Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Metal-Free Thioesterification of Amides Generating Acyl Thioesters

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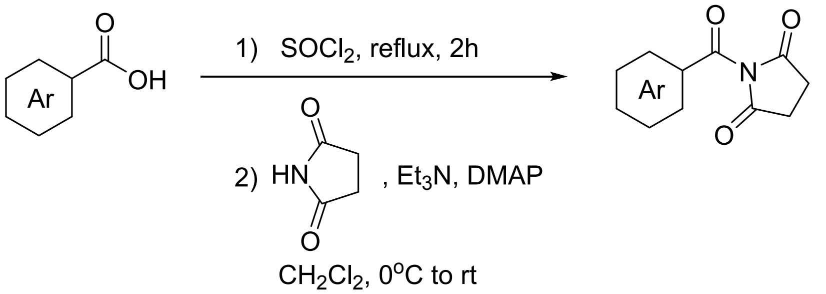
Table of contents

1. General Information

All starting materials reported in the manuscript have been previously described in literature or prepared by the method reported previously. Amides were prepared by standard methods. All products reported in the manuscript have been previously described in literature unless stated otherwise [1-9]. The reactions were carried out in schlenk tubes of 25 mL under air/ N_2 atmosphere. Reagents were used as received unless otherwise noted, and solvents were purified according to standard operation procedures. Column chromatography was performed using Silica Gel 60 (200–300 mesh). The reactions were monitored by GC and GC-MS, GC-MS results were recorded on GC-MS QP2010, and GC analysis was performed on GC 2014. The ^1H, and ^{13}C NMR spectra were recorded on a Brucker ADVANCE III spectrometer at 400 MHz, and 100 MHz respectively, and chemical shifts were reported in parts per million (ppm). The electron ionization (EI) method was used as the ionization method for the HRMS measurement, and the mass analyzer type is TOF for EI. All solvents and reagents were purchased from Energy Chemical, Alfa Aesar, and Aladdin.

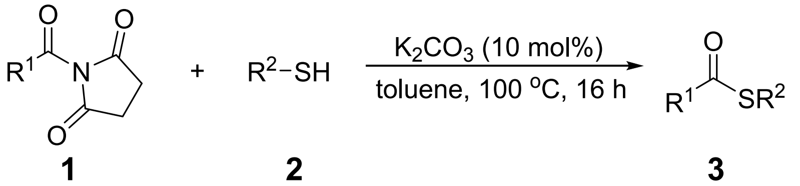
2. Experimental Procedure

2.1 Preparation of the Starting Materials



Thionyl chloride (9 mL) was added to the carboxylic acid (1.0 equiv, 10.0 mmol) and the mixture was refluxed for 2 h. After cooling down to room temperature, the resulting solution was concentrated under *vacuo* to provide the corresponding acyl chloride. An oven-dried Schlenk flask (100 mL) equipped with a stirring bar was charged with Succinimide (10 mmol, 1.0 equiv) and *N*,*N*-dimethyl-4-aminopyridine (0.25 equiv, 2.5 mmol). The reaction flask was then placed under argon atmosphere and subjected to evacuation/backfilling for 3 cycles under high vacuum. Dry dichloromethane (50 mL) was added into the flask which was cooled to 0 °C. Triethylamine (2.0 equiv, 20.0 mmol) was transferred into the reaction mixture followed by slow addition of acyl chloride with vigorous stirring at 0 °C. The reaction mixture was stirred at room temperature overnight. After completion, the reaction mixture was diluted with Et_2O (20 mL) and filtered. The organic layer was washed with HCl (1.0 M, 30 mL), brine (30 mL), dried over anhydrous $MgSO_4$, and concentrated under *vacuo*. The crude product was purified by column chromatography over silica gel (200-300 mesh) using petroleum ethyl acetate/ether as an eluent to give analytically pure product.

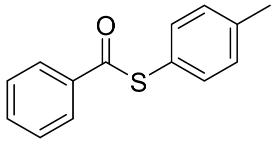
2.2 General Experimental Procedure for the Synthesis of Thioester.



In an oven dried 25 mL Schlenk tube charged with amides **1** (0.2 mmol), Thiophenol **2** (0.24 mmol, 1.2 equiv) and K_2CO_3 (0.02 mmol, 10 mol %). Subsequently, toluene (2 mL) was added under air/ N_2. The reaction mixture was reacted at 100 °C for 16 h. After completion of the reaction, the reaction mixture was concentrated under vacuum. The desired product was isolated by column chromatography over silica gel (200-300 mesh) using ethyl acetate /petroleum ether as an eluent.

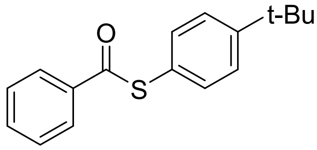
3. Characterization Data for the Products

S-(*p*-tolyl) benzothioate (3a)



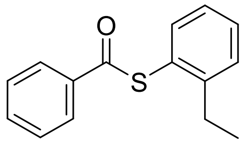
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 96% yield (43.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.53 (dd, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 139.8, 136.7, 135.1, 133.6, 130.1, 128.7, 127.5, 123.8, 21.4. MS (EI): m/z = 228.1. This compound is known.[1]

S-(4-(tert-butyl)phenyl) benzothioate (3b)



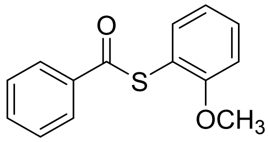
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 72% yield (38.9 mg). mp: 78–79 °C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.2 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.55-7.49 (m, 6H), 1.41 (s,9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 152.8, 136.8, 134.7, 133.6, 128.8, 127.5, 126.4, 123.9, 34.8, 31.3. MS (EI): m/z = 270.1.

S-(2-ethylphenyl) benzothioate (3c)



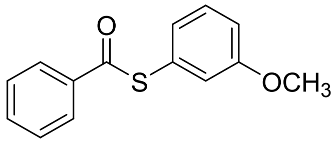
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with PE/ EA (50/1) to afford colorless liquid in 95% yield (46.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.54-7.40 (m, 5H), 7.31 (t, *J* = 7.4 Hz, 1H), 2.84-2.79 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.1, 148.2, 137.0, 136.8, 133.6, 130.5, 129.3, 128.8, 127.6, 126.8, 126.1, 27.6, 15.2. MS (EI): m/z = 242.1

S-(2-methoxyphenyl) benzothioate (3d)



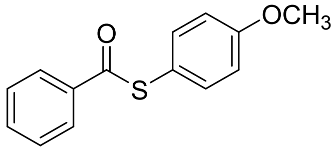
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with PE/ EA (50/1) to afford a white solid in 90% yield (43.9 mg). mp: 107–109 °C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.42-7.36 (m, 4H), 6.98-6.93 (m, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.3, 159.8, 137.3, 136.8, 133.5, 131.8, 128.7, 127.6, 121.2, 115.4, 111.7, 56.1. MS (EI): m/z = 244.1.

S-(3-methoxyphenyl) benzothioate (3e)



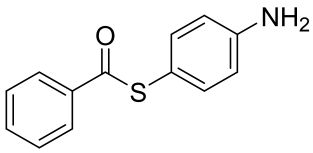
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with PE/ EA (50/1) to afford a white solid in 91% yield (44.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 2.0 Hz, 1H), 7.00-6.98 (m, 1H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.1, 160.0, 136.7, 133.7, 130.0, 128.8, 128.3, 127.5, 127.3, 120.1, 115.8, 55.4. MS (EI): m/z = 244.1. This compound is known. [2]

S-(4-methoxyphenyl) benzothioate (3f)



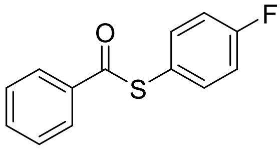
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with PE/ EA (50/1) to afford a white solid in 88% yield (42.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.2 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.53 (dd, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 160.8, 136.6, 133.6, 128.7, 127.5, 117.9, 115.0 , 55.4. MS (EI): m/z = 244.1. This compound is known. [1]

S-(4-aminophenyl) benzothioate (3g)



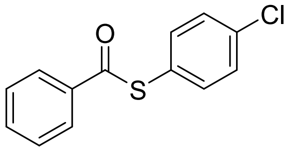
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with PE /EA (2/1) to afford a white solid in 71% yield (32.5 mg). mp: 113–115 °C ; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.95 (d, *J* = 7.2, 2H), 7.71 (t, *J* = 7.8,1H), 7.58 (dd, *J* = 7.6, 2H), 7.16 (d, *J* = 8.4, 2H), 6.73 (d, *J* = 8.4, 2H), 3.53 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 191.8, 148.0, 136.8, 136.5, 133.4, 128.7, 127.4, 115.7, 114.5. MS (EI): m/z = 229.1.

S-(4-fluorophenyl) benzothioate (3h)



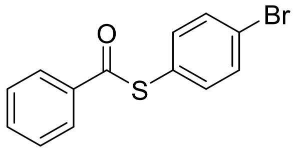
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 84% yield (39.0 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.08 (d, *J* = 7.2 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.56-7.52 (m,4H), 7.21 (dd, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 190.06, 163.65 (d, $J_{C\text{-}F}$ = 248.6 Hz), 137.20 (d, $J_{C\text{-}F}$ = 8.5 Hz), 136.4, 133.8, 128.84, 127.5, 122.7 (d, $J_{C\text{-}F}$ = 3.3 Hz), 116.6 (d, $J_{C\text{-}F}$ = 21.9 Hz). MS (EI): m/z = 232.1. This compound is known. [1]

S-(4-chlorophenyl) benzothioate (3i)



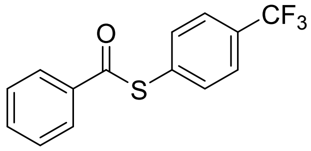
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 87% yield (43.2 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.06 (d, *J* = 8.8Hz, 2H), 7.67 (t, *J* = 7.4Hz, 1H), 7.55 (d, *J* = 7.6Hz, 2H), 7.51-7.47 (m, 4H); ^{13}C NMR (100MHz, CDCl$_3$): δ 189.6, 136.3, 136.0, 133.9, 129.5, 128.8, 127.5, 125.9. MS (EI): m/z = 248.0. This compound is known. [1]

S-(4-bromophenyl) benzothioate (3j)



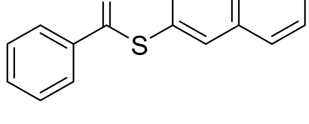
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 83% yield (48.5 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.06 (d, *J* = 7.2 Hz, 2H), 7.69-7.63 (m, 3H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 189.4, 136.5, 136.4, 133.9, 132.5, 128.8, 127.5, 126.5, 124.3. MS (EI): m/z = 292.0. This compound is known. [1]

S-(4-(trifluoromethyl)phenyl) benzothioate (3k)



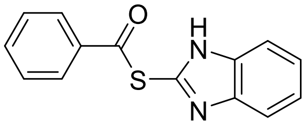
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 87% yield (49.1 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.07 (d, *J* = 7.2 Hz, 2H), 7.77-7.67 (m, 5H), 7.55 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 188.9, 136.2, 135.2, 134.1, 132.2, 131.5(q, J_{C-F} = 32.6 Hz, J_{C-F} = 65.2 Hz), 128.9, 127.6, 126.0(q, J_{C-F} = 3.5 Hz, J_{C-F} = 7.2 Hz),123.8(q, J_{C-F} = 270.9 Hz, J_{C-F} = 541.7 Hz). MS (EI): m/z = 282.1. This compound is known. [2]

S-(naphthalen-2-yl) benzothioate (3l)



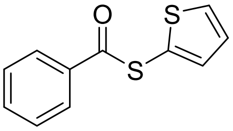
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 89% yield (47.0 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.11 (d, *J* = 7.2 Hz, 3H), 7.98-7.89 (m, 3H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.61-7.54 (m,5H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 190.4, 136.7, 135.0, 133.7, 133.7, 133.5, 131.4, 128.9, 128.8, 128.0, 127.9, 127.5, 127.2, 126.6, 124.7. MS (EI): m/z = 264.1. This compound is known. [1]

S-(1H-benzo[d]imidazol-2-yl) benzothioate (3m)



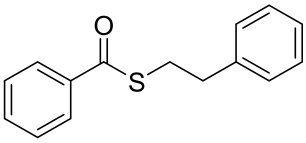
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with PE /EA (2/1) to afford a white solid in 62% yield (31.5 mg). mp: 187–189 °C ; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 13.25 (s, 1H), 7,84 (d, *J* = 7.6 Hz, 2H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.55 (dd, *J* = 7.8 Hz, 2H), 7.32-7.19 (m,4H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 170.0, 169.7, 135.0, 132.9, 132.3, 132.0, 131.04, 129.3, 125.1, 123.6, 111.9, 110.6. MS (EI): m/z = 254.1.

S-(thiophen-2-yl) benzothioate (3n)



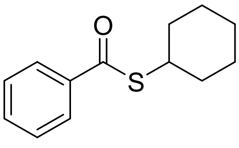
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 79% yield (34.8 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.08-8.06 (m, 2H), 7.69-7.65 (m, 2H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.32-7.30 (m, 1H), 7.23-7.20 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 189.8, 136.4, 136.0, 134.0, 132.2, 128.9, 128.0, 127.6, 124.2. MS (EI): m/z = 220.0. This compound is known. [3]

S-phenethyl benzothioate (3o)



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford colorless liquid in 95% yield (46.0 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.88 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.35 (dd, *J* = 7.6 Hz, 2H), 7.25-7.13 (m, 5H), 3.23 (t, *J* = 7.8 Hz, 2H), 2.89 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 191.8, 140.1, 137.2, 133.4, 128.7, 128.6, 128.6, 127.2, 126.6, 36.0, 30.5. MS (EI): m/z = 242.0. This compound is known. [4]

S-cyclohexyl benzothioate (3p)

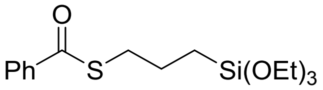


The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford colorless liquid in 93% yield (40.9 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.88 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.36 (dd, *J* = 7.8 Hz, 2H), 3.68-3.63 (m, 1H), 1.97-1.94 (m, 2H), 1.73-1.67 (m, 2H), 1.50-1.18 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 191.9, 137.5, 133.1, 128.5, 127.1, 42.5, 33.2, 26.0, 25.6. MS (EI): m/z = 220.1. This compound is known. [4]

S-heptyl benzothioate (3q)

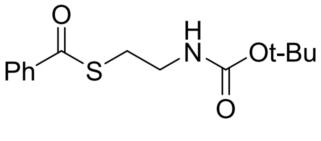
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford colorless liquid in 91% yield (40.4 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.49 (dd, *J* = 7.8 Hz, 2H), 3.12 (t, *J* = 7.4 Hz, 2H), 1.76-1.68 (m, 2H), 1.51-1.44 (m, 2H), 1.38-1.34 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 192.2, 137.3, 133.2, 128.5, 127.2 , 31.4, 29.5, 29.1, 28.6, 22.5, 14.0. MS (EI): m/z = 222.1. This compound is known. [5]

S-(3-(triethoxysilyl)propyl) benzothioate (3r)



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford colorless liquid in 94% yield (64.3 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.37 (dd, *J* =7.6 Hz, 2H), 3.78-3.73 (m, 6H), 3.04 (t, *J* = 7.4 Hz, 2H), 1.77-1.69 (m, 2H), 1.16 (t, *J* = 6.8 Hz, 9H), 0.71 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 192.0, 137.2, 133.2, 128.5, 127.2, 58.4, 31.9, 23.3, 18.3, 10.1. MS (EI): m/z = 342.0. This compound is known. [6]

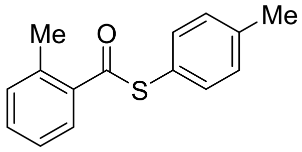
S-(2-((tert-butoxycarbonyl)amino)ethyl) benzothioate (3s)



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with PE /EA (2/1) to afford colorless liquid in 91% yield (51.1 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.50 (dd, *J* = 7.8 Hz, 2H), 4.94 (s, 1H), 3.44 (t, *J* = 6.2

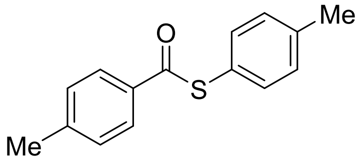
Hz, 2H), 3.26 (t, *J* = 6.4 Hz, 2H), 1.487.63 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 191.7, 155.8, 136.8, 133.5, 128.6, 127.3, 79.5, 40.4, 29.1, 28.4. MS (EI): m/z = 281.1. This compound is known. [7]

S-(p-tolyl) 2-methylbenzothioate (3t)



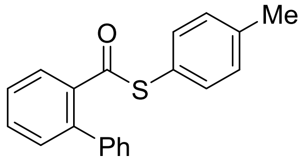
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 84% yield (40.7 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.47 (dd, *J* = 8.6 Hz, 3H), 7.37-7.30 (m, 4H), 2.54 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 192.7, 139.8, 137.4, 136.9, 134.9, 131.9, 131.7, 130.1, 128.6, 125.8, 124.7, 21.4, 20.8. MS (EI): m/z = 242.1. This compound is known. [8]

S-(p-tolyl) 4-methylbenzothioate (3u)



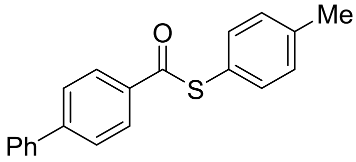
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 90% yield (43.6 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.21-7.18 (m, 4H), 2.35 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 190.1, 144.5, 139.7, 135.1, 134.2, 130.1, 129.4, 127.6, 124.0, 21.7, 21.4. MS (EI): m/z = 242.1. This compound is known. [1]

S-(p-tolyl) [1,1'-biphenyl]-2-carbothioate (3v)



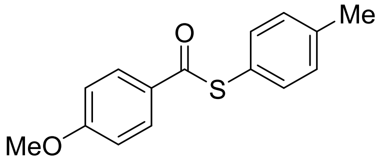
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 85% yield (51.7 mg). mp: 92–94 °C ; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.81 (d, *J* = 8.4 Hz, 1H), 7.62 (t, *J* = 8.2 Hz, 1H), 7.53-7.44 (m, 7H), 7.31-7.26 (m, 4H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 194.0, 140.4, 140.1, 139.7, 138.5, 134.4, 131.2, 130.8, 130.1, 129.1, 128.3, 127.8, 127.7, 127.3, 124.5, 21.4. MS (EI): m/z = 304.1.

S-(p-tolyl) [1,1'-biphenyl]-4-carbothioate (3w)



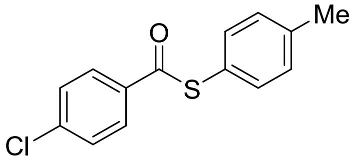
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 71% yield (43.2 mg). mp: 141–143 °C ; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.15 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.54 (dd, *J* = 7.4 Hz, 2H), 7.48-7.46 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.47 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 190.1, 146.3, 139.8, 139.8, 135.4, 135.1, 130.1, 129.0, 128.3, 128.0, 127.4, 127.3, 123.8, 21.4. MS (EI): m/z = 304.1.

S-(p-tolyl) 4-methoxybenzothioate (3x)



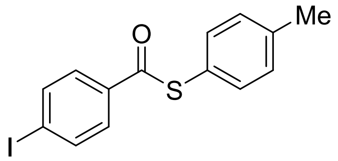
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 81% yield (41.8 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.99 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 3.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 189.0, 164.0, 139.7, 135.2, 130.1, 129.7, 129.5, 124.1, 113.9, 55.6, 21.4. MS (EI): m/z = 258.1. This compound is known. [1]

S-(p-tolyl) 4-chlorobenzothioate (3y)



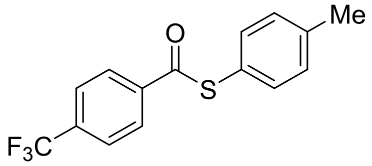
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 79% yield (41.4 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 189.5, 140.0, 140.0, 135.1 135.0, 130.2, 129.1, 128.8, 123.4, 21.4. MS (EI): m/z = 262.1. This compound is known. [1]

S-(p-tolyl) 4-iodobenzothioate (3z)



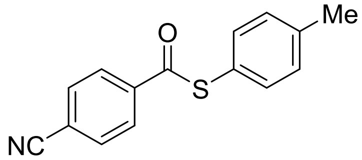
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 76% yield (53.8 mg). mp: 116–117 °C ; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.15 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 189.6, 140.4, 139.9, 134.9, 132.6, 130.3, 127.9, 122.6, 117.8, 117.2, 116.8, 21.4. MS (EI): m/z = 354.0.

S-(p-tolyl) 4-(trifluoromethyl)benzothioate (3aa)



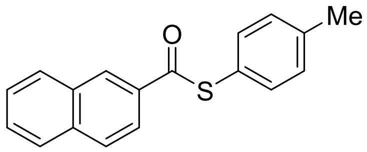
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 82% yield (48.5 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.18 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 189.8, 140.2, 139.5, 134.9 (q, $J_{C\text{-}F}$ = 32.7 Hz, $J_{C\text{-}F}$ = 65.3 Hz), 134.9, 130.3, 127.8, 126.7 (q, $J_{C\text{-}F}$ = 207.3 Hz, $J_{C\text{-}F}$ = 601.0 Hz), 125.8 (q, $J_{C\text{-}F}$ = 3.2 Hz, $J_{C\text{-}F}$ = 6.8 Hz), 123.0, 21.4. MS (EI): m/z = 296.1. This compound is known. [1]

S-(p-tolyl) 4-cyanobenzothioate (3ab)



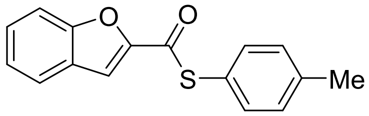
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 77% yield (39.0 mg). mp: 120–121 °C ; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 190.0, 140.0, 138.0, 136.4, 135.0, 130.2, 128.8, 123.26, 101.3, 21.4. MS (EI): m/z = 253.1.

S-(p-tolyl) naphthalene-2-carbothioate (3ac)



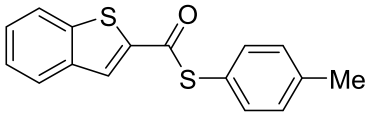
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 95% yield (50.4 mg). mp: 120–121 °C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 1H), 8.09-8.06 (m, 2H), 7.95 (dd, J = 8.2 Hz, 2H), 7.69-7.61 (m, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5, 139.8, 135.9, 135.1, 134.0, 132.5, 130.1, 129.6, 129.0, 128.6, 128.6, 127.9, 127.0, 123.9, 123.3, 21.4. MS (EI): m/z = 265.0.

S-(p-tolyl) benzofuran-2-carbothioate (3ad)



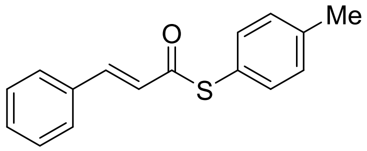
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a yellow solid in 55% yield (29.5 mg). mp: 101–103 °C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 7.6 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.66 (s, 1H), 7.56 (dd, J = 8.0 Hz, 1H), 7.49 (d, J = 2.0 Hz, 2H), 7.40 (dd, J = 7.6 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.0, 155.6, 150.8, 140.2, 135.0, 130.2, 128.2, 127.0, 124.1, 123.2, 122.4, 112.5, 111.7, 21.4. MS (EI): m/z = 268.1.

S-(p-tolyl) benzo[b]thiophene-2-carbothioate (3ae)



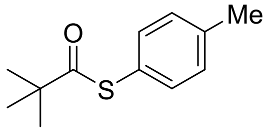
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 71% yield (40.3 mg). mp: 127–129 °C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.98-7.92 (m, 2H), 7.55-7.47 (m, 4H), 7.33 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.9, 142.0, 140.9, 140.1, 138.7, 135.0, 130.2 128.6, 127.4, 125.9, 125.2, 123.1, 122.9, 21.4. MS (EI): m/z = 284.1.

S-(p-tolyl) (E)-3-phenylprop-2-enethioate (3af)



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 60% yield (30.5 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.72 (d, *J* = 16.0 Hz, 1H), 7.62-7.60 (m, 2H), 7.46-7.41 (m, 5H), 7.31 (d, *J* = 2.0 Hz, 2H), 6.84 (d, *J* = 15.6 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 188.5, 141.4, 139.8, 134.6, 134.1, 130.7, 130.1, 129.0, 128.5, 124.2, 124.1, 21.4. MS (EI): m/z = 254.1. This compound is known. [8]

S-(p-tolyl) 2,2-dimethylpropanethioate (3ag)



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford colorless liquid in 96% yield (39.9 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 205.0, 139.3, 134.9, 129.9, 124.6, 46.9, 27.5, 21.3. MS (EI): m/z = 208.1. This compound is known. [9]

4. References

[1] H. Cao, L. McNamee and H. Alper. *J. Org. Chem.* **2008**, *73*, 3530.

[2] Z. Qiao and X. Jiang. *Org. Lett.* **2016**, *18*, 1550.

[3] G. Rong, J. Mao, D. Liu, H. Yan, Y. Zheng and J. Chen. *RSC Adv.*, **2015**, *5*, 26461.

[4] J. Chung, U. R. Seo, S. Chun and Y. K. Chung. *ChemCatChem*. **2016**, *8*, 318.

[5] H. K. Moon, G. H. Sung, B. R. Kim, J. K. Park, Y.-J. Yoon and H. J. Yoon. *Adv. Synth. Catal*. **2016**, *358*, 1725.

[6] R. W. Cruse, R. J. Pickwell, E. R. Pohl and K. J. Weller. U.S. Pat. Appl. Publ., 20040210001, 2004.

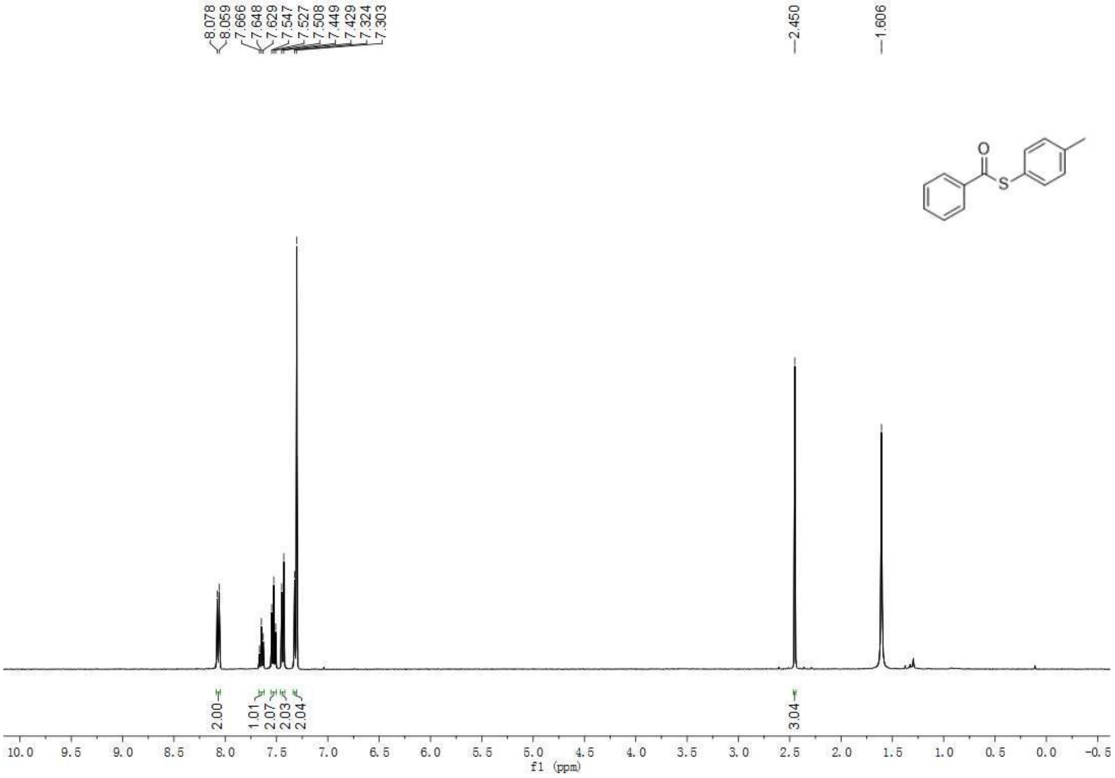
[7] G.-P. Lu and C. Cai. *Adv. Synth. Catal.* **2013**, *355*, 1271.

[8] R. Wittenberg, J. Srogl, M. Egi and L. S. Liebeskind. *Org. Lett.,* **2003**, *5*, 3033.

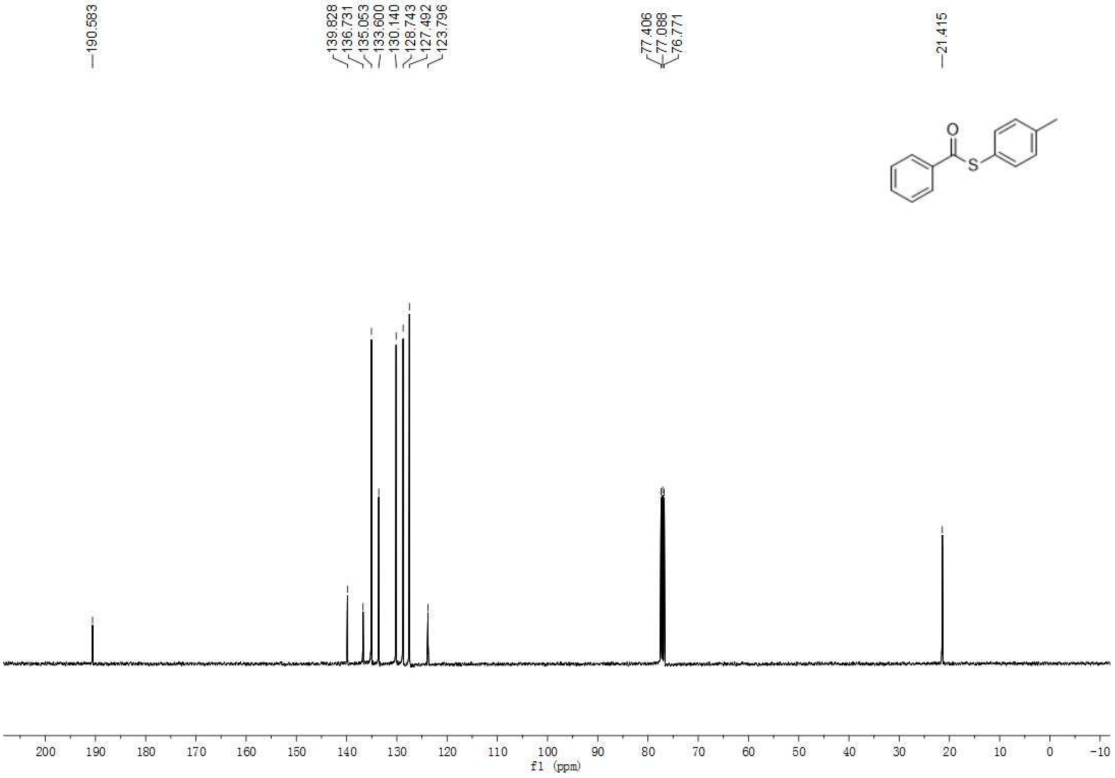
[9] B. Kang and S. H. Hong. *Chem. Sci*., **2017**, *8*, 6613.

5. Copies of ^{1}H, ^{13}C NMR Spectra of the Products

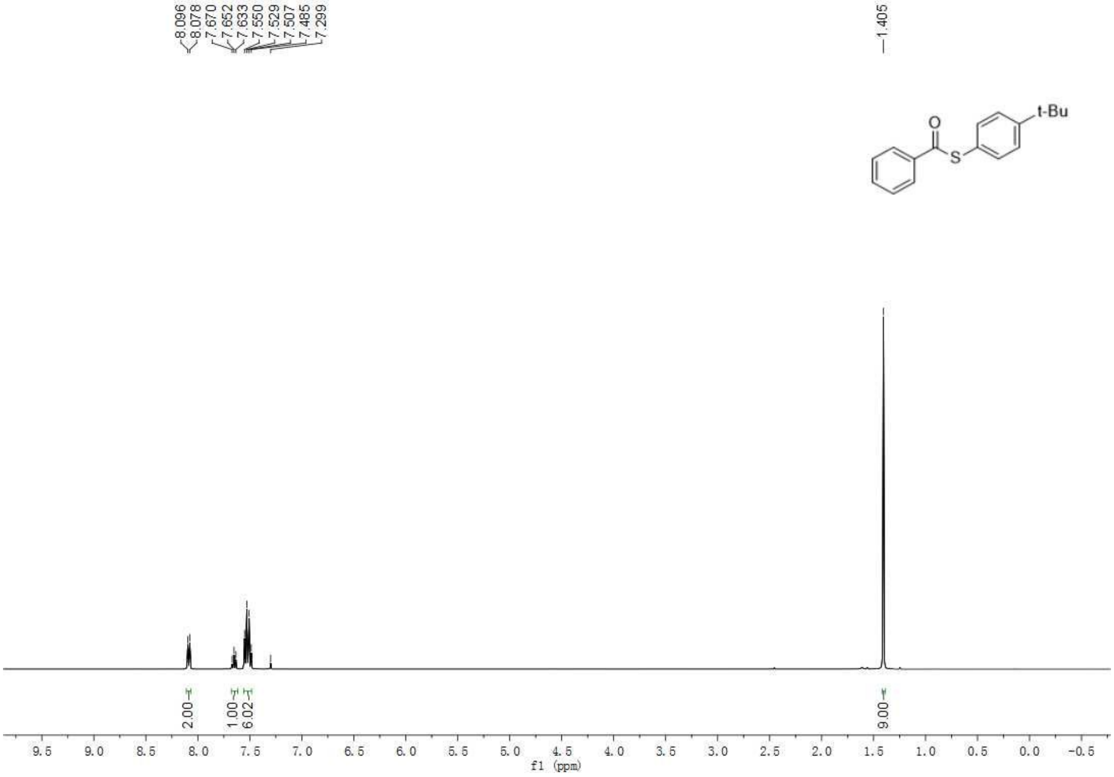
^{1}H NMR Spectrum of S-(p-tolyl) benzothioate **(3a)**



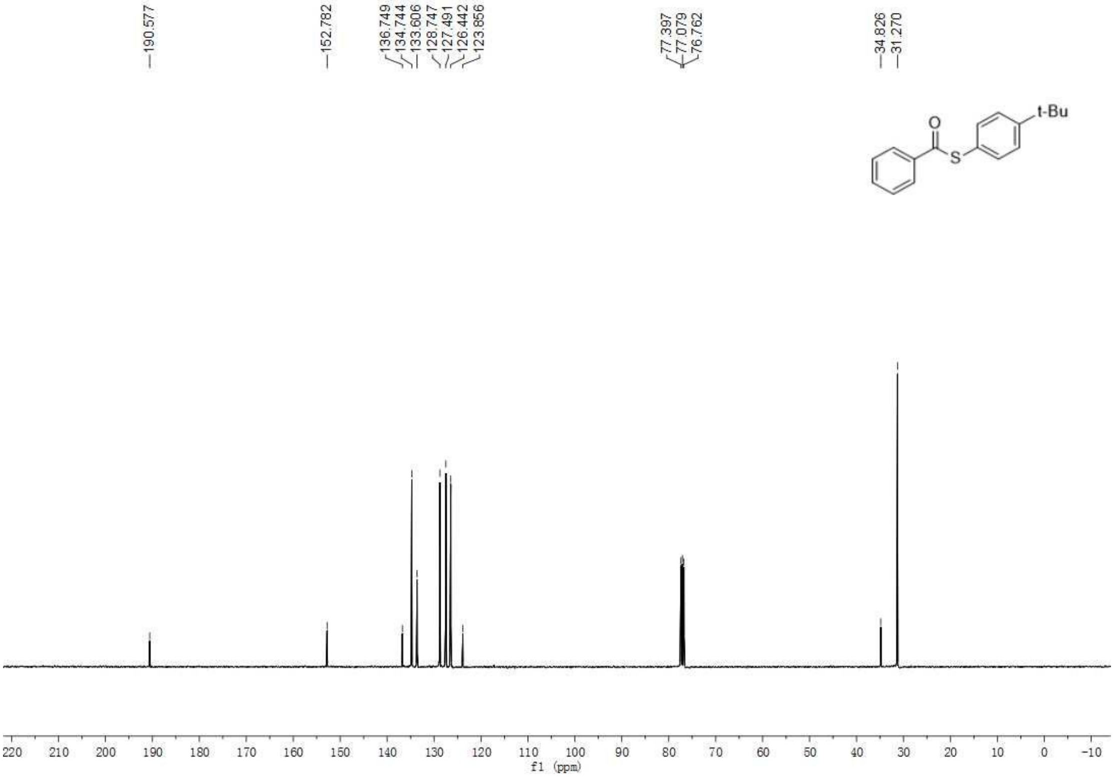
^{13}C NMR Spectrum of S-(p-tolyl) benzothioate **(3a)**



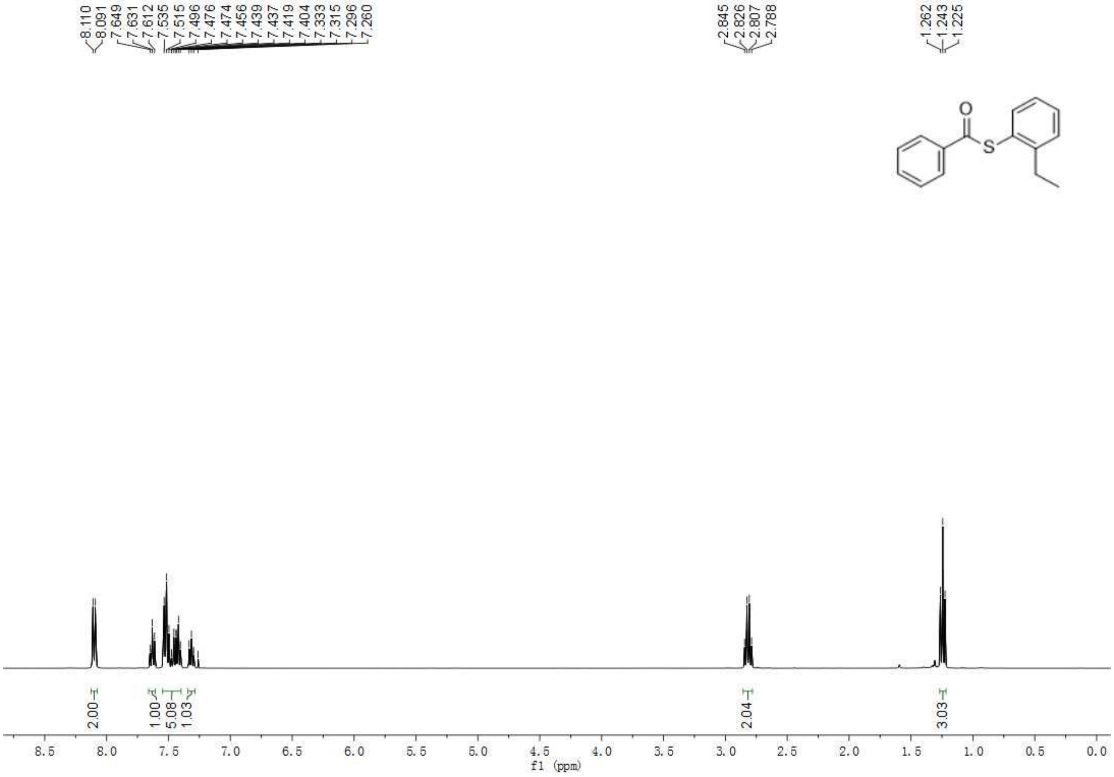
^{1}H NMR Spectrum of S-(4-(tert-butyl)phenyl) benzothioate **(3b)**



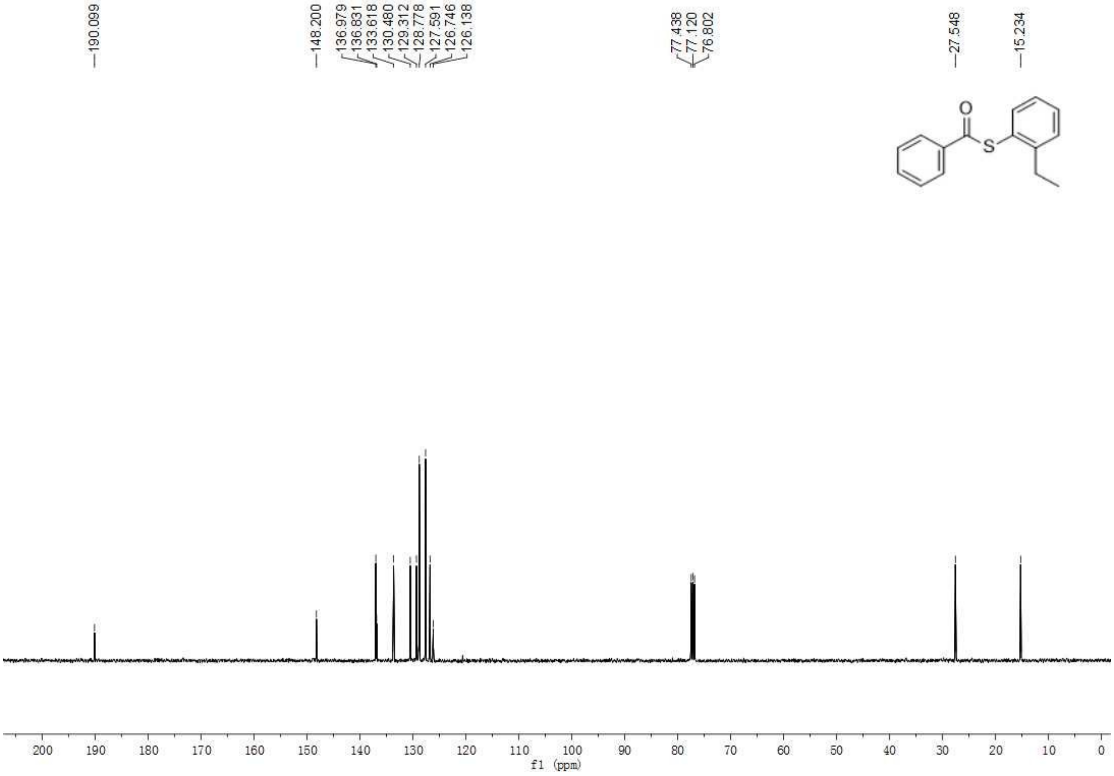
^{13}C NMR Spectrum of S-(4-(tert-butyl)phenyl) benzothioate **(3b)**



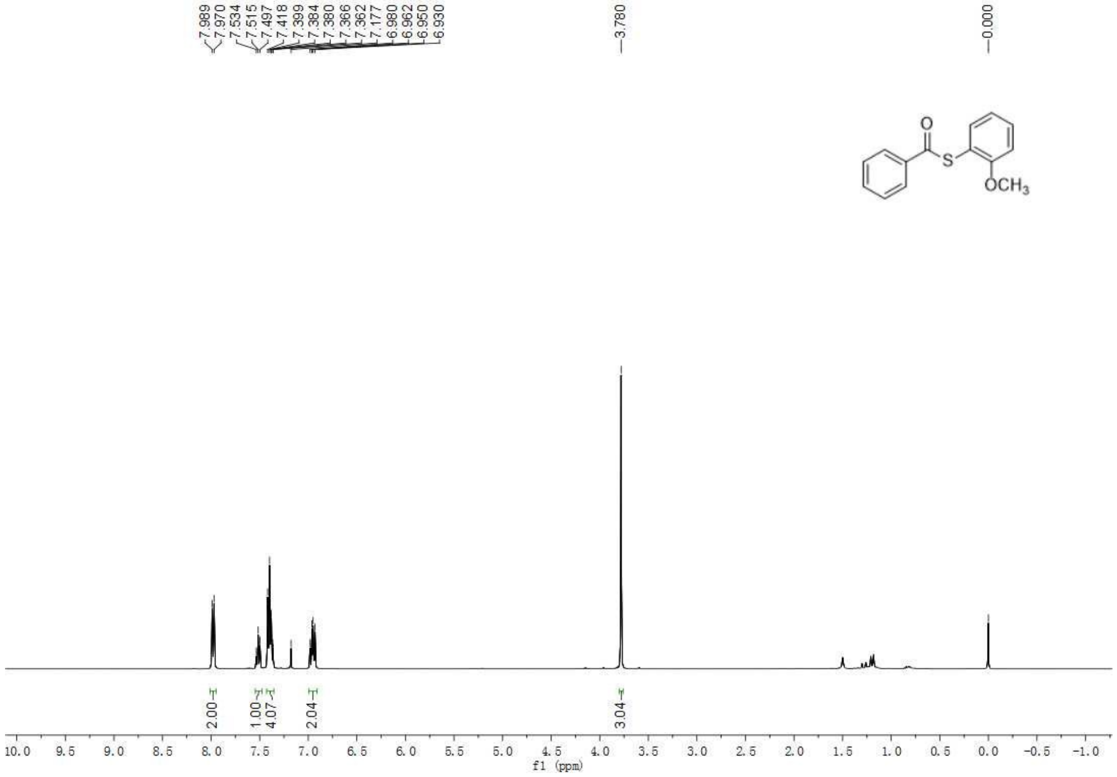
^{1}H NMR Spectrum of S-(2-ethylphenyl) benzothioate **(3c)**



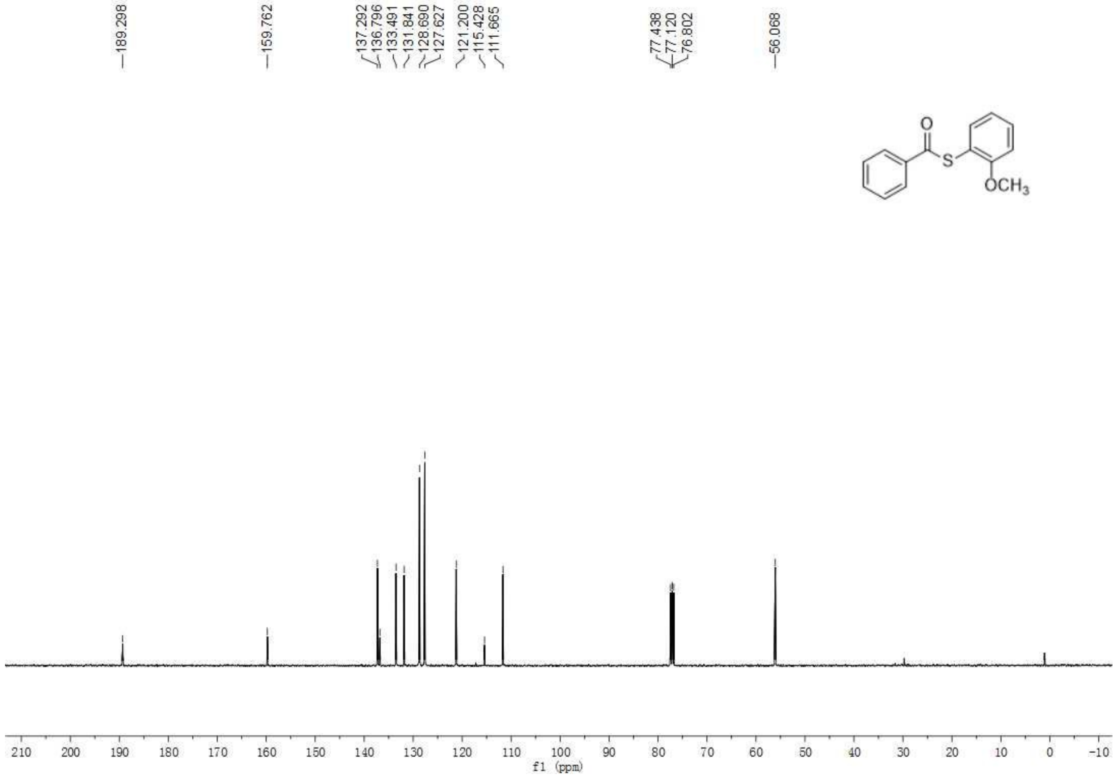
^{13}C NMR Spectrum of S-(2-ethylphenyl) benzothioate **(3c)**



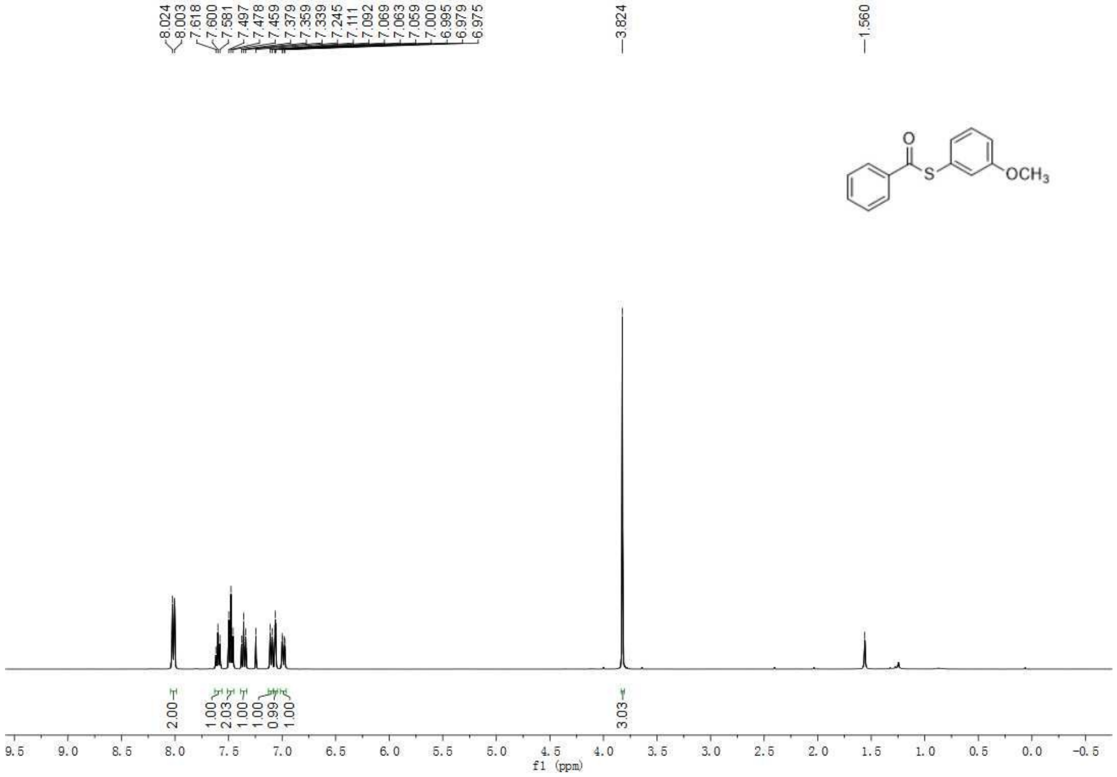
^{1}H NMR Spectrum of S-(2-methoxyphenyl) benzothioate **(3d)**



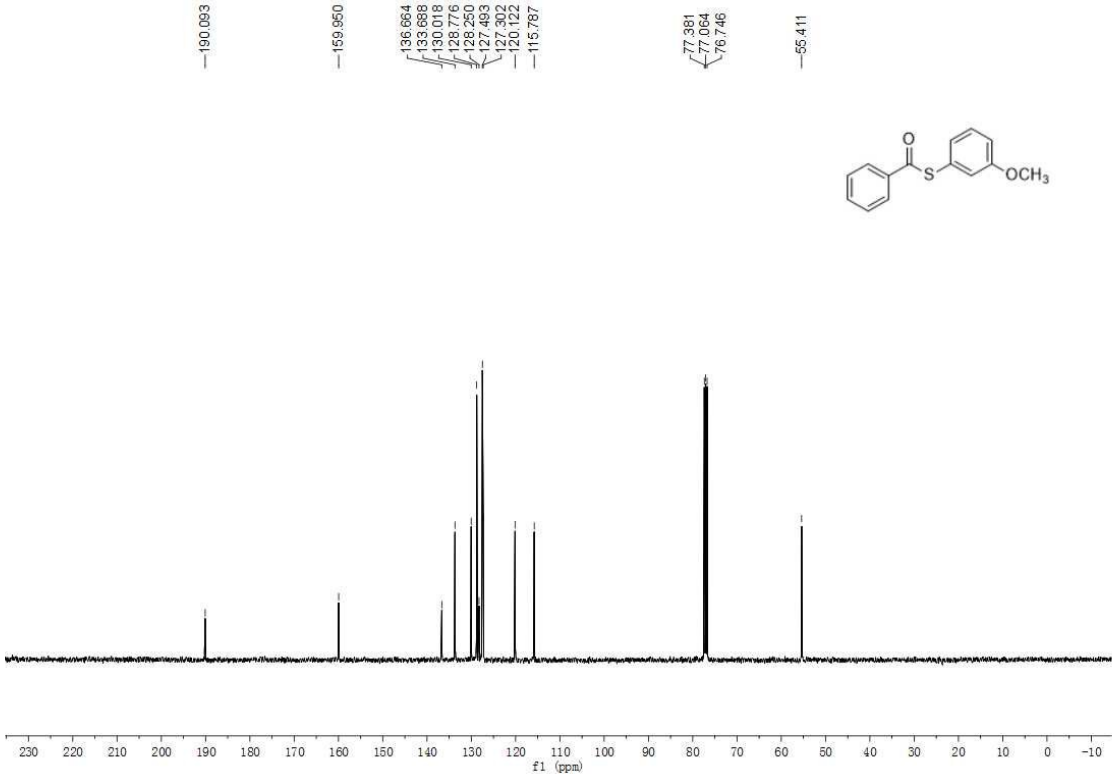
^{13}C NMR Spectrum of S-(2-methoxyphenyl) benzothioate **(3d)**



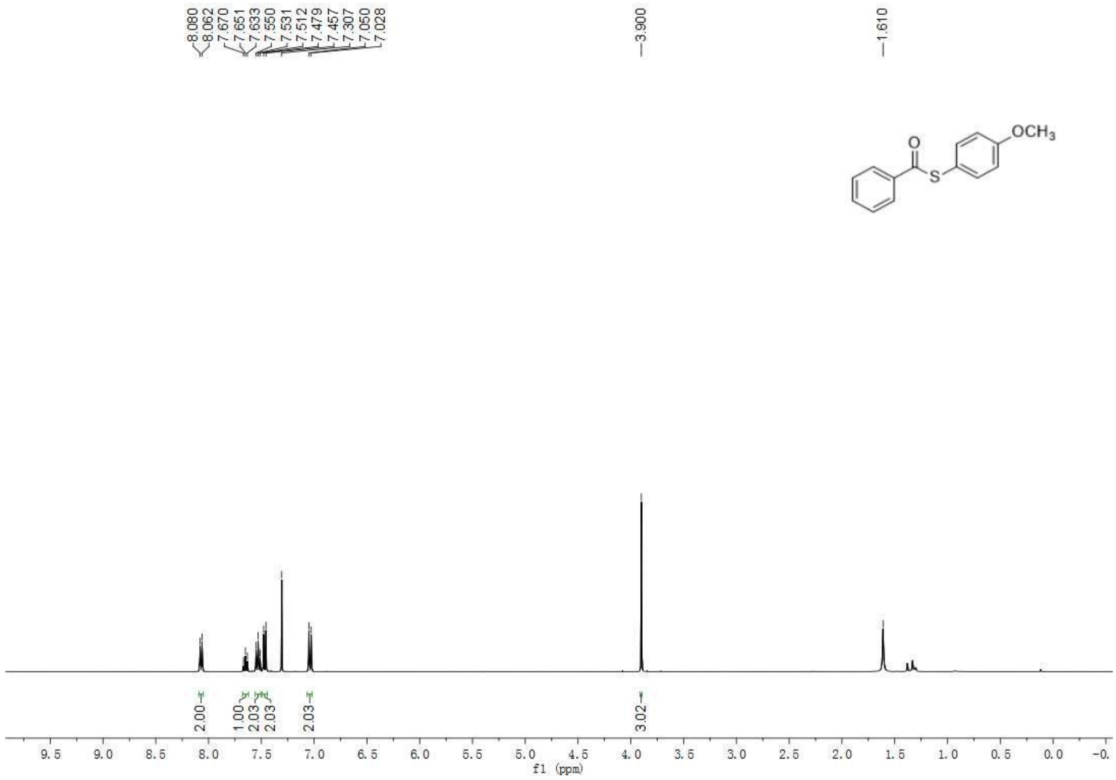
^{1}H NMR Spectrum of S-(3-methoxyphenyl) benzothioate **(3e)**



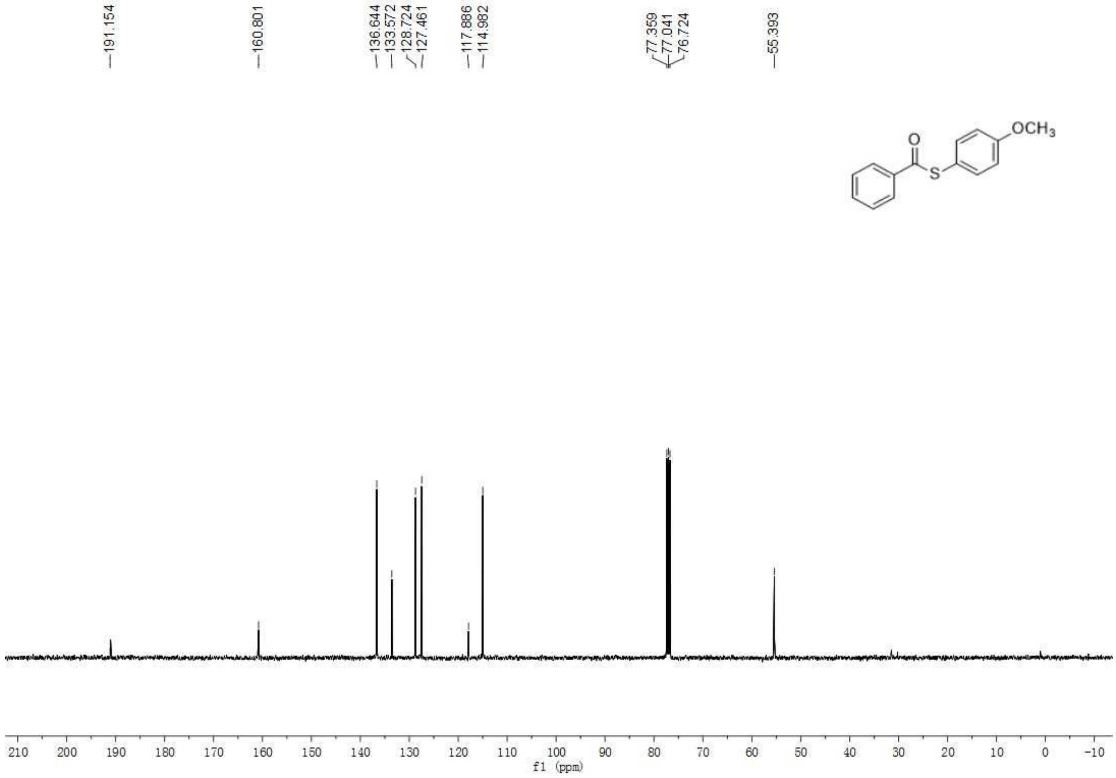
^{13}C NMR Spectrum of S-(3-methoxyphenyl) benzothioate **(3e)**



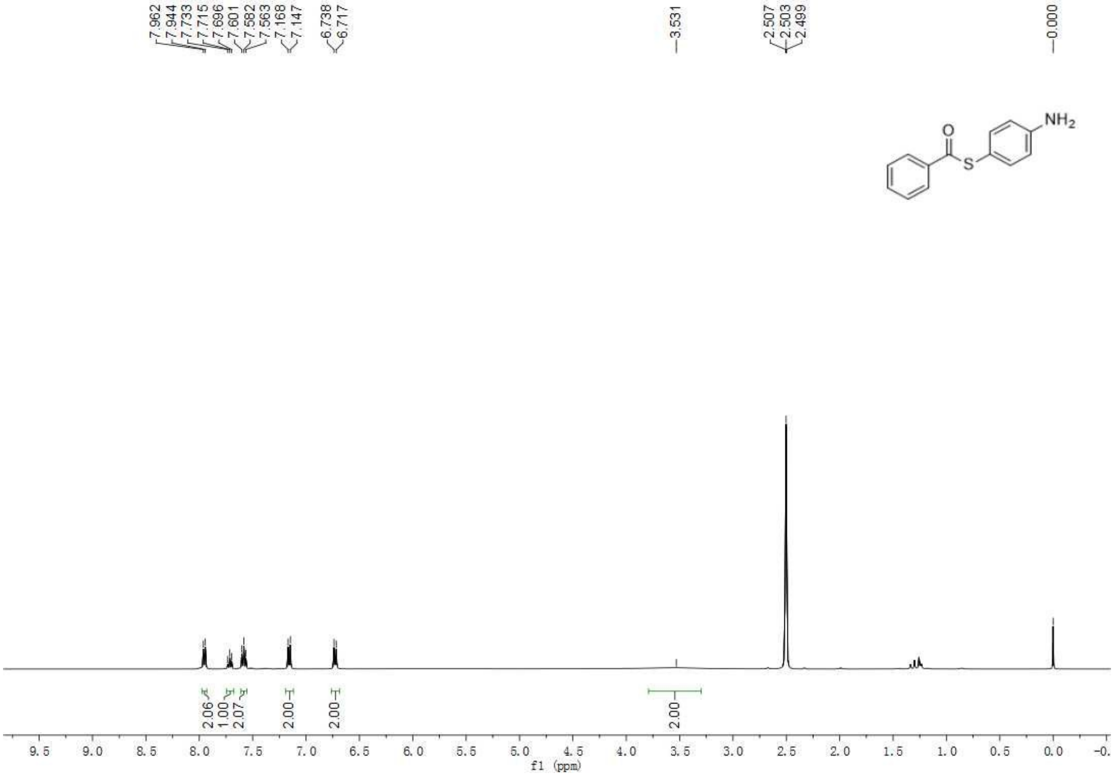
^{1}H NMR Spectrum of S-(4-methoxyphenyl) benzothioate **(3f)**



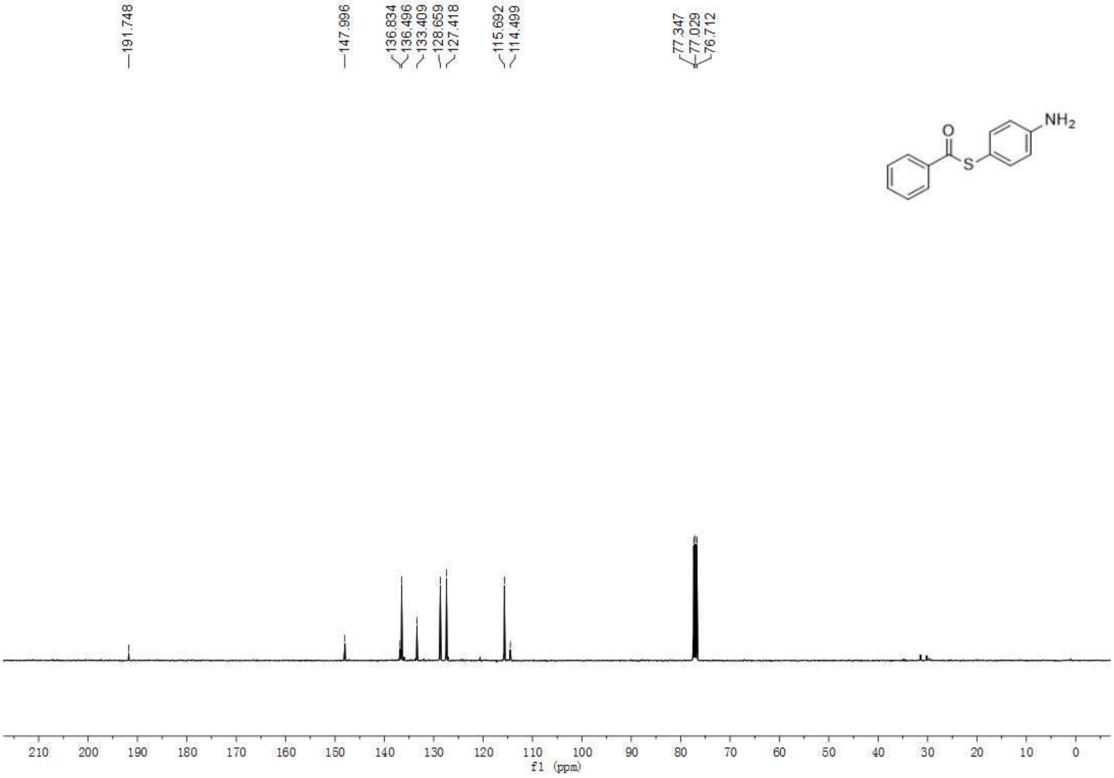
^{13}C NMR Spectrum of S-(4-methoxyphenyl) benzothioate **(3f)**



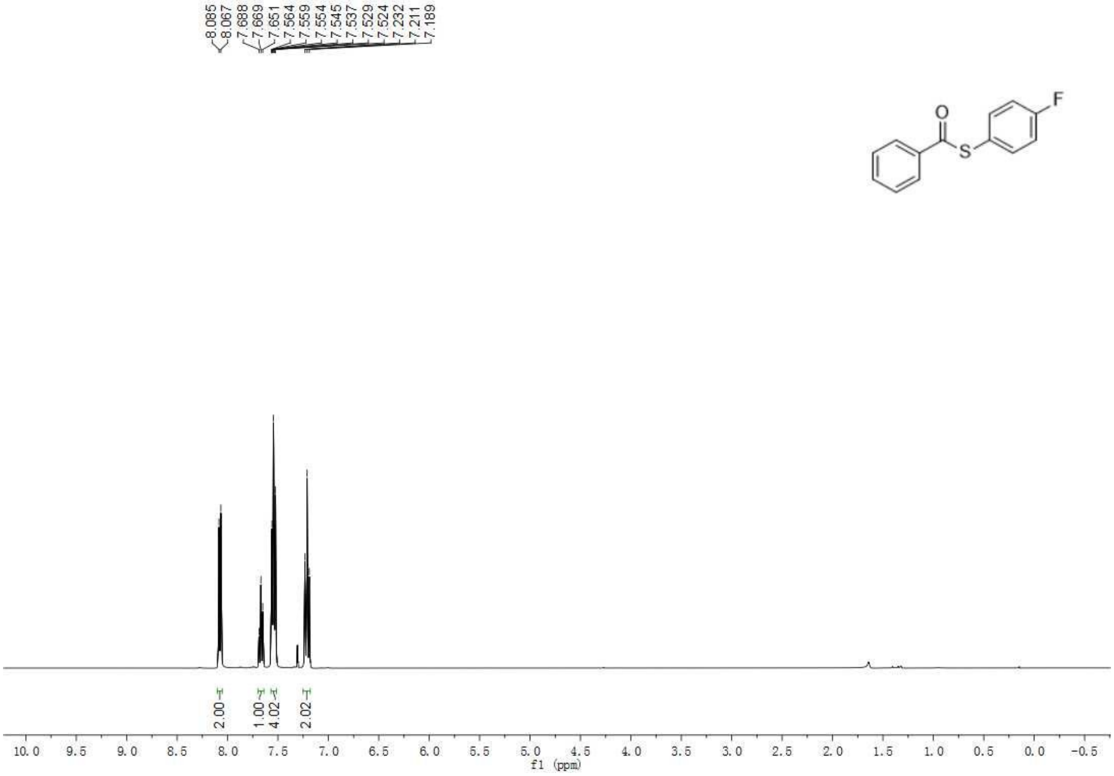
^{1}H NMR Spectrum of **S-**(4-aminophenyl) benzothioate **(3g)**



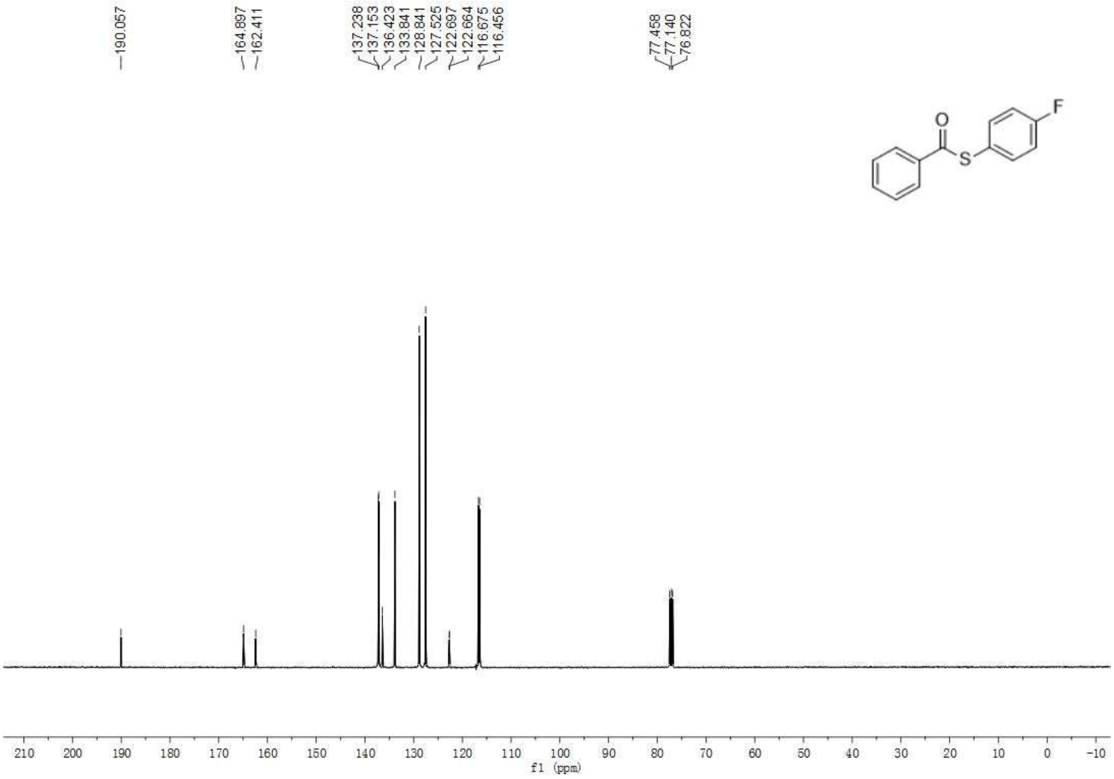
^{13}C NMR Spectrum of S-(4-aminophenyl) benzothioate **(3g)**



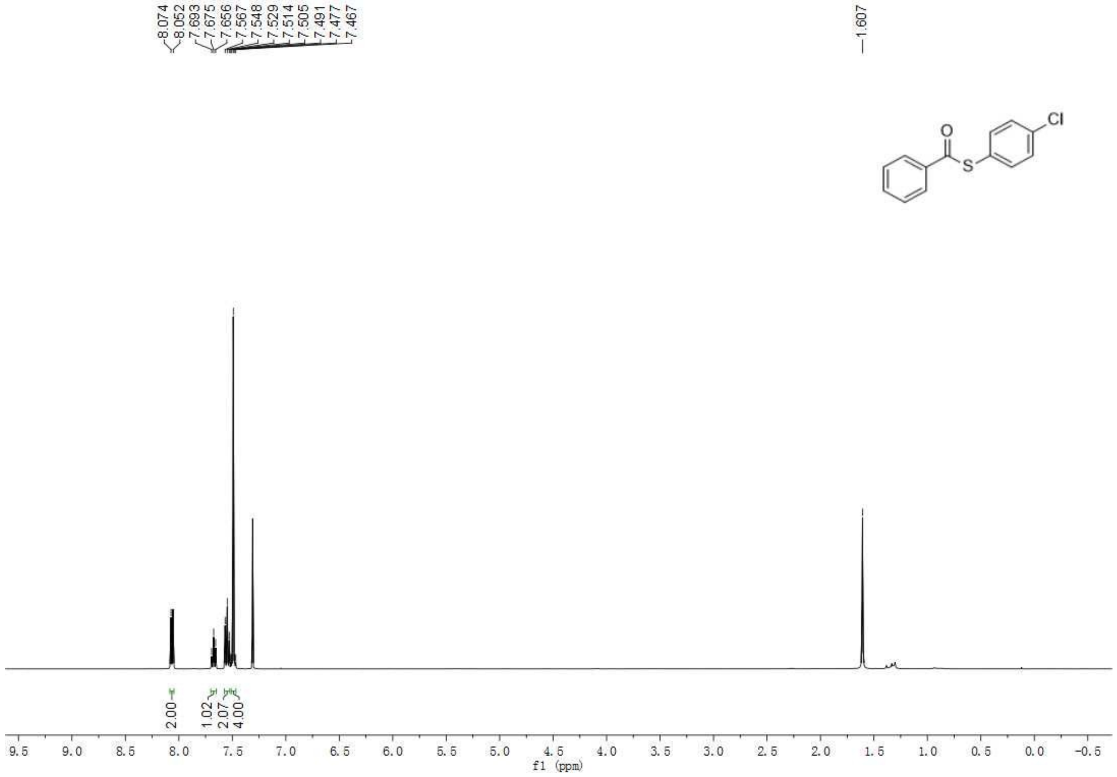
^{1}H NMR Spectrum of S-(4-fluorophenyl) benzothioate **(3h)**



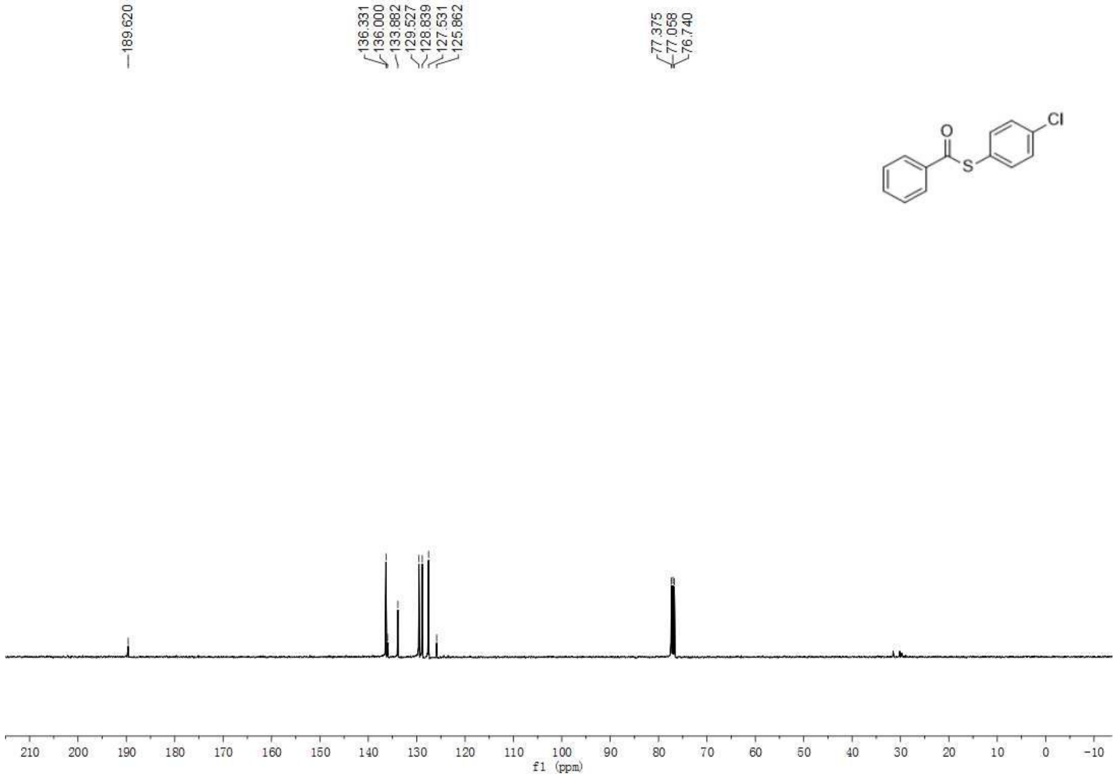
^{13}C NMR Spectrum of S-(4-fluorophenyl) benzothioate **(3h)**



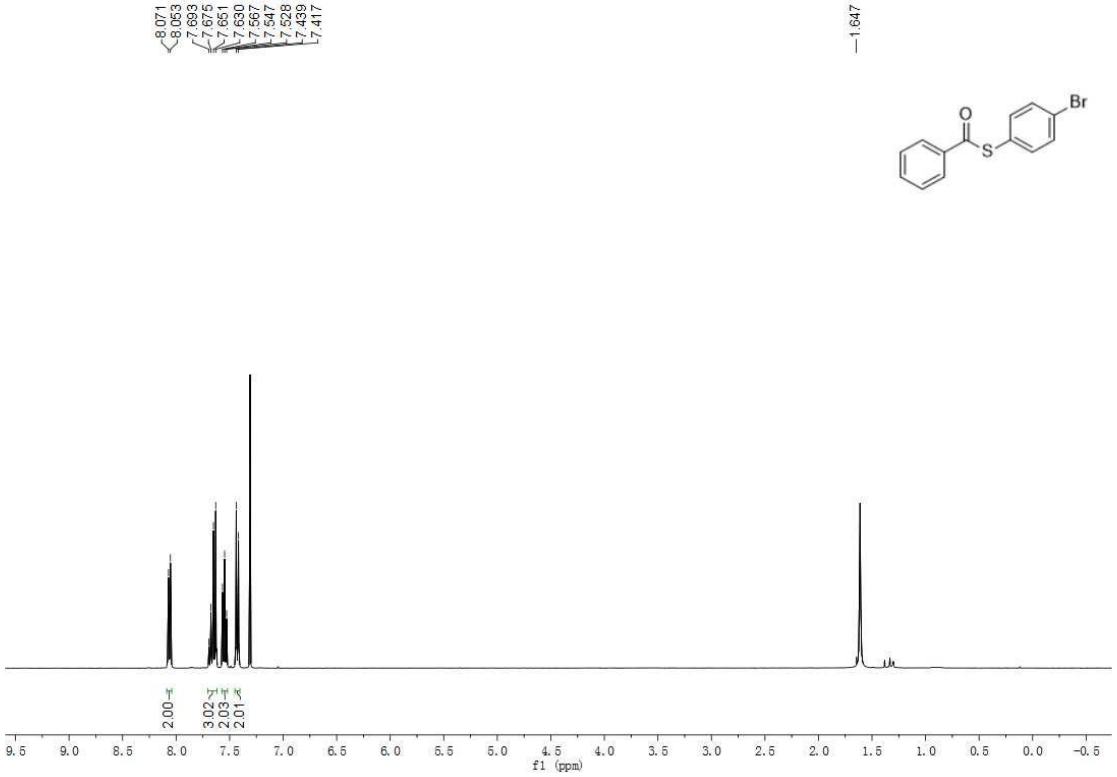
^{1}H NMR Spectrum of S-(4-chlorophenyl) benzothioate **(3i)**



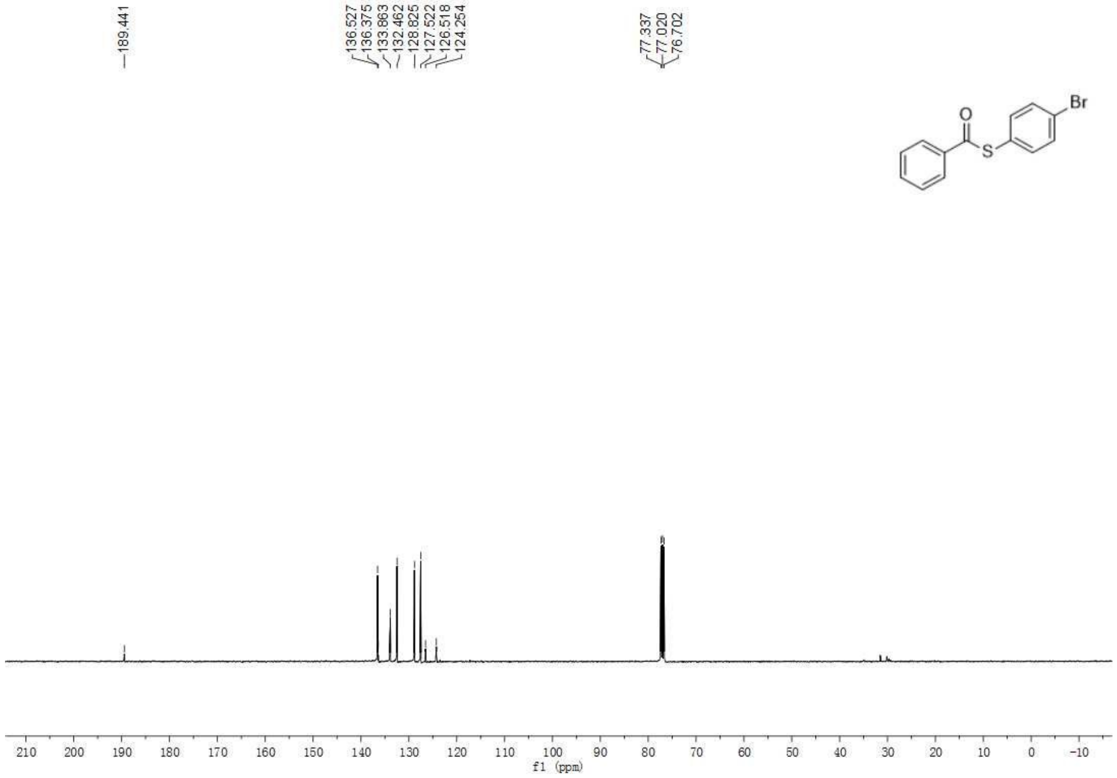
^{13}C NMR Spectrum of S-(4-chlorophenyl) benzothioate **(3i)**



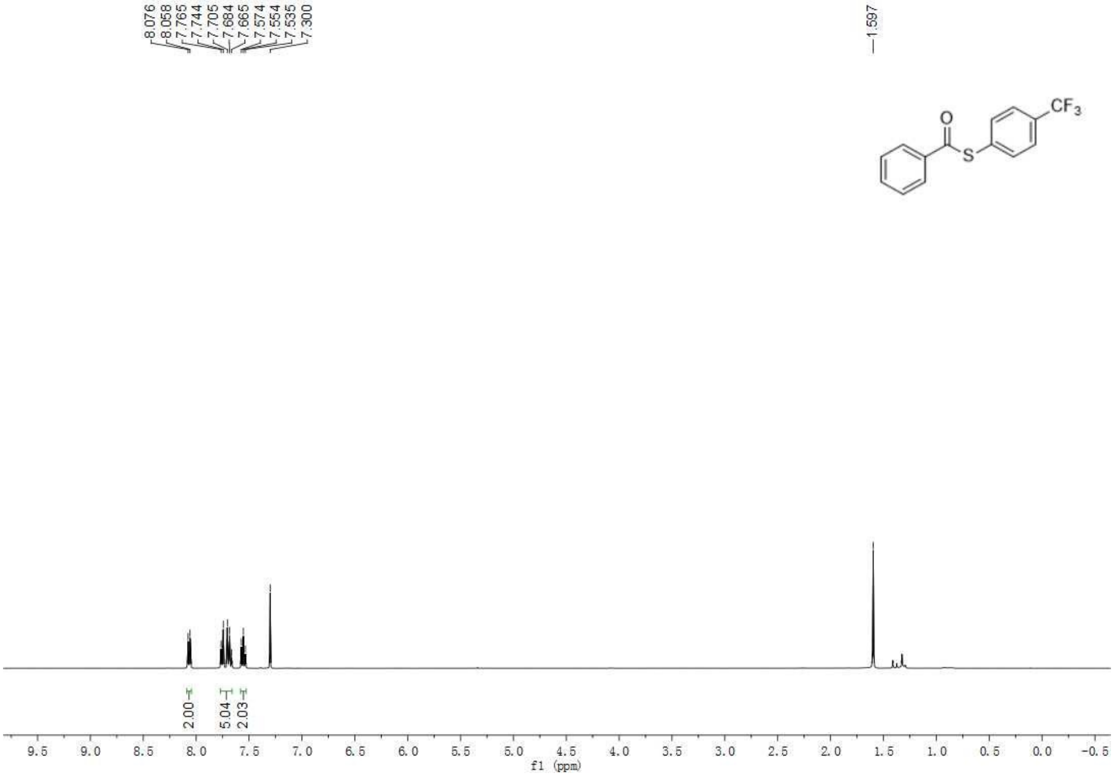
^{1}H NMR Spectrum of S-(4-bromophenyl) benzothioate **(3j)**



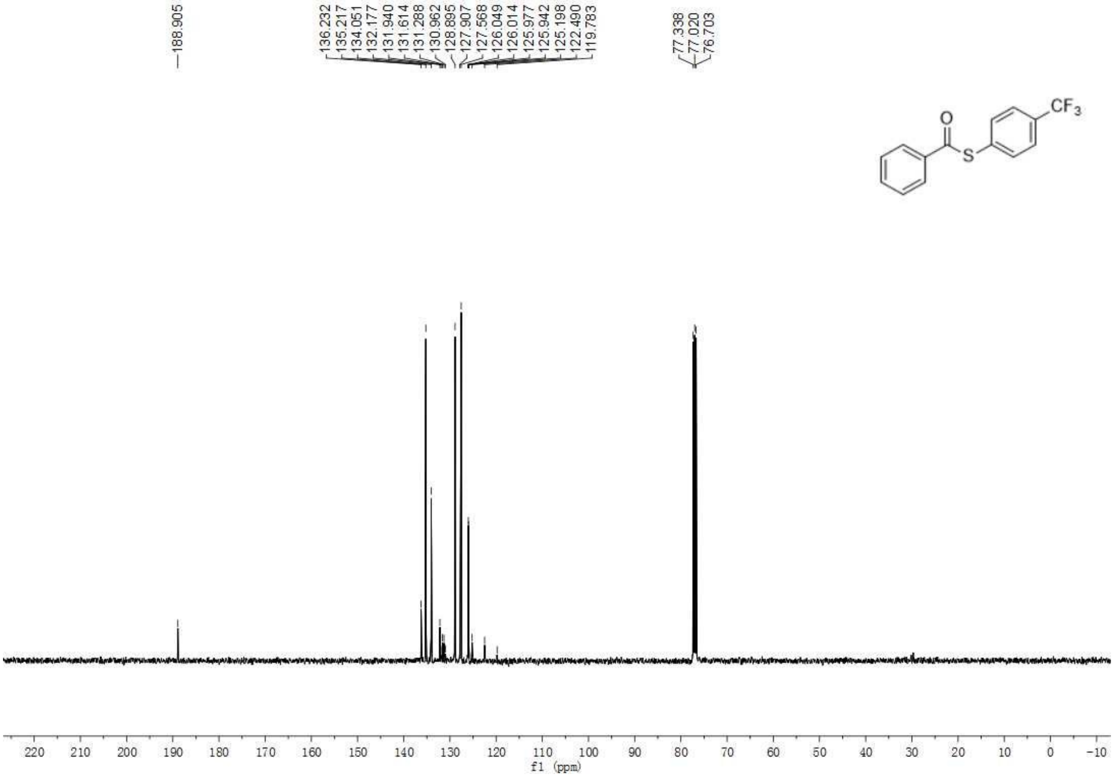
^{13}C NMR Spectrum of S-(4-bromophenyl) benzothioate **(3j)**



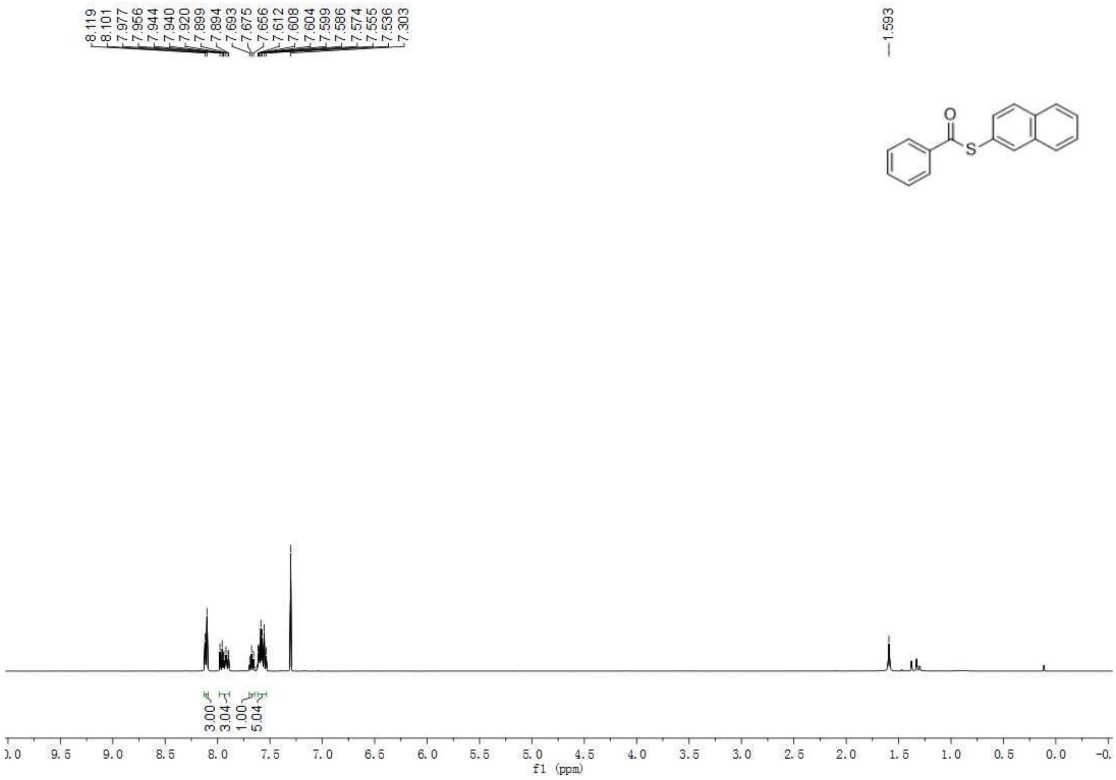
^{1}H NMR Spectrum of S-(4-(trifluoromethyl)phenyl) benzothioate **(3k)**



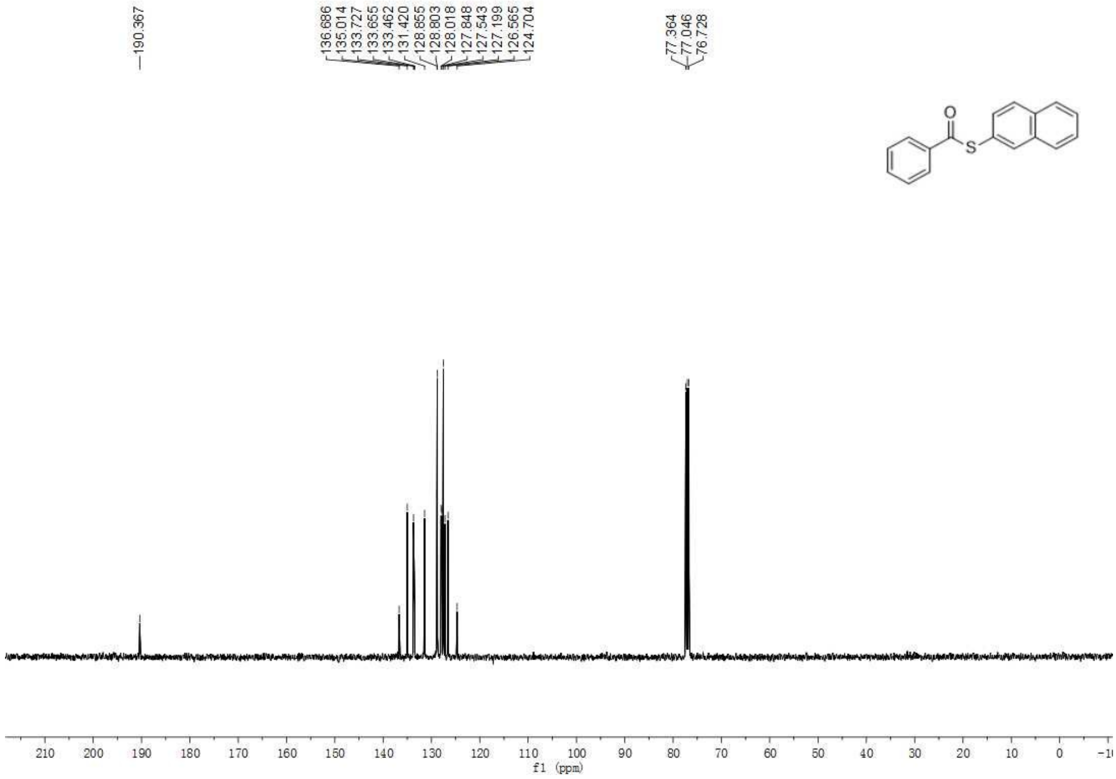
^{13}C NMR Spectrum of S-(4-(trifluoromethyl)phenyl) benzothioate **(3k)**



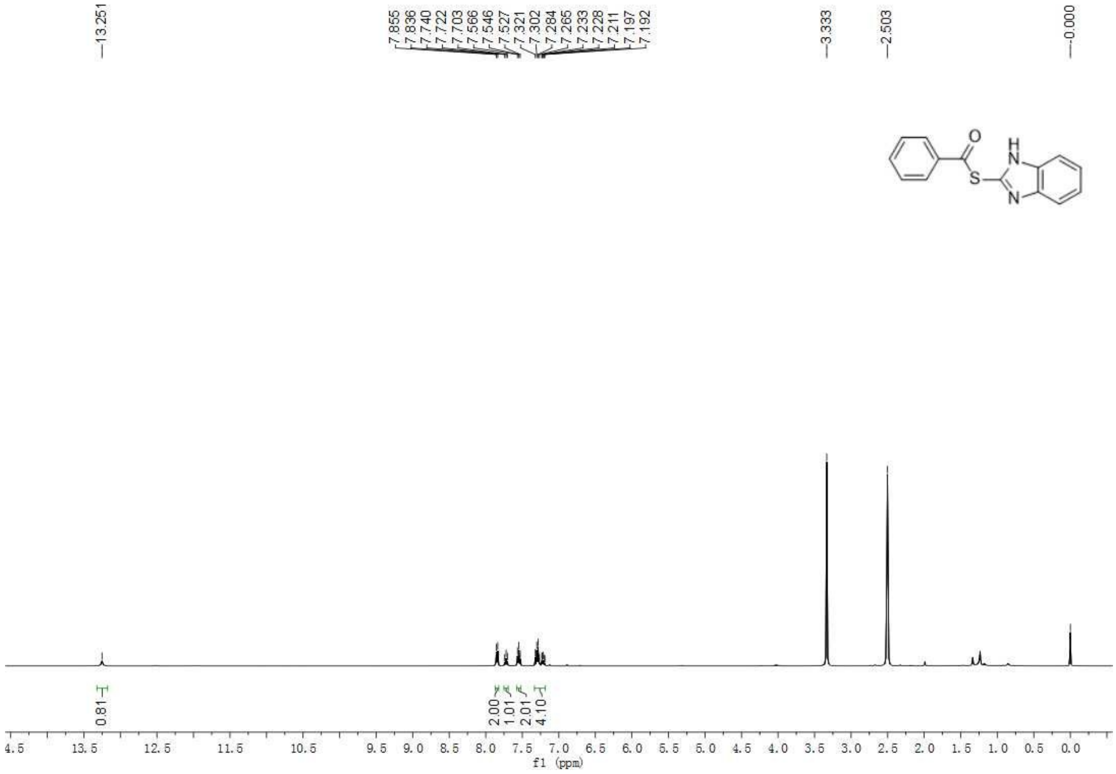
^{1}H NMR Spectrum of S-(naphthalen-2-yl) benzothioate **(3l)**



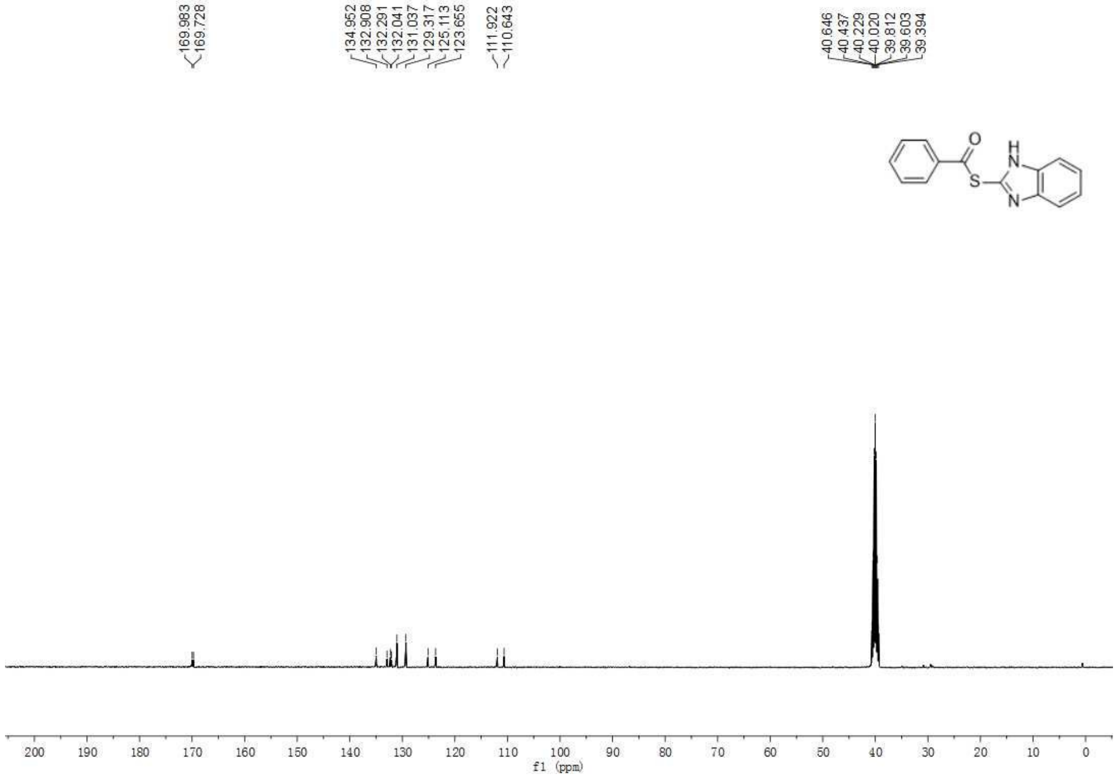
^{13}C NMR Spectrum of S-(naphthalen-2-yl) benzothioate **(3l)**



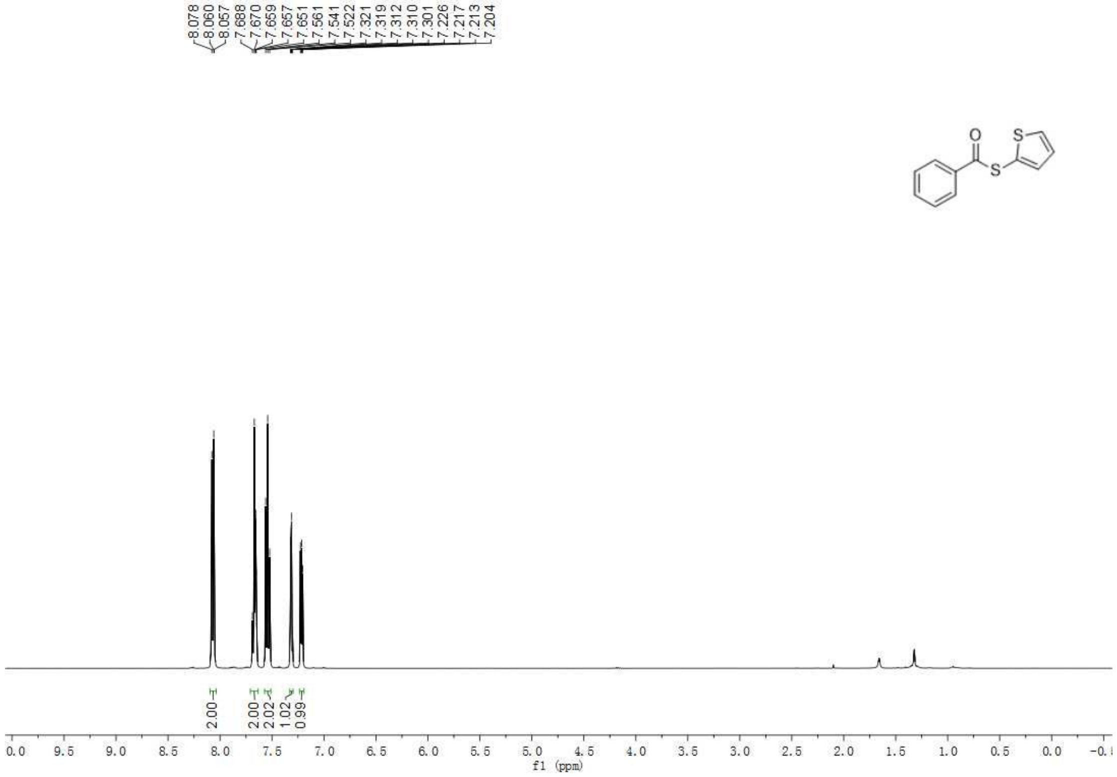
^{1}H NMR Spectrum of S-(1H-benzo[d]imidazol-2-yl) benzothioate **(3m)**



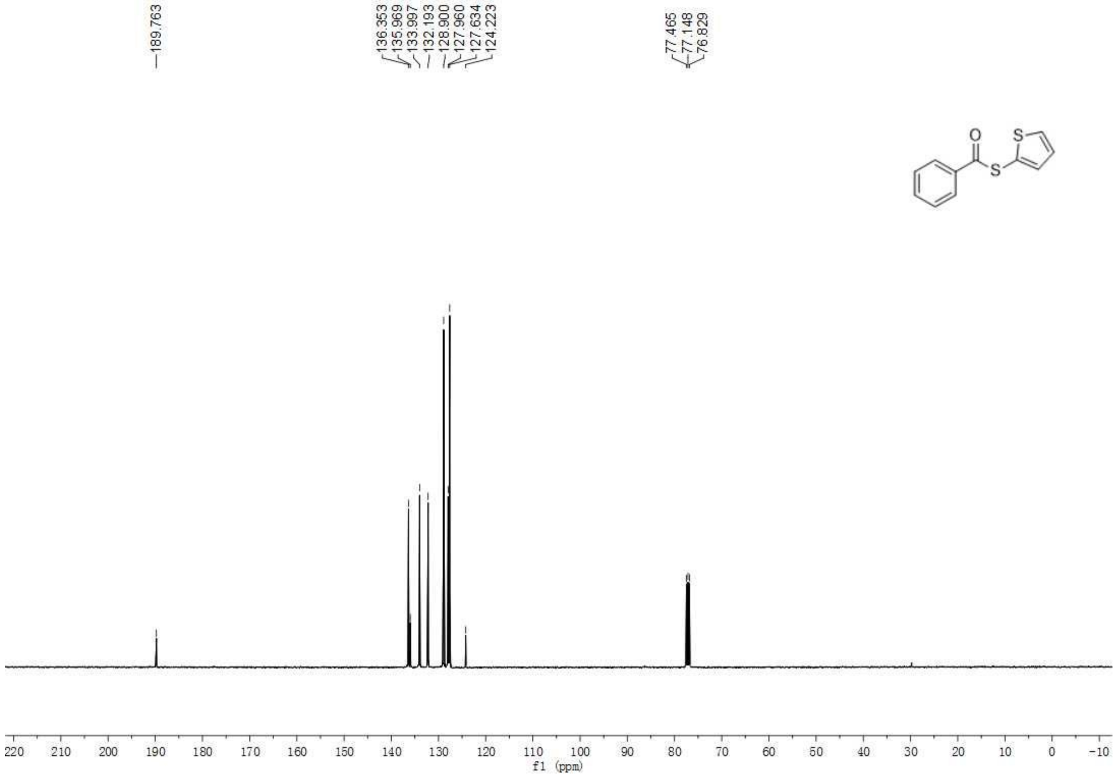
^{13}C NMR Spectrum of S-(1H-benzo[d]imidazol-2-yl) benzothioate **(3m)**



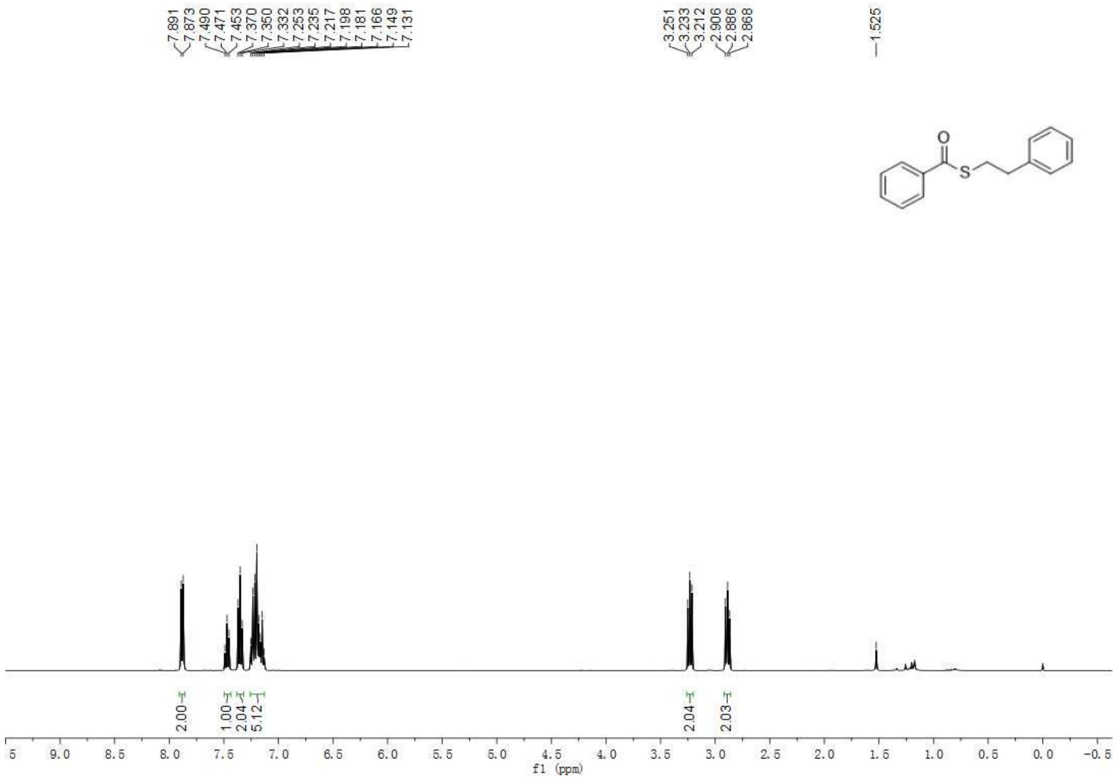
^{1}H NMR Spectrum of S-(thiophen-2-yl) benzothioate **(3n)**



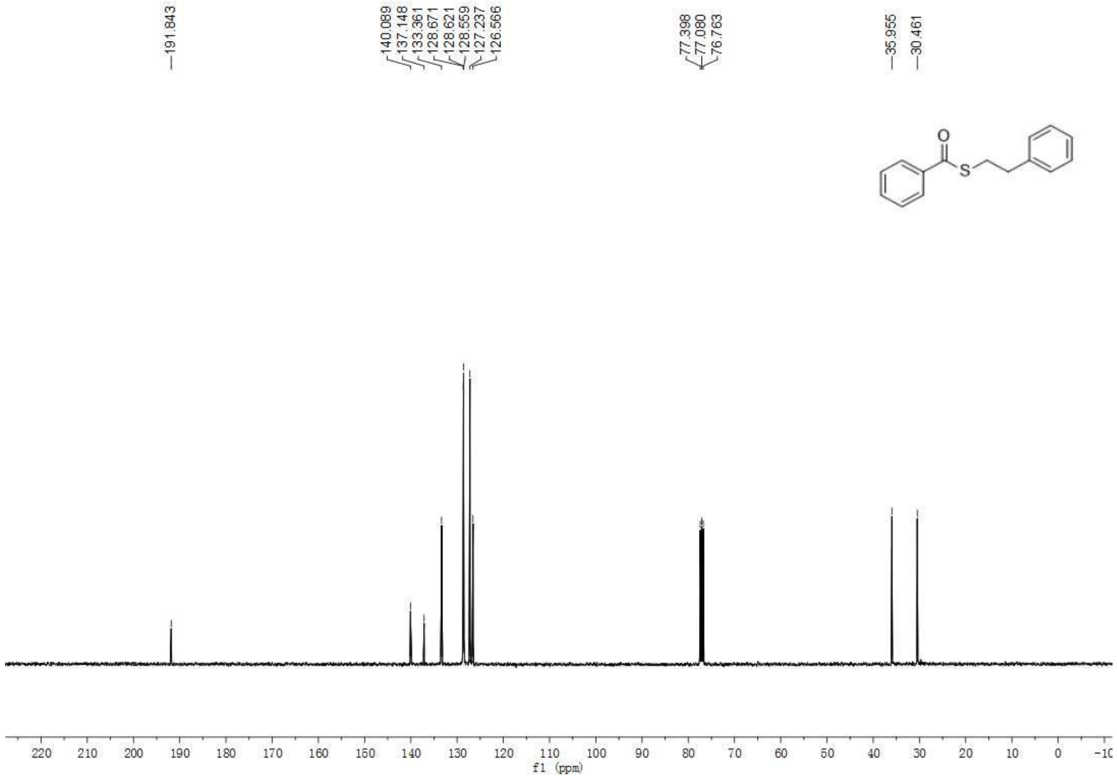
^{13}C NMR Spectrum of S-(thiophen-2-yl) benzothioate **(3n)**



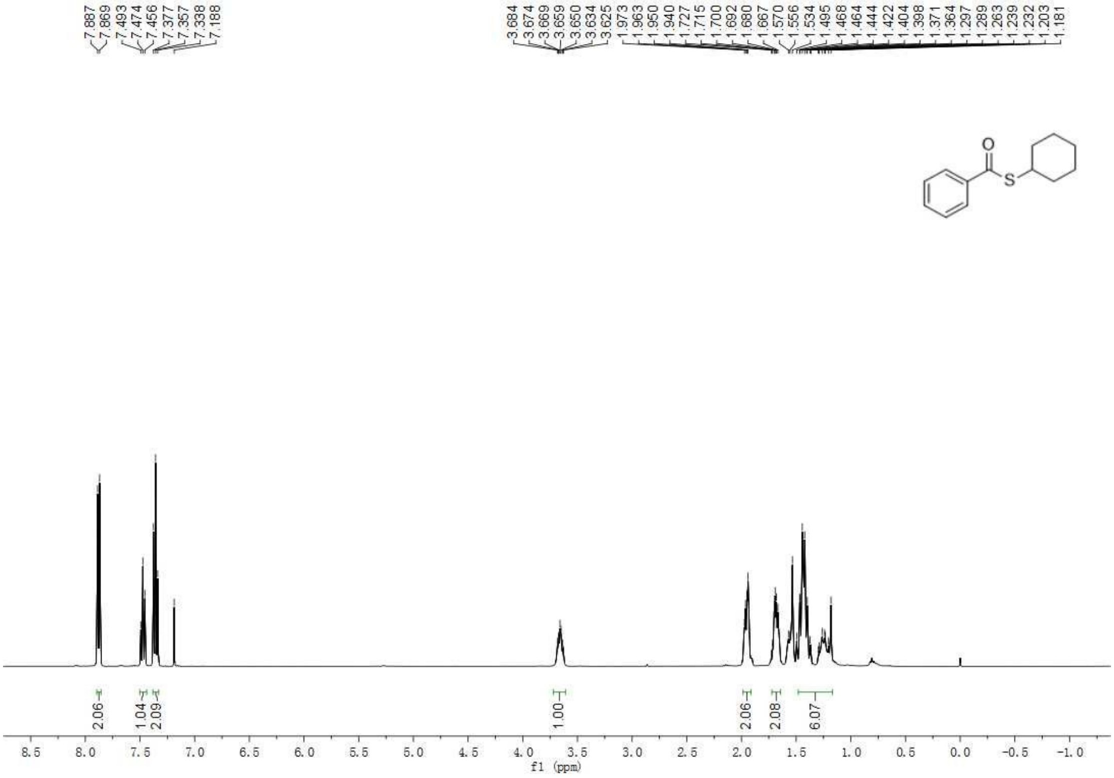
^{1}H NMR Spectrum of S-phenethyl benzothioate **(3o)**



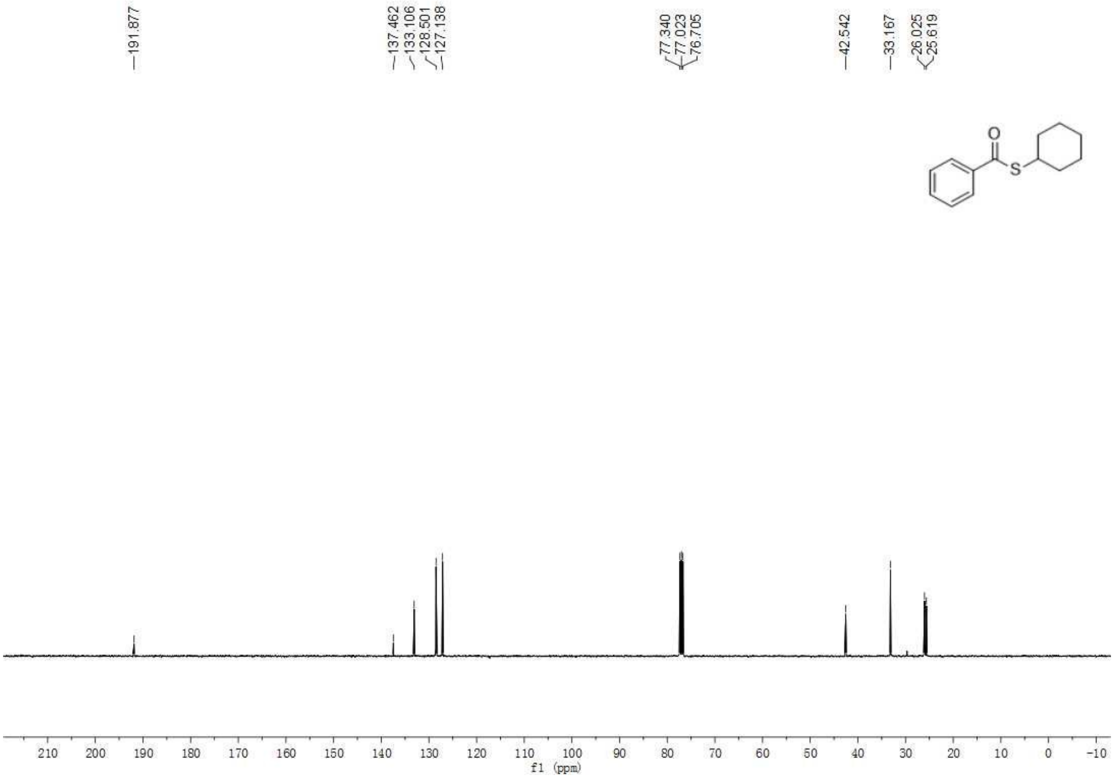
^{13}C NMR Spectrum of S-phenethyl benzothioate **(3o)**



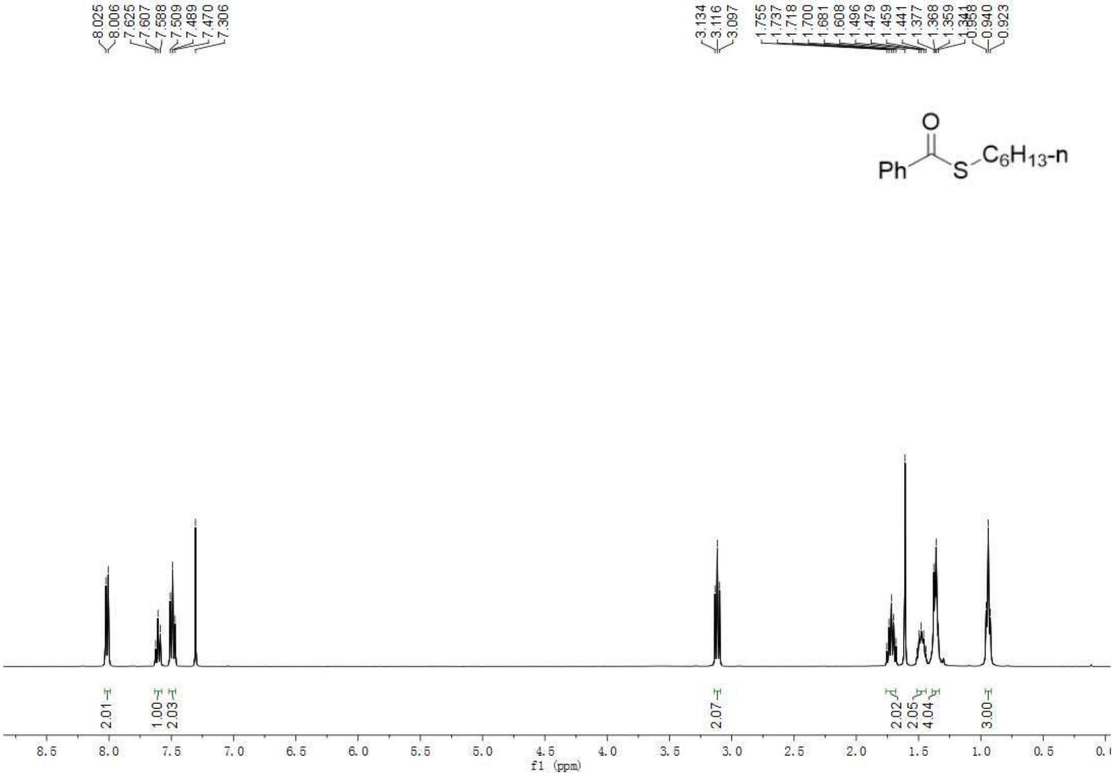
^{1}H NMR Spectrum of S-cyclohexyl benzothioate **(3p)**



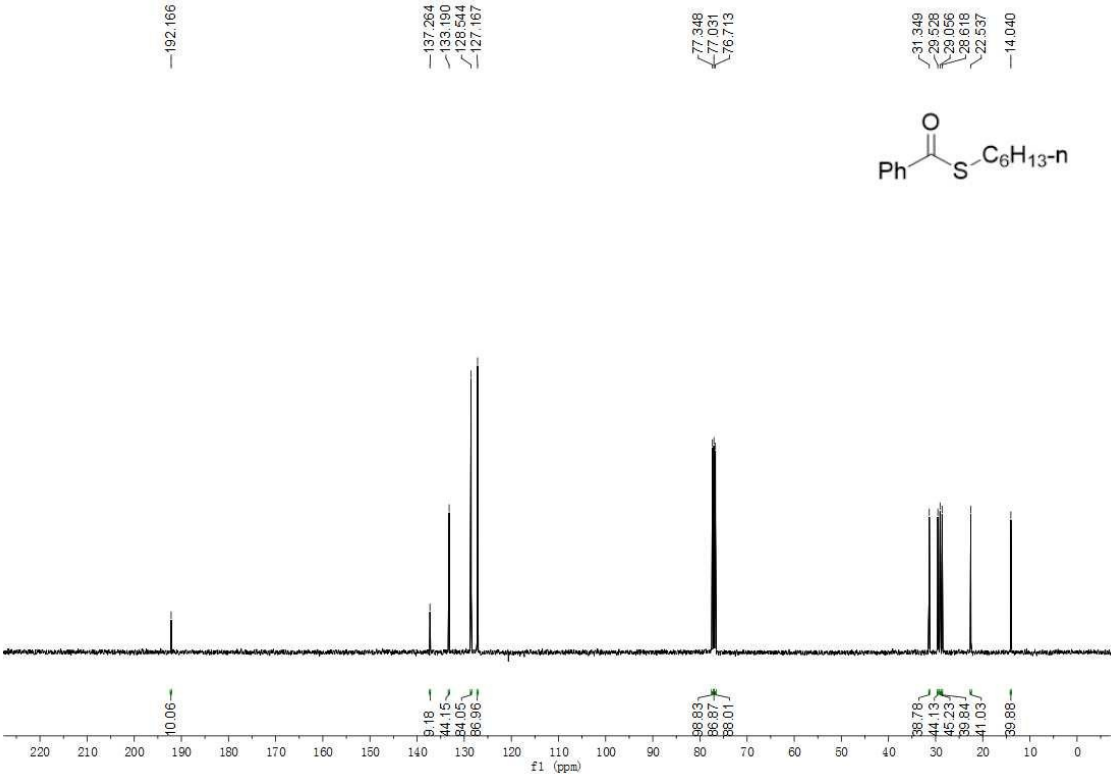
^{13}C NMR Spectrum of S-cyclohexyl benzothioate **(3p)**



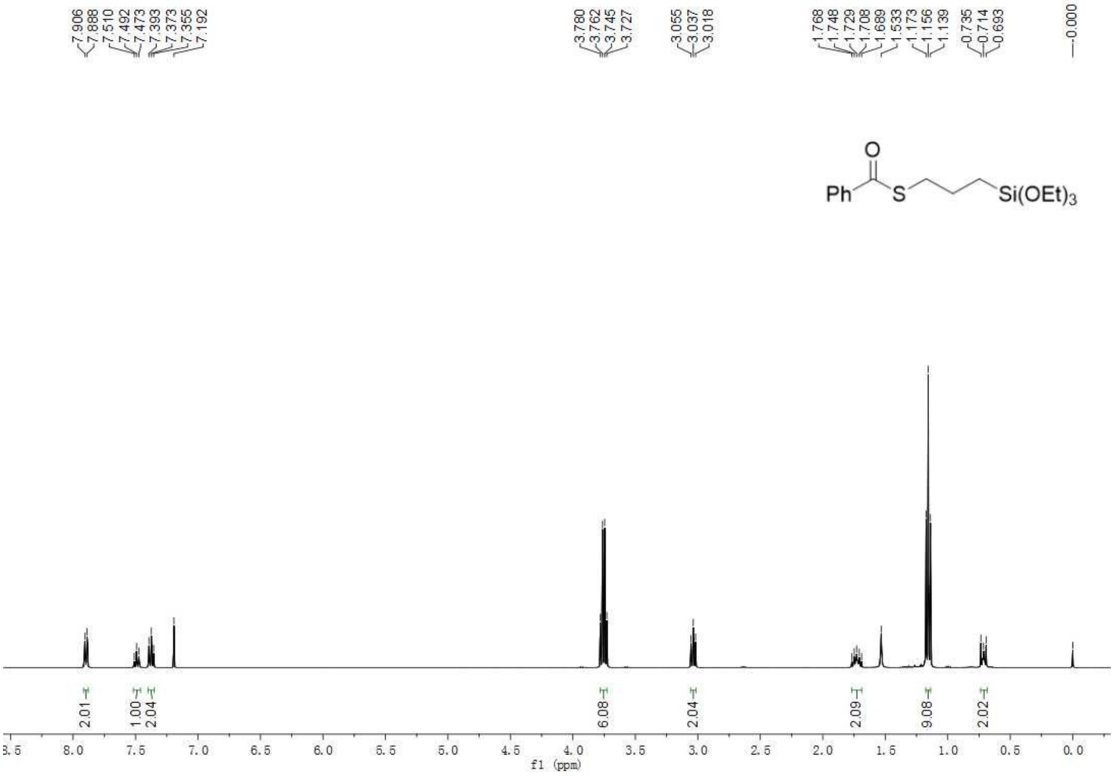
^{1}H NMR Spectrum of S-heptyl benzothioate **(3q)**



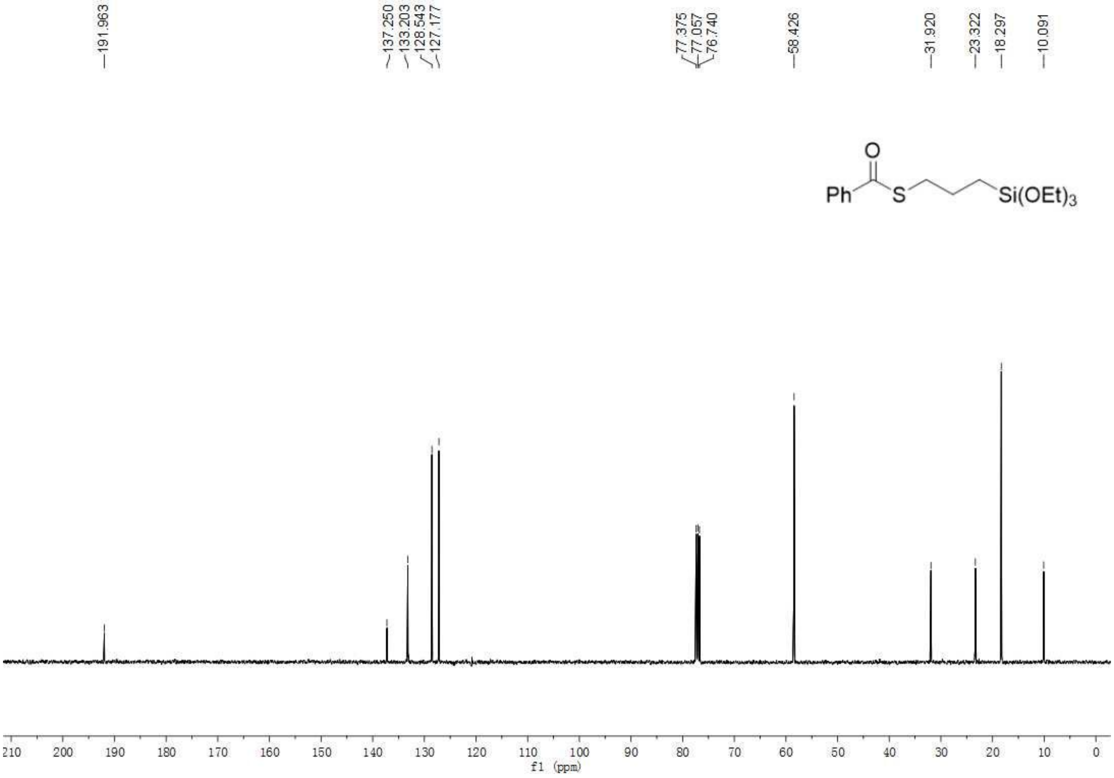
^{13}C NMR Spectrum of S-heptyl benzothioate **(3q)**



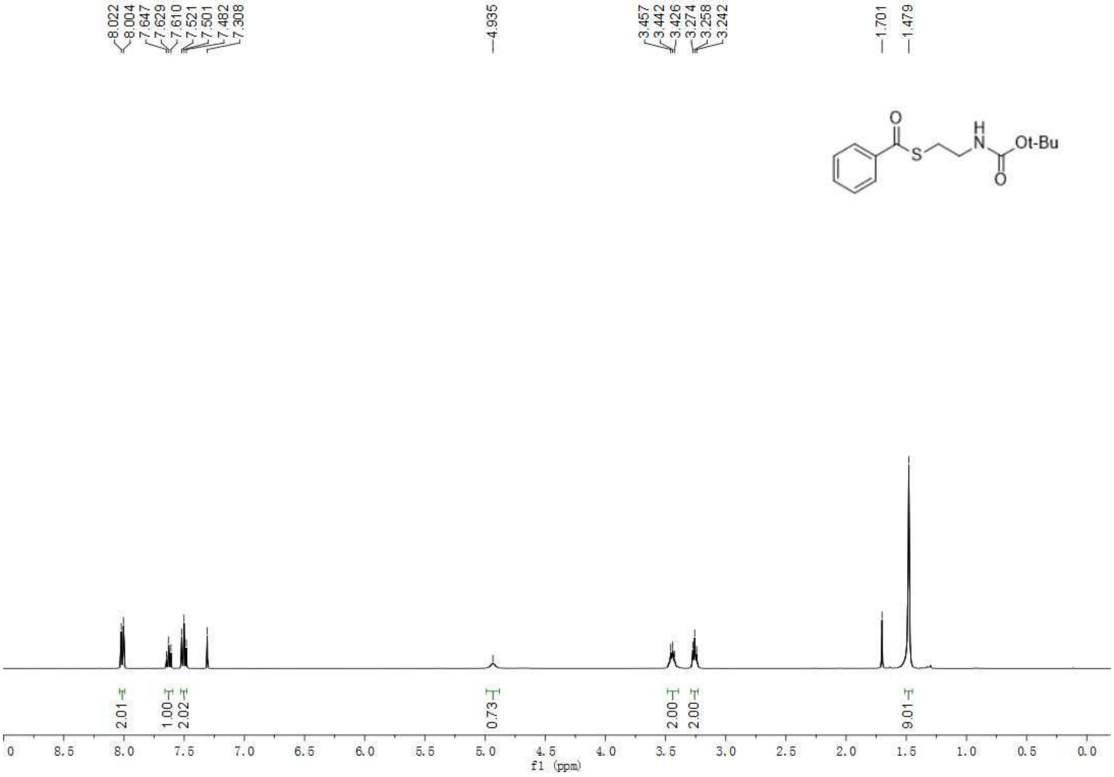
^{1}H NMR Spectrum of S-(3-(triethoxysilyl)propyl) benzothioate **(3r)**



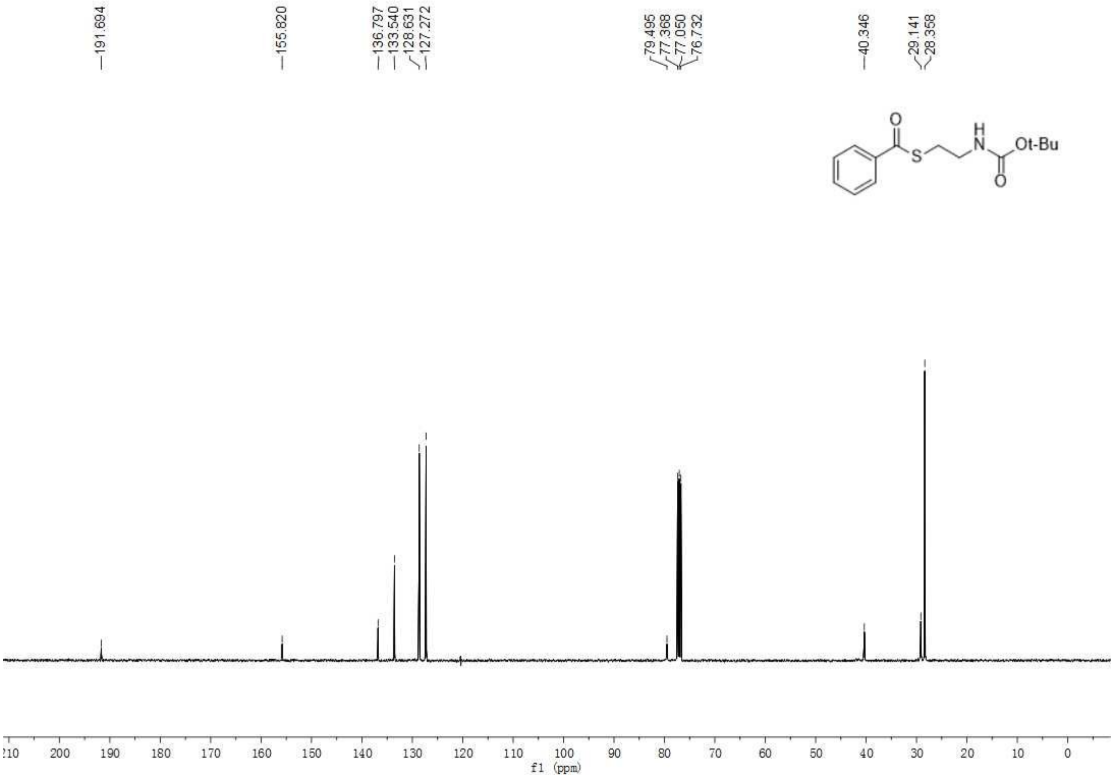
^{13}C NMR Spectrum of S-(3-(triethoxysilyl)propyl) benzothioate **(3r)**



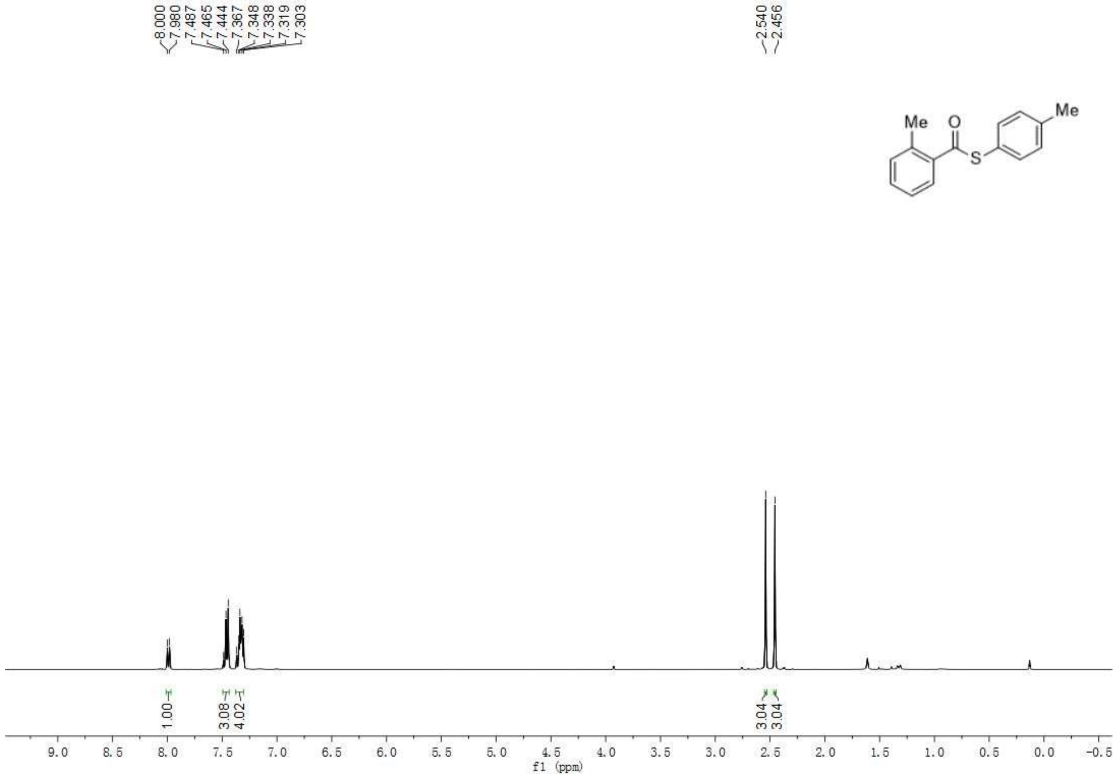
^{1}H NMR Spectrum of S-(2-((tert-butoxycarbonyl)amino)ethyl) benzothioate **(3s)**



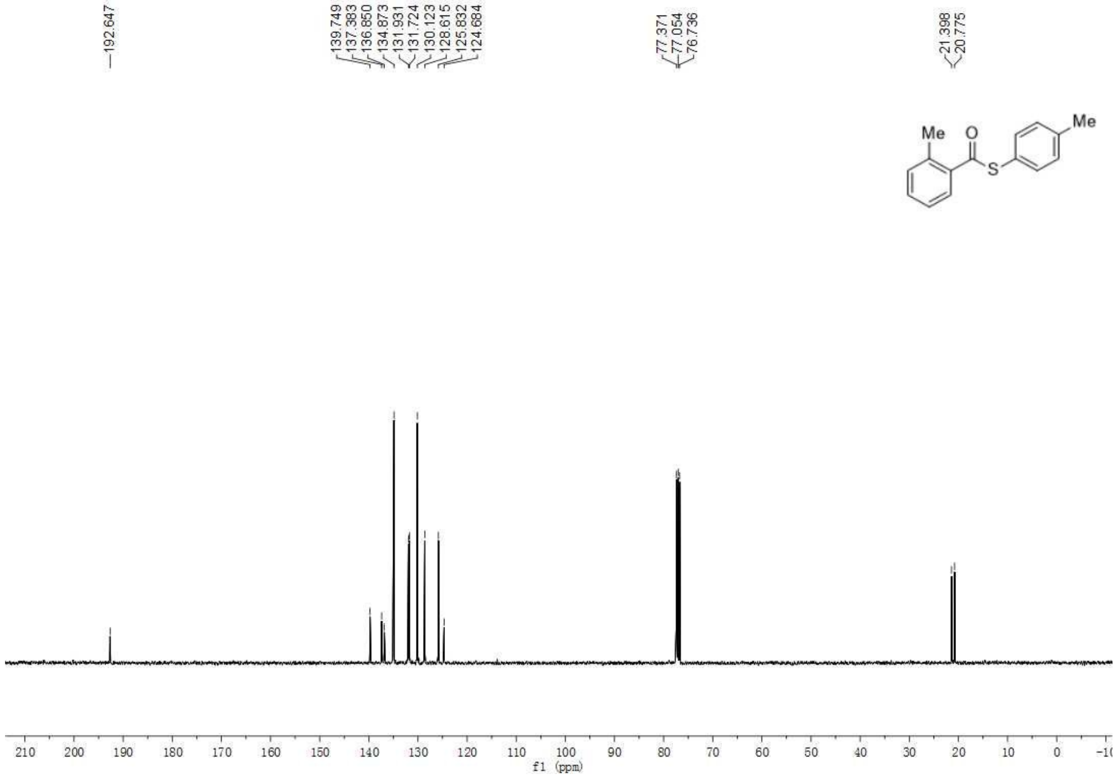
^{13}C NMR Spectrum of S-(2-((tert-butoxycarbonyl)amino)ethyl) benzothioate **(3s)**



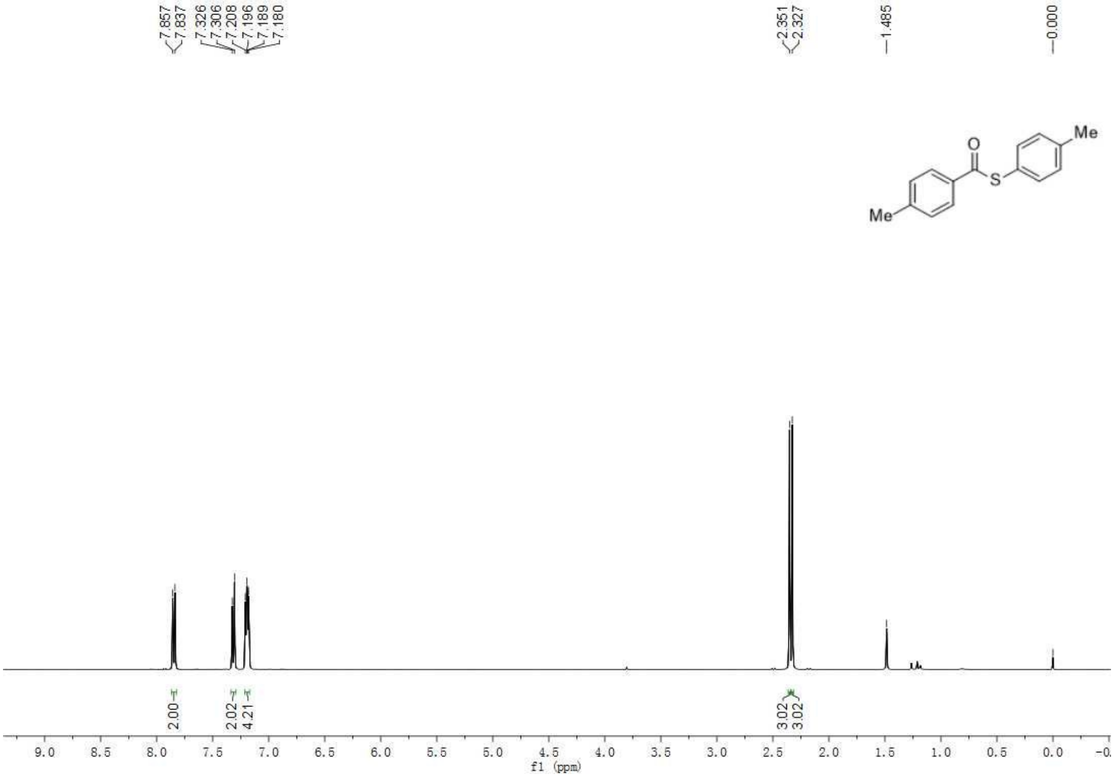
^{1}H NMR Spectrum of S-(p-tolyl) 2-methylbenzothioate **(3t)**



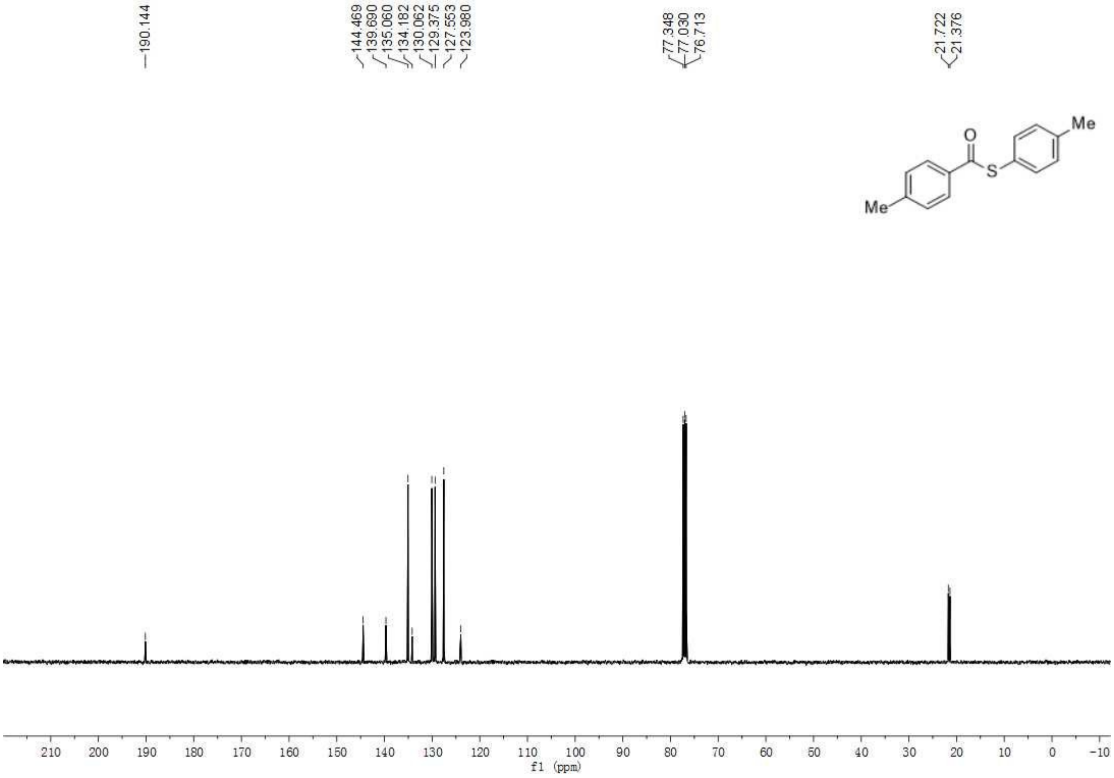
^{13}C NMR Spectrum of S-(p-tolyl) 2-methylbenzothioate **(3t)**



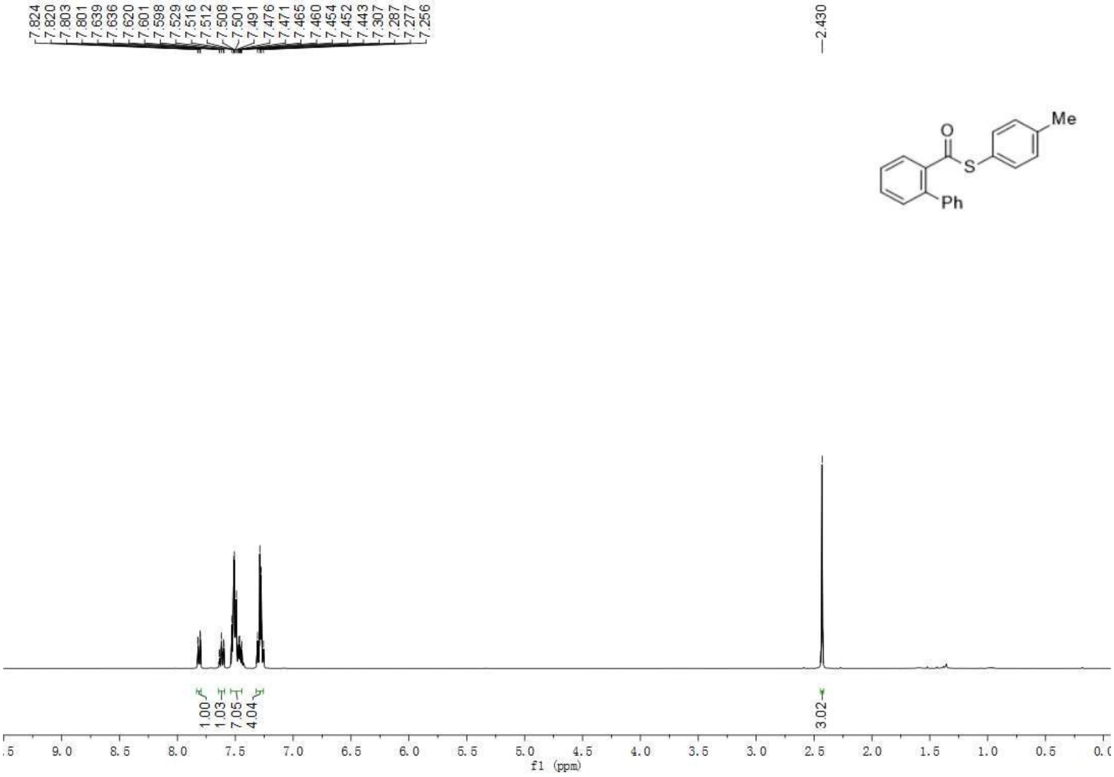
^{1}H NMR Spectrum of S-(p-tolyl) 4-methylbenzothioate **(3u)**



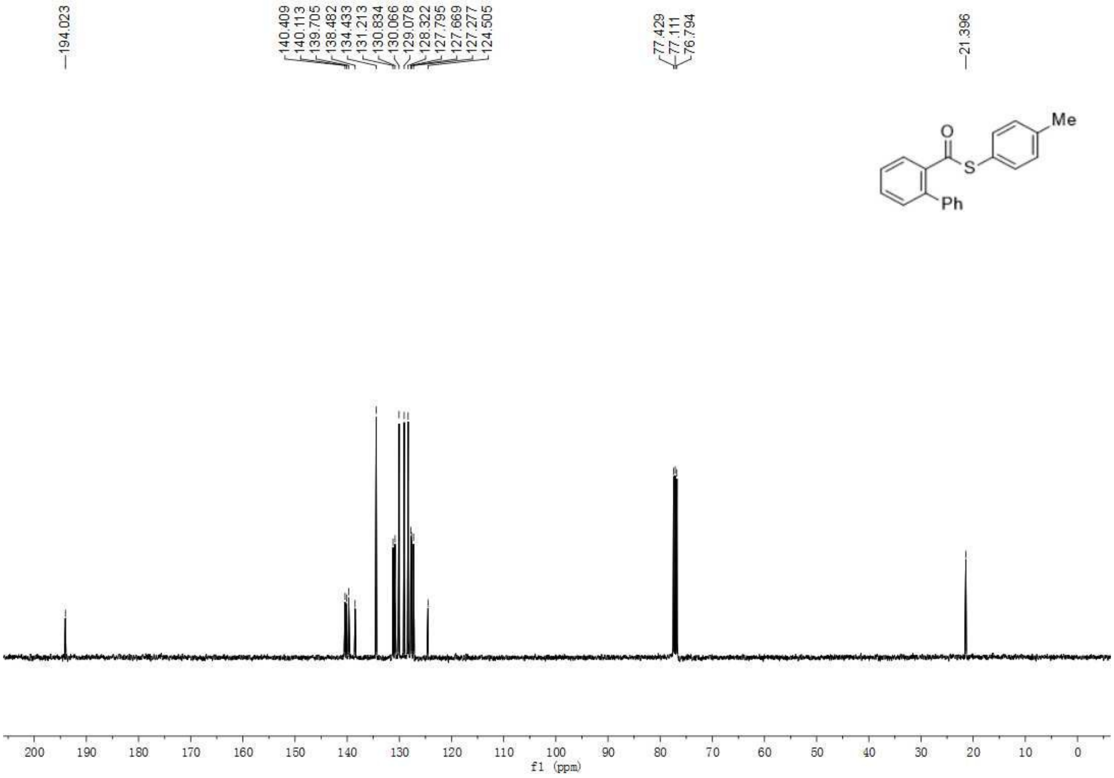
^{13}C NMR Spectrum of S-(p-tolyl) 4-methylbenzothioate **(3u)**



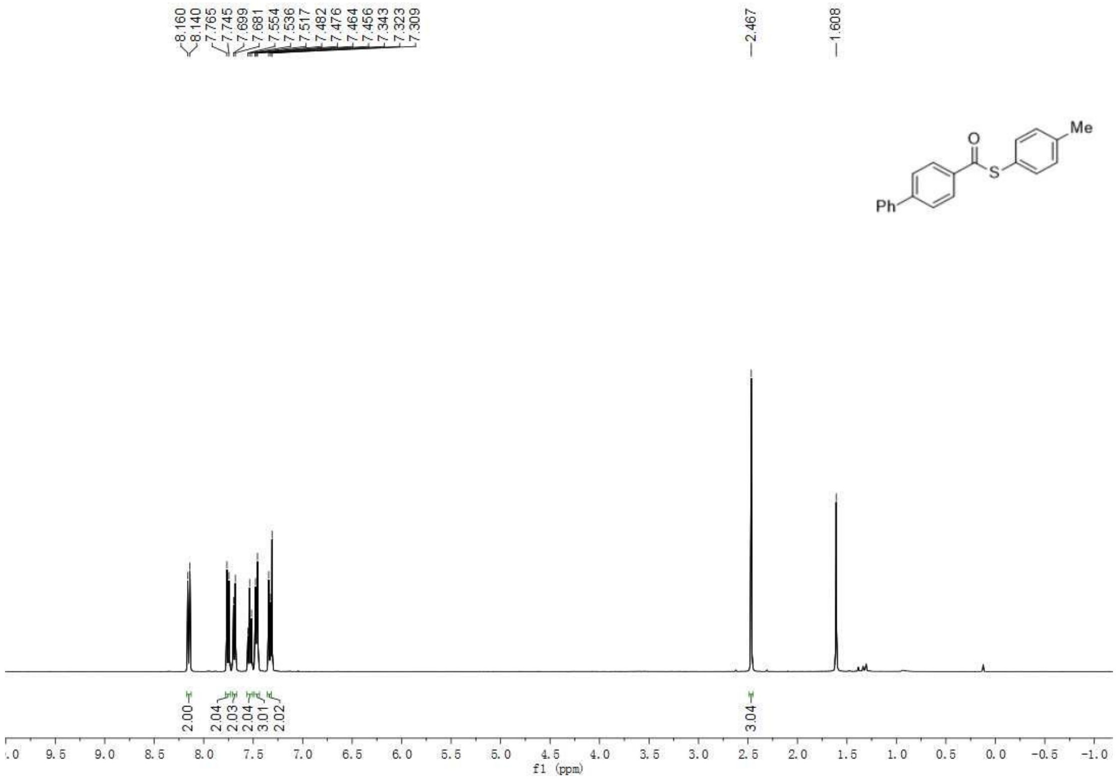
^1H NMR Spectrum of S-(p-tolyl) [1,1'-biphenyl]-2-carbothioate **(3v)**



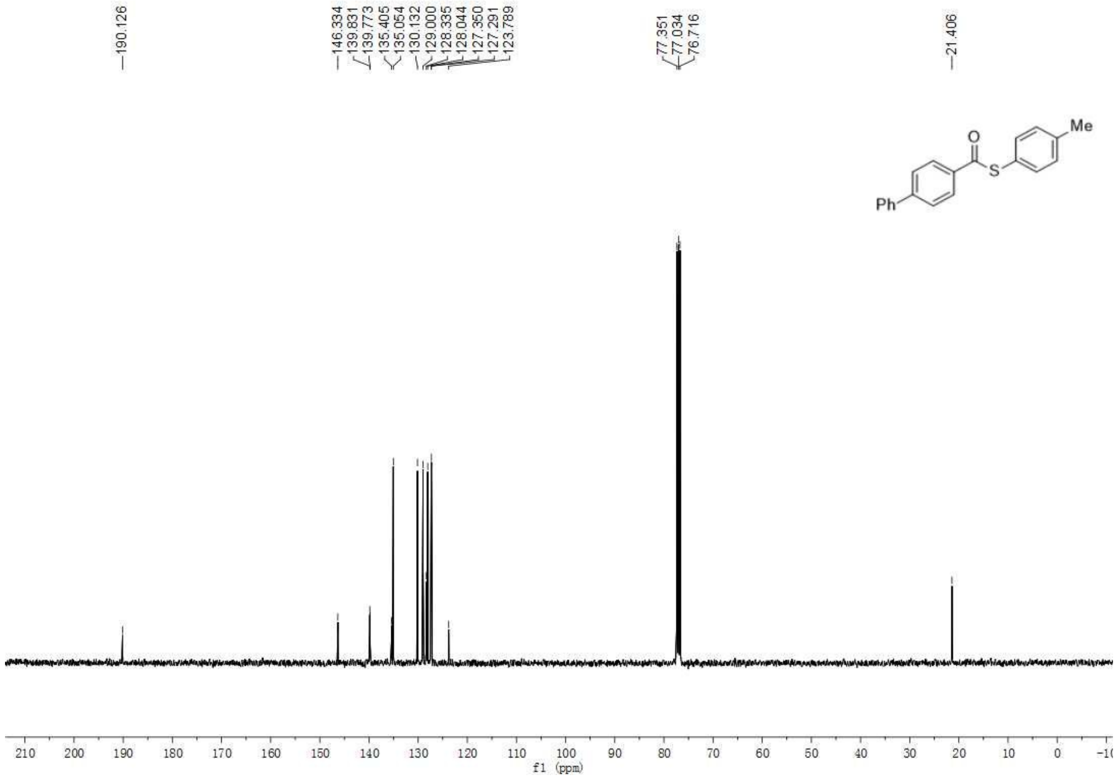
^{13}C NMR Spectrum of S-(p-tolyl) [1,1'-biphenyl]-2-carbothioate **(3v)**



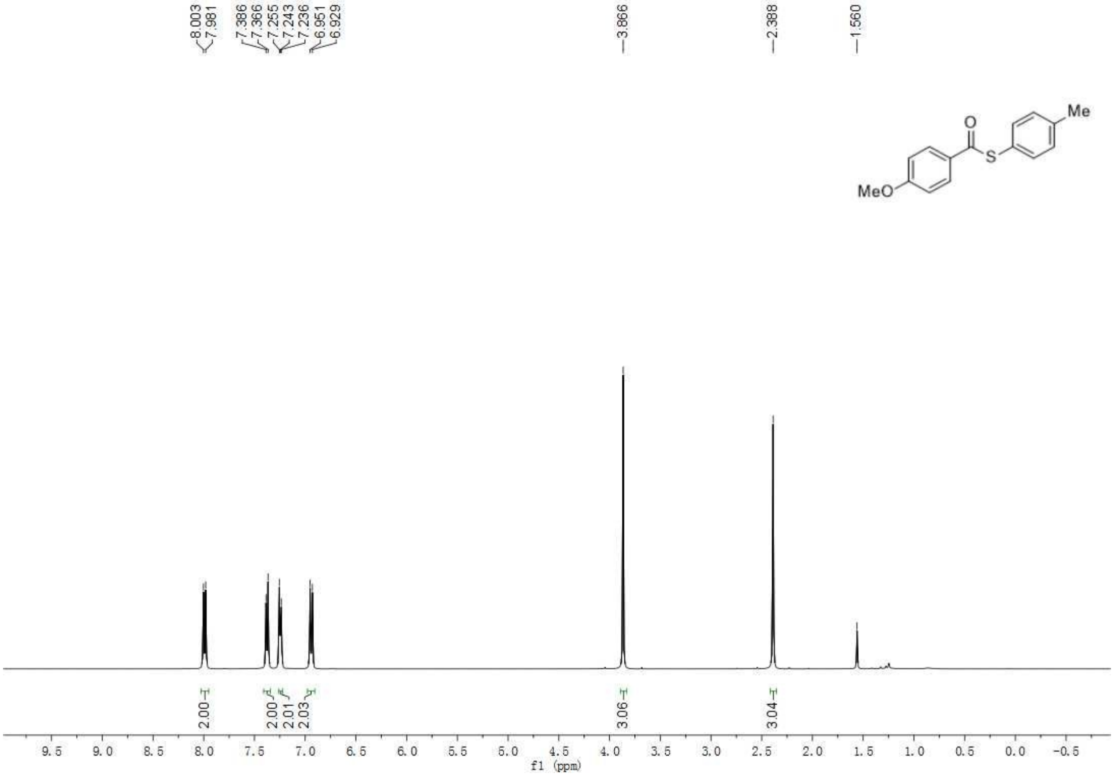
^{1}H NMR Spectrum of S-(p-tolyl) [1,1'-biphenyl]-4-carbothioate **(3w)**



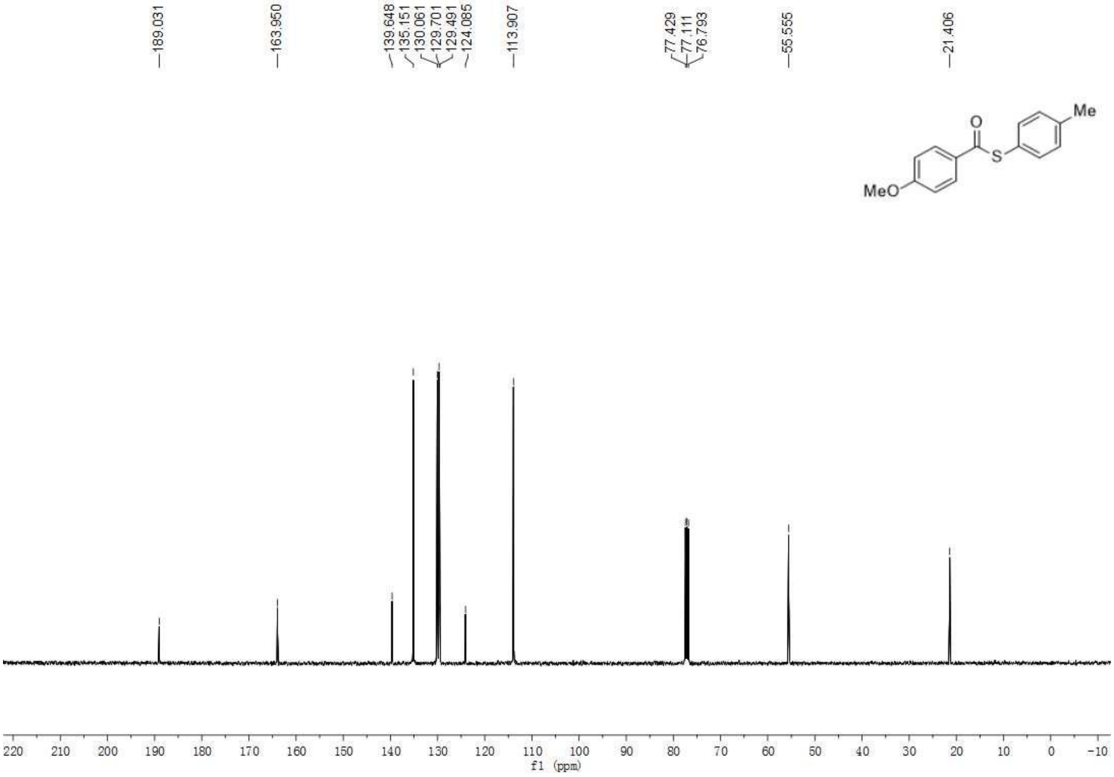
^{13}C NMR Spectrum of S-(p-tolyl) [1,1'-biphenyl]-4-carbothioate **(3w)**



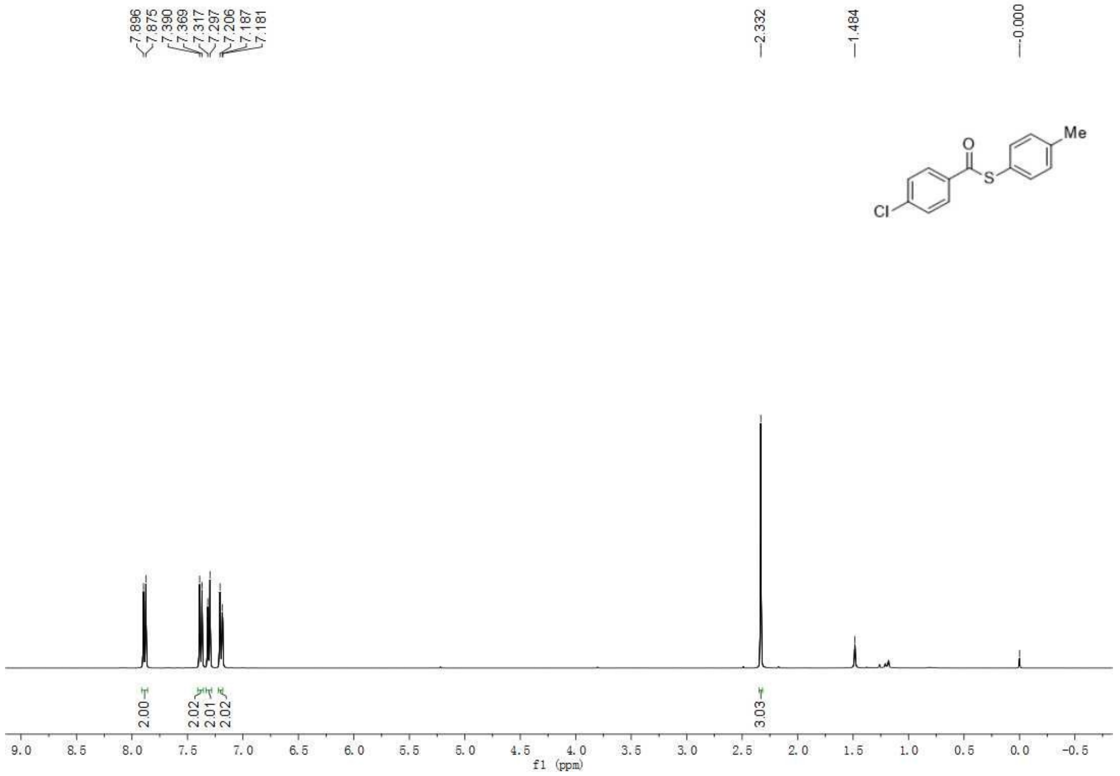
^{1}H NMR Spectrum of S-(p-tolyl) 4-methoxybenzothioate **(3x)**



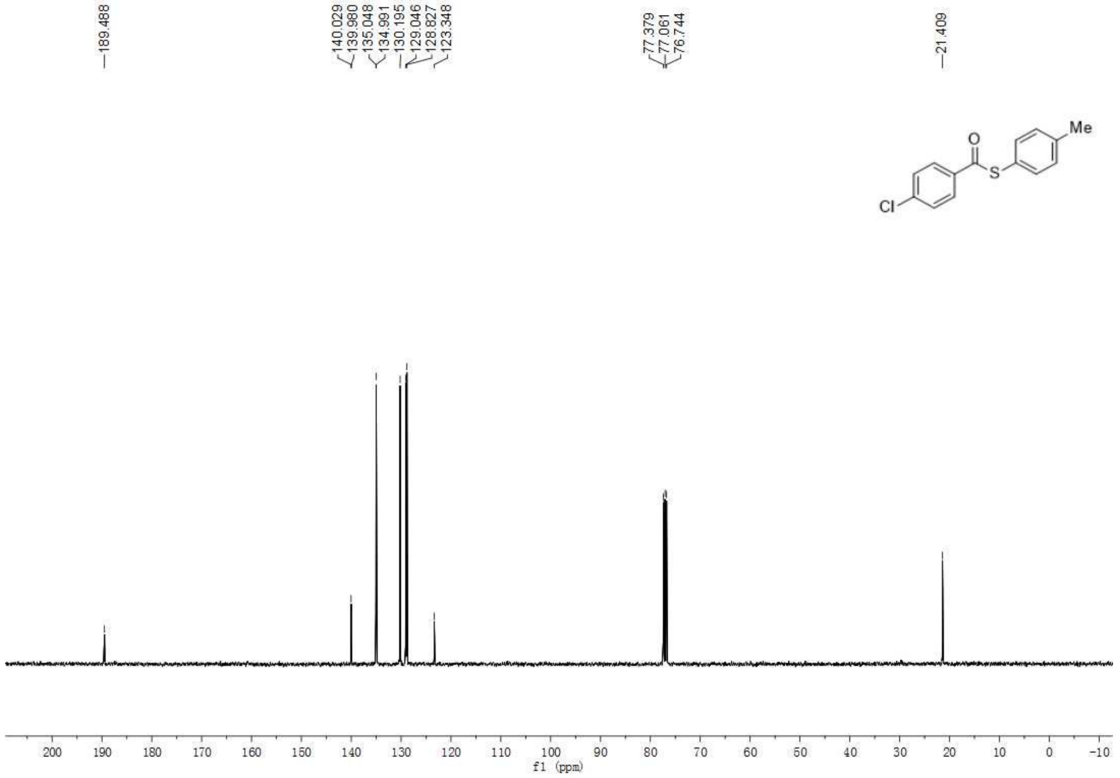
^{13}C NMR Spectrum of S-(p-tolyl) 4-methoxybenzothioate **(3x)**



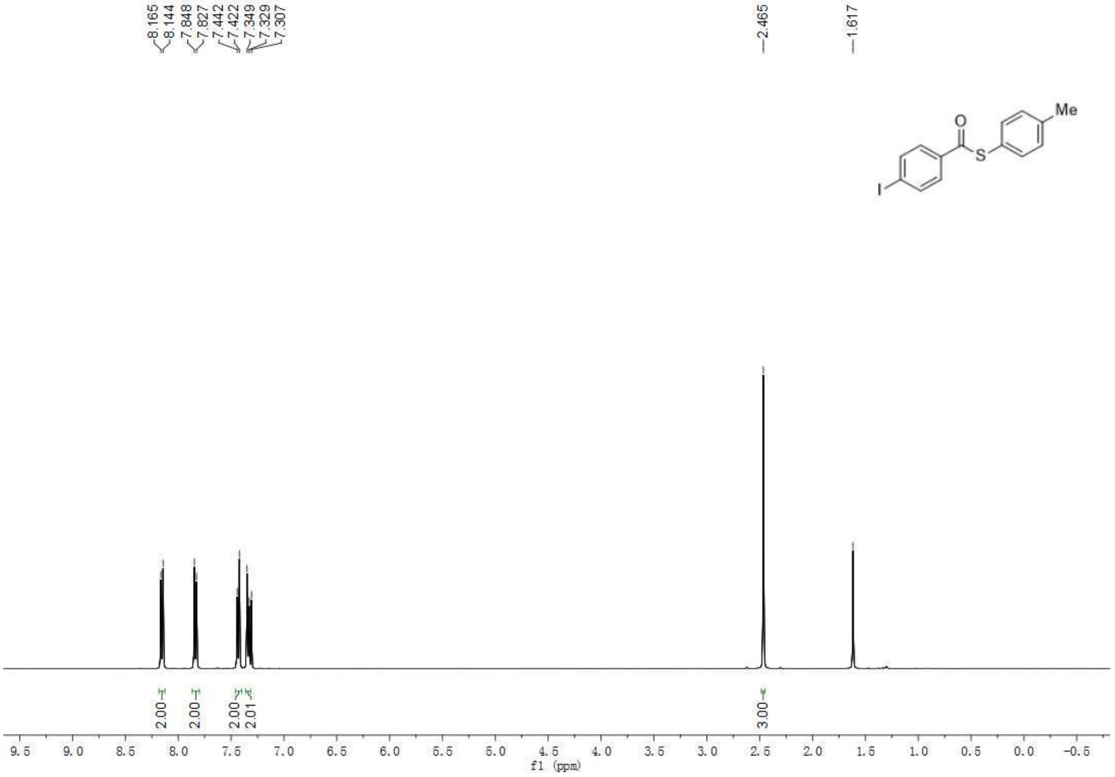
^{1}H NMR Spectrum of S-(p-tolyl) 4-chlorobenzothioate **(3y)**



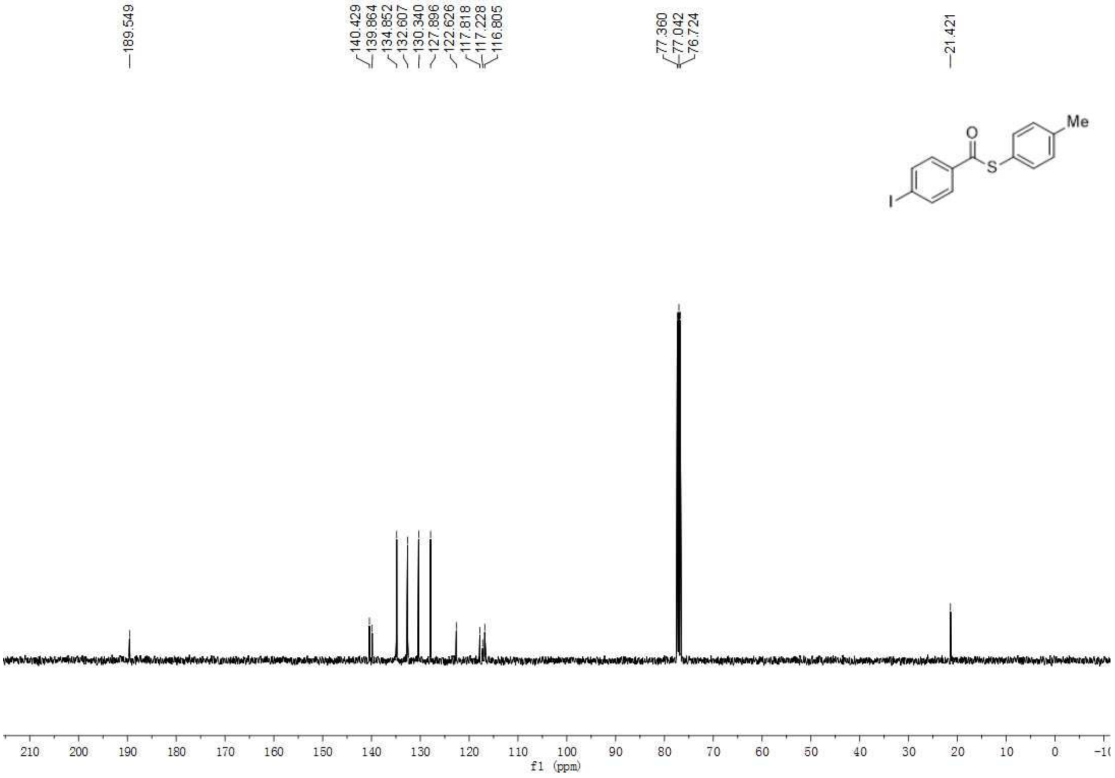
^{13}C NMR Spectrum of S-(p-tolyl) 4-chlorobenzothioate **(3y)**



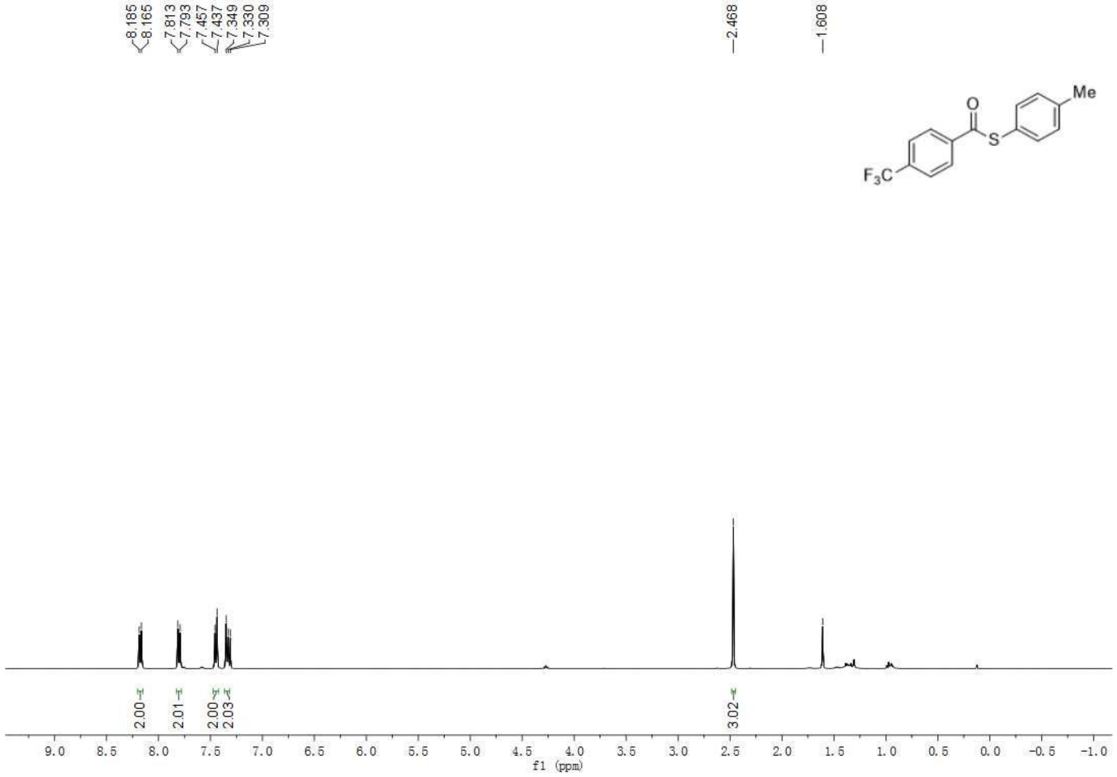
^{1}H NMR Spectrum of S-(p-tolyl) 4-iodobenzothioate **(3z)**



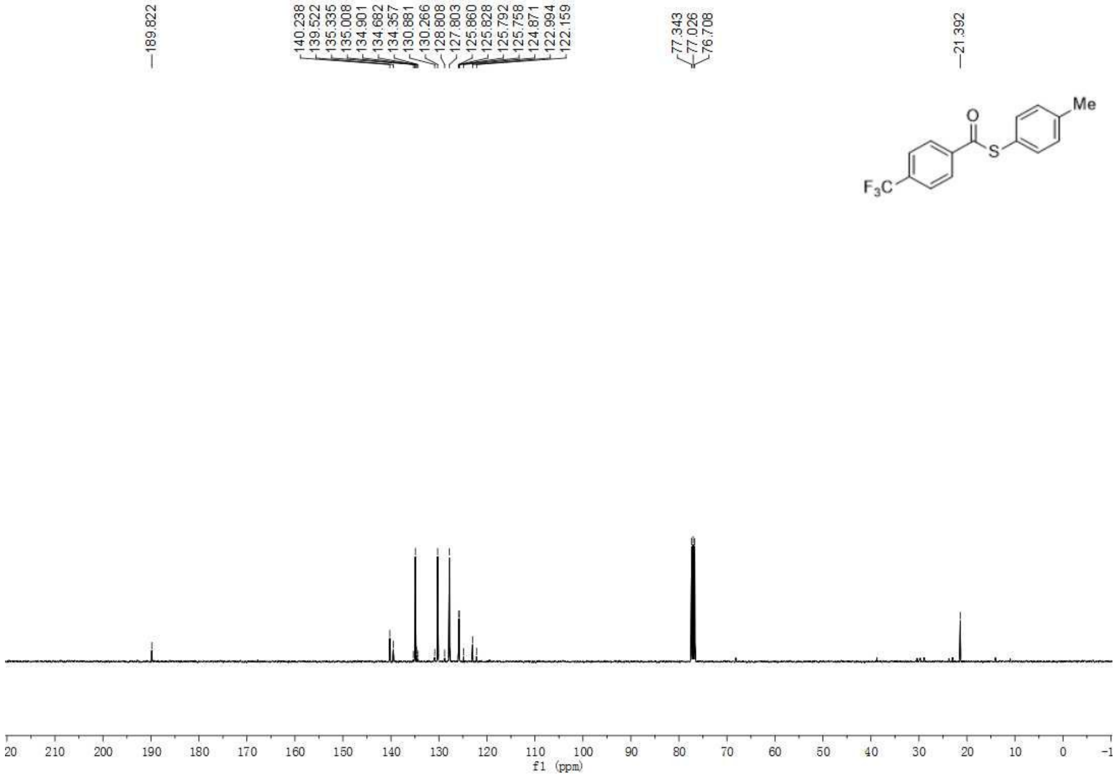
^{13}C NMR Spectrum of S-(p-tolyl) 4-iodobenzothioate **(3z)**



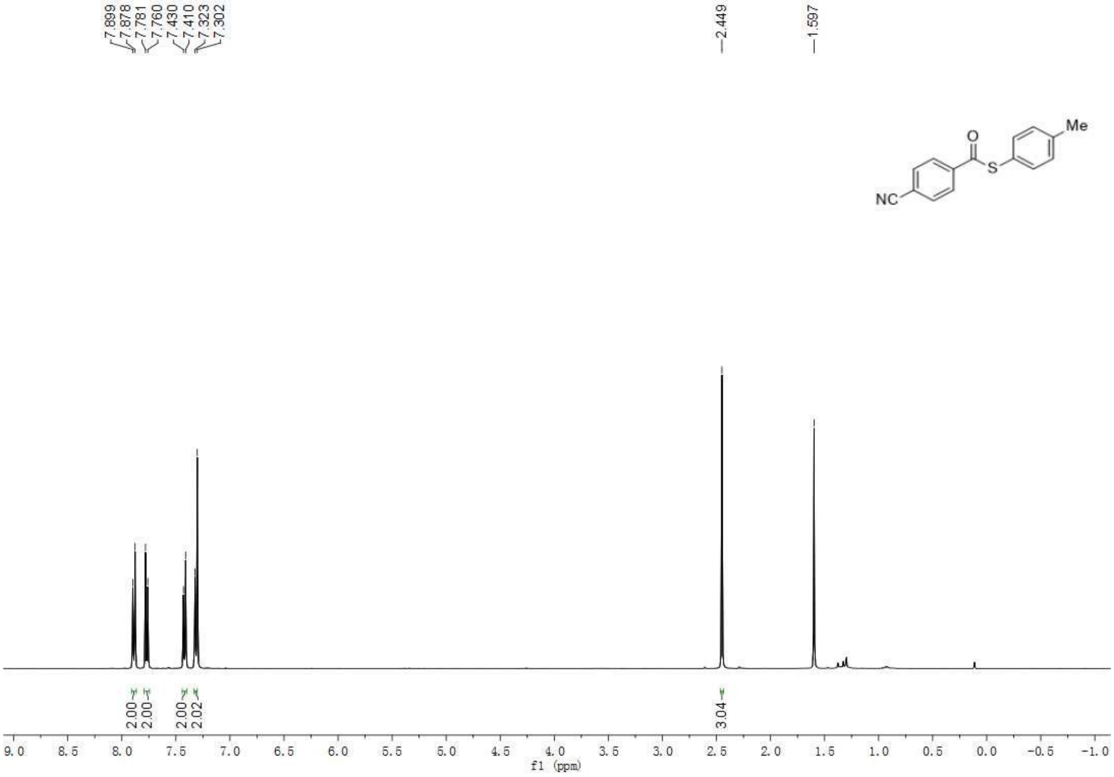
^{1}H NMR Spectrum of S-(p-tolyl) 4-(trifluoromethyl)benzothioate **(3aa)**



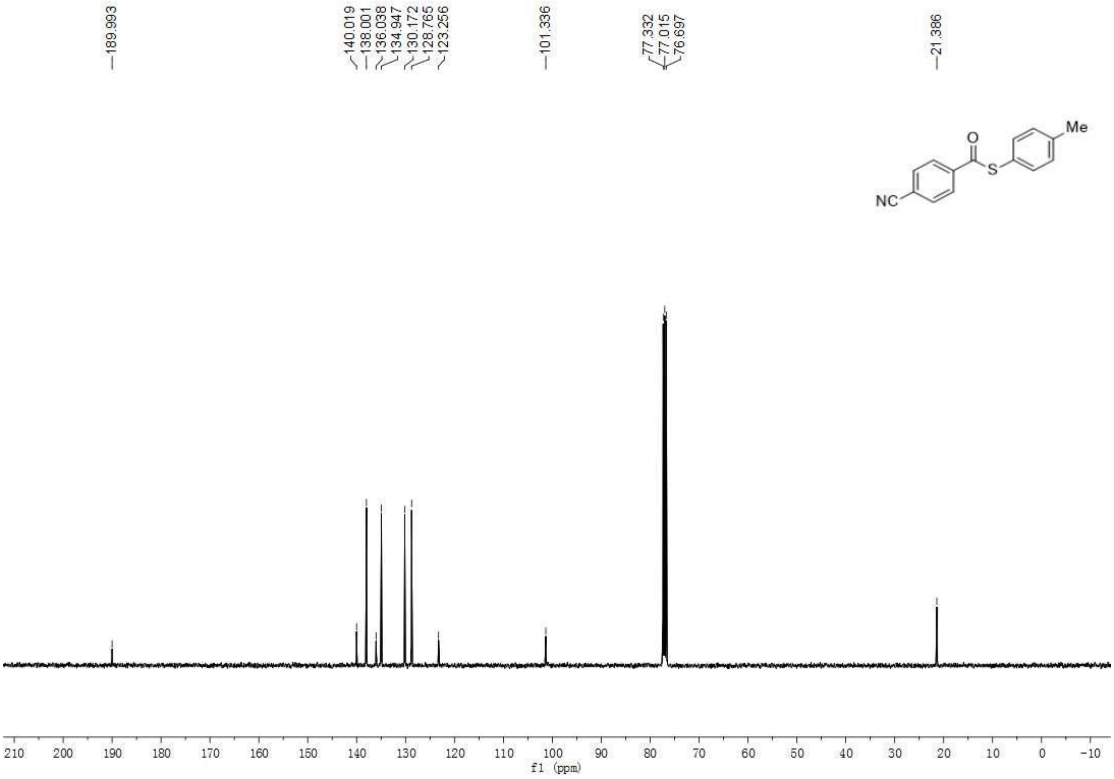
^{13}C NMR Spectrum of S-(p-tolyl) 4-(trifluoromethyl)benzothioate **(3aa)**



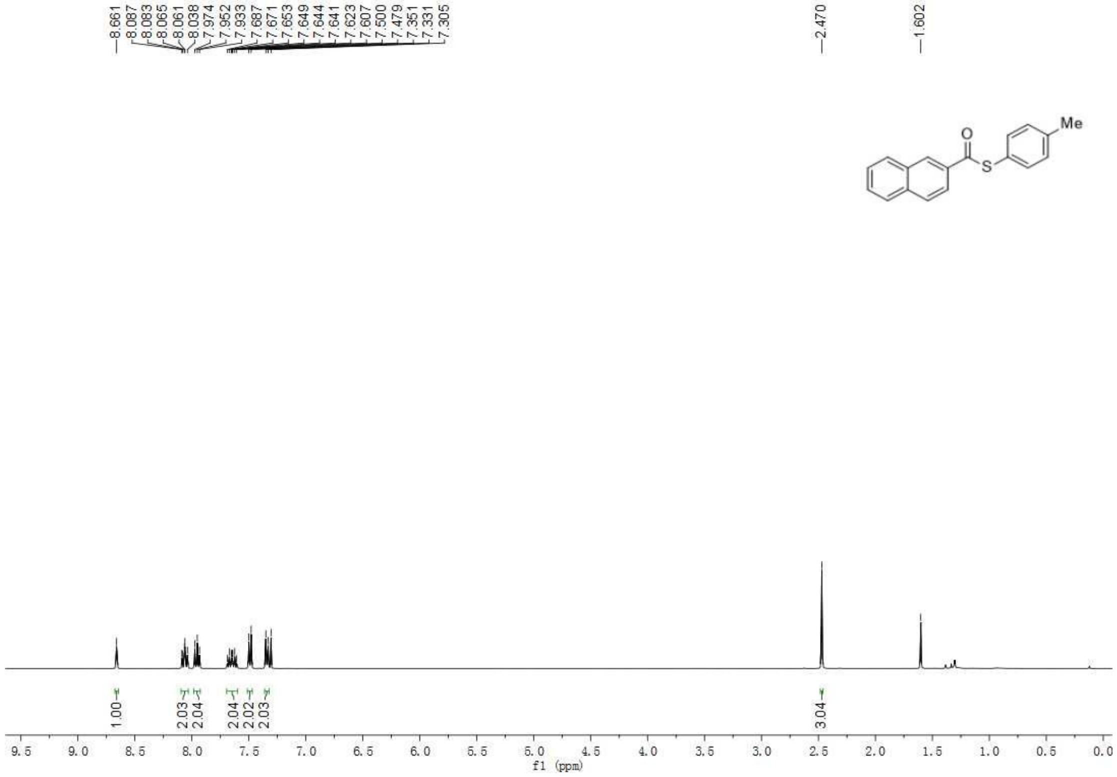
^{1}H NMR Spectrum of S-(p-tolyl) 4-cyanobenzothioate **(3ab)**



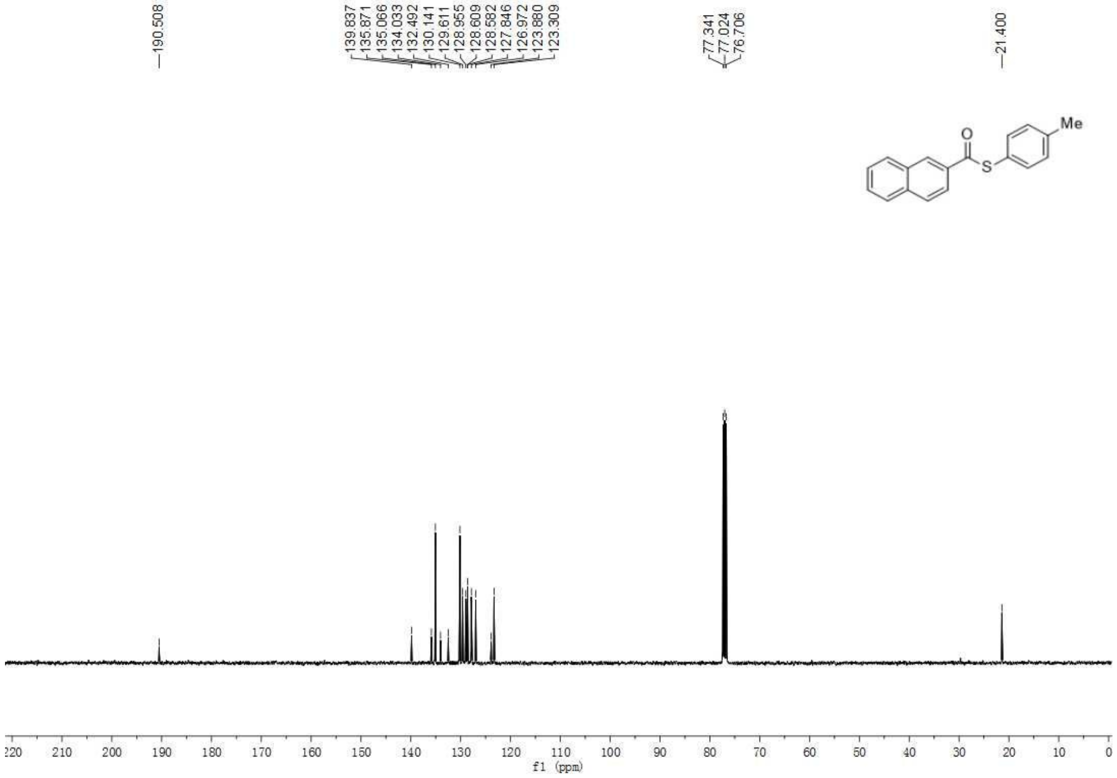
^{13}C NMR Spectrum of S-(p-tolyl) 4-cyanobenzothioate **(3ab)**



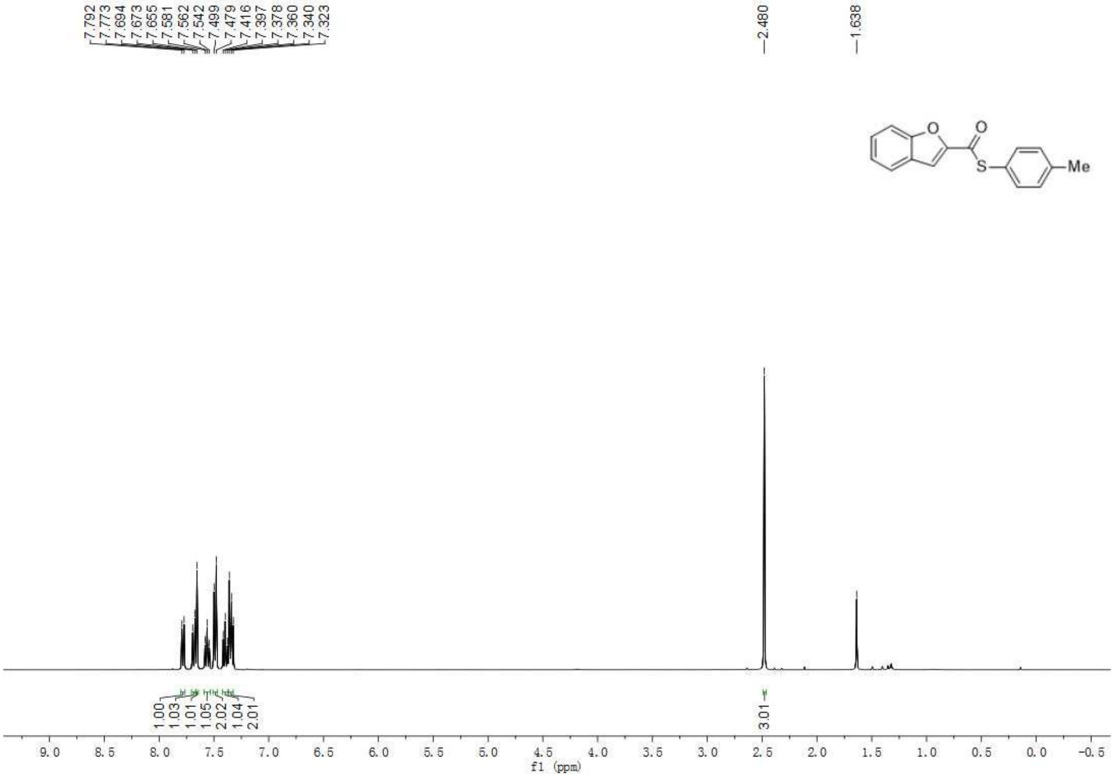
^{1}H NMR Spectrum of S-(p-tolyl) naphthalene-2-carbothioate **(3ac)**



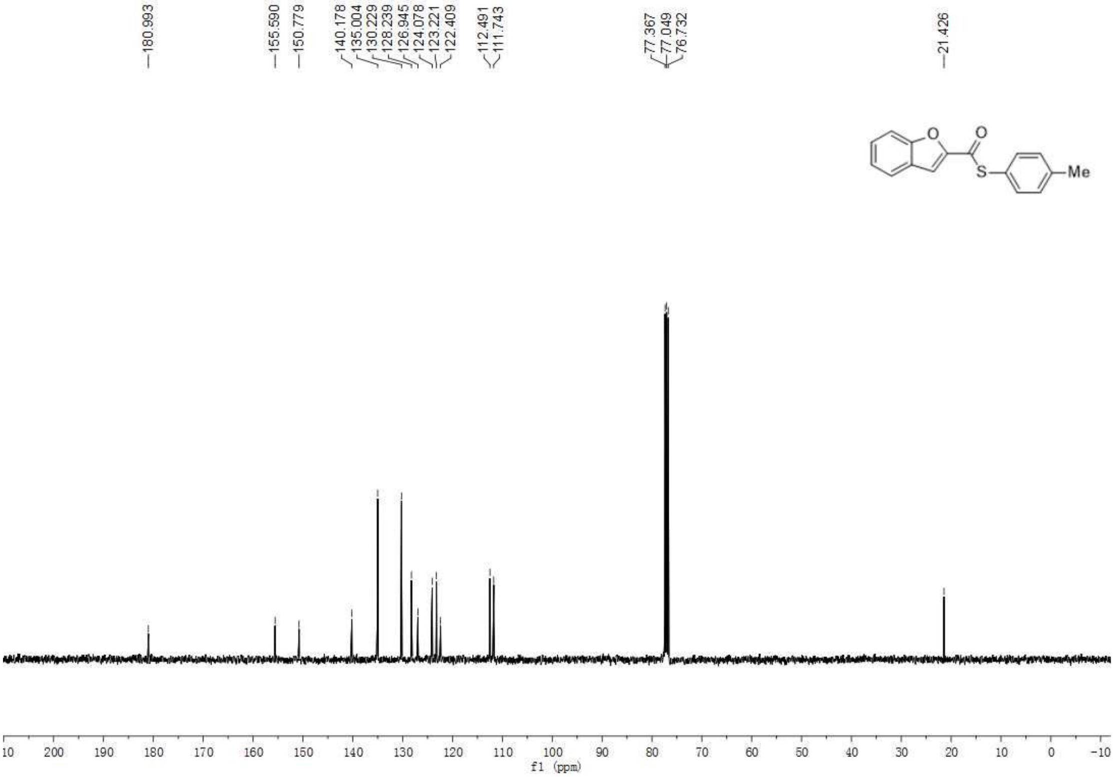
^{13}C NMR Spectrum of S-(p-tolyl) naphthalene-2-carbothioate **(3ac)**



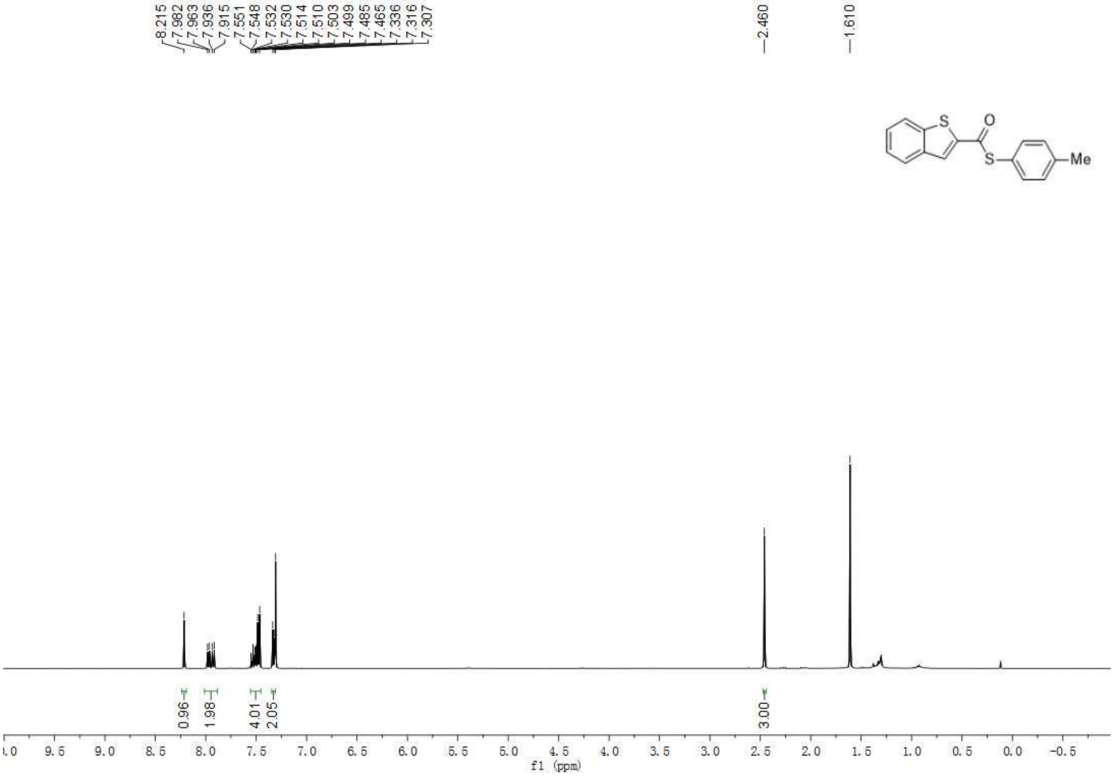
^{1}H NMR Spectrum of S-(p-tolyl) benzofuran-2-carbothioate **(3ad)**



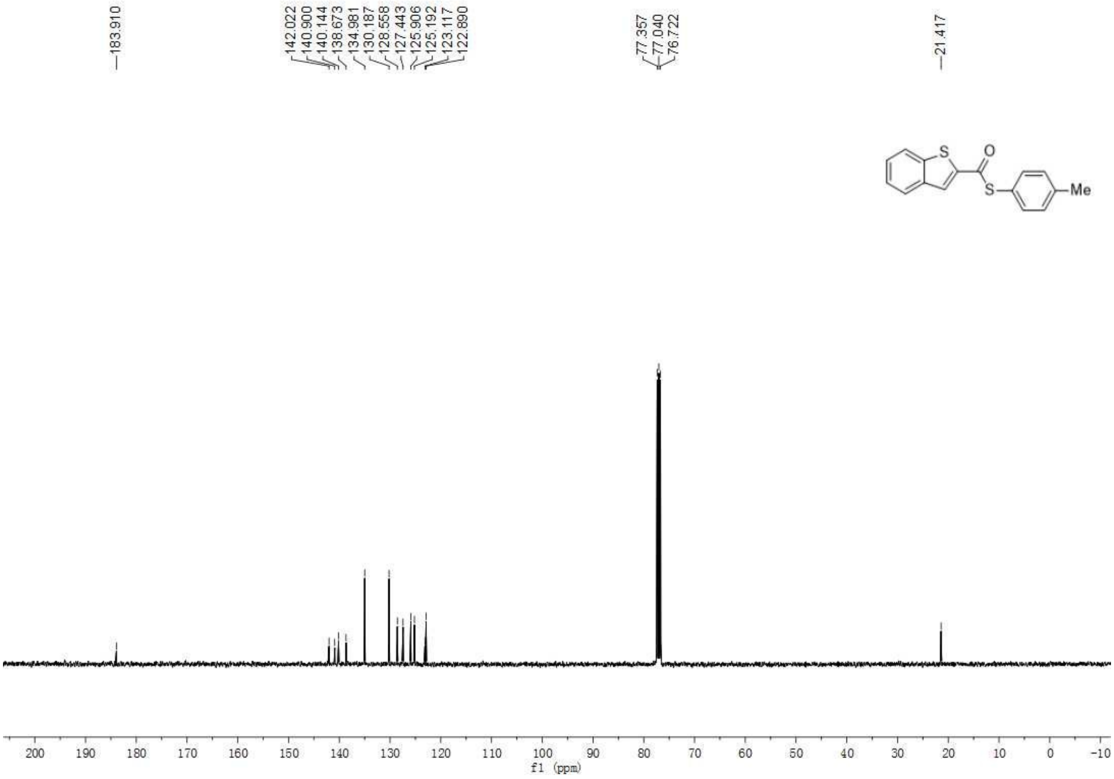
^{13}C NMR Spectrum of S-(p-tolyl) benzofuran-2-carbothioate **(3ad)**



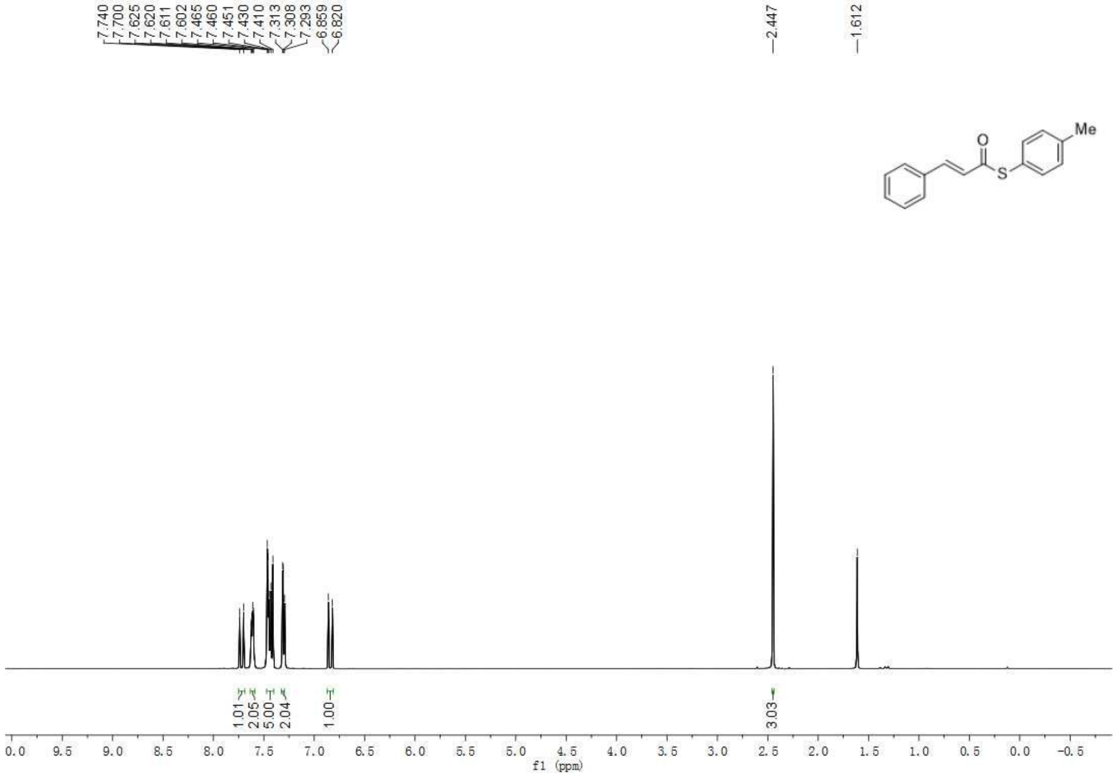
^{1}H NMR Spectrum of S-(p-tolyl) benzo[b]thiophene-2-carbothioate **(3ae)**



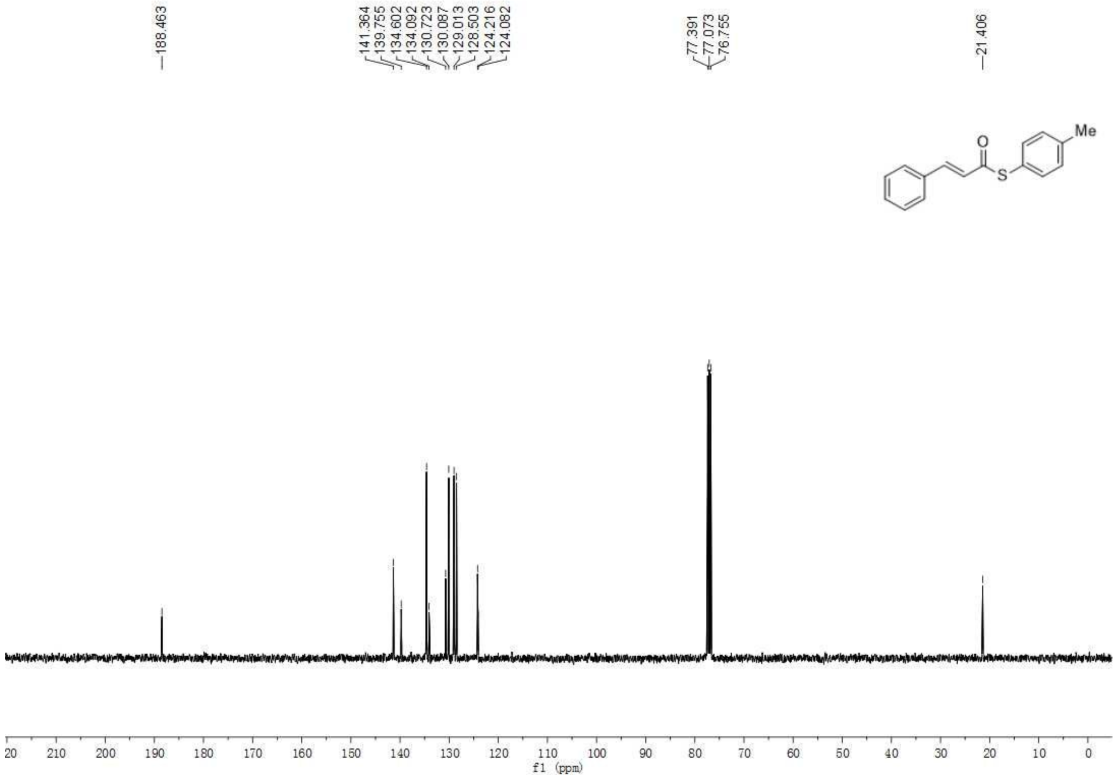
^{13}C NMR Spectrum of S-(p-tolyl) benzo[b]thiophene-2-carbothioate **(3ae)**



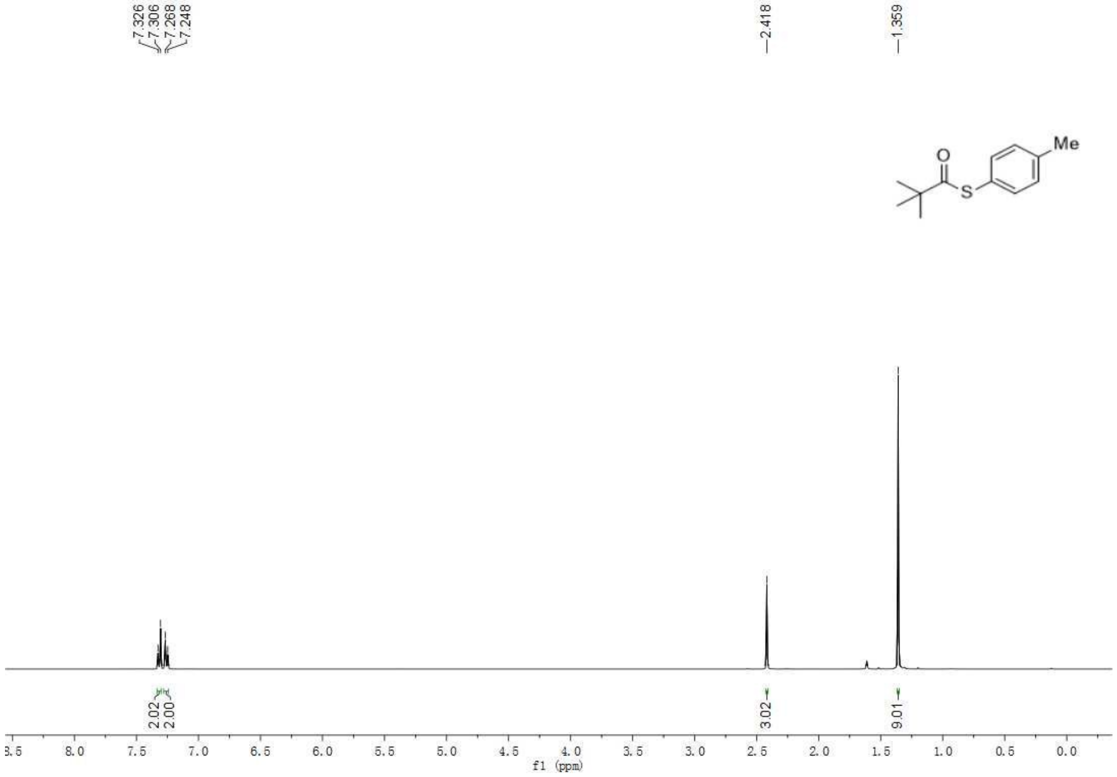
^{1}H NMR Spectrum of S-(p-tolyl) (E)-3-phenylprop-2-enethioate **(3af)**



^{13}C NMR Spectrum of S-(p-tolyl) (E)-3-phenylprop-2-enethioate **(3af)**



^{1}H NMR Spectrum of S-(p-tolyl) 2,2-dimethylpropanethioate **(3ag)**



^{13}C NMR Spectrum of S-(p-tolyl) 2,2-dimethylpropanethioate **(3ag)**