Electronic Supplementary Information

Transamidation of Thioamides with Nucleophilic Amines: Thioamide N–C(S) Activation by Ground-State-Destabilization

Jin Zhang,*[,†] Hui Zhao,[†] Guangchen Li,[‡] Xinhao Zhu,[†] Linqin Shang,[†] Yang He[†] Xin Liu,[†] Yangmin Ma[†] and Michal Szostak*[,‡]

[†]*College of Chemistry and Chemical Engineering, Key Laboratory of Chemical Additives for China National Light Industry, Shaanxi University of Science and Technology, Xi'an 710021, China*

[‡]*Department of Chemistry, Rutgers University, 73 Warren Street, Newark, New Jersey 07102, United States*

Table of Contents S1

Corresponding Author:

Shaanxi University of Science and Technology
6 Xuefu Road, Xi'an 710021, China
E-mail: zhangjin@sust.edu.cn

Department of Chemistry, Rutgers University
73 Warren Street, Newark, NJ 07102, United States
E-mail: michal.szostak@rutgers.edu

1. General Information

Commercially available chemicals were purchased from commercial suppliers and used as received without further purification. All reactions were performed in oven-dried or flame-dried glassware. TLC analysis was carried out on glass plates coated with silica gel 60 F254. The plates were visualized using a 254 nm ultraviolet lamp. Purification was performed by chromatography using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Ascend spectrometers at 400 , 500 or 600 MHz (^{1}H NMR), 100 MHz or 150 MHz (^{13}C NMR) and 376 MHz (^{19}F NMR). For ^{1}H NMR, tetramethylsilane (TMS) (δ = 0) in $CDCl_3$ was used as an internal standard. For ^{13}C NMR, $CDCl_3$ (δ = 77.0) was used as an internal standard. The following abbreviations were used: s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad. All coupling constants (*J*) are reported in hertz (Hz). ^{1}H NMR and ^{13}C NMR data are given for all compounds in the Supporting Information for characterization purposes.

2. Experimental Procedures and Characterization Data

- **General Procedure for the Synthesis of Thioamides.**

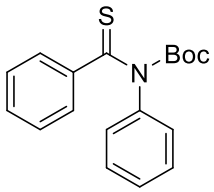
All starting materials reported in the manuscript have been previously described in literature and prepared by the method reported previously unless indicated otherwise. Thioamides were prepared by Amides and P_2S_5 that have been previously described in literature.[1]

General procedure for the synthesis N, N-Boc/Boc thioamides: An oven-dried flask equipped with a stir bar was charged with a primary thioamide (2.0 mmol, 1.0 equiv), dimethylaminopyridine (0.10 mmol, 5 mol%) and THF (0.20 M). Di-*tert*-butyl dicarbonate (3.0 equiv) was added dropwise to the reaction mixture with vigorous stirring at 0 ℃, and the reaction mixture was stirred for 15 h at 25 °C. After the indicated time, the reaction mixture was diluted with ethyl acetate (50 mL), the organic layer was washed with water (1 x 30 mL), brine (1 x 30 mL), dried over Na_2SO_4, and concentrated. The crude reaction mixture was purified by chromatography on silica gel (PE/EA = 40:1).

General procedure for the synthesis of N-mono-Boc thioamides: An oven-dried flask equipped with a stir bar was charged with a secondary thioamide (2.0 mmol, 1.0 equiv), dimethylaminopyridine (0.10 mmol, 5 mol%) and THF (0.20 M). Di-*tert*-butyl dicarbonate (1.1 equiv) was added dropwise to the reaction mixture with vigorous stirring at 0 ℃, and the reaction mixture was stirred for 15 h at 25 °C. After the indicated time, the reaction mixture was diluted with ethyl acetate (50 mL), the organic layer was washed with water (1 x 30 mL), brine (1 x 30 mL), dried over Na_2SO_4, and concentrated. The crude reaction mixture was purified by chromatography on silica gel (PE/EA = 40:1).

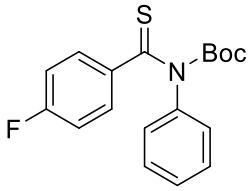
- **Characterization Data of Starting Materials**

Thioamides used in this study were prepared by procedures reported in the literature. Spectroscopic data match those reported in the literature. All other thioamide starting materials were prepared by methods described in the manuscript. [2]



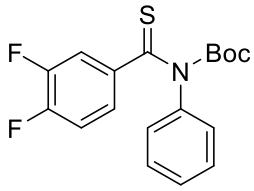
1a

***tert*-Butyl phenyl(phenylcarbonothioyl)carbamate (1a).** Yellow solid. Spectroscopic properties matched those described previously.[2]



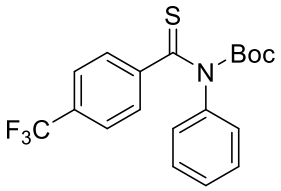
1b

***tert*-Butyl (4-fluorophenylcarbonothioyl)(phenyl)carbamate (1b).** Yellow solid.^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.67 (m, 2H), 7.43 (d, J = 7.2 Hz, 2H), 7.35 (d, J = 7.1 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.04 (d, J = 7.2 Hz, 2H), 1.22 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 209.2 (s, -**C**=S, 1C), 164.3 (d, J = 253.7 Hz, -**C**$_{(Ph)}$-F, 1C) ,152.5 (s, -**C**=O, 1C), 143.8 (s, **C**$_{Ph}$ –C=S, 1C), 142.5 (s, **C**$_{Ph}$ -N, 1C), 129.5 (s, **C**$_{Ph}$, 2C), 129.3(d, J = 9.1 Hz, **C**$_{Ph}$, 1C), 128.1 (s, **C**$_{Ph}$, 2C), 127.8 (s, **C**$_{Ph}$, 2C), 115.2 (d, J = 22.7 Hz, **C**$_{Ph}$, 2C), 84.5 (s, -**C**-$(CH_3)_3$, 1C), 27.4 (s, -C-**$(CH_3)_3$**, 3C). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.6 -108.5 (m, 1F). HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}FNO_2S^+$:332.1115; Found: 332.1109.



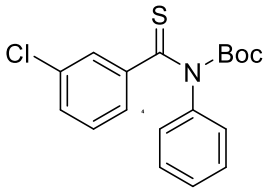
1c

***tert*-Butyl (3,4-difluorophenylcarbonothioyl)(phenyl)carbamate (1c).** Yellow solid. Spectroscopic properties matched those described previously.[2]



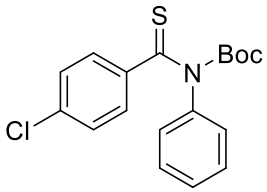
1d

***tert*-Butyl phenyl(4-(trifluoromethyl)phenylcarbonothioyl)carbamate (1d)**. Yellow solid. Spectroscopic properties matched those described previously.[2]



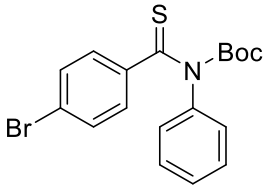
1e

***tert*-Butyl (3-chlorophenylcarbonothioyl)(phenyl)carbamate (1e)**. Yellow solid. Spectroscopic properties matched those described previously.[2]



1f

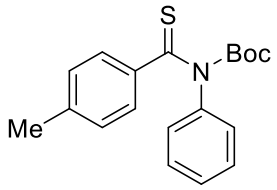
***tert*-Butyl (4-chlorophenylcarbonothioyl)(phenyl)carbamate (1f).** Yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, J = 8.5 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H), 7.42 (dd, J = 14.5, 7.9 Hz, 3H), 7.31 (d, J = 5.2 Hz, 2H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.2 (s, -**C**=S, 1C), 152.5 (s, -**C**=O, 1C), 144.7 (s, **C$_{Ph}$** –C=S, 1C), 143.8 (s, **C$_{Ph}$** –Cl, 1C), 137.0 (s, **C$_{Ph}$** –N, 1C), 129.6 (s, **C$_{Ph}$**, 2C), 128.5 (s, **C$_{Ph}$**, 2C), 128.4 (s, **C$_{Ph}$**, 2C), 128.3 (s, **C$_{Ph}$**, 1C), 127.9 (s, **C$_{Ph}$**, 2C), 84.8 (s, -**C**-$(CH_3)_3$, 1C), 27.5 (s, -C-**$(CH_3)_3$**, 3C). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{18}ClNO_2S^+$: 370.0639; Found: 370.0638.



1g

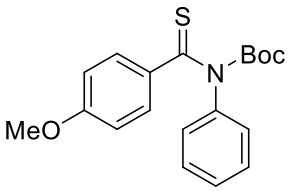
***tert*-Butyl (4-bromophenylcarbonothioyl)(phenyl)carbamate (1g).** Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.54 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.3 Hz, 2H),

7.43 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.25 (d, J = 7.7 Hz, 2H), 1.23 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 209.1 (s, -**C**=S, 1C), 152.4 (s, -**C**=O, 1C), 145.0 (s, $\mathbf{C}_{\mathbf{Ph}}$–C=S, 1C), 143.7 (s, $\mathbf{C}_{\mathbf{Ph}}$, 1C), 131.3 (s, $\mathbf{C}_{\mathbf{Ph}}$–N, 1C), 129.6 (s, $\mathbf{C}_{\mathbf{Ph}}$, 2C), 128.4 (s, $\mathbf{C}_{\mathbf{Ph}}$, 2C), 128.2 (s, $\mathbf{C}_{\mathbf{Ph}}$, 2C), 127.9 (s, $\mathbf{C}_{\mathbf{Ph}}$, 2C), 125.3 (s, $\mathbf{C}_{\mathbf{Ph}}$–Br, 1C), 84.8 (s, -**C**-$(CH_3)_3$, 1C), 27.5 (s, -C-$\mathbf{(CH_3)_3}$, 3C). HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}BrNO_2S^+$: 392.0314; Found: 392.0414.



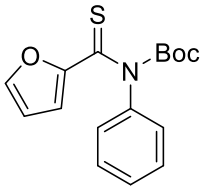
1h

***tert*-Butyl (4-methylphenylcarbonothioyl)(phenyl)carbamate (1h)**. Yellow solid. Spectroscopic properties matched those described previously.[2]



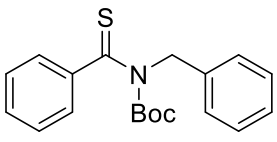
1i

***tert*-Butyl (4-methoxyphenylcarbonothioyl)(phenyl)carbamate (1i).** Yellow solid. Spectroscopic properties matched those described previously.[2]



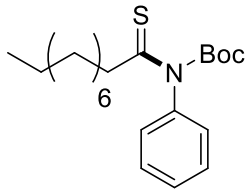
1j

***tert*-Butyl (furan-2-carbonothioyl)(phenyl)carbamate (1j)**. Yellow solid. Spectroscopic properties matched those described previously.[2]



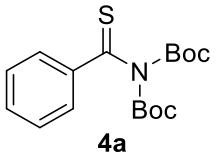
1k

***tert*-Butyl benzyl(phenylcarbonothioyl)carbamate (1k).** Yellow solid. Spectroscopic properties matched those described previously.[2]



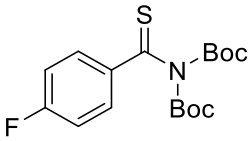
1l

***tert*-Butyl decanethioyl(phenyl)carbamate(1l).** Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.11 (d, J = 7.5 Hz, 2H), 3.31 – 3.26 (m, 2H), 1.87 – 1.78 (m, 2H), 1.40 (s, 9H), 1.37 – 1.13 (m, 12H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 216.4 (s, -**C**=S, 1C), 151.8 (s, -**C**=O, 1C), 143.4 (s, **C$_{Ph}$**–N-, 1C), 129.2 (s, **C$_{Ph}$**, 2C), 128.0 (s, **C$_{Ph}$**, 2C), 127.8 (s, **C$_{Ph}$**, 1C), 84.3 (s, -**C**-$(CH_3)_3$, 1C), 47.2 (s, S=C-**CH_2**-CH_2, 1C), 31.9 (s, -CH_2-**CH_2-**, 1C), 30.5 (s, -CH_2-**CH_2-**, 1C), 29.5 (s, -CH_2-**CH_2-**, 1C), 29.4 (s, -CH_2-**CH_2-**, 1C), 29.3 (s, -CH_2-**CH_2-**, 1C), 29.2 (s, -CH_2-**CH_2-**, 1C), 27.6 (s, -C-**(CH_3)$_3$**, 3C), 22.7 (s, -**CH_2**-CH_3, 1C), 14.1 (s, -CH_2-**CH_3**, 1C). HRMS calcd for $C_{21}H_{33}NO_2SNa$ $[M + Na]^+$ 386.2118, found 386.2124.



4a

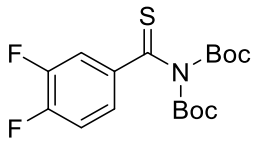
***tert*-Butyl (*tert*-butoxycarbonyl)(phenylcarbonothioyl)carbamate (4a).** Yellow solid. Spectroscopic properties matched those described previously.[2]



4b

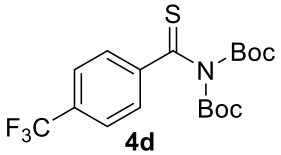
***tert*-Butyl (4-fluorophenylcarbonothioyl)(phenyl)carbamate (4b).**Yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.66 (m, 2H), 7.08 (t, J = 8.2 Hz, 2H), 1.48 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 205.6 (s, -**C**=S, 1C), 165.3 (d, J = 256.7 Hz, F-**C$_{Ph}$**, 1C), 150.4 (s, -**C**=O, 2C), 140.6 (s, **C$_{Ph}$**-C=S,1C), 130.0 (d, J = 9.1 Hz, **C$_{Ph}$**, 2C), 115.5 (d, J = 22.2 Hz, **C$_{Ph}$**, 2C), 85.3 (s, -**C**-$(CH_3)_3$, 2C), 27.5 (s, -C-**(CH_3)$_3$**, 6C). ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.8 - -103.9 (m, 1F). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$

Calcd for $C_{17}H_{22}FNO_4S^+$: 378.1146; Found: 378.1140.



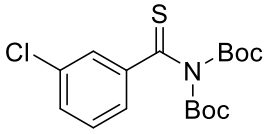
4c

***tert*-Butyl (*tert*-butoxycarbonyl)(3,4-difluorophenylcarbonothioyl) carbamate (4c).** Yellow solid. Spectroscopic properties matched those described previously.[2]



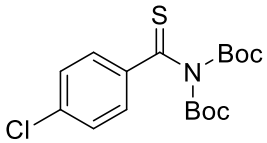
4d

***tert*-Butyl phenyl(4-(trifluoromethyl)phenylcarbonothioyl)carbamate (4d).** Yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (q, J = 8.1 Hz, 4H), 1.47 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.0 (s, -**C**=S, 1C), 157.5 (s, -**C**=O, 2C), 140.6 (s, **C$_{Ph}$**-C=S,1C), 136.4 (q, J = 47.7 Hz, **C$_{Ph}$**-CF_3, 1C), 129.3 (s, **C$_{Ph}$**, 2C), 128.2 (s, J = 4.2 Hz, **C$_{Ph}$**, 2C), 123.7 (q, J = 272.6 Hz, -**C**F_3, 1C), 85.0 (s, -**C**-$(CH_3)_3$, 2C), 27.7 (s, -C-**$(CH_3)_3$**, 6C). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9 (s, 1F), -63.1 (s, 1F), -63.5 (s, 1F). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{22}F_3NO_4S^+$: 428.1114; Found: 428.1113.



4e

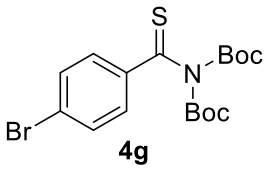
***tert*-Butyl (*tert*-butoxycarbonyl)(3-chlorophenylcarbonothioyl) carbamate (4e).** Yellow solid. Spectroscopic properties matched those described previously.[2]



4f

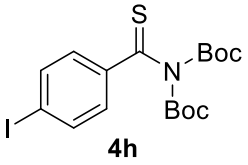
***tert*-Butyl (4- chlorophenylcarbonothioyl)(phenyl)carbamate (4f).** Yellow solid.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 1.44 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 205.1 (s, -**C**=S, 1C), 150.0 (s, -**C**=O, 2C), 142.2 (s, **C$_{Ph}$**-C=S, 1C), 138.0 (s, **C$_{Ph}$**-Cl, 1C), 133.2 (s, **C$_{Ph}$**, 2C), 129.5 (s, **C$_{Ph}$**, 2C),

85.0 (s, -**C**-$(CH_3)_3$, 2C), 27.2 (s, -C-**$(CH_3)_3$**, 6C). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{18}ClNO_2S^+$: 370.0639; Found: 370.0638.



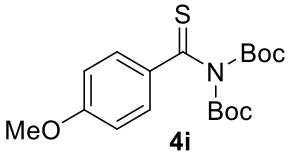
4g

***tert*-Butyl (4-bromophenylcarbonothioyl)(*tert*-butoxycarbonyl) carbamate (4g)**. Yellow solid. Spectroscopic properties matched those described previously.[2]



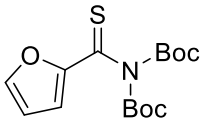
4h

***tert*-Butyl (4- iodophenylcarbonothioyl)(phenyl)carbamate (4h).** Yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 1.43 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.8 (s, -**C**=S, 1C), 150.2 (s, -**C**=O, 2C), 143.4 (s, **C$_{Ph}$**-C=S, 1C), 137.4 (s, **C$_{Ph}$**, 2C), 128.8 (s, **C$_{Ph}$**, 2C), 99.1 (s, **C$_{Ph}$**-I, 1C), 85.3 (s, -**C**-$(CH_3)_3$, 2C), 27.4 (s, -C-**$(CH_3)_3$**, 6C). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{22}INO_4S^+$: 486.0206; Found: 486.0207.



4i

***tert*-Butyl (4-methoxyphenylcarbonothioyl)(phenyl)carbamate (4i).** Yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H), 1.42 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.2 (s, -**C**=S, 1C), 163.6 (s, -**C$_{Ph}$**-OCH_3, 1C), 150.7 (s, -**C**=O, 2C), 137.4 (s, **C$_{Ph}$**-C=S, 1C), 130.3 (s, **C$_{Ph}$**, 2C), 113.7 (s, **C$_{Ph}$**, 2C), 84.7 (s, -**C**-$(CH_3)_3$, 2C), 55.7 (s, C_{Ph}-**CH_3**, 1C), 27.6 (s, -C-**$(CH_3)_3$**, 6C). HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}NO_5S^+$: 368.1526; Found: 368.1526.

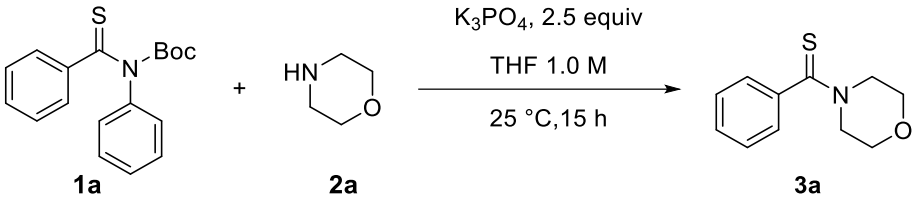


4j

***tert*-Butyl (*tert*-butoxycarbonyl)(furan-2-carbonothioyl)carbamate (4j).** Yellow solid. Spectroscopic properties matched those described previously.[2]

- **Characterization Data of Products**

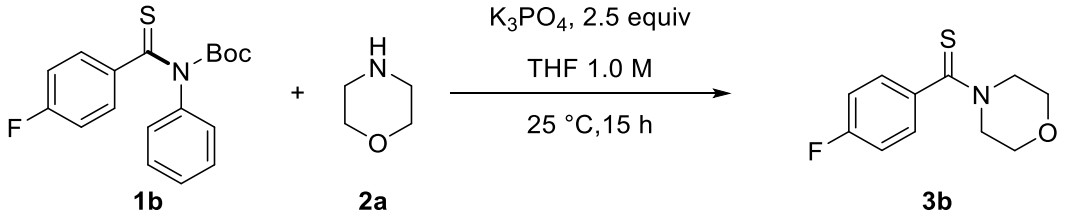
Morpholino(phenyl)methanethione(3a, Table 1, entry 1)



1a 2a 3a

According to the general procedure, the reaction of *tert*-Butyl phenyl(phenylcarbonothioyl) carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 86 % yield (17.8 mg). Yellow solid. Spectroscopic properties matched those described previously.[3]

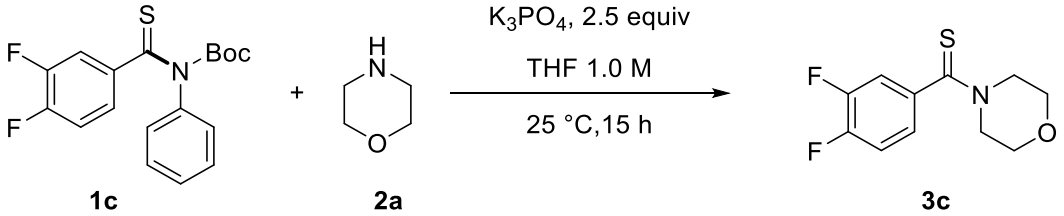
(4-Fluorophenyl)(morpholino)methanethione (3b, Scheme 2)



1b 2a 3b

According to the general procedure, the reaction of *tert*-Butyl (4-fluorophenylcarbonothioyl)(phenyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 57 % yield (13.0 mg). Spectroscopic properties matched those described previously.[4]

(3,4-Difluorophenyl)(morpholino)methanethione (3c, Scheme 2)

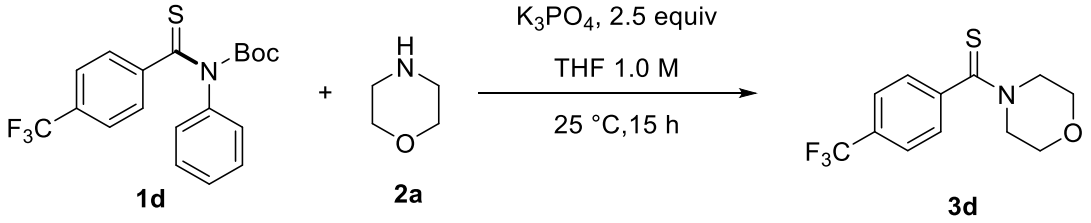


1c 2a 3c

According to the general procedure, the reaction of *tert*-Butyl (4-fluorophenylcarbonothioyl)(phenyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the

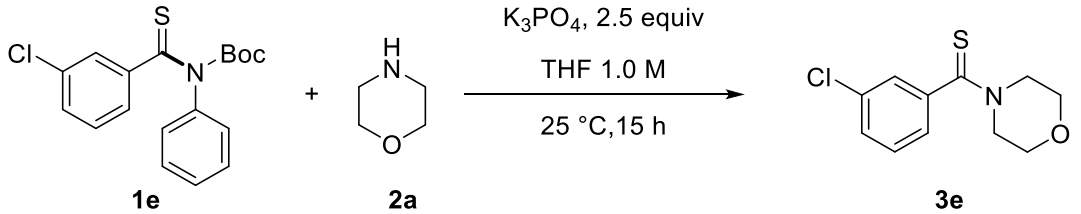
standard work-up as described above and chromatography the title compound in 69 % yield (17.0 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (q, J = 7.4 Hz, 2H), 7.08 (d, J = 6.1 Hz, 1H), 4.45 (s, 2H), 3.93 (s, 2H), 3.68 (d, J = 14.2 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1 (s, -**C**=S, 1C), 151.6 (dd, J = 60.6 Hz, J = 18.6 Hz, F-**C$_{Ph}$**, 1C), 149.1 (dd, J = 50.5 Hz, J = 18.8 Hz, F-**C$_{Ph}$**, 1C), 139.1(t, J = 4.7 Hz, **C$_{Ph}$**-C-C=S, 1C), 122.4 (q, J = 3.9 Hz, **C$_{Ph}$**, 1C), 117.6 (d, J = 17.7 Hz, **C$_{Ph}$**, 1C), 116.0 (d, J = 18.7 Hz, **C$_{Ph}$**, 1C), 66.7 (s, -O-**CH$_2$**-CH_2-, 1C), 66.5 (s, -O-**CH$_2$**-CH_2-, 1C), 52.7 (s, -O-CH_2-**CH$_2$**-, 1C), 49.8 (s, -O-CH_2-**CH$_2$**-, 1C). ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.0 (m, 1F), -136.3 (m, 1F). HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{12}F_2NOS^+$: 244.0602; Found: 244.0596.

Morpholino(4-(trifluoromethyl)phenyl)methanethione (3d, Scheme 2)



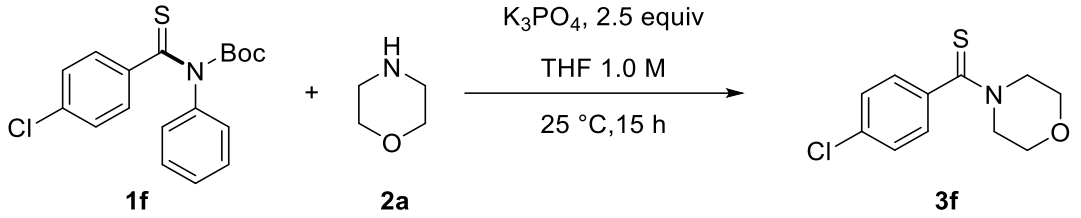
According to the general procedure, the reaction of *tert*-Butyl phenyl(4-(trifluoromethyl)phenylcarbonothioyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 76 % yield (20.5 mg). Spectroscopic properties matched those described previously.[5]

(3-Chlorophenyl)(morpholino)methanethione (3e, Scheme 2)



According to the general procedure, the reaction of *tert*-Butyl (3-chlorophenylcarbonothioyl)(phenyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 62 % yield (21.0 mg). Spectroscopic properties matched those described previously.[3]

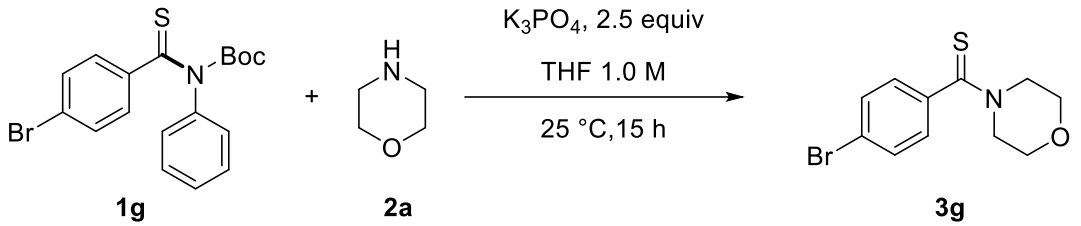
(4-Chlorophenyl)(morpholino)methanethione (3f, Scheme 2)



1f **2a** **3f**

According to the general procedure, the reaction of *tert*-Butyl (4-chlorophenylcarbonothioyl)(phenyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 53 % yield (17.5 mg). Spectroscopic properties matched those described previously.[4]

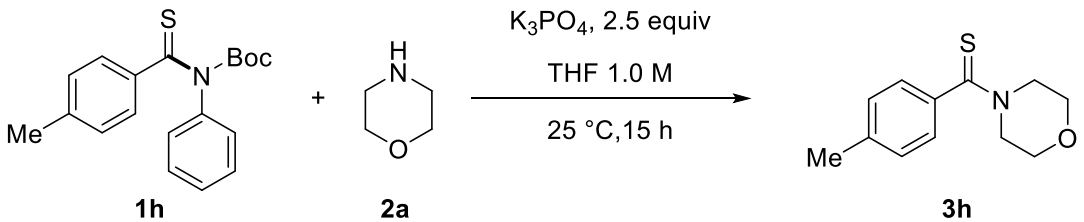
(4-Bromophenyl)(morpholino)methanethione (3g, Scheme 2)



1g **2a** **3g**

According to the general procedure, the reaction of *tert*-Butyl (4-bromophenylcarbonothioyl)(phenyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 65 % yield (18.5 mg). Spectroscopic properties matched those described previously.[4]

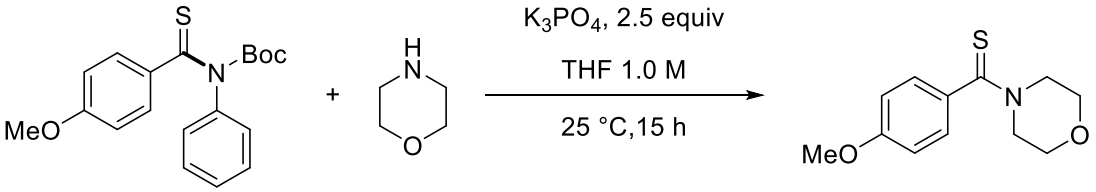
Morpholino(*p*-tolyl)methanethione (3h, Scheme 2)



1h **2a** **3h**

According to the general procedure, the reaction of *tert*-Butyl (4-methylphenylcarbonothioyl)(phenyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 76 % yield (17.0 mg). Spectroscopic properties matched those described previously.[3]

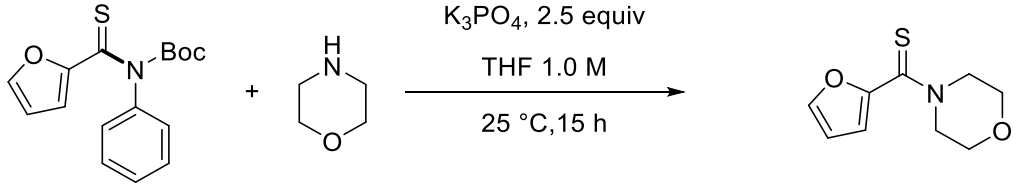
(4-Methoxyphenyl)(morpholino)methanethione (3i, Scheme 2)



1i **2a** **3i**

According to the general procedure, the reaction of *tert*-Butyl (4-methoxyphenylcarbonothioyl)(phenyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 80 % yield (19.0 mg). Spectroscopic properties matched those described previously.[3]

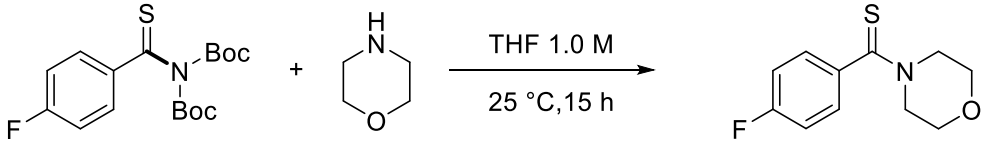
Furan-2-yl(morpholino)methanethione (3j, Scheme 2)



1j **2a** **3j**

According to the general procedure, the reaction of *tert*-Butyl (furan-2-carbonothioyl)(phenyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 65 % yield (12.8 mg). Spectroscopic properties matched those described previously.[6]

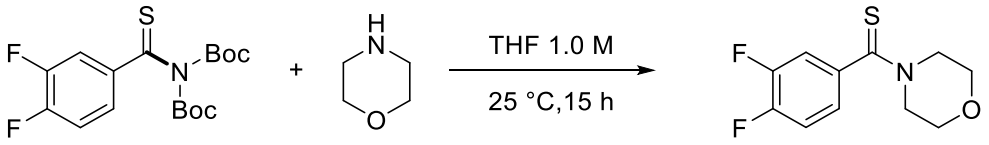
(4-Fluorophenyl)(morpholino)methanethione (3b, Scheme 3)



4b **2a** **3b**

According to the general procedure, the reaction of *tert*-Butyl (4-fluorophenylcarbonothioyl)(phenyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 91 % yield (20.5 mg). Spectroscopic properties matched those described previously.[4]

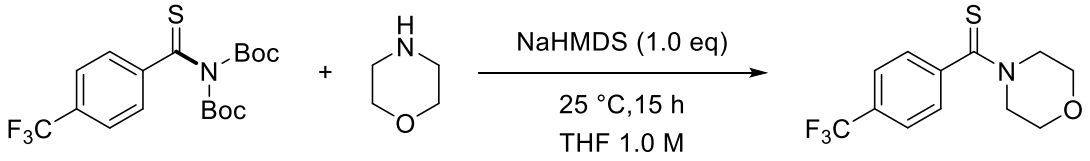
(3,4-Difluorophenyl)(morpholino)methanethione (3c, Scheme 3)



4c **2a** **3c**

According to the general procedure, the reaction of *tert*-Butyl (3,4-difluorophenylcarbonothioyl)(phenyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 50 % yield (12.2 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (q, J = 7.4 Hz, 2H), 7.08 (d, J = 6.1 Hz, 1H), 4.45 (s, 2H), 3.93 (s, 2H), 3.68 (d, J = 14.2 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1 (s, -**C**=S, 1C), 151.6 (dd, J = 60.6 Hz, J = 18.6 Hz, F-**C$_{Ph}$**, 1C), 149.1 (dd, J = 50.5 Hz, J = 18.8 Hz, F-**C$_{Ph}$**, 1C), 139.1(t, J = 4.7 Hz, **C$_{Ph}$**, 1C), 122.4 (q, J = 3.9 Hz, **C$_{Ph}$**, 1C), 117.6 (d, J = 17.7 Hz, **C$_{Ph}$**, 1C), 116.0 (d, J = 18.7 Hz, **C$_{Ph}$**, 1C), 66.7 (s, -O-**CH$_2$**-CH_2-, 1C), 66.5 (s, -O-**CH$_2$**-CH_2-, 1C), 52.7 (s, -O-CH_2-**CH$_2$**-, 1C), 49.8 (s, -O-CH_2-**CH$_2$**-, 1C). ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.0 (m, 1F), -136.3 (m, 1F). HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{12}F_2NOS^+$:244.0602; Found: 244.0596.

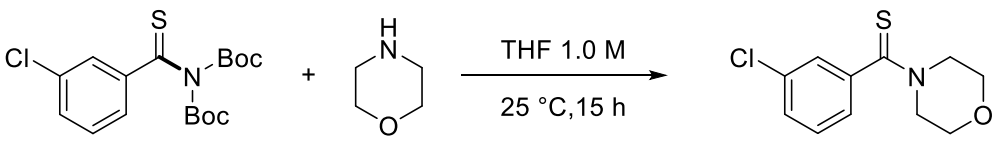
Morpholino(4-(trifluoromethyl)phenyl)methanethione (3d, Scheme 3)



4d **2a** **3d**

According to the general procedure, the reaction of *tert*-Butyl phenyl(4-(trifluoromethyl)phenylcarbonothioyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) and NaHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 60 % yield (16.6 mg). Spectroscopic properties matched those described previously.[5]

(3-Chlorophenyl)(morpholino)methanethione (3e, Scheme 3)

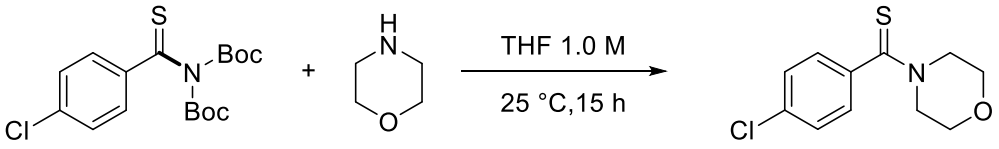


4e **2a** **3e**

According to the general procedure, the reaction of *tert*-Butyl (3-

chlorophenylcarbonothioyl)(phenyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 58 % yield (13.9 mg). Spectroscopic properties matched those described previously.[3]

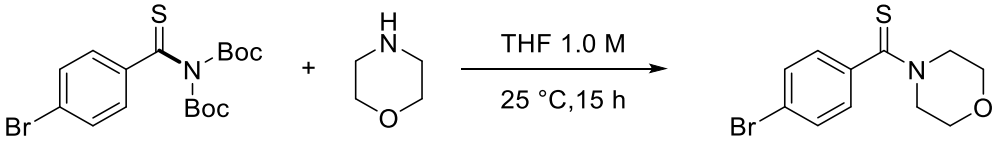
(4-Chlorophenyl)(morpholino)methanethione (3f, Scheme 3)



4f **2a** **3f**

According to the general procedure, the reaction of *tert*-Butyl (4-chlorophenylcarbonothioyl)(phenyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 52 % yield (12.5mg). Spectroscopic properties matched those described previously.[4]

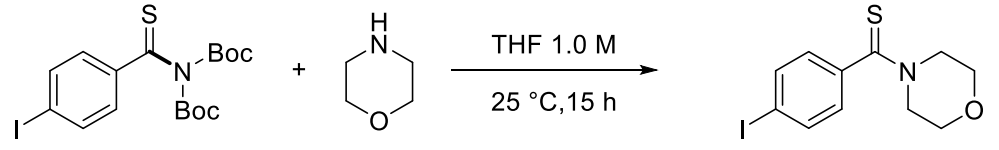
(4-Bromophenyl)(morpholino)methanethione (3g, Scheme 3)



4g **2a** **3g**

According to the general procedure, the reaction of *tert*-Butyl (4-bromophenylcarbonothioyl)(phenyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 59 % yield (17.0 mg). Spectroscopic properties matched those described previously.[4]

(4-Iodophenyl)(morpholino)methanethione (3k, Scheme 3)

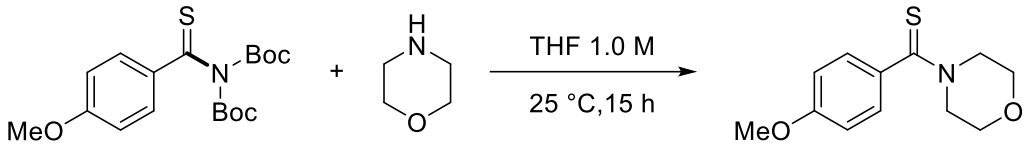


4k **2a** **3k**

According to the general procedure, the reaction of *tert*-Butyl (4-iodophenylcarbonothioyl)(phenyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as

described above and chromatography the title compound in 68 % yield (23.0 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.71 (d, J = 8.3 Hz, 2H), 7.04 (d, J = 8.3 Hz, 2H), 4.47 – 4.34 (m, 2H), 3.96 – 3.82 (m, 2H), 3.62 (dt, J = 27.1, 4.1 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.6 (s, -**C**=S, 1C), 141.8 (s, **C$_{Ph}$**-C=S, 1C), 137.7(s, **C$_{Ph}$**, 2C), 127.7 (s, **C$_{Ph}$**, 2C), 94.9 (s, **C$_{Ph}$**-I, 1C). 66.7 (s, -O-**CH$_2$**-CH_2-, 1C), 66.5 (s, -O-**CH$_2$**-CH_2-, 1C), 52.6(s, -O-CH_2-**CH$_2$**-, 1C), 49.5(s, -O-CH_2-**CH$_2$**-, 1C). HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{12}INOS^+$:333.9757; Found: 333.9759.

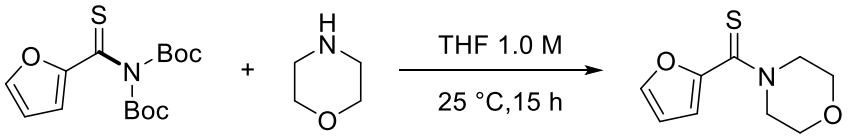
(4-Methoxyphenyl)(morpholino)methanethione（3i, Scheme 3）



4i **2a** **3i**

According to the general procedure, the reaction of *tert*-Butyl (4-methoxyphenylcarbonothioyl)(phenyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 55 % yield (13.0 mg). Spectroscopic properties matched those described previously[3]

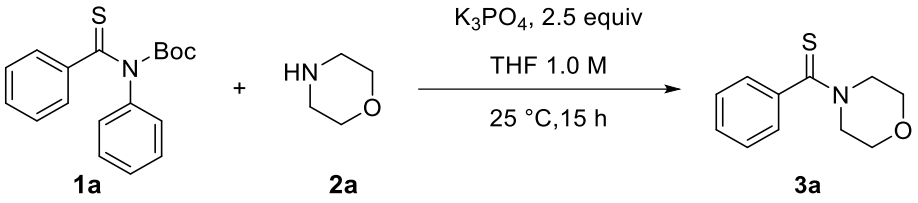
Furan-2-yl(morpholino)methanethione (3j, Scheme 3)



4j **2a** **3j**

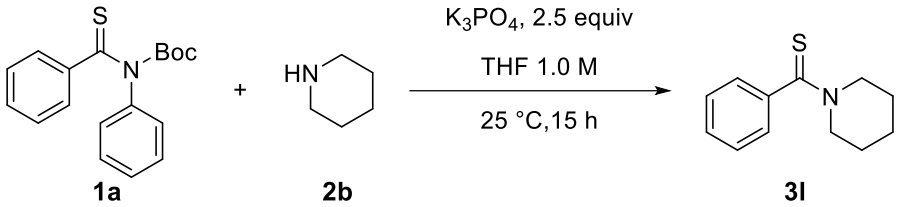
According to the general procedure, the reaction of *tert*-Butyl (furan-2-carbonothioyl)(phenyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 56 % yield (11.1 mg). Spectroscopic properties matched those described previously.[6]

Morpholino(phenyl)methanethione (3a, Scheme 4)



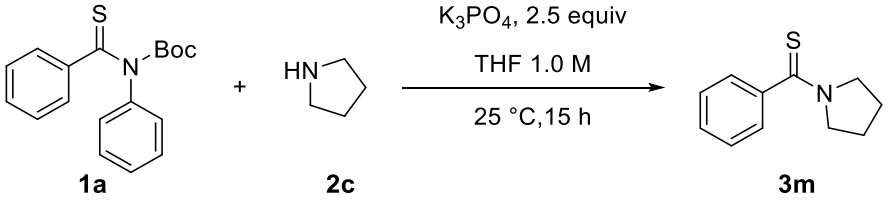
According to the general procedure, the reaction of *tert*-Butyl phenyl(phenylcarbonothioyl) carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 86 % yield (17.8 mg). Yellow solid. Spectroscopic properties matched those described previously.[2]

Phenyl(piperidin-1-yl)methanethione (3l, Scheme 4)



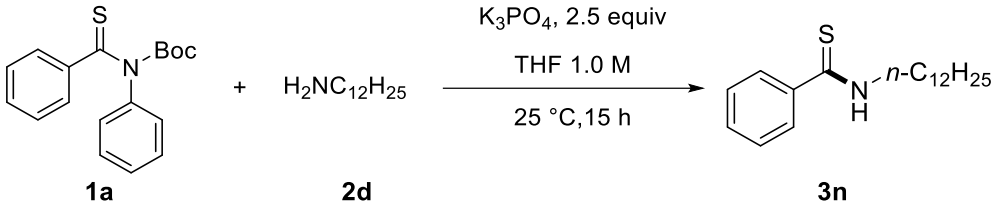
According to the general procedure, the reaction of *tert*-Butyl phenyl(phenylcarbonothioyl) carbamate (0.10 mmol, 1.0 equiv), piperidine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 63 % yield (13.1 mg). Yellow solid. Spectroscopic properties matched those described previously.[4]

Phenyl(pyrrolidin-1-yl)methanethione (3m, Scheme 4)



According to the general procedure, the reaction of *tert*-Butyl phenyl(phenylcarbonothioyl) carbamate (0.10 mmol, 1.0 equiv), pyrrolidine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 81 % yield (15.6 mg). Yellow solid. Spectroscopic properties matched those described previously.[4]

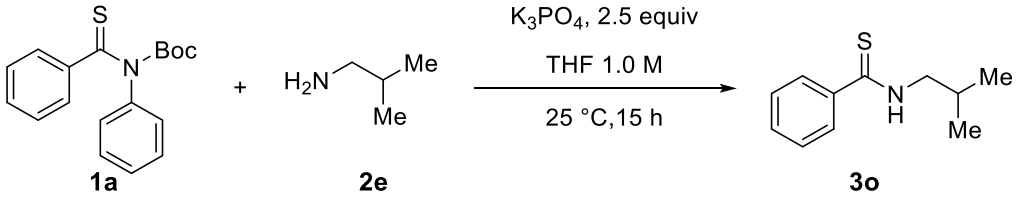
***N*-Dodecylbenzothioamide (3n, Scheme 4)**



1a **2d** **3n**

According to the general procedure, the reaction of *tert*-Butyl phenyl(phenylcarbonothioyl) carbamate (0.10 mmol, 1.0 equiv), dodecan-1-amine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 88 % yield (26.8 mg). Yellow solid. Spectroscopic properties matched those described previously.[7]

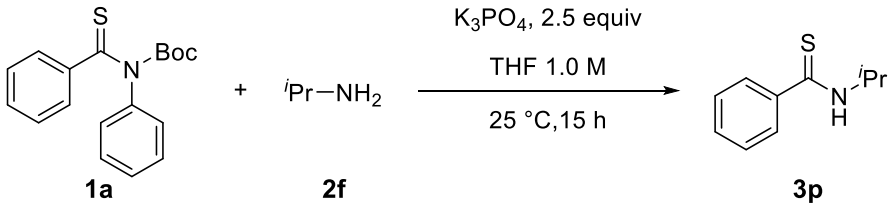
***N*-Isobutylbenzothioamide (3o, Scheme 4)**



1a **2e** **3o**

According to the general procedure, the reaction of *tert*-Butyl phenyl(phenylcarbonothioyl) carbamate (0.10 mmol, 1.0 equiv), 2-methylpropan-1-amine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 57 % yield (11.0 mg). Yellow solid. Spectroscopic properties matched those described previously.[8]

***N*-Isopropylbenzothioamide (3p, Scheme 4)**

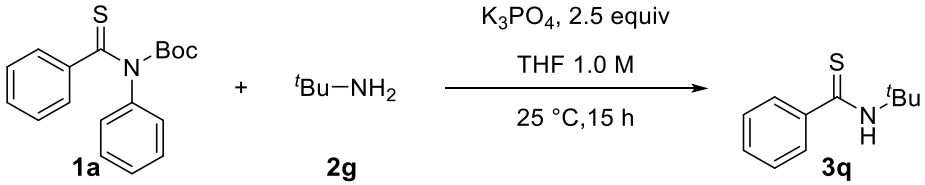


1a **2f** **3p**

According to the general procedure, the reaction of *tert*-Butyl phenyl(phenylcarbonothioyl) carbamate (0.10 mmol, 1.0 equiv), propan-2-amine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the

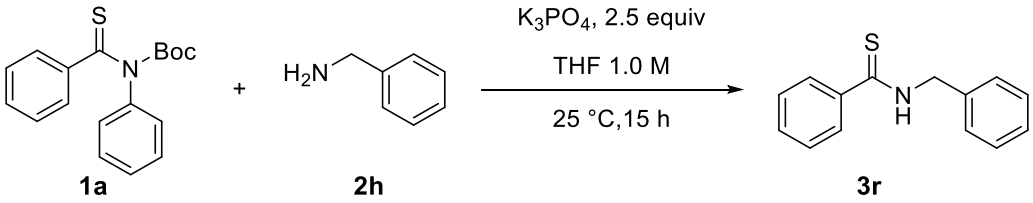
standard work-up as described above and chromatography the title compound in 72 % yield (13.0 mg). Yellow solid. Spectroscopic properties matched those described previously.[9]

***N*-(*tert*-Butyl)benzothioamide (3q, Scheme 4)**



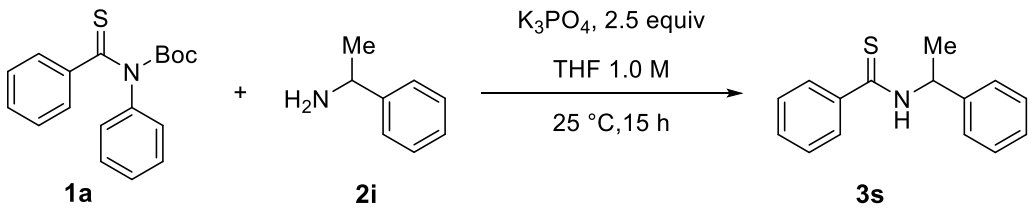
According to the general procedure, the reaction of *tert*-Butyl phenyl(phenylcarbonothioyl) carbamate (0.10 mmol, 1.0 equiv), 2-methylpropan-2-amine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 75 % yield (14.5 mg). Yellow solid. Spectroscopic properties matched those described previously.[6]

***N*-Benzylbenzothioamide (3r, Scheme 4)**



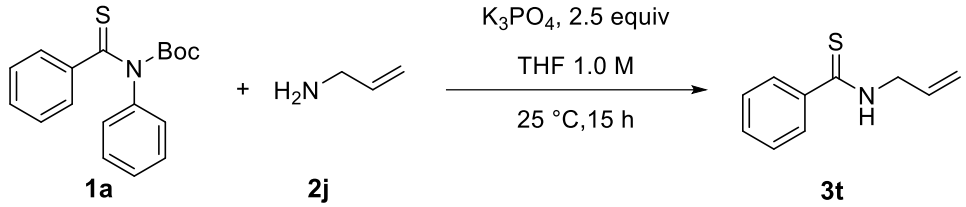
According to the general procedure, the reaction of *tert*-Butyl phenyl(phenylcarbonothioyl) carbamate (0.10 mmol, 1.0 equiv), phenylmethanamine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 80 % yield (18.2 mg). Yellow solid. Spectroscopic properties matched those described previously.[9]

***N*-(1-Phenylethyl)benzothioamide (3s, Scheme 4)**



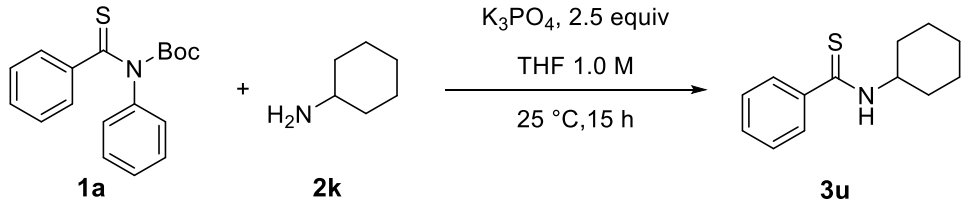
According to the general procedure, the reaction of *tert*-Butyl phenyl(phenylcarbonothioyl) carbamate (0.10 mmol, 1.0 equiv), 1-phenylethan-1-amine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 83 % yield (20.0 mg). Yellow solid. Spectroscopic properties matched those described previously.[10]

***N*-Allylbenzothioamide (3t, Scheme 4)**



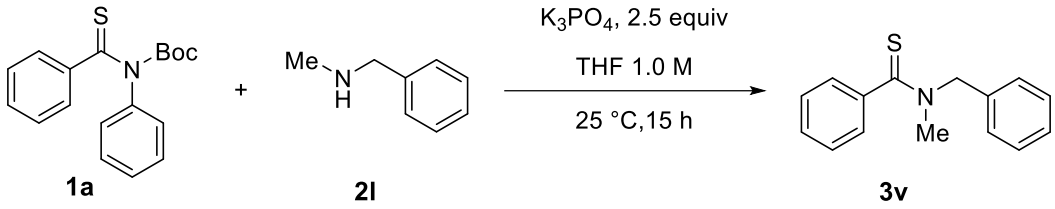
According to the general procedure, the reaction of *tert*-Butyl phenyl(phenylcarbonothioyl) carbamate (0.10 mmol, 1.0 equiv), prop-2-en-1-amine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 81 % yield (14.4 mg). Yellow solid. Spectroscopic properties matched those described previously.[11]

***N*-Cyclohexylbenzothioamide (3u, Scheme 4)**



According to the general procedure, the reaction of *tert*-Butyl phenyl(phenylcarbonothioyl) carbamate (0.10 mmol, 1.0 equiv), cyclohexanamine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 77 % yield (16.9 mg). Yellow solid. Spectroscopic properties matched those described previously.[9]

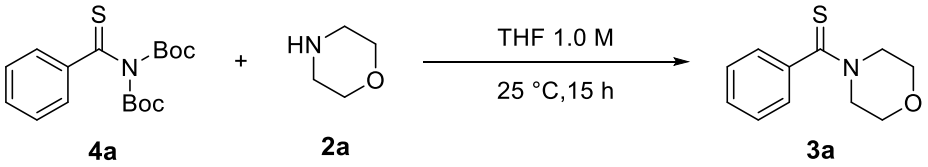
***N*-Benzyl-*N*-methylbenzothioamide (3v, Scheme 4)**



1a 2l 3v

According to the general procedure, the reaction of *tert*-Butyl phenyl(phenylcarbonothioyl) carbamate (0.10 mmol, 1.0 equiv), N-methyl-1-phenylmethanamine (2.0 equiv) and K_3PO_4 (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 80 % yield (19.3 mg). Yellow solid. Spectroscopic properties matched those described previously.[12]

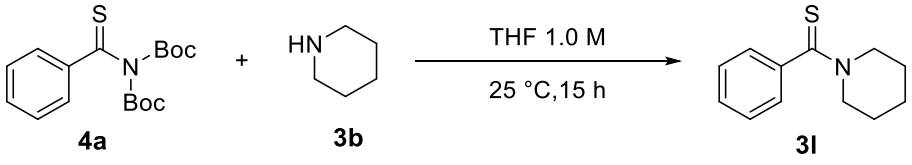
Morpholino(phenyl)methanethione (3a, Scheme 5)



4a 2a 3a

According to the general procedure, the reaction of *tert*-Butyl (*tert*-butoxycarbonyl) (phenylcarbonothioyl)carbamate (0.10 mmol, 1.0 equiv), morpholine (2.0 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 75 % yield (15.6 mg). Yellow solid. Spectroscopic properties matched those described previously.[2]

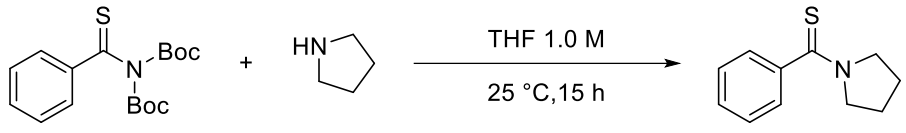
Phenyl(piperidin-1-yl)methanethione (3l, Scheme 5)



4a 3b 3l

According to the general procedure, the reaction of *tert*-Butyl (*tert*-butoxycarbonyl) (phenylcarbonothioyl)carbamate (0.10 mmol, 1.0 equiv), piperidine (2.0 equiv) in THF (1.0 M) at 120 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 63 % yield (14.0 mg). Yellow solid. Spectroscopic properties matched those described previously.[4]

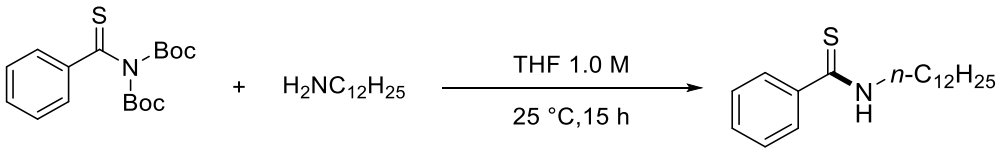
Phenyl(pyrrolidin-1-yl)methanethione (3m, Scheme 5)



4a **2c** **3m**

According to the general procedure, the reaction of *tert*-Butyl (*tert*-butoxycarbonyl) (phenylcarbonothioyl)carbamate (0.10 mmol, 1.0 equiv), pyrrolidine (2.0 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 85 % yield (16.4 mg). Yellow solid. Spectroscopic properties matched those described previously.[4]

***N*-Dodecylbenzothioamide (3n, Scheme 5)**



4a **2d** **3n**

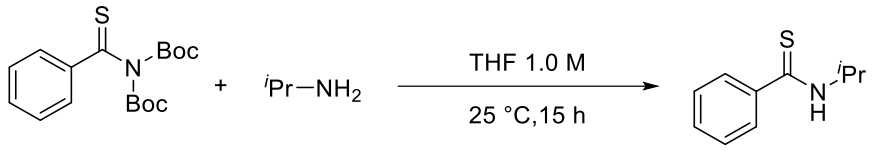
According to the general procedure, the reaction of *tert*-Butyl (*tert*-butoxycarbonyl) (phenylcarbonothioyl)carbamate (0.10 mmol, 1.0 equiv), 6-(trifluoromethyl)pyridin-3-amine (2.0 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 93 % yield (28.3 mg). Yellow solid. Spectroscopic properties matched those described previously.[7]

***N*-Isobutylbenzothioamide (3o, Scheme 5)**

4a **2e** **3o**

According to the general procedure, the reaction of *tert*-Butyl (*tert*-butoxycarbonyl) (phenylcarbonothioyl)carbamate (0.10 mmol, 1.0 equiv), 6-(trifluoromethyl)pyridin-3-amine (2.0 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 86 % yield (16.6 mg). Yellow solid. Spectroscopic properties matched those described previously.[8]

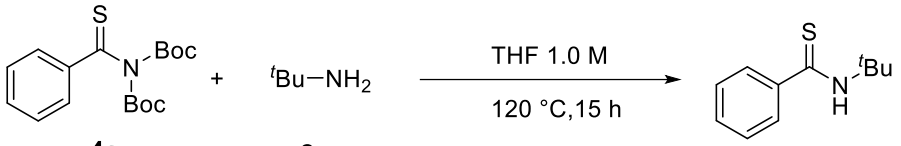
***N*-Isopropylbenzothioamide (3p, Scheme 5)**



4a **2f** **3p**

According to the general procedure, the reaction of *tert*-Butyl (*tert*-butoxycarbonyl) (phenylcarbonothioyl)carbamate (0.10 mmol, 1.0 equiv), propan-2-amine (2.0 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 59 % yield (13.6 mg). Yellow solid. Spectroscopic properties matched those described previously.[9]

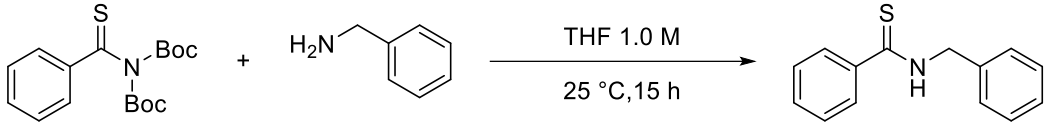
***N*-(*tert*-Butyl)benzothioamide (3q, Scheme 5)**



4a **2g** **3q**

According to the general procedure, the reaction of *tert*-Butyl (*tert*-butoxycarbonyl) (phenylcarbonothioyl)carbamate (0.10 mmol, 1.0 equiv), 2-methylpropan-2-amine (2.0 equiv) in THF (1.0 M) at 120 ℃ for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 59 % yield (11.4 mg). Yellow solid. Spectroscopic properties matched those described previously.[6]

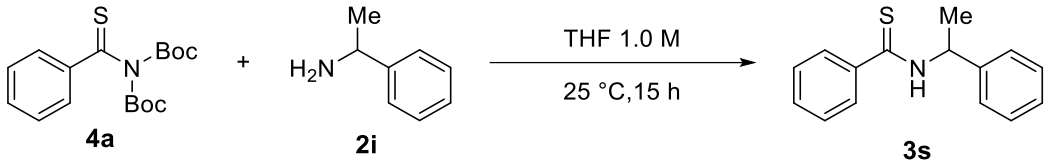
***N*-Benzylbenzothioamide (3r, Scheme 5)**



4a **2h** **3r**

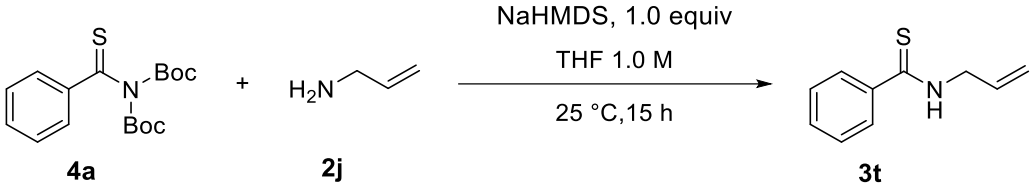
According to the general procedure, the reaction of *tert*-Butyl (*tert*-butoxycarbonyl) (phenylcarbonothioyl)carbamate (0.10 mmol, 1.0 equiv), phenylmethanamine (2.0 equiv) in THF (1.0 M) at 25 ℃ for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 84 % yield (19.1 mg). Yellow solid. Spectroscopic properties matched those described previously.[9]

***N*-(1-Phenylethyl)benzothioamide (3s, Scheme 5)**



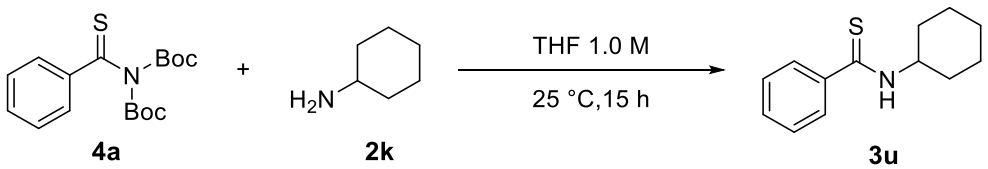
According to the general procedure, the reaction of *tert*-Butyl (*tert*-butoxycarbonyl) (phenylcarbonothioyl)carbamate (0.10 mmol, 1.0 equiv), 1-phenylethan-1-amine (2.0 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 80 % yield (19.3 mg). Yellow solid. Spectroscopic properties matched those described previously.[10]

***N*-Allylbenzothioamide (3t, Scheme 5)**



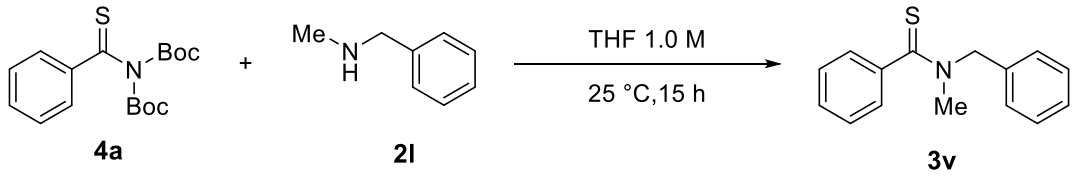
According to the general procedure, the reaction of *tert*-Butyl (*tert*-butoxycarbonyl) (phenylcarbonothioyl)carbamate (0.10 mmol, 1.0 equiv), prop-2-en-1-amine (2.0 equiv) and NaHMDS (1.0 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 85 % yield (15.1 mg). Yellow solid. Spectroscopic properties matched those described previously.[11]

***N*-Cyclohexylbenzothioamide (3u, Scheme 5)**



According to the general procedure, the reaction of *tert*-Butyl (*tert*-butoxycarbonyl) (phenylcarbonothioyl)carbamate (0.10 mmol, 1.0 equiv), cyclohexanamine (2.0 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 86 % yield (18.9 mg). Yellow solid. Spectroscopic properties matched those described previously.[9]

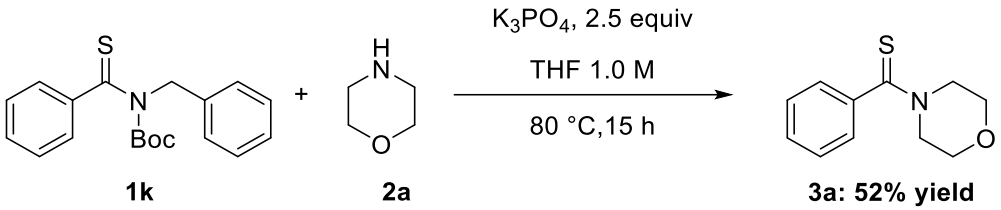
***N*-Benzyl-*N*-methylbenzothioamide (3v, Scheme 5)**



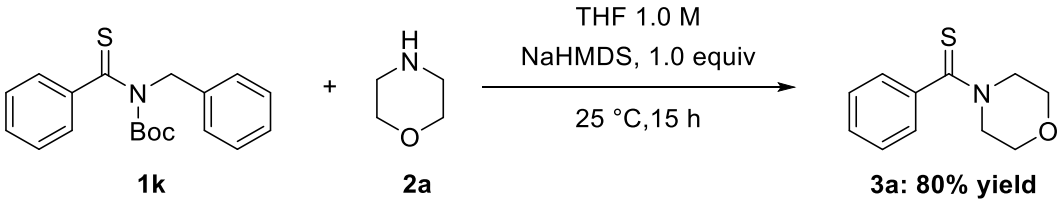
According to the general procedure, the reaction of *tert*-butyl (*tert*-butoxycarbonyl) (phenylcarbonothioyl)carbamate (0.10 mmol, 1.0 equiv), *N*-methyl-1-phenylmethanamine (2.0 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 85 % yield (21.0 mg). Yellow solid. Spectroscopic properties matched those described previously.[12]

3. Mechanistic Studies Referred to from the Main Manuscript

(1) Transamidation of *N*-alkyl-*N*-Boc-thioamides (Scheme 6)

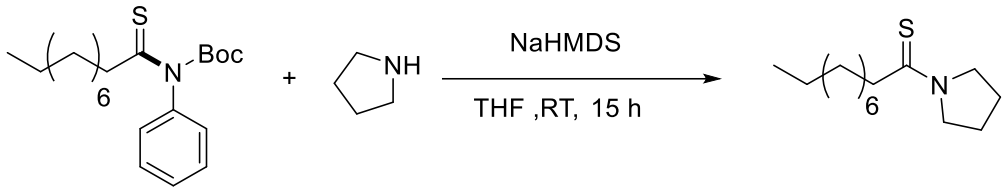


An oven-dried vial equipped with a stir bar was charged with *tert*-butyl benzyl(phenylcarbonothioyl)carbamate (1.0 equiv), morpholine (2.0 equiv), THF (1 M) and K_3PO_4 (2.5 equiv) were sequentially added with vigorous stirring at 80 ℃, and the reaction mixture was stirred at 25 °C for an indicated time. After the indicated time, the reaction mixture was quenched with NH_4Cl (aq., 1.0 M, 1 mL), iluted with CH_2Cl_2 (10 mL), the organic layer was washed with water (1 x 10 mL), brine (1 x 10 mL), dried and concentrated. A sample was analyzed by ^1H NMR ($CDCl_3$, 600 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples.



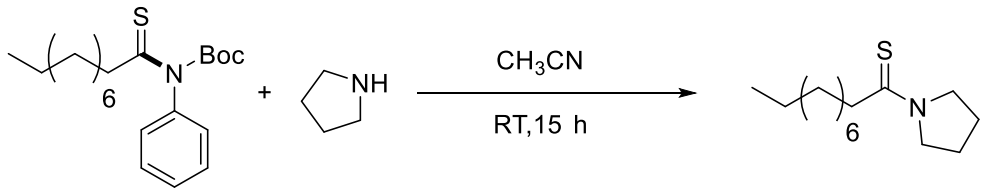
An oven-dried vial equipped with a stir bar was charged with *tert*-Butyl benzyl(phenylcarbonothioyl)carbamate (1.0 equiv), morpholine (2.0 equiv), THF (1 M) and NaHMDS (1.0 equiv) were sequentially added with vigorous stirring at 25 °C, and the reaction mixture was stirred at 25 °C for an indicated time. After the indicated time, the reaction mixture was quenched with NH_4Cl (aq., 1.0 M, 1 mL), iluted with CH_2Cl_2 (10 mL), the organic layer was washed with water (1 x 10 mL), brine (1 x 10 mL), dried and concentrated. A sample was analyzed by ^1H NMR ($CDCl_3$, 600 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples.

(2) Transamidation of aliphatic *N*-mono-*N*-Boc-thioamides (Scheme 7)



1l **2c** **3w: <5 % yield**
1l: >95 %recovery

An oven-dried vial equipped with a stir bar was charged with *tert*-Butyl pentanethioyl(phenyl)carbamate (1.0 equiv), pyrrolidine (2.0 equiv), THF (1 M) and NaHMDS (2.5 equiv) were sequentially added with vigorous stirring at 25 °C, and the reaction mixture was stirred at 25 °C for an indicated time. After the indicated time, the reaction mixture was quenched with NH_4Cl (aq., 1.0 M, 1 mL), iluted with CH_2Cl_2 (10 mL), the organic layer was washed with water (1 x 10 mL), brine (1 x 10 mL), dried and concentrated. A sample was analyzed by ^1H NMR ($CDCl_3$, 600 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples.

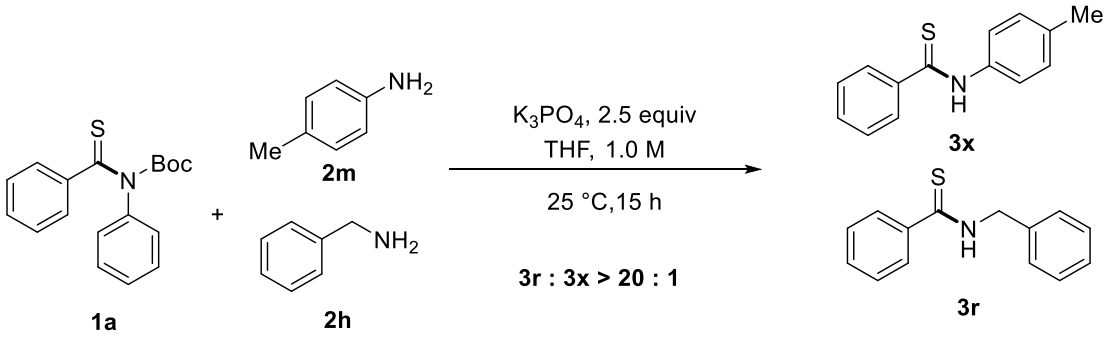


1l **2c** **3w: 87 % yield**

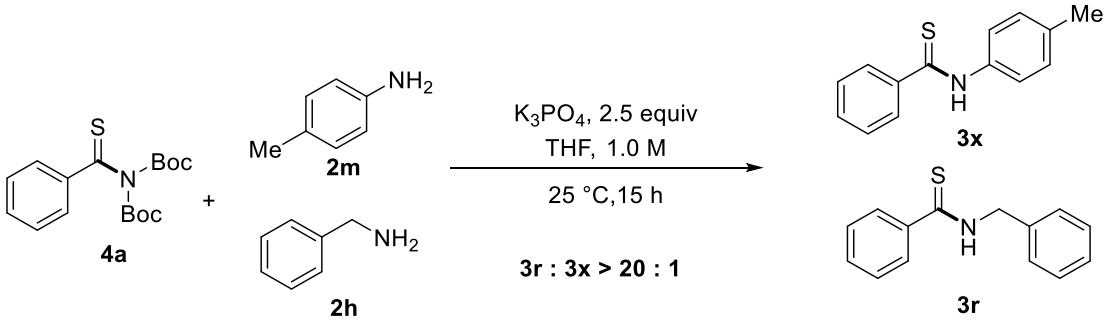
An oven-dried vial equipped with a stir bar was charged with *tert*-Butyl pentanethioyl(phenyl)carbamate (1.0 equiv), pyrrolidine (2.0 equiv), CH_3CN (1 M) and were sequentially added with vigorous stirring at 25 °C, and the reaction mixture was stirred at 25 °C for an indicated time. After the indicated time, the reaction mixture was quenched with NH_4Cl (aq., 1.0 M, 1 mL), iluted with CH_2Cl_2 (10 mL), the organic layer was washed with water (1 x 10 mL), brine (1 x 10 mL), dried and concentrated. A sample was analyzed by ^1H NMR ($CDCl_3$, 600 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (EtOAc/hexanes) afforded the title product (Yellow oil, 21.0 mg, 87% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 3.86 (t, J = 7.0 Hz, 2H), 3.62 (t, J = 6.9 Hz, 2H), 2.72 – 2.66 (m, 2H), 2.07 (p, J = 6.7 Hz, 2H), 1.98

(p, J = 6.7 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.37 – 1.24 (m, 12H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.0 (s, **C**=S,1C) , 53.8 (s, -N-**CH_2**-, 1C), 50.5 (s, -N-**CH_2**-, 1C), 44.3 (s, -N-CH_2-**CH_2**-, 1C), 31.9(s, -N-CH_2-**CH_2**-, 1C), 29.5 (s, -**CH_2**-, 1C), 29.5(s, -**CH_2**-, 1C), 29.4(s, -**CH_2**-, 1C), 29.3(s, -**CH_2**-, 1C), 29.0(s, -**CH_2**-, 1C), 26.4(s, -**CH_2**-, 1C), 24.4(s, -**CH_2**-, 1C), 22.7(s, -**CH_2**-, 1C), 14.1 (s, -**C**H_3,1C). HRMS calcd for $C_{14}H_{28}NS$ (M + H) 242.1937, found 242.1934.

(3) Selectivity in transamidation of *N*-mono-*N*-Boc and *N,N*-Boc$_2$-thioamides (Scheme 8)



An oven-dried vial equipped with a stir bar was charged with tert-Butyl phenyl(phenylcarbonothioyl)carbamate (1.0 equiv), p-toluidine (2.0 equiv), phenylmethanamine (2.0 equiv) , THF (1 M) and K_3PO_4 (2.5 equiv) were sequentially added with vigorous stirring at 25 °C, and the reaction mixture was stirred at 25 °C for an indicated time. After the indicated time, the reaction mixture was quenched with NH_4Cl (aq., 1.0 M, 1 mL), diluted with CH_2Cl_2 (10 mL), the organic layer was washed with water (1 x 10 mL), brine (1 x 10 mL), dried and concentrated. A sample was analyzed by ^{1}H NMR ($CDCl_3$, 600 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples.



An oven-dried vial equipped with a stir bar was charged with *tert*-Butyl (*tert*-

butoxycarbonyl)(furan-2-carbonothioyl)carbamate (1.0 equiv), p-toluidine (2.0 equiv), phenylmethanamine (2.0 equiv) , THF (1 M) and K_3PO_4 (2.5 equiv) were sequentially added with vigorous stirring at 25 °C, and the reaction mixture was stirred at 25 °C for an indicated time. After the indicated time, the reaction mixture was quenched with NH_4Cl (aq., 1.0 M, 1 mL), diluted with CH_2Cl_2 (10 mL), the organic layer was washed with water (1 x 10 mL), brine (1 x 10 mL), dried and concentrated. A sample was analyzed by ^1H NMR ($CDCl_3$, 600 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples.

4. ^{1}H and ^{13}C NMR Spectra

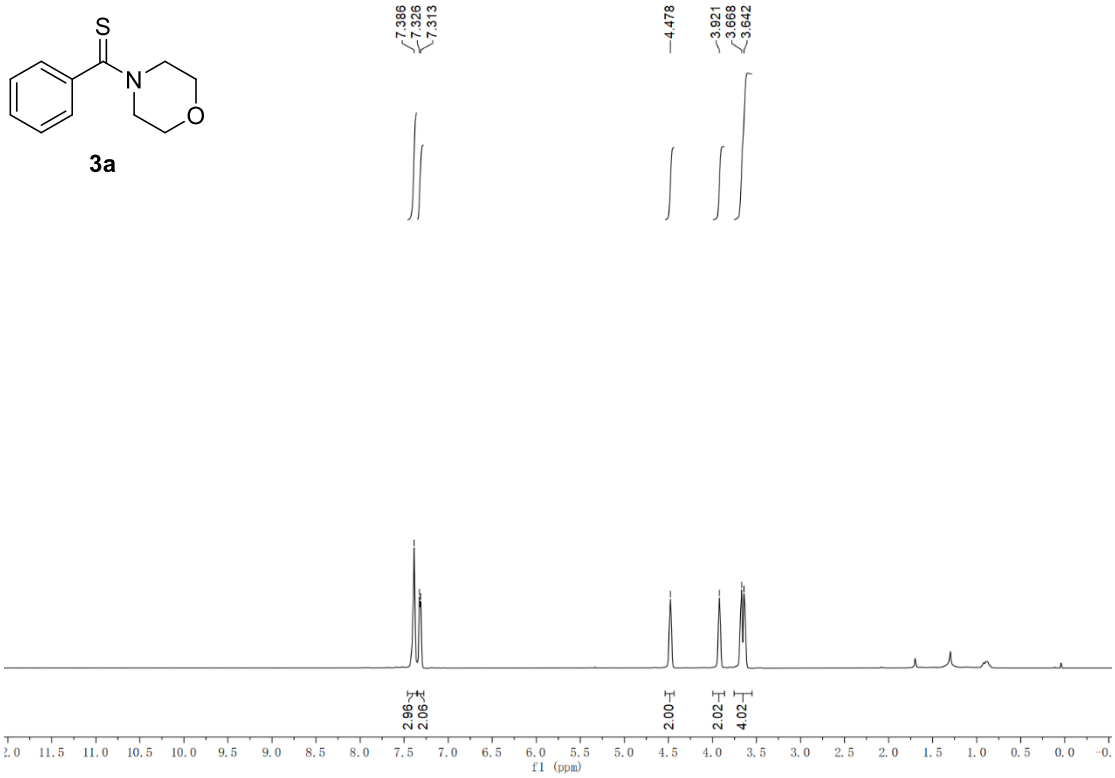


Figure S1 ^{1}H NMR Spectrum of Morpholino(phenyl)methanethione(**3a**)

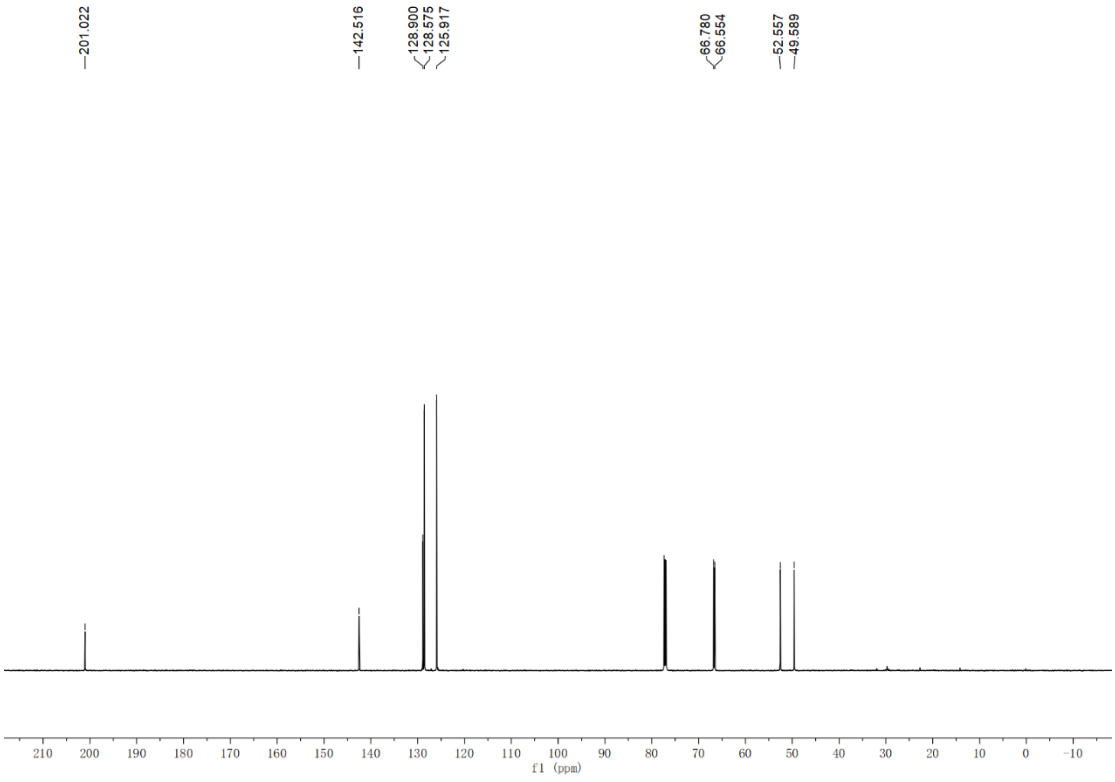


Figure S2 ^{13}C NMR Spectrum of Morpholino(phenyl)methanethione(**3a**)

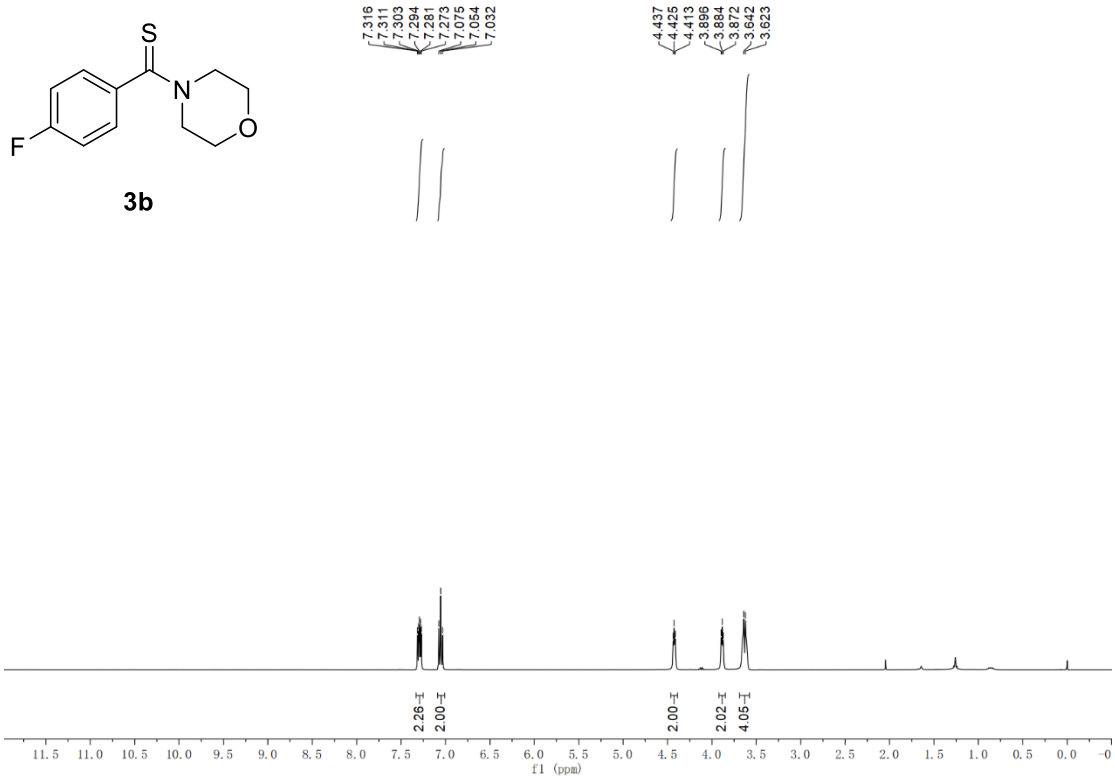


Figure S3 ^{1}H NMR Spectrum of (4-Fluorophenyl)(Morpholino)methanethione (**3b**)

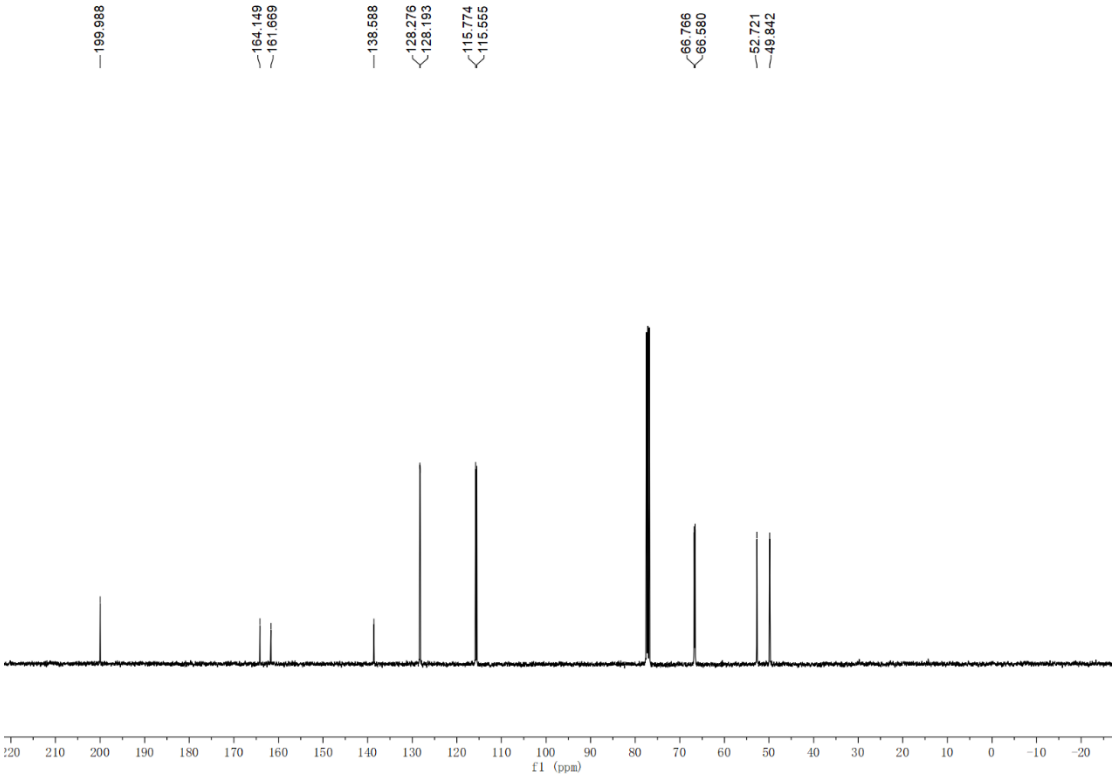


Figure S4 ^{13}C NMR Spectrum of (4-Fluorophenyl)(Morpholino)methanethione (**3b**)

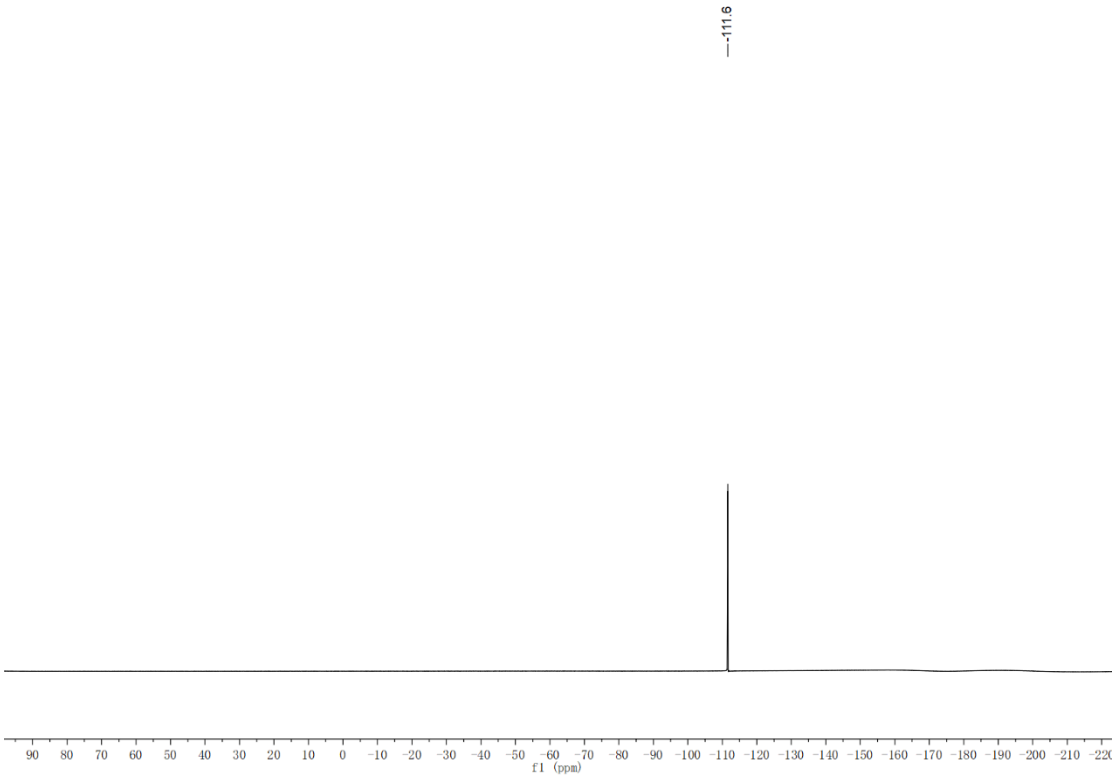


Figure S5 ^{19}F NMR Spectrum of (4-Fluorophenyl)(Morpholino)methanethione (**3b**)

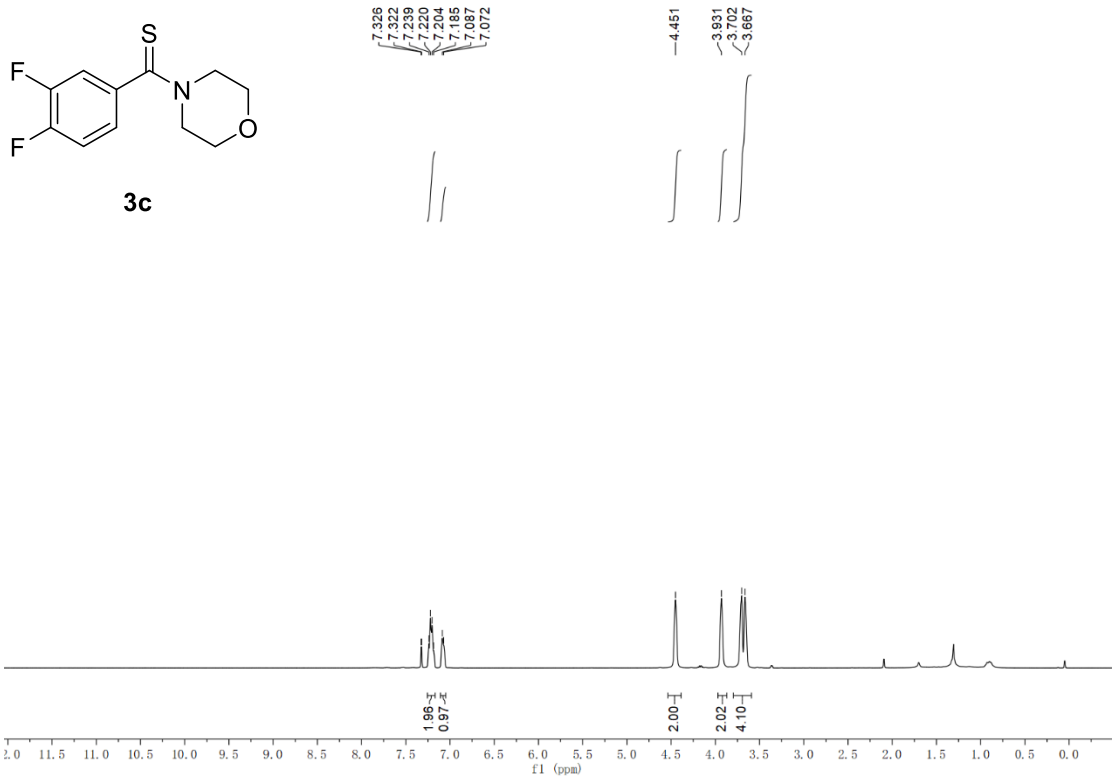


Figure S6 ^{1}H NMR Spectrum of (3,4-Difluorophenyl)(Morpholino)methanethione (**3c**)

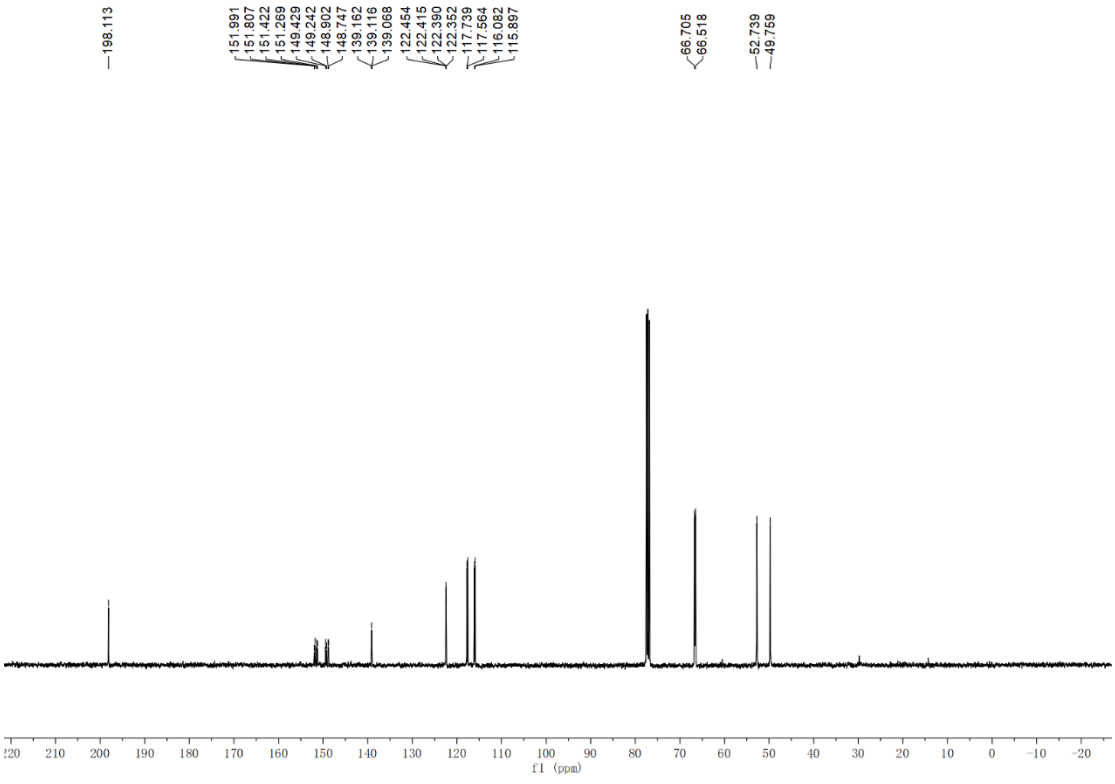


Figure S7 ^{13}C NMR Spectrum of (3,4-Difluorophenyl)(Morpholino)methanethione (**3c**)

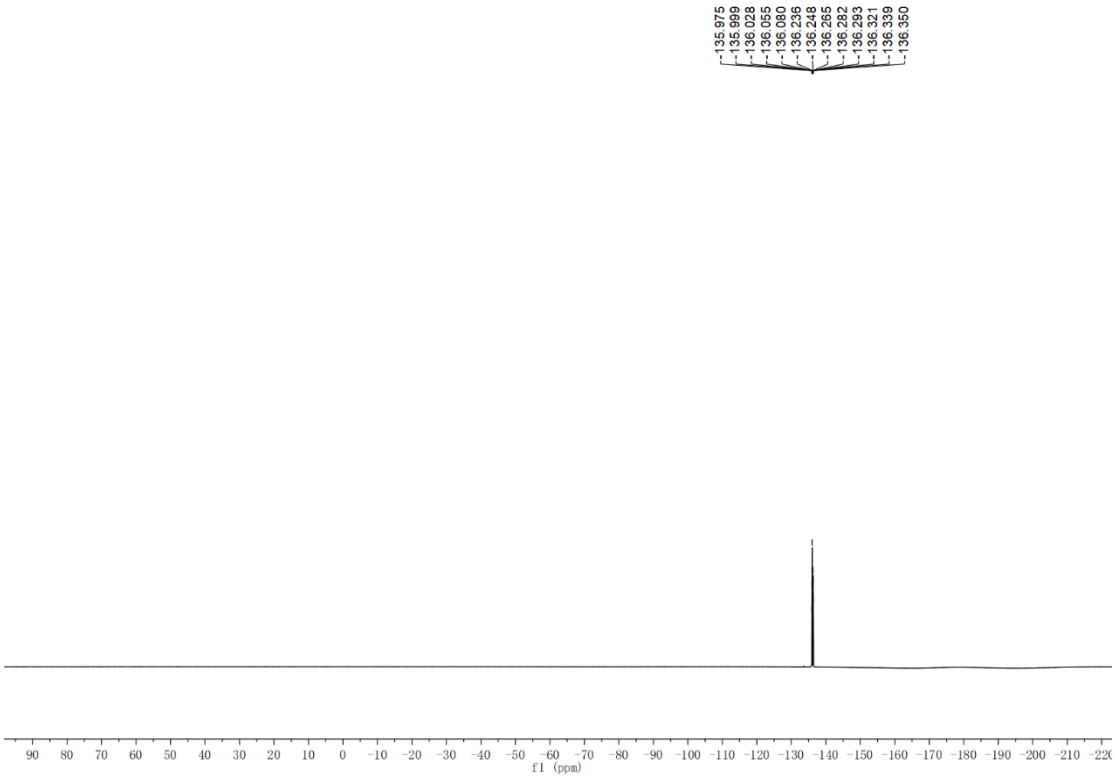


Figure S8 ^{19}F NMR Spectrum of (3,4-Difluorophenyl)(Morpholino)methanethione (**3c**)

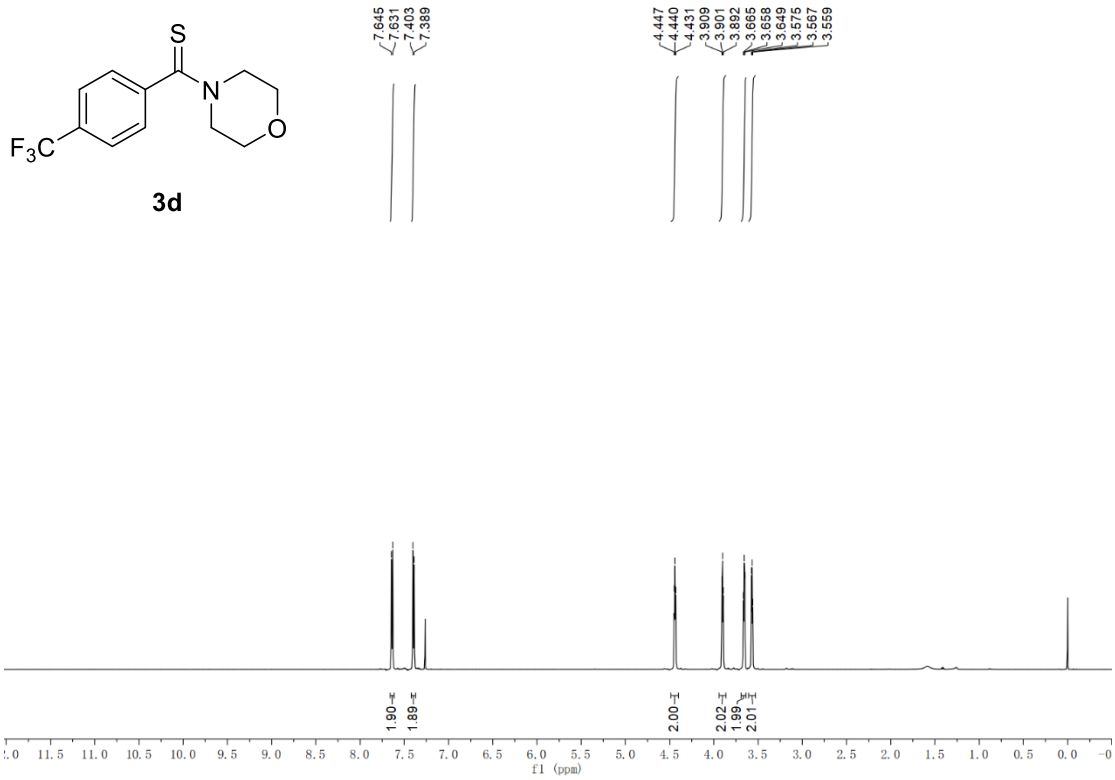


Figure S9 ^{1}H NMR Spectrum of Morpholino(4-(trifluoromethyl)phenyl)methanethione (**3d**)

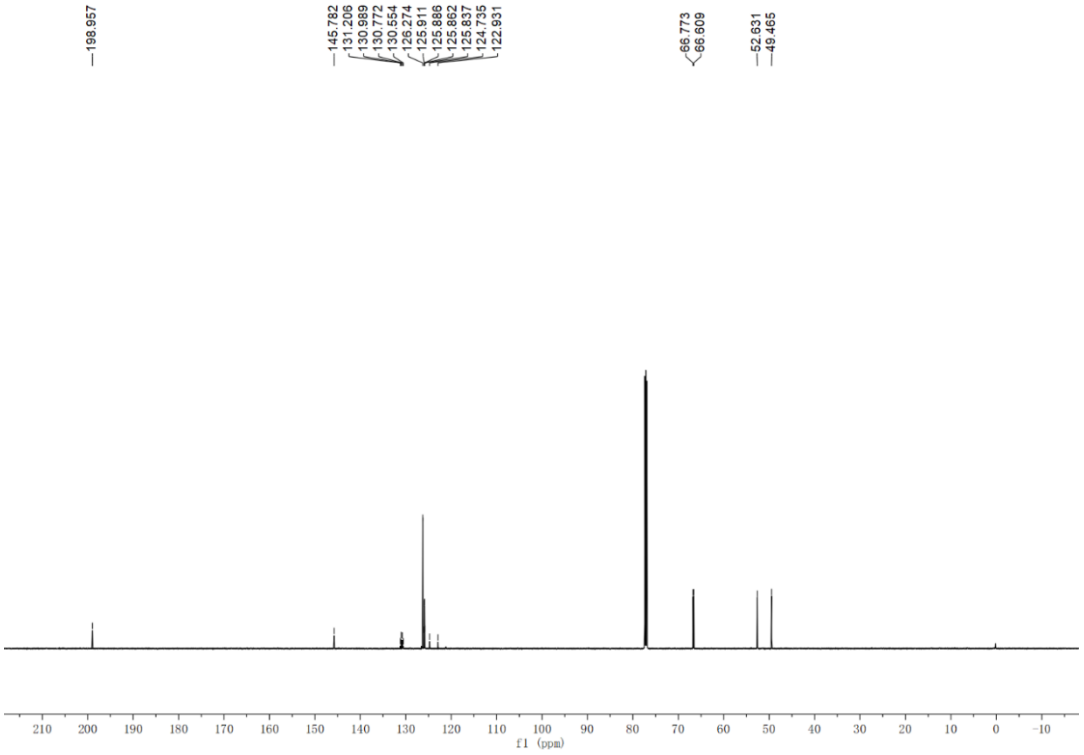


Figure S10 ^{13}C NMR Spectrum of Morpholino(4-(trifluoromethyl)phenyl)methanethione (**3d**)

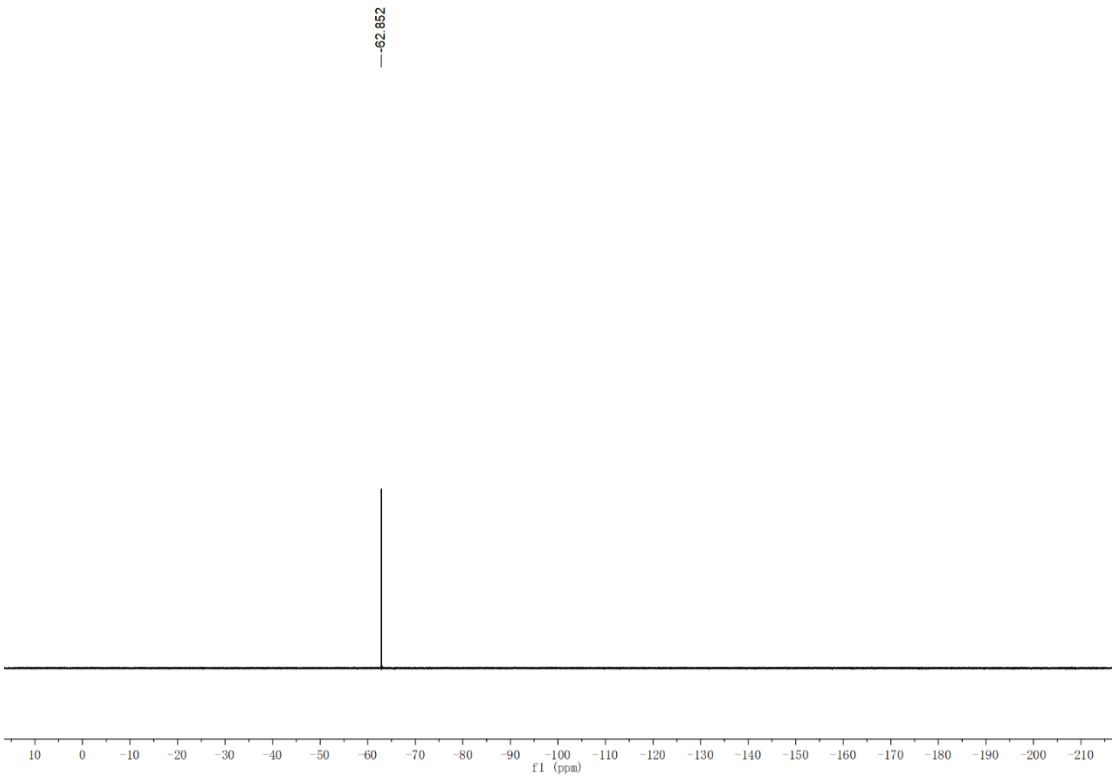


Figure S11 ^{19}F NMR Spectrum of Morpholino(4-(trifluoromethyl)phenyl)methanethione (**3d**)

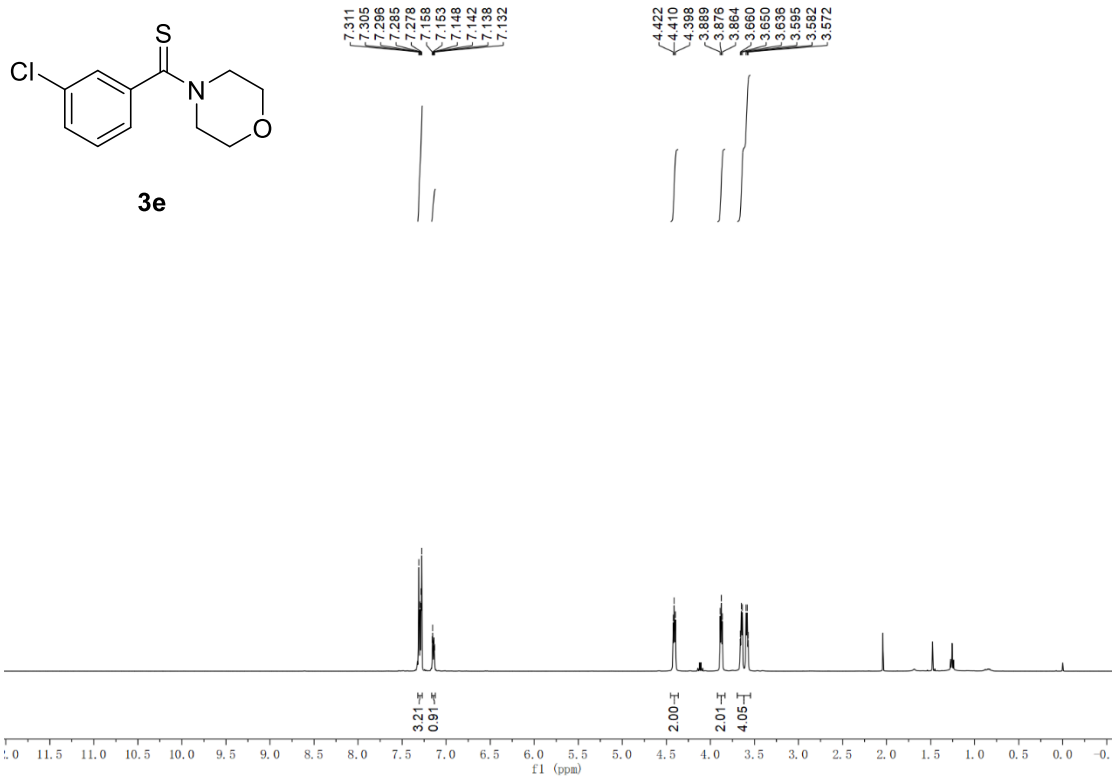


Figure S12 ^{1}H NMR Spectrum of (3-Chlorophenyl)(Morpholino)methanethione (**3e**)

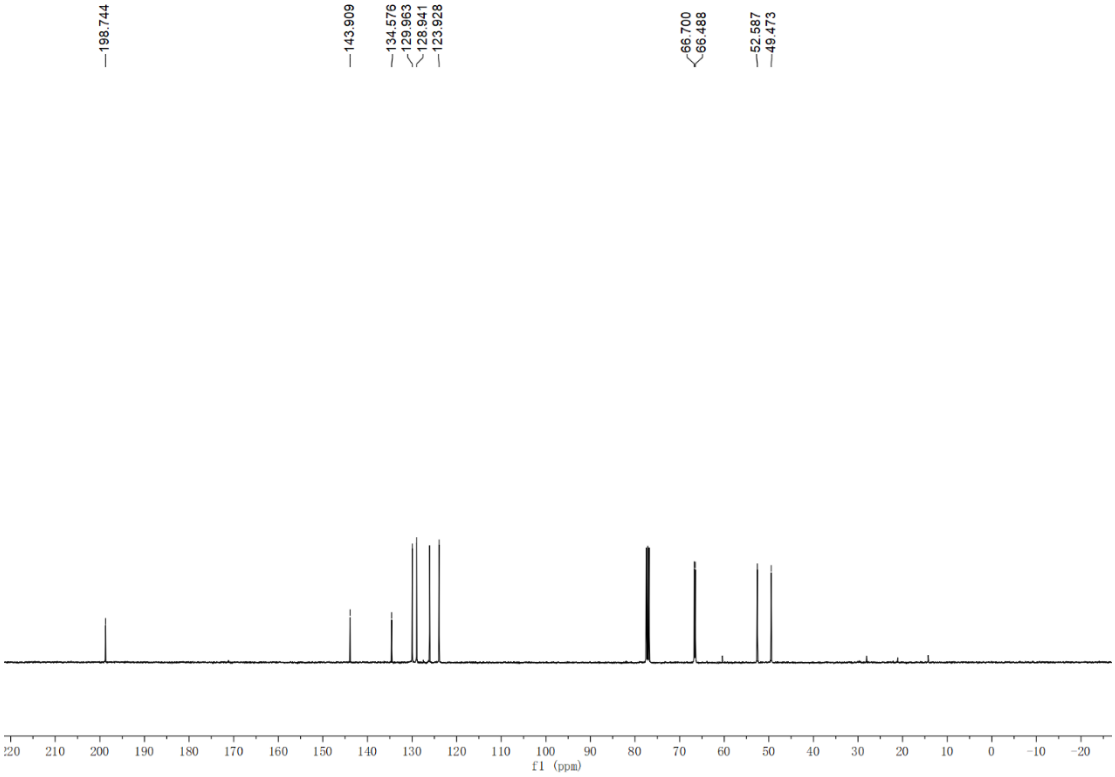


Figure S13 ^{13}C NMR Spectrum of (3-Chlorophenyl)(Morpholino)methanethione (**3e**)

Figure S14 ^{1}H NMR Spectrum of (4-Chlorophenyl)(Morpholino)methanethione (**3f**)

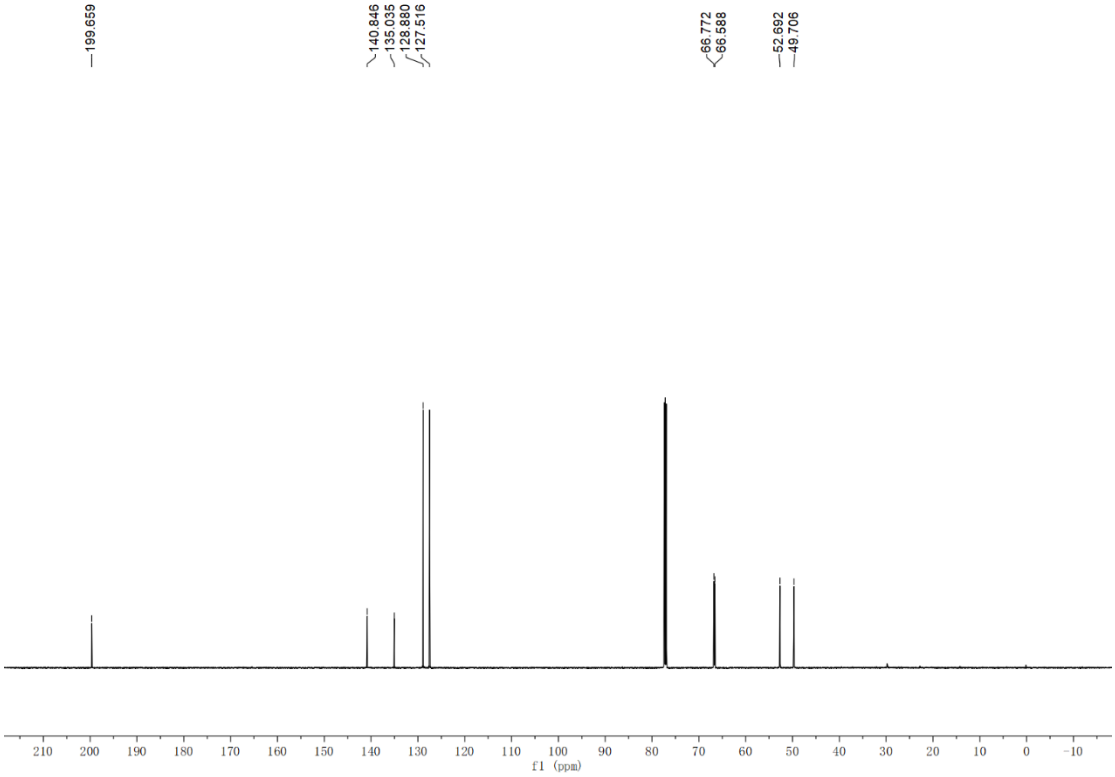


Figure S15 ^{13}C NMR Spectrum of (4-Chlorophenyl)(Morpholino)methanethione (**3f**)

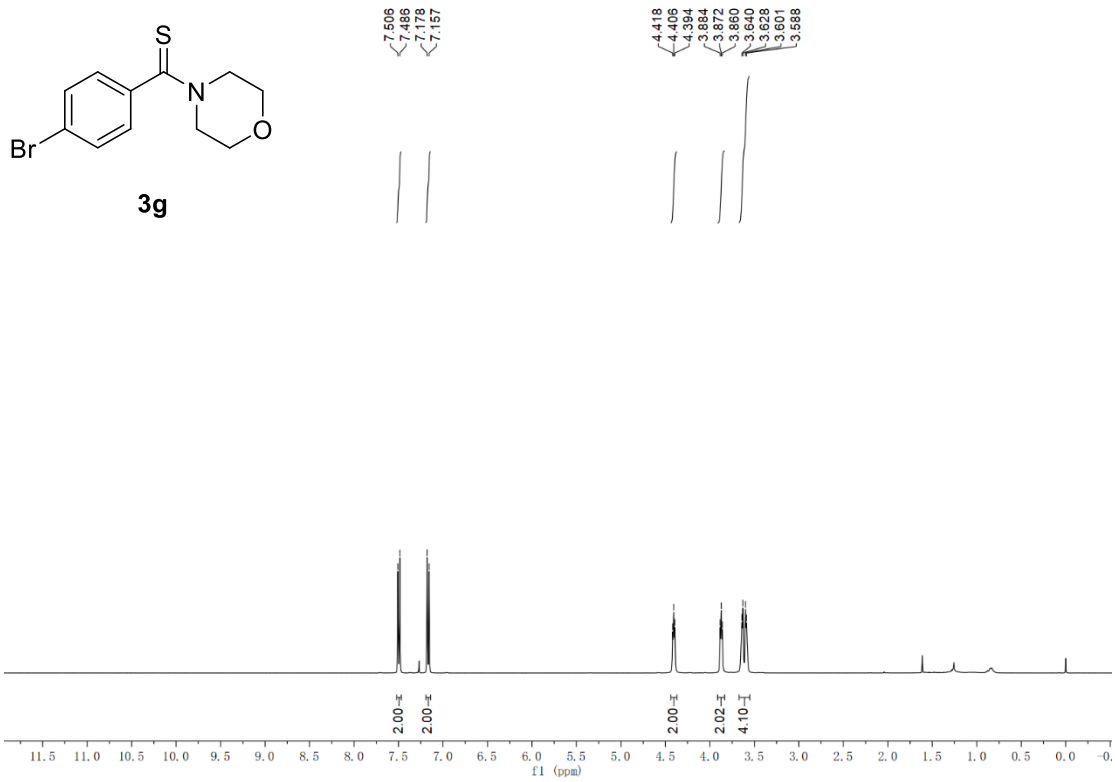


Figure S16 ^{1}H NMR Spectrum of (4-Bromophenyl)(Morpholino)methanethione (**3g**)

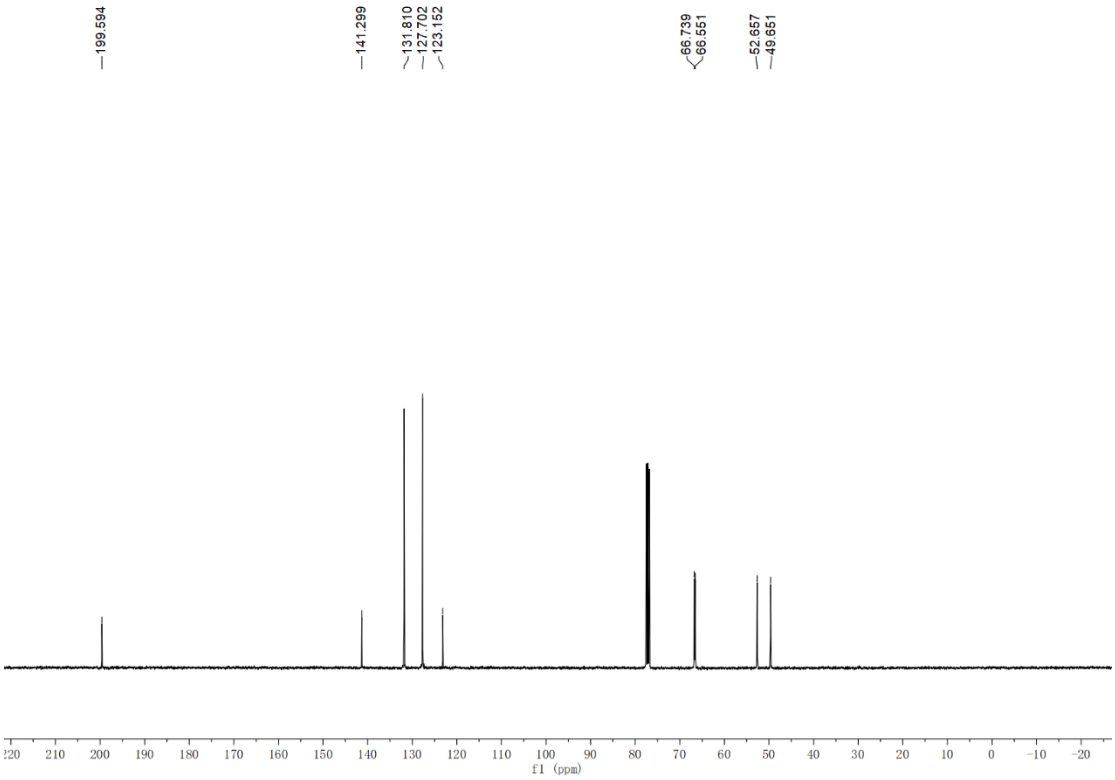


Figure S17 ^{13}C NMR Spectrum of (4-Bromophenyl)(Morpholino)methanethione (**3g**)

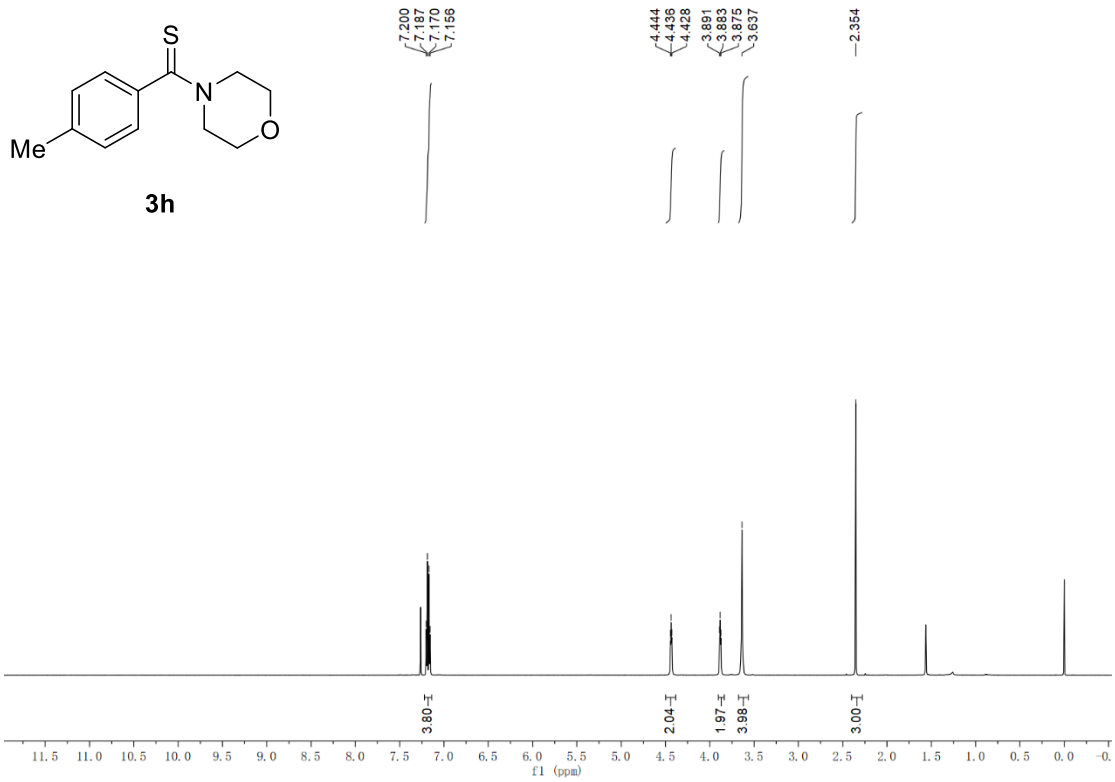


Figure S18 ^{1}H NMR Spectrum of Morpholino(p-tolyl)methanethione (**3h**)

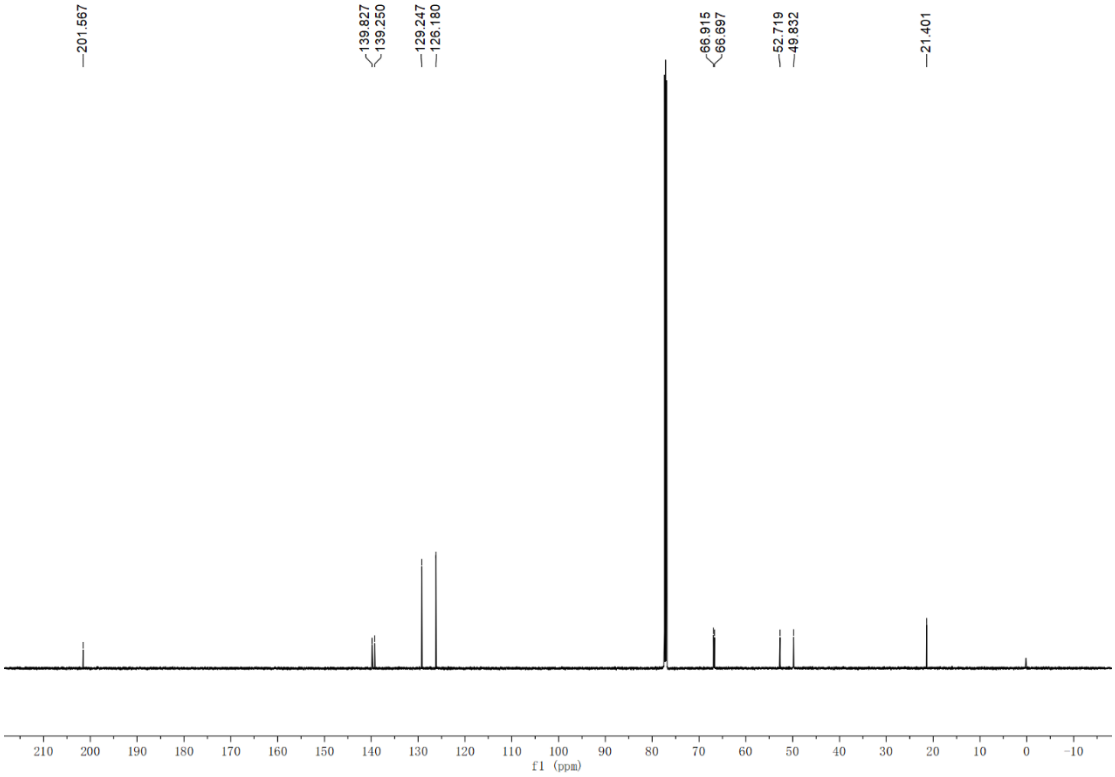


Figure S19 ^{13}C NMR Spectrum of Morpholino(p-tolyl)methanethione (**3h**)

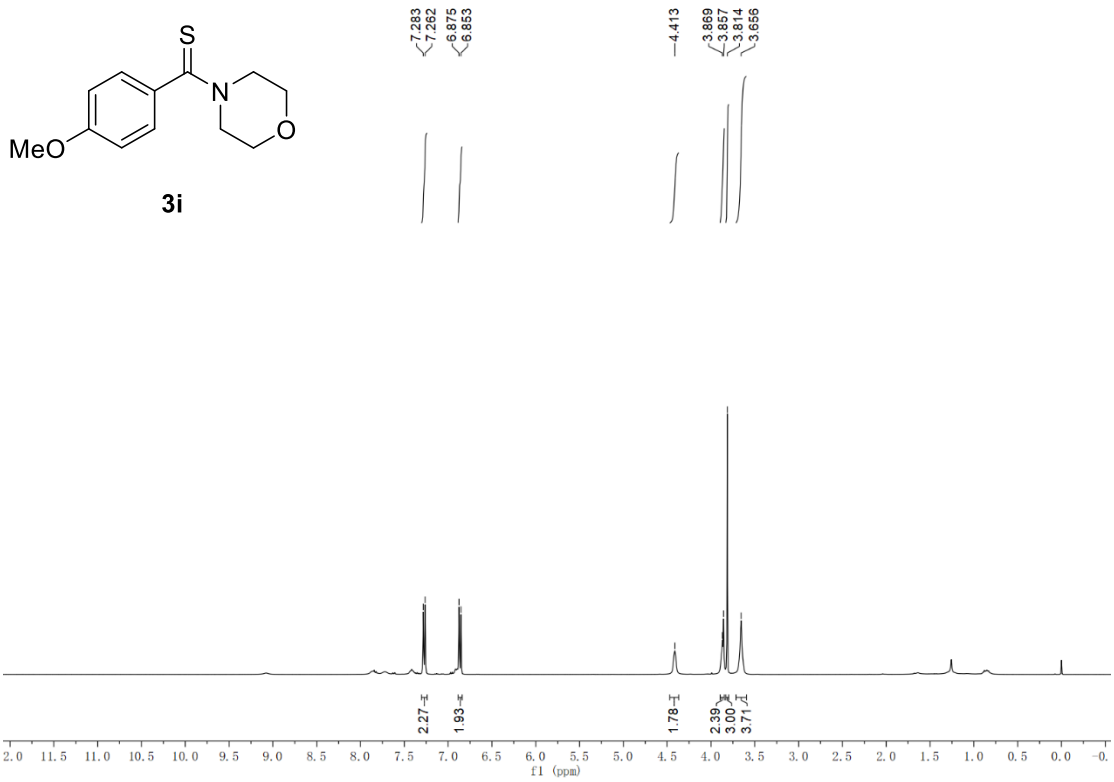


Figure S20 ^{1}H NMR Spectrum of (4-Methoxyphenyl)(morpholino)methanethione (**3i**)

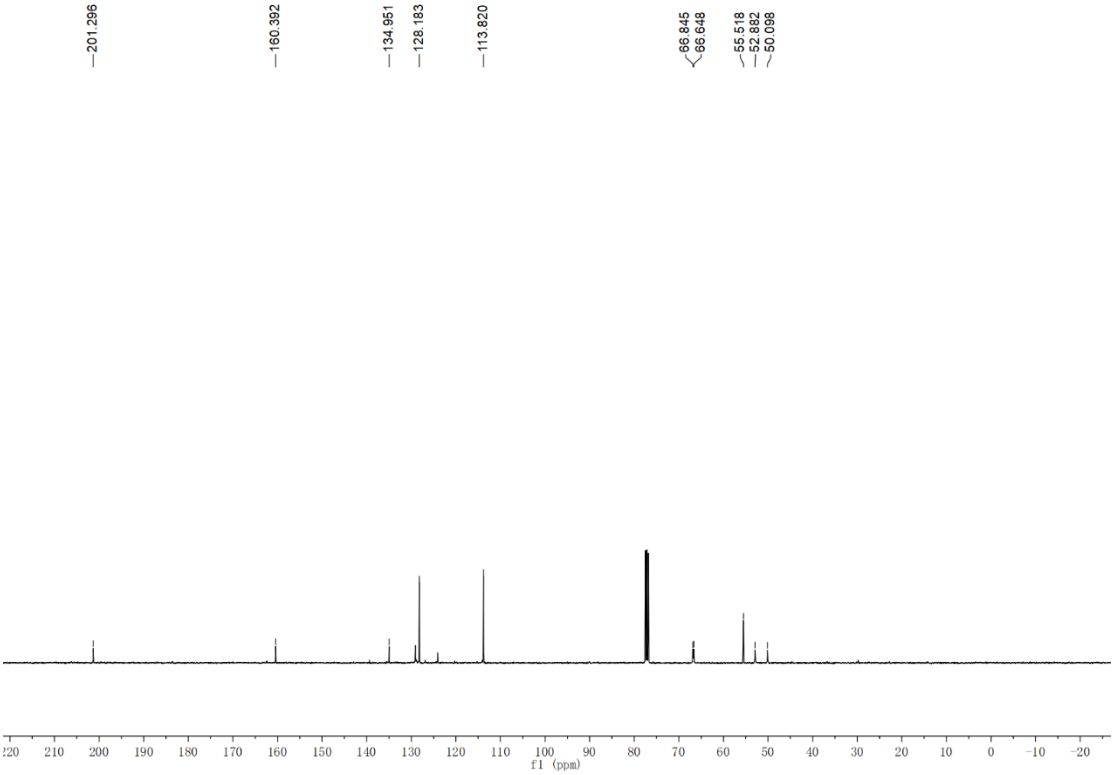


Figure S21 ^{13}C NMR Spectrum of (4-Methoxyphenyl)(morpholino)methanethione (**3i**)

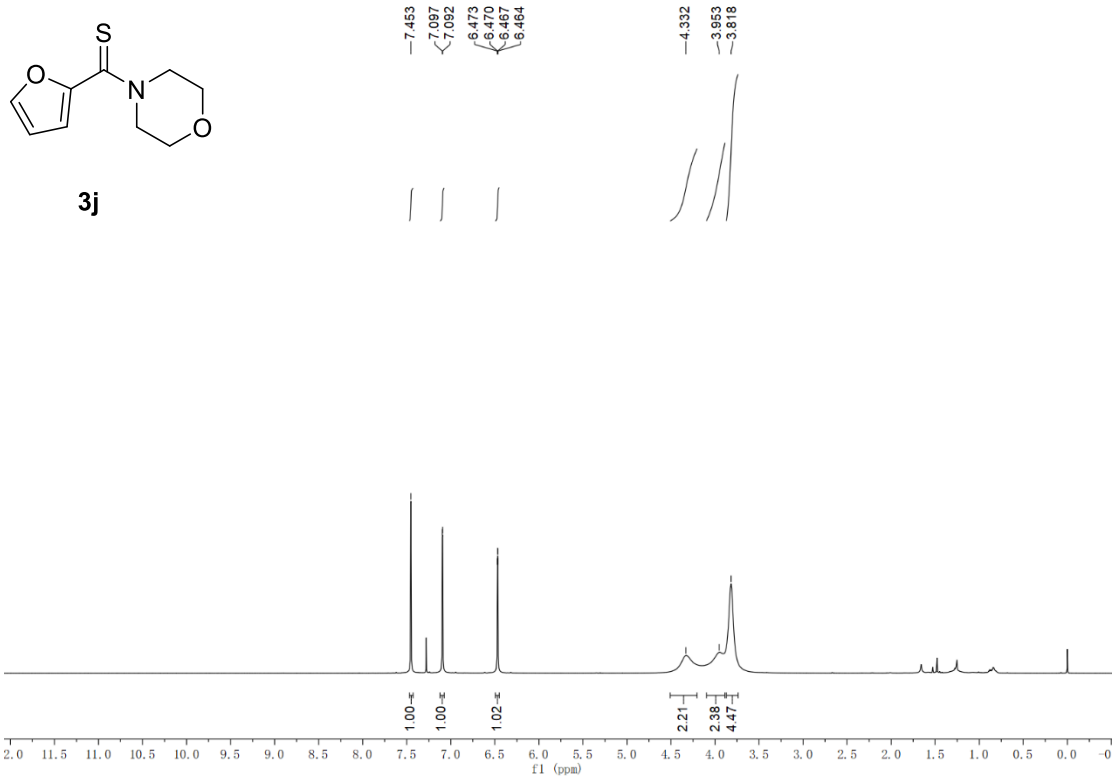


Figure S22 ^{1}H NMR Spectrum of Furan-2-yl(morpholino)methanethione (**3j**)

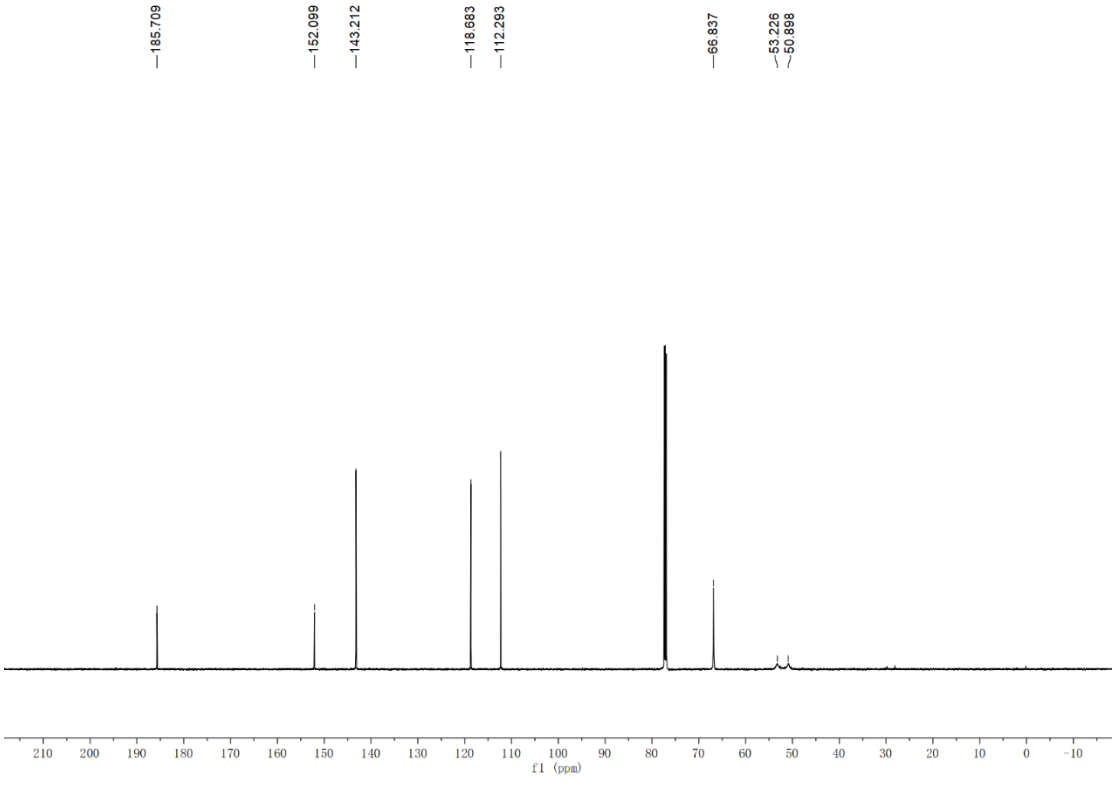


Figure S23 ^{13}C NMR Spectrum of Furan-2-yl(morpholino)methanethione (**3j**)

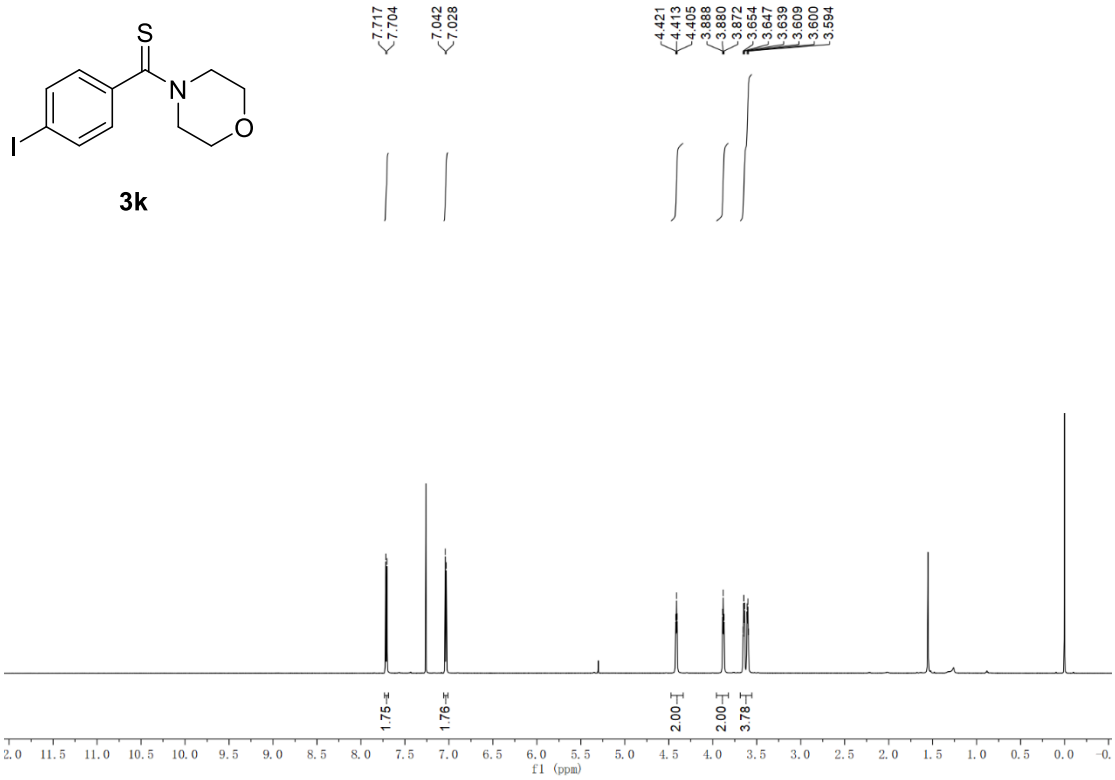


Figure S24 ^{1}H NMR Spectrum of (4-Iodophenyl)(Morpholino)methanethione (**3k**)

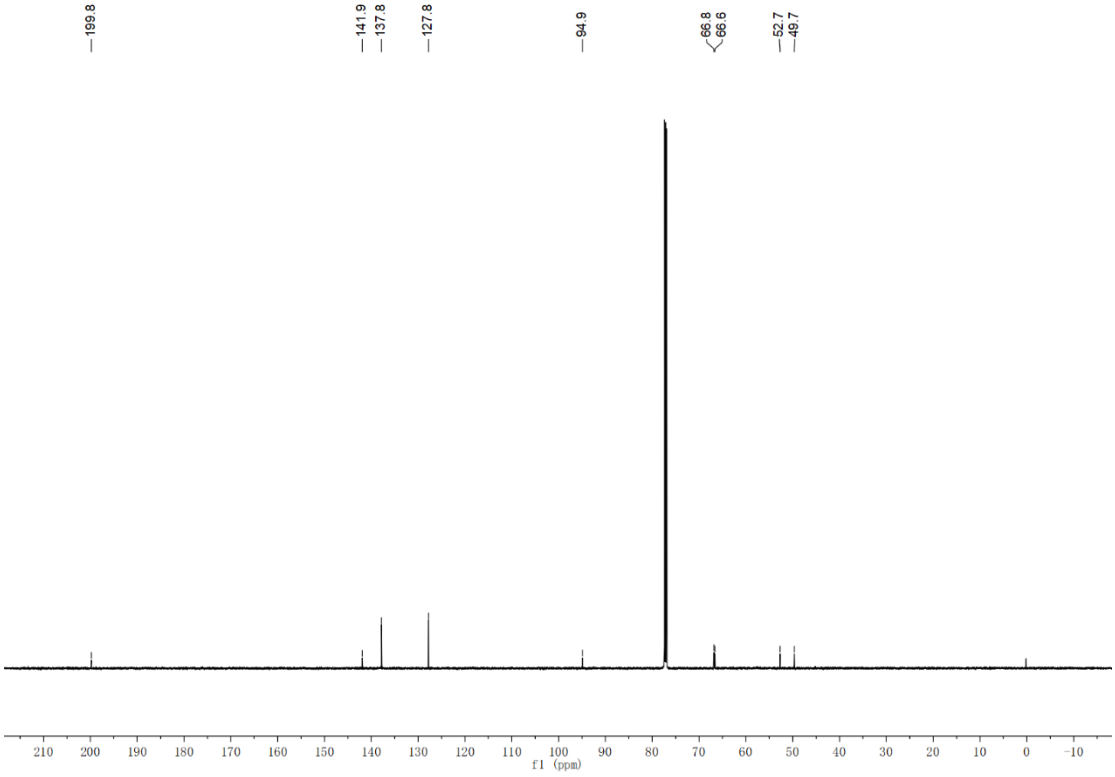


Figure S25 ^{13}C NMR Spectrum of (4-Iodophenyl)(Morpholino)methanethione (**3k**)

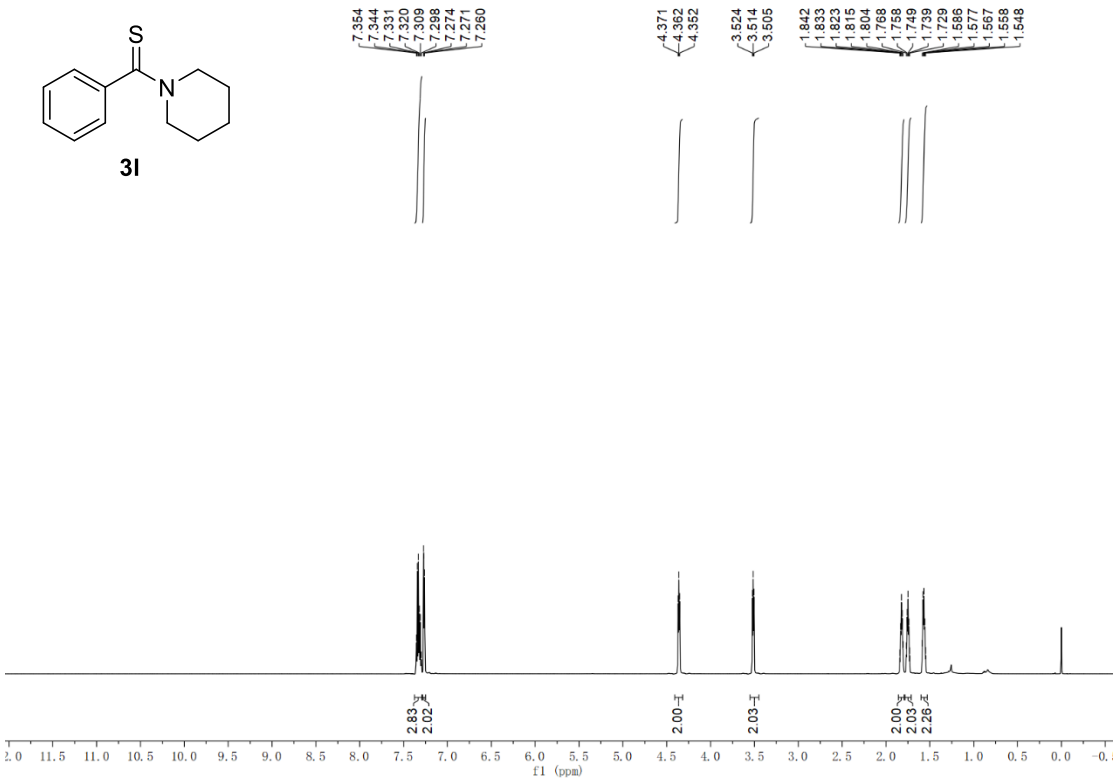


Figure S26 ^{1}H NMR Spectrum of Phenyl(piperidin-1-yl)methanethione(**3l**)

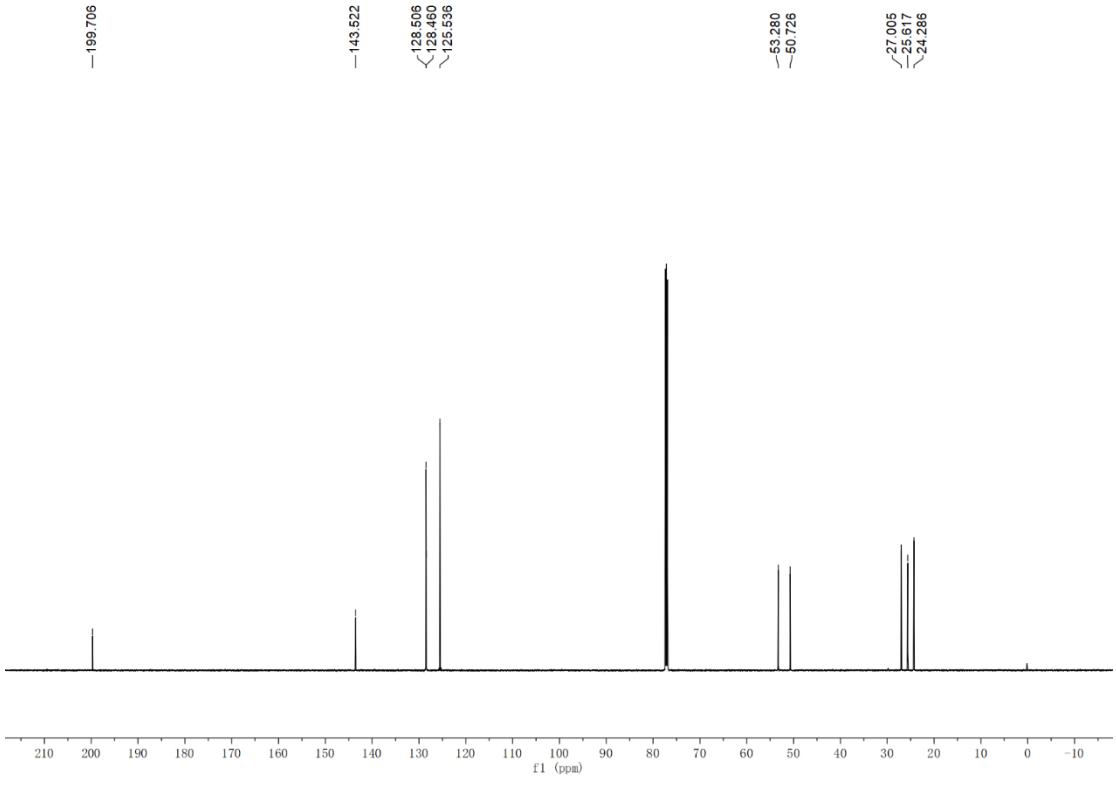


Figure S27 ^{13}C NMR Spectrum of Phenyl(piperidin-1-yl)methanethione(**3l**)

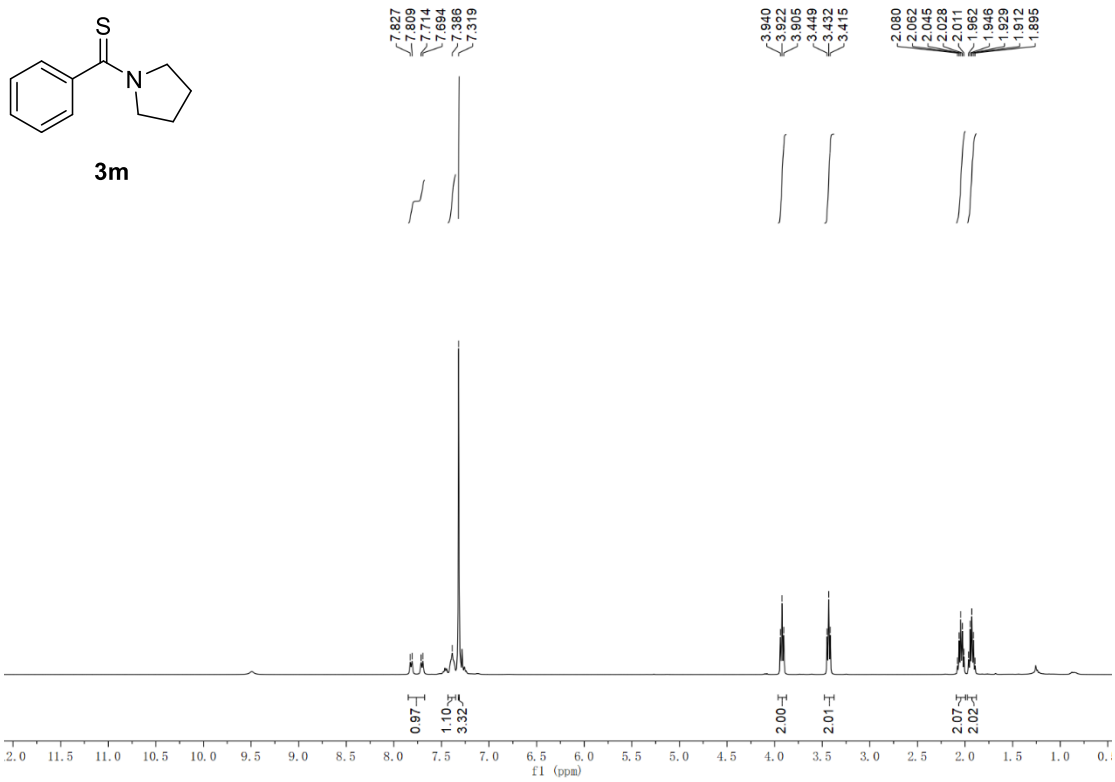


Figure S28 ^{1}H NMR Spectrum of Phenyl(pyrrolidin-1-yl)methanethione(**3m**)

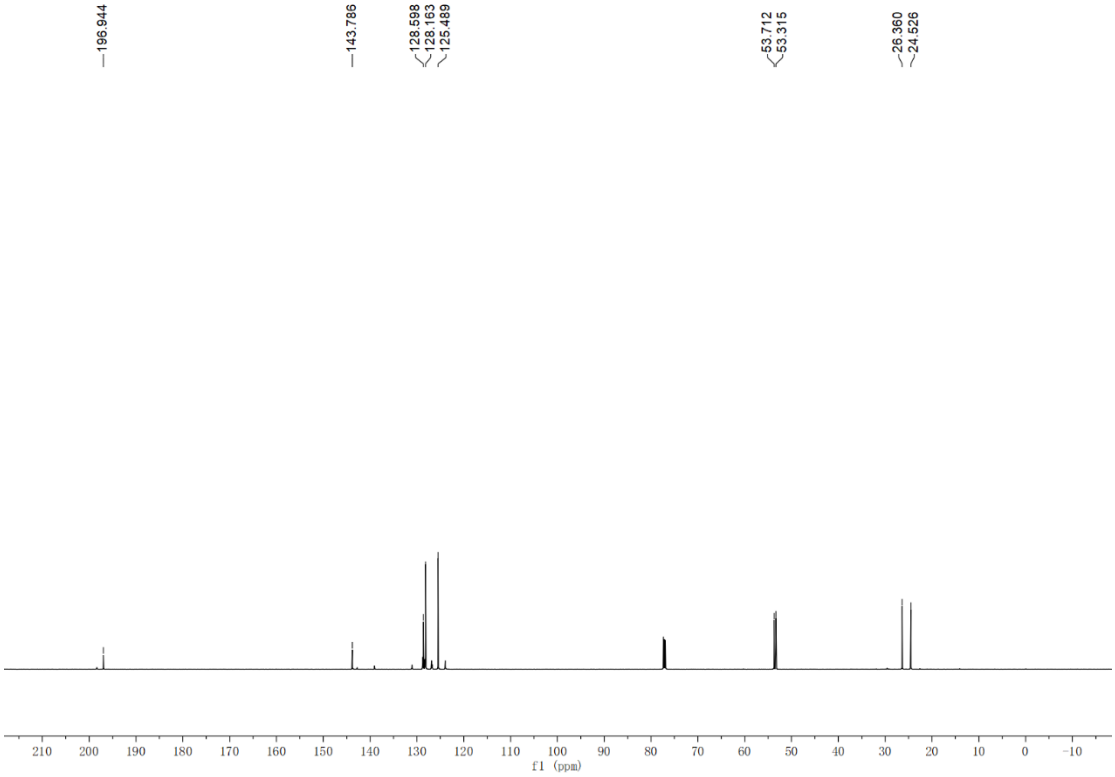


Figure S29 ^{13}C NMR Spectrum of Phenyl(pyrrolidin-1-yl)methanethione(**3m**)

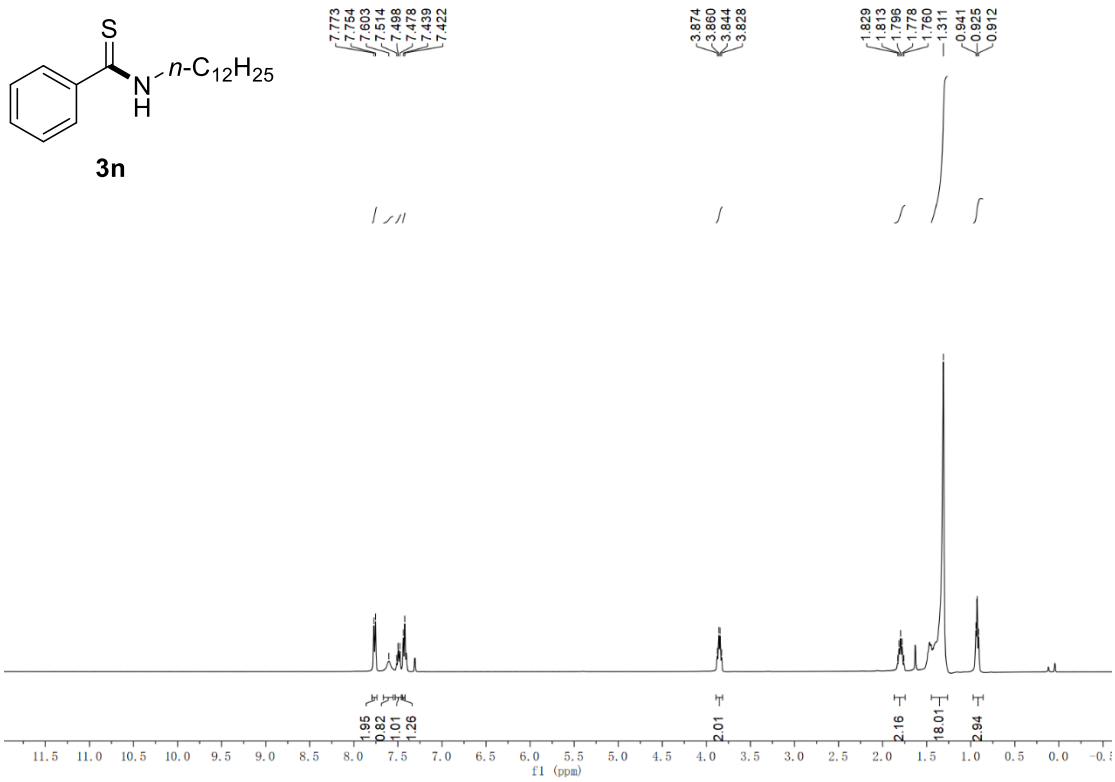


Figure S30 ^{1}H NMR Spectrum of *N*-Dodecylbenzothioamide(**3n**)

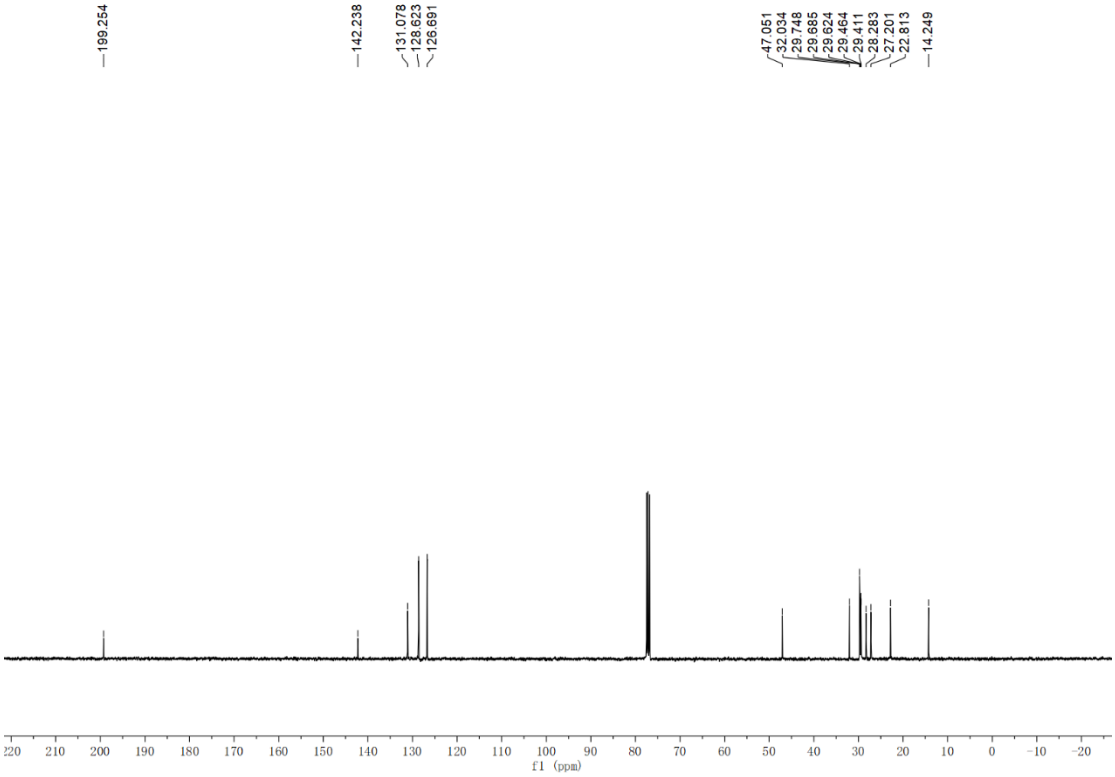


Figure S31 ^{13}C NMR Spectrum of *N*-Dodecylbenzothioamide(**3n**)

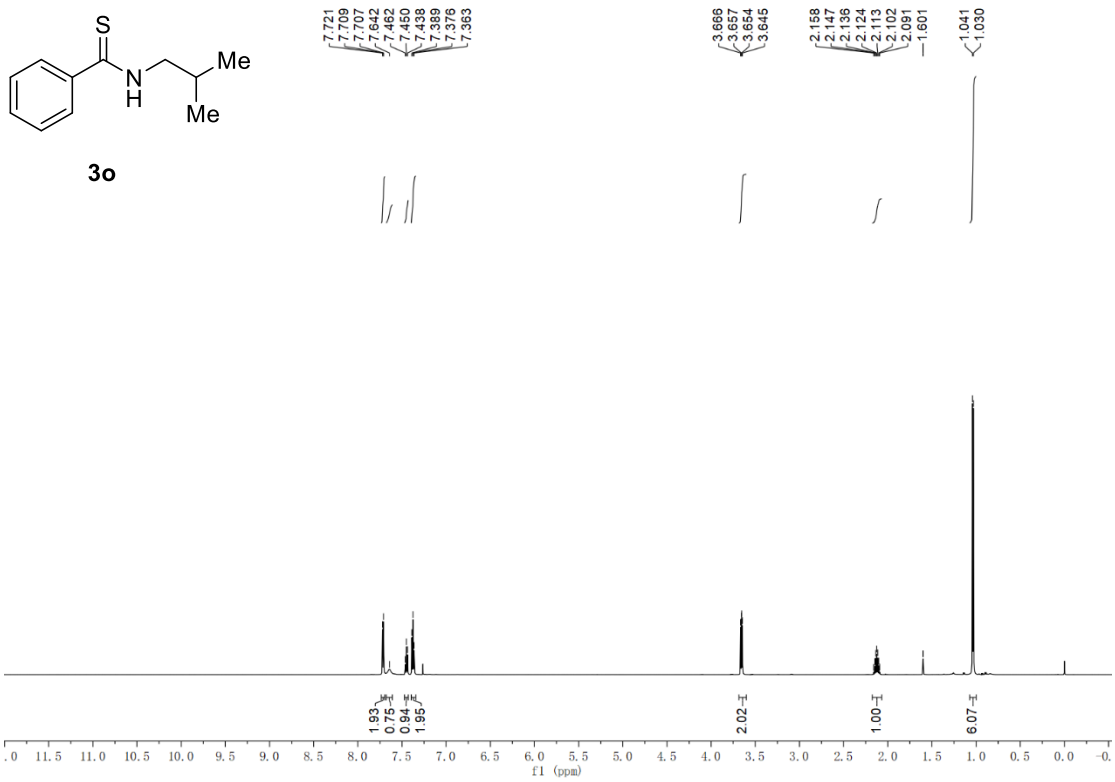


Figure S32 ^{1}H NMR Spectrum of *N*-Isobutylbenzothioamide(**3o**)

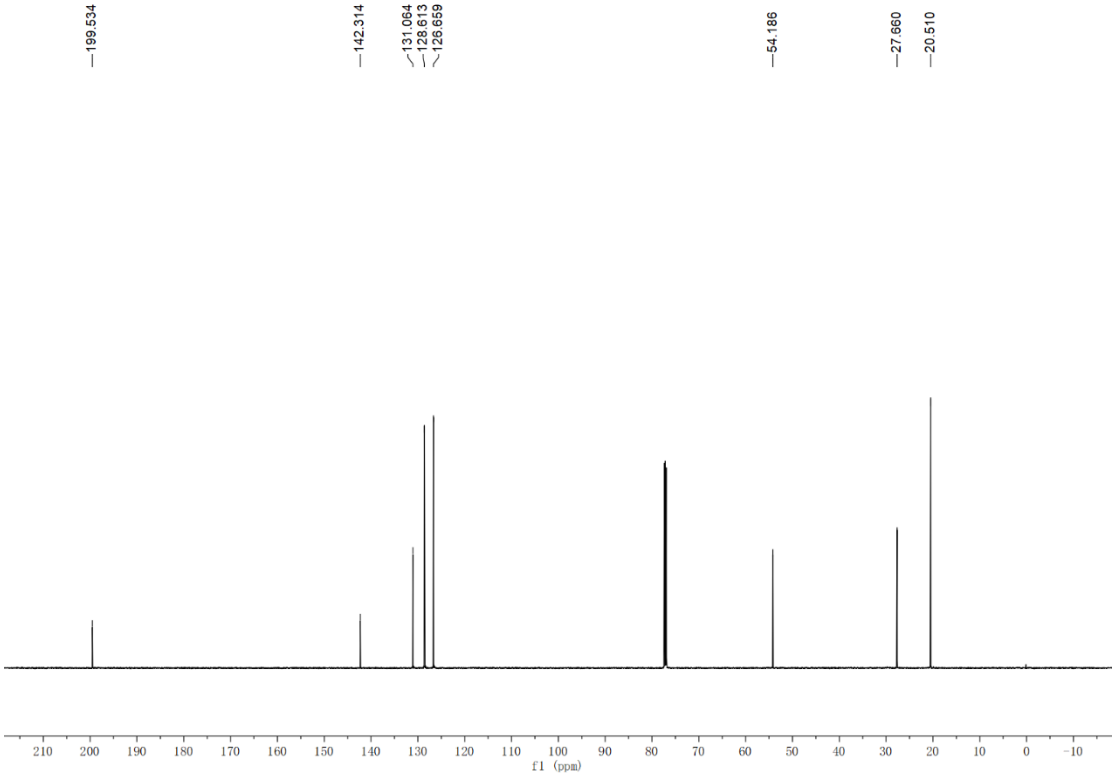


Figure S33 ^{13}C NMR Spectrum of *N*-Isobutylbenzothioamide(**3o**)

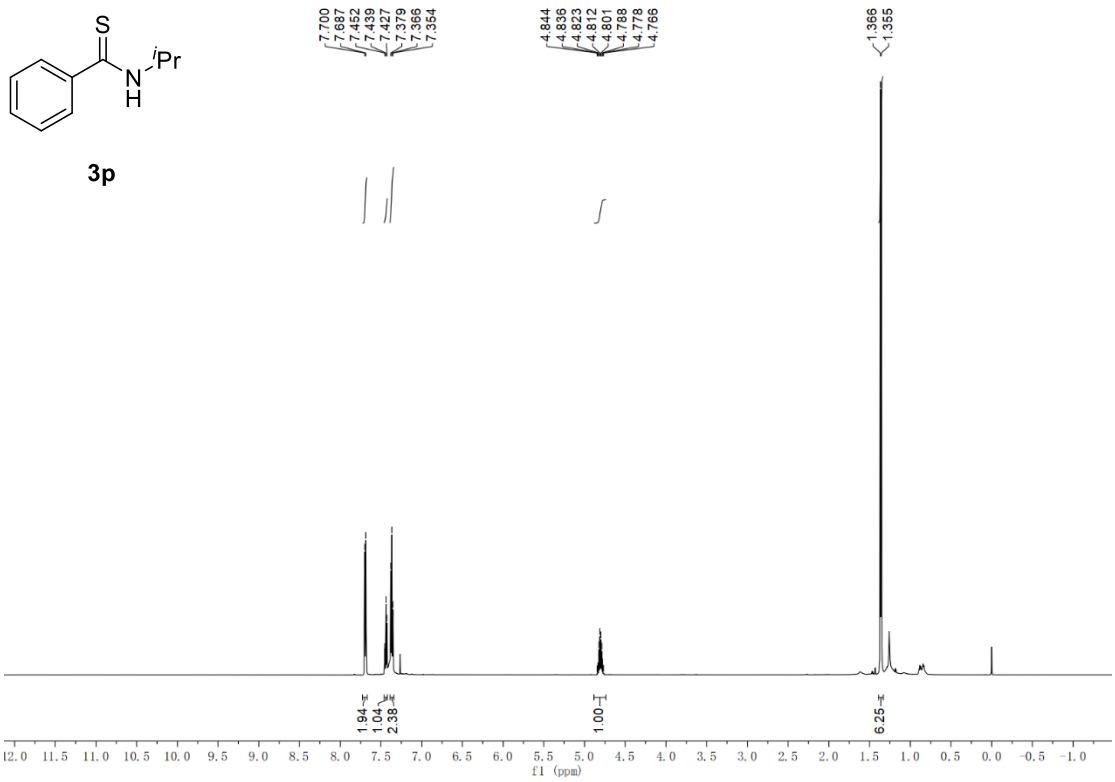


Figure S34 ^{1}H NMR Spectrum of *N*-Isopropylbenzothioamide(**3p**)

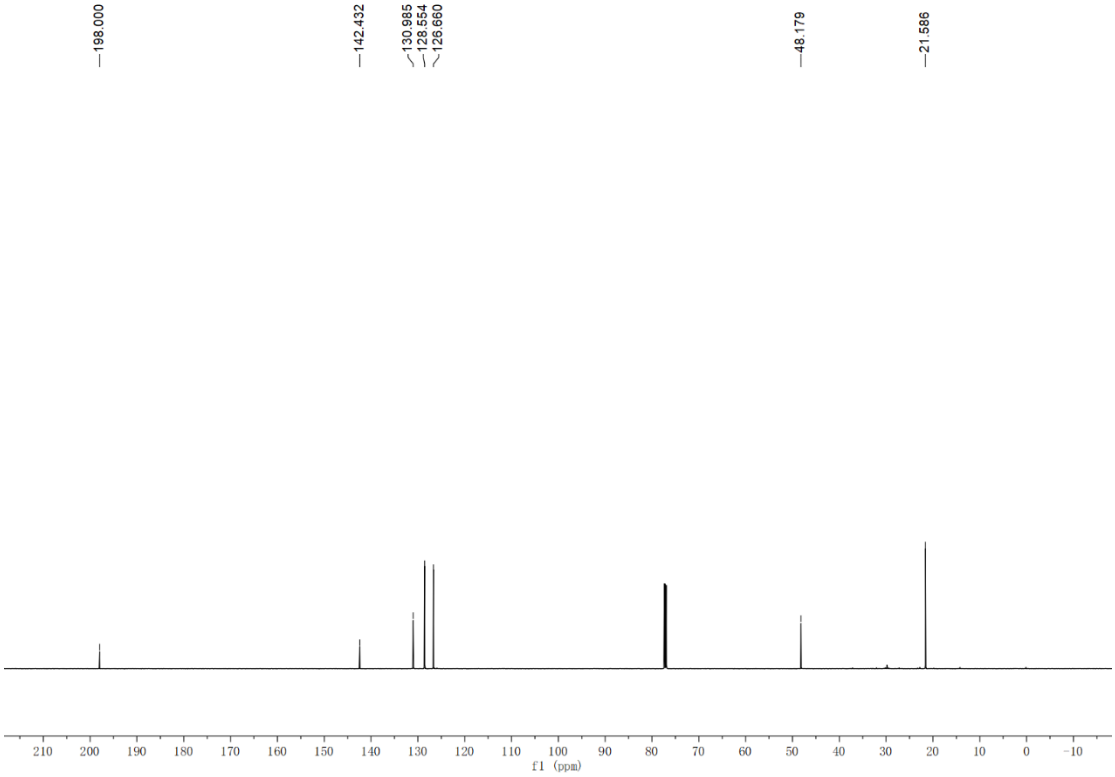


Figure S35 ^{13}C NMR Spectrum of *N*-Isopropylbenzothioamide(**3p**)

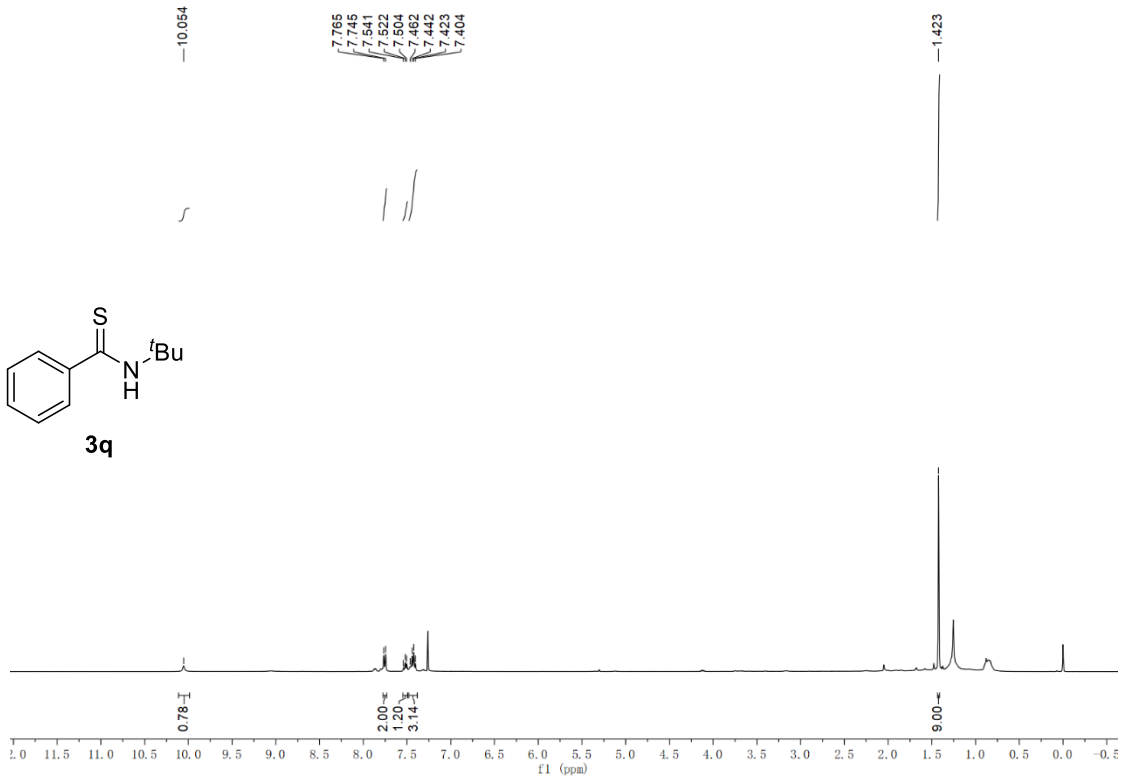


Figure S36 ^{1}H NMR Spectrum of *N*-(tert-Butyl)benzothioamide(**3q**)

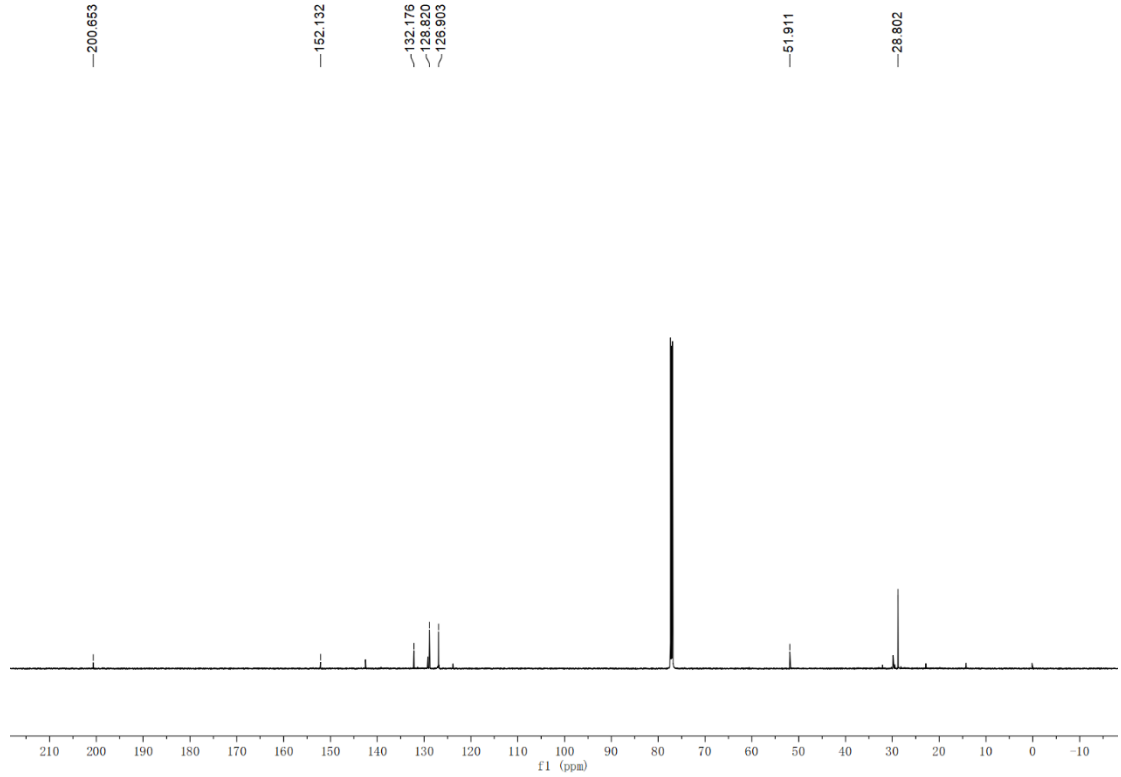


Figure S37 ^{13}C NMR Spectrum of *N*-(tert-Butyl)benzothioamide(**3q**)

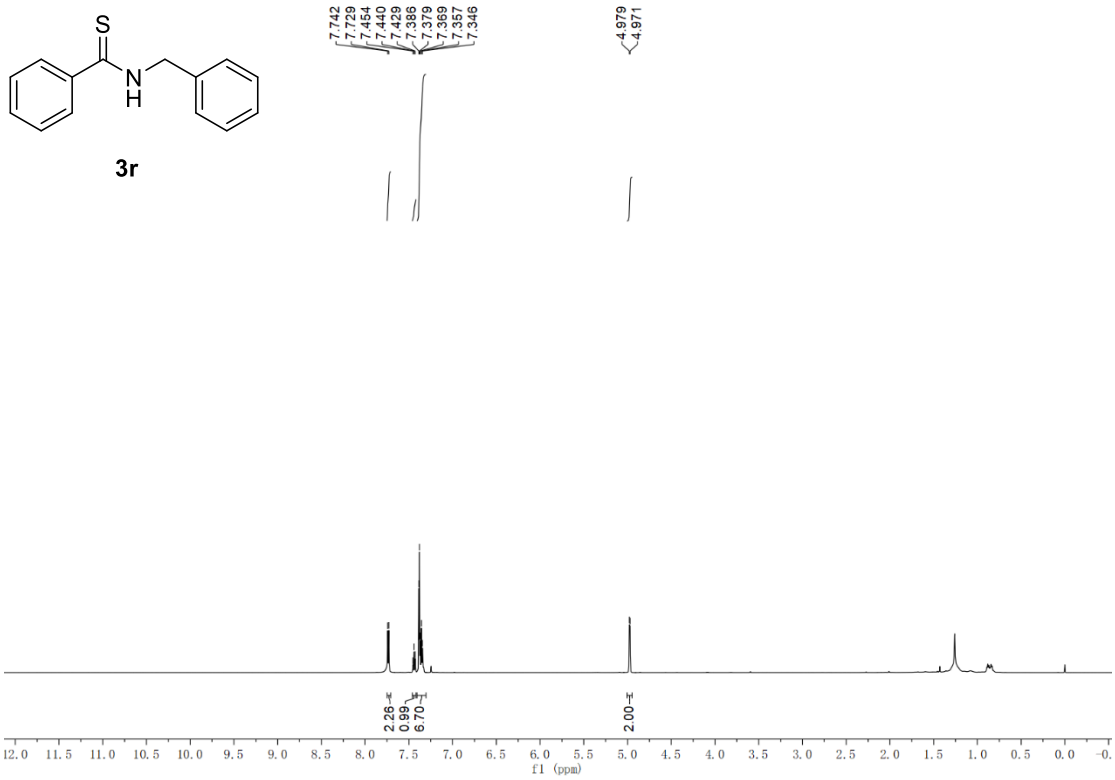


Figure S38 ^{1}H NMR Spectrum of *N*-Benzylbenzothioamide(**3r**)

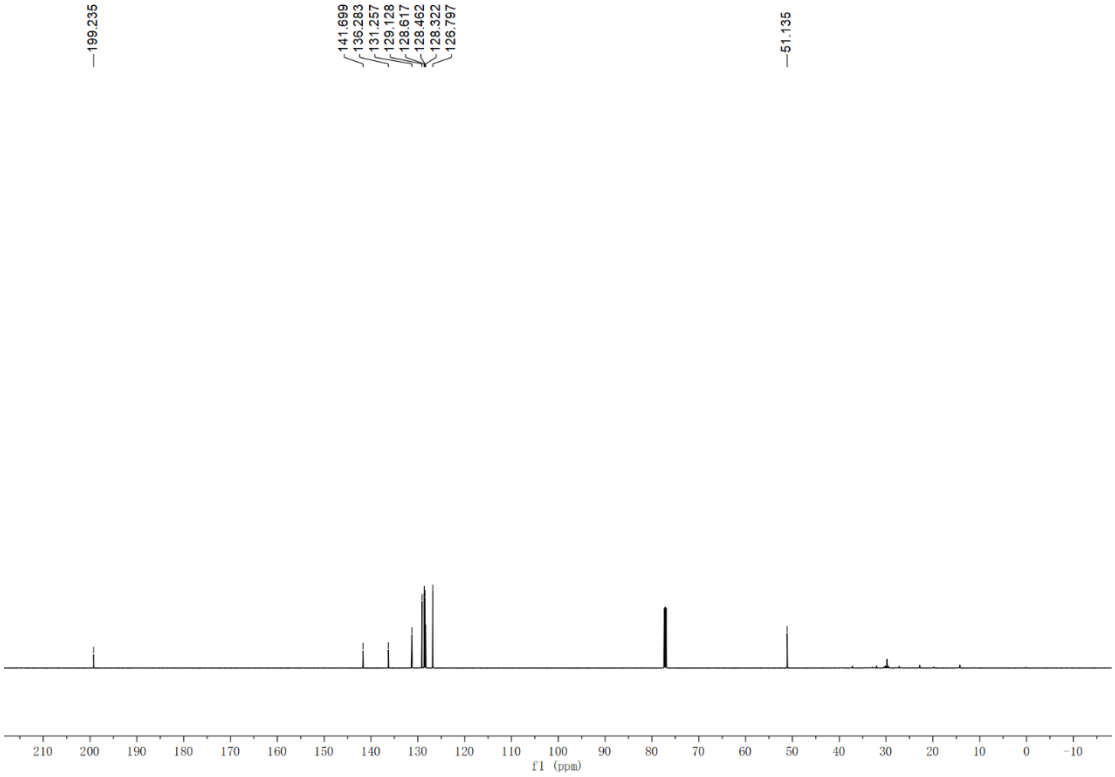


Figure S39 ^{13}C NMR Spectrum of *N*-Benzylbenzothioamide(**3r**)

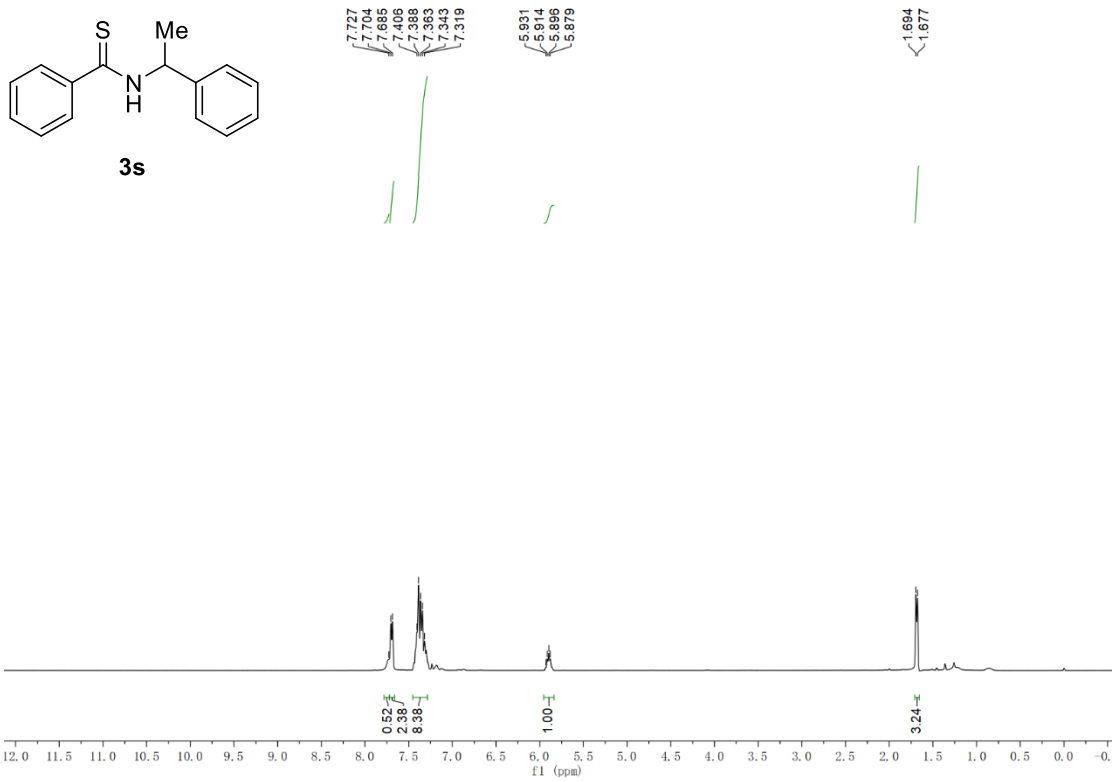


Figure S40 ^{1}H NMR Spectrum of *N*-(1-Phenylethyl)benzothioamide(**3s**)

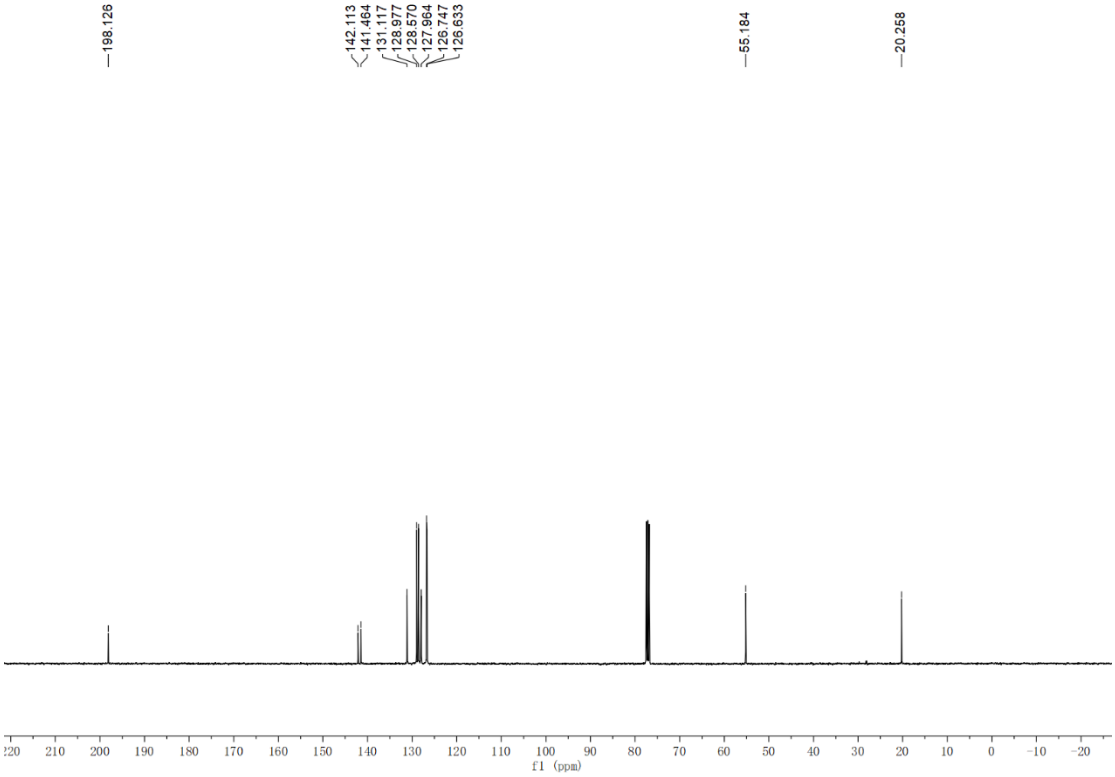


Figure S41 ^{13}C NMR Spectrum of *N*-(1-Phenylethyl)benzothioamide(**3s**)

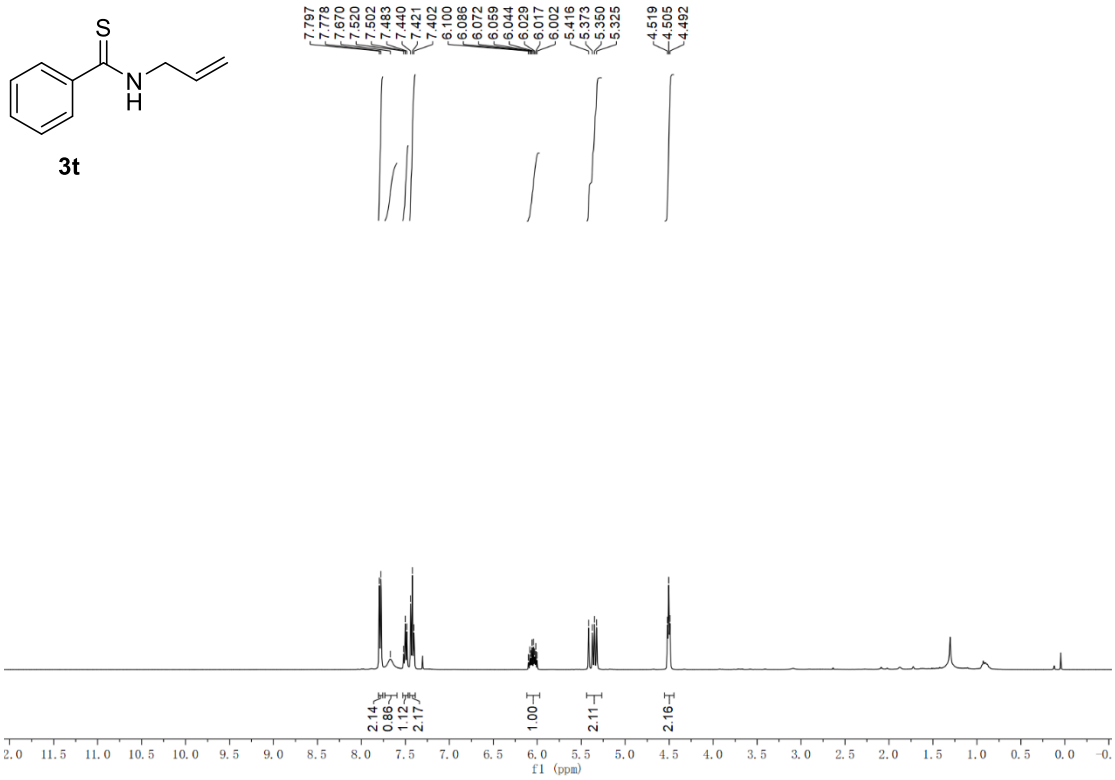


Figure S42 ^{1}H NMR Spectrum of *N*-Allylbenzothioamide(**3t**)

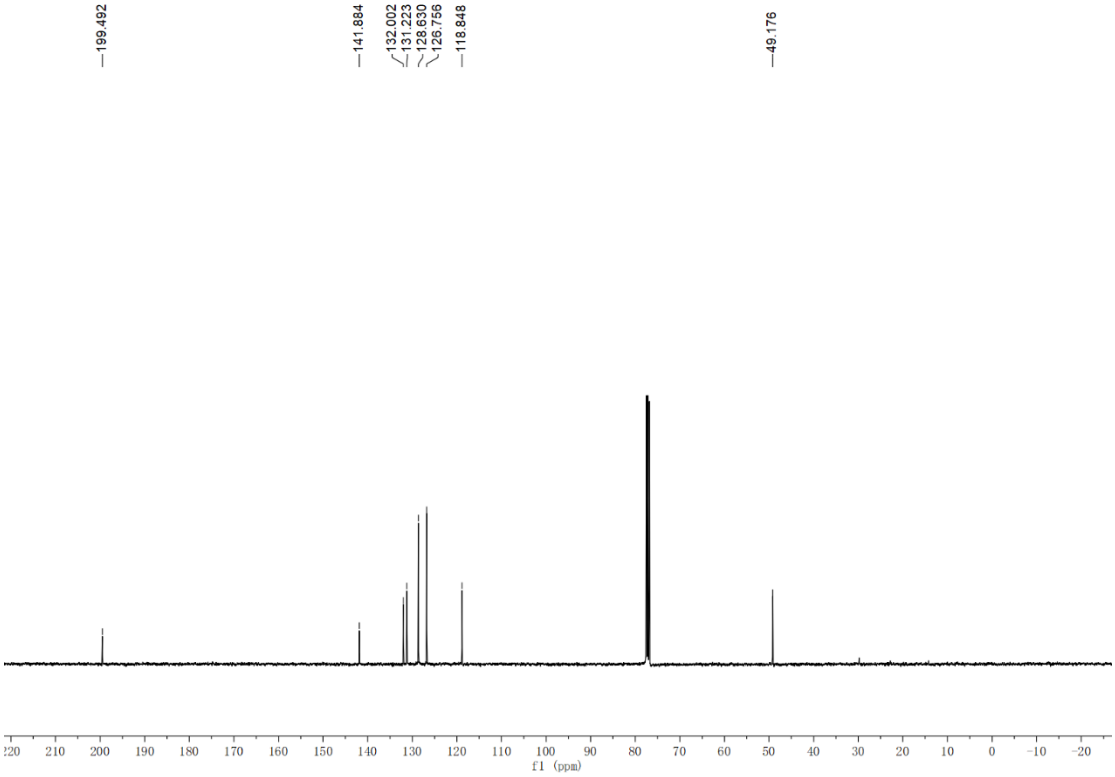


Figure S43 ^{13}C NMR Spectrum of *N*-Allylbenzothioamide(**3t**)

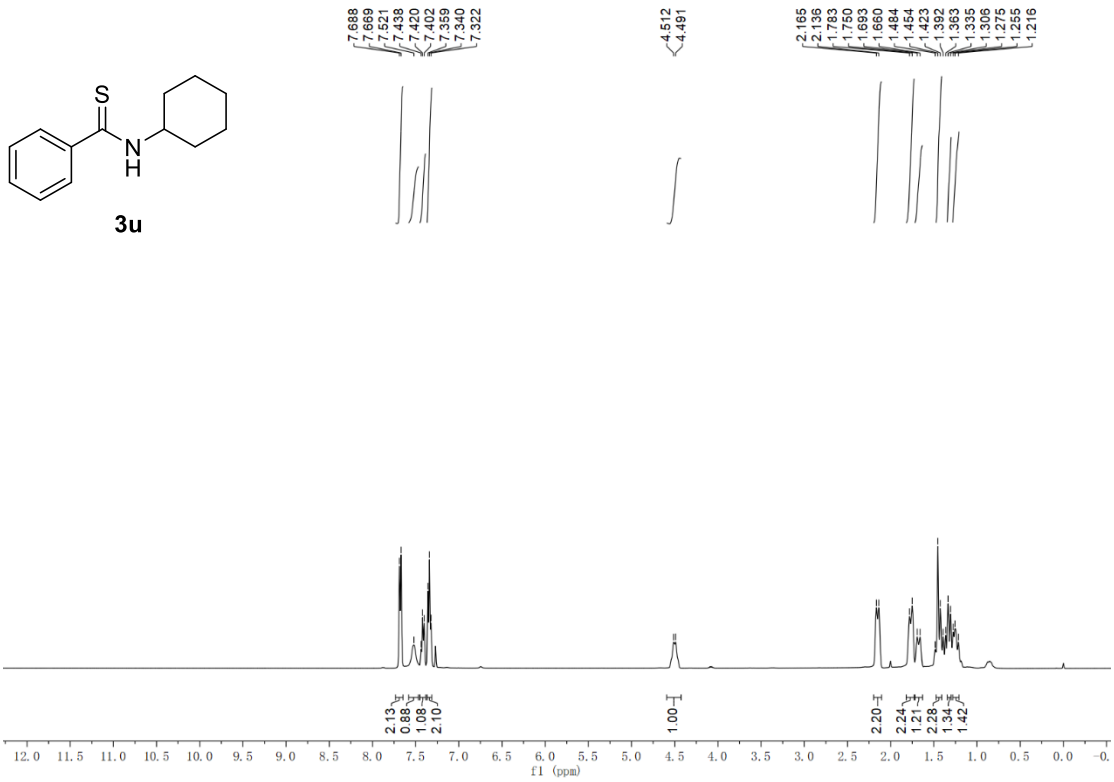


Figure S44 ^{1}H NMR Spectrum of *N*-Cyclohexylbenzothioamide(**3u**)

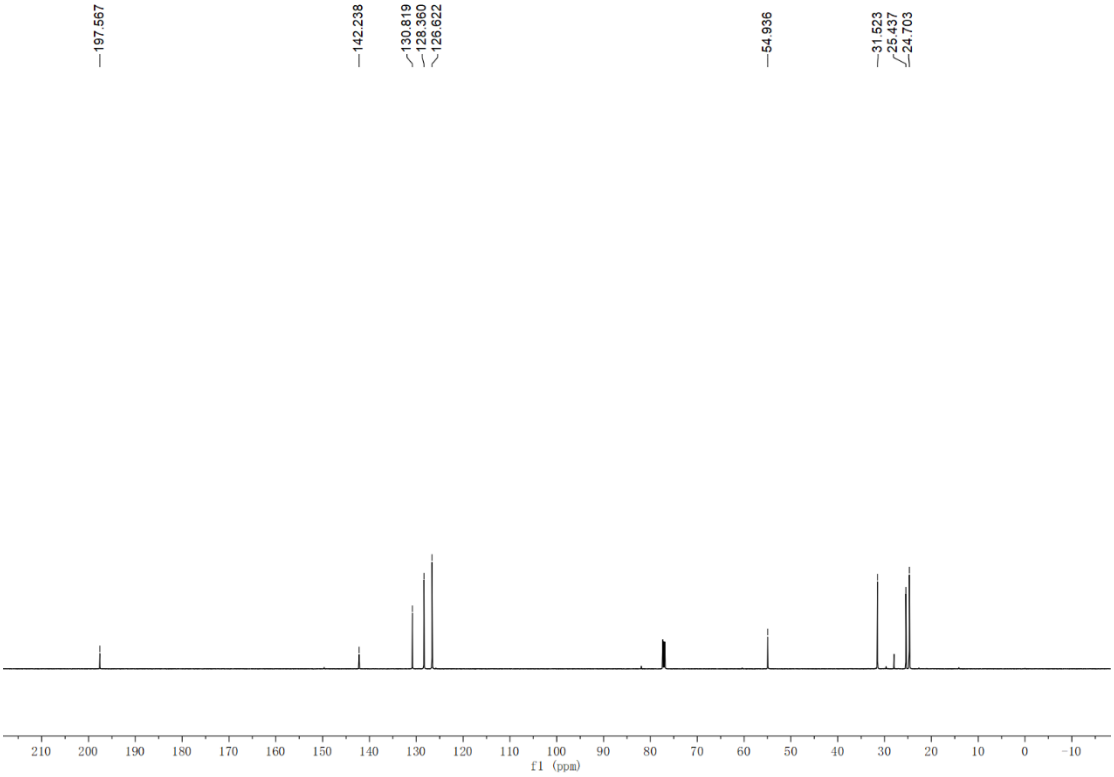


Figure S45 ^{13}C NMR Spectrum of *N*-Cyclohexylbenzothioamide(**3u**)

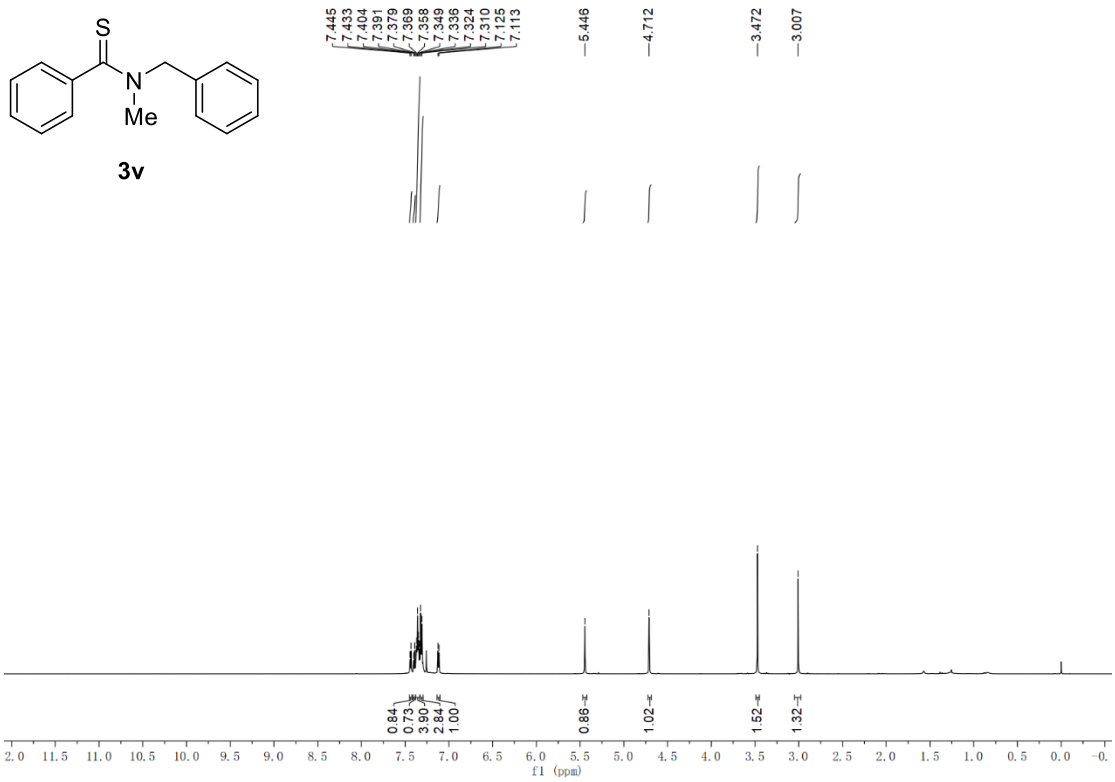


Figure S46 ^{1}H NMR Spectrum of *N*-Benzyl-N-methylbenzothioamide(**3v**)

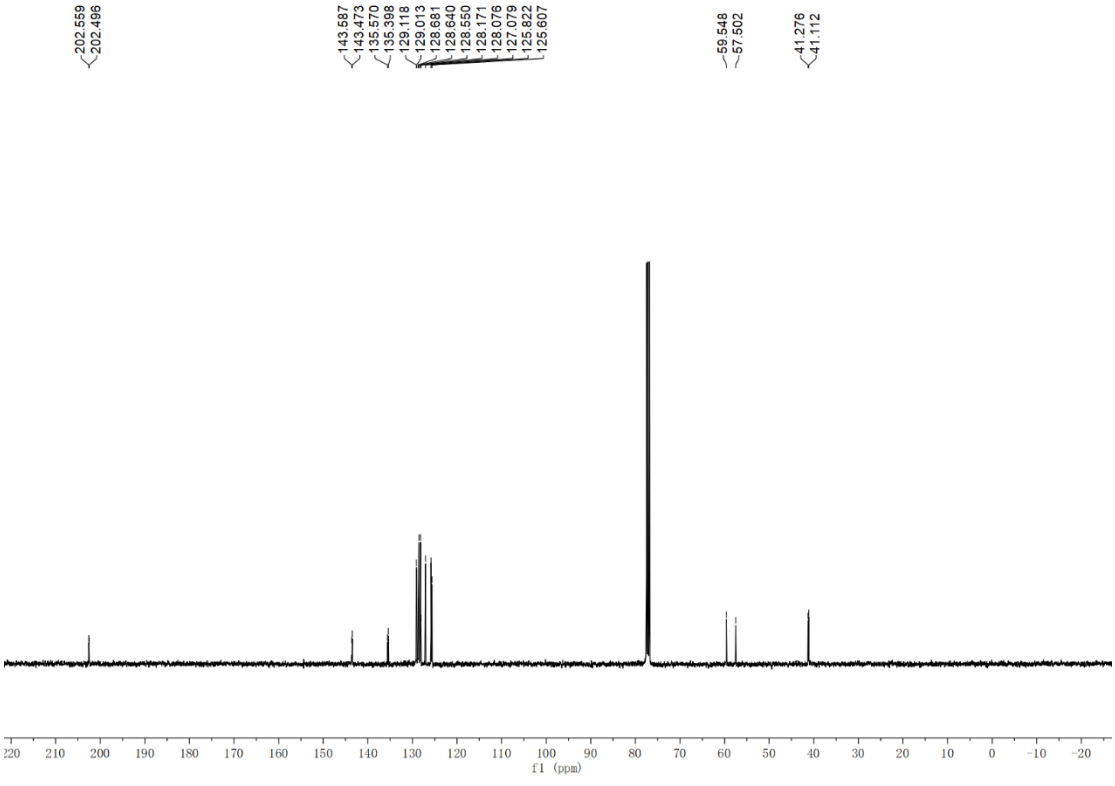


Figure S47 ^{13}C NMR Spectrum of *N*-Benzyl-N-methylbenzothioamide(**3v**)

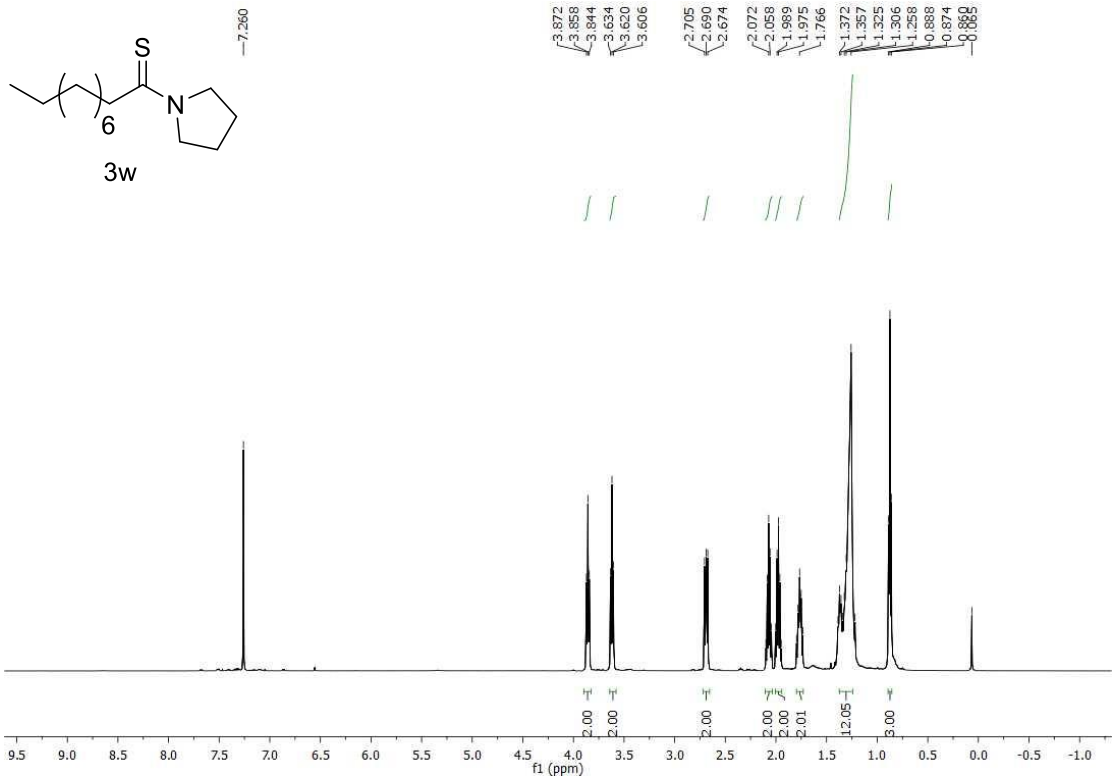


Figure S48 ^{1}H NMR Spectrum of 1-(pyrrolidin-1-yl)pentane-1-thione (**3w**)

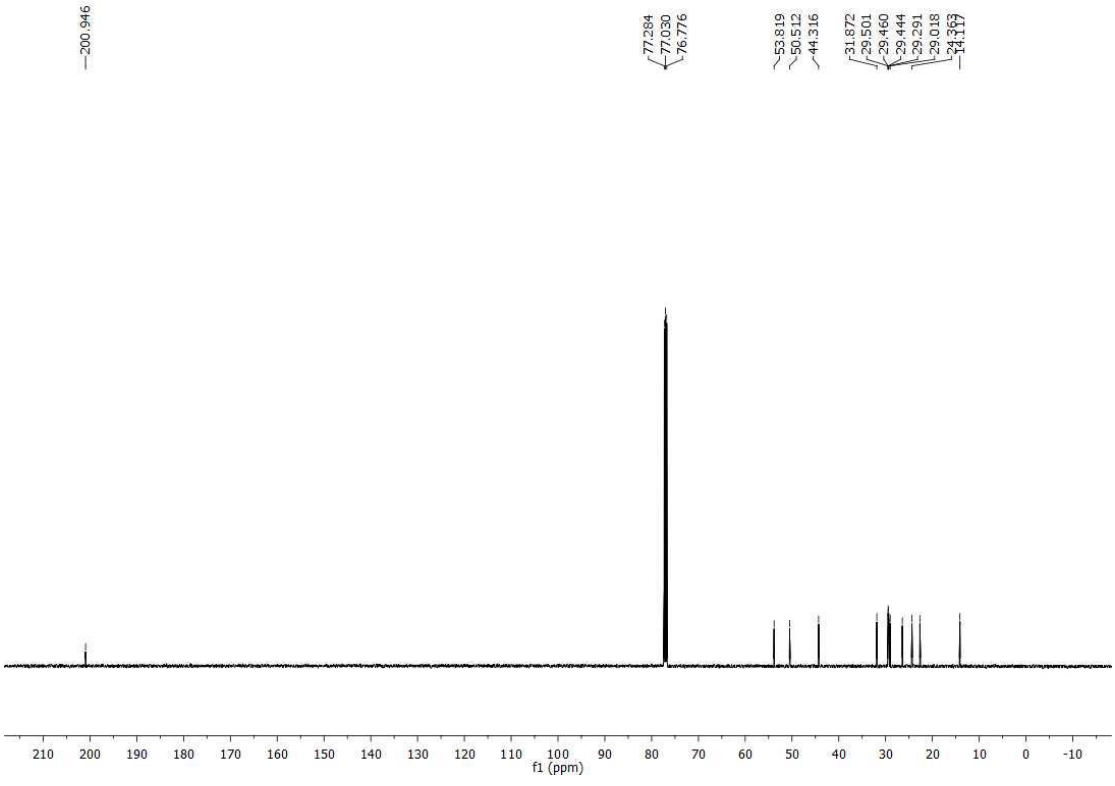


Figure S49 ^{13}C NMR Spectrum of 1-(pyrrolidin-1-yl)pentane-1-thione (**3w**)

5. References

1. Zhang, J.; Liu, Z.; Yin, Z.; Yang, X.; Ma, Y.; Szostak, R.; Szostak, M., Preference of cis-Thioamide Structure in N-Thioacyl-N-methylanilines. Organic Letters 2020, 22, 9500-9505.
2. Li, G.; Xing, Y.; Zhao, H.; Zhang, J.; Hong, X.; Szostak, M., Chemoselective Transamidation of Thioamides by Transition-Metal-Free N−C(S) Transacylation. Angewandte Chemie International Edition 2022, e202200144.
3. Li, J.; Ren, X.; Li, G.; Liang, H.; Zhao, Y.; Wang, Z.; Li, H.; Yuan, B., Mixed bases mediated synthesis of thioamides in water. Journal of Sulfur Chemistry 2020, 41, 229-237.
4. Khatri, C. K.; Mali, A. S.; Chaturbhuj, G. U., Sulfated polyborate catalyzed Kindler reaction: a rapid, efficient, and green protocol. Monatshefte für Chemie - Chemical Monthly 2017, 148, 1463-1468.
5. Liu, L.; Guo, Z.; Xu, K.; Hui, S.; Zhao, X.; Wu, Y., Transition-metal-free cleavage of C–C double bonds: a three-component reaction of aromatic alkenes with S8and amides towards aryl thioamides. Organic Chemistry Frontiers 2018, 5, 3315-3318.
6. Qiu, R.; Xu, X.; Chen, S.; Li, Y.; Chen, J.; Su, L.; Tang, Z.; Au, C.-T., Iodine-Promoted Synthesis of Thioamides from 1,2-Dibenzyl-sulfane and Difurfuryl Disulfide. Synlett 2016, 27, 2339-2344.
7. Sheng, H.; Zeng, R.; Wang, W.; Luo, S.; Feng, Y.; Liu, J.; Chen, W.; Zhu, M.; Guo, Q., An Efficient Heterobimetallic Lanthanide Alkoxide Catalyst for Transamidation of Amides under Solvent-Free Conditions. Advanced Synthesis & Catalysis 2017, 359, 302-313.
8. Phakhodee, W.; Duangkamol, C.; Wiriya, N.; Pattarawarapan, M., A convenient one-pot synthesis of N-substituted amidoximes and their application toward 1,2,4-oxadiazol-5-ones. RSC Advances 2018, 8, 38281-38288.
9. Chen, J.; Mei, L.; Liu, J.; Zhong, C.; Yuan, B.; Li, Q., Microwave-assisted iodine-catalyzed oxidative coupling of dibenzyl(difurfuryl)disulfides with amines: a rapid and efficient protocol for thioamides. RSC Advances 2019, 9, 28576-28580.

10. Pace, V.; Castoldi, L.; Monticelli, S.; Safranek, S.; Roller, A.; Langer, T.; Holzer, W., A Robust, Eco-Friendly Access to Secondary Thioamides through the Addition of Organolithium Reagents to Isothiocyanates in Cyclopentyl Methyl Ether (CPME). Chemistry 2015, 21, 18966-70.
11. Abazid, A. H.; Hollwedel, T. N.; Nachtsheim, B. J., Stereoselective Oxidative Cyclization of N-Allyl Benzamides to Oxaz(ol)ines. Organic Letters 2021, 23, 5076-5080.
12. Pastor, I.; Gisbert, P., Oxidative Coupling–Thionation of Amines Mediated by Iron-Based Imidazolium Salts for the Preparation of Thioamides. Synthesis 2018, 50, 3031-3040.