

A Convergent Paired Electrolysis Strategy Enables Cross-Coupling of Methylarenes with Imines

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1. General Information

All reactions were carried out under Ar atmosphere unless otherwise noted. All reagents and solvents were obtained from commercial suppliers and used without further purification. Reactions were monitored by TLC on silica gel plates (GF₂₅₄), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AVANCE III-400 spectrometer at room temperature. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplet; broad (br). High resolution mass spectra were obtained using an Agilent 6210 Series TOF LC-MS equipped with electrospray ionization (ESI) probe operating in positive ion mode.

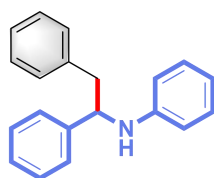
2. Reaction Condition Optimization

entry	electrode	mediator	solvent	electrolyte	yield(%) ^b
1	RVC(+)-Pt(-)	--	CH ₃ CN	Et ₄ NPF ₆	0
2	RVC(+)-Pt(-)	TEMPO	CH ₃ CN	Et ₄ NPF ₆	0
3	RVC(+)-Pt(-)	CpFe	CH ₃ CN	Et ₄ NPF ₆	0
4	RVC(+)-Pt(-)	ⁱ Pr ₃ SiSH	CH ₃ CN	Et ₄ NPF ₆	32
5	RVC(+)-Pt(-)	K ₃ Fe(CN) ₄	CH ₃ CN	Et ₄ NPF ₆	0
6	RVC(+)-Pt(-)	ⁱ Pr ₃ SiSH	DCM	Et ₄ NPF ₆	6
7	RVC(+)-Pt(-)	ⁱ Pr ₃ SiSH	DMA	Et ₄ NPF ₆	54
8	RVC(+)-RVC(-)	ⁱ Pr ₃ SiSH	DMA	Et ₄ NPF ₆	67
9	RVC(+)-RVC(-)	PhSH	DMA	Et ₄ NPF ₆	0
10	RVC(+)-RVC(-)	CH ₃ COSH	DMA	Et ₄ NPF ₆	0
11	RVC(+)-RVC(-)	MeCOOCH ₂ SH	DMA	Et ₄ NPF ₆	0
12	Pt(+)-Pt(-)	ⁱ Pr ₃ SiSH	DMA	Et ₄ NPF ₆	30
13	RVC(+)-RVC(-)	ⁱ Pr ₃ SiSH	DMA	ⁿ Bu ₄ NClO ₄	87(84) ^c
14	RVC(+)-RVC(-)	ⁱ Pr ₃ SiSH	DMA	LiClO ₄	35

Reaction condition: 0.2 mmol **1a**, 1.0 mmol **2a**, 0.02 mmol mediator, 0.4 mmol electrolyte, 4 mL solvent, Ar, constant current= 6 mA, 24 h. [b] Yields based on analysis of the ¹H NMR spectra of the crude product mixture using CH₂Br₂ as an internal standard. [c] Isolated yield of **3a**.

3. General Procedure for Cross-Coupling of Methylarenes with Imines

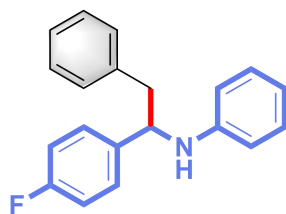
The test cube was charged with a stir bar, 0.2 mmol imines, 1.0 mmol methylarenes, 0.02 mmol triisopropylsilanethiol, 0.4 mmol $n\text{Bu}_4\text{NClO}_4$ and 4 mL DMA. Then the assembled electrodes were placed into the solution. The silica gel plug was sealed with film. The mixture was electrolyzed at a constant current of 6 mA until the imines was completely consumed. The RVC electrodes were ultrasonic washed with ethyl acetate twice. The combined mixture was washed with H_2O (25 mL \times 2), brine, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography to afford the final products.



3a, 84% yield

The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3a**, (84%, 45.9 mg), a colorless sticky oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.18 (m, 8H), 7.12 (d, J = 8.2 Hz, 2H), 7.04 (dd, J = 8.6, 7.4 Hz, 2H), 6.62 (t, J = 7.8 Hz, 1H), 6.45 (d, J = 7.6 Hz, 2H), 4.58 (dd, J = 8.2, 5.7 Hz, 1H), 4.12 (br s, 1H), 3.13 (dd, J = 14.0, 5.7 Hz, 1H), 3.01 (dd, J = 14.0, 8.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.23, 143.39, 137.64, 129.17, 128.98, 128.53, 128.50, 127.02, 126.68, 126.41, 117.44, 113.59, 59.18, 45.13.

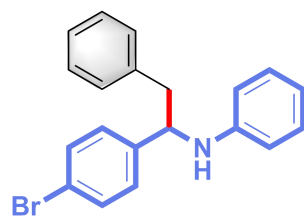
HRMS (ESI) Calculated for $\text{C}_{20}\text{H}_{20}\text{N}^+$ ($[\text{M}+\text{H}]^+$): 274.1590, found: 274.1594.



3b, 72% yield

The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3b**, (72%, 41.9 mg), a colorless sticky oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.30 (dd, *J* = 8.1, 4.9 Hz, 5H), 7.15 – 6.99 (m, 6H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.52 – 6.43 (m, 2H), 4.59 (d, *J* = 6.3 Hz, 1H), 4.13 (br s, 1H), 3.12 (dd, *J* = 13.8, 7.9 Hz, 1H), 3.05 (dd, *J* = 13.8, 8.0 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 161.84 (d, *J* = 244.7 Hz), 147.01, 138.96 (d, *J* = 3.1 Hz), 137.32, 129.11 (d, *J* = 17.7 Hz), 128.56, 127.92 (d, *J* = 8.0 Hz), 126.79, 117.66, 115.46, 115.25, 113.63, 58.62, 45.22.

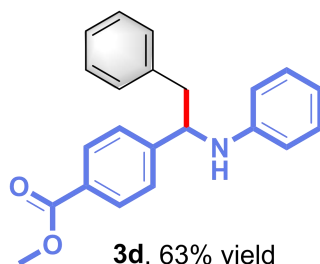
HRMS (ESI) Calculated for C₂₀H₁₉FN⁺ ([M+H]⁺): 292.1496, found: 292.1490.



3c, 71% yield

The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3c**, (71%, 49.8 mg), a colorless sticky oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.15 (m, 5H), 7.11 – 7.01 (m, 4H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.42 (d, *J* = 9.5 Hz, 2H), 4.53 (dd, *J* = 7.8, 6.1 Hz, 1H), 4.09 (br s, 1H), 3.08 (dd, *J* = 13.9, 5.9 Hz, 1H), 2.99 (dd, *J* = 13.9, 8.0 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 146.88, 142.48, 137.12, 131.64, 129.18, 129.04, 128.61, 128.22, 126.87, 120.71, 117.76, 113.63, 58.72, 45.01.

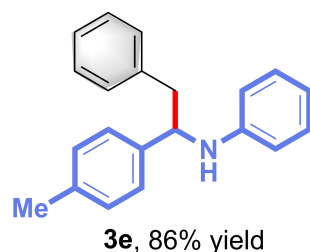
HRMS (ESI) Calculated for C₂₀H₁₉BrN⁺ ([M+H]⁺): 352.0695, found: 352.0696.



3d, 63% yield

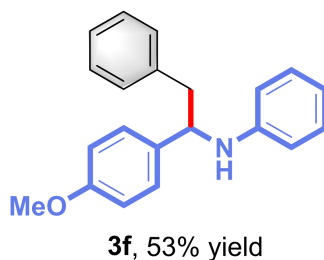
The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3d**, (63%, 41.8 mg), a colorless sticky oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.60 – 7.51 (m, 3H), 7.42 – 7.31 (m, 4H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 8.5 Hz, 2H), 4.93 (dd, *J* = 7.7, 6.1 Hz, 1H), 4.44 (br s, 1H), 4.19 (s, 3H), 3.41 (dd, *J* = 13.9, 5.9 Hz, 1H), 3.32 (dd, *J* = 13.9, 8.0 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 166.93, 148.85, 146.83, 136.98, 129.91, 129.16, 129.02, 128.59, 126.88, 126.50, 117.77, 113.58, 59.09, 51.99, 44.80.

HRMS (ESI) Calculated for C₂₂H₂₂NO₂⁺ ([M+H]⁺): 332.1645, found: 332.1649.



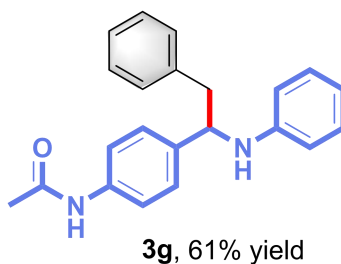
The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3e**, (86%, 49.4 mg), a colorless sticky oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.19 (m, 5H), 7.16 – 7.10 (m, 4H), 7.08 – 7.02 (m, 2H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 7.7 Hz, 2H), 4.56 (dd, *J* = 8.2, 5.7 Hz, 1H), 4.10 (br s, 1H), 3.13 (dd, *J* = 14.0, 5.6 Hz, 1H), 3.00 (dd, *J* = 14.0, 8.3 Hz, 1H), 2.33 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 147.32, 137.81, 136.54, 129.24, 129.17, 128.96, 128.49, 126.62, 126.30, 117.36, 113.58, 58.89, 45.16, 21.08.

HRMS (ESI) Calculated for C₂₁H₂₂N⁺ ([M+H]⁺): 288.1747, found: 288.1743.



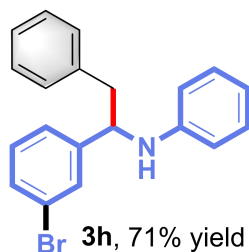
The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3f**, (53%, 32.1 mg), a colorless sticky oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.22 (dd, *J* = 13.6, 7.9 Hz, 5H), 7.16 – 7.02 (m, 4H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.45 (d, *J* = 8.5 Hz, 2H), 4.53 (t, *J* = 6.9 Hz, 1H), 4.09 (br s, 1H), 3.76 (s, 3H), 3.08 (dd, *J* = 13.9, 5.9 Hz, 1H), 2.99 (dd, *J* = 13.9, 7.9 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 158.54, 147.28, 137.74, 135.32, 129.19, 128.96, 128.45, 127.44, 126.59, 117.36, 113.88, 113.59, 58.58, 55.17, 45.17.

HRMS (ESI) Calculated for C₂₁H₂₂NO⁺ ([M+H]⁺): 304.1696, found: 304.1695.



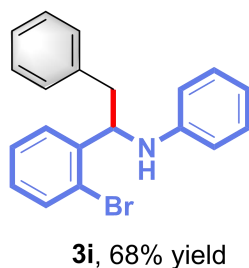
The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3g**, (61%, 40.3 mg), a colorless sticky oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.5 Hz, 3H), 7.32 – 7.18 (m, 5H), 7.14 – 6.99 (m, 4H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.44 (d, *J* = 8.5 Hz, 2H), 4.54 (dd, *J* = 7.8, 6.1 Hz, 1H), 4.08 (br s, 1H) 3.09 (dd, *J* = 13.9, 7.6 Hz, 1H), 2.98 (dd, *J* = 13.9, 8.0 Hz, 1H), 2.12 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.34, 139.30, 137.50, 136.73, 129.16, 128.96, 128.50, 126.98, 126.68, 120.04, 117.47, 113.61, 58.71, 45.02, 24.48.

HRMS (ESI) Calculated for C₂₂H₂₃N₂O⁺ ([M+H]⁺): 331.1805, found: 331.1809.



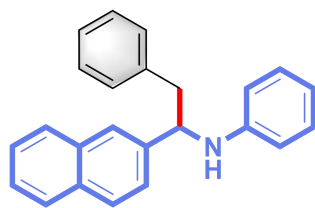
The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3h**, (71%, 49.8 mg), a colorless sticky oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.41 (t, $J = 1.7$ Hz, 1H), 7.29 (dt, $J = 7.8, 1.5$ Hz, 1H), 7.24 – 7.13 (m, 4H), 7.10 – 6.96 (m, 5H), 6.57 (t, $J = 7.3$ Hz, 1H), 6.35 (d, $J = 8.6$ Hz, 2H), 4.45 (dd, $J = 8.3, 5.7$ Hz, 1H), 4.11 (br s, 1H), 3.03 (dd, $J = 14.0, 5.6$ Hz, 1H), 2.90 (dd, $J = 14.0, 8.4$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.90, 146.11, 137.09, 130.22, 130.14, 129.44, 129.13, 129.05, 128.63, 126.91, 125.12, 122.76, 117.80, 113.62, 58.88, 45.09.

HRMS (ESI) Calculated for $\text{C}_{20}\text{H}_{19}\text{BrN}^+$ ($[\text{M}+\text{H}]^+$): 352.0695, found: 352.0699.



The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3i**, (68%, 47.7 mg), a colorless sticky oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, $J = 7.0$ Hz, 1H), 7.43 (d, $J = 7.7$ Hz, 1H), 7.31 - 7.21 (m, 6H), 7.11 (t, $J = 6.8$ Hz, 1H), 7.03 (t, $J = 7.9$ Hz, 2H), 6.61 (t, $J = 7.3$ Hz, 1H), 6.36 (d, $J = 7.7$ Hz, 2H), 4.99 (dd, $J = 9.5, 3.9$ Hz, 1H), 4.10 (br s, 1H), 3.30 (dd, $J = 14.3, 3.8$ Hz, 1H), 2.75 (dd, $J = 14.2, 9.5$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.79, 141.80, 137.54, 133.03, 129.08, 129.01, 128.67, 128.63, 127.90, 127.85, 126.89, 122.90, 117.69, 113.54, 58.07, 42.76.

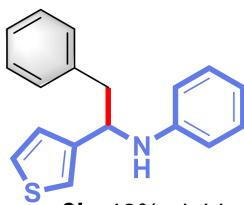
HRMS (ESI) Calculated for $\text{C}_{20}\text{H}_{19}\text{BrN}^+$ ($[\text{M}+\text{H}]^+$): 352.0695, found: 352.0697.



3j, 51% yield

The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3j**, (51%, 32.9 mg), a colorless sticky oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.73 (m, 4H), 7.50 – 7.40 (m, 3H), 7.29 – 7.19 (m, 3H), 7.14 (d, $J = 8.0$ Hz, 2H), 7.02 (t, $J = 7.9$ Hz, 2H), 6.60 (t, $J = 7.3$ Hz, 1H), 6.48 (d, $J = 7.7$ Hz, 2H), 4.74 (dd, $J = 8.2, 5.7$ Hz, 1H), 4.12 (br s, 1H), 3.22 (dd, $J = 14.0, 5.6$ Hz, 1H), 3.07 (dd, $J = 14.0, 8.3$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.27, 140.99, 137.57, 133.49, 132.82, 129.19, 128.99, 128.57, 128.38, 127.85, 127.65, 126.75, 125.95, 125.54, 125.10, 124.73, 117.54, 113.69, 59.42, 45.09.

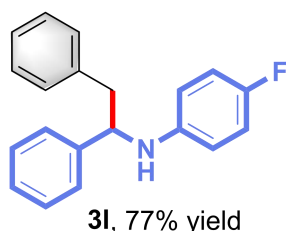
HRMS (ESI) Calculated for $\text{C}_{24}\text{H}_{22}\text{N}^+$ ($[\text{M}+\text{H}]^+$): 324.1747, found: 324.1752.



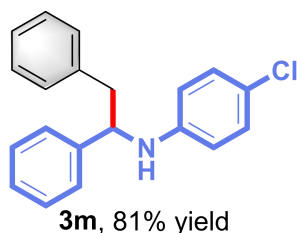
3k, 48% yield

The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3k**, (48%, 26.8 mg), a colorless sticky oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.20 (m, 4H), 7.12 – 7.08 (m, 4H), 7.03 – 7.00 (m, 2H), 6.67 (t, $J = 7.3$ Hz, 1H), 6.53 (d, $J = 8.6$ Hz, 2H), 4.75 (t, $J = 6.7$ Hz, 1H), 3.18 – 3.08 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.20, 144.59, 137.53, 129.26, 129.07, 128.42, 126.10, 125.89, 120.96, 117.58, 113.55, 55.19, 43.82.

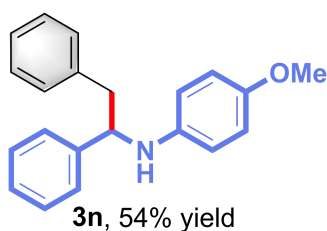
HRMS (ESI) Calculated for $\text{C}_{18}\text{H}_{18}\text{NS}^+$ ($[\text{M}+\text{H}]^+$): 280.1154, found: 280.1158.



The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3l**, (77%, 44.8 mg), a colorless sticky oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.18 (m, 8H), 7.11 (d, $J = 6.8$ Hz, 2H), 6.73 (t, $J = 8.8$ Hz, 2H), 6.36 (dd, $J = 8.2, 5.2$ Hz, 2H), 4.50 (dd, $J = 8.1, 5.8$ Hz, 1H), 3.90 (br s, 1H), 3.12 (dd, $J = 14.0, 5.6$ Hz, 1H), 2.98 (dd, $J = 14.0, 8.3$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.93, 154.59, 143.20, 137.56, 129.15, 128.58, 128.54, 126.94 (d, $J = 38.6$ Hz), 126.40, 115.38 (d, $J = 22.3$ Hz), 114.45, 114.38, 59.78, 45.18. **HRMS (ESI)** Calculated for $\text{C}_{20}\text{H}_{19}\text{FN}^+$ ($[\text{M}+\text{H}]^+$): 292.1496, found: 292.1495.

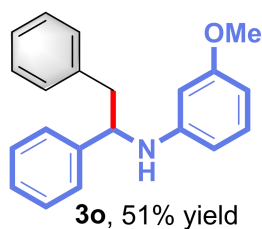


The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3m**, (81%, 49.7 mg), a colorless sticky oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.13 (m, 8H), 7.03 (d, $J = 8.1$ Hz, 2H), 6.90 (d, $J = 8.9$ Hz, 2H), 6.28 (d, $J = 8.9$ Hz, 2H), 4.46 (dd, $J = 8.2, 5.7$ Hz, 1H), 4.01 (br s, 1H), 3.06 (dd, $J = 14.0, 5.6$ Hz, 1H), 2.92 (dd, $J = 14.0, 8.2$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.74, 142.85, 137.39, 129.14, 128.80, 128.62, 128.57, 127.20, 126.80, 126.35, 122.09, 114.69, 59.24, 45.04. **HRMS (ESI)** Calculated for $\text{C}_{20}\text{H}_{19}\text{ClN}^+$ ($[\text{M}+\text{H}]^+$): 308.1201, found: 308.1207.



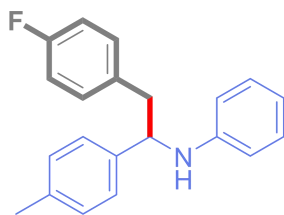
The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3n**, (54%, 32.7 mg), a colorless sticky oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.18 (m, 8H), 7.12 (d, J = 6.7 Hz, 2H), 6.64 (d, J = 9.0 Hz, 2H), 6.40 (d, J = 8.9 Hz, 2H), 4.50 (dd, J = 8.3, 5.7 Hz, 1H), 3.96 (br s, 1H), 3.66 (s, 3H), 3.11 (dd, J = 13.9, 5.6 Hz, 1H), 2.99 (dd, J = 13.9, 8.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.04, 143.66, 141.49, 137.79, 129.18, 128.52, 128.49, 126.99, 126.65, 126.48, 114.88, 114.62, 60.05, 55.67, 45.24.

HRMS (ESI) Calculated for $\text{C}_{21}\text{H}_{22}\text{NO}^+$ ($[\text{M}+\text{H}]^+$): 304.1696, found: 304.1697.



The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3o**, (51%, 30.9 mg), a colorless sticky oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.08 (m, 10H), 6.77 – 6.54 (m, 3H), 6.32 (d, J = 8.7 Hz, 1H), 4.79 (br s, 1H), 4.53 (t, J = 6.9 Hz, 1H), 3.80 (s, 3H), 3.11 (d, J = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.83, 143.52, 137.94, 137.29, 129.28, 128.44, 128.32, 126.93, 126.48, 121.09, 116.46, 111.21, 109.46, 59.45, 55.56, 45.26.

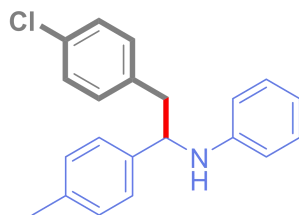
HRMS (ESI) Calculated for $\text{C}_{21}\text{H}_{22}\text{NO}^+$ ($[\text{M}+\text{H}]^+$): 304.1696, found: 304.1699.



3p, 79% yield

The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3p**, (79%, 48.2 mg), a colorless sticky oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.02 (m, 8H), 6.95 (t, $J = 8.7$ Hz, 2H), 6.64 (t, $J = 7.3$ Hz, 1H), 6.48 (d, $J = 7.7$ Hz, 2H), 4.62 – 4.46 (m, 1H), 4.09 (br s, 1H), 3.13 – 2.96 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.69 (d, $J = 244.7$ Hz), 147.16, 139.96, 136.68, 133.45, 130.59, 129.15 (d, $J = 23.2$ Hz), 126.34, 117.50, 115.25 (d, $J = 21.2$ Hz), 113.56, 58.95, 44.13, 21.08.

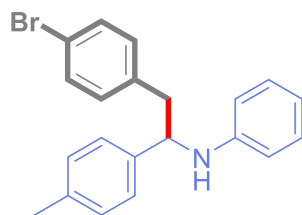
HRMS (ESI) Calculated for $\text{C}_{21}\text{H}_{21}\text{FN}^+$ ($[\text{M}+\text{H}]^+$): 306.1653, found: 306.1658.



3q, 81% yield

The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3q**, (81%, 52.1 mg), a colorless sticky oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 6.98 (m, 10H), 6.65 (t, $J = 7.3$ Hz, 1H), 6.49 (d, $J = 8.5$ Hz, 2H), 4.55 (t, $J = 6.9$ Hz, 1H), 4.05 (br s, 1H), 3.09 - 2.98 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.07, 139.81, 136.73, 136.23, 132.41, 130.55, 129.28, 129.04, 128.53, 126.33, 117.54, 113.55, 58.76, 44.21, 21.08.

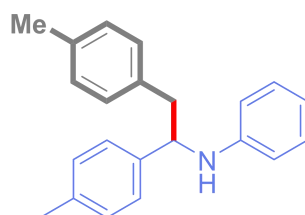
HRMS (ESI) Calculated for $\text{C}_{21}\text{H}_{21}\text{ClN}^+$ ($[\text{M}+\text{H}]^+$): 322.1357, found: 322.1351.



3r, 61% yield

The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3r**, (61%, 44.5 mg), a colorless sticky oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, $J = 8.3$ Hz, 2H), 7.21 – 7.04 (m, 6H), 6.97 (d, $J = 8.3$ Hz, 2H), 6.65 (t, $J = 7.3$ Hz, 1H), 6.49 (d, $J = 8.6$ Hz, 2H), 4.55 (t, $J = 6.9$ Hz, 1H), 4.05 (br s, 1H), 3.10 – 2.94 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.04, 139.77, 136.74, 131.48, 130.94, 129.29, 129.04, 126.33, 120.49, 117.56, 113.55, 58.69, 44.25, 21.08.

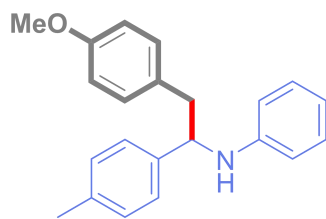
HRMS (ESI) Calculated for $\text{C}_{21}\text{H}_{21}\text{BrN}^+$ ($[\text{M}+\text{H}]^+$): 366.0852, found: 366.0856.



3s, 72% yield

The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3s**, (72%, 43.3 mg), a colorless sticky oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.14 (d, $J = 7.9$ Hz, 2H), 7.07 – 6.90 (m, 8H), 6.53 (t, $J = 7.3$ Hz, 1H), 6.37 (d, $J = 7.8$ Hz, 2H), 4.44 (dd, $J = 8.2, 5.6$ Hz, 1H), 4.02 (br s, 1H), 3.01 (dd, $J = 14.0, 5.4$ Hz, 1H), 2.85 (dd, $J = 14.0, 8.4$ Hz, 1H), 2.24 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.39, 140.54, 136.46, 136.14, 134.65, 129.22, 129.19, 129.02, 128.93, 126.29, 117.28, 113.58, 58.88, 44.78, 21.09, 21.03.

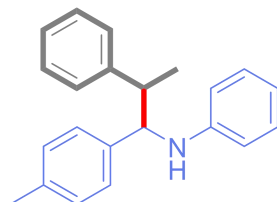
HRMS (ESI) Calculated for $\text{C}_{22}\text{H}_{24}\text{N}^+$ ($[\text{M}+\text{H}]^+$): 302.1903, found: 302.1903.



3t, 61% yield

The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3t**, (61%, 38.7 mg), a colorless sticky oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.22 (d, $J = 8.0$ Hz, 2H), 7.11 - 7.04 (m, 6H), 6.82 (d, $J = 8.6$ Hz, 2H), 6.63 (t, $J = 7.3$ Hz, 1H), 6.47 (d, $J = 7.7$ Hz, 2H), 4.57 - 4.46 (m, 1H), 4.11 (br s, 1H), 3.79 (s, 3H), 3.08 (dd, $J = 14.1, 5.7$ Hz, 1H), 2.94 (dd, $J = 14.1, 8.1$ Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.33, 147.39, 140.46, 136.47, 130.15, 129.75, 129.21, 128.95, 126.32, 117.32, 113.89, 113.59, 58.99, 55.21, 44.27, 21.09.

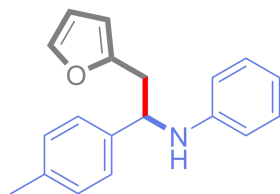
HRMS (ESI) Calculated for $\text{C}_{22}\text{H}_{24}\text{NO}^+$ ($[\text{M}+\text{H}]^+$): 318.1852, found: 318.1847.



3u, 79% yield, (1:1 dr)

The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3u**, (79%, 47.6 mg), a colorless sticky oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.34 - 6.92 (m, 11H), 6.57 (dd, $J = 13.1, 6.9$ Hz, 1H), 6.40 (dd, $J = 35.5, 8.5$ Hz, 2H), 4.50 (d, $J = 5.4$ Hz, 0.5H), 4.31 (d, $J = 8.3$ Hz, 0.5H), 4.13 (br s, 1H), 3.22 (dd, $J = 7.4, 5.6$ Hz, 0.5H), 2.97 (p, $J = 7.1$ Hz, 0.5 H), 2.31 (s, 1.5H), 2.27 (s, 1.5H), 1.31 (d, $J = 7.2$ Hz, 1.5H), 1.15 (d, $J = 7.0$ Hz, 1.5H).

HRMS (ESI) Calculated for $\text{C}_{22}\text{H}_{24}\text{N}^+$ ($[\text{M}+\text{H}]^+$): 302.1903, found: 302.1907.



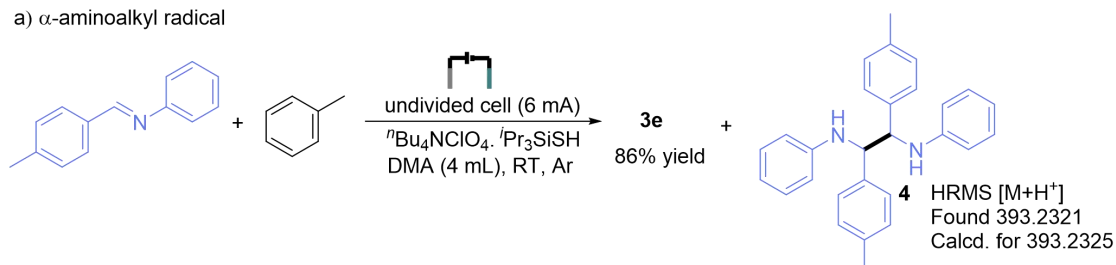
3v, 41% yield

The reaction was carried out according to the general procedure on 0.2 mmol scale (24 h). The residue was purified by flash column chromatography (petroleum ether: ethyl acetate, 100/1-50/1) to afford **3v**, (41%, 22.7 mg), a colorless sticky oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 6.99 (m, 6H), 6.62 (t, $J = 7.3$ Hz, 1H), 6.48 (d, $J = 7.7$ Hz, 2H), 6.29 – 6.23 (m, 1H), 6.01 (d, $J = 3.1$ Hz, 1H), 4.60 (d, $J = 5.2$ Hz, 1H), 4.28 (br s, 1H), 3.10 (dd, $J = 15.2, 5.1$ Hz, 1H), 3.01 (dd, $J = 15.2, 8.5$ Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.16, 141.70, 140.08, 136.66, 129.29, 128.97, 126.06, 117.38, 113.53, 110.25, 107.35, 57.14, 37.33, 21.07. Spectral data are in agreement with the literature.

HRMS (ESI) Calculated for $\text{C}_{19}\text{H}_{20}\text{NO}^+$ ($[\text{M}+\text{H}]^+$): 278.1539, found: 278.1544.

4. Mechanistic experiments

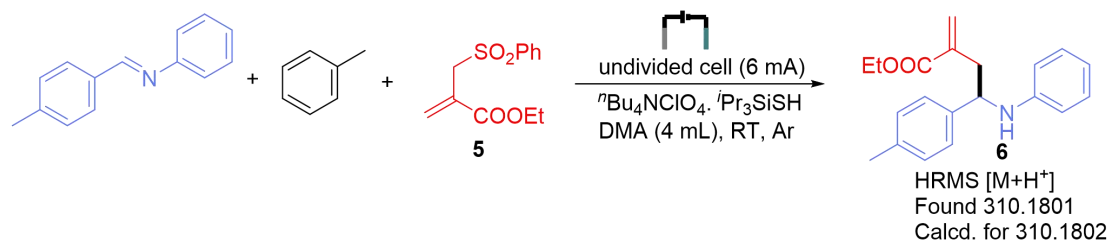
a) α -aminoalkyl radical



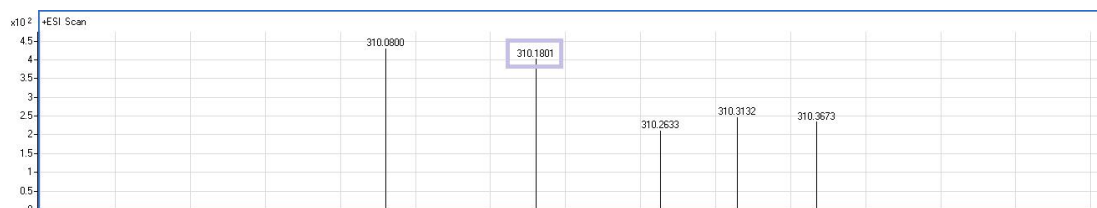
The test cube was charged with a stir bar, 0.2 mmol (E)-N-phenyl-1-(p-tolyl)methanimine 39.1 mg, 1.0 mmol 1.0 mmol toluene 92.1 mg, 0.02 mmol triisopropylsilylanethiol, 0.4 mmol $n\text{Bu}_4\text{NClO}_4$ and 4 mL DMA. Then the assembled electrodes were placed into the solution. The silica gel plug was sealed with film. The mixture was electrolyzed at a constant current of 6 mA for 24 h. The resulting crude mixture was detected by **ESI-HRMS**.



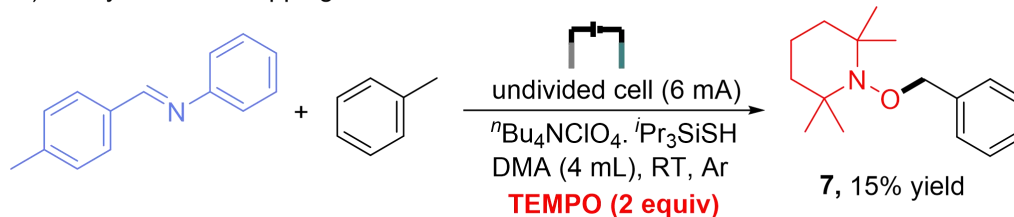
b) α -aminoalkyl radical trapping



The test cube was charged with a stir bar, 0.2 mmol (E)-N-phenyl-1-(p-tolyl)methanimine 39.1 mg, 1.0 mmol 1.0 mmol toluene 92.1 mg, 0.02 mmol triisopropylsilanethiol, 0.4 mmol ⁿBu₄NClO₄, 0.4 mmol **5** 101.7 mg, and 4 mL DMA. Then the assembled electrodes were placed into the solution. The silica gel plug was sealed with film. The mixture was electrolyzed at a constant current of 6 mA for 24 h. The resulting crude mixture was detected by **ESI-HRMS**.



c) benzylic radical trapping

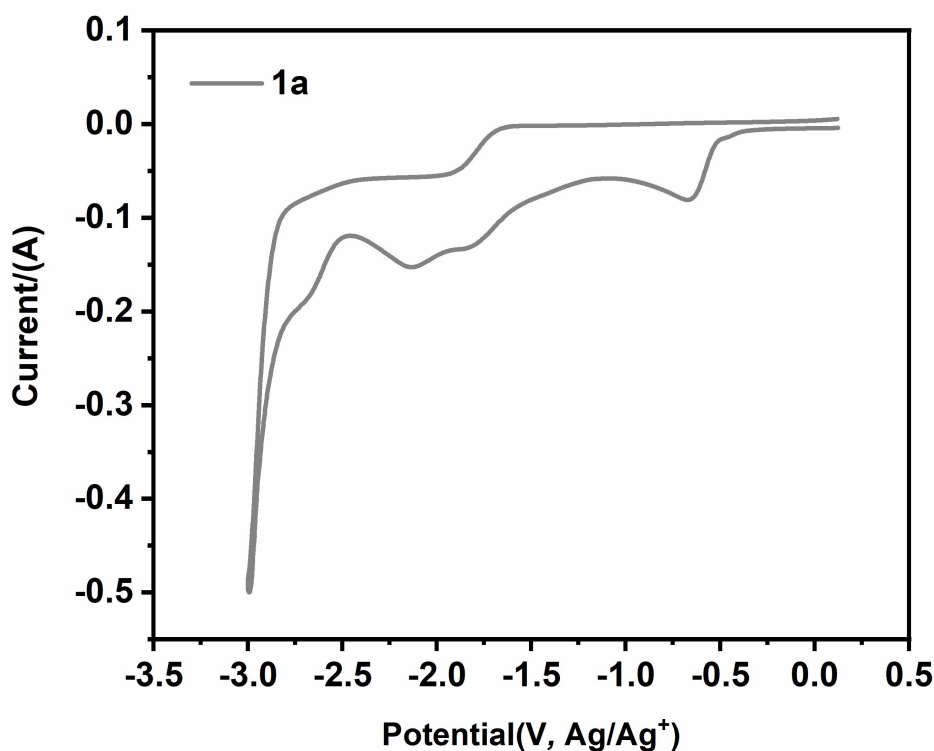


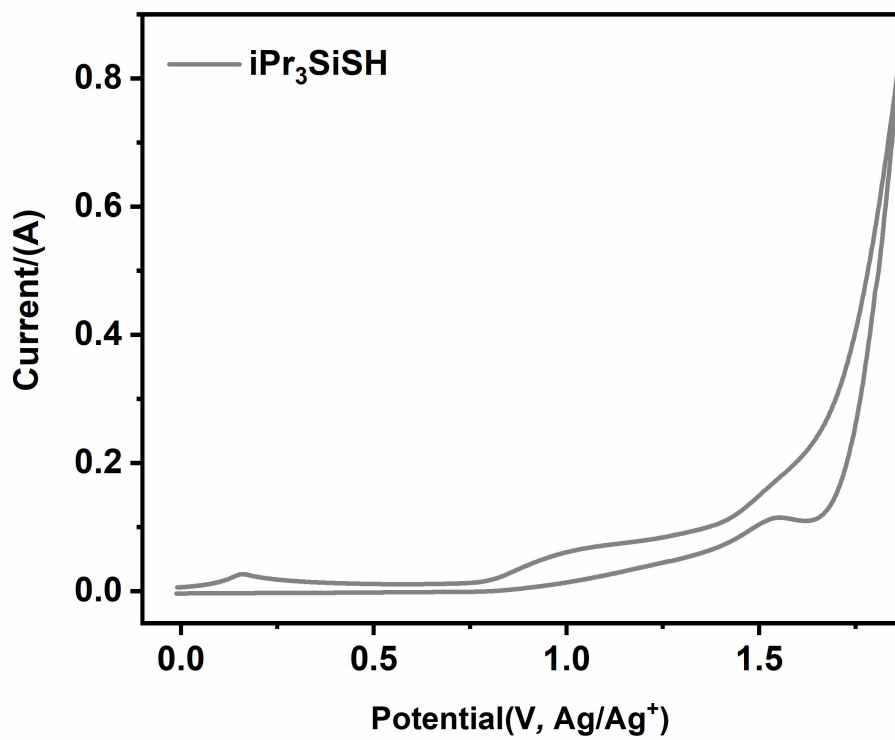
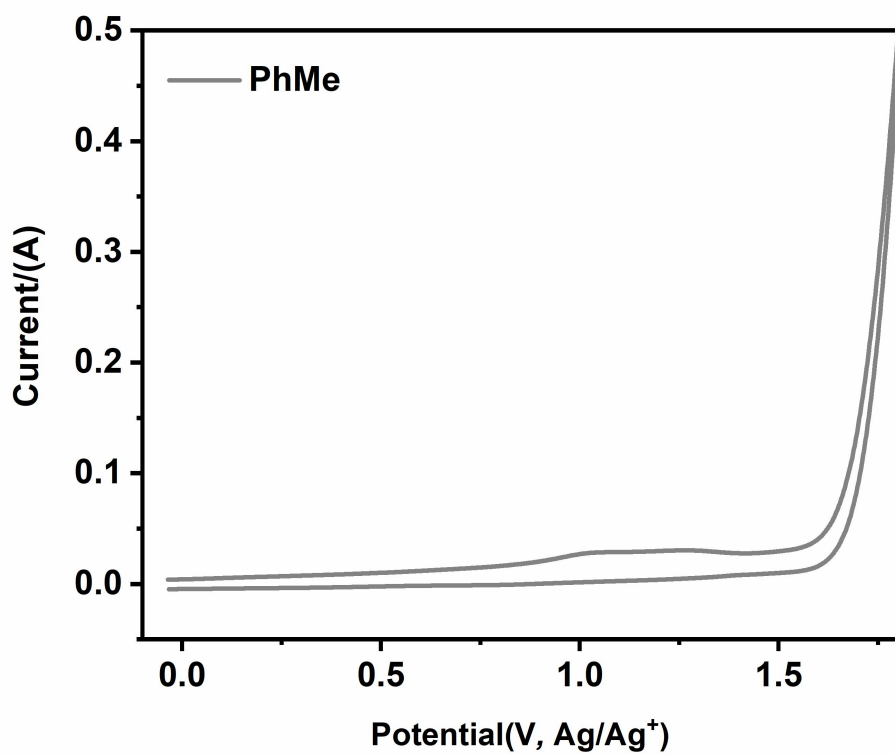
The test cube was charged with a stir bar, 0.2 mmol (E)-N-phenyl-1-(p-tolyl)methanimine 39.1 mg, 1.0 mmol 1.0 mmol toluene 92.1 mg, 0.02 mmol triisopropylsilanethiol, 0.4 mmol ⁿBu₄NClO₄, 0.4 mmol TEMPO 62.4 mg, and 4 mL DMA. Then the assembled electrodes were placed into the solution. The silica gel plug was sealed with film. The mixture was electrolyzed at a constant current of 6 mA for 24 h. The mixture was electrolyzed at a constant current of 6 mA

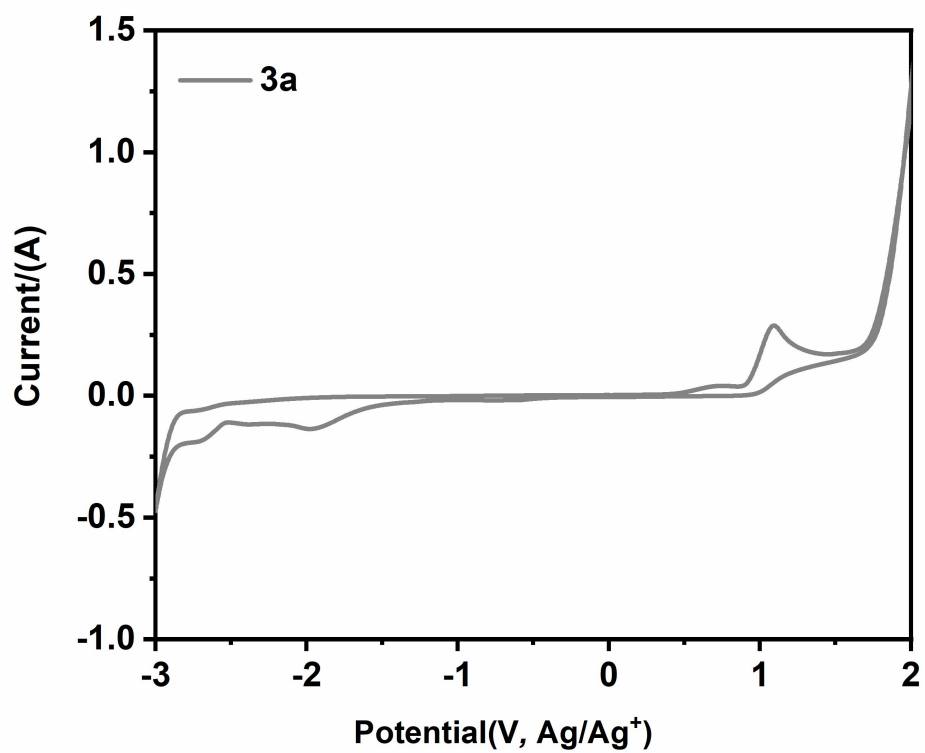
for 24 h. The RVC electrodes were ultrasonic washed with ethyl acetate twice. The combined mixture was washed with H₂O (30 mL ×2), brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography to afford compound **7** (7.4 mg, 15% yield). ¹H NMR (400 MHz; CDCl₃). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.56 – 7.05 (m, 5H), 4.75 (s, 2H), 1.55 – 1.28 (m, 6H), 1.18 (s, 6H), 1.08 (s, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 138.32, 128.20, 127.43, 127.27, 78.73, 60.01, 39.74, 33.10, 20.31, 17.13. Spectral data are in agreement with the literature.¹

Cyclic Voltammetry Studies

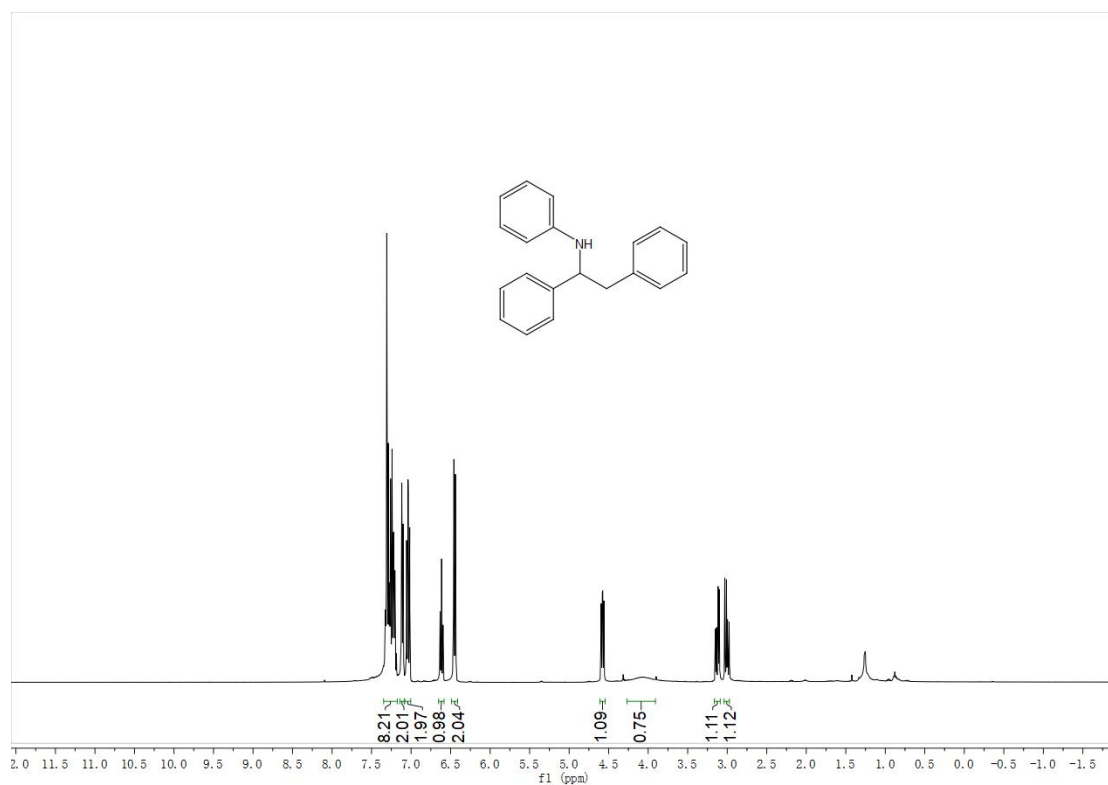
CV was performed using solutions of substrate (0.01 mol/L) prepared in DMA with ⁿBu₄NClO₄ (0.1 mol/L) as electrolyte. A glassy carbon disk electrode (diameter 3 mm), a Pt wire (diameter 1 mm) and a SCE (fill the salt bridge with 1.5 mL electrolyte) were used as the working electrode, counter electrode and reference electrode, respectively. The scan rate was 100 mV/s.

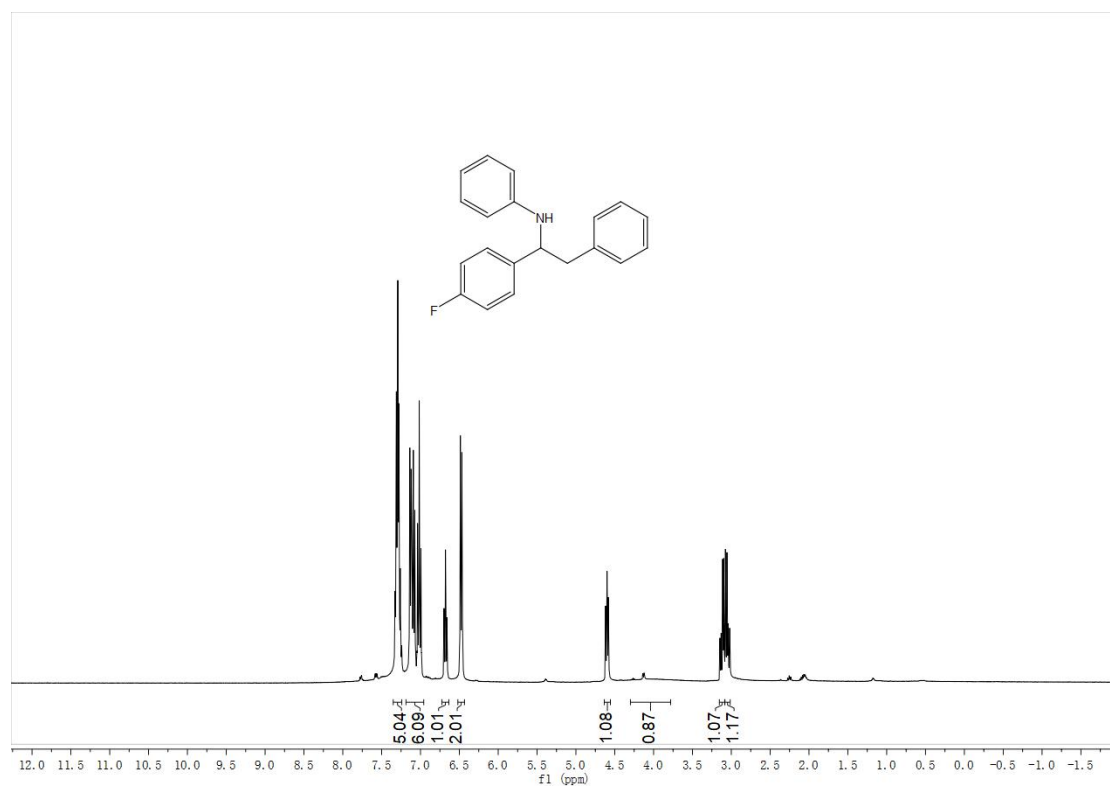
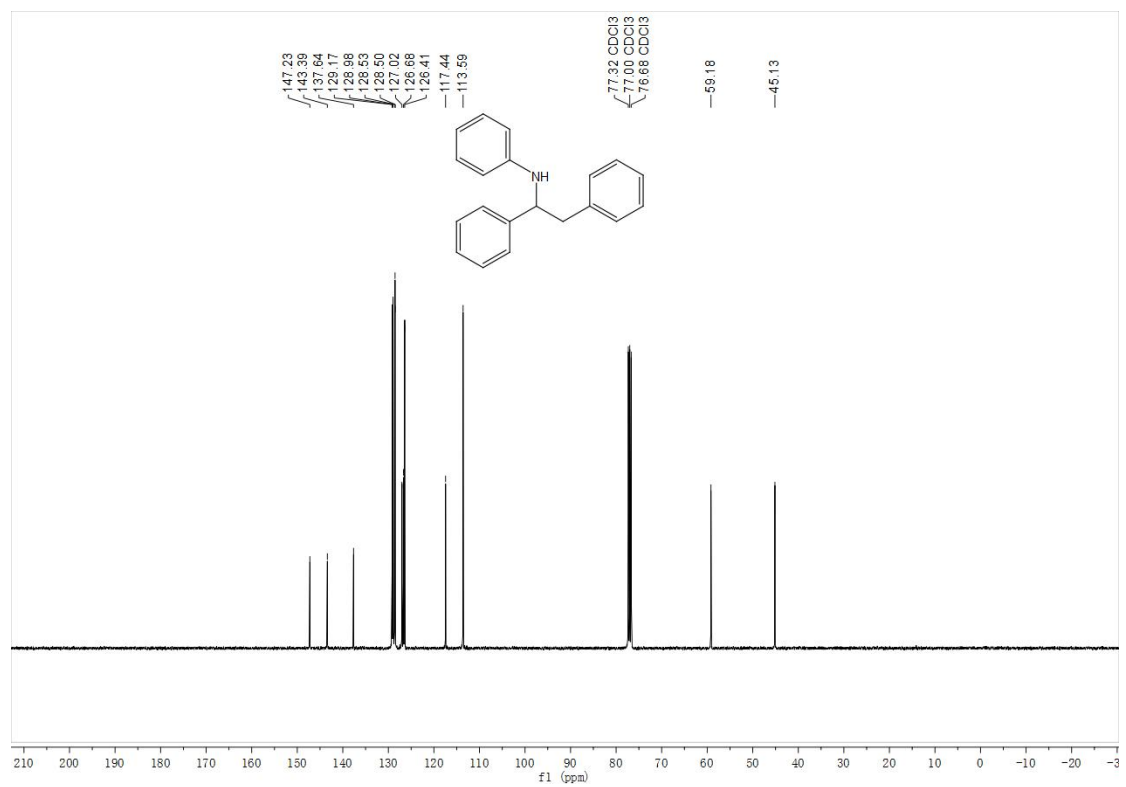


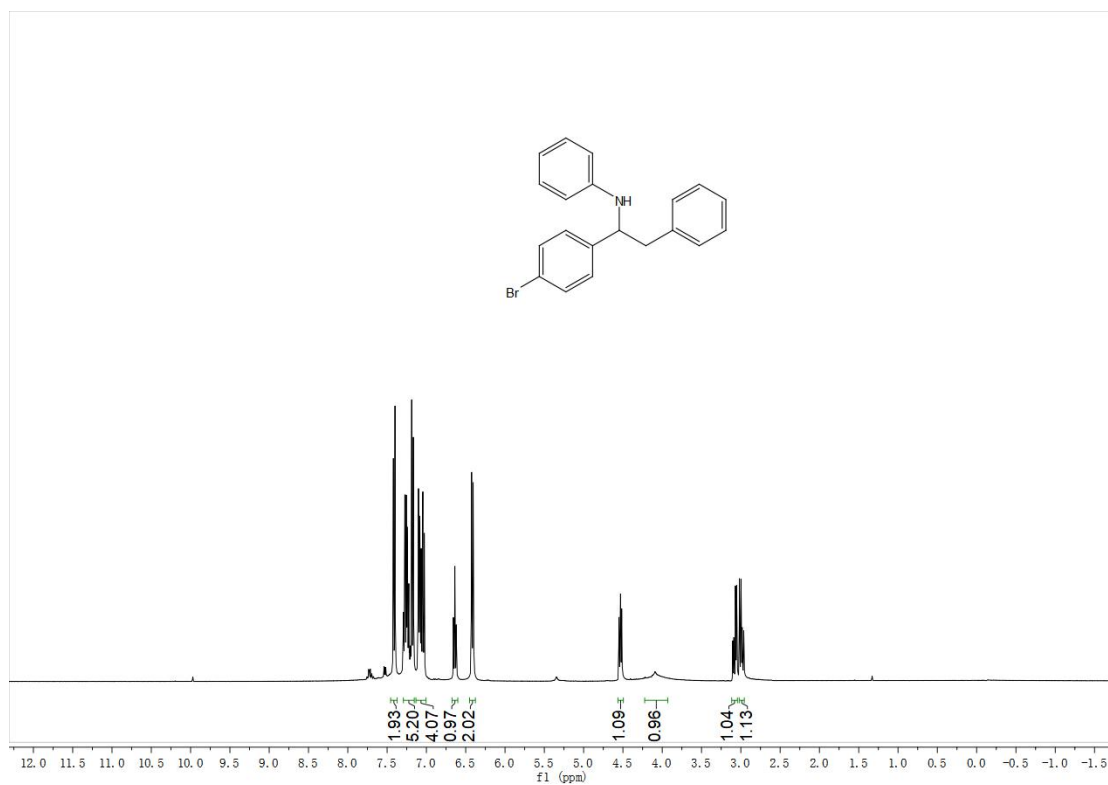
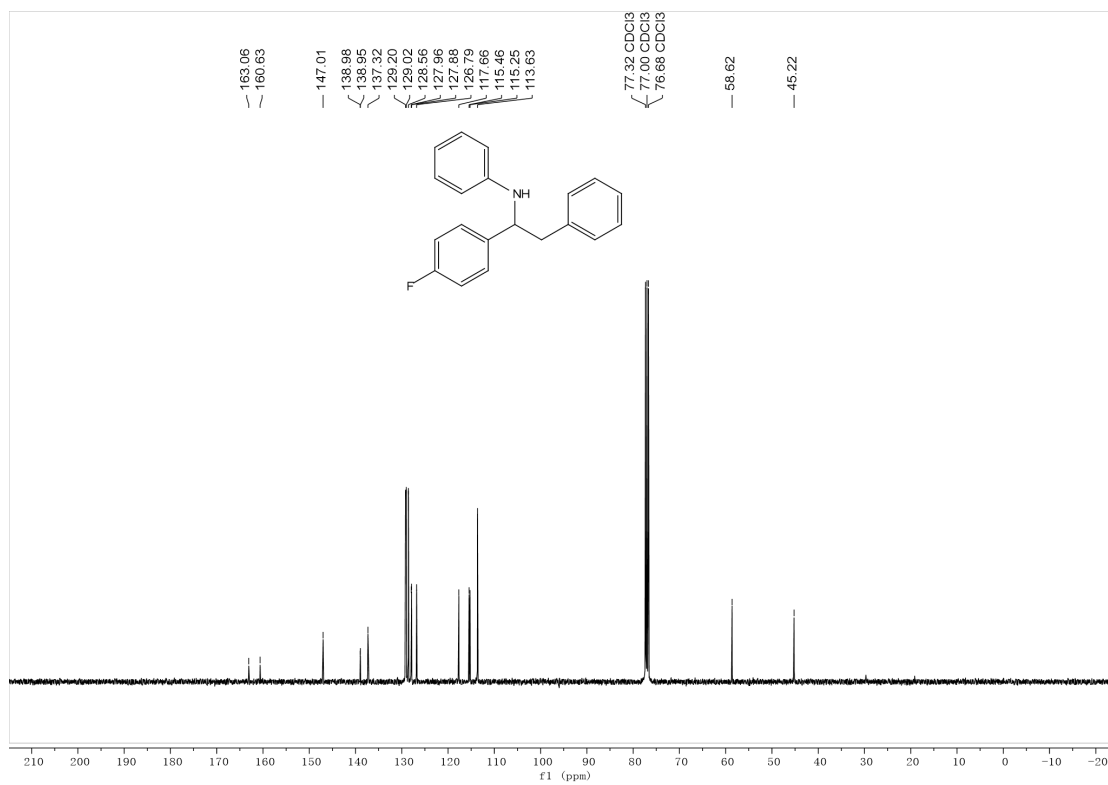


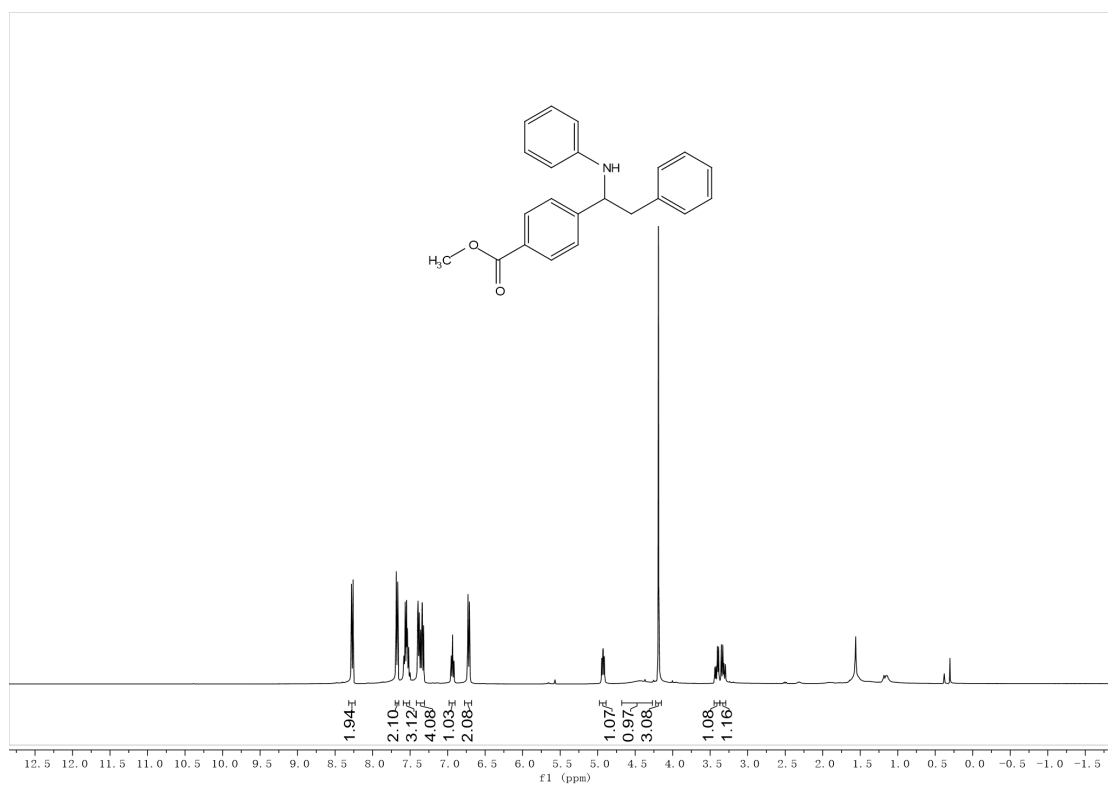
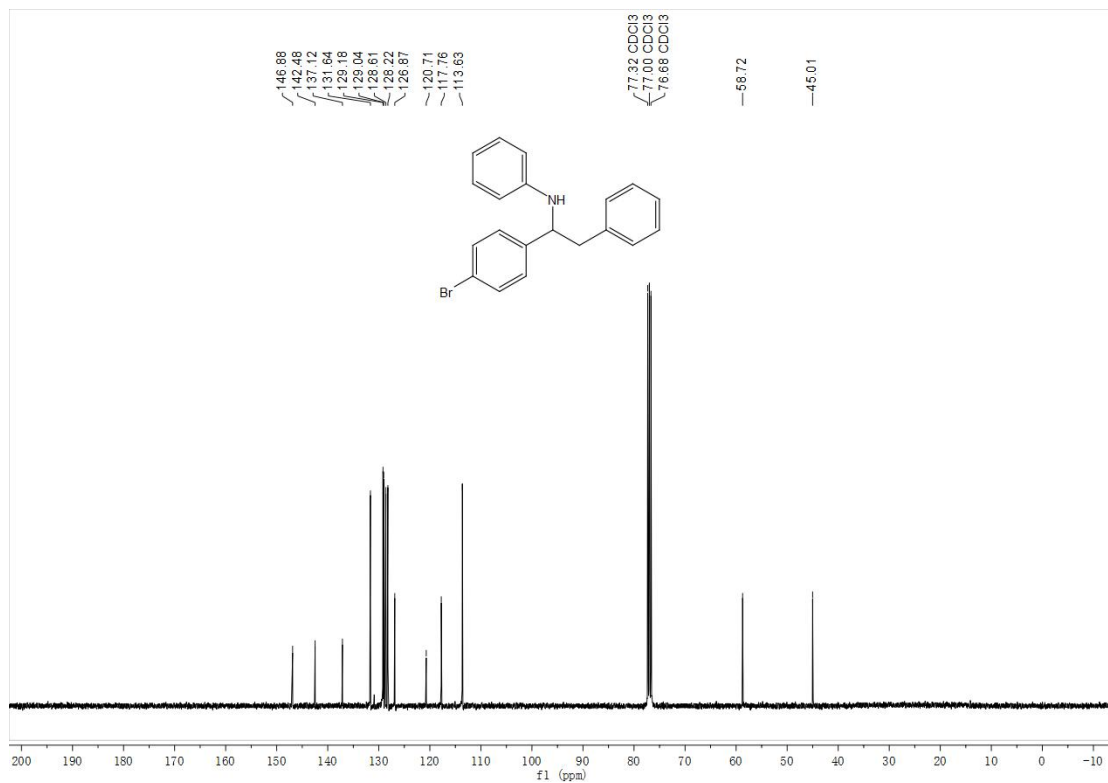


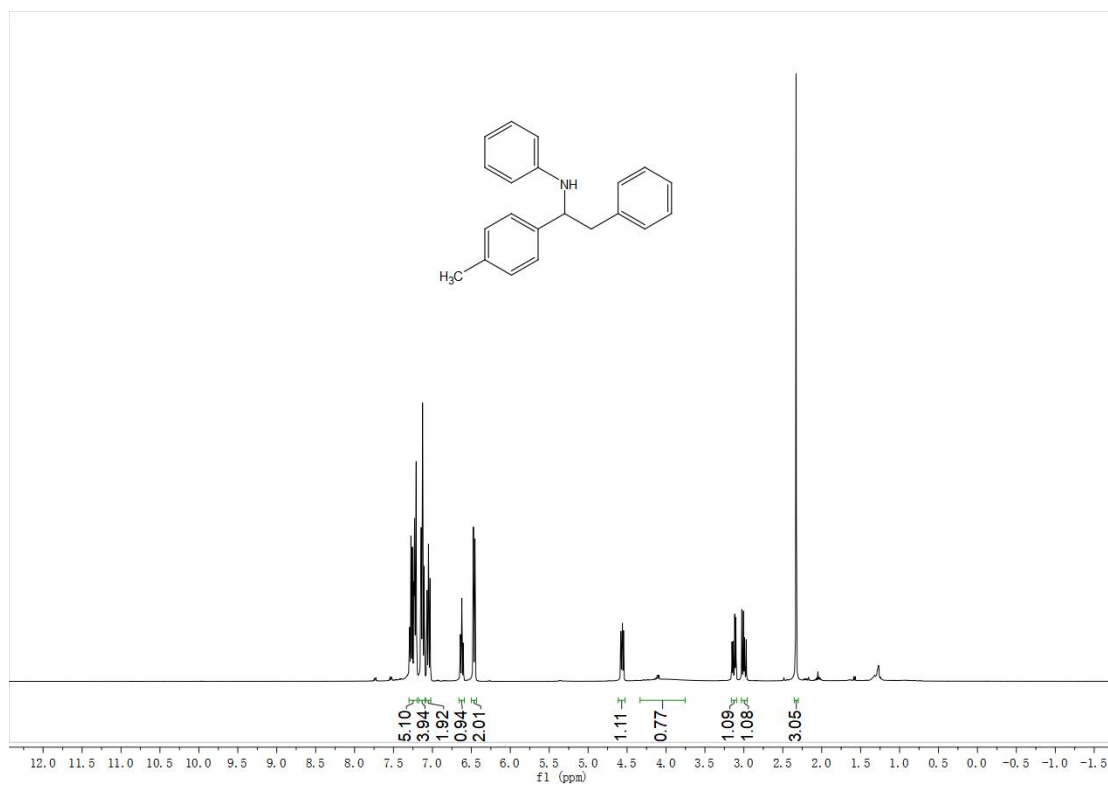
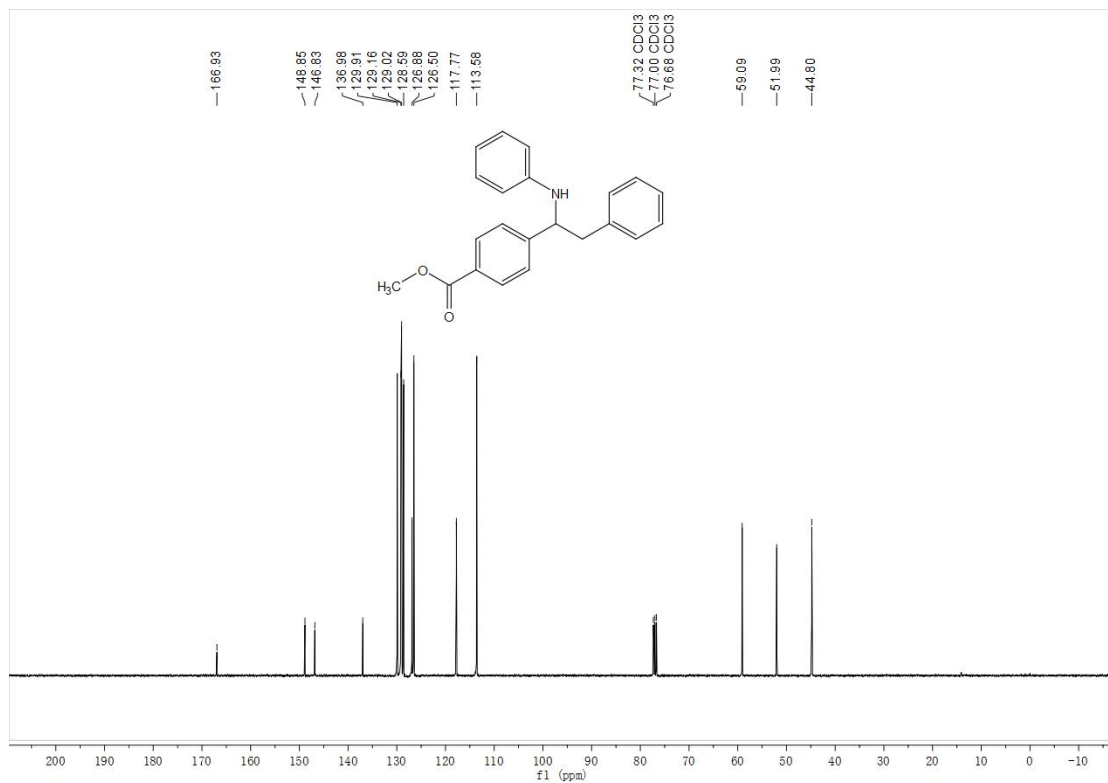
6. Copies of ¹H NMR, ¹³C NMR Spectra

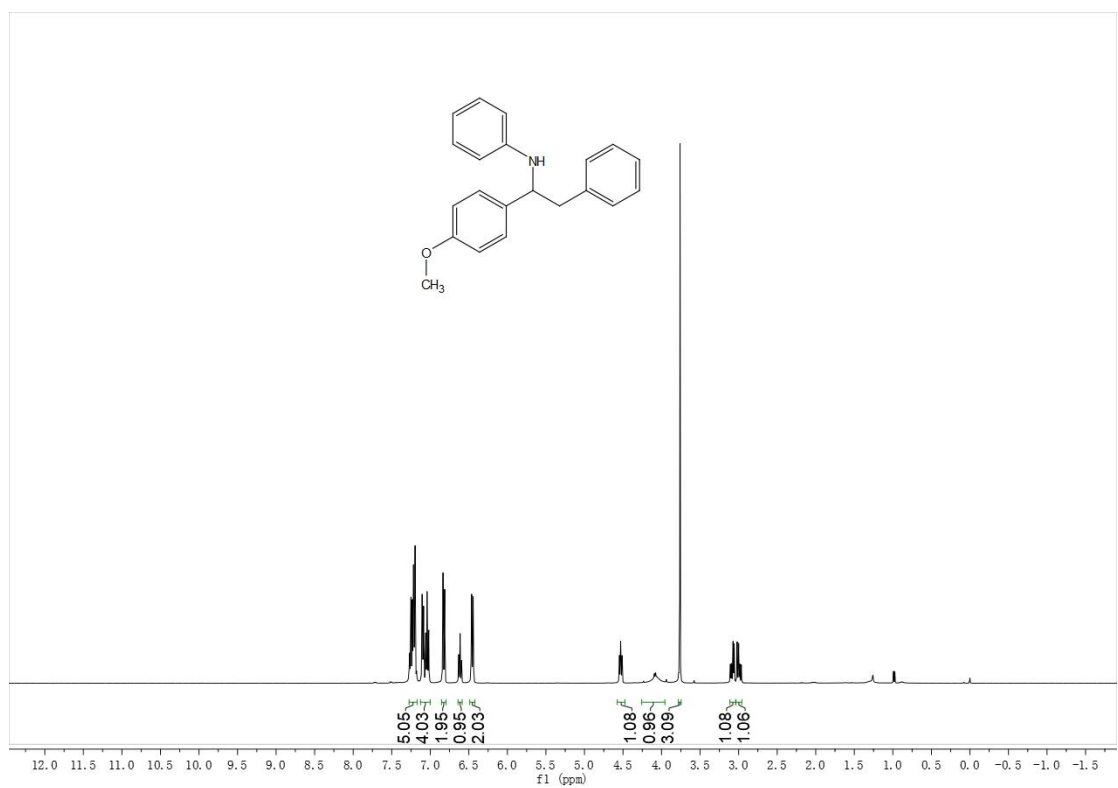
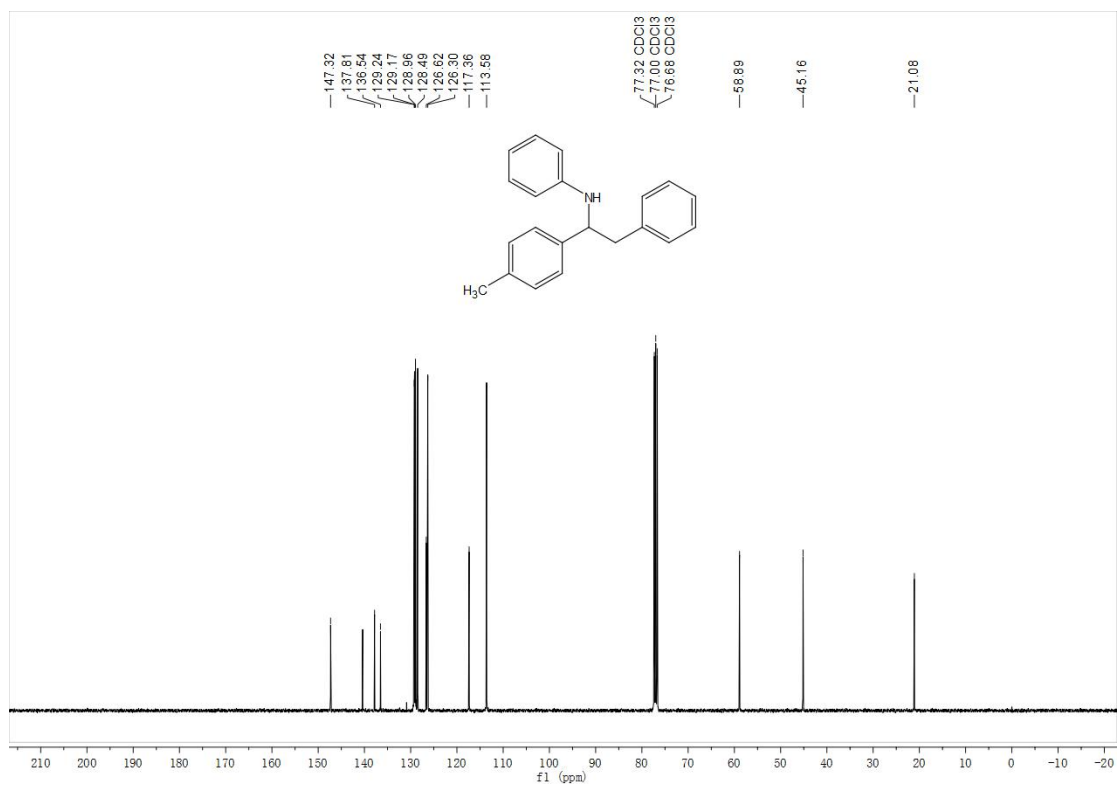


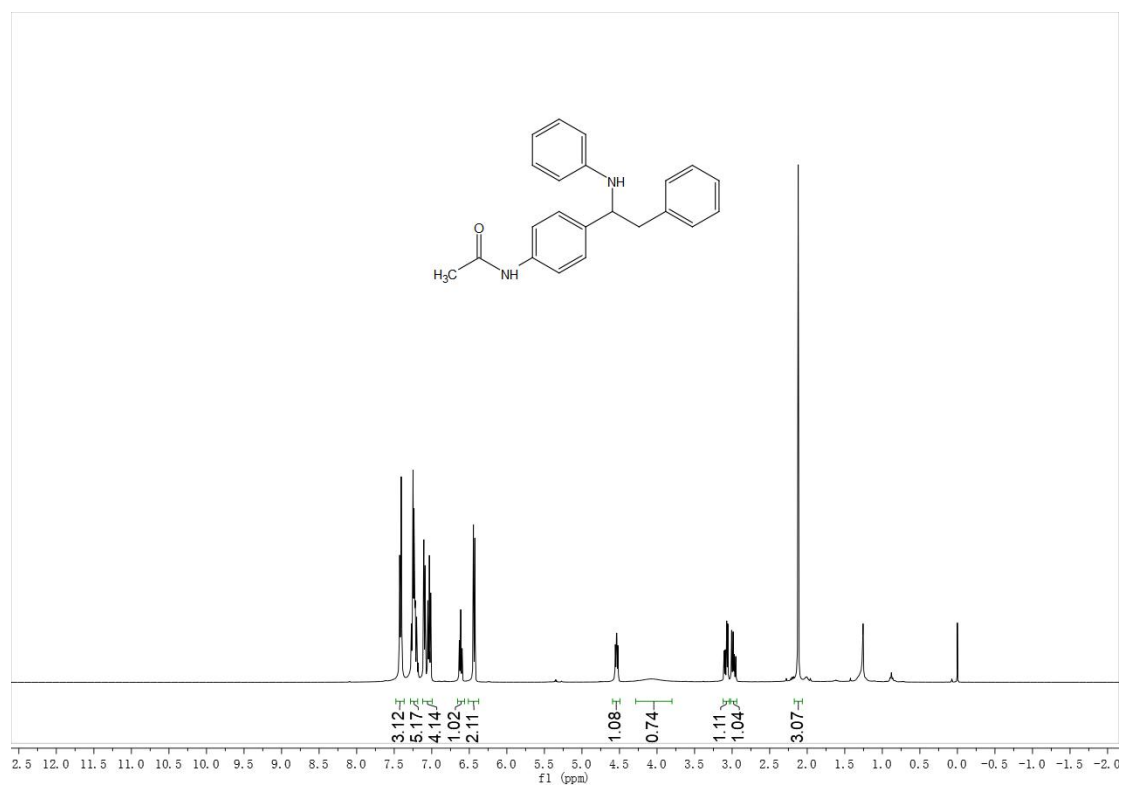
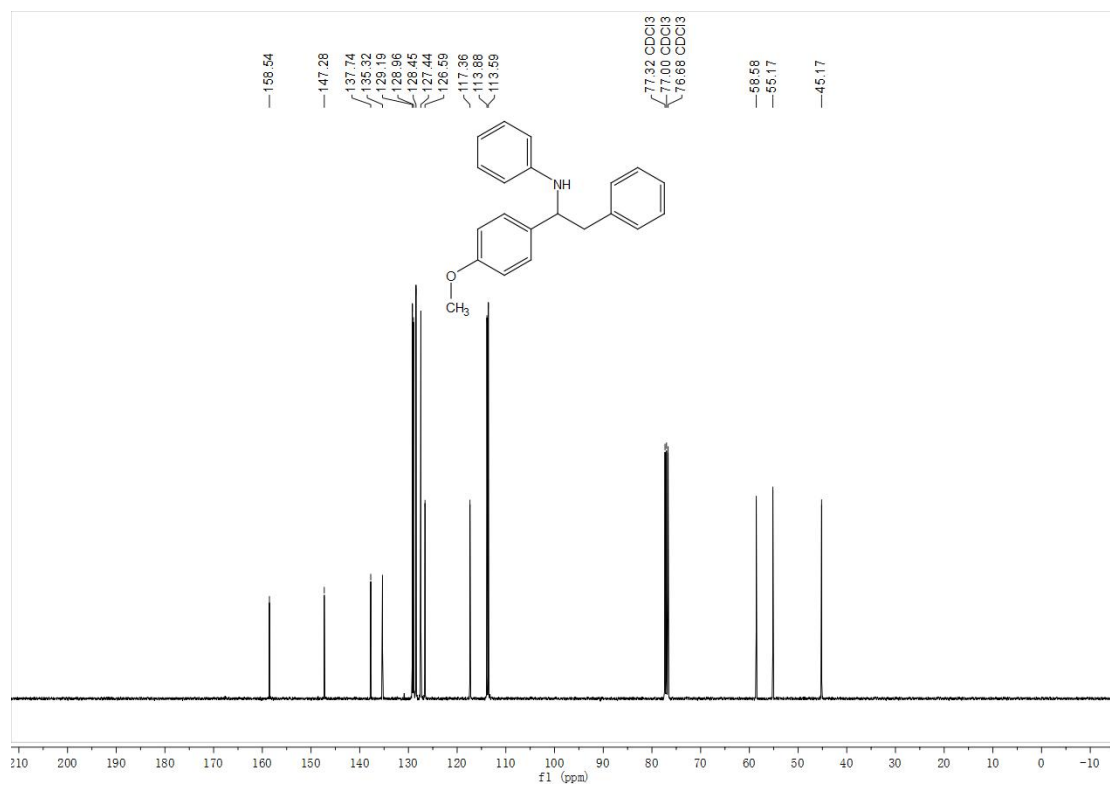


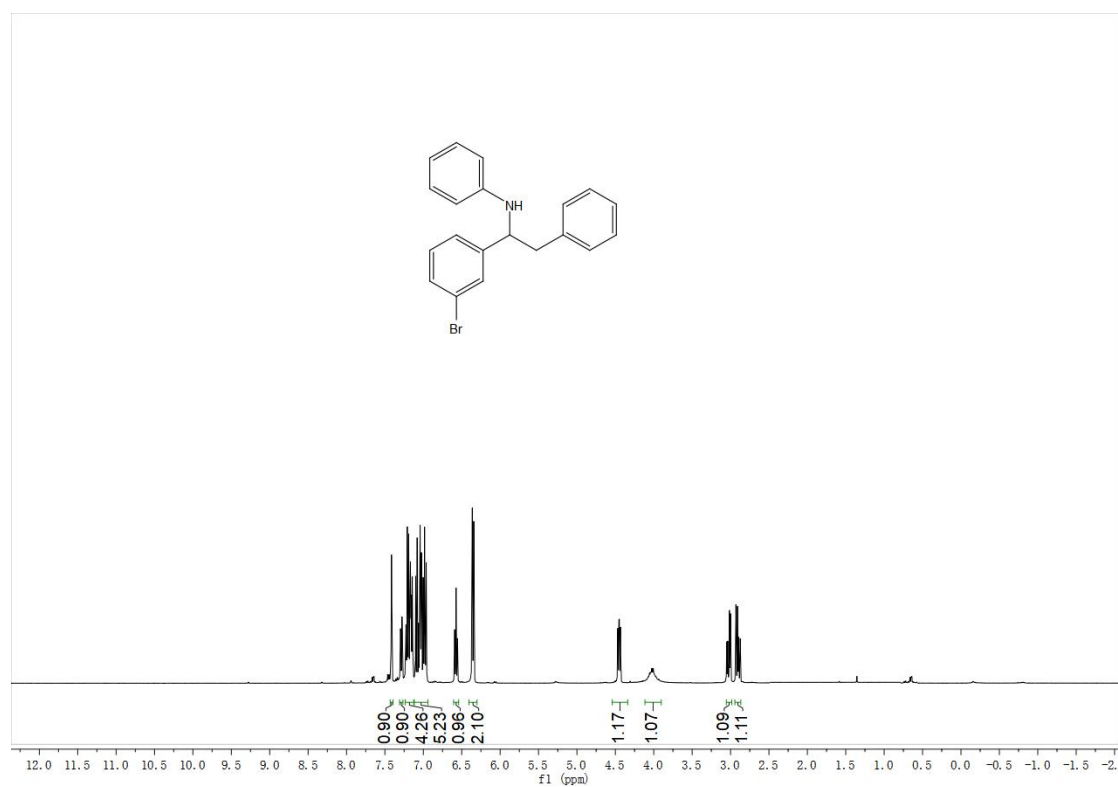
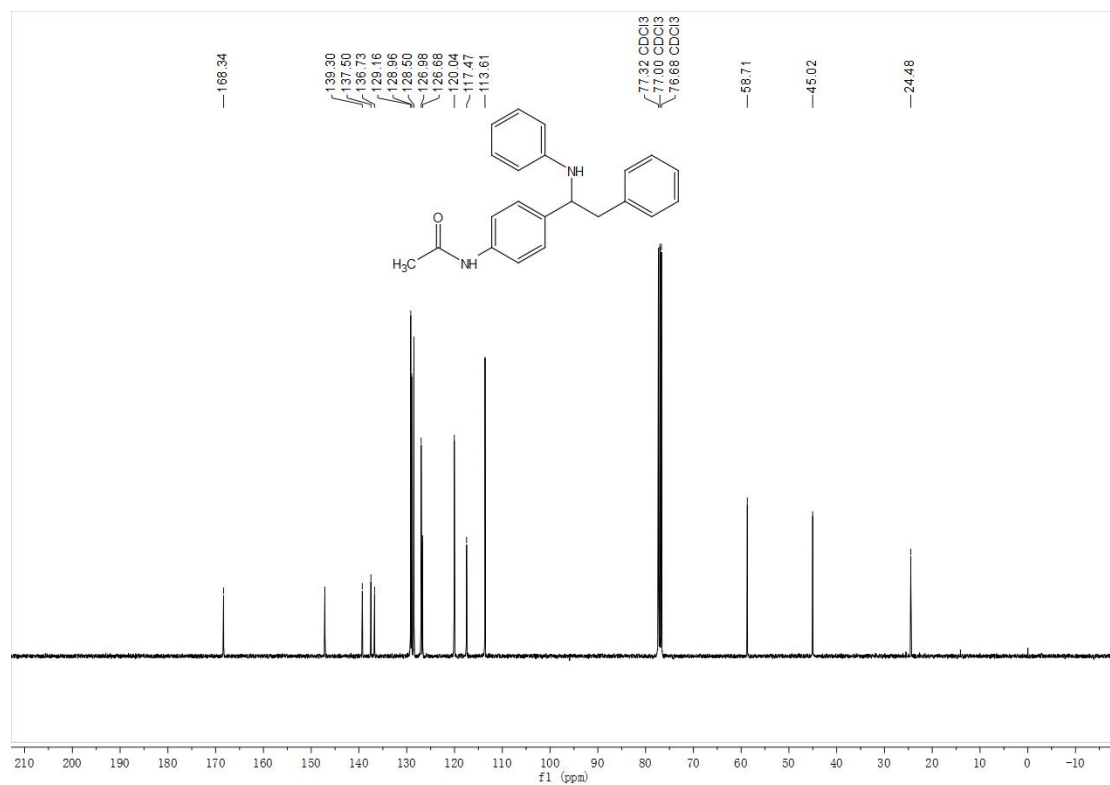


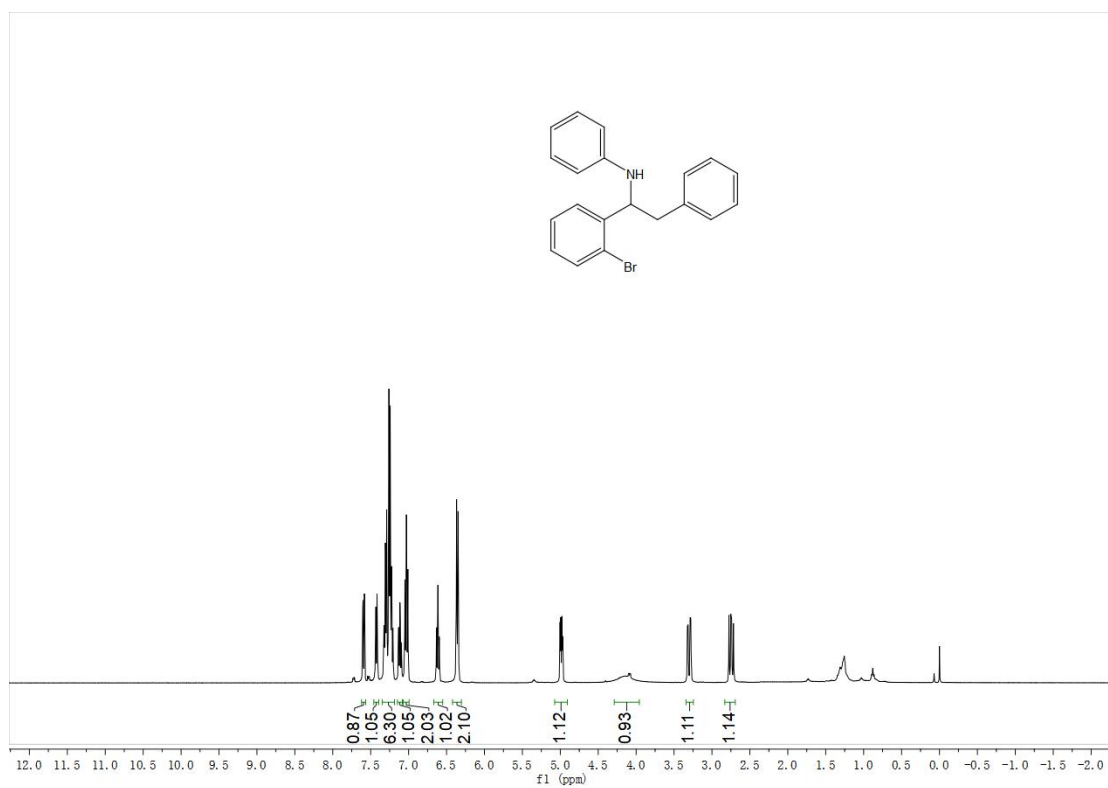
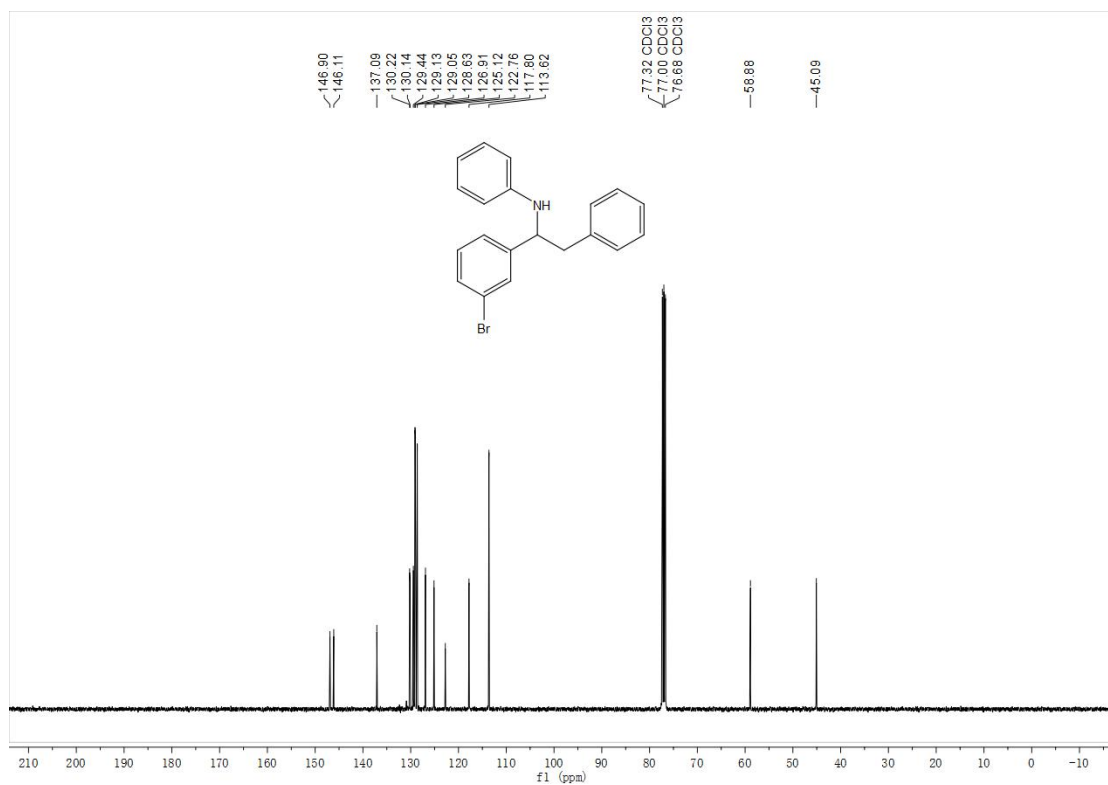


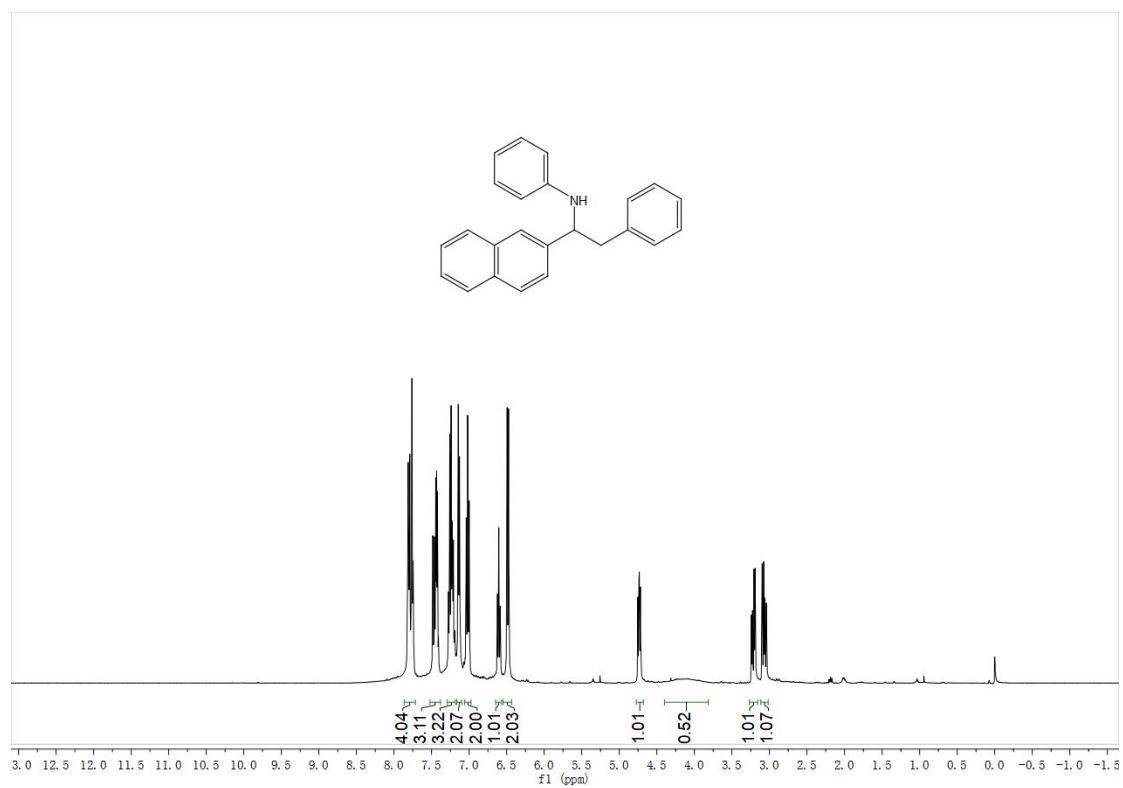
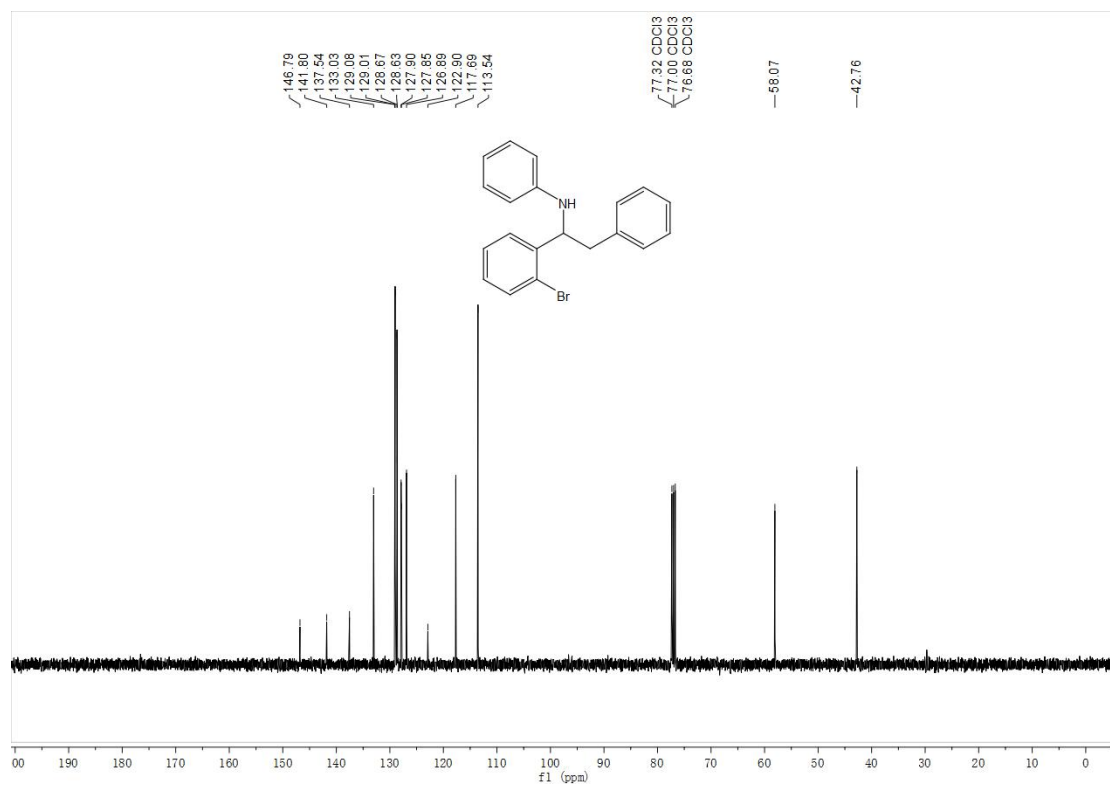


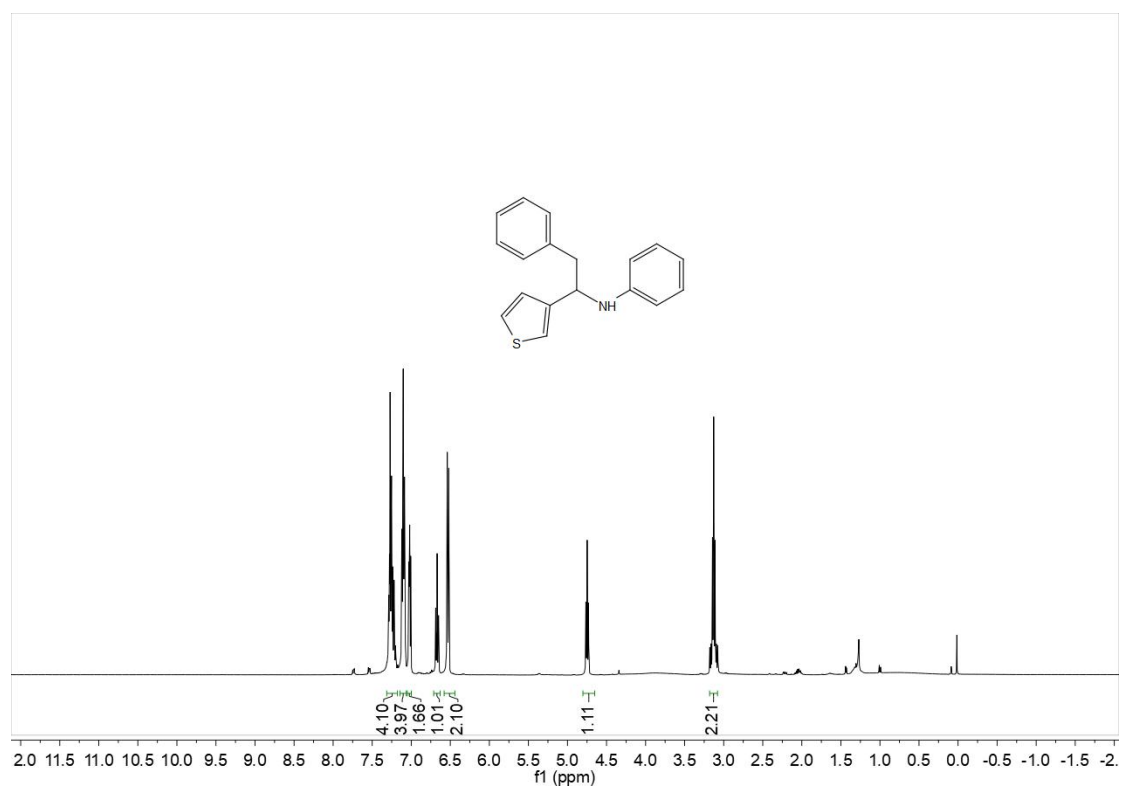
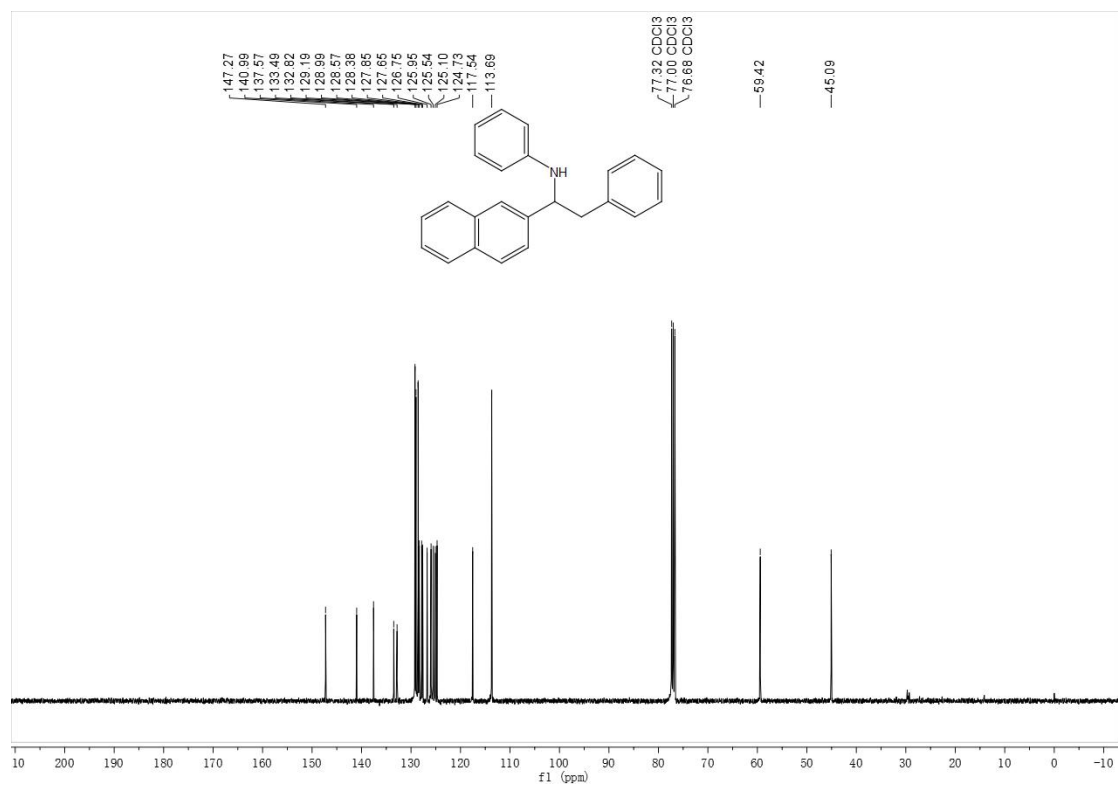


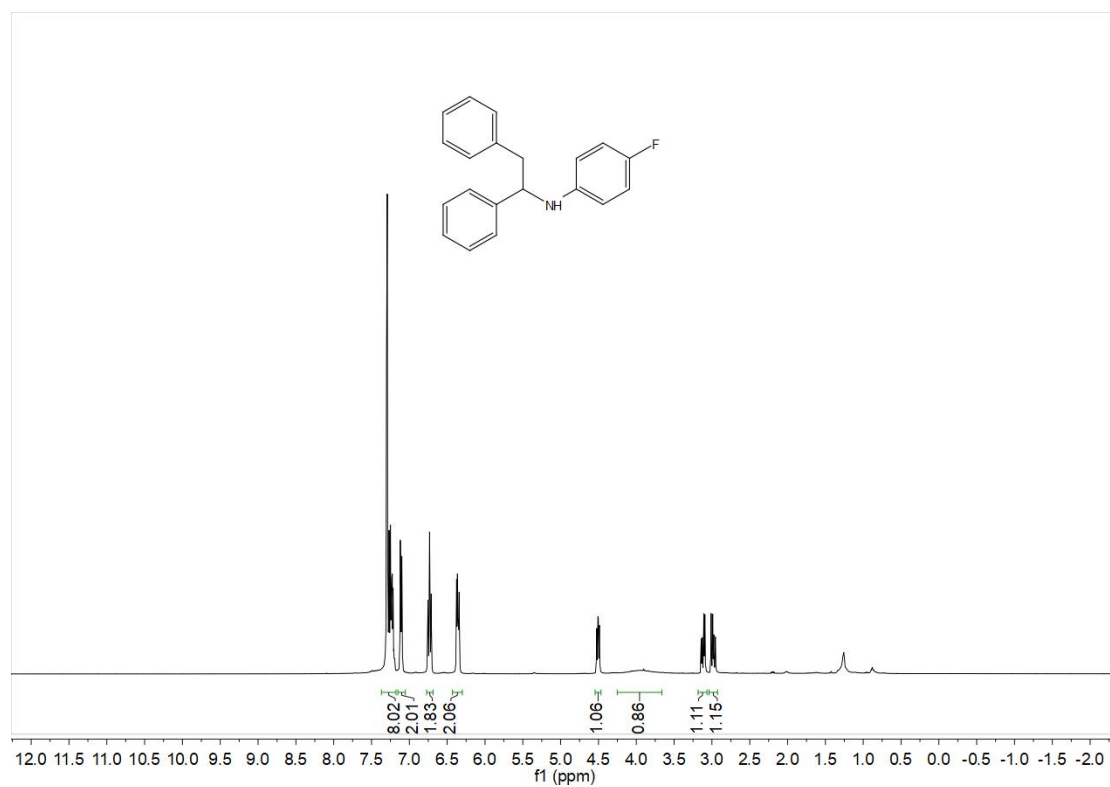
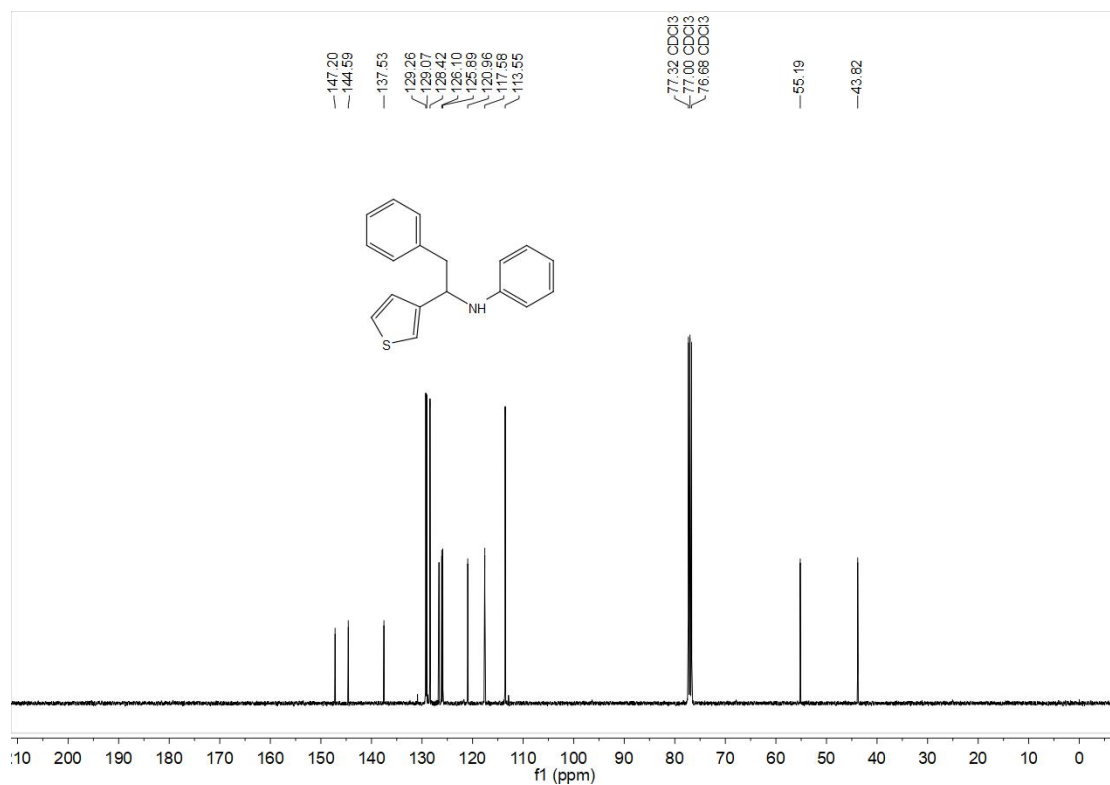


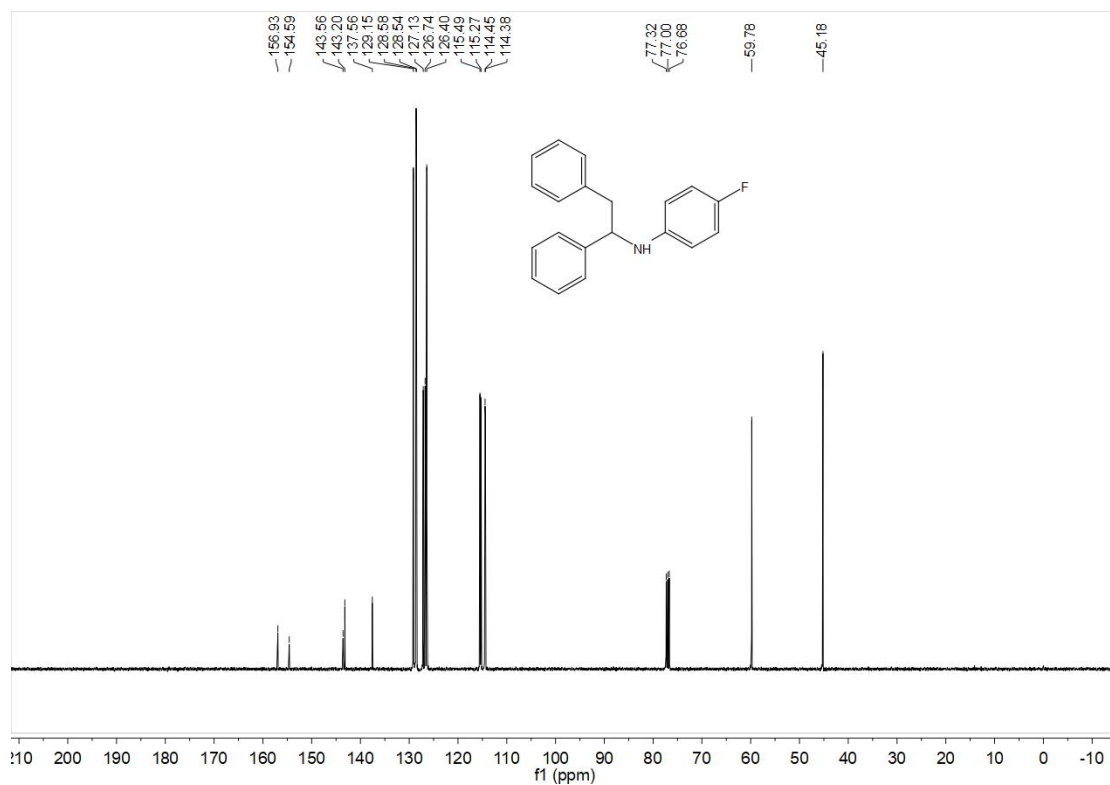


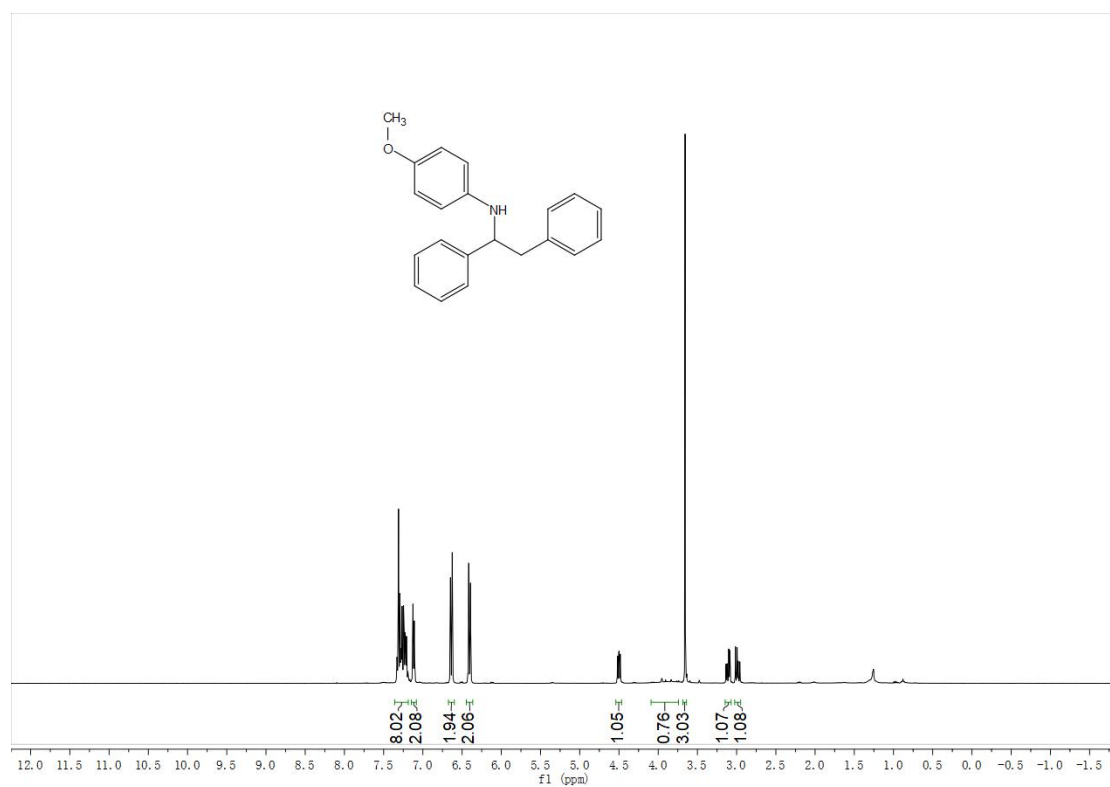
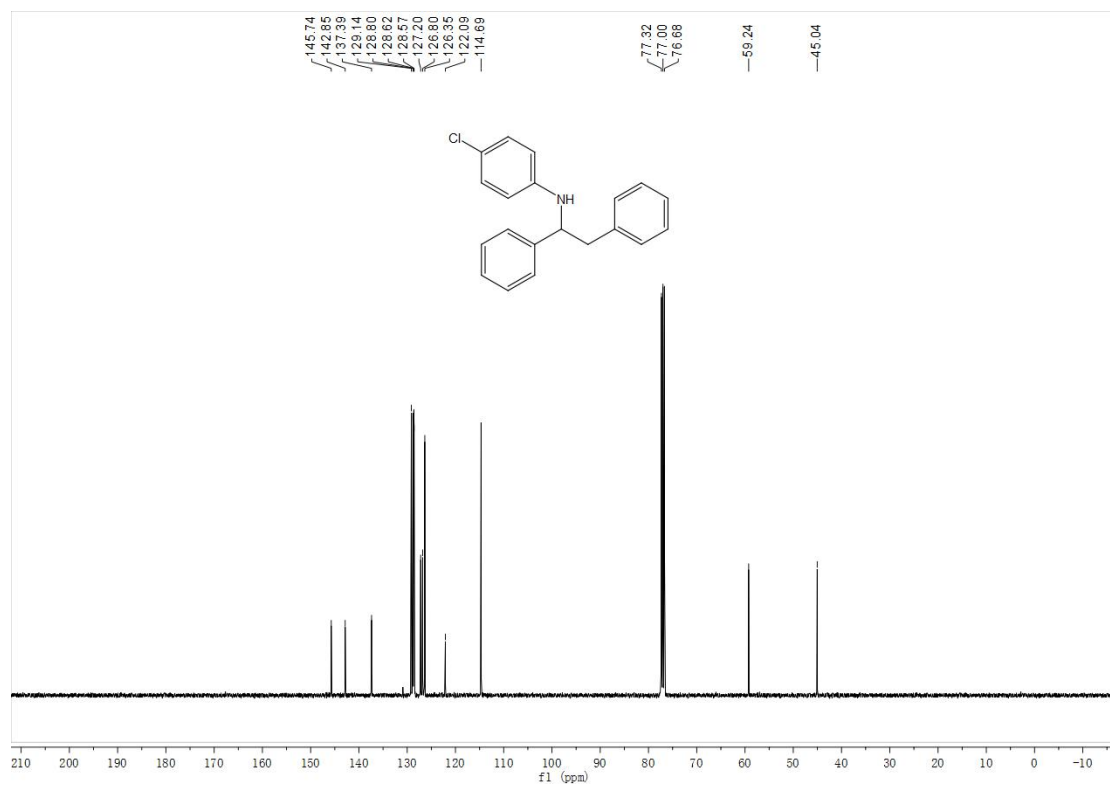


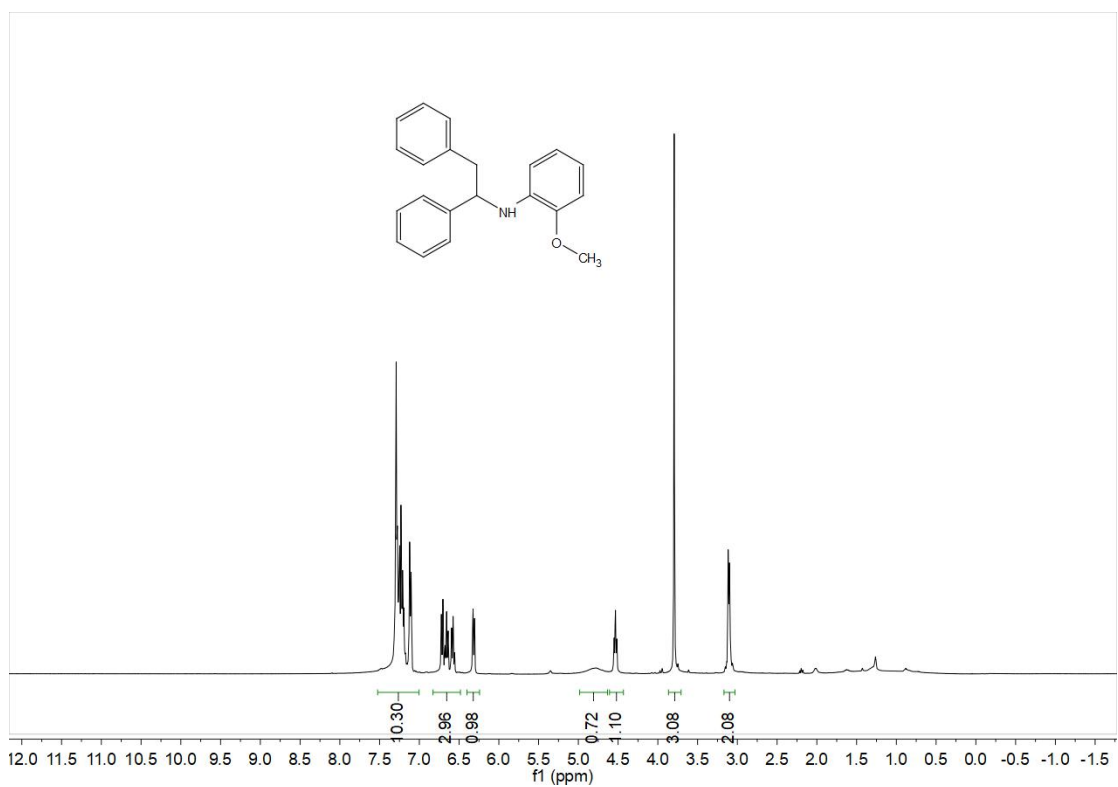
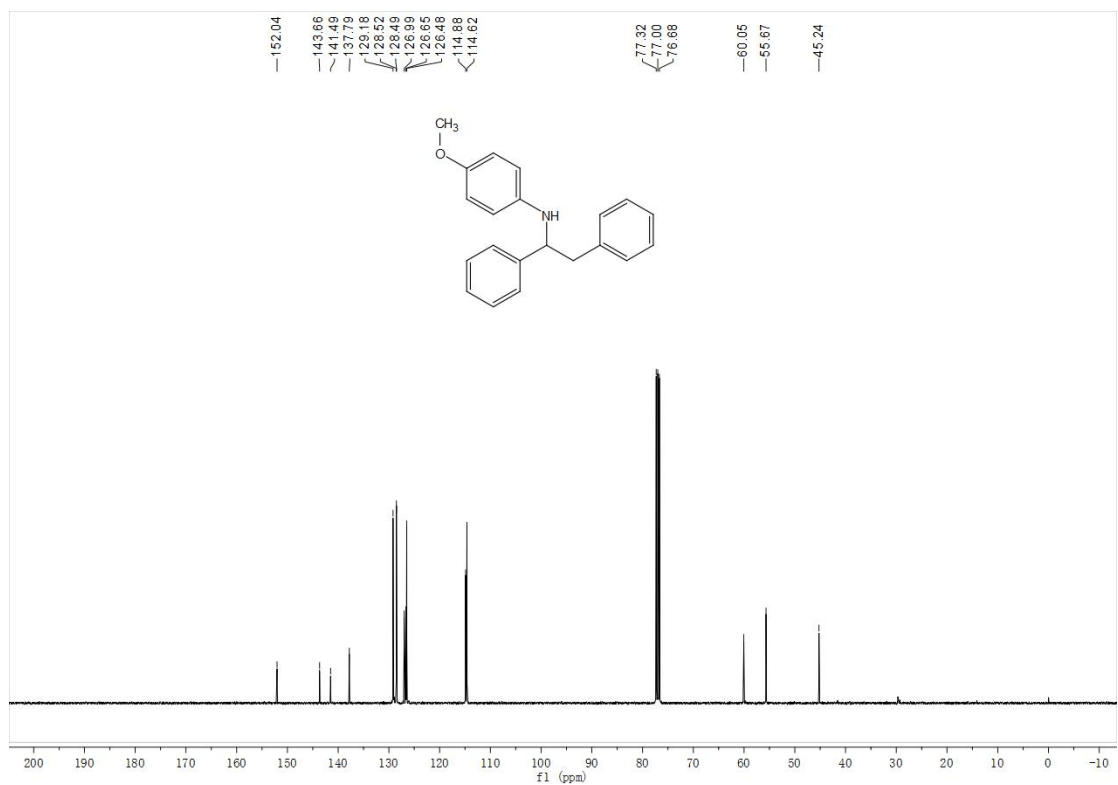


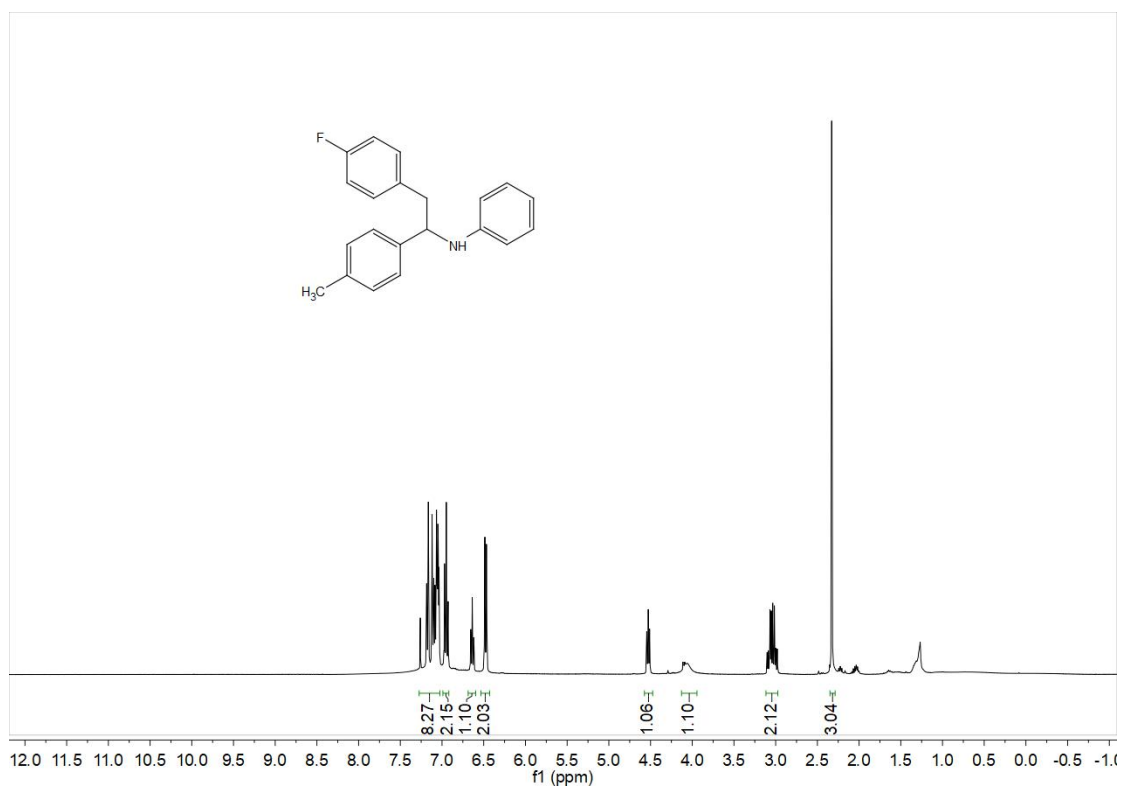
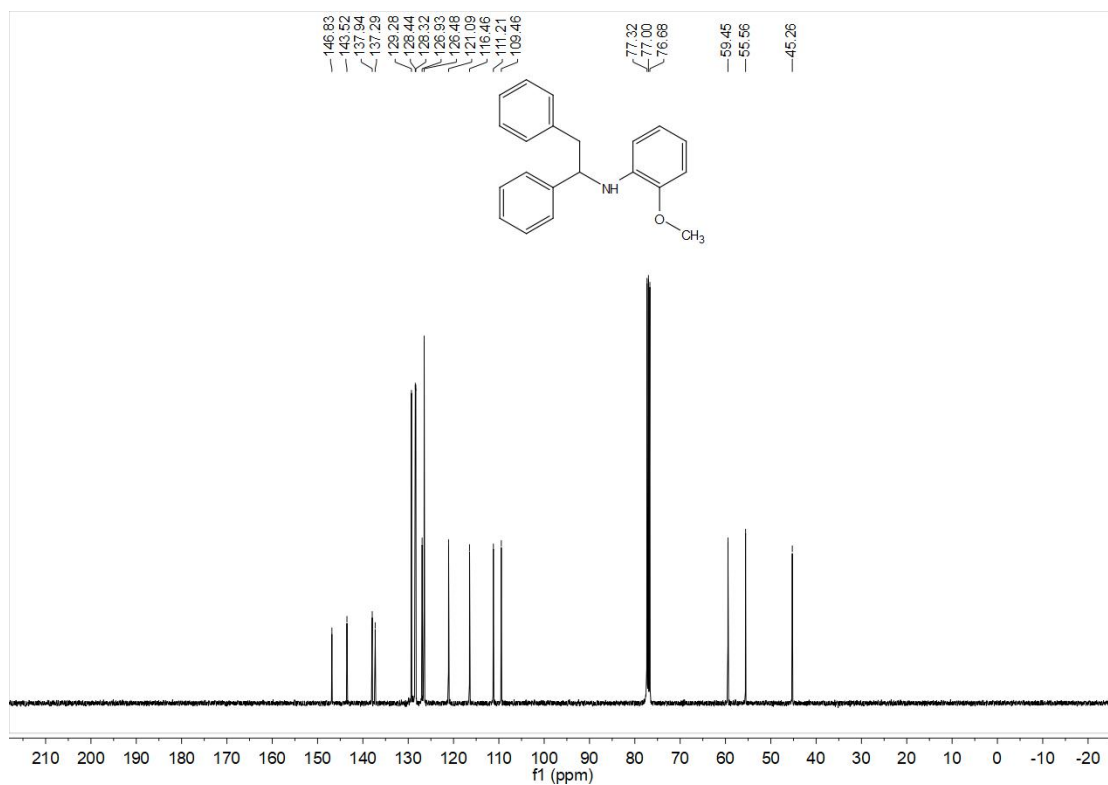


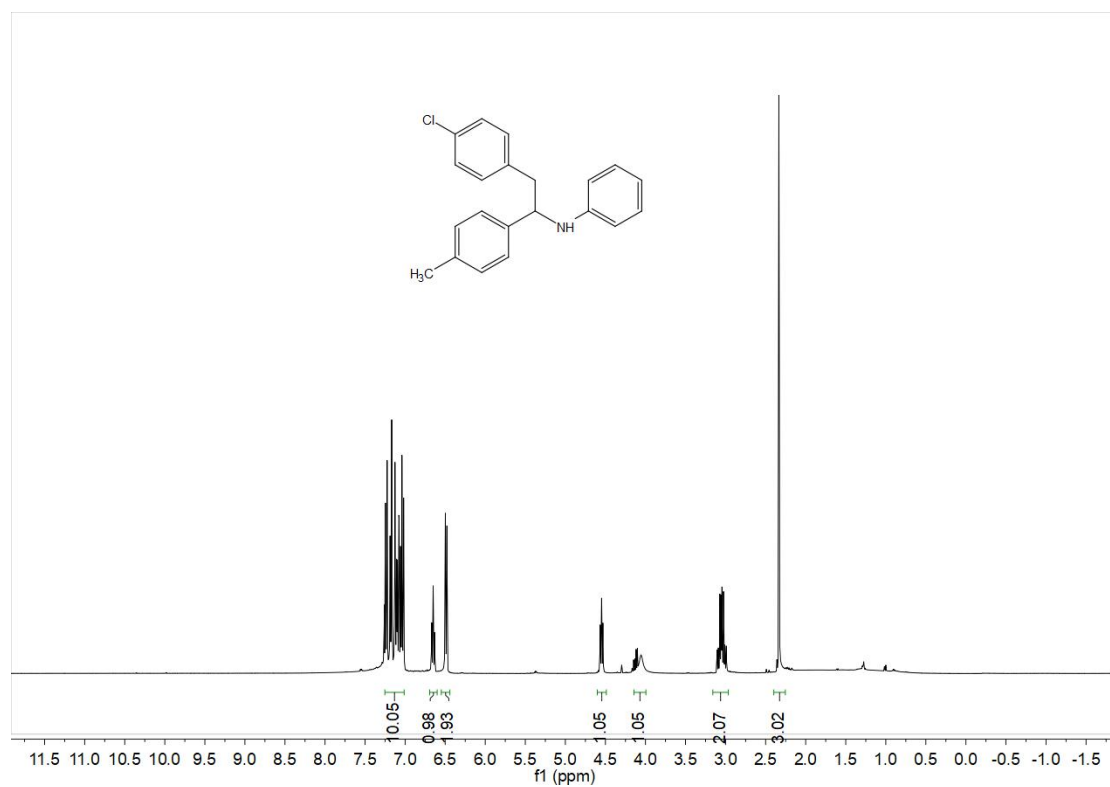
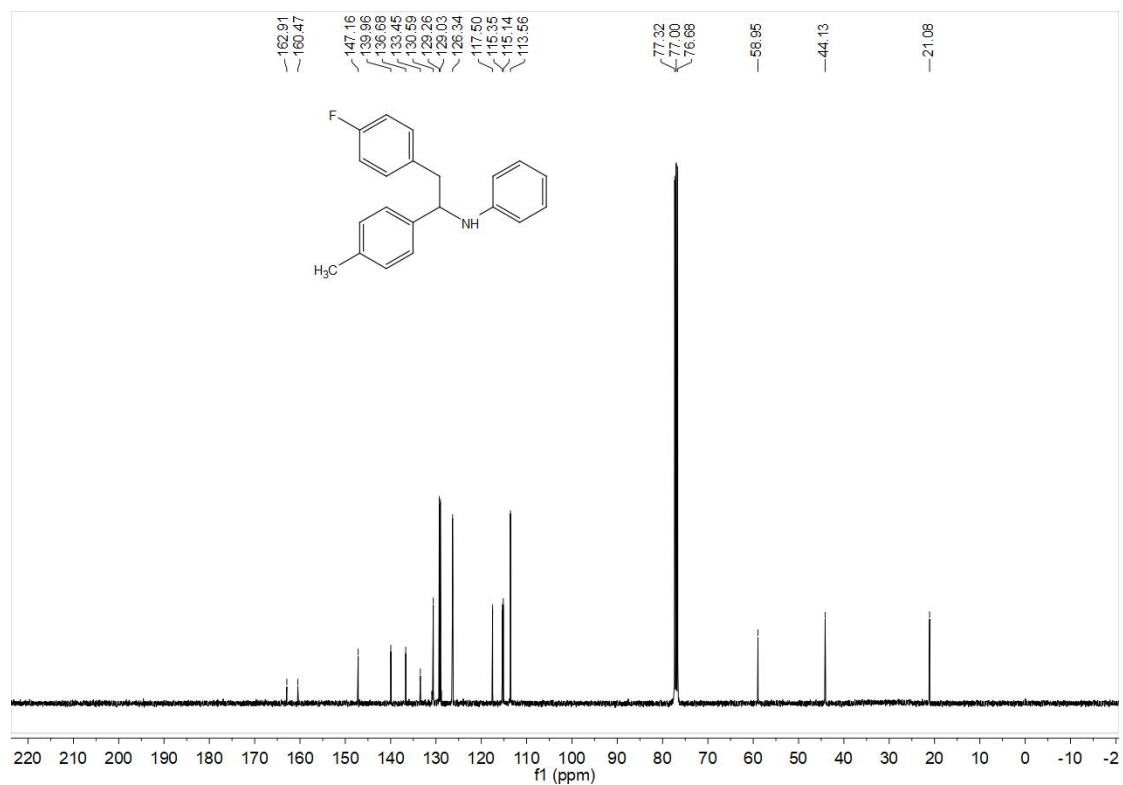


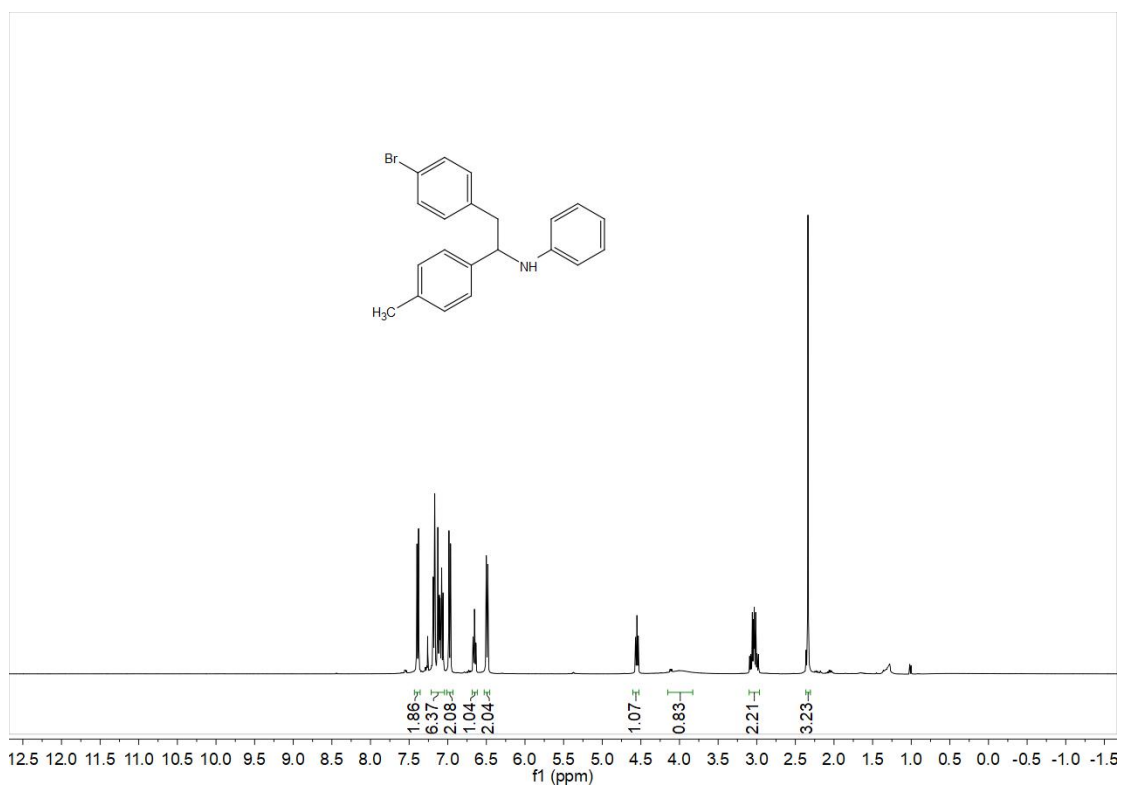
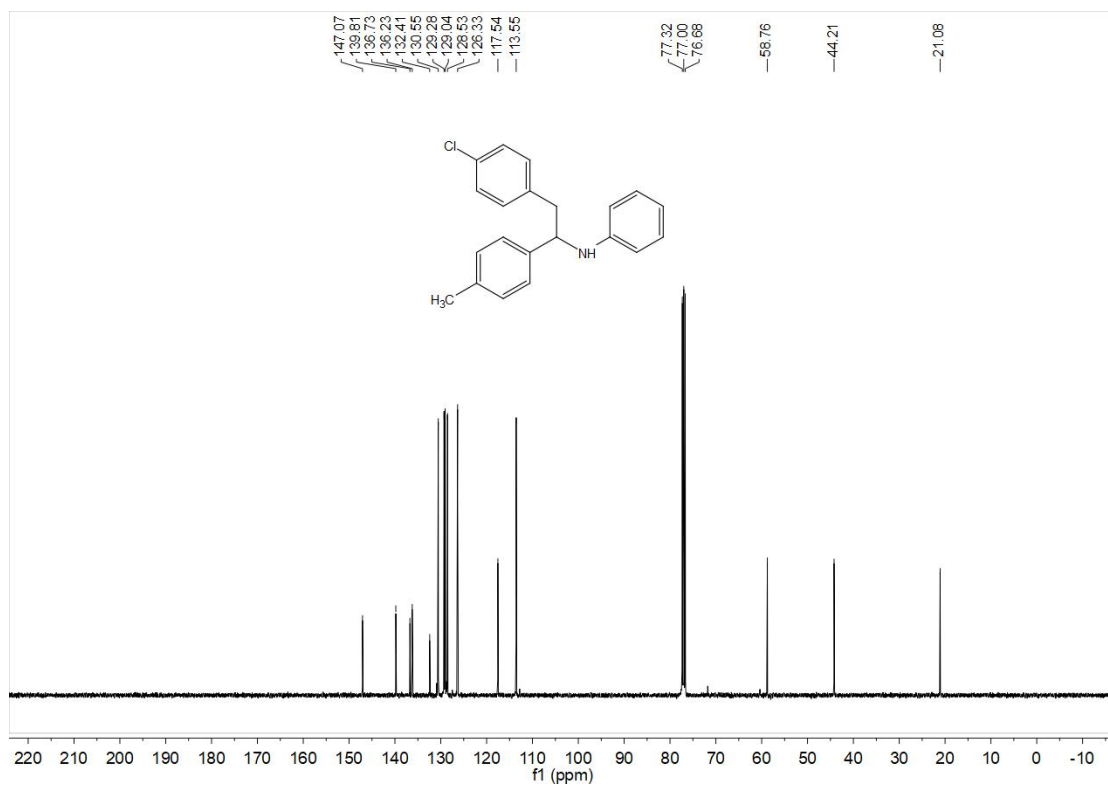


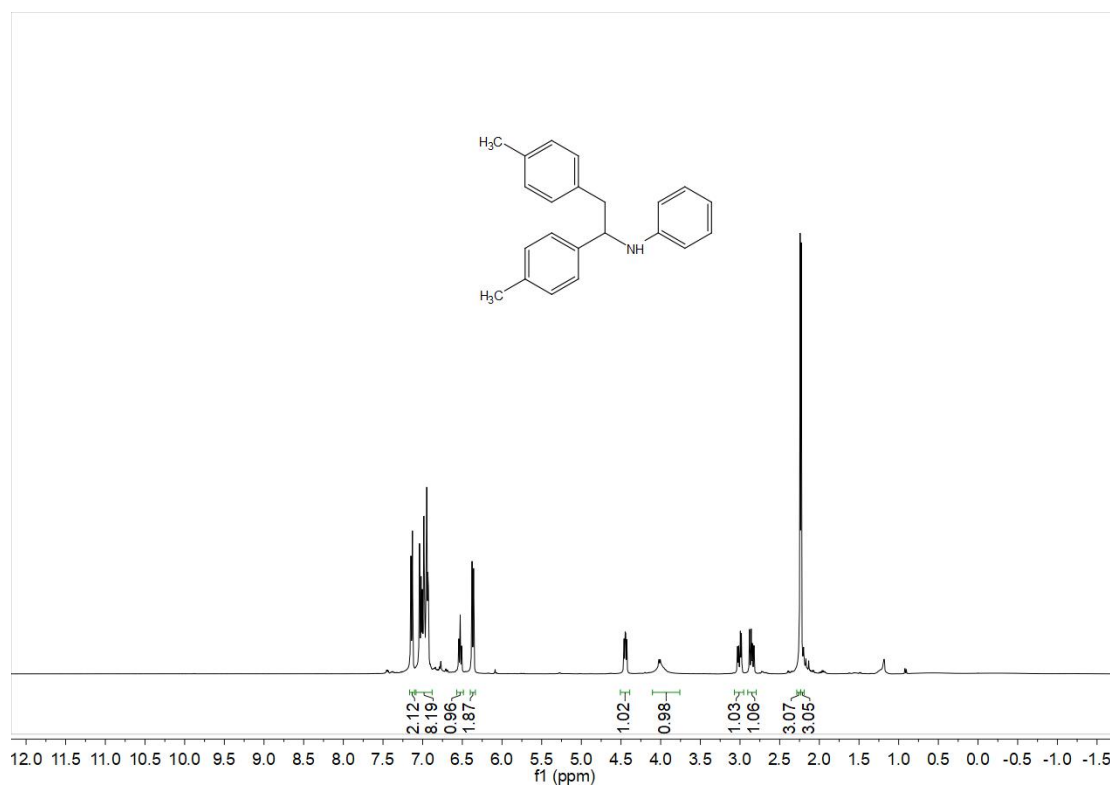
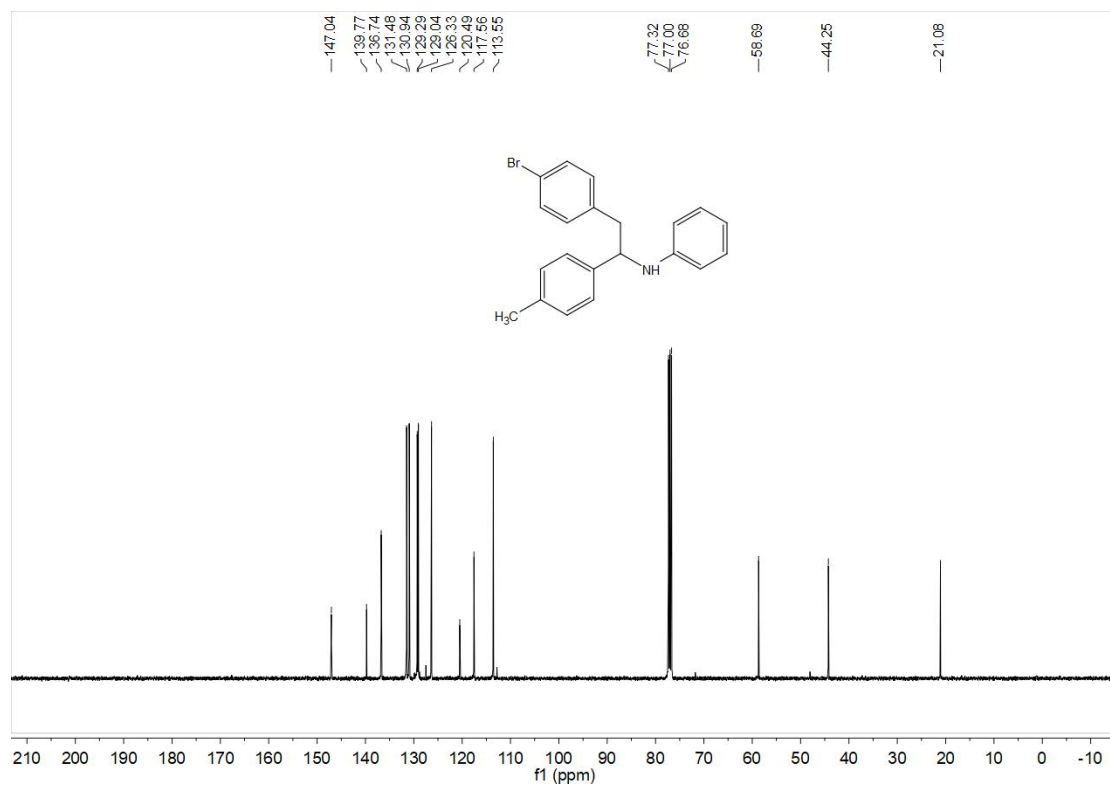


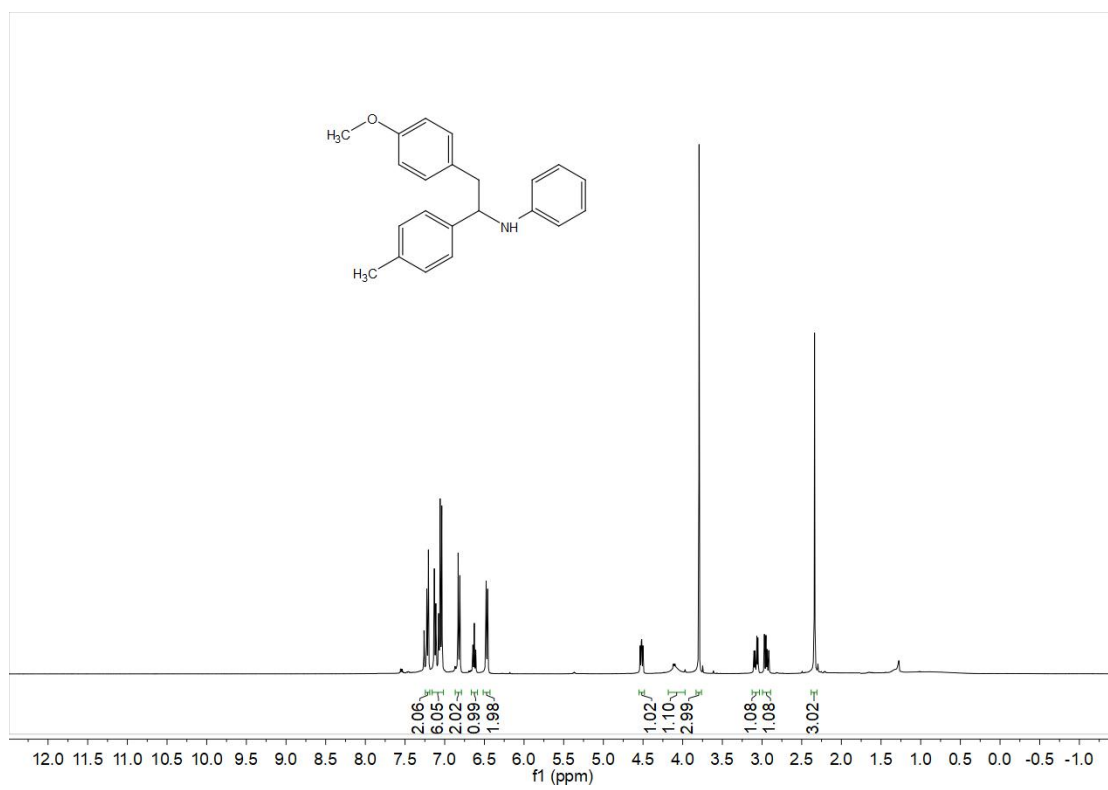
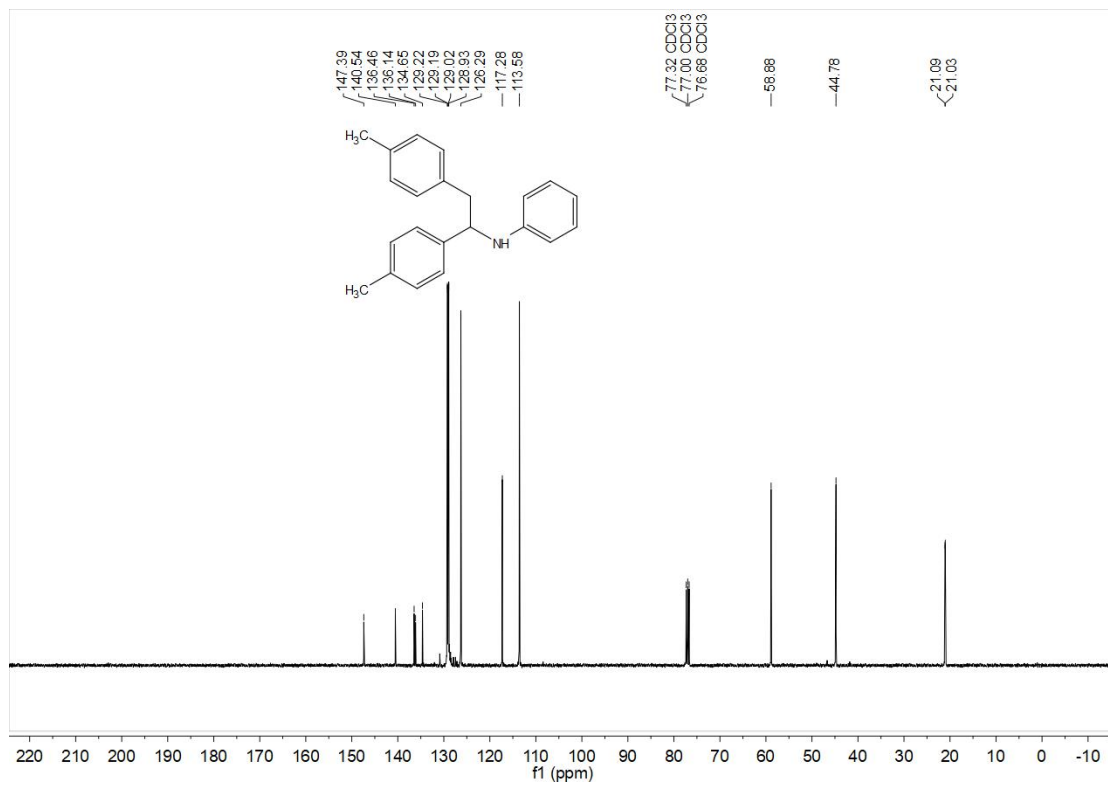


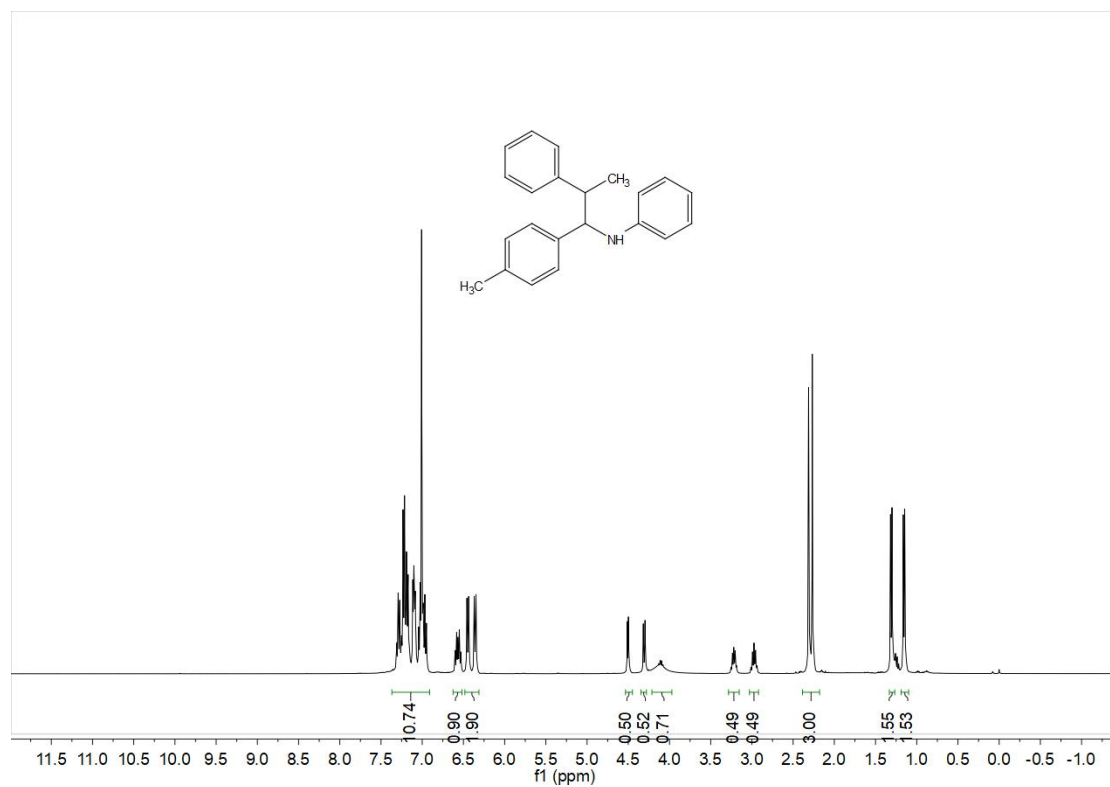
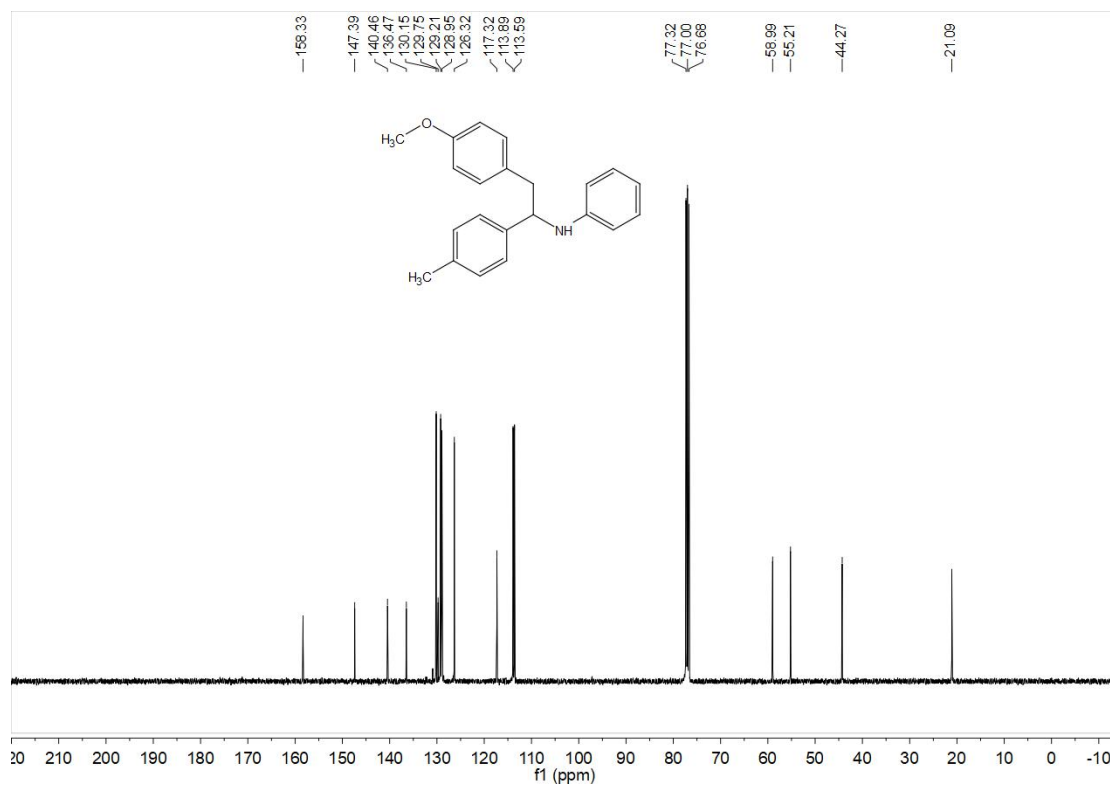


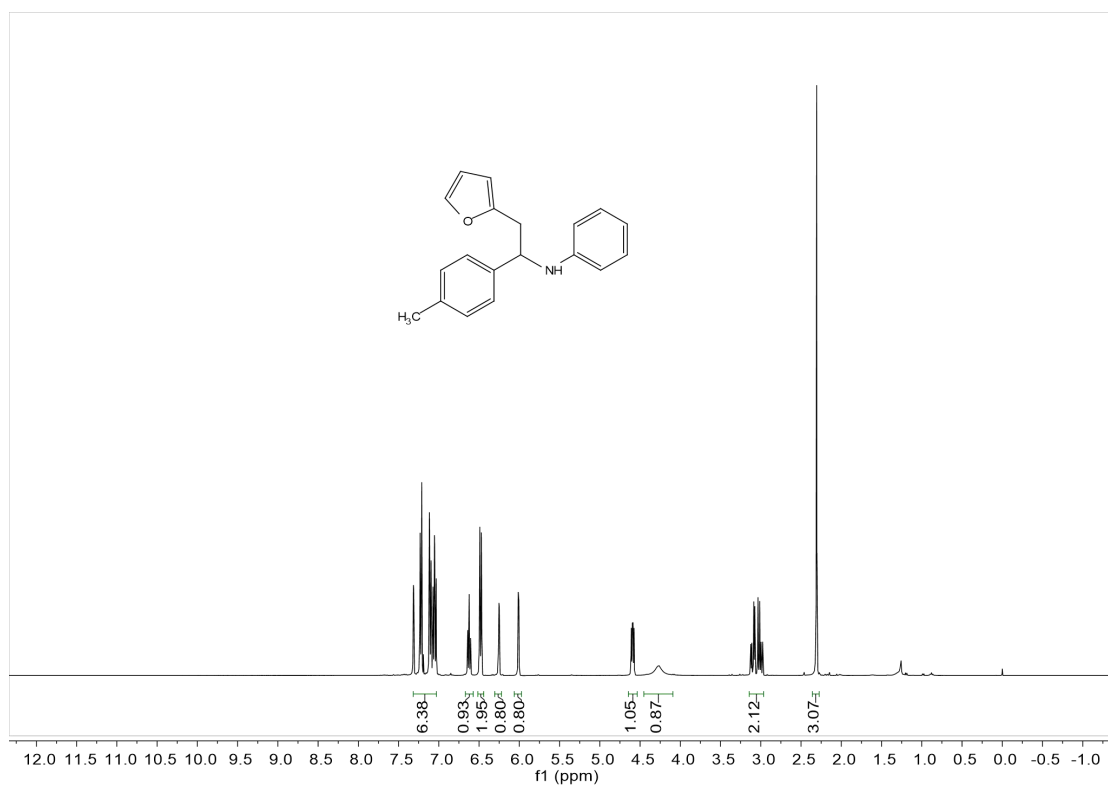
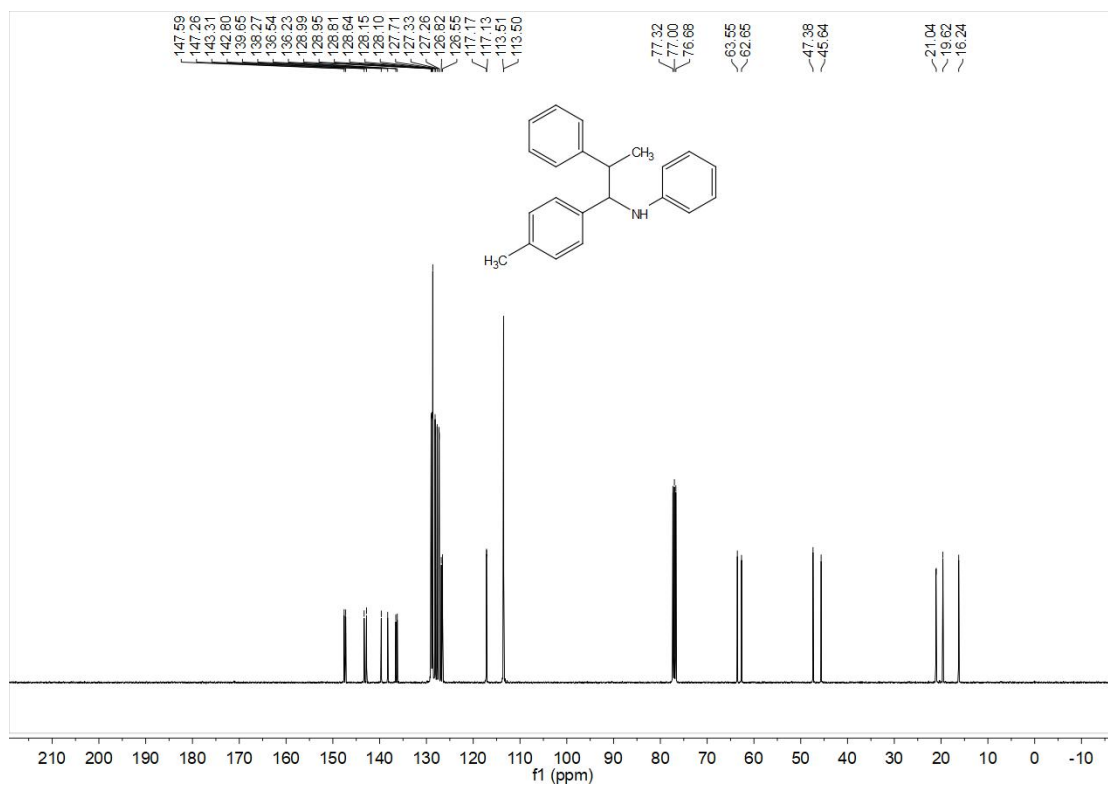


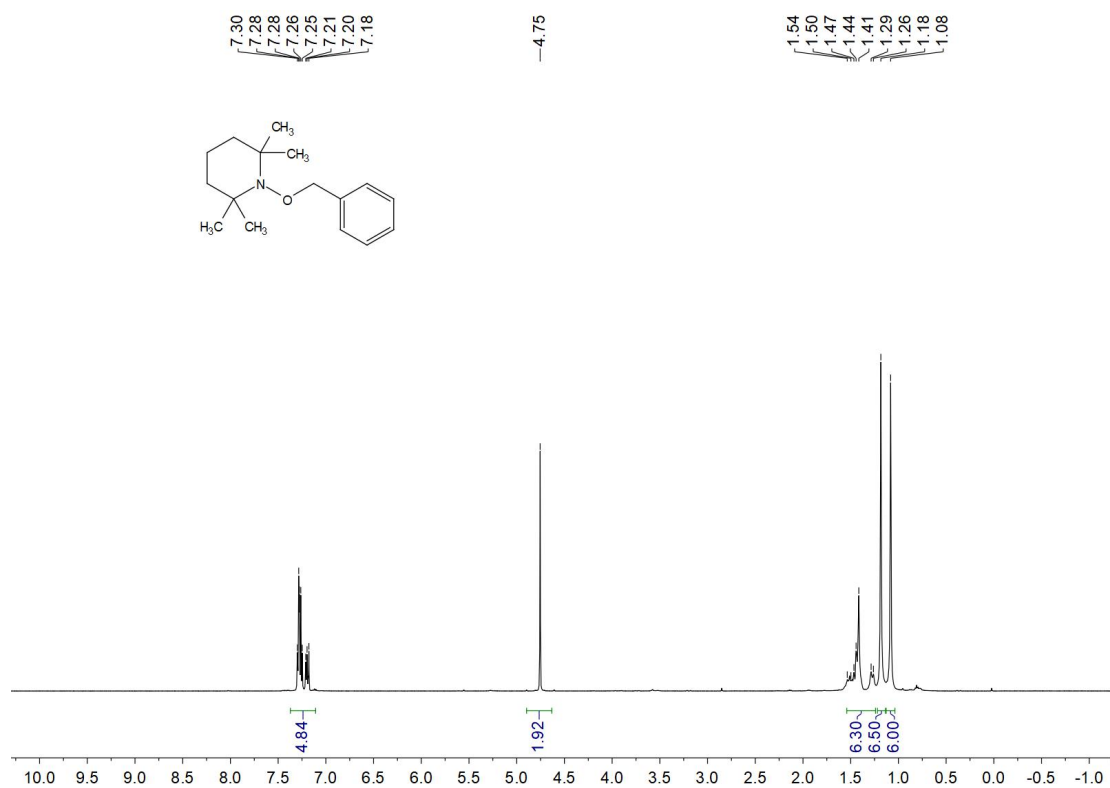
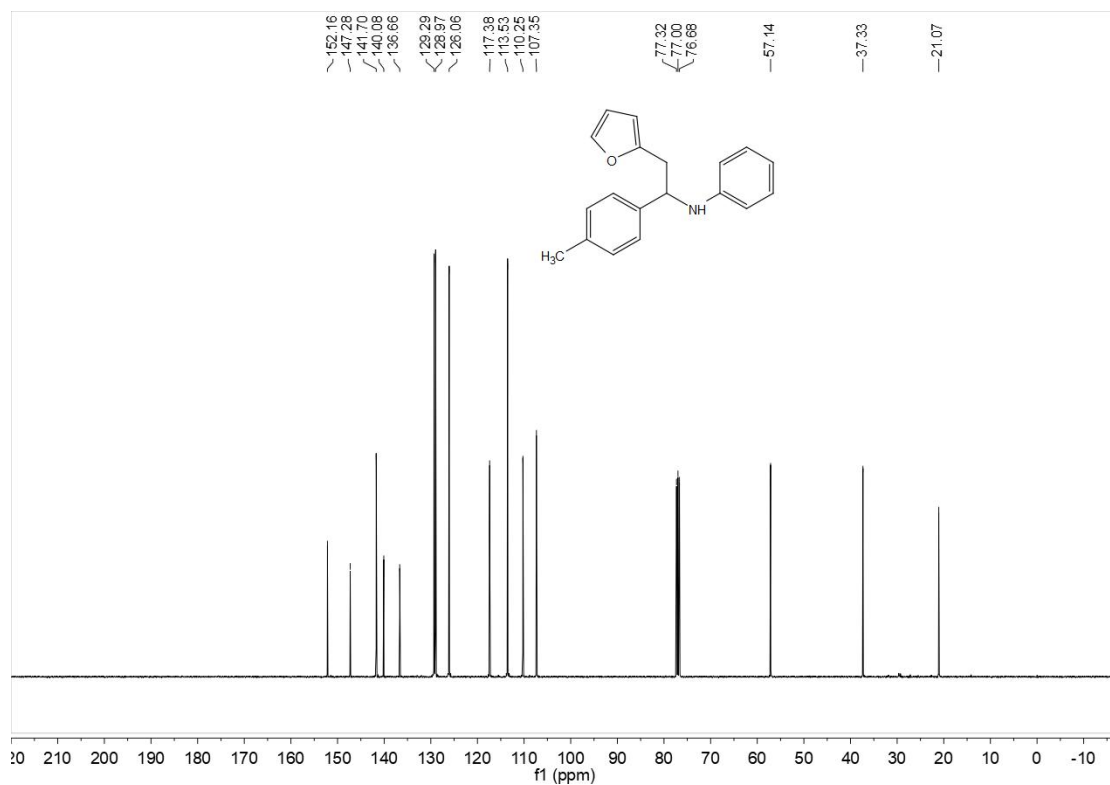


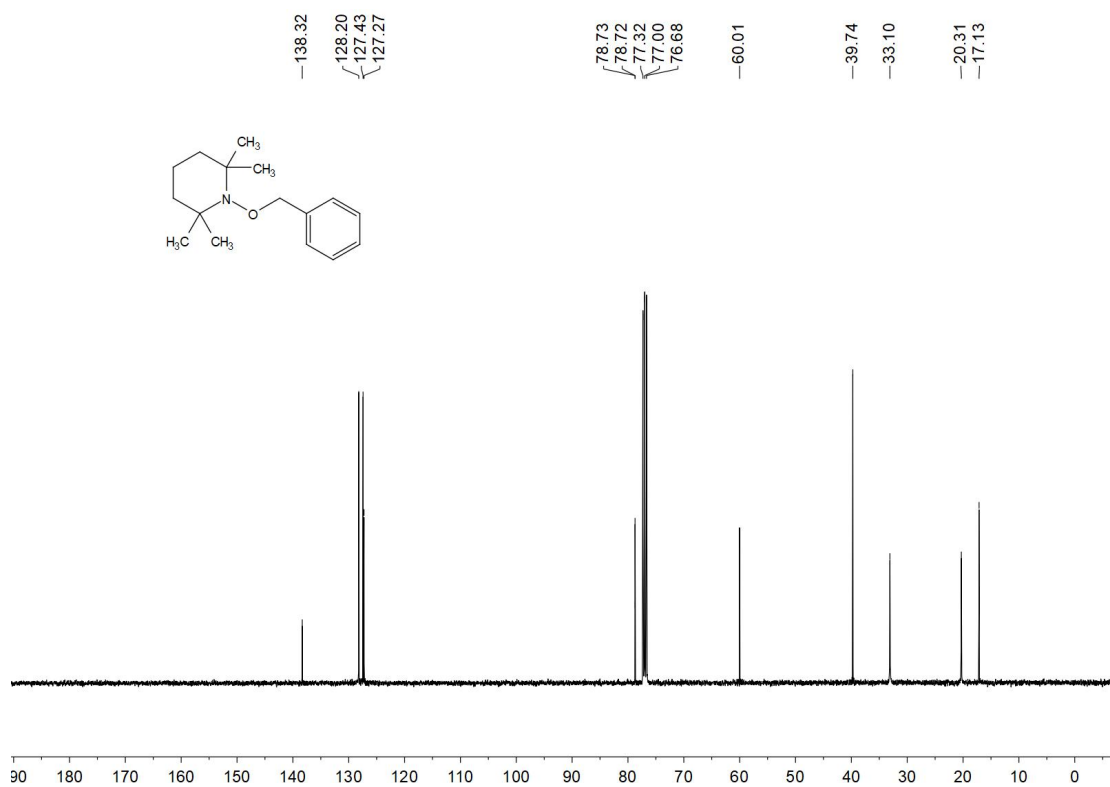












6. References

1. Y. Yasu, T. Koike, and M. Akita, *Adv. Synth. Catal.* **2012**, 354, 3414–3420.