Palladium-Catalyzed Carbonylation of Benzylic Ammonium Salts via C-N Bond Activation under atmosphere pressure

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Supporting Information

Part 1. General informations

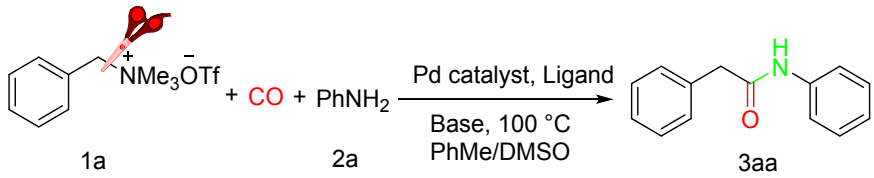
1. Analytical methods. All the reactions were monitored by thin-layer chromatography (TLC) or LC-MS (EI); products purification was done using silica gel column chromatography. $^{1}H/^{13}C$ NMR spectra were recorded on Bruker avance 400 MHz and Bruker AMX 400 MHz spectrometer at 400/100 MHz, respectively, in $CDCl_3$ unless otherwise stated, using either TMS or the undeuterated solvent residual signal as the reference. Chemical shifts are given in ppm and are measured relative to $CDCl_3$ or DMSO-d_6 as an internal standard. Mass spectra were obtained by the electrospray ionization time-of-flight (ESI-TOF) mass spectrometry. GC yields were obtained using biphenyl as an internal standard. Flash column chromatography purification of compounds was carried out by gradient elution using ethyl acetate (EA) in light petroleum ether (PE). Melting points were determined on an X-4 digital display microscope apparatus.

Part 2. Optimization details

General Procedure A: Carbonylation of **1a** and **2a** with CO (Table 1)

Ammonium salts **1a** (119.6 mg, 0.40 mmol), $PdCl_2$(dppf) (4.4 mg, 0.006 mmol), PPh_3 (15.7 mg, 0.06 mmol) and Na_2CO_3 (42.4 mg, 0.40 mmol) were added into a 25 mL Schlenk tube equipped with a magnetic stirred bar. The reaction mixture was degassed 3 times by CO and stirred under CO balloon. Toluene (1.0 mL), amine **2a** (18.6 mg, 0.20 mmol) and DMSO (0.2 mL) were then added into the tube by syringe. The reaction mixture was heated to 100 ºC and monitored by TLC. Upon completion, the reaction was diluted by AcOEt (5 mL), The reaction was extracted with EA (20 mL x 3). The combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash column chromatography (PE/EA = 4:1) afford the amide **3aa**. Alternatively, 1,1'-biphenyl (30.8 mg, 0.2 mmol) was added into the residue as internal standard (k = 1.235), and the yield of the product **3aa** was determined by GC analysis.

Table 1. Optimization for the reaction of *N*,*N*,*N*-trimethyl-1-phenylmethan-aminium trifluoromethanesulfonate (**1a**) and aniline (**2a**)[a]



Entry	Cat. (X mol%)	Ligand (Y mol%)	Solvent	Base	Yield[b] (%)
1	$PdCl_2$ (5)	PPh_3 (10)	PhMe/DMSO	EtN_3	22
2	$Pd(PPh_3)_4$ (5)	PPh_3 (10)	PhMe/DMSO	EtN_3	34
3	$PdCl_2(PPh_3)_2$ (5)	PPh_3 (10)	PhMe/DMSO	EtN_3	48
4	$PdCl_2$(dppf) (5)	PPh_3 (10)	PhMe/DMSO	EtN_3	66(65)[c]
5	$Pd(OAc)_2$ (5)	PPh_3 (10)	PhMe/DMSO	EtN_3	trace
6	$Pd(TFA)_2$ (5)	PPh_3 (10)	PhMe/DMSO	EtN_3	trace
7	$Pd(acac)_2$ (5)	PPh_3 (10)	PhMe/DMSO	EtN_3	trace
8	$PdCl_2$(dppf) (5)	BINAP (10)	PhMe/DMSO	EtN_3	60
9	$PdCl_2$(dppf) (5)	dppf (10)	PhMe/DMSO	EtN_3	62
10	$PdCl_2$(dppf) (5)	Xantphos (10)	PhMe/DMSO	EtN_3	55
11	$PdCl_2$(dppf) (5)	1,10-Phen (10)	PhMe/DMSO	EtN_3	31
12	$PdCl_2$(dppf) (5)	--	PhMe/DMSO	EtN_3	30
13	$PdCl_2$(dppf) (5)	PPh_3 (10)	PhMe/DMSO	Pyridine	0
14	$PdCl_2$(dppf) (5)	PPh_3 (10)	PhMe/DMSO	DBU	trace

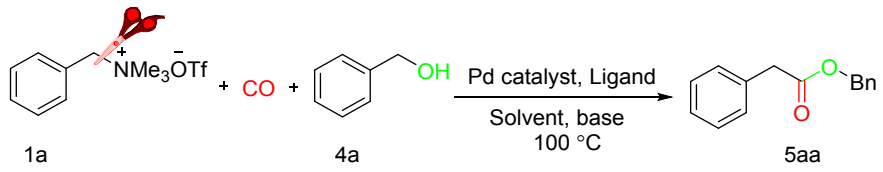
15	$PdCl_2$(dppf) (5)	PPh_3 (10)	PhMe/DMSO	KO^tBu	trace
16	$PdCl_2$(dppf) (5)	PPh_3 (10)	PhMe/DMSO	K_2CO_3	71
17	$PdCl_2$(dppf) (5)	PPh_3 (10)	PhMe/DMSO	Na_2CO_3	80
18	$PdCl_2$(dppf) (5)	PPh_3 (10)	PhMe	Na_2CO_3	58
19	$PdCl_2$(dppf) (5)	PPh_3 (10)	DMF	Na_2CO_3	trace
20	$PdCl_2$(dppf) (5)	PPh_3 (10)	1,4-dioxane	Na_2CO_3	0
21	$PdCl_2$(dppf) (5)	PPh_3 (10)	(PhMe/DMSO)[d]	Na_2CO_3	75
22	$PdCl_2$(dppf) (5)	PPh_3 (10)	(PhMe/DMSO)[e]	Na_2CO_3	82
23	$PdCl_2$(dppf) (5)	PPh_3 (10)	(PhMe/DMSO)[e]	Na_2CO_3	70
24	$PdCl_2$(dppf) (5)	PPh_3 (5)	(PhMe/DMSO)[e]	Na_2CO_3	58
25	$PdCl_2$(dppf) (5)	PPh_3 (20)	(PhMe/DMSO)[e]	Na_2CO_3	88
26	$PdCl_2$(dppf) (5)	PPh_3 (30)	(PhMe/DMSO)[e]	Na_2CO_3	91(90)[c]
27	***$PdCl_2$(dppf) (3)***	***PPh_3 (30)***	***(PhMe/DMSO)[e]***	***Na_2CO_3***	***97(97)[c]***
28	$PdCl_2$(dppf) (3)	PPh_3 (30)	(PhMe/DMSO)[e]	Na_2CO_3[f]	87
29[g]	$PdCl_2$(dppf) (3)	PPh_3 (30)	(PhMe/DMSO)[e]	Na_2CO_3	trace
30[h]	$PdCl_2$(dppf) (3)	PPh_3 (30)	(PhMe/DMSO)[e]	Na_2CO_3	0

[a] General reaction condition: **1a** (0.40 mmol), **2a** (0.20 mmol), catalyst (X mol %), ligand (Y mol %), base (0.40 mmol) in PhMe/DMSO (1.0 mL/0.1 mL) under 1 atm CO at 100 °C for 12 h. [b] Yield were determined by GC analysis. [c] Isolated yield. [d] PhMe/DMSO (0.75 mL/0.25 mL). [e] PhMe/DMSO (1.0 mL/0.2 mL). [f] Na_2CO_3 (0.20 mmol). [g] 80 °C instead of 100 °C. [h] 60 °C instead of 100℃.

General Procedure B: Carbonylation of 1a and 4a with CO (Table 2)

Ammonium salts **1a** (59.8 mg, 0.2 mmol), $PdCl_2$(dppf) (14.6 mg, 0.02 mmol), and Na_2CO_3 (21.2 mg, 0.2 mmol) was added to a 25 mL schlenk tube equipped with a magnetic stirred bar, and a balloon filled with CO was connected to the Schlenk tube through the side arm after exhaust the air,. benzyl alcohol **2a** (108 mg, 1.0 mmol) and toluene (2.0 mL) were then injected into the tube by syringe. The reaction was then heated to 100 ºC and stirred corresponding time. Upon completion, the reaction was quenched by AcOEt (5 mL). The reaction was extracted with EA (20 mL x 3). The combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash column chromatography (PE/EA = 50:1) afford the amide **3aa**. Alternatively, 1,1'-biphenyl (30.8 mg, 0.2 mmol) was added into the residue as internal standard (k=1.108). The yield of the product **5aa** was determined by GC analysis.

Table 2. Optimization for the reaction of N,N,N-trimethyl-1-phenylmethan -aminium trifluoromethanesulfonate (1a) and benzyl alcohol (4a)[a]



1a 4a 5aa

Entry	Cat. (X mol%)	Ligand (Y mol%)	Solvent	Base	Yield[b] (%)
1	$PdCl_2(dppf)$ (5)	PPh_3 (10)	PhMe	Na_2CO_3	25
2	$Pd(PPh_3)_4$ (5)	PPh_3 (10)	PhMe	Na_2CO_3	17
3	$PdCl_2(PPh_3)_2$ (5)	PPh_3 (10)	PhMe	Na_2CO_3	trace
4	$Pd(acac)_2$ (5)	PPh_3 (10)	PhMe	Na_2CO_3	trace
5	$Pd(OAc)_2$ (5)	PPh_3 (10)	PhMe	Na_2CO_3	ND
6	$PdCl_2$ (5)	PPh_3 (10)	PhMe	Na_2CO_3	ND
7	$Pd_2(dba)_3$ (5)	PPh_3 (10)	PhMe	Na_2CO_3	ND
8	$PdCl_2(dppf)$ (5)	BINAP (10)	PhMe	Na_2CO_3	trace
9	$PdCl_2(dppf)$ (5)	dppe (10)	PhMe	Na_2CO_3	19
10	$PdCl_2(dppf)$ (5)	dppf (10)	PhMe	Na_2CO_3	20
11	$PdCl_2(dppf)$ (5)	Xantphos (10)	PhMe	Na_2CO_3	ND
12	$PdCl_2(dppf)$ (5)	--	PhMe	Na_2CO_3	24
13	$PdCl_2(dppf)$ (5)	--	1,4-dioxane	Na_2CO_3	trace
14	$PdCl_2(dppf)$ (5)	--	DMF	Na_2CO_3	ND
15	$PdCl_2(dppf)$ (5)	--	$PhCH_2OH$	Na_2CO_3	72(70)[c]
16	$PdCl_2(dppf)$ (5)	--	PhMe/DMSO (1:1)	Na_2CO_3	17
17	$PdCl_2(dppf)$ (5)	--	PhMe/DMF (1:1)	Na_2CO_3	16
18[d]	$PdCl_2(dppf)$ (5)	--	PhMe	Na_2CO_3	34
19[e]	$PdCl_2(dppf)$ (5)	--	PhMe	Na_2CO_3	66
20[f]	$PdCl_2(dppf)$ (5)	--	PhMe	Na_2CO_3	79
21[g]	$PdCl_2(dppf)$ (5)	--	PhMe	Na_2CO_3	77
22[h]	$PdCl_2(dppf)$ (5)	--	PhMe	Na_2CO_3	47
23[i]	$PdCl_2(dppf)$ (5)	--	PhMe	Na_2CO_3	69
24	$PdCl_2(dppf)$ (5)	--	PhMe	K_2CO_3	76
25	$PdCl_2(dppf)$ (5)	--	PhMe	Cs_2CO_3	10
26	$PdCl_2(dppf)$ (5)	--	PhMe	$NaHCO_3$	29
27	$PdCl_2(dppf)$ (5)	--	PhMe	DBU	trace
28	$PdCl_2(dppf)$ (3)	--	PhMe	Na_2CO_3	10
29	$PdCl_2(dppf)$ (10)	--	PhMe	Na_2CO_3	84(82)

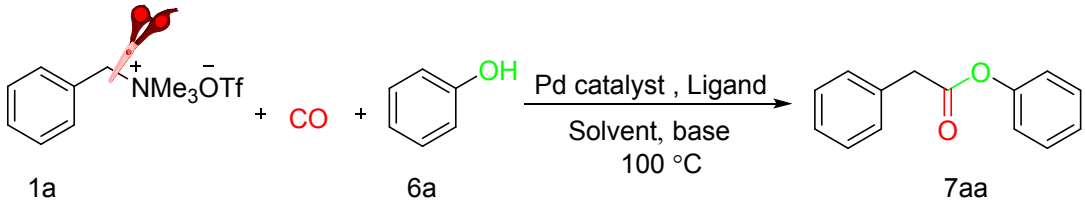
30	$PdCl_2$(dppf) (15)	--	PhMe	Na_2CO_3	81
31	***$PdCl_2$(dppf) (10)***	**--**	***PhMe***	***Na_2CO_3[j]***	***84(82)***
32	$PdCl_2$(dppf) (10)	--	PhMe	Na_2CO_3[k]	75
33[l]	$PdCl_2$(dppf) (10)	--	PhMe	Na_2CO_3	37
34[m]	$PdCl_2$(dppf) (10)	--	PhMe	Na_2CO_3	50

[a]Reaction condition: 1a (0.2 mmol), 2a (0.2 mmol), catalyst (X mol%), ligand (Y mol%), base (0.4 mmol) in PhMe (2.0 mL) under 1 atm CO at 100 ℃ for 12 h. [b]Yield were determined by GC analysis. [c]Isolated yield; [d]1a: 4a=1:3; [e]1a: 4a=1:4; [f]1a: 4a=1:5; [g]1a: 4a=1:7; [h]1a: 4a=3:1; [i]1a: 4a=3:1; [j]Na_2CO_3 (0.2 mmol, 1 equiv); [k]Na_2CO_3(0.1 mmol, 0.5 equiv); [l]90 ℃ instead of 100℃; [m]110 ℃ instead of 100℃.

General Procedure C: Carbonylation of 1a and 6a with CO (Table 3)

Ammonium salts **1a** (59.8 mg, 0.2 mmol), $PdCl_2$(dppf) (14.6 mg, 0.02 mmol), dppp (16.5 mg, 0.04 mmol), and Na_2CO_3 (21.2 mg, 0.2 mmol) was added to a 25 mL schlenk tube equipped with a magnetic stirred bar, and a balloon filled with CO was connected to the Schlenk tube through the side arm after exhaust the air, phenol **6a** (56.4 mg, 0.6 mmol) and toluene (2.0 mL) were then injected into the tube by syringe. The reaction was then heated to 100 ℃ and stirred corresponding time. Upon completion, the reaction was quenched by AcOEt (5 mL). The reaction was extracted with EA (20 mL x 3). The combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash column chromatography (PE/EA = 50:1) afford the amide **3aa**. Alternatively, 1,1'-biphenyl (30.8 mg, 0.2 mmol) was added into the residue as internal standard (k=1.026). The yield of the product **7aa** was determined by GC analysis.

Table 3. Optimization for the reaction of N,N,N-trimethyl-1-phenylmethan -aminium trifluoromethanesulfonate (1a) and phenol (4a)[a]



1a 6a 7aa

Entry	Cat. (X mol%)	Ligand (Y mol%)	Solvent	Base	Yield[b] (%)
1	$PdCl_2$(dppf) (10)	--	PhMe	Na_2CO_3	13
2	$PdCl_2$(dppf) (10)	TFP (20)	PhMe	Na_2CO_3	17
3	$PdCl_2$(dppf) (10)	BINAP (20)	PhMe	Na_2CO_3	69
4	$PdCl_2$(dppf) (10)	dppe (20)	PhMe	Na_2CO_3	19
5	**$PdCl_2$(dppf) (10)**	**dppp (20)**	**PhMe**	**Na_2CO_3**	**82(81)[c]**
6	$PdCl_2$(dppf) (10)	dppf (20)	PhMe	Na_2CO_3	70
7	$PdCl_2$(dppf) (10)	PPh_3 (20)	PhMe	Na_2CO_3	28
8	$Pd(PPh_3)_4$ (10)	PPh_3 (20)	PhMe	Na_2CO_3	19
9	$PdCl_2$ (10)	PPh_3 (20)	PhMe	Na_2CO_3	14
10	$Pd(acac)_2$ (10)	PPh_3 (20)	PhMe	Na_2CO_3	trace
11	$Pd(OAc)_2$ (10)	PPh_3 (20)	PhMe	Na_2CO_3	trace
12	$PdCl_2$(dppf) (10)	dppp (20)	DMF	Na_2CO_3	trace
13	$PdCl_2$(dppf) (10)	dppp (20)	DMSO	Na_2CO_3	trace
14	$PdCl_2$(dppf) (10)	dppp (20)	1,4-dioxane	Na_2CO_3	31
15	$PdCl_2$(dppf) (10)	dppp (20)	PhMe	$NaHCO_3$	62
16	$PdCl_2$(dppf) (10)	dppp (20)	PhMe	K_2CO_3	48
17	$PdCl_2$(dppf) (10)	dppp (20)	PhMe	^tBuONa	trace
18	$PdCl_2$(dppf) (10)	dppp (20)	PhMe	DBU	trace
19	$PdCl_2$(dppf) (5)	dppp (20)	PhMe	Na_2CO_3	59
20	$PdCl_2$(dppf) (5)	dppp (10)	PhMe	Na_2CO_3	33
21	$PdCl_2$(dppf) (3)	dppp (10)	PhMe	Na_2CO_3	25
22	$PdCl_2$(dppf) (3)	dppp (30)	PhMe	Na_2CO_3	70
23	$PdCl_2$(dppf) (5)	dppp (20)	PhMe	Na_2CO_3	77
24[d]	$PdCl_2$(dppf) (10)	dppp (20)	PhMe	Na_2CO_3	79(77)[c]
25[e]	$PdCl_2$(dppf) (10)	dppp (20)	PhMe	Na_2CO_3	68
26[f]	$PdCl_2$(dppf) (10)	dppp (20)	PhMe	Na_2CO_3	trace
27[g]	$PdCl_2$(dppf) (10)	dppp (20)	PhMe	Na_2CO_3	45

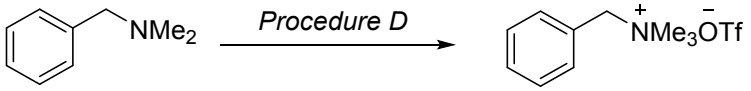
[a]Reaction condition: 1a (0.2 mmol), 6a (0.6 mmol), catalyst (X mol%), ligand (Y mol%), base (0.2 mmol) in PhMe (2.0 mL) under 1 atm CO at 100 ℃ for 12 h. [b]Yield were determined by GC analysis. [c]Isolated yield; [d]Na_2CO_3 (0.4 mmol 2.0 equiv); [e]Na_2CO_3 (0.1 mmol 0.5 equiv); [f]90 ℃ instead of 100℃; [g]110 ℃ instead of 100℃

Part 3: Synthesis of Benzylic Ammonium Salts

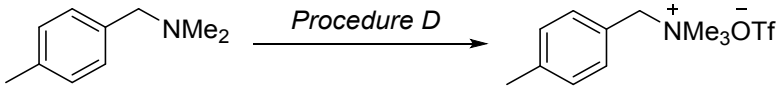
General Procedure D (Preparation of Benzyl Ammonium Triflates): Preparation of N,N,N-Trimethyl-1-phenylmethanaminium trifluoromethanesulfonate

Dimethylbenzylamine (2.5 g, 18.5 mmol, 1.0 equiv) was dissolved in Et_2O (15 mL, 4.0 M). MeOTf (2.7 mL, 23.9 mmol, 1.3 equiv) was added dropwise at 0 °C. White precipitate formed immediately. After complete addition the reaction mixture was stirred for an additional 30 minutes at 0 °C. The precipitate was isolated by filtration and washed with Et_2O (2 x 20 mL). The resulting solid was dried under vacuum to give salt 1a (5.17 g, 94%) as a white solid (mp 97–99 °C)

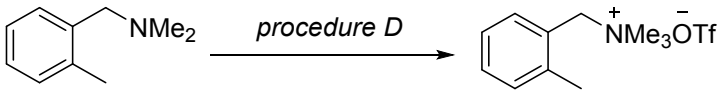
Substituted dimethyl benzyl amines were prepared either from the benzyl amines using Escheweiler–Clarke conditions[1]or via reductive amination of the benzaldehyde or acetophenone derivative[2].



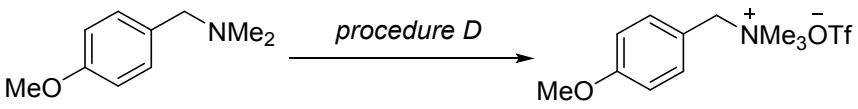
N,N,N-trimethyl-1-phenylmethanaminium trifluoromethanesulfonate, was synthesized following the procedure D from dimethyl benzyl amine, white soild, 95%, Mp: 97-99° C, Analytical data were in agreement with previous reports.[3]



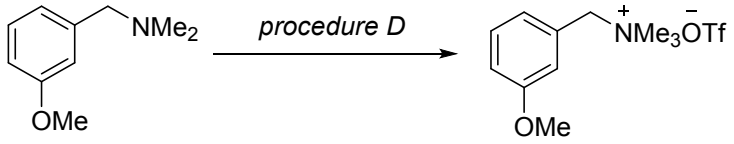
N,N,N-trimethyl-1-(p-tolyl)methanaminium trifluoromethanesulfonate, was synthesized following the procedure D from corresponding dimethyl benzyl amine, white soild, 95%, Mp: 110-113° C, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.41 (d, J = 7.8 Hz, 2H), 7.33 (d, J = 7.5 Hz, 2H), 4.46 (s, 2H), 3.00 (s, 9H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 140.5, 133.1, 123.0, 125.8, 121.1(d, $J_{C\text{-}F}$ = 320.5 Hz), 68.2, 52.1, 21.3. FTIR(KBr): 3037, 1488, 1483, 1263, 1230, 1152, 1035. HRMS(ESI) calcd for $C_{11}H_{18}N^+$[M-OTf]$^+$ 164.1434, found 164.1442.



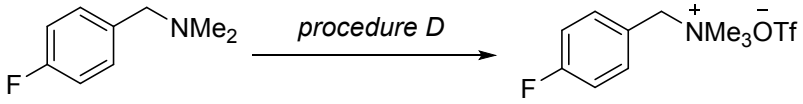
N,N,N-trimethyl-1-(o-tolyl)methanaminium trifluoromethanesulfonate, was synthesized following the procedure D from corresponding dimethyl benzyl amine, white soild, 90%, Mp: 116-118° C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.49 - 7.30 (m, 4H), 4.55 (d, J = 3.0 Hz, 2H), 3.05 (d, J = 2.9 Hz, 9H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 140.3, 134.7, 132.0, 130., 127.2, 126.6, 121.2(d, $J_{C\text{-}F}$ = 320.4 Hz), 65.6, 52.4, 20.1. FTIR(KBr): 3039, 1496, 1279, 1278, 1258, 1228, 1161, 1146, 1034. HRMS(ESI) calcd for $C_{12}H_{18}N^+$[M-OTf]$^+$ 164.1434, found 164.1438.



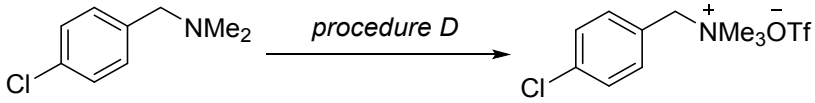
1-(4-methoxyphenyl)-N,N,N-trimethylmethanaminium trifluoromethanesulfonate, was synthesized following the procedure D from corresponding dimethyl benzyl amine, white soild, 95%, Mp: 94-95° C, Analytical data were in agreement with previous reports.[3]



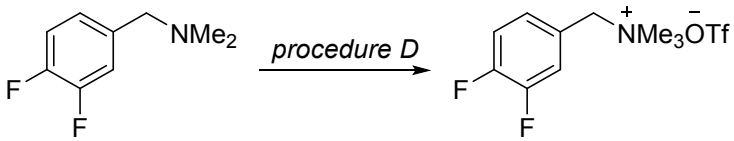
1-(3-methoxyphenyl)-N,N,N-trimethylmethanaminium, trifluoromethanesulfonate, was synthesized following the procedure D from corresponding dimethyl benzyl amine, light brown soild, 89%, Mp: 59-62° C, Analytical data were in agreement with previous reports.[3]



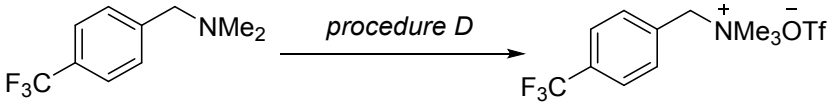
1-(4-fluorophenyl)-N,N,N-trimethylmethanaminium trifluoromethanesulfonate, was synthesized following the procedure D from corresponding dimethyl benzyl amine, white soild, 89%, Mp: 130-132° C.^{1}H NMR (400 MHz, DMSO-d_6) δ 7.66 – 7.55 (m, 2H), 7.41 – 7.31 (m, 2H), 4.51 (d, J = 3.2 Hz, 2H), 3.01 (d, J = 2.7 Hz, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.7 (d, $J_{C\text{-}F}$ = 247.6 Hz), 135.6 (d, $J_{C\text{-}F}$ = 8.8 Hz), 125.2, 121.2 (d, $J_{C\text{-}F}$ = 322.9 Hz), 116.4 (d, $J_{C\text{-}F}$ = 22.2 Hz), 67.5, 52.2. FTIR(KBr): 3036, 1512, 1488, 1263, 1228, 1261, 1156, 1035 HRMS(ESI) calcd for $C_{10}H_{15}FN^{+}$[M-OTf]$^{+}$ 168.1183, found 168.1189.



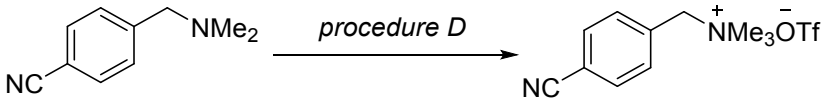
1-(4-chlorophenyl)-N,N,N-trimethylmethanaminium trifluoromethanesulfonate, was synthesized following the procedure D from corresponding dimethyl benzyl amine, white soild, 90%, Mp: 120-122° C. ^{1}H NMR (400 MHz, DMSO) δ 7.62 – 7.54(m,4H), 4.54 (dd, J = 19.5, 2.9 Hz, 2H), 3.02 (d, J = 2.3 Hz, 9H). ^{13}C NMR (101 MHz, DMSO) δ 135.8, 135.1, 129.5, 127.8, 121.2 (d, J = 320.3 Hz),67.4, 52.3. FTIR(KBr): 3038, 1488, 1261, 1156, 1035. HRMS(ESI) calcd for $C_{10}H_{15}ClN^{+}$[M-OTf]$^{+}$ 184.0888, found 184.0892



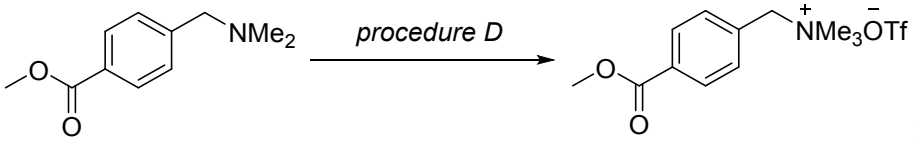
1-(3,4-difluorophenyl)-N,N,N-trimethylmethanaminium trifluoromethanesulfonate, was synthesized following the procedure D from corresponding dimethyl benzyl amine,white soild, 88%, Mp: 117-119° C, Analytical data were in agreement with previous reports.[3]



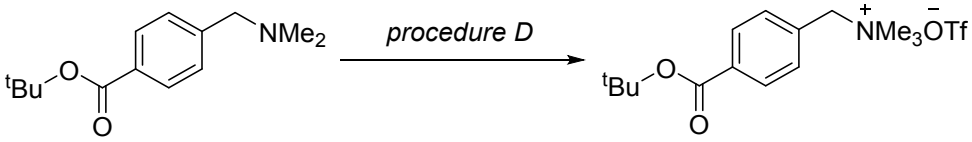
N,N,N-trimethyl-1-(4-(trifluoromethyl)phenyl)methanaminium trifluoromethanesulfonate, was synthesized following the procedure D from corresponding dimethyl benzyl amine, white soild, 90%, Mp: 117-119° C, Analytical data were in agreement with previous reports.



1-(4-cyanophenyl)-N,N,N-trimethylmethanaminium trifluoromethanesulfonate, was synthesized following the procedure D from corresponding dimethyl benzyl amine, white soild, 90%, Mp: 133-135° C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 4.61 (s, 2H), 3.05 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 134.2, 133.9, 133.2, 121.2 (d, $J_{C\text{-}F}$ = 320.6 Hz), 118.7, 113.6, 67.4, 52.6. FTIR(KBr): 3038, 2230, 1485, 1493, 1285, 1260, 1156, 1028. HRMS(ESI) calcd for $C_{11}H_{15}N_2^+$[M-OTf]$^+$ 175.1230, found 175.1238

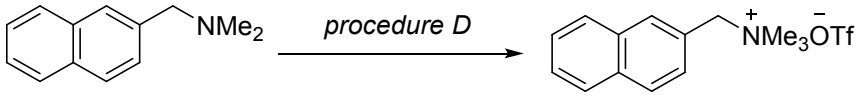


1-(4-(methoxycarbonyl)phenyl)-N,N,N-trimethylmethanaminium trifluoromethane sulfonate, was synthesized following the procedure D from corresponding dimethyl benzyl amine, white soild, 92%, Mp: 168-171° C, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.08 (d, J = 7.6 Hz,2H), 7.69 (d, J = 8.1 Hz, 2H), 4.60 (d, J = 3.0 Hz,2H), 3.89 (d, J = 1.5 Hz, 3H), 3.05 (d, J = 3.5 Hz, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.2, 133.7, 131.7,130.0, 121.2(d, $J_{C\text{-}F}$ = 320.6 Hz),67.6, 52.9, 52.5. FTIR(KBr): 3034, 1728, 1282, 1259, 1163, 1032, 1032. HRMS(ESI) calcd for $C_{12}H_{18}NO_2^+$[M-OTf]$^+$ 208.1332, found 208.1340



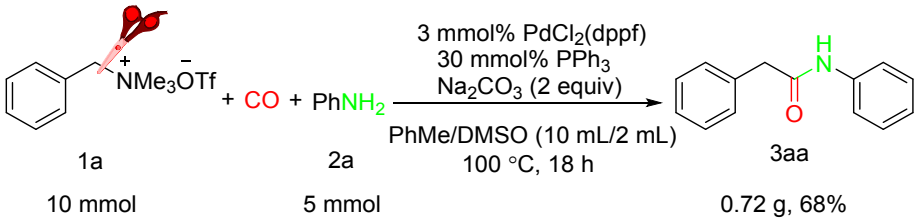
1-(4-(tert-butoxycarbonyl)phenyl)-N,N,N-trimethylmethanaminium trifluoromethanesulfonate, was synthesized following the procedure D from corresponding dimethyl benzyl amine, white soild, 92%, Mp: 114-116° C, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 9.5 Hz, 2H), 4.59 (d, J =

2.2 Hz, 2H), 3.04 (d, J = 2.4 Hz, 9H), 1.56 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.9, 133.6, 133.4, 133.2, 129.9, 121.2(d, $J_{C\text{-}F}$ = 314.3 Hz), 81.8, 67.7, 52.5, 28.2. FTIR(KBr): 3037, 2994, 1696, 1492, 1304, 1141, 1123, 1031. HRMS(ESI) calcd for $C_{15}H_{24}NO_2^+$[M-OTf]$^+$ 250.1802, found 250.1809



N,N,N-trimethyl-1-(naphthalen-2-yl)methanaminium trifluoromethanesulfonate, was synthesized following the procedure D from corresponding dimethyl benzyl amine, white soild, 90%, Mp: 108-110° C, Analytical data were in agreement with previous reports.[3]

Part 4: Scale-up experiment



According to Procedure A, ammonium salts **1a** (2.99 g, 10 mmol), $PdCl_2$(dppf) (109.8 mg, 0.15 mmol), PPh_3 (393 mg, 1.5 mmol), and Na_2CO_3 (1.06 g, 10 mmol) was added to a 50 mL schlenk flask equipped with a magnetic stirred bar, a and a balloon filled with CO was connected to the Schlenk tube through the side arm after exhaust the air, DMSO (2 mL), amine **2a** (18.6 mg, 0.2 mmol) and toluene (10 mL) were then injected into the tube by syringe. The reaction was then heated to 100 ºC and stirred 18 h (Fig 1). Upon completion, the reaction was quenched by AcOEt (5 mL). The reaction was extracted with EA (60 mL x 3). The combined organic layers were washed with brine (60 mL) and dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash column chromatography (silica gel, hexanes:EtOAc= 4:1), 0.72 g (68%) 3aa was obtained as light yellow solid .

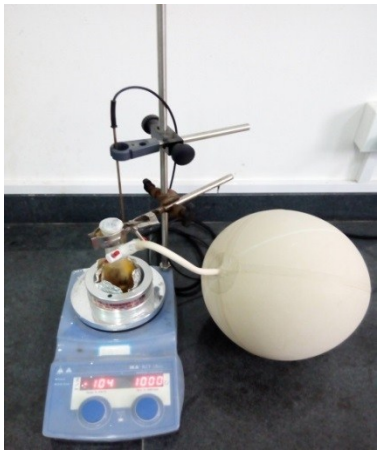
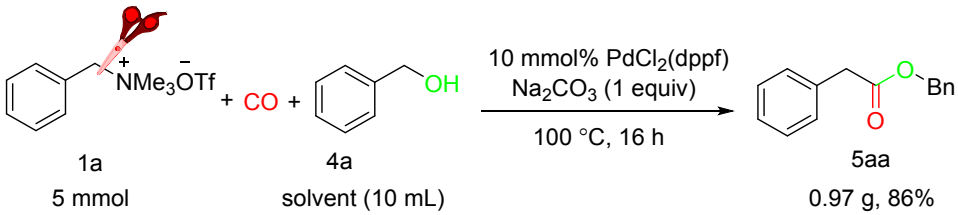
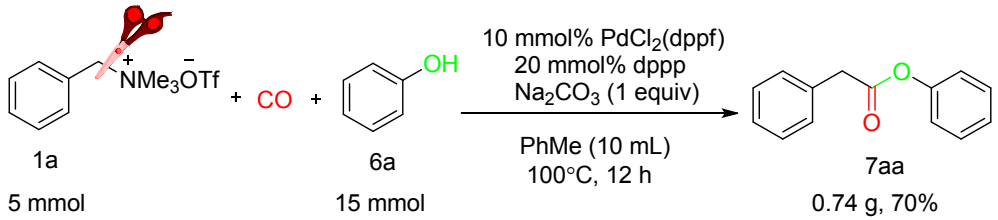


Fig 1



According to Procedure B, ammonium salts **1a** (1.50 g, 5 mmol), $PdCl_2$(dppf) (366 mg, 0.5 mmol), and Na_2CO_3 (530 mg, 5 mmol) was added to a 50 mL schlenk flask equipped with a magnetic stirred bar, and a balloon filled with CO was connected to the Schlenk tube through the side arm after exhaust the air,, benzyl alchol **4a** (10 mL) were then injected into the tube by syringe. The reaction was then heated to 100 ºC and stirred 16 h. Upon completion. The reaction was extracted with EA

(60 mL x 3). The combined organic layers were washed with brine (60 mL) and dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash column chromatography (silica gel, hexanes:EtOAc= 100:1), 0.97 g (86%) 5aa was obtained as yellow liquid .



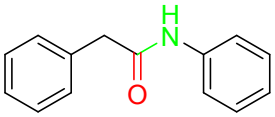
1a
5 mmol

6a
15 mmol

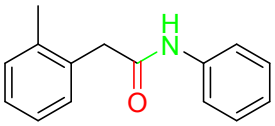
7aa
0.74 g, 70%

According to Procedure C, ammonium salts **1a** (1.50 g, 5 mmol), $PdCl_2$(dppf) (370 mg, 0.5 mmol), dppp (415 mg, 1 mmol), Na_2CO_3 (530 mg, 5 mmol), and phenol **6a** (1.4 g, 15 mmol) was added to a 50 mL schlenk flask equipped with a magnetic stirred bar, and a balloon filled with CO was connected to the Schlenk tube through the side arm after exhaust the air, toluene (10 mL) were then injected into the tube by syringe. The reaction was then heated to 100 ºC and stirred 12 h (Fig 1). Upon completion, the reaction was quenched by AcOEt (5 mL). The reaction was extracted with EA (60 mL x 3). The combined organic layers were washed with brine (60 mL) and dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash column chromatography (silica gel, hexanes:EtOAc= 100:1), 0.74 g (70%) 3aa was obtained as colorless liquid .

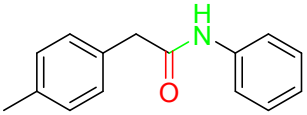
Part 5. Characterization of carbonylation products of amines(3aa—3bj)



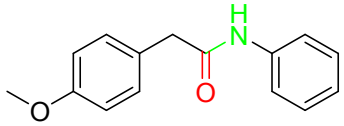
N,2-diphenylacetamide (3aa)[4,5], this compound was prepared according to General Procedure A for 12 h, Yield：97% (40.9 mg), light yellow solid，Mp：118 – 120℃ ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.29 (d, 7H), 7.28 – 7.23 (m, 2H), 7.08 (t, *J* =7.4Hz, 1H), 3.70 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 137.7, 134.6, 129.5, 129.2, 128.9, 127.6, 124.5, 120.0, 44.8. HRMS(ESI$^+$) calculated for $C_{14}H_{13}NO$ $[M+H]^+$: 212.1075; found: 212.1077.



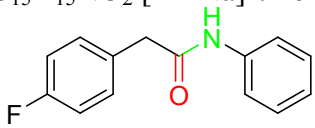
N-phenyl-2-(o-tolyl)acetamide (3ab)[40748-53-6], this compound was prepared according to General Procedure A for 12 h, Yield：95% (42.6 mg), light yellow solid，Mp：133 - 135℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.9 Hz, 2H), 7.28 – 7.21 (m, 7H), 7.06 (t, *J* = 7.2 Hz, 1H), 3.70 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 137.6, 137.3, 133.0, 130.9, 130.5, 128.9, 128.1, 126.8, 124.4, 120.0, 42.8, 19.5. HRMS(ESI$^+$) calculated for $C_{15}H_{15}NO$ $[M+H]^+$: 226.1232; found: 226.1237.



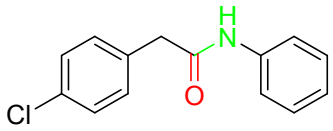
N-phenyl-2-(p-tolyl)acetamide (3ac)[5], this compound was prepared according to General Procedure A for 12 h, Yield：95% (42.7 mg), yellow solid，Mp：156 - 158℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.29 (dd, *J* = 10.0, 5.4 Hz, 3H), 7.23 (s, 4H), 7.10 (t, *J* = 7.3 Hz, 1H), 3.71 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 137.7, 137.4, 131.4, 130.0, 129.5, 128.9, 124.4, 119.9, 44.5, 21.1. HRMS(ESI$^+$) calculated for $C_{15}H_{15}NO$ $[M+Na]^+$: 248.1051; found: 248.1055.



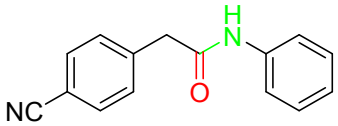
2-(4-methoxyphenyl)-N-phenylacetamide (3ad)[5], this compound was prepared according to General Procedure A for 10 h, Yield：96% (46.2 mg), yellow solid，Mp：115 - 117℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.15 (dd, *J* = 18.4, 8.2 Hz, 4H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 2H), 3.71 (s, 3H), 3.54 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 159.1, 137.8, 130.6, 128.9, 126.5, 124.4, 119.9, 114.5, 55.3, 43.8. HRMS(ESI$^+$) calculated for $C_{15}H_{15}NO_2$ $[M+Na]^+$: 264.1000; found: 264.1004.



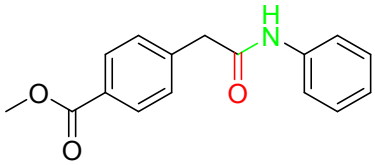
2-(4-fluorophenyl)-N-phenylacetamide (3ae)[5], this compound was prepared according to General Procedure A for 16 h, Yield：81% (37.2 mg), light yellow solid，Mp：124 - 126℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.0 Hz, 2H), 7.31 – 7.22 (m, 4H), 7.11 – 7.01 (m, 3H), 3.66 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 162.24 (d, $J_{C\text{-}F}$ = 246.4 Hz), 137.6, 131.1 (d, $J_{C\text{-}F}$ = 8.0 Hz), 130.3 (d, $J_{C\text{-}F}$= 3.4 Hz), 129.0, 124.6, 120.0, 116.0 (d, $J_{C\text{-}F}$ = 22.5 Hz), 43.8; HRMS(ESI$^+$) calculated for $C_{14}H_{12}FNO$ $[M+H]^+$: 230.0981; found: 230.0978.



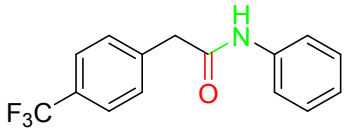
2-(4-chlorophenyl)-N-phenylacetamide (3af)[7], this compound was prepared according to General Procedure A for 12 h, Yield：89% (43.7 mg), light yellow solid，Mp：170 - 172℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.19 (s, 1H), 7.60 (d, J = 7.9 Hz, 2H), 7.37 (q, J = 8.6 Hz, 4H), 7.30 (t, J = 7.8 Hz, 2H), 7.04 (t, J = 7.3 Hz, 1H), 3.66 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 139.2, 135.1, 131.4, 131.1, 128.8, 128.3, 123.4, 119.2, 42.5. HRMS(ESI$^+$) calculated for $C_{14}H_{12}ClNO$ $[M+H]^+$: 246.0686; found: 246.0685



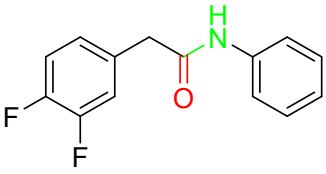
2-(4-cyanophenyl)-N-phenylacetamide (3ag), this compound was prepared according to General Procedure A for 14 h, Yield：85% (40.3 mg), yellow solid，Mp：156 - 159℃; ^{1}H NMR (400 MHz, DMSO) δ 10.26 (s, 1H), 7.81 (d, J = 8.1 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.1 Hz, 2H), 7.31 (t, J = 7.8 Hz, 2H), 7.05 (t, J = 7.3 Hz, 1H), 3.79 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.2, 141.9, 139.1, 132.2, 130.4, 128.8, 123.5, 119.3, 119.0, 109.6, 43.2. FTIR(KBr)：1668 cm^{-1} ($CH_2\underline{CO}NR_1R_2$), HRMS(ESI$^+$) calculated for $C_{15}H_{12}N_2O[M+H]^+$: 237.1028; found: 237.1032.



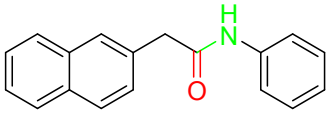
methyl 4-(2-oxo-2-(phenylamino)ethyl)benzoate (3ah), this compound was prepared according to General Procedure A for 12 h**,** Yield：94% (50.8 mg), white solid，Mp：164 - 166℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.25 (s, 1H), 7.95 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 7.8 Hz, 2H), 7.50 (d, J = 7.9 Hz, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.05 (t, J = 7.3 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.5, 166.2, 141.7, 139.2, 129.7, 129.3, 128.9, 128.1, 123.4, 119.2, 52.1, 43.3. FTIR(KBr)：1664 cm^{-1} ($CH_2\underline{CO}NR_1R_2$), HRMS(ESI$^+$) calculated for $C_{16}H_{15}NO_3[M+Na]^+$: 292.0950; found: 292.0953.



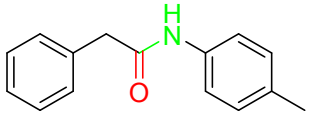
N-phenyl-2-(4-(trifluoromethyl)phenyl)acetamide (3ai), this compound was prepared according to General Procedure A for 8 h, Yield：98% (54.7 mg), light red solid，Mp：135 - 138℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.25 (s, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.1 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 7.8 Hz, 2H), 7.06 (t, J = 7.3 Hz, 1H), 3.80 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 141.2 (d, $J_{C\text{-}F}$ = 1.0 Hz), 139.5, 130.5, 129.2, 127.8 (d, $J_{C\text{-}F}$ = 31.4 Hz), 125.5 (q, $J_{C\text{-}F}$ = 7.1 Hz), 124.9 (d, $J_{C\text{-}F}$ = 270.2 Hz), 123.8, 119.7, 43.4. FTIR(KBr)：1658 cm^{-1} ($CH_2\underline{CO}NR_1R_2$), HRMS(ESI$^+$) calculated for $C_{15}H_{12}F_3NO[M+H]^+$: 280.0949; found: 280.0947.



2-(3,4-difluorophenyl)-N-phenylacetamide (3aj), this compound was prepared according to General Procedure A for 8 h, Yield：95% (47.2 mg), light yellow solid，Mp：108 - 110℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.19 (s, 1H), 7.62 (d, J = 7.9 Hz, 2H), 7.40 (dd, J = 16.2, 8.6 Hz, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.19 (s, 1H), 7.05 (t, J = 7.3 Hz, 1H), 3.69 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.6, 150.1 (dd, $J_{C\text{-}F}$ = 70.3, 12.4 Hz), 147.6 (dd, $J_{C\text{-}F}$ = 69.3, 12.5 Hz), 139.2, 133.7 (dd, $J_{C\text{-}F}$ = 6.3, 3.8 Hz), 128.9, 126.1 (dd, $J_{C\text{-}F}$= 6.3, 3.3 Hz), 123.4, 119.3, 118.3 (d, $J_{C\text{-}F}$ = 17.1 Hz), 117.2 (d, $J_{C\text{-}F}$ = 16.9 Hz), 42.2. FTIR(KBr)：1655 cm^{-1} ($CH_2\underline{CO}NR_1R_2$), HRMS(ESI$^+$) calculated for $C_{14}H_{11}F_2NO[M+H]^+$: 248.0887; found: 248.0884.

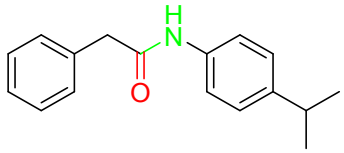


N,2-diphenylacetamide (3ak), this compound was prepared according to General Procedure A For 14 h, Yield 63% (32.8 mg), white solid，Mp：118 - 120℃ ; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.24 (s, 1H), 7.88 (d, J = 8.0 Hz, 3H), 7.85 (s, 1H), 7.63 (d, J = 7.8 Hz, 2H), 7.54 –7.47 (m, 3H), 7.31 (t, J = 7.8 Hz, 2H), 7.05 (t, J = 7.4 Hz, 1H), 3.84 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.5, 139.7, 134.2, 133.5, 132.3, 129.2, 128.2, 128.1, 126.6, 126.1, 123.72 (s), 119.7, 43.9. FTIR(KBr)：1658 cm^{-1} ($CH_2\underline{CO}NR_1R_2$); HRMS(ESI$^+$) calculated for $C_{18}H_{15}NO[M+H]^+$: 262.1232; found: 262.1238.

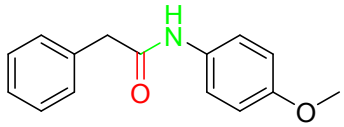


2-phenyl-N-(p-tolyl)acetamide (3al)[5], this compound was prepared according to General Procedure A for 12 h, Yield：87% (39.3 mg), white solid，Mp：128 - 131℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ

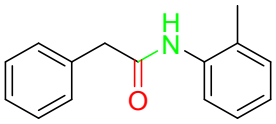
7.38 (s, 1H), 7.31 – 7.24 (m, 2H), 7.21 (d, J = 7.3 Hz, 5H), 6.97 (d, J = 8.0 Hz, 2H), 3.56 (s, 2H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 135.2, 134.7, 134.1, 129.5, 129.4, 129.1, 127.5, 120.1, 44.7, 20.9. HRMS(ESI$^+$) calculated for $C_{15}H_{15}NO$ [M+H]$^+$: 248.1051; found: 248.1053.



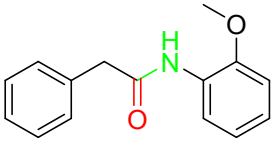
N-(4-isopropylphenyl)-2-phenylacetamide (3am), this compound was prepared according to General Procedure A for 8 h, Yield： 96% (48.5 mg), white solid，Mp：134 - 136℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.34 (m, 2H), 7.31 (t, J = 5.4 Hz, 5H), 7.11 (d, J = 8.4 Hz, 2H), 3.68 (s, 2H), 2.88 – 2.78 (m, 1H), 1.20 (s, 2H), 1.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 145.2, 135.4, 134.7, 129.5, 129.1, 127.5, 126.8, 120.2, 44.7, 33.6, 24.0. FTIR(KBr)：1658 cm^{-1} (CH_2CONR_1R_2), HRMS(ESI$^+$) calculated for $C_{17}H_{19}NO$[M+H]$^+$: 276.1364; found: 276.1366.



N-(4-methoxyphenyl)-2-phenylacetamide (3an)[6], this compound was prepared according to General Procedure A for 12 h**,** Yield：89% (42.7 mg), light yellow solid，Mp：121 – 124℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 8H), 6.77 (d, J = 8.6 Hz, 2H), 3.73 (s, 3H), 3.63 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 156.5, 134.8, 130.9, 129.4, 129.0, 127.4, 122.0, 114.0, 55.5, 44.4. HRMS(ESI$^+$) calculated for $C_{15}H_{15}NO_2$[M+H]$^+$: 264.1000; found: 264.1005.

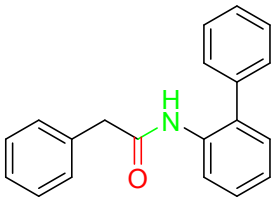


2-phenyl-N-(o-tolyl)acetamide (3ao)[6], this compound was prepared according to General Procedure A for 8 h**,** Yield 99% (44.6 mg), white solid，Mp：158 - 161℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.0 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.26 (d, J = 7.3 Hz, 3H), 7.08 (t, J = 7.5 Hz, 1H), 6.99 (d, J = 7.2 Hz, 1H), 6.91 (dd, J = 14.6, 7.1 Hz, 2H), 3.67 (s, 2H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 135.6, 134.7, 130.4, 129.7, 129.4, 128.3, 127.8, 126.8, 125.0, 122.3, 44.9, 17.1. HRMS(ESI$^+$) calculated for $C_{15}H_{15}NO$[M+H]$^+$: 248.1051; found: 248.1052.

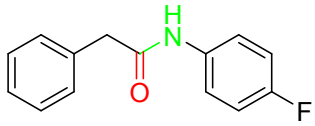


N-(2-methoxyphenyl)-2-phenylacetamide (3ap)[8], this compound was prepared according to General Procedure A for 8 h, Yield 99% (47.7 mg), white solid，Mp：158 - 161℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 7.8 Hz, 1H), 7.72 (s, 1H), 7.32 – 7.27 (m, 2H), 7.27 – 7.22 (m, 3H), 6.90

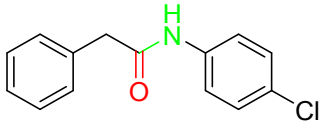
(t, J = 7.7 Hz, 1H), 6.83 (t, J = 7.7 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 3.65 (s, 2H), 3.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) 168.9, 147.9, 134.6, 129.5, 129.0, 127.5, 127.5, 123.7, 121.0, 119.5, 110.0, 55.6, 45.1. HRMS(ESI$^+$) calculated for $C_{15}H_{15}NO_2$ $[M+H]^+$: 264.1000; found: 264.1004.



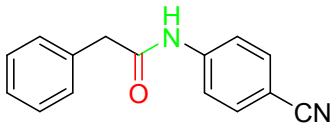
N-([1,1'-biphenyl]-2-yl)-2-phenylacetamide (3aq), this compound was prepared according to General Procedure A for 12 h, Yield 90% (47.7 mg), white solid，Mp：158 - 161℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.2 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.29 – 7.23 (m, 3H), 7.19 (s, 2H), 7.11 (d, J = 6.5 Hz, 2H), 7.03 (d, J = 6.5 Hz, 5H), 3.58 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 137.6, 134.7, 133.8, 132.1, 129.9, 129.3, 129.1, 128.9, 128.8, 128.3, 127.6, 127.4, 124.1, 120.9, 45.1. FTIR(KBr)：1655 cm^{-1} (CH_2CONR_1R_2); HRMS(ESI$^+$) calculated for $C_{20}H_{17}NO[M+H]^+$: 310.1208; found: 310.1208.



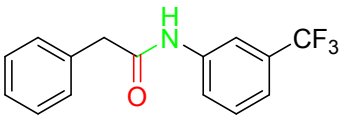
N-(4-fluorophenyl)-2-phenylacetamide (3ar)[7], this compound was prepared according to General Procedure A for 10 h, Yield：95% (43.7 mg), brown solid，Mp：133 - 135℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.22 (s, 1H), 7.63 (dd, J = 8.9, 5.0 Hz, 2H), 7.35 – 7.30 (m, 4H), 7.27 – 7.23 (m, 1H), 7.13 (t, J = 8.8 Hz, 2H), 3.64 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.5, 158.44 (d, $J_{C\text{-}F}$ = 239.7 Hz), 136.4, 136.1 (d, $J_{C\text{-}F}$ = 2.6 Hz),.129.6, 128.8, 127.0, 121.4 (d, $J_{C\text{-}F}$= 7.8 Hz), 115.7 (d, $J_{C\text{-}F}$ = 22.2 Hz), 43.7. HRMS(ESI$^+$) calculated for $C_{14}H_{12}FNO[M+H]^+$: 230.0981; found: 230.0981.



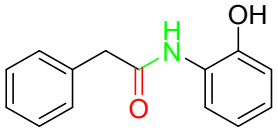
N-(4-chlorophenyl)-2-phenylacetamide (3as)[5,7], this compound was prepared according to General Procedure A for 14 h, Yield：87% (42.8 mg), light yellow solid，Mp：170 - 172℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, J = 7.7, 5.4 Hz, 5H), 7.30 (d, J = 7.4 Hz, 3H), 7.21 (d, J = 8.7 Hz, 2H), 3.70 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 136.2, 134.2, 129.5, 129.3, 128.9, 127.8, 126.4, 121.2, 44.7. HRMS(ESI$^+$) calculated for $C_{14}H_{12}ClNO[M+H]^+$: 246.0686; found: 246.0684.



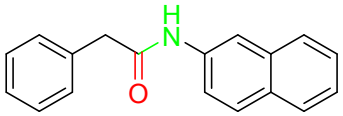
N-(4-cyanophenyl)-2-phenylacetamide(3at)[6], this compound was prepared according to General Procedure A for 12 h, Yield：95% (44.7 mg), yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.62 (s, 1H), 7.78 (q, *J* = 8.5 Hz, 4H), 7.34 (d, *J* = 3.8 Hz, 4H), 7.26 (d, *J* = 3.4 Hz, 1H), 3.71 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.1, 143.5, 135.5, 133.4, 129.3, 128.4, 126.8, 119.2, 119.1, 105.1, 43.4. HRMS(ESI$^+$) calculated for $C_{15}H_{12}N_2O$[M+H]$^+$: 237.1028; found: 237.1030.



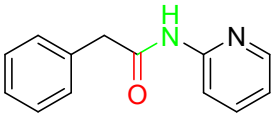
2-phenyl-N-(3-(trifluoromethyl)phenyl)acetamide (3au)[5], this compound was prepared according to General Procedure A for 8 h, Yield：98% (54.7 mg), light yellow solid，Mp：84 - 86℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.65 (s, 1H), 7.52 (d, *J* = 7.3 Hz, 1H), 7.27 – 7.17 (m, 7H), 3.60 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 138.2, 134.1, 131.6 (q, *J* = 32.6 Hz), 129.4, 129.3, 127.8, 123.8 (q, J_{C-F} = 270.7 Hz), 123.0, 121.0 (d, J_{C-F} = 3.7 Hz), 119.7, 116.6 (d, J_{C-F} = 3.6 Hz), 44.7. FTIR(KBr)：1639 cm^{-1} ($CH_2\underline{CO}NR_1R_2$), HRMS(ESI$^+$) calculated for $C_{15}H_{12}F_3NO$[M+H]$^+$: 280.0949; found: 280.0948.



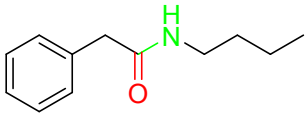
N-(2-hydroxyphenyl)-2-phenylacetamide (3av), this compound was prepared according to General Procedure A for 12 h, Yield：78% (35.3 mg), yellow solid，Mp：61 - 64℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.79 (s, 1H), 9.34 (s, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.30 (m, 4H), 7.27 – 7.22 (m, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 3.75 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.5, 147.6, 136.1, 129.2, 128.3, 126.5, 126.3, 124.5, 121.9, 118.9, 115.5, 42.9. FTIR(KBr)：1639 cm^{-1} ($CH_2\underline{CO}NR_1R_2$), HRMS(ESI$^+$) calculated for $C_{14}H_{13}NO_2$[M+H]$^+$: 250.0844; found: 250.0846.



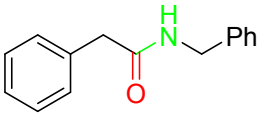
N-(naphthalen-2-yl)-2-phenylacetamide (3aw)[5], this compound was prepared according to General Procedure A for 14 h, Yield：76% (39.6 mg), brown solid，Mp：157 - 160℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.39 (s, 1H), 8.32 (s, 1H), 7.85 (d, *J* = 4.7 Hz, 1H), 7.82(d, *J* = 3.0 Hz, 1H), 7.62 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.42(d, *J* = 7.8 Hz, 3H), 7.37 (s, 1H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.2 Hz, 1H), 3.72 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.5, 136.9, 136.1, 133.5, 129.8, 129.2, 128.4, 128.4, 127.5, 127.3, 126.6, 126.5, 124.6, 120.0, 115.3, 43.5. HRMS (ESI$^+$) calculated for $C_{18}H_{15}NO$ [M+H]$^+$: 284.1051; found: 284.1050.



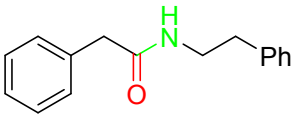
2-phenyl-N-(pyridin-2-yl)acetamide (3ax), this compound was prepared according to General Procedure A for 12 h, Yield：89% (37.6 mg), brown solid，Mp：123 - 124℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.18 – 8.06 (m, 2H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.29 – 7.23 (m, 2H), 7.21 (d, *J* = 7.0 Hz, 3H), 6.95 – 6.87 (m, 1H), 3.65 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 151.4, 147.6, 138.4, 134.1, 129.4, 129.1, 127.6, 119.9, 114.2, 44.8. FTIR(KBr)：1639 cm^{-1} ($CH_2\underline{CO}NR_1R_2$),：1640 cm^{-1} ($CH_2\underline{CO}NR_1R_2$), HRMS(ESI$^+$) calculated for $C_{13}H_{12}N_2O$ $[M+H]^+$: 213.1028; found: 213.1024.



N-butyl-2-phenylacetamide (3ay)[4], this compound was prepared according to General Procedure A for 12 h**,** Yield：79% (30.1 mg), brown solid，Mp：53 - 55℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.2 Hz, 2H), 7.30 (d, *J* = 7.1 Hz, 1H), 7.26 (dd, *J* = 5.4, 4.4 Hz, 2H), 5.45 (s, 1H), 3.56 (s, 2H), 3.20 (dd, *J* = 13.1, 6.9 Hz, 2H), 1.40 (dt, *J* = 14.8, 7.2 Hz, 2H), 1.25 (dd, *J* = 15.0, 7.4 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 135.1, 129.5, 129.0, 127.3, 43.9, 39.4, 31.5, 20.0, 13.7. HRMS(ESI$^+$) calculated for $C_{12}H_{17}NO$ $[M+H]^+$: 192.1388; found: 192.1391.

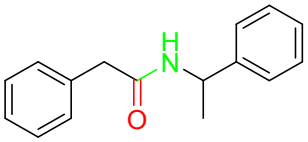


N-benzyl-2-phenylacetamide (3az)[4], this compound was prepared according to General Procedure A for 12 h, Yield：72% (32.4 mg), yellow solid，Mp：123 - 125℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.26 (t, *J* = 7.0 Hz, 6H), 7.16 (d, *J* = 7.2 Hz, 2H), 5.87 (s, 1H), 4.39 (d, *J* = 5.7 Hz, 2H), 3.60 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 138.2, 134.8, 129.4, 129.0, 128.6, 127.5, 127.4, 127.4, 43.8, 43.6. HRMS (ESI$^+$) calculated for $C_{15}H_{15}NO$ $[M+H]^+$: 226.1232; found: 226.1229.

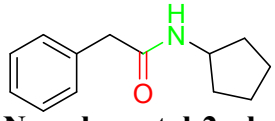


N-phenethyl-2-phenylacetamide (3ba), this compound was prepared according to General Procedure A for 10 h, Yield：81% (38.6 mg), yellow solid，Mp：92 - 95℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.3 Hz, 2H), 7.26 (dd, *J* = 14.0, 6.8 Hz, 3H), 7.16 (d, *J* = 6.9 Hz, 3H), 7.02 (d, *J* = 7.0 Hz, 2H), 5.43 (s, 1H), 3.52 (s, 2H), 3.45 (dd, *J* = 12.9, 6.5 Hz, 2H), 2.71 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 138.7, 134.8, 129.5, 129.0, 128.7, 128.6, 127.3, 126.4, 43.9,

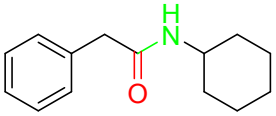
40.7, 35.5. FTIR(KBr)：1639 cm^{-1} ($CH_2\underline{CO}NR_1R_2$),：1640 cm^{-1} ($CH_2\underline{CO}NR_1R_2$), HRMS ($ESI^+$) calculated for $C_{16}H_{17}NO$ $[M+Na]^+$: 262.1208; found: 262.1210.



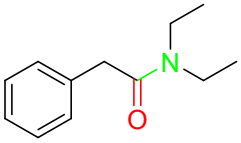
2-phenyl-N-(1-phenylethyl)acetamide (3bb), this compound was prepared according to General Procedure A for 10 h, Yield：91% (43.4 mg), white solid，Mp：115 - 117℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.1 Hz, 2H), 7.31 – 7.22 (m, 6H), 7.18 (d, *J* = 7.0 Hz, 2H), 5.16 – 5.06 (m, 1H), 3.56 (s, 2H), 1.39 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 143.1, 135.0, 129.4, 129.0, 128.6, 127.3, 127.3, 126.0, 48.8, 43.9, 21.8. FTIR(KBr)：1641 cm^{-1} ($CH_2\underline{CO}NR_1R_2$), HRMS($ESI^+$) calculated for $C_{16}H_{17}NO$ $[M+Na]^+$: 262.1208; found: 262.1206.



N-cyclopentyl-2-phenylacetamide (3bc), this compound was prepared according to General Procedure A for 16 h, Yield：63% (25.8 mg), yellow solid，Mp：116 - 119℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 2H), 5.40 (s, 1H), 4.18 (dd, *J* = 13.9, 7.0 Hz, 1H), 3.54 (s, 2H), 1.92 (dd, *J* = 12.1, 6.1 Hz, 2H), 1.55 (s, 4H), 1.28 – 1.22 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 135.2, 129.4, 129.0, 127.2, 51.3, 43.9, 33.0, 23.6. FTIR(KBr)：1641 cm^{-1} ($CH_2\underline{CO}NR_1R_2$), HRMS($ESI^+$) calculated for $C_{13}H_{17}NO$ $[M+Na]^+$: 226.1208; found: 226.1207.

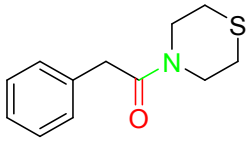


N-cyclohexyl-2-phenylacetamide (3bd)[8], this compound was prepared according to General Procedure A for 12 h, Yield：85% (36.9 mg), light yellow solid，Mp：131 - 133℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.3 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 7.1 Hz, 2H), 5.40 (s, 1H), 3.80 – 3.69 (m, 1H), 3.53 (s, 2H), 1.84 – 1.81 (m, 2H), 1.66 – 1.54 (m, 2H), 1.37 – 1.21 (m, 2H), 1.06 – 0.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 135.2, 129.3, 128.9, 127.2, 48.2, 44.0, 32.9, 25.4, 24.7. HRMS(ESI^+) calculated for $C_{14}H_{19}NO$ $[M+Na]^+$: 240.1364; found: 240.1367.

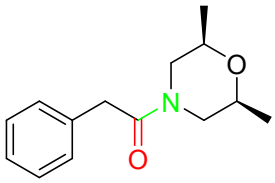


N,N-diethyl-2-phenylacetamide (3be)[8], this compound was prepared according to General Procedure A for 12 h, Yield：55% (21.2 mg), white solid，Mp：57-59℃; ^1H NMR (400 MHz,

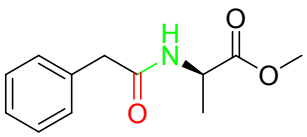
$CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.28 – 7.23 (m, 3H), 3.70 (s, 2H), 3.39 (q, *J* = 7.1 Hz, 2H), 3.30 (q, *J* = 7.1 Hz, 2H), 1.15 – 1.06 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 135.6, 128.6,128.6, 126.7, 42.4, 40.9, 40.2, 14.2, 13.0. HRMS(ESI$^+$) calculated for $C_{12}H_{17}NO$ $[M+Na]^+$: 214.1208; found: 214.1206.



2-phenyl-1-thiomorpholinoethan-1-one (3bf), this compound was prepared according to General Procedure A for 12 h, Yield： 55% (24.4 mg), yellow solid，Mp：83 - 85℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.3 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 3H), 3.92 – 3.87 (m, 2H), 3.73 (s, 2H), 3.71 – 3.68 (m, 2H), 2.60 – 2.55 (m, 2H), 2.33 – 2.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 134.8, 128.9, 128.5, 127.0, 48.8, 44.4, 41.4, 27.5, 27.3. FTIR(KBr)：1649 cm^{-1} ($CH_2\underline{CO}NR_1R_2$), HRMS(ESI$^+$) calculated for $C_{12}H_{15}NOS$ $[M+Na]^+$: 244.0772; found: 244.0769.

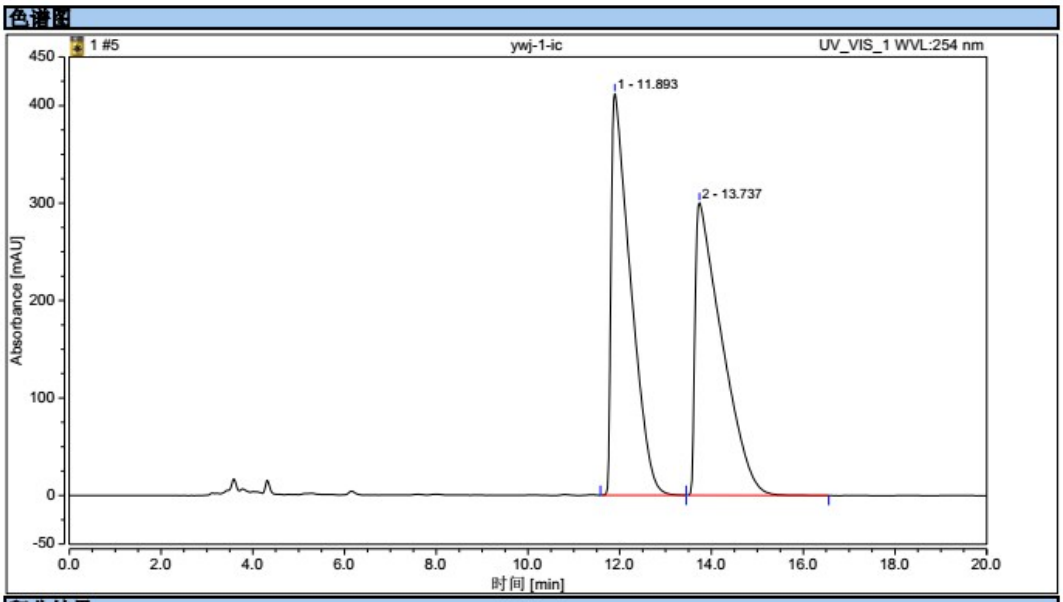


1-((2S,6R)-2,6-dimethylmorpholino)-2-phenylethan-1-one (3bg), this compound was prepared according to General Procedure A for 12 h, Yield：79% (37.0 mg), yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 6.9 Hz, 3H), 4.48 (d, *J* = 13.2 Hz, 1H), 3.73 (s, 2H), 3.63 (d, *J* = 13.1 Hz, 1H), 3.52 – 3.42 (m, 1H), 3.27 – 3.17 (m, 1H), 2.76 – 2.66 (m, 1H), 2.37 – 2.26 (m, 1H), 1.17 (d, *J* = 6.2 Hz, 3H), 1.07 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.32 (s), 134.9, 128.8, 128.5, 126.9, 71.9, 71.6, 51.7, 47.2, 41.1, 18.7, 18.6. FTIR(thin film)：1644 cm^{-1} ($CH_2\underline{CO}NR_1R_2$), HRMS(ESI$^+$) calculated for $C_{14}H_{19}NO_2$ $[M+Na]^+$: 256.1313; found: 256.1317.



(S)-Methyl 2-(2-phenylacetamido)propanoate (3bh), this compound was prepared according to General Procedure A for 12 h (α-amino-esters was in the hydrochloride form), Yield：83% (36.7 mg), yellow solid，Mp：63 - 65℃; ^{1}H NMR (400 MHz, $CDCl_3$) 7.36 (t, *J* = 7.0 Hz, 2H), 7.29 (t, *J* = 8.1 Hz, 3H), 6.07 (s, 1H), 4.58 (m, *J* = 7.2 Hz, 1H), 3.71 (s, 3H), 3.59 (s, 2H), 1.34 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 170.5, 134.6, 129.4, 129.0, 127.4, 52.4, 48.1, 43.6, 18.3.

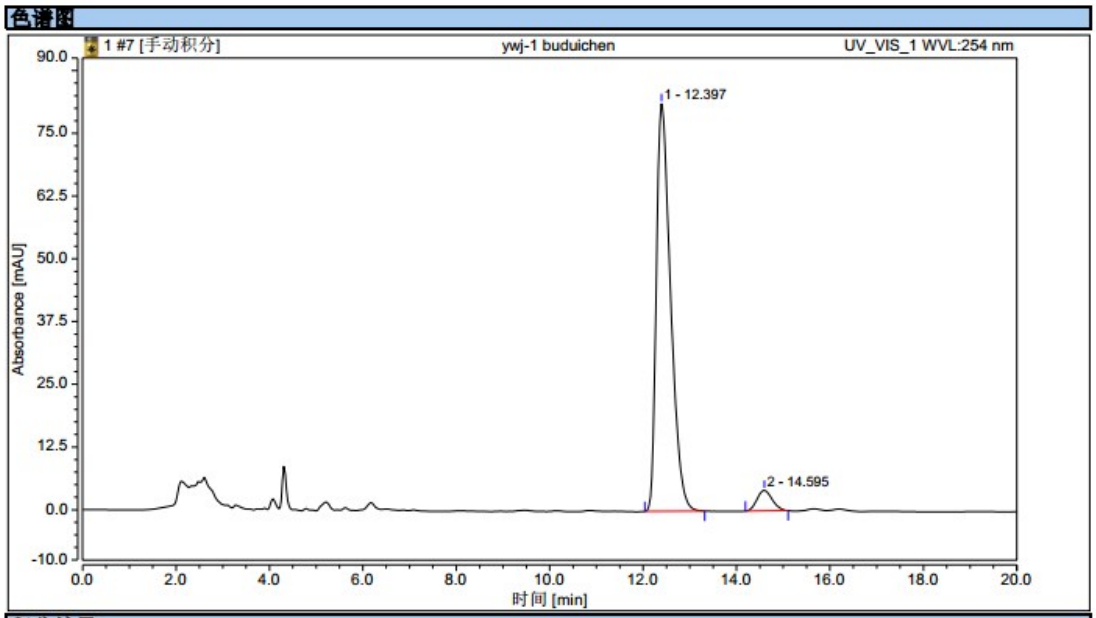
FTIR(KBr)：1613 cm^{-1} ($CH_2\underline{CO}NR_1R_2$), HRMS(ESI$^+$) calculated for $C_{12}H_{15}NO_3$ $[M+Na]^+$: 244.0950; found: 244.0952. HPLC (Chiral IC, n-hexane:isopropanol=75:25, flow rate = 1.0 mL/min), tR= 11.893, 13.737 min, ee = 90%.



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		11.893	202.477	412.210	49.91	57.83	n.a.
2		13.737	203.173	300.575	50.09	42.17	n.a.
总和:			**405.650**	**712.785**	**100.00**	**100.00**	

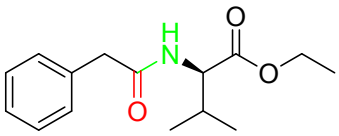
(Rac-HPLC spectrum)



积分结果

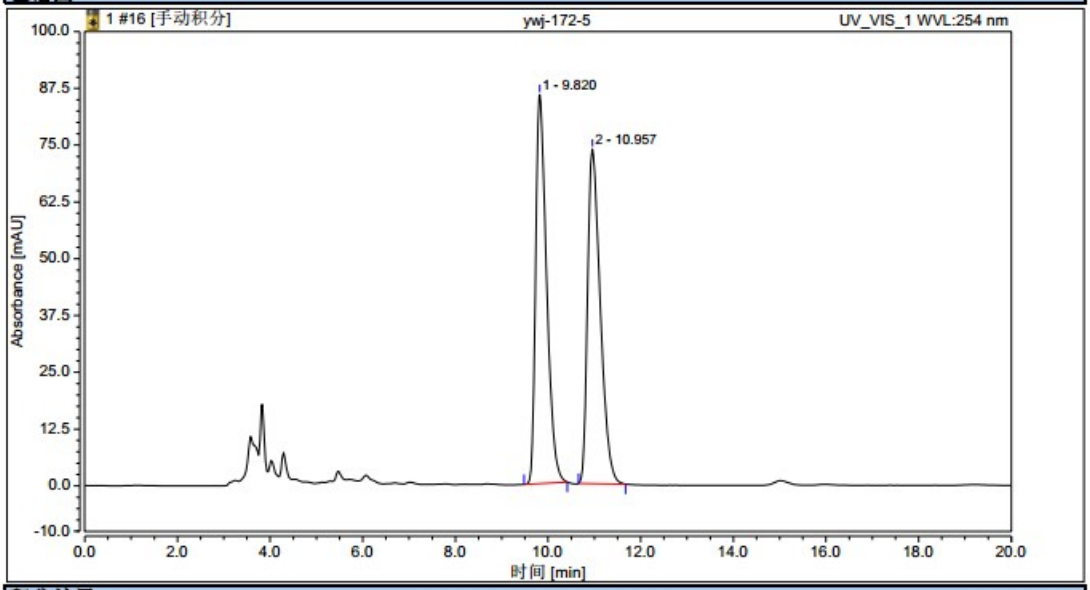
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		12.397	28.702	81.180	94.87	95.22	n.a.
2		14.595	1.551	4.078	5.13	4.78	n.a.
总和:			**30.254**	**85.258**	**100.00**	**100.00**	

(3aj HPLC spectrum)



(S)-Ethyl 3-methyl-2-(2-phenylacetamido)butanoate (3bi)，this compound was prepared according to General Procedure A for 12 h **(**α-amino-esters was in the hydrochloride form， equal dppf instead of PPh_3), Yield：42% (22.3 mg), yellow solid，Mp：58 - 60℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, *J* = 9.7, 2H), 7.30 (t, *J* = 6.6 Hz, 3H), 5.89 (d, *J* = 7.9 Hz, 1H), 4.52 (dd, *J* = 8.8, 4.8 Hz, 1H), 4.21 – 4.09 (m, 2H), 3.62 (s, 2H), 2.16 – 2.05 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.86 (d, *J* = 6.9 Hz, 3H), 0.77 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 170.8, 134.8, 129.4, 129.1, 127.5, 61.2, 57.0, 43.8, 31.3, 18.9, 17.6, 14.2. FTIR(KBr)：1640 cm^{-1} ($CH_2\underline{CO}NR_1R_2$), HRMS(ESI$^+$) calculated for $C_{12}H_{15}NO_3$ $[M+Na]^+$: 264.1600; found: 264.1601. HPLC (Chiral IC, n-hexane:isopropanol=75:25, flow rate = 1.0 mL/min), tR= 9.820, 10.957 min, ee = 100%.

色谱图

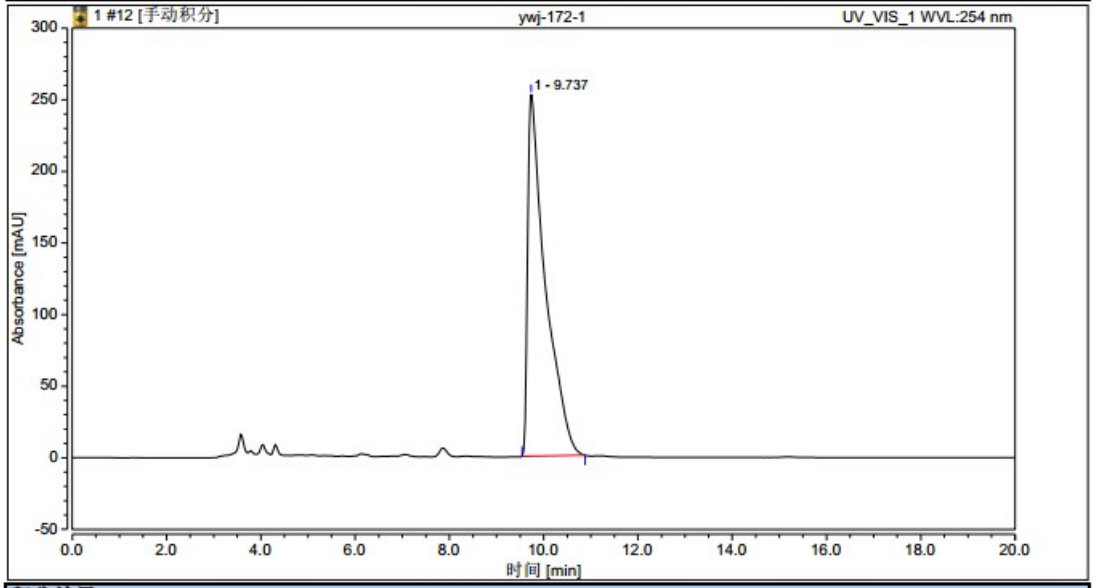


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		9.820	23.445	85.635	50.05	53.76	n.a.
2		10.957	23.397	73.661	49.95	46.24	n.a.
总和:			**46.842**	**159.296**	**100.00**	**100.00**	

(Rac-HPLC spectrum)

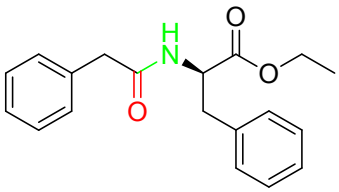
色谱图



积分结果

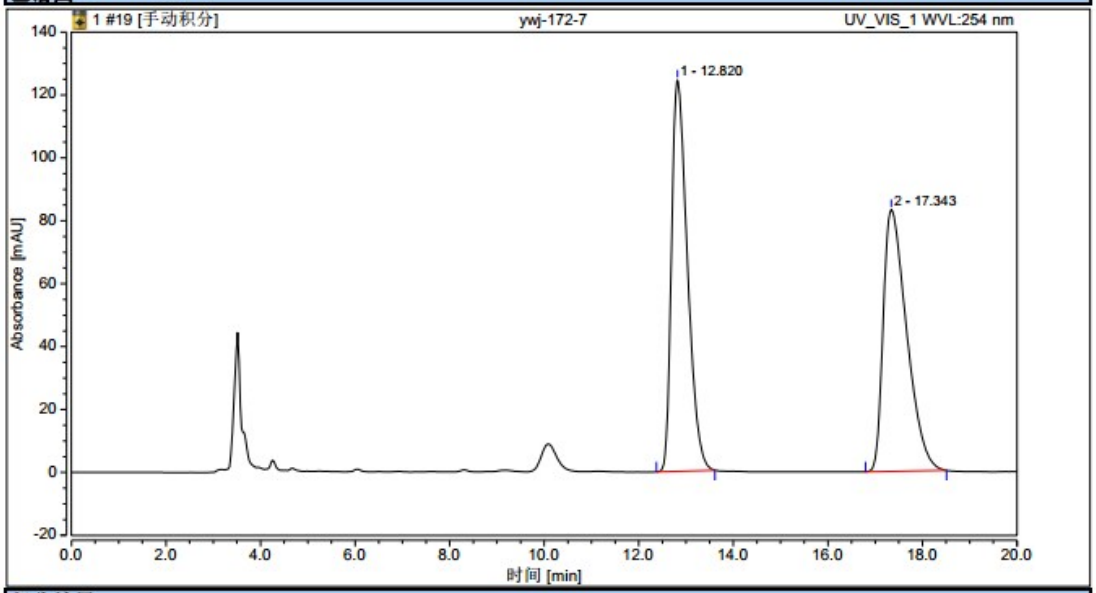
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		9.737	109.909	252.405	100.00	100.00	n.a.
总和:			**109.909**	**252.405**	**100.00**	**100.00**	

(3ak HPLC spectrum)



(S)-Ethyl 3-phenyl-2-(2-phenylacetamido)propanoate (3bj)，this compound was prepared according to General Procedure A for 16 h (α -amino-esters was in the hydrochloride form， equal dppf instead of PPh_3), Yield：39% (22.9 mg), brown oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 3H), 7.21 – 7.16 (m, 5H), 6.91 (dd, *J* = 6.5, 3.0 Hz, 2H), 5.84 (d, *J* = 7.3 Hz, 1H), 4.87 – 4.79(m, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.55 (s, 2H), 3.10 – 2.97 (m, 2H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 170.4, 135.7, 134.5, 129.4, 129.2, 129.0, 128.5, 127.4, 127.0, 61.5, 53.0, 43.7, 37.7, 14.1. FTIR(KBr)：1655 cm^{-1} ($CH_2\underline{CO}NR_1R_2$), HRMS(ESI$^+$) calculated for $C_{12}H_{15}NO_3$ $[M+H]^+$: 312.1600; found: 312.1594. HPLC (Chiral IC, n-hexane:isopropanol=75:25, flow rate = 1.0 mL/min), tR= 12.820, 17.343 min, ee = 94%.

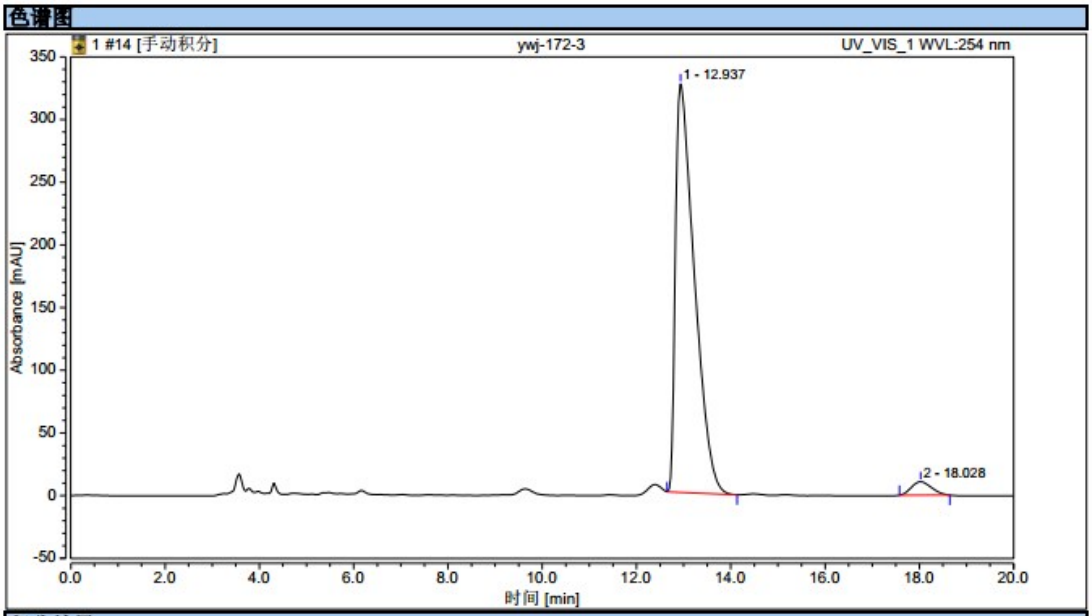
色谱图



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		12.820	48.330	124.447	50.27	59.91	n.a.
2		17.343	47.808	83.271	49.73	40.09	n.a.
总和:			**96.138**	**207.719**	**100.00**	**100.00**	

(Rac-HPLC spectrum)

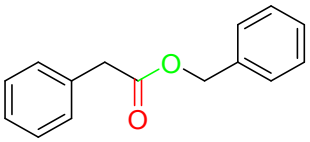


积分结果

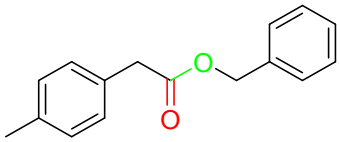
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		12.937	151.150	325.740	96.60	96.80	n.a.
2		18.028	5.328	10.758	3.40	3.20	n.a.
总和:			156.478	336.499	100.00	100.00	

(3al HPLC spectrum)

Part 6.Characterization of carbonylation products of esters (reaction with alcohols) (5aa—5ay)

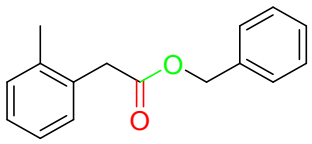


Benzyl 2-phenylacetate (5aa)[102-16-9], this compound was prepared according to General Procedure B for 12 h, Yield: 82% (36.7 mg), light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.06 (m, 10H), 5.12 (s, 2H), 3.66 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 135.9, 133.9, 129.3, 128.6, 128.6, 128.2, 128.1, 127.2, 66.6, 41.4. HRMS(ESI$^+$) calculated for $C_{15}H_{14}O_2$ [M+Na$^+$] 249.0891, found 249.0890.

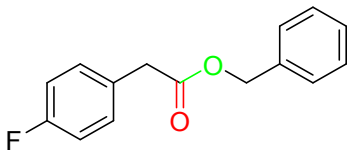


Benzyl 2-(p-tolyl)acetate (5ab), this compound was prepared according to General Procedure B for 10 h, Yield: 86% (41.2 mg), light green liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 5H), 7.14 (m, 4H), 5.11 (s, 2H), 3.62 (s, 2H), 2.32 (s,3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 136.8,

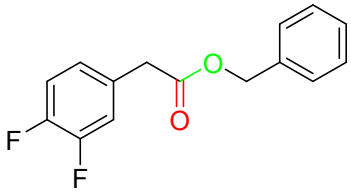
136.0, 130.9, 129.3, 129.2, 128.6, 128.2, 128.2, 66.6, 41.0, 21.1. FTIR(thin film): 1738 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{16}H_{16}O_2$ [M+H$^+$] 241.1229, found 241.1220.



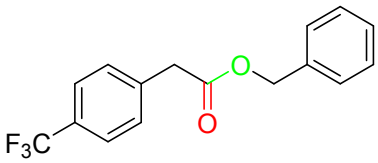
Benzyl 2-(o-tolyl)acetate (5ac), Yield: 86% (41.1 mg), this compound was prepared according to General Procedure B for 10 h, light green liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 5H), 7.24 – 7.12 (m, 4H), 5.14 (s, 2H), 3.67 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 136.9, 136.0, 132.7, 130.4, 130.2, 128.5, 128.2, 128.1, 127.5, 126.2, 66.6, 39.2, 19.6. FTIR(thin film): 1739 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{16}H_{16}O_2$ [M+H$^+$] 241.1229, found 241.1223.



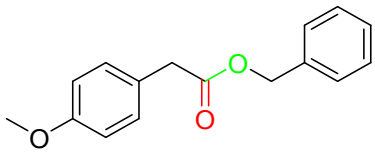
Benzyl 2-(4-fluorophenyl)acetate (5ad), this compound was prepared according to General Procedure B for 12 h, Yield: 82% (39.9 mg), light green liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 5H), 7.36 – 7.21 (m, 2H), 6.99 (t, J = 8.7 Hz, 2H), 5.13 (s, 2H), 3.63 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 162.1 (d, $J_{C\text{-}F}$= 245.4 Hz), 135.8, 130.9 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.7 (d, $J_{C\text{-}F}$ = 3.3 Hz), 128.6, 128.3, 128.2, 115.4 (d, $J_{C\text{-}F}$ = 21.5 Hz), 66.8, 40.5. FTIR(thin film): 1731 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{15}H_{13}FO_2$ [M +H$^+$] 245.0978, found 245.0972.



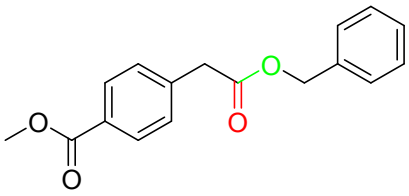
Benzyl 2-(3,4-difluorophenyl)acetate (5ae), this compound was prepared according to General Procedure B for 12 h, Yield: 81% (47.7 mg), light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 5H), 7.14 – 7.04 (m, 2H), 7.00 – 6.95 (m, 1H), 5.13 (s, 2H), 3.61 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 151.18 (dd, $J_{C\text{-}F}$ = 51.6, 12.7 Hz), 148.71 (dd, $J_{C\text{-}F}$ = 50.9, 12.7 Hz), 135.6, 130.7 (dd, $J_{C\text{-}F}$ = 50.9, 6.1 Hz), 128.6, 128.4, 128.3, 125.4 (dd, $J_{C\text{-}F}$ = 6.2, 3.7 Hz), 118.4 (d, $J_{C\text{-}F}$ = 17.7 Hz), 117.3 (d, $J_{C\text{-}F}$ = 17.4 Hz), 66.9, 40.3 (d, $J_{C\text{-}F}$ = 1.2 Hz).. FTIR(thin film): 1738 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{15}H_{12}F_2O_2$ [M+Na$^+$] 285.0703, found 285.0695.



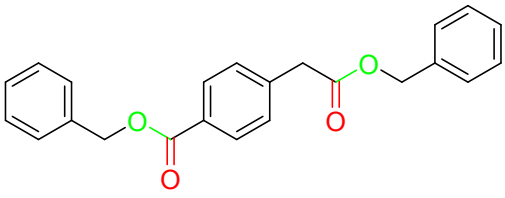
Benzyl 2-(4-(trifluoromethyl)phenyl)acetate (5af), this compound was prepared according to General Procedure B for 10 h, Yield: 80% (47.1 mg), light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.36 – 7.27 (m, 5H), 5.14 (s, 2H), 3.72 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 139.9 (d, J_{C-F} = 4.8 Hz), 133.7, 130.4 (q, J_{C-F} = 32.5 Hz), 129.3, 128.7, 128.0, 127.3, 125.5 (q, J_{C-F} = 3.8 Hz), 124.1 (q, J_{C-F} = 272.1 Hz),, 65.6, 41.4. FTIR(thin film)：1731 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{16}H_{13}F_3O_2$ [M+H$^+$] 295.0946, found 295.0940.



Benzyl 2-(4-methoxyphenyl)acetate (5ag), this compound was prepared according to General Procedure B for 14 h, Yield: 62% (31.8 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 5H), 7.20 (d, J = 8.7 Hz, 2H), 6.85(d, J = 8.8 Hz,2H), 5.12 (s, 2H), 3.79 (s, 3H), 3.60 (s,2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 158.8, 136.0, 130.4, 128.6, 128.2, 128.2, 126.0, 114.1, 66.6, 55.3, 40.5. FTIR(thin film)：1735 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{16}H_{16}O_3$ [M+H$^+$]257.1178, found 241.1172.

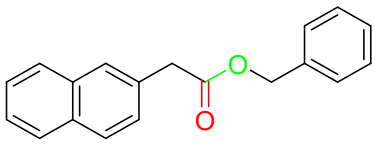


Methyl 4-(2-(benzyloxy)-2-oxoethyl)benzoate (5ah), this compound was prepared according to General Procedure B for 12 h, Yield: 66% (37.1 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.99(d, J = 8.4 Hz,2H), 7.41 – 7.28 (m, 7H), 5.14 (s, 2H), 3.90 (s, 3H), 3.72 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 166.9, 139.0, 135.7, 129.9, 129.4, 129.1, 128.6, 128.4, 128.2, 66.9, 52.1, 41.3. FTIR(thin film)：1740 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{17}H_{16}O_4$ [M+H$^+$] 285.1127, found 285.1131.

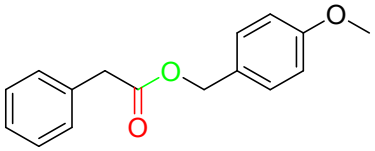


Benzyl-4-(2-(benzyloxy)-2-oxoethyl)benzoate (5ai), this compound was prepared according to General Procedure B for 16 h, Yield: 40%/45%, (27.5 mg/ 30.8), from 4-chloro/bromo benzylic ammonium salts, yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.3 Hz, 2H), 7.49 – 7.18 (m, 12H), 5.35 (s, 2H), 5.13 (s, 2H), 3.71 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 166.2, 139.2, 136.1, 135.7, 130.0, 129.4, 129.1, 128.6, 128.6, 128.4, 128.3, 128.2, 128.2, 66.9, 66.7, 41.3.

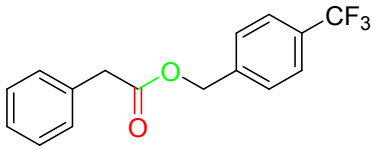
FTIR(thin film)：1731 cm^{-1} ($CH_2\underline{CO}OR$); HRMS(ESI$^+$) calculated for $C_{23}H_{20}O_4$ [M+Na^+] 383.1259, found 383.1261.



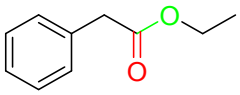
Benzyl 2-(naphthalen-2-yl)acetate (5aj), this compound was prepared according to General Procedure B for 16 h, Yield: 47% (25.9 mg), light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, *m*, 3H), 7.72 (s, 1H), 7.47 – 7.39 (m, 3H), 7.36 – 7.29 (m, 5H), 5.15 (s, 2H), 3.83 (s,2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 135.9, 133.5, 132.6, 131.4, 128.6, 128.3, 128.2, 128.1, 127.7, 127.7, 127.4, 126.2, 125.9, 66.8, 41.6. FTIR(thin film)：1731 cm^{-1} ($CH_2\underline{CO}OR$); HRMS(ESI$^+$) calculated for $C_{19}H_{16}O_2$ [M+H^+] 277.1229, found 277.1236.



4-methoxybenzyl 2-phenylacetate (5ak), this compound was prepared according to General Procedure B for 12 h, Yield: 57% (29.2 mg), yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 7H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.06 (s, 2H), 3.79 (s, 3H), 3.62 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 159.7, 134.0, 130.0, 129.3, 128.6, 128.0, 127.1, 114.0, 66.5, 55.3, 41.4. FTIR(thin film)：1740 cm^{-1} ($CH_2\underline{CO}OR$); HRMS(ESI$^+$) calculated for $C_{16}H_{16}O_2$ [M+H^+] 257.1178, found 257.1180.

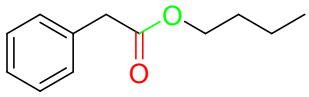


4-(trifluoromethyl)benzyl 2-phenylacetate (5al), this compound was prepared according to General Procedure B for 10 h, Yield: 79% (46.7 mg), yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.24 (m, 5H), 5.17 (s, 2H), 3.69 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) 171.2, 139.9 (d, $J_{C\text{-}F}$ = 1.2 Hz), 133.7, 130.4 (d, $J_{C\text{-}F}$= 32.5 Hz), 129.3, 128.7, 128.0, 127.3, 125.5 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.1 (d, $J_{C\text{-}F}$ = 272.1 Hz), 65.6, 41.4. FTIR(thin film)：1729 cm^{-1} ($CH_2\underline{CO}OR$); HRMS(ESI$^+$) calculated for $C_{16}H_{13}F_3O_2$ [M+H^+] 295.0946, found 295.0950.

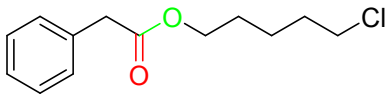


Ethyl 2-phenylacetate (5am), this compound was prepared according to General Procedure B for 16 h, Yield: 48% (15.8 mg), 20 mol% xantphos extra added，^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 6.97

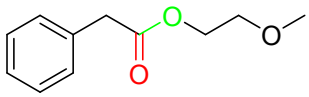
(m, 4H), 4.14 (q, J = 7.1 Hz, 2H), 3.61 (s, 2H), 1.24 (t, J = 7.1 Hz, 3H). FTIR(thin film)：1738 cm^{-1} (CH_2COOR); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 134.2, 129.3, 128.6, 127.0, 60.9, 41.5, 14.2. HRMS(ESI$^+$) calculated for $C_{10}H_{12}O_2$ [M+Na^+] 187.0735, found 187.0739.



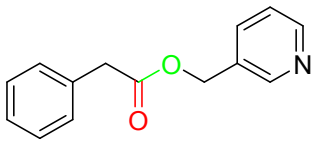
Butyl 2-phenylacetate (5an), this compound was prepared according to General Procedure B For 12 h, Yield: 54% (21.1 mg), yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 5H), 4.09 (t, J = 6.7 Hz, 2H), 3.61 (s, 2H), 1.62 – 1.54(m, 4H), 1.38 – 1.31(m, 2H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 134.3, 129.3, 128.6, 127.1, 64.8, 41.5, 30.7, 19.1, 13.7. FTIR(thin film)：1736 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{12}H_{16}O_2$ [M+Na^+] 215.1048, found 215.1043.



5-chloropentyl 2-phenylacetate (5ao), this compound was prepared according to General Procedure B for 10 h, Yield: 61% (26.3 mg), yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 5H), 4.10 (t, J = 6.5 Hz, 2H), 3.61 (s, 2H), 3.49 (t, J = 6.6 Hz, 2H), 1.80 – 1.71 (m, 2H), 1.69 – 1.61 (m, 2H), 1.51 – 1.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 134.1, 129.3, 128.6, 127.1, 64.6, 44.8, 41.5, 32.1, 27.9, 23.3. FTIR(thin film)：1736 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{13}H_{17}ClO_2$ [M+H^+] 241.0995, found 241.0990.

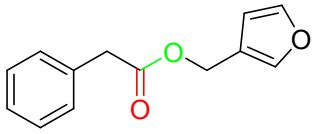


2-methoxyethyl 2-phenylacetate (5ap), this compound was prepared according to General Procedure B for 10 h, Yield: 59% (22.9 mg), yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 5H), 4.25 (t, J = 5.4, 2H), 3.66 (s,2 H), 3.58 (t, J = 4.1 Hz, 2H), 3.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 134.0, 129.3, 128.6, 127.1, 70.4, 63.9, 59.0, 41.2. FTIR(thin film)：1737 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{11}H_{14}O_3$ [M+Na^+] 263.0841, found 263.0835.

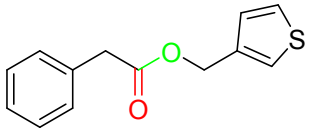


Pyridin-3-ylmethyl 2-phenylacetate (5aq), this compound was prepared according to General Procedure B for 12 h, Yield: 65% (29.5 mg), yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 – 8.53 (m,2H), 7.68 – 7.59 (m, 1H), 7.37 – 7.22 (m, 6H), 5.14 (s, 2H), 3.67 (s, 2H). ^{13}C NMR (100

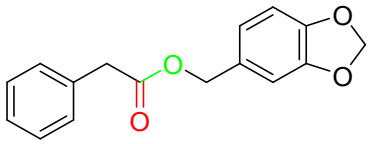
MHz, $CDCl_3$) δ 171.2, 149.5, 149.4, 136.0, 133.6, 131.6, 129.2, 128.7, 127.3, 123.5, 64.0, 41.3. FTIR(thin film)：1738 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{14}H_{13}NO_2$ [M+H$^+$] 228.1025, found 228.1019.



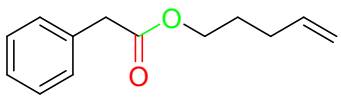
Furan-3-ylmethyl 2-phenylacetate (5ar), this compound was prepared according to General Procedure B for 12 h, Yield: 54% (24.1 mg), yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 0.6 Hz, 1H), 7.37 (d, *J* = 1.5 Hz, 1H), 7.34 –7.25 (m, 5H), 6.39 (s, 1H), 5.00 (s, 2H), 3.63 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 143.4, 141.6, 133.9, 129.3, 128.6, 127.2, 120.4, 110.5, 58.2, 41.3. FTIR(thin film)：1738 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{13}H_{12}O_3$ [M+H$^+$] 217.0865, found 217.0866.



Thiophen-3-ylmethyl 2-phenylacetate (5as), this compound was prepared according to General Procedure B for 12 h, Yield: 63% (29.2 mg), yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 6H), 7.23 (s, 2H), 7.03 (d, *J* = 4.9 Hz, 1H), 5.12 (s, 2H), 3.64 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 136.7, 133.9, 129.3, 128.6, 127.5, 127.2, 126.2, 124.2, 61.7, 41.3. FTIR(thin film)：1736 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{13}H_{12}O_2S$[M+Na$^+$] 255.0456, found 255.0450.

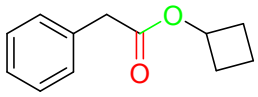


Benzo[d][1,3]dioxol-5-ylmethyl 2-phenylacetate (5at), this compound was prepared according to General Procedure B for 10 h, Yield: 74% (37.1 mg), yellow solid; Mp：112-114 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 5H), 6.81– 6.74 (m, 3H), 5.94 (s, 2H), 5.02 (s, 2H), 3.64 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 147.9, 147.7, 134.0, 129.7, 129.3, 128.6, 127.2, 122.2, 109.0, 108.3, 101.2, 66.6, 41.4. FTIR(KBr)：1736 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{16}H_{14}O_3$ [M+Na$^+$] 277.0841, found 277.0838.

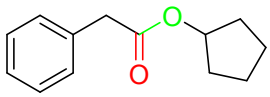


Pent-4-en-1-yl 2-phenylacetate (5au), this compound was prepared according to General Procedure B for 10 h, Yield: 80% (32.6 mg), yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 5H),

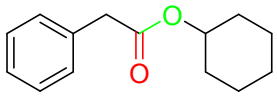
5.83 – 5.70 (m, 1H), 5.03 – 4.93 (m, 2H), 4.10 (t, J = 9.0 Hz, 2H), 3.61 (s,2H), 2.07 (dd, J = 14.3, 7.3 Hz, 2H), 1.76 – 1.57 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 137.5, 134.2, 129.3, 128.6, 127.1, 115.3, 64.3, 41.5, 30.0, 27.9. FTIR(thin film)：1761 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{13}H_{16}O_2$ [M+Na$^+$] 227.1048, found 227.1043.



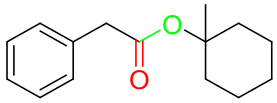
Cyclobutyl 2-phenylacetate (5av), this compound was prepared according to General Procedure B for 10 h, Yield: 77% (29.1 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.20 (m, 5H), 5.07 – 4.83 (m, 1H), 3.58 (s, 2H), 2.44 – 2.26 (m, 2H), 2.09 – 1.58 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 134.2, 129.3, 128.6, 127.0, 69.3, 41.4, 30.3, 13.6. FTIR(thin film)：1736 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{12}H_{14}O_2$ [M+Na$^+$] 213.0891, found 213.0886.



Cyclopentyl 2-phenylacetate (5aw), this compound was prepared according to General Procedure B for 12 h**,** Yield: 61% (24.8 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.18 (m, 5H), 5.24 – 5.13 (m, 1H), 3.57 (s, 2H), 1.89 – 1.78 (m, 2H), 1.72 – 1.62 (m, 4H), 1.60 – 1.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 134.4, 129.2, 128.5, 127.0, 77.6, 41.8, 32.7, 23.7. FTIR (thin film)：1734 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{13}H_{16}O_2$ [M+Na$^+$] 227.1048, found 227.1047.



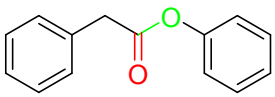
Cyclohexyl 2-phenylacetate (5ax), this compound was prepared according to General Procedure B for 12 h, Yield: 66% (28.6 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 5H), 4.81 – 4.73 (m, 1H), 3.59 (s, 2H), 1.86 – 1.77 (m, 2H), 1.74 – 1.64 (m, 2H), 1.55 – 1.25 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 134.5, 129.2, 128.5, 127.0, 73.1, 41.9, 31.6, 25.4, 23.7. FTIR(thin film)：1732 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{14}H_{18}O_2$ [M+H$^+$] 219.1385, found 219.1385.



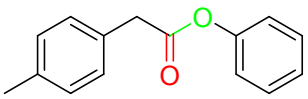
1-methylcyclohexyl 2-phenylacetate (5ay), this compound was prepared according to General Procedure B for 16 h, Yield: 20% (9.4 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.31 (m, 3H), 7.29 (d, J = 2.6 Hz, 2H), 3.58 (s, 2H), 1.47 (s, 3H), 1.46 – 1.27 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 134.9, 129.4, 128.5, 126.9, 82.4, 43.0, 36.6, 25.6, 25.4, 22.0. FTIR(thin

film)：1731 cm^{-1} (CH_2COOR); HRMS(ESI^+) calculated for $C_{15}H_{20}O_2$[$M+Na^+$] 255.1361, found 255.1364.

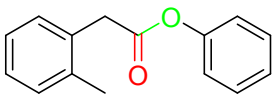
Part 7.Characterization of carbonylation products of esters (reaction with phenols) (7aa—7ay)



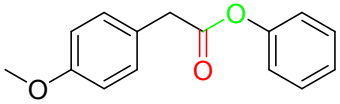
Phenyl 2-phenylacetate (7aa)[722-01-0], this compound was prepared according to General Procedure C for 8 h, Yield: 81% (34.3 mg), colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 7H), 7.20 (t, J = 7.4 Hz, 1H), 7.05 (d, J = 7.8 Hz, 2H), 3.86 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 150.8, 133.5, 129.4, 129.3, 128.8, 127.4, 125.9, 121.5, 41.5. HRMS(ESI^+) calculated for $C_{14}H_{12}O_2$ [$M+H^+$] 213.0916, found 213.0910.



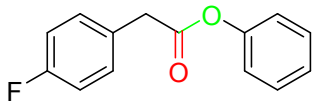
Phenyl 2-(p-tolyl)acetate(7ab), this compound was prepared according to General Procedure C for 8 h, Yield: 88% (40.2 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 10.7, 5.1 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.23 – 7.14 (m, 3H), 7.08 – 7.01 (m, 2H), 3.80 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 150.8, 137.0, 130.4, 129.4, 129.4, 129.2, 125.8, 121.5, 41.1, 21.1. FTIR (thin film)：1746 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{15}H_{14}O_2$ [M+Na$^+$] 249.0891, found 249.0886.



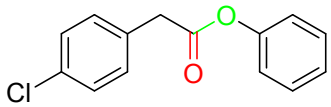
Phenyl 2-(m-tolyl)acetate(7ac), this compound was prepared according to General Procedure C for 10 h**,** Yield: 70% (31.6 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 3H), 7.25 – 7.17 (m, 4H), 7.05 (m, d, *J* = 8.8 Hz, 2H), 3.87 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 150.8, 136.9, 132.3, 130.5, 130.3, 129.4, 127.7, 126.3, 125.9, 121.5, 39.4 19.7. FTIR (thin film)：1754 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{15}H_{14}O_2$ [M+Na$^+$] 249.0891, found 249.0895.



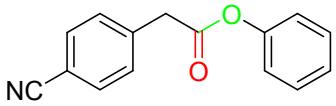
Phenyl 2-(4-methoxyphenyl)acetate (7ad), this compound was prepared according to General Procedure C for 8 h, Yield: 85% (41.2 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 6.8 Hz, 2H), 3.80 (s, 3H), 3.79 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 158.9, 150.8, 130.4, 129.4, 125.8, 125.5, 121.5, 114.2, 55.3, 40.6. FTIR (thin film)：1754 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{15}H_{14}O_3$ [M+H$^+$] 243.1021, found 243.1016.



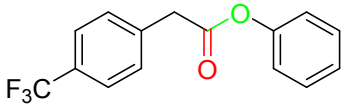
Phenyl 2-(4-fluorophenyl)acetate (7ae), this compound was prepared according to General Procedure C for 8 h, Yield: 85% (39.1mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 4H), 7.22 (dd, *J* = 12.7, 5.3 Hz, 1H), 7.08 – 7.02 (m, 4H), 3.82 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 162.2 (d, $J_{C\text{-}F}$ = 245.8 Hz), 150.7, 131.0 (d, $J_{C\text{-}F}$ = 8.1 Hz), 129.5, 129.2 (d, $J_{C\text{-}F}$ = 3.2 Hz), 126.0, 121.4, 115.6 (d, $J_{C\text{-}F}$ = 21.5 Hz), 40.6. FTIR (thin film)：1755 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{14}H_{11}FO_2$ [M+Na$^+$] 253.0641, found 253.0635.



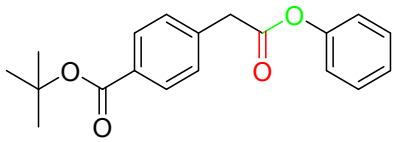
Phenyl 2-(4-chlorophenyl)acetate (7af), this compound was prepared according to General Procedure C for 10 h, Yield: 80% (39.2mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 6H), 7.22 (dd, *J* = 12.4, 5.0 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 2H), 3.82 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 150.6, 133.4, 131.9, 130.7, 129.5, 128.9, 126.0, 121.4, 40.7. FTIR (thin film): 1762 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{14}H_{11}ClO_2$ [M +Na$^+$] 269.0345, found 269.0340.



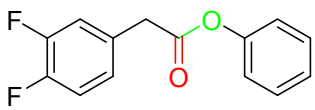
Phenyl 2-(4-cyanophenyl)acetate (7ag), this compound was prepared according to General Procedure C for 12 h, Yield: 56% (26.5 mg), white solid; Mp: 64-66 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.24(m, *J* = 8.4 Hz, 1H), 7.06 (m, *J* = 8.0 Hz, 2H), 3.93 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 150.5, 138.7, 132.5, 130.3, 129.5, 126.2, 121.3, 118.6, 111.5, 41.3. FTIR (KBr): 1749 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{15}H_{11}FO_2$ [M+H$^+$] 260.0687, found 260.0682.



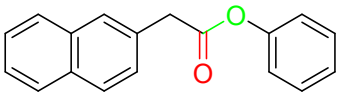
Phenyl 2-(4-(trifluoromethyl)phenyl)acetate (7ah), this compound was prepared according to General Procedure C for 14 h**,** Yield: 48% (27.0 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.37(t, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 8.4 Hz, 2H), 3.92 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 150.8, 137.4, 129.8, 129.8(d, $J_{C\text{-}F}$ = 128.0 Hz), 129.5, 126.1, 125.7 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.1 (d, $J_{C\text{-}F}$ = 272.0 Hz), 121.4, 41.1. FTIR (thin film): 1756 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{15}H_{11}F_3O_2$ [M+Na$^+$] 303.0609, found 303.0603.



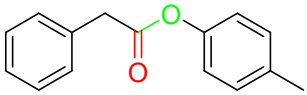
Tert-butyl 4-(2-oxo-2-phenoxyethyl)benzoate (7ai), this compound was prepared according to General Procedure C for 12 h, Yield: 67% (42.0 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.04 (d,7.6 Hz, 2H), 3.90 (s, 2H), 1.60 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 165.5, 150.7, 138.0, 131.2, 129.9, 129.5, 129.2, 126.0, 121.4, 81.1, 41.4, 28.2. FTIR (thin film): 1757 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{19}H_{20}O_4$ [M+Na$^+$] 313.1440, found 313.1445.



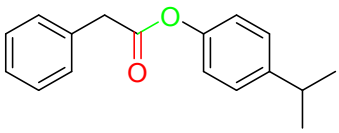
Phenyl 2-(3,4-difluorophenyl)acetate (7aj), this compound was prepared according to General Procedure C for 10 h, Yield: 83% (41.2 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, J = 8.0 Hz, 2H), 7.25 – 7.19 (m, 2H), 7.18 – 7.02 (m, 4H), 3.81 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 151.3 (dd, J = 47.0, 12.7 Hz), 150.6, 148.8 (dd, J = 46.5, 12.5 Hz), 130.2 (q, $J_{C\text{-}F}$ = 40.0 Hz), 129.5, 126.1, 125.5 (dd, $J_{C\text{-}F}$ = 39.6, 9.6 Hz), 121.4, 118.5 (d, J = 17.7 Hz), 117.5 (d, J = 17.3 Hz), 40.4. FTIR (thin film)：1761 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{14}H_{10}F_2O_2$ [M+Na$^+$] 271.0547, found 271.0548.



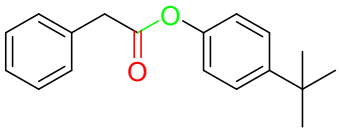
Phenyl 2-(naphthalen-2-yl)acetate (7ak), this compound was prepared according to General Procedure C for 12 h, Yield: 32% (16.9 mg), white solid; Mp：109-110 ℃， ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (t, J = 8.8 Hz, 4H), 7.50 (m, J = 9.2, 8.0, 2.7 Hz, 3H), 7.34 (t, J = 7.9 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 8.8 Hz,2H), 4.02 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 150.8, 133.5, 132.6, 131.0, 129.4, 128.5, 128.2, 127.8, 127.7, 127.3, 126.3, 126.0, 125.9, 121.5, 41.7. FTIR (KBr)：1755 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{18}H_{14}O_2$ [M+Na$^+$] 285.0891, found 285.0886.



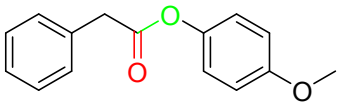
P-tolyl 2-phenylacetate (7al), this compound was prepared according to General Procedure C for 8 h**,** Yield: 83% (37.5 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 5H), 7.13 (d, J = 8.3 Hz, 2H), 6.93 (d, J = 8.3 Hz, 2H), 3.83 (s, 2H), 2.31 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 148.6, 135.5, 133.6, 129.9, 129.3, 128.7, 127.3, 121.1, 41.4, 20.9. FTIR (thin film)：1740 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{15}H_{14}O_2$ [M +Na$^+$] 249.0891, found 249.0893.



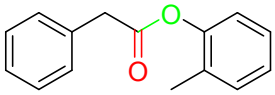
4-isopropylphenyl 2-phenylacetate (7am), this compound was prepared according to General Procedure C for 10 h**,** Yield: 89% (45.2 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.25 (m, 5H), 7.19 (d, J = 8.5 Hz, 2H), 6.96 (d, J = 8.5 Hz, 2H), 3.83 (s, 2H), 2.94 –2.82 (m, 1H), 1.22 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 148.7, 146.4, 133.6, 129.3, 128.7, 127.3, 127.3, 121.1, 41.5, 33.6, 24.0. FTIR (thin film)：1762 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{17}H_{18}O_2$ [M+Na$^+$] 277.1204, found 277.1199.



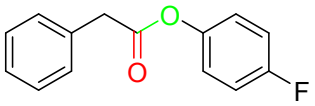
4-(tert-butyl)phenyl 2-phenylacetate (7an), this compound was prepared according to General Procedure C for 8 h, Yield: 84% (44.9 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 6H), 7.31 – 7.26 (m, 1H), 7.00 – 6.95 (m, 2H), 3.84 (s, 2H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 148.7, 148.5, 133.7, 129.3, 128.7, 127.3 126.3, 120.8, 41.5, 34.5, 31.4. FTIR (thin film)：1759 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{18}H_{20}O_2$ [M+Na$^+$] 291.1361, found 291.1356.



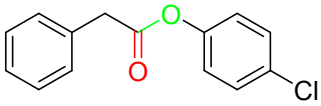
4-methoxyphenyl 2-phenylacetate (7ao)， this compound was prepared according to General Procedure C for 10 h, Yield: 87% (42.1 mg), colorless liquid;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 4H), 7.33 – 7.27 (m, 1H), 6.97 (d, J = 9.2 Hz, 2H), 6.85(d, J = 9.2 Hz, 2H), 3.83 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 157.3, 144.3, 133.6, 129.3, 128.7, 127.3, 122.2, 114.4, 55.6, 41.4. FTIR (thin film)：1739 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{15}H_{14}O_3$ [M+Na$^+$] 265.0841, found 265.0835.



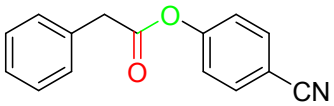
O-tolyl 2-phenylacetate (7ap), this compound was prepared according to General Procedure C for 8 h, Yield: 76% (34.3 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 –7.33 (m, 4H), 7.29 (t, J = 7.2 Hz, 1H), 7.17 (t, J = 7.2 Hz, 2H), 7.13 – 7.07 (m, 1H), 6.97 (d, J = 7.8 Hz, 1H), 3.86 (s, 2H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 149.4, 133.6, 131.2, 130.2, 129.4, 128.8, 127.4, 126.9, 126.1, 121.8, 41.5, 16.0. FTIR (thin film)：1754 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{15}H_{14}O_2$ [M+Na$^+$] 249.0891, found 249.0886



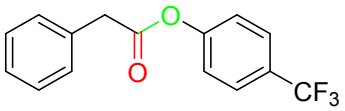
4-fluorophenyl 2-phenylacetate (7aq), this compound was prepared according to General Procedure C for 12 h, Yield: 80% (36.7 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H), 7.06 – 6.99 (m, 4H), 3.85 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 160.3 (d, $J_{C\text{-}F}$ = 244.2 Hz), 146.6 (d, $J_{C\text{-}F}$ = 2.7 Hz), 133.4, 129.3, 128.8, 127.5, 122.9 (d, $J_{C\text{-}F}$= 8.5 Hz), 116.0 (d, $J_{C\text{-}F}$ = 23.5 Hz), 41.3. FTIR (thin film)：1759 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{14}H_{11}FO_2$ [M+Na$^+$] 253.0641, found 253.0635.



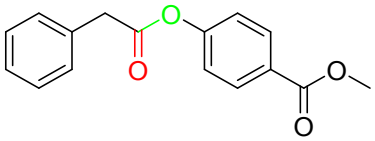
4-chlorophenyl 2-phenylacetate (7ar), this compound was prepared according to General Procedure C for 8 h, Yield: 89% (43.7 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 4.4 Hz, 4H), 7.33 – 7.27 (m, 3H), 7.02 – 6.97 (m, 2H), 3.84 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 149.3, 133.3, 131.3, 129.5, 129.3, 128.8, 127.5, 122.9, 41.4. FTIR (thin film)：1747 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{14}H_{11}ClO_2$ [M+Na$^+$]269.0345, found 269.0340.



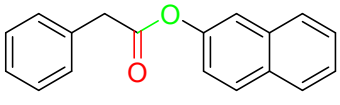
4-cyanophenyl 2-phenylacetate (7as), this compound was prepared according to General Procedure C for 10 h, Yield: 92% (43.7 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.8 Hz, 2H), 7.42 – 7.28 (m, 5H), 7.20 (d, J = 8.7 Hz, 2H), 3.88 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 154.0, 133.7, 132.8, 129.3, 128.9, 127.7, 122.7, 118.2, 109.8, 41.3. FTIR(thin film)：1766 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{15}H_{11}NO_2$ [M+Na$^+$] 260.0687, found 260.0682.



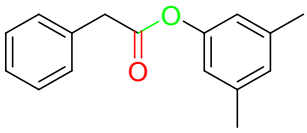
4-(trifluoromethyl)phenyl 2-phenylacetate (7at), this compound was prepared according to General Procedure C for 8 h**,** Yield: 91% (50.9 mg), yellow liquid;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.8 Hz, 2H), 7.39 – 7.30 (m, 5H), 7.19 (d, J = 8.4 Hz, 2H), 3.87 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 153.3, 133.1, 129.4, 128.9, 128.2 (q, $J_{C\text{-}F}$= 32.9 Hz), 127.6, 126.8 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.9 (d, $J_{C\text{-}F}$ = 271.9 Hz), 122.0, 41.4. FTIR(thin film)：1750 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{15}H_{11}F_3O_2$ [M+Na$^+$] 303.0609, found 303.0603.



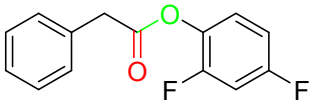
Methyl 4-(2-phenylacetoxy)benzoate (7au), this compound was prepared according to General Procedure C for 10 h, Yield: 58%(31.3 mg), white solid; Mp：88-89 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 4.3 Hz, 3H), 7.32 (t, J = 4.2 Hz 1H), 7.14 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H), 3.87 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 166.3, 154.4, 133.1, 131.1, 129.3, 128.8, 127.8, 127.5, 121.5, 52.2, 41.4. FTIR(KBr)：1745 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{16}H_{14}O_4$ [M+H$^+$] 271.0970, found 271.0965.



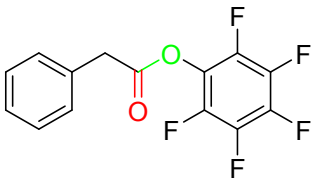
Naphthalen-2-yl 2-phenylacetate (7av), this compound was prepared according to General Procedure C for 10 h, Yield: 58% (30.2 mg), white solid; Mp：82-83 ℃，^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.9 Hz, 2H), 7.79 – 7.75 (m, 1H), 7.53 (d, J = 2.1 Hz, 1H), 7.50 – 7.36 (m, 6H), 7.35 – 7.29 (m, 1H), 7.19 (dd, J = 8.9, 2.3 Hz, 1H), 3.91 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 148.5, 133.8, 133.5, 131.5, 129.4, 129.4, 128.9, 127.8, 127.7, 127.5, 126.6, 125.8, 121.0, 118.5, 41.5. FTIR(KBr)：1760 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{18}H_{14}O_2$ [M+Na$^+$] 285.0891, found 285.0886.



3,5-dimethylphenyl 2-phenylacetate (7aw), this compound was prepared according to General Procedure C for 10 h, Yield:71% (34.1 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 4H), 7.32 –7.26 (m, 1H), 6.84 (s, 1H), 6.66 (s, 2H), 3.83 (s, 2H), 2.28 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 150.7, 139.3, 133.6, 129.3, 128.7, 127.6, 127.3, 119.0, 41.5, 21.2. FTIR(thin film)：1758 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{16}H_{16}O_2$ [M+Na$^+$] 263.1048, found 263.1043.



2,4-difluorophenyl 2-phenylacetate (7ax), this compound was prepared according to General Procedure C for 10 h, Yield: 73% (36.2 mg), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 7.08 – 7.00 (m, 1H), 6.93 – 6.78 (m, 2H), 3.89 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 161.5 (dd, $J_{C\text{-}F}$ = 247.4, 10.5 Hz), 155.4 (dd, $J_{C\text{-}F}$ = 252.1, 12.5 Hz), 134.6 (dd, $J_{C\text{-}F}$ = 13.0, 4.0 Hz), 133.0, 129.3, 128.8, 127.5, 124.2 (dd, $J_{C\text{-}F}$ = 9.9, 2.0 Hz), 111.2 (dd, $J_{C\text{-}F}$ = 23.1, 3.9 Hz), 105.1 (dd, $J_{C\text{-}F}$ = 26.9, 22.4 Hz), 40.8. FTIR(thin film)：1752 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{14}H_{10}F_2O_2$ [M+Na$^+$] 271.0547, found 271.0548.



Perfluorophenyl 2-phenylacetate (7ay), this compound was prepared according to General Procedure C for 12 h, Yield: 48% (28.7 mg), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.29 (m, 5H), 3.97 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 132.1, 129.3, 129.0, 127.9, 40.2. FTIR(thin film)：1748 cm^{-1} (CH_2COOR); HRMS(ESI$^+$) calculated for $C_{14}H_8F_5NO$ [M + Na$^+$] 324.0424, found 324.0430.

Part 8: References：

(1) Icke, R. N.; Wisegarver, B. B.; Alles, G. A. *Org. Synth.* **1955**, *Coll. Vol. 3*, 723.

(2) The reductive aminations were carried out according to literature procedure, except that Me_2NH was formed in situ from $Me_2N{\cdot}HCl$ and Et_3N. See: Bhattacharyya, S. *Synth. Commun.* **2000**, *30*, 2001.

(3) Maity, P.; Shacklady-McAtee, D. M.; Yap, G. P. A.; Sirianni, E. R.; Watson, M. P. *J. Am. Chem. Soc.* **2013,** *135*, 280.

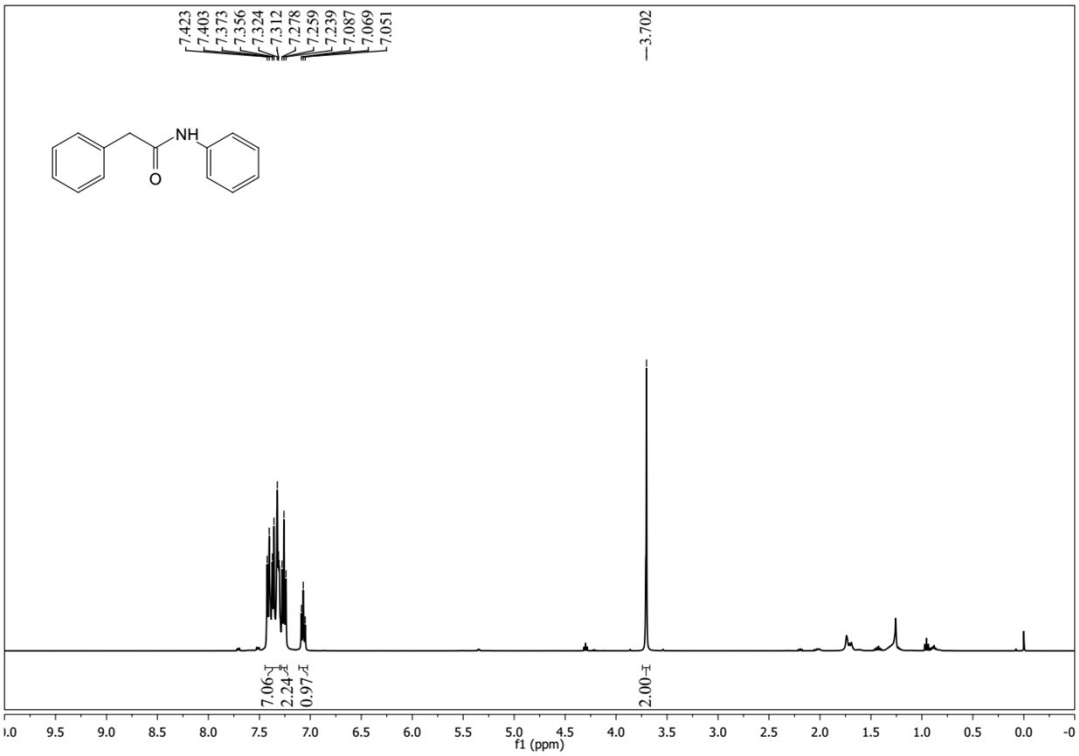
(4) Gu, L.; Lim, J.; Cheong, J. L.; Lee, S. S. *Chem. Commun.* **2014,** *50*, 7017.

(5) Huang, H.; Tang, L.; Xi, Y.; He, G.; Zhu, H. *Tetrahedron Lett* **2016,** *57*, 1873.

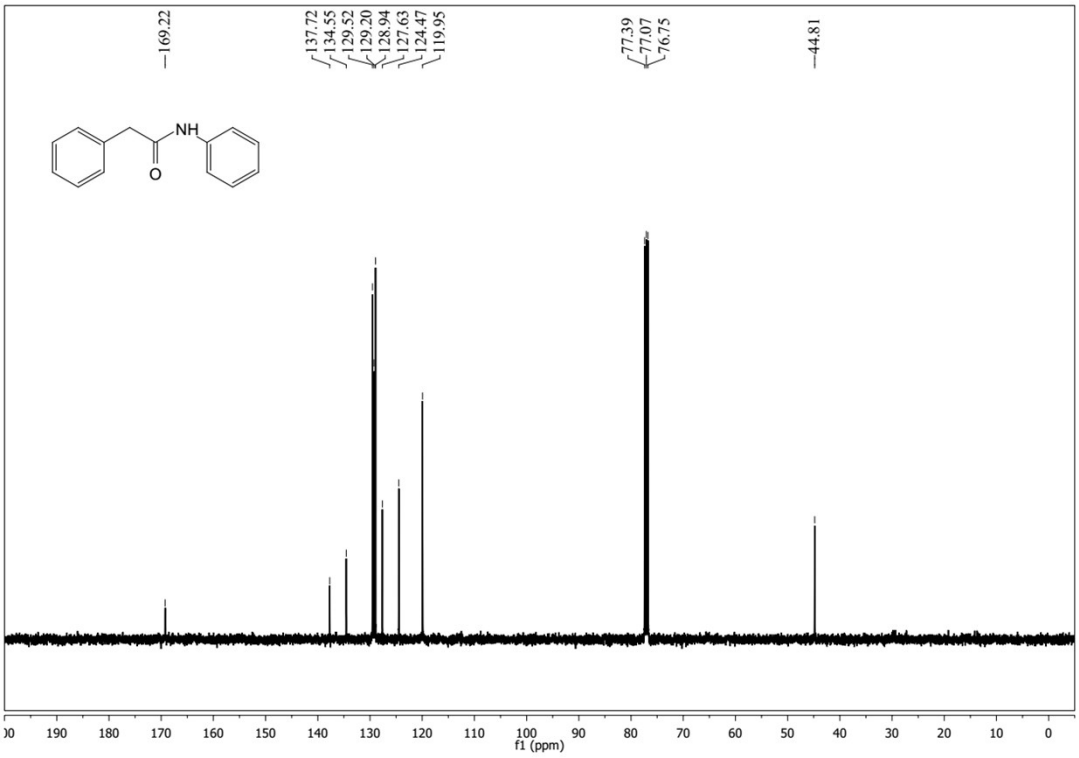
(6) Mamillapalli, N. C.; Sekar, G. *Adv. Synth. Catal* **2015,** *357*, 3273.
(7) Liu, H.; Laurenczy, G.; Yan, N.; Dyson, P. J. *Chem. Commun.* **2014,** *50*, 341.
(8) Xie, P.; Xia, C.; Huang, H. *Org Lett* **2013,** *15*, 3370-3.

Part 9. ^{1}H NMR and ^{13}C NMR Spectra

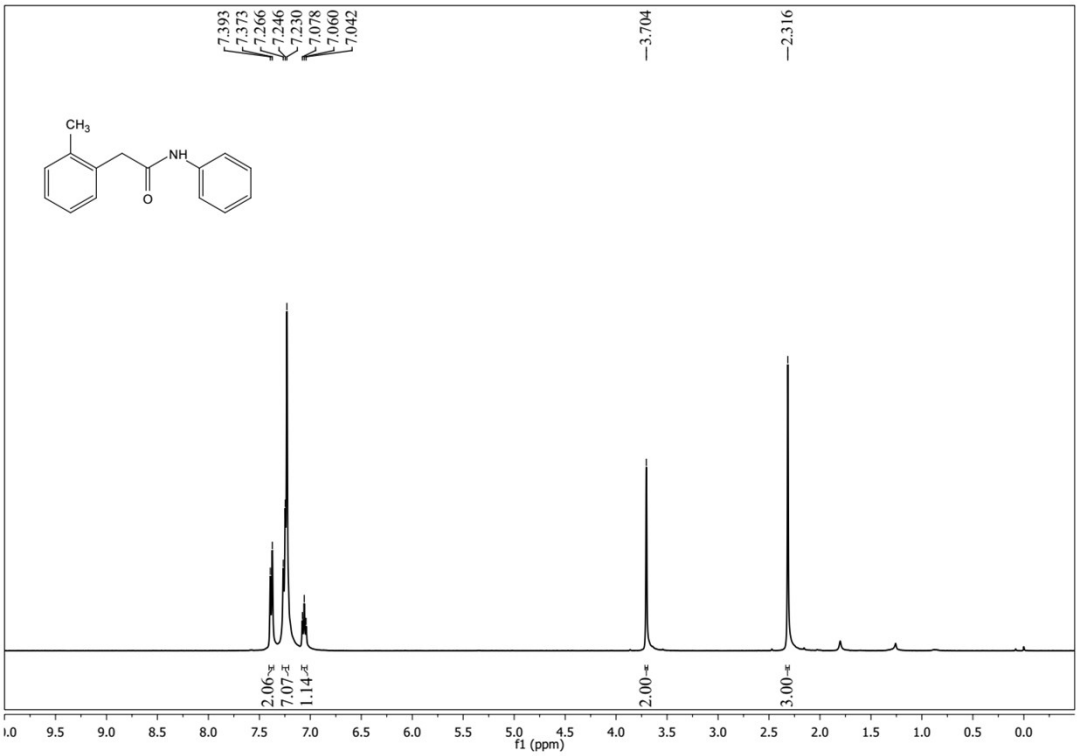
^{1}H NMR Spectra of 3aa



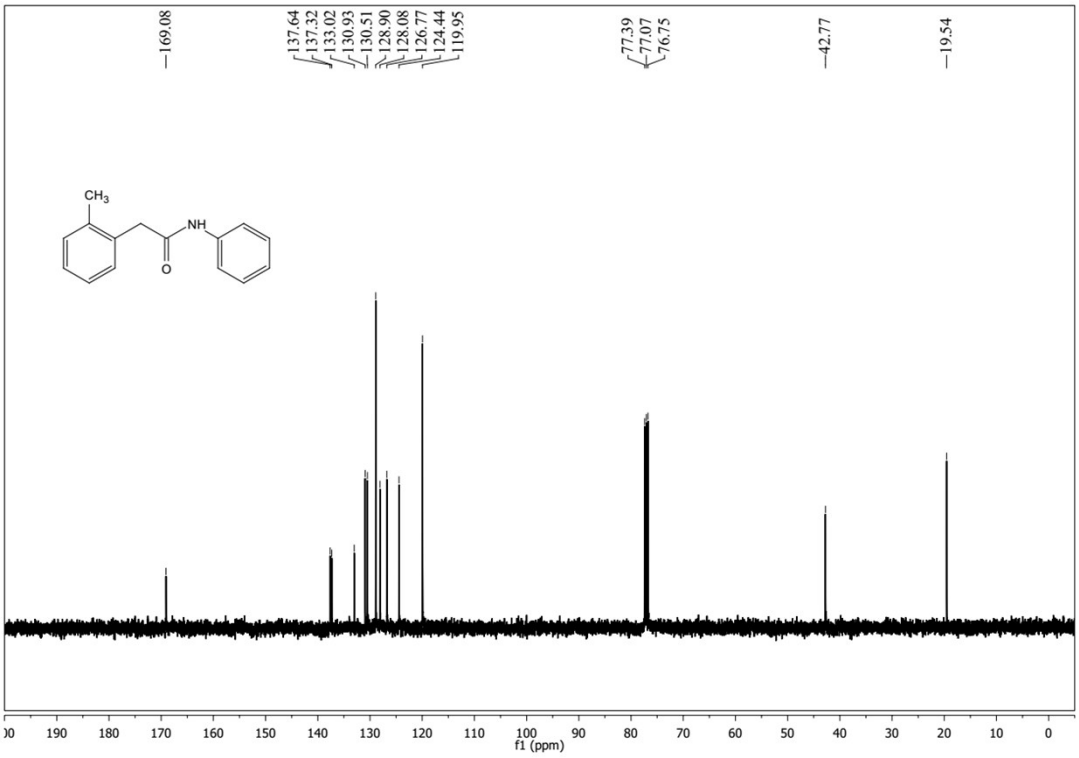
^{13}C NMR Spectra of 3aa



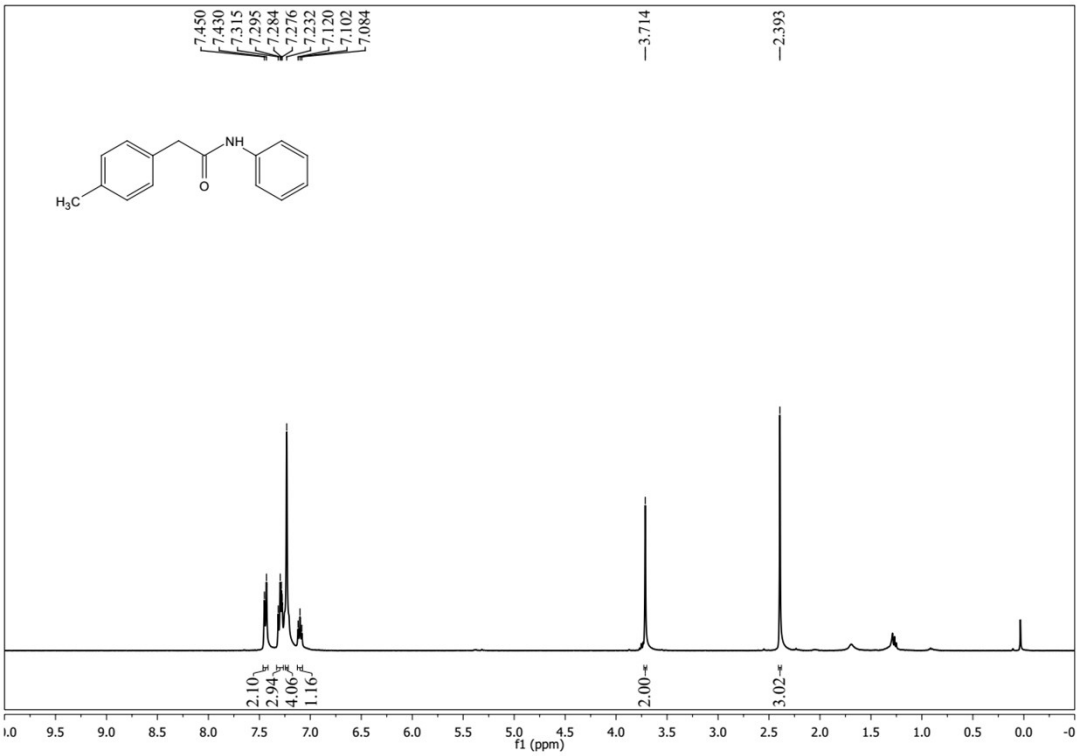
^{1}H NMR Spectra of 3ab



^{13}C NMR Spectra of 3ab



^{1}H NMR Spectra of 3ac



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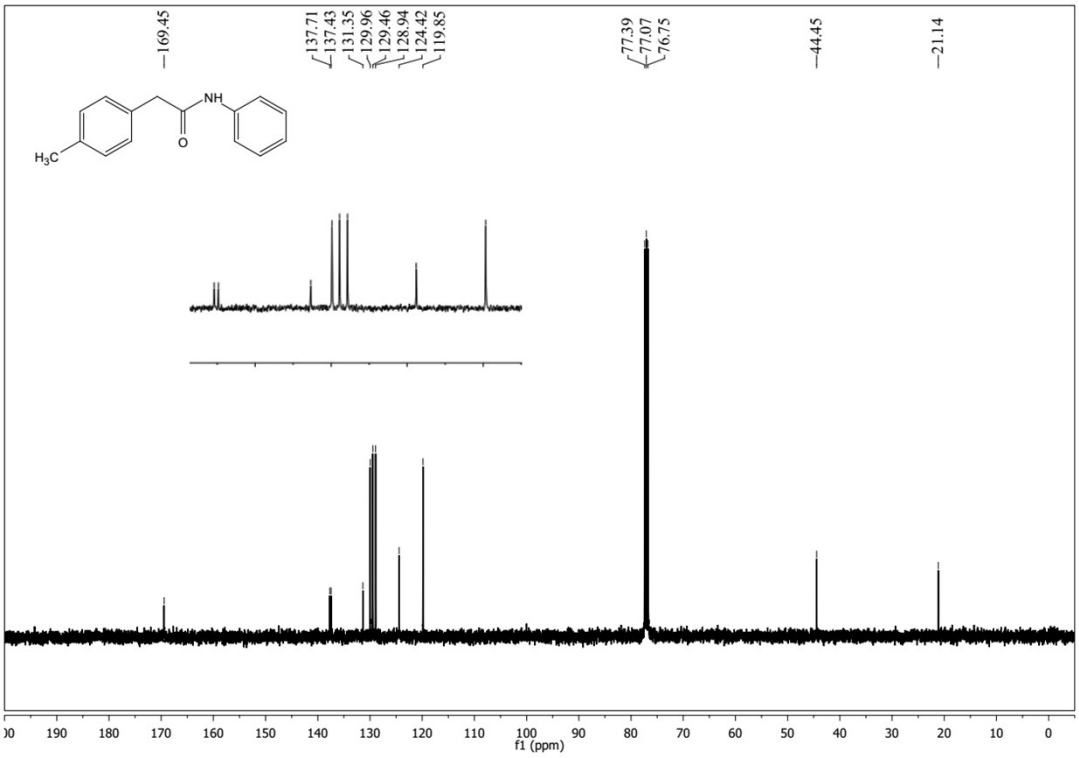
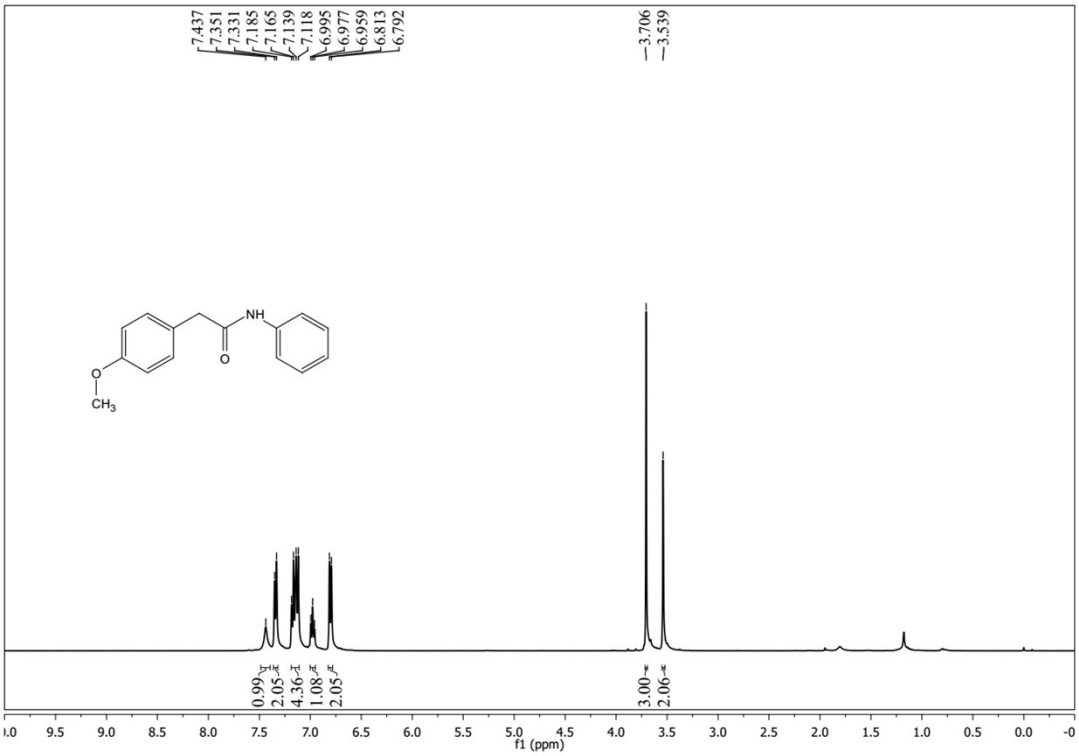
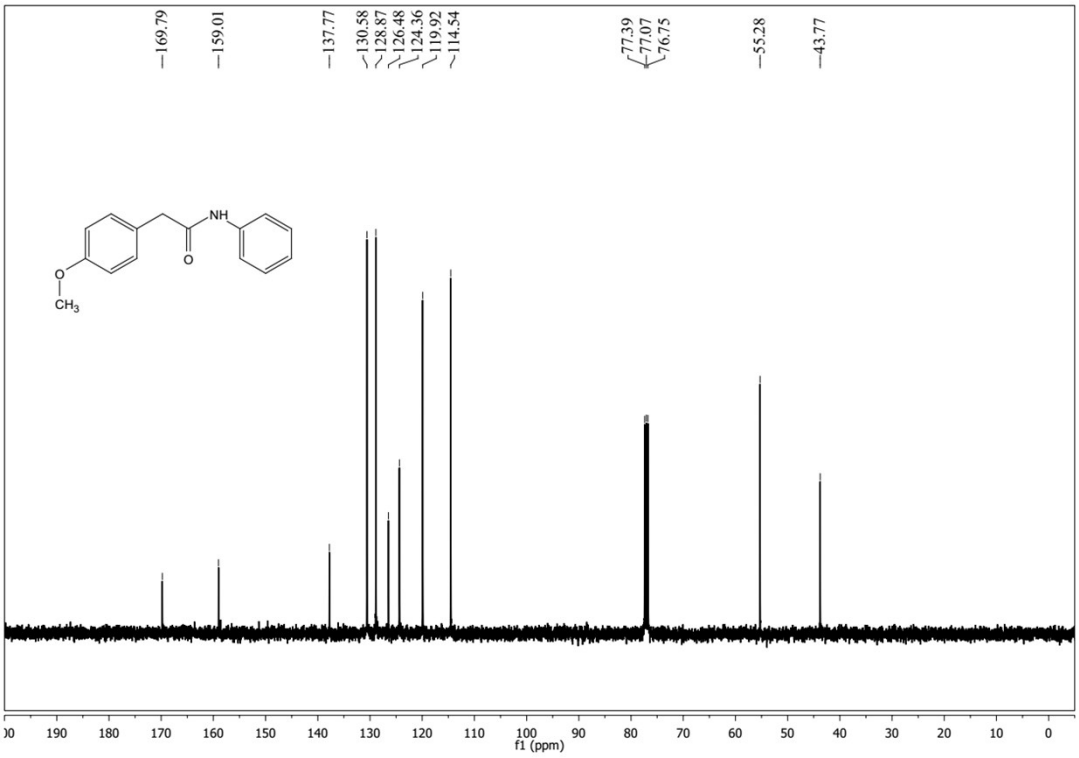


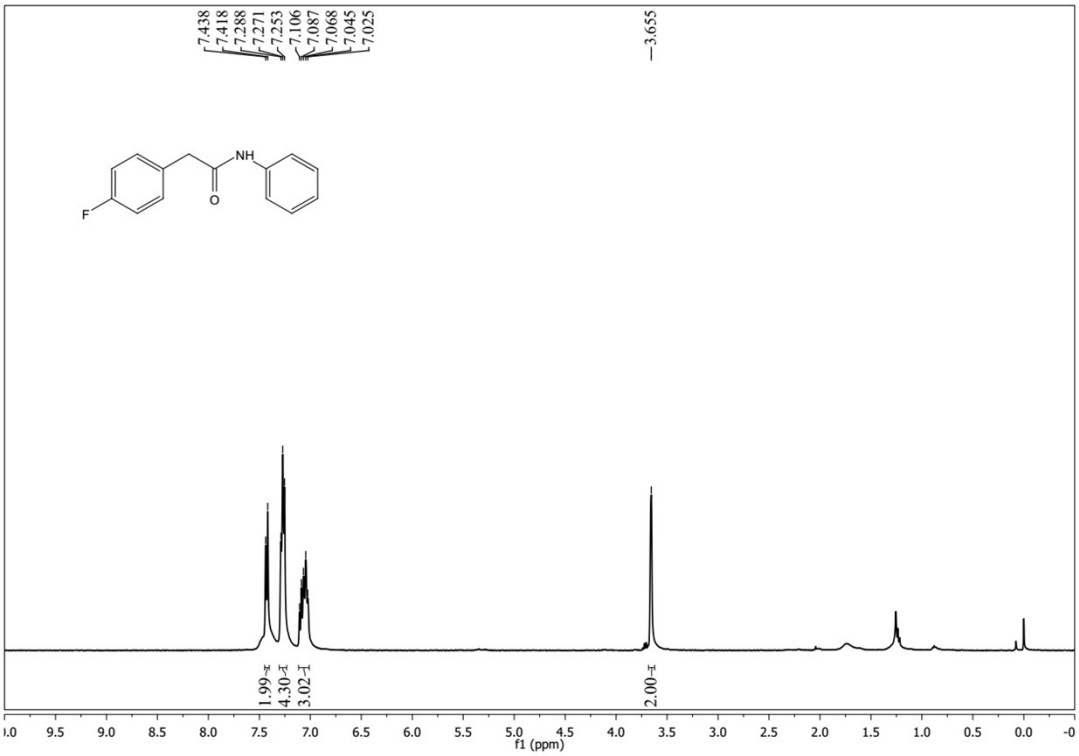
^{1}H NMR Spectra of 3ad



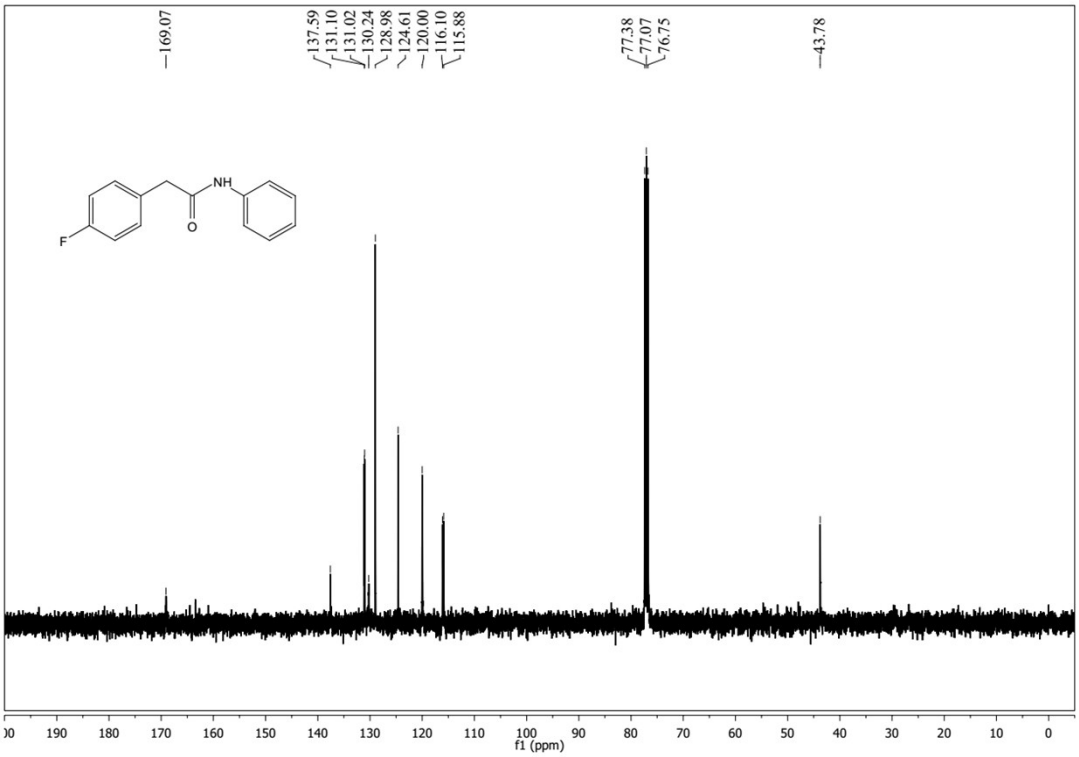
^{13}C NMR Spectra of 3ad



^{1}H NMR Spectra of 3ae



^{13}C NMR Spectra of 3ae



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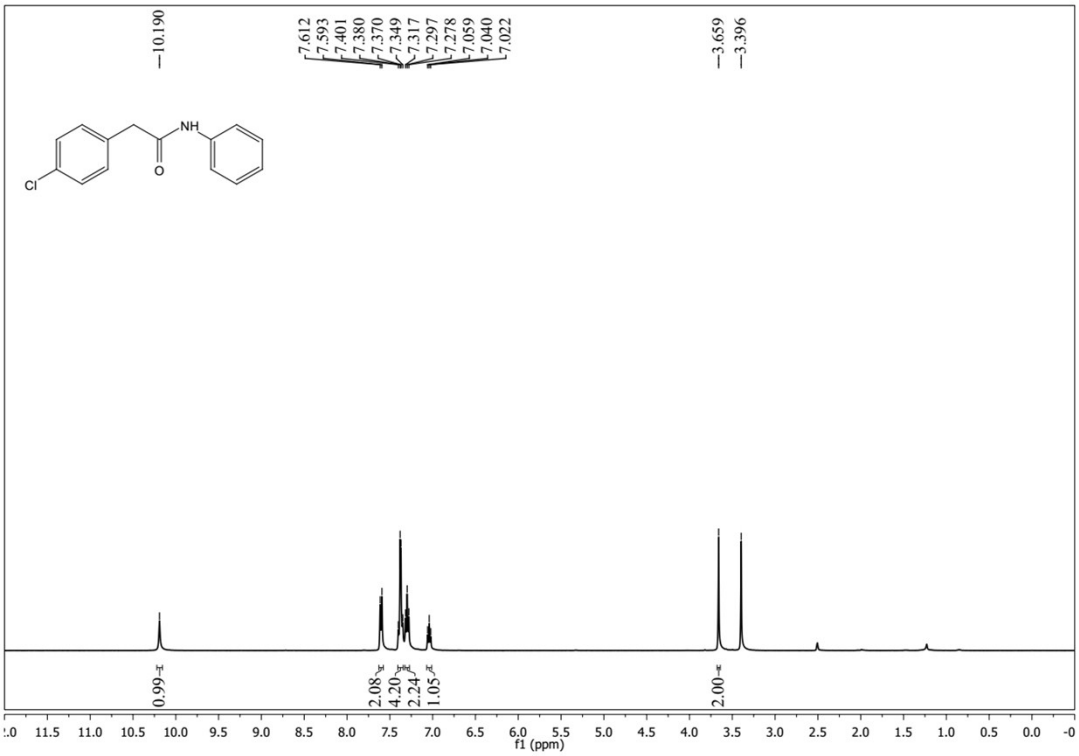
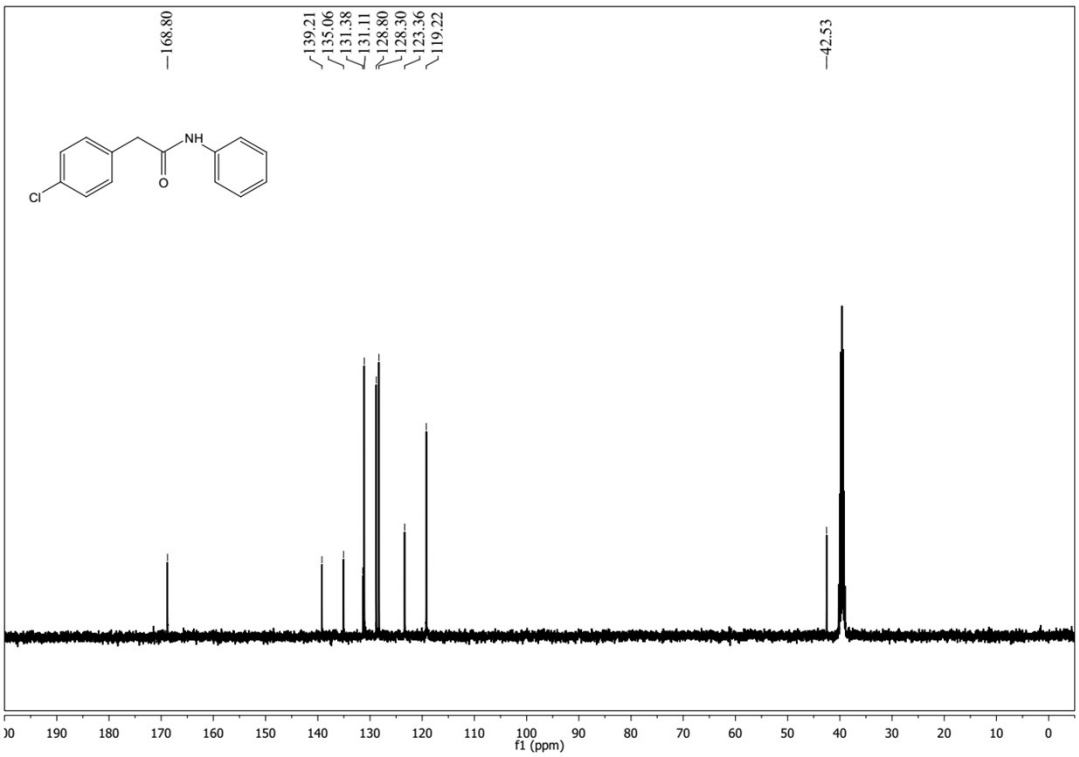
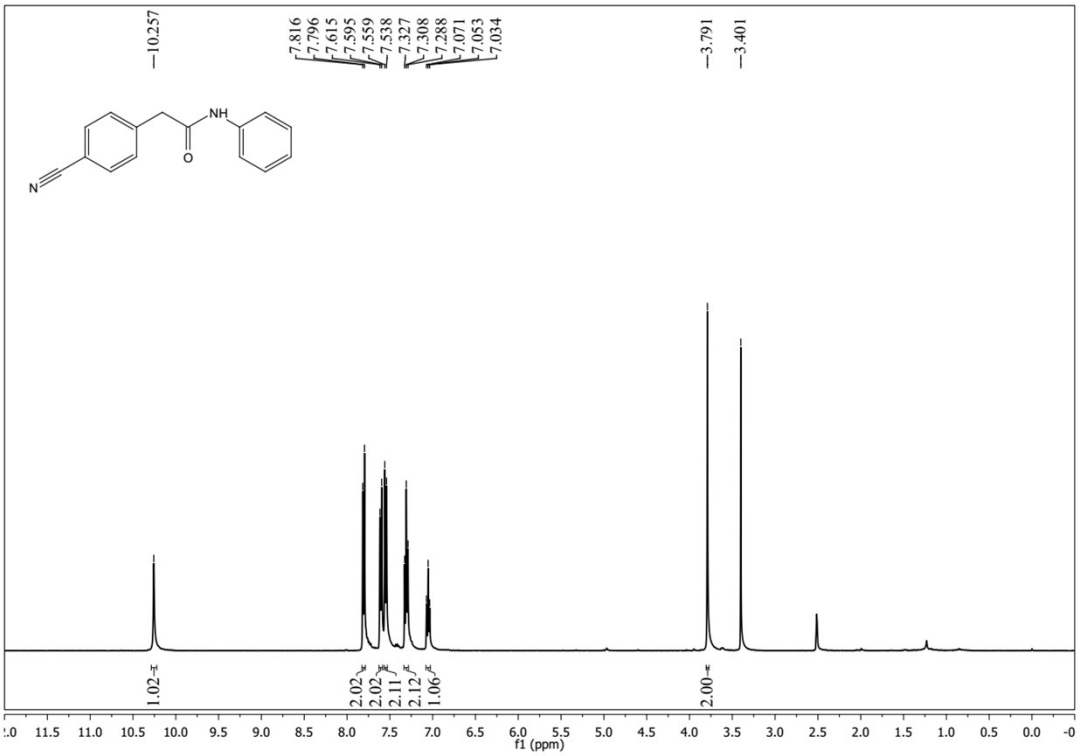


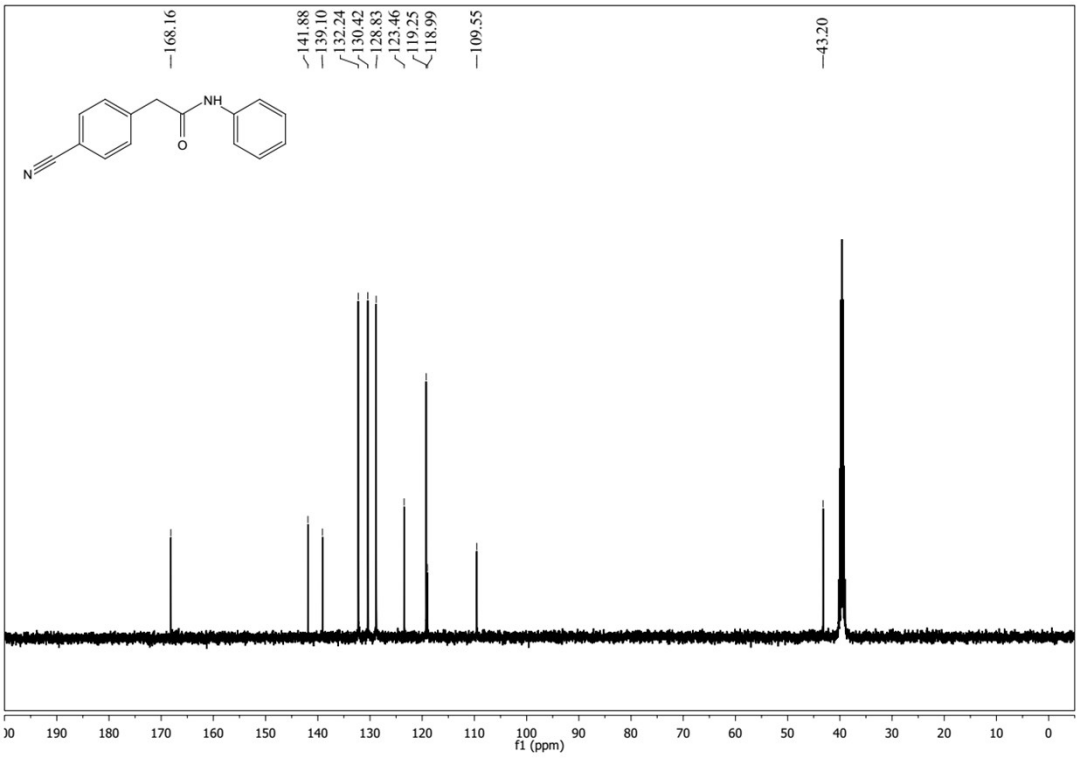
^{13}C NMR Spectra of 3af



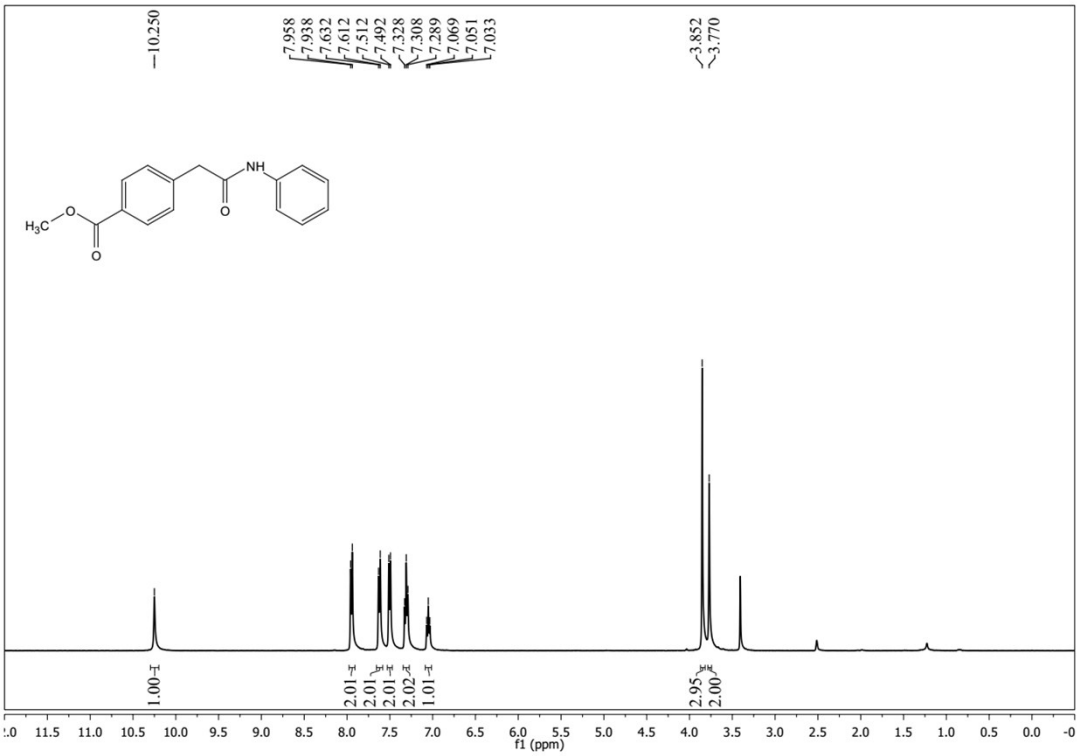
^{1}H NMR Spectra of 3ag



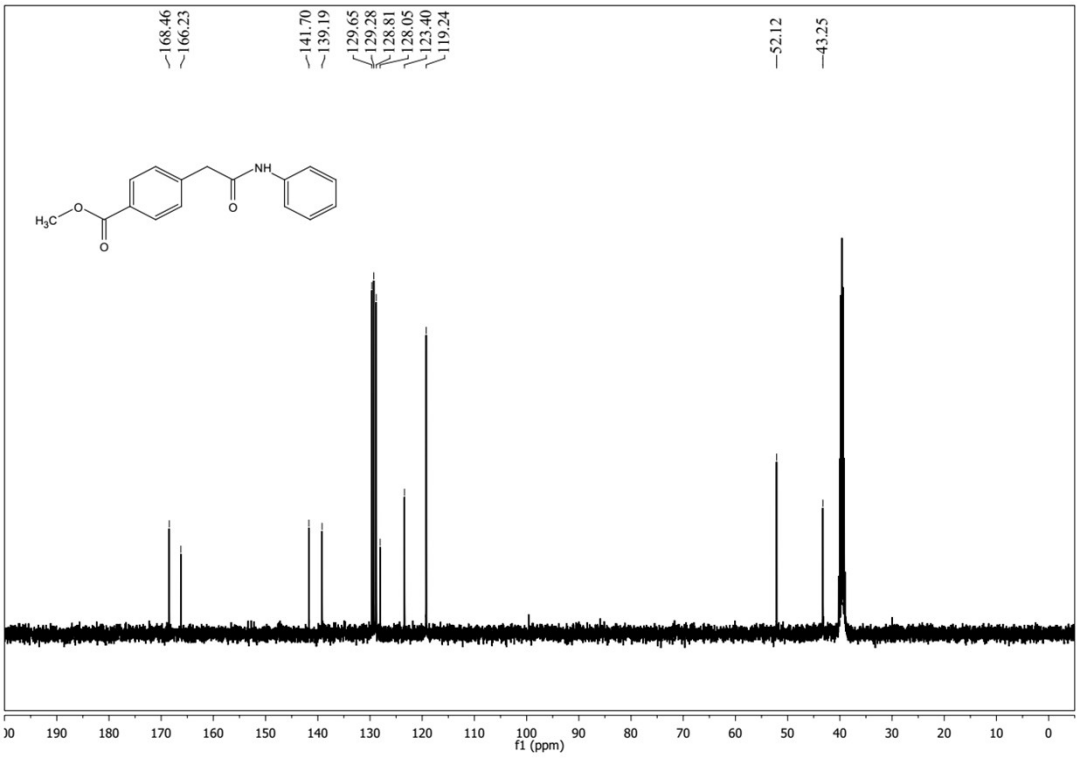
^{13}C NMR Spectra of 3ag



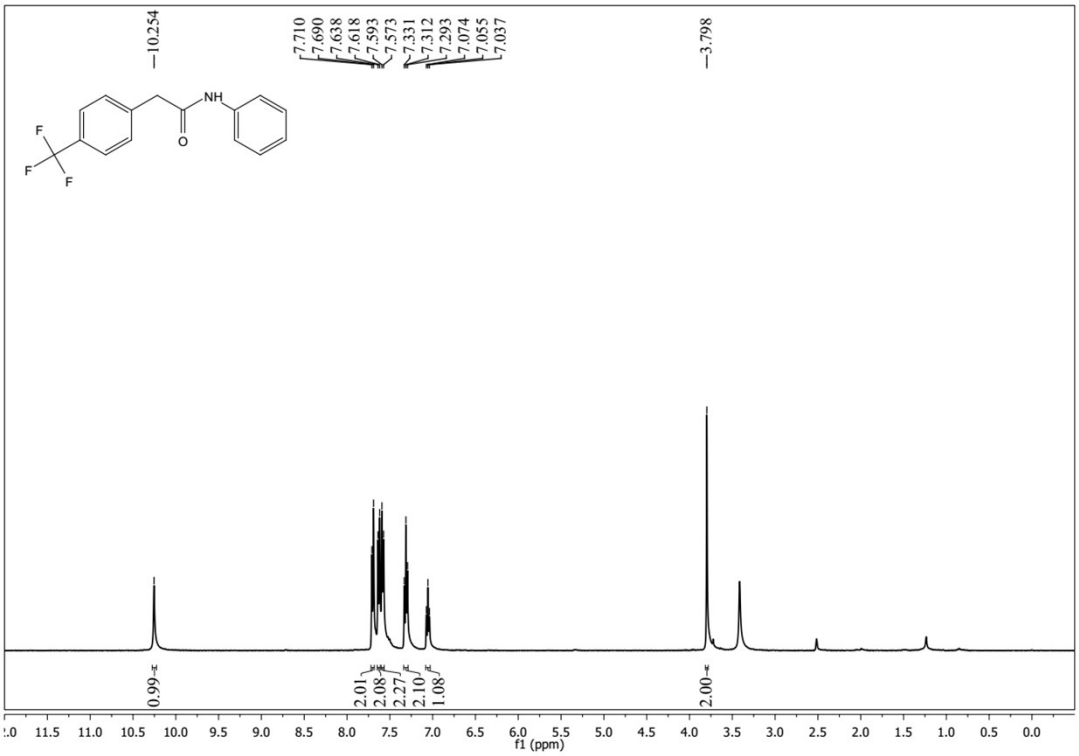
^{1}H NMR Spectra of 3ah



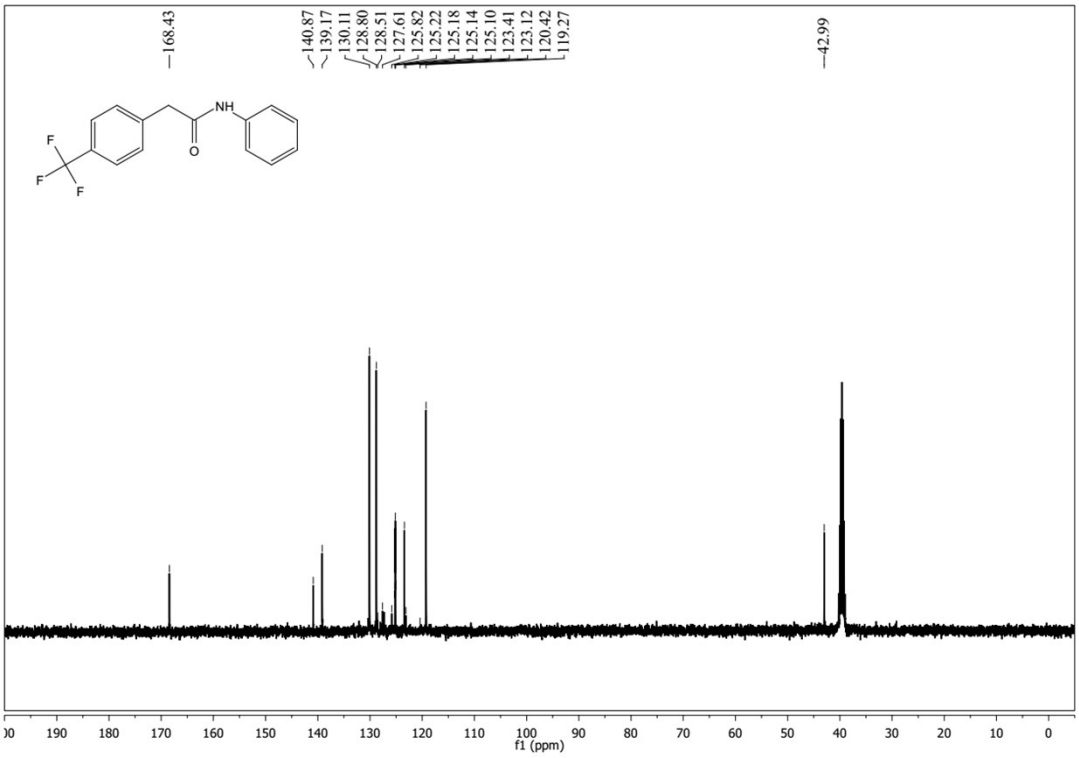
^{13}C NMR Spectra of 3ah



^{1}H NMR Spectra of 3ai



^{13}C NMR Spectra of 3ai



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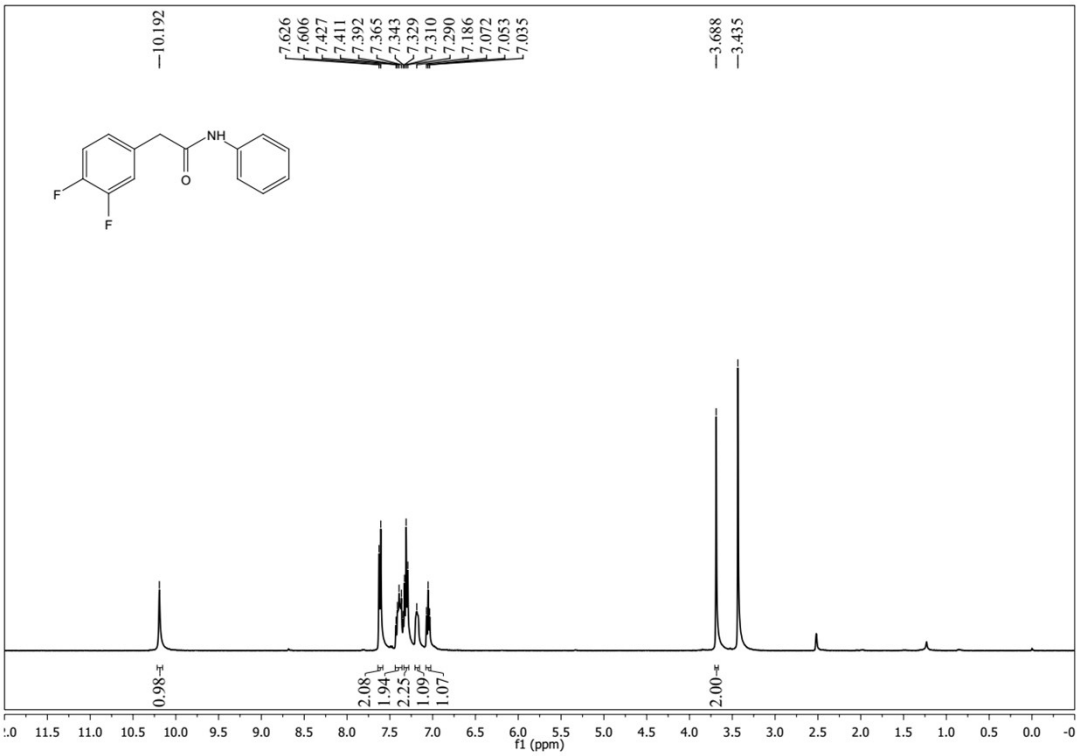
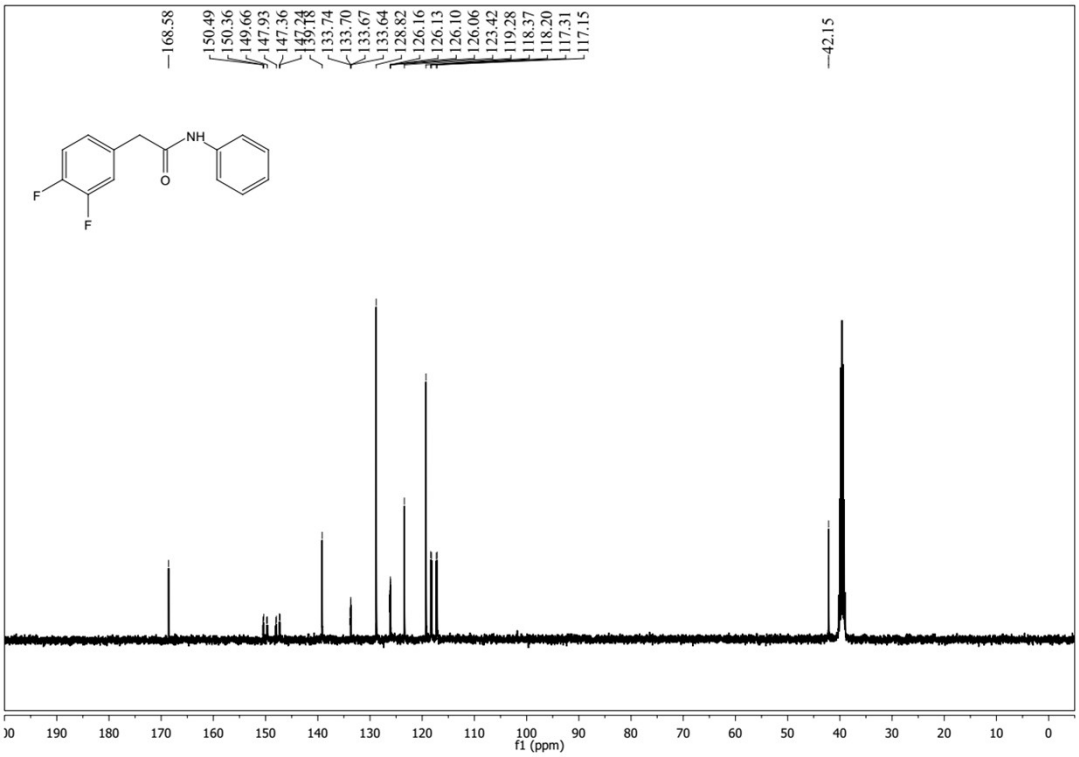


^{13}C NMR Spectra of 3aj



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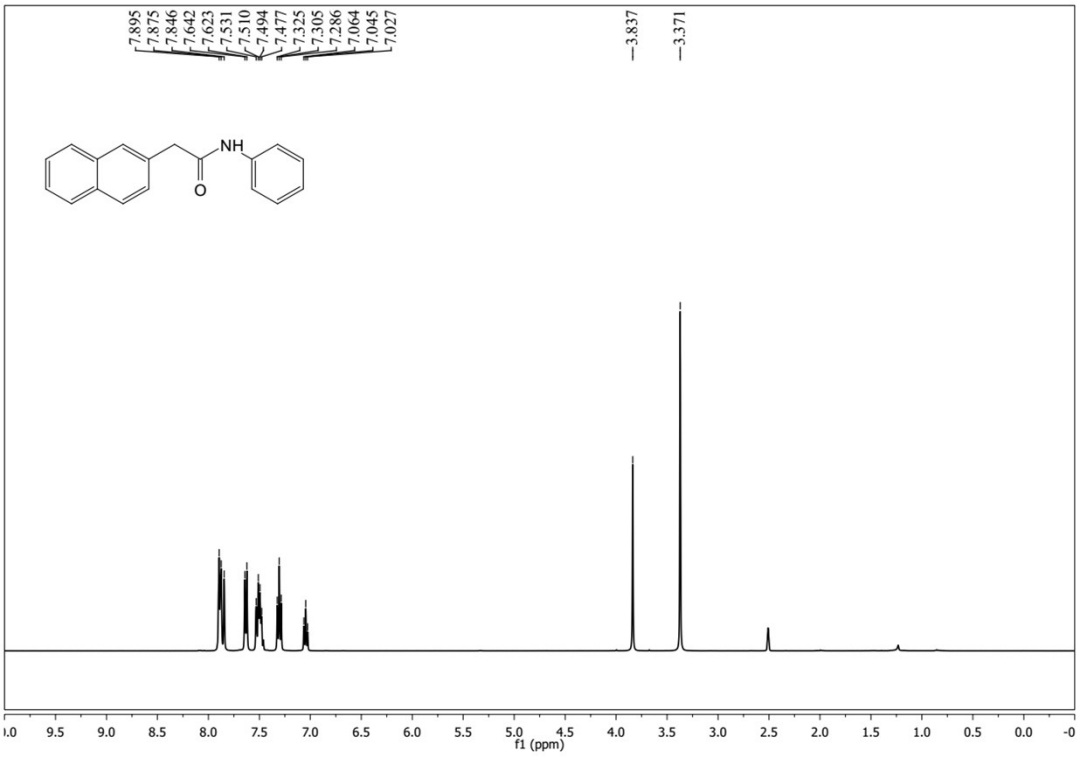
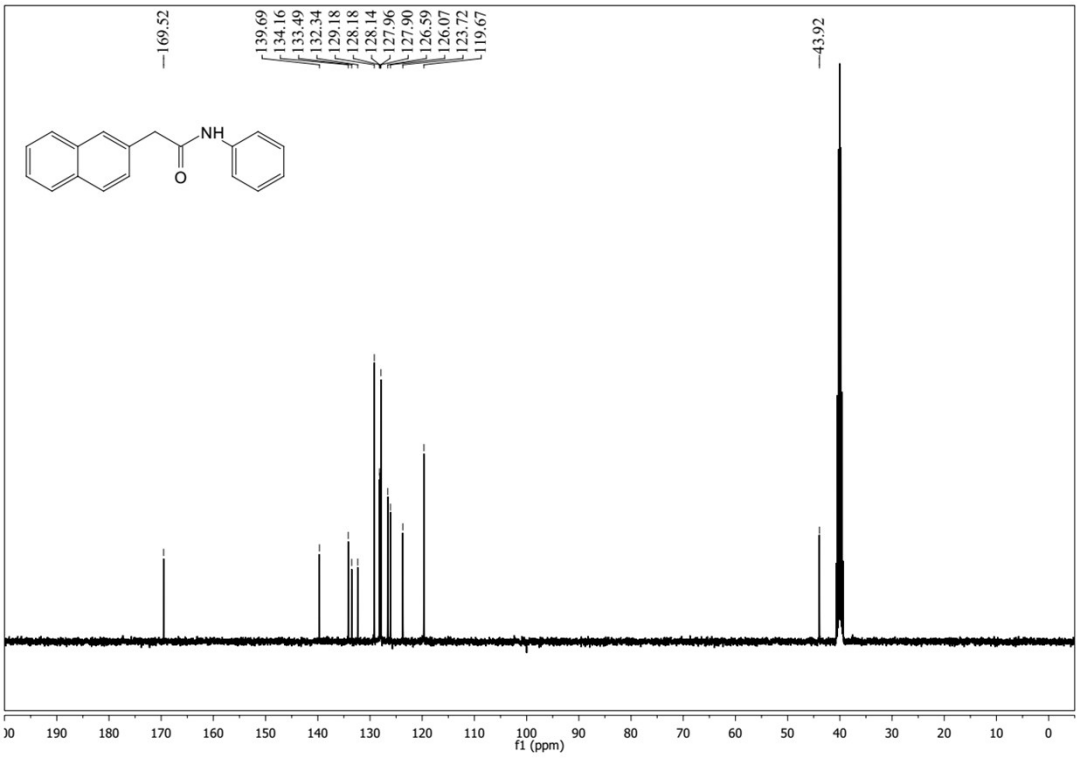
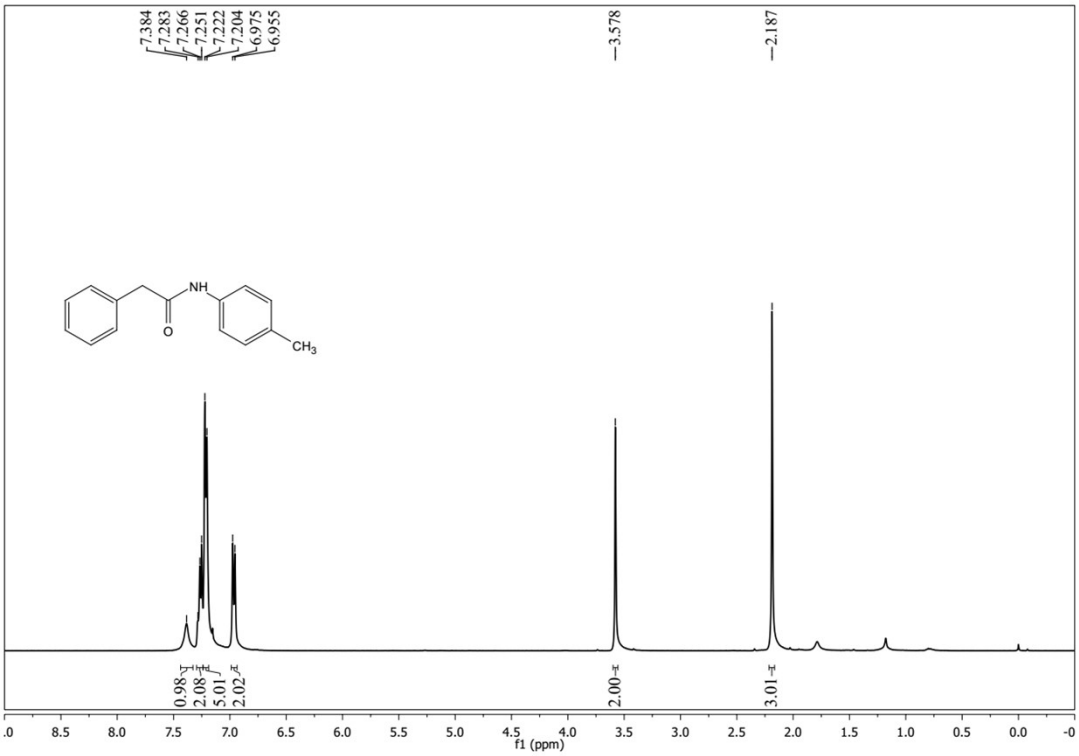


^{13}C NMR Spectra of 3ak



^{1}H NMR Spectra of 3al



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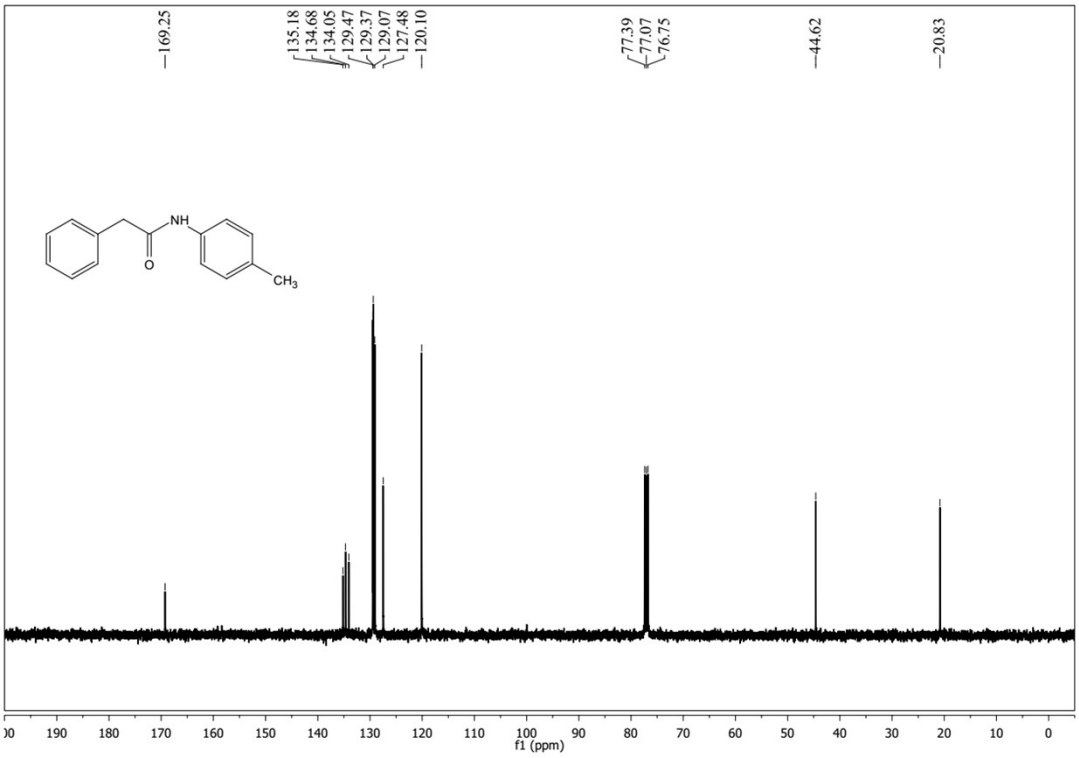
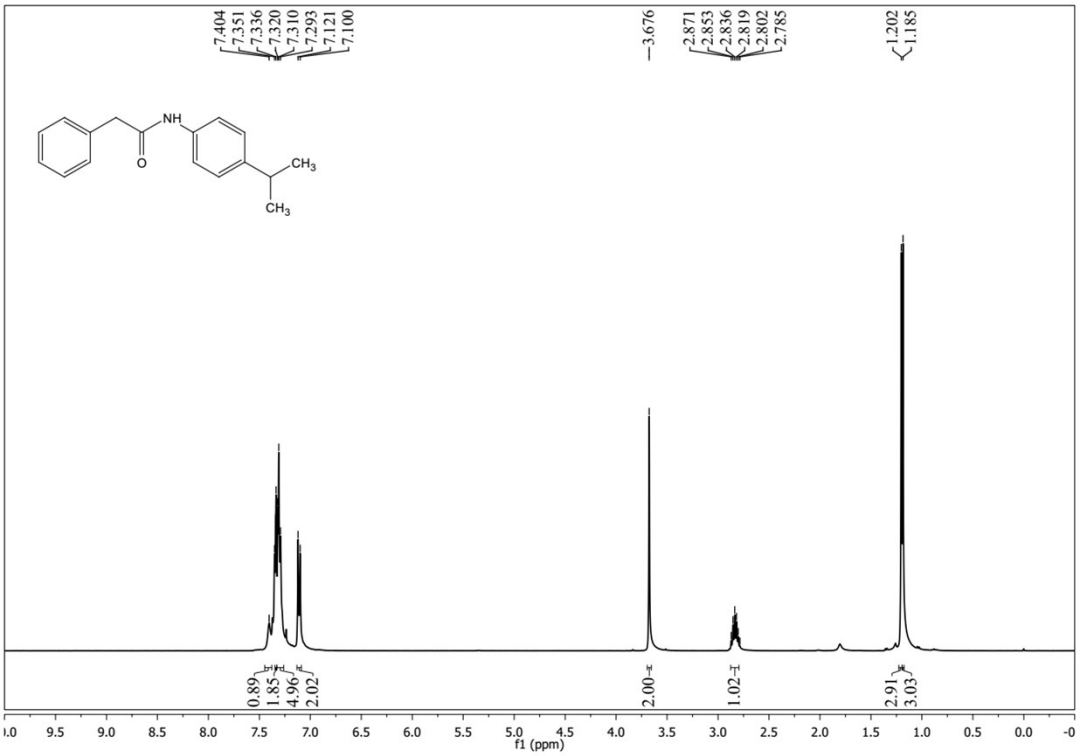
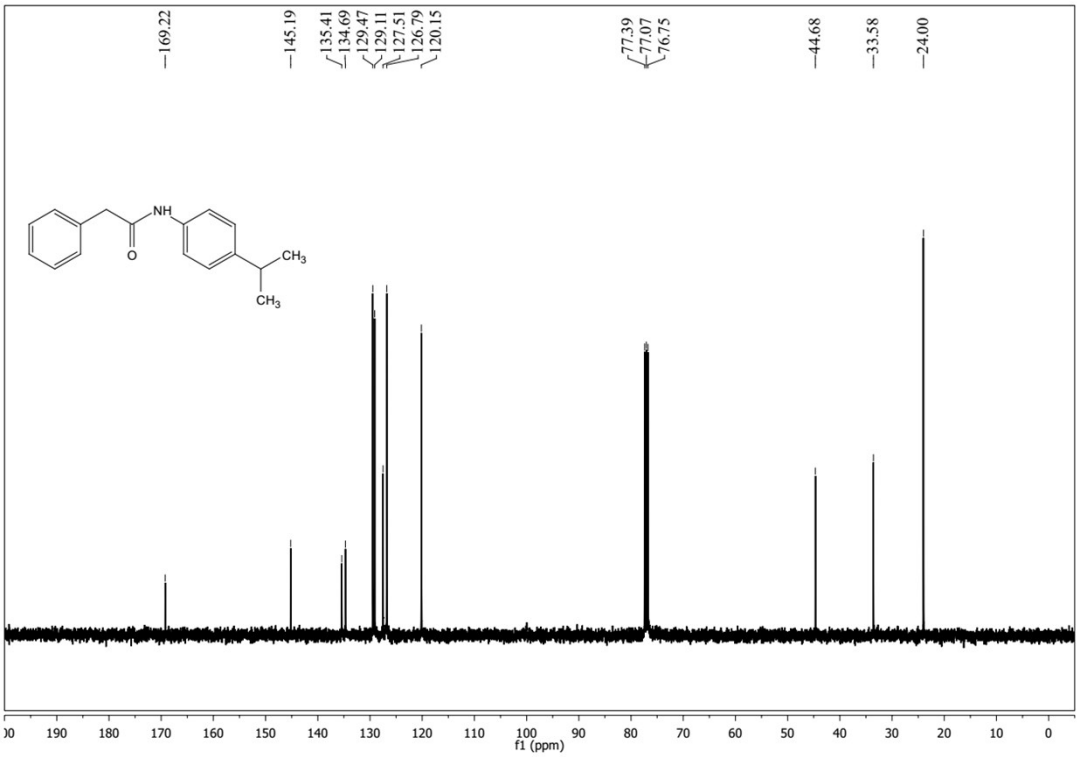


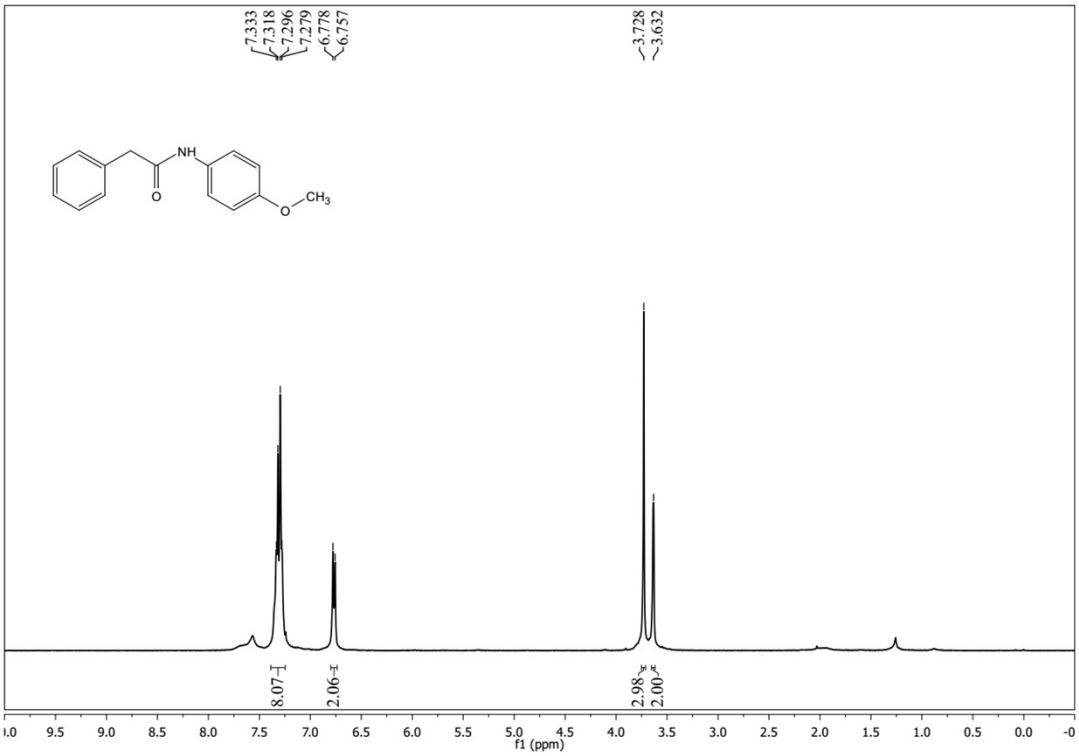
^{1}H NMR Spectra of 3am



^{13}C NMR Spectra of 3am



^{1}H NMR Spectra of 3an



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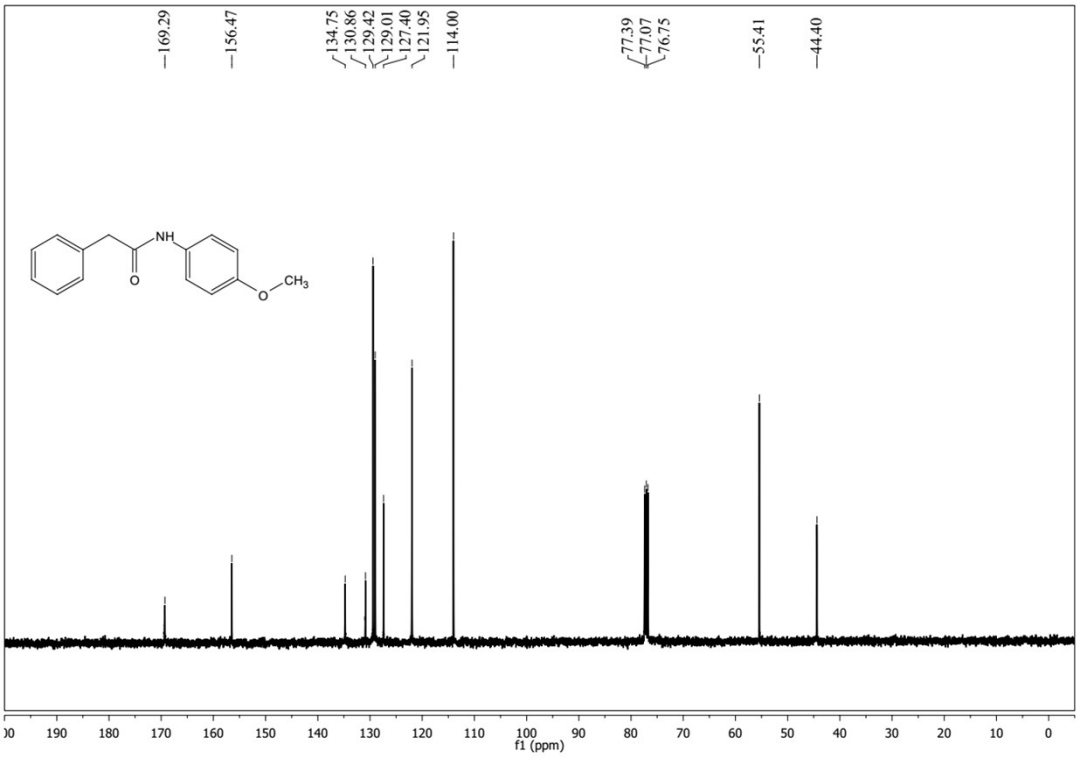
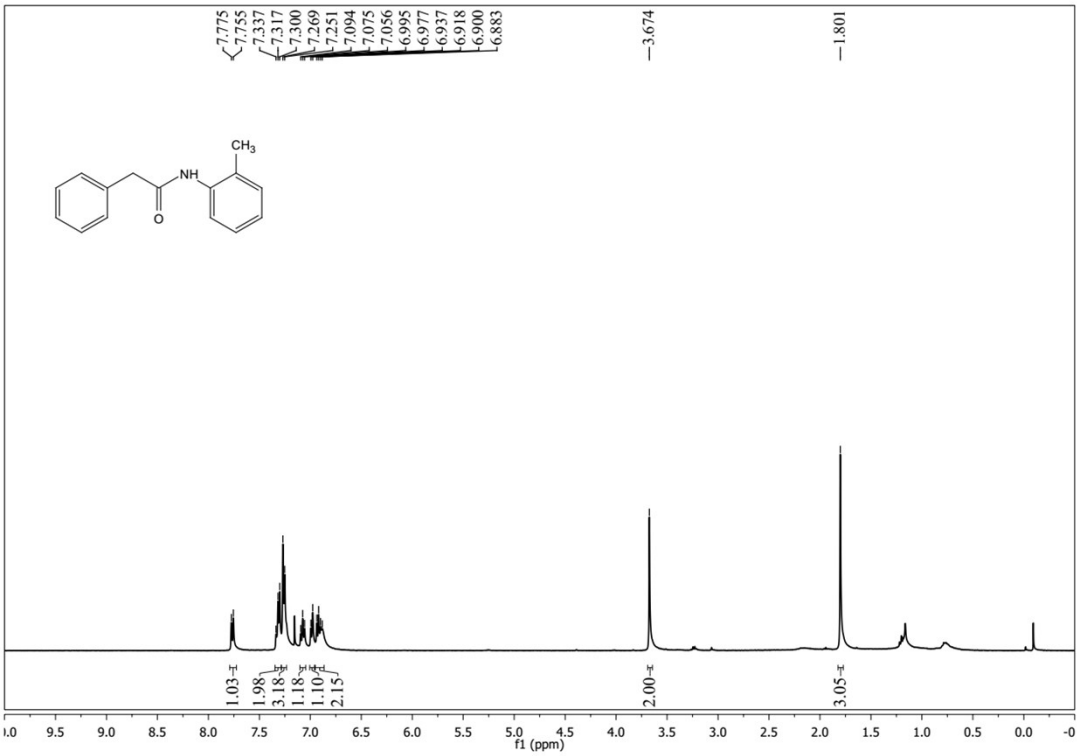
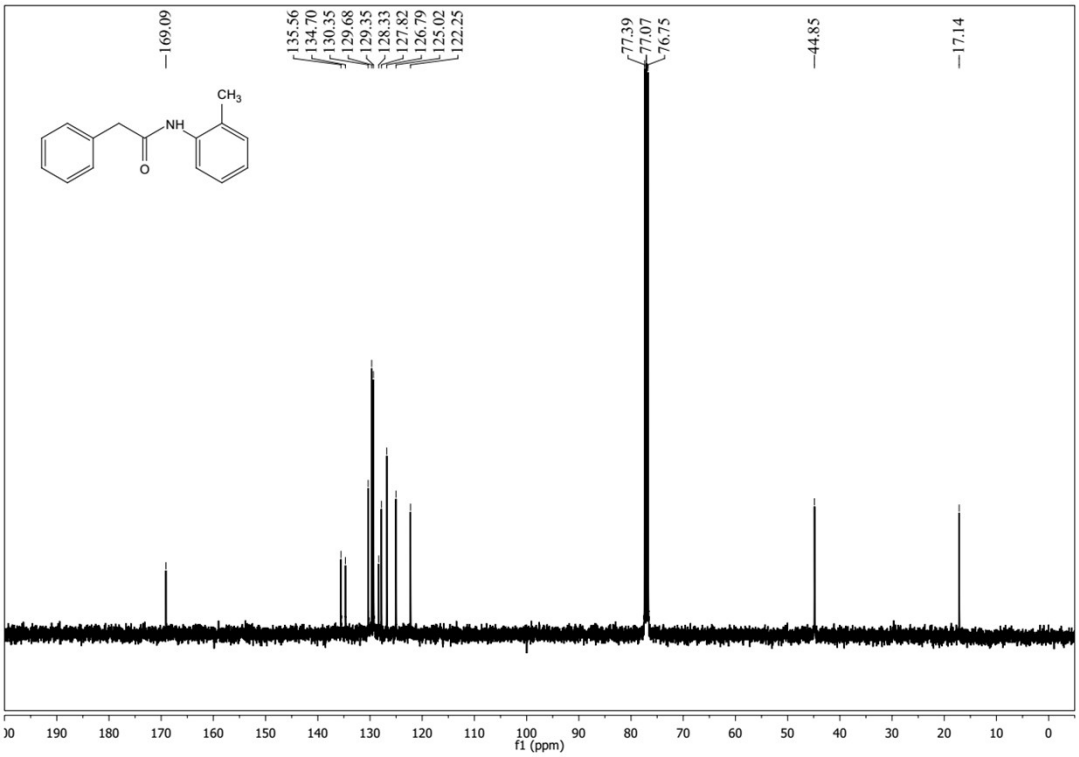


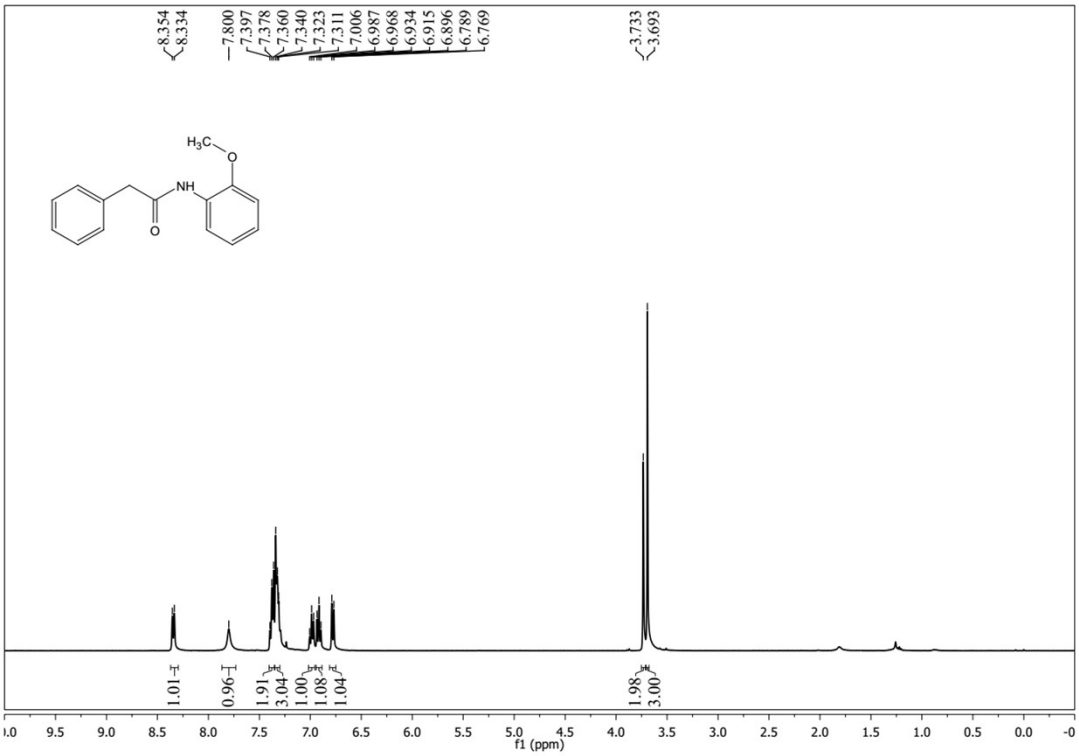
^{1}H NMR Spectra of 3ao



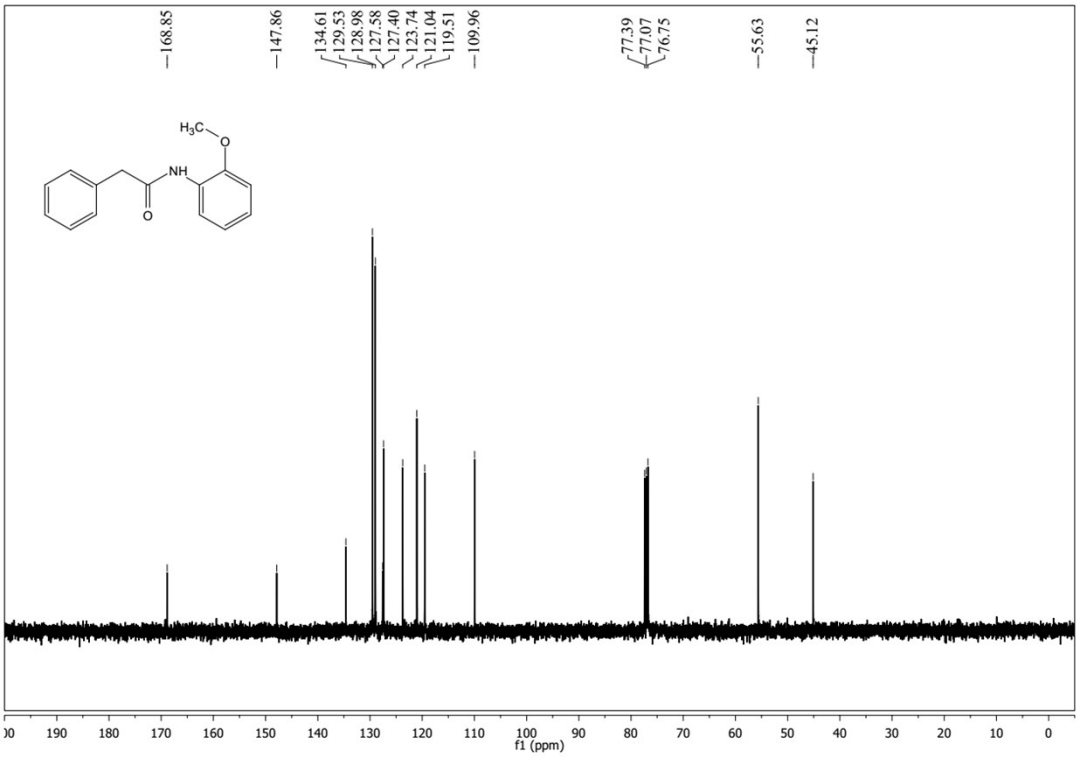
^{13}C NMR Spectra of 3ao



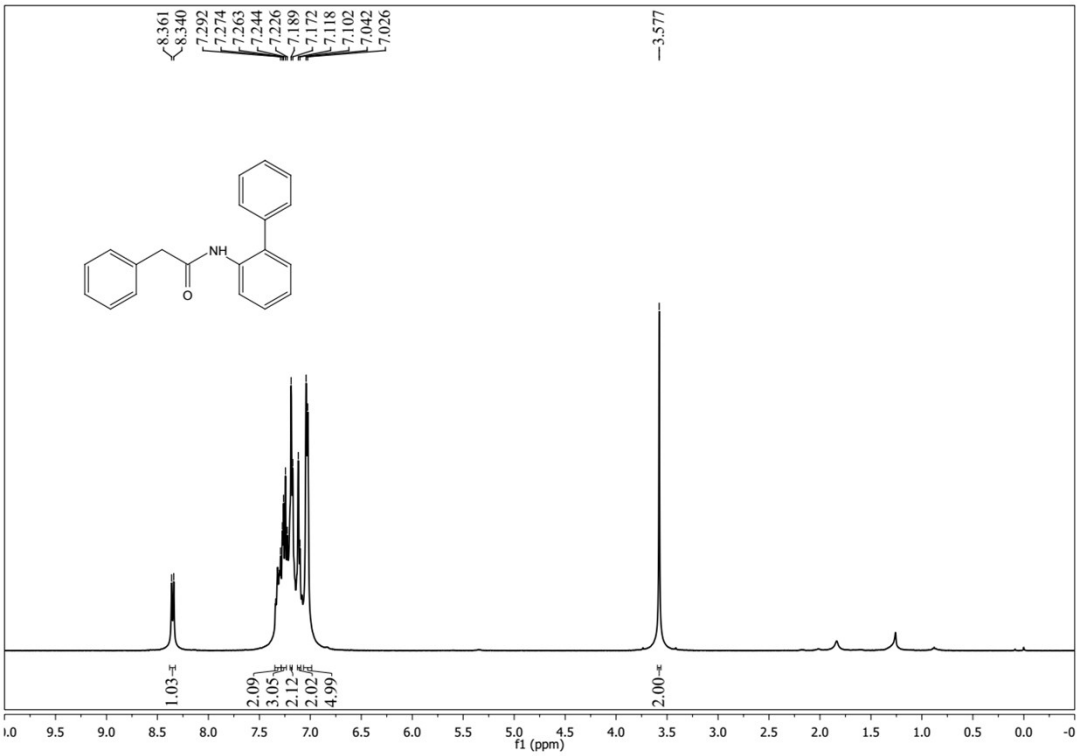
^{1}H NMR Spectra of 3ap



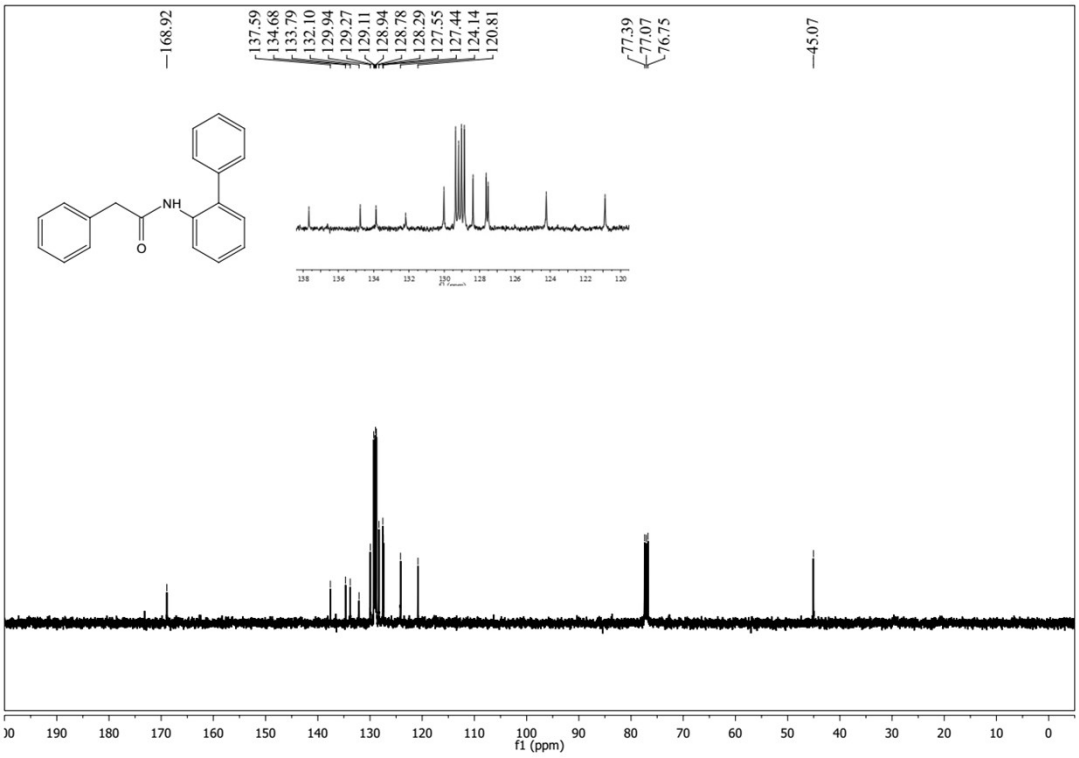
^{13}C NMR Spectra of 3ap



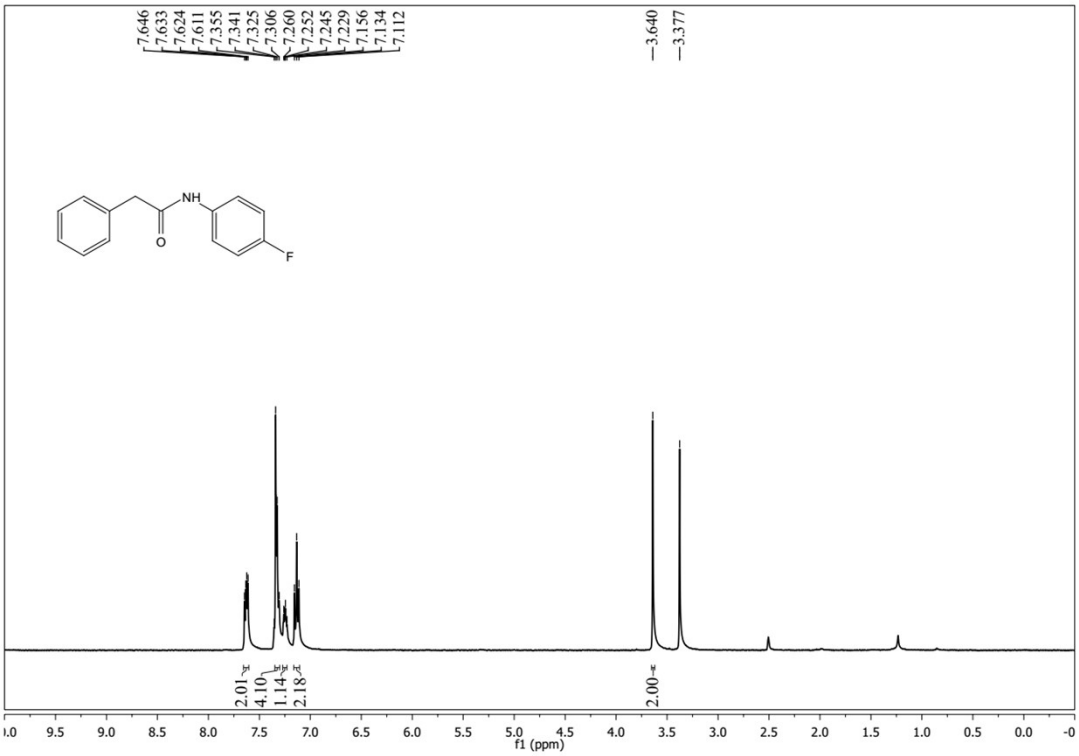
^{1}H NMR Spectra of 3aq



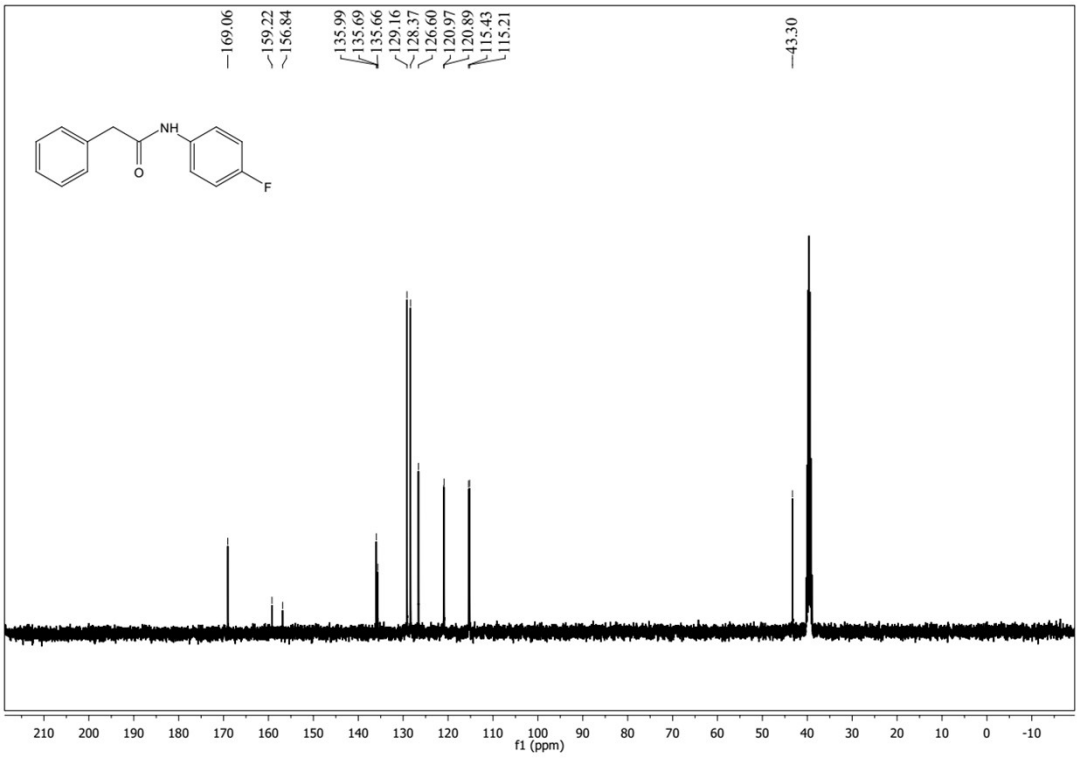
^{13}C NMR Spectra of 3aq



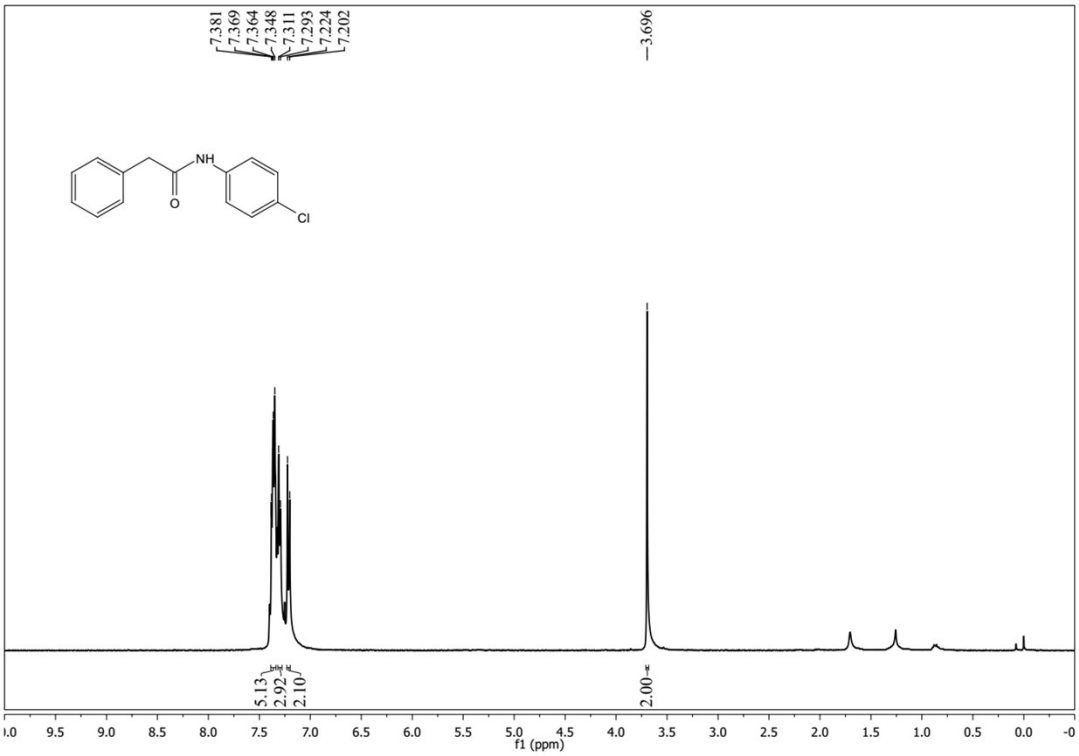
^{1}H NMR Spectra of 3ar



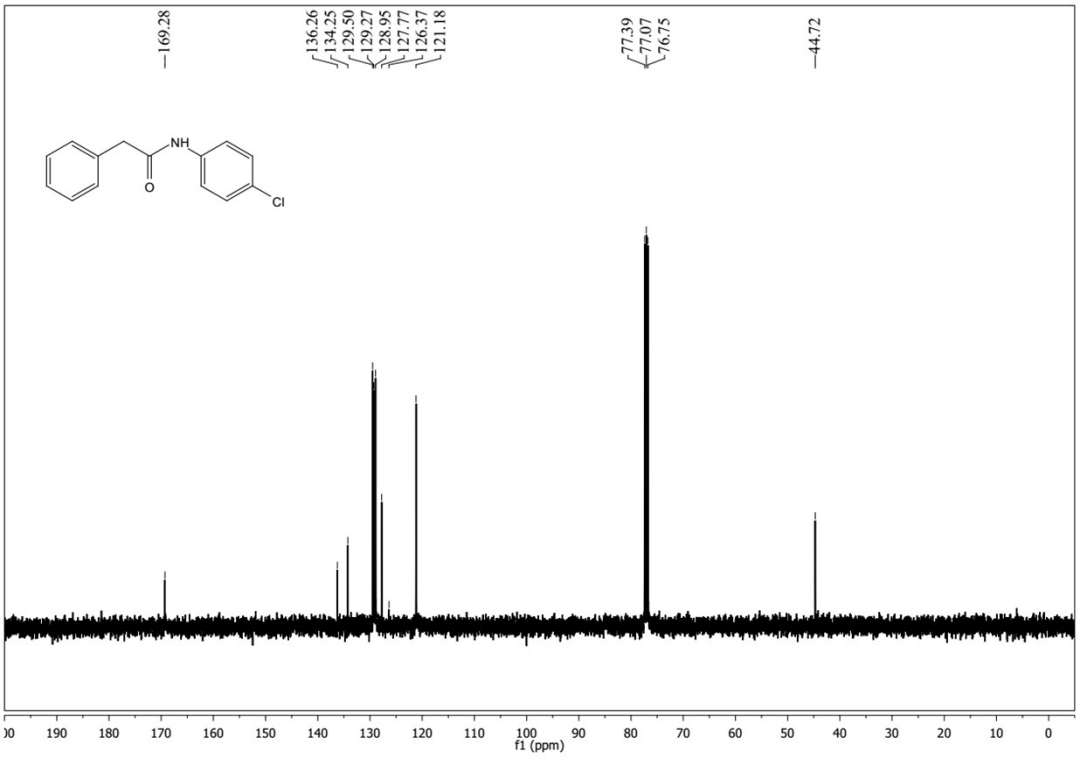
^{13}C NMR Spectra of 3ar



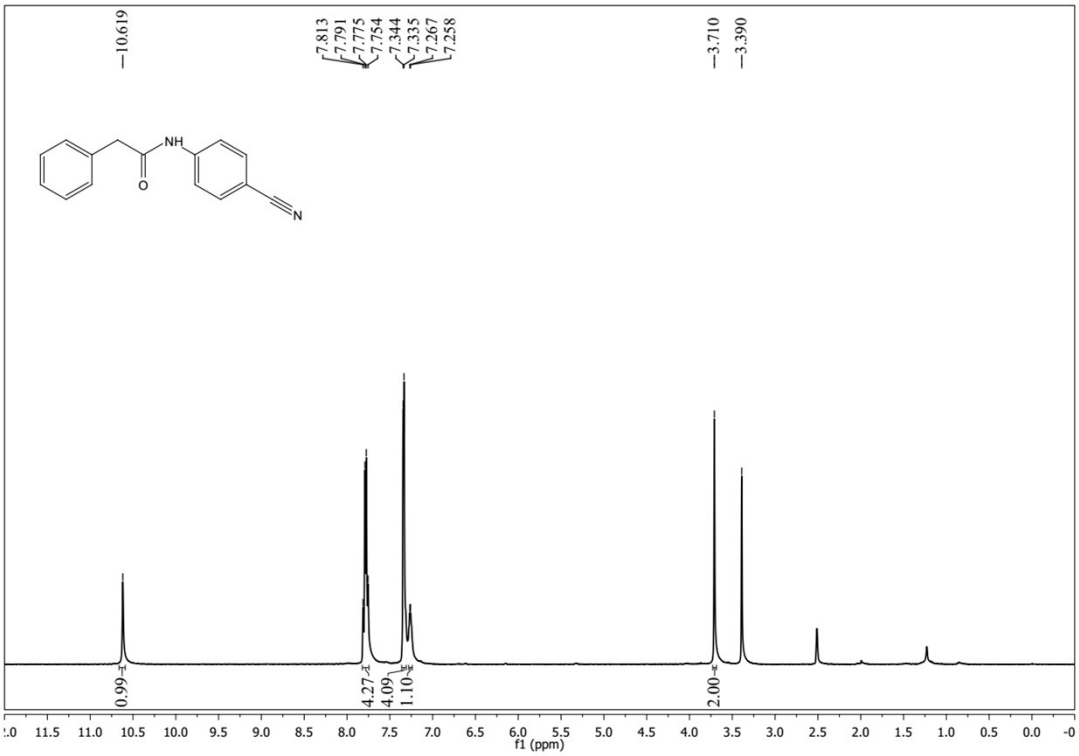
^{1}H NMR Spectra of 3as



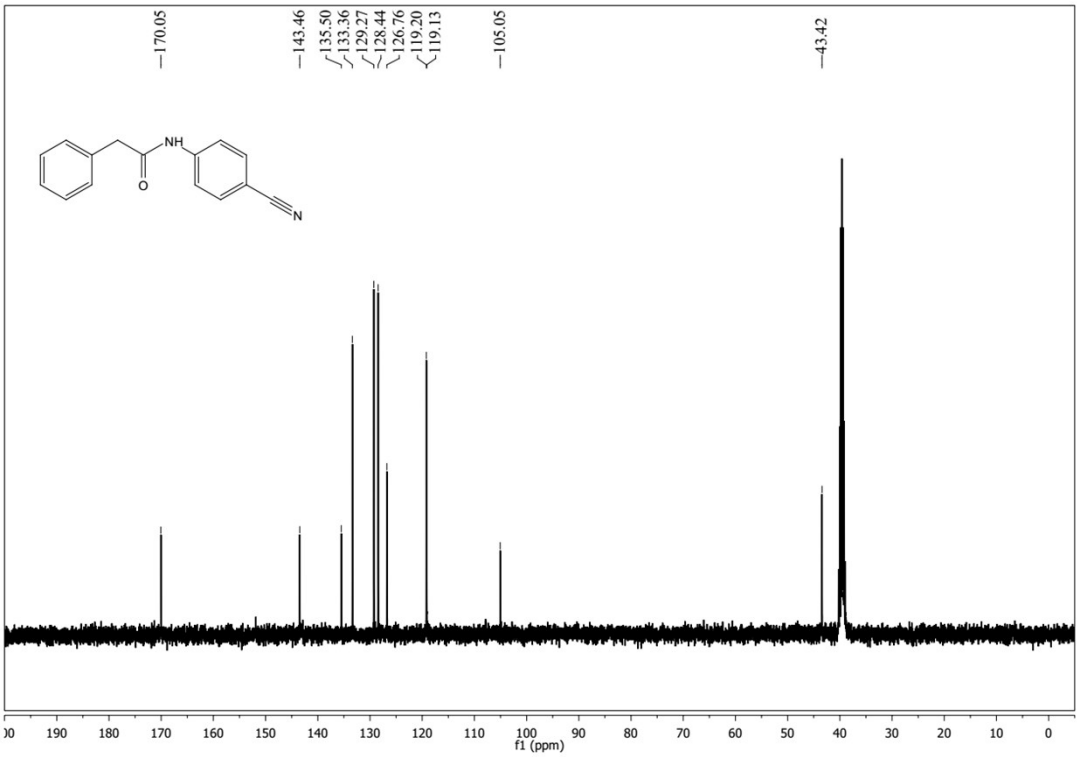
^{13}C NMR Spectra of 3as



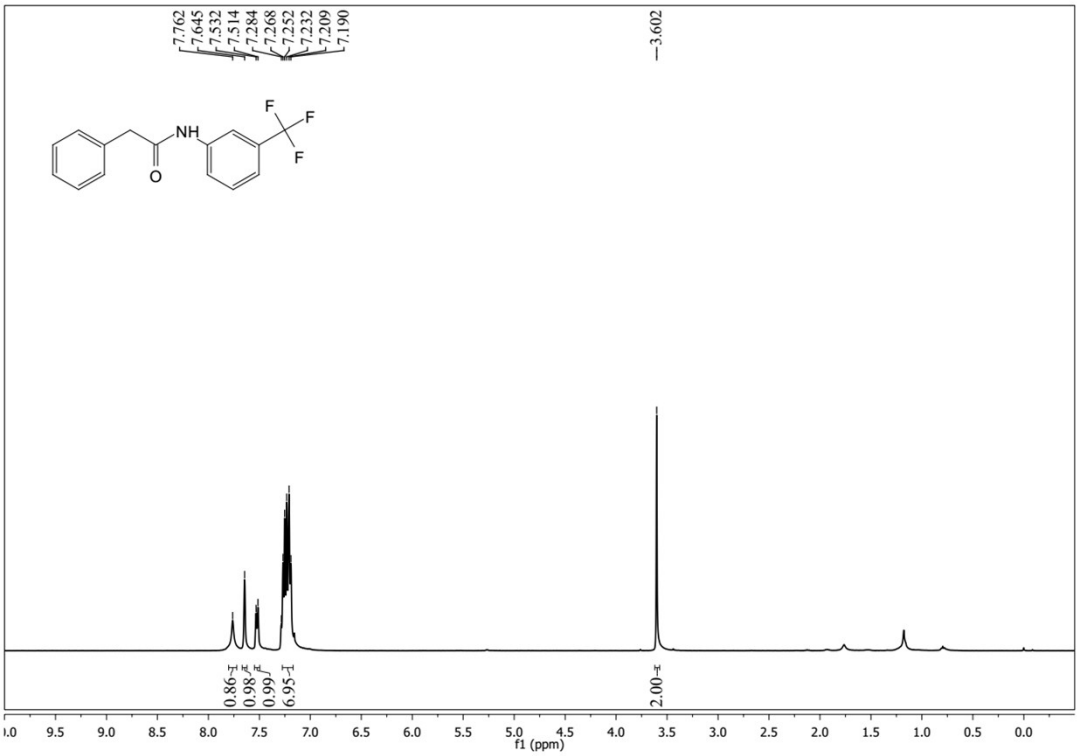
^{1}H NMR Spectra of 3at



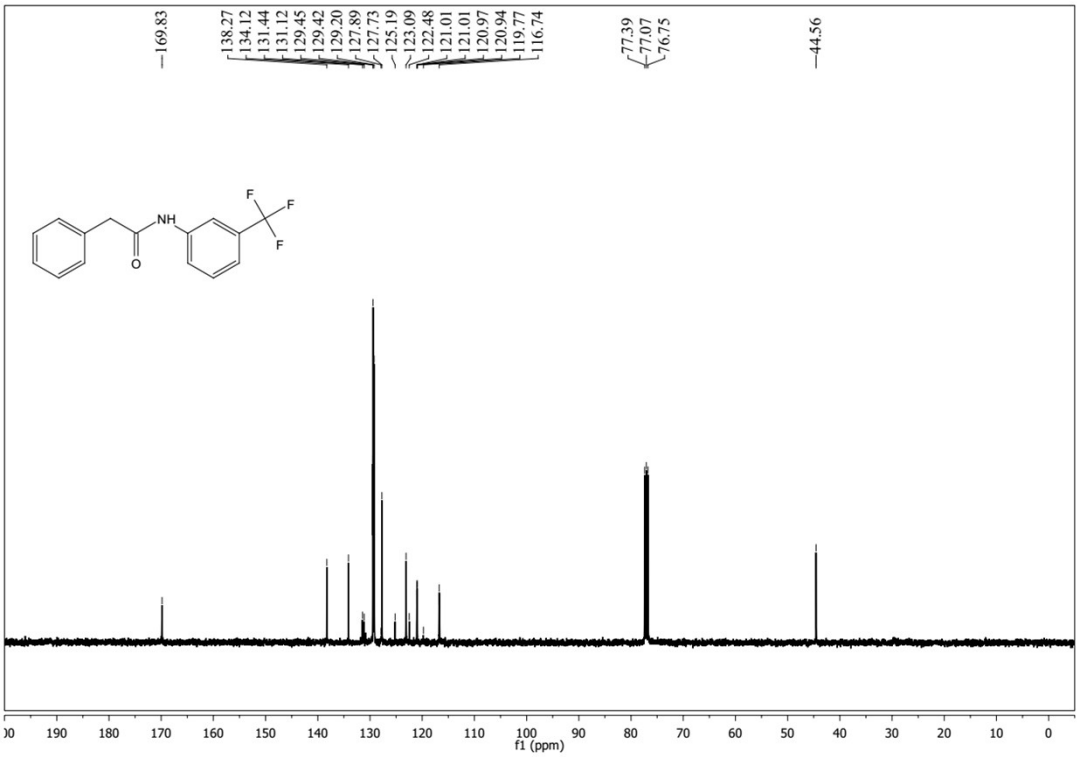
^{13}C NMR Spectra of 3at



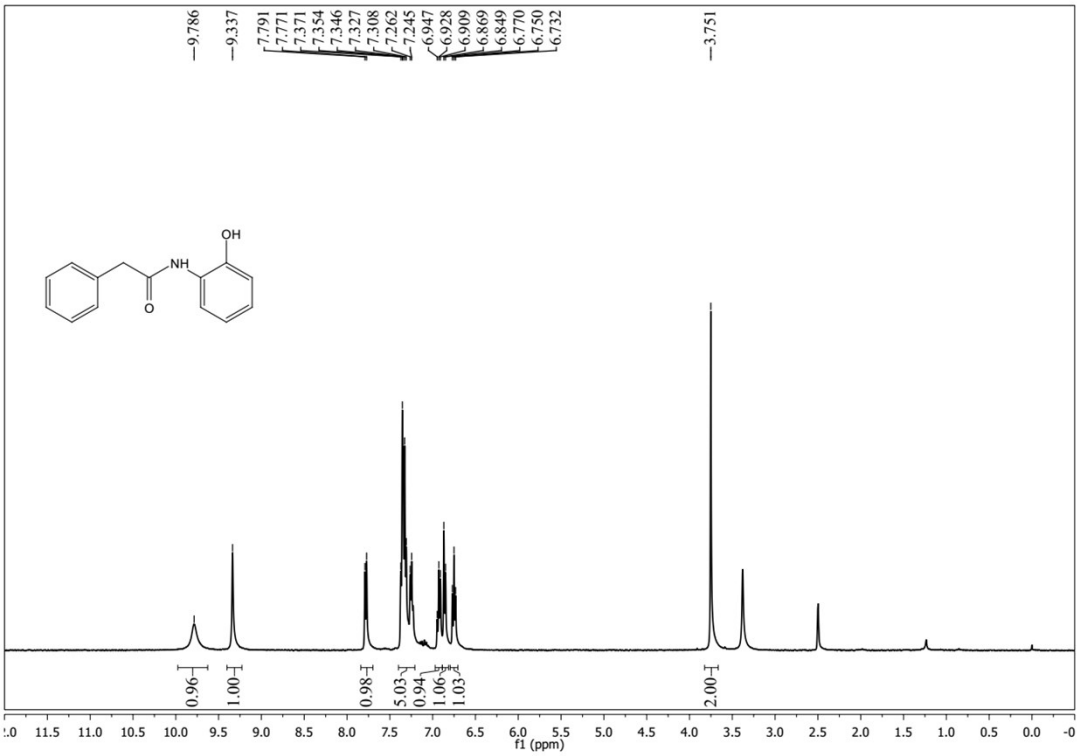
^{1}H NMR Spectra of 3au



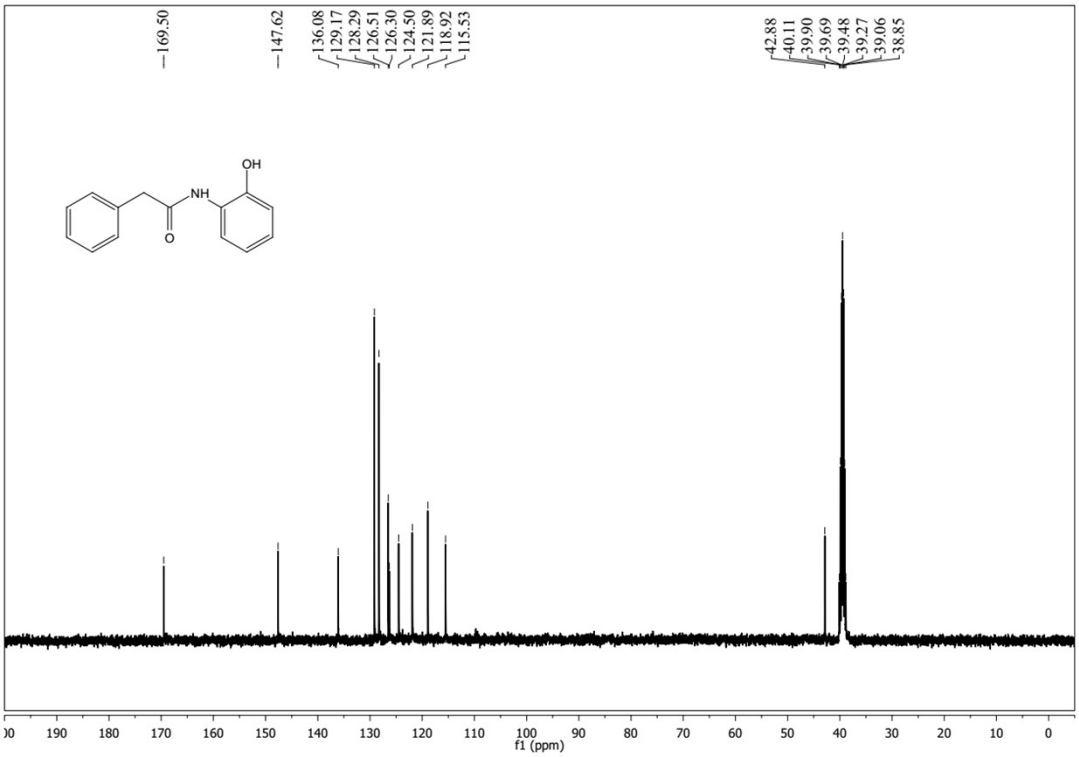
^{13}C NMR Spectra of 3au



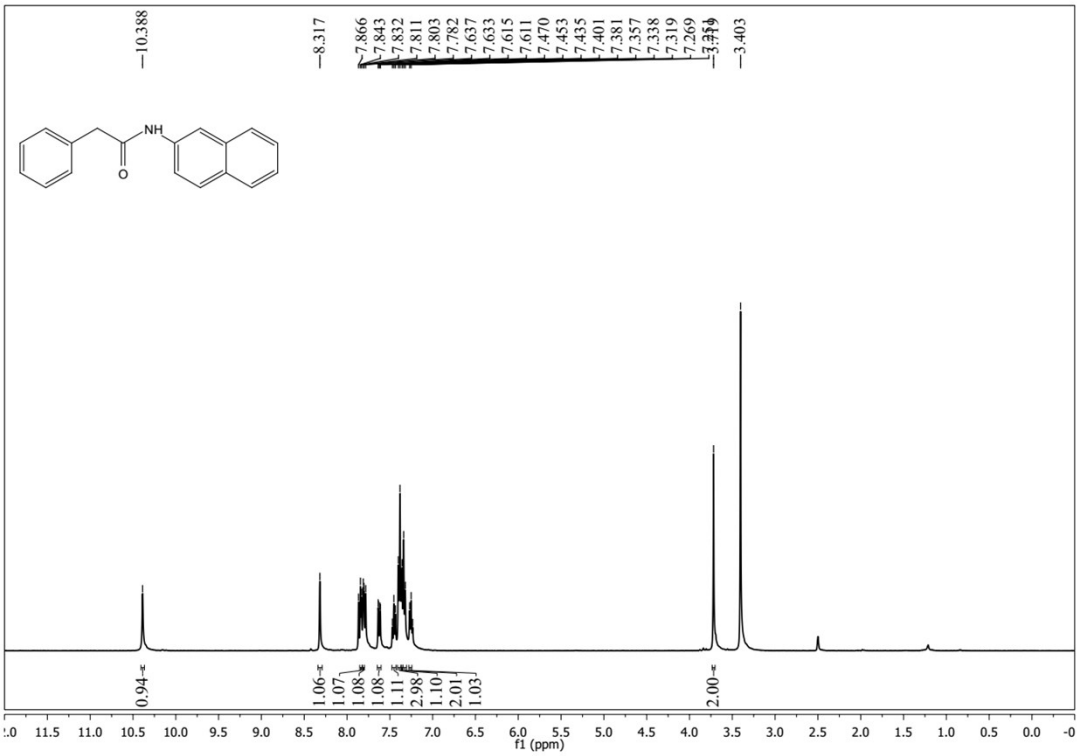
^{1}H NMR Spectra of 3av



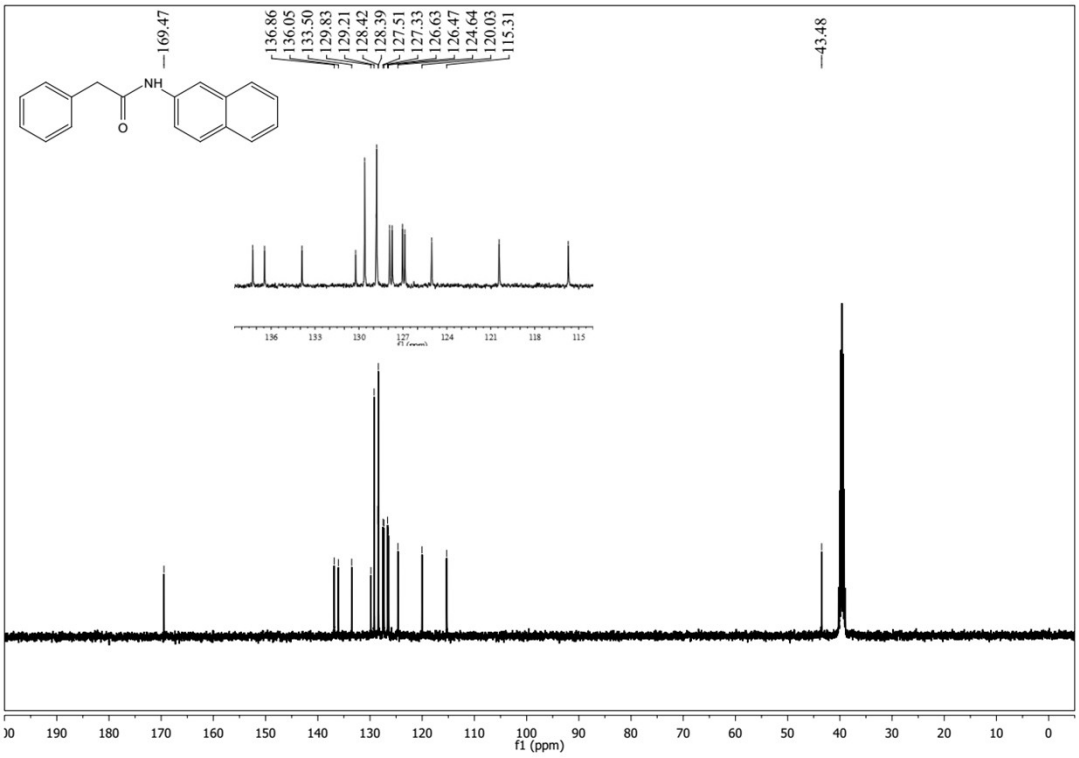
^{13}C NMR Spectra of 3av



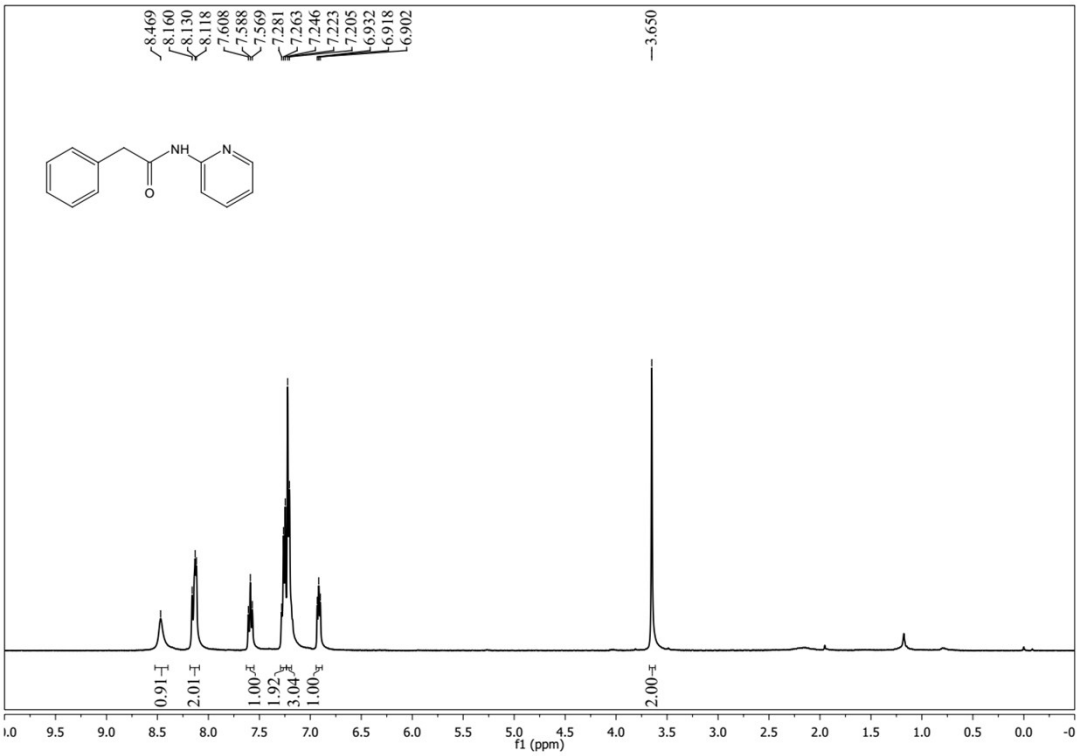
^{1}H NMR Spectra of 3aw



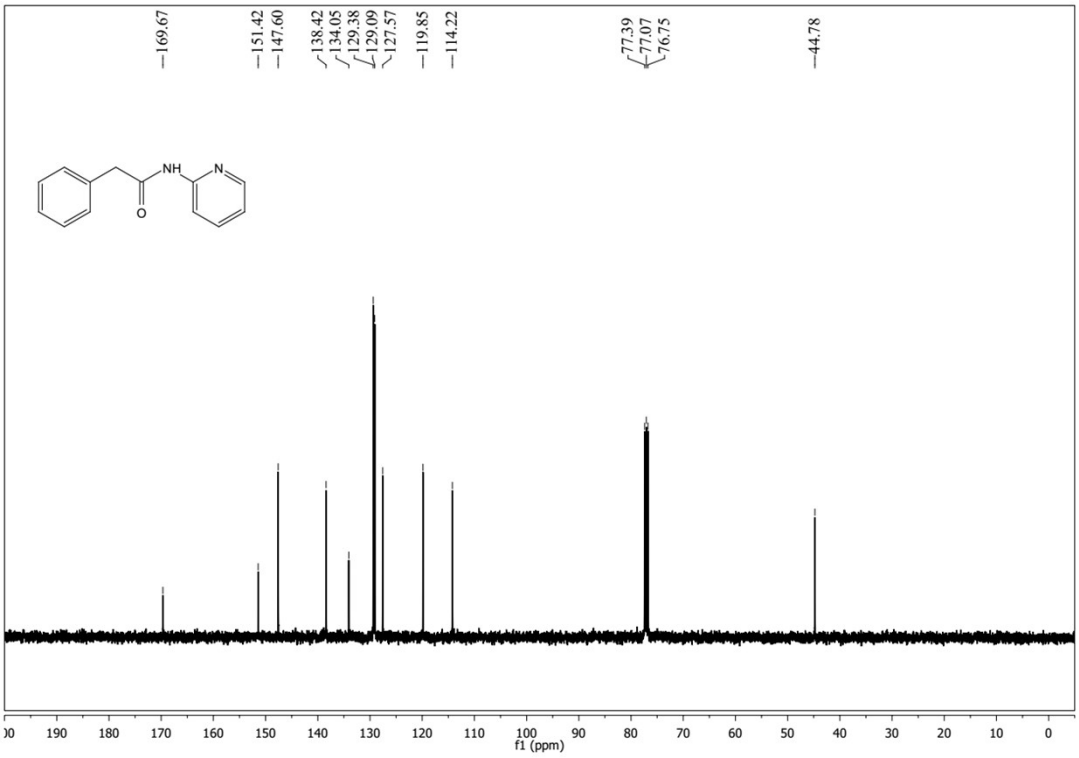
^{13}C NMR Spectra of 3aw



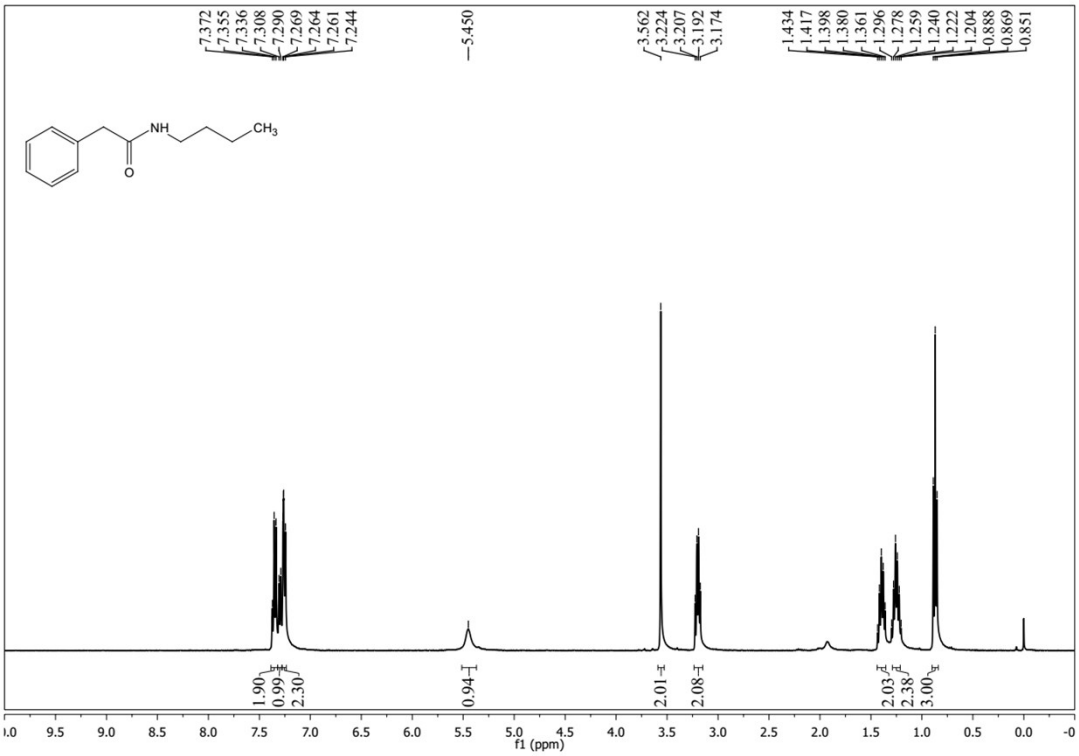
^{1}H NMR Spectra of 3ax



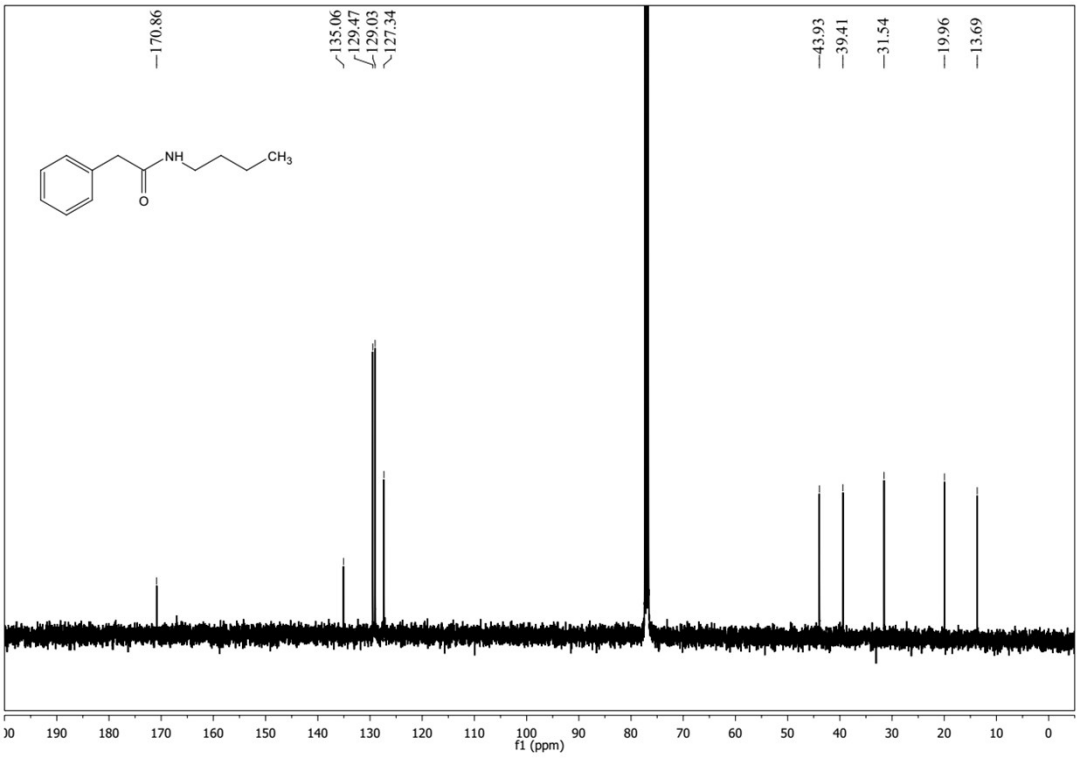
^{13}C NMR Spectra of 3ax



^{1}H NMR Spectra of 3ay



^{13}C NMR Spectra of 3ay



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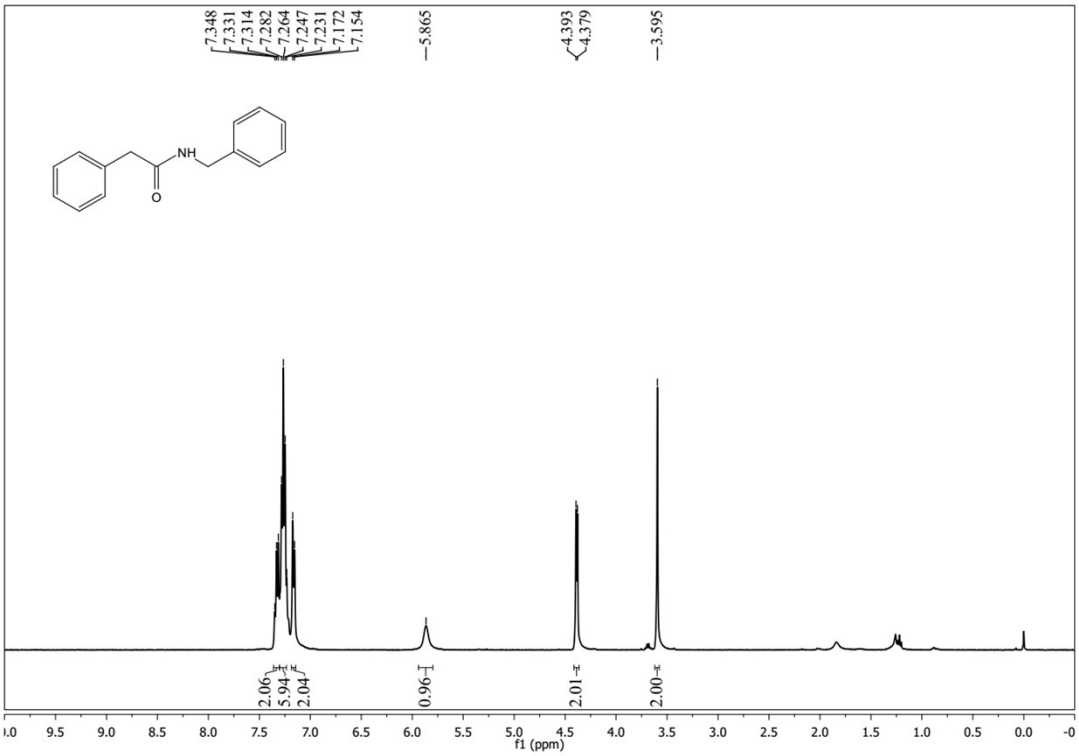

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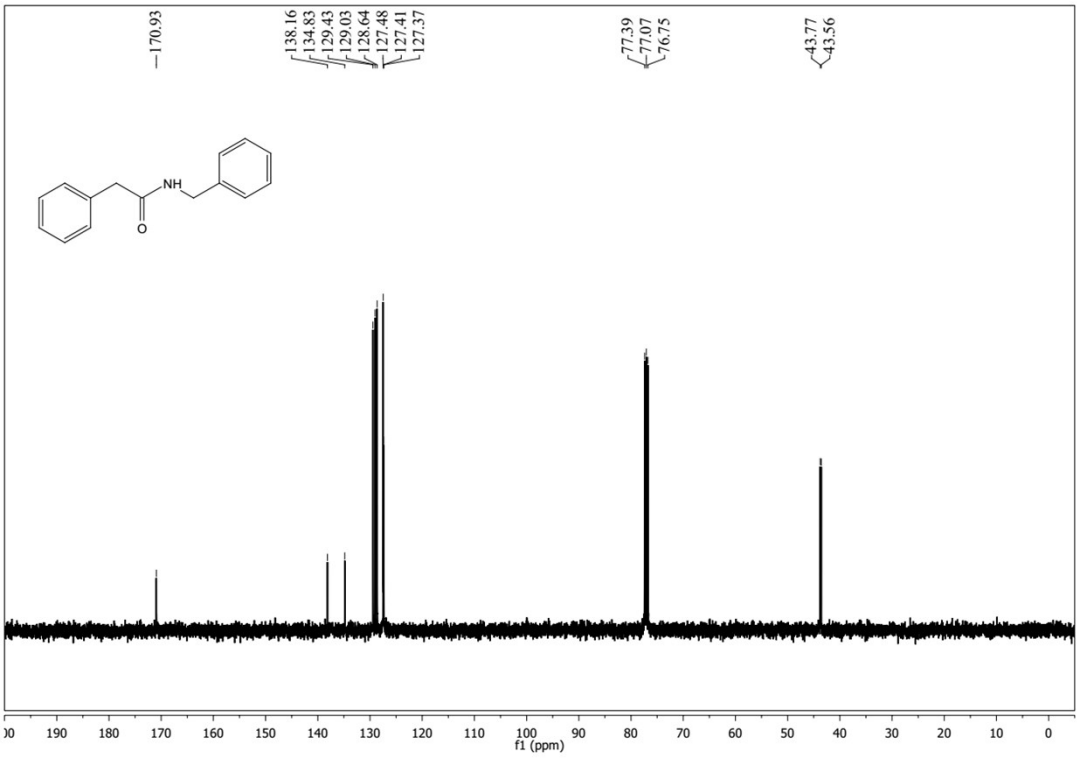
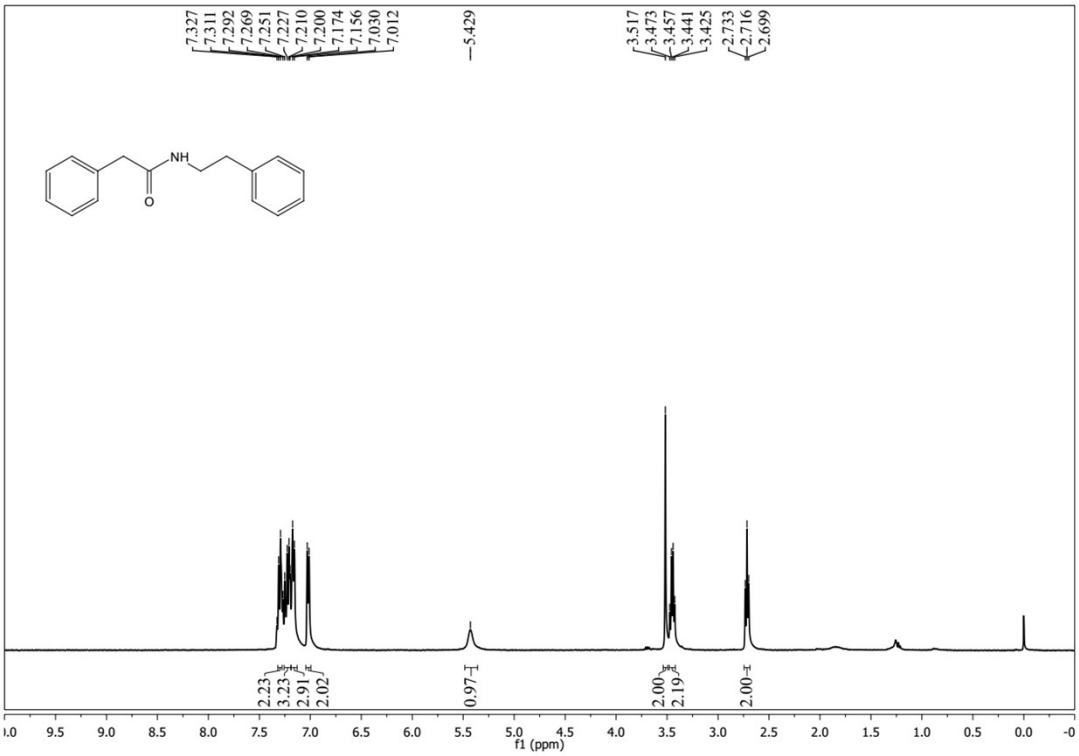
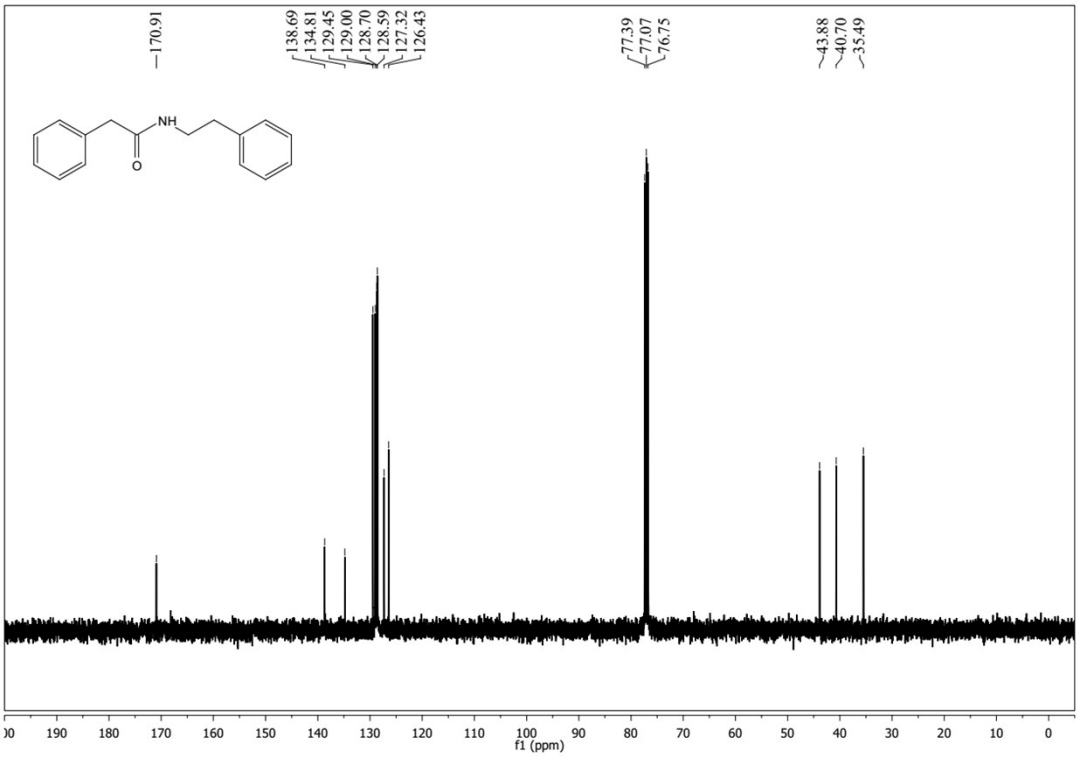


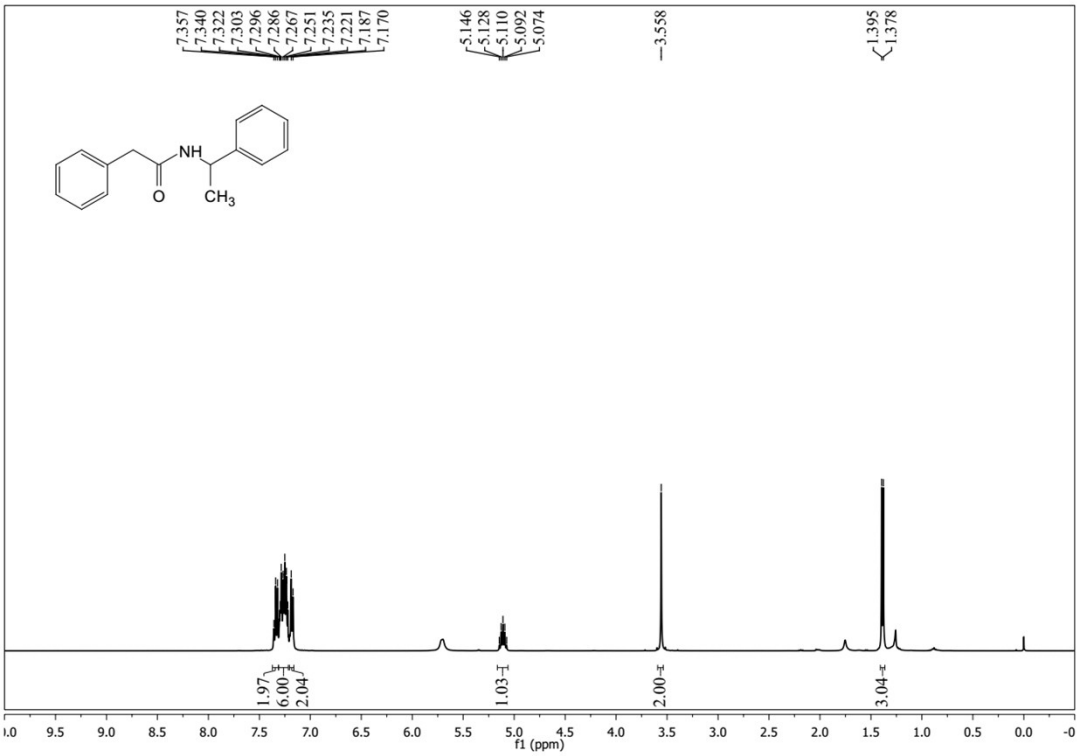
^{1}H NMR Spectra of 3ba



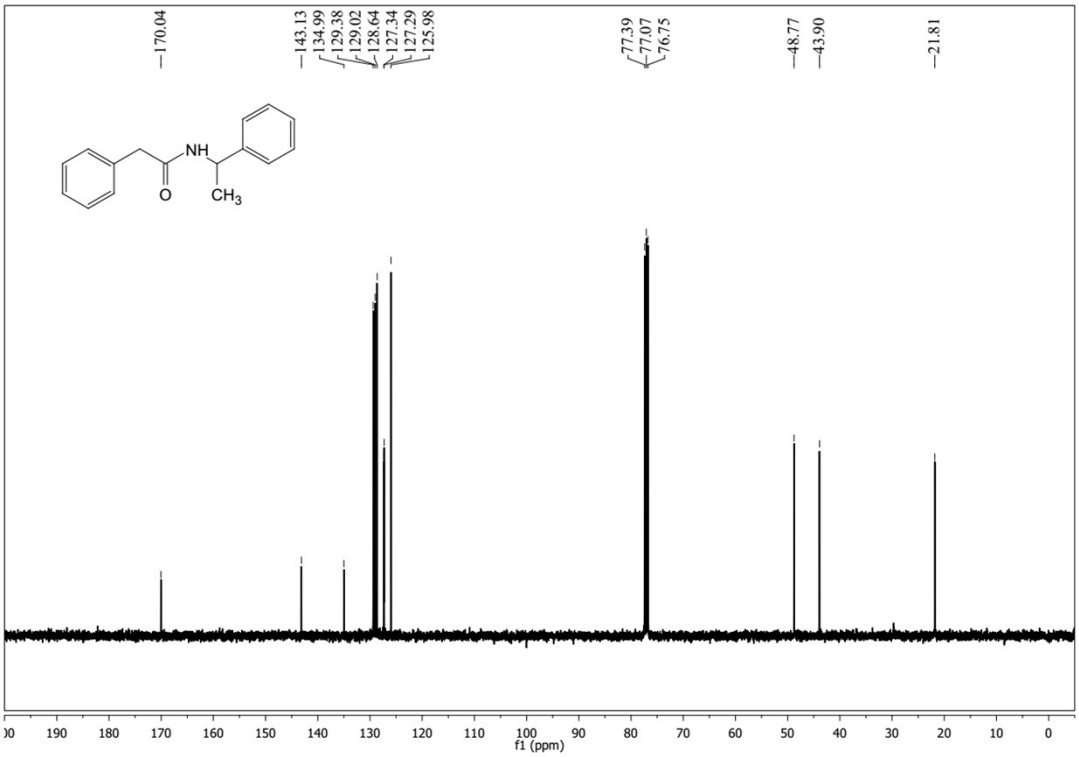
^{13}C NMR Spectra of 3ba



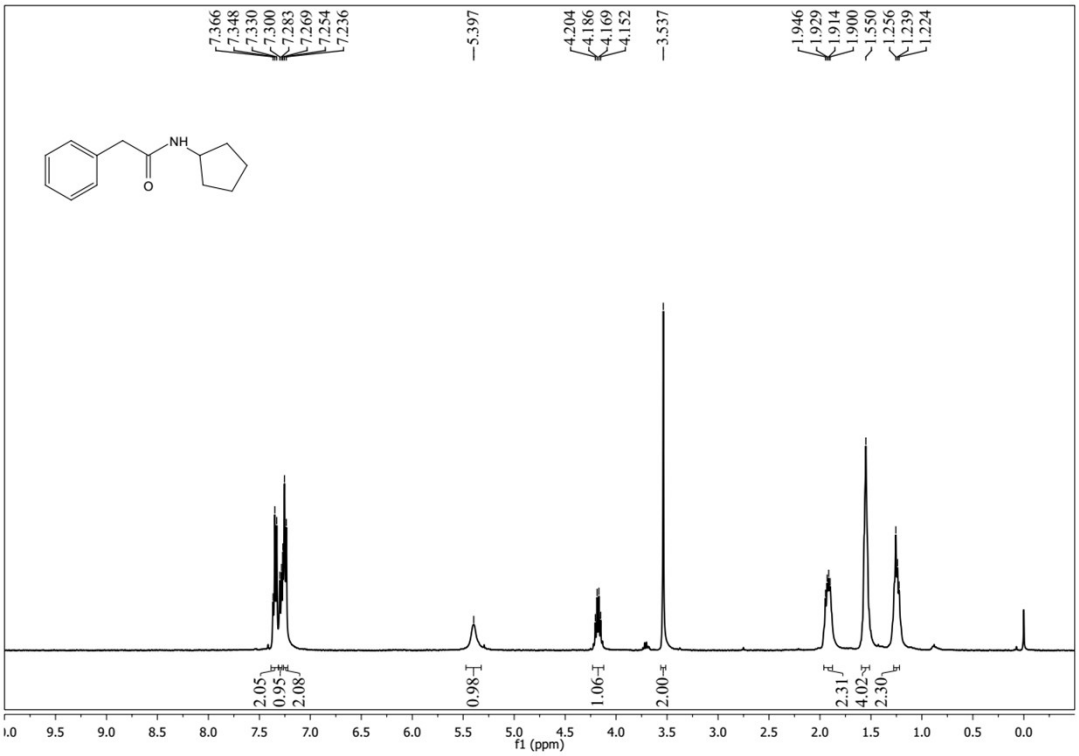
^{1}H NMR Spectra of 3bb



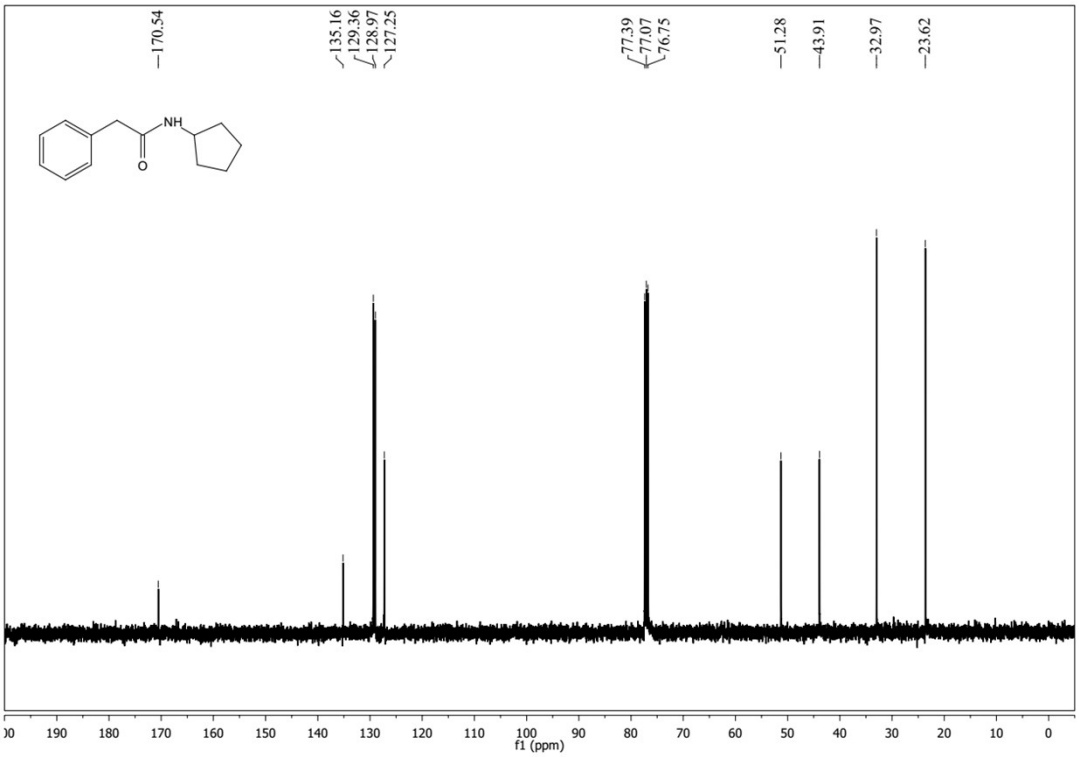
^{13}C NMR Spectra of 3bb



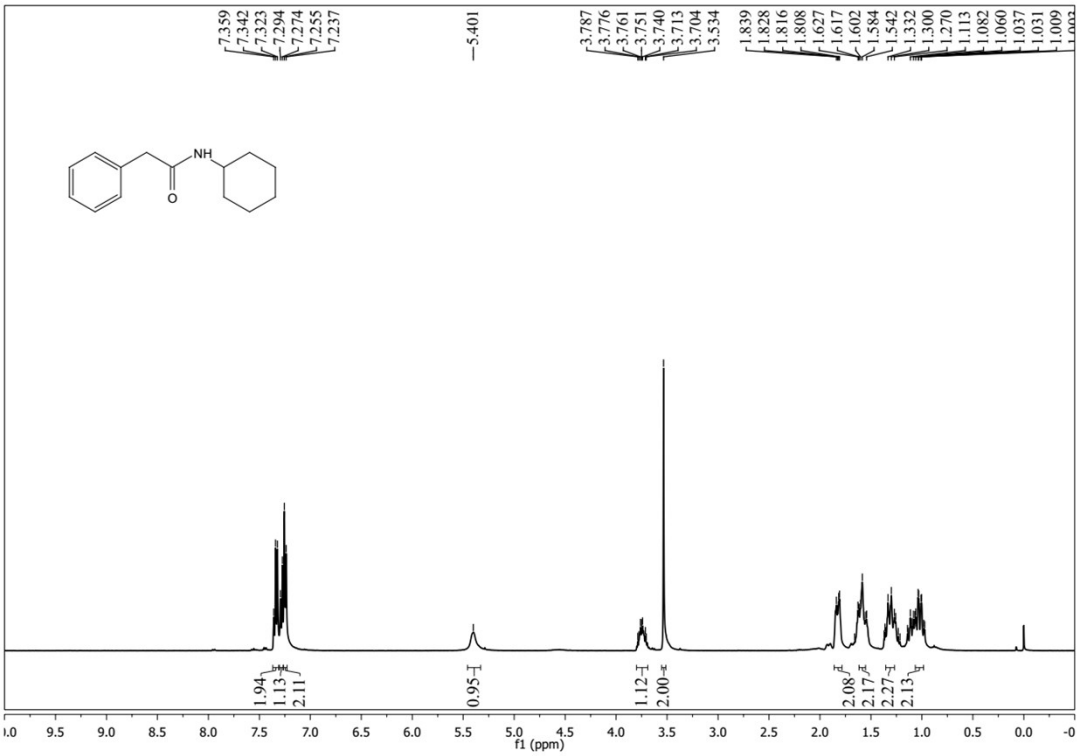
^{1}H NMR Spectra of 3bc



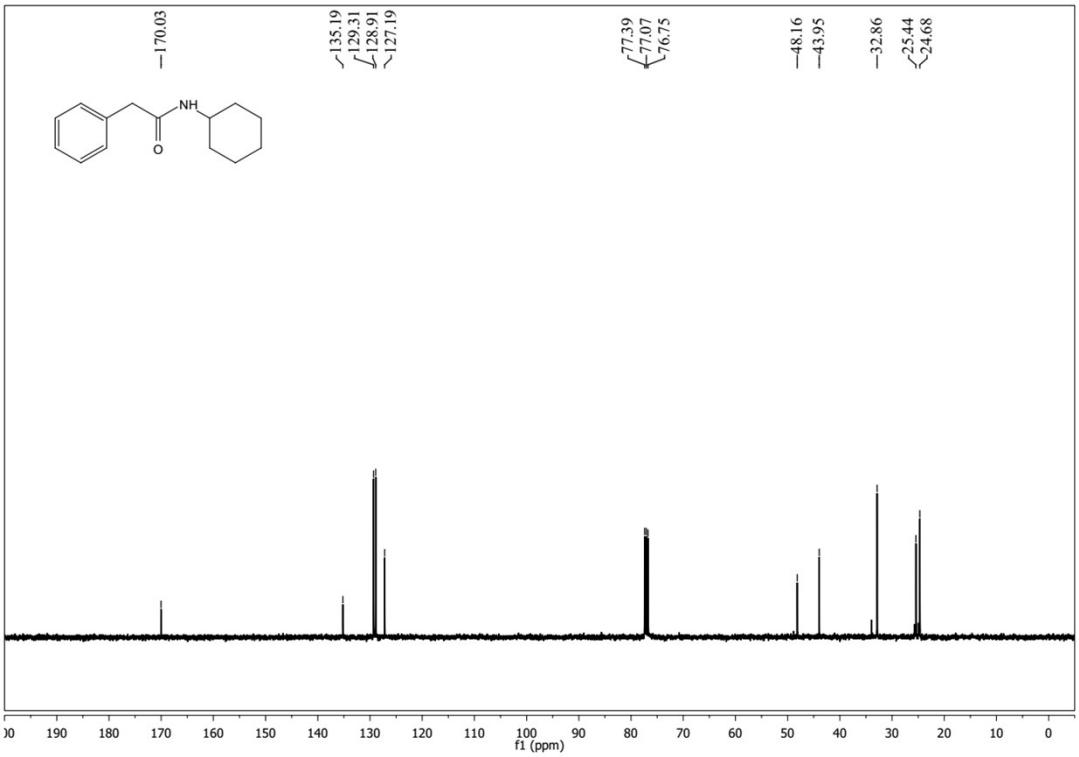
^{13}C NMR Spectra of 3bc



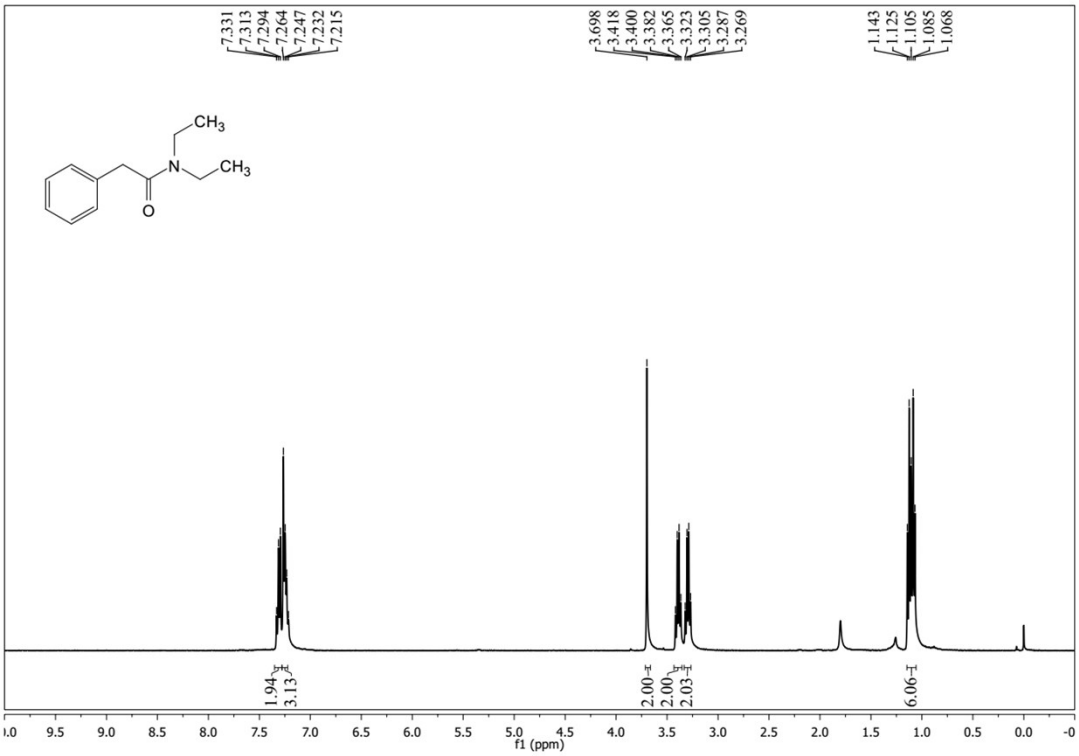
^{1}H NMR Spectra of 3bd



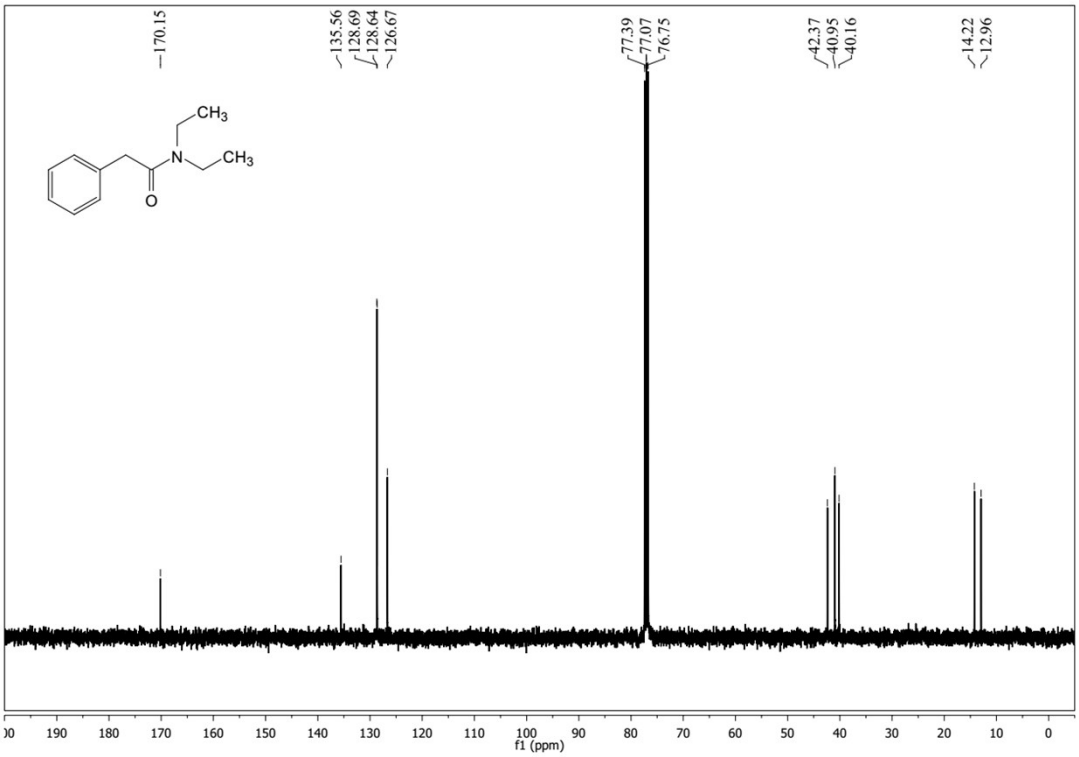
^{13}C NMR Spectra of 3bd



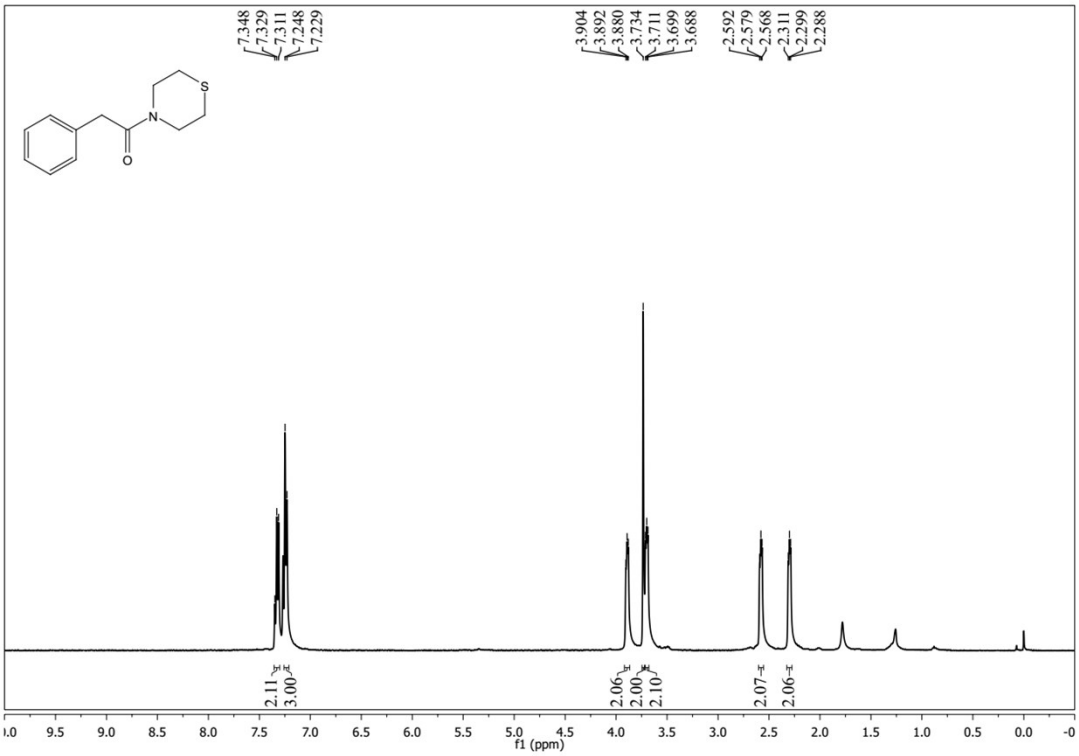
^{1}H NMR Spectra of 3be



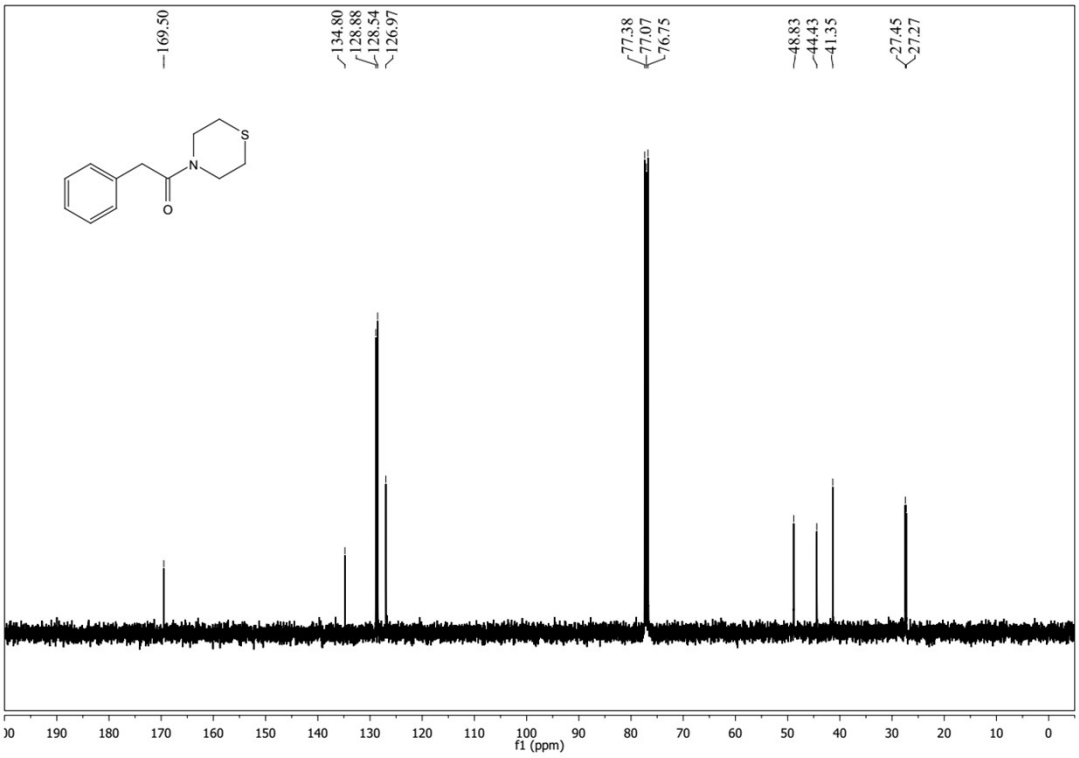
^{13}C NMR Spectra of 3be



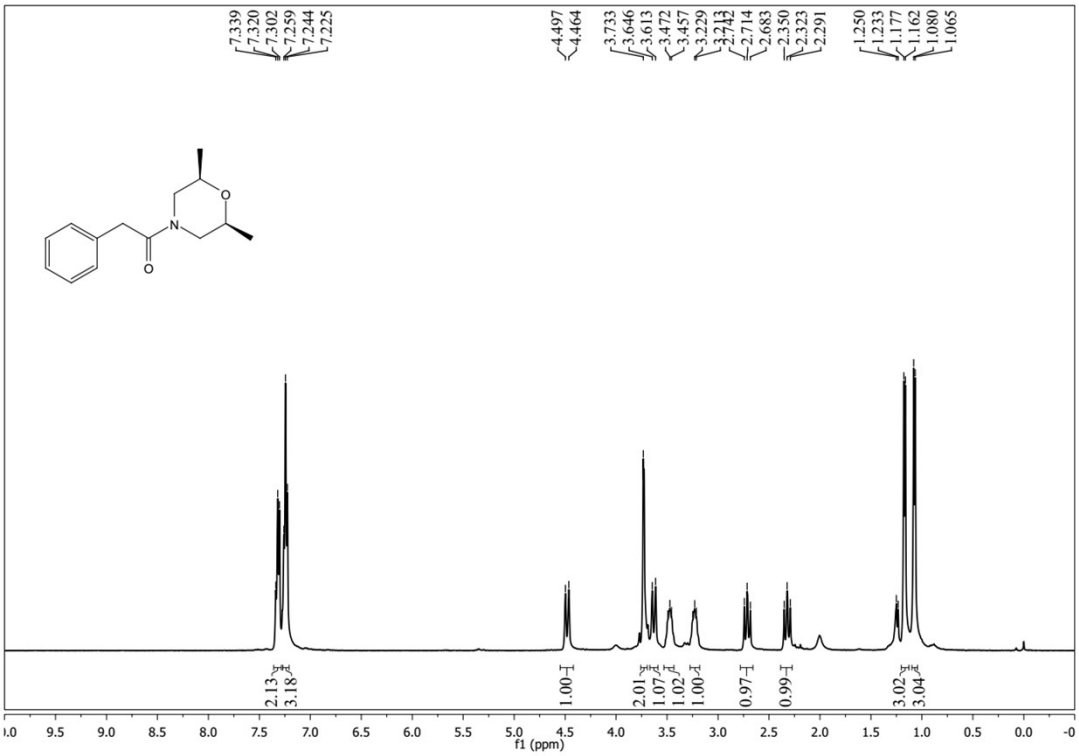
^{1}H NMR Spectra of 3bf



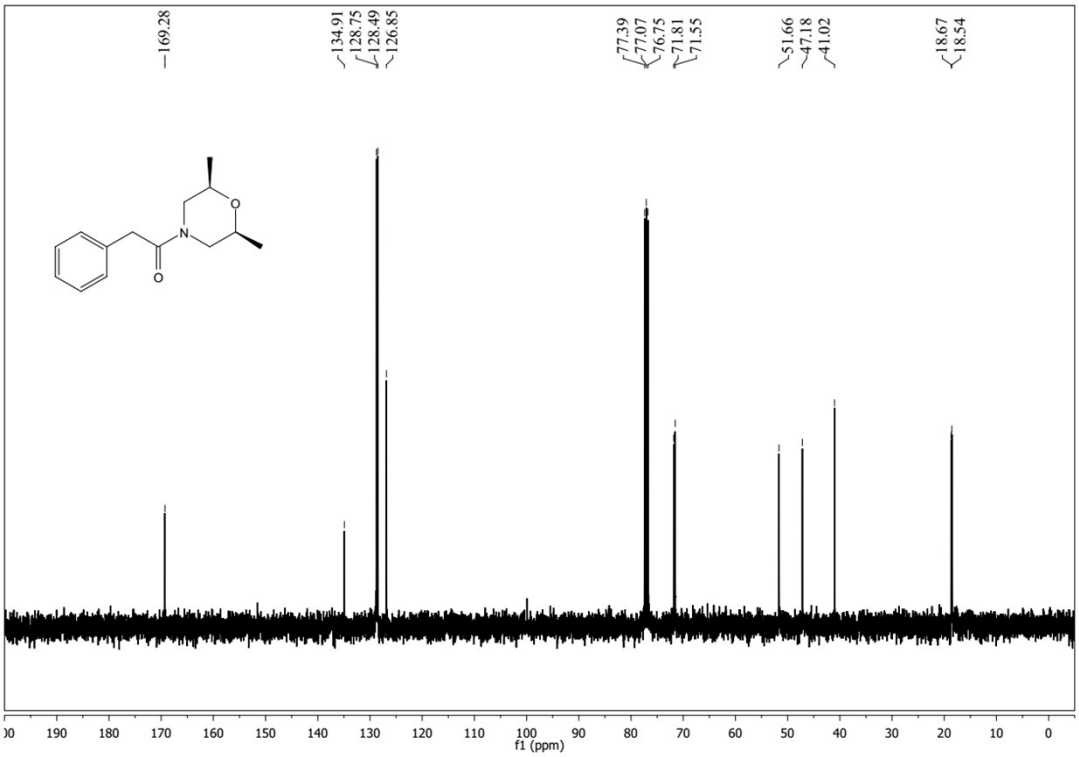
^{13}C NMR Spectra of 3bf



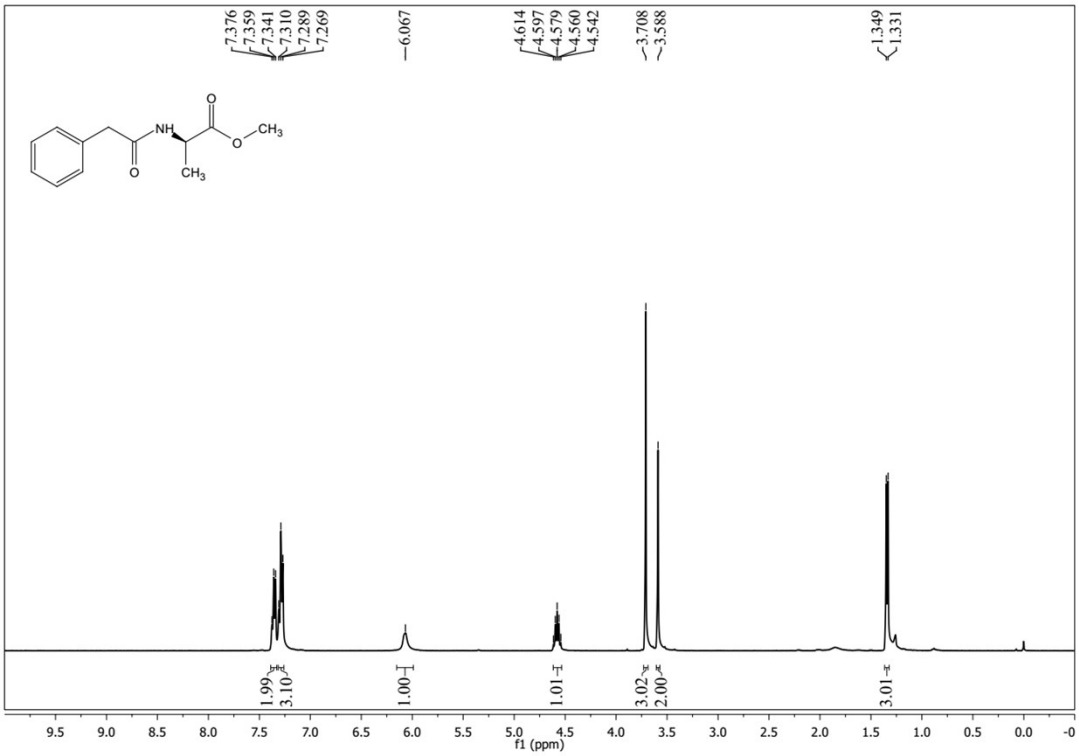
^{1}H NMR Spectra of 3bg



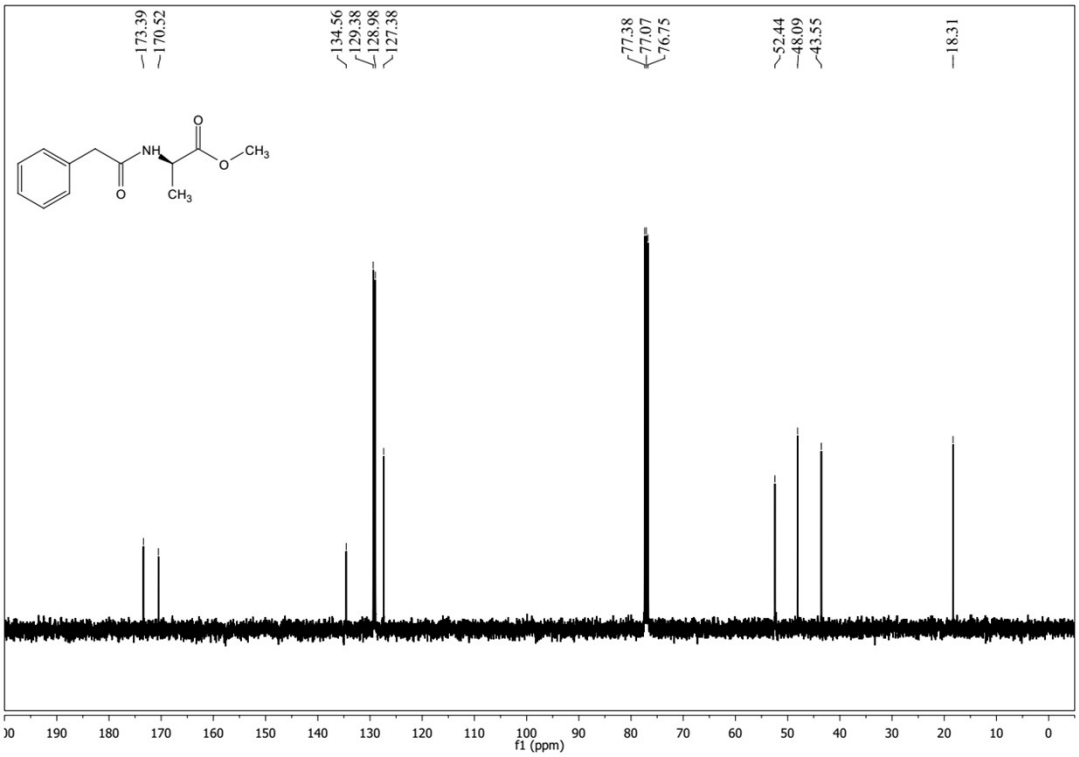
^{13}C NMR Spectra of 3bg



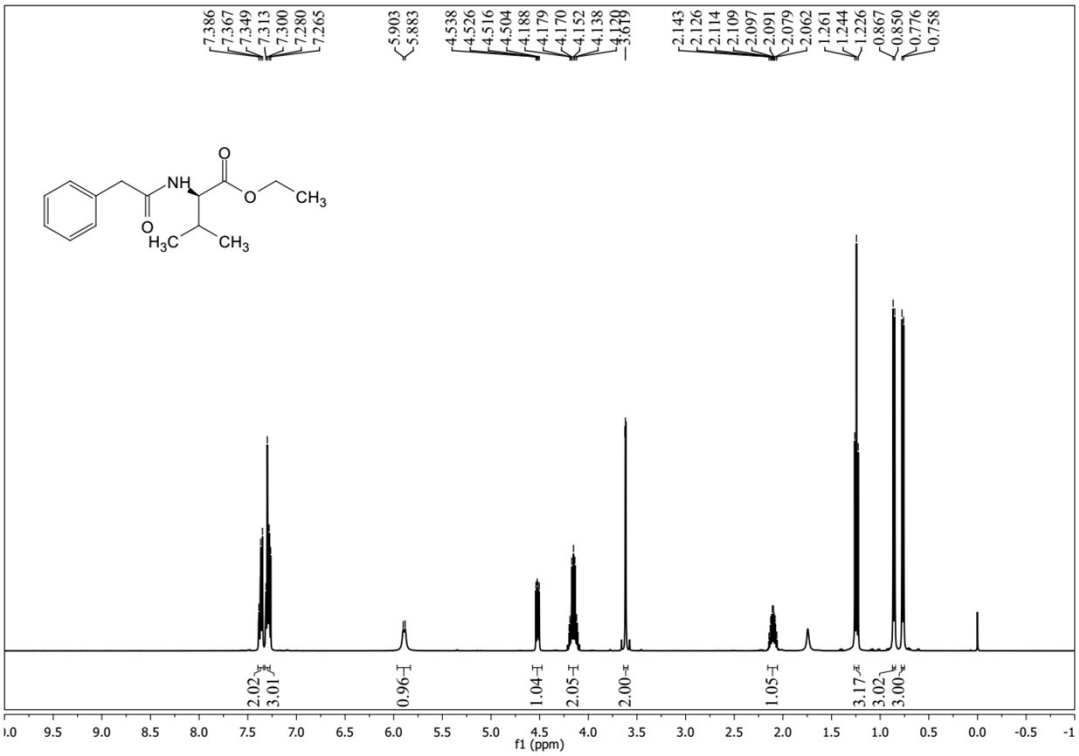
^{1}H NMR Spectra of 3bh



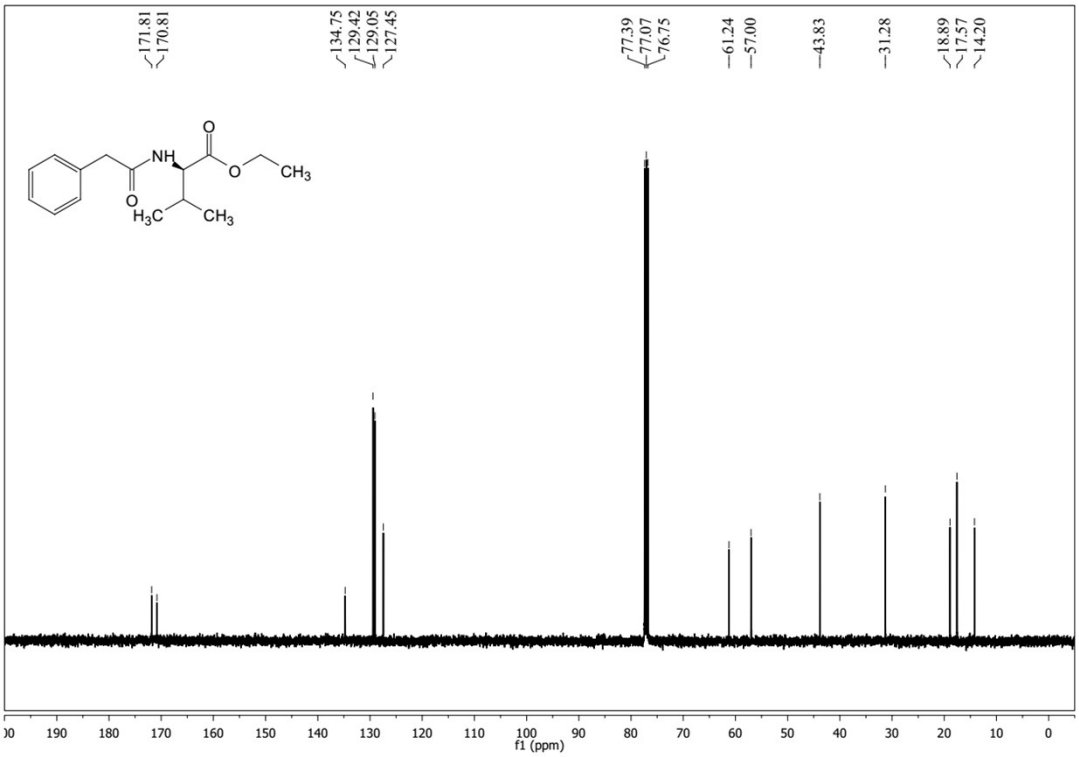
^{13}C NMR Spectra of 3bh



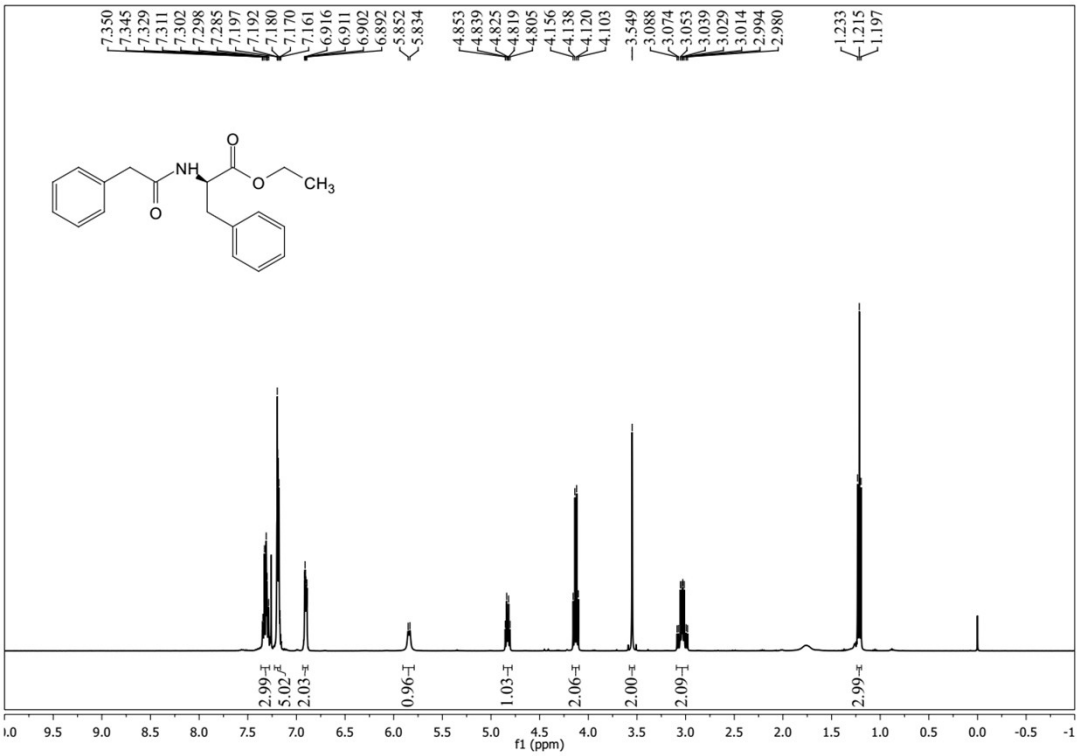
^{1}H NMR Spectra of 3bi



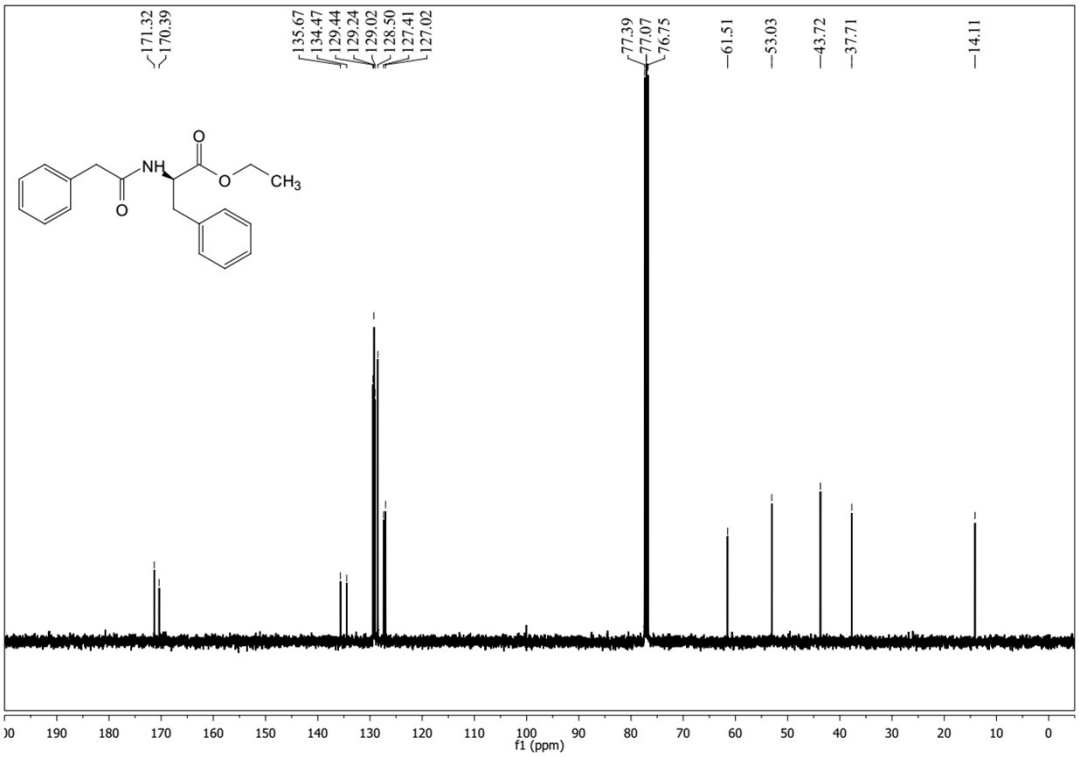
^{13}C NMR Spectra of 3bi



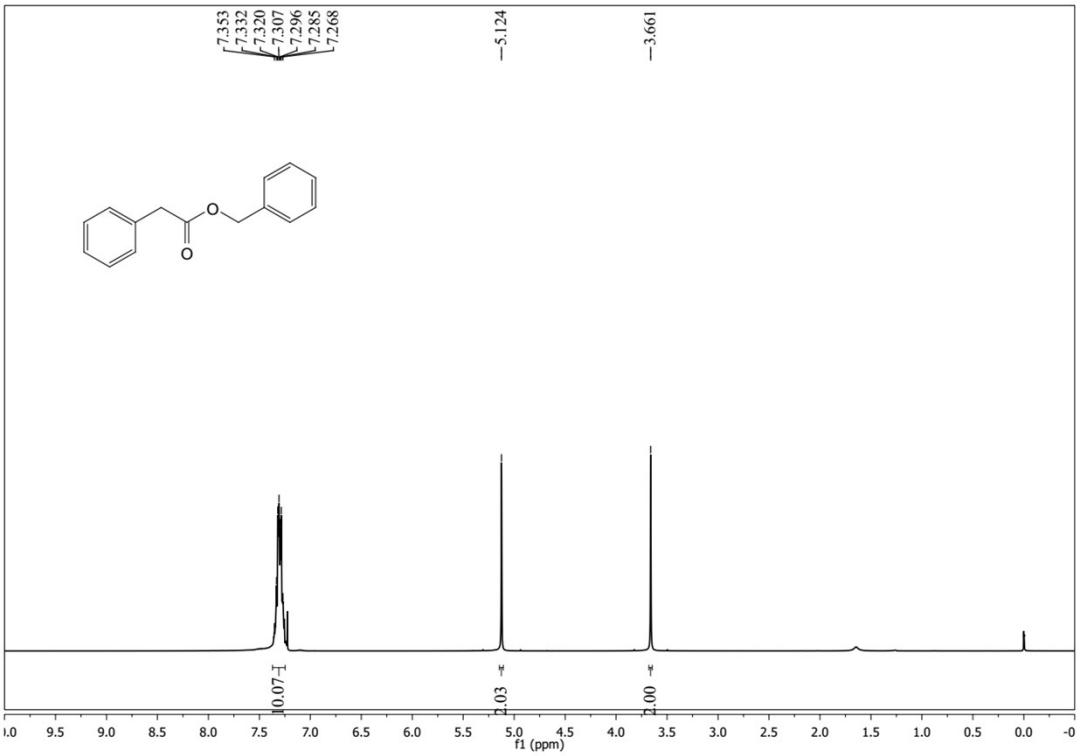
^{1}H NMR Spectra of 3bj



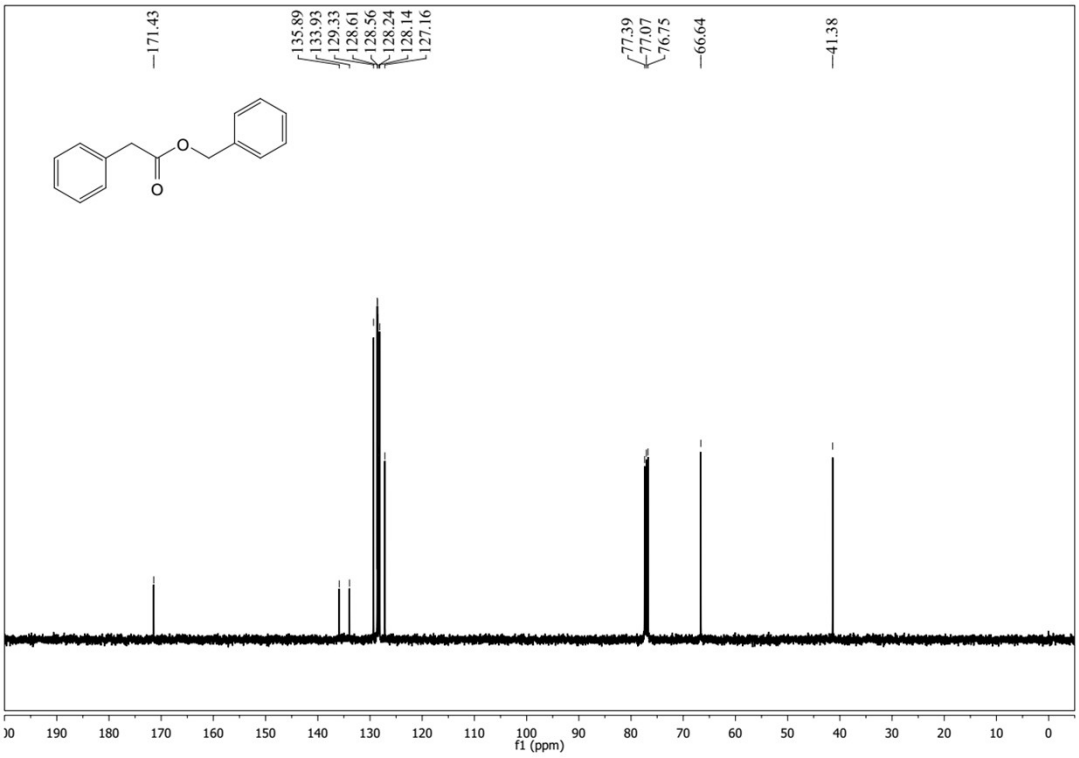
^{13}C NMR Spectra of 3bj



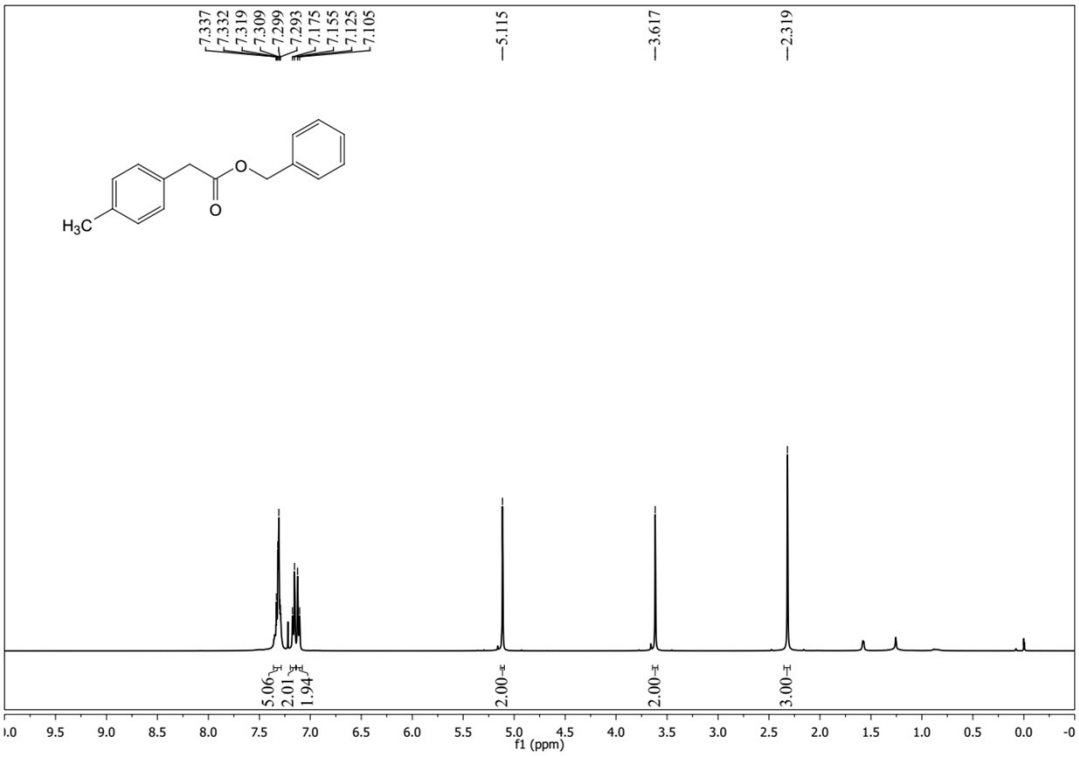
^{1}H NMR Spectra of 5aa



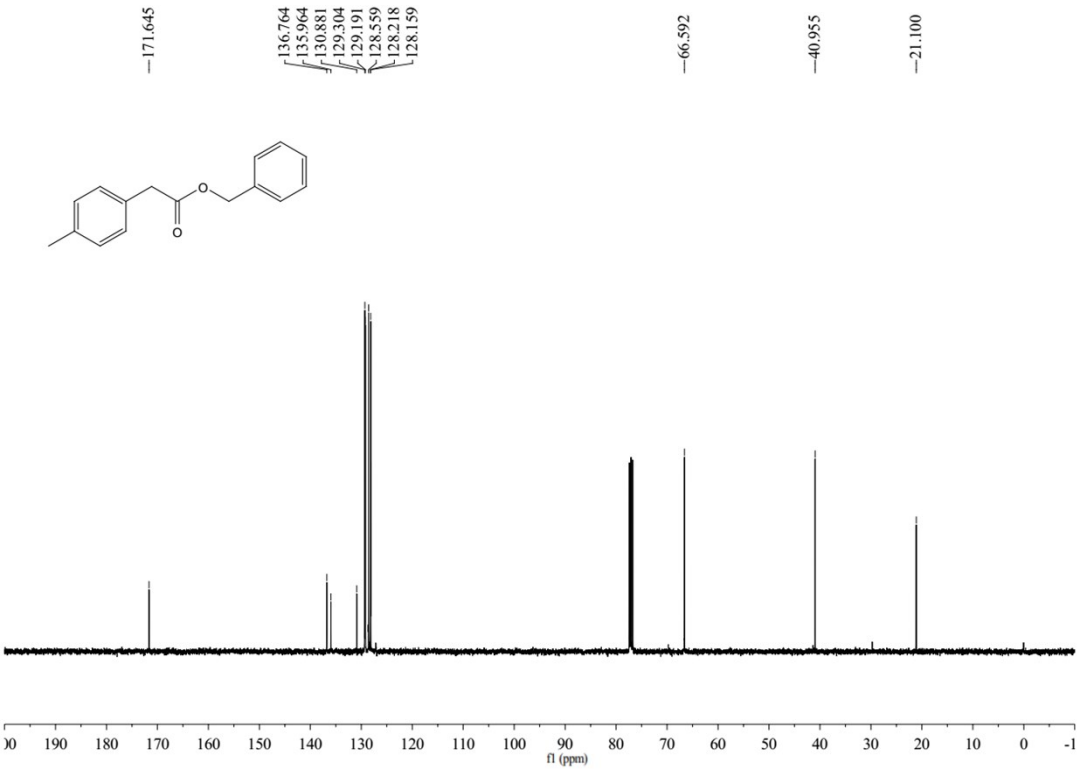
^{13}C NMR Spectra of 5aa



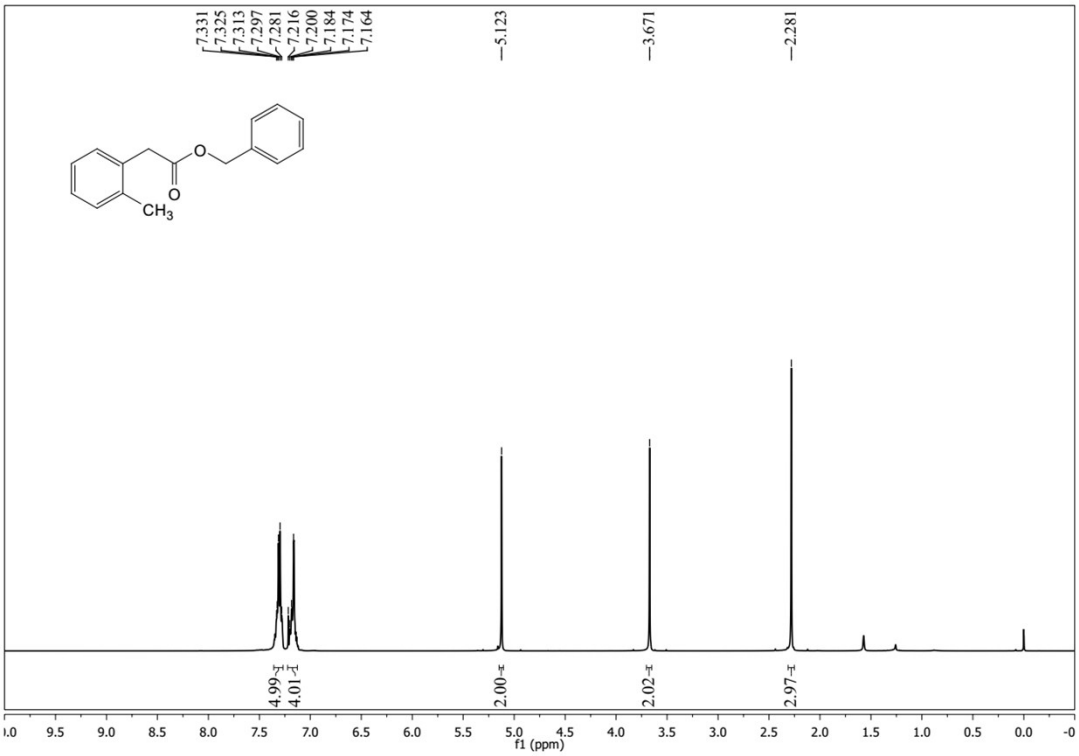
^{1}H NMR Spectra of 5ab



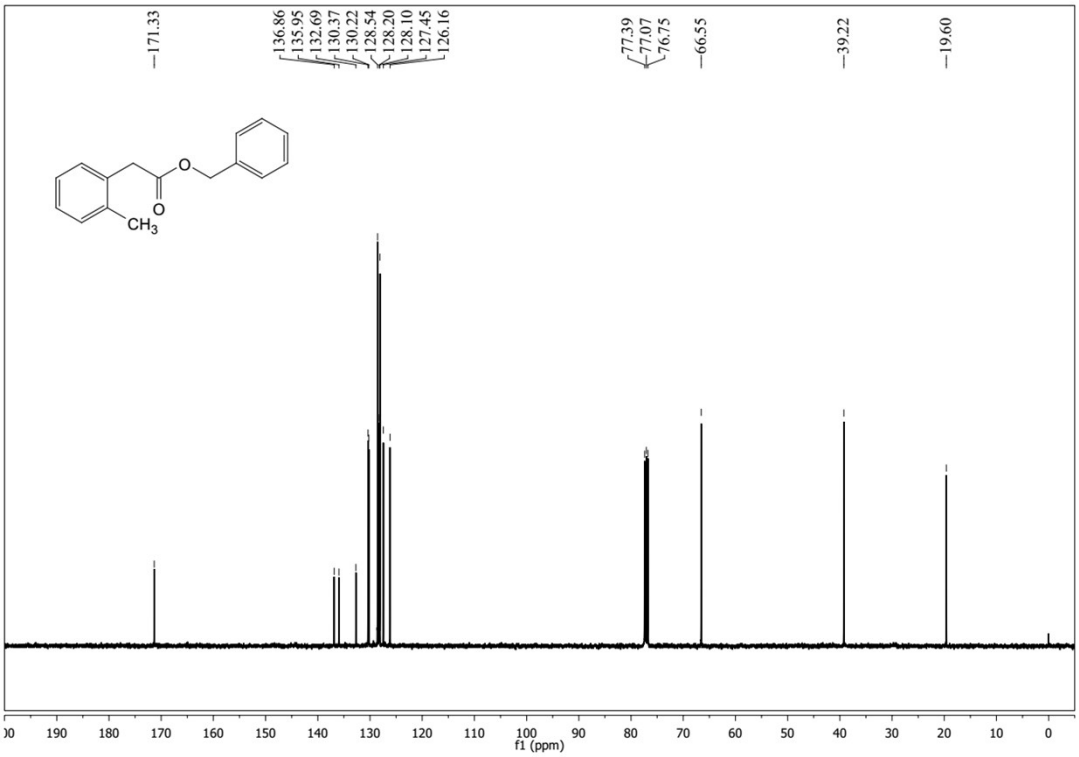
^{13}C NMR Spectra of 5ab



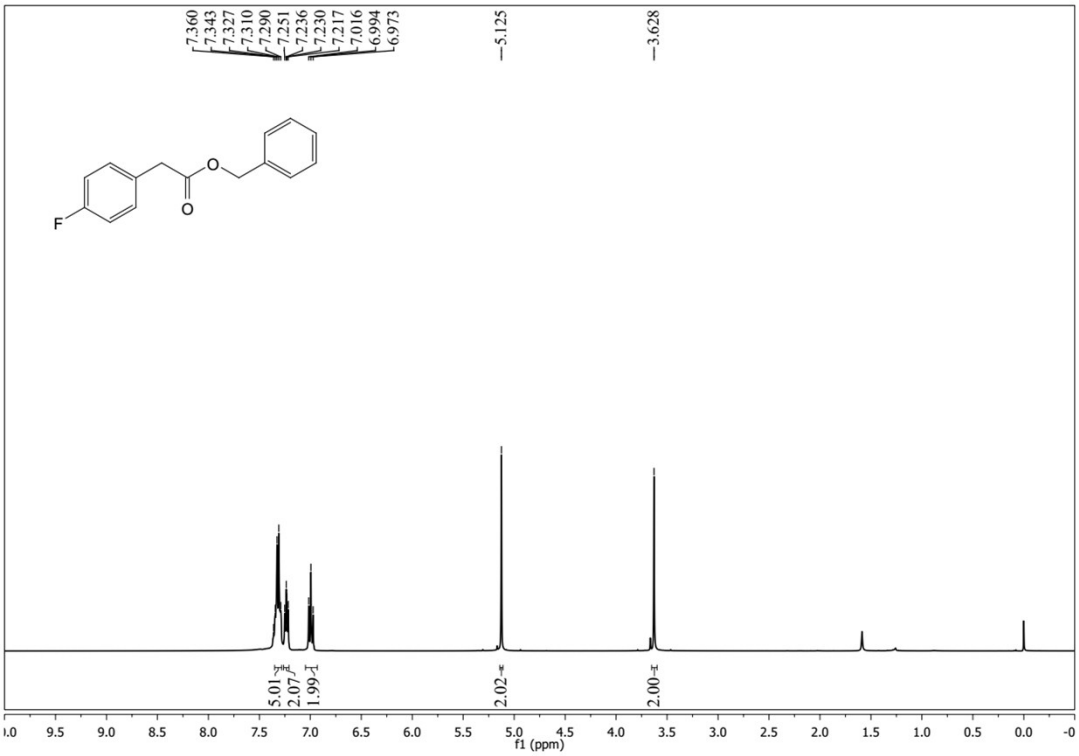
^{1}H NMR Spectra of 5ac



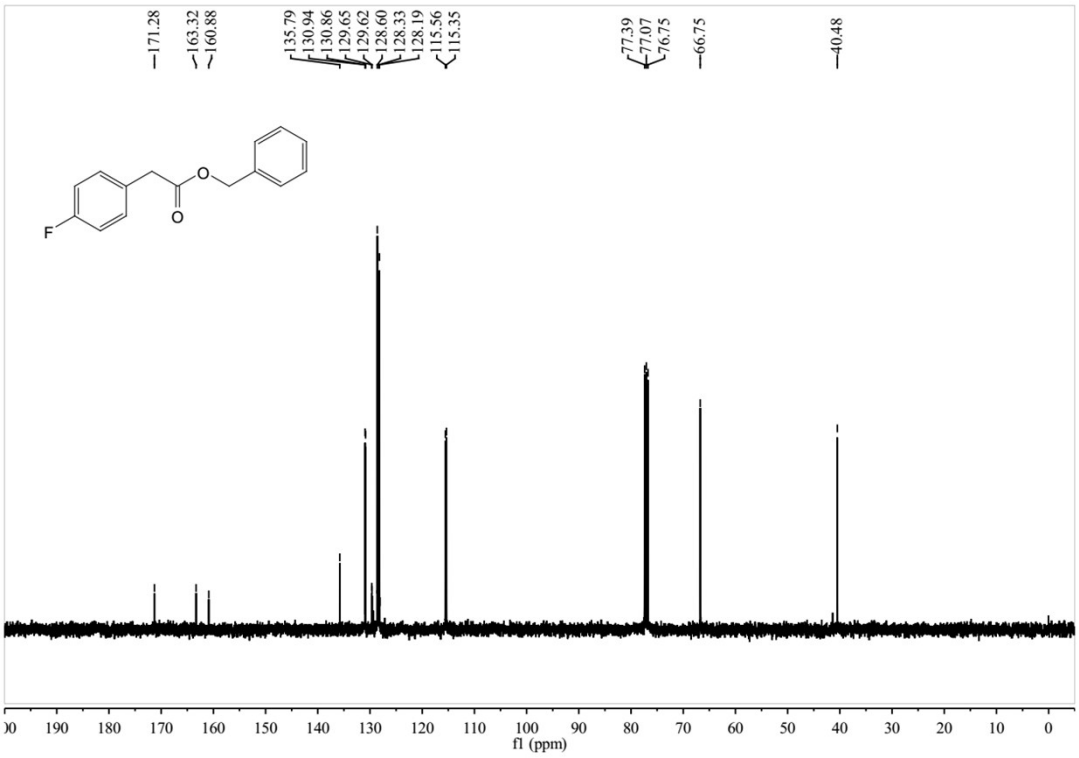
^{13}C NMR Spectra of 5ac



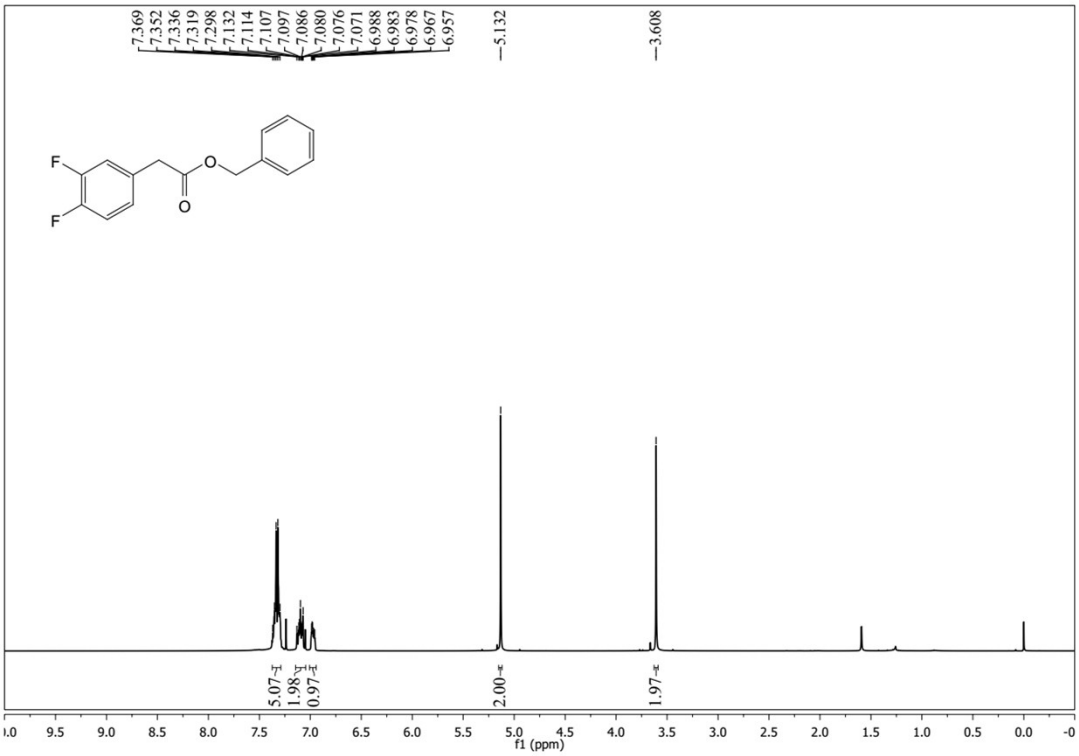
^{1}H NMR Spectra of 5ad



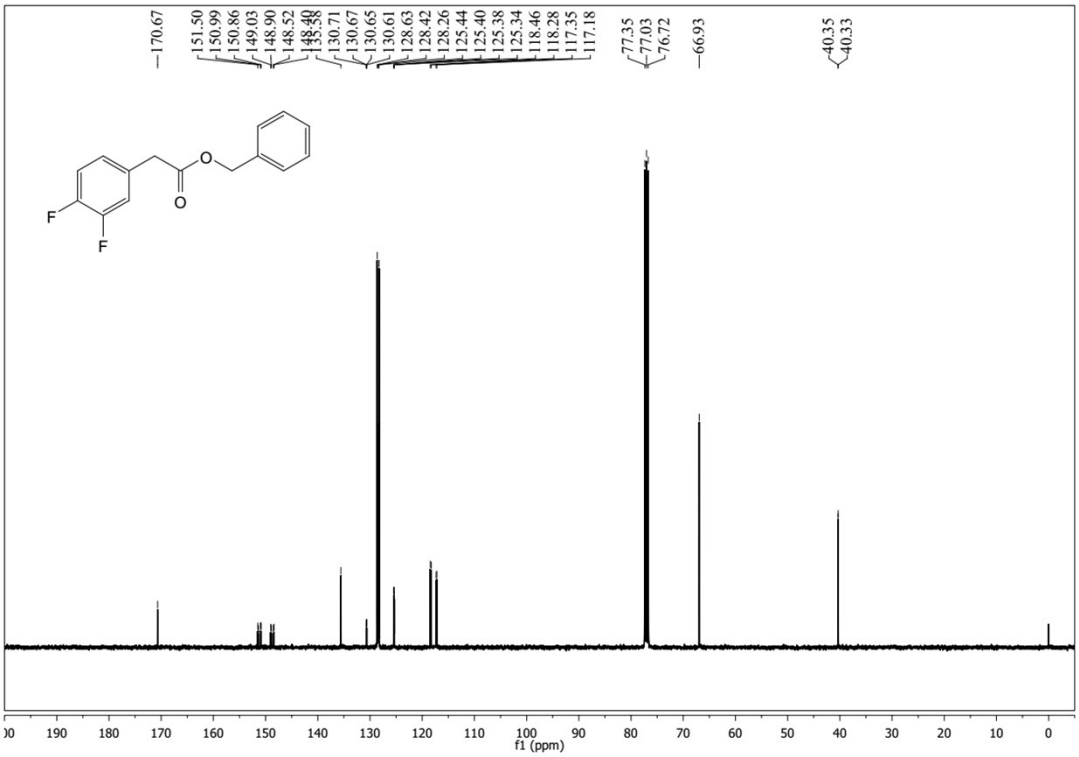
^{13}C NMR Spectra of 5ad



^{1}H NMR Spectra of 5ae



^{13}C NMR Spectra of 5ae



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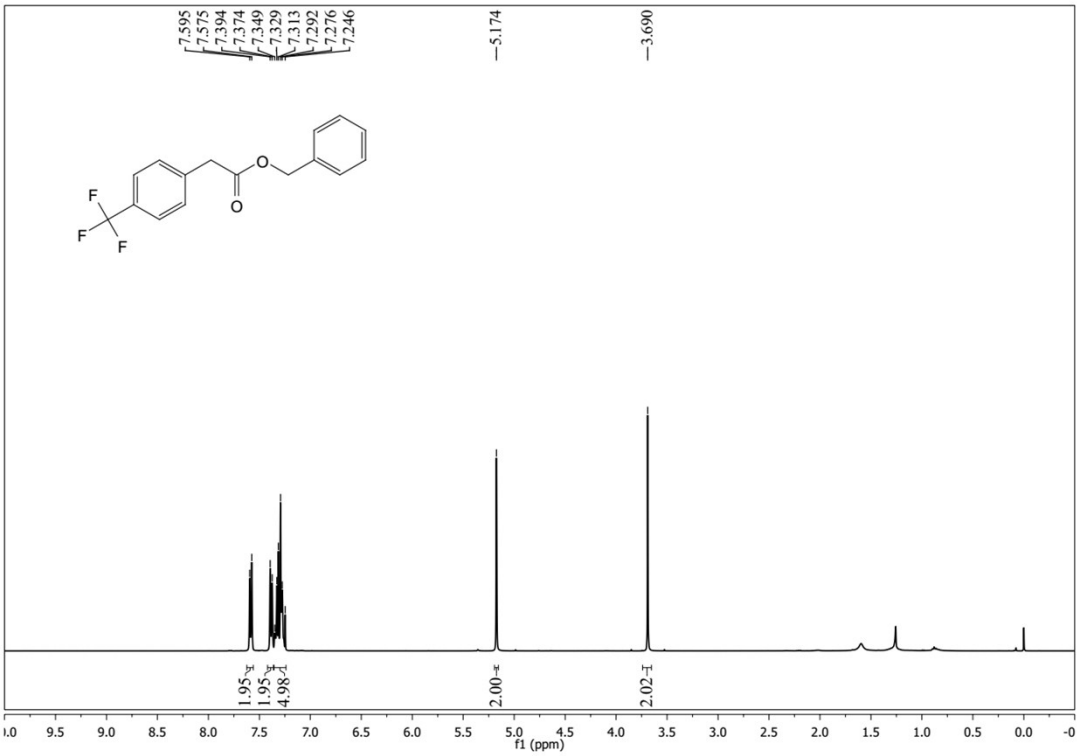
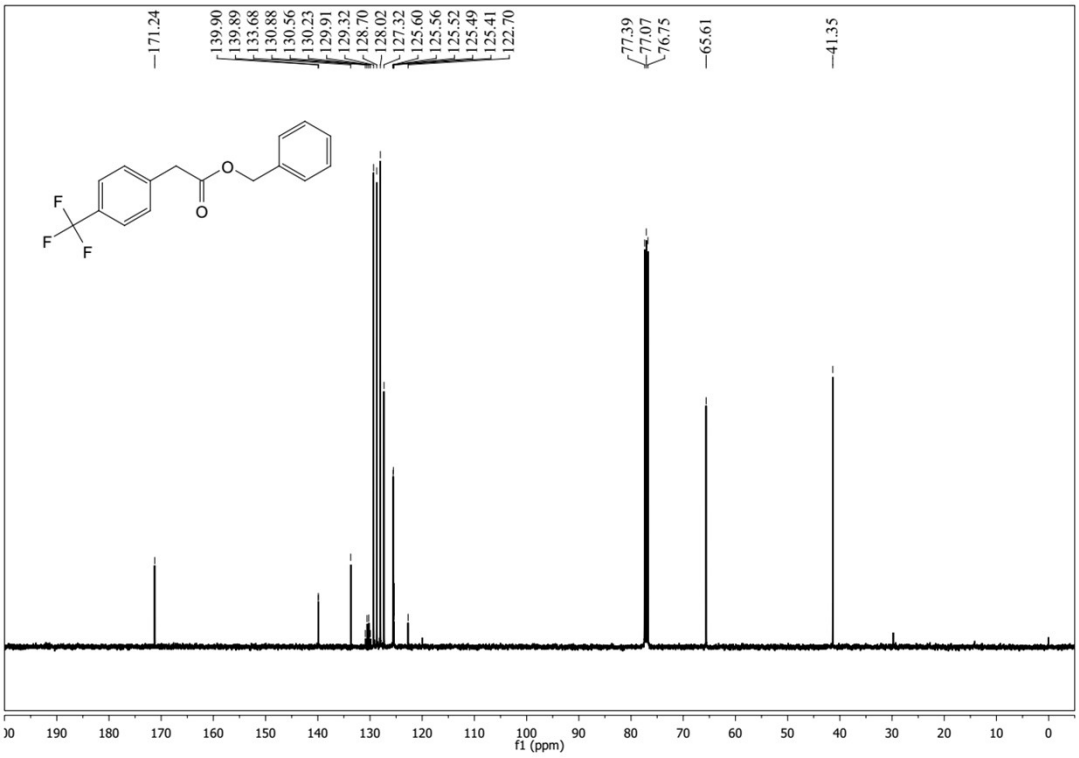
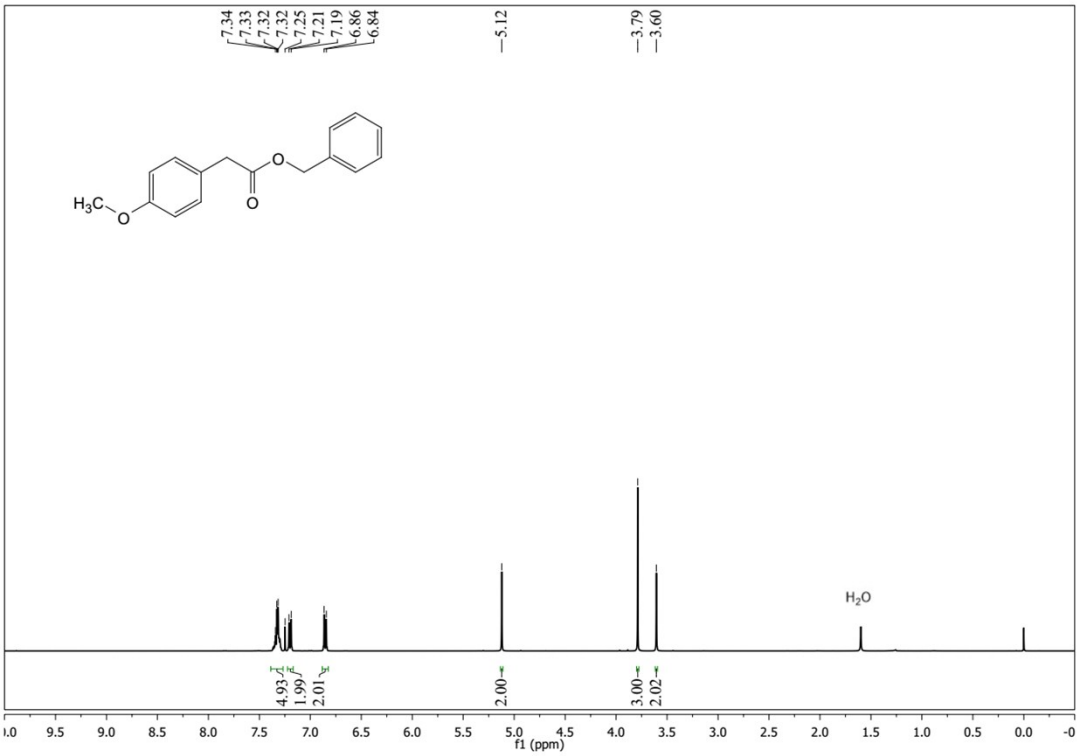


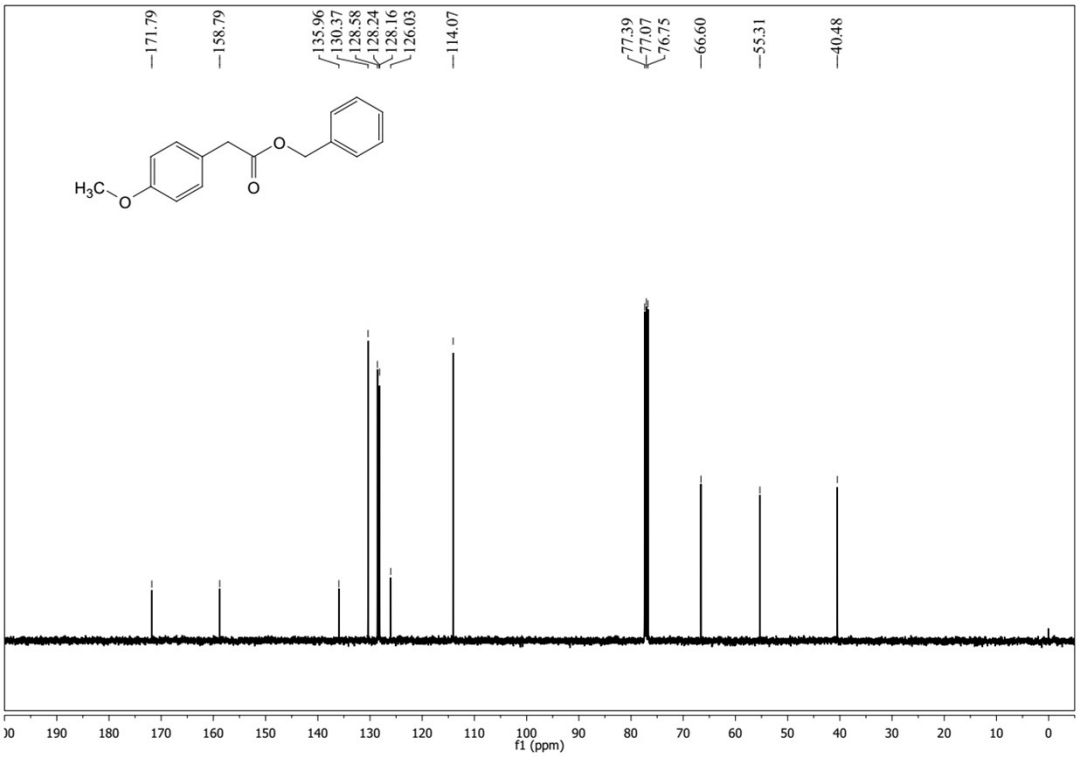
^{13}C NMR Spectra of 5af



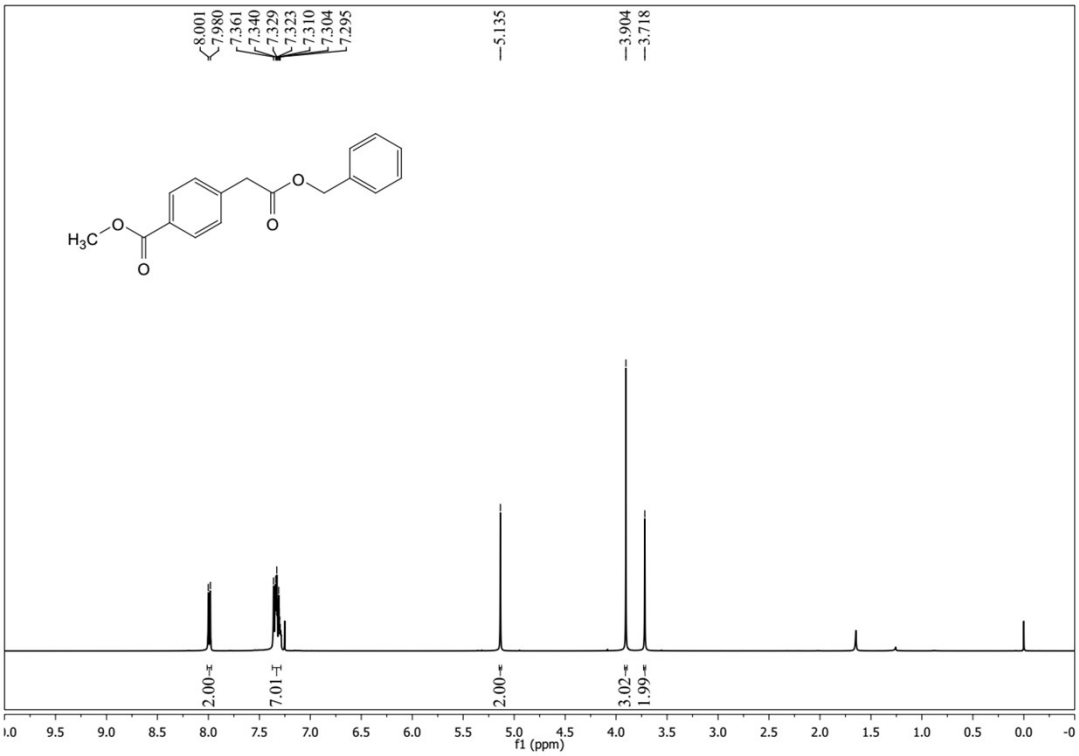
^{1}H NMR Spectra of 5ag



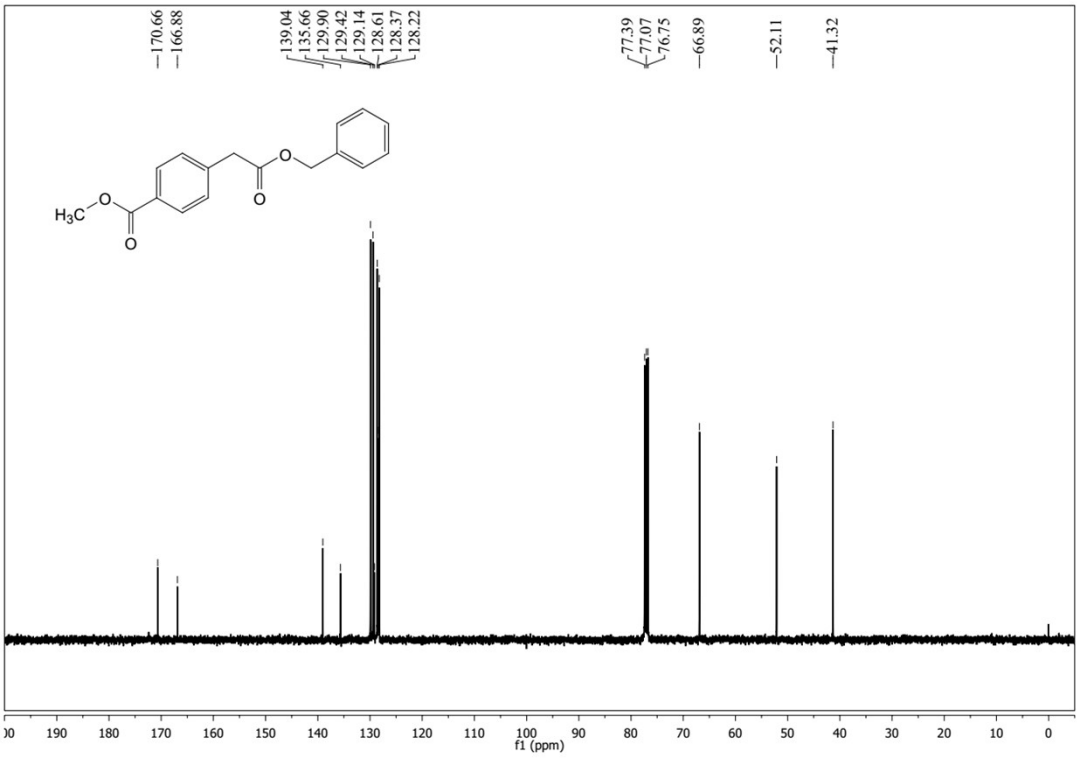
^{13}C NMR Spectra of 5ag



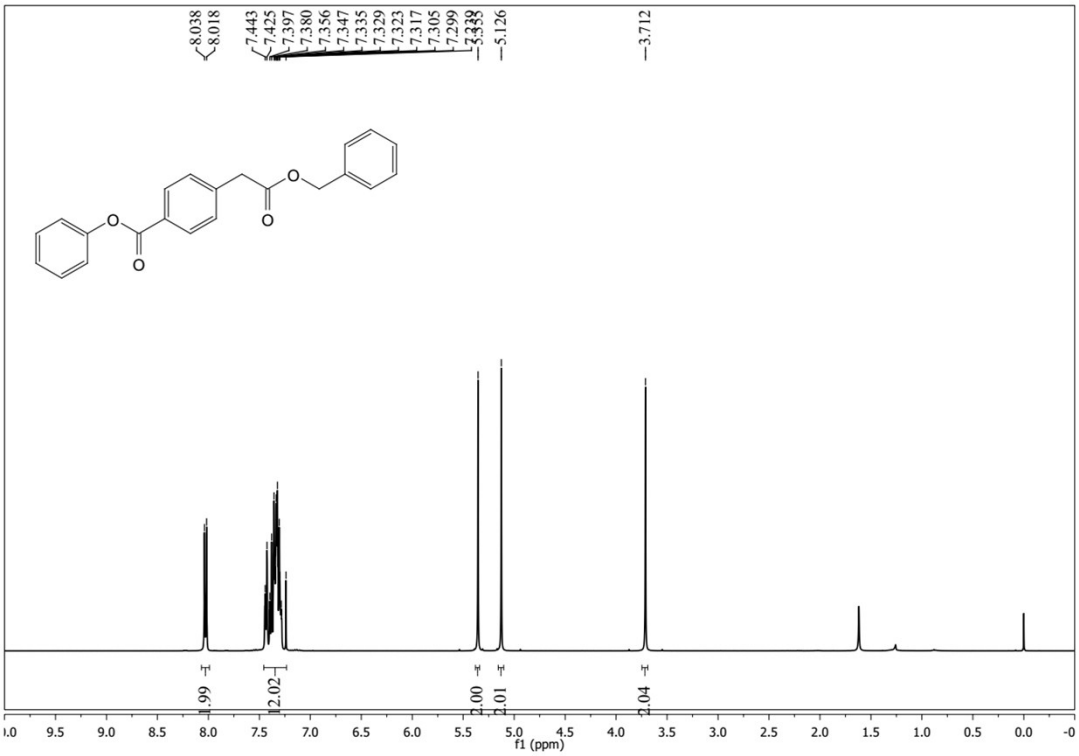
^{1}H NMR Spectra of 5ah



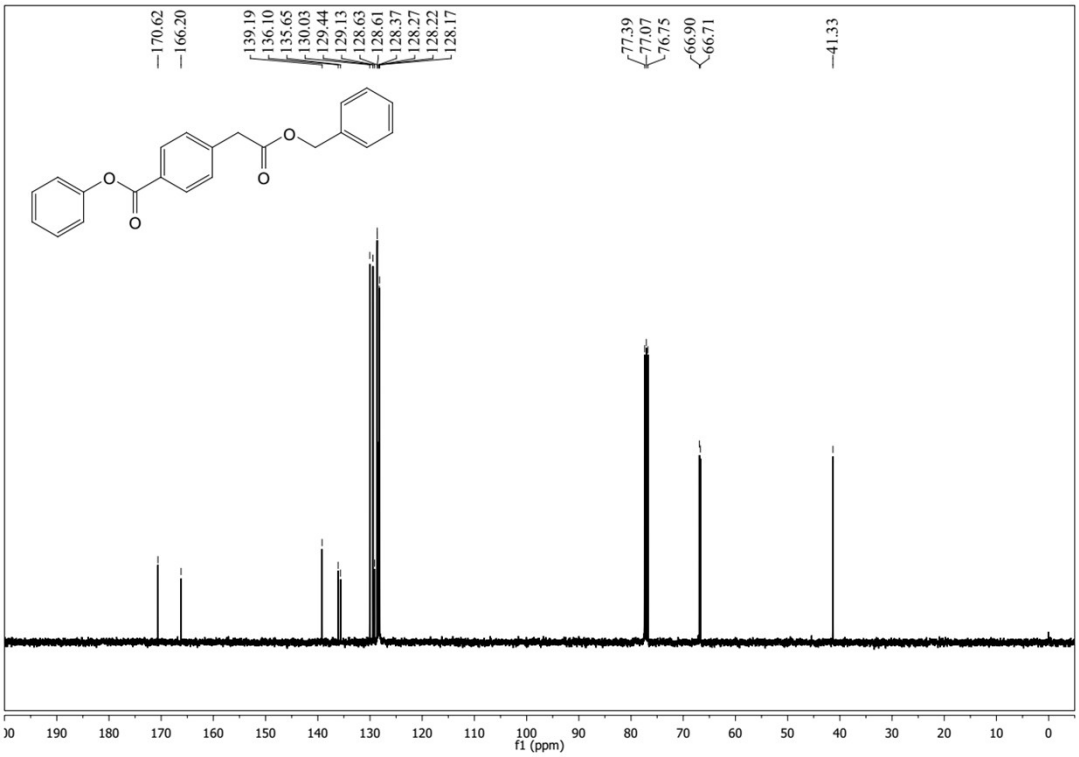
^{13}C NMR Spectra of 5ah



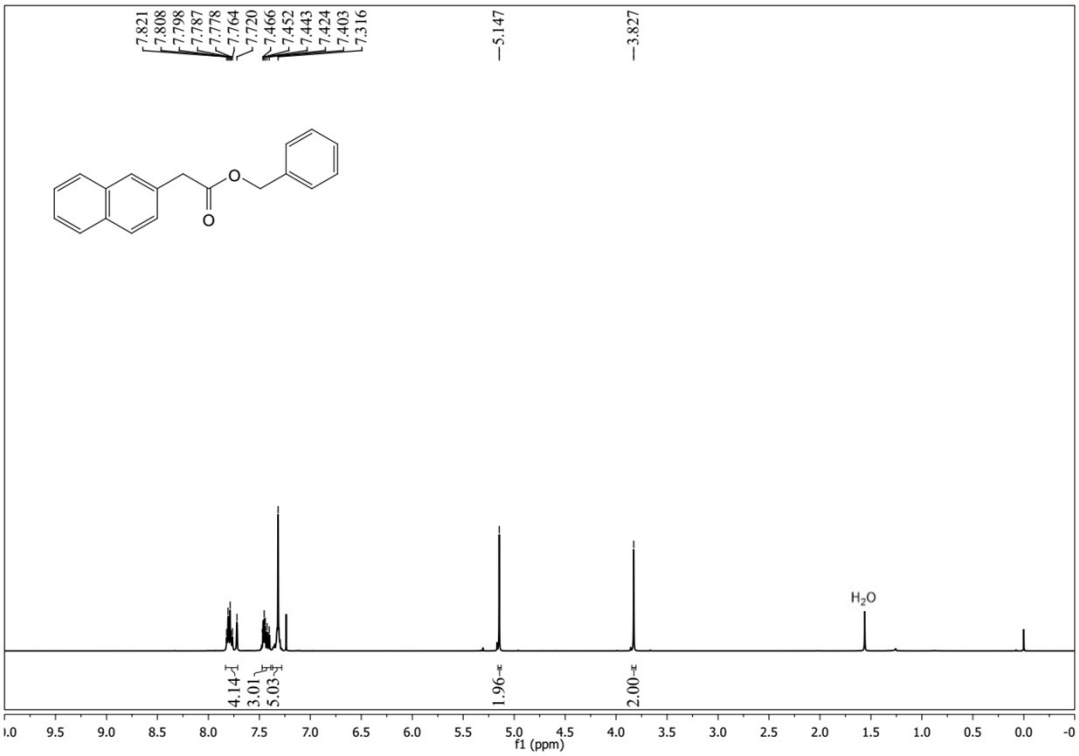
^{1}H NMR Spectra of 5ai



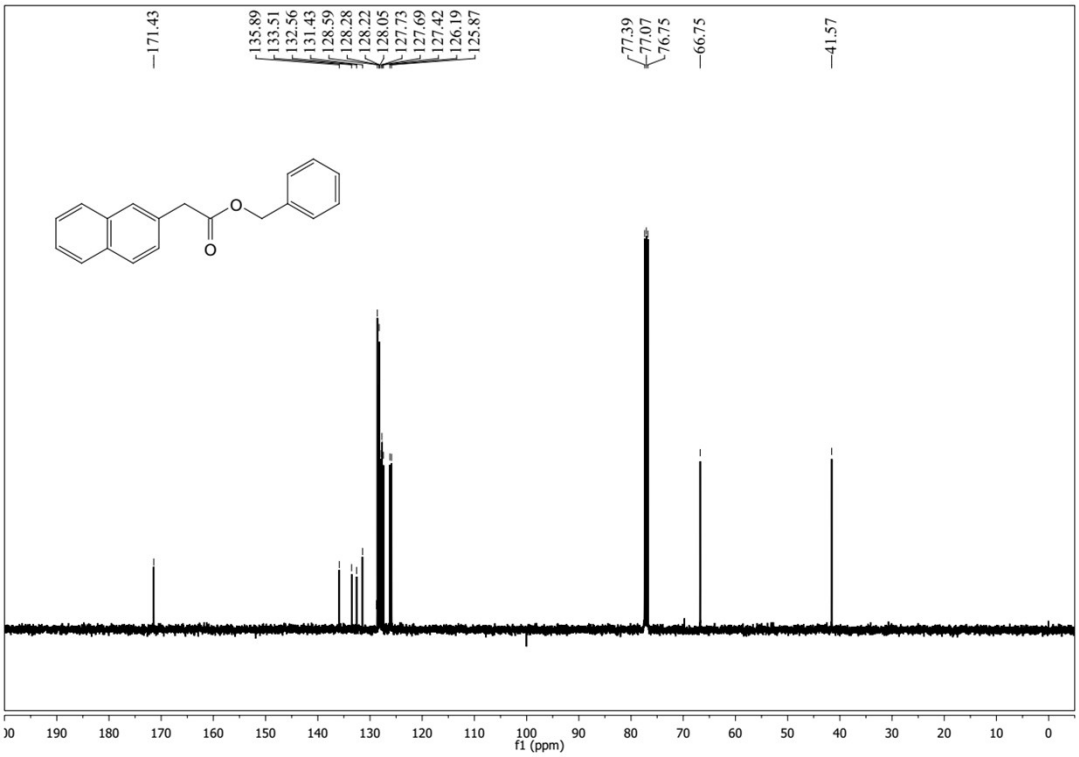
^{13}C NMR Spectra of 5ai



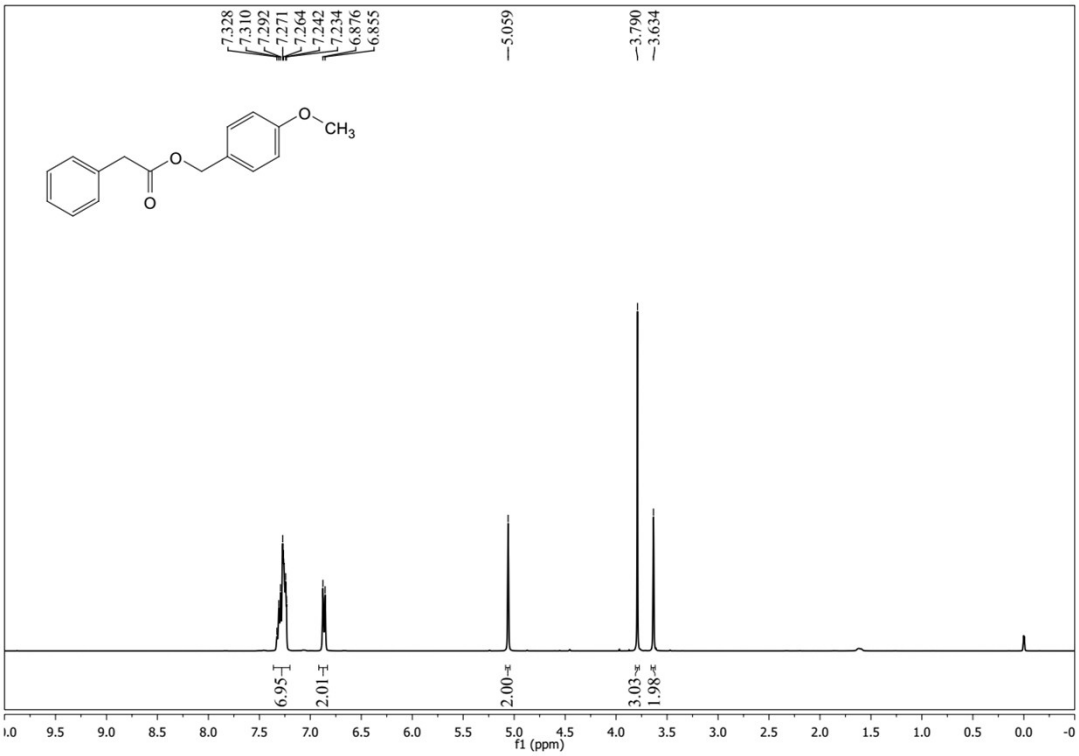
^{1}H NMR Spectra of 5aj



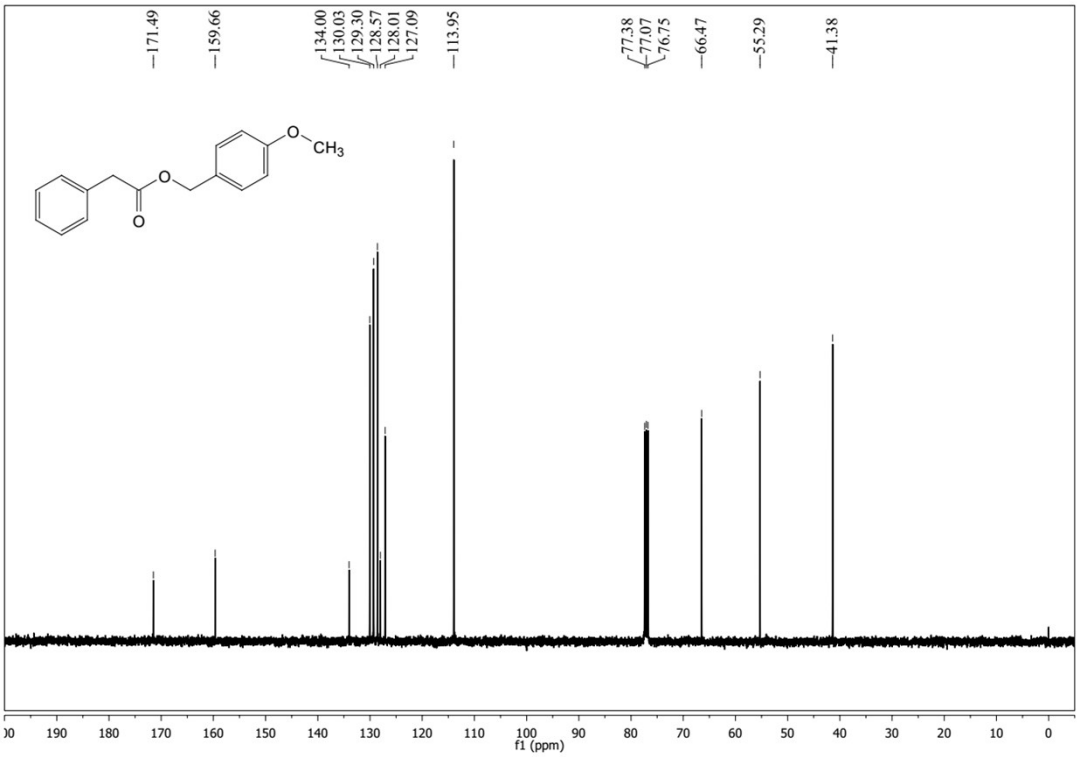
^{13}C NMR Spectra of 5aj



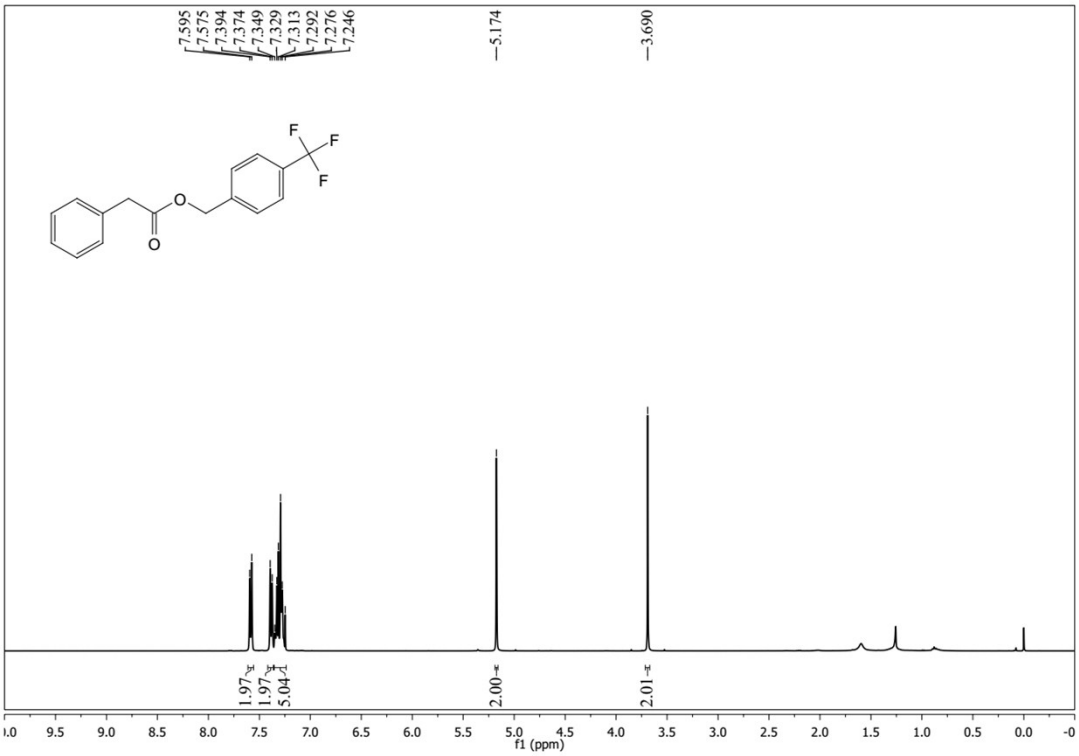
^{1}H NMR Spectra of 5ak



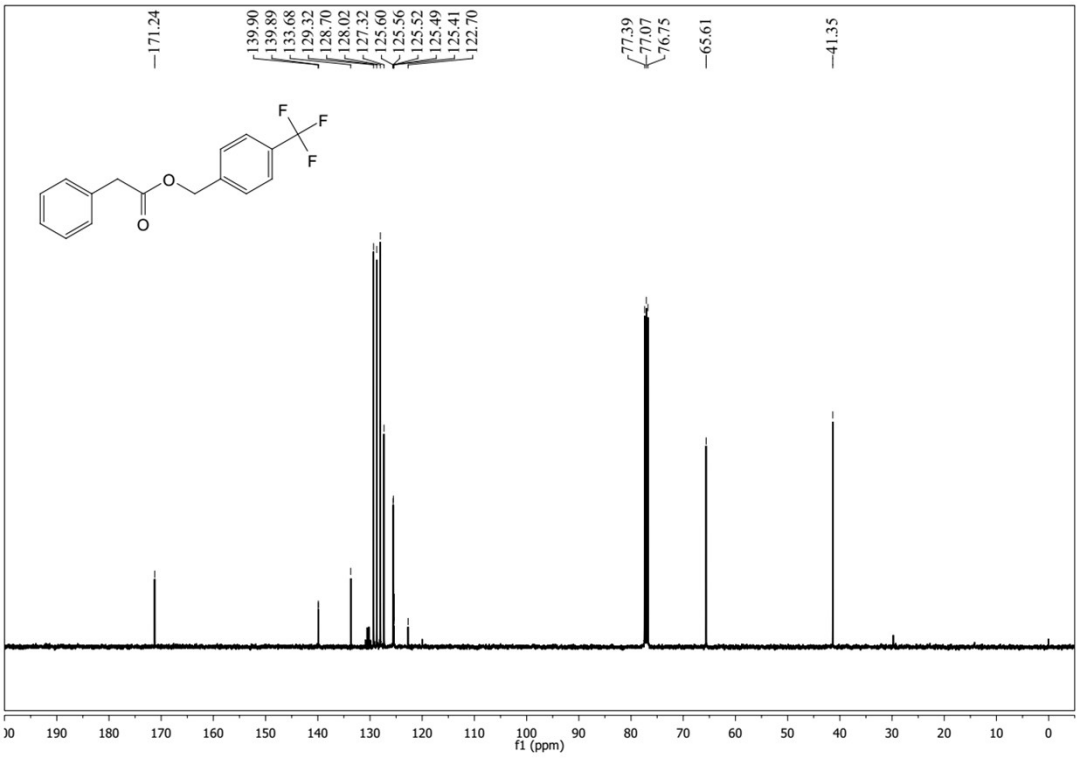
^{13}C NMR Spectra of 5ak



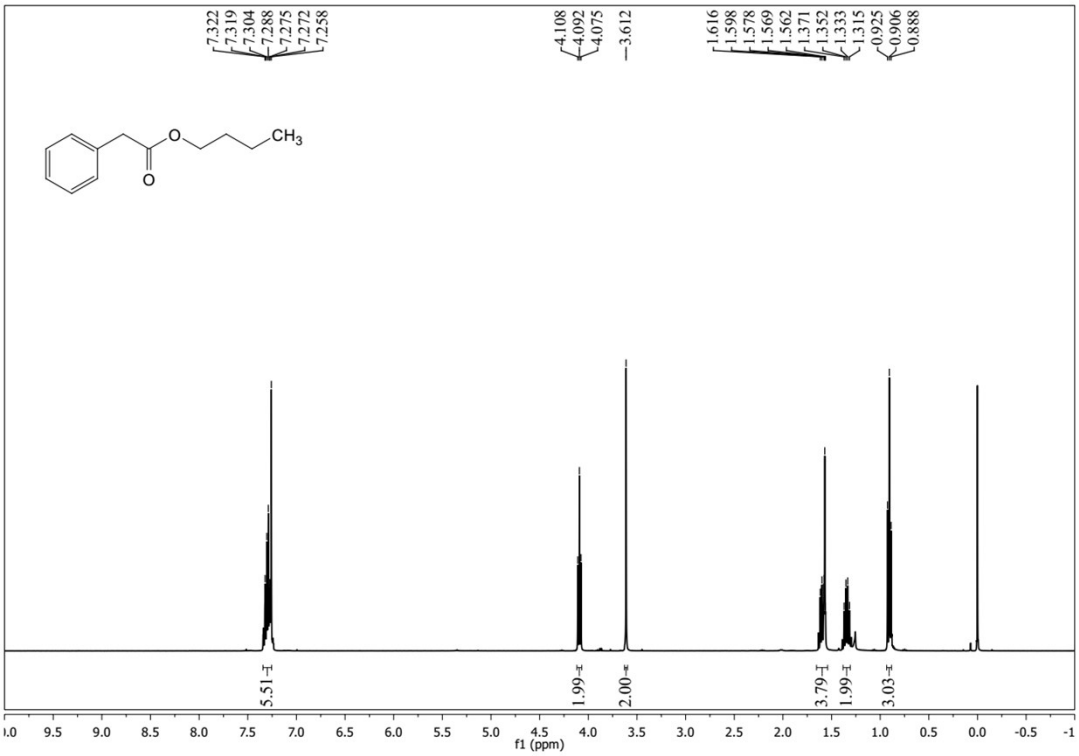
^{1}H NMR Spectra of 5al



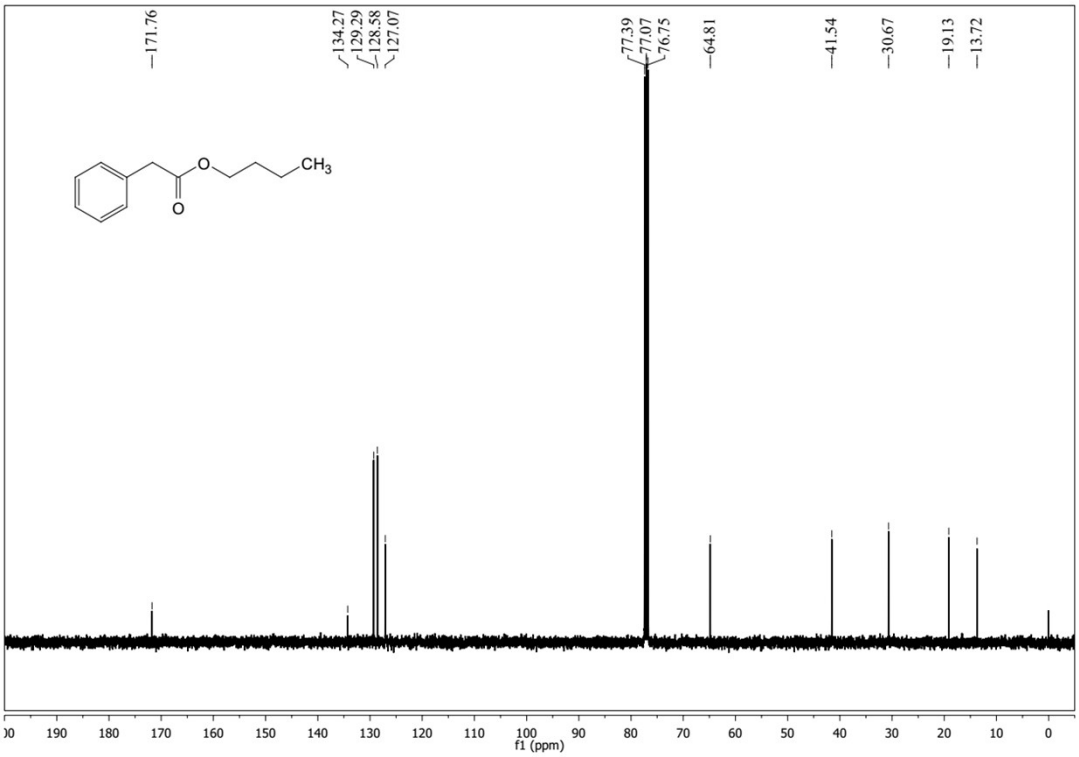
^{13}C NMR Spectra of 5al



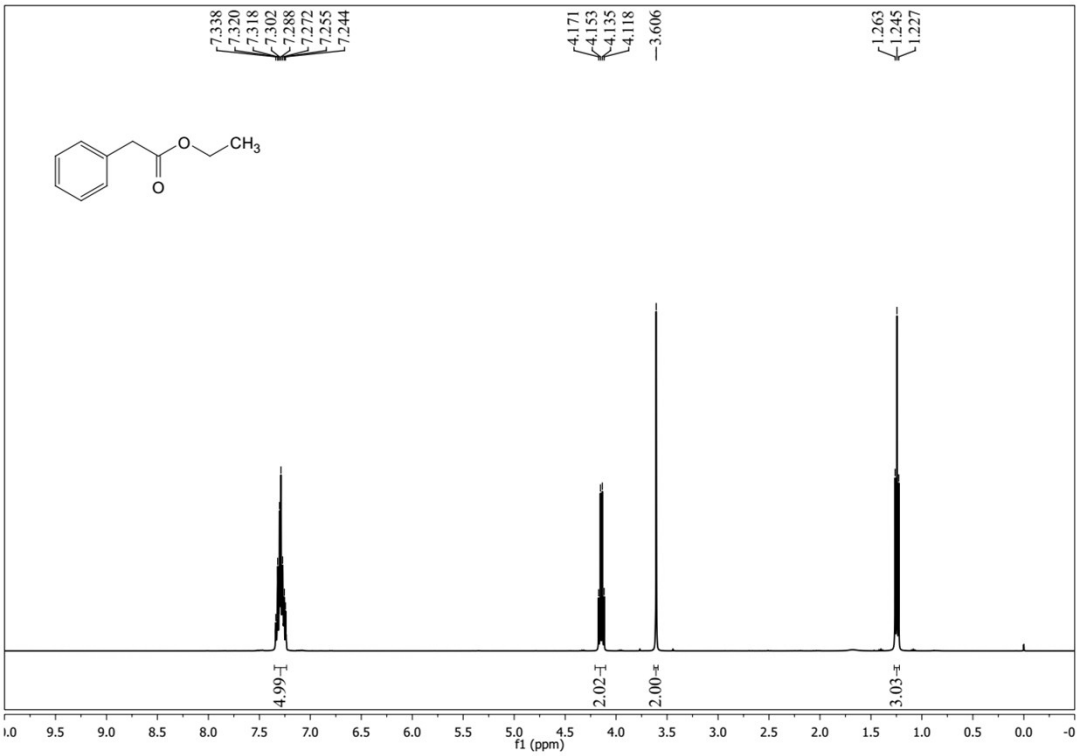
^{1}H NMR Spectra of 5am



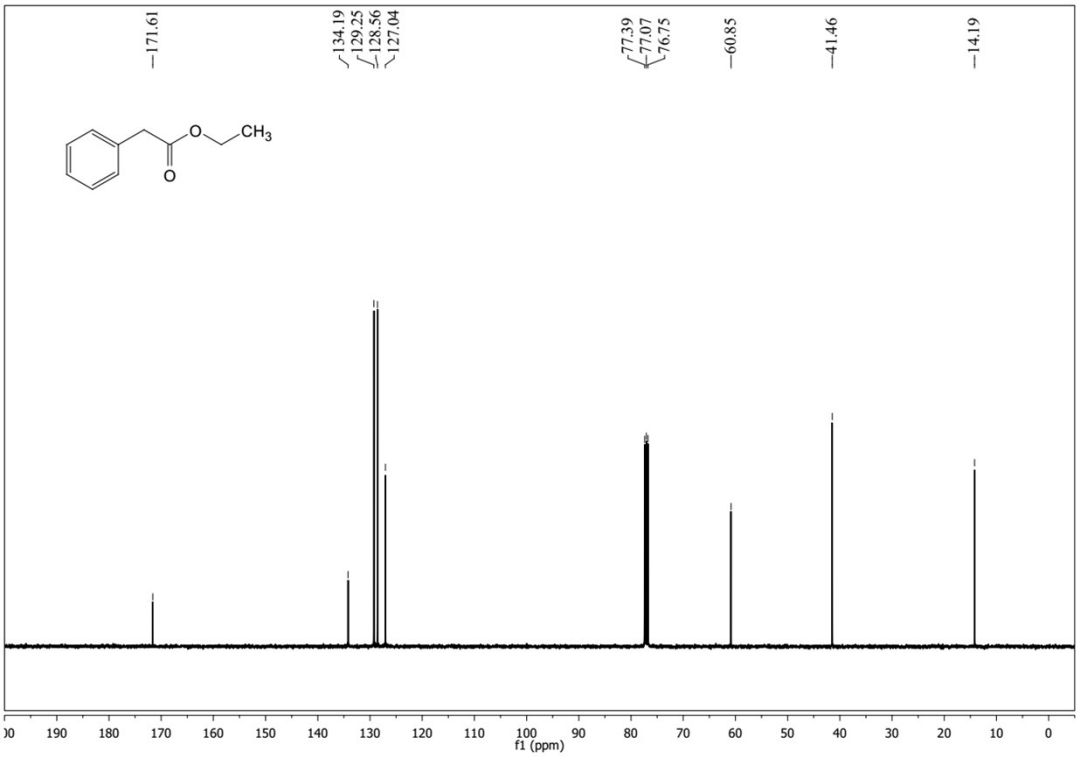
^{13}C NMR Spectra of 5am



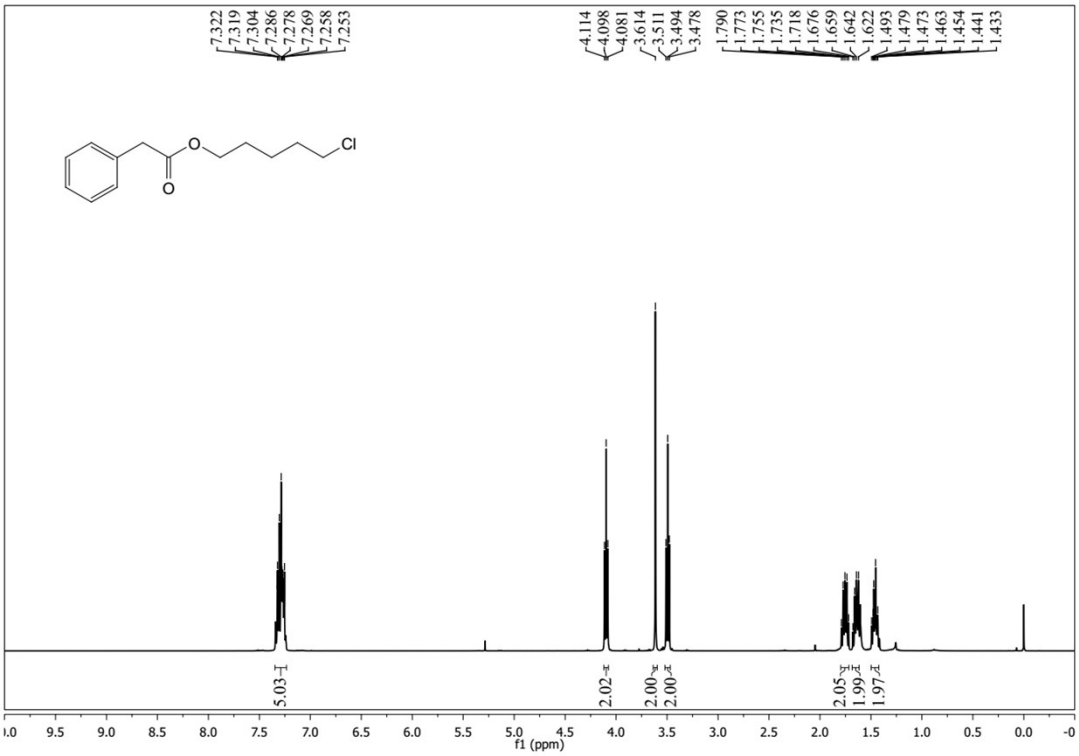
^{1}H NMR Spectra of 5an



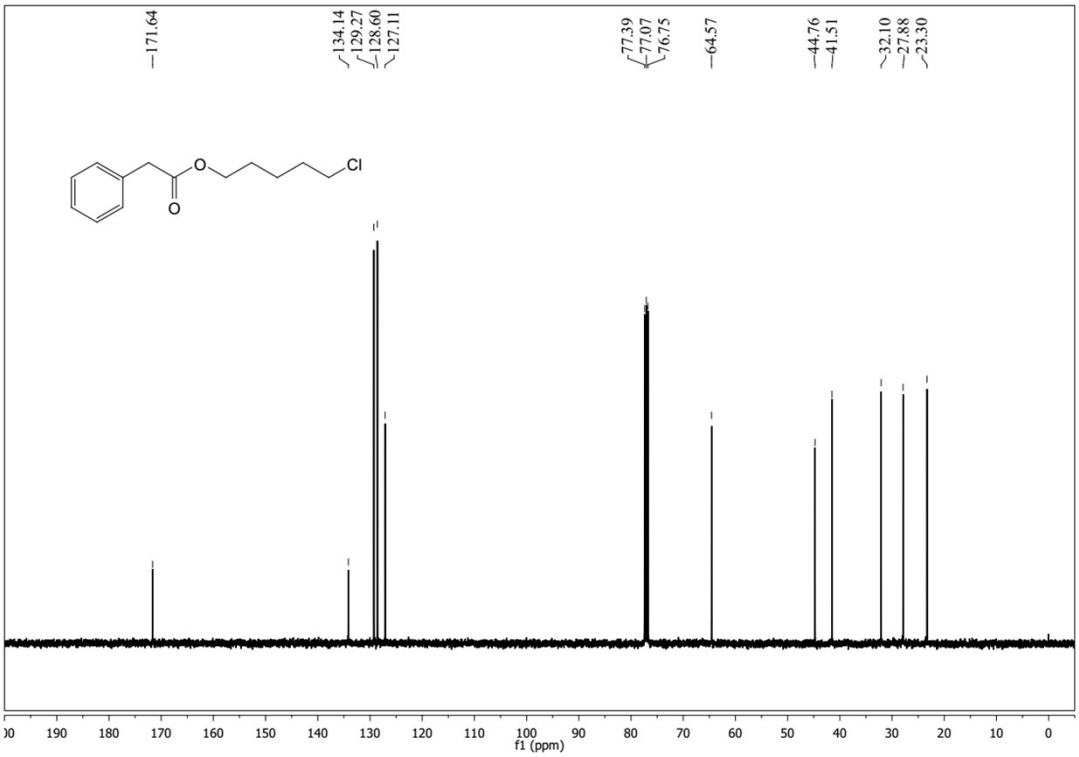
^{13}C NMR Spectra of 5an



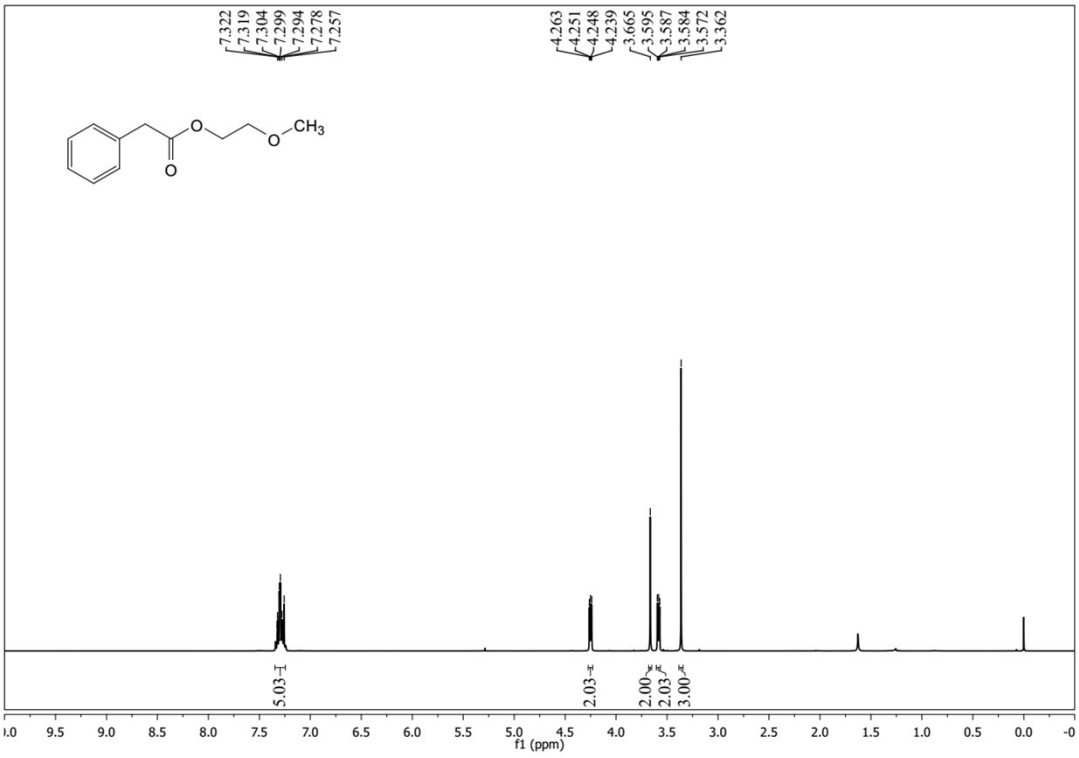
^{1}H NMR Spectra of 5ao



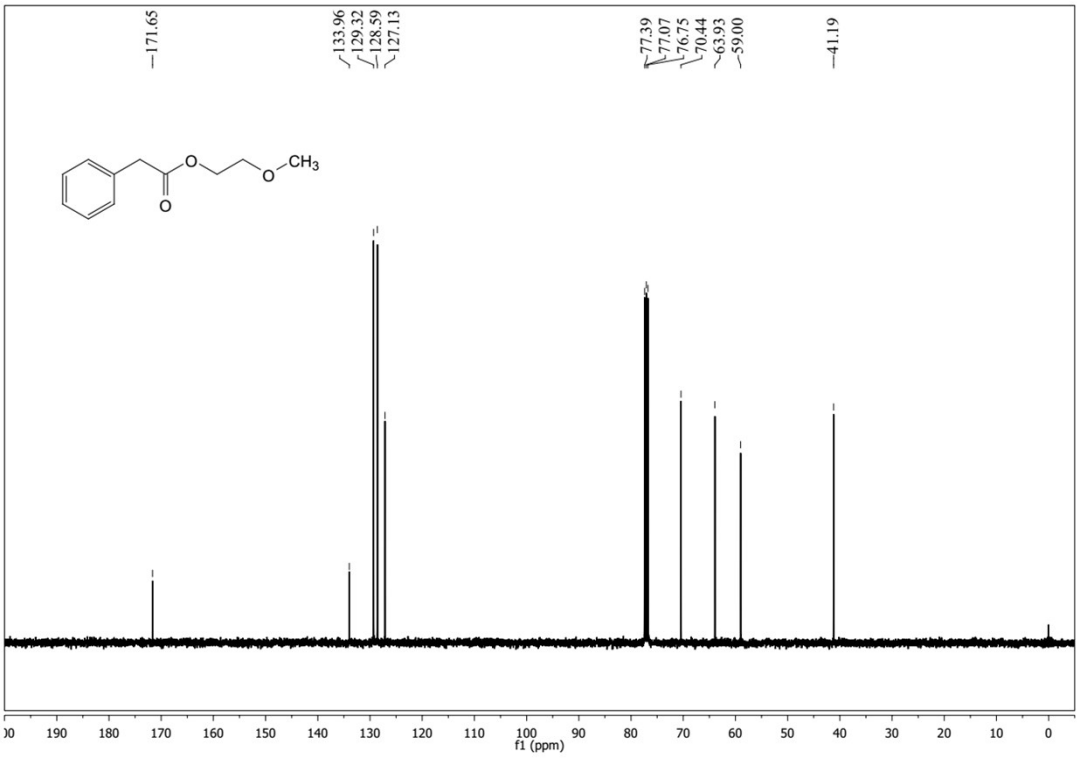
^{13}C NMR Spectra of 5ao



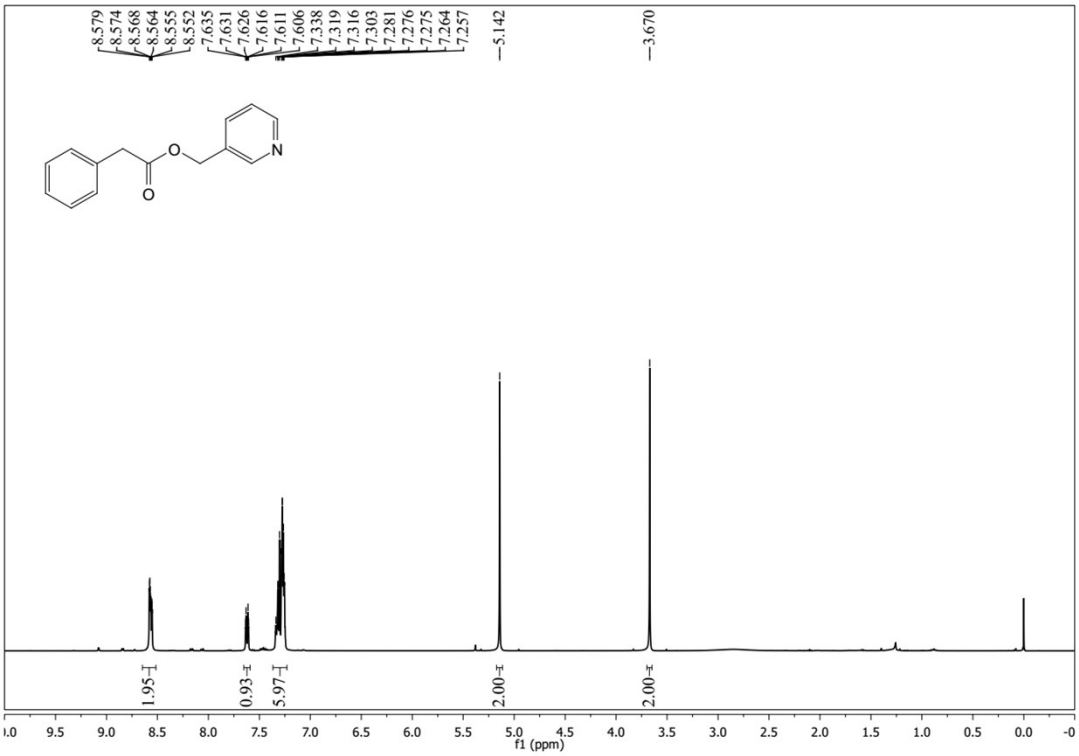
^{1}H NMR Spectra of 5ap



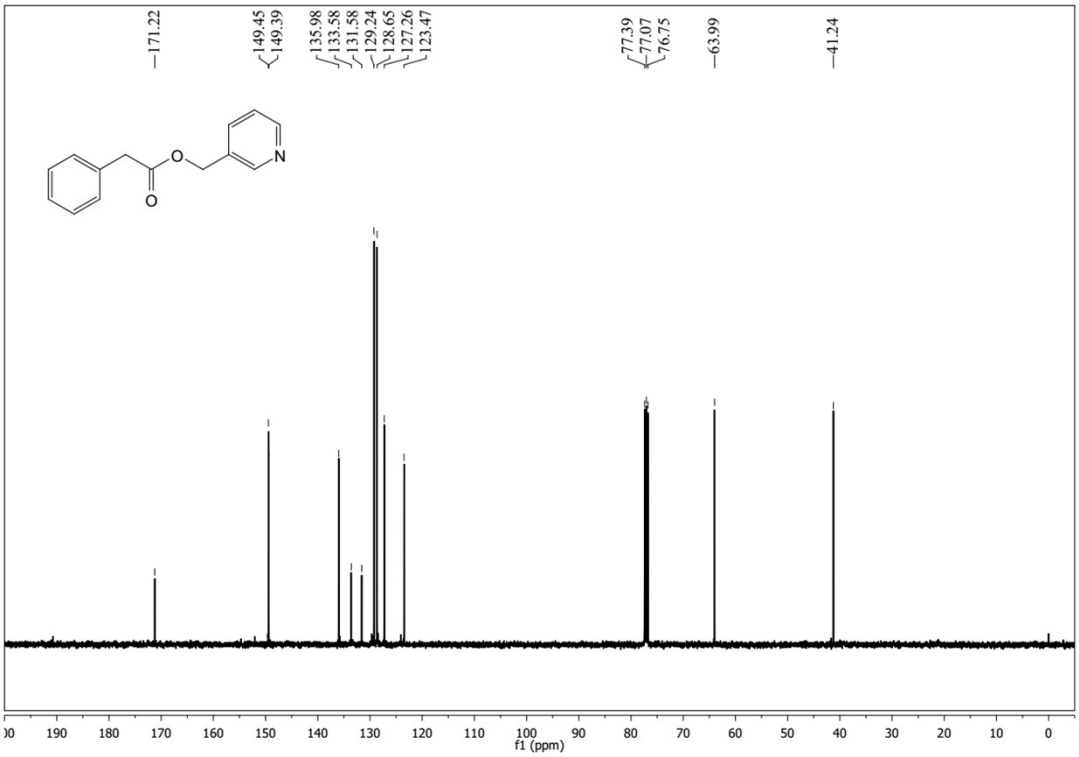
^{13}C NMR Spectra of 5ap



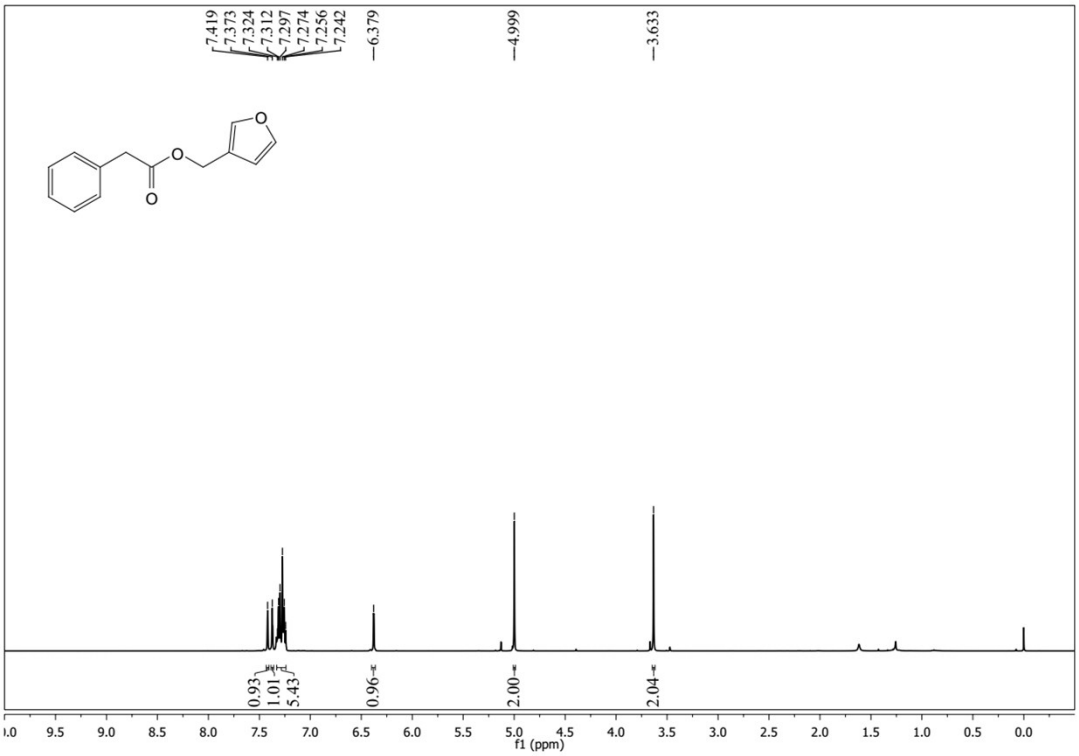
^{1}H NMR Spectra of 5aq



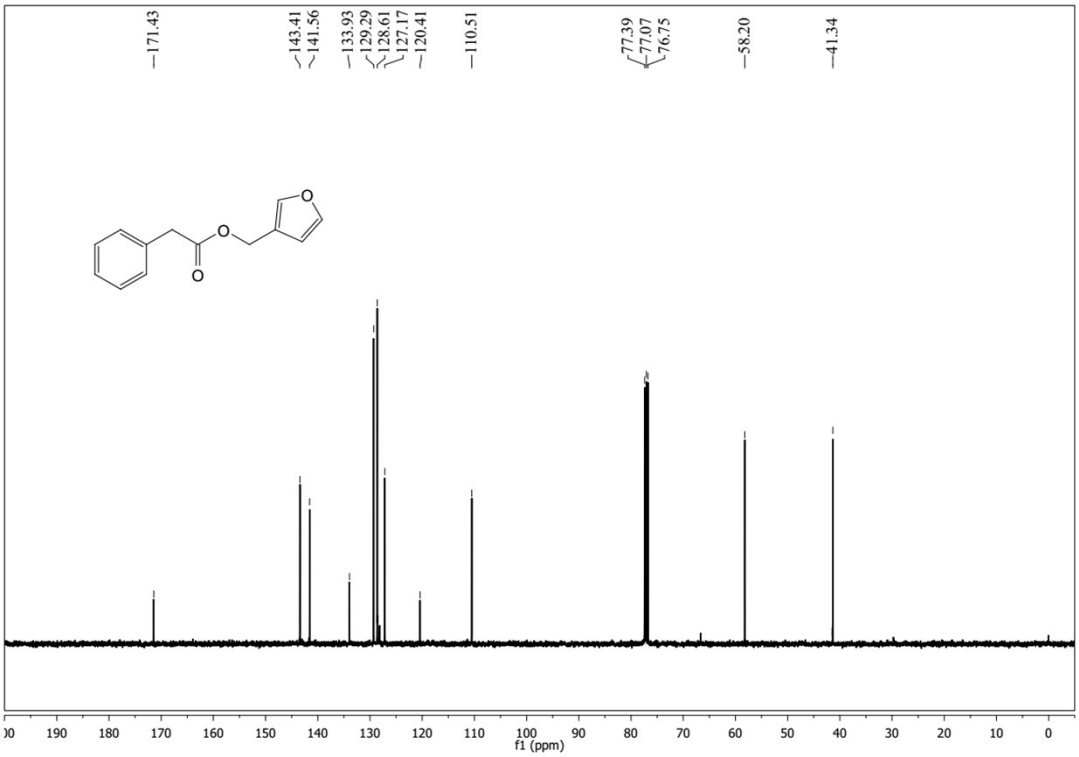
^{13}C NMR Spectra of 5aq



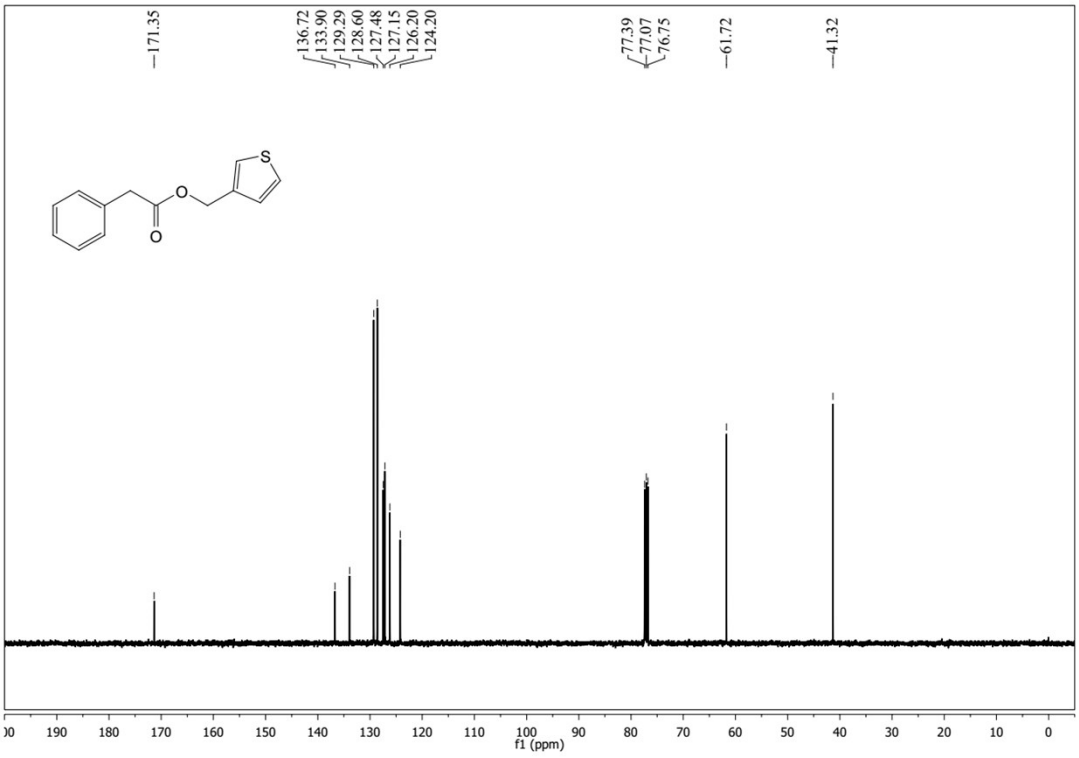
^{1}H NMR Spectra of 5ar



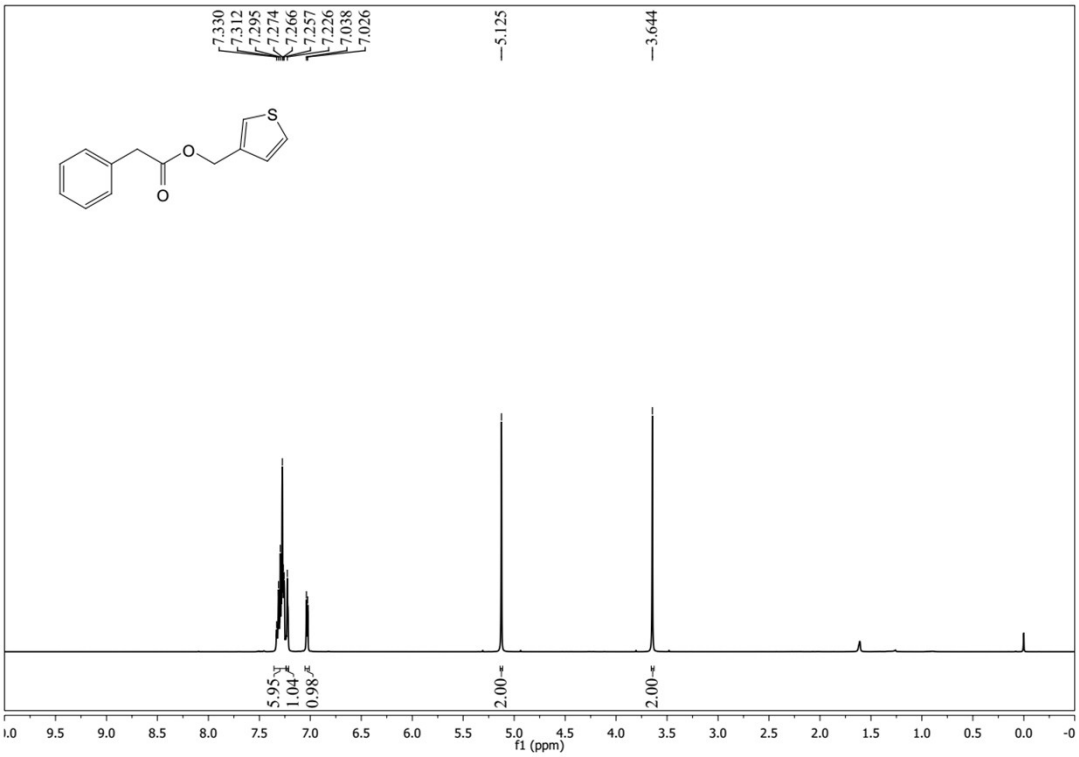
^{13}C NMR Spectra of 5ar



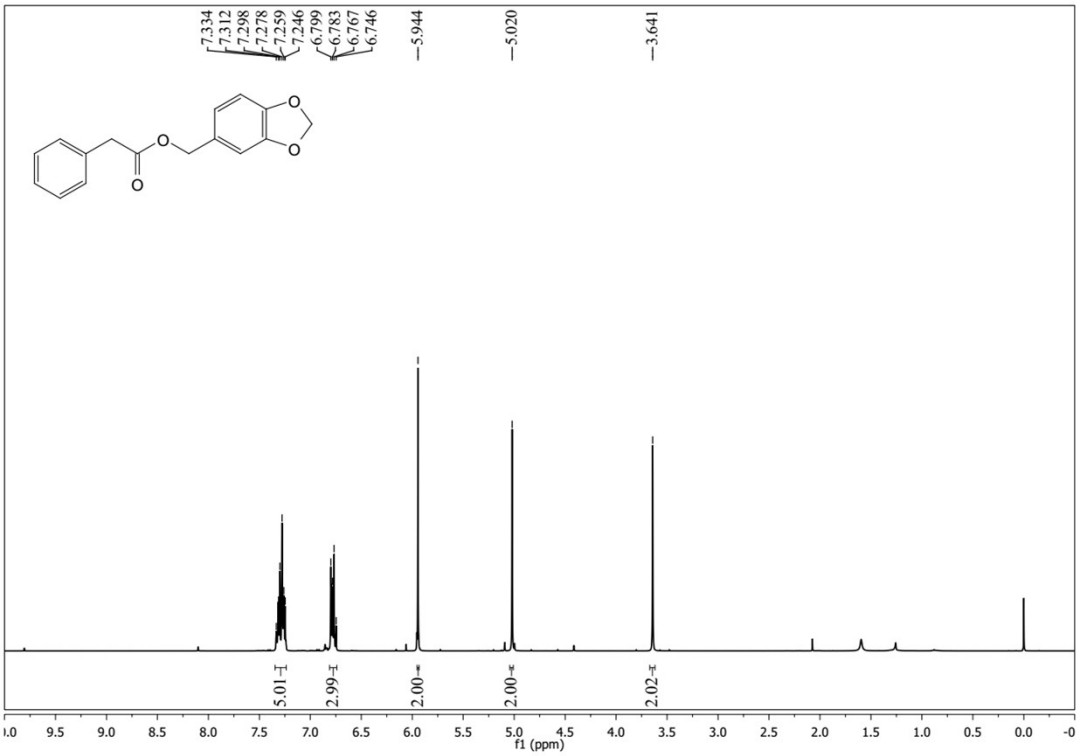
^{1}H NMR Spectra of 5as



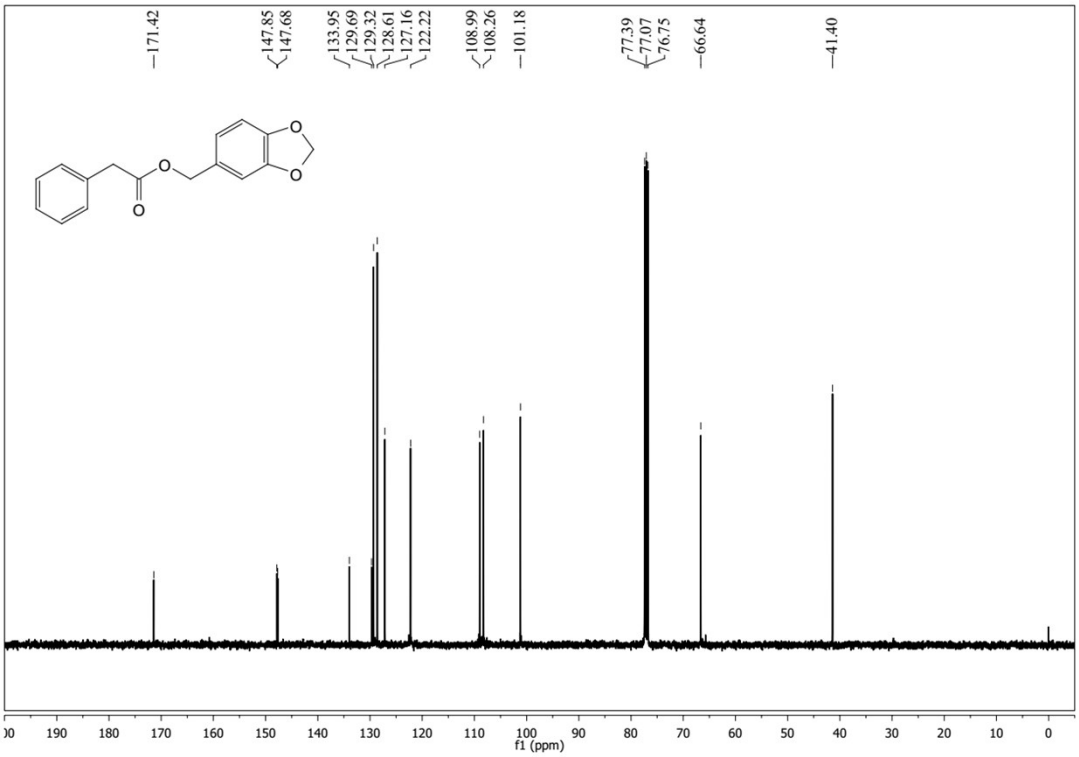
^{13}C NMR Spectra of 5as



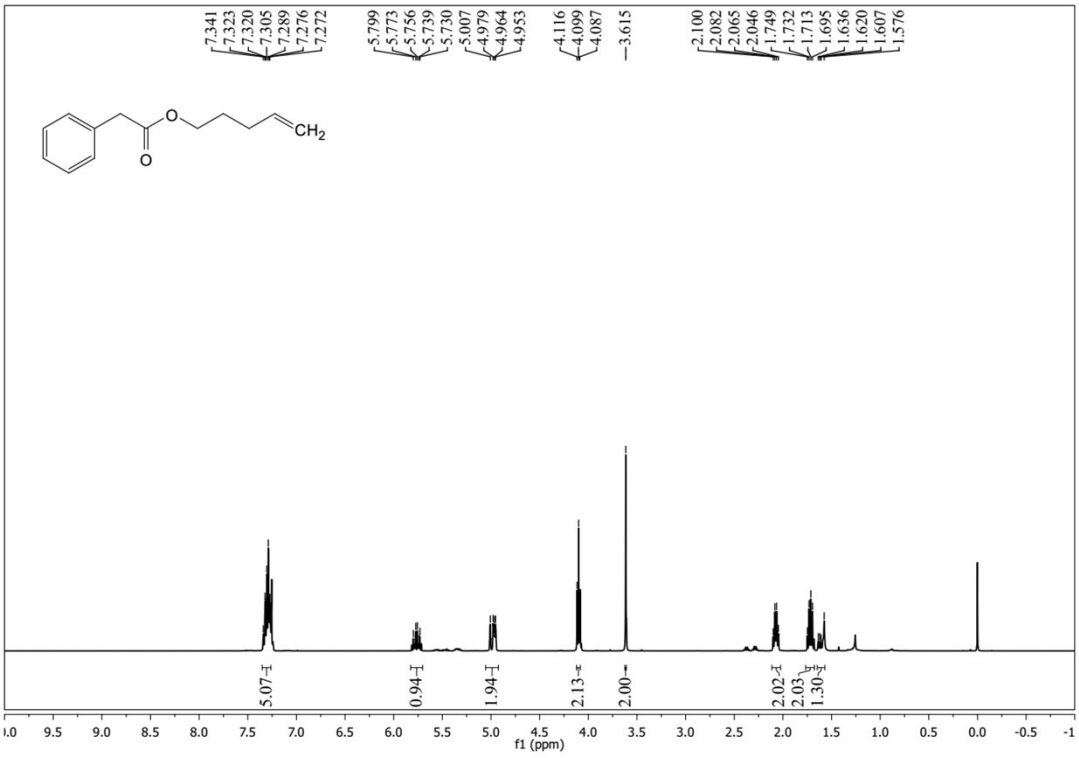
^{1}H NMR Spectra of 5at



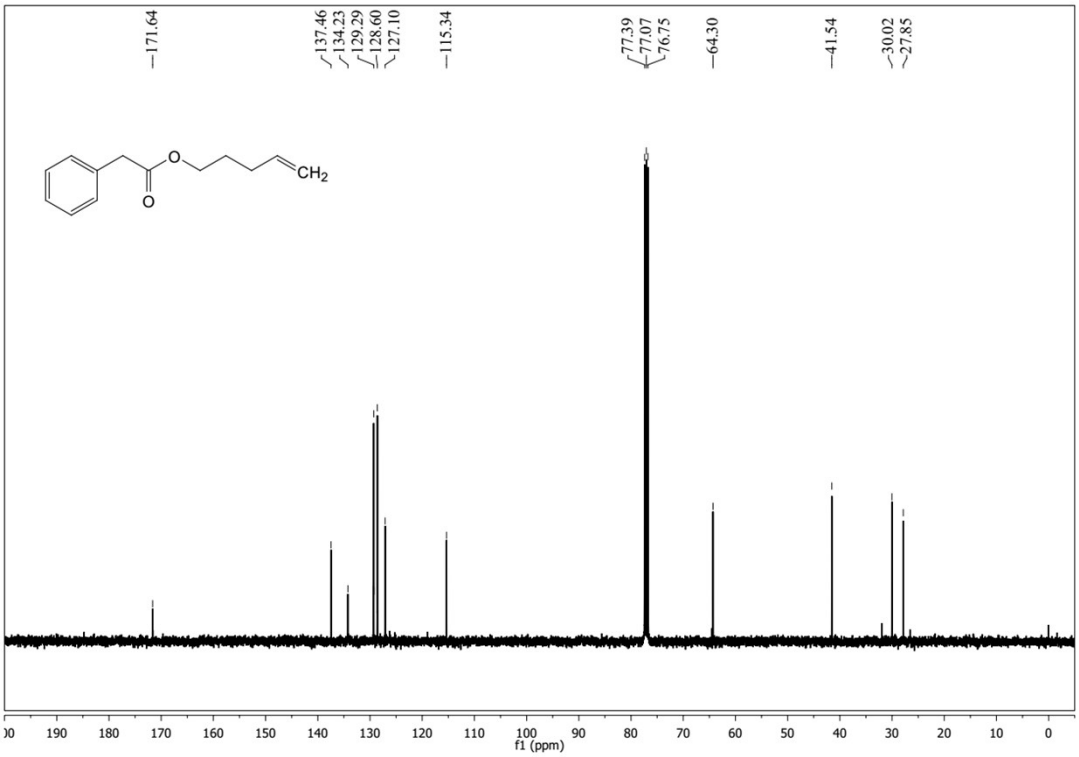
^{13}C NMR Spectra of 5at



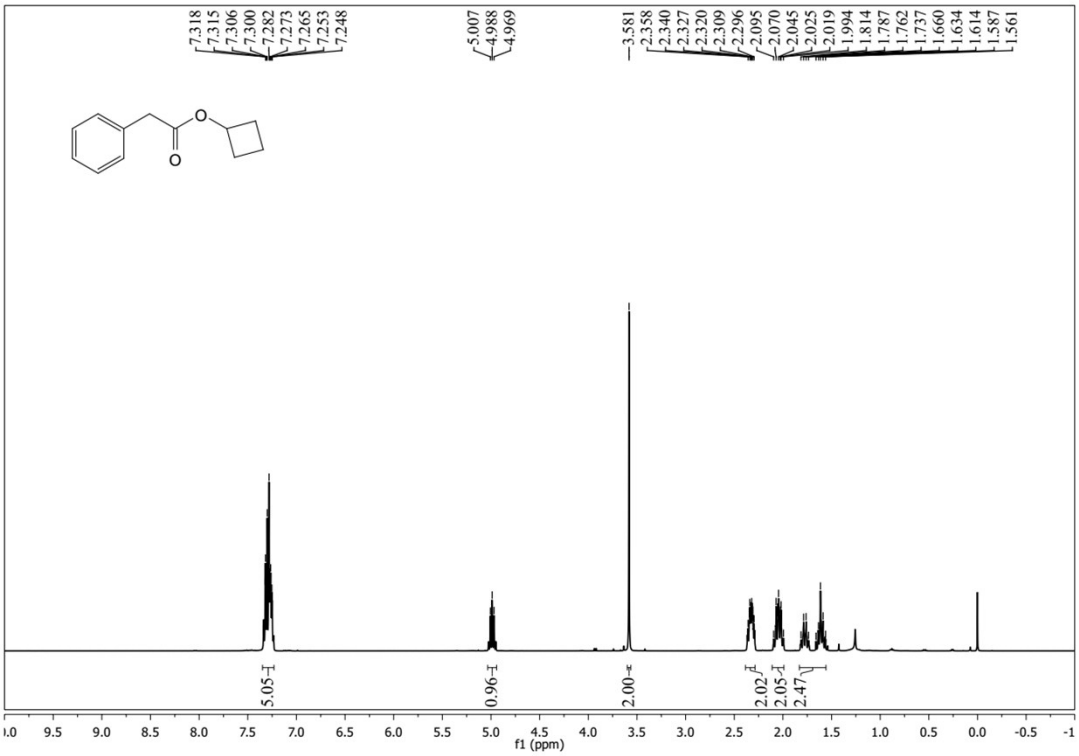
^{1}H NMR Spectra of 5au



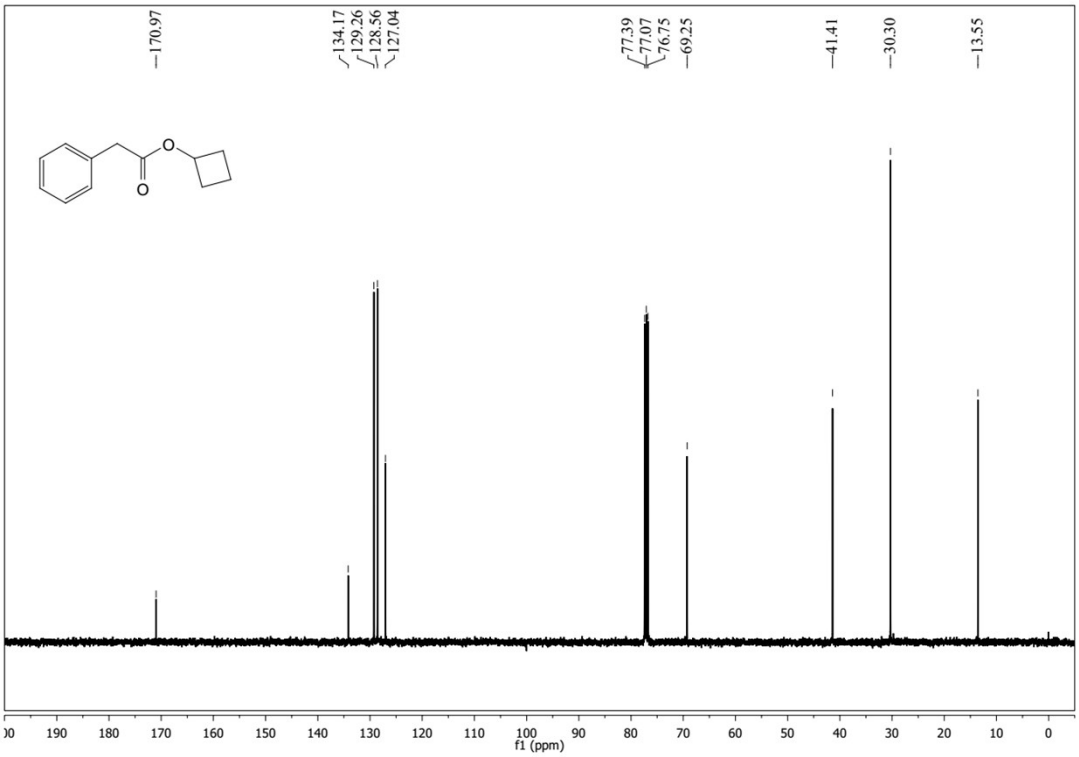
^{13}C NMR Spectra of 5au



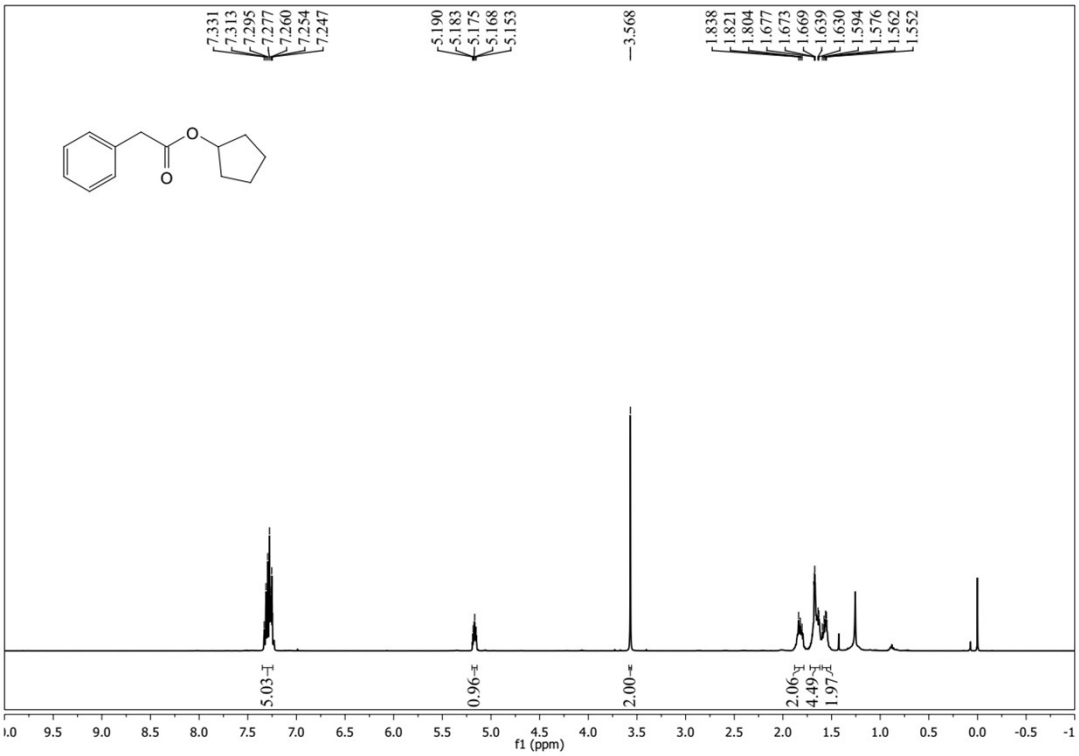
^{1}H NMR Spectra of 5av



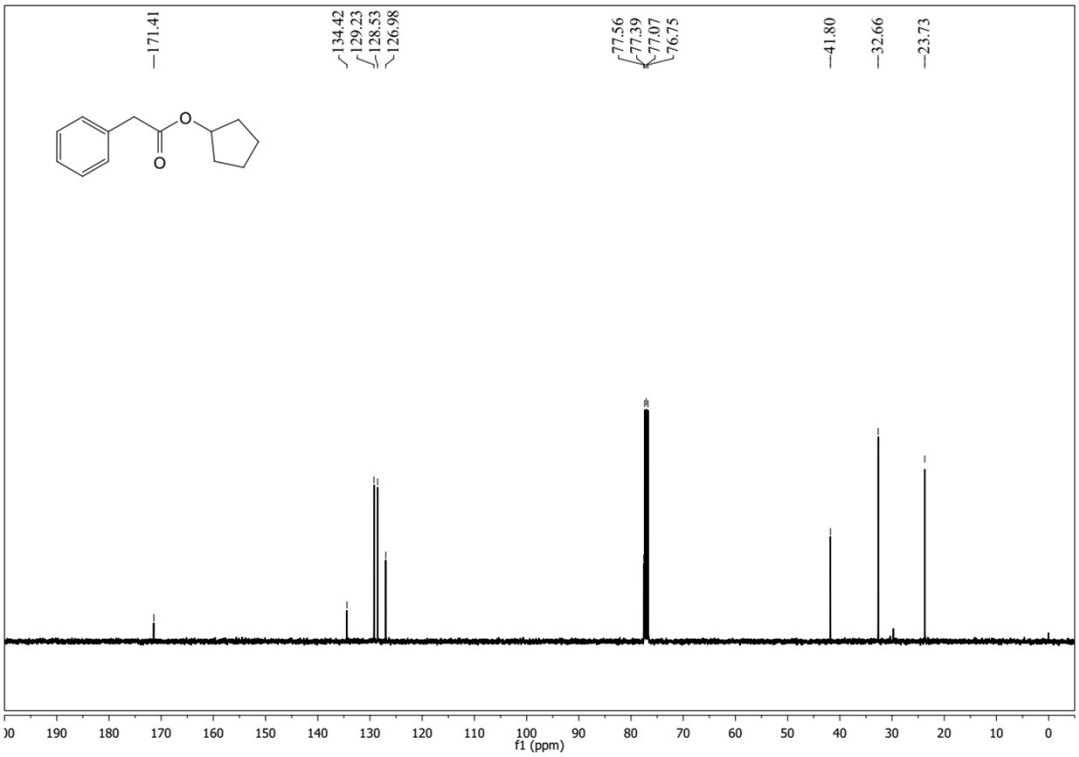
^{13}C NMR Spectra of 5av



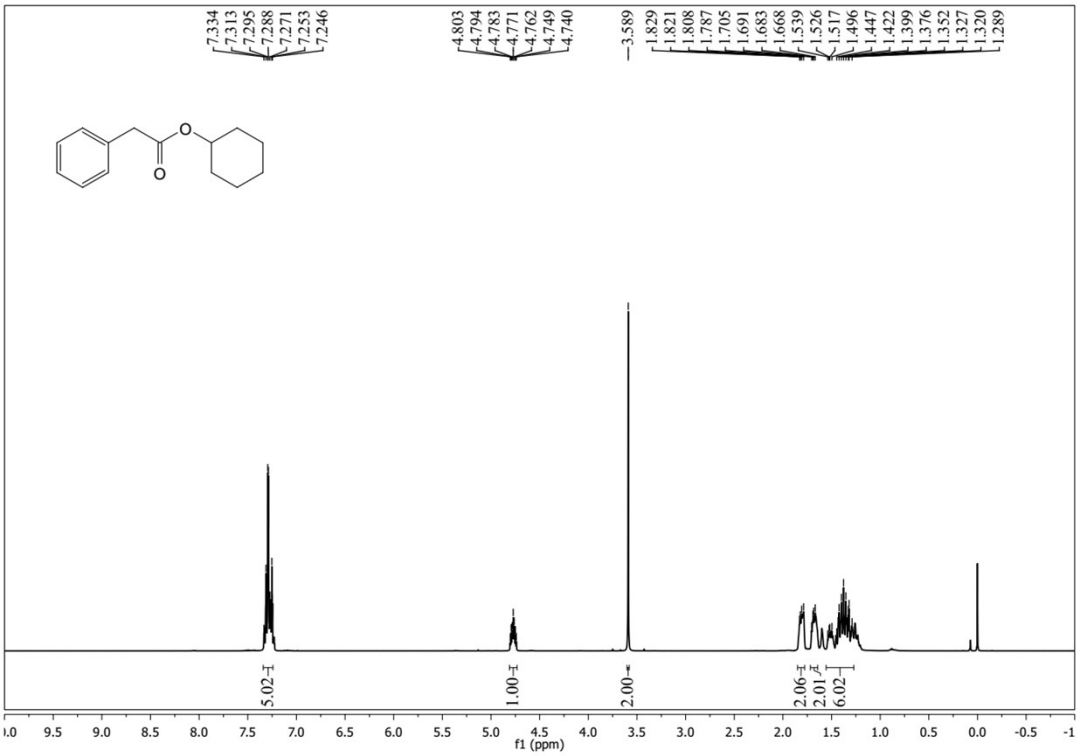
^{1}H NMR Spectra of 5aw



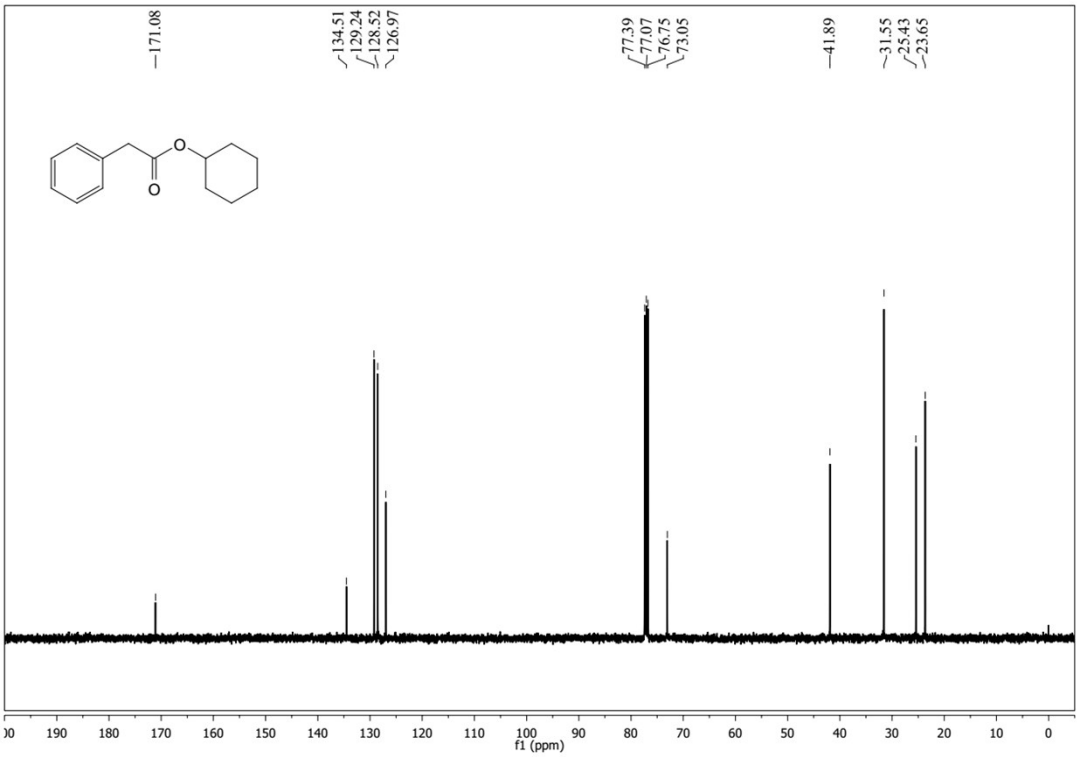
^{13}C NMR Spectra of 5aw



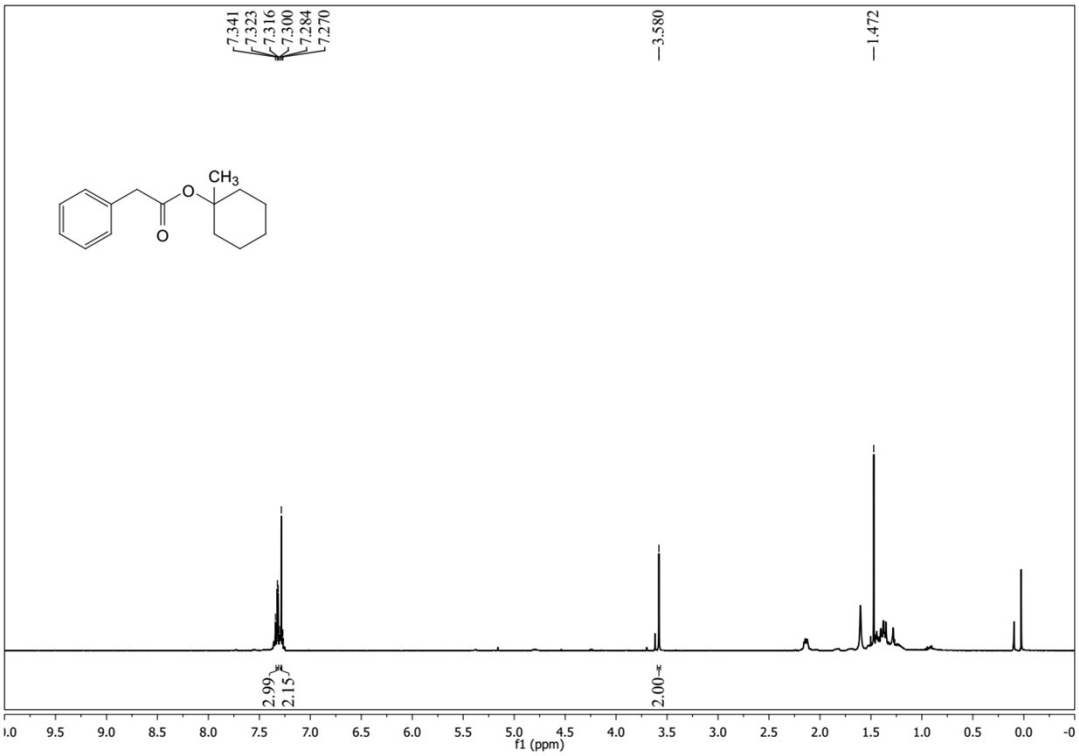
^{1}H NMR Spectra of 5ax



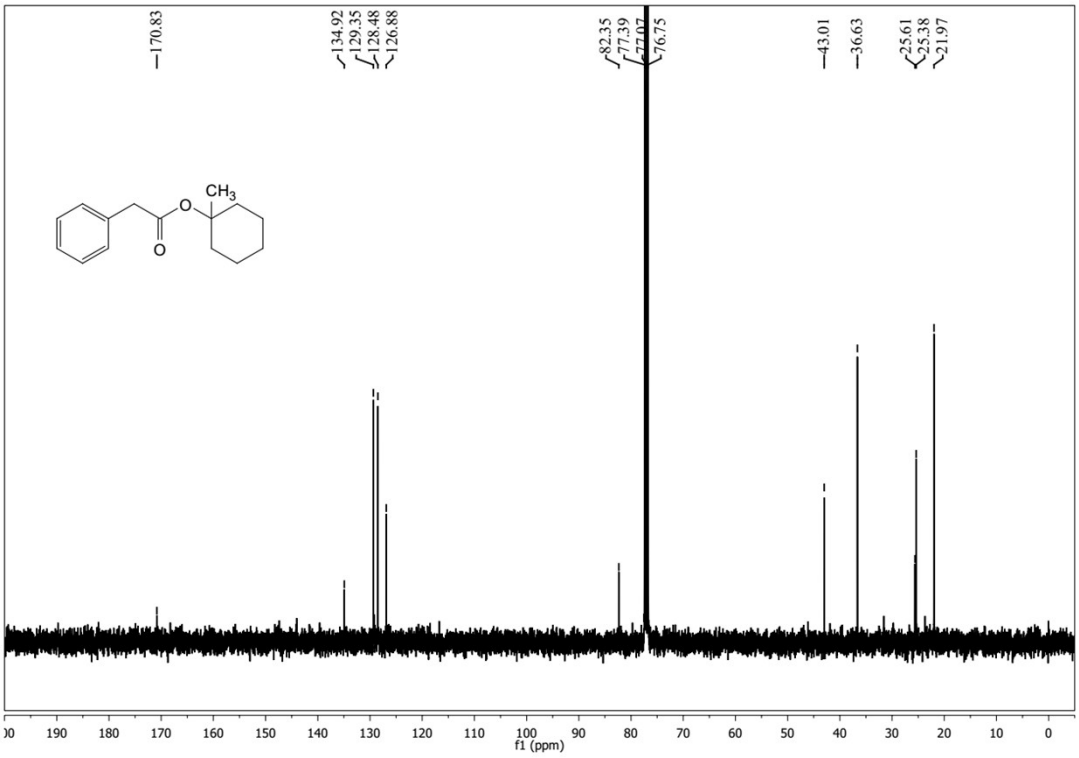
^{13}C NMR Spectra of 5ax



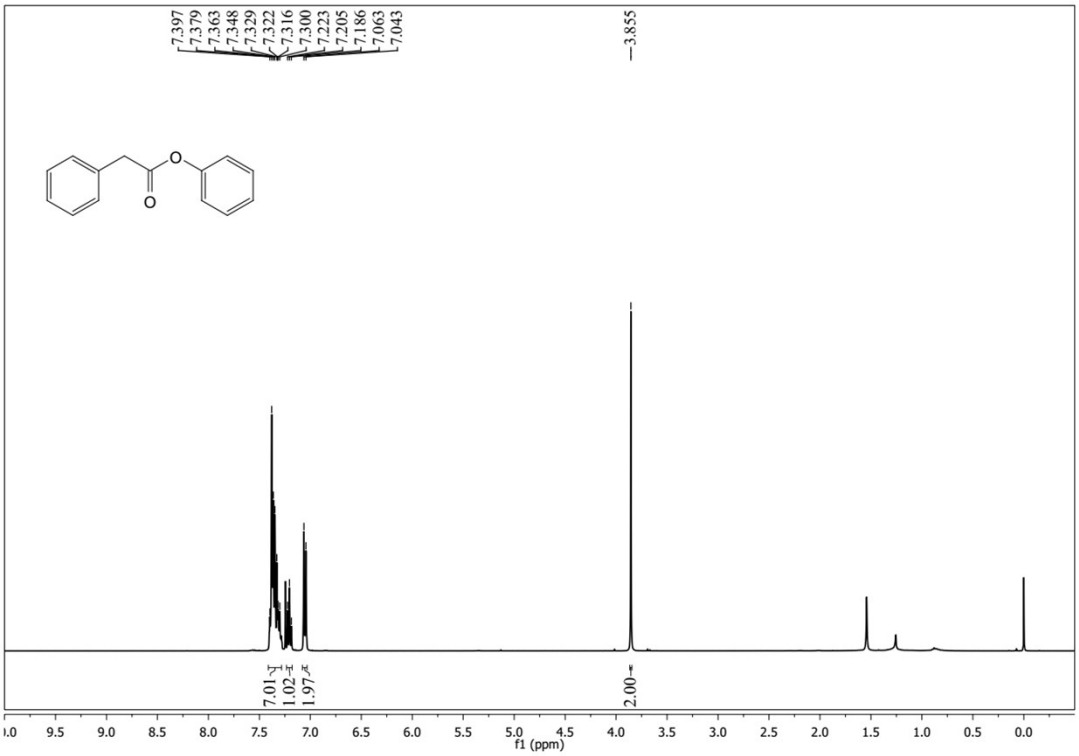
^{1}H NMR Spectra of 5ay



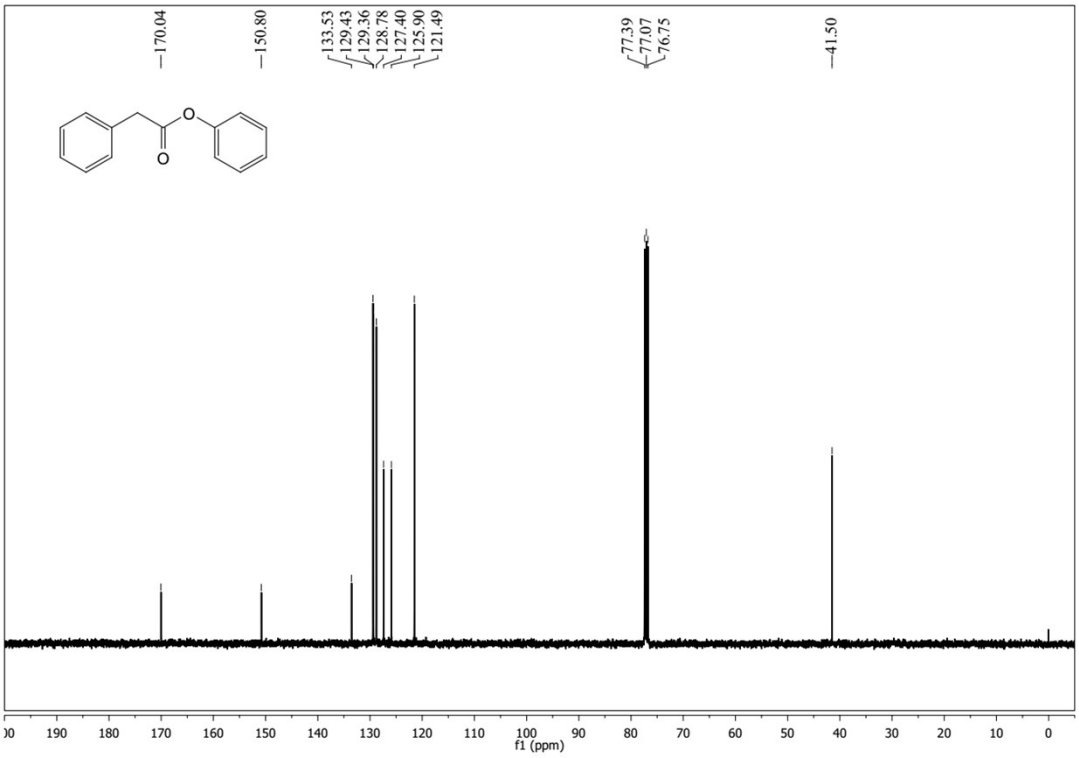
^{13}C NMR Spectra of 5ay



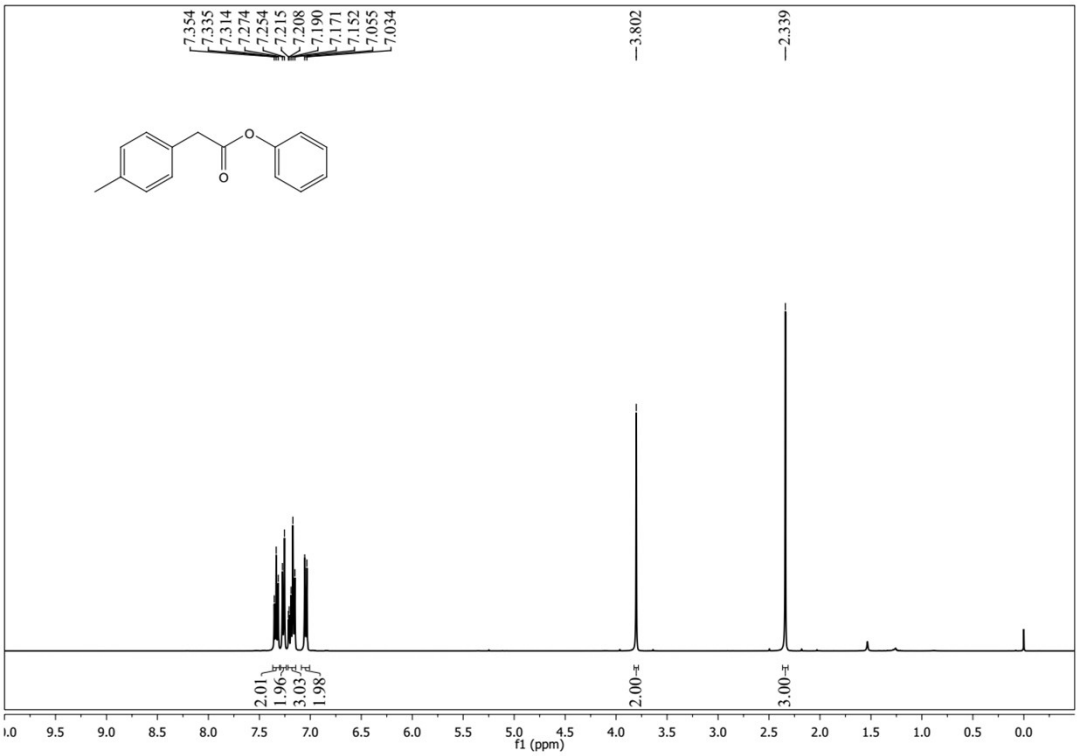
^{1}H NMR Spectra of 7aa



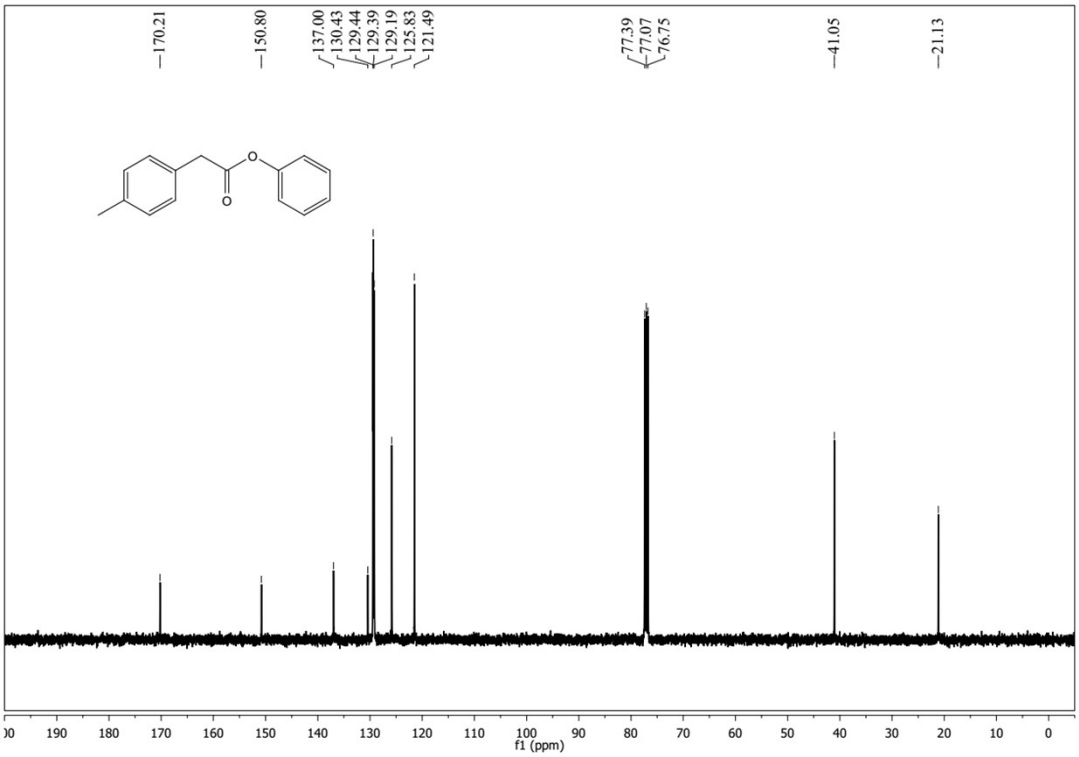
^{13}C NMR Spectra of 7aa



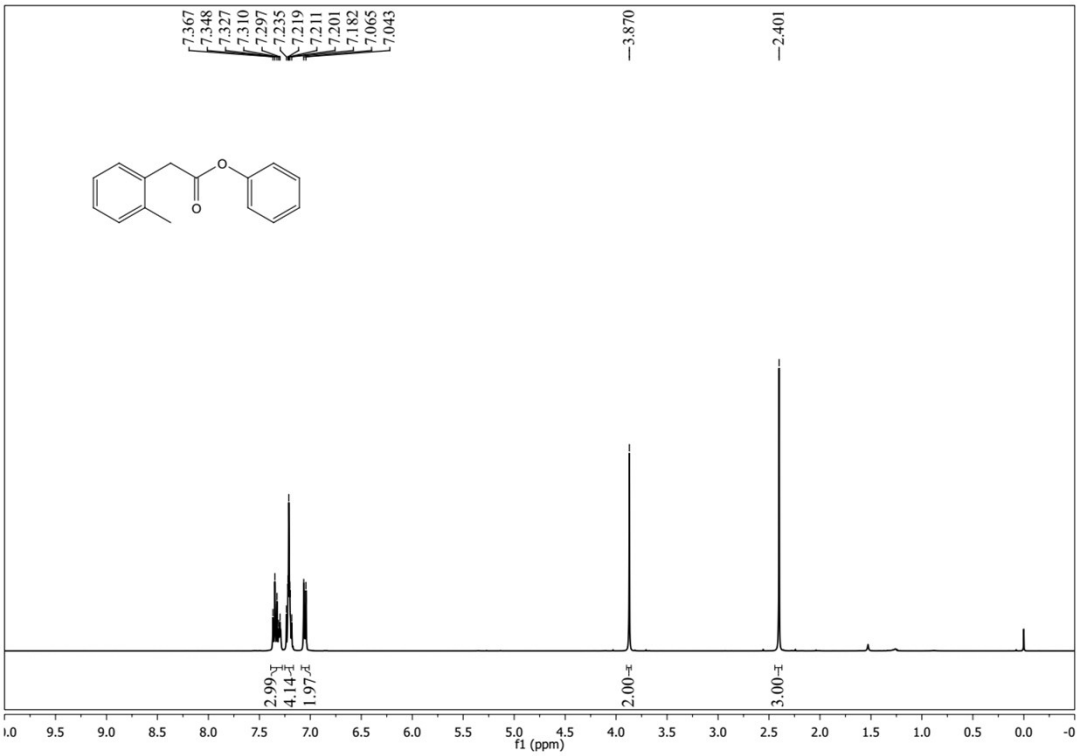
^{1}H NMR Spectra of 7ab



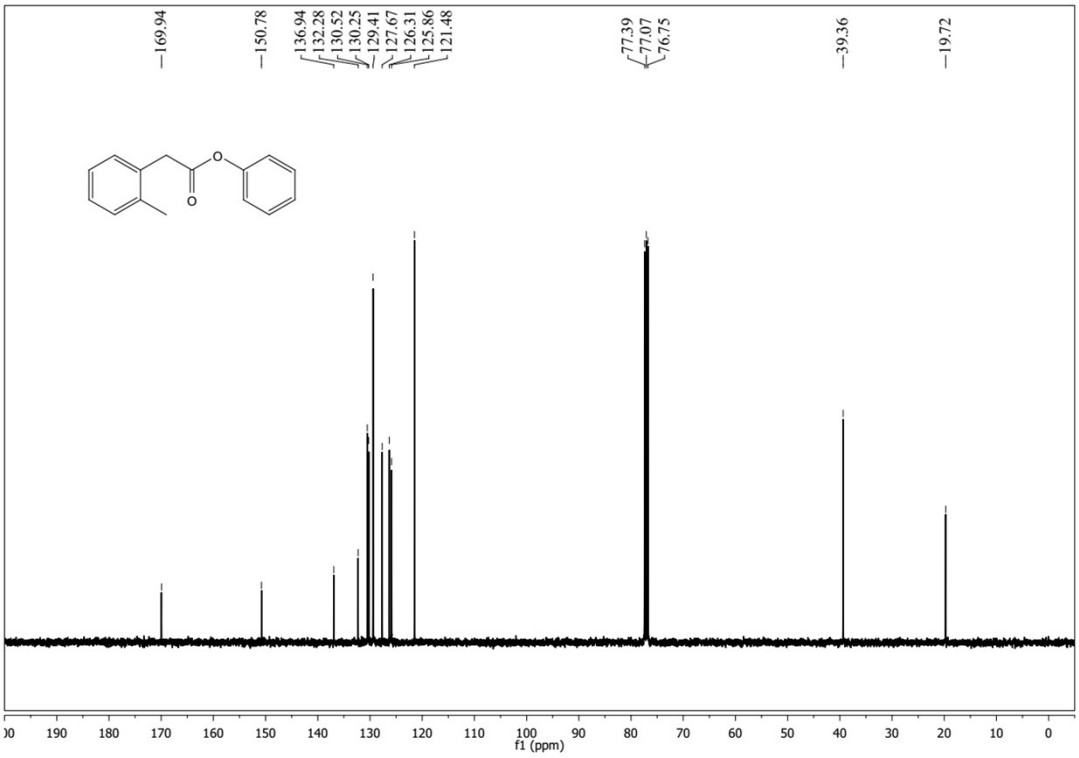
^{13}C NMR Spectra of 7ab



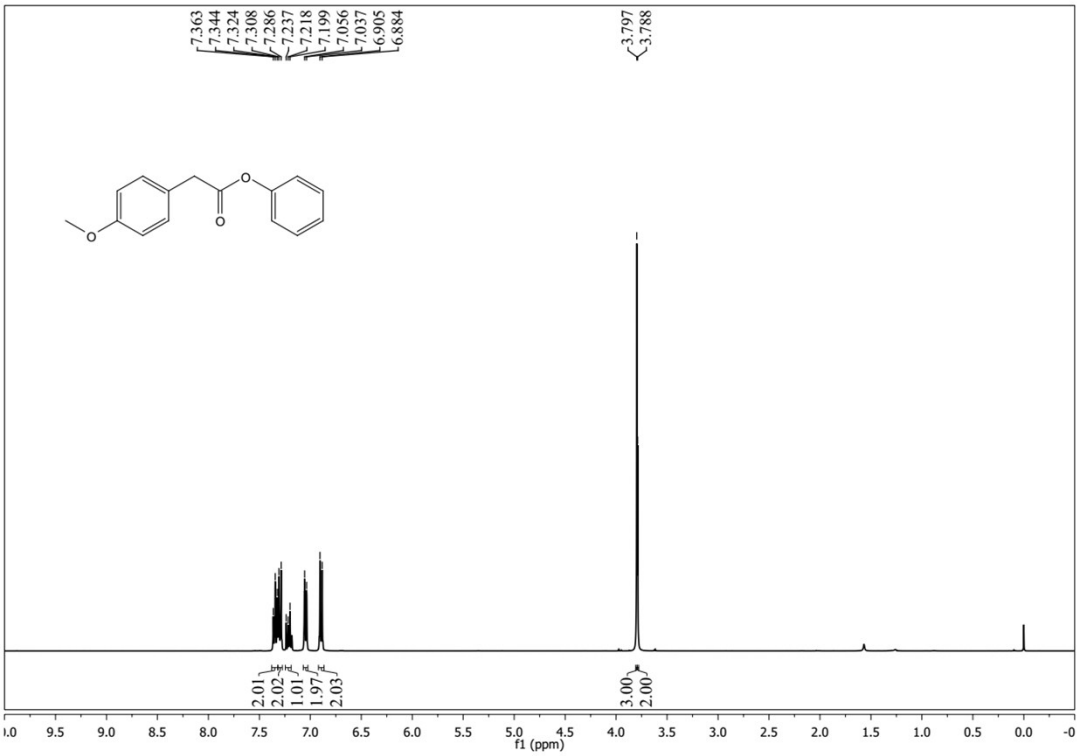
^{1}H NMR Spectra of 7ac



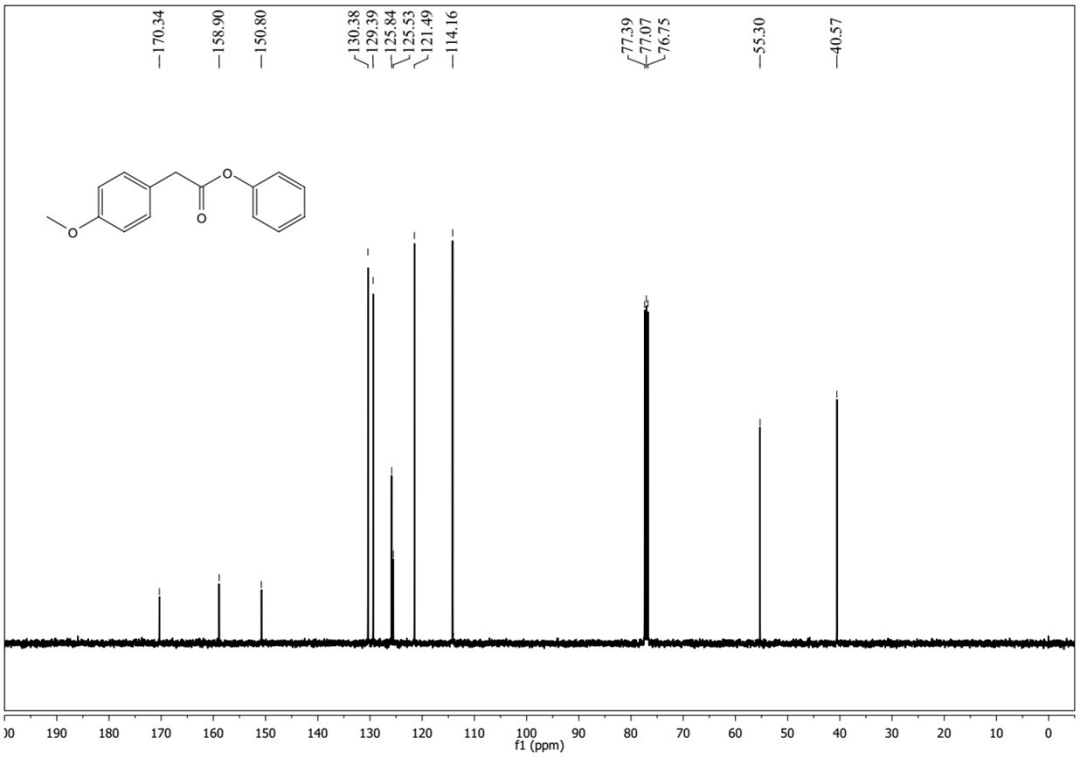
^{13}C NMR Spectra of 7ac



^{1}H NMR Spectra of 7ad



^{13}C NMR Spectra of 7ad



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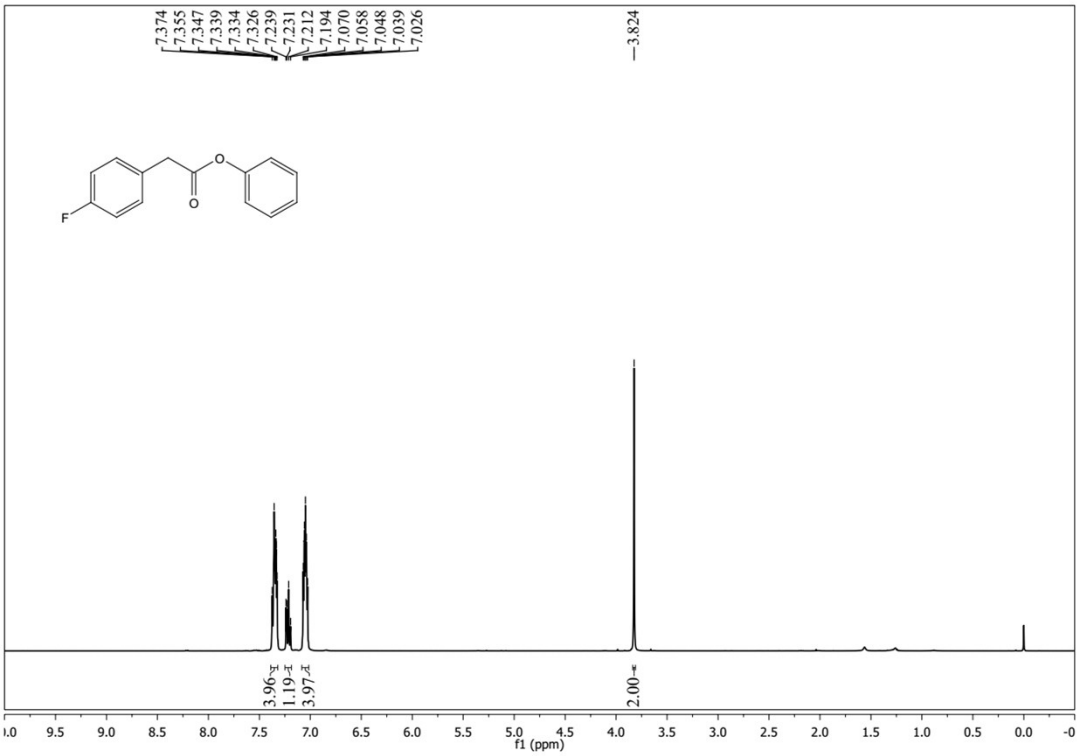

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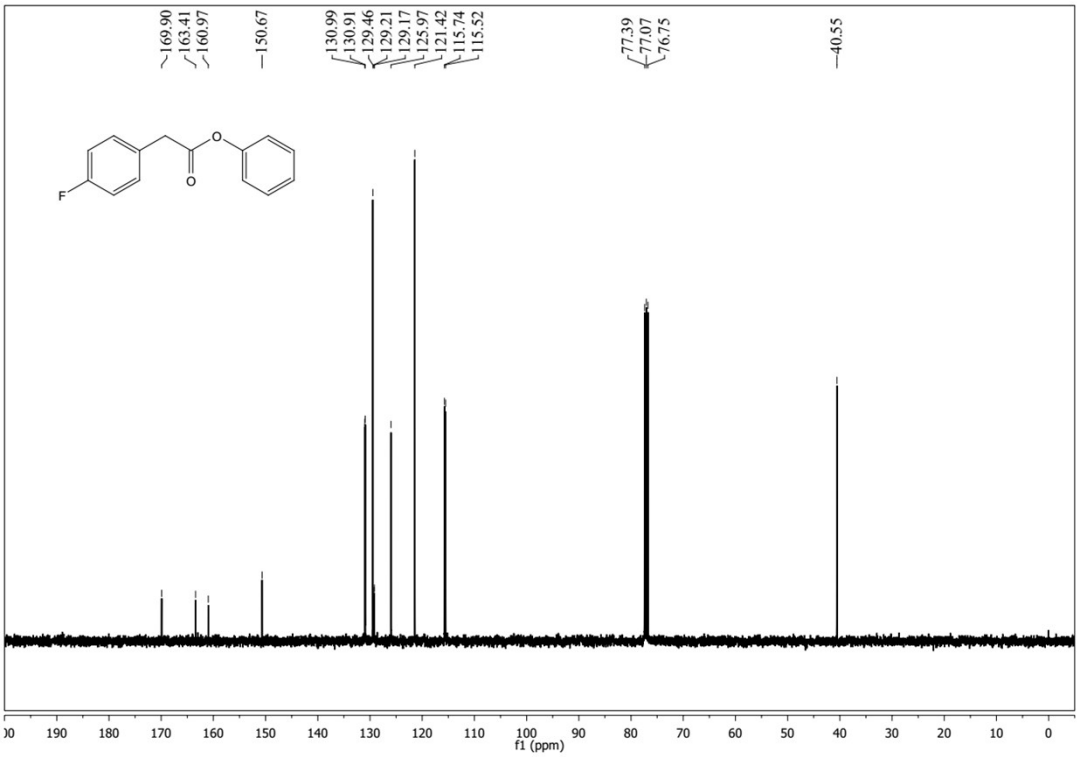

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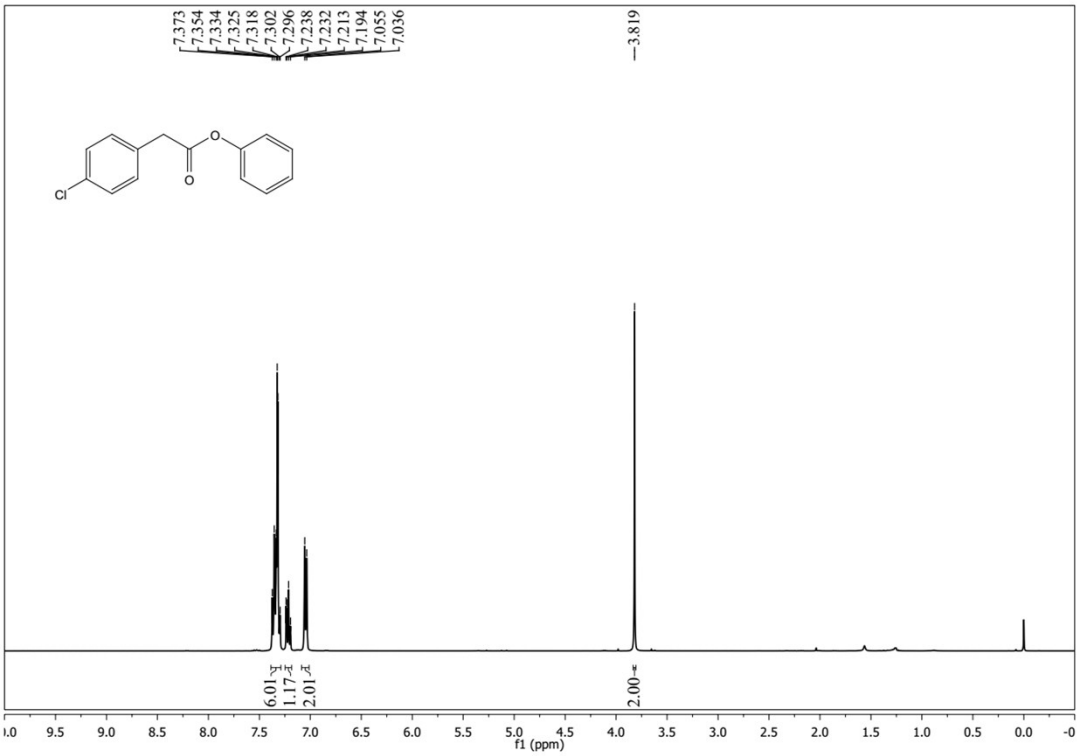
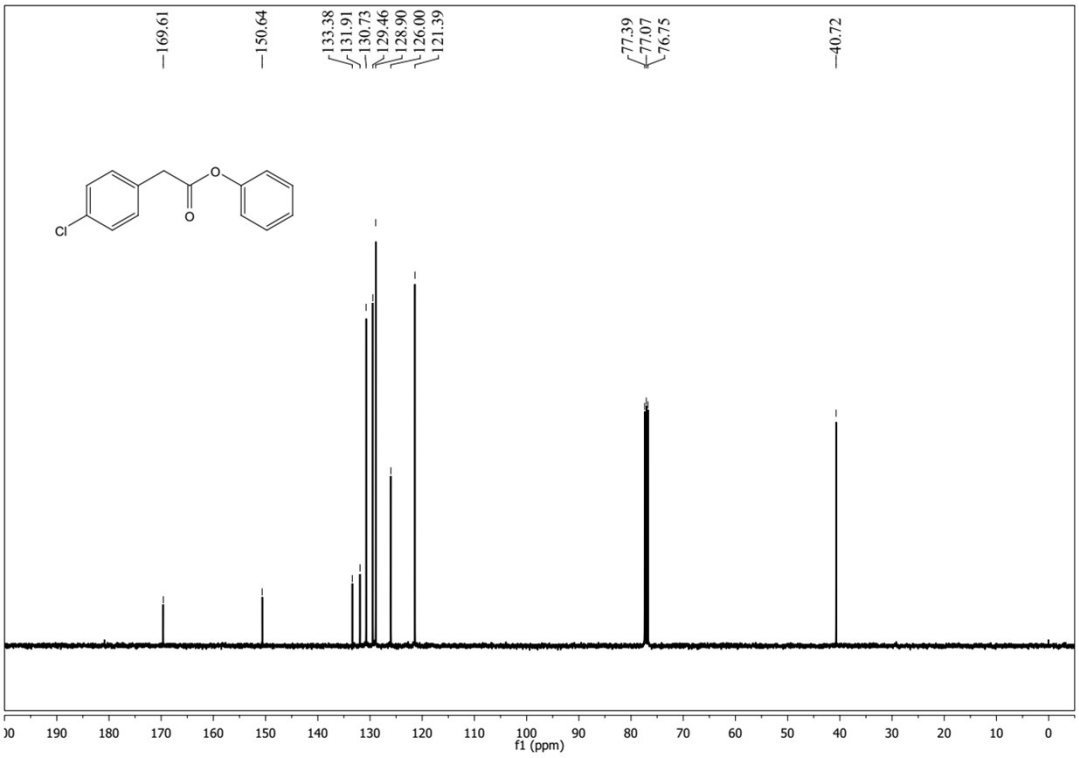
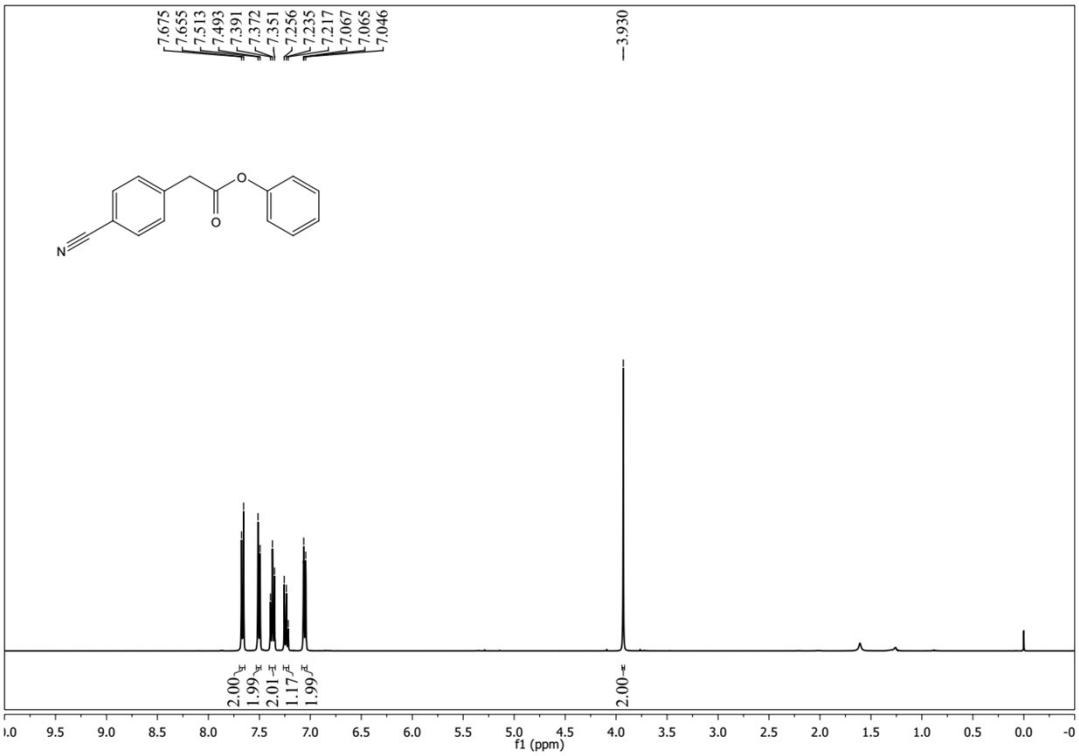


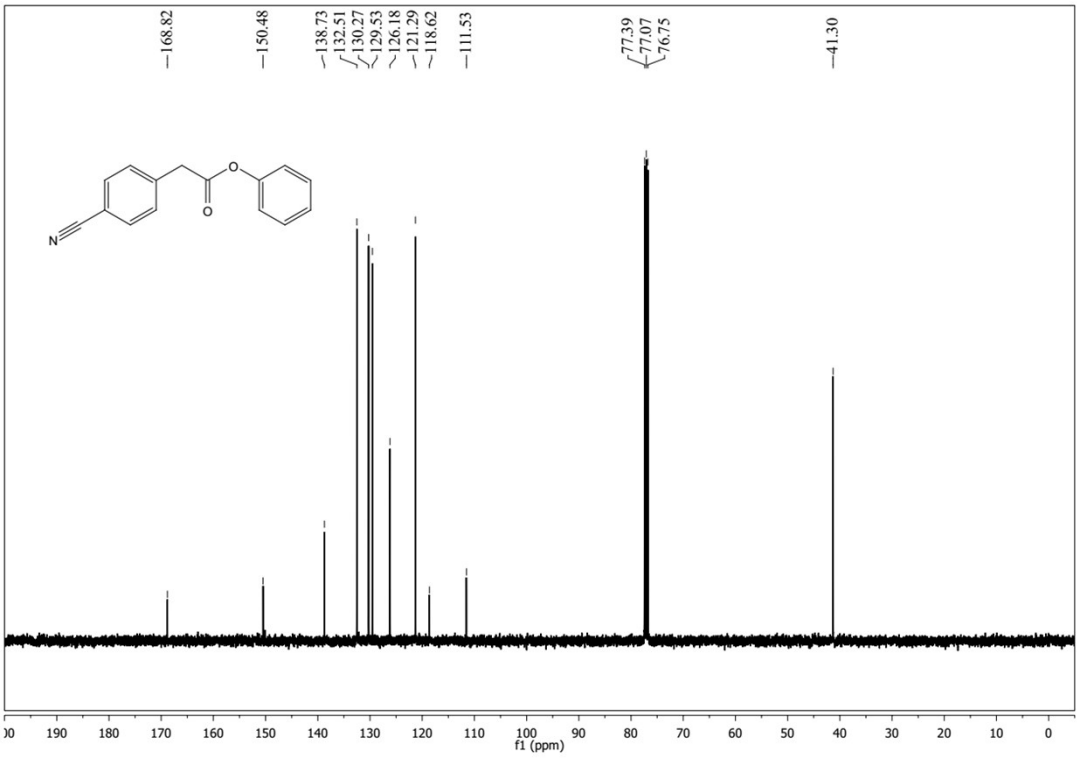
^{13}C NMR Spectra of 7af



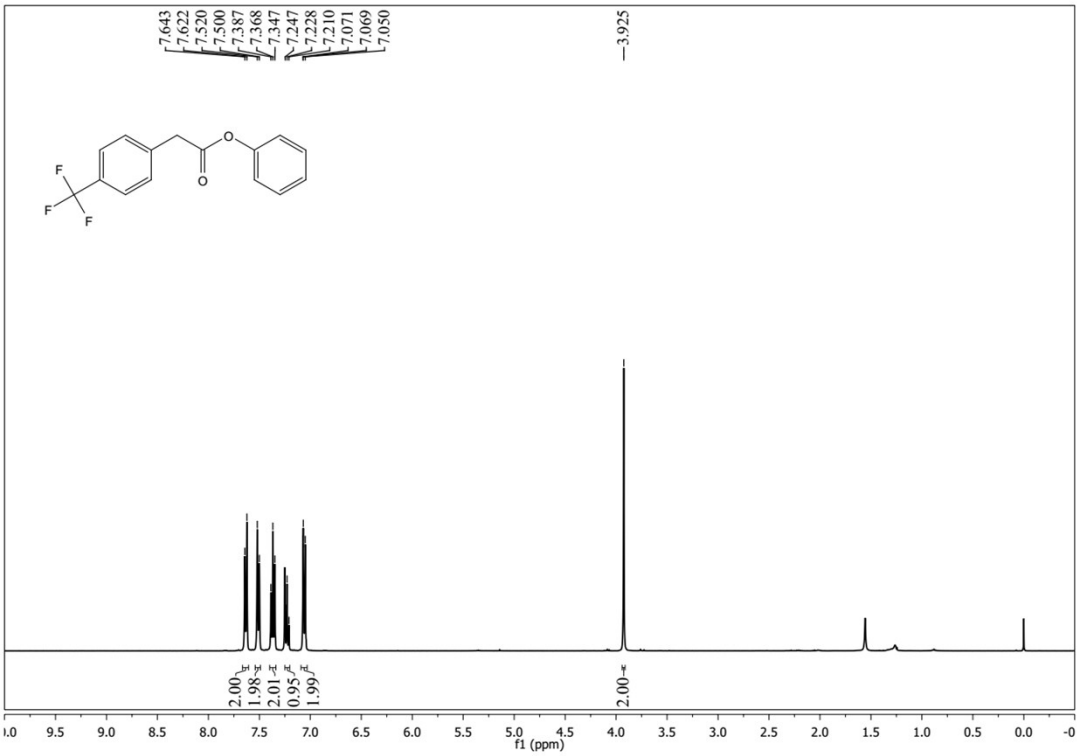
^{1}H NMR Spectra of 7ag



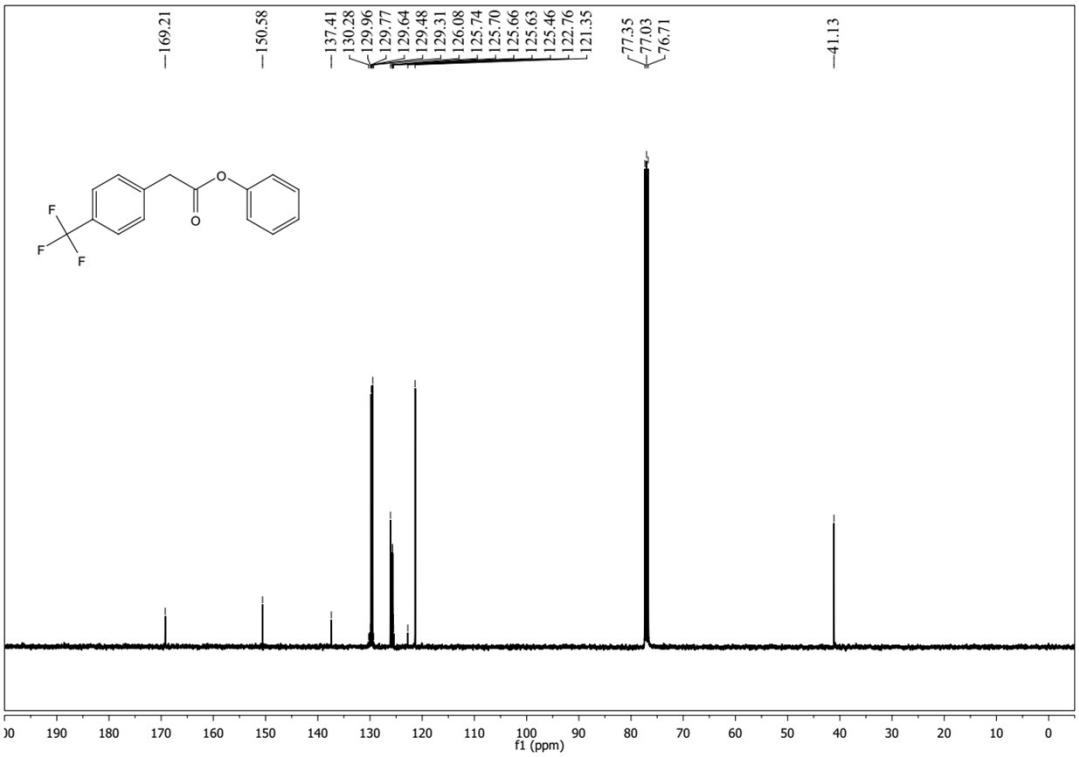
^{13}C NMR Spectra of 7ag



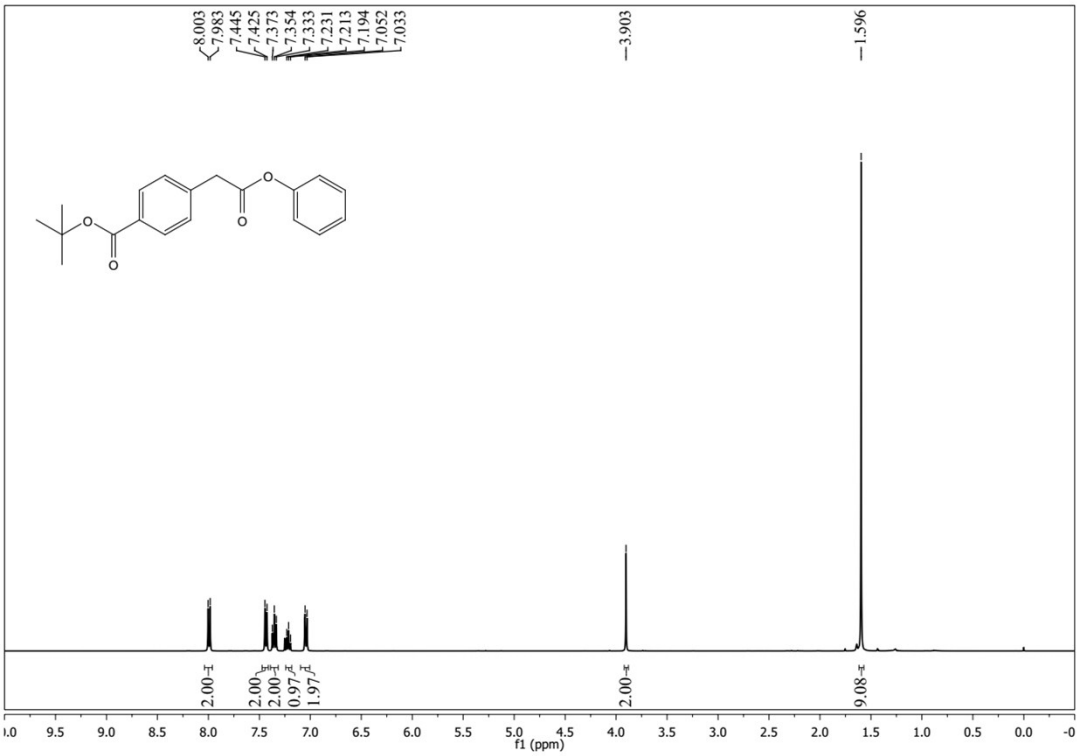
^{1}H NMR Spectra of 7ah



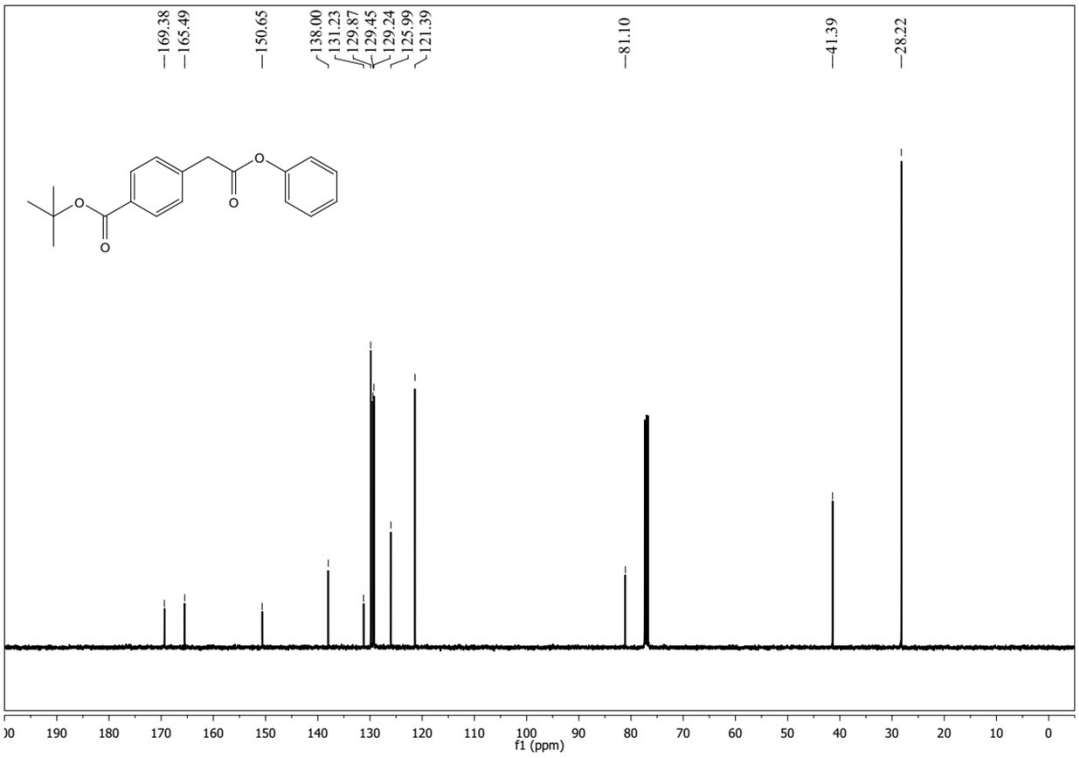
^{13}C NMR Spectra of 7ah



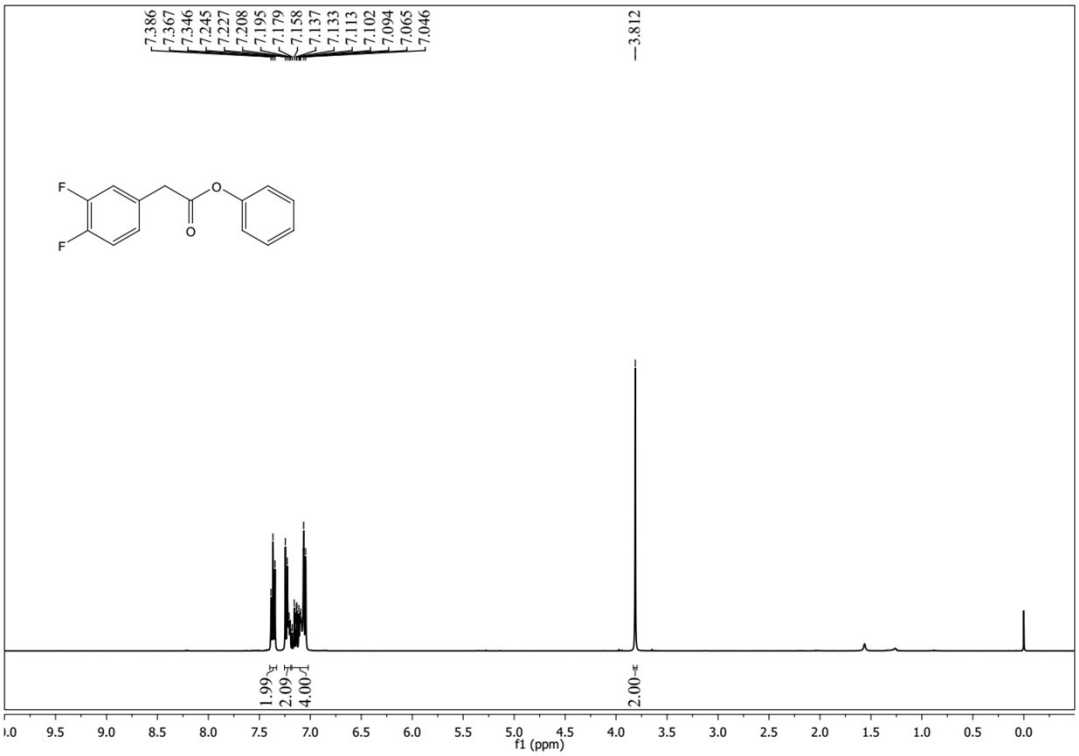
^{1}H NMR Spectra of 7ai



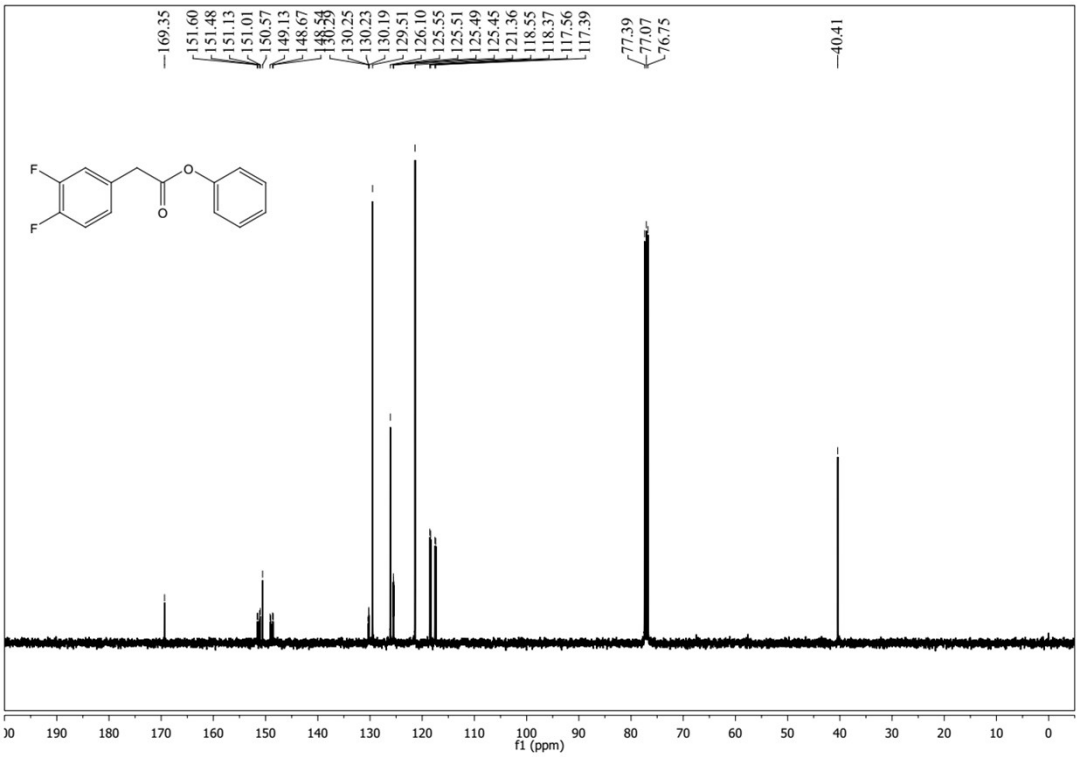
^{13}C NMR Spectra of 7ai



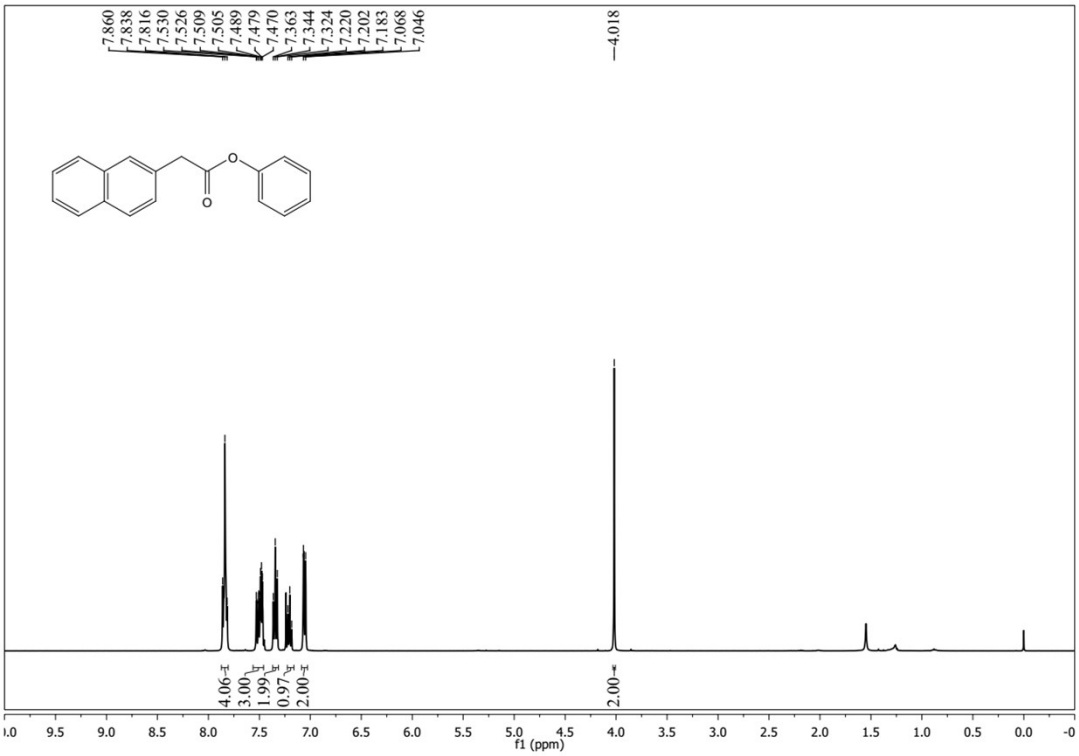
^{1}H NMR Spectra of 7aj



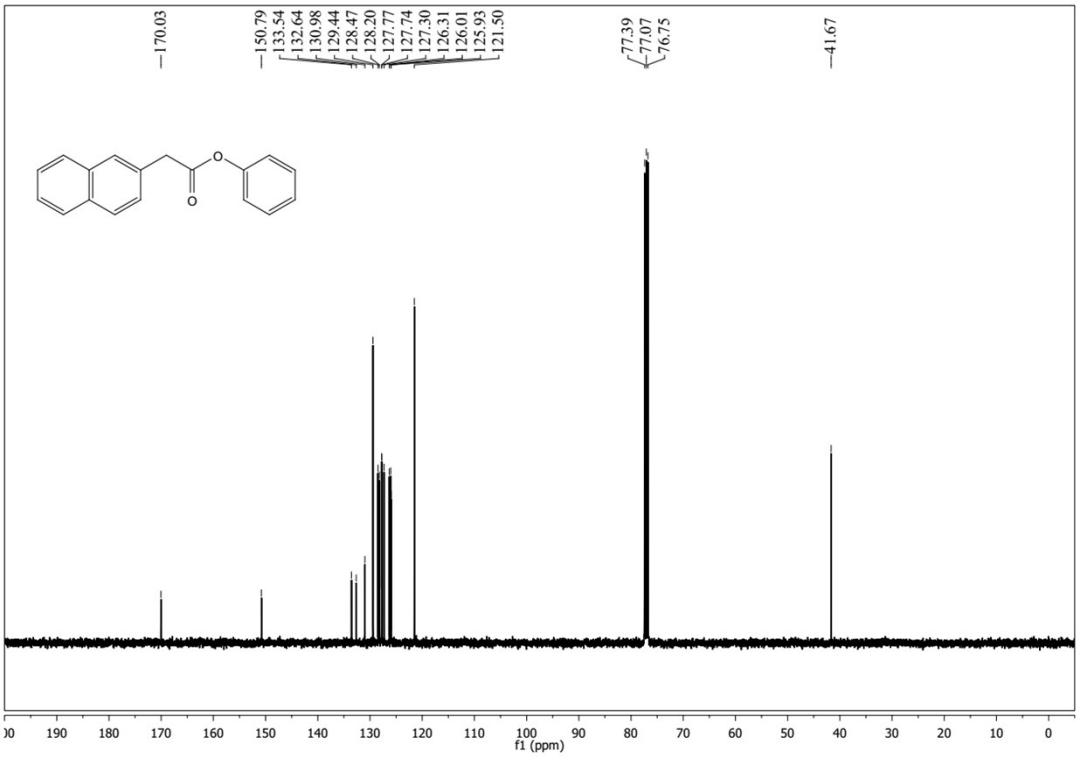
^{13}C NMR Spectra of 7aj



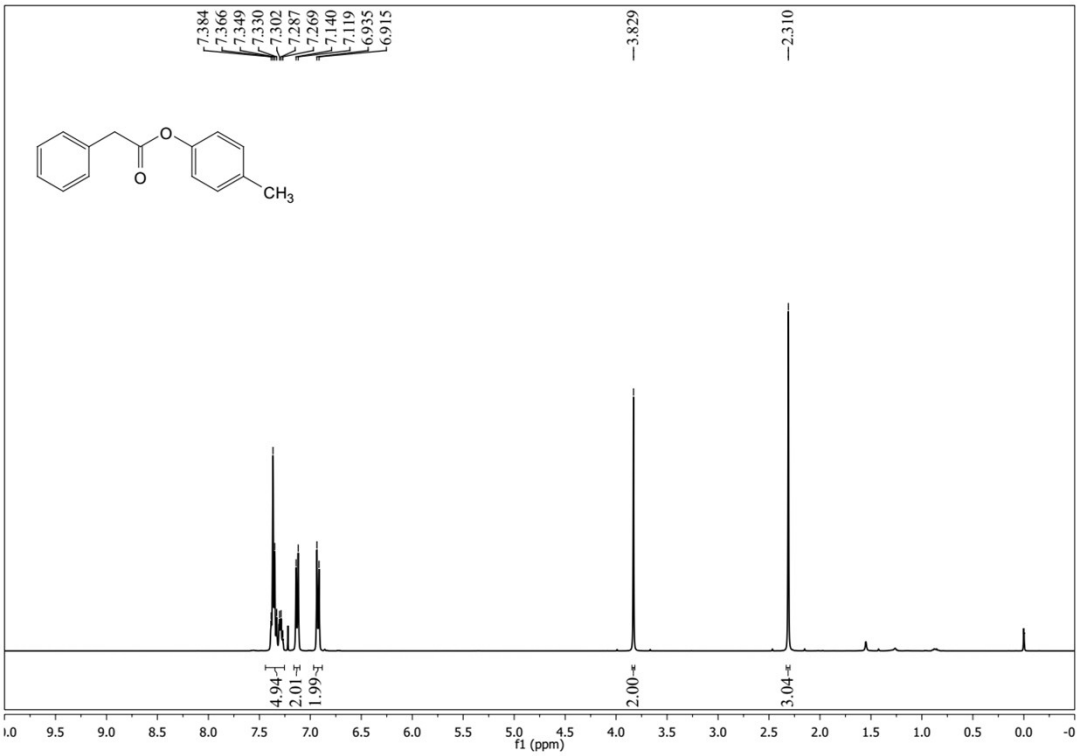
^{1}H NMR Spectra of 7ak



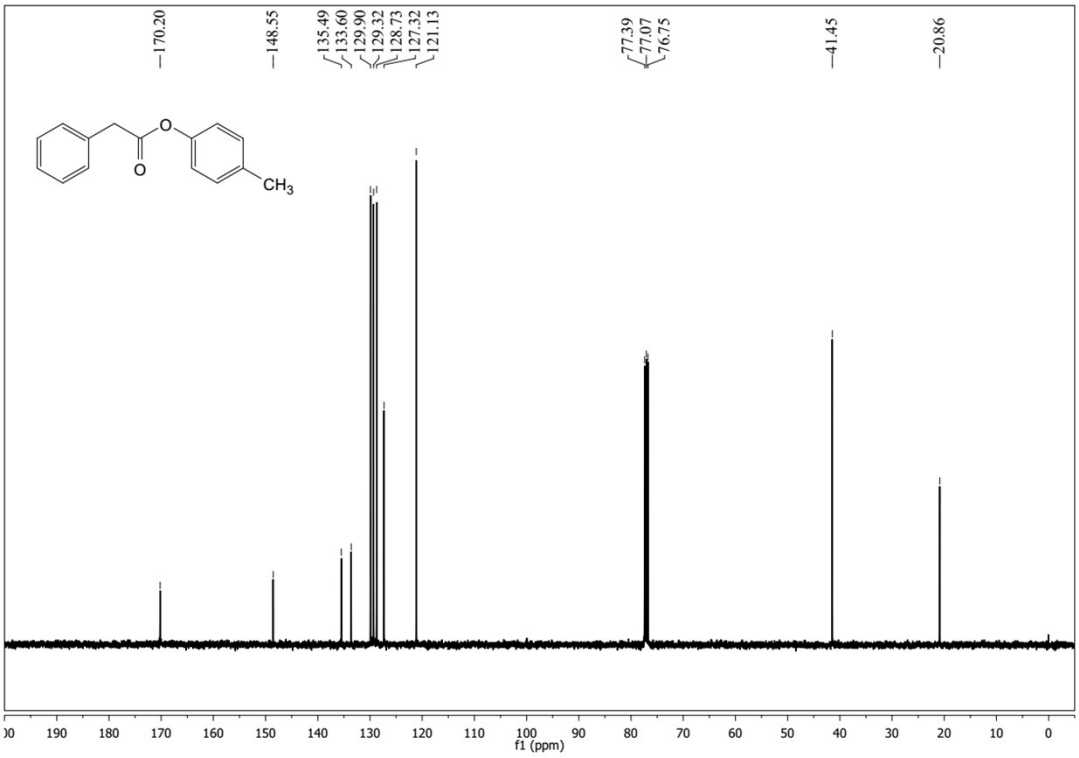
^{13}C NMR Spectra of 7ak



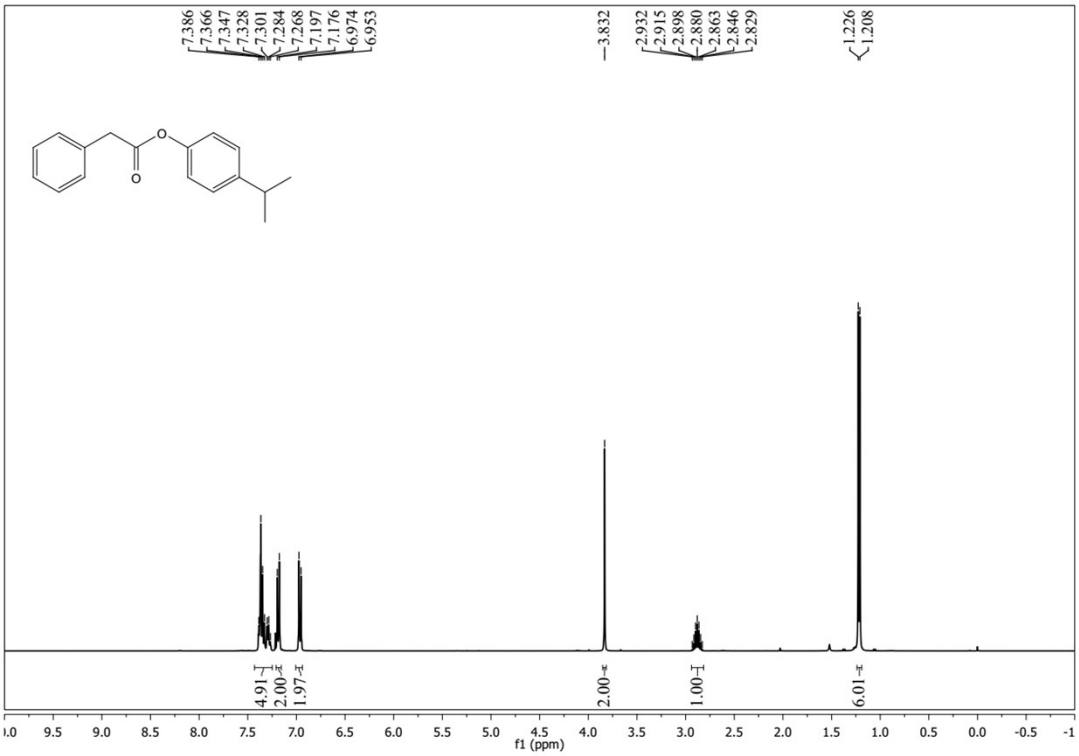
^{1}H NMR Spectra of 7al



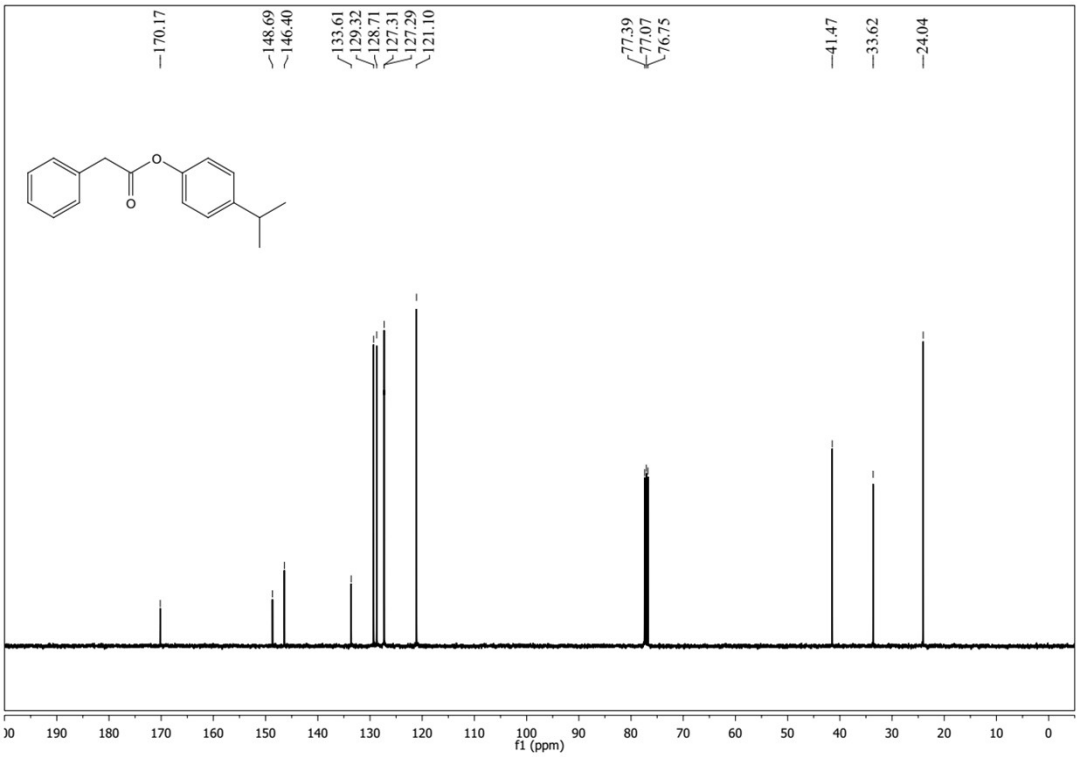
^{13}C NMR Spectra of 7al



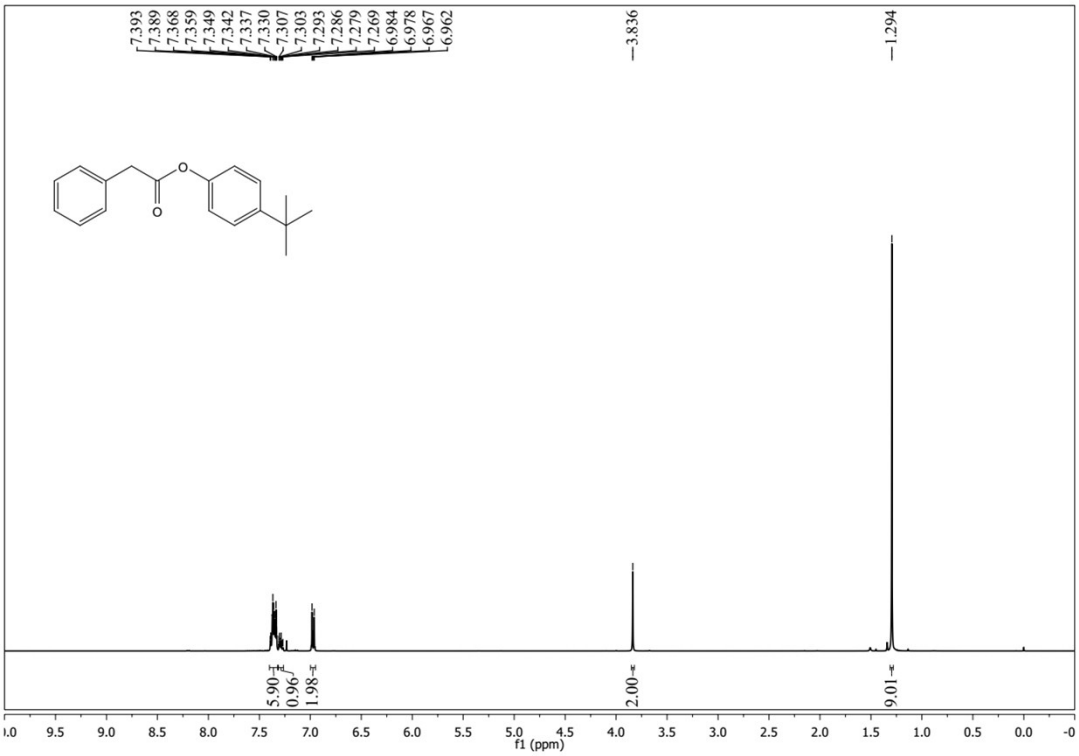
^{1}H NMR Spectra of 7am



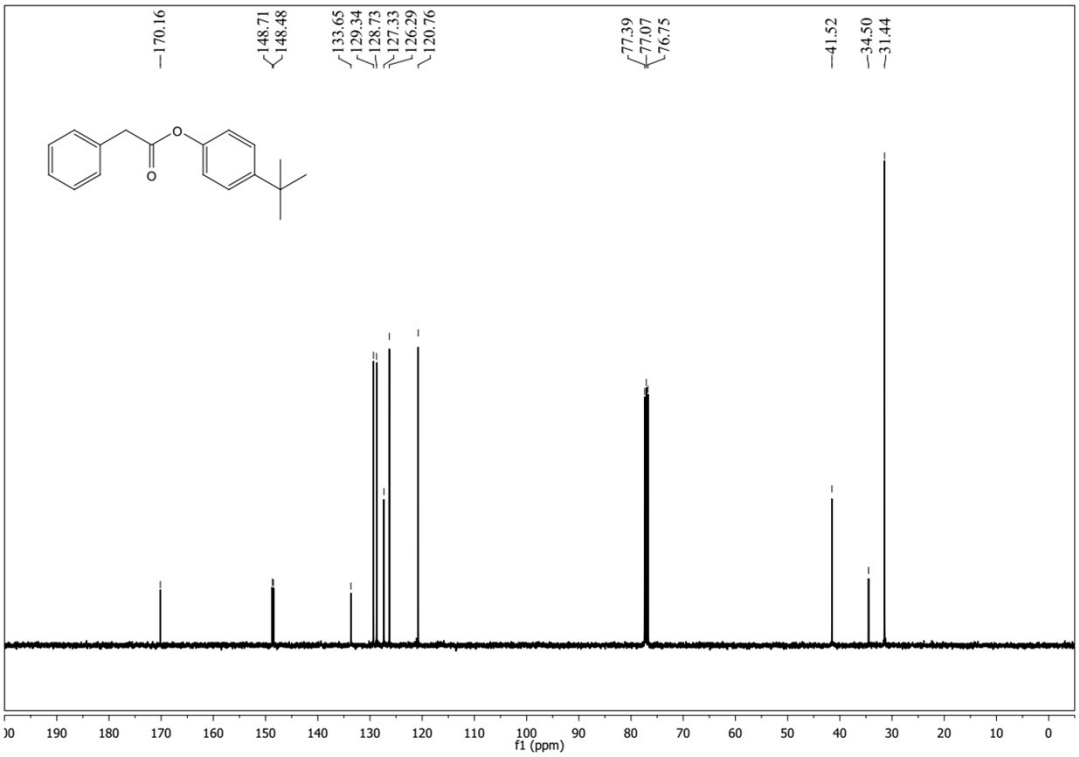
^{13}C NMR Spectra of 7am



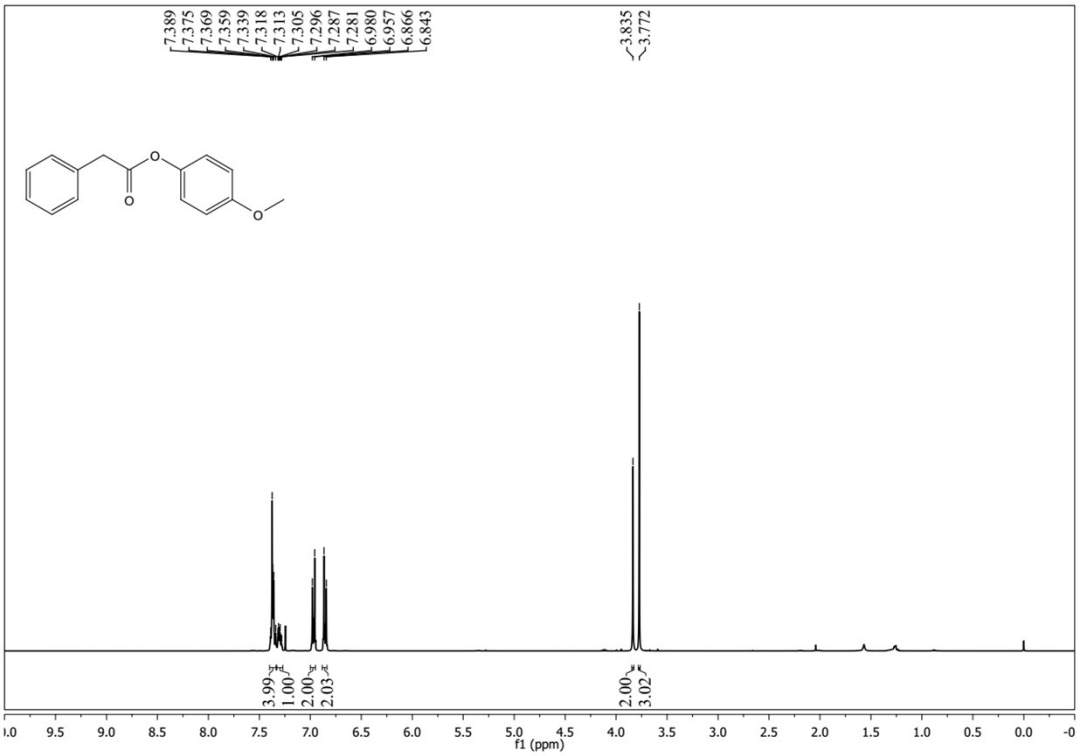
^{1}H NMR Spectra of 7an



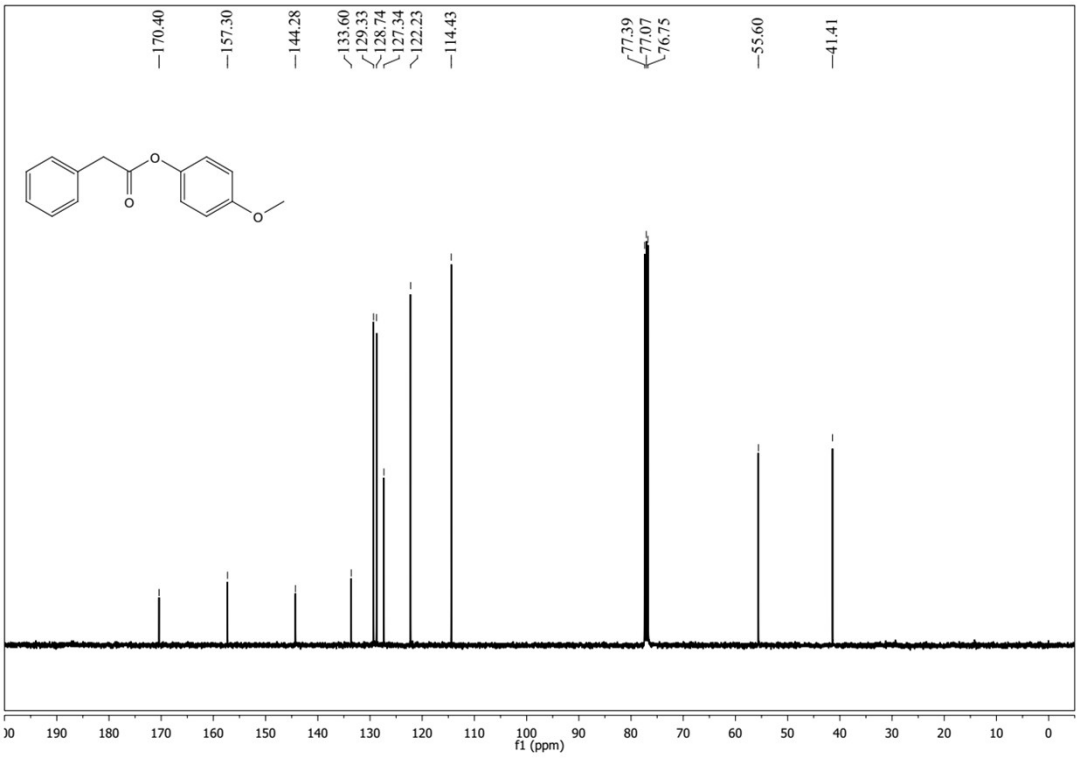
^{13}C NMR Spectra of 7an



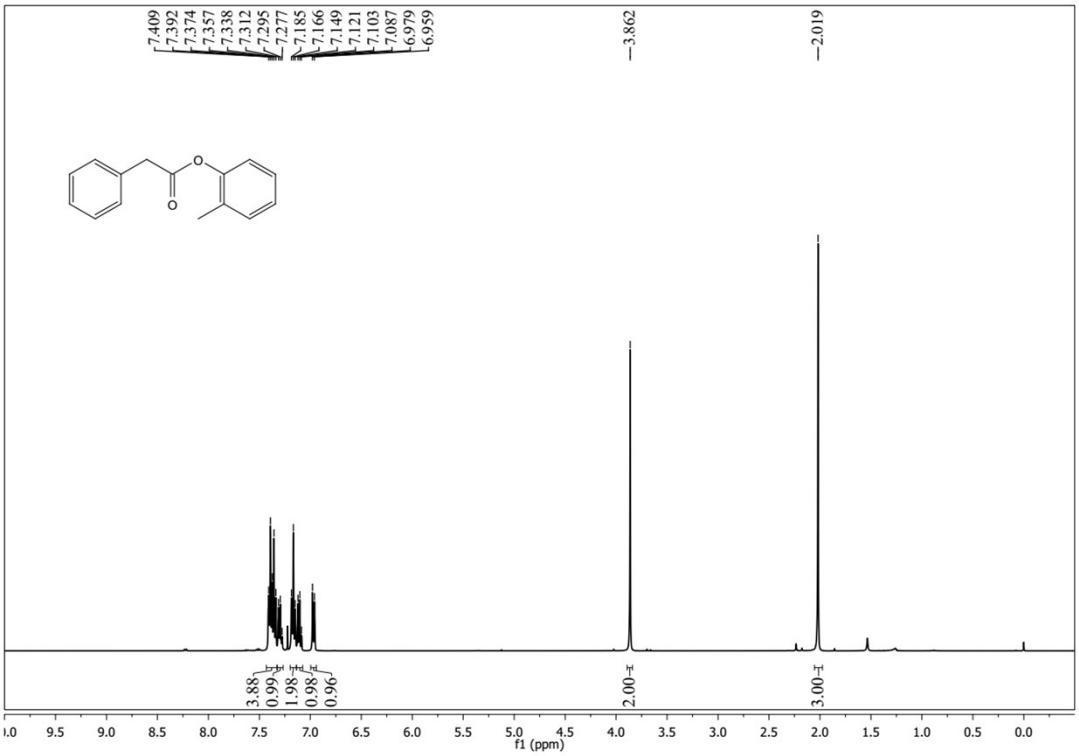
^{1}H NMR Spectra of 7ao



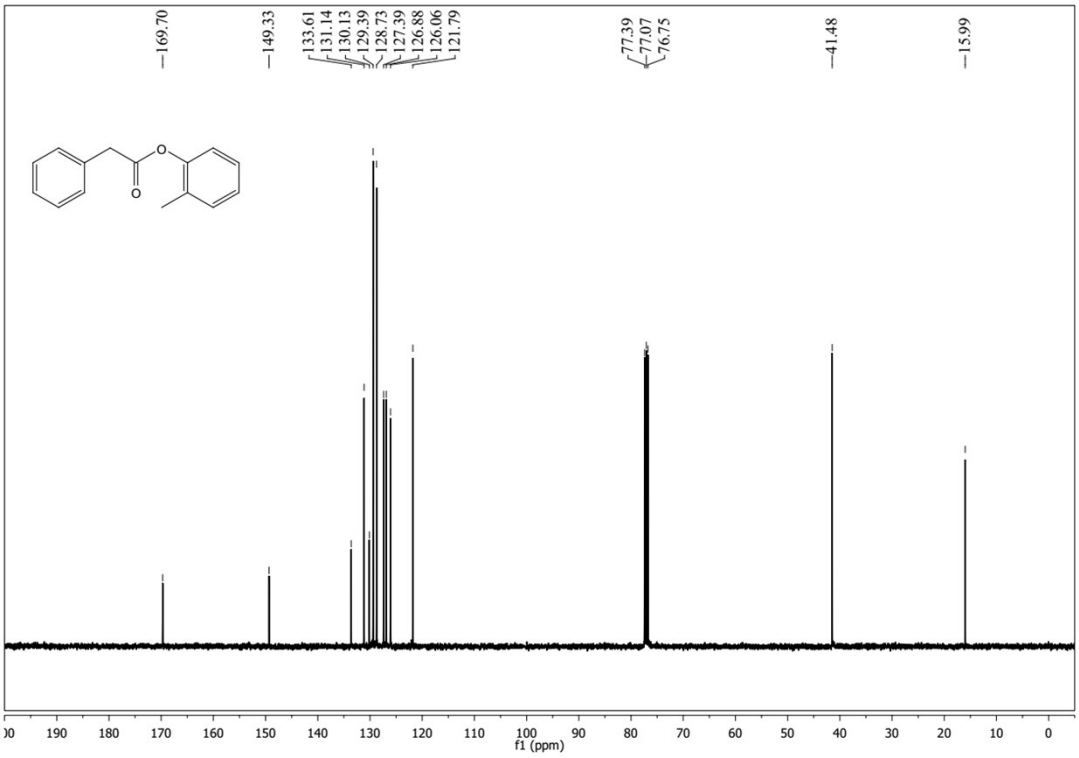
^{13}C NMR Spectra of 7ao



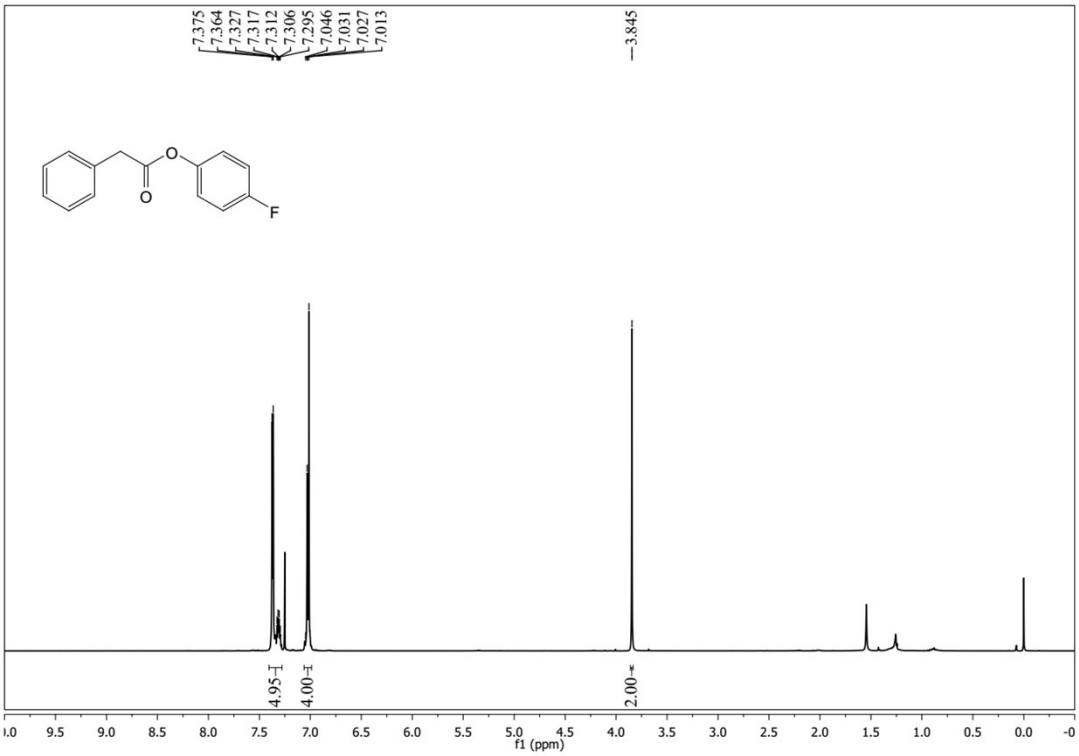
^{1}H NMR Spectra of 7ap



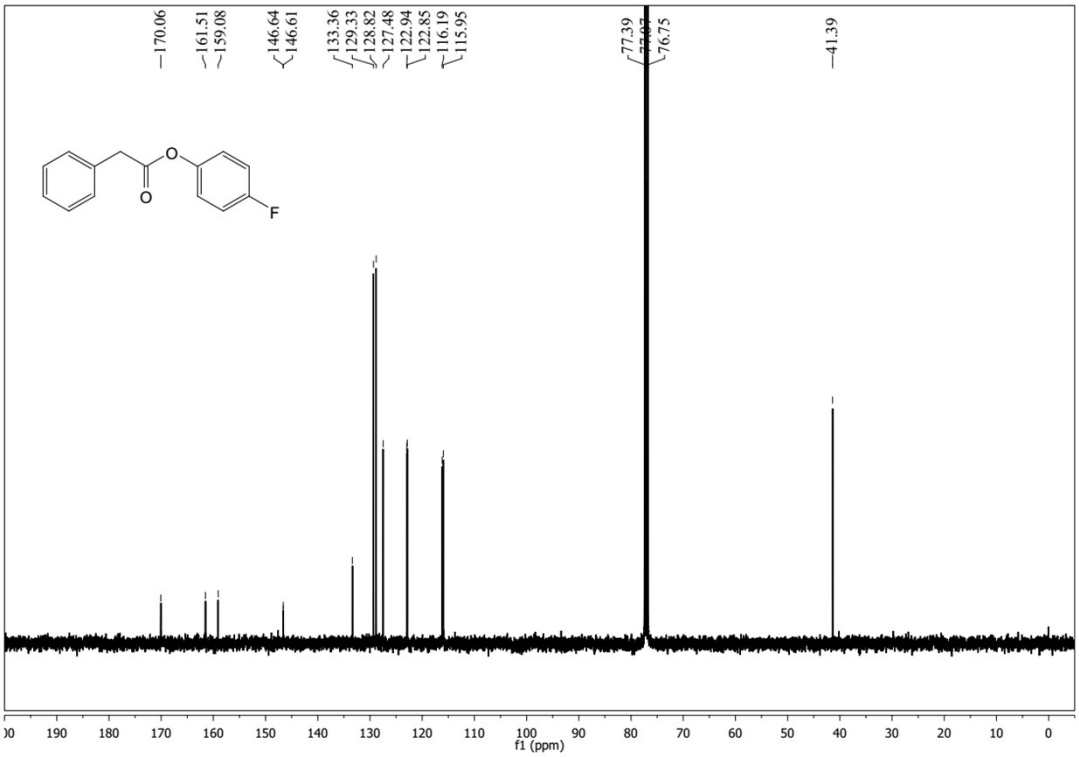
^{13}C NMR Spectra of 7ap



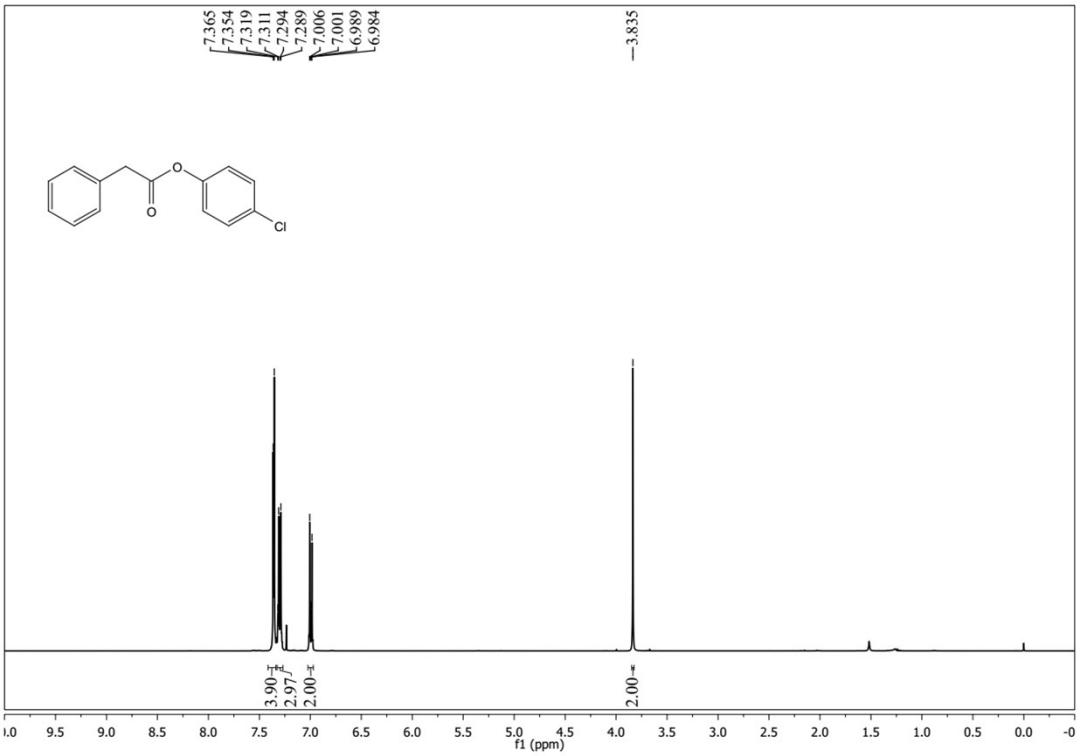
^{1}H NMR Spectra of 7aq



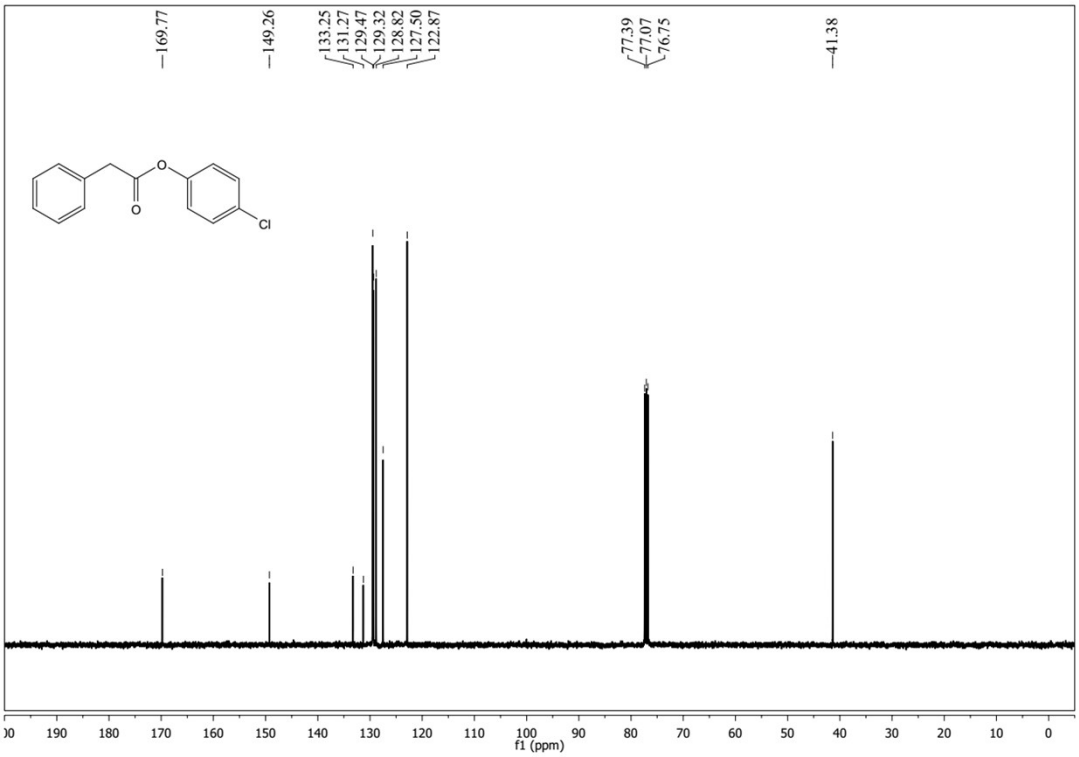
^{13}C NMR Spectra of 7aq



^{1}H NMR Spectra of 7ar



^{13}C NMR Spectra of 7ar



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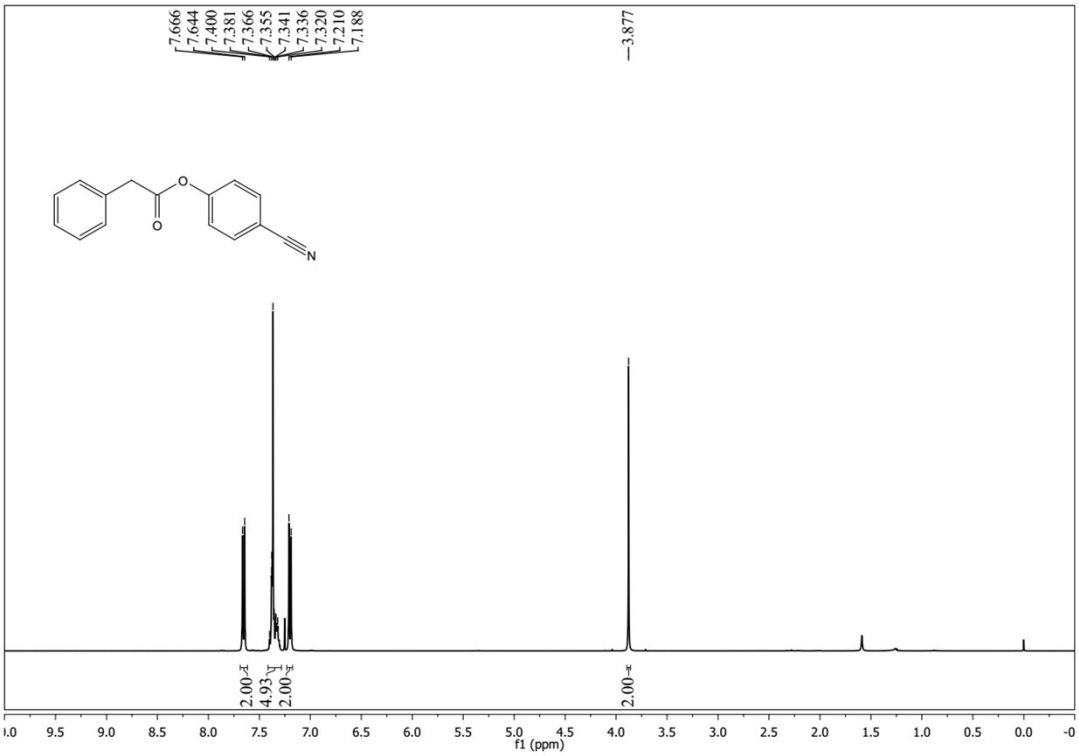
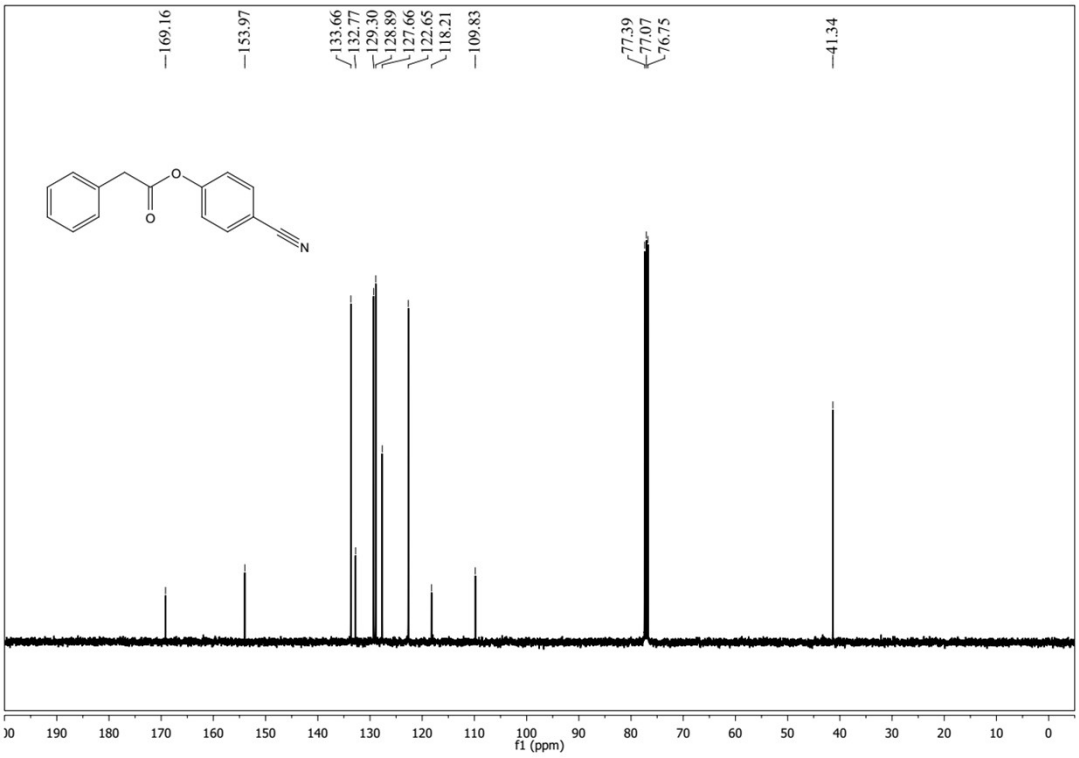
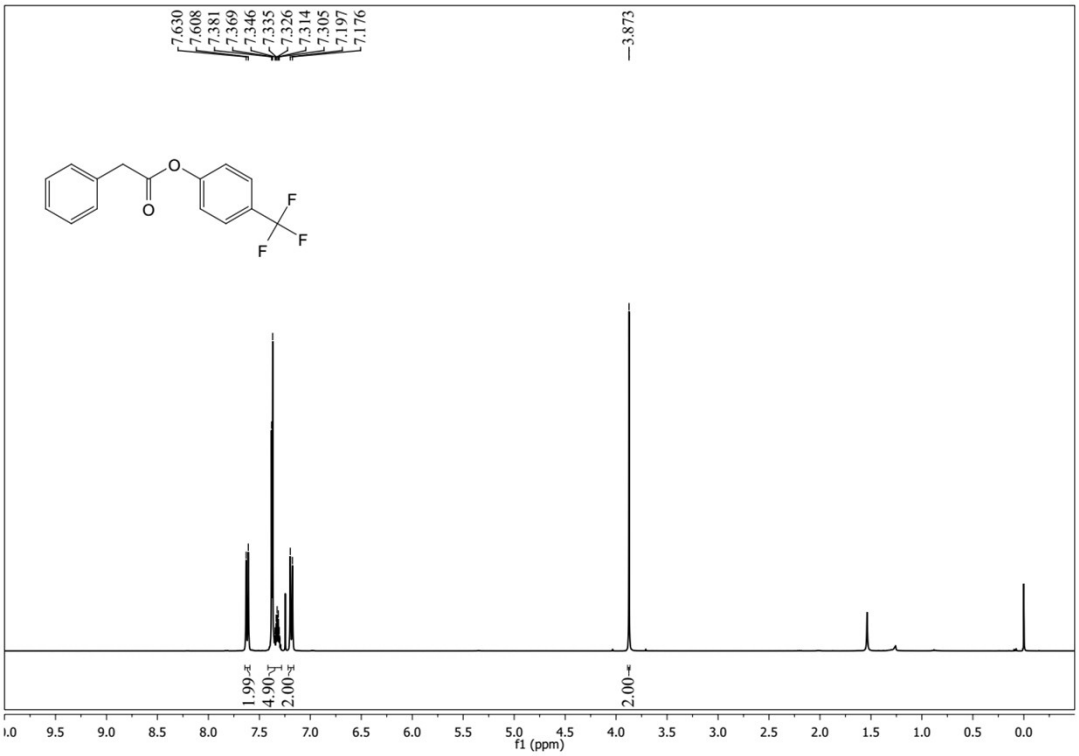


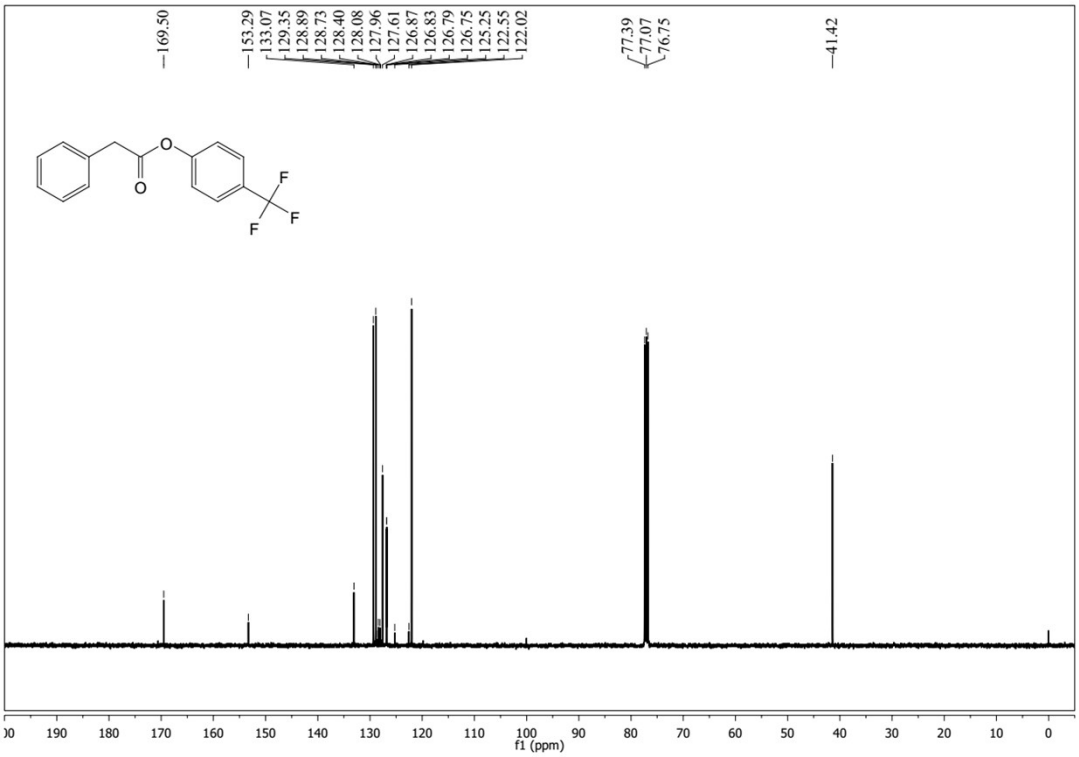
^{13}C NMR Spectra of 7as



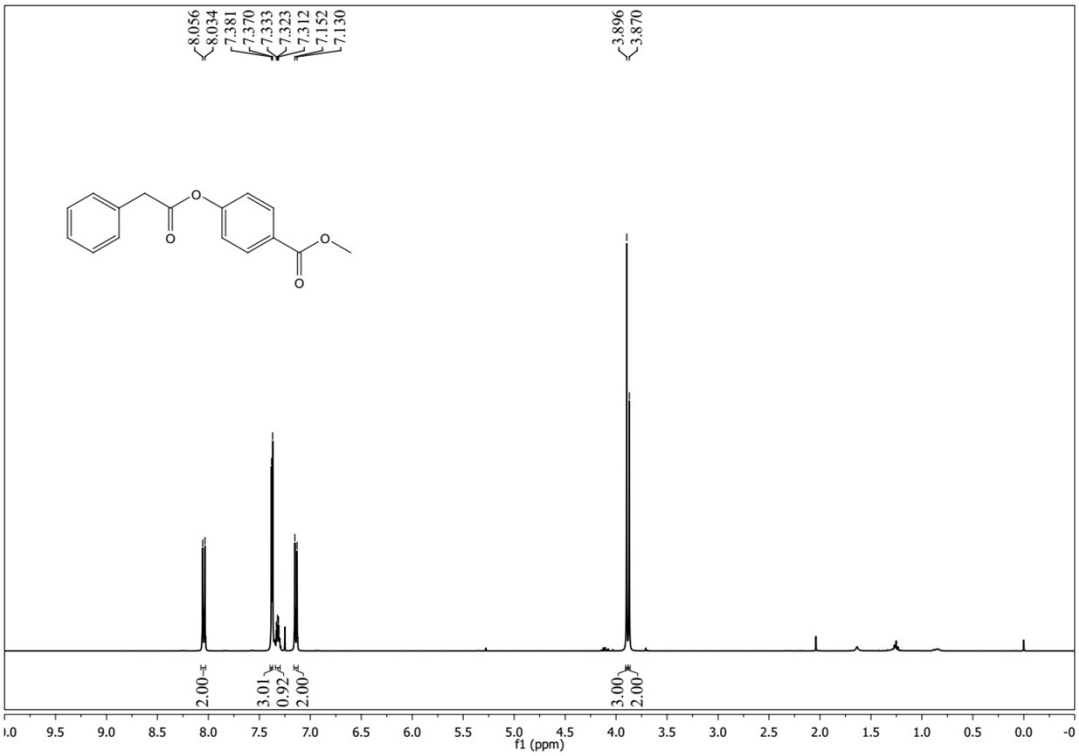
^{1}H NMR Spectra of 7at



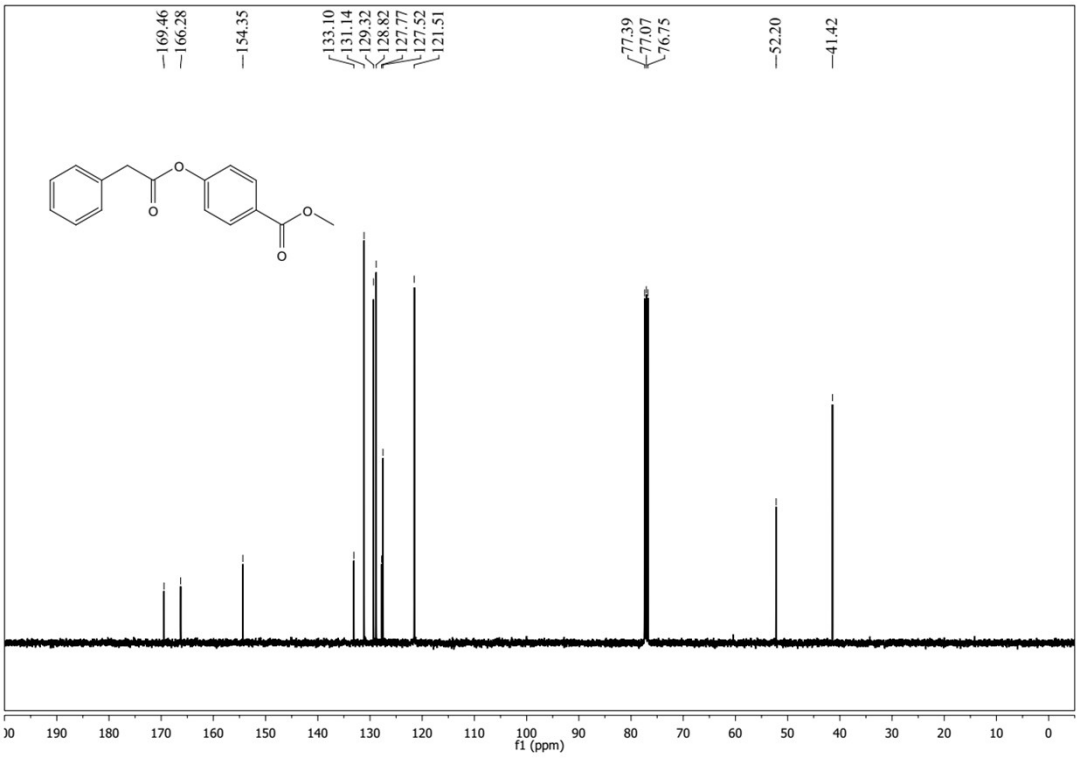
^{13}C NMR Spectra of 7at



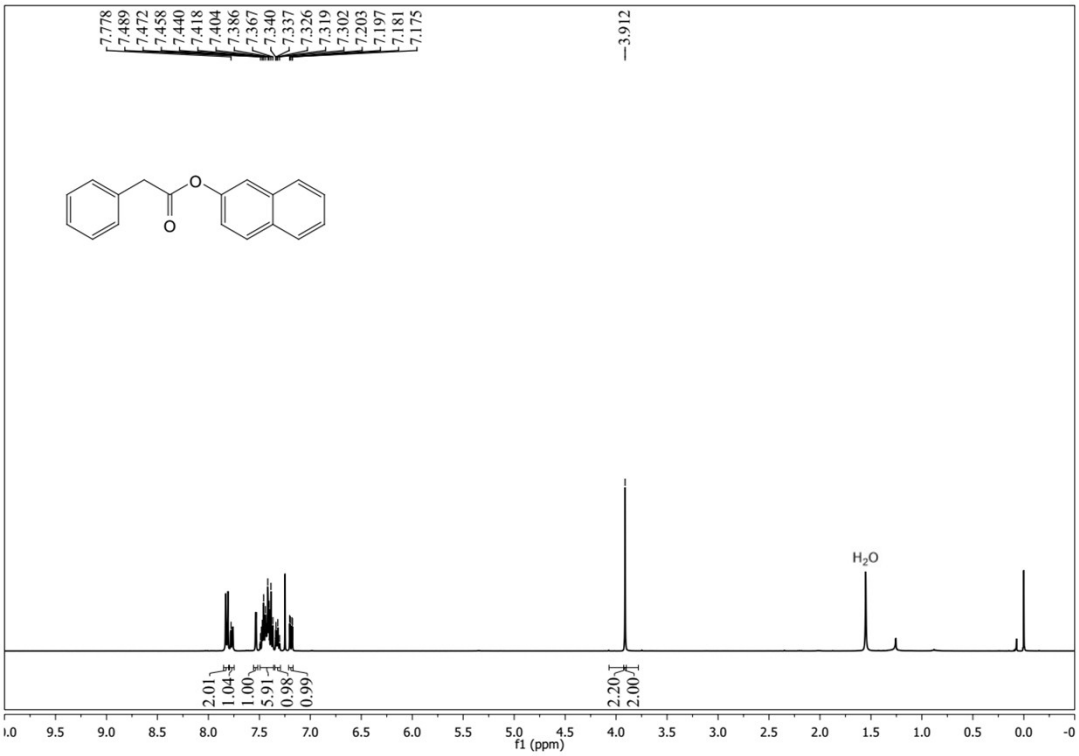
^{1}H NMR Spectra of 7au



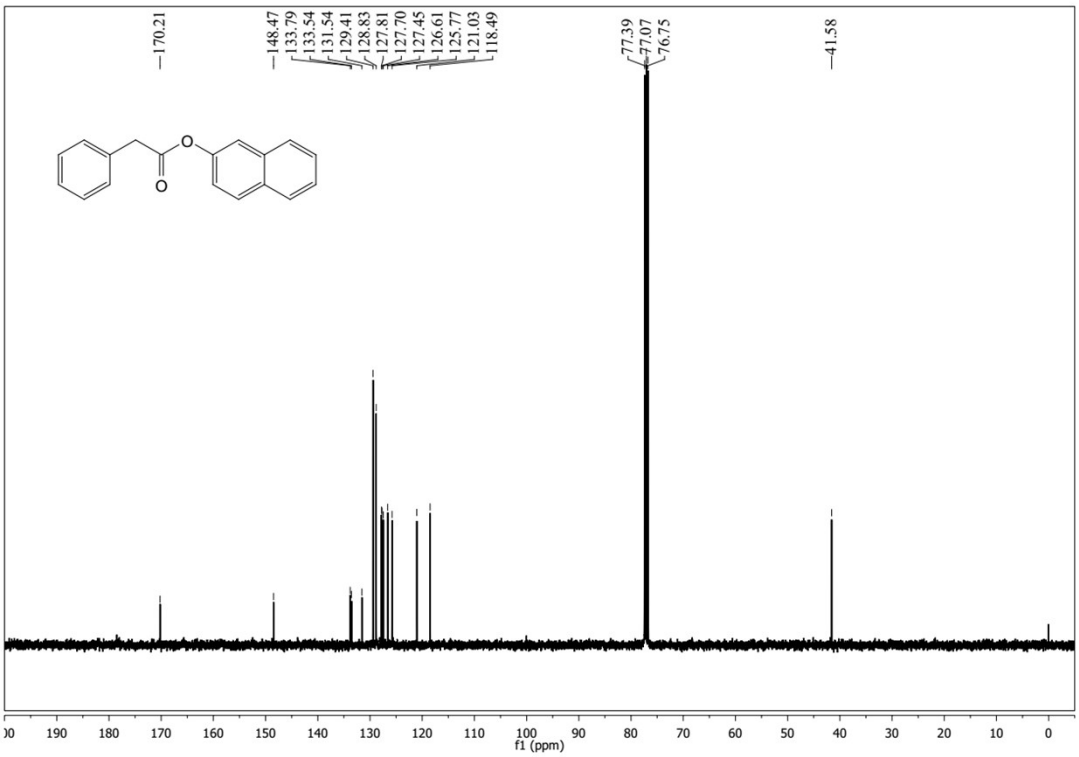
^{13}C NMR Spectra of 7au



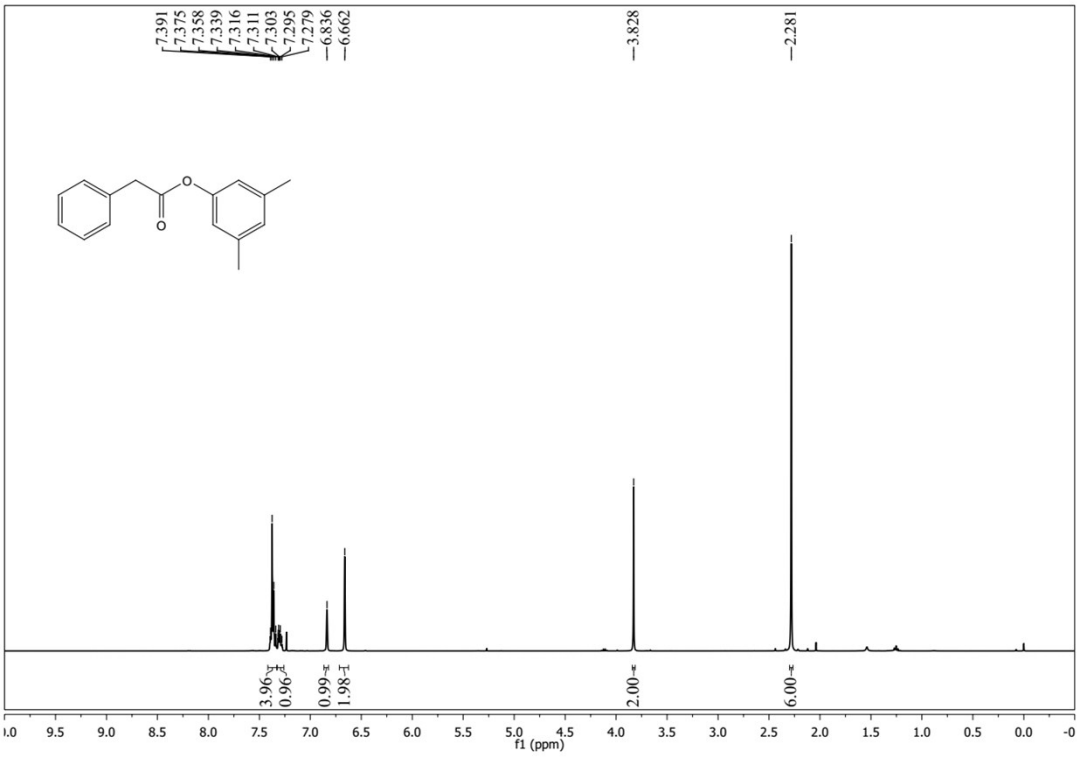
^{1}H NMR Spectra of 7av



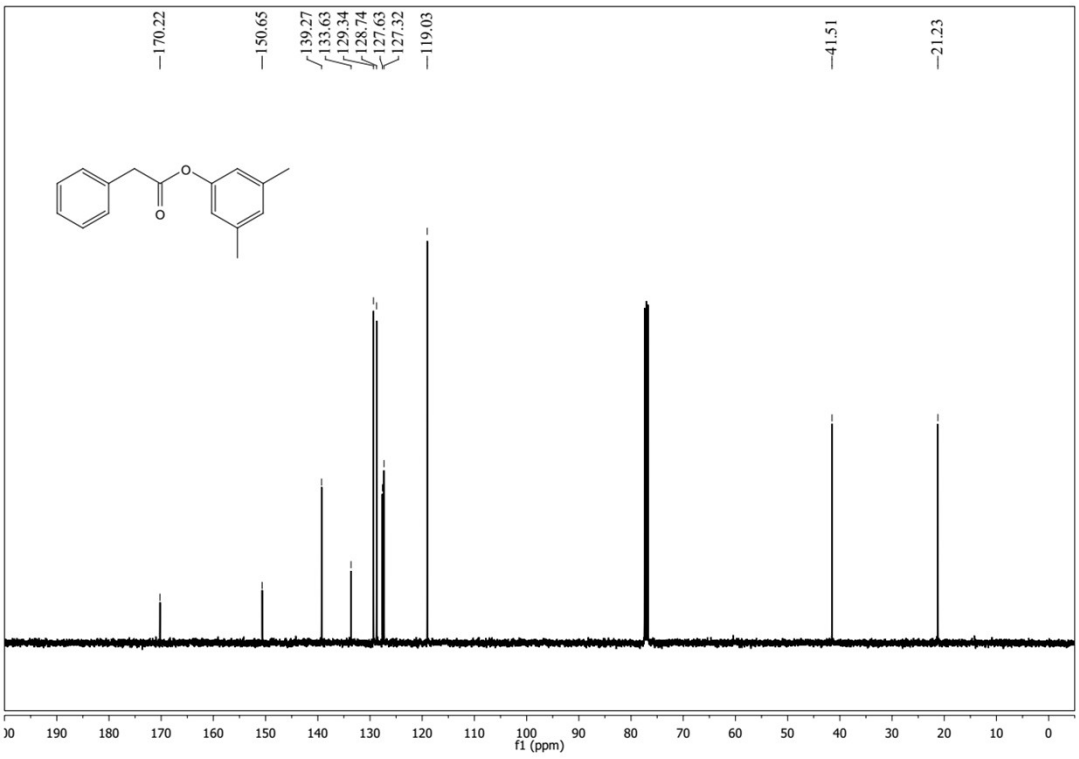
^{13}C NMR Spectra of 7av



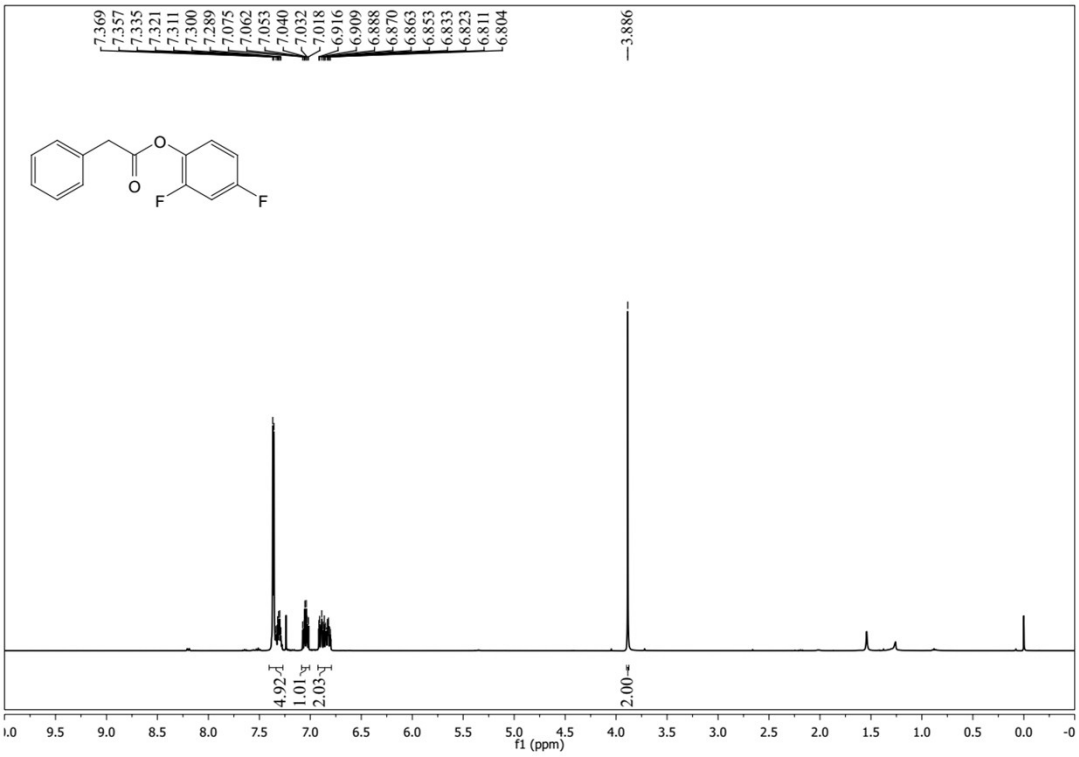
^{1}H NMR Spectra of 7aw



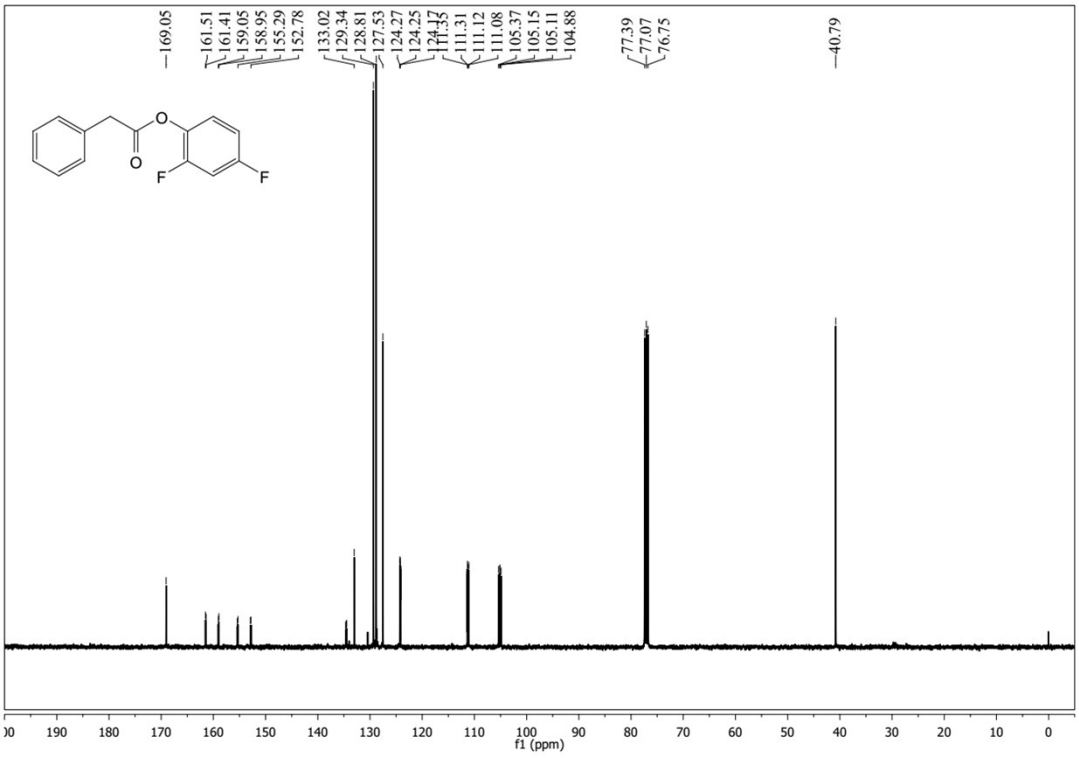
^{13}C NMR Spectra of 7aw



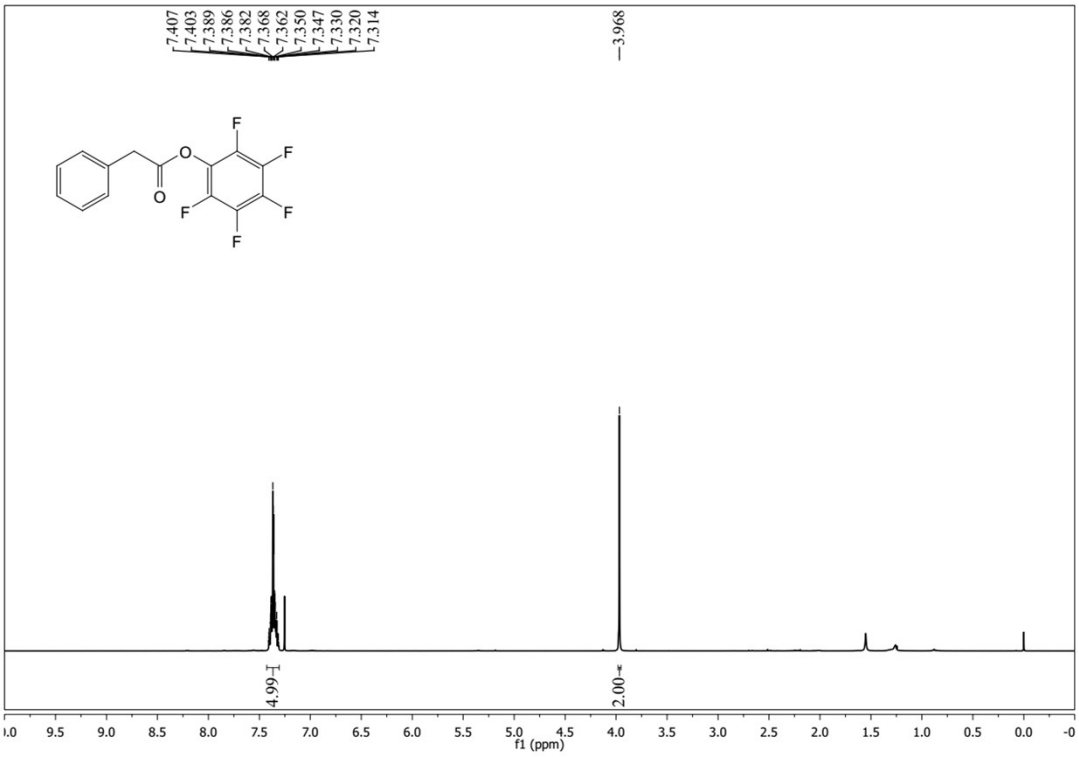
^{1}H NMR Spectra of 7ax



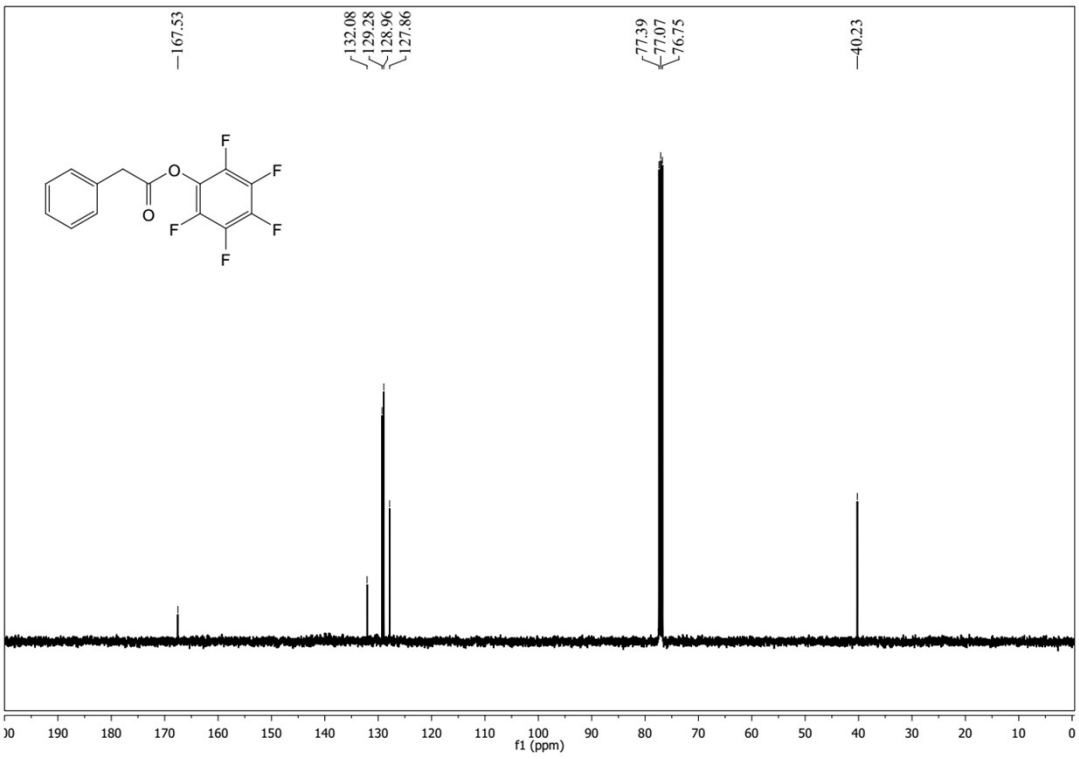
^{13}C NMR Spectra of 7ax

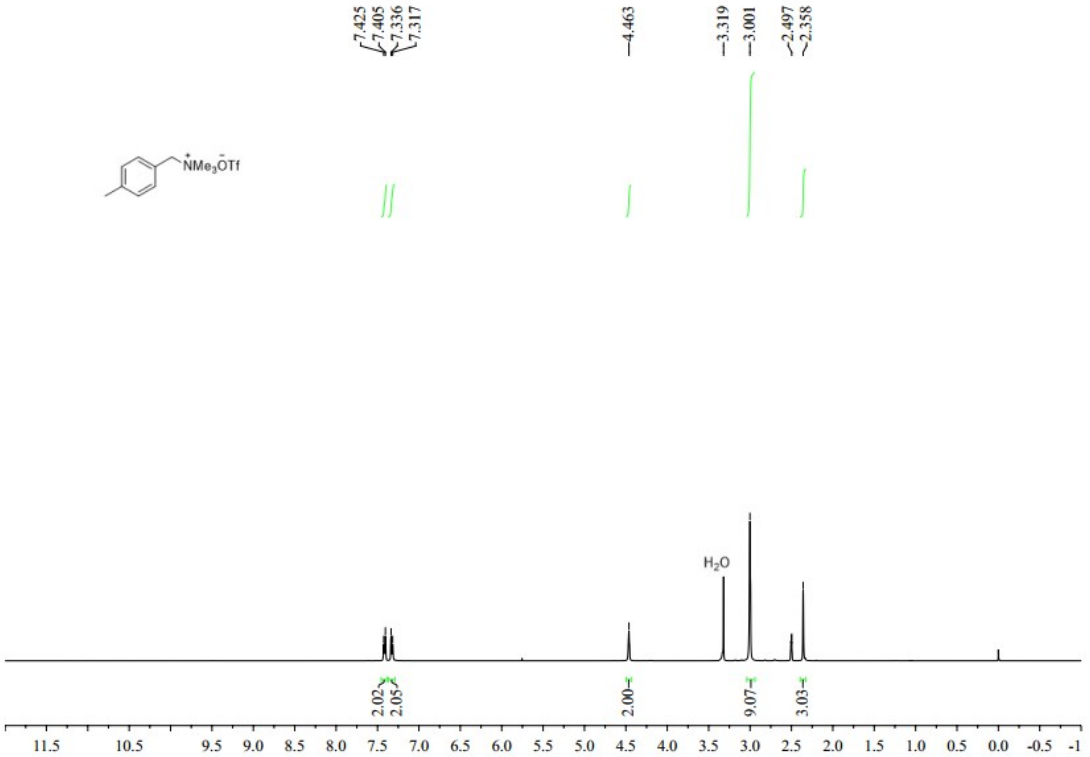


^{1}H NMR Spectra of 7ay



^{13}C NMR Spectra of 7ay

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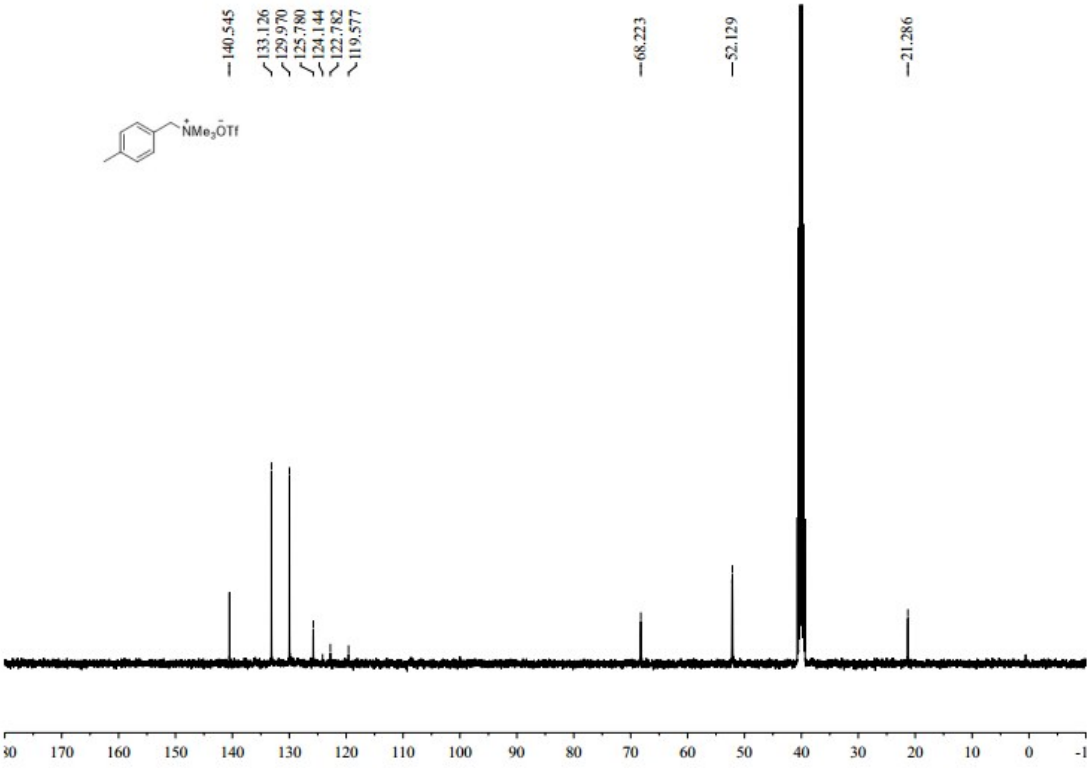
7.336
7.317
4.463
3.319
3.001
2.497
2.358
NMe3OTf
H2O
2.02
2.05
2.00
9.07
3.03
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1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133.126
129.970
125.780
124.144
122.782
119.577
68.223
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21.286
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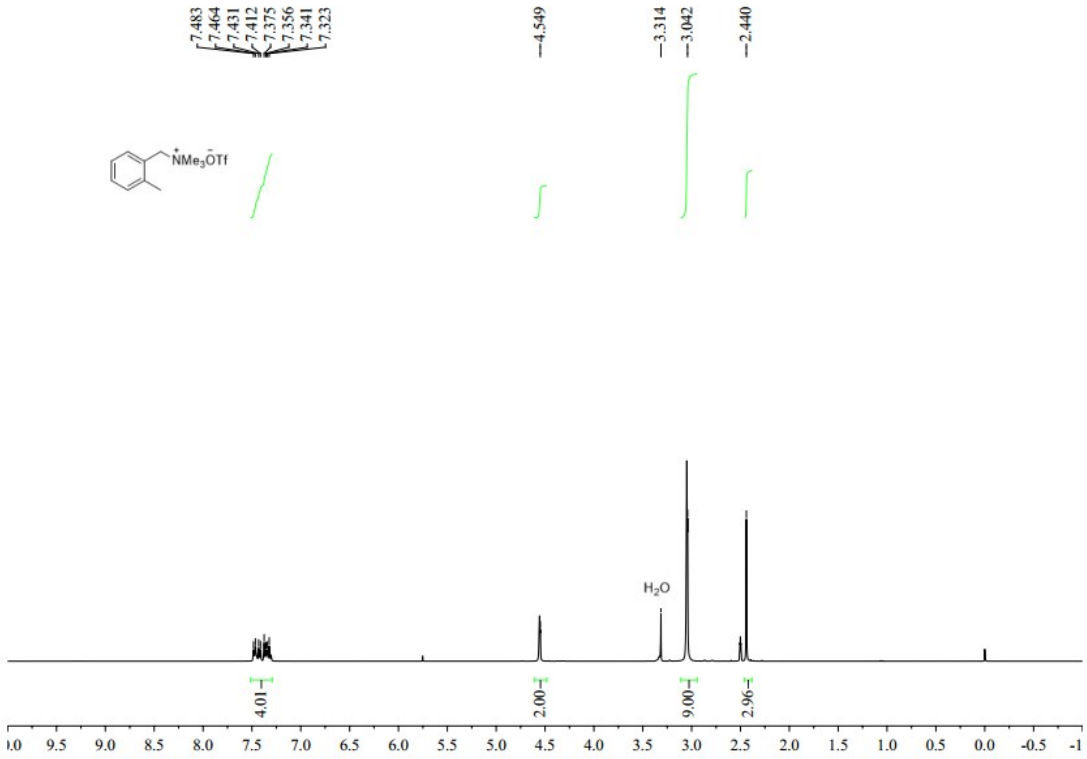
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1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7.464
7.431
7.412
7.375
7.356
7.341
7.323
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3.314
3.042
2.440
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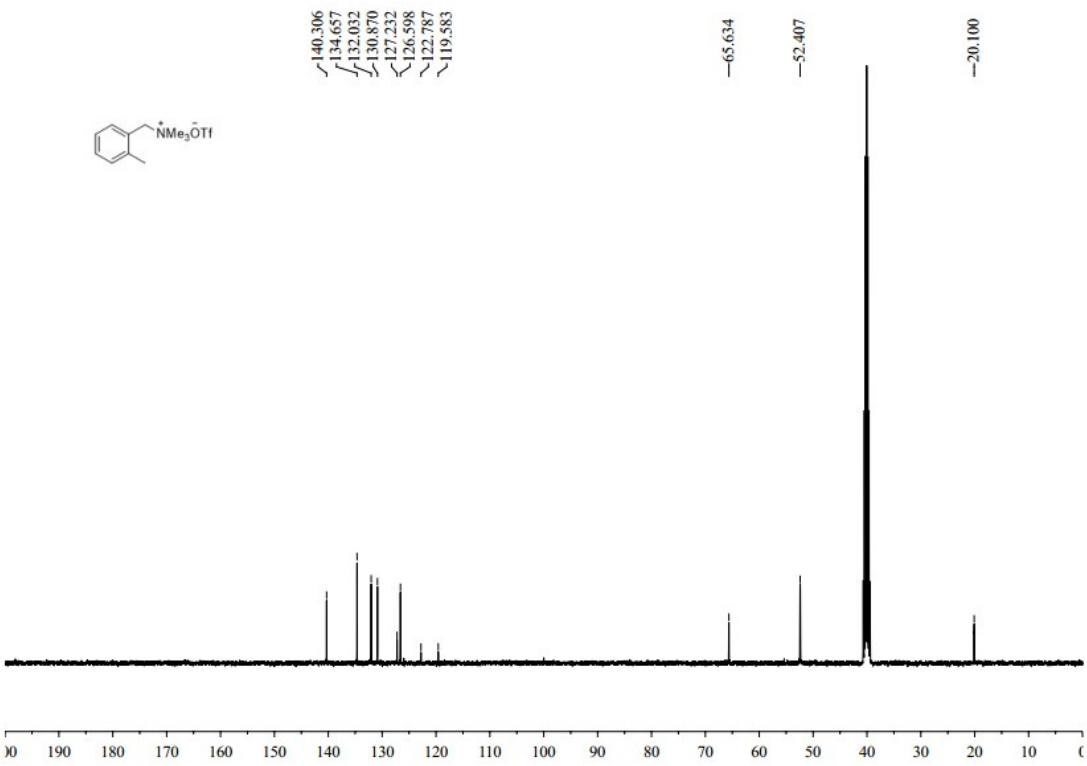
H2O
4.01
2.00
9.00
2.96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130.870
127.232
126.598
122.787
119.583
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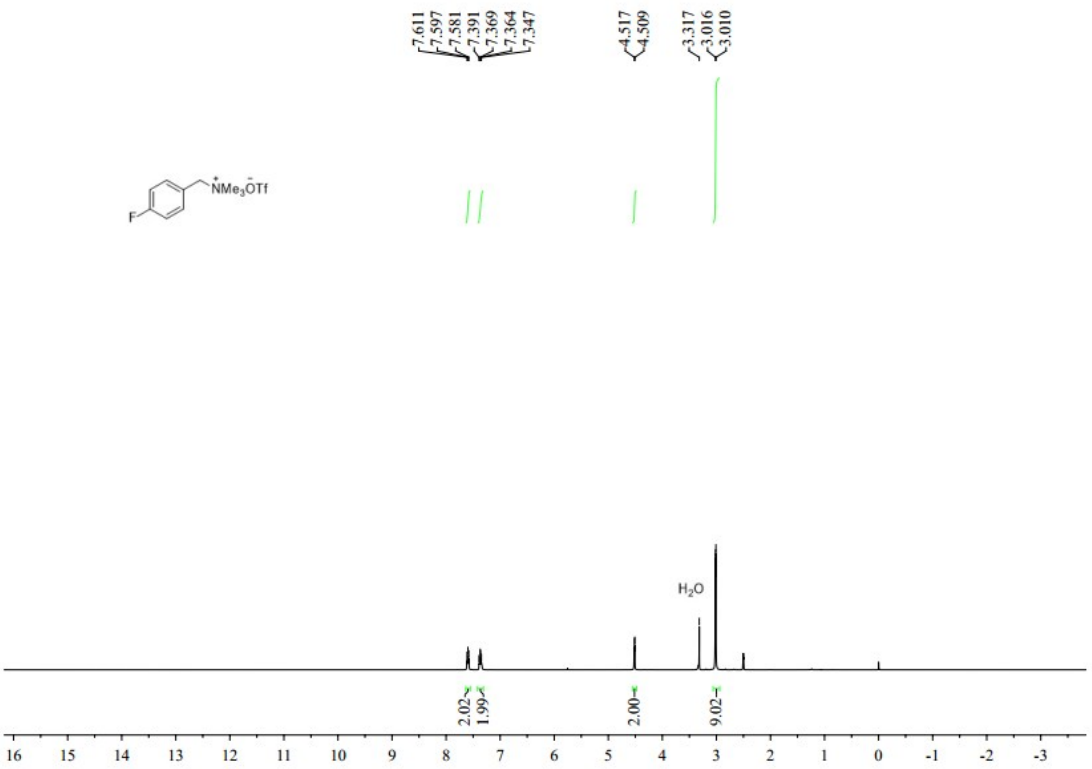
20.100
NMe3OTf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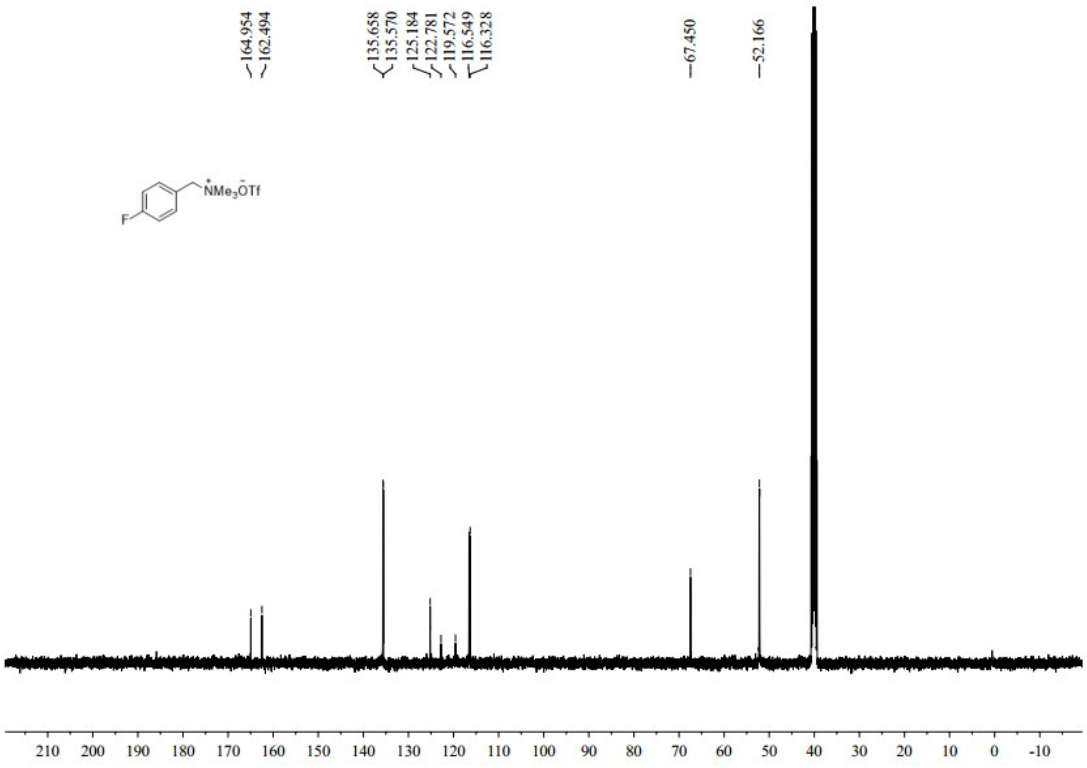
7.597
7.581
7.391
7.369
7.364
7.347
4.517
4.509
3.317
3.016
3.010
NMe3OTf
F
H2O
2.02
1.99
2.00
9.02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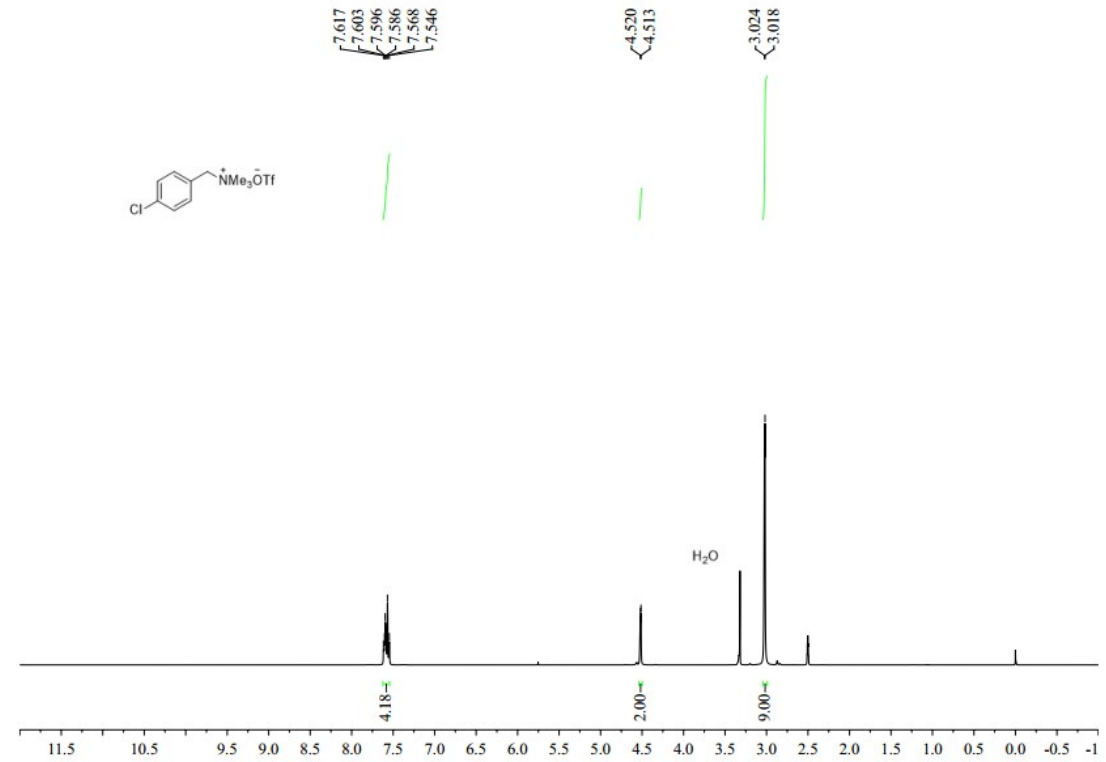
F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7.586
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3.024
3.018
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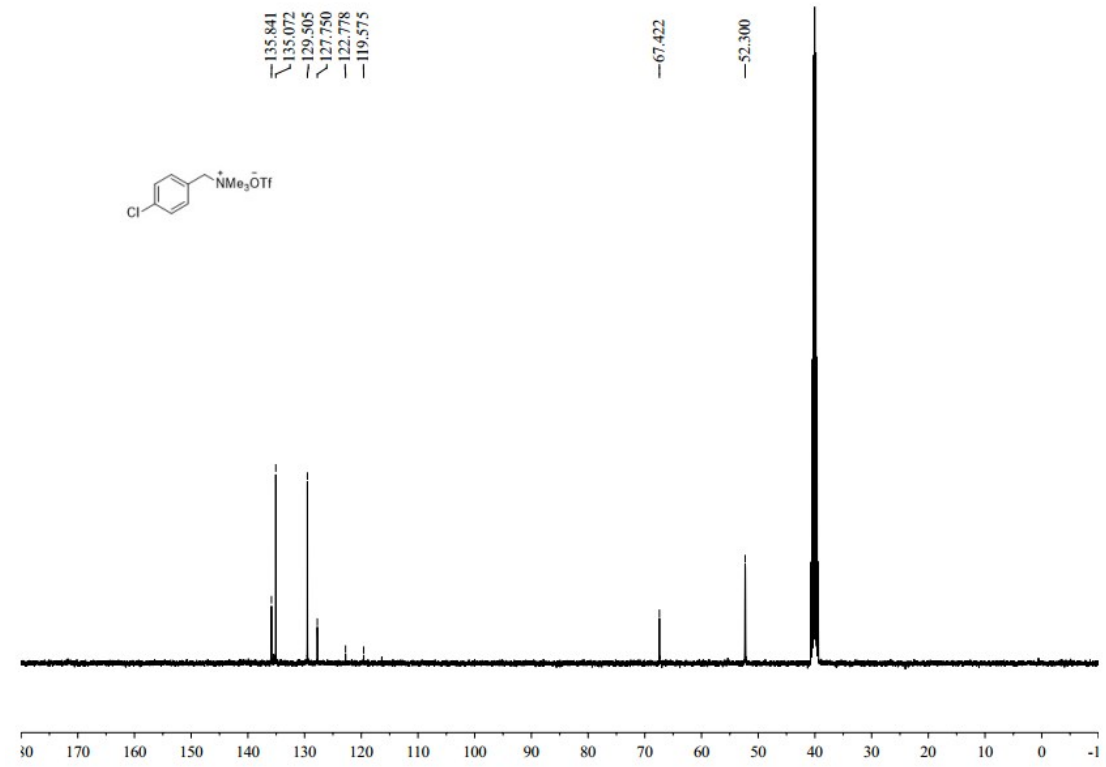
Cl
H2O
4.18
2.00
9.00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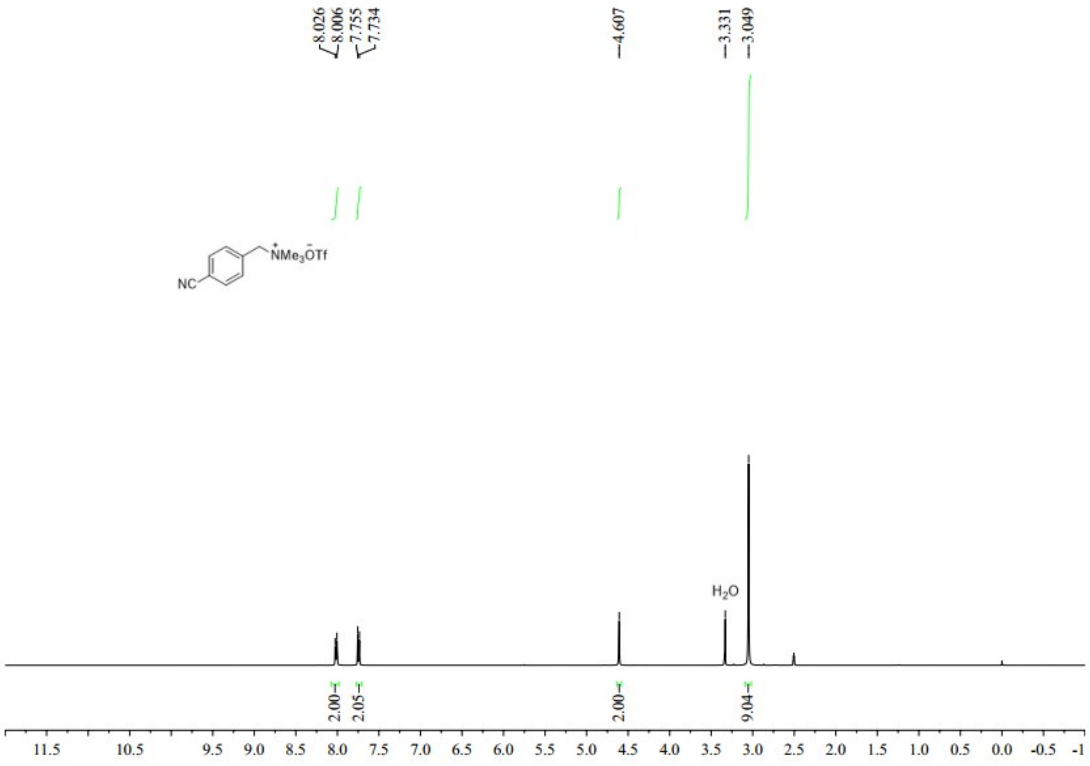
Cl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8.006
7.755
7.734
4.607
3.331
3.049
NC
NMe3OTf
H2O
2.00
2.05
2.00
9.04
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
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2.0
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1.0
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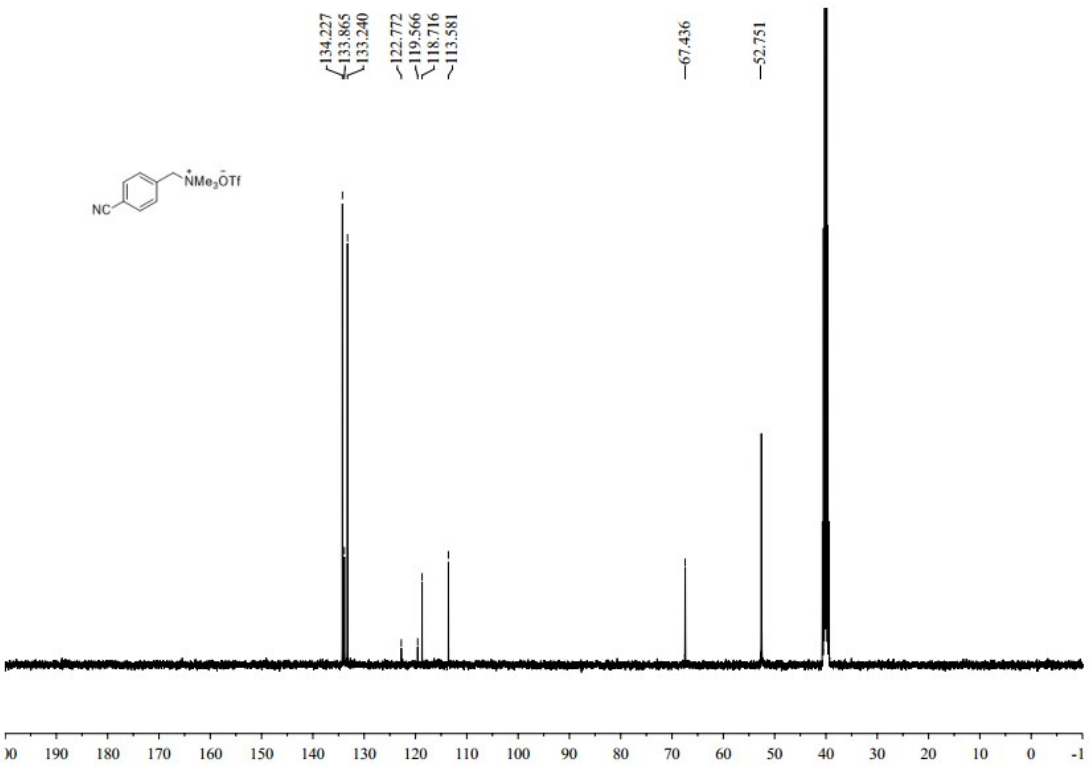
0.0
-0.5
-1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133.240
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113.581
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NC
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120
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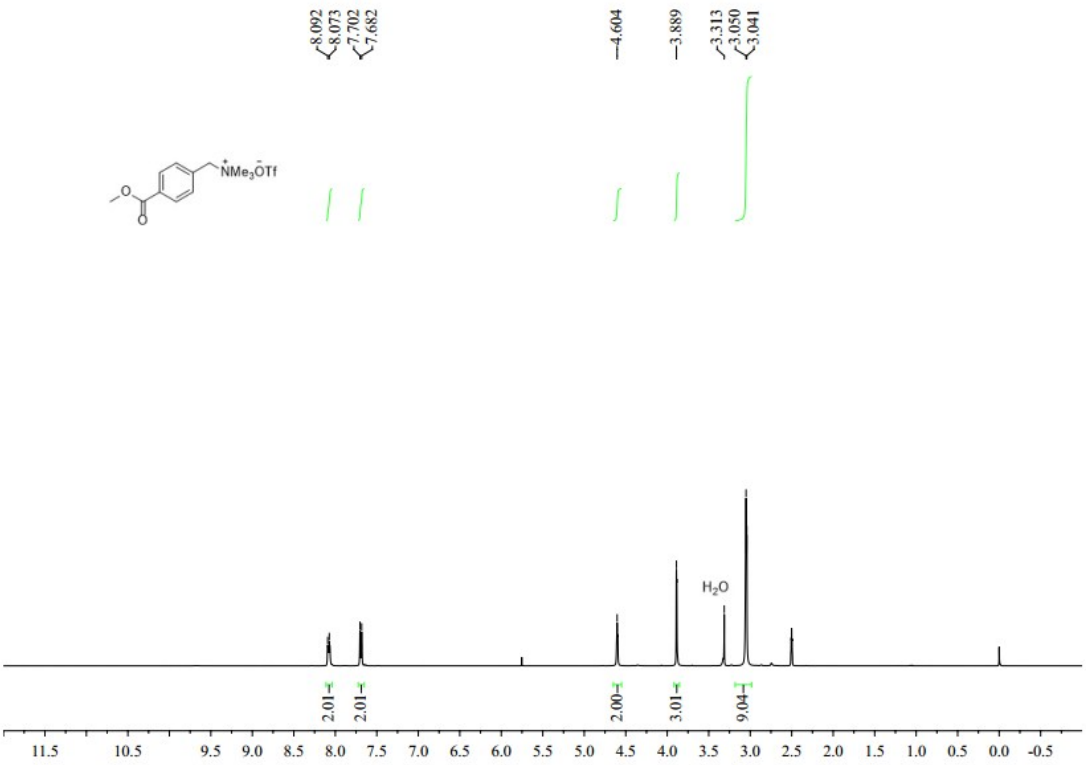
100
90
80
70
60
50
40
30
20
10
0
-1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7.702
7.682
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3.050
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NMe3OTf
H2O
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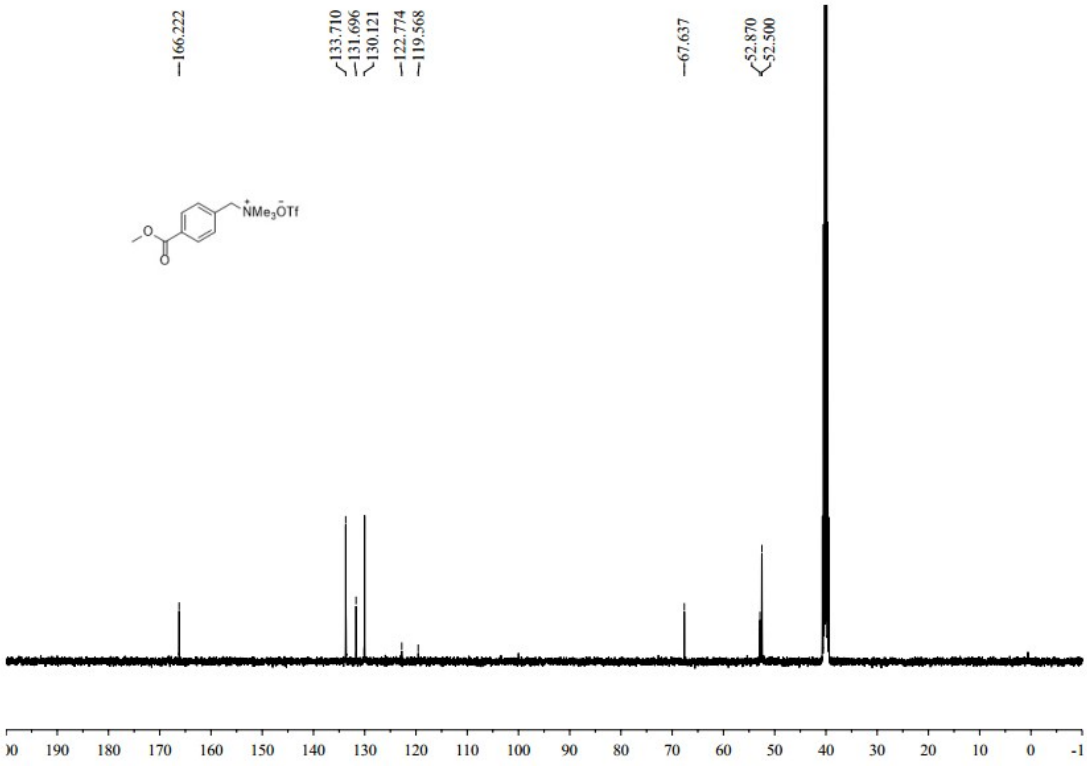
2.01
2.00
3.01
9.04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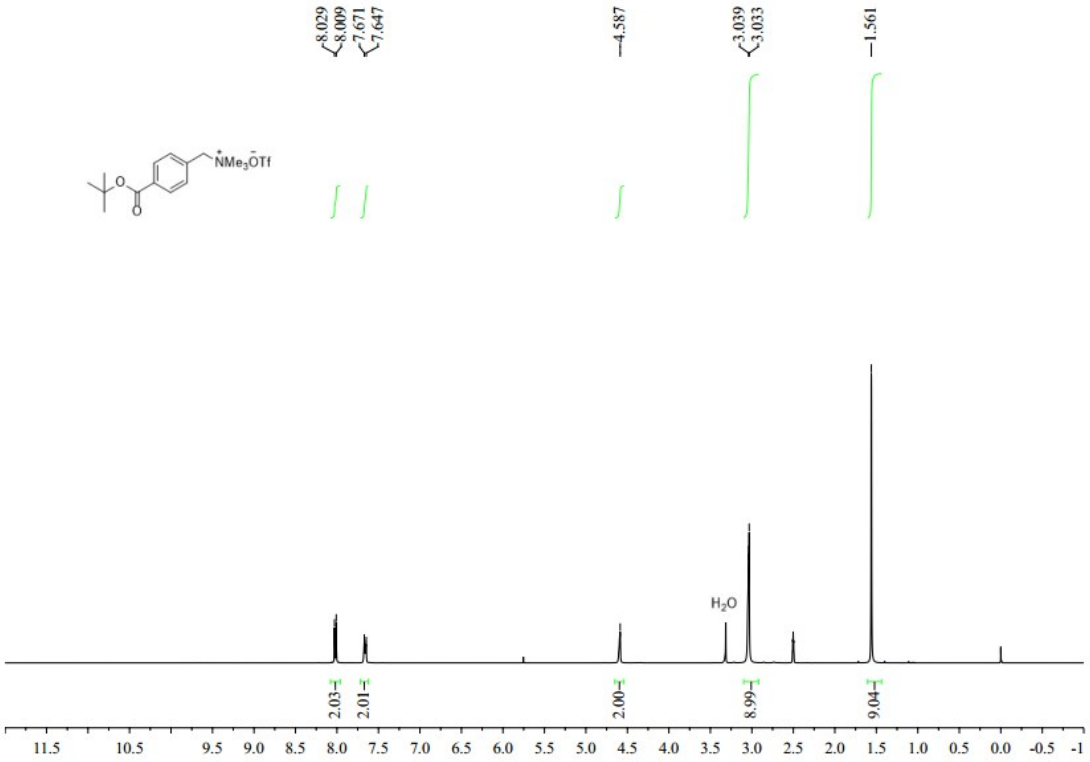
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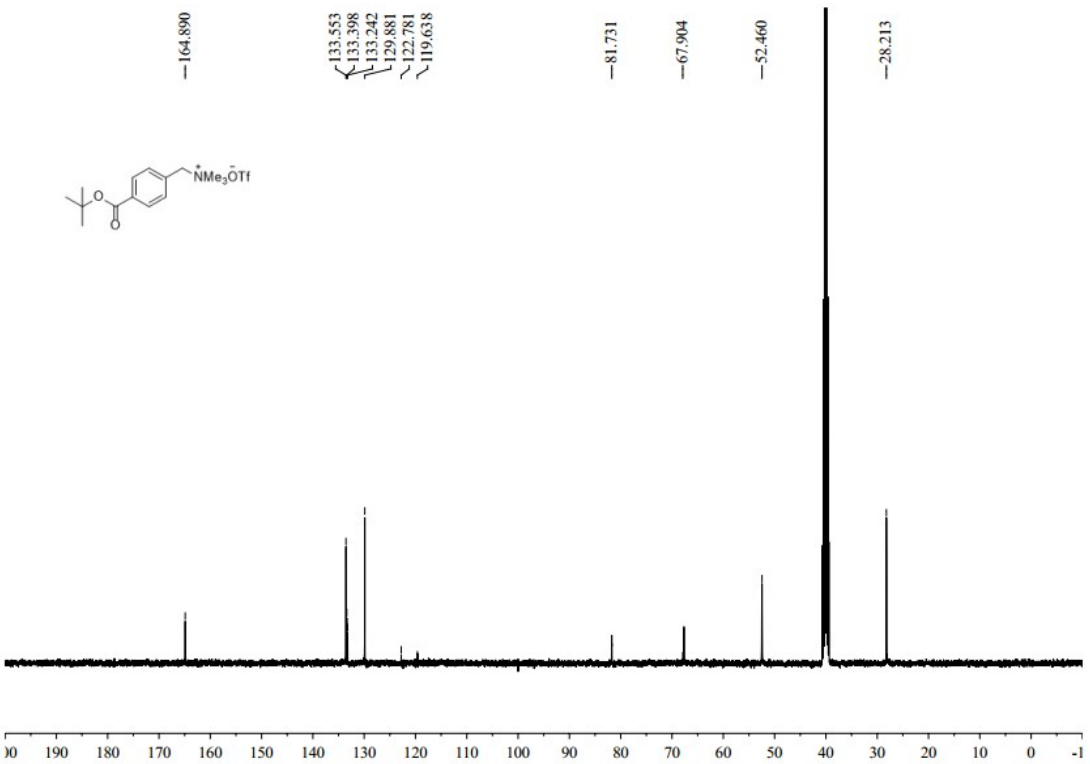
8.99
9.04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