Supporting Information

Electrochemical induced Aminochlorination of Alkenes

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1. General Information

All manipulations were carried out by standard Schlenk techniques. Unless otherwise stated, analytical grade solvents and commercially available reagents were used to conduct the reactions. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 ℃). Gradient flash chromatography was conducted and eluted with a continuous gradient from petroleum to the ethyl acetate. All the new compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS or GCMS. The known compounds were characterized by ^{1}H NMR and ^{13}C NMR, ^{19}F NMR. The ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. The chemical shifts (δ) were given in part per million relatives to internal tetramethyl silane (TMS, 0 ppm for ^{1}H NMR), $CDCl_3$ (77.16 ppm for ^{13}C NMR). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT Premier or JEOL AccuTOF-MS and ccurate masses were reported for the molecular ion + Hydrogen $(M+H)^+$ or molecular ion + Sodium $(M+Na)^+$. GCMS spectra were measured with a GCMS-QP2010SE. Hydrogen gas content was analyzed by gas chromatography (7890-II, Tianmei, China, TCD, nitrogen as a carrier gas and 5 Å molecular sieve column, a thermal conductivity detector). Electrolysis experiments were performed using a dual display potentiostat (DJS-292B) or galvanostat (made in China). The carbon block (15 mm×15 mm×2 mm) (made in China) was purchased as anode electrode. The Nickel plate (15 mm×15 mm×1 mm) (made in China) was purchased as the cathode electrode. Cyclic voltammograms were obtained on a CHI 605E potentiostat.

2. Experimental procedure

2.1 General procedure for the synthesis of *N*-(2-chloro-2-phenylethyl)benzamide and *N*-(2-chloro-1-phenylethyl)benzamide:

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar. The bottle was equipped with carbon block (15 mm×15 mm×2 mm) and nickel electrode (15 mm×15 mm×1 mm). A solution of styrene (0.5 mmol, 92.7 mg), benzamide (1.5 mmol, 3 equiv., 182.6 mg) and $TBAPF_6$

(0.5 mmol, 1 equiv., 193.7 mg) in DCE (10 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 10 mA at 80 ˚C for 6 h. After completion of the reaction, the reaction system was quenched by ethyl acetate. The aqueous solution was extracted with CH_2Cl_2 (3 × 20 mL) and the combined extracts were dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product was obtained by flash column chromatography on silica gel (eluent: petroleum / ethyl acetate = 5:1). Product ratios were determined for isolated yield.

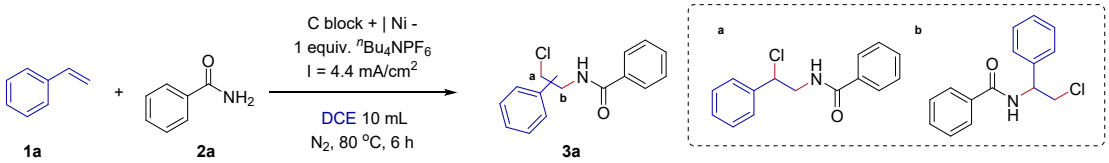
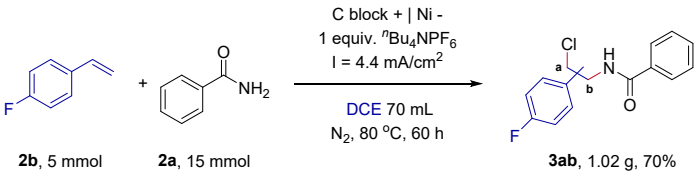


Figure S1. Synthesis 2-chloroalkylamines

2.2 Procedure for gram scale synthesis:

In an oven-dried undivided three-necked bottle (100 mL) equipped with a stir bar. The bottle was equipped with carbon block (15 mm×15 mm×2 mm) and nickel electrode (15 mm×15 mm×1 mm). A solution of 4-fluorostyrene (5 mmol, 0.61 g), benzamide (15 mmol, 3 equiv., 1.8 g) and $TBAPF_6$ (5 mmol, 1.9 g) in DCE (70 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 10 mA at 80 ˚C for 60 h. After completion of the reaction, the reaction system was quenched by ethyl acetate. The aqueous solution was extracted with CH_2Cl_2 (3 × 40 mL) and the combined extracts were dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product was obtained by flash column chromatography on silica gel (eluent: petroleum / ethyl acetate = 5:1).



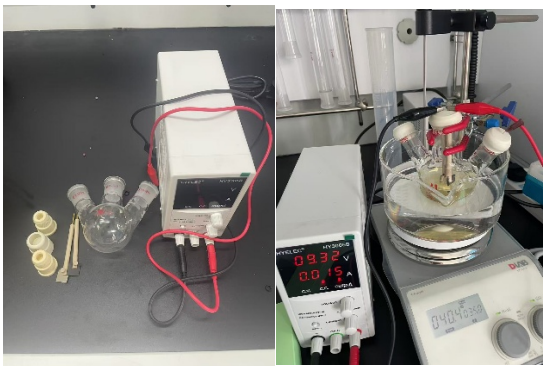


Figure S2. The gram scale synthesis.

2.3 Procedure for the further transformation experiment

In a schlenk tube with a stir bar. The schlenk tube was equipped with the product and sodium acetate

(0.5 mmol, 41.0 mg) in DCE (10 mL) stirring under nitrogen atmosphere 80 ˚C for 4.25 h. After completion of the reaction, the reaction system was quenched by ethyl acetate. The aqueous solution was extracted with CH_2Cl_2 (3 × 20 mL) and the combined extracts were dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product was obtained by flash column chromatography on silica gel (eluent: petroleum / ethyl acetate = 5:1).

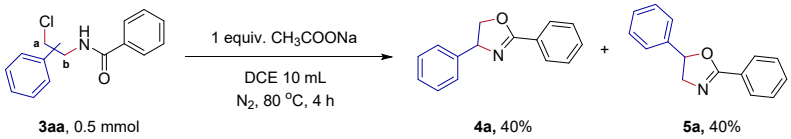


Figure S3. The further transformation experiment.

2.4 Procedure for the synthesis of alkenes:

To a suspension of triphenylphosphonium bromide (1.5 equiv.) in THF at 0 °C was added ^{t}BuOK (1.5 equiv.). The reaction was warmed to ambient temperature and stirred for 0.5 h. The ketone or aldehyde (1.0 equiv.) was added. The resulting mixture was stirred at rt until complete consumption of the carbonyl substrate (monitored by TLC or ^{1}H NMR). H_2O (20 mL) was added to quench the reaction. The resulting mixture was extracted with Et_2O (2 x 50 mL). The combined organic solution was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with EtOAc/hexanes to afford the alkene.

2.5 Procedure for the chloride trapping experiment

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar. The bottle was equipped with carbon block (15 mm×15 mm×2 nm) and nickel electrode (15 mm×15 mm×1 mm). A solution of styrene (0.5 mmol, 52.0 mg), benzamide (1.5 mmol, 3 equiv., 182.6 mg) and $TBAPF_6$ (0.5 mmol, 1 equiv., 193.7mg) in DCE (10 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 10 mA at 80 ˚C for 2 h. After completion of the reaction, the $AgNO_3$ (in CH_3CN) was added in the liquid.

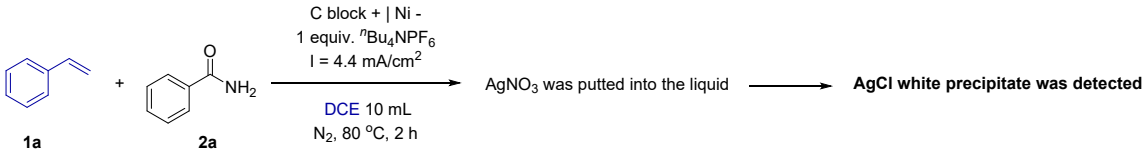


Figure S4. The chloride trapping experiment.

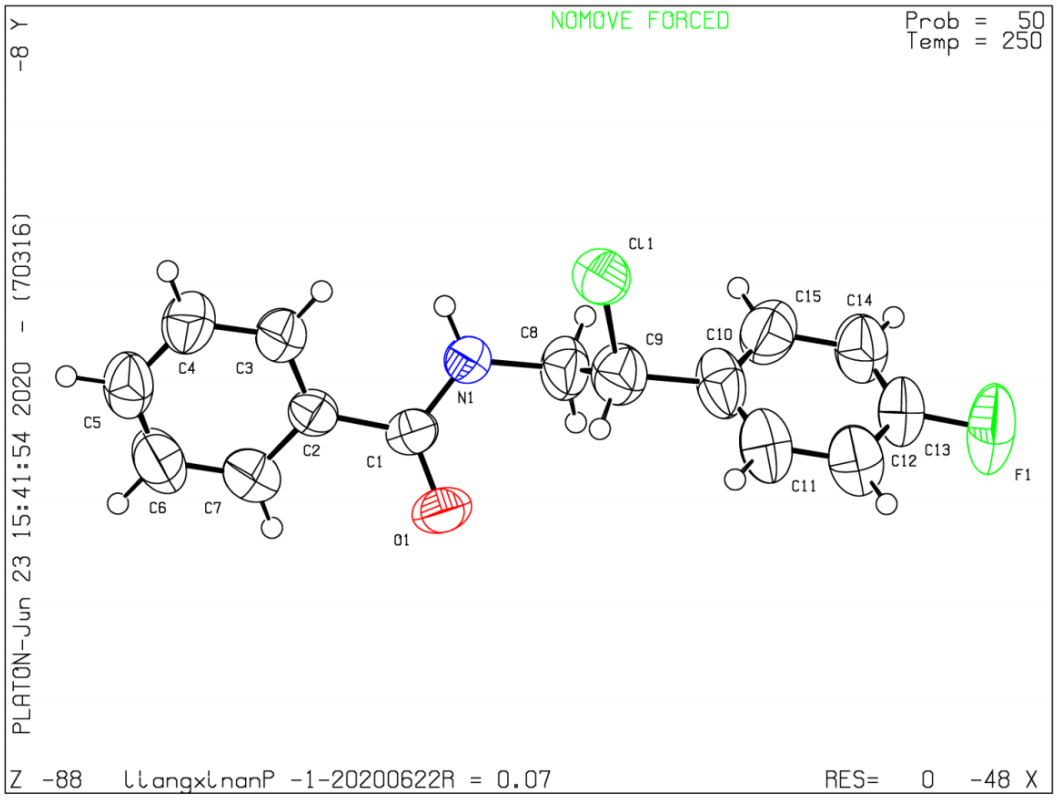
2.6 General procedure for cyclic voltammetry (CV) experiments:

Cyclic voltammetry experiments were performed in a three-electrode cell connected to a Schlenk

line at room temperature. The working electrode was a steady glassy carbon disk electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution, and separated from reaction by a salt bridge. DCE (10 ml) containing $^{n}Bu_4NPF_6$ (0.5 mmol) were poured into the electrochemical cell in all experiments. The scan rate was 0.1 V/s, ranging from 0 V to 2.5 or 3.0 V.

2.7 X-ray structure of 3aba

CCDC:2422837



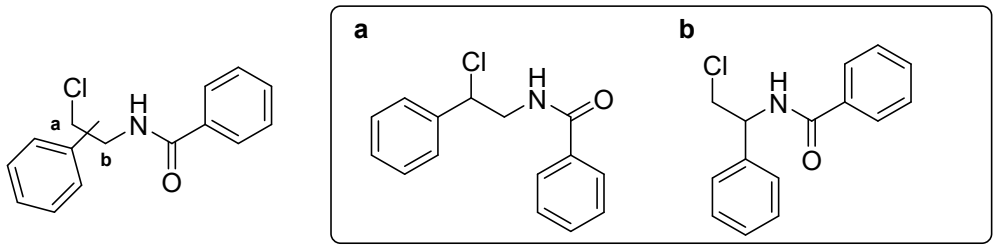
Bond precision: C-C = 0.0067 A Wavelength=1.54184
Cell: a=5.1084(2) b=10.9354(3) c=12.2655(4)
alpha=80.540(3) beta=87.394(3) gamma=81.359(2)
Temperature: 250 K

	Calculated	Reported
Volume	668.04(4)	668.04(4)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C15 H13 Cl F N O	C15 H13 Cl F N O
Sum formula	C15 H13 Cl F N O	C15 H13 Cl F N O
Mr	277.71	277.71

Dx,g cm^{-3}	1.381	1.381
Z	2	2
Mu (mm^{-1})	2.566	2.566
F000	288.0	288.0
F000’	289.55	
h,k,lmax	6,12,14	5,12,14
Nref	2261	2248
Tmin,Tmax	0.912,0.926	0.756,1.000
Tmin’	0.814	

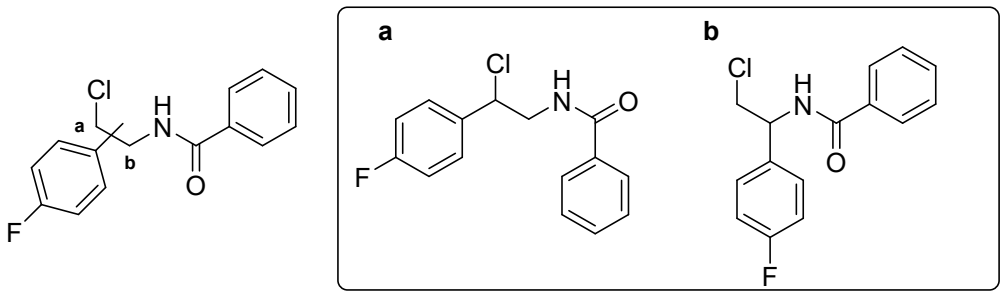
Correction method= # Reported T Limits: Tmin=0.756 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 0.994 Theta(max)= 64.995
R(reflections)= 0.0737(1934) wR2(reflections)= 0.2170(2248)
S = 1.083 Npar= 172

3. Characterization of products



3aa

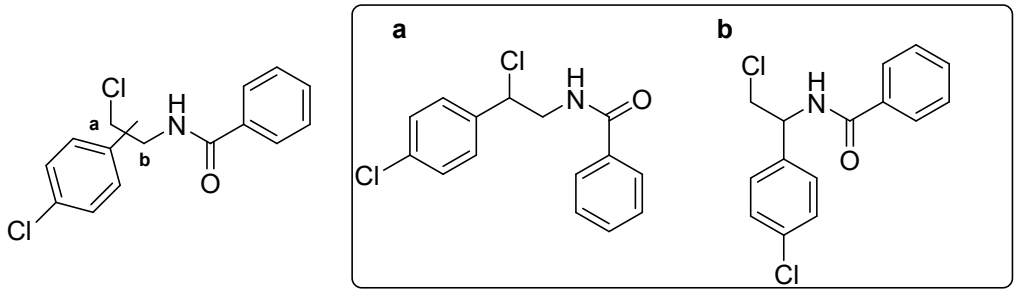
N-(2-chloro-2-phenylethyl)benzamide and N-(2-chloro-1-phenylethyl)benzamide : 111 mg pale yellow liquid was obtained, corresponding to 86% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 29.6, 7.3 Hz, 2H), 7.56 – 7.31 (m, 8H), 6.87 – 6.78 (m, 0.5H), 6.60 (s, 0.5H), 5.63 – 5.53 (m, 0.5H), 5.15 (dd, J = 8.4, 4.8 Hz, 0.5H), 4.12 (dt, J = 12.5, 5.9 Hz, 0.5H), 3.99 (d, J = 4.7 Hz, 1H), 3.83 – 3.73 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.68, 167.11, 138.72, 138.50, 134.13, 134.05, 132.01, 131.92, 129.03, 128.98, 128.82, 128.79, 128.32, 127.29, 127.19, 127.08, 126.83, 62.33, 53.98, 47.88, 47.65. **HRMS (ESI)** calcd for $C_{15}H_{15}ClNO^{+}$, $[M+H]^{+}$, 260.0837, found 260.0837[1].



3ab

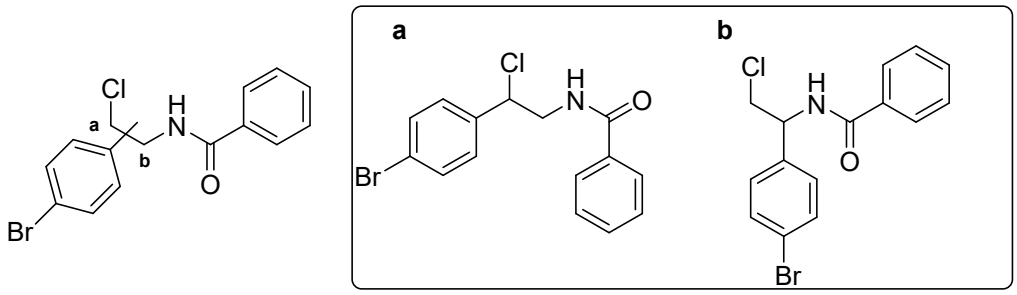
N-(2-chloro-2-(4-fluorophenyl)ethyl)benzamide and N-(2-chloro-1-(4-fluorophenyl)ethyl)benzamide : 105 mg pale yellow liquid was obtained, corresponding to 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.72 (m, 2H), 7.57 – 7.46 (m, 1H), 7.45 – 7.33 (m, 4H), 7.18 – 7.09 (m, 0.5H), 7.04 (td, *J* = 8.6, 5.8 Hz, 2H), 6.87 – 6.78 (m, 0.5H), 5.51 (dt, *J* = 7.6, 5.5 Hz, 0.5H), 5.14 (dd, *J* = 8.9, 5.0 Hz, 0.5H), 4.09 – 4.01 (m, 0.5H), 3.98 – 3.89 (m, 1H), 3.73 (s, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.79, 167.22, 164.02, 163.68, 161.56, 161.23, 134.66, 134.63, 134.52, 134.49, 133.95, 133.84, 132.02, 131.94, 130.71, 129.60, 129.14, 129.05, 128.75, 128.61, 128.53, 127.22, 127.07, 116.86, 116.64, 115.97, 115.90, 115.76, 115.69, 61.39, 53.63, 47.68. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -112.45, -113.88. HRMS (ESI) calcd for $C_{15}H_{14}ClFNO^+$, $[M+H]^+$, 278.0742, found 278.0741.



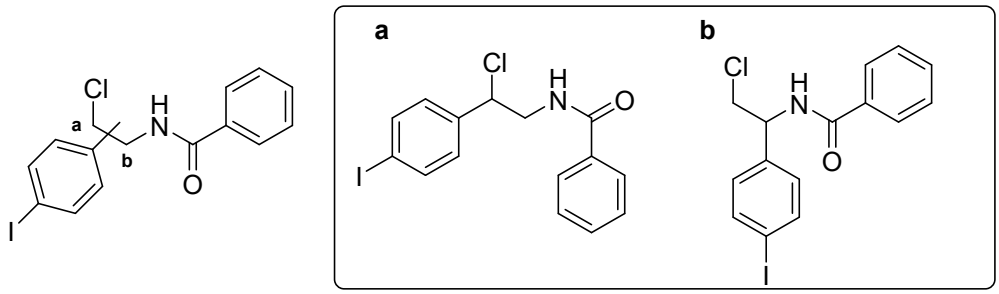
3ac

N-(2-chloro-2-(4-chlorophenyl)ethyl)benzamide and N-(2-chloro-1-(4-chlorophenyl)ethyl)benzamide : 104 mg pale yellow liquid was obtained, corresponding to 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.72 (m, 2H), 7.59 – 7.50 (m, 1H), 7.49 – 7.41 (m, 2H), 7.41 – 7.31 (m, 4H), 6.93 – 6.80 (m, 0.5H), 6.68 – 6.57 (m, 0.5H), δ 5.49 (dd, 0.5H), 5.11 (dd, *J* = 8.5, 5.1 Hz, 0.5H), 4.04 (dt, *J* = 13.6, 5.9 Hz, 0.5H), 3.93 (d, *J* = 5.2 Hz, 1H), 3.76 – 3.66 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.78, 167.16, 137.26, 137.12, 134.82, 134.12, 133.94, 133.79, 132.15, 132.02, 129.15, 129.11, 128.85, 128.82, 128.69, 128.22, 127.19, 127.07, 61.39, 53.46, 47.73, 47.63. **HRMS (ESI)** calcd for $C_{15}H_{14}Cl_2FNO^+$, $[M+H]^+$, 294.0447, found 294.0447.



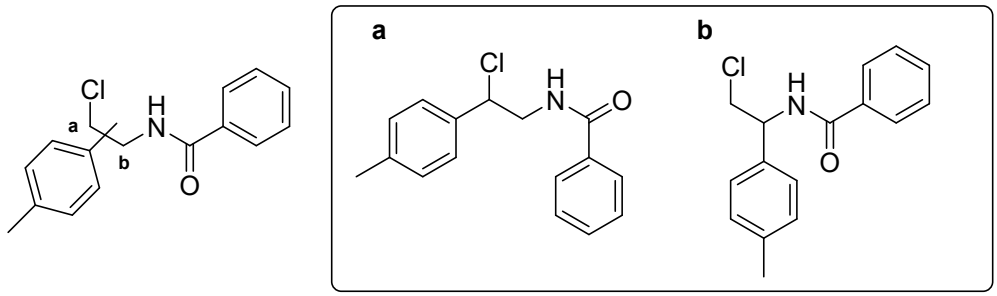
3ad

N-(2-(4-bromophenyl)-2-chloroethyl)benzamide and N-(1-(4-bromophenyl)-2-chloroethyl)benzamide : 134 mg pale yellow liquid was obtained, corresponding to 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 26.8, 7.9 Hz, 2H), 7.46 (dq, *J* = 23.7, 7.4, 6.5 Hz, 5H), 7.27 (dd, *J* = 13.2, 7.7 Hz, 2H), 7.08 (d, *J* = 7.4 Hz, 0.5H), 6.85 – 6.73 (m, 0.5H), 5.49 (d, *J* = 6.5 Hz, 0.5H), 5.11 (dd, *J* = 8.5, 5.1 Hz, 0.5H), 4.10 – 3.99 (m, 0.5H), 3.93 (d, *J* = 5.2 Hz, 1H), 3.77 – 3.61 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.79, 167.20, 137.77, 137.70, 133.90, 133.75, 132.09, 132.05, 132.00, 131.98, 128.96, 128.77, 128.56, 127.21, 127.07, 122.93, 122.19, 61.30, 53.65, 47.62, 47.53. **HRMS (ESI)** calcd for $C_{15}H_{14}BrClFNO^+$, $[M+H]^+$, 337.9942, found 337.9942.



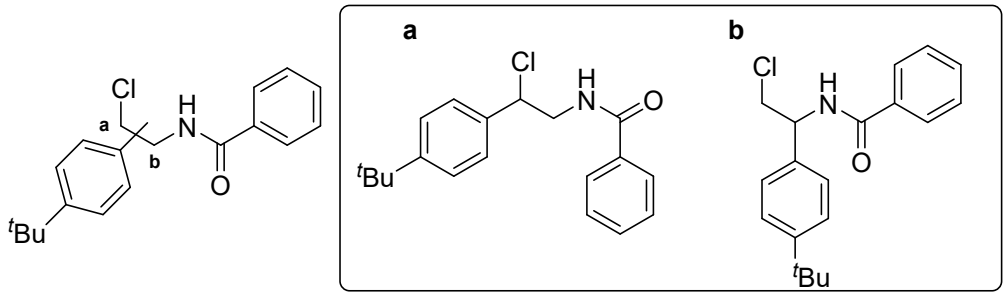
3ae

N-(2-chloro-2-(4-iodophenyl)ethyl)benzamide and N-(2-chloro-1-(4-iodophenyl)ethyl)benzamide : 84.6 mg pale yellow liquid was obtained, corresponding to 44% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 1H), 7.76 – 7.64 (m, 2H), 7.57 – 7.48 (m, 1H), 7.46 – 7.31 (m, 3H), 7.14 (dd, *J* = 16.4, 8.4 Hz, 2H), 7.07 – 6.90 (m, 0.5H), 6.78 – 6.58 (m, 0.5H), 5.48 (dd, *J* = 5.2, 2.4 Hz, 0.5H), 5.19 – 5.04 (m, 0.5H), 4.14 – 4.00 (m, 0.5H), 3.99 – 3.90 (m, 1H), 3.80 – 3.65 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.69, 167.10, 138.37, 138.31, 137.96, 137.90, 133.85, 133.70, 132.04, 131.93, 129.08, 128.89, 128.73, 128.24, 127.20, 127.15, 127.12, 127.02, 126.74, 94.67, 93.82, 62.20, 61.38, 54.00, 53.62, 47.75, 47.46. **HRMS (ESI)** calcd for $C_{15}H_{14}ICIFNO^+$, $[M+H]^+$, 385.9803, found 385.9802.



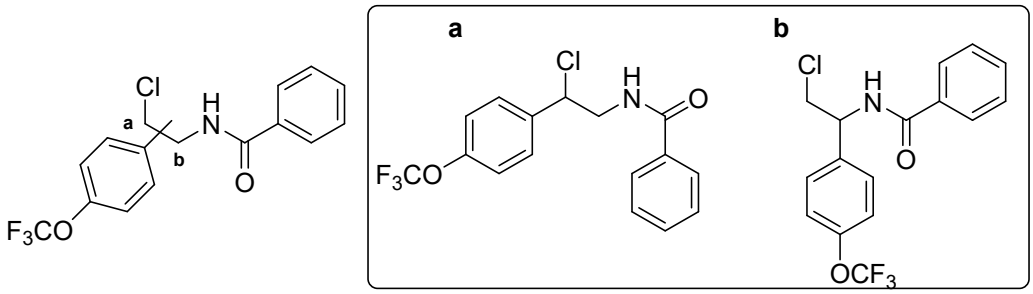
3af

N-(2-chloro-2-(p-tolyl)ethyl)benzamide and N-(2-chloro-1-(p-tolyl)ethyl)benzamide : 98.2 mg pale yellow liquid was obtained, corresponding to 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.71 (m, 2H), 7.55 – 7.47 (m, 1H), 7.47 – 7.39 (m, 2H), 7.34 – 7.23 (m, 2H), 7.21 – 7.13 (m, 2H), 6.92 – 6.63 (m, 1H), 5.56 – 5.43 (m, 0.6H), 5.21 – 5.07 (m, 0.4H), 4.14 – 4.03 (m, 0.4H), 3.96 (d, *J* = 5.4 Hz, 1H), 3.76 (m, 0.6H), 2.37 – 2.31 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.67, 167.11, 138.91, 138.06, 135.82, 135.58, 134.19, 134.14, 131.89, 131.83, 129.63, 129.61, 128.74, 127.19, 127.19, 127.09, 126.75, 62.27, 53.92, 47.77, 21.29, 21.22. **HRMS (ESI)** calcd for $C_{16}H_{17}ClNO^+$, $[M+H]^+$, 274.0993, found 274.0993.



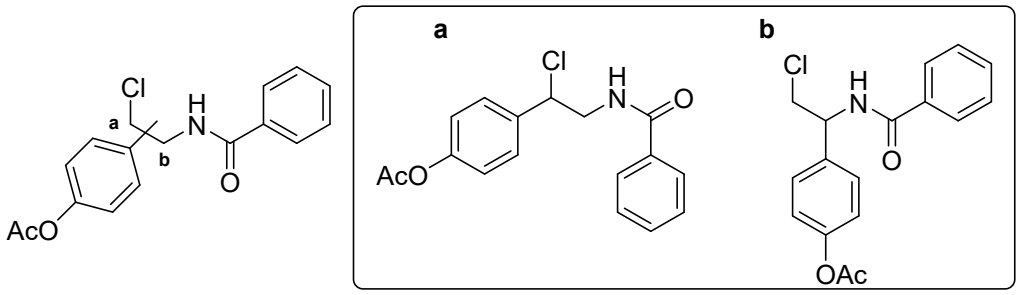
3ag

N-(2-(4-(tert-butyl)phenyl)-2-chloroethyl)benzamide and N-(1-(4-(tert-butyl)phenyl)-2-chloroethyl)benzamide : 130.7 mg pale yellow liquid was obtained, corresponding to 83% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 22.8, 8.0 Hz, 2H), 7.56 – 7.46 (m, 1H), 7.45 – 7.30 (m, 6H), 7.03 – 6.66 (m, 1H), 5.64 – 5.42 (m, 0.5H), 5.22 – 5.03 (m, 0.5H), 4.21 – 4.04 (m, 0.5H), 3.97 (d, *J* = 5.3 Hz, 1H), 3.81 – 3.62 (m, 0.5H), 1.31 (d, *J* = 5.7 Hz, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.71, 167.16, 152.05, 151.17, 135.71, 135.50, 134.16, 134.11, 131.88, 131.83, 130.44, 129.41, 128.72, 127.20, 127.10, 126.96, 126.60, 126.56, 125.87, 62.31, 53.84, 47.65, 47.55, 34.75, 34.64, 31.38, 31.35, 31.29. **HRMS (ESI)** calcd for $C_{19}H_{23}ClNO^+$, $[M+H]^+$, 316.1463, found 316.1463.



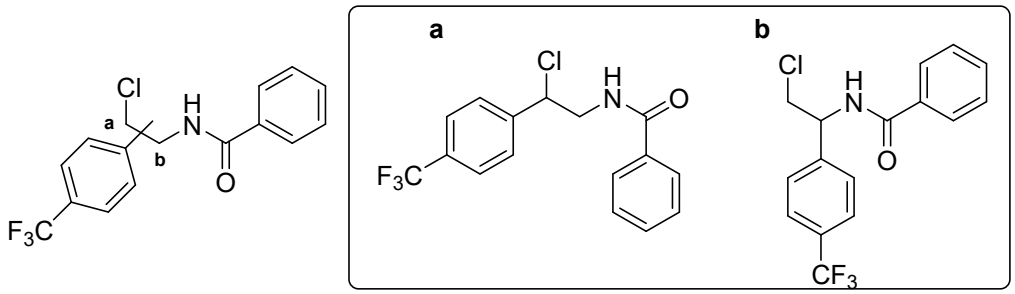
3ah

N-(2-chloro-2-(4-(trifluoromethoxy)phenyl)ethyl)benzamide and N-(2-chloro-1-(4-(trifluoromethoxy)phenyl)ethyl)benzamide : 94.3 mg pale yellow liquid was obtained, corresponding to 55% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.71 (m, 2H), 7.52 (m, 1H), 7.48 – 7.39 (m, 4H), 7.25 – 7.16 (m, 2H), 7.05 – 6.56 (m, 1H), 5.64 – 5.48 (m, 0.5H), 5.22 – 5.11 (m, 0.5H), 4.17 – 4.04 (m, 0.5H), 3.99 – 3.91 (m, 1H), 3.78 – 3.62 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.87, 167.24, 149.40, 148.98, 137.41, 137.35, 133.92, 133.75, 133.45, 132.17, 132.04, 129.80, 128.87, 128.84, 128.82, 128.35, 127.21, 127.08, 121.37, 121.33, 61.22, 53.48, 47.74, 47.67. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -57.81, -57.82. **HRMS (ESI)** calcd for $C_{16}H_{14}ClF_3NO_2^+$, $[M+H]^+$, 344.0660, found 344.0660.



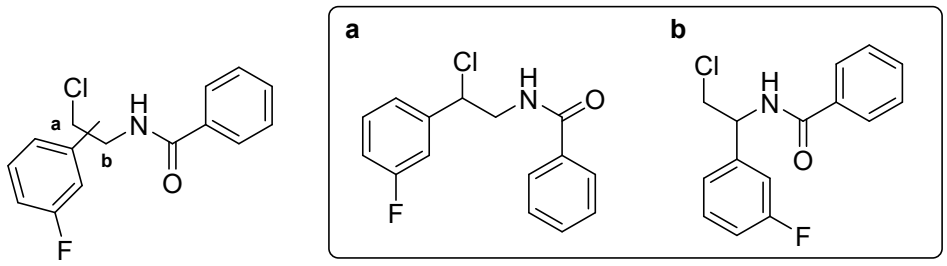
3ai

4-(2-benzamido-1-chloroethyl)phenyl acetate and 4-(1-benzamido-2-chloroethyl)phenyl acetate: 139.4 mg pale yellow liquid was obtained, corresponding to 88% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.70 (m, 2H), 7.55 – 7.31 (m, 5H), 7.19 (d, *J* = 7.9 Hz, 0.7H), 7.14 – 7.01 (m, 1H), 6.94 – 6.86 (m, 0.3H), 5.64 – 5.36 (m, 0.7H), 5.17 – 5.09 (m, 0.3H), 4.04 – 3.95 (m, 0.3H), 3.88 (d, *J* = 5.6 Hz, 1H), 3.77 – 3.67 (m, 0.7H), 2.28 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.62, 169.49, 167.84, 167.28, 150.78, 150.33, 136.33, 136.26, 133.92, 133.85, 131.92, 131.85, 128.67, 128.66, 128.44, 128.02, 127.22, 127.08, 122.01, 121.96, 61.27, 53.79, 47.68, 47.29, 21.20. **HRMS (ESI)** calcd for $C_{17}H_{17}ClNO_3^+$, $[M+H]^+$, 318.0891, found 318.0891. ^{1}H NMR (400 MHz, Chloroform-*d*)



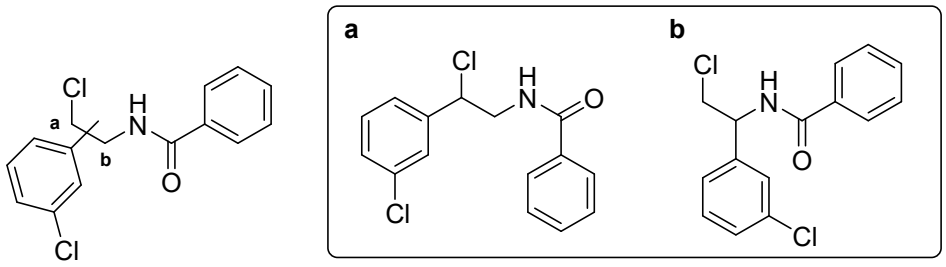
3aj

N-(2-chloro-2-(4-(trifluoromethyl)phenyl)ethyl)benzamide and N-(2-chloro-1-(4-(trifluoromethyl)phenyl)ethyl)benzamide : 117.7 mg pale yellow liquid was obtained, corresponding to 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.73 (m, 2H), 7.67 – 7.61 (m, 2H), 7.60 – 7.49 (m, 3H), 7.49 – 7.42 (m, 2H), 7.09 – 6.61 (m, 1H), 5.68 – 5.48 (m, 0.5H), 5.28 – 5.16 (m, 0.5H), 4.17 – 4.07 (m, 0.5H), 4.05 – 3.91 (m, 1H), 3.78 – 3.66 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.84, 167.22, 142.62, 142.58, 134.38, 133.85, 133.63, 132.26, 132.10, 129.15, 128.90, 128.85, 127.77, 127.24, 127.21, 127.08, 126.01, 125.98, 125.94, 125.90, 61.21, 53.67, 47.70. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.59, -62.67. **HRMS (ESI)** calcd for $C_{16}H_{14}ClF_3NO^+$, $[M+H]^+$, 328.0711, found 328.0710.



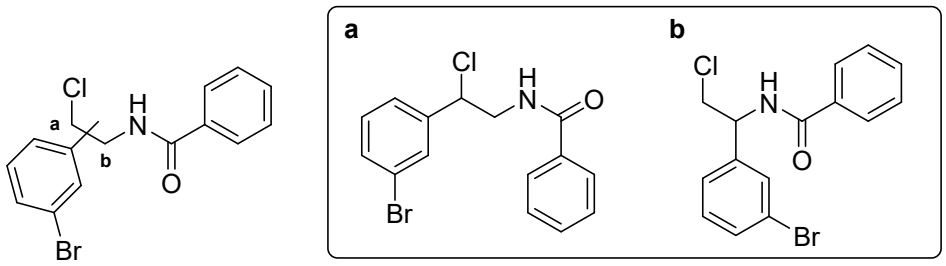
3ak

N-(2-chloro-2-(3-fluorophenyl)ethyl)benzamide and N-(2-chloro-1-(3-fluorophenyl)ethyl)benzamide : 99.7 mg pale yellow liquid was obtained, corresponding to 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.73 (m, 2H), 7.57 – 7.51 (m, 1H), 7.49 – 7.43 (m, 2H), 7.40 – 7.33 (m, 1H), 7.24 – 6.99 (m, 3H), 6.91 – 6.58 (m, 1H). 5.65 – 5.53 (m, 0.5H), 5.20 – 5.10 (m, 0.5H), 4.20 – 4.07 (m, 0.5H), 4.04 – 3.92 (m, 1H), 3.80 – 3.57 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.76, 167.14, 164.32, 164.16, 161.87, 161.71, 141.18, 141.12, 133.98, 133.78, 132.18, 132.03, 130.61, 130.53, 128.89, 128.84, 127.21, 127.08, 123.05, 123.02, 122.53, 122.50, 116.14, 115.93, 115.37, 115.16, 114.51, 114.29, 114.04, 113.82, 61.35, 53.49, 47.82, 47.67. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -111.77, -112.01. **HRMS (ESI)** calcd for $C_{15}H_{14}ClFNO^+$, $[M+H]^+$, 278.0742, found 278.0742.



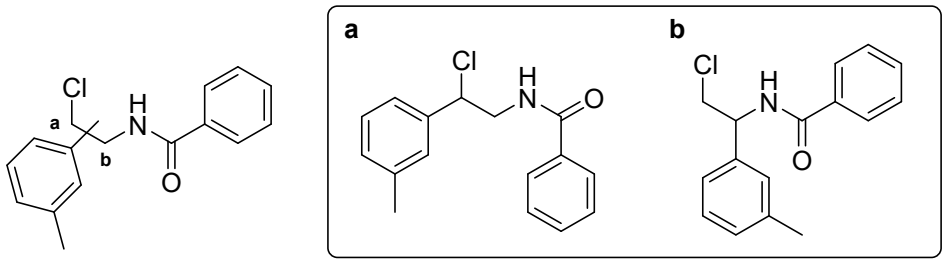
3al

N-(2-chloro-2-(3-chlorophenyl)ethyl)benzamide and N-(2-chloro-1-(3-chlorophenyl)ethyl)benzamide : 126 mg pale yellow liquid was obtained, corresponding to 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.70 (m, 2H), 7.56 – 7.47 (m, 1H), 7.45 – 7.35 (m, 3H), 7.33 – 7.24 (m, 3H), 7.17 – 6.69 (m, 1H), 5.61 – 5.40 (m, 0.5H), 5.17 – 5.06 (m, 0.5H), 4.12 – 4.00 (m, 0.5H), 4.00 – 3.87 (m, 1H), 3.76 – 3.64 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.84, 167.24, 140.75, 140.66, 134.77, 134.75, 133.90, 133.70, 132.10, 131.98, 130.19, 129.11, 128.77, 128.43, 127.47, 127.25, 127.09, 126.96, 125.52, 125.15, 61.17, 53.73, 47.63, 47.59. **HRMS (ESI)** calcd for $C_{15}H_{14}Cl_2NO^+$, $[M+H]^+$, 294.0447, found 294.0447.



3am

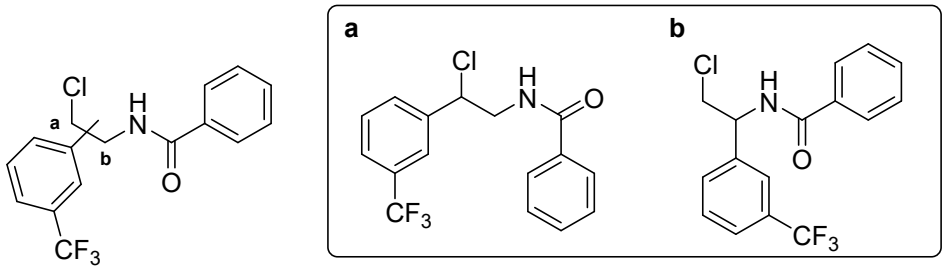
N-(2-(3-bromophenyl)-2-chloroethyl)benzamide and N-(1-(3-bromophenyl)-2-chloroethyl)benzamide : 126.3 mg pale yellow liquid was obtained, corresponding to 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.71 (m, 2H), 7.57 – 7.49 (m, 2H), 7.48 – 7.30 (m, 5H), 6.97 – 6.46 (m, 1H), 5.64 – 5.46 (m, 0.5H), 5.19 – 5.06 (m, 0.5H), 4.16 – 4.04 (m, 0.5H), 4.03 – 3.87 (m, 1H), 3.75 – 3.68 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.79, 167.13, 140.91, 133.95, 133.73, 132.19, 132.11, 132.04, 131.43, 130.51, 130.40, 129.87, 128.99, 128.87, 128.84, 127.23, 127.19, 127.10, 126.82, 126.01, 125.60, 123.06, 122.93, 61.23, 53.50, 47.76, 47.70. **HRMS (ESI)** calcd for $C_{15}H_{14}BrClNO^+$, $[M+H]^+$, 337.9942, found 337.9941.



3an

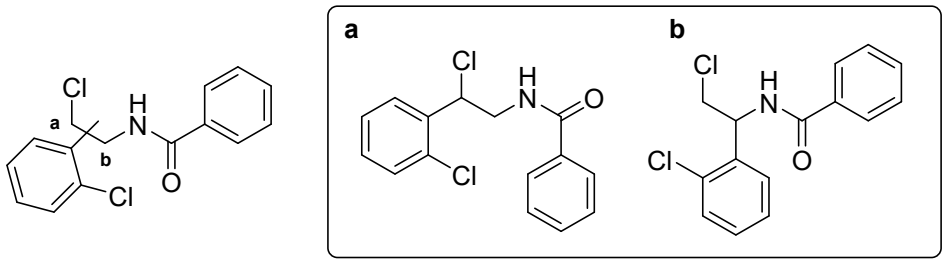
N-(2-chloro-2-(m-tolyl)ethyl)benzamide and N-(2-chloro-1-(m-tolyl)ethyl)benzamide : 103.7 mg pale yellow liquid was obtained, corresponding to 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.69

(m, 2H), 7.56 – 7.39 (m, 3H), 7.30 – 7.08 (m, 4H), 6.96 – 6.59 (m, 1H), 5.60 – 5.42 (m, 0.5H), 5.18 – 5.02 (m, 0.5H), 4.17 – 4.03 (m, 0.5H), 3.96 (d, *J* = 5.4 Hz, 1H), 3.83 – 3.67 (m, 0.5H), 2.36 (d, *J* = 3.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.71, 167.13, 138.73, 138.68, 138.63, 138.46, 134.14, 134.07, 131.94, 131.88, 129.77, 129.08, 128.84, 128.76, 127.94, 127.60, 127.20, 127.08, 124.28, 123.77, 62.40, 54.12, 47.79, 47.64, 21.63, 21.50. **HRMS (ESI)** calcd for $C_{16}H_{17}ClNO^+$, $[M+H]^+$, 274.0993, found 274.0993.



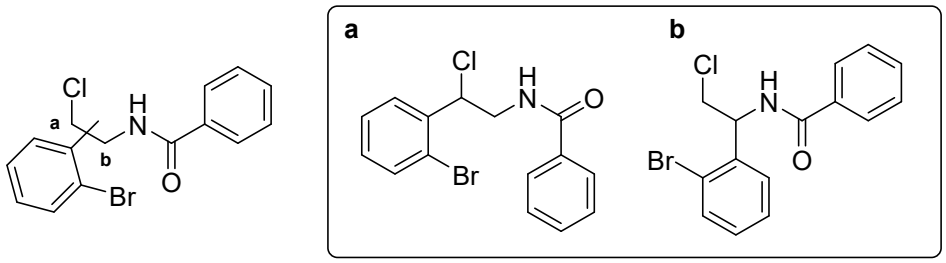
3ao

N-(2-chloro-2-(3-(trifluoromethyl)phenyl)ethyl)benzamide and N-(2-chloro-1-(3-(trifluoromethyl)phenyl)ethyl)benzamide : 86.6 mg pale yellow liquid was obtained, corresponding to 53% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 29.2, 7.2 Hz, 2H), 7.72 – 7.57 (m, 3H), 7.55 – 7.40 (m, 4H), 7.14 – 6.65 (m, 1H), 5.72 – 5.52 (m, 0.3H), 5.29 – 5.16 (m, 0.7H), 4.18 – 4.03 (m, 0.3H), 4.04 – 3.87 (m, 1H), 3.83 – 3.65 (m, 0,7H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.89, 167.28, 139.77, 133.89, 133.68, 132.21, 132.06, 130.71, 130.40, 129.52, 129.46, 128.86, 128.82, 127.24, 127.08, 125.85, 125.82, 125.78, 125.74, 125.22, 125.19, 125.15, 124.23, 124.19, 124.15, 124.12, 123.58, 123.54, 61.28, 53.74, 47.74, 47.68. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.53, -62.62. **HRMS (ESI)** calcd for $C_{16}H_{14}ClF_3NO^+$, $[M+H]^+$, 328.0711, found 328.0710.



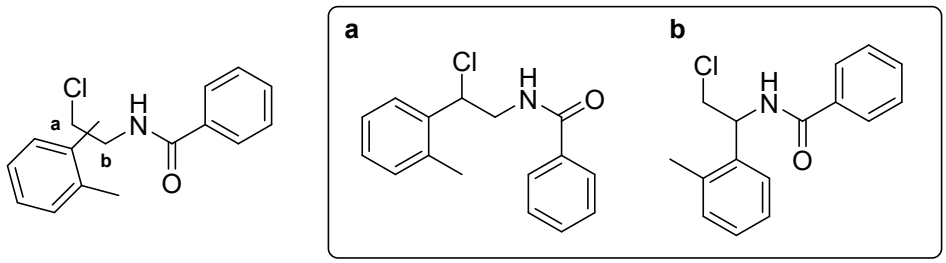
3ap

N-(2-chloro-2-(2-chlorophenyl)ethyl)benzamide and N-(2-chloro-1-(2-chlorophenyl)ethyl)benzamide : 120.1 mg pale yellow liquid was obtained, corresponding to 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.73 (m, 2H), 7.65 – 7.28 (m, 7H), 7.11 – 6.54 (m, 1H). 5.95 – 5.82 (m, 0.5H), 5.73 – 5.53 (m, 0.5H), 4.26 – 4.08 (m, 0.5H), 4.09 – 3.93 (m, 1H), 3.90 – 3.73 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.72, 166.96, 136.11, 135.85, 134.06, 133.82, 133.15, 132.92, 132.01, 131.83, 130.24, 130.01, 129.87, 129.47, 128.91, 128.76, 128.69, 128.52, 127.52, 127.21, 127.14, 127.10, 58.07, 52.19, 46.40, 26.98. **HRMS (ESI)** calcd for $C_{15}H_{14}Cl_2NO^+$, $[M+H]^+$, 294.0447, found 294.0446. ^{1}H NMR (400 MHz, Chloroform-*d*)



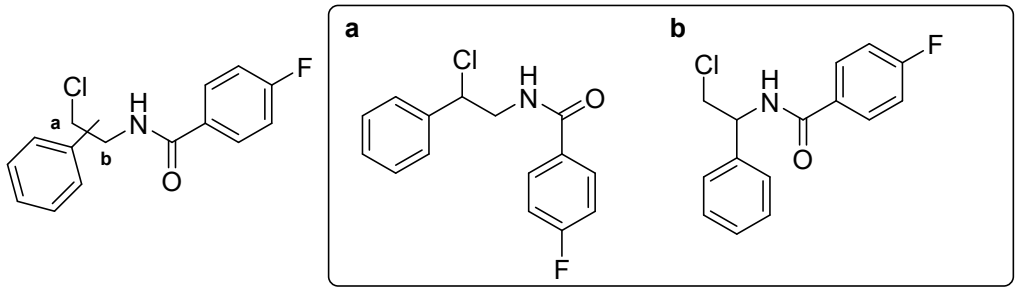
3aq

N-(2-(2-bromophenyl)-2-chloroethyl)benzamide and N-(1-(2-bromophenyl)-2-chloroethyl)benzamide : 109.8 mg pale yellow liquid was obtained, corresponding to 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, 2H), 7.66 – 7.54 (m, 2H), 7.53 – 7.33 (m, 4H), 7.24 – 7.05 (m, 1H), 6.51 (d, *J* = 123.6 Hz, 1H), 5.69 – 5.60 (m, 0.5H), 4.19 – 4.09 (m, 0.5H), 3.89 – 3.78 (m, 0.5H), 3.73 (q, *J* = 6.9 Hz, 1H), 3.09 (t, *J* = 6.9 Hz, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.75, 167.65, 138.42, 137.77, 134.56, 134.09, 133.19, 133.07, 131.87, 131.57, 131.21, 130.33, 128.97, 128.74, 128.66, 128.48, 128.19, 127.81, 127.12, 126.96, 124.67, 123.42, 60.66, 46.45, 39.96, 35.80. **HRMS (ESI)** calcd for $C_{15}H_{14}BrClNO^+$, $[M+H]^+$, 337.9942, found 337.9942.



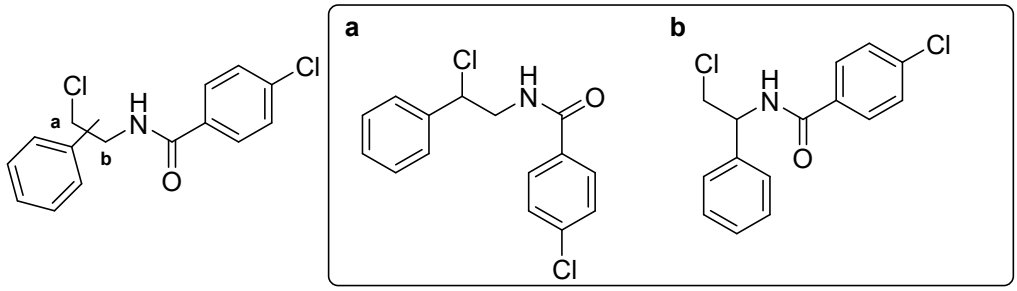
3ar

N-(2-chloro-2-(o-tolyl)ethyl)benzamide and N-(2-chloro-1-(o-tolyl)ethyl)benzamide : 95.5 mg pale yellow liquid was obtained, corresponding to 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 2H), 7.59 – 7.33 (m, 4H), 7.26 – 7.16 (m, 3H), 7.02 – 6.74 (m, 1H), 5.70 (q, *J* = 6.3 Hz, 0.7H), 5.44 (dd, *J* = 9.3, 4.5 Hz, 0.3H), 4.10 (dd, *J* = 7.1, 4.5 Hz, 0.7H), 3.97 – 3.83 (m, 1H), 3.75 – 3.61 (m, 0.3H), 2.43 (d, *J* = 8.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.85, 167.09, 136.86, 136.82, 136.30, 135.95, 134.05, 133.95, 131.87, 131.07, 130.83, 128.72, 128.69, 128.19, 127.17, 127.09, 126.70, 126.64, 126.43, 125.62, 58.94, 51.04, 46.90, 46.36, 19.44, 19.26. **HRMS (ESI)** calcd for $C_{16}H_{17}ClNO^+$, $[M+H]^+$, 274.0993, found 274.0993.



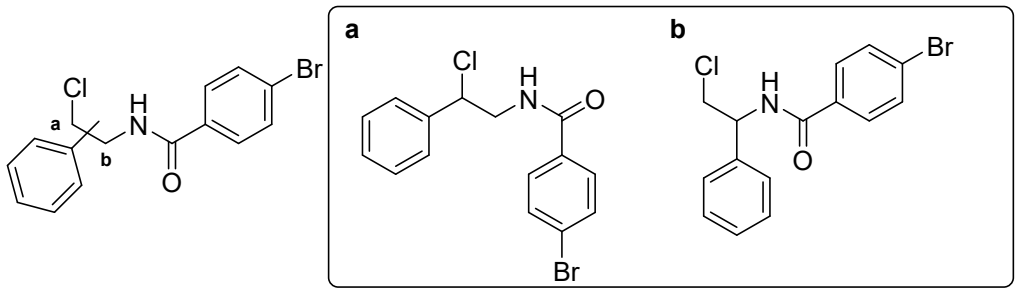
3as

N-(2-chloro-2-phenylethyl)-4-fluorobenzamide and N-(2-chloro-1-phenylethyl)-4-fluorobenzamide : 102.5 mg pale yellow liquid was obtained, corresponding to 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.72 (m, 2H), 7.45 – 7.30 (m, 5H), 7.13 (t, 2H), 6.97 – 6.58 (m, 1H), 5.59 – 5.47 (m, 0.5H), 5.14 (dd, *J* = 9.0, 5.0 Hz, 0.5H), 4.12 – 4.03 (m, 0.5H), 3.96 (d, *J* = 5.4 Hz, 1H), 3.84 – 3.67 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.69, 166.27, 166.22, 166.18, 163.76, 163.71, 138.67, 130.32, 130.29, 130.26, 130.23, 129.65, 129.57, 129.52, 129.43, 129.04, 128.99, 128.97, 128.36, 127.26, 126.81, 126.31, 115.92, 115.70, 62.22, 54.27, 47.70. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -107.44, -107.45, -107.55, -107.56. **HRMS (ESI)** calcd for $C_{15}H_{14}ClFNO^+$, $[M+H]^+$, 278.0742, found 278.0741.



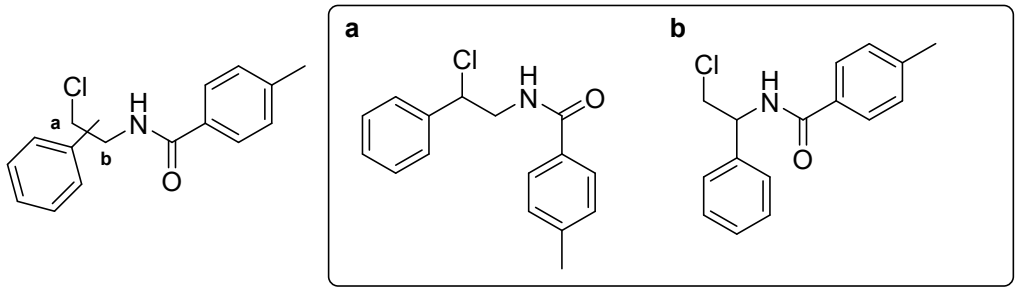
3at

4-chloro-N-(2-chloro-2-phenylethyl)benzamide and 4-chloro-N-(2-chloro-1-phenylethyl)benzamide : 107.3 mg pale yellow liquid was obtained, corresponding to 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 26.1, 8.4 Hz, 2H), 7.43 – 7.30 (m, 7H), 7.15 – 6.72 (m, 1H), 5.59 – 5.45 (m, 0.5H), 5.14 (dd, *J* = 8.9, 5.0 Hz, 0.5H), 4.11 – 4.00 (m, 0.5H), 3.95 (d, *J* = 5.6 Hz, 1H), 3.80 – 3.65 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.74, 166.27, 138.62, 138.47, 138.15, 138.10, 132.47, 132.42, 129.02, 128.97, 128.95, 128.69, 128.55, 128.35, 127.23, 126.80, 62.09, 54.40, 47.69, 47.58. **HRMS (ESI)** calcd for $C_{15}H_{14}Cl_2NO^+$, $[M+H]^+$, 294.0447, found 294.0447.



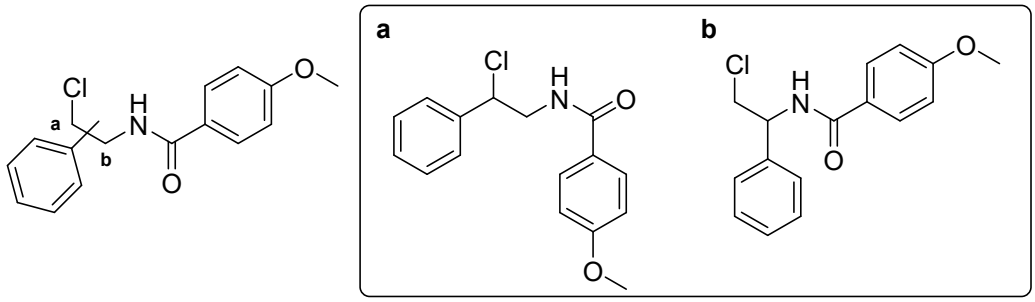
3au

4-bromo-N-(2-chloro-2-phenylethyl)benzamide and 4-bromo-N-(2-chloro-1-phenylethyl)benzamide : 118.3 mg pale yellow liquid was obtained, corresponding to 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.57 (m, 2H), 7.56 – 7.50 (m, 2H), 7.45 – 7.31 (m, 5H), 7.07 – 6.53 (m, 1H), 5.57 – 5.45 (m, 0.5H), 5.14 (dd, *J* = 8.9, 5.0 Hz, 0.5H), 4.13 – 4.01 (m, 0.5H), 3.96 (d, *J* = 5.5 Hz, 1H), 3.82 – 3.69 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.81, 166.32, 138.61, 138.42, 132.95, 132.89, 131.98, 129.05, 129.00, 128.98, 128.85, 128.72, 128.39, 127.25, 126.81, 126.67, 126.60, 62.13, 54.32, 47.69, 47.63. **HRMS (ESI)** calcd for $C_{15}H_{14}BrClNO^+$, $[M+H]^+$, 337.9942, found 337.9941.



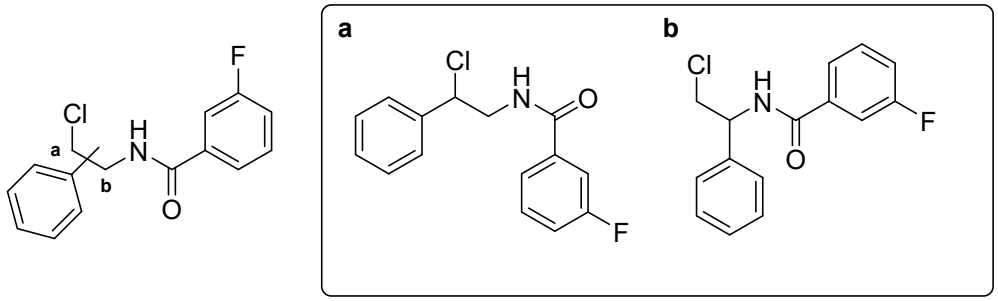
3av

N-(2-chloro-2-phenylethyl)-4-methylbenzamide and N-(2-chloro-1-phenylethyl)-4-methylbenzamide : 88.7 mg pale yellow liquid was obtained, corresponding to 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 30.0, 8.2 Hz, 2H), 7.51 – 7.29 (m, 6H), 7.25 – 7.20 (m, 1H), 6.78 (dd, *J* = 93.4, 6.3 Hz, 1H), 5.60 – 5.51 (m, 0.5H), 5.15 (dd, *J* = 8.9, 5.0 Hz, 0.5H), 4.14 – 4.05 (m, 0.5H), 3.98 (d, *J* = 5.3 Hz, 1H), 3.81 – 3.70 (m, 0.5H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.63, 167.07, 142.46, 142.36, 138.78, 138.63, 131.21, 131.14, 130.82, 130.33, 129.57, 129.40, 128.95, 128.92, 128.23, 127.28, 127.20, 127.08, 126.84, 126.71, 126.67, 62.32, 53.96, 47.86, 47.59, 22.27, 21.60. **HRMS (ESI)** calcd for $C_{16}H_{17}ClNO^+$, $[M+H]^+$, 274.0993, found 274.0993.



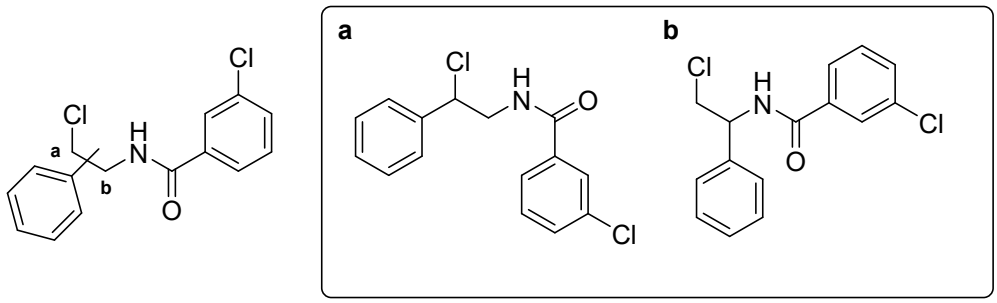
3aw

N-(2-chloro-2-phenylethyl)-4-methoxybenzamide and N-(2-chloro-1-phenylethyl)-4-methoxybenzamide: 94 mg pale yellow liquid was obtained, corresponding to 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 29.7, 8.6 Hz, 2H), 7.45 – 7.31 (m, 5H), 6.96 – 6.89 (m, 2H), 6.87 – 6.56 (m, 1H), 5.59 – 5.44 (m, 0.5H), 5.14 (dd, *J* = 8.9, 5.0 Hz, 0.5H), 4.17 – 4.04 (m, 0.5H), 3.98 (d, *J* = 5.3 Hz, 1H), 3.84 (s, 3H), 3.79 – 3.71 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.20, 166.65, 162.52, 162.46, 138.82, 138.72, 129.07, 128.93, 128.91, 128.21, 127.28, 126.84, 126.31, 126.24, 113.91, 62.39, 55.53, 53.98, 47.89, 47.61. **HRMS (ESI)** calcd for $C_{16}H_{17}ClNO_2^+$, $[M+H]^+$, 290.0942, found 290.0941.



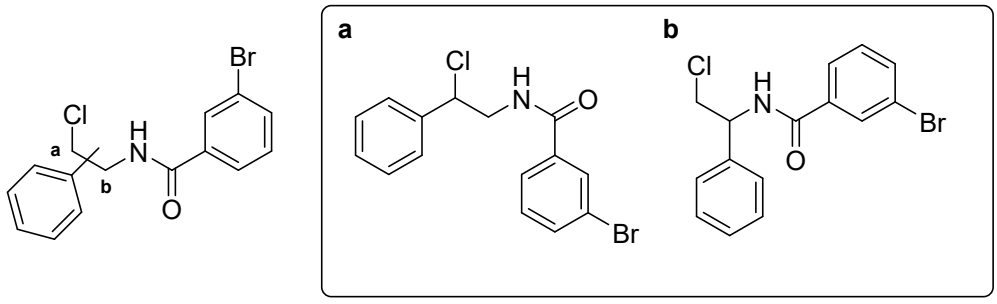
3ax

N-(2-chloro-2-phenylethyl)-3-fluorobenzamide and N-(2-chloro-1-phenylethyl)-3-fluorobenzamide : 69.2 mg pale yellow liquid was obtained, corresponding to 50% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.50 (m, 2H), 7.46 – 7.30 (m, 5H), 7.25 – 7.17 (m, 1H), 6.93 – 6.49 (m, 1H), 5.63 – 5.43 (m, 0.7H), 5.22 – 5.05 (m, 0.3H), 4.58 – 4.21 (m, 0.7H), 4.03 – 3.91 (m, 1H), 3.84 – 3.70 (m, 0.3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.99, 165.90, 164.11, 161.64, 136.34, 136.27, 130.55, 130.47, 129.10, 129.02, 128.48, 127.26, 126.80, 122.61, 122.53, 122.50, 119.15, 118.93, 114.80, 114.57, 62.18, 54.19, 47.71. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -111.44, -111.50. **HRMS (ESI)** calcd for $C_{15}H_{14}ClFNO^+$, $[M+H]^+$, 278.0742, found 278.0742.



3ay

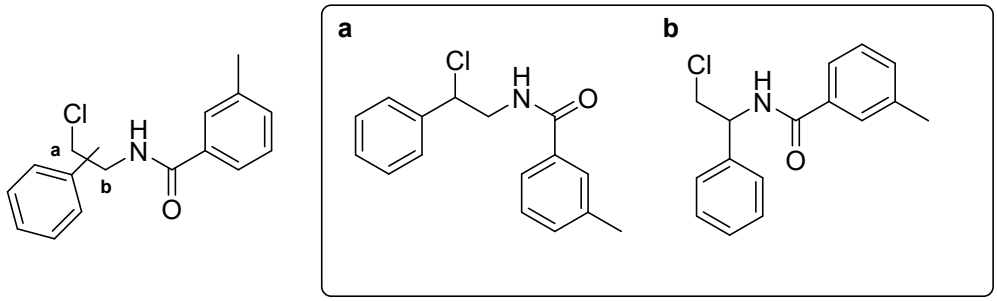
3-chloro-N-(2-chloro-2-phenylethyl)benzamide and 3-chloro-N-(2-chloro-1-phenylethyl)benzamide : 117.6 mg pale yellow liquid was obtained, corresponding to 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.72 (m, 1H), 7.64 (dd, *J* = 30.8, 7.7 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.31 (m, 6H), 6.95 – 6.57 (m, 1H), 5.59 – 5.47 (m, 0.5H), 5.14 (dd, *J* = 9.0, 4.9 Hz, 0.5H), 4.15 – 4.05 (m, 0.5H), 4.01 – 3.92 (m, 1H), 3.81 – 3.66 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.43, 165.90, 138.55, 138.27, 135.88, 135.81, 134.93, 132.00, 131.94, 130.12, 130.10, 129.08, 129.02, 129.00, 128.43, 127.55, 127.51, 127.25, 126.80, 125.31, 125.14, 62.14, 54.28, 47.72, 47.63. **HRMS (ESI)** calcd for $C_{15}H_{14}Cl_2NO^+$, $[M+H]^+$, 294.0447, found 294.0447.



3az

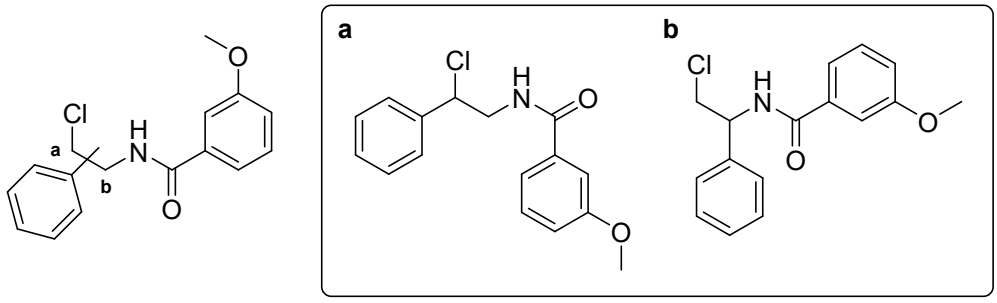
3-bromo-N-(2-chloro-2-phenylethyl)benzamide and 3-bromo-N-(2-chloro-1-phenylethyl)benzamide : 133.5 mg pale yellow liquid was obtained, corresponding to 79% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 21.7 Hz, 1H), 7.77 – 7.60 (m, 2H), 7.50 – 7.30 (m, 6H), 6.82 – 6.45 (m, 1H), 5.64 – 5.51 (m, 0.5H), 5.19 – 5.10 (m, 0.5H), 4.19 – 4.07 (m, 0.5H), 4.04 – 3.92 (m, 1H), 3.84 – 3.69 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.27, 165.70, 138.55, 138.21, 136.11, 136.03, 135.00, 134.92, 130.42, 130.39, 129.13, 129.07, 129.04, 128.48, 127.27, 126.81, 125.76, 125.60, 123.02,

123.01, 62.21, 54.16, 47.74, 47.70. **HRMS (ESI)** calcd for $C_{15}H_{14}BrClNO^+$, $[M+H]^+$, 337.9942, found 337.9941.



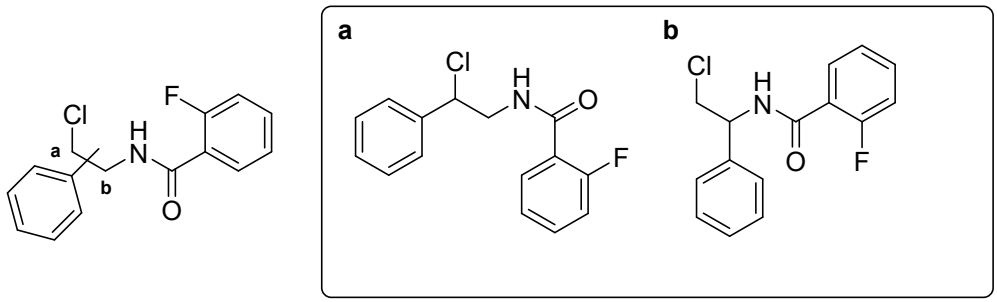
3ba

N-(2-chloro-2-phenylethyl)-3-methylbenzamide and N-(2-chloro-1-phenylethyl)-3-methylbenzamide : 109.2 mg pale yellow liquid was obtained, corresponding to 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.50 (m, 2H), 7.47 – 7.41 (m, 1H), 7.41 – 7.34 (m, 3H), 7.34 – 7.28 (m, 3H), 7.02 – 6.62 (m, 1H), 5.62 – 5.42 (m, 0.5H), 5.15 (dd, *J* = 9.0, 5.0 Hz, 0.5H), 4.14 – 4.05 (m, 0.5H), 3.97 (d, *J* = 5.3 Hz, 1H), 3.81 – 3.70 (m, 0.5H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.92, 167.36, 138.75, 138.64, 138.61, 138.58, 134.06, 134.00, 132.68, 132.60, 128.95, 128.91, 128.62, 128.59, 128.23, 127.91, 127.86, 127.27, 126.83, 124.15, 124.00, 62.26, 54.03, 47.77, 47.61, 21.45. **HRMS (ESI)** calcd for $C_{16}H_{17}ClNO^+$, $[M+H]^+$, 274.0993, found 274.0992.



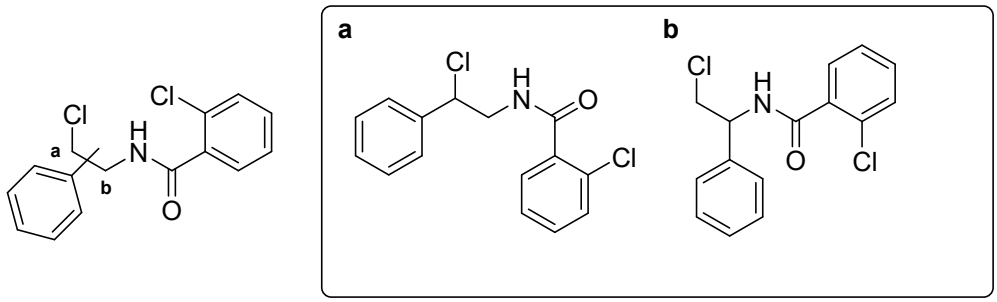
3bb

N-(2-chloro-2-phenylethyl)-3-methoxybenzamide and N-(2-chloro-1-phenylethyl)-3-methoxybenzamide : 69.4 mg pale yellow liquid was obtained, corresponding to 48% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.31 (m, 8H), 7.10 – 7.03 (m, 1H), 6.95 – 6.60 (m, 1H), 5.59 – 5.50 (m, 0.5H), 5.15 (dd, *J* = 8.9, 5.1 Hz, 0.5H), 4.13 – 4.04 (m, 0.5H), 3.98 (d, *J* = 5.3 Hz, 1H), 3.83 (s, 3H), 3.80 – 3.67 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.56, 167.00, 159.91, 138.71, 138.50, 135.56, 135.48, 129.76, 129.00, 128.95, 128.29, 127.27, 126.81, 118.88, 118.81, 118.10, 118.06, 112.61, 112.42, 62.20, 55.56, 55.54, 54.11, 47.77, 47.65. **HRMS (ESI)** calcd for $C_{16}H_{17}ClNO_2^+$, $[M+H]^+$, 290.0942, found 290.0941.



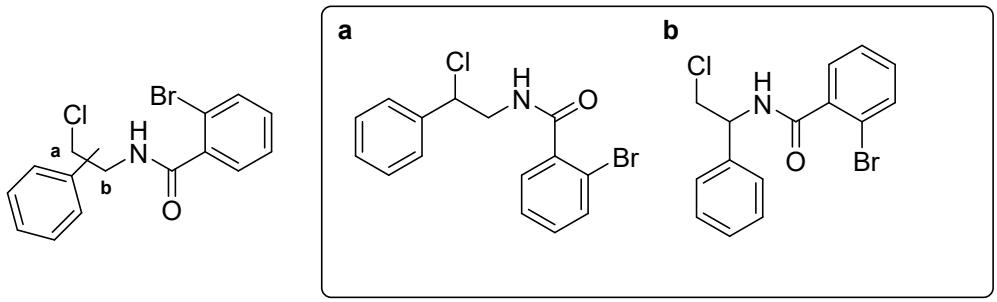
3bc

N-(2-chloro-2-phenylethyl)-2-fluorobenzamide and N-(2-chloro-1-phenylethyl)-2-fluorobenzamide :76.1 mg pale yellow liquid was obtained, corresponding to 55% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 – 8.01 (m, 1H), 7.53 – 7.44 (m, 2H), 7.42 – 7.37 (m, 3H), 7.35 – 7.32 (m, 1H), 7.30 – 7.26 (m, 1H), 7.19 – 7.06 (m, 2H), 5.65 – 5.54 (m, 0.5H), 5.16 (dd, *J* = 8.9, 5.0 Hz, 0.5H), 4.22 – 4.09 (m, 0.5H), 4.03 – 3.92 (m, 1H), 3.87 – 3.75 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.54, 163.51, 162.94, 162.91, 162.14, 162.03, 159.68, 159.56, 138.71, 138.45, 133.88, 133.78, 133.69, 132.30, 132.28, 132.14, 132.12, 129.00, 128.96, 128.30, 127.27, 126.79, 125.06, 125.03, 124.99, 124.96, 120.68, 120.63, 120.57, 120.52, 116.35, 116.10, 61.98, 54.28, 47.95, 47.73. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -113.14, -113.33. **HRMS (ESI)** calcd for $C_{15}H_{14}ClFNO^+$, $[M+H]^+$, 278.0742, found 278.0741.



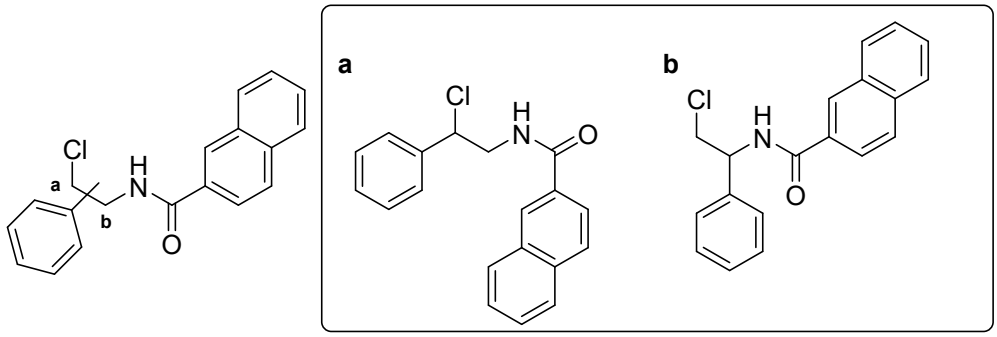
3bd

2-chloro-N-(2-chloro-2-phenylethyl)benzamide and 2-chloro-N-(2-chloro-1-phenylethyl)benzamide : 32.3 mg pale yellow liquid was obtained, corresponding to 22% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.61 (m, 1H), 7.54 – 7.30 (m, 8H), 7.09 – 6.50 (m, 1H), 5.63 – 5.49 (m, 0.5H), 5.26 – 5.10 (m, 0.5H), 4.18 – 4.08 (m, 0.5H), 4.05 – 3.90 (m, 1H), 3.88 – 3.72 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.57, 165.91, 138.64, 138.52, 138.03, 134.45, 134.26, 131.92, 131.83, 131.73, 131.61, 130.76, 130.54, 130.39, 130.35, 130.20, 128.98, 128.94, 128.90, 128.87, 128.72, 128.70, 128.26, 128.23, 127.28, 127.23, 127.15, 127.09, 126.93, 126.80, 126.74, 126.61, 99.98, 62.24, 61.70, 54.35, 47.68, 47.56. **HRMS (ESI)** calcd for $C_{15}H_{14}Cl_2NO^+$, $[M+H]^+$, 294.0447, found 294.0447.



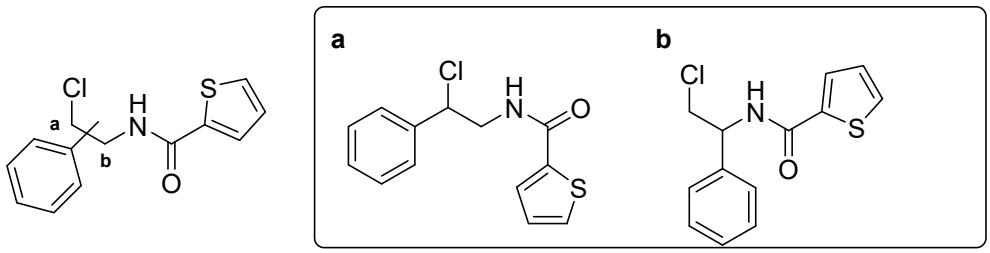
3be

2-bromo-N-(2-chloro-2-phenylethyl)benzamide and 2-bromo-N-(2-chloro-1-phenylethyl)benzamide : 72.7 mg pale yellow liquid was obtained, corresponding to 43% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.71 (m, 1H), 7.62 – 7.55 (m, 1H), 7.49 – 7.31 (m, 7H), 6.87 – 6.42 (m, 1H), 5.56 (dt, *J* = 7.7, 5.1 Hz, 0.5H), 5.18 (dd, *J* = 8.8, 5.3 Hz, 0.5H), 4.16 – 4.07 (m, 0.5H), 4.05 – 3.92 (m, 1H), 3.86 – 3.76 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.79, 167.15, 138.58, 138.00, 137.28, 137.16, 133.57, 133.56, 131.70, 131.60, 129.91, 129.63, 129.06, 128.98, 128.96, 128.94, 128.78, 128.76, 128.36, 127.74, 127.67, 127.38, 127.28, 127.18, 127.07, 126.95, 119.38, 62.28, 61.73, 54.39, 47.57. **HRMS (ESI)** calcd for $C_{15}H_{14}BrClNO^+$, $[M+H]^+$, 337.9942, found 337.9941.



3bf

N-(2-chloro-2-phenylethyl)-2-naphthamide and N-(2-chloro-1-phenylethyl)-2-naphthamide : 78.8 mg pale yellow liquid was obtained, corresponding to 51% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 – 8.21 (m, 1H), 8.02 – 7.84 (m, 4H), 7.66 – 7.54 (m, 2H), 7.50 – 7.32 (m, 5H), 7.03 – 6.61 (m, 1H), 5.74 – 5.52 (m, 0.5H), 5.21 (dd, *J* = 9.0, 4.9 Hz, 0.5H), 4.25 – 4.15 (m, 0.5H), 4.10 – 4.02 (m, 1H), 3.89 – 3.77 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.80, 167.29, 138.75, 138.61, 134.92, 134.89, 132.61, 131.28, 131.23, 129.05, 128.98, 128.96, 128.94, 128.64, 128.29, 127.91, 127.90, 127.84, 127.79, 127.71, 127.30, 126.91, 126.90, 123.70, 123.57, 62.28, 54.27, 47.78, 47.75. **HRMS (ESI)** calcd for $C_{19}H_{17}ClNO^+$, $[M+H]^+$, 310.0993, found 310.0993.



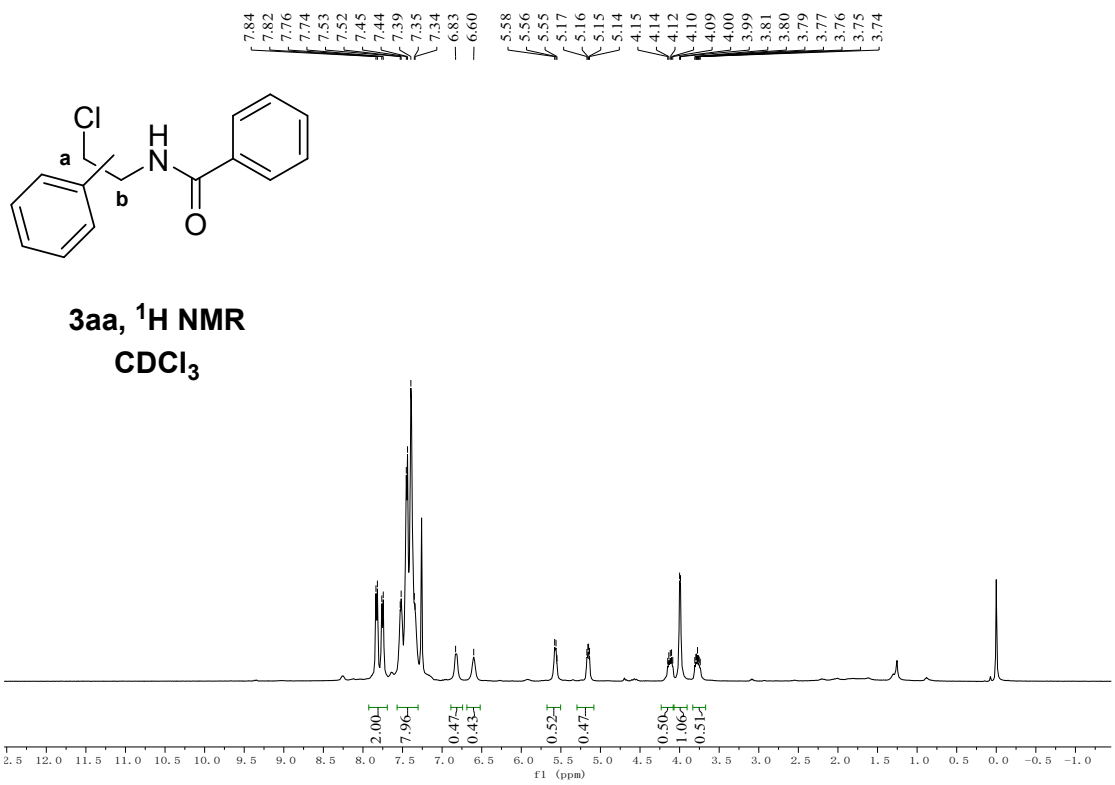
3bg

N-(2-chloro-2-phenylethyl)thiophene-2-carboxamide and N-(2-chloro-1-phenylethyl)thiophene-2-carboxamide : 106.1 mg pale yellow liquid was obtained, corresponding to 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.48 (m, 2H), 7.38 (ddt, *J* = 15.9, 11.4, 5.2 Hz, 5H), 7.10 – 7.02 (m, 1H), 6.88 – 6.57 (m, 1H), 5.58 – 5.47 (m, 0.5H), 5.14 (dd, *J* = 8.9, 4.9 Hz, 0.5H), 4.12 – 4.02 (m, 0.5H), 3.97 (d, *J* = 5.6 Hz, 1H), 3.78 – 3.68 (m, 0.5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.10, 161.60, 138.63, 138.38, 130.70, 130.57, 129.47, 129.01, 128.96, 128.67, 128.53, 128.33, 127.85, 127.26, 126.85, 126.54, 62.24, 54.09, 47.63, 47.58. **HRMS (ESI)** calcd for $C_{13}H_{13}ClNOS^{+}$, $[M+H]^{+}$, 266.0401, found 266.0401.

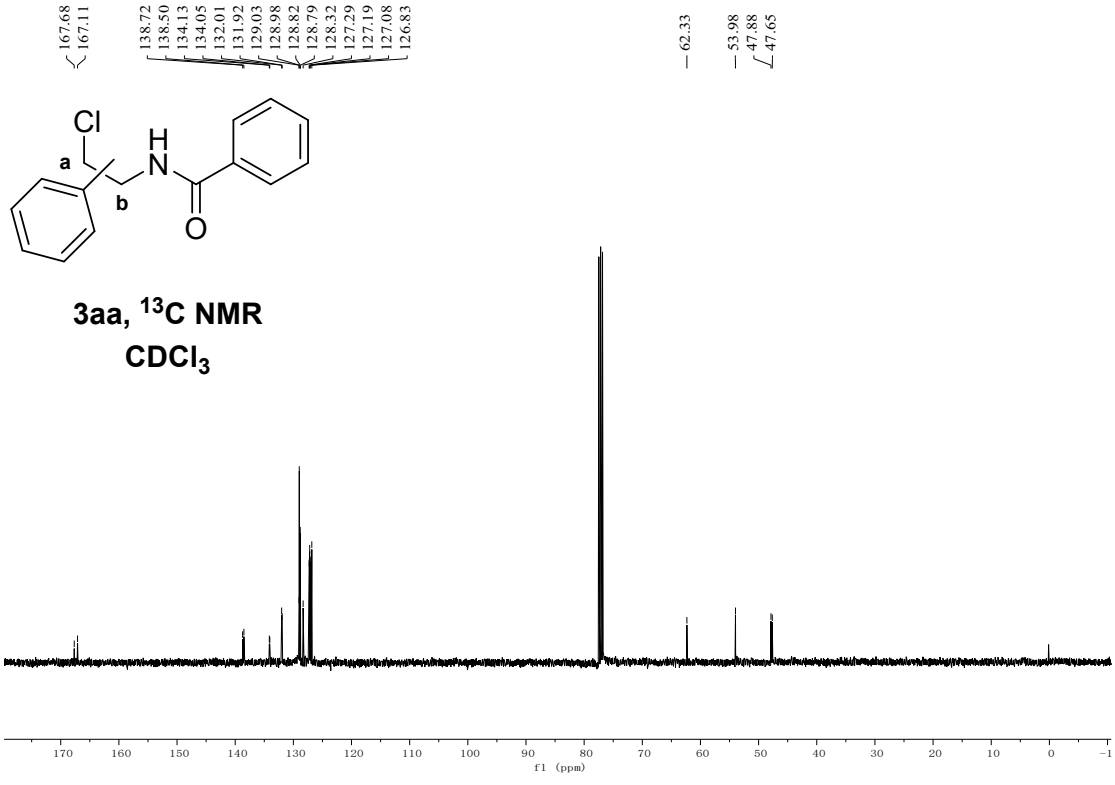
4. References

1. Pill, T.; Polborn, K.; Beck, W., *Chem. Ber.* 2006, *123*, 11-17.

5. NMR spectra of products



3aa, ^{1}H NMR
$CDCl_3$



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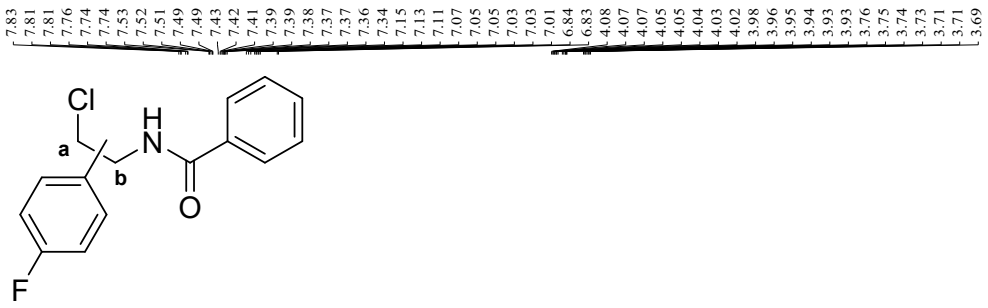
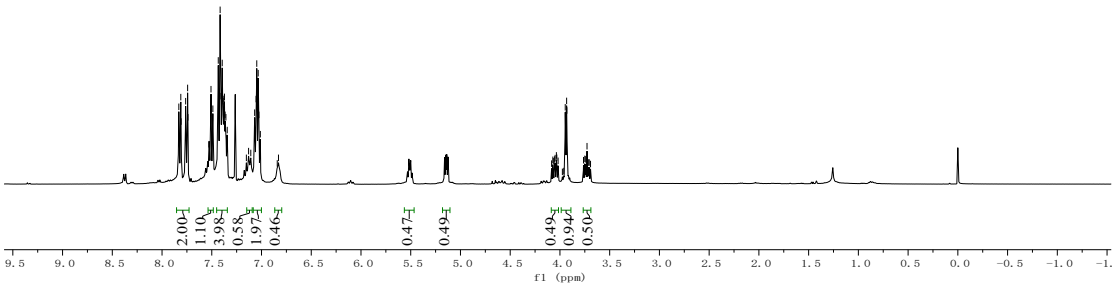
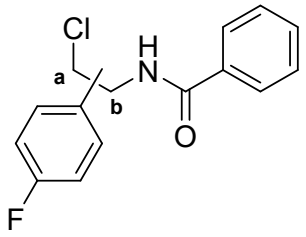
$CDCl_3$



3ab, ^{1}H NMR

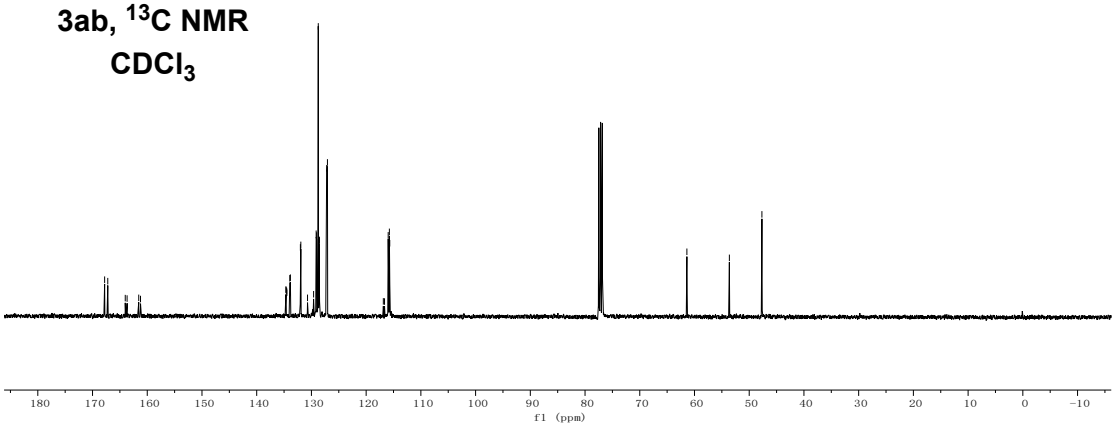
$CDCl_3$



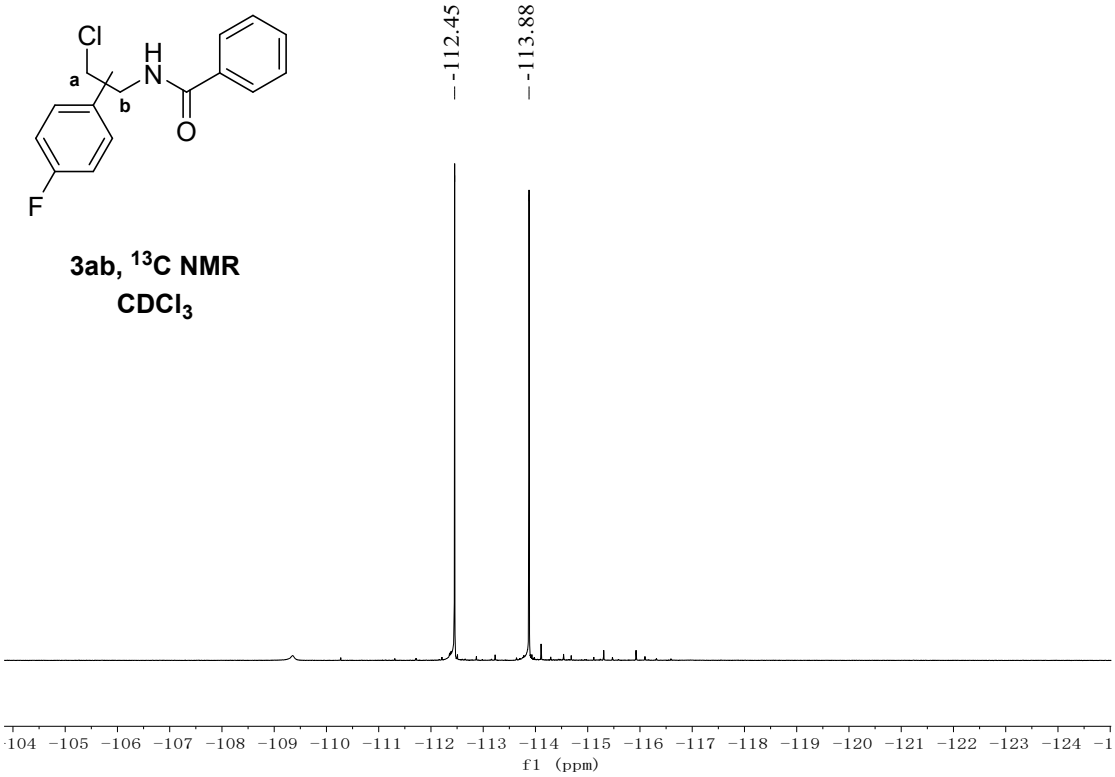


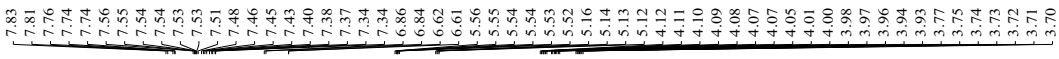
3ab, ^{13}C NMR

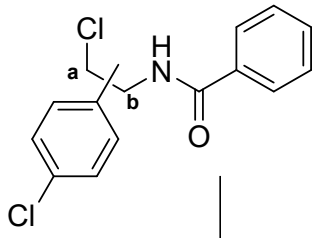
$CDCl_3$



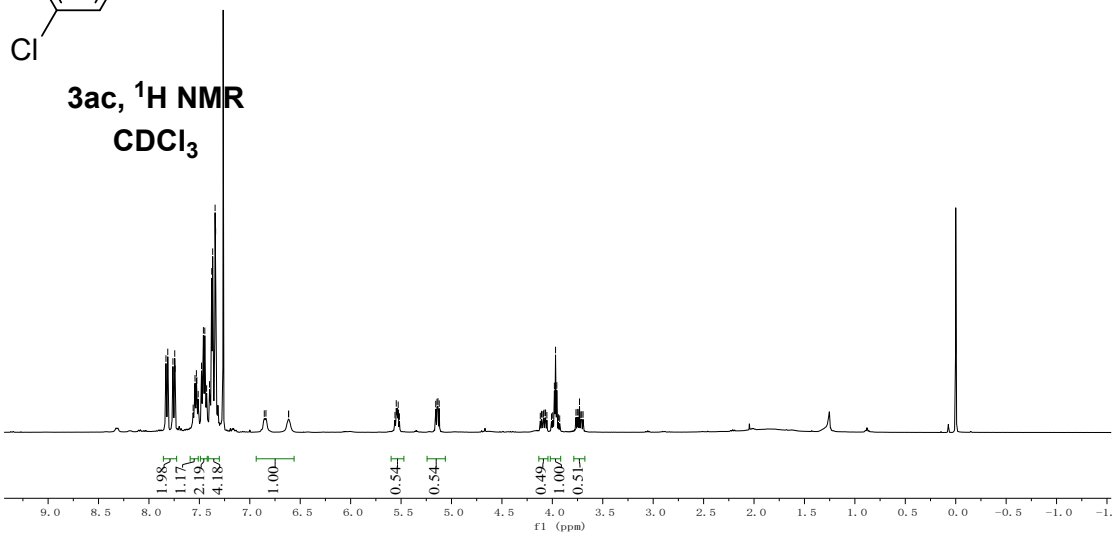
3ab, ^{13}C NMR
$CDCl_3$

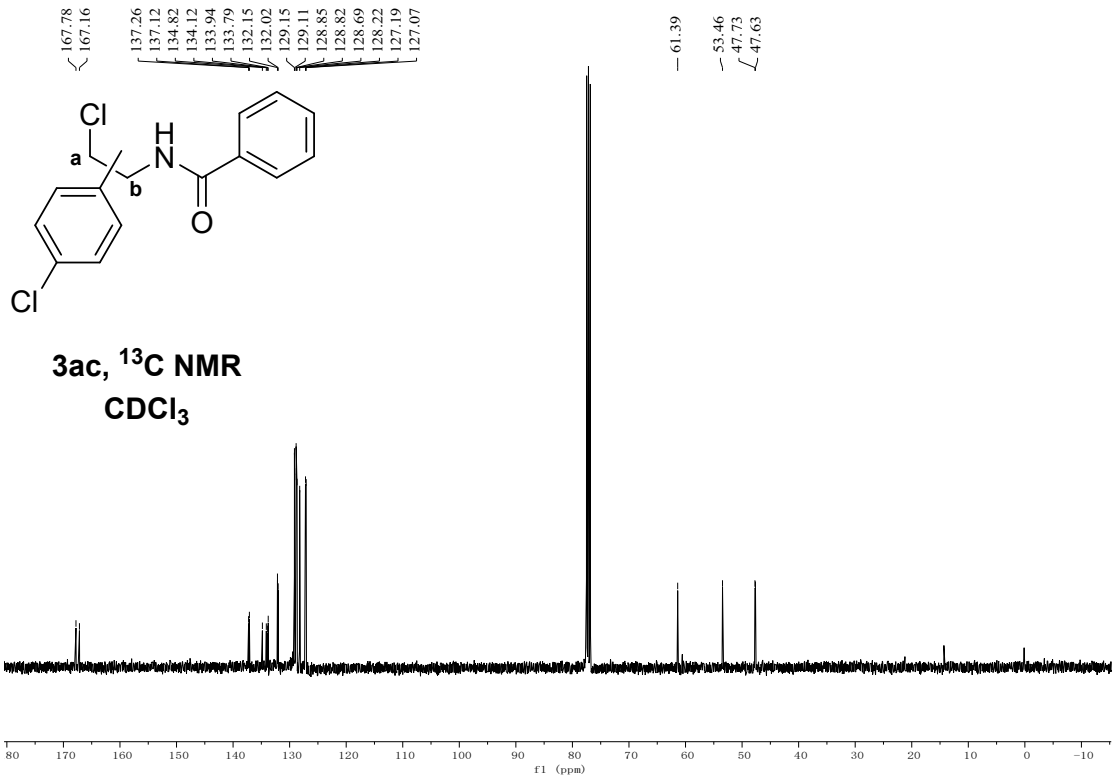






3ac, ^{1}H NMR
$CDCl_3$





3ac, ^{13}C NMR

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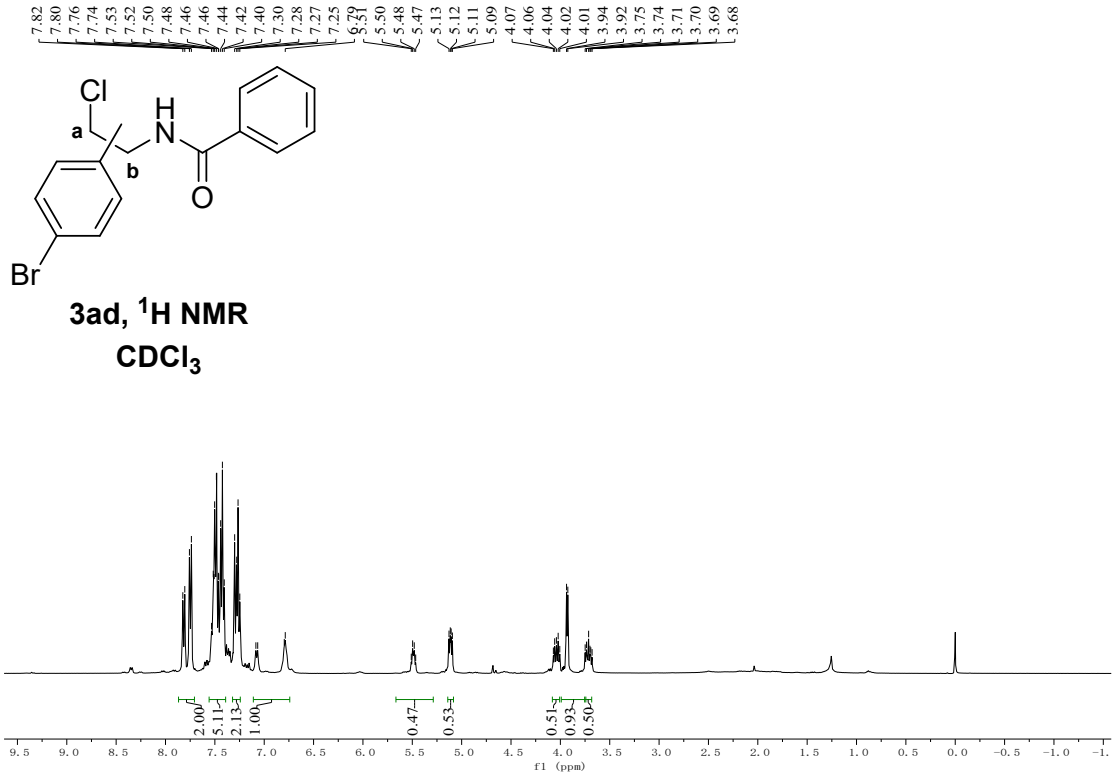

3ad, ^{1}H NMR

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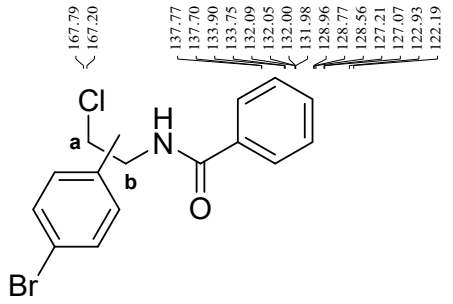

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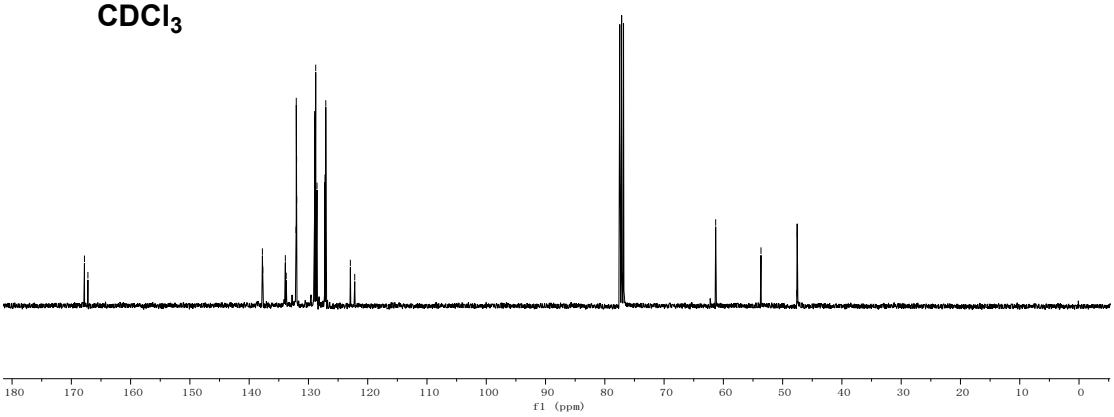
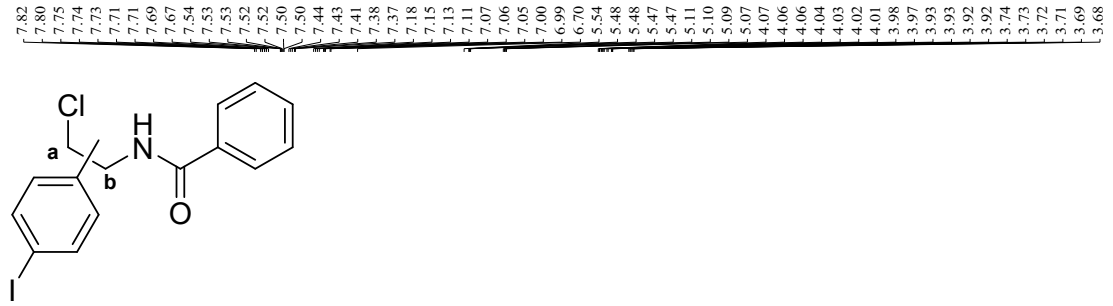
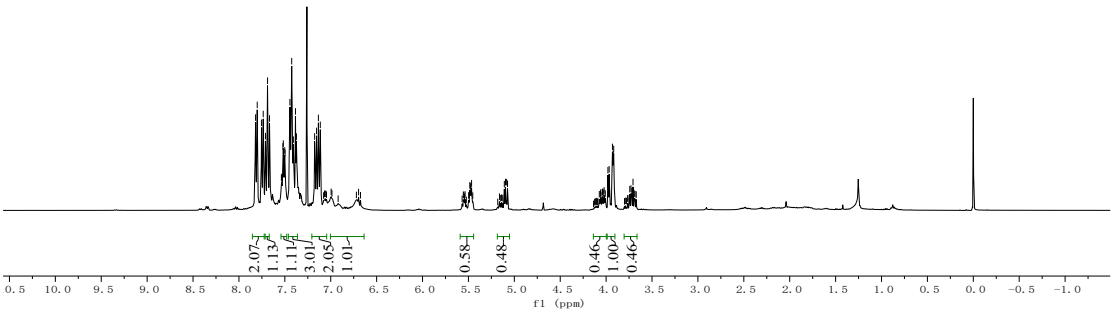
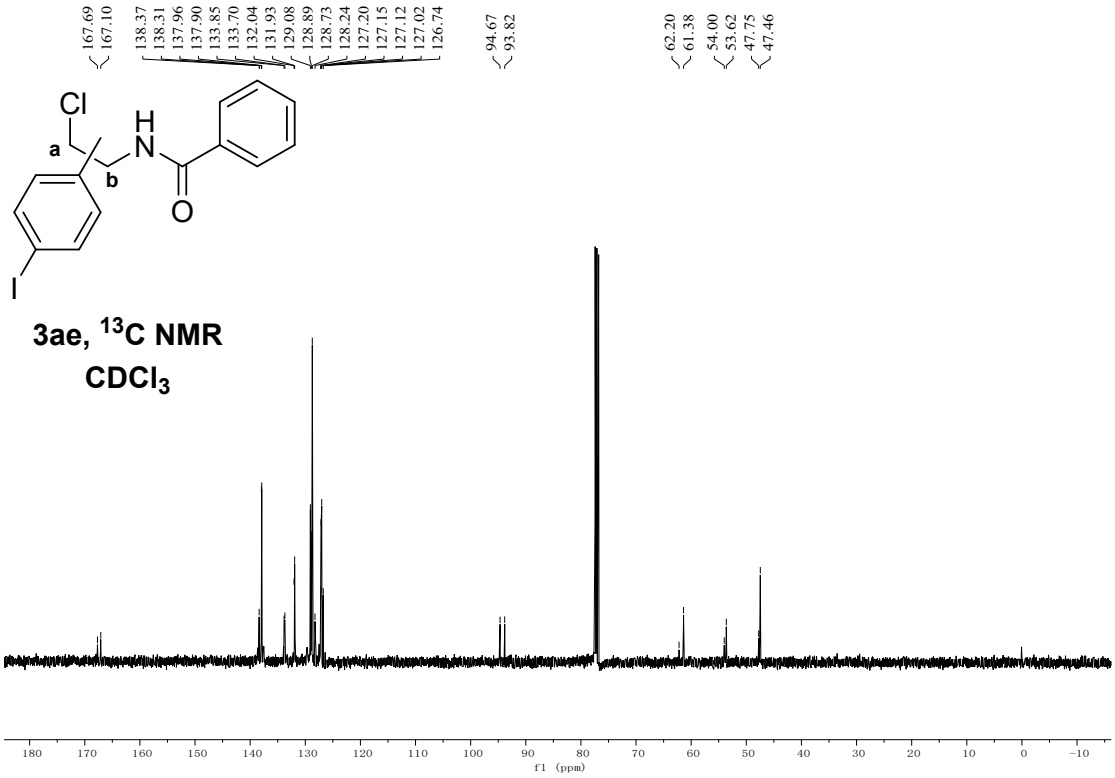




3ae, ^{1}H NMR

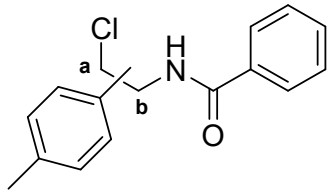
$CDCl_3$





3ae, ^{13}C NMR

$CDCl_3$



3af, ^{1}H NMR

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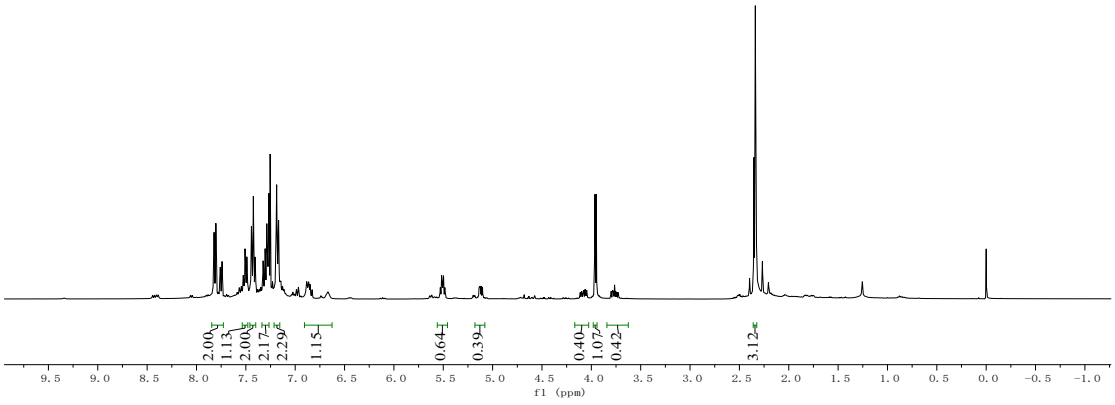

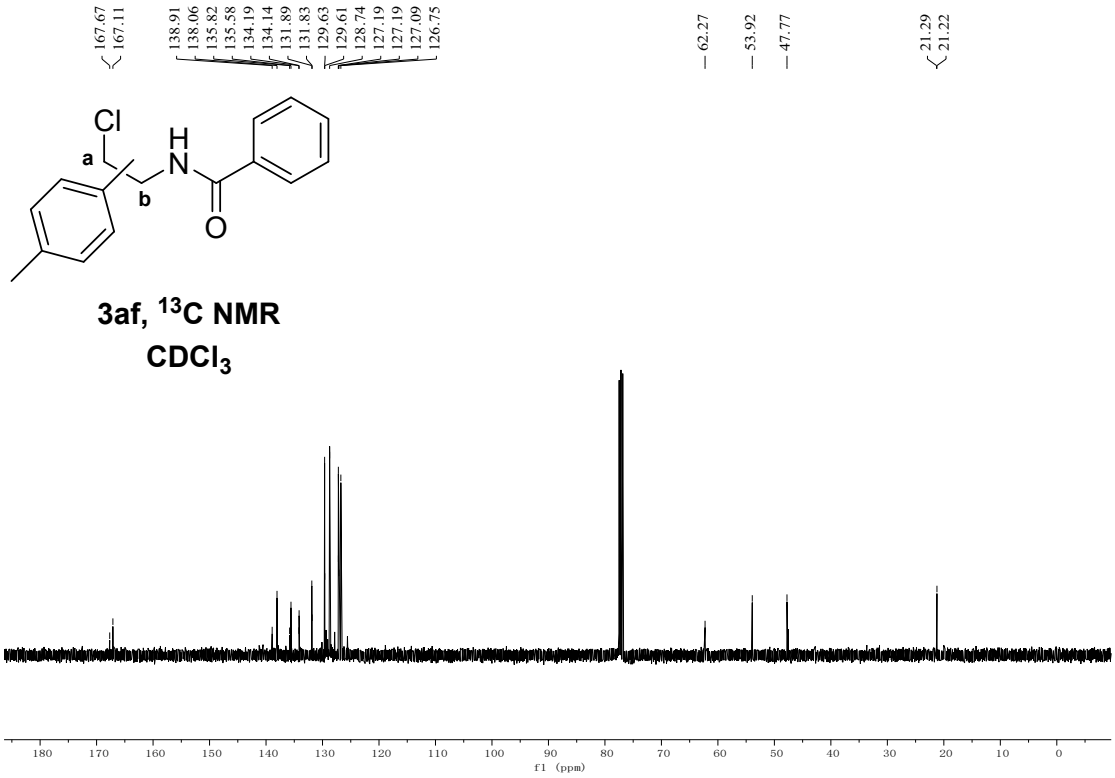

3af, ^{13}C NMR

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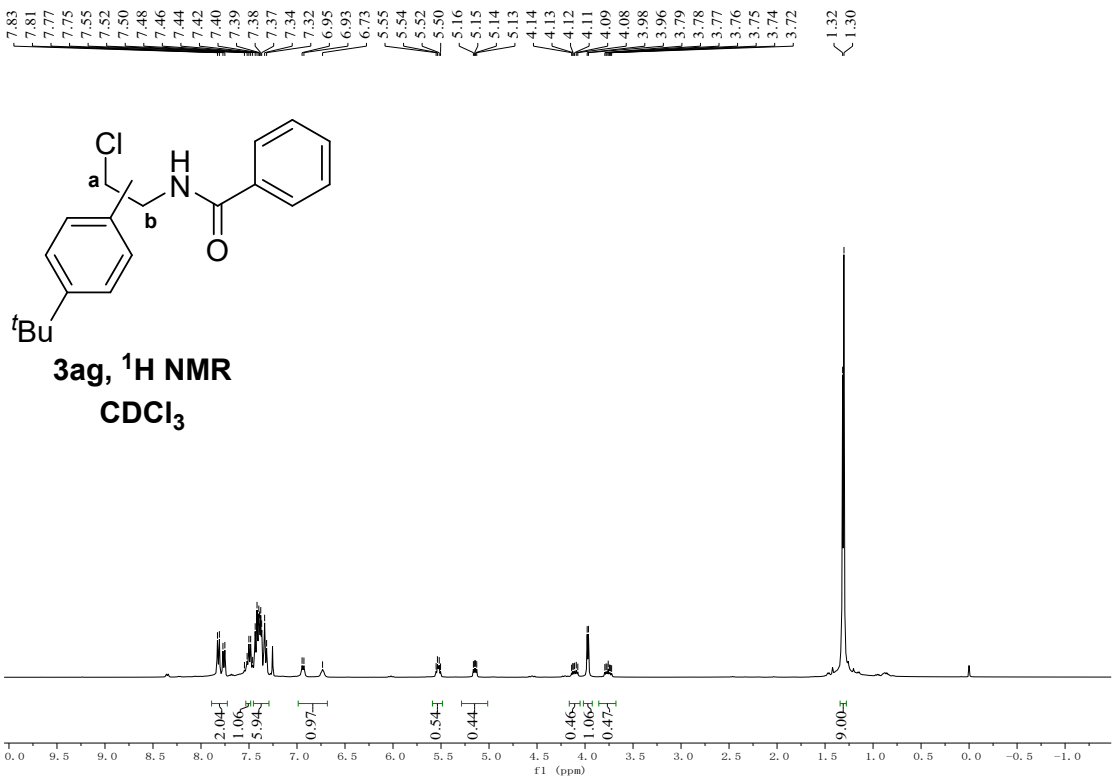

3ag, ^{1}H NMR

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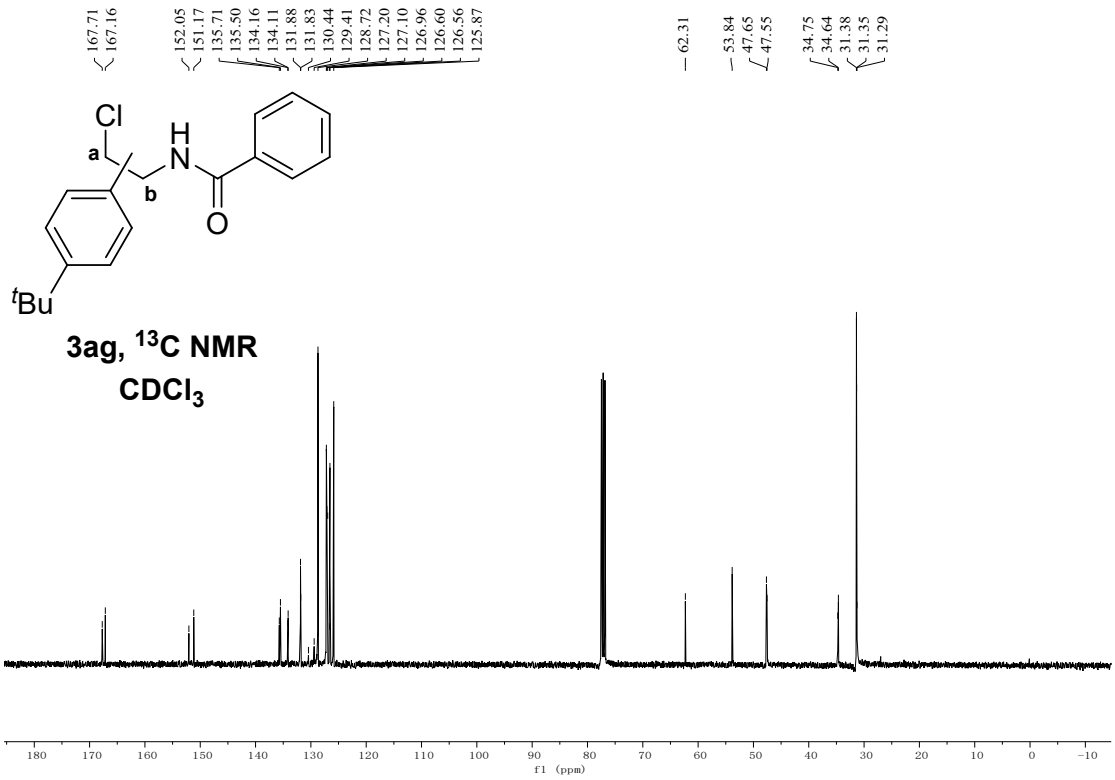

3ag, ^{13}C NMR

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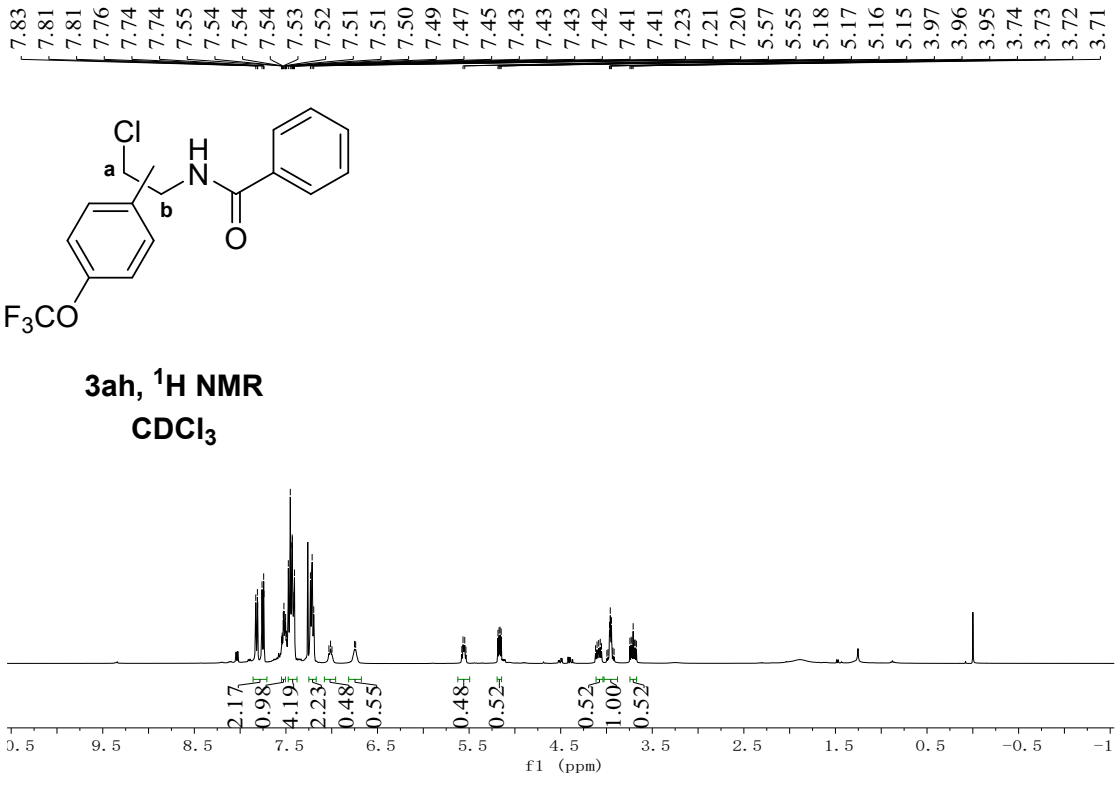
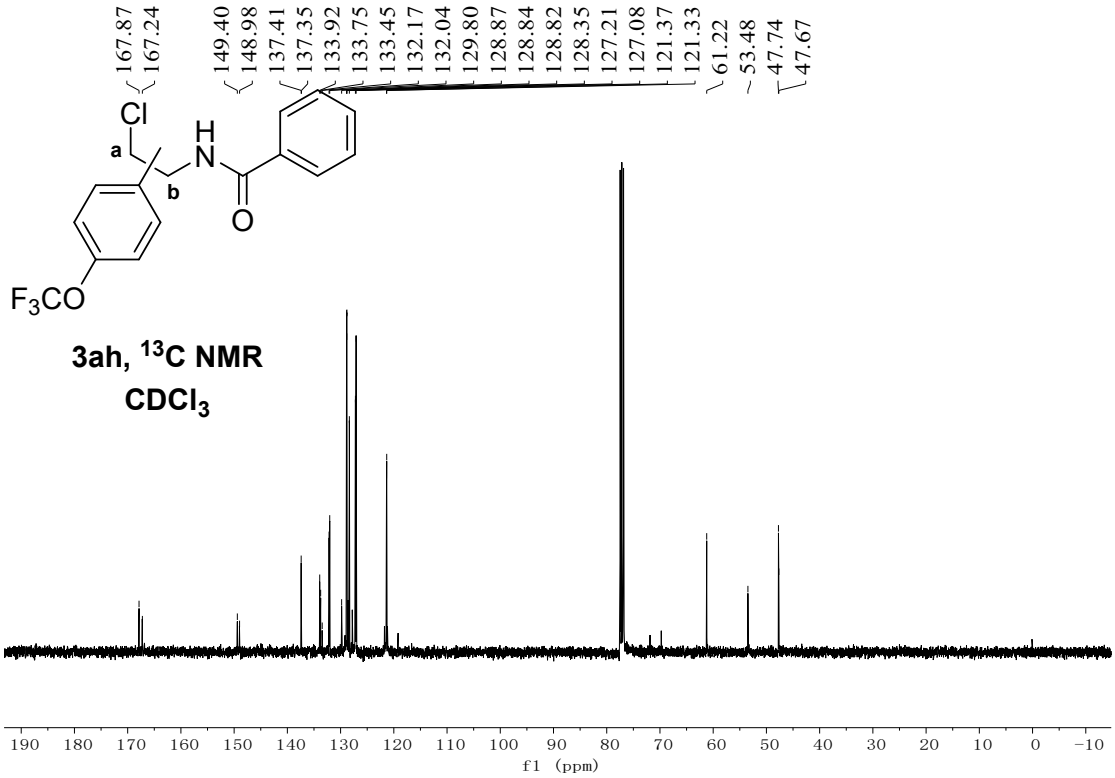


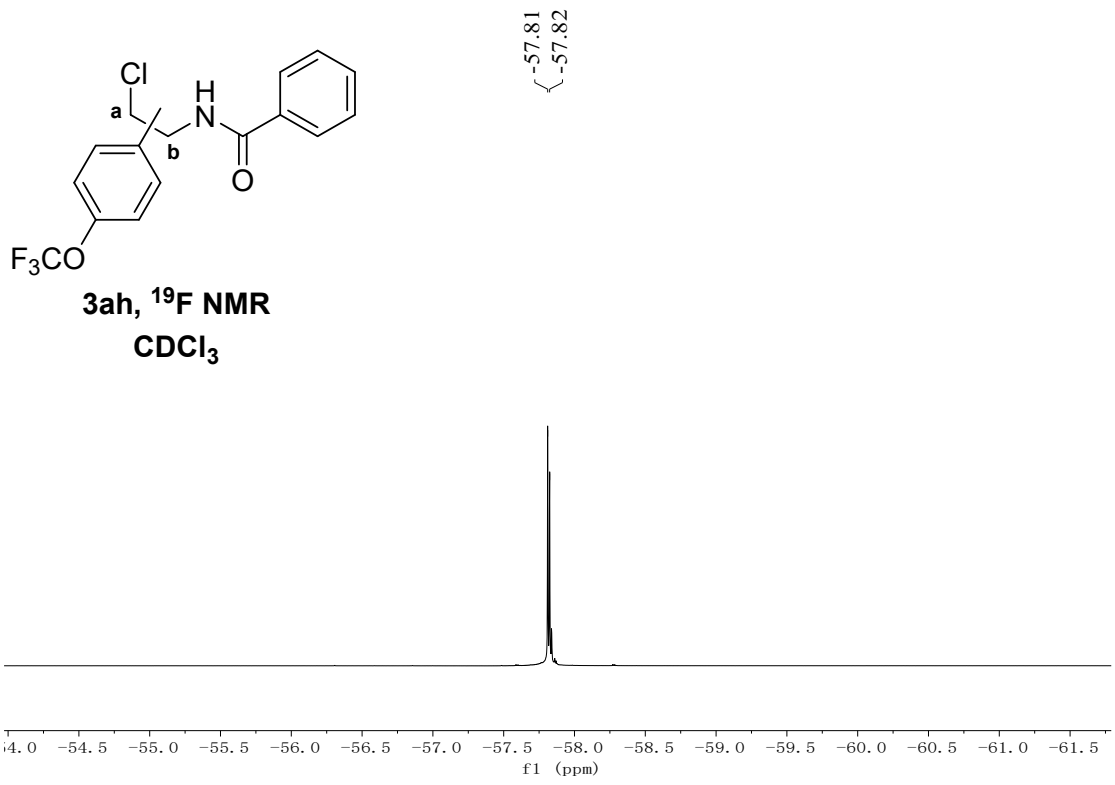
3ah, ^{1}H NMR

$CDCl_3$



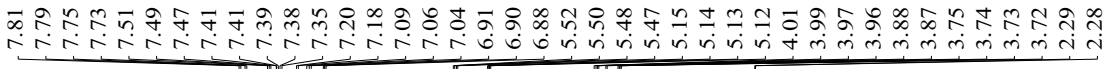
3ah, ^{13}C NMR

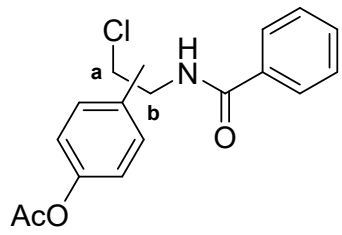
$CDCl_3$



3ah, ^{19}F NMR

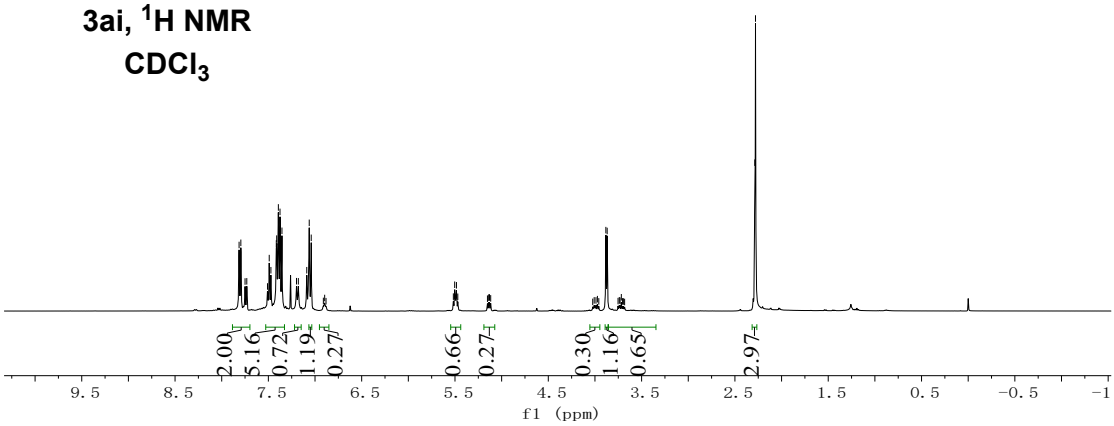
$CDCl_3$

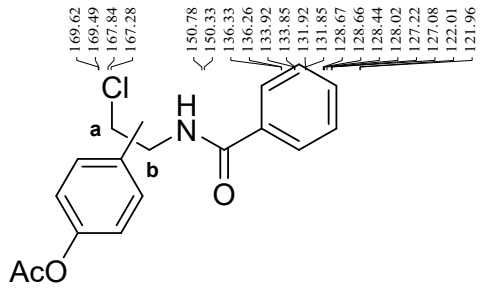




3ai, ^{1}H NMR

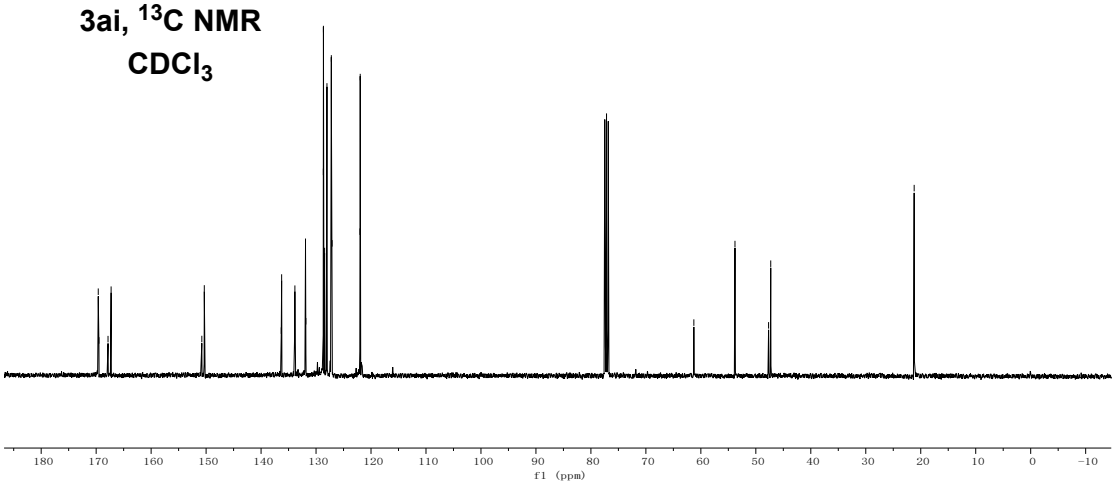
$CDCl_3$

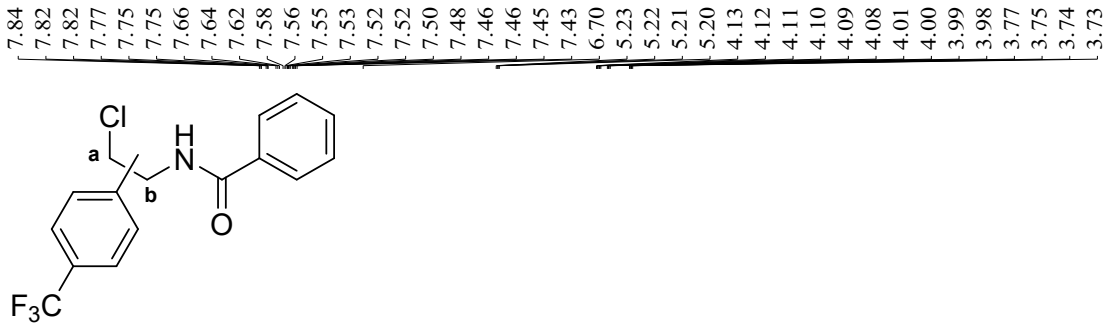




3ai, ^{13}C NMR

$CDCl_3$





3aj, ^{1}H NMR

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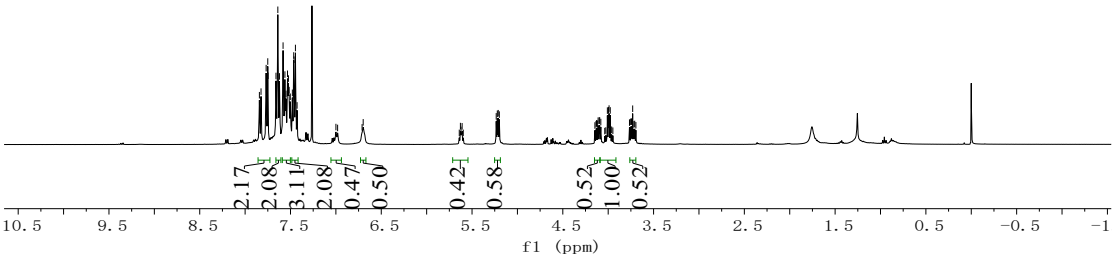
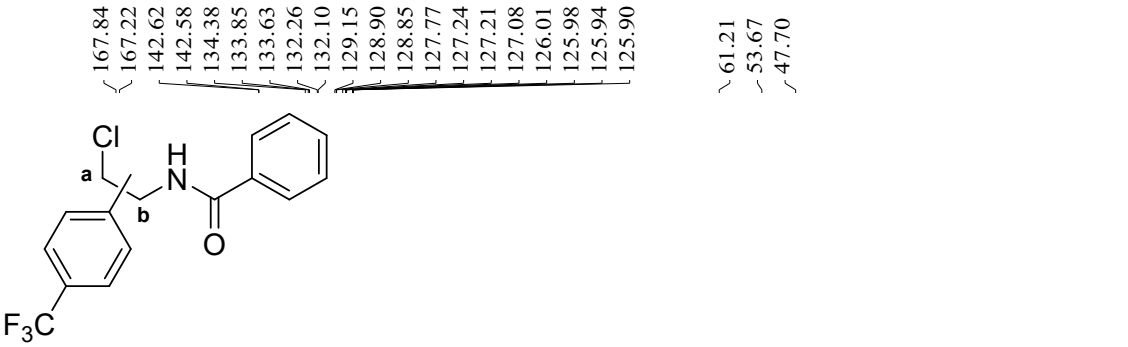
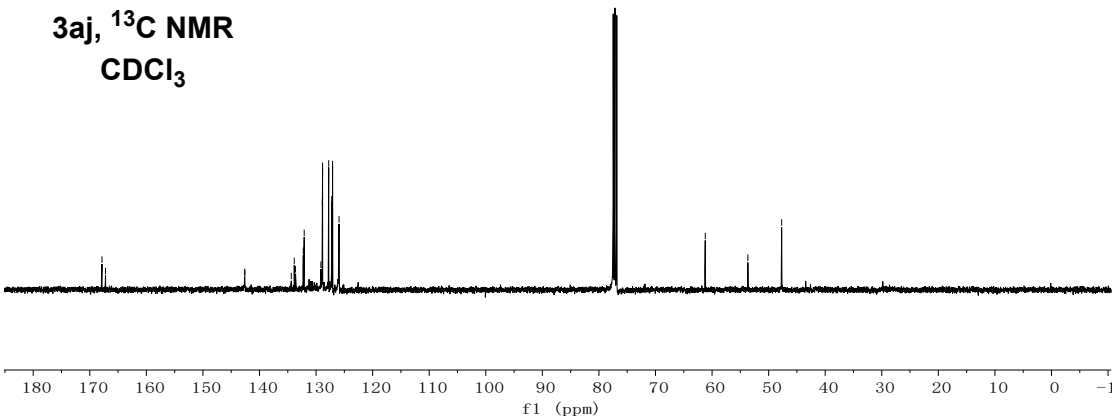
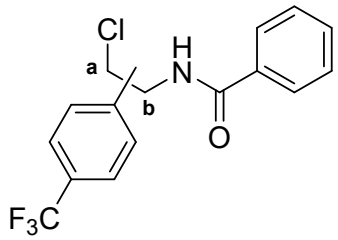




3aj, ^{13}C NMR

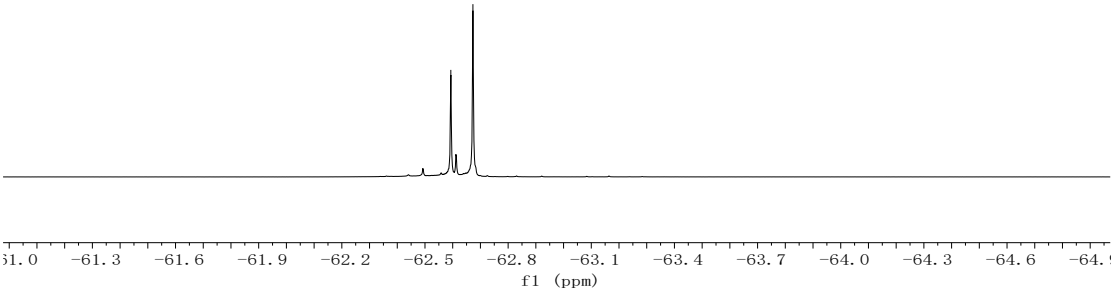
$CDCl_3$



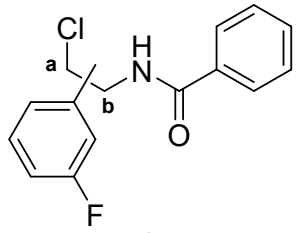


-62.59
-62.67

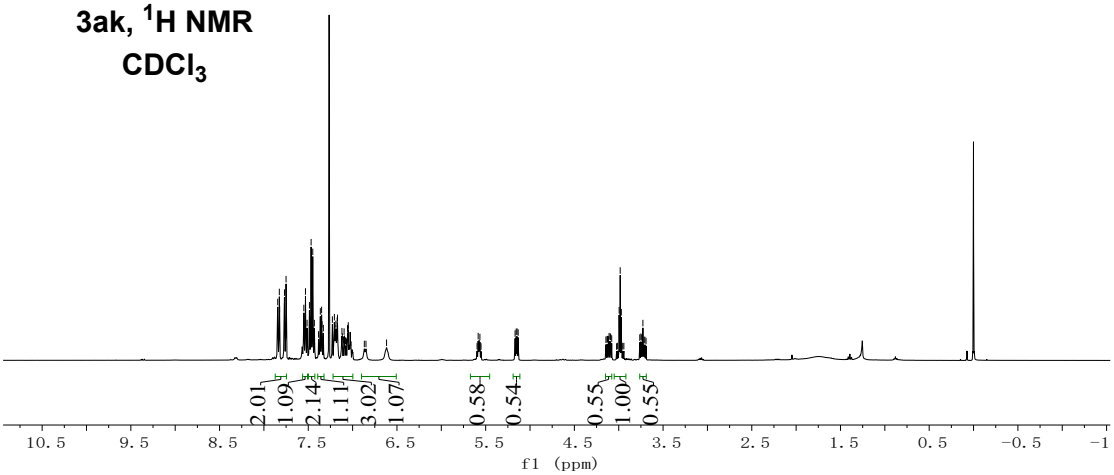
3aj, ^{19}F NMR
$CDCl_3$

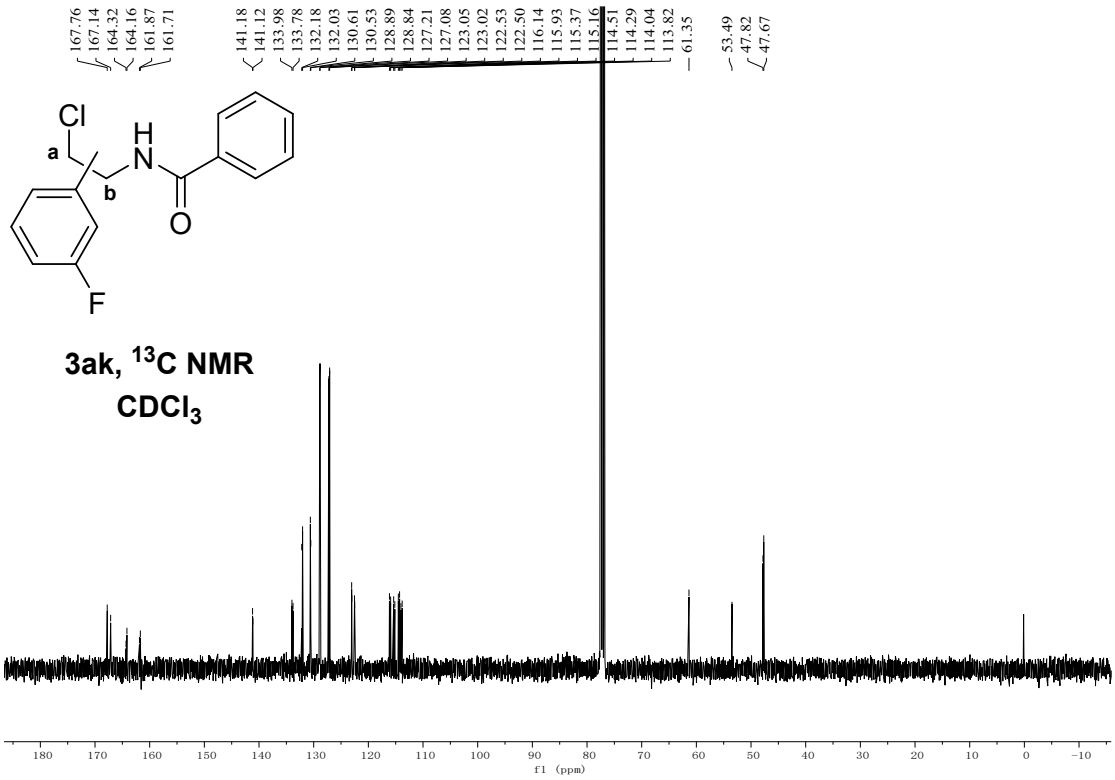


7.84 7.83 7.82 7.77 7.75 7.75 7.55 7.53 7.52 7.51 7.49 7.47 7.45 7.43 7.38 7.36 7.35 7.34 7.33 7.23 7.21 7.20 7.19 7.18 7.17 7.17 7.12 7.10 7.06 7.06 7.05 7.05 5.17 5.16 5.15 5.13 4.00 3.98 3.97 3.73



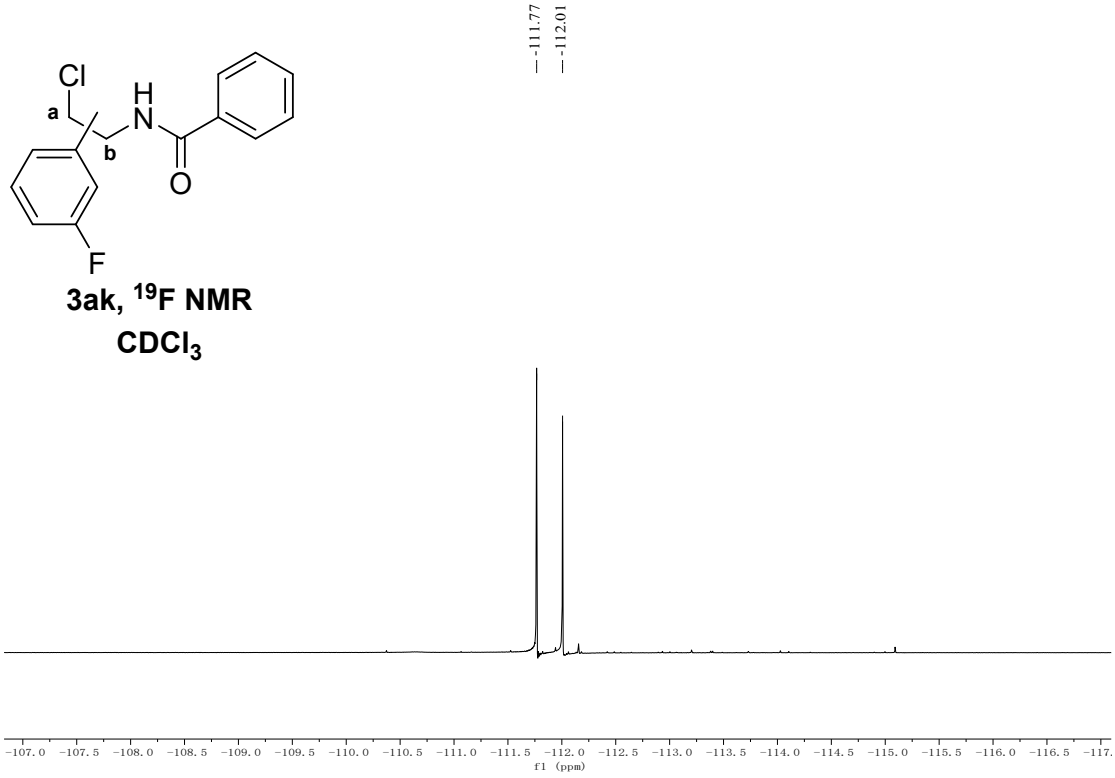
3ak, ^{1}H NMR
$CDCl_3$





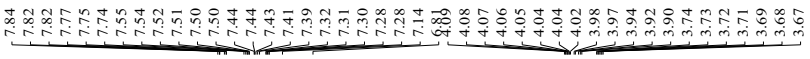
3ak, ^{13}C NMR

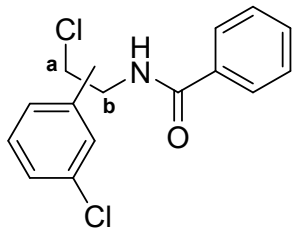
$CDCl_3$



3ak, ^{19}F NMR

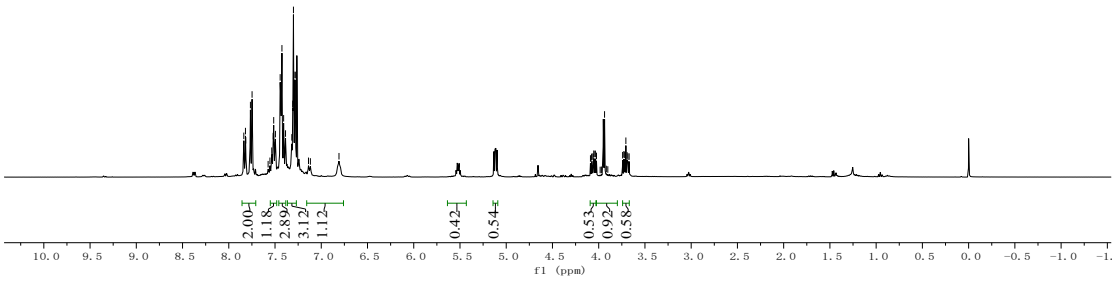
$CDCl_3$

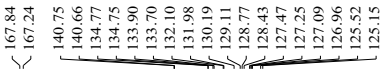


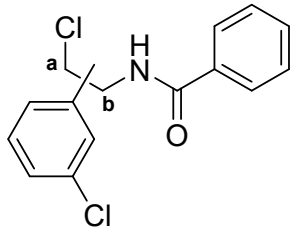


3al, ^{1}H NMR

$CDCl_3$

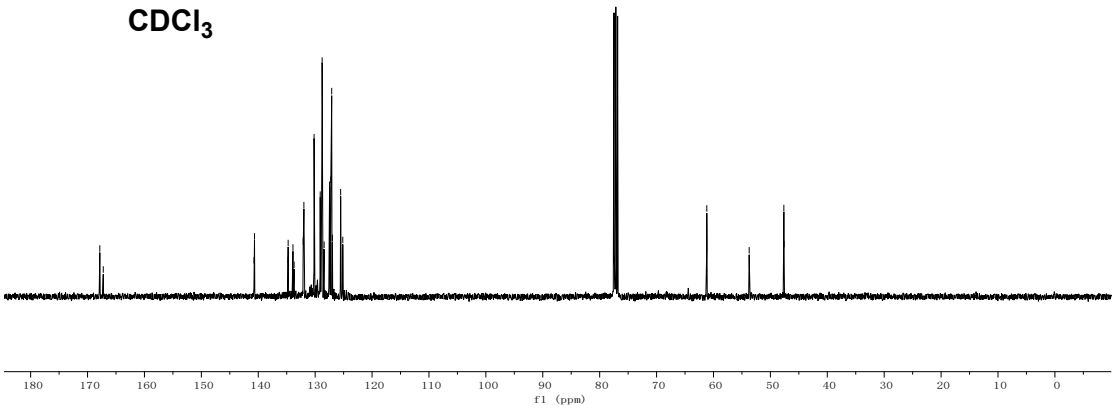


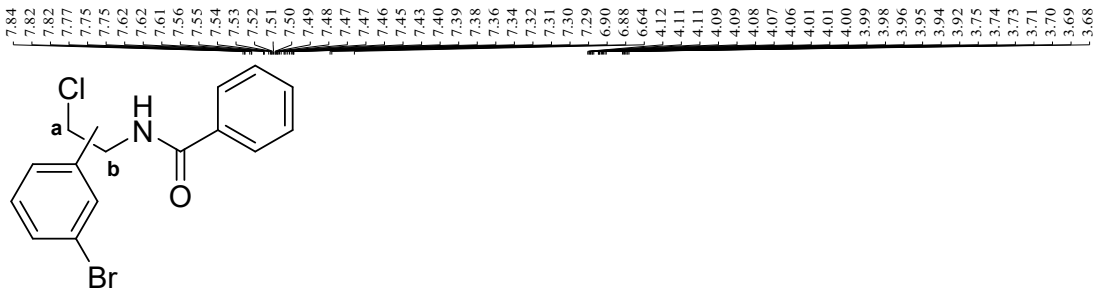




3al, ^{13}C NMR

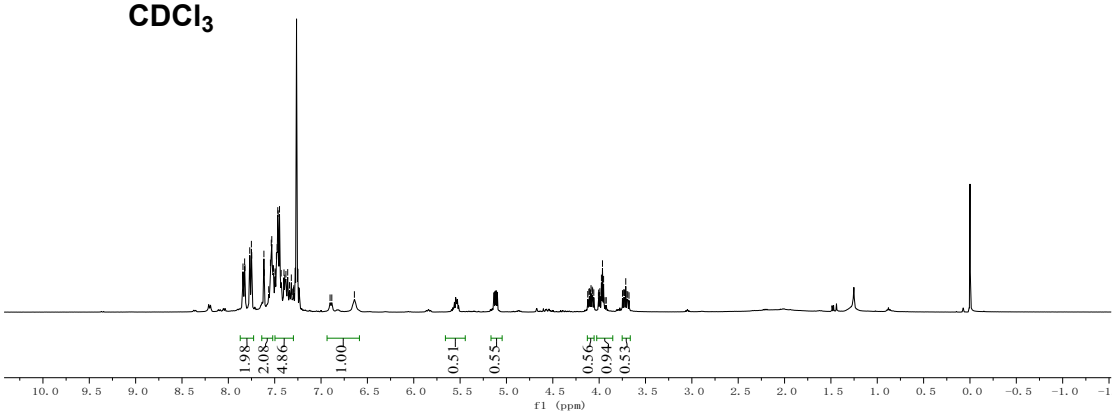
$CDCl_3$

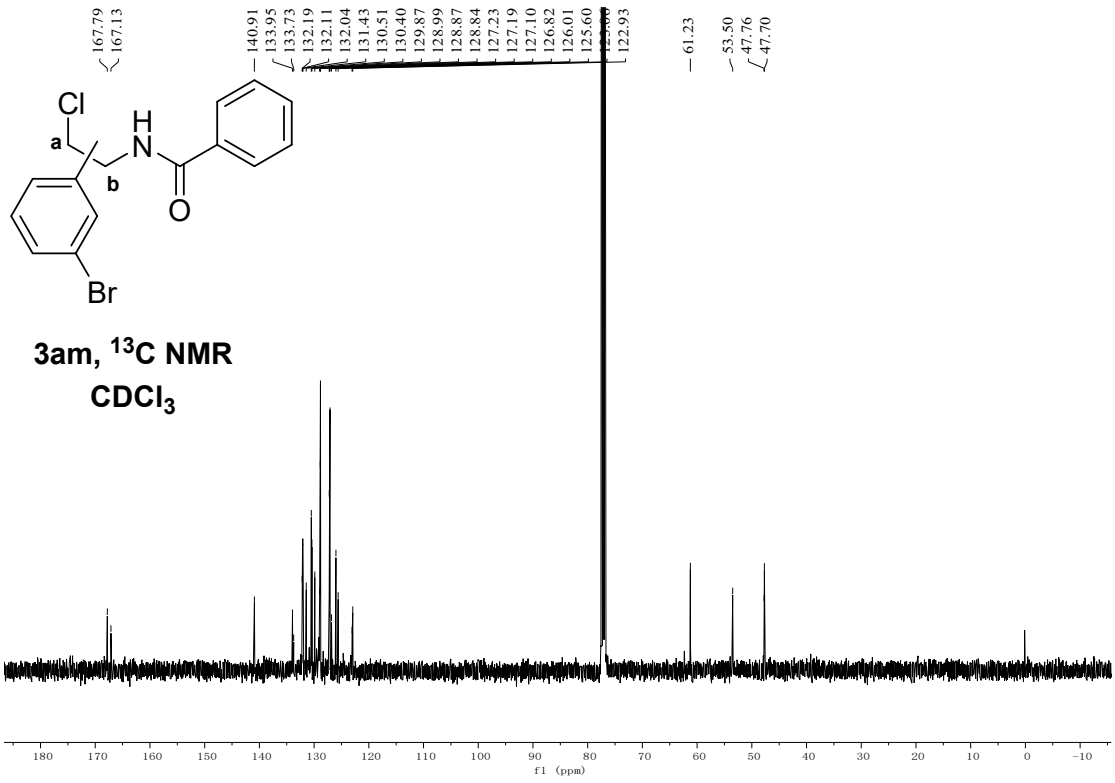




3am, ^{1}H NMR

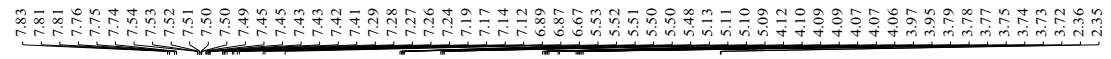
$CDCl_3$

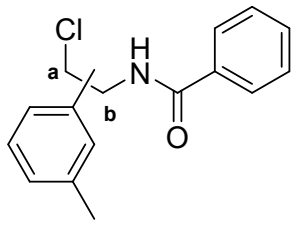




3am, ^{13}C NMR

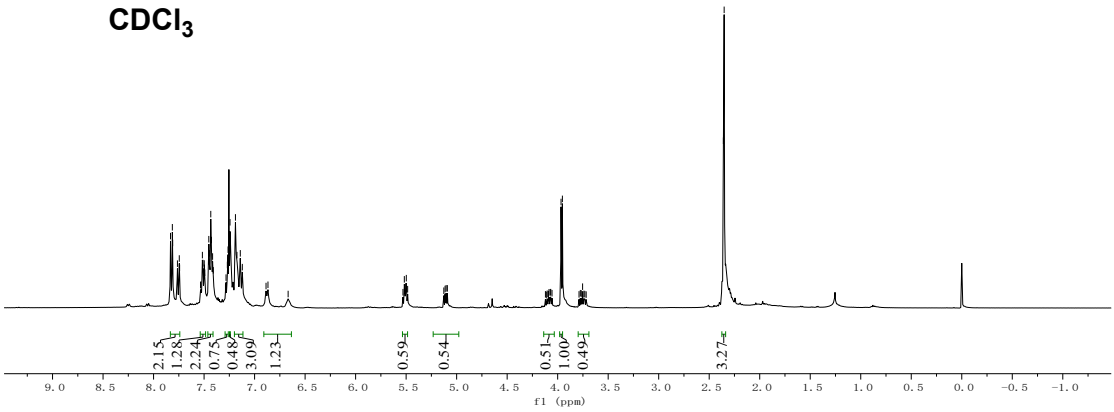
$CDCl_3$

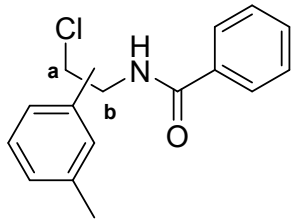




3an, ^{1}H NMR

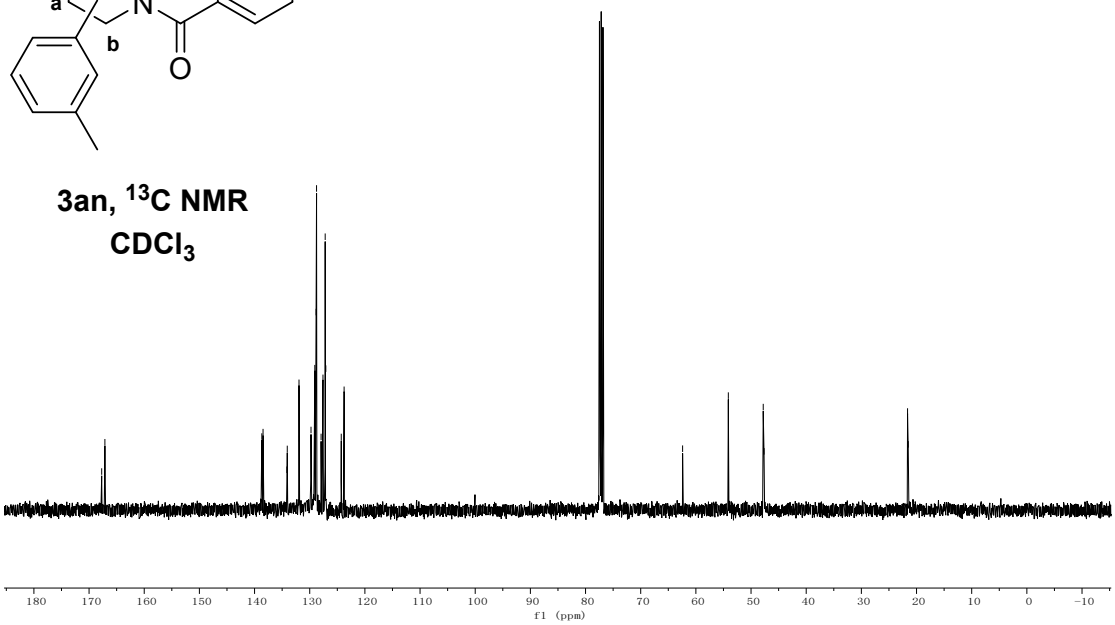
$CDCl_3$

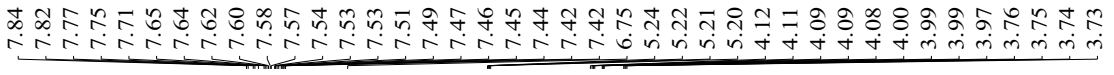


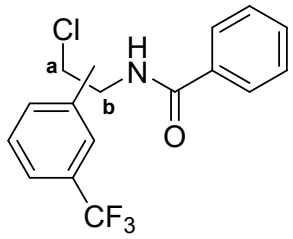


3an, ^{13}C NMR

$CDCl_3$

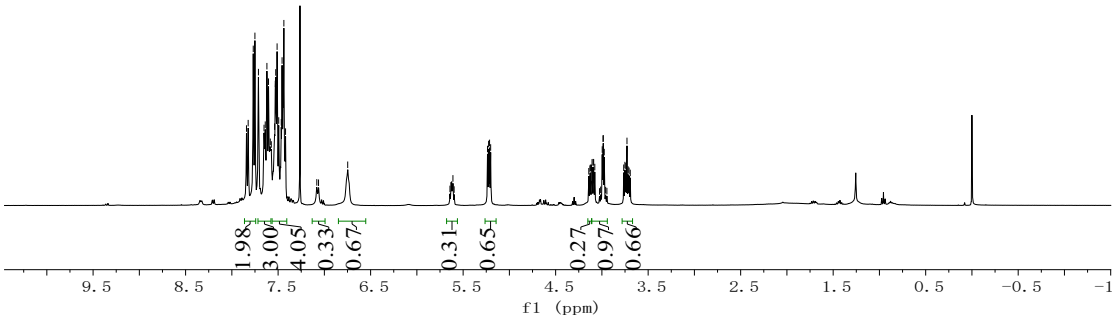


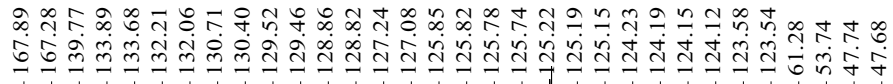


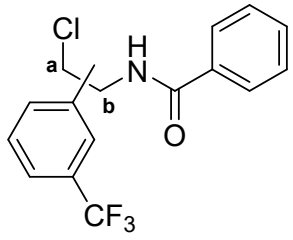


3ao, ^{1}H NMR

$CDCl_3$

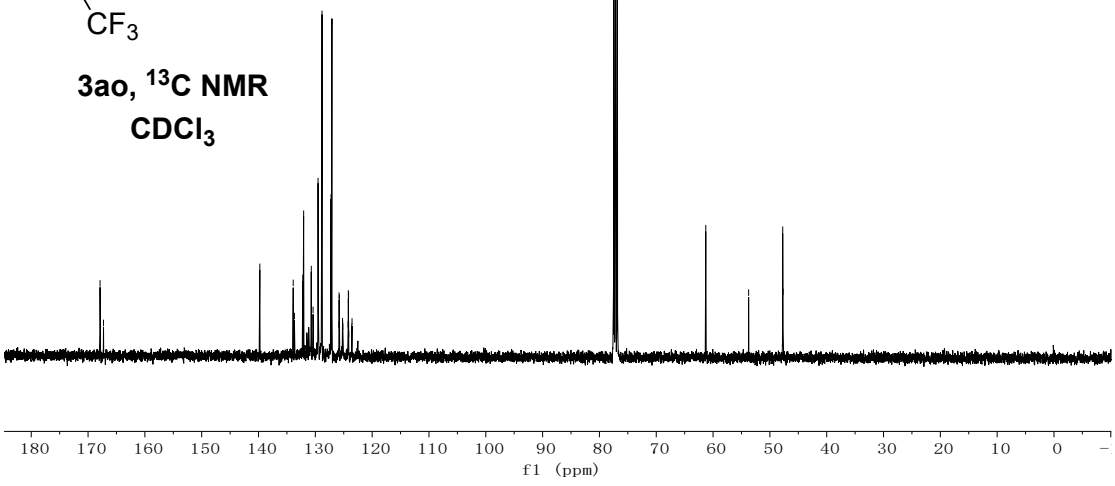




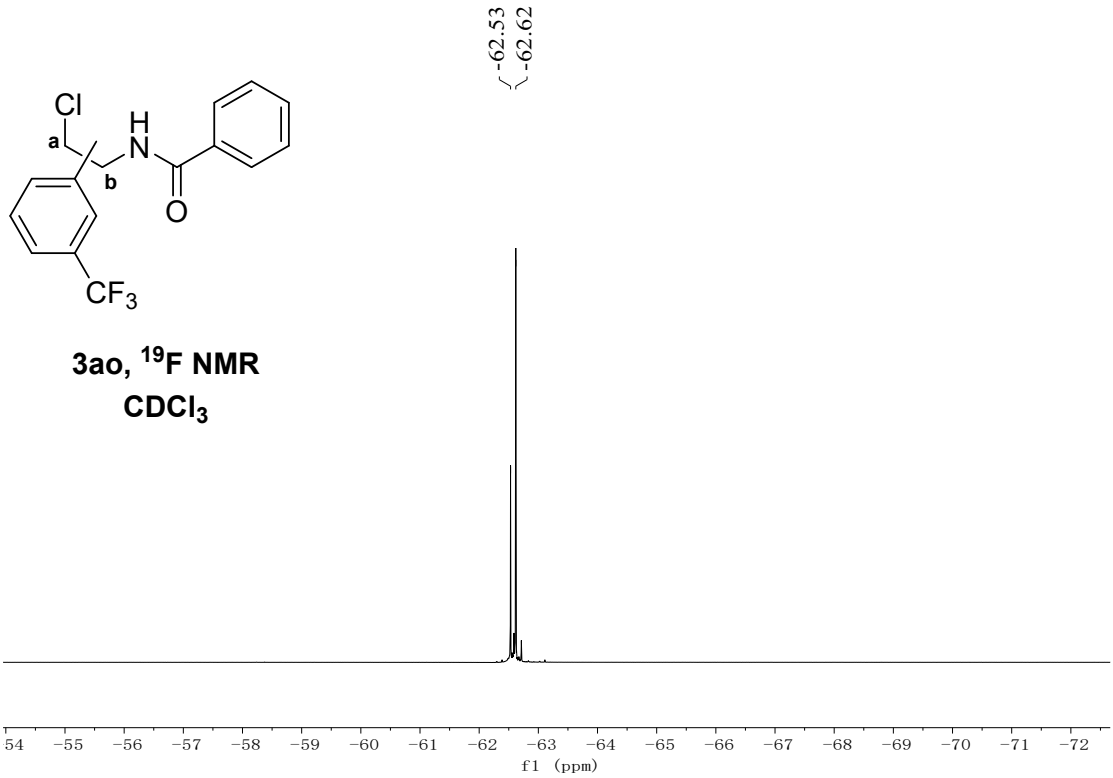


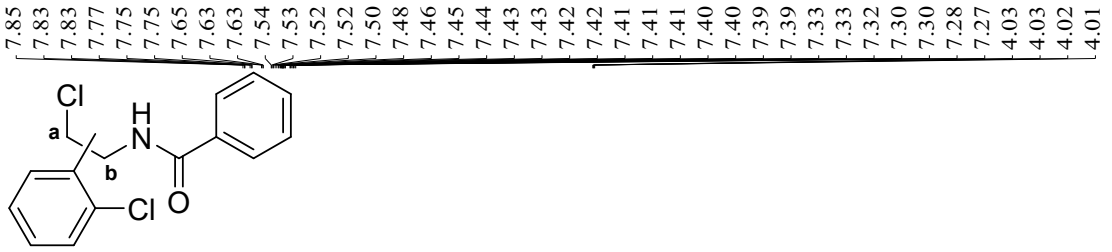
3ao, ^{13}C NMR

$CDCl_3$

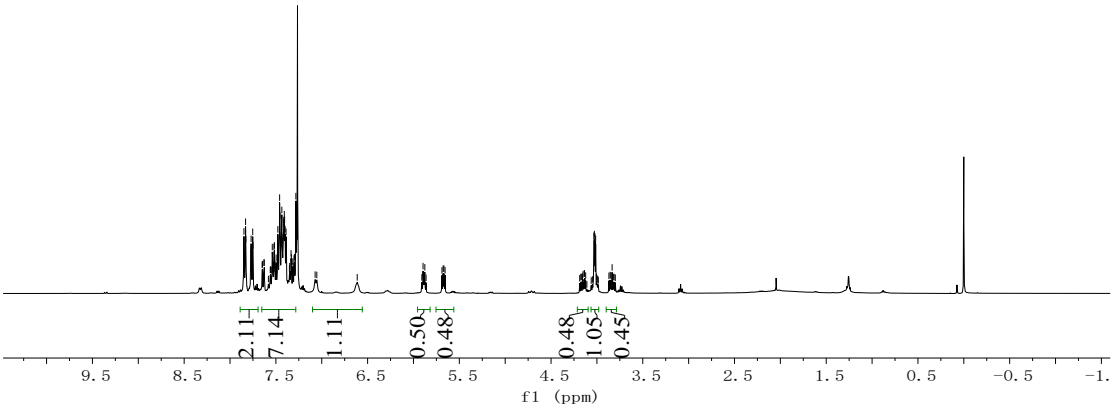


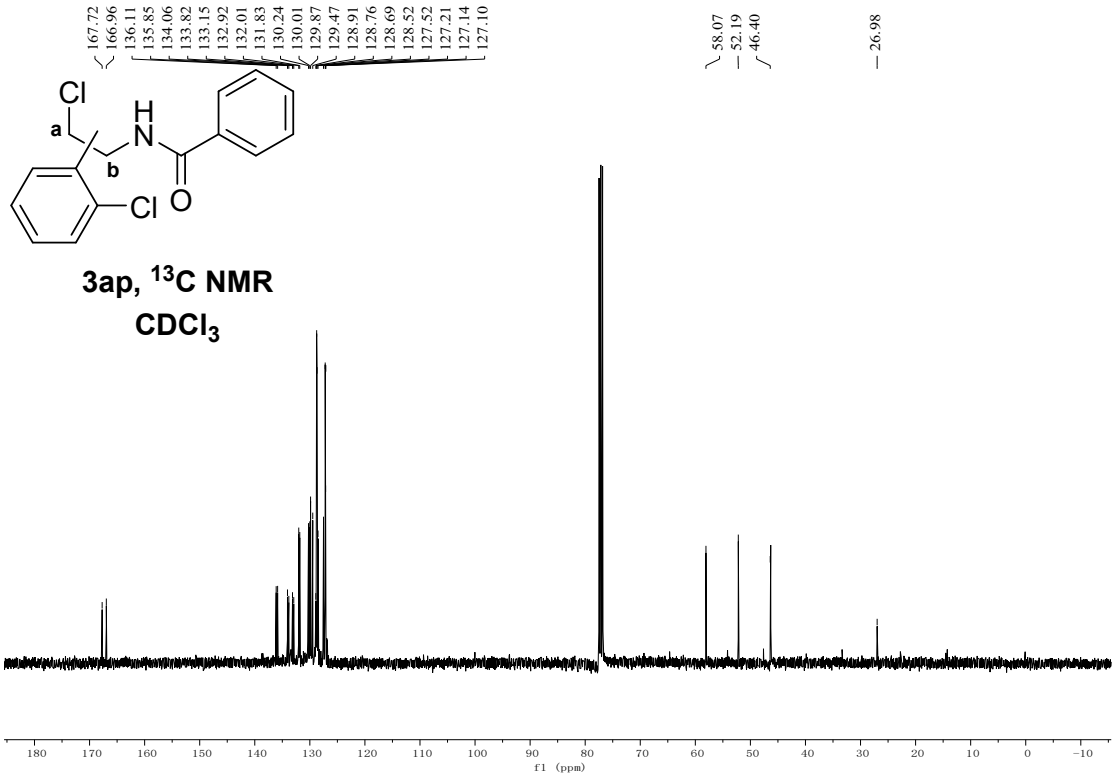
3ao, ^{19}F NMR
$CDCl_3$





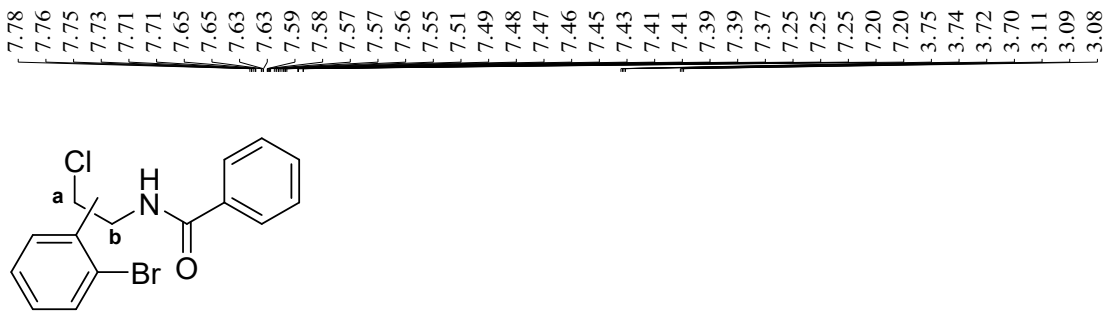
3ap, ^{1}H NMR
$CDCl_3$





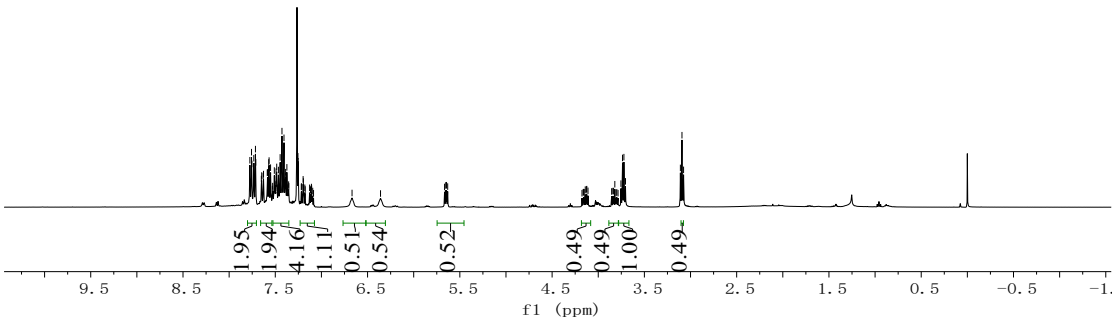
3ap, ^{13}C NMR

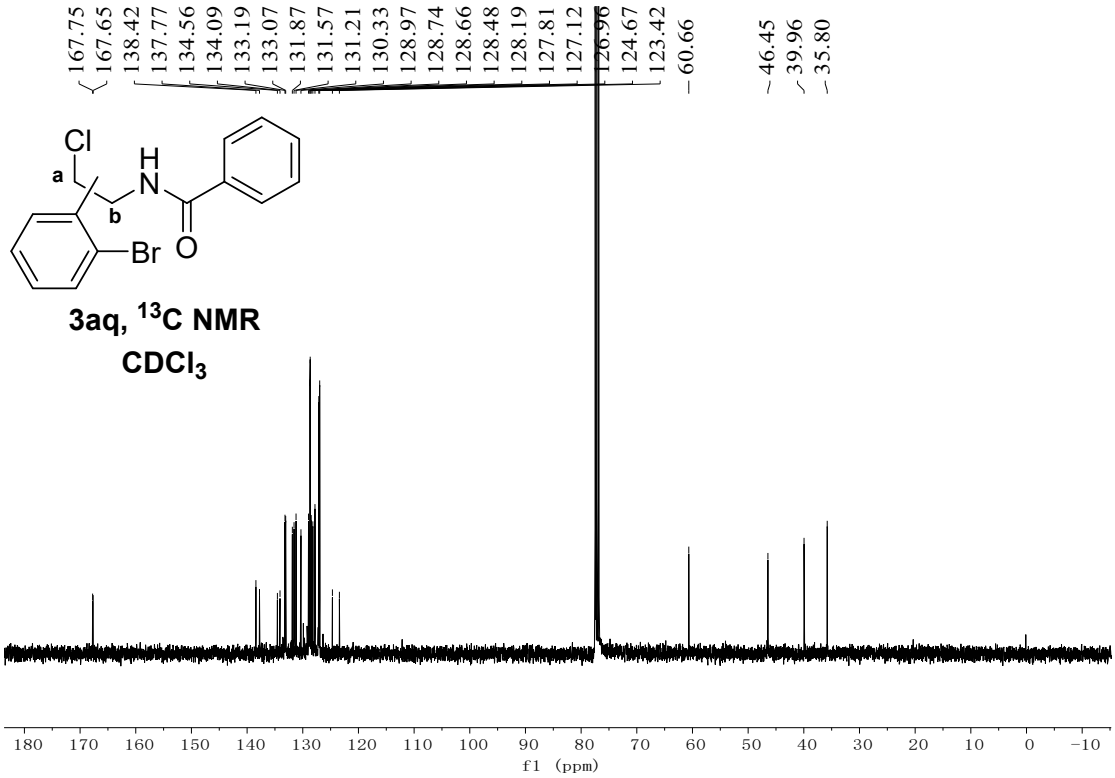
$CDCl_3$



3aq, ^{1}H NMR

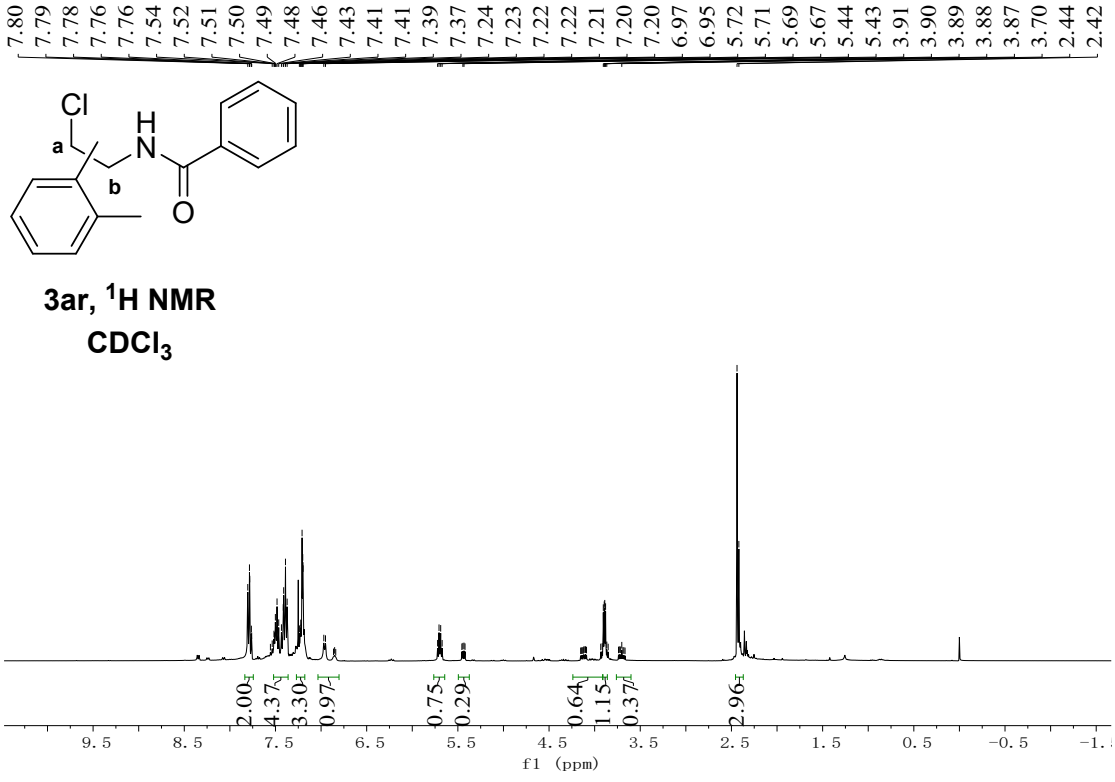
$CDCl_3$





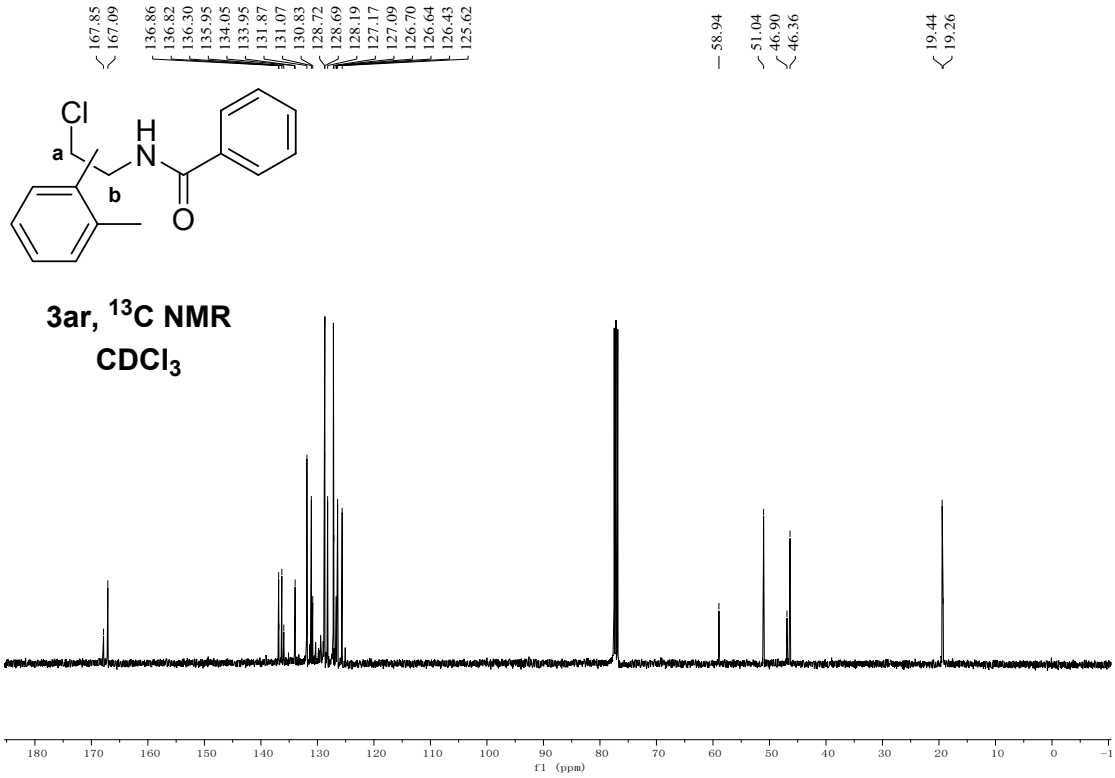
3aq, ^{13}C NMR

$CDCl_3$

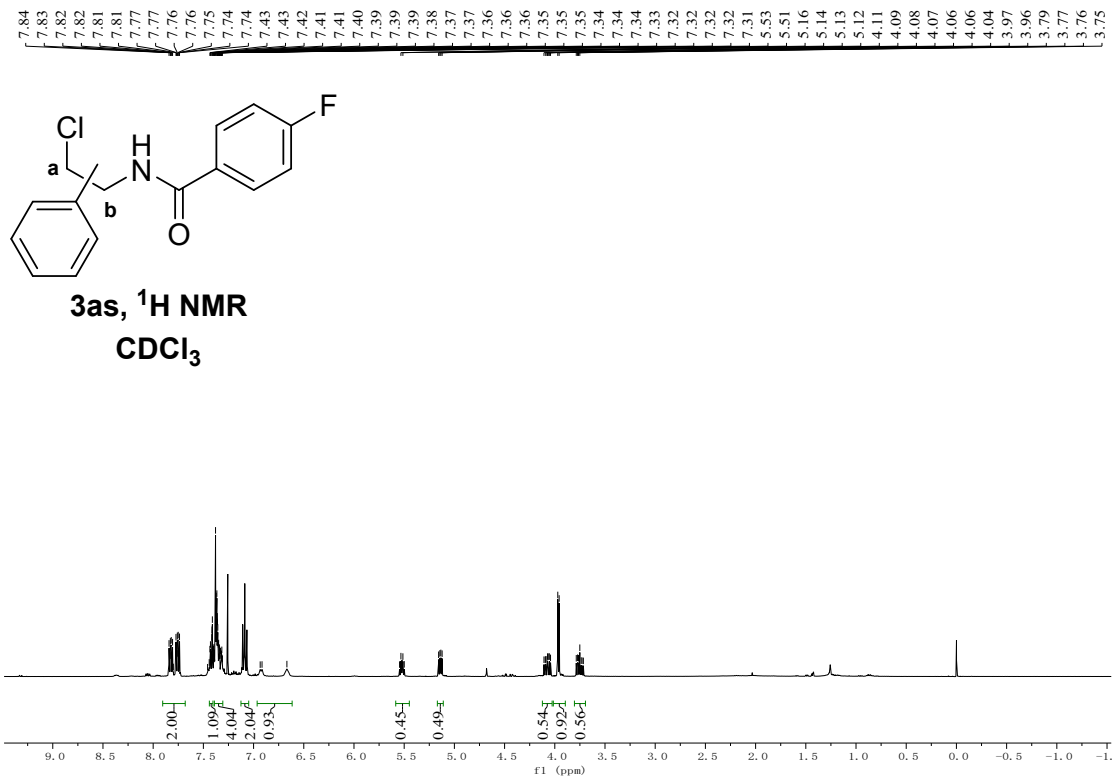


3ar, ^{1}H NMR

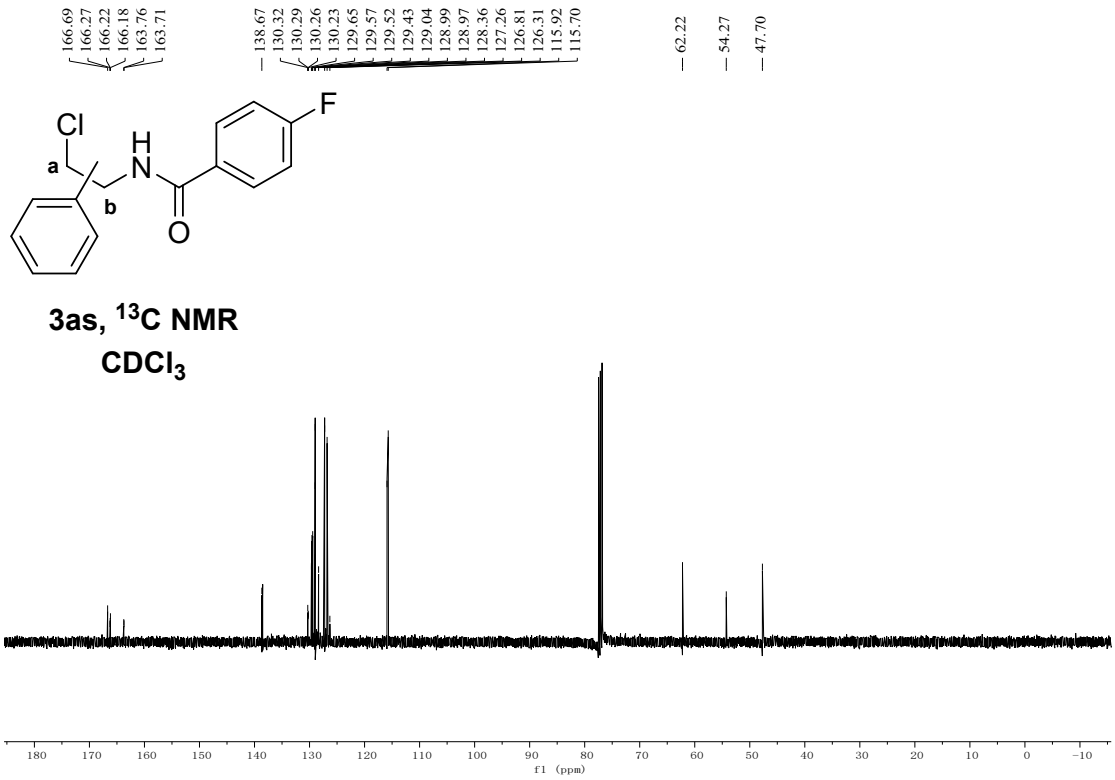
$CDCl_3$



3ar, ^{13}C NMR
$CDCl_3$

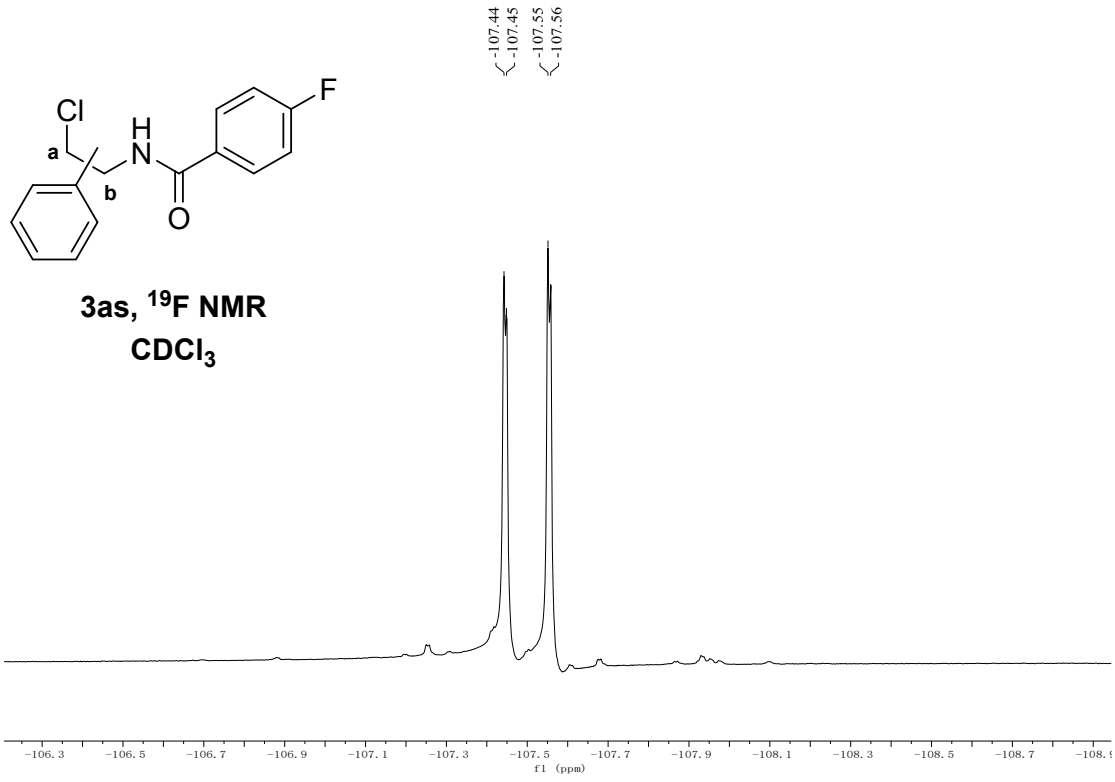


3as, ^{1}H NMR
$CDCl_3$



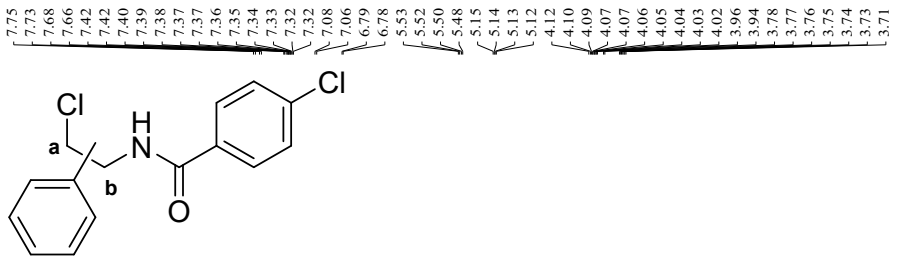
3as, ^{13}C NMR

$CDCl_3$



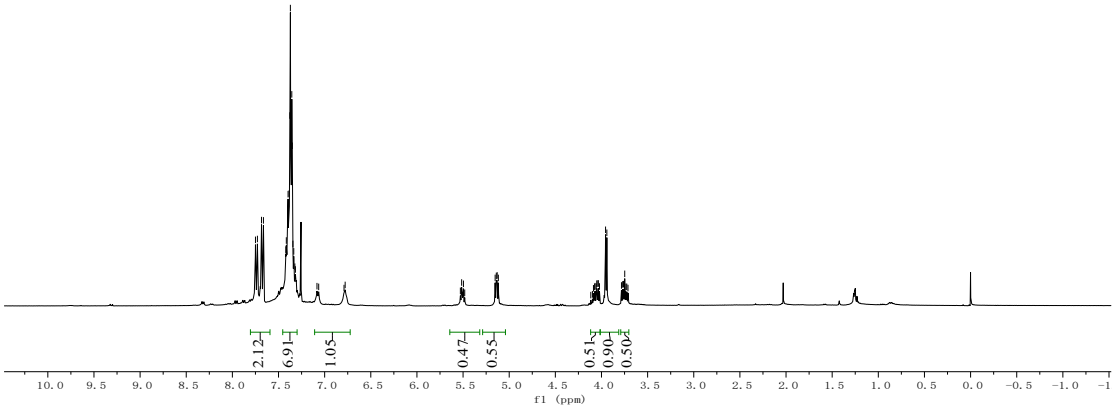
3as, ^{19}F NMR

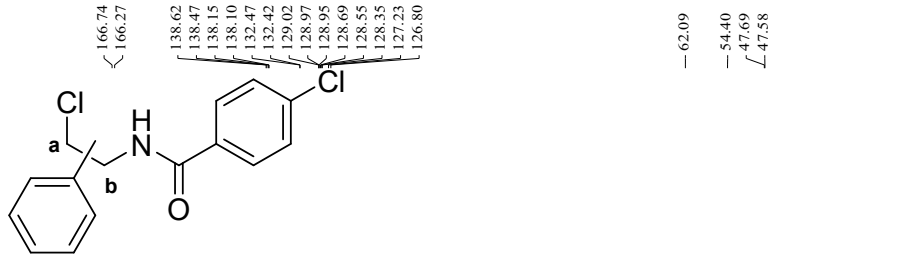
$CDCl_3$



3at, ^{1}H NMR

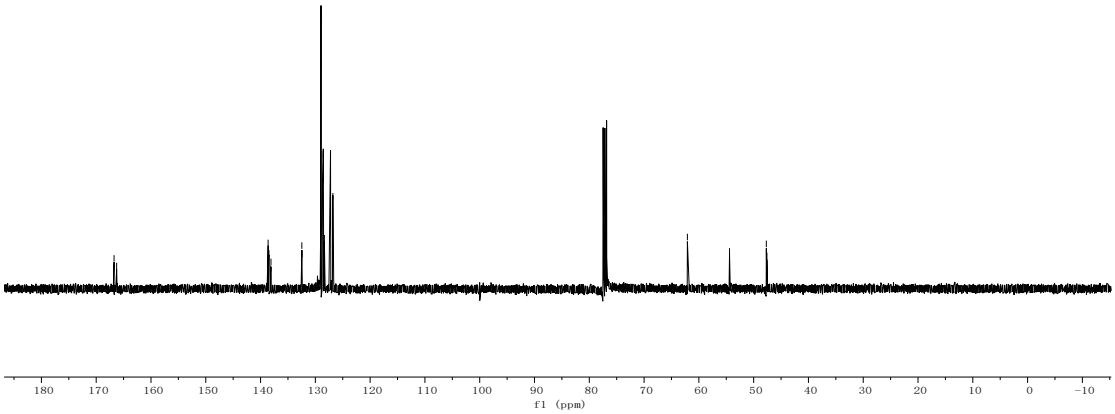
$CDCl_3$

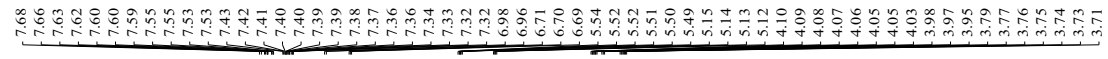


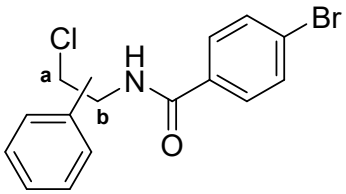


3at, ^{13}H NMR

$CDCl_3$

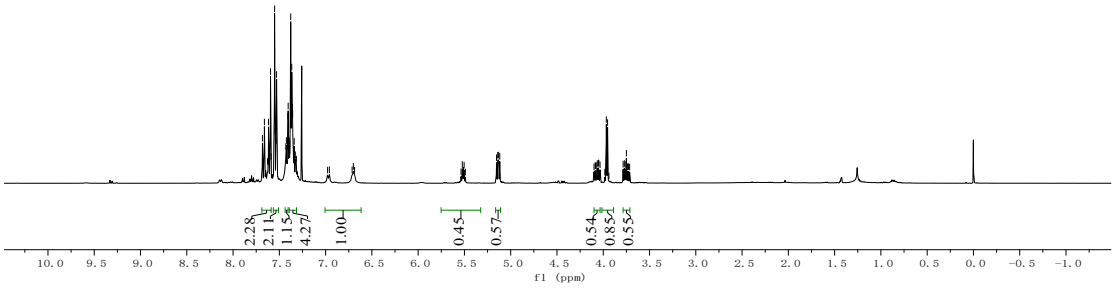


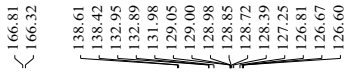


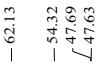


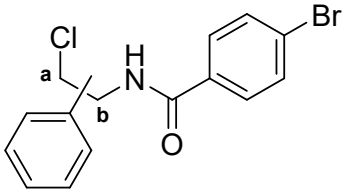
3au, ^{1}H NMR

$CDCl_3$



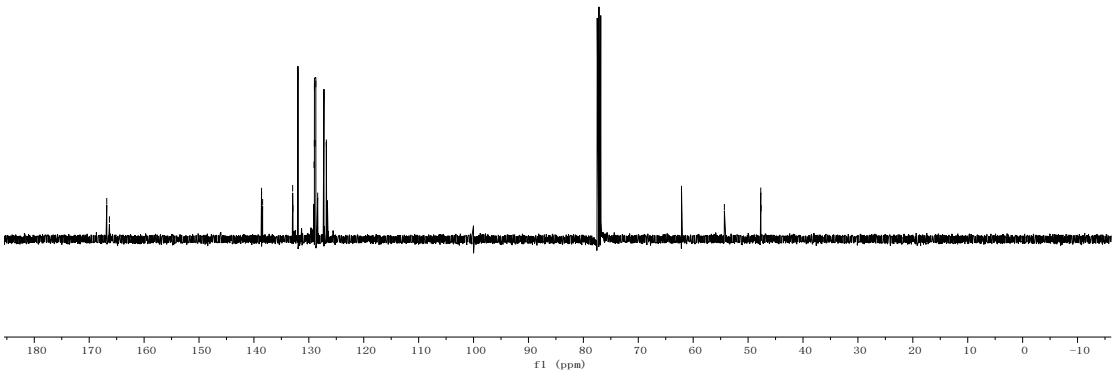


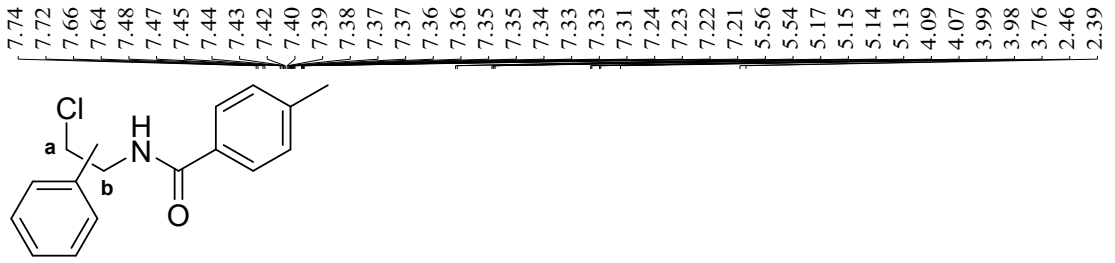




3au, ^{13}C NMR

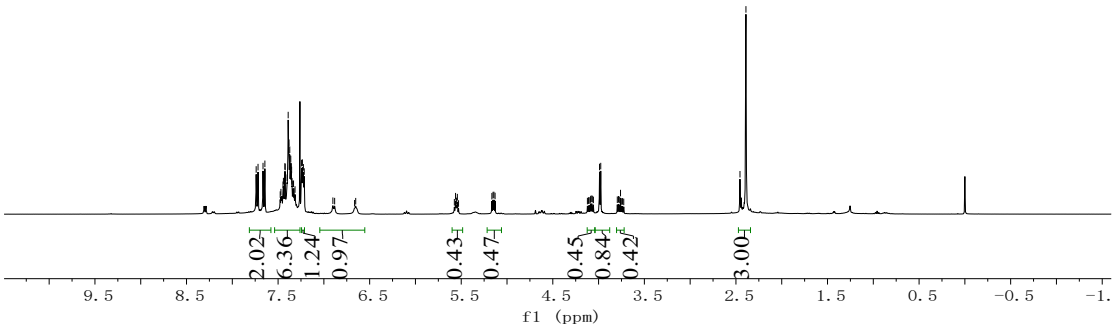
$CDCl_3$

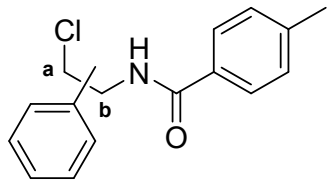




3av, ^{1}H NMR

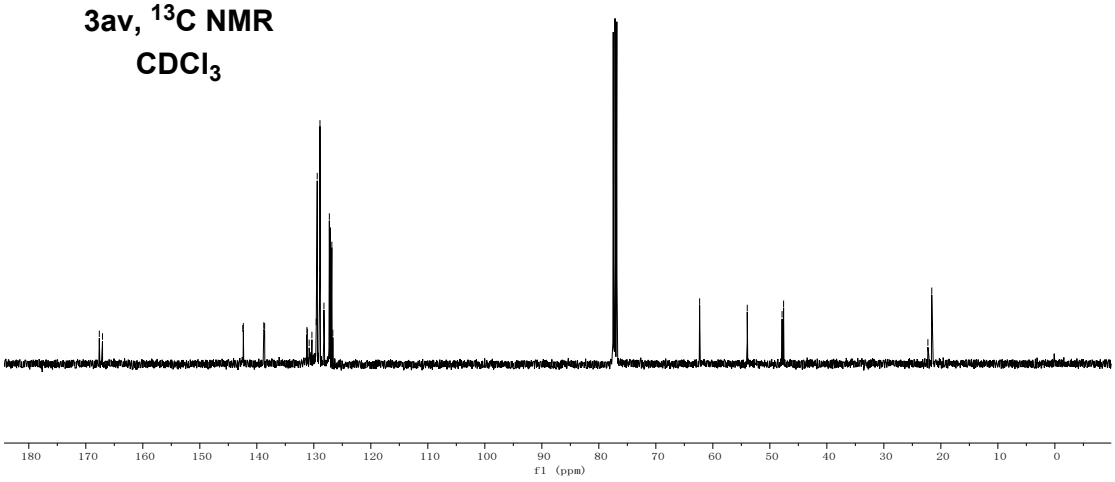
$CDCl_3$

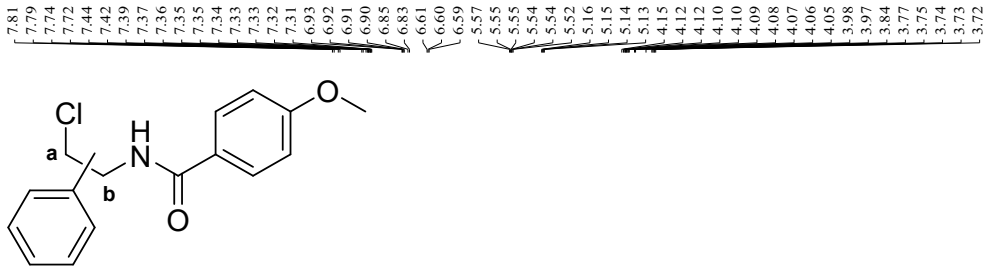




3av, ^{13}C NMR

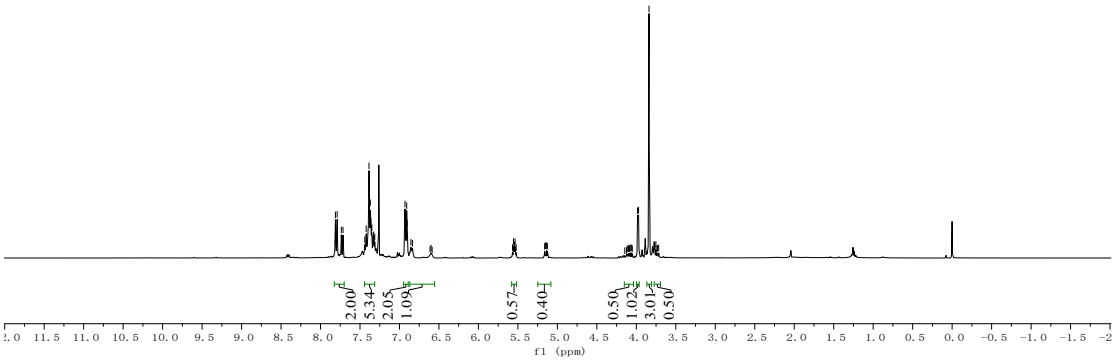
$CDCl_3$

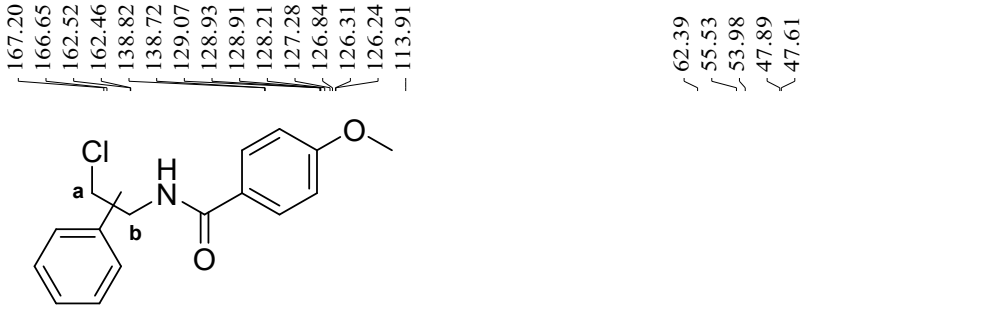




3aw, ^{1}H NMR

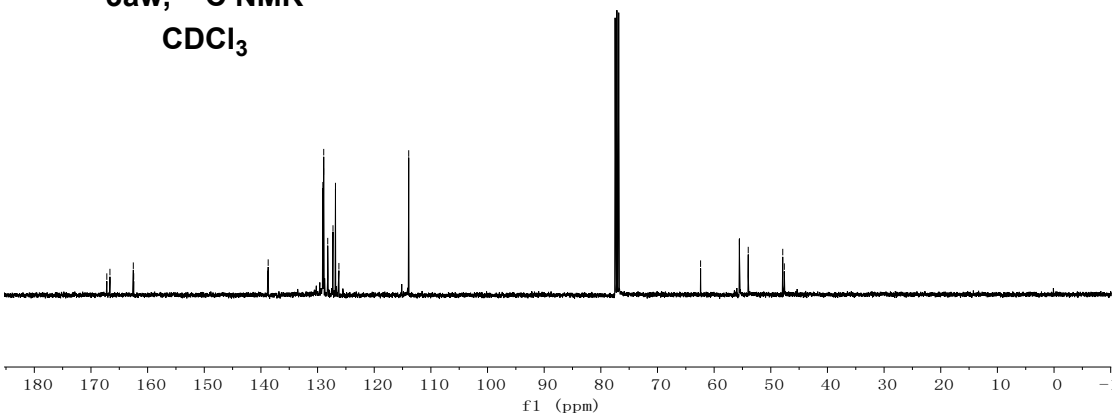
$CDCl_3$

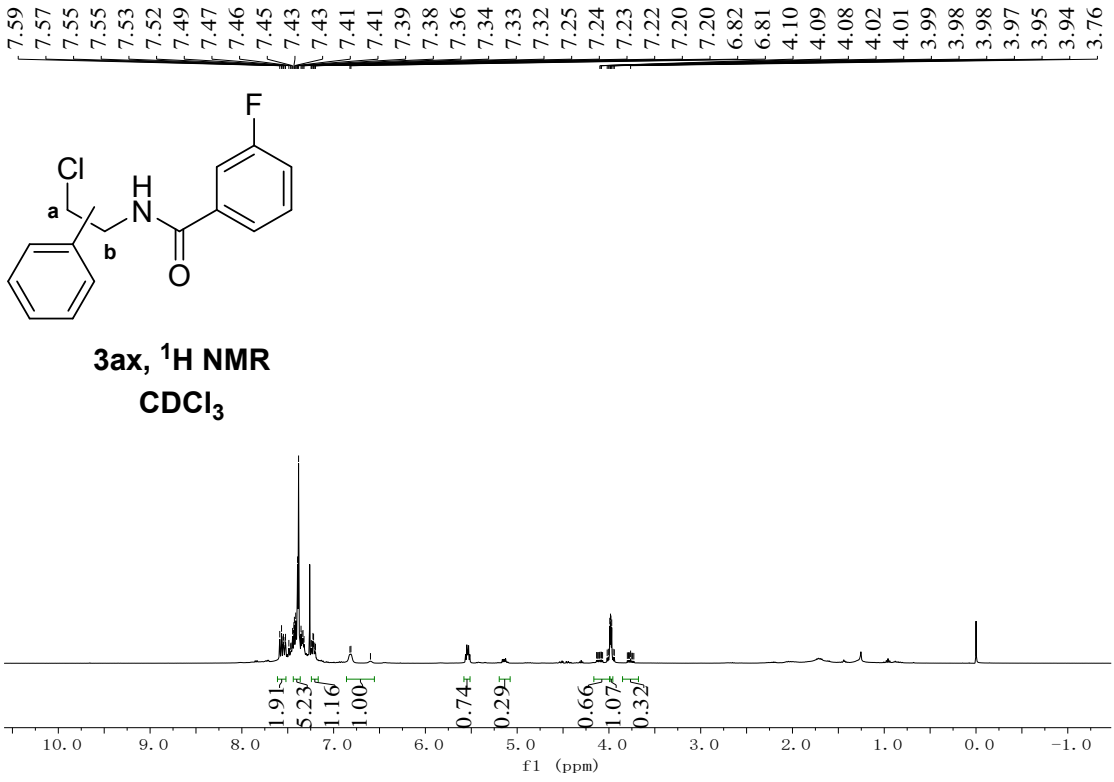




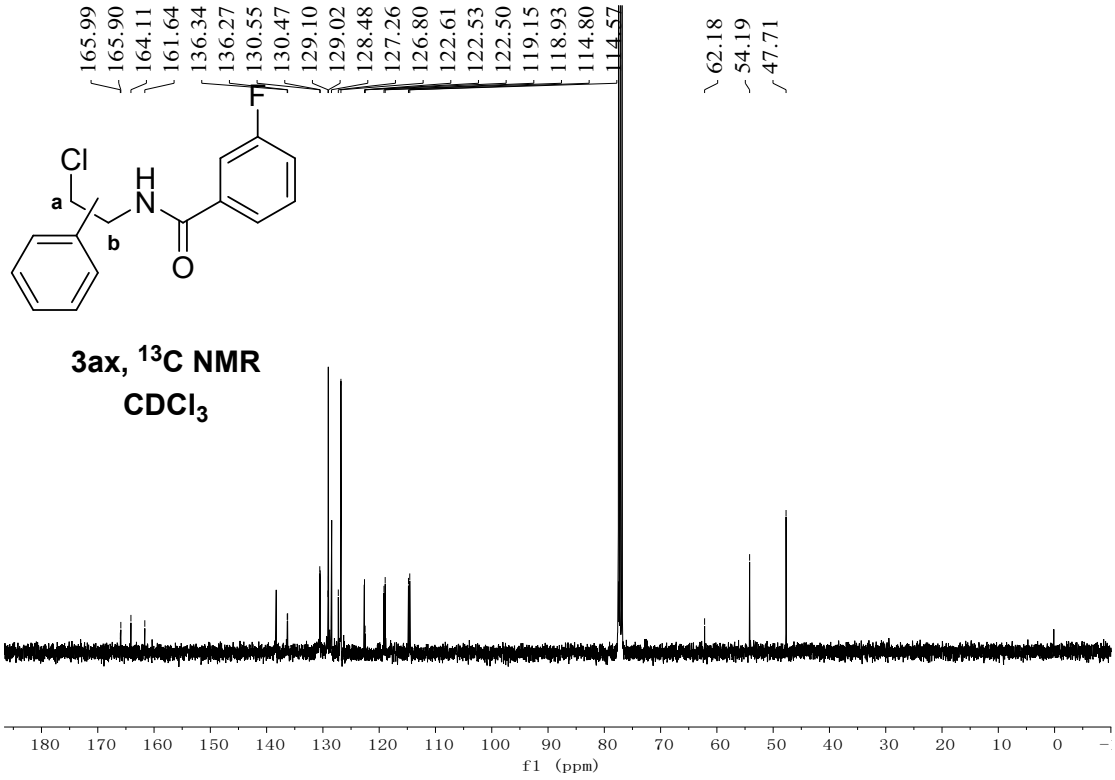
3aw, ^{13}C NMR

$CDCl_3$

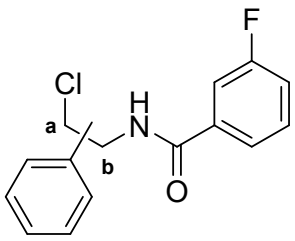




3ax, ^{1}H NMR
$CDCl_3$

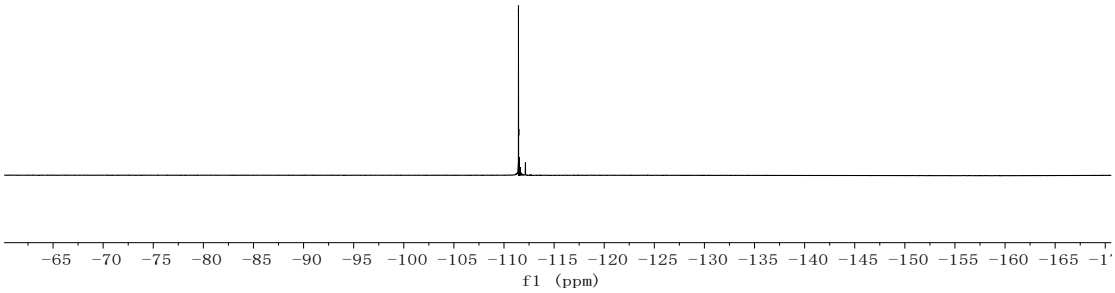


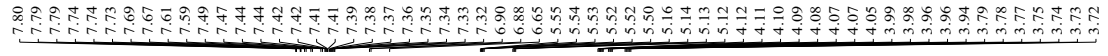
3ax, ^{13}C NMR
$CDCl_3$

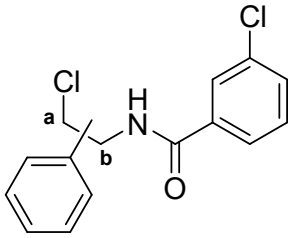


-111.44
-111.50

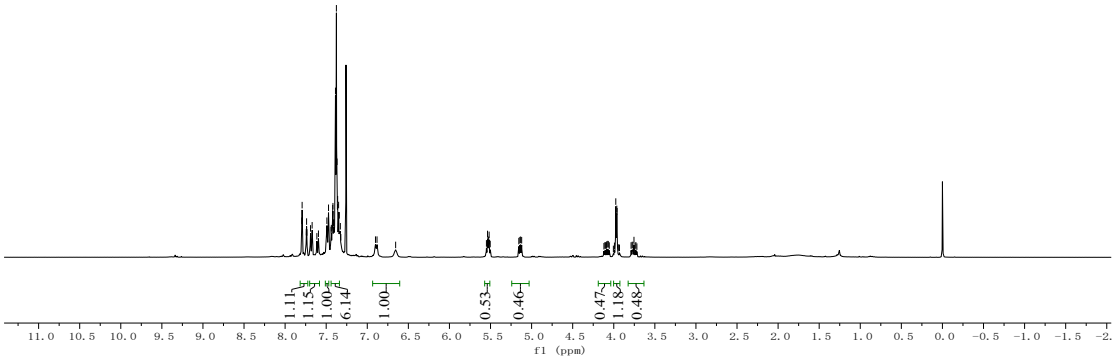
3ax, ^{19}F NMR
$CDCl_3$

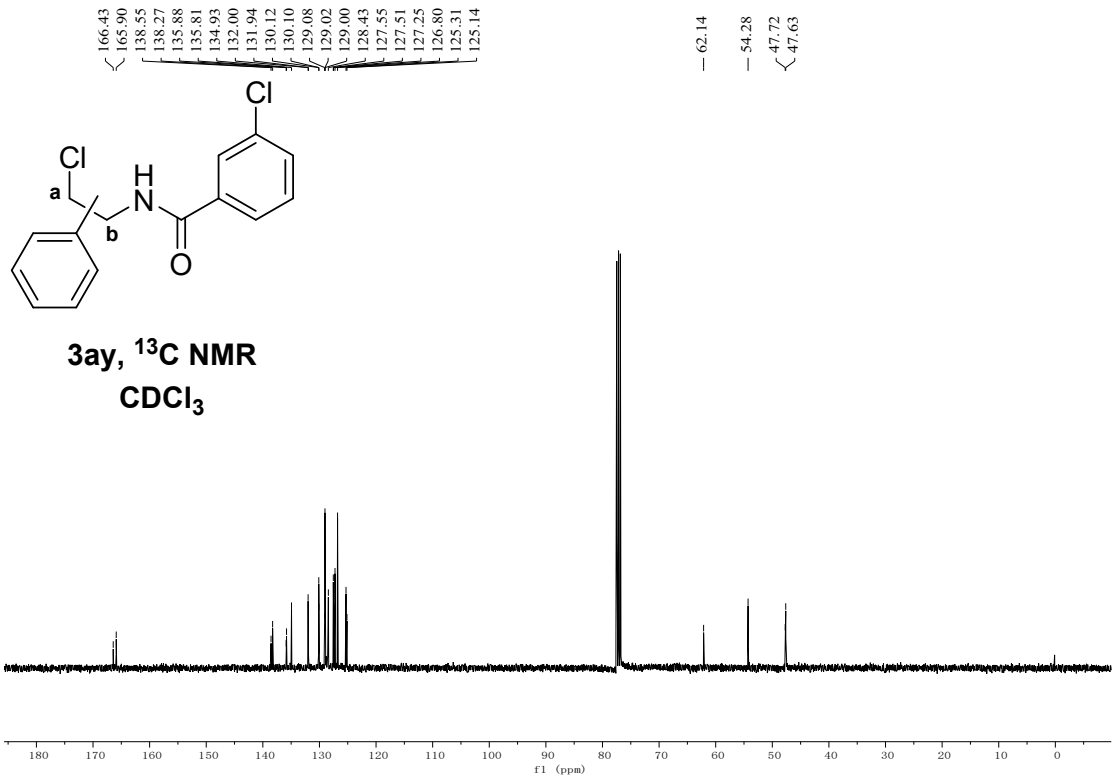




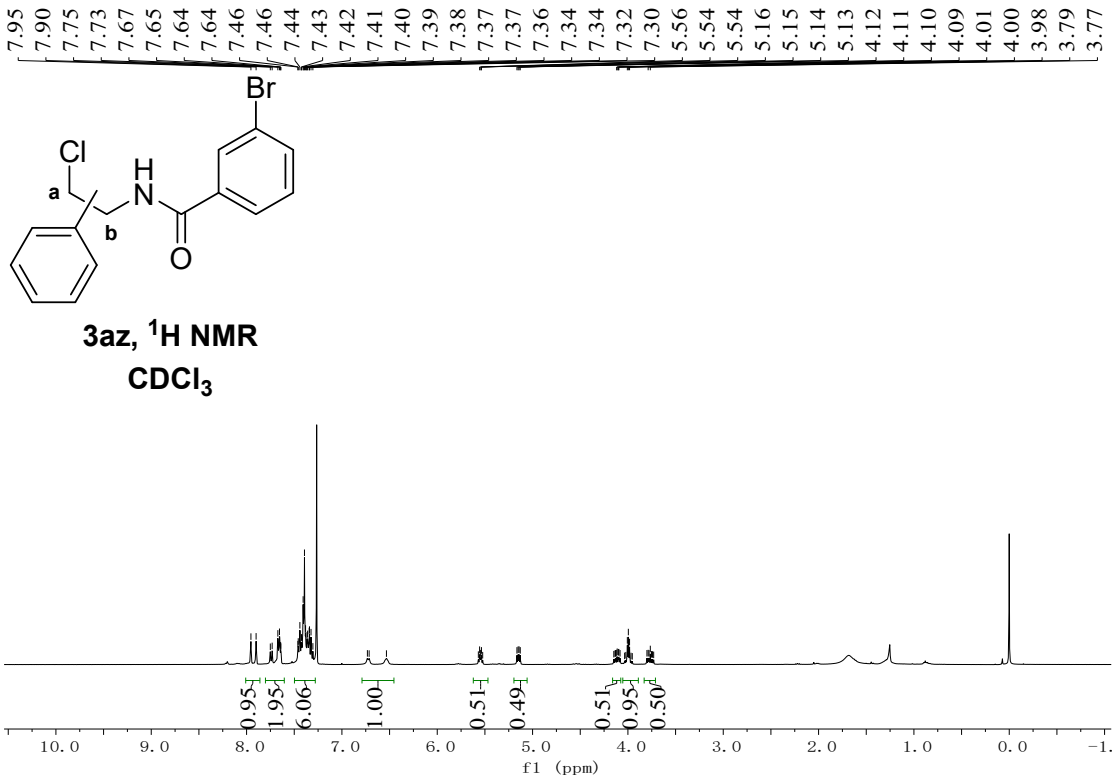


3ay, ^{1}H NMR
$CDCl_3$





3ay, ^{13}C NMR
$CDCl_3$



3az, ^{1}H NMR
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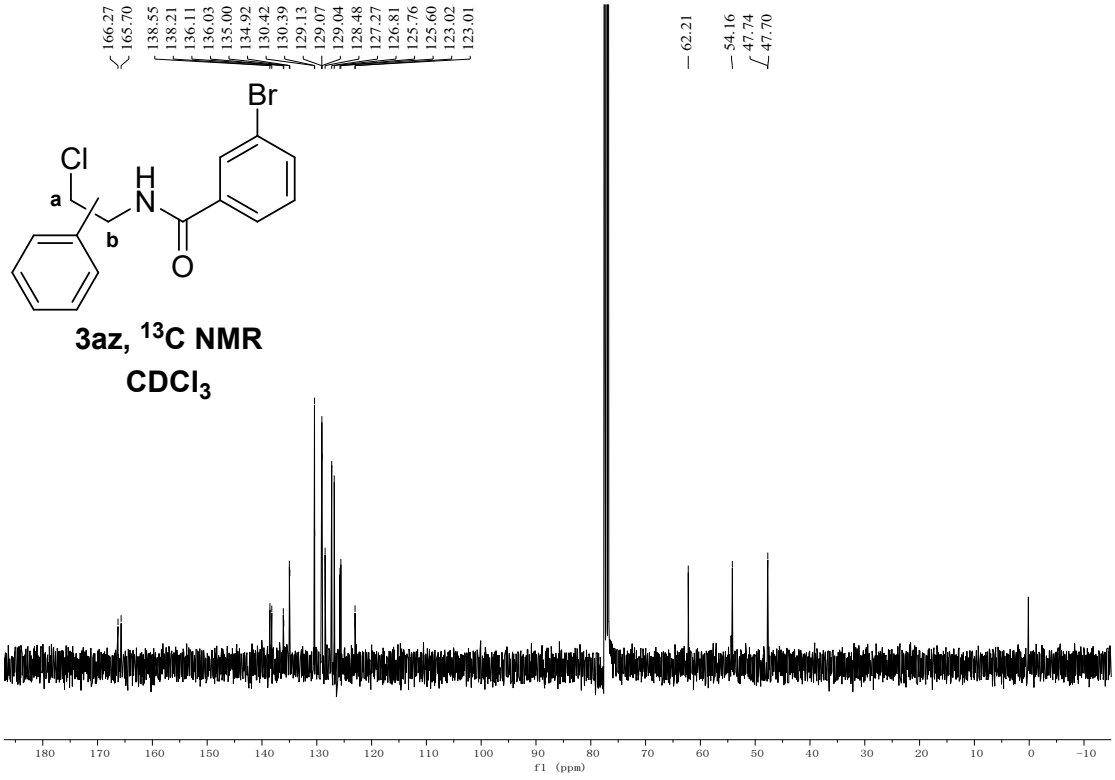

3az, ^{13}C NMR

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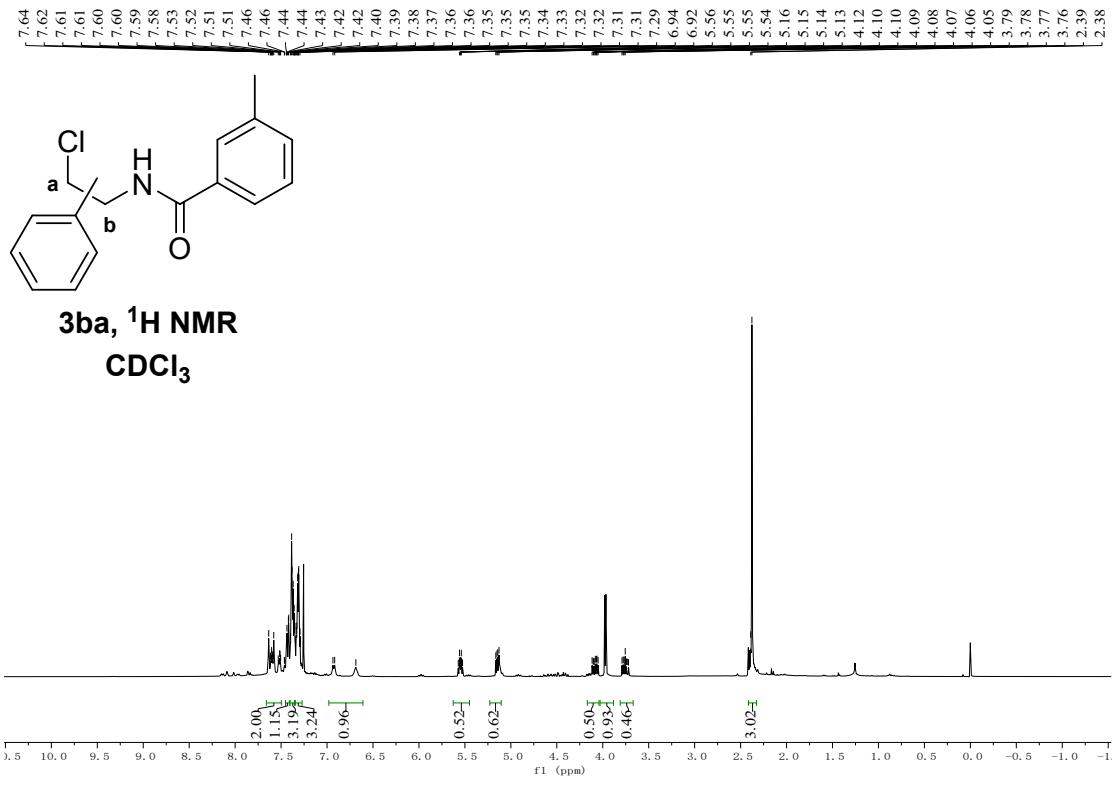

3ba, ^{1}H NMR

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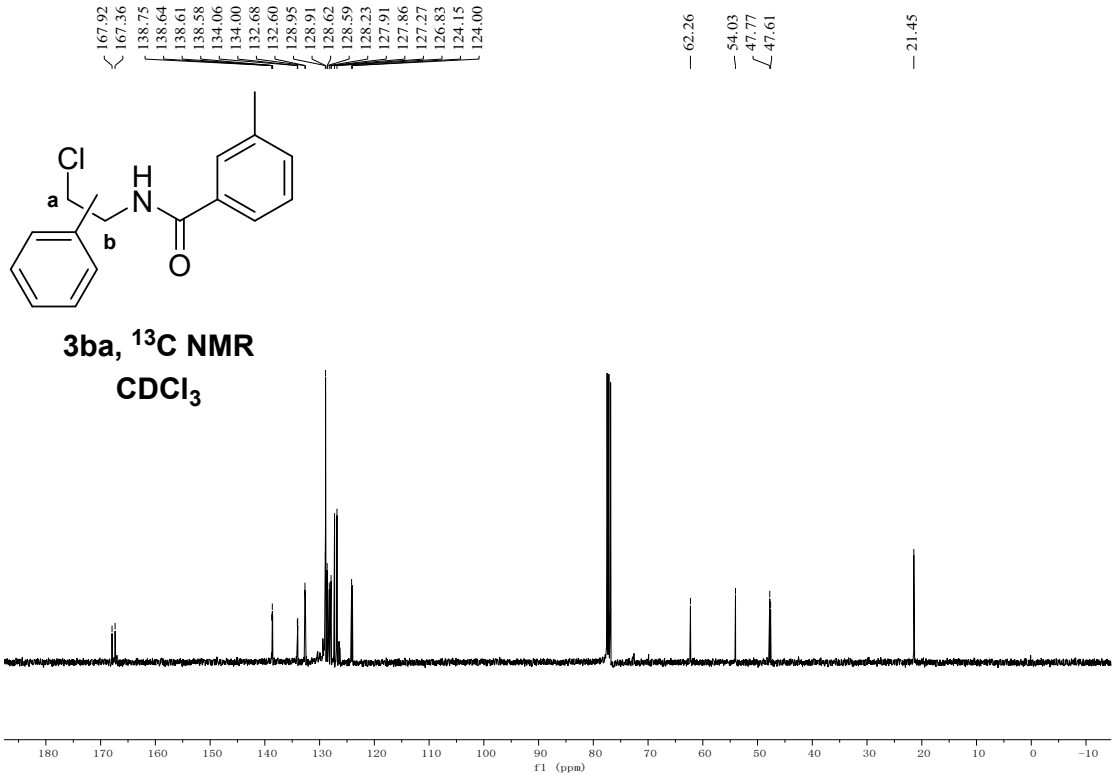

3ba, ^{13}C NMR

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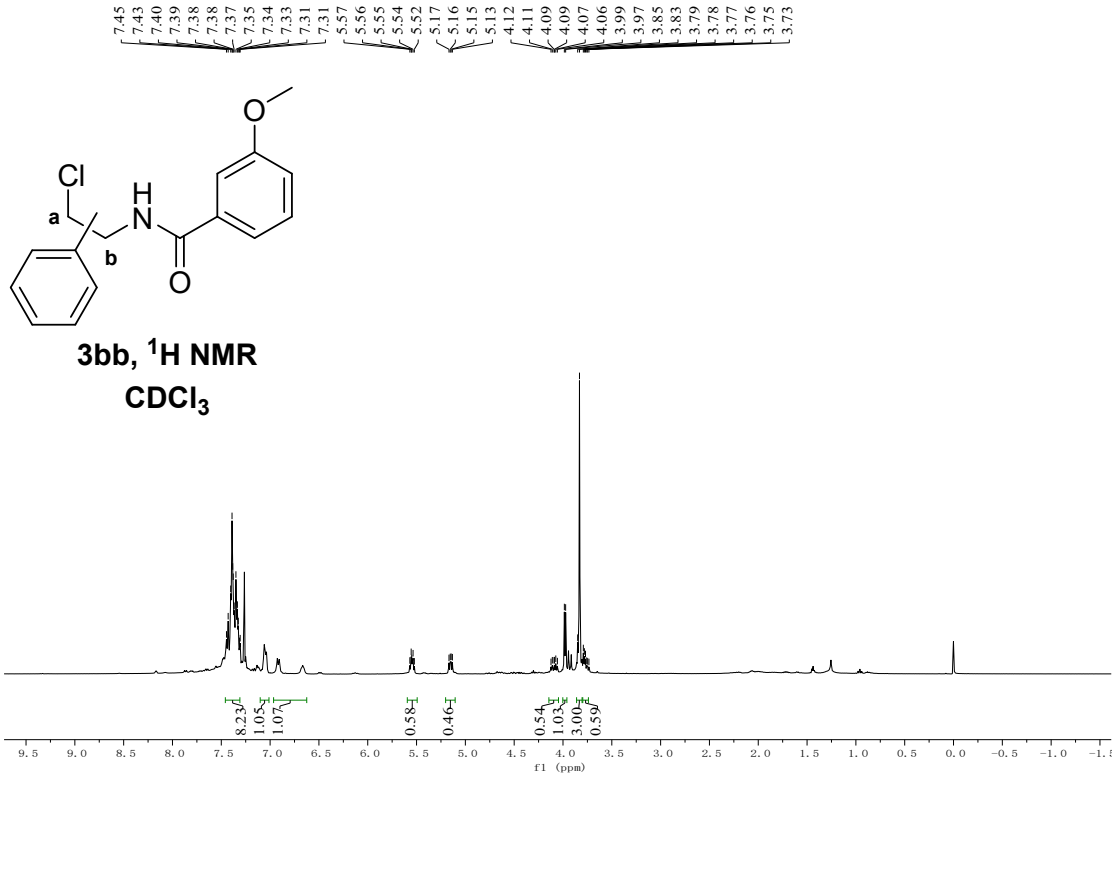

3bb, ^{1}H NMR

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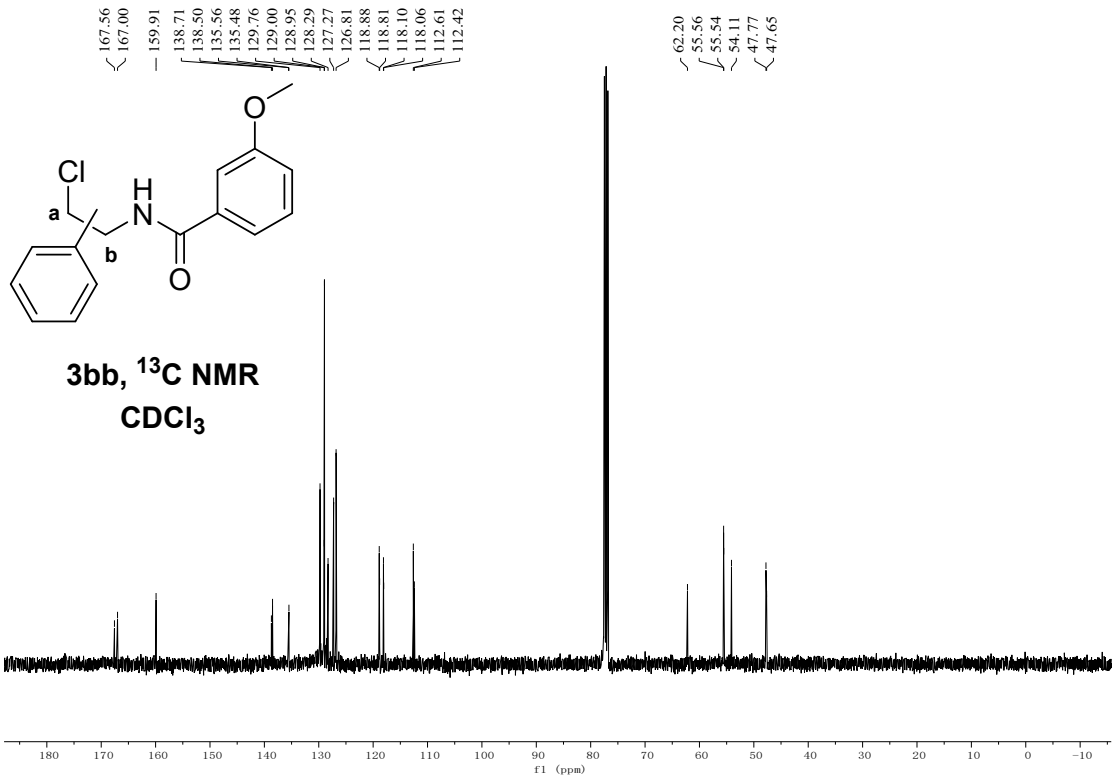
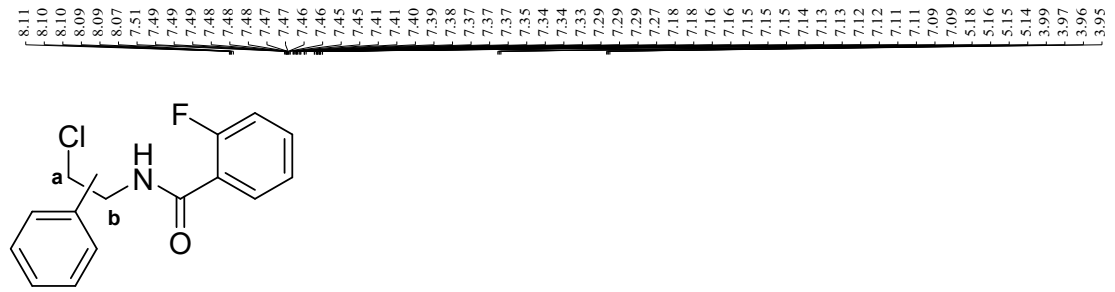


3bb, ^{13}C NMR
$CDCl_3$



3bc, ^{1}H NMR
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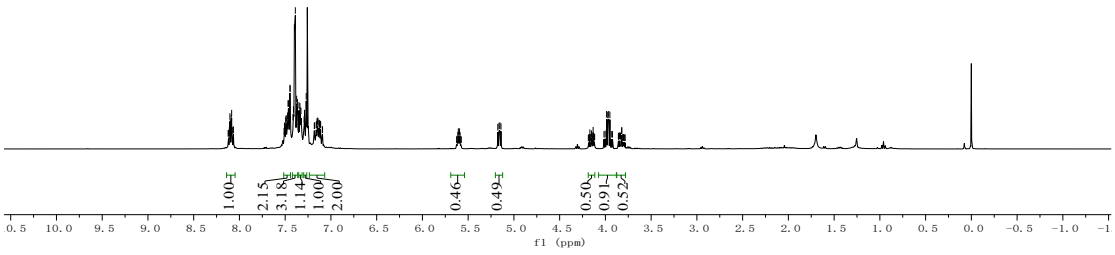

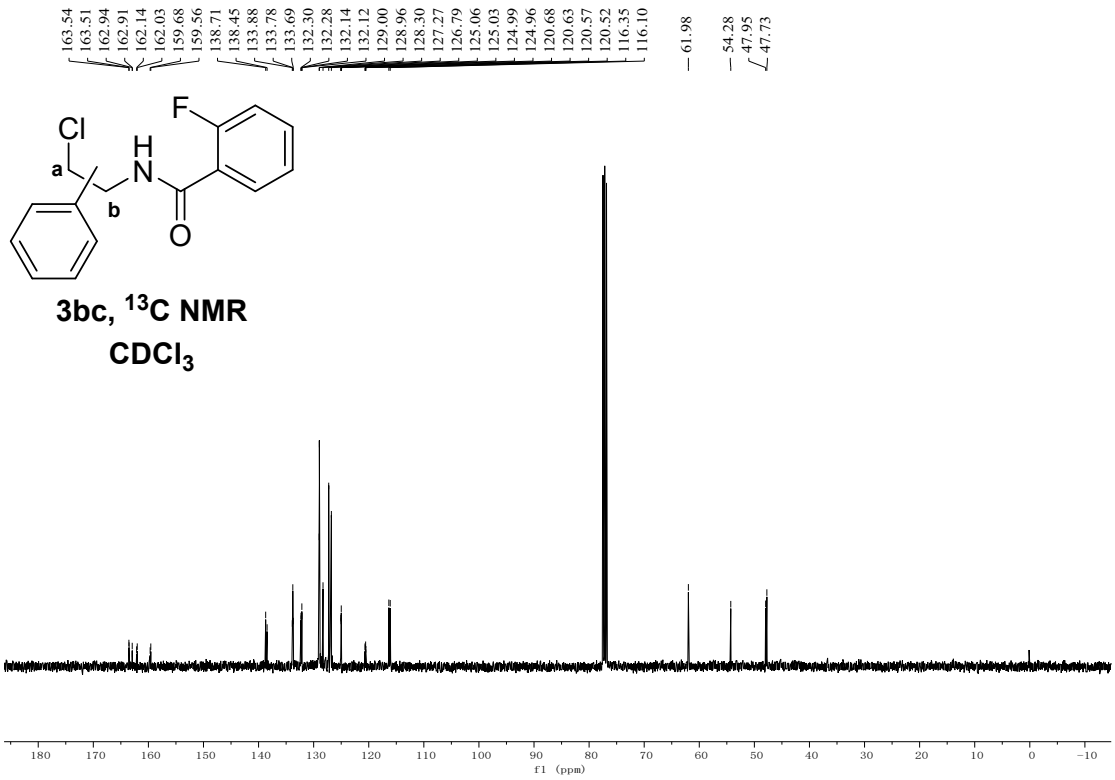

3bc, ^{13}C NMR

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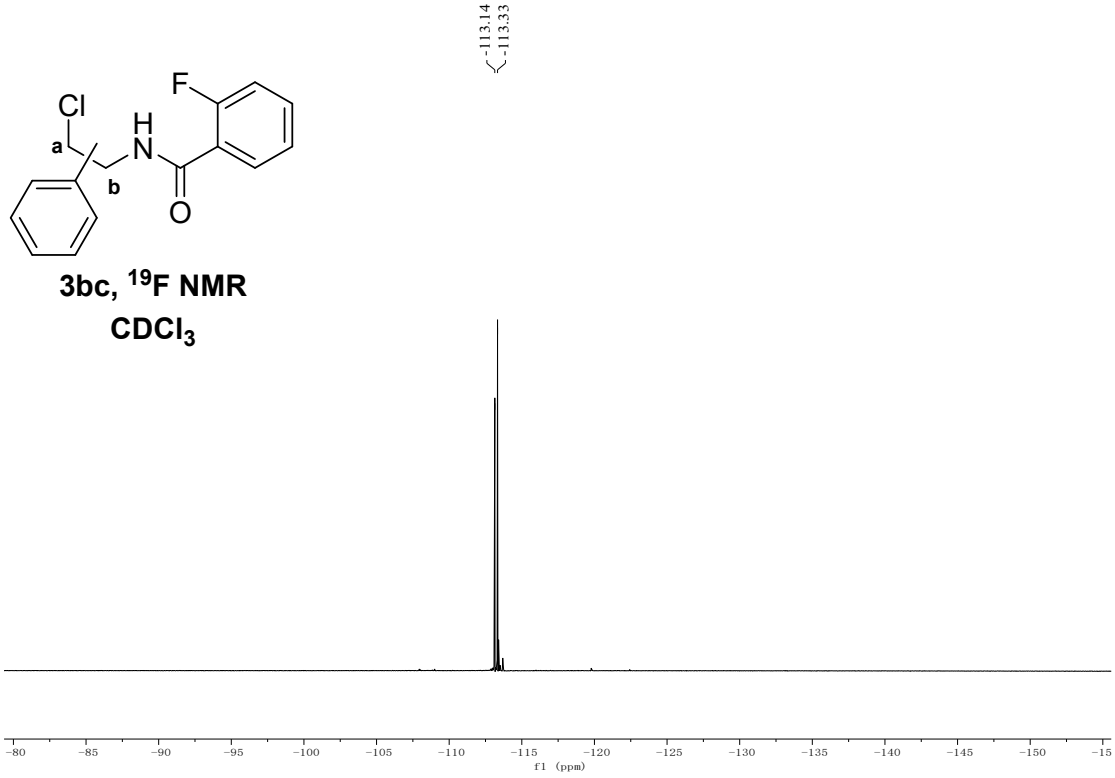

3bc, ^{19}F NMR

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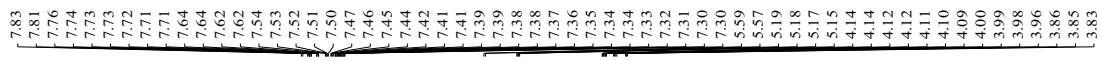

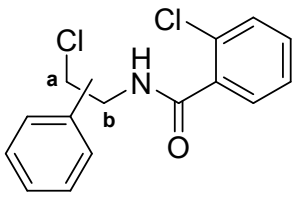

3bd, ^{1}H NMR

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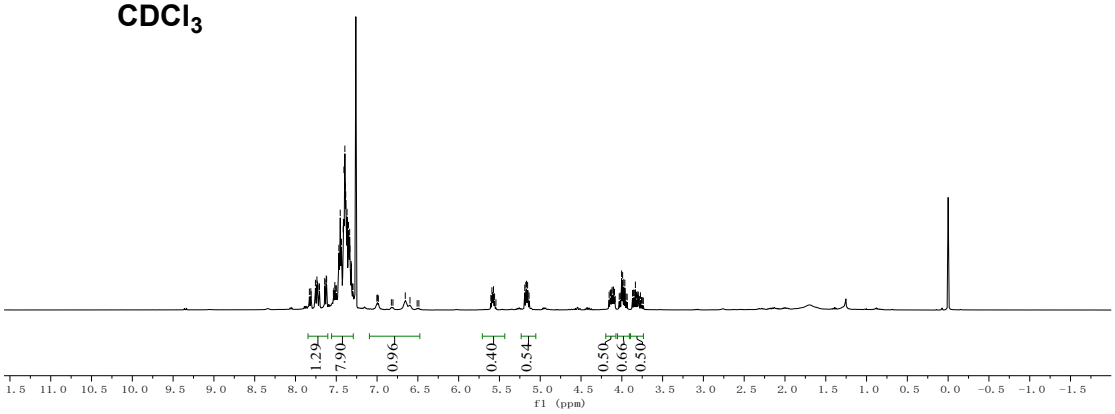

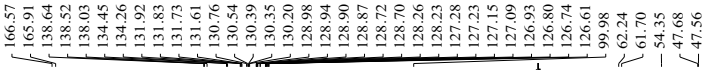

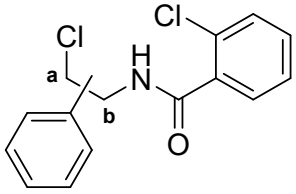

3bd, ^{13}C NMR

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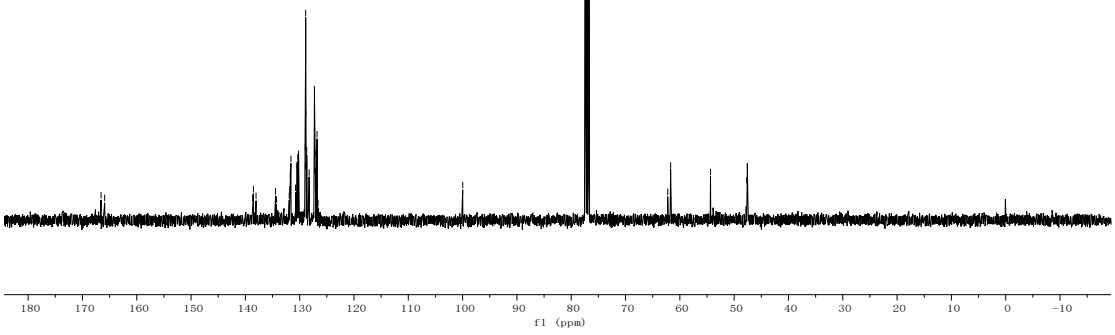
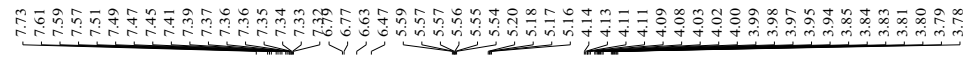
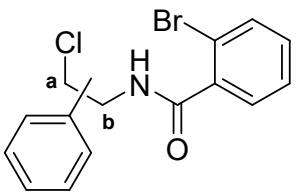
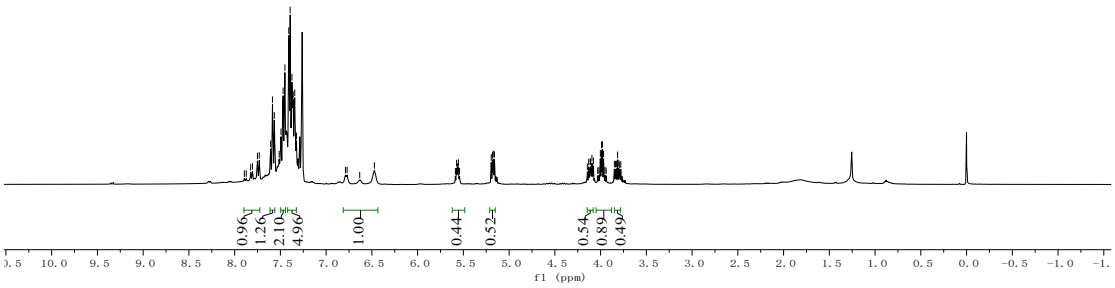


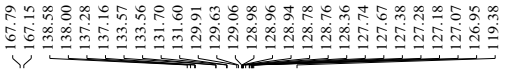


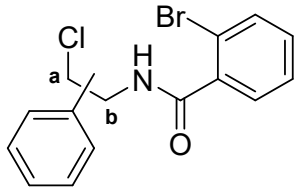


3be, ^{1}H NMR

$CDCl_3$

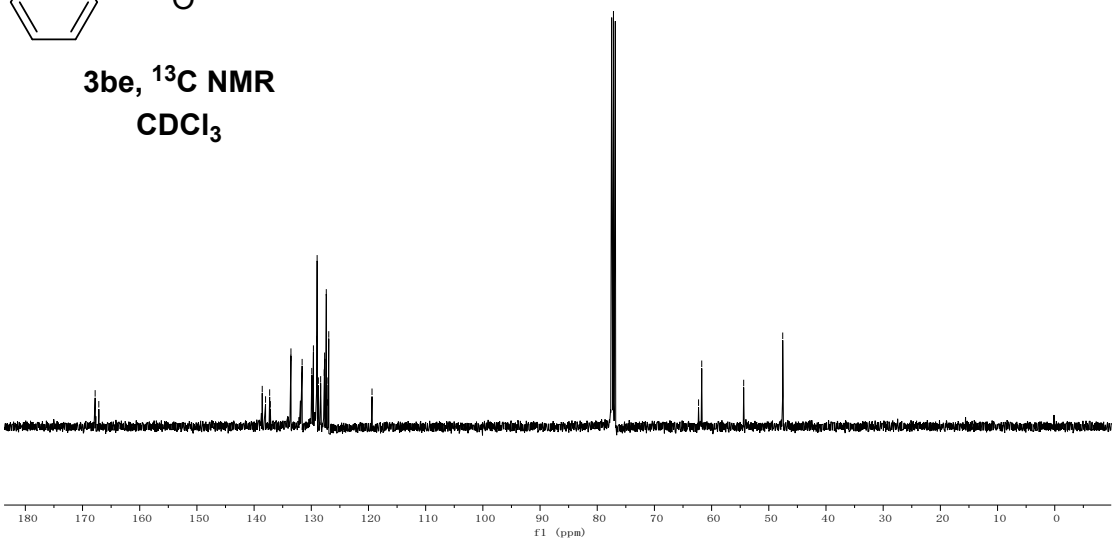


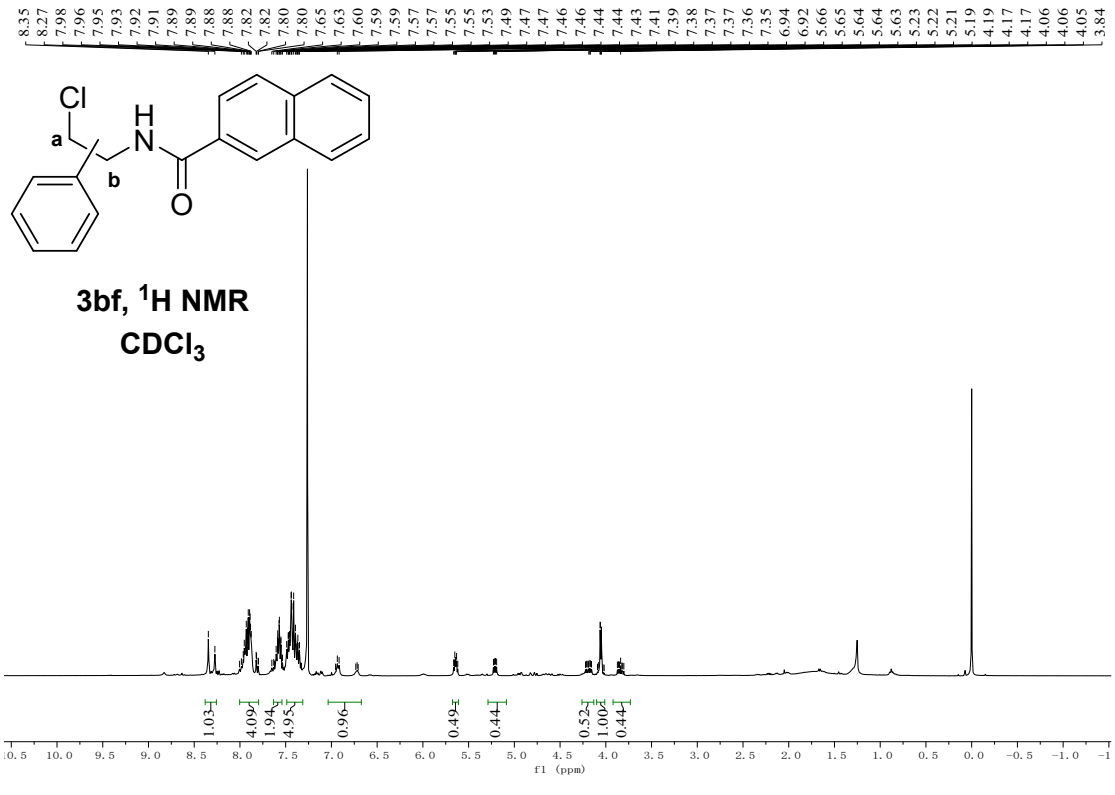




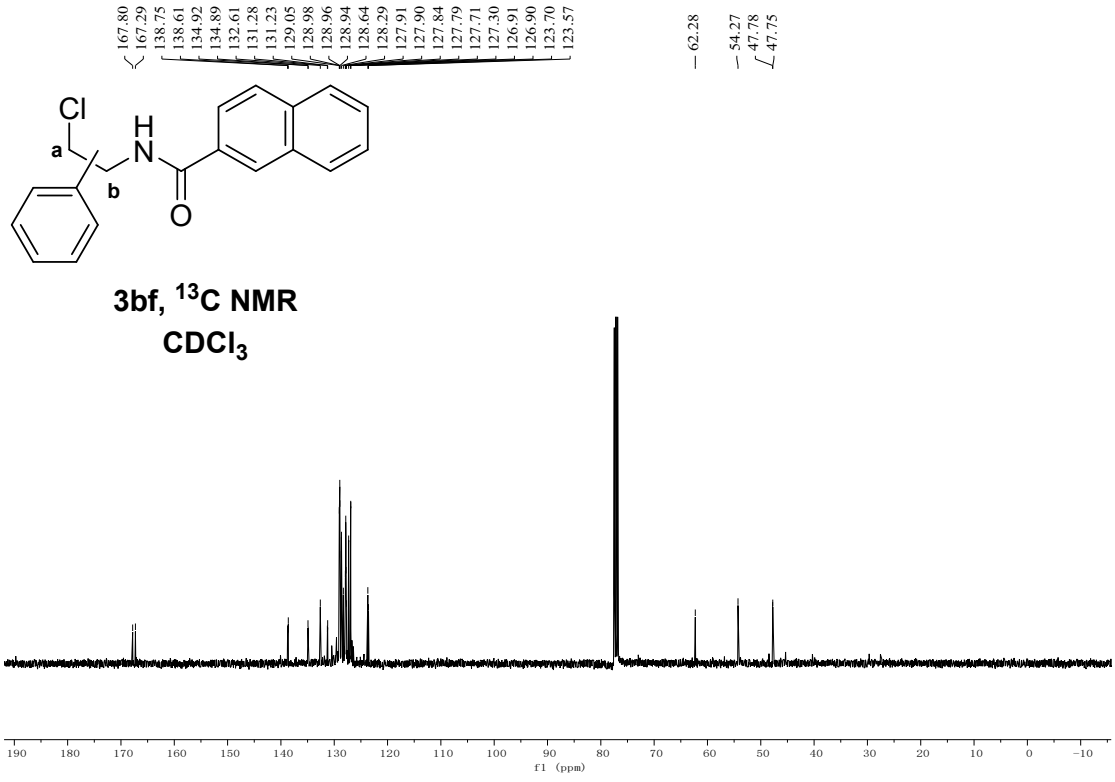
3be, ^{13}C NMR

$CDCl_3$

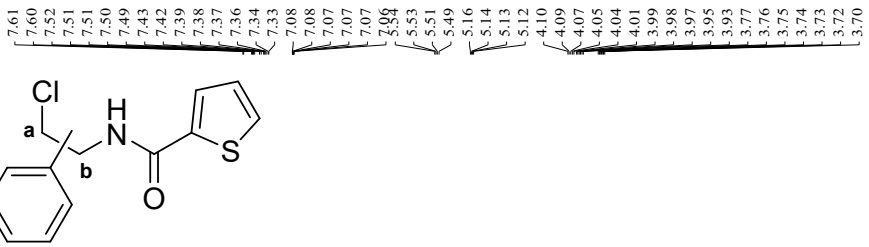




3bf, ^{1}H NMR
$CDCl_3$

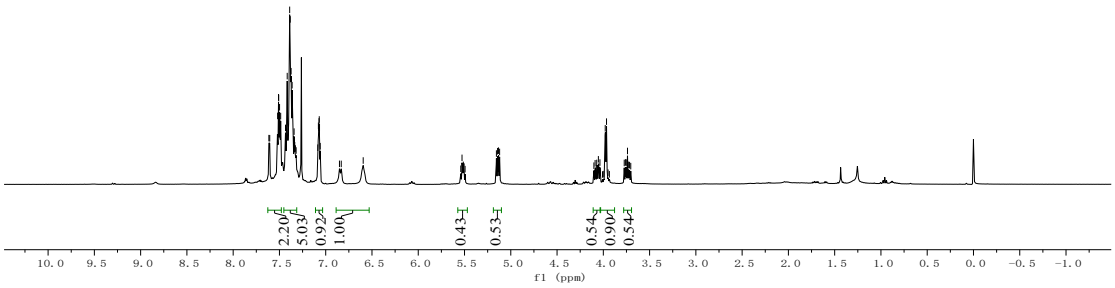


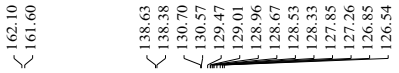
3bf, ^{13}C NMR
$CDCl_3$

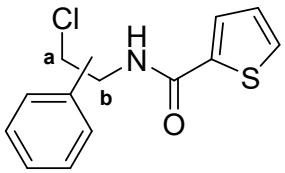


3bg, ^{1}H NMR

$CDCl_3$







3bg, ^{13}C NMR

$CDCl_3$