Visible Light-Promoted Alkylation of Polar π-Bonds (C=O and C=N) Using Potassium Organotrifluoroborates

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SUPPLEMENTARY INFORMATION

General Information

Unless otherwise noted, all reagents were purchased from commercial sources and used as received. *N*-(Benzylidene)aniline (**2a**) was prepared according to the method of Bigelow and Eatough.[1] Solvents were degassed and dried using a PureSolv Solvent Purification System by Innovative Technology. Melting points were measured on an Electrothermal IA9100 digital melting point apparatus and are uncorrected. ^{1}H NMR spectra were obtained at 300 MHz or 400 MHz; ^{13}C NMR spectra were obtained at 75 MHz or 100 MHz. Chemical shifts are reported in parts per million (δ) using the solvent residual proton or carbon signal ($CDCl_3$: δH 7.26 ppm, δC 77.3 ppm; d6-DMSO: δH 2.50 ppm, δC 39.5 ppm) as an internal reference. FTIR spectra were recorded on a ThermoScientific Nicolet iS10 or Avatar 370 spectrometer. GC/EI-MS analyses were performed on an Agilent Technologies 7890 GC equipped with 30 m x 0.32 mm Agilent HP-5 column coupled to an Agilent Technologies 5975C MSD. Flash column chromatography was carried out using silica gel (grade 60, 230 – 400 mesh). Feit 16 W PAR 38 blue LED reflector floodlights were purchased from Amazon.com; the emission spectrum was measured with an Ocean Optics Red Tide USB650 spectrophotometer.

General Procedure for Visible Light-Promoted Alkylation of Imines.

An appropriate potassium organotrifluoroborate (**1**, 0.38 mmol), **2a** (0.25 mmol), ***Ir-dF(CF$_3$)-dtb*** (7.1 mg, 0.0063 mmol, 2.5 mol %), and CH_2Cl_2 (5 mL) were added to an oven dried 25 mL Schlenk tube equipped with a Teflon stir bar and rubber septum. The solution was sparged with argon for 15 minutes, and then placed between two Feit 16 W blue LED floodlights (~9 cm away, Figure S1; emission spectrum shown in Figure S2). Unless otherwise indicated, the solution was illuminated with stirring for 46 h; the temperature was maintained at approximately 30 °C by a fan blowing across the reaction vessel. The reaction mixture was quenched with saturated aqueous NH_4Cl (20 mL), and extracted with (3 x 10 mL) of CH_2Cl_2. The combined organic layers were dried (Na_2SO_4), evaporated, and purified by flash column chromatography (hexanes/ethyl acetate) to give the product.

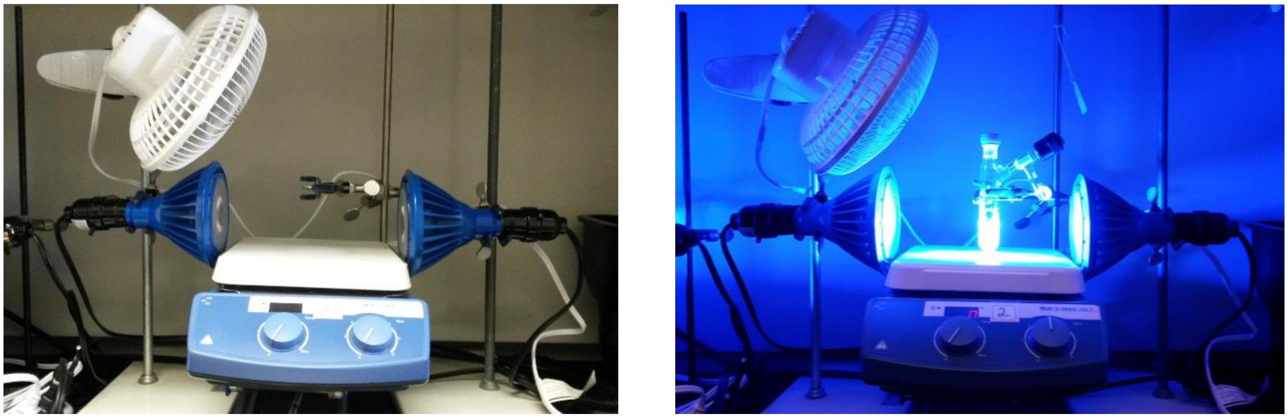


Figure S1

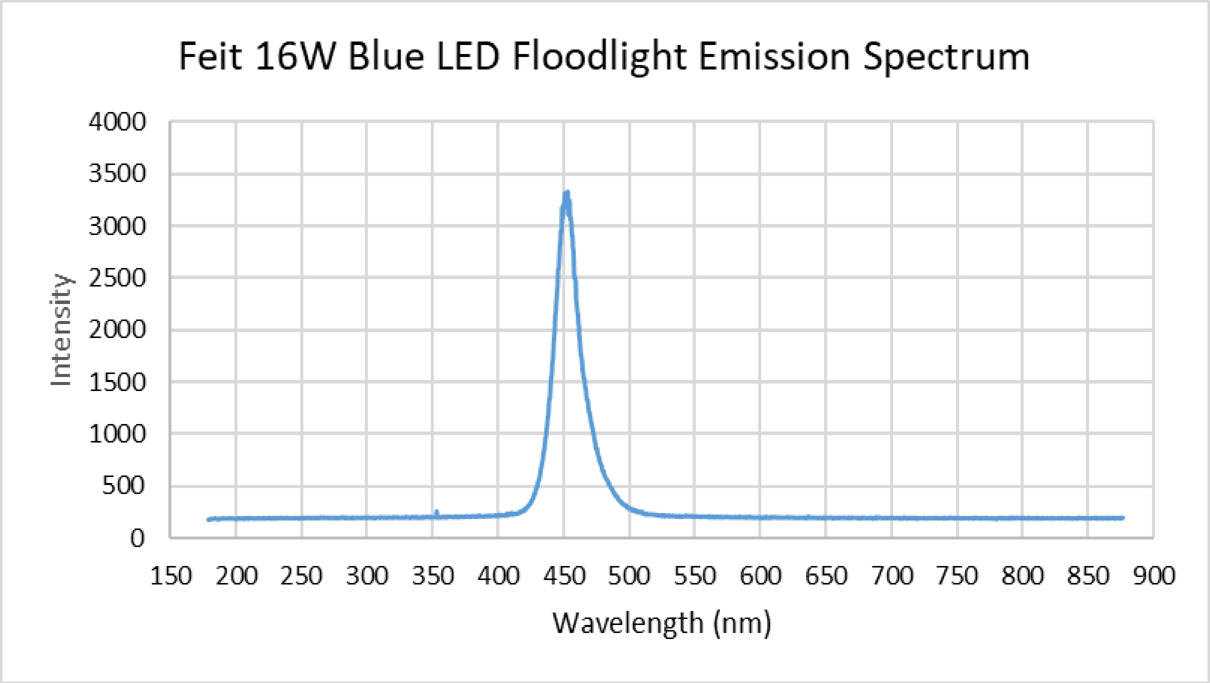
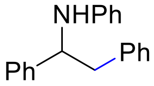


Figure S2

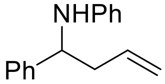
Compound Data for Amines (3)

N-(1,2-Diphenylethyl)aniline (**3a**).



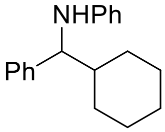
Pale yellow oil. Yield: 70%. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.38-7.19 (m, 8H), 7.18-7.11 (m, 2H), 7.10-7.02 (m, 2H), 6.68-6.61 (m, 1H), 6.51-6.44 (m, 2H), 4.62-4.56 (m, 1H), 4.12 (br s, 1H), 3.20-2.97 (m, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 147.4, 143.5, 137.8, 129.3, 129.1, 128.7, 128.6, 127.1, 126.8, 126.5, 117.6, 113.7, 59.3, 45.3. EI-MS: m/z 273 (M^+, 1), 183 (32), 182 (100), 180 (20), 104 (30), 91 (17), 77 (49). These data are in agreement with reported literature data.[2]

N-(1-Phenyl-3-buten-1-yl)aniline (**3b**)



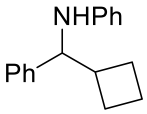
Orange oil. Yield: 70%. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.49-7.20 (m, 5H), 7.16-7.04 (m, 2H), 6.72-6.61 (m, 1H), 6.56-6.46 (m, 2H), 5.86-5.68 (m, 1H), 5.26-5.12 (m, 2H), 4.45-4.36 (m, 1H), 4.18 (br s, 1H), 2.69-2.42 (m, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 147.4, 143.6, 134.7, 129.1, 128.7, 127.1, 126.4, 118.4, 117.4, 113.6, 57.2, 43.4. IR (ATR): 3407 cm^{-1} (N-H). EI-MS: m/z 223 (M^+, 2), 183 (18), 182 (100), 104 (23), 77 (39). These data are in agreement with reported literature data.[2]

N-(1-Cyclohexyl-1-phenylmethyl)aniline (**3c**)



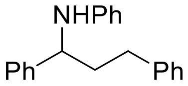
Orange oil. Yield: 72%. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.31-7.16 (m, 5H), 7.10-7.01 (m, 2H), 6.64-6.56 (m, 1H), 6.52-6.45 (m, 2H), 5.86-5.68 (m, 1H), 4.15 (br s, 1H), 4.11 (d, J = 6.3 Hz, 1H), 4.18 (br s, 1H), 1.94-1.44 (m, 6H), 1.30-0.94 (m, 5H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 147.8, 142.7, 129.1, 128.3, 127.3, 126.8, 117.0, 113.2, 63.5, 45.0, 30.3, 29.5, 26.5, 26.5, 26.4. IR (ATR): 3422 cm^{-1} (N-H). EI-MS: m/z 265 (M^+, 3), 183 (18), 182 (100), 104 (15), 91 (13), 77 (25). These data are in agreement with reported literature data.[3]

N-(1-Cyclobutyl-1-phenylmethyl)aniline (**3e**)



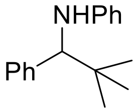
Pale yellow oil. Yield: 50%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.40-7.46 (m, 4H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 2H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 7.7 Hz, 2H), 4.16 (d, *J* = 8.8 Hz, 1H), 4.01 (br s, 1H), 2.59-2.46 (m, 1H), 2.19-2.07 (m, 1H), 1.96-1.73 (m, 5H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 147.8, 142.6, 129.1, 128.5, 127.0, 126.6, 117.2, 113.4, 63.8, 42.6, 26.2, 25.6, 17.6. IR (ATR): 3410 cm^{-1} (N-H). EI-MS: m/z 237 (M^+, 6), 183 (14), 182 (100), 144 (12), 129 (17), 115 (20), 104 (12), 91 (25), 77 (30). HRMS calculated for $C_{17}H_{20}N$ (M + H): 238.1590, found: 238.1590.

N-(1,3-Diphenylpropyl)aniline (**3f**)



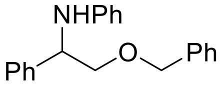
Illuminated for 168 h. Yellow oil. Yield: 41%. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.37-7.13 (m, 10H), 7.08 (t, *J* = 7.5 Hz, 2H), 6.64 (t, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 8.5 Hz, 2H), 4.35 (t, *J* = 6.8 Hz, 1H), 4.12 (br s, 1H), 2.80-2.62 (m, 2H), 2.24-2.04 (m, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 147.2, 143.8, 141.5, 129.2, 128.7, 128.6, 128.5, 127.1, 126.6, 126.1, 117.5, 113.5, 57.9, 40.2, 32.7. IR (ATR): 3409 cm^{-1} (N-H). EI-MS: m/z 287 (M^+, 4), 194 (16), 183 (18), 182 (100), 115 (15), 104 (20), 93 (17), 91 (55), 77 (32). These data are in agreement with reported literature data.[4]

N-(2,2-Dimethyl-1-phenylpropyl)aniline (**3g**)

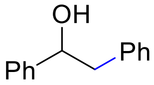


Orange oil. Yield: 72%. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.35-7.17 (m, 5H), 7.05 (t, *J* = 7.4 Hz, 2H), 6.59 (t, J = 7.4 Hz, 1H), 6.49 (d, J = 7.7 Hz, 2H), 4.26 (br s, 1H), 4.05 (s, 1H), 1.00 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 147.8, 141.3, 129.1, 128.6, 127.8, 126.9, 117.0, 113.3, 67.3, 35.0, 27.2. IR (ATR): 3438 cm^{-1} (N-H). EI-MS: m/z 239 (M^+, 3), 183 (22), 182 (100), 181 (36), 180 (47), 104 (24), 77 (55). These data are in agreement with reported literature data.[5]

N-(2-Phenoxy-1-phenylethyl)aniline (**3h**)



Yellow oil. Yield: 61%. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.45-7.22 (m, 10H), 7.05 (t, *J* = 8.0 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 2H), 6.52 (d, *J* = 7.7 Hz, 2H), 4.83-4.49 (m, 4H), 3.74 (dd, *J* = 10.0, 4.0 Hz, 1H), 3.59 (t, *J* = 9.2 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 147.4, 140.6, 137.9, 129.1, 128.8, 128.6, 127.9, 127.8, 127.6, 127.0, 118.0, 114.3, 74.4, 73.1, 58.5. IR (ATR): 3391 cm^{-1} (N-H). EI-MS: m/z 303 (M^+, 5), 183 (37), 182 (100), 180 (13), 104 (34), 91 (45), 77 (50). HRMS calculated for $C_{21}H_{22}NO$ (M + H): 304.1696, found: 304.1697.



*1,2-Diphenylethanol (**4**).*

Potassium benzyltrifluoroborate (**1a**, 75.2 mg, 0.38 mmol), diphenyl phosphate (, ***Ir-dF(CF$_3$)-dtb*** (7.1 mg, 0.0063 mmol, 2.5 mol %), and CH_2Cl_2 (5 mL) were added to an oven dried 25 mL Schlenk tube equipped with a Teflon stir bar and rubber septum. The vessel was sealed, then evacuated and purged with argon three times. Benzaldehyde (26.5 mg, 25.5 µL, 0.25 mmol) was added, followed by dry, degassed CH_2Cl_2 (5 mL). The greenish yellow hazy mixture was placed between two Feit 16 W blue LED floodlights (~9 cm away, Figure S1; emission spectrum shown in Figure S2), and illuminated with stirring for 46 h; the temperature was maintained at approximately 30 °C by means of a fan.. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (20 mL), and extracted with (3 x 10 mL) of CH_2Cl_2. For determination of yield by NMR, the combined organic layers were dried (Na_2SO_4), a known amount of 1,3,5-trimethoxybenzene (~0.14 mmol) was added to the dried organic extract, and the solution was evaporated and analyzed by ^{1}H-NMR, using the integration ratio of the signals at 4.9 (**4**, dd, 1H) and 6.1 ($C_6H_3(OCH_3)_3$, s, 3H) to determine product yield. For product isolation, the combined organic layers were dried (Na_2SO_4), evaporated, and purified by flash column chromatography (hexanes/ethyl acetate) to give 19.8 mg (40%) of **4** as an off-white powder. Mp: 63-64 °C (lit:[6] 64 °C). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.39-7.16 (m, 10H), 4.90 (dd, *J* = 8.3, 5.0 Hz, 1H), 3.08-2.92 (m, 2H), 1.80 (br s, 1H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 143.9, 138.1, 129.6, 128.6, 128.5, 127.7, 126.7, 126.0, 75.4, 46.2. IR (ATR): 3302 cm^{-1} (O-H). EI-MS: m/z 198 (M^+, 1), 181 (12), 180 (80), 179 (80), 178 (55), 176 (10), 165 (42), 152 (14), 107 (100), 105 (14). These data are in agreement with those reported in the literature.[6]

Light-Dark Experiment.

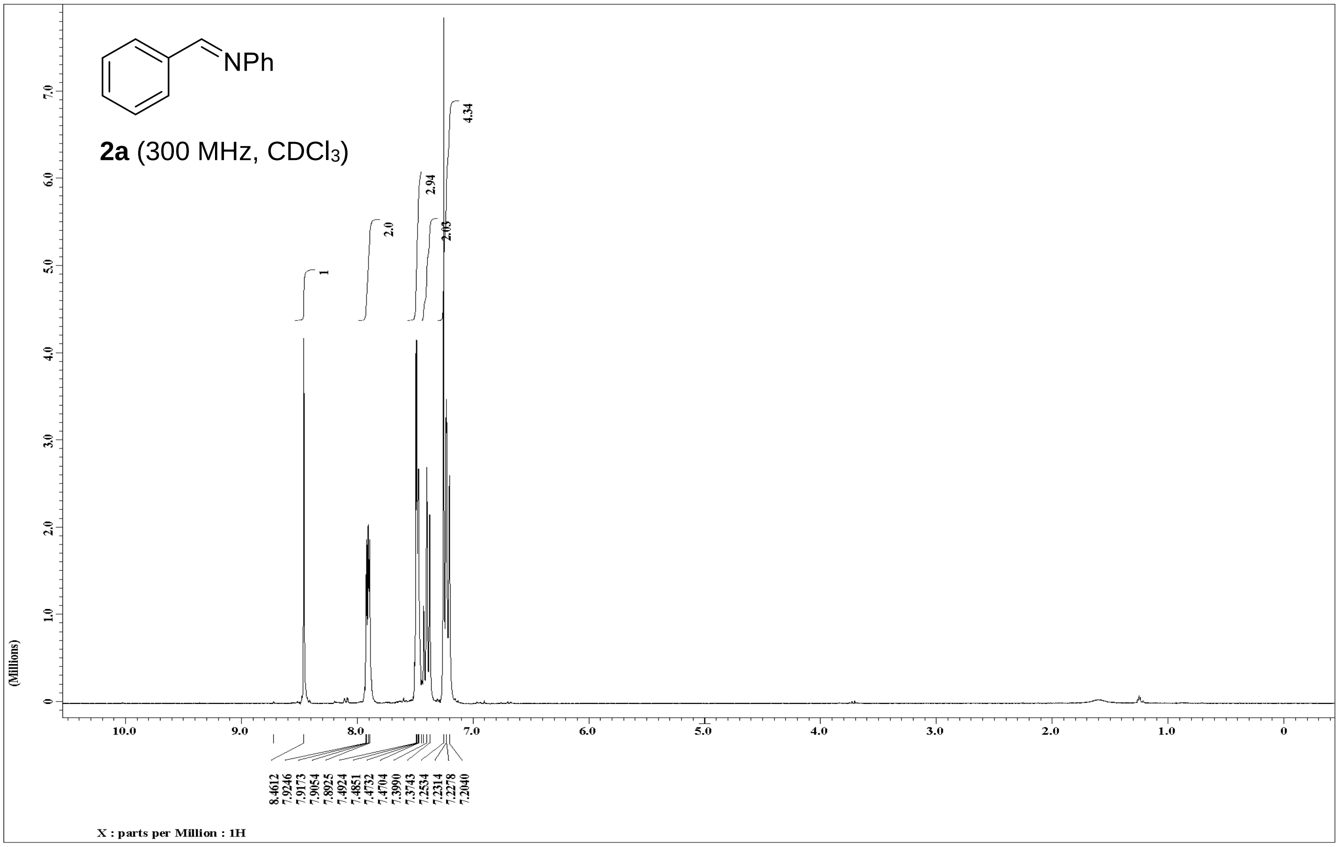
Potassium benzyltrifluoroborate (**1a**, 54.5 mg, 0.38 mmol), benzalaniline (**2a**, 45.4 mg, 0.25 mmol), ***Ir-dF(CF_3)-dtb*** (7.1 mg, 0.0063 mmol, 2.5 mol %), and CH_2Cl_2 (5 mL) were added to an oven dried 25 mL Schlenk tube equipped with a Teflon stir bar and rubber septum. Decane (145 µL) was added as an internal standard. The solution was sparged with argon for 15 minutes, then placed between two 16 W blue LEDs (~9 cm away, Figure S1). The solution was illuminated with stirring for a period of time (usually 10 min), and sampled for GC/MS analysis at the end of the illumination period. The solution was stirred in the dark (kept in a sealed cardboard box, usually 30 min), and sampled for GC/MS analysis at the end of the "dark" stir period. Progress of the reaction was measured by the ratio of GC area of product **3a** to GC area of decane (IS). Results are tabulated below.

Time (min)	GC Area Ratio (**3a**/IS)	Illumination (off/on)
0	0.00	on
10	0.22	
10	0.22	off
40	0.21	
40	0.21	on
50	0.44	
50	0.44	off
80	0.47	
80	0.47	on
90	0.62	
90	0.62	off
1050	0.60	
1050	0.60	on
1060	0.88	
1060	0.88	off
1090	0.84	
1090	0.84	on
1100	1.00	
1100	1.00	off
1130	1.04	
1130	1.04	on
1140	1.01	
1140	1.01	off
1170	1.04	
1170	1.04	on
1180	1.02	

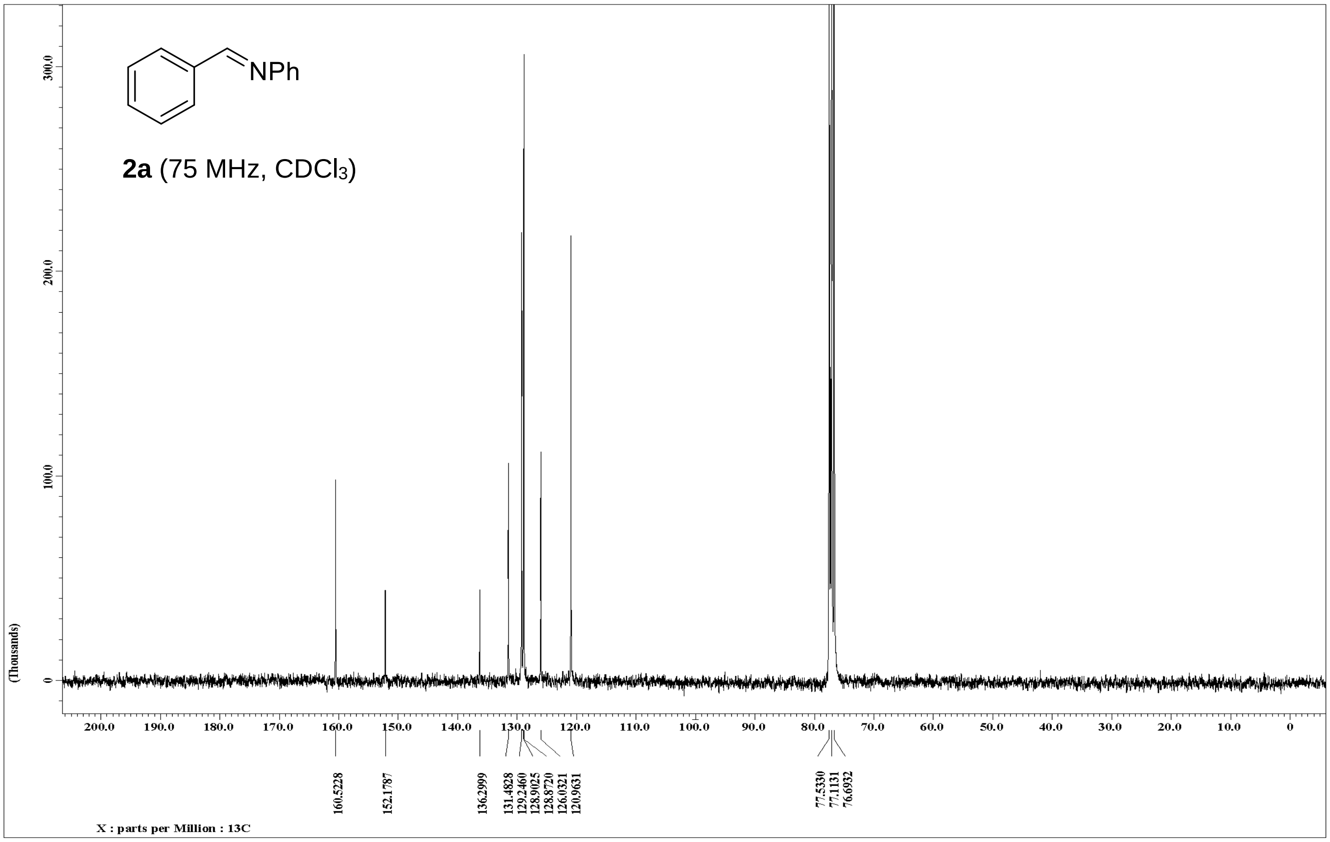
References

1. Bigelow, L. A.; Eatough, H. *Org. Synth.* **1928**, *8*, 22-23.
2. Zhang, Y.; Yan, T.; Cheng, W.; Zuo, J.; Zhao, W. *Tetrahedron Lett.* **2009,** *50*, 2925-2928.
3. Shen, Z. L.; Cheong, H. L.; Loh, T. P. *Chem. Eur. J.* **2008,** *14*, 1875-1880.
4. Chen, N.; Dai, X. J.; Wang, H.; Li, C. J. *Angew. Chem. Int. Ed.* **2017,** *56*, 6260-6263.
5. Russell, G. A.; Wang, L.; Rajaratnam, R. *J. Org. Chem.* **1996,** *61*, 8988-8991.
6. Lewis, F. W.; McCabe, T. C.; Grayson, D. H. *Tetrahedron* **2011**, *67*, 7517-7528.

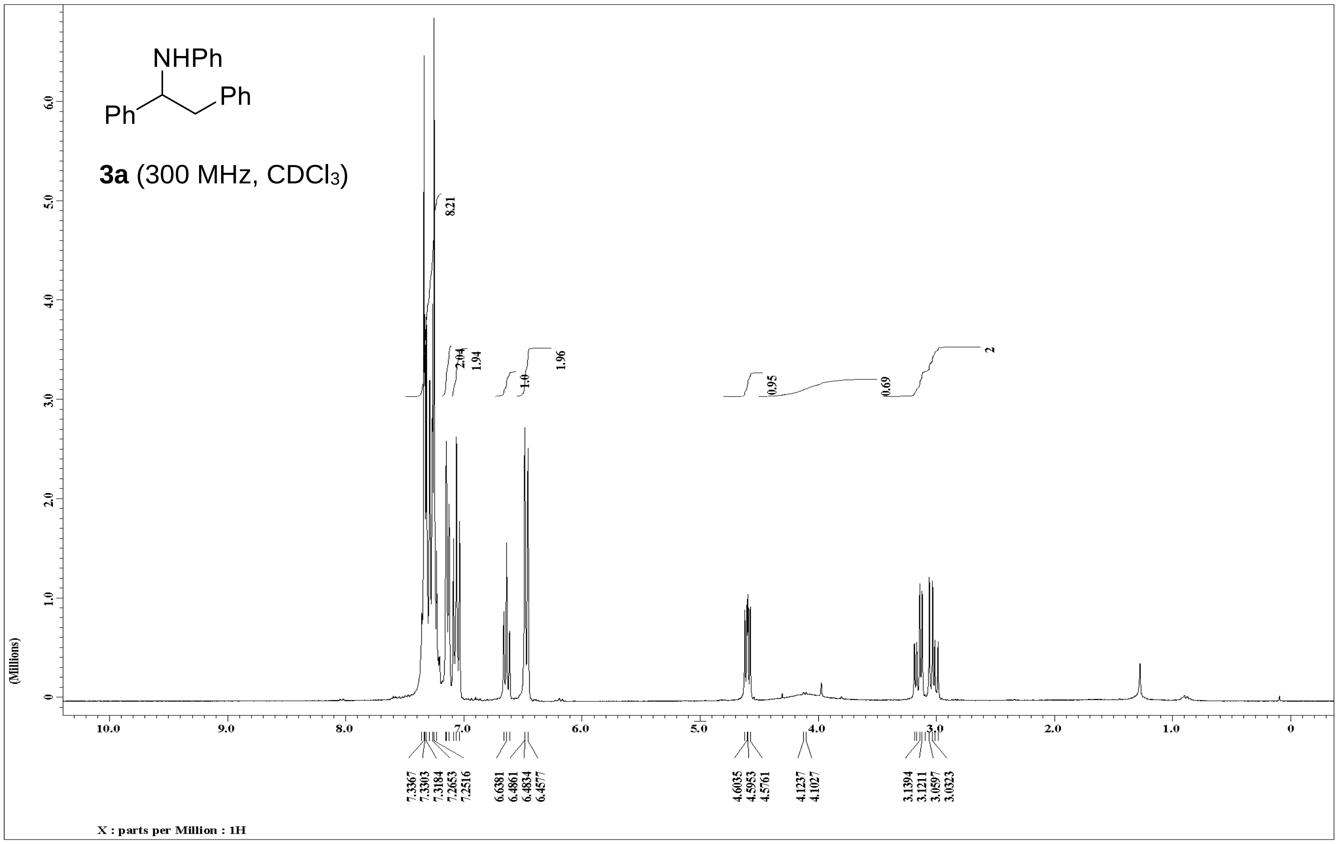
COMPOUND SPECTRA

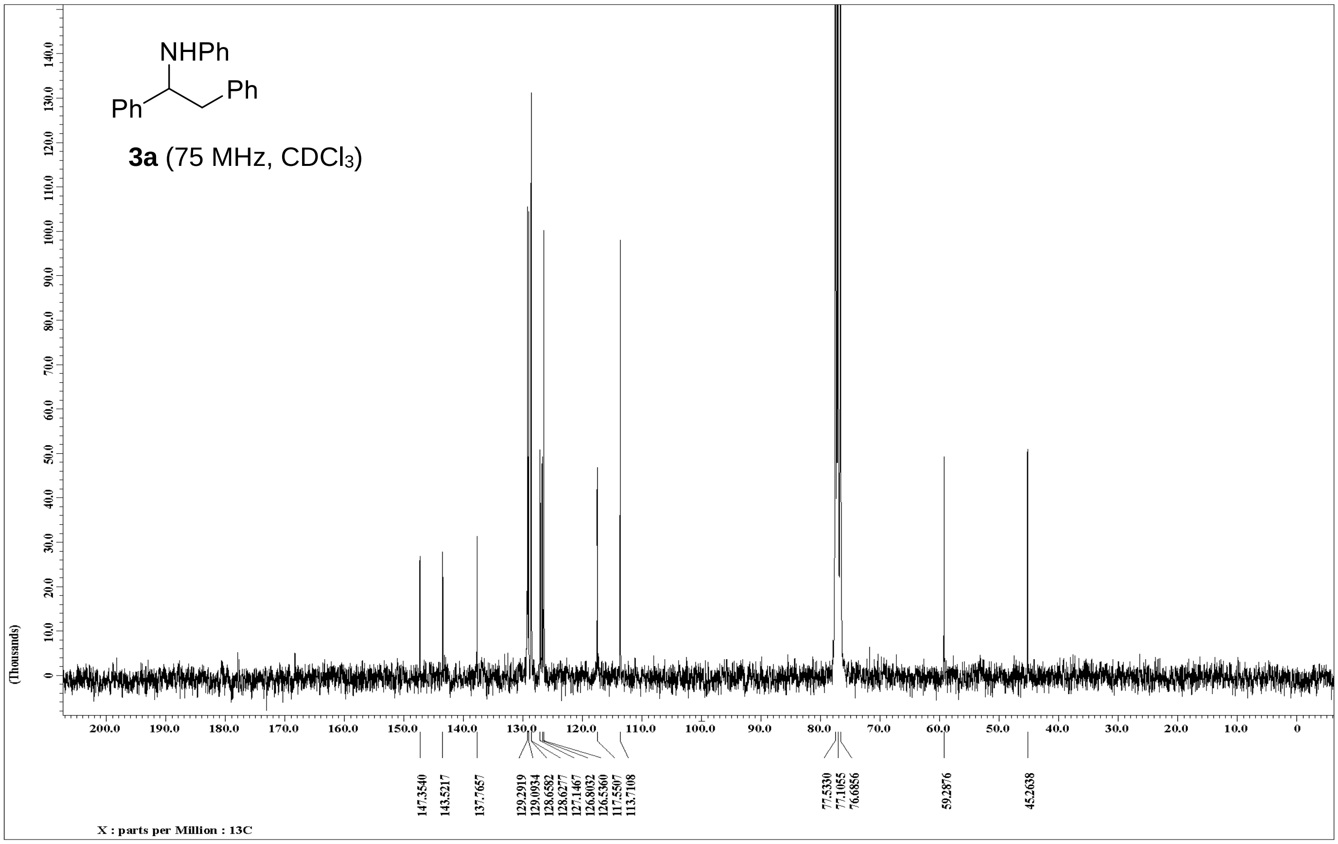


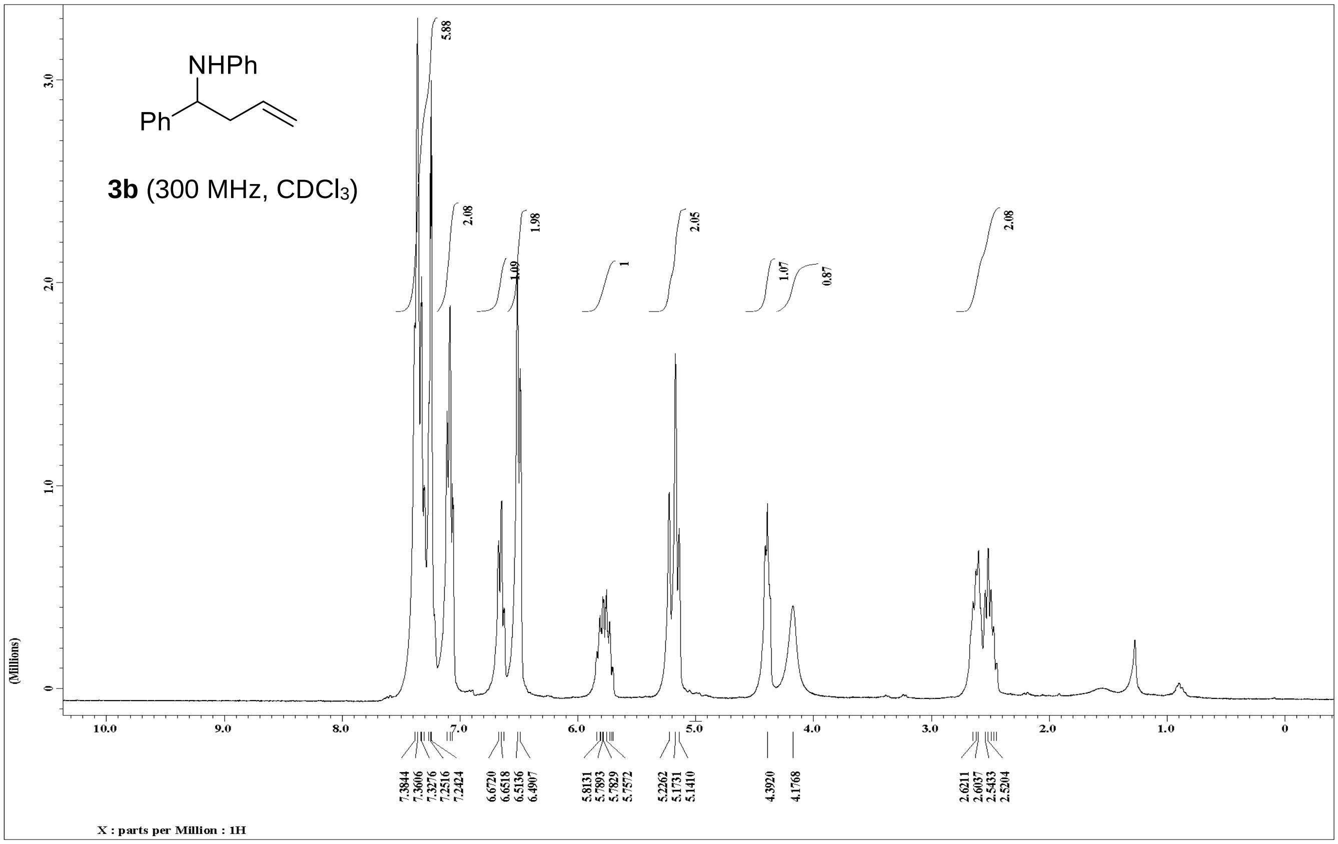
2a (300 MHz, CDCl$_3$)

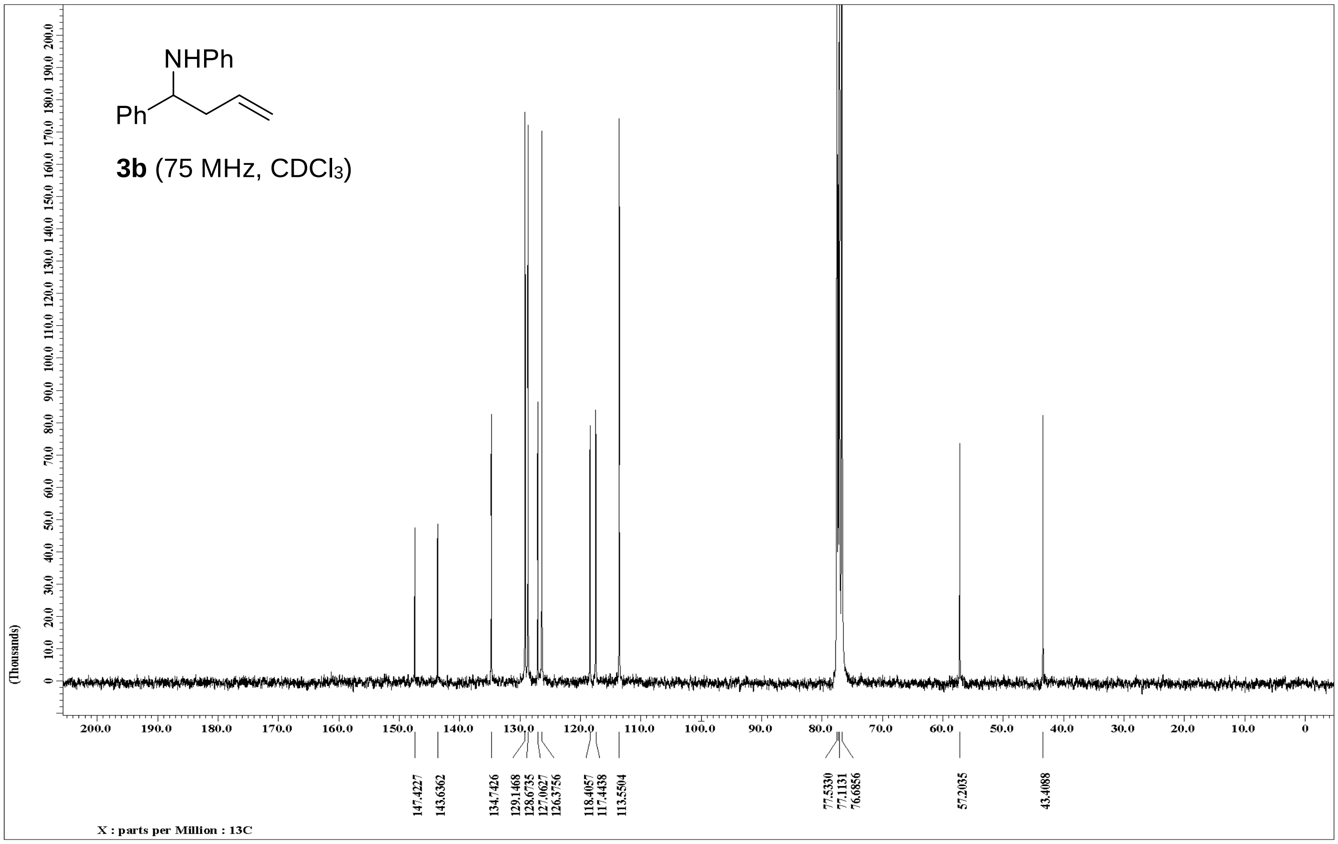


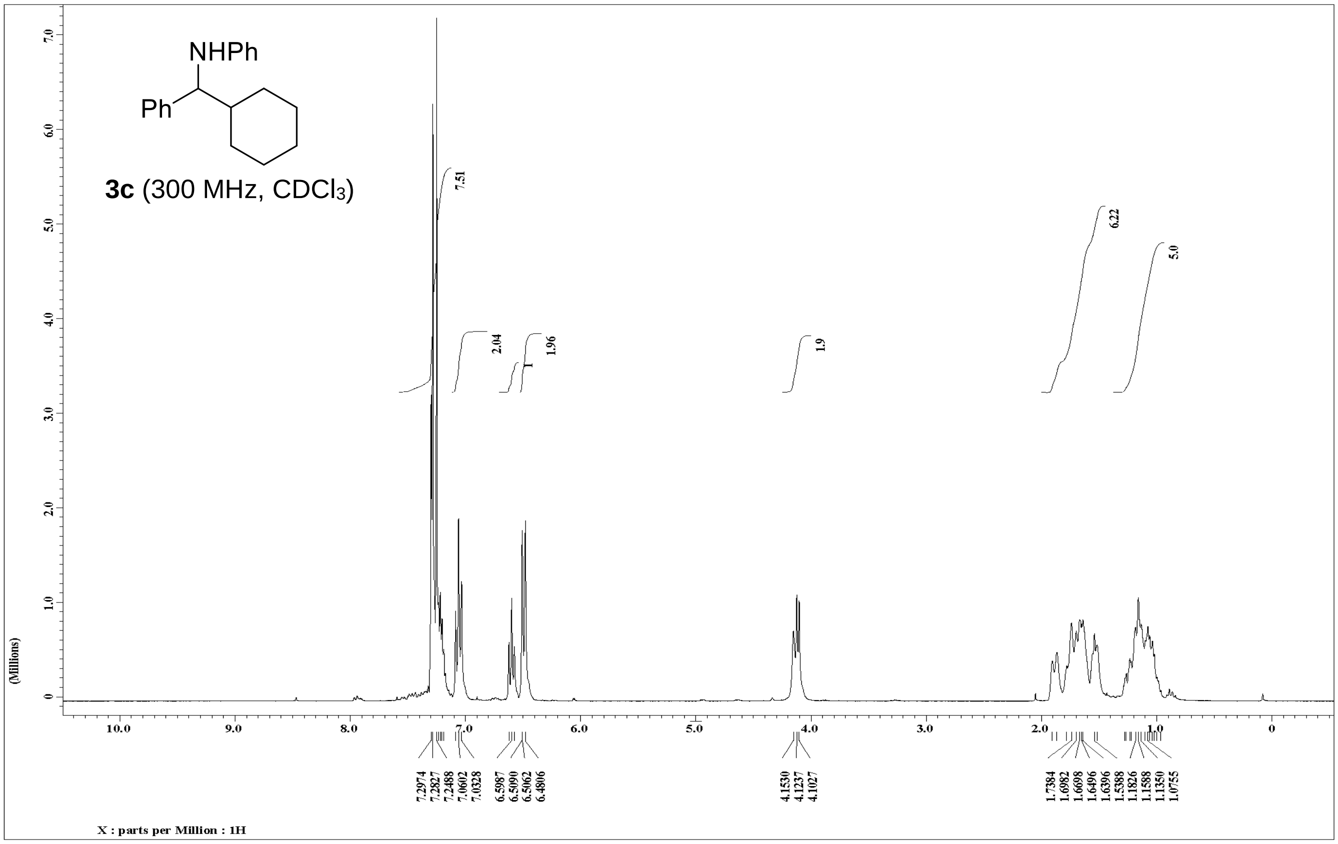
2a (75 MHz, CDCl$_3$)

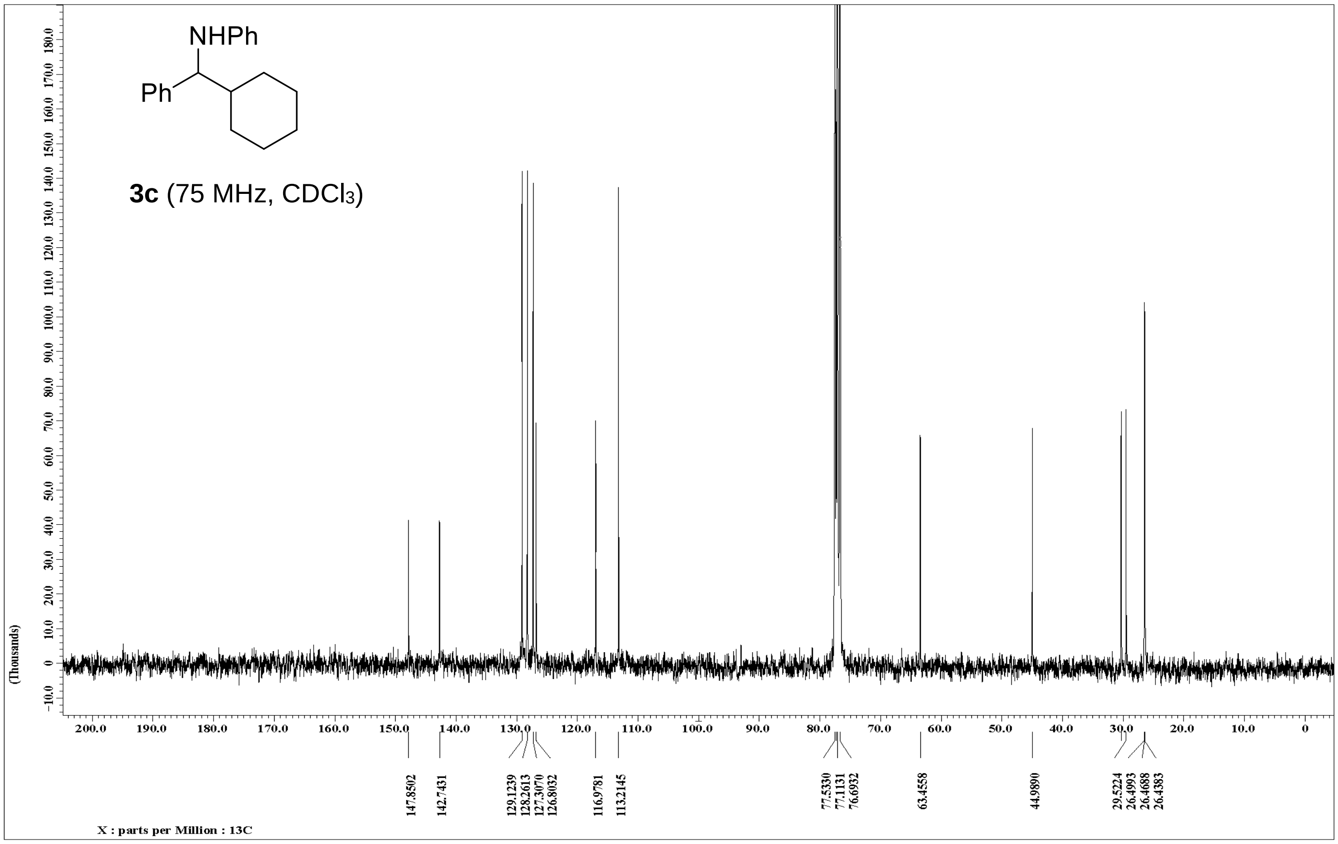

NHPh
Ph
Ph
3a (300 MHz, CDCl3)
8.21
2.04
1.94
1.0
1.96
0.95
0.69
2
(Millions)
0
1.0
2.0
3.0
4.0
5.0
6.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3367
7.3303
7.3184
7.2653
7.2516
6.6381
6.4861
6.4834
6.4577
4.6035
4.5953
4.5761
4.1237
4.1027
3.1394
3.1211
3.0597
3.0323
X : parts per Million : 1H

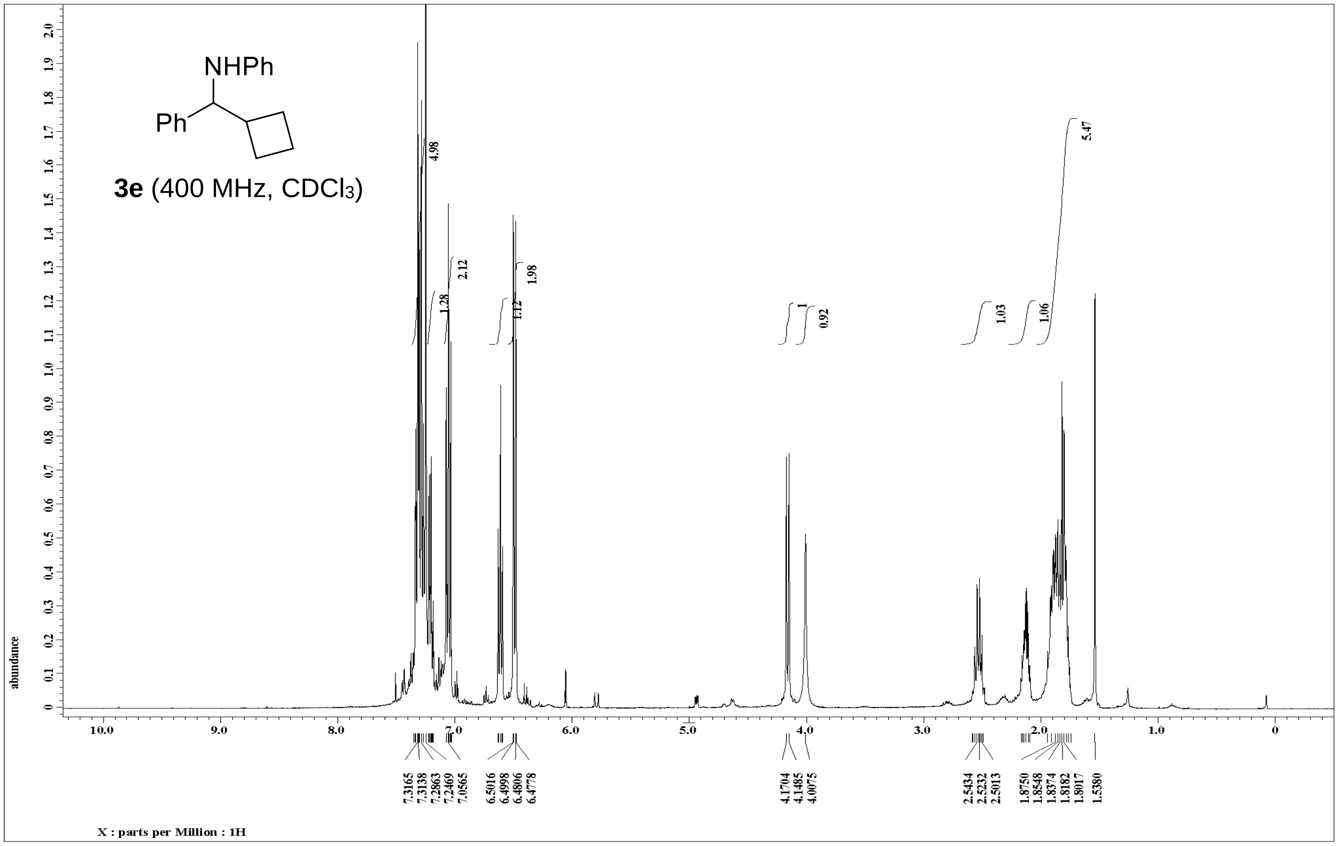

NHPh
Ph
Ph
3a (75 MHz, CDCl3)
(Thousands)
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
147.3540
143.5217
137.7657
129.2919
129.0934
128.6582
128.6277
127.1467
126.8032
126.5360
117.5507
113.7108
77.5330
77.1055
76.6856
59.2876
45.2638
X : parts per Million : 13C

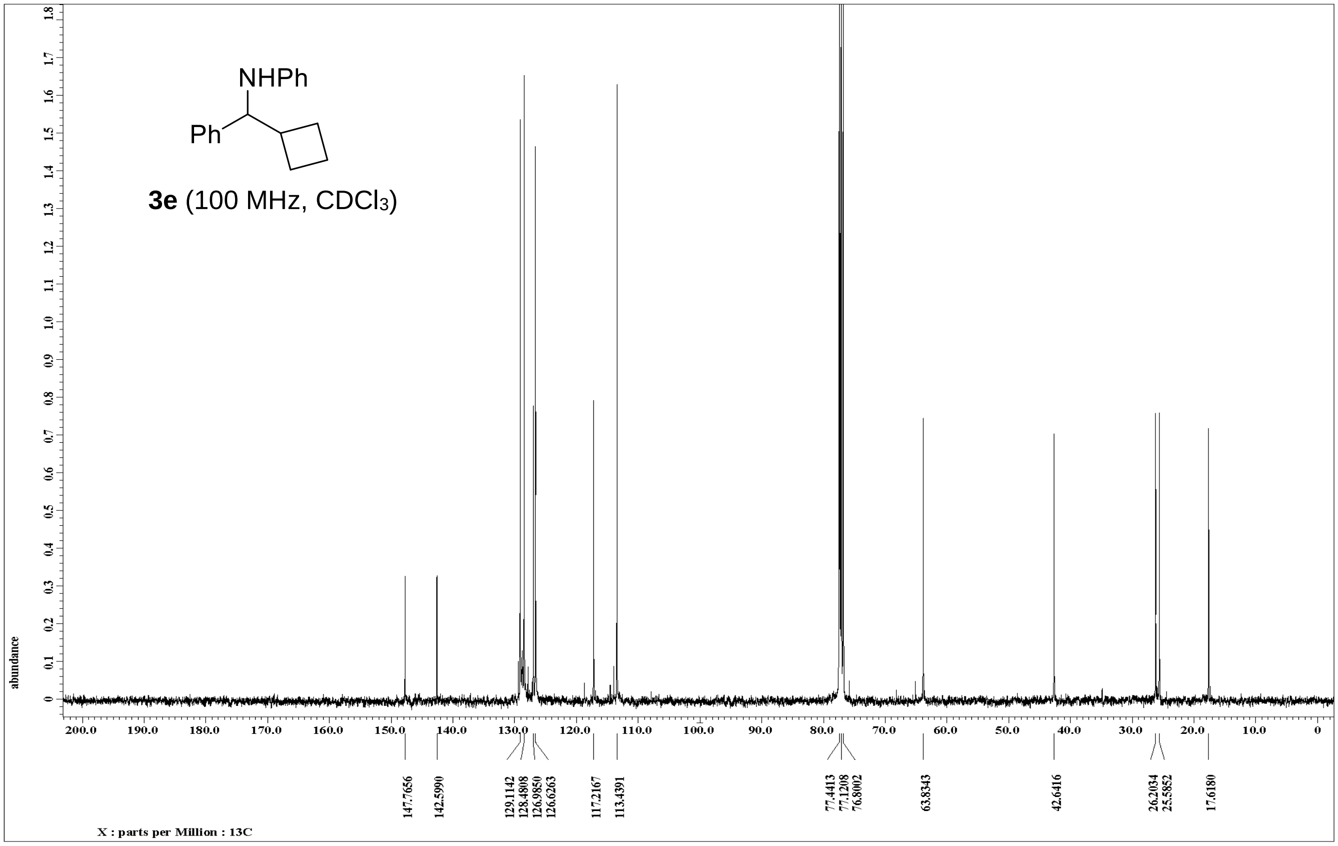

3b (300 MHz, $CDCl_3$)

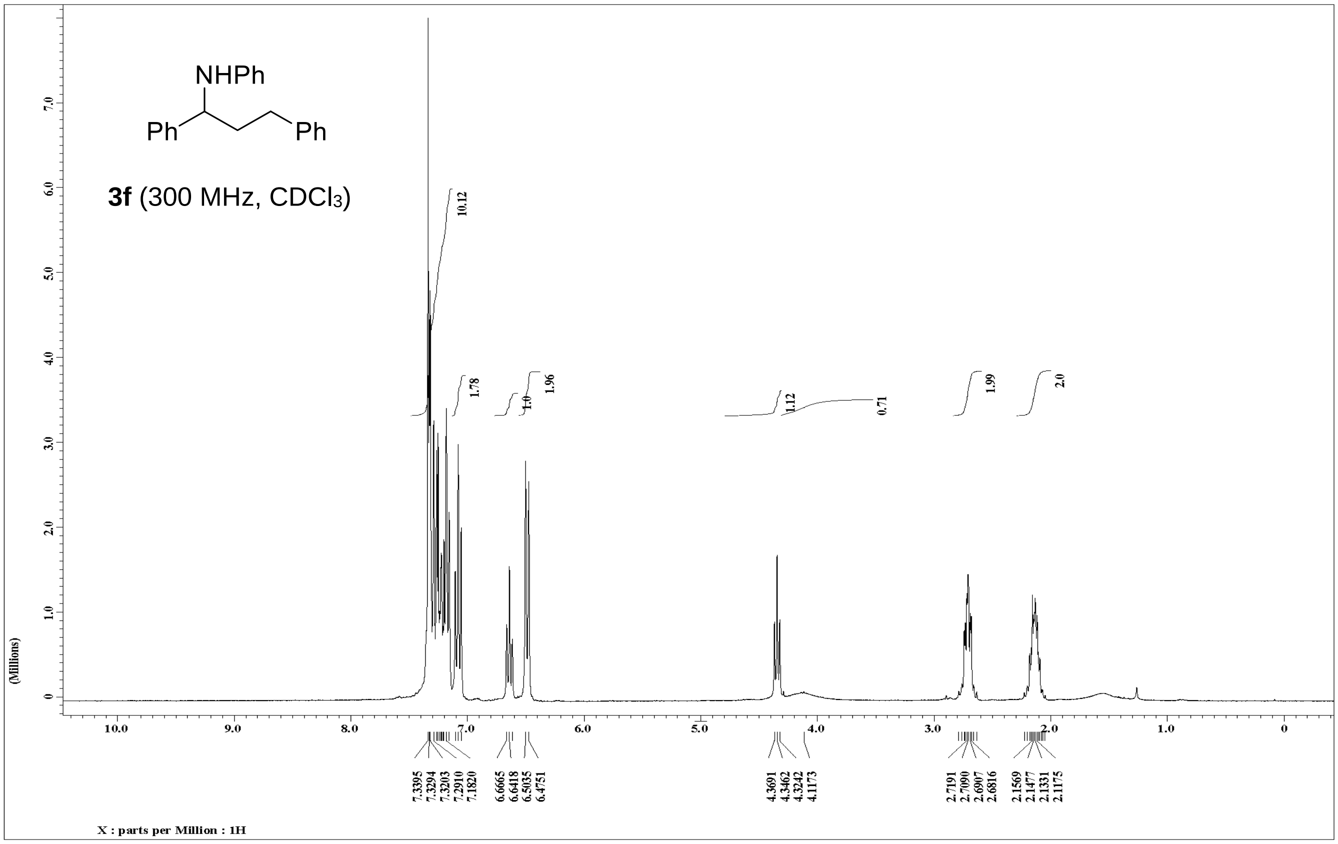

3b (75 MHz, $CDCl_3$)

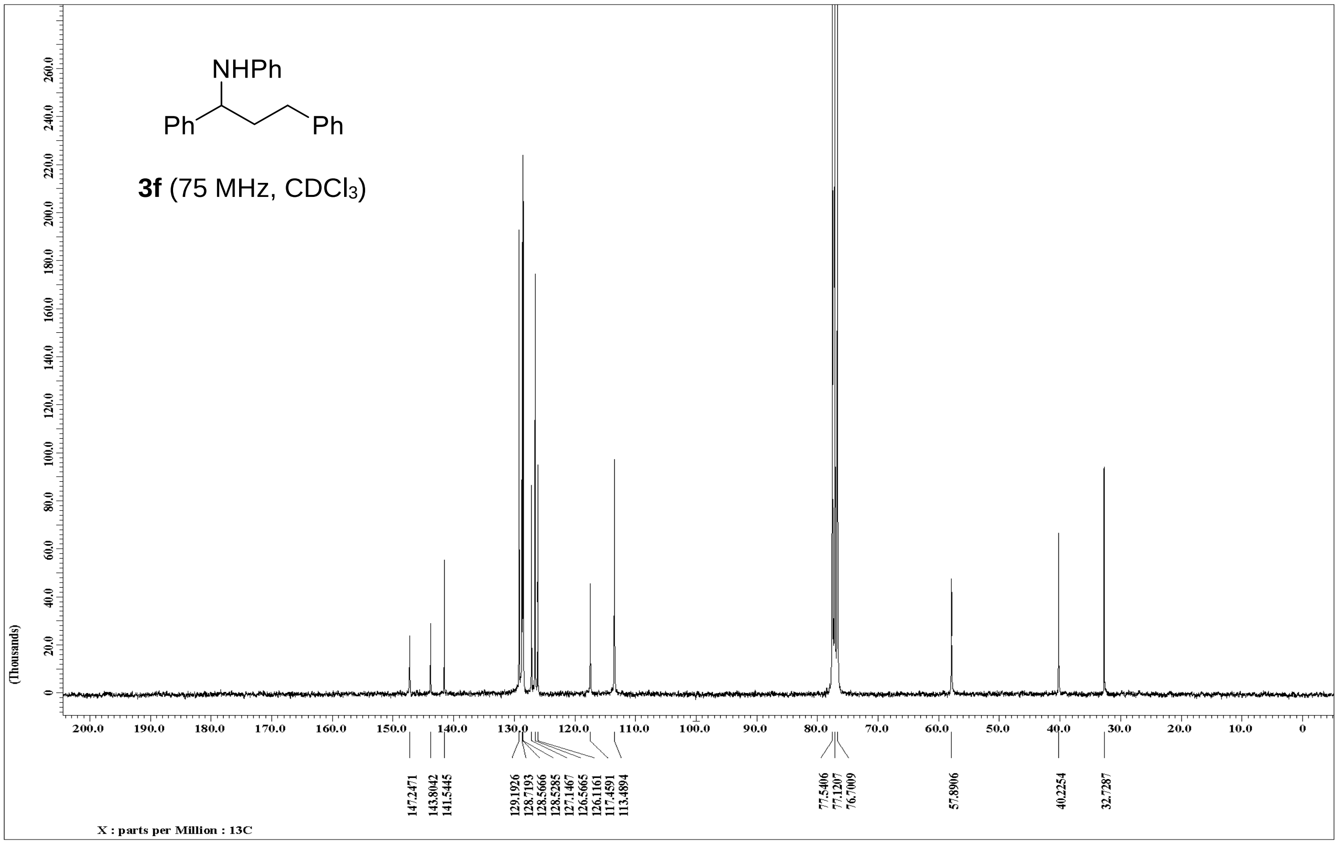

NHPh
Ph
3c (300 MHz, CDCl3)
(Millions)
7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.51
2.04
1.96
1.9
6.22
5.0
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.2974
7.2827
7.2488
7.0602
7.0328
6.5987
6.5090
6.5062
6.4806
4.1530
4.1237
4.1027
1.7384
1.6982
1.6698
1.6496
1.6396
1.5388
1.1826
1.1588
1.1350
1.0755
X : parts per Million : 1H

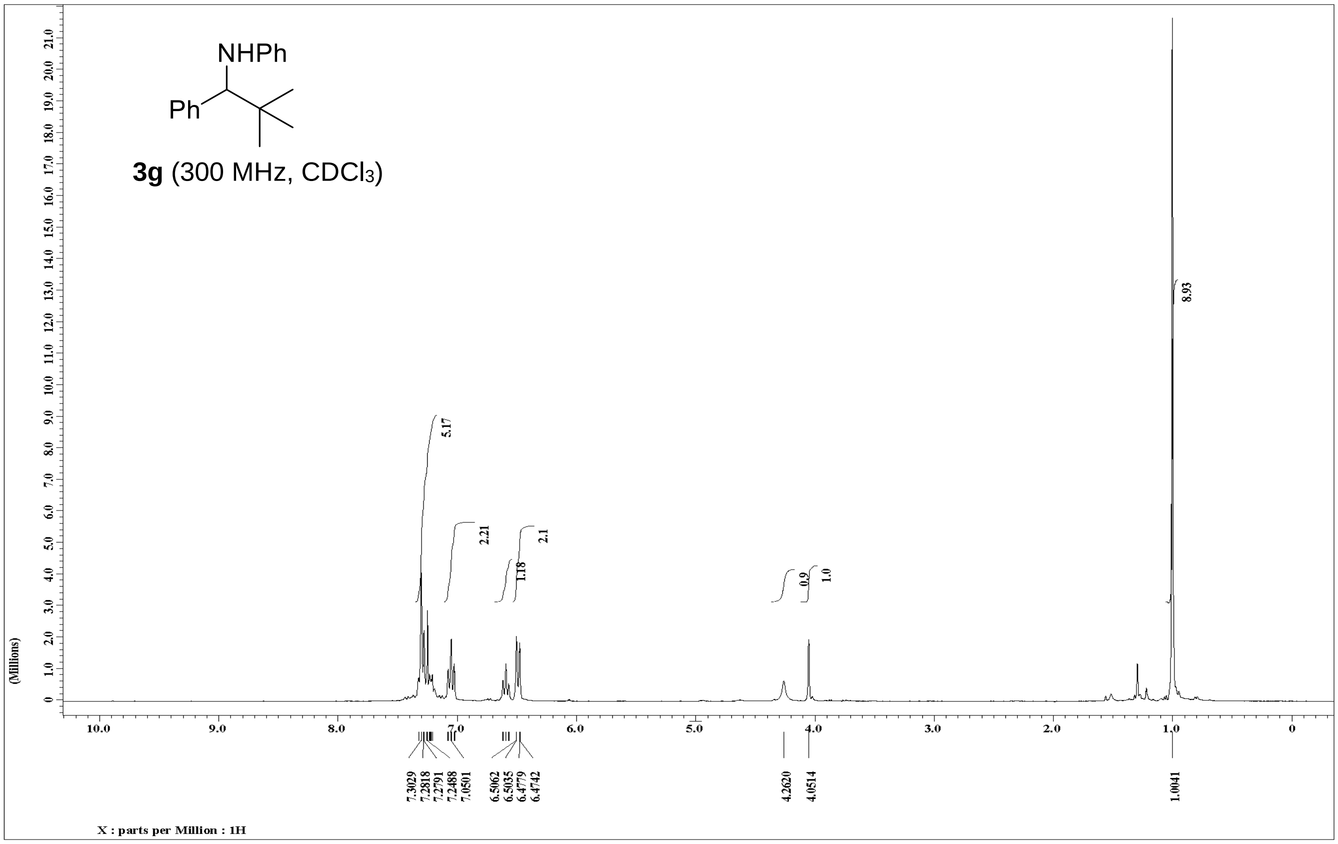

NHPh
Ph
3c (75 MHz, CDCl3)
(Thousands)
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
147.8502
142.7431
129.1239
128.2613
127.3070
126.8032
116.9781
113.2145
77.5330
77.1131
76.6932
63.4558
44.9890
29.5224
26.4993
26.4688
26.4383
X : parts per Million : 13C


NHPh
Ph
3e (400 MHz, CDCl3)
abundance
4.98
2.12
1.28
1.98
1.12
1
0.92
1.03
1.06
5.47
7.3165
7.3138
7.2863
7.2469
7.0565
6.5016
6.4998
6.4806
6.4778
4.1704
4.1485
4.0075
2.5434
2.5232
2.5013
1.8750
1.8548
1.8374
1.8182
1.8017
1.5380
X : parts per Million : 1H

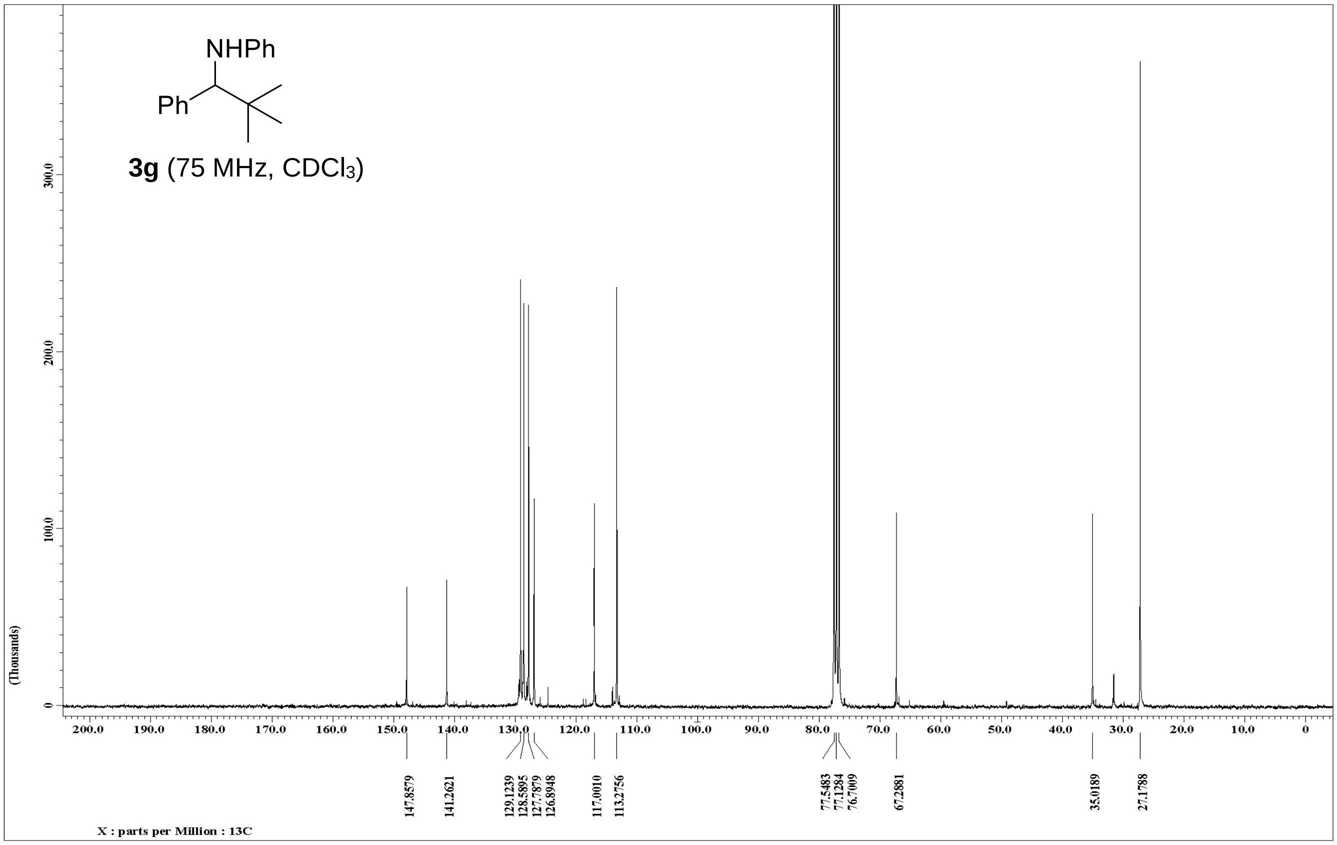

NHPh
Ph
3e (100 MHz, CDCl3)
abundance
147.7656
142.5990
129.1142
128.4808
126.9850
126.6263
117.2167
113.4391
77.4413
77.1208
76.8002
63.8343
42.6416
26.2034
25.5852
17.6180
X : parts per Million : 13C


NHPh
Ph
Ph
3f (300 MHz, CDCl3)
10.12
1.78
1.0
1.96
1.12
0.71
1.99
2.0
7.3395
7.3294
7.3203
7.2910
7.1820
6.6665
6.6418
6.5035
6.4751
4.3691
4.3462
4.3242
4.1173
2.7191
2.7090
2.6907
2.6816
2.1569
2.1477
2.1331
2.1175
(Millions)
X : parts per Million : 1H

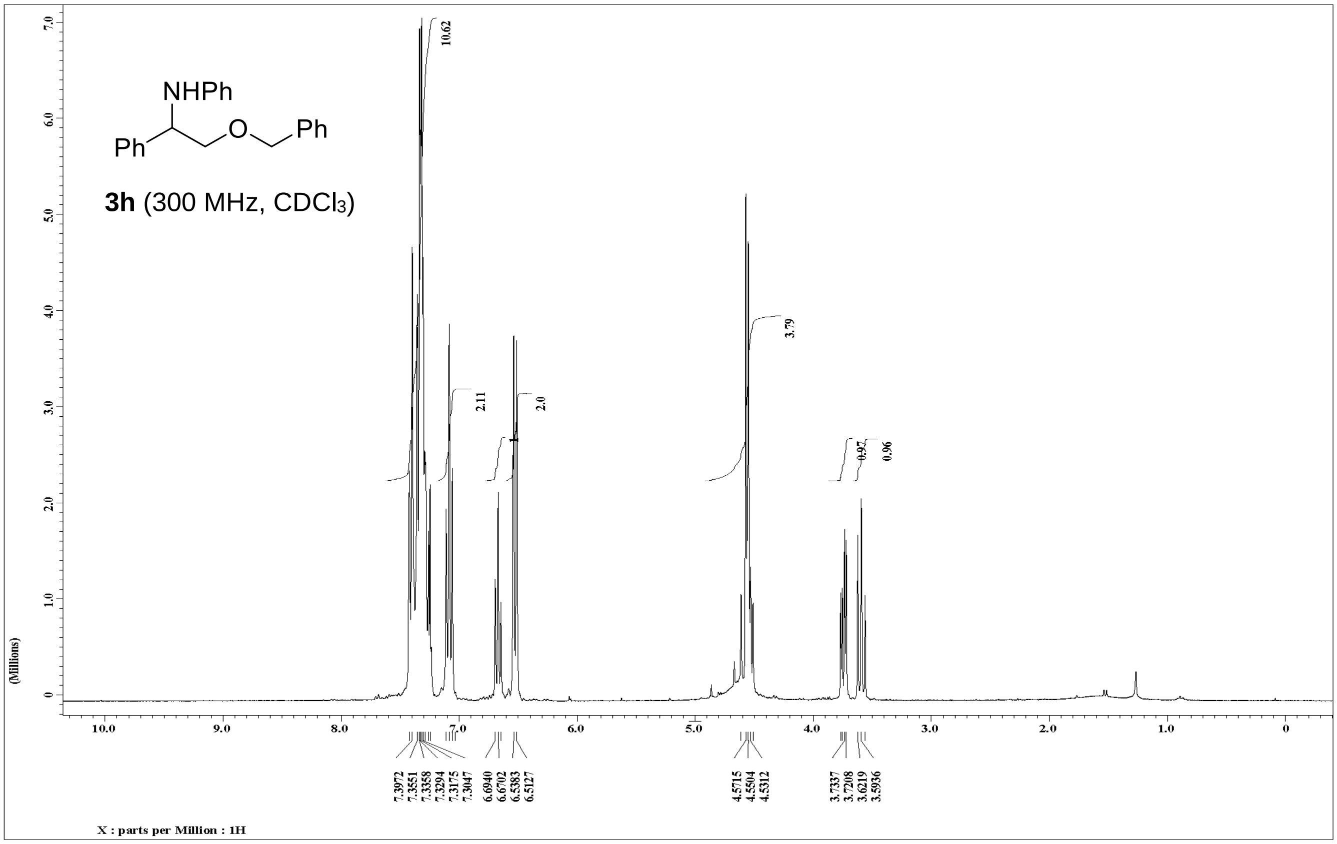

NHPh
Ph
Ph
3f (75 MHz, CDCl3)
147.2471
143.8042
141.5445
129.1926
128.7193
128.5666
128.5285
127.1467
126.5665
126.1161
117.4591
113.4894
77.5406
77.1207
76.7009
57.8906
40.2254
32.7287
(Thousands)
X : parts per Million : 13C

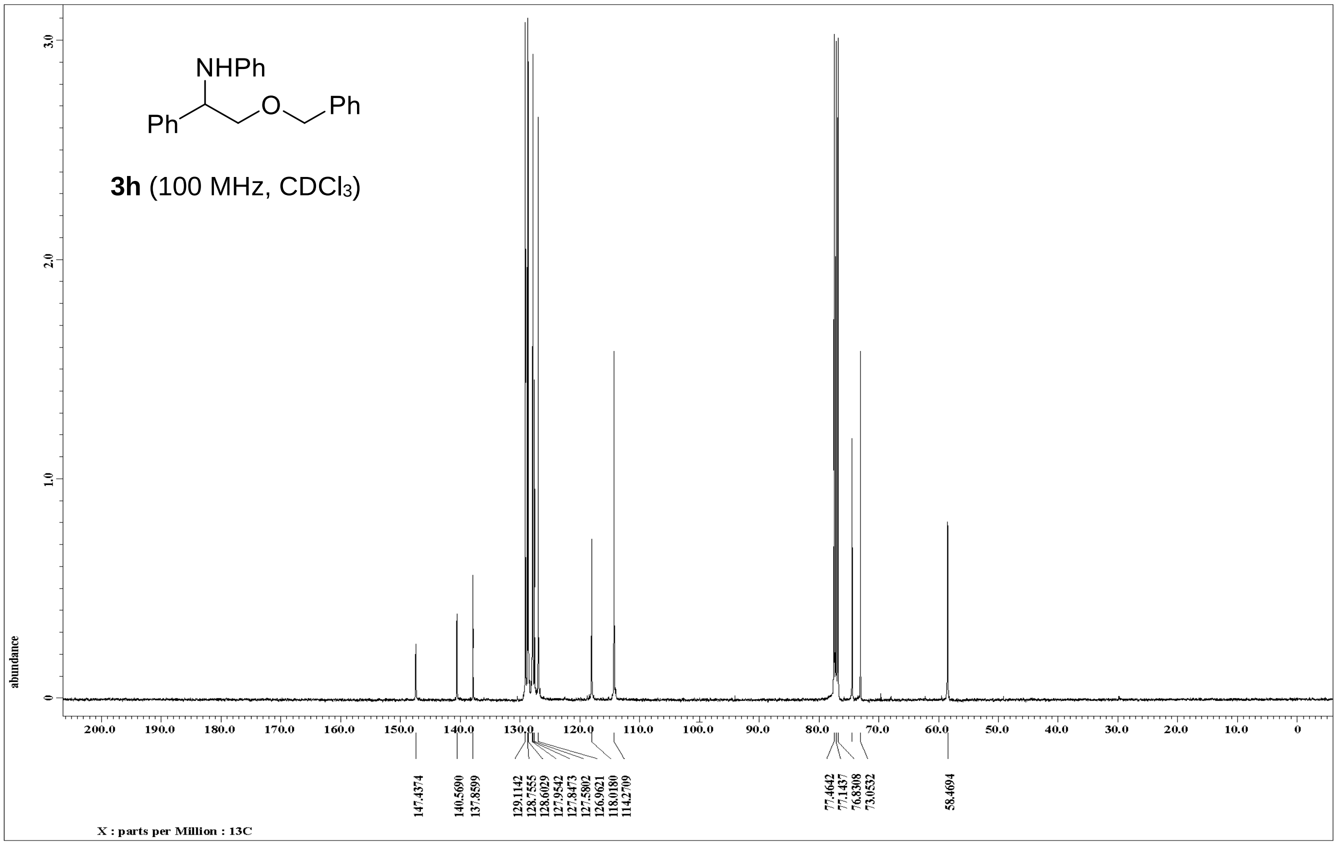


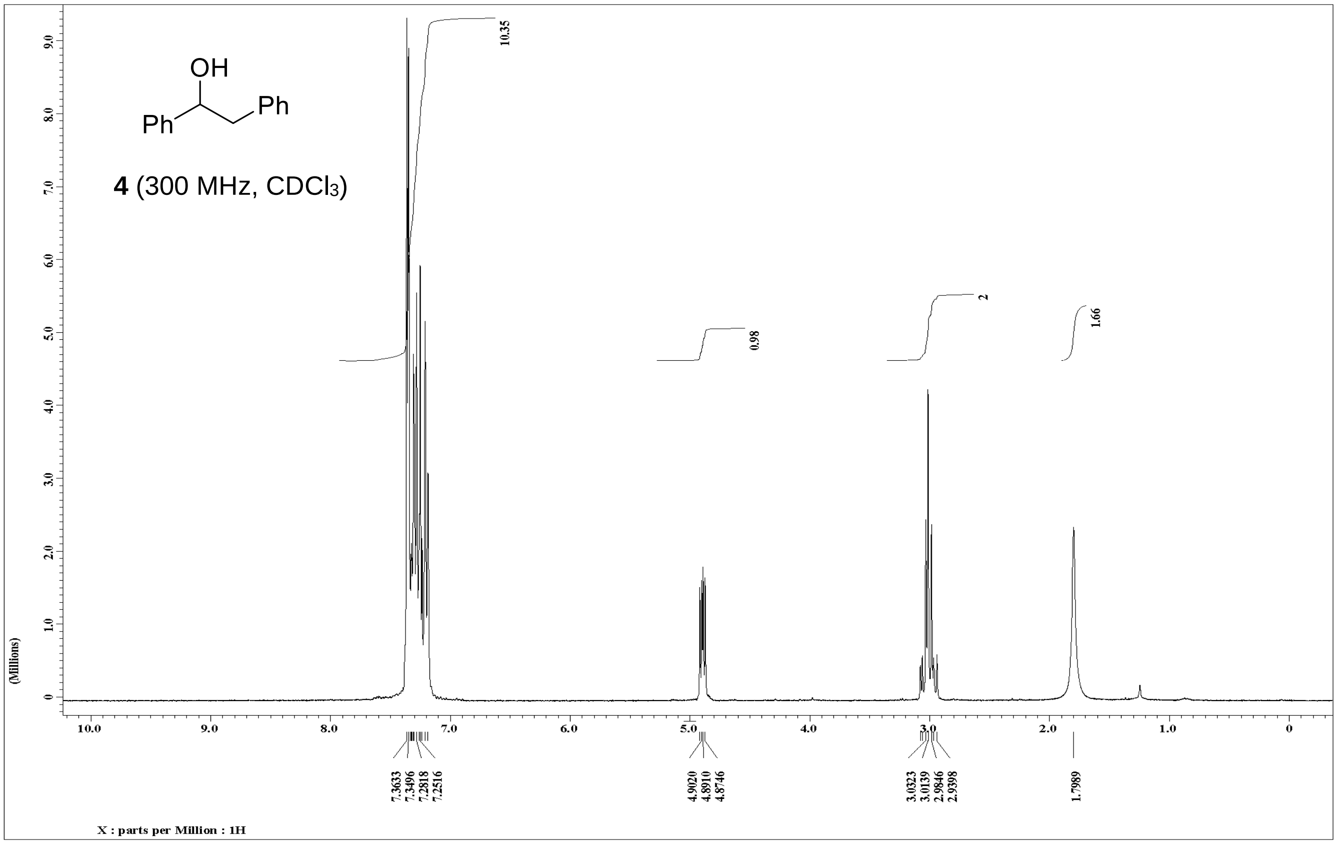
3g (300 MHz, $CDCl_3$)

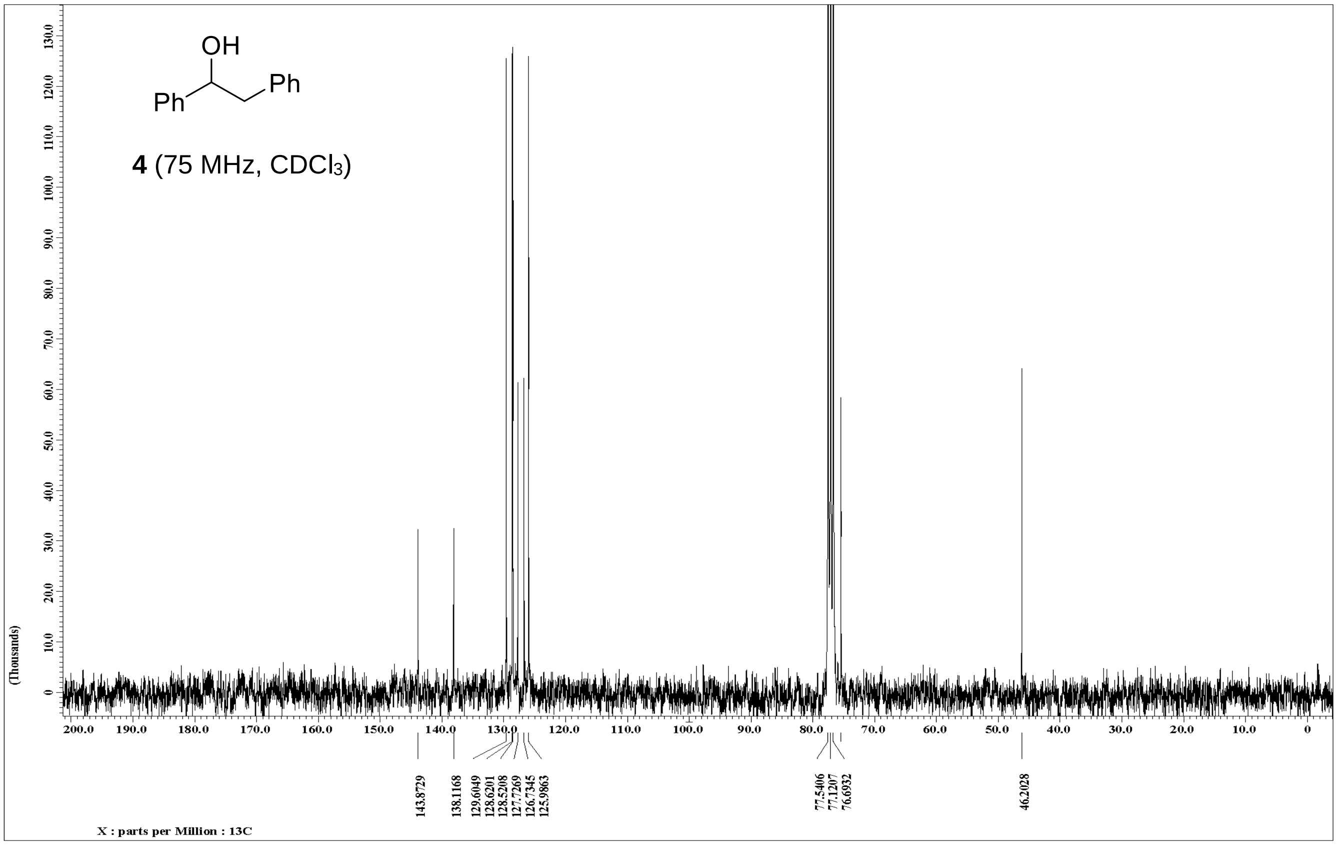


3g (75 MHz, $CDCl_3$)


3h (300 MHz, $CDCl_3$)


3h (100 MHz, $CDCl_3$)


OH
Ph
Ph
4 (300 MHz, CDCl3)
10.35
0.98
2
1.66
(Millions)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3633
7.3496
7.2818
7.2516
4.9020
4.8910
4.8746
3.0323
3.0139
2.9846
2.9398
1.7989
X : parts per Million : 1H


OH
Ph
Ph
4 (75 MHz, CDCl3)
(Thousands)
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
143.8729
138.1168
129.6049
128.6201
128.5208
127.7269
126.7345
125.9863
77.5406
77.1207
76.6932
46.2028
X : parts per Million : 13C