

Supporting Information

Manganese(III)-Promoted Thiocarbonylation of Alkylborates with Disulfides: Synthesis of Aliphatic Thioesters

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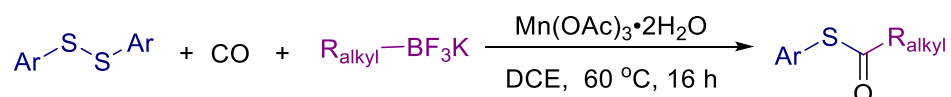
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1 General information

Reagents, solvents and analytical methods:

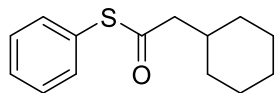
Unless otherwise noted, all reactions were carried out under a carbon monoxide or nitrogen atmosphere. Potassium alkyltrifluoroborates were not commercially available were synthesized according to existing methods (*Angew. Chem., Int. Ed.* **2012**, *51*, 528-532; *ACS Catal.* **2016**, *6*, 8332-8335; *J. Am. Chem. Soc.* **2014**, *136*, 2280-2283). All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (b. p. 30-60 °C) and ethyl acetate as eluent. ¹H and ¹³C NMR spectra were taken on Bruker AVANCE III 400 MHz spectrometers and CDCl₃ (¹H NMR δ 7.26, ¹³C NMR δ 77.0) as solvent. All coupling constants (*J*) are reported in Hz with the following abbreviations: s = singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, q = quadruplet, m = multiplet, br = broad. Gas chromatography (GC) analyses were performed on an Agilent HP-7890A instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d. 0.25 μm film thickness) using argon as carrier gas. Gas chromatography mass spectrometer (GC-MS) analyses were performed on an Shimadzu QP2020 NX instrument. High resolution mass spectra (HRMS) were recorded on Agilent 8890-7250 and Agilent Q-TOF 6540. Because of the high toxicity of carbon monoxide, all of the reactions should be performed in an autoclave. The laboratory should well-equipped with a CO detector and alarm system.

2. General procedure



A 4 mL screw-cap vial was charged with disulfides (0.1 mmol), potassium alkyltrifluoroborates (0.45 mmol), Mn(OAc)₃•2H₂O (0.55 mmol, 147.4 mg) and an oven-dried stirring bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. After DCE (1.0 mL), was added with a syringe under N₂ atmosphere, the vial was moved to an alloy plate and put into a Parr 4560 series autoclave (300 mL) under N₂ atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 60 bar CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer. The reaction mixture was heated to 60 °C for 16 h. The reaction mixture was then diluted with EtOAc, filtered through silica gel with copious washings (Et₂O or EtOAc), concentrated, and purified by column chromatography.

3. Spectroscopic data of products



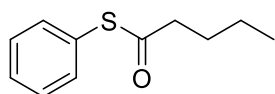
S-phenyl 2-cyclohexylethanoate (1)

The title compound was prepared from 1,2-diphenyldisulfane (21.8 mg, 0.1 mmol) and potassium cyclohexylmethyltrifluoroborate (91.8 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA=50:1) to give the product as a colorless oil (42 mg, 90%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.34 - 7.30 (m, 5H), 2.45 (d, $J = 7.0$ Hz, 2H), 1.82 (dtq, $J = 10.9, 7.2, 3.5$ Hz, 1H), 1.74 - 1.54 (m, 5H), 1.24 - 1.06 (m, 3H), 0.94 (qd, $J = 12.0, 3.3$ Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 196.9, 134.4, 129.3, 129.1, 128.2, 51.2, 35.7, 32.9, 26.1, 26.0.

HRMS (EI): Calcd. for C₁₄H₁₈OS [M]⁺ 234.1073, found: 234.1077.



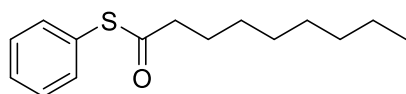
S-phenyl pentanoate (2)

The title compound was prepared from 1,2-diphenyldisulfane (21.8 mg, 0.1 mmol) and potassium butyltrifluoroborate (73.8 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA=50:1) to give the product as a yellow oil (27 mg, 70%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 - 7.30 (m, 5H), 2.58 (t, $J = 7.5$ Hz, 2H), 1.72 - 1.57 (m, 2H), 1.32 (ddd, $J = 14.9, 7.5, 1.3$ Hz, 2H), 0.94 - 0.79 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 197.6, 134.5, 129.3, 129.2, 128.0, 43.5, 27.7, 22.1, 13.7.

HRMS (EI): Calcd. for C₁₁H₁₄OS [M]⁺ 194.0760, found: 194.0755.



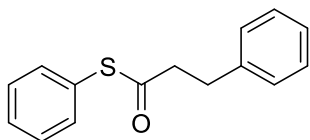
S-phenyl nonanoate (3)

The title compound was prepared from 1,2-diphenyldisulfane (21.8 mg, 0.1 mmol) and potassium octyltrifluoroborate (99 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA=50:1) to give the product as a yellow oil (45 mg, 90%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.35 - 7.30 (m, 5H), 2.57 (t, $J = 7.5$ Hz, 2H), 1.63 (p, $J = 7.4$ Hz, 2H), 1.29 - 1.13 (m, 10H), 0.81 (t, $J = 6.8$ Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 197.6, 134.5, 129.3, 129.2, 128.0, 43.8, 31.8, 29.2, 29.1, 29.0, 25.6, 22.7, 14.1.

HRMS (EI): Calcd. for C₁₅H₂₂OS [M]⁺ 250.1386, found: 250.1379.



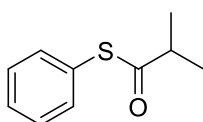
S-phenyl 3-phenylpropanethioate (4)

The title compound was prepared from 1,2-diphenyldisulfane (21.8 mg, 0.1 mmol) and potassium phenethyltrifluoroborate (95.4 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (39 mg, 81%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.35 - 7.28 (m, 5H), 7.23 - 7.17 (m, 2H), 7.15 - 7.10 (m, 3H), 2.96 - 2.90 (m, 2H), 2.90 - 2.85 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 196.7, 140.0, 134.5, 129.5, 129.3, 128.6, 128.4, 127.7, 126.5, 45.2, 31.4.

HRMS (EI): Calcd. for C₁₅H₁₄OS [M]⁺ 242.0760, found: 242.0750.



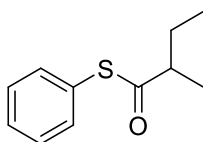
S-phenyl 2-methylpropanethioate (7)

The title compound was prepared from 1,2-diphenyldisulfane (21.8 mg, 0.1 mmol) and potassium isopropyltrifluoroborate (67.5 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (28 mg, 78%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.34 - 7.30 (m, 5H), 2.78 (p, *J* = 6.9 Hz, 1H), 1.19 (s, 3H), 1.18 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 201.9, 134.6, 129.2, 129.1, 127.9, 43.0, 19.4.

HRMS (EI): Calcd. for C₁₀H₁₂OS [M]⁺ 180.0603, found: 180.0598.



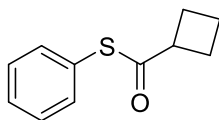
S-phenyl 2-methylbutanethioate (8)

The title compound was prepared from 1,2-diphenyldisulfane (21.8 mg, 0.1 mmol) and potassium *sec*-butyltrifluoroborate (73.8 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (35 mg, 90%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.39 - 7.26 (m, 5H), 2.60 (h, *J* = 6.9 Hz, 1H), 1.73 (dt, *J* = 13.6, 7.3 Hz, 1H), 1.53 - 1.40 (m, 1H), 1.16 (d, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 201.6, 134.5, 129.2, 129.1, 128.0, 50.0, 27.2, 17.2, 11.6.

HRMS (EI): Calcd. for C₁₁H₁₄OS [M]⁺ 194.0760, found: 194.0760.



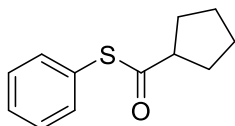
S-phenyl cyclobutanecarbothioate (10)

The title compound was prepared from 1,2-diphenyldisulfane (21.8 mg, 0.1 mmol) and potassium cyclobutyltrifluoroborate (72.9 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a yellow oil (35 mg, 91%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.26 (m, 5H), 3.38 (pd, J = 8.4, 1.0 Hz, 1H), 2.43 – 2.25 (m, 2H), 2.17 (dddd, J = 16.9, 8.6, 4.3, 2.6 Hz, 2H), 1.95 – 1.79 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 199.4, 134.6, 129.2, 129.1, 127.9, 46.6, 26.1, 18.0.

HRMS (EI): Calcd. for C₁₁H₁₂OS [M]⁺ 192.0603, found: 192.0597.



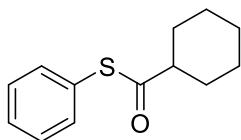
S-phenyl cyclopentanecarbothioate (11)

The title compound was prepared from 1,2-diphenyldisulfane (21.8 mg, 0.1 mmol) and potassium cyclopentyltrifluoroborate (79.2 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a yellow oil (35 mg, 85%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.25 (m, 5H), 3.02 (p, J = 7.9 Hz, 1H), 1.84 (dtd, J = 14.9, 7.6, 5.3 Hz, 4H), 1.72 – 1.60 (m, 2H), 1.59 – 1.50 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 199.9, 133.5, 128.1, 128.1, 127.1, 51.9, 29.6, 24.9.

HRMS (EI): Calcd. for C₁₂H₁₄OS [M]⁺ 206.0760, found: 206.0758.



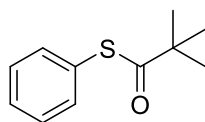
S-phenyl cyclohexanecarbothioate (12)

The title compound was prepared from 1,2-diphenyldisulfane (21.8 mg, 0.1 mmol) and potassium cyclohexyltrifluoroborate (85.5 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (44 mg, >99%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.33 - 7.29 (m, 5H), 2.53 (tt, J = 11.4, 3.6 Hz, 1H), 1.98 – 1.87 (m, 2H), 1.73 (dt, J = 12.0, 3.1 Hz, 2H), 1.45 (qd, J = 11.9, 3.5 Hz, 2H), 1.30 – 1.09 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 200.8, 134.6, 129.2, 129.1, 128.0, 52.5, 29.6, 25.5.

HRMS (EI): Calcd. for C₁₃H₁₆OS [M+H]⁺ 220.0917, found: 220.0910.



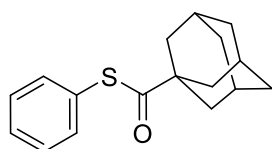
S-phenyl 2,2-dimethylpropanethioate (13)

The title compound was prepared from 1,2-diphenyldisulfane (21.8 mg, 0.1 mmol) and potassium *tert*-butyltrifluoroborate (73.8 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (22 mg, 57%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.34 - 7.30 (m, 5H), 1.24 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 204.657, 137.500, 134.989, 129.083, 128.456, 30.970, 27.440.

HRMS (EI): Calcd. for C₁₁H₁₄OS [M]⁺ 194.0760, found: 194.0754.



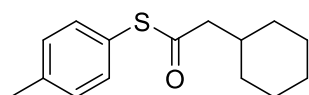
S-phenyl (3*r*,5*r*,7*r*)-adamantane-1-carbothioate (14)

The title compound was prepared from 1,2-diphenyldisulfane (21.8 mg, 0.1 mmol) and potassium ((3*r*,5*r*,7*r*)-adamantan-1-yl)trifluoroborate (108.9 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a white solid (54 mg, >99%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.34 - 7.29 (m, 5H), 2.01 (p, *J* = 3.3 Hz, 3H), 1.93 (d, *J* = 3.0 Hz, 6H), 1.67 (q, *J* = 3.4 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 203.2, 134.0, 128.0, 128.0, 127.0, 48.0, 38.3, 35.4, 27.2.

HRMS (EI): Calcd. for C₁₇H₂₀OS [M]⁺ 227.1229, found: 227.1221.



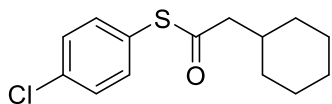
S-(*p*-tolyl) 2-cyclohexylethanethioate (15)

The title compound was prepared from 1,2-di-*p*-tolyl disulfane (24.6 mg, 0.1 mmol) and potassium cyclohexylmethyltrifluoroborate (91.8 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (47 mg, 95%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 2.43 (d, *J* = 7.0 Hz, 2H), 2.28 (s, 3H), 1.81 (dtq, *J* = 10.9, 7.2, 3.5 Hz, 1H), 1.74 - 1.54 (m, 5H), 1.23 - 1.04 (m, 3H), 0.99 - 0.86 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 197.4, 139.5, 134.4, 130.0, 124.6, 51.1, 35.7, 32.9, 26.2, 26.0, 21.3.

HRMS (ESI-TOF): Calcd. for C₁₅H₂₀OS [M]⁺ 248.1235, found: 248.1230.



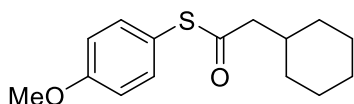
S-(4-chlorophenyl) 2-cyclohexylethanethioate (16)

The title compound was prepared from 1,2-bis(4-chlorophenyl)disulfane (28.7 mg, 0.1 mmol) and potassium cyclohexylmethyltrifluoroborate (91.8 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA=50:1) to give the product as a colorless oil (44 mg, 82%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 8.6 Hz, 2H), 2.45 (d, J = 7.0 Hz, 2H), 1.81 (ddh, J = 14.4, 7.0, 3.5 Hz, 1H), 1.73 – 1.55 (m, 5H), 1.23 – 1.05 (m, 3H), 1.00 – 0.88 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 196.3, 135.7, 135.6, 129.4, 126.6, 51.3, 35.7, 32.9, 26.1, 26.0.

HRMS (ESI-TOF): Calcd. for C₁₄H₁₇ClOS [M+H]⁺ 268.0683, found: 268.0685.



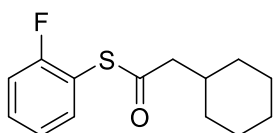
S-(4-methoxyphenyl) 2-cyclohexylethanethioate (17)

The title compound was prepared from 1,2-bis(4-methoxyphenyl)disulfane (27.8 mg, 0.1 mmol) and potassium cyclohexylmethyltrifluoroborate (91.8 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA=50:1) to give the product as a colorless oil (44 mg, 83%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 3.73 (s, 3H), 2.43 (d, J = 7.0 Hz, 2H), 1.81 (tp, J = 10.8, 3.5 Hz, 1H), 1.73 – 1.55 (m, 5H), 1.25 – 1.05 (m, 3H), 0.98 – 0.87 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 197.9, 160.6, 136.0, 118.9, 114.8, 55.3, 51.0, 35.7, 32.9, 26.1, 26.0.

HRMS (EI): Calcd. for C₁₅H₂₀O₂S [M]⁺ 268.0683, found: 268.0675.



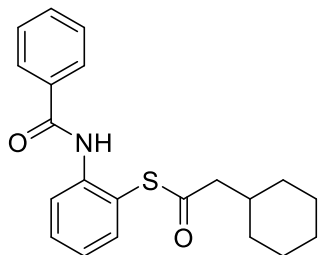
S-(2-fluorophenyl) 2-cyclohexylethanethioate (18)

The title compound was prepared from 1,2-bis(2-fluorophenyl)disulfane (25.4 mg, 0.1 mmol) and potassium cyclohexylmethyltrifluoroborate (91.8 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA=50:1) to give the product as a colorless oil (41 mg, 81%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.33 (qt, J = 8.1, 1.7 Hz, 2H), 7.15 – 7.04 (m, 2H), 2.48 (d, J = 7.1 Hz, 2H), 1.83 (ddh, J = 14.4, 7.0, 3.5 Hz, 1H), 1.76 – 1.56 (m, 5H), 1.25 – 1.05 (m, 3H), 1.01 – 0.88 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 195.0, 162.1 (d, J = 242.4 Hz), 136.6, 132.0 (d, J = 8.5 Hz), 124.6 (d, J = 3.8 Hz), 116.2 (d, J = 22.0 Hz), 115.5 (d, J = 17.5 Hz), 51.1, 35.8, 32.9, 26.1, 26.0.

HRMS (EI): Calcd. for C₁₄H₁₇FOS [M]⁺ 252.0979, found: 252.0986.



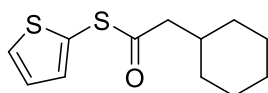
S-(2-benzamidophenyl) 2-cyclohexylethanethioate (19)

The title compound was prepared from *N,N'*-(disulfaneylbis(2,1-phenylene))dibenzamide (45.7 mg, 0.1 mmol) and potassium cyclohexylmethyltrifluoroborate (91.8 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 10:1) to give the product as a colorless oil (18 mg, 26%).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.48 (s, 1H), 8.39 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.84 – 7.73 (m, 2H), 7.52 – 7.33 (m, 5H), 7.10 (td, *J* = 7.6, 1.3 Hz, 1H), 2.51 (d, *J* = 7.1 Hz, 2H), 1.80 (ddh, *J* = 14.5, 7.0, 3.5 Hz, 1H), 1.66 – 1.53 (m, 5H), 1.18 – 1.00 (m, 3H), 0.97 – 0.85 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 196.5, 165.2, 139.8, 135.9, 134.8, 132.0, 131.6, 128.8, 127.1, 124.8, 122.4, 117.9, 51.3, 35.8, 32.9, 26.0, 25.9.

HRMS (ESI-TOF): Calcd. for C₂₁H₂₃NO₂S [M+H]⁺ 354.1522, found: 354.1526.



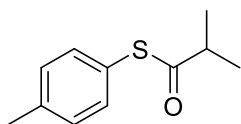
S-(thiophen-2-yl) 2-cyclohexylethanethioate (20)

The title compound was prepared from 1,2-di(thiophen-2-yl)disulfane (23 mg, 0.1 mmol) and potassium cyclohexylmethyltrifluoroborate (91.8 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (31 mg, 65%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 5.3, 1.3 Hz, 1H), 7.14 (dd, *J* = 3.6, 1.3 Hz, 1H), 7.10 (dd, *J* = 5.3, 3.6 Hz, 1H), 2.52 (d, *J* = 7.0 Hz, 2H), 1.88 (ddq, *J* = 11.1, 7.4, 3.8 Hz, 1H), 1.80 – 1.66 (m, 5H), 1.29 – 1.14 (m, 3H), 1.05 – 0.94 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 196.8, 135.5, 131.6, 127.8, 125.2, 50.6, 35.6, 32.9, 26.1, 26.0.

HRMS (EI): Calcd. for C₁₂H₁₆OS₂ [M]⁺ 240.0643, found: 240.0649.



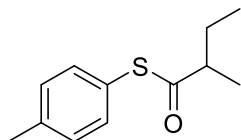
S-(*p*-tolyl) 2-methylpropanethioate (21)

The title compound was prepared from 1,2-di-*p*-tolylsulfane (24.6 mg, 0.1 mmol) and potassium isopropyltrifluoroborate (67.5 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (29 mg, 75%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 2.77 (p, *J* = 6.9 Hz, 1H), 2.29 (s, 3H), 1.18 (d, *J* = 6.9 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 202.4, 139.4, 134.6, 130.0, 124.4, 42.9, 21.3, 19.4.

HRMS (EI): Calcd. for C₁₁H₁₄OS [M]⁺ 194.0760, found: 194.0762.



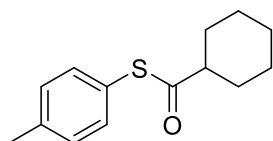
S-(*p*-tolyl) 2-methylbutanethioate (22)

The title compound was prepared from 1,2-di-*p*-tolyl disulfane (24.6 mg, 0.1 mmol) and potassium *sec*-butyltrifluoroborate (73.8 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (42 mg, >99%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 2.59 (h, *J* = 6.9 Hz, 1H), 2.28 (s, 3H), 1.72 (dt, *J* = 13.7, 7.3 Hz, 1H), 1.45 (ddd, *J* = 13.9, 7.6, 6.5 Hz, 1H), 1.15 (d, *J* = 6.9 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 202.0, 139.4, 134.5, 130.0, 124.5, 49.9, 27.2, 21.3, 17.2, 11.6.

HRMS (EI): Calcd. for C₁₂H₁₆OS [M]⁺ 208.0916, found: 208.0912.



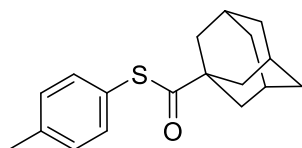
S-(*p*-tolyl) cyclohexanecarbothioate (23)

The title compound was prepared from 1,2-di-*p*-tolyl disulfane (24.6 mg, 0.1 mmol) and potassium cyclohexyltrifluoroborate (85.5 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (47 mg, >99%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 2.51 (tt, *J* = 11.4, 3.6 Hz, 1H), 2.28 (s, 3H), 1.96 – 1.87 (m, 2H), 1.73 (dt, *J* = 12.5, 3.4 Hz, 2H), 1.44 (qd, *J* = 11.9, 3.4 Hz, 2H), 1.28 – 1.14 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 201.2, 139.4, 134.6, 129.9, 124.4, 52.4, 29.6, 25.6, 25.5, 21.3.

HRMS (EI): Calcd. for C₁₄H₁₈OS [M]⁺ 234.1073, found: 234.1067.



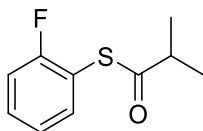
S-(*p*-tolyl) (3*r*,5*r*,7*r*)-adamantane-1-carbothioate (24)

The title compound was prepared from 1,2-di-*p*-tolyl disulfane (24.6 mg, 0.1 mmol) and potassium ((3*r*,5*r*,7*r*)-adamantan-1-yl)trifluoroborate (108.9 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a white solid (57 mg, >99%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H), 2.01 (p, *J* = 3.2 Hz, 3H), 1.92 (d, *J* = 3.0 Hz, 6H), 1.67 (q, *J* = 3.3 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 203.6, 138.2, 133.9, 128.9, 123.4, 48.0, 38.3, 35.4, 27.2, 20.3.

HRMS (EI): Calcd. for C₁₈H₂₂OS [M]⁺ 286.1386, found: 286.1375.



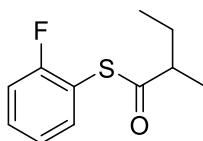
S-(2-fluorophenyl) 2-methylpropanethioate (25)

The title compound was prepared from 1,2-bis(2-fluorophenyl)disulfane (25.4 mg, 0.1 mmol) and potassium isopropyltrifluoroborate (67.5 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (27 mg, 68%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.28 (m, 2H), 7.14 – 7.03 (m, 2H), 2.81 (p, *J* = 6.9 Hz, 1H), 1.20 (d, *J* = 6.9 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 200.0, 162.2 (d, *J* = 252.2 Hz), 136.8, 131.9 (d, *J* = 8.3 Hz), 124.6 (d, *J* = 3.9 Hz), 116.2 (d, *J* = 22.3 Hz), 115.4 (d, *J* = 18.5 Hz), 43.1, 19.3.

HRMS (EI): Calcd. for C₁₀H₁₁FOS [M]⁺ 198.0509, found: 198.0501.



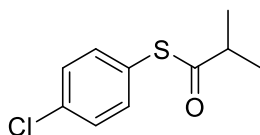
S-(2-fluorophenyl) 2-methylbutanethioate (26)

The title compound was prepared from 1,2-bis(2-fluorophenyl)disulfane (25.4 mg, 0.1 mmol) and potassium *sec*-butyltrifluoroborate (73.8 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a yellow oil (35 mg, 68%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.33 (td, *J* = 7.3, 5.7 Hz, 2H), 7.15 – 7.04 (m, 2H), 2.64 (h, *J* = 6.9 Hz, 1H), 1.74 (dt, *J* = 13.7, 7.4 Hz, 1H), 1.53 – 1.44 (m, 1H), 1.17 (d, *J* = 6.9 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 198.6, 161.1 (d, *J* = 252.2 Hz), 135.7, 130.9 (d, *J* = 8.3 Hz), 123.6 (d, *J* = 3.6 Hz), 115.1 (d, *J* = 22.6 Hz), 114.4 (d, *J* = 18.9 Hz), 49.0, 26.2, 16.1, 10.5.

HRMS (EI): Calcd. for C₁₁H₁₃FOS [M]⁺ 212.0666, found: 212.0656.



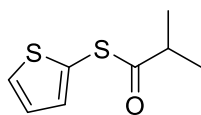
S-(4-chlorophenyl) 2-methylpropanethioate (27)

The title compound was prepared from 1,2-bis(4-chlorophenyl)disulfanedisulfane (25.4 mg, 0.1 mmol) and potassium isopropyltrifluoroborate (67.5 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (34 mg, 80%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 2.77 (p, *J* = 6.9 Hz, 1H), 1.18 (d, *J* = 6.9 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 201.3, 135.8, 135.6, 129.4, 126.4, 43.1, 19.3.

HRMS (EI): Calcd. for C₁₀H₁₁ClOS [M]⁺ 214.0214, found: 214.0214.



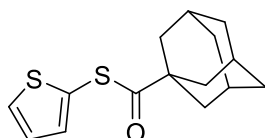
S-(thiophen-2-yl) 2-methylpropanethioate (28)

The title compound was prepared from 1,2-di(thiophen-2-yl)disulfane (23 mg, 0.1 mmol) and potassium isopropyltrifluoroborate (67.5 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (15 mg, 40%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.47 (dd, *J* = 5.3, 1.3 Hz, 1H), 7.07 (dd, *J* = 3.6, 1.3 Hz, 1H), 7.03 (dd, *J* = 5.3, 3.6 Hz, 1H), 2.79 (p, *J* = 6.9 Hz, 1H), 1.19 (d, *J* = 6.9 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 201.6, 135.6, 131.6, 127.8, 125.0, 42.6, 19.3.

HRMS (EI): Calcd. for C₈H₁₀OS₂ [M]⁺ 186.0168, found: 186.0167.



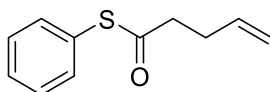
S-(thiophen-2-yl) (3*r*,5*r*,7*r*)-adamantane-1-carbothioate (29)

The title compound was prepared from 1,2-di(thiophen-2-yl)disulfane (23 mg, 0.1 mmol) and potassium ((3*r*,5*r*,7*r*)-adamantan-1-yl)trifluoroborate (108.9 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (40 mg, 72%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 (dd, *J* = 5.2, 1.4 Hz, 1H), 7.06 – 6.96 (m, 2H), 2.05 – 1.99 (m, 3H), 1.93 (d, *J* = 2.9 Hz, 6H), 1.71 – 1.63 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 202.6, 134.7, 130.5, 126.7, 124.1, 48.2, 38.1, 35.3, 27.1.

HRMS (EI): Calcd. for C₁₅H₁₈OS₂ [M]⁺ 278.0794, found: 278.0792.



S-phenyl pent-4-enethioate (32)

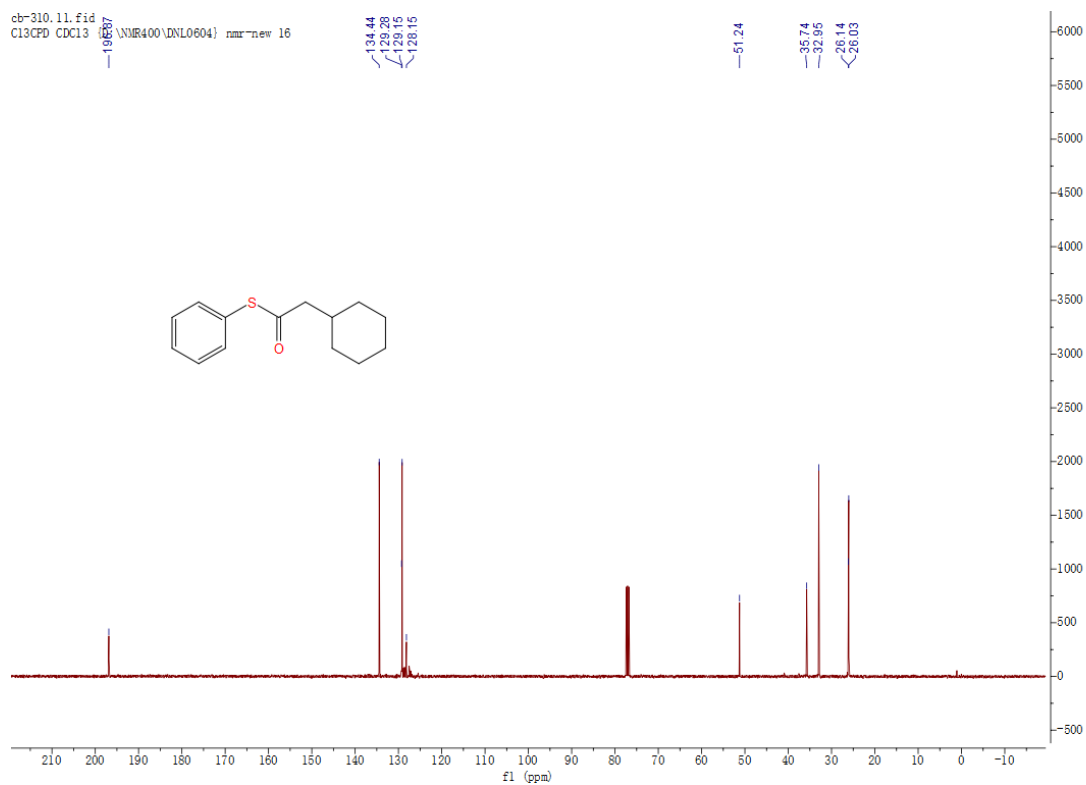
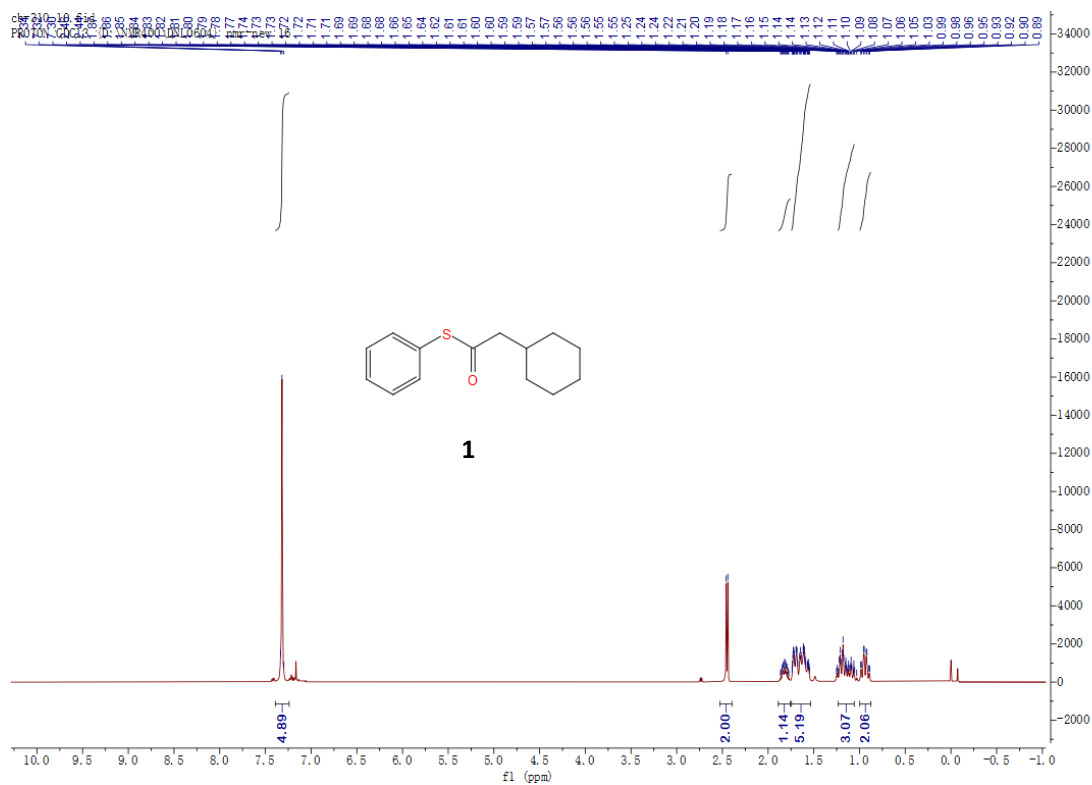
The title compound was prepared from 1,2-diphenyldisulfane (21.8 mg, 0.1 mmol) and potassium cyclopropylmethyltrifluoroborate (72.9 mg, 0.45 mmol) according to general procedure. The crude residue was purified by flash chromatography (PE/EA = 50:1) to give the product as a colorless oil (21 mg, 55%).

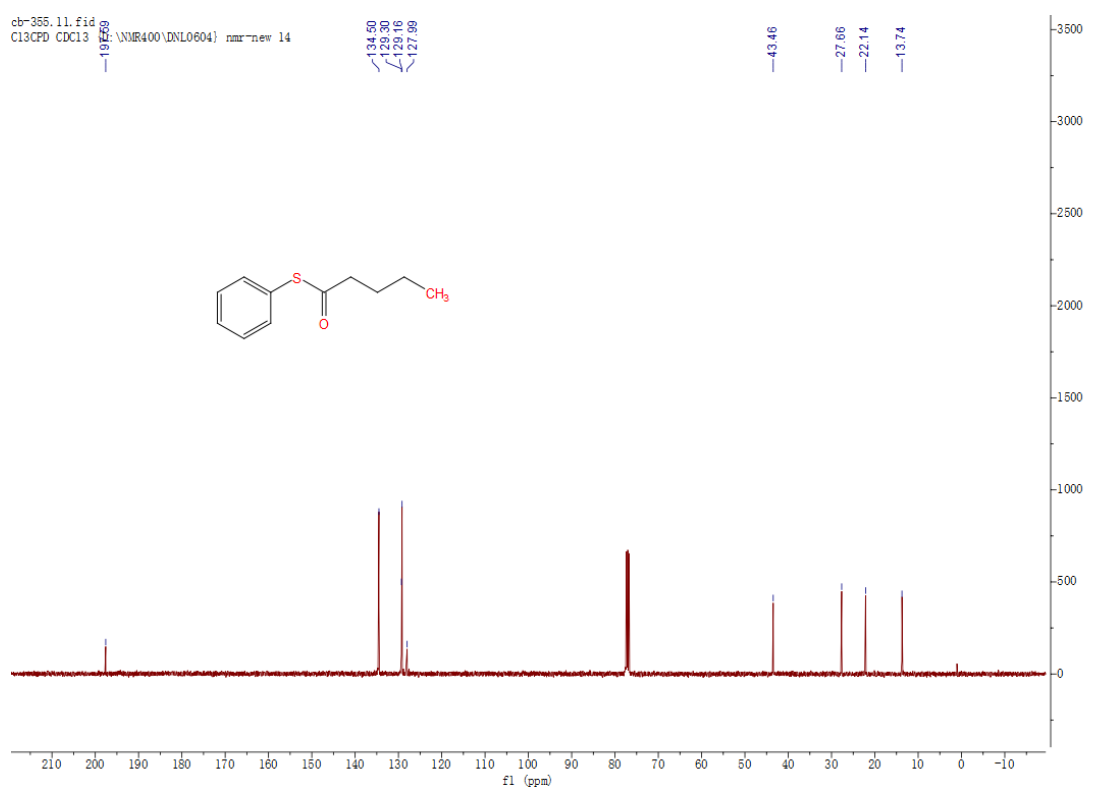
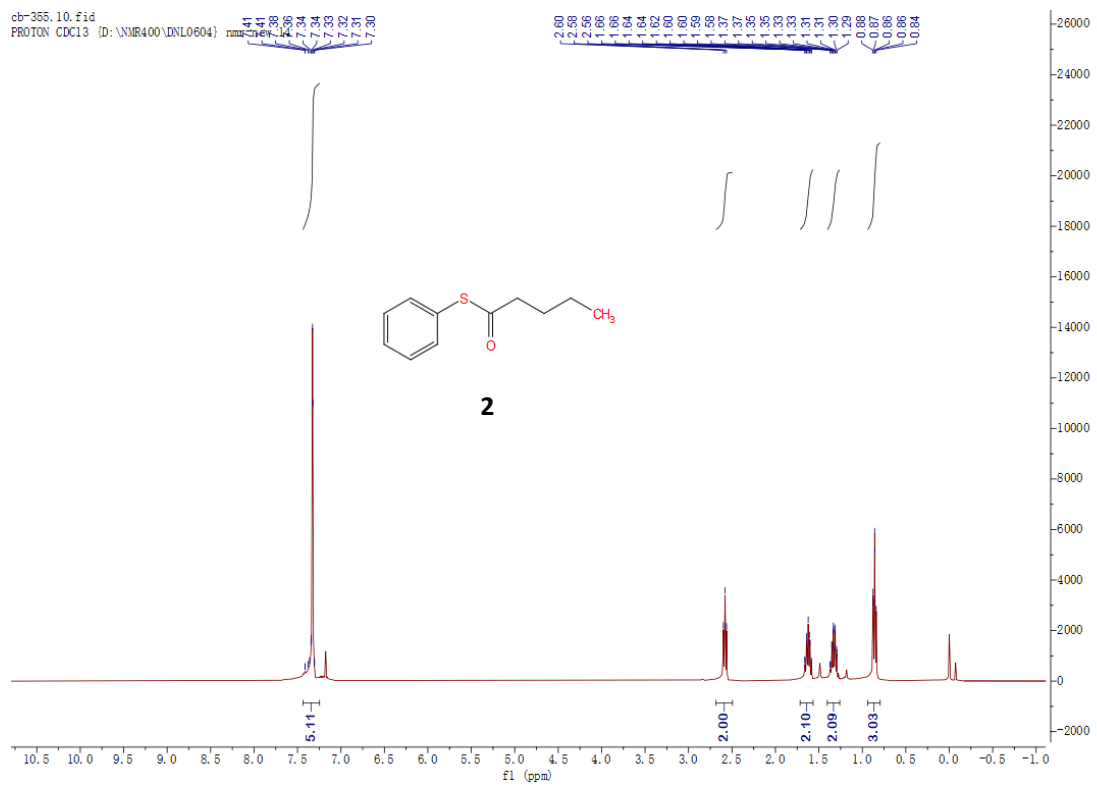
¹H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.31 (m, 5H), 5.76 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.12 – 4.91 (m, 2H), 2.68 (dd, *J* = 8.3, 6.7 Hz, 2H), 2.44 – 2.35 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 196.8, 136.1, 134.5, 129.4, 129.2, 127.8, 116.0, 42.8, 29.4.

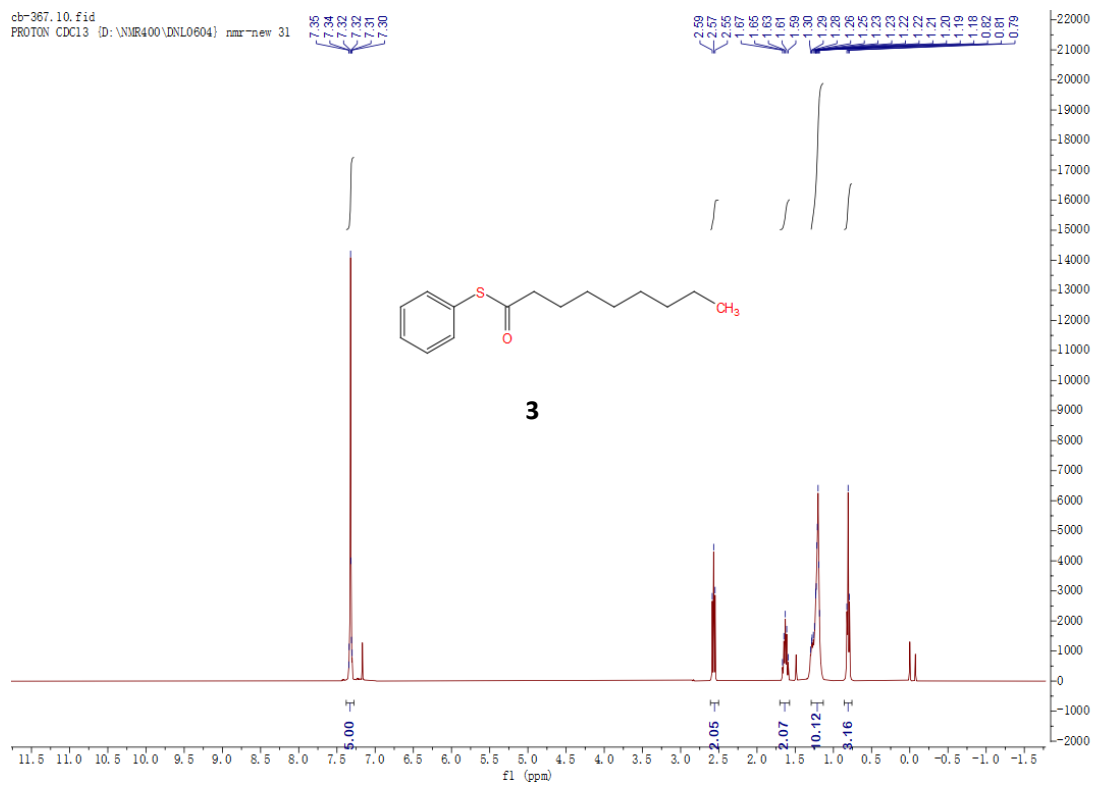
HRMS (EI): Calcd. for C₁₁H₁₂OS [M]⁺ 192.0603, found: 192.0607.

4. Copies of NMR spectra for products

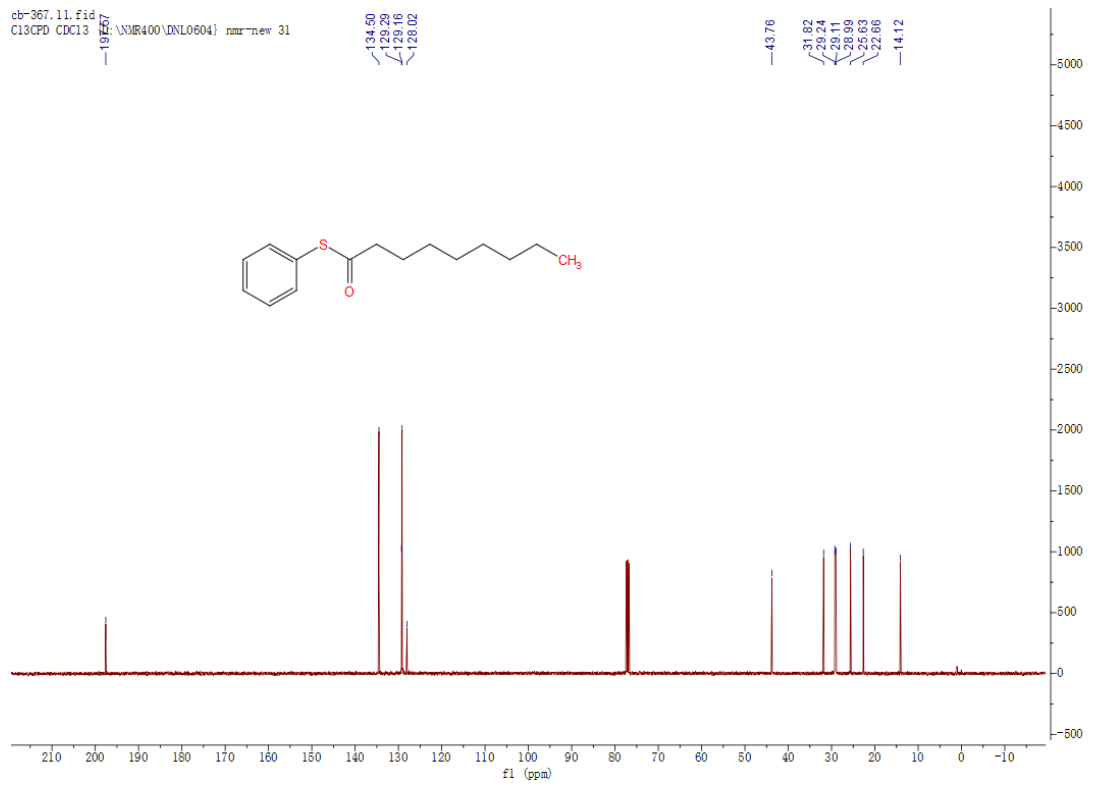


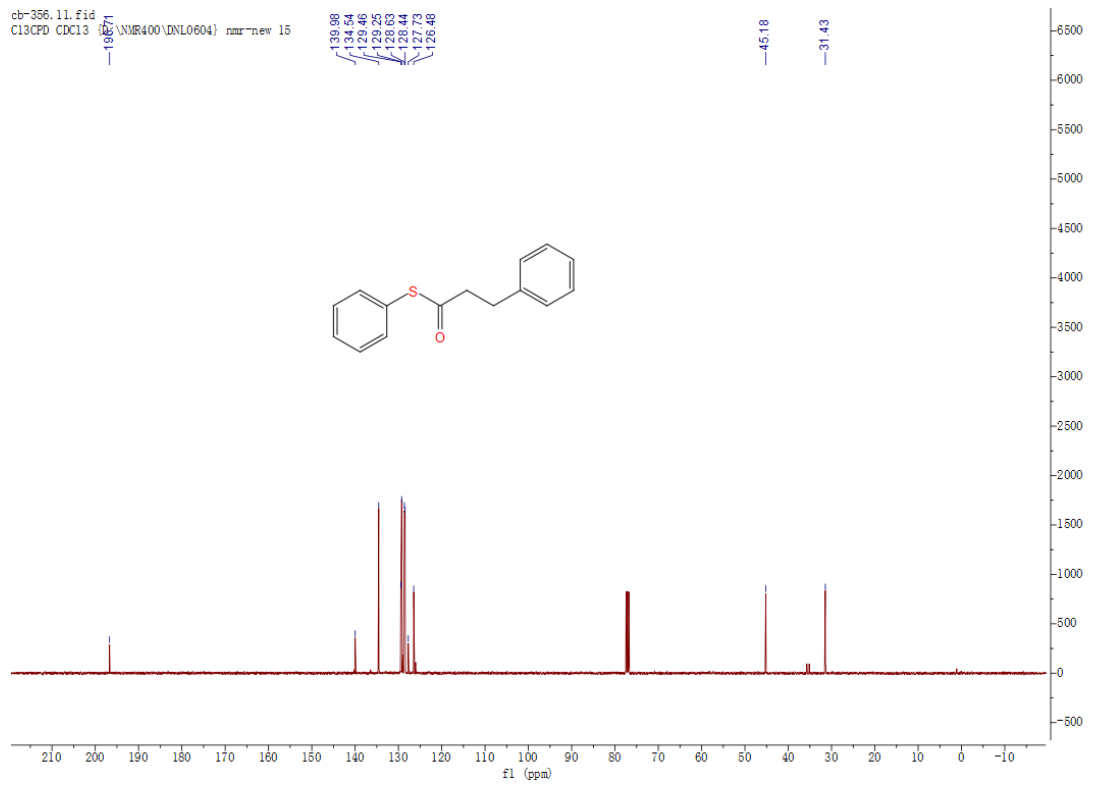
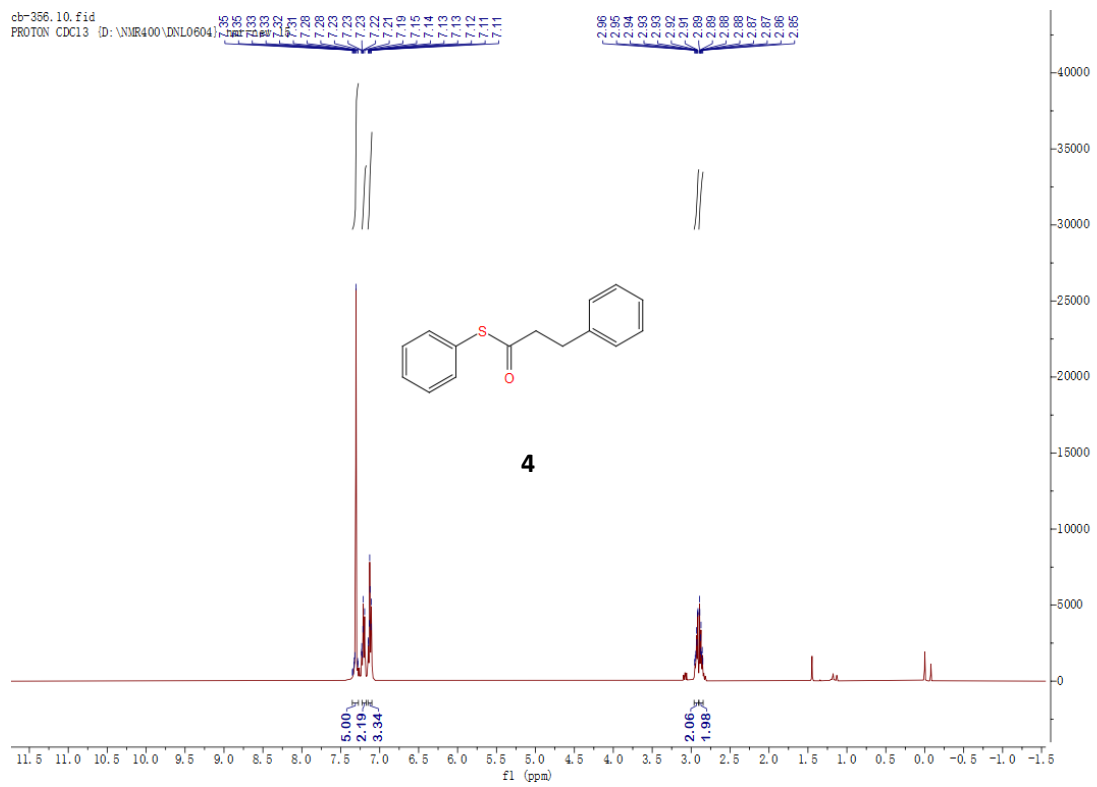


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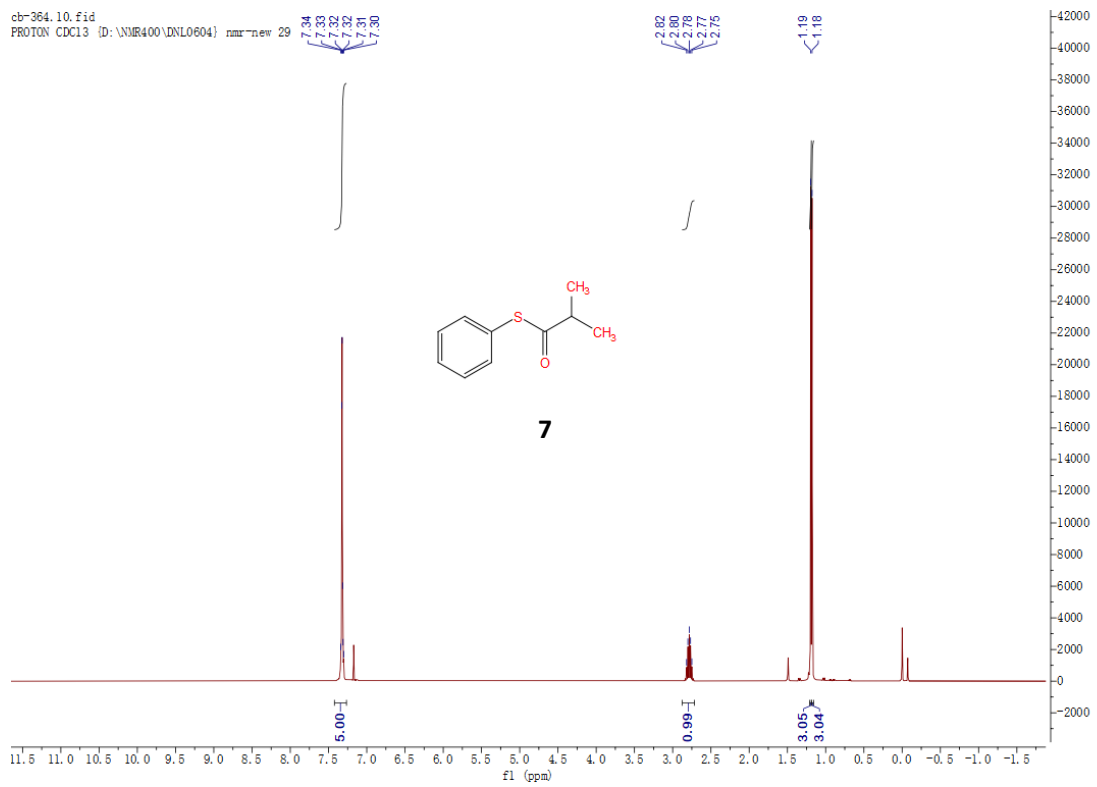


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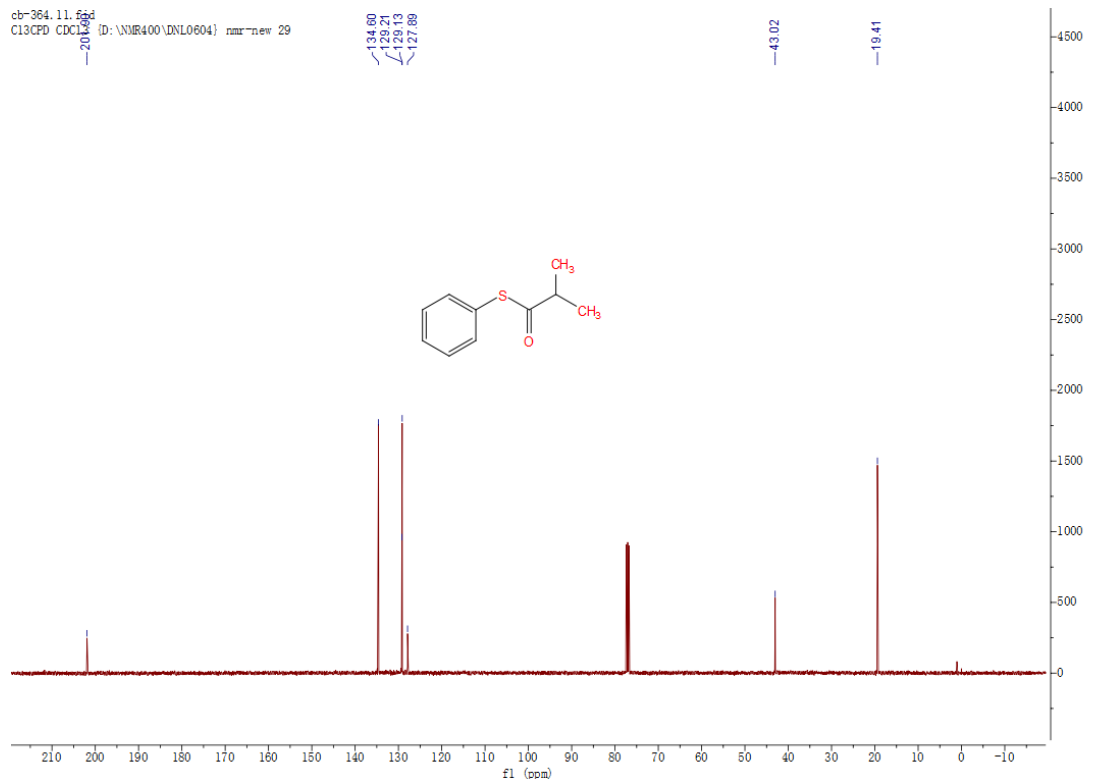




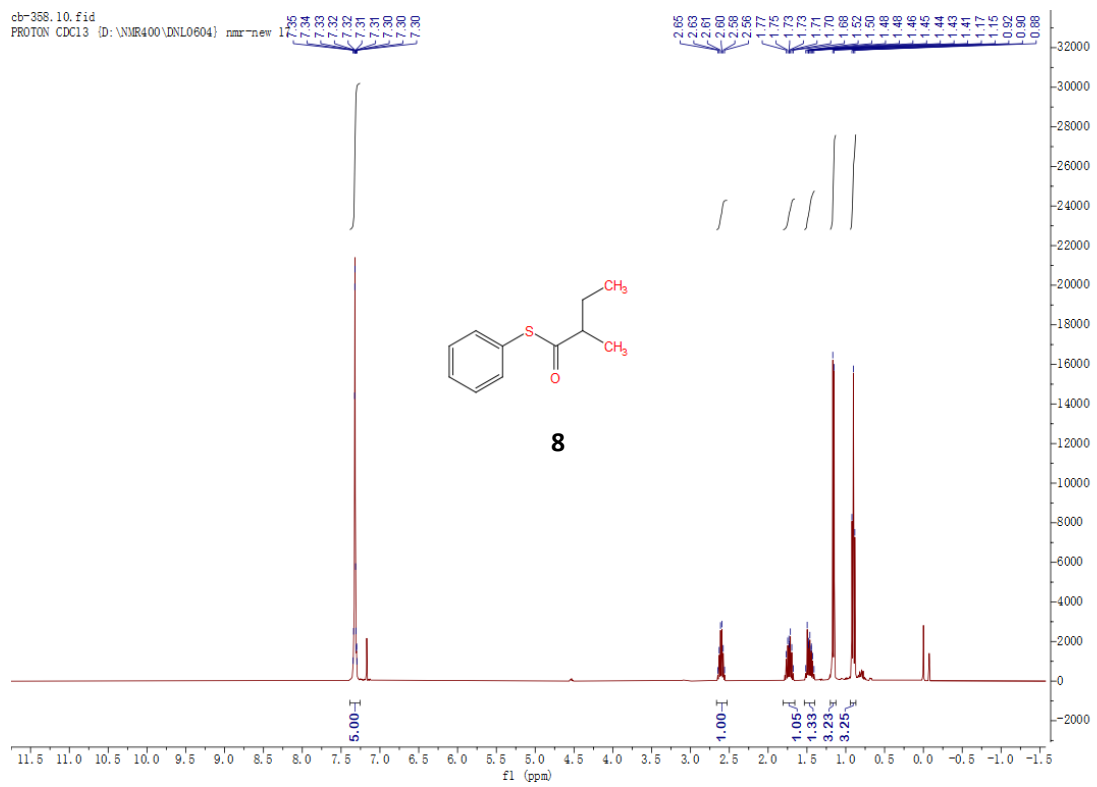
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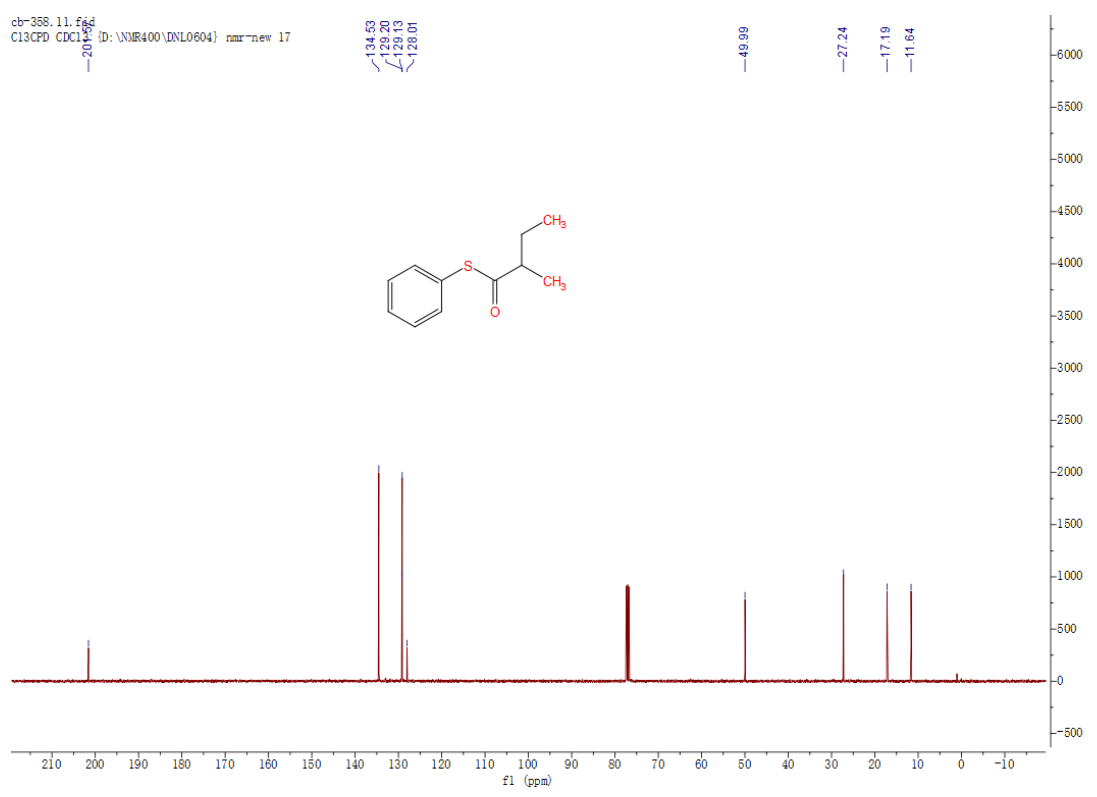
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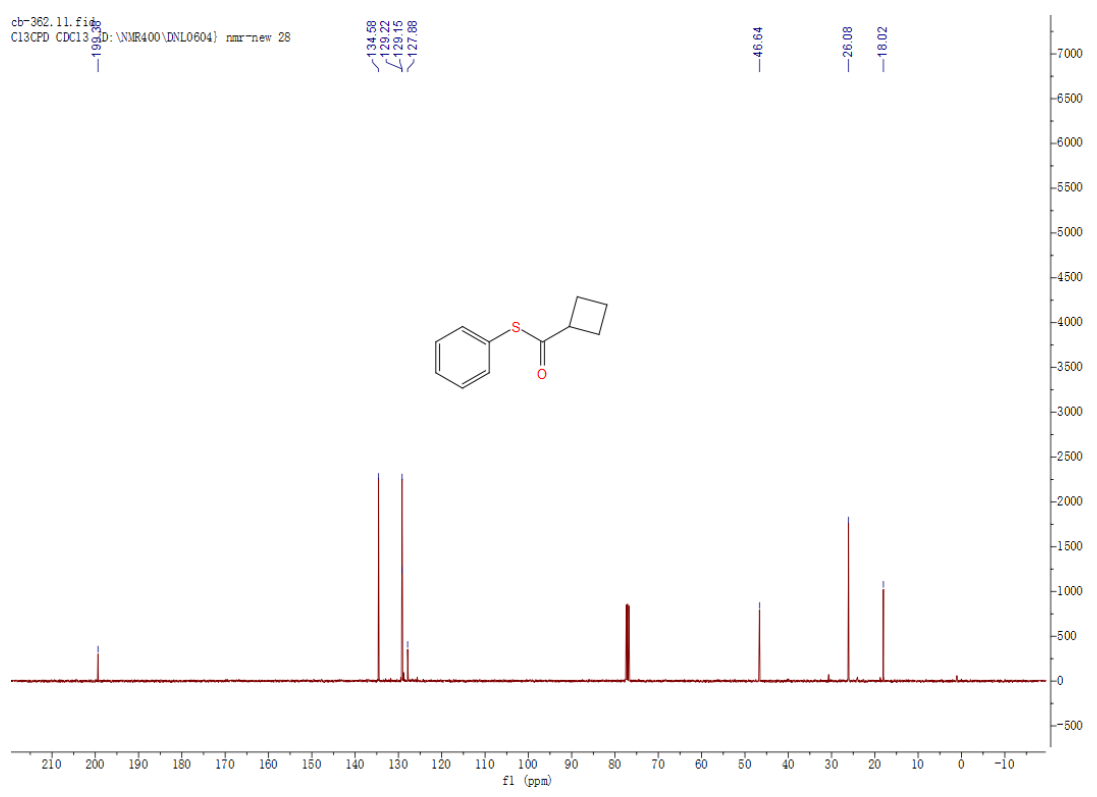
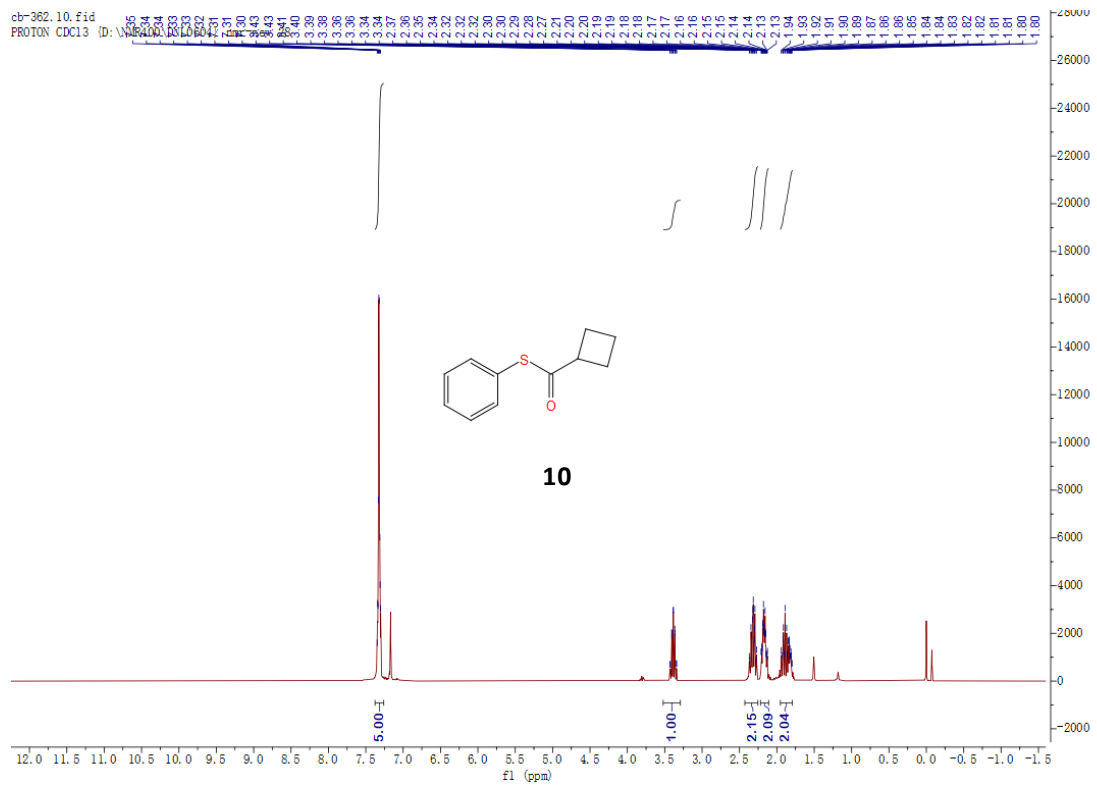


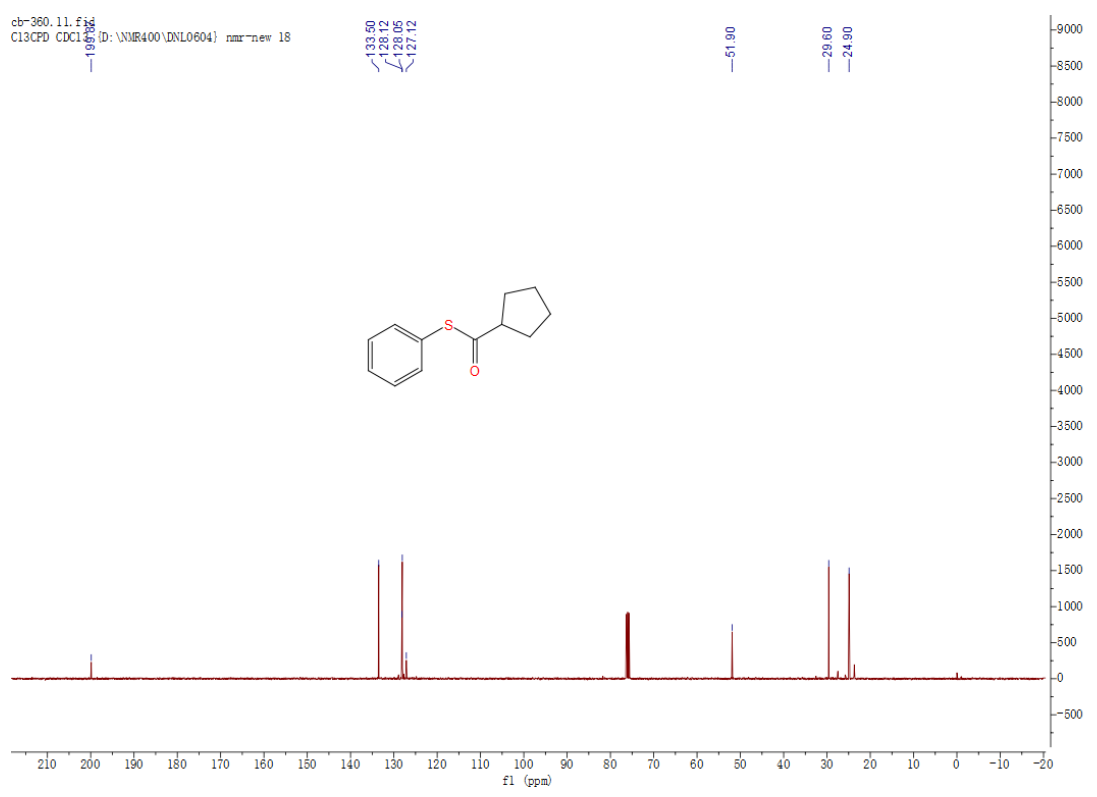
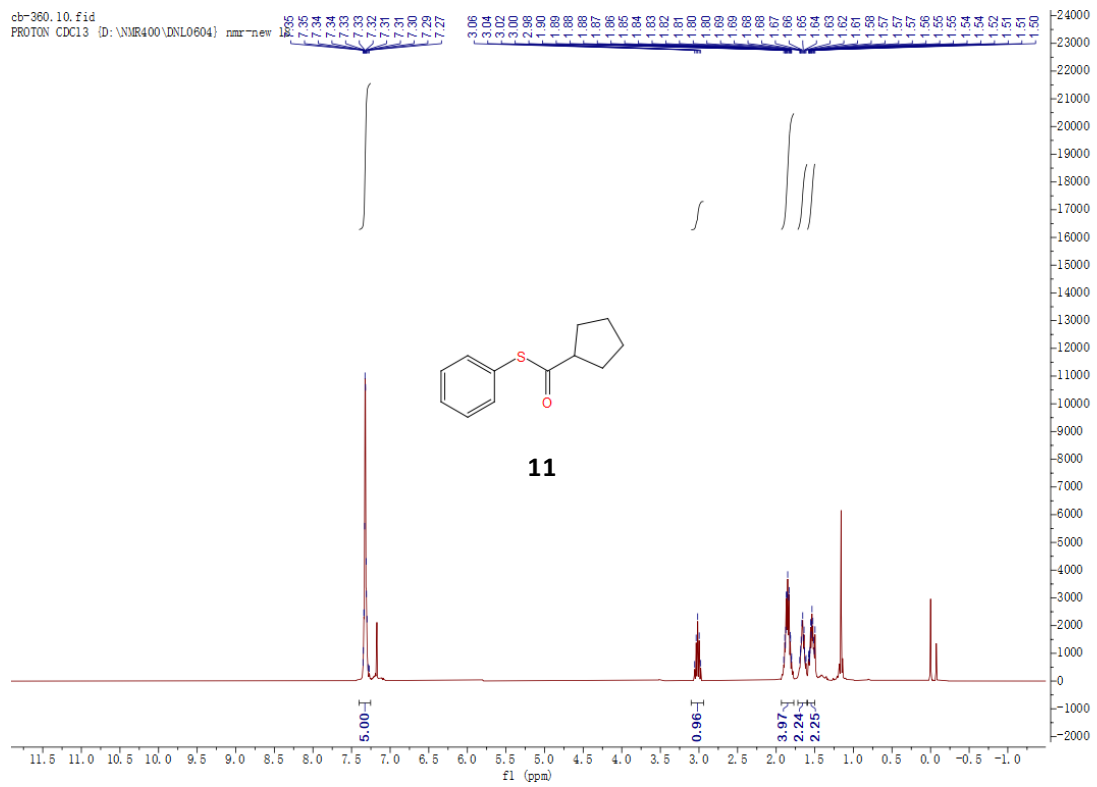
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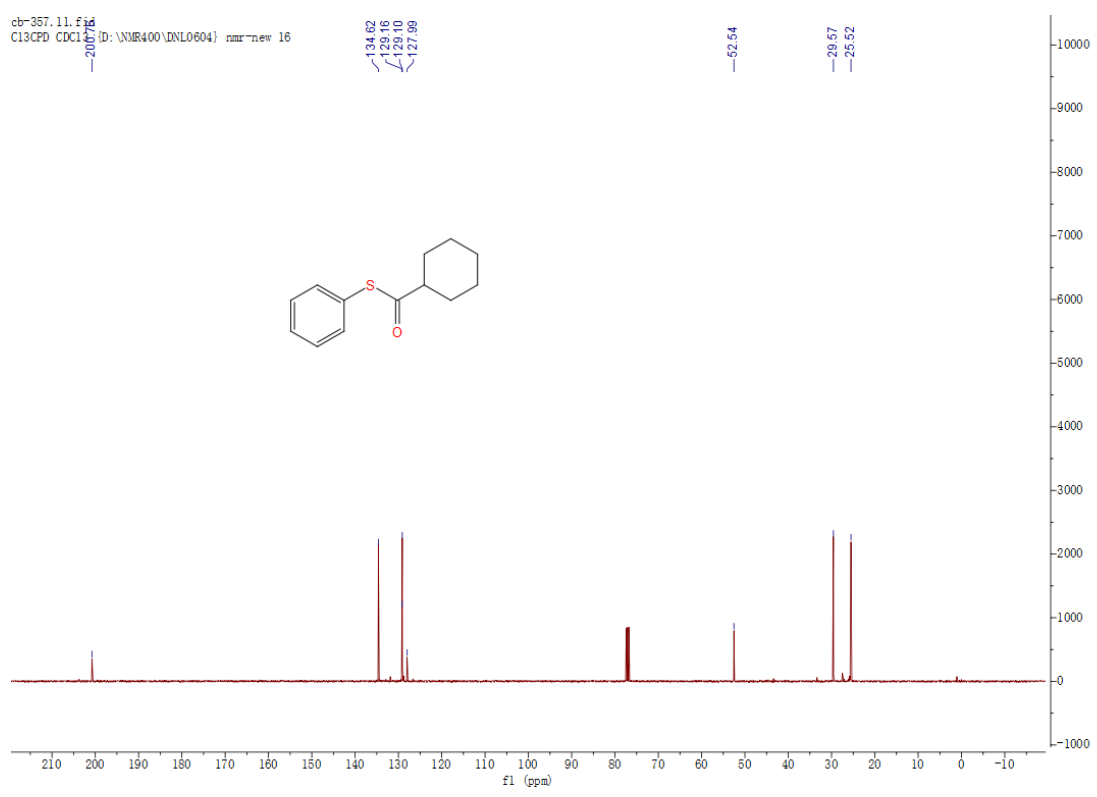
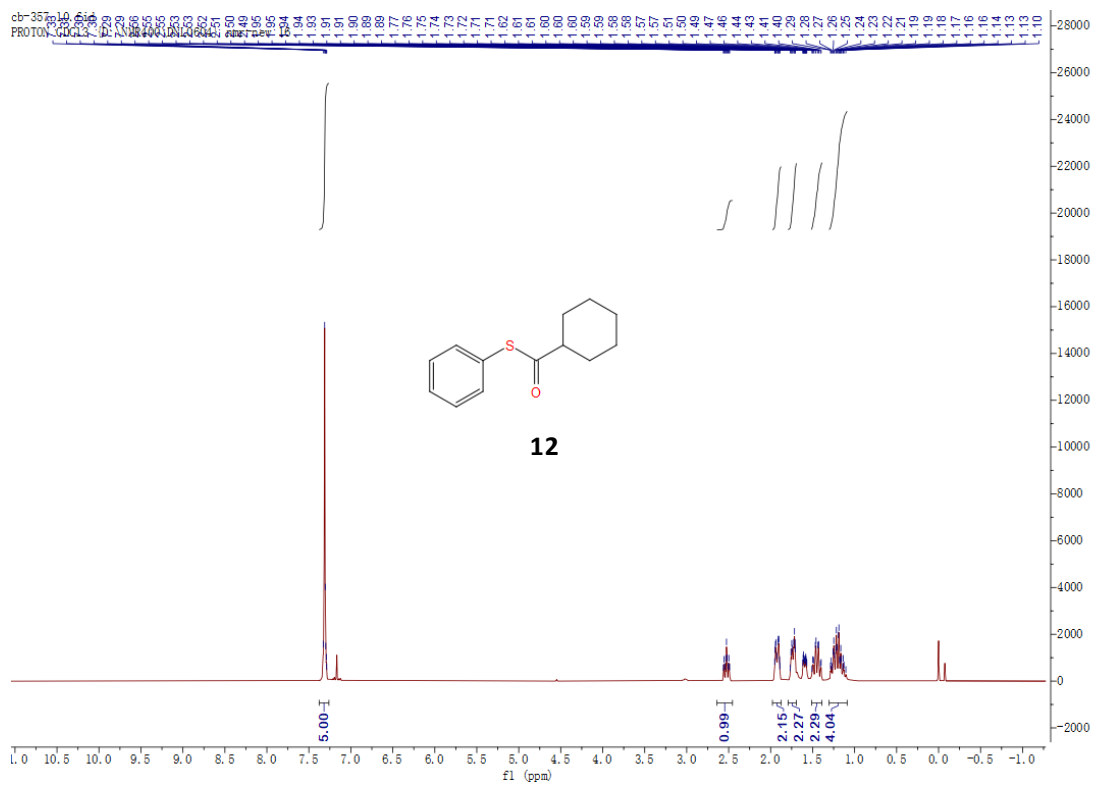


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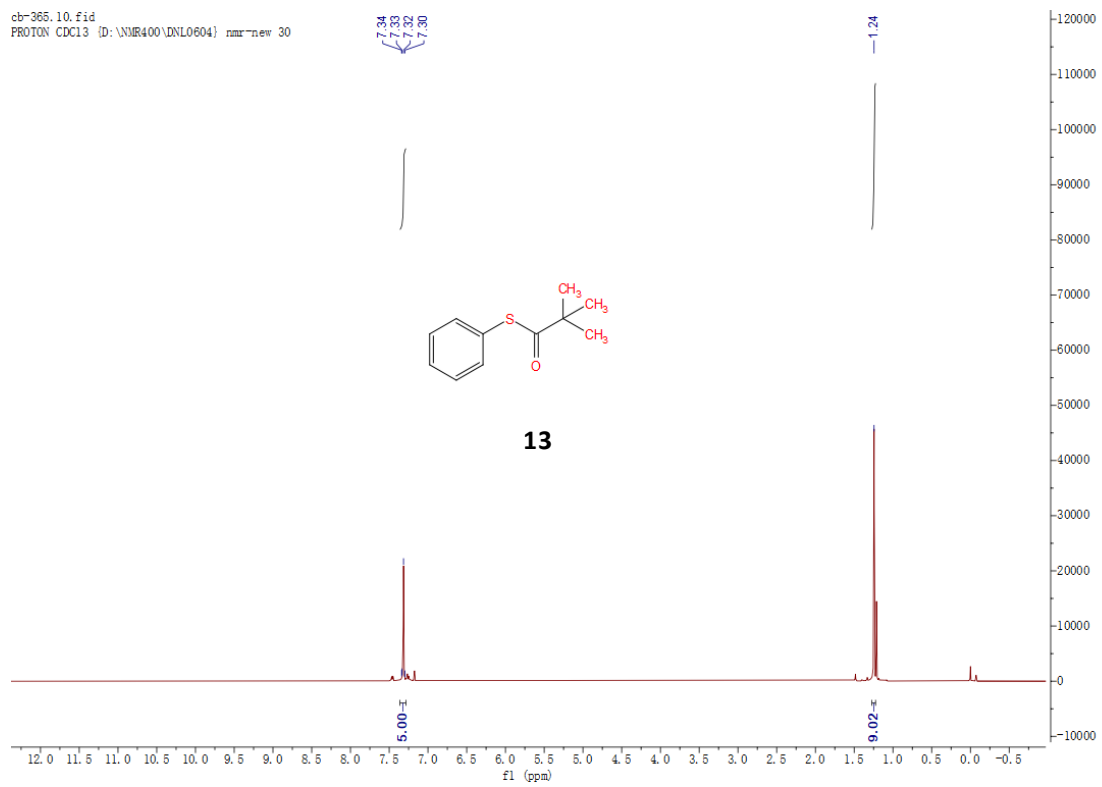




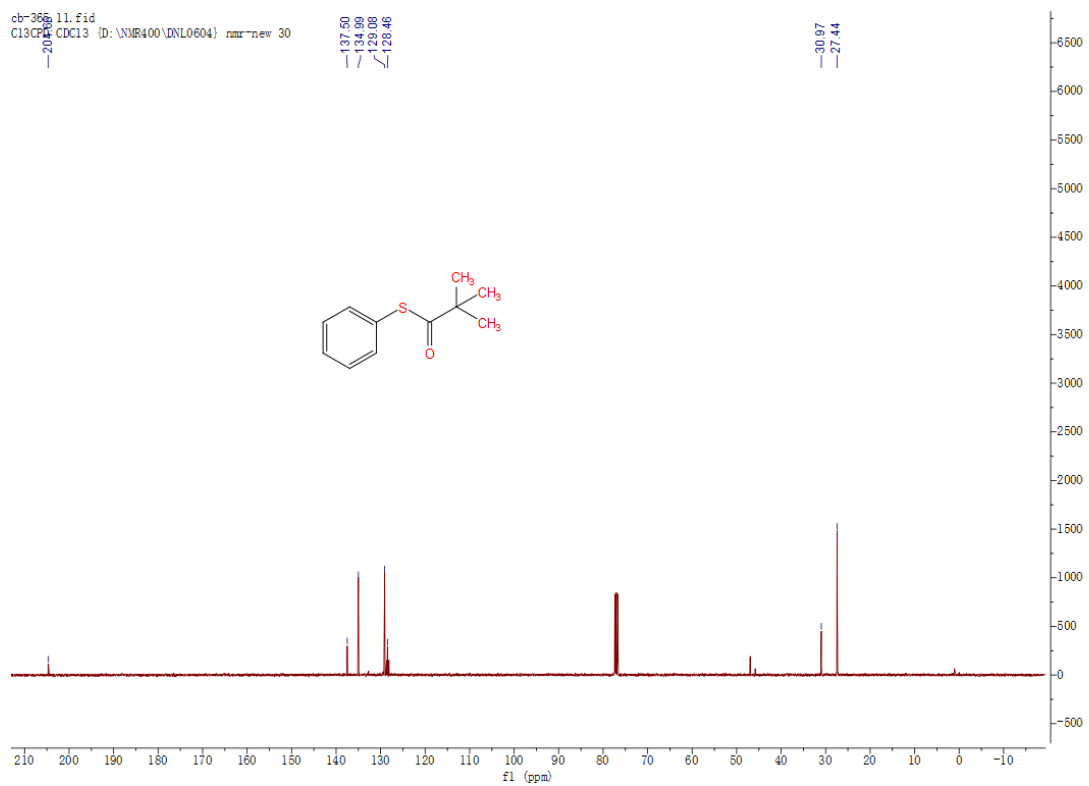




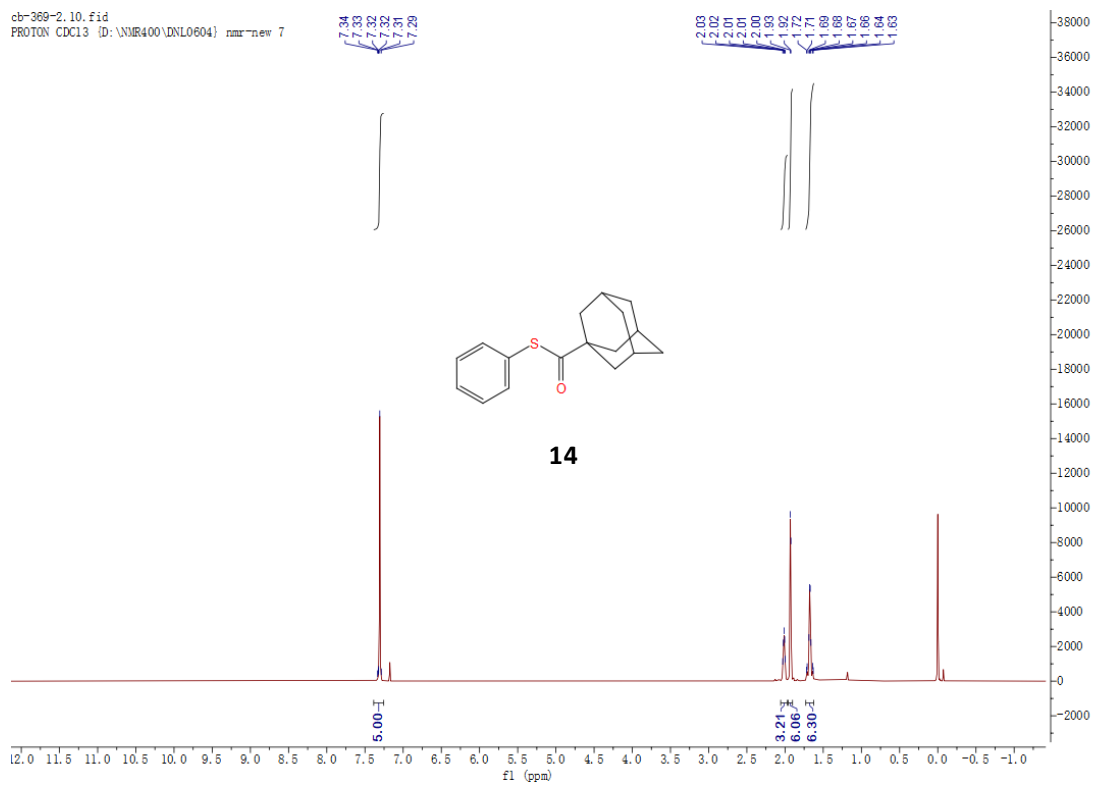
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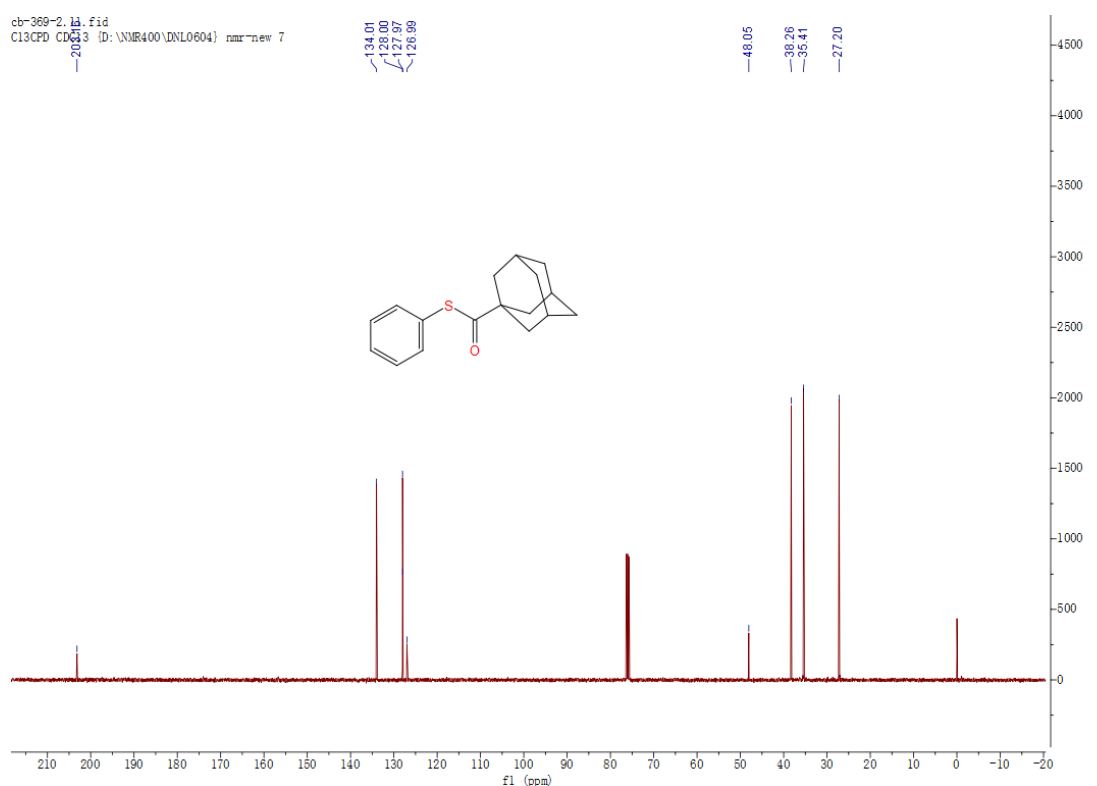
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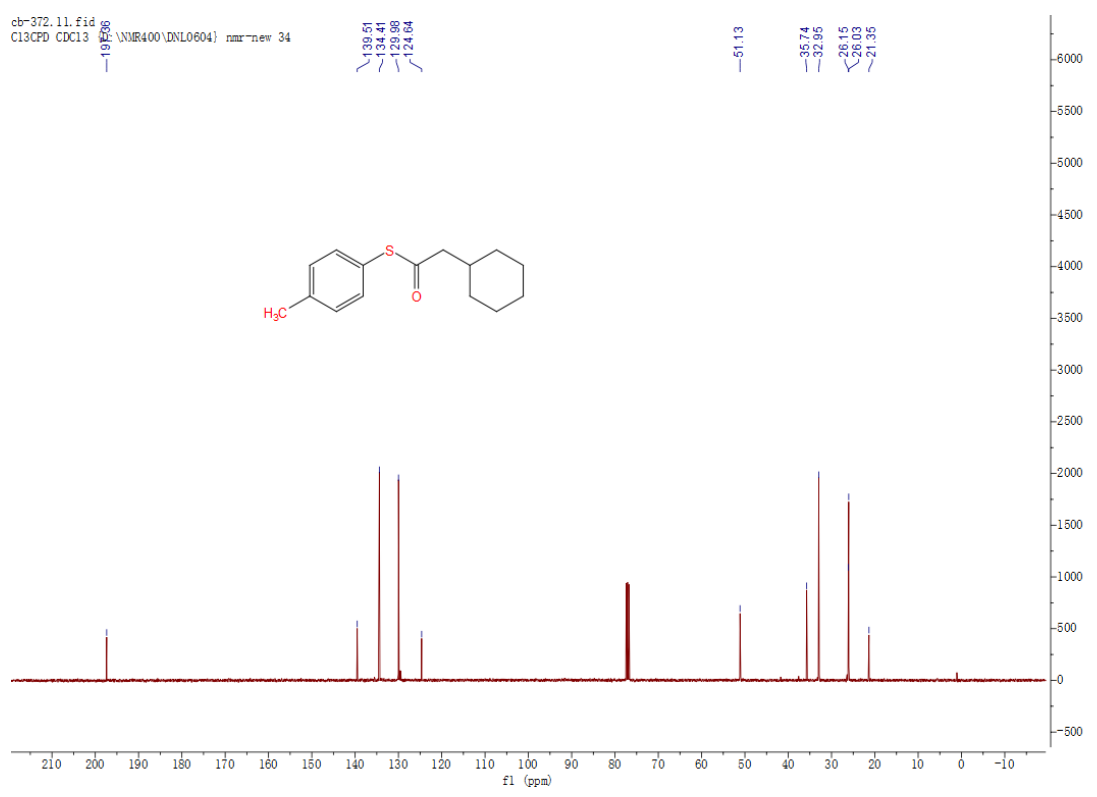
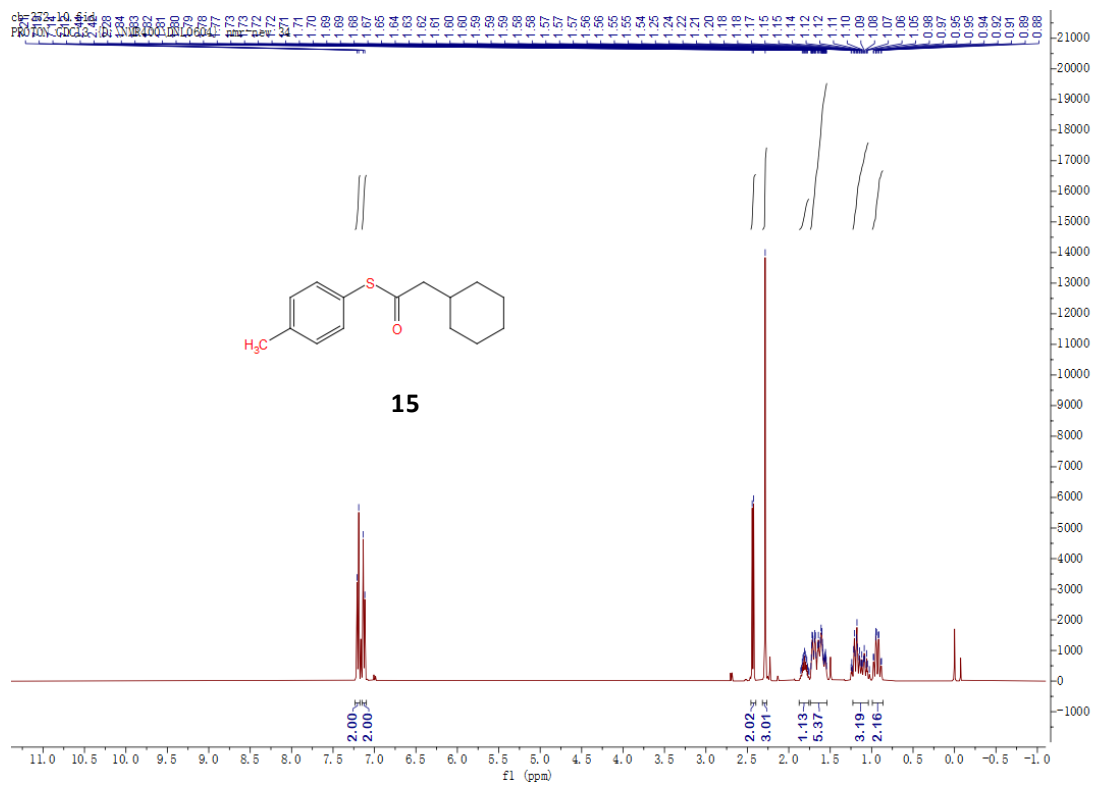


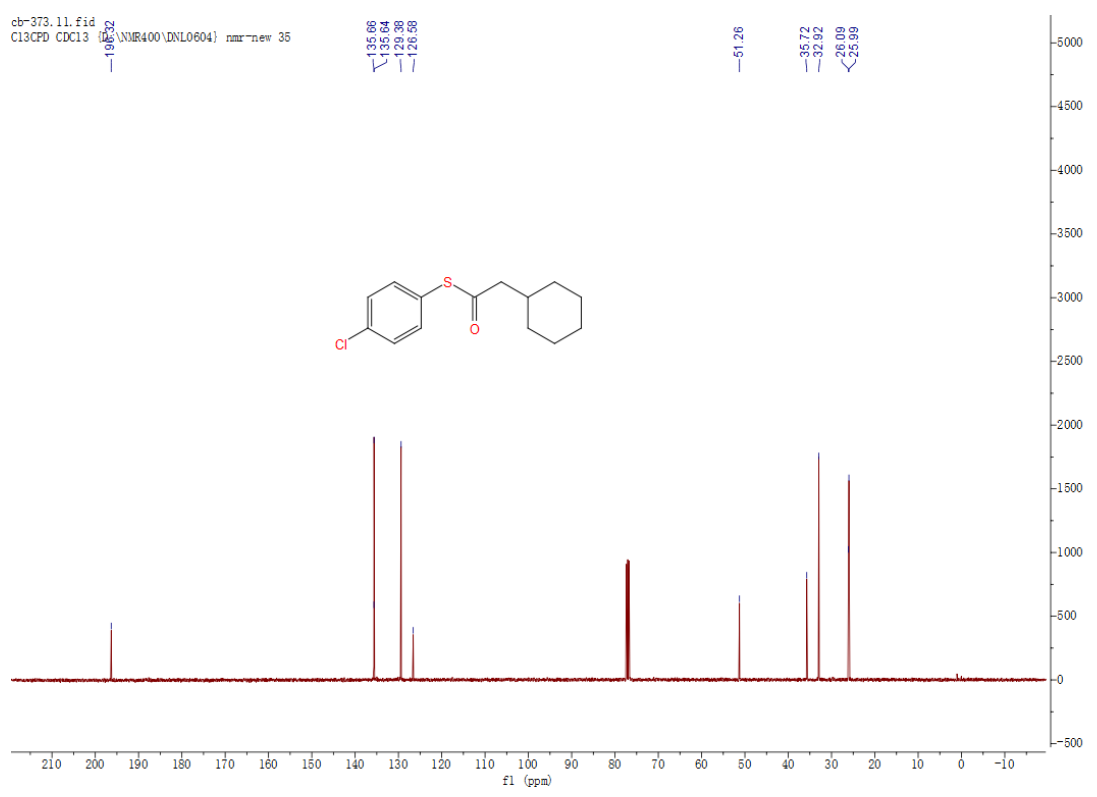
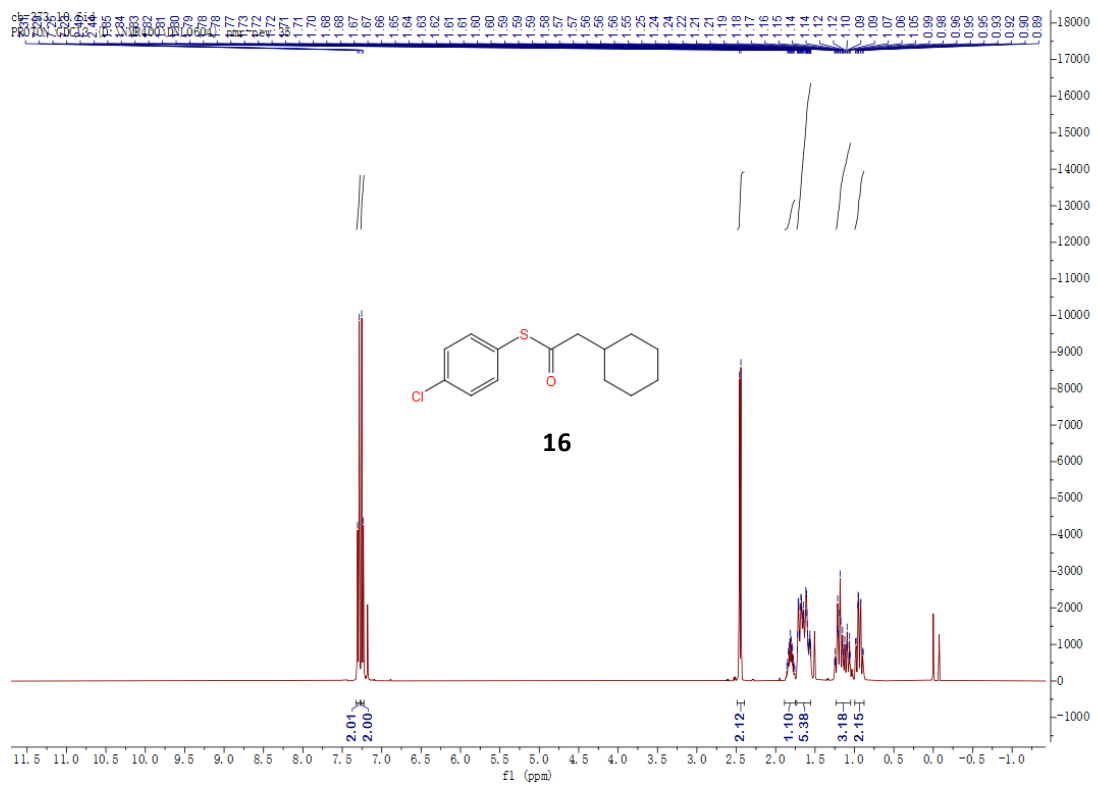
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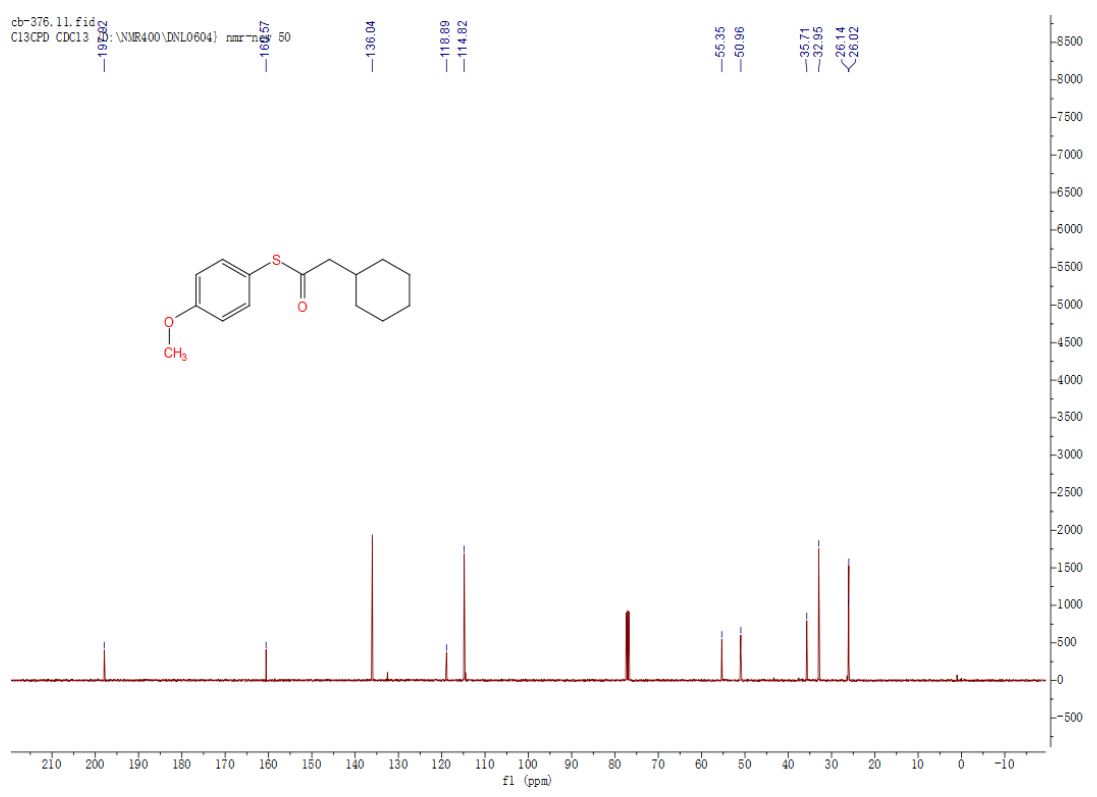
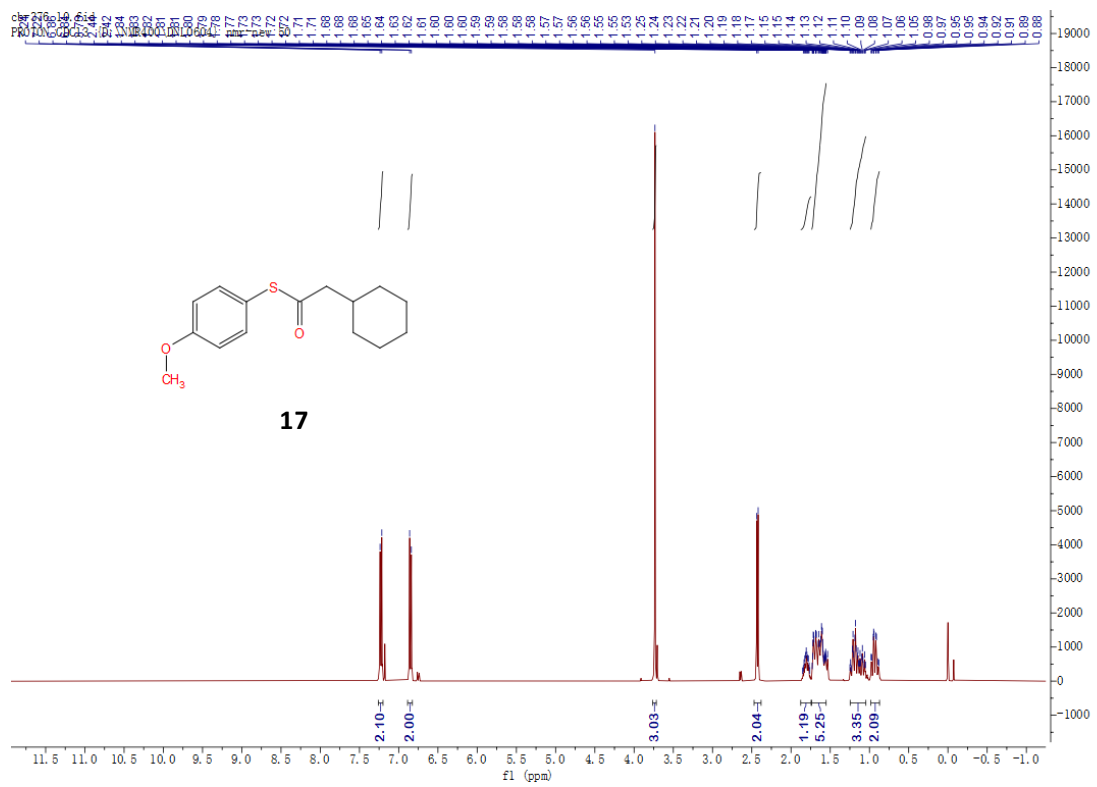


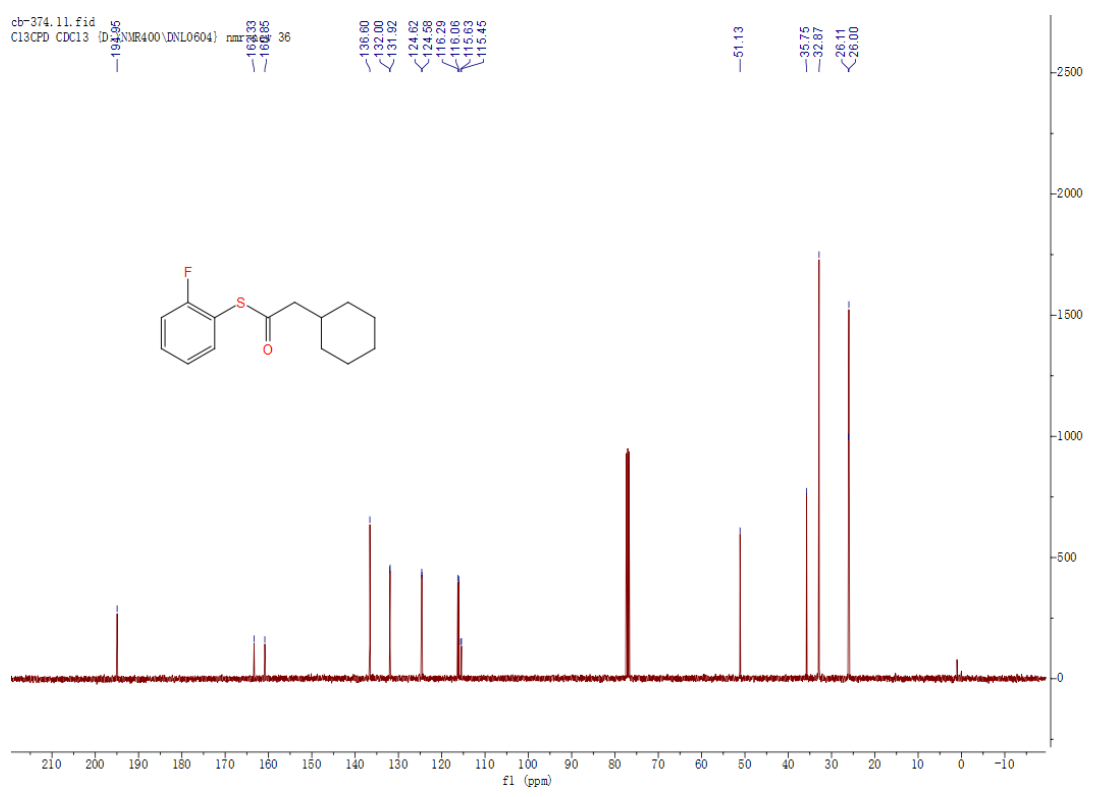
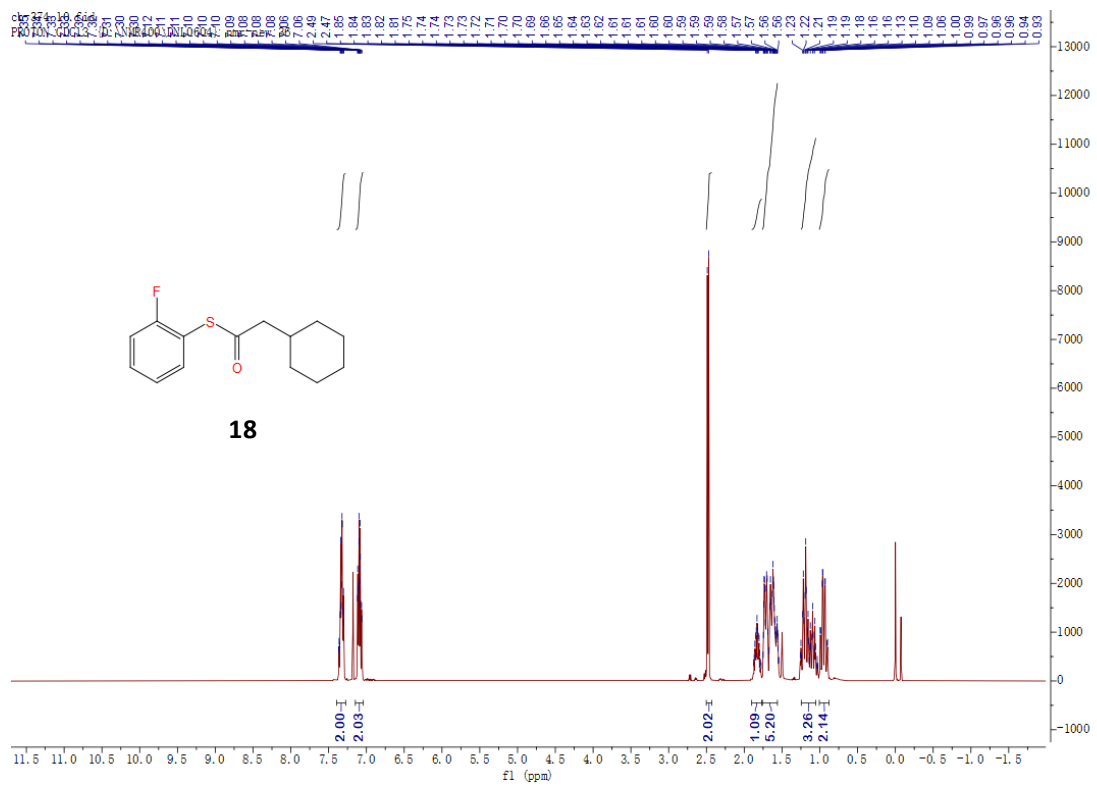
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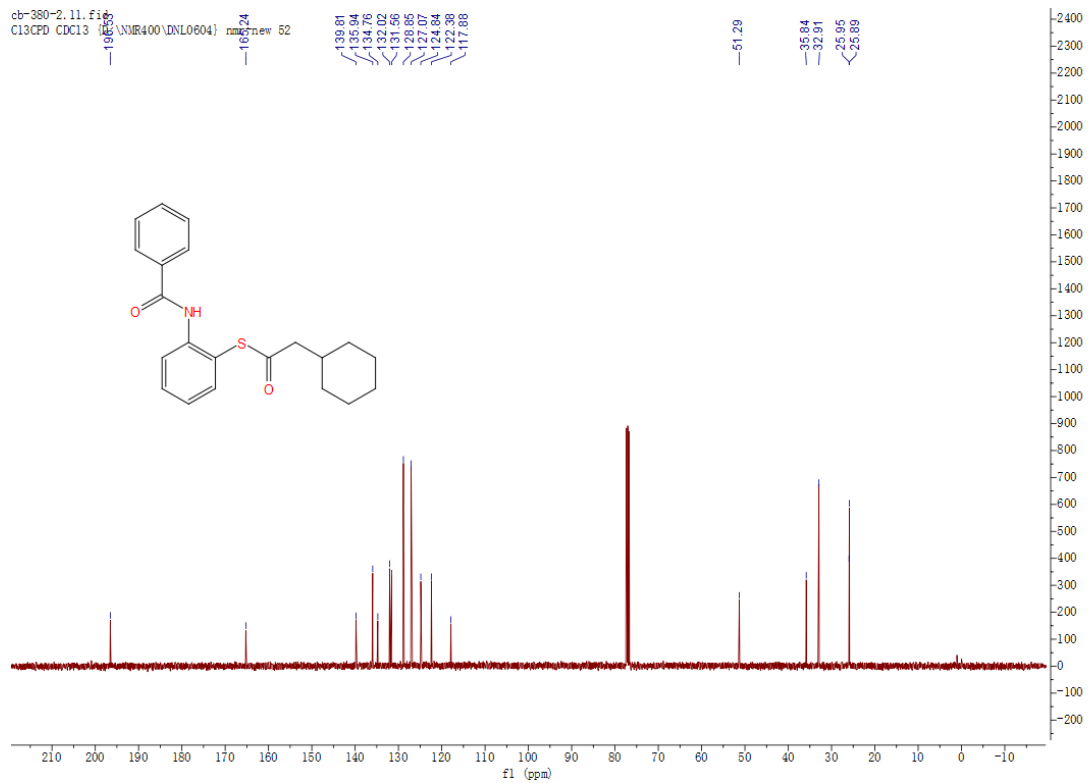
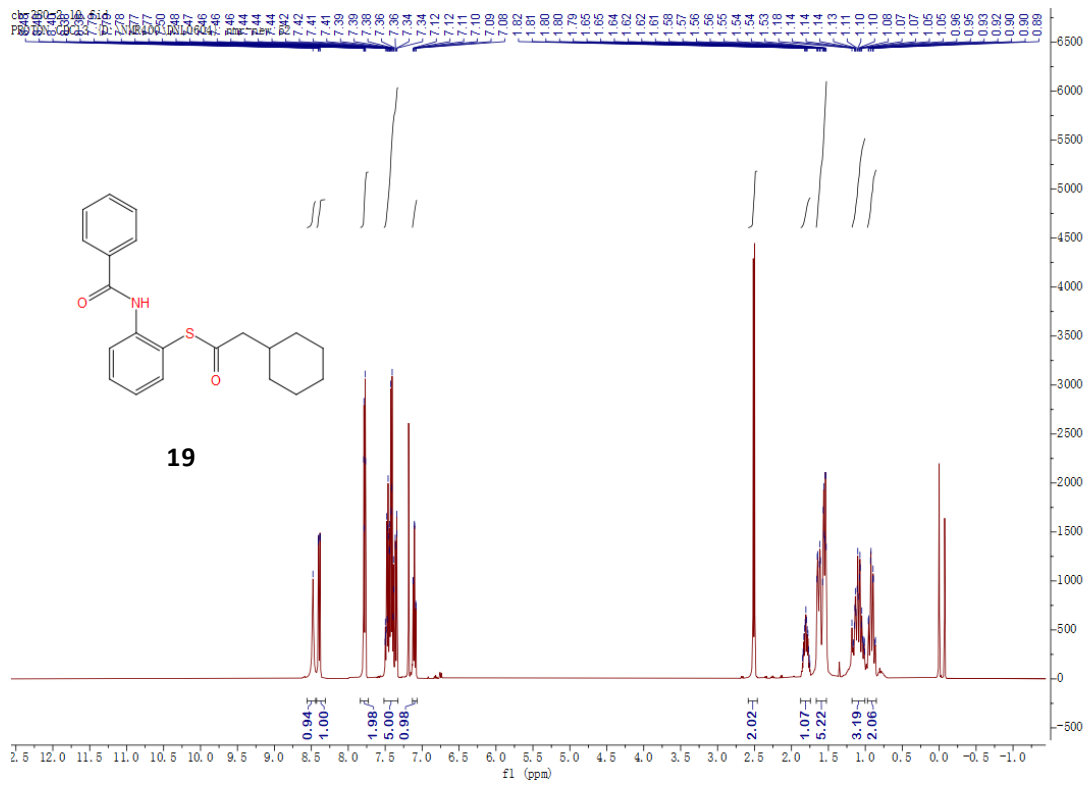


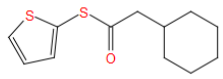
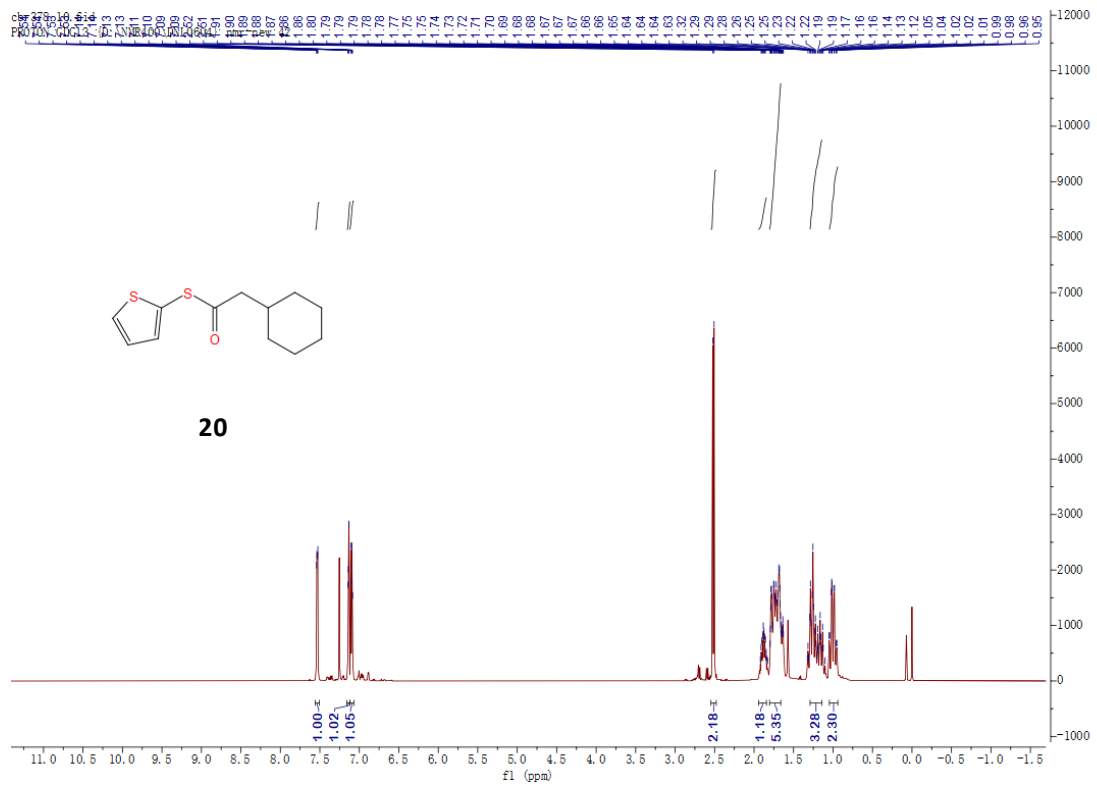




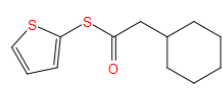
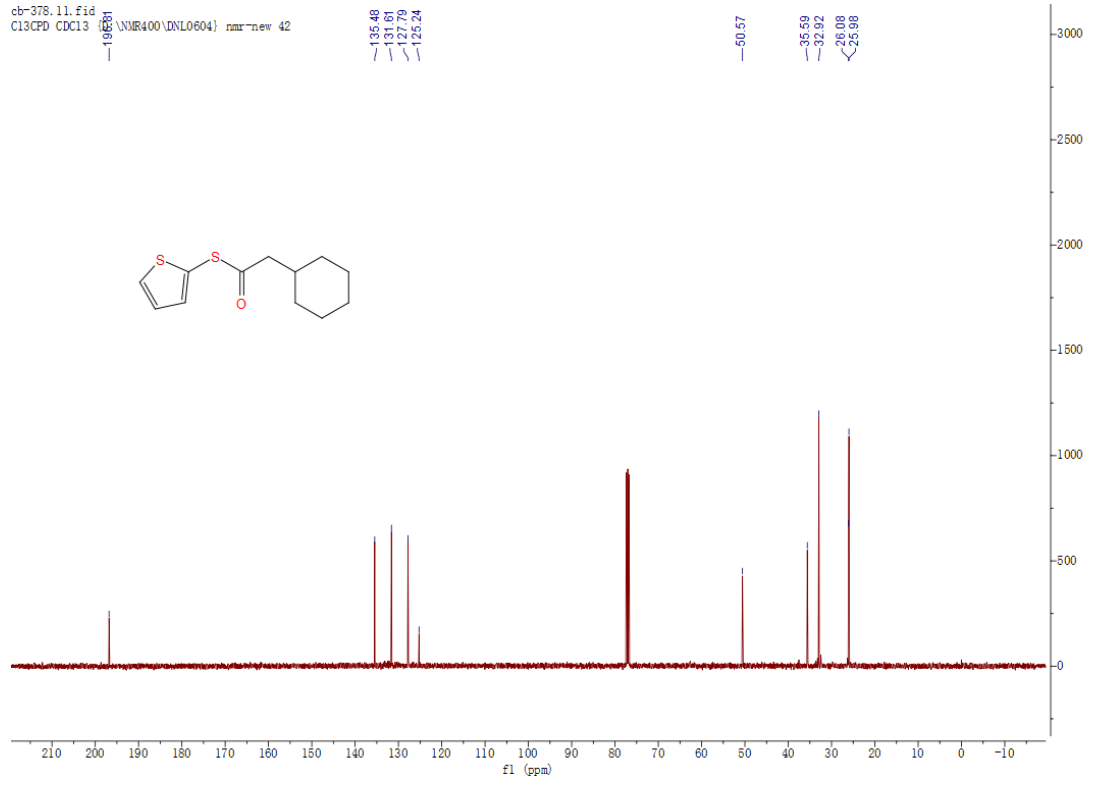




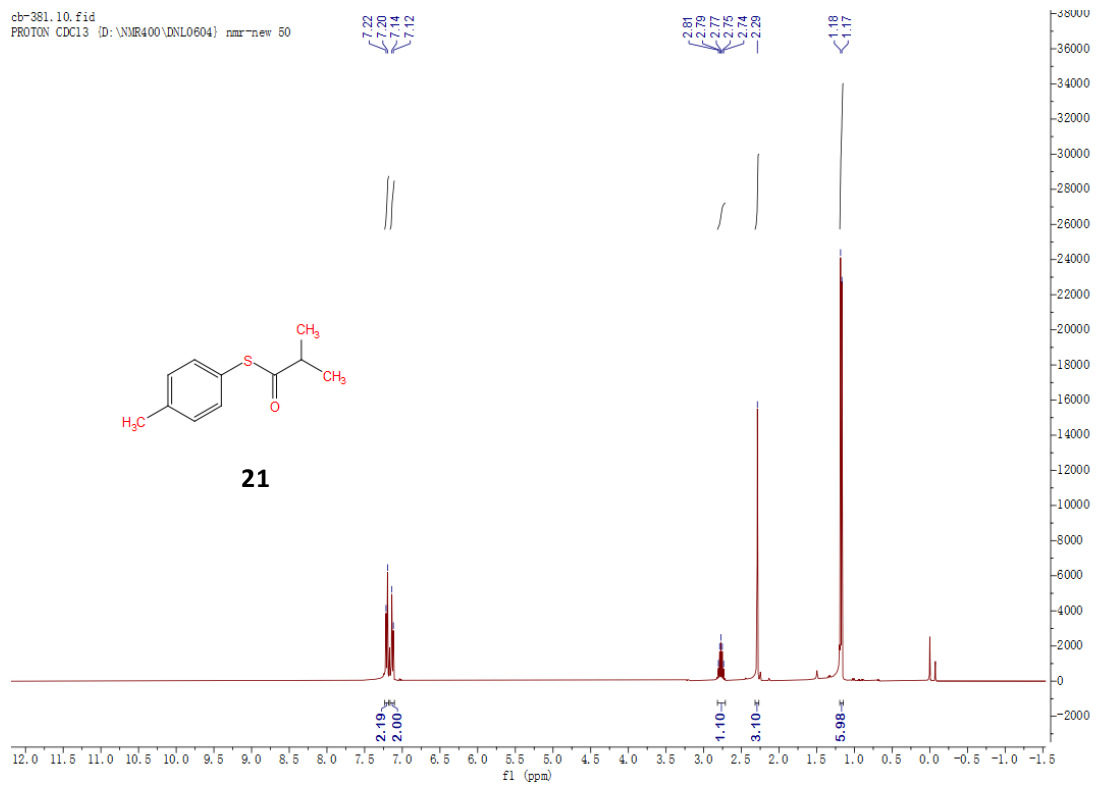




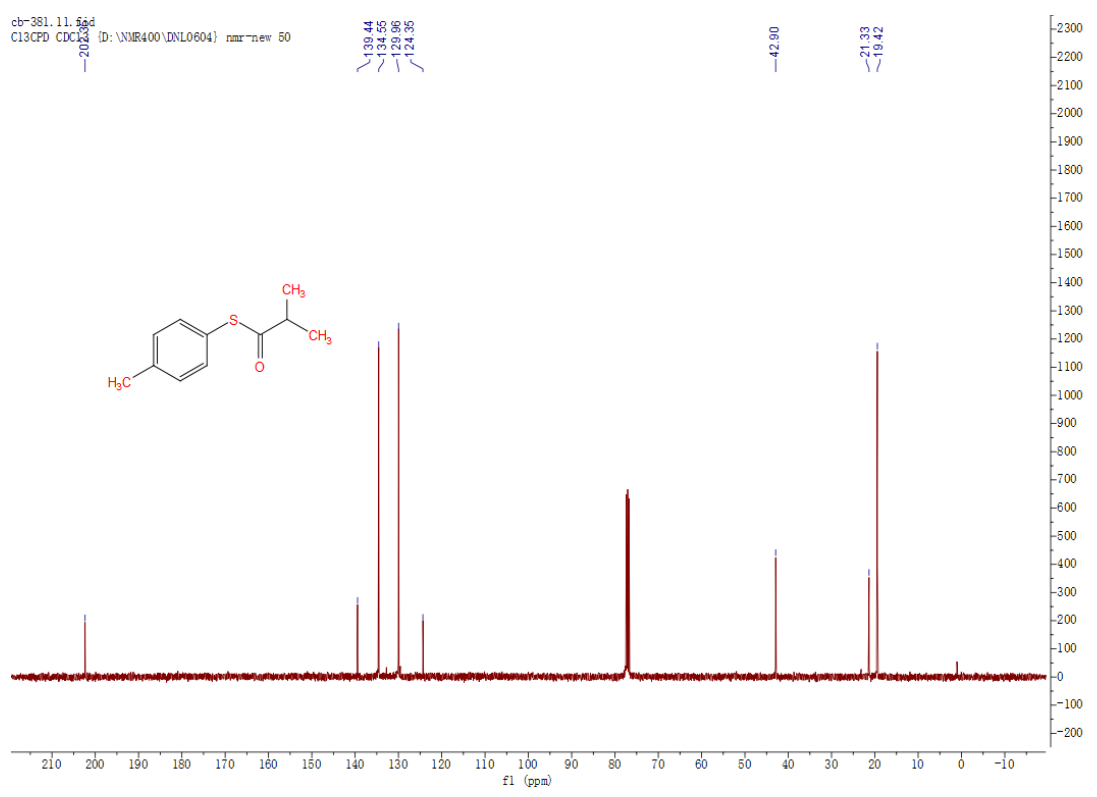
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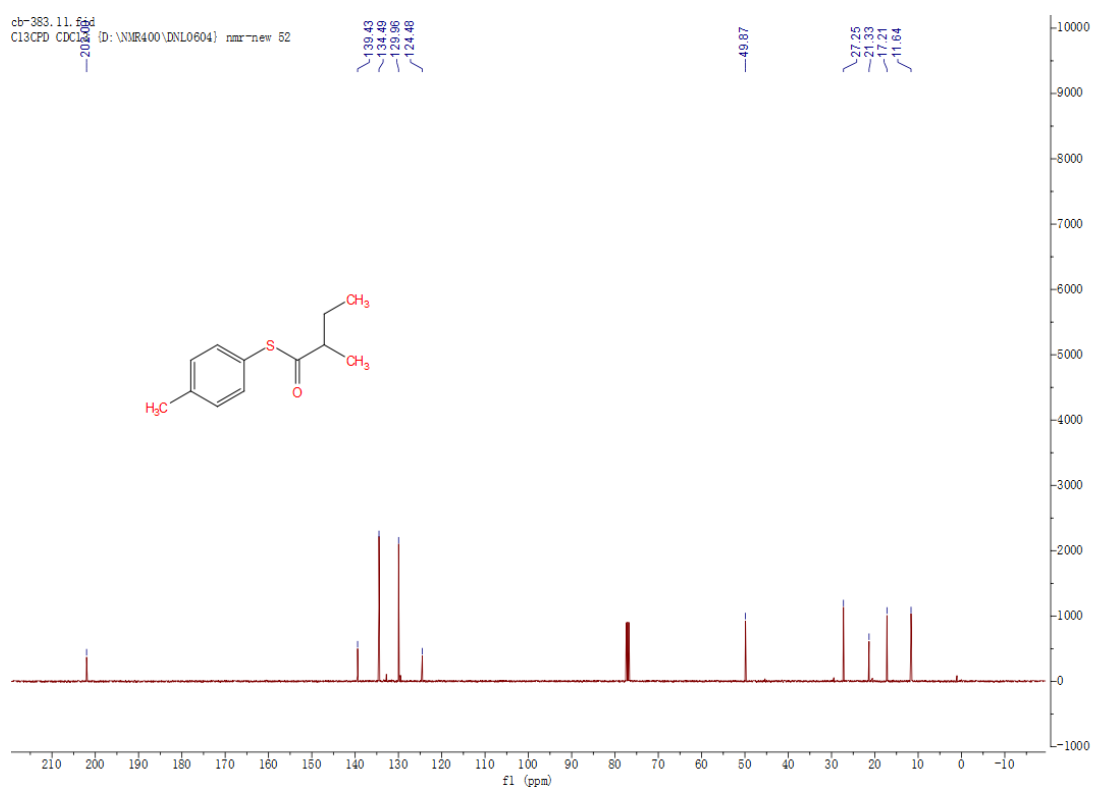
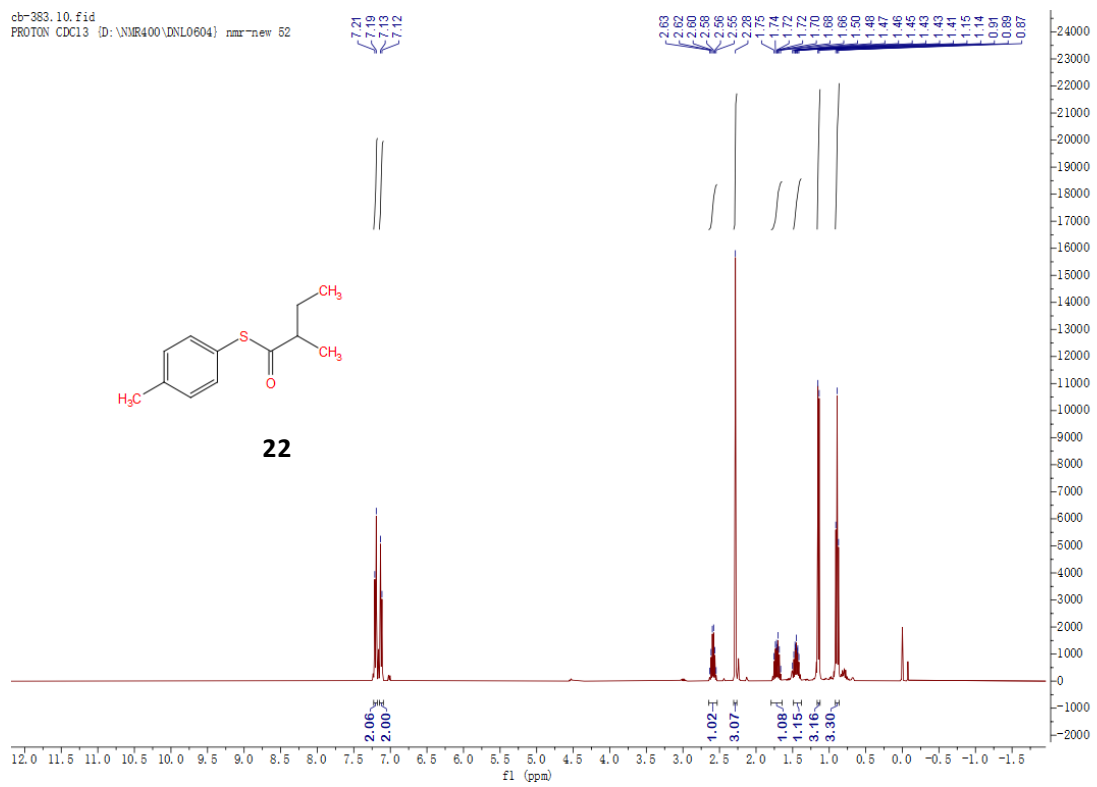
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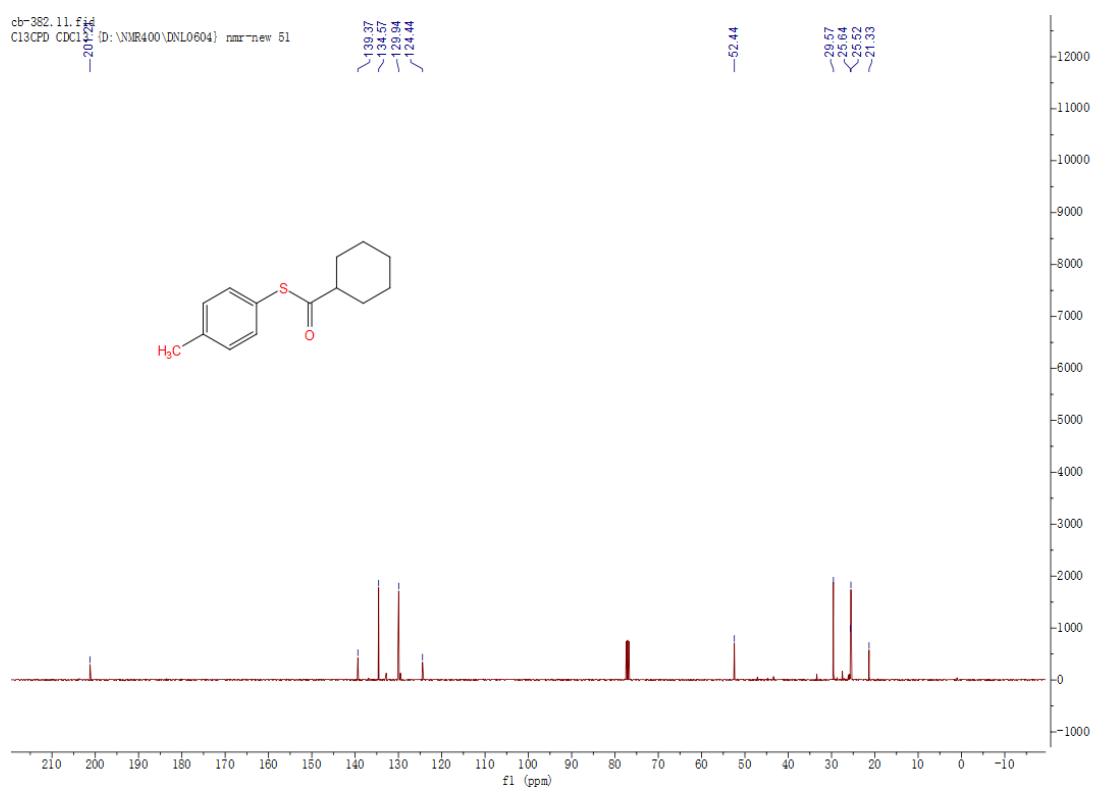
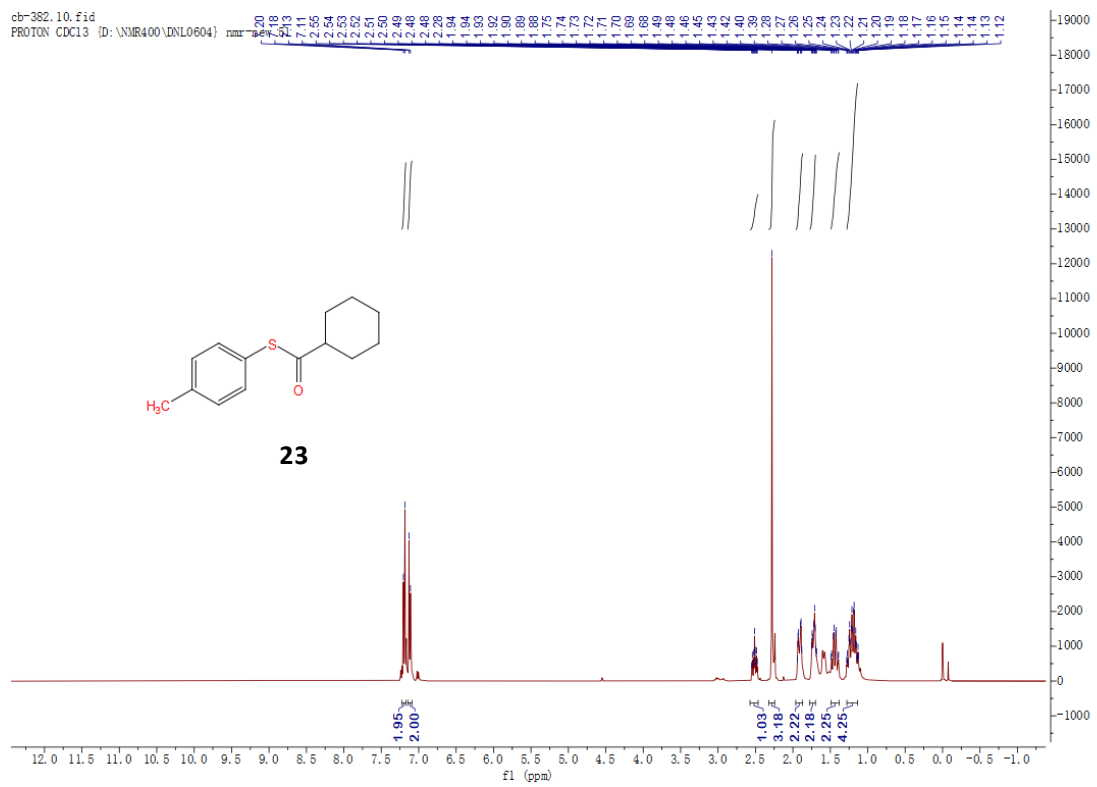


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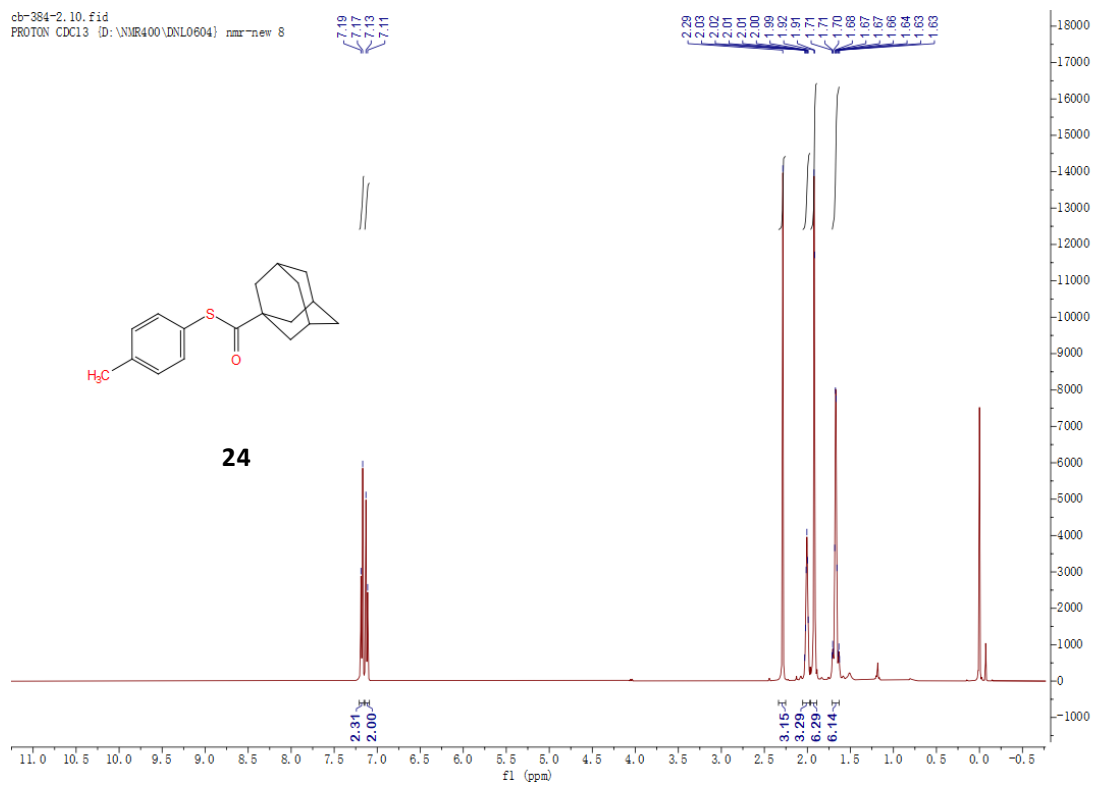


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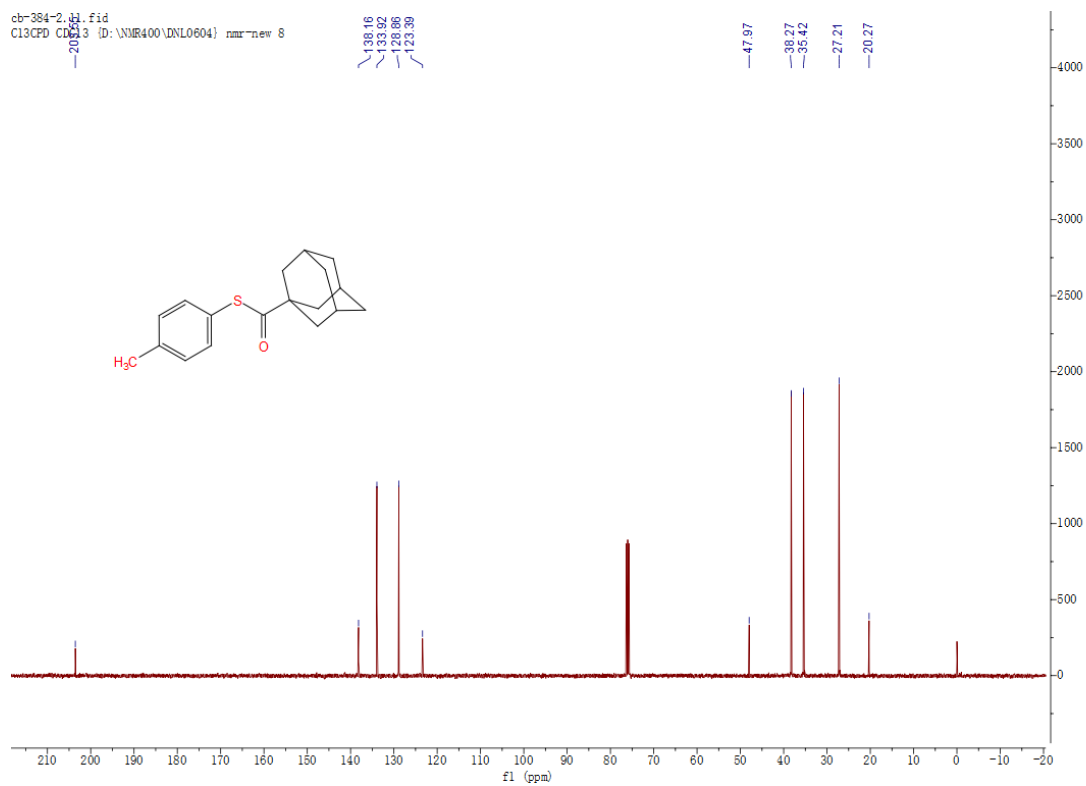




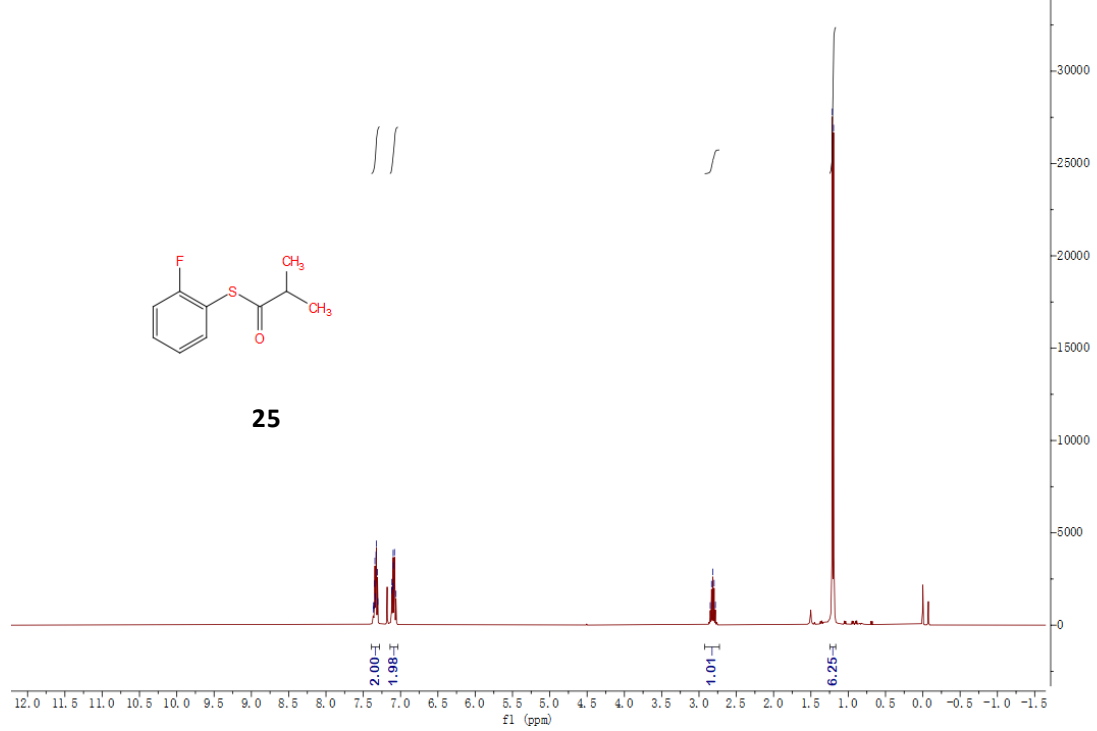
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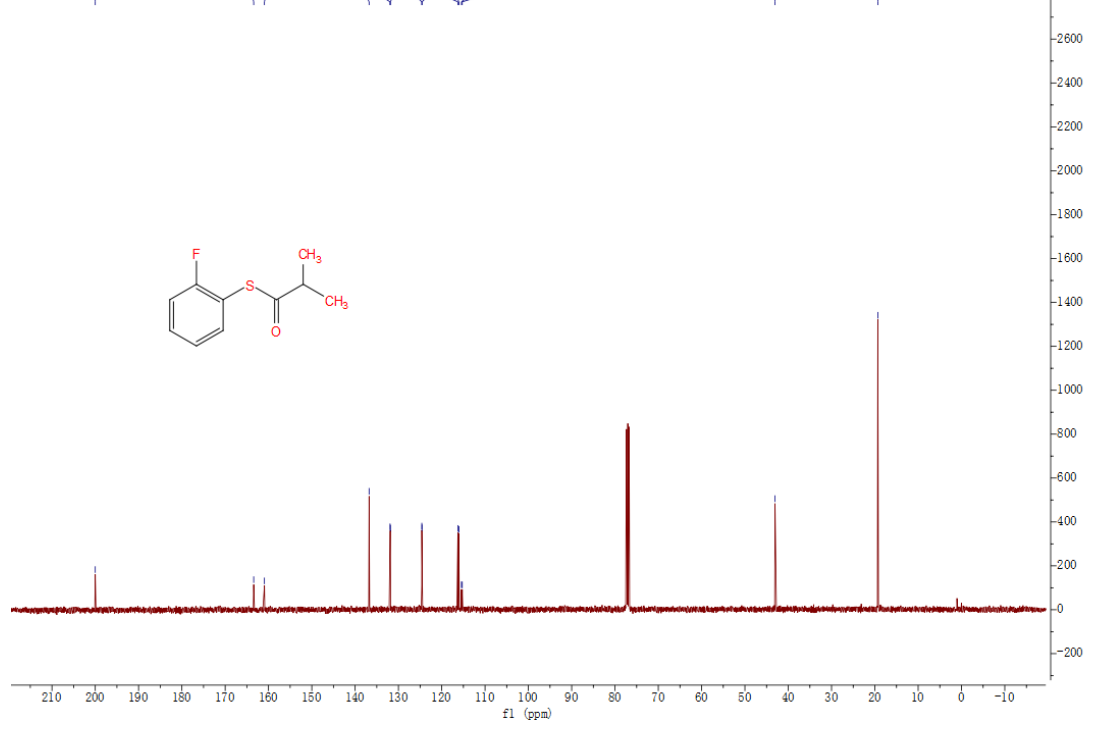
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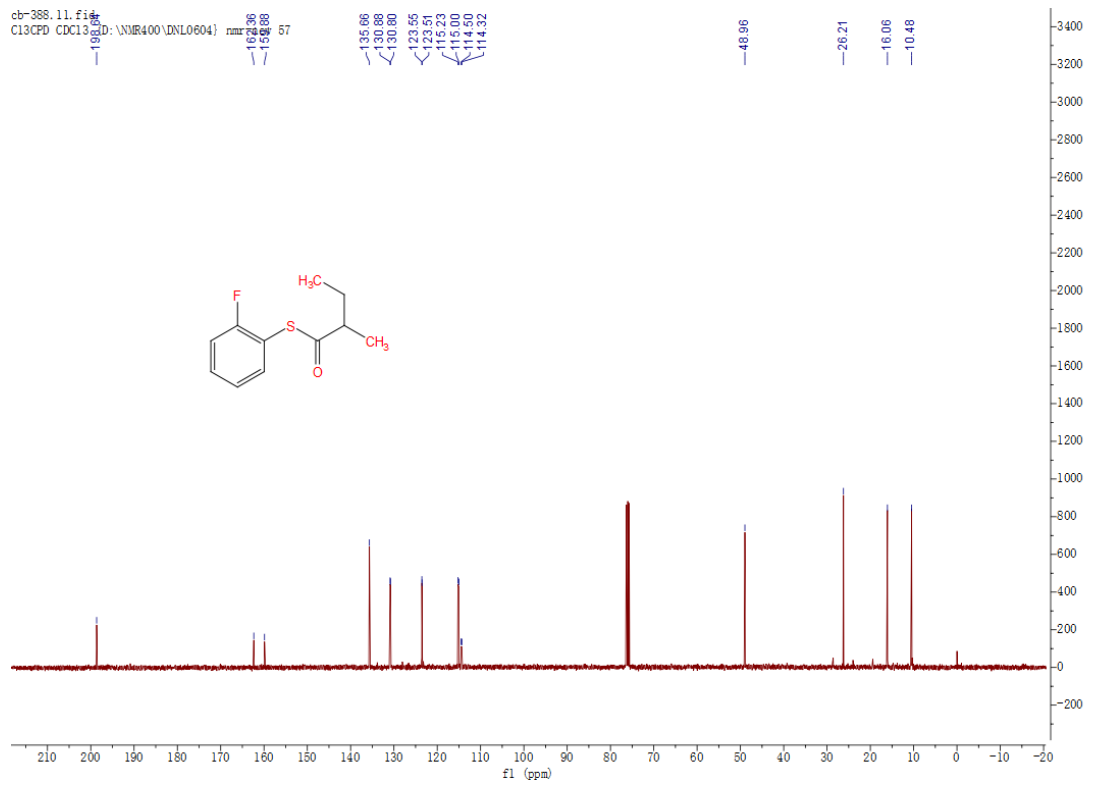
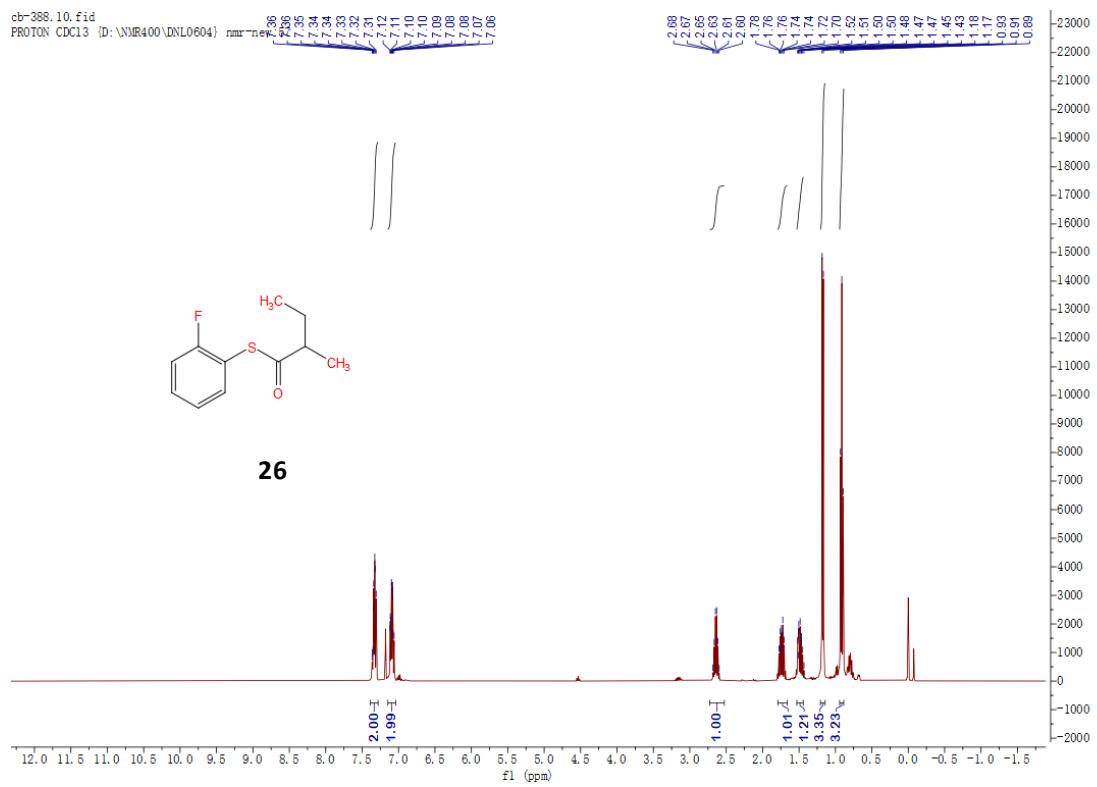


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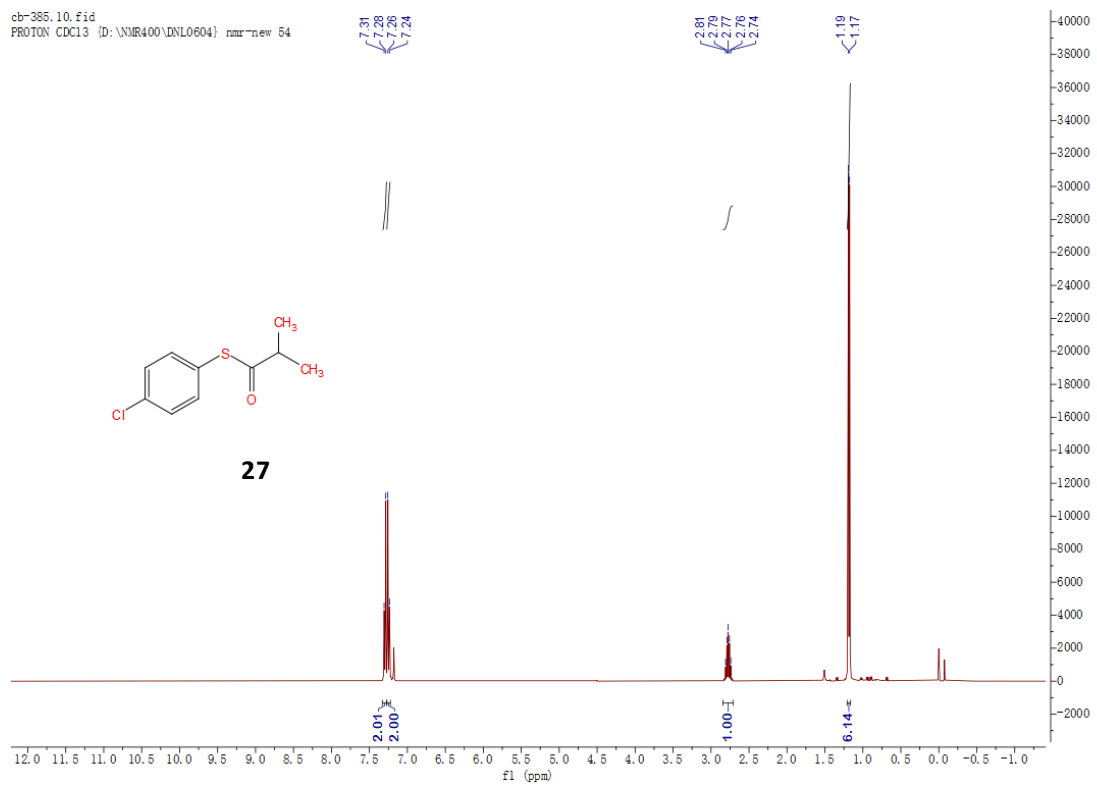


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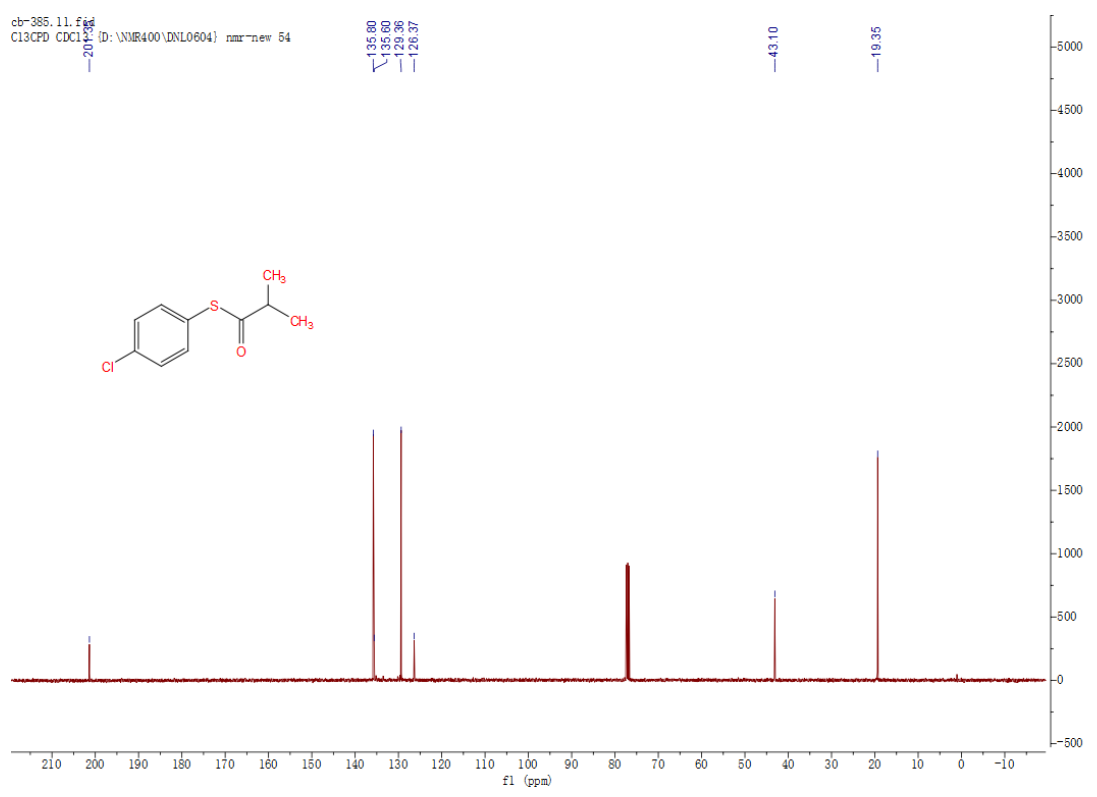




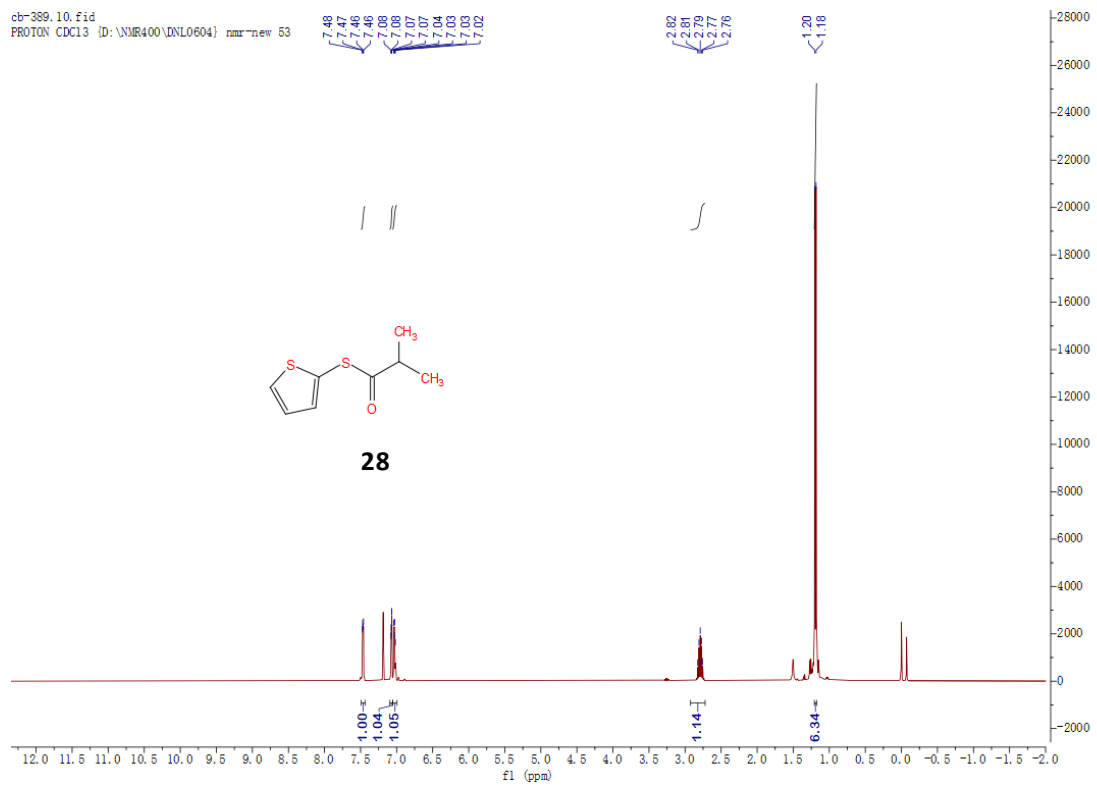
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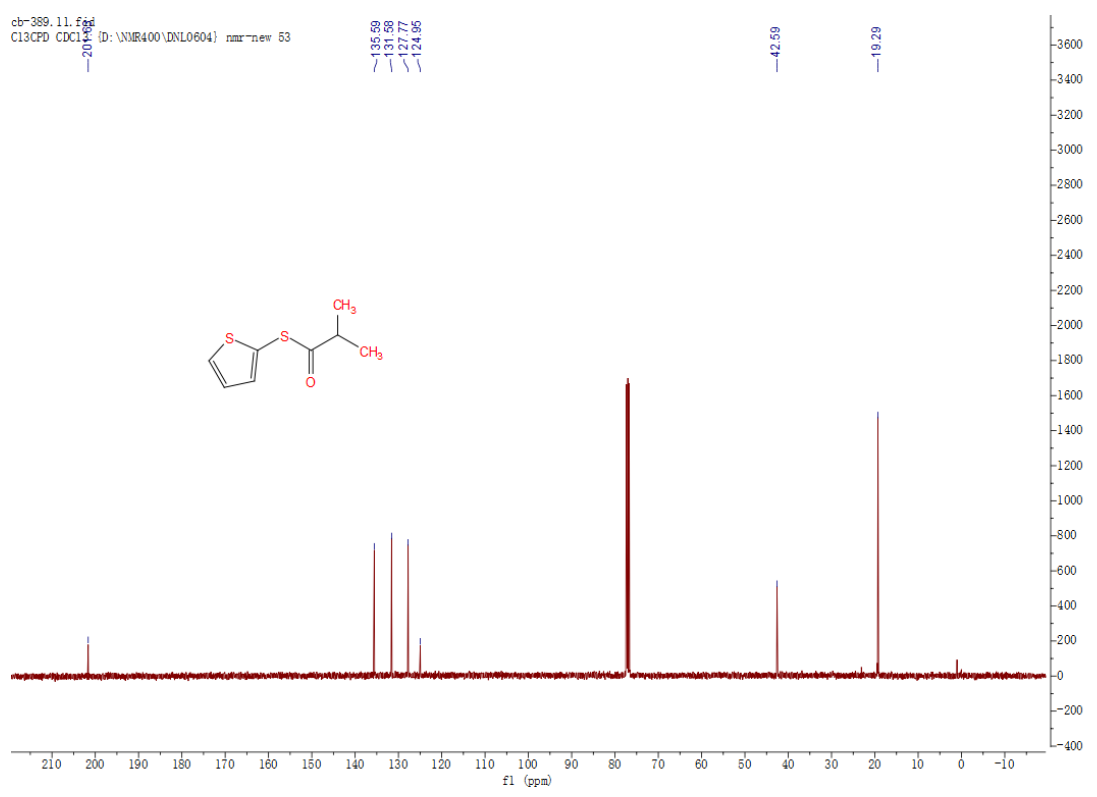
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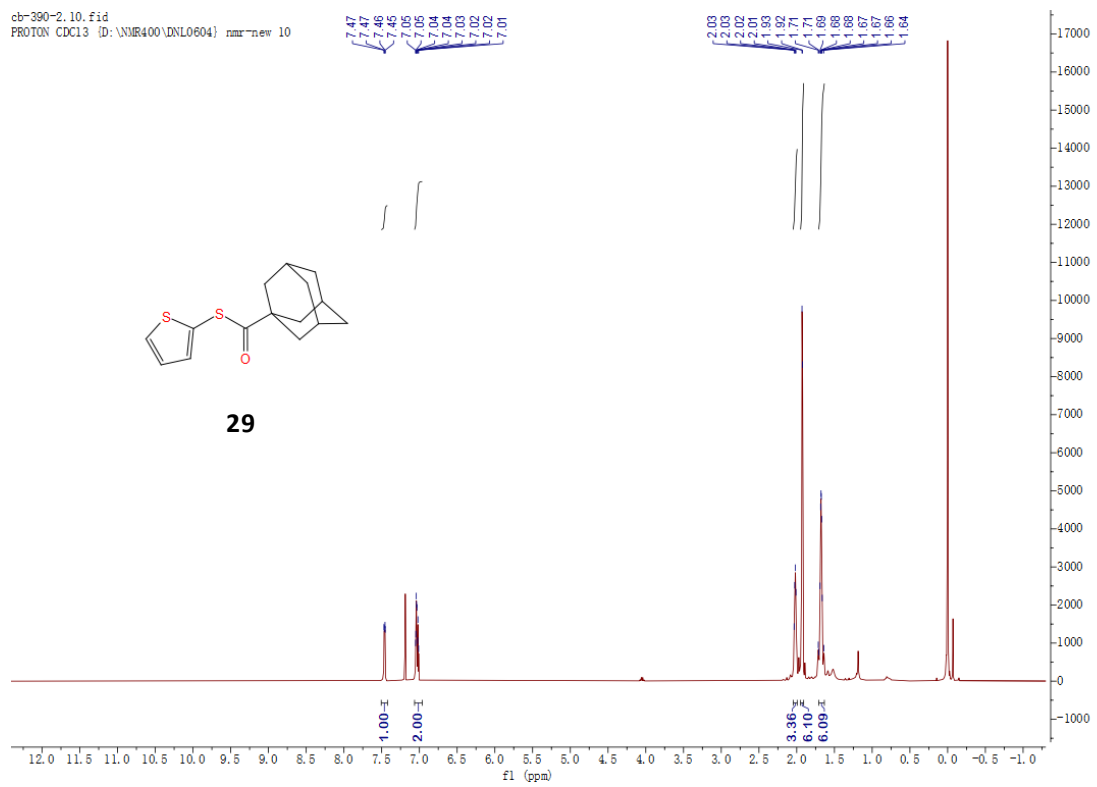
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C13CPD CDCl3 [D:\NMR400\DNL0604] nmr-new 53



cb-390-2.10.fid
PROTON CDCl3 (D:\NMR400\DNL0604) nmr-new 10



cb-390-2.10.fid
C13CPD CDCl3 (D:\NMR400\DNL0604) nmr-new 10

