Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

NHC-catalyzed Thioesterification of Aldehydes by External Redox Activation

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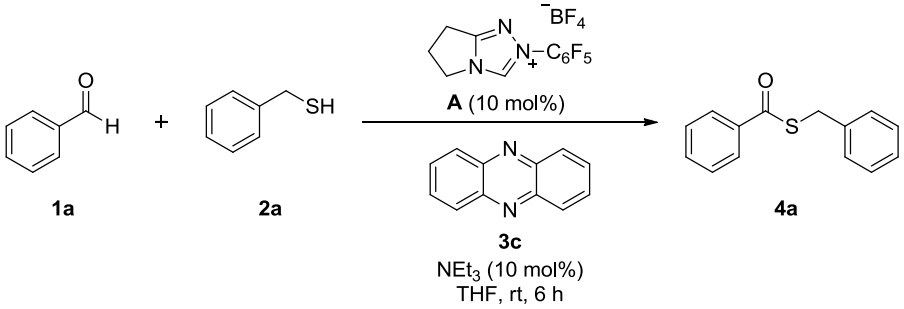
General. All reactions were carried out under a positive atmosphere of argon in dried glassware unless otherwise noted. Solvents were dried and distilled according to standard protocols. All melting points were measured on YAMAMOTO micro melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 500 MHz and at 125 MHz, respectively; Tetramethylsilane (TMS) was used as an internal standard. IR spectra were recorded on a JASCO FT/IR-410 or FT/IR-4100 Fourier-transform infrared spectrometer. Low and High resolution mass spectra were recorded on JEOL JMS-01SG-2 or JMS-HX/HX 110A mass spectrometer. Elemental analysis were performed on YANACO CHN CORDER MT-6 spectrometer. Column chromatography was performed on Merck silica gel 60 (230-400 mesh), Reactions and chromatography fraction were analyzed employing pre-coated silica gel plate (Merck Silica Gel F_{254}).

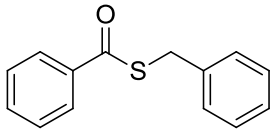
Material. Unless otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and were used without purification. Catalyst **A** was prepared according to the known procedure reported by Rovis, T. *et al*[1], and catalyst **B** was purchased from Tokyo Kasei Co. Oxidants **3a**[2] and **3b**[3] were prepared according to the known procedure respectively. Other oxidants were purchased from commercial suppliers.

Typical procedure for NHC-catalyzed thioesterification of aromatic aldehydes (Table 2, entry 1).



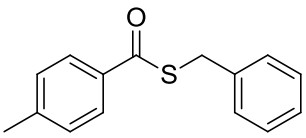
To a screw-capped test tube equipped with a magnetic stir bar and charged with phenazine **3c** (64.9 mg, 0.36 mmol, 1.2 equiv.) and NHC-precatalyst **A** (10.9 mg, 0.03 mmol, 10 mol%) was added THF (0.6 mL, 0.5 M). The aldehyde **1a** (0.3 mmol) and benzyl mercaptan **2a** (39 µL, 0.33 mmol, 1.1 equiv.) were added, followed by triethylamine (4.2 µL, 0.03 mmol, 10 mol%). After being stirred at ambient temperature for 6 hours under argon atmosphere, the reaction mixture was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexane : diethyl ether = 1 : 0 to 50 : 1) to give **4a** (64.2 mg, 94% yield).

Characterization data (Table 2)



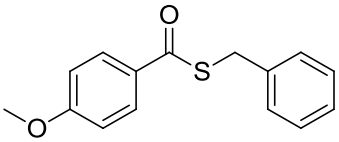
***S*-Benzyl benzothioate (4a)**[4]:

Colerless oil; IR (neat) 1660, 1598, 1580, 1493, 1449, 1204, 1174, 908 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.43 (dt, J_1 = 7.8 Hz, J_2 = 7.2 Hz, 2H), 7.37 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.24 (m, 1H), 4.32 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.8, 153.8, 148.5, 136.8, 134.6, 129.0, 128.7, 127.5, 123.5, 33.3; Anal. Calcd for $C_{14}H_{12}OS$: C, 73.65; H, 5.30; Found: C, 73.74; H, 5.23.



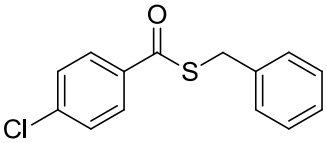
***S*-Benzyl 4-methylbenzothioate (4b)**:

Colorless crystals; mp 42-42.5 ºC; IR (neat) 1645, 1600, 1493, 1451, 1405, 1204, 1171, 904 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.26-7.22 (m, 3H), 4.30 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.9, 144.3, 137.6, 134.2, 129.3, 129.0, 128.6, 127.3, 127.2, 33.2, 21.7; Anal. Calcd for $C_{15}H_{14}OS$: C, 74.34; H, 5.82; Found: C, 74.21; H, 5.87.



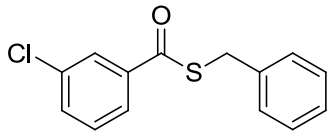
***S*-Benzyl 4-methoxybenzothioate (4c)**[5]:

Colorless crystals; mp 51-52 °C; IR (neat) 1646, 1597, 1502, 1453, 1306, 1254, 1212, 1166, 1025, 909 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.25-7.22 (m, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 4.30 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.7, 163.8, 137.7, 129.6, 129.4, 128.9, 128.6, 127.2, 113.7, 55.5, 33.2; Anal. Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46; Found: C, 69.53; H, 5.65.



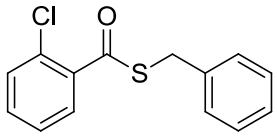
***S*-Benzyl 4-chlorobenzothioate (4d)**:

White solid; mp 53-54 °C (lit.[6]: 53-54.5 °C); IR (neat) 1660, 1584, 1486, 1452, 1398, 1201, 1087, 912 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.27-7.24 (m, 1H), 4.32 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.1, 139.8, 137.2, 135.1, 128.9, 128.9, 128.7, 128.6, 127.4, 33.4; Anal. Calcd for $C_{14}H_{11}ClOS$: C, 64.00; H, 4.22; Found: C, 64.05; H, 4.33.



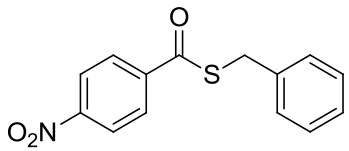
_S_-Benzyl 3-chlorobenzothioate (4e):

Pale yellow oil; IR (neat) 1660, 1571, 1495, 1470, 1454, 1419, 1198, 959, 935 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.39-7.36 (m, 3H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.27-7.24 (m, 1H), 4.32 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.1, 138.3, 137.0, 134.9, 133.3, 129.9, 129.0, 128.7, 127.5, 127.3, 125.4, 33.5; Anal. Calcd for $C_{14}H_{11}ClOS$: C, 64.00; H, 4.22; Found: C, 64.22; H, 4.22.



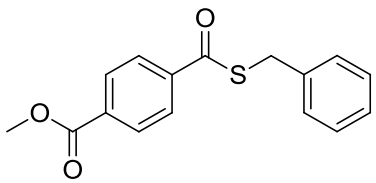
_S_-Benzyl 2-chlorobenzothioate (4f)[7]:

Pale yellow oil; IR (neat) 1675, 1586, 1495, 1462, 1432, 1262, 1202, 966, 913 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (m, 1H), 7.44-7.25 (m, 8H), 4.32 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.3, 137.1, 136.9, 132.3, 130.9, 130.9, 129.3, 128.9, 128.7, 127.4, 126.7, 34.3; Anal. Calcd for $C_{14}H_{11}ClOS$: C, 64.00; H, 4.22; Found: C, 64.22; H, 4.26.



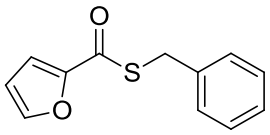
_S_-Benzyl 4-nitrobenzothioate (4g)[8]:

Colorless crystals; mp 81-82 °C; IR (neat) 1641, 1600, 1518, 1346, 1319, 1194, 922, 846 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.6 Hz, 2H), 8.10 (d, *J* = 8.6 Hz, 2H), 7.38-7.25 (m, 5H), 4.36 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.8, 150.5, 141.3, 136.6, 129.0, 128.8, 128.3, 127.6, 123.9, 33.8; Anal. Calcd for $C_{14}H_{11}NO_3S$: C, 61.52; H, 4.06; N, 5.12; Found: C, 61.27; H, 4.12; N, 5.07.



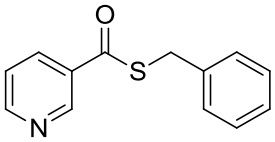
Methyl [4-(benzylthio)carbonyl]benzoate (4h):

Colorless needle; mp 87-88 °C; IR (neat) 1725, 1658, 1493, 1449, 1433, 1403, 1286, 1218, 1112, 917 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 2H), 8.01 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.27-7.24 (m, 1H), 4.34 (s, 2H), 3.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.7, 166.0, 140.0, 137.0, 134.2, 129.8, 129.0, 128.7, 127.4, 127.2, 52.4, 33.5 ; Anal. Calcd for $C_{16}H_{14}O_3S$: C, 67.11; H, 4.93; Found: C, 66.96; H, 4.87.



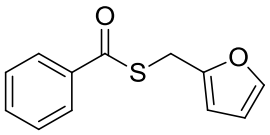
_S_-Benzyl furan-2-carbothioate (4i)[9]:

Pale yellow oil; IR (neat) 1649, 1566, 1466, 1385, 1253, 1221, 1154, 1016, 955, 848 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (m, 1H), 7.35 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.2 Hz, 2H), 7.26-7.23 (m, 1H), 7.19 (d, J = 3.4 Hz, 1H), 6.51 (m, 1H), 4.29 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.8, 150.6, 146.2, 137.3, 128.9, 128.6, 127.3, 115.7, 112.2, 32.3; Anal. Calcd for $C_{12}H_{10}O_2S$: C, 66.03; H, 4.62; Found: C, 65.78; H, 4.42.



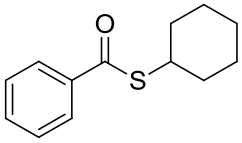
_S_-Benzyl pyridine-3-carbothioate (4j):

Yellow oil; IR (neat) 1662, 1582, 1453, 1416, 1217, 915 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.78 (m, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.41-7.37 (m, 3H), 7.32 (t, J = 7.5 Hz, 2H), 7.28-7.25 (m, 1H), 4.35 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.8, 153.8, 148.5, 136.8, 134.5, 132.3, 128.9, 128.7, 127.5, 123.5, 33.3; Anal. Calcd for $C_{13}H_{11}NOS$: C, 68.09; H, 4.84; N, 6.11; Found: C, 68.18; H, 5.11; N, 5.82.



_S_-(Furan-2-ylmethyl) benzothioate (4k)[10]:

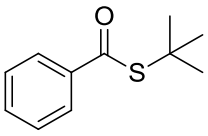
Pale yellow oil; IR (neat) 1664, 1597, 1502, 1447, 1214, 1176, 1152, 1011, 933, 911, 786, 763 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.44 (dt, J_1 = 8.0 Hz, J_2 = 7.5 Hz, 2H), 7.35 (m, 1H), 6.30 (m, 2H), 4.35 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.7, 150.4, 142.3, 136.6, 133.5, 128.6, 127.3, 110.6, 108.1, 25.7; Anal. Calcd for $C_{12}H_{10}O_2S$: C, 66.03; H, 4.62; Found: C, 66.11; H, 4.54.



_S_-Cyclohexyl benzothioate (4l)[11]:

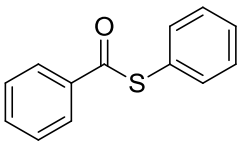
Colorless oil; IR (neat) 2928, 2853, 1659, 1580, 1447, 1203, 1174, 911 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.43 (dt, J_1 = 8.0 Hz, J_2 = 7.5 Hz, 2H), 3.73 (m, 1H), 2.04-2.02 (m, 2H), 1.77-1.75 (m, 2H), 1.64-1.62 (m, 1H), 1.58-1.43 (m, 4H), 1.36-1.32 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.8, 137.4, 133.1, 128.5, 127.1, 42.5, 33.1,

26.0, 25.6; Anal. Calcd for $C_{13}H_{16}OS$: C, 70.87; H, 7.32; Found: C, 70.95; H, 7.57.



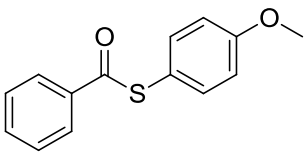
_S_-_tert_-Butyl benzothioate (4m)[12]:

Colorless oil; IR (neat) 2962, 2921, 1656, 1580, 1477, 1450, 13643, 1202, 1160, 905 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 7.8 Hz, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.41 (dt, J_1 = 7.8 Hz, J_2 = 7.5 Hz, 2H), 1.58 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) 192.8, 138.3, 132.9, 128.4, 126.9, 48.1, 30.0; Anal. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26; Found: C, 67.85; H, 7.32.



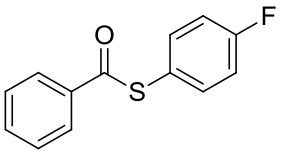
_S_-Phenyl benzothioate (4n)[4]:

White solid; mp 53.5-54 °C ; IR (neat) 3060, 2924, 1664, 1579, 1477, 1442, 1391, 1307, 1198, 1176, 890 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 7.5 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.53-7.45 (m, 7H); ^{13}C NMR (126 MHz, $CDCl_3$) 190.2, 136.6, 135.1, 133.7, 129.5, 129.2, 128.7, 127.5, 127.3; Anal. Calcd for $C_{13}H_{10}OS$: C, 72.87; H, 4.70; Found: C, 72.54; H, 4.69.



_S_-(4-Methoxyphenyl) benzothioate (4o)[10]:

White crystals; mp 94-94.5 °C ; IR (neat) 3088, 3053, 3026, 2964, 2933, 2842, 1665, 1588, 1491, 1445, 1287, 1246, 1205, 1170, 1021, 899, 819 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$) δ 8.02 (d, J = 7.5 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.49-7.46 (m, 2H), 7.42 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 8.6 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) 191.0, 160.8, 136.7, 136.6, 133.5, 128.7, 127.4, 117.9, 114.9, 55.3; Anal. Calcd for $C_{14}H_{12}O_2S$: C, 68.63; H, 4.95; Found: C, 68.56; H, 5.20.

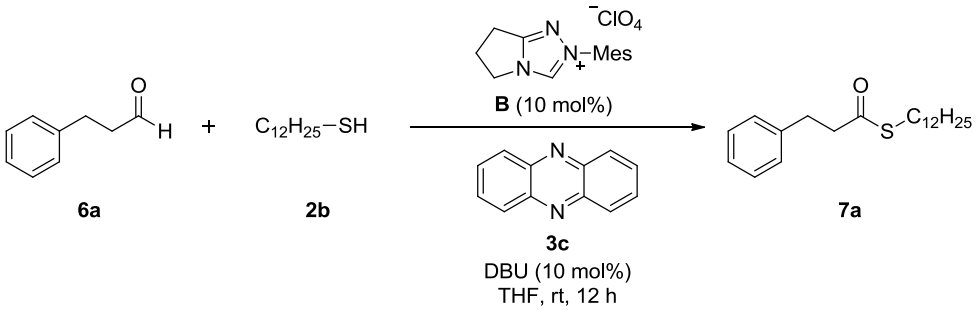


_S_-(4-Fluorophenyl) benzothioate (4p)[10]:

White crystals; mp 48-49 °C ; IR (neat) 3071, 1673, 1585, 1485, 1446, 1396, 1223, 1203, 1174, 1155, 897, 823, 775, 683, 640 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$) δ 8.01 (d, J = 7.7 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.51-7.48 (m, 4H), 7.16 (t, J = 8.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) 190.1,

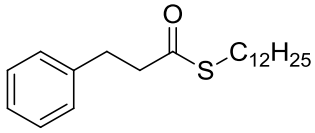
163.6 ($J_{C\text{-}F}$ = 250 Hz), 137.1 ($J_{C\text{-}F}$ = 9.6 Hz), 136.4, 133.8, 128.8, 127.5, 122.6, 116.5 ($J_{C\text{-}F}$ = 22.8 Hz); Anal. Calcd for $C_{13}H_9FOS$: C, 67.22; H, 3.91; Found: C, 66.96; H, 3.74.

Typical Procedure for thioesterification of aliphatic aldehydes (Table 4, entry 1).



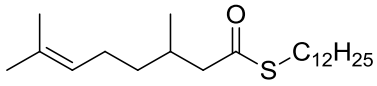
To a screw-capped test tube equipped with a magnetic stir bar and charged with phenazine **3c** (81.1 mg, 0.45 mmol, 1.5 equiv.) and NHC-precatalyst **B** (9.8 mg, 0.03 mmol, 10 mol%) was added THF (0.6 mL, 0.5 M). The aldehyde **6a** (0.3 mmol) and dodecane thiol **2b** (79 µL, 0.45 mmol, 1.5 equiv.) were added, followed by DBU (4.5 µL, 0.03 mmol, 10 mol%). After being stirred at ambient temperature for 12 hours under argon atmosphere, the reaction mixture was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexane : diethyl ether = 1 : 0 to 50 : 1) to give **7a** (78.7 mg, 86% yield).

Characterization data (Table 4)



***S*-Dodecyl 3-phenylpropanethioate (7a)**:

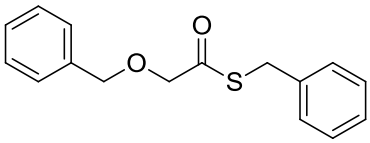
Colorless oil; IR (neat) 2924, 2853, 1690, 1496, 1457, 1046, 972 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 7.22-7.18 (m, 3H), 2.98 (t, J = 7.2 Hz, 2H), 2.88-2.84 (m, 4H), 1.56-1.52 (m, 3H), 1.26 (m, 17H), 0.88 (t, J = 12.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.7, 140.1, 128.5, 128.3, 126.3, 45.5, 31.9, 31.5, 29.6, 29.6, 29.5, 29.5, 29.3, 29.1, 28.9, 28.8, 22.7, 14.1; Anal. Calcd for $C_{21}H_{34}OS$: C, 75.39; H, 10.24; Found: C, 75.19; H, 10.40.



***S*-Dodecyl 3,7-dimethyloct-6-enethioate (7b)**:

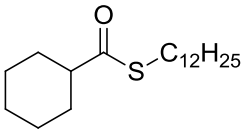
Colerless oil; IR (neat) 2958, 2923, 2853, 1691, 1460, 1379, 1220, 1116, 1012 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.08 (t, J = 6.6 Hz, 1H), 2.87 (t, J = 7.4 Hz, 2H), 2.56-2.52 (m, 2H), 2.37-2.33 (m, 2H), 2.06-1.92 (m, 3H), 1.68 (s, 3H), 1.60-1.52 (m, 5H), 1.25 (m, 20H), 0.94 (d, J = 6.6 Hz, 2H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.3, 131.6, 124.2, 51.3, 36.7, 31.9, 30.8, 29.6, 29.6, 29.6, 29.5, 29.3, 29.1, 28.9, 28.8, 25.7, 25.4, 22.7, 19.4, 17.7, 14.1; Anal. Calcd for

$C_{22}H_{42}OS$: C, 74.51; H, 11.94; Found: C, 74.26; H, 12.12.



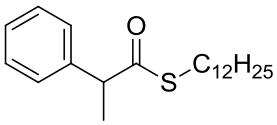
_S_-Benzyl 2-(benzyloxy)ethanethioate (7c):

Colorless oil; IR (neat) 3062, 3030, 2925, 1684, 1453, 1129, 1089, 1008 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36-7.22 (m, 10H), 4.64 (s, 2H), 4.18 (s, 2H), 4.15 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.3, 137.3, 136.8, 128.9, 128.6, 128.5, 128.1, 127.9, 127.3, 74.8, 74.0, 32.2; Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92; Found: C, 70.65; H, 5.85.



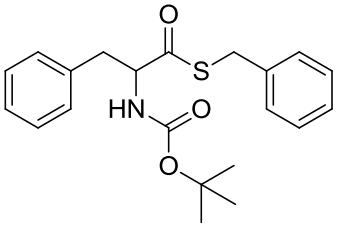
_S_-Dodecyl cyclohexanecarbothioate (7d):

Colerless oil; IR (neat) 2925, 2853, 2688, 1451, 1220, 969 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.84 (t, J = 7.2 Hz, 2H), 2.49-2.43 (m ,1H), 1.92-1.90 (m, 2H), 1.80-1.77 (m, 2H), 1.67-1.62 (m, 1H), 1.58-1.52 (m, 2H), 1.50-1.42 (m, 2H), 1.25 (m, 21H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.3, 52.7, 31.9, 29.6, 29.6, 29.5, 29.3, 29.1, 28.8, 28.4, 25.6, 25.5, 22.7, 14.1; Anal. Calcd for $C_{19}H_{36}OS$: C, 73.01; H, 11.61; Found: C, 73.17; H, 11.87.



_S_-Dodecyl 2-phenylpropanethioate (7e):

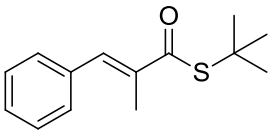
Colerless oil; IR (neat) 2924, 2853, 1687, 1454, 1374, 1219, 995, 945 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34-7.25 (m, 5H), 3.90-3.85 (m, 1H), 2.87-2.77 (m, 2H), 1.53-1.50 (m, 5H), 1.23 (m, 18H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.3, 140.0, 128.6, 127.9, 127.3, 54.2, 31.9, 29.6, 29.5, 29.4, 29.4, 29.3, 29.1, 28.8, 22.7, 18.4, 14.1; Anal. Calcd for $C_{21}H_{34}OS$: C, 75.39; H, 10.24; Found: C, 75.63; H, 10.35.



_S_-Benzyl 2-[(*tert*-butoxycarbonyl)amino]-3-phenylpropanethioate (7f)[9]:

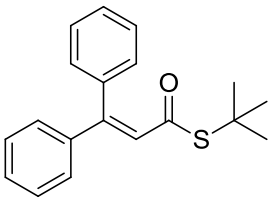
White crystals; mp 102 °C ; IR (neat) 3357, 3060, 3030, 3006, 2979, 2933, 2907, 1684, 1516, 1448, 1314, 1250, 1220, 1168, 1070, 996 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31-7.23 (m, 8H), 7.07 (m,

2H), 4.88 (d, *J* = 8.0 Hz, 1H), 4.65 (m, 1H), 4.14-4.06 (m, 2H), 3.13-3.03 (m, 2H), 1.39 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.4, 154.9, 137.1, 135.5, 129.4, 128.9, 128.6, 128.5, 127.3, 127.0, 80.3, 60.8, 38.3, 33.3, 28.2; Anal. Calcd for $C_{21}H_{25}NO_3S$: C, 67.89; H, 6.78; N, 3.77; Found: C, 67.64; H, 6.70; N, 3.77.



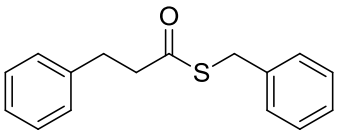
(*E*)-*S*-*tert*-Butyl 2-methyl-3-phenylprop-2-enethioate (7g):

Colorless oil; IR (neat) 2961, 2921, 2864, 1648, 1450, 1362, 1219, 1158, 1016, 988, 953, 903 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.39-7.31 (m, 5H), 2.11 (s, 3H), 1.54 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.4, 137.3, 136.1, 135.7, 129.7, 128.4, 128.3, 47.7, 29.9, 14.0; Anal. Calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74; Found: C, 71.98; H, 8.00.



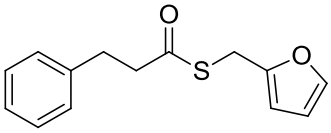
***S*-*tert*-Butyl 3,3-diphenylprop-2-enethioate (7h)**:

Pale yellow crystals; mp 111.5-112 °C ; IR (neat) 2955, 2920, 2860, 1669, 1586, 1571, 1490, 1446, 1363, 1219, 1155, 1030, 1009, 992, 955 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.22 (m, 10H), 6.48 (s, 1H), 1.43 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.2, 151.8, 141.0, 138.7, 129.6, 129.3, 128.5, 128.3, 128.3, 127.9, 124.9, 48.3, 29.7; HRMS (FAB$^-$): Calcd for $C_{19}H_{20}OS$ (M^+) 296.1235, Found: 296.1236.



***S*-Benzyl 3-phenylpropanethioate (7i)[5]**:

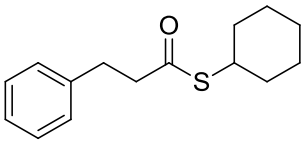
Colerless oil; IR (neat) 3062, 3029, 2925, 1687, 1603, 1495, 1452, 1411, 1219, 1045, 974 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.15 (m, 10H), 4.11 (s, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.86 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.8, 139.9, 137.5, 128.8, 128.6, 128.5, 128.3, 127.2, 126.3, 45.2, 33.1, 31.4; Anal. Calcd for $C_{16}H_{16}OS$: C, 74.96; H, 6.29; Found: C, 74.72; H, 6.33.



***S*-(Furan-2-ylmethyl) 3-phenylpropanethioate (7j)[7]**:

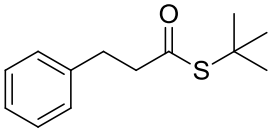
Yellow oil; IR (neat) 3120, 3061, 2931, 1662, 1582, 1501, 1448, 1398, 1206, 1175, 1151, 1009, 909

cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32-7.16 (m, 6H), 6.29 (m, 1H), 6.20 (m, 1H), 4.15 (s, 2H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.88 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.3, 150.4, 142.2, 139.9, 128.5, 128.3, 126.4, 110.6, 107.9, 45.3, 31.3, 25.6; Anal. Calcd for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73; Found: C, 68.05; H, 5.76.



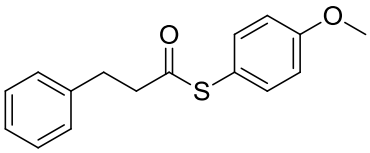
_S_-Cyclohexyl 3-phenylpropanethioate (7k)[13]:

Colerless oil; IR (neat) 2928, 2853, 1684, 1449, 1344, 1263, 1219, 1045, 970, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.21-7.17 (m, 3H), 3.55-3.50 (m, 1H), 2.96 (t, *J* = 7.4 Hz, 2H), 2.81 (t, *J* = 7.4 Hz, 2H), 1.90-1.88 (m, 2H), 1.70-1.67 (m, 2H), 1.59-1.56 (m, 1H), 1.46-1.35 (m, 4H), 1.27-1.25 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.5, 140.2, 128.5, 128.3, 126.2, 45.6, 42.2, 33.0, 31.5, 25.9, 25.5; Anal. Calcd for $C_{15}H_{20}OS$: C, 72.53; H, 8.12; Found: C, 72.24; H, 8.41.



S-tert-Butyl 3-phenylpropanethioate (7l):

Colerless oil; IR (neat) 2963, 2925, 2865, 1681, 1454, 1364, 1219, 1160, 1043, 964, 909 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.21-7.17 (m, 3H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.75 (t, *J* = 7.4 Hz, 2H), 1.45 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.5, 140.3, 128.5, 128.3, 126.2, 48.0, 46.0, 31.4, 29.8; Anal. Calcd for $C_{13}H_{18}OS$: C, 70.22; H, 8.16; Found: C, 70.38; H, 8.10.



_S_-(4-Methoxyphenyl) 3-phenylpropanethioate (7m)[14]:

White crystals; mp 58-58.5 °C; IR (neat) 3026, 2952, 2903, 2835, 1704, 1589, 1491, 1457, 1288, 1242, 1171, 1028, 970, 832, 814, 772, 735, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31-7.28 (m, 4H), 7.23-7.20 (m, 3H), 6.93 (d, *J* = 5.8 Hz, 2H), 3.82 (s, 3H), 3.01 (t, *J* = 7.4 Hz, 2H), 2.94 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.7, 160.6, 140.0, 136.1, 128.5, 128.4, 126.3, 118.3, 114.8, 55.3, 44.8, 31.4; Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92; Found: C, 70.51; H, 5.85.

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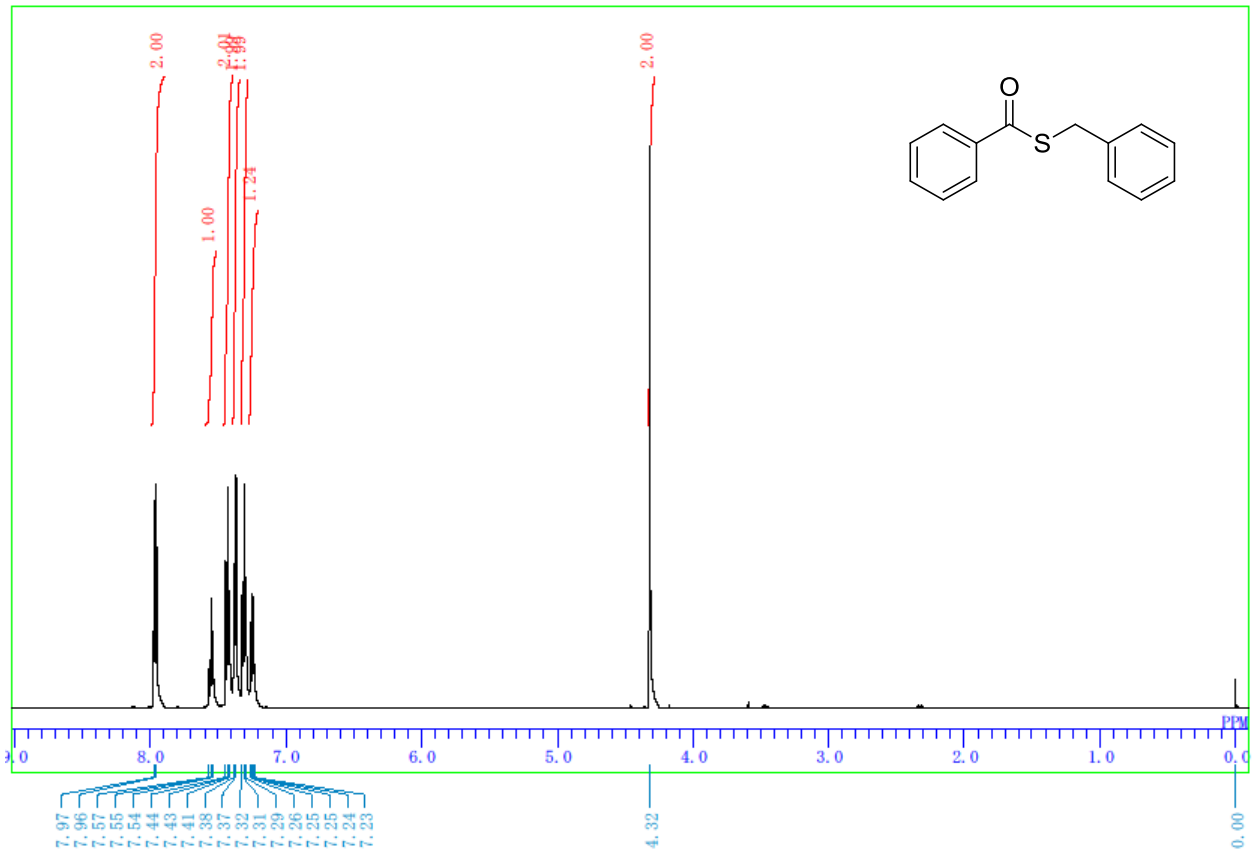
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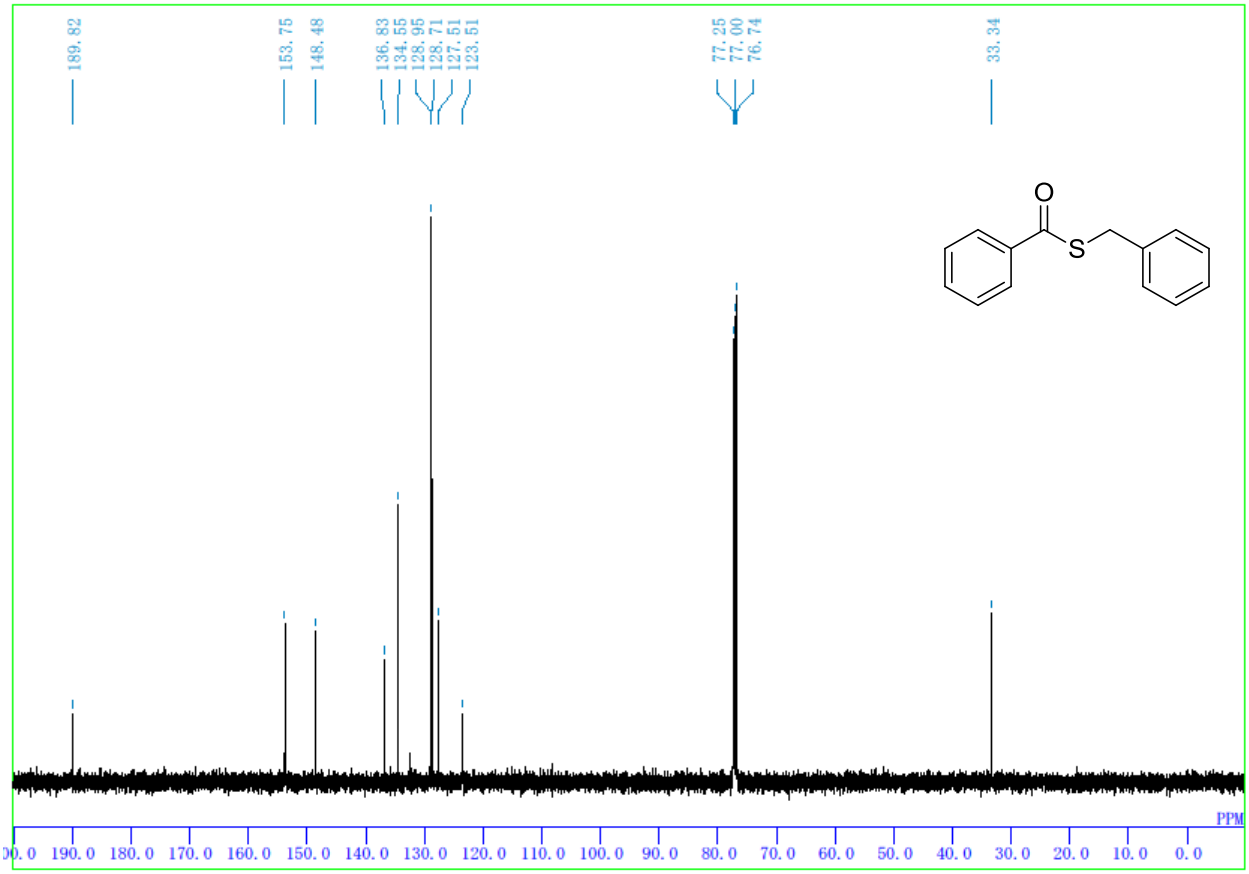
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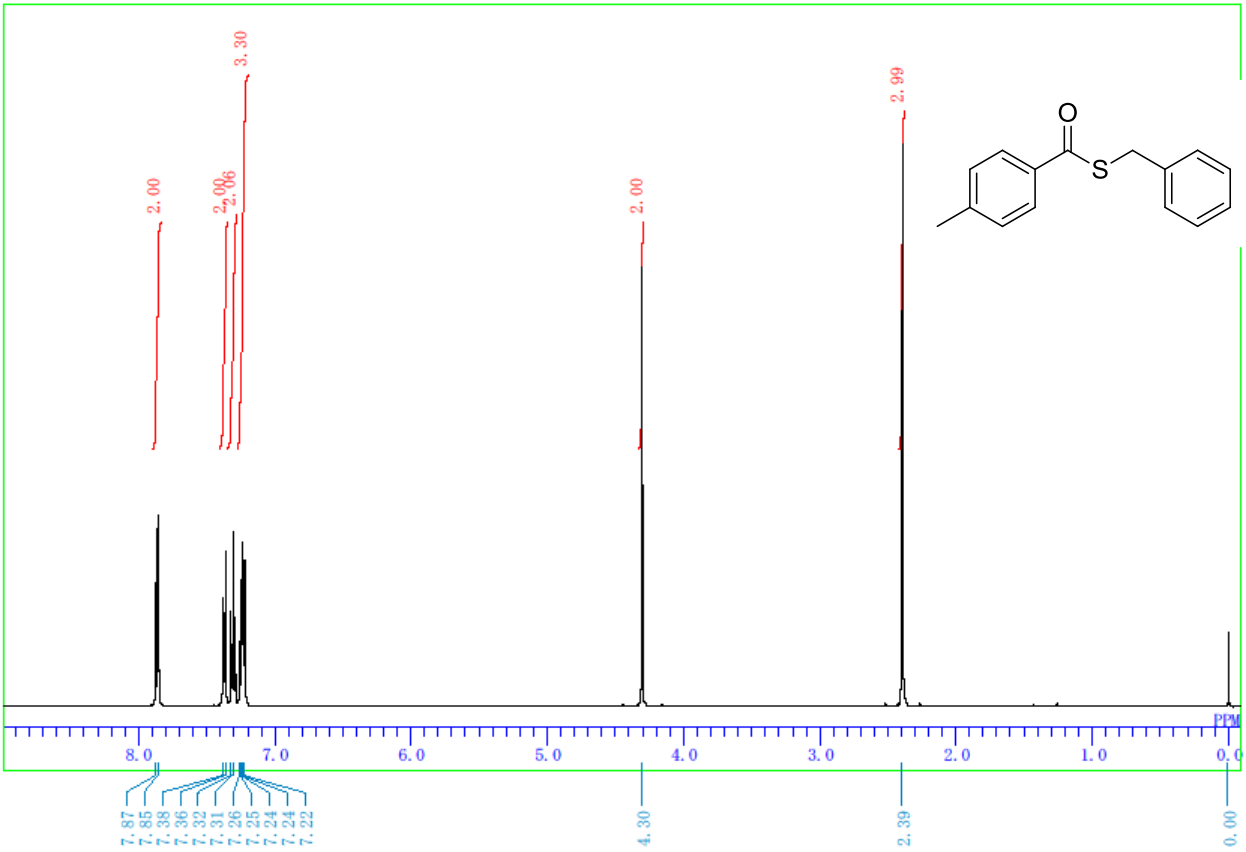
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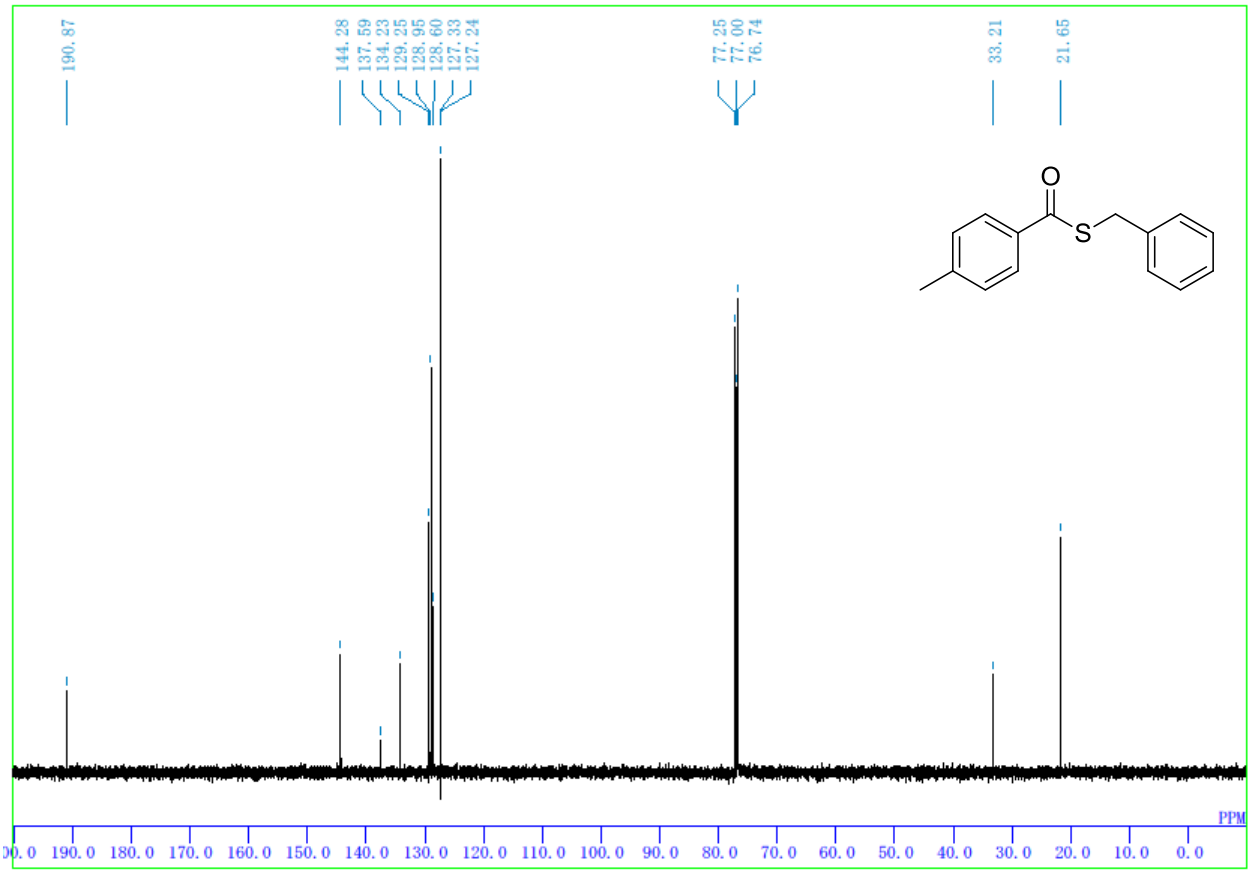
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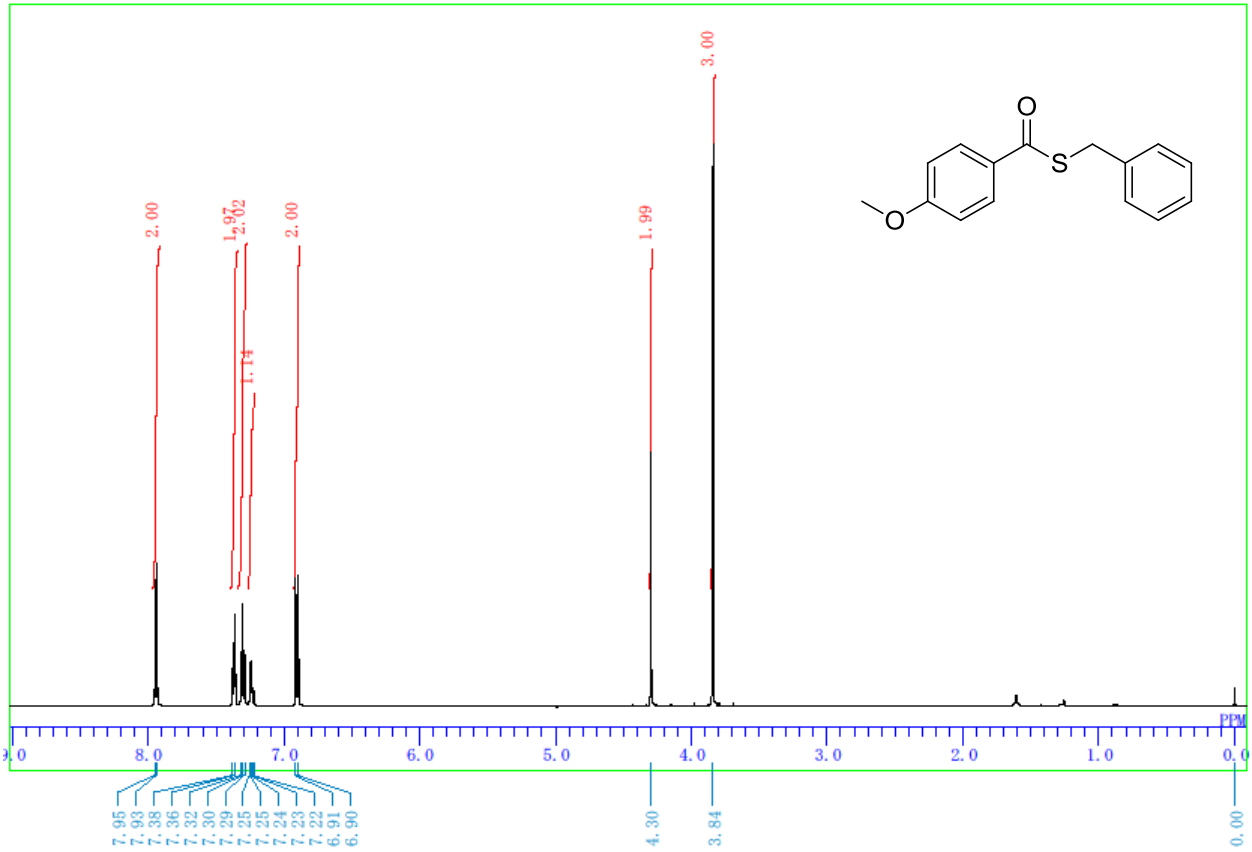
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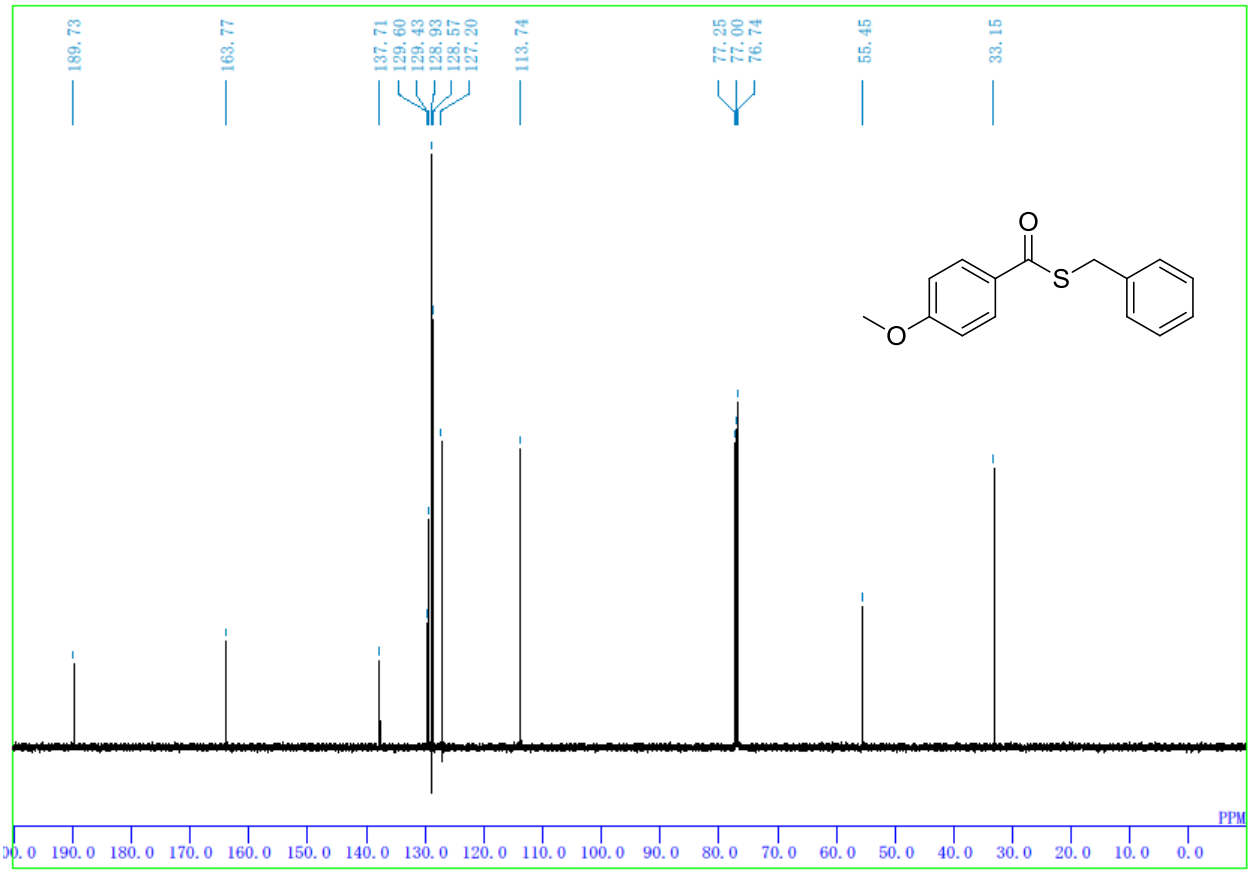
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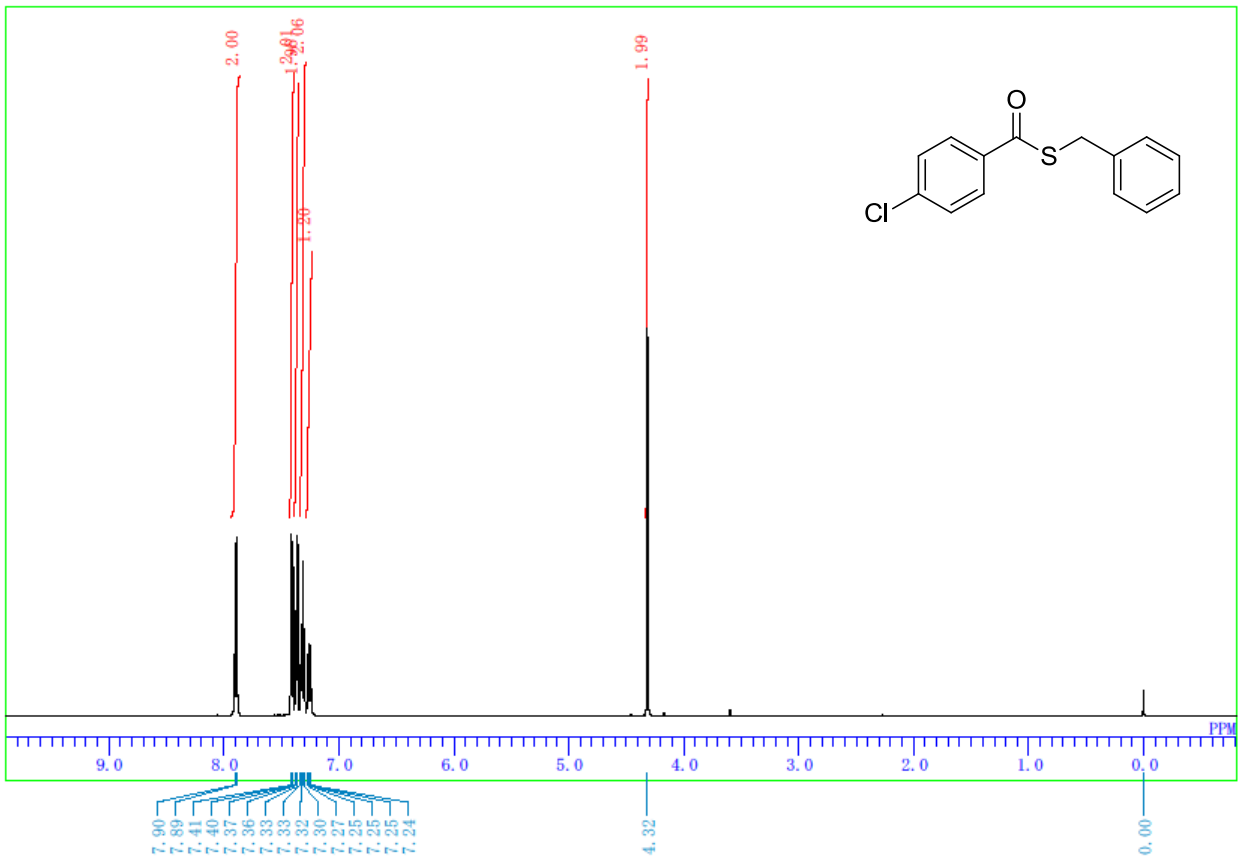
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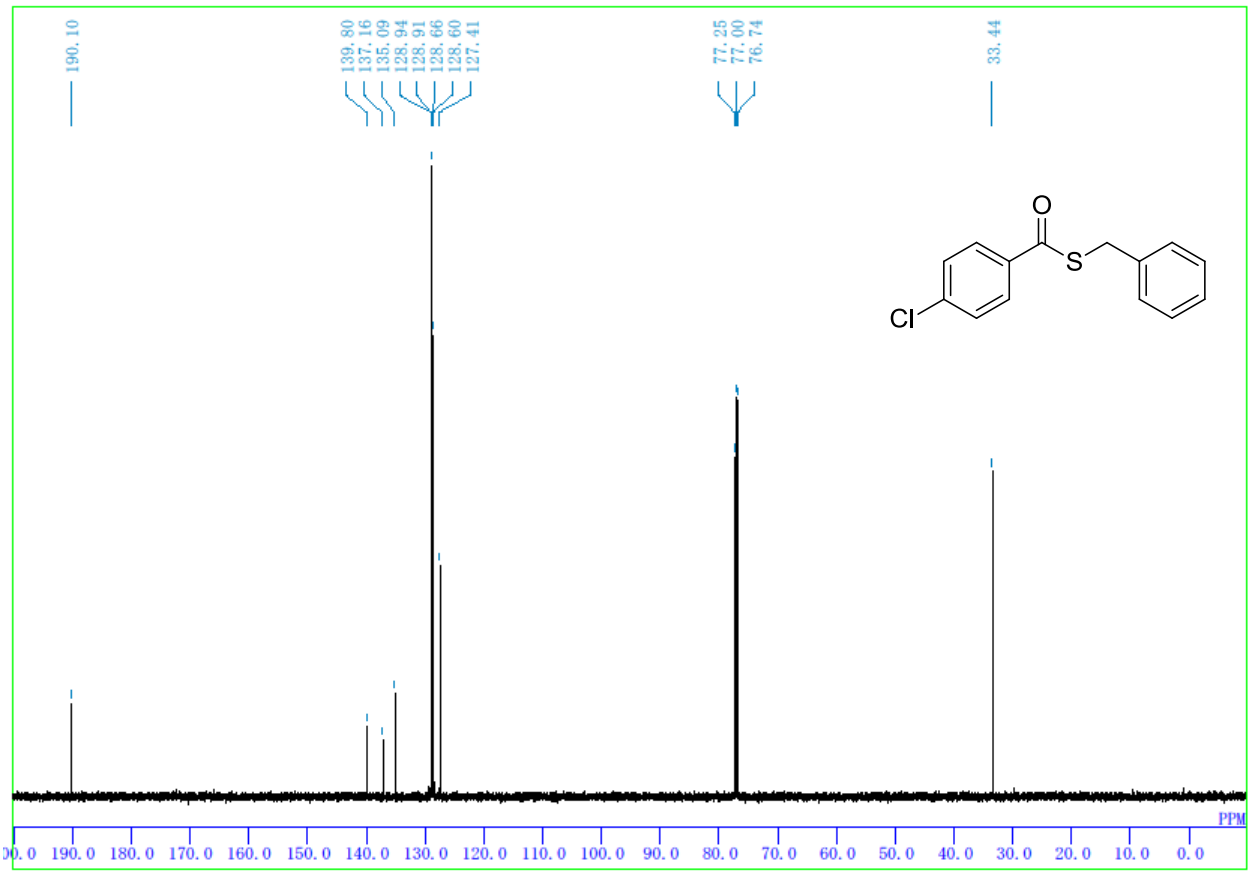
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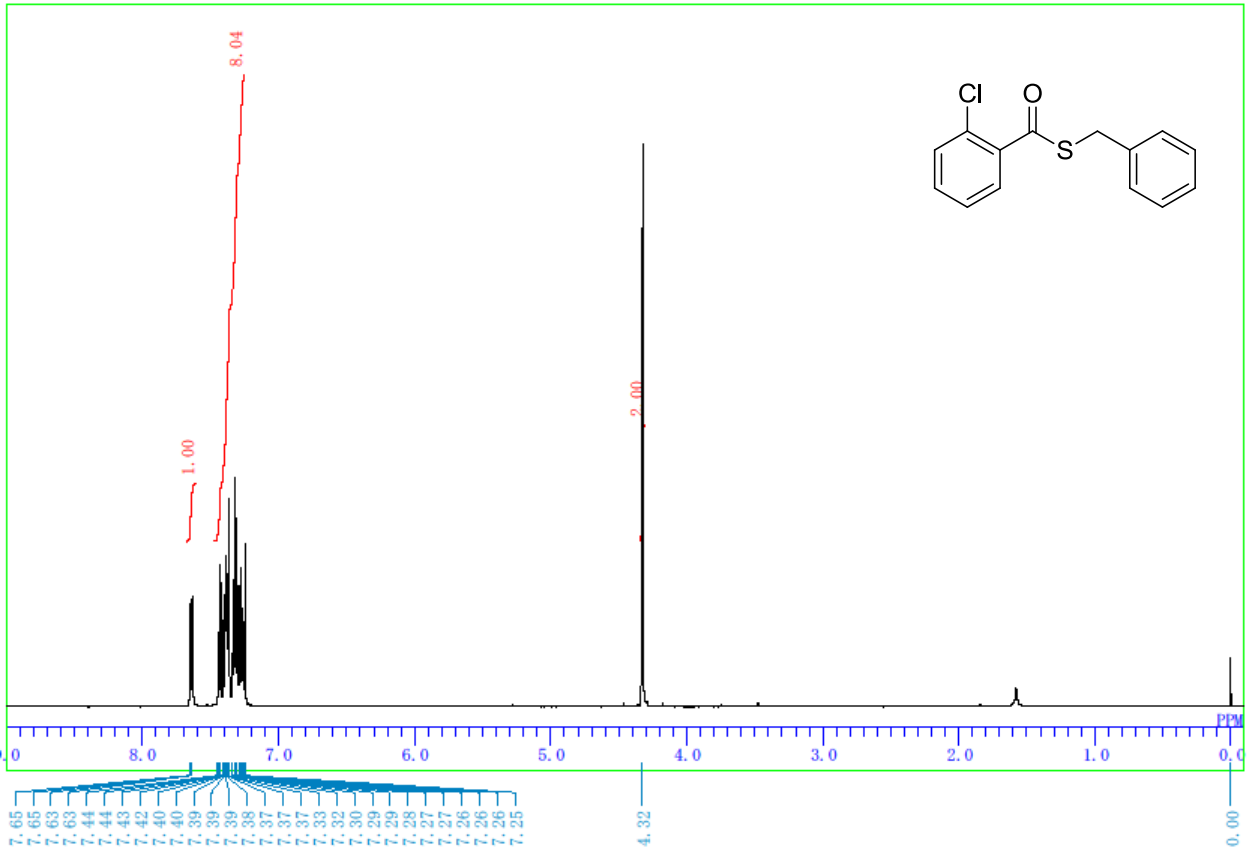
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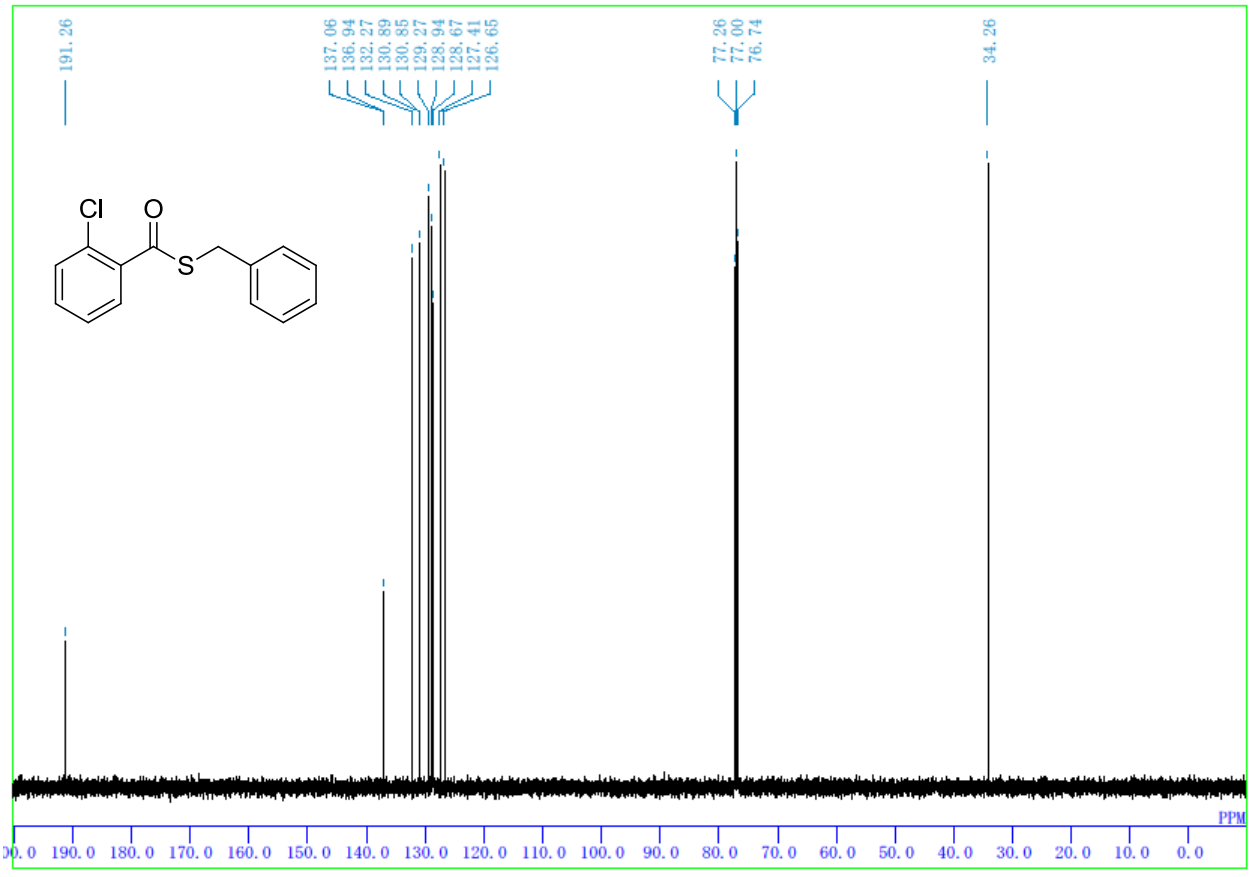
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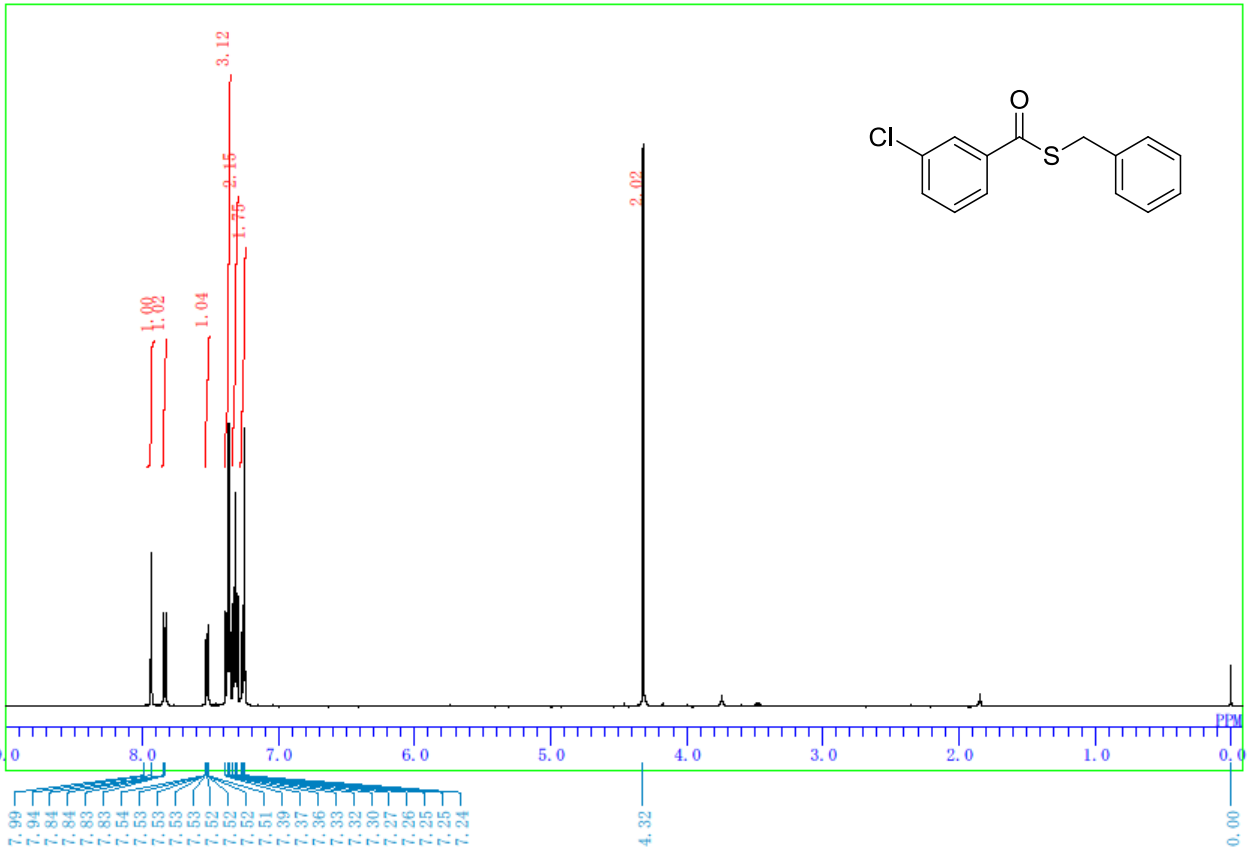
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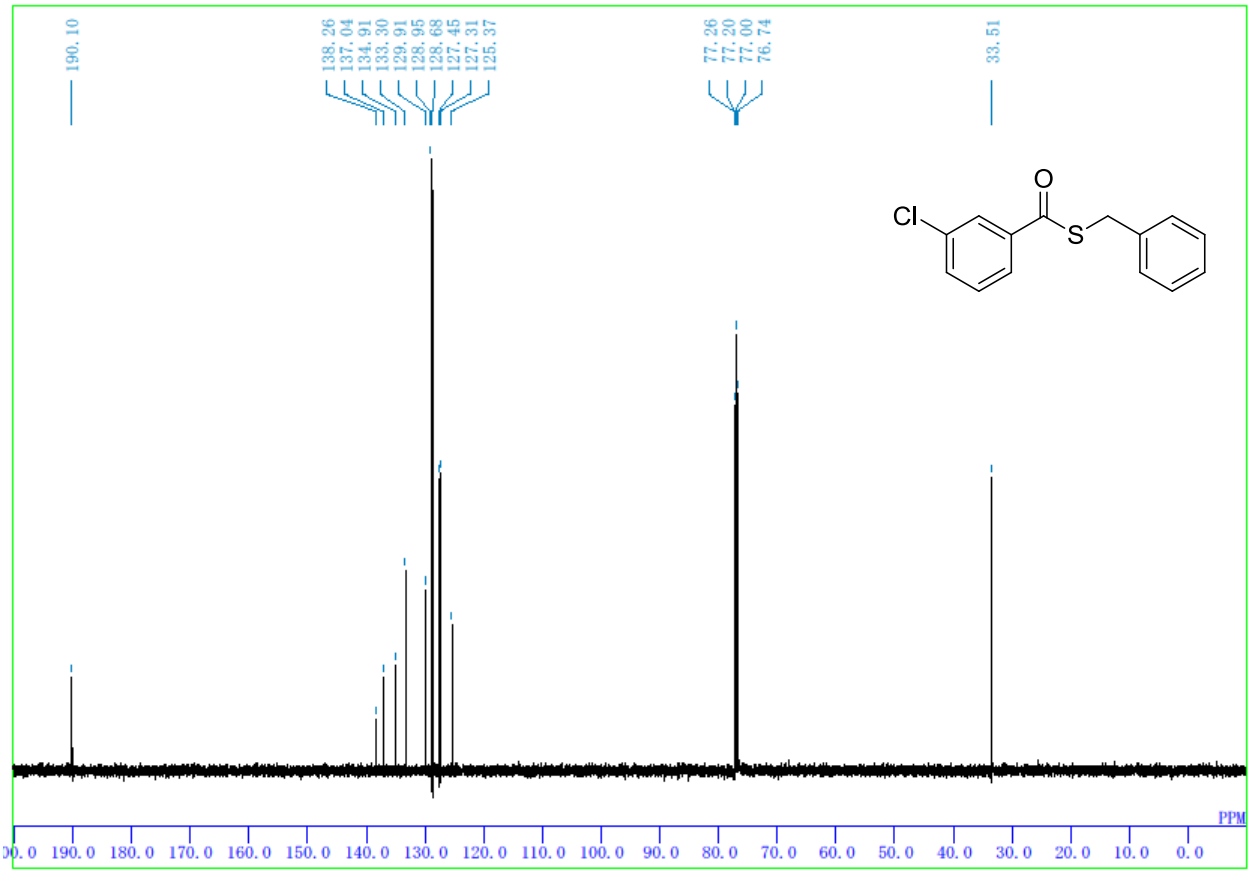
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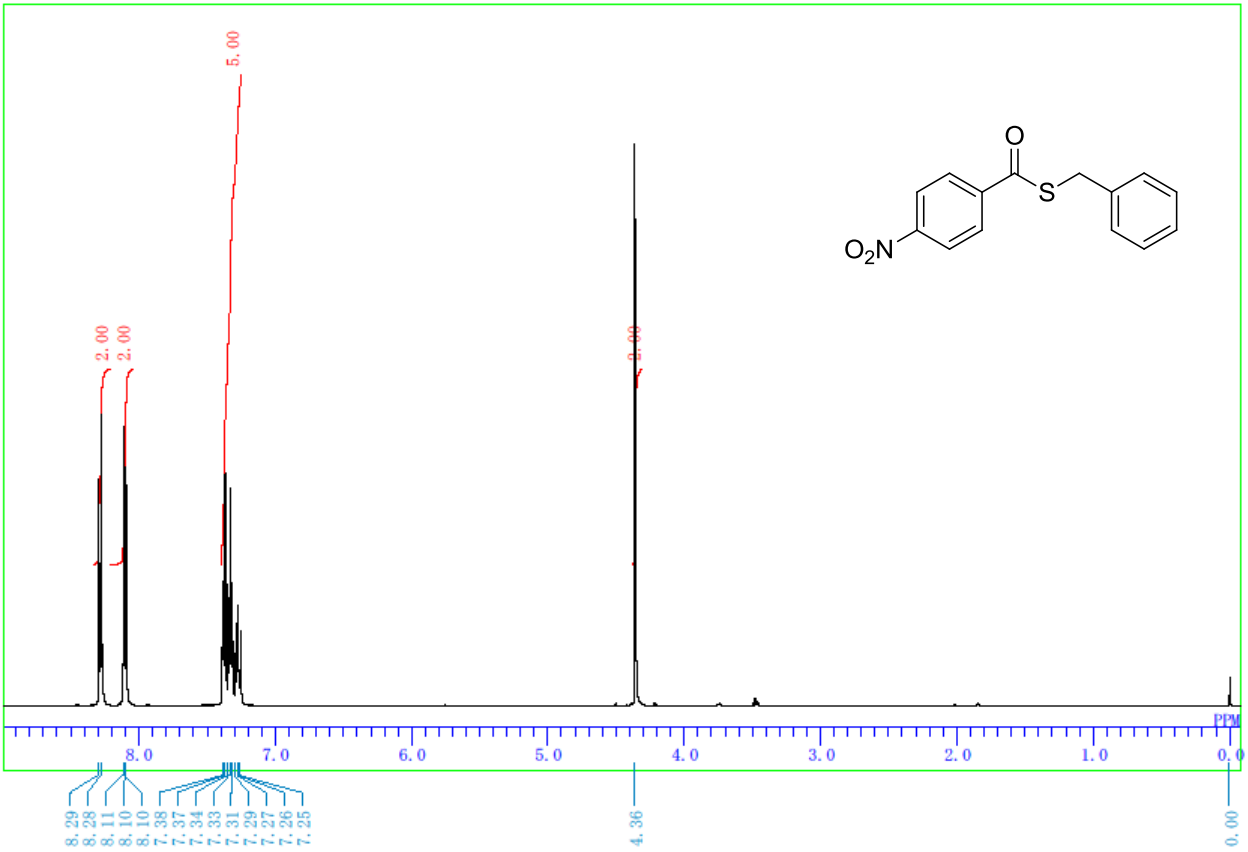
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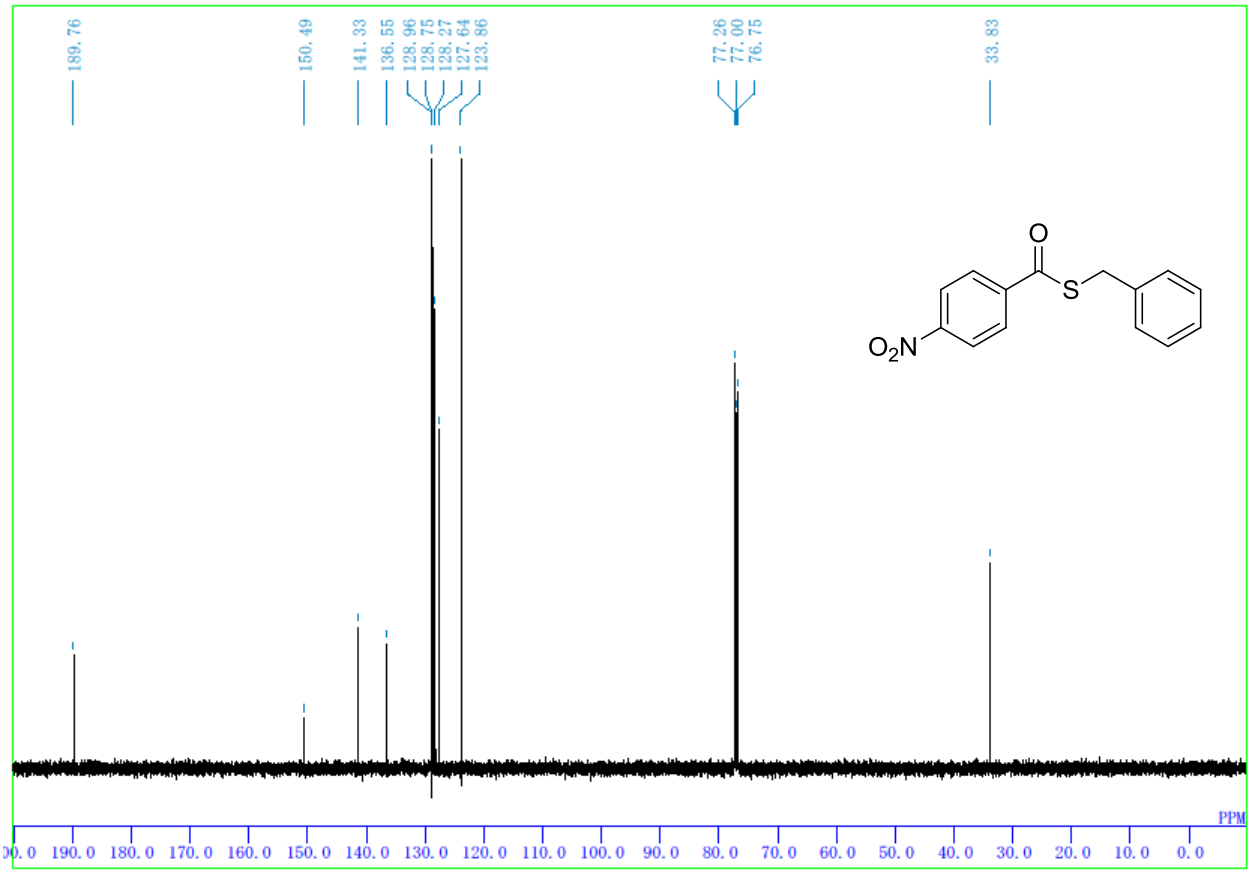
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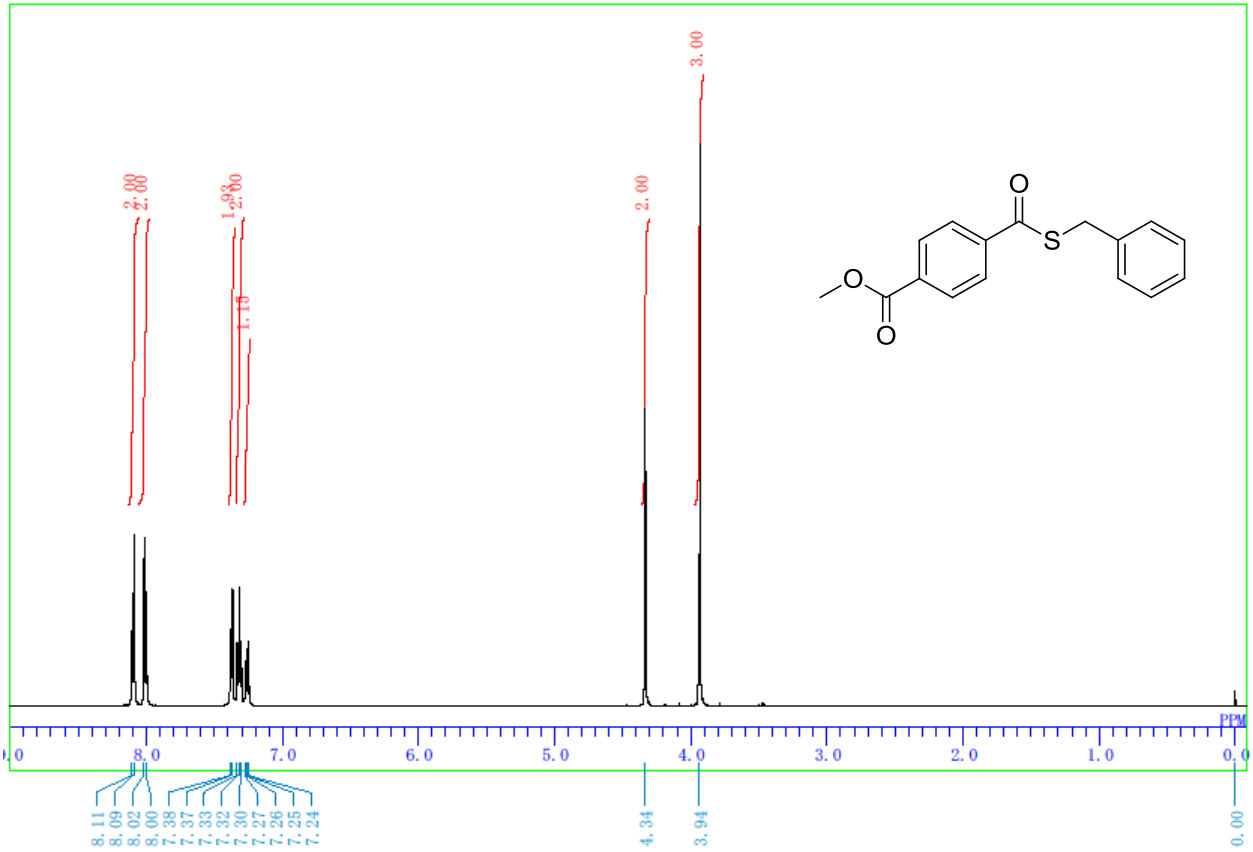
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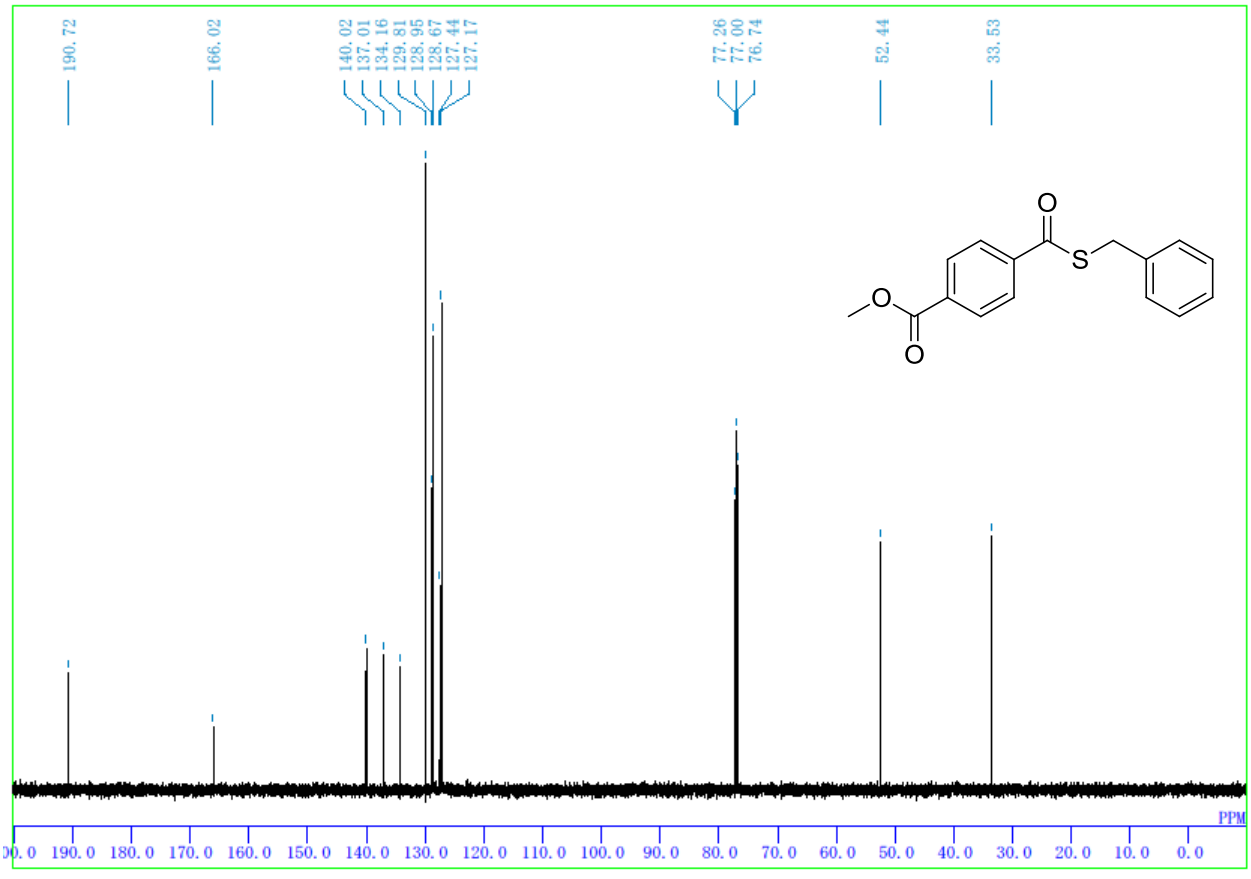
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O
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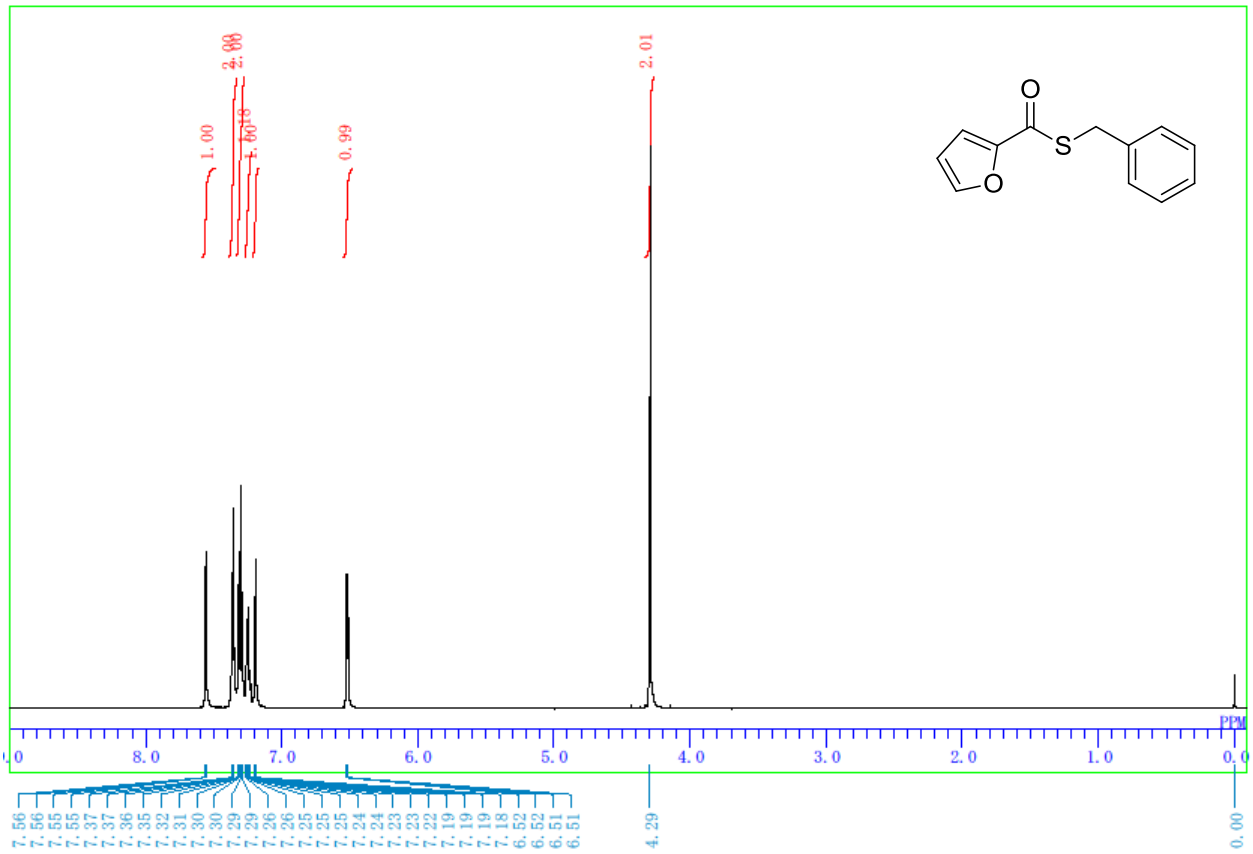
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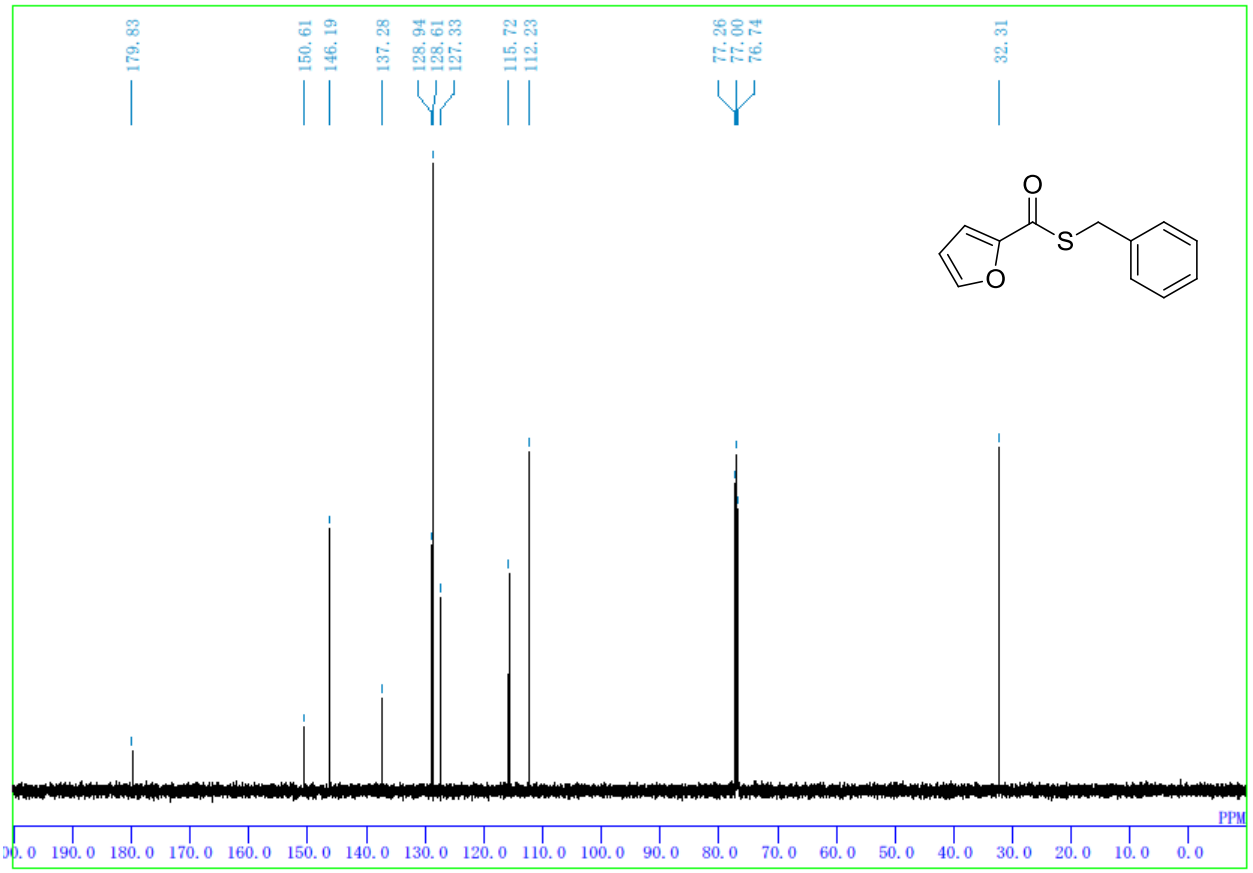
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PPM
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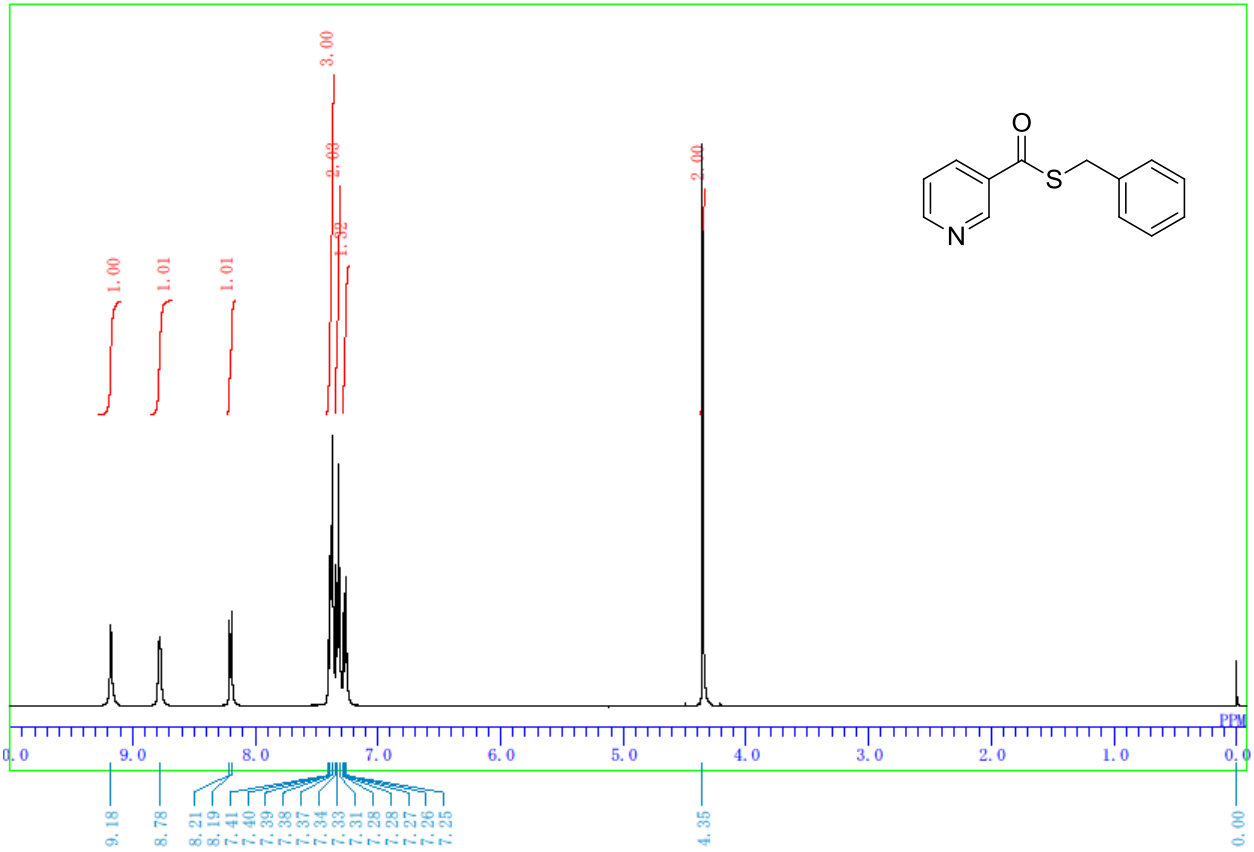
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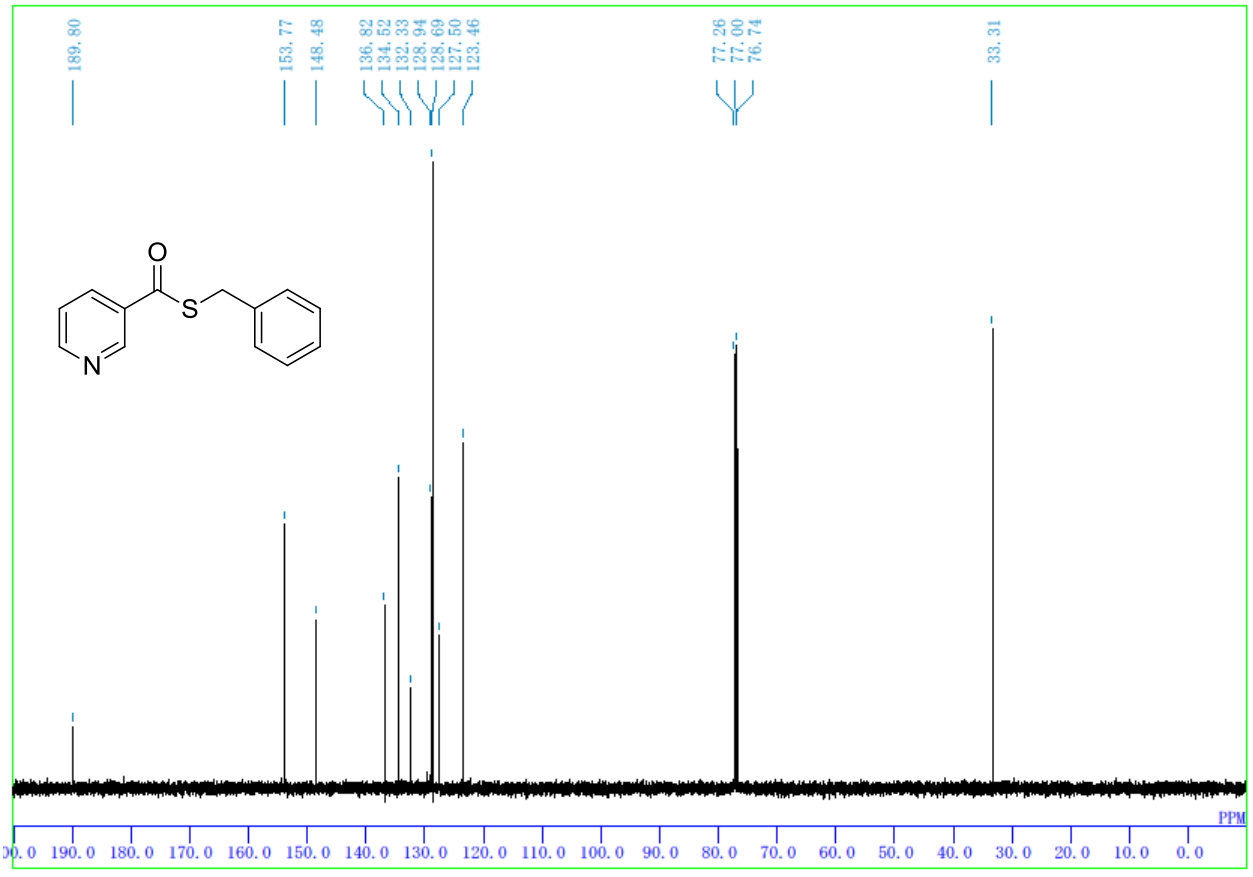
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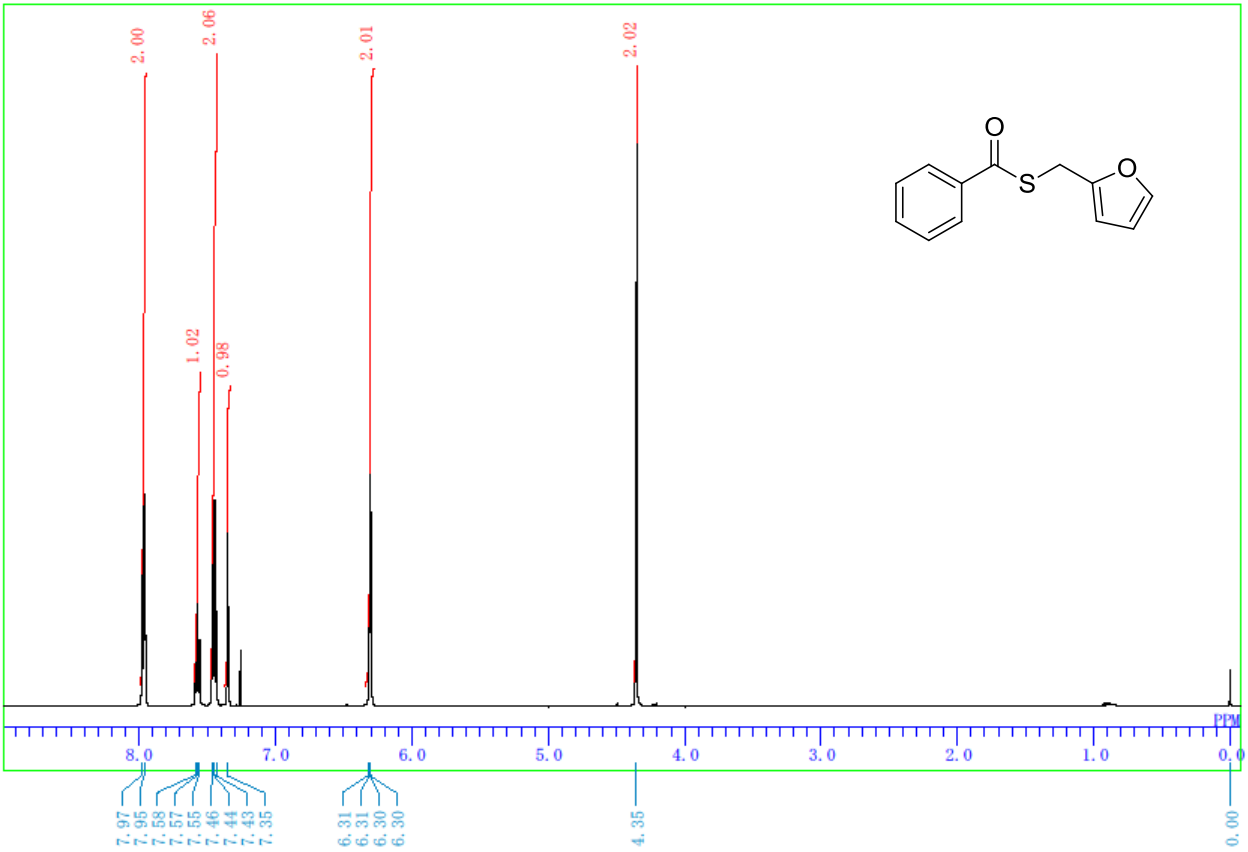
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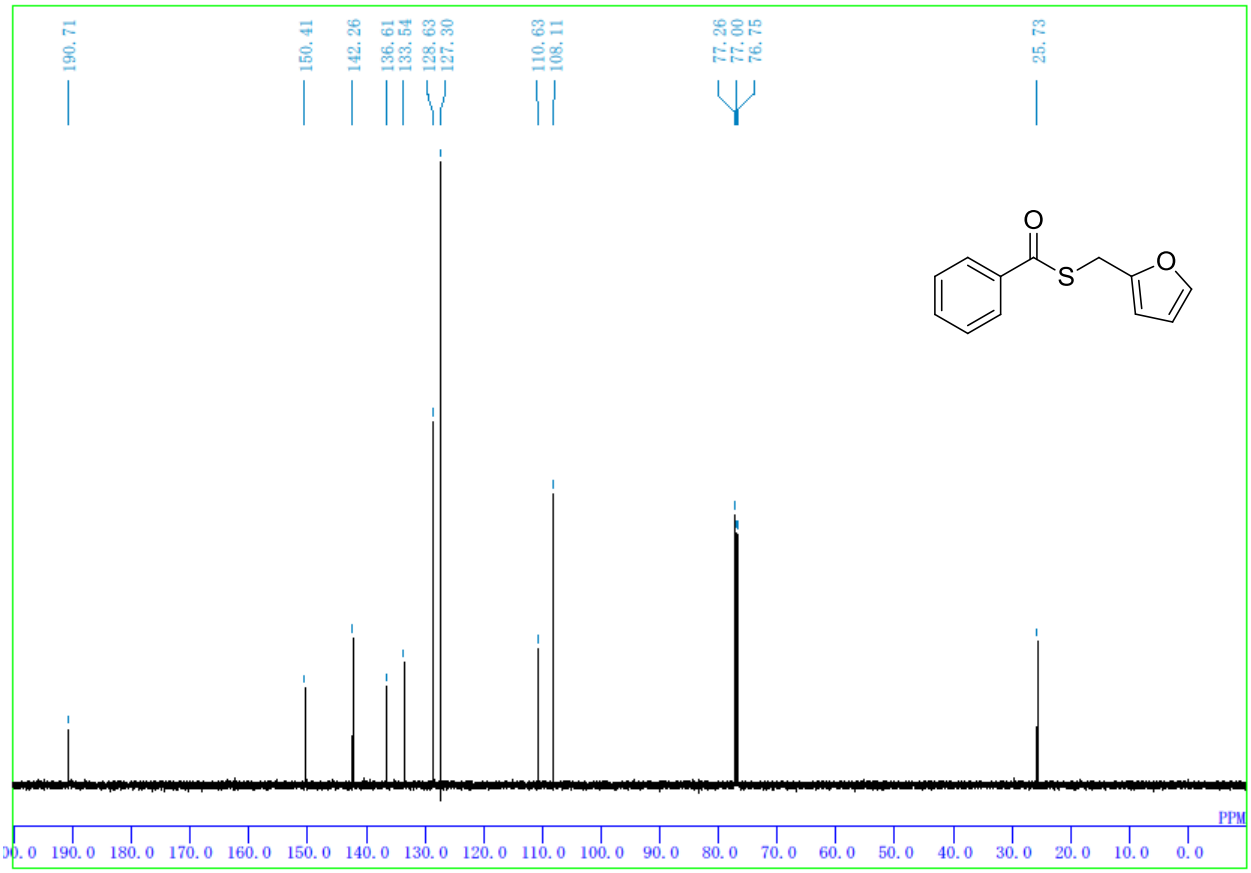
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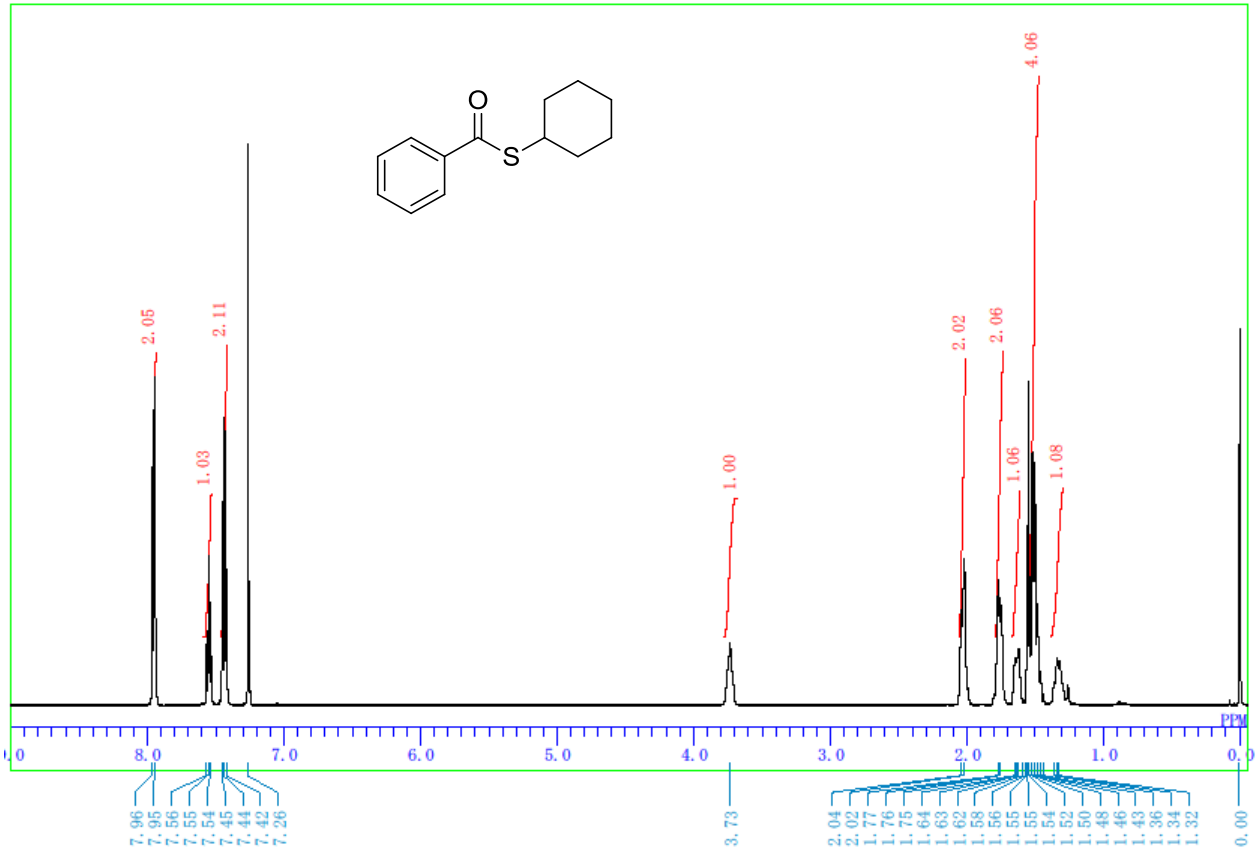
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1.76
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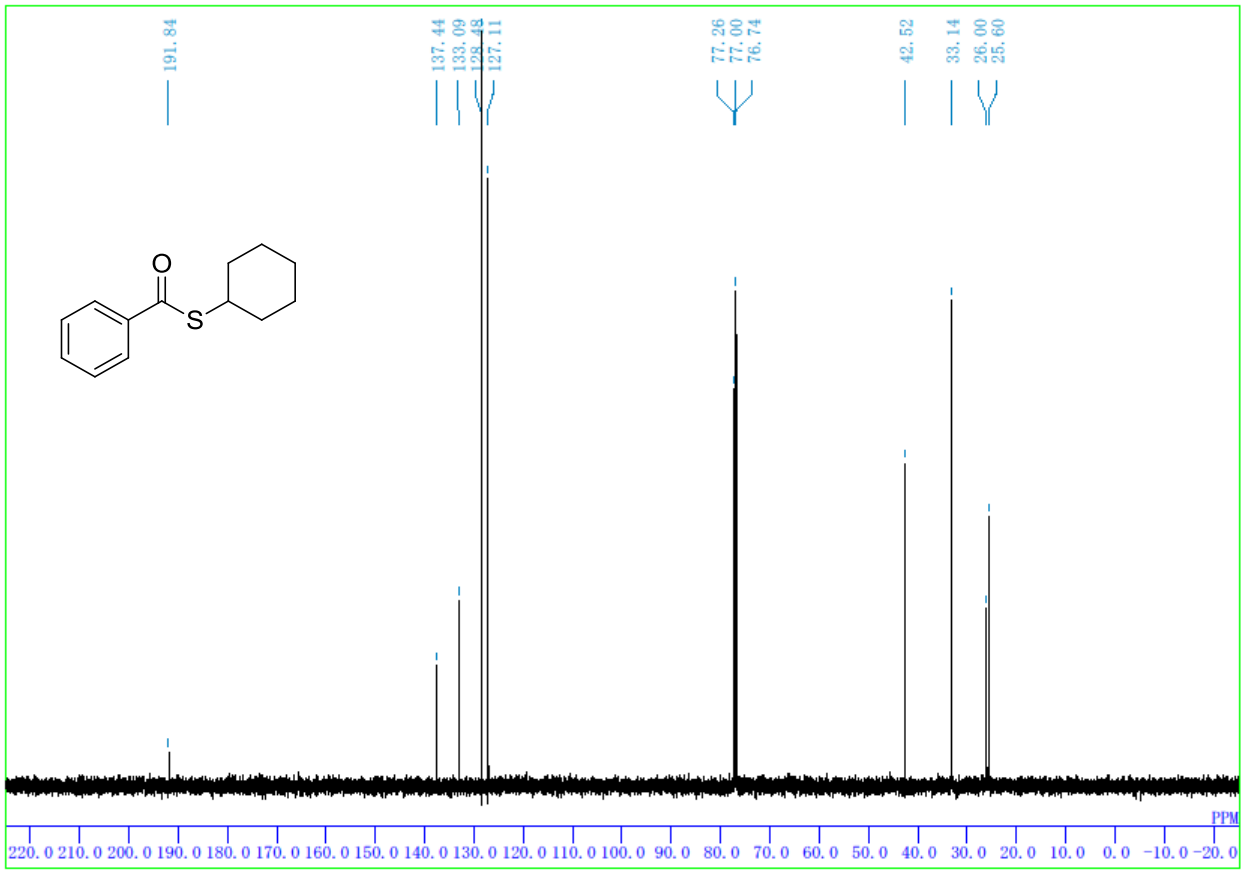
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33.14
26.00
25.60
PPM
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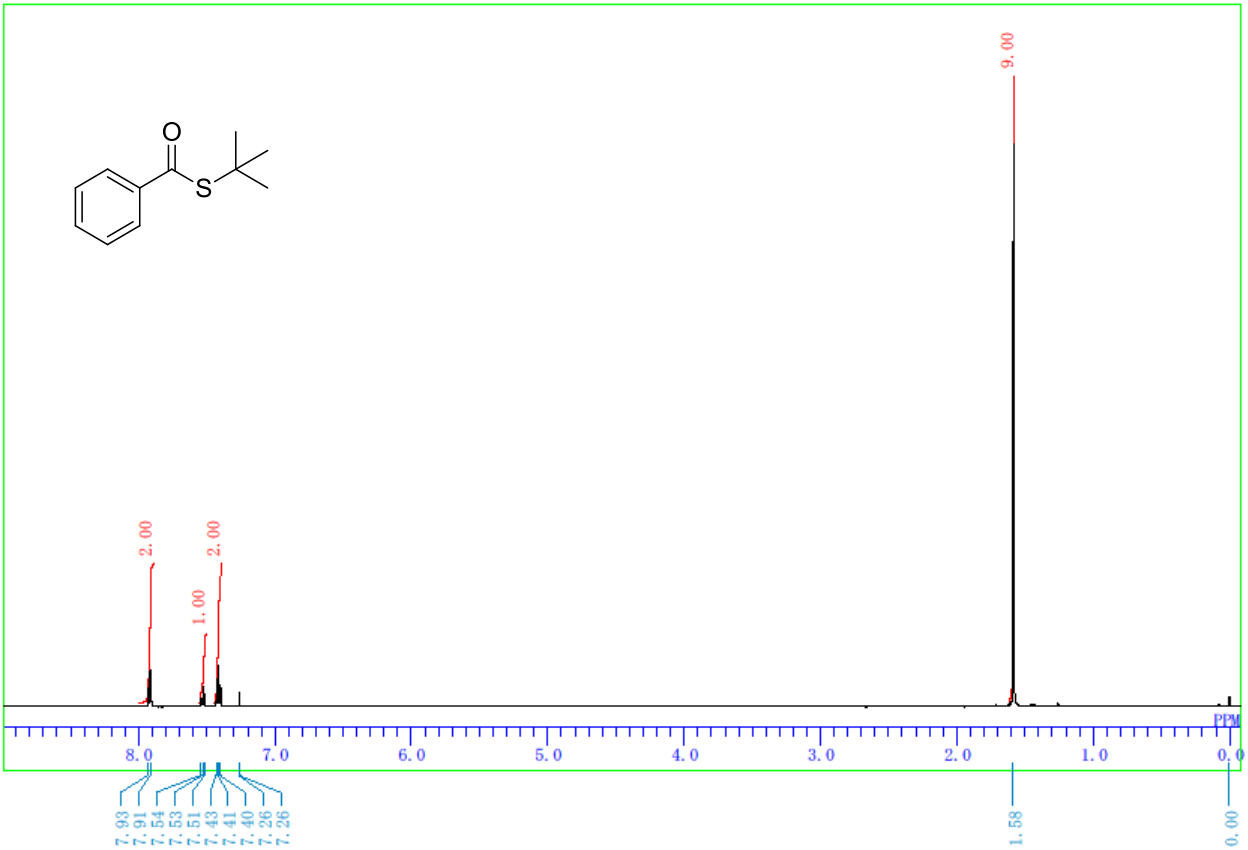
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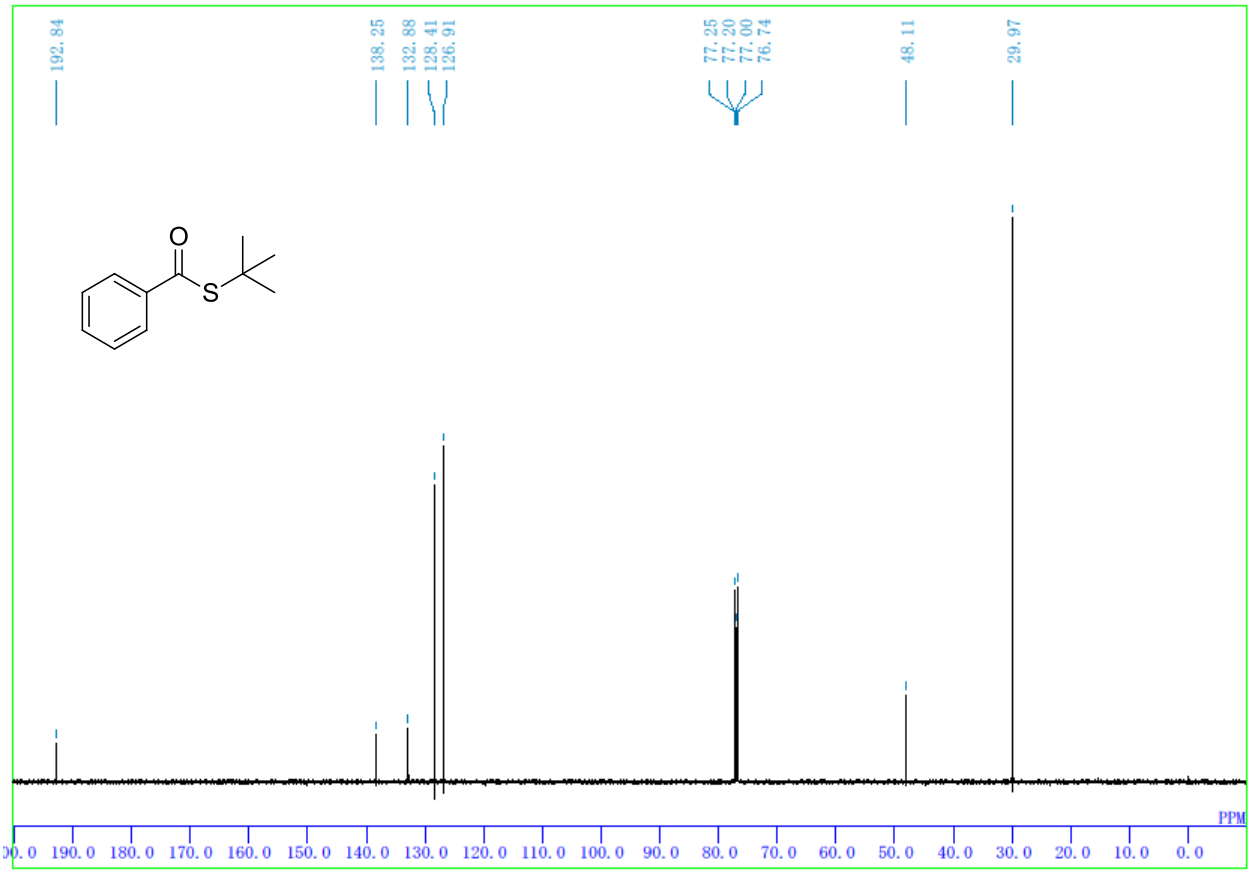
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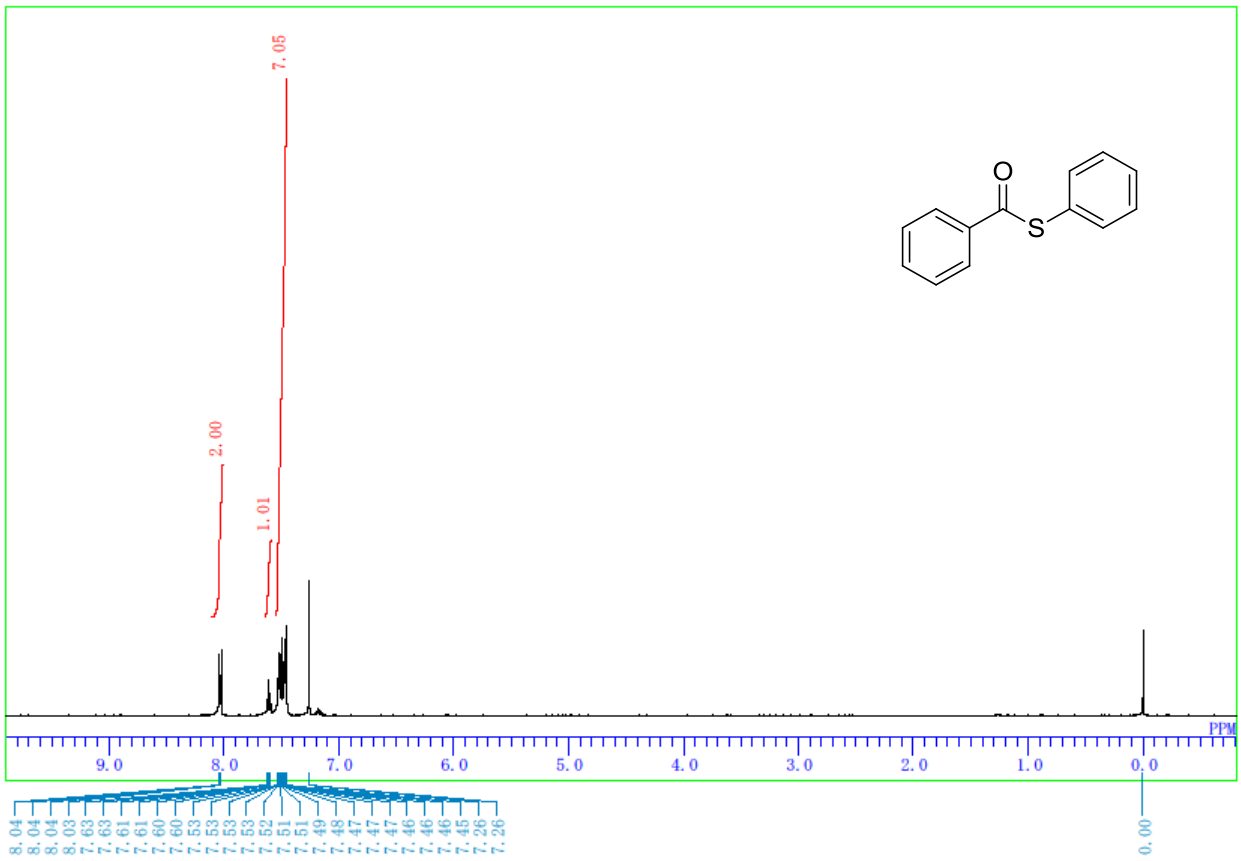
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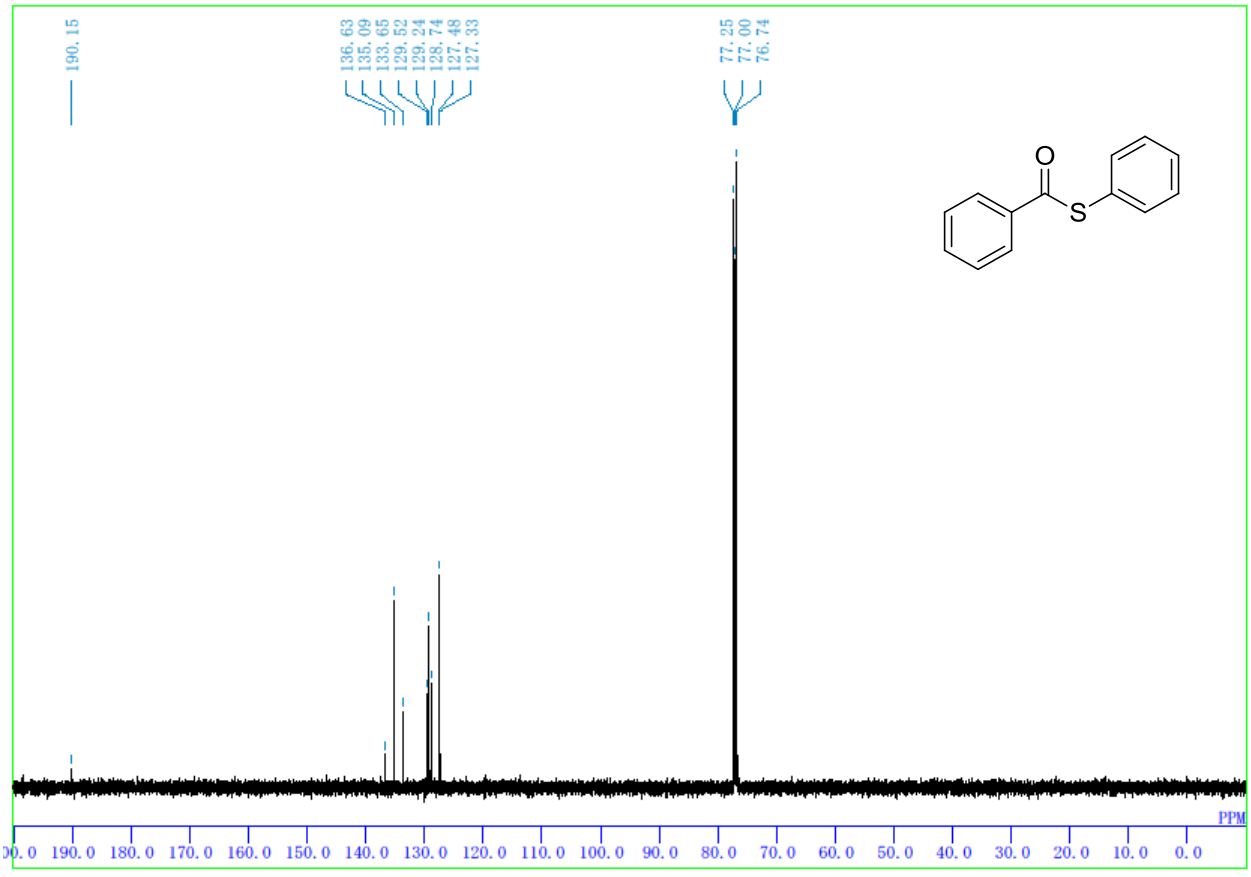
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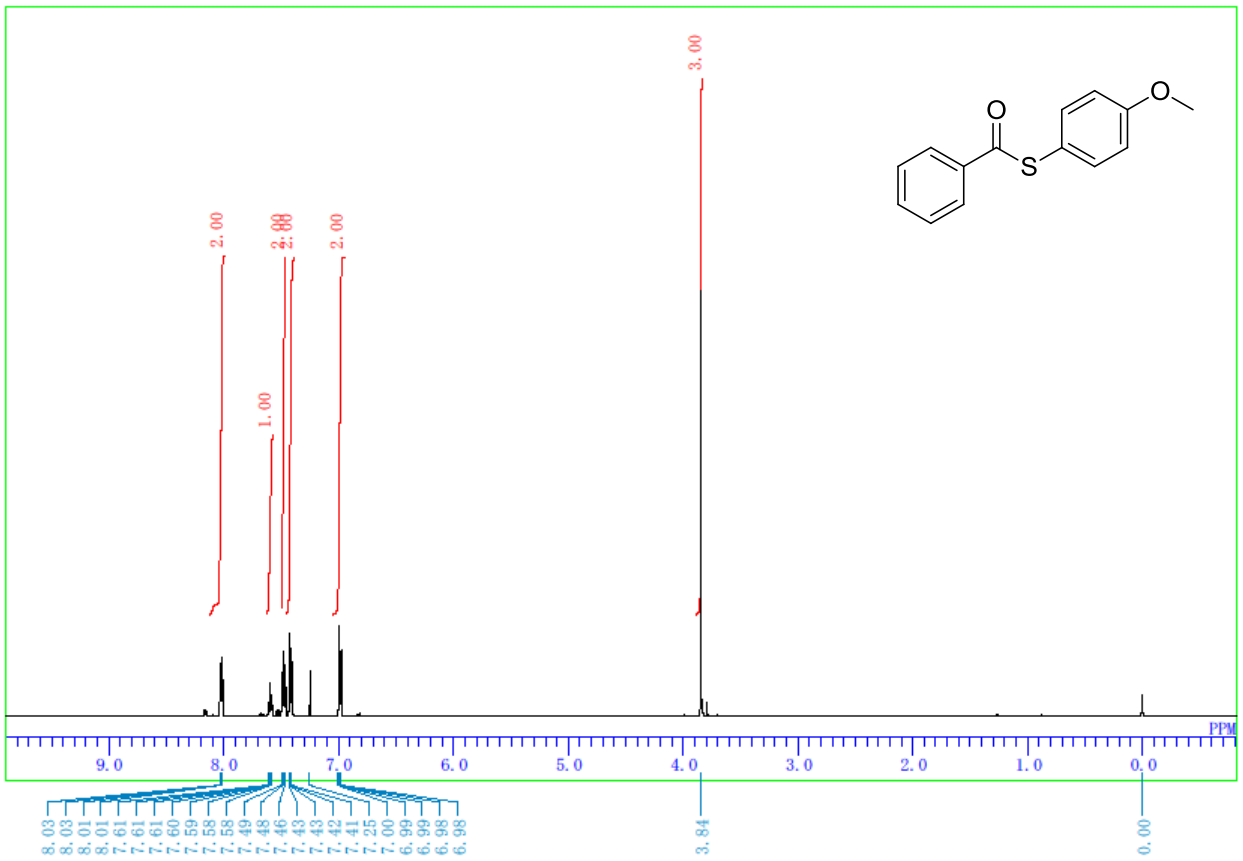
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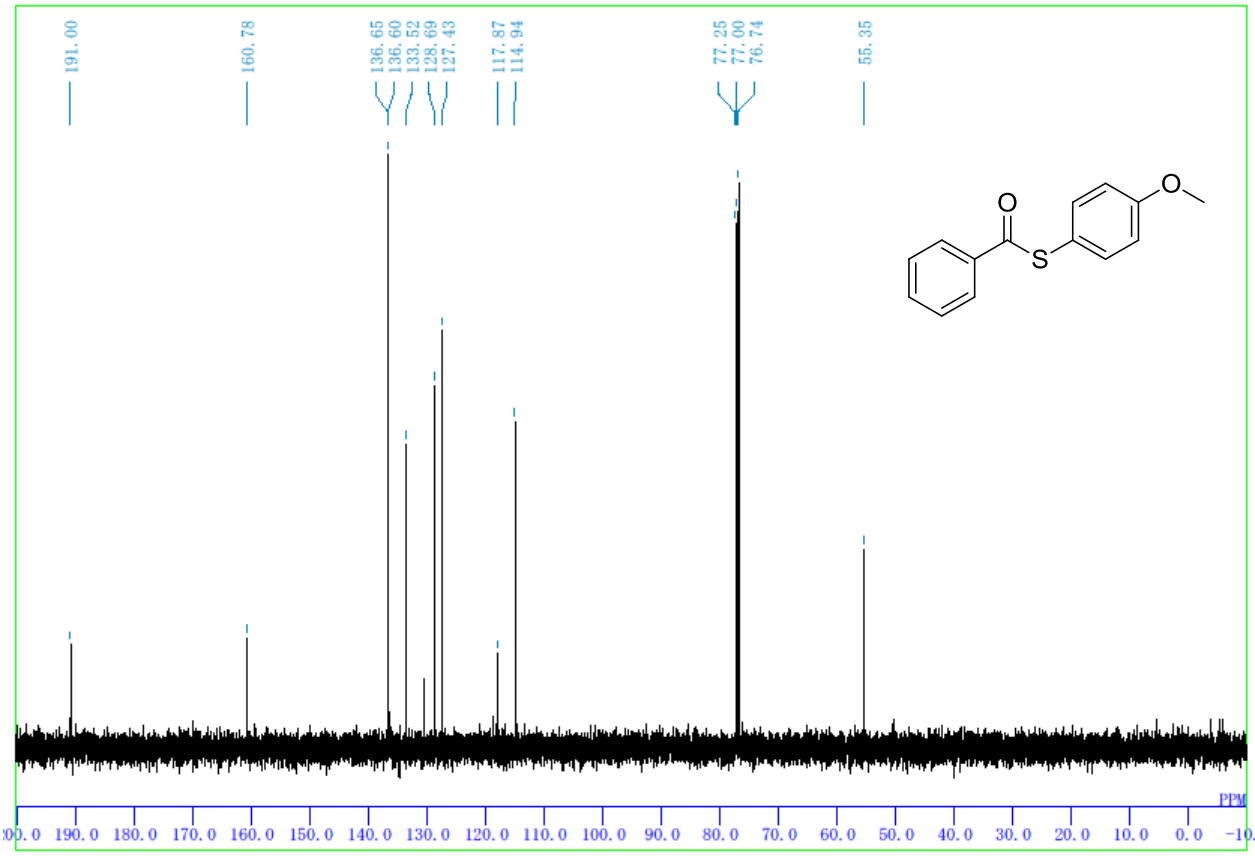
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PPM
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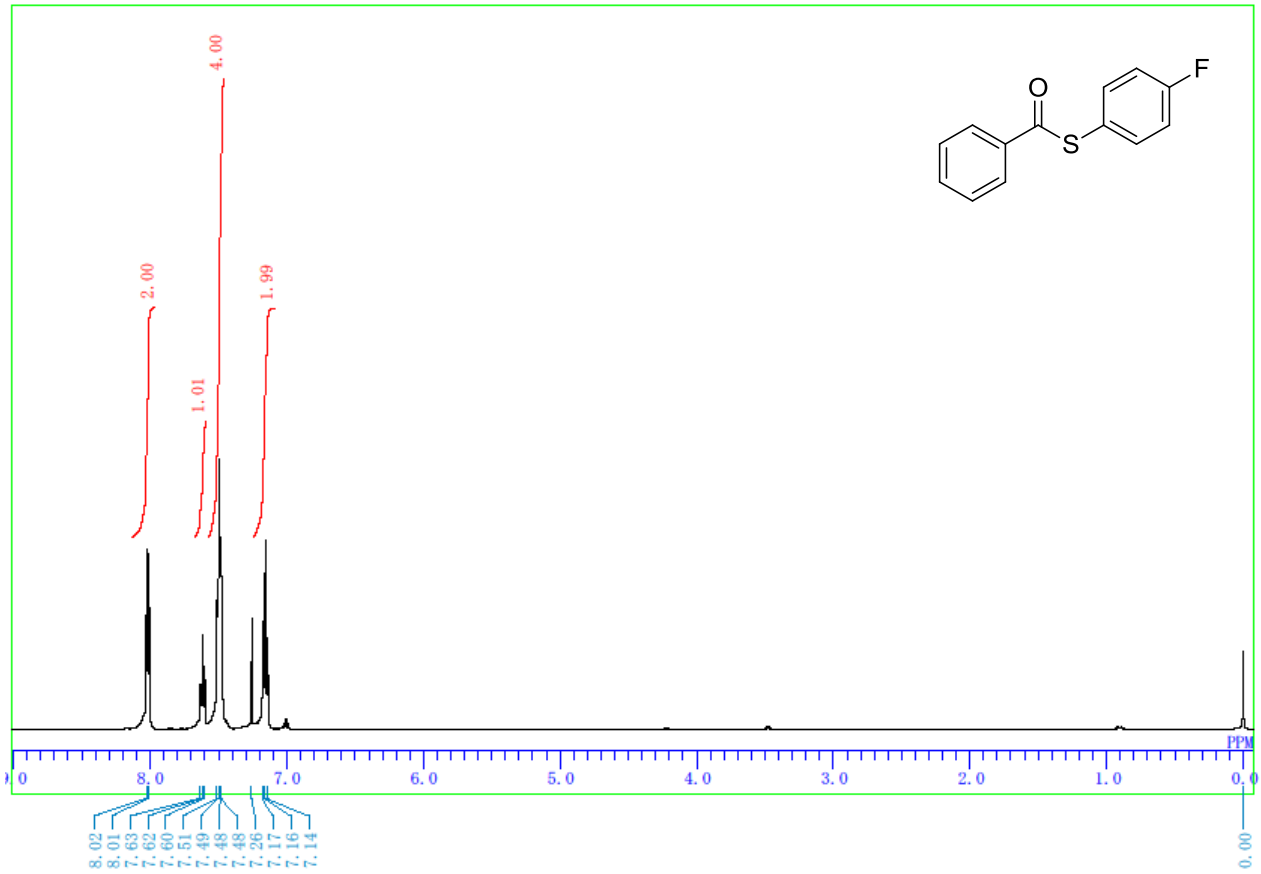
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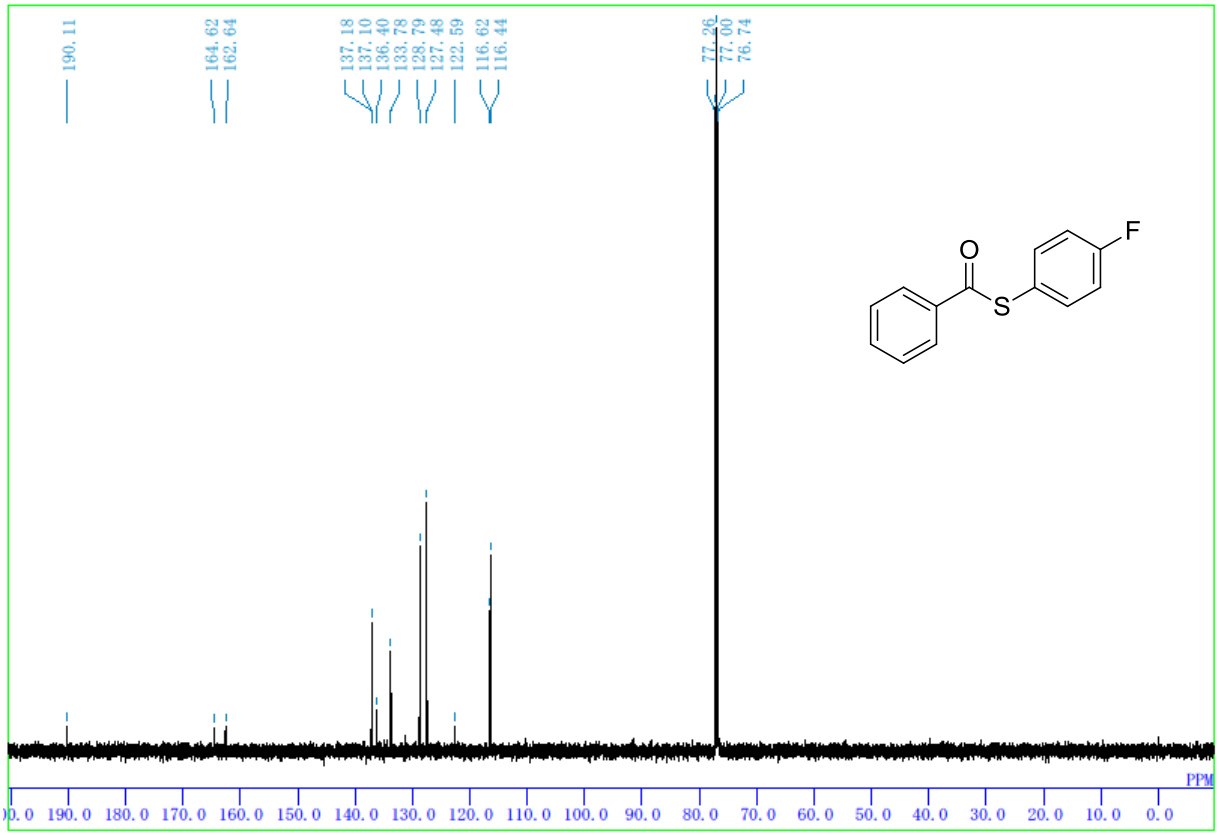
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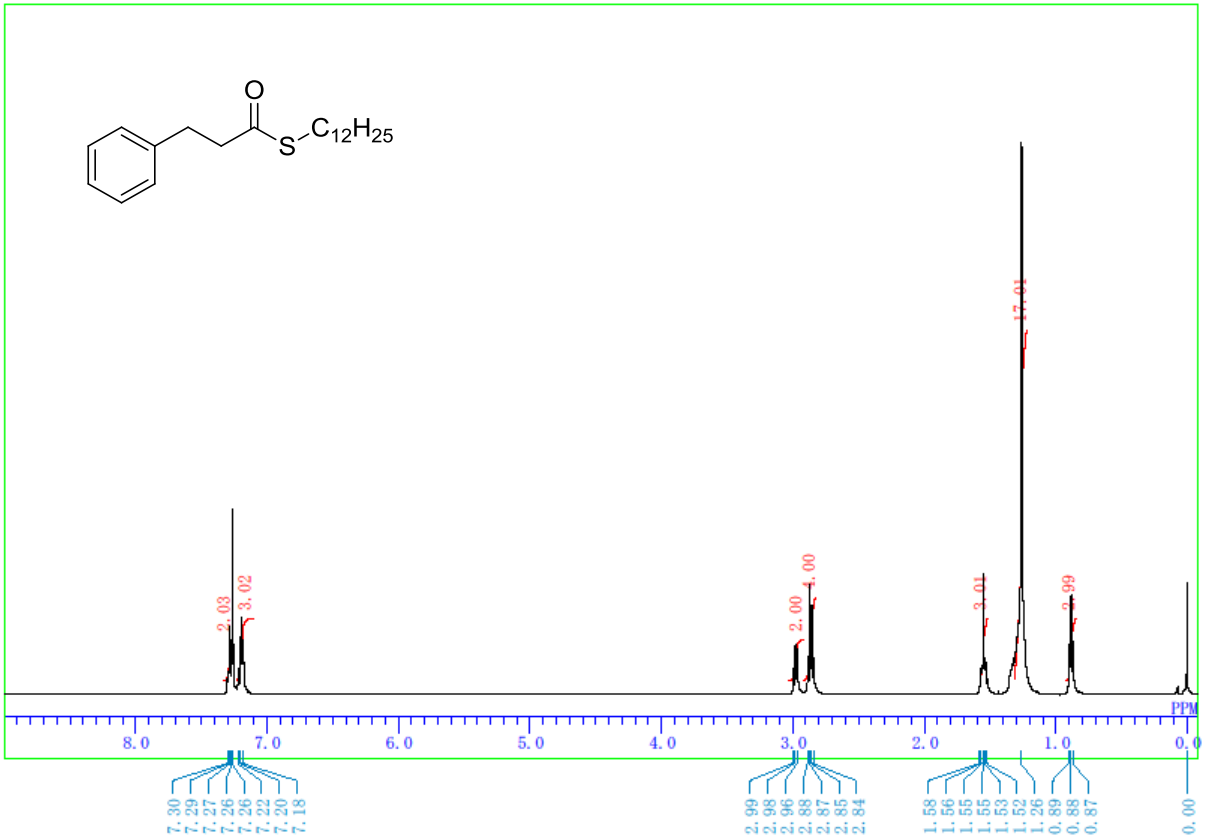
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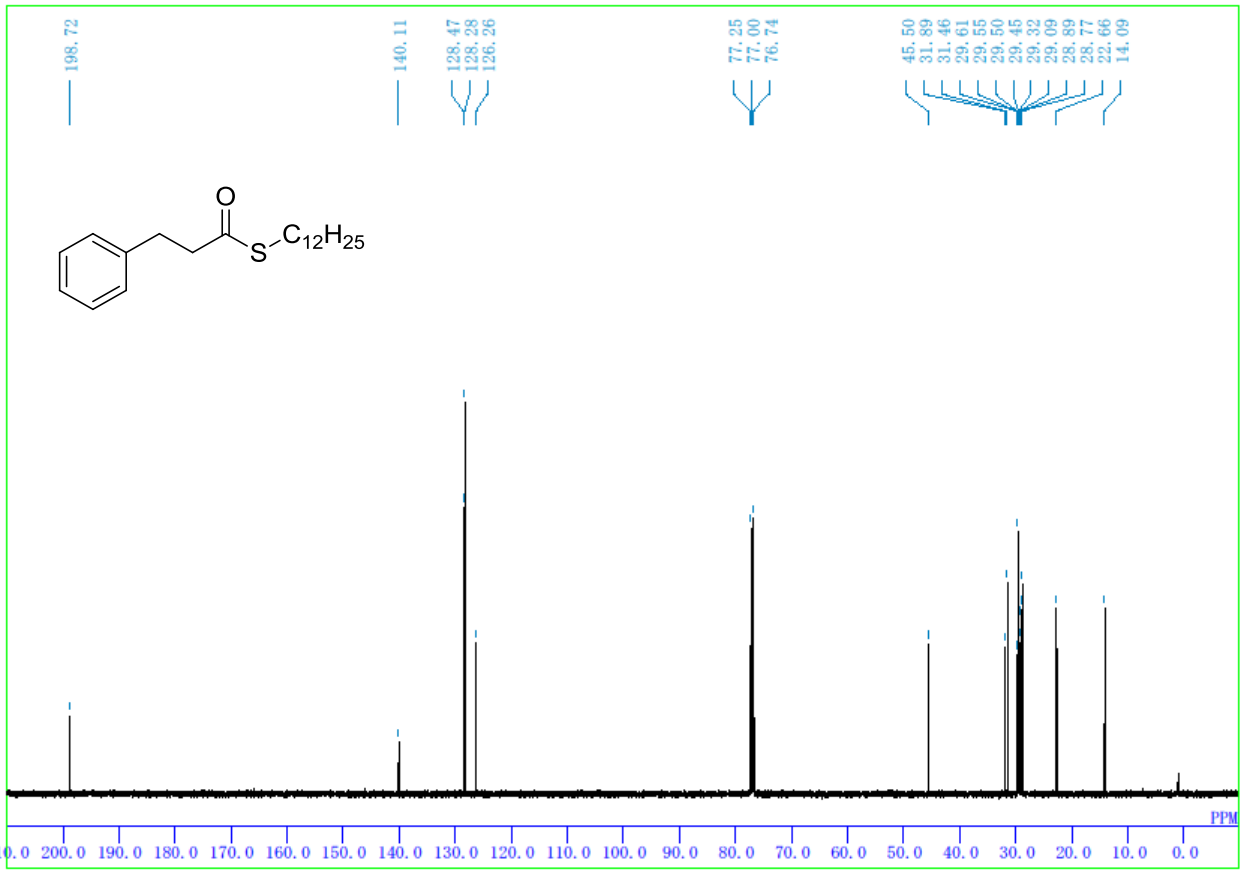
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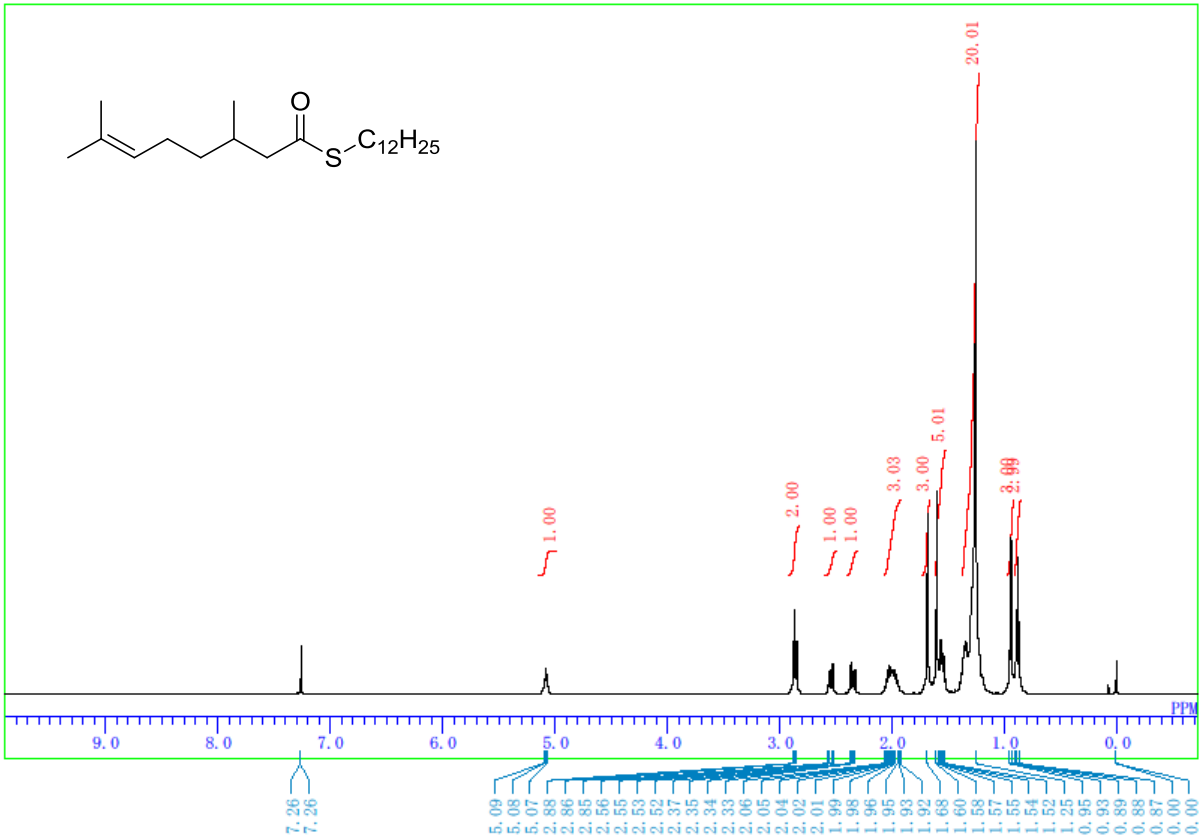
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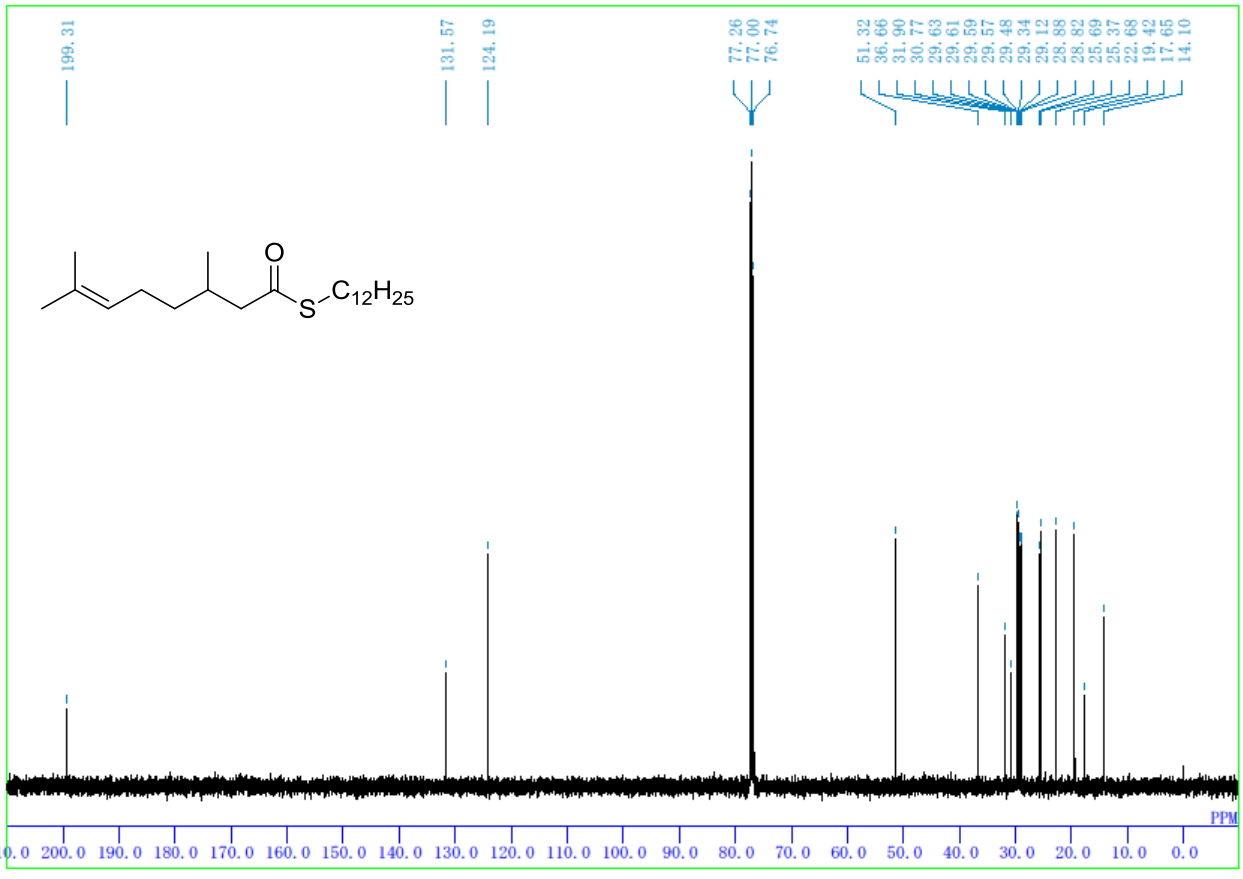
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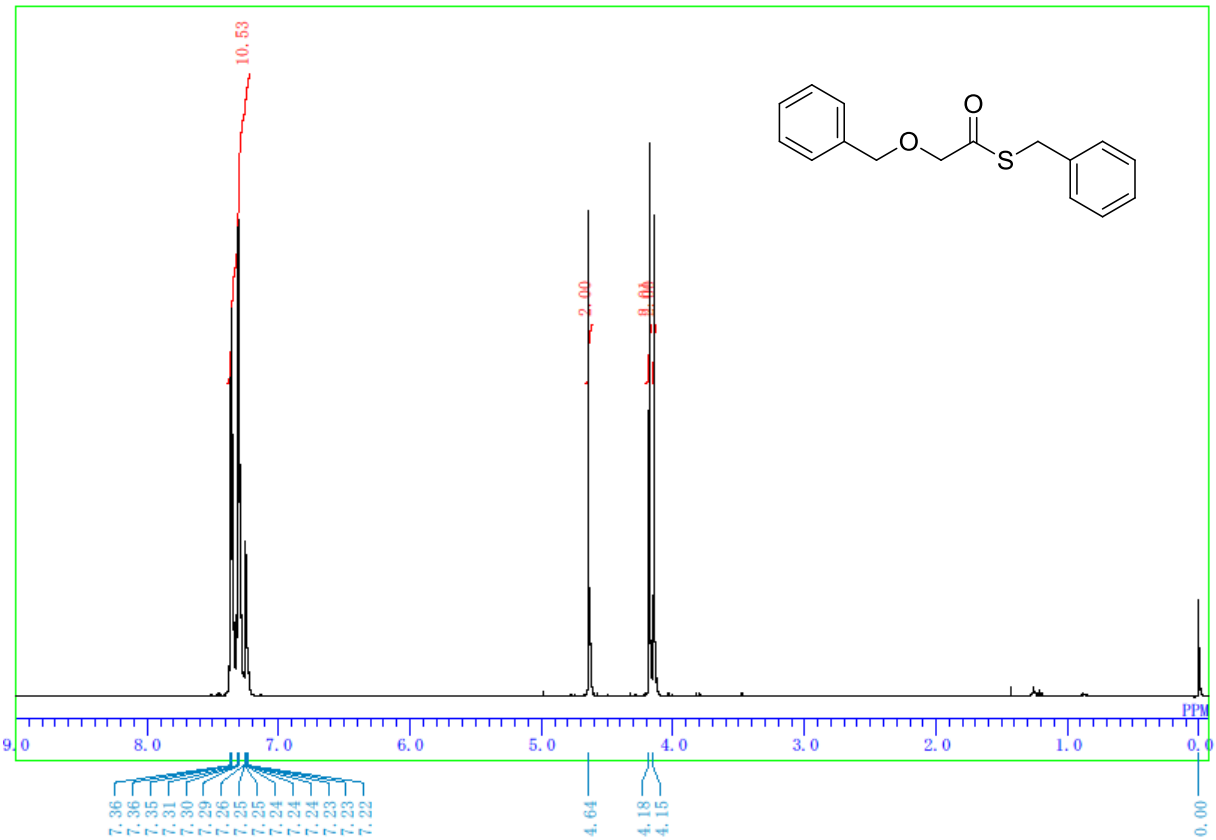
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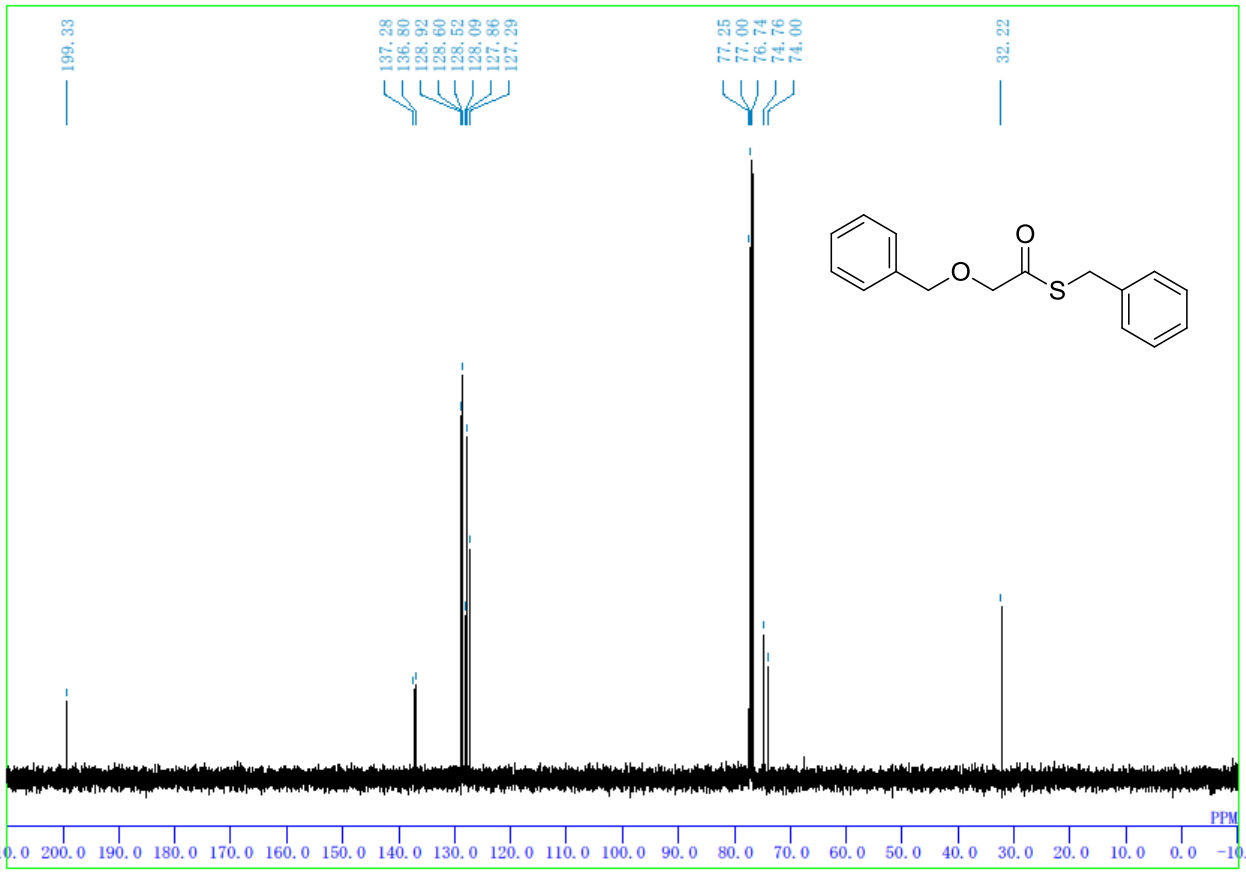
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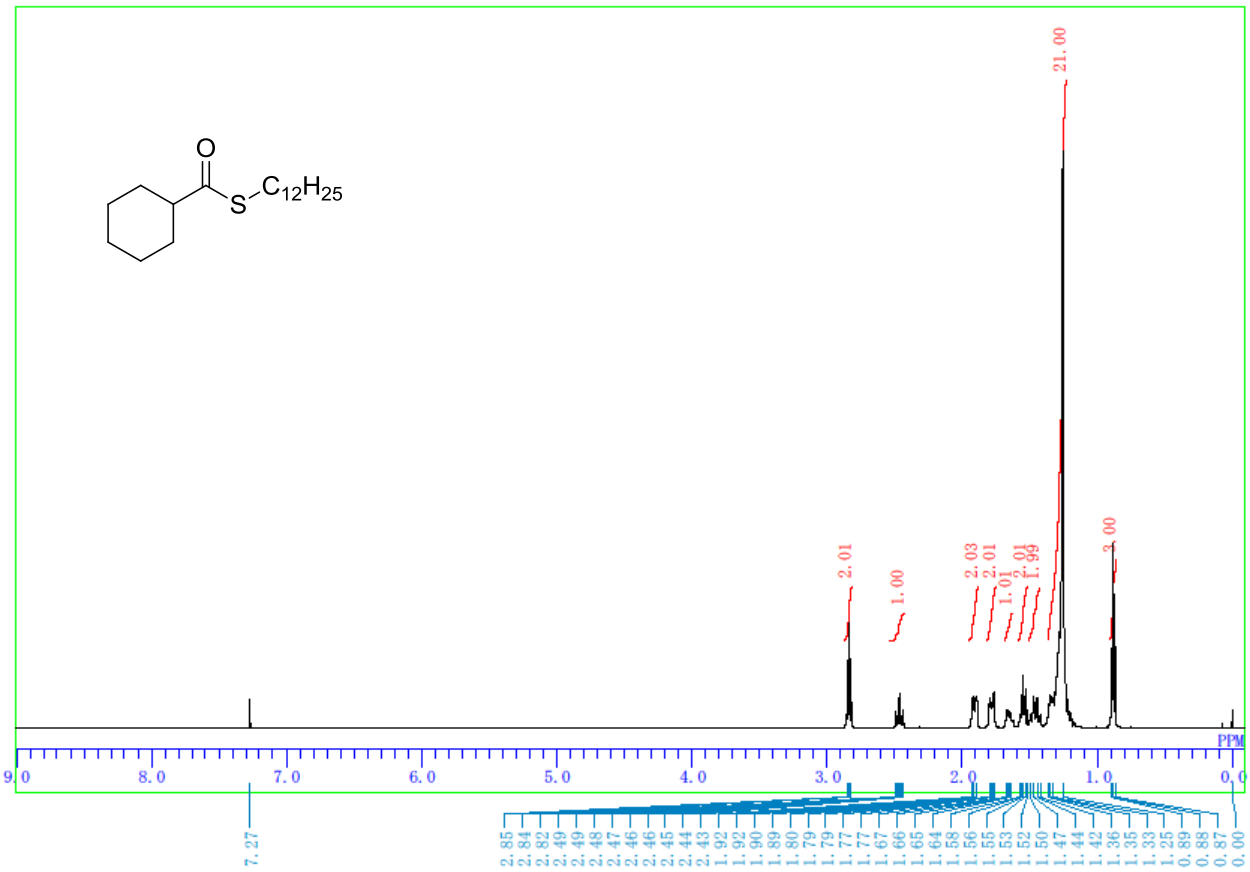
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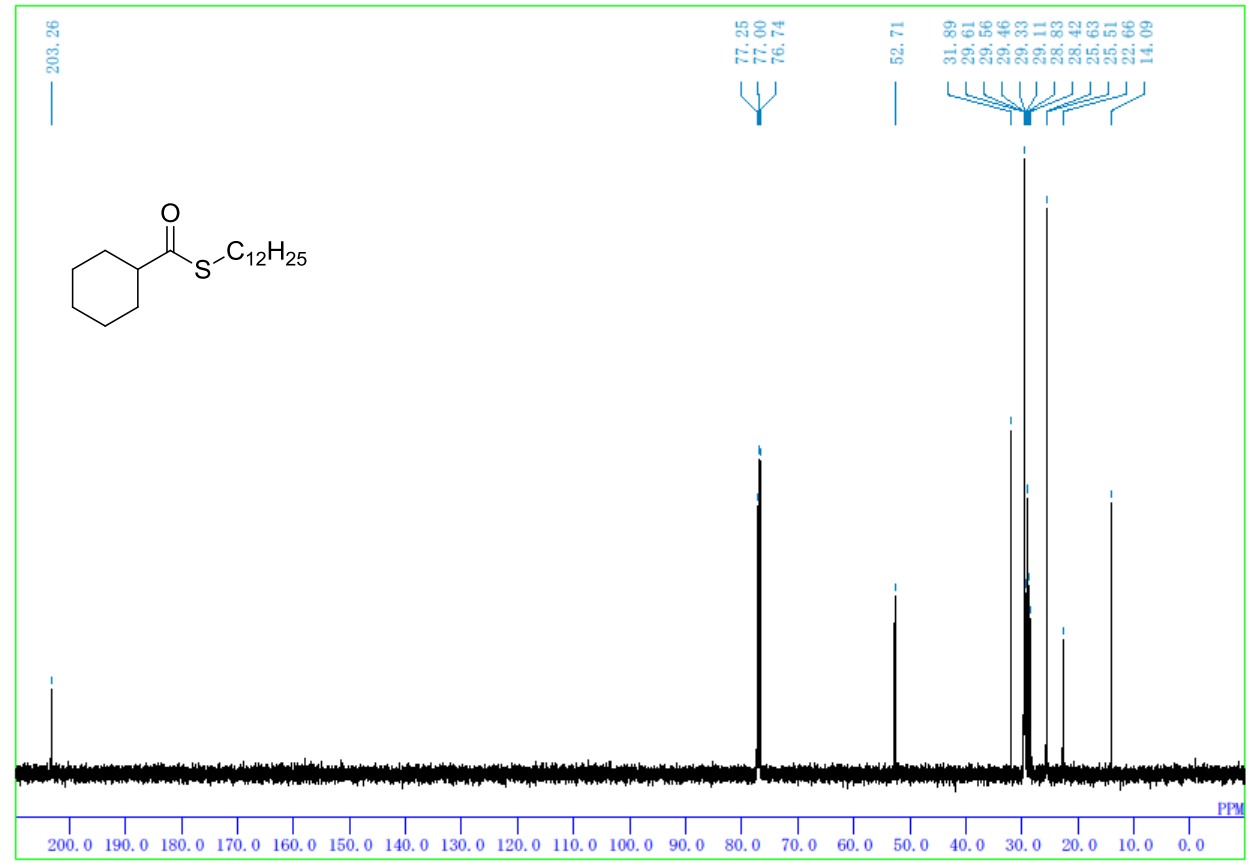
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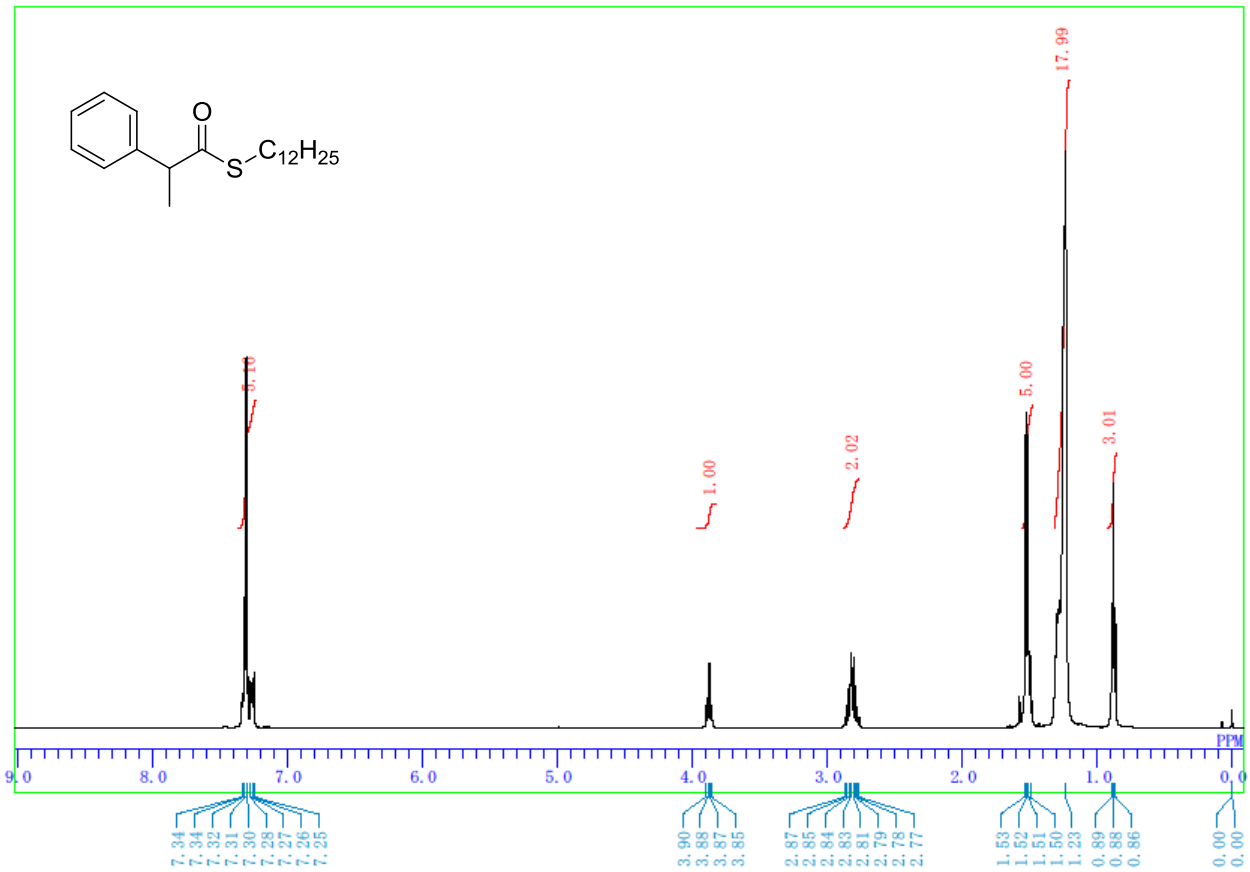
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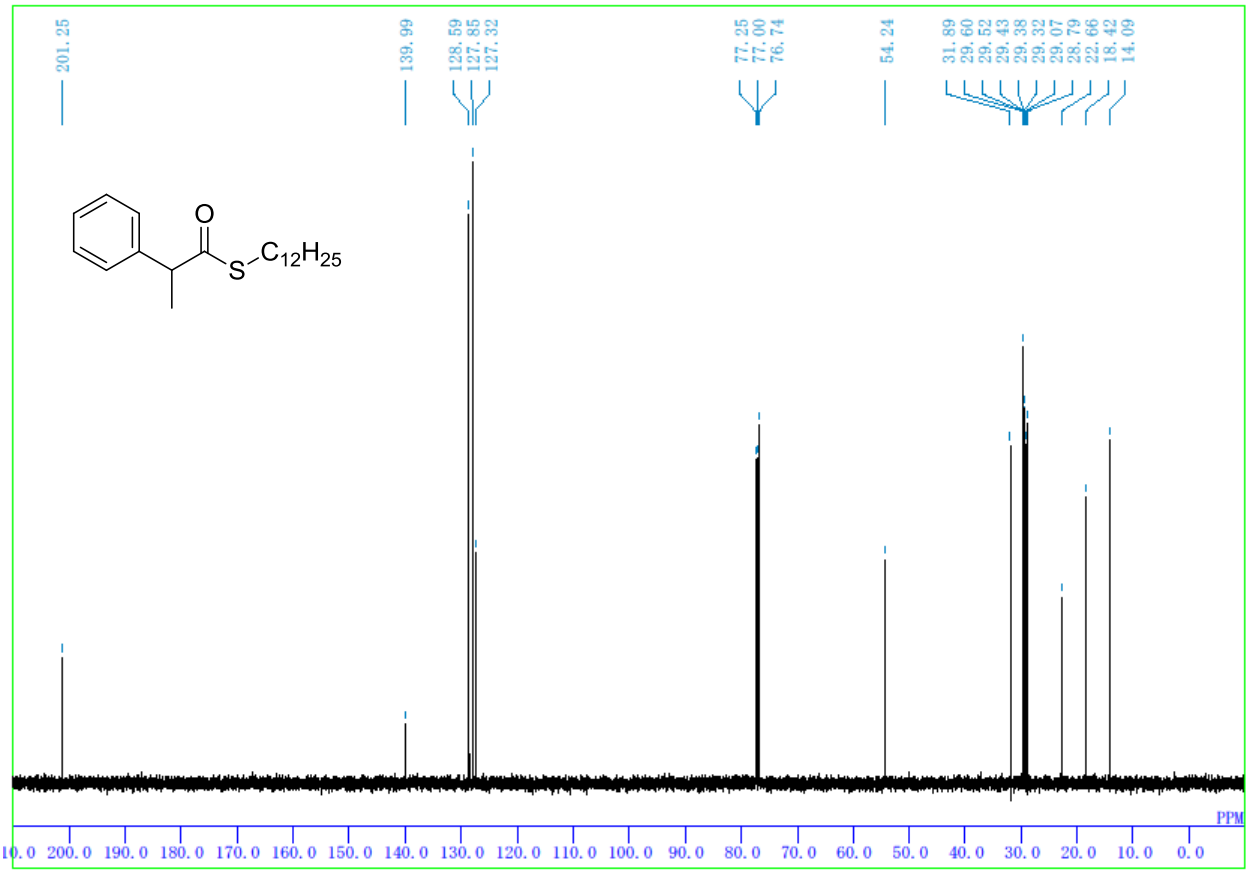
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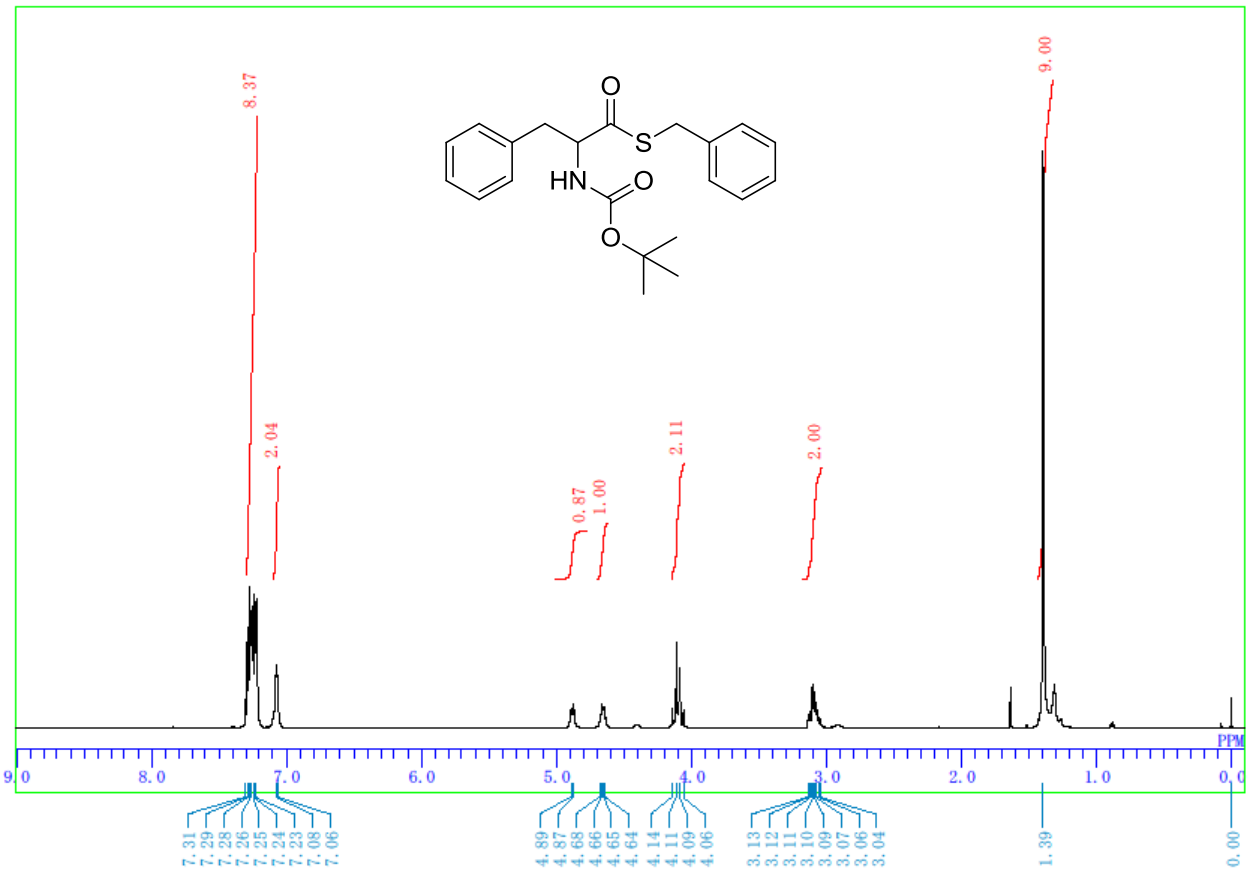
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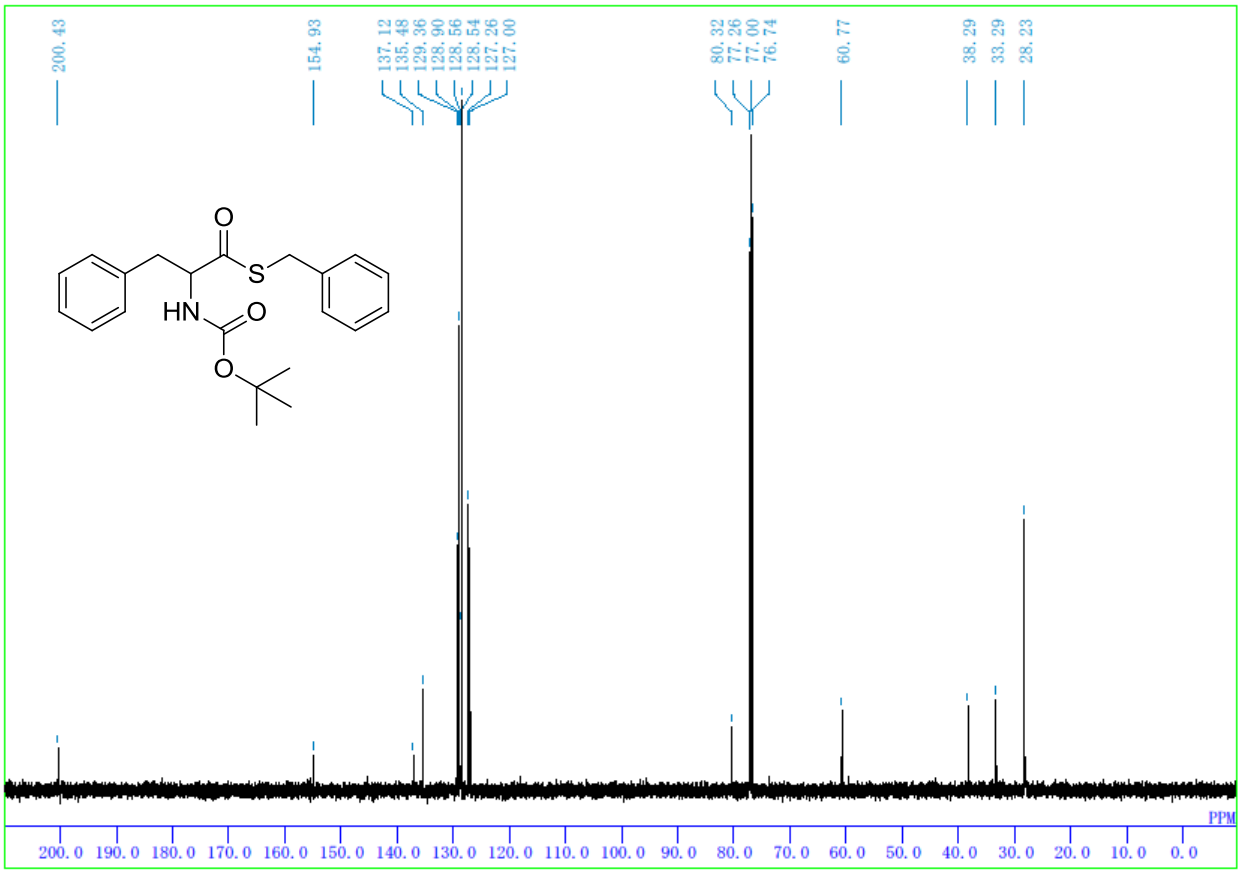
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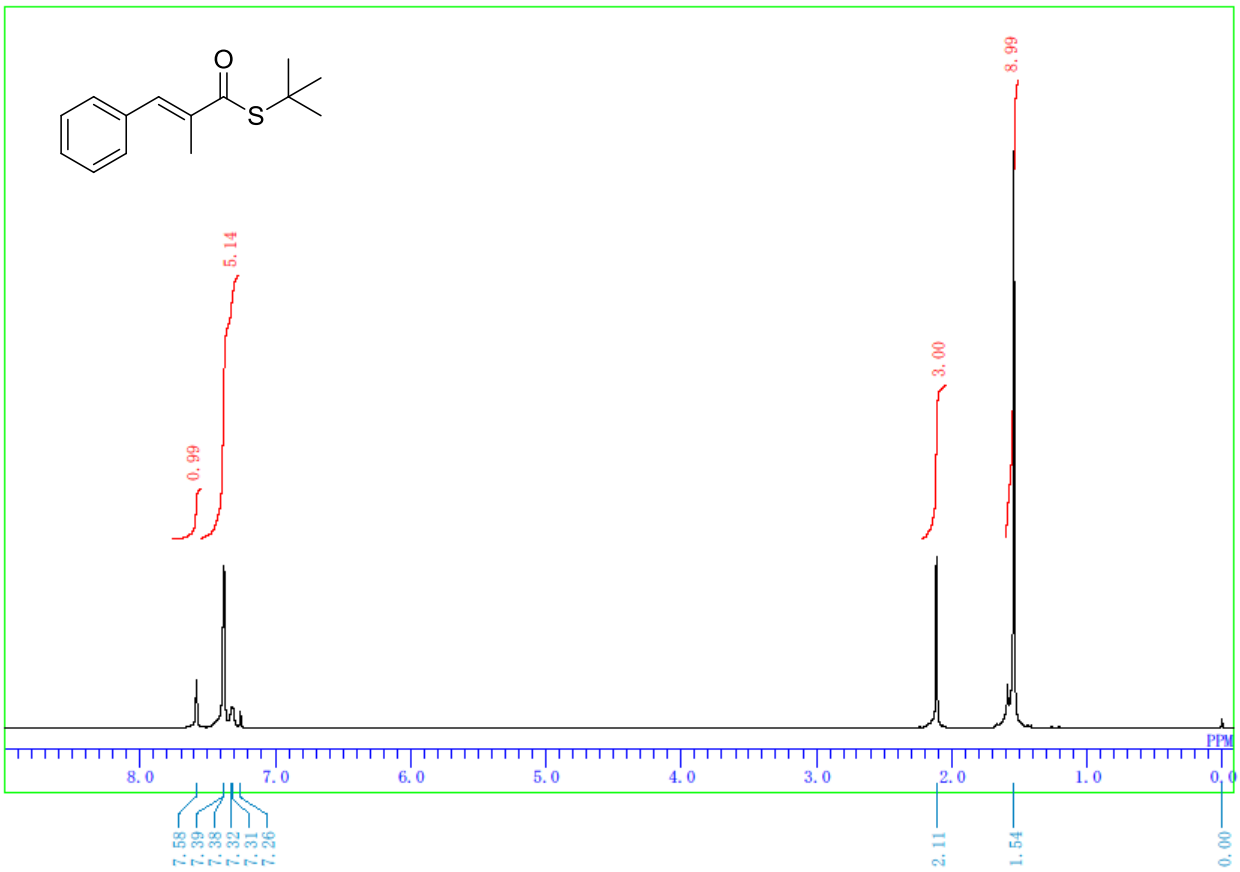
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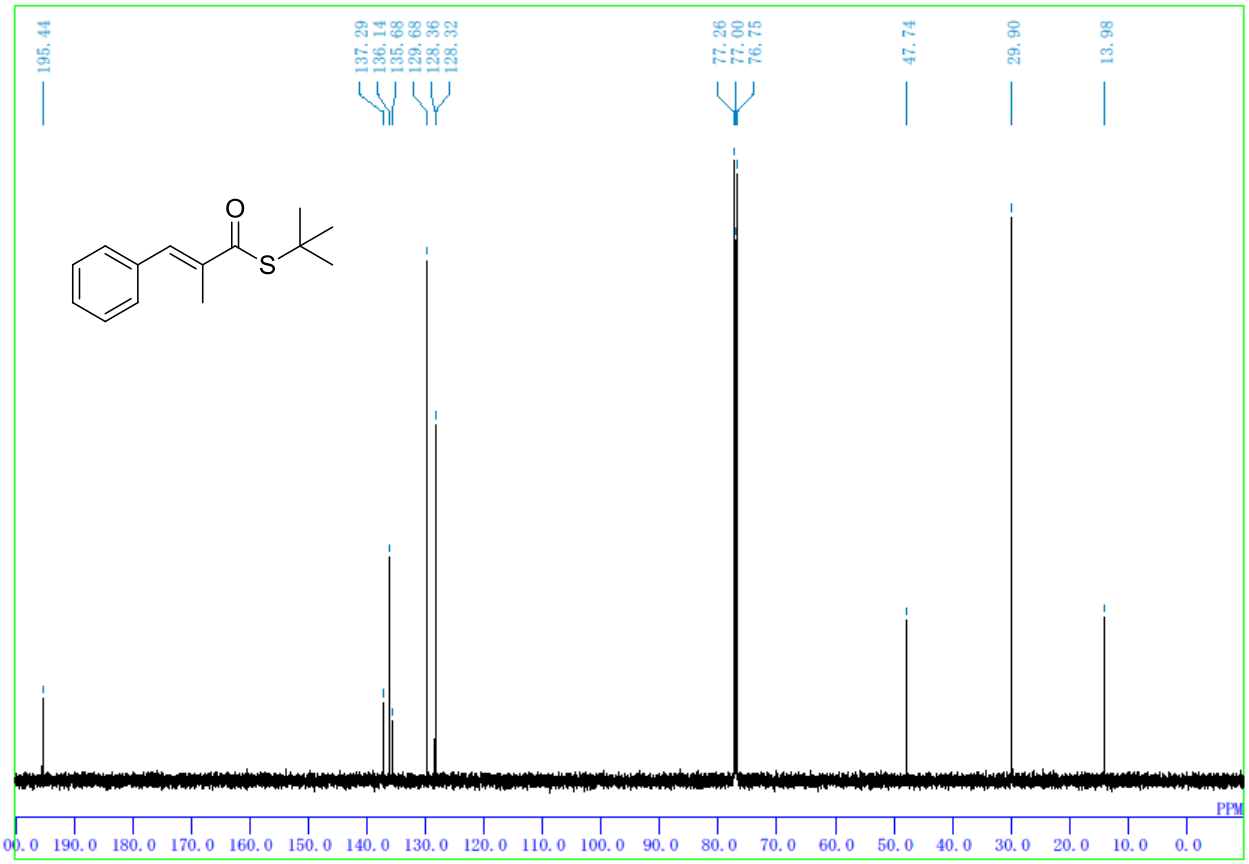
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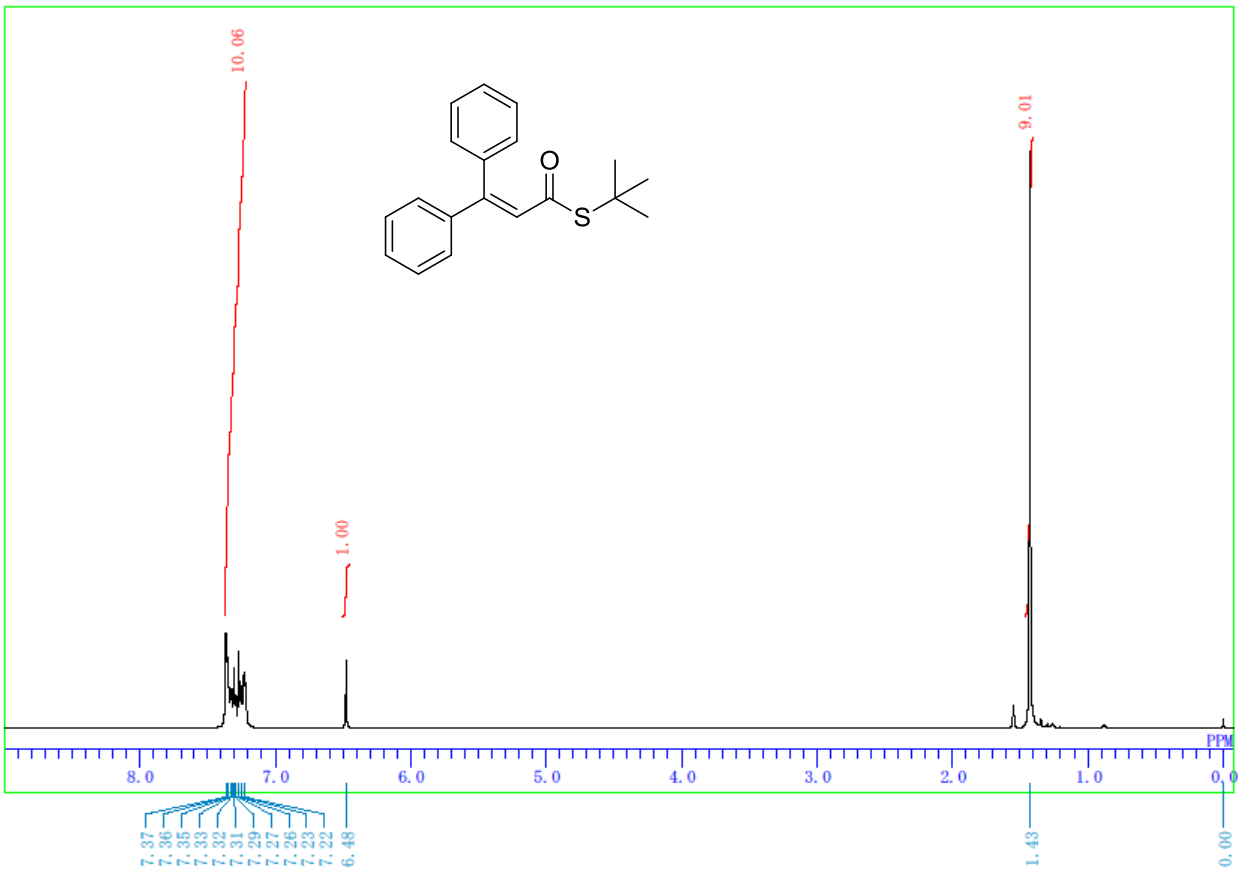
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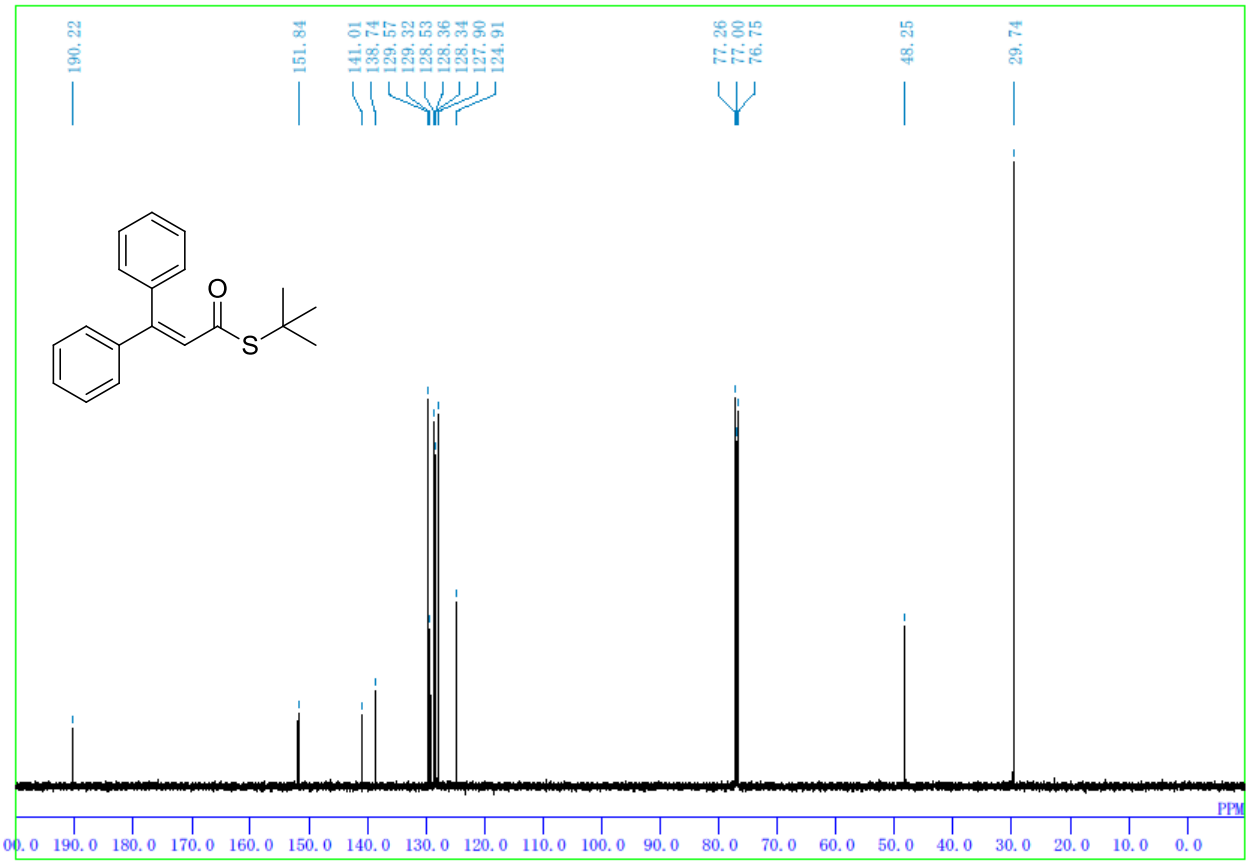
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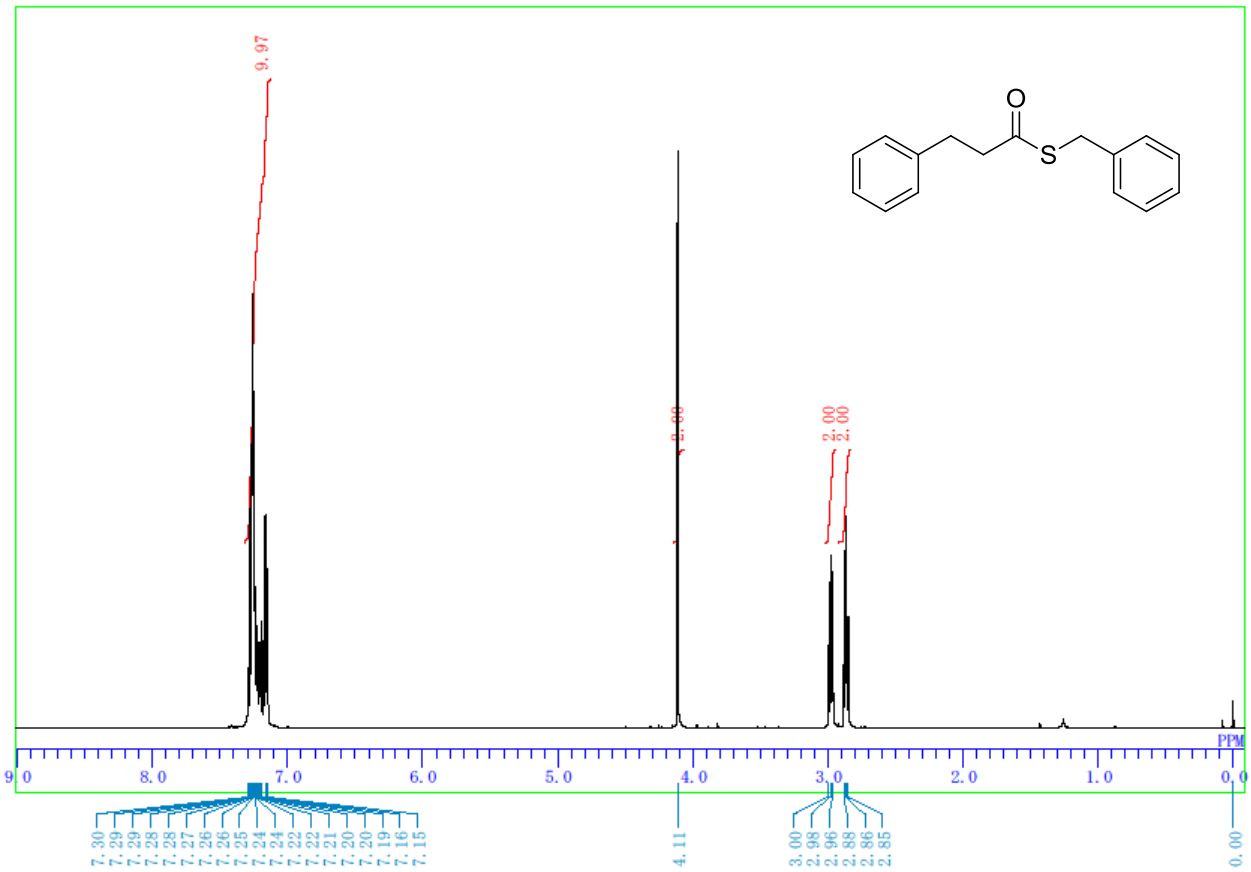
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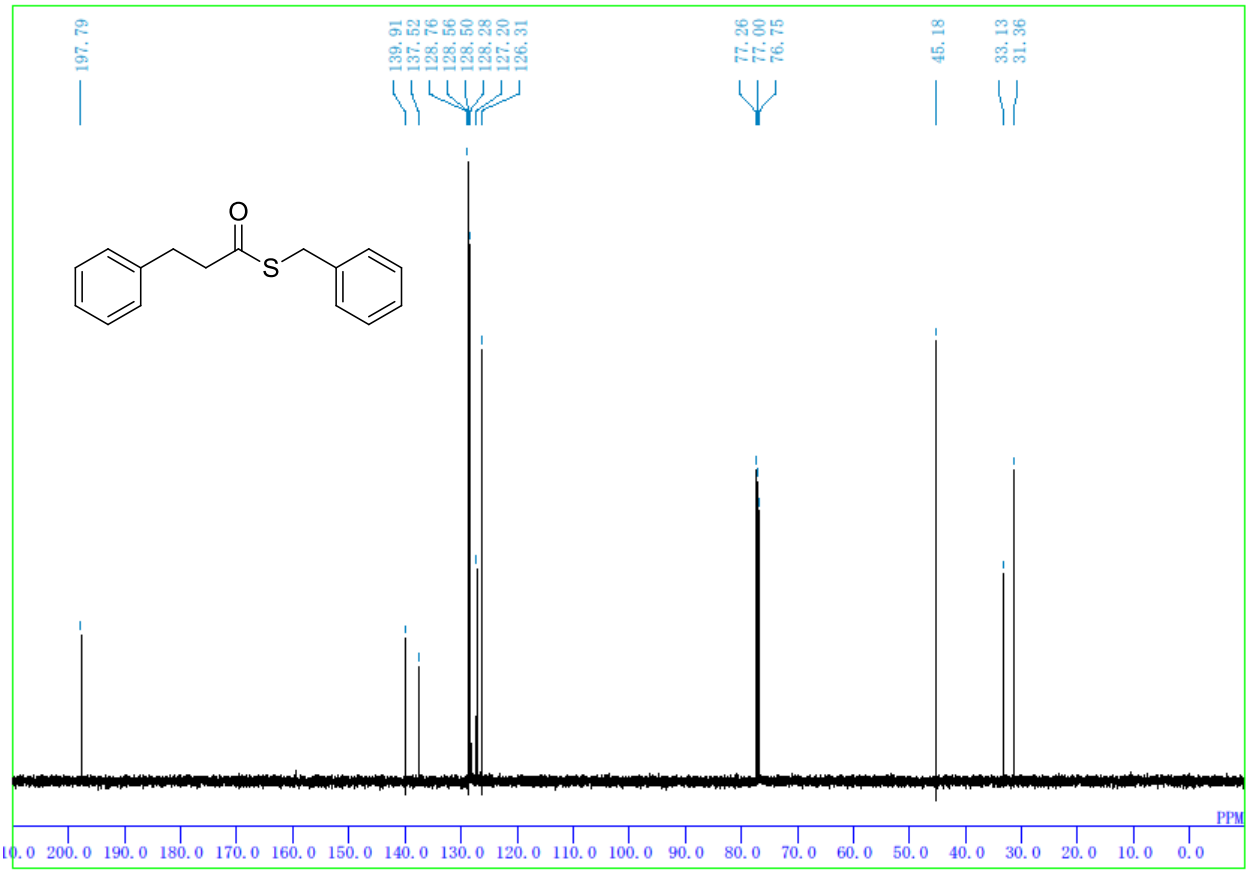
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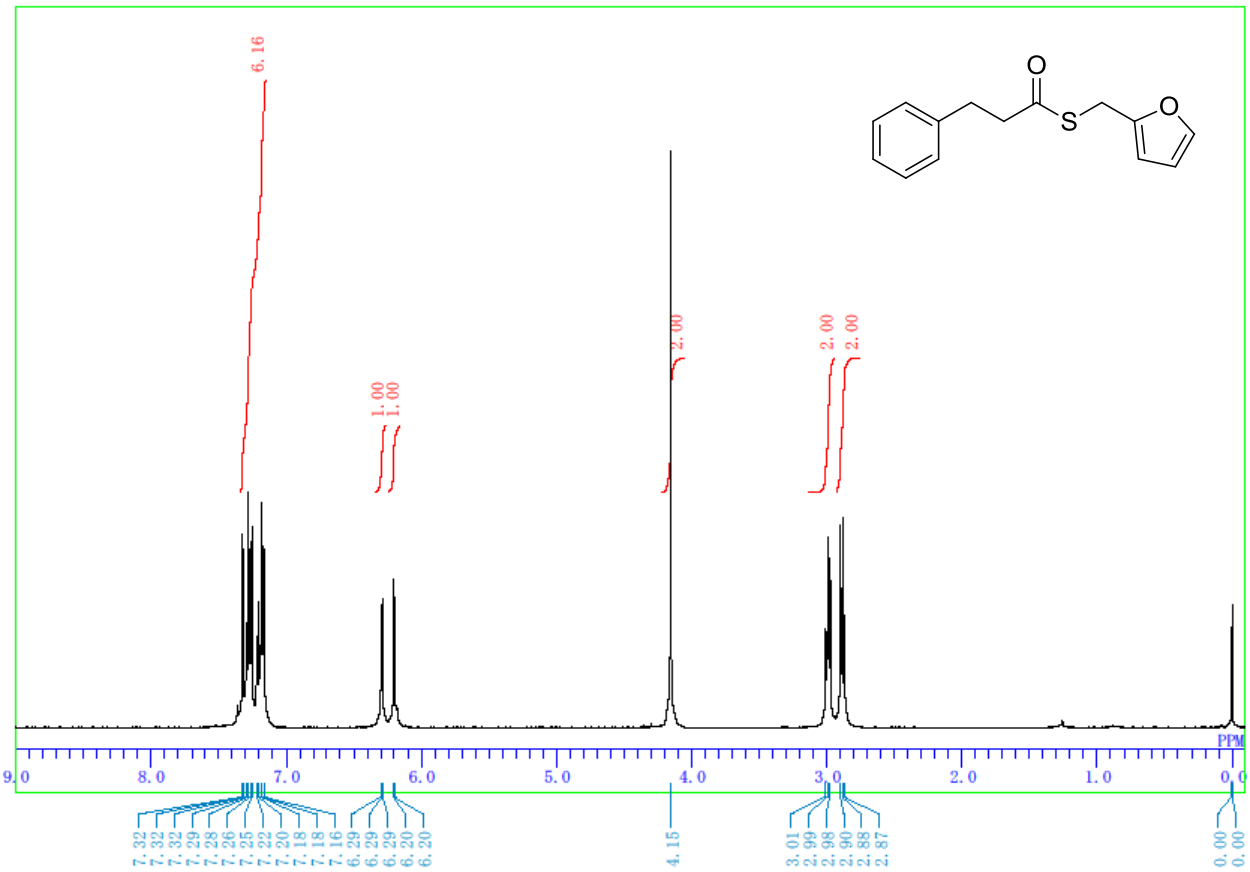
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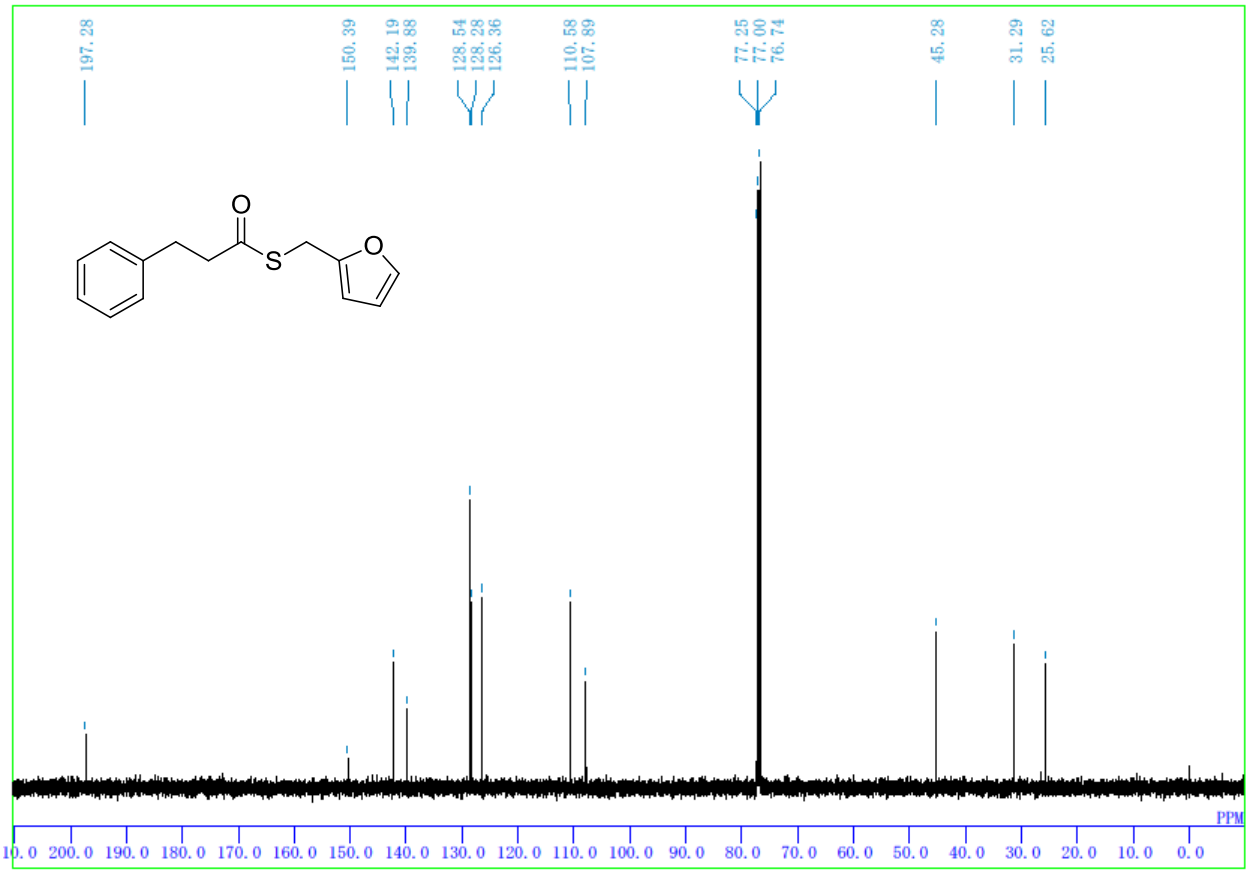
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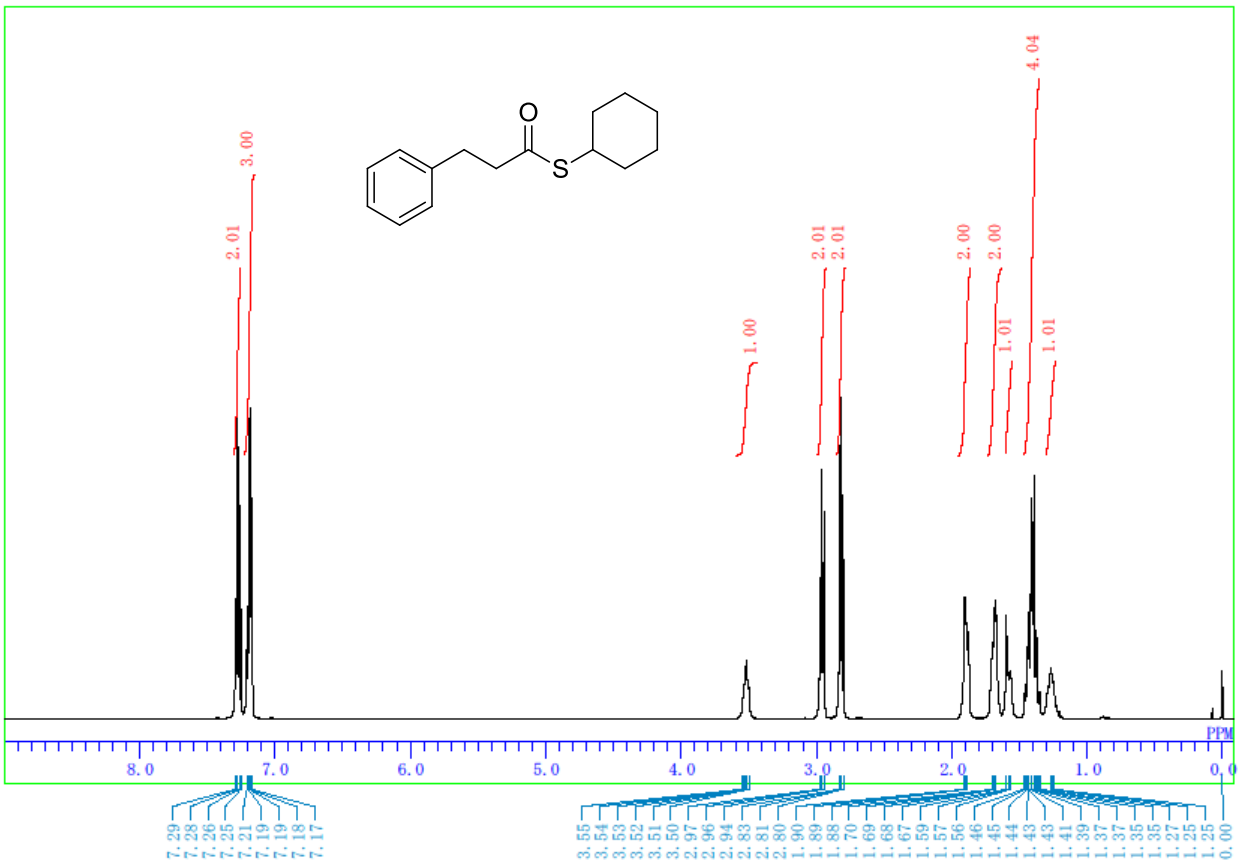
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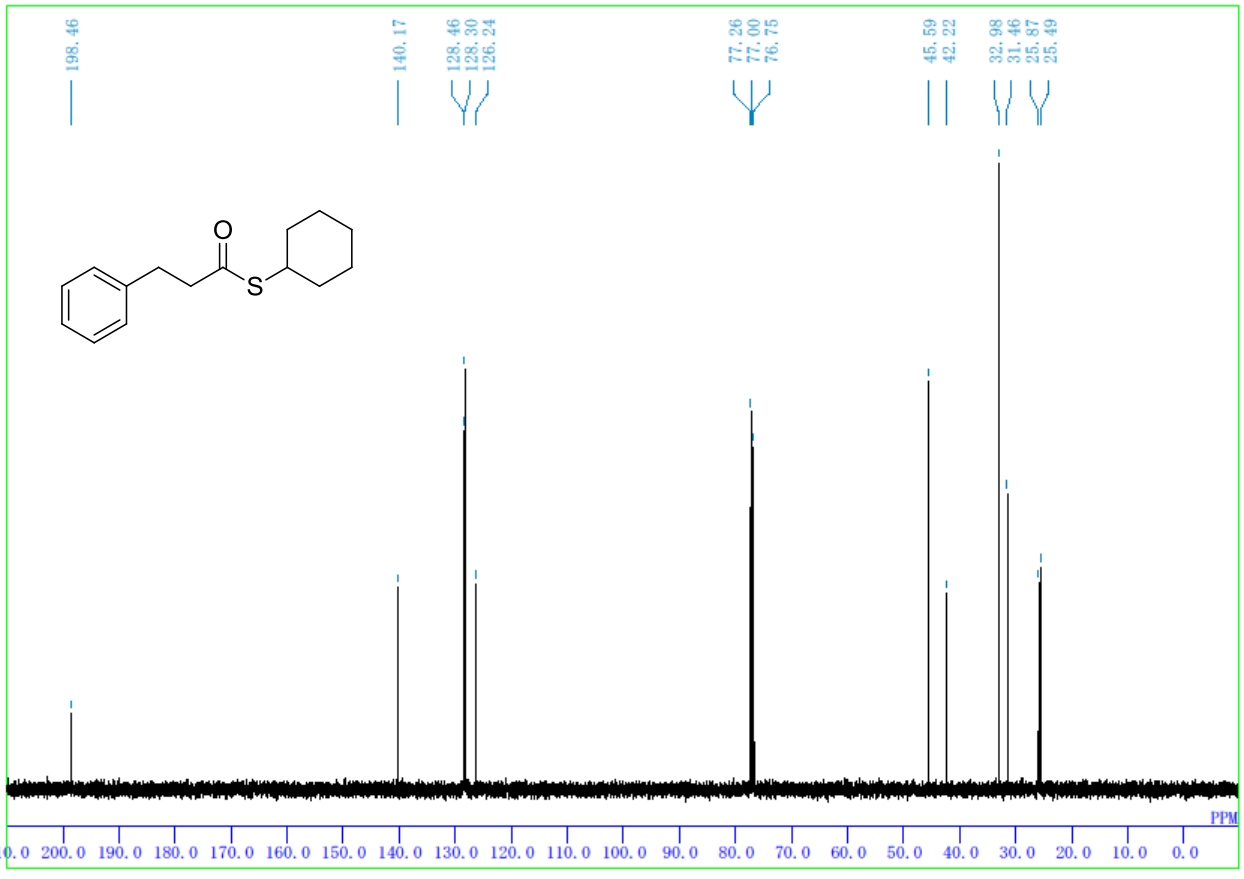
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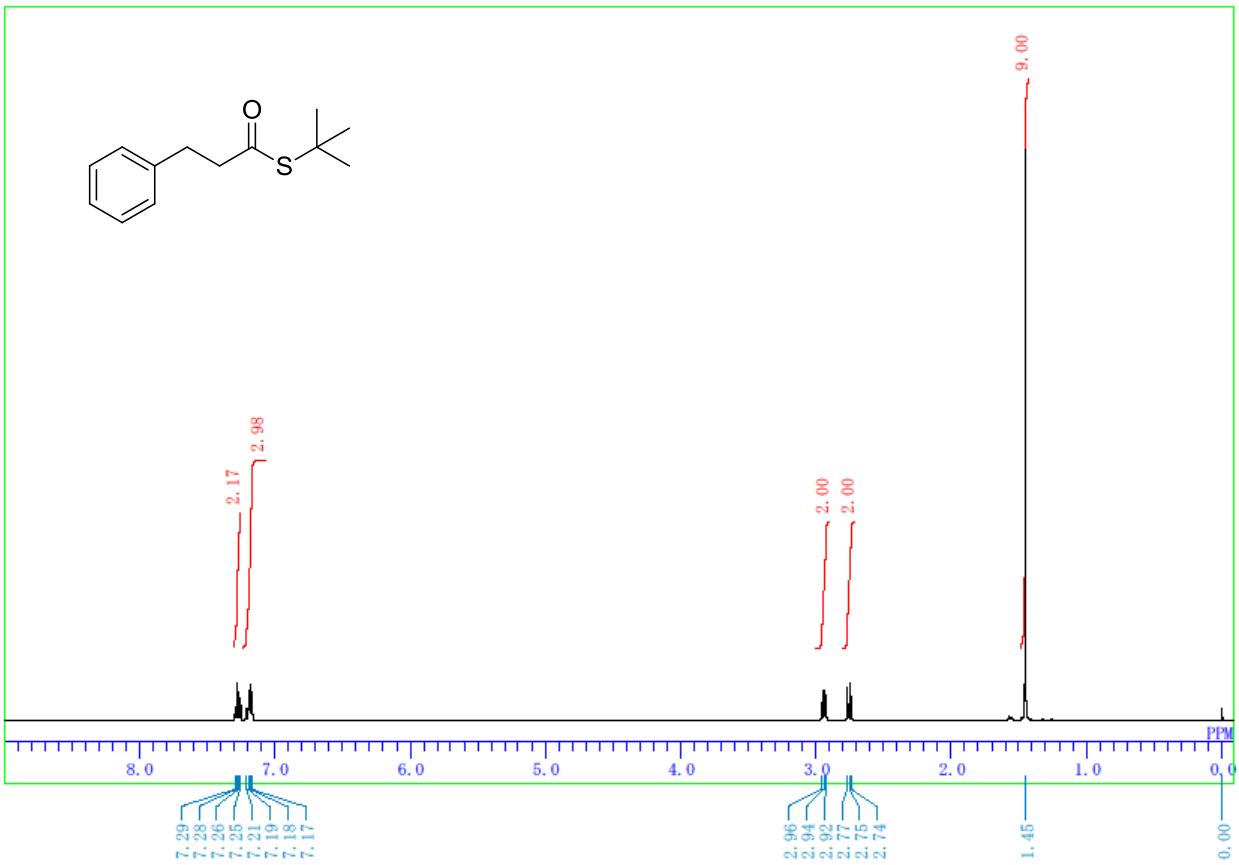
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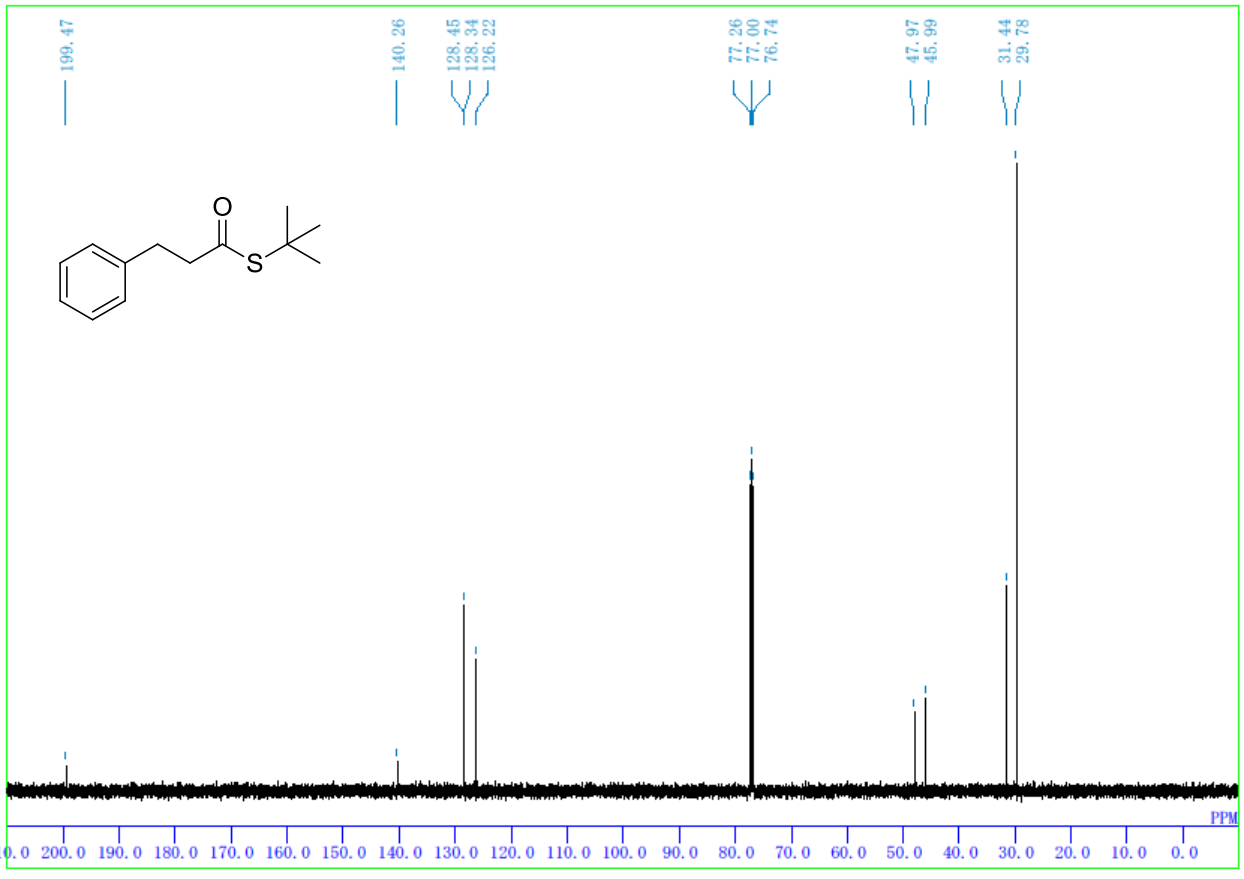
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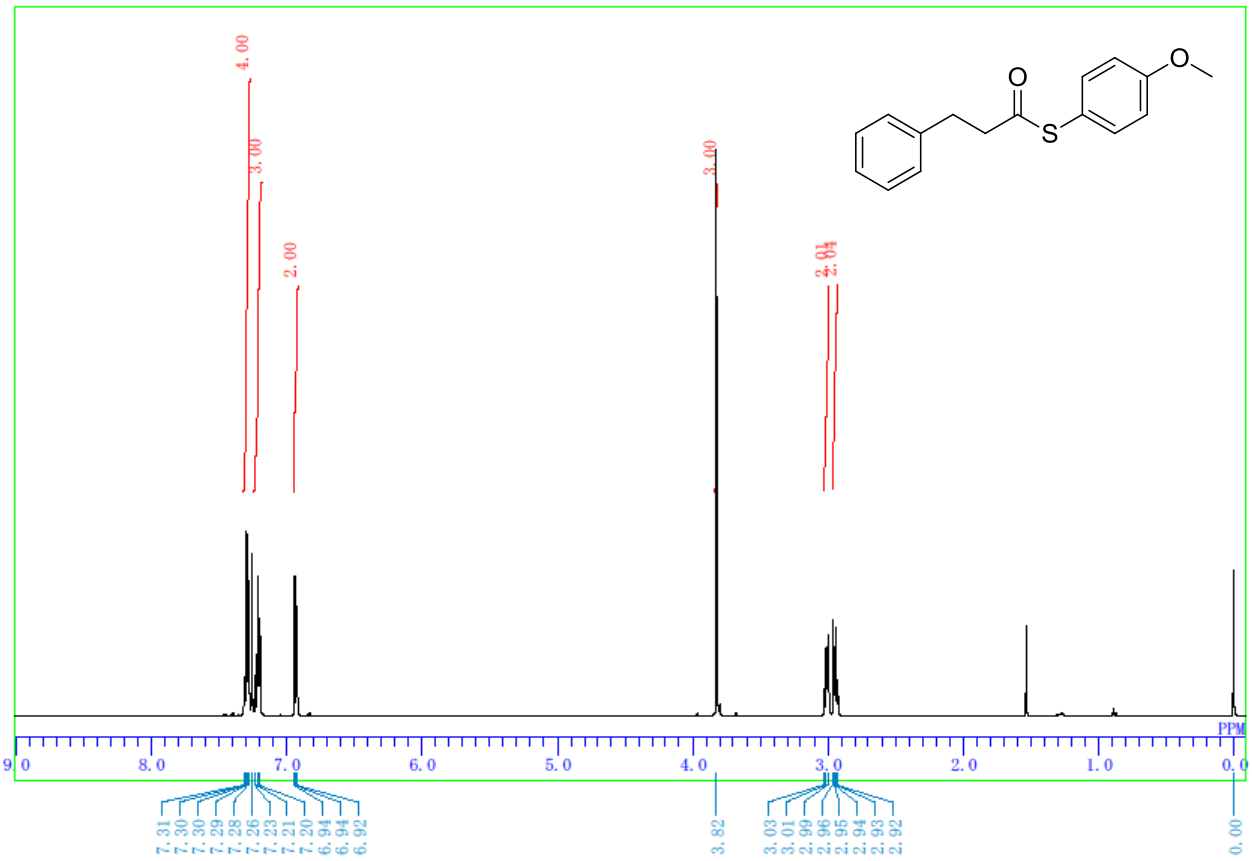
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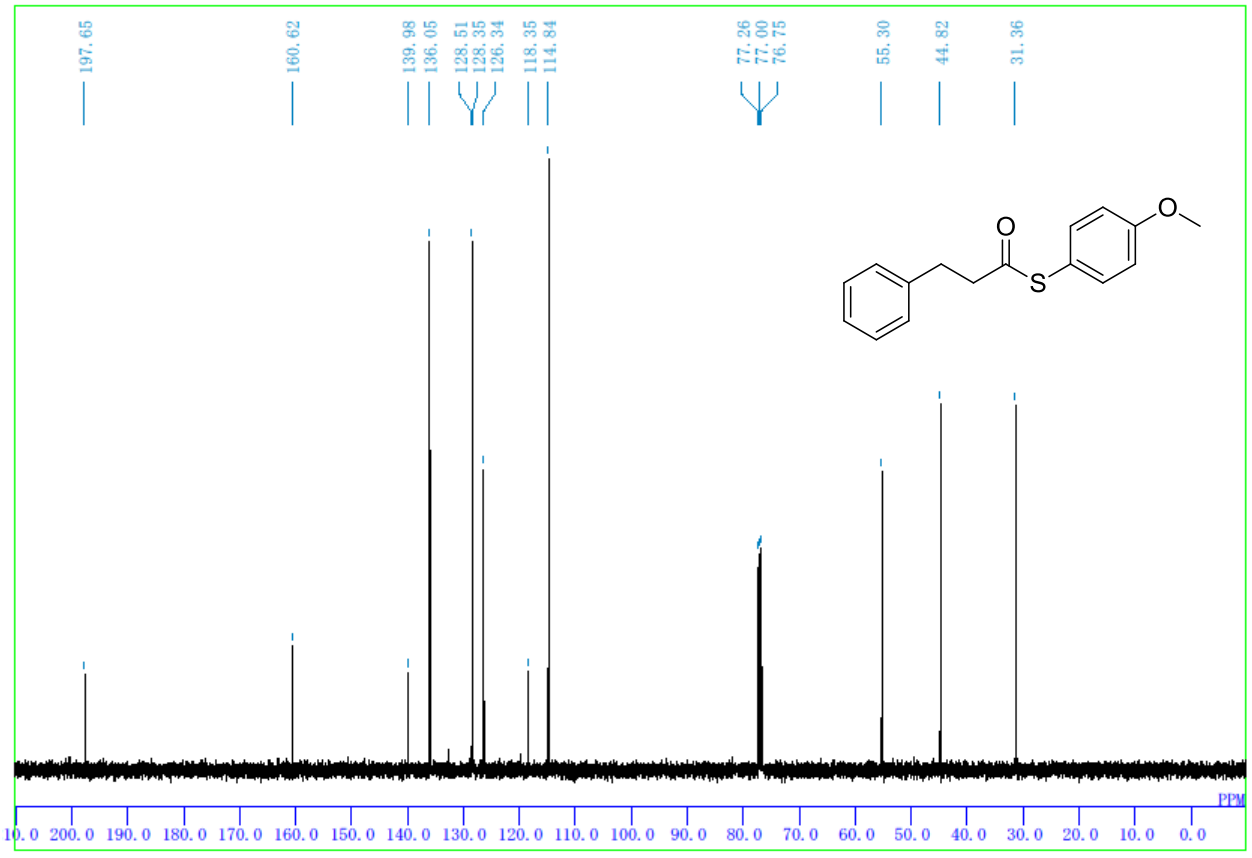
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