Supporting Information

Transition-metal-catalyst-free synthesis of anthranilic acid derivatives by transfer hydrogenative coupling of 2-nitroaryl methanols with alcohols/amines

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Table of contents

General information

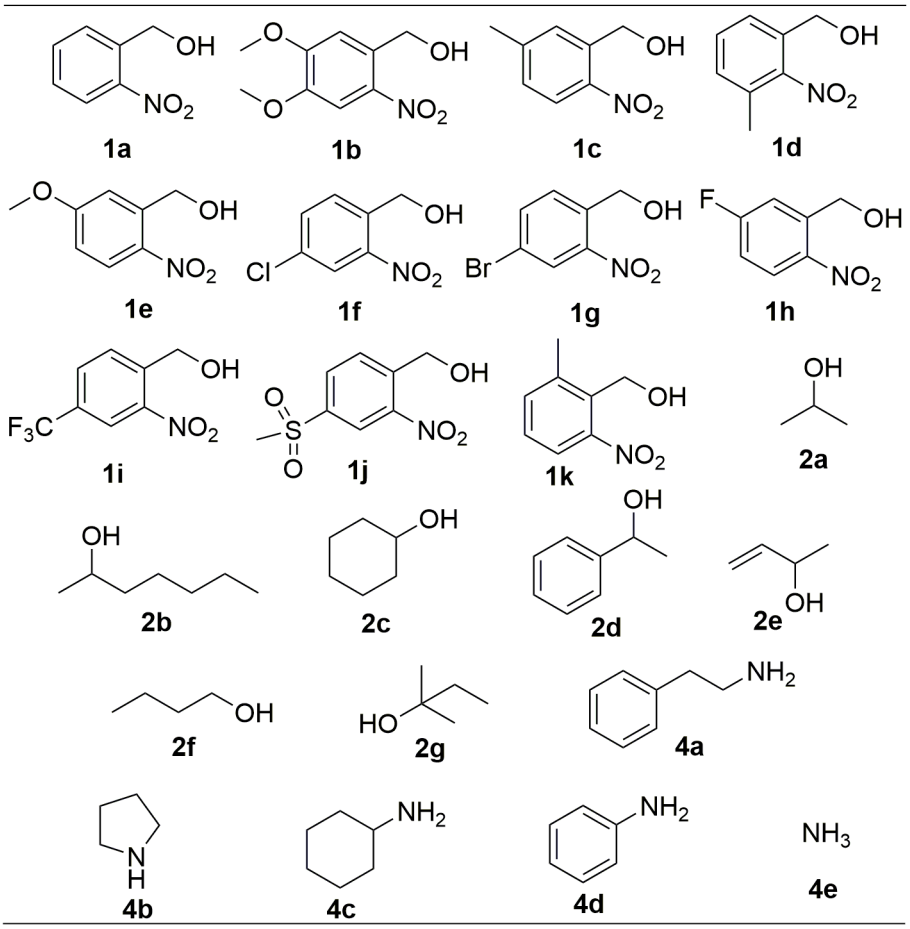
All the obtained products were characterized by melting points (m.p), ^{1}H-NMR, ^{13}C-NMR and infrared spectra (IR). Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; IR spectra were recorded on a FTLA2000 spectrometer; ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Bruker-400 and referenced to 7.26 ppm for chloroform solvent with TMS as internal standard (0 ppm) or 2.50 ppm for DMSO-d_6. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; Unless otherwise stated,, all the reagents were purchased from commercial sources (J&K Chemic, TCI, Fluka, Acros, SCRC), used without further purification.

Substrates preparation

2-nitroaryl methanols **1a** to **1i** and **1k** are known compounds and they were prepared via the literature procedures.[1,2] **1j** is unknown compound and it was prepared also via the literature procedures.[1,2]

Application

3-phenethyl-2-phenyl-2,3-dihydroquinazolin-4(1H)-one **6a** was known compound and prepared via the literature procedure.[3]



Scheme S1. Substrates employed for synthesizing anthranilic acid derivatives

Typical procedure for synthesis of isopropyl 2-aminobenzoate (3aa)

Under N_2 atmosphere, (2-nitrophenyl)methanol (0.5 mmol, 76.5 mg), Cs_2CO_3 (0.2 mmol, 65.2 mg) and propan-2-ol (1 mL) were introduced in a Schlenk tube (25 mL), successively. Then, the Schlenk tube was closed and the resulting mixture was stirred at 100 ℃ for 16 h. After cooling down to room temperature, the reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica, eluting with petroleum ether (60-90 ℃) : ethyl acetate (30 : 1) to give isopropyl 2-aminobenzoate **3aa** as clear oil liquid (71.6 mmg, 80%).

Typical procedure for synthesis of 2-amino-N-phenethylbenzamide (5aa)

Under N_2 atmosphere, (2-nitrophenyl)methanol (0.5 mmol, 76.5 mg), Cs_2CO_3 (0.2 mmol, 65.2 mg), 2-phenylethan-1-amine (1.0 ml) and propan-2-ol (3 mmol, 18.0 mg) were introduced in a Schlenk tube (25 mL), successively. Then, the Schlenk tube was closed and the resulting mixture was stirred at 110 ℃ for 16 h. After cooling down to room temperature, the reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica, eluting with petroleum ether : ethyl acetate (4:1) to give 2-amino-N-phenethylbenzamide **5aa** as gray solid (78.0 mmg, 65%).

Reference

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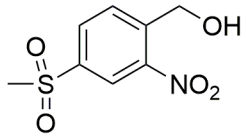
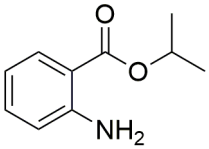
Analytic data of the obtained compounds

(1) (4-(methylsulfonyl)-2-nitrophenyl)methanol**(1j)**



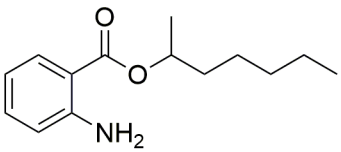
Yield: 90%, Yellow solid, m.p: 141-142 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.52 (s, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 5.80 (t, *J* = 5.6 Hz, 1H), 4.92 (d, *J* = 5.2 Hz, 2H), 3.34 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 147.10, 144.62, 140.66, 132.16, 130.14, 123.81, 60.32, 43.72. IR (KBr): 3527, 1535, 1388, 1353, 1320, 1159, 1141, 1049, 974, 767, 752, 525 cm^{-1}. HRMS (ESI): Calcd. for $C_8H_9NNaO_5S$ $[M+Na]^+$: 254.0094; found: 254.0093.

(2) isopropyl 2-aminobenzoate **(3aa)**[4]



Yield: 80%, Clear oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.22-7.28 (m, 1H), 6.60-6.70 (m, 2H), 5.68 (br, 2H), 5.15-5.28 (m, 1H), 1.36 (d, *J* = 5.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.71, 150.44, 133.85, 131.25, 116.66, 116.20, 111.54, 67.60, 22.02. IR (KBr): 3482, 3371, 3036, 2963, 1686, 1615, 1246, 1100, 751 cm^{-1}. MS (EI, m/z): 179.08 $[M]^+$.

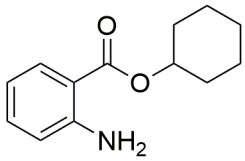
(3) Heptan-2-yl 2-aminobenzoate **(3ab)**



Yield: 83%, Clear oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.12-7.22 (m, 1H), 6.52-6.61 (m, 2H), 5.64 (br, 2H), 4.96-5.10 (m, 1H), 1.59-1.69 (m, 1H), 1.45-1.55 (m, 1H), 1.18-1.32 (m, 9H), 0.77-0.84 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.82, 150.47, 133.84, 131.21, 116.67, 116.20, 111.55, 72.99, 36.08,

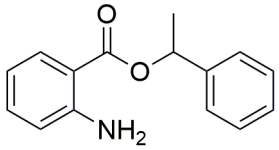
31.71, 25.15, 22.56, 20.14, 14.01. IR (KBr): 3484, 3372, 2956, 2861, 1686, 1615, 1245, 1103, 750 cm^{-1}. MS (EI, m/z): 235.18 $[M]^+$. HRMS (ESI): Calcd. for $C_{14}H_{22}NO_2$ $[M+H]^+$: 236.1645; found: 236.1644.

(4) Cyclohexyl 2-aminobenzoate **(3ac)**[5]



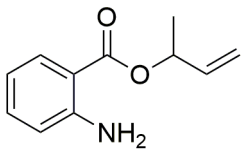
Yield: 82%, Pale yellow oil liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.20-7.29 (m, 1H), 6.59-6.70 (m, 2H), 5.70 (br, 2H), 4.94-5.04 (m, 1H), 1.86-2.00 (m, 2H), 1.72-1.83 (m, 2H), 1.50-1.65 (m, 3H), 1.28-1.50 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.61, 150.46, 133.85, 131.27, 116.67, 116.22, 116.61, 72.33, 31.21, 25.54, 23.69. IR (KBr): 3482, 3370, 3085, 2935, 2858, 1685, 1616, 1244, 1105, 751 cm^{-1}. MS (EI, m/z): 219.12 $[M]^+$.

(5) 1-phenylethyl 2-aminobenzoate **(3ad)**[5]



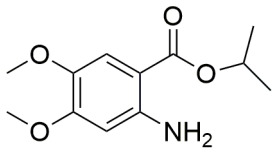
Yield: 85%, Pale yellow oil liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.22-7.31 (m, 2H), 6.60-6.70 (m, 2H), 6.08 (q, *J* = 12.0 Hz, 1H), 5.68 (br, 2H), 1.65 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.35, 150.64, 142.16, 134.11, 131.28, 128.57, 127.78, 125.92, 116.69, 116.26, 111.07, 72.24, 22.60. IR (KBr): 3483, 3370, 3034, 2925, 2856, 1686, 1611, 1241, 1027, 749 cm^{-1}. MS (EI, m/z): 241.04 $[M]^+$.

(6) But-3-en-2-yl 2-aminobenzoate **(3ae)**[6]



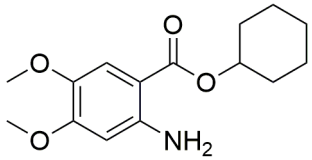
Yield: 80%, Clear oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 6.60-6.70 (m, 2H), 5.90-6.02 (m, 1H), 5.51-5.61 (m, 1H), 5.32 (d, *J* = 17.2 Hz, 1H), 5.17 (d, *J* = 10.4 Hz, 1H), 1.44 (d, *J* = 5.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.36, 150.58, 138.03, 134.04, 131.23, 116.68, 116.24, 115.51, 111.15, 70.80, 20.16. IR (KBr): 3485, 3374, 2926, 2855, 1688, 1616, 1244, 1103, 928, 751 cm^{-1}. MS (EI, m/z): 191.16 $[M]^+$.

(7) Isopropyl 2-amino-4,5-dimethoxybenzoate **(3ba)**[7]



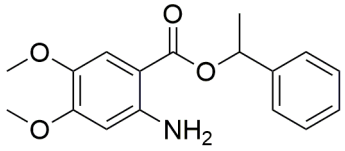
Yield: 78%, Orange solid, m.p: 97-98 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (s, 1H), 6.14 (s, 1H), 5.39 (br, 2H), 5.15-5.24 (m, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 1.36 (d, *J* = 5.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.33, 154.73, 147.05, 140.51, 113.18, 102.86, 99.40, 67,35, 56.57, 55.73, 22.09. IR (KBr): 3467, 3358, 3078, 2984, 2940, 1684, 1653, 1246, 1105 cm^{-1}. MS (EI, m/z): 239.12 $[M]^+$.

(8) cyclohexyl 2-amino-4,5-dimethoxybenzoate **(3bc)**



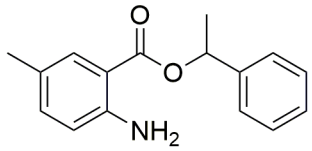
Yield: 78%, Orange solid, m.p: 119-120 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (s, 1H), 6.14 (s, 1H), 5.26 (br, 2H), 4.92-5.02 (m, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 1.88-2.00 (m, 2H), 1.73-1.83 (m, 2H), 1.51-1.63 (m, 3H), 1.28-1.50 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.21, 154.74, 147.03, 140.53, 113.25, 102.96, 99.41, 72.15, 56.56, 55.74, 31.81, 25.53, 23.79. IR (KBr): 3472, 3362, 2934, 2858, 1678, 1594, 1248, 1207, 1165 cm^{-1}.MS (EI, m/z): 279.22 $[M]^+$. HRMS (ESI): Calcd. for $C_{15}H_{22}NO_4$ $[M+H]^+$: 280.1543; found: 280.1539.

(9) 1-phenylethyl 2-amino-4,5-dimethoxybenzoate **(3bd)**



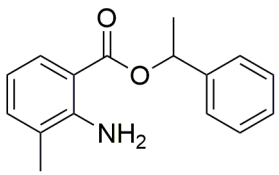
Yield: 76%, Brown oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.47 (m, 3H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.23-7.31 (m, 1H), 6.02-6.16 (m, 2H), 5.57 (br, 2H), 3.83 (s, 6H), 1.65 (d, *J* = 5.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.97, 155.06, 147.45, 142.36, 140.57, 128.56, 127.71, 125.85, 113.29, 102.35, 99.38, 71.97, 56.70, 55.75, 22.04. IR (KBr): 3475, 3365, 3063, 2978, 2867, 1681, 1624, 1250, 1164 cm^{-1}. MS (EI, m/z): 301.13 $[M]^+$. HRMS (ESI): Calcd. for $C_{17}H_{19}NNaO_4$ $[M+Na]^+$: 324.1206; found: 324.1207.

(10) 1-phenylethyl 2-amino-5-methylbenzoate **(3cd)**



Yield: 75%, Pale yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (s, 1H), 7.22-7.47 (m, 5H), 7.08 (q, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 6.08 (q, *J* = 13.2 Hz, 1H), 5.45 (br, 2H), 2.24 (s, 3H), 1.65 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.38, 148.50, 142.21, 135.25, 130.81, 128.56, 127.76, 125.95, 125.37, 116.88, 111.98, 72.15, 22.54, 20.33. IR (KBr): 3484, 3374, 3029, 2980, 2861, 1687, 1626, 1261, 1090 cm^{-1}. MS (EI, m/z): 255.05 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_{18}NO_2$ $[M+H]^+$: 256.1332; found: 256.1329.

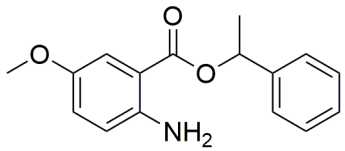
(11) 1-phenylethyl 2-amino-3-methylbenzoate **(3dd)**



Yield: 67%, Pale yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 6.8 Hz, 2H), 7.29 (d, *J* = 6.8 Hz, 1H), 7.19

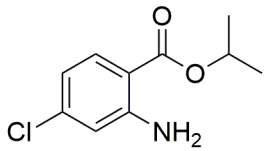
(d, *J* = 7.2 Hz, 1H), 6.60 (t, *J* = 7.2 Hz, 1H), 6.08 (q, *J* = 12.8 Hz, 1H), 2.15 (s, 3H), 1.65 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.78, 149.14, 142.24, 134.83, 129.22, 128.54, 127.72, 125.88, 122.99, 115.62, 110.57, 72.19, 22.61, 17.40. IR (KBr): 3470, 3370, 3031, 2974, 2855, 1685, 1612, 1240, 1079 cm^{-1}. MS (EI, m/z): 255.24 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_{18}NO_2$ $[M+H]^+$: 256.1332; found: 256.1327.

(12) 1-phenylethyl 2-amino-5-methoxybenzoate **(3ed)**



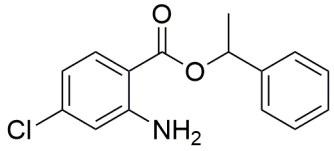
Yield: 62%, Pale yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.51 (m, 7H), 6.95,6.97 (dd, J_1 = 4.0 Hz, J_2 = 8.8 Hz, 1H), 6.62 (d, *J* = 8.8 Hz, 1H), 3,78 (s, 3H), 1.66 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.01, 150.58, 145.18, 142.05, 128.57, 127.80, 125.91, 122.69, 118.20, 114.09, 111.28, 72.41, 56.01, 22.53. IR (KBr): 3448, 3371, 2926, 2854, 1691, 1590, 1213, 1092 cm^{-1}. MS (EI, m/z): 271.05 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_{18}NO_3$ $[M+H]^+$: 272.1281; found: 272.1280.

(13) Isopropyl 2-amino-4-chlorobenzoate **(3fa)**[8]



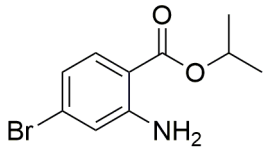
Yield: 78%, Pale yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.0 Hz, 1H), 6.65 (s, 1H), 6.58,6.60 (dd, J_1 = 0.8 Hz, J_2 = 8.4 Hz, 1H), 5.79 (br, 2H), 5.15-5.26 (m, 1H), 1.35 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.10, 151.19, 139.26, 132.64, 116.59, 115.89, 110.02, 67.93, 21.97. IR (KBr): 3485, 3369, 2981, 2927, 1688, 1613, 1243, 906, 693 cm^{-1}. MS (EI, m/z): 213.01 $[M]^+$; 215.04 $[M+2]^+$

(14) 1-phenylethyl 2-amino-4-chlorobenzoate **(3fd)**



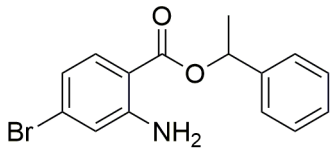
Yield: 80%, Pale yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.4 Hz, 1H), 7.22-7.47 (m, 5H), 6.57-6.67 (m, 2H), 6.06 (q, *J* = 12.4 Hz, 1H), 5.68 (br, 2H), 1.64 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.76, 151.38, 141.92, 140.05, 132.65, 128.61, 127.90, 125.93, 116.67, 115.59, 109.56, 72.55, 22.51. IR (KBr): 3486, 3370, 3032, 2926, 2855, 1689, 1611, 1239, 1094, 763, 696 cm^{-1}.MS (EI, m/z): 275.00 $[M]^+$; 277.07 $[M+2]^+$. HRMS (ESI): Calcd. for $C_{15}H_{15}ClNO_2$ $[M+H]^+$: 276.0786; found: 276.0781.

(15) Isopropyl 2-amino-4-bromobenzoate **(3ga)**



Yield: 75%, Pale yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.0 Hz, 1H), 6.82 (s, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.75 (br, 2H), 5.14-5.25 (m, 1H), 1.35 (d, *J* = 5.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.21, 151.23, 132.63, 128.41, 119.41, 118.96, 110.37, 67.97, 21.97. IR (KBr): 3483, 3367, 2981, 2929, 1687, 1609, 1242, 1091, 892, 767 cm^{-1}. MS (EI, m/z): 256.96 $[M]^+$; 259.01 $[M+2]^+$. HRMS (ESI): Calcd. for $C_{10}H_{13}BrNO_2$ $[M+H]^+$: 258.0124; found: 258.0116.

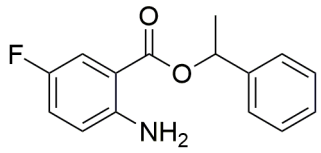
(16) 1-phenylethyl 2-amino-4-bromobenzoate **(3gd)**



Yield: 82%, Pale yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.21-7.45 (m, 5H), 6.79 (s, 1H), 6.75 (d, *J* = 8.8 Hz, 1H), 6.01-6.10 (m, 1H), 5.75 (br, 2H), 1.64 (d, *J* = 5.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.89, 151.42, 141.91, 132.64, 128.74, 128.63, 127.93, 125.94, 119.50, 119.04, 109.91,

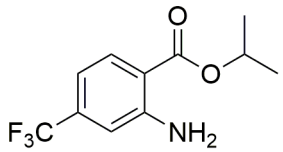
72.59, 22.53. IR (KBr): 3485, 3369, 2981, 2927, 1689, 1608, 1239, 1063, 763, 696 cm^{-1}. MS (EI, m/z): 319.11 $[M]^+$; 321.11 $[M+2]^+$. HRMS (ESI): Calcd. for $C_{15}H_{15}BrNO_2$ $[M+H]^+$: 320.0281; found: 320.0277.

(17) 1-phenylethyl 2-amino-5-fluorobenzoate **(3hd)**



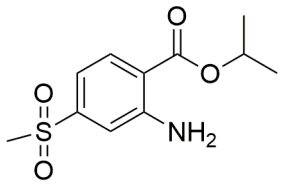
Yield: 76%, Pale yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62,7.64 (dd, J_1 = 2.8 Hz, J_2 = 9.6 Hz, 1H), 7.42 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 7.2 Hz, 2H), 7.24-7.32 (m, 1H), 6.98-7.06 (m, 1H), 6.55-6.65 (m, 1H), 6.07 (q, J = 13.2 Hz, 1H), 5.51 (br, 2H), 1.65 (d, J = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 116.50, 153.95(d, J_{C-F} = 116.5 Hz), 147.18, 141.80, 128.62, 127.93, 125.95, 122.05(d, J_{C-F} = 11.5 Hz), 117.85(d, J_{C-F} = 3.5 Hz), 116.14(d, J_{C-F} = 11.5 Hz), 110.96(d, J_{C-F} = 3.5 Hz), 72.72, 22.49. IR (KBr): 3486, 3373, 3035, 2982, 2857, 1678, 1594, 1248, 1207, 1165 cm^{-1}. MS (EI, m/z): 259.08 $[M]^+$. HRMS (ESI): Calcd. for $C_{15}H_{15}FNO_2$ $[M+H]^+$: 260.1081; found: 260.1080.

(18) isopropyl 2-amino-4-(trifluoromethyl)benzoate **(3ia)**



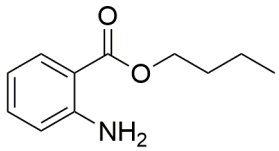
Yield: 81%, Pale yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.4 Hz, 1H), 6.89 (d, J = 1.6 Hz, 1H), 6.84,6.82 (dd, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 1H), 5.82 (br, 2H), 5.32-5.17 (m, 1H), 1.37 (d, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.87, 150.19, 135.24 (d, J = 32.0 Hz), 132.16, 124.95, 122.24, 113.79, 113.37 (q, J = 4.0 Hz), 112.20 (q, J = 4.0 Hz), 68.36, 21.93. IR (KBr): 3703, 2985, 1699, 1594, 1456, 1443, 1244, 1171, 1129, 1094, 909, 782, 748, 705 cm^{-1}. HRMS (ESI): Calcd. for $C_{11}H_{13}F_3NO_2$ $[M+H]^+$: 248.0893; found: 248.0892.

(19) isopropyl 2-amino-4-(methylsulfonyl)benzoate **(3ja)**



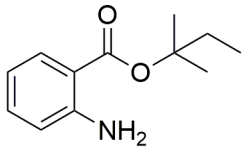
Yield: 86%, Pale yellow oil liquid, m.p: 96-97 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.25 (s, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.10 (br, 2H), 5.16-5.32 (m, 1H), 3.04 (s, 3H), 1.38 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.55, 150.62, 144.66, 132.82, 115.31, 114.93, 113.25, 68.71, 44.09, 21.90. IR (KBr): 3472, 3364, 2982, 2929, 1692, 1614, 1247, 1097 cm^{-1}. MS (EI, m/z): 257.14 $[M]^+$. HRMS (ESI): Calcd. for $C_{11}H_{15}NNaO_4S$ $[M+Na]^+$: 280.0614; found: 280.0612.

(20) butyl 2-aminobenzoate **(3af)**[9]



Yield: 48%, Pale yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.91 (m, 1H), 7.21-7.30 (m, 1H), 6.59-6.72 (m, 2H), 5.35 (br, 2H), 4.27 (t, *J* = 6.4 Hz, 2H), 1.70-1.81 (m, 2H), 1.43-1.55 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.25, 154.40, 133.97, 131.22, 116.71, 116.30, 111.19, 64.20, 30.83, 19.34, 13.78. IR (KBr): 3696, 2956, 1689, 1588, 1294, 1245, 1103, 1096, 751 cm^{-1}. MS (EI, m/z): 193.12 $[M]^+$.

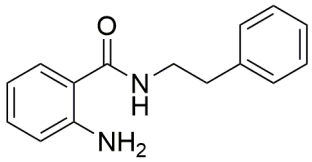
(21) tert-pentyl 2-aminobenzoate **(3ag)**



Yield: 35%, Pale yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.88 (m, 1H), 7.21-7.26 (m, 1H), 6.53-6.80 (m, 2H), 1.91 (q, *J* = 14.8 Hz, 2H), 1.56 (s, 6H), 0.97 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.62, 150.33, 133.54, 131.43, 116.72, 116.18, 112.66, 83.11, 33.90, 25.81, 8.63. IR (KBr): 3702, 2975, 1687, 1585,

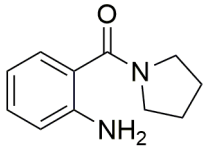
1558, 1487, 1459, 1295, 1252, 1155, 1107, 920, 751 cm^{-1}. HRMS (ESI): Calcd. for $C_{12}H_{18}NO_2$ $[M+H]^+$: 208.1332; found: 208.1331.

(22) 2-amino-N-phenethylbenzamide **(5aa)**[10]



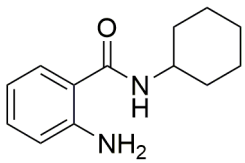
Yield: 65%, Gray solid, m.p: 90-91 ℃; ^1H NMR (400 MHz, $CDCl_3$): δ 7.13-7.35 (m, 7H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.59 (t, *J* = 7.2 Hz, 1H), 6.10 (br, 1H), 5.54 (br, 2H), 3.62-3.72 (m, 2H), 2.91 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.32, 148.63, 138.99, 132.22, 128.83, 128.73, 127.04, 126.59, 117.30, 116.64, 116.29, 40.81, 35.75. IR (KBr): 3472, 3293, 3193, 3030, 2924, 2859, 1629, 1582, 1526, 1300, 1259, 744, 694 cm^{-1}. MS (EI, m/z): 240.15 $[M]^+$.

(23) (2-aminophenyl)(pyrrolidin-1-yl)methanone **(5ab)**[11]



Yield: 45%, Brown solid, m.p: 86-87 ℃; ^1H NMR (400 MHz, $CDCl_3$): δ 7.06-7.24 (m, 2H), 6.60-6.75 (m, 2H), 4.66 (br, 2H), 3.25-3.65 (m, 4H), 1.63-1.97 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.53, 145.95, 130.67, 127.96, 120.78, 117.05, 116.66, 49.53, 45.97, 26.31, 24.44. IR (KBr): 3439, 3147, 2962, 2925, 2872, 1679, 1609, 1406, 750 cm^{-1}. MS (EI, m/z): 190.18 $[M]^+$.

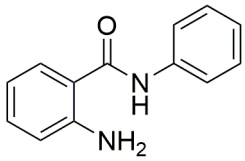
(24) 2-amino-N-cyclohexylbenzamide **(5ac)**[12]



Yield: 72%, Yellow solid, m.p: 152-153 ℃; ^1H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.58-6.74 (m, 2H), 5.93 (br, 1H), 5.47 (br, 2H), 3,85-3.99 (m, 1H), 2.01 (d, *J* = 11.2 Hz, 2H), 1.60-1.80 (m, 4H), 1.34-1.52 (m, 2H),

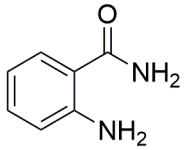
1.17-1.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.49, 148.59, 130.25, 127.01, 117.25, 116.75, 116.58, 48.31, 33.24, 25.61, 24.92. IR (KBr): 3475, 3367, 3306, 3050, 2930, 2854, 1669, 1626, 1537, 1320, 1264, 749, 668 cm^{-1}. MS (EI, m/z): 218.13 $[M]^+$.

(25) 2-amino-N-phenylbenzamide **(5ad)**[13]



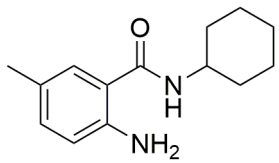
Yield: 51%, White solid, m.p: 131-132 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (br, 1H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.20-7.28 (m, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 6.66-6.75 (m, 1H), 5.48 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.58, 148.98, 137.88, 132.76, 129.07, 127.18, 124.51, 120.57, 117.56, 116.86, 116.28. IR (KBr): 3467, 3362, 3282, 3121, 2958, 2918, 2852, 1634, 1587, 1528, 1402, 1248, 747, 688 cm^{-1}. MS (EI, m/z): 212.05 $[M]^+$.

(26) 2-aminobenzamide **(5ae)**[14]



Yield: 20%, brown solid, m.p: 112-113 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): 7.71 (br, 1H), δ 7.52 (d, J = 8.0 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 7.04 (br, 1H), 6.67 (d, J = 8.4 Hz, 1H), 6.54 (s, 2H), 6.47 (t, J = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.30, 150.18, 131.87, 128.74, 116.40, 114.37, 113.70. IR (KBr): 3412, 1628, 1401, 1315, 1257, 744 cm^{-1}. MS (EI, m/z): 136.09 $[M]^+$.

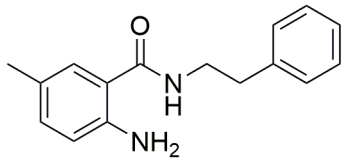
(27) 2-amino-N-cyclohexyl-5-methylbenzamide **(5cc)**[15]



Yield: 53%, Gray solid, m.p: 186-187 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (s, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 5.90 (br, 1H), 5.27 (br, 2H),

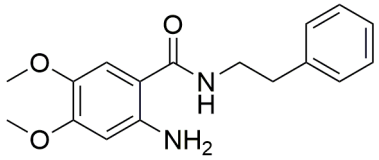
3.85-4.01 (m, 1H), 2.24 (s, 3H), 1.98-2.06 (m, 2H), 1.60-1.80 (m, 4H), 1.37-1.49 (m, 2H), 1.18-1.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.51, 146.10, 132.88, 127.10, 125.85, 117.48, 116.96, 48.30, 33.28, 25.63, 24.95, 20.36. IR (KBr): 3412, 3297, 3132, 2927, 2854, 1628, 1584, 1529, 1401, 1150, 825, 600 cm^{-1}. MS (EI, m/z): 232.16 $[M]^+$.

(28) 2-amino-5-methyl-N-phenethylbenzamide **(5ca)**



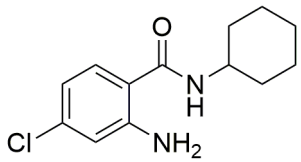
Yield: 67%, Gray solid, m.p: 113-115 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.35 (m, 2H), 7.21-7.27 (m, 3H), 6.95-7.03 (m, 2H), 6.58 (d, *J* = 8.4 Hz, 1H), 6.10 (br, 1H), 5.24 (br, 2H), 3.66 (q, *J* = 13.2 Hz, 2H), 2.91 (t, *J* = 6.8 Hz, 2H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.34, 146.16, 139.05, 133.06, 128.87, 128.69, 127.23, 126.57, 125.87, 117.49, 116.53, 40.83, 35.80, 20.23. IR (KBr): 3459, 3415, 3293, 3026, 2923, 2859, 1633, 1578, 1403, 693 cm^{-1}. MS (EI, m/z): 254.15 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_{19}N_2O$ $[M+H]^+$: 255.1492; found: 255.1495.

(29) 2-amino-4,5-dimethoxy-N-phenethylbenzamide **(5ba)**



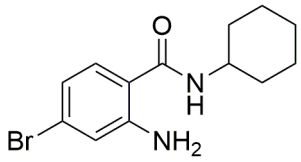
Yield: 60%, Black solid, m.p: 110-112 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.34 (m, 7H), 6.67 (s, 1H), 6.16 (s, 1H), 6.10 (br, 1H), 5.31 (br, 2H), 3.81 (s, 3H), 3.72 (s, 3H), 3.64 (q, *J* = 12.8 Hz, 2H), 2.90 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.91, 153.16, 144.65, 140.78, 139.18, 128.89, 128.67, 126.55, 110.92, 107.42, 100.84, 56.84, 55.72, 40.75, 35.76. IR (KBr): 3457, 3345, 3336, 2925, 2856, 2758, 1637, 1590, 1504, 1504, 1257, 1218, 699, 607 cm^{-1}. MS (EI, m/z): 300.15 $[M]^+$. HRMS (ESI): Calcd. for $C_{17}H_{21}N_2O_3$ $[M+H]^+$: 301.1547; found: 301.1550.

(30) 2-amino-4-chloro-N-cyclohexylbenzamide **(5fc)**[16]



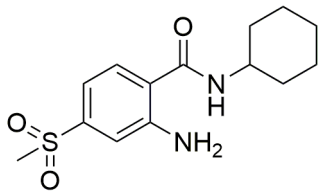
Yield: 70%, Yellow solid, m.p: 173-174 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.4 Hz, 1H), 6.65 (s, 1H), 6.58 (d, *J* = 8.4 Hz, 1H), 5.89 (br, 1H), 5.61 (br, 2H), 5.82-5.96 (m, 1H), 1.94-2.05 (m, 2H), 1.60-1.82 (m, 4H), 1.35-1.47 (m, 2H), 1.17-1.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.77, 149.73, 137.78, 128.28, 116.55, 116.51, 114.94, 48.46, 33.19, 25.56, 24.92. IR (KBr): 3467, 3348, 3285, 3053, 2930, 2853, 1619, 1576, 1532, 1255 cm^{-1}. MS (EI, m/z): 252.08 $[M]^+$; 254.13 $[M+2]^+$.

(31) 2-amino-4-bromo-N-cyclohexylbenzamide **(5gc)**



Yield: 72%, Brown solid, m.p: 181-182 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.4 Hz, 1H), 6.82 (s, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 5.88 (br, 1H), 5.59 (s, *2*H), 3.80-3.96 (m, 1H), 1.93-2.05 (m, 2H), 1.60-1.78 (m, 4H), 1.35-1.47 (m, 2H), 1.17-1.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.82, 149.80, 128.32, 126.18, 119.54, 119.41, 115.35, 48.46, 33.18, 25.57, 24.91. IR (KBr): 3465, 3349, 3285, 3044, 2927, 2854, 1618, 1572, 1530, 1253 cm^{-1}. MS (EI, m/z): 296.06 $[M]^+$; 298.05 $[M+2]^+$. HRMS (ESI): Calcd. for $C_{13}H_{18}BrN_2O$ $[M+H]^+$: 297.0597; found: 297.0593.

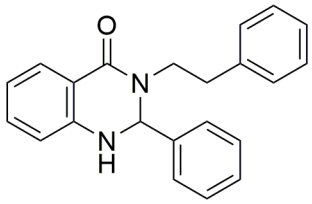
(32) 2-amino-N-cyclohexyl-4-(methylsulfonyl)benzamide **(5jc)**



Yield: 73%, Pale yellow solid, m.p: 191-193 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.20 (s, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.04 (br, 1H), 5.75 (br, 2H), 3.85-4.01 (m, 1H), 3.02 (s, 3H), 1.95-2.06 (m, 2H), 1.62-1.81 (m, 4H), 1.37-1.49 (m,

2H), 1.28-1.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.12, 148.98, 143.14, 128.39, 120.71, 115.31, 114.07, 48.77, 44.23, 33.07, 25.50, 24.90. IR (KBr): 3471, 3363, 3142, 2925, 2853, 1621, 1576, 1532, 1402, 1143 cm^{-1}. MS (EI, m/z): 296.08 $[M]^+$. HRMS (ESI): found $[M-H]^+$: 295.0800.

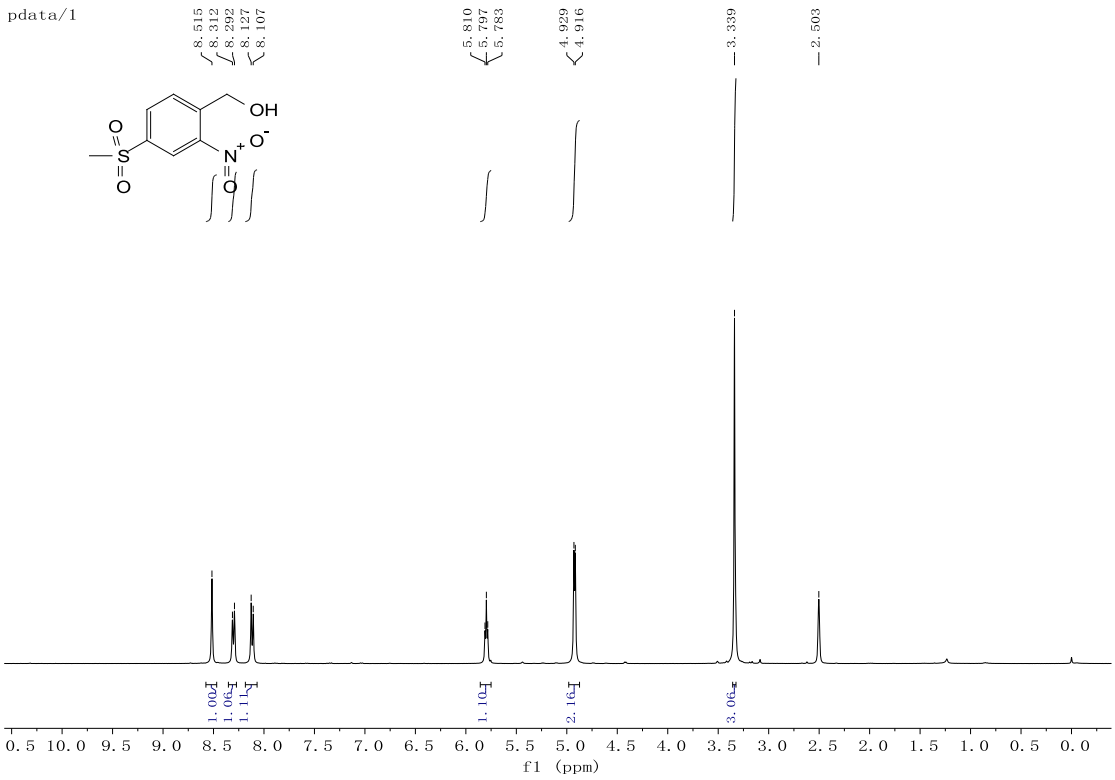
(33) 3-phenethyl-2-phenyl-2,3-dihydroquinazolin-4(1H)-one**(6a)**[17]



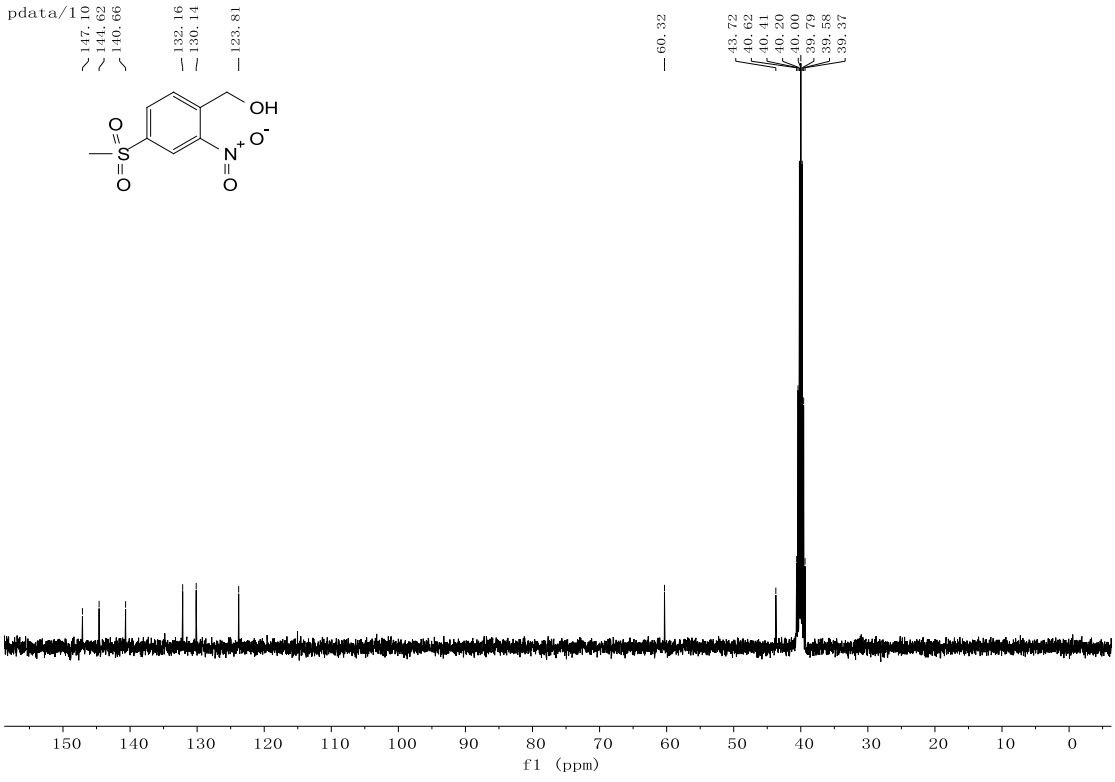
Yield: 62%, brown solid, m.p: 145-146 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.6 Hz, 1H), 7.34 (s, 5H), 7.18-7.24 (m, 4H), 7.10 (d, *J* = 7.2 Hz, 2H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 5.55 (s, 1H), 4.50 (s, 1H), 3.98-4.11 (m, 1H), 3.03-2.91 (m, 2H), 2.72-2.82 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.34, 145.40, 139.70, 139.29, 133.54, 129.53, 129.08, 128.99, 128.58, 128.55, 126.97, 126.45, 119.38, 116.31, 114.46, 73.07, 47.04, 34.34. IR (KBr): 3306, 1603, 1504, 1452, 1403, 1312, 747, 695 cm^{-1}. MS (EI, m/z): 328.20 $[M]^+$.

NMR spectra of the obtained compounds

^{1}H- NMR spectrum of 1j

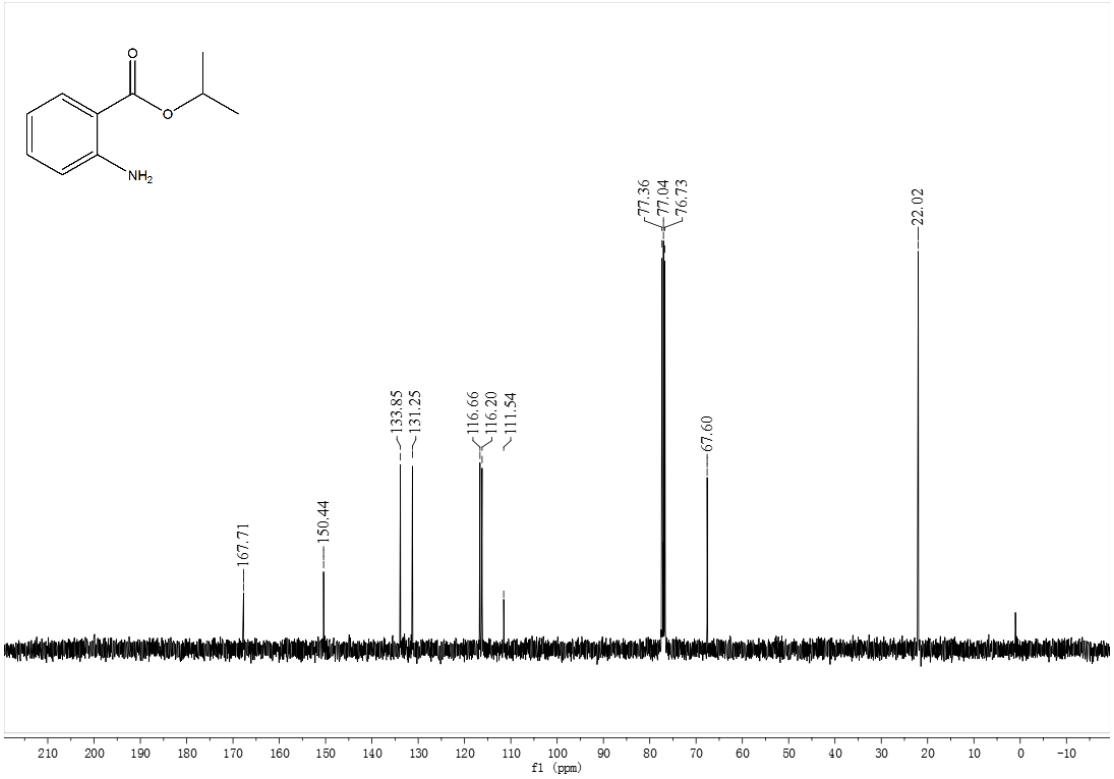


^{13}C-NMR spectrum of 1j

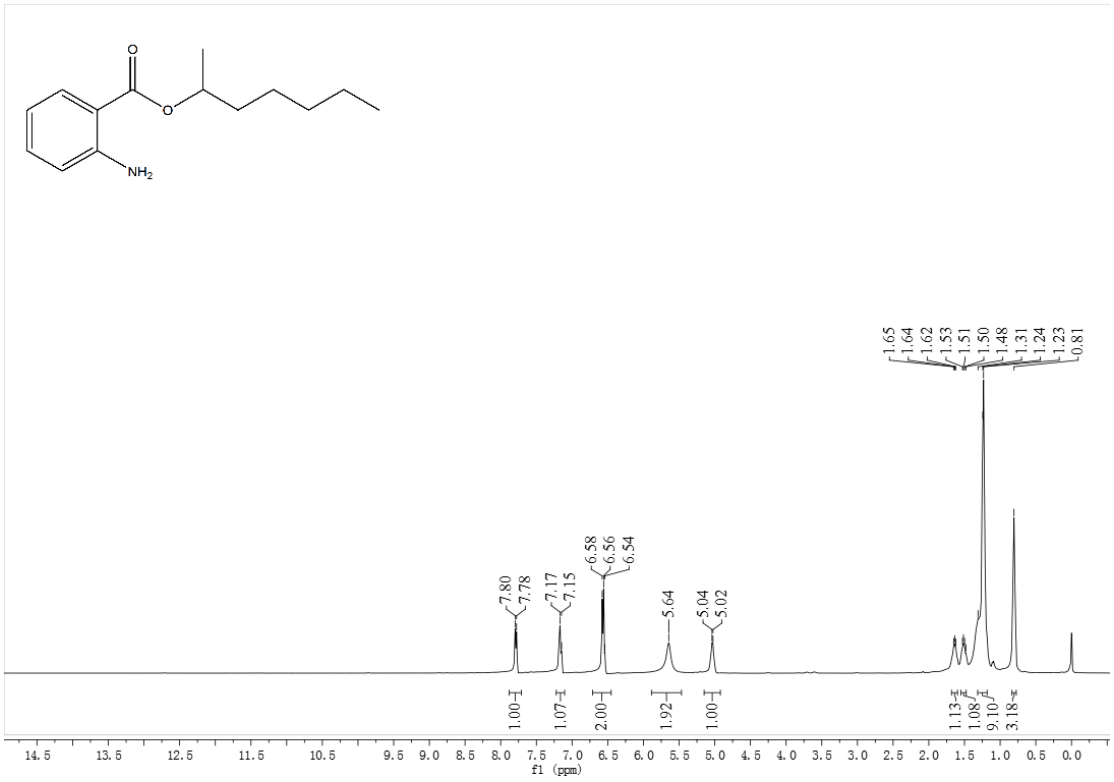


^{1}H- NMR spectrum of 3aa

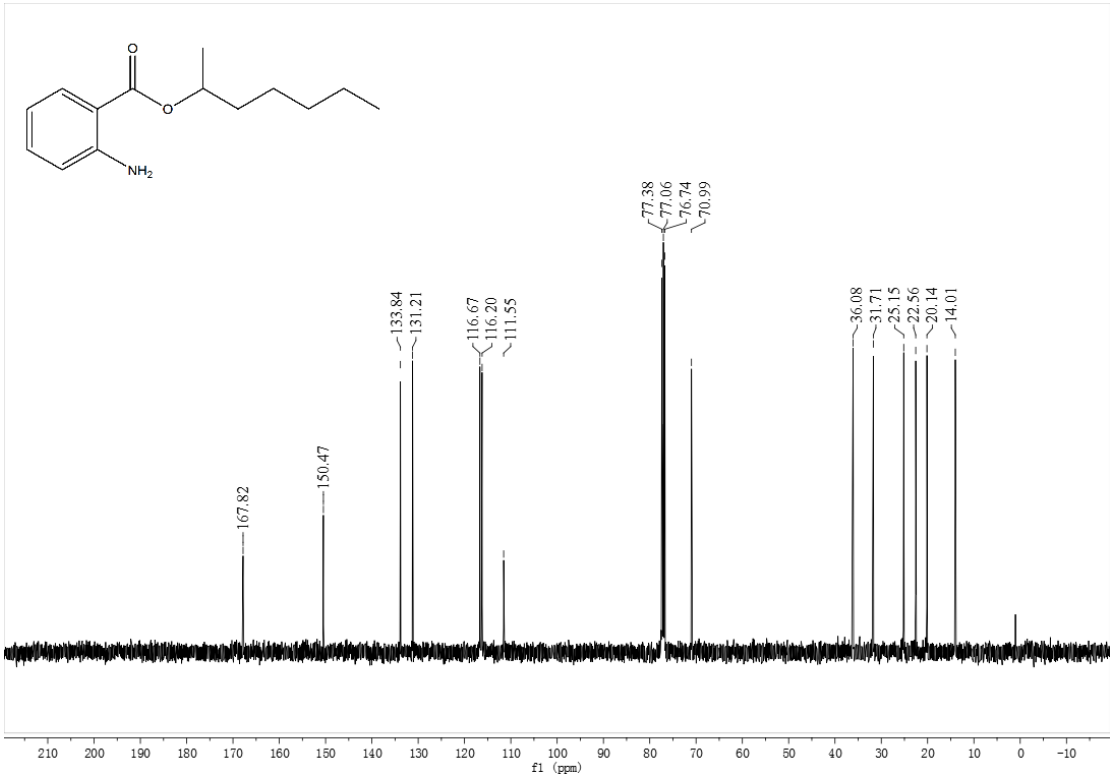
^{13}C-NMR spectrum of 3aa



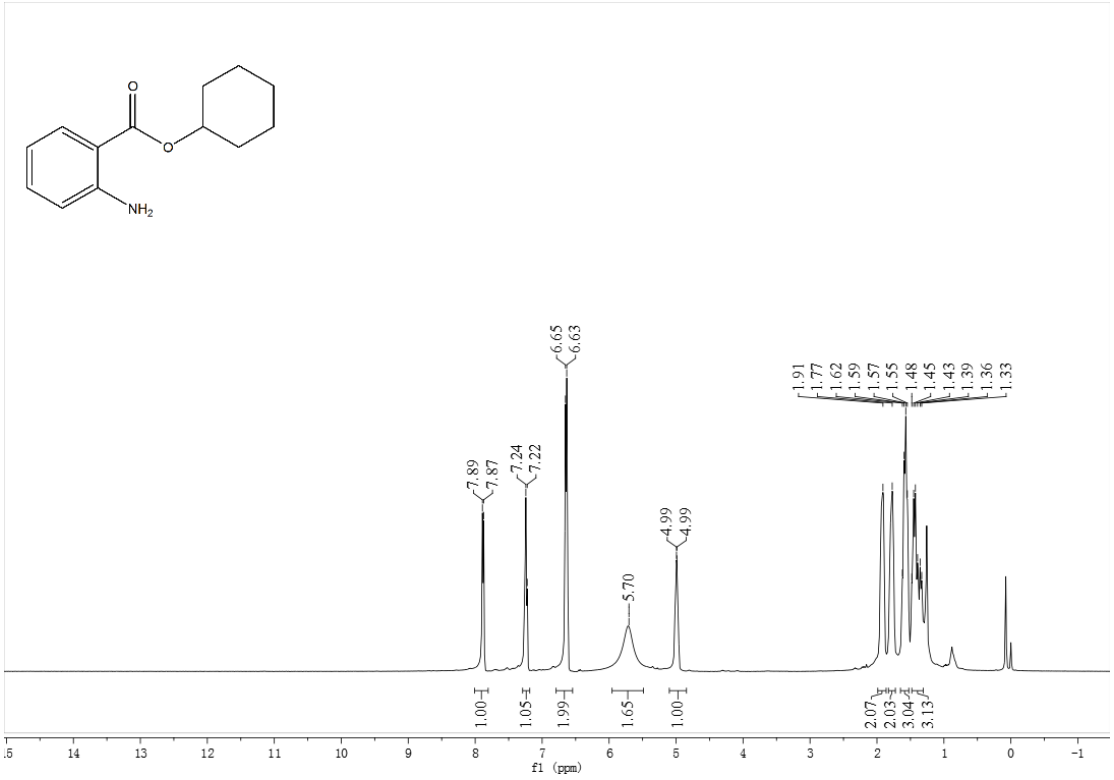
^{1}H- NMR spectrum of 3ab



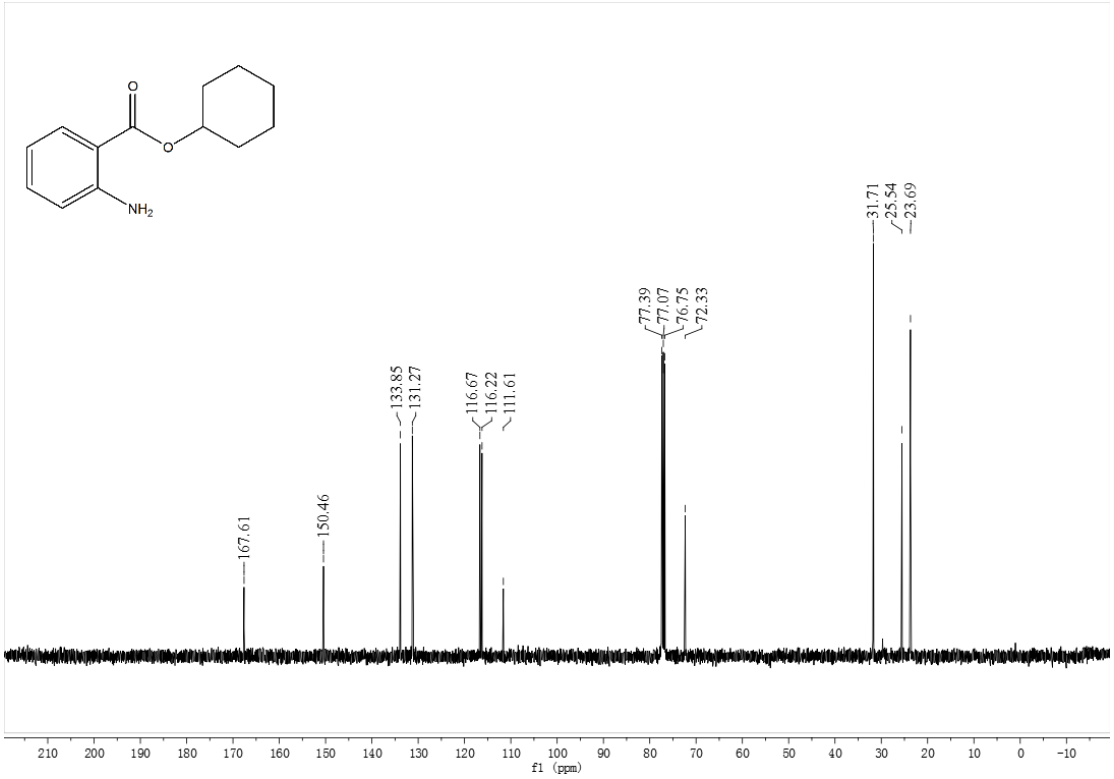
^{13}C-NMR spectrum of 3ab



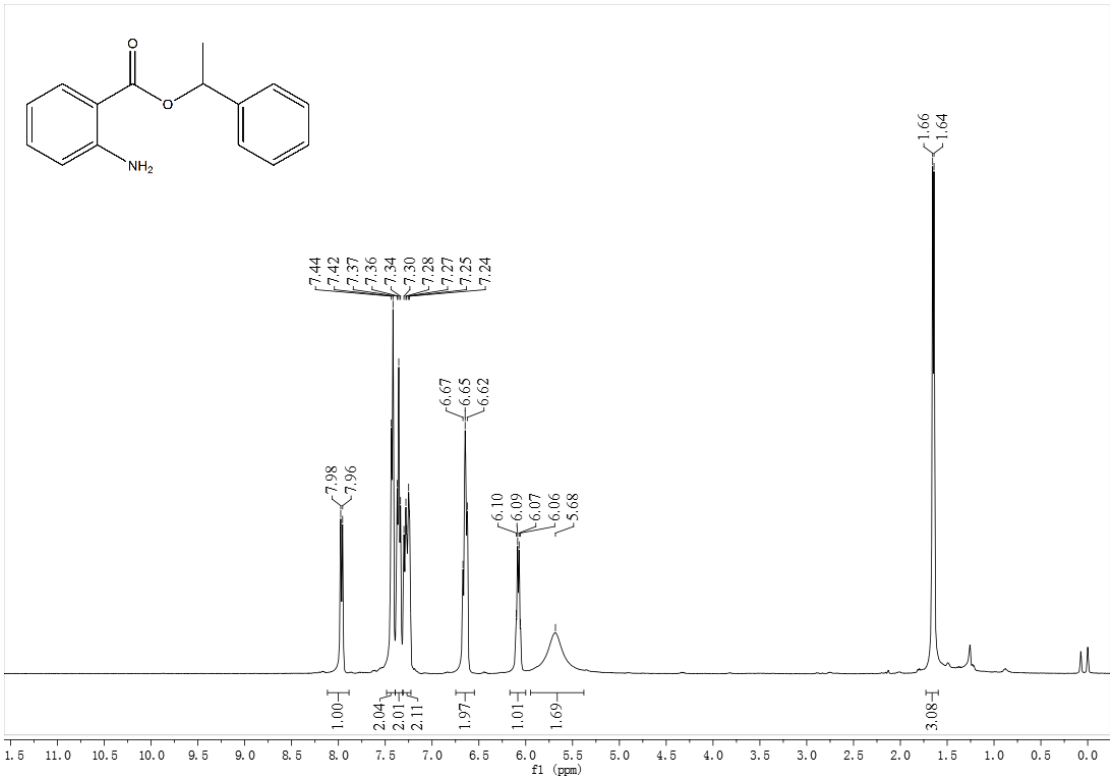
^{1}H- NMR spectrum of 3ac



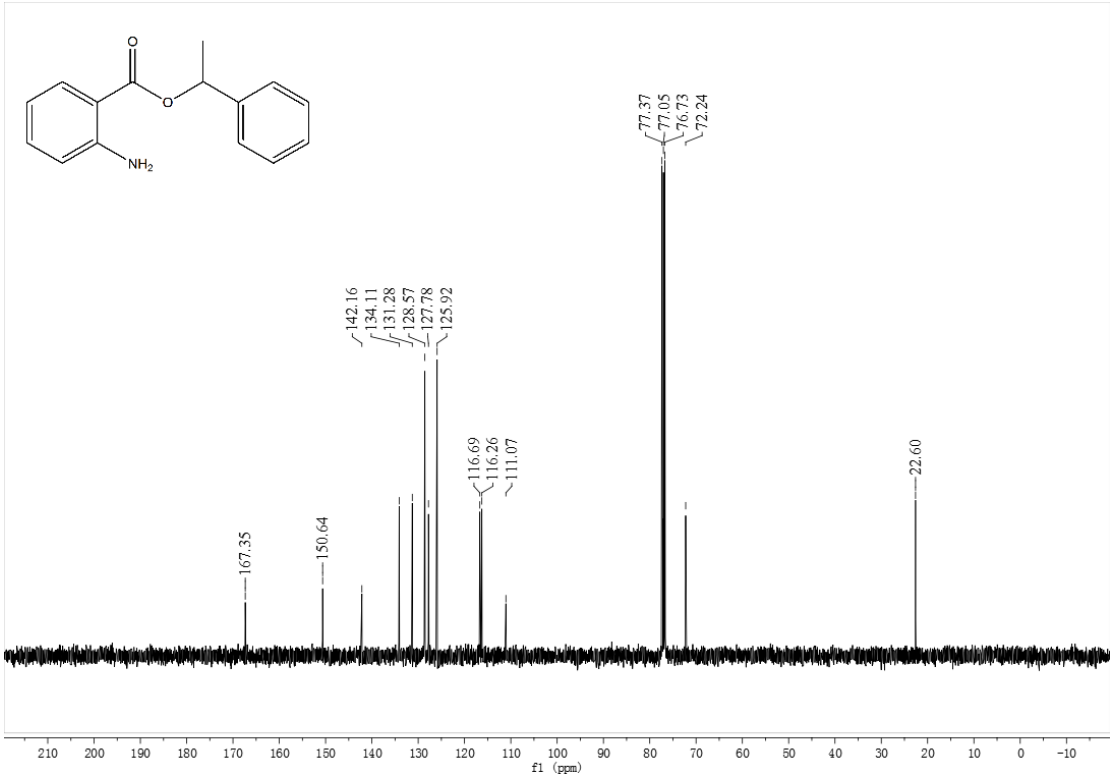
^{13}C-NMR spectrum of 3ac



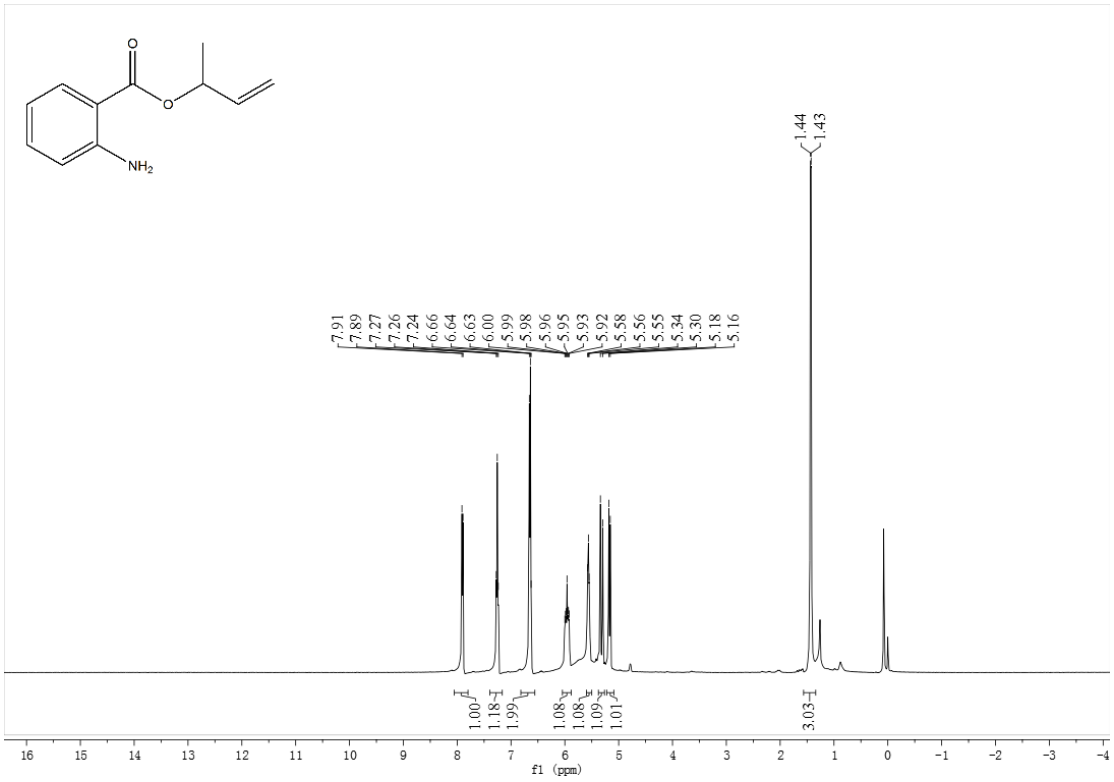
^{1}H- NMR spectrum of 3ad



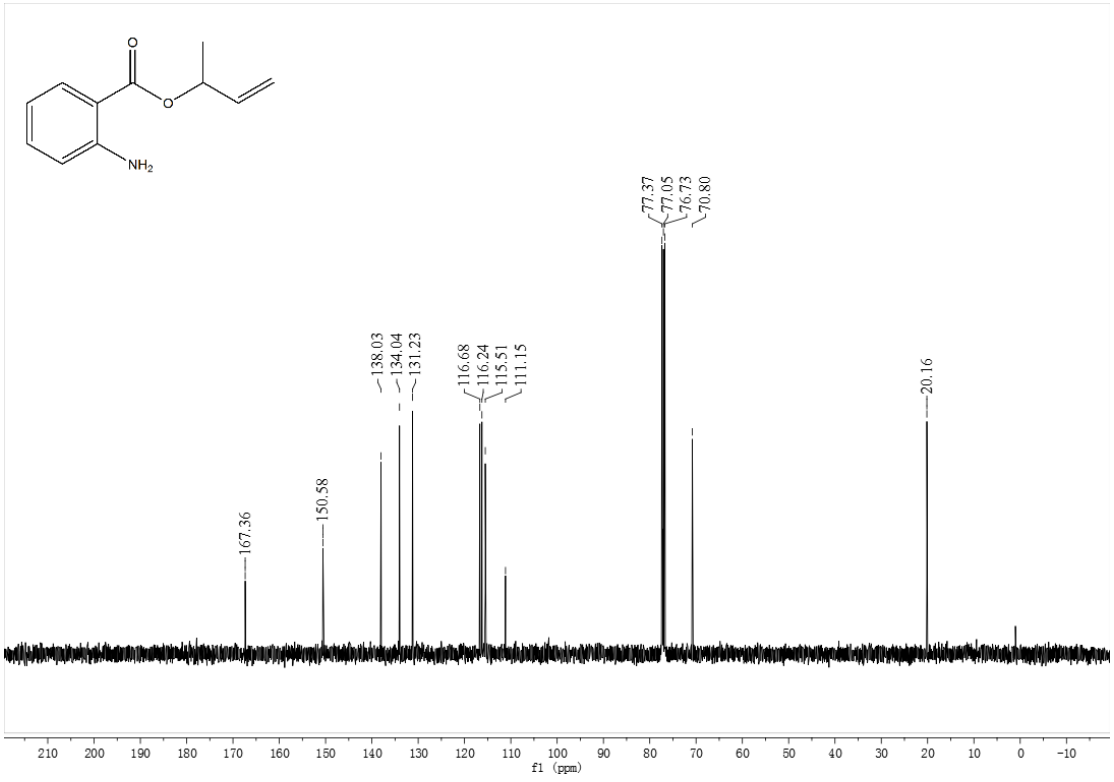
^{13}C-NMR spectrum of 3ad



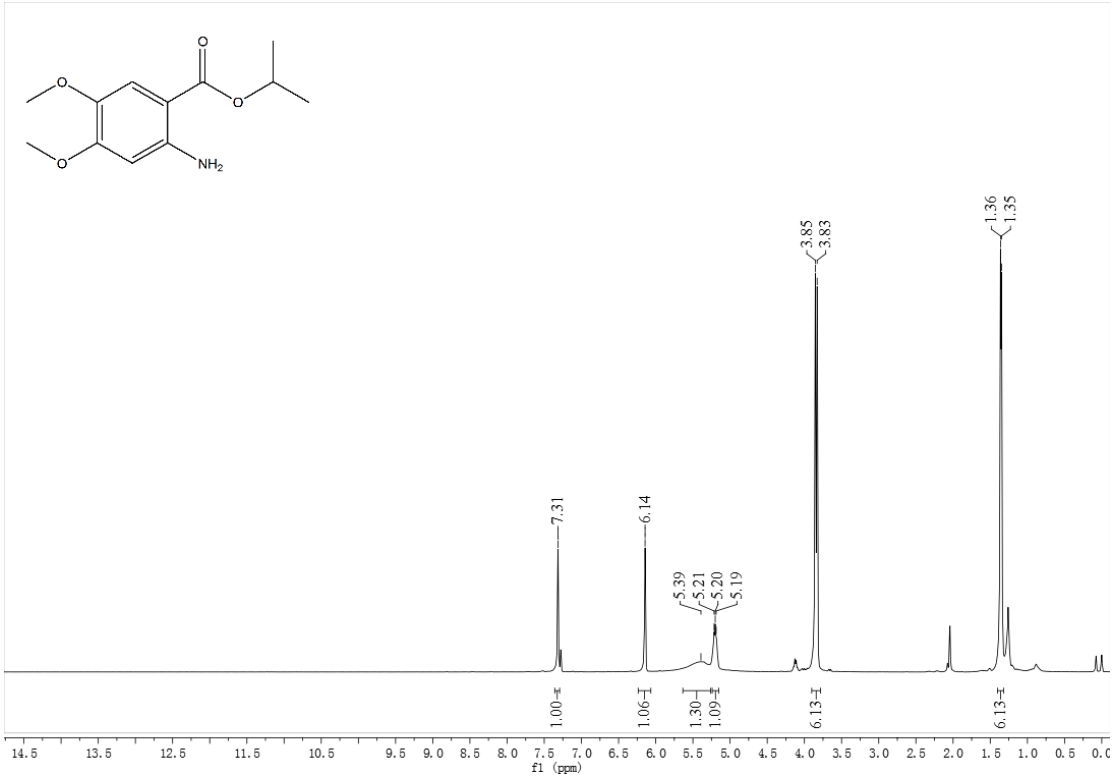
^{1}H- NMR spectrum of 3ae



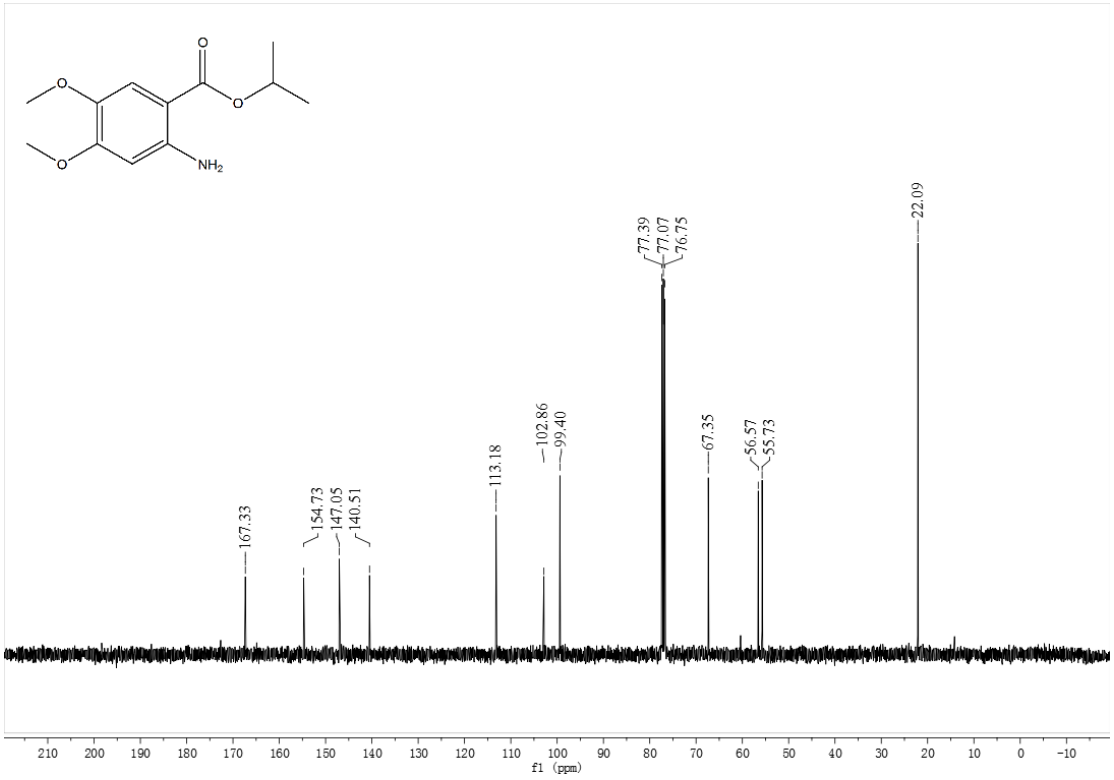
^{13}C-NMR spectrum of 3ae



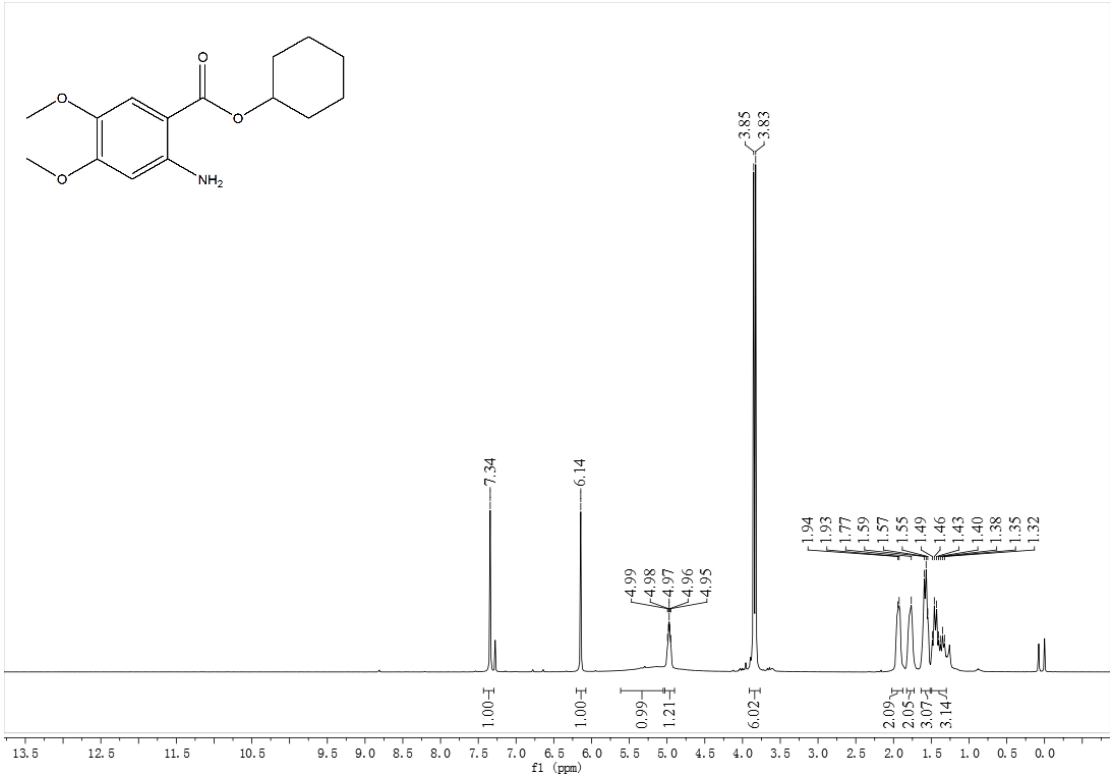
^{1}H- NMR spectrum of 3ba



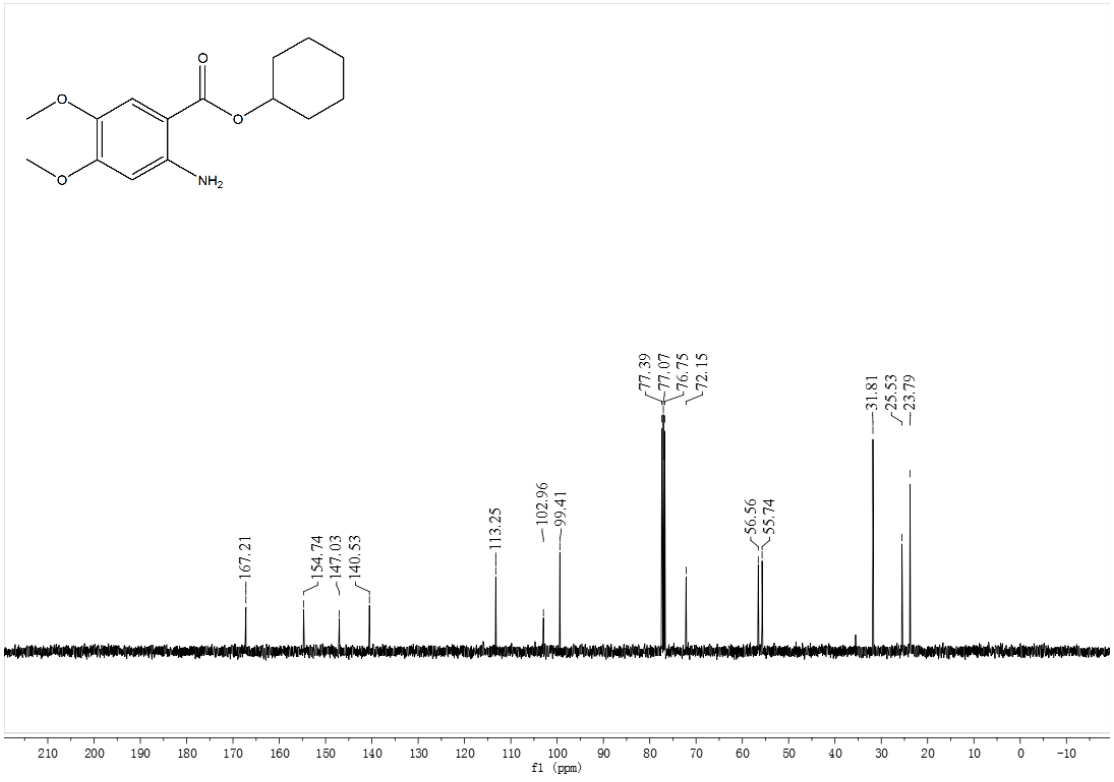
^{13}C-NMR spectrum of 3ba



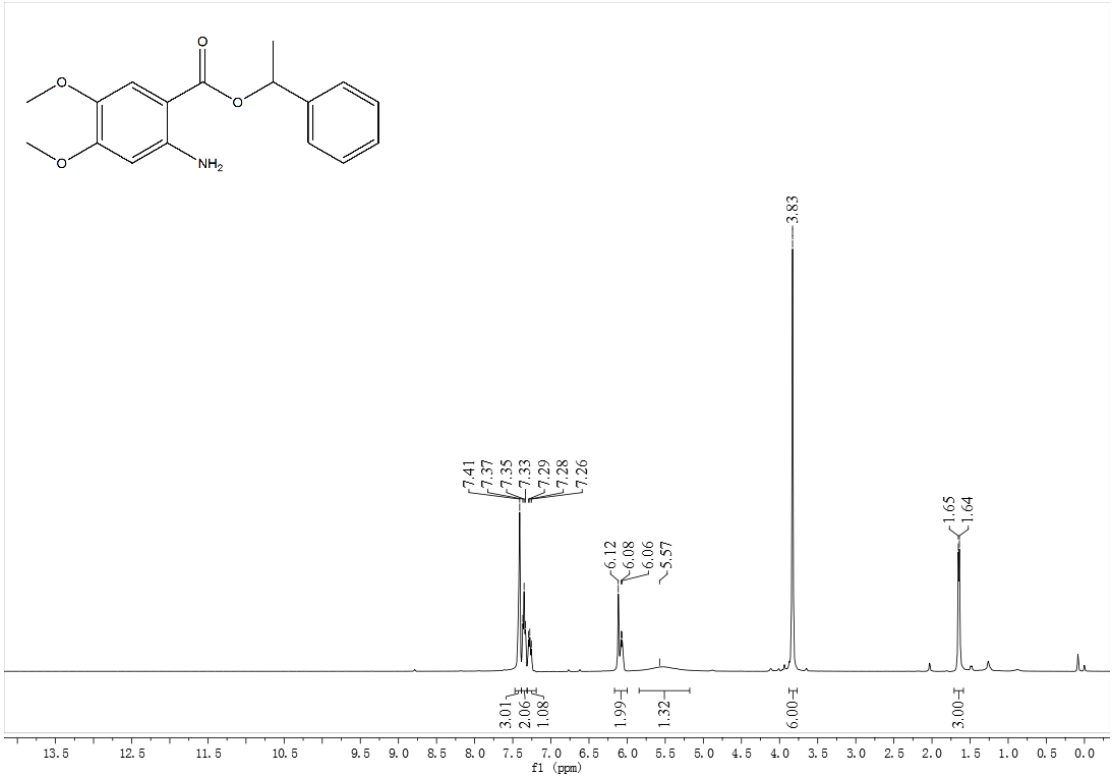
^{1}H- NMR spectrum of 3bc



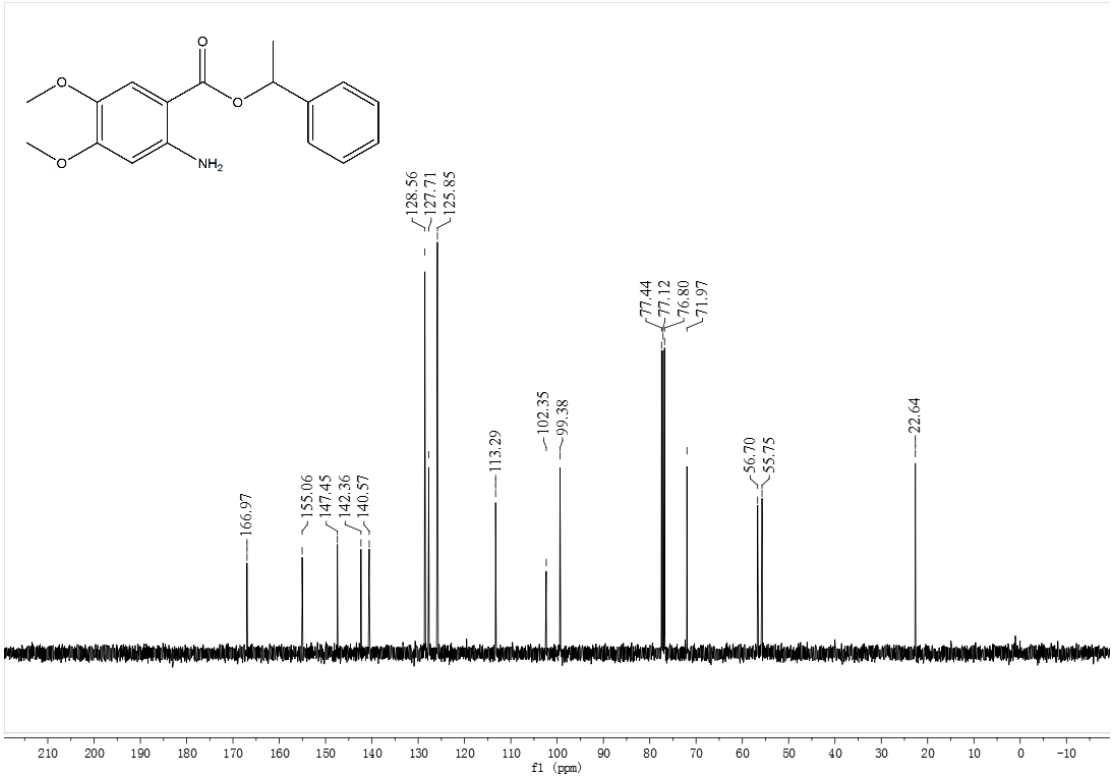
^{13}C-NMR spectrum of 3bc



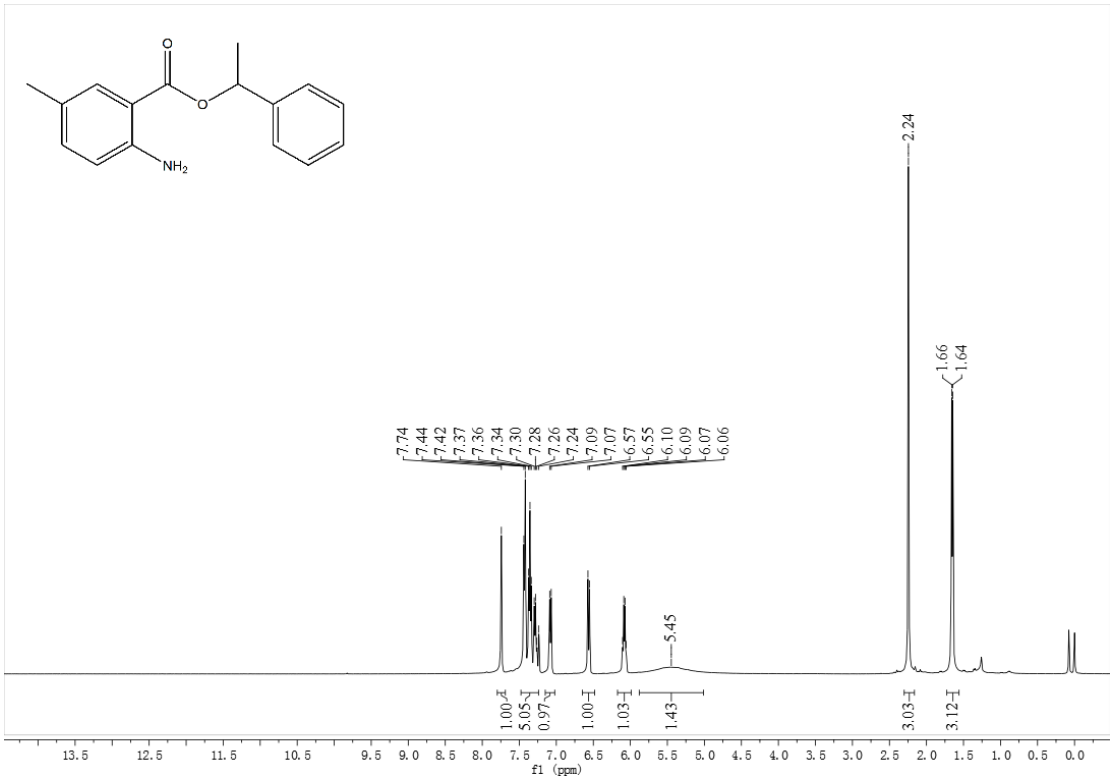
^{1}H- NMR spectrum of 3bd



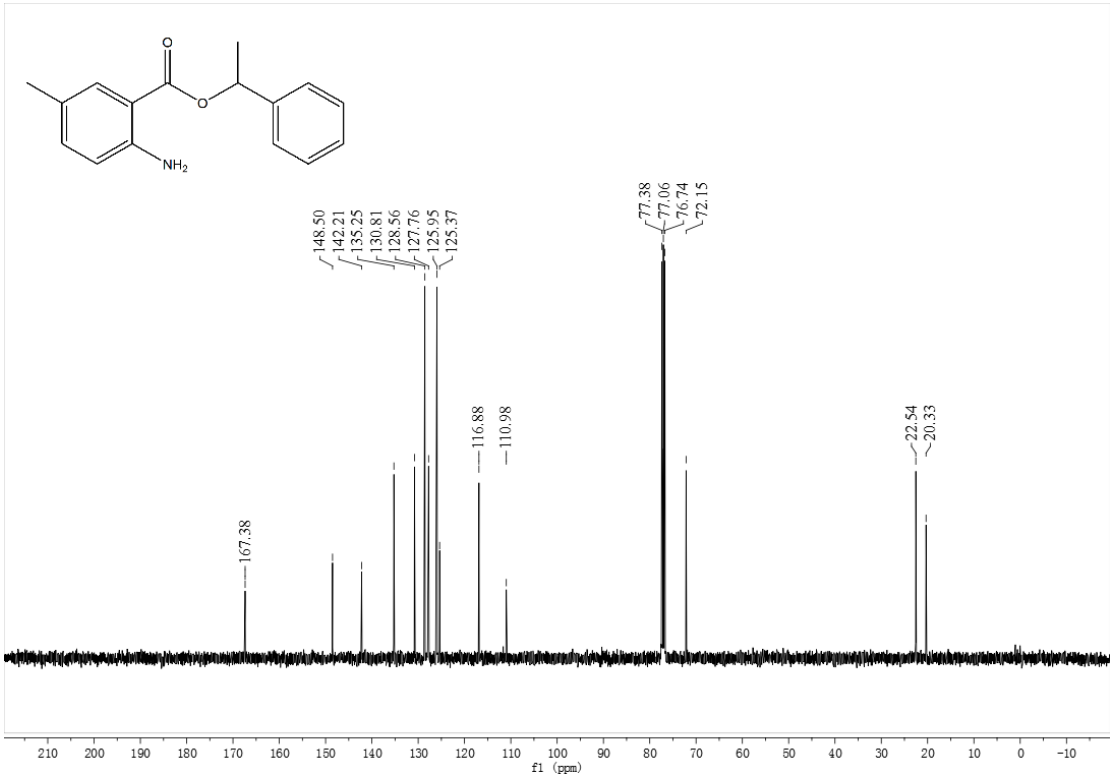
^{13}C-NMR spectrum of 3bd



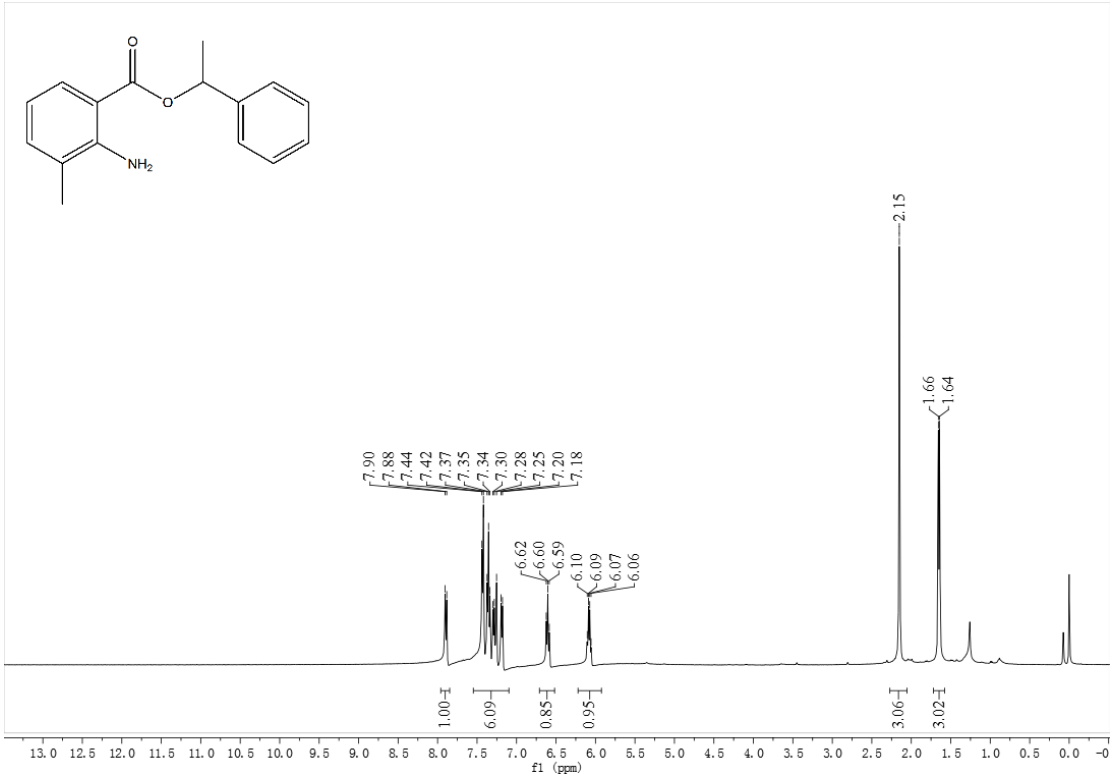
^{1}H- NMR spectrum of 3cd



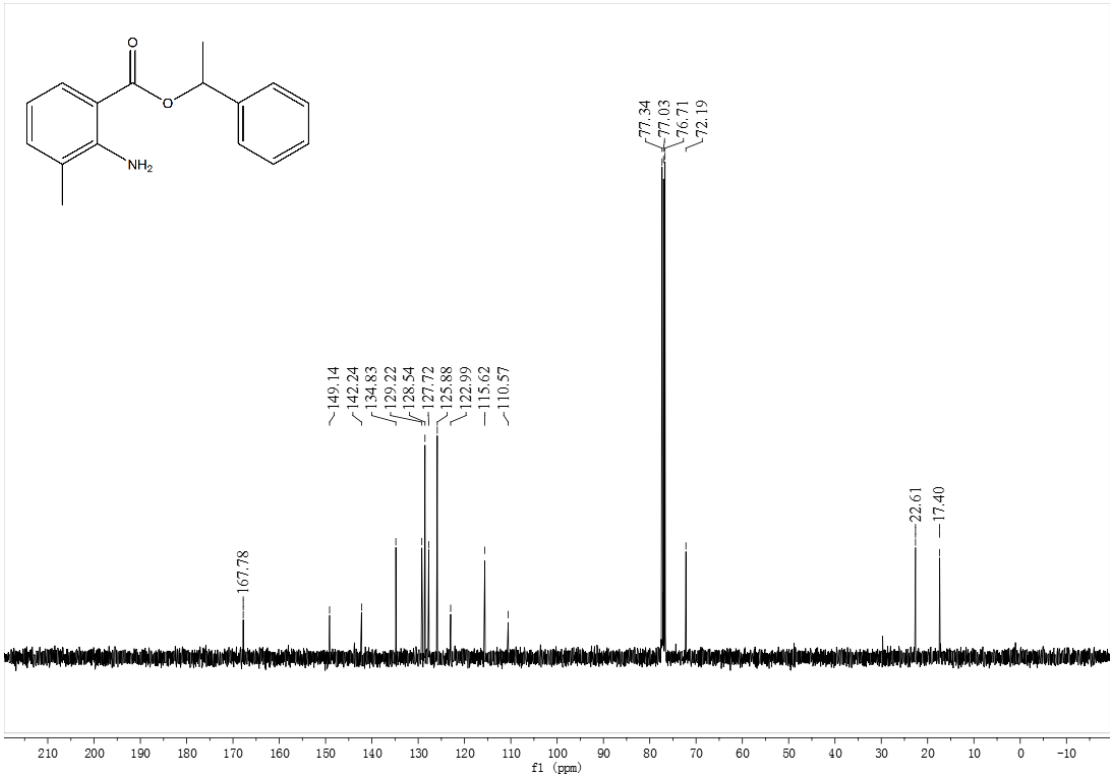
^{13}C-NMR spectrum of 3cd



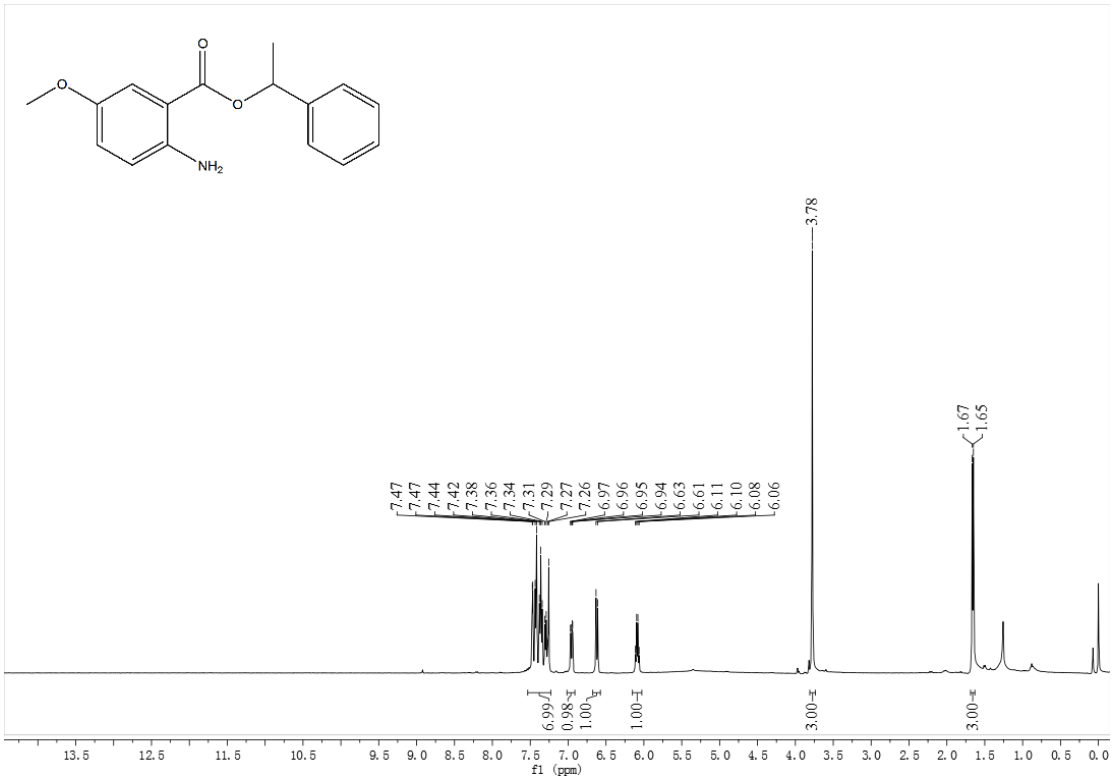
^{1}H- NMR spectrum of 3dd



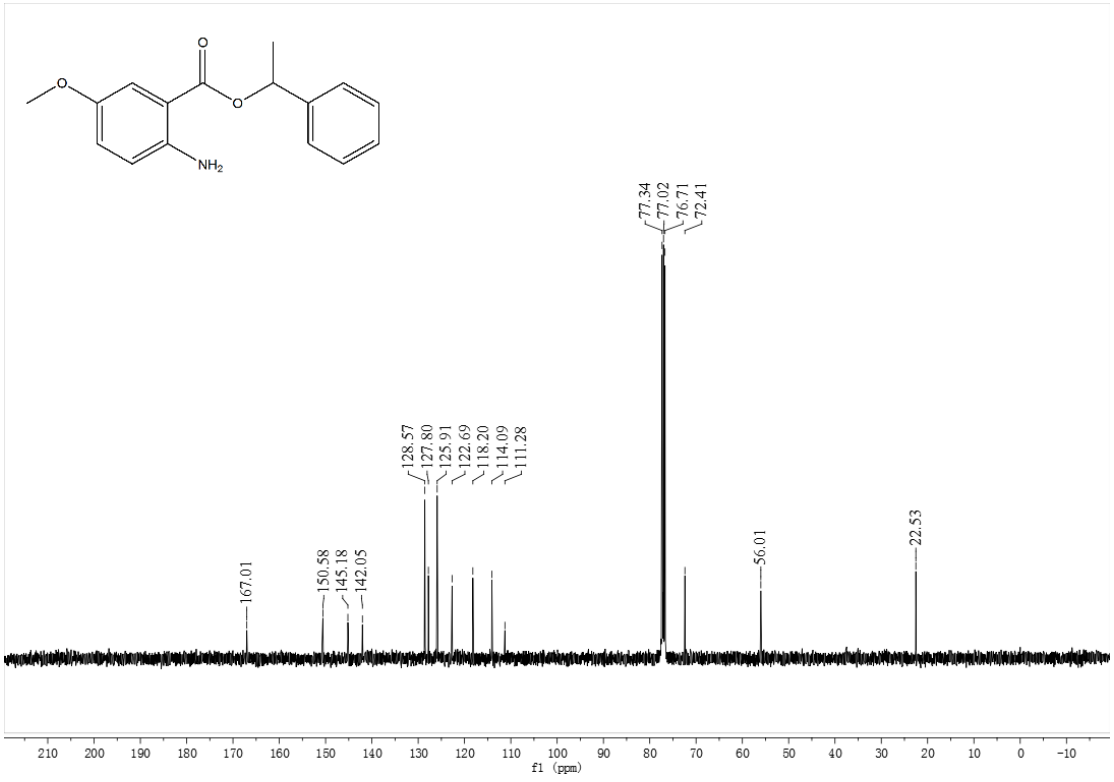
^{13}C-NMR spectrum of 3dd



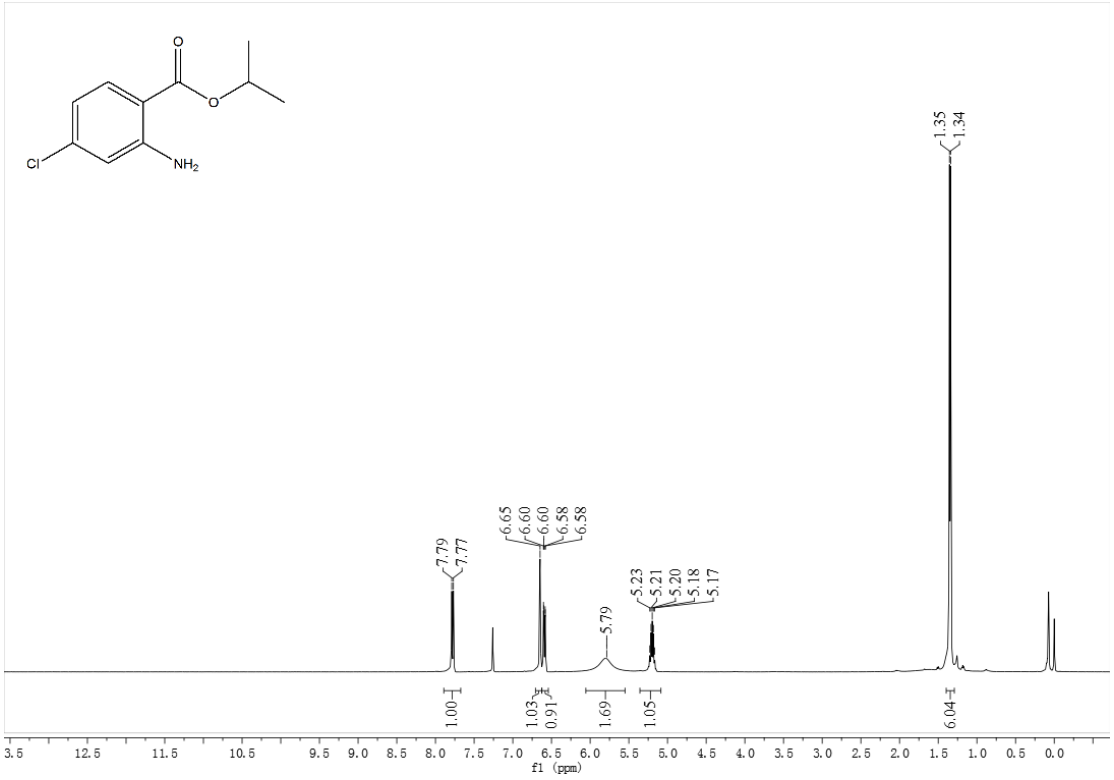
^{1}H- NMR spectrum of 3ed



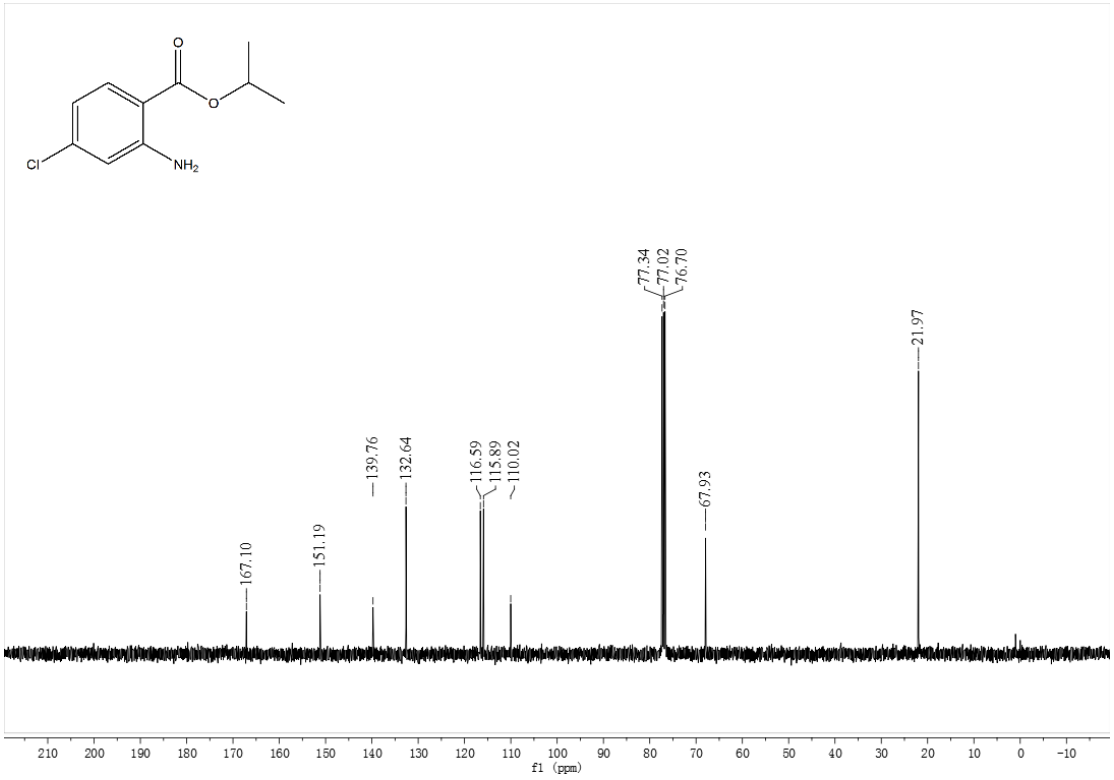
^{13}C-NMR spectrum of 3ed



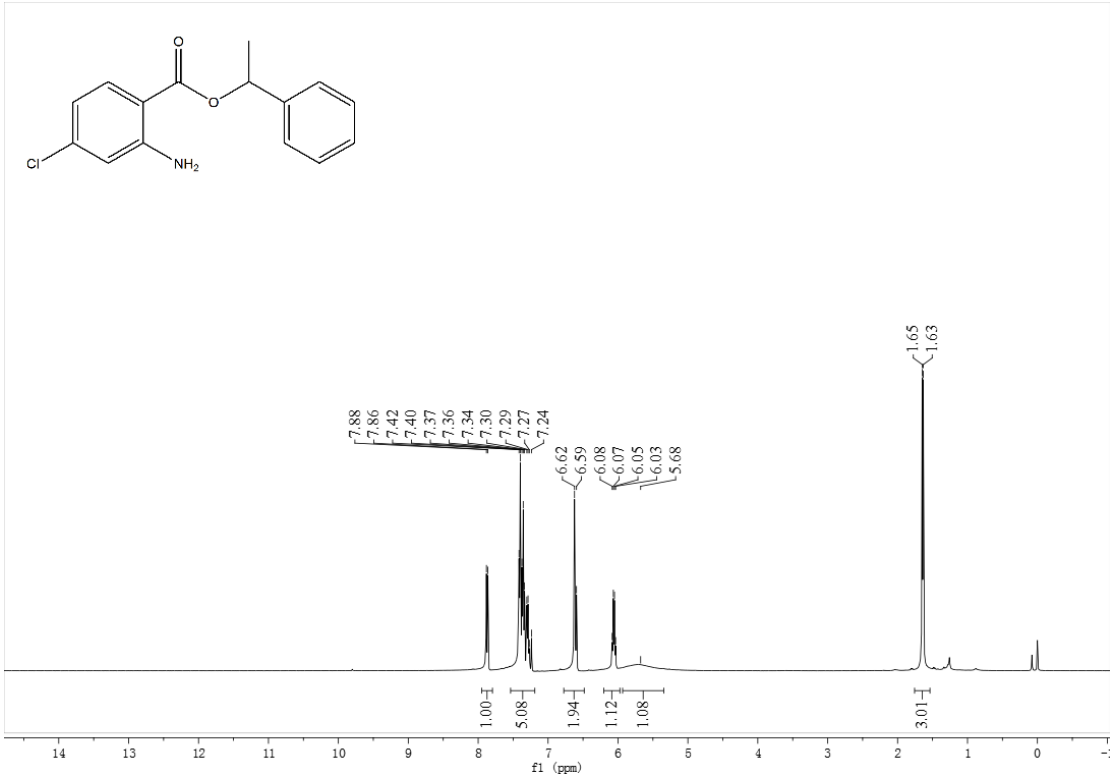
^{1}H- NMR spectrum of 3fa



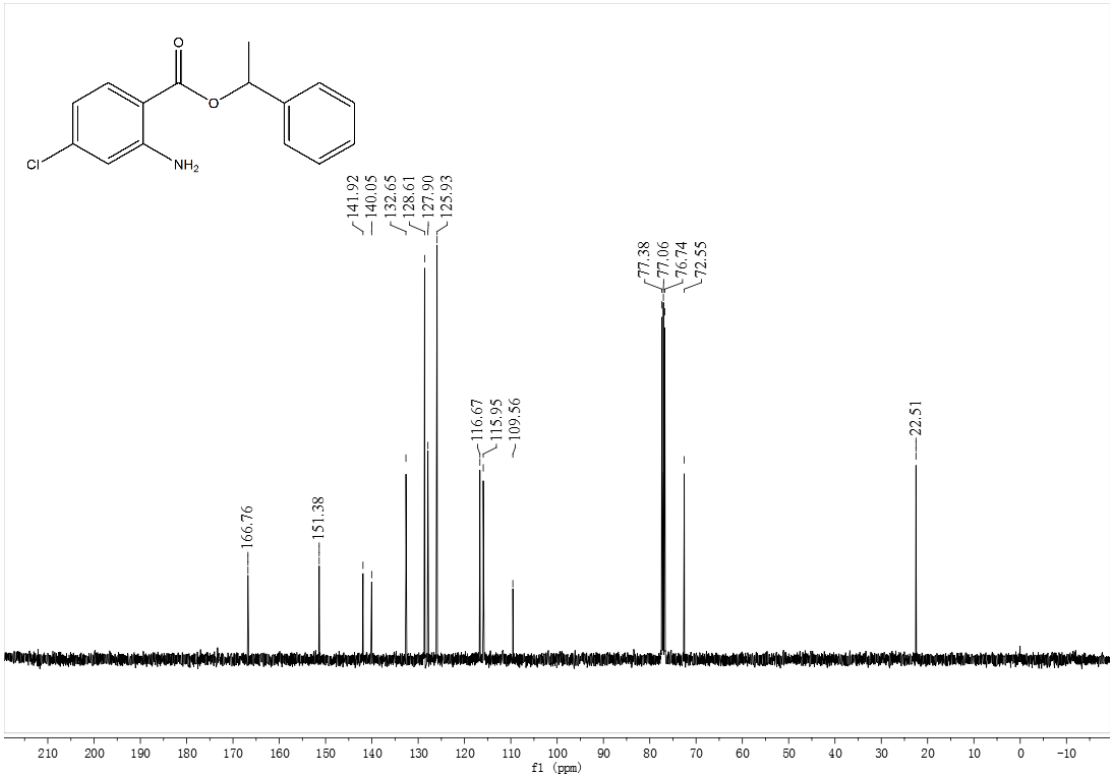
^{13}C-NMR spectrum of 3fa



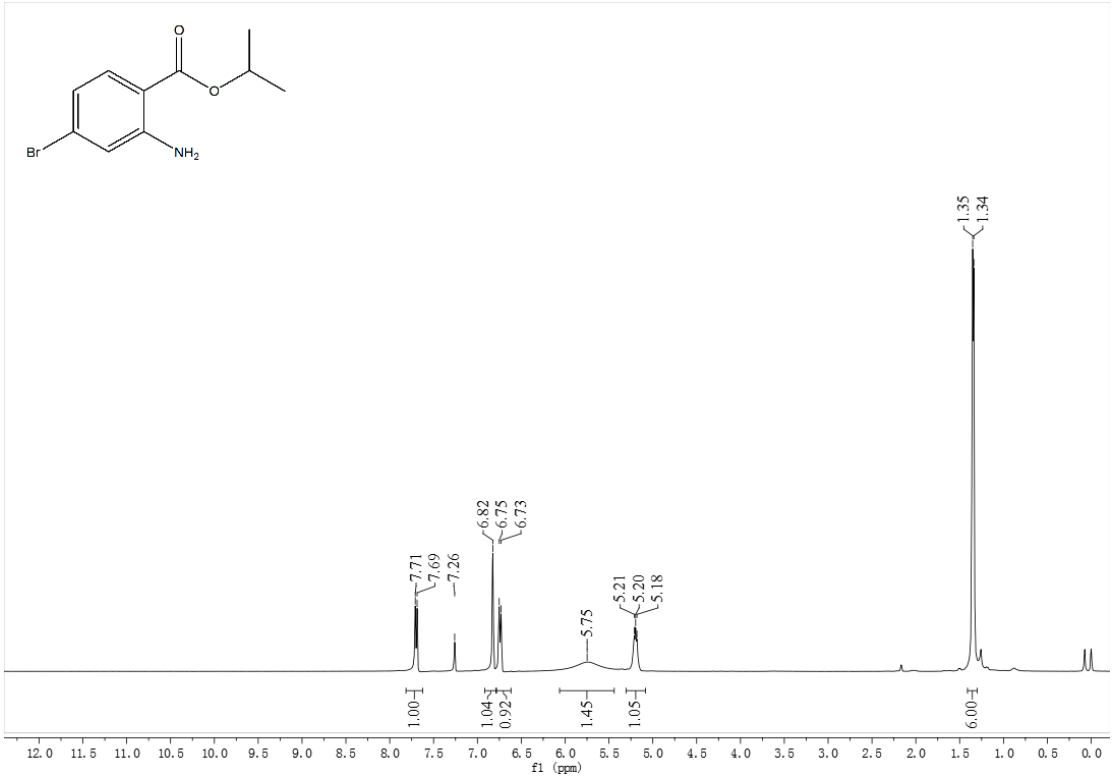
^{1}H- NMR spectrum of 3fd



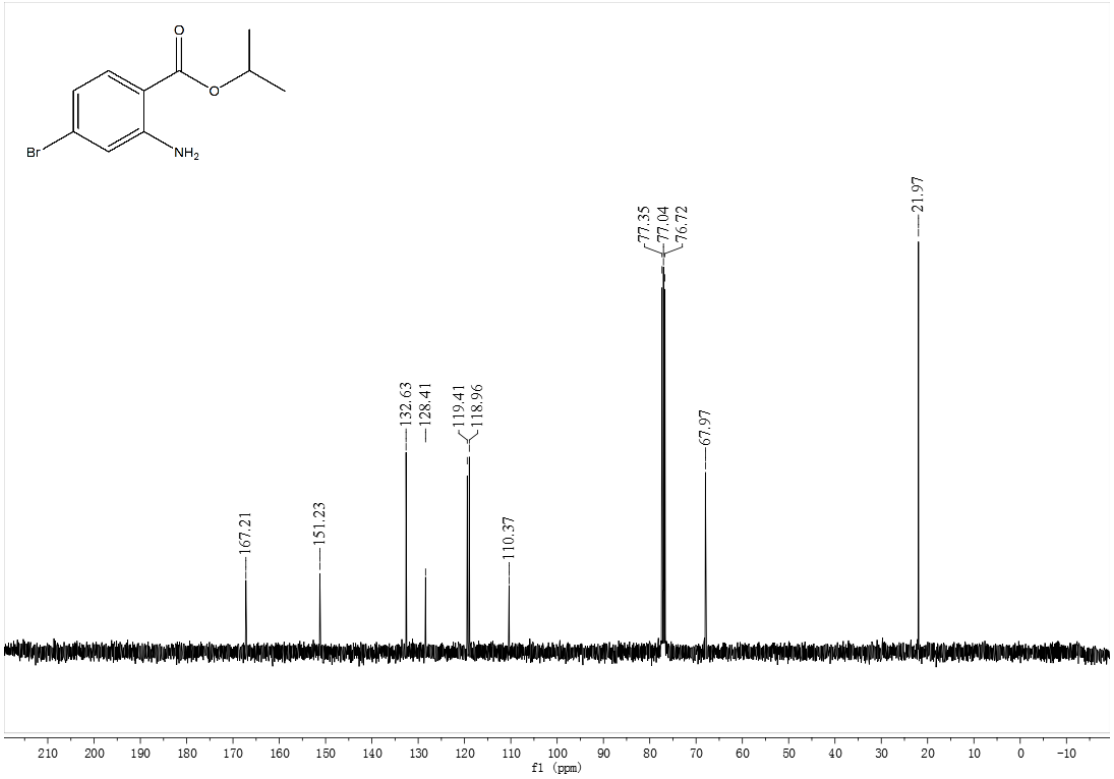
^{13}C-NMR spectrum of 3fd



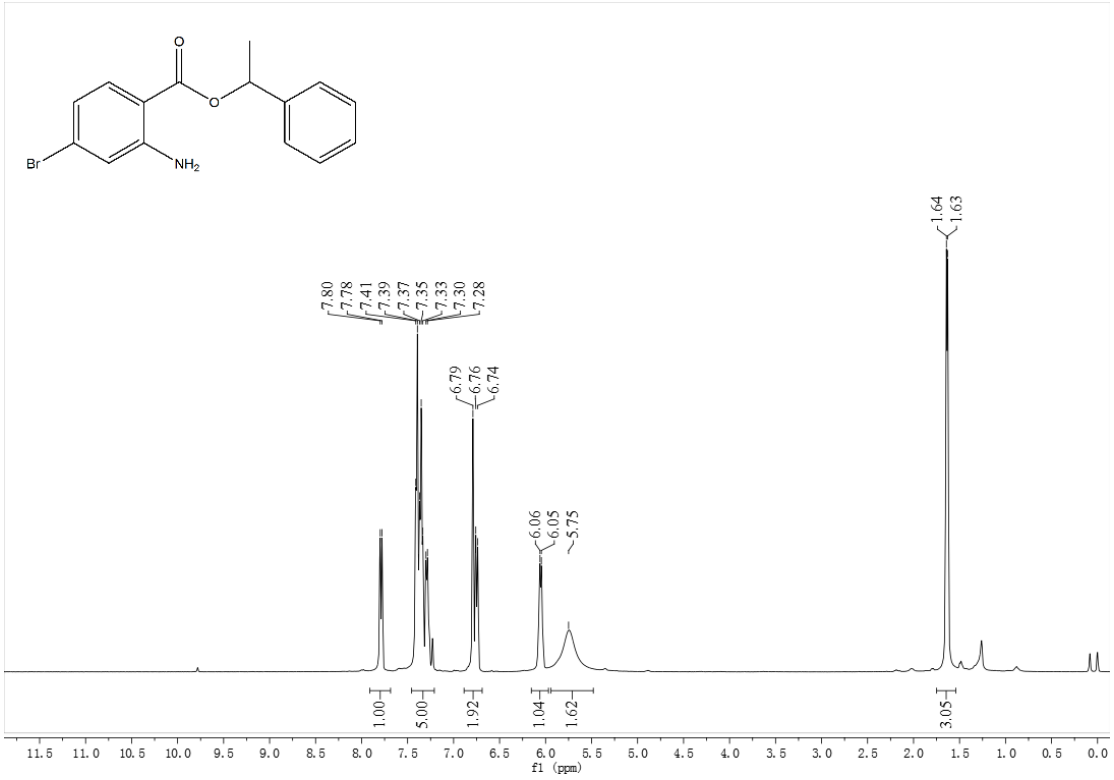
^{1}H- NMR spectrum of 3ga



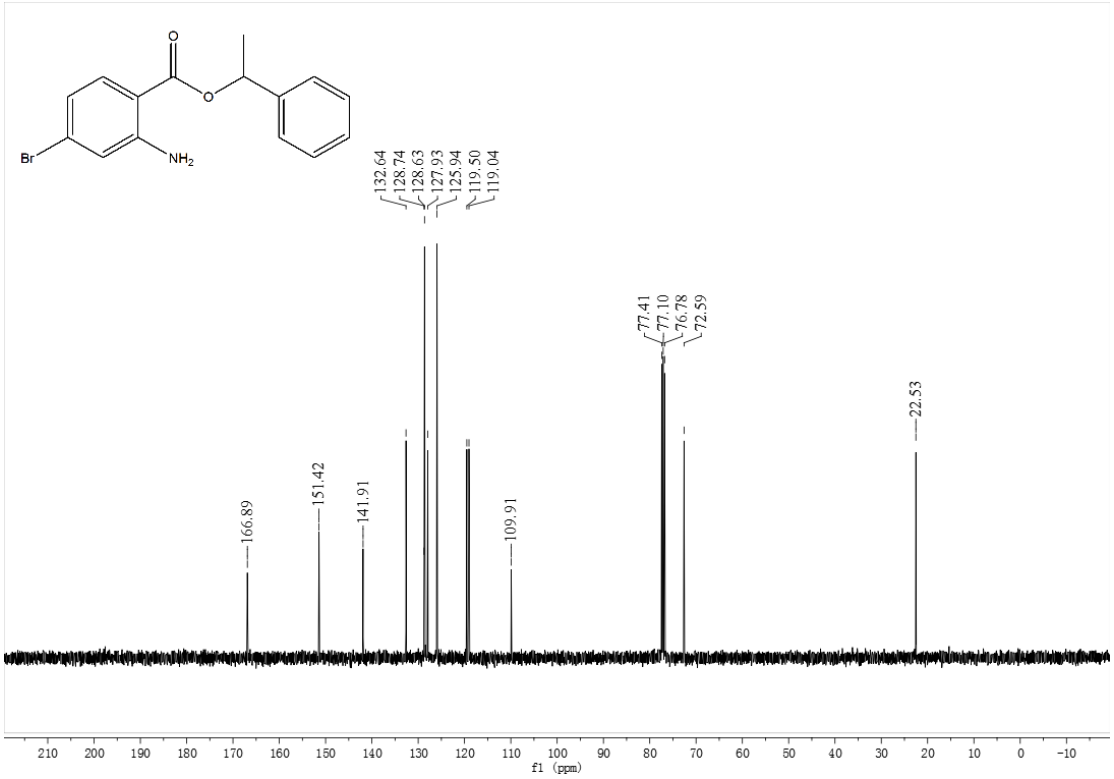
^{13}C-NMR spectrum of 3ga



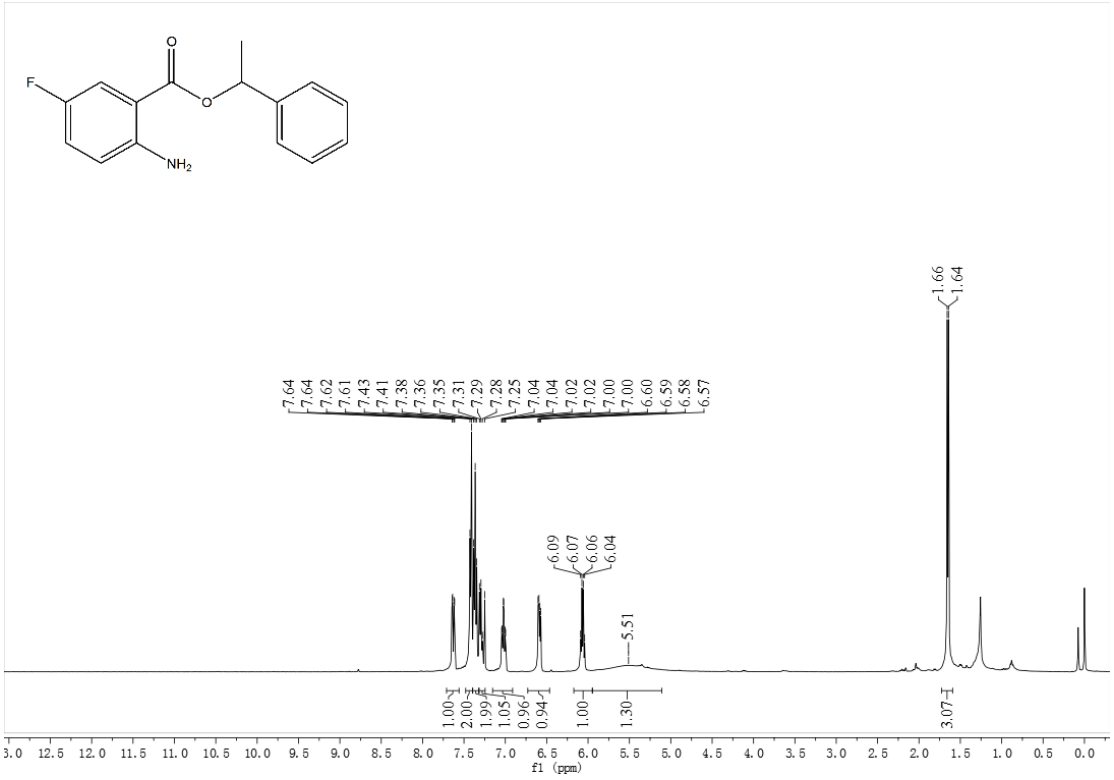
^{1}H- NMR spectrum of 3gd



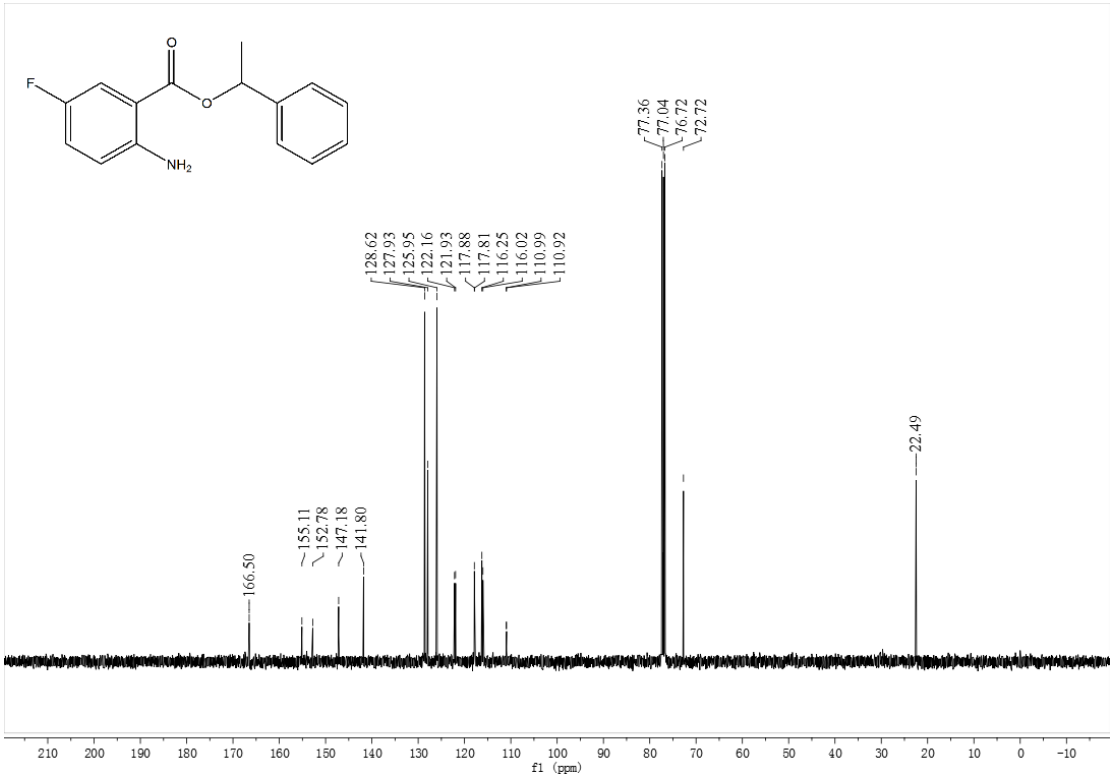
^{13}C-NMR spectrum of 3gd



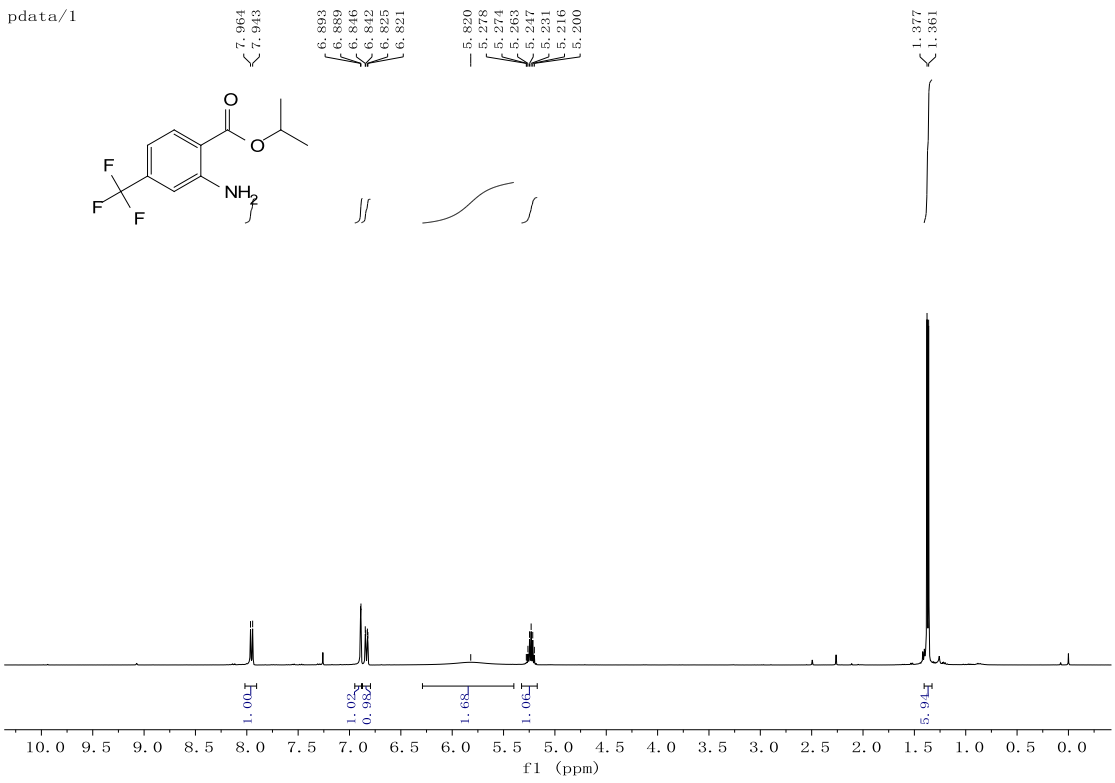
^{1}H- NMR spectrum of 3hd



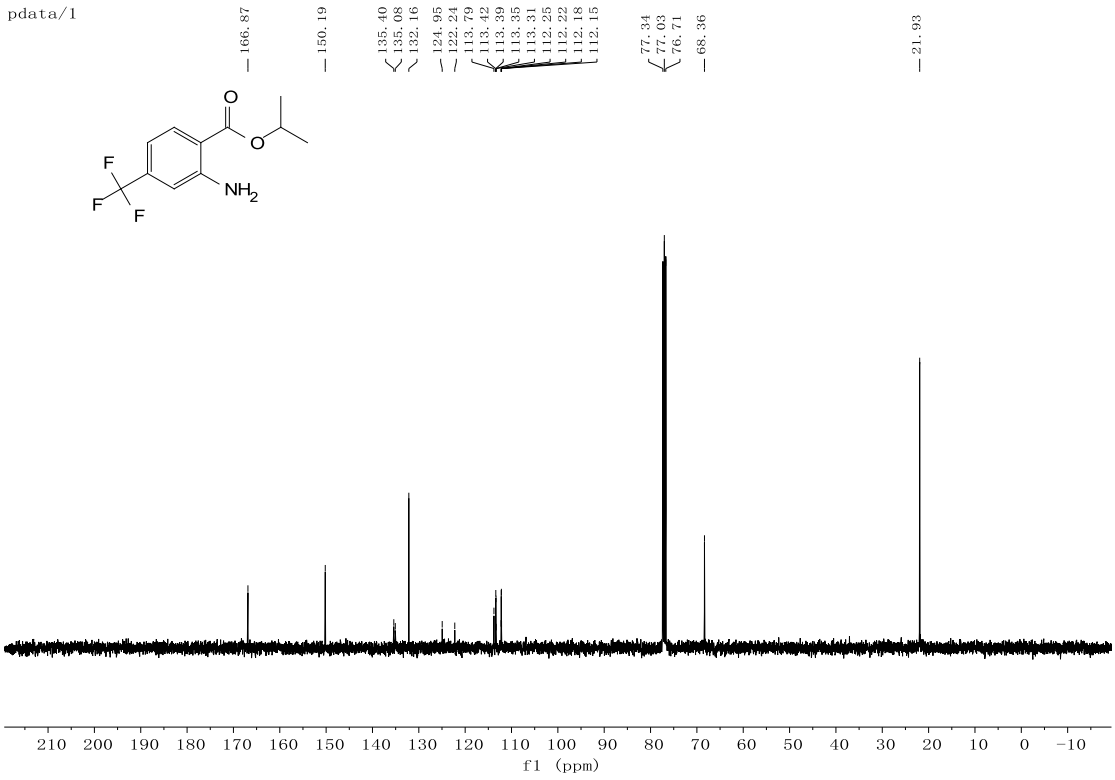
^{13}C-NMR spectrum of 3hd



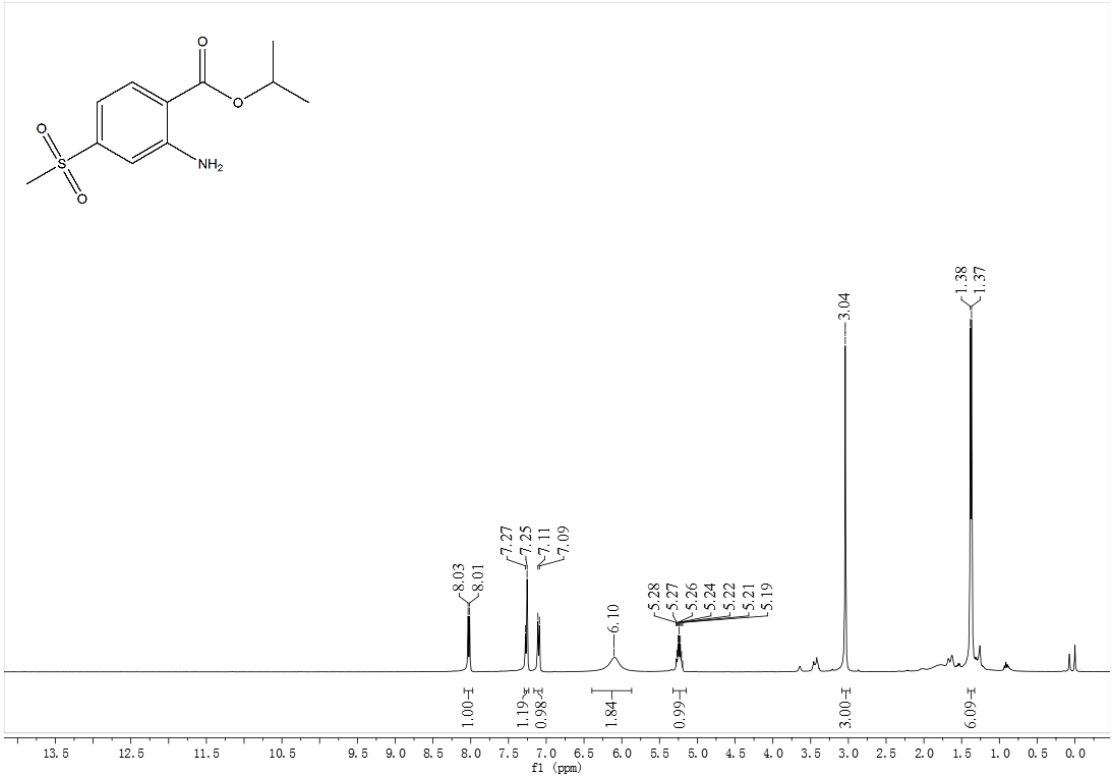
^{1}H- NMR spectrum of 3ia



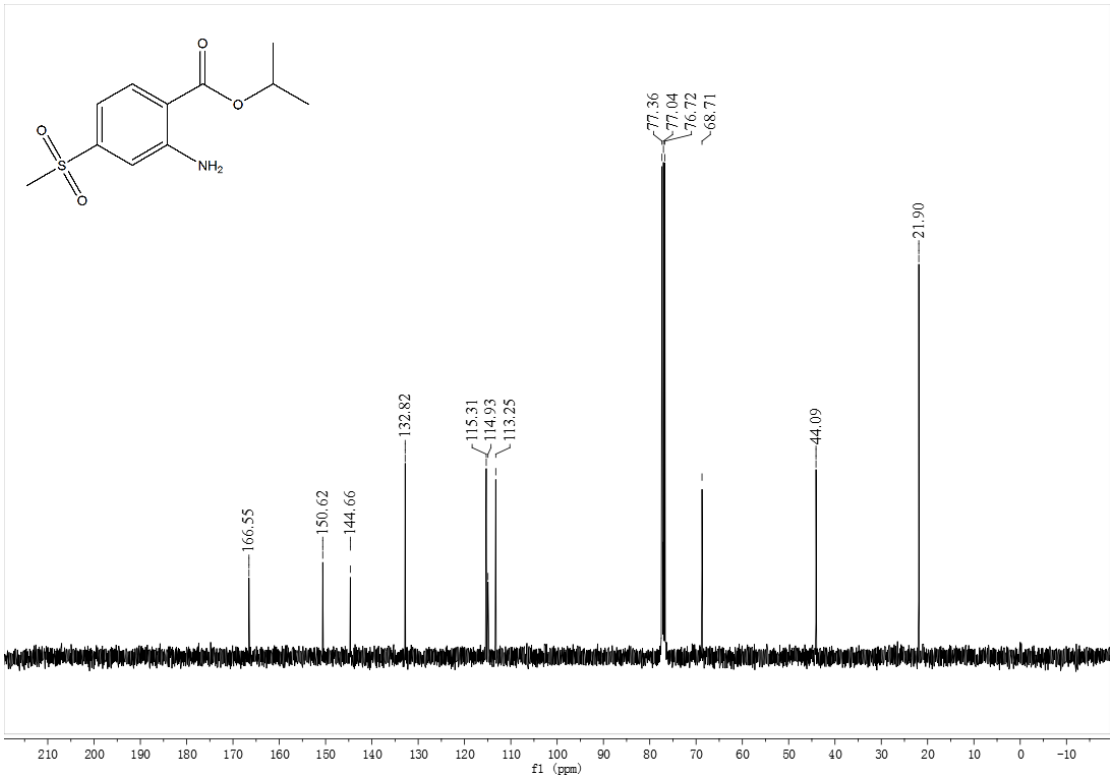
^{13}C-NMR spectrum of 3ia



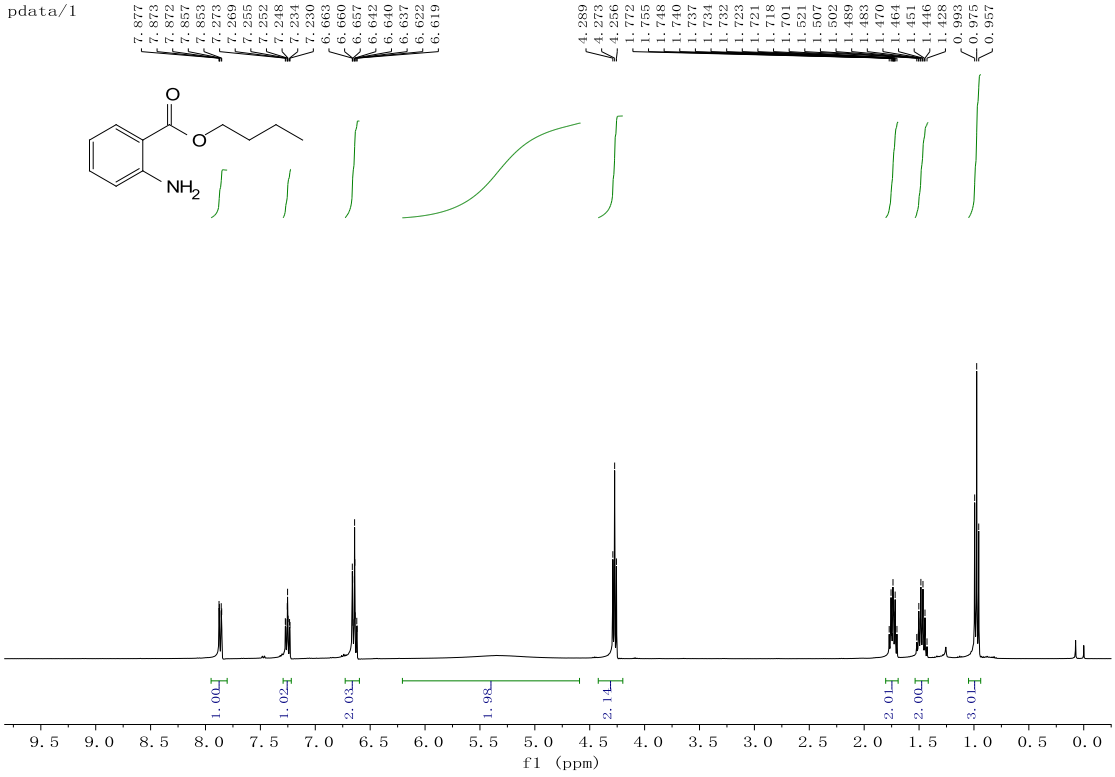
^{1}H- NMR spectrum of 3ja



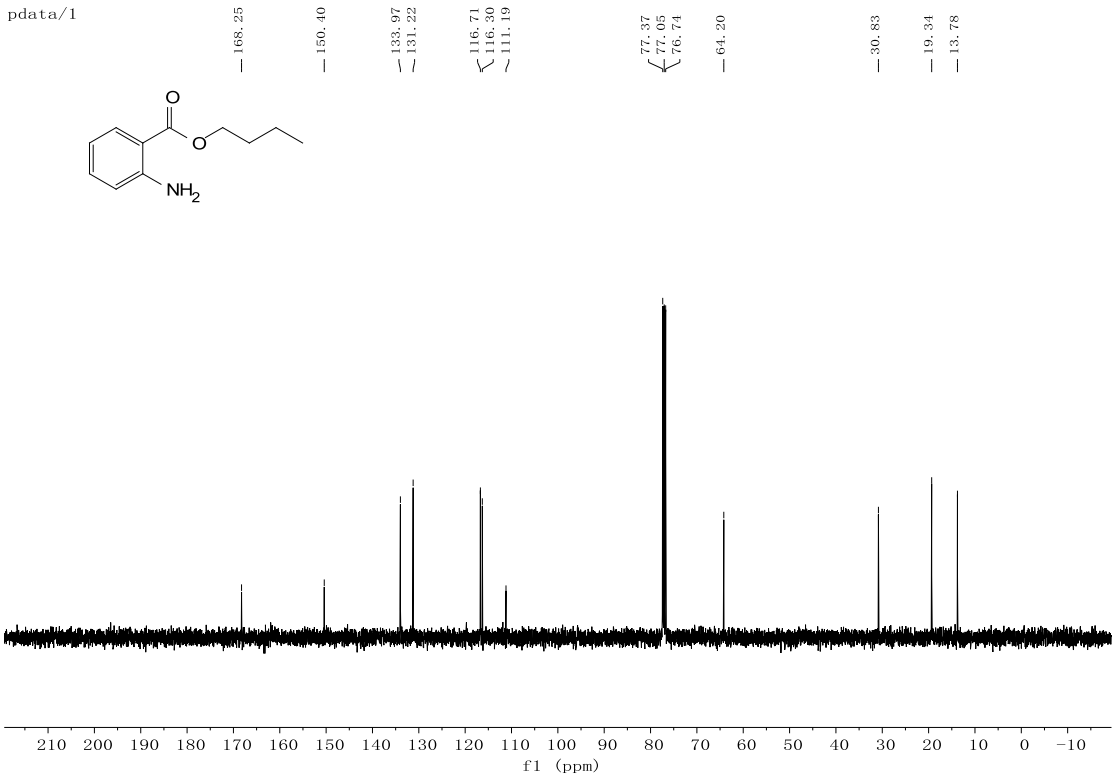
^{13}C-NMR spectrum of 3ja



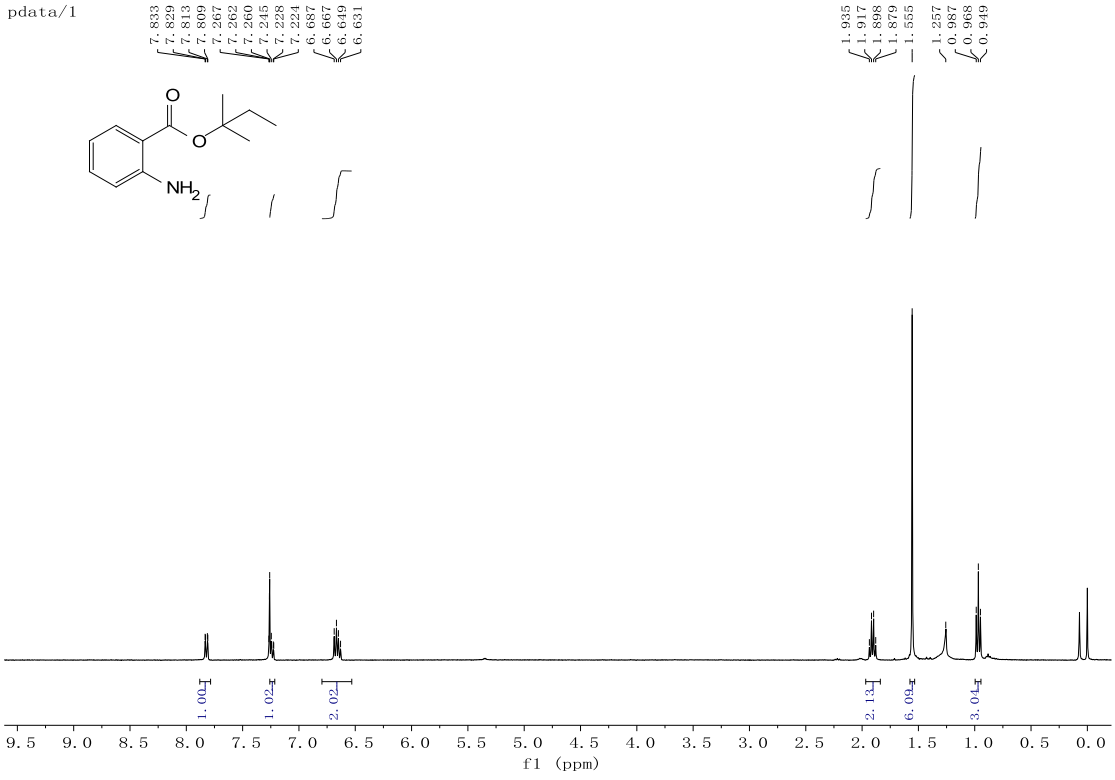
^{1}H- NMR spectrum of 3af



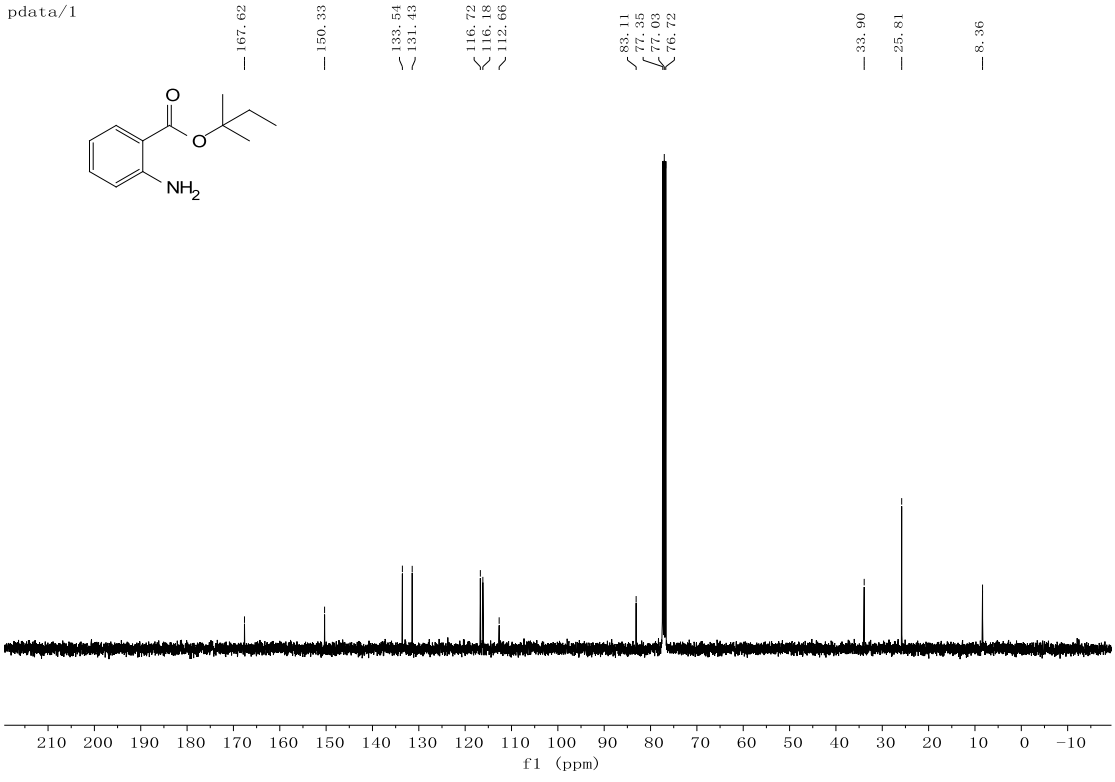
^{13}C-NMR spectrum of 3af



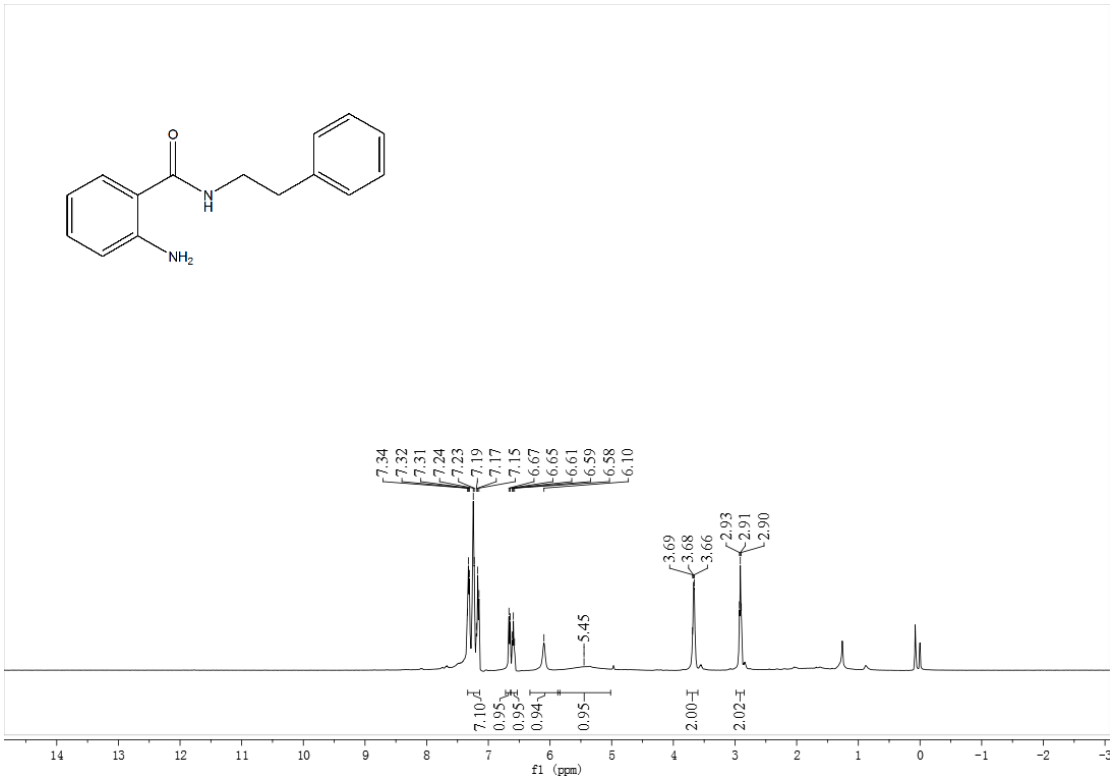
^{1}H- NMR spectrum of 3ag



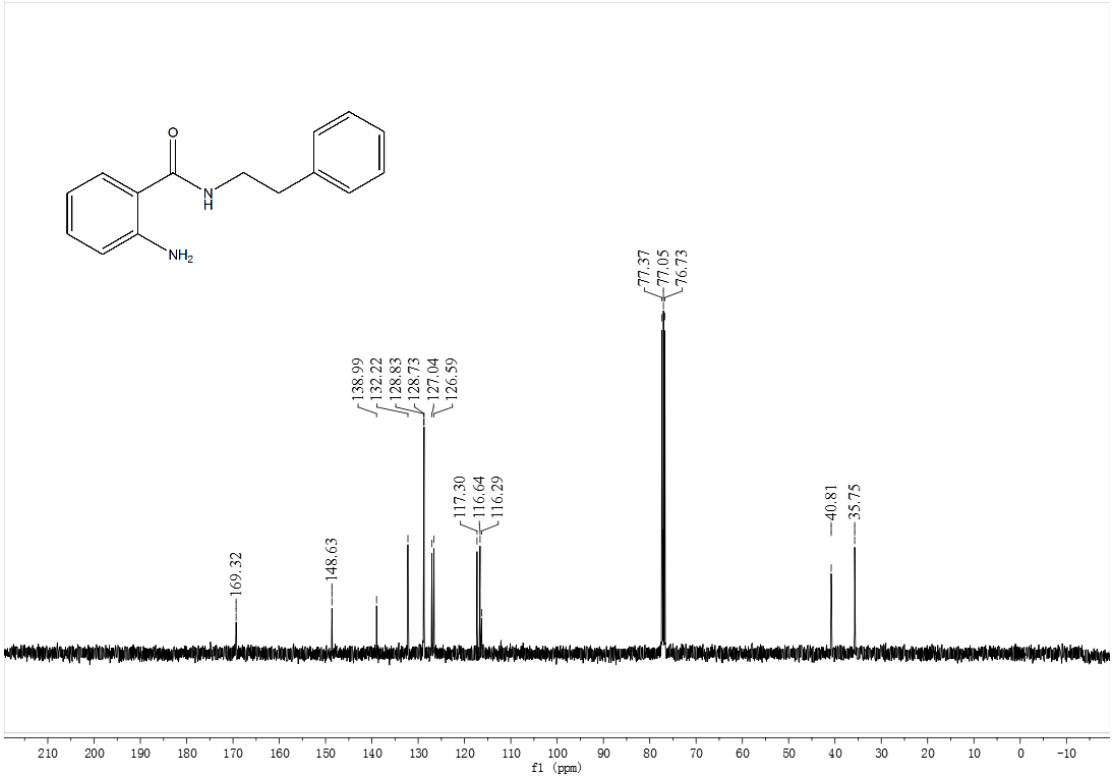
^{13}C-NMR spectrum of 3ag



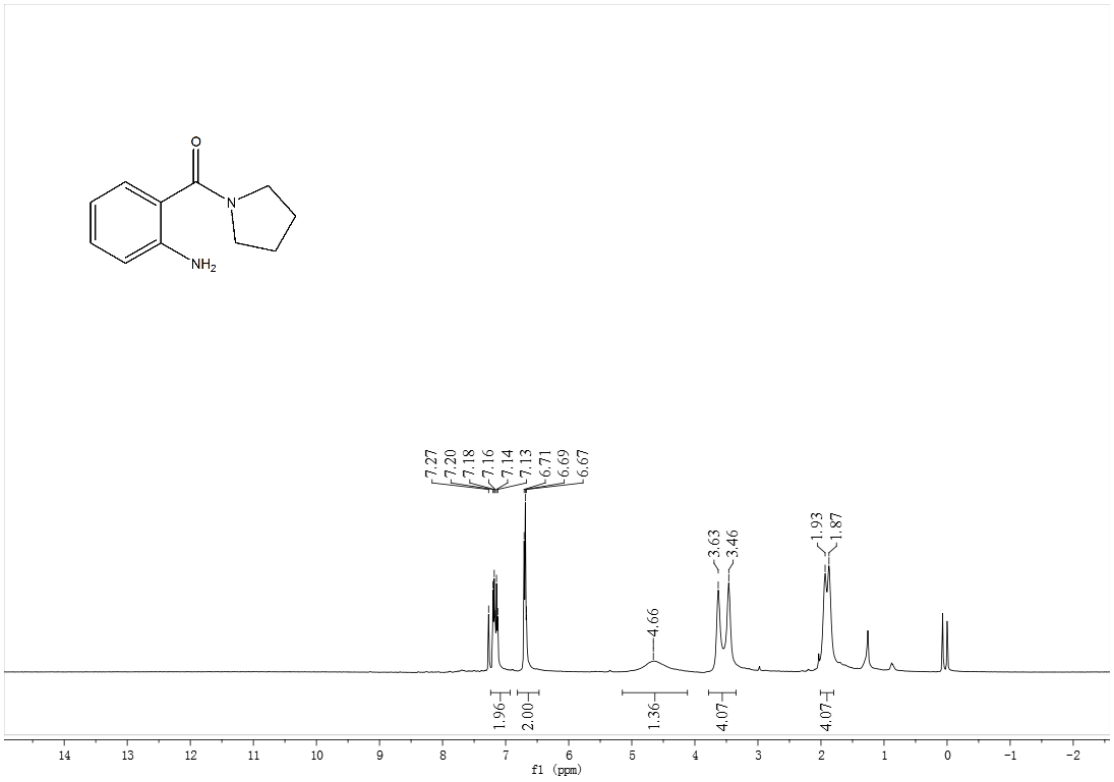
^{1}H- NMR spectrum of 5aa



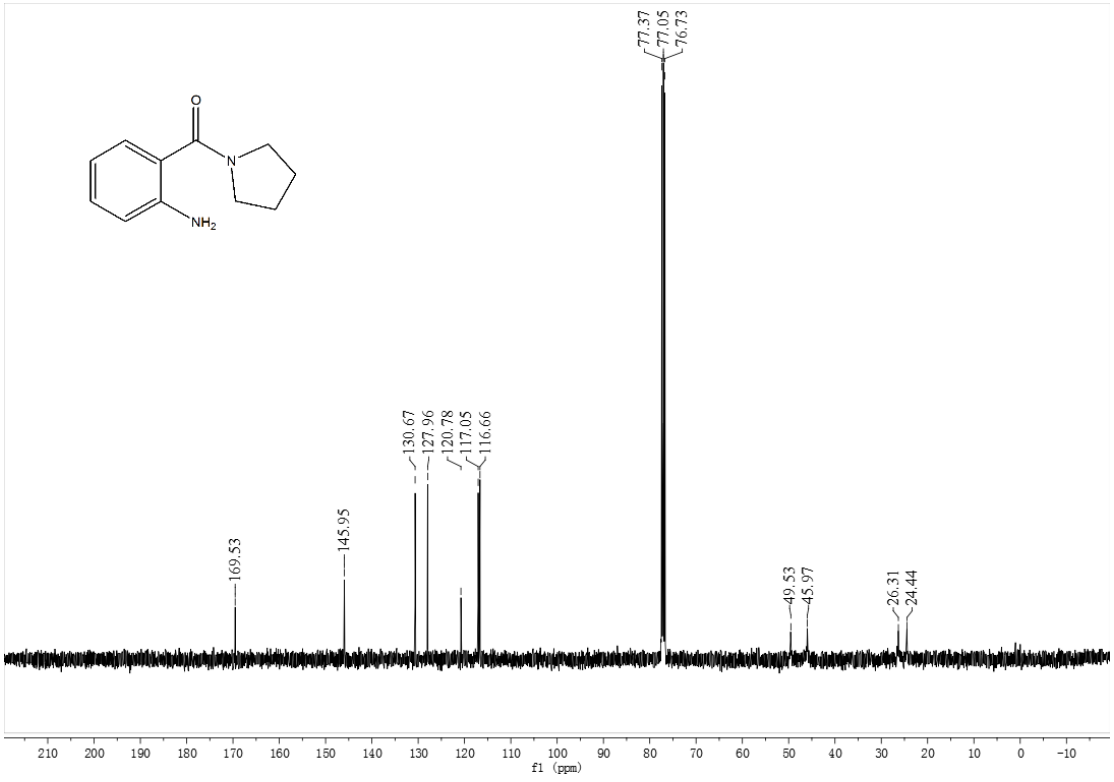
^{13}C-NMR spectrum of 5aa



^{1}H- NMR spectrum of 5ab

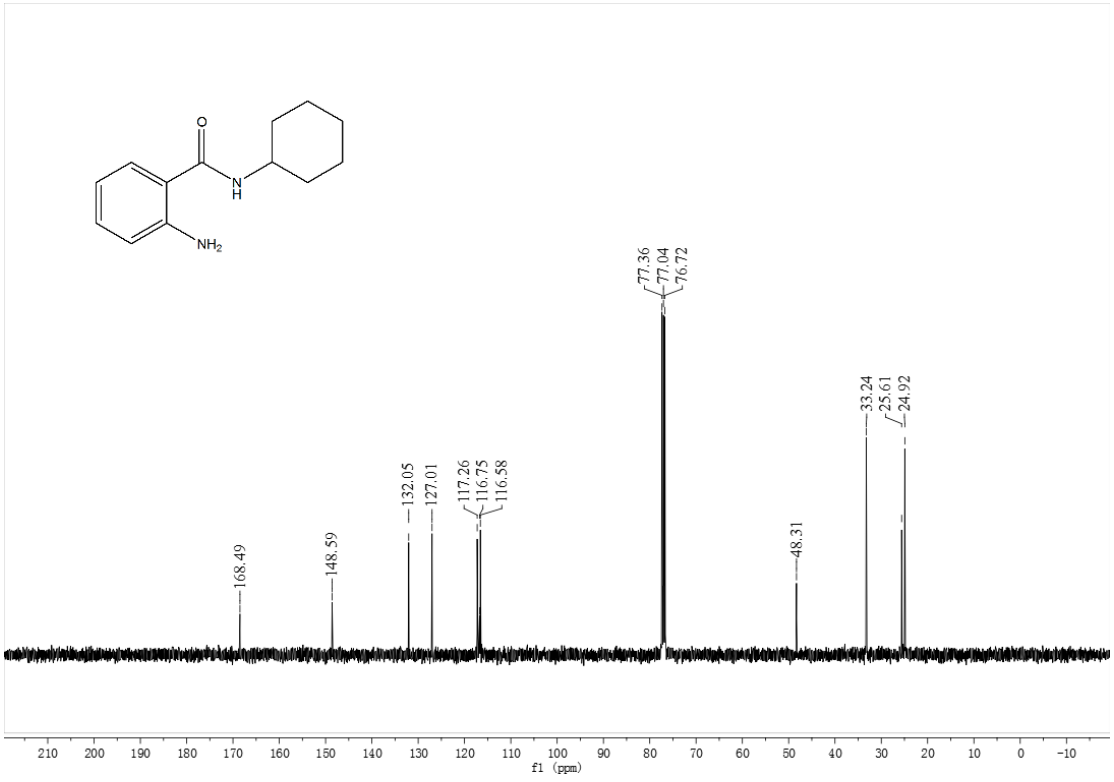


^{13}C-NMR spectrum of 5ab

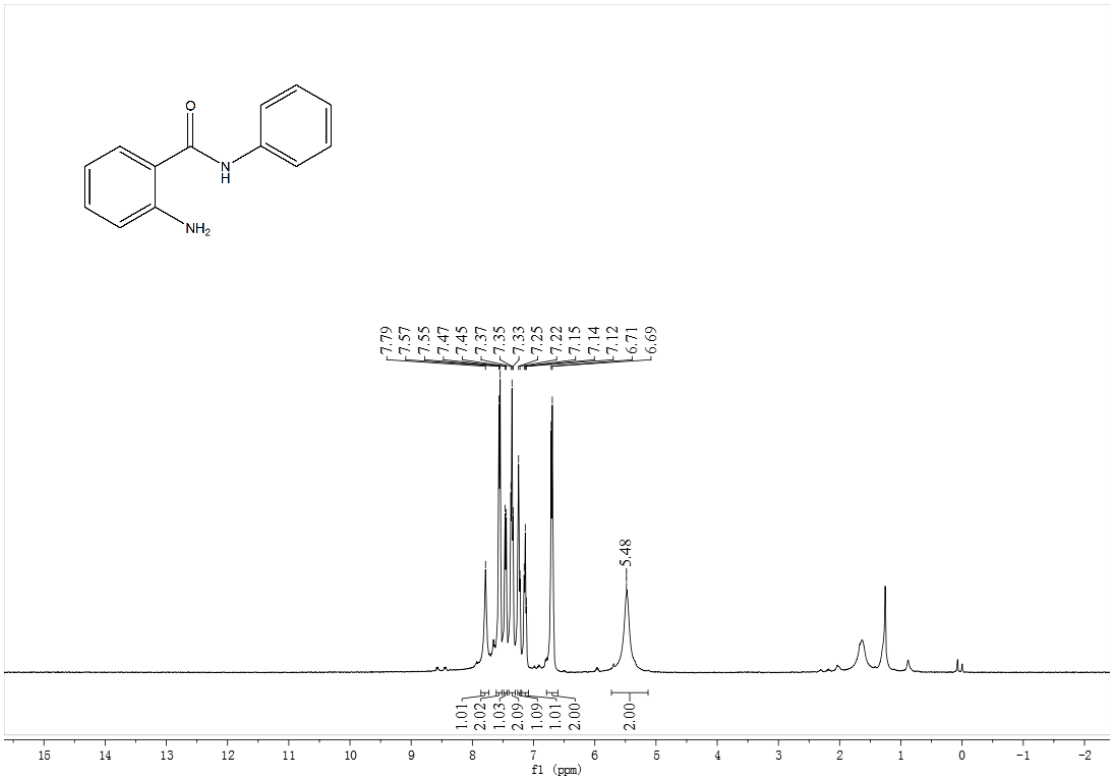


^{1}H- NMR spectrum of 5ac

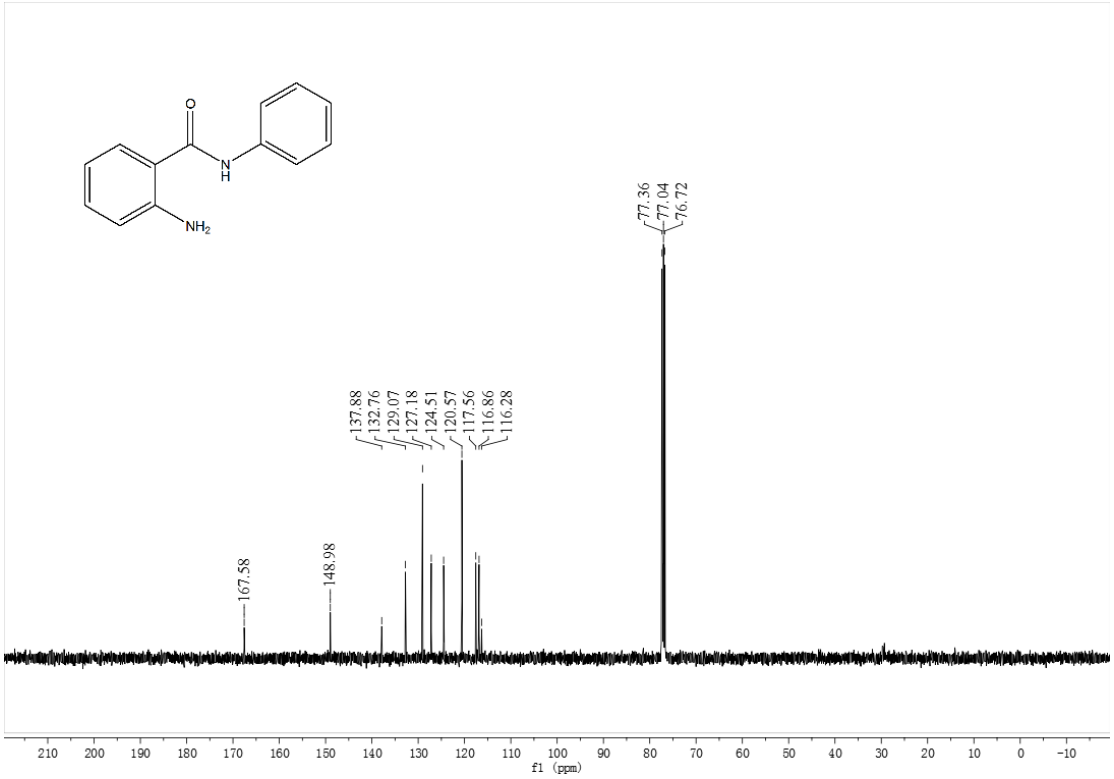
^{13}C-NMR spectrum of 5ac



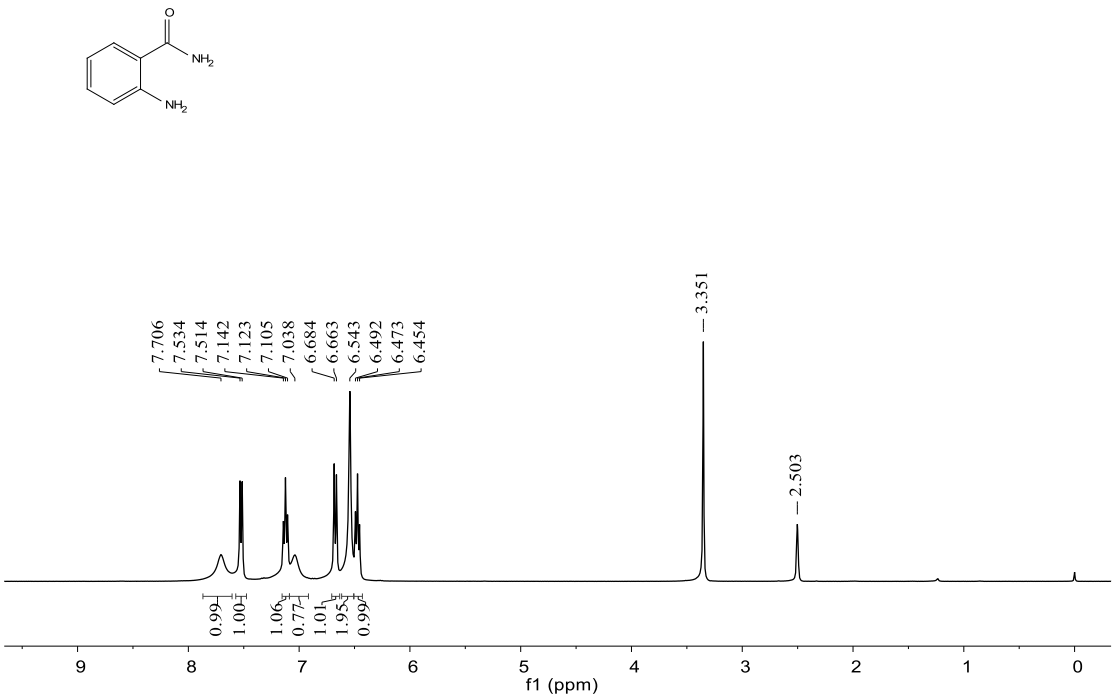
^{1}H- NMR spectrum of 5ad



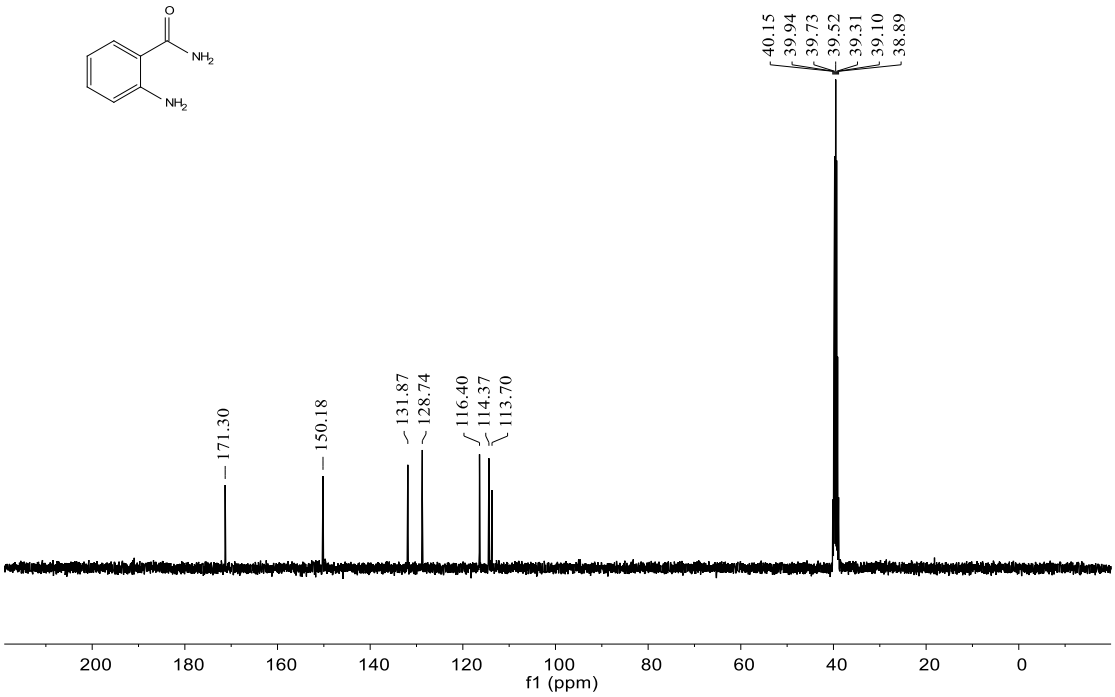
^{13}C-NMR spectrum of 5ad



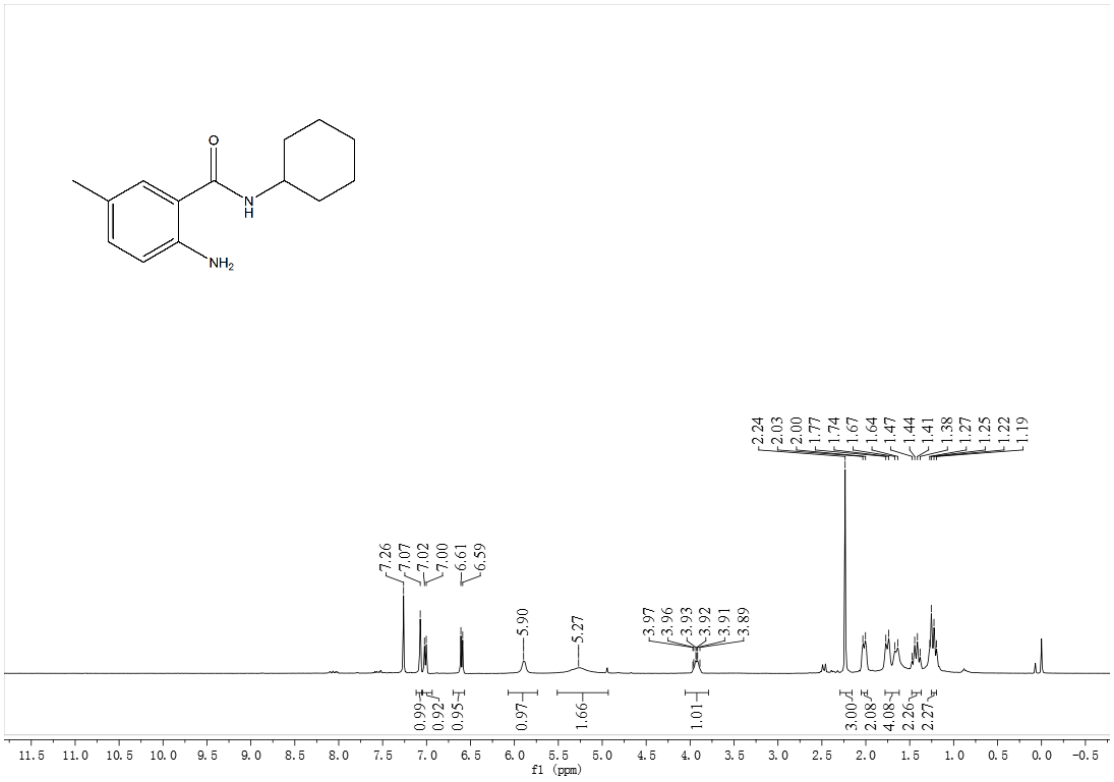
^{1}H- NMR spectrum of 5ae



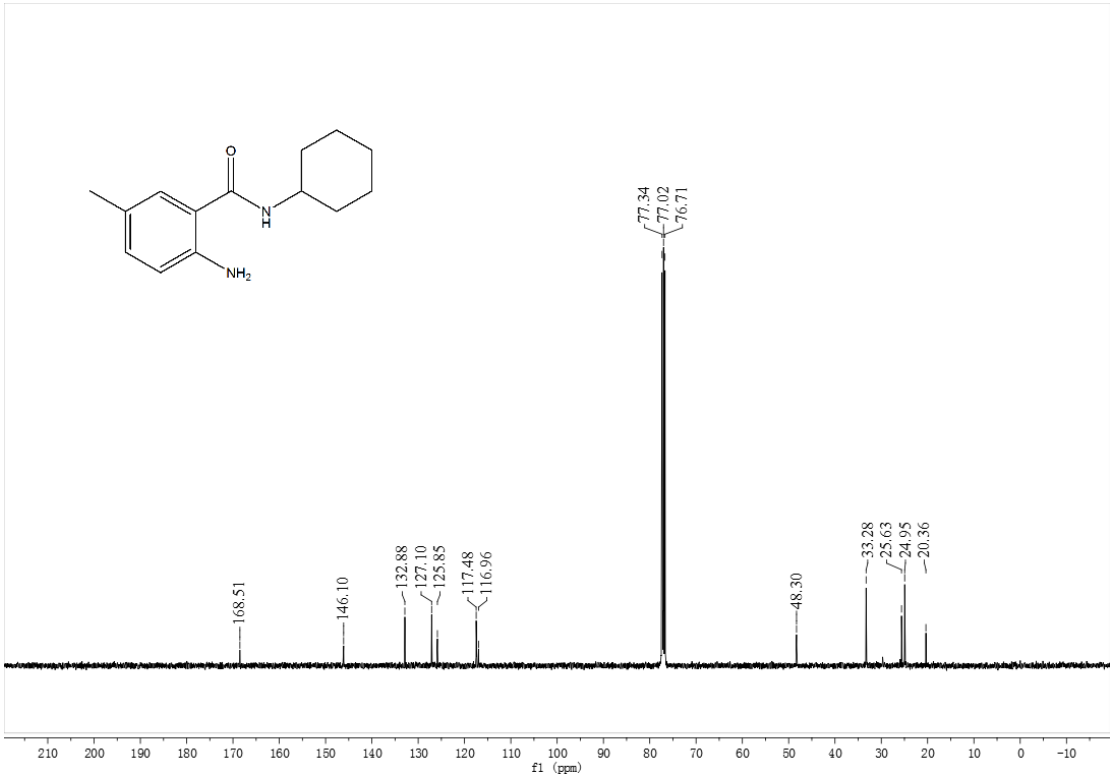
^{13}C-NMR spectrum of 5ae



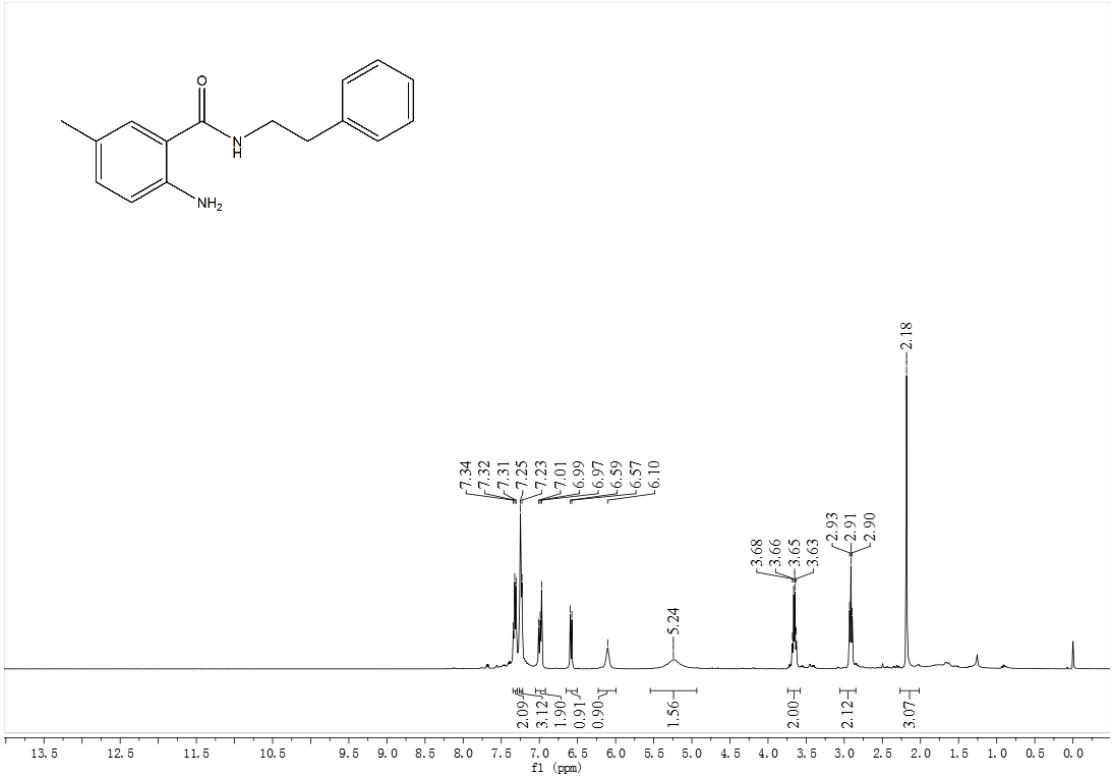
^{1}H- NMR spectrum of 5cc



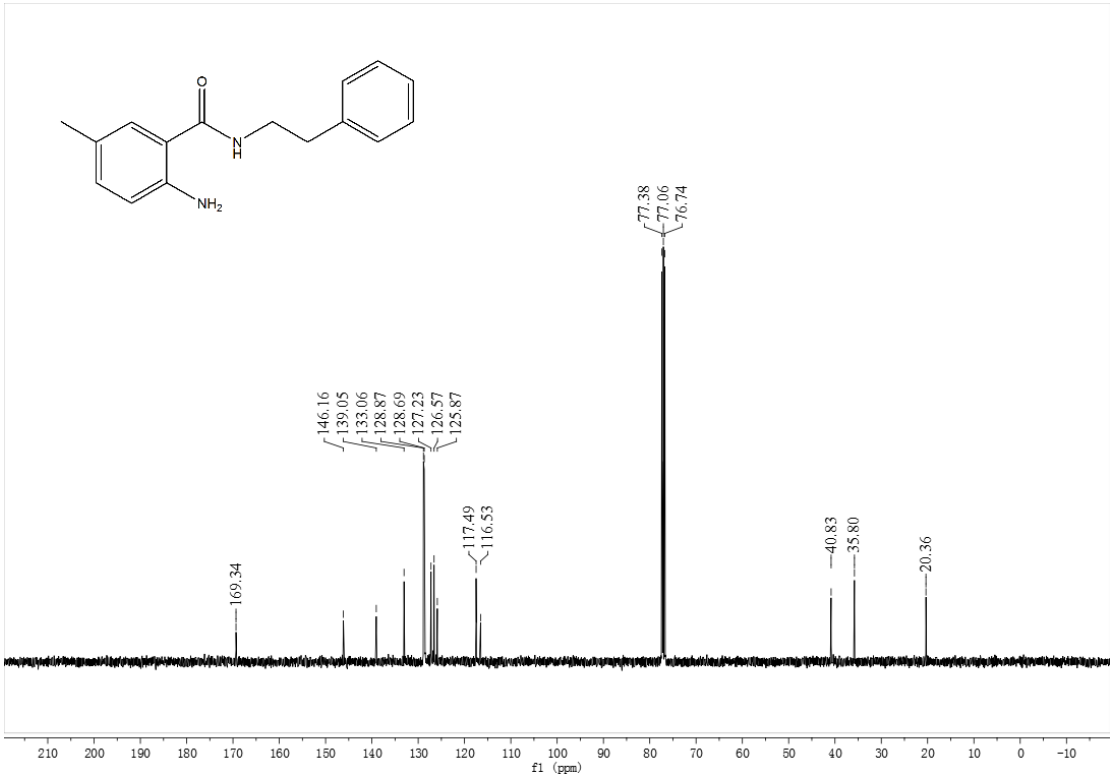
^{13}C-NMR spectrum of 5cc



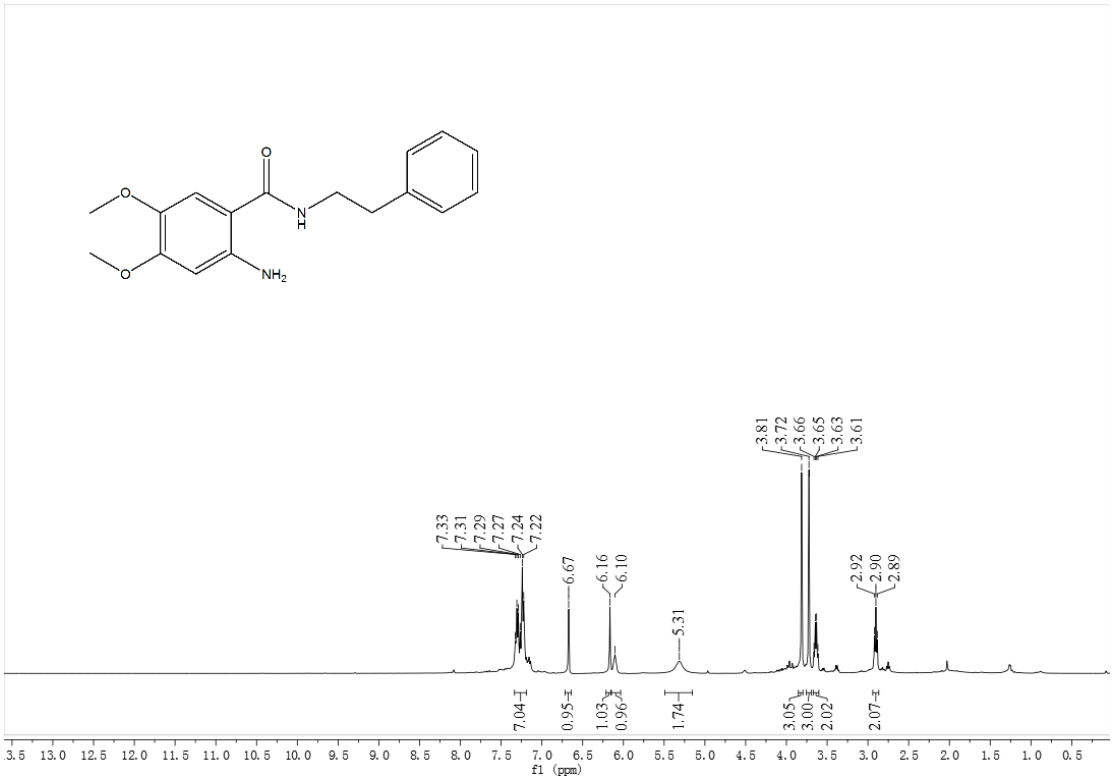
^{1}H- NMR spectrum of 5ca



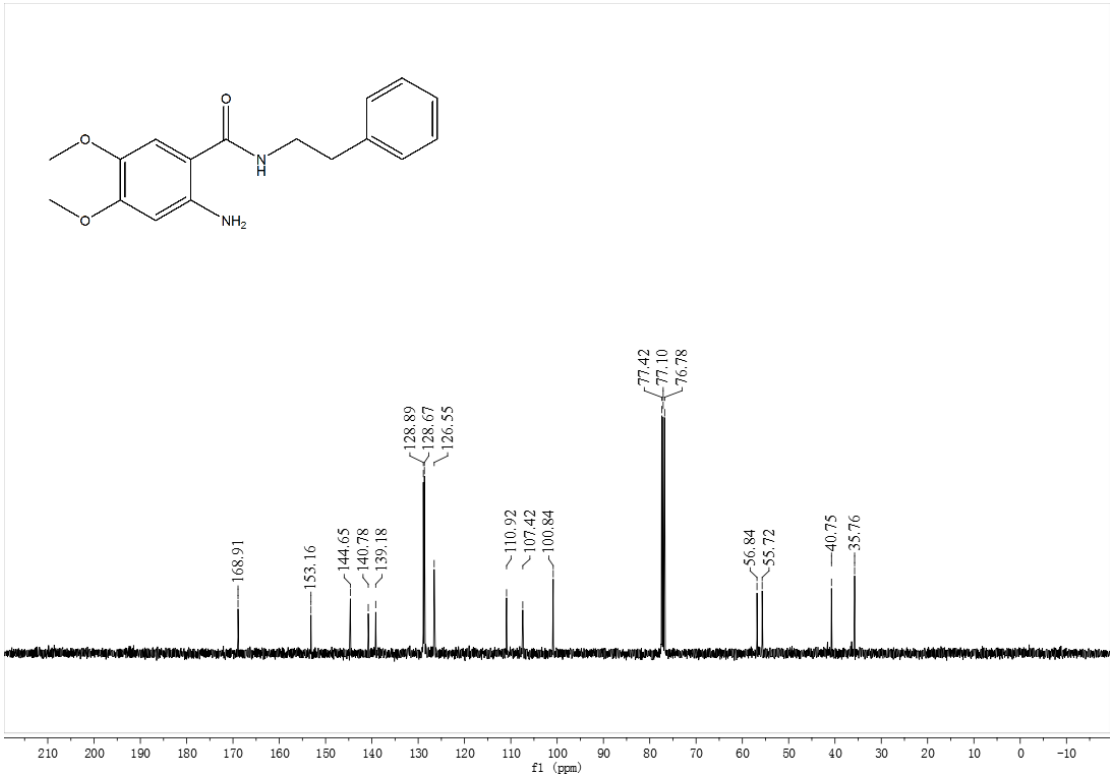
^{13}C-NMR spectrum of 5ca



^{1}H- NMR spectrum of 5ba

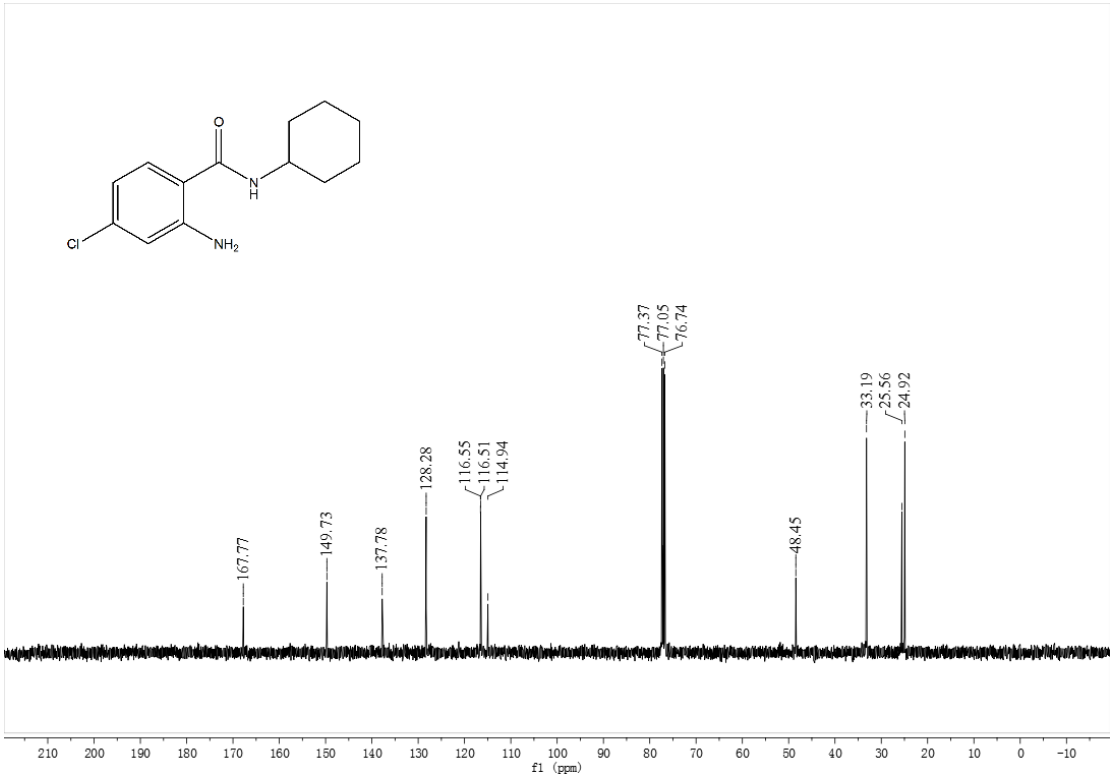


^{13}C-NMR spectrum of 5ba



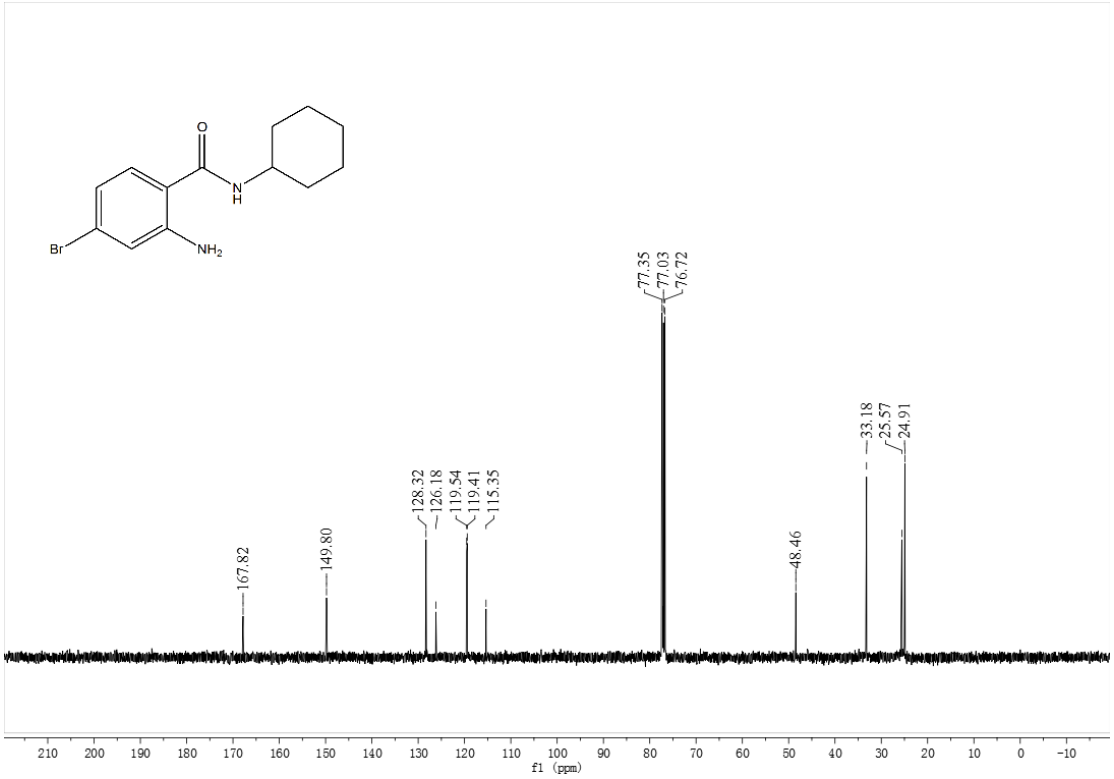
^{1}H- NMR spectrum of 5fc

^{13}C-NMR spectrum of 5fc

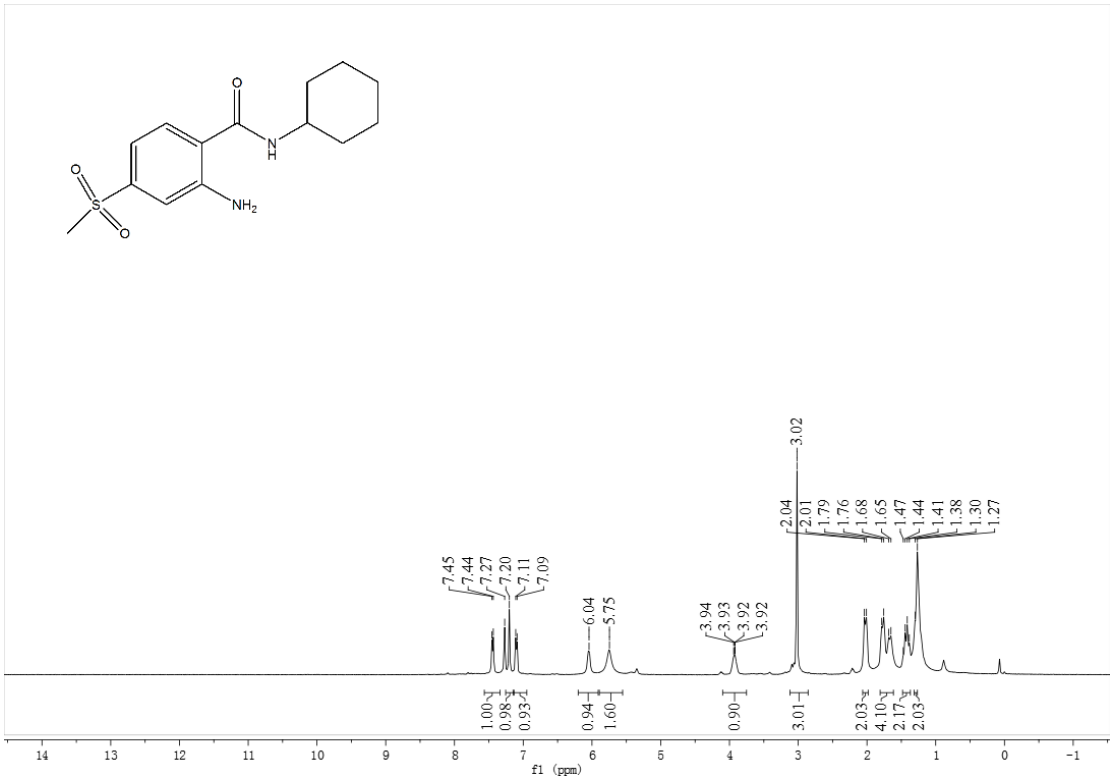


^{1}H- NMR spectrum of 5gc

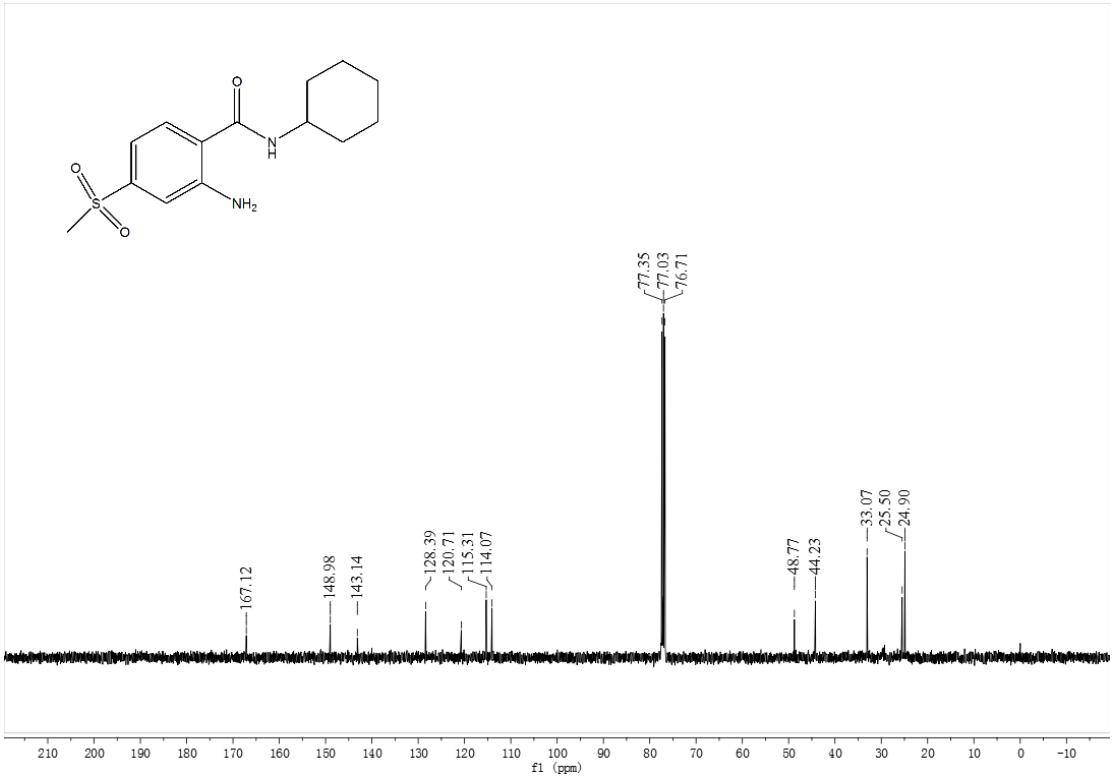
^{13}C-NMR spectrum of 5gc



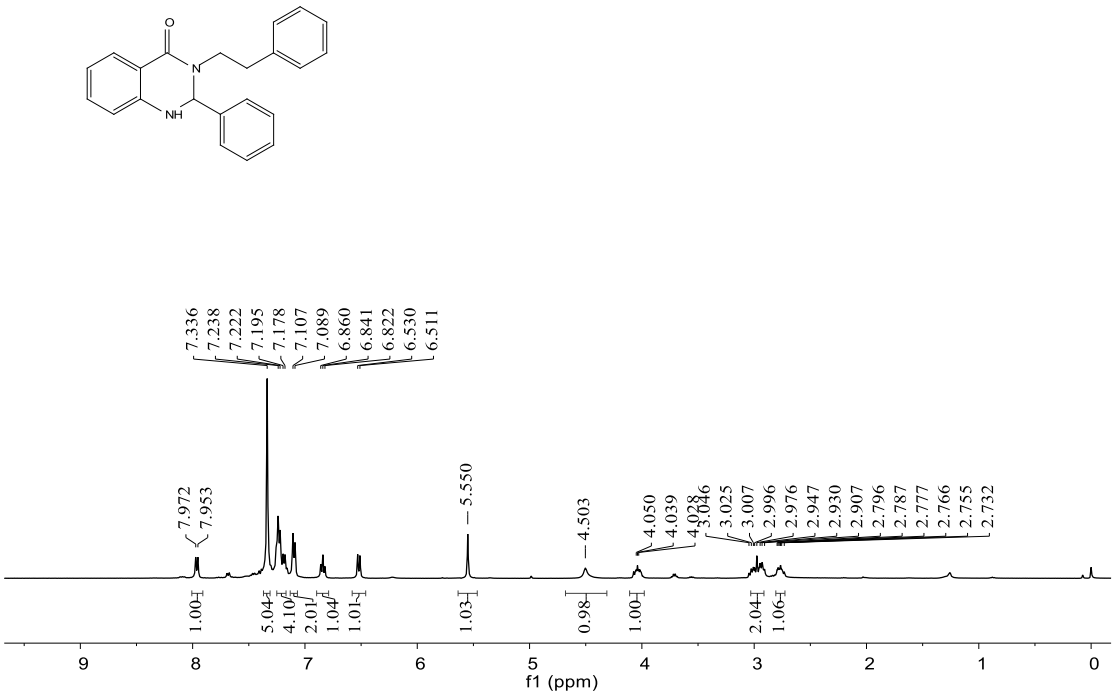
^{1}H- NMR spectrum of 5jc



^{13}C-NMR spectrum of 5jc



^{1}H- NMR spectrum of 6a



^{13}C-NMR spectrum of 6a