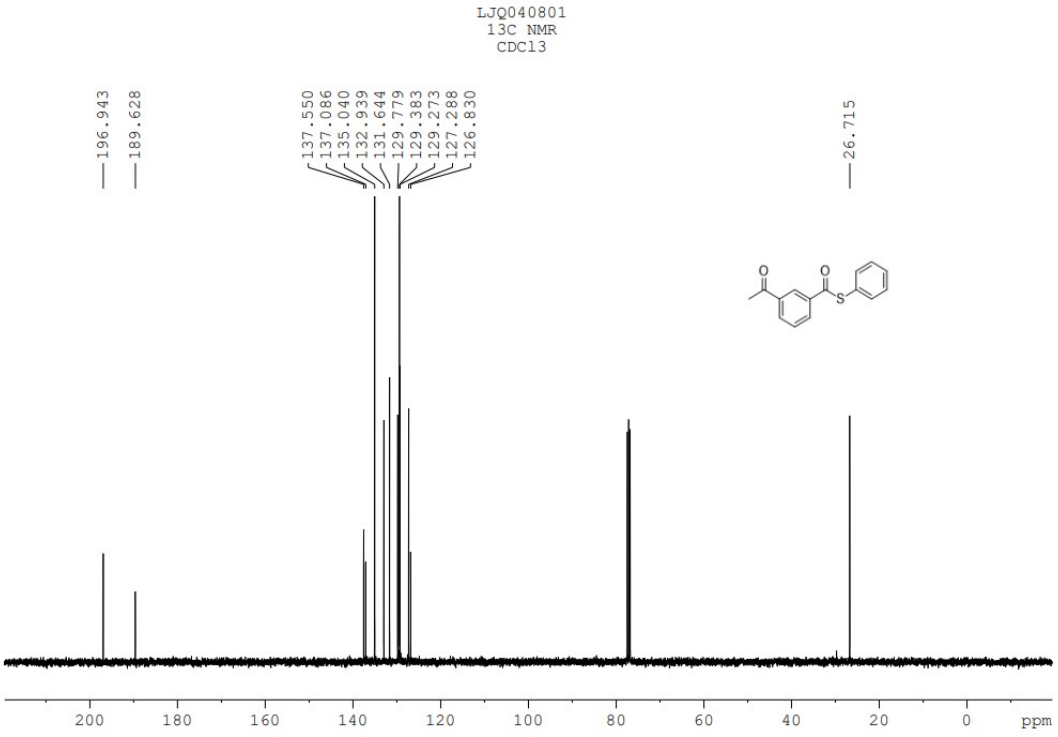
8.204
8.200
8.197
7.636
7.617
7.597
7.558
7.552
7.549
7.544
7.540
7.537
7.533
7.505
7.500
7.496
7.488
7.486
7.480
8.230
8.226
8.224
8.220
8.216
8.214
8.211
8.206
8.204
8.200
7.636
7.617
7.597
7.558
7.552
7.549
7.544
7.540
7.537
7.533
7.500
7.496
7.488
7.486
7.480
2.678
O
O
S
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
ppm
0.976
2.000
1.003
5.021
9
8
7
6
5
4
3
2
1
ppm
0.976
2.000
1.003
5.021
3.010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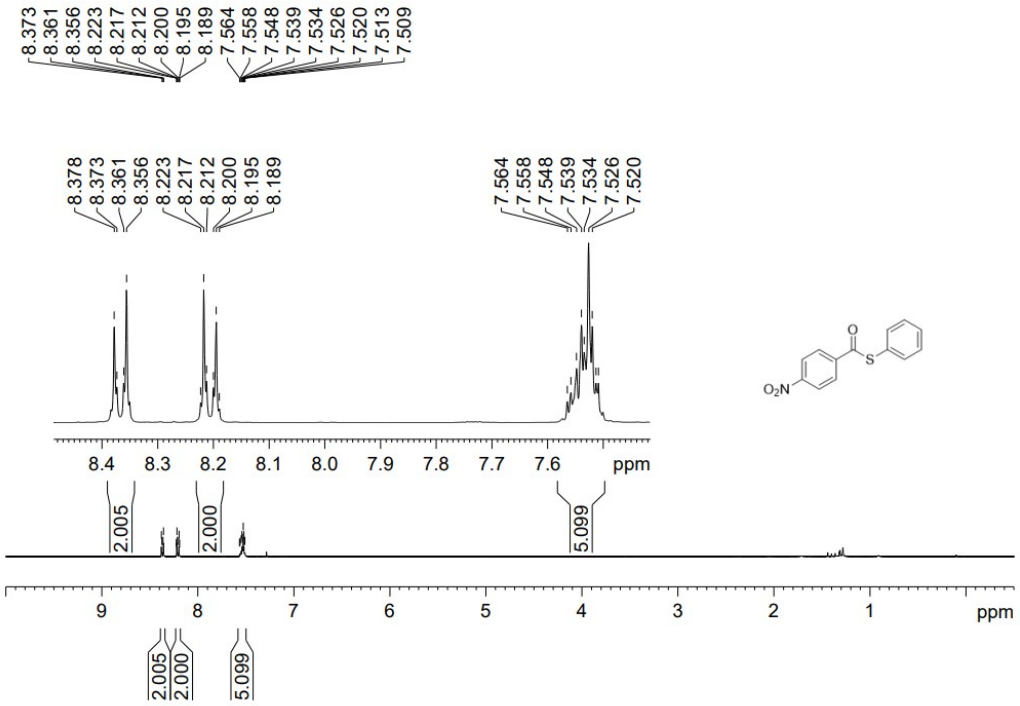
13C NMR
CDCl3
196.943
189.628
137.550
137.086
135.040
132.939
131.644
129.779
129.383
129.273
127.288
126.830
26.715
200
180
160
140
120
100
80
60
40
20
0
ppm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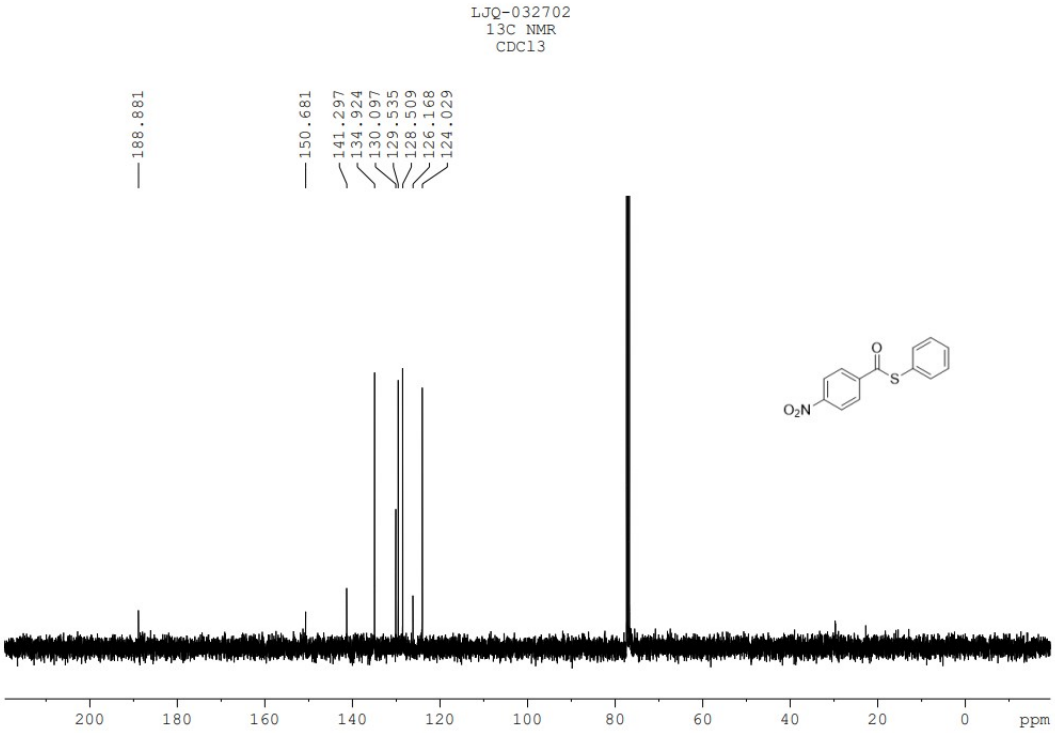
8.361
8.356
8.223
8.217
8.212
8.200
8.195
8.189
7.564
7.558
7.548
7.539
7.534
7.526
7.520
7.513
7.509
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
ppm
2.005
2.000
5.099
9
8
7
6
5
4
3
2
1
ppm


LJQ-032702
13C NMR
CDCl3
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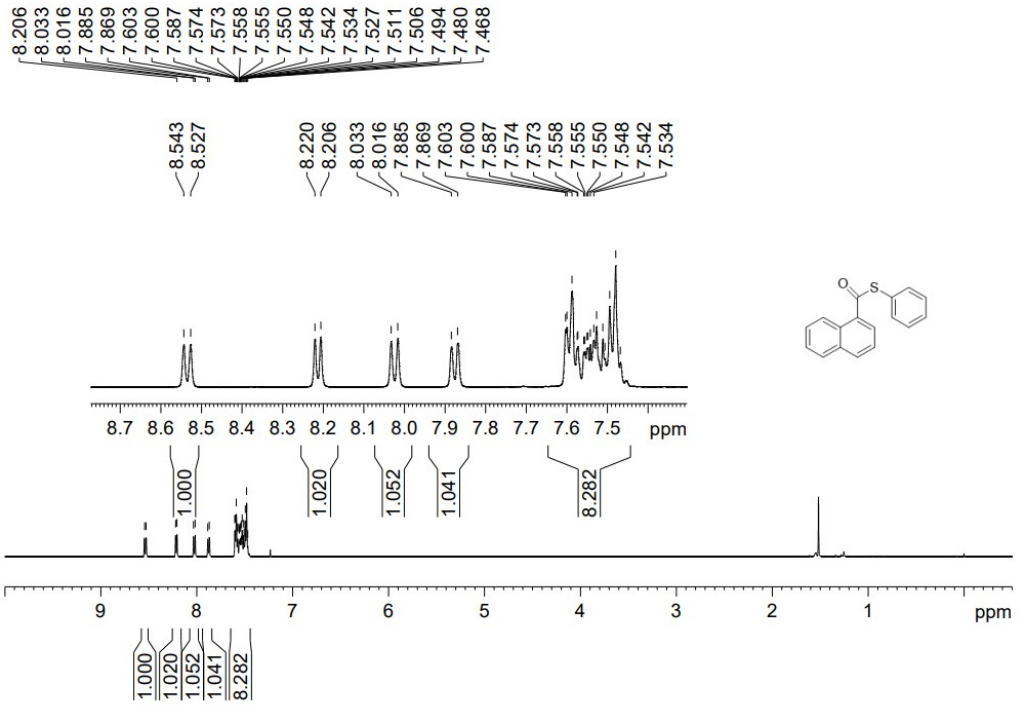
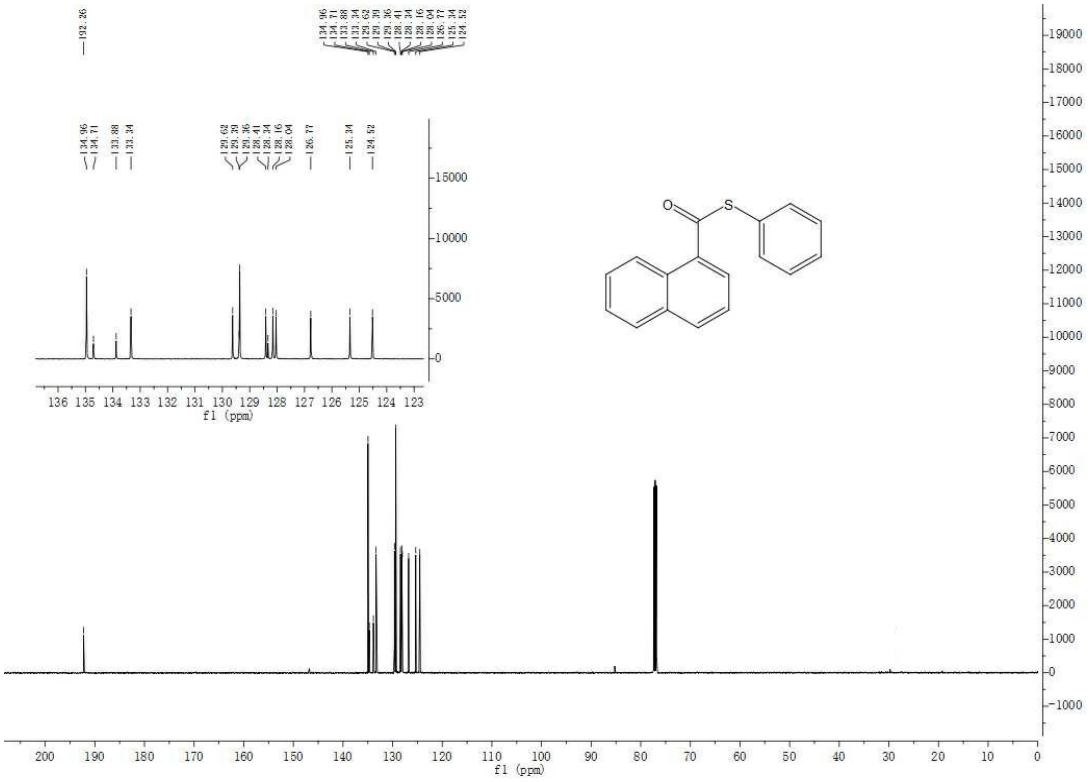
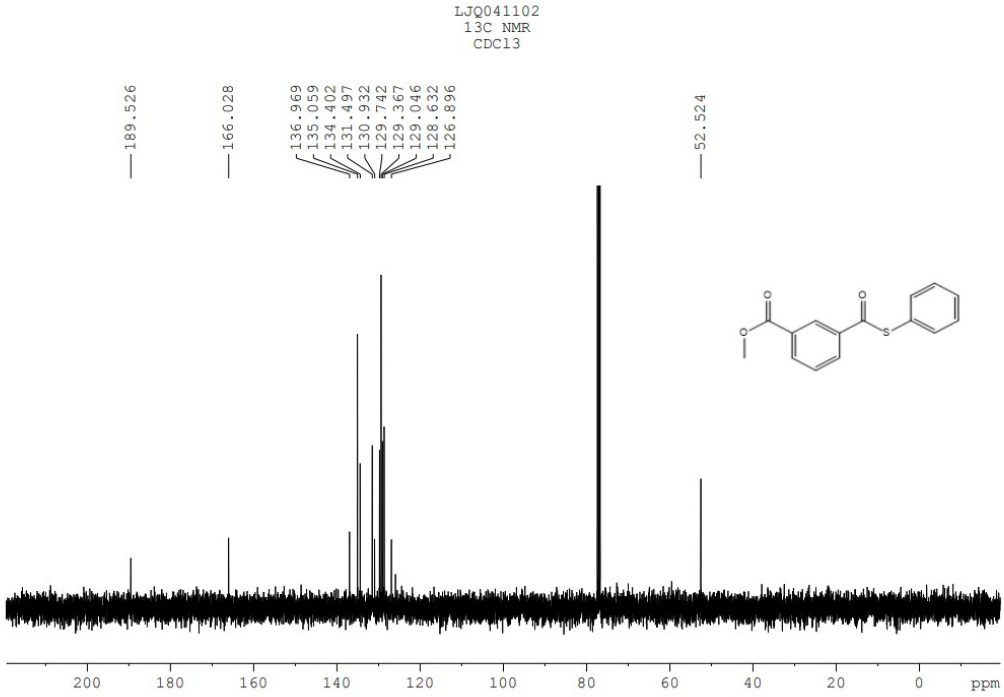
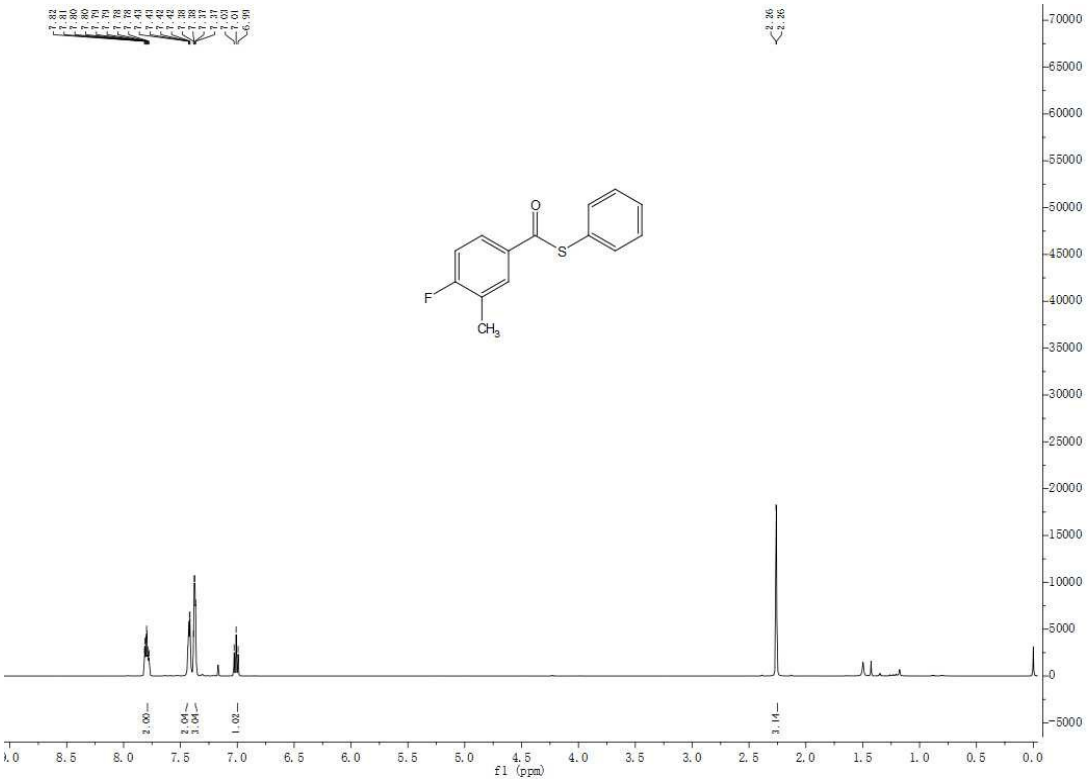
150.681
141.297
134.924
130.097
129.535
128.509
126.168
124.029
200
180
160
140
120
100
80
60
40
20
0
ppm

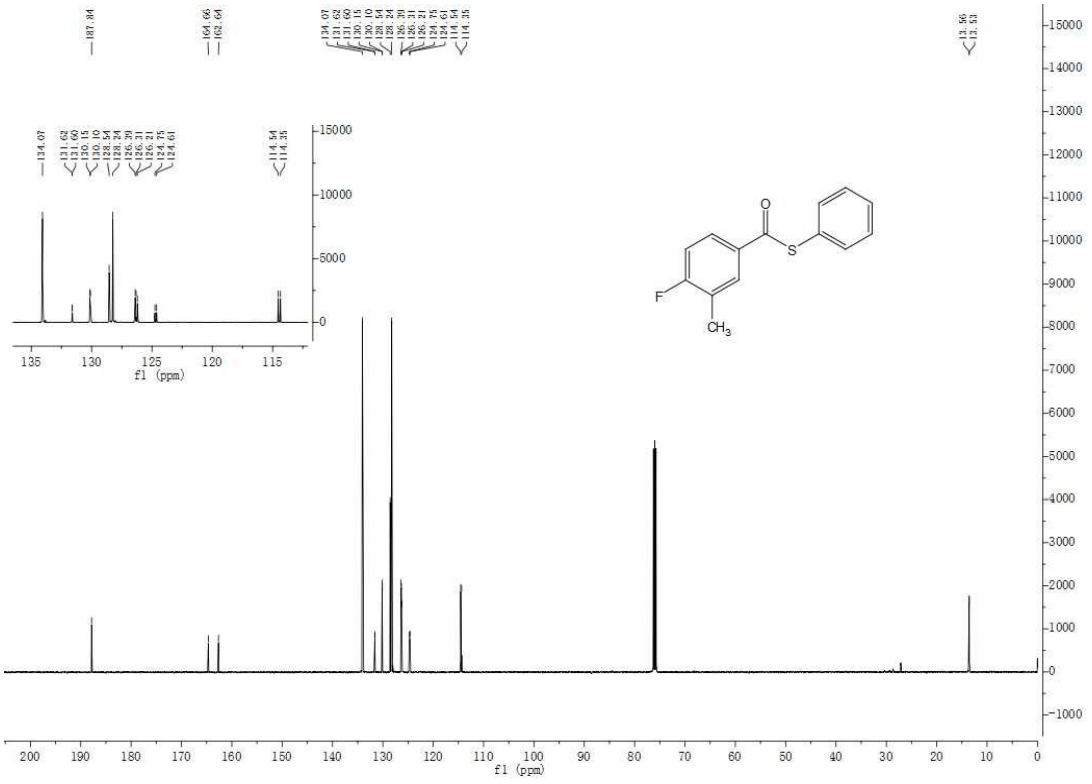

8.206
8.033
8.016
7.885
7.869
7.603
7.600
7.587
7.574
7.573
7.558
7.555
7.550
7.548
7.542
7.534
7.527
7.511
7.506
7.494
7.480
7.468
8.543
8.527
8.220
8.206
8.033
8.016
7.885
7.869
7.603
7.600
7.587
7.574
7.573
7.558
7.555
7.550
7.548
7.542
7.534
8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5
ppm
1.000
1.020
1.052
1.041
8.282
9
8
7
6
5
4
3
2
1
ppm
1.000
1.020
1.052
1.041
8.282

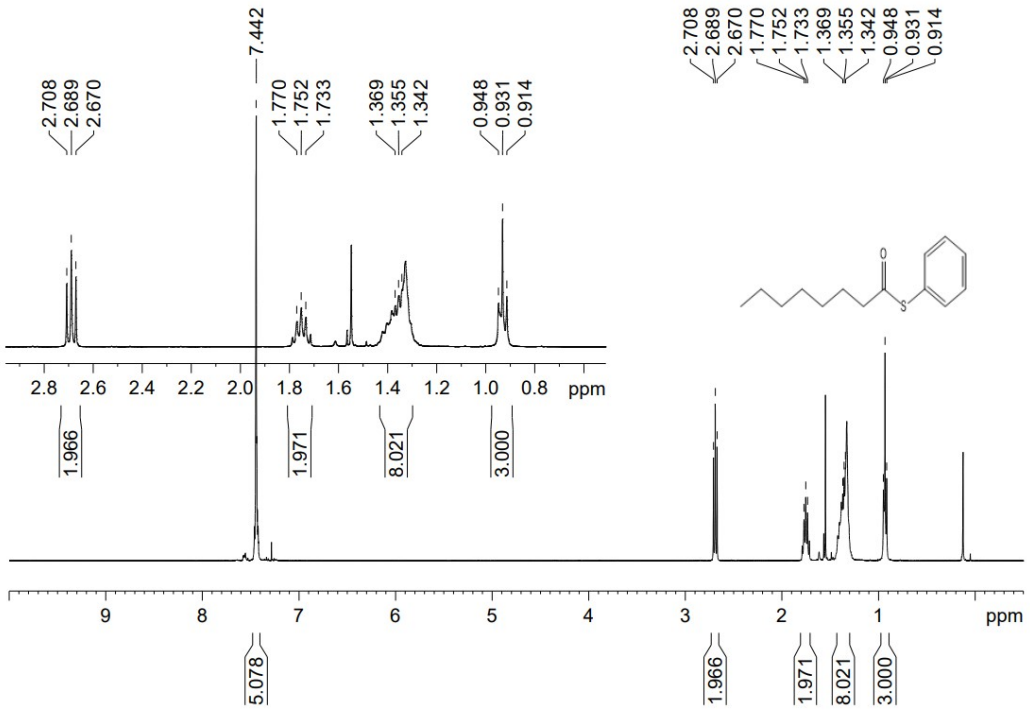

192.26
134.96
134.71
133.88
133.34
129.62
129.39
129.36
128.41
128.26
128.16
128.04
126.77
125.34
124.52
f1 (ppm)


8.311
8.292
8.222
8.221
8.203
8.202
7.626
7.606
7.587
7.566
7.558
7.553
7.549
7.546
7.542
7.509
7.505
7.499
7.496
7.488
8.719
8.714
8.710
3.994
ppm
1.000
1.022
1.018
1.053
2.069
3.010
3.028


LJQ041102
13C NMR
CDCl3
189.526
166.028
136.969
135.059
134.402
131.497
130.932
129.742
129.367
129.046
128.632
126.896
52.524
O
O
O
S
200
180
160
140
120
100
80
60
40
20
0
ppm


O
S
F
CH3
f1 (ppm)


O
S
F
CH3
f1 (ppm)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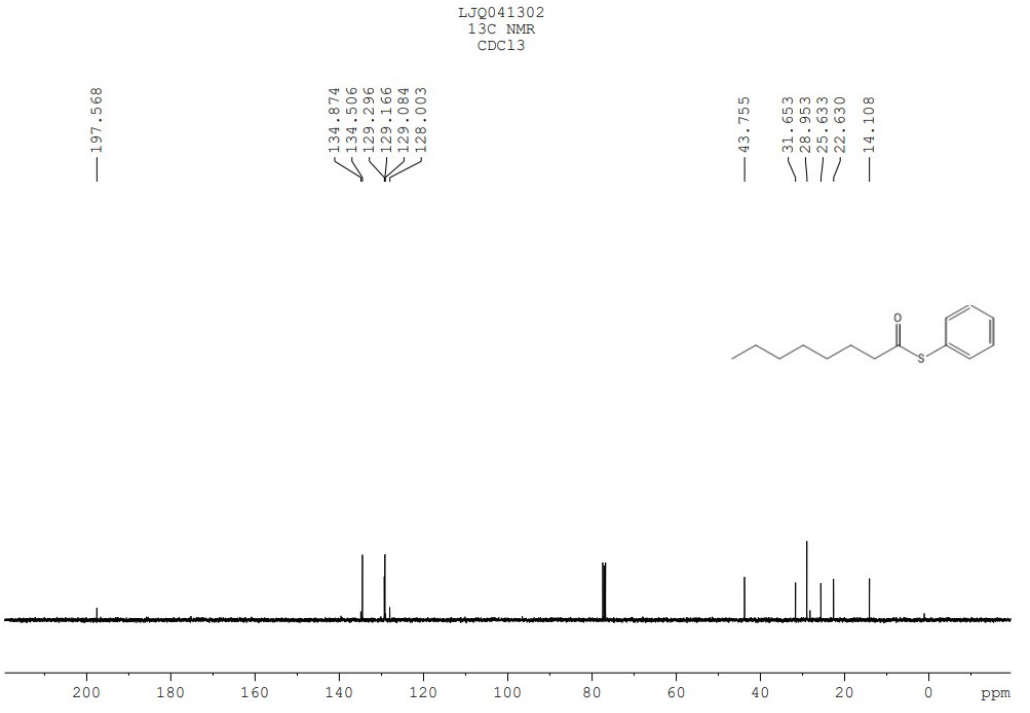
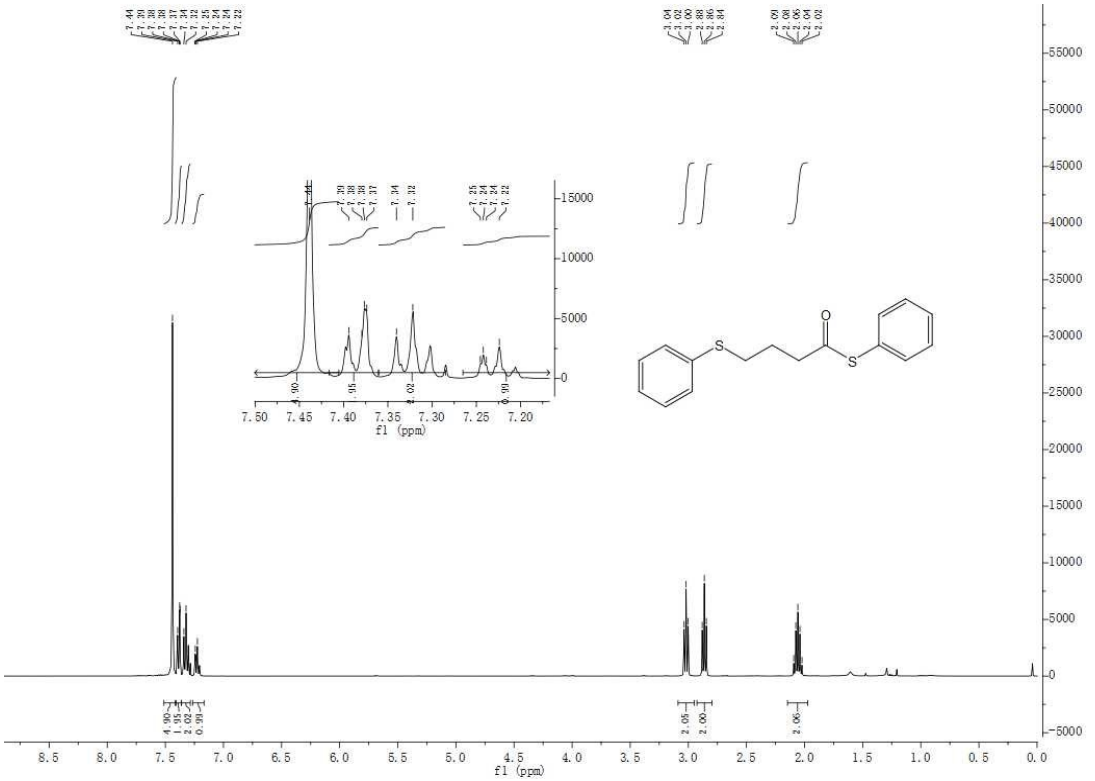
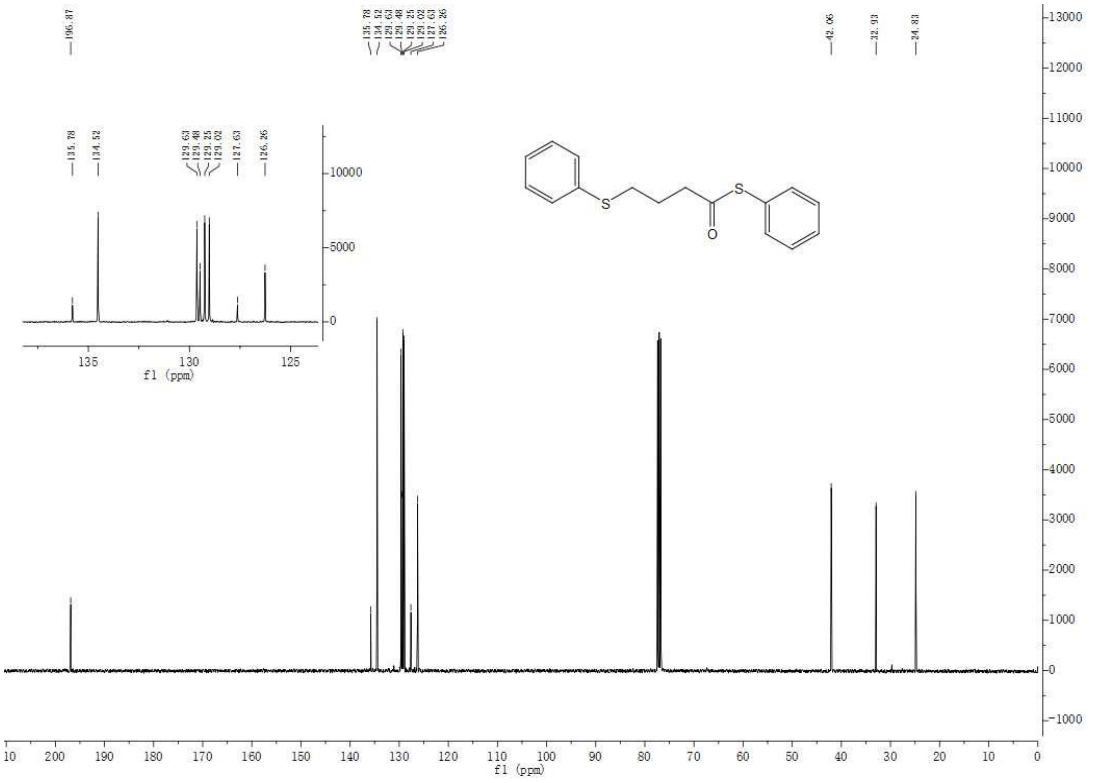
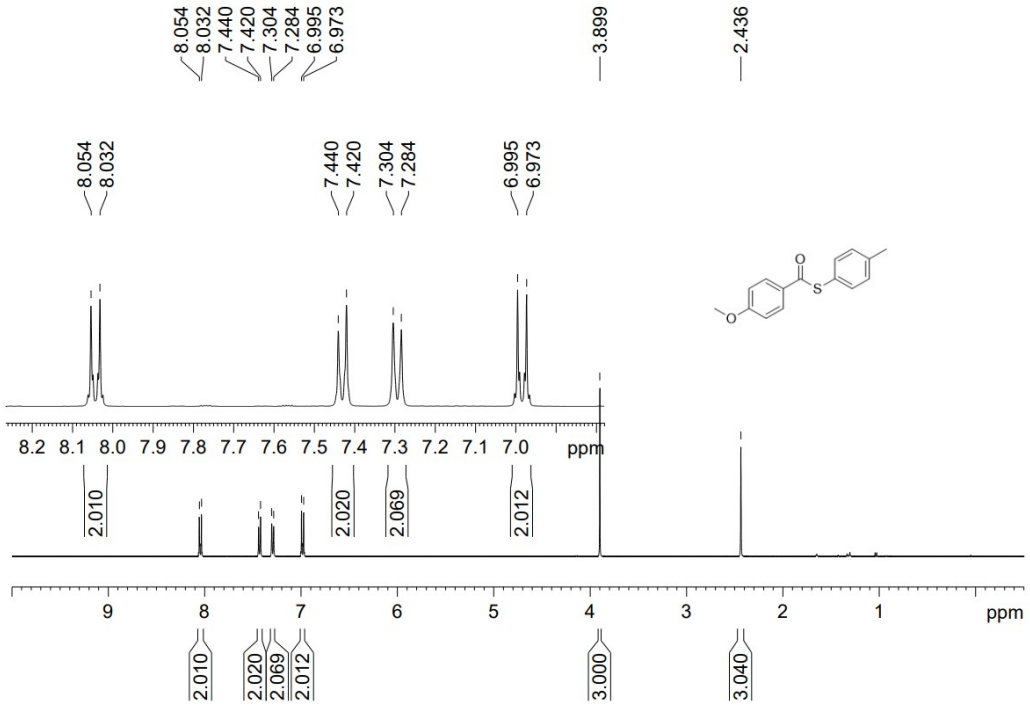
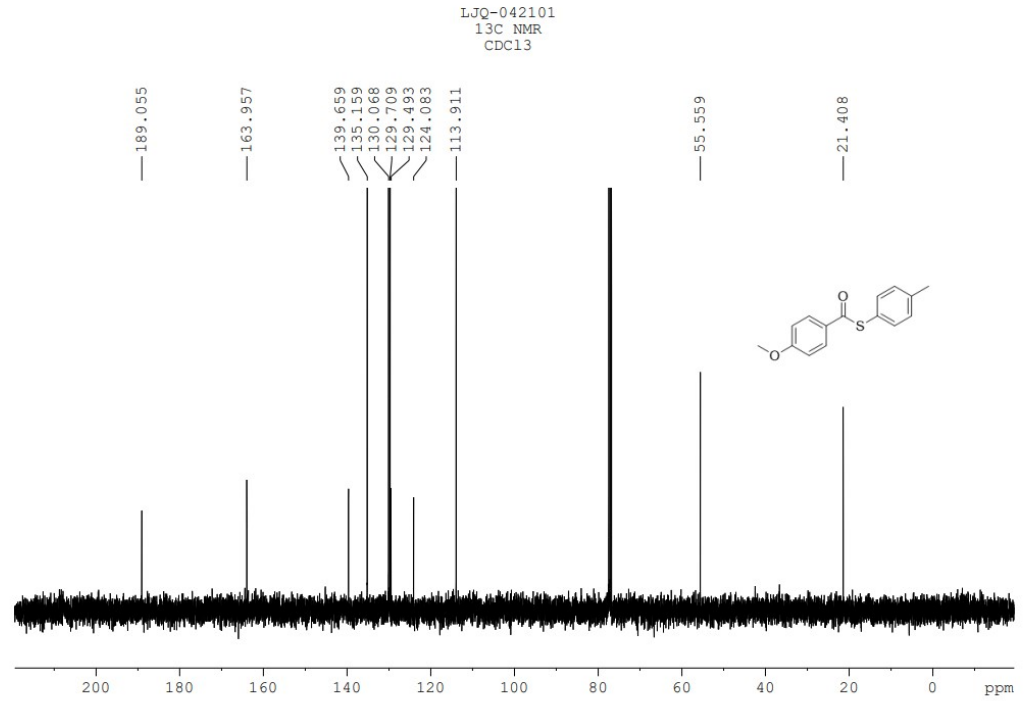
2.689
2.670
7.442
1.770
1.752
1.733
1.369
1.355
1.342
0.948
0.931
0.914
ppm
1.966
1.971
8.021
3.000
5.078

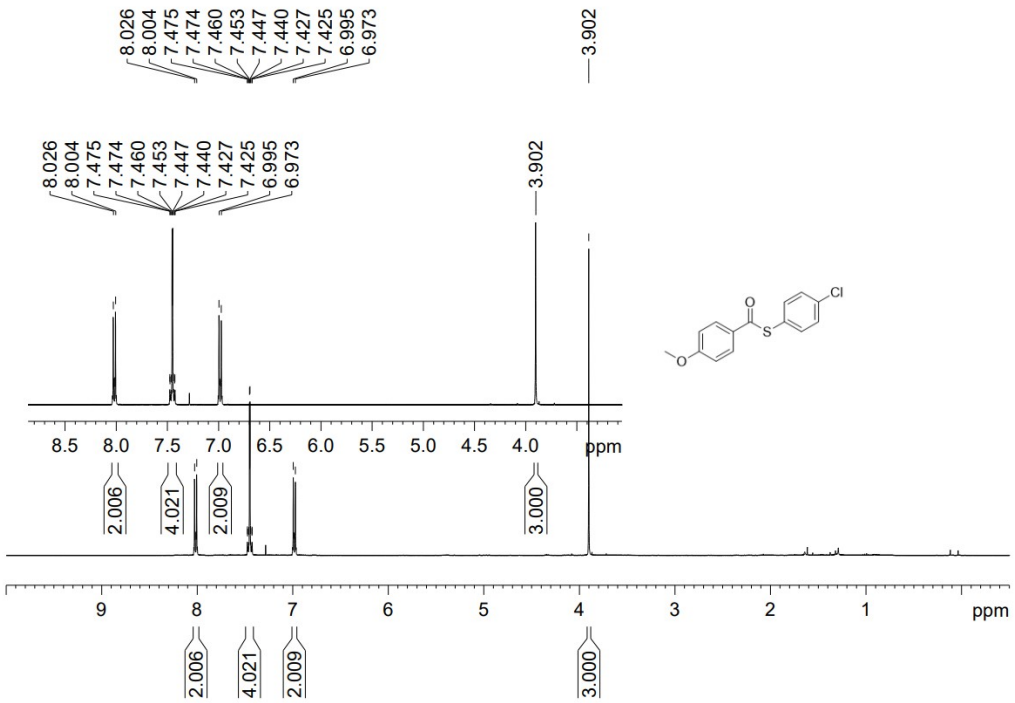

LJQ041302
13C NMR
CDC13
197.568
134.874
134.506
129.296
129.166
129.084
128.003
43.755
31.653
28.953
25.633
22.630
14.108
ppm

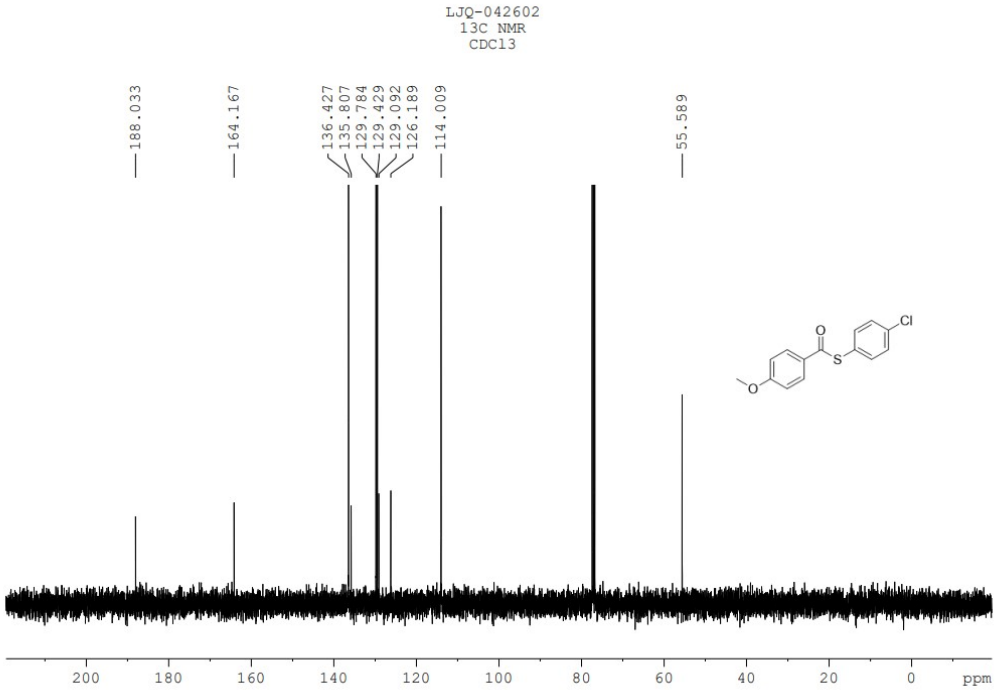

f1 (ppm)

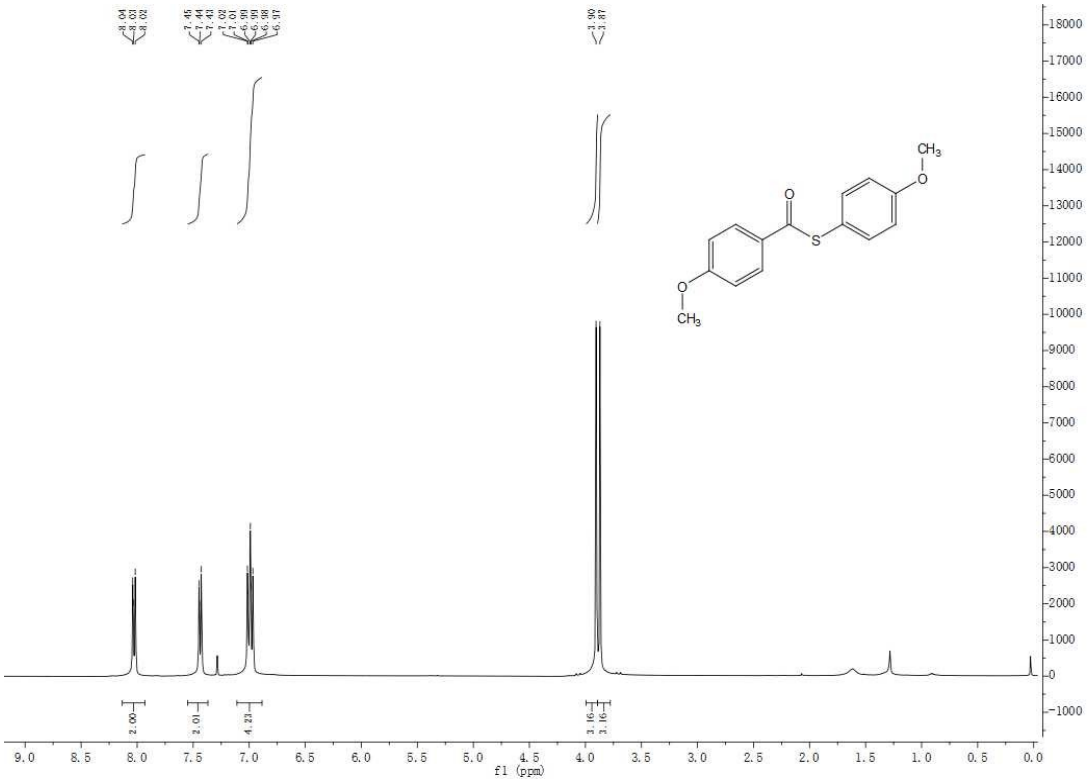

f1 (ppm)

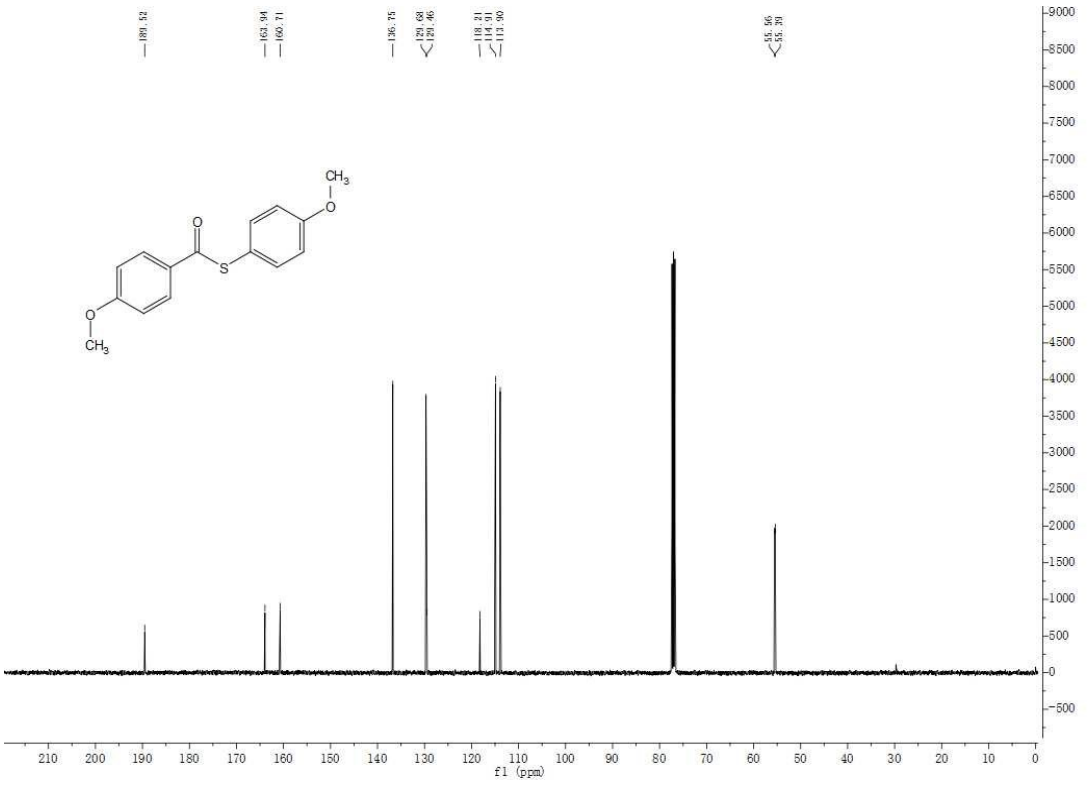

8.054
8.032
7.440
7.420
7.304
7.284
6.995
6.973
3.899
2.436
ppm
2.010
2.020
2.069
2.012
3.000
3.040

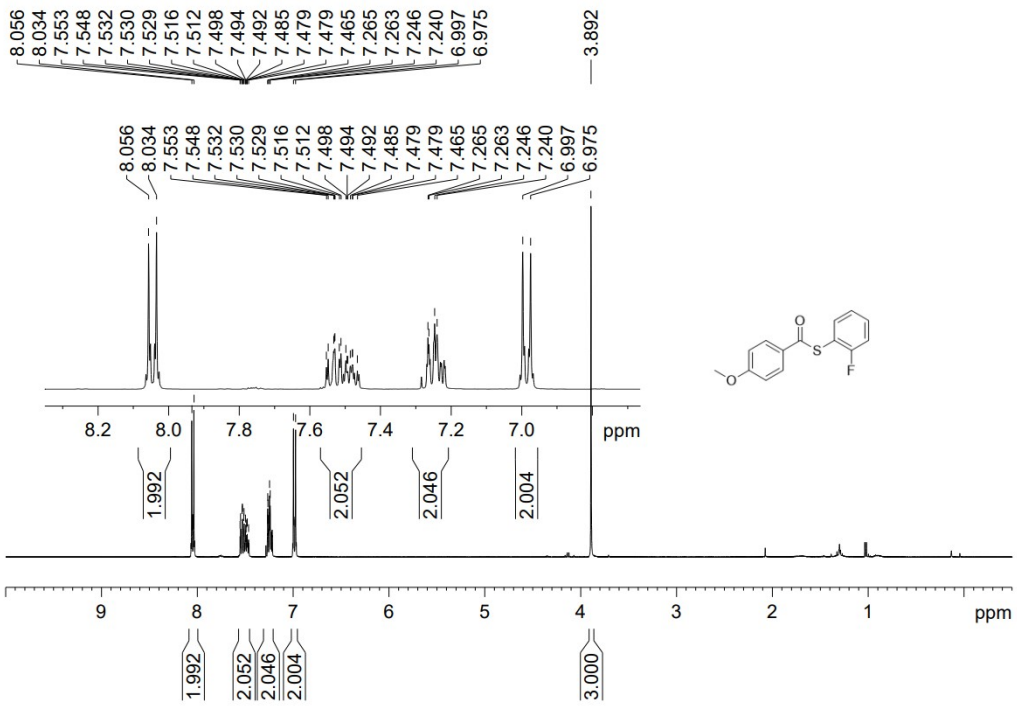

LJQ-042101
13C NMR
CDCl3
189.055
163.957
139.659
135.159
130.068
129.709
129.493
124.083
113.911
55.559
21.408
ppm

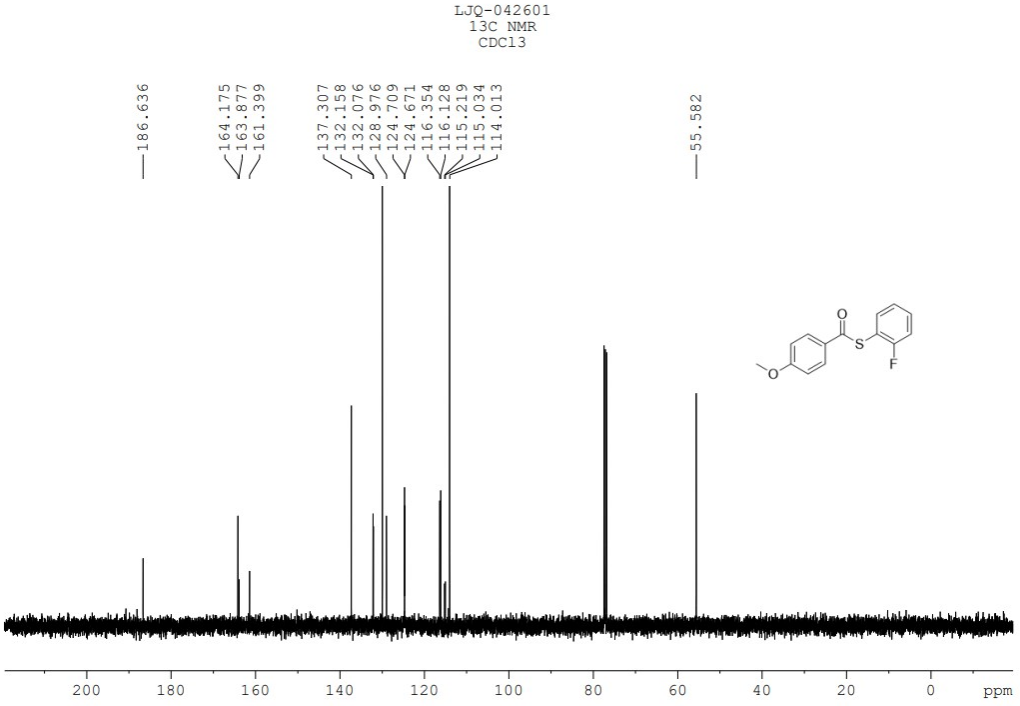

8.026
8.004
7.475
7.474
7.460
7.453
7.447
7.440
7.427
7.425
6.995
6.973
3.902
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 ppm
2.006
4.021
2.009
3.000
9 8 7 6 5 4 3 2 1 ppm
Cl
O
S
O

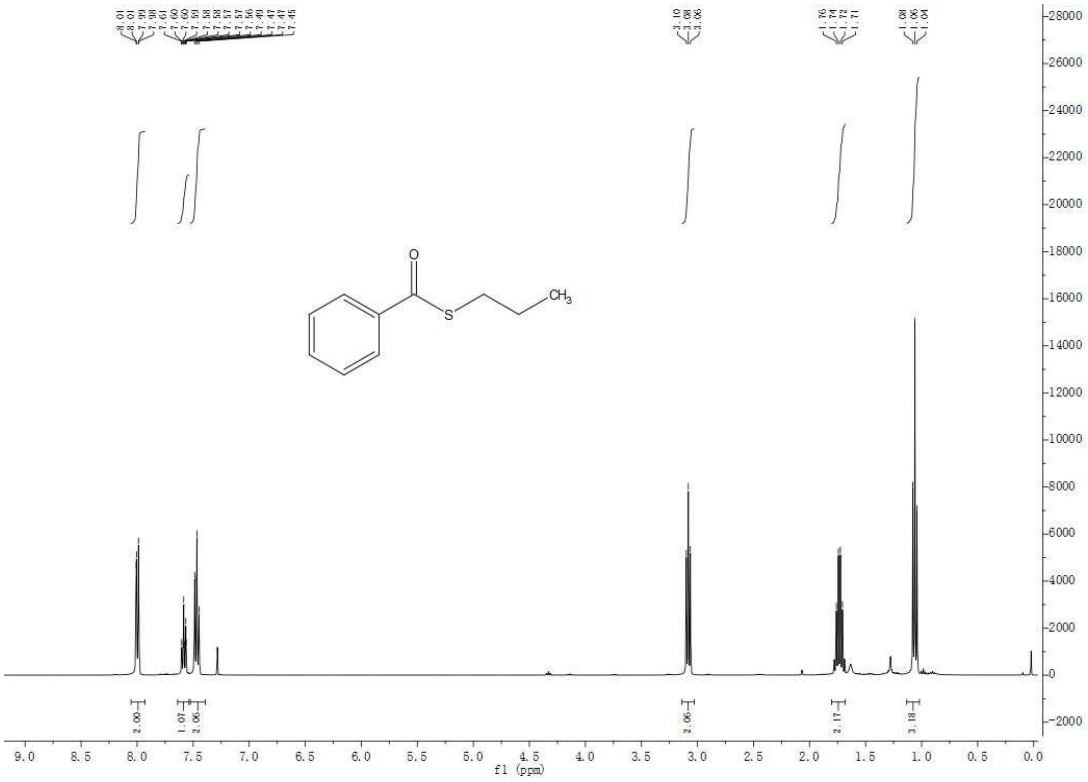

LJQ-042602
13C NMR
CDCl3
188.033
164.167
136.427
135.807
129.784
129.429
129.092
126.189
114.009
55.589
200 180 160 140 120 100 80 60 40 20 0 ppm
Cl
O
S
O

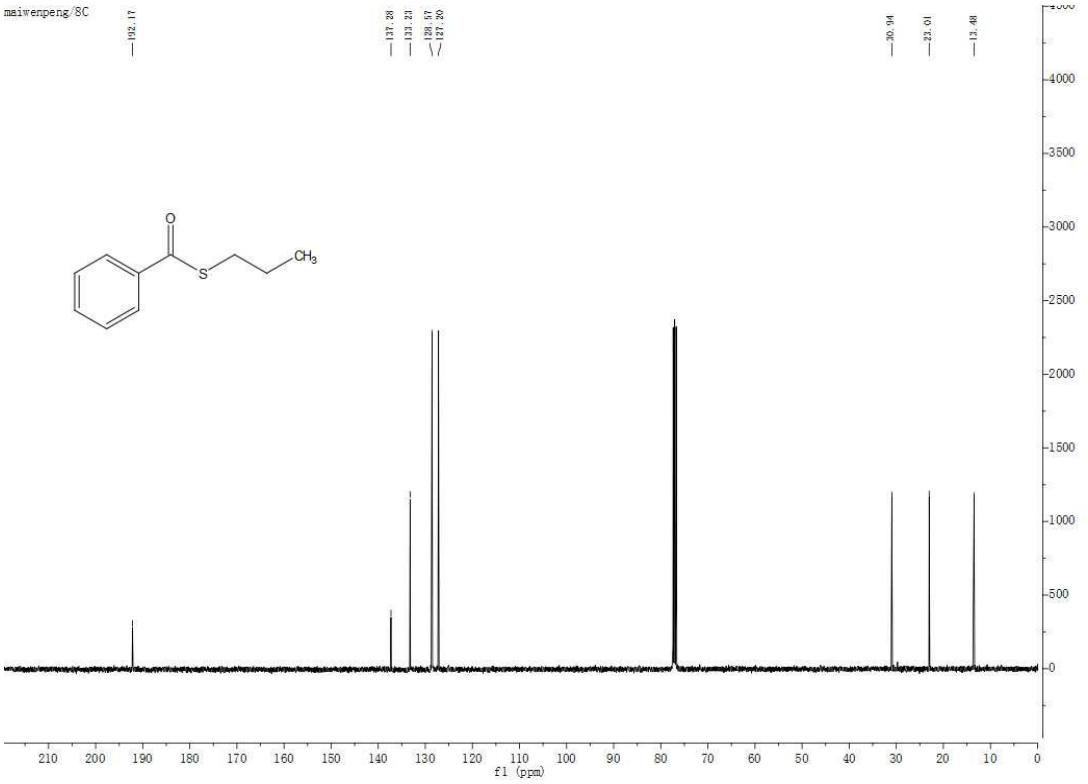

8.04
8.03
8.02
7.45
7.44
7.43
7.02
7.01
6.99
6.98
6.97
3.90
3.87
CH3
O
S
O
CH3
2.00
2.01
4.23
3.16
3.16
f1 (ppm)

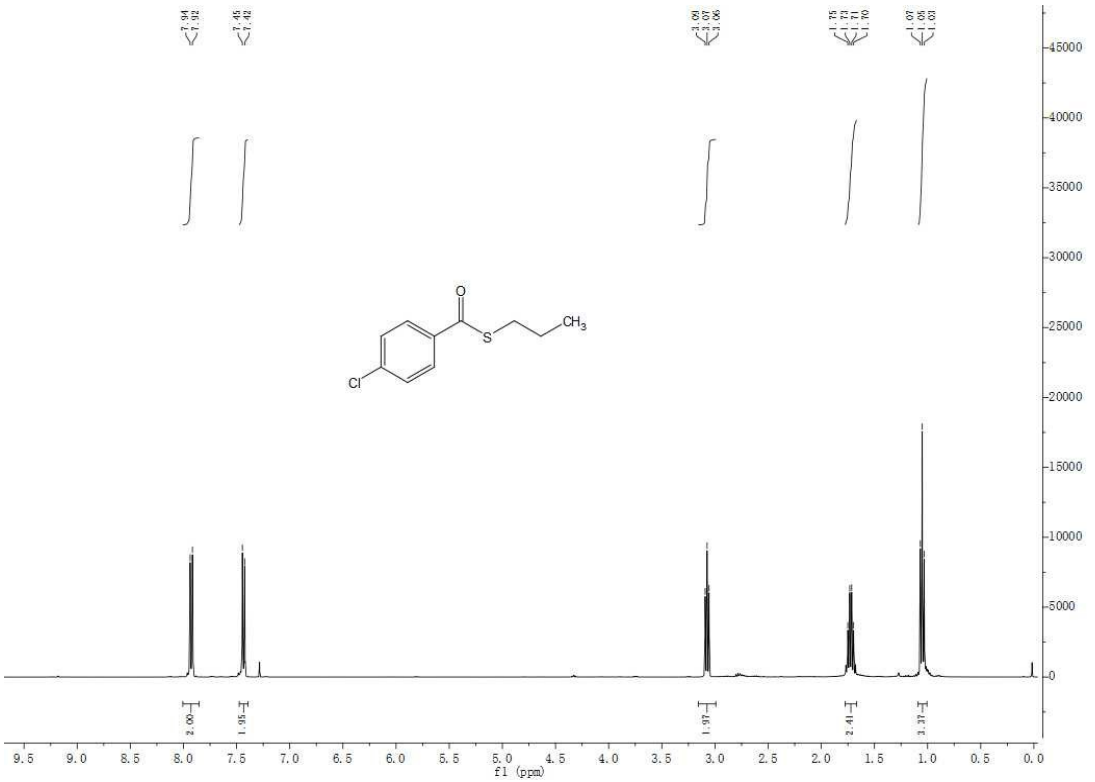

189.52
163.94
160.71
136.75
129.68
129.46
118.21
114.91
113.90
55.56
55.39
CH3
O
O
S
O
CH3
f1 (ppm)

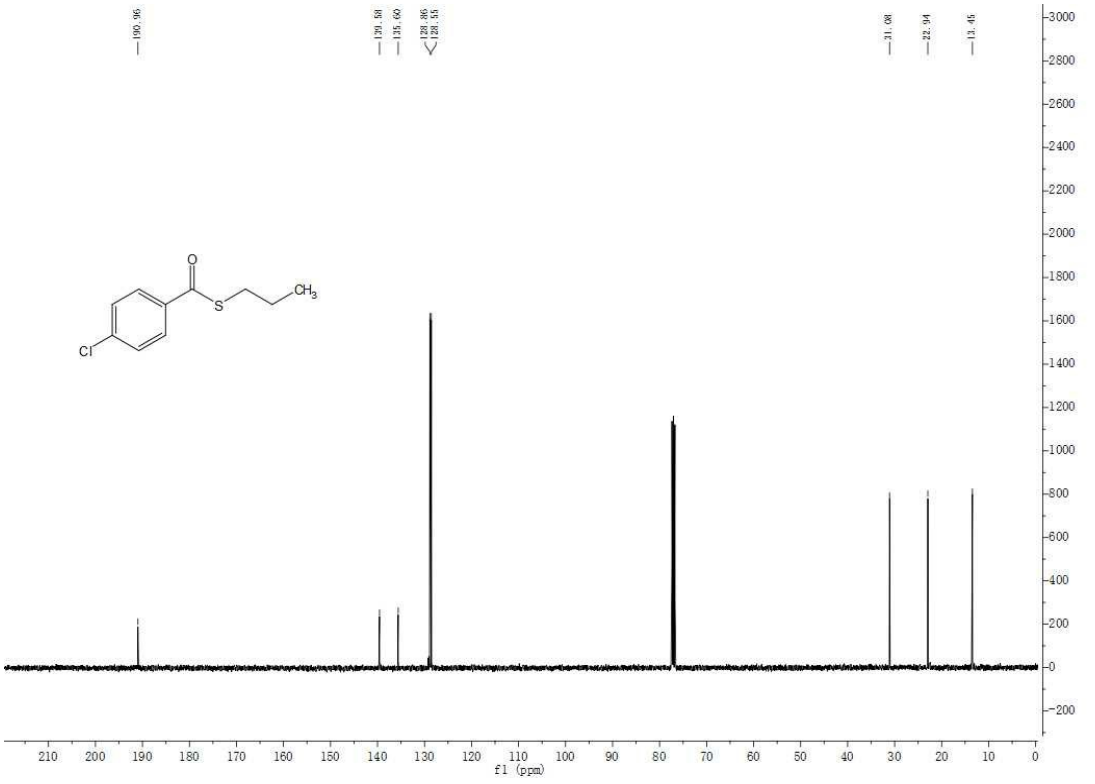

8.056
8.034
7.553
7.548
7.532
7.530
7.529
7.516
7.512
7.498
7.494
7.492
7.485
7.479
7.465
7.265
7.263
7.246
7.240
6.997
6.975
3.892
8.2
8.0
7.8
7.6
7.4
7.2
7.0
ppm
1.992
2.052
2.046
2.004
9
8
7
6
5
4
3
2
1
ppm
1.992
2.052
2.046
2.004
3.000
O
S
F
O


LJQ-042601
13C NMR
CDCl3
186.636
164.175
163.877
161.399
137.307
132.158
132.076
128.976
124.709
124.671
116.354
116.128
115.219
115.034
114.013
55.582
200
180
160
140
120
100
80
60
40
20
0
ppm
O
S
F
O


O
S
CH3
f1 (ppm)


maiwenpeng/8C
192.17
137.28
133.23
128.57
127.20
30.94
23.01
13.48
O
S
CH3
f1 (ppm)


7.94
7.92
7.45
7.42
3.09
3.07
3.06
1.75
1.73
1.71
1.70
1.07
1.05
1.03
O
S
CH3
Cl
2.00
1.95
1.97
2.41
3.37
f1 (ppm)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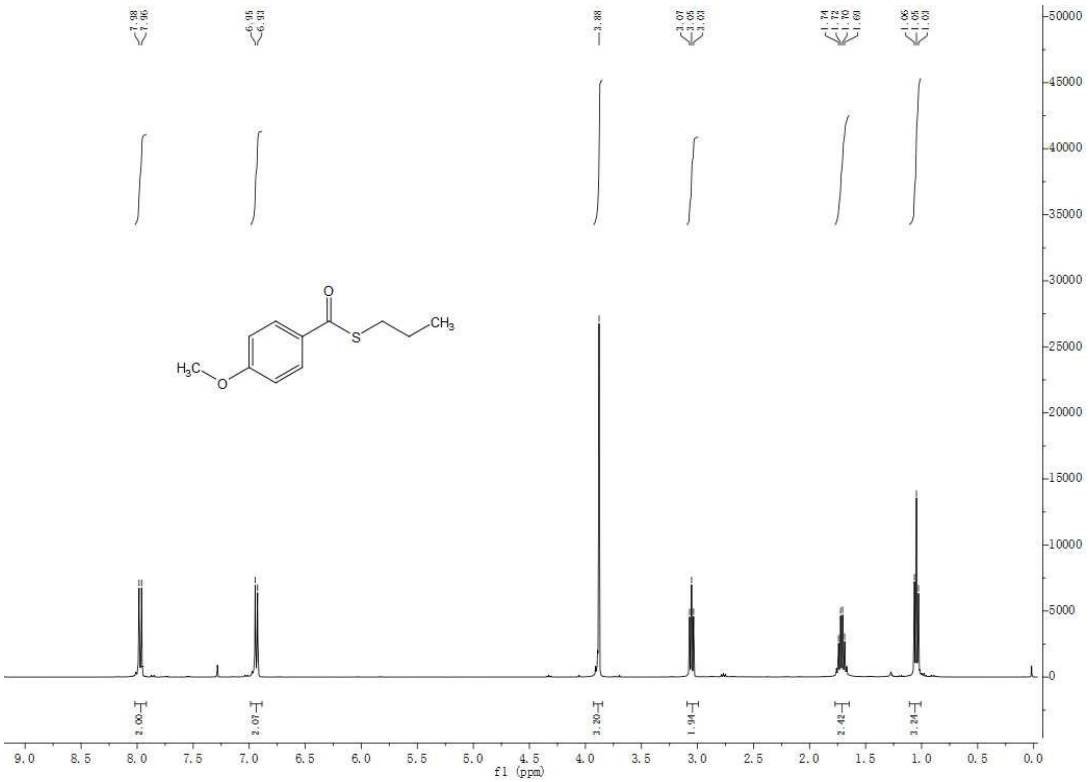
139.58
135.69
128.86
128.51
31.08
22.94
13.45
O
S
CH3
Cl
f1 (ppm)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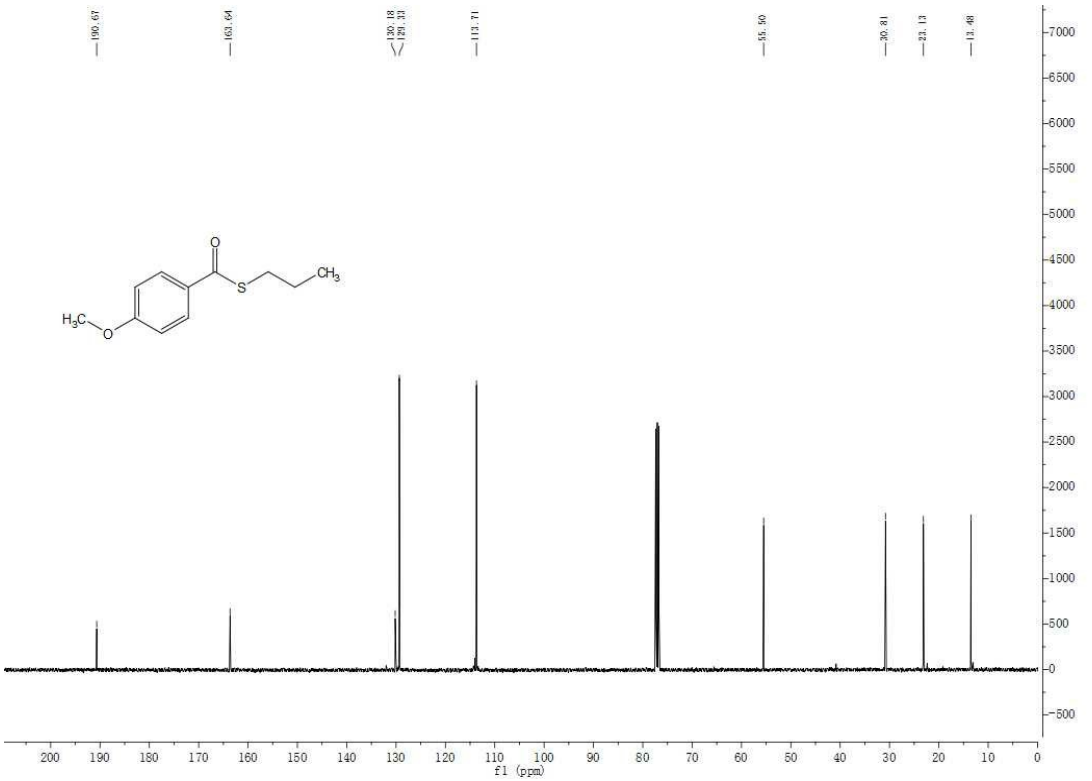
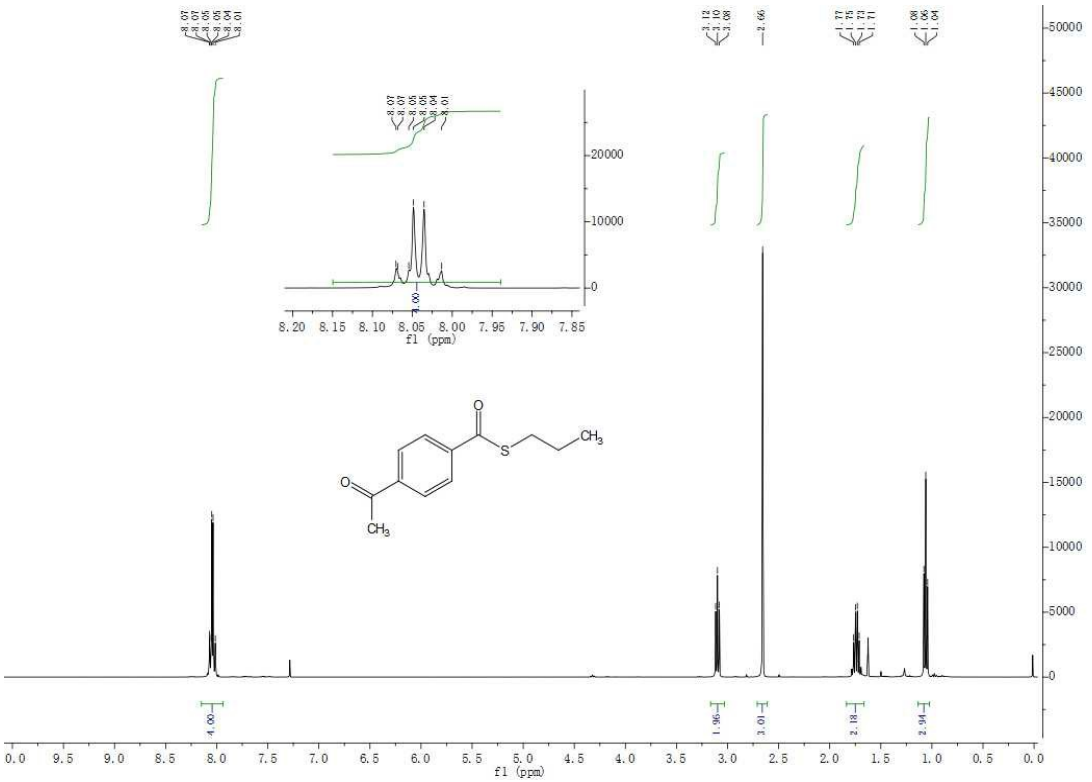
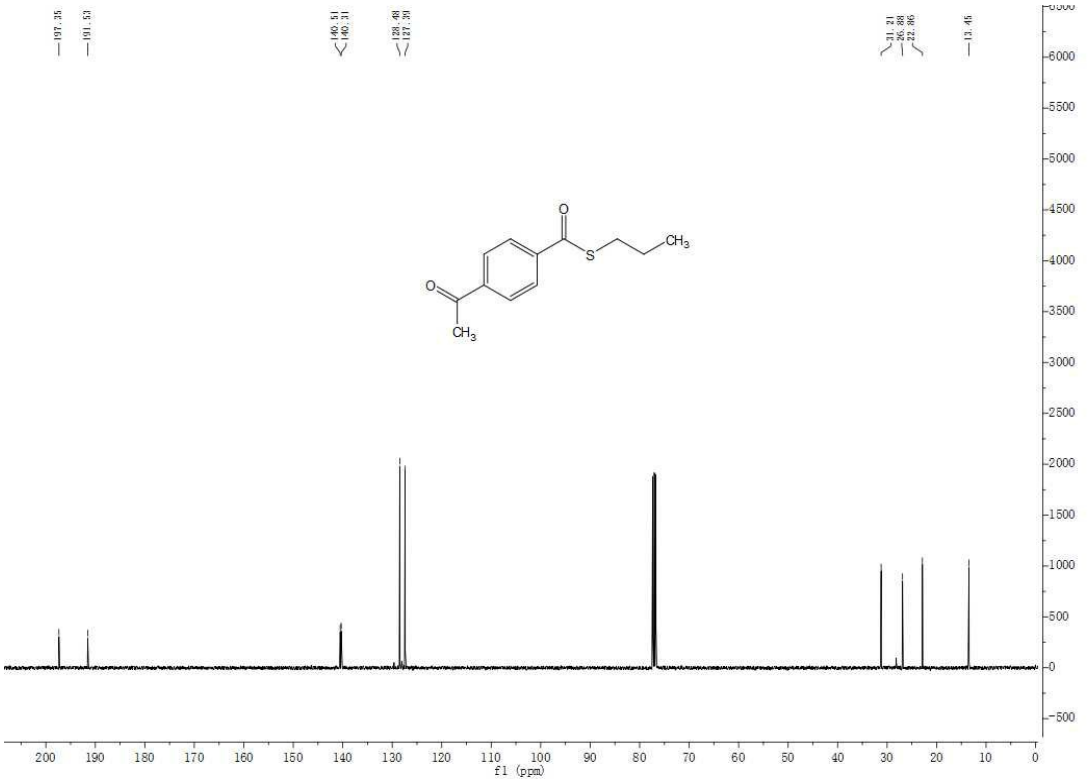
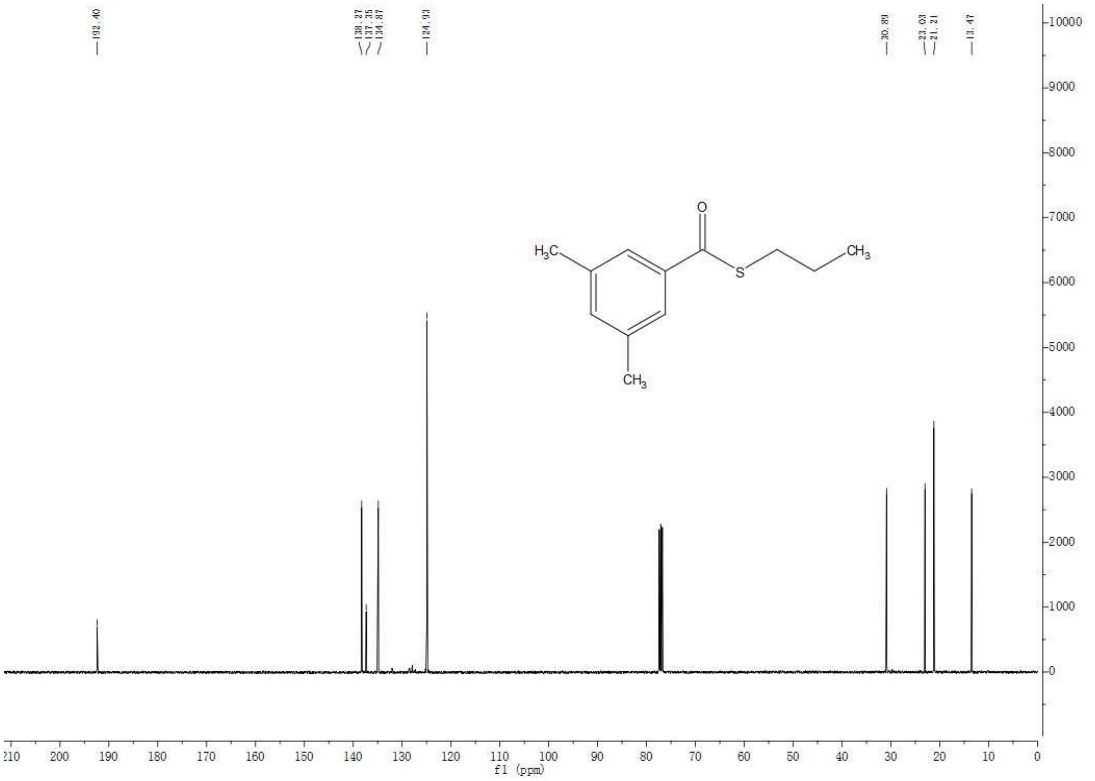
7.96
6.95
6.93
3.88
2.67
2.65
1.69
1.74
1.72
1.70
1.69
1.66
1.65
1.63
O
S
CH3
H3C
O
2.00
2.07
3.20
1.94
2.42
3.24
f1 (ppm)

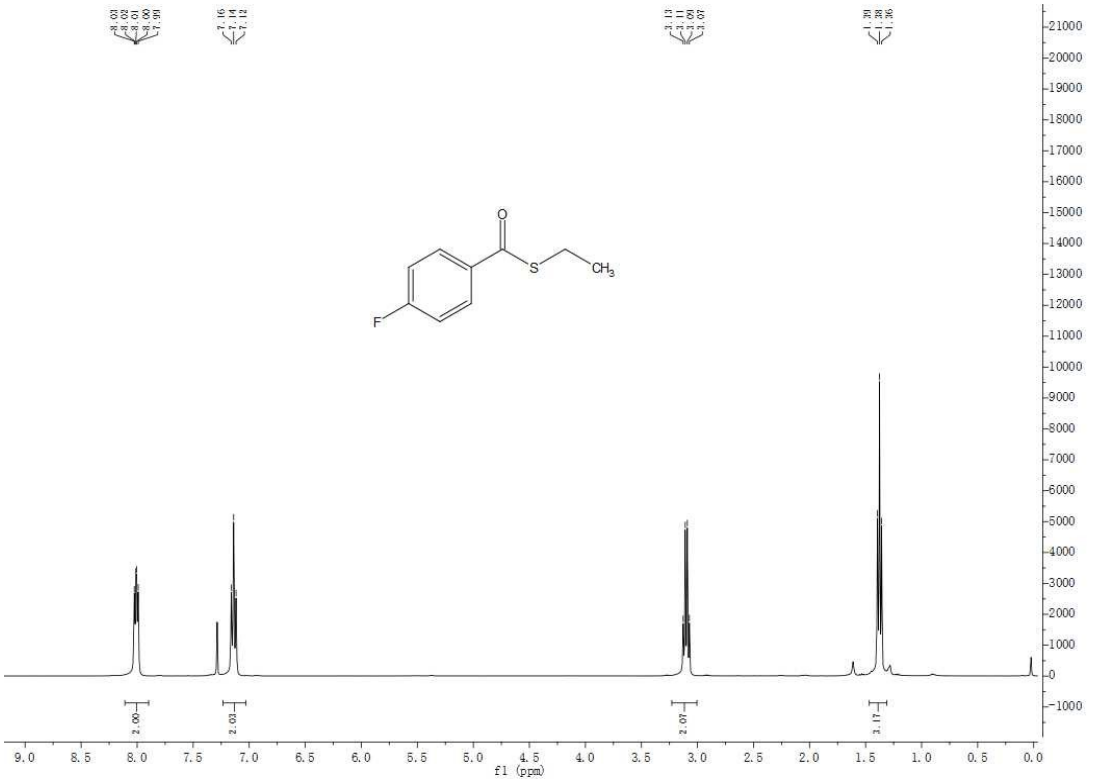

190.67
163.64
130.18
129.33
113.71
55.50
30.81
23.13
13.48
O
S
CH3
H3C
O
f1 (ppm)

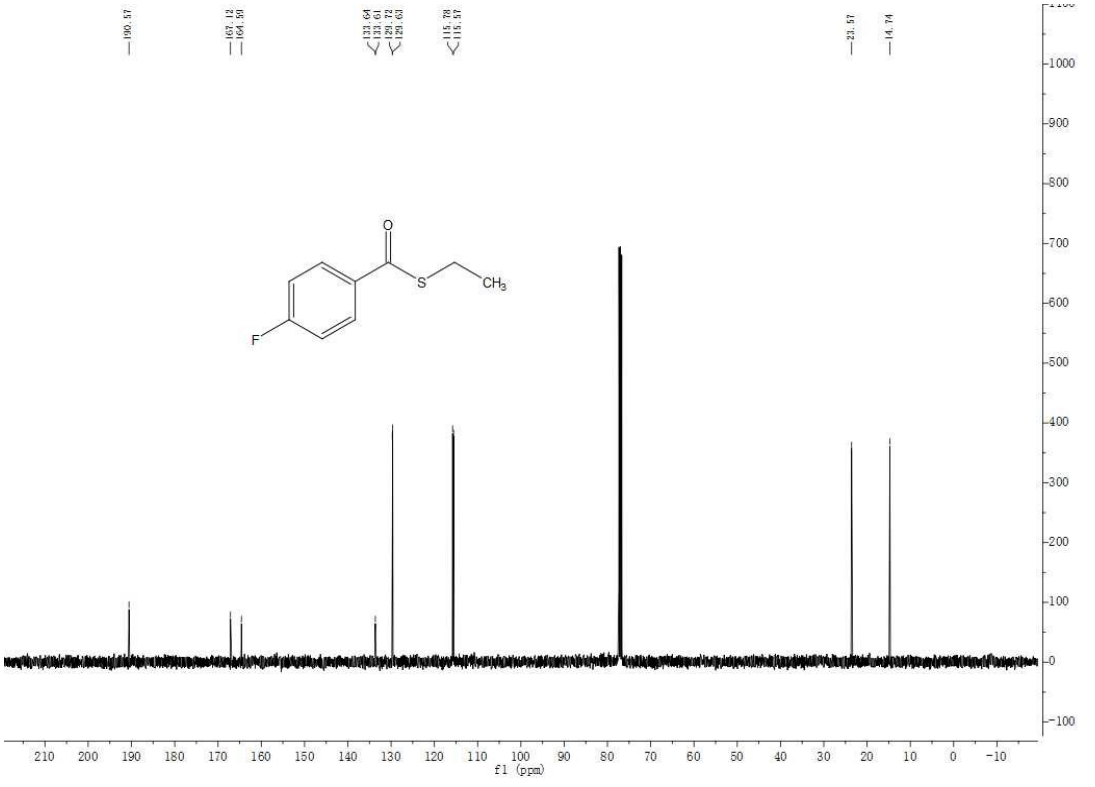

8.07
8.07
8.05
8.05
8.04
8.04
8.01
8.01
3.12
3.10
3.08
2.66
1.77
1.75
1.73
1.71
1.08
1.06
1.04
4.00
1.96
3.01
2.18
2.94
f1 (ppm)
O
S
CH3
O
CH3

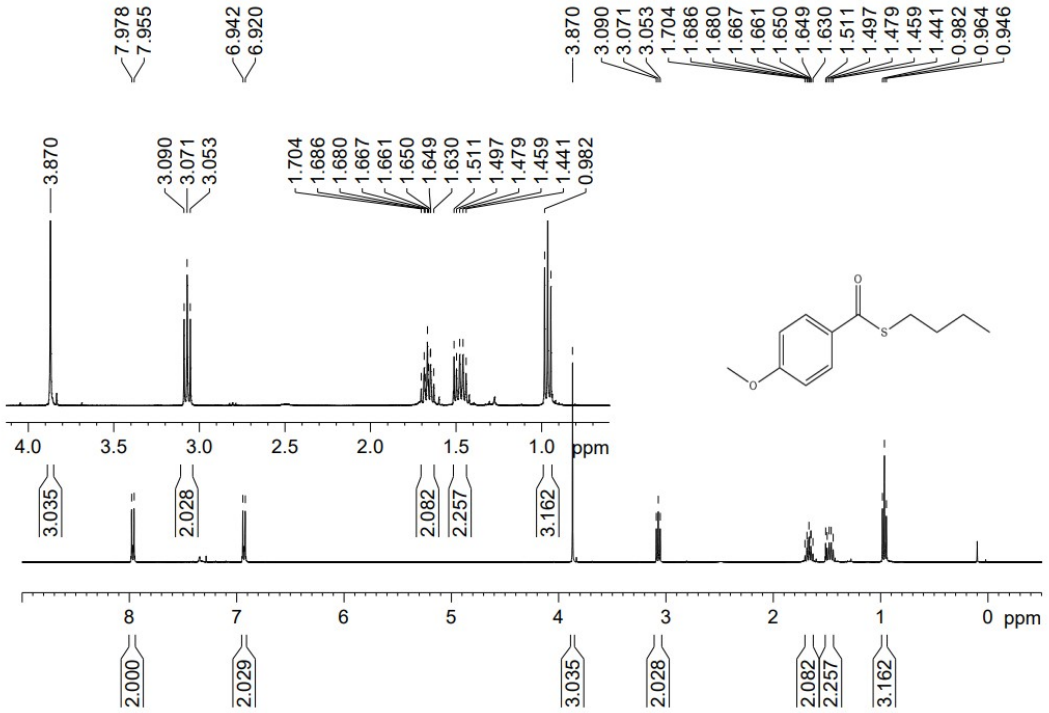

197.35
191.53
140.51
140.31
138.48
137.30
31.21
25.88
22.86
13.46
f1 (ppm)
O
S
CH3
O
CH3


7.61
7.60
7.21
2.88
2.86
2.84
2.38
1.75
1.73
1.71
1.69
1.07
1.06
1.04
H3C
O
S
CH3
CH3
2.00
0.97
2.05
6.27
2.19
3.12
f1 (ppm)

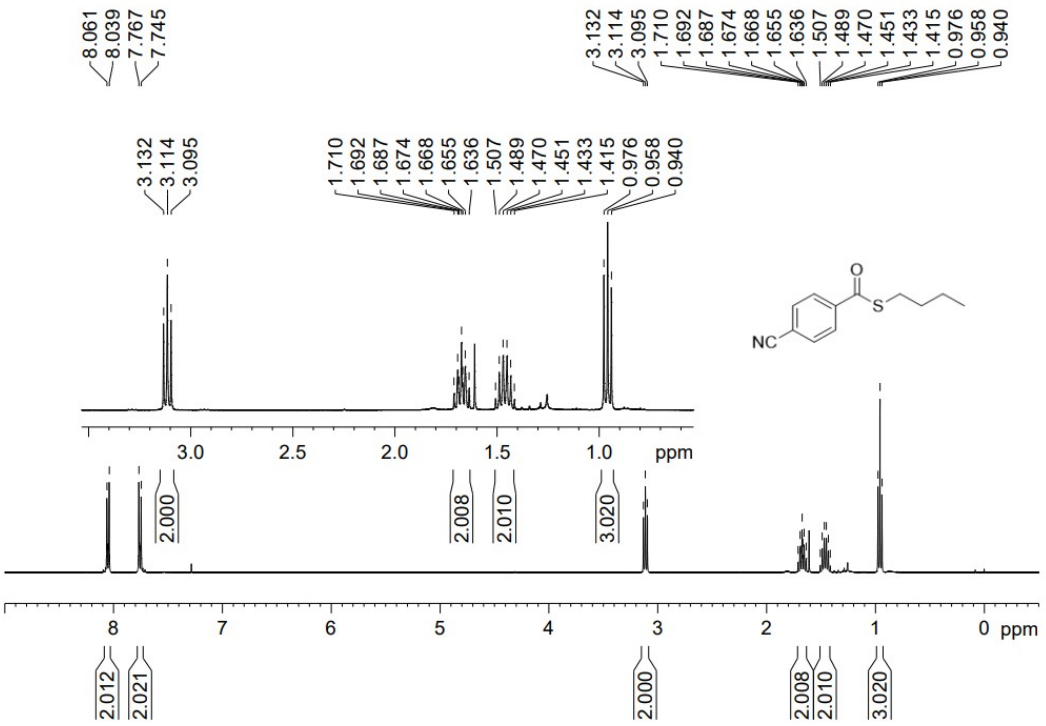

192.40
138.27
137.35
134.87
124.93
30.89
23.03
21.21
13.47
H3C
O
S
CH3
CH3
f1 (ppm)

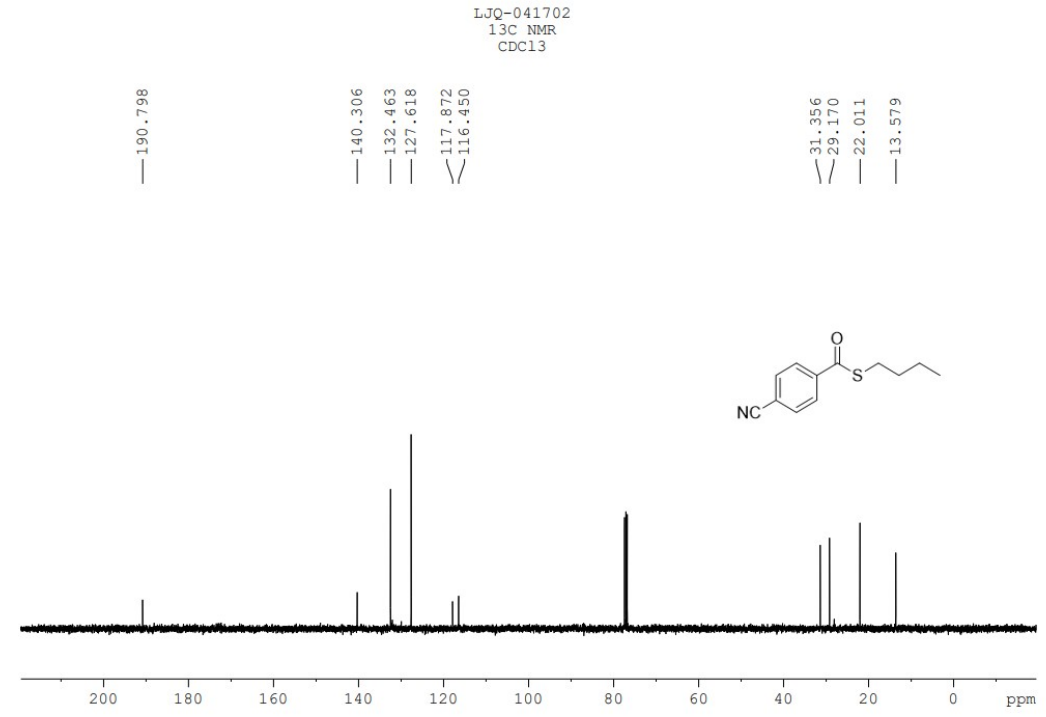

8.02
8.01
8.00
7.99
7.16
7.14
7.12
3.13
3.11
3.09
3.07
1.39
1.38
1.36
O
S
CH3
F
2.00
2.03
2.07
3.17
f1 (ppm)

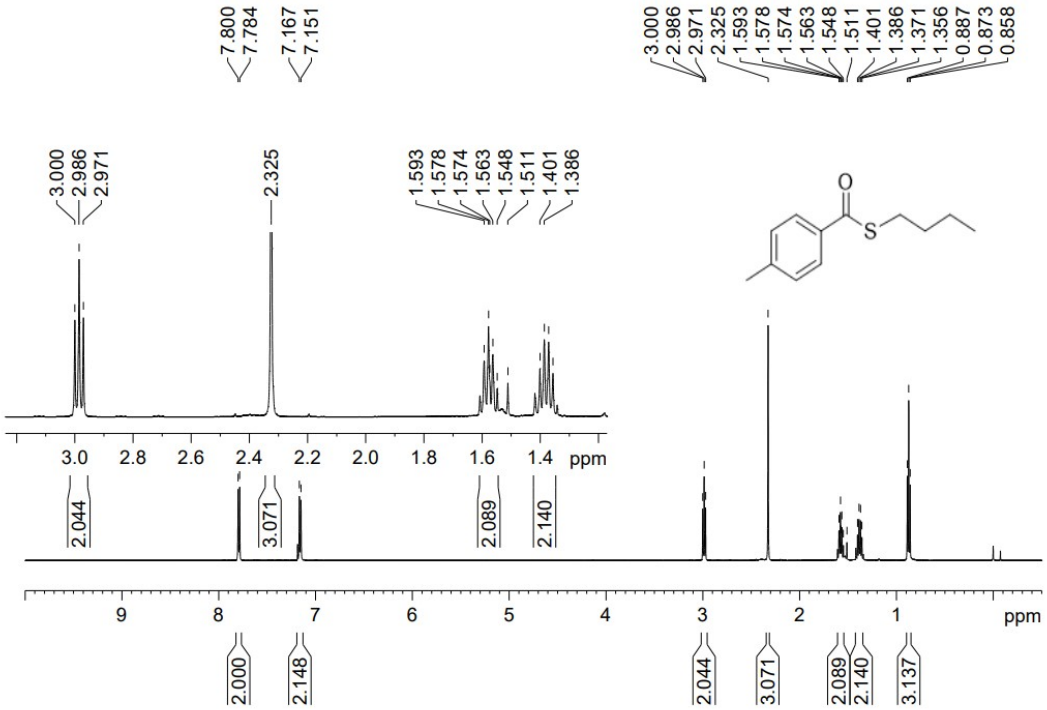

190.57
167.12
164.59
133.64
133.61
129.72
129.63
115.78
115.57
23.57
14.74
O
S
CH3
F
f1 (ppm)

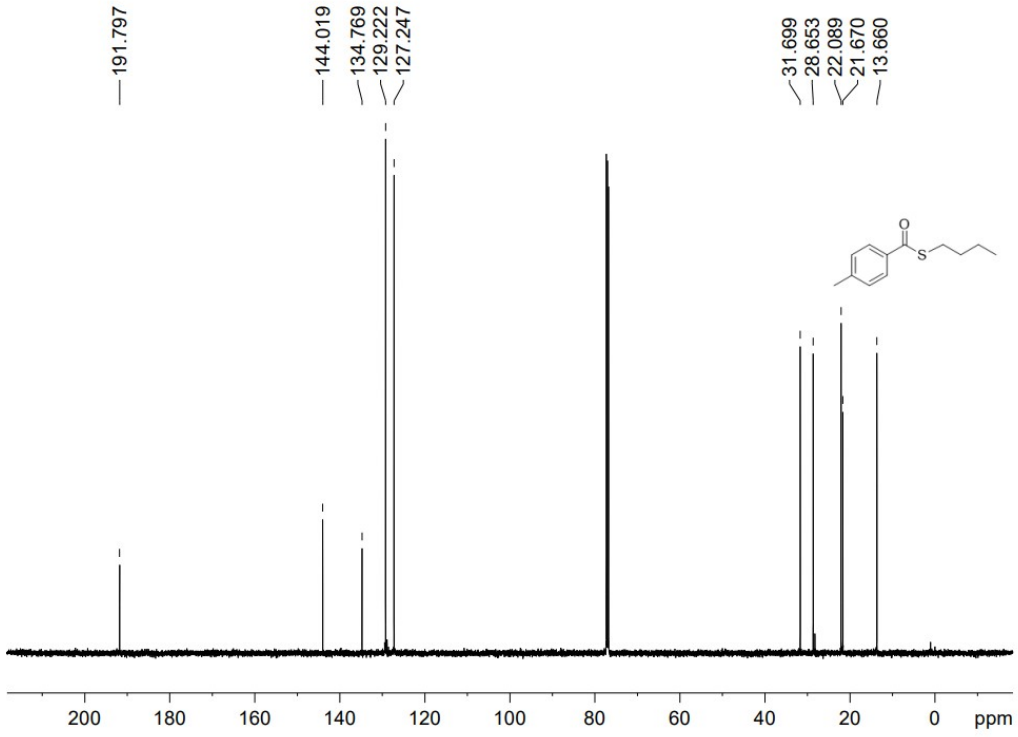

7.978
7.955
6.942
6.920
3.870
3.090
3.071
3.053
1.704
1.686
1.680
1.667
1.661
1.650
1.649
1.630
1.511
1.497
1.479
1.459
1.441
0.982
0.964
0.946
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
3.035
2.028
2.082
2.257
3.162
8
7
6
5
4
3
2
1
0 ppm
2.000
2.029
3.035
2.028
2.082
2.257
3.162


LJQ-0418
13C NMR
CDCl3
190.659
163.631
130.175
129.310
113.693
55.478
31.775
28.610
22.077
13.649
200
180
160
140
120
100
80
60
40
20
0
ppm


8.061
8.039
7.767
7.745
3.132
3.114
3.095
1.710
1.692
1.687
1.674
1.668
1.655
1.636
1.507
1.489
1.470
1.451
1.433
1.415
0.976
0.958
0.940
NC
O
S
3.0
2.5
2.0
1.5
1.0
ppm
2.000
2.008
2.010
3.020
8
7
6
5
4
3
2
1
0 ppm
2.012
2.021
2.000
2.008
2.010
3.020

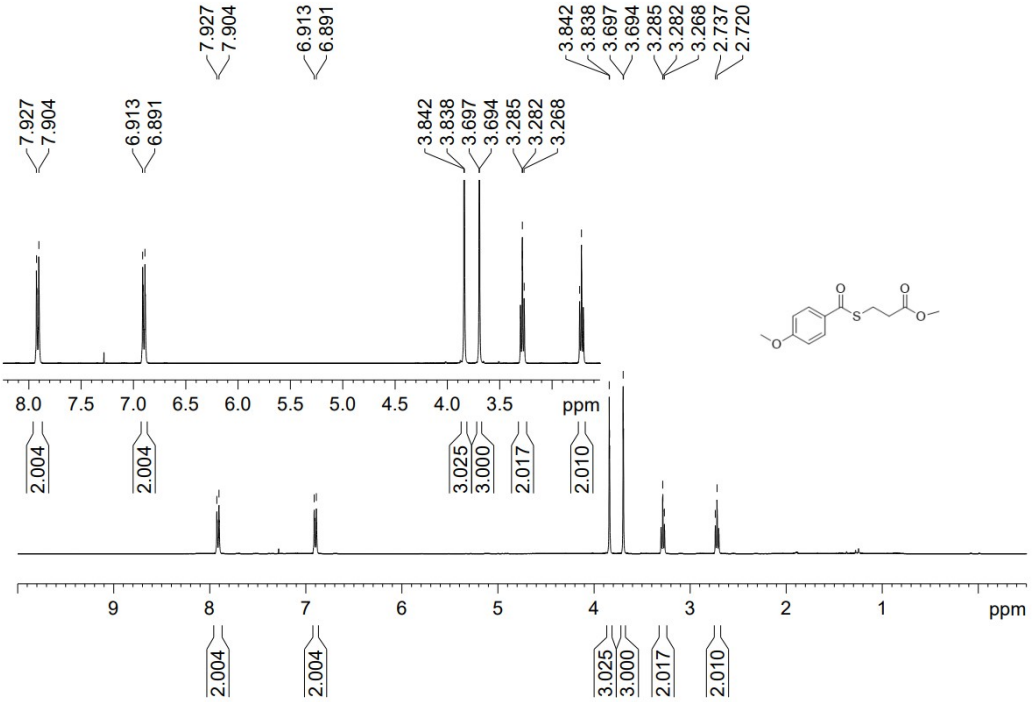

LJQ-041702
13C NMR
CDCl3
190.798
140.306
132.463
127.618
117.872
116.450
31.356
29.170
22.011
13.579
NC
O
S
200
180
160
140
120
100
80
60
40
20
0
ppm

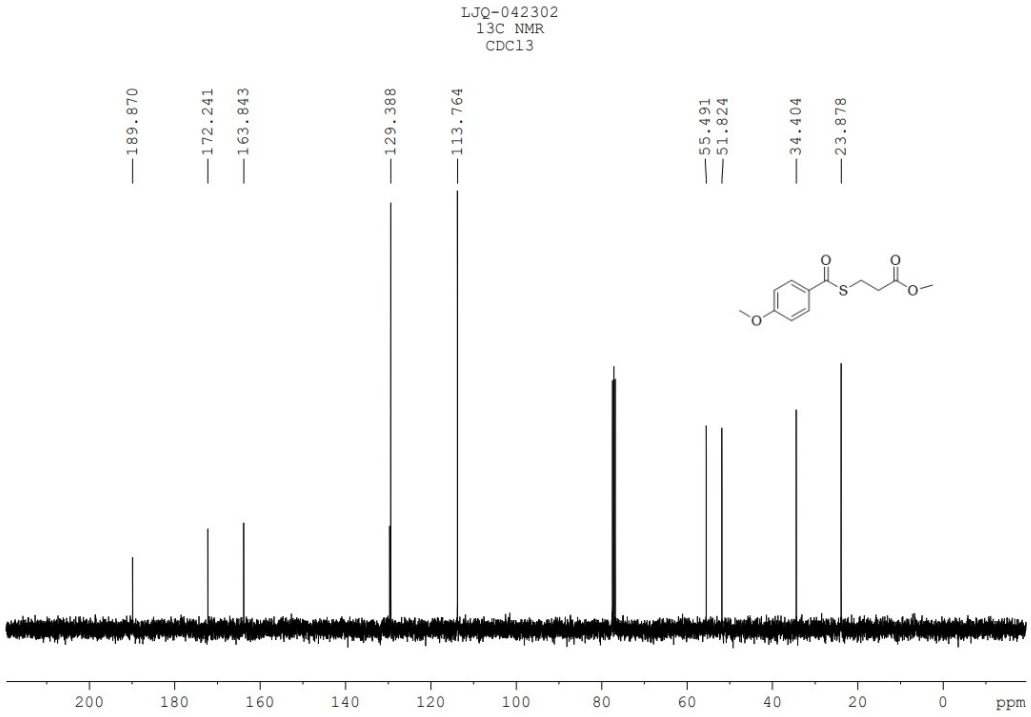

7.800
7.784
7.167
7.151
3.000
2.986
2.971
2.325
1.593
1.578
1.574
1.563
1.548
1.511
1.401
1.386
1.371
1.356
0.887
0.873
0.858
O
S
ppm
2.044
3.071
2.089
2.140
2.000
2.148
3.137

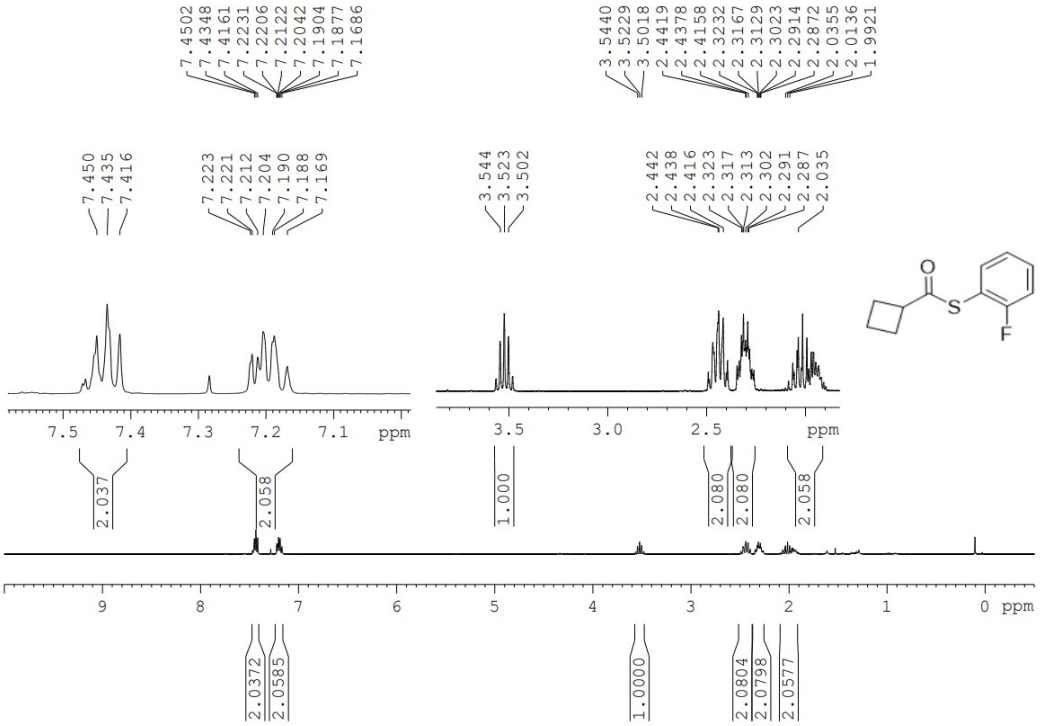

191.797
144.019
134.769
129.222
127.247
31.699
28.653
22.089
21.670
13.660
O
S
ppm

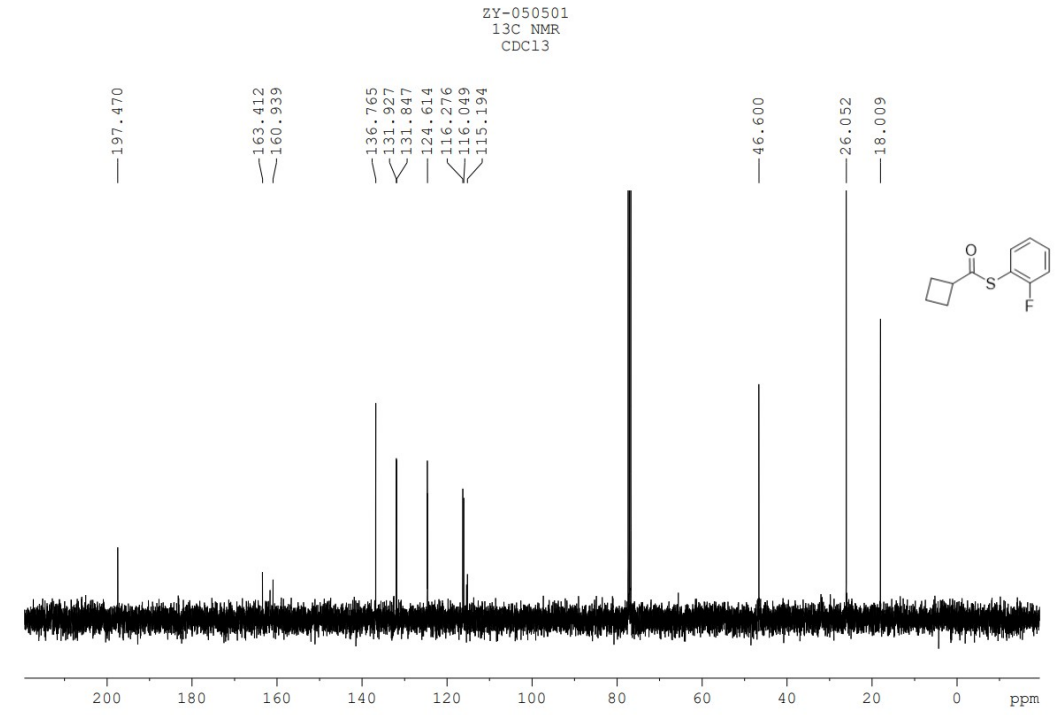

191.51
172.20
136.80
133.53
128.65
127.24
51.90
34.28
24.03
O
O
S
O
CH3
f1 (ppm)

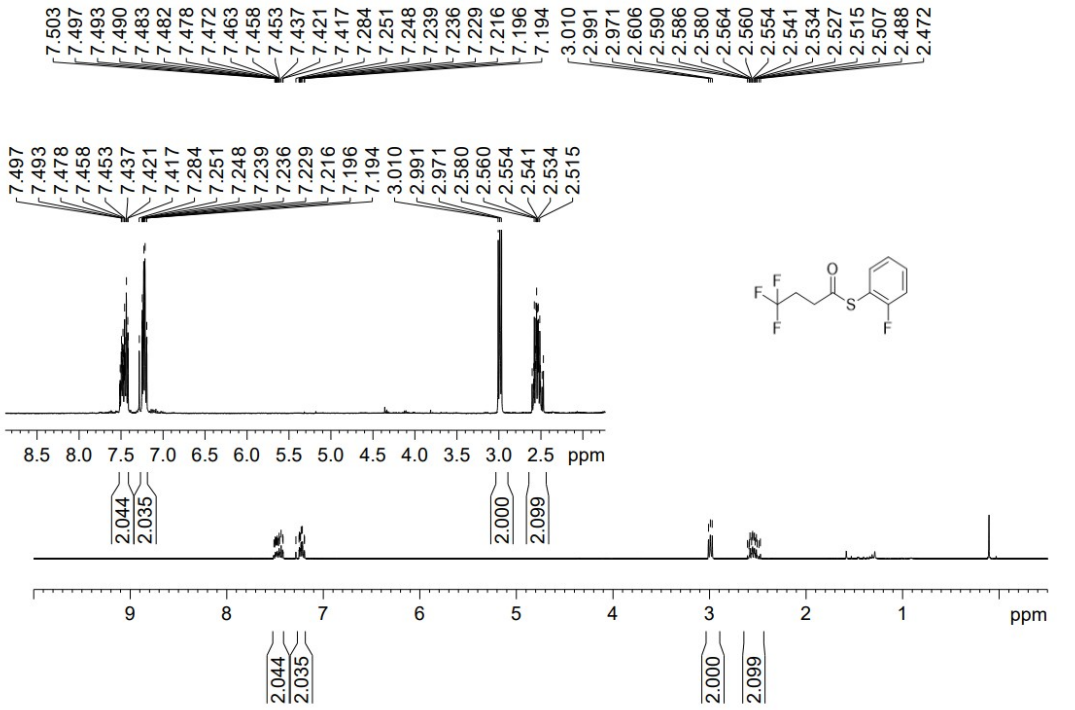

191.51
172.20
136.80
133.53
128.65
127.24
51.90
34.28
24.03
O
O
S
O
CH3
f1 (ppm)

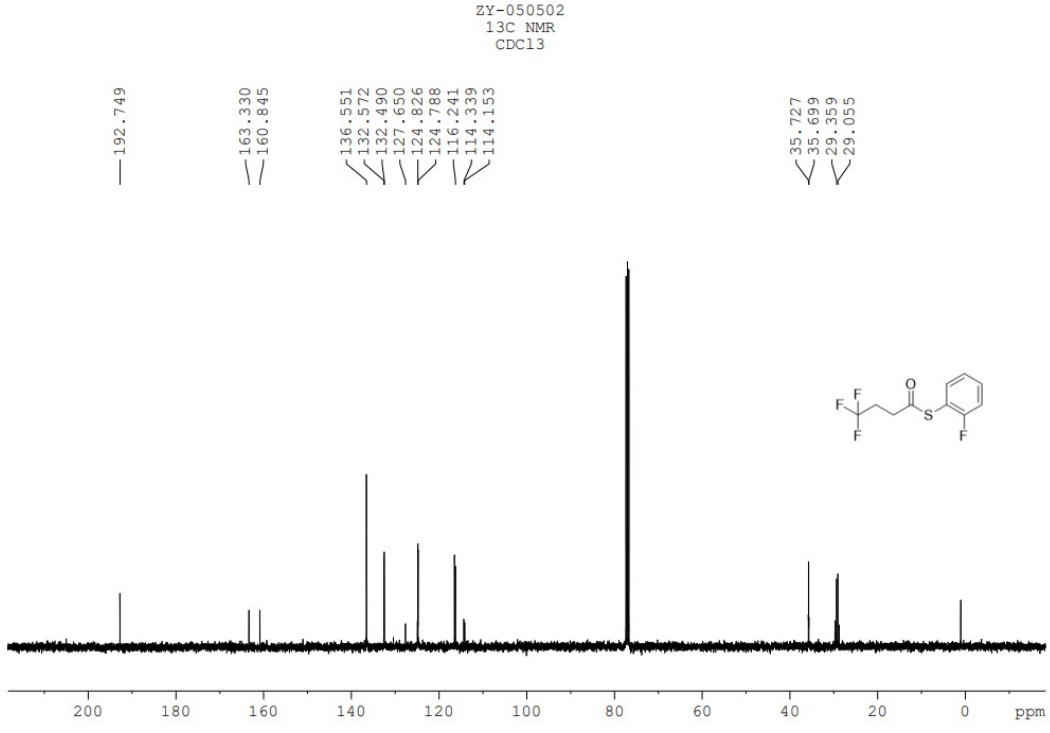

7.927
7.904
6.913
6.891
3.842
3.838
3.697
3.694
3.285
3.282
3.268
2.737
2.720
ppm
2.004
2.004
3.025
3.000
2.017
2.010

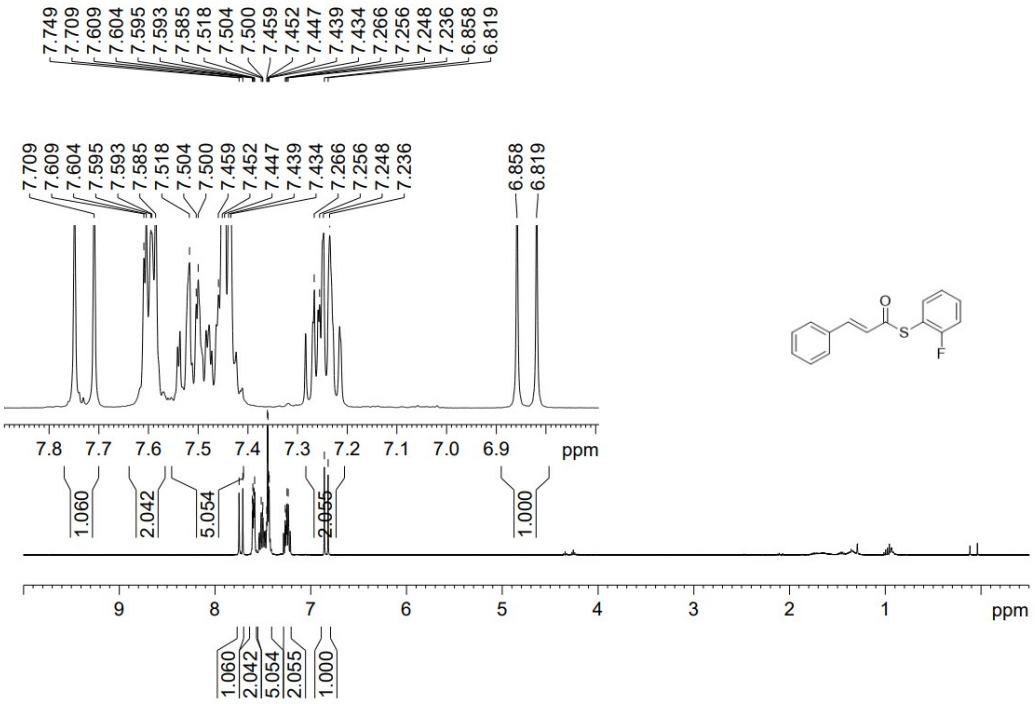

LJQ-042302
13C NMR
CDCl3
189.870
172.241
163.843
129.388
113.764
55.491
51.824
34.404
23.878
ppm

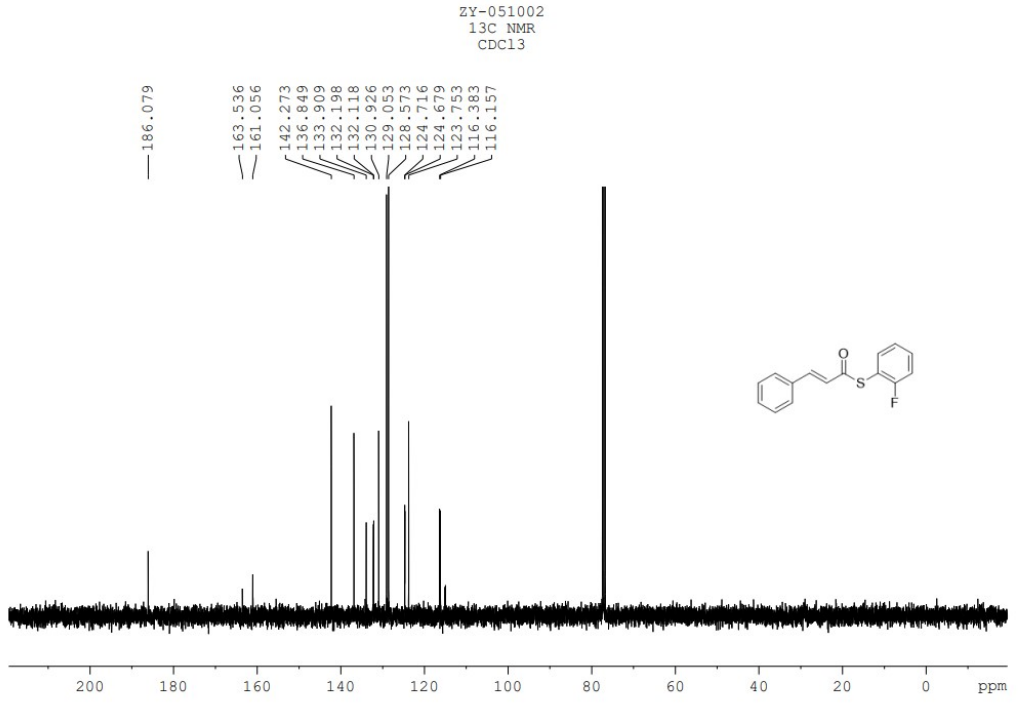

7.4502
7.4348
7.4161
7.2231
7.2206
7.2122
7.2042
7.1904
7.1877
7.1686
3.5440
3.5229
3.5018
2.4419
2.4378
2.4158
2.3232
2.3167
2.3129
2.3023
2.2914
2.2872
2.0355
2.0136
1.9921
7.450
7.435
7.416
7.223
7.221
7.212
7.204
7.190
7.188
7.169
3.544
3.523
3.502
2.442
2.438
2.416
2.323
2.317
2.313
2.302
2.291
2.287
2.035
O
S
F
7.5
7.4
7.3
7.2
7.1
ppm
3.5
3.0
2.5
ppm
2.037
2.058
1.000
2.080
2.080
2.058
9
8
7
6
5
4
3
2
1
0 ppm
2.0372
2.0585
1.0000
2.0804
2.0798
2.0577

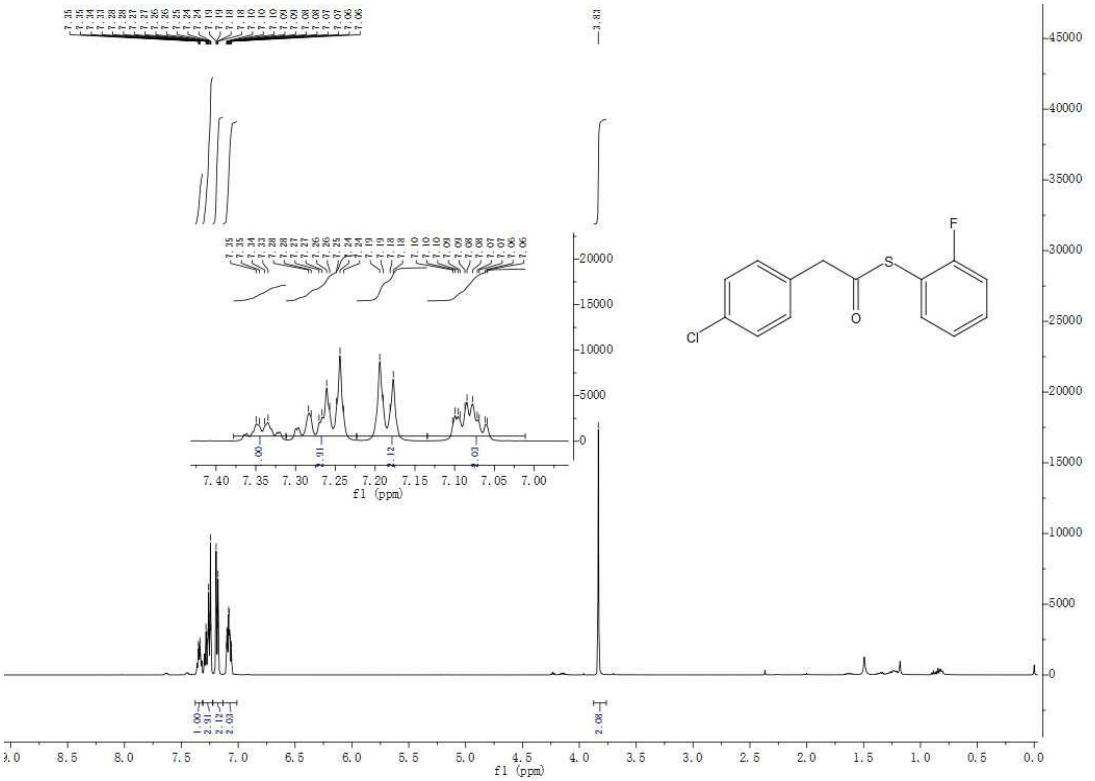

ZY-050501
13C NMR
CDC13
197.470
163.412
160.939
136.765
131.927
131.847
124.614
116.276
116.049
115.194
46.600
26.052
18.009
O
S
F
200
180
160
140
120
100
80
60
40
20
0
ppm

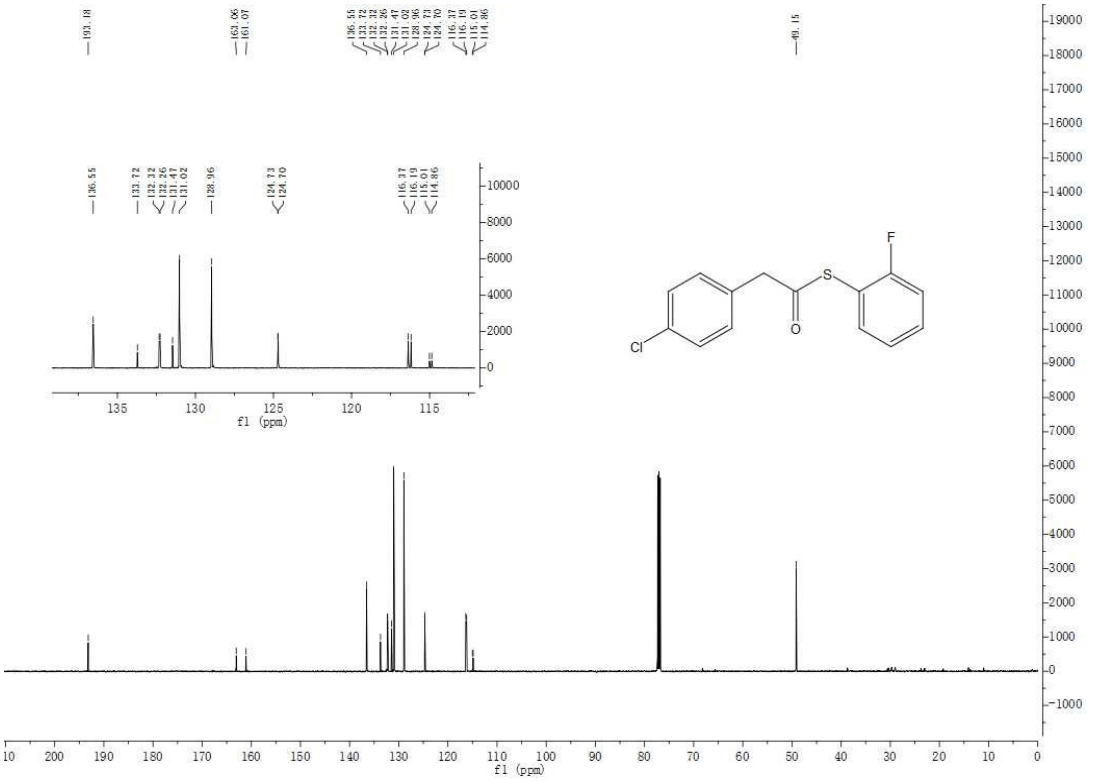

7.503
7.497
7.493
7.490
7.483
7.482
7.478
7.472
7.463
7.458
7.453
7.437
7.421
7.417
7.284
7.251
7.248
7.239
7.236
7.229
7.216
7.196
7.194
3.010
2.991
2.971
2.606
2.590
2.586
2.580
2.564
2.560
2.554
2.541
2.534
2.527
2.515
2.507
2.488
2.472
F
F
F
O
S
F
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
2.044
2.035
2.000
2.099
9 8 7 6 5 4 3 2 1 ppm

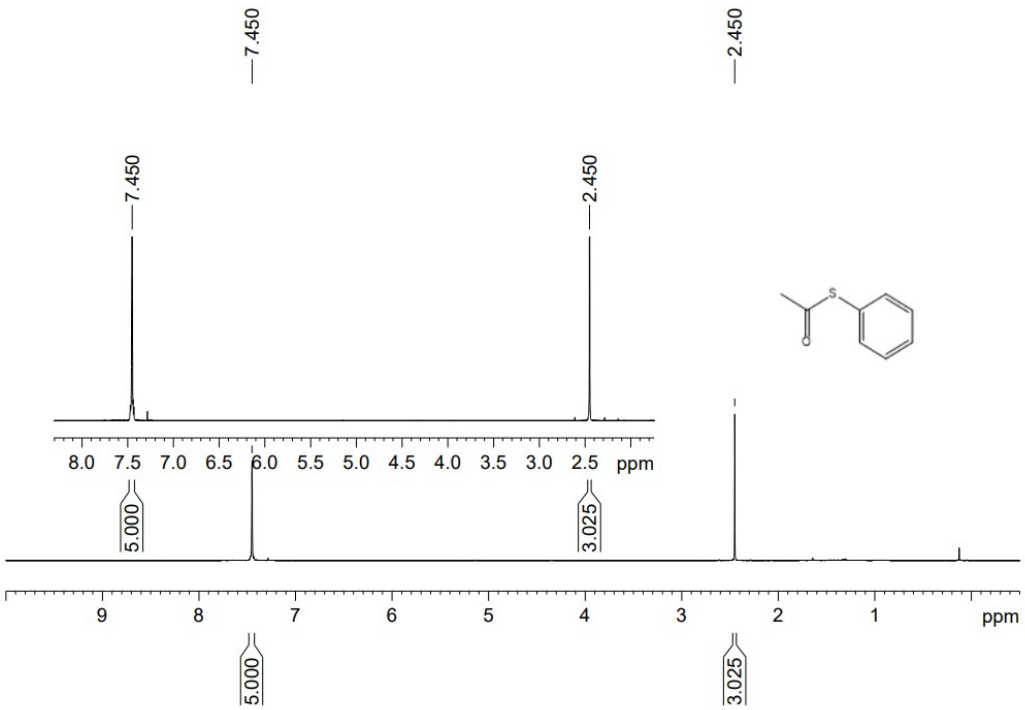

ZY-050502
13C NMR
CDCl3
192.749
163.330
160.845
136.551
132.572
132.490
127.650
124.826
124.788
116.241
114.339
114.153
35.727
35.699
29.359
29.055
F
F
F
O
S
F
200 180 160 140 120 100 80 60 40 20 0 ppm

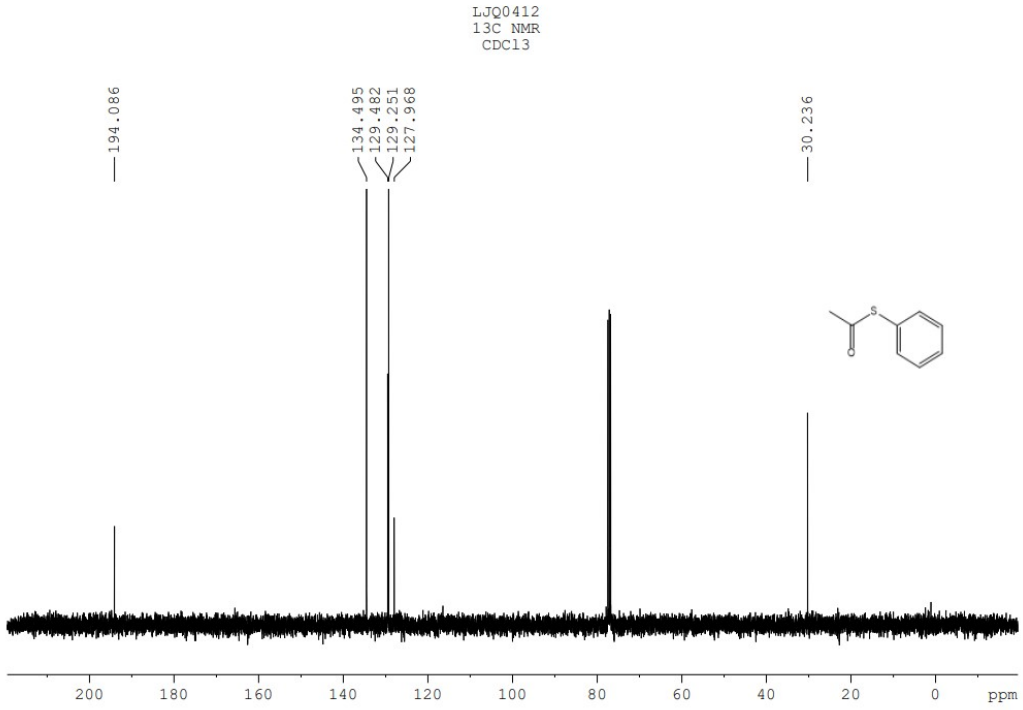

7.749
7.709
7.609
7.604
7.595
7.593
7.585
7.518
7.504
7.500
7.459
7.452
7.447
7.439
7.434
7.266
7.256
7.248
7.236
6.858
6.819
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
ppm
1.060
2.042
5.054
2.055
1.000
9
8
7
6
5
4
3
2
1
ppm
O
S
F

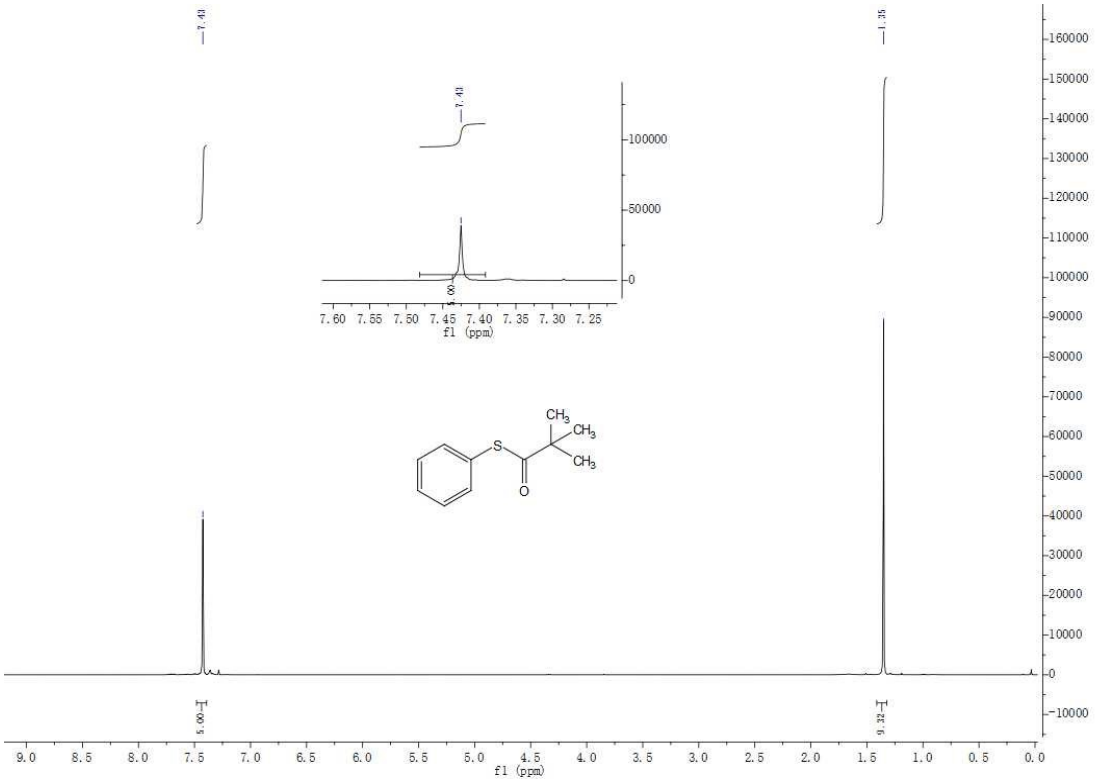

ZY-051002
13C NMR
CDCl3
186.079
163.536
161.056
142.273
136.849
133.909
132.198
132.118
130.926
129.053
128.573
124.716
124.679
123.753
116.383
116.157
200
180
160
140
120
100
80
60
40
20
0
ppm
O
S
F

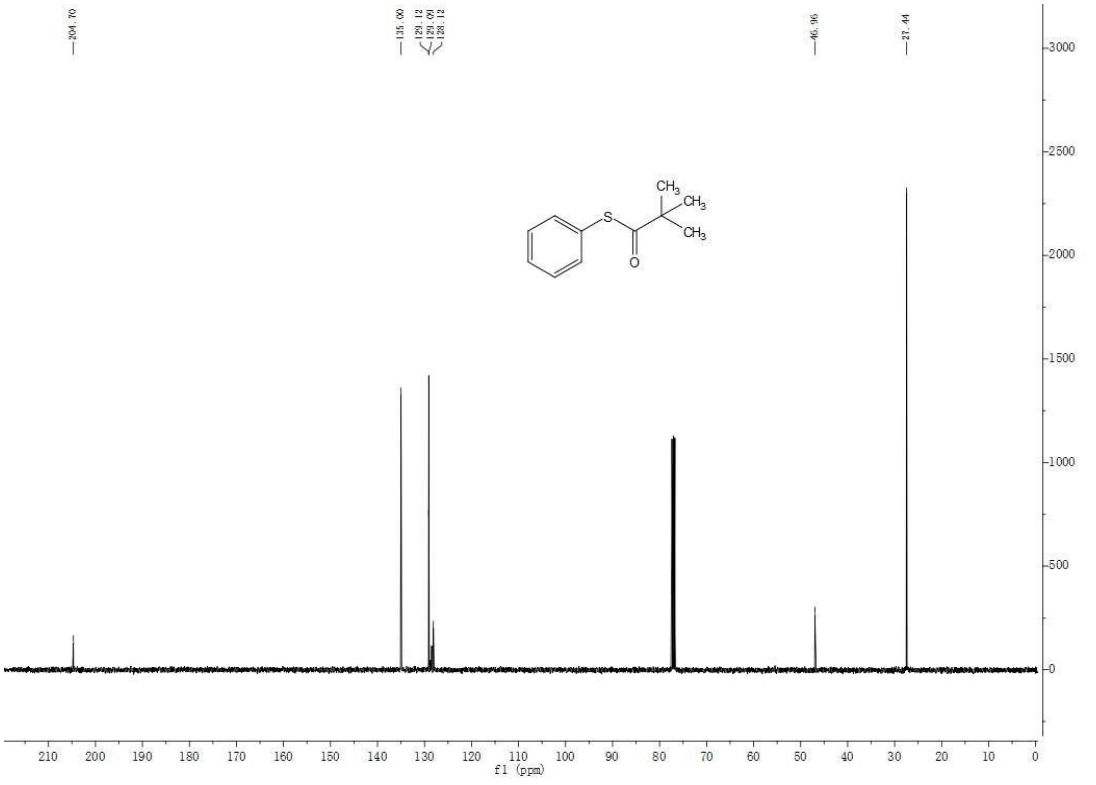

F
S
O
Cl
f1 (ppm)


F
S
O
Cl
f1 (ppm)


7.450
2.450
7.450
2.450
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
5.000
3.025
9 8 7 6 5 4 3 2 1 ppm
5.000
3.025


LJQ0412
13C NMR
CDCl3
194.086
134.495
129.482
129.251
127.968
30.236
200 180 160 140 120 100 80 60 40 20 0 ppm


7.43
1.35
5.00
9.32
f1 (ppm)


204.70
135.00
129.12
129.05
128.12
46.96
27.44
f1 (ppm)