Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

DIC–Borane-Catalyzed Selective Methylation of Primary Amines with CO_2 Using Boranes as Reducing Agents

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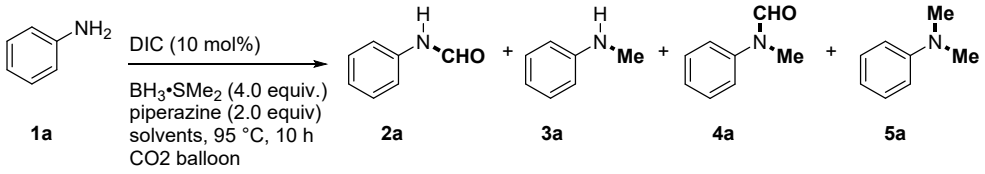
1. General Information.

Unless otherwise noted, materials were purchased from Adamas, Energy-Chemical, and other commercial suppliers and were used as received. Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on VARIAN-400 (400 MHz) or Bruker AV-400 (400 MHz) NMR spectrometers. Chemical shifts (δ) are reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. Gas chromatographic (GC) analysis was performed on a Shimadzu GC-2010 system equipped with an FID detector and a capillary column, and the tridecane as the internal standard. High-resolution mass spectra (HRMS) were obtained with a MICROTOF-10454 Premier LC HR mass spectrometer.

2. Solvent screening.

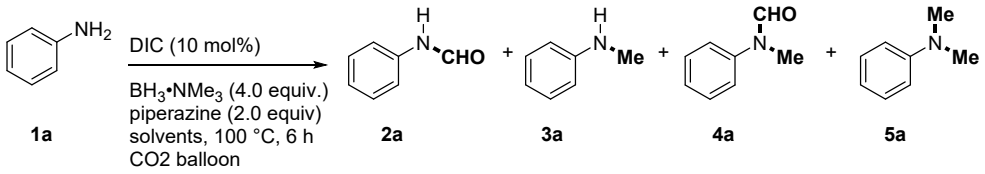
Table S1. Solvent screening for mono-methylation.[a]



Entry	Solvent	Yield of **2a**/%	Yield of **3a**/%	Yield of **4a**/%	Yield of **5a**/%
1	Toluene	-	86	-	-
2	Glyme	-	-	-	-
3	1,4-dioxane	-	56	-	-
4	DCE	-	-	-	-
5	THF	35	-	-	-

[a] Condition: $PhNH_2$ (0.3 mmol), $BH_3{\cdot}SMe_2$ (4.0 equiv.), DIC (10 mol%), solvent (0.4 mL), piperazine (2.0 equiv.), 95 °C, 10 h.

Table S2. Solvent screening for di-methylation.[a]

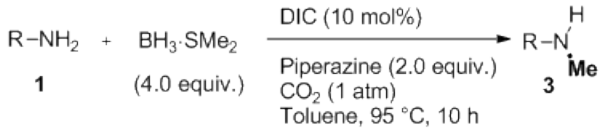


Entry	Solvent	Yield of **2a**/%	Yield of **3a**/%	Yield of **4a**/%	Yield of **5a**/%
1	Toluene	28	26	23	21
2	Glyme	-	-	-	95
3	1,4-dioxane	2	2	4	67
4	DCE	-	4	-	55
5	THF	3	7	5	52

[a] Condition: $PhNH_2$ (0.3 mmol), $BH_3{\cdot}NMe_3$ (4.0 equiv.), DIC (10 mol%), solvent (0.2 mL), 100 °C, 6 h.

3. General Procedure and Spectral Data of Products.

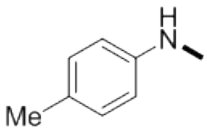
3.1 General Procedure for Synthesis of *N*-Methylaniline.



In a Schlenk tube was placed aniline (0.3 mmol), piperazine (51.7 mg, 0.6 mmol), $BH_3{\cdot}SMe_2$ (120.0 μL, 10 mol/L, 1.2 mmol), *N,N′*-diisopropylcarbodiimide (3.7 mg, 0.03 mmol), toluene (0.4 mL). The resulting mixture was stirred with a CO_2 balloon at 95 ºC for 10 h, and then allowed to room temperature. The reaction was quenched by saturated aqueous NaCl (1 mL). The aqueous layer was extracted with EtOAc (2 mL x

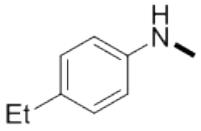
3). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, EtOAc/PE).

_N_,4-Dimethylaniline (3b)



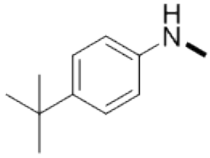
The typical procedure was applied to *p*-toluidine (32.1 mg, 0.3 mmol). Yield: 21.8 mg, 60 %, brown oil, R_f = 0.7 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 2H), 3.64 (br, 1H), 2.98 (s, 3H), 2.48 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.0, 129.5, 126.1, 112.4, 30.8, 20.2. The physical and spectral data were consistent with those previously reported.[1]

4-Ethyl-*N*-methylaniline (3c)



The typical procedure was applied to 4-ethylaniline (36.4 mg, 0.3 mmol). Yield: 26.8 mg, 66 %, yellow oil; R_f = 0.8 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (20:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.05 (d, *J* = 8.0 Hz, 2H), 6.59 (d, *J* = 8.0 Hz, 2H), 3.36 (br, 1H), 2.84 (s, 3H), 2.57 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.3, 133.1, 128.5, 112.6, 31.0, 27.9, 16.0. The physical and spectral data were consistent with those previously reported.[2]

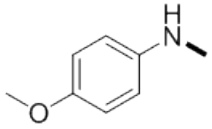
4-(*tert*-Butyl)-*N*-methylaniline (3d)



The typical procedure was applied to 4-(*tert*-butyl)aniline (44.8 mg, 0.3 mmol). Yield: 26.6 mg, 54 %, yellow oil; R_f = 0.9 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.23 (d, *J* = 8.0 Hz, 2H), 6.59 (d, *J* = 8.0 Hz, 2H), 3.58 (br, 1H), 2.83 (s, 3H), 1.29 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.0,

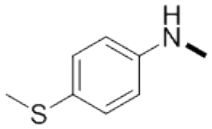
140.1, 126.0, 112.2, 33.9, 31.6, 31.0. The physical and spectral data were consistent with those previously reported.[2]

4-Methoxy-*N*-methylaniline (3e)



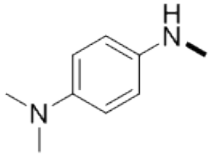
The typical procedure was applied to 4-methoxyaniline (37.0 mg, 0.3 mmol). Yield: 29.0 mg, 71 %, yellow oil; R_f = 0.7 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.81 (d, J = 8.0 Hz, 2H), 6.60 (d, J = 8.0 Hz, 2H), 3.76 (s, 3H), 3.09 (br, 1H) 2.81 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.0, 143.7, 114.9, 113.6, 55.8, 31.6. The physical and spectral data were consistent with those previously reported.[3]

***N*-Methyl-4-(methylthio)aniline (3f)**



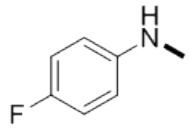
The typical procedure was applied to 4-(methylthio)aniline (41.8 mg, 0.3 mmol). Yield: 19.4 mg, 42 %, yellow oil, R_f = 0.7 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24 (d, J = 8.0 Hz, 2H), 6.56 (d, J = 8.0 Hz, 2H), 3.65 (br, 1H), 2.83 (s, 3H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.2, 131.6, 124.0, 112.9, 30.7, 19.3. The physical and spectral data were consistent with those previously reported.[4]

***N*^{1},*N*^{1},*N*^{4}-Trimethylbenzene-1,4-diamine (3g)**



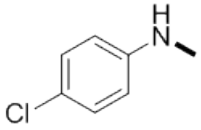
The typical procedure was applied to N^1,N^1-dimethylbenzene-1,4-diamine (40.9 mg, 0.3 mmol). Yield: 25.7 mg, 57 %, brown oil; R_f= 0.5 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (5:1),^{1}H NMR (DMSO-d_6, 400 MHz):^{1}H NMR (400 MHz, DMSO-d_6): δ 6.64 (d, J = 8.0 Hz, 2H), 6.46 (d, J = 8.0 Hz, 2H), 4.95 (br, 1H), 2.70 (s, 6H), 2.60 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 142.8, 142.6, 115.5, 112.8, 42.0, 30.7. The physical and spectral data were consistent with those previously reported.[5]

4-Fluoro-*N*-methylaniline (3h)



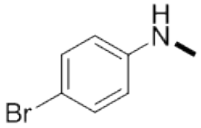
The typical procedure was applied to 4-fluoroaniline (33.3 mg, 0.3 mmol). Yield: 23.3 mg, 62%, yellow oil; R_f = 0.7 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.91 (t, J = 8.0 Hz, 2H), 6.54 (dd, J = 8.0, 4.0 Hz, 2H), 3.47 (br, 1H), 2.81 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.8 (d, $^1J_{C\text{-}F}$ = 240.0 Hz), 145.7, 115.6 (d, $^2J_{C\text{-}F}$ = 20.0 Hz), 113.2 (d, $^3J_{C\text{-}F}$ = 10.0 Hz), 31.3. The physical and spectral data were consistent with those previously reported.[1]

4-Chloro-*N*-methylaniline (3i)



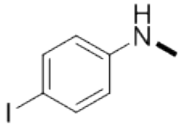
The typical procedure was applied to 4-choroaniline (38.3 mg, 0.3 mmol). Yield: 27.8 mg, 66 %, yellow oil; R_f = 0.7 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.13 (d, J = 8.0 Hz, 2H), 6.53 (d, J = 8.0 Hz, 2H), 3.70 (br, 1H), 2.81 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.8, 128.9, 121.7, 113.4, 30.8. The physical and spectral data were consistent with those previously reported.[1]

4-Bromo-*N*-methylaniline (3j)



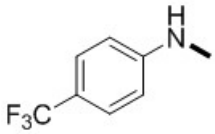
The typical procedure was applied to 4-bromoaniline (51.6 mg, 0.3 mmol). Yield: 35.0 mg, 63 %, yellow oil; R_f = 0.7 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26 (d, J = 8.0 Hz, 2H), 6.48 (d, J = 8.0 Hz, 2H), 3.72 (br, 1H) 2.81 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.2, 131.8, 113.9, 108.7, 30.7. The physical and spectral data were consistent with those previously reported.[1]

4-Iodo-*N*-methylaniline (3k)



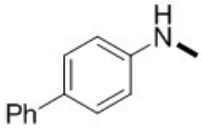
The typical procedure was applied to 4-iodoaniline (65.7 mg, 0.3 mmol). Yield: 30.7 mg, 44 %, brown oil, R_f = 0.7 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 (d, J = 8.0 Hz, 2H), 6.39 (d, J = 8.0 Hz, 2H), 3.75 (br, 1H), 2.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.8, 137.7, 114.6, 77.7, 30.5. The physical and spectral data were consistent with those previously reported.[6]

_N_-Methyl-4-(trifluoromethyl)aniline (3l)



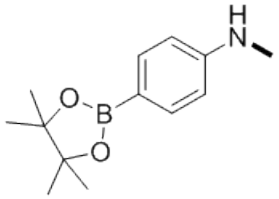
The typical procedure was applied to 4-(trifluoromethyl)aniline (48.3 mg, 0.3 mmol). Yield: 16.1 mg, 31 %, yellow solid, R_f = 0.4 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (20:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 (d, J = 8.0 Hz, 2H), 6.61 (d, J = 8.0 Hz, 2H), 3.94 (br, 1H), 2.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.6, 126.5 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 122.4 (d, $^1J_{C\text{-}F}$= 260.0 Hz), 118.5 (q, $^2J_{C\text{-}F}$ = 30.0 Hz), 111.4, 30.1. The physical and spectral data were consistent with those previously reported.[7]

_N_-Methyl-[1,1'-biphenyl]-4-amine (3m)



The typical procedure was applied to [1,1'-biphenyl]-4-amine(50.8 mg, 0.3 mmol). Yield: 36.0 mg, 66 %, orange oil, R_f = 0.7 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1), ^{1}H NMR ($CDCl_3$, 400 MHz):) δ 7.42 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.26 (t, J = 8.0 Hz, 2H), 7.13 (t, J = 8.0 Hz, 1H), 6.54 (d, J = 8.0 Hz, 2H), 3.37 (br, 1H) 2.72 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.7, 141.2, 130.1, 128.6, 127.8, 126.2, 126.0, 112.6, 30.7. The physical and spectral data were consistent with those previously reported.[8]

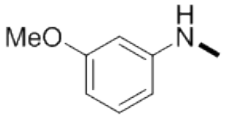
_N_-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (3n)



The typical procedure was applied to 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (65.7 mg, 0.3 mmol). Yield:

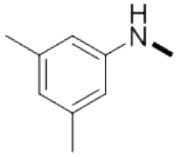
46.2 mg, 66 %, yellow solid; R_f = 0.8 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (10:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (d, *J* = 8.0 Hz, 2H), 6.58 (d, *J* = 8.0 Hz, 2H), 3.94 (br, 1H), 2.85 (s, 3H), 1.33 (s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.7, 136.3 (two carbons are overlapped), 111.4, 83.1, 30.2, 24.8. The physical and spectral data were consistent with those previously reported.[9]

3-Methoxy-*N*-methylaniline (3o)



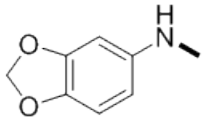
The typical procedure was applied to 3-methoxyaniline (36.9 mg, 0.3 mmol). Yield: 33.3 mg, 81 %, yellow oil; R_f = 0.6 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (5:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.10 (t, *J* = 8.0 Hz, 1H), 6.29 (d, *J* = 8.0 Hz, 1H), 6.24 (d, *J* = 8.0 Hz, 1H), 6.18 (d, *J* = 4.0 Hz, 1H), 3.79 (s, 3H), 2.83 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.8, 150.7, 129.9, 105.6, 102.3, 98.3, 55.0, 30.7. The physical and spectral data were consistent with those previously reported.[1]

***N*,3,5-Trimethylaniline (3p)**



The typical procedure was applied to 3,5-dimethylaniline (36.4 mg, 0.3 mmol). Yield: 25.1 mg, 62 %, yellow oil; R_f = 0.7 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.40 (s, 1H), 6.28 (s, 2H), 3.46 (br, 1H), 2.83 (s, 3H), 2.27 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.4, 138.8, 119.3, 110.4, 30.8, 21.5. The physical and spectral data were consistent with those previously reported.[10]

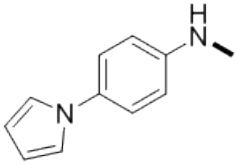
***N*-Methylbenzo[*d*][1,3]dioxol-5-amine (3q)**



The typical procedure was applied to benzo[*d*][1,3]dioxol-5-amine (41.1 mg, 0.3 mmol). Yield: 23.2 mg, 51 %, brown oil; R_f = 0.7 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (10:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.68 (d, *J* = 8.0 Hz, 1H), 6.25 (d, *J* = 4.0 Hz, 1H), 6.05 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.14 (br, 1H), 5.85 (s, 2H), 2.79 (s, 3H). ^{13}C NMR ($CDCl_3$,

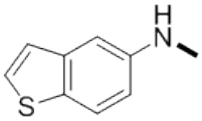
100 MHz): δ 148.3, 145.2, 139.5, 108.6, 103.8, 100.5, 95.6, 31.6. The physical and spectral data were consistent with those previously reported.[2]

_N_-Methyl-4-(1_H_-pyrrol-1-yl)aniline (3r)



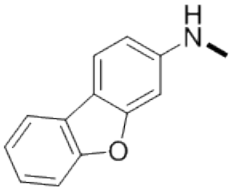
The typical procedure was applied to 4-(1*H*-pyrrol-1-yl)aniline (47.5 mg, 0.3 mmol). Yield: 35.5 mg, 69 %, yellow solid; R_f = 0.7 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (20:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25 (d, *J* = 12.0 Hz, 2H), 7.01 (t, *J* = 4.0 Hz, 2H), 6.67 (d, *J* = 12.0 Hz, 2H), 6.34 (t, *J* = 4.0 Hz, 2H), 3.77 (br, 1H), 2.88 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.5, 131.7, 122.4, 119.7, 112.7, 109.2, 30.9. The physical and spectral data were consistent with those previously reported.[11]

_N_-Methylbenzo[*b*]thiophen-5-amine (3s)



The typical procedure was applied to benzo[*b*]thiophen-5-amine (44.8 mg, 0.3 mmol). Yield: 28.9 mg, 59 %, brown oil; R_f = 0.8 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (20:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 4.0 Hz, 1H), 7.20 (d, *J* = 4.0 Hz, 1H), 7.00 (d, *J* = 4.0 Hz, 1H), 6.74 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.71 (br, 1H), 2.90 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.9, 141.0, 129.2, 126.7, 123.3, 122.7, 113.8, 104.2, 31.1. The physical and spectral data were consistent with those previously reported.[12]

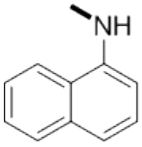
_N_-Methyldibenzo[*b*,*d*]furan-3-amine (3t)



The typical procedure was applied to dibenzo[*b*,*d*]furan-3-amine (55.0 mg, 0.3 mmol). Yield: 37.7 mg, 64 %, yellow solid; R_f = 0.7 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (20:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.13 (m, 2H), 6.75 (d, *J* = 4.0 Hz, 1H), 6.63 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.01 (br, 1H), 2.92 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.4, 155.7, 149.8, 125.0, 124.6, 122.5, 121.0, 119.1,

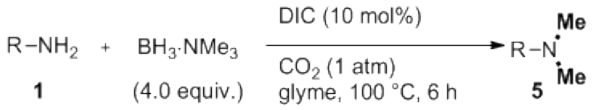
114.2, 111.0, 109.7, 93.7, 30.9. The physical and spectral data were consistent with those previously reported.[13]

_N_-Methylnaphthalen-1-amine (3u)



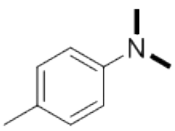
The typical procedure was applied to 1-naphthylamine (43.0 mg, 0.3 mmol). Yield: 15.3 mg, 50 %, brown oil, R_f = 0.7 (PE/EtOAc =10/1); purified by column chromatography eluting with PE/EtOAc (30:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (ddd, J = 12.0, 8.0, 4.0 Hz, 2H), 7.50 – 7.41 (m, 2H), 7.39 (t, J = 8.0 Hz, 1H), 7.29 – 7.19 (m, 1H), 6.62 (d, J = 8.0 Hz, 1H), 4.45 (br, 1H), 3.03 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.5, 134.2, 128.6, 126.6, 125.7, 124.7, 123.4, 119.7, 117.3, 103.7, 31.0. The physical and spectral data were consistent with those previously reported.[14]

2.2 General Procedure for Synthesis of _N,N_-Dimethylaniline.



In a Schlenk tube was placed aniline (0.3 mmol), BH_3·NMe_3 (87.54 mg, 1.2 mmol), *N,N'*-diisopropylcarbodiimide (3.7 mg, 0.03 mmol), glyme (0.2 mL). The resulting mixture was stirred with a CO_2 balloon at 100 ºC for 6 h, and then allowed to room temperature. The reaction was quenched by saturated aqueous NaCl (1 mL). The aqueous layer was extracted with EtOAc (2 mL x 3). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, EtOAc/PE).

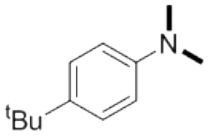
***N,N*,4-Trimethylaniline (5b)**



The typical procedure was applied to *N*,4-dimethylaniline (32.1 mg, 0.3 mmol). Yield: 30.8 mg, 76 %, yellow oil; R_f= 0.8 (PE/EtOAc = 10/1);

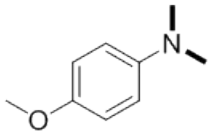
purified by column chromatography eluting with PE/EtOAc (30:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.06 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 2H), 2.90 (s, 6H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.8, 129.6, 126.1, 113.2, 41.1, 20.3. The physical and spectral data were consistent with those previously reported. [15]

4-(*tert*-Butyl)-*N,N*-dimethylaniline (5d)



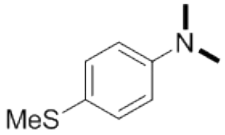
The typical procedure was applied to 4-(tert-butyl)aniline (44.8 mg, 0.3 mmol). Yield: 46.0 mg, 87 %, white solid; R_f = 0.8 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 2.95 (s, 6H), 1.33 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.4, 139.5, 125.8, 112.7, 40.9, 33.7, 31.5. The physical and spectral data were consistent with those previously reported. [16]

4-Methoxy-*N,N*-dimethylaniline (5e)



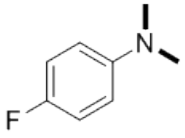
The typical procedure was applied to 4-methoxyaniline (37.0 mg, 0.3 mmol). Yield: 35.9 mg, 79 %, yellow oil; R_f = 0.8 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.85 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 3.77 (s, 3H), 2.87 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.0, 145.8, 114.9, 114.6, 55.7, 41.8. The physical and spectral data were consistent with those previously reported. [15]

***N,N*-Dimethyl-4-(methylthio)aniline (5f)**



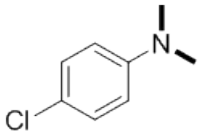
The typical procedure was applied to 4-(methylthio)aniline (41.8 mg, 0.3 mmol). Yield: 38.9 mg, 78 %, yellow oil; R_f = 0.8 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 2H), 2.95 (s, 6H), 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.4, 131.3, 123.3, 113.1, 40.5, 19.2. The physical and spectral data were consistent with those previously reported.[17]

4-Fluoro-*N*,*N*-dimethylaniline (5h)



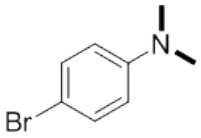
The typical procedure was applied to 4-fluoroaniline (33.3 mg, 0.3 mmol). Yield: 27.0 mg, 65 %, yellow oil, R_f= 0.8 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.95 (t, J = 8.0 Hz, 2H), 6.77 – 6.49 (m, 2H), 2.90 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.6 (d, $^1J_{C\text{-}F}$ = 240.0 Hz), 147.5, 115.4 (d, $^2J_{C\text{-}F}$ = 20.0 Hz), 114.0 (d, $^3J_{C\text{-}F}$ = 10.0 Hz), 41.4. The physical and spectral data were consistent with those previously reported.[15]

4-Chloro-*N*,*N*-dimethylaniline (5i)



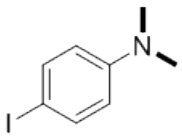
The typical procedure was applied to 4-chloroaniline (38.3 mg, 0.3 mmol). Yield: 37.8 mg, 81 %, yellow oil, R_f= 0.8 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.18 (d, J = 8.0 Hz, 2H), 6.64 (d, J = 8.0 Hz, 2H), 2.93 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.1, 128.8, 121.4, 113.6, 40.6. The physical and spectral data were consistent with those previously reported. [15]

4-Bromo-*N*,*N*-dimethylaniline (5j)



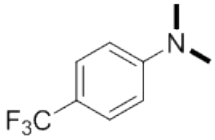
The typical procedure was applied to 4-bromoaniline (51.6 mg, 0.3 mmol). Yield: 53.0 mg, 89 %, light yellow solid; R_f= 0.8 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 (d, J = 8.0 Hz, 2H), 6.59 (d, J = 8.0 Hz, 1H), 2.93 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.4, 131.6, 114.0, 108.4, 40.5. The physical and spectral data were consistent with those previously reported. [15]

4-Iodo-*N*,*N*-dimethylaniline (5k)



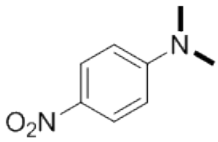
The typical procedure was applied to 4-iodoaniline (65.7 mg, 0.3 mmol). Yield: 59.3 mg, 80 %, yellow solid; R_f = 0.8 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, J = 8.0 Hz, 2H), 6.50 (d, J = 8.0 Hz, 2H), 2.93 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.9, 137.5, 114.6, 76.7, 40.3. The physical and spectral data were consistent with those previously reported. [15]

_N,N_-Dimethyl-4-(trifluoromethyl)aniline (5l)



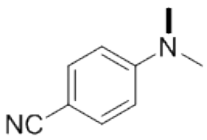
The typical procedure was applied to 4-(trifluoromethyl)aniline (48.3 mg, 0.3 mmol). Yield: 38.3 mg, 68 %, yellow solid; R_f= 0.8 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 (d, J = 8.0 Hz, 2H), 6.72 (d, J = 8.0 Hz, 2H), 3.03 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 126.3, (q, $^3J_{C\text{-}F}$=4.0 Hz), 125.2 (d, $^1J_{C\text{-}F}$=270.0 Hz), 117.5 (d, $^2J_{C\text{-}F}$=30.0 Hz), 111.1, 40.1. The physical and spectral data were consistent with those previously reported. [15]

_N,N_-Dimethyl-4-nitroaniline (5v)



The typical procedure was applied to _N_-methyl-4-nitroaniline (41.4 mg, 0.3 mmol). Yield: 40.4 mg, 81 %, yellow solid; R_f = 0.7 (PE/EtOAc = 2/1); purified by column chromatography eluting with PE/EtOAc (5:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (d, J = 8.0 Hz, 2H), 6.59 (d, J = 8.0 Hz, 2H), 3.12 (s, 6H). ^{13}C NMR ($CDCl_3$, 100MHz): δ 154.2, 136.9, 126.1, 110.2, 40.2. The physical and spectral data were consistent with those previously reported. [15]

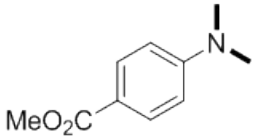
4-(Dimethylamino)benzonitrile (5w)



The typical procedure was applied to 4-aminobenzonitrile (35.4 mg, 0.3 mmol). Yield: 23.7 mg, 54 %, white solid; R_f= 0.6 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (10:1); ^{1}H NMR

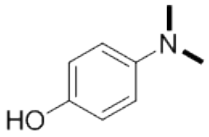
($CDCl_3$, 400 MHz): δ 7.45 (d, J = 8.0 Hz, 2H), 6.63 (d, J = 8.0 Hz, 2H), 3.03 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.4, 133.3, 120.7, 111.3, 97.1, 39.9. The physical and spectral data were consistent with those previously reported. [15]

Methyl 4-(dimethylamino)benzoate (5x)



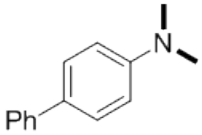
The typical procedure was applied to methyl 4-aminobenzoate (45.3 mg, 0.3 mmol). Yield: 38.5 mg, 72 %, yellow oil; R_f = 0.8 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (10:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.90 (d, J = 8.0 Hz, 2H), 6.63 (d, J = 8.0 Hz, 2H), 3.85 (s, 3H), 3.02 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.4, 153.2, 131.2, 116.8, 110.6, 51.4, 39.9. The physical and spectral data were consistent with those previously reported.[18]

4-(Dimethylamino)phenol (5y)



The typical procedure was applied to 4-aminophenol (32.7 mg, 0.3 mmol). Yield: 25.2 mg, 61 %, black solid; R_f = 0.7 (PE/EtOAc = 2/1); purified by column chromatography eluting with PE/EtOAc (5:1); ^1H NMR (DMSO-d_6, 400 MHz): δ 8.61 (s, 1H), 6.62 (s, 4H), 2.73 (s, 6H).^{13}C NMR (DMSO-d_6, 100 MHz) δ 149.3, 144.4, 115.6, 115.0, 41.6. The physical and spectral data were consistent with those previously reported.[19]

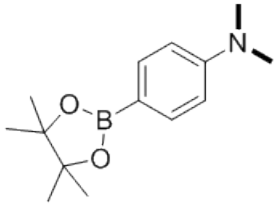
***N,N*-Dimethyl-[1,1'-biphenyl]-4-amine (5m)**



The typical procedure was applied to [1,1'-biphenyl]-4-amine (50.8 mg, 0.3 mmol). Yield: 48.6 mg, 82 %, white solid; R_f = 0.8 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.63 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 8.0 Hz, 2H), 7.32 (s, 1H), 6.87 (d, J = 8.0 Hz, 2H), 3.04 (s, 6H). ^{13}C NMR

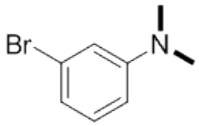
($CDCl_3$, 100 MHz): δ 149.9, 141.1, 129.1, 128.6, 127.6, 126.2, 125.9, 112.7, 40.5. The physical and spectral data were consistent with those previously reported. [15]

***N,N*-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (5n)**



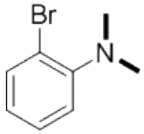
The typical procedure was applied to 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (65.7 mg, 0.3 mmol). Yield: 55.9 mg, 75 %, yellow solid; R_f = 0.7 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (20:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 2H), 2.99 (s, 6H), 1.34 (s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.5, 136.1 (two carbons are overlapped), 111.2, 83.1, 40.1, 24.8. The physical and spectral data were consistent with those previously reported.[20]

3-Bromo-*N,N*-dimethylaniline (5z)



The typical procedure was applied to 3-bromoaniline (51.6 mg, 0.3 mmol). Yield: 47.9 mg, 80 %, light yellow solid; R_f= 0.8 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (10:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.10 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 4.0 Hz, 2H), 6.64 (d, *J* = 8.0 Hz, 1H), 2.96 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 130.2, 123.3, 119.0, 115.0, 110.8, 40.3. The physical and spectral data were consistent with those previously reported.[21]

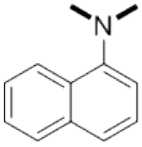
2-Bromo-*N,N*-dimethylaniline (5aa)



The typical procedure was applied to 2-bromoaniline (51.6 mg, 0.3 mmol). Yield: 48.3 mg, 81 %, light yellow solid; R_f= 0.8 (PE/EtOAc = 10/1); purified by column chromatography eluting with PE/EtOAc (30:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.89 (t, *J* = 8.0 Hz, 1H), 2.81 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.8,

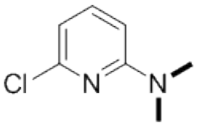
133.8, 128.0, 123.9, 120.4, 119.1, 44.2. The physical and spectral data were consistent with those previously reported.[22]

_N,N_-Dimethylnaphthalen-1-amine (5u)



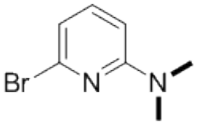
The typical procedure was applied to naphthalen-1-amine (43.0 mg, 0.3 mmol). Yield: 40.6 mg, 79 %, white solid; R_f = 0.8 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (10:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.25 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H),, 7.51 (m, 3H), 7.44 – 7.33 (m, 1H), 7.09 (d, J = 4.0 Hz, 1H)., 2.92 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 134.7, 128.7, 128.3, 125.7, 125.7, 125.1, 124.1, 122.8, 113.9, 45.2. The physical and spectral data were consistent with those previously reported. [15]

6-Chloro-_N,N_-dimethylpyridin-2-amine (5ab)



The typical procedure was applied to 6-chloropyridin-2-amine (38.6 mg, 0.3 mmol). Yield: 37.6 mg, 80 %, colorless oil; R_f = 0.8 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (10:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 (t, J = 8.0 Hz, 1H), 6.51 (d, J = 8.0 Hz, 1H), 6.34 (d, J = 8.0 Hz, 1H), 3.06 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.1, 149.2, 139.2, 110.2, 103.5, 37.9. The physical and spectral data were consistent with those previously reported.[23]

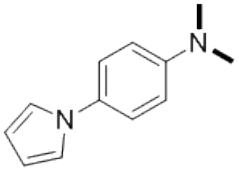
6-Bromo-_N,N_-dimethylpyridin-2-amine (5ac)



The typical procedure was applied to 6-bromopyridin-2-amine (51.9 mg, 0.3 mmol). Yield: 45.5 mg, 76 %, colorless oil; R_f = 0.8 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (10:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24 (t, J = 8.0 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 6.37 (d, J = 8.0 Hz, 1H), 3.06 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.1, 140.1, 139.0,

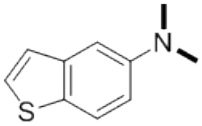
114.1, 103.8, 37.9. The physical and spectral data were consistent with those previously reported.[24]

_N,N_-Dimethyl-4-(1_H_-pyrrol-1-yl)aniline (5r)



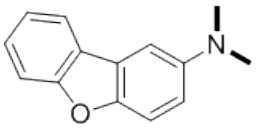
The typical procedure was applied to 4-(1*H*-pyrrol-1-yl)aniline (47.5 mg, 0.3 mmol). Yield: 43.3 mg, 78 %, yellow solid; R_f = 0.8 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (20:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 4.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.33 (t, *J* = 4.0 Hz, 2H), 3.00 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.9, 131.2, 122.1, 119.7, 113.0, 109.3, 40.8. The physical and spectral data were consistent with those previously reported.[25]

_N,N_-Dimethylbenzo[_b_]thiophen-5-amine (5s)



The typical procedure was applied to benzo[*b*]thiophen-5-amine (44.8 mg, 0.3 mmol). Yield: 47.0 mg, 88 %, yellow solid; R_f = 0.9 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (20:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 4.0 Hz, 1H), 6.99 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.02 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.7, 140.9, 129.0, 126.7, 123.5, 122.5, 113.3, 106.3, 41.4. The physical and spectral data were consistent with those previously reported.[26]

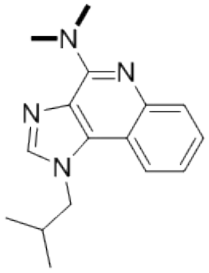
_N,N_-Dimethyldibenzo[_b,d_]furan-2-amine (5t)



The typical procedure was applied to dibenzo[*b,d*]furan-2-amine (54.9 mg, 0.3 mmol). Yield: 55.4 mg, 87 %, yellow solid; R_f = 0.9 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (20:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.27 (m, 2H), 6.89 (d, *J* = 4.0 Hz, 1H), 6.79 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.06 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ

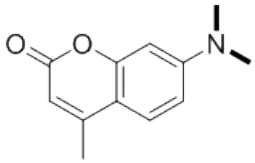
158.5, 155.9, 151.0, 125.1, 124.8, 122.5, 120.9, 119.2, 113.6, 111.1, 108.9, 94.7, 41.0. The physical and spectral data were consistent with those previously reported.[27]

1-*iso*-Butyl-*N,N*-dimethyl-1*H*-imidazo[4,5-*c*]quinolin-4-amine (5ad)



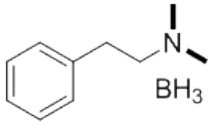
The typical procedure was applied to 1-isobutyl-1*H*-imidazo[4,5-*c*]quinolin-4-amine (48.1 mg, 0.2 mmol). Yield: 33.7 mg, 63 %, white solid; R_f = 0.6 (PE/EtOAc = 2/1); purified by column chromatography eluting with PE/EtOAc (3:1), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (t, *J* = 8.0 Hz, 2H), 7.76 (s, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.30 (s, 1H), 4.30 (d, *J* = 8.0 Hz, 2H), 3.63 (s, 6H), 2.64 – 2.24 (m, 1H), 1.05 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.1, 145.1, 140.7, 133.8, 129.9, 127.4, 127.2, 121.3, 119.6, 114.7, 55.0, 39.5, 28.5, 19.7. The physical and spectral data were consistent with those previously reported. HRMS(ESI) m/z: [M + H]+ Calcd for $C_{16}H_{21}N_4$ 269.1761; Found 269.1759.

7-(Dimethylamino)-4-methyl-2*H*-chromen-2-one (5ae)



The typical procedure was applied to 7-amino-4-methyl-2*H*-chromen-2-one (52.6 mg, 0.3 mmol). Yield: 26.6 mg, 44 %, light yellow solid; R_f = 0.5 (PE/EtOAc = 2/1); purified by column chromatography eluting with PE/EtOAc (3:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39 (d, *J* = 8.0 Hz, 1H), 6.61 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.50 (s, 1H), 5.96 (q, *J* = 4.0 Hz, 1H), 3.04 (s, 6H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.1, 155.6, 152.9, 152.8, 125.2, 109.6, 109.2, 108.7, 98.2, 40.1, 18.5. The physical and spectral data were consistent with those previously reported.[28]

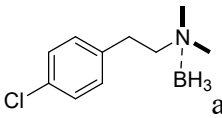
Borane-*N,N*-dimethyl-2-phenylethan-1-amine complex(5af)



The typical procedure was applied to 2-phenylethan-1-amine (36.4 mg, 0.3 mmol). Yield: 26.6 mg, 54 %, white solid; R_f = 0.8 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (30:1);

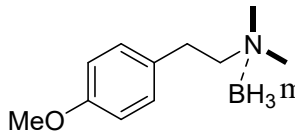
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 (t, J = 8.0 Hz, 2H), 7.28 – 7.14 (m, 3H), 3.09 – 3.03 (m, 2H), 3.00 – 2.95 (m, 2H), 2.66 (s, 6H), 2.21 – 1.52 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.9, 128.7 (two carbons are overlapped), 126.7, 66.1, 51.7, 30.8. ^{11}B NMR ($CDCl_3$, 128 MHz): δ -10.0 (q, J = 102.4 Hz). The physical and spectral data were consistent with those previously reported.[29]

Borane-2-(4-chlorophenyl)-*N,N*-dimethylethan-1-amine complex (5ag)



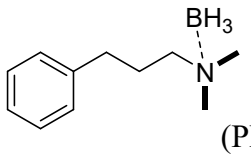
The typical procedure was applied to 2-(4-chlorophenyl)ethan-1-amine (46.7 mg, 0.3 mmol). Yield: 36.7 mg, 62 %, white solid, R_f = 0.4 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (30:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.21 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 3.03 – 2.93 (m, 2H), 2.85 (m, 2H), 2.58 (s, 6H), 1.98 – 1.54 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.4, 132.5, 130.1, 128.8, 65.9, 51.8, 30.2. ^{11}B NMR ($CDCl_3$, 128 MHz): δ -10.0 (q, J = 98.6 Hz). HRMS(ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{15}ClN$ 184.0887; Found 184.0890 (Only amine was observed. The BH_3 was removed under ESI mode).

Borane-2-(4-methoxyphenyl)-*N,N*-dimethylethan-1-amine complex (5ah)



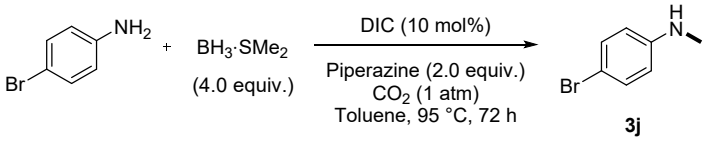
The typical procedure was applied to 2-(4-methoxyphenyl)ethan-1-amine (45.4 mg, 0.3 mmol). Yield: 37.7 mg, 65 %, white solid, R_f = 0.4 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (30:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.12 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H), 3.79 (s, 3H), 3.05 – 2.96 (m, 2H), 2.93 (m, 2H), 2.65 (s, 6H), 2.06 – 1.59 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.3, 129.9, 129.7, 114.1, 66.3, 55.3, 51.7, 29.9. ^{11}B NMR ($CDCl_3$, 128 MHz): δ -10.1 (q, J = 98.6 Hz). HRMS(ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{18}ON$ 180.1382; Found 180.1377 (Only amine was observed. The BH_3 was removed under ESI mode).

Borane-*N,N*-dimethyl-3-phenylpropan-1-amine complex (5ai)

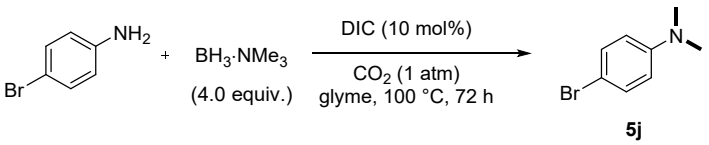


The typical procedure was applied to 3-phenylpropan-1-amine (40.6 mg, 0.3 mmol). Yield: 29.2 mg, 55 %, white solid, R_f = 0.4 (PE/EtOAc = 5/1); purified by column chromatography eluting with PE/EtOAc (30:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 (t, J = 8.0 Hz, 2H), 7.25 – 7.13 (m, 3H), 2.84 – 2.73 (m, 2H), 2.62 (t, J = 8.0 Hz, 2H), 2.56 (s, 6H), 2.19 – 1.96 (m, 2H), 1.79 – 1.26 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.6, 128.5, 128.2, 126.2, 64.1, 51.3, 33.3, 25.5. ^{11}B NMR ($CDCl_3$, 128 MHz): δ -10.0 (q, J = 89.6 Hz). The physical and spectral data were consistent with those previously reported.[29]

4. Gram-Scale Reaction



In a 100 mL Schlenk tube was placed 4-bromoaniline (860.3 mg, 5.0 mmol), piperazine (861.4 mg, 10.0 mmol), BH_3·SMe_2 (2.0 mL, 10 mol/L, 20.0 mmol), *N,N′*-diisopropylcarbodiimide (63.1 mg, 0.5 mmol), toluene (6.0 mL). The resulting mixture was stirred with a CO_2 balloon at 95 ºC for 72 h, and then allowed to room temperature. The reaction was quenched by saturated brine (10 mL). The aqueous layer was extracted with EtOAc (30 mL x 3). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, EtOAc/PE). Yield: 407.5 mg, 44 %, yellow oil.

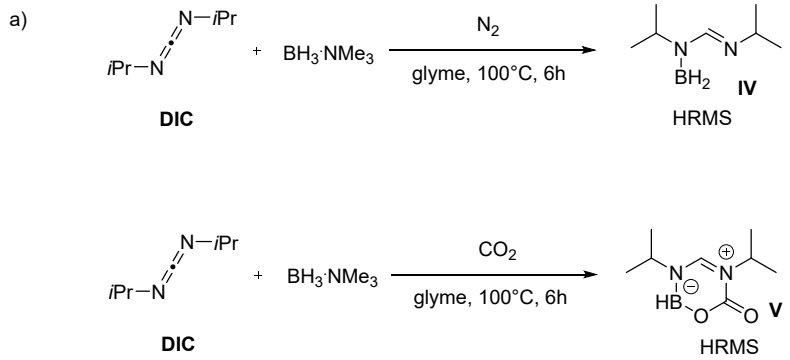


In a 100 mL Schlenk tube was placed 4-bromoaniline (860.3 mg, 5.0 mmol), BH_3·NMe_3 (1459.0 mg, 20.0 mmol), *N,N′*-diisopropylcarbodiimide (63.1 mg, 0.5 mmol), glyme (3.0 mL). The resulting mixture was stirred with a CO_2 balloon at 100 ºC for 72 h, and

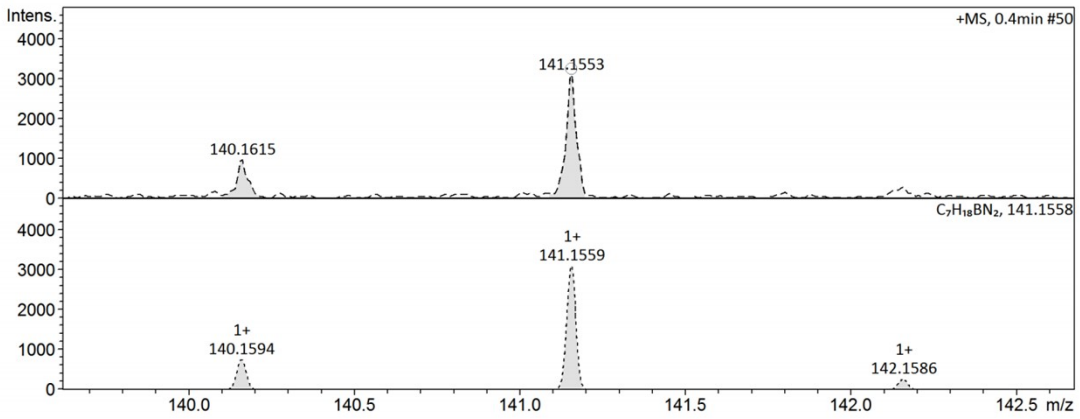
then allowed to room temperature. The reaction was quenched by saturated brine (10 mL). The aqueous layer was extracted with EtOAc (30 mL x 3). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, EtOAc/PE). Yield: 633.5 mg, 64 %, light yellow solid.

5. Mechanistic Studies:

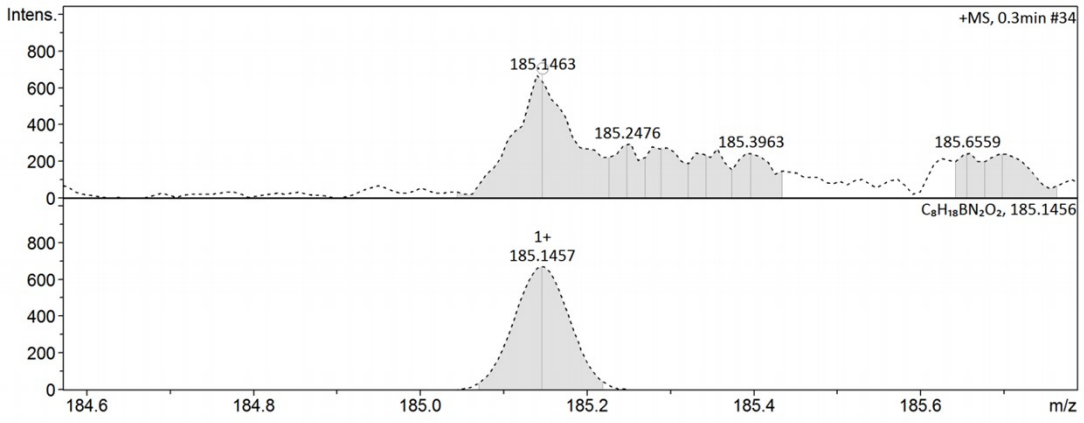
Scheme S1. HRMS experiments.



a) In a Schlenk tube was placed $BH_3{\cdot}NMe_3$ (14.6 mg, 0.2 mmol), DIC (25.2 mg, 0.2 mmol), glyme (0.1 mL). The resulting mixture was stirred under N_2 atmosphere at 100 ºC (heating block) for 6 h, and then allowed to room temperature. The resulting mixture **IV** was added MeCN in glovebox for HRMS analysis. HRMS(ESI) m/z: [M+H]+ Calcd for $C_7H_{18}BN_2$ 141.1558; Found 141.1553.

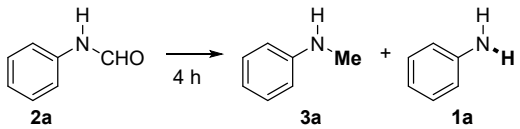


In a Schlenk tube was placed $BH_3{\cdot}NMe_3$ (14.6 mg, 0.2 mmol), DIC (25.2 mg, 0.2 mmol), glyme (0.1 mL). The resulting mixture was stirred under CO_2 atmosphere at 100 ºC (heating block) for 6 h, and then allowed to room temperature. The resulting mixture **V** was added MeCN in glovebox for HRMS analysis. HRMS(ESI) m/z: [M+H]+ Calcd for $C_8H_{18}BN_2O_2$ 185.1456; Found 185.1463.



Scheme S2. Control experiments.

b)

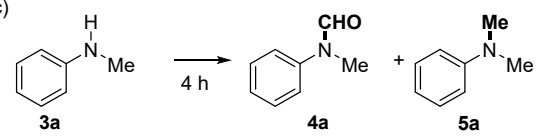


	2a	3a	1a
monomethylated conditions:		63%	37%
dimethylated conditions:		35%	6%

b) In a Schlenk tube was placed **2a** (36.3 mg, 0.3 mmol), piperazine (51.7 mg, 0.6 mmol), $BH_3{\cdot}SMe_2$ (120.0 μL, 10 mol/L, 1.2 mmol), DIC (3.7 mg, 0.03 mmol), toluene (0.4 mL). The resulting mixture was stirred with a N_2 atmosphere at 95 ºC for 4 h, and then allowed to room temperature. The reaction was quenched by saturated aqueous NaCl (1 mL). The yield was determined by GC with tridecane as the internal standard.

In a Schlenk tube was placed **2a** (36.3 mg, 0.3 mmol), $BH_3{\cdot}NMe_3$ (87.5 mg, 1.2 mmol), DIC (3.7 mg, 0.03 mmol), glyme (0.2 mL). The resulting mixture was stirred with a N_2 atmosphere at 100 ºC for 4 h, and then allowed to room temperature. The reaction was quenched by saturated aqueous NaCl (1 mL). The yield was determined by GC with tridecane as the internal standard.

c)



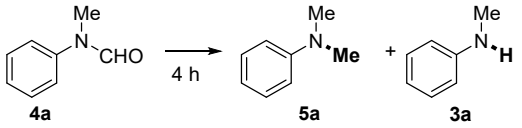
3a **4a** **5a**

monomethylated conditions:	0%	4%
dimethylated conditions:	8%	92%

c) In a Schlenk tube was placed **3a** (32.1 mg, 0.3 mmol), piperazine (51.7 mg, 0.6 mmol), $BH_3{\cdot}SMe_2$ (120.0 μL, 10 mol/L, 1.2 mmol), DIC (3.7 mg, 0.03 mmol), toluene (0.4 mL). The resulting mixture was stirred with a CO_2 balloon at 95 ºC for 4 h, and then allowed to room temperature. The reaction was quenched by saturated aqueous NaCl (1 mL). The yield was determined by GC with tridecane as the internal standard.

In a Schlenk tube was placed **3a** (32.1 mg, 0.3 mmol), $BH_3{\cdot}NMe_3$ (87.5 mg, 1.2 mmol), DIC (3.7 mg, 0.03 mmol), glyme (0.2 mL). The resulting mixture was stirred with a CO_2 balloon at 100 ºC for 4 h, and then allowed to room temperature. The reaction was quenched by saturated aqueous NaCl (1 mL). The yield was determined by GC with tridecane as the internal standard.

d)



4a **5a** **3a**

monomethylated conditions:	56%	13%
dimethylated conditions:	33%	19%

d) In a Schlenk tube was placed **4a** (40.5 mg, 0.3 mmol), piperazine (51.7 mg, 0.6 mmol), $BH_3{\cdot}SMe_2$ (120.0 μL, 10mol/L, 1.2 mmol), DIC (3.7 mg, 0.03 mmol), toluene (0.4 mL). The resulting mixture was stirred with a CO_2 balloon at 95 ºC for 4 h, and then allowed to room temperature. The reaction was quenched by saturated aqueous NaCl (1 mL). The yield was determined by GC with tridecane as the internal standard.

In a Schlenk tube was placed **4a** (40.5 mg, 0.3 mmol), $BH_3{\cdot}NMe_3$ (87.5 mg, 1.2 mmol), DIC (3.7 mg μL, 0.03 mmol), glyme (0.2 mL). The resulting mixture was

stirred with a CO_2 balloon at 100 ºC for 4 h, and then allowed to room temperature. The reaction was quenched by saturated aqueous NaCl (1 mL). The yield was determined by GC with tridecane as the internal standard.

6. References

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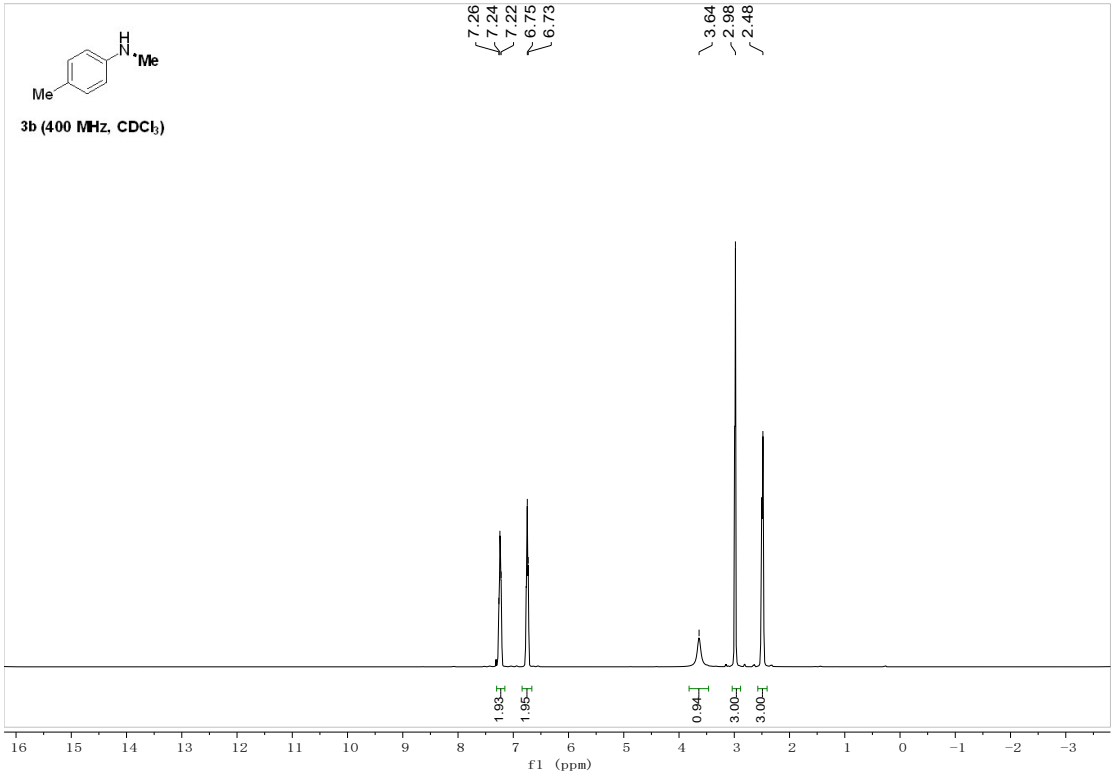
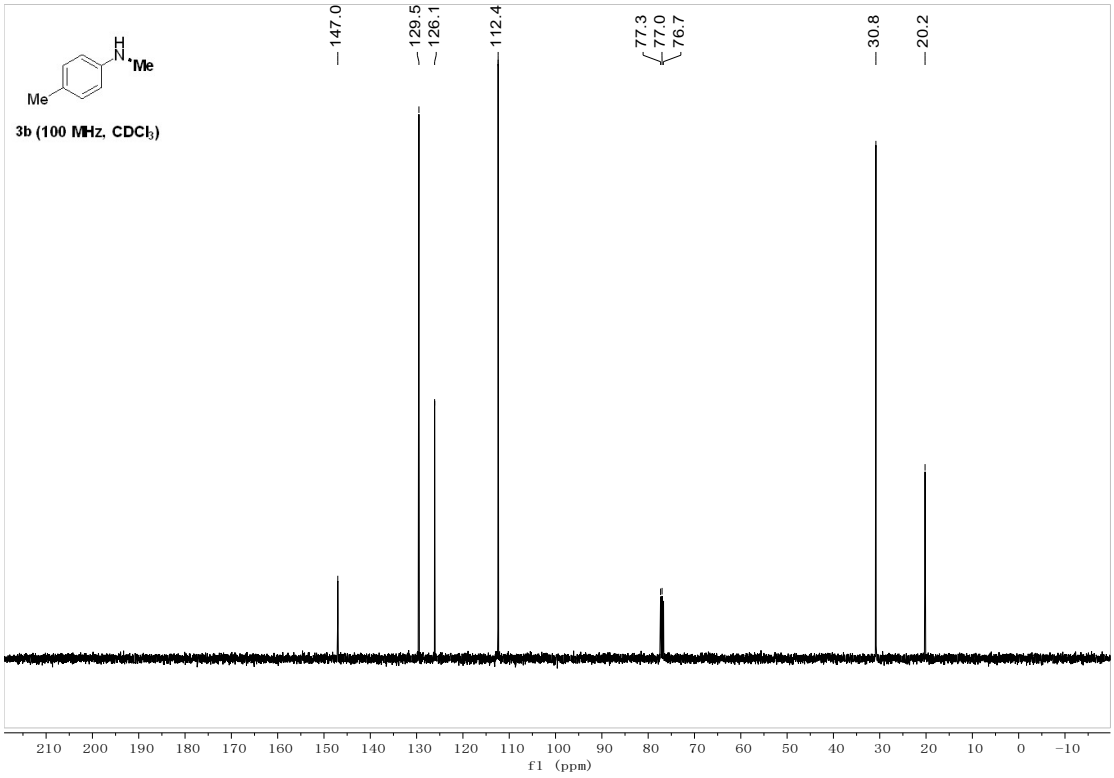
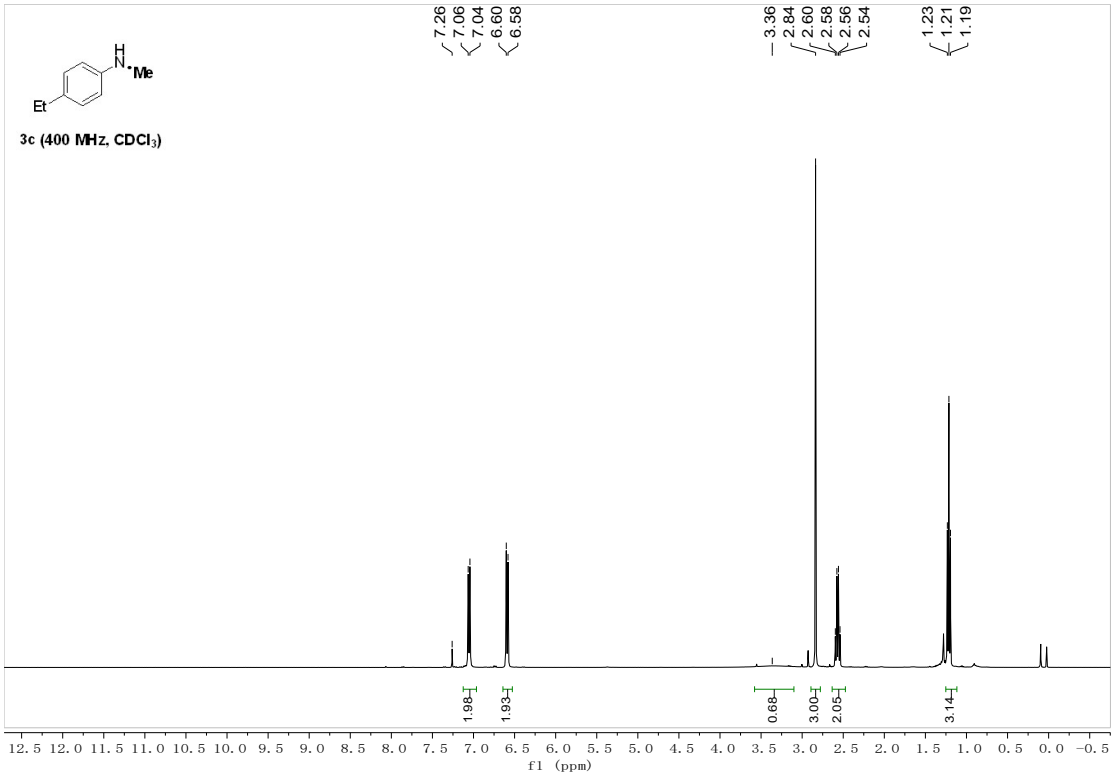
7. ^{1}H and ^{13}C NMR Spectra



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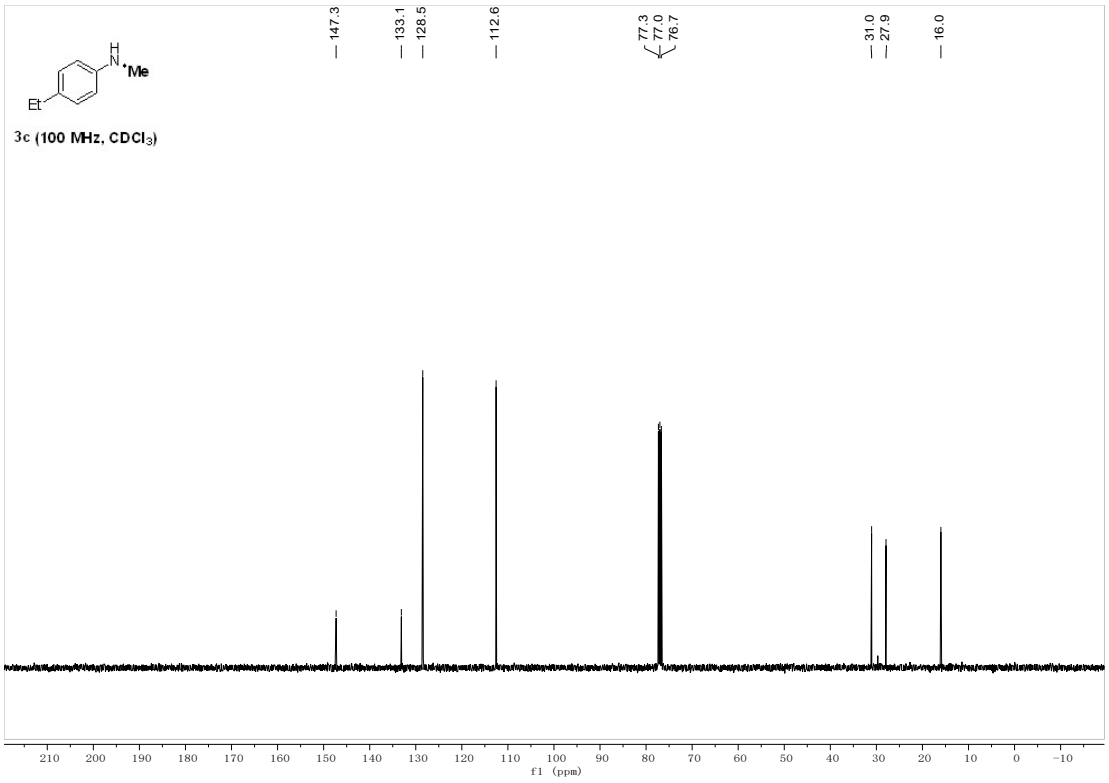
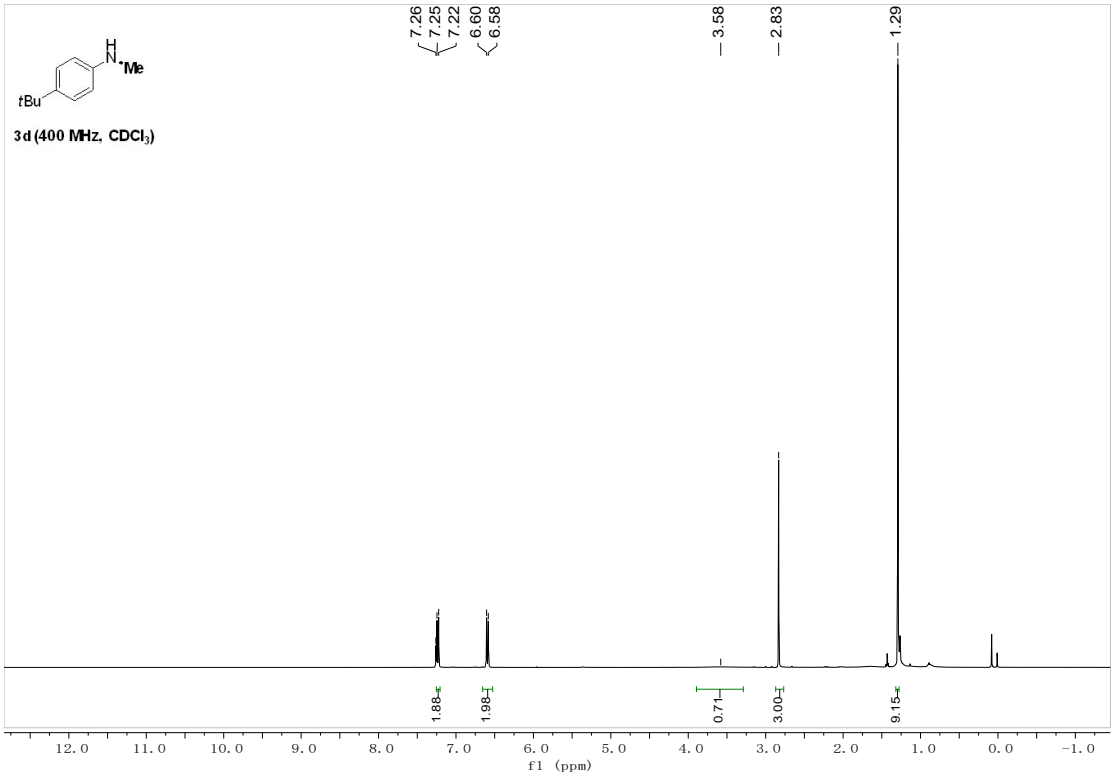
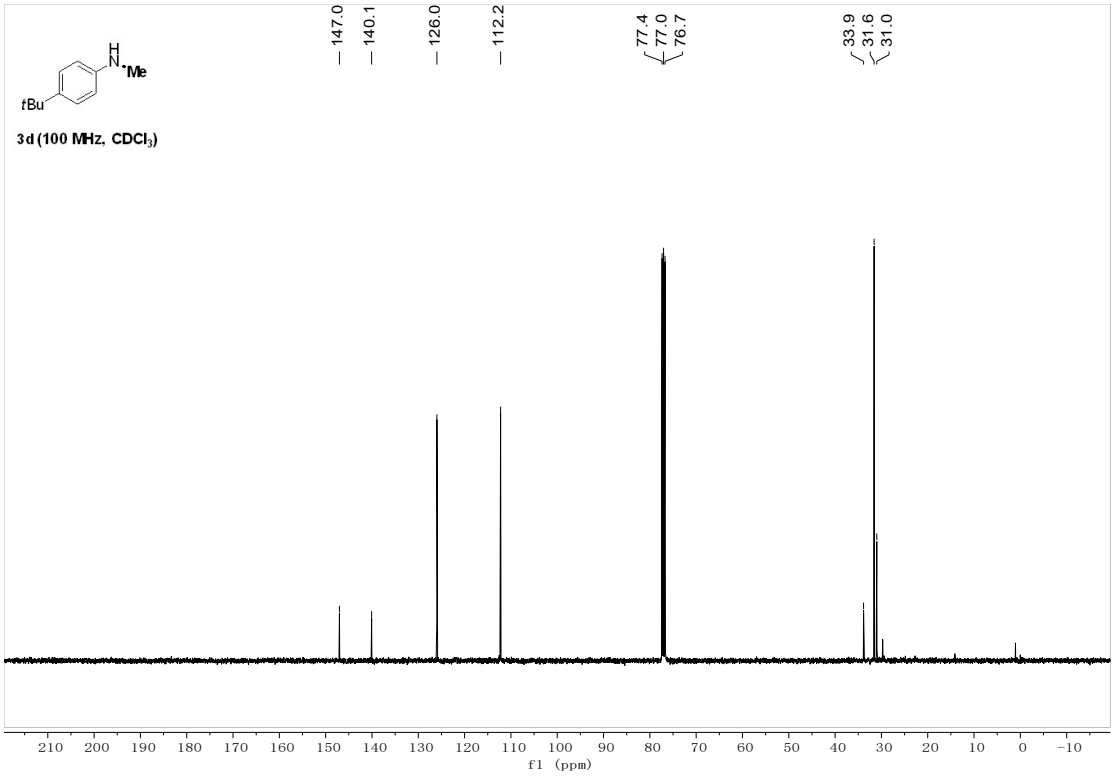
7.06
7.04
6.60
6.58
3.36
2.84
2.60
2.58
2.56
2.54
1.23
1.21
1.19
Et
H
N
Me
3c (400 MHz, CDCl3)
1.98
1.93
0.68
3.00
2.05
3.14
f1 (ppm)

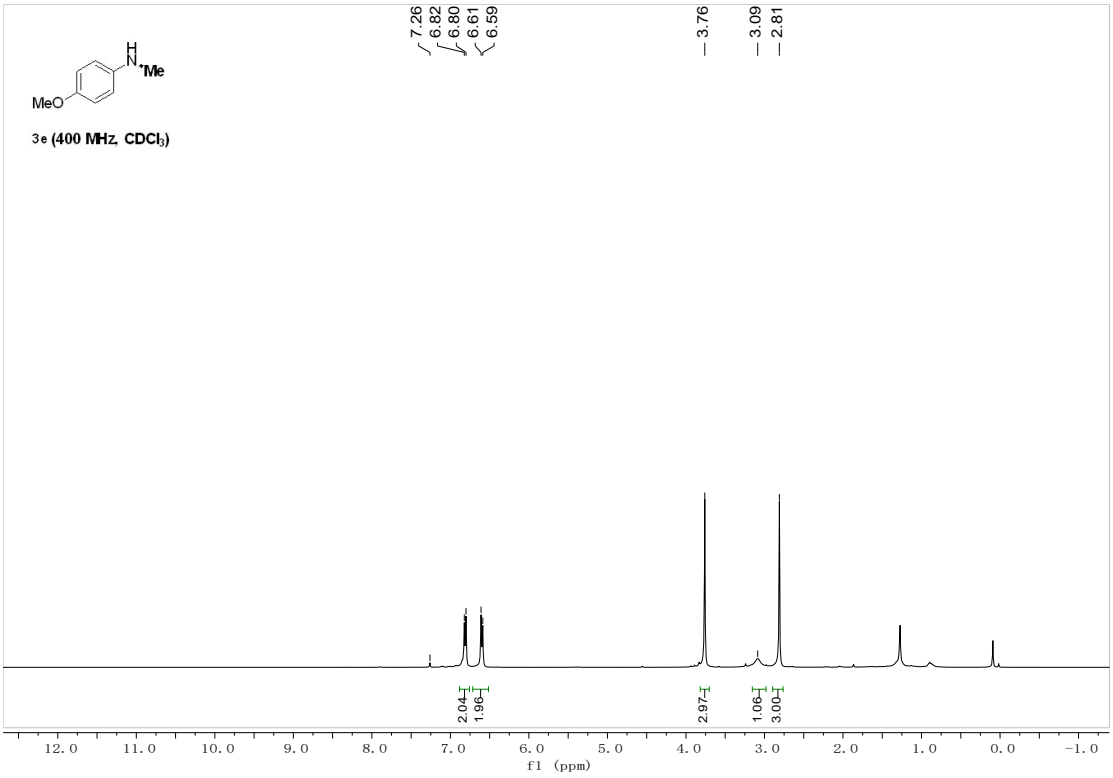

147.3
133.1
128.5
112.6
77.3
77.0
76.7
31.0
27.9
16.0
Et
H
N
Me
3c (100 MHz, CDCl3)
f1 (ppm)



3d (400 MHz, $CDCl_3$)



3d (100 MHz, $CDCl_3$)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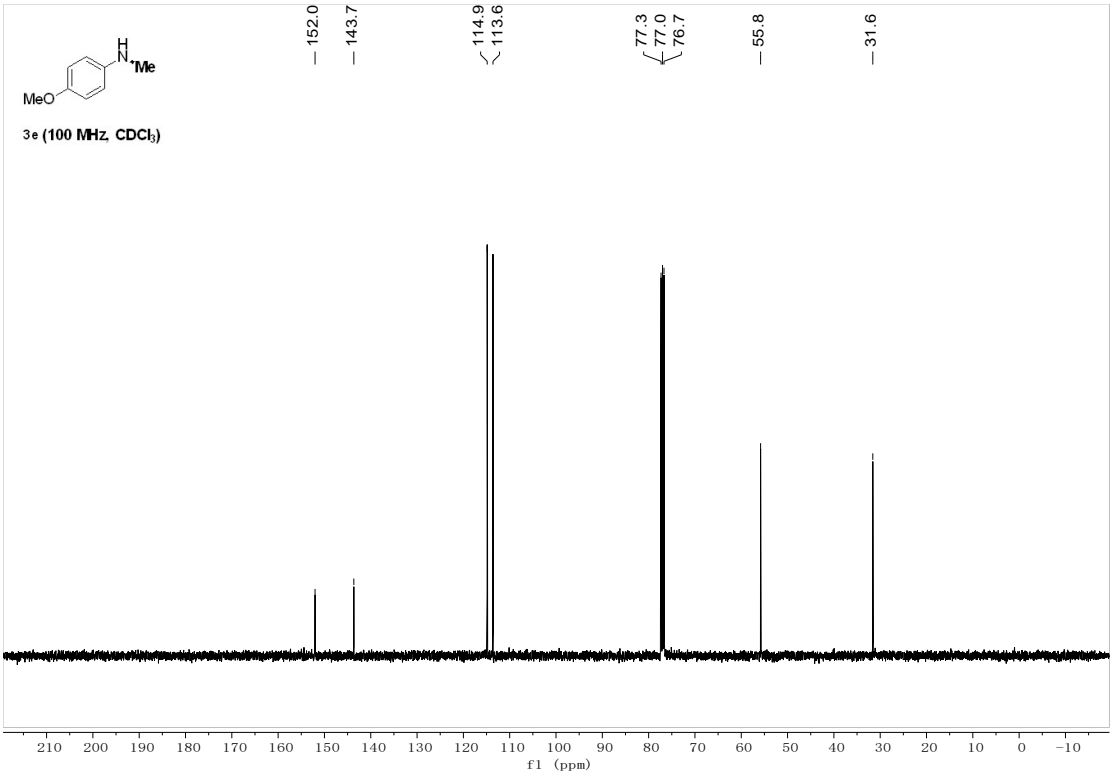
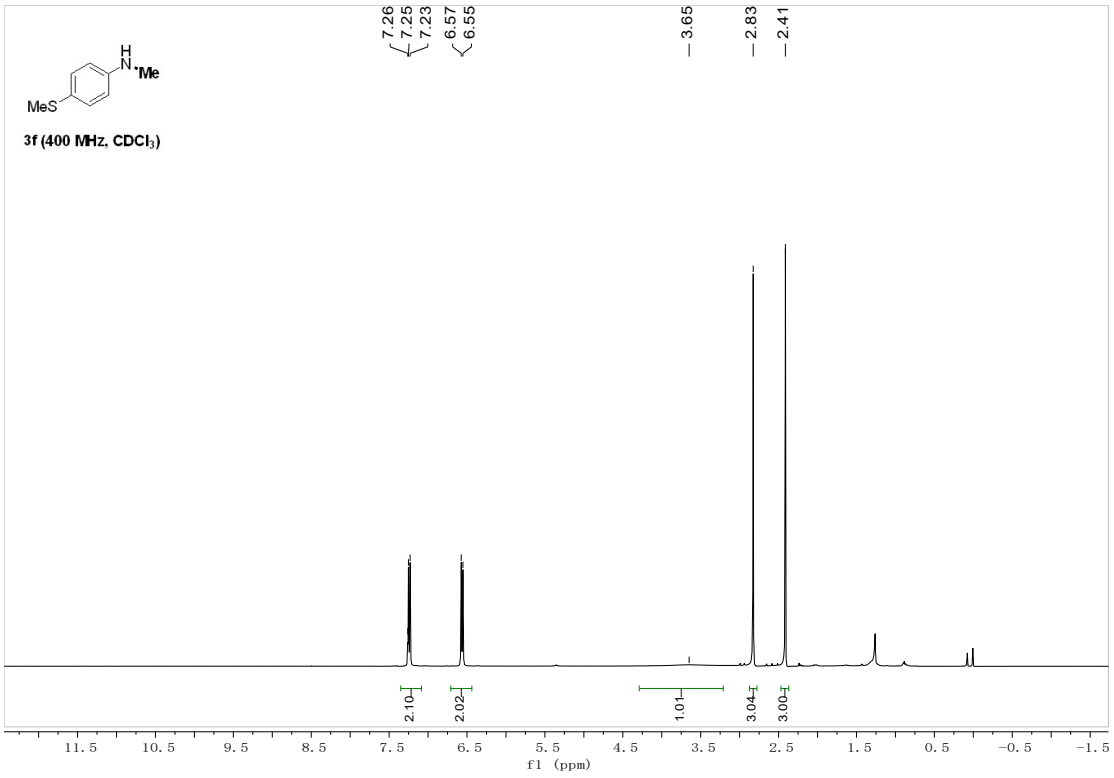
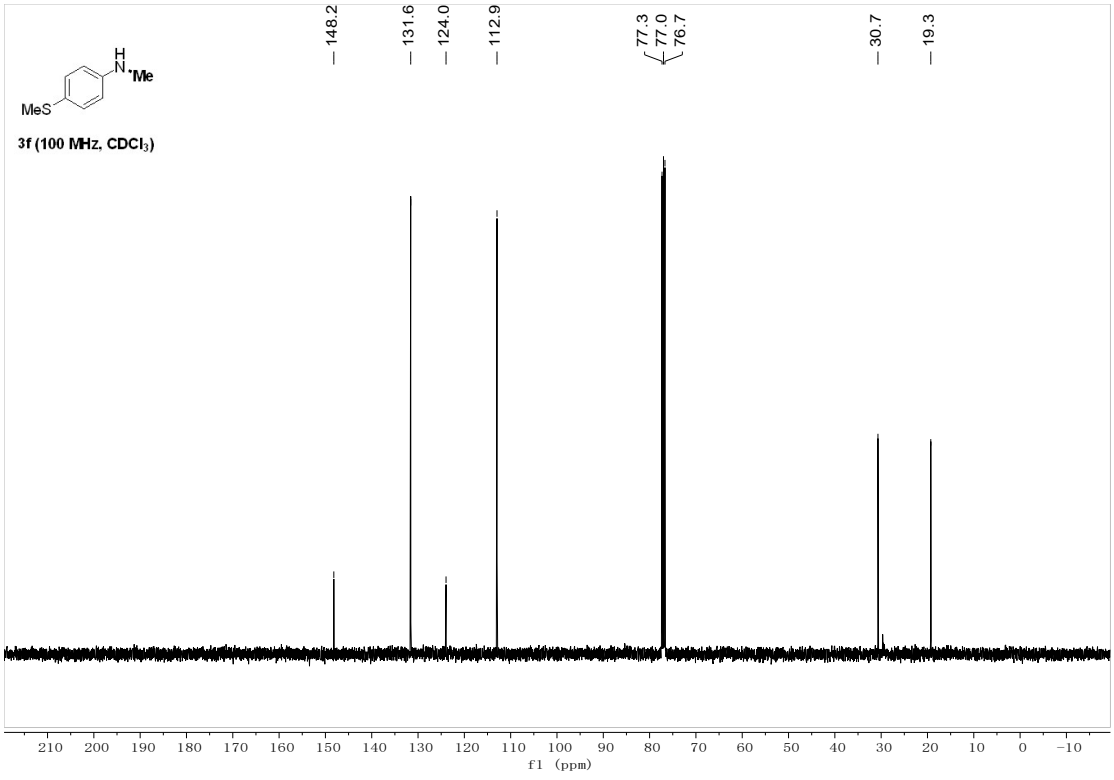
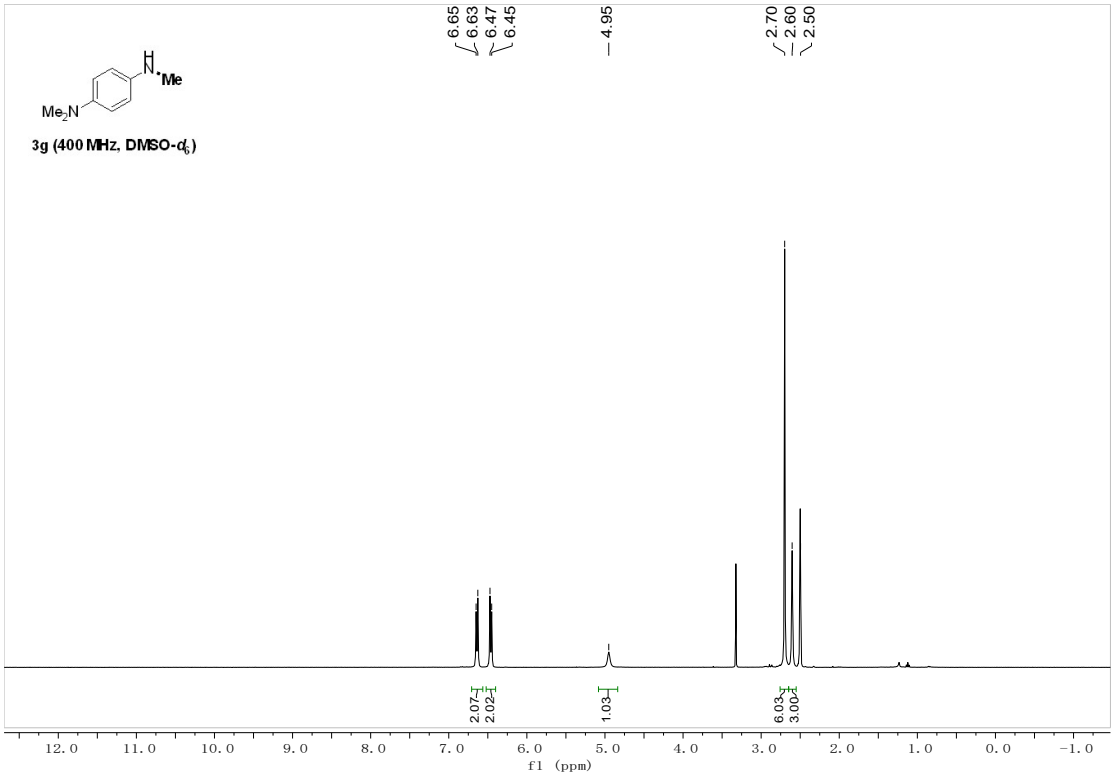
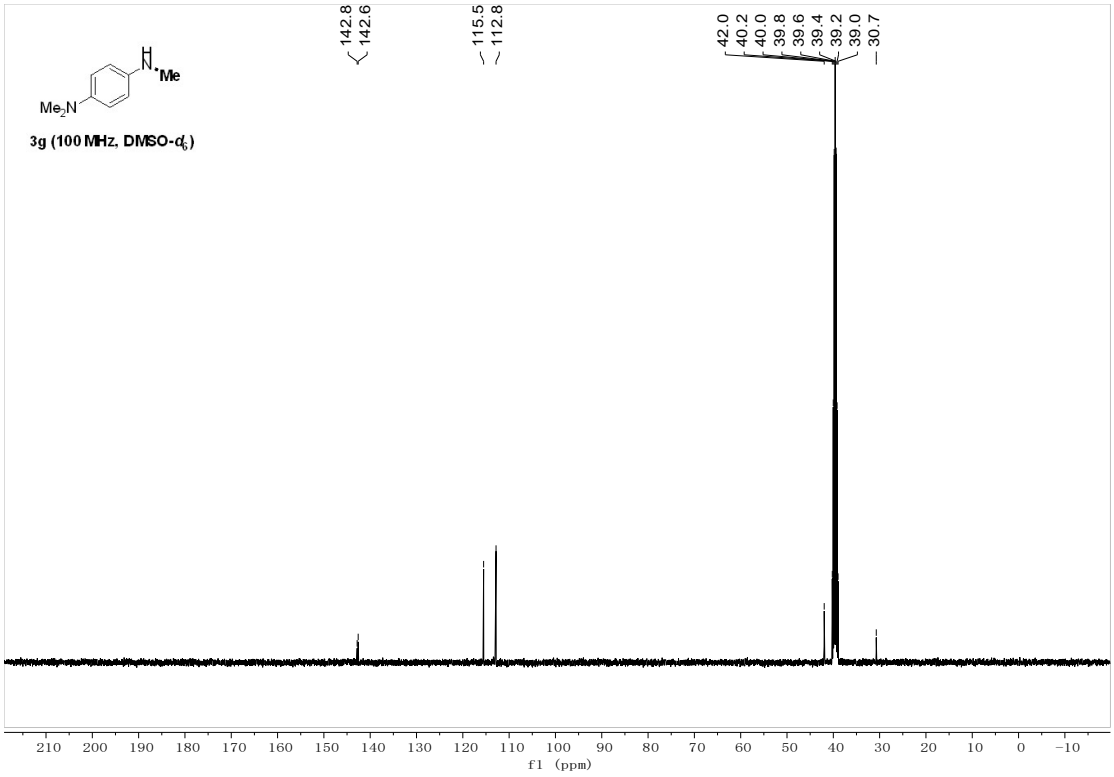
6.82
6.80
6.61
6.59
3.76
3.09
2.81
MeO
N
H
Me
3e (400 MHz, CDCl3)
2.04
1.96
2.97
1.06
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.0
f1 (ppm)

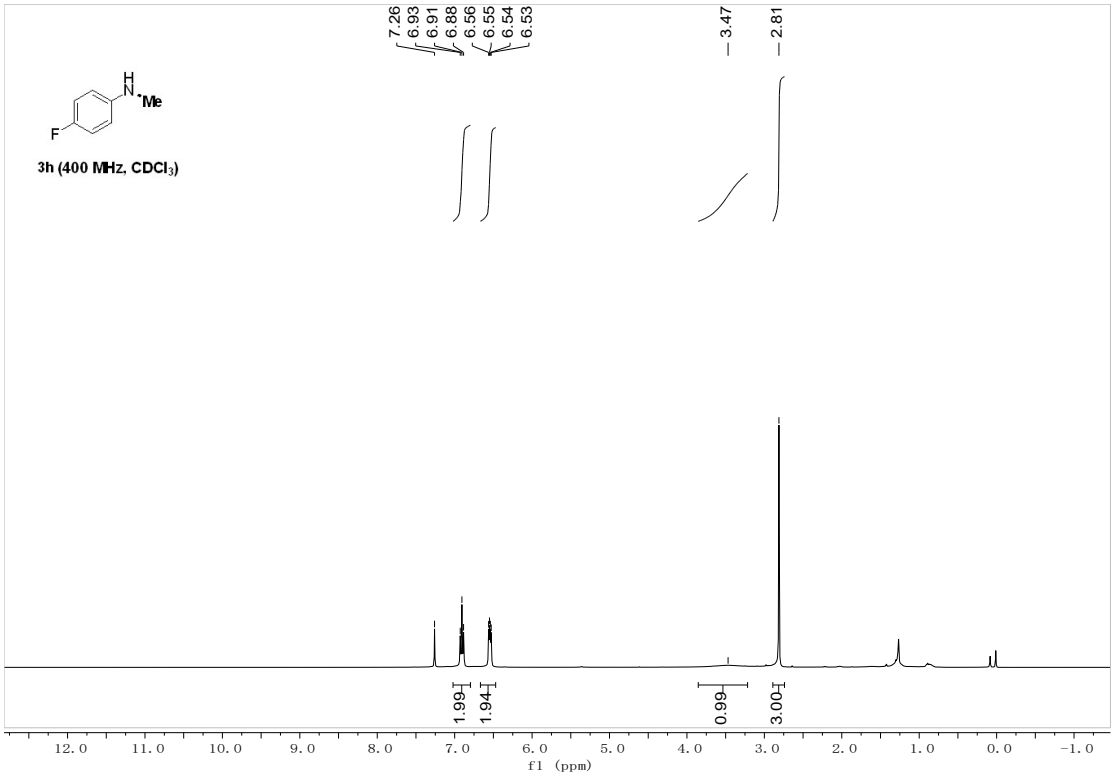

152.0
143.7
114.9
113.6
77.3
77.0
76.7
55.8
31.6
MeO
N
H
Me
3e (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.26
7.25
7.23
6.57
6.55
3.65
2.83
2.41
MeS
H
N
Me
3f (400 MHz, CDCl3)
2.10
2.02
1.01
3.04
3.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
−1.5
f1 (ppm)

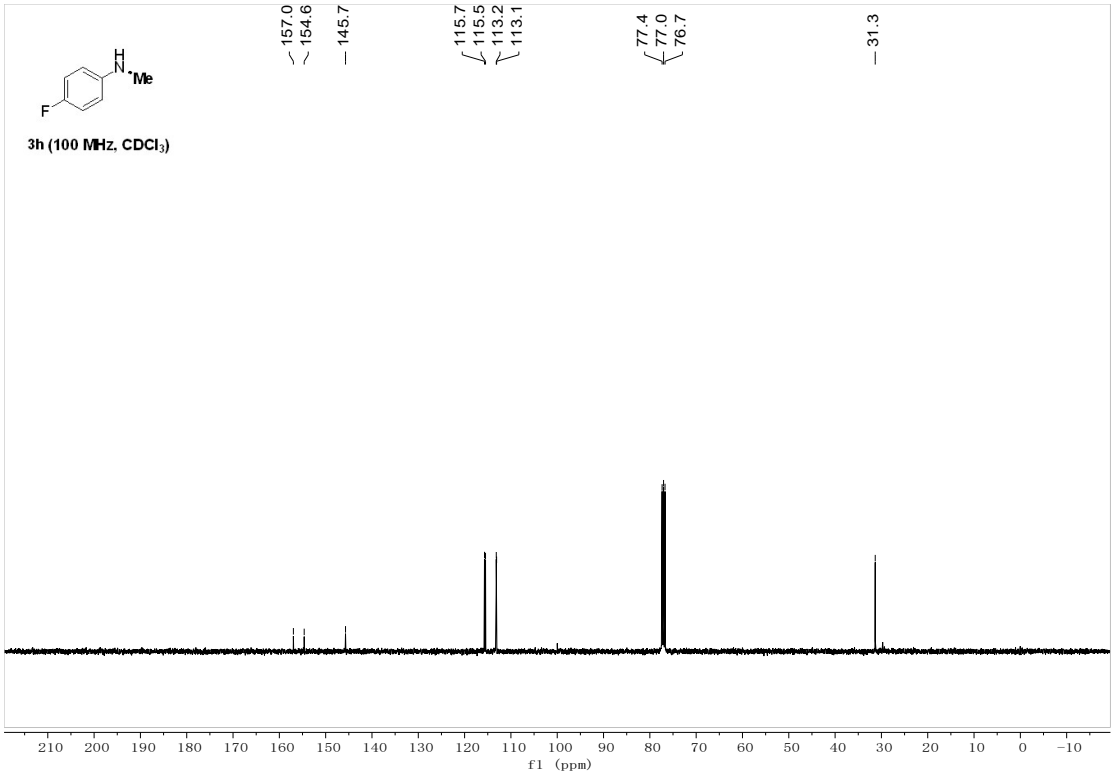

148.2
131.6
124.0
112.9
77.3
77.0
76.7
30.7
19.3
MeS
H
N
Me
3f (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


6.65
6.63
6.47
6.45
4.95
2.70
2.60
2.50
Me2N
N
H
Me
3g (400 MHz, DMSO-d6)
2.07
2.02
1.03
6.03
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.0
f1 (ppm)

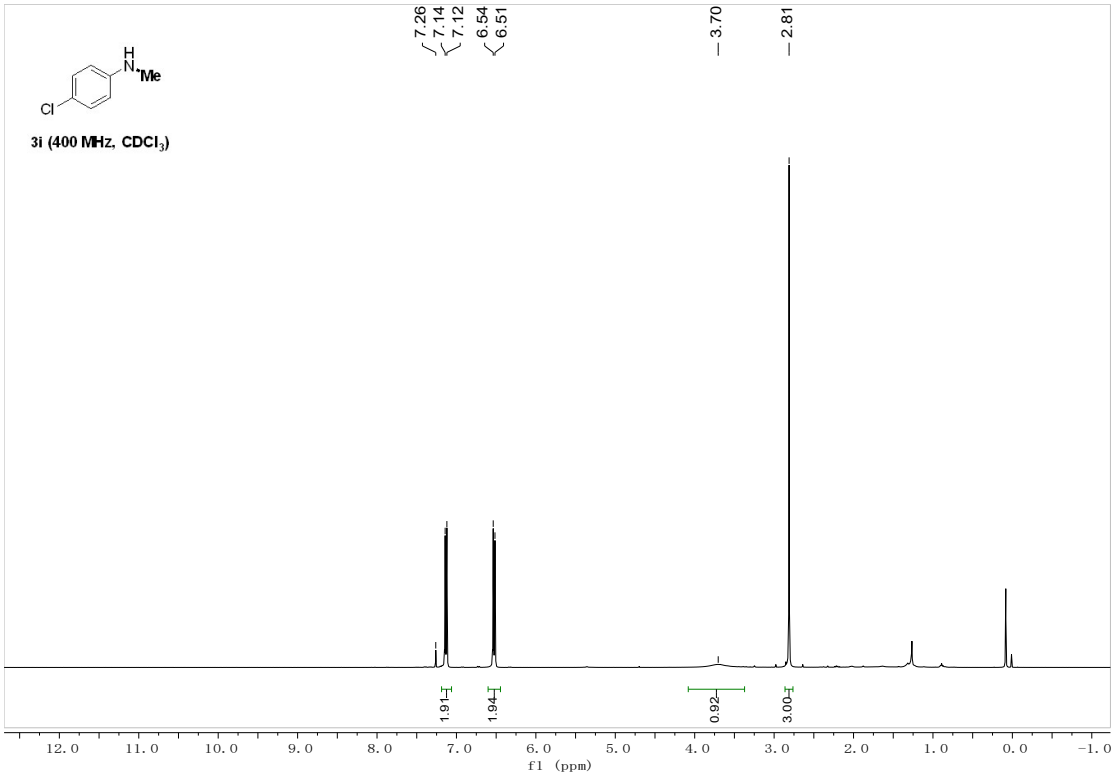

142.8
142.6
115.5
112.8
42.0
40.2
40.0
39.8
39.6
39.4
39.2
39.0
30.7
Me2N
N
H
Me
3g (100 MHz, DMSO-d6)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

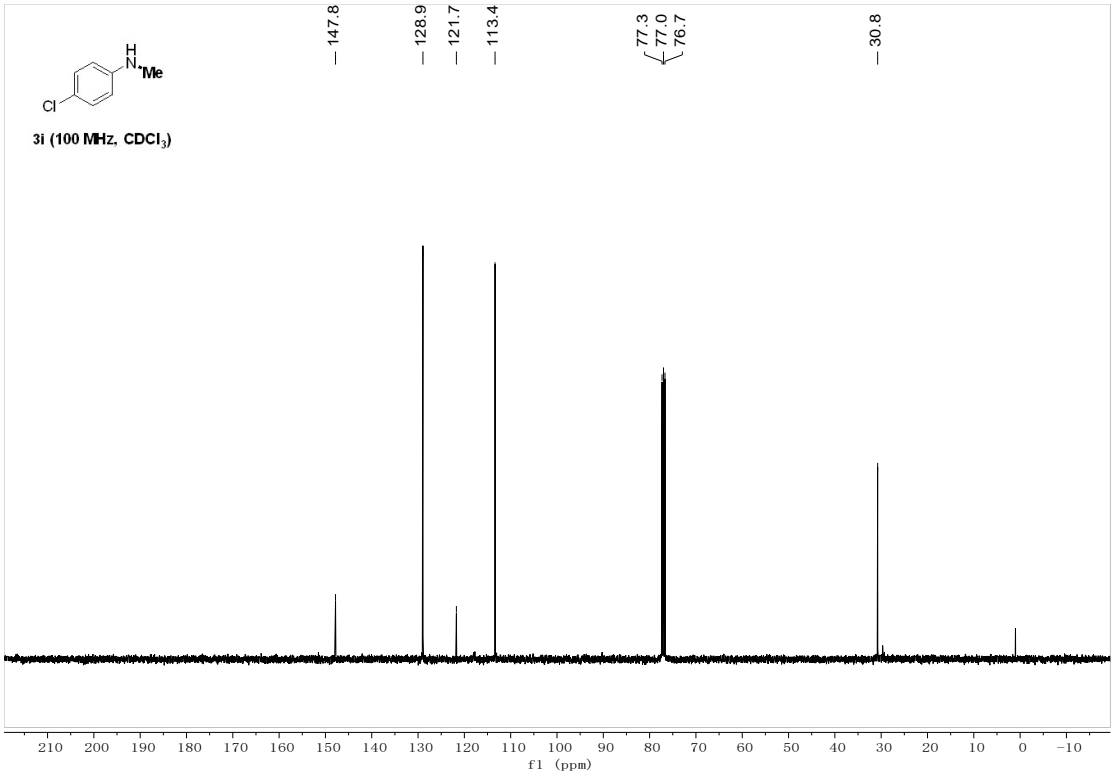


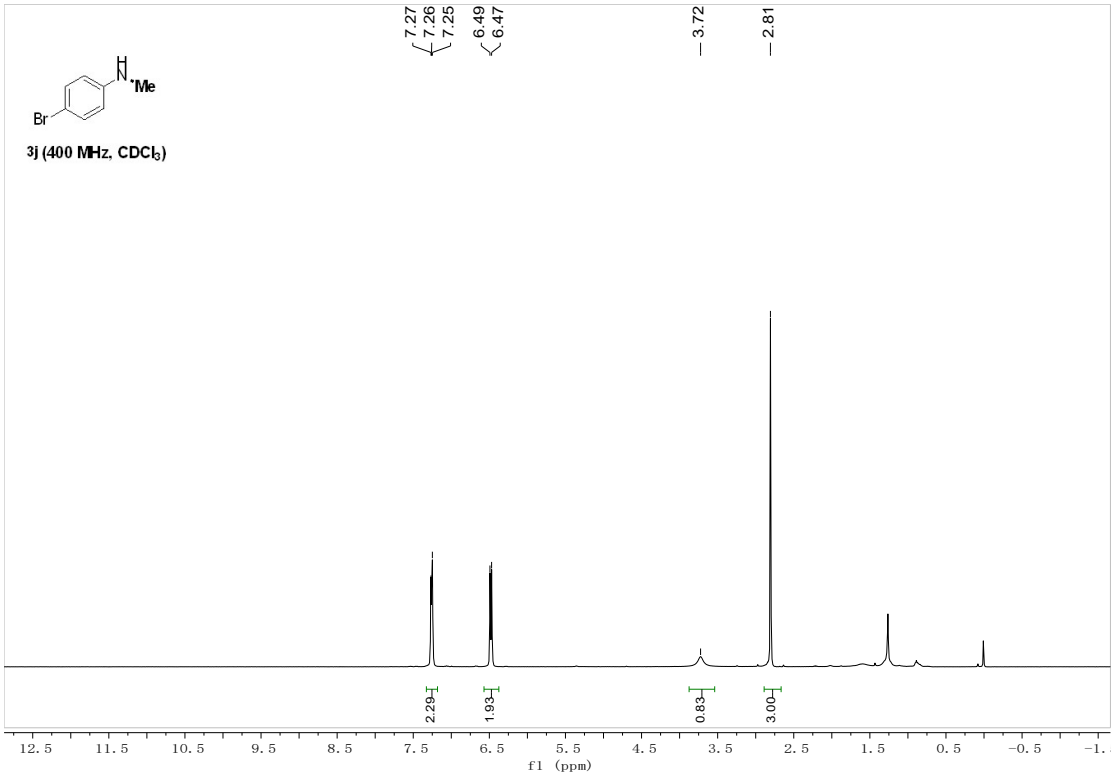
3h (400 MHz, $CDCl_3$)

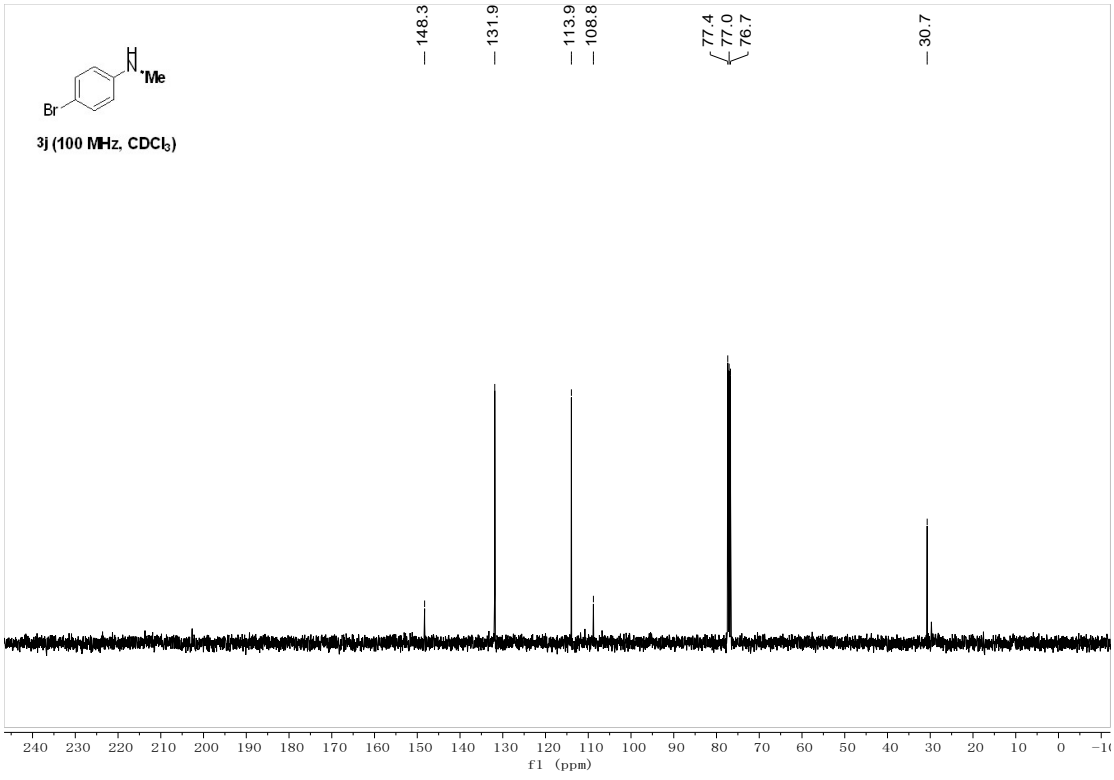


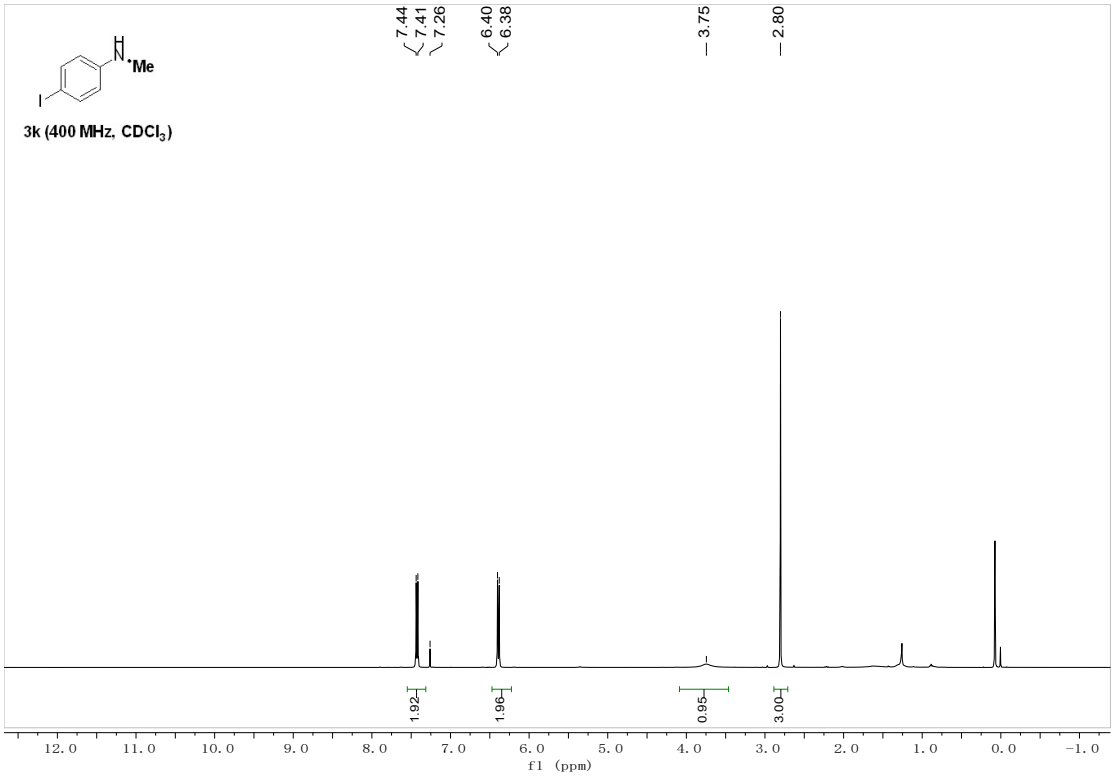
3h (100 MHz, $CDCl_3$)

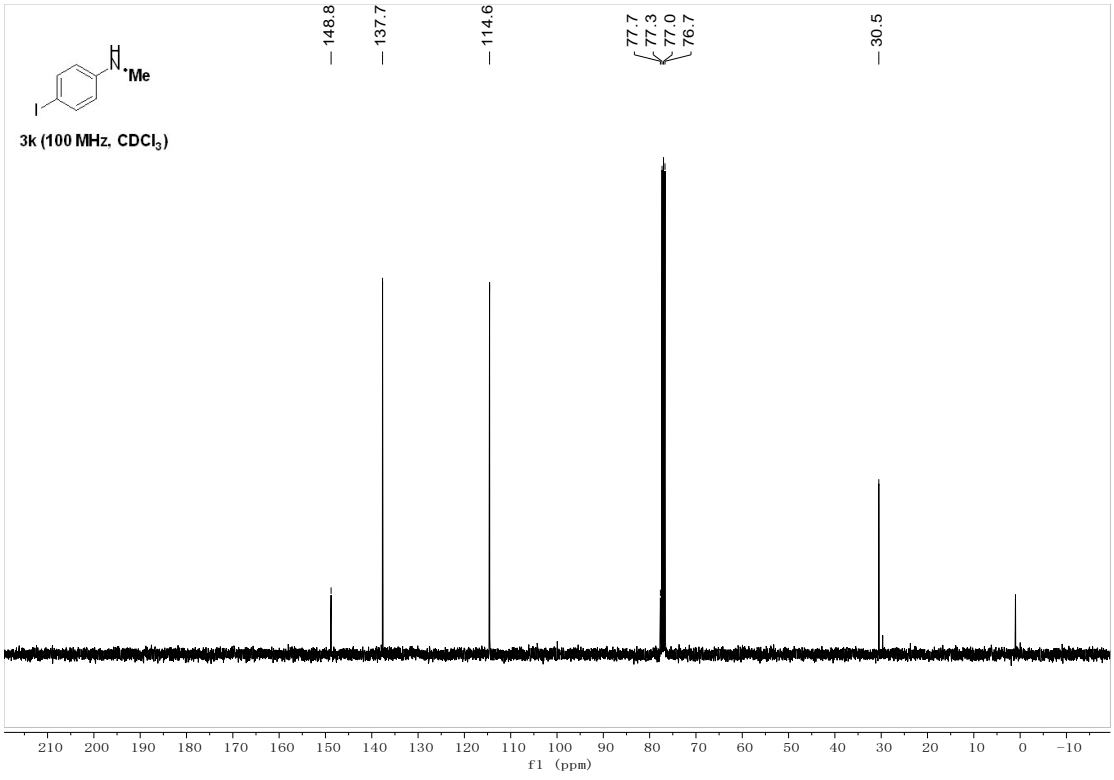

7.26
7.14
7.12
6.54
6.51
3.70
2.81
H
N
Me
Cl
3i (400 MHz, CDCl3)
1.91
1.94
0.92
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

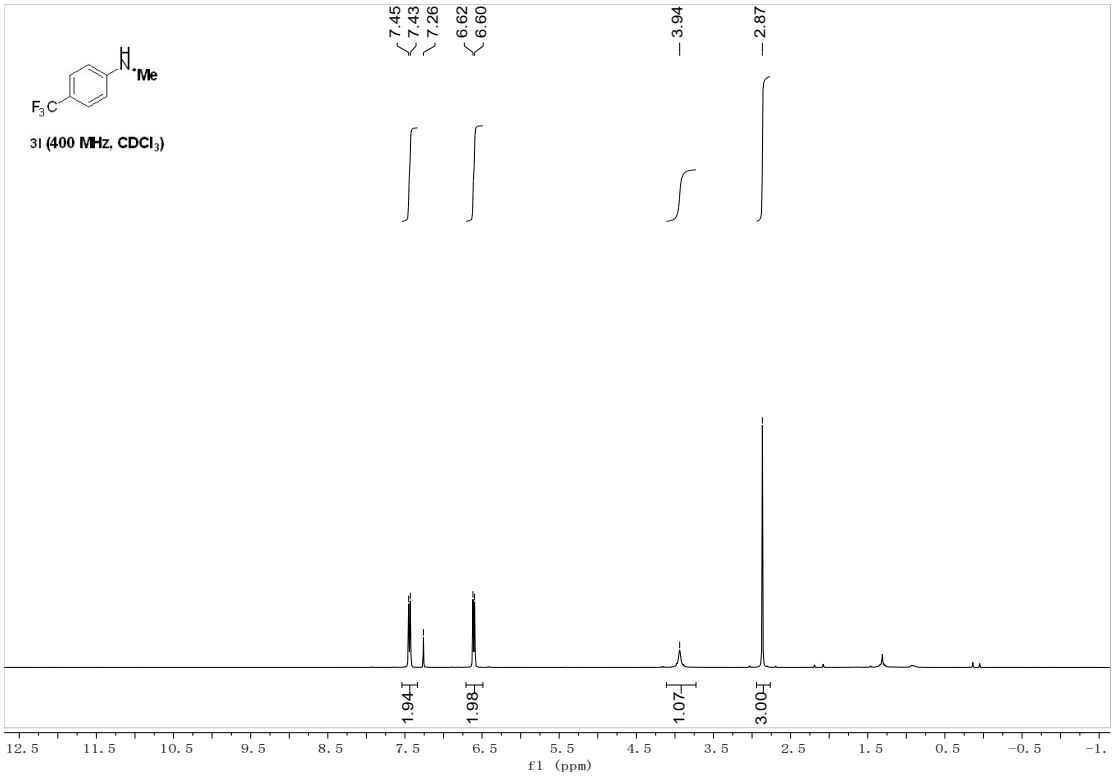

147.8
128.9
121.7
113.4
77.3
77.0
76.7
30.8
H
N
Me
Cl
3i (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

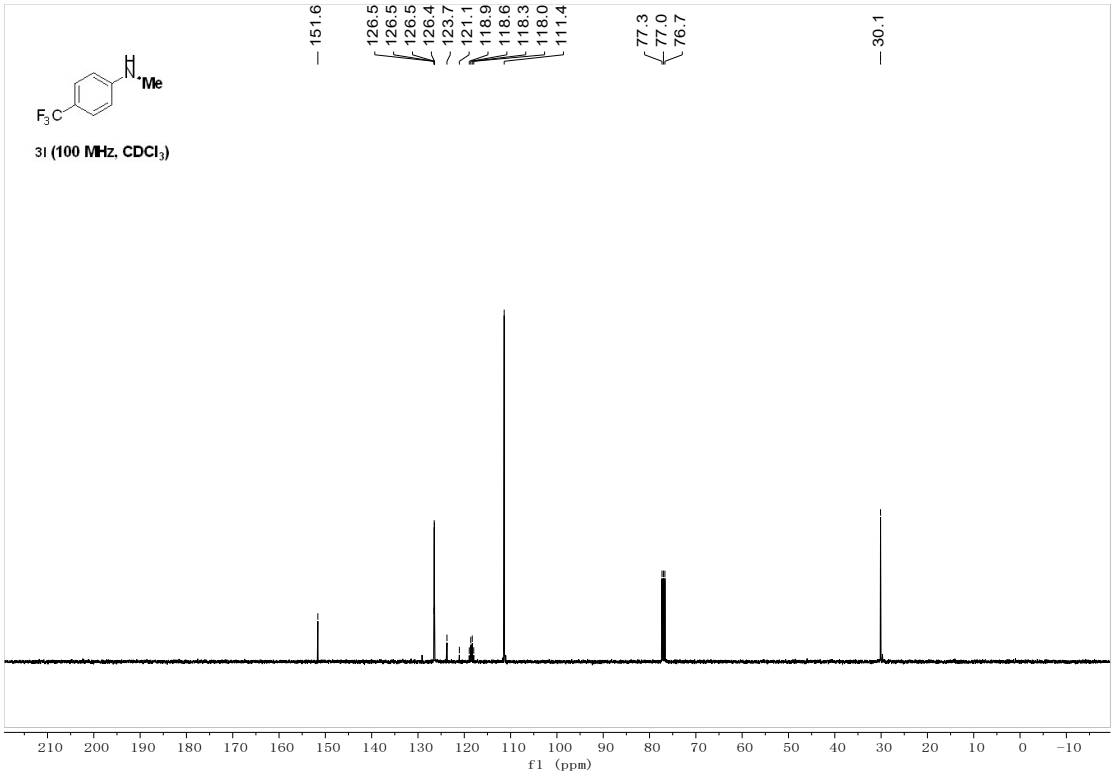

7.27
7.26
7.25
6.49
6.47
3.72
2.81
Br
N
H
Me
3j (400 MHz, CDCl3)
2.29
1.93
0.83
3.00
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)


148.3
131.9
113.9
108.8
77.4
77.0
76.7
30.7
Br
N
H
Me
3j (100 MHz, CDCl3)
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.44
7.41
7.26
6.40
6.38
3.75
2.80
Me
3k (400 MHz, CDCl3)
1.92
1.96
0.95
3.00
f1 (ppm)


148.8
137.7
114.6
77.7
77.3
77.0
76.7
30.5
Me
3k (100 MHz, CDCl3)
f1 (ppm)


7.45
7.43
7.26
6.62
6.60
3.94
2.87
Me
F3C
3l (400 MHz, CDCl3)
1.94
1.98
1.07
3.00
f1 (ppm)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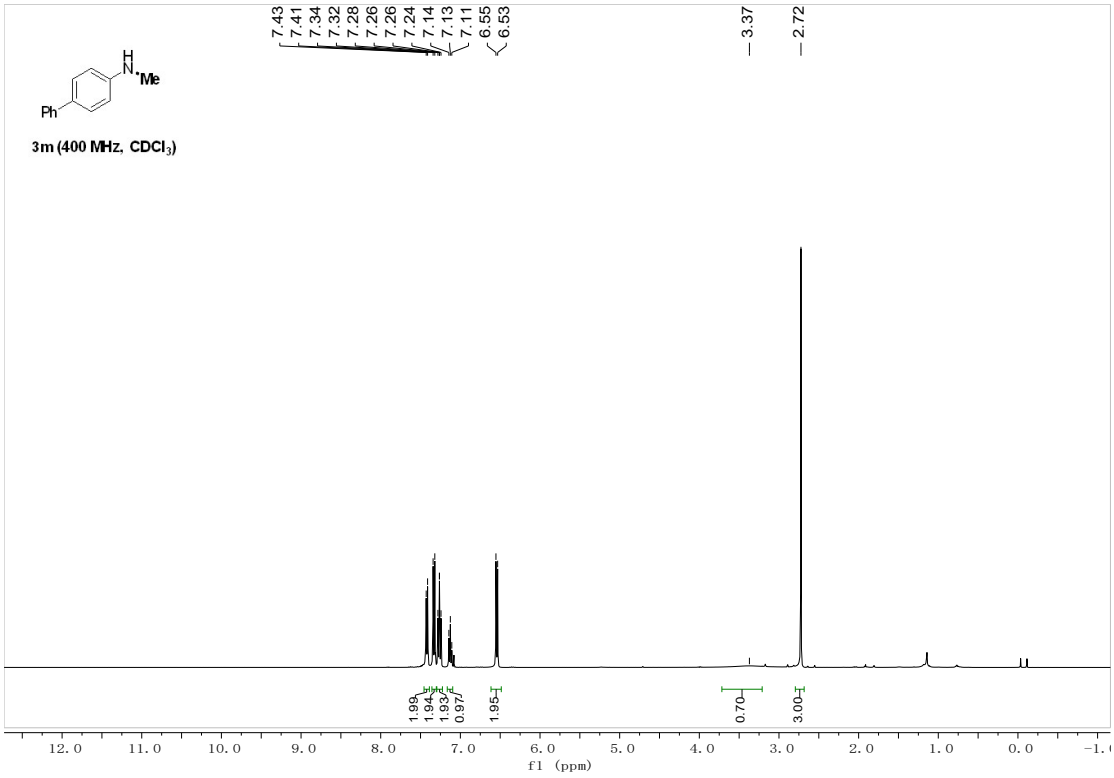
126.5
126.5
126.5
126.4
123.7
121.1
118.9
118.6
118.3
118.0
111.4
77.3
77.0
76.7
30.1
Me
F3C
3l (100 MHz, CDCl3)
f1 (ppm)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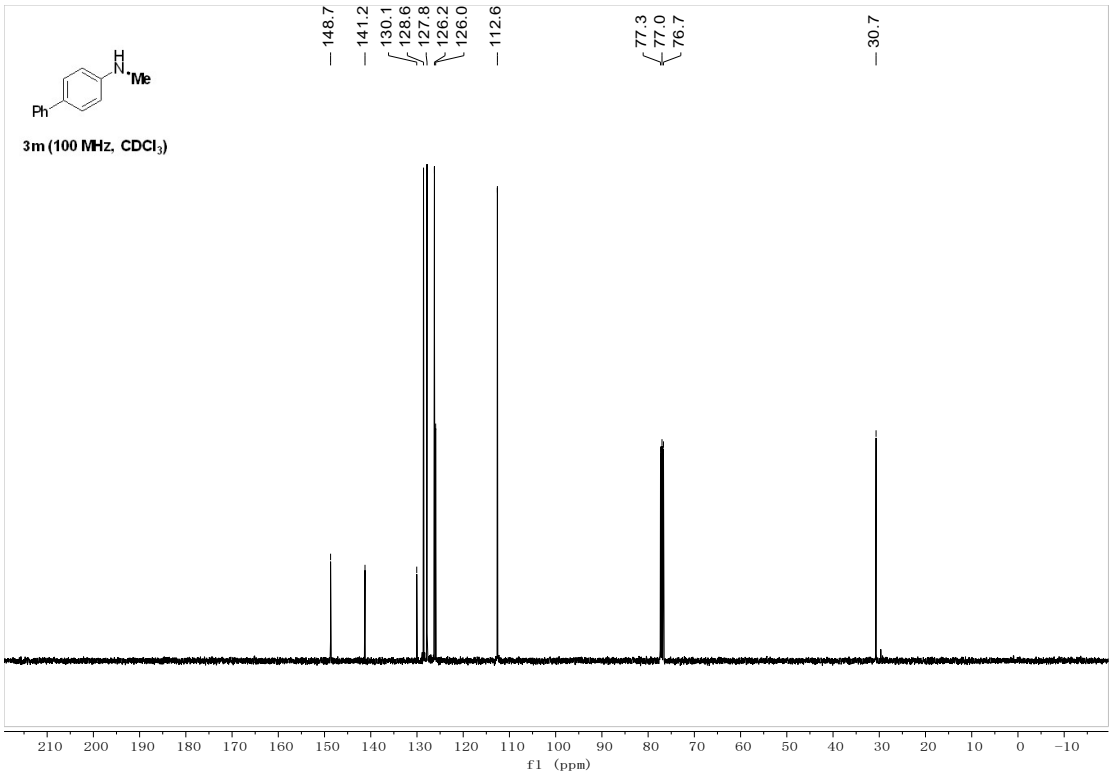
7.41
7.34
7.32
7.28
7.26
7.26
7.24
7.14
7.13
7.11
6.55
6.53
3.37
2.72
Ph
N
H
Me
3m (400 MHz, CDCl3)
1.99
1.94
1.93
0.97
1.95
0.70
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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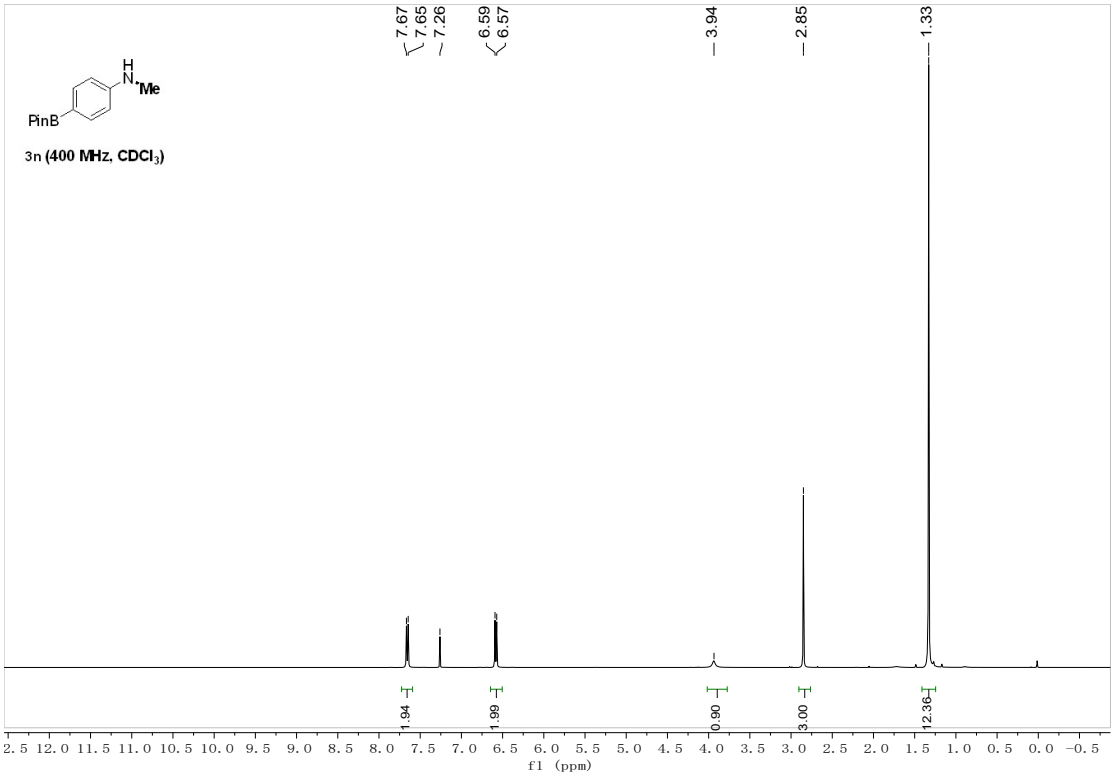
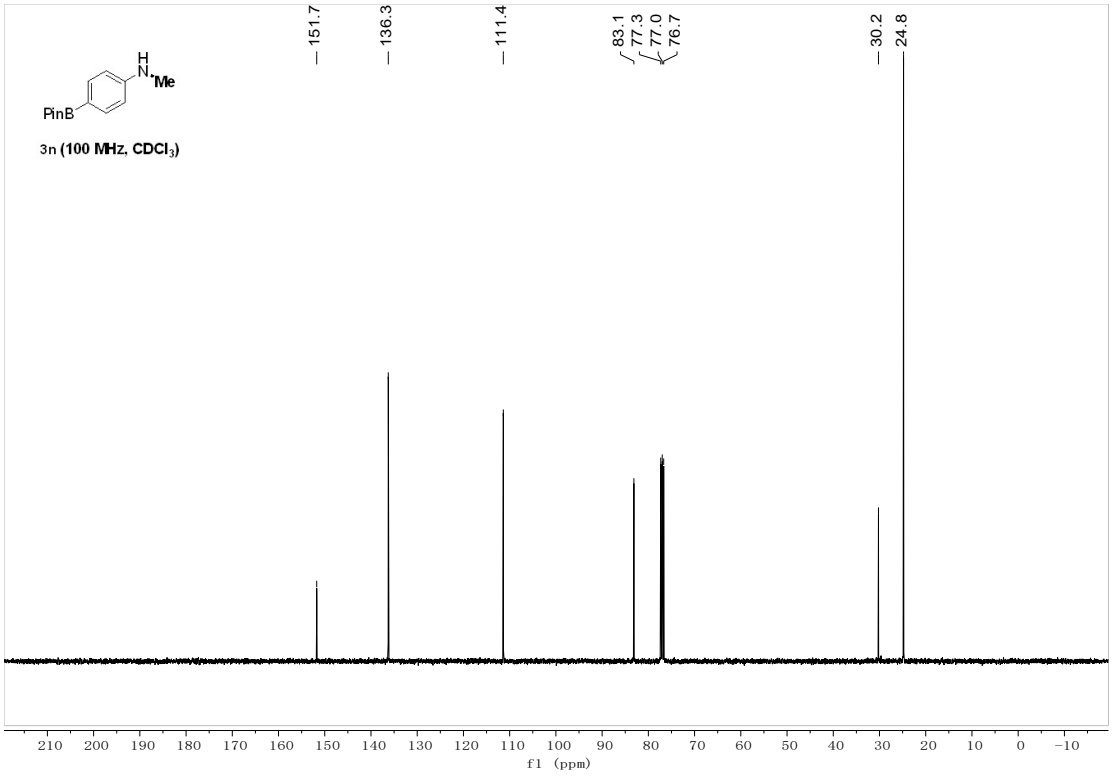
130.1
128.6
127.8
126.2
126.0
112.6
77.3
77.0
76.7
30.7
Ph
N
H
Me
3m (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.67
7.65
7.26
6.59
6.57
3.94
2.85
1.33
H
N
Me
PinB
3n (400 MHz, CDCl3)
1.94
1.99
0.90
3.00
12.36
f1 (ppm)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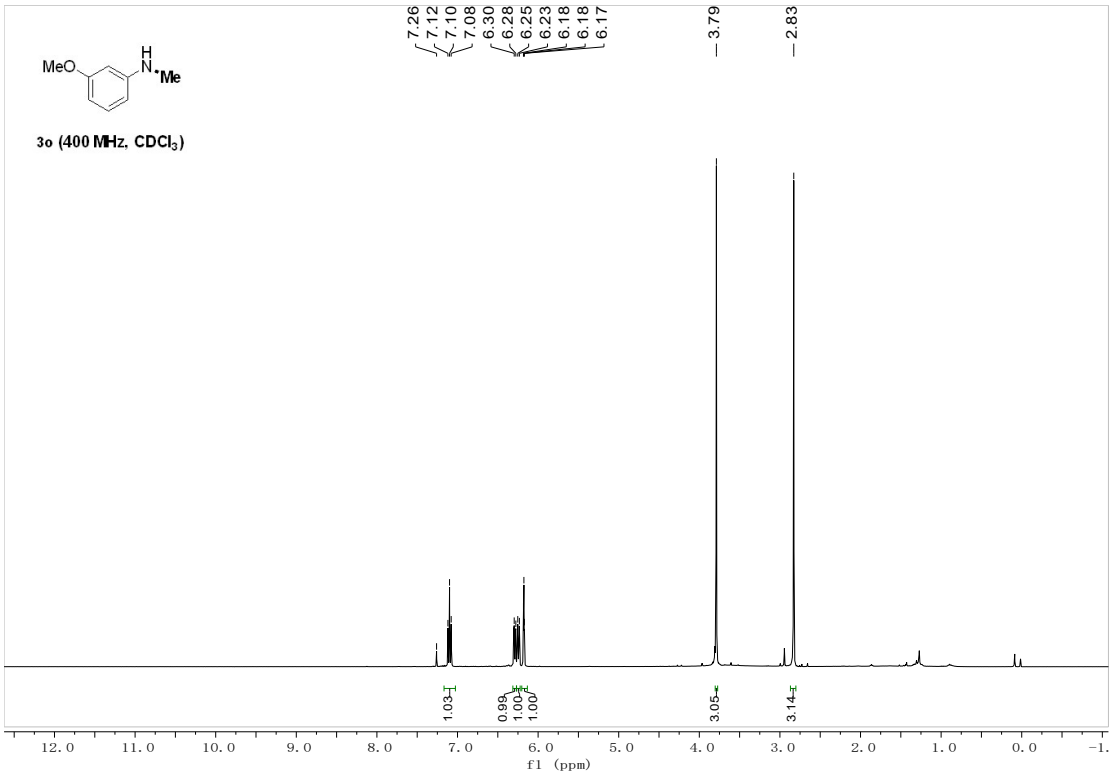
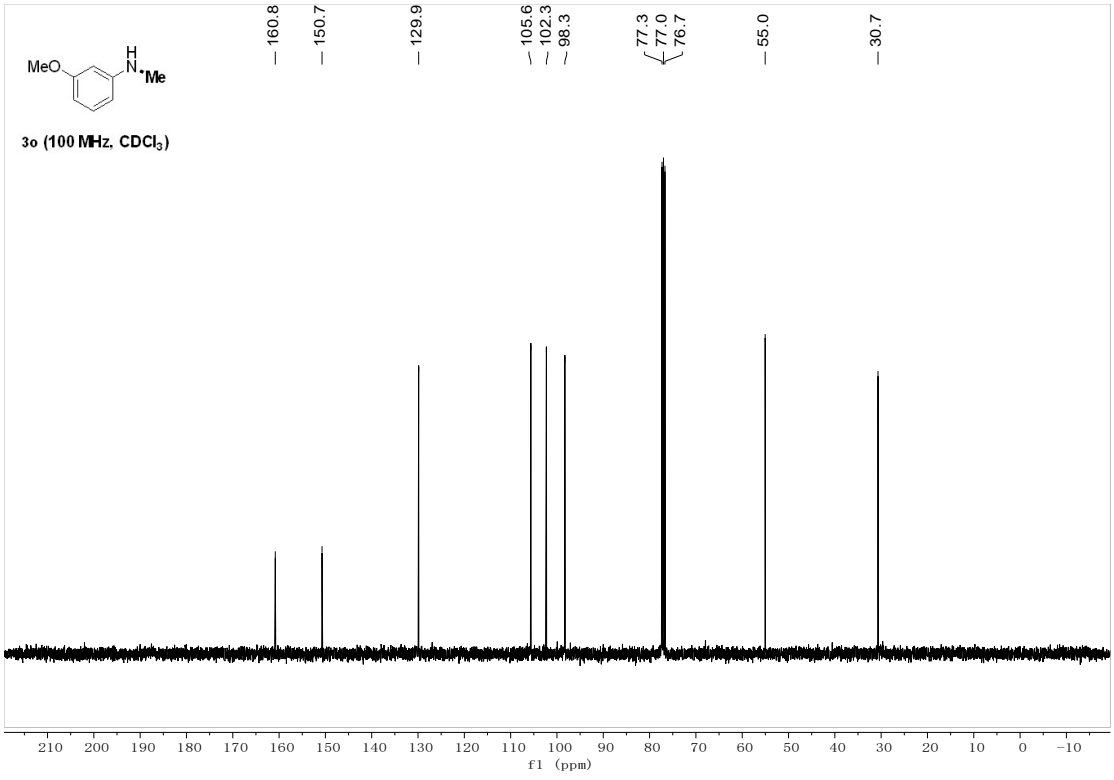
136.3
111.4
83.1
77.3
77.0
76.7
30.2
24.8
H
N
Me
PinB
3n (100 MHz, CDCl3)
f1 (ppm)


7.26
7.12
7.10
7.08
6.30
6.28
6.25
6.23
6.18
6.18
6.17
3.79
2.83
MeO
H
N
Me
3o (400 MHz, CDCl3)
1.03
0.99
1.00
1.00
3.05
3.14
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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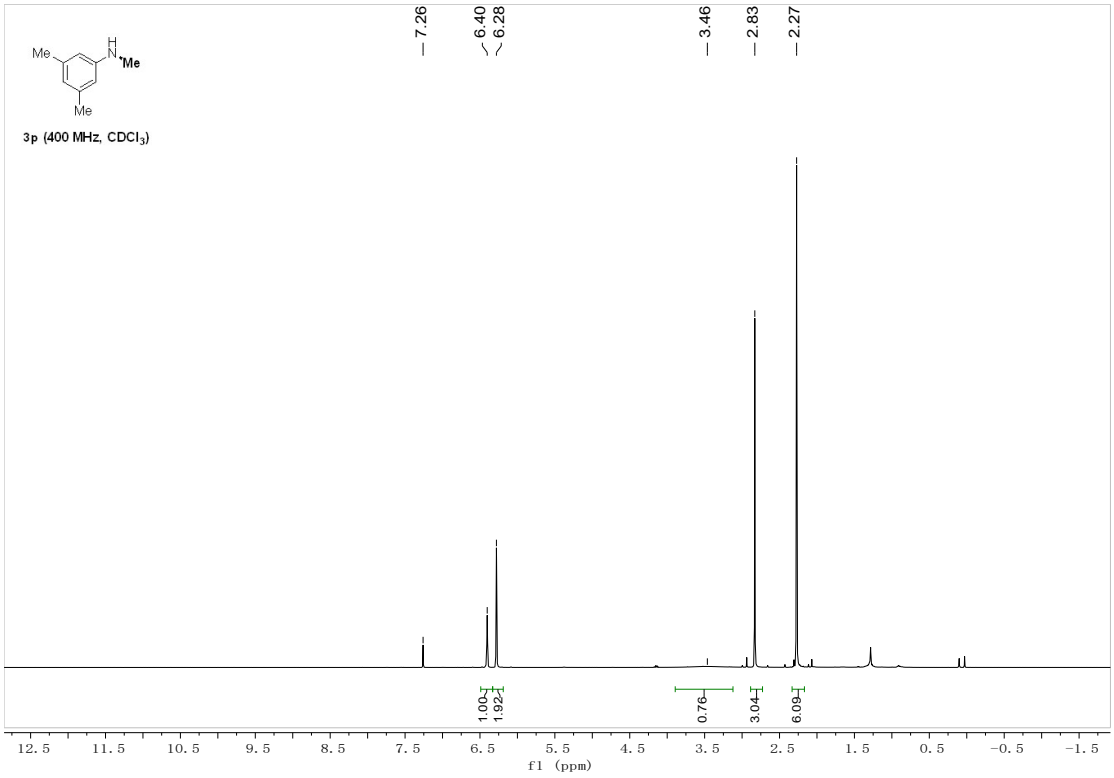
105.6
102.3
98.3
77.3
77.0
76.7
55.0
30.7
MeO
H
N
Me
3o (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.26
6.40
6.28
3.46
2.83
2.27
Me
N
H
Me
Me
3p (400 MHz, CDCl3)
1.00
1.92
0.76
3.04
6.09
12.5
11.5
10.5
9.5
8.5
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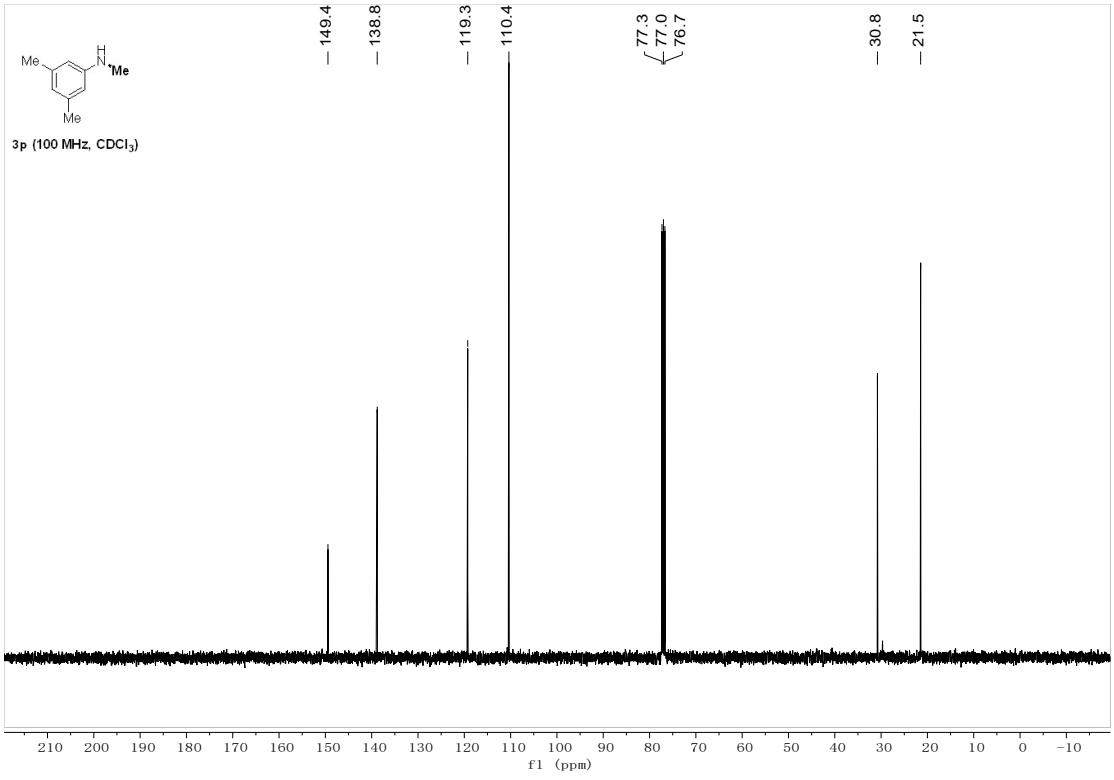
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
−1.5
f1 (ppm)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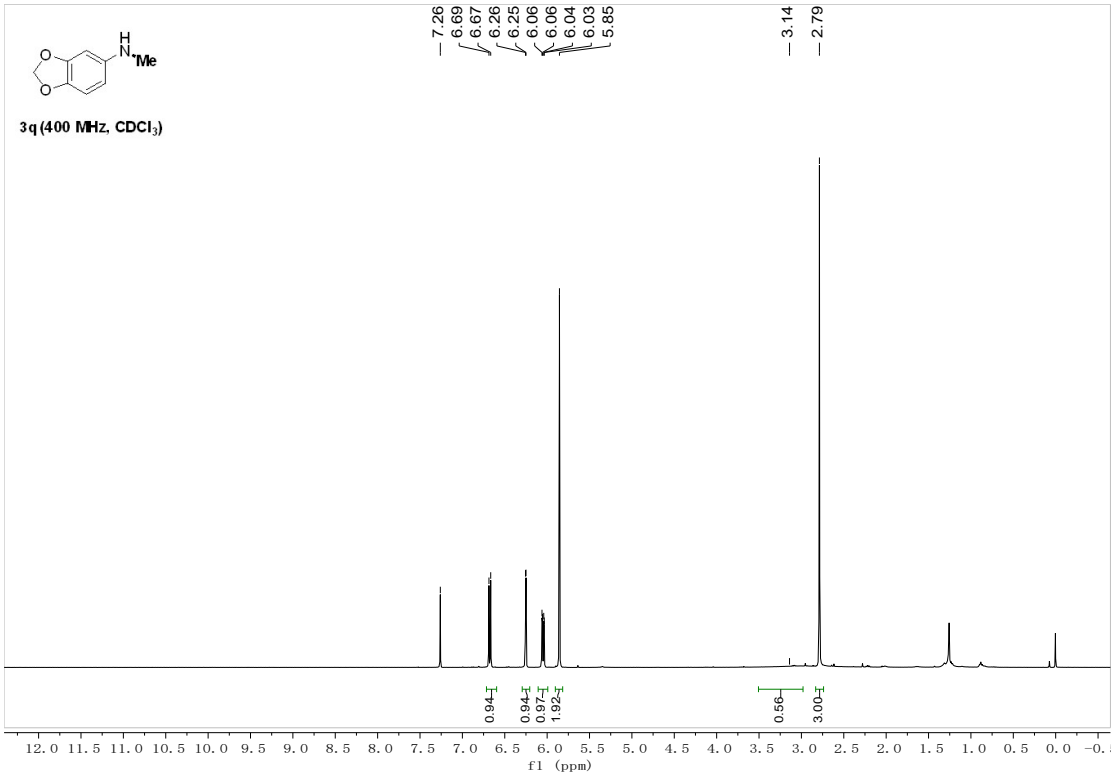
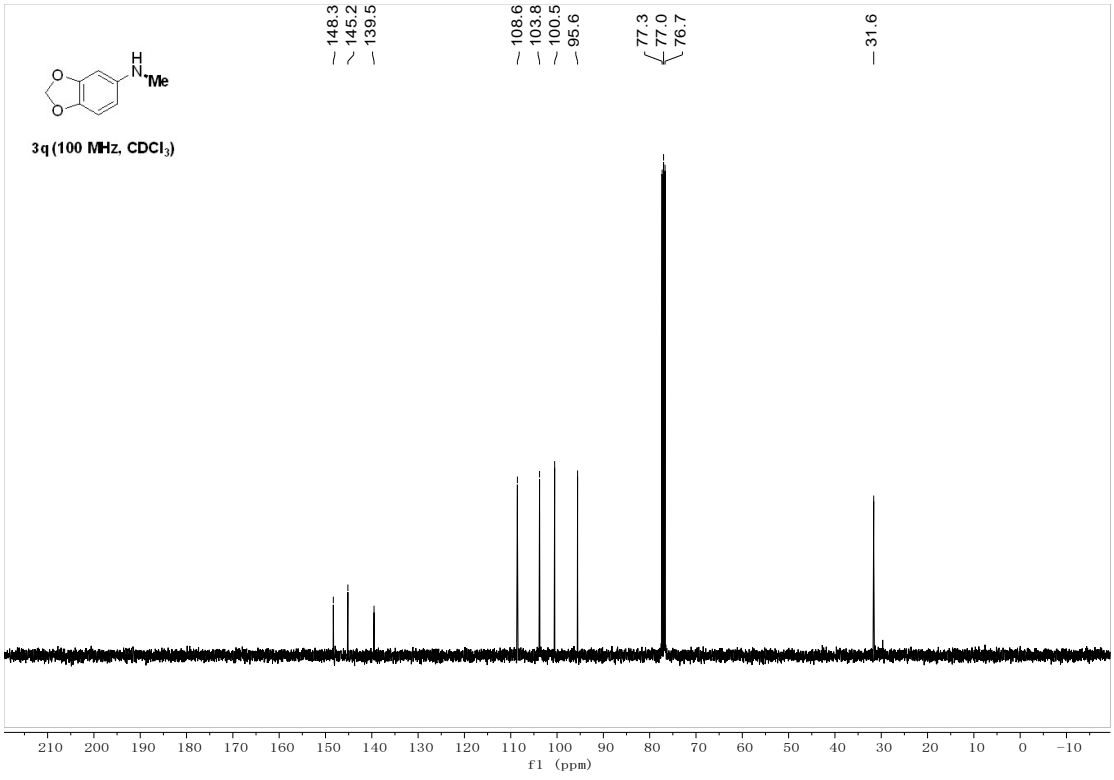
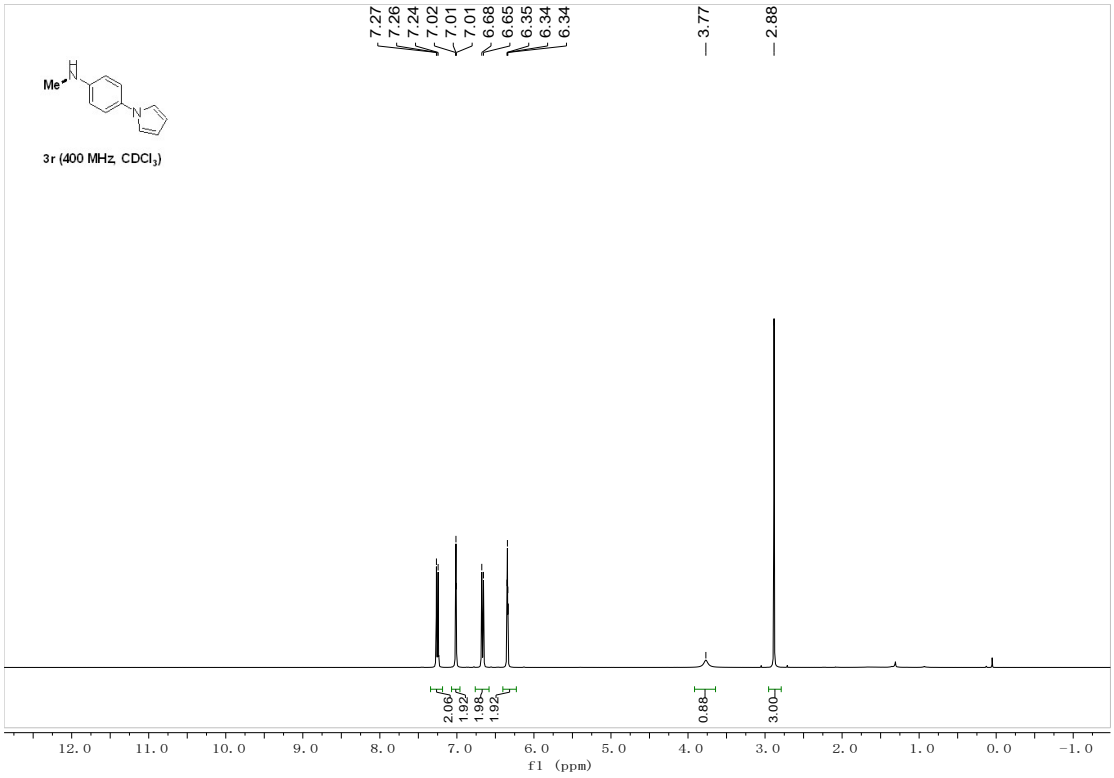
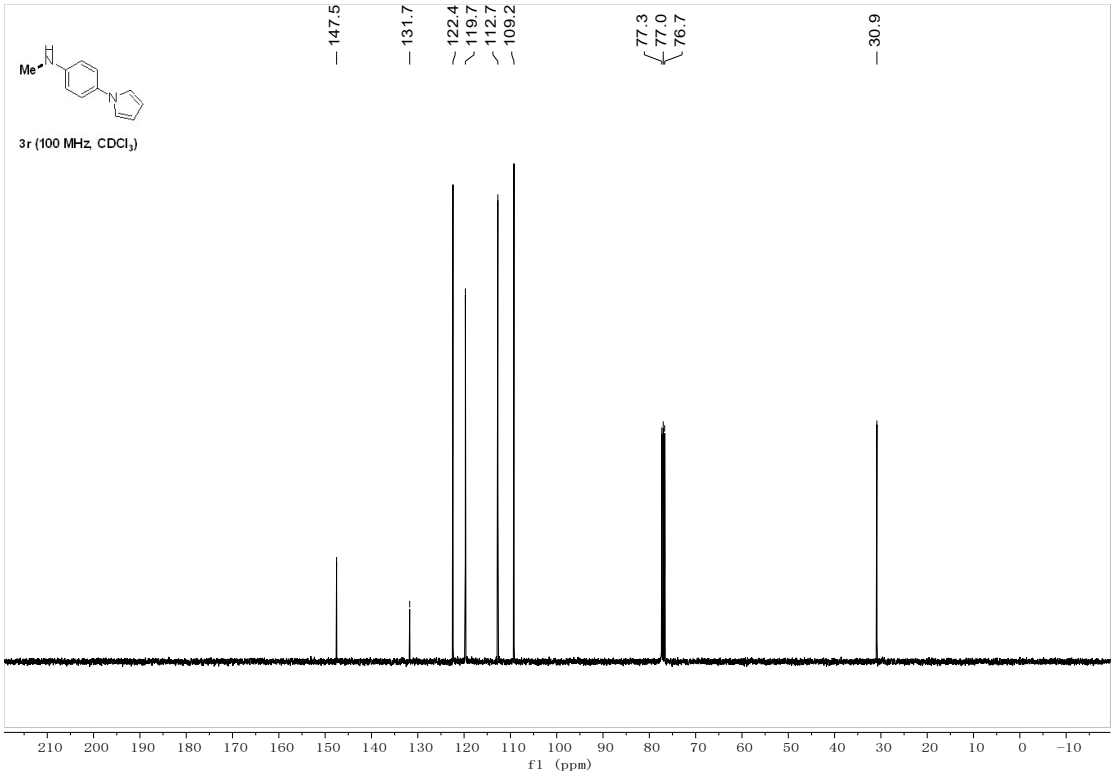
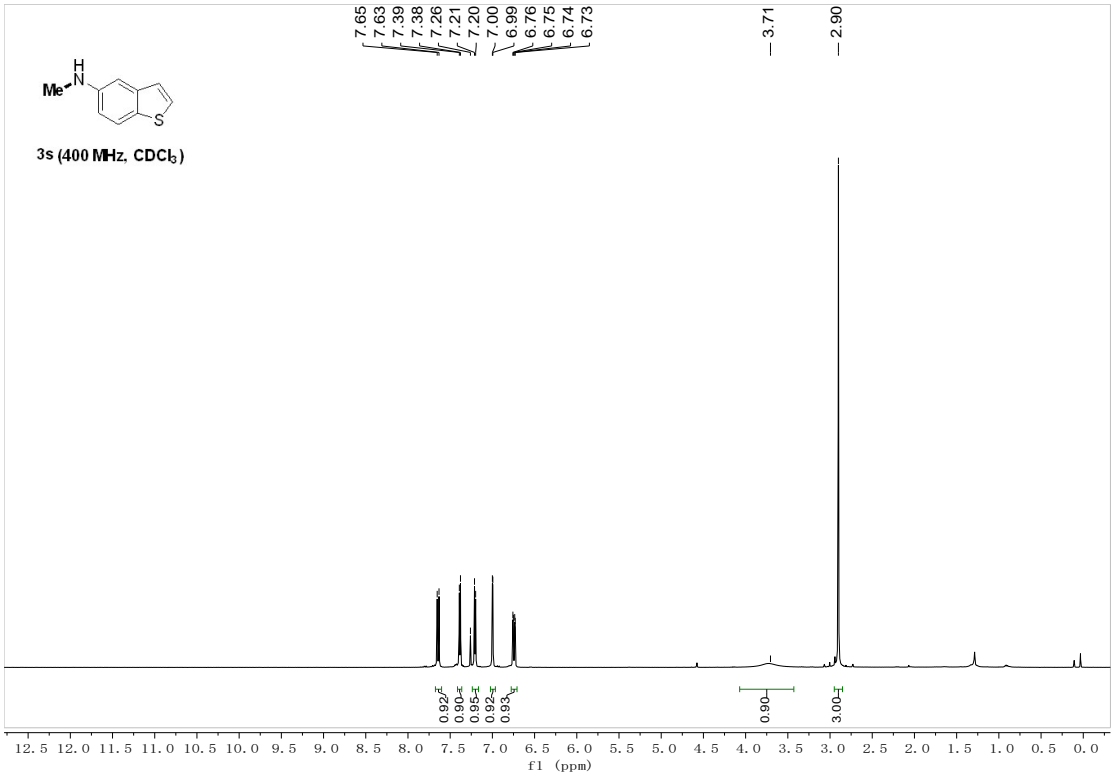
119.3
110.4
77.3
77.0
76.7
30.8
21.5
Me
N
H
Me
Me
3p (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

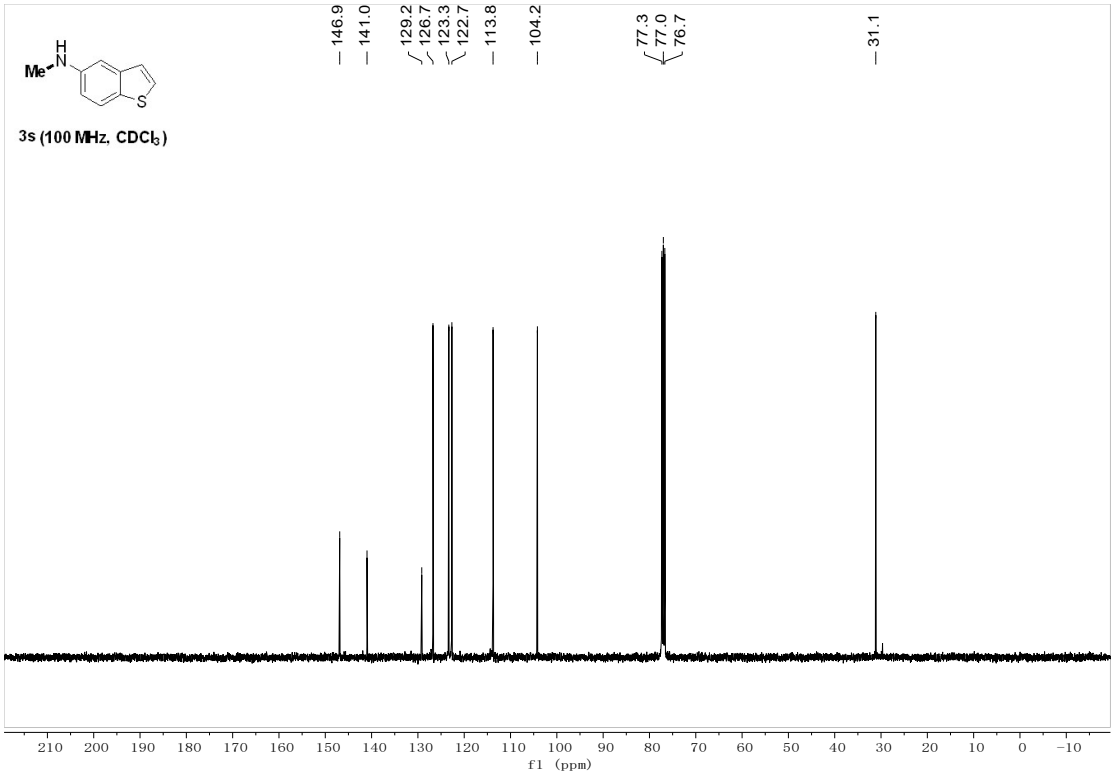

7.26
6.69
6.67
6.26
6.25
6.06
6.06
6.04
6.03
5.85
3.14
2.79
3q (400 MHz, CDCl3)
0.94
0.94
0.97
1.92
0.56
3.00
f1 (ppm)

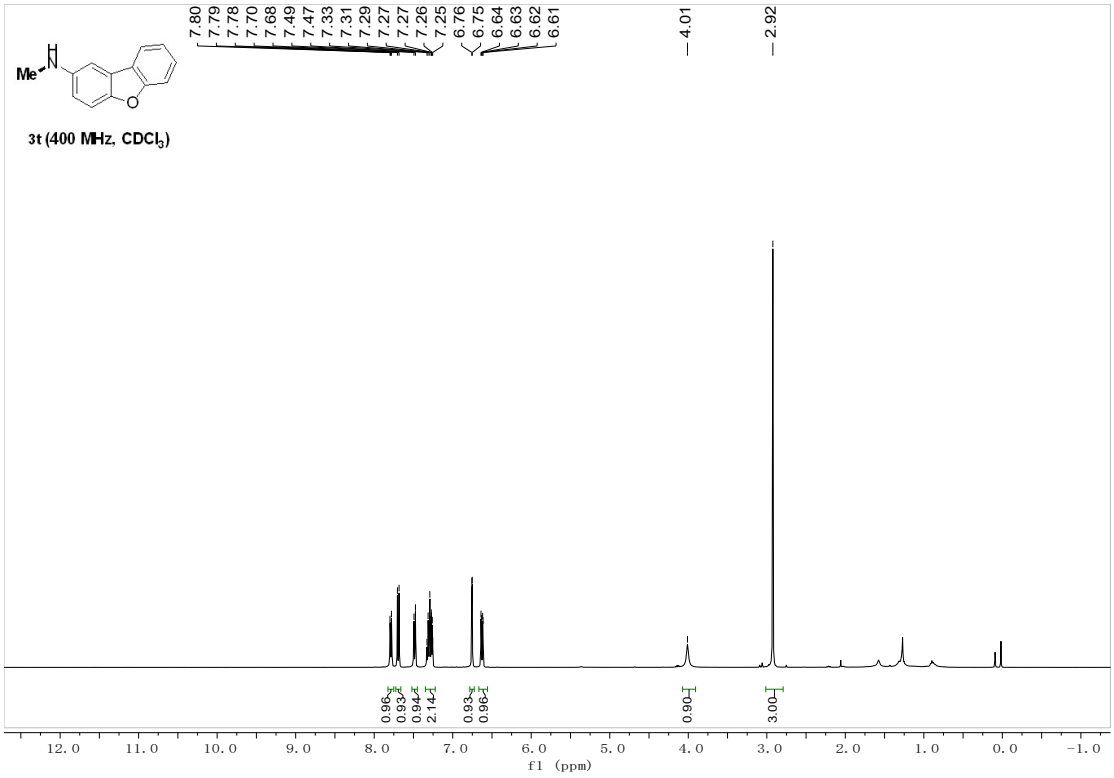

148.3
145.2
139.5
108.6
103.8
100.5
95.6
77.3
77.0
76.7
31.6
3q (100 MHz, CDCl3)
f1 (ppm)

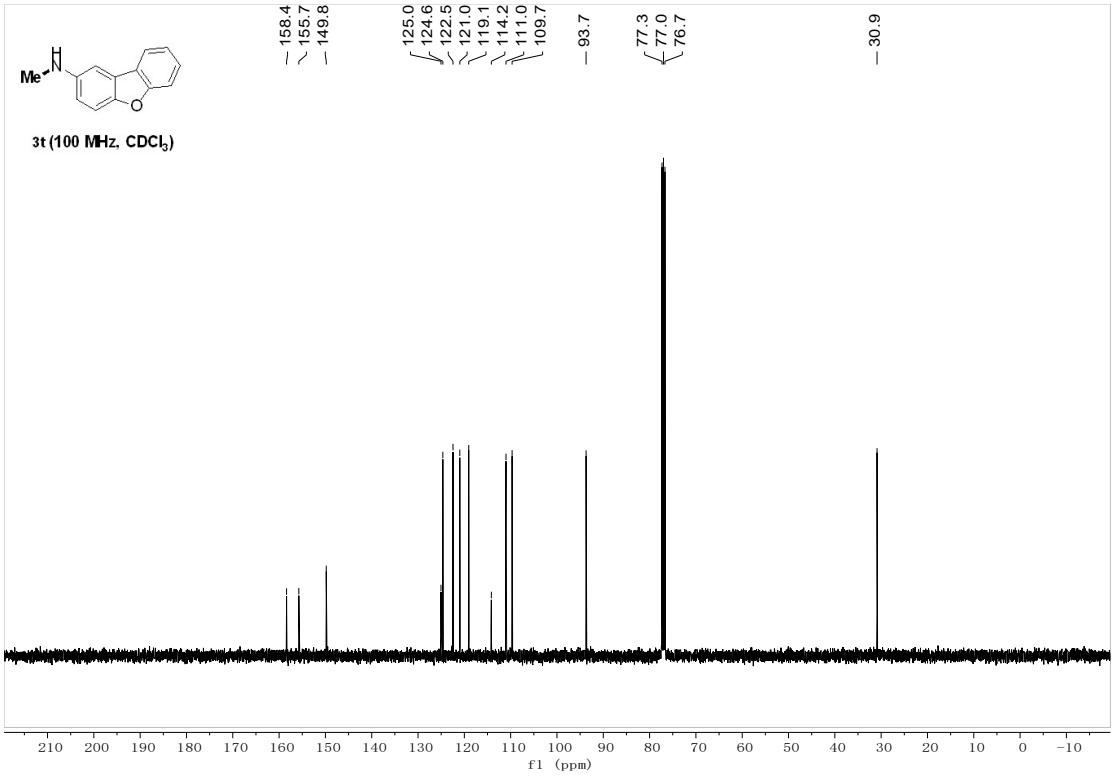

7.27
7.26
7.24
7.02
7.01
7.01
6.68
6.65
6.35
6.34
6.34
3.77
2.88
Me
N
H
N
3r (400 MHz, CDCl3)
2.06
1.92
1.98
1.92
0.88
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

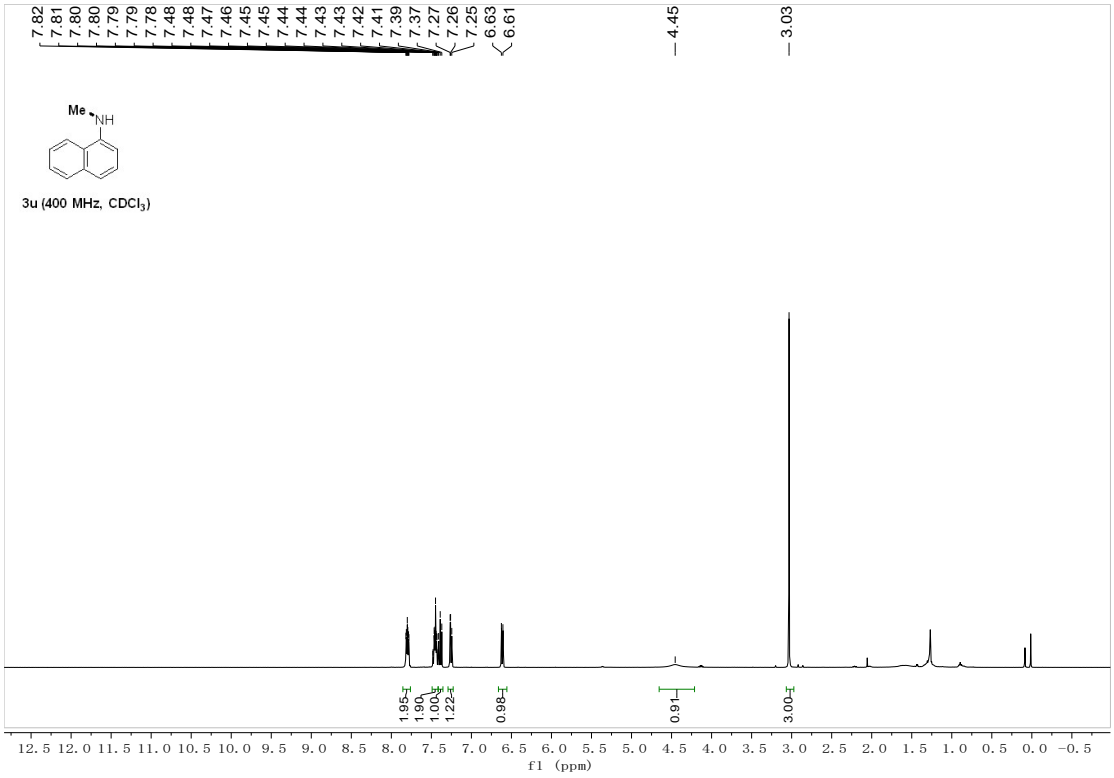

147.5
131.7
122.4
119.7
112.7
109.2
77.3
77.0
76.7
30.9
Me
N
H
N
3r (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

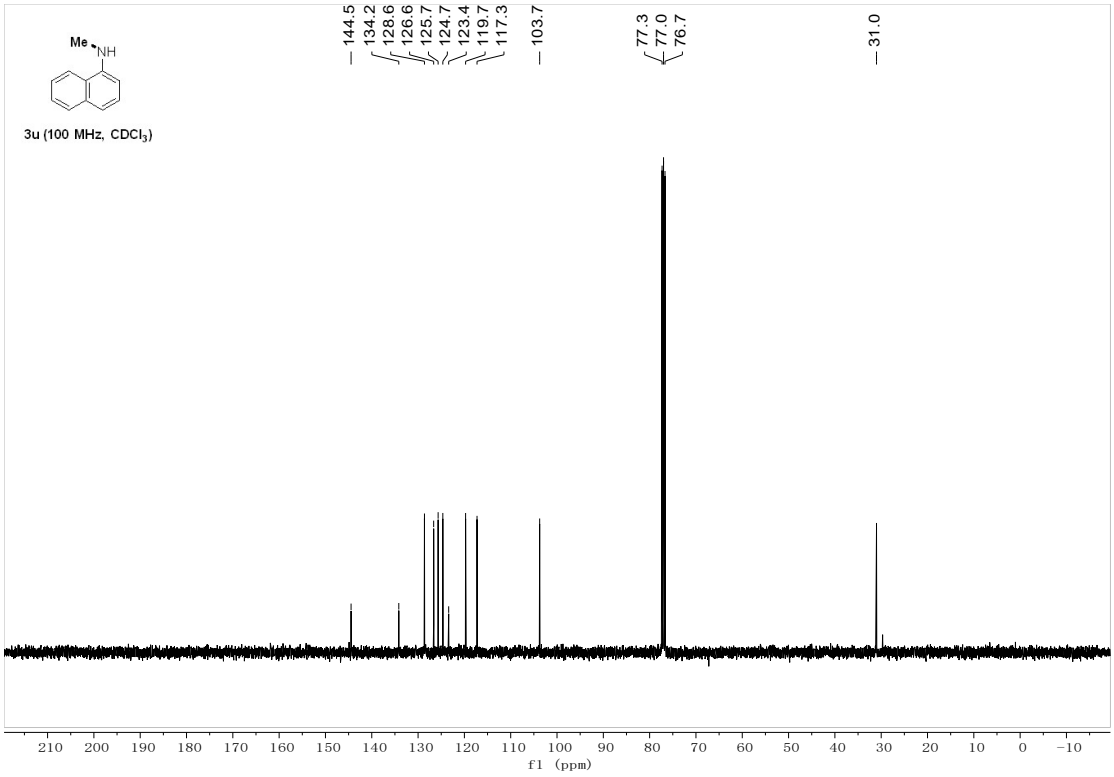

7.65
7.63
7.39
7.38
7.26
7.21
7.20
7.00
6.99
6.76
6.75
6.74
6.73
3.71
2.90
Me
H
N
S
3s (400 MHz, CDCl3)
0.92
0.90
0.95
0.92
0.93
0.90
3.00
f1 (ppm)

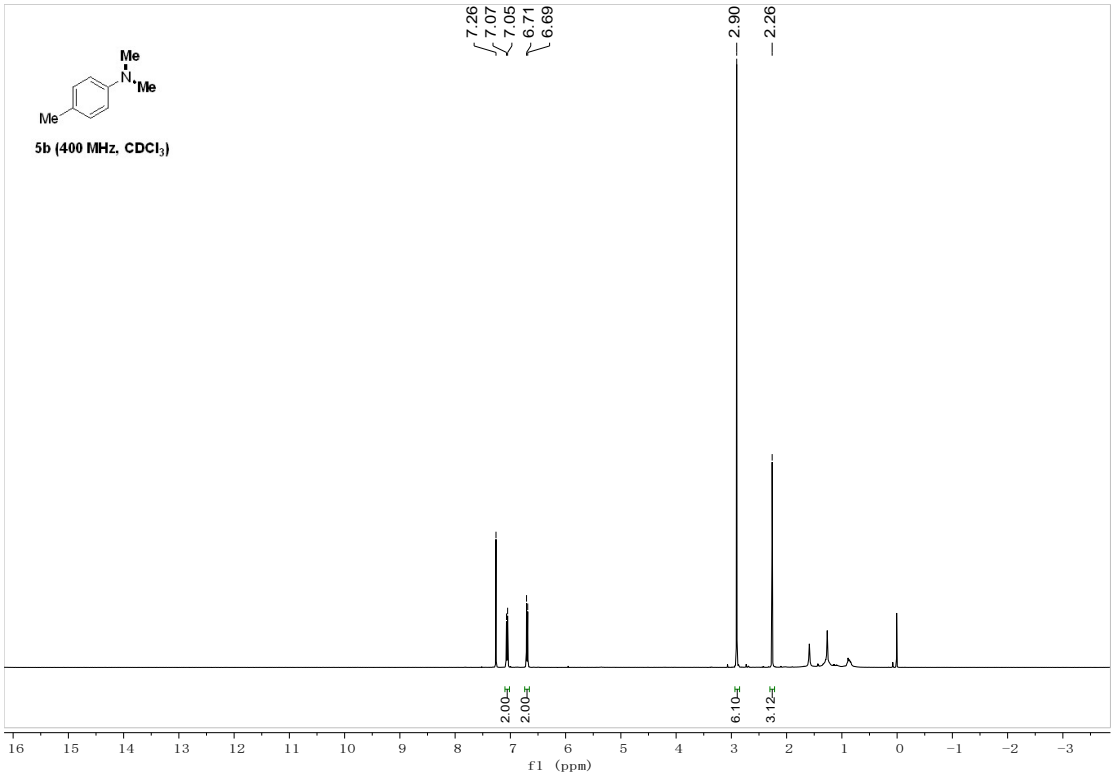

146.9
141.0
129.2
126.7
123.3
122.7
113.8
104.2
77.3
77.0
76.7
31.1
Me
H
N
S
3s (100 MHz, CDCl3)
f1 (ppm)

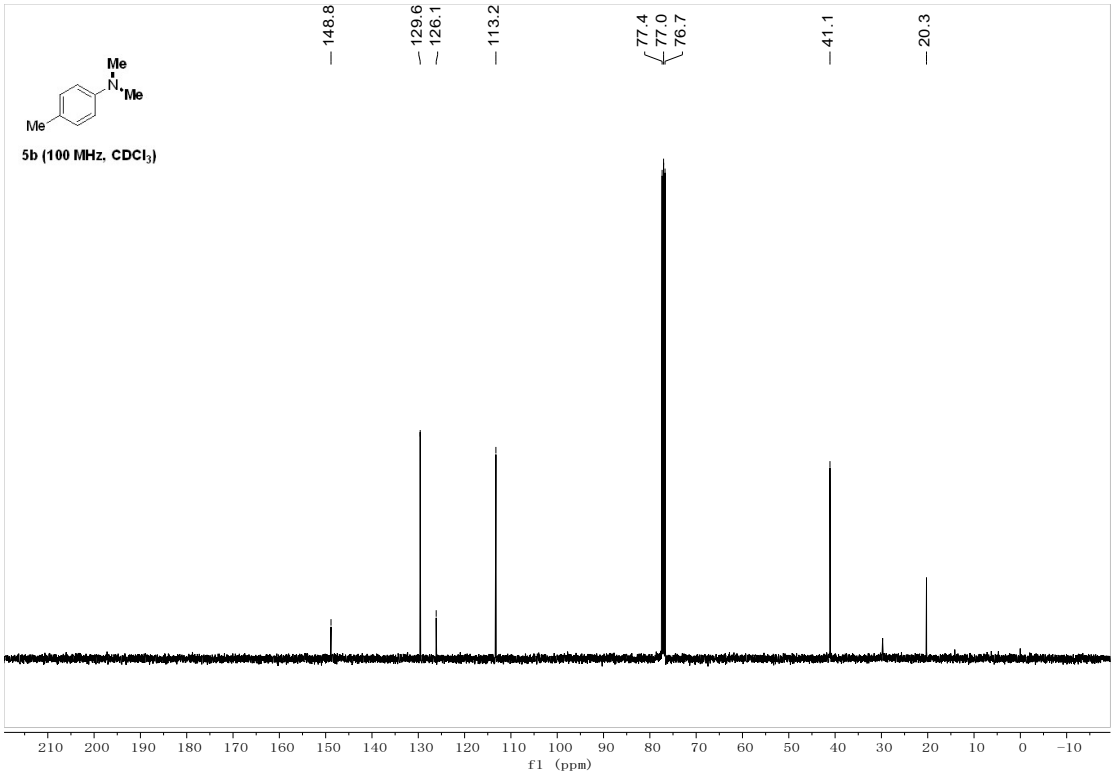

7.80
7.79
7.78
7.70
7.68
7.49
7.47
7.33
7.31
7.29
7.27
7.27
7.26
7.25
6.76
6.75
6.64
6.63
6.62
6.61
4.01
2.92
Me
N
H
O
3t (400 MHz, CDCl3)
0.96
0.93
0.94
2.14
0.93
0.96
0.90
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.0
f1 (ppm)

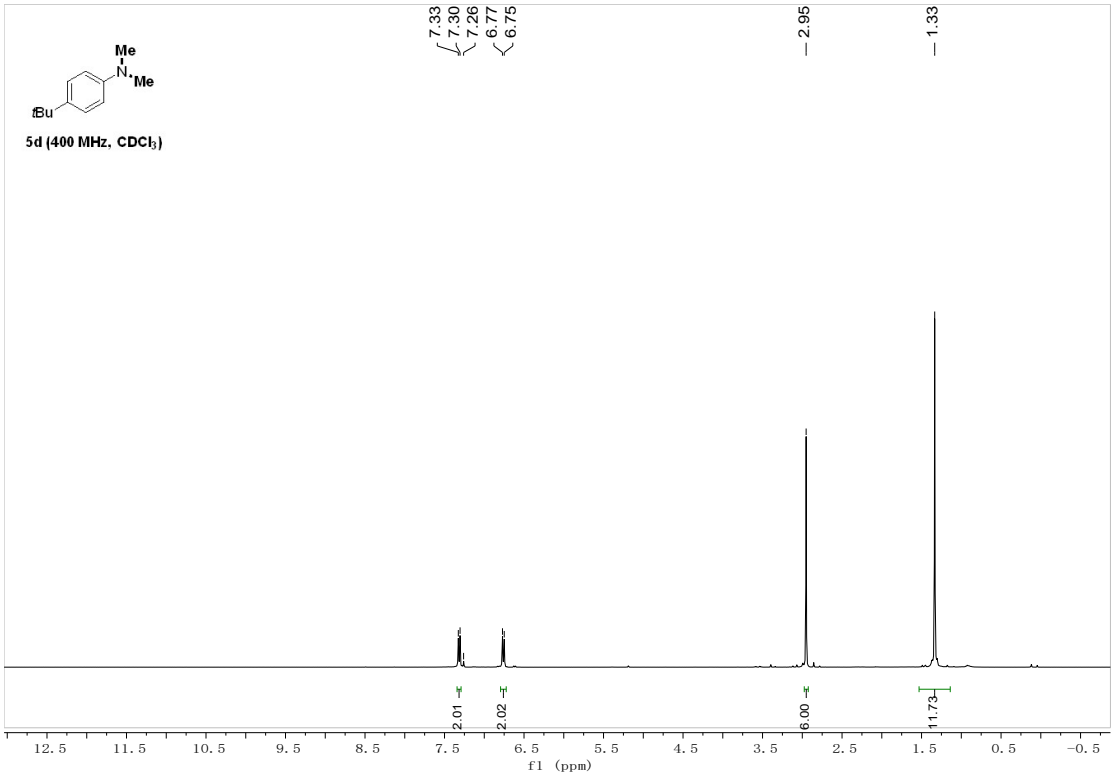

158.4
155.7
149.8
125.0
124.6
122.5
121.0
119.1
114.2
111.0
109.7
93.7
77.3
77.0
76.7
30.9
Me
N
H
O
3t (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

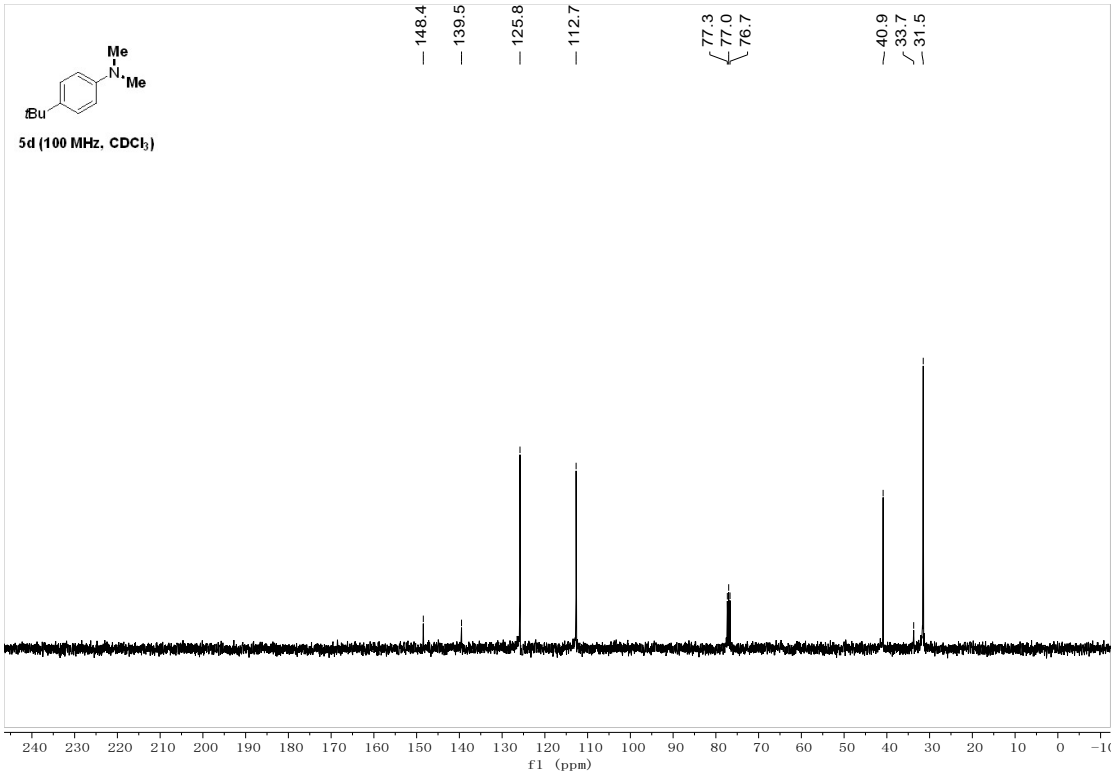

7.82
7.81
7.80
7.80
7.79
7.79
7.78
7.48
7.48
7.47
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.41
7.39
7.37
7.27
7.26
7.25
6.63
6.61
4.45
3.03
Me
NH
3u (400 MHz, CDCl3)
1.95
1.90
1.00
1.22
0.98
0.91
3.00
f1 (ppm)

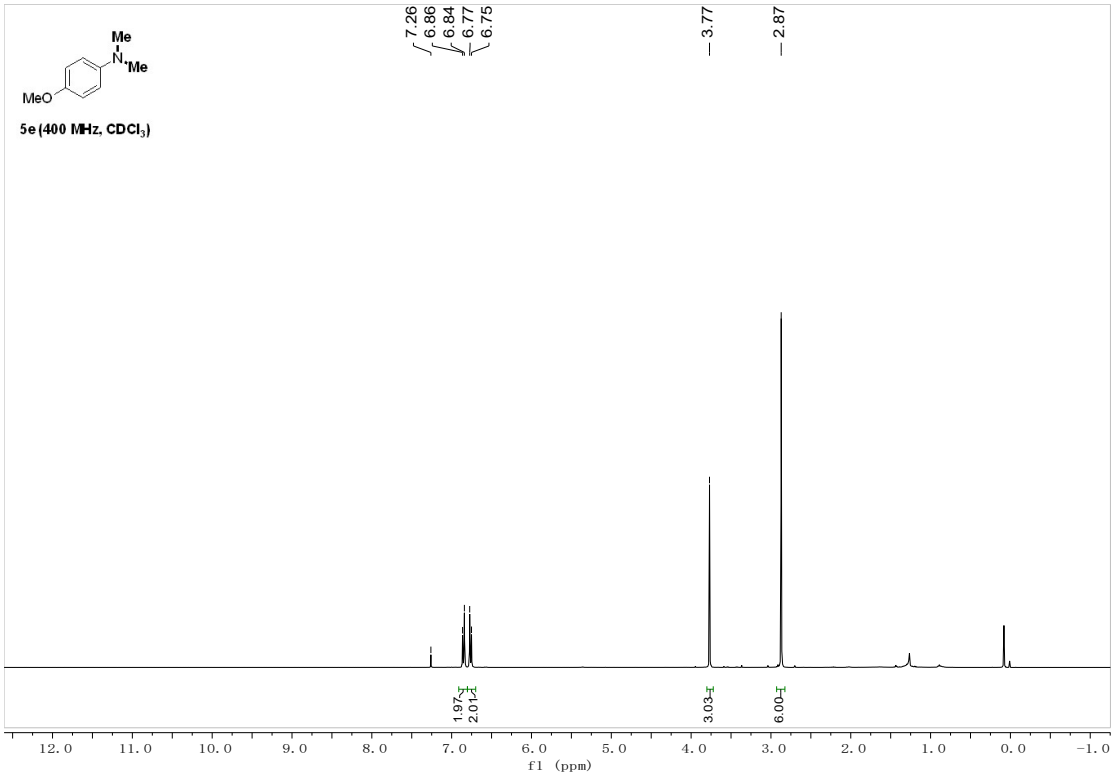

144.5
134.2
128.6
126.6
125.7
124.7
123.4
119.7
117.3
103.7
77.3
77.0
76.7
31.0
Me
NH
3u (100 MHz, CDCl3)
f1 (ppm)

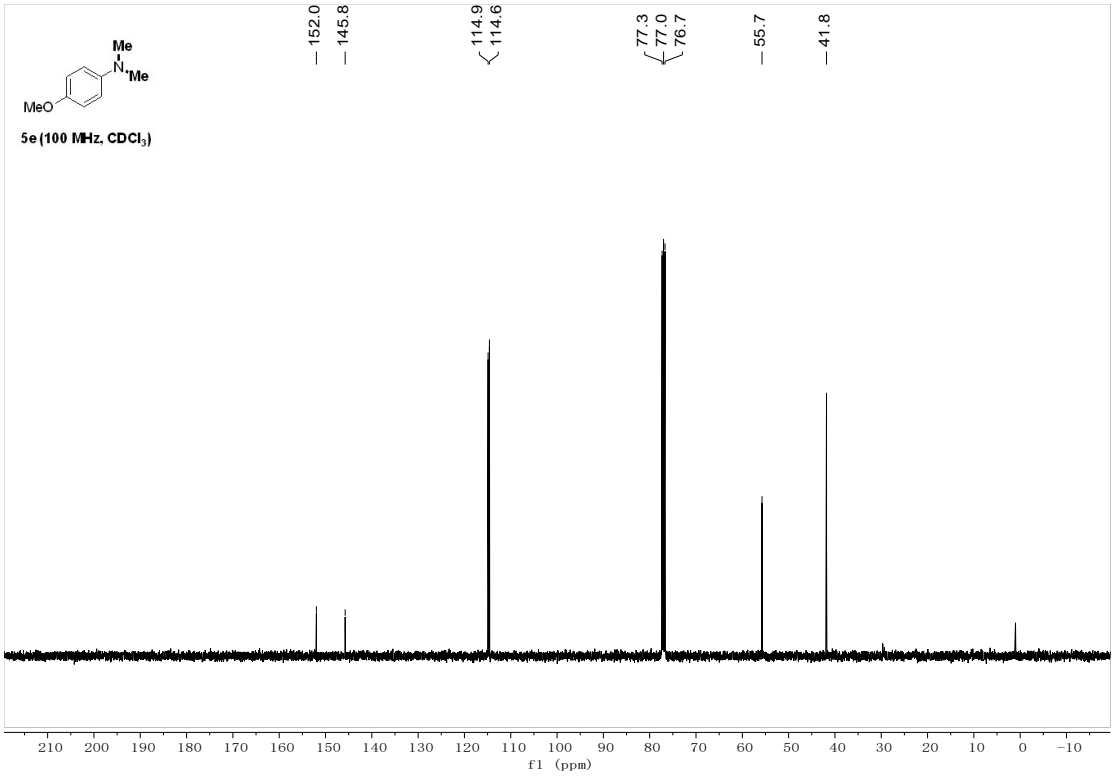

7.26
7.07
7.05
6.71
6.69
2.90
2.26
Me
N
Me
Me
5b (400 MHz, CDCl3)
2.00
2.00
6.10
3.12
f1 (ppm)

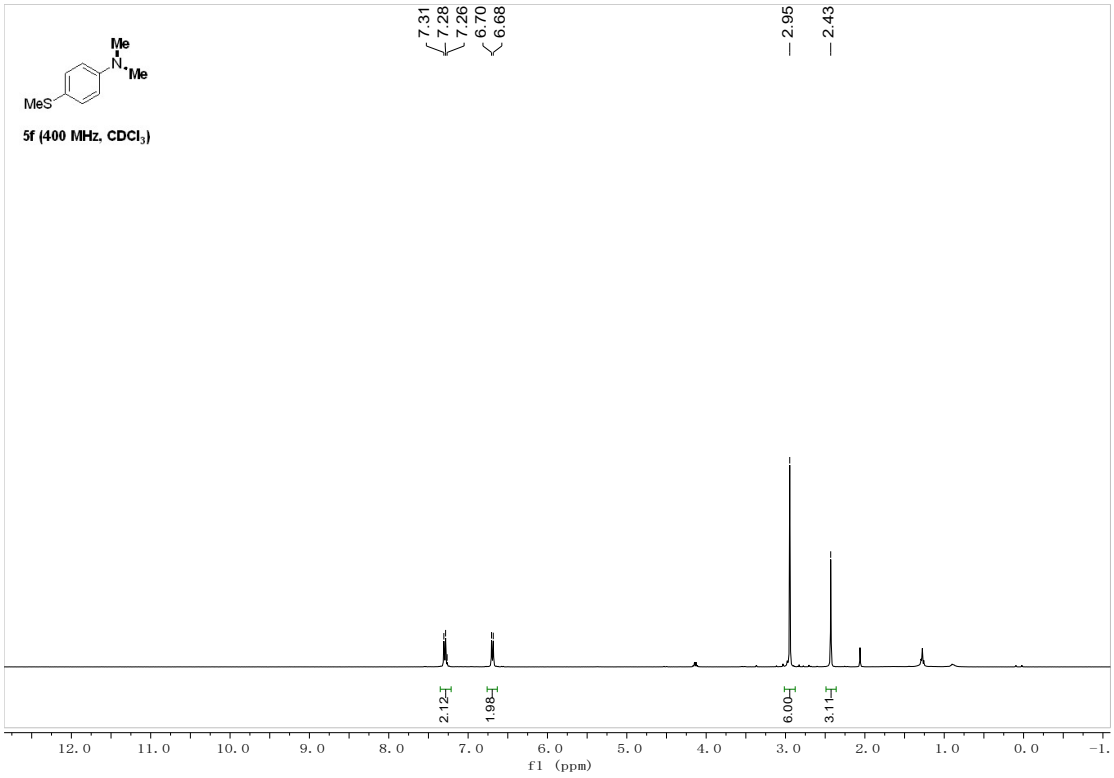

148.8
129.6
126.1
113.2
77.4
77.0
76.7
41.1
20.3
Me
N
Me
Me
5b (100 MHz, CDCl3)
f1 (ppm)

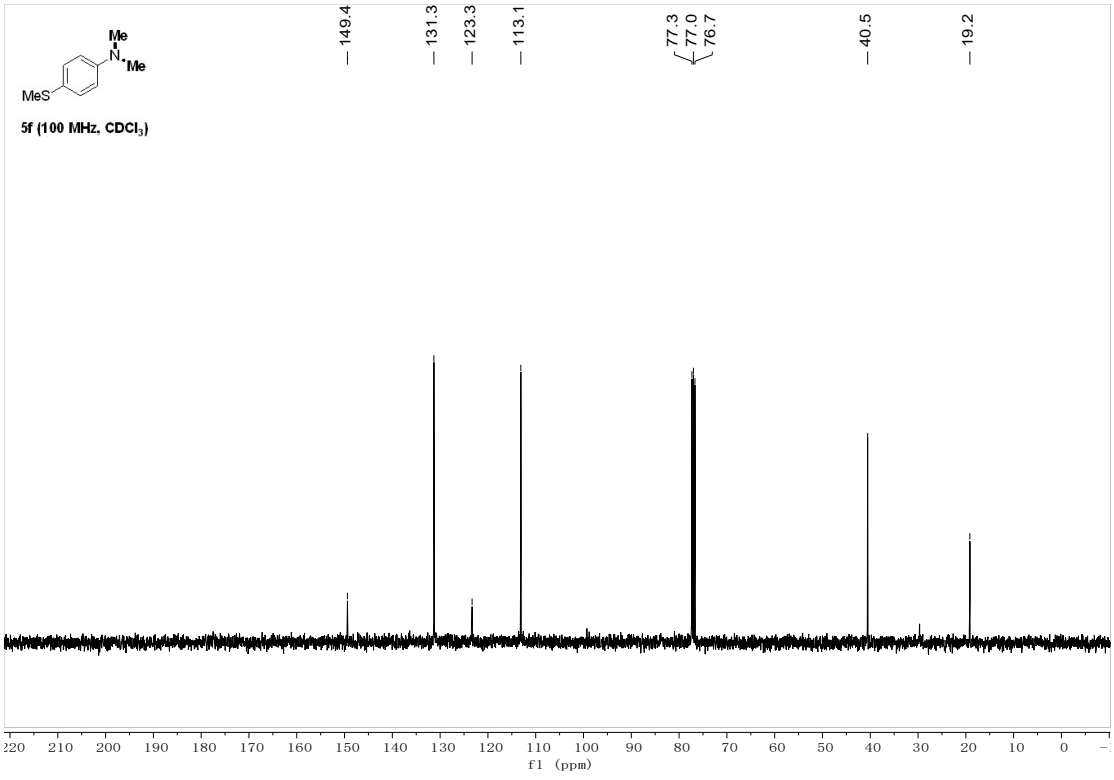

7.33
7.30
7.26
6.77
6.75
2.95
1.33
Me
N
Me
tBu
5d (400 MHz, CDCl3)
2.01
2.02
6.00
11.73
f1 (ppm)

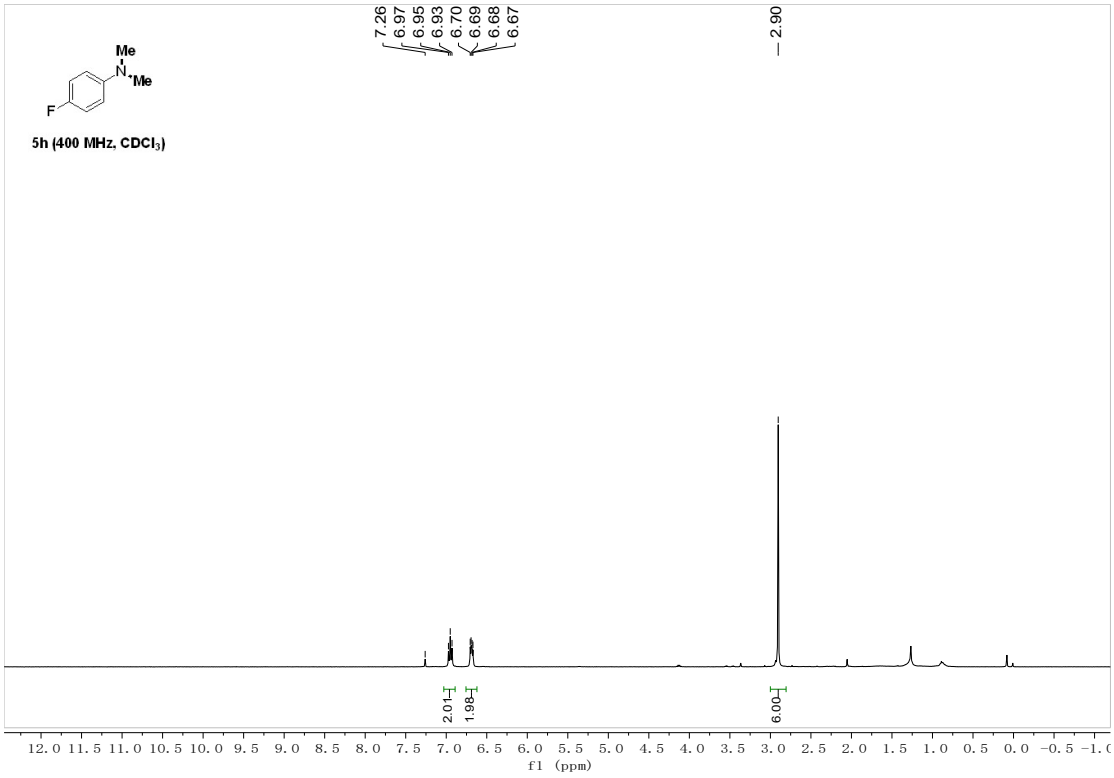

148.4
139.5
125.8
112.7
77.3
77.0
76.7
40.9
33.7
31.5
Me
N
Me
tBu
5d (100 MHz, CDCl3)
f1 (ppm)

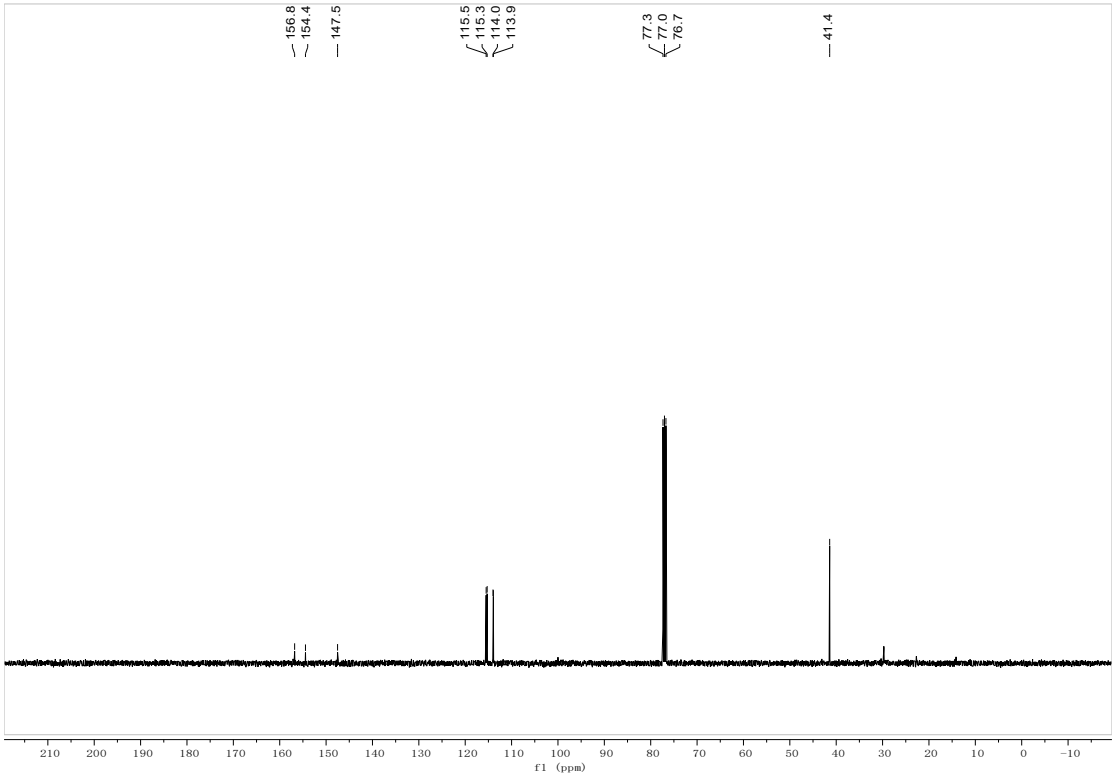

Me
N
Me
MeO
5e (400 MHz, CDCl3)
7.26
6.86
6.84
6.77
6.75
3.77
2.87
1.97
2.01
3.03
6.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.0
f1 (ppm)

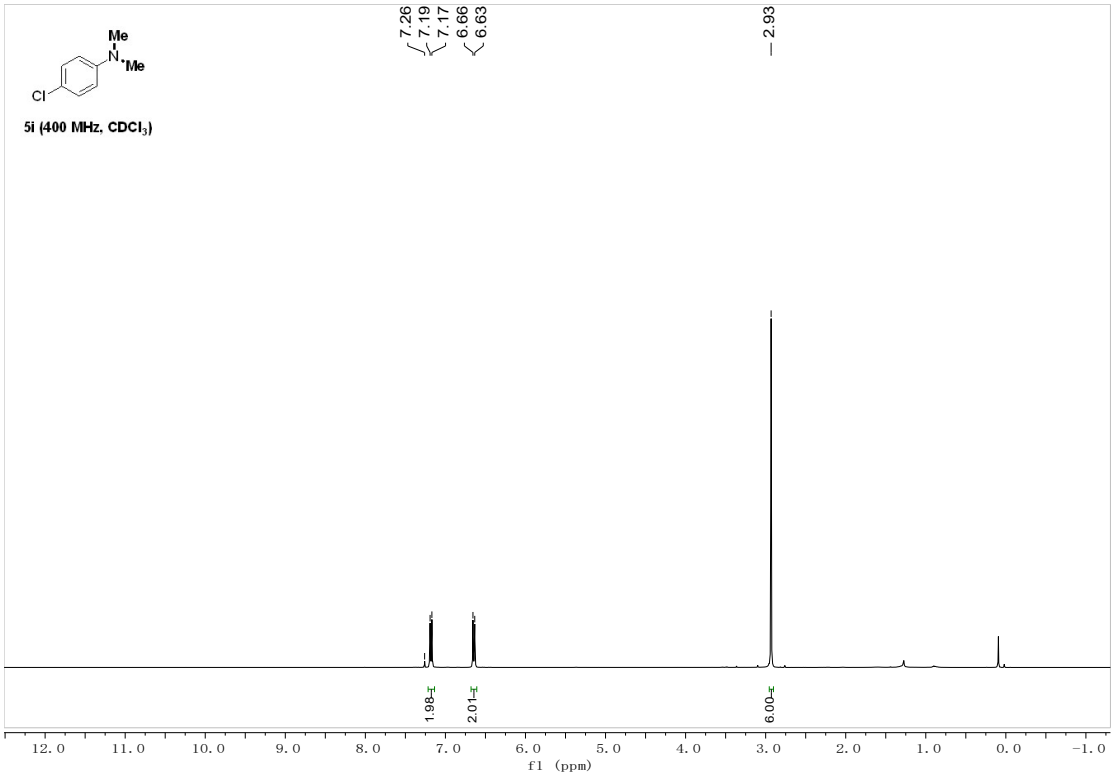

Me
N
Me
MeO
5e (100 MHz, CDCl3)
152.0
145.8
114.9
114.6
77.3
77.0
76.7
55.7
41.8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

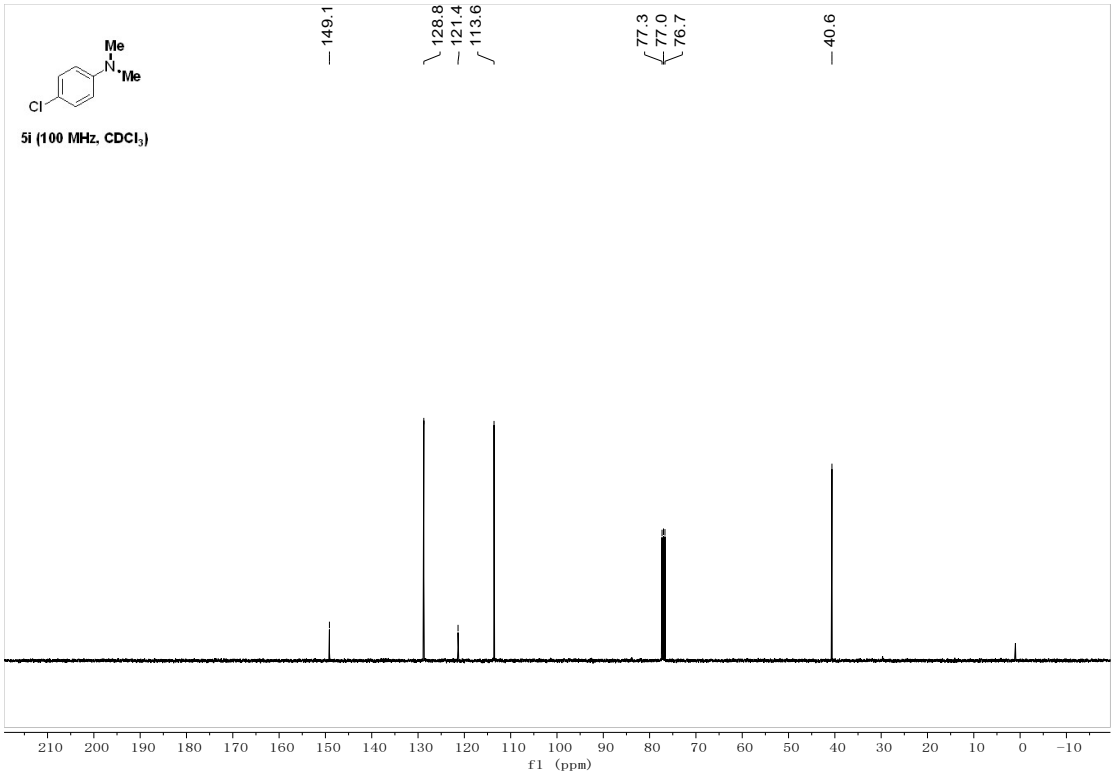

Me
N
Me
MeS
5f (400 MHz, CDCl3)
7.31
7.28
7.26
6.70
6.68
2.95
2.43
2.12
1.98
6.00
3.11
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

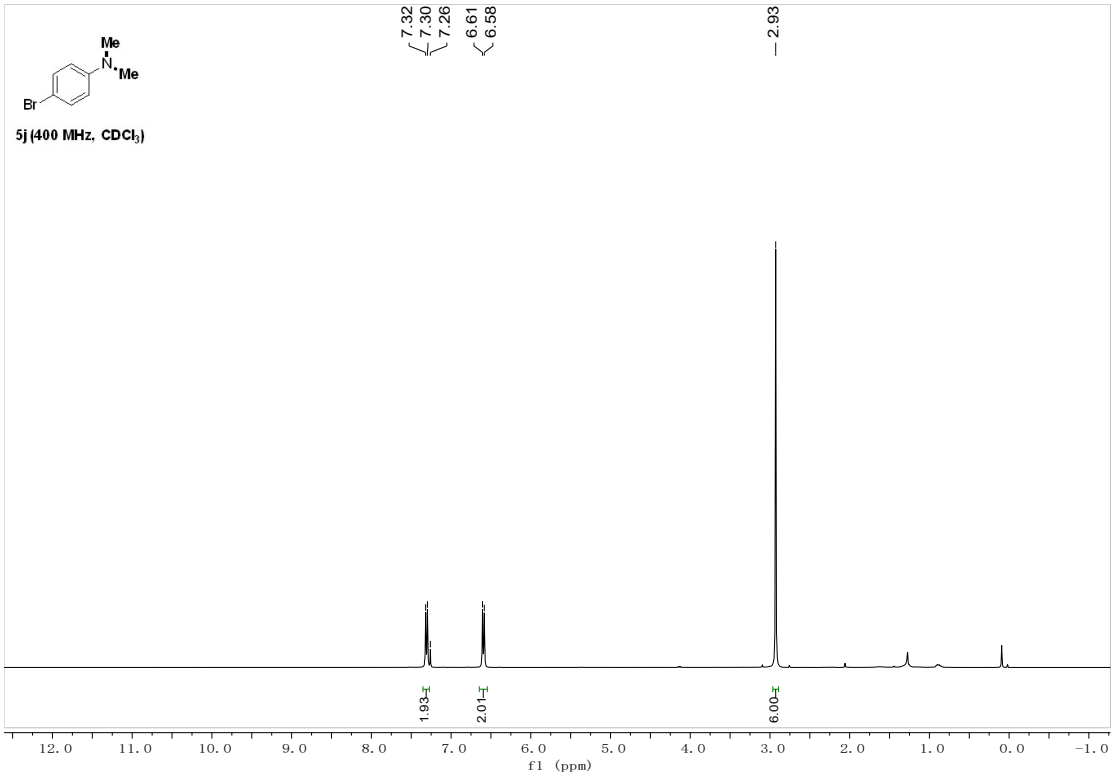

Me
N
Me
MeS
5f (100 MHz, CDCl3)
149.4
131.3
123.3
113.1
77.3
77.0
76.7
40.5
19.2
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

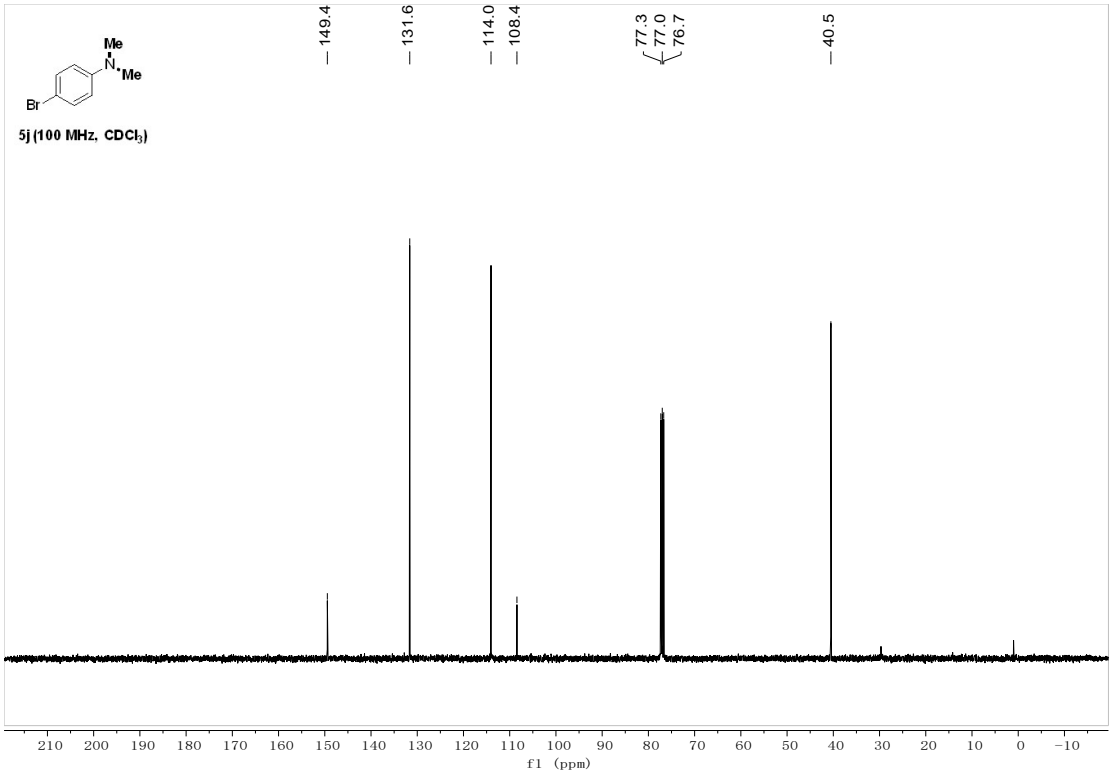

Me
N
Me
F
5h (400 MHz, CDCl3)
7.26
6.97
6.95
6.93
6.70
6.69
6.68
6.67
2.90
2.01
1.98
6.00
f1 (ppm)

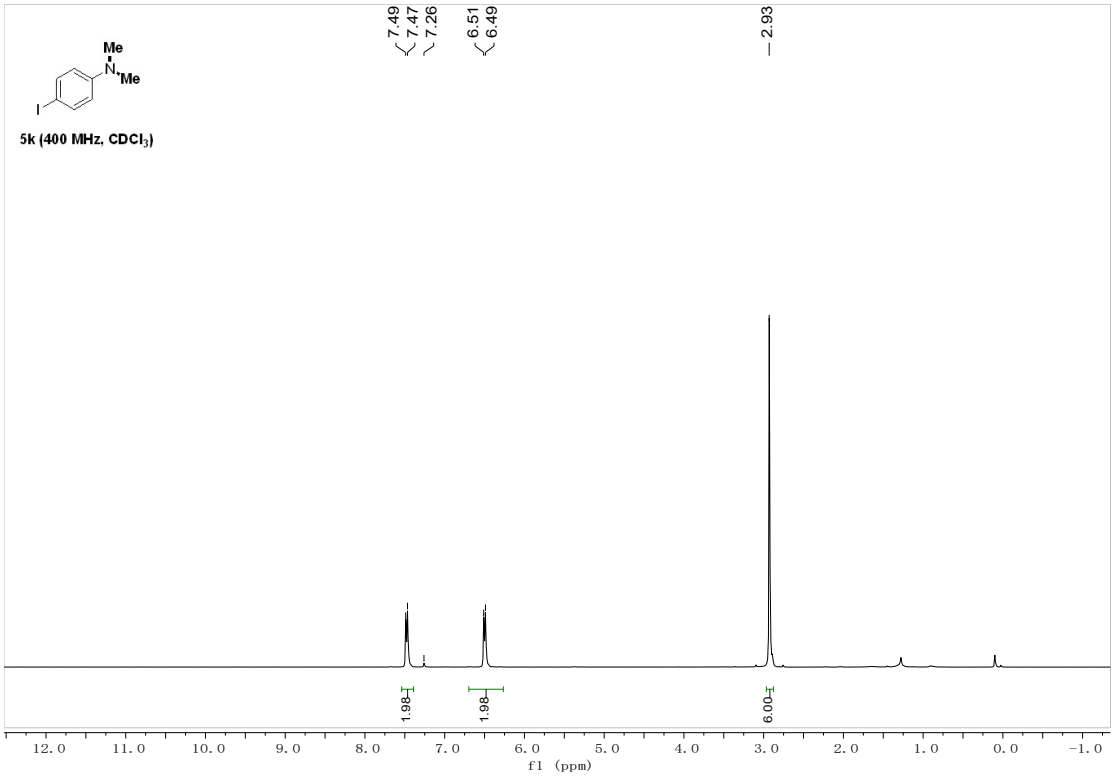

156.8
154.4
147.5
115.5
115.3
114.0
113.9
77.3
77.0
76.7
41.4
f1 (ppm)

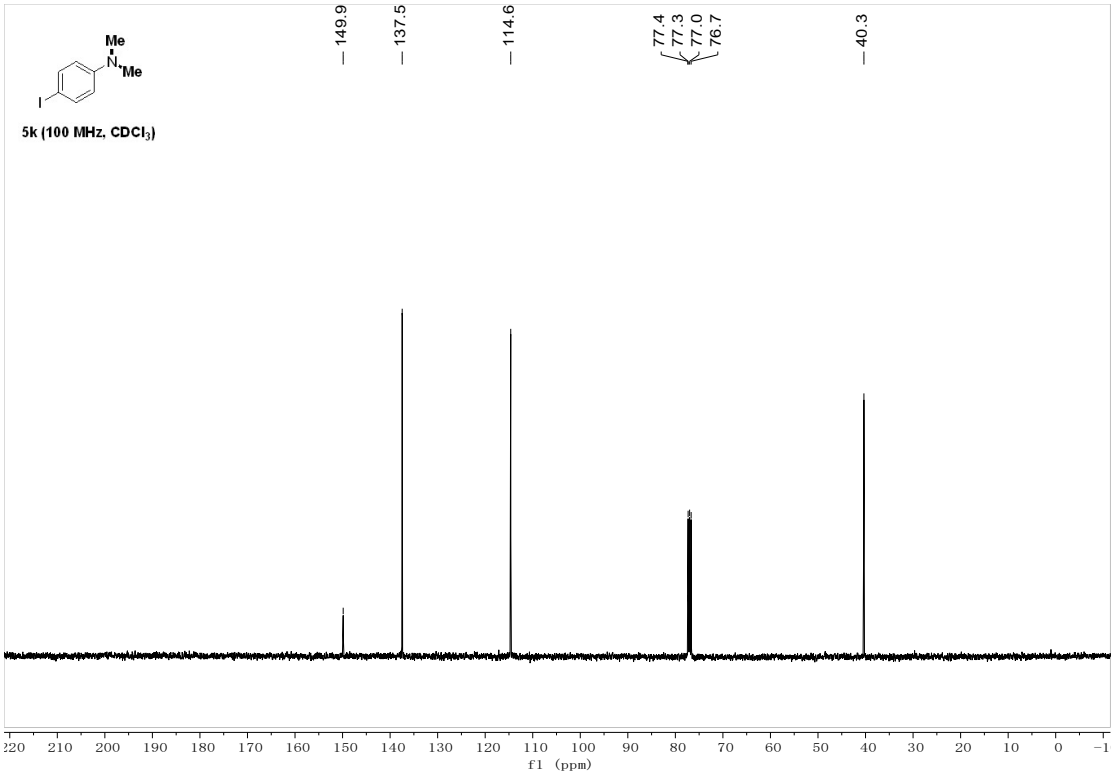

Me
N
Me
Cl
5i (400 MHz, CDCl3)
7.26
7.19
7.17
6.66
6.63
2.93
1.98
2.01
6.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

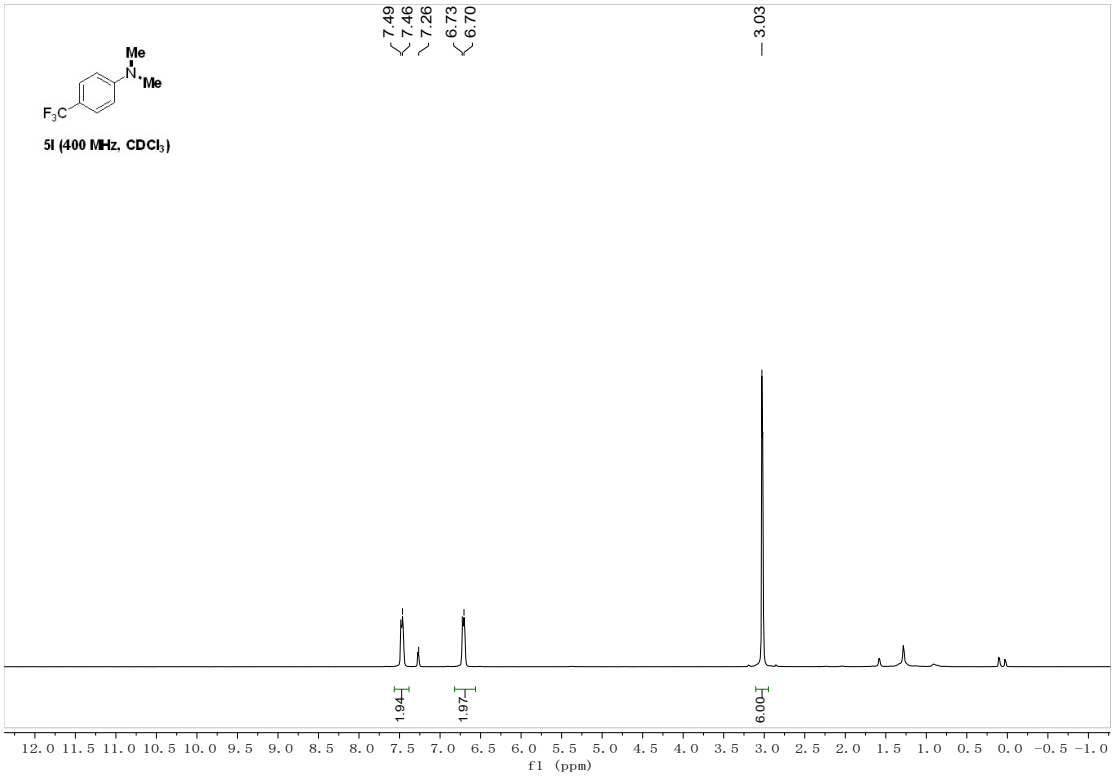

Me
N
Me
Cl
5i (100 MHz, CDCl3)
149.1
128.8
121.4
113.6
77.3
77.0
76.7
40.6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

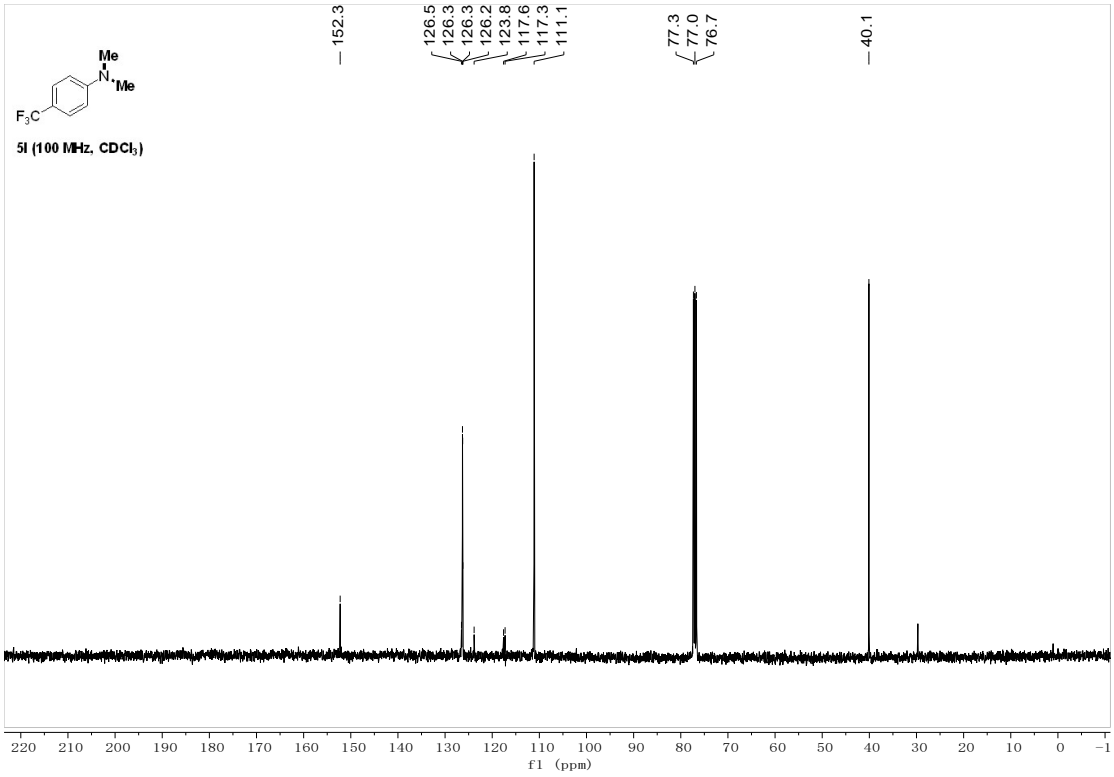

Me
N
Me
Br
5j (400 MHz, CDCl3)
7.32
7.30
7.26
6.61
6.58
2.93
1.93
2.01
6.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

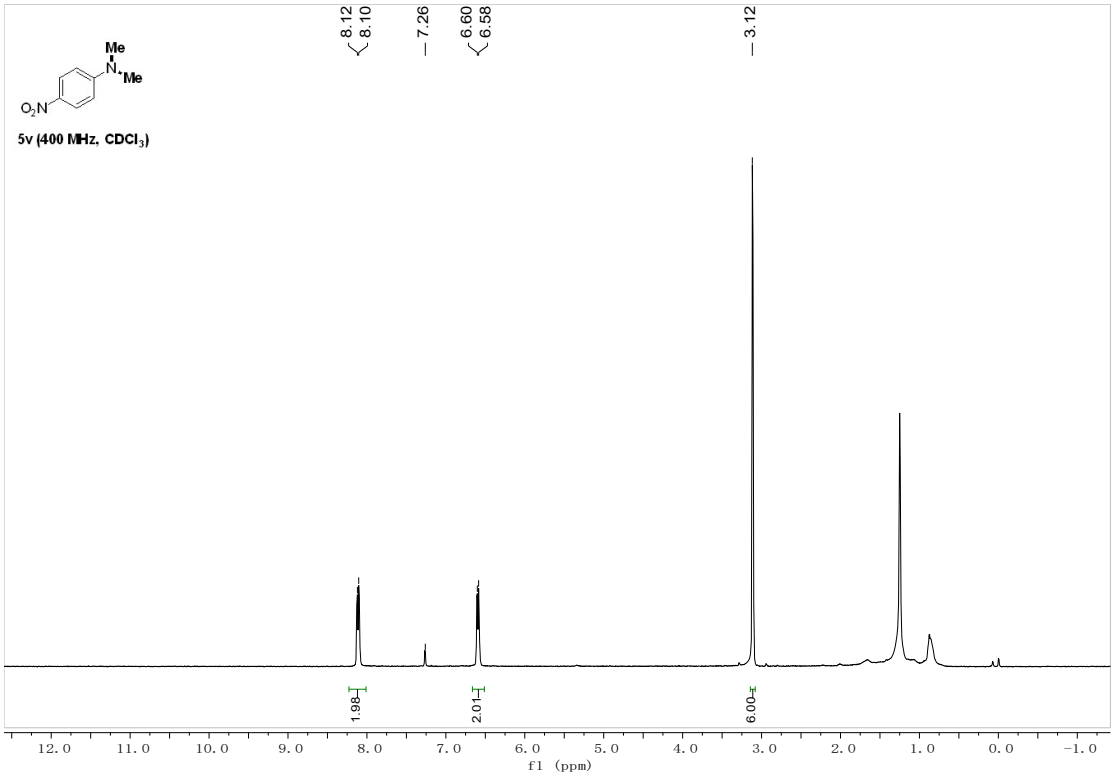

Me
N
Me
Br
5j (100 MHz, CDCl3)
149.4
131.6
114.0
108.4
77.3
77.0
76.7
40.5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

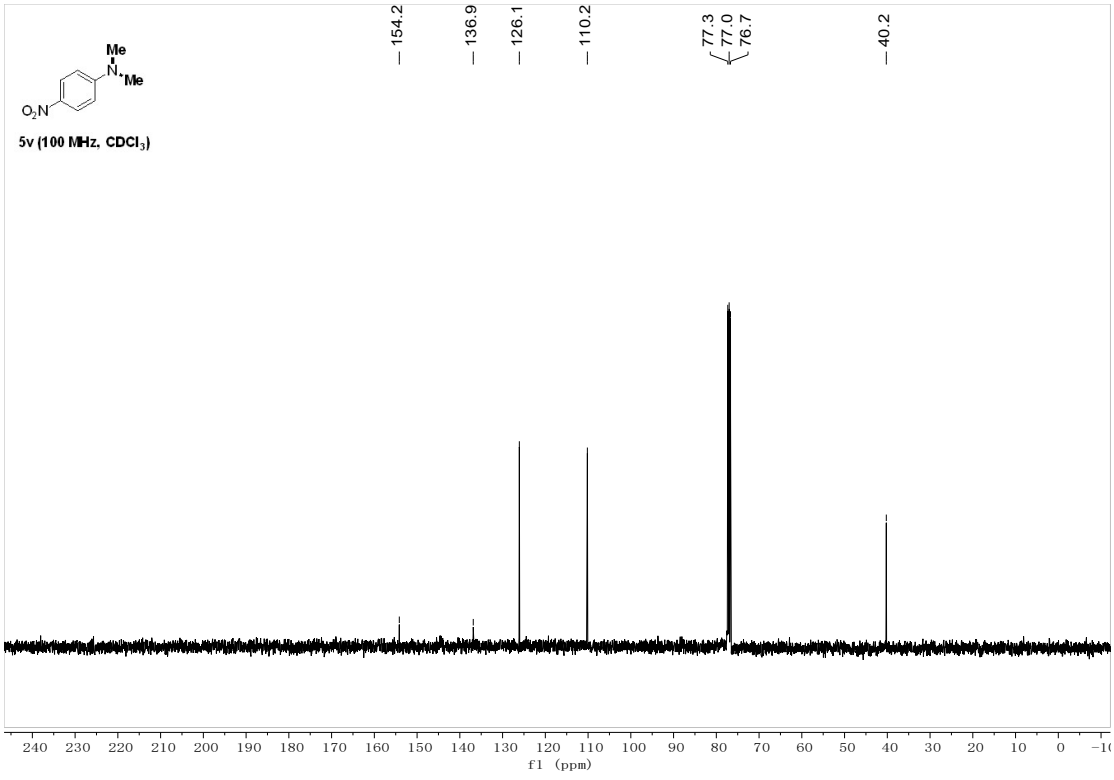

7.49
7.47
7.26
6.51
6.49
2.93
Me
N
Me
I
5k (400 MHz, CDCl3)
1.98
1.98
6.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

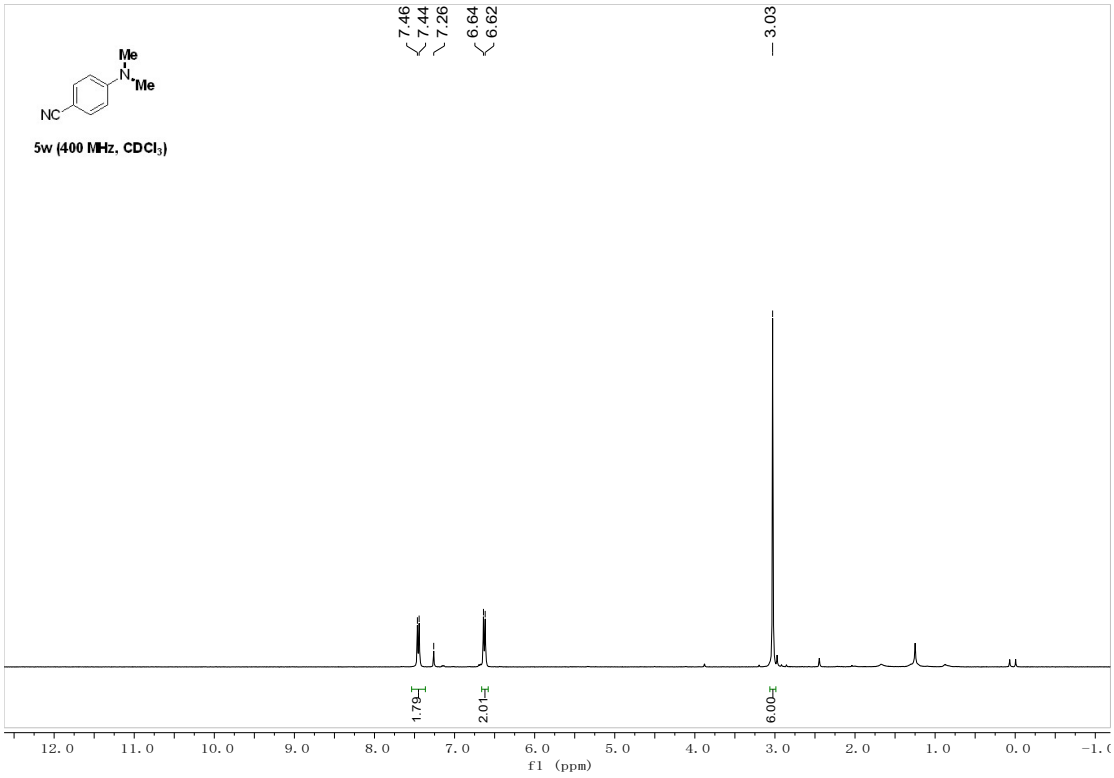

149.9
137.5
114.6
77.4
77.3
77.0
76.7
40.3
Me
N
Me
I
5k (100 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

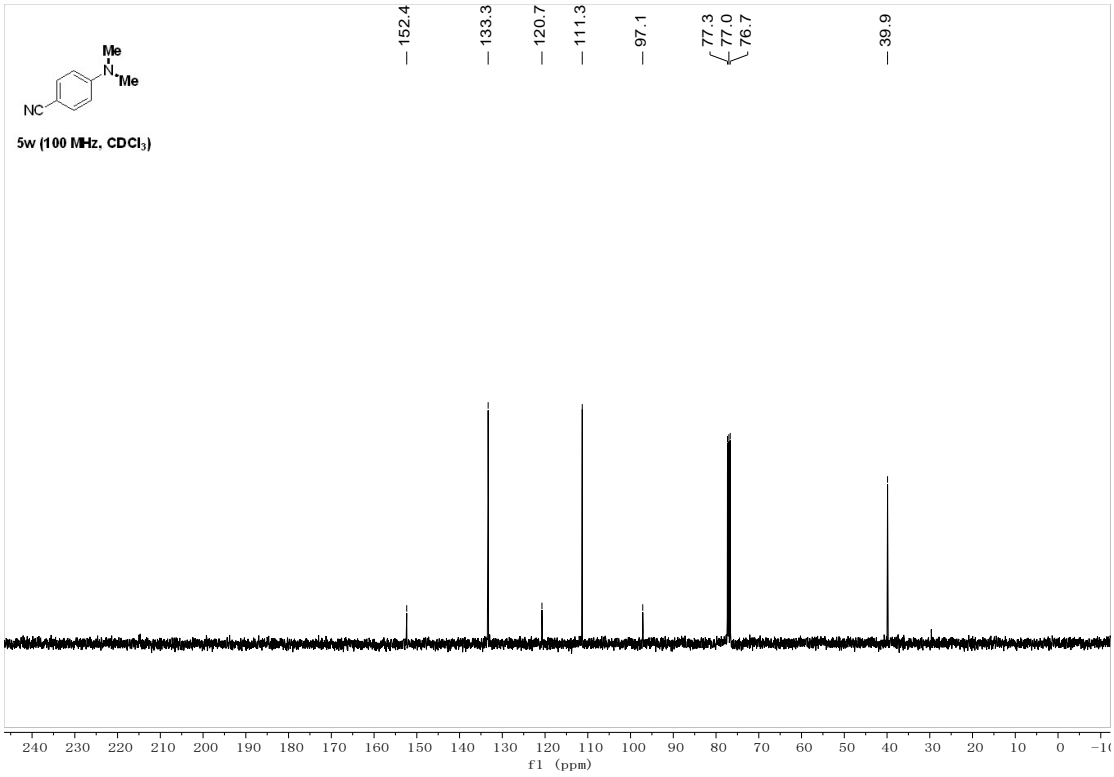

7.49
7.46
7.26
6.73
6.70
3.03
Me
N
Me
F3C
5l (400 MHz, CDCl3)
1.94
1.97
6.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

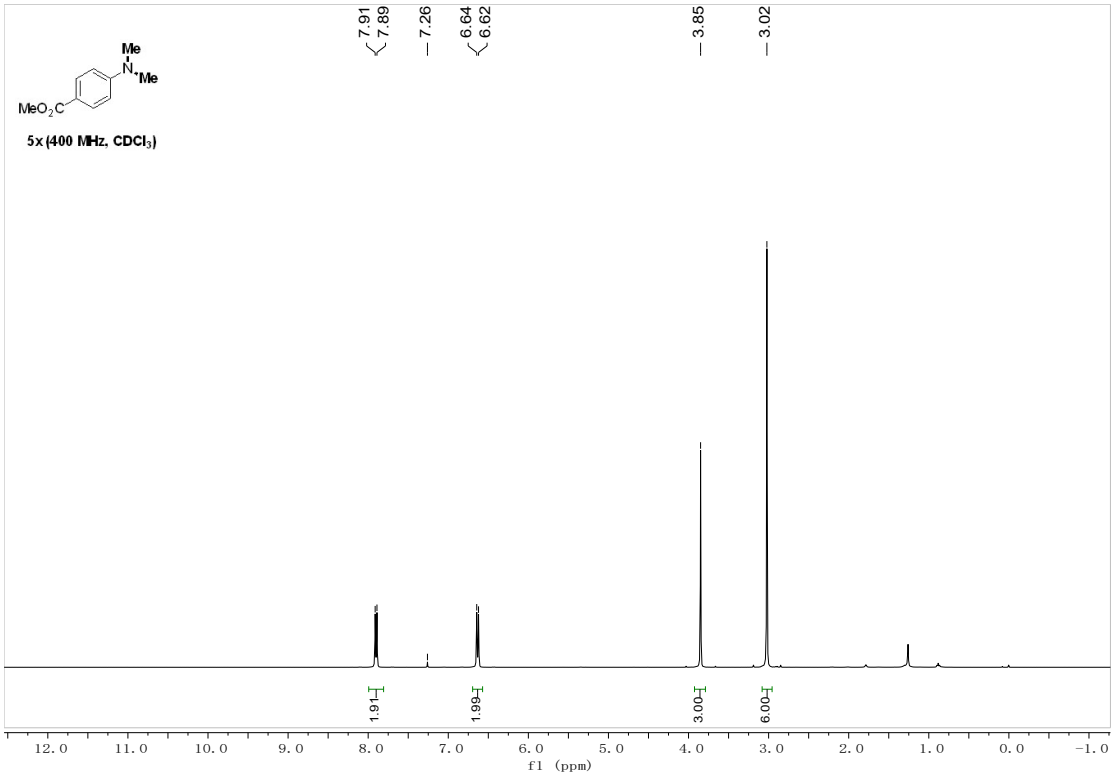

152.3
126.5
126.3
126.3
126.2
123.8
117.6
117.3
111.1
77.3
77.0
76.7
40.1
Me
N
Me
F3C
5l (100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

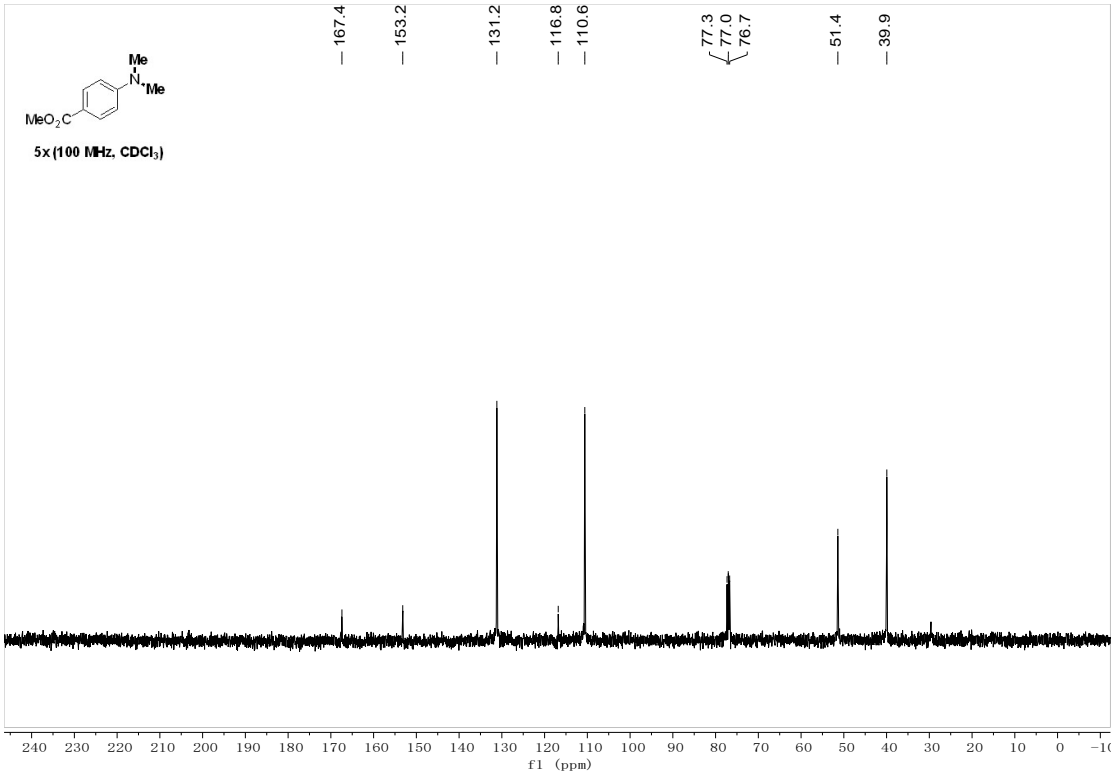

Me
N
Me
O2N
5v (400 MHz, CDCl3)
8.12
8.10
7.26
6.60
6.58
3.12
1.98
2.01
6.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.0
f1 (ppm)

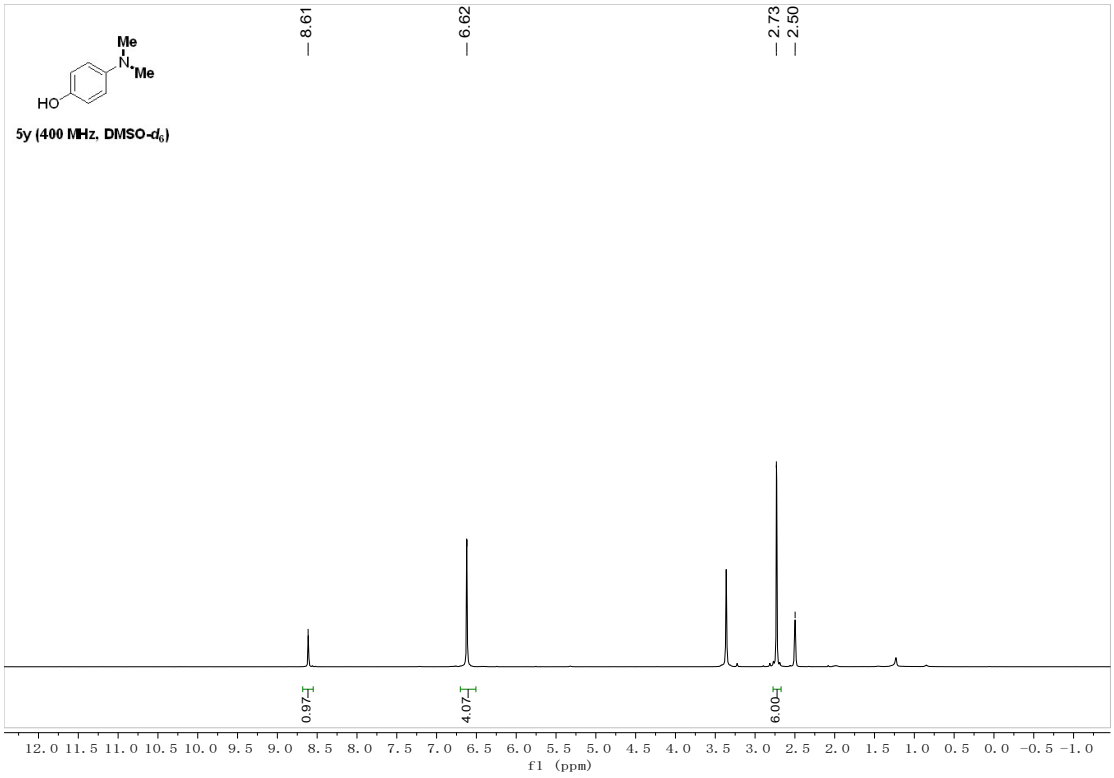

Me
N
Me
O2N
5v (100 MHz, CDCl3)
154.2
136.9
126.1
110.2
77.3
77.0
76.7
40.2
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

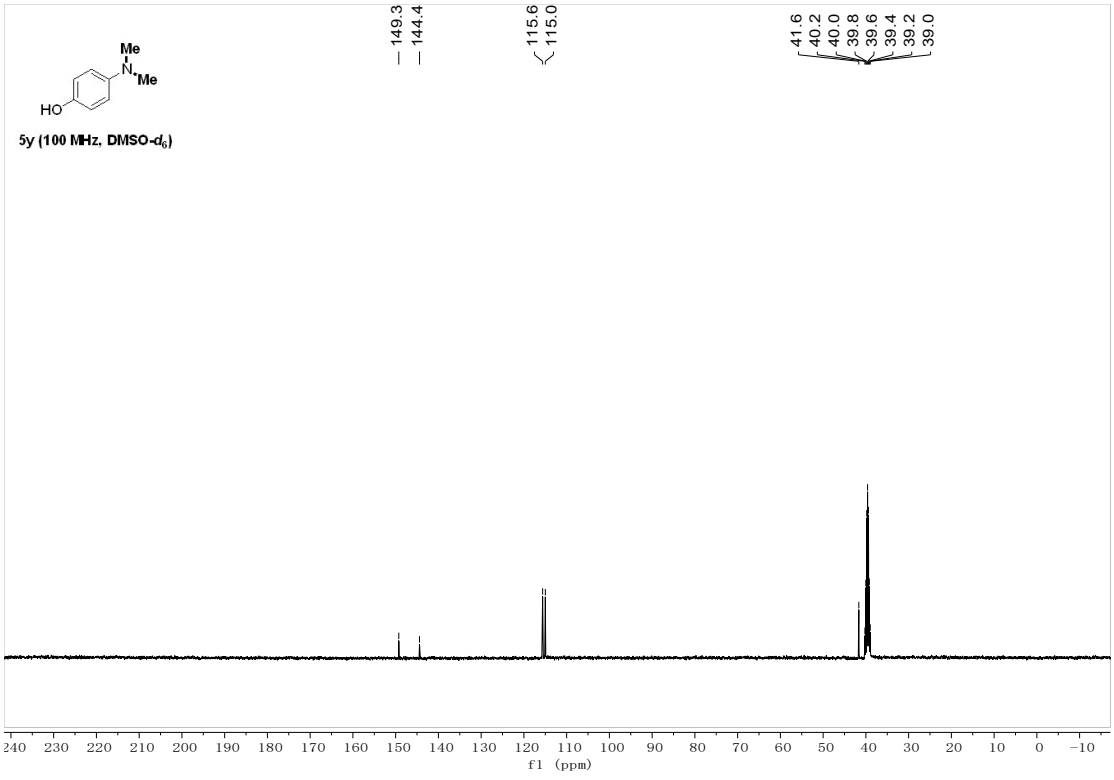

7.46
7.44
7.26
6.64
6.62
3.03
Me
N
Me
NC
5w (400 MHz, CDCl3)
1.79
2.01
6.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

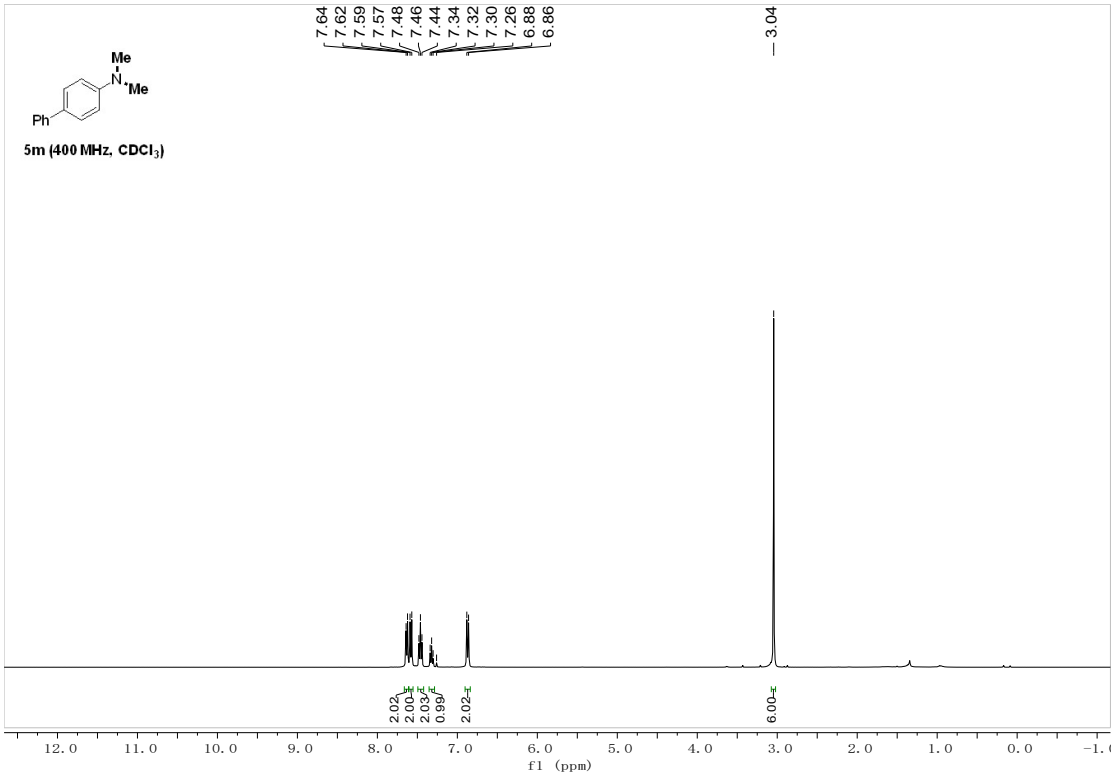

152.4
133.3
120.7
111.3
97.1
77.3
77.0
76.7
39.9
Me
N
Me
NC
5w (100 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

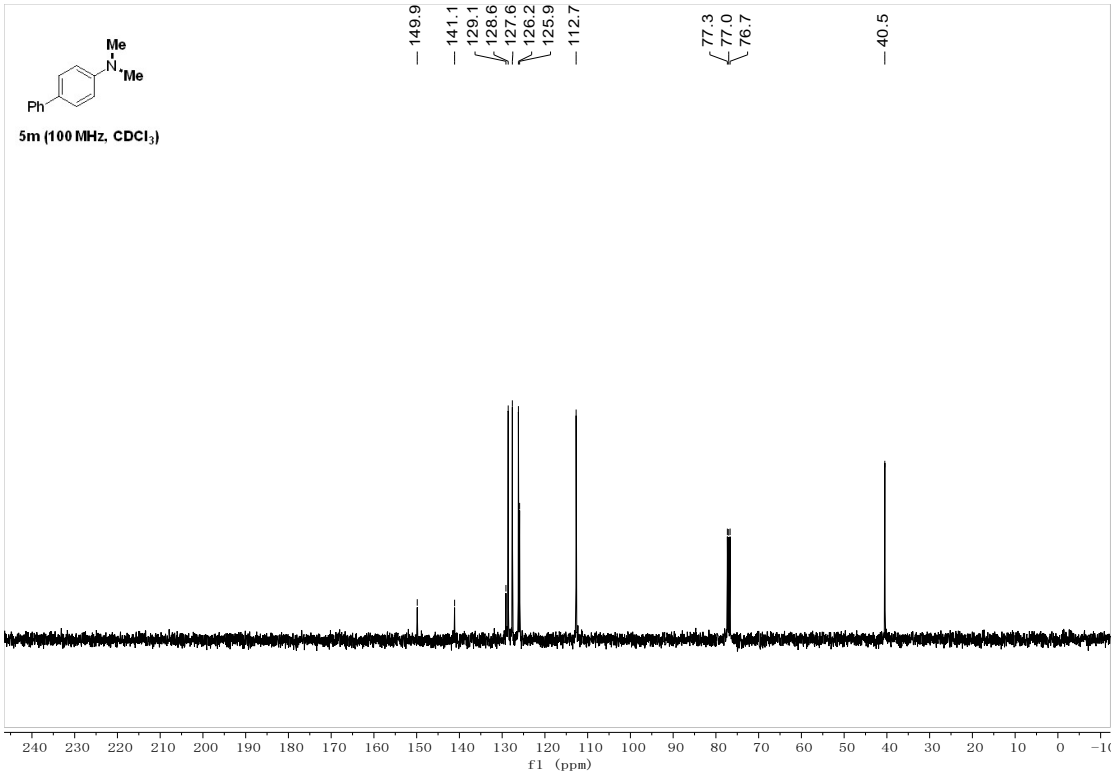

7.91
7.89
7.26
6.64
6.62
3.85
3.02
Me
N
Me
MeO2C
5x (400 MHz, CDCl3)
1.91
1.99
3.00
6.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.0
f1 (ppm)

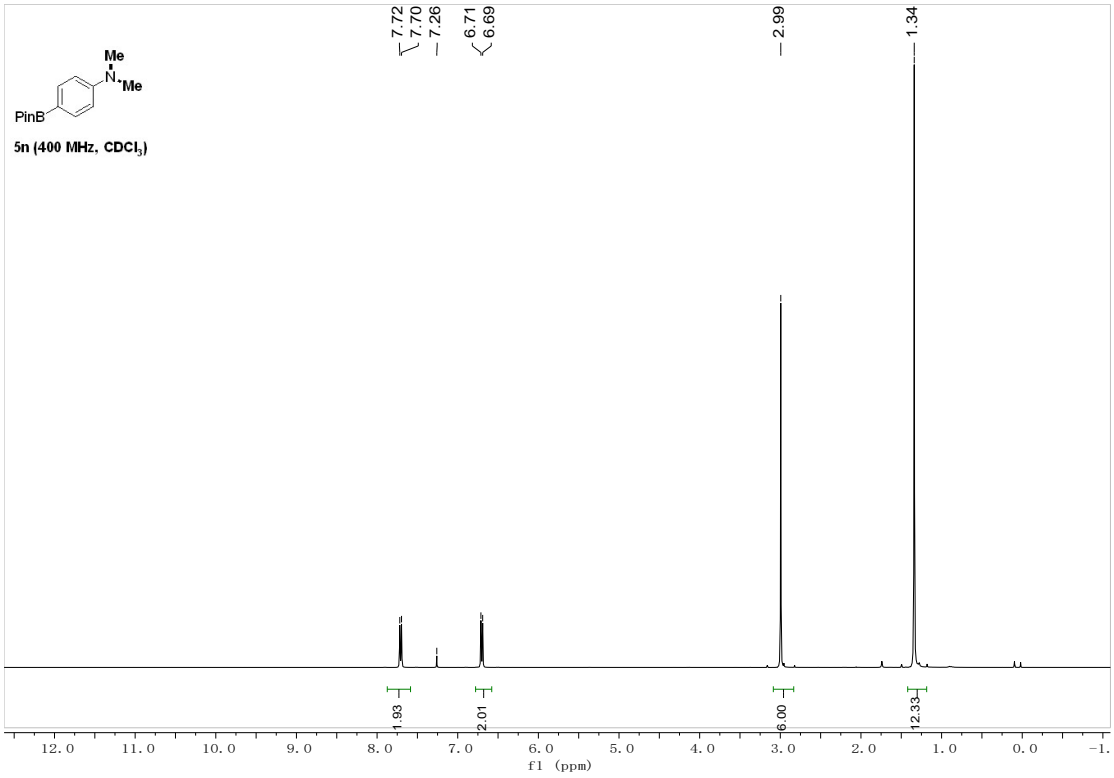

167.4
153.2
131.2
116.8
110.6
77.3
77.0
76.7
51.4
39.9
Me
N
Me
MeO2C
5x (100 MHz, CDCl3)
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

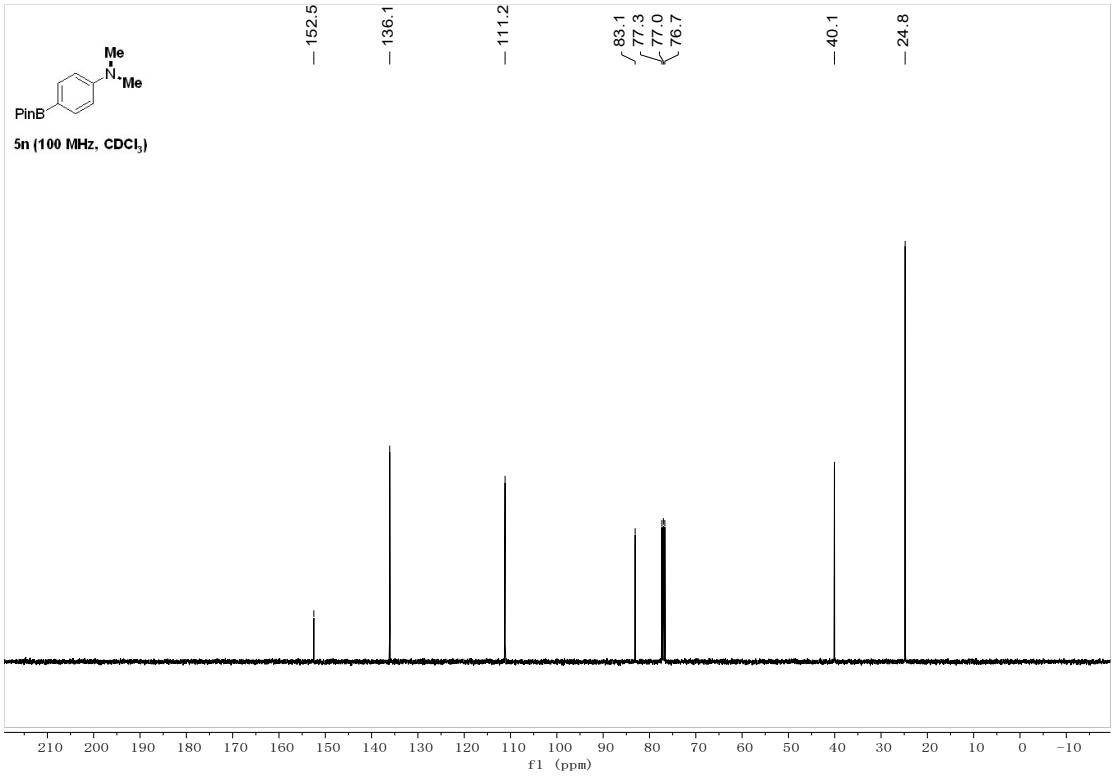

Me
N
Me
HO
5y (400 MHz, DMSO-d_6)
8.61
6.62
2.73
2.50
0.97
4.07
6.00
f1 (ppm)

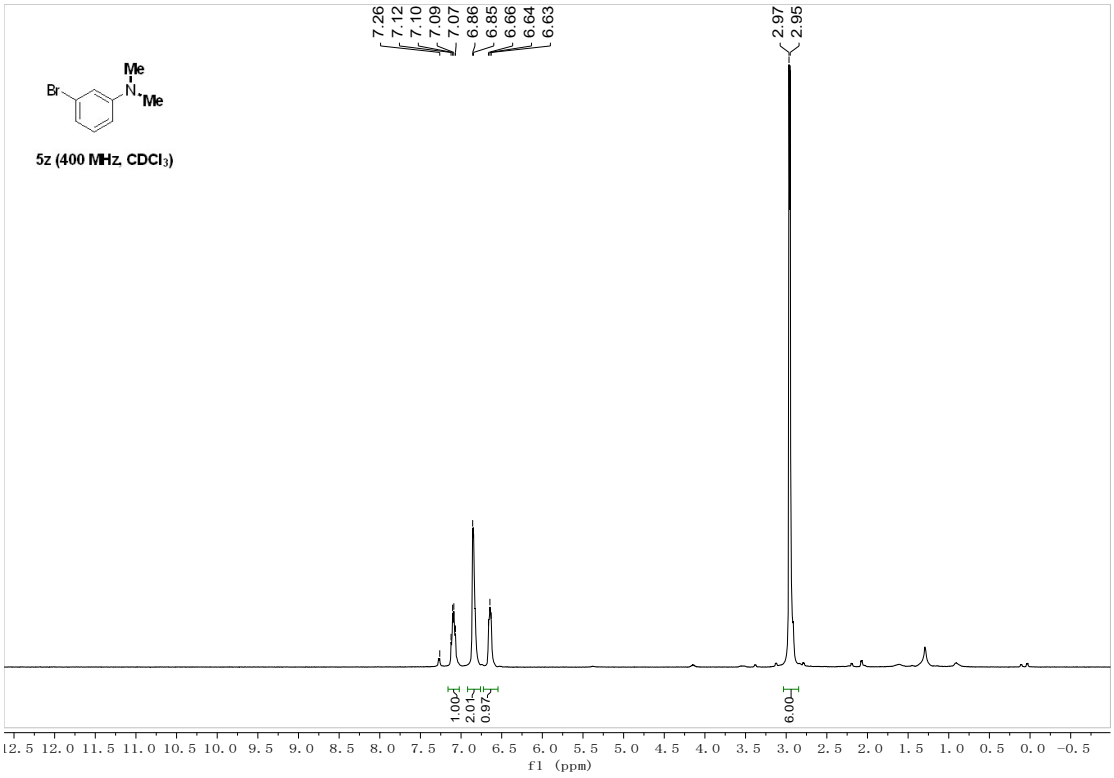

Me
N
Me
HO
5y (100 MHz, DMSO-d_6)
149.3
144.4
115.6
115.0
41.6
40.2
40.0
39.8
39.6
39.4
39.2
39.0
f1 (ppm)

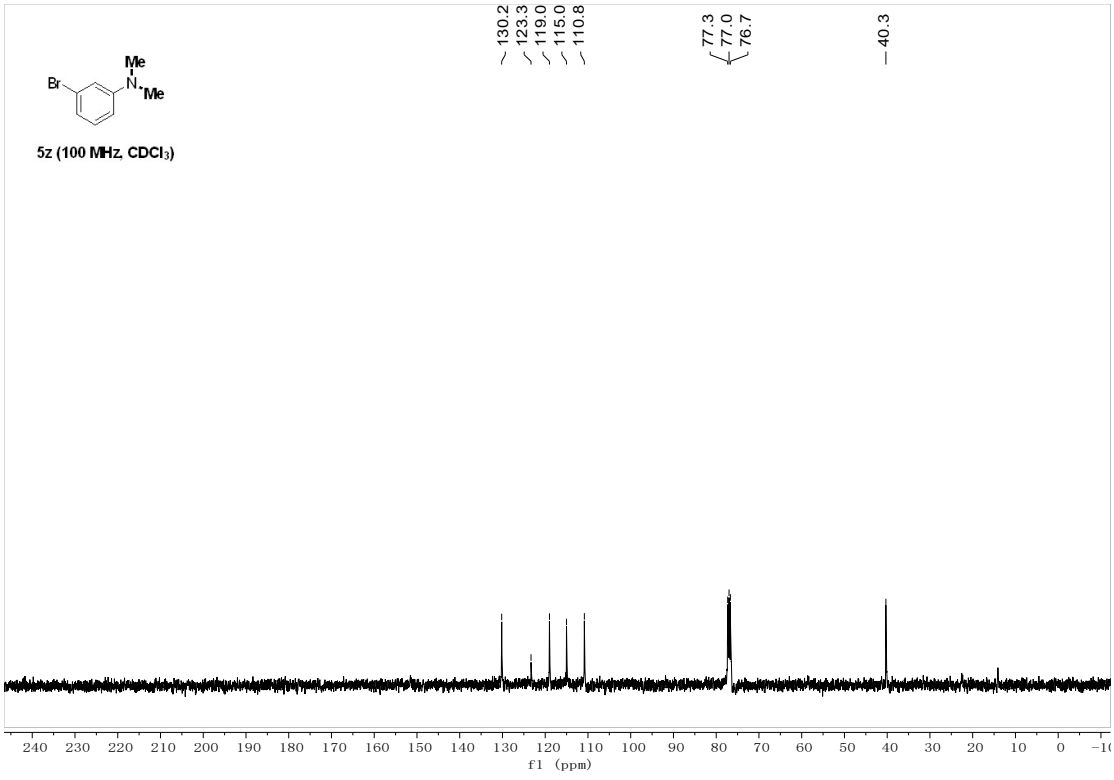

7.64
7.62
7.59
7.57
7.48
7.46
7.44
7.34
7.32
7.30
7.26
6.88
6.86
3.04
Me
N
Me
Ph
5m (400 MHz, CDCl3)
2.02
2.00
2.03
0.99
2.02
6.00
f1 (ppm)

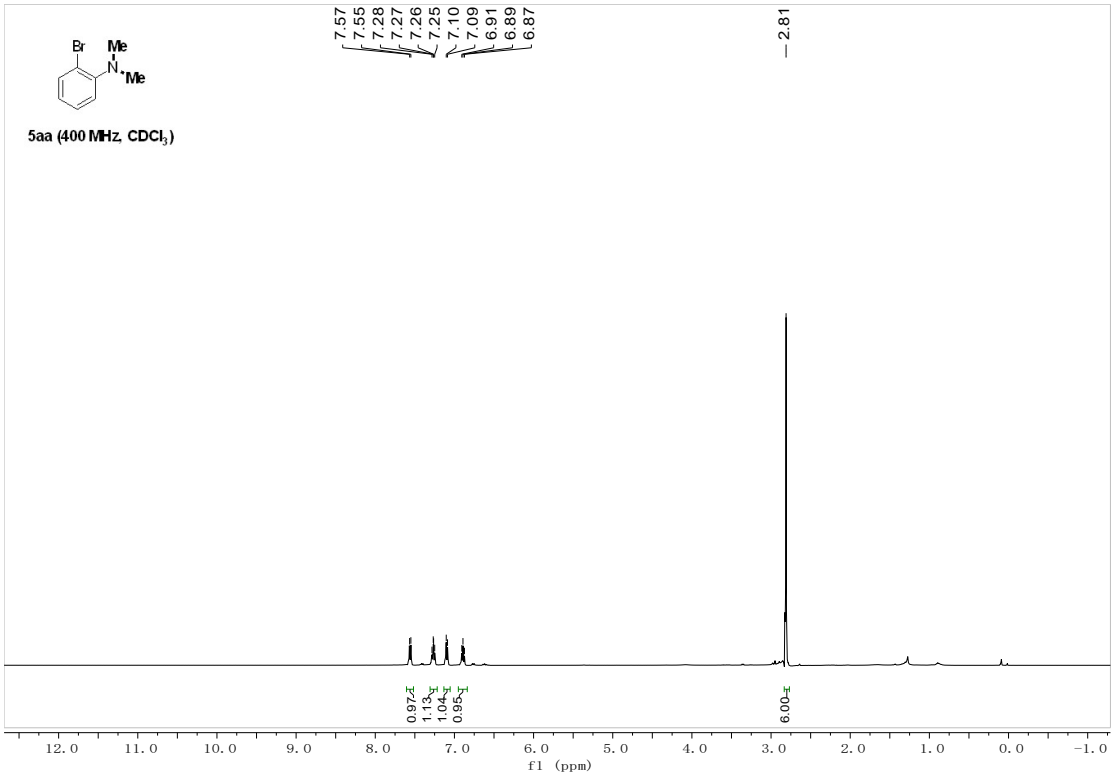

149.9
141.1
129.1
128.6
127.6
126.2
125.9
112.7
77.3
77.0
76.7
40.5
Me
N
Me
Ph
5m (100 MHz, CDCl3)
f1 (ppm)

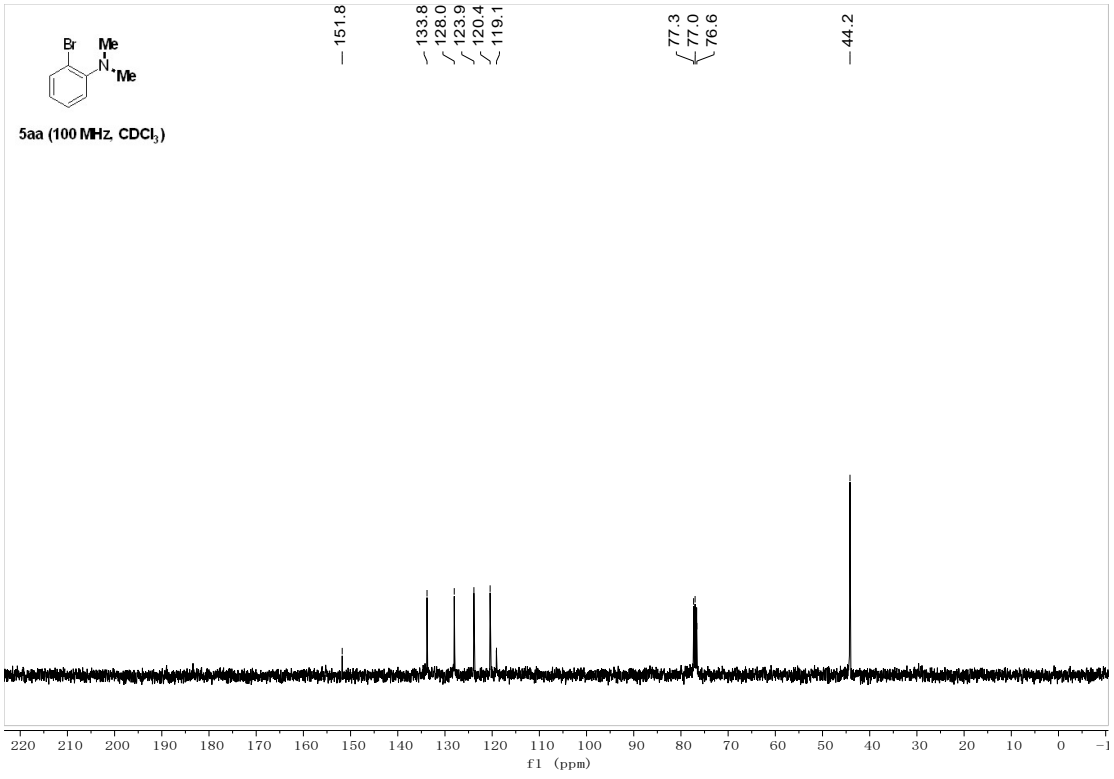

Me
N
Me
PinB
5n (400 MHz, CDCl3)
7.72
7.70
7.26
6.71
6.69
2.99
1.34
1.93
2.01
6.00
12.33
f1 (ppm)

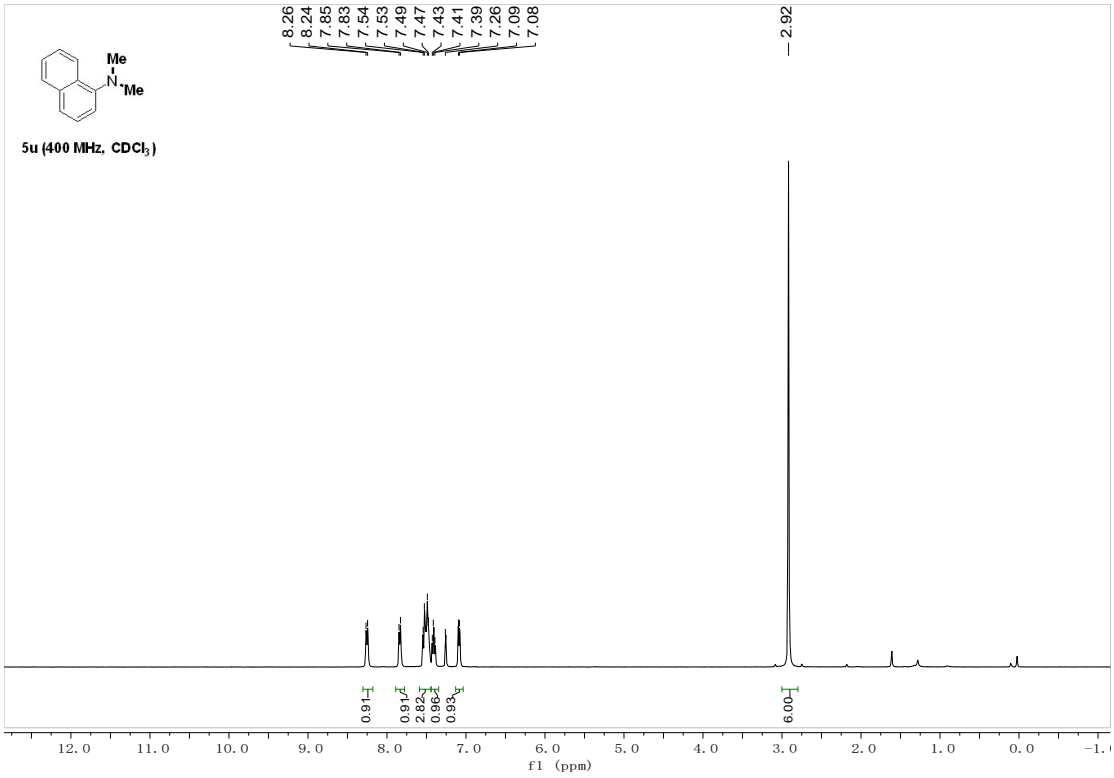

Me
N
Me
PinB
5n (100 MHz, CDCl3)
152.5
136.1
111.2
83.1
77.3
77.0
76.7
40.1
24.8
f1 (ppm)

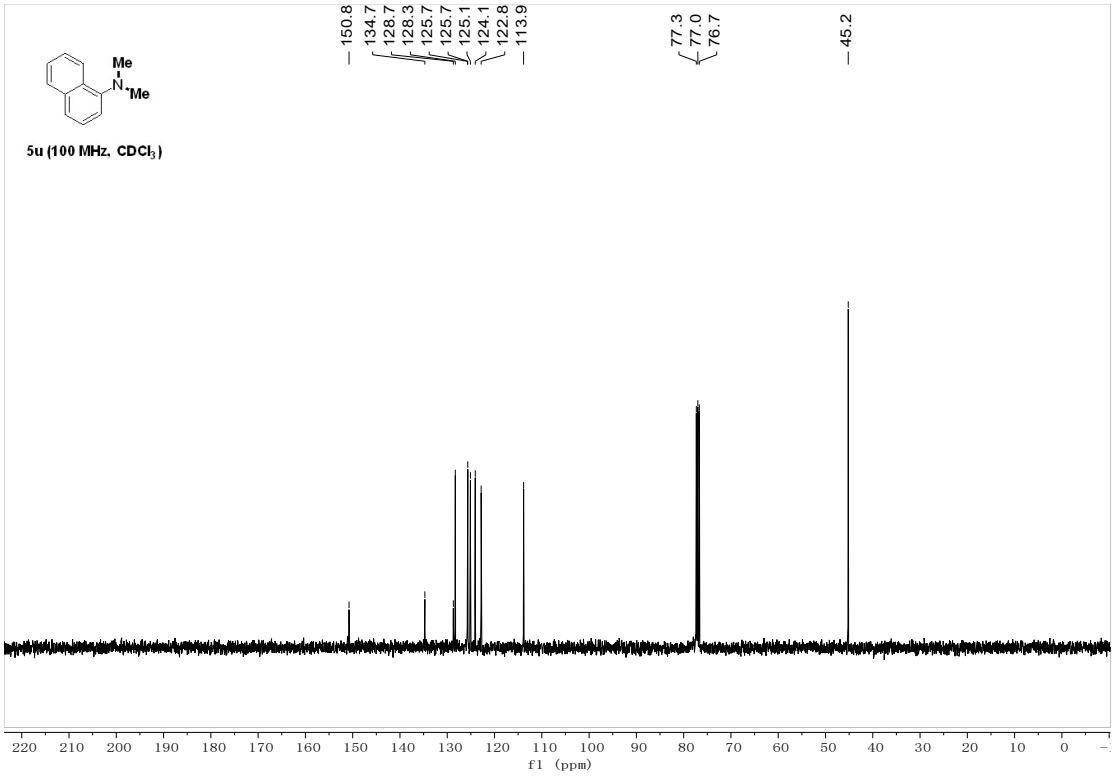

7.26
7.12
7.10
7.09
7.07
6.86
6.85
6.66
6.64
6.63
2.97
2.95
Me
N
Me
Br
5z (400 MHz, CDCl3)
1.00
2.01
0.97
6.00
f1 (ppm)

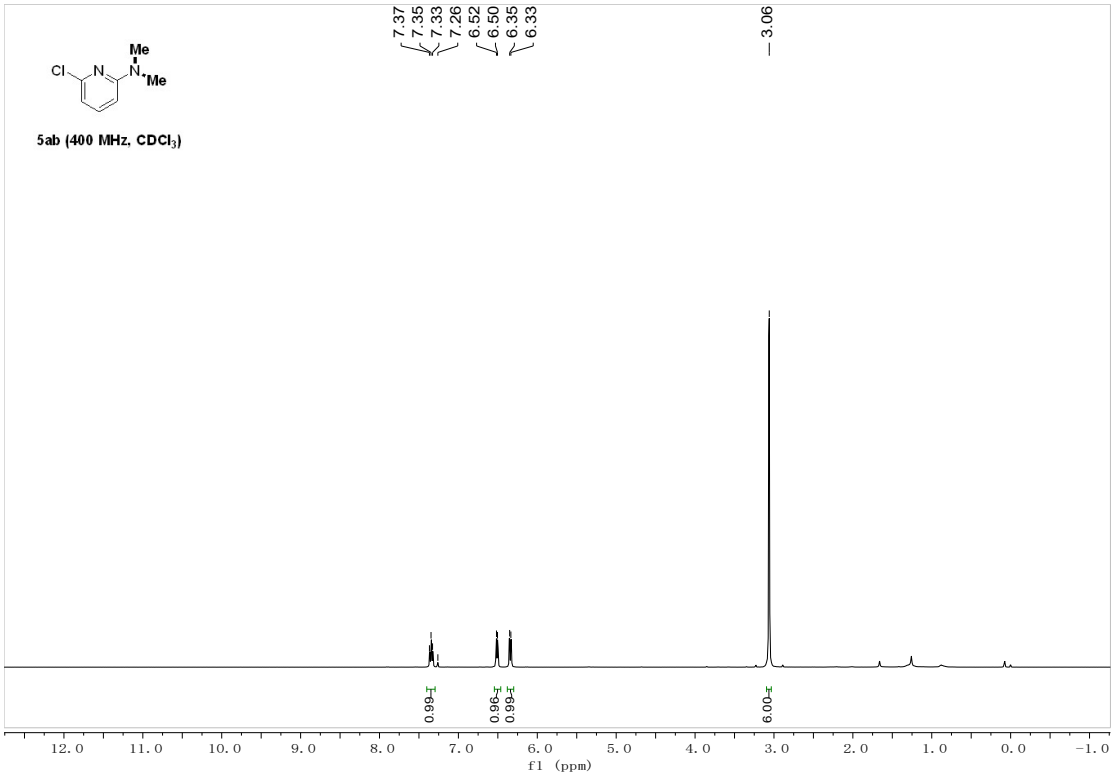

130.2
123.3
119.0
115.0
110.8
77.3
77.0
76.7
40.3
Me
N
Me
Br
5z (100 MHz, CDCl3)
f1 (ppm)

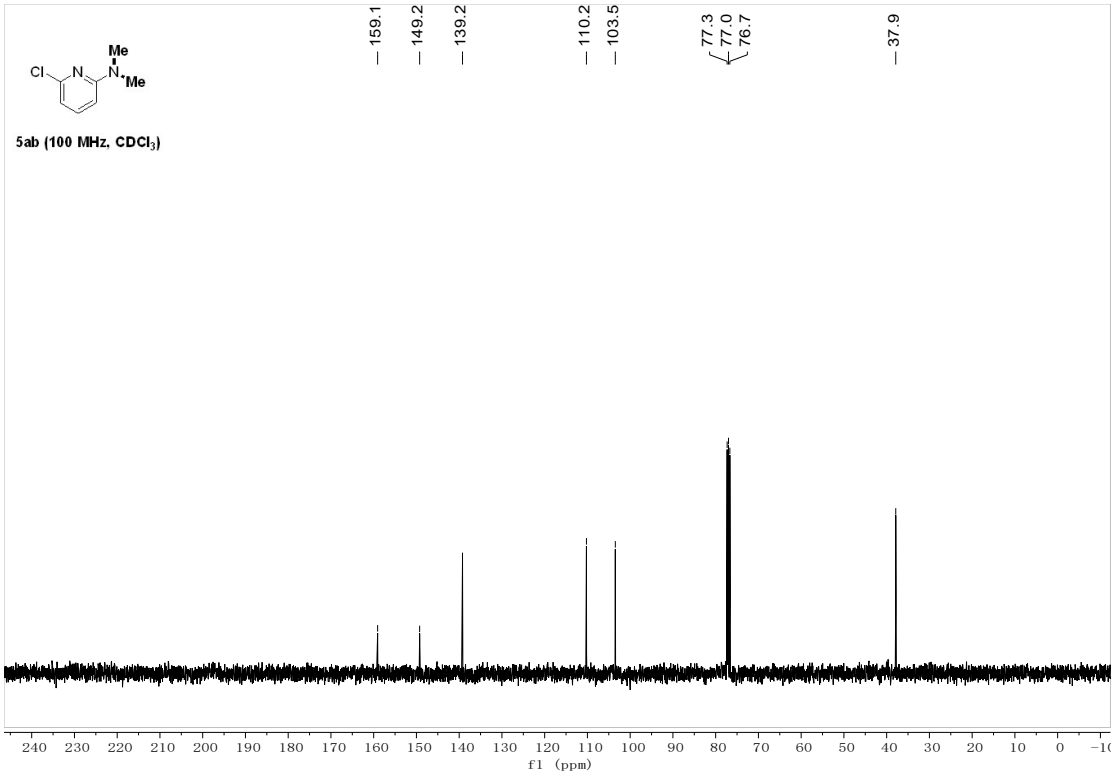

Br
Me
N
Me
5aa (400 MHz, CDCl3)
7.57
7.55
7.28
7.27
7.26
7.25
7.10
7.09
6.91
6.89
6.87
2.81
0.97
1.13
1.04
0.95
6.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

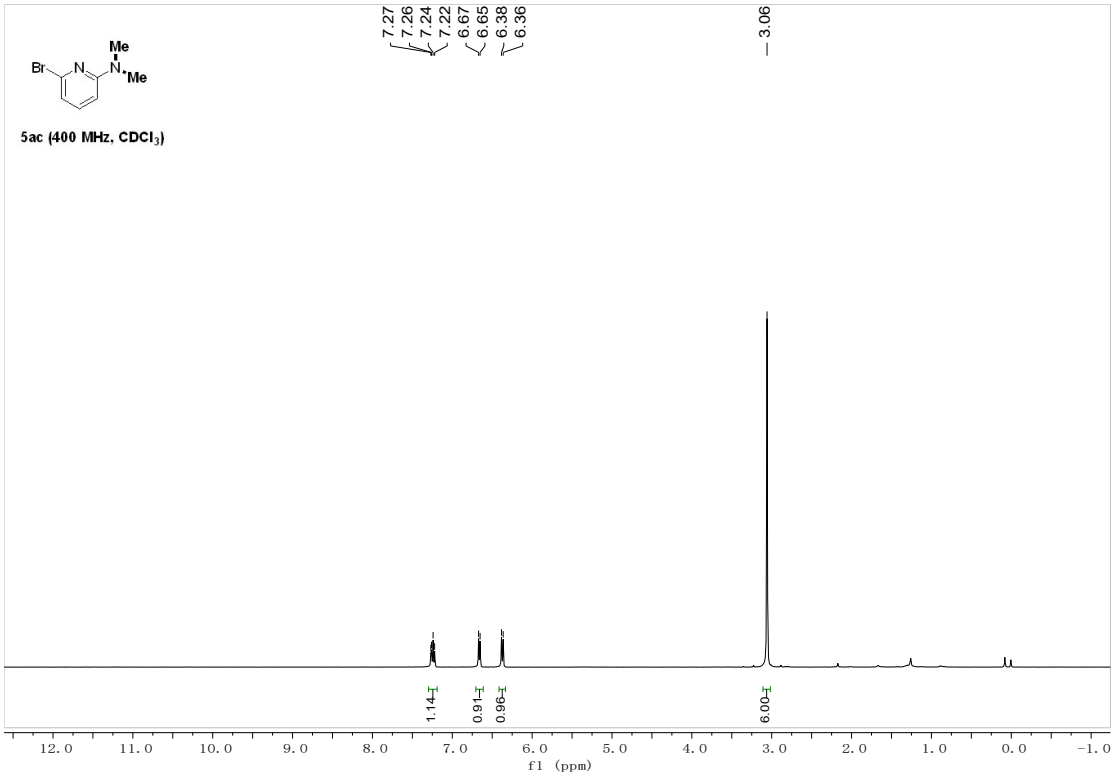

Br
Me
N
Me
5aa (100 MHz, CDCl3)
151.8
133.8
128.0
123.9
120.4
119.1
77.3
77.0
76.6
44.2
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

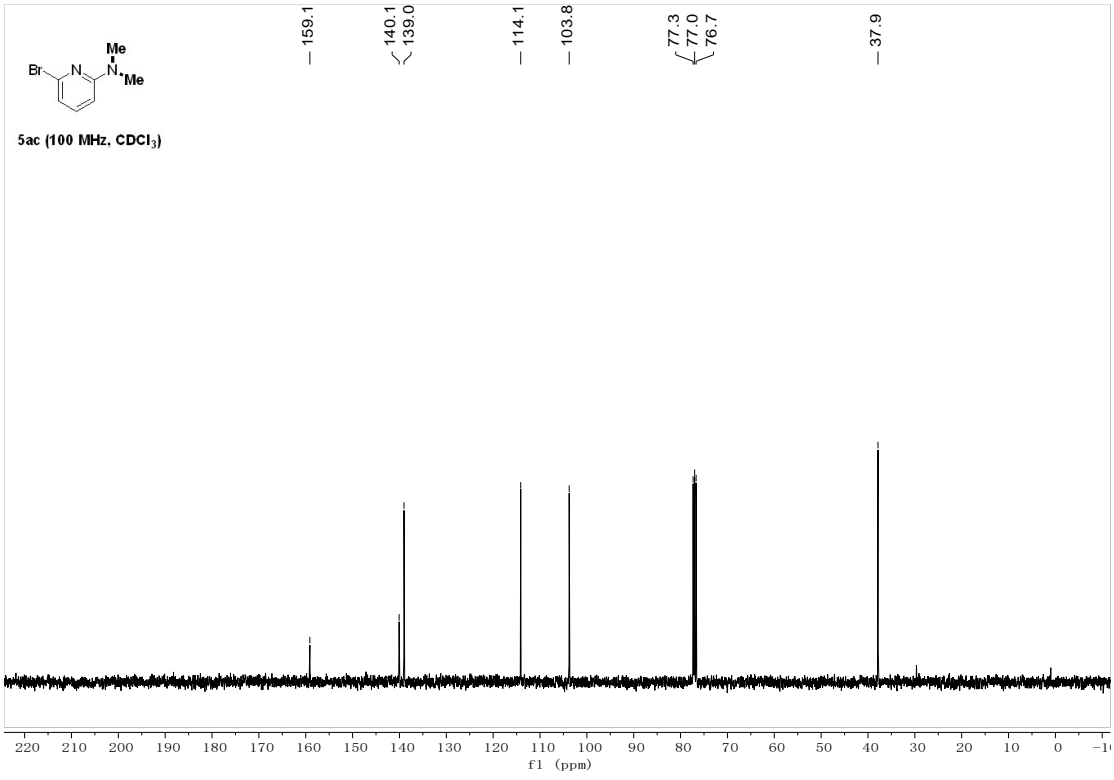

8.26
8.24
7.85
7.83
7.54
7.53
7.49
7.47
7.43
7.41
7.39
7.26
7.09
7.08
2.92
Me
N
Me
5u (400 MHz, CDCl3)
0.91
0.91
2.82
0.96
0.93
6.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

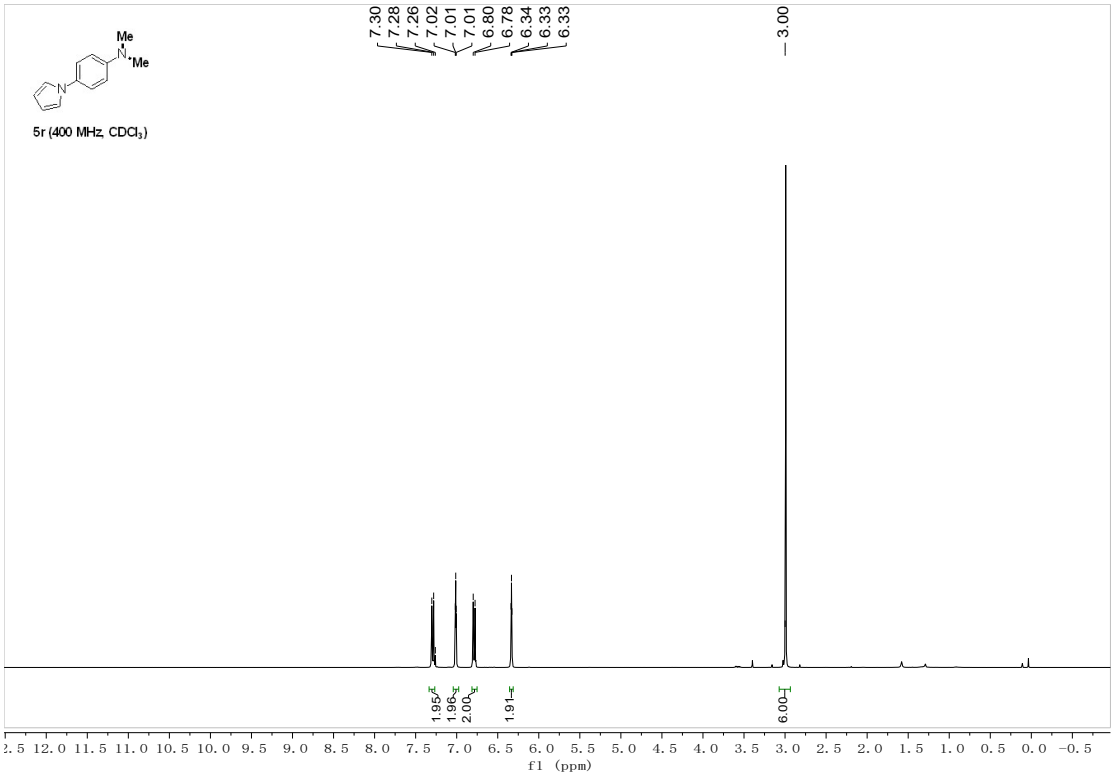

150.8
134.7
128.7
128.3
125.7
125.7
125.1
124.1
122.8
113.9
77.3
77.0
76.7
45.2
Me
N
Me
5u (100 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

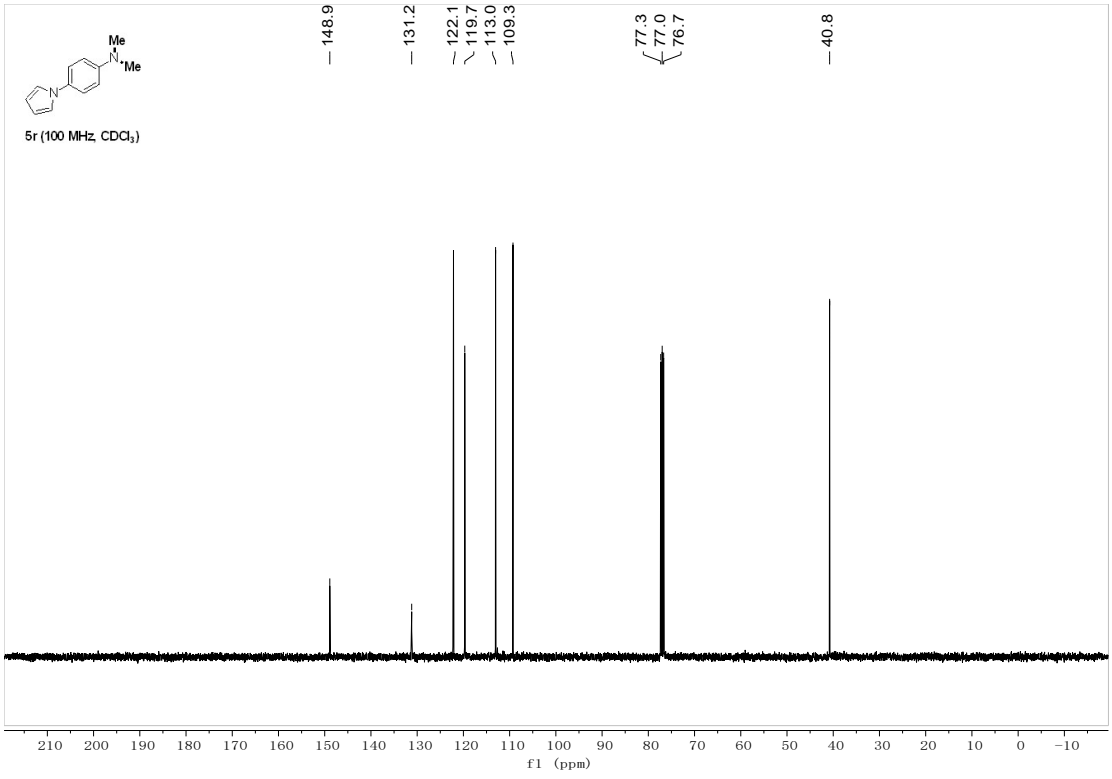

Me
Cl
N
N
Me
5ab (400 MHz, CDCl3)
7.37
7.35
7.33
7.26
6.52
6.50
6.35
6.33
3.06
0.99
0.96
0.99
6.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.0
f1 (ppm)

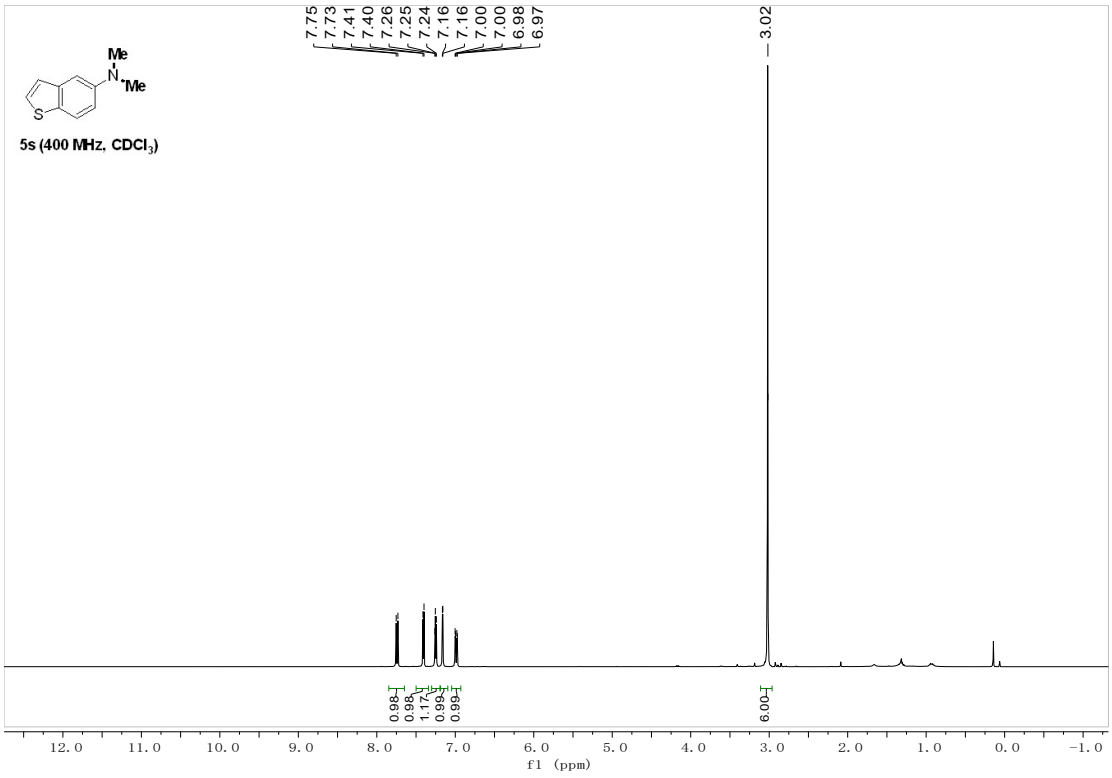

Me
Cl
N
N
Me
5ab (100 MHz, CDCl3)
159.1
149.2
139.2
110.2
103.5
77.3
77.0
76.7
37.9
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

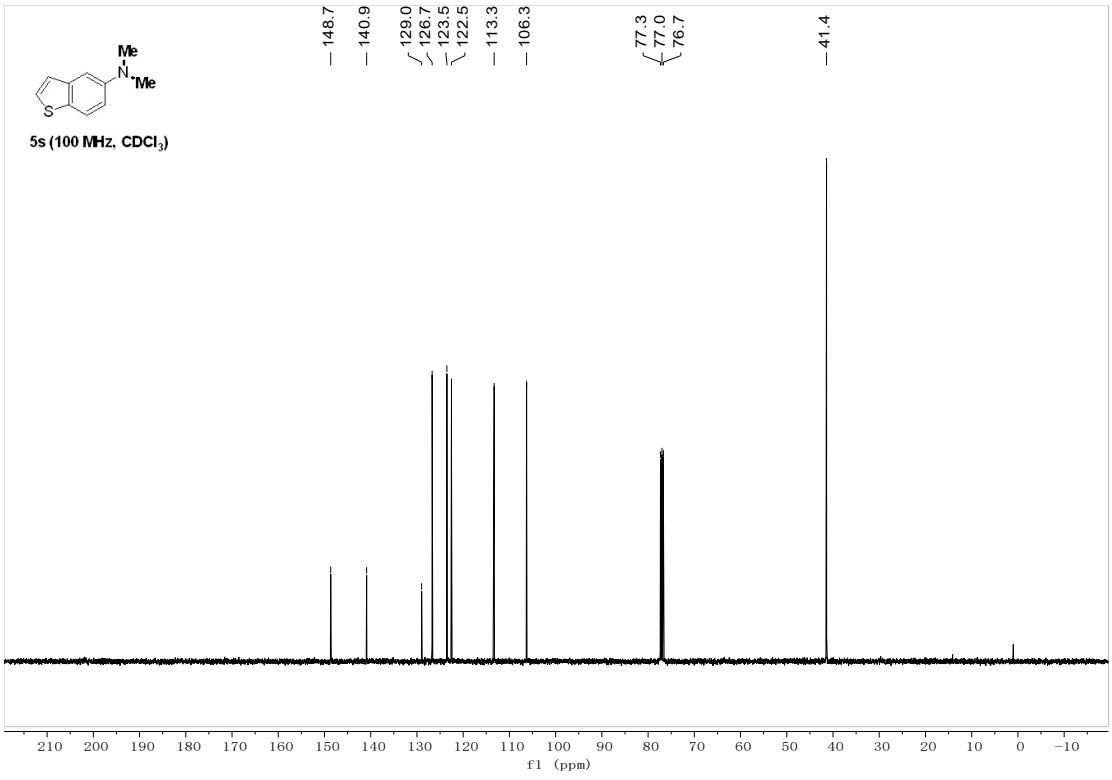

Me
Br
N
N
Me
5ac (400 MHz, CDCl3)
7.27
7.26
7.24
7.22
6.67
6.65
6.38
6.36
3.06
1.14
0.91
0.96
6.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.0
f1 (ppm)

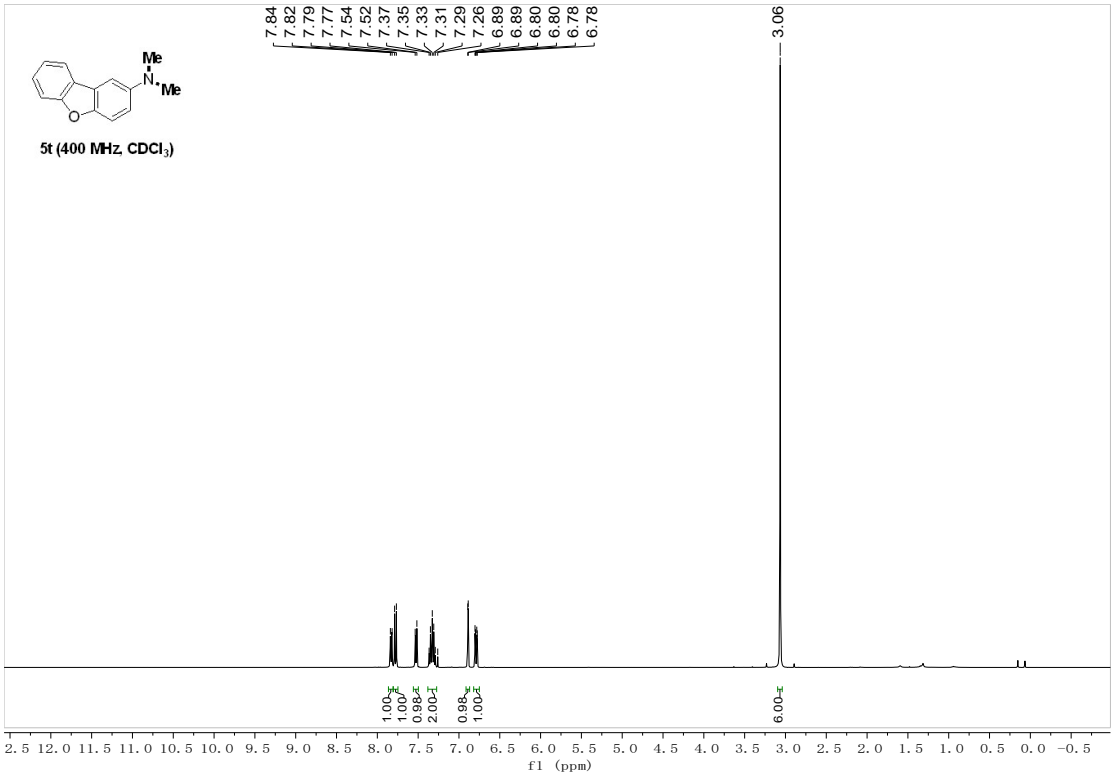

Me
Br
N
N
Me
5ac (100 MHz, CDCl3)
159.1
140.1
139.0
114.1
103.8
77.3
77.0
76.7
37.9
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

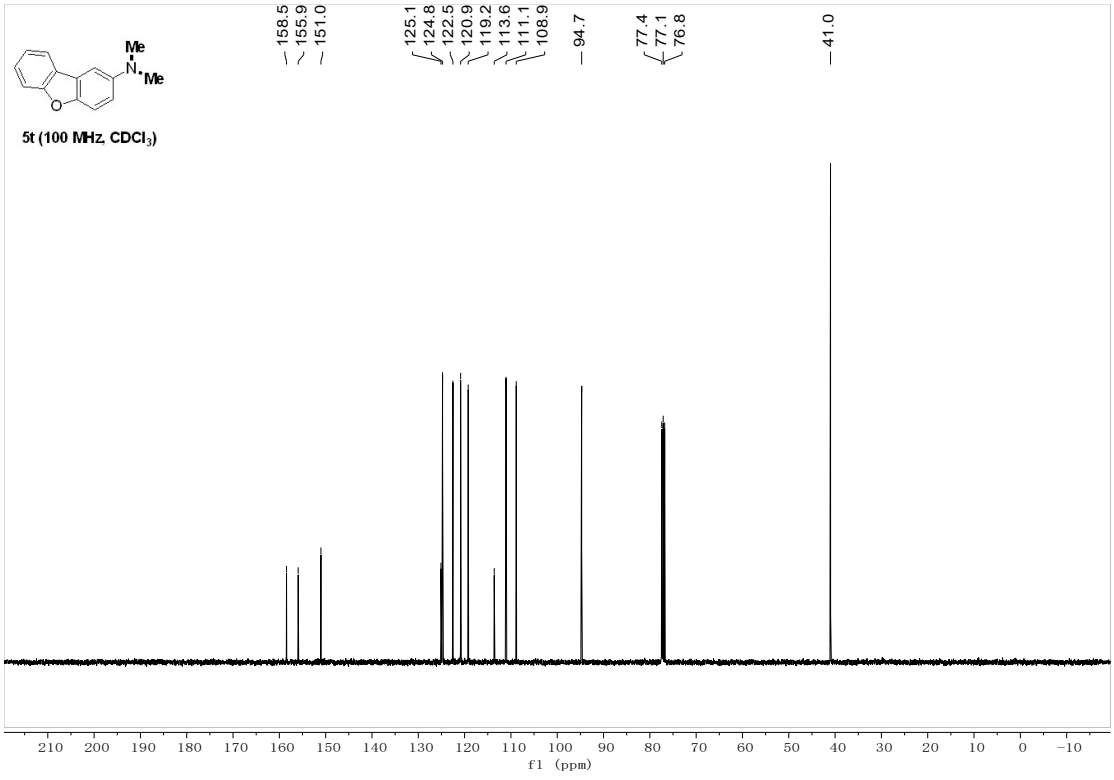

7.30
7.28
7.26
7.02
7.01
7.01
6.80
6.78
6.34
6.33
6.33
3.00
Me
N
Me
5r (400 MHz, CDCl3)
1.95
1.96
2.00
1.91
6.00
f1 (ppm)

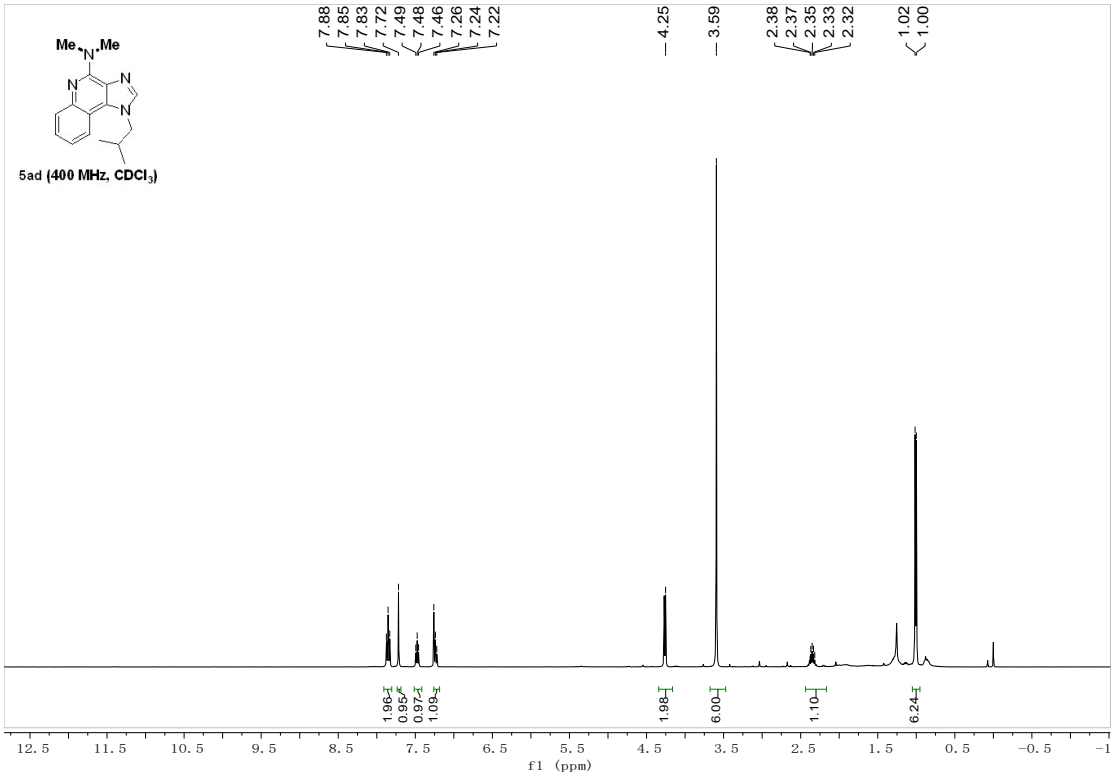

148.9
131.2
122.1
119.7
113.0
109.3
77.3
77.0
76.7
40.8
Me
N
Me
5r (100 MHz, CDCl3)
f1 (ppm)

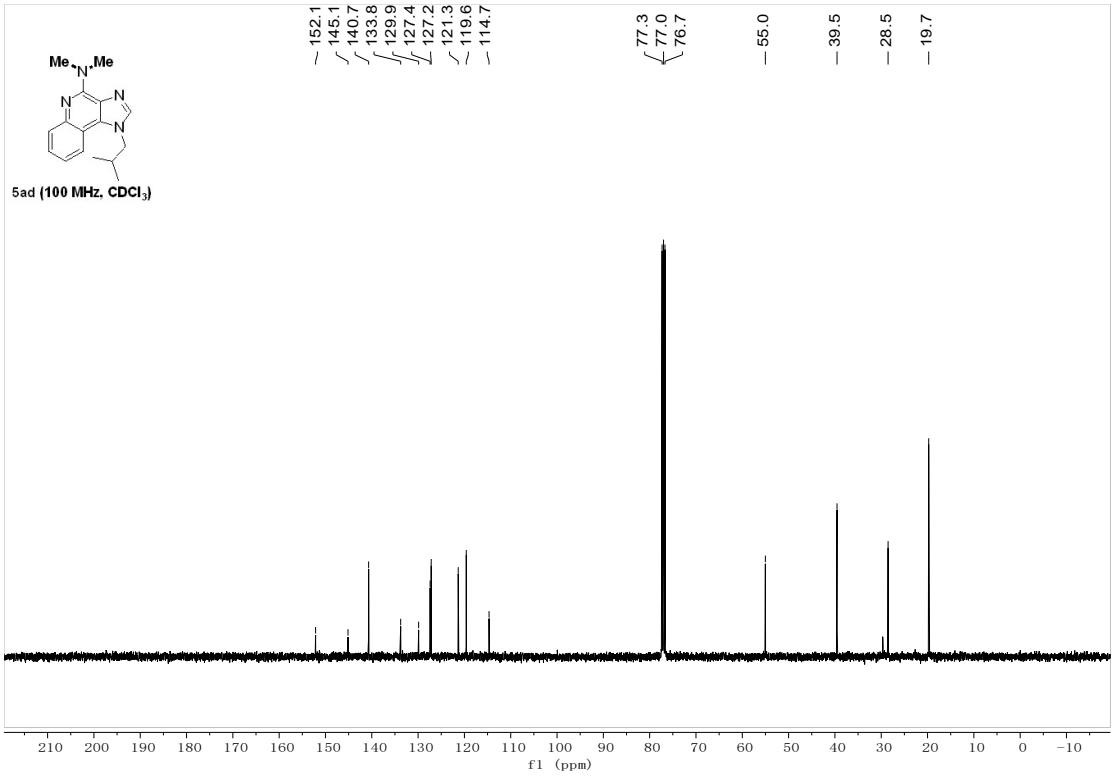

7.75
7.73
7.41
7.40
7.26
7.25
7.24
7.16
7.16
7.00
7.00
6.98
6.97
3.02
Me
N
Me
S
5s (400 MHz, CDCl3)
0.98
0.95
1.17
0.99
0.99
6.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

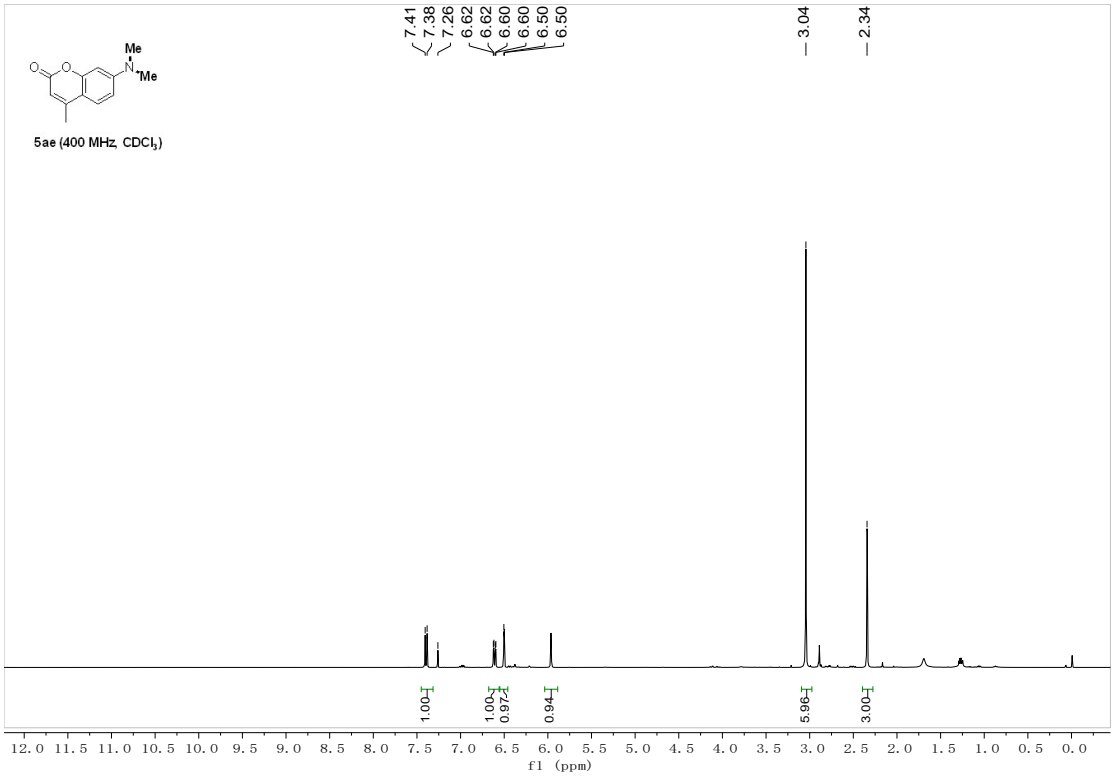

148.7
140.9
129.0
126.7
123.5
122.5
113.3
106.3
77.3
77.0
76.7
41.4
Me
N
Me
S
5s (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

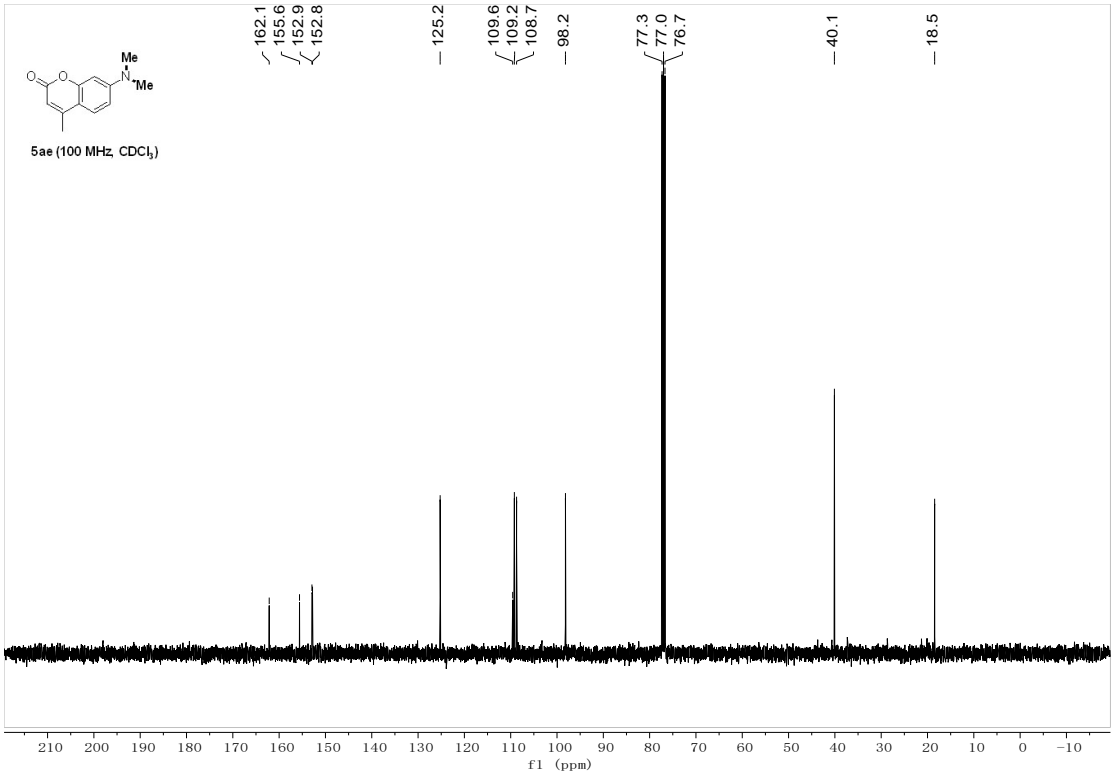

7.84
7.82
7.79
7.77
7.54
7.52
7.37
7.35
7.33
7.31
7.29
7.26
6.89
6.89
6.80
6.80
6.78
6.78
3.06
Me
N
Me
O
5t (400 MHz, CDCl3)
1.00
1.00
0.98
2.00
0.98
1.00
6.00
f1 (ppm)

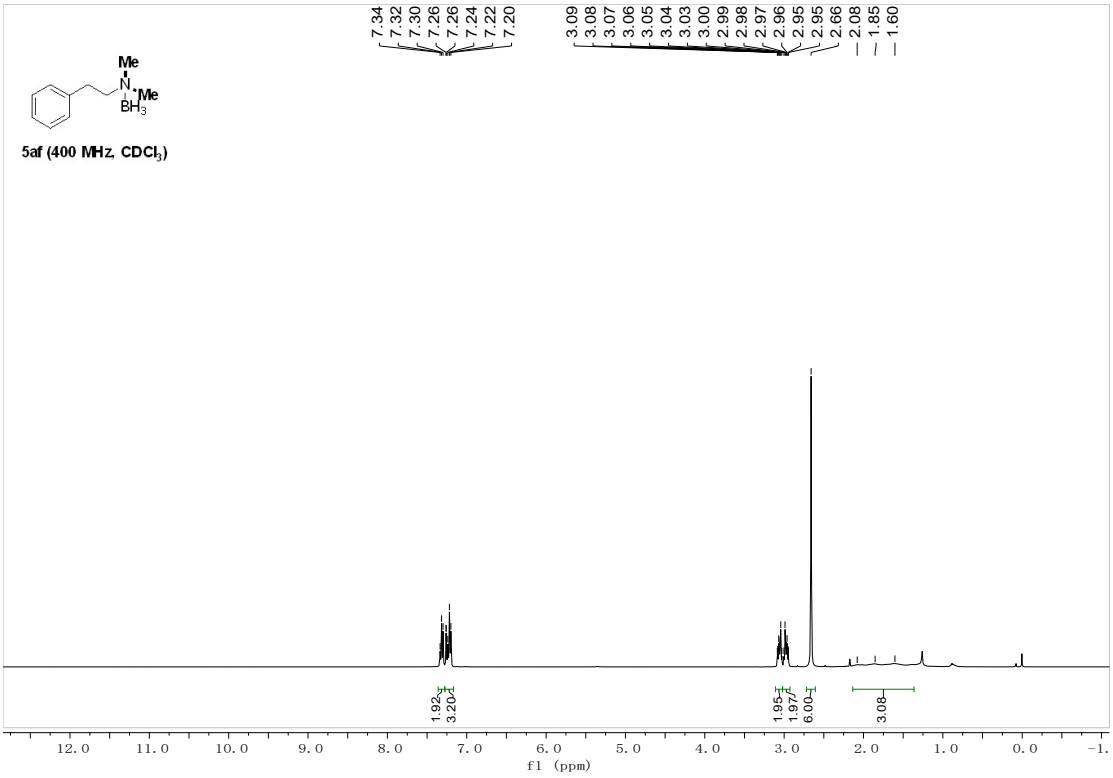

158.5
155.9
151.0
125.1
124.8
122.5
120.9
119.2
113.6
111.1
108.9
94.7
77.4
77.1
76.8
41.0
Me
N
Me
O
5t (100 MHz, CDCl3)
f1 (ppm)

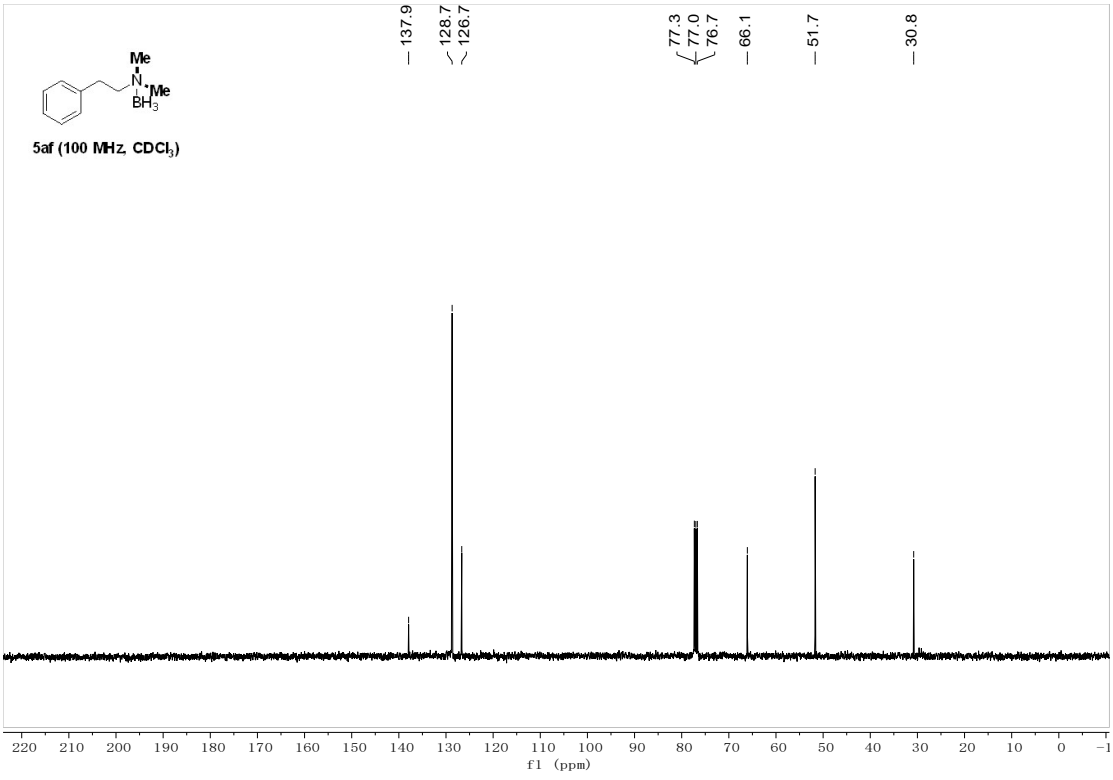

7.88
7.85
7.83
7.72
7.49
7.48
7.46
7.26
7.24
7.22
4.25
3.59
2.38
2.37
2.35
2.33
2.32
1.02
1.00
Me
N
Me
5ad (400 MHz, CDCl3)
1.96
0.95
0.97
1.09
1.98
6.00
1.10
6.24
f1 (ppm)

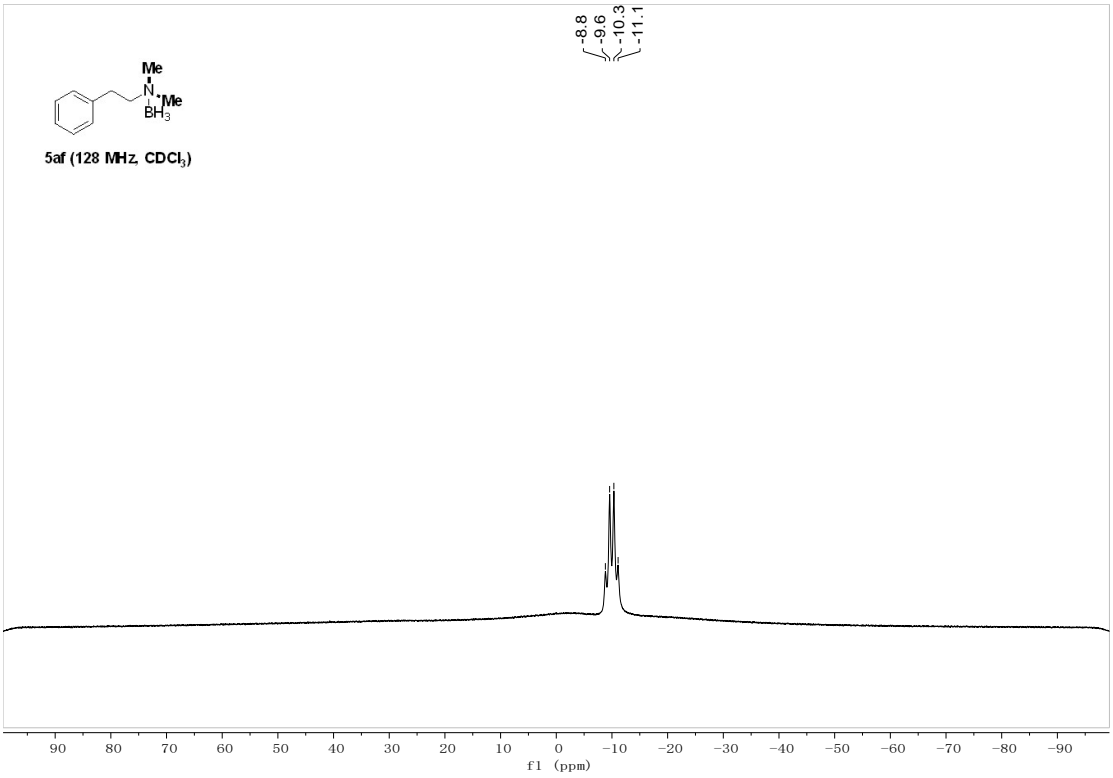

152.1
145.1
140.7
133.8
129.9
127.4
127.2
121.3
119.6
114.7
77.3
77.0
76.7
55.0
39.5
28.5
19.7
Me
N
Me
5ad (100 MHz, CDCl3)
f1 (ppm)

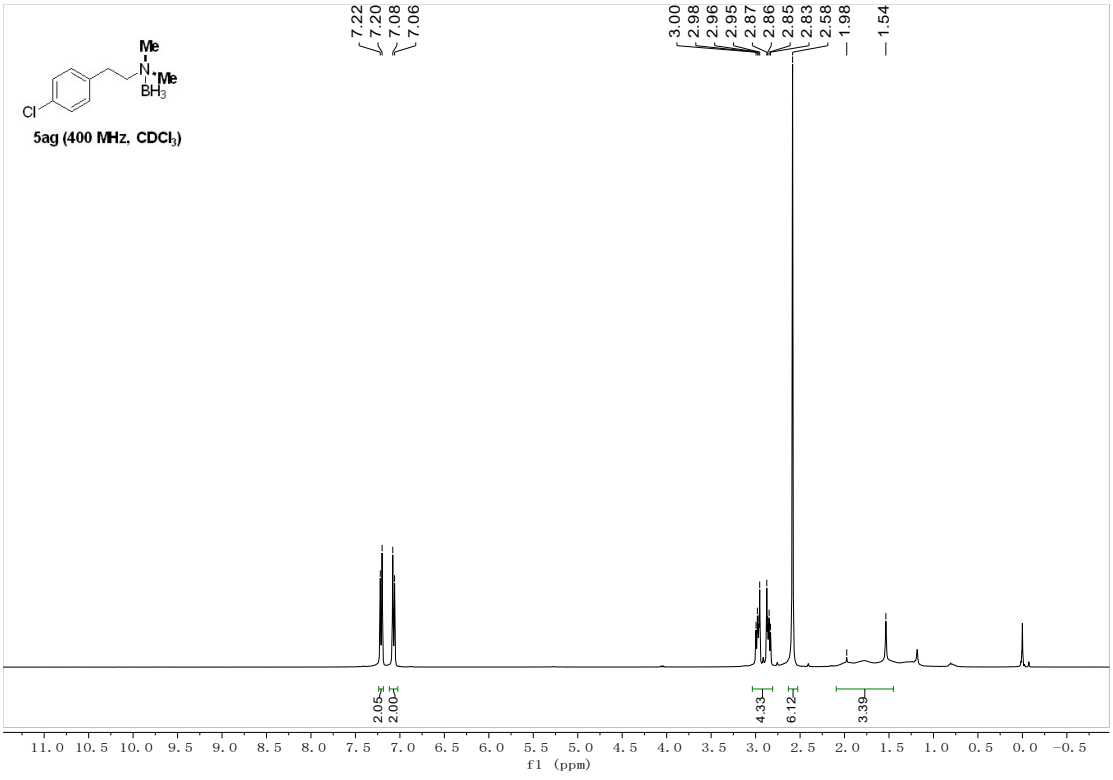

Me
N
Me
O
O
5ae (400 MHz, CDCl3)
7.41
7.38
7.26
6.62
6.62
6.60
6.60
6.50
6.50
3.04
2.34
1.00
1.00
0.97
0.94
5.96
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

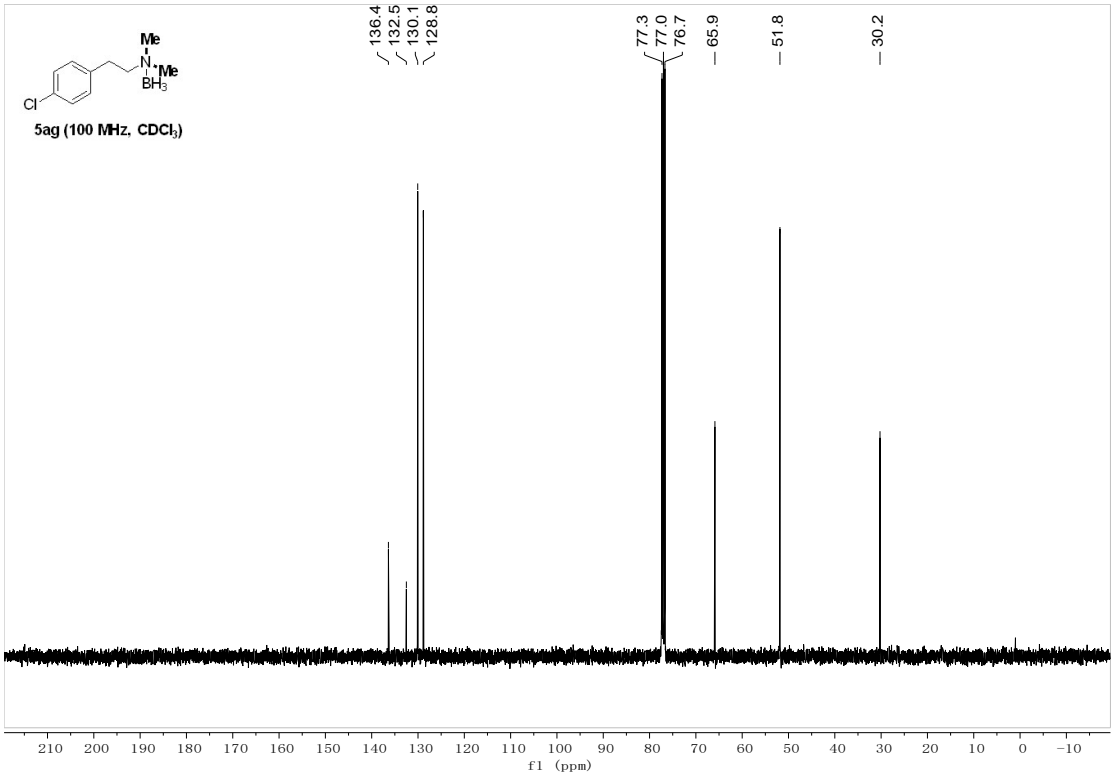

Me
N
Me
O
O
5ae (100 MHz, CDCl3)
162.1
155.6
152.9
152.8
125.2
109.6
109.2
108.7
98.2
77.3
77.0
76.7
40.1
18.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

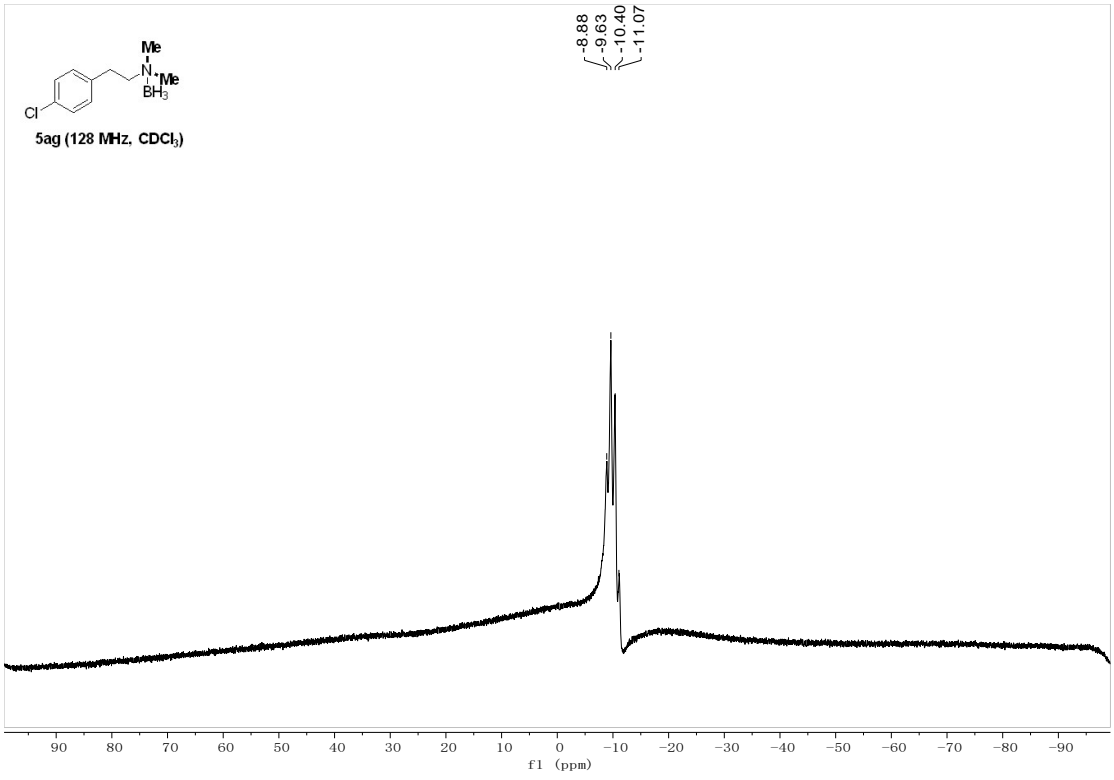

7.34
7.32
7.30
7.26
7.26
7.24
7.22
7.20
3.09
3.08
3.07
3.06
3.05
3.04
3.03
3.00
2.99
2.98
2.97
2.96
2.95
2.95
2.66
2.08
1.85
1.60
Me
N
Me
BH3
5af (400 MHz, CDCl3)
1.92
3.20
1.95
1.97
6.00
3.08
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

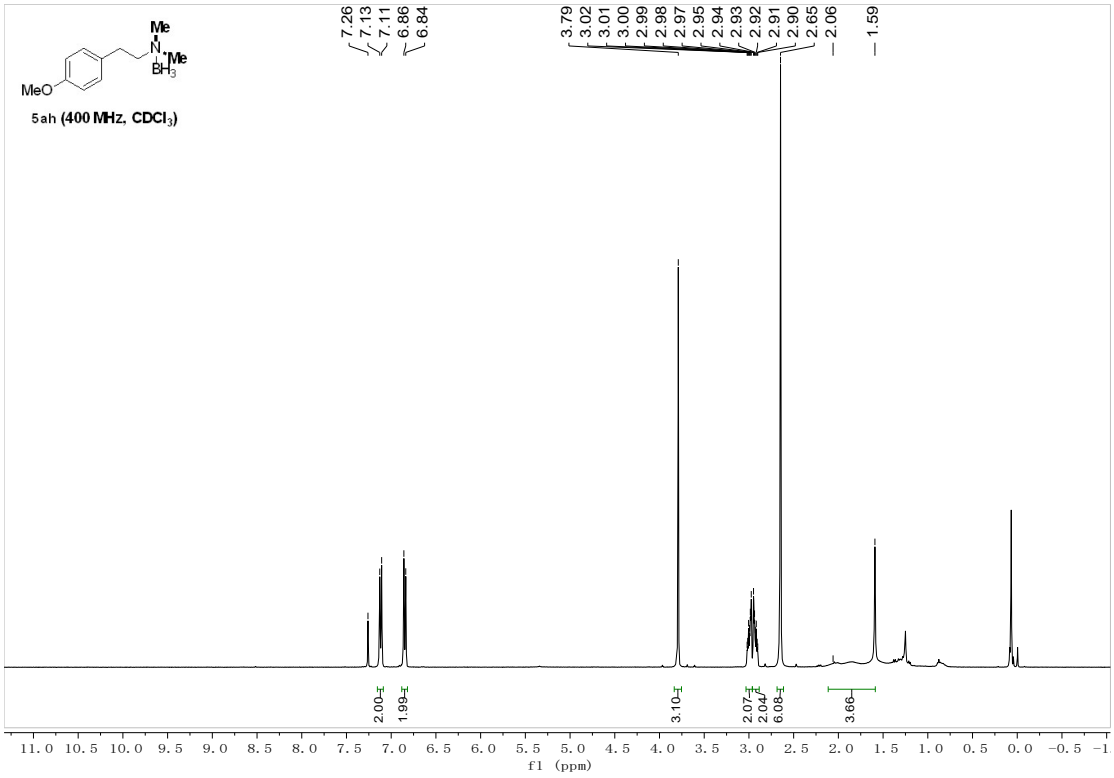

137.9
128.7
126.7
77.3
77.0
76.7
66.1
51.7
30.8
Me
N
Me
BH3
5af (100 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

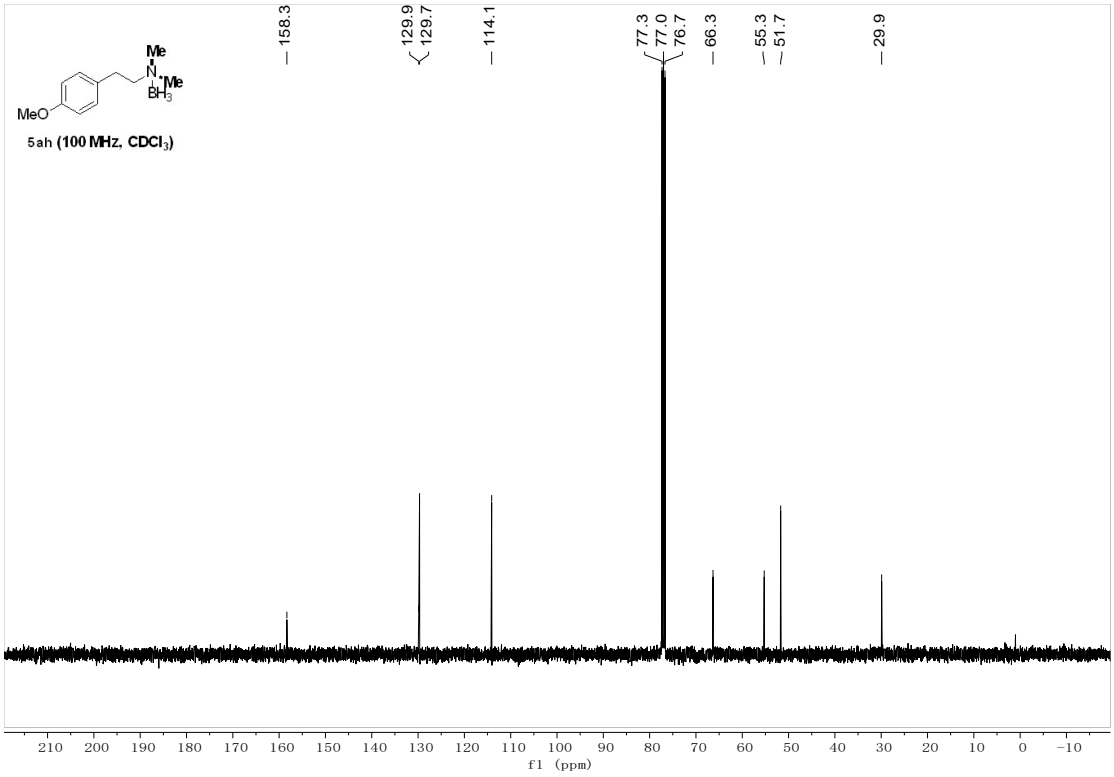

-8.8
-9.6
-10.3
-11.1
Me
N
Me
BH3
5af (128 MHz, CDCl3)
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

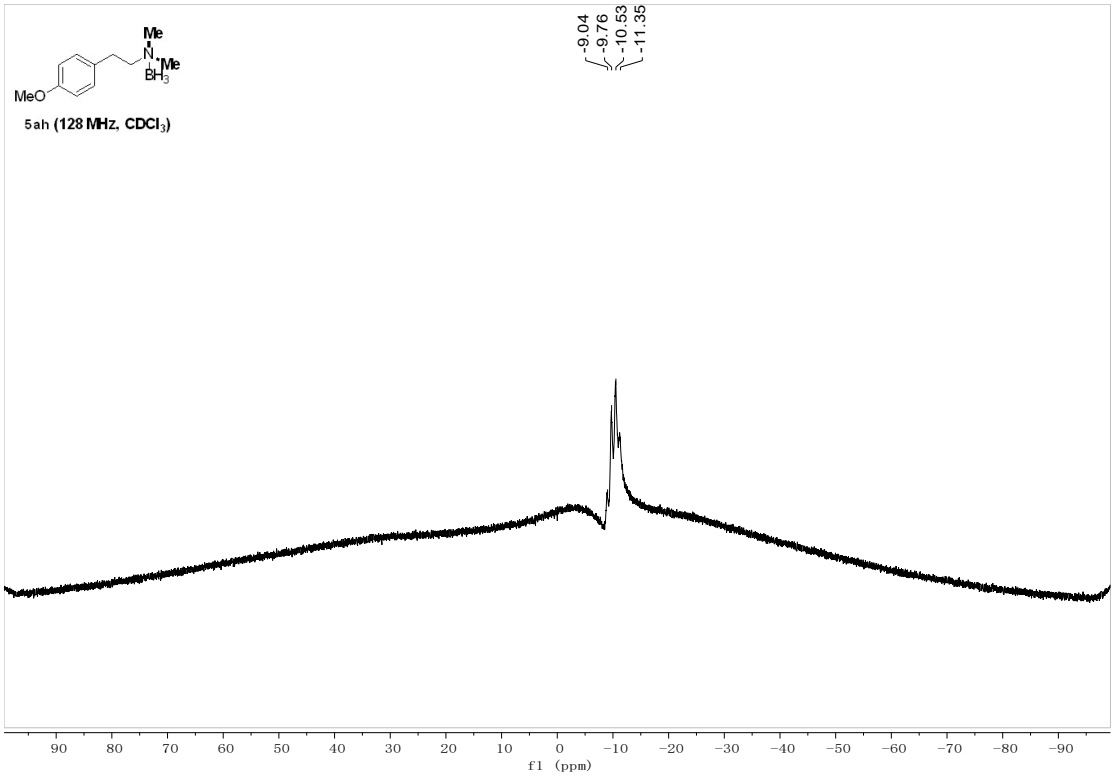

7.22
7.20
7.08
7.06
3.00
2.98
2.96
2.95
2.87
2.86
2.85
2.83
2.58
1.98
1.54
Me
N
Me
BH3
Cl
5ag (400 MHz, CDCl3)
2.05
2.00
4.33
6.12
3.39
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

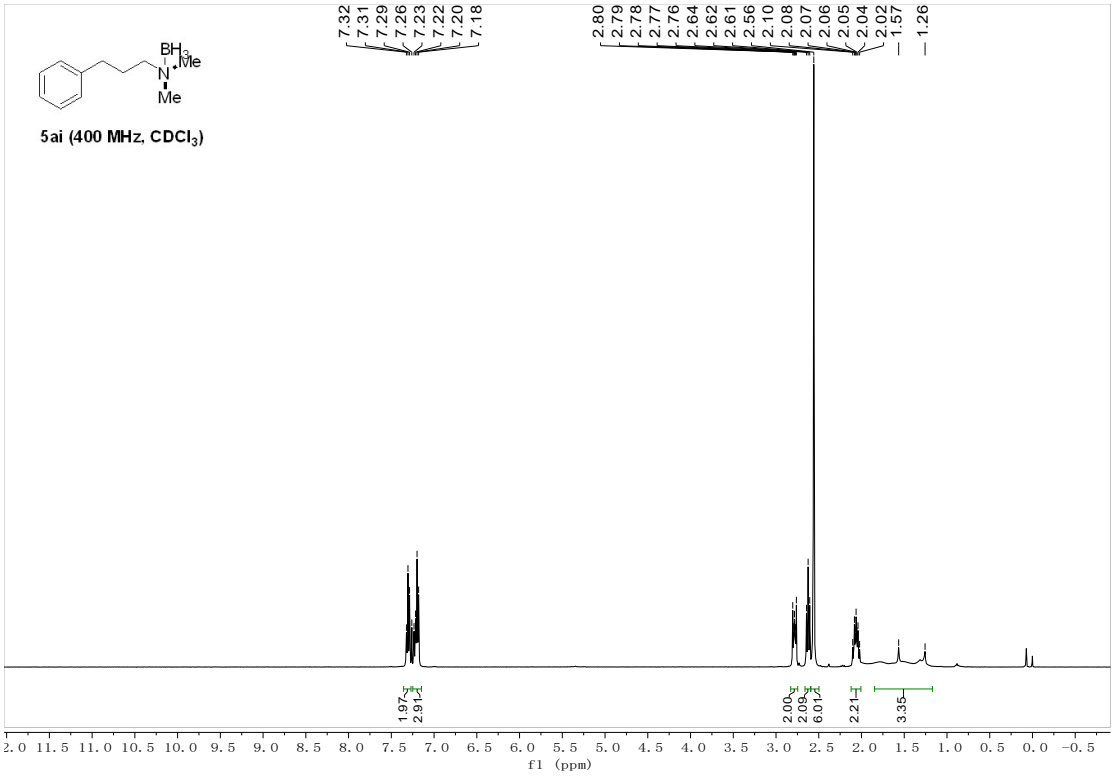

Me
N
Me
BH3
Cl
5ag (100 MHz, CDCl3)
136.4
132.5
130.1
128.8
77.3
77.0
76.7
65.9
51.8
30.2
f1 (ppm)

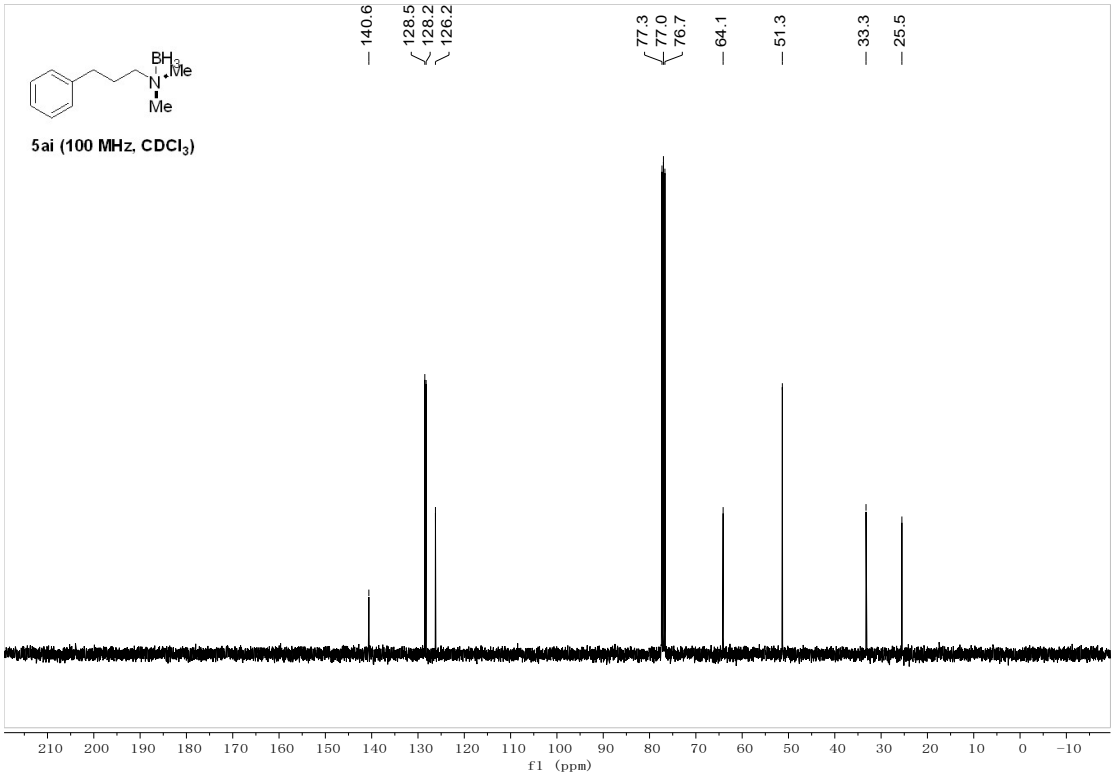

Me
N
Me
BH3
Cl
5ag (128 MHz, CDCl3)
-8.88
-9.63
-10.40
-11.07
f1 (ppm)

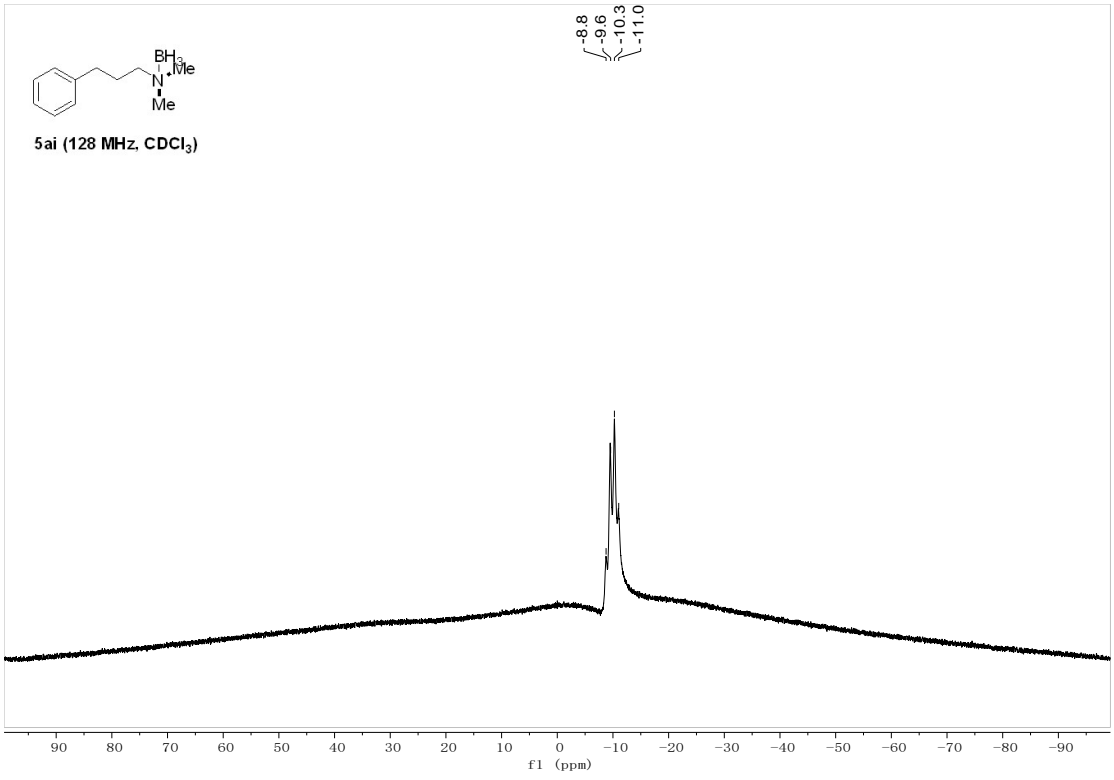

Me
N
Me
BH3
MeO
5ah (400 MHz, CDCl3)
7.26
7.13
7.11
6.86
6.84
3.79
3.02
3.01
3.00
2.99
2.98
2.97
2.95
2.94
2.93
2.92
2.91
2.90
2.65
2.06
1.59
2.00
1.99
3.10
2.07
2.04
6.08
3.66
f1 (ppm)


Me
N
Me
BH3
MeO
5ah (100 MHz, CDCl3)
158.3
129.9
129.7
114.1
77.3
77.0
76.7
66.3
55.3
51.7
29.9
f1 (ppm)


Me
N
Me
BH3
MeO
5ah (128 MHz, CDCl3)
-9.04
-9.76
-10.53
-11.35
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)


BH3
Me
N
Me
Me
5ai (400 MHz, CDCl3)
7.32
7.31
7.29
7.26
7.23
7.22
7.20
7.18
2.80
2.79
2.78
2.77
2.76
2.64
2.62
2.61
2.56
2.10
2.08
2.07
2.06
2.05
2.04
2.02
1.57
1.26
1.97
2.91
2.00
2.09
6.01
2.21
3.35
2.0 11.5 11.0 10.5 10.0 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
f1 (ppm)


140.6
128.5
128.2
126.2
77.3
77.0
76.7
64.1
51.3
33.3
25.5
BH3
Me
N
Me
5ai (100 MHz, CDCl3)
f1 (ppm)


-8.8
-9.6
-10.3
-11.0
BH3
Me
N
Me
5ai (128 MHz, CDCl3)
f1 (ppm)