Supporting Information

Direct N alkylation of sulfur-containing amines

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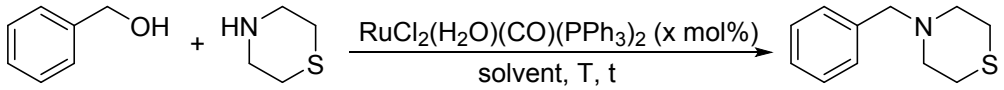
1. General information

NMR data were obtained on Bruker AVANCE Ⅲ 500MHz for ^{1}H at 500 MHz and for ^{13}C at 125 MHz with TMS as the internal standard. HRMS data were measured on an Agilent 6120 LC/TOF-MS with ESI source or Waters Premier GC/TOF-MS with EI source. In each case, enantiomeric excess was determined on a chiral column in comparison with authentic racemates by chiral HPLC, using a JASCO LC-2000 Plus system, consisting of MD-2010 HPLC diode array detector. Column chromatography and flash chromatography experiments were conducted using silica gel GF254 (200-300mesh) eluting with ethyl ether and petroleum ether. TLC experiments were carried out on glass-backed silica plates. Unless otherwise noted, chemicals were used without purification as commercially available.

2. General procedures

Table S1. Optimization of the Reaction Conditions[a, b]



1a **2a** **3aa**

Entry	M_{1a} : M_{2a}	Load of **cat.**/mol%	Solvent	Temperature/°C	Time/h	Yield/%
1	2:1	0.2	-	150	5	71
2	2:1	0.5	-	150	5	8
3	2:1	1	-	150	5	28
4	2:1	1	-	140	5	52
5	2:1	1	-	160	5	43
6	2:1	1	Toluene	150	5	53
7	2:1	1	Xylene	150	5	58
8	2:1	1	DMSO	150	5	26
9	2:1	1	-	150	10	65
10	3:1	1	-	150	5	86
11	5:1	1	-	150	5	95

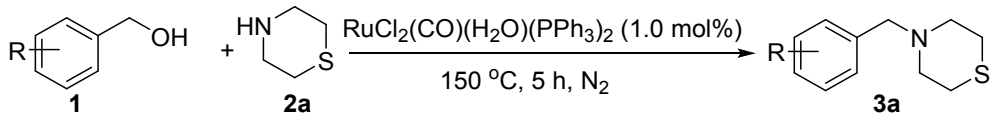
[a]Reaction conditions: benzyl alcohol **1a**, thiomorpholine **2a** (1.0 mmol) and $RuCl_2(H_2O)(CO)(PPh_3)_2$, solvent (1.0 mL) were heated for 5-8 h under N_2. [b]Isolated yields.

General procedures for the synthesis of $RuCl_2(CO)(H_2O)(PPh_3)_2$, $RuCl_2(CO)(CH_3CN)(PPh_3)_2$

$RuCl_3$ (1.0 mmol, 0.21 g) and triphenylphosphine (3.0 mmol, 0.79 g) were refluxed in formaldehyde aqueous solution (10 mL, 40 w./w.%) and ethylene glycol methyl ether (10 mL) for 40 min to produce yellow solid. Then, the soild was purified by flite, washed with alcohol and water (10 mL×3), dried to obtain catalyst

$RuCl_2(CO)(H_2O)(PPh_3)_2$ (0.63 g, 85% yield). Furthermore, the catalyst $RuCl_2(CO)(H_2O)(PPh_3)_2$ (1.0 mmol, 0.74 g) was refluxed in acetonitrile (20 mL) to obtain catalyst $RuCl_2(CO)(CH_3CN)(PPh_3)_2$ (0.72 g, 94% yield).

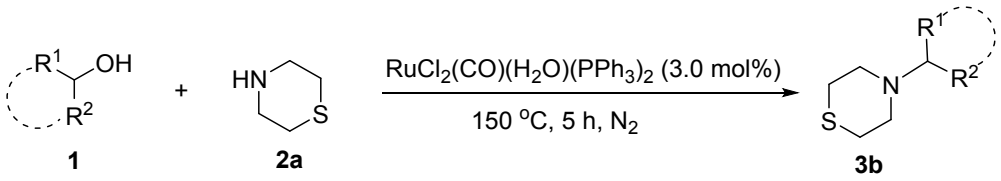
General procedures for the synthesis of products 3a



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

To a 10-mL of Schlenk tube was added alcohols **1** (5.0 mmol), thiomorpholine **2a** (1.0 mmol) and $RuCl_2(CO)(H_2O)(PPh_3)_2$ (1.0 mol%), nitrogen replacement and sealed. The mixture was stirred at 150 °C for 5 h. Then the mixture was diluted with EtOAc (10 mL), and cancentrated under vacuum. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (20:1 to 5:1) to afford products **3a**.

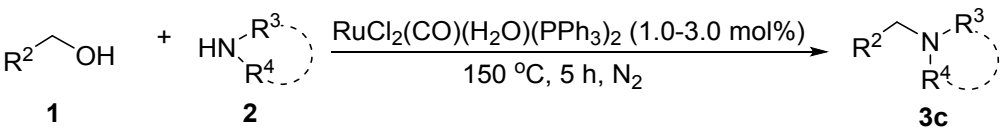
General procedures for the synthesis of products 3b



1 **2a** **3b**

To a 10-mL of Schlenk tube was added alcohols **1** (5.0 mmol), thiomorpholine **2a** (1.0 mmol) and $RuCl_2(CO)(H_2O)(PPh_3)_2$ (3.0 mol%), nitrogen replacement and sealed. The mixture was stirred at 150 °C for 5 h. Then the mixture was diluted with EtOAc (10 mL), and cancentrated under vacuum. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (20:1 to 5:1) to afford products **3b**.

General procedures for the synthesis of products 3c

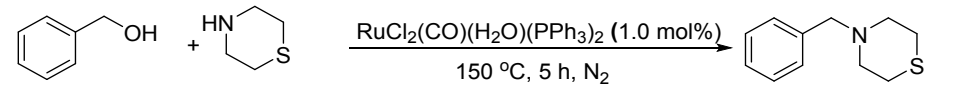


1 **2** **3c**

To a 10-mL of Schlenk tube was added alcohol **1** (5.0 mmol), amine **2** (1.0 mmol) and $RuCl_2(CO)(H_2O)(PPh_3)_2$ (1.0-3.0 mol%), nitrogen replacement and sealed. The mixture was stirred at 150 °C for 5 h. Then the mixture was diluted with EtOAc (10 mL), and cancentrated under vacuum. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (20:1 to 5:1) to afford

products **3c**.

3. Multigram-scale synthesis of the product 3aa

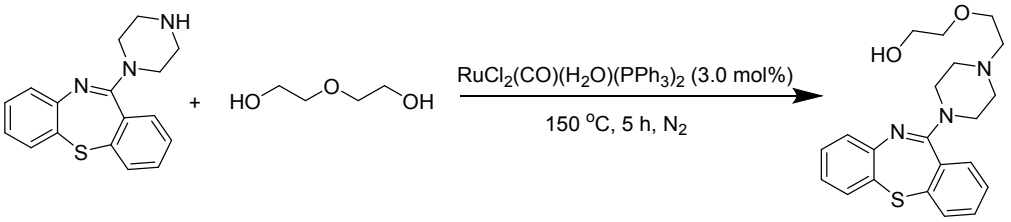


1a, 50.0 mmol **2a**, 10.0 mmol **3aa**, 1.79 g, 93% yield

To a 50-mL of Schlenk tube was added benzyl alcohol **1a** (5.4 g, 50.0 mmol), thiomorpholine **2a** (1.03 g, 10.0 mmol) and $RuCl_2(CO)(H_2O)(PPh_3)_2$ (1.0 mol%), nitrogen replacement and sealed. The mixture was stirred at 150 °C for 5 h. Then the mixture was diluted with EtOAc (100 mL), and cancentrated under vacuum. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (20:1) to afford the product **3aa** 1.79 g in 93% yield.

4. Synthesis of the quetiapine 6

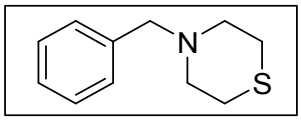
To a 10-mL of Schlenk tube was added diethylene glycol (212 mg, 2.0 mmol), intermediate **5** (295 mg, 1.0 mmol), toluene 1 mL and $RuCl_2(CO)(H_2O)(PPh_3)_2$ (3.0 mol%), nitrogen replacement and sealed. The mixture was stirred at 150 °C for 5 h. Then the mixture was diluted with EtOAc (10 mL), and cancentrated under vacuum. The residue was purified by flash chromatography on silica gel with methylene chloride/methanol (20:1) to afford the quetiapine **6**.



5 **6**

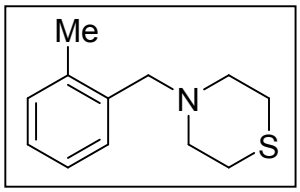
5. Characterization of products

4-benzylthiomorpholine (**3aa**)



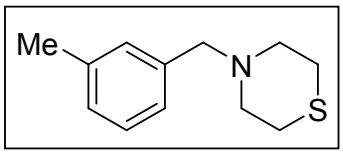
Yield: 183.3 mg, 95%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 4H), 7.30 – 7.25 (m, 1H), 3.54 (s, 2H), 2.77 – 2.65 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.01, 129.00 (2C), 128.20 (2C), 127.05, 63.64, 54.87 (2C), 27.97 (2C). **HRMS** (ES+) *m/z* calcd for $C_{11}H_{15}NS$ ($[M+H]^+$) 194.0998, found 194.0999.

4-(2-methylbenzyl)thiomorpholine (**3ab**)



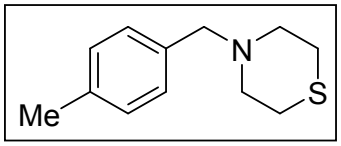
Yield: 167.7 mg, 81%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 1H), 7.22 – 7.13 (m, 3H), 3.48 (s, 2H), 2.73 (dd, *J* = 6.3, 2.8 Hz, 4H), 2.67 (dd, *J* = 5.4, 4.0 Hz, 4H), 2.37 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.58, 136.19, 130.31, 129.83, 127.10, 125.46, 61.56, 54.99 (2C), 28.15 (2C), 19.22. **HRMS** (ES+) *m/z* calcd for $C_{12}H_{17}NS$ ($[M+H]^+$) 208.1154, found 208.1155.

4-(3-methylbenzyl)thiomorpholine (**3ac**)



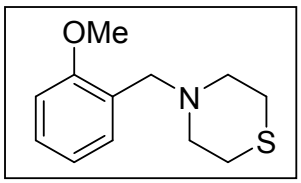
Yield: 192.5 mg, 93%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.5 Hz, 1H), 7.15 – 7.07 (m, 3H), 3.50 (s, 2H), 2.76 – 2.66 (m, 8H), 2.37 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.88, 137.83, 129.79, 128.10, 127.84, 126.16, 63.69, 54.92 (2C), 27.97 (2C), 21.37. **HRMS** (ES+) *m/z* calcd for $C_{12}H_{17}NS$ ($[M+H]^+$) 208.1154, found 208.1158.

4-(4-methylbenzyl)thiomorpholine (**3ad)**



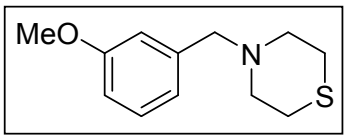
Yield: 194.5 mg, 94%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 3.50 (s, 2H), 2.75 – 2.65 (m, 8H), 2.38 – 2.32 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.69, 134.88, 129.04 (2C), 128.92 (2C), 63.41, 54.86 (2C), 28.01 (2C), 21.07. **HRMS** (ES+) *m/z* calcd for $C_{12}H_{17}NS$ ($[M+H]^+$) 208.1154, found 208.1155.

4-(2-methoxybenzyl)thiomorpholine (**3ae**)



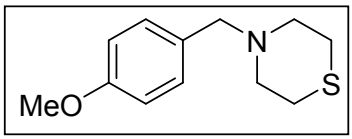
Yield: 151.6 mg, 68%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.25 (td, *J* = 8.0, 1.7 Hz, 1H), 6.97 – 6.92 (m, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 3.83 (s, 3H), 3.60 (s, 2H), 2.81 – 2.74 (m, 4H), 2.74 – 2.67 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.82, 130.31, 128.04, 126.01, 120.30, 110.46, 56.66, 55.39, 54.86 (2C), 27.96 (2C). **HRMS** (ES+) *m/z* calcd for $C_{12}H_{17}NOS$ ($[M+H]^+$) 224.1104, found 224.1107.

4-(3-methoxybenzyl)thiomorpholine (**3af**)



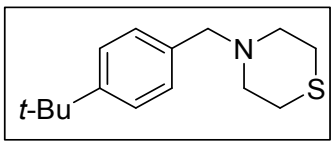
Yield: 178.4 mg, 80%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 1H), 6.93 – 6.88 (M, 2H), 6.84 – 6.78 (m, 1H), 3.82 (s, 3H), 3.51 (s, 2H), 2.76 – 2.66 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.68, 139.81, 129.17, 121.30, 114.48, 112.46, 63.57, 55.18, 54.92 (2C), 28.01 (2C). **HRMS** (ES+) *m/z* calcd for $C_{12}H_{17}NOS$ ($[M+H]^+$) 224.1104, found 224.1110.

4-(4-methoxybenzyl)thiomorpholine (**3ag**)



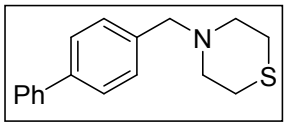
Yield: 187.3 mg, 84%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 6.89 – 6.84 (m, 2H), 3.81 (s, 3H), 3.47 (s, 2H), 2.75 – 2.63 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.78, 130.23 (2C), 129.93, 113.63 (2C), 63.05, 55.25, 54.78 (2C), 27.99 (2C). **HRMS** (ES+) *m/z* calcd for $C_{12}H_{17}NOS$ ($[M+H]^+$) 224.1104, found 224.1103.

4-(4-(*tert*-butyl)benzyl)thiomorpholine (**3ah**)



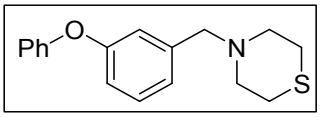
Yield: 146.9 mg, 59%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 3.51 (s, 2H), 2.76 – 2.66 (m, 8H), 1.34 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.02, 134.85, 128.78 (2C), 125.13 (2C), 63.35, 54.90 (2C), 34.46, 31.40 (3C), 28.02 (2C). **HRMS** (ES+) *m/z* calcd for $C_{15}H_{23}NS$ ($[M+H]^+$) 250.1624, found 250.1625.

4-([1,1'-biphenyl]-4-ylmethyl)thiomorpholine (**3ai**)



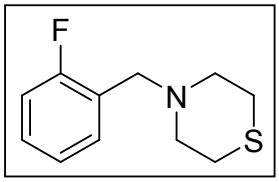
Yield: 250.2mg, 93%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.60 – 7.55 (m, 2H), 7.49 – 7.43 (m, 2H), 7.43 – 7.34 (m, 3H), 3.59 (s, 2H), 2.82 – 2.66 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.94, 140.08, 137.14, 129.45 (2C), 128.75 (2C), 127.19, 127.04 (2C), 127.00 (2C), 63.35, 54.96 (2C), 28.05 (2C). **HRMS** (ES+) *m/z* calcd for $C_{17}H_{19}NS$ ($[M+H]^+$) 270.1311, found 270.1312.

4-(3-phenoxybenzyl)thiomorpholine (**3aj**)



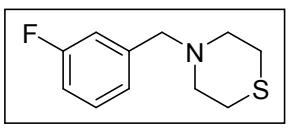
Yield: 242.3 mg, 85%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 7.15 – 7.09 (m, 1H), 7.07 (d, J = 7.6 Hz, 1H), 7.05 – 7.00 (m, 3H), 6.91 (dd, J = 8.1, 1.9 Hz, 1H), 3.52 (s, 2H), 2.78 – 2.64 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.27 (2C), 140.30, 129.71 (2C), 129.48, 123.78, 123.17, 119.36, 118.79 (2C), 117.50, 63.26, 54.88 (2C), 27.99 (2C). **HRMS** (ES+) *m/z* calcd for $C_{17}H_{19}NOS$ ($[M+H]^+$) 286.1260, found 286.1265.

4-(2-fluorobenzyl)thiomorpholine (**3ak**)



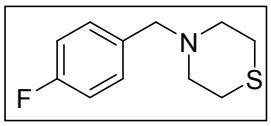
Yield: 147.7 mg, 70%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 (td, J = 7.5, 1.7 Hz, 1H), 7.28 – 7.21 (m, 1H), 7.12 (td, J = 7.5, 1.0 Hz, 1H), 7.06 – 7.01 (m, 1H), 3.61 (s, 2H), 2.79 – 2.73 (m, 4H), 2.73 – 2.67 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.43 (d, $^1J_{C\text{-}F}$ = 246.6 Hz, 1C), 131.41 (d, $^3J_{C\text{-}F}$ = 4.54 Hz, 1C), 128.82 (d, $^3J_{C\text{-}F}$ = 8.3 Hz, 1C), 124.45 (d, $^2J_{C\text{-}F}$ = 14.6 Hz, 1C), 123.85 (d, $^4J_{C\text{-}F}$ = 3.5 Hz, 1C), 115.27 (d, $^2J_{C\text{-}F}$ = 22.2 Hz, 1C), 55.96 (d, $J_{C\text{-}F}$ = 1.76 Hz, 1C), 54.62 (2C), 27.98 (2C). **HRMS** (ES+) *m/z* calcd for $C_{11}H_{14}FNS$ ($[M+H]^+$) 212.0904, found 212.0909.

4-(3-fluorobenzyl)thiomorpholine (**3al**)



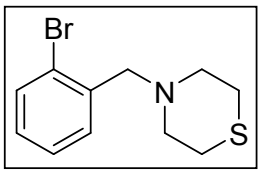
Yield: 196.2 mg, 93%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 1H), 7.07 (dd, J = 10.5, 4.4 Hz, 2H), 6.95 (td, J = 8.5, 2.4 Hz, 1H), 3.52 (s, 2H), 2.77 – 2.63 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.97 (d, $^1J_{C\text{-}F}$ = 246.1 Hz, 1C), 140.99 (d, $^3J_{C\text{-}F}$ = 6.9 Hz, 1C), 129.63 (d, $^3J_{C\text{-}F}$ = 8.2 Hz, 1C), 124.35 (d, $^4J_{C\text{-}F}$ = 2.8 Hz, 1C), 115.54 (d, $^2J_{C\text{-}F}$ = 21.3 Hz, 1C), 113.95 (d, $^2J_{C\text{-}F}$ = 21.2 Hz, 1C), 63.03 (d, $J_{C\text{-}F}$ = 1.8 Hz, 1C), 54.91 (2C), 28.00 (2C). **HRMS** (ES+) *m/z* calcd for $C_{11}H_{14}FNS$ ($[M+H]^+$) 212.0904, found 212.0905.

4-(4-fluorobenzyl)thiomorpholine (**3am**)



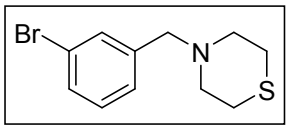
Yield: 175.1 mg, 83%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.20 (m, 2H), 7.06 – 6.95 (m, 2H), 3.49 (s, 2H), 2.75 – 2.58 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.01 (d, $^1J_{C\text{-}F}$ = 245.3 Hz, 1C), 131.75, 130.42 (d, $^3J_{C\text{-}F}$ = 8.1 Hz, 2C), 115.02 (d, $^2J_{C\text{-}F}$ = 21.3 Hz, 2C), 62.82, 54.82 (2C), 28.00 (2C). **HRMS** (ES+) *m/z* calcd for $C_{11}H_{14}FNS$ ($[M+H]^+$) 212.0904, found 212.0906.

4-(2-bromobenzyl)thiomorpholine (**3an**)



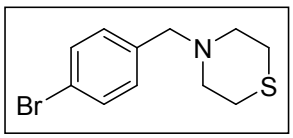
Yield: 165.9 mg, 61%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.46 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.29 (td, *J* = 7.5, 1.5 Hz, 1H), 7.12 (td, *J* = 7.7, 1.7 Hz, 1H), 3.61 (s, 2H), 2.82 – 2.75 (m, 4H), 2.73 – 2.65 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.45, 132.71, 130.53, 128.38, 127.13, 124.60, 62.37, 54.88 (2C), 28.00 (2C). **HRMS** (ES+) *m/z* calcd for $C_{11}H_{14}BrNS$ ($[M+H]^+$) 274.0082, found 274.0093.

4-(3-bromobenzyl)thiomorpholine (**3ao**)



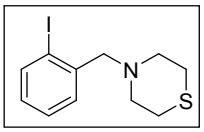
Yield: 261.1 mg, 96%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.40 – 7.36 (m, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 3.47 (s, 2H), 2.73 – 2.63 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.62, 131.72, 130.12, 129.74, 127.41, 122.41, 62.87, 54.81 (2C), 27.91 (2C). **HRMS** (ES+) *m/z* calcd for $C_{11}H_{14}BrNS$ ($[M+H]^+$) 274.0082, found 274.0092.

4-(4-bromobenzyl)thiomorpholine (**3ap**)



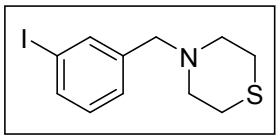
Yield: 251.2 mg, 92%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 3.47 (s, 2H), 2.74 – 2.62 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.18, 131.37 (2C), 130.63 (2C), 120.90, 62.90, 54.88 (2C), 27.99 (2C). **HRMS** (ES+) *m/z* calcd for $C_{11}H_{14}BrNS$ ($[M+H]^+$) 274.0082, found 274.0085.

4-(2-iodobenzyl)thiomorpholine (**3aq**)



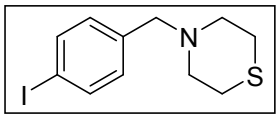
Yield: 315.8 mg, 99%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.32 (td, *J* = 7.5, 1.7 Hz, 1H), 6.96 (td, *J* = 7.7, 1.7 Hz, 1H), 3.54 (s, 2H), 2.84 – 2.74 (m, 4H), 2.74 – 2.63 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.55 (2C), 130.28, 128.74, 127.95, 100.58, 67.08, 54.81 (2C), 28.04 (2C). **HRMS** (ES+) *m/z* calcd for $C_{11}H_{14}INS$ ($[M+H]^+$) 319.9964, found 319.9966.

4-(3-iodobenzyl)thiomorpholine (**3ar**)



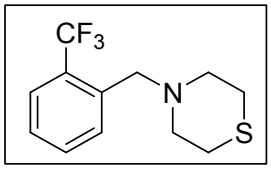
Yield: 312.6 mg, 98%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 6.4 Hz, 1H), 7.06 (t, *J* = 7.7 Hz, 1H), 3.46 (s, 2H), 2.75 – 2.65 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.64, 137.81, 136.21, 130.02, 128.20, 94.41, 62.86, 54.88 (2C), 27.95 (2C). **HRMS** (ES+) *m/z* calcd for $C_{11}H_{14}INS$ ($[M+H]^+$) 319.9964, found 319.9970.

4-(4-iodobenzyl)thiomorpholine (**3as**)



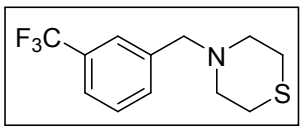
Yield: 293.5 mg, 92%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 3.46 (s, 2H), 2.76 – 2.62 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.87, 137.36 (2C), 130.94 (2C), 92.41, 62.99, 54.89 (2C), 27.99 (2C). **HRMS** (ES+) *m/z* calcd for $C_{11}H_{14}INS$ ($[M+H]^+$) 319.9964, found 319.9969.

4-(2-(trifluoromethyl)benzyl)thiomorpholine (**3at**)



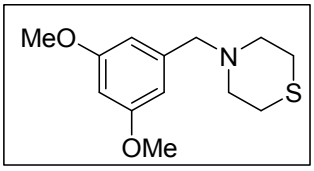
Yield: 148.8 mg, 57%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 3.68 (s, 2H), 2.73 (td, *J* = 9.4, 3.4 Hz, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.79, 131.73, 130.15, 128.68 (q, $^{2}J_{C\text{-}F}$ = 30.2 Hz, 1C), 126.81, 125.78 (q, $^{3}J_{C\text{-}F}$ = 5.9 Hz, 1C), 124.5 (q, $^{1}J_{C\text{-}F}$ = 274.6 Hz, 1C), 58.90, 55.08 (2C), 28.11 (2C). **HRMS** (ES+) *m/z* calcd for $C_{12}H_{14}F_3NS$ ($[M+H]^+$) 262.0872, found 262.0879.

4-(3-(trifluoromethyl)benzyl)thiomorpholine (**3au**)



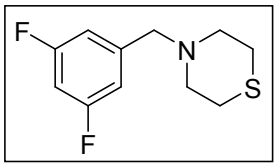
Yield: 255.8 mg, 98%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.52 (d, J = 7.7 Hz, 2H), 7.44 (t, J = 7.7 Hz, 1H), 3.57 (s, 2H), 2.77 – 2.65 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.39, 132.18, 130.68 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz, 1C), 128.71, 125.50 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz, 1C), 124.22 (q, $^{1}J_{C\text{-}F}$ = 272.8 Hz, 1C), 129.98 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz, 1C), 63.07, 54.94 (2C), 27.99 (2C). **HRMS** (ES+) *m/z* calcd for $C_{12}H_{14}F_3NS$ ($[M+H]^+$) 262.0872, found 262.0878.

4-(3,5-dimethoxybenzyl)thiomorpholine (**3av**)



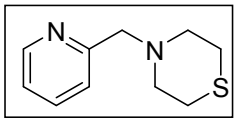
Yield: 202.4 mg, 80%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.50 (d, J = 2.3 Hz, 2H), 6.37 (t, J = 2.3 Hz, 1H), 3.80 (s, 6H), 3.47 (s, 2H), 2.70 (q, J = 6.7 Hz, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.75 (2C), 140.66, 106.78 (2C), 98.99, 63.69, 55.30 (2C), 54.92 (2C), 28.00 (2C). **HRMS** (ES+) *m/z* calcd for $C_{13}H_{19}NO_2S$ ($[M+H]^+$) 254.1209, found 254.1217.

4-(3,5-difluorobenzyl)thiomorpholine (**3aw**)



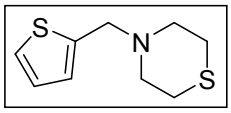
Yield: 132.8, 58%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 – 6.85 (m, 2H), 6.69 (tt, J = 8.9, 2.4 Hz, 1H), 3.49 (s, 2H), 2.76 – 2.65 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.03 (dd, $^{1}J_{C\text{-}F}$ = 248.2, 12.7 Hz, 2C), 142.72 (t, $^{3}J_{C\text{-}F}$ = 8.7 Hz, 1C), 111.19 (dd, $^{2}J_{C\text{-}F}$ = 19.3, 5.7 Hz, 2C), 102.40 (t, $^{2}J_{C\text{-}F}$ = 25.4 Hz, 1C), 62.70 (t, $^{4}J_{C\text{-}F}$ = 2.0 Hz, 1C), 54.90 (2C), 27.98 (2C). **HRMS** (ES+) *m/z* calcd for $C_{11}H_{13}F_2NS$ ($[M+H]^+$) 230.0810, found 230.0820.

4-(pyridin-2-ylmethyl)thiomorpholine (**3ax**)



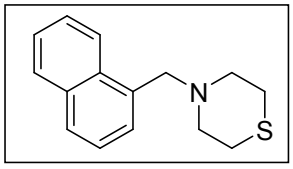
Yield: 155.2mg, 80%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.41 (m, 1H), 7.50 (m, 1H), 7.25 (d, J = 7.7 Hz, 1H), 7.25 (d, J = 7.7 Hz, 1H), 7.02 (m, 2H), 2.61 (m, 4H), 2.58 – 2.49 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.00, 148.82, 135.99, 122.70, 121.66, 64.79, 54.67 (2C), 27.50 (2C). **HRMS** (ES+) *m/z* calcd for $C_{10}H_{14}N_2S$ ($[M+H]^+$) 195.0950, found 195.0958.

4-(thiophen-2-ylmethyl)thiomorpholine (**3ay**)



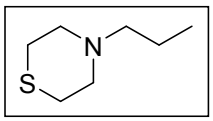
Yield: 173.1 mg, 87%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 - 7.23(m, 1H), 6.98 – 6.94 (m, 1H), 6.93 – 6.89 (m, 1H), 3.75 (s, 2H), 2.81- 2.73 (m, 4H), 2.73 – 2.65 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.46, 126.48, 126.08, 125.12, 57.89, 54.61 (2C), 28.02 (2C). **HRMS** (ES+) *m/z* calcd for $C_9H_{13}NS_2$ ($[M+H]^+$) 200.0562, found 200.0561.

4-(naphthalen-1-ylmethyl)thiomorpholine (**3az**)



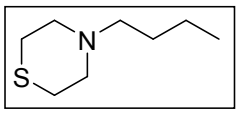
Yield: 155.5 mg, 64%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.3 Hz, 1H), 7.91 – 7.86 (m, 1H), 7.81 (dd, *J* = 7.0, 2.1 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.47 – 7.40 (m, 2H), 3.94 (s, 2H), 2.85 – 2.78 (m, 4H), 2.71 – 2.64 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 133.87, 133.79, 132.52, 128.39, 128.01, 127.44, 125.71, 125.62, 125.05, 124.73, 61.84, 55.10 (2C), 28.09 (2C). **HRMS** (ES+) *m/z* calcd for $C_{15}H_{17}NS$ ($[M+H]^+$) 244.1154, found 244.1158.

4-propylthiomorpholine (**3ba**)



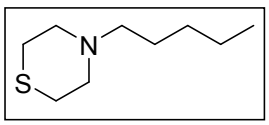
Yield: 126.2 mg, 87%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.76 – 2.62 (m, 8H), 2.35 – 2.27 (m, 2H), 1.54 – 1.43 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 61.35, 54.99 (2C), 27.97 (2C), 19.58, 11.87. **HRMS** (ES+) *m/z* calcd for $C_7H_{15}NS$ ($[M+H]^+$) 146.0998, found 146.1000.

4-butylthiomorpholine (**3bb**)



Yield: 120.8 mg, 76%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.76 – 2.63 (m, 8H), 2.39 – 2.30 (m, 2H), 1.51 – 1.40 (m, 2H), 1.35 – 1.22 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 59.17, 55.03 (2C), 28.63, 27.98 (2C), 20.71, 13.99. **HRMS** (ES+) *m/z* calcd for $C_8H_{17}NS$ ($[M+H]^+$) 160.1154, found 160.1158.

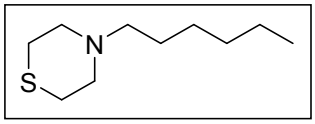
4-pentylthiomorpholine (**3bc**)



Yield: 145.3 mg, 84%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.74 – 2.62 (m, 8H), 2.37 - 2.29 (m, 2H), 1.52 – 1.40 (m, 2H), 1.37 – 1.21 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 59.47,

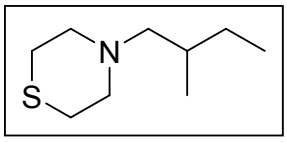
55.03 (2C), 29.74, 27.97 (2C), 26.16, 22.57, 14.01. **HRMS** (ES+) *m/z* calcd for $C_9H_{19}NS$ ($[M+H]^+$) 174.1311, found 174.1309.

4-hexylthiomorpholine (**3bd**)



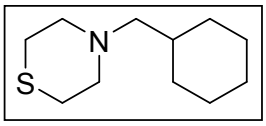
Yield: 166.4 mg, 89%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.76 – 2.63 (m, 8H), 2.38 – 2.31 (m, 2H), 1.51 – 1.41 (m, 2H), 1.35 – 1.23 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 59.52, 55.06 (2C), 31.76, 28.00 (2C), 27.24, 26.47, 22.59, 14.02. **HRMS** (ES+) *m/z* calcd for $C_{10}H_{21}NS$ ($[M+H]^+$) 188.1467, found 188.1464.

4-(2-methylbutyl)thiomorpholine (**3be**)



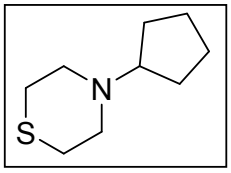
Yield: 141.9 mg, 82%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.76 – 2.54 (m, 8H), 2.19 (dd, *J* = 12.3, 6.7 Hz, 1H), 2.06 (dd, *J* = 12.3, 7.8 Hz, 1H), 1.56 (dt, *J* = 14.2, 7.1 Hz, 1H), 1.50 – 1.34 (m, 1H), 1.14 – 1.00 (m, 1H), 0.93 – 0.81 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 65.97, 55.58 (2C), 31.87, 28.00, 27.67 (2C), 17.77, 11.32. **HRMS** (ES+) *m/z* calcd for $C_9H_{19}NS$ ($[M+H]^+$) 174.1311, found 174.1310.

4-(cyclohexylmethyl)thiomorpholine (**3bf**)



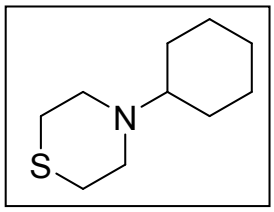
Yield: 173.1 mg, 87%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.70 – 2.59 (m, 8H), 2.12 (d, *J* = 7.1 Hz, 2H), 1.78 – 1.61 (m, 5H), 1.52 – 1.41 (m, 1H), 1.27 – 1.09 (m, 3H), 0.91 – 0.77 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 66.28, 55.61 (2C), 35.03, 31.85 (2C), 27.99 (2C), 26.79, 26.13 (2C). **HRMS** (ES+) *m/z* calcd for $C_{11}H_{21}NS$ ($[M+H]^+$) 200.1467, found 200.1474.

4-cyclopentylthiomorpholine (**3bg**)



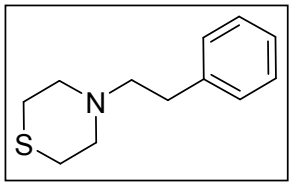
Yield: 152.2 mg, 89%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.81 – 2.73 (m, 4H), 2.73 – 2.67 (m, 4H), 2.64 (td, *J* = 8.9, 4.5 Hz, 1H), 1.89 – 1.78 (m, 2H), 1.72 – 1.61 (m, 2H), 1.59 – 1.48 (m, 2H), 1.44 – 1.34 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 67.54, 53.75 (2C), 29.83 (2C), 27.91 (2C), 24.10 (2C). **HRMS** (ES+) *m/z* calcd for $C_9H_{17}NS$ ($[M+H]^+$) 172.1154, found 172.1162.

4-cyclohexylthiomorpholine (**3bh**)



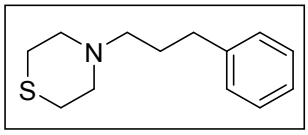
Yield: 112.9 mg, 61%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.90 – 2.79 (m, 4H), 2.73 – 2.61 (m, 4H), 2.39 – 2.25 (m, 1H), 1.79 (d, *J* = 8.5 Hz, 4H), 1.67 – 1.58 (m, 1H), 1.32 – 1.16 (m, 4H), 1.08 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 65.44, 51.39 (2C), 28.61 (2C), 28.54 (2C), 26.39, 26.19 (2C). **HRMS** (ES+) *m/z* calcd for $C_{10}H_{19}NS$ ($[M+H]^+$) 186.1311, found 186.1317.

4-phenethylthiomorpholine (**3bi**)



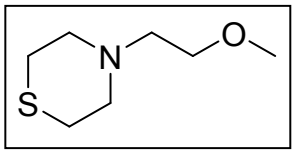
Yield: 124.2 mg, 60%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 2.87 – 2.76 (m, 6H), 2.76 – 2.70 (m, 4H), 2.69 – 2.62 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.21, 128.69 (2C), 128.40 (2C), 126.07, 61.19, 54.92 (2C), 33.10, 27.97 (2C). **HRMS** (ES+) *m/z* calcd for $C_{12}H_{17}NS$ ($[M+H]^+$) 208.1154, found 208.1156.

4-(3-phenylpropyl)thiomorpholine (**3bj**)



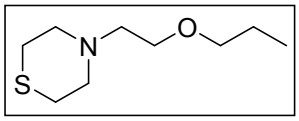
Yield: 132.6 mg, 60%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 2.76 – 2.67 (m, 8H), 2.67 – 2.61 (m, 2H), 2.46 – 2.38 (m, 2H), 1.87 – 1.78 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.00, 128.35 (2C), 128.29 (2C), 125.76, 58.55, 54.95 (2C), 33.56, 28.12, 27.93 (2C). **HRMS** (ES+) *m/z* calcd for $C_{13}H_{19}NS$ ($[M+H]^+$) 222.1311, found 222.1317.

4-(2-methoxyethyl)thiomorpholine (**3bk**)



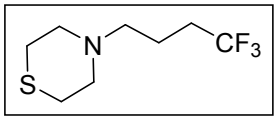
Yield: 90.2 mg, 56%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.50 (t, *J* = 5.6 Hz, 2H), 3.34 (s, 3H), 2.80 – 2.74 (m, 4H), 2.72 – 2.67 (m, 4H), 2.61 (t, *J* = 5.6 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 69.93, 58.88, 58.56, 55.27 (2C), 27.71 (2C). **HRMS** (ES+) *m/z* calcd for $C_7H_{15}NOS$ ($[M+H]^+$) 162.0947, found 162.0948.

4-(2-propoxyethyl)thiomorpholine (**3bl**)



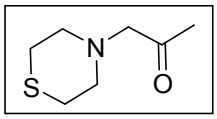
Yield: 132.3 mg, 70%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.57 – 3.51 (m, 2H), 3.37 (t, *J* = 6.7 Hz, 2H), 2.83 – 2.73 (m, 4H), 2.71 – 2.64 (m, 4H), 2.61 (t, *J* = 5.9 Hz, 2H), 1.63 – 1.53 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 72.88, 68.20, 58.52, 55.26 (2C), 27.81 (2C), 22.77, 10.53. **HRMS** (ES+) *m/z* calcd for $C_9H_{19}NOS$ ([M+H]$^+$) 190.1260, found 190.1266.

4-(4,4,4-trifluorobutyl)thiomorpholine (**3bm**)



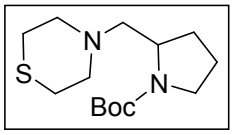
Yield: 164.0 mg, 77%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.71 – 2.56 (m, 8H), 2.36 (t, *J* = 7.1 Hz, 2H), 2.15 – 2.01 (m, 2H), 1.68 (dt, *J* = 14.8, 7.4 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 127.24 (q, $^1J_{C\text{-}F}$ = 276.7 Hz, 1C), 57.33, 54.80 (2C), 31.38 (q, $^2J_{C\text{-}F}$ = 28.7 Hz, 1C), 27.88 (2C), 19.04 (q, $^3J_{C\text{-}F}$ = 2.6 Hz, 1C). **HRMS** (ES+) *m/z* calcd for $C_8H_{14}F_3NS$ ([M+H]$^+$) 214.0872, found 214.0878.

1-thiomorpholinopropan-2-one (**3bn**)



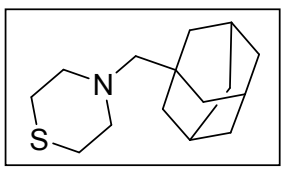
Yield:116.1 mg, 73%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.18 (s, 2H), 2.76 – 2.67 (m, 8H), 2.13 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 206.66, 68.78, 55.07 (2C), 27.73 (2C), 27.62. **HRMS** (ES+) *m/z* calcd for $C_7H_{13}NOS$ ([M+H]$^+$) 160.0791, found 160.0790.

tert-butyl 2-(thiomorpholinomethyl)pyrrolidine-1-carboxylate (**3bo**)



Yield: 143.0 mg, 50%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.98 – 3.68 (m, 1H), 3.39 – 3.17 (m, 2H), 2.92 – 2.80 (m, 2H), 2.72 – 2.46 (m, 7H), 2.11 (dd, *J* = 12.2, 10.1 Hz, 1H), 1.94 – 1.75 (m, 4H), 1.45 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.38, 79.23, 61.75, 55.79, 55.04 (2C), 46.16, 29.68, 28.52 (3C), 27.94 (2C), 22.58. **HRMS** (ES+) *m/z* calcd for $C_{14}H_{26}N_2O_2S$ ([M+H]$^+$) 287.1788, found 287.1795.

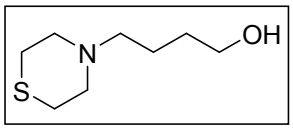
4-(adamantan-1-ylmethyl)thiomorpholine (**3bp**)



Yield: 130.5 mg, 52%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.78 – 2.70 (m, 4H), 2.67 – 2.57 (m, 4H), 1.94 (s, 5H), 1.72 (dd, *J* = 15.6, 7.4 Hz, 4H), 1.62 (d, *J* = 11.3 Hz, 3H), 1.45 (d, *J* = 2.3 Hz, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 71.73, 57.64 (2C), 40.78 (3C), 37.26 (3C), 35.15, 28.46 (3C), 28.26 (2C). **HRMS**

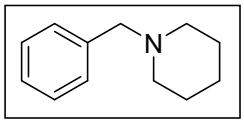
(ES+) *m/z* calcd for $C_{15}H_{25}NS$ ([M+H]$^+$) 252.1780, found 252.1788.

4-thiomorpholinobutan-1-ol (**3bq**)



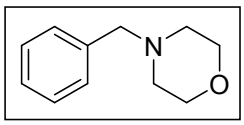
Yield: 124.3 mg, 71%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.59 – 3.49 (m, 2H), 2.79 – 2.62 (m, 8H), 2.43 - 2.32 (m, 2H), 1.67 – 1.58 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 62.48, 59.23, 54.96 (2C), 32.26, 27.48 (2C), 24.88. **HRMS** (ES+) *m/z* calcd for $C_8H_{17}NOS$ ([M+H]$^+$) 176.1104, found 176.1110.

1-benzylpiperidine (**3ca**)



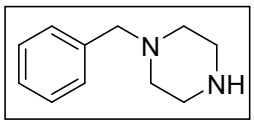
Yield: 171.5 mg, 98%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 4H), 7.29 – 7.24 (m, 1H), 3.50 (s, 2H), 2.40 (s, 4H), 1.64 – 1.57 (m, 4H), 1.51 – 1.41 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.65, 129.23 (2C), 128.09 (2C), 126.82, 63.91, 54.51 (2C), 26.00 (2C), 24.41. **HRMS** (ES+) *m/z* calcd for $C_{12}H_{18}N$ ([M+H]$^+$) 176.1434, found 176.1433.

4-benzylmorpholine (**3cb**)



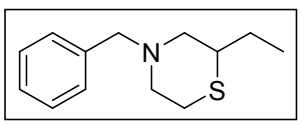
Yield: 169.9 mg, 96%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.30 – 7.25 (m, 1H), 3.76 – 3.70 (m, 4H), 3.52 (s, 2H), 2.47 (t, *J* = 4.2 Hz, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.74, 129.22 (2C), 128.26 (2C), 127.16, 67.02 (2C), 63.48, 53.63 (2C). **HRMS** (ES+) *m/z* calcd for $C_{11}H_{16}NO$ ([M+H]$^+$) 178.1226, found 176.1231.

1-benzylpiperazine (**3cc**)



Yield: 112.6 mg, 64%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 4H), 7.28 – 7.23 (m, 1H), 3.49 (s, 2H), 2.88 (t, *J* = 4.9 Hz, 4H), 2.42 (s, 4H), 2.22 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.01, 129.22 (2C), 128.18 (2C), 127.01, 63.67, 54.40 (2C), 45.99 (2C). **HRMS** (ES+) *m/z* calcd for $C_{11}H_{17}N_2$ ([M+H]$^+$) 177.1386, found 177.1394.

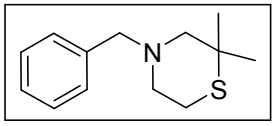
4-benzyl-2-ethylthiomorpholine (**3cd**)



Yield: 137.0 mg, 62%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.20 (m, 5H), 3.55 (q, *J* = 13.3 Hz, 2H), 3.08 – 2.94 (m, 2H), 2.89 – 2.80 (m, 2H), 2.64 – 2.53 (m, 1H), 2.42 – 2.33 (m, 1H), 2.18 (dd, *J* = 11.6,

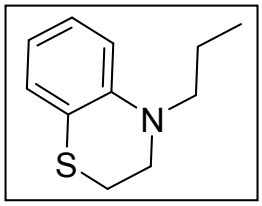
9.4 Hz, 1H), 1.64 – 1.41 (m, 2H), 0.99 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.19, 128.89 (2C), 128.18 (2C), 126.99, 63.44, 60.98, 54.61, 42.75, 27.68, 26.54, 11.53. **HRMS** (ES+) *m/z* calcd for $C_{13}H_{19}NS$ ($[M+H]^+$) 222.1311, found 222.1319.

4-benzyl-2,2-dimethylthiomorpholine (**3ce**)



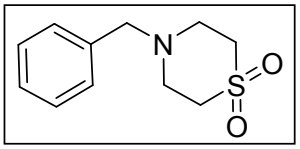
Yield: 150.3 mg, 68%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.32 (m, 5H), 3.55 (s, 2H), 2.84 – 2.65 (m, 4H), 2.44 (s, 2H), 1.37 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.75, 128.61 (2C), 128.16 (2C), 126.91, 67.42, 63.35, 54.83, 39.91, 27.89 (2C), 26.20. **HRMS** (ES+) *m/z* calcd for $C_{13}H_{19}NS$ ($[M+H]^+$) 222.1311, found 222.1319.

4-propyl-3,4-dihydro-2H-benzo[b][1,4]thiazine (**3cf**)



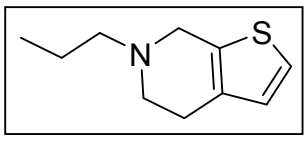
Yield: 111.9 mg, 58%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.09 (d, *J* = 7.6 Hz, 1H), 7.07 – 7.00 (m, 1H), 6.72 (d, *J* = 8.3 Hz, 1H), 6.65 (t, *J* = 7.4 Hz, 1H), 3.70 – 3.61 (m, 2H), 3.33 – 3.25 (m, 2H), 3.11 – 3.03 (m, 2H), 1.71 (dd, *J* = 15.0, 7.5 Hz, 2H), 1.02 (td, *J* = 7.3, 1.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.21, 127.71, 125.73, 117.26, 116.70, 112.48, 54.25, 49.85, 25.55, 19.47, 11.38. **HRMS** (ES+) *m/z* calcd for $C_{11}H_{15}NS$ ($[M+H]^+$) 194.0998, found 194.0996.

4-benzylthiomorpholine 1,1-dioxide (**3cg**)



Yield: 220.5 mg, 98%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.20 (m, 5H), 3.65 (s, 2H), 3.13 – 3.03 (m, 4H), 3.00 – 2.93 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.18, 128.69 (2C), 128.46 (2C), 127.56, 61.32, 51.35 (2C), 50.44 (2C). **HRMS** (ES+) *m/z* calcd for $C_{11}H_{15}NO_2S$ ($[M+H]^+$) 226.0896, found 226.0903.

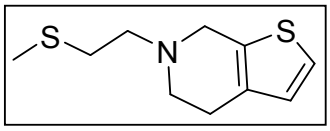
6-propyl-4,5,6,7-tetrahydrothieno[2,3-c]pyridine (**3ch**)



Yield: 128.5 mg, 71%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.08 (d, *J* = 5.1 Hz, 1H), 6.73 (d, *J* = 5.1 Hz, 1H), 3.57 (t, *J* = 1.6 Hz, 2H), 2.91 (t, *J* = 5.7 Hz, 2H), 2.80 (t, *J* = 5.7 Hz, 2H), 2.56 – 2.48 (m, 2H),

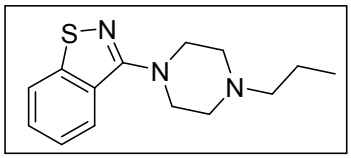
1.67 – 1.57 (m, 2H), 0.97 (dd, *J* = 8.8, 6.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 133.96, 133.43, 125.23, 122.54, 59.91, 53.14, 50.94, 25.48, 20.54, 11.95. **HRMS** (ES+) *m/z* calcd for $C_{10}H_{15}NS$ ($[M+H]^+$) 182.0998, found 182.0994.

6-(2-(methylthio)ethyl)-4,5,6,7-tetrahydrothieno[2,3-c]pyridine (**3ci**)



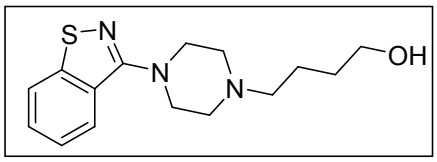
Yield: 153.4 mg, 72%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.08 (d, *J* = 5.1 Hz, 1H), 6.73 (d, *J* = 5.1 Hz, 1H), 3.62 (t, *J* = 1.5 Hz, 2H), 2.91 (t, *J* = 5.4 Hz, 2H), 2.87 – 2.78 (m, 4H), 2.75 – 2.70 (m, 2H), 2.16 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 133.47, 133.25, 125.12, 122.66, 57.11, 52.90, 50.77, 31.80, 25.30, 15.83. **HRMS** (ES+) *m/z* calcd for $C_{10}H_{15}NS_2$ ($[M+H]^+$) 214.0719, found 214.0725.

3-(4-propylpiperazin-1-yl)benzo[d]isothiazole (**3cj**)



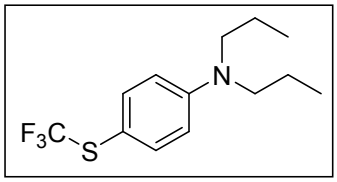
Yield: 201.0 mg, 77%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 59.3, 8.2 Hz, 2H), 7.37 (dt, *J* = 15.2, 7.3 Hz, 2H), 3.60 – 3.49 (m, 4H), 2.70 – 2.61 (m, 4H), 2.42 – 2.33 (m, 2H), 1.61 – 1.48 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.83, 152.64, 127.94, 127.35, 123.81, 123.71, 120.41, 60.63, 52.94 (2C), 49.96 (2C), 19.89, 11.87. **HRMS** (ES+) *m/z* calcd for $C_{14}H_{19}N_3S$ ($[M+H]^+$) 262.1372, found 262.1384.

4-(4-(benzo[d]isothiazol-3-yl)piperazin-1-yl)butan-1-ol (**3ck**)



Yield: 209.5 mg, 72%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.51 – 7.43 (m, 1H), 7.39 – 7.32 (m, 1H), 3.68 – 3.53 (m, 6H), 2.79 – 2.69 (m, 4H), 2.50 (t, *J* = 5.5 Hz, 2H), 1.77 – 1.66 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.53, 152.80, 127.93, 127.50, 123.87, 123.77, 120.56, 62.65, 58.64, 52.79 (2C), 49.56 (2C), 32.33, 24.98. **HRMS** (ES+) *m/z* calcd for $C_{15}H_{21}N_{3O}S$ ($[M+H]^+$) 292.1478, found 292.1475.

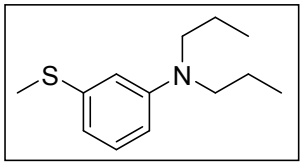
N,N-dipropyl-4-((trifluoromethyl)thio)aniline (**3cl**)



Yield: 257.6 mg, 93%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 6.66 – 6.59 (m, 2H), 3.34 – 3.22 (m, 4H), 1.72 – 1.60 (m, 4H), 0.97 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.98,

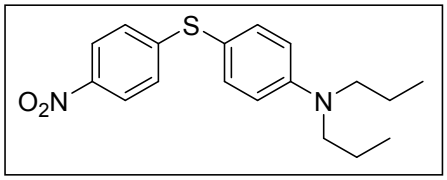
138.13 (2C), 129.88 (q, $^{1}J_{C\text{-}F}$ = 309.2 Hz, 1C), 111.90 (2C), 106.98, 52.79 (2C), 20.28 (2C), 11.34 (2C). **HRMS** (ES+) *m/z* calcd for $C_{13}H_{18}F_3NS$ ([M+H]$^+$) 278.1185, found 278.1197.

3-(methylthio)-N,N-dipropylaniline (**3cm**)



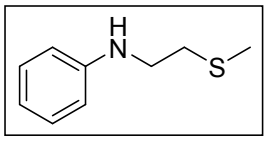
Yield: 198.5 mg, 89%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16 (t, *J* = 8.0 Hz, 1H), 6.59 (d, *J* = 7.0 Hz, 2H), 6.49 (dd, *J* = 9.0, 2.0 Hz, 1H), 3.34 – 3.22 (m, 4H), 2.52 (s, 3H), 1.66 (dd, *J* = 15.1, 7.5 Hz, 4H), 0.98 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.45, 138.88, 129.44, 113.49, 110.10, 109.08, 52.80 (2C), 20.38 (2C), 16.01, 11.39 (2C). **HRMS** (ES+) *m/z* calcd for $C_{13}H_{21}NS$ ([M+H]$^+$) 224.1467, found 224.1476.

4-((4-nitrophenyl)thio)-N,N-dipropylaniline (**3cn**)



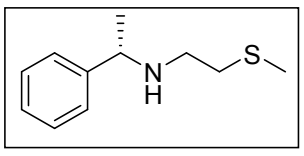
Yield: 181.5 mg, 55%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H), 7.39 – 7.31 (m, 2H), 7.15 – 7.08 (m, 2H), 6.72 – 6.66 (m, 2H), 3.34 – 3.27 (m, 4H), 1.73 – 1.61 (m, 4H), 0.98 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.86, 149.39, 144.66, 137.09 (2C), 125.03 (2C), 123.79 (2C), 112.61 (2C), 111.96, 52.79 (2C), 20.35 (2C), 11.40 (2C). **HRMS** (ES+) *m/z* calcd for $C_{18}H_{22}N_2O_2S$ ([M+H]$^+$) 331.1475, found 331.1483.

N-(2-(methylthio)ethyl)aniline (**4a**)



Yield: 83.5 mg, 50%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24 – 7.12 (m, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.62 (dd, *J* = 8.5, 0.8 Hz, 2H), 4.05 (s, 1H), 3.30 (t, *J* = 6.5 Hz, 2H), 2.73 (t, *J* = 6.5 Hz, 2H), 2.09 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.68, 129.19 (2C), 117.60, 112.97 (2C), 41.77, 33.48, 14.87. **HRMS** (ES+) *m/z* calcd for $C_9H_{13}NS$ ([M+H]$^+$) 168.0841, found 168.0844.

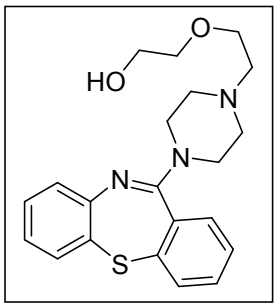
(*S*)-2-(methylthio)-N-(1-phenylethyl)ethan-1-amine (**4b**)



Yield: 194.3mg, 70%, ee > 99%. The enantiomeric excess was determined by HPLC on Daicel Chiralpak IA-H with hexane/i-PrOH (98:2) as the eluent, Flow: 1 mL/min; UV = 210 nm; t_{minor} =

23.555 min, t_{major} = 30.272 min. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.29 – 7.23 (m, 1H), 3.80 (q, *J* = 6.6 Hz, 1H), 2.77 – 2.57 (m, 4H), 2.04 (s, 3H), 1.72 (s, 1H), 1.39 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.55, 128.47 (2C), 126.95, 126.55 (2C), 57.99, 45.35, 34.58, 24.42, 15.07. **HRMS** (ES+) *m/z* calcd for $C_{11}H_{17}NS$ ($[M+H]^+$) 196.1154, found 196.1161.

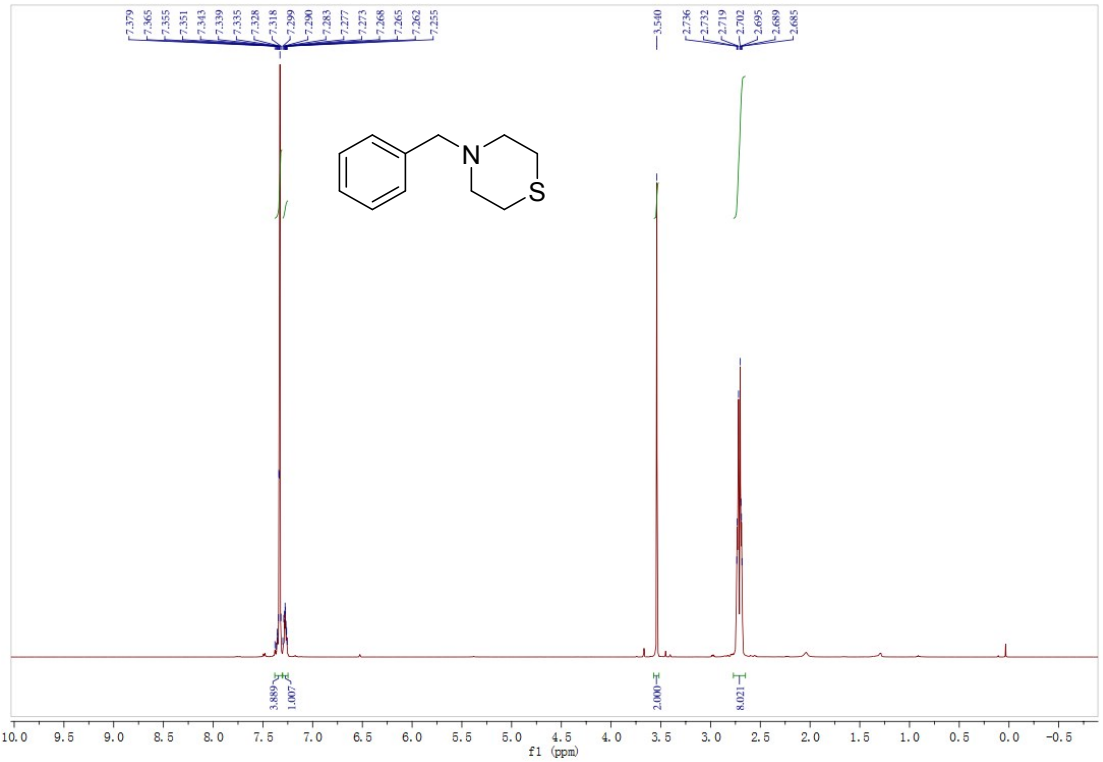
Quetiapine (**6**)

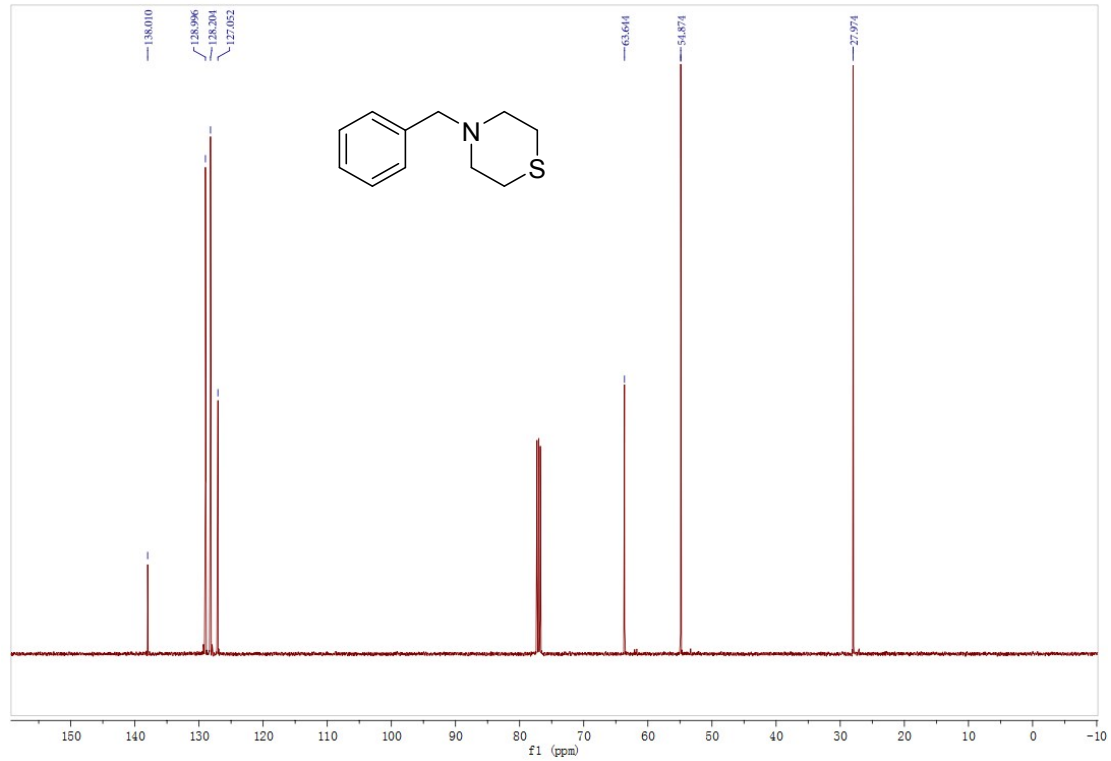


Yield: 268.1 mg, 70%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 1H), 7.39 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.37 – 3.28 (m, 3H), 7.18 (td, *J* = 8.0, 1.5 Hz, 1H), 7.08 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.89 (td, *J* = 7.6, 1.4 Hz, 1H), 3.78 – 3.74 (m, 2H), 3.73 – 3.69 (m, 2H), 3.69 – 3.65 (m, 3H), 3.64 – 3.58 (m, 5H), 2.71 – 2.62 (m, 3H), 2.61 – 2.51 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.60, 148.81, 139.89, 134.02, 132.15, 132.13, 130.79, 129.08, 128.93, 128.27, 127.94, 125.26, 122.83, 72.41, 72.33, 67.43, 61.85 (2C), 61.62, 57.93 (2C). **HRMS** (ES+) *m/z* calcd for $C_{21}H_{25}N_3O_2S$ ($[M+H]^+$) 384.1740, found 384.1745.

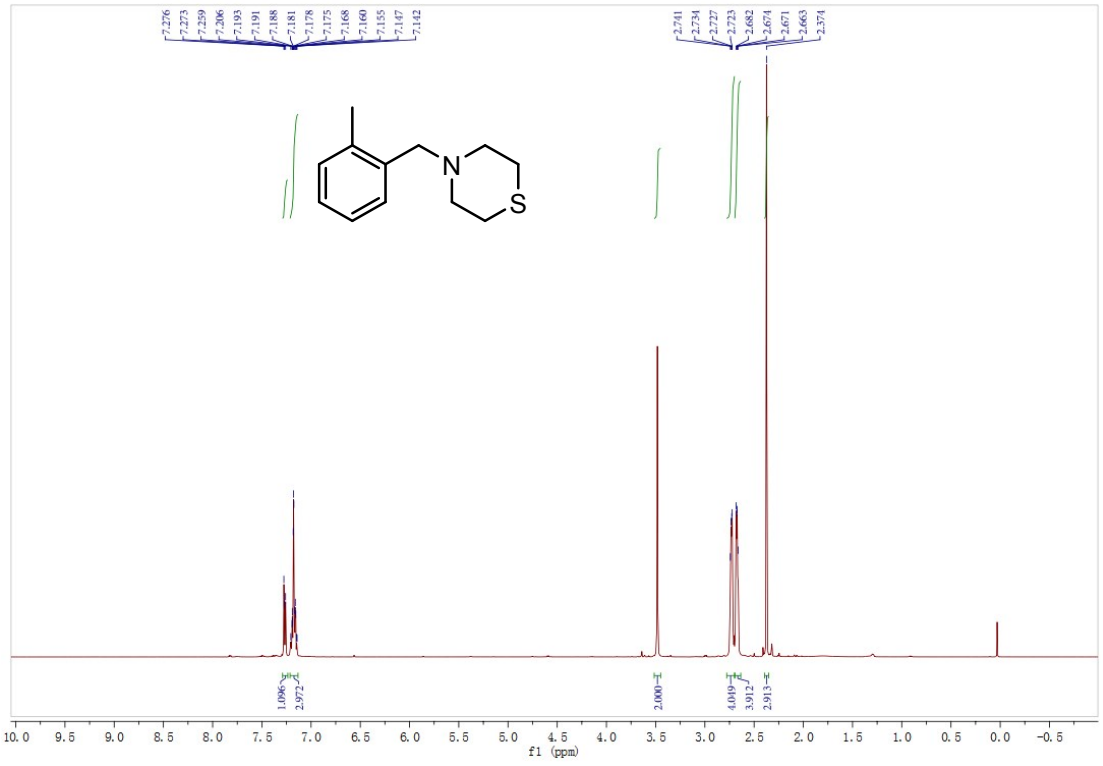
6. ^{1}H, ^{13}C NMR spectra

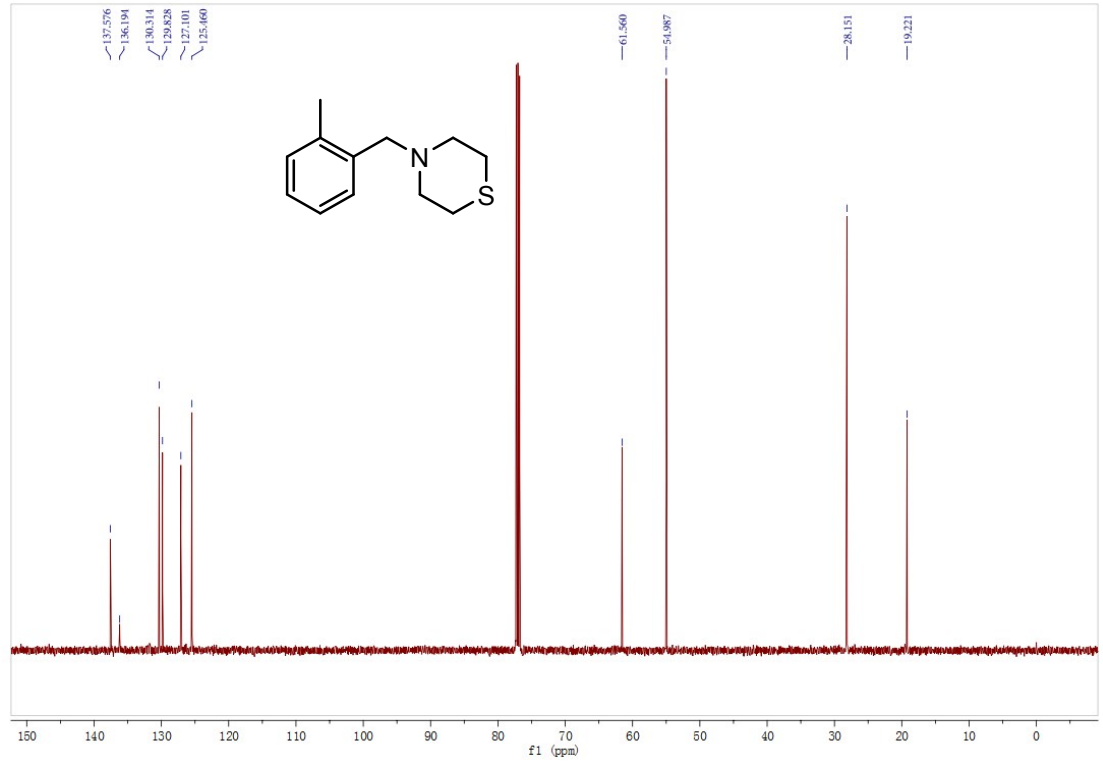
4-benzylthiomorpholine (**3aa**)



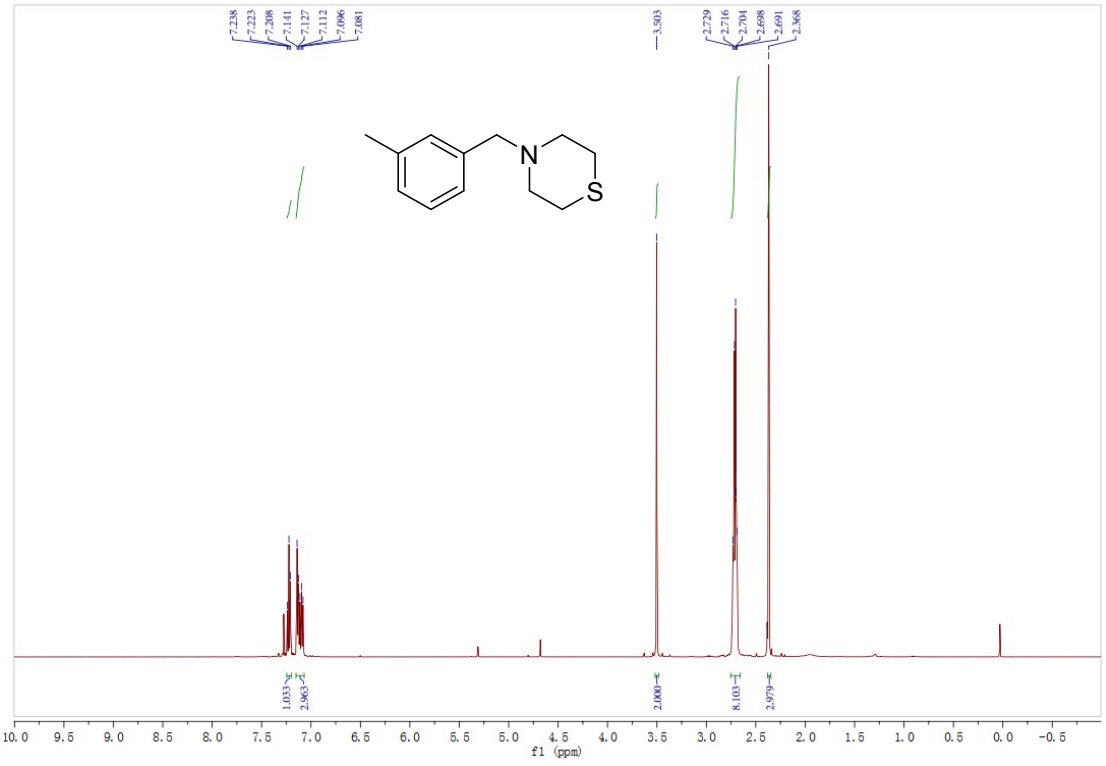


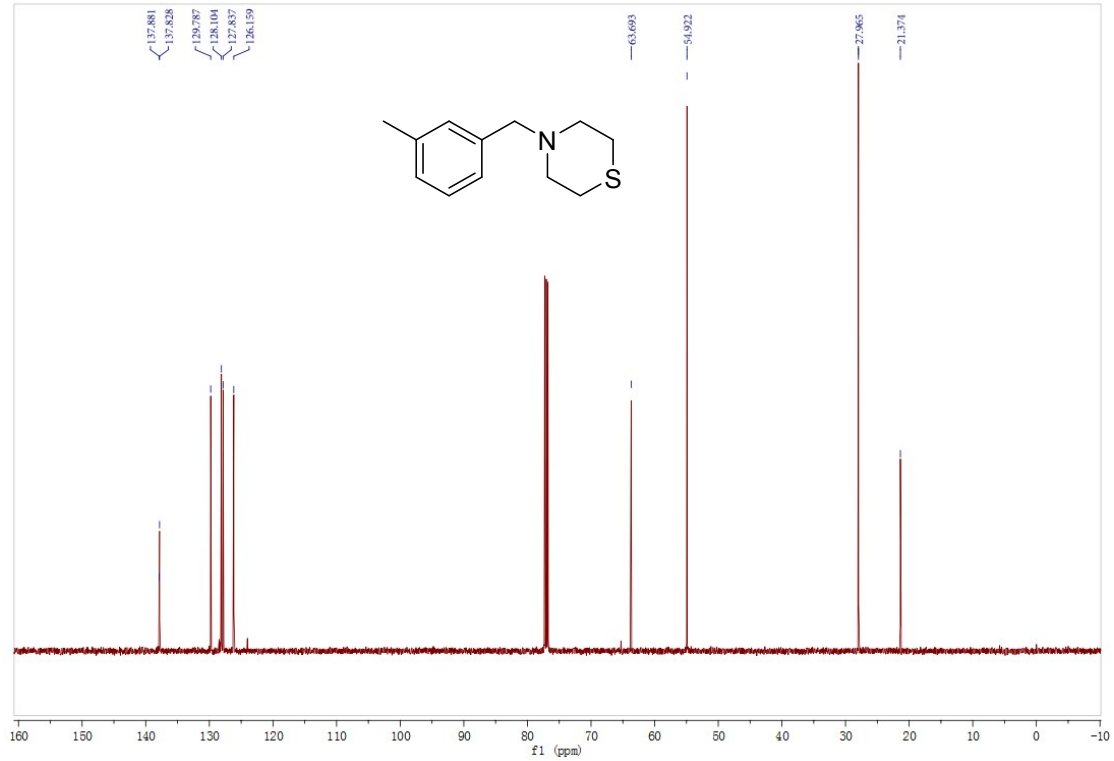
4-(2-methylbenzyl)thiomorpholine (**3ab**)



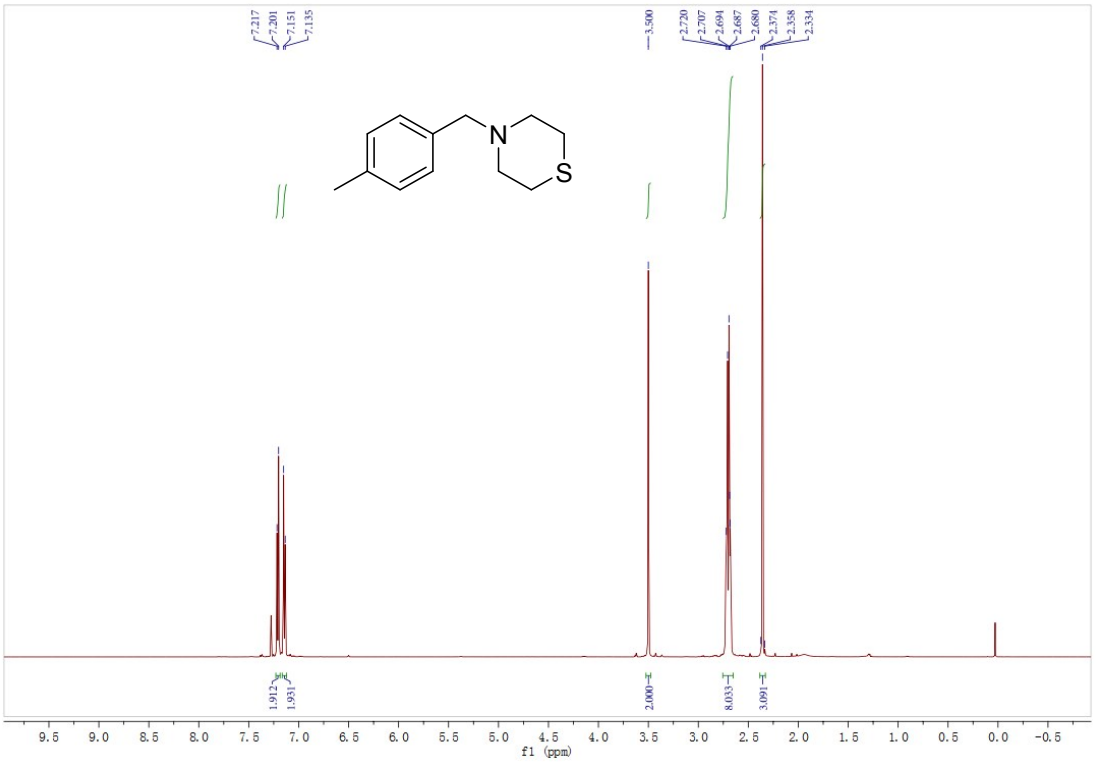


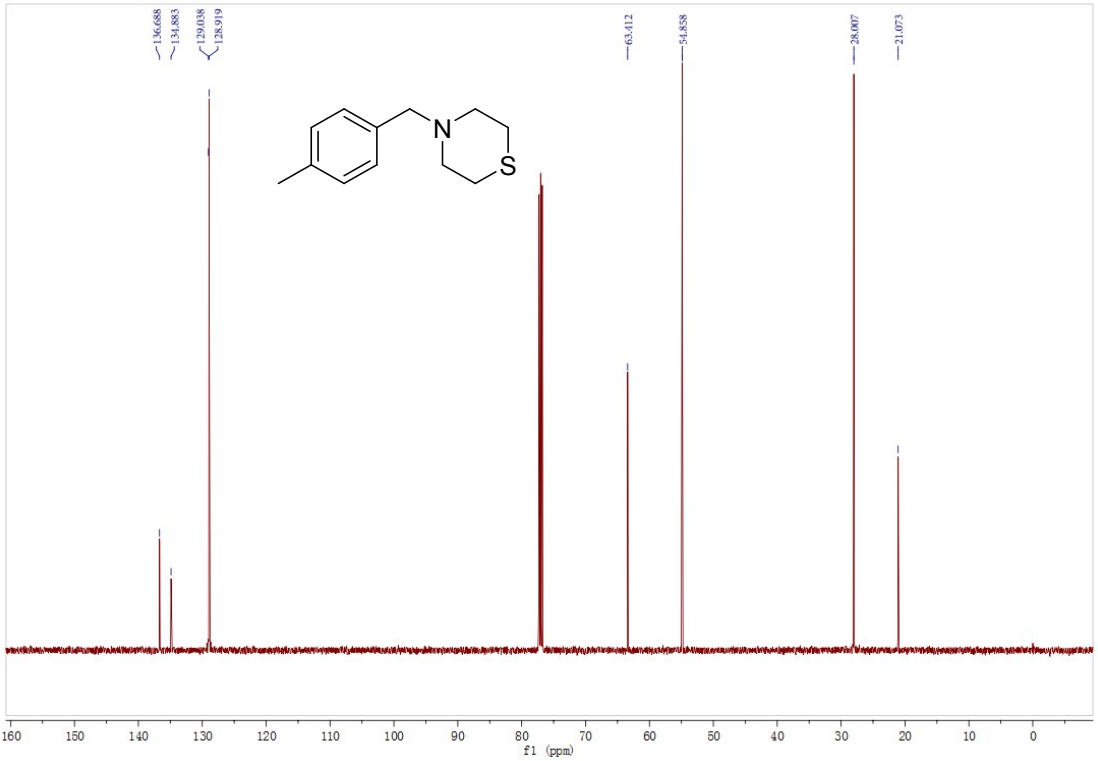
4-(3-methylbenzyl)thiomorpholine (**3ac**)



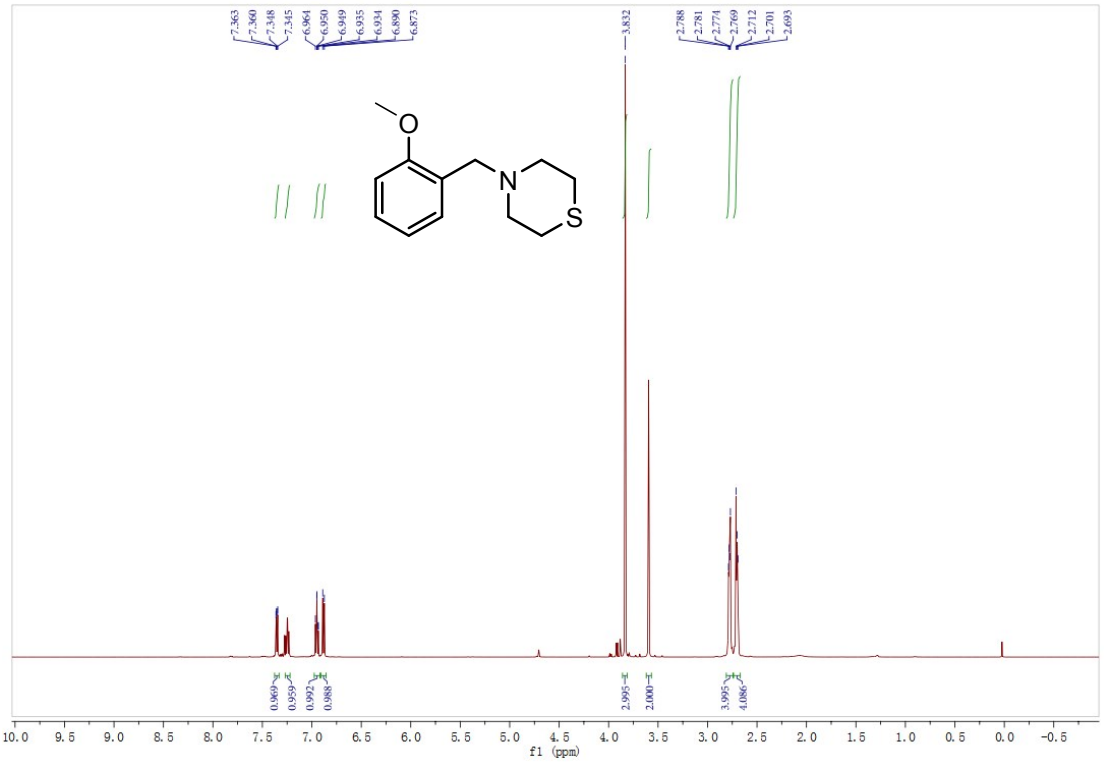


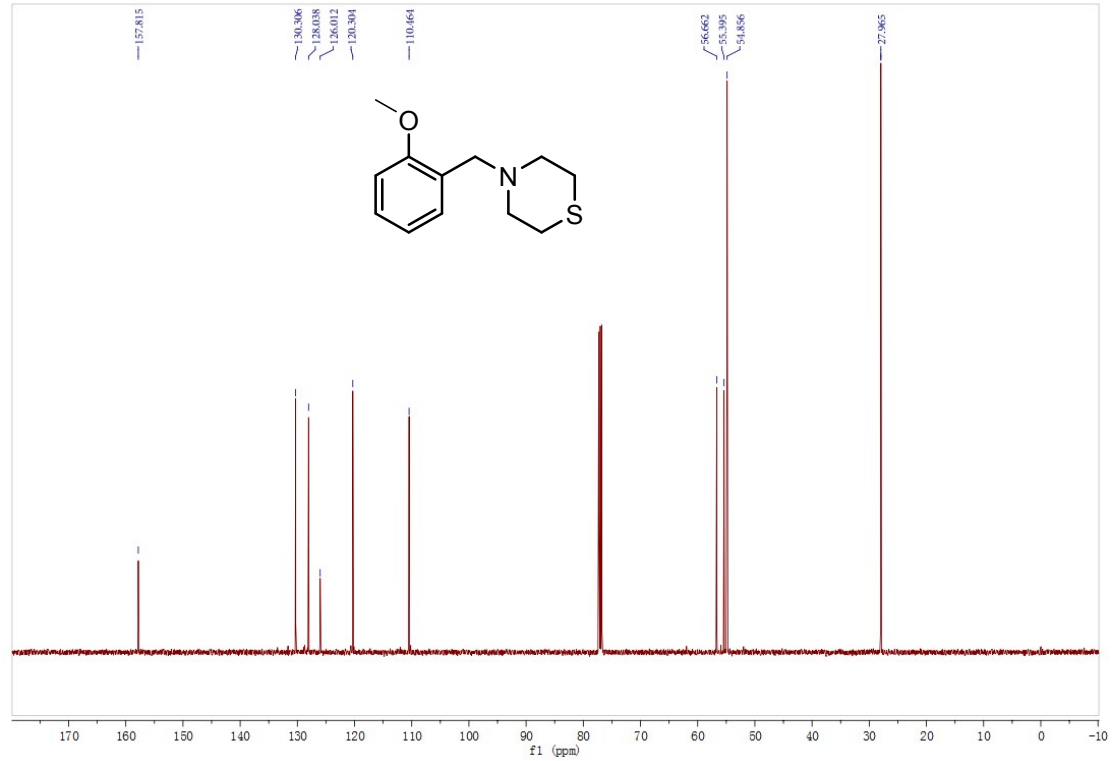
4-(4-methylbenzyl)thiomorpholine (**3ad**)



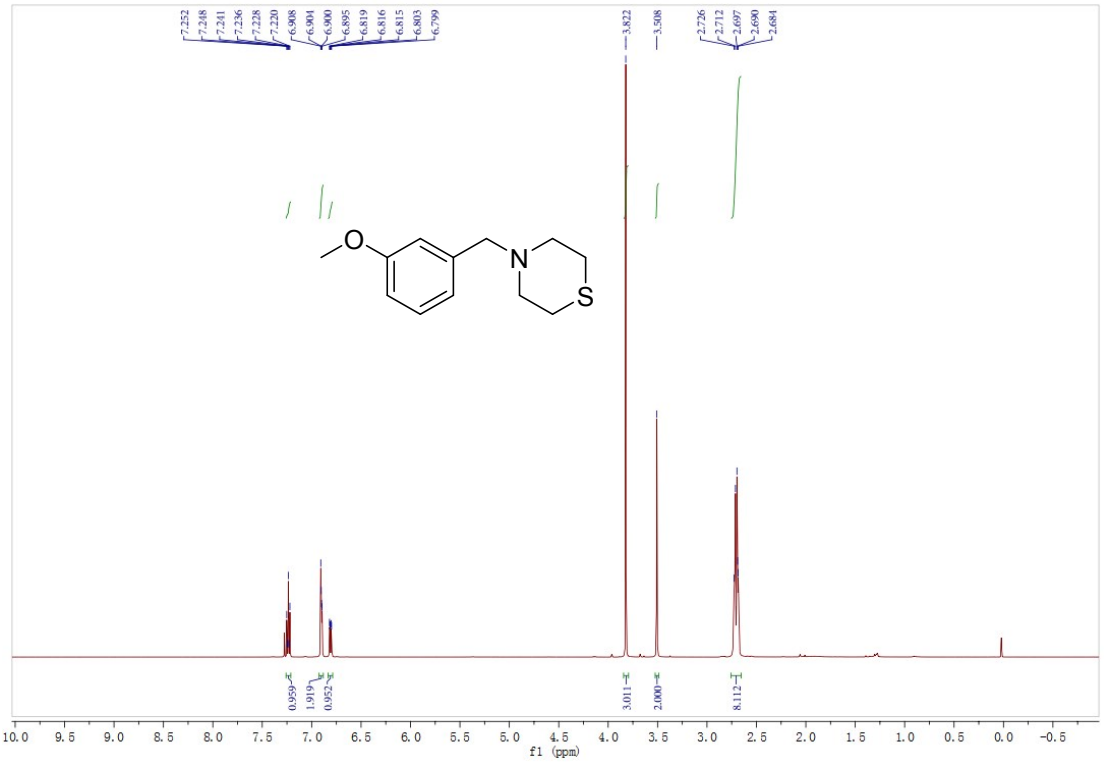


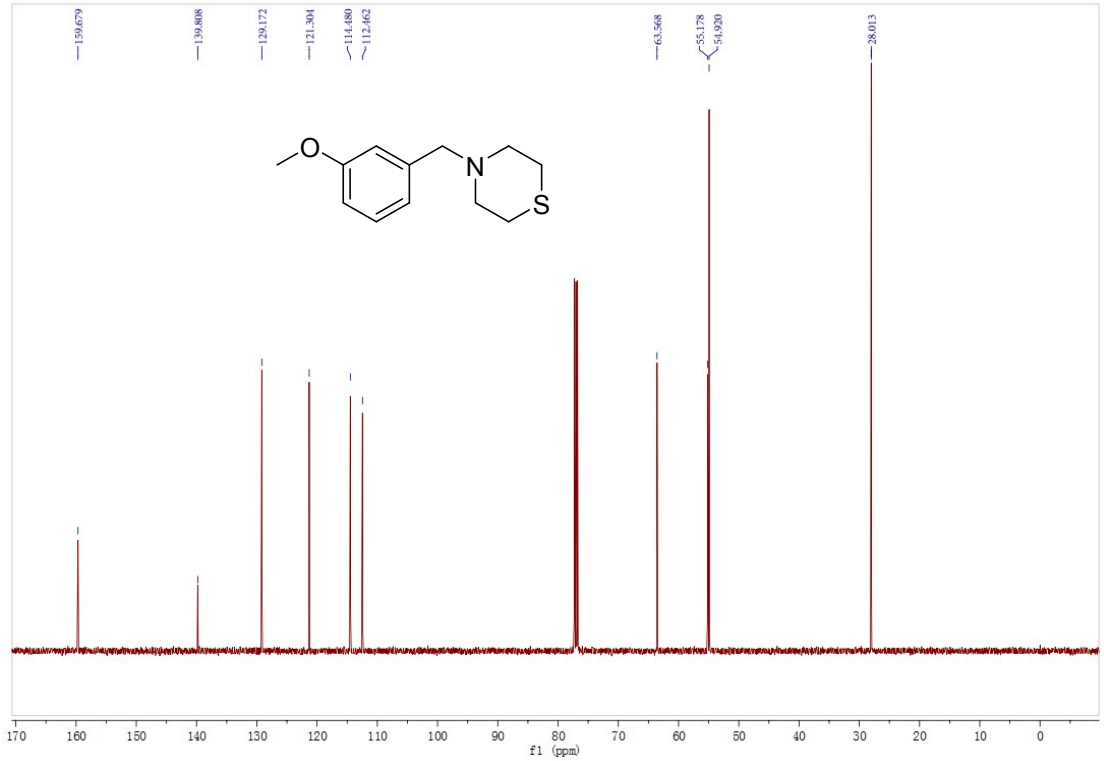
4-(2-methoxybenzyl)thiomorpholine (**3ae**)



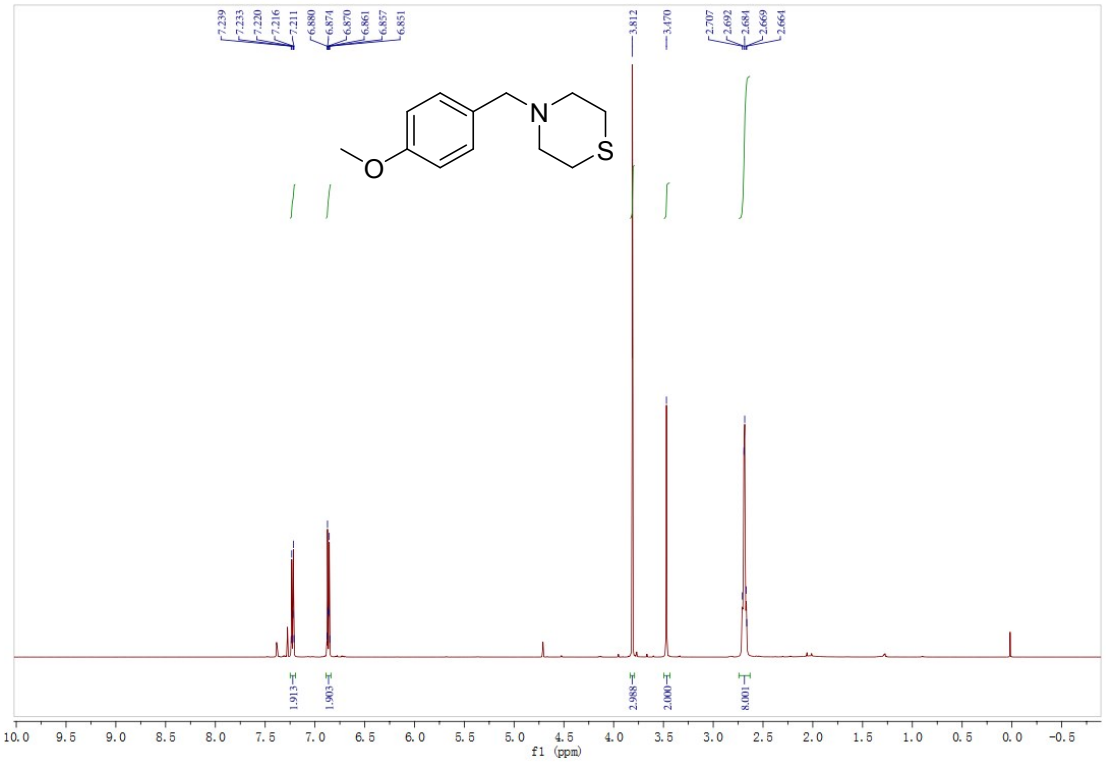


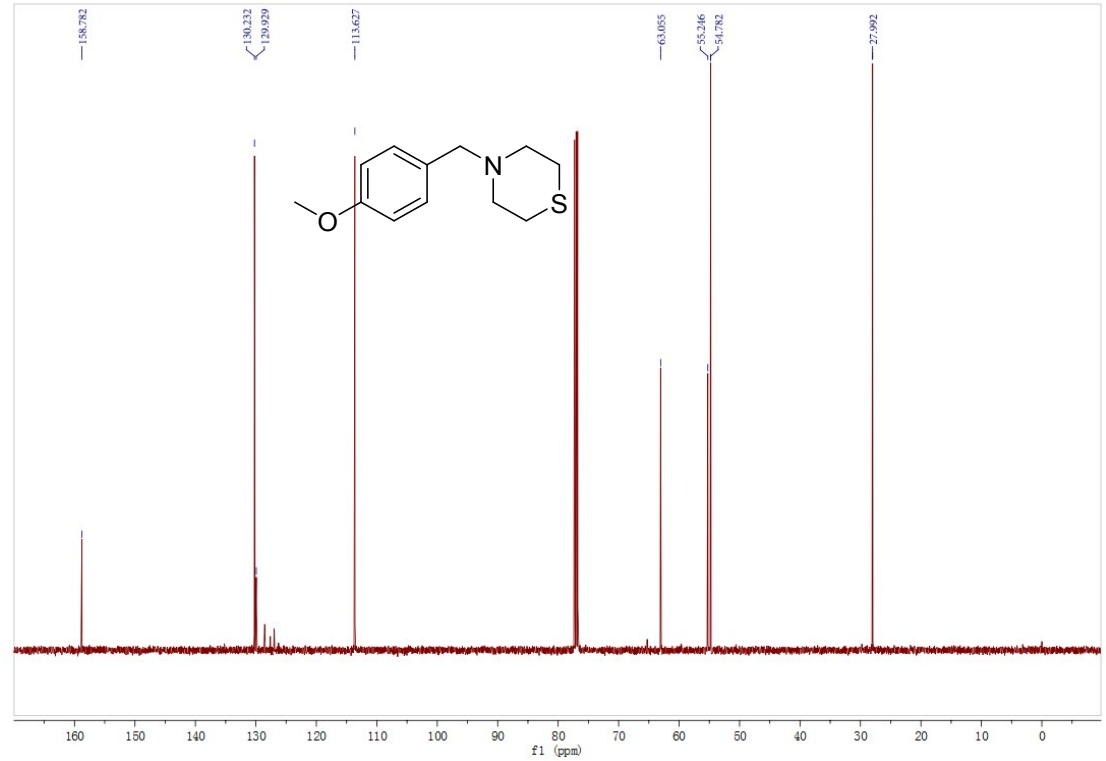
4-(3-methoxybenzyl)thiomorpholine (**3af**)



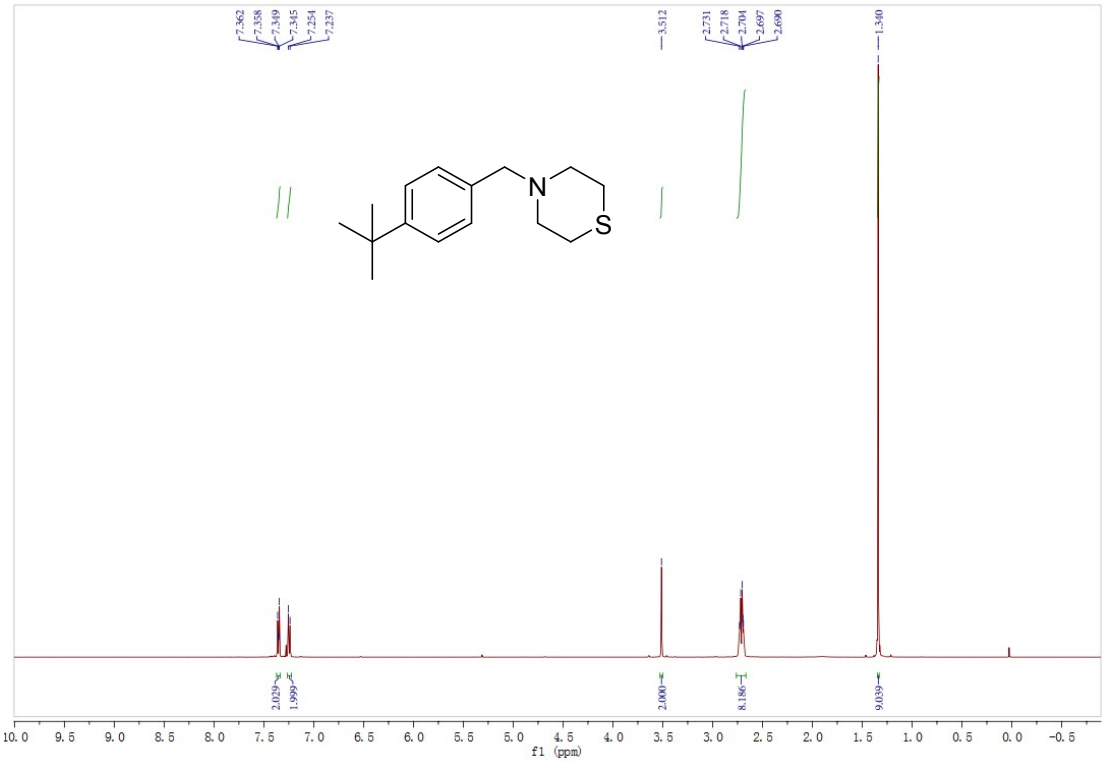


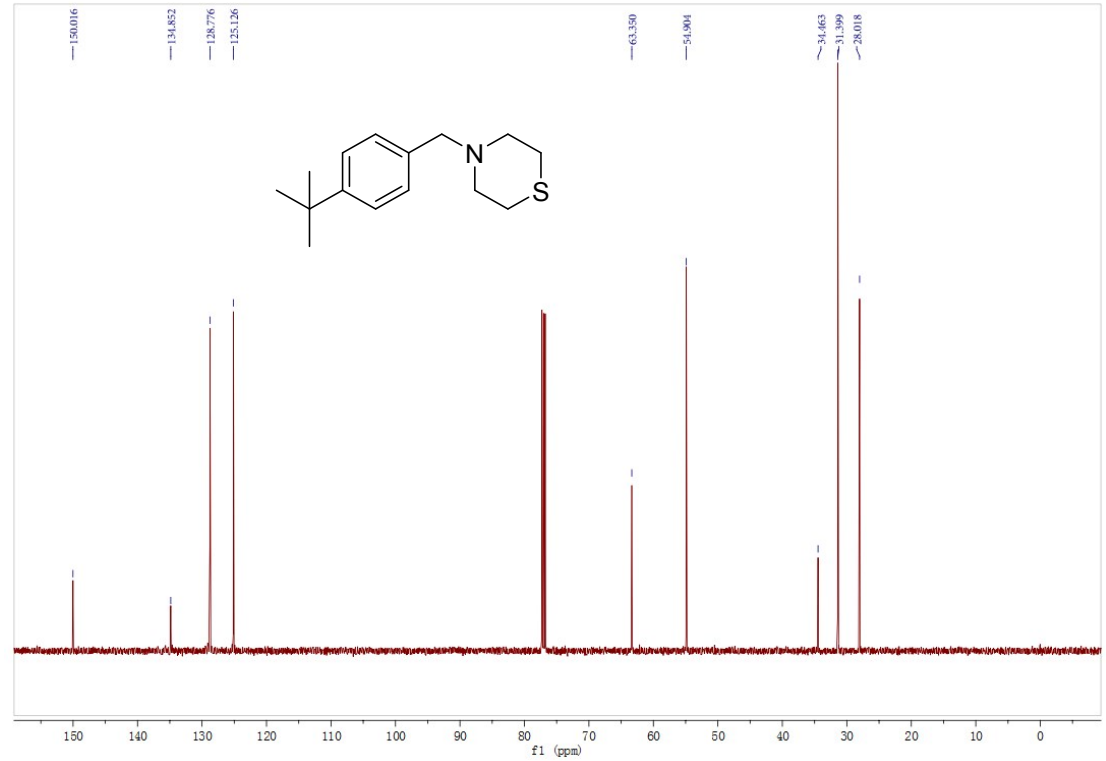
4-(4-methoxybenzyl)thiomorpholine (**3ag**)



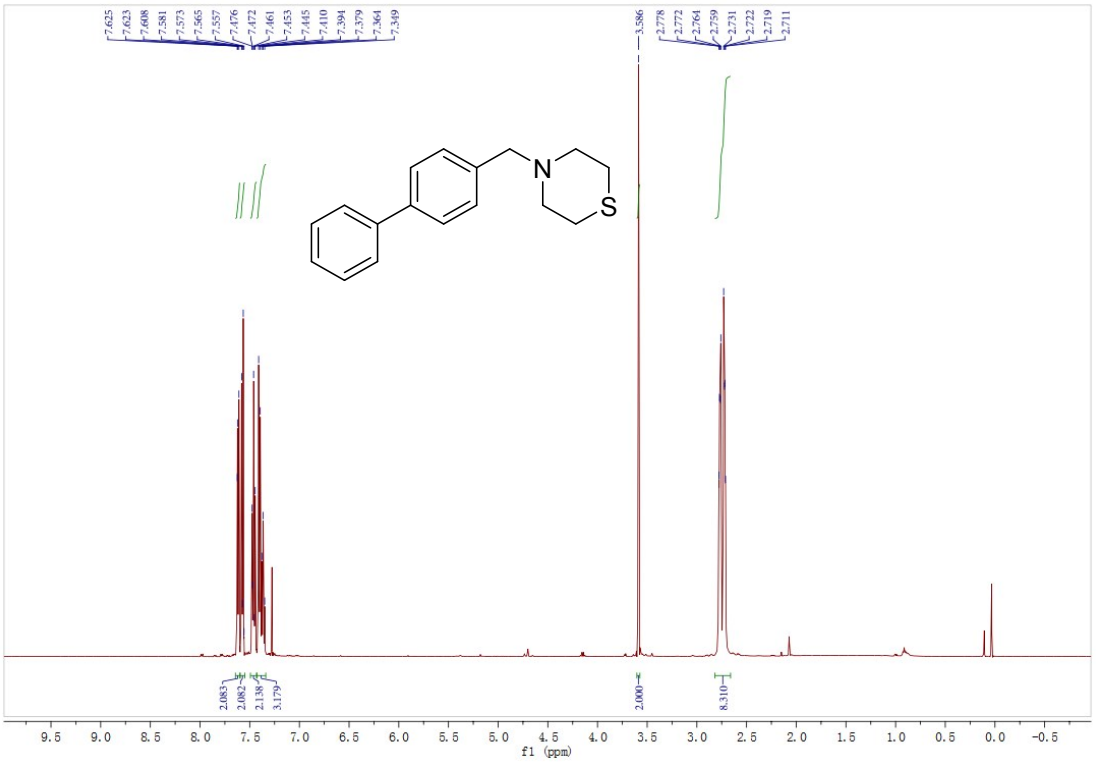


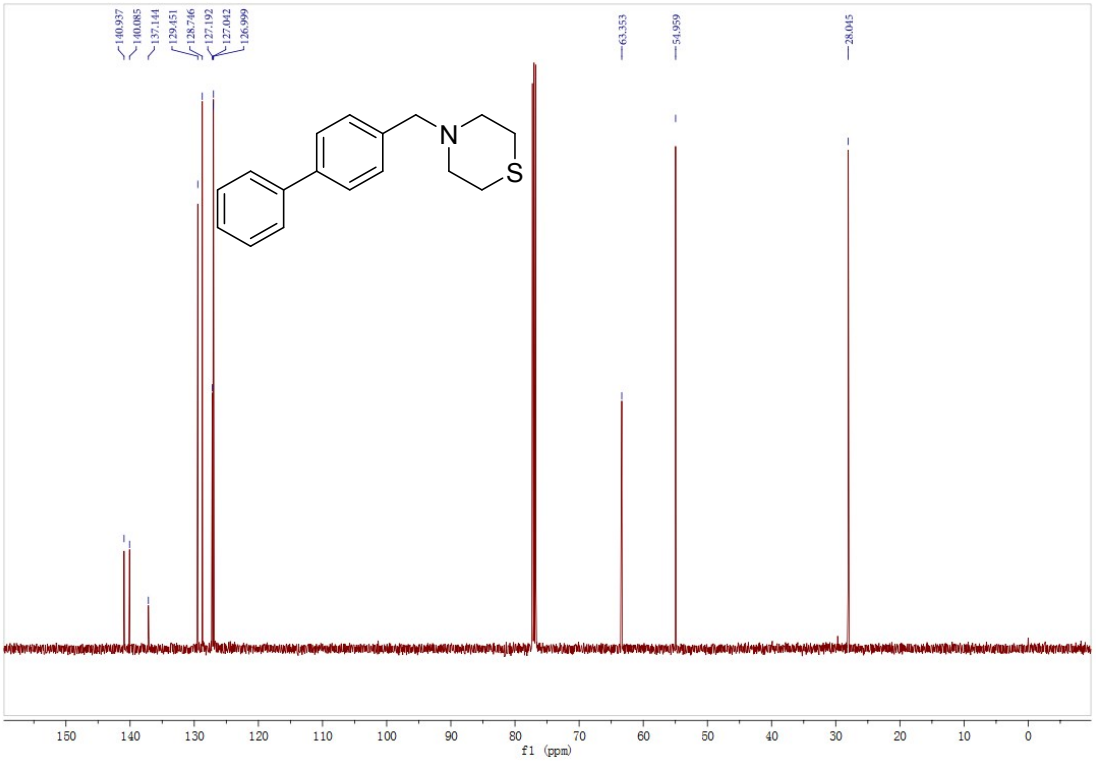
4-(4-(*tert*-butyl)benzyl)thiomorpholine (**3ah**)



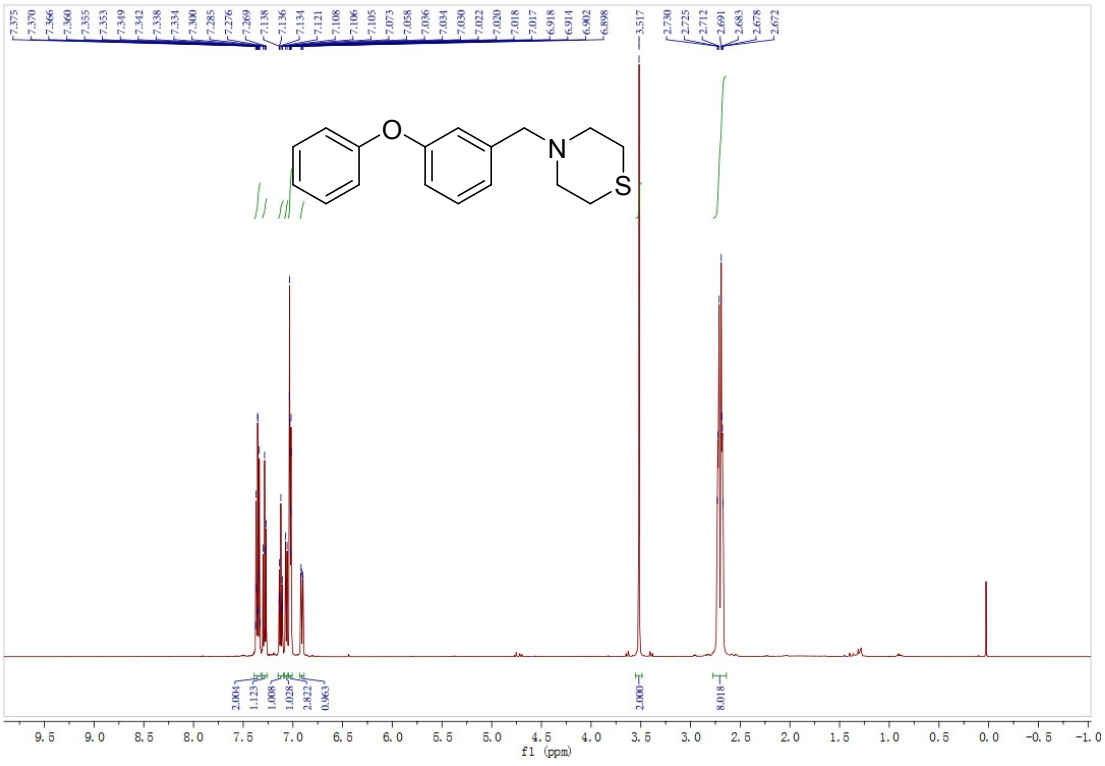


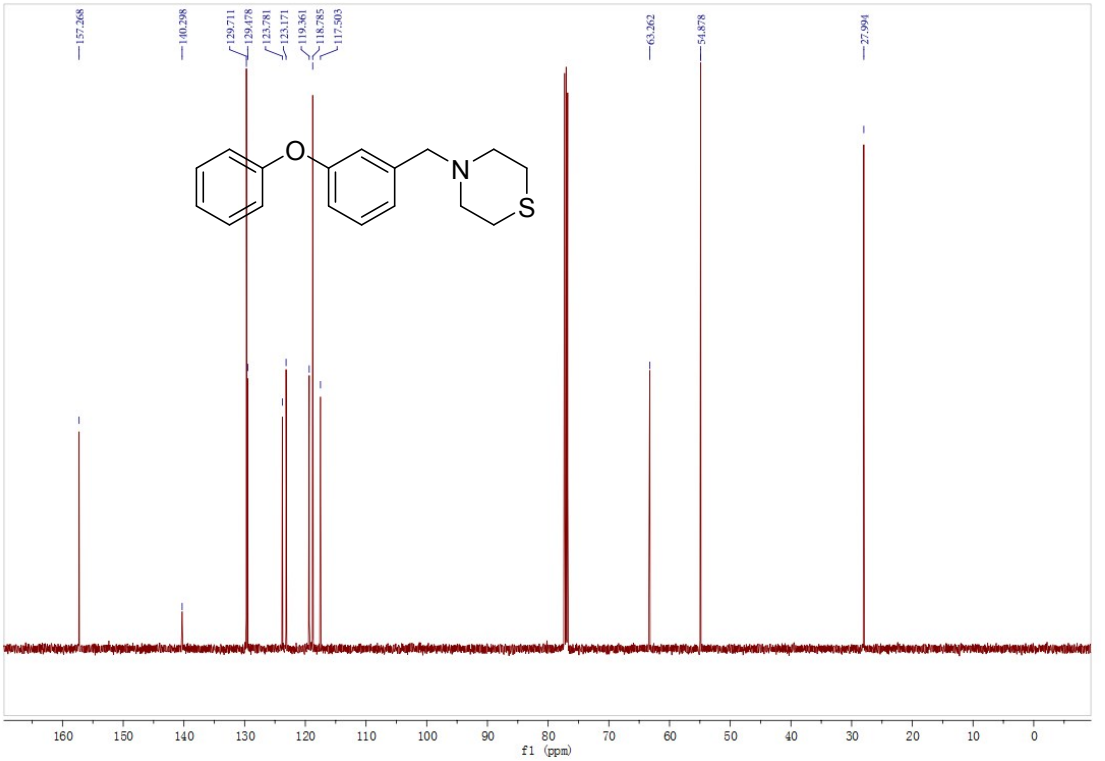
4-([1,1'-biphenyl]-4-ylmethyl)thiomorpholine (**3ai**)



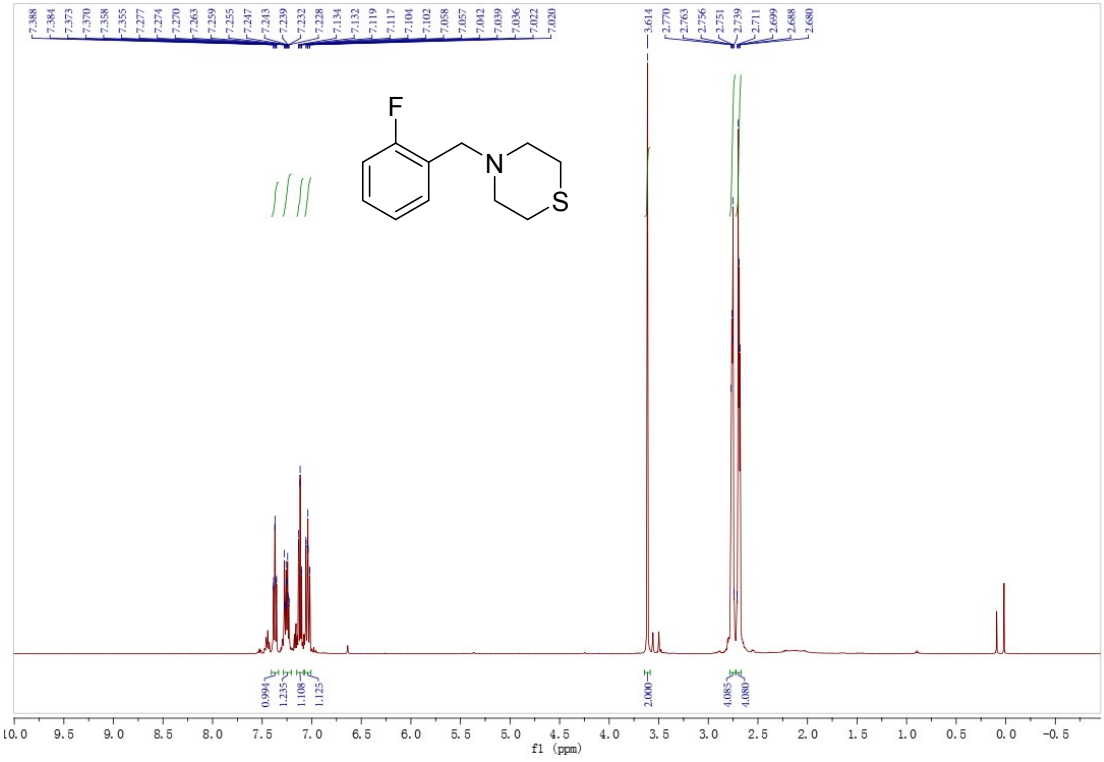


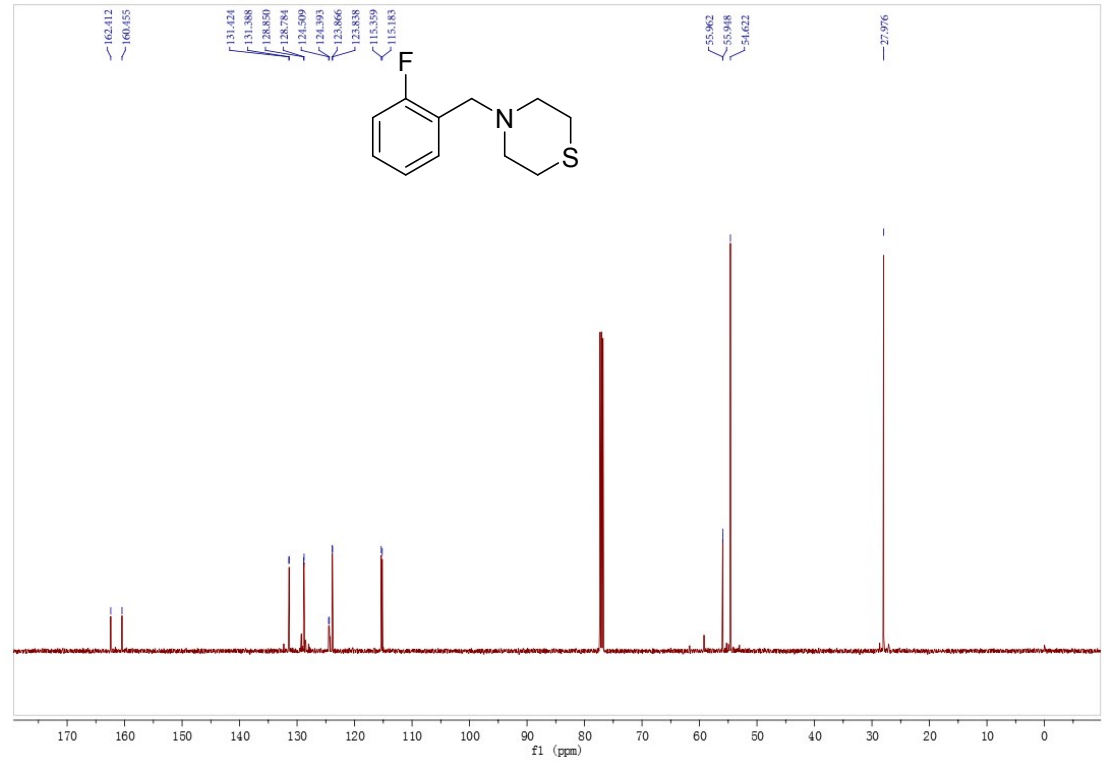
4-(3-phenoxybenzyl)thiomorpholine (**3aj**)



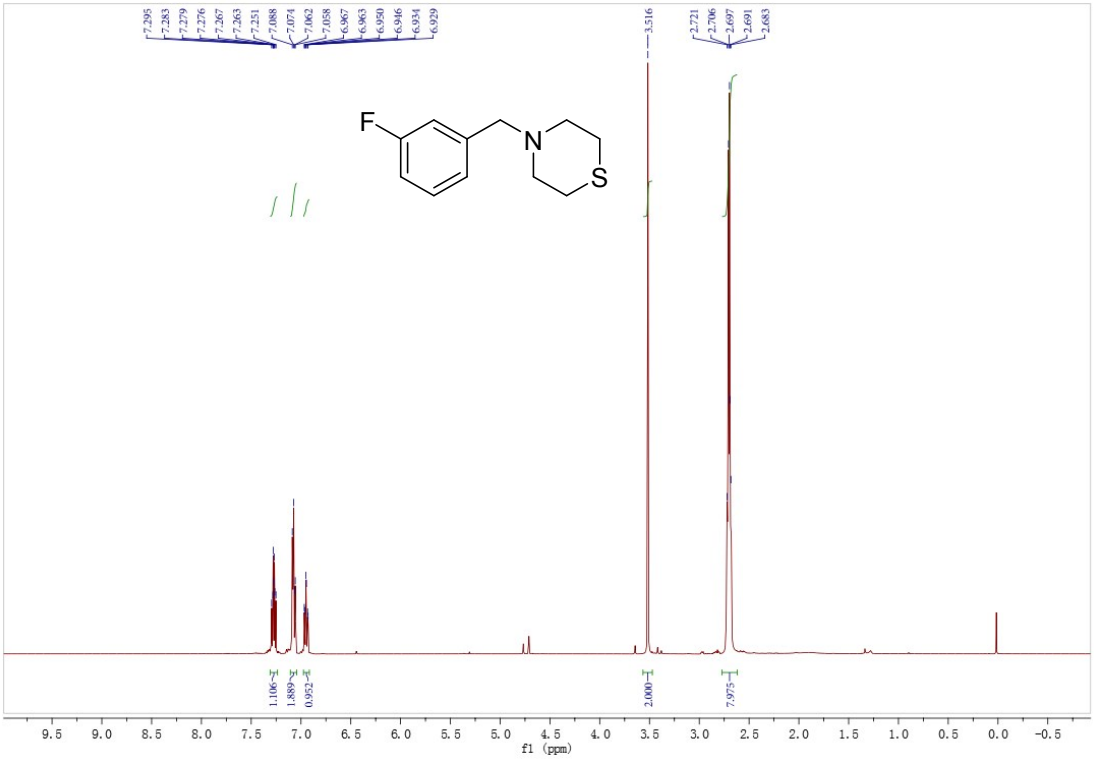


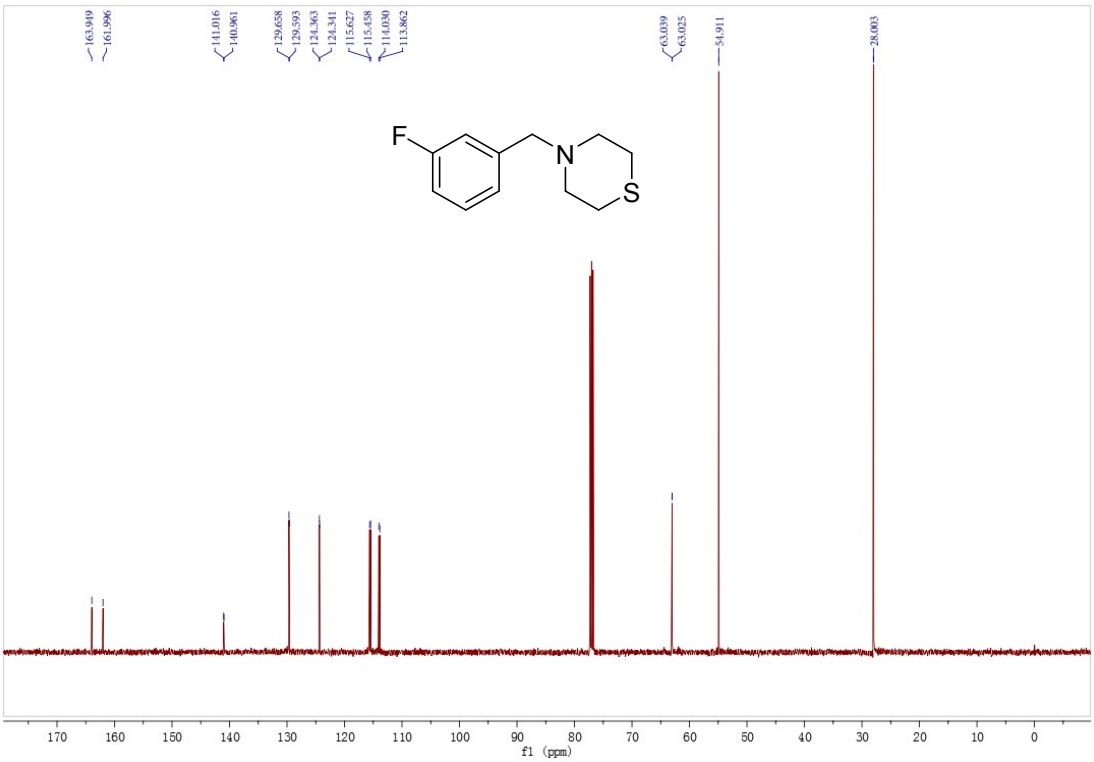
4-(2-fluorobenzyl)thiomorpholine (**3ak**)



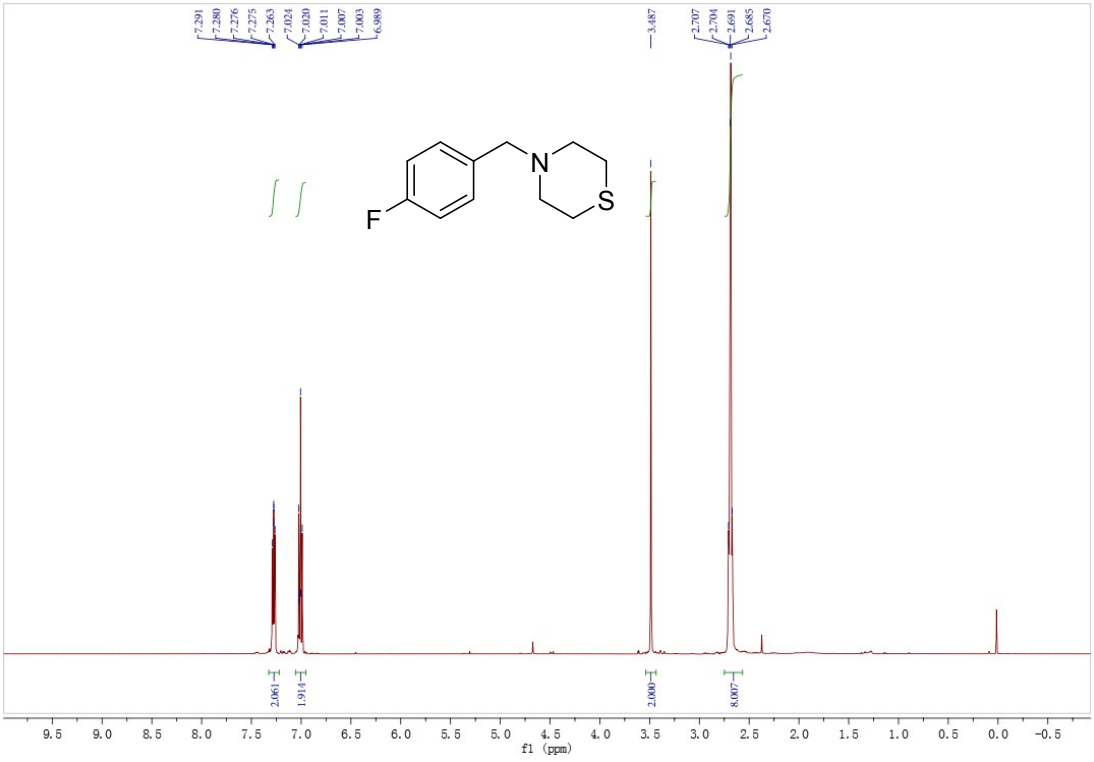


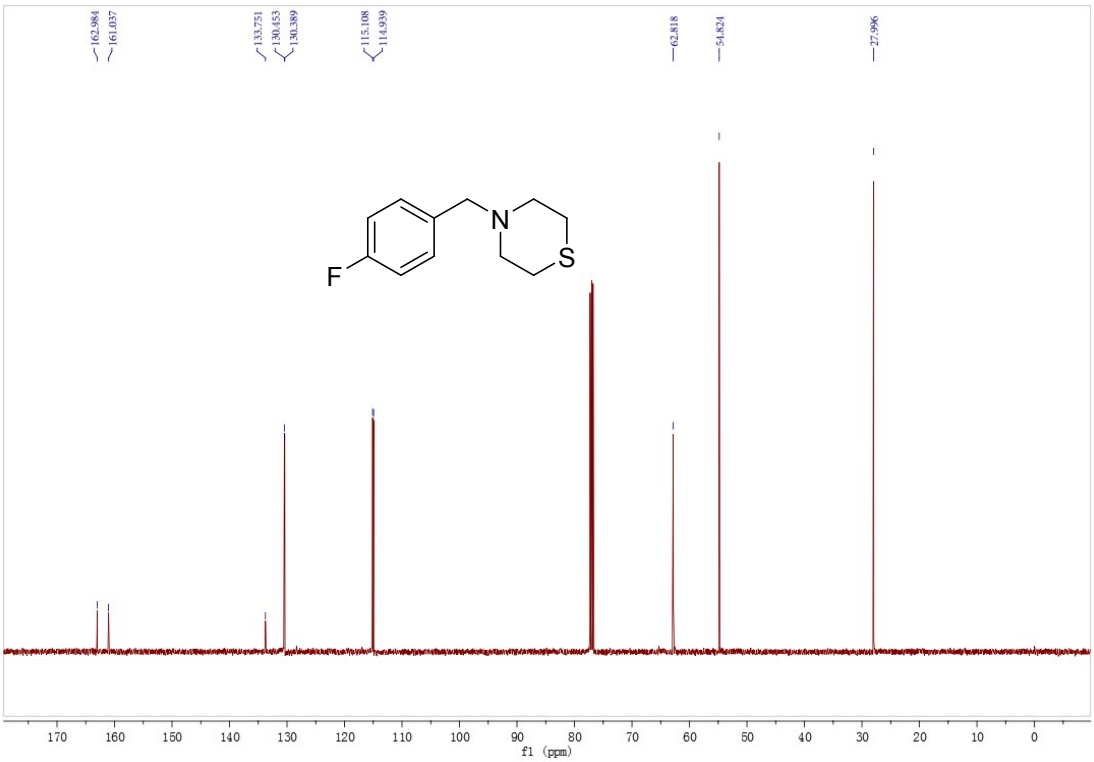
4-(3-fluorobenzyl)thiomorpholine (**3al**)



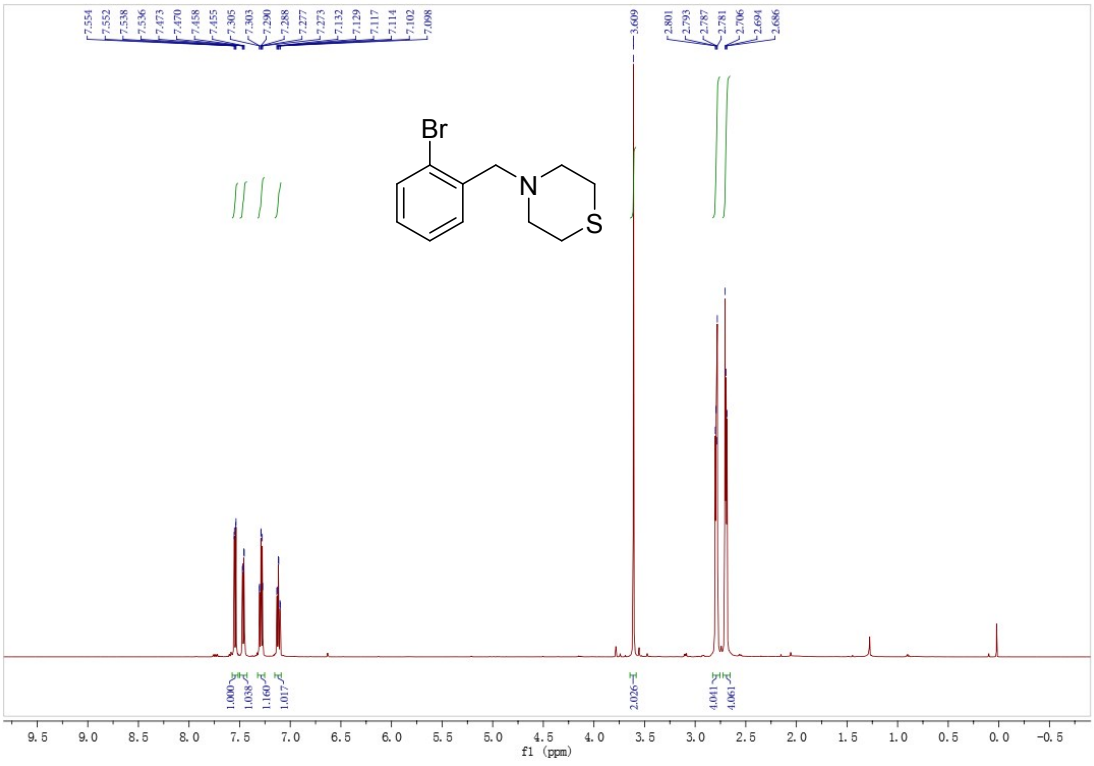


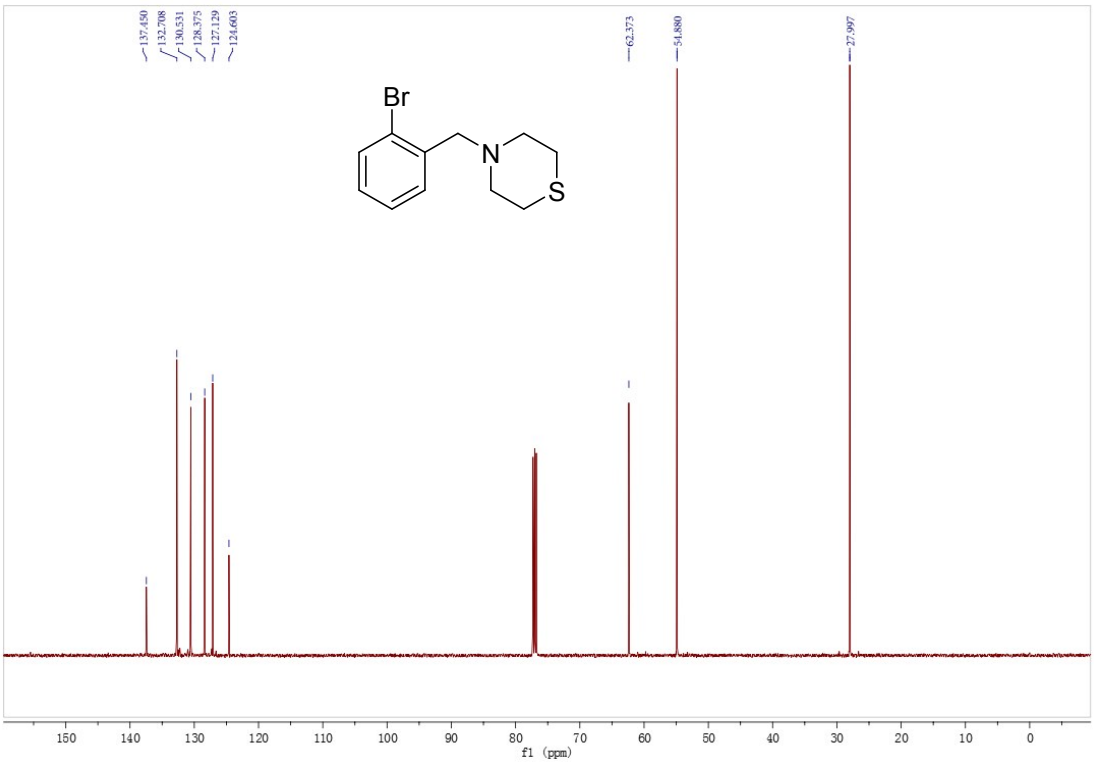
4-(4-fluorobenzyl)thiomorpholine (**3am**)



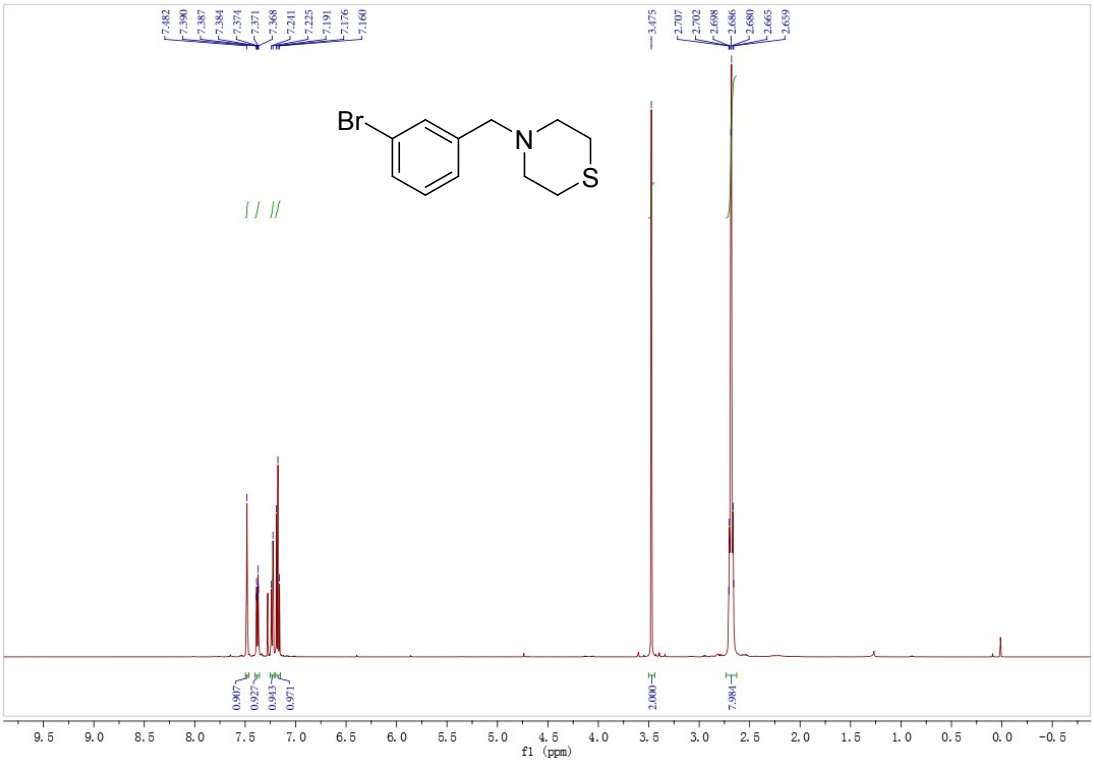


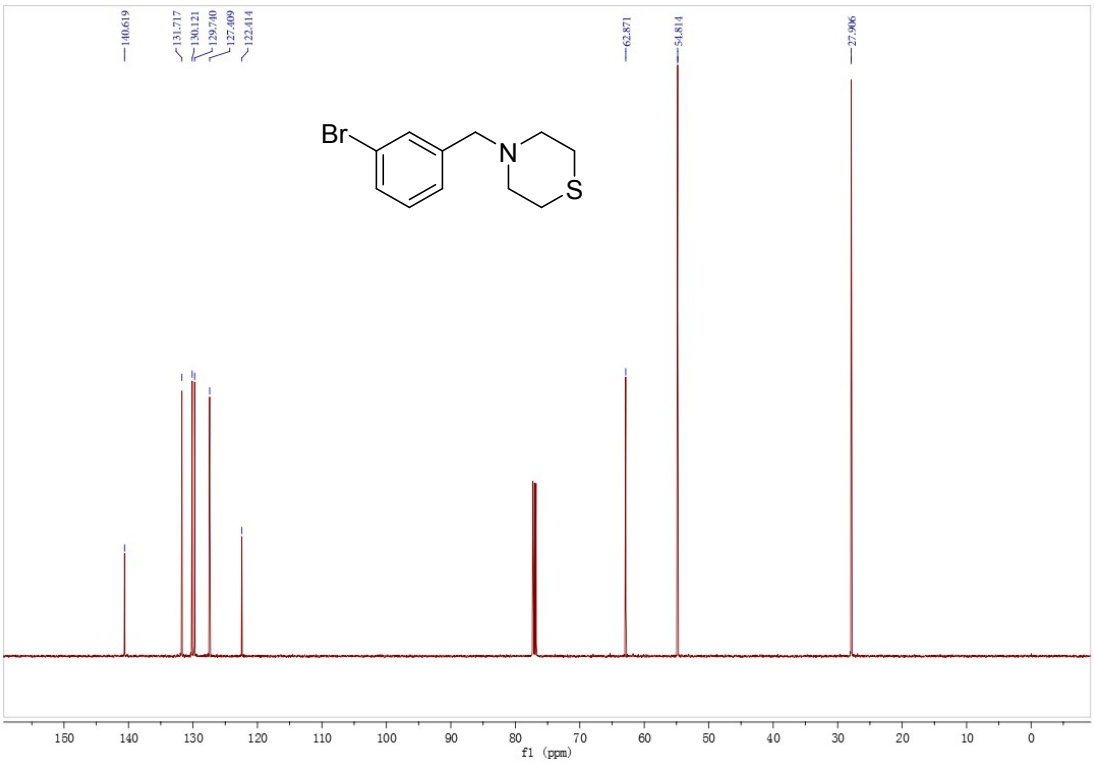
4-(2-bromobenzyl)thiomorpholine (**3an**)



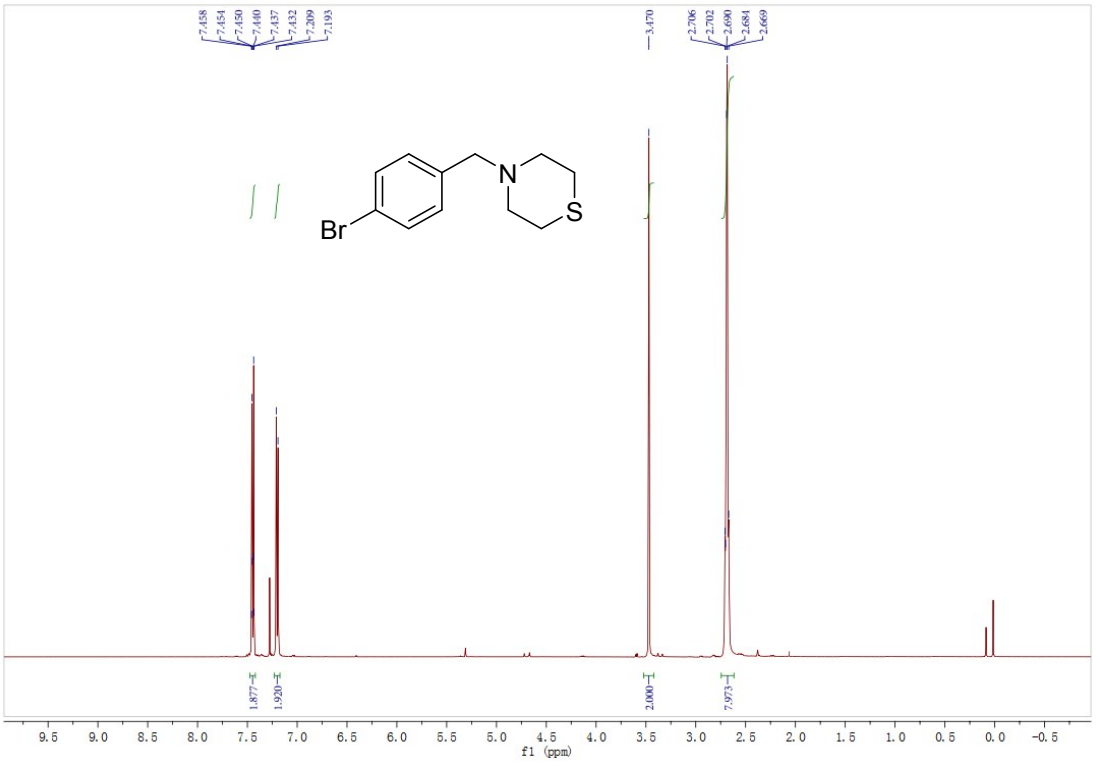


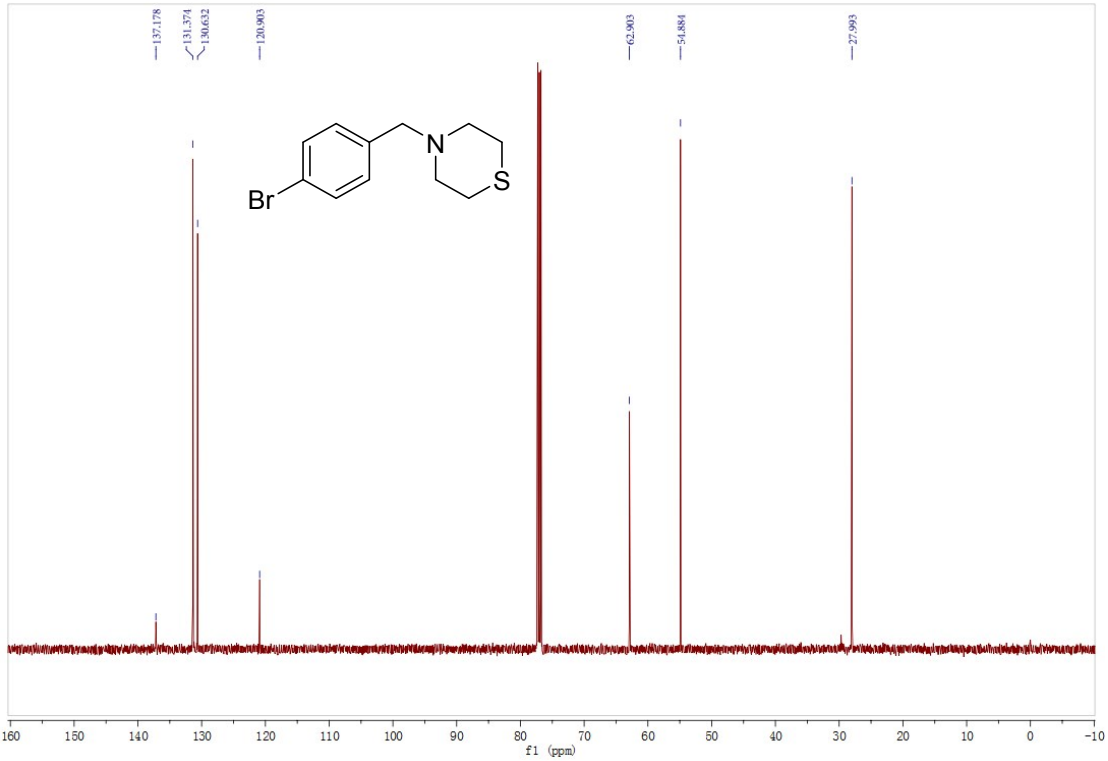
4-(3-bromobenzyl)thiomorpholine (**3ao**)



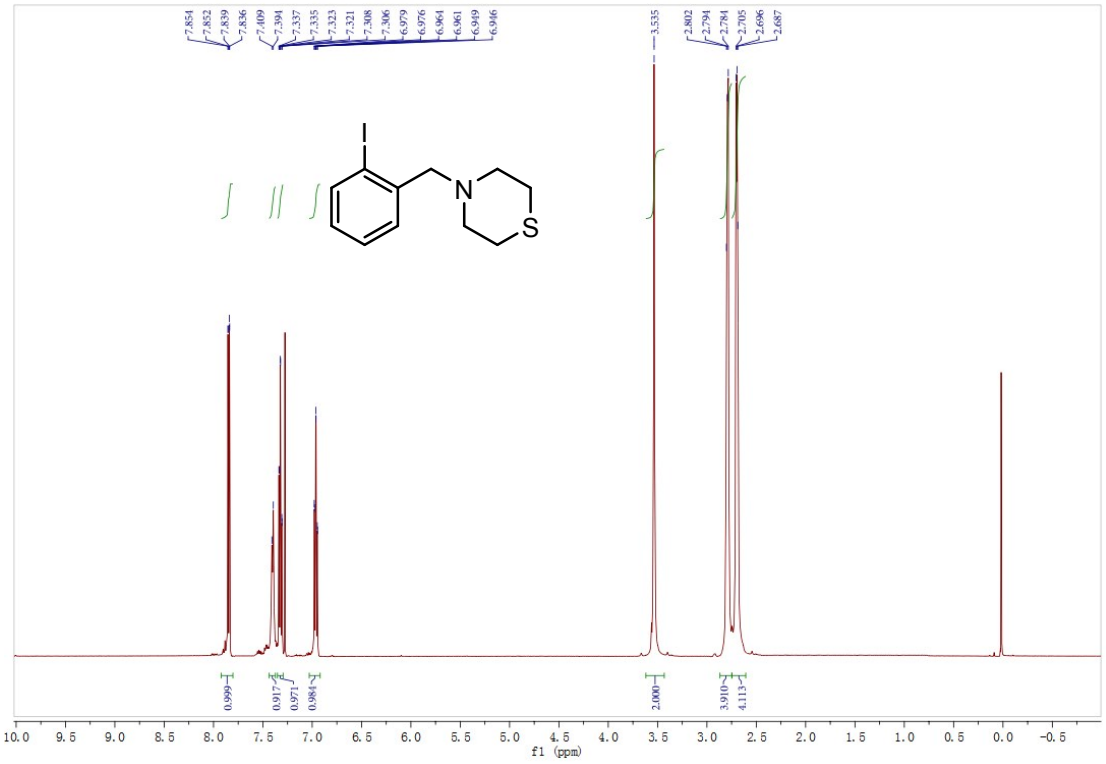


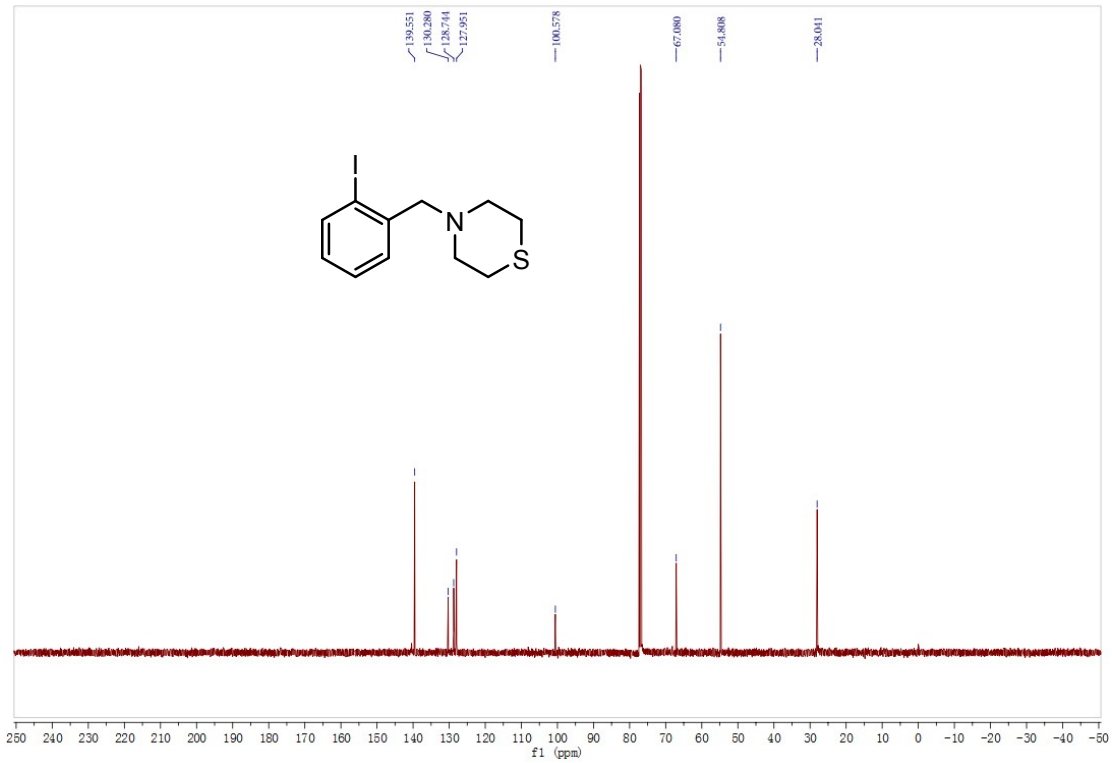
4-(4-bromobenzyl)thiomorpholine (**3ap**)



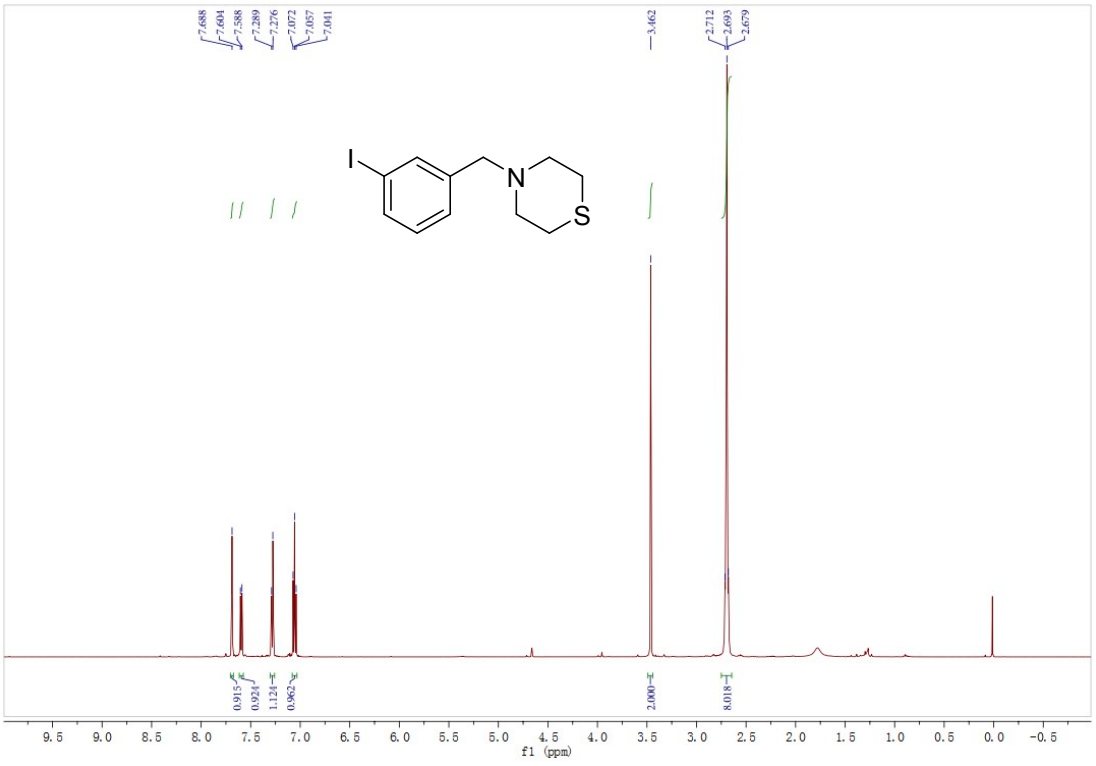


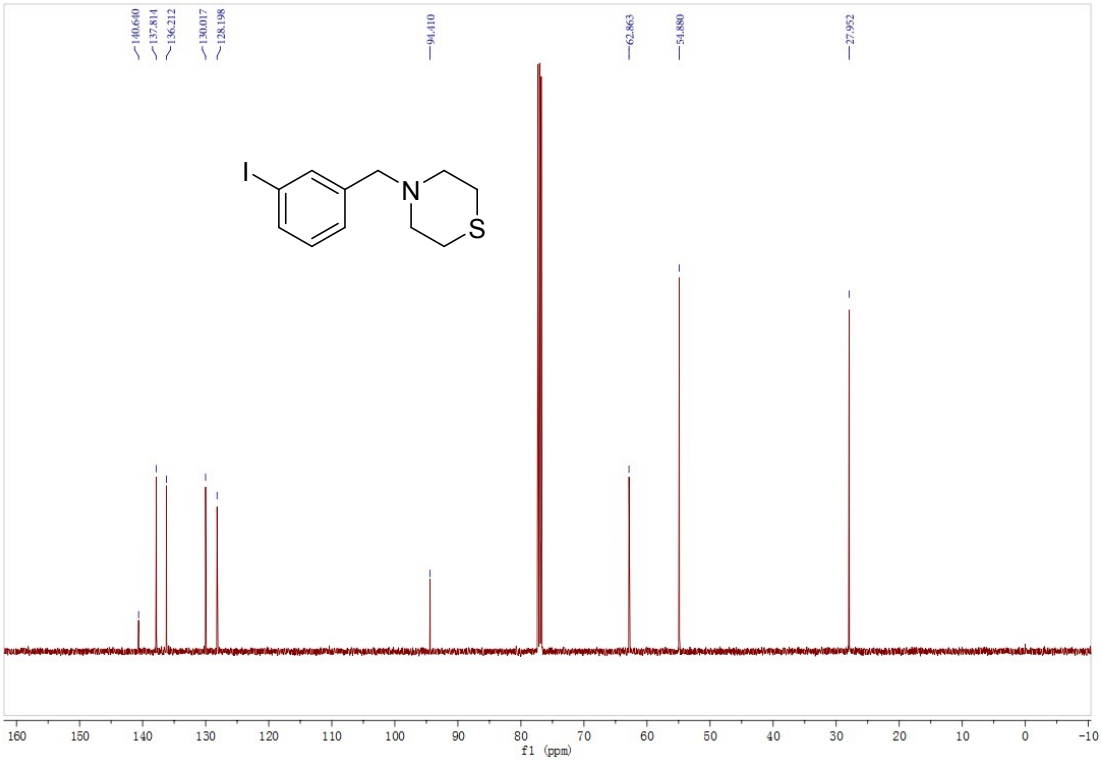
4-(2-iodobenzyl)thiomorpholine (**3aq**)



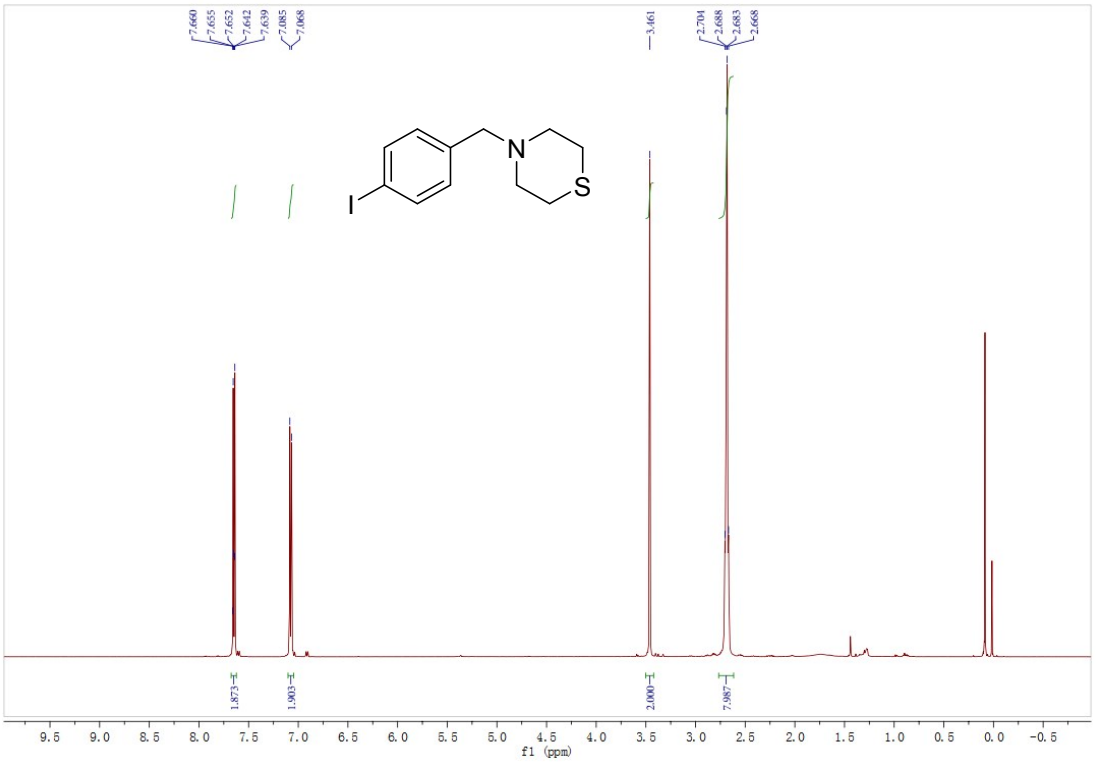


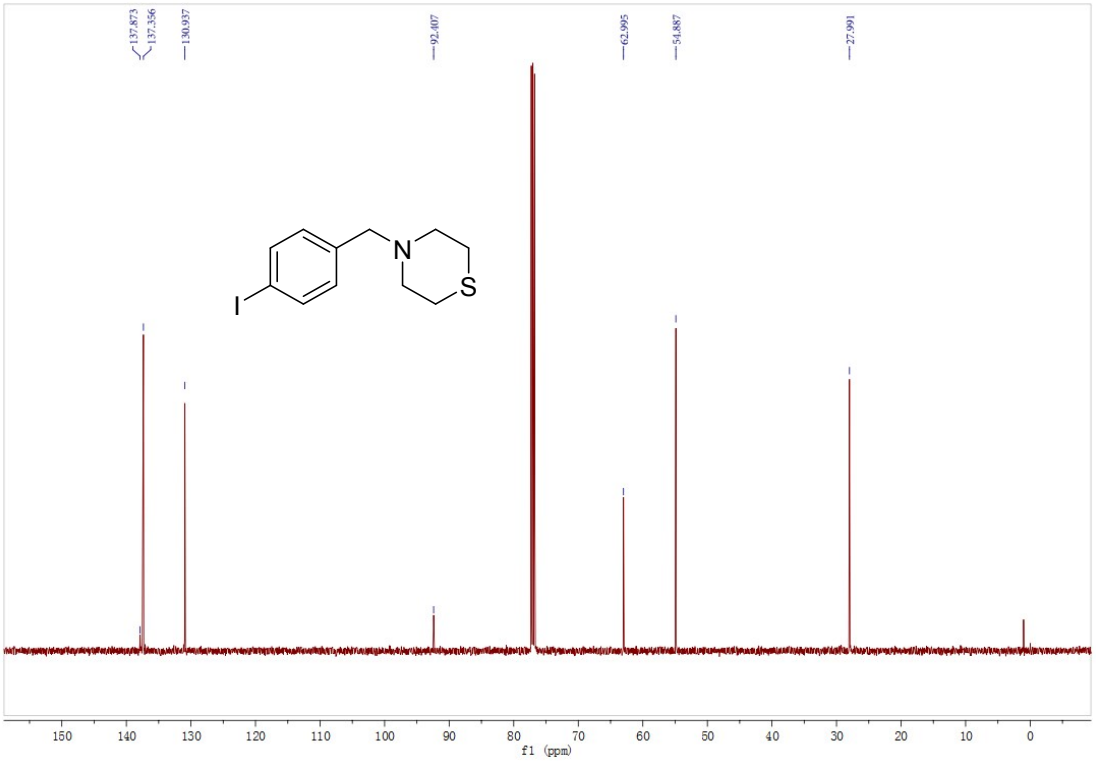
4-(3-iodobenzyl)thiomorpholine (**3ar**)



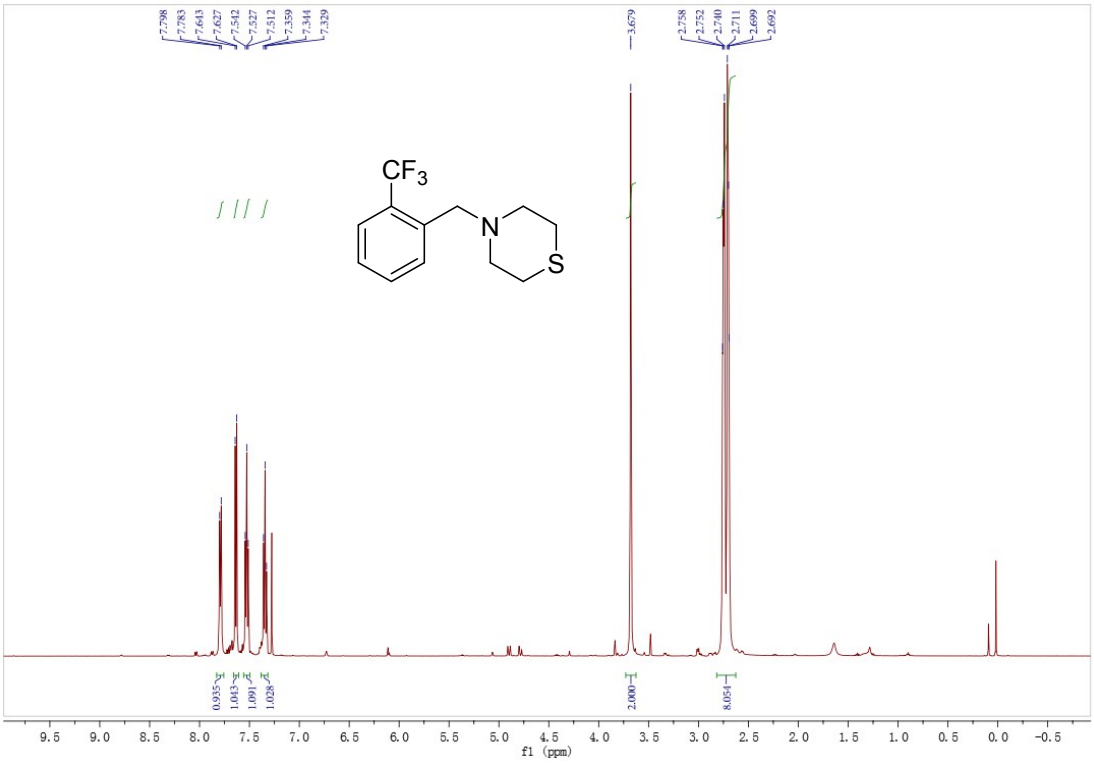


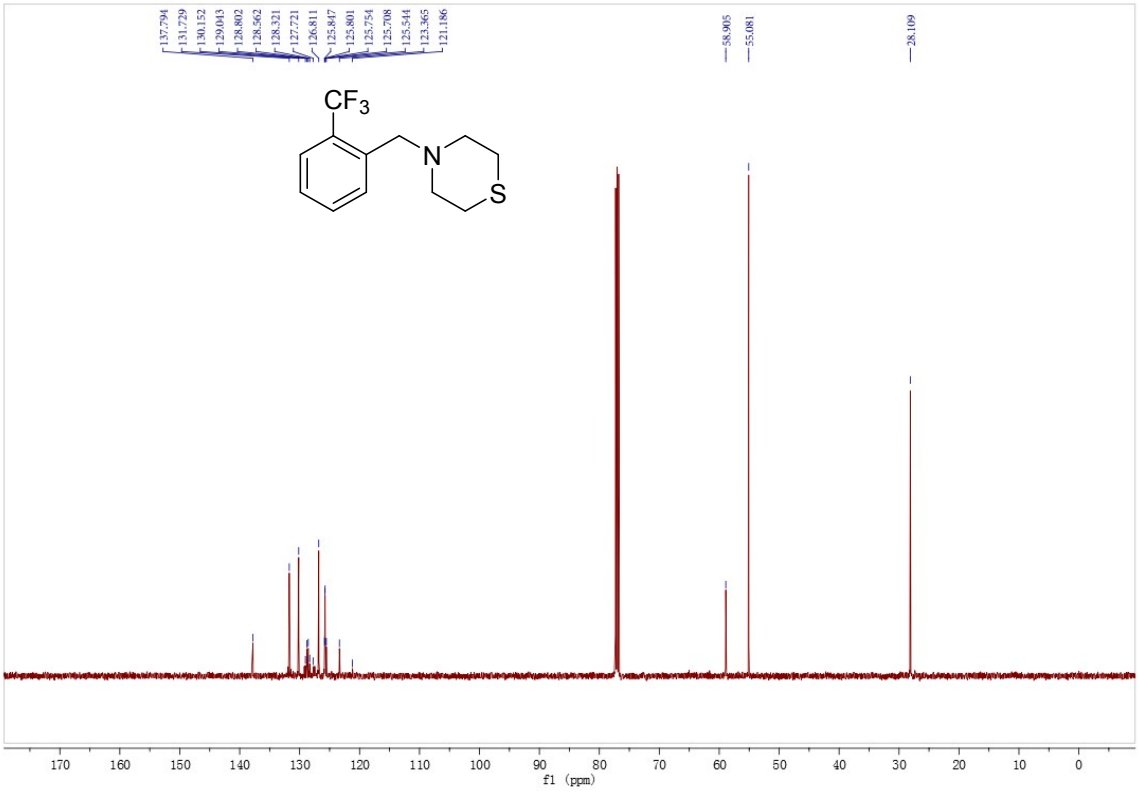
4-(4-iodobenzyl)thiomorpholine (**3as**)



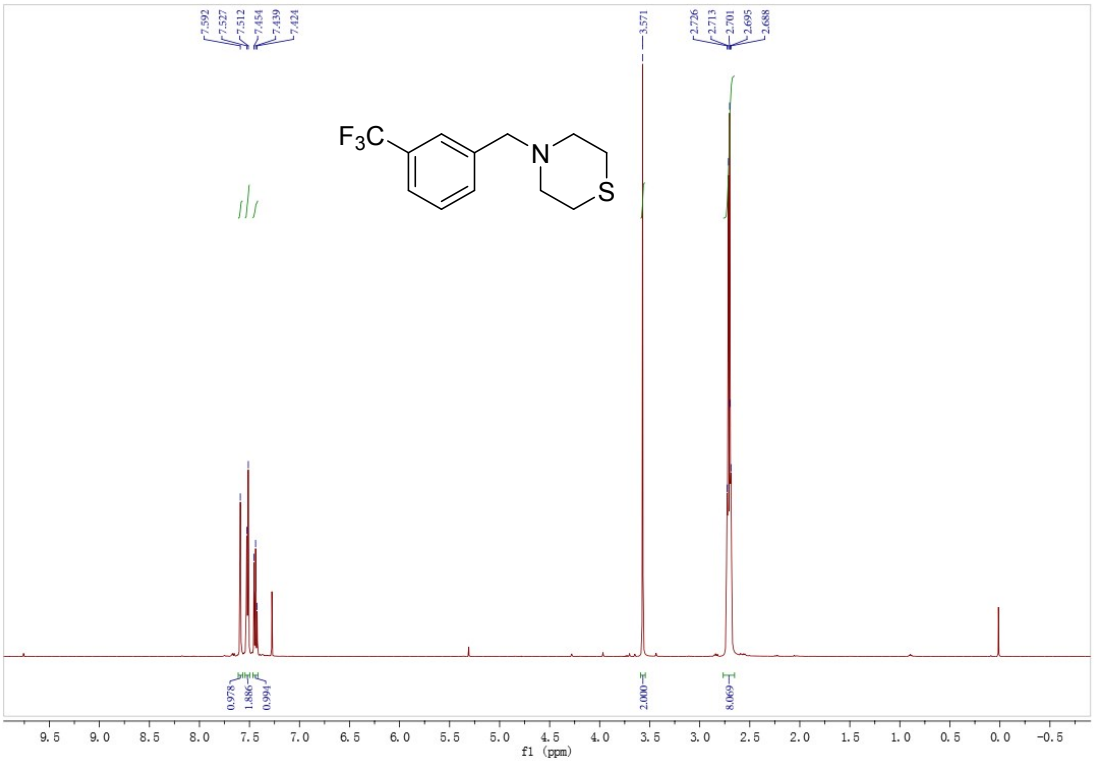


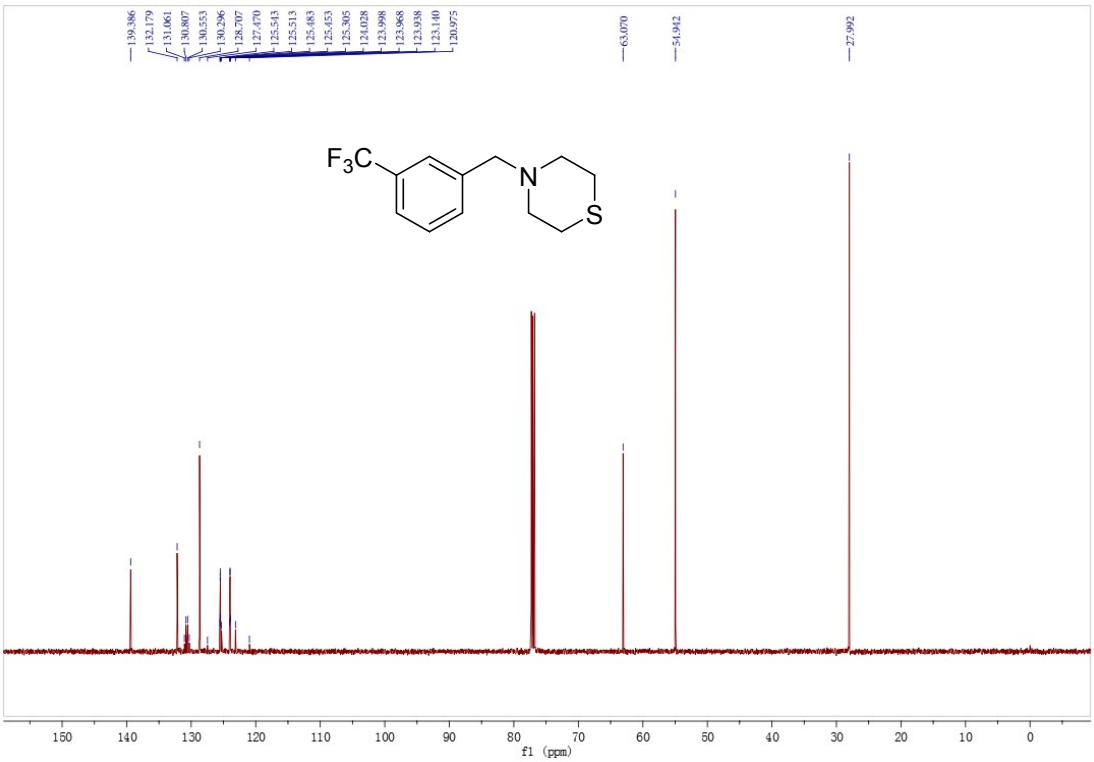
4-(2-(trifluoromethyl)benzyl)thiomorpholine (**3at**)



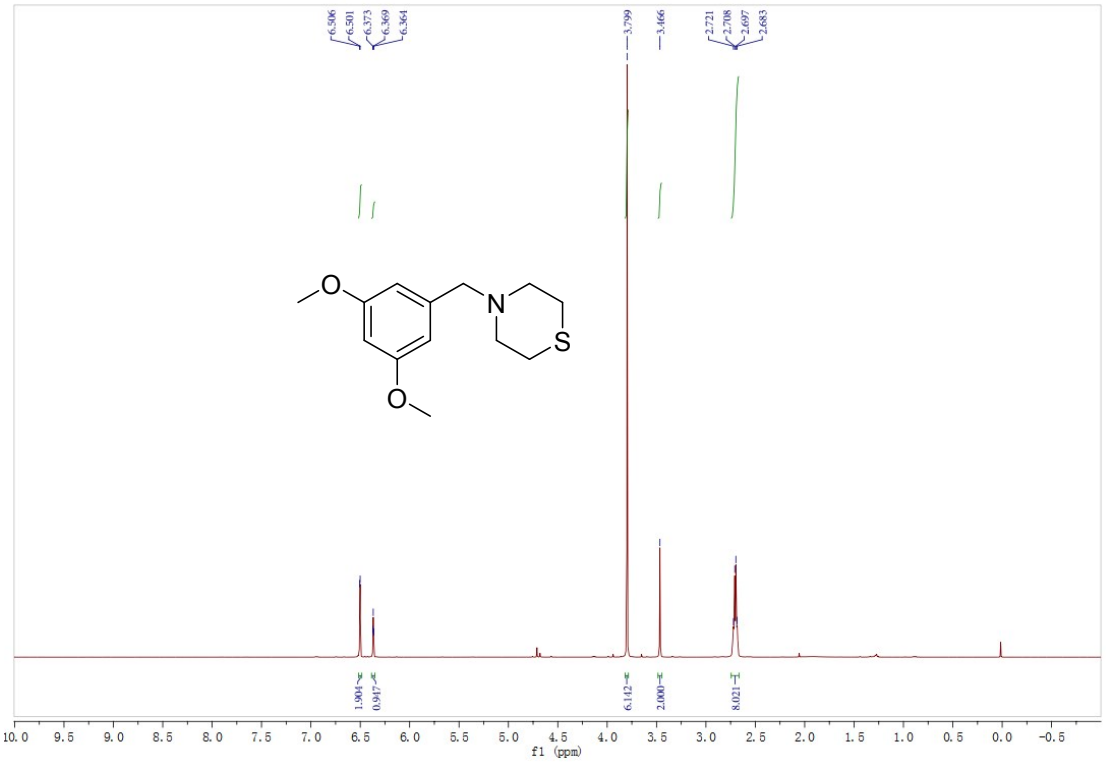


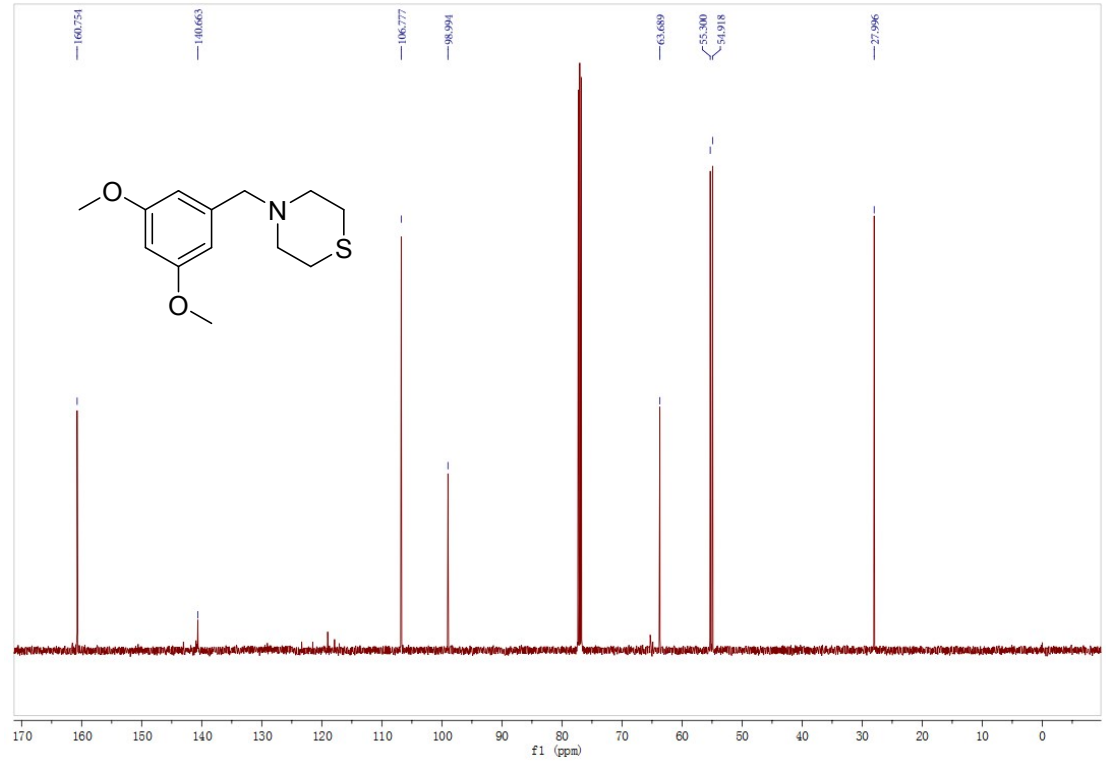
4-(3-(trifluoromethyl)benzyl)thiomorpholine (**3au**)



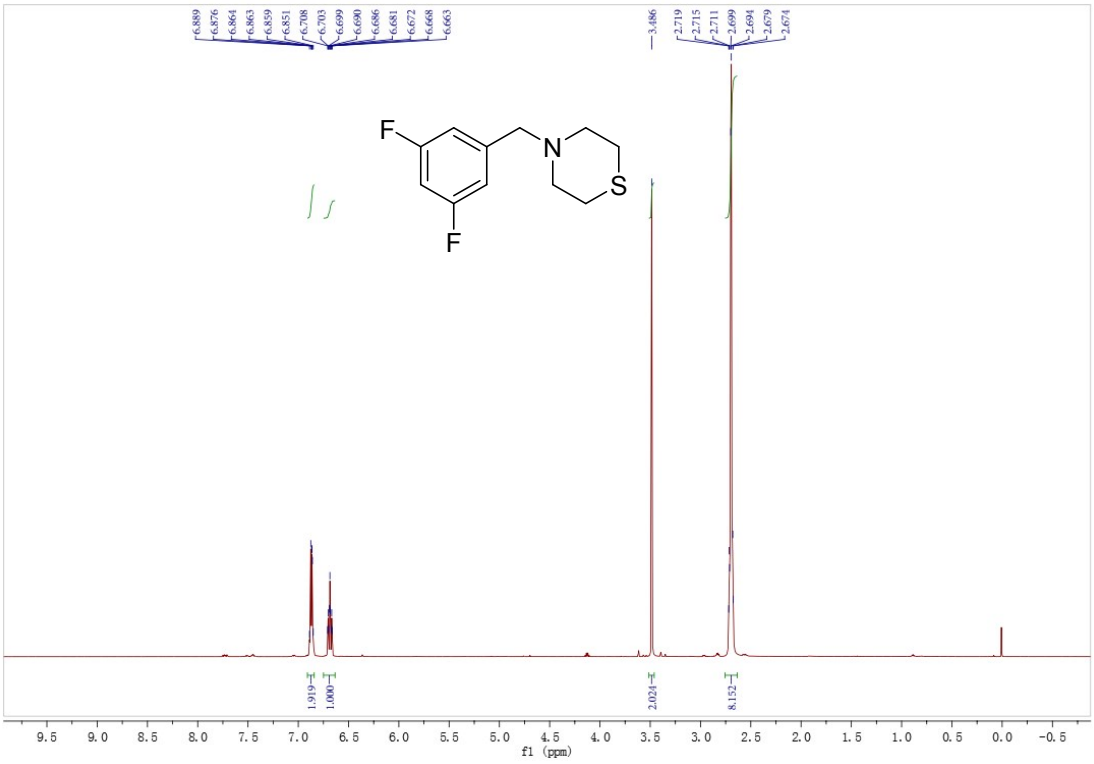


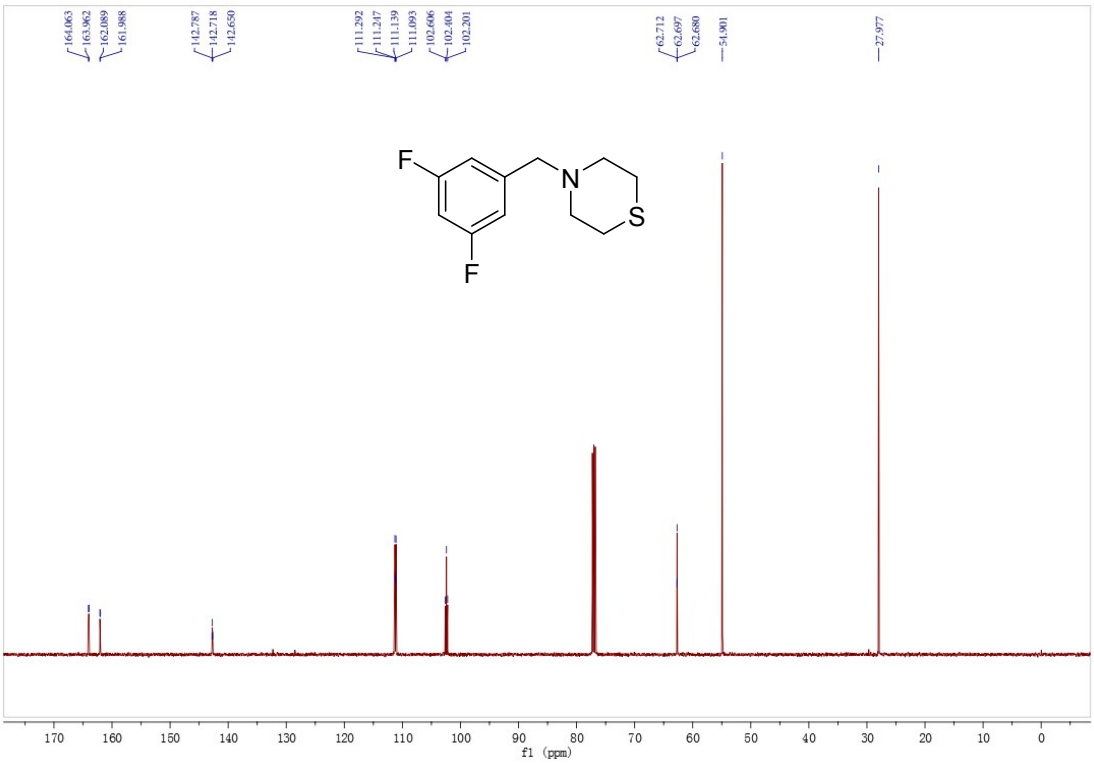
4-(3,5-dimethoxybenzyl)thiomorpholine (**3av**)



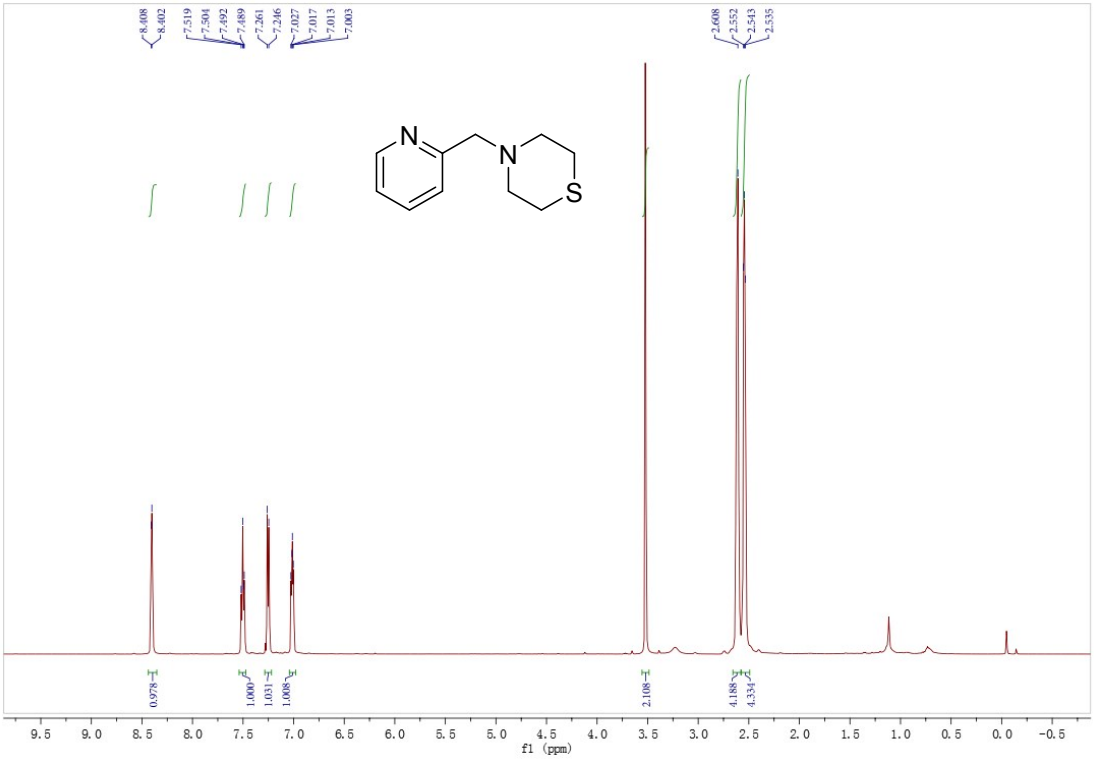


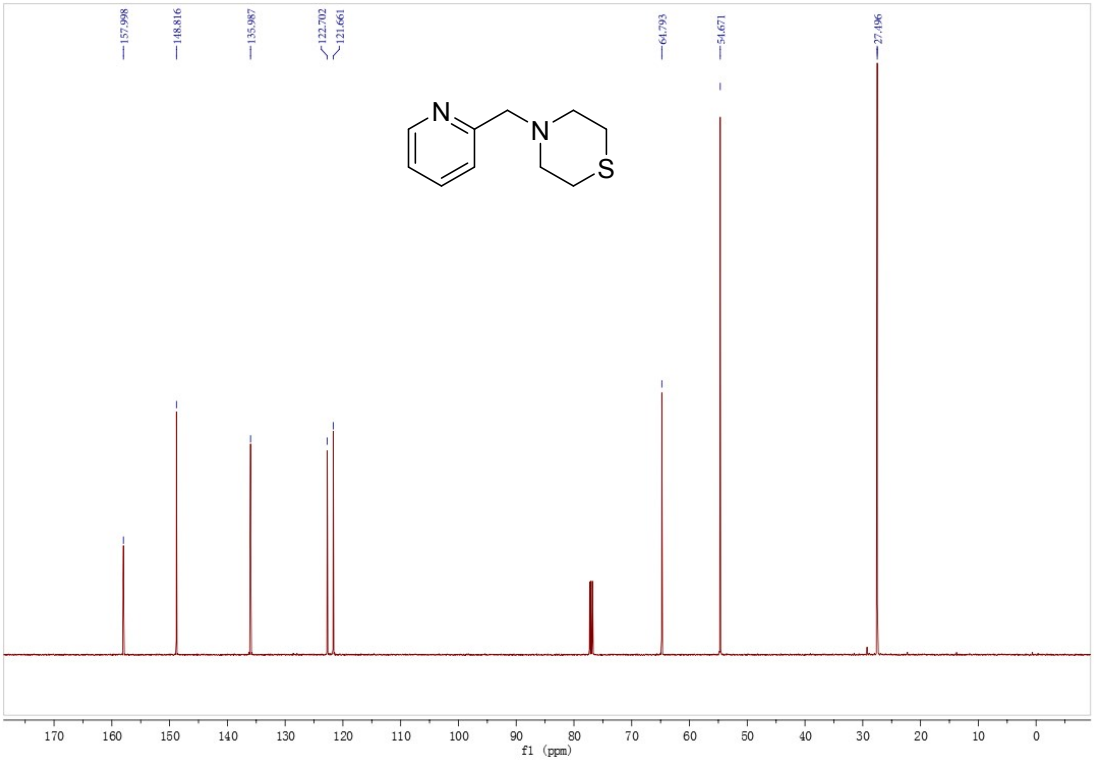
4-(3,5-difluorobenzyl)thiomorpholine (**3aw**)



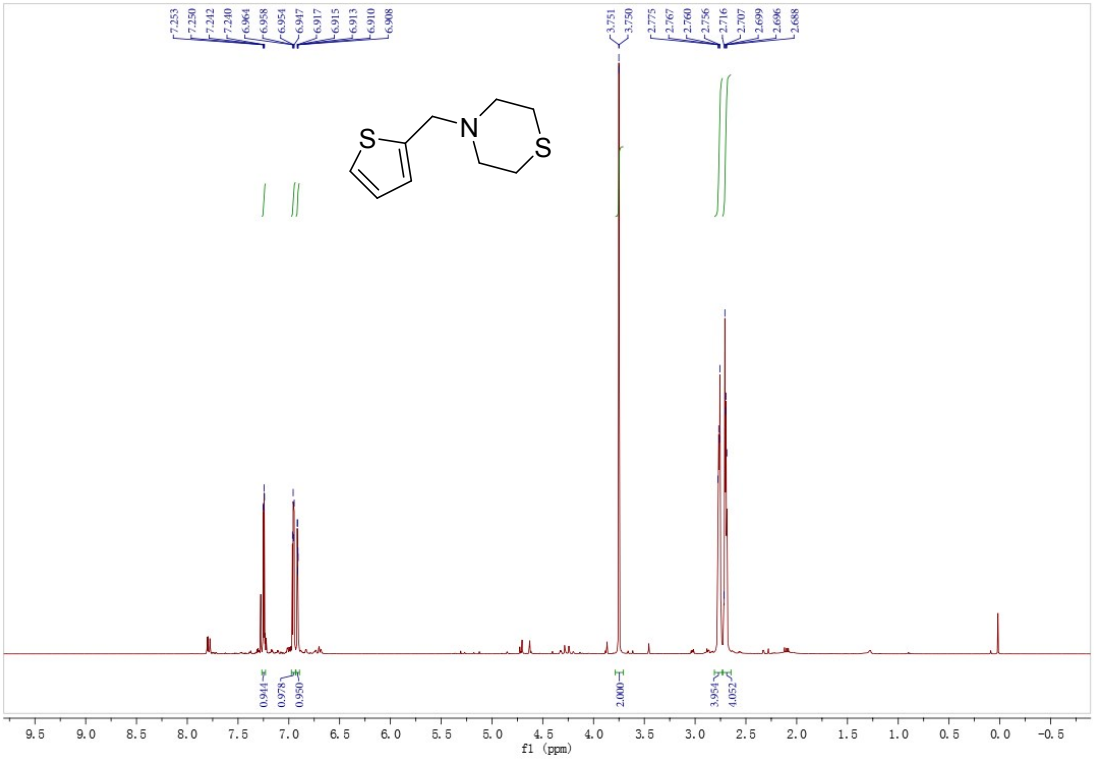


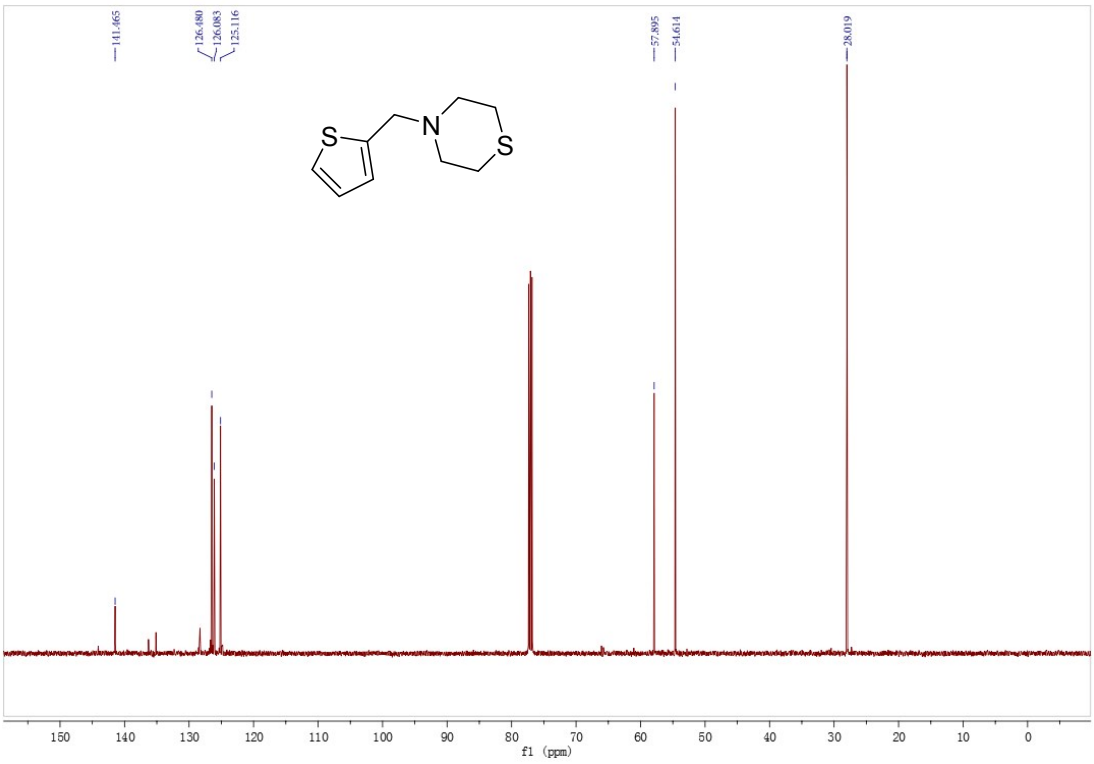
4-(pyridin-2-ylmethyl)thiomorpholine (**3ax**)



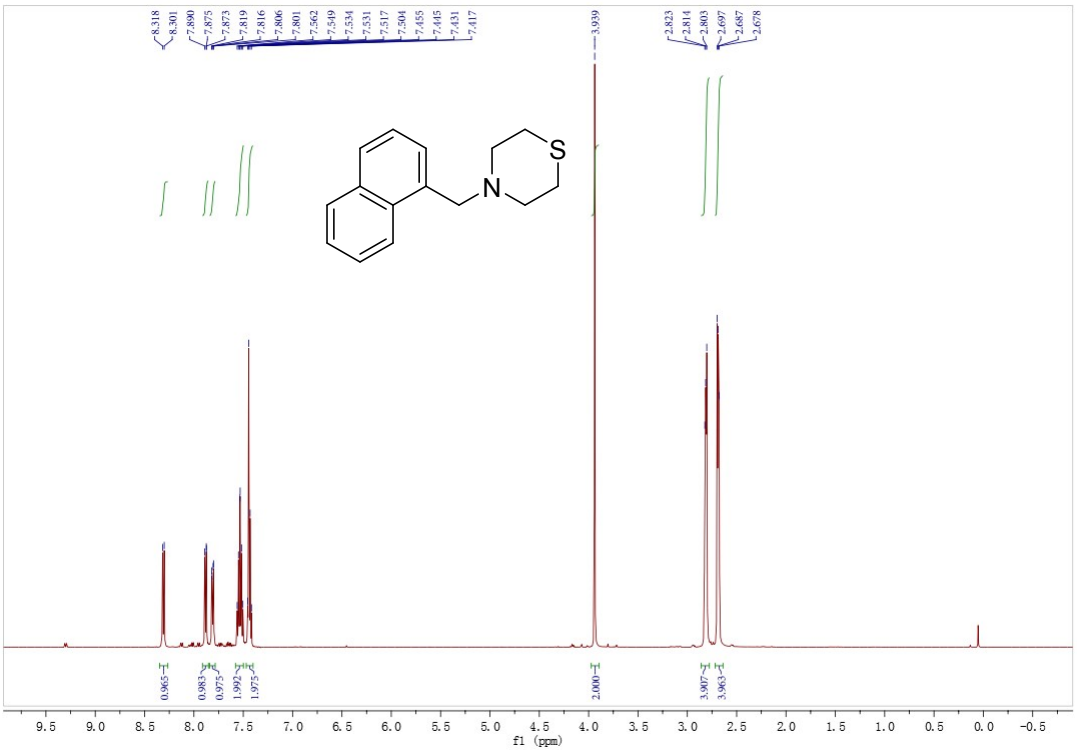


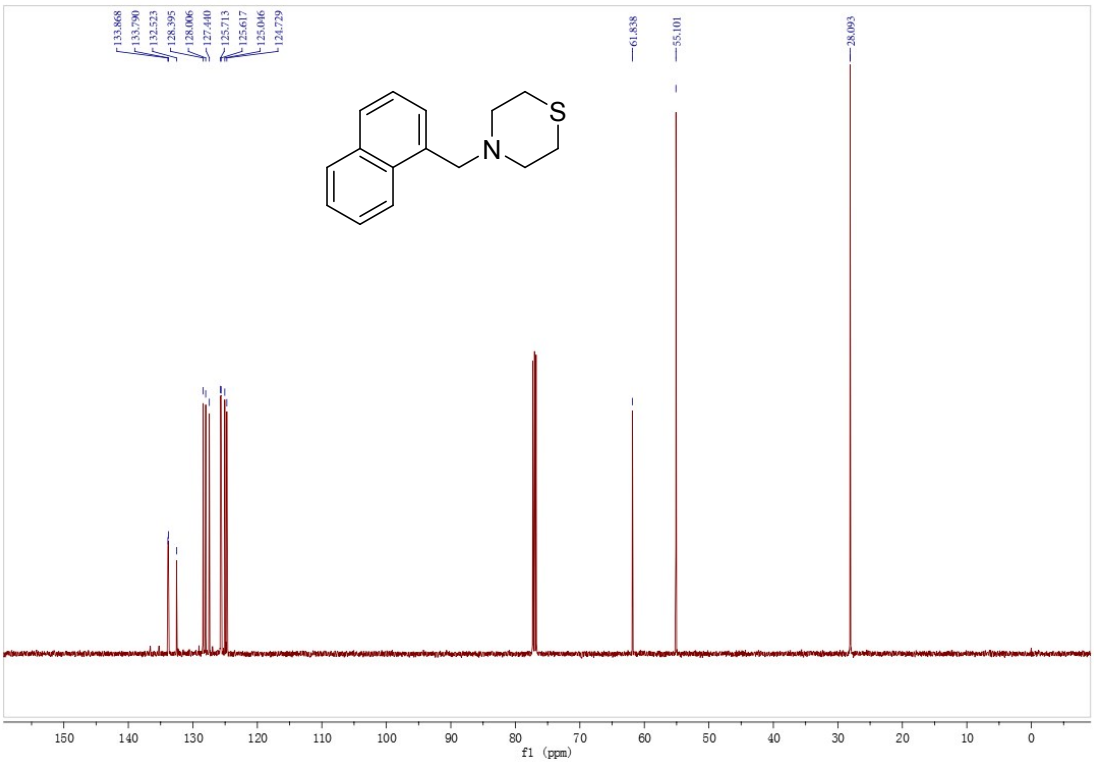
4-(thiophen-2-ylmethyl)thiomorpholine (**3ay**)



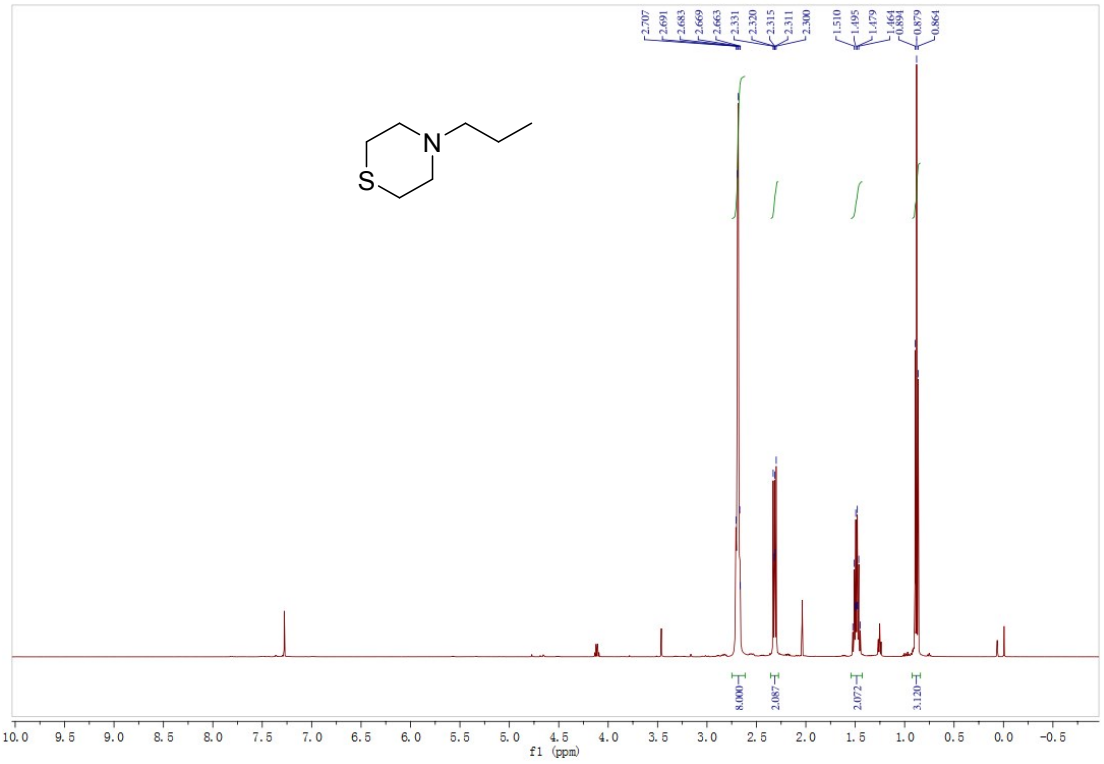


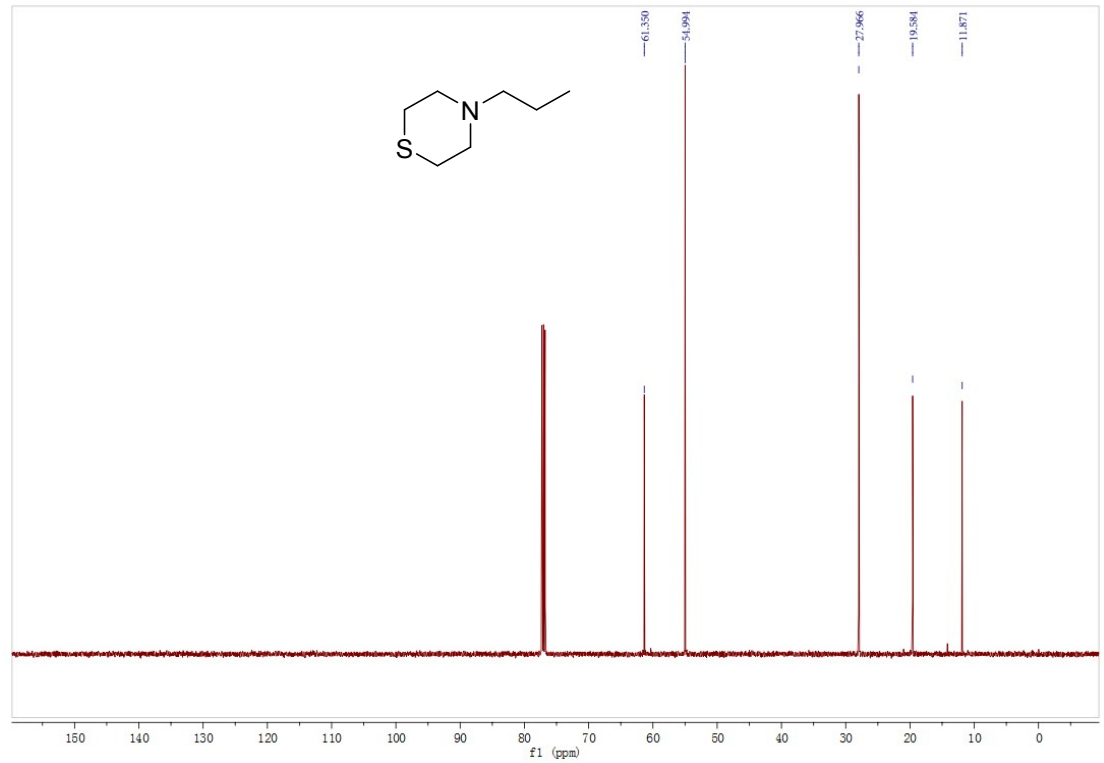
4-(naphthalen-1-ylmethyl)thiomorpholine (**3az**)



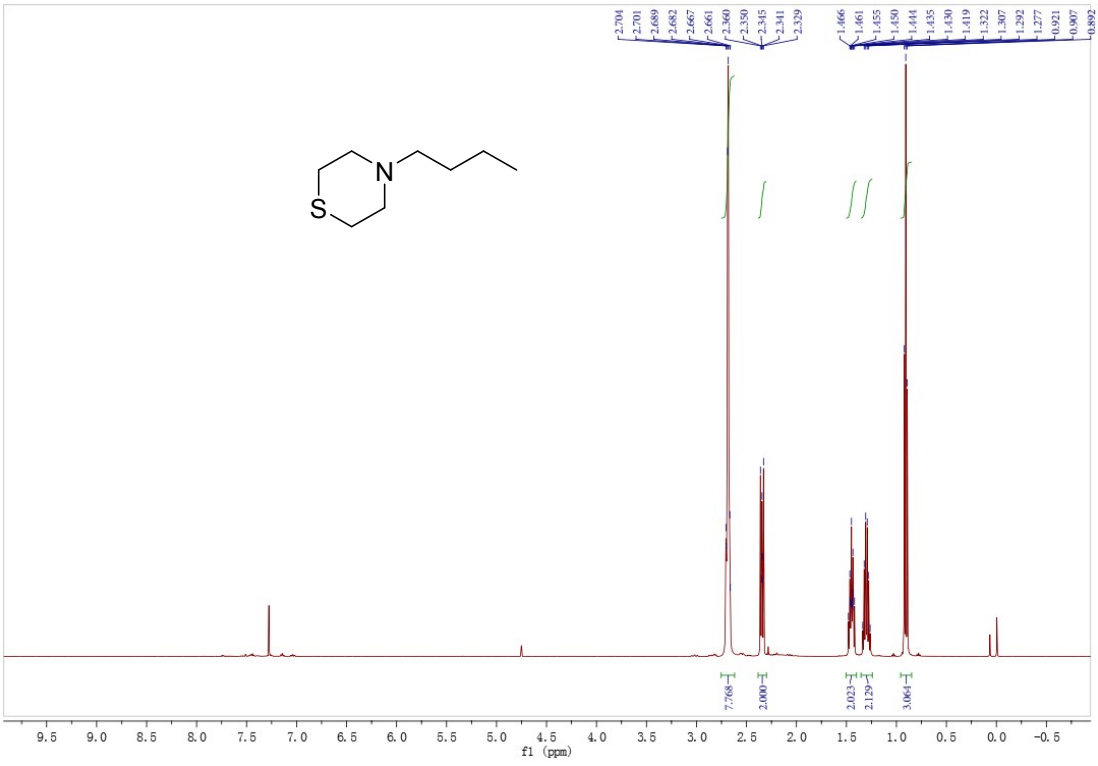


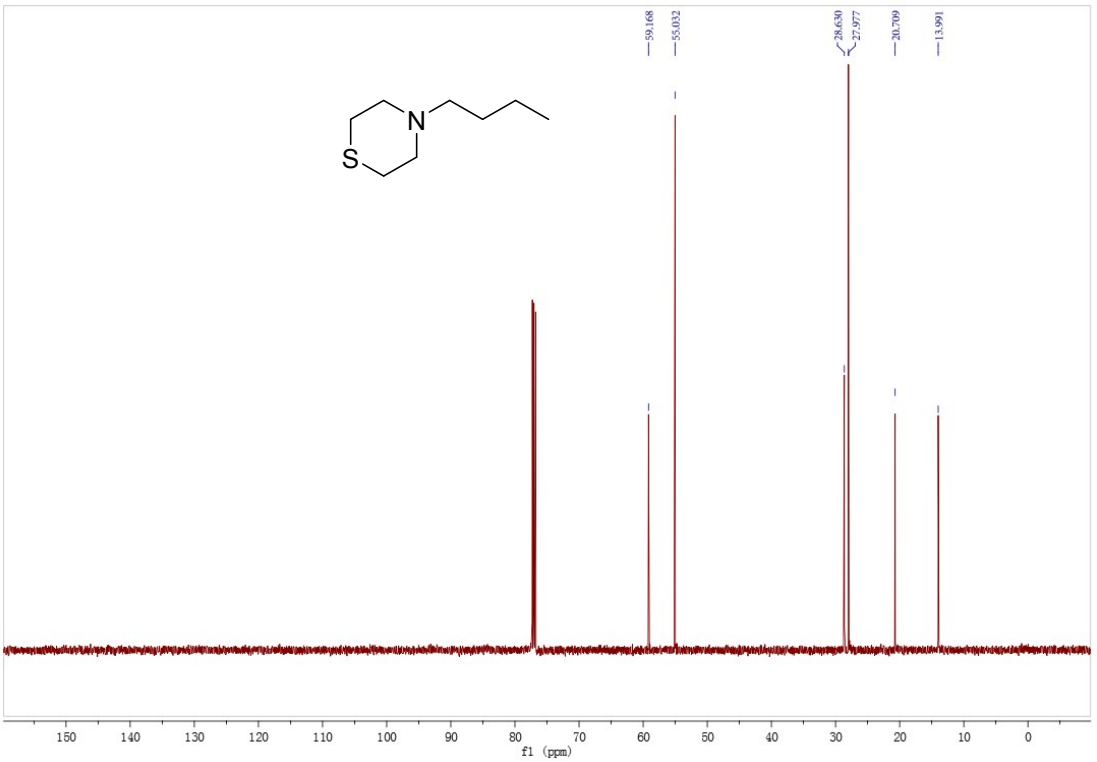
4-propylthiomorpholine (**3ba**)



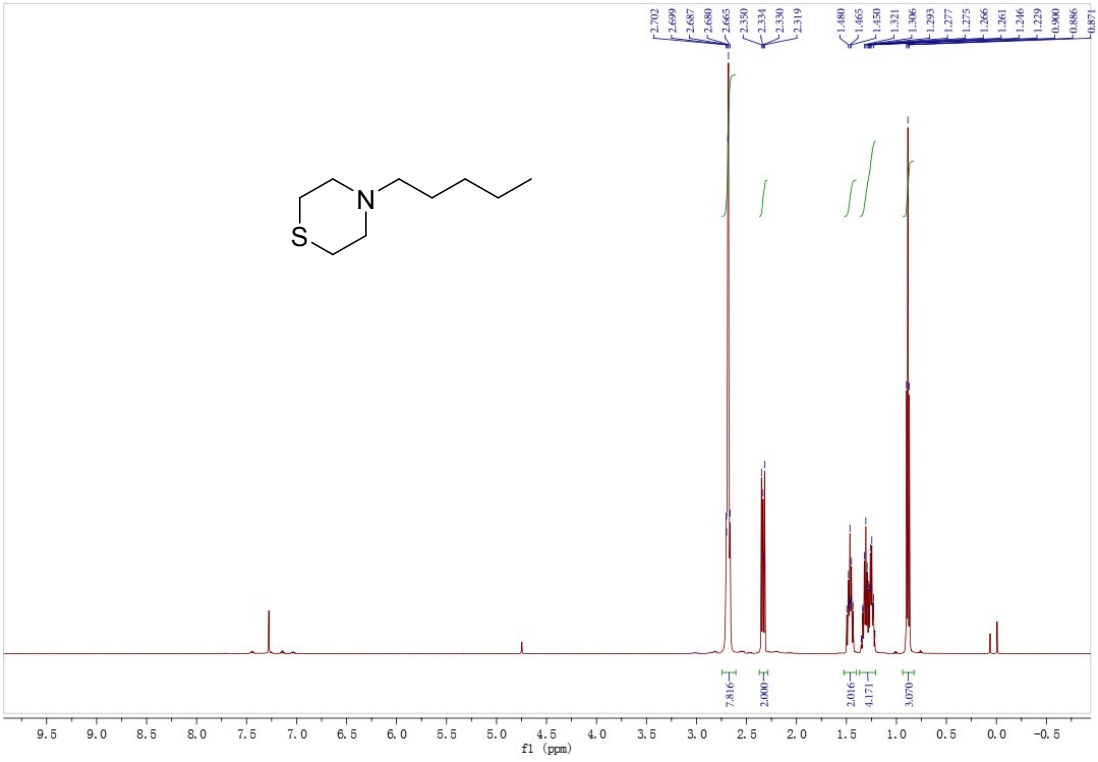


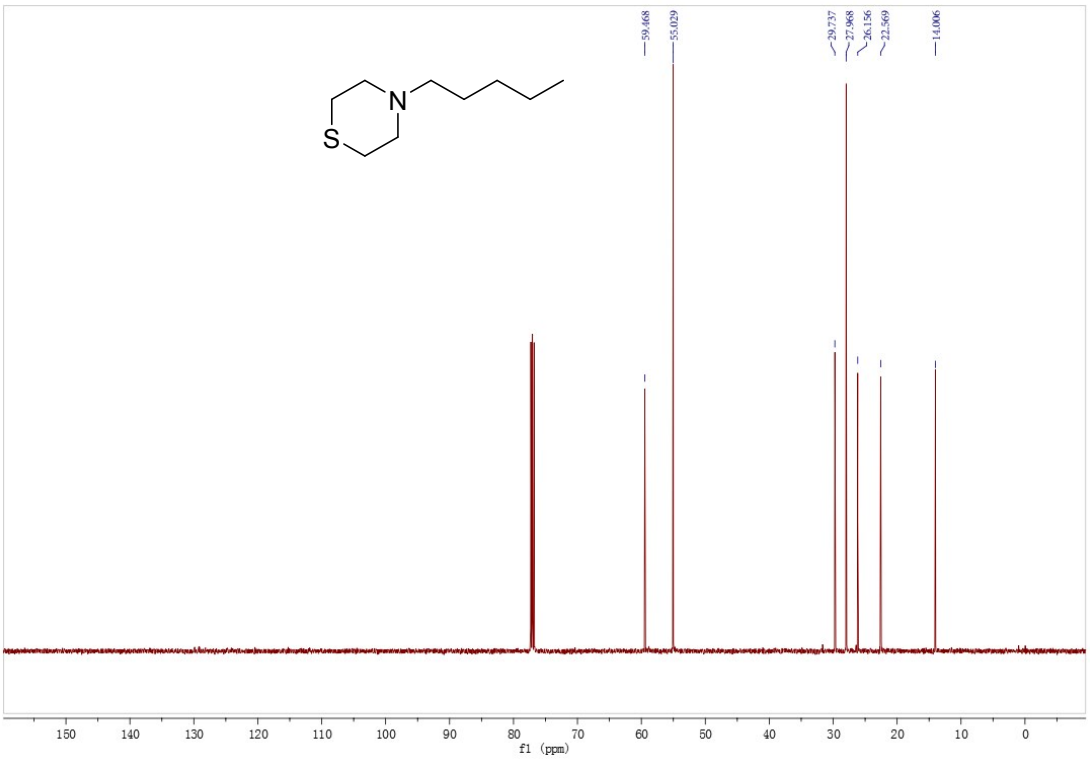
4-butylthiomorpholine (**3bb**)



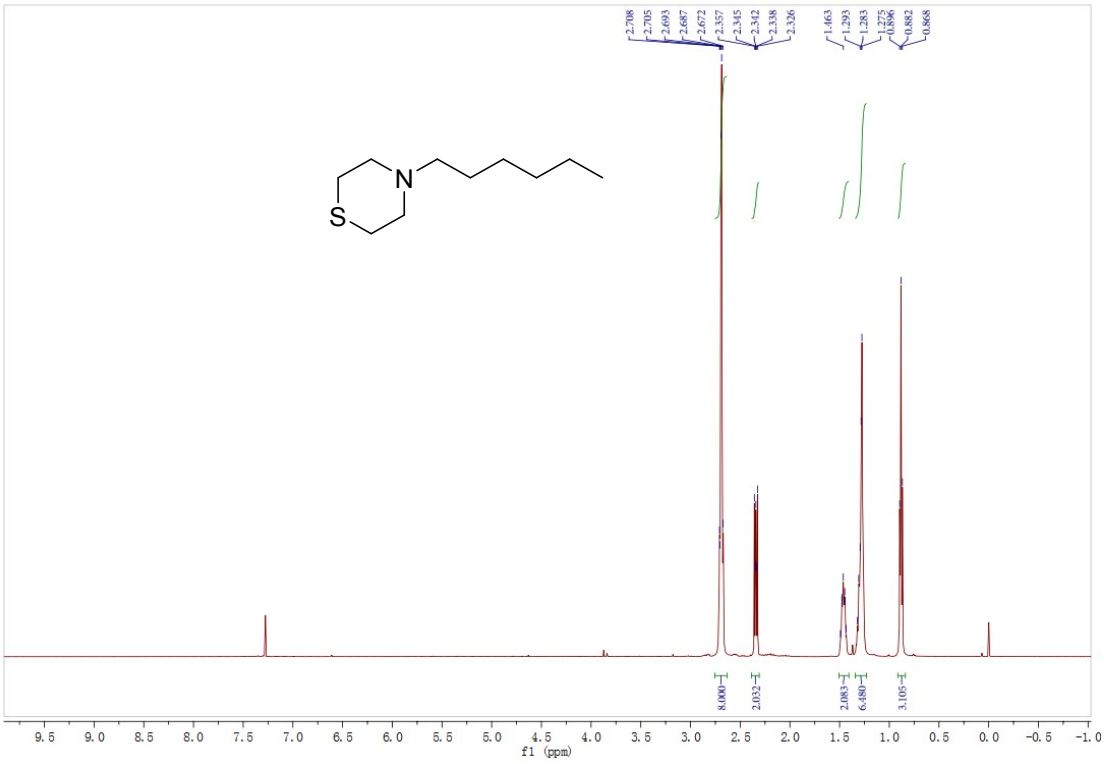


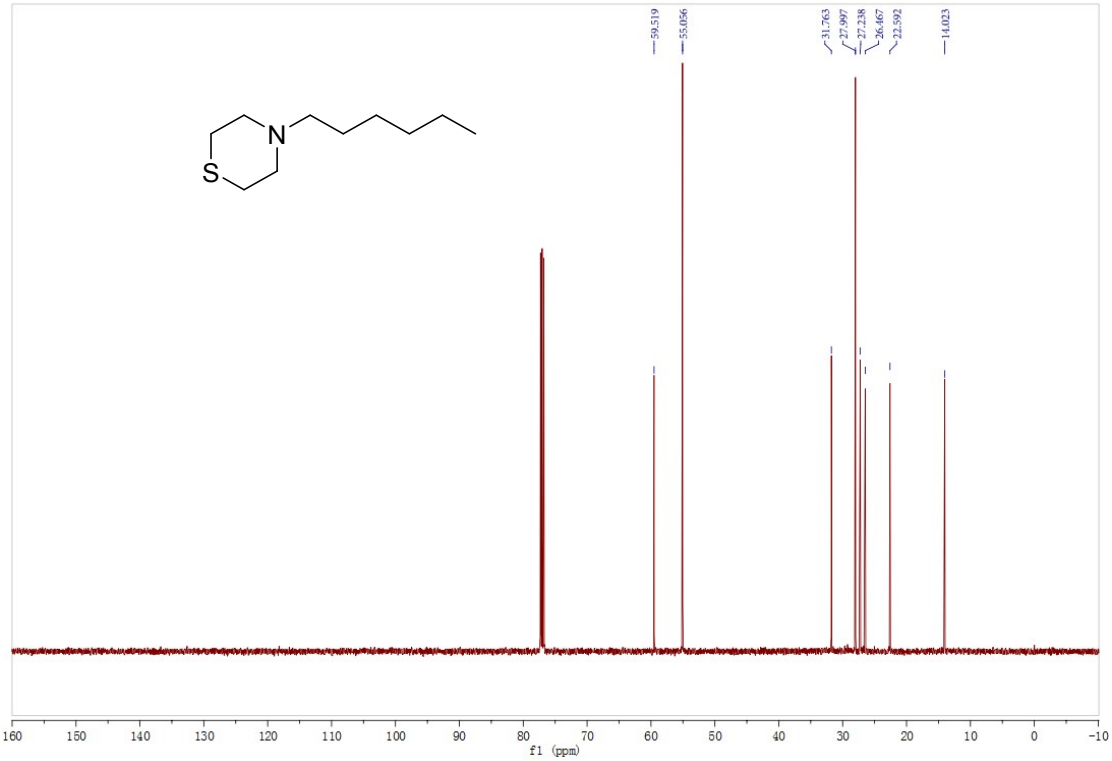
4-pentylthiomorpholine (**3bc**)



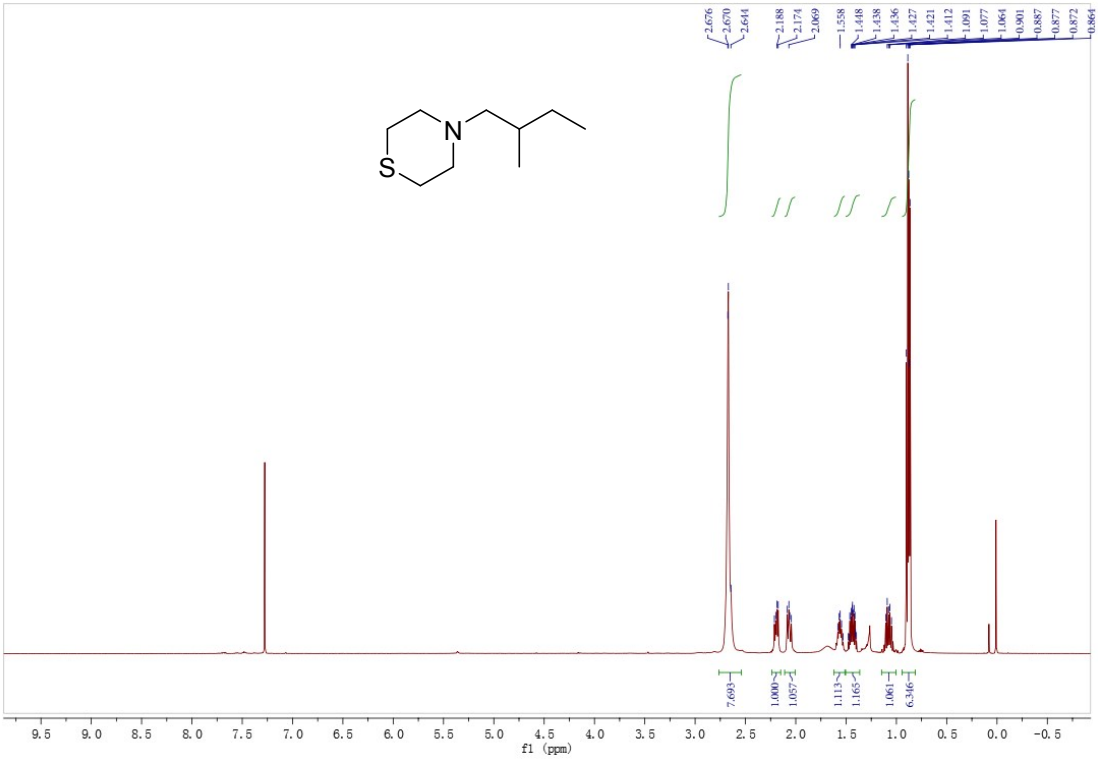


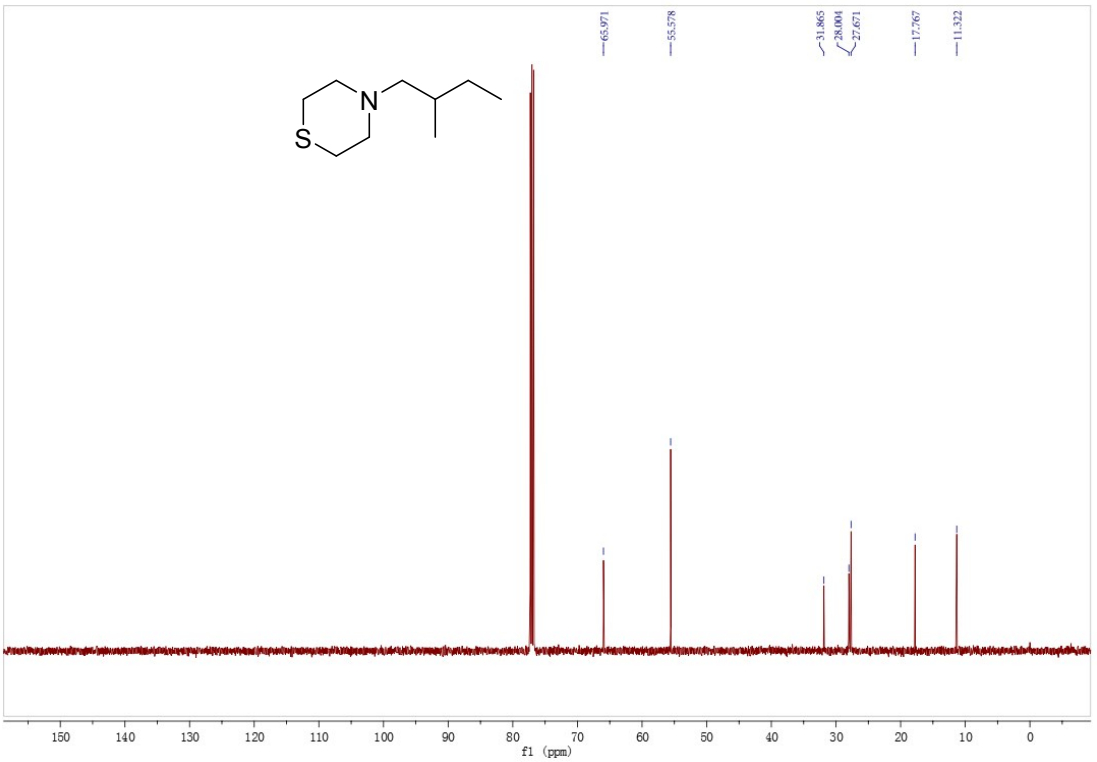
4-hexylthiomorpholine (**3bd**)



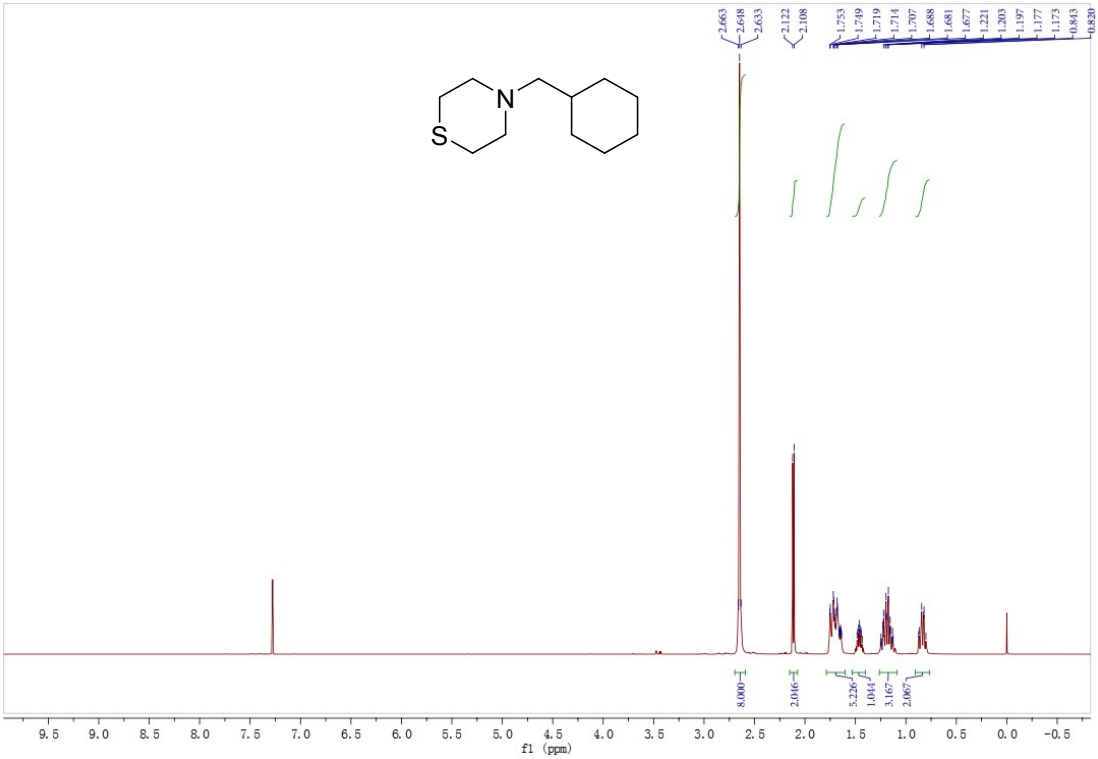


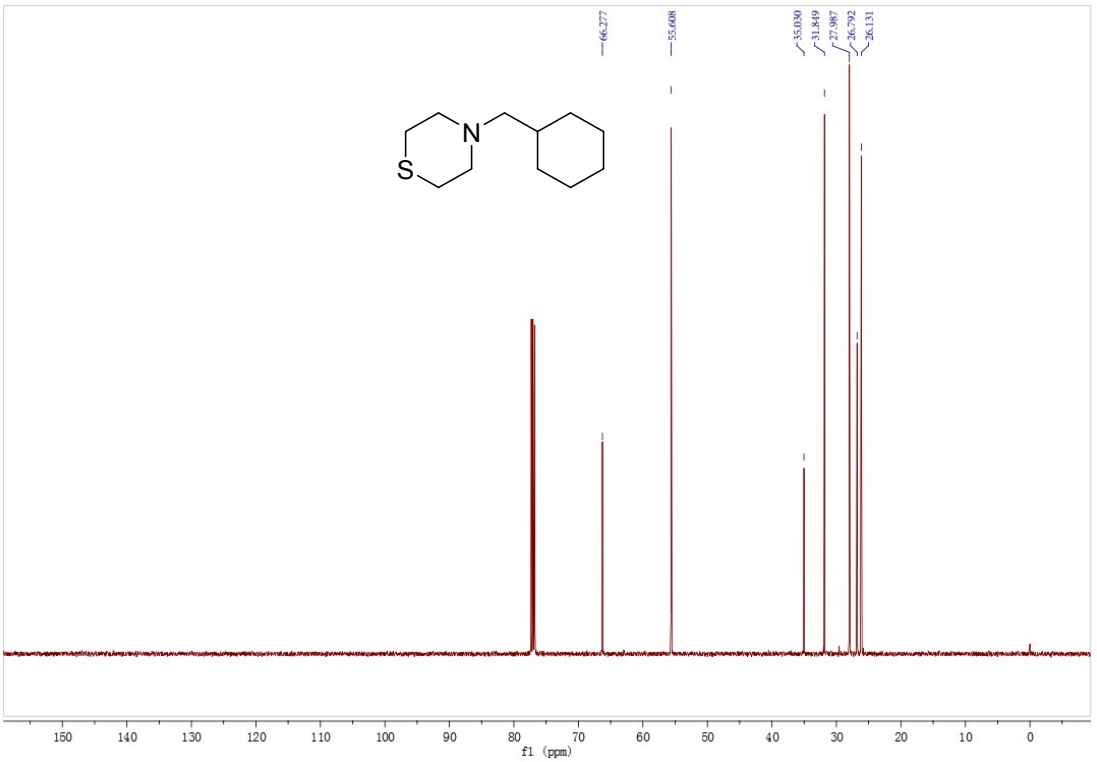
4-(2-methylbutyl)thiomorpholine (**3be**)



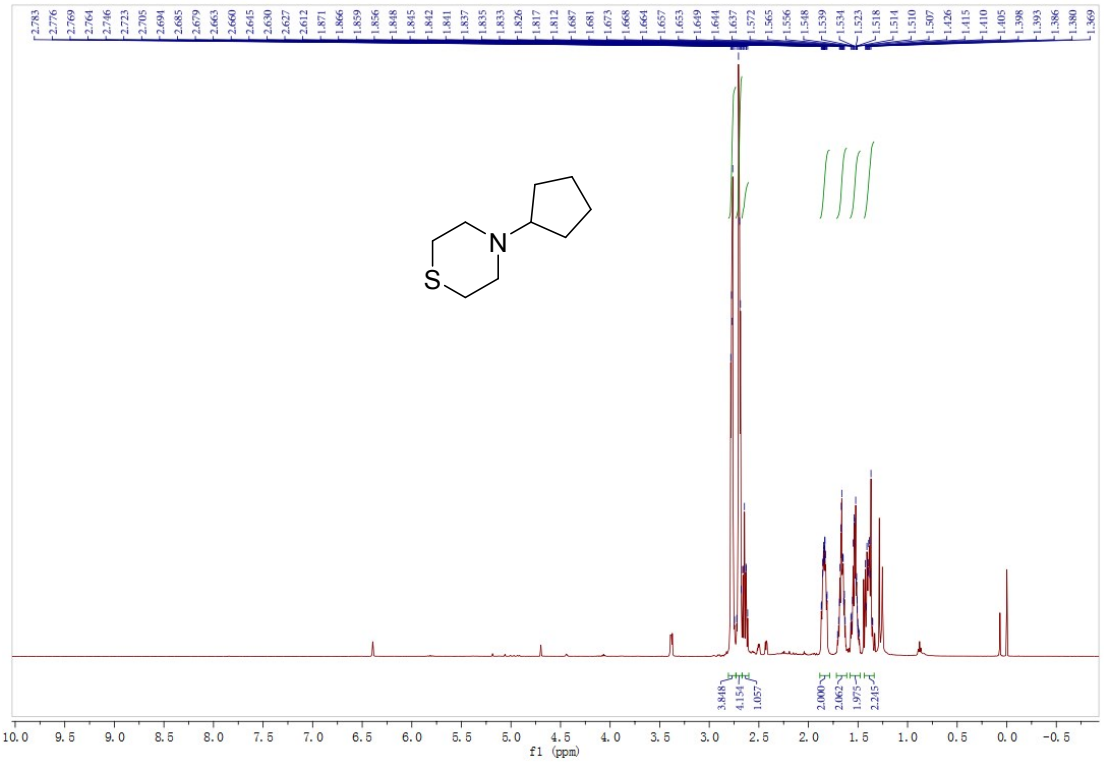


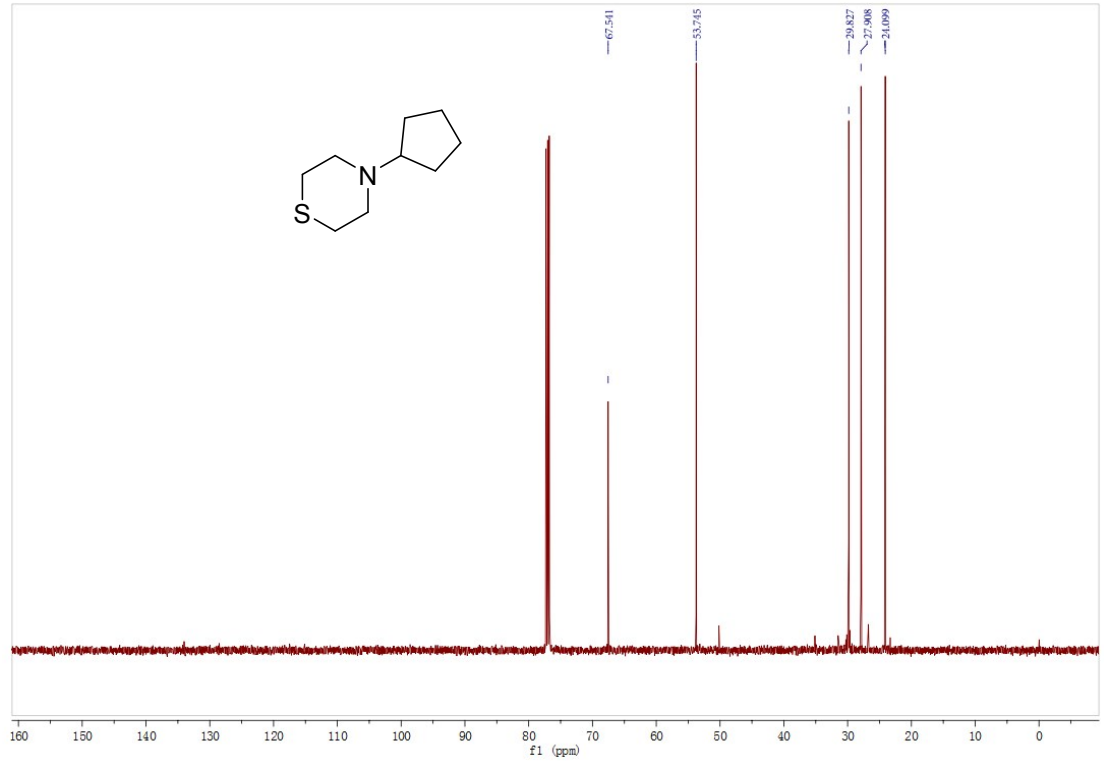
4-(cyclohexylmethyl)thiomorpholine (**3bf**)



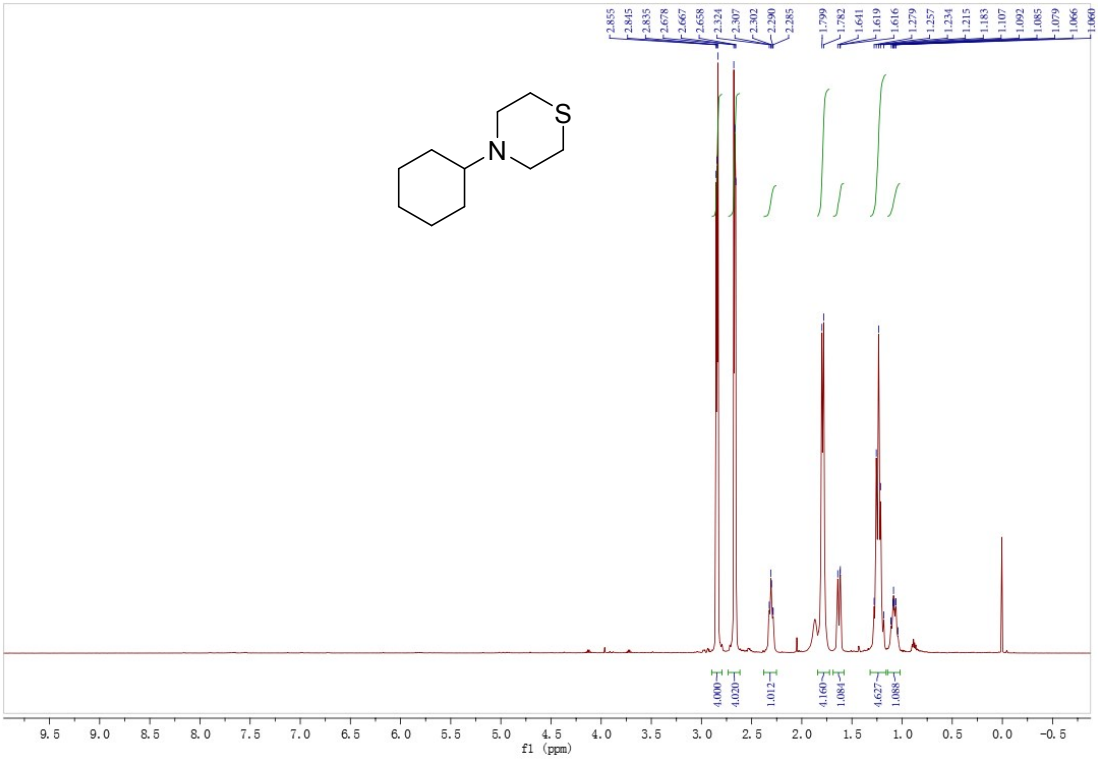


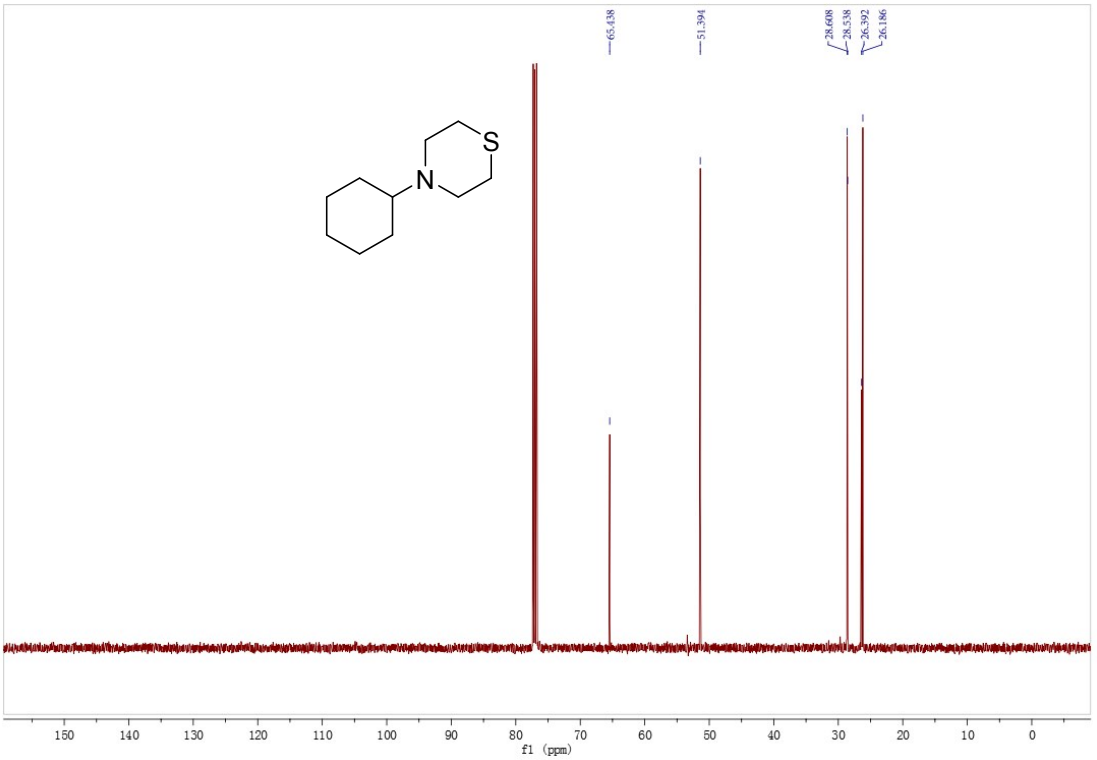
4-cyclopentylthiomorpholine (**3bg**)



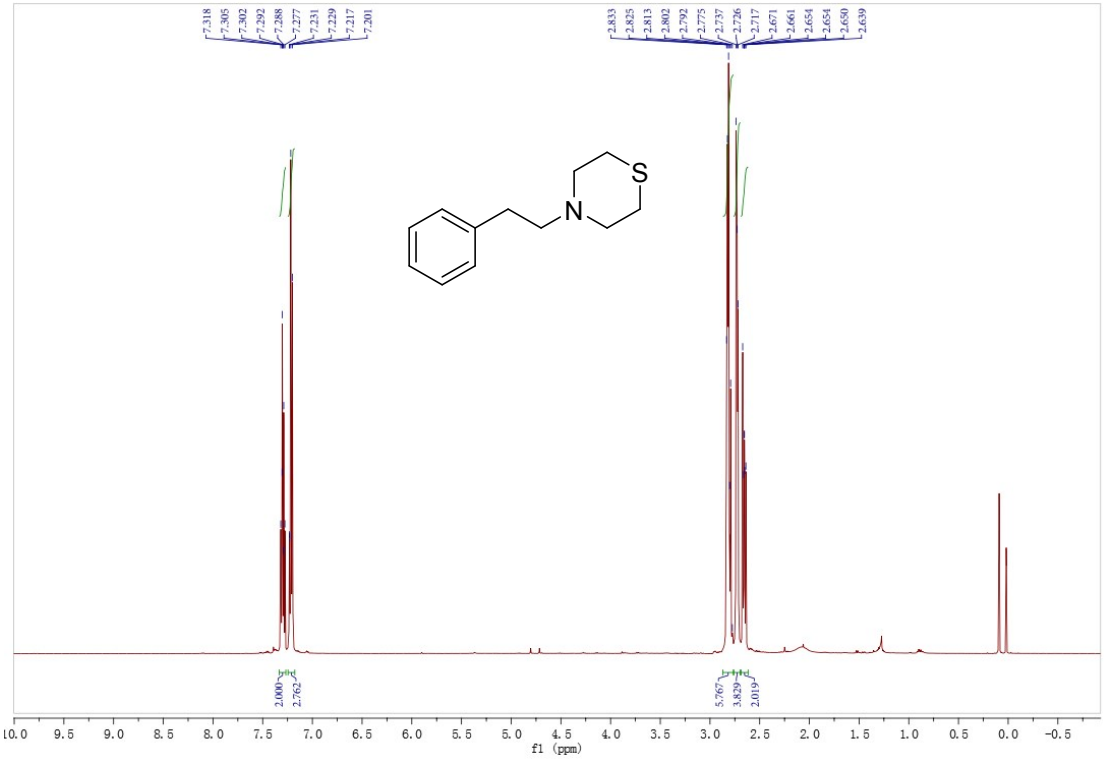


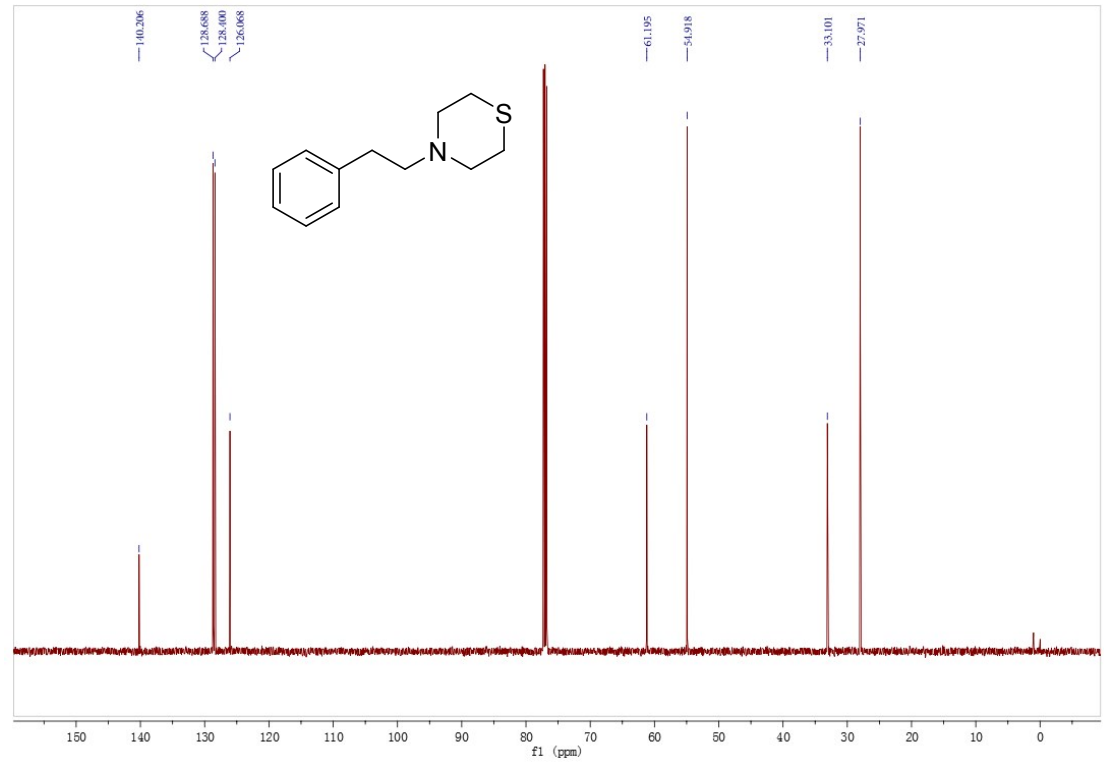
4-cyclohexylthiomorpholine (**3bh**)



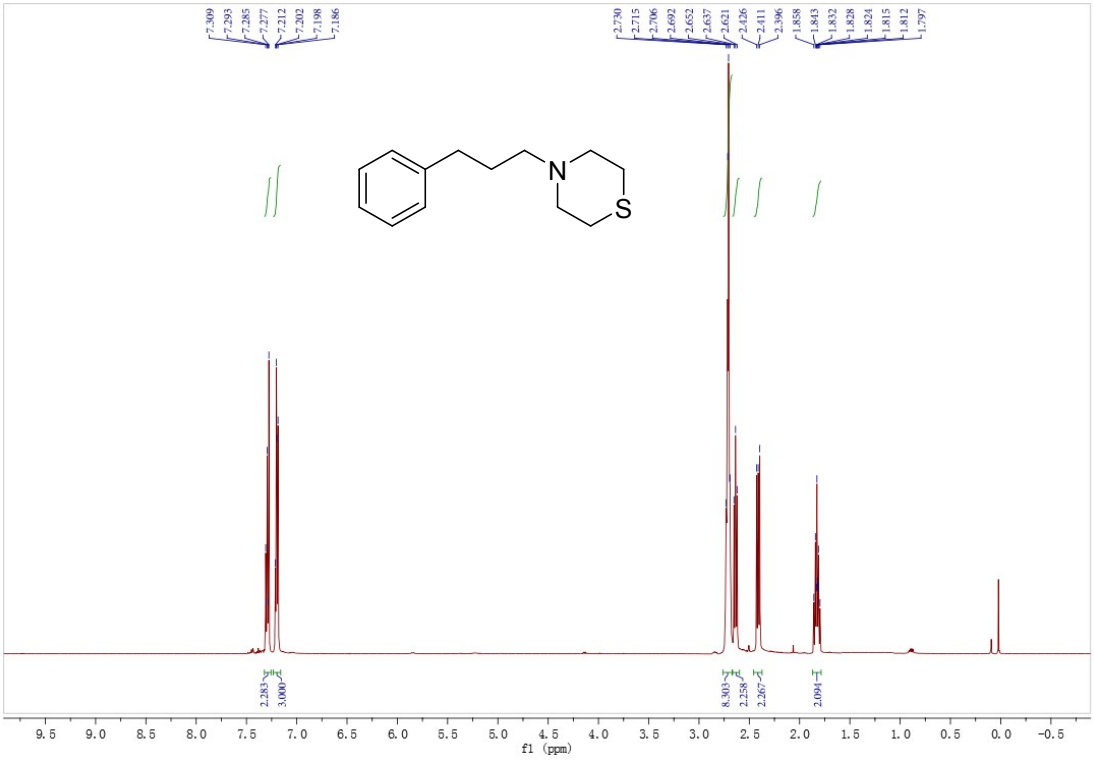


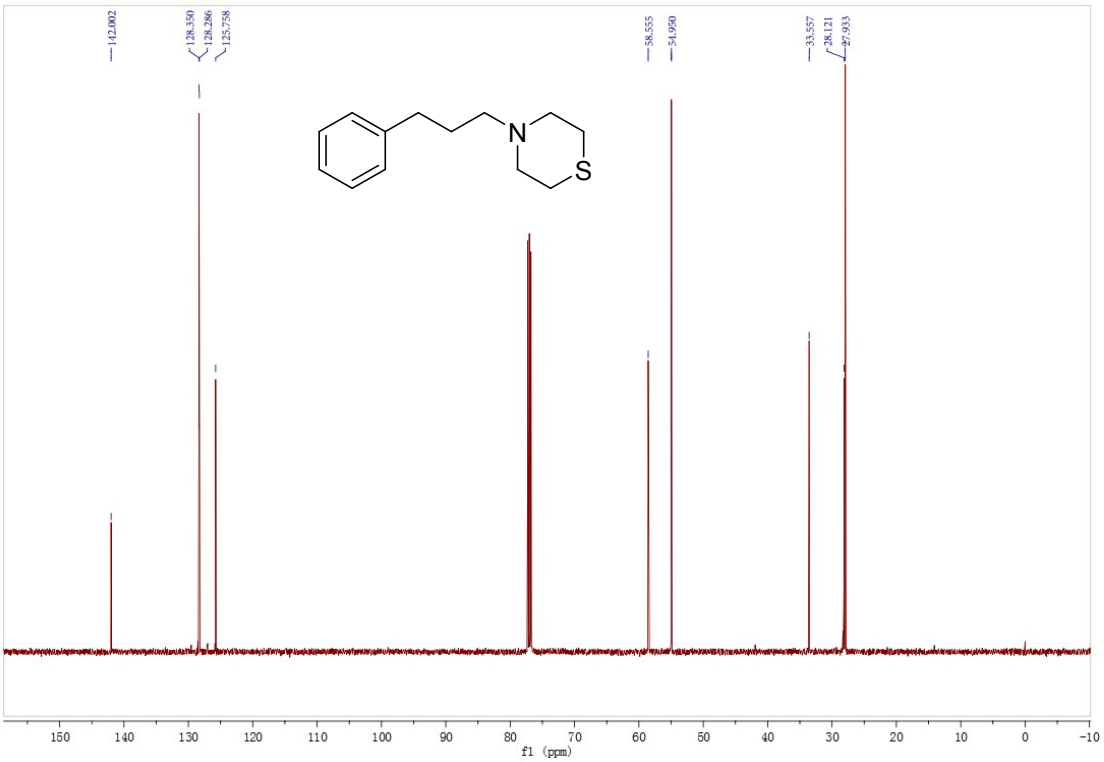
4-phenethylthiomorpholine (**3bi**)



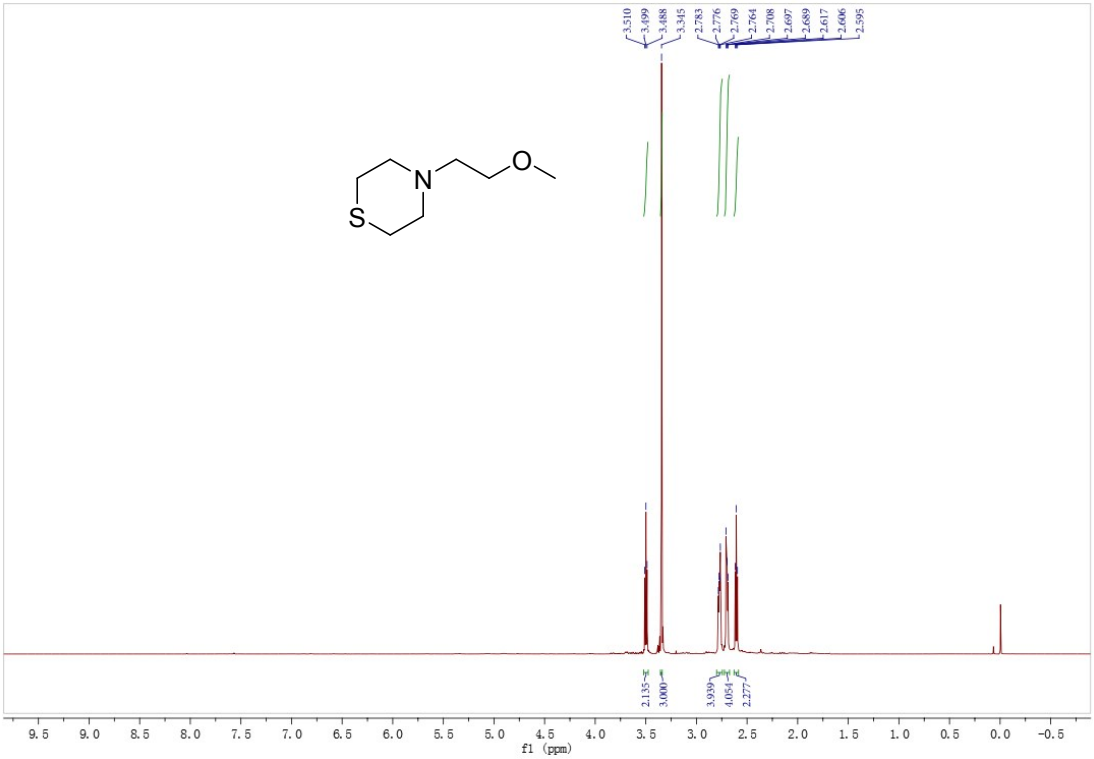


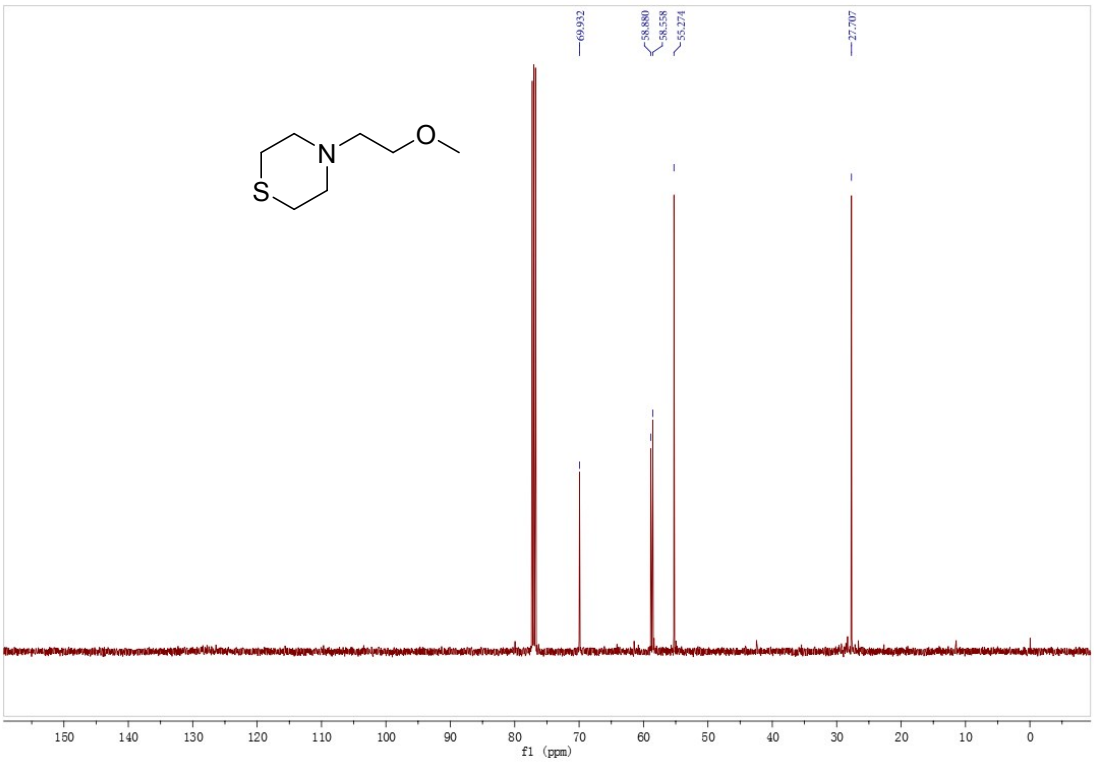
4-(3-phenylpropyl)thiomorpholine (**3bj**)



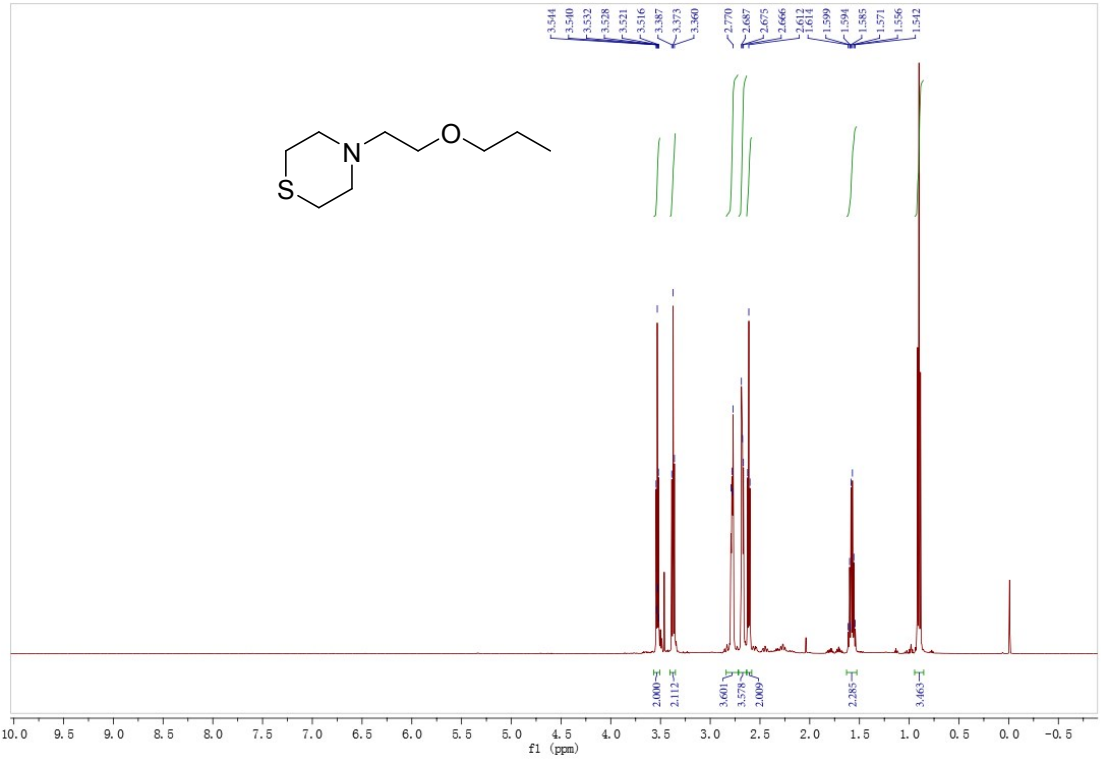


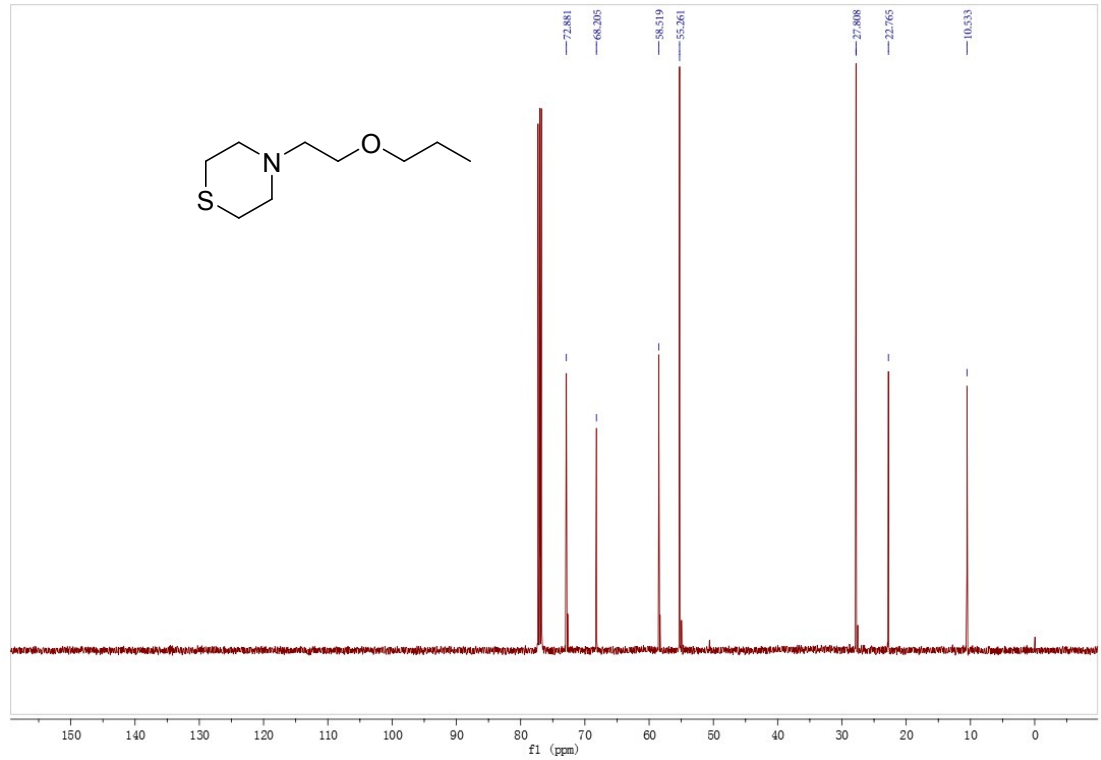
4-(2-methoxyethyl)thiomorpholine (**3bk**)



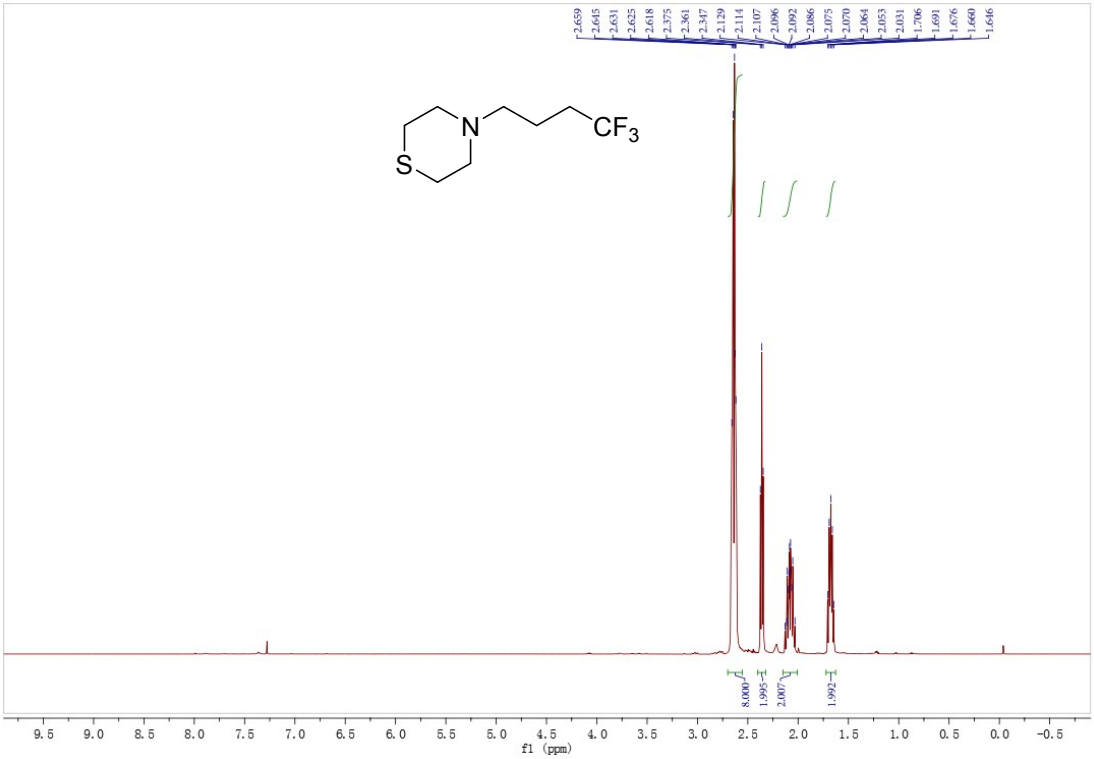


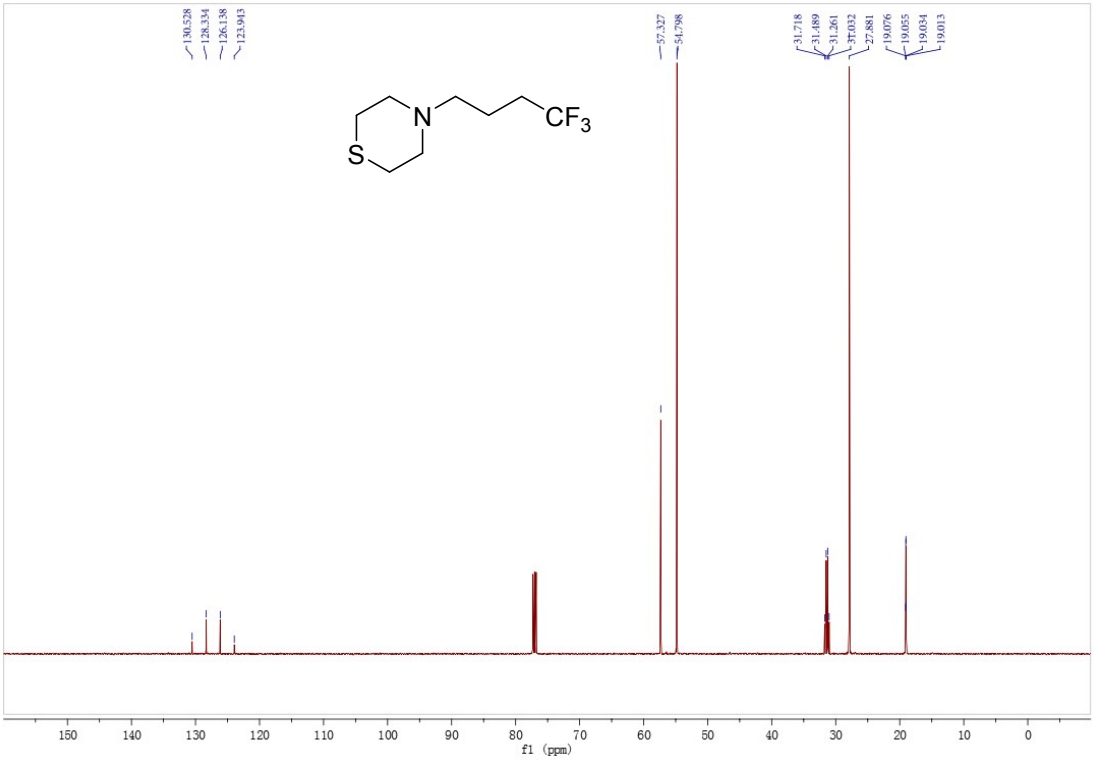
4-(2-propoxyethyl)thiomorpholine (**3bl**)



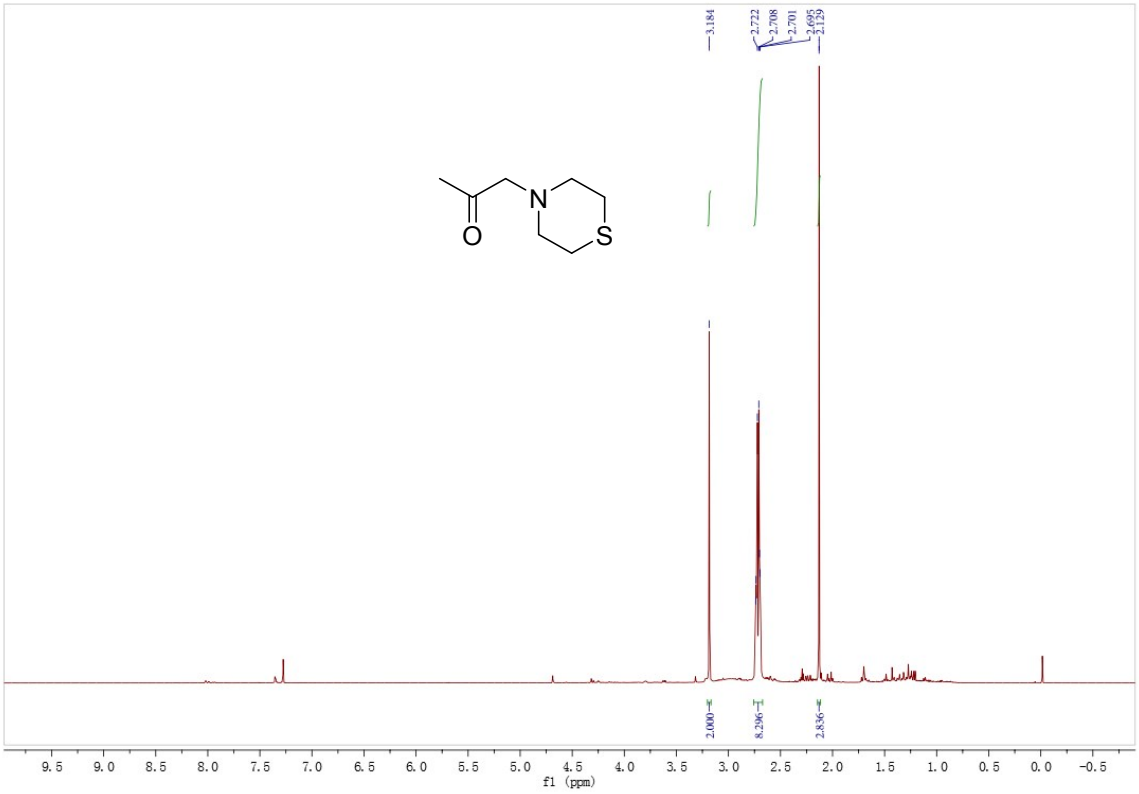


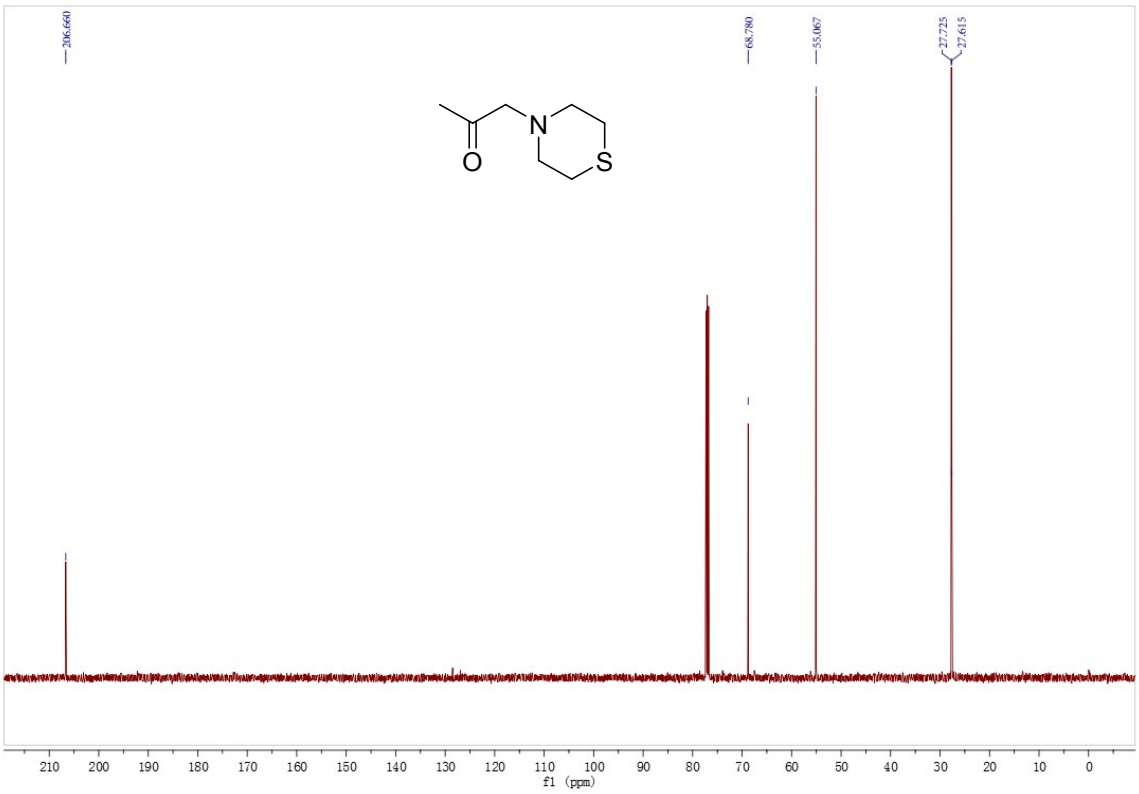
4-(4,4,4-trifluorobutyl)thiomorpholine (**3bm**)



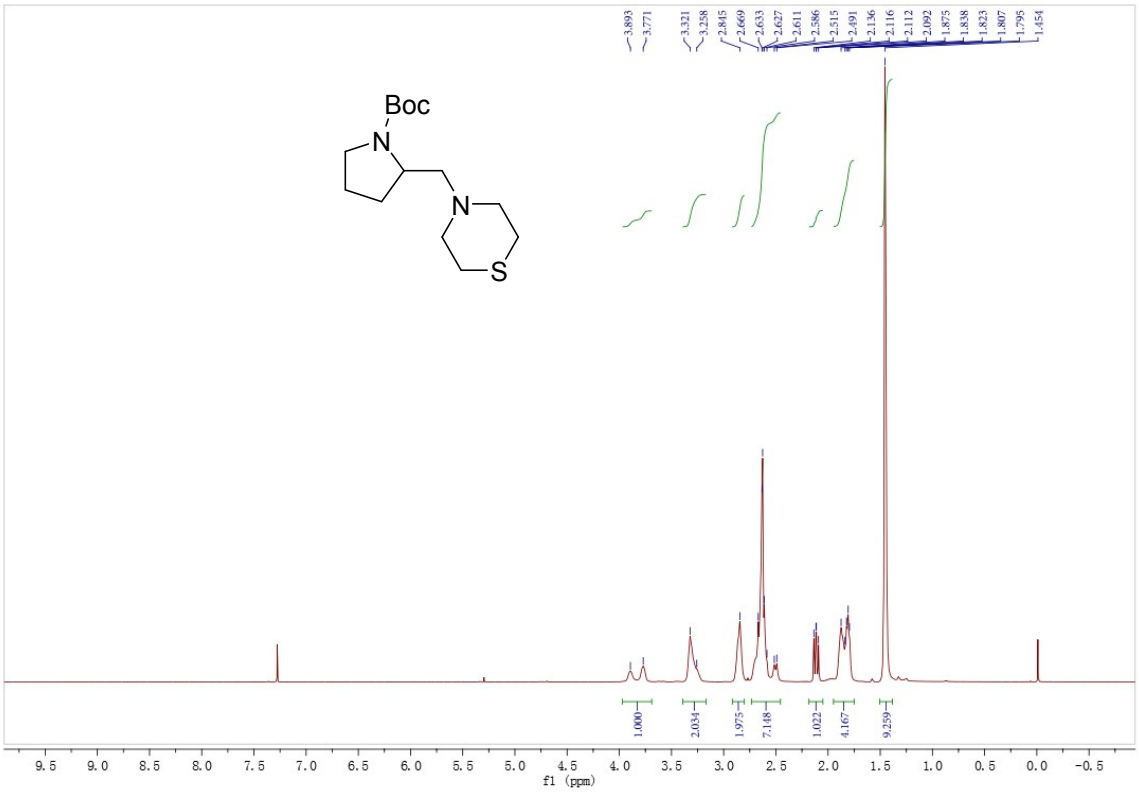


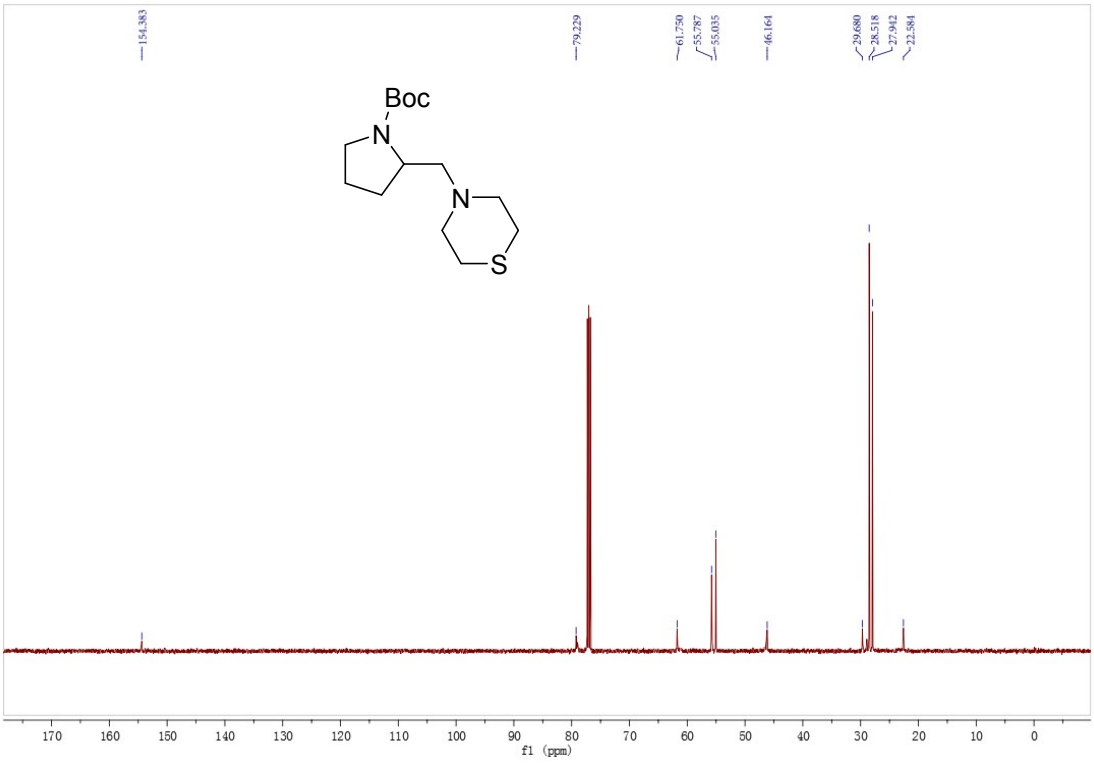
1-thiomorpholinopropan-2-one (**3bn**)



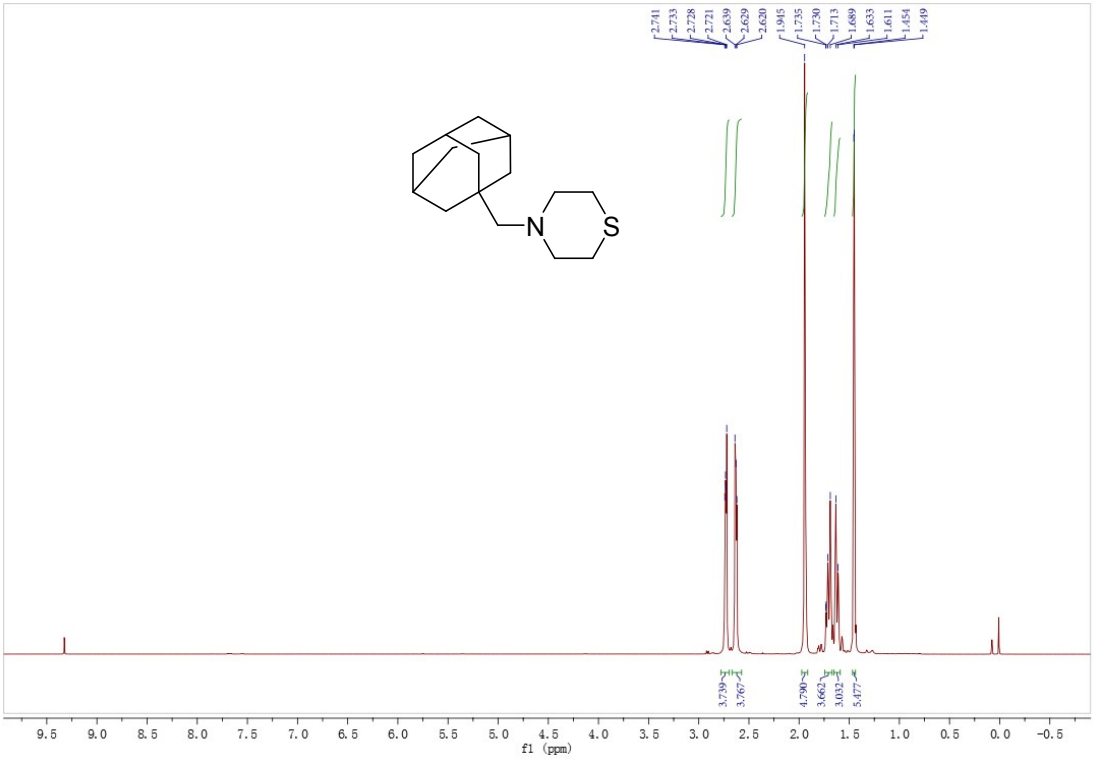


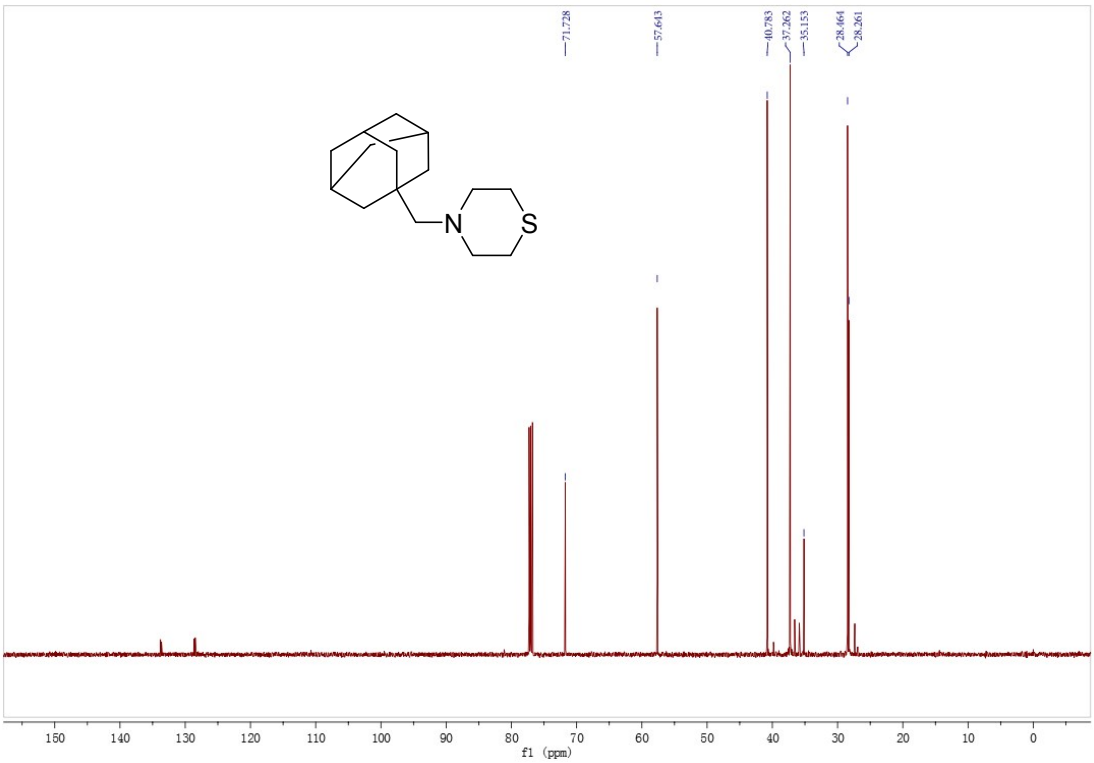
tert-butyl 2-(thiomorpholinomethyl)pyrrolidine-1-carboxylate (**3bo**)



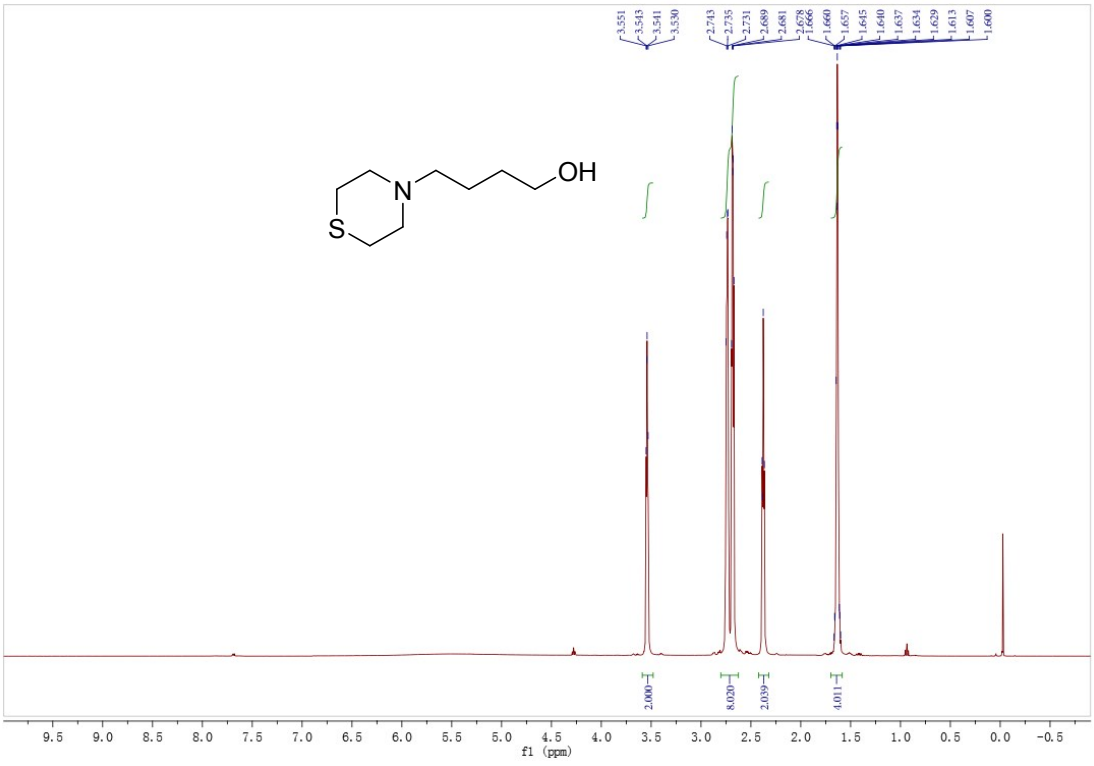


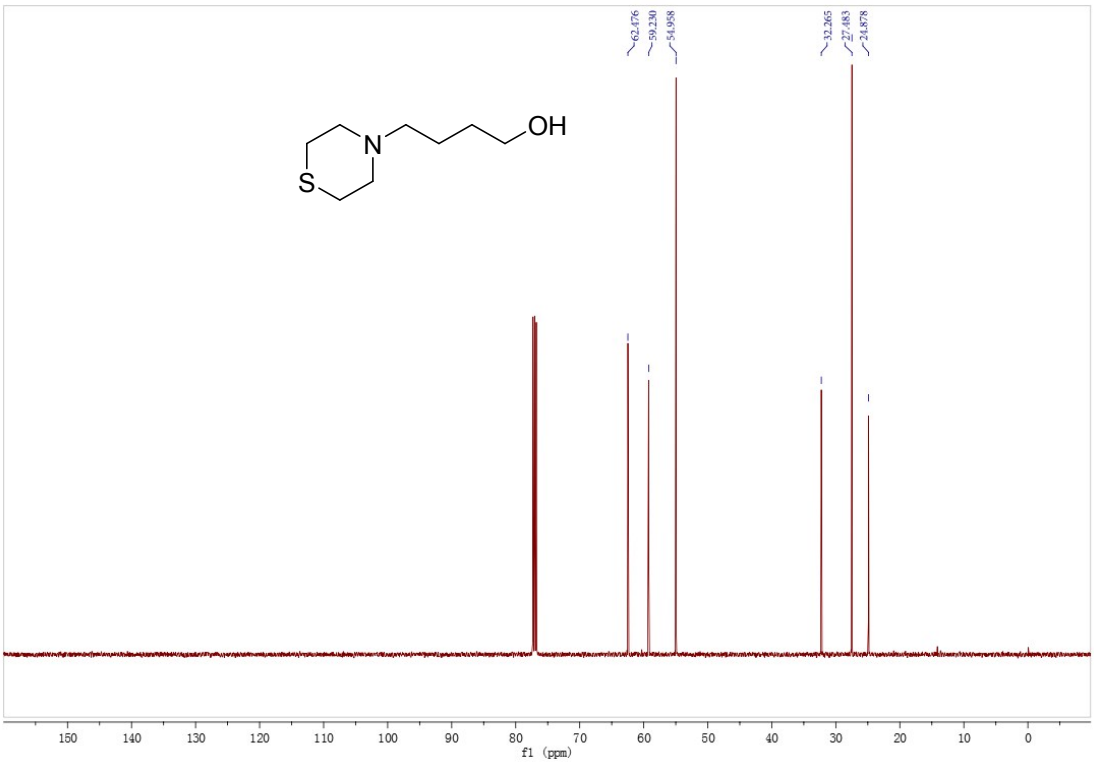
4-(adamantan-1-ylmethyl)thiomorpholine (**3bp**)



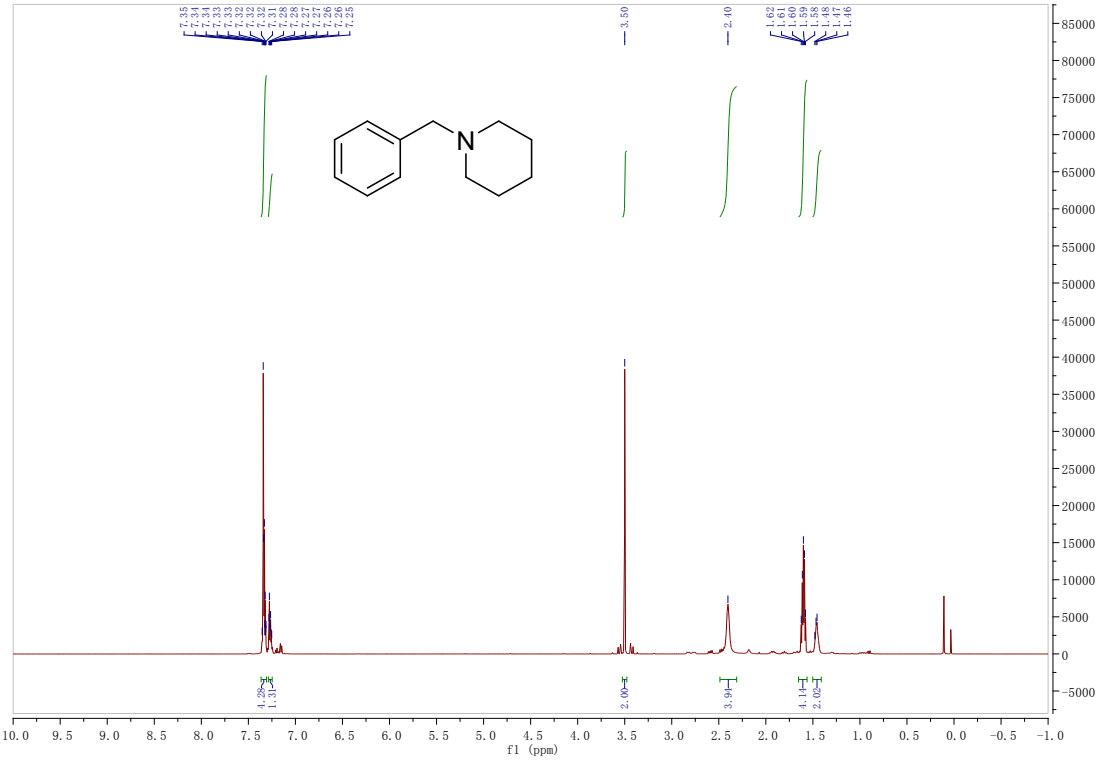


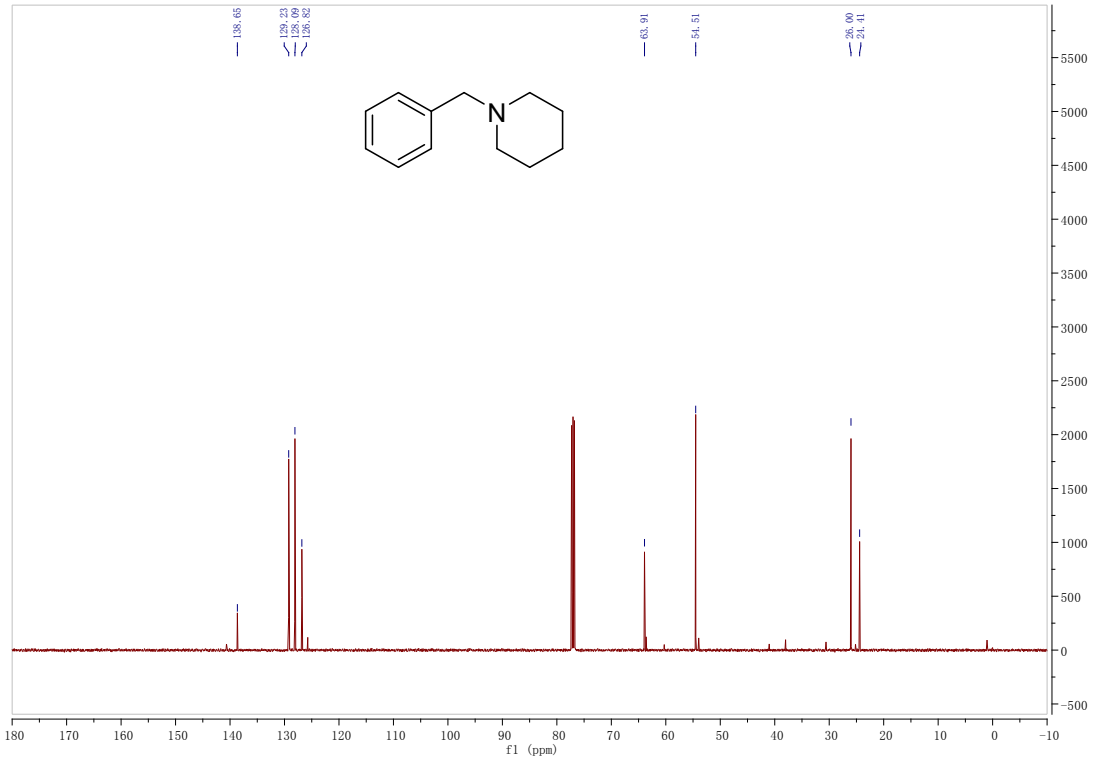
4-thiomorpholinobutan-1-ol (**3bq**)



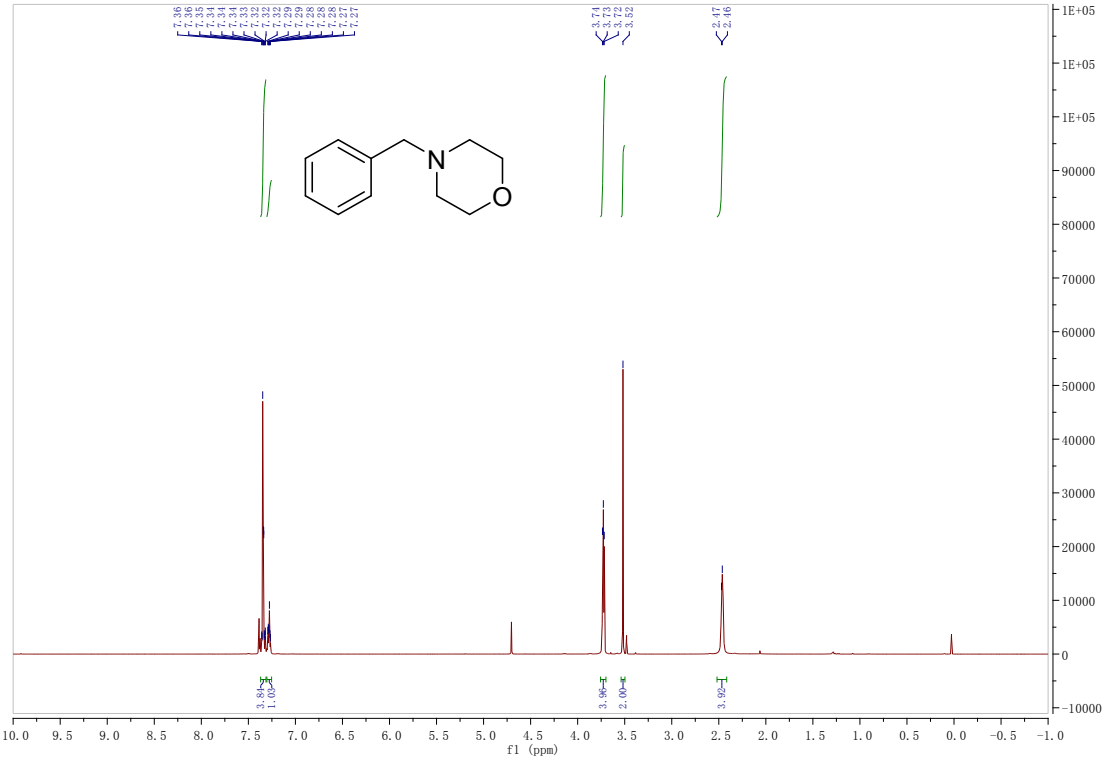


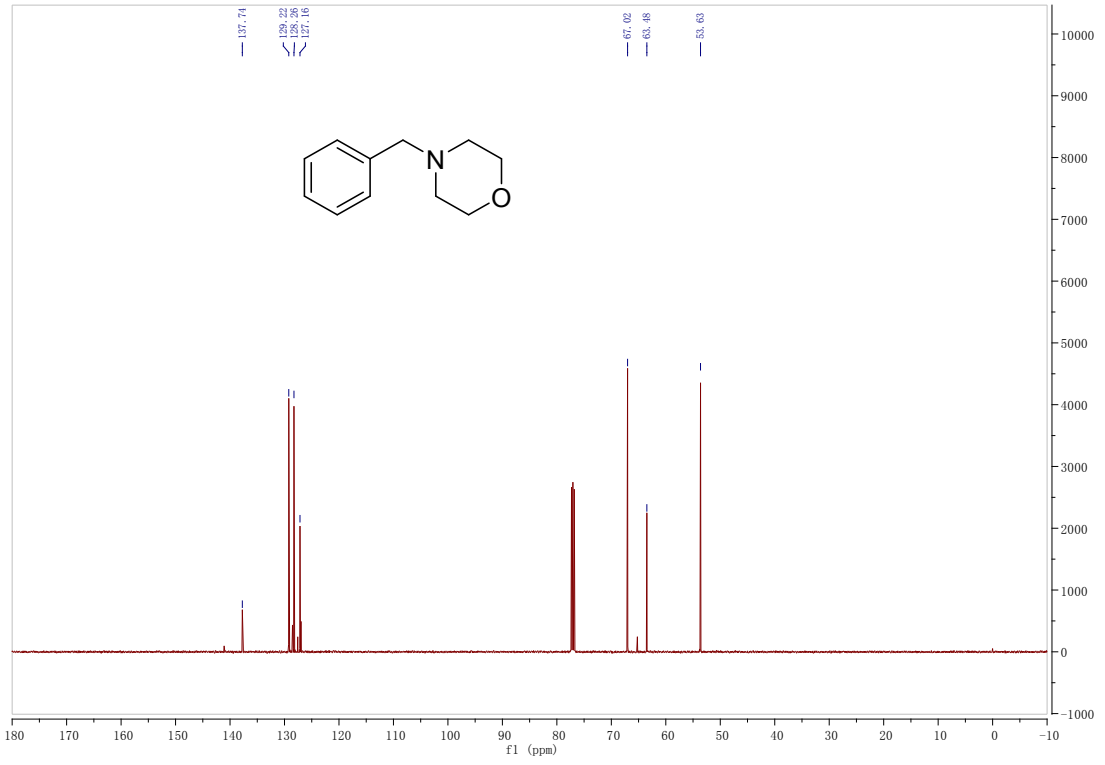
1-benzylpiperidine (**3ca**)



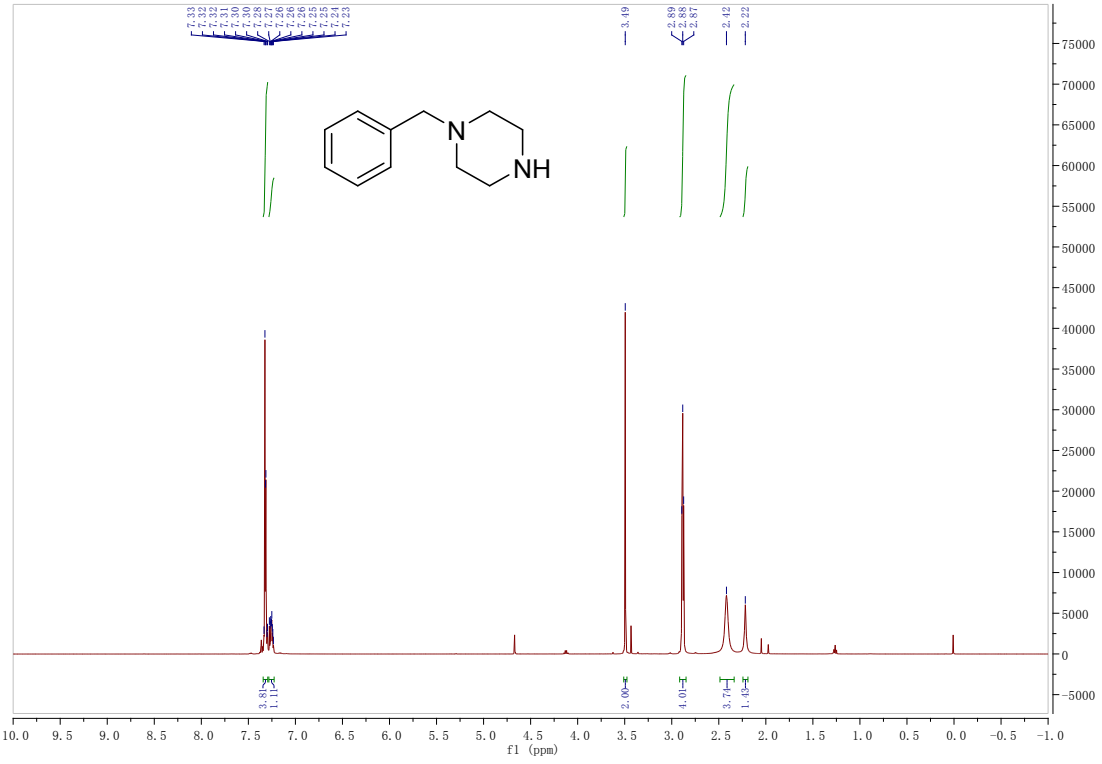


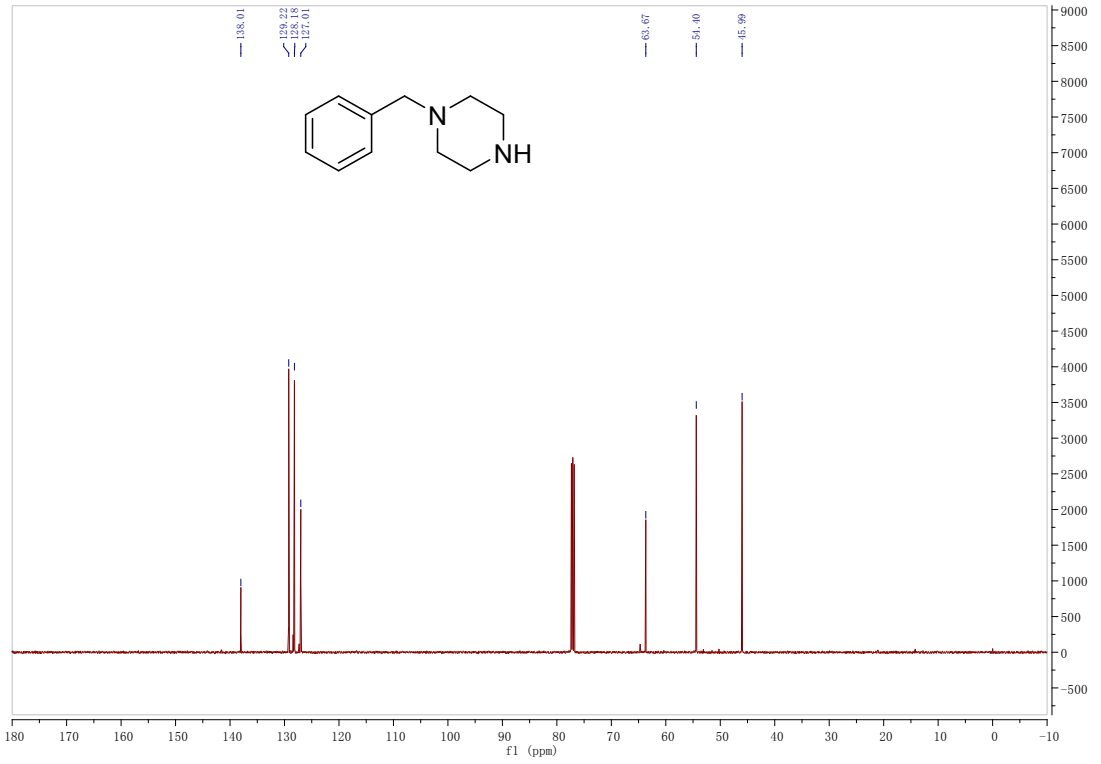
4-benzylmorpholine (**3cb**)



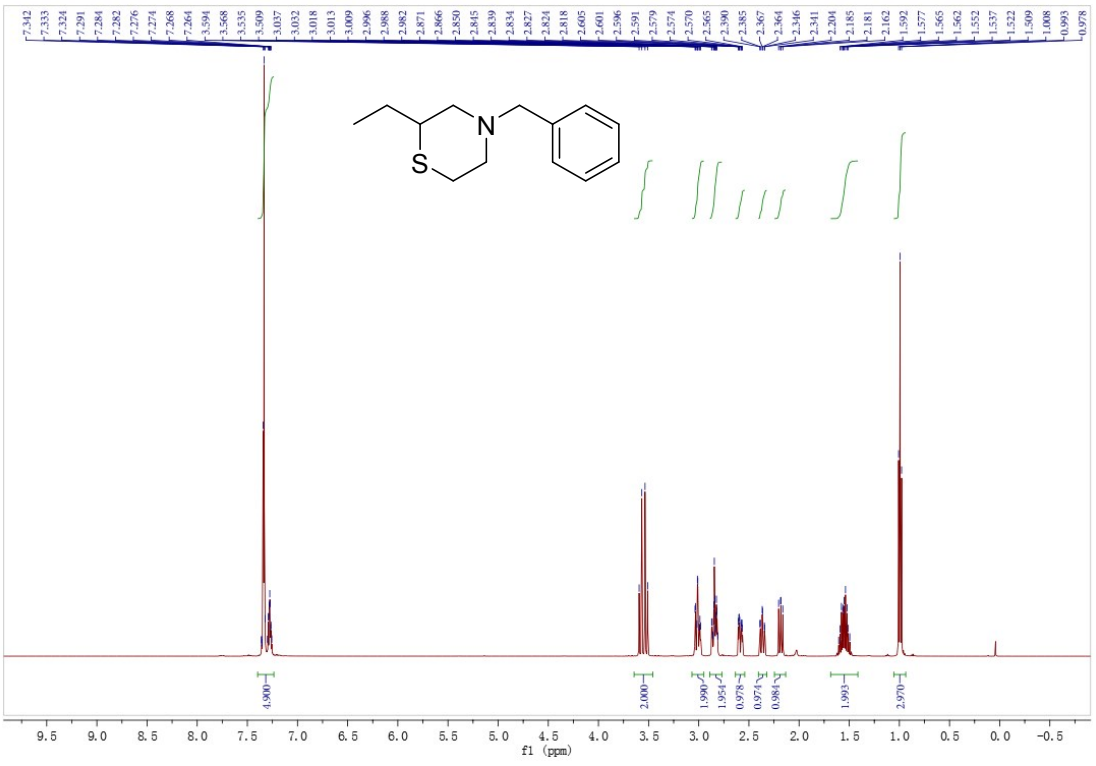


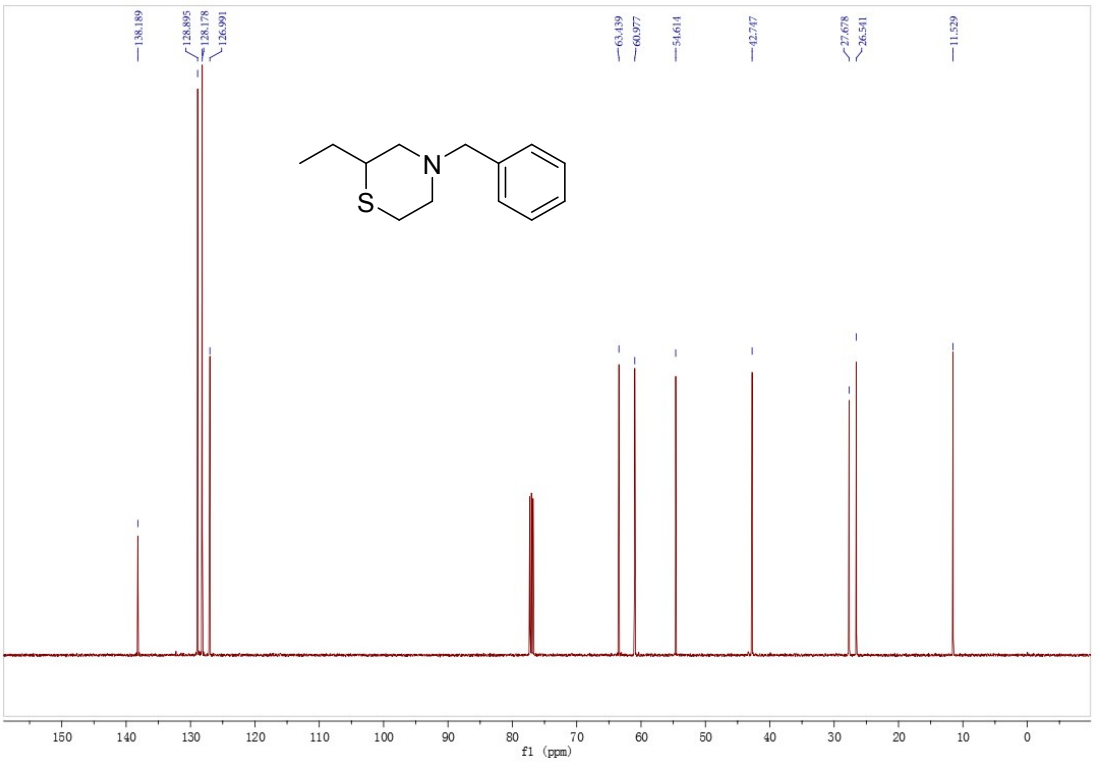
1-benzylpiperazine (**3cc**)



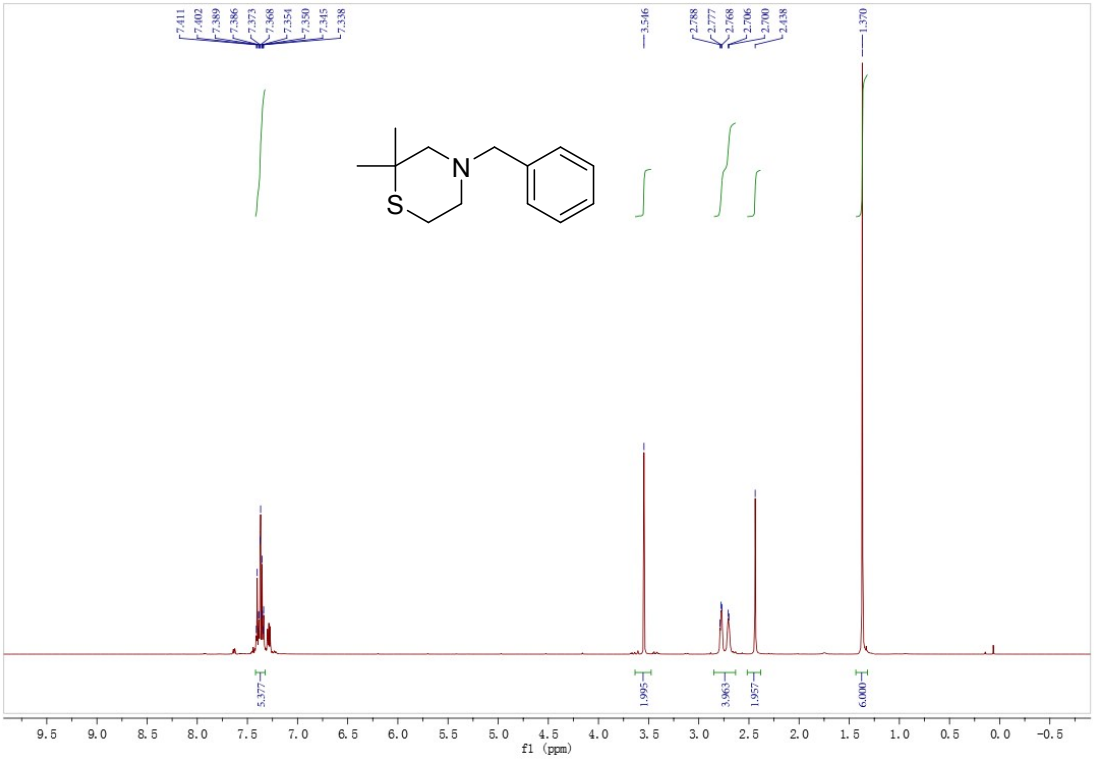


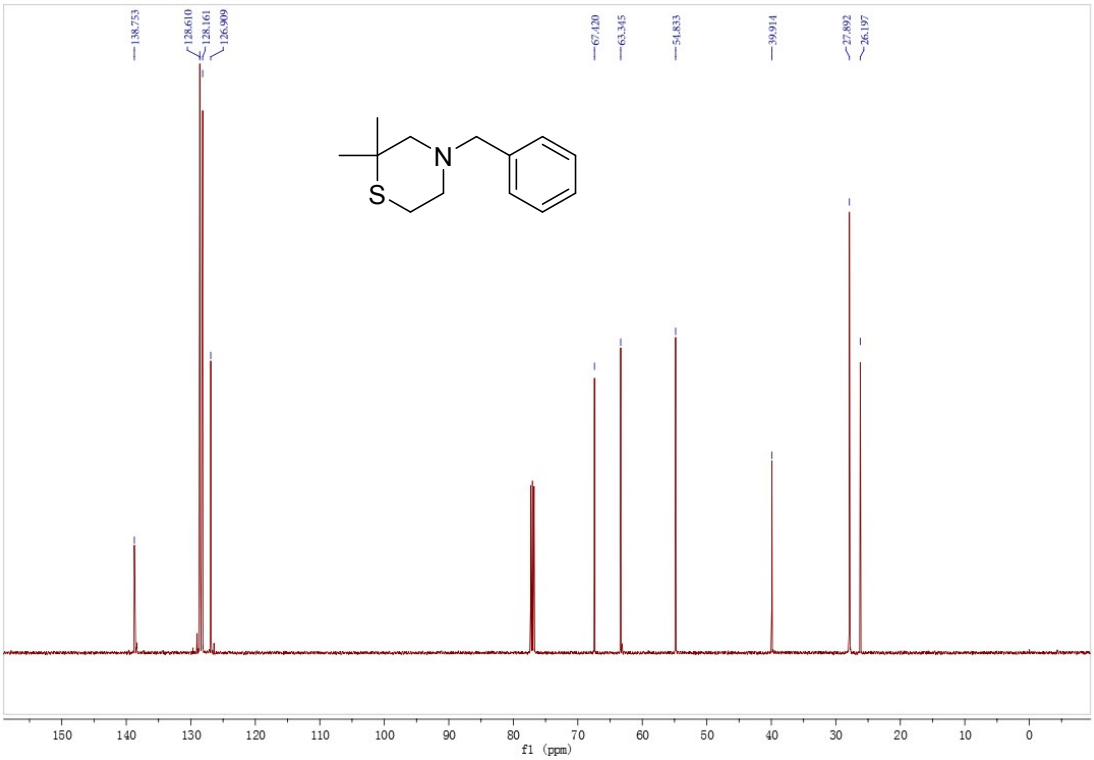
4-benzyl-2-ethylthiomorpholine (**3cd**)



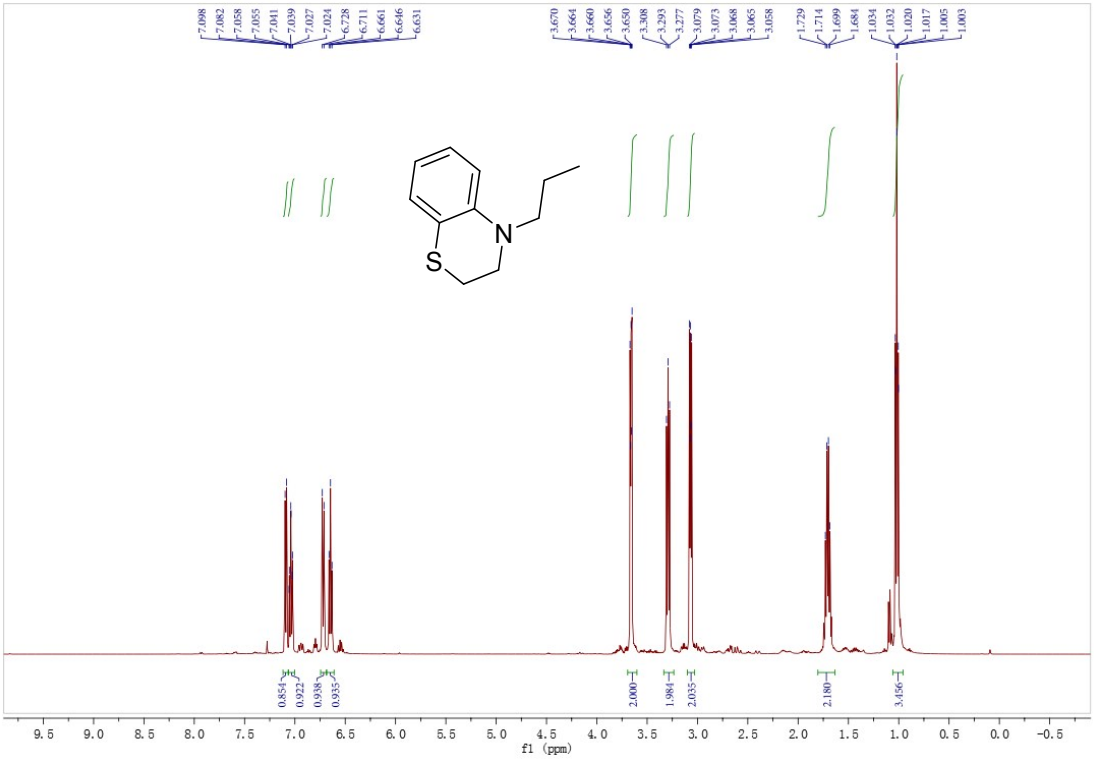


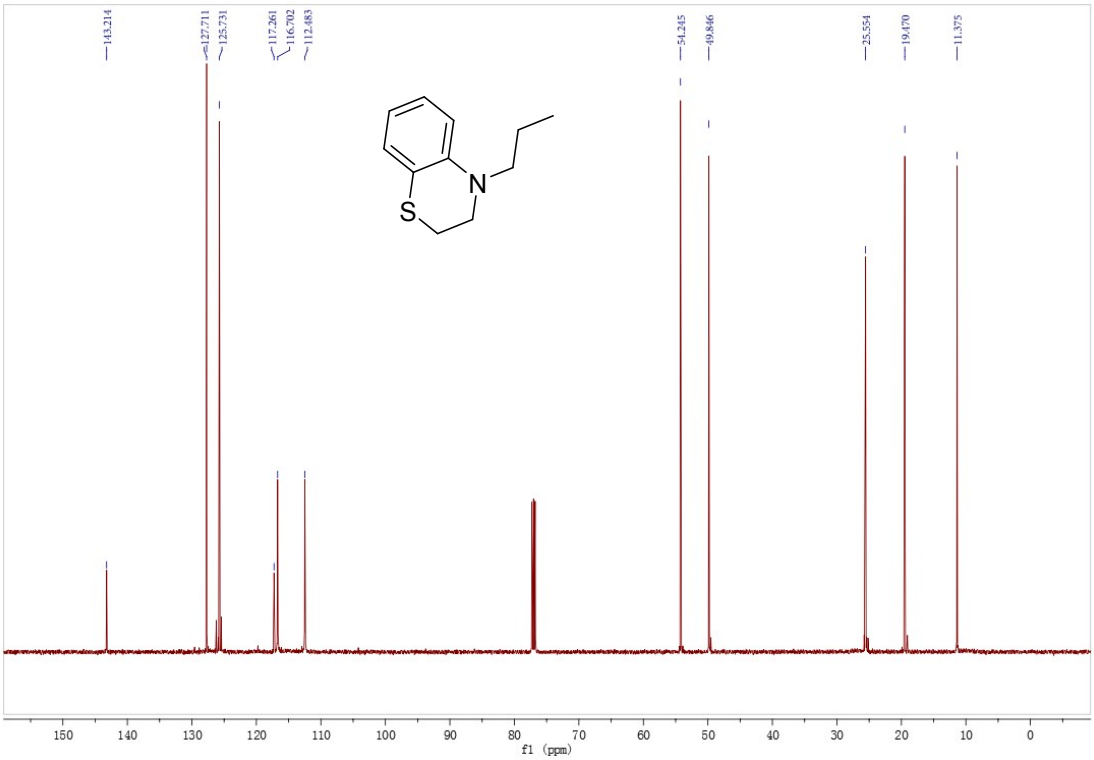
4-benzyl-2,2-dimethylthiomorpholine (**3ce**)



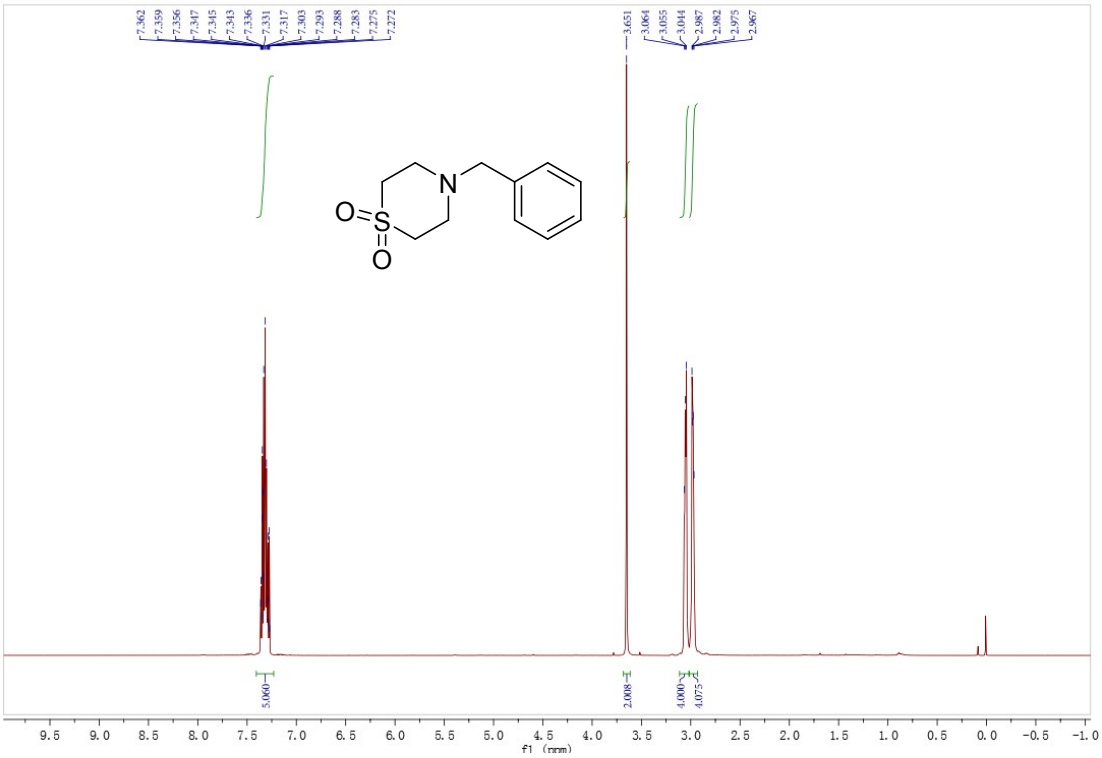


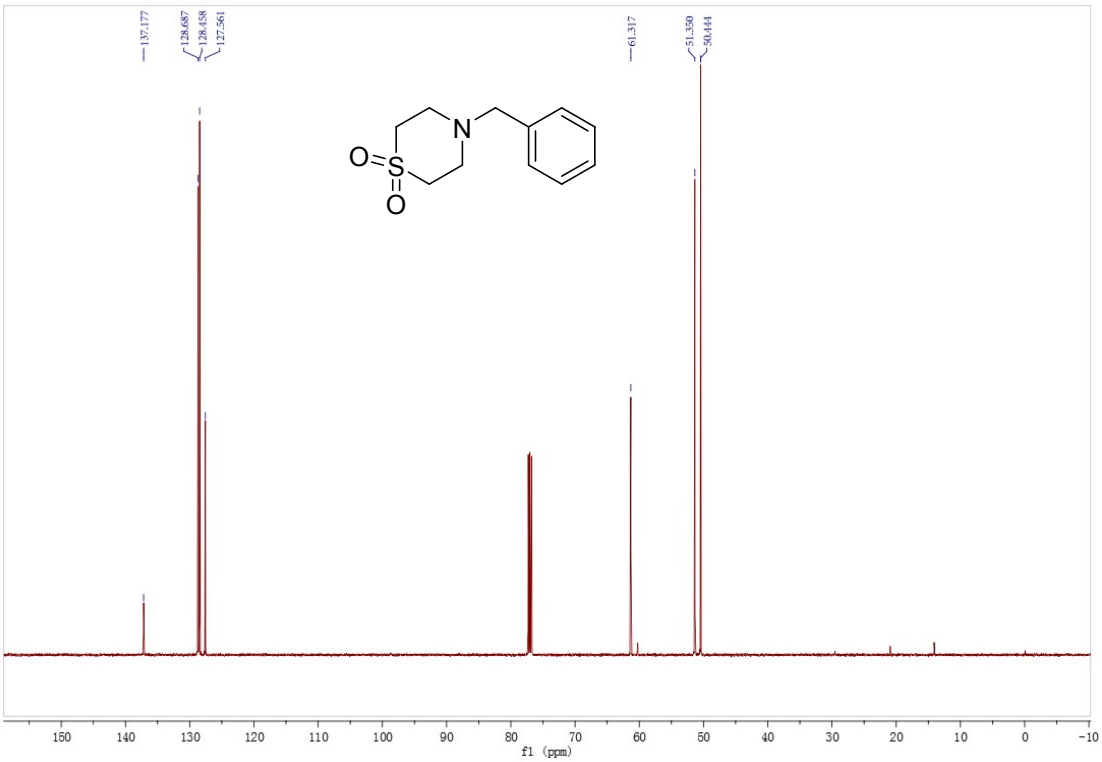
4-propyl-3,4-dihydro-2H-benzo[b][1,4]thiazine (**3cf**)



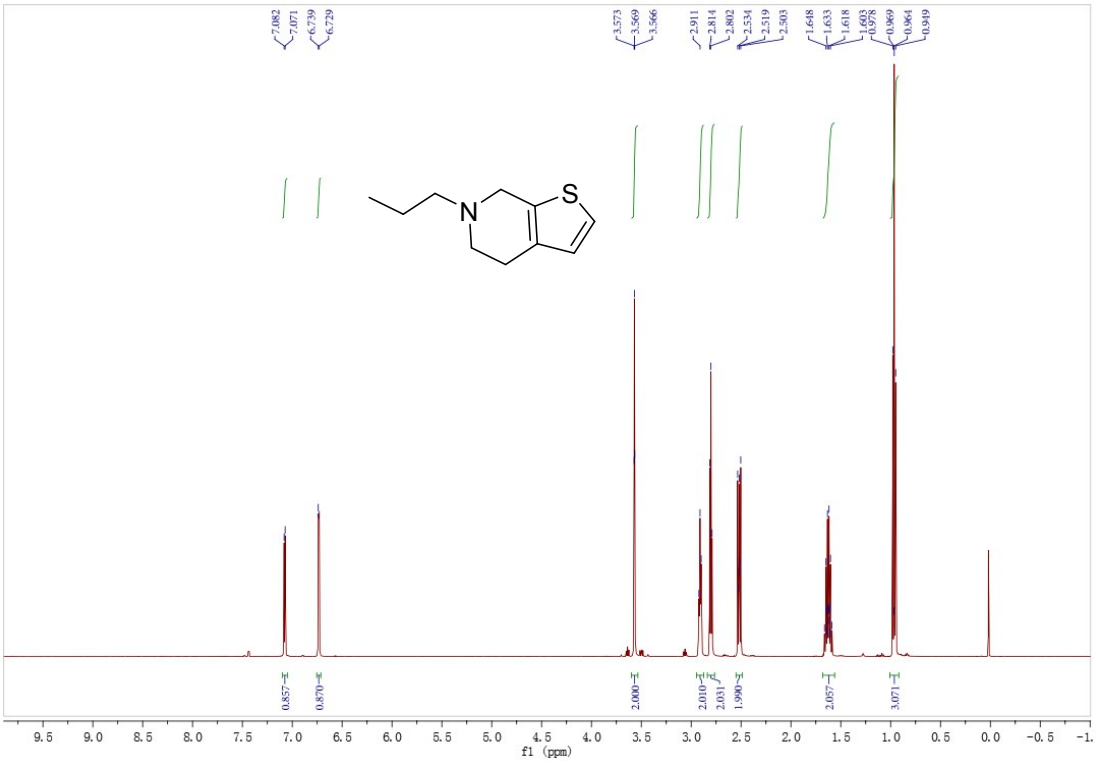


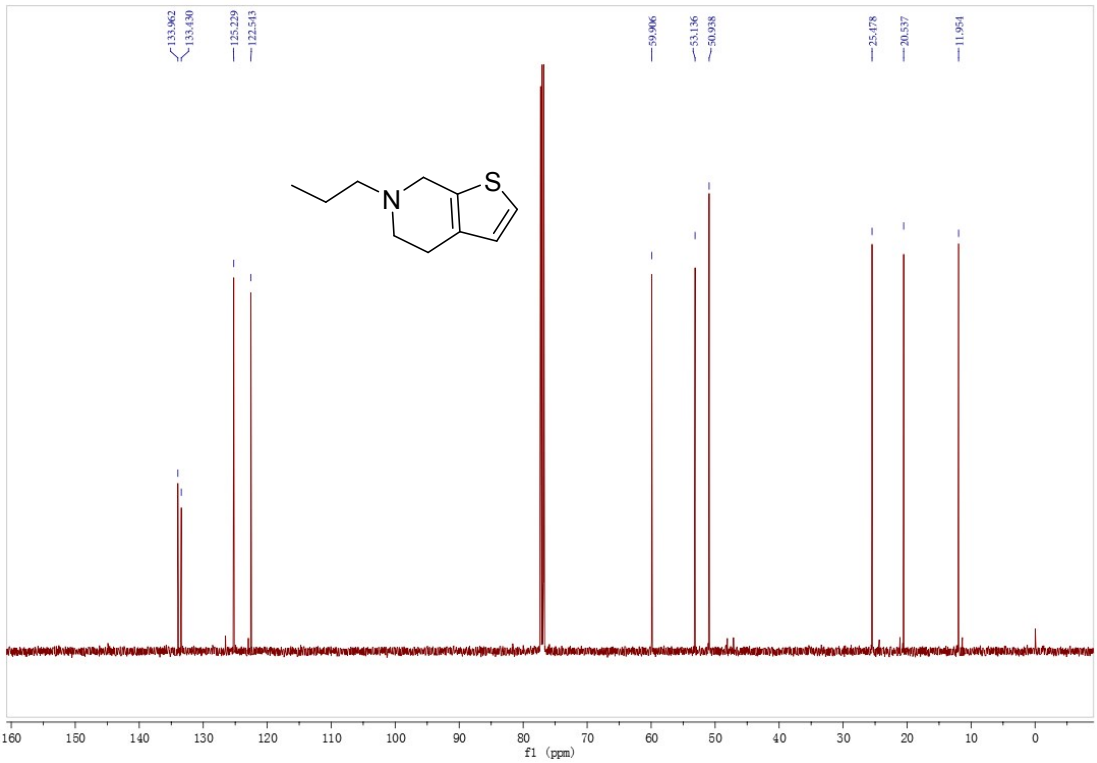
4-benzylthiomorpholine 1,1-dioxide (**3cg**)



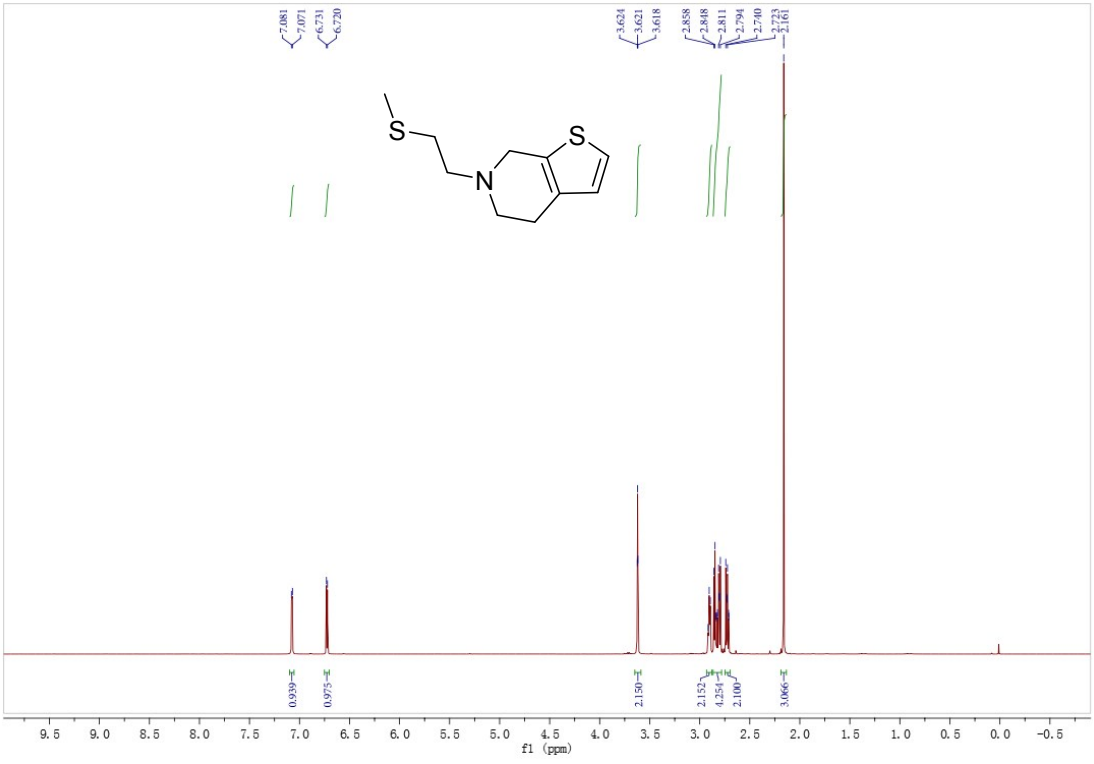


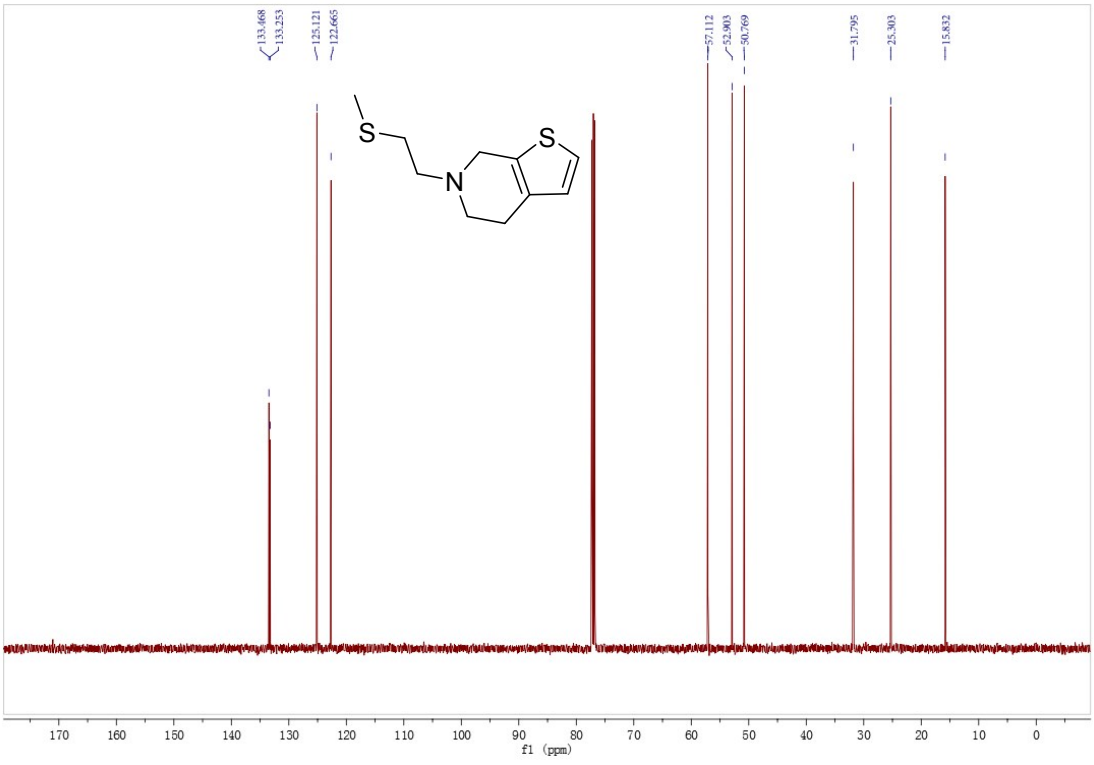
6-propyl-4,5,6,7-tetrahydrothieno[2,3-c]pyridine (**3ch**)



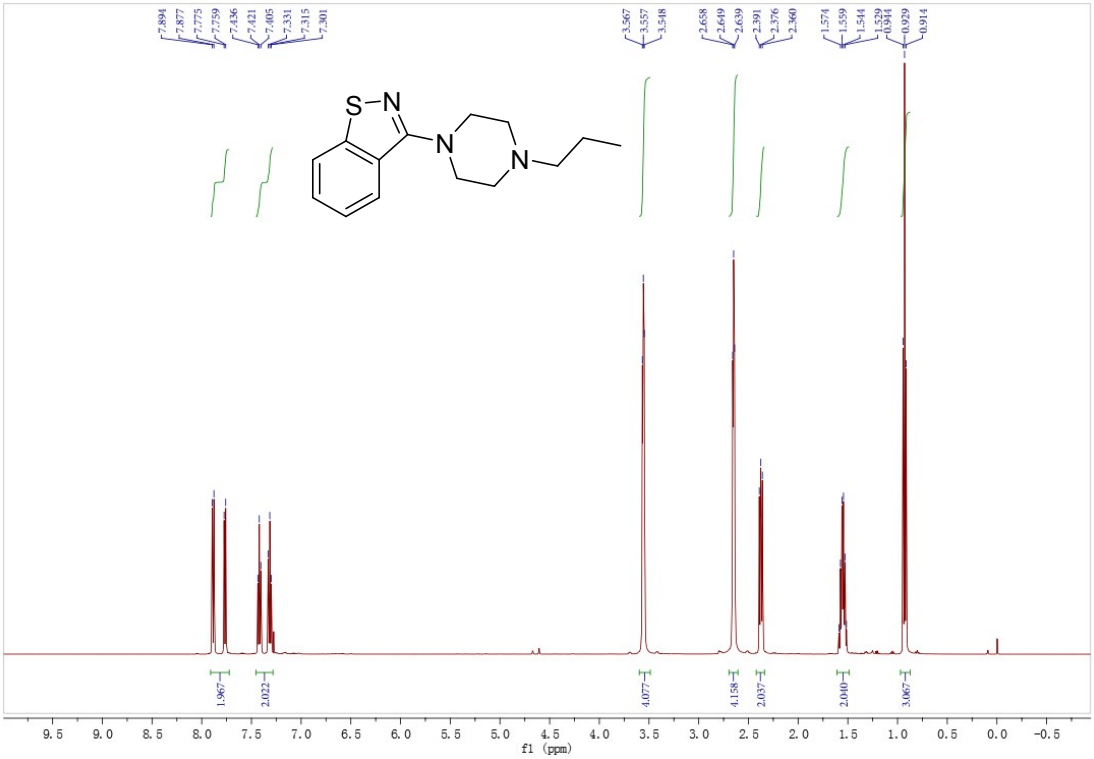


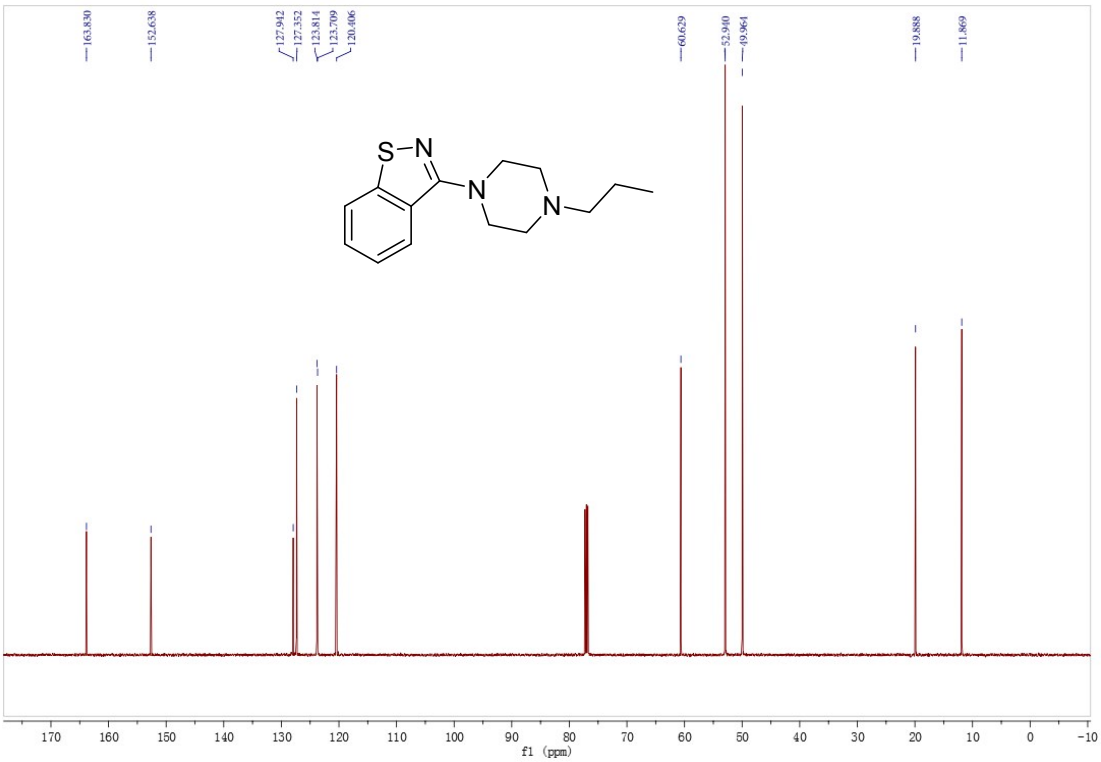
6-(2-(methylthio)ethyl)-4,5,6,7-tetrahydrothieno[2,3-c]pyridine (**3ci**)



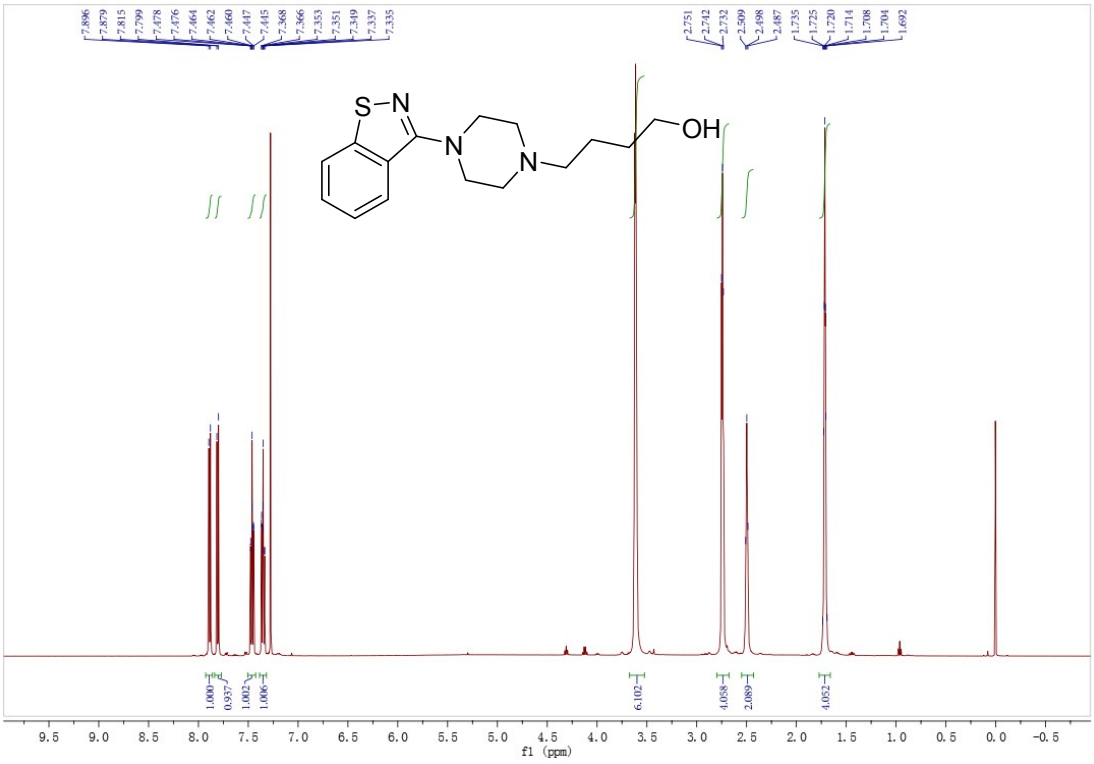


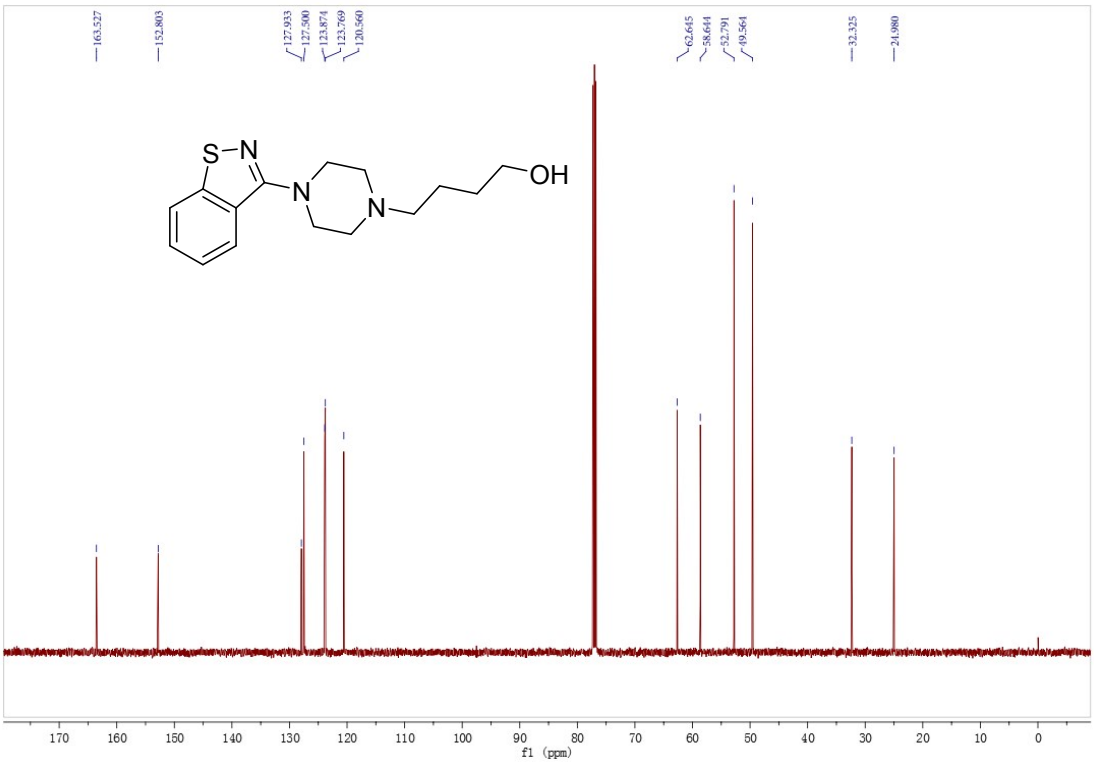
3-(4-propylpiperazin-1-yl)benzo[d]isothiazole (**3cj**)



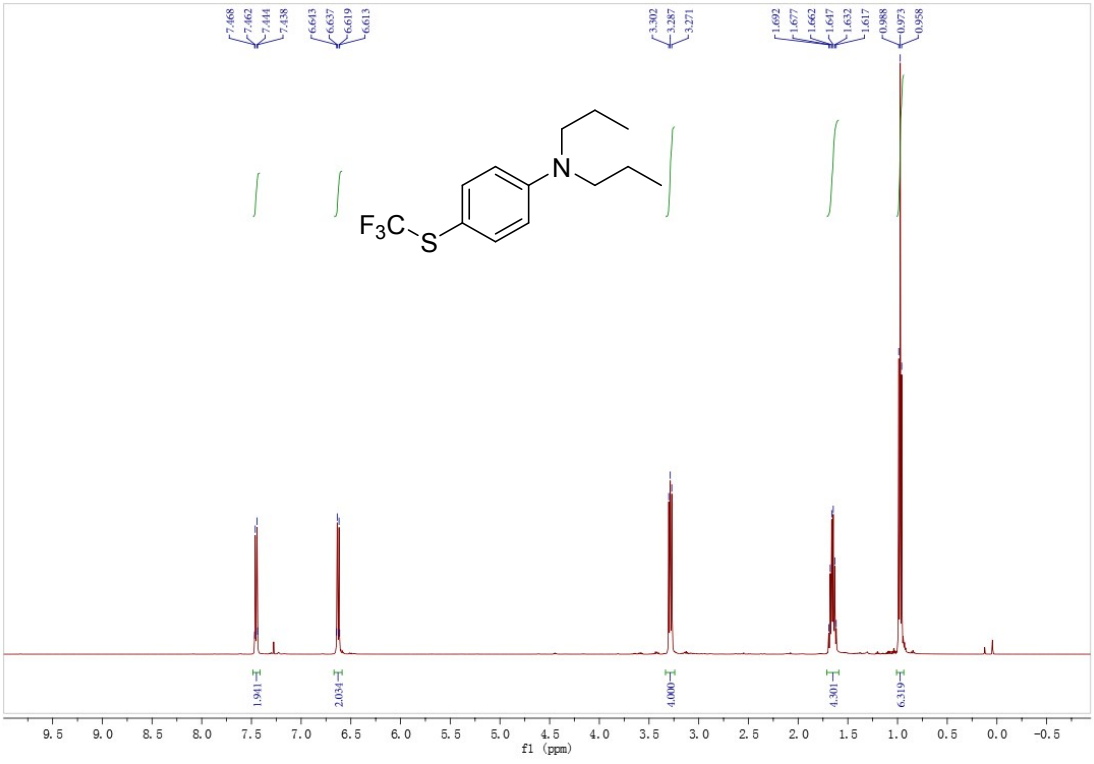


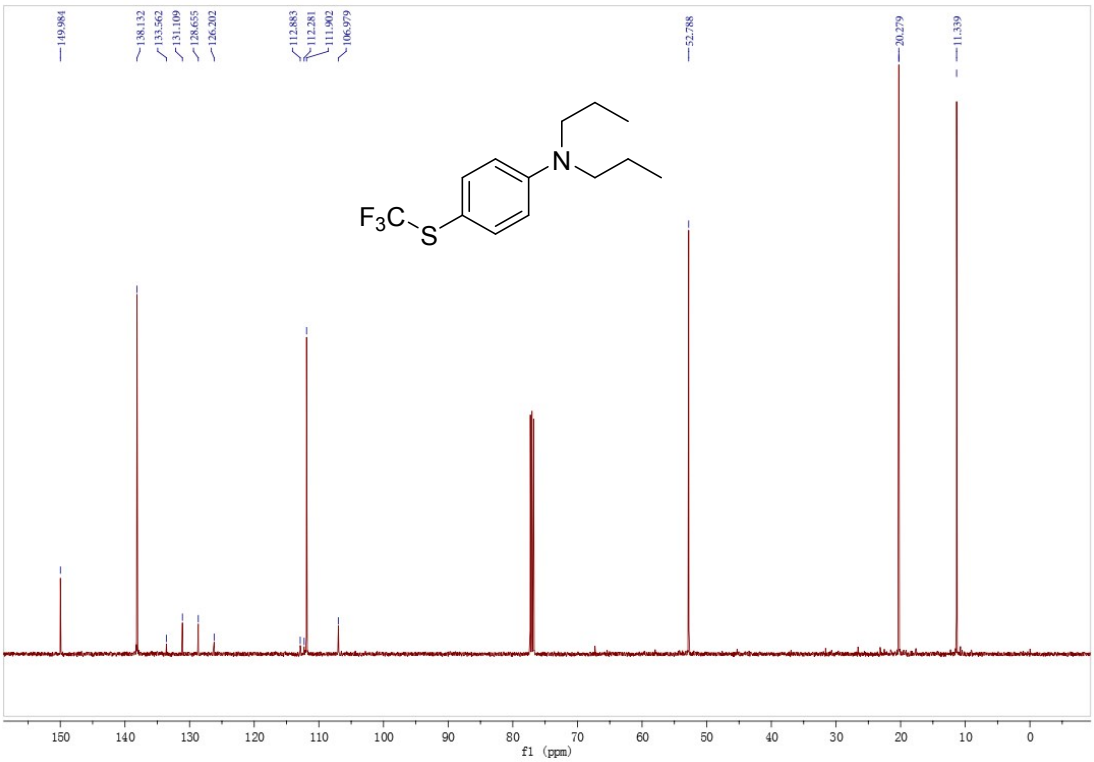
4-(4-(benzo[d]isothiazol-3-yl)piperazin-1-yl)butan-1-ol (**3ck**)



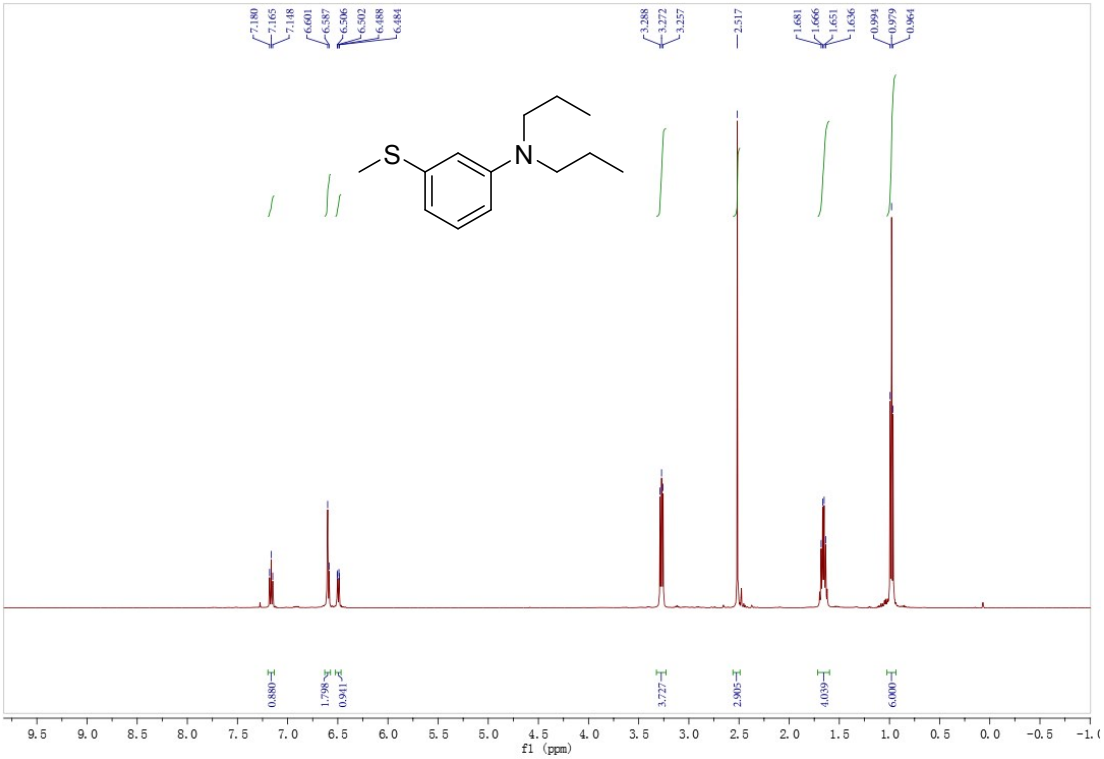


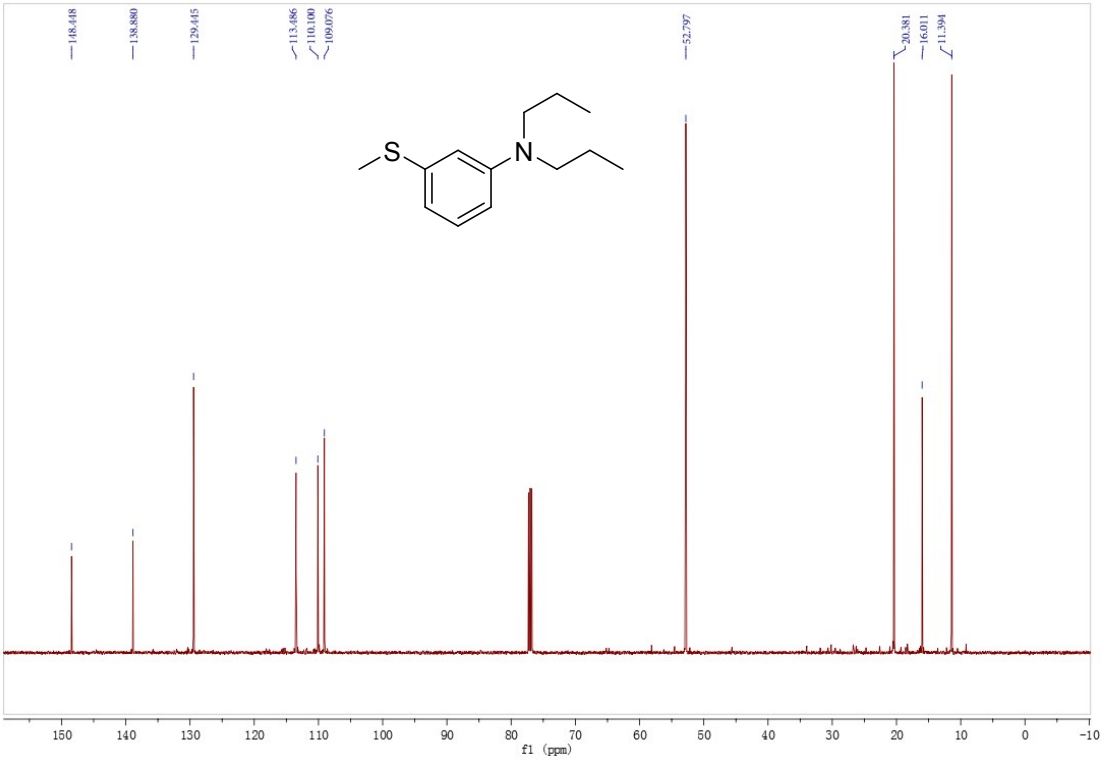
N,N-dipropyl-4-((trifluoromethyl)thio)aniline (**3cl**)



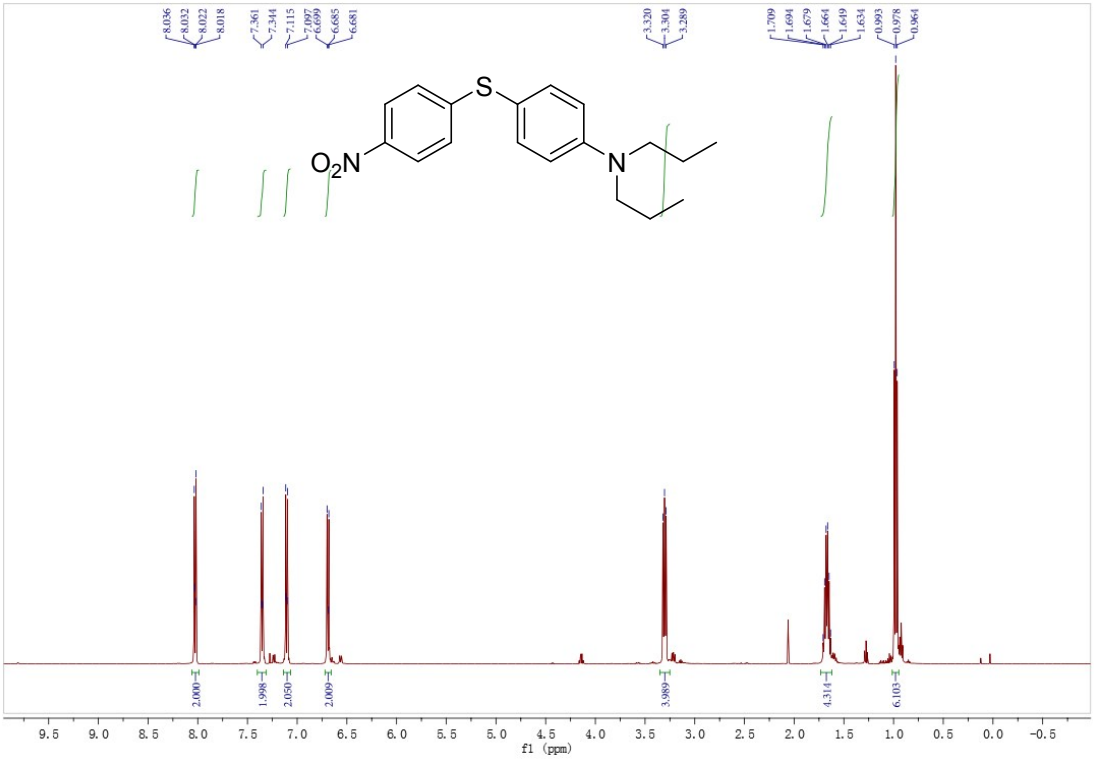


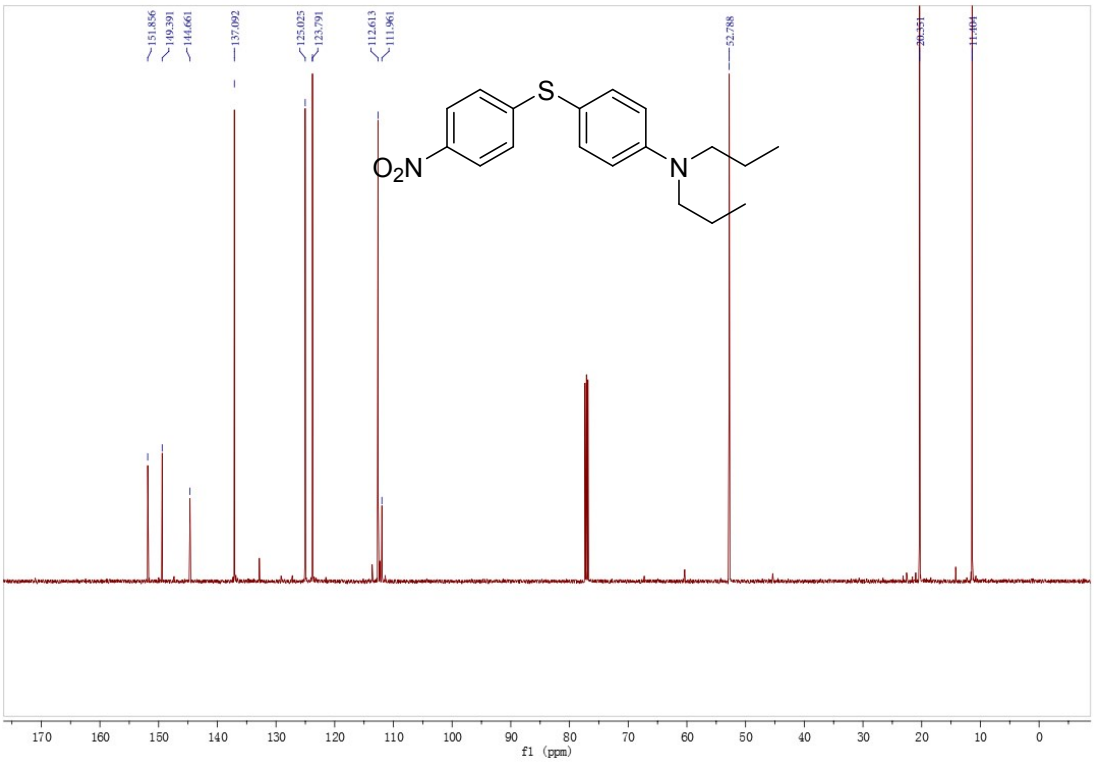
3-(methylthio)-N,N-dipropylaniline (**3cm**)



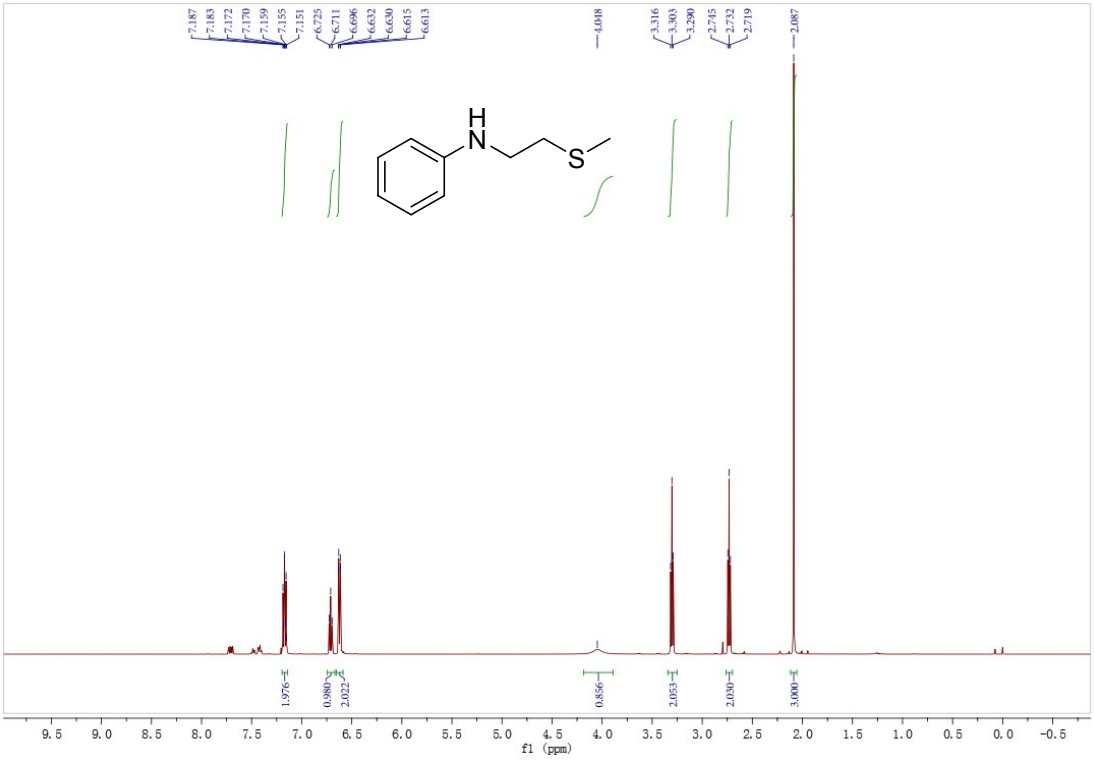


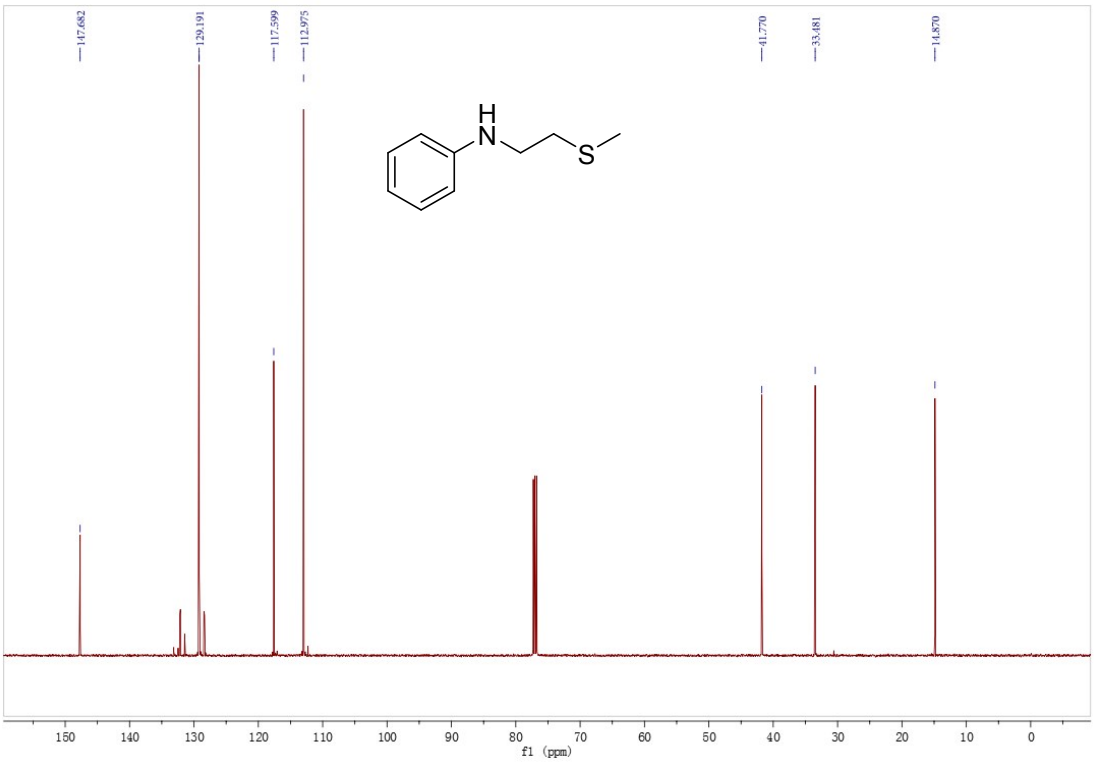
4-((4-nitrophenyl)thio)-N,N-dipropylaniline (**3cn**)



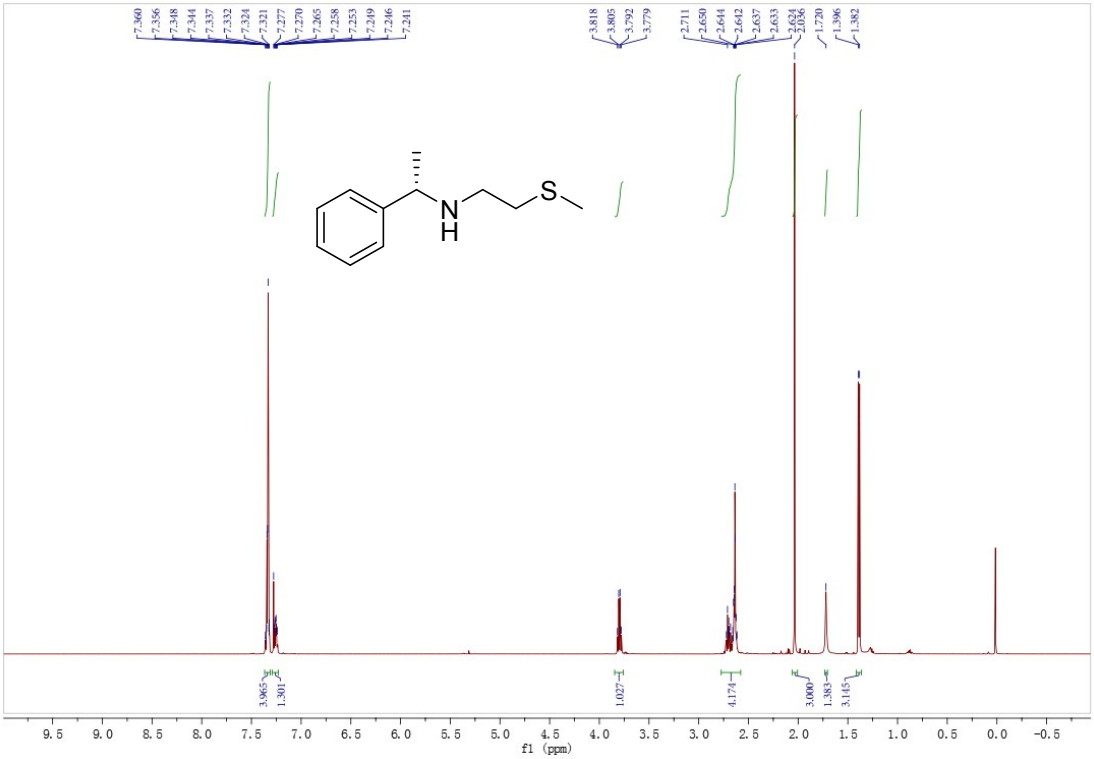


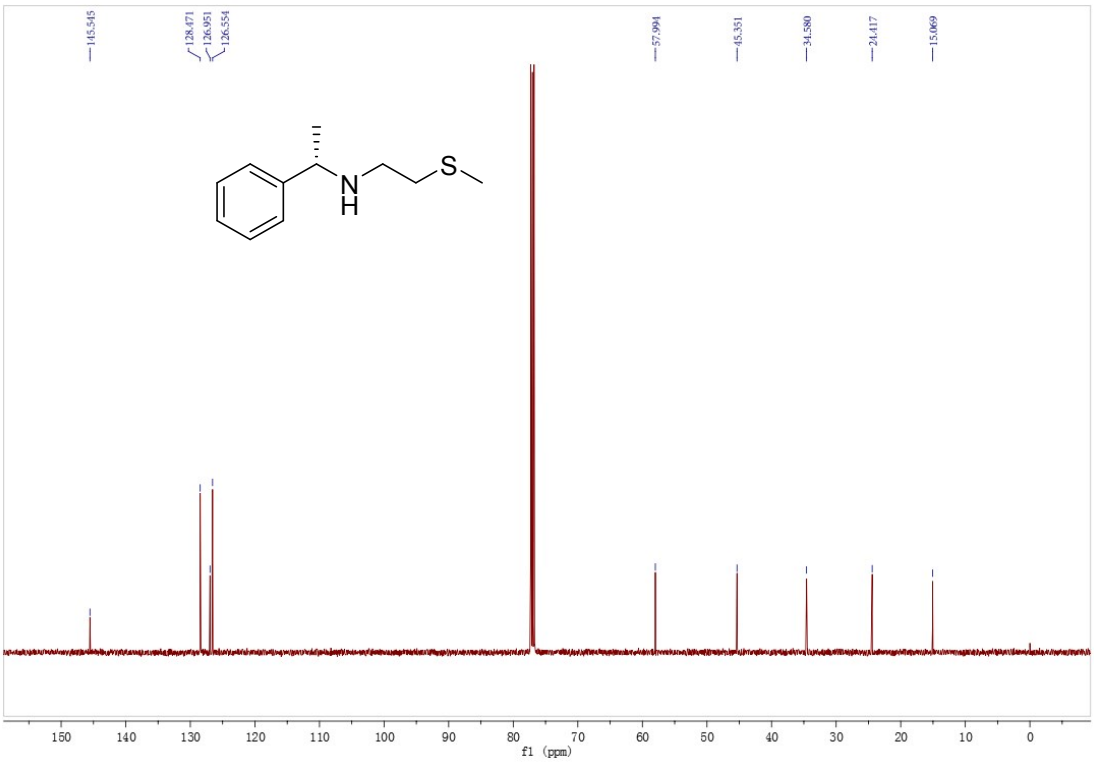
N-(2-(methylthio)ethyl)aniline (**4a**)



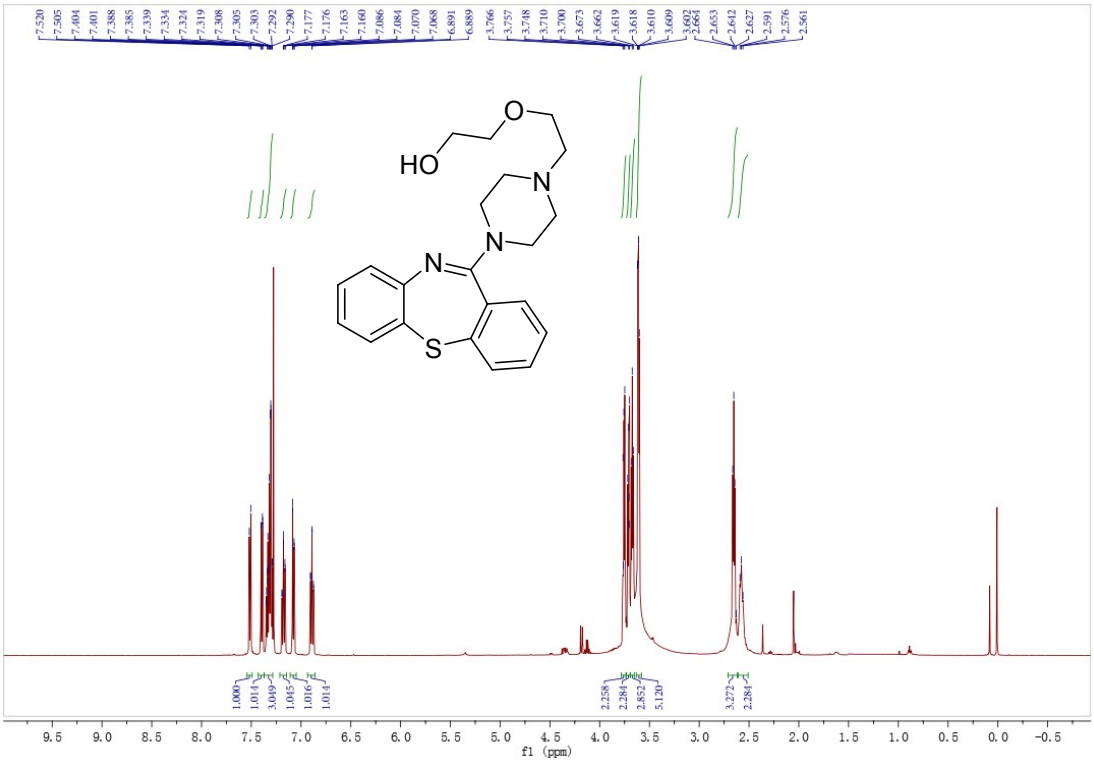


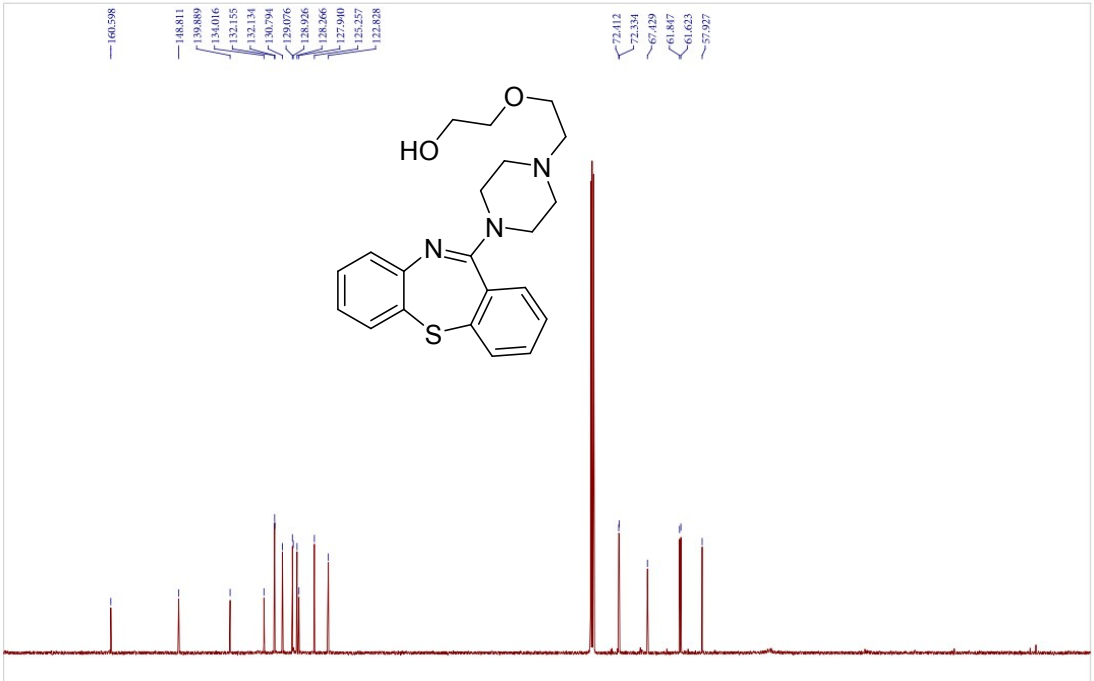
(*S*)-2-(methylthio)-N-(1-phenylethyl)ethan-1-amine (**4b**)





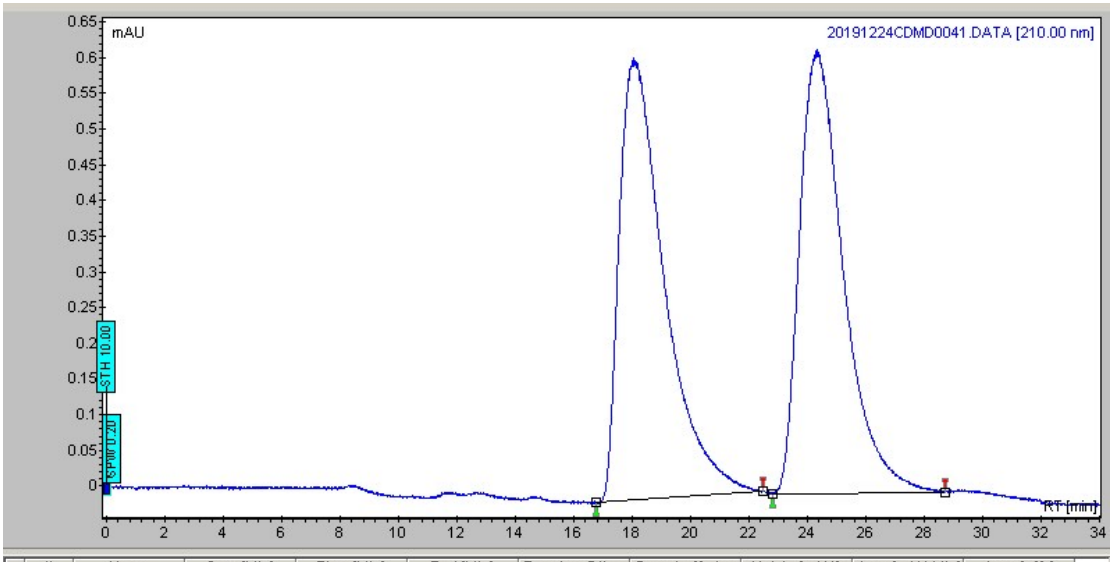
Quetiapine (**6**)



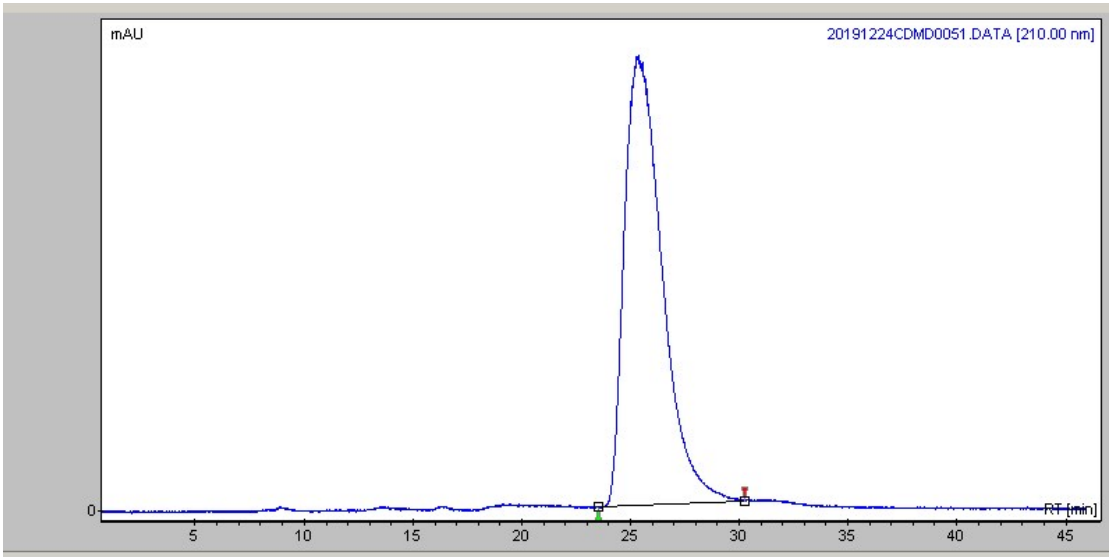


7. HPLC chromatograms of the compound 4b

(*S*)-2-(methylthio)-N-(1-phenylethyl)ethan-1-amine

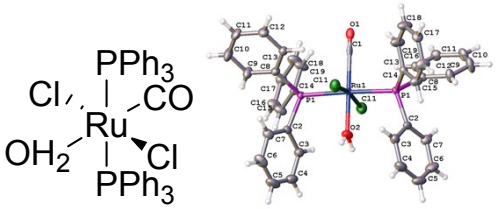


#	Name	Start [Min]	Time [Min]	End [Min]	Ret. time Offset	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	16.747	18.065	22.456	0.000	50.68	0.6	1.1	50.677
2	UNKNOWN	22.789	24.292	28.689	0.000	49.32	0.6	1.1	49.323
Total						100.00	1.2	2.2	100.000



#	Name	Start [Min]	Time [Min]	End [Min]	Ret. time Offset	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	23.555	25.371	30.272	0.000	100.00	0.9	1.8	100.000
Total						100.00	0.9	1.8	100.000

8. Crystallographic data of $RuCl_2(H_2O)(CO)(PPh_3)_2$



(ellipsoid contour at 50% probability level)

Table 1. Crystal data and structure refinement for wmj18080_0m.

Identification code	wmj18080_0m	
Empirical formula	C37 H32 Cl2 O2 P2 Ru	
Formula weight	742.53	
Temperature	172.99 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 24.1640(5) Å	α= 90°.
	b = 9.5229(2) Å	β= 116.6390(10)°.
	c = 15.7986(3) Å	γ = 90°.
Volume	3249.53(12) $Å^3$	
Z	4	
Density (calculated)	1.518 Mg/m^3	
Absorption coefficient	4.370 mm^{-1}	
F(000)	1512	
Crystal size	0.15 x0.11 x0.10 mm^3	
Theta range for data collection	6.270 to 54.924°.	
Index ranges	-29<=h<=29, -11<=k<=11, -19<=l<=18	
Reflections collected	19347	
Independent reflections	3046 [R(int) = 0.0437]	
Completeness to theta = 53.594°	98.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.5319	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3046 / 12 / 208	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0304, wR2 = 0.0804	
R indices (all data)	R1 = 0.0310, wR2 = 0.0808	
Extinction coefficient	0.00131(14)	

Largest diff. peak and hole	1.285 and -0.850 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for wmj18080_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	5000	3258(1)	7500	16(1)
Cl(1)	5557(1)	3521(1)	9180(1)	33(1)
P(1)	5932(1)	3315(1)	7304(1)	16(1)
O(2)	5000	5502(4)	7500	36(1)
C(1')	5000	5502(4)	7500	36(1)
O(1')	5000	6450(20)	7500	48(3)
C(1)	5000	1095(5)	7500	22(1)
O(1)	5000	212(4)	7500	23(1)
O(2')	5000	1095(5)	7500	22(1)
C(2)	6197(1)	5127(2)	7378(2)	20(1)
C(3)	5832(1)	6084(3)	6674(2)	28(1)
C(4)	5984(1)	7497(3)	6765(2)	37(1)
C(5)	6495(2)	7979(3)	7556(2)	40(1)
C(6)	6864(2)	7047(3)	8245(2)	38(1)
C(7)	6717(1)	5620(3)	8160(2)	27(1)
C(8)	6603(1)	2327(2)	8139(2)	20(1)
C(9)	7149(1)	2334(3)	8040(2)	32(1)
C(10)	7658(1)	1566(3)	8650(2)	39(1)
C(11)	7626(1)	766(3)	9359(2)	32(1)
C(12)	7088(1)	735(3)	9455(2)	27(1)
C(13)	6576(1)	1515(2)	8852(2)	22(1)
C(14)	5889(1)	2664(2)	6186(2)	19(1)
C(15)	6057(1)	3457(3)	5603(2)	30(1)
C(16)	6048(2)	2870(3)	4791(2)	35(1)
C(17)	5879(1)	1499(3)	4555(2)	29(1)
C(18)	5713(2)	697(3)	5131(2)	40(1)
C(19)	5711(2)	1280(3)	5933(2)	35(1)

Table 3. Bond lengths [Å] and angles [°] for wmj18080_0m.

Ru(1)-Cl(1)#1	2.3907(7)
Ru(1)-Cl(1)	2.3907(7)
Ru(1)-P(1)	2.4067(6)
Ru(1)-P(1)#1	2.4066(6)
Ru(1)-O(2)	2.137(3)
Ru(1)-C(1')	2.137(3)
Ru(1)-C(1)	2.060(4)
Ru(1)-O(2')	2.060(4)
P(1)-C(2)	1.827(2)
P(1)-C(8)	1.826(2)
P(1)-C(14)	1.831(2)
O(2)-H(2A)	0.9018
O(2)-H(2B)	0.9020
C(1')-O(1')	0.905(17)
C(1)-O(1)	0.841(4)
C(1)-H(2'A)#1	0.781(2)
C(1)-H(2'B)#1	0.781(2)
O(1)-H(2'A)#1	0.842(2)
O(1)-H(2'B)#1	0.842(2)
O(2')-H(2'A)	0.7813
O(2')-H(2'B)	0.7812
C(2)-C(3)	1.402(3)
C(2)-C(7)	1.390(3)
C(3)-H(3)	0.9500
C(3)-C(4)	1.385(4)
C(4)-H(4)	0.9500
C(4)-C(5)	1.383(5)
C(5)-H(5)	0.9500
C(5)-C(6)	1.378(5)
C(6)-H(6)	0.9500
C(6)-C(7)	1.395(4)
C(7)-H(7)	0.9500
C(8)-C(9)	1.397(3)
C(8)-C(13)	1.392(3)
C(9)-H(9)	0.9500
C(9)-C(10)	1.382(4)

C(10)-H(10)	0.9500
C(10)-C(11)	1.385(4)
C(11)-H(11)	0.9500
C(11)-C(12)	1.375(4)
C(12)-H(12)	0.9500
C(12)-C(13)	1.391(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.385(3)
C(14)-C(19)	1.389(4)
C(15)-H(15)	0.9500
C(15)-C(16)	1.390(4)
C(16)-H(16)	0.9500
C(16)-C(17)	1.369(4)
C(17)-H(17)	0.9500
C(17)-C(18)	1.377(4)
C(18)-H(18)	0.9500
C(18)-C(19)	1.387(4)
C(19)-H(19)	0.9500

Cl(1)#1-Ru(1)-Cl(1)	167.99(4)
Cl(1)-Ru(1)-P(1)#1	87.05(2)
Cl(1)#1-Ru(1)-P(1)#1	92.68(2)
Cl(1)-Ru(1)-P(1)	92.68(2)
Cl(1)#1-Ru(1)-P(1)	87.05(2)
P(1)#1-Ru(1)-P(1)	177.40(3)
O(2)-Ru(1)-Cl(1)	83.993(18)
O(2)-Ru(1)-Cl(1)#1	83.994(18)
O(2)-Ru(1)-P(1)	88.702(13)
O(2)-Ru(1)-P(1)#1	88.702(13)
C(1')-Ru(1)-Cl(1)	83.993(18)
C(1')-Ru(1)-P(1)	88.702(13)
C(1)-Ru(1)-Cl(1)	96.007(18)
C(1)-Ru(1)-Cl(1)#1	96.006(18)
C(1)-Ru(1)-P(1)	91.298(13)
C(1)-Ru(1)-P(1)#1	91.298(14)
C(1)-Ru(1)-O(2)	180.0
O(2')-Ru(1)-Cl(1)	96.007(18)
O(2')-Ru(1)-P(1)	91.298(13)

O(2')-Ru(1)-C(1')	180.0
C(2)-P(1)-Ru(1)	109.58(7)
C(2)-P(1)-C(14)	104.36(10)
C(8)-P(1)-Ru(1)	118.33(8)
C(8)-P(1)-C(2)	105.53(11)
C(8)-P(1)-C(14)	99.82(10)
C(14)-P(1)-Ru(1)	117.68(8)
Ru(1)-O(2)-H(2A)	127.9
Ru(1)-O(2)-H(2B)	127.9
H(2A)-O(2)-H(2B)	104.1
Ru(1)-C(1')-H(2A)#1	127.937(2)
Ru(1)-C(1')-H(2B)#1	127.928(5)
H(2A)#1-C(1')-H(2B)#1	104.1
O(1')-C(1')-Ru(1)	180.0
H(2A)#1-O(1')-H(2B)#1	127.6
Ru(1)-C(1)-H(2'A)#1	117.6(3)
Ru(1)-C(1)-H(2'B)#1	117.6(3)
O(1)-C(1)-Ru(1)	180.0
O(1)-C(1)-H(2'A)#1	62.4(3)
O(1)-C(1)-H(2'B)#1	62.4(3)
H(2'A)#1-C(1)-H(2'B)#1	124.9
C(1)-O(1)-H(2'A)#1	55.3(2)
C(1)-O(1)-H(2'B)#1	55.3(2)
H(2'A)#1-O(1)-H(2'B)#1	110.7
Ru(1)-O(2')-H(2'A)	117.6
Ru(1)-O(2')-H(2'B)	117.6
H(2'A)-O(2')-H(2'B)	124.9
C(3)-C(2)-P(1)	119.02(19)
C(7)-C(2)-P(1)	121.83(19)
C(7)-C(2)-C(3)	118.8(2)
C(2)-C(3)-H(3)	119.8
C(4)-C(3)-C(2)	120.4(2)
C(4)-C(3)-H(3)	119.8
C(3)-C(4)-H(4)	119.9
C(5)-C(4)-C(3)	120.3(3)
C(5)-C(4)-H(4)	119.9
C(4)-C(5)-H(5)	120.0
C(6)-C(5)-C(4)	119.9(3)

C(6)-C(5)-H(5)	120.0
C(5)-C(6)-H(6)	119.8
C(5)-C(6)-C(7)	120.3(3)
C(7)-C(6)-H(6)	119.8
C(2)-C(7)-C(6)	120.2(3)
C(2)-C(7)-H(7)	119.9
C(6)-C(7)-H(7)	119.9
C(9)-C(8)-P(1)	119.65(18)
C(13)-C(8)-P(1)	121.45(18)
C(13)-C(8)-C(9)	118.8(2)
C(8)-C(9)-H(9)	119.7
C(10)-C(9)-C(8)	120.6(2)
C(10)-C(9)-H(9)	119.7
C(9)-C(10)-H(10)	120.0
C(9)-C(10)-C(11)	120.0(3)
C(11)-C(10)-H(10)	120.0
C(10)-C(11)-H(11)	120.0
C(12)-C(11)-C(10)	120.0(2)
C(12)-C(11)-H(11)	120.0
C(11)-C(12)-H(12)	119.8
C(11)-C(12)-C(13)	120.5(2)
C(13)-C(12)-H(12)	119.8
C(8)-C(13)-H(13)	120.0
C(12)-C(13)-C(8)	120.1(2)
C(12)-C(13)-H(13)	120.0
C(15)-C(14)-P(1)	123.39(18)
C(15)-C(14)-C(19)	118.2(2)
C(19)-C(14)-P(1)	118.33(18)
C(14)-C(15)-H(15)	119.8
C(14)-C(15)-C(16)	120.4(2)
C(16)-C(15)-H(15)	119.8
C(15)-C(16)-H(16)	119.5
C(17)-C(16)-C(15)	120.9(2)
C(17)-C(16)-H(16)	119.5
C(16)-C(17)-H(17)	120.4
C(16)-C(17)-C(18)	119.2(2)
C(18)-C(17)-H(17)	120.4
C(17)-C(18)-H(18)	119.9

C(17)-C(18)-C(19)	120.3(3)
C(19)-C(18)-H(18)	119.9
C(14)-C(19)-H(19)	119.5
C(18)-C(19)-C(14)	120.9(2)
C(18)-C(19)-H(19)	119.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for wmj18080_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	15(1)	19(1)	16(1)	0	9(1)	0
Cl(1)	29(1)	41(1)	30(1)	-9(1)	14(1)	-2(1)
P(1)	16(1)	17(1)	17(1)	2(1)	10(1)	1(1)
O(2)	41(2)	20(2)	58(2)	0	33(2)	0
C(1')	41(2)	20(2)	58(2)	0	33(2)	0
O(1')	32(7)	77(11)	39(7)	0	19(6)	0
C(1)	10(1)	48(2)	9(1)	0	6(1)	0
O(1)	17(2)	37(2)	14(1)	0	6(1)	0
O(2')	10(1)	48(2)	9(1)	0	6(1)	0
C(2)	23(1)	18(1)	25(1)	-1(1)	16(1)	-1(1)
C(3)	27(1)	25(1)	34(1)	3(1)	17(1)	2(1)
C(4)	47(2)	24(1)	50(2)	7(1)	31(2)	6(1)
C(5)	63(2)	21(1)	52(2)	-9(1)	40(2)	-9(1)
C(6)	49(2)	36(2)	35(2)	-15(1)	24(1)	-18(1)
C(7)	33(1)	29(1)	23(1)	-3(1)	15(1)	-5(1)
C(8)	21(1)	20(1)	18(1)	2(1)	9(1)	3(1)
C(9)	26(1)	45(2)	30(1)	14(1)	18(1)	10(1)
C(10)	26(1)	58(2)	38(2)	15(1)	20(1)	16(1)
C(11)	26(1)	40(2)	27(1)	8(1)	9(1)	13(1)
C(12)	28(1)	29(1)	23(1)	6(1)	10(1)	3(1)
C(13)	22(1)	23(1)	22(1)	2(1)	11(1)	1(1)
C(14)	19(1)	20(1)	20(1)	1(1)	10(1)	2(1)
C(15)	44(2)	25(1)	26(1)	-4(1)	21(1)	-8(1)
C(16)	53(2)	33(1)	28(1)	-1(1)	27(1)	-7(1)
C(17)	33(1)	34(1)	24(1)	-6(1)	16(1)	0(1)
C(18)	64(2)	25(1)	46(2)	-11(1)	38(2)	-9(1)
C(19)	60(2)	22(1)	40(2)	-3(1)	36(2)	-8(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}The ^{3}) for wmj18080_0m.

	x	y	z	U(eq)
H(2A)	5193	6084	7997	54
H(2B)	4807	6084	7003	54
H(2'A)	4881	715	7011	32
H(2'B)	5120	715	7989	32
H(3)	5480	5760	6130	33
H(4)	5735	8138	6284	44
H(5)	6592	8952	7624	48
H(6)	7220	7377	8781	46
H(7)	6974	4983	8638	33
H(9)	7171	2870	7549	38
H(10)	8029	1588	8583	47
H(11)	7975	239	9778	38
H(12)	7066	176	9937	32
H(13)	6207	1494	8927	26
H(15)	6180	4407	5760	35
H(16)	6160	3429	4394	42
H(17)	5877	1105	4001	35
H(18)	5600	-258	4977	48
H(19)	5585	723	6316	43