Electronic Supplementary Information

Copper-Catalyzed *N*-Alkylation of Amides and Amines with Alcohols Employing the Aerobic Relay Race Methodology

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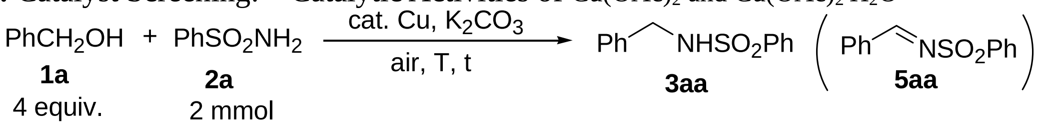
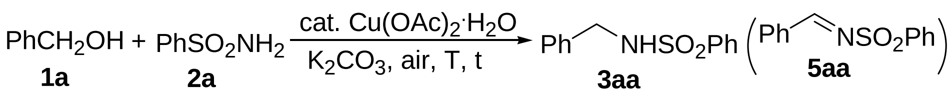
Table S1. Catalyst Screening:[a] Catalytic Activities of $Cu(OAc)_2$ and $Cu(OAc)_2 \cdot H_2O$



run	Cu (mol%)	K_2CO_3 (mol%)	T, t	**3aa%**[b]
1[c]	$Cu(OAc)_2$ (1)	20	150 °C, 12 h	>99
2[c]	$Cu(OAc)_2 \cdot H_2O$ (1)	20	150 °C, 12 h	>99
3[d]	$Cu(OAc)_2$ (5)	100	120 °C, 12 h	>99
4[d]	$Cu(OAc)_2 \cdot H_2O$ (5)	100	120 °C, 12 h	>99
5	$Cu(OAc)_2$ (5)	10	150 °C, 12 h	>99
6	$Cu(OAc)_2 \cdot H_2O$ (5)	10	150 °C, 12 h	>99

[a] Commercial **1a** without any treatment was used. [b] GC yield based on **2a**. [c] Repeating the literature condition (*Angew. Chem. Int. Ed.* **2009**, *48*, 5912; *Adv. Synth. Catal.* **2009**, *351*, 2949). [d] Our original condition (*Chin. Chem. Lett.* **2011**, *22*, 1021; *J. Org. Chem.* **2011**, *76*, 5759).

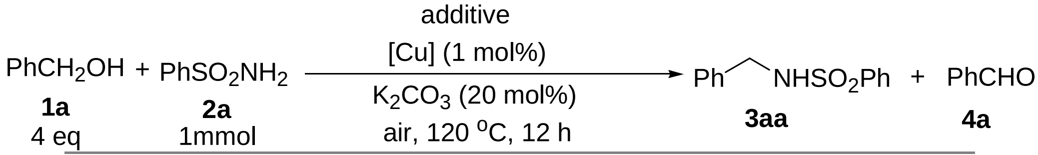
Table S2. Condition Screening and Optimization.



run	Cu (mol%)/**1a** (mol/mol)	K_2CO_3 (mol%)/**1a** (mol/mol)	T, t	**3aa%**[a]
1[b]	2, 0.0033	100, 0.167	120 °C, 12 h	70
2[b]	2, 0.0033	50, 0.083	120 °C, 12 h	56
3[c]	1, 0.0025	100, 0.25	120 °C, 12 h	97
4[c]	1, 0.0025	50, 0.125	120 °C, 12 h	89
5[c]	1, 0.0025	10, 0.025	120 °C, 12 h	31
6[c]	1, 0.0025	50, 0.125	135 °C, 12 h	99
7[c]	1, 0.0025	20, 0.05	135 °C, 12 h	77
8[c]	1, 0.0025	10, 0.025	135 °C, 12 h	41
9[c]	1, 0.0025	20, 0.05	150 °C, 12 h	99
10[c]	1, 0.0025	20, 0.05	150 °C, 12 h	99[e]
11[c]	1, 0.0025	10, 0.025	150 °C, 12 h	31[e]
12[d]	1, 0.0078	10, 0.077	135 °C, 24 h	89

[a] Commercial **1a** was directly used without further treatment. GC yield based on **2a**. Usually high **3aa**/**5aa** ratios (>99/1) were obtained. [b] Reactions with 6 mmol **1a** and 1 mmol **2a**. [c] Reactions with 4 mmol **1a** and 1 mmol **2a**. [d] Reactions with 2.6 mmol **1a** and 2 mmol **2a**. [e] Anhydrous $Cu(OAc)_2$ was used.

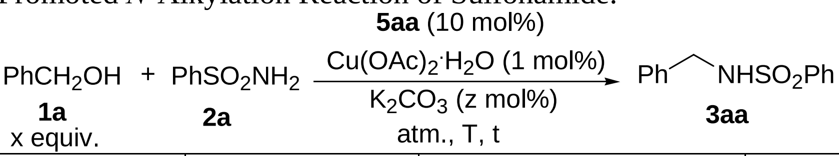
Table S3. Additive Effects on Cu-Catalyzed Aerobic *N*-Alkylation of Sulfonamide in the Presence of Large Excess Alcohol.[a]



Run	[Cu] (1 mol%)	additive (mol%)	**3aa**[b]	**4a**[b]
1		-	57	6
2[c]		O_2	30	34 (**5aa**, 29)
3	$Cu(OAc)_2{\cdot}H_2O$	Bipy (1 mol%)	71	6
4		Bipy (1 mol%) TEMPO (2 mol%)	99	12
5		Bipy (1 mol%)	ND	-
6	$Cu(OAc)_2{\cdot}H_2O$ (under N_2)	Bipy (1 mol%) TEMPO (2 mol%)	ND	-
7		-	Trace	-
8	$CuBr_2$	Bipy (1 mol%) TEMPO (2 mol%)	96	15
9		-	66	6
10	$CuCl_2{\cdot}2H_2O$	Bipy (1 mol%) TEMPO (2 mol%)	99	9
11		-	59	6
12	$Cu(NO_3)_2{\cdot}3H_2O$	Bipy (1 mol%) TEMPO (2 mol%)	99	12
13		-	ND	-
14	$CuSO_4$	Bipy (1 mol%) TEMPO (2 mol%)	83	8
15		-	44	5
16	CuI	Bipy (1 mol%) TEMPO (2 mol%)	88	9

[a] Absolute **1a** (100% GC purity) was used. [b] GC yield. [c] Reaction carried out under pure O_2 (1 atm.) in a 20 mL tube (ca. 90 mol% O_2).

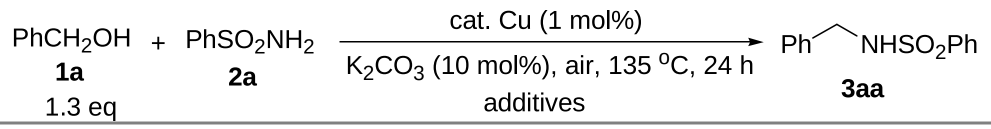
Table S4. Imine-Promoted *N*-Alkylation Reaction of Sulfonamide.[a]



Run	**1a** (equiv.)	K_2CO_3 (mol%)	atm., T, t	**3aa**%[a]
1	4	20	air, 120 ^oC, 12 h	72
2	4	20	N_2, 120 ^oC, 12 h	67
3	1.3	10	air, 135 ^oC, 24 h	91
4	1.3	10	N_2, 135 ^oC, 24 h	95

[a] Absolute **1a** (100% GC purity) was used.

Table S5. Additive Effects under the Optimized Reaction Condition (in the Presence of Reduced Alcohol Loadings).



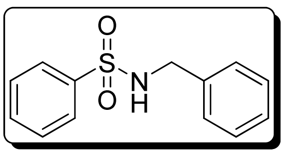
run	Cu	Additives (mol%)	**3aa**%[a] A (pure **1a**) [b]	C (2% **4a**)[c]
1	$Cu(OAc)_2 \cdot H_2O$	-	79	93
2	$Cu(OAc)_2 \cdot H_2O$	Bipy (1)	56	65
3	$Cu(OAc)_2 \cdot H_2O$	1,10-phenanthroline (1)	35	---------[d]
4	$Cu(OAc)_2 \cdot H_2O$	TEMPO (2)	---------	36
5	$Cu(OAc)_2 \cdot H_2O$	Bipy (1), TEMPO (2)	---------	70
6	$CuCl_2 \cdot 2H_2O$	-	63	---------
7	$CuCl_2 \cdot 2H_2O$	Bipy (1)	33	---------
8	$CuCl_2 \cdot 2H_2O$	1,10-phenanthroline (1)	42	---------
9	CuI	-	83[e,f]	
10	CuI	Bipy (1), TEMPO (2)	64[e]	

[a] GC yield based on **2a**. [b] Sample A of **1a**: Absolute **1a** (100% purity confirmed by GC) was used. [c] Sample C of **1a**: An older sample of **1a** (containing 2.28% PhCHO as detected by GC) was degassed and used. [d] The reactions were not conducted. [e] In 18 h. [f] No reaction occurred when the same reaction was run under nitrogen.

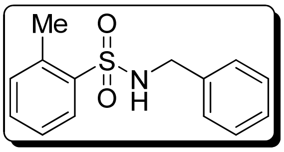
General. Substrates, bases and catalysts are all purchased. All reactions were carried out in sealed Schlenk tubes and monitored by TLC, GC-MS and/or ^{1}H NMR. Unless otherwise noted, substrates and catalysts were used as purchased without further purification and degassing in reactions carried out under air. As analyzed, samples of commercial benzyl alcohol are usually contaminated by trace amount of benzaldehyde. Thus, in control reactions and mechanistic studies where needed, absolute alcohols (freshly distilled from CaH_2, degassed and stored under N_2 in a Schlenk flask, 100% purity without any contaminants as confirmed by GC analysis) was used as noted. Products were purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluent. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-III 500 instrument (500 MHz for ^{1}H and 125.4 MHz for ^{13}C NMR spectroscopy). Unless otherwise noted, $CDCl_3$ was used as the solvent. Chemical shift values for ^{1}H and ^{13}C NMR were referred to internal Me_4Si (0 ppm). Mass spectra were measured on a Shimadzu GCMS-QP2010 Plus spectrometer (EI). HRMS (EI) analysis was performed by the Analytical Center at the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

Typical Procedure for Copper-Catalyzed Aerobic *N*-Alkylation of Amides and Amines with Alcohols. The mixture of benzenesulfonamide **2a** (0.471 g, 3.0 mmol), $Cu(OAC)_2 \cdot H_2O$ (0.006 g, 0.03 mmol, 1 mol%), and K_2CO_3 (0.042 g, 0.3 mmol, 10 mol%) in benzyl alcohol **1a** (0.39 mL, 3.9 mmol, 1.3 equiv.) was stirred at 135°C under air in a sealed 20 mL Schlenk tube and monitored by TLC and/or GC-MS. The reaction was then quenched with ethyl acetate and the crude product was purified by column chromatography with ethyl acetate and petroleum ether (60-90 ^{o}C) as eluent, giving *N*-benzylbenzenesulfonamide **3aa** in 78% isolated yield.

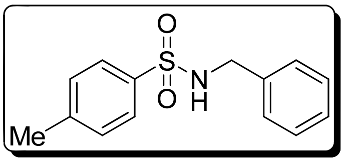
Characterization of Products:



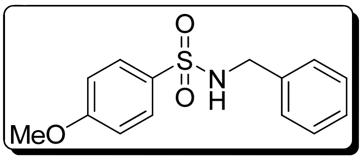
***N*-Benzylbenzenesulfonamide (3aa).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88-7.86 (m, 2H), 7.60-7.57 (m, 1H), 7.52-7.49 (m, 2H), 7.27-7.25 (m, 3H), 7.19-7.18 (m, 2H), 4.83 (b, 1H), 4.14 (d, J = 6.2 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 139.9, 136.3, 132.6, 129.1, 128.6, 127.84, 127.81, 127.1, 47.2. MS (EI): m/z (%) 246 (0.26), 143 (4.63), 141 (3.97), 125 (5.14), 106 (100), 104 (12), 91 (14), 79 (21), 78 (15), 77 (43), 65 (5), 51 (17). This compound was known. [1]



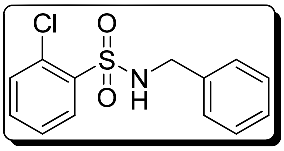
***N*-Benzyl-o-toluenesulfonamide (3ab).** White oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, J = 7.7 Hz, 1H), 7.48-7.45 (m, 1H), 7.34-7.27 (m, 5H), 7.17-7.15 (m, 2H), 4.67 (b, 1H), 4.12 (d, J = 6.1 Hz, 2H), 2.62 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 137.9, 137.1, 136.5, 132.7, 132.5, 129.4, 128.5, 127.8, 127.7, 126.1, 47.0, 20.2. MS (EI): *m/z* (%) 261 (0.13), 157 (2), 155 (1), 106 (100), 91 (50), 77 (12), 65 (18). This compound was known.[6]



***N*-Benzyl-*p*-toluenesulfonamide (3ac).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 8.1 Hz, 2H), 7.32-7.25 (m, 5H), 7.20-7.19 (m, 2H), 4.66 (b, 1H), 4.12 (d, J = 6.2 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 143.4, 136.9, 136.4, 129.7, 128.6, 127.8, 127.7, 127.2, 47.2, 21.5. MS (EI): *m/z* (%) 261 (0.1), 260 (0.2), 157 (3), 107 (10), 106 (100), 92 (13), 91 (39), 79 (17), 77 (11). This compound was known.[5]

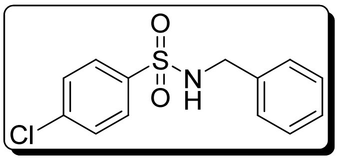


***N*-Benzyl-4-methoxybenzenesulfonamide (3ad).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, J = 8.9 Hz, 2H), 7.30-7.27 (m, 3H), 7.20-7.19 (m, 2H), 6.98 (d, J = 8.9 Hz, 2H), 4.57 (bt, J = 5.7 Hz, 1H), 4.12 (d, J = 6.2 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 163.0, 136.3, 131.5, 129.3, 128.7, 127.92, 127.89, 114.3, 55.6, 47.3. MS (EI): *m/z* (%) 277 (3), 212 (1), 171 (4), 155 (14), 127 (2), 123 (20), 108 (26), 106 (100), 91 (15), 79 (13), 77 (28), 64 (8). This compound was known.[5]

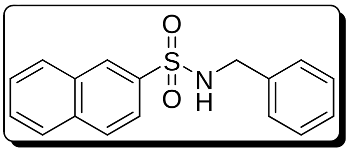


***N*-Benzyl-*2*-chlorobenzenesulfonamide (3ae).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, J = 8.1 Hz, 1H), 7.50-7.45 (m, 2H), 7.40-7.37 (m, 1H), 7.25-7.17 (m, 5H), 5.32 (b, 1H), 4.12 (d, J = 6.2 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 137.3, 135.7, 133.7, 131.5, 131.4, 131.2, 128.7, 128.0, 127.9, 127.2, 47.5. MS (EI): *m/z* (%) 281 (0.1), 280 (0.2), 176 (5), 159 (5), 111 (13), 106 (100), 104

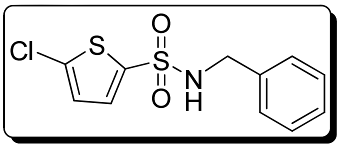
(15), 91 (17), 79 (18), 77 (18), 75 (10). This compound was known.[1]



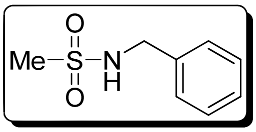
***N*-Benzyl-4-chlorobenzenesulfonamide (3af).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.78 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 4.3 Hz, 1H), 7.28-7.26 (m, 2H), 7.19-7.17 (m, 2H), 4.87 (bt, *J* = 5.8 Hz, 1H), 4.15 (d, *J* = 6.1 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): *δ* 139.1, 138.6, 136.0, 129.3, 128.7, 128.5, 127.90, 127.86, 47.2. MS (EI): *m/z* (%) 281 (0.1), 280 (0.2), 112 (6), 111 (16), 107 (8), 106 (100), 104 (15), 91 (15), 79 (19), 77 (15), 75 (10). This compound was known.[5]



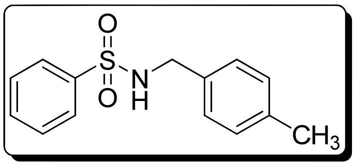
***N*-Benzyl-2-naphthalenesulfonamide (3ag).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 8.45 (b, 1H), 7.98-7.92 (m, 3H), 7.85-7.83 (m, 1H), 7.66-7.62 (m, 2H), 7.25-7.18 (m, 5H), 4.71 (bt, *J* = 5.8 Hz, 1H), 4.18 (d, *J* = 6.1 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): *δ* 136.7, 136.2, 134.8, 132.1, 129.5, 129.2, 128.8, 128.6, 128.5, 127.9, 127.8, 127.5, 122.3, 47.3. MS (EI): *m/z* (%) 298 (2), 297 (11), 192 (5), 175 (2), 144 (8), 128 (50), 127 (57), 115 (8), 106 (100), 91 (16), 79 (11), 77 (19). This compound was known.[5]



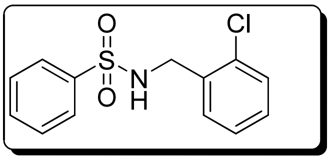
***N*-Benzyl-5-chlorothiophene-2-sulfonamide (3ah).** Yellow solid. ^{1}H NMR (500MHz, $CDCl_3$): *δ* 7.35-7.22 (m, 6H), 6.89 (d, *J* = 3.9 Hz, 1H), 5.03 (b, 1H), 4.21 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): *δ* 138.9, 137.4, 135.7, 131.7, 128.8, 128.1, 127.9, 126.7, 47.5. MS (EI): *m/z* (%) 287 (3), 252 (2), 222 (3), 181 (4), 165 (5), 133 (19), 118 (22), 106 (100), 91 (38), 79 (19), 51 (8). This compound was known.[1]



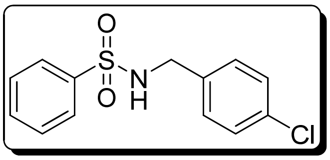
***N*-Benzylmethanesulfonamide (3ai).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.36-7.27 (m, 5H), 5.20 (b, 1H), 4.27 (d, *J* = 6.2 Hz, 2H), 2.80 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): *δ* 136.8, 128.8, 128.0, 127.9, 47.1, 40.9. MS (EI): *m/z* (%) 185 (1.2), 107 (8), 106 (100), 105 (18), 104 (44), 91 (29), 79 (31), 78 (12), 77 (20), 65(8), 51 (11). This compound was known.[1]



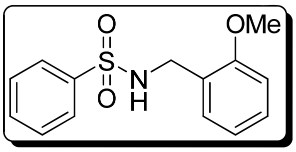
***N*-(4-Methylbenzyl)benzenesulfonamide (3ba).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89-7.87 (m, 2H), 7.61-7.58 (m, 1H), 7.54-7.51 (m, 2H), 7.10-7.06 (m, 4H), 4.58 (b, 1H), 4.11 (d, *J* = 6.1 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 143.5, 137.0, 136.3, 129.7, 128.7, 127.94, 127.89, 127.2, 47.3, 21.5. MS (EI): *m/z* (%) 261 (0.4), 246 (0.1), 195 (0.3), 165 (0.3), 143 (3), 125 (3), 120 (100), 118 (30), 105 (13), 91 (18), 77 (33), 65 (9), 63 (2), 51 (10). This compound was known.[10]



***N*-(2-Chlorobenzyl)benzenesulfonamide (3ca).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81-7.79 (m, 2H), 7.51-7.48 (m, 1H), 7.42-7.39 (m, 2H), 7.28-7.26 (m, 1H), 7.22-7.20 (m, 1H), 7.15-7.09(m, 2H), 5.48 (b, 1H), 4.24 (d, *J* = 6.5 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 140.0, 133.8, 133.3, 132.6, 130.1, 129.4, 129.2, 129.0, 126.99, 126.94, 45.0. MS (EI): *m/z* (%) 281 (0.25), 246 (1.73), 142 (32), 141 (15), 140 (100), 125 (17), 113 (7), 89 (5), 77 (47), 51 (14). This compound was known.[3]



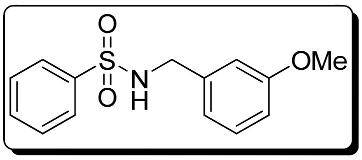
***N*-(4-Chlorobenzyl)benzenesulfonamide (3da).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84-7.82 (m, 2H), 7.59-7.56 (m, 1H), 7.50-7.47 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 5.17 (b, 1H), 4.10 (d, *J* = 6.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.9, 134.9, 133.7, 132.8, 129.21, 129.17, 128.8, 127.0, 46.6. MS (EI): *m/z* (%) 281 (0.09), 280 (0.11), 142 (32), 140 (100), 138 (13), 125 (18), 113 (8), 89 (6), 77 (46). This compound was known.[2]



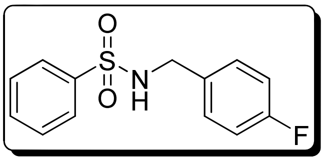
***N*-(2-Methoxybenzyl)-benzenesulfonamide (3ea).** White oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.60-7.57 (m, 1H), 7.52-7.49 (m, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.7

Hz, 2H), 4.76 (bt, J = 5.7 Hz, 1H), 4.07 (d, J = 6.1 Hz, 1H), 3.77 (s, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 159.4, 140.1, 132.7, 129.3, 129.1, 128.7, 128.2, 127.1, 114.1, 114.0, 55.3, 46.9. MS (EI): *m/z* (%) 277 (5), 137 (9), 136 (100), 134 (20), 121 (15), 119 (13), 107 (11), 91 (25), 77 (37), 51 (13). This compound was known.[9]

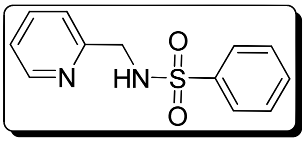
***N*-(4-Methoxybenzyl)benzenesulfonamide (3fa).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 7.2 Hz, 2H), 7.48-7.47 (m, 1H), 7.41-7.38 (m, 2H), 7.20-7.16 (m, 1H), 7.06-7.04 (m, 1H), 6.81-6.78 (m, 1H), 6.72 (d, J = 8.2 Hz, 1H), 5.14 (bt, J = 6.0 Hz, 1H), 4.17 (d, J = 6.4 Hz, 2H), 3.73 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 159.2, 140.0, 132.6, 129.2, 129.1, 128.3, 127.1, 114.0, 55.3, 46.7. MS (EI): *m/z* (%) 277 (5), 141 (2), 135 (100), 121 (29), 77 (26). This compound was known.[4]



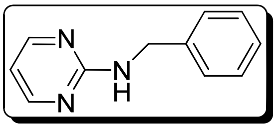
***N*-(3-Methoxybenzyl)benzenesulfonamide (3ga).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, J = 7.7 Hz, 2H), 7.54-7.51 (m, 1H), 7.45-7.42 (m, 2H), 7.12-7.09 (m, 1H), 6.63-6.69 (m, 3H), 5.41 (b, 1H), 4.07 (d, J = 6.4 Hz, 2H), 3.66 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 159.7, 140.0, 137.9, 132.6, 129.6, 129.1, 127.0, 120.0, 113.6, 113.1, 55.1, 47.1. MS (EI): *m/z* (%) 277 (14), 141 (4), 136 (100), 121 (8), 109 (16), 105 (19), 77 (26), 65 (7), 51 (10). This compound was known.[11]



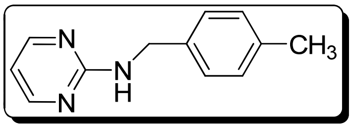
***N*-(4-Fluorobenzyl)benzenesulfonamide (3ha).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82-7.80 (m, 2H), 7.56-7.53 (m, 1H), 7.46-7.43 (m, 2H), 7.14-7.11 (m, 2H), 6.90-6.86 (m, 2H), 5.50 (b, 1H), 4.07 (d, J = 6.3 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 162.8 (d, $J_{C\text{-}F}$ = 246 Hz), 139.9, 132.7, 132.2 (d, $J_{C\text{-}F}$ = 2.5 Hz), 129.6 (d, $J_{C\text{-}F}$ = 8.75 Hz), 129.1, 127.0, 115.4 (d, $J_{C\text{-}F}$ = 21.3 Hz), 46.5. MS (EI): *m/z* (%) 264 (0.2), 143 (6), 124 (100), 109 (16), 97 (13), 77 (27), 51 (10). HRMS Calcd for $C_{13}H_{13}FNO_2S$ (M+H): 266.0646; found: 266.0637.



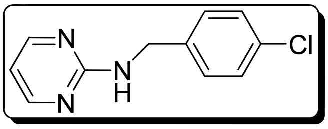
***N*-(2-Pyridylmethyl)benzenesulfonamide (3ia).** Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45 (d, J = 4.7 Hz, 1H), 7.86 (d, J = 7.5 Hz, 2H), 7.61-7.58 (m, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.15 (t, J = 6.7 Hz, 2H), 6.00 (s, 1H), 4.27 (d, J = 5.3 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 154.8, 149.0, 139.7, 136.8, 132.6, 129.0, 127.2, 122.7, 122.0, 47.4. MS (EI): *m/z* (%) 247 (0.5), 185 (6), 184 (45), 183 (27), 168 (3), 156 (2), 141 (13), 125 (2), 107 (100), 106 (55), 92 (13), 80 (29), 79 (57), 78 (32), 77 (76), 65 (9), 51 (42). This compound was known.[12]



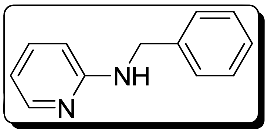
***N*-Benzyl-(2-pyrimidyl)amine (3aj).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, J = 4.5 Hz, 2H), 7.37-7.32 (m, 4H), 7.28-7.27 (m, 1H), 6.54 (t, J = 4.8 Hz 1H), 5.63 (b, 1H), 4.64 (d, J = 5.9 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 162.3, 158.1, 139.1, 128.6, 127.5, 127.3, 110.9, 45.5. MS (EI): *m/z* (%) 186 (12), 185 (90), 184 (63), 157 (5), 144 (3), 129 (3), 108 (19), 106 (100), 91 (47), 79 (40), 77 (13), 65 (28). This compound was known.[16]



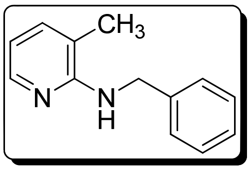
***N*-(4-Methylbenzyl)-(2-pyrimidyl)amine (3bj).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (s, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 6.53-6.51 (m, 1H), 5.68 (b, 1H), 4.59 (d, J = 5.8 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 162.4, 158.1, 136.9, 136.0, 129.3, 127.5, 110.76, 45.3, 21.1. MS (EI): *m/z* (%) 199 (100), 198 (52), 184 (62), 120 (50), 105 (46), 106 (26), 79 (34), 80 (15), 65 (7), 53 (12). This compound was known.[14]



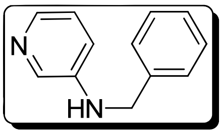
***N*-(4-Chlorobenzyl)-(2-pyrimidyl)amine (3dj).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, J = 4.5 Hz, 2H), 7.30–7.27 (m, 4H), 6.54 (t, J = 4.8 Hz, 1H), 5.88 (b, 1H), 4.61 (d, J = 6.1 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 162.3, 158.1, 137.8, 132.9, 128.8, 128.7, 111.0, 44.7. MS (EI): *m/z* (%) 221 (34), 220 (29), 219 (100), 184 (41), 142 (26), 141 (7), 140 (84), 125 (43), 108 (18), 89 (31), 80 (35), 63 (11), 53 (20). This compound was known.[12]



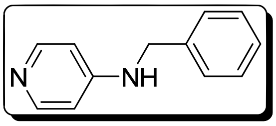
***N*-Benzyl-(2-pyridyl)amine (3ak).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, J = 4.5 Hz, 1H), 7.41-7.32 (m, 5H), 7.28-7.26 (m, 1H), 6.60-6.58 (m, 1H), 6.37 (d, J = 8.4 Hz, 1H), 4.87 (b, 1H), 4.51 (d, J = 5.8 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 158.7, 148.2, 139.2, 137.5, 128.6, 127.4, 127.2, 113.2, 106.8, 46.4. MS (EI): *m/z* (%) 184 (14), 183 (100), 153 (5), 127 (5), 116 (2), 106 (34), 79(11), 66 (4). This compound was known.[16]



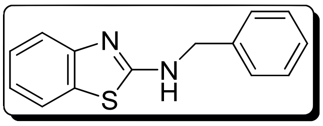
***N*-Benzyl-[2-(3-methylpyridyl)]amine (3al).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, J = 4.9 Hz, 1H), 7.39-7.32 (m, 4H), 7.28-7.22 (m, 2H), 6.55-6.53 (m, 1H), 4.68 (d, J = 5.3 Hz, 2H), 4.36 (b, 1H), 2.07 (s, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 156.7, 145.5, 140.1, 136.9, 128.6, 127.9, 127.2, 116.5, 112.9, 45.8, 16.95. MS (EI): *m/z* (%) 198 (83), 197 (25), 181 (5), 121 (10), 106 (100), 91 (39), 79 (11), 65 (29). This compound was known.[15]



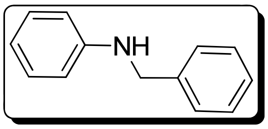
***N*-Benzyl-(3-pyridyl)amine (3am).** Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, J = 2.8 Hz, 1H), 7.96 (d, J = 4.7 Hz, 1H), 7.354-7.345 (m, 4H), 7.30-7.27 (m, 1H), 7.07-7.04 (m, 1H), 6.87 -6.85 (m, 1H), 4.33 (d, J = 5.4 Hz, 2H), 4.18 (b, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 144.0, 138.9, 138.5, 136.1, 128.8, 127.6, 127.4, 123.5, 118.7, 47.9. MS (EI): *m/z* (%) 184 (38), 183 (5), 92 (9), 91 (100), 78 (7), 77 (2), 65 (13), 51 (6). This compound was known.[7]



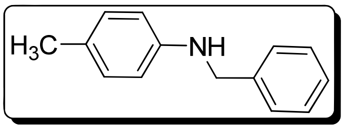
***N*-Benzyl-(4-pyridyl)amine (3an).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, J = 6.1 Hz, 2H), 7.38-7.29 (m, 5H), 6.47 (d, J = 6.2 Hz, 2H), 4.73 (b, 1H), 4.37 (d, J = 5.3 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 153.2, 150.0, 136.5, 133.4, 129.0, 128.5, 107.8, 46.2. MS (EI): *m/z* (%) 185 (5), 184 (40), 154(0.7), 128 (1), 107 (7), 105 (6), 92 (8), 91 (100), 78 (11), 65 (16), 51 (12). This compound was known.[17]



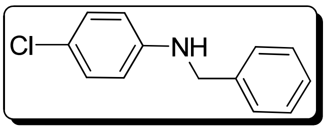
***N*-Benzylbenzo[*d*]thiazol-2-amine (3ao).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 8.1 Hz, 1H),7.40-7.35 (m, 4H), 7.32-7.28 (m, 2H), 7.11-7.07 (m, 1H), 5.72 (b, 1H), 4.65 (s, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 167.2, 152.4, 137.5, 130.6, 128.9, 127.9, 127.7, 126.0, 121.8, 120.8, 119.2, 49.4. MS (EI): *m/z* (%) 242 (3) 241 (8), 240 (46), 239 (25), 212 (4), 163 (3), 136 (15), 106 (27), 92 (8), 91 (100), 65 (25), 51 (4).This compound was known.[8]



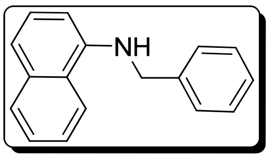
***N*-Benzylaniline (3ap).** Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-7.32 (m, 4H), 7.28-7.26 (m, 1H), 7.19-7.16 (m, 2H), 6.73-6.70 (m, 1H), 6.65-6.63 (m, 2H), 4.33 (s, 2H), 4.04 (b, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 148.1, 139.4, 129.3, 128.6, 127.5, 127.2, 117.6, 112.9, 48.4. MS (EI): *m/z* (%) 183 (56), 182 (21), 106 (22), 104 (11), 92 (9), 91 (100), 77 (18), 65 (15), 51 (7). This compound was known.[17]



***N*-Benzyl-4-methylaniline (3aq).** Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47-7.37 (m, 5H), 7.10-7.08 (m, 2H), 6.67-6.65 (m, 2H), 4.39 (s, 2H), 3.97 (b, 1H), 2.35 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 146.1, 139.8, 129.9, 128.7, 127.6, 127.3, 126.8, 113.1, 48.7, 20.5. MS (EI): *m/z* (%) 197 (66), 196 (26), 120 (26), 106 (5), 92 (9), 91 (100), 89 (3), 79 (4), 78 (3), 65 (14), 51 (3). This compound was known.[17]



***N*-Benzyl-4-chloroaniline (3ar).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.30 (m, 5H), 7.14 (d, J = 8.4 Hz, 2H), 6.58-6.55 (m, 2H), 4.32 (s, 2H), 4.08 (b, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.6, 138.9, 129.0, 128.7, 127.4, 127.1, 113.9, 48.3. MS (EI): *m/z* (%) 218 (8), 217 (39), 216 (7), 111 (5), 92 (8), 91 (100), 75 (4), 65 (11), 51 (3). This compound was known.[17]



***N*-Benzylnaphthalen-1-amine (3as).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84-7.80 (m, 2H), 7.47-7.30 (m, 9H), 6.64 (d, J = 7.5 Hz, 1H), 4.71 (b, 1H), 4.51 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.2, 139.1, 134.3, 128.73, 128.71, 127.7, 127.4, 126.6, 125.7, 124.8, 123.4, 119.9, 117.6, 104.8, 48.6. MS (EI): *m/z* (%) 234 (20), 233(98), 232 (23), 154 (5), 142 (24), 127 (11), 115 (41), 101 (2), 91 (100), 77 (5), 65 (11), 51 (2). This compound was known.[18]

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Elementary Reactions and Mechanistic Studies

Table S6. Cu-Mediated Alcohol Oxidation.

$$\underset{\substack{\textbf{1a}\\ \text{4mmol}}}{PhCH_2OH} \xrightarrow[K_2CO_3,\ N_2/air, T, t]{\text{cat. Cu}} \underset{\textbf{4a}}{PhCHO} + \underset{\textbf{6a}}{PhCH_2OAc}$$

Run	Cu (mol%)	K_2CO_3 (mol%)	condition	**4a**%[a]	**6a**%[a]
1	$Cu(OAC)_2{\cdot}H_2O$ (5)	-	N_2, 120 °C, 6 h	NR	
2	$Cu(OAC)_2{\cdot}H_2O$ (5)	50	N_2, 120 °C, 12 h	NR	
3	$Cu(OAC)_2{\cdot}H_2O$ (5)	-	air, 120 °C, 6 h	2.8	
4	$Cu(OAC)_2{\cdot}H_2O$ (5)	50	air, 120 °C, 6 h 12 h	4.4 5.8	
5	$Cu(OAC)_2{\cdot}H_2O$ (5)	-	N_2, 150 °C, 6 h 12 h	2.3 2.4	 13
6	$Cu(OAC)_2{\cdot}H_2O$ (5)	-	N_2, 180 °C, 6 h 12 h	2.8 2.7	 10
7	$Cu(OAC)_2{\cdot}H_2O$ (10)	-	N_2, 150 °C, 6 h 12 h	5 4 (4)	17 18 (13)
8	$Cu(OAC)_2{\cdot}H_2O$ (20)	-	N_2, 150 °C, 6 h 12 h	5.4 5.5 (8)	33 39 (33)
9	CuI (10)	-	N_2, 150 °C, 6 h	NR	
10	CuI (20)	-	N_2, 150 °C, 6 h	NR	
11	CuI (50)	-	N_2, 150 °C, 6 h	NR	

[a] Absolute **1a** was used. GC yield (NMR yield in parenthesis).

Table S7. Cu-Promoted Condensation of Sulfonamides with Aldehydes.[a]

$$\underset{\substack{\textbf{2a}\\ \text{1 mmol}}}{PhSO_2NH_2} + \underset{\substack{\textbf{4a}\\ \text{6 equiv.}}}{PhCHO} \xrightarrow[K_2CO_3,\ atm., T, t]{\text{cat. } Cu(OAc)_2{\cdot}H_2O} \underset{\textbf{5aa}}{PhSO_2N{=}CH_2Ph}$$

run	[Cu] (mol%)	K_2CO_3（mol%）	condition	**5aa** yield (%)[b]
1	-	-	N_2, 120 °C, 8 h	65
2	5	-	N_2, 120 °C, 4 h	95
3	5	-	air, 120 °C, 4 h 8 h	87 96
4	-	100	N_2, 120 °C, 8 h	78
5	-	100	air, 120 °C, 4 h 8 h	84 93

[a] Newly distilled **4a** was used. [b] GC yield based on **2a**.

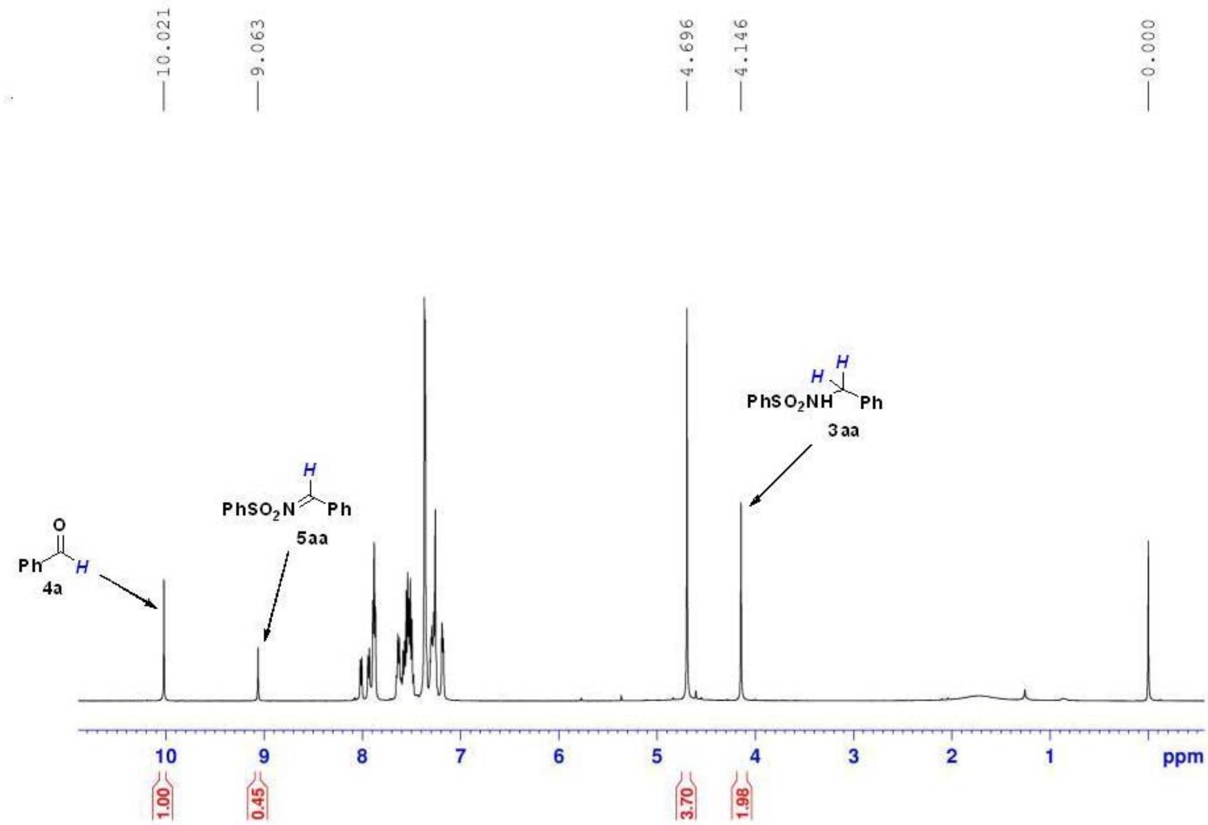
Table S8. Cu-Catalyzed Transfer Hydrogenation.

$$\underset{\substack{\textbf{1a}\\ x\ \text{equiv.}}}{PhCH_2OH} + \underset{\textbf{5aa}}{PhSO_2N{=}CHPh} \xrightarrow[K_2CO_3\ (z\ mol\%),\ atm.,\ T,\ t]{Cu(OAc)_2\cdot H_2O\ (y\ mol\%)} \underset{\textbf{3aa}}{PhSO_2NHCH_2Ph} + \underset{\textbf{4a}}{PhCHO}$$

Run	x, y, z	condition	**3aa** yield (%)	**4a** yield (%)	**4a/3aa**[c]
1[a]	6, 0, 0	N_2, 120 °C, 8 h	-	-	-
2[a]	6, 5, 0	N_2, 120 °C, 2 h	26	49	-
3[a]	6, 5, 100	N_2, 120 °C, 2 h	95	32	-
4[a]	6, 5, 100	air, 120 °C, 2 h	58	87	-
5[a]	1.3, 1, 20	N_2, 100 °C, 8 h	93	52	-
6[b]	1.3, 1, 20	N_2, 100 °C, 4 h	69	69	1.00/1.00
		6 h	83	70	0.84/1.00

[a] Detected by GC. [b] Detected by NMR. [c] mol/mol by NMR.

(1) Table S7, Run 6, 100 °C, 4 h:

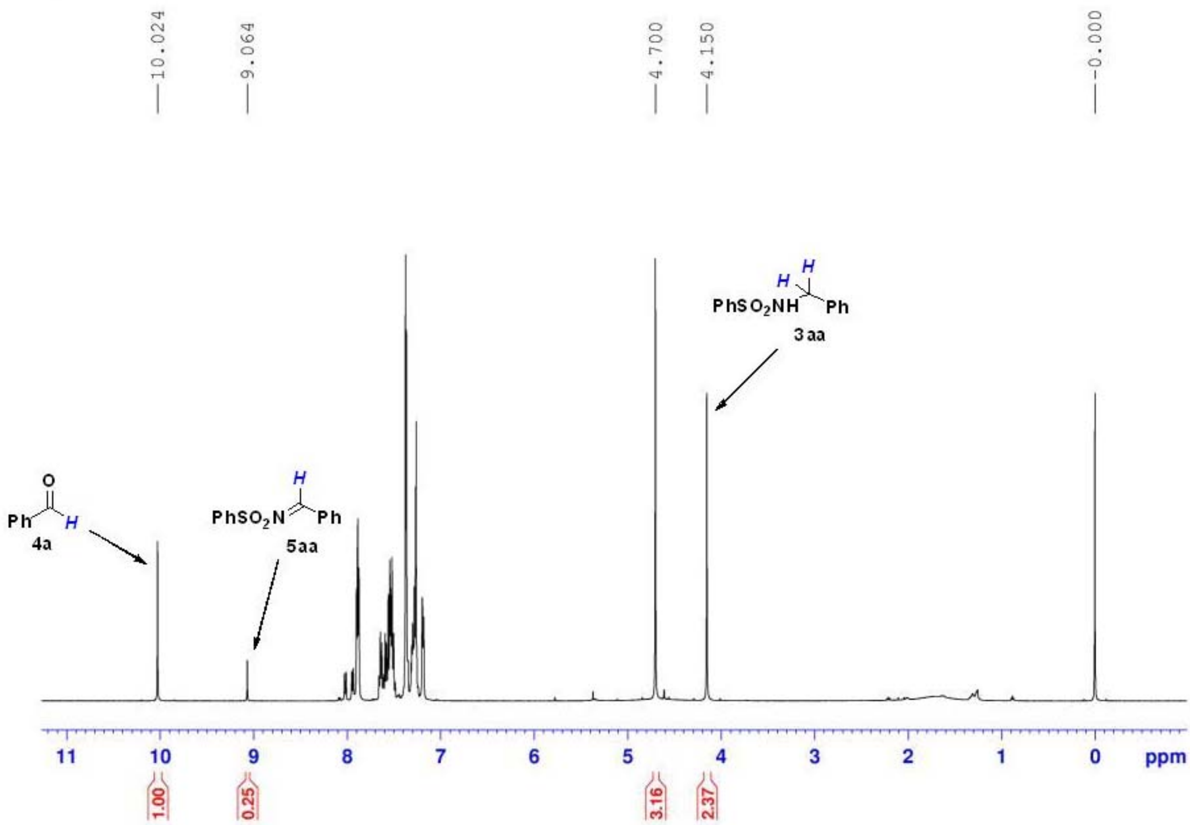


3aa% = (1.98/2)/(1.98/2+0.45)% = 69%

4a% = 1.00 /(1.98/2+0.45)% = 69%

4a/3aa (mol/mol) = 69/69 = 1.00/1.00

(2) Table S7, Run 6, 100°C, 6 h:

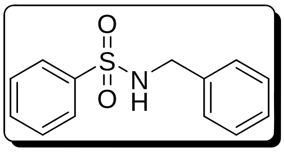


3aa% = (2.37/2)/(2.37/2+0.25)% = 83%

4a% = 1.00 /(2.37/2+0.25)% = 70%

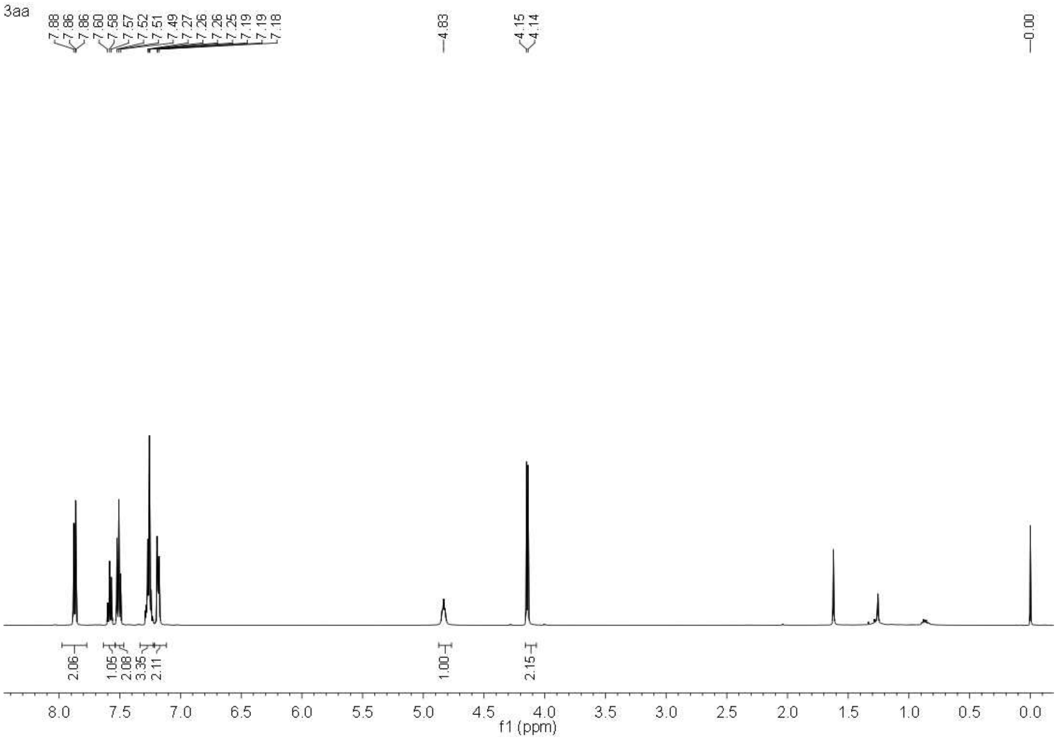
4a/3aa (mol/mol) = 70/83 = 0.84/1.00

^{1}H and ^{13}C NMR Spectra of the Products

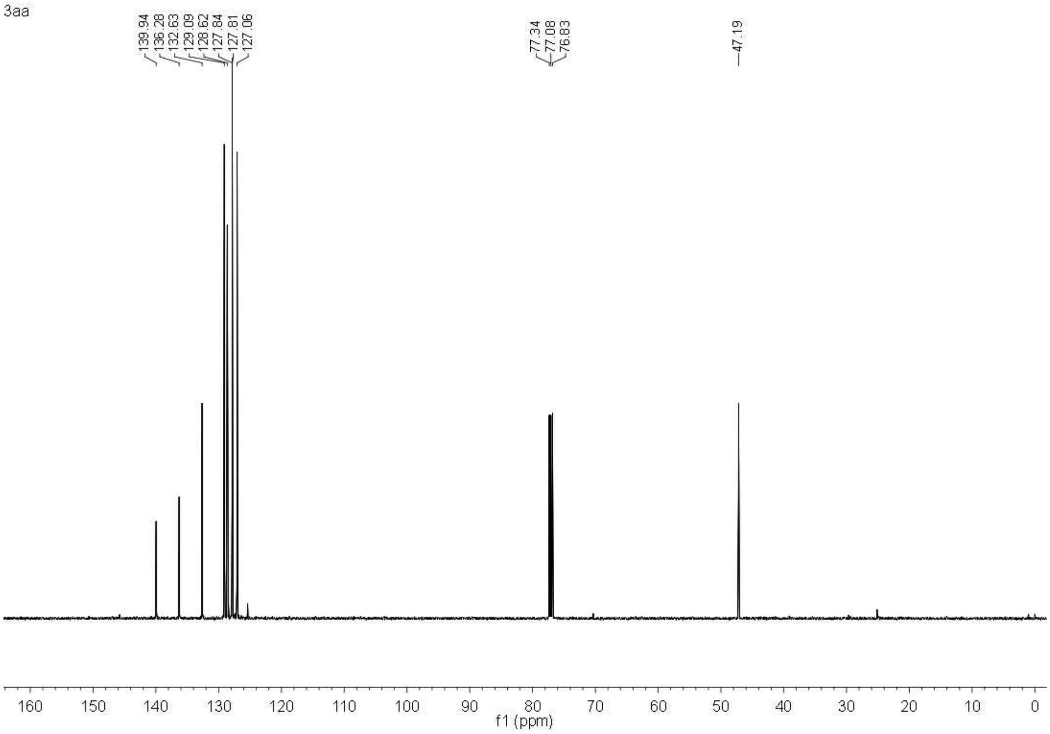


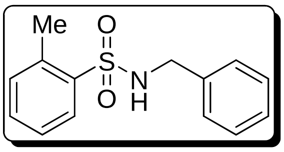
3aa

^{1}H NMR



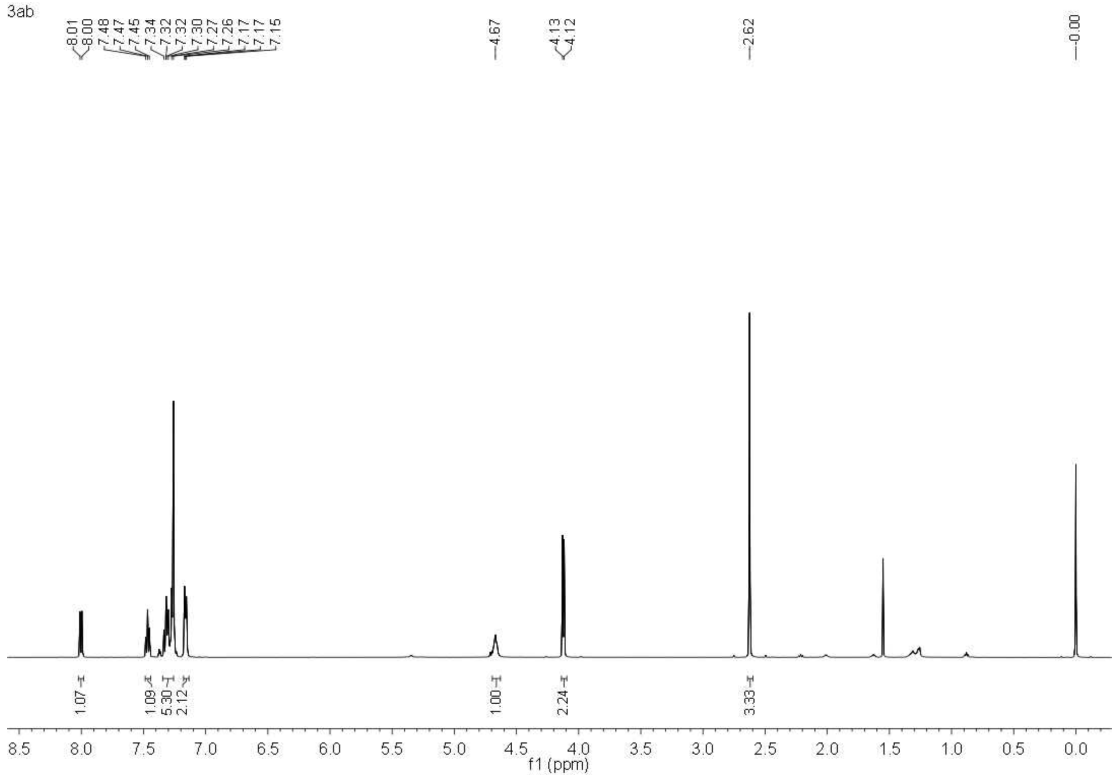
^{13}C NMR



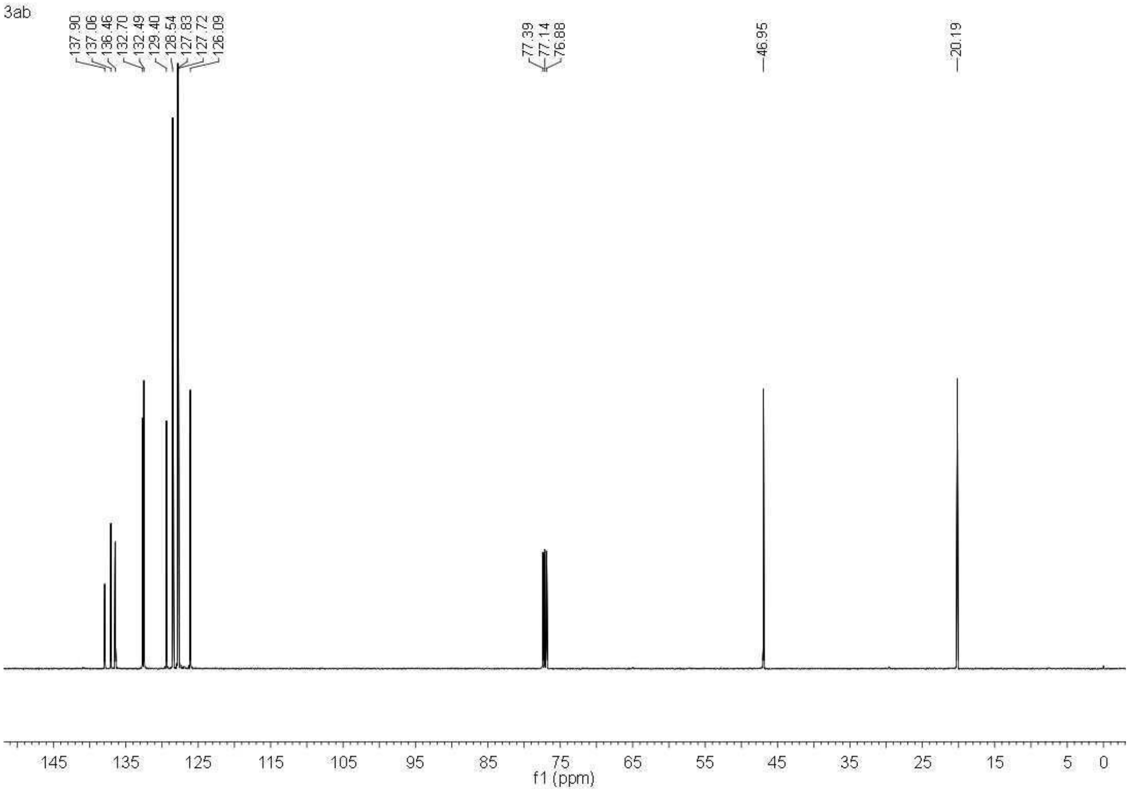


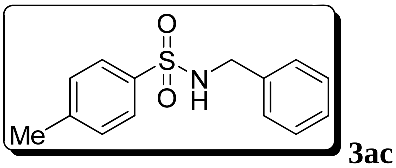
3ab

^{1}H NMR

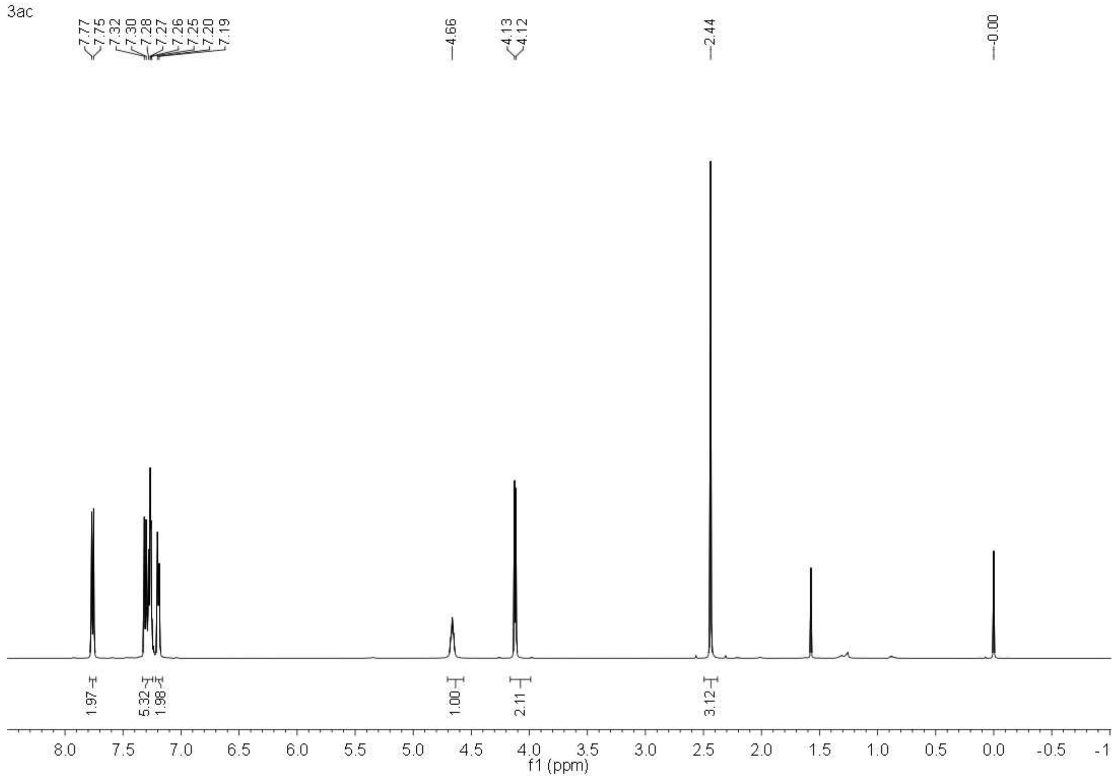


^{13}C NMR

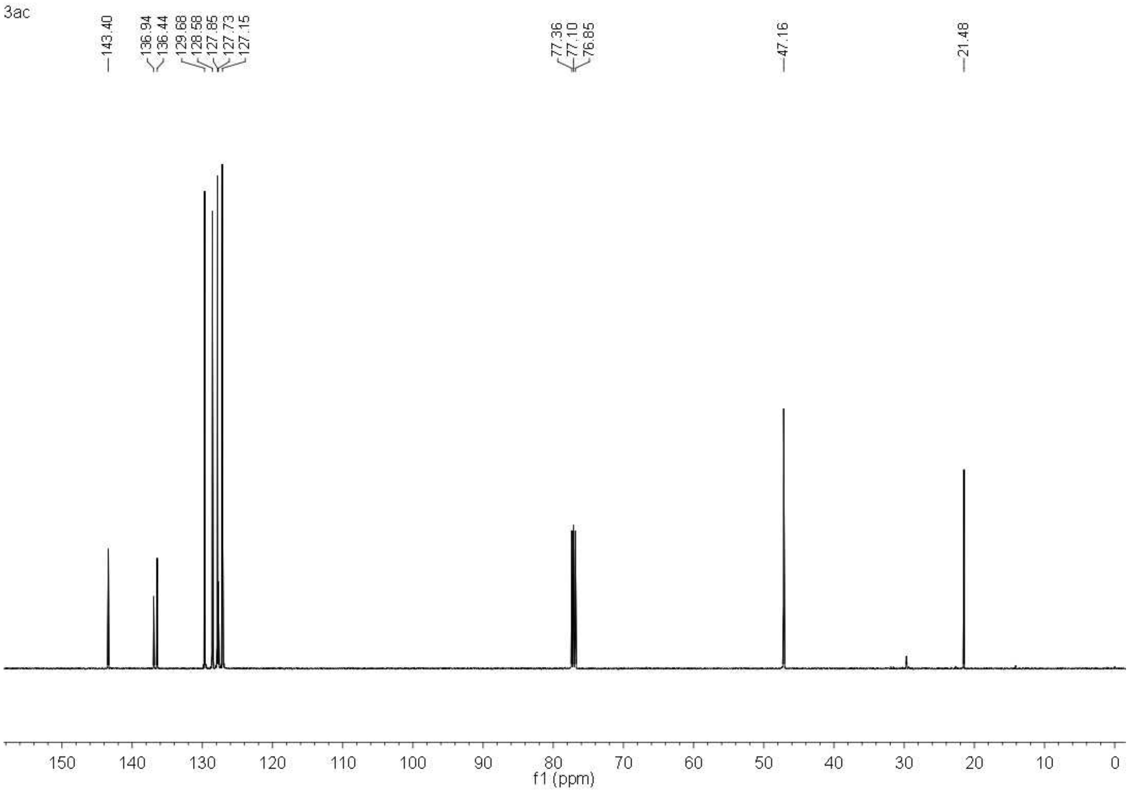


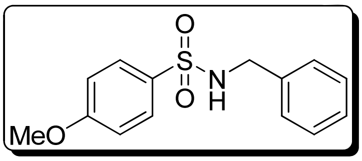


^{1}H NMR



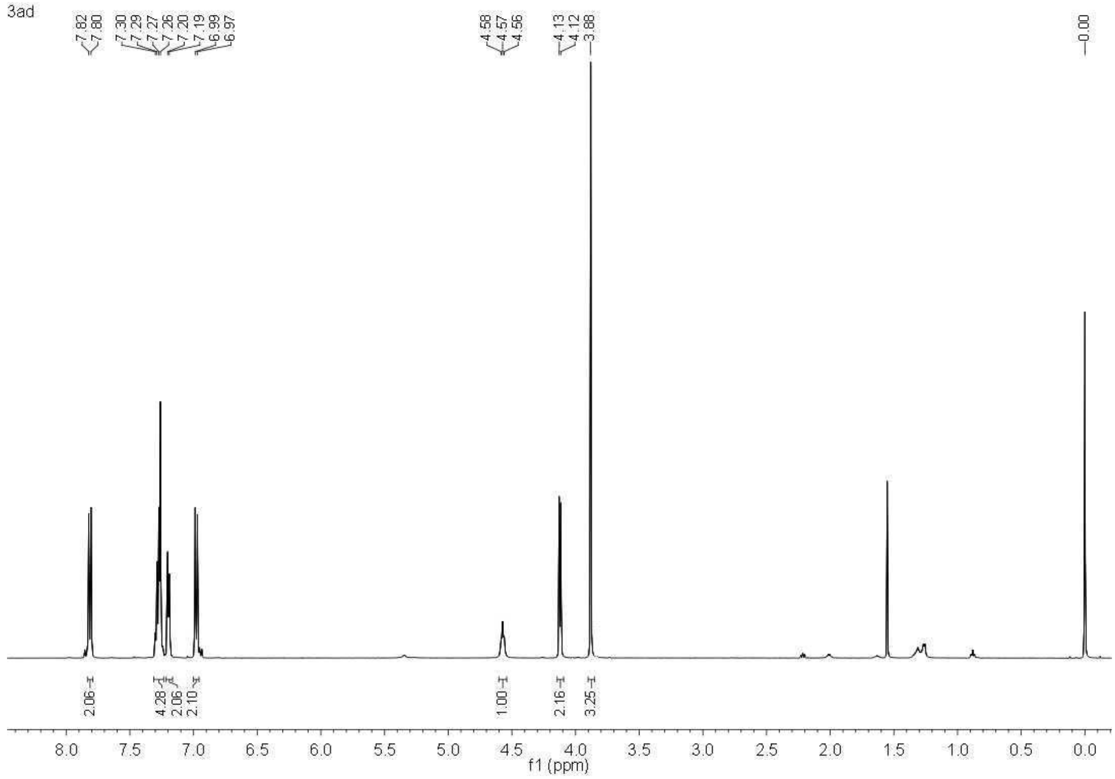
^{13}C NMR



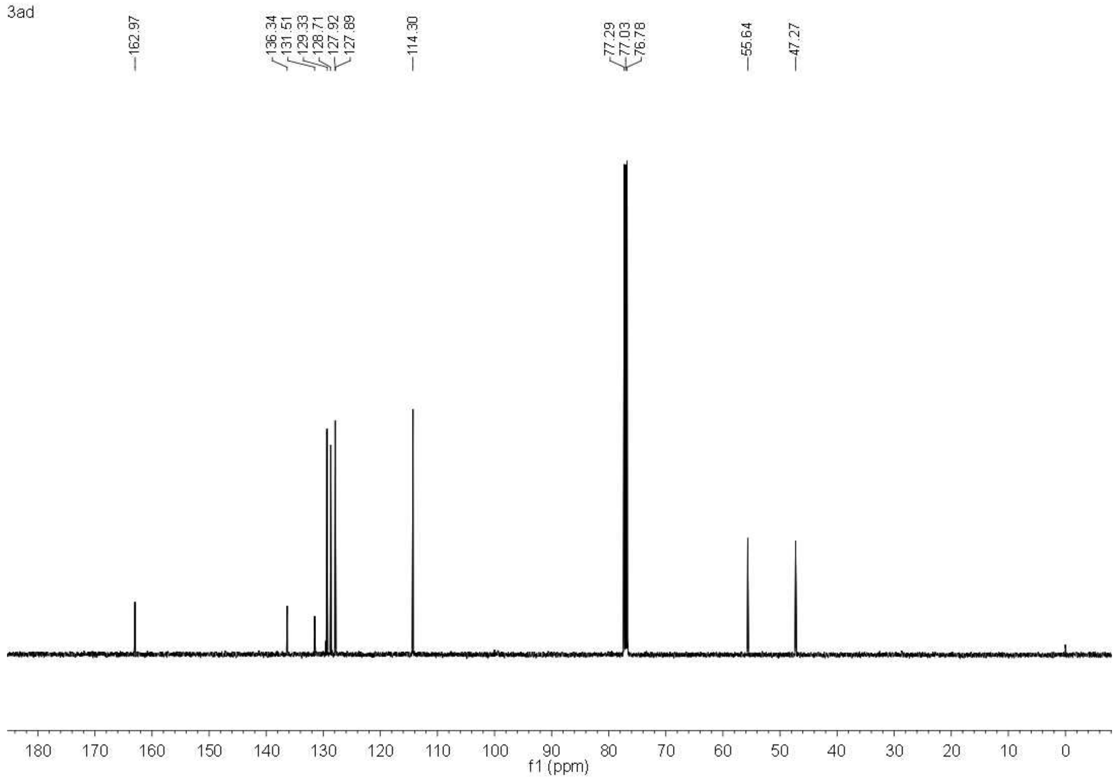


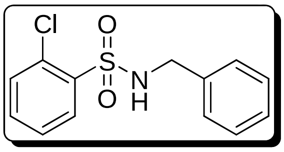
3ad

^{1}H NMR



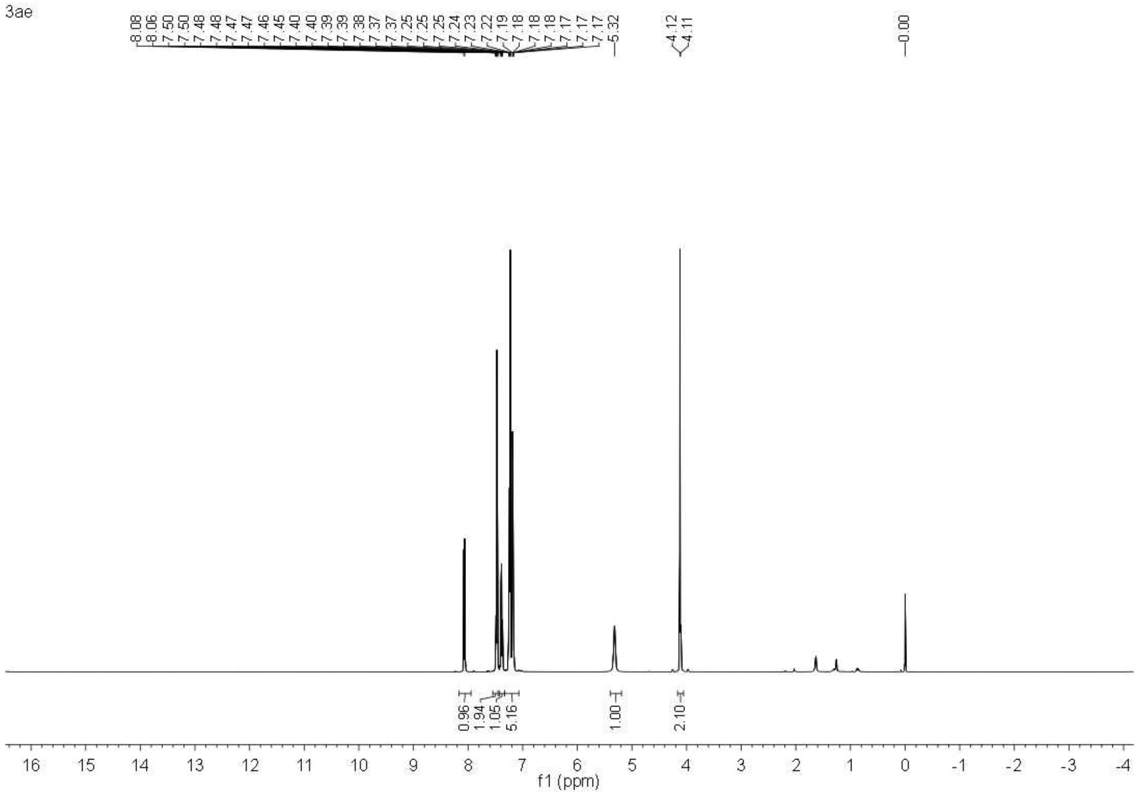
^{13}C NMR



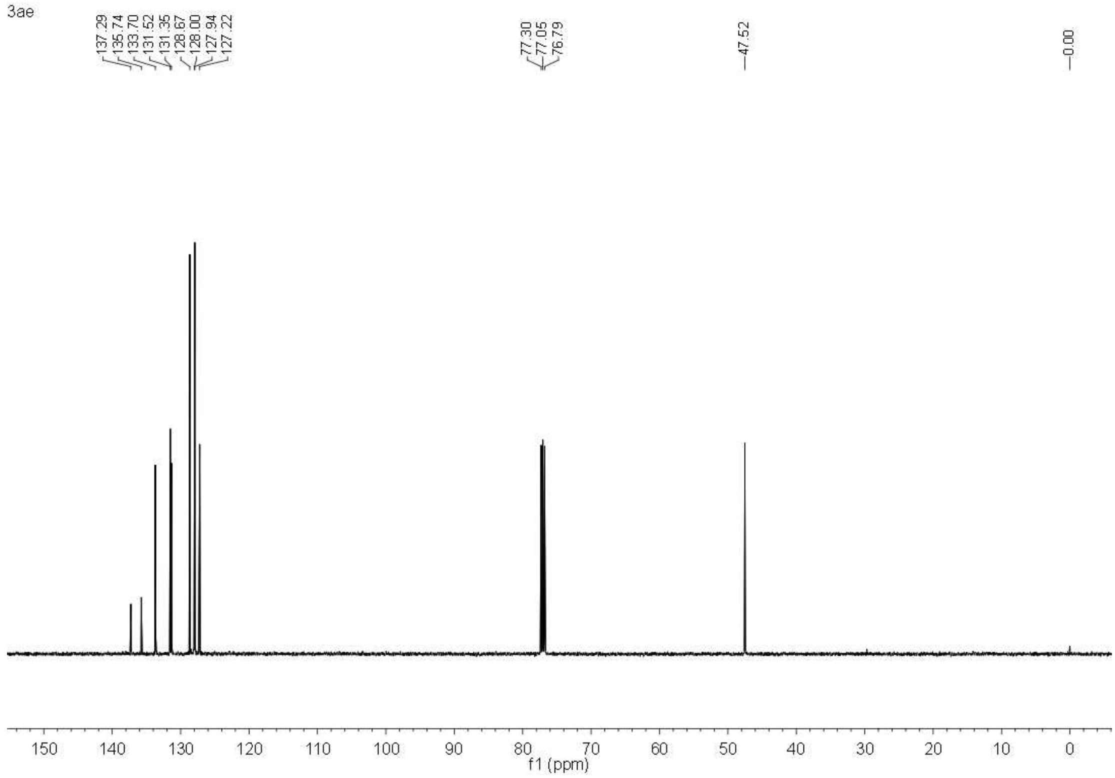


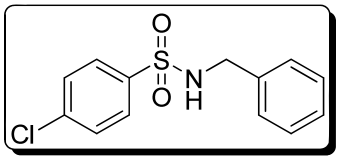
3ae

^{1}H NMR



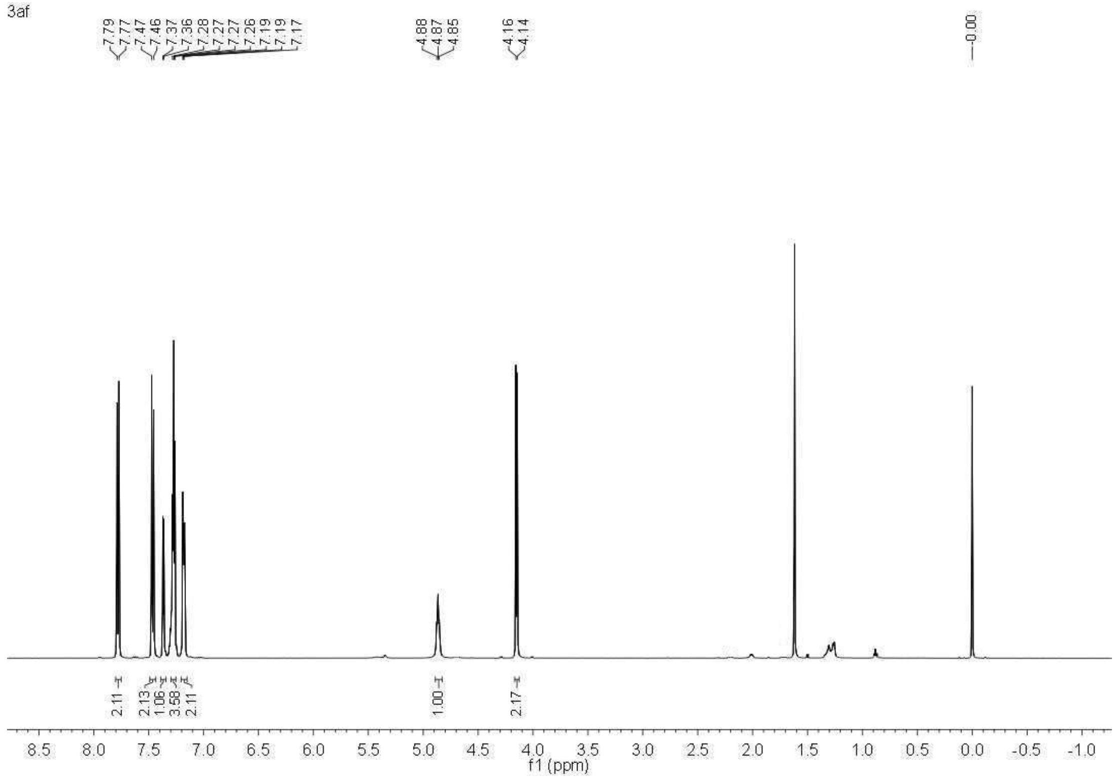
^{13}C NMR



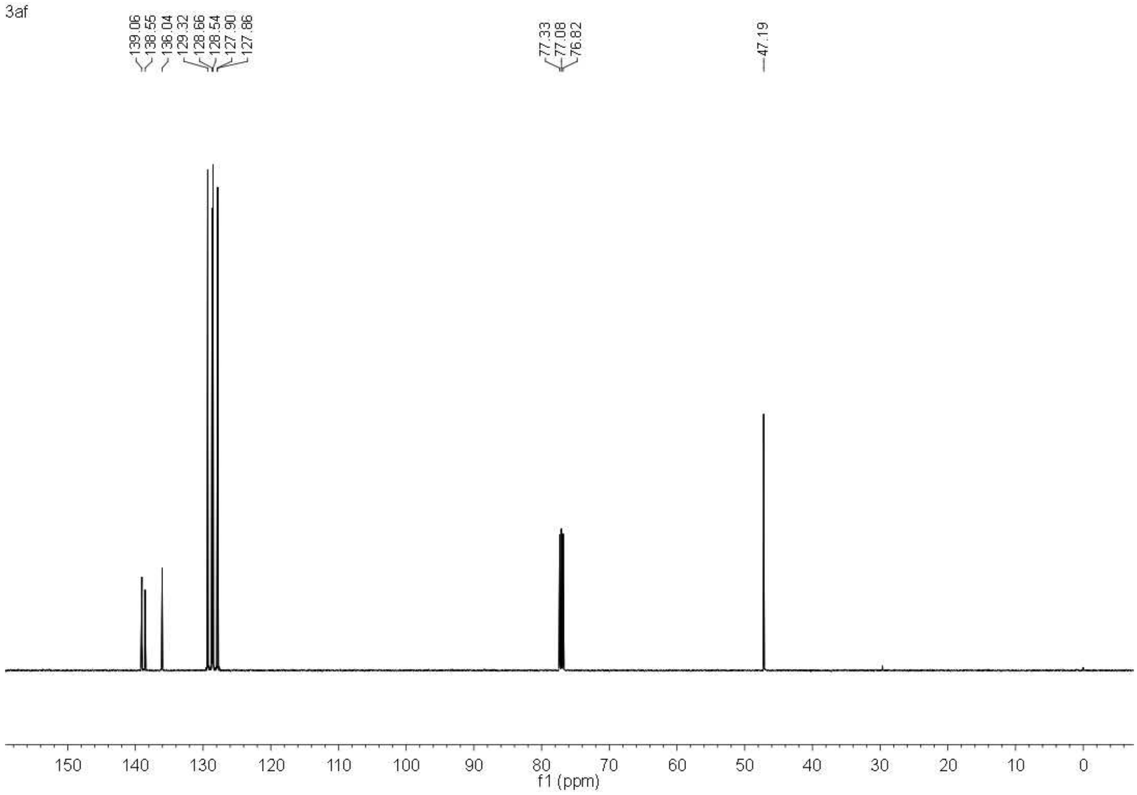


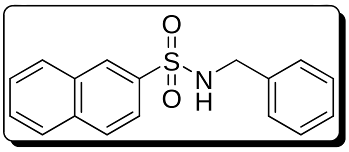
3af

^{1}H NMR



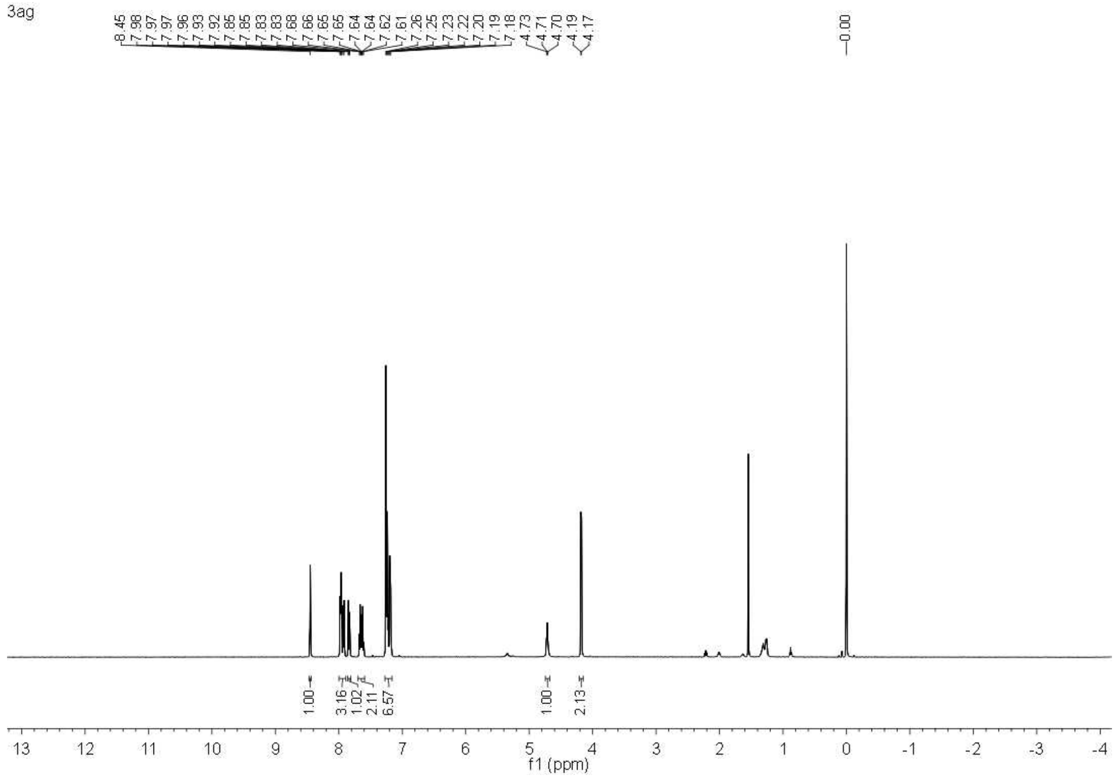
^{13}C NMR



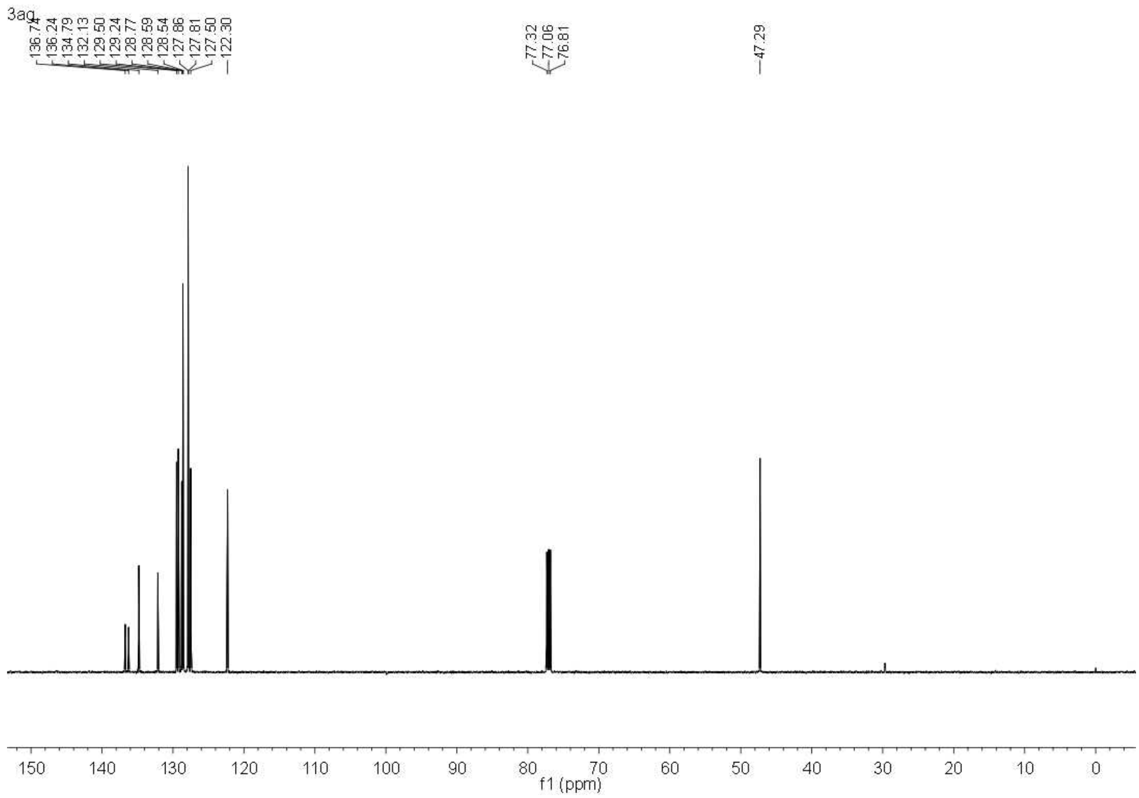


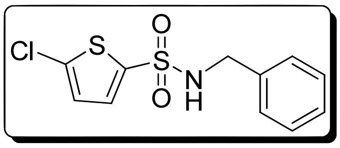
3ag

^{1}H NMR



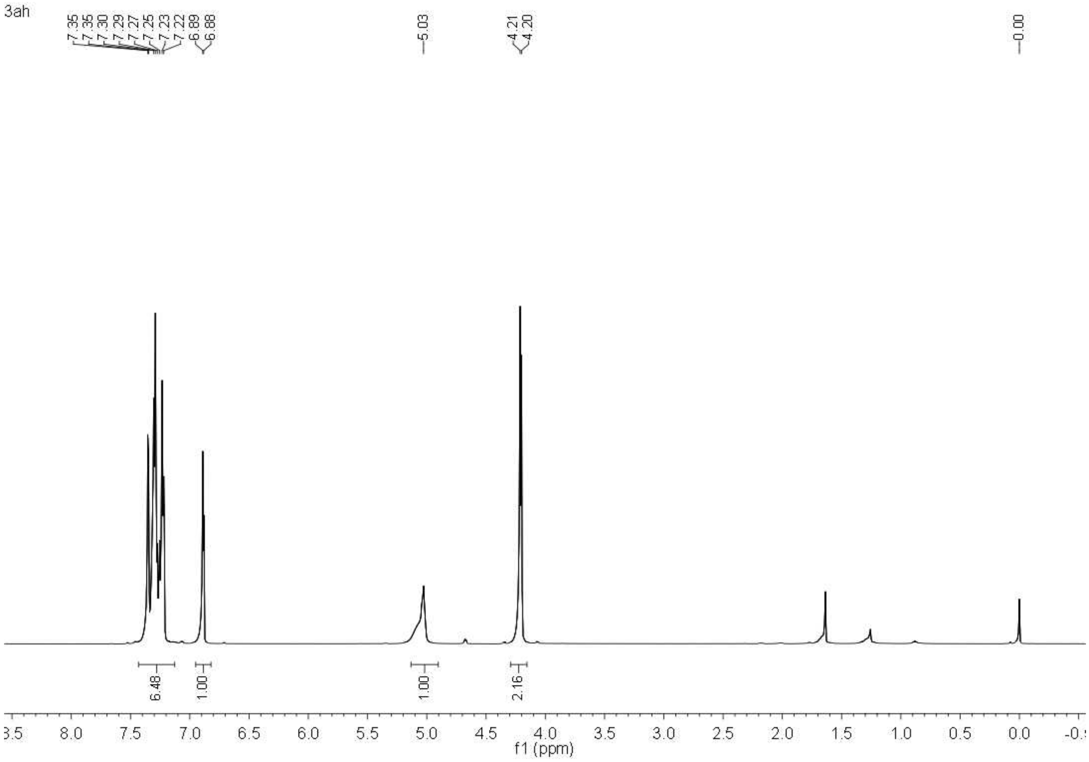
^{13}C NMR



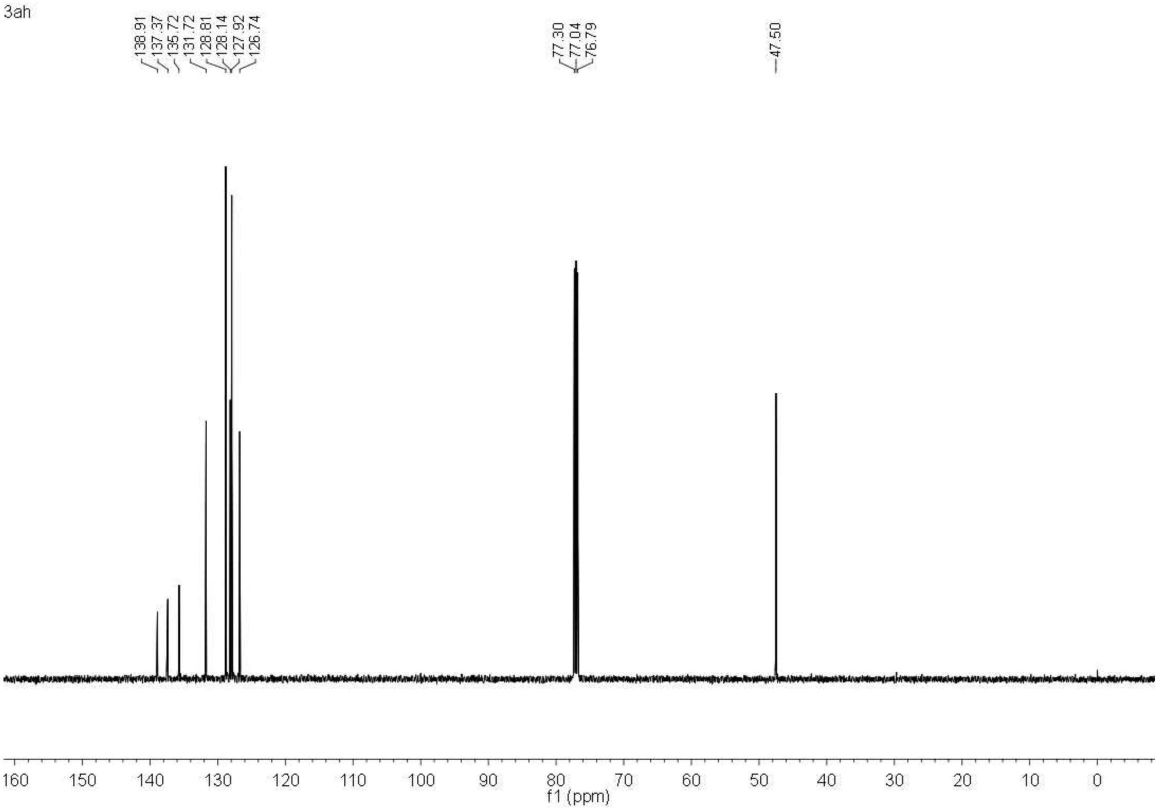


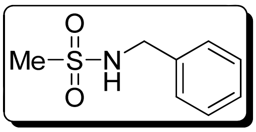
3ah

^{1}H NMR



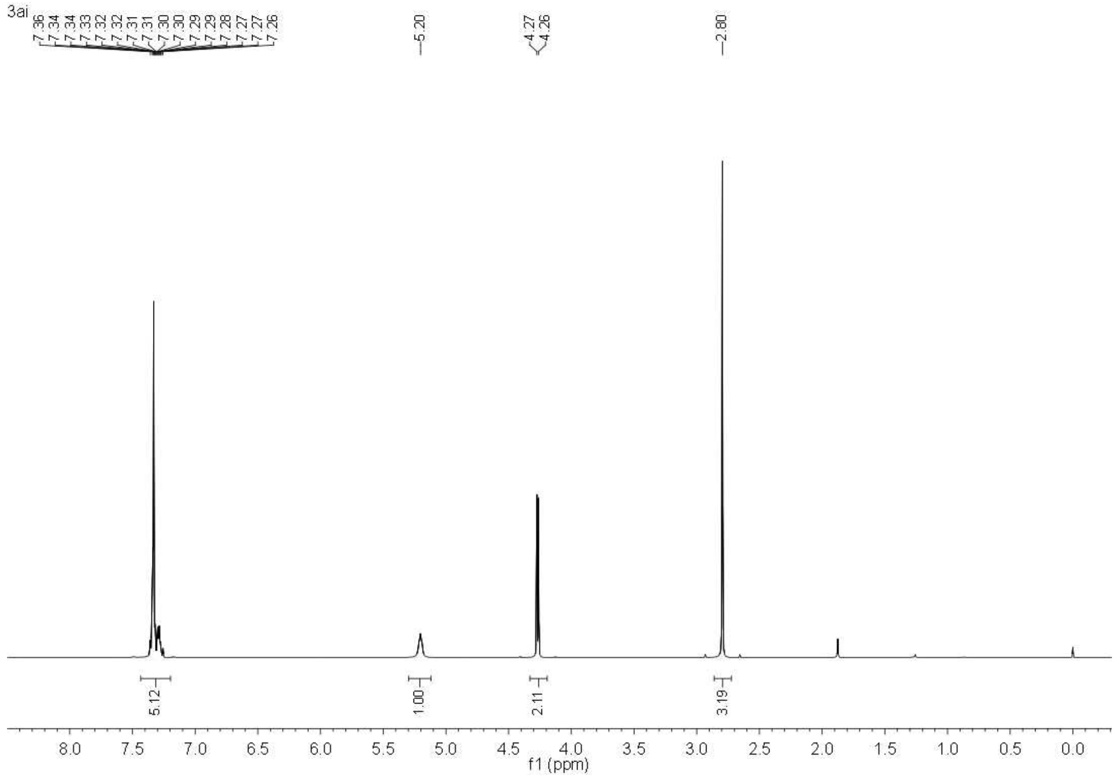
^{13}C NMR



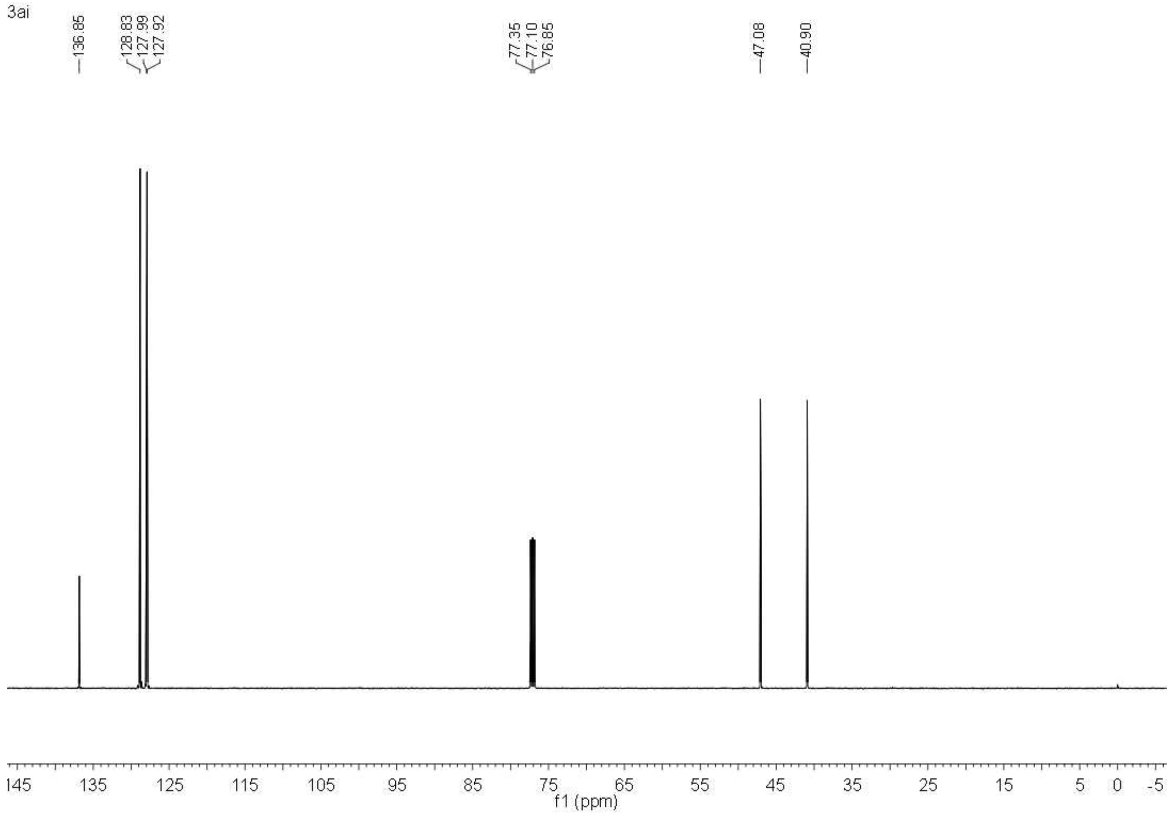


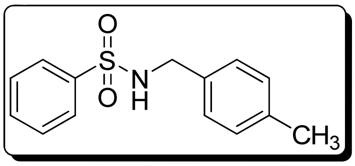
3ai

[1]H NMR



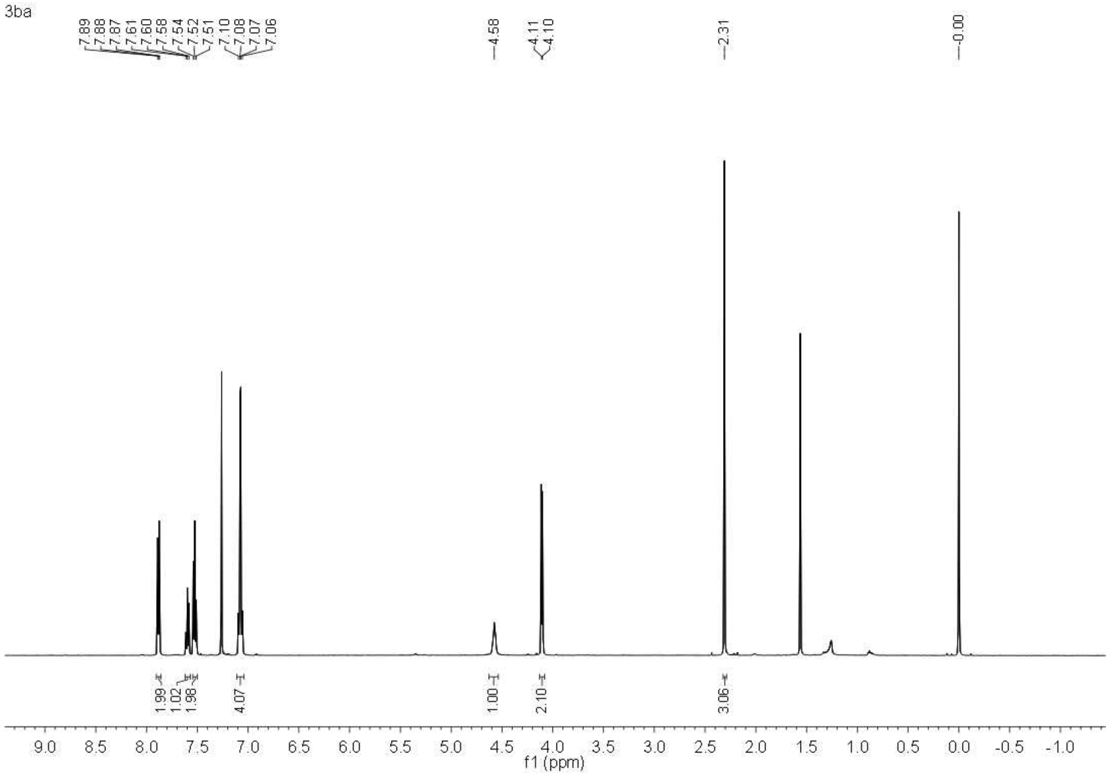
[13]C NMR



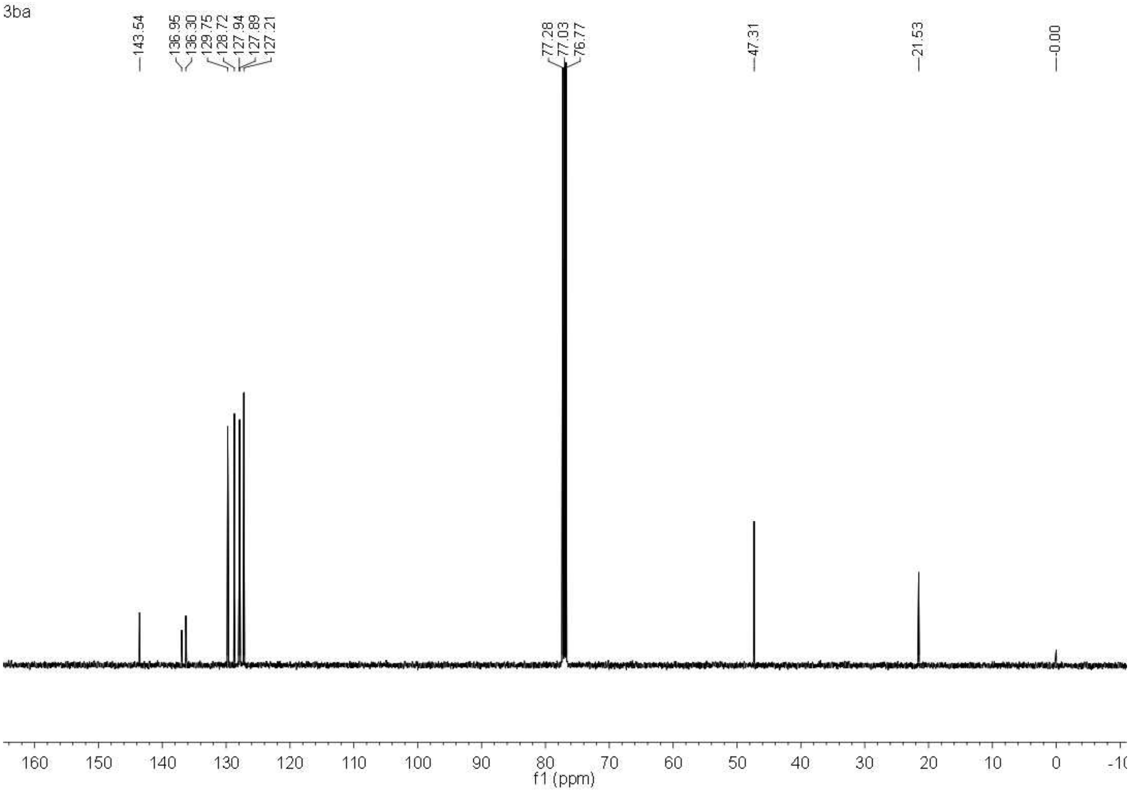


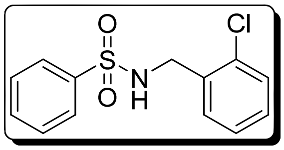
3ba

^{1}H NMR



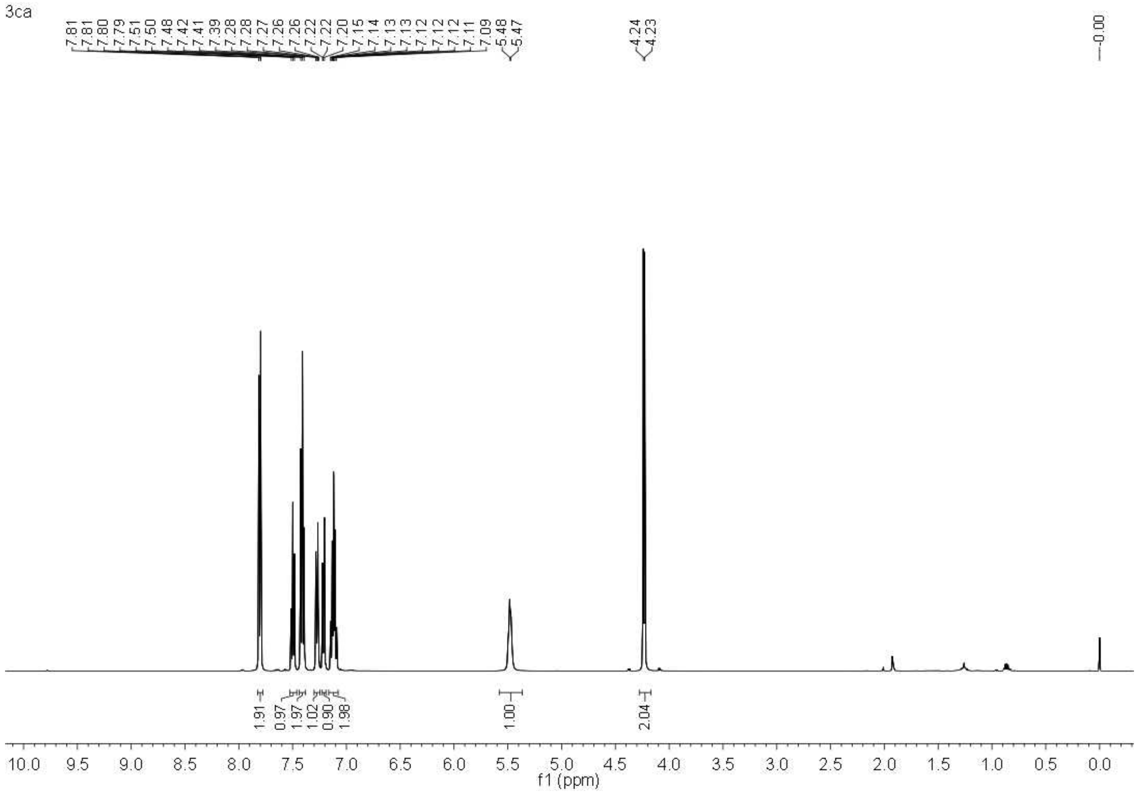
^{13}C NMR



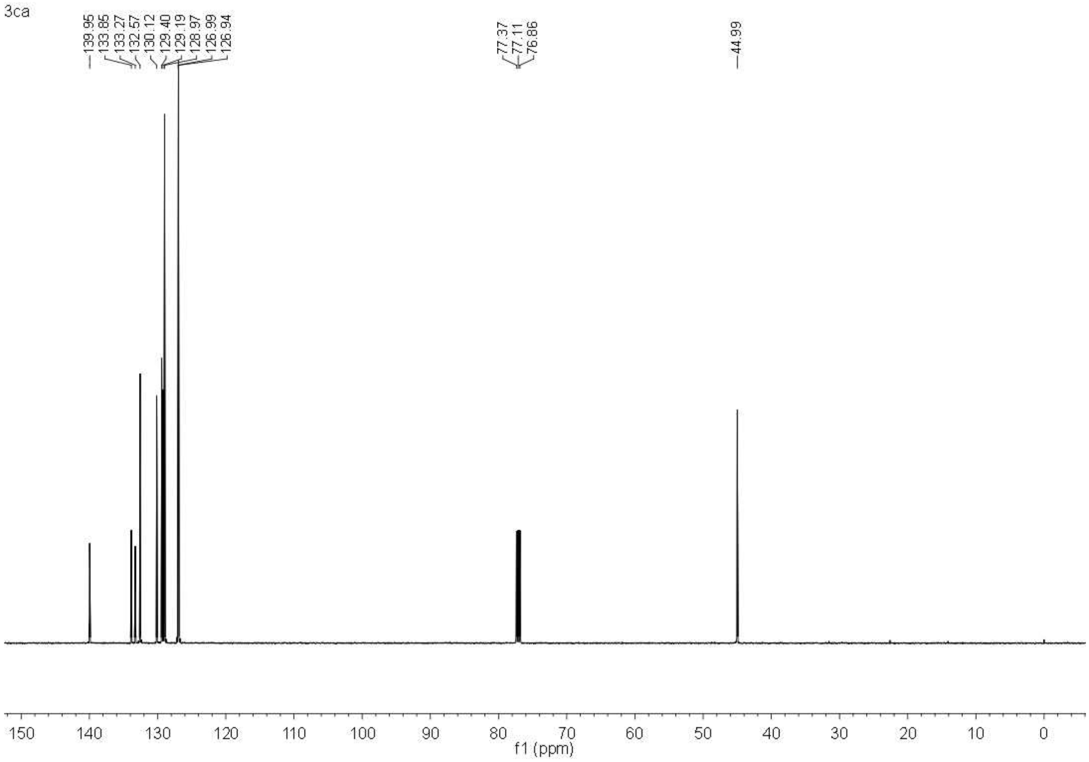


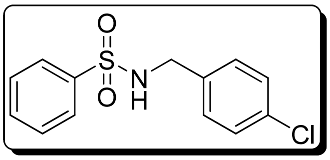
3ca

^{1}H NMR



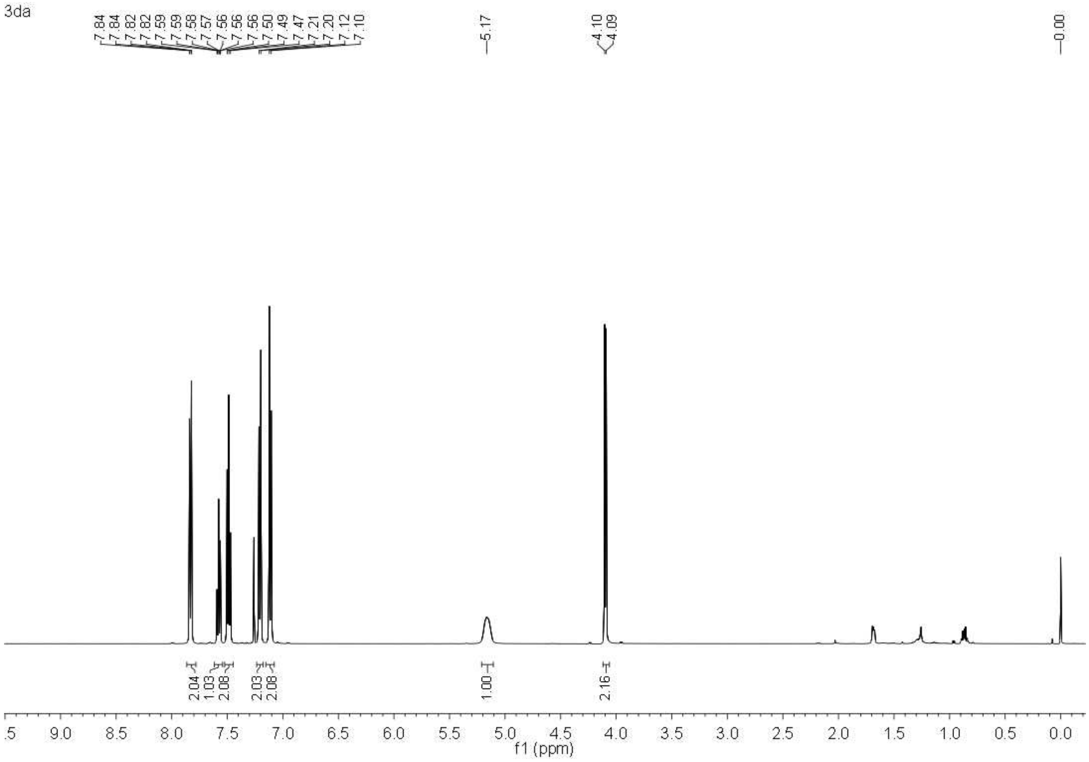
^{13}C NMR



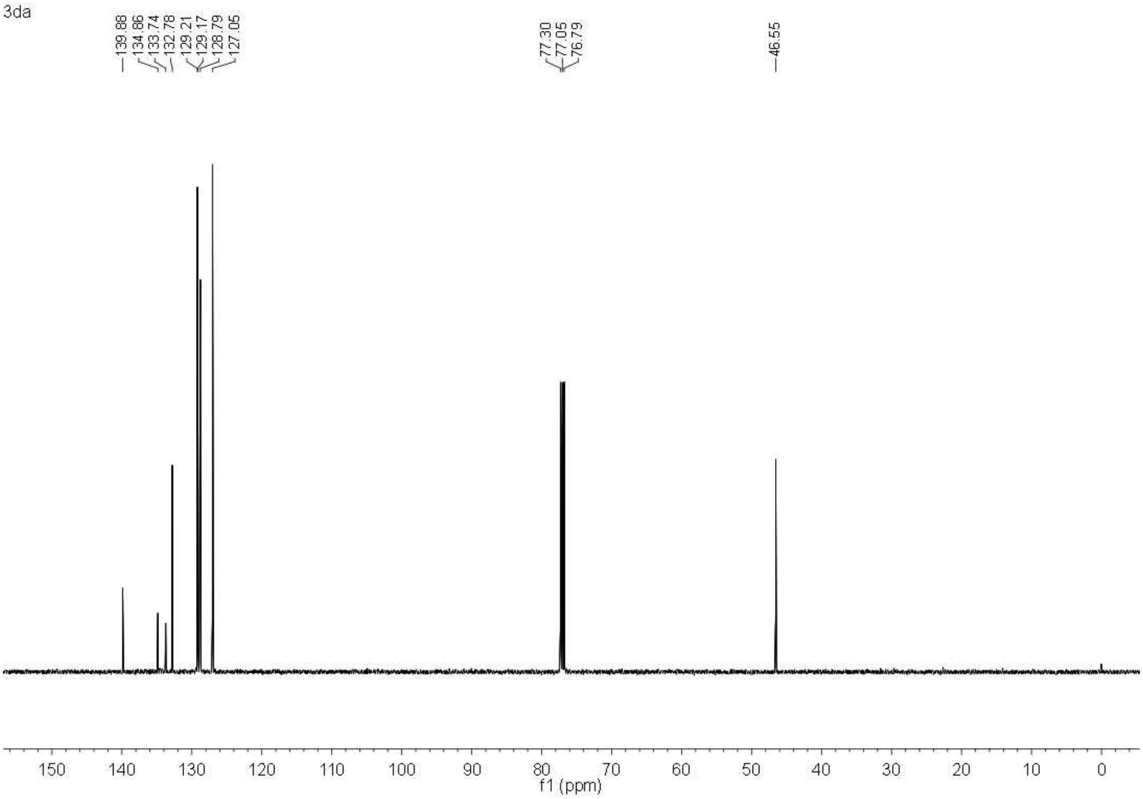


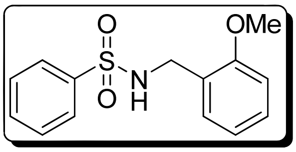
3da

^{1}H NMR



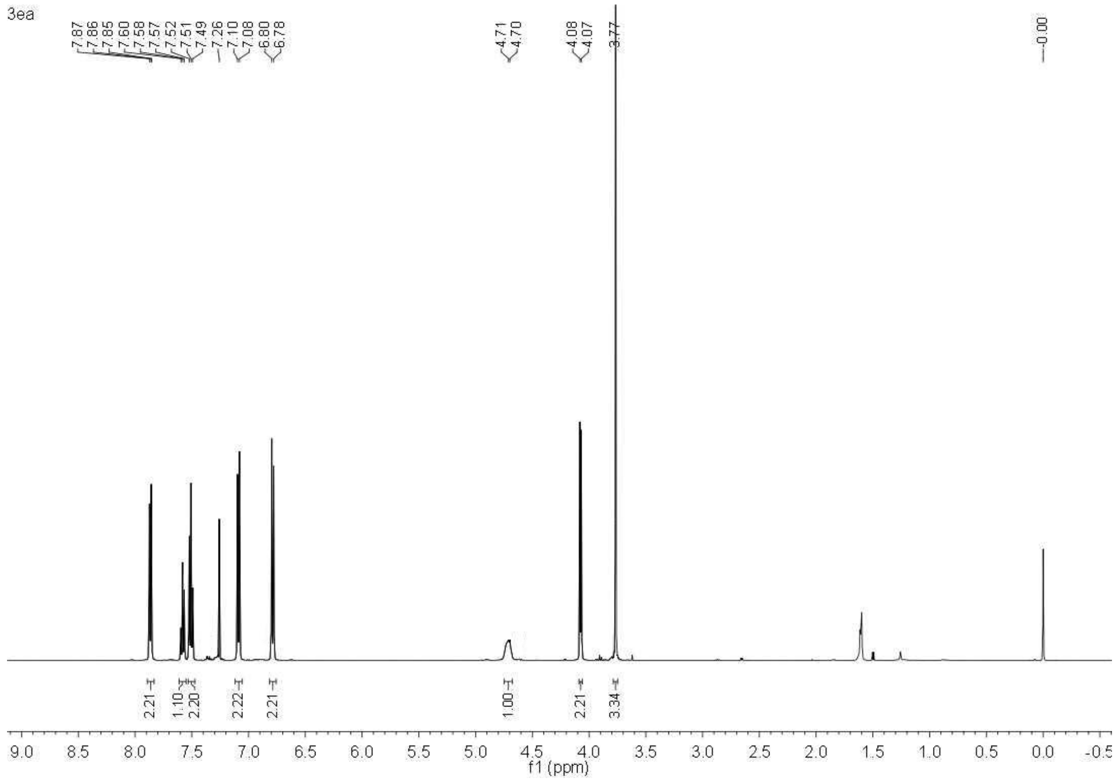
^{13}C NMR



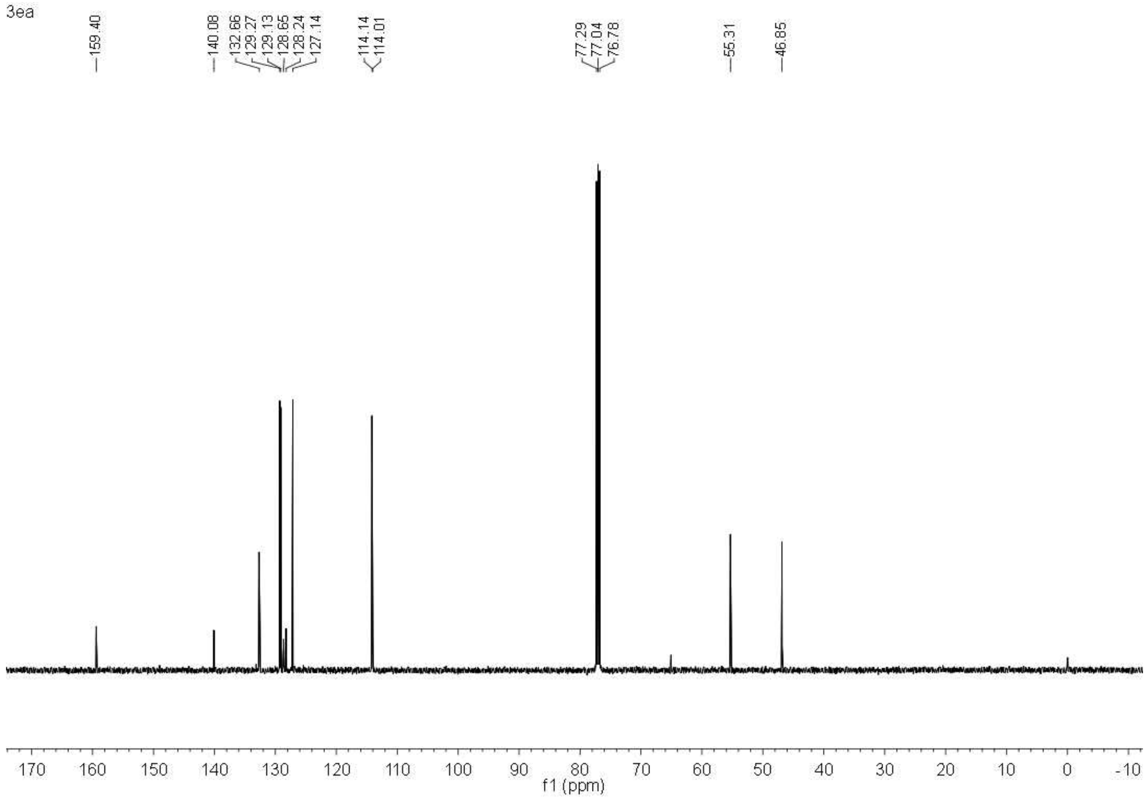


3ea

^{1}H NMR

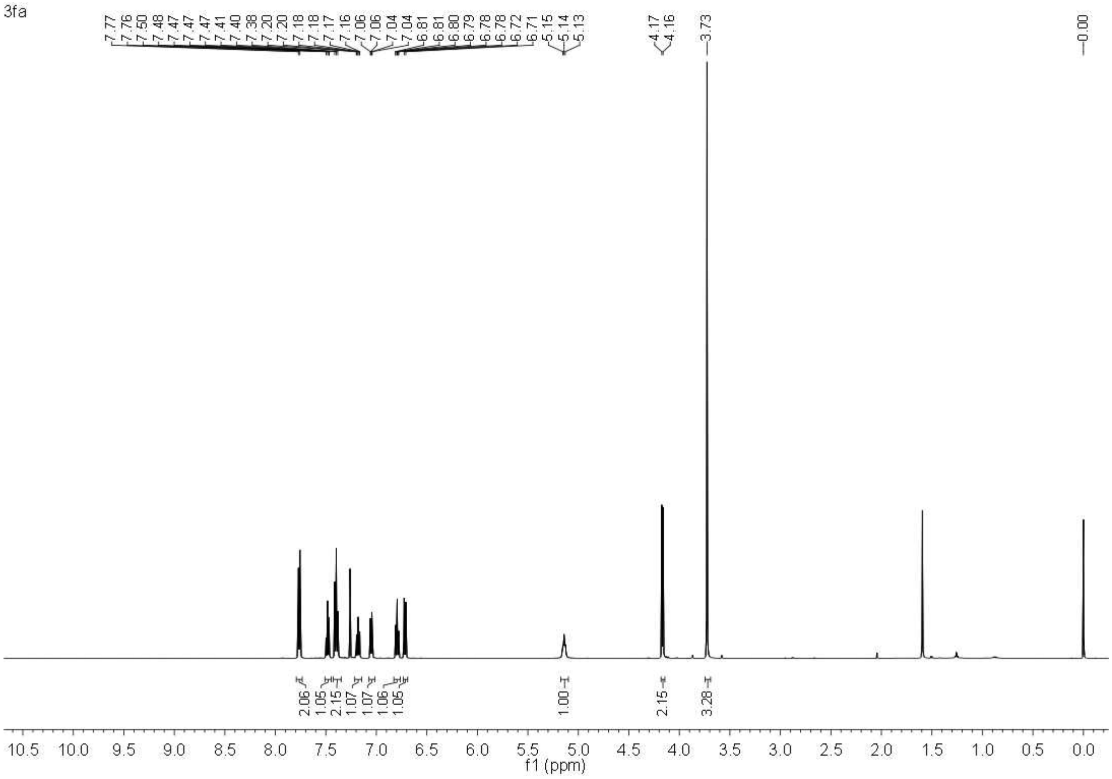


^{13}C NMR

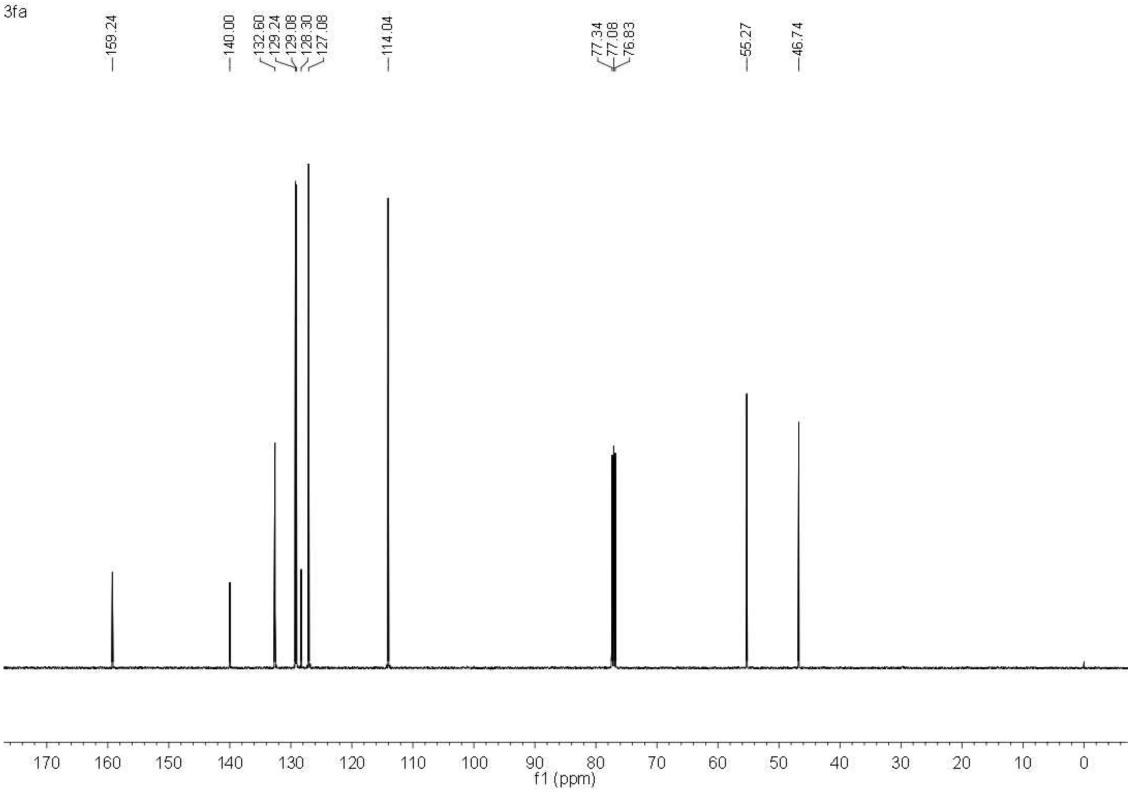


3fa

^{1}H NMR

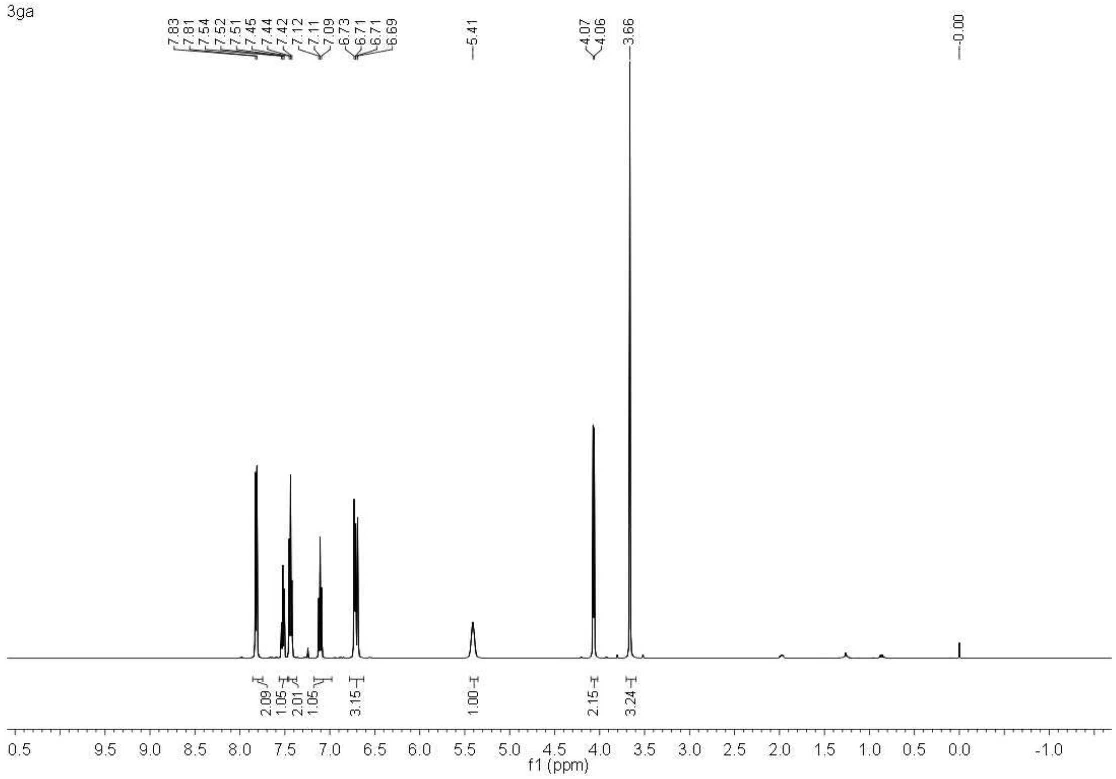


^{13}C NMR

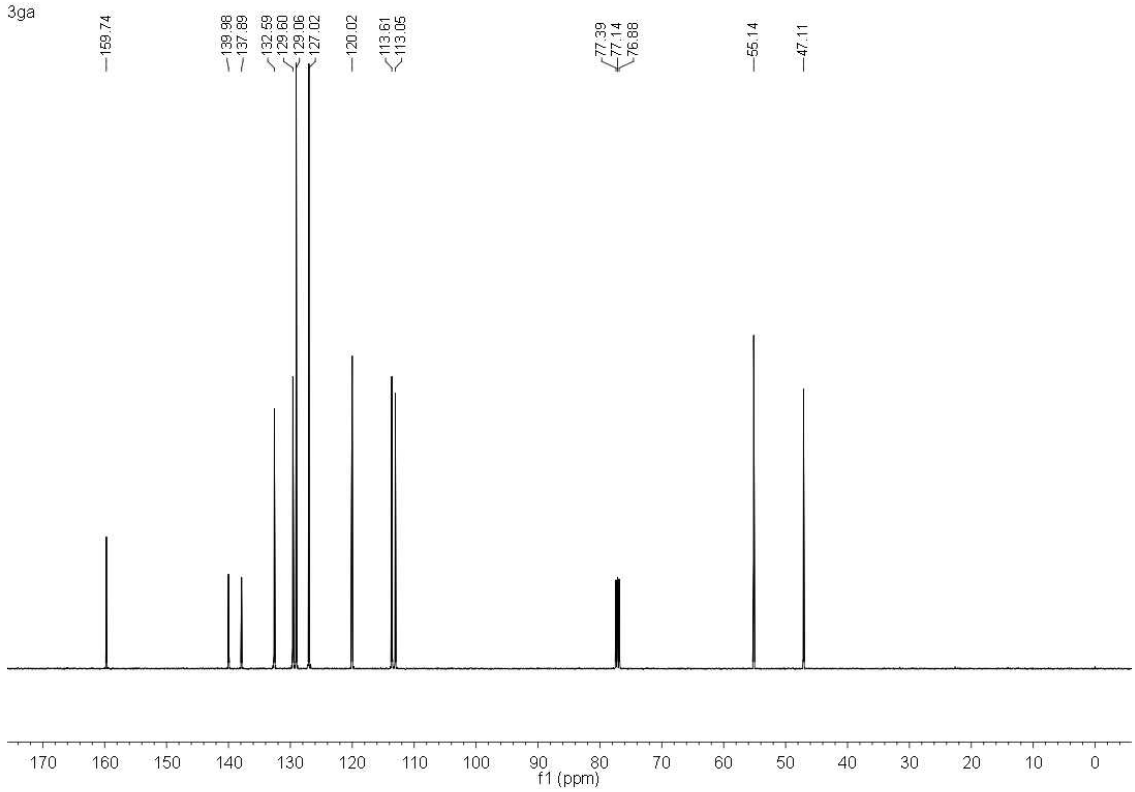


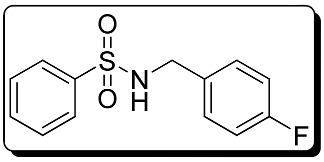
3ga

^{1}H NMR



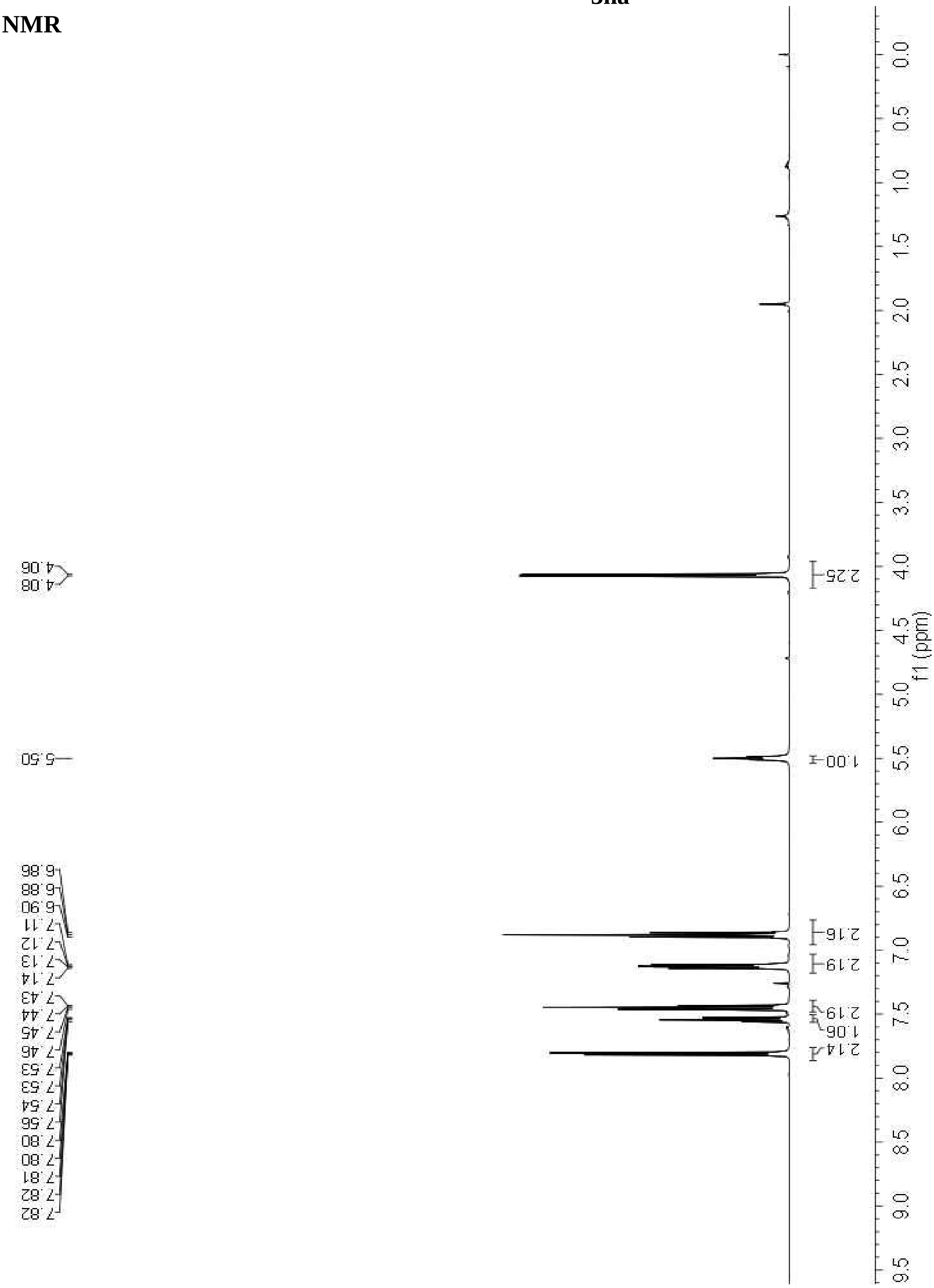
^{13}C NMR



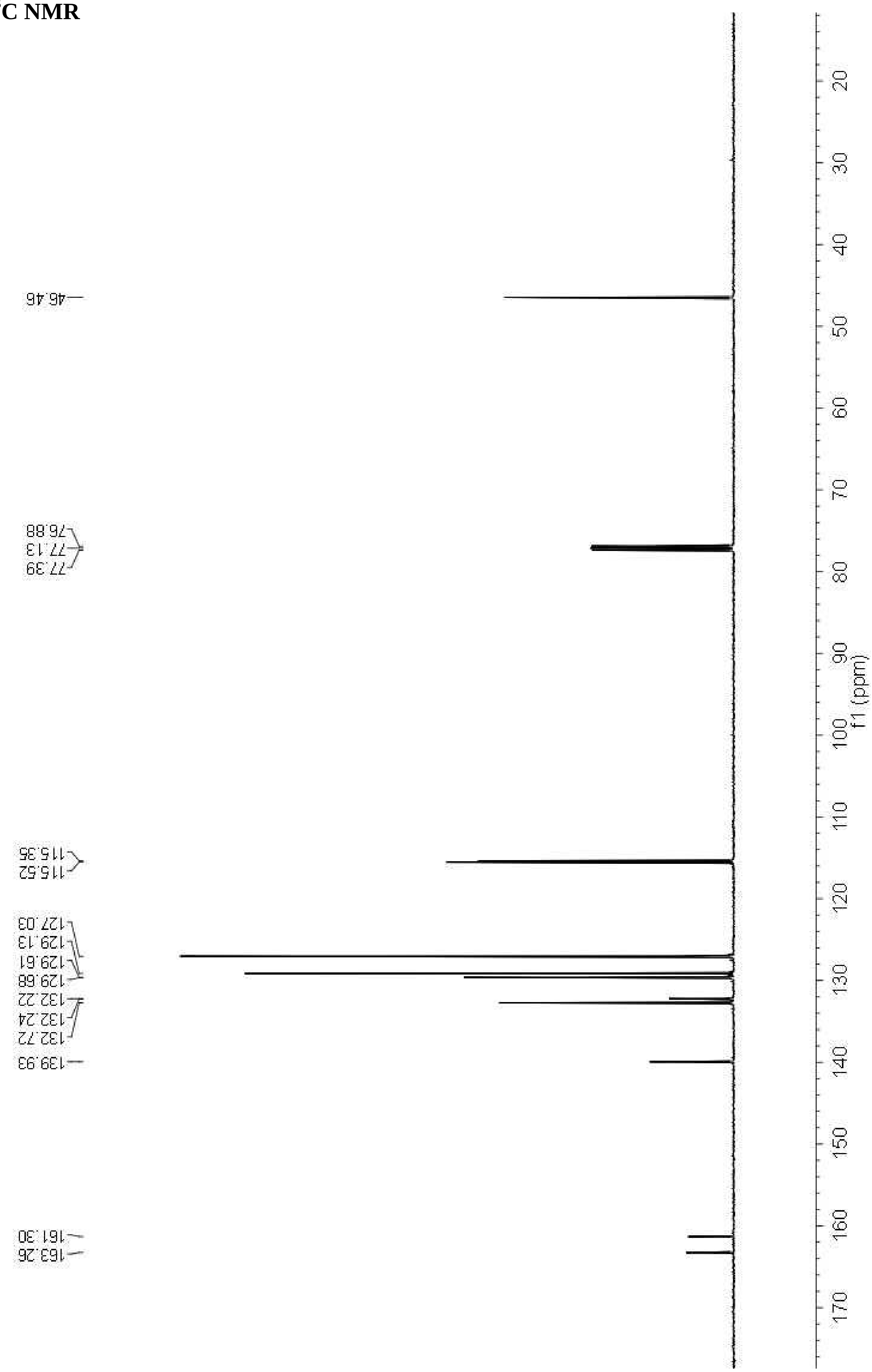


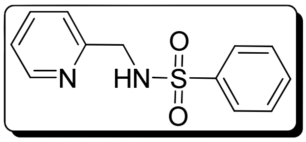
3ha

[1]H NMR


4.06
4.08
5.50
6.86
6.88
6.90
7.11
7.12
7.13
7.14
7.43
7.44
7.45
7.46
7.53
7.53
7.54
7.56
7.80
7.80
7.81
7.82
7.82
2.25
1.00
2.16
2.19
2.19
1.06
2.14
f1 (ppm)

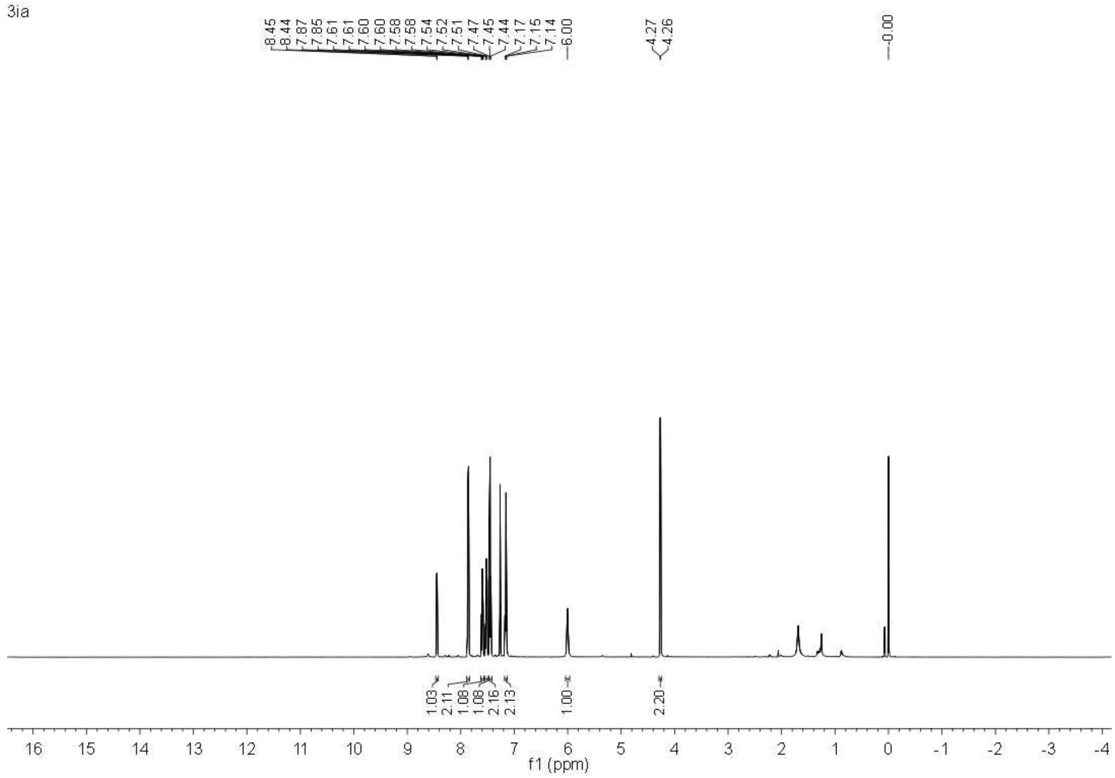
^{13}C NMR


46.46
76.88
77.13
77.39
115.35
115.52
127.03
129.13
129.61
129.68
132.22
132.24
132.72
139.93
161.30
163.26
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
f1 (ppm)

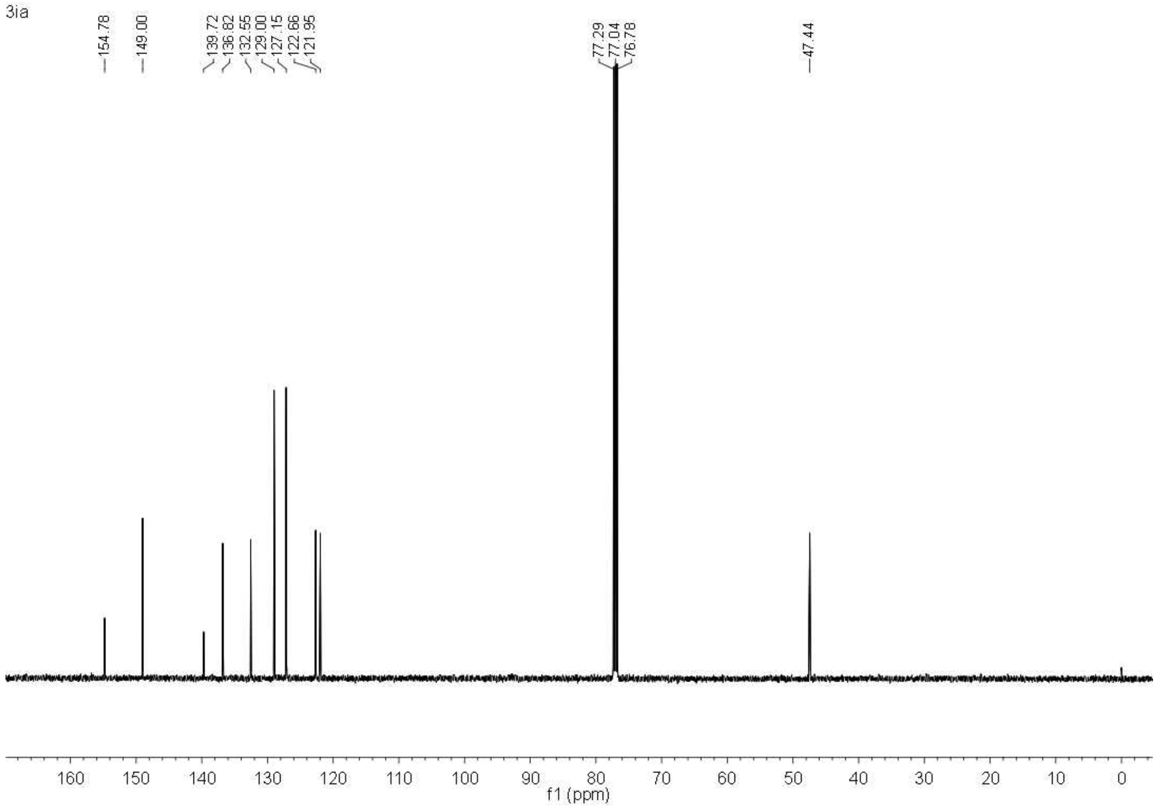


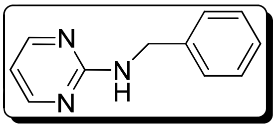
3ia

^{1}H NMR



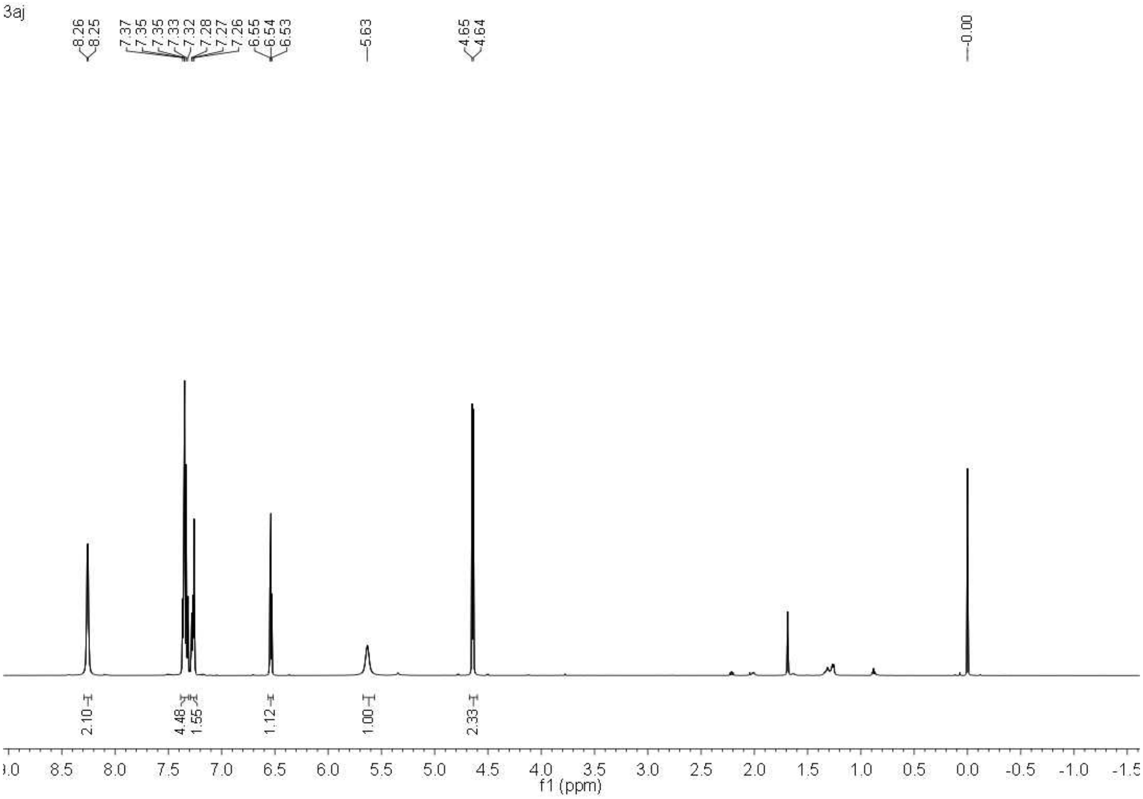
^{13}C NMR



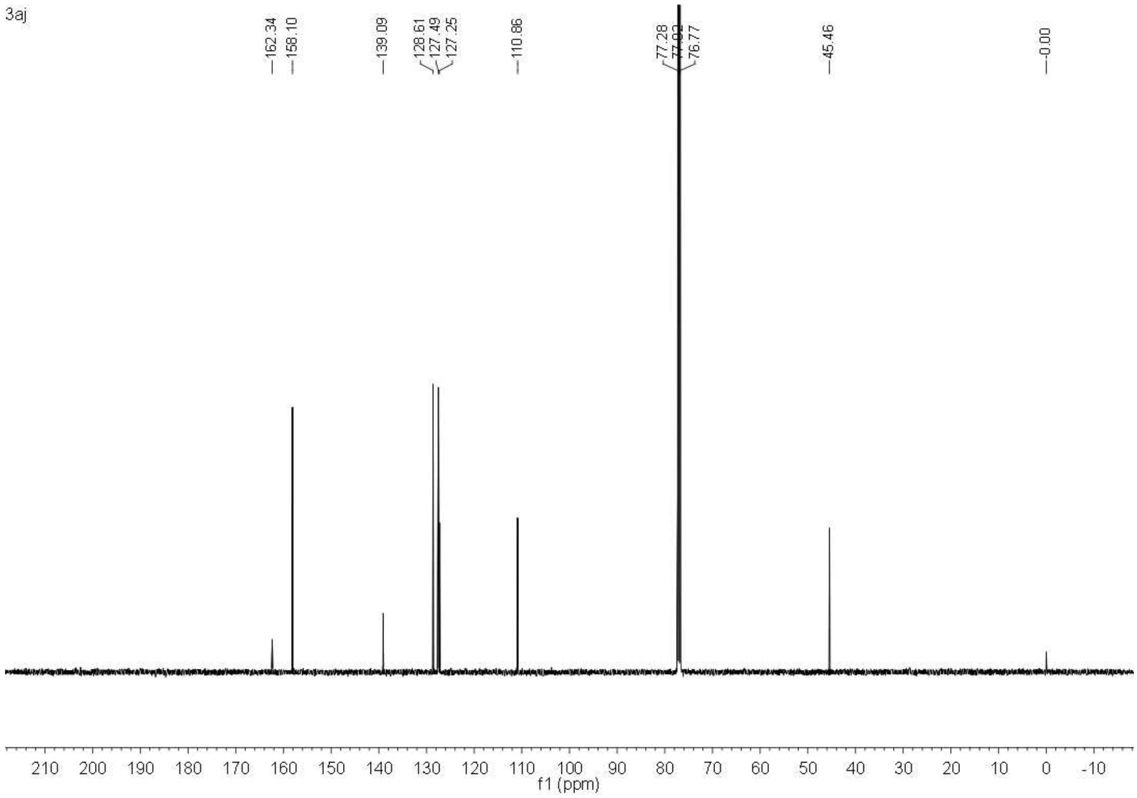


3aj

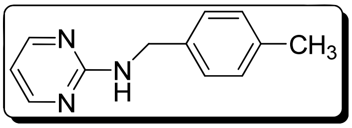
^{1}H NMR



^{13}C NMR

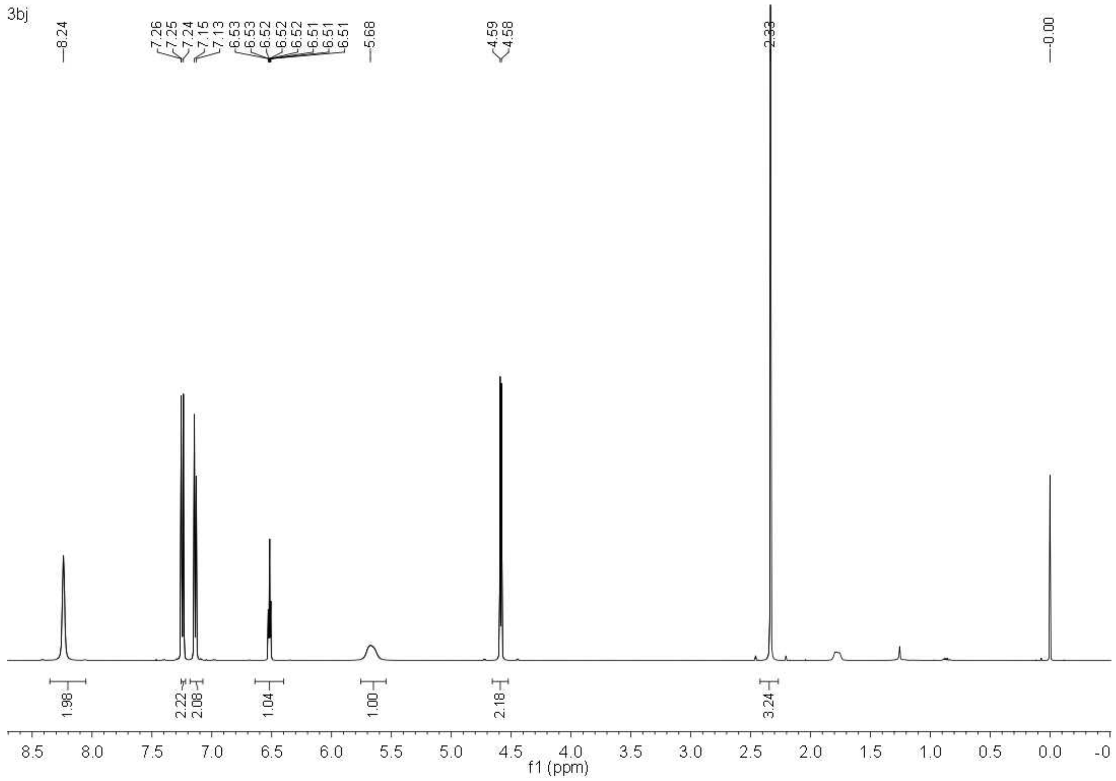


Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

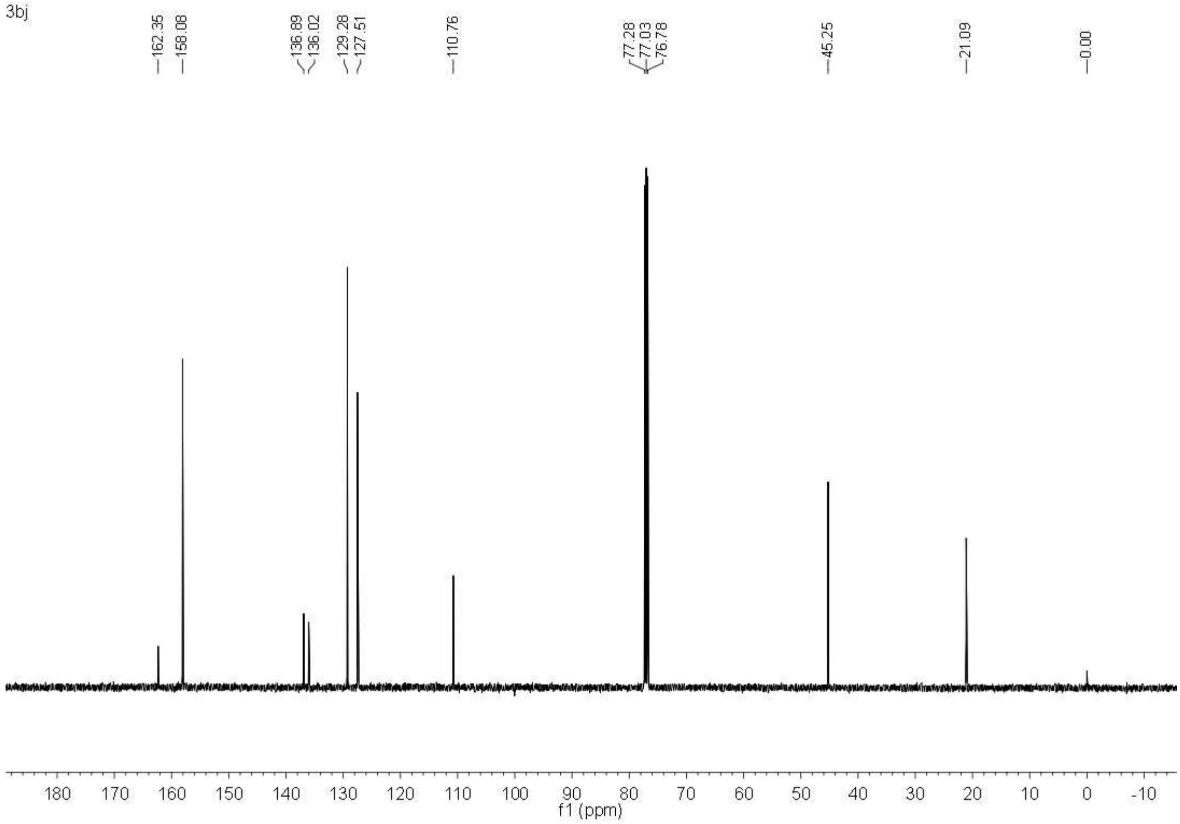


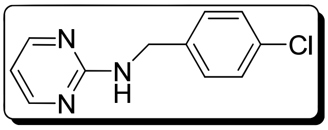
3bj

^{1}H NMR



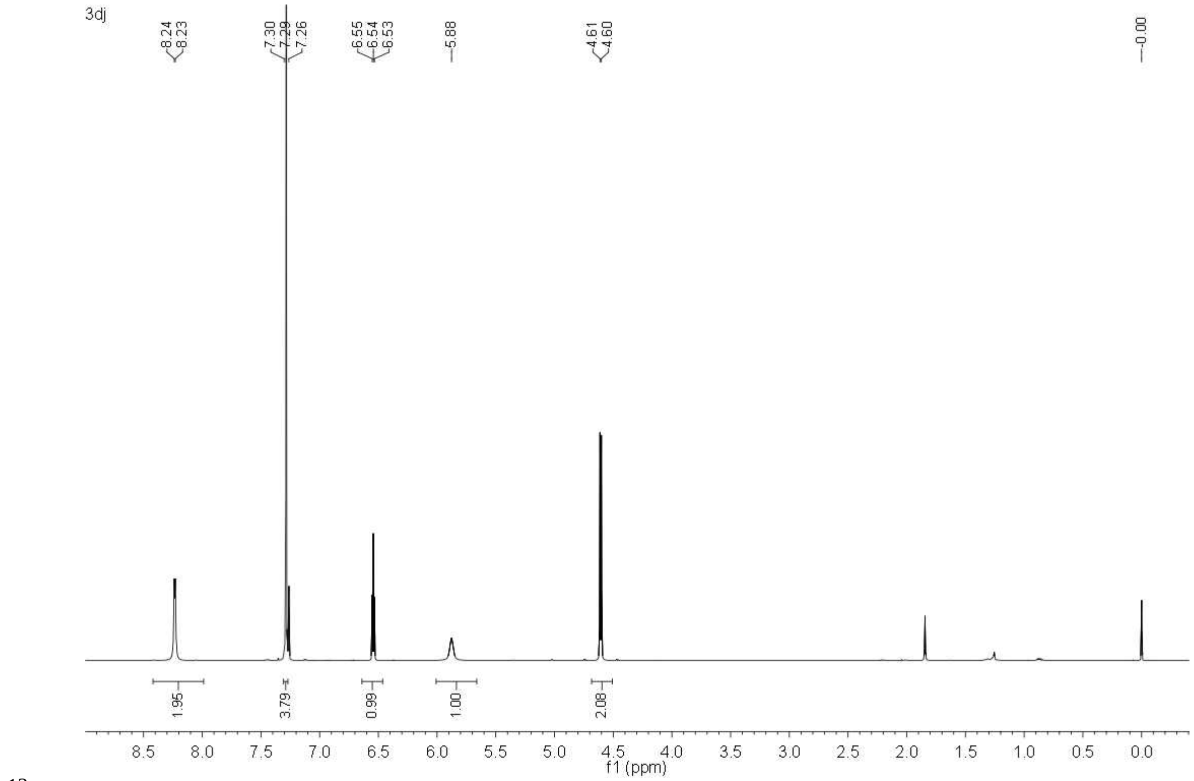
^{13}C NMR



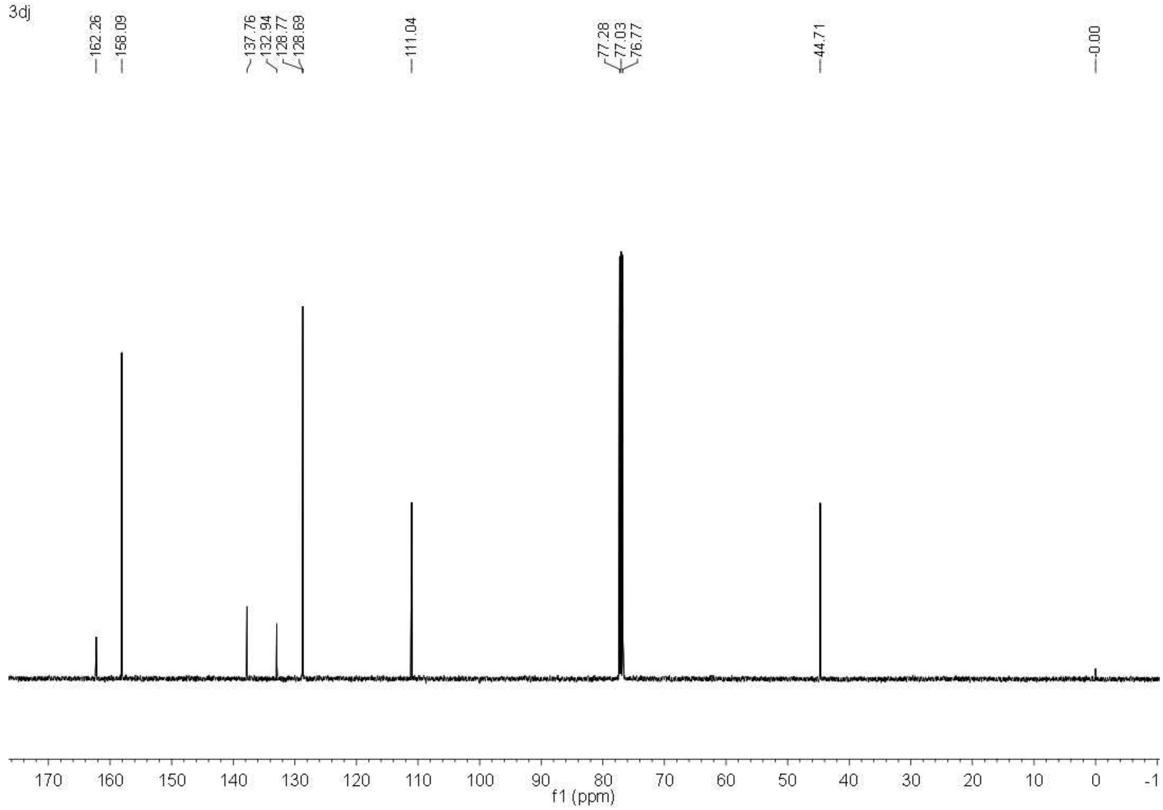


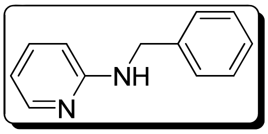
3dj

^{1}H NMR



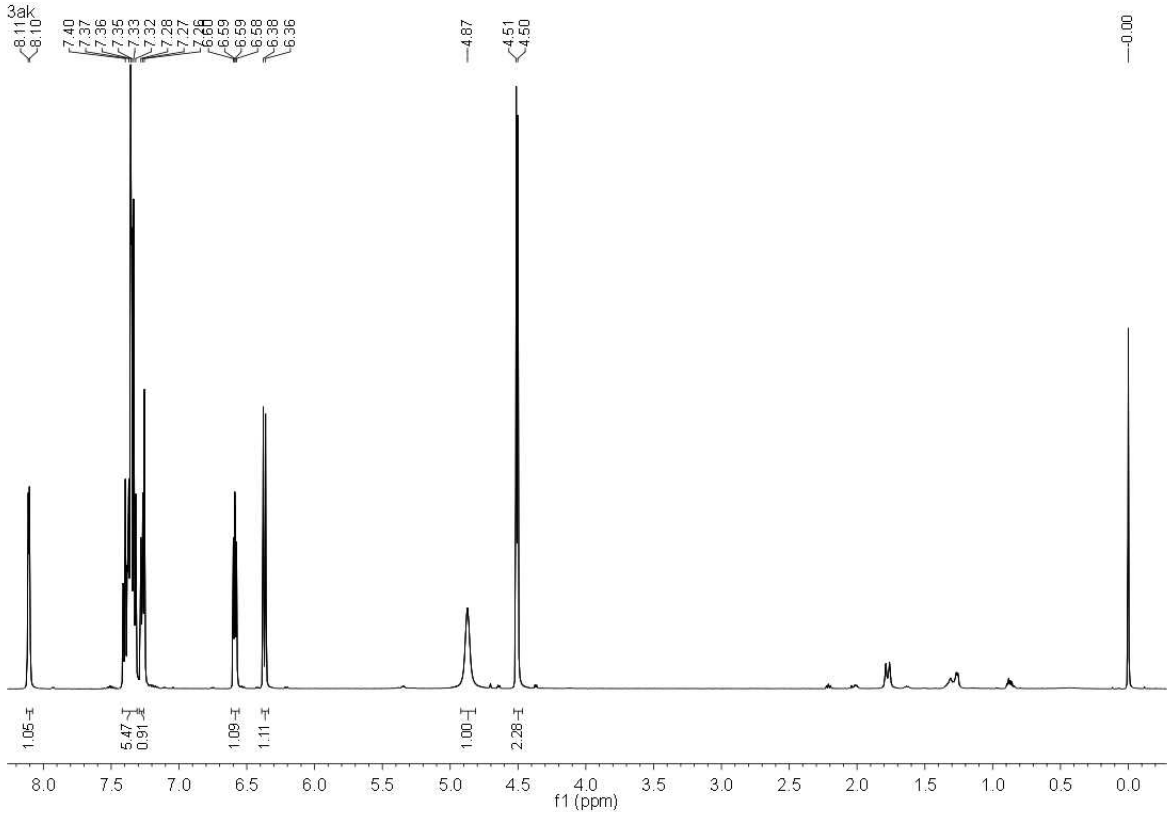
^{13}C NMR



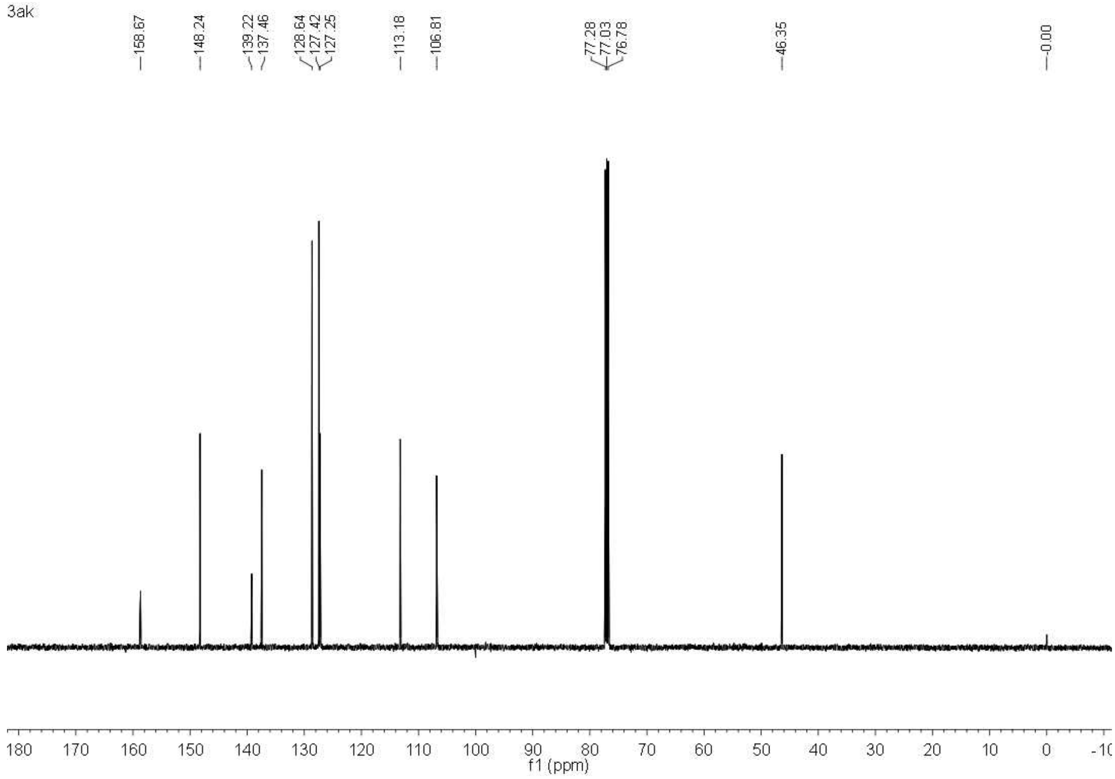


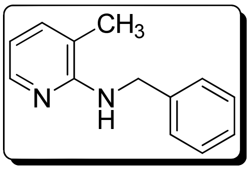
3ak

^{1}H NMR



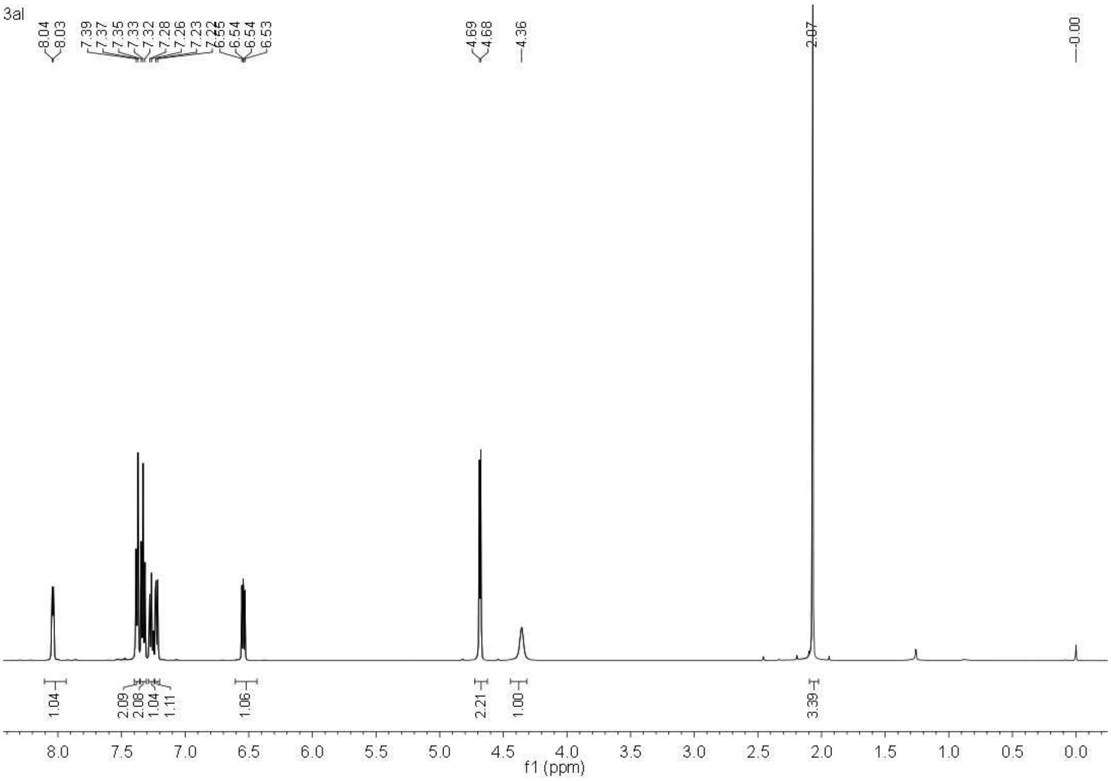
^{13}C NMR



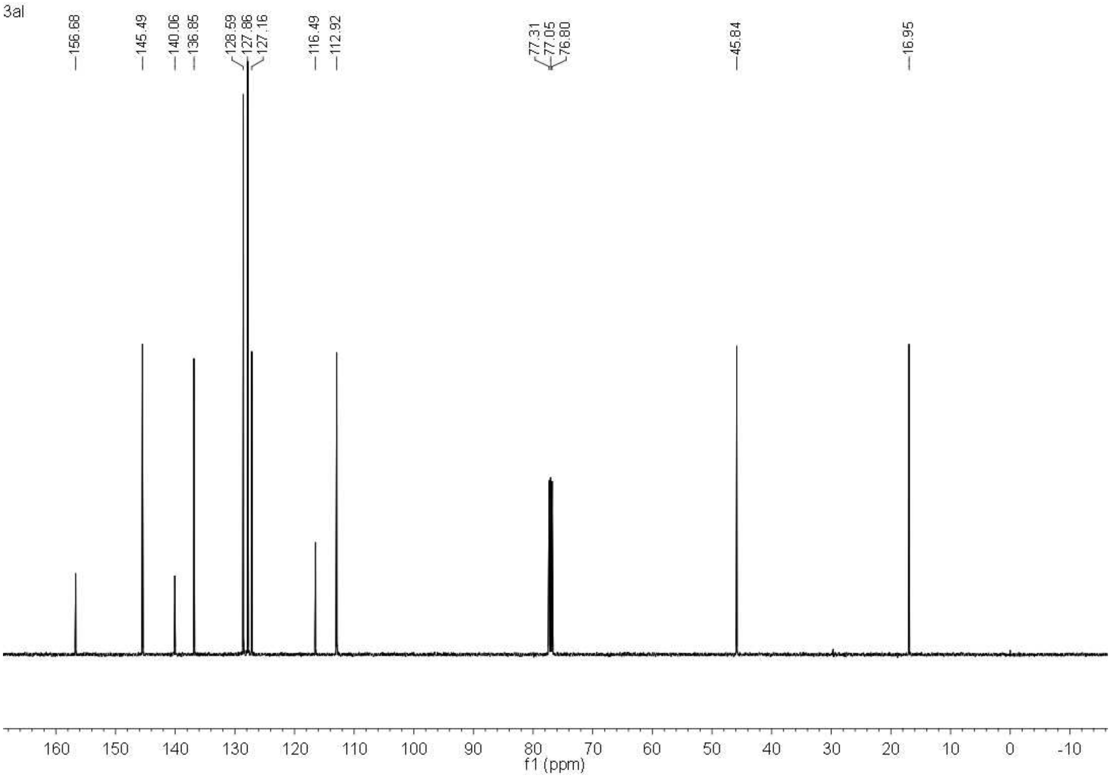


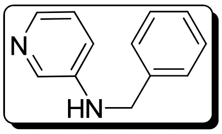
3al

^{1}H NMR



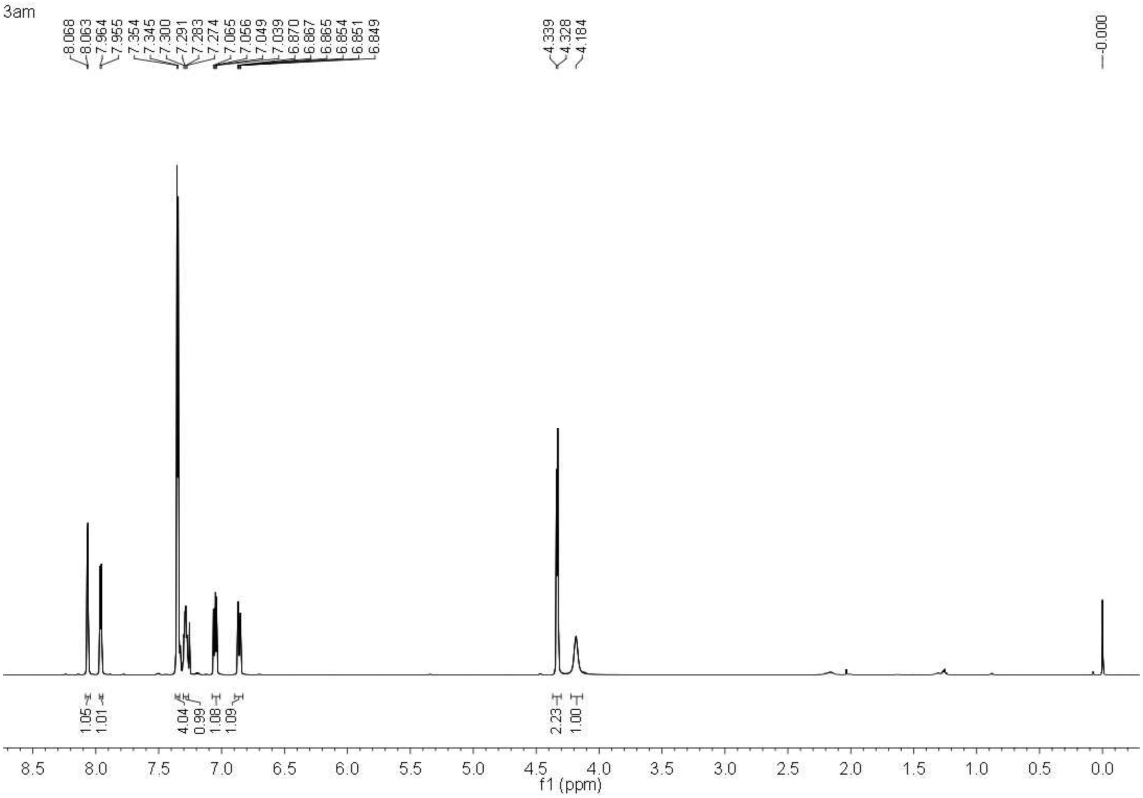
^{13}C NMR



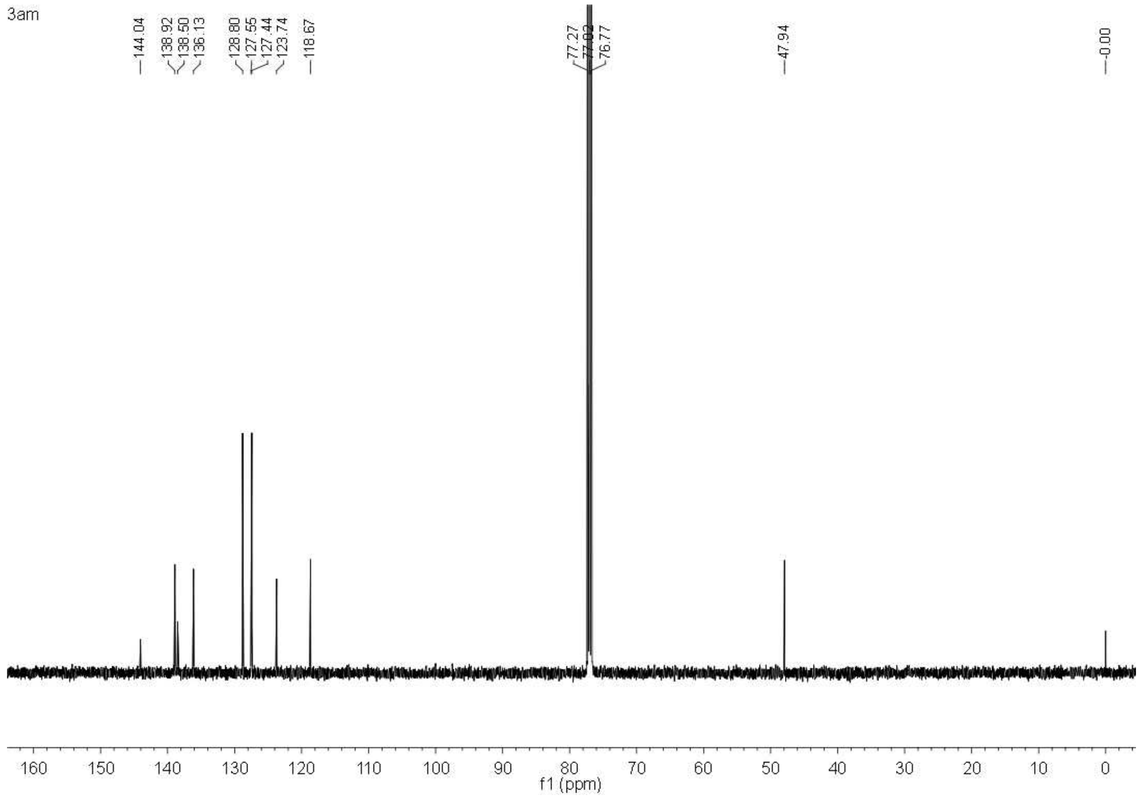


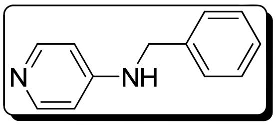
3am

^{1}H NMR



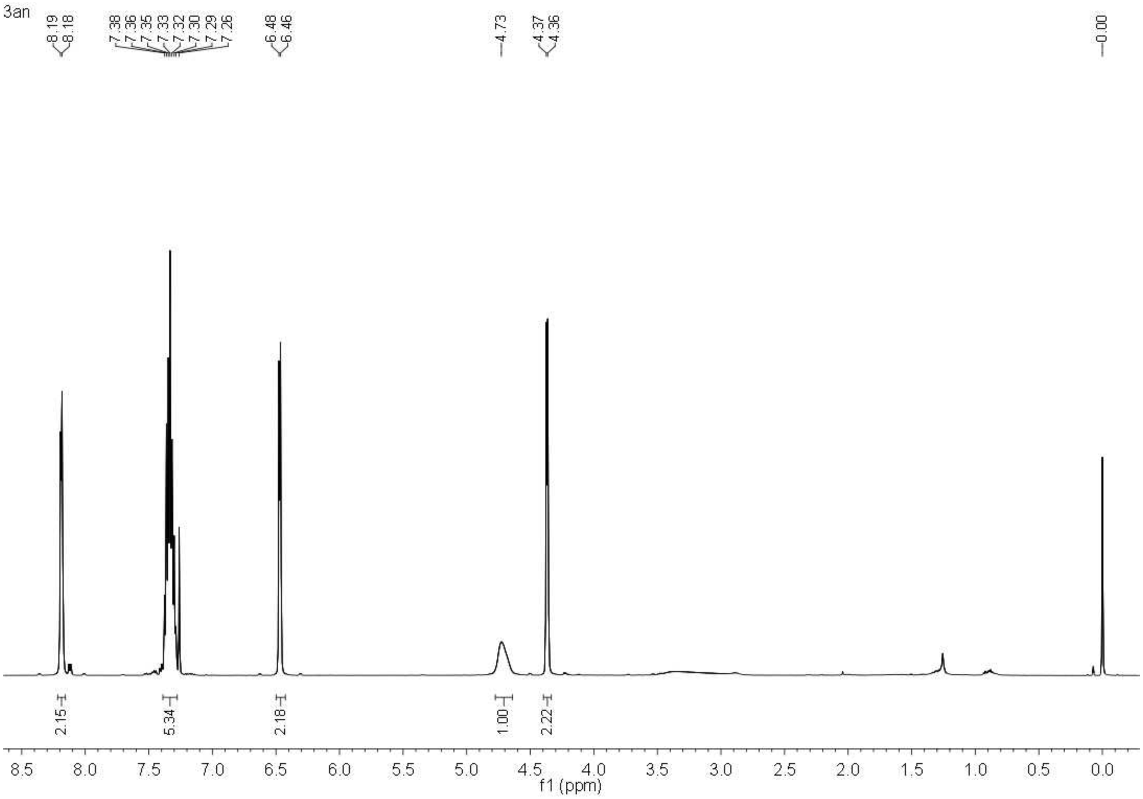
^{13}C NMR



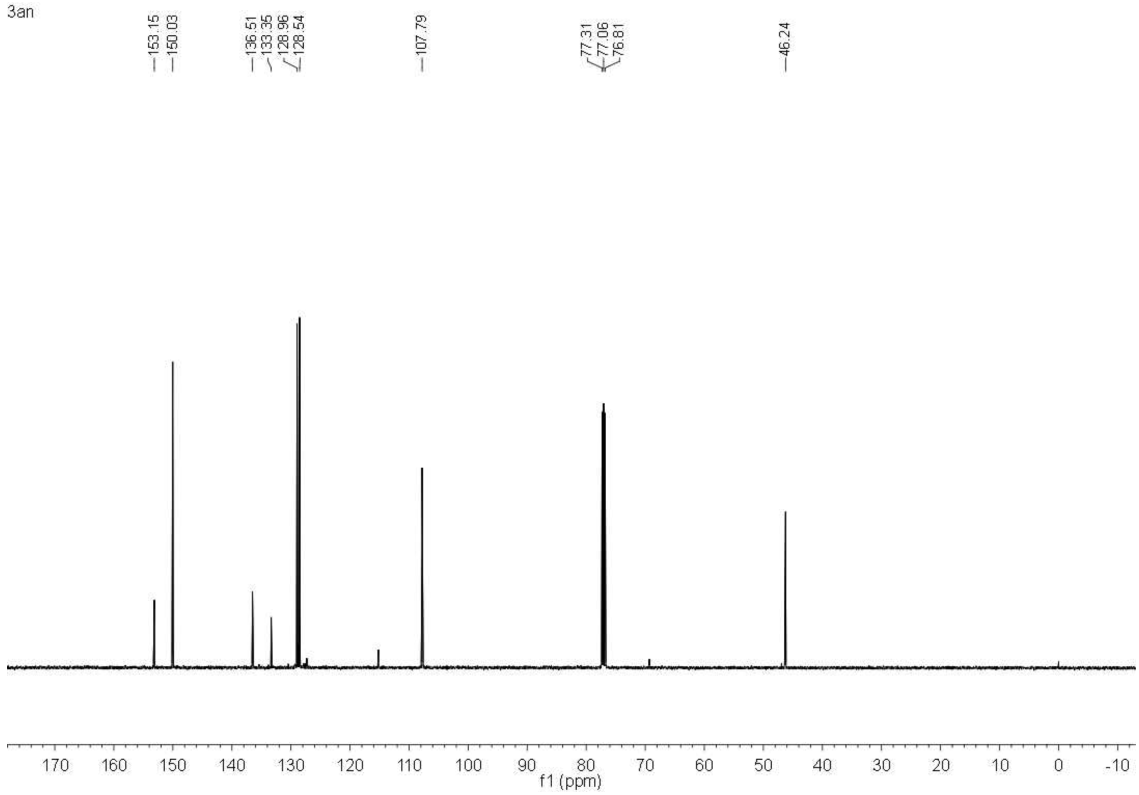


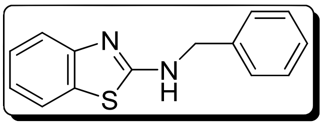
3an

^{1}H NMR



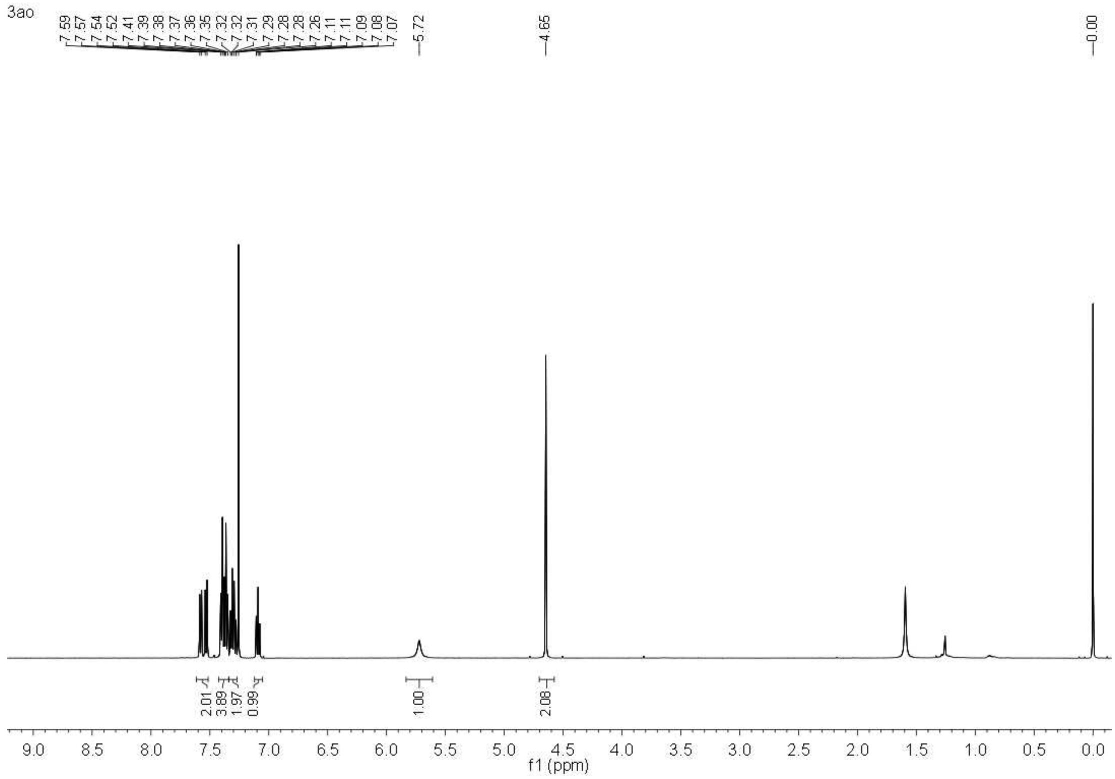
^{13}C NMR





3ao

^{1}H NMR



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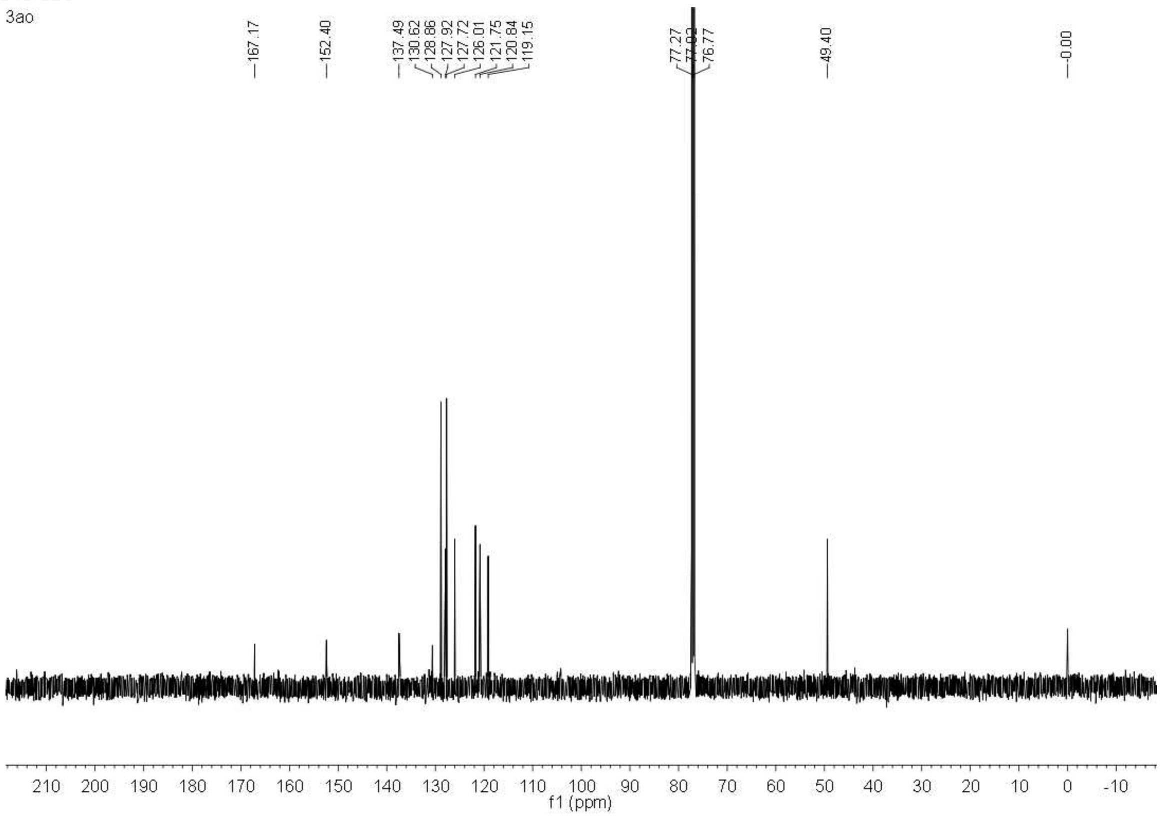
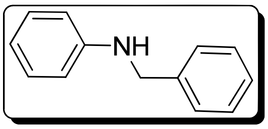
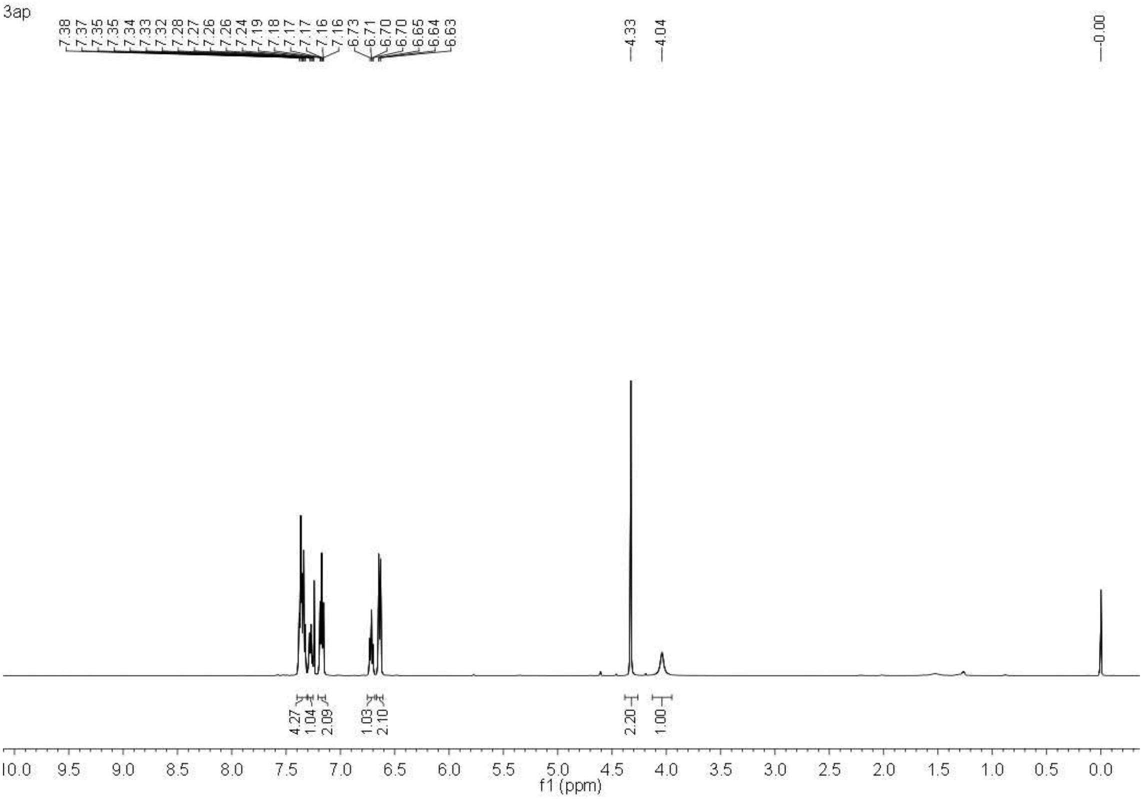




3ap

^{1}H NMR



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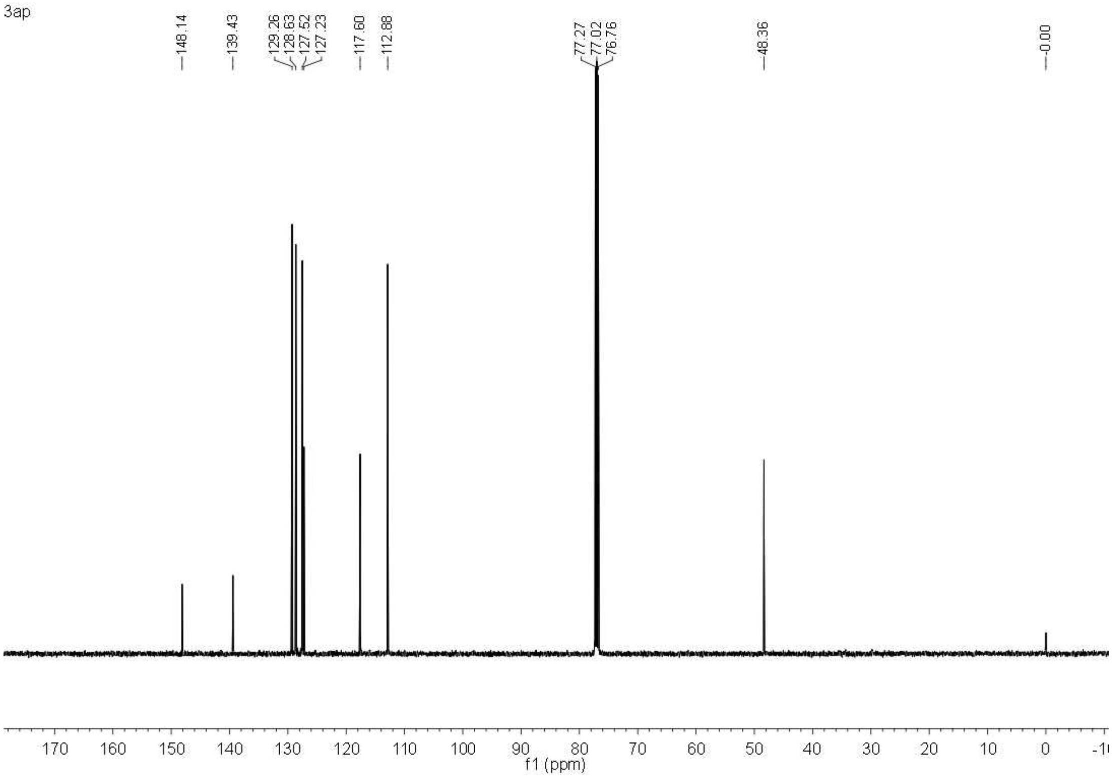
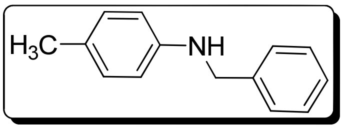
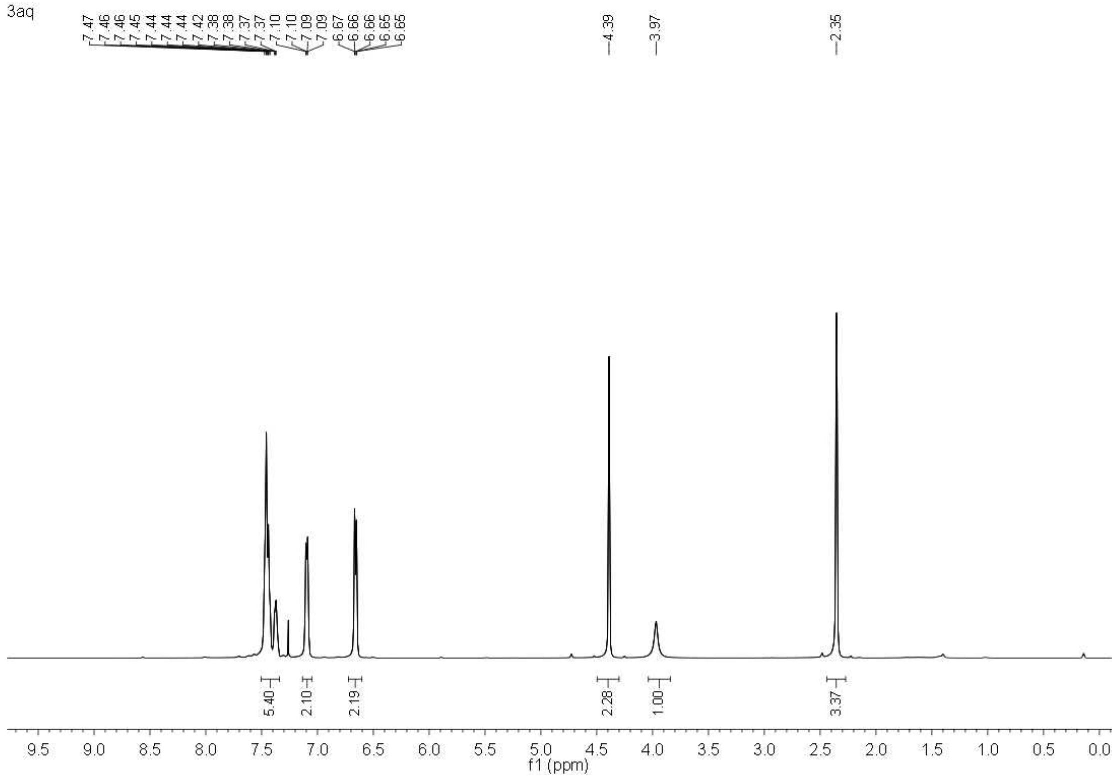




3aq

^{1}H NMR



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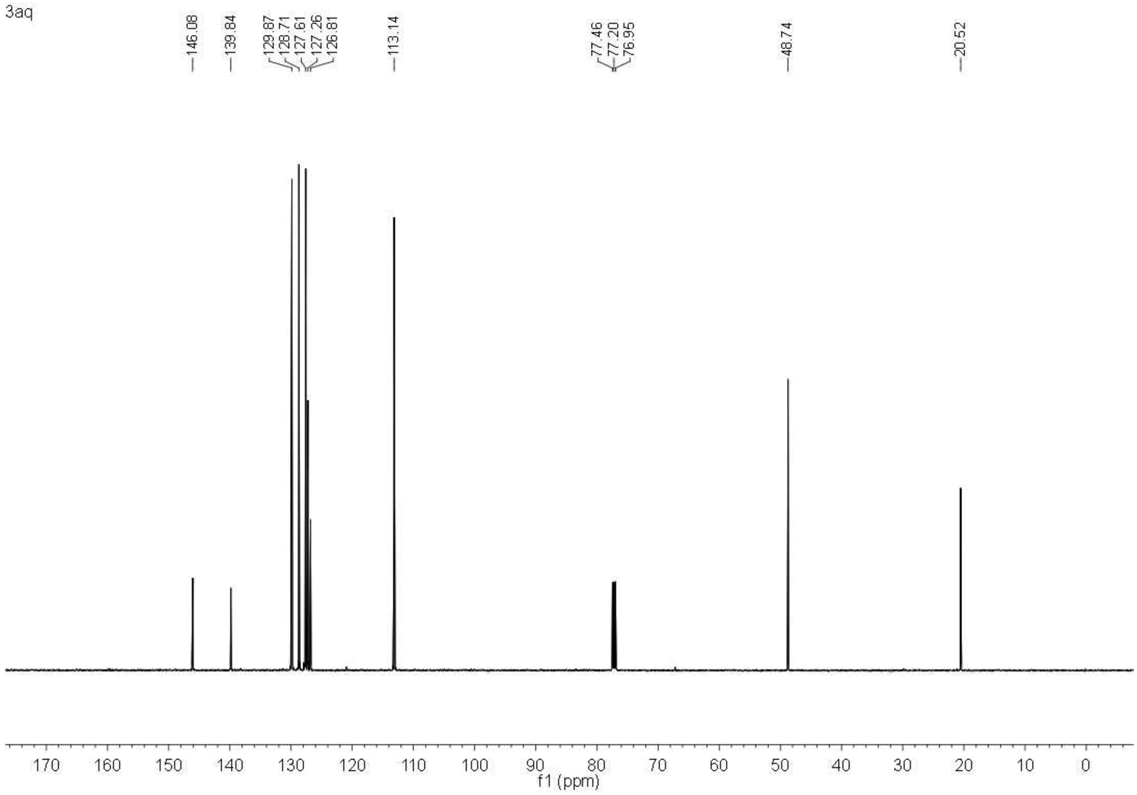
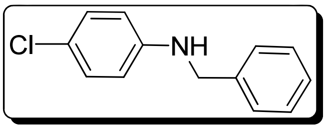
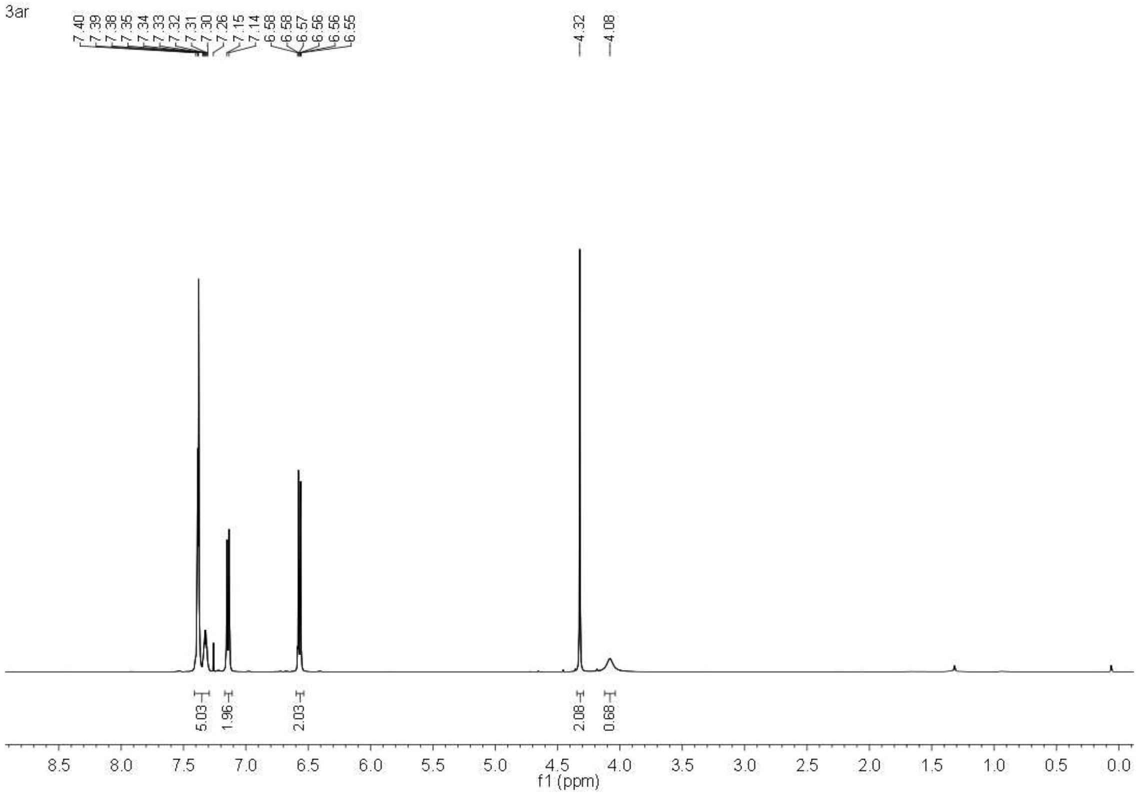


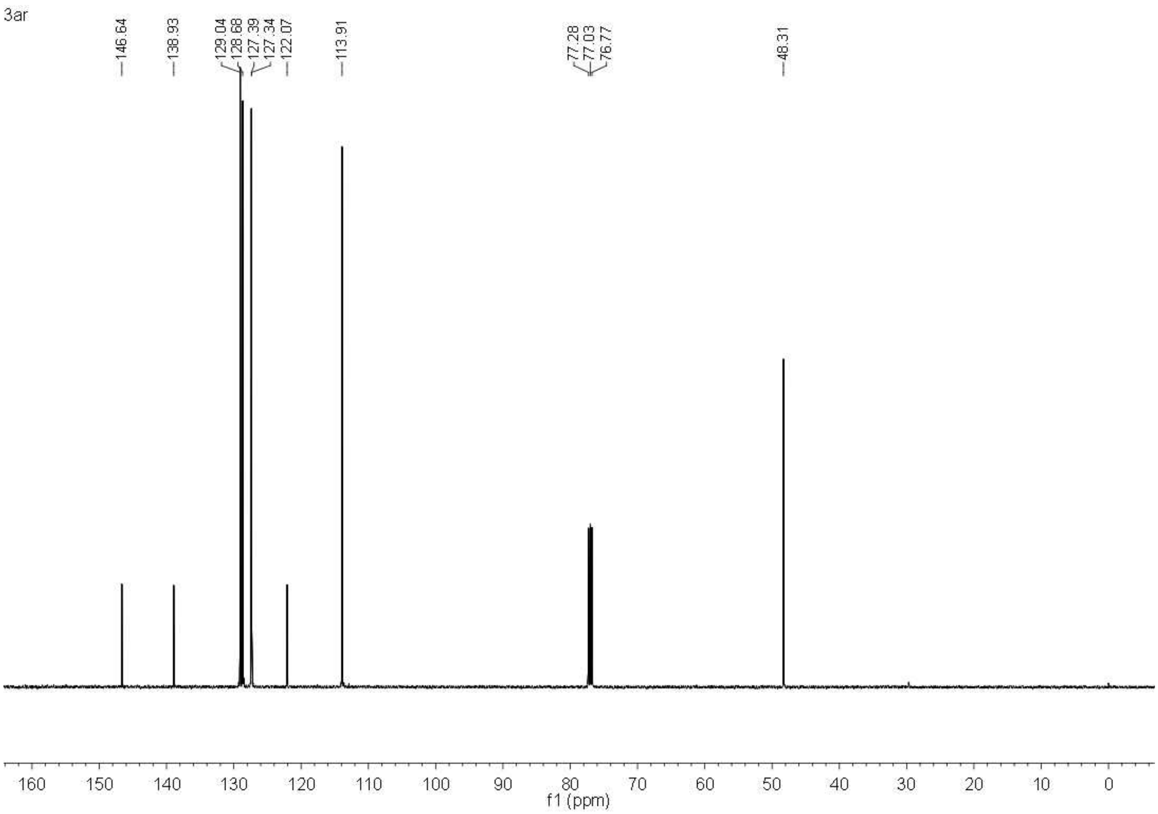


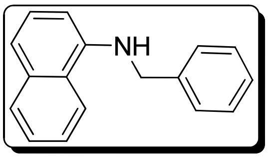
3ar

^{1}H NMR



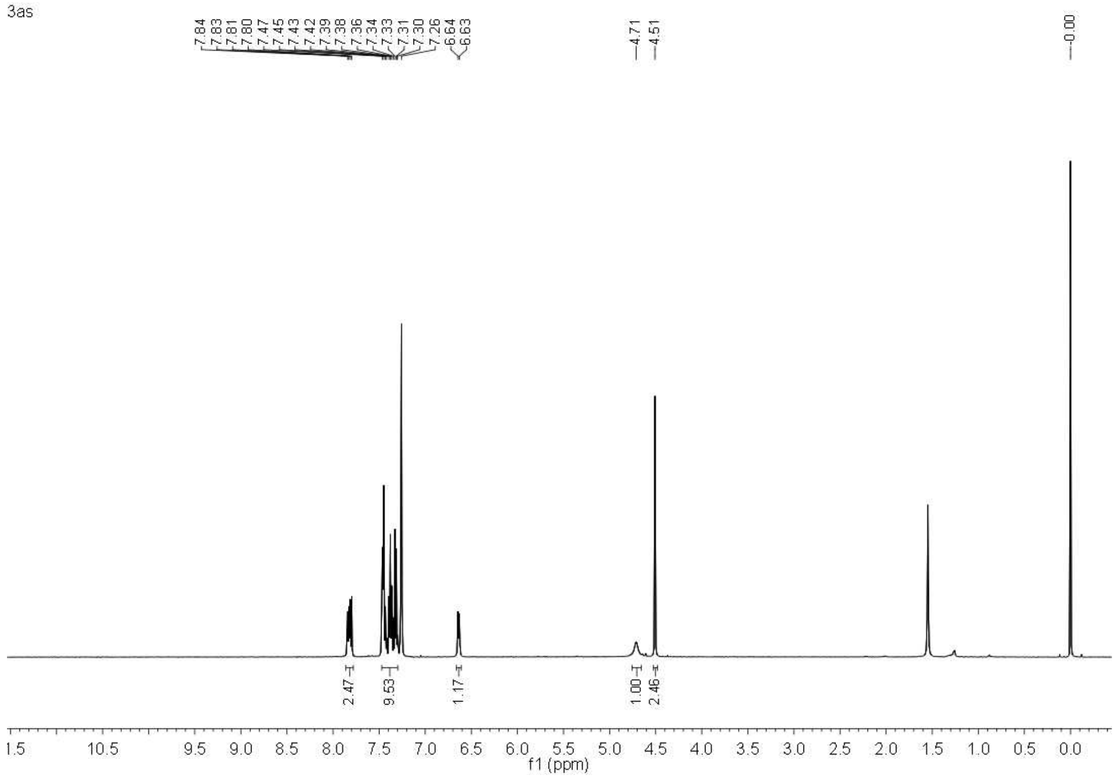
^{13}C NMR





3as

^{1}H NMR



^{13}C NMR