Supporting Information for

UiO-type Metal-Organic Frameworks with NHC or metal-NHC Functionalities for *N*-Methylation Using CO_2 as the Carbon Source

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Experimental Procedures

General Methods

The starting chemicals and solvents were purchased from commercial suppliers (Sigma-Aldrich, Alfa Aesar, TCI, and Adamas-beta) without further purification. Elemental analyses (EA) for C, H, and N were operated on a FLASH EA 1112 (Cl for Dionex ICS3000) element analyser. Powder X-ray diffraction (PXRD) patterns were recorded using a BRUKER D2 PHASER X-ray diffractometer equipped with a Cu sealed tube (λ = 1.54184 Å) at 30 kV and 10 mA with a scan speed of 0.2 s/step, a step size of 0.02 ° in 2θ, and a 2θ range of 3.5~40 °. Scanning electron microscopy (SEM) was carried out on a Pheom Pro instrument using a 10 kV energy source under vacuum. Metallic element content detection for Zr, Zn and Cu were carried out on a PERKIN ELMER OPTIMA 8300 inductively coupled plasma optical emission spectrometer (ICP-OES). X-ray photoelectron spectroscopy (XPS) was performed on an AXIS ULTRA DLD spectrometer, and the data was analyzed by the PSPEAK 41 software. Nuclear magnetic resonance (NMR) spectra were carried out on an ADVANCE III HD spectrometer (600 MHz); chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for tetramethylsilane (TMS). GC-MS data were tested with ThermoFisher Trace 1300-ISQ (EI). UiO-68-NHC[S1], $IPrZnCl_2$[S2] and IPrCuCl[S3] was synthesized according to the previously reported procedure.

Experimental

Synthesis of UiO-68-(NHC)ZnCl$_2$. $ZnCl_2$ (0.273 g, 2 mmol) was dissolved in a round bottom flask with 5 ml CH_3OH, following by the introduction of UiO-68-NHC (122 mg, 1 mmol eq. of NHC-ligand). The flask was fixed onto a mechanical shaker with a constant shaking rate of 120 c.p.m. at 60 ℃ for 1 h. The solids were isolated via centrifugation and washed thoroughly with fresh DMA methanol (3×10 mL). The solids were left to soak in methanol for characterization or catalysis.

Synthesis of UiO-68-(NHC)CuCl. CuCl(0.198 g, 2 mmol) was dissolved in a round bottom flask with 5 ml CH_3OH, following by the introduction of UiO-68-NHC (122 mg, 1 mmol NHC-ligand). The flask was fixed onto a mechanical shaker with a constant shaking rate of 120 c.p.m. at 60 ℃ for 1 h. The solids were isolated via centrifugation and washed thoroughly with fresh DMA (3×10 mL) and methanol (3×10 mL). The solids were left to soak in methanol for characterization or catalysis.

Gas Sorption. Fresh UiO-68-(NHC)$ZnCl_2$/UiO-68-(NHC)CuCl (ca. 30 mg) were prepared and washed with benzene (3x5 ml) and then soaked in benzene overnight, followed by isolation and loading into a pre-weighted BET sample tube. The samples were degassed at 0 ℃ in an ice bath for 12 h and at room temperature for another 12 h, and finally heated at 60 ℃ for 6 h on a MICROMERITICS ASAP

2020 adsorption analyser under the outgas rate of less than 5 mm Hg. The sample tube was re-weighed to obtain a consistent dry mass for the degassed sample. Gas sorption isotherms were recorded volumetrically at 77 K for N_2, 273 K and 298 K for CO_2, respectively. Brunauer-Emmett-Teller (BET) surface area data were calculated using N_2 adsorption data at 77 K in the relative pressure range of 0.05~0.3 P/P_0. The exact surface area was averaged by the analyses of three independent samples. Isosteric heat of adsorption (Qst) for CO_2 were calculated by applying the Clausius-Clapeyron equation:

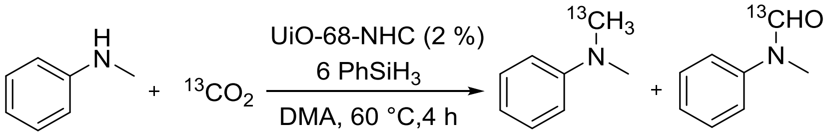
$$\left(\frac{\delta \ln P}{\delta T}\right)_\theta = \frac{Qst}{RT^2}$$

to two sets of adsorption data collected at two different temperatures, in which P = equilibrium pressure, T = temperature, θ = adsorption capacity devided by surface area, and R = 0.00831 kJ/mol·K.

Methylation of Amines. UiO-68-NHC (13 mg, containing 0.00529 mmol NHC according to the formula of $Zr_6O_4(OH)_4(tpdc\text{-}NH_2)_{3.78}(NHC)_{2.22}$) was added to a round bottom flask with 2 mL of solvent, then amine (0.25 mmol) and phenylsilane (380 ul, 1.5 mmol) was added to the flask, subsequently. The flask was sealed, and CO_2 was introduced into the flask via a balloon. The flask was fixed onto a mechanical shaker with a constant shaking rate of 120 c.p.m. at 60 ℃ for 2 h to complete the catalytic reaction. The catalyst was separated by filtration, rinsed by DMA (3×10 mL) for the next run. The reaction mixture was diluted with dichloromethane before the GC-MS analysis. The catalytic yields were determined by GC/MS using biphenyl as an internal standard. The desired products were obtained by flash chromatography on silica gel with petroleumether/ethyl acetate.

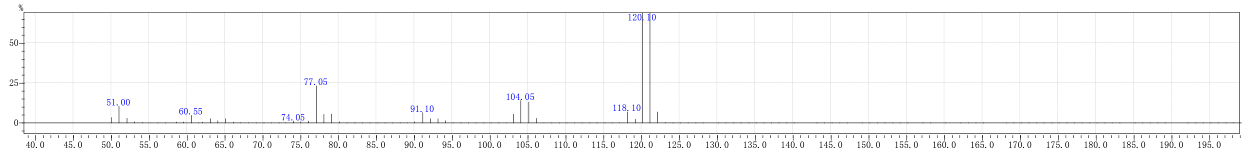
Methylation of 4-(methylamino)benzoic acid. UiO-68-(NHC)$ZnCl_2$/UiO-68-(NHC)CuCl (15 mg, containing 0.011~0.0113 mmol metal-NHC sites) was added to a round bottom flask with 2 mL of DMA, then 4-(methylamino)benzoic acid (37.79 mg, 0.25 mmol) and phenylsilane (380 ul, 1.5 mmol) was added to the flask, subsequently. The flask was sealed, and CO_2 was introduced into the flask via a balloon. The flask was fixed onto a mechanical shaker with a constant shaking rate of 120 c.p.m. at 60 ℃ for 4 h to complete the catalytic reaction. The catalyst was separated by filtration, rinsed by DMA (3×10 mL), and then directly used for the next run. The solution pH was adjusted to 14 using 10 wt. % KOH aqueous solution. The solvents were then removed by vacuum evaperation, and the residue was washed by dichloromethane (3×10 mL) before tuning pH to 1 by 1 M HCl. The solids were isolated via centrifugation and dried under vacuum. The catalytic yields were determined by ^{1}H-NMR using methanol as an internal standard.

Labelling Experiment. UiO-68-NHC (13 mg) was added to a round bottom flask with 2 mL of solvent, then amine (0.25 mmol) and phenylsilane (380 ul, 1.5 mmol) was added to the flask, subsequently. The flask was sealed, and $^{13}CO_2$ was introduced into the flask via a balloon. The flask was fixed onto a mechanical shaker with a constant shaking rate of 120 c.p.m. at 60 ℃ for 2 h to complete the catalytic reaction. The reaction mixture diluted with dichloromethane before the GC-MS analysis.

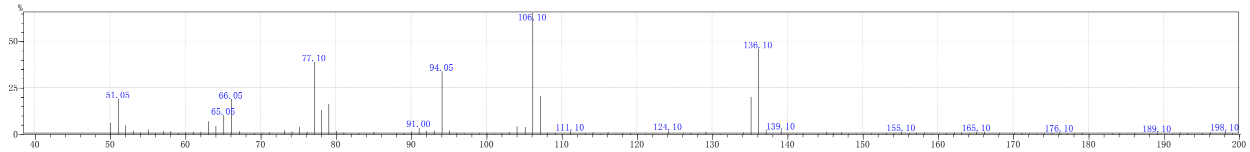


1a 1b 1c

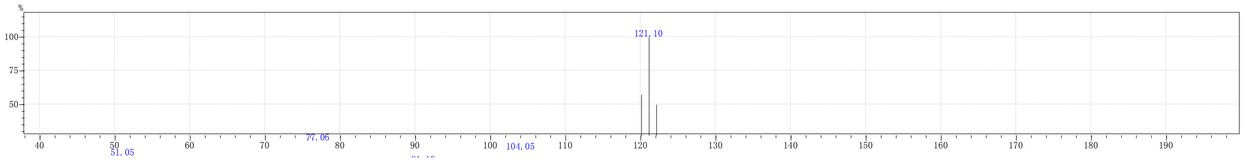
The EI-MS spectra of 13C-labelled 1b:



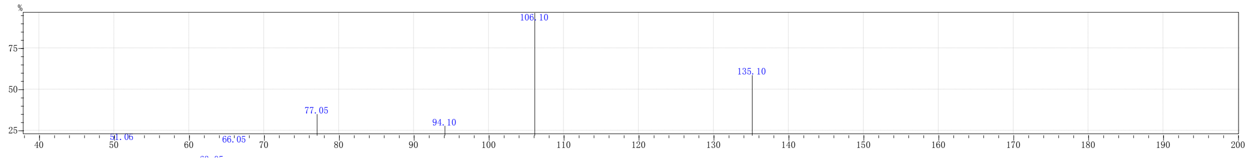
The EI-MS spectra of 13C-labelled 1c:



The EI-MS spectra of 1b:



The EI-MS spectra of 1c:



Kinetic Profile of the Conversion.

2 mL DMA and UiO-68-NHC (13 mg) was added to a round bottom flask, then 1.5 mmol phenylsilane and 0.25 mmol N-Methylaniline was introduced, and CO_2 was introduced into the flask via

a balloon. Eight reactions with the same reaction conditions but at different time intervals were performed. The flasks were fixed onto a mechanical shaker with a constant shaking rate of 120 c.p.m. at 60 ℃ to complete the catalytic reaction in 15 min, 30 min, 45 min, 60 min, 75 min, 90 min, 105 min, 120 min. The reaction was filtered, followed by GC-MS studies.

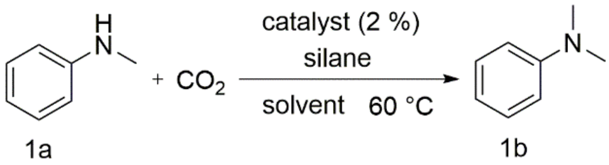
Similarity, UiO-68-(NHC)$ZnCl_2$/UiO-68-(NHC)CuCl (15 mg) and 2 mL DMA was added to a round bottom flask, then 1.5 mmol phenylsilane and 0.25 mmol 4-(methylamino)benzoic acid was introduced, and CO_2 was introduced into the flask via a balloon. Eight reactions with the same reaction conditions but at different time intervals were performed. The flasks were fixed onto a mechanical shaker with a constant shaking rate of 120 c.p.m. at 60 ℃ to complete the catalytic reaction in 30 min, 60 min, 90 min, 120 min, 150 min, 180 min, 210 min, 240 min. The reaction was filtered, followed by ^{1}H-NMR studies. Hot-filtration test was performed in 30 min at reaction temperature by filtrating the MOF catalyst, which is shut down the converson of methylation of 4-(methylamino)benzoic acid.

Mercury Poisoning Tests. Hg(0) poisoning test was done in the methylation of 4-(methylamino)benzoic acid with phenylsilane and UiO-68-(NHC)$ZnCl_2$/UiO-68-(NHC)CuCl. After 120 min of reaction time, the conversion was determined by ^{1}H-NMR. Then mercury (0.5 ml) was added to the reaction mixture and the reaction was continued for another 120 min.

Capture and Exchange Experiments. UiO-68-(NHC)$ZnCl_2$/UiO-68-(NHC)CuCl (10 mg) was introduced to a flask with 4-(methylamino)benzoic acid (5 mmol) in DMSO-d_6 at 60 ℃ for 4 h. The solids were isolated via centrifugation and washed by methanol (3×10 mL), dried under vacuum, followed by ^{1}H-NMR studies.

Supporting Figures and Tables

Table S1. Optimization of N-methylation of N-methylaniline using CO_2.[a]



Entry	Reductant	Ratio[b]	Solvent	Temperature (°C)	Time(h)	Yield(%)[c]
1	$PhSiH_3$	1:2	DMA	60	2	50(2)
2	$PhSiH_3$	1:4	DMA	60	2	85(1)
3	$PhSiH_3$	1:6	DMA	60	2	92(1)
4	$PhSiH_3$	1:8	DMA	60	2	94(1)
5	$PhSiH_3$	1:2	DMA	60	12	52(3)
6	$PhSiH_3$	1:6	DMA	50	2	82(2)
7	$PhSiH_3$	1:6	DMA	70	2	76(3)
8	$PhSiHMe_2$	1:6	DMA	60	2	trace
9	H_2	---	DMA	60	12	0
10	$PhSiH_3$	1:6	toluene	60	2	0
11	$PhSiH_3$	1:6	THF	60	2	0
12	$PhSiH_3$	1:6	DMSO	60	2	trace
13	$PhSiH_3$	1:6	DMF	60	2	87(2)
14	$PhSiH_3$	1:6	CH_3CN	60	2	trace

[a]Reaction conditions: N-methylaniline (0.25 mmol), catalyst (2 mol% based on amines), $PhSiH_3$ (1.5 mmol), solvent (2 mL), CO_2 (1 atm), 60 °C, 2 h. [b]Molar ratio of amine: silane. [c]Yields determined by GC-MS using biphenyl as an internal standard, three independent trials, values in the parenthesis are error bars for catalysis.

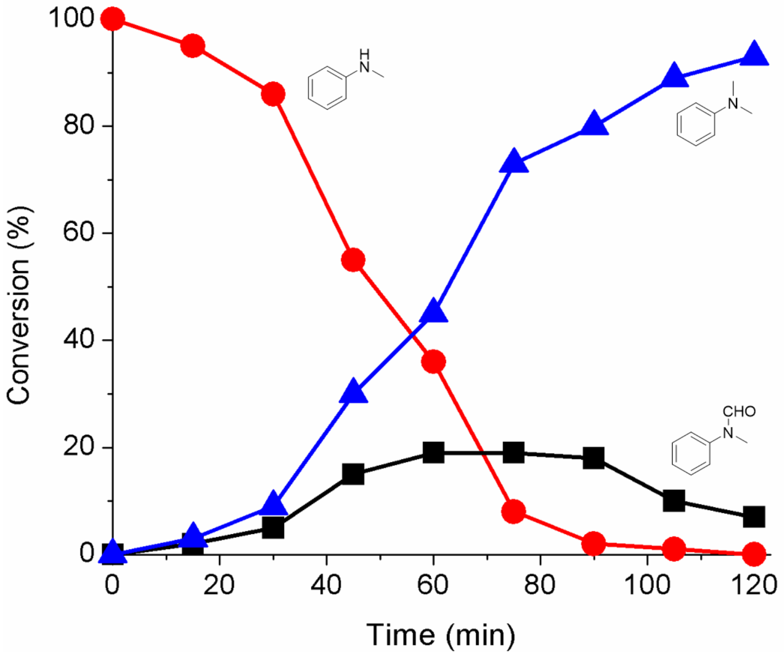


Figure S1. Kinetic profile of UiO-68-NHC catalyzed methylation of N-methylaniline.

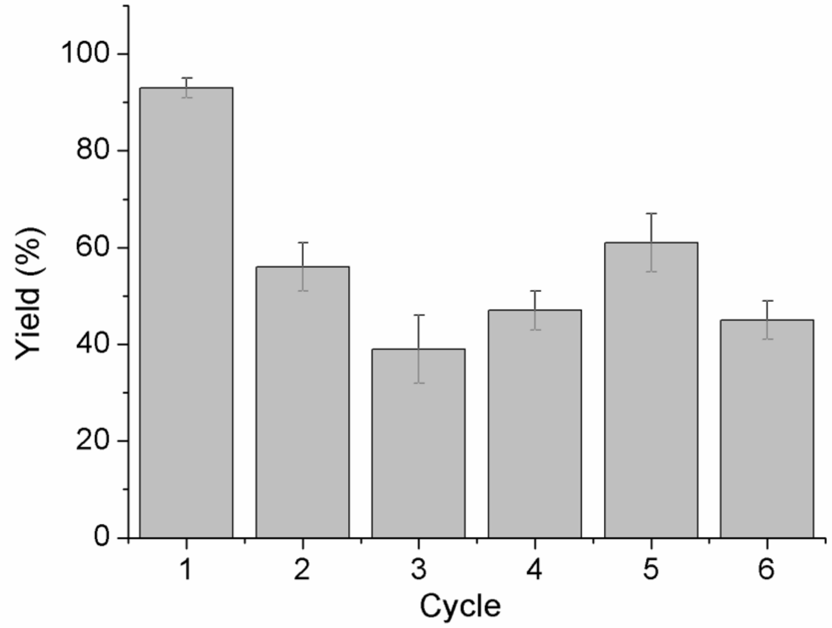


Figure S2. Recyclability test of UiO-68-NHC for methylation of N-methylaniline to N,N-dimethylaniline.

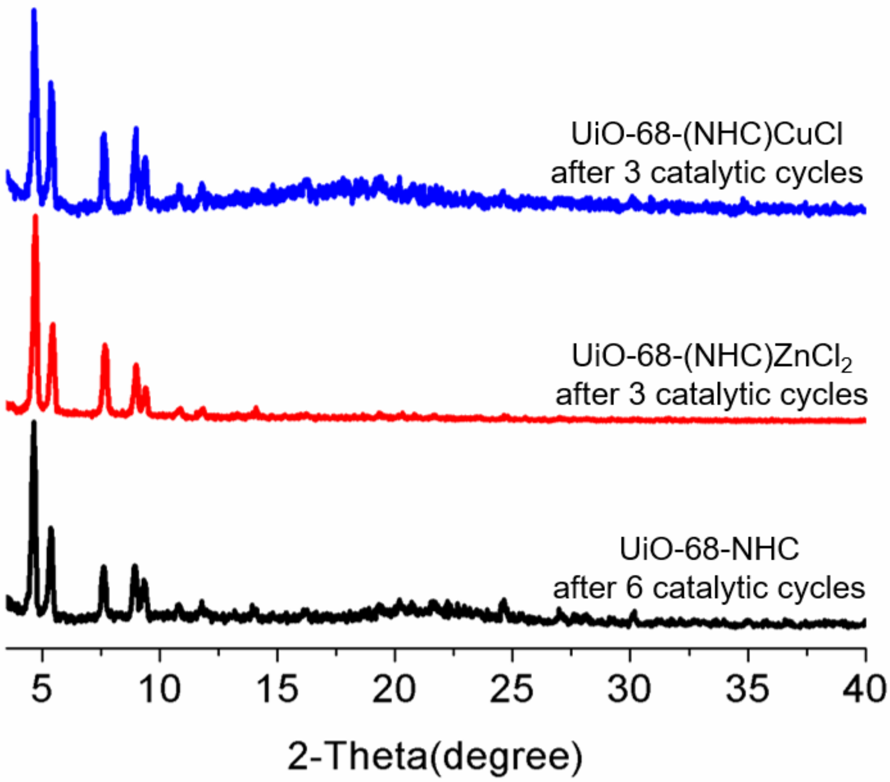


Figure S3. PXRD of UiO-68-NHC after 6 catalytic cycles, UiO-68-(NHC)ZnCl$_2$ after 3 catalytic cycles and UiO-68-(NHC)CuCl after 3 catalytic cycles.

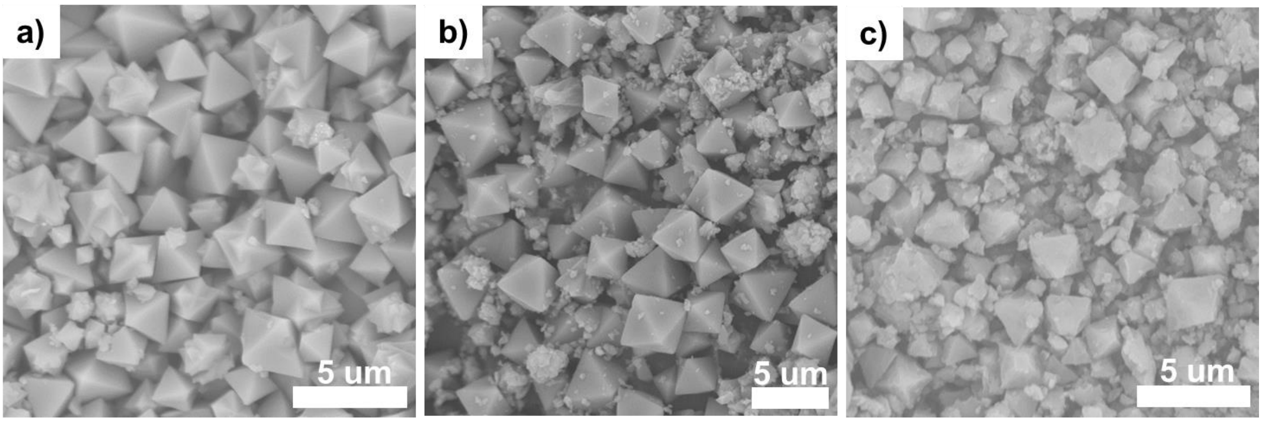


Figure S4. SEM images of UiO-68-NHC (a), UiO-68-NHC after 1 catalytic cycle (b), UiO-68-NHC after 6 catalytic cycles (c).

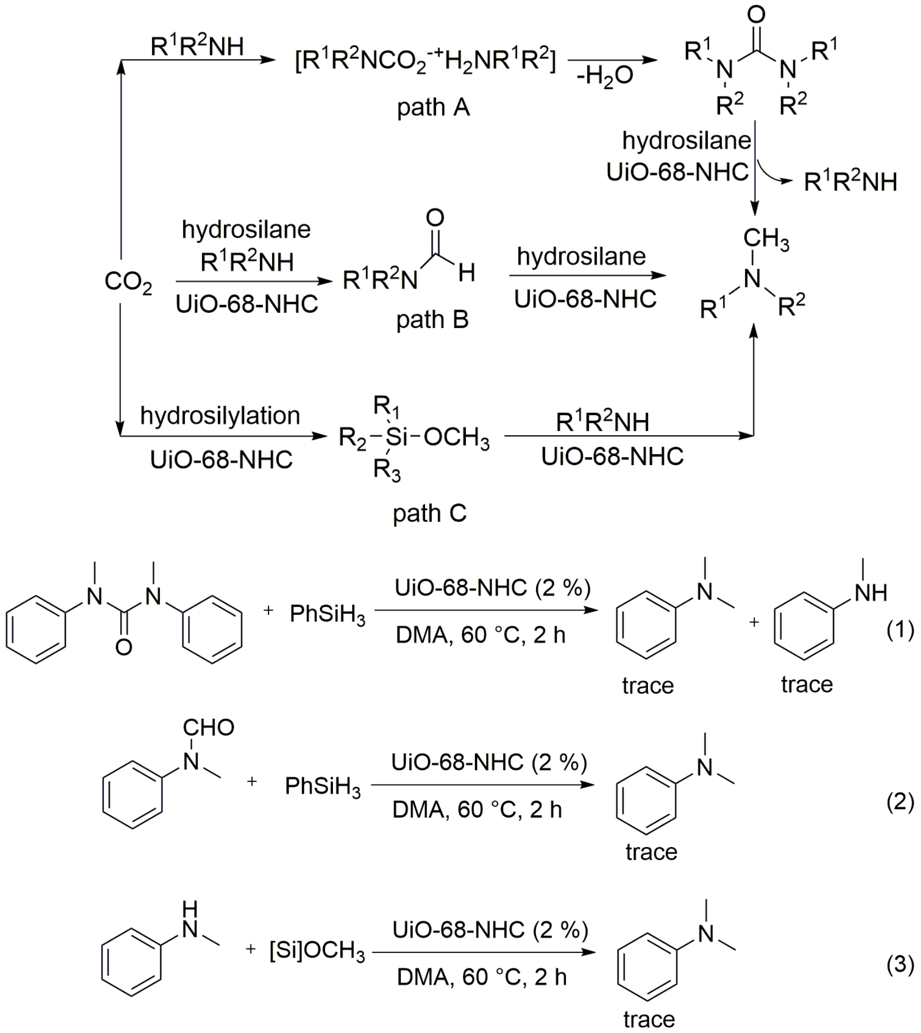


Figure S5. Top: three proposed pathways for methylation of amines with CO_2 catalyzed by UiO-68-NHC; bottom: the catalytic results of using different precursors to support the mechanistic studies of N-methylation catalyzed by UiO-68-NHC.

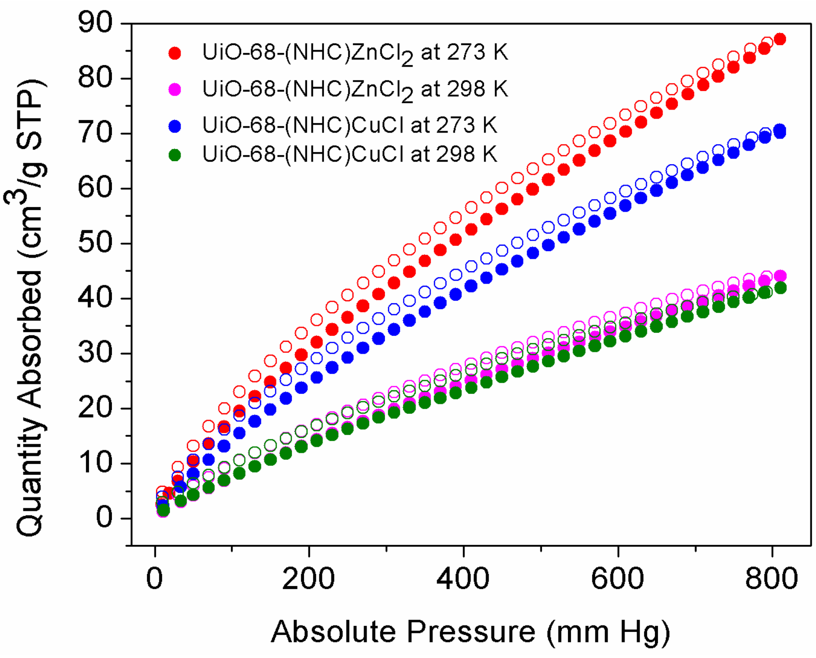


Figure S6. CO_2 sorption of UiO-68-(NHC)ZnCl$_2$ and UiO-68-(NHC)CuCl at 273 K and 298 K.

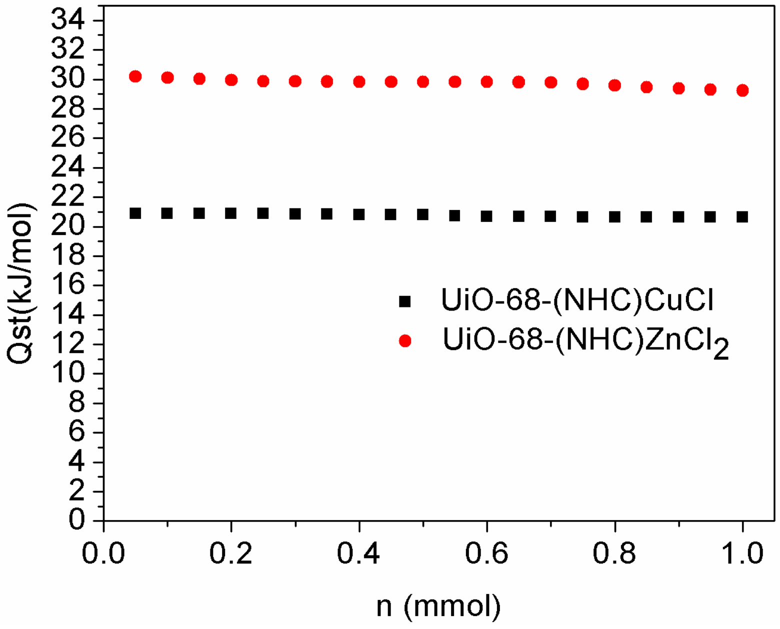


Figure S7. Qst profile of UiO-68-(NHC)ZnCl$_2$ (red) and UiO-68-(NHC)CuCl (black) for CO_2.

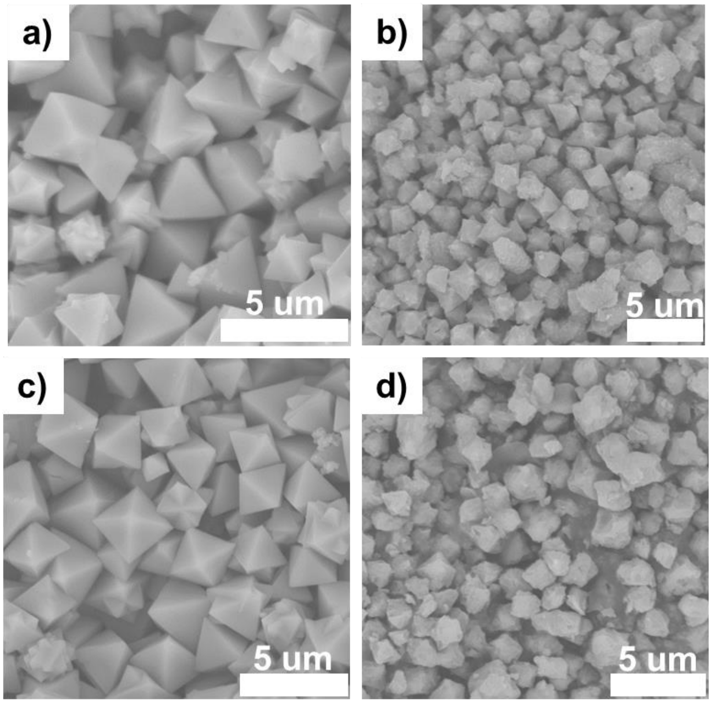


Figure S8. SEM images of UiO-68-(NHC)ZnCl$_2$ (a), UiO-68-(NHC)ZnCl$_2$ after 3 catalytic cycles (b), UiO-68-(NHC)CuCl (c) and UiO-68-(NHC)CuCl after 3 catalytic cycles (d).

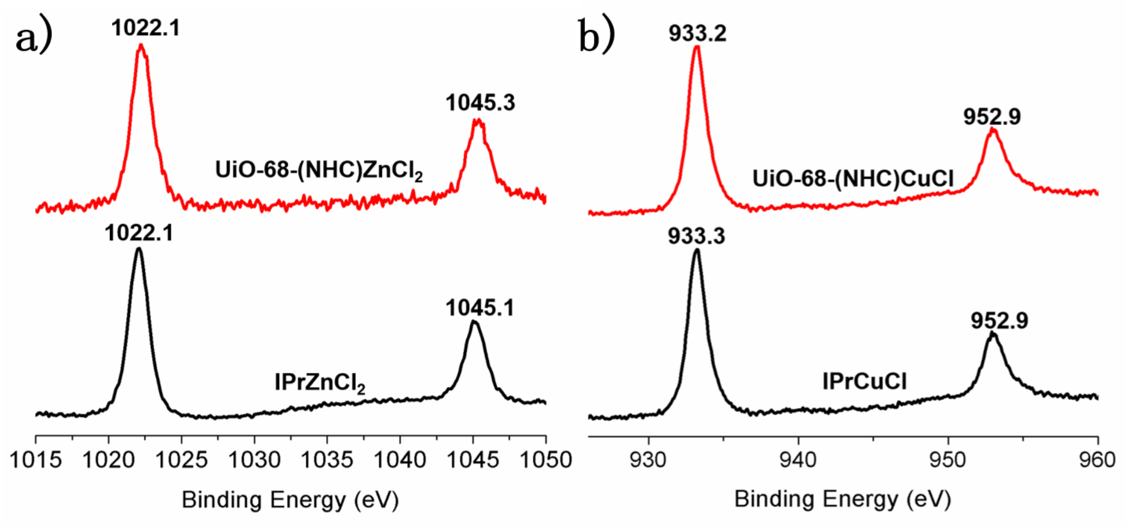


Figure S9. XPS spectra of IPrZnCl$_2$ and UiO-68-(NHC)ZnCl$_2$(a), IPrCuCl and UiO-68-(NHC)CuCl(b).

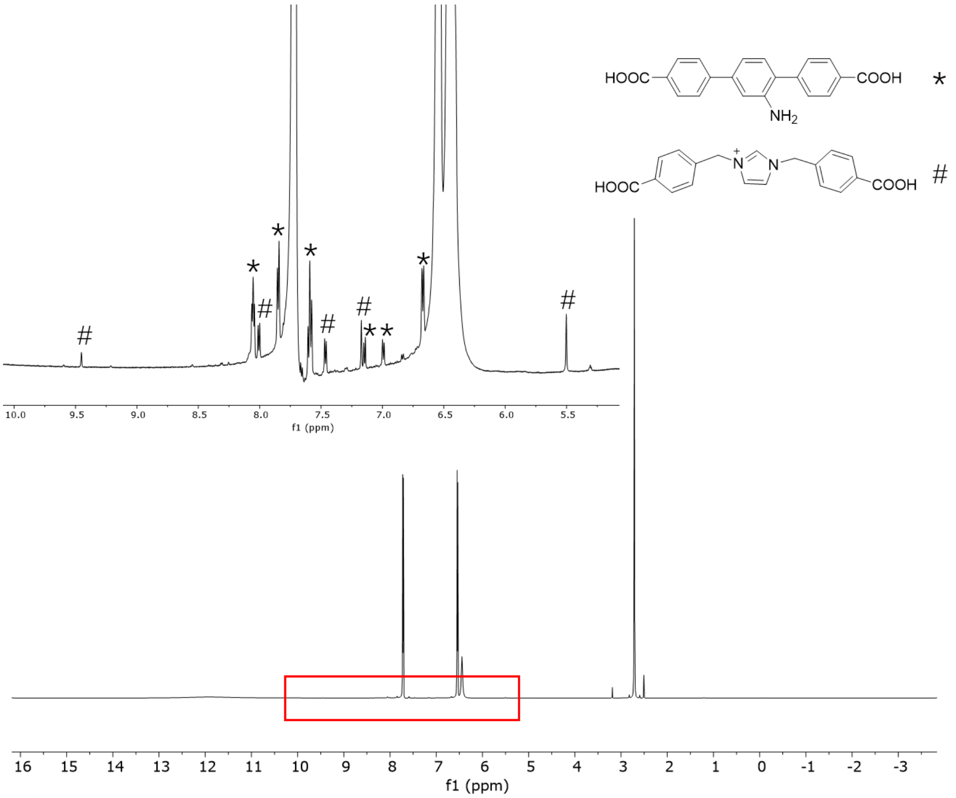


Figure S10. ^{1}H-NMR spectra of the supernatant between UiO-68-(NHC)ZnCl$_2$ and 100 equivalent of 4-(methylamino)benzoic acid.

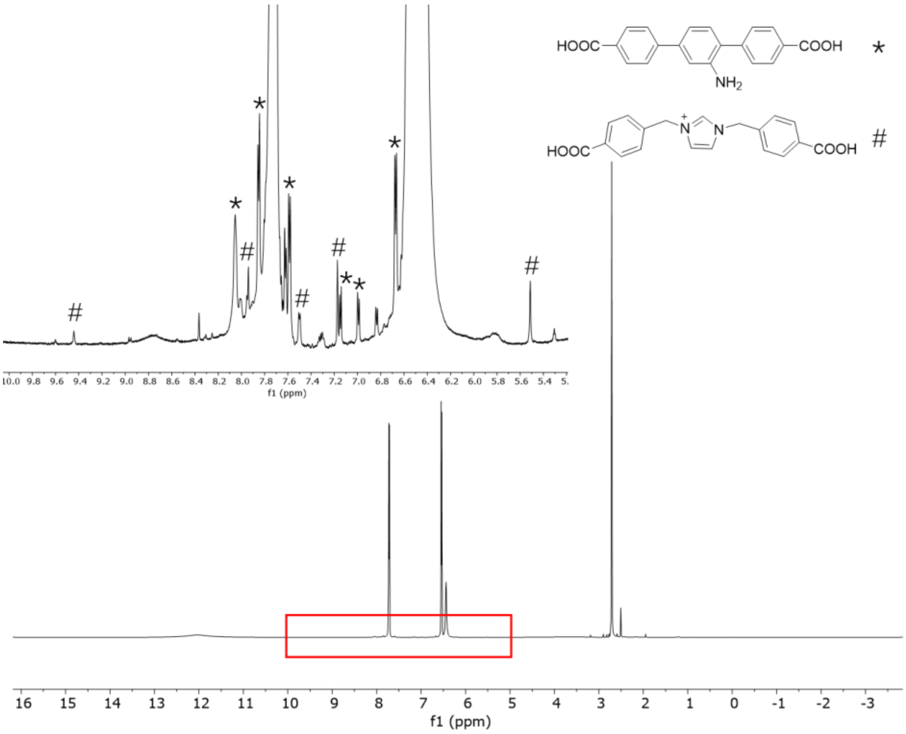


Figure S11. ^{1}H-NMR spectra of the supernatant between UiO-68-(NHC)CuCl and 100 equivalent of 4-(methylamino)benzoic acid.

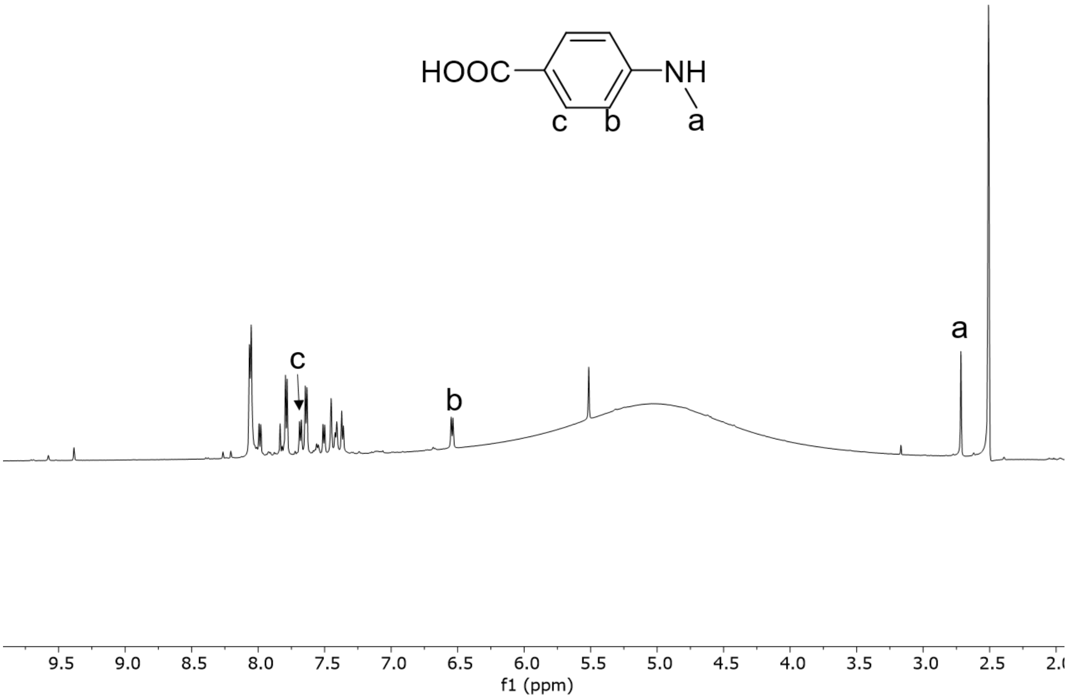


Figure S12. ^{1}H-NMR spectra of UiO-68-(NHC)$ZnCl_2$ digested with HF/DMSO-d_6 after soaking in 100 equivalent of 4-(methylamino)benzoic acid.

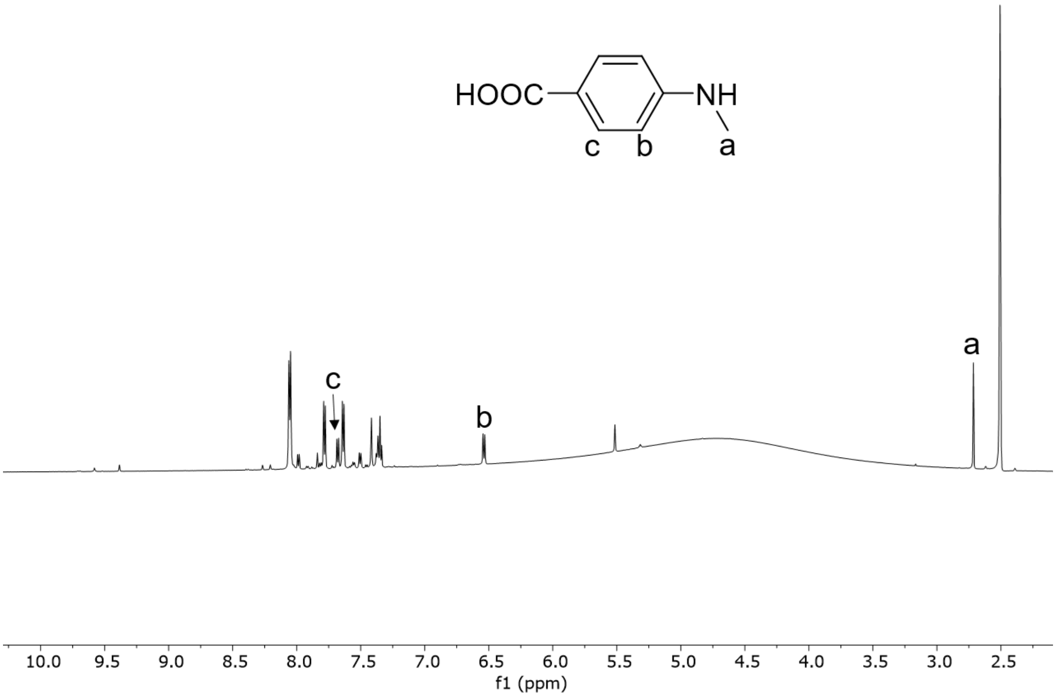


Figure S13. ^{1}H-NMR spectra of UiO-68-(NHC)CuCl digested with HF/DMSO-d_6 after soaking in 100 equivalent of 4-(methylamino)benzoic acid.

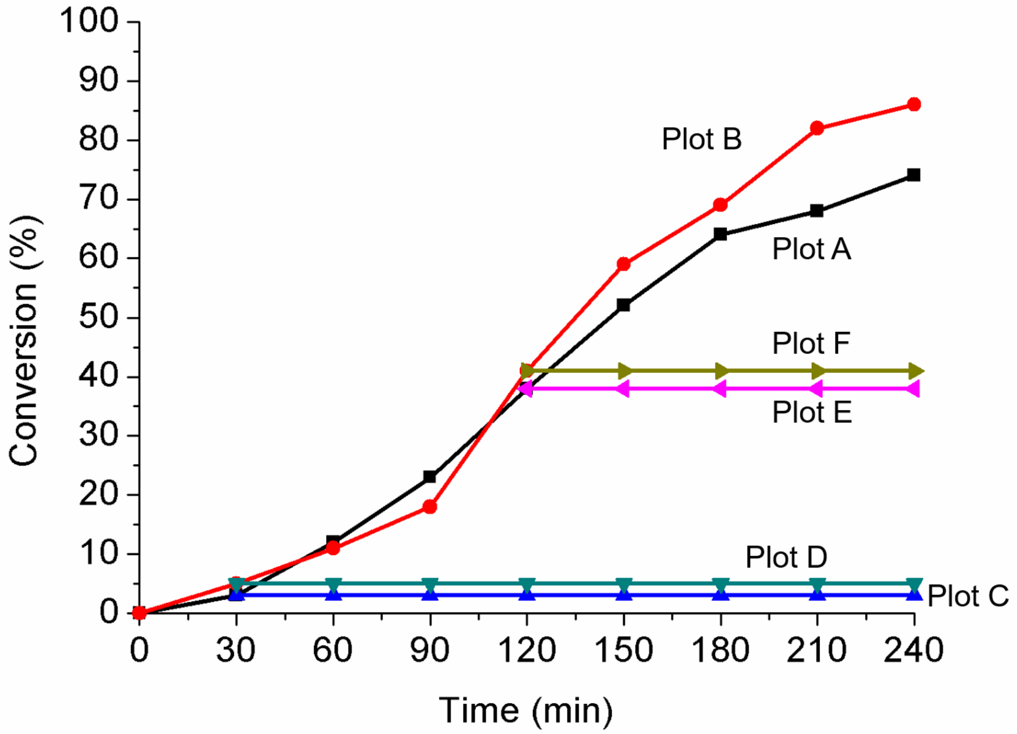


Figure S14. Kinetic profile of methylation of 4-(methylamino)benzoic acid catalyzed by UiO-68-(NHC)$ZnCl_2$ (plot A) or UiO-68-(NHC)CuCl (plot B). Hot filtration: removal of UiO-68-(NHC)$ZnCl_2$ (plot C) or UiO-68-(NHC)CuCl (plot D) after 30 min reaction. Mercury poisoning: Hg(0) was added to the reaction catalyzed by UiO-68-(NHC)$ZnCl_2$ (plot E) or UiO-68-(NHC)CuCl (plot F) at 120 min.

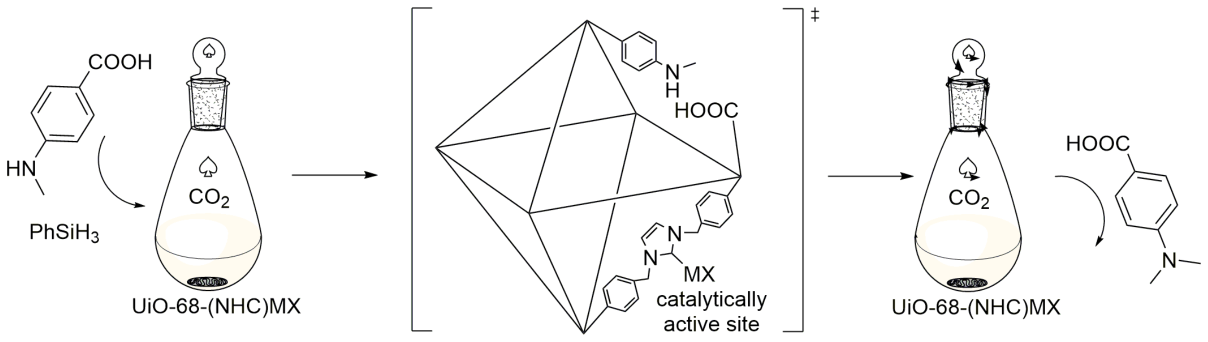


Figure S15. Scheme of MOF-catalyzed N-methylation of 4-(methylamino)benzoic acid.

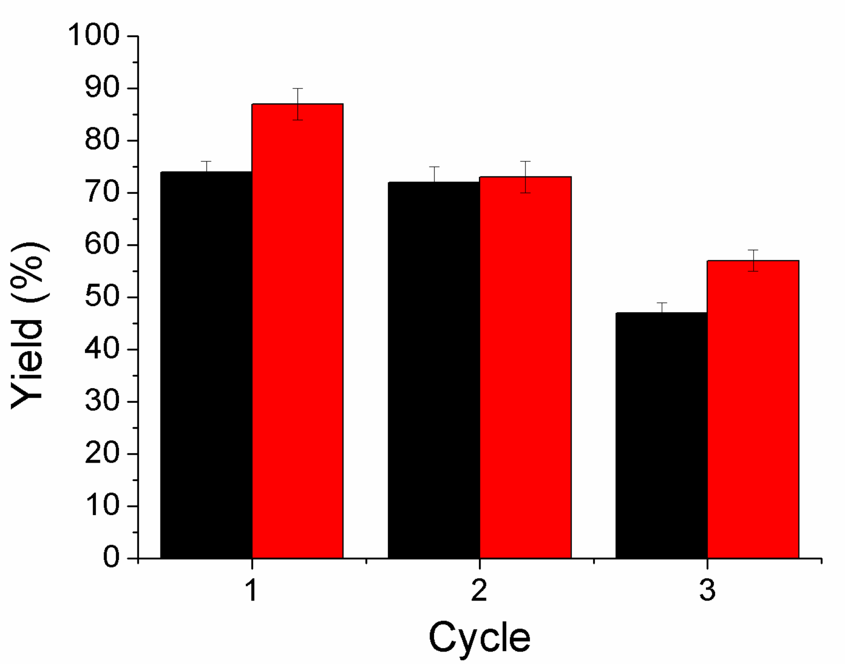
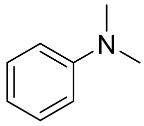


Figure S16. Recyclability test of UiO-68-(NHC)ZnCl$_2$(black)/UiO-68-(NHC)CuCl(red) catalyzing methylation of 4-(methylamino)benzoic acid.



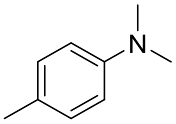
1b, 93%

N,*N*-dimethylaniline

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 – 7.46 (m, 1H), 7.00 – 6.95 (m, 2H), 3.14 (d, *J* = 3.5 Hz, 4H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ = 150.62, 129.07, 116.61, 112.62, 40.53.

MS (EI): m/z (rel. int.) 121.



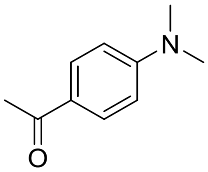
2b, 64%

N,*N*,4-trimethylaniline

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 7.23 – 7.09 (m, 2H), 6.84 – 6.70 (m, 2H), 2.98 (s, 6H), 2.35 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ = 148.93, 129.68, 126.15, 113.30, 41.14, 20.35.

MS (EI): m/z (rel. int.) 135.



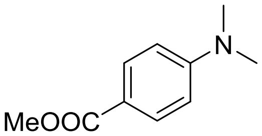
3b, 60%

1-(4-(dimethylamino)phenyl)ethan-1-one

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 7.87 (dd, *J*=9.4, 2.4, 1H), 6.94 – 6.39 (m, 1H), 3.05 (s, 2H), 2.51 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ = 196.48, 153.47, 130.61, 125.42, 110.68, 40.12, 26.09.

MS (EI): m/z (rel. int.) 163.



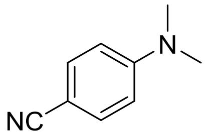
4b, 62%

methyl 4-(dimethylamino)benzoate

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 7.89 (dd, *J*=9.0, 1.9, 1H), 6.61 (dd, *J*=9.0, 1.9, 1H), 3.84 (d, *J*=1.9, 1H), 3.00 (d, *J*=2.1, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ = 167.50, 153.28, 131.25, 116.88, 110.68, 51.47, 40.01.

MS (EI): m/z (rel. int.) 179.



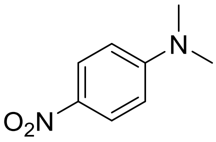
5b, 26%

4-(dimethylamino)benzonitrile

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 7.37 (d, *J*=8.6, 1H), 6.57 (d, *J*=8.6, 1H), 2.97 (d, *J*=2.2, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ = 152.28, 133.09, 120.64, 111.22, 96.78, 39.70.

MS (EI): m/z (rel. int.) 146.



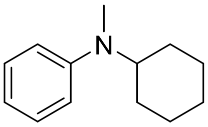
6b, 20%

N,*N*-dimethyl-4-nitroaniline

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 8.27 – 7.97 (m, 1H), 6.75 – 6.41 (m, 1H), 3.12 (s, 4H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ = 154.32, 137.00, 126.22, 110.32, 40.37.

MS (EI): m/z (rel. int.) 166.



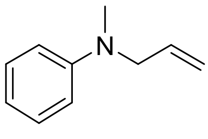
7b, 91%

N-cyclohexyl-*N*-methylaniline

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 7.21 (t, *J*=7.5, 1H), 6.77 (d, *J*=8.0, 1H), 6.67 (t, *J*=7.2, 1H), 3.55 (t, *J*=11.5, 1H), 2.76 (s, 1H), 1.80 (dd, *J*=34.2, 12.4, 2H), 1.67 (d, *J*=13.3, 1H), 1.44 (q, *J*=12.5, 1H), 1.38 – 1.30 (m, 4H), 1.13 (t, *J*=12.8, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ = 150.31, 129.23, 116.34, 113.27, 58.25, 31.29, 30.18, 26.35, 26.08.

MS (EI): m/z (rel. int.) 189.



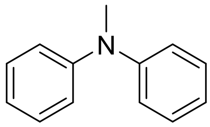
8b, 84%

N-allyl-*N*-methylaniline

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 7.23 – 7.09 (m, 1H), 6.65 (dq, *J*=12.2, 4.7, 3.6, 2H), 5.82 – 5.72 (m, 1H), 5.13 – 5.04 (m, 1H), 3.87 – 3.83 (m, 1H), 2.89 – 2.85 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ = 149.62, 133.94, 129.24, 116.52, 116.27, 112.56, 55.39, 38.13.

MS (EI): *m/z* (rel. int.) 147.



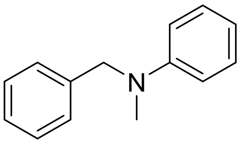
9b, 40%

N-methyl-*N*-phenylaniline

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 7.32 – 7.27 (m, 1H), 7.02 (dt, *J*=7.8, 1.1, 1H), 6.95 (tt, *J*=7.3, 1.1, 1H), 3.32 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ = 149.16, 129.33, 121.39, 120.58, 40.38.

MS (EI): m/z (rel. int.) 183.



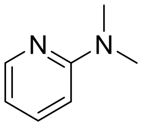
10b, 99%

N-benzyl-*N*-methylaniline

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 7.51 (t, *J*=7.2, 1H), 7.46 – 7.39 (m, 3H), 6.98 – 6.90 (m, 2H), 4.71 (d, *J*=2.1, 1H), 3.19 (d, *J*=2.2, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ = 149.77, 139.08, 129.24, 128.61, 126.90, 126.78, 116.59, 112.40, 56.62, 38.52.

MS (EI): m/z (rel. int.) 197.



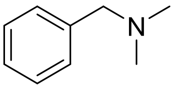
11b, 29%

N,*N*-dimethylpyridin-2-amine

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 8.01 (d, *J*=5.2, 1H), 7.22 (td, *J*=8.0, 6.9, 2.2, 2H), 6.34 (t, *J*=5.9, 2H), 6.28 (d, *J*=8.7, 2H), 2.86 (d, *J*=3.3, 12H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ = 158.93, 147.44, 136.63, 111.02, 105.37, 37.56.

MS (EI): m/z (rel. int.) 122.



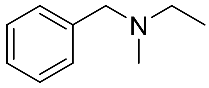
12b, 36%

N,*N*-dimethyl-1-phenylmethanamine

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 7.32 (d, *J*=6.5, 1H), 7.26 (td, *J*=5.7, 2.6, 0H), 3.43 (s, 1H), 2.25 (s, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ = 138.99, 129.19, 128.32, 127.12, 64.52, 45.48.

MS (EI): m/z (rel. int.) 135.



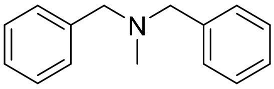
13b, 48%

N-benzyl-*N*-methylethanamine

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 7.38 (td, *J*=8.2, 5.9, 4H), 7.33 – 7.27 (m, 1H), 3.55 (s, 2H), 2.51 (q, *J*=7.2, 2H), 2.26 (d, *J*=1.4, 3H), 1.20 – 1.15 (m, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ = 139.13, 129.04, 128.15, 126.84, 61.97, 51.17, 41.62, 12.46.

MS (EI): m/z (rel. int.) 149.



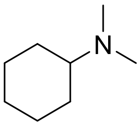
14b, 73%

N-benzyl-*N*-methyl-1-phenylmethanamine

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 7.53 (d, *J*=7.8, 1H), 7.47 (t, *J*=7.6, 1H), 7.39 (t, *J*=7.5, 1H), 3.67 (s, 1H), 2.34 (d, *J*=1.7, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ = 139.36, 128.96, 128.27, 126.98, 61.92, 42.28.

MS (EI): m/z (rel. int.) 211.



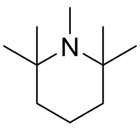
15b, 64%

N,*N*-dimethylcyclohexanamine

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 1.84 (d, *J*=3.3, 1H), 1.72 (dd, *J*=12.7, 8.5, 0H), 1.47 – 1.41 (m, 0H), 1.37 (dd, *J*=12.8, 4.2, 0H), 1.20 (dt, *J*=13.7, 3.9, 0H), 0.91 – 0.62 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ = 63.13, 40.87, 28.35, 25.72, 25.15.

MS (EI): m/z (rel. int.) 127.



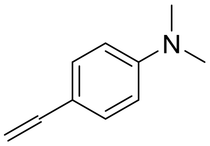
16b, 99%

1,2,2,6,6-pentamethylpiperidine

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 2.12 (d, *J*=2.3, 1H), 1.46 – 1.39 (m, 1H), 1.37 – 1.29 (m, 1H), 0.93 (d, *J*=3.7, 4H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ = 53.62, 41.17, 28.39, 26.23, 17.86.

MS (EI): m/z (rel. int.) 155.



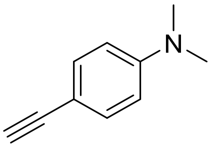
17b, 45%

N,*N*-dimethyl-4-vinylaniline

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 7.28 (ddd, *J*=8.3, 5.0, 2.8, 1H), 6.71 – 6.44 (m, 2H), 5.62 – 5.44 (m, 1H), 5.09 – 4.91 (m, 1H), 2.91 (dd, *J*=5.0, 3.1, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ = 150.30, 136.70, 127.22, 126.23, 112.37, 109.36, 40.54.

MS (EI): m/z (rel. int.) 147.



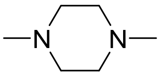
18b, 63%

4-ethynyl-*N*,*N*-dimethylaniline

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 7.38 (dd, *J*=9.0, 2.4, 1H), 6.63 (dd, *J*=9.0, 2.3, 1H), 3.00 (d, *J*=2.2, 1H), 2.98 (d, *J*=2.4, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ = 150.46, 133.29, 111.76, 108.79, 84.97, 74.91, 40.25.

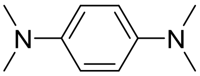
MS (EI): m/z (rel. int.) 145.



19b, 63%

1,4-dimethylpiperazine

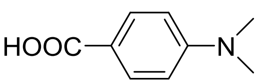
^{1}H NMR (600 MHz, Chloroform-*d*) δ = 2.45 (s, 1H), 2.29 (s, 1H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ = 54.51, 45.46.
MS (EI): m/z (rel. int.) 114.



20b, 60%[b]

N^{1},*N*^{1},*N*^{4},*N*^{4}-tetramethylbenzene-1,4-diamine

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 6.84 (s, 1H), 2.90 (s, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ = 144.05, 115.43, 42.10.
MS (EI): m/z (rel. int.) 164.



21b

4-(dimethylamino)benzoic acid

^{1}H NMR (600 MHz, DMSO-d_6) δ = 12.13 (s, 1H), 7.77 (d, *J*=9.0, 1H), 6.89 – 6.57 (m, 2H), 2.97 (s, 5H).

^{13}C NMR (151 MHz, DMSO-d_6) δ = 167.62, 153.10, 130.98, 116.98, 110.78, 39.65.

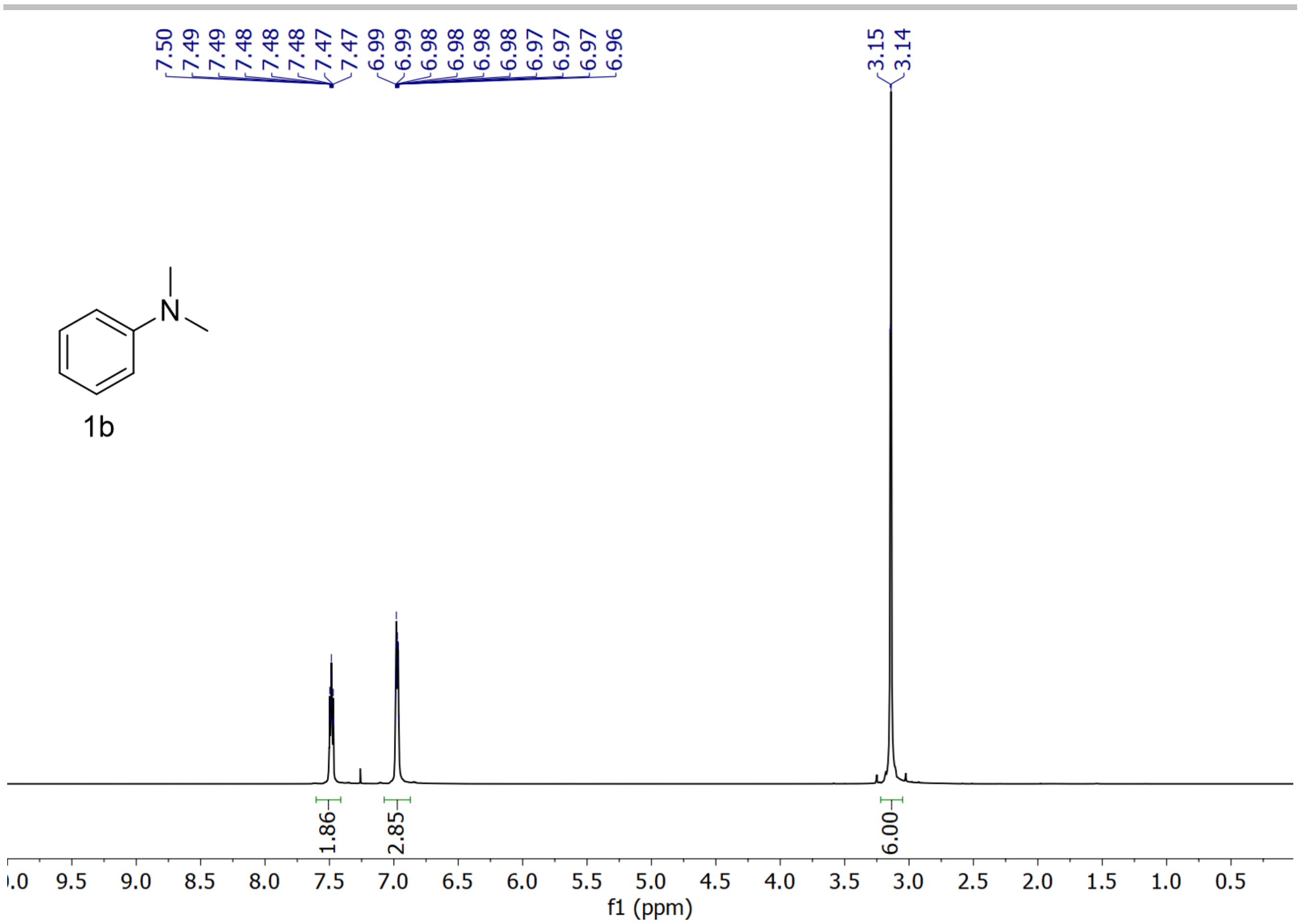
MS (EI): m/z (rel. int.) 165.

References

[S1] X. Zhang, J. Sun, G. Wei, Z. Liu, H. Yang, K. Wang, H. Fei, *Angew. Chem. Int. Ed.* **2019**, *58*, 2844-2849.

[S2] O. Jacquet, X. Frogneux, C. Das Neves Gomes, T. Cantat, *Chem. Sci.* **2013**, *4*, 2127-2137.

[S3] V. Jurkauskas, J. P. Sadighi, S. L. Buchwald, *Org. Lett.* **2003**, *5*, 2417-2420.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6.97
6.97
6.96
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2.85
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8.0
7.5
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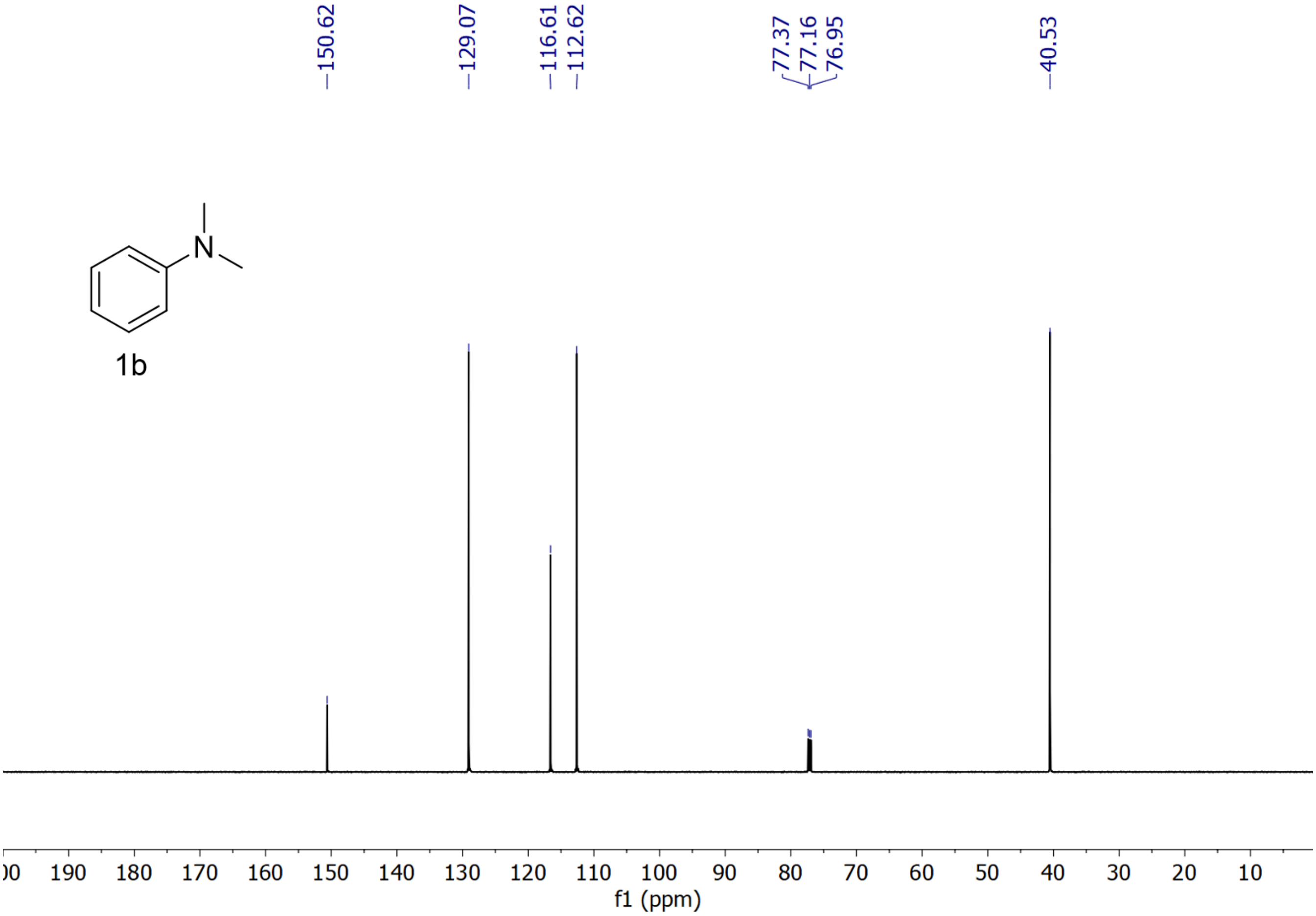
f1 (ppm)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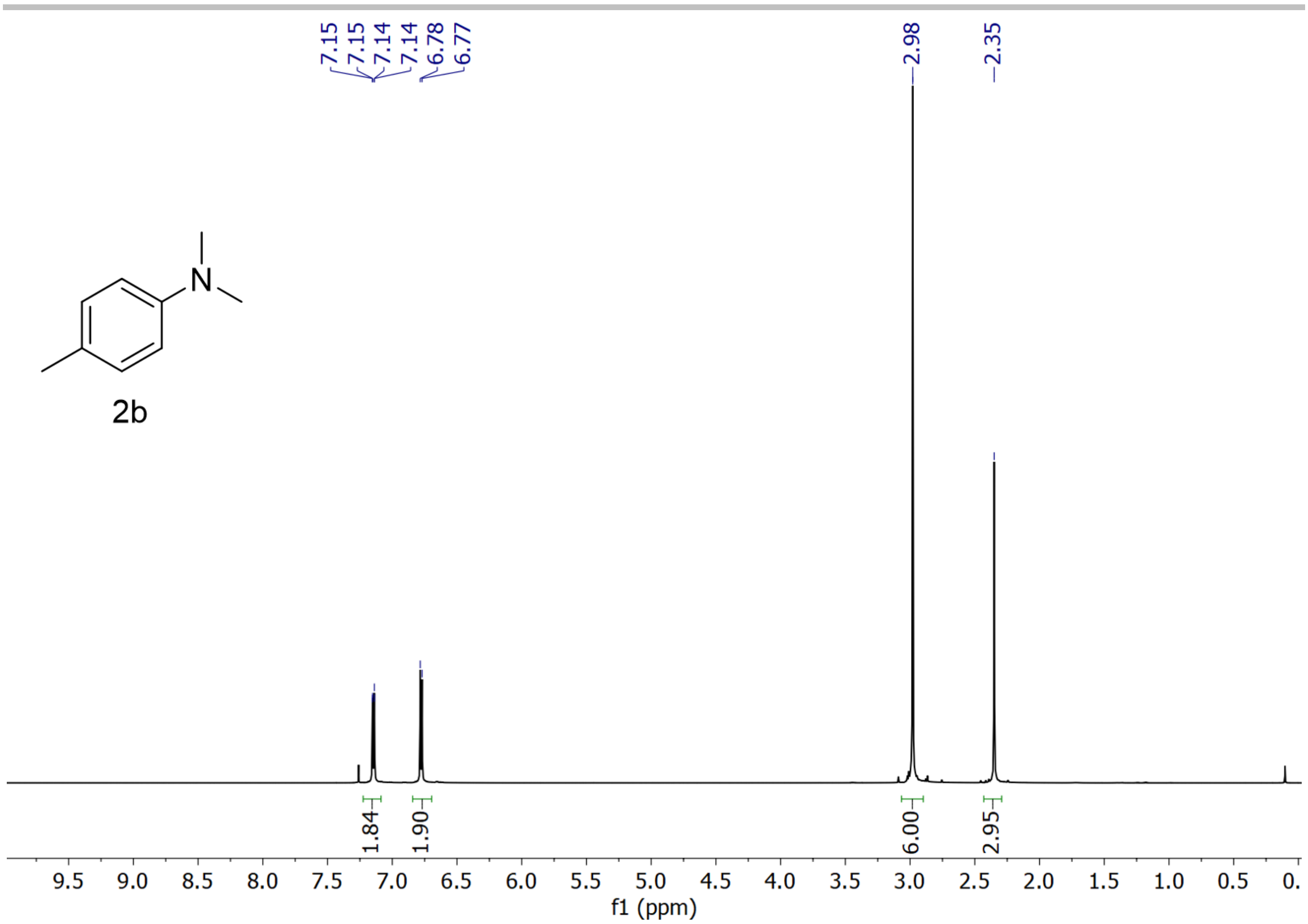
10
f1 (ppm)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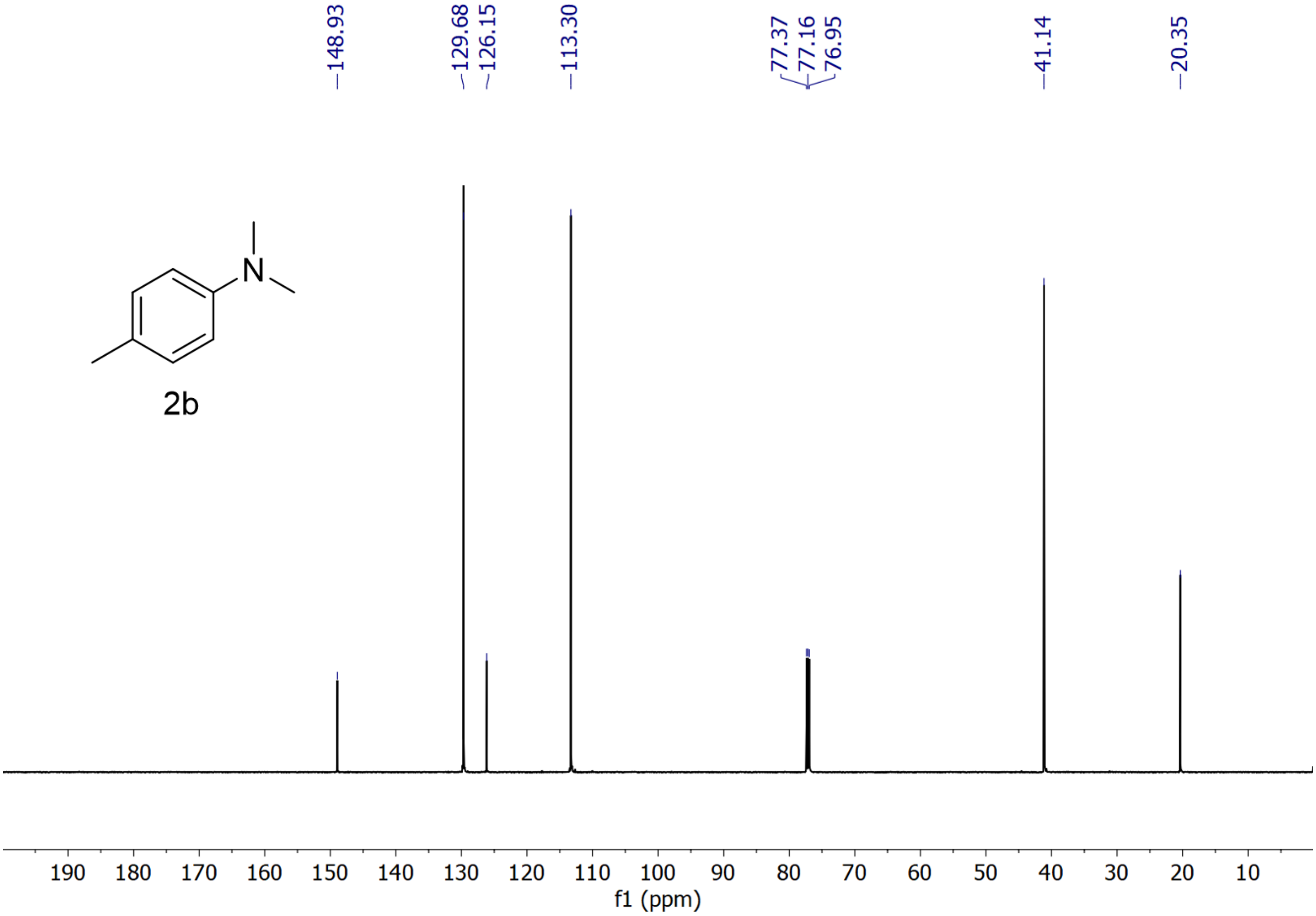
f1 (ppm)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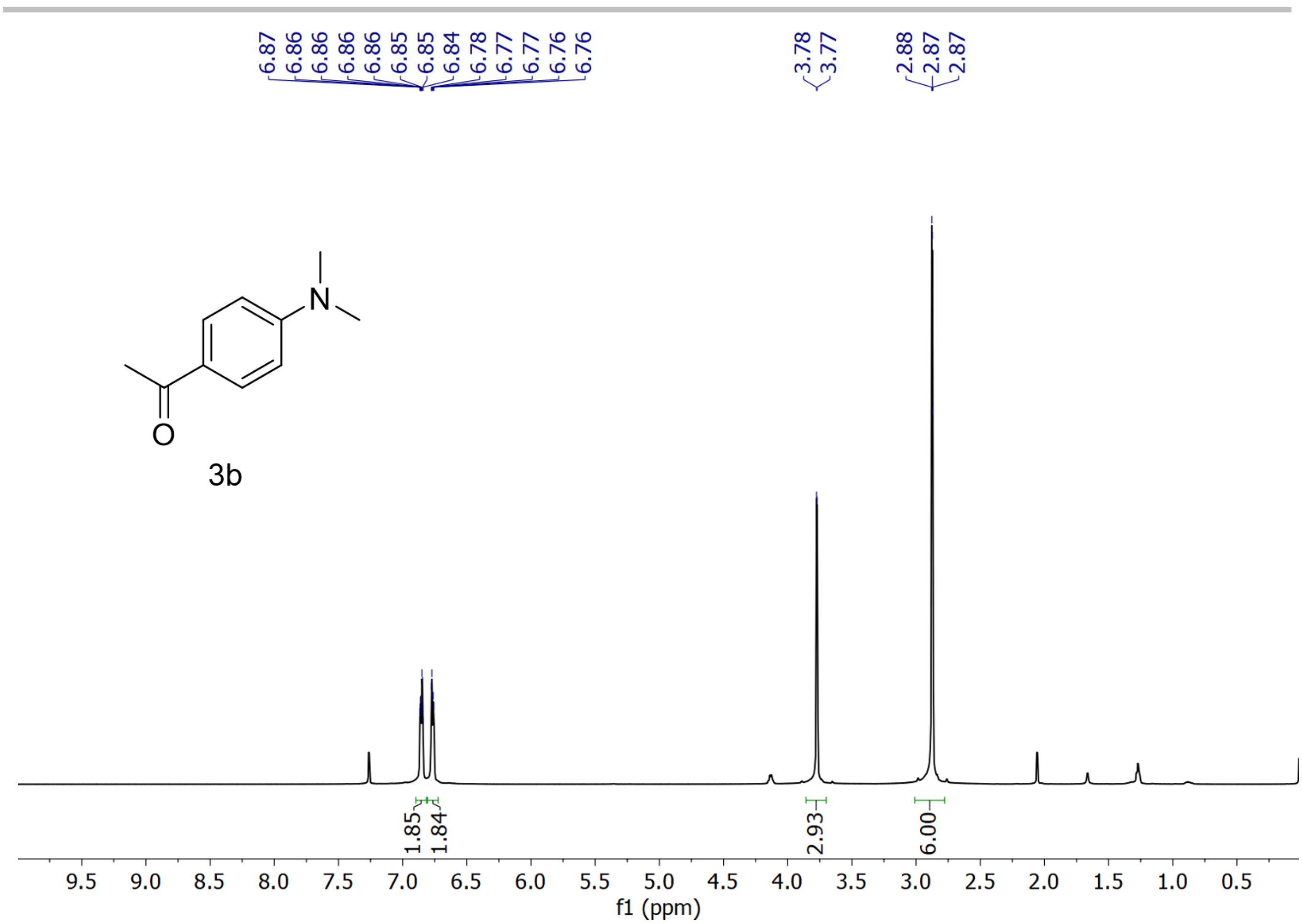
f1 (ppm)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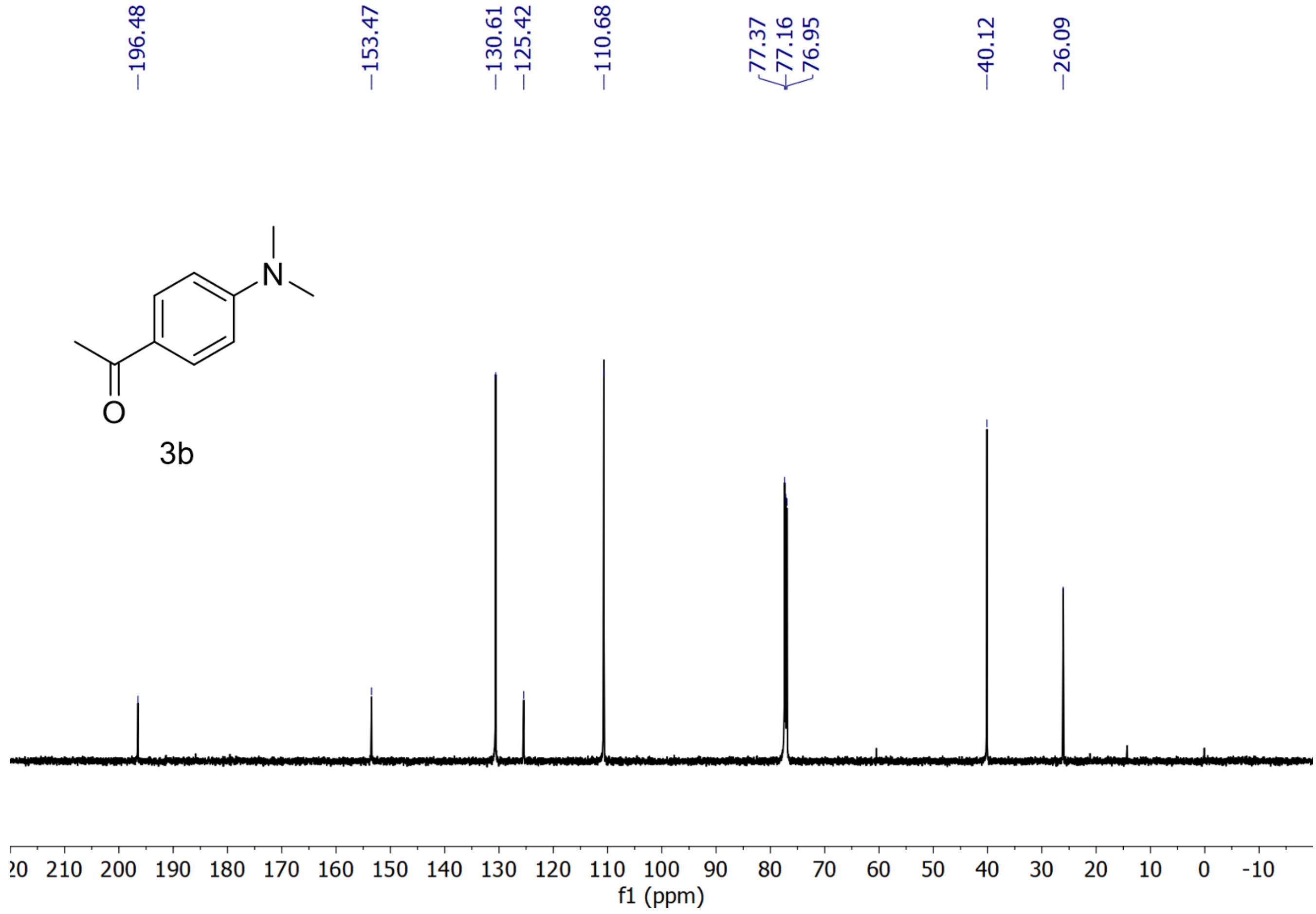
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O
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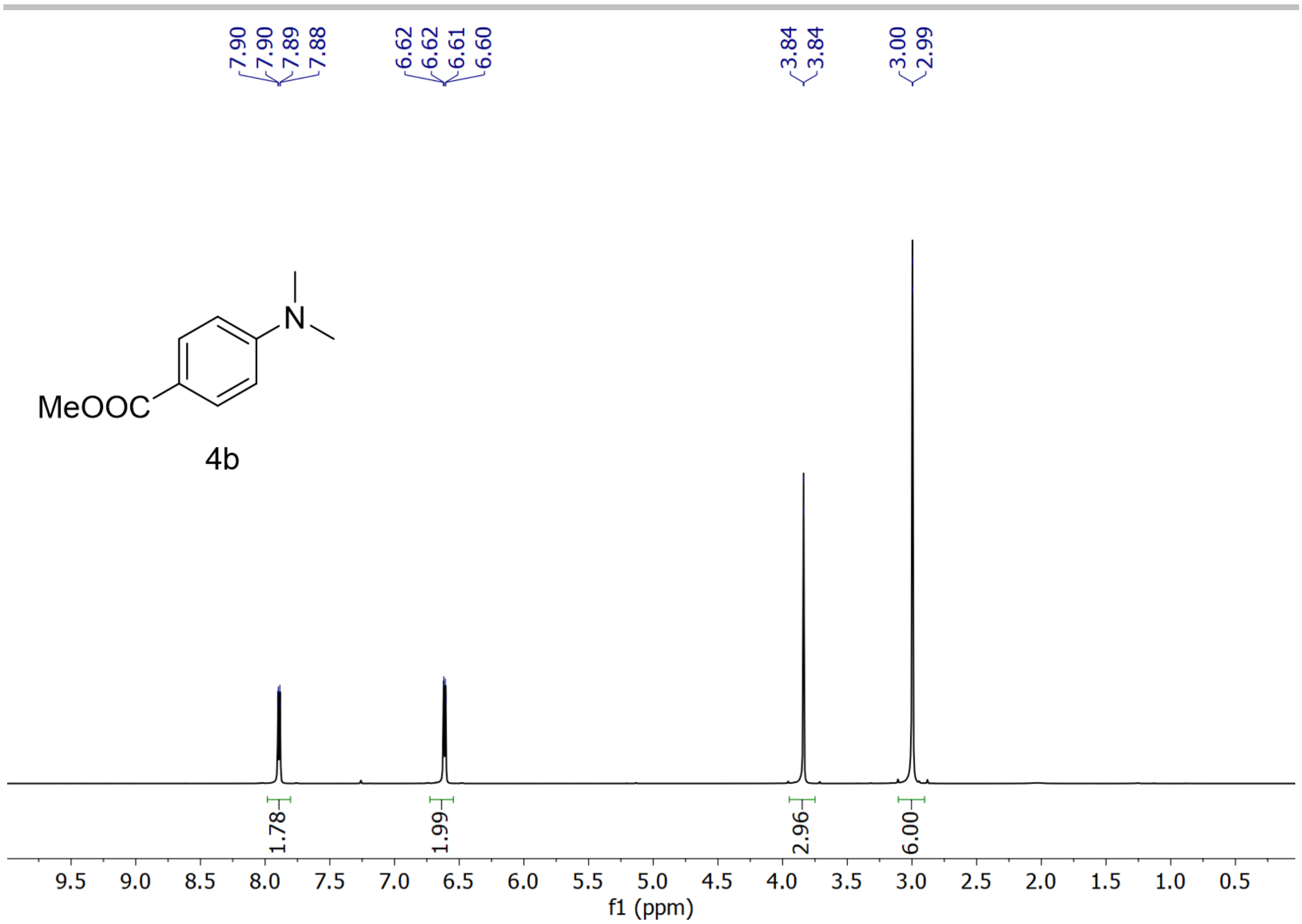
f1 (ppm)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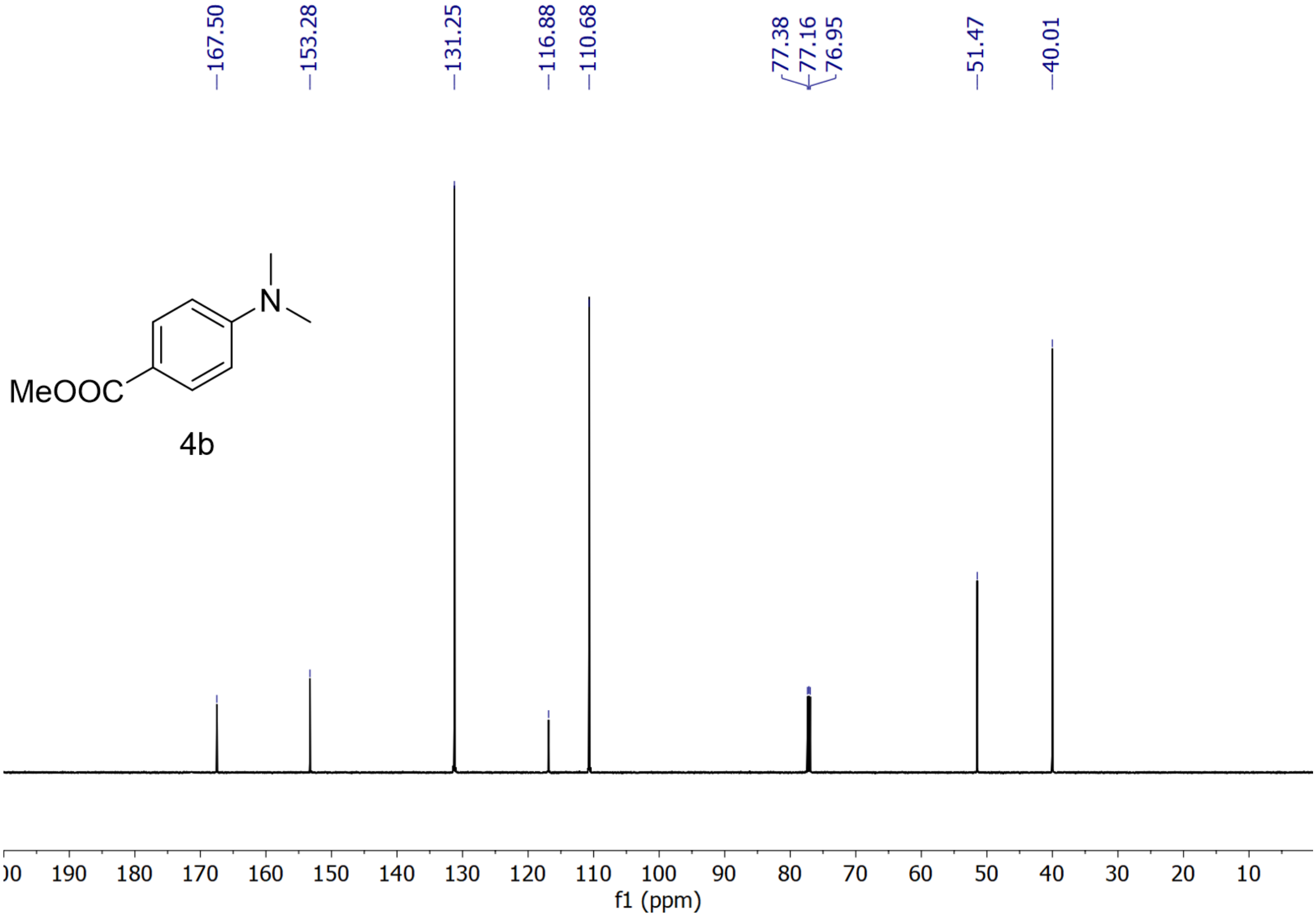
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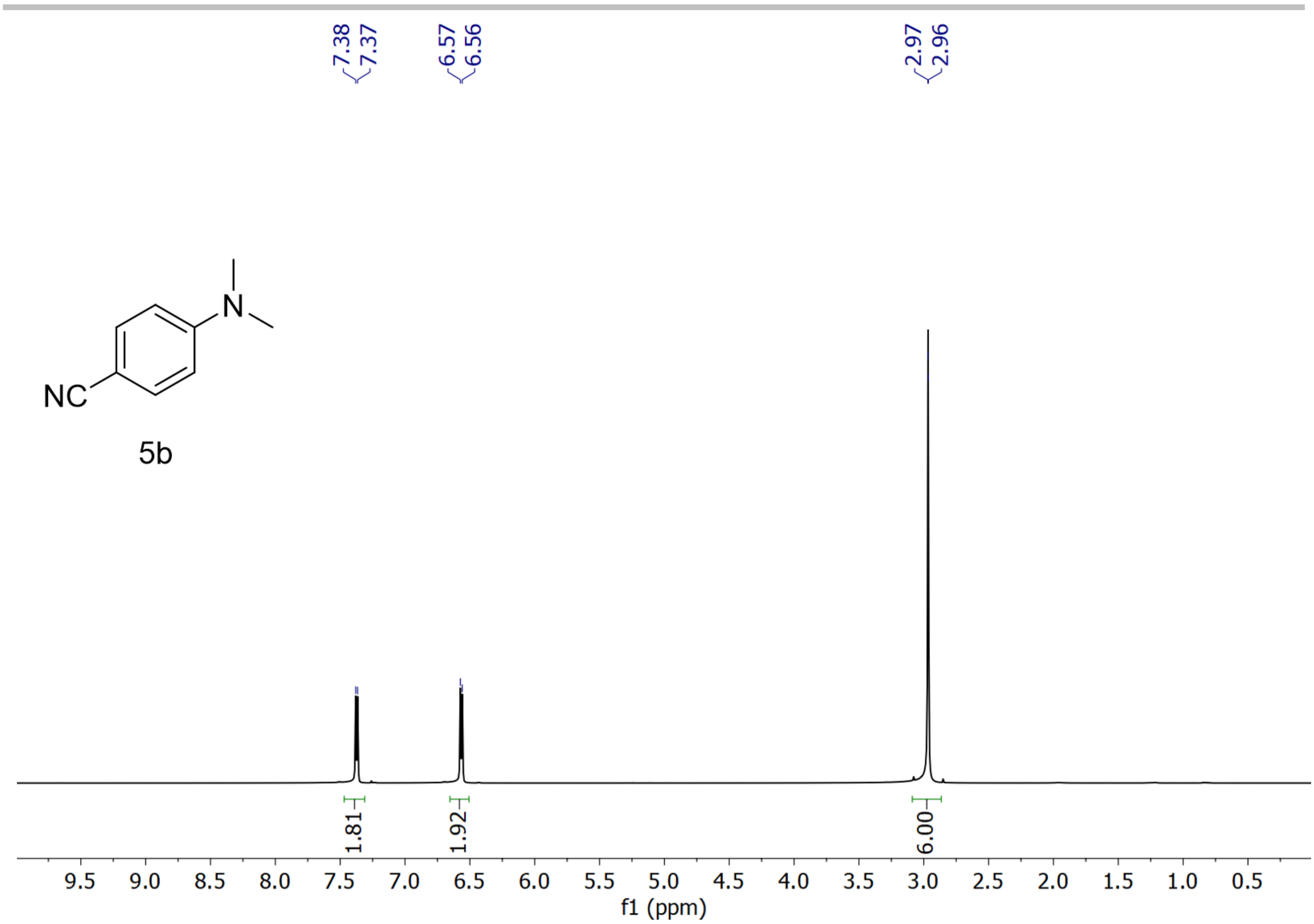
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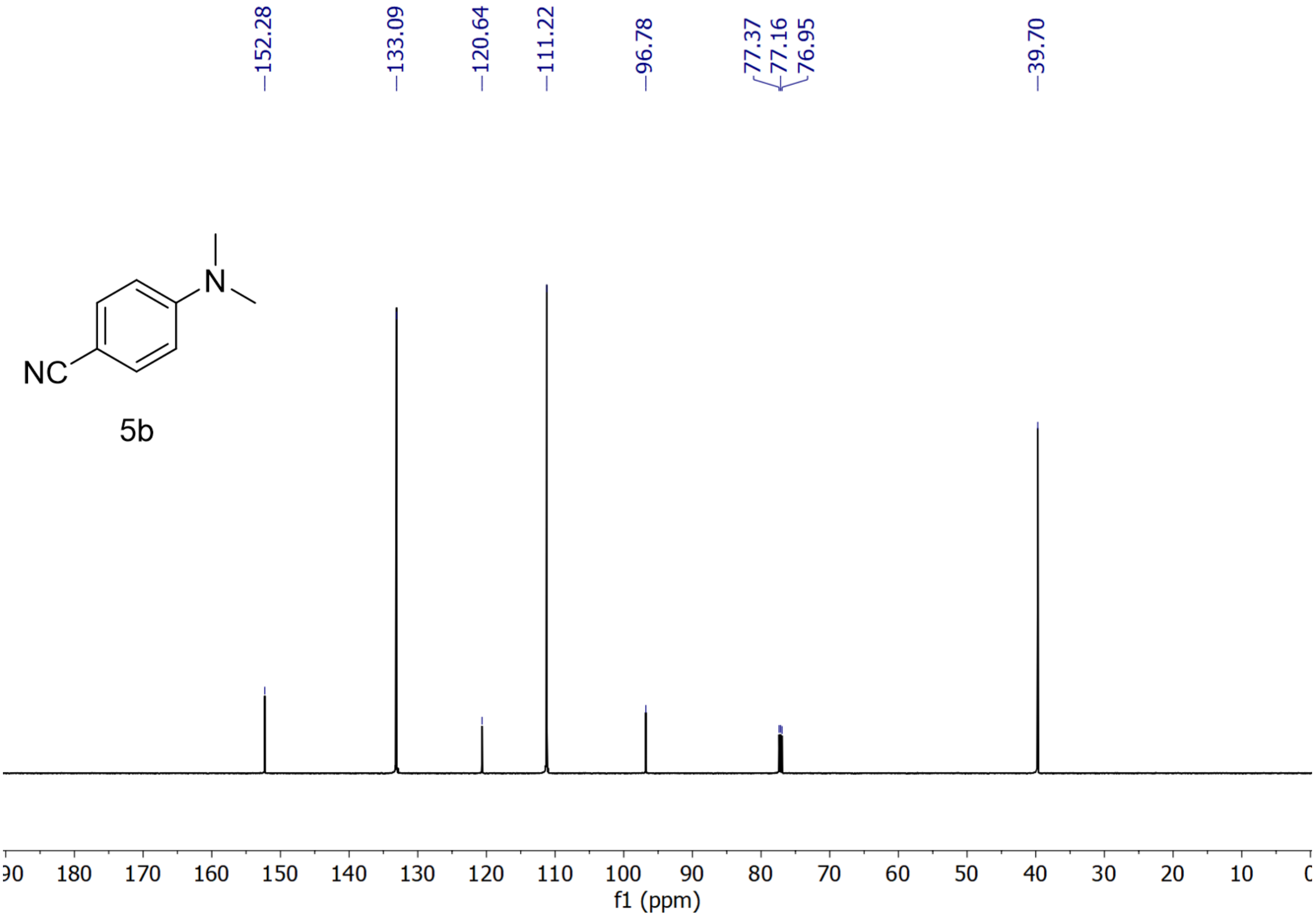
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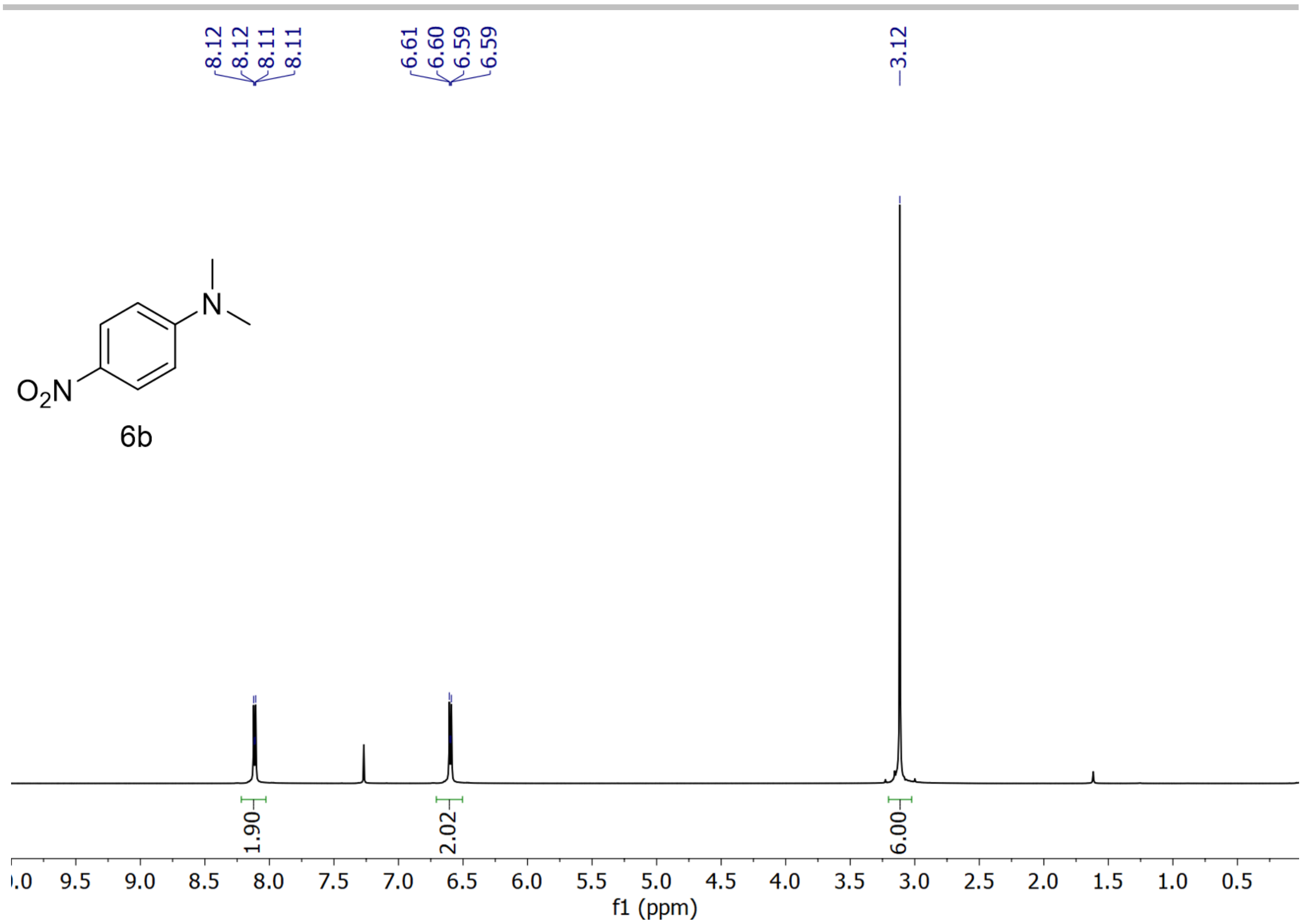
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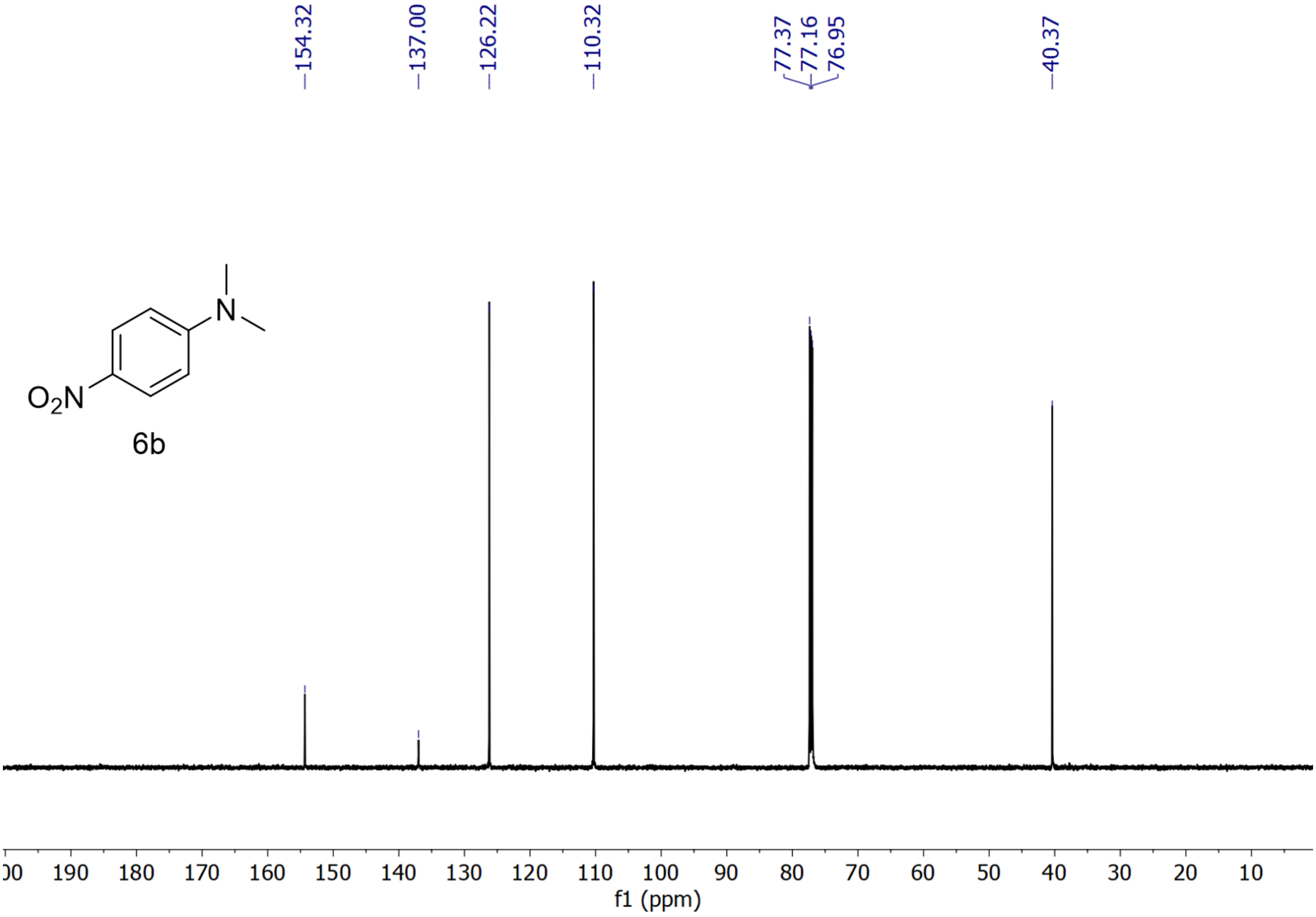
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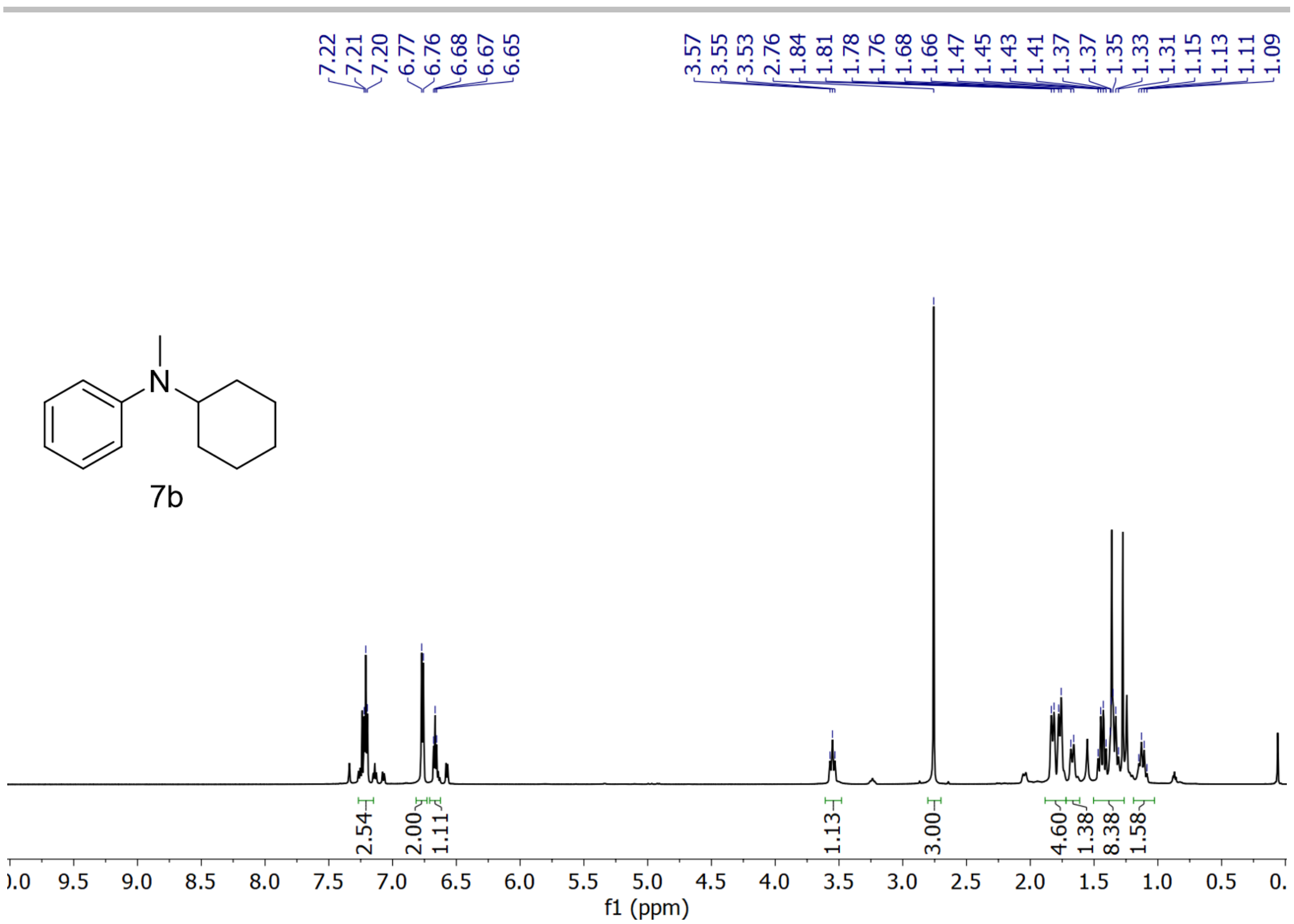
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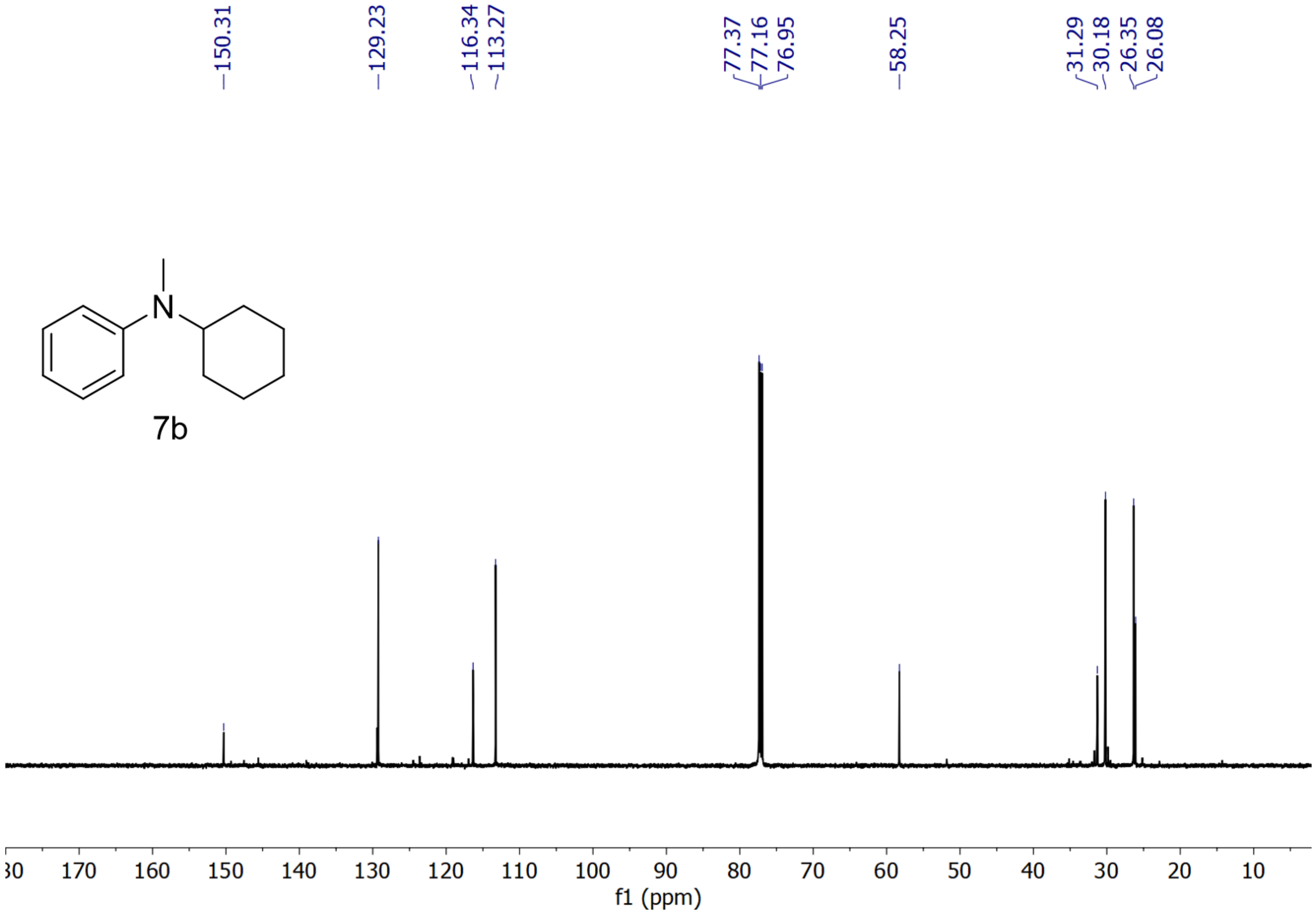
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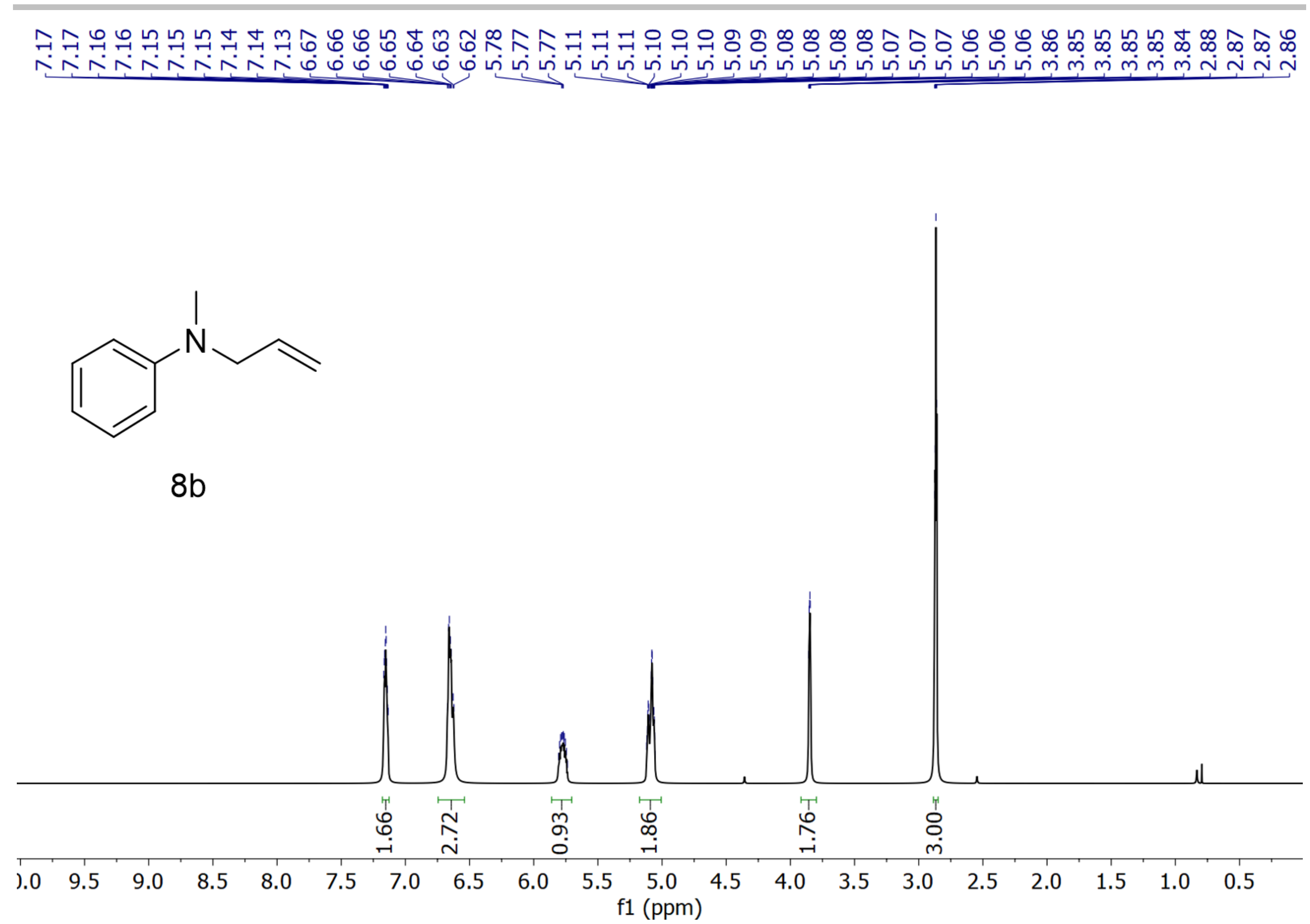
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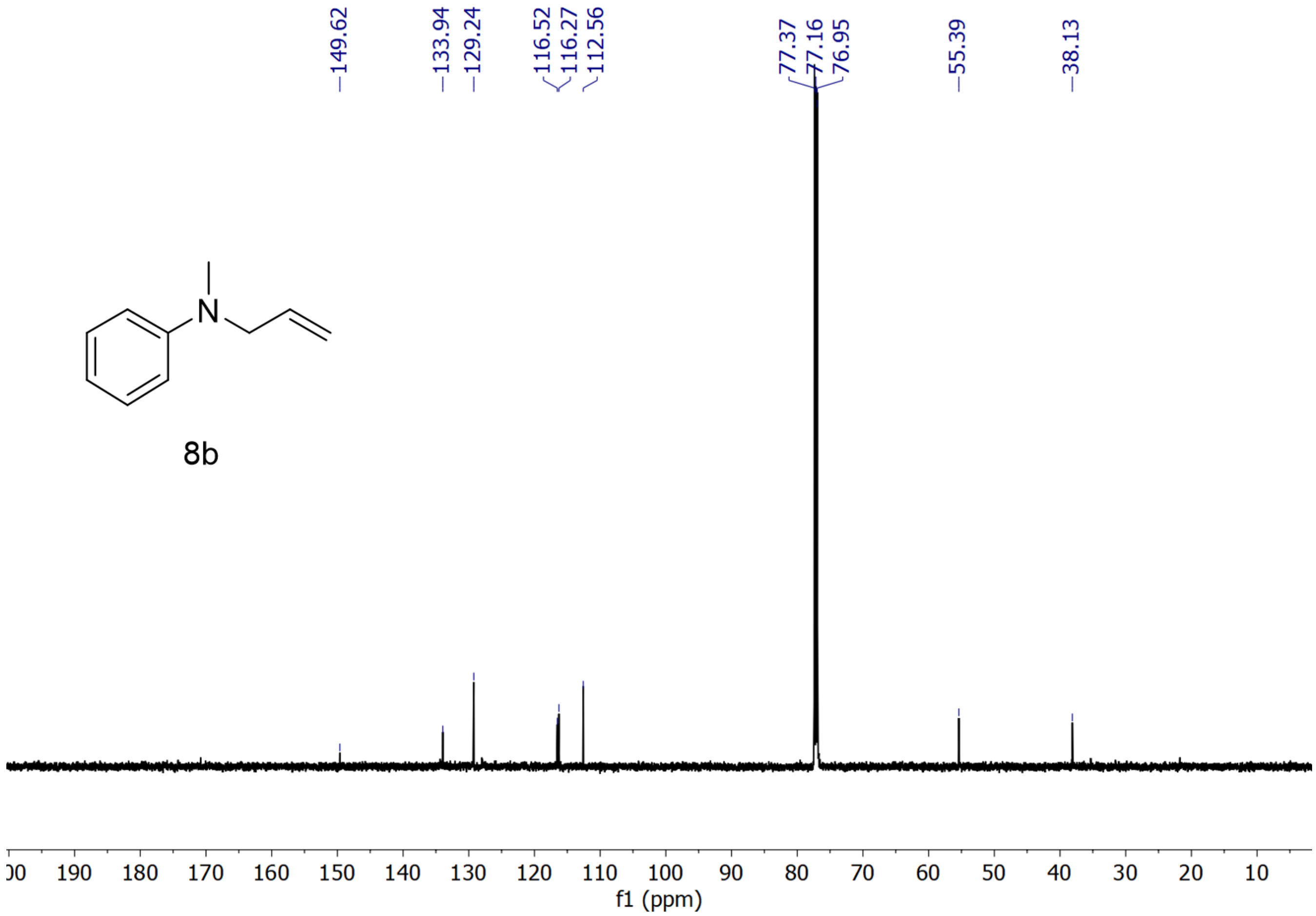
f1 (ppm)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77.16
76.95
55.39
38.13
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8b
)0
190
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130
120
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100
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80
70
60
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30
20
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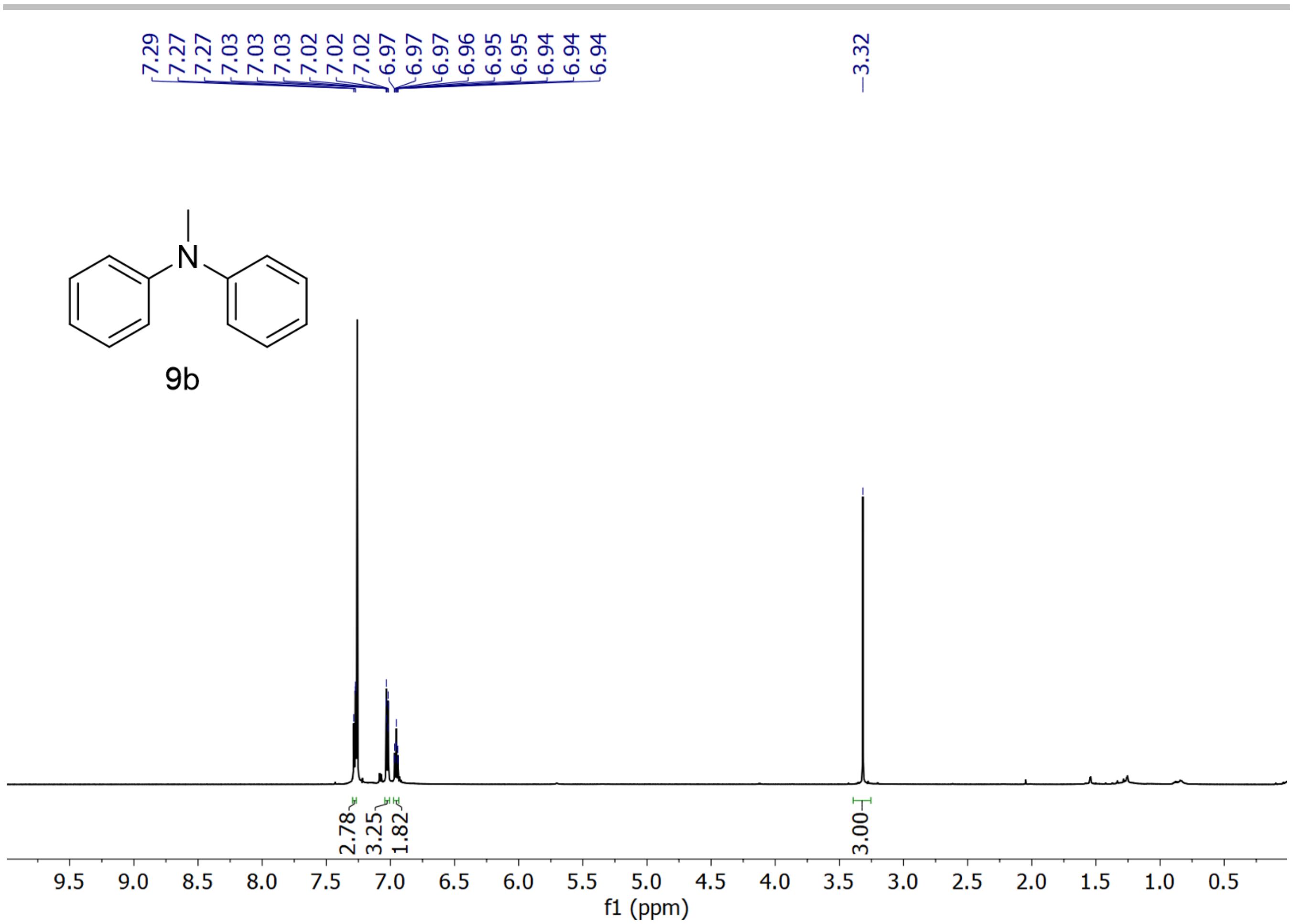
f1 (ppm)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7.03
7.02
7.02
7.02
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6.97
6.97
6.96
6.95
6.95
6.94
6.94
6.94
3.32
N
9b
2.78
3.25
1.82
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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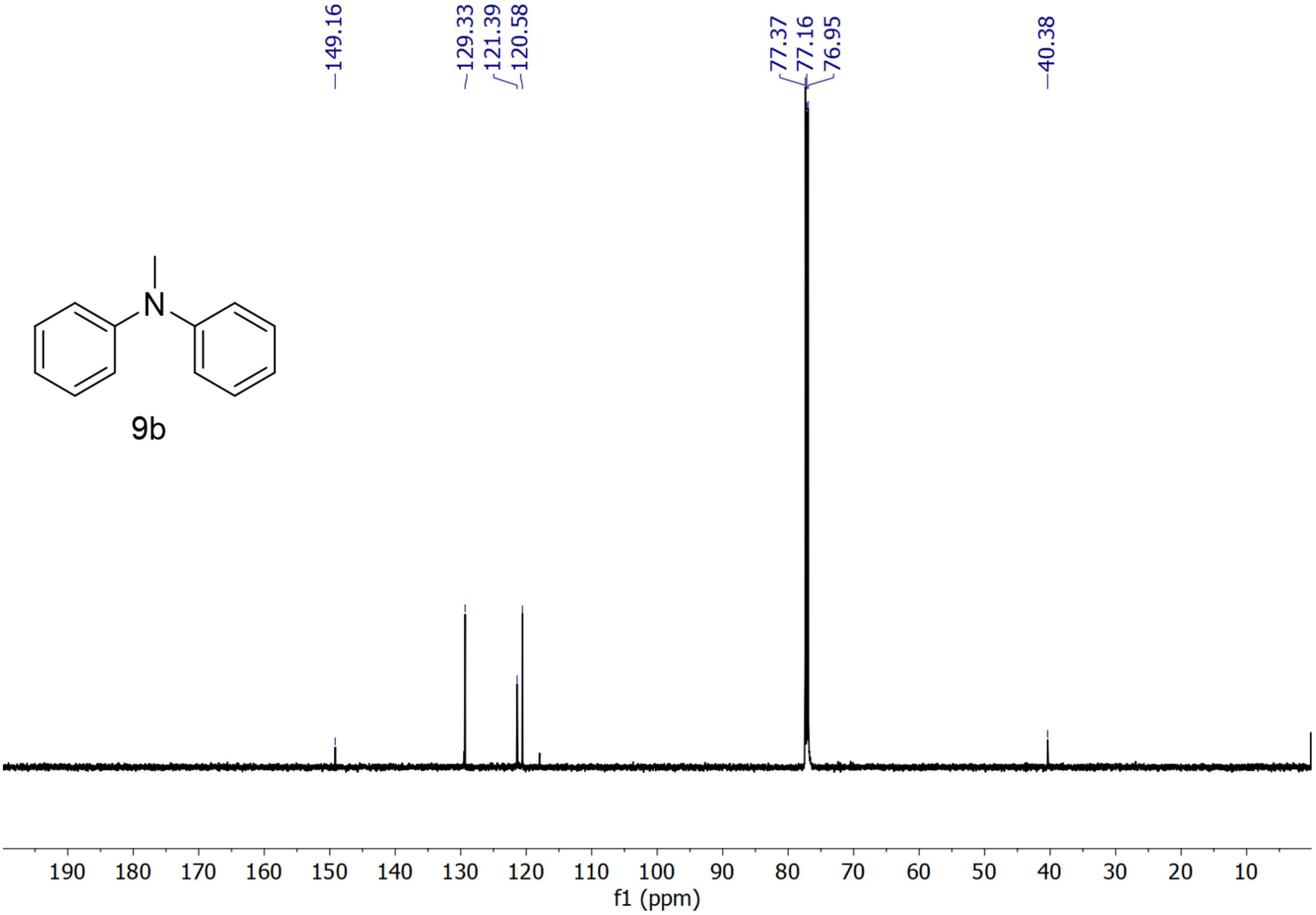
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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77.37
77.16
76.95
40.38
N
9b
190
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160
150
140
130
120
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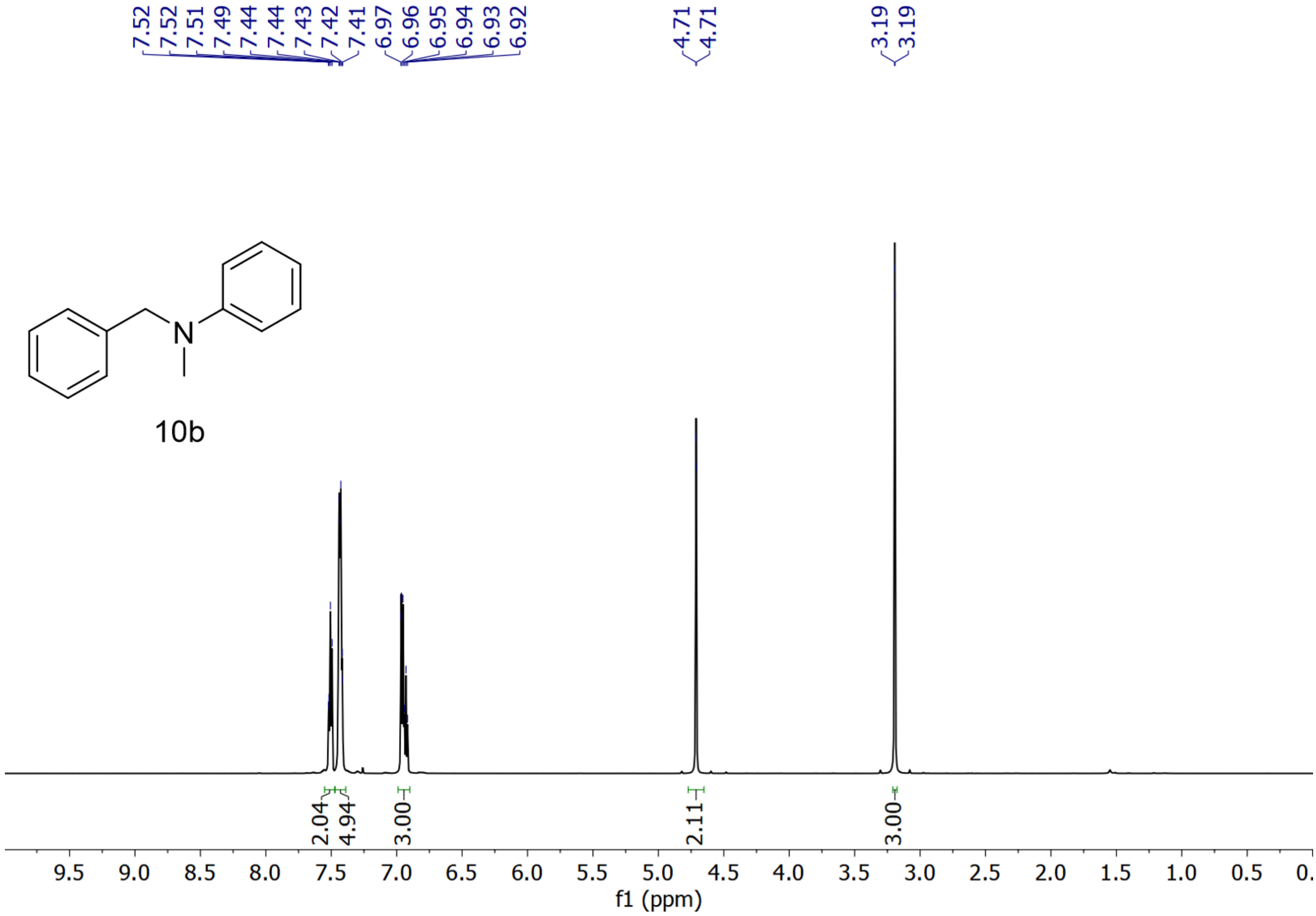
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.52
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7.44
7.44
7.43
7.42
7.41
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6.96
6.95
6.94
6.93
6.92
4.71
4.71
3.19
3.19
N
10b
2.04
4.94
3.00
2.11
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
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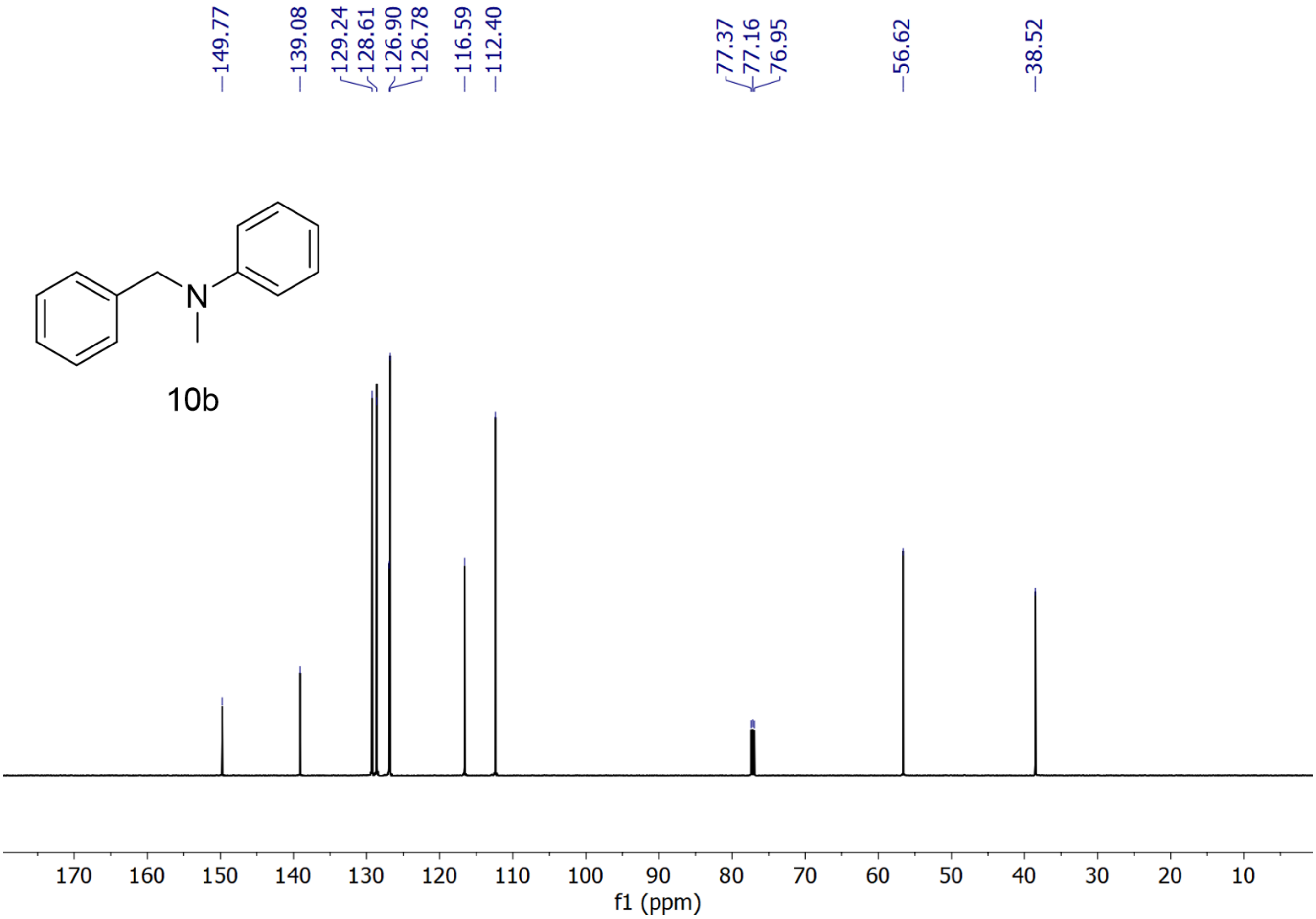
1.5
1.0
0.5
0.
f1 (ppm)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112.40
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77.16
76.95
56.62
38.52
N
10b
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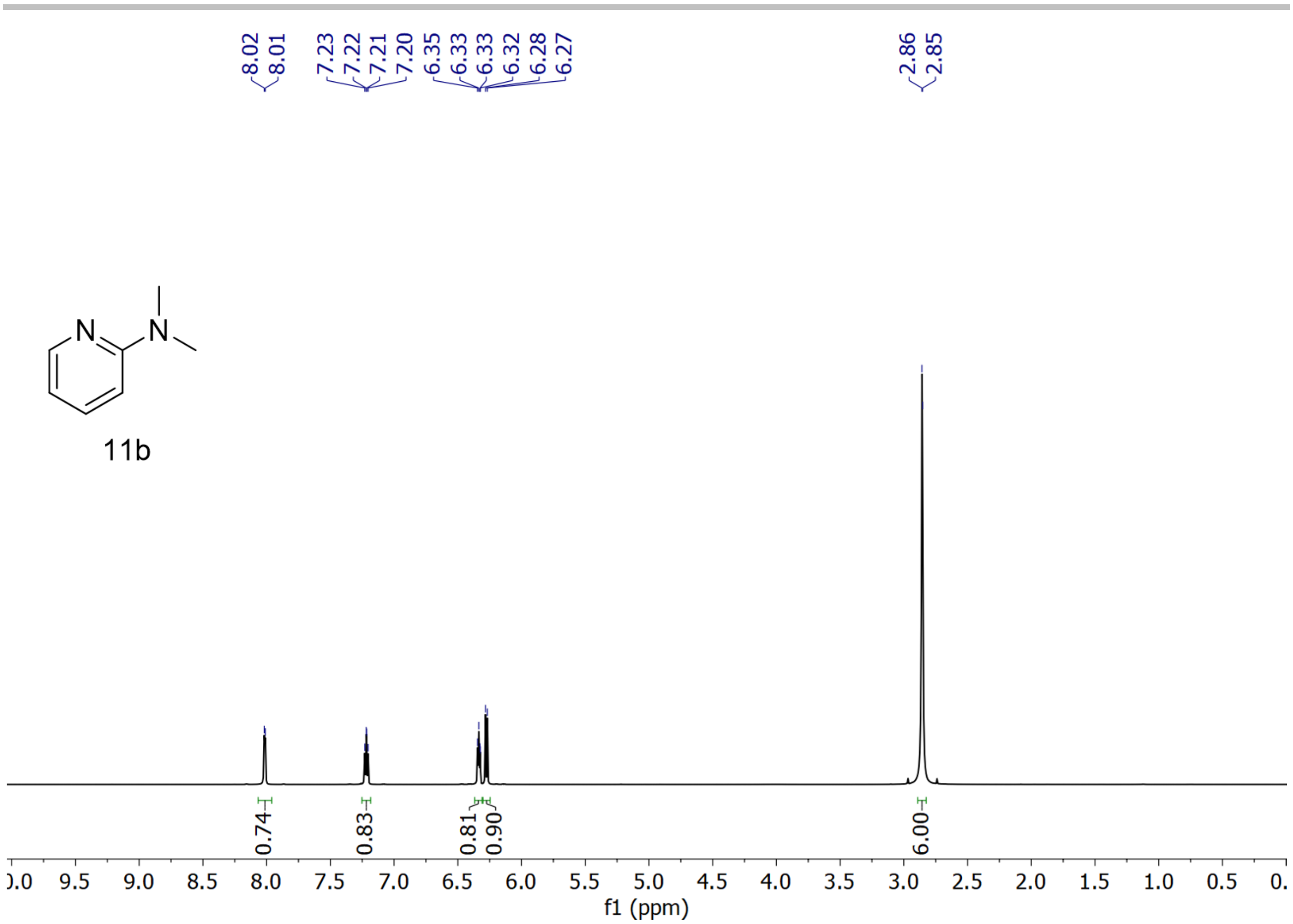
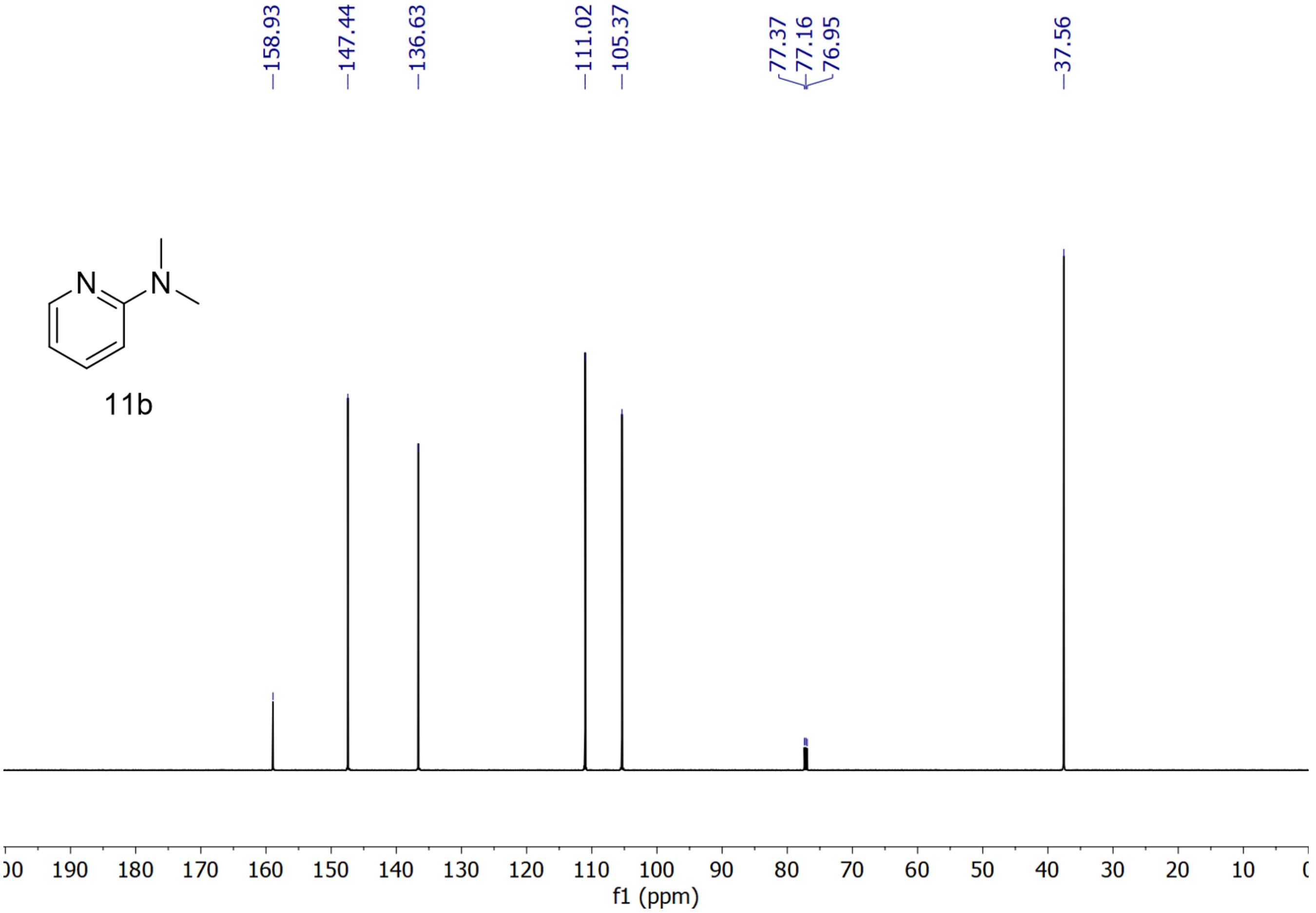
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.02
8.01
7.23
7.22
7.21
7.20
6.35
6.33
6.33
6.32
6.28
6.27
2.86
2.85
11b
0.74
0.83
0.81
0.90
6.00
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
f1 (ppm)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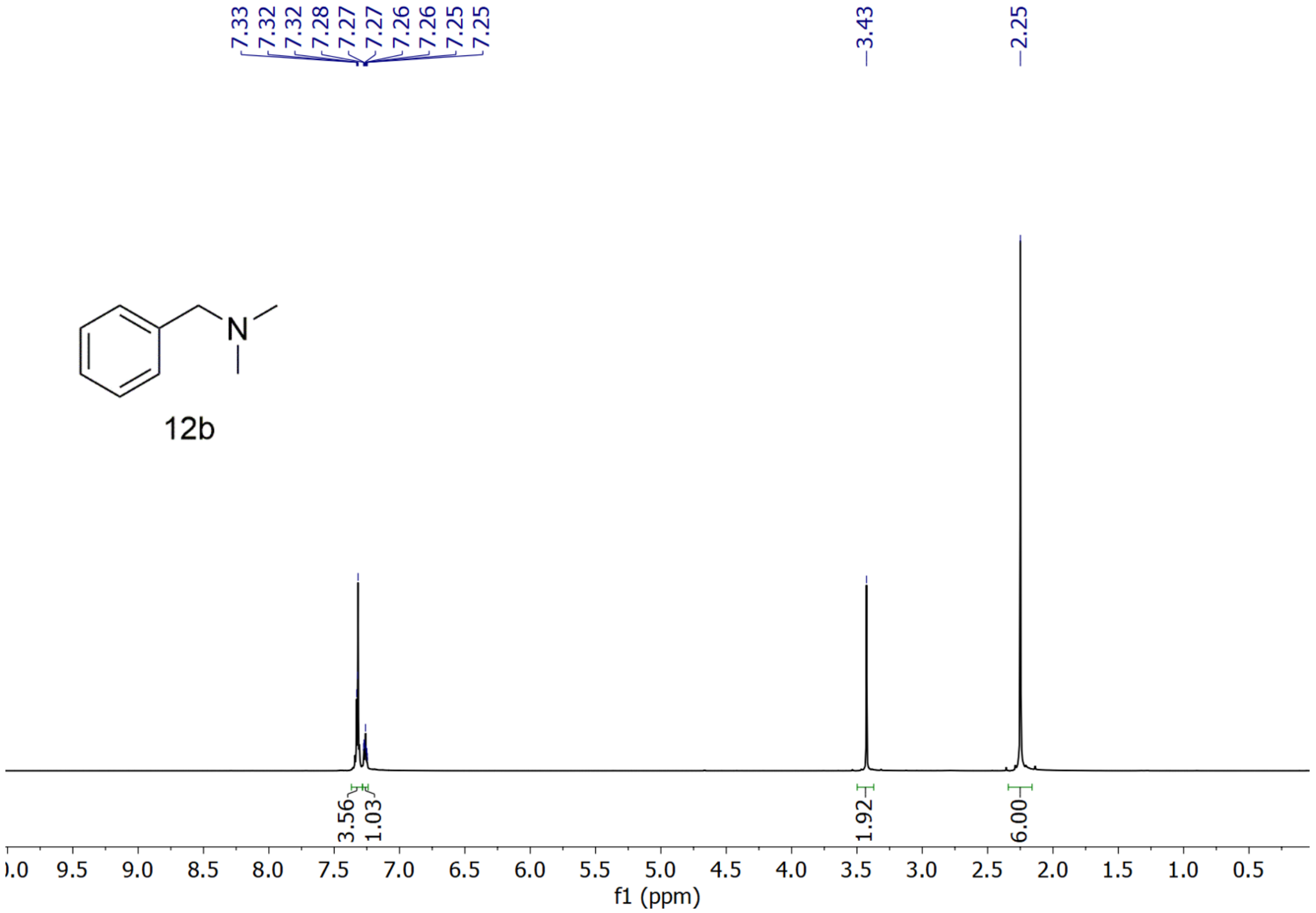
147.44
136.63
111.02
105.37
77.37
77.16
76.95
37.56
11b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.33
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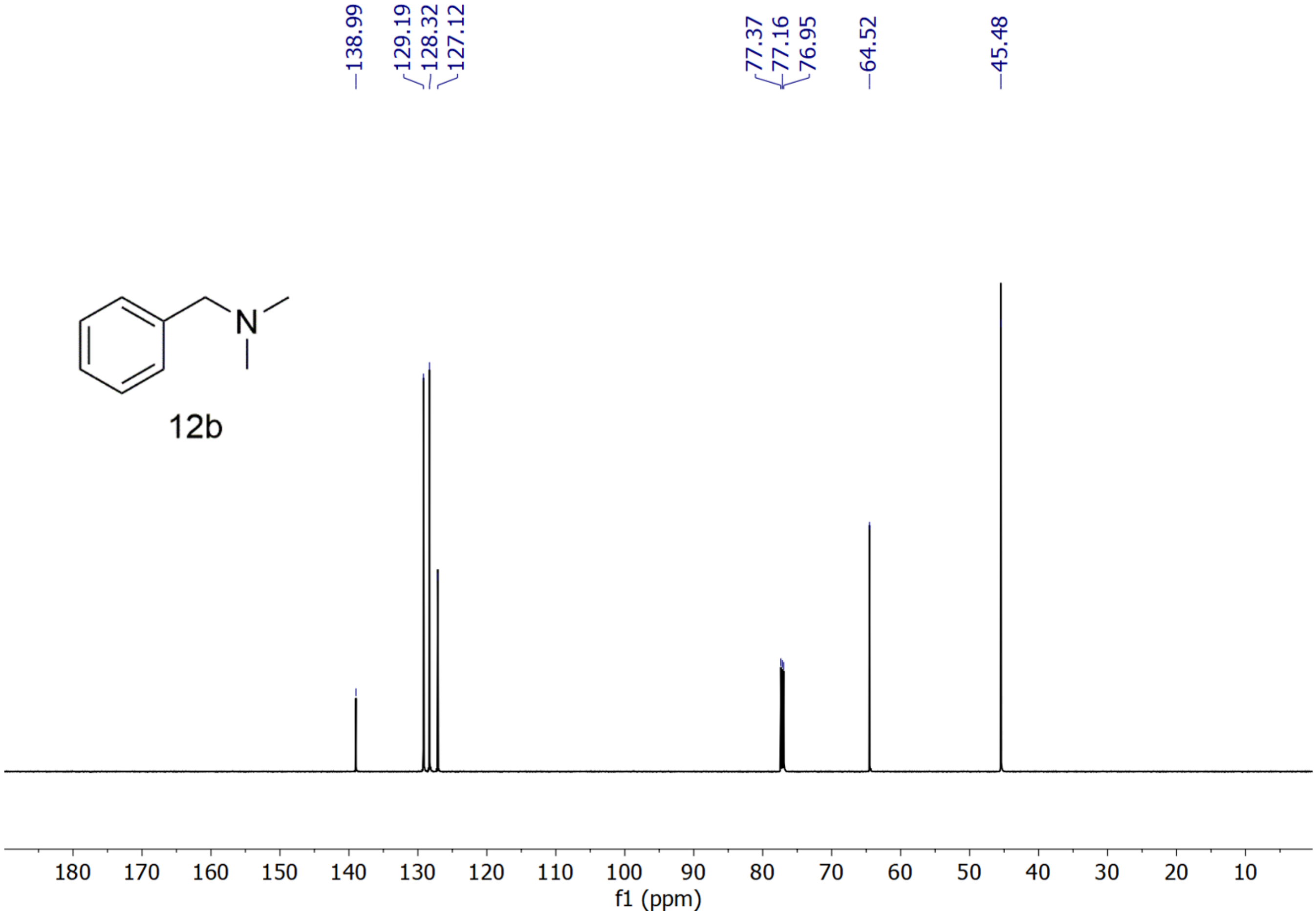
7.28
7.27
7.27
7.26
7.26
7.25
7.25
3.43
2.25
12b
3.56
1.03
1.92
6.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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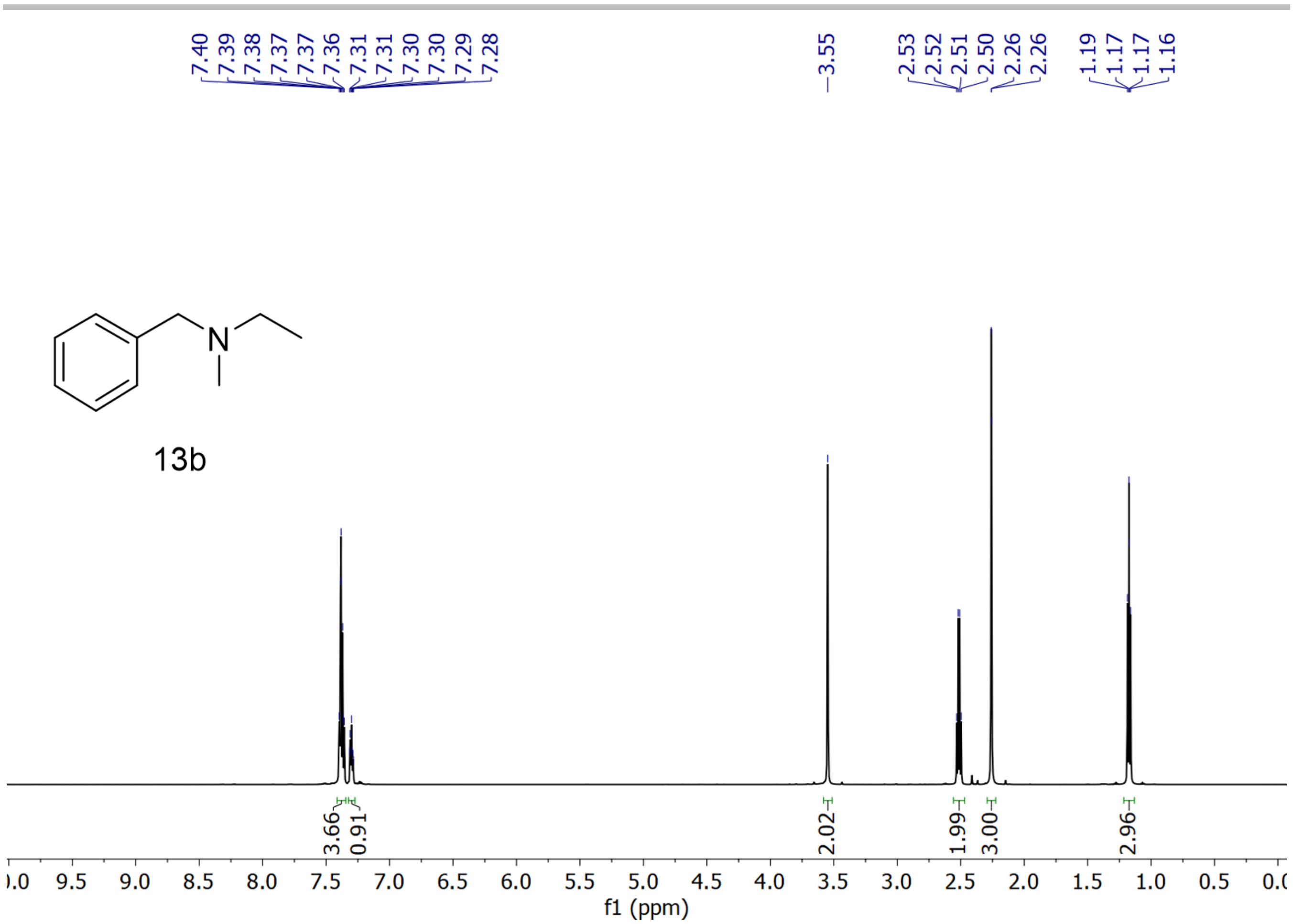
129.19
128.32
127.12
77.37
77.16
76.95
64.52
45.48
12b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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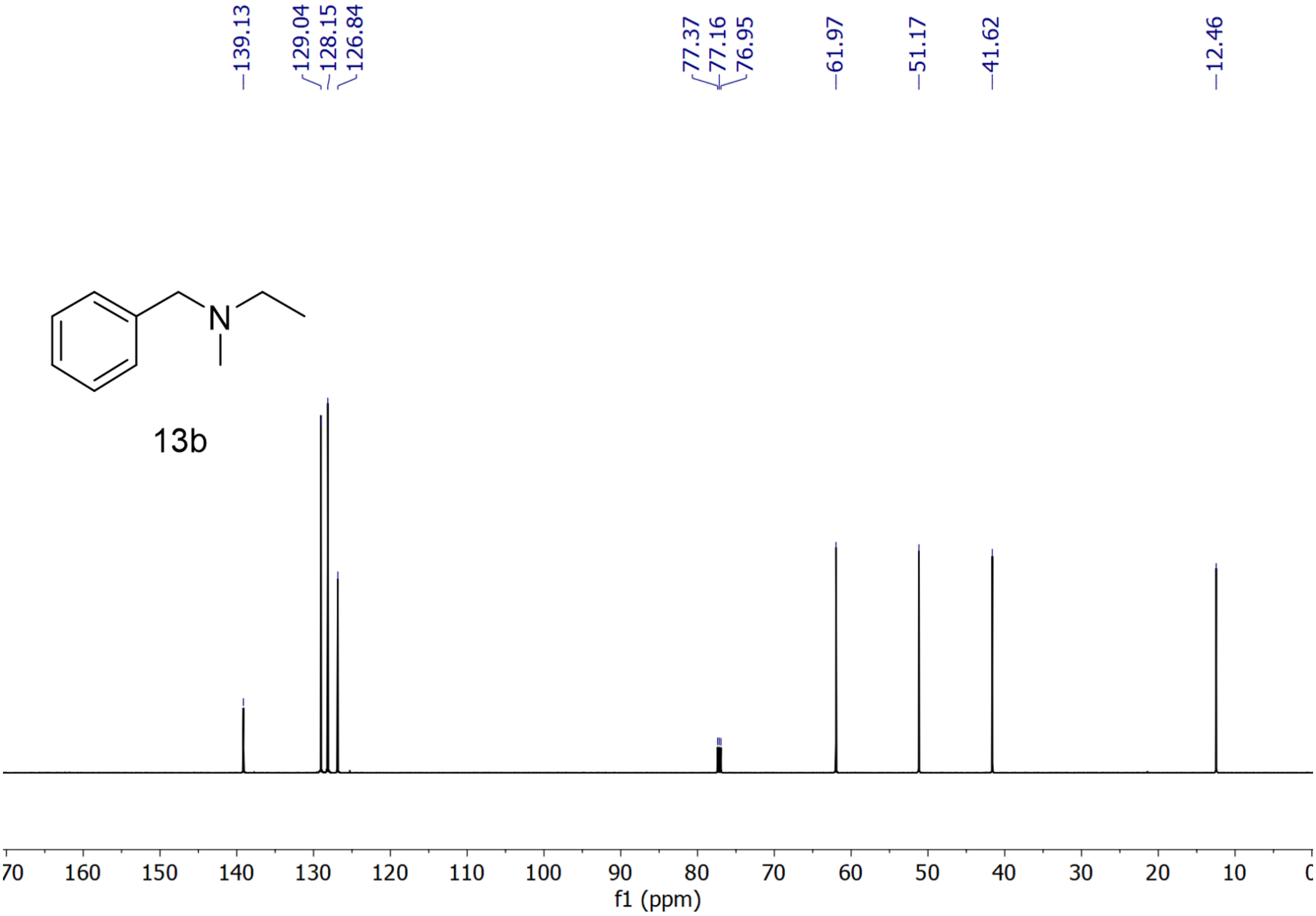
7.38
7.37
7.37
7.36
7.31
7.31
7.30
7.30
7.29
7.28
3.55
2.53
2.52
2.51
2.50
2.26
2.26
1.19
1.17
1.17
1.16
13b
3.66
0.91
2.02
1.99
3.00
2.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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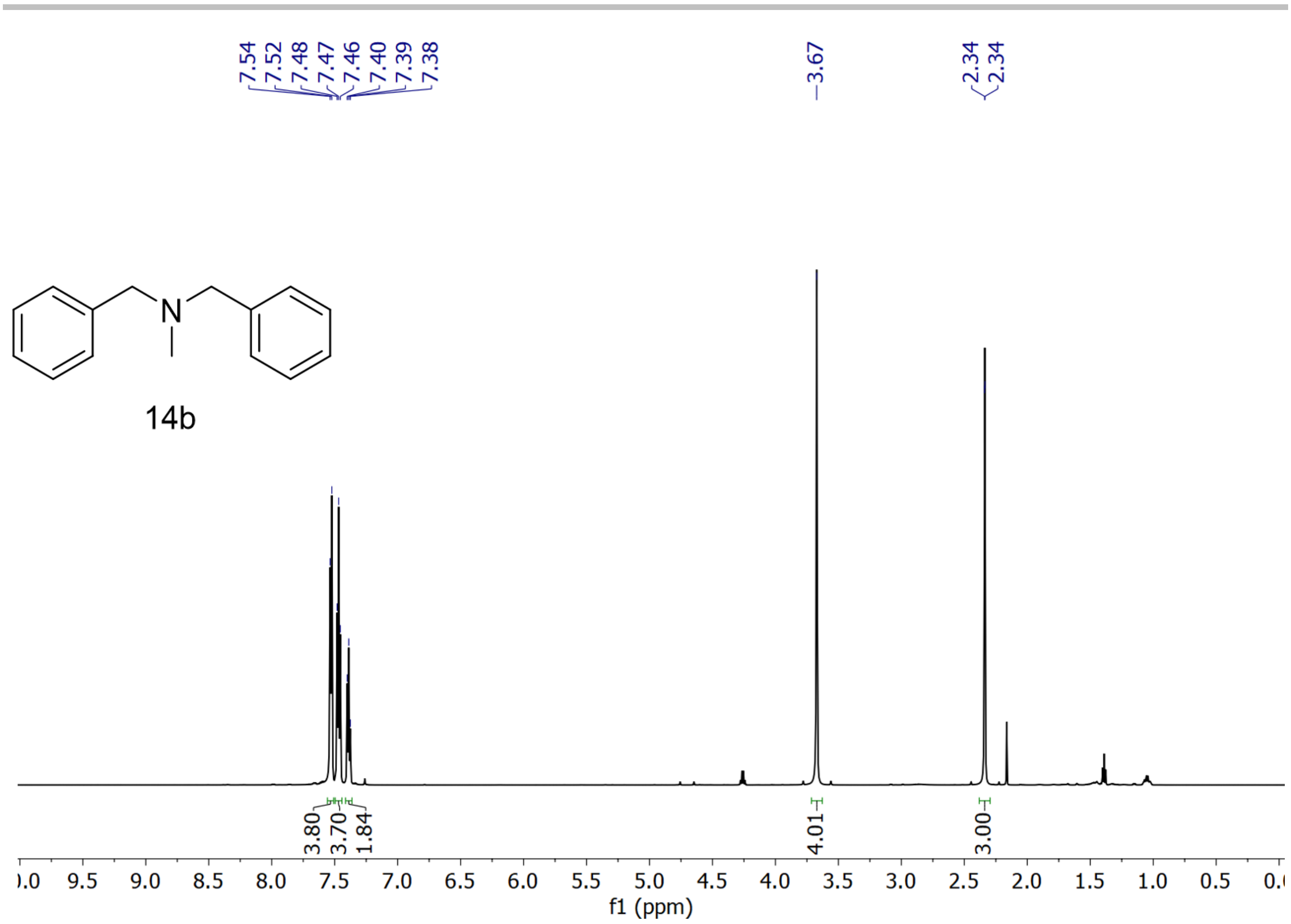
129.04
128.15
126.84
77.37
77.16
76.95
61.97
51.17
41.62
12.46
13b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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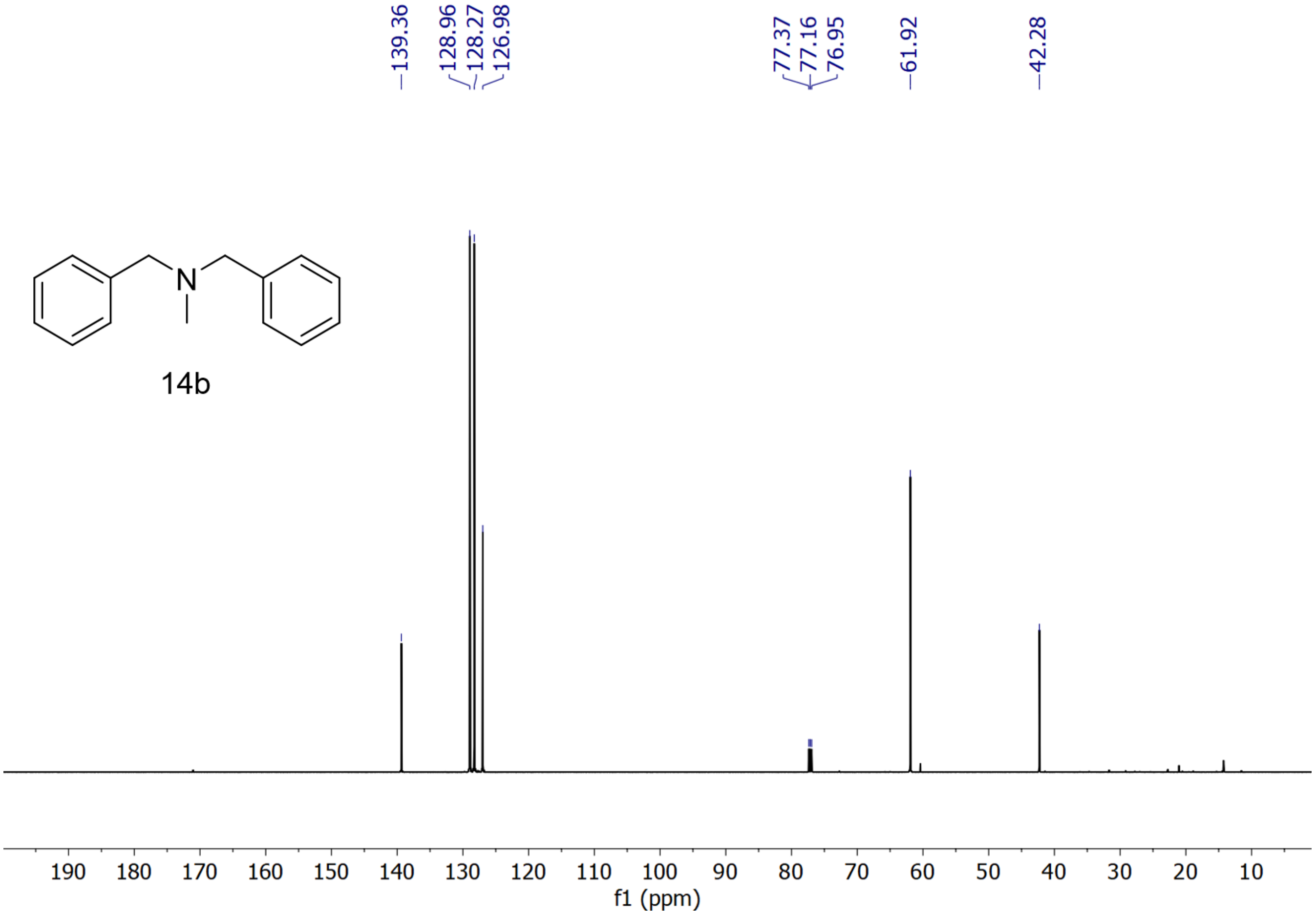
7.52
7.48
7.47
7.46
7.40
7.39
7.38
3.67
2.34
2.34
N
14b
3.80
3.70
1.84
4.01
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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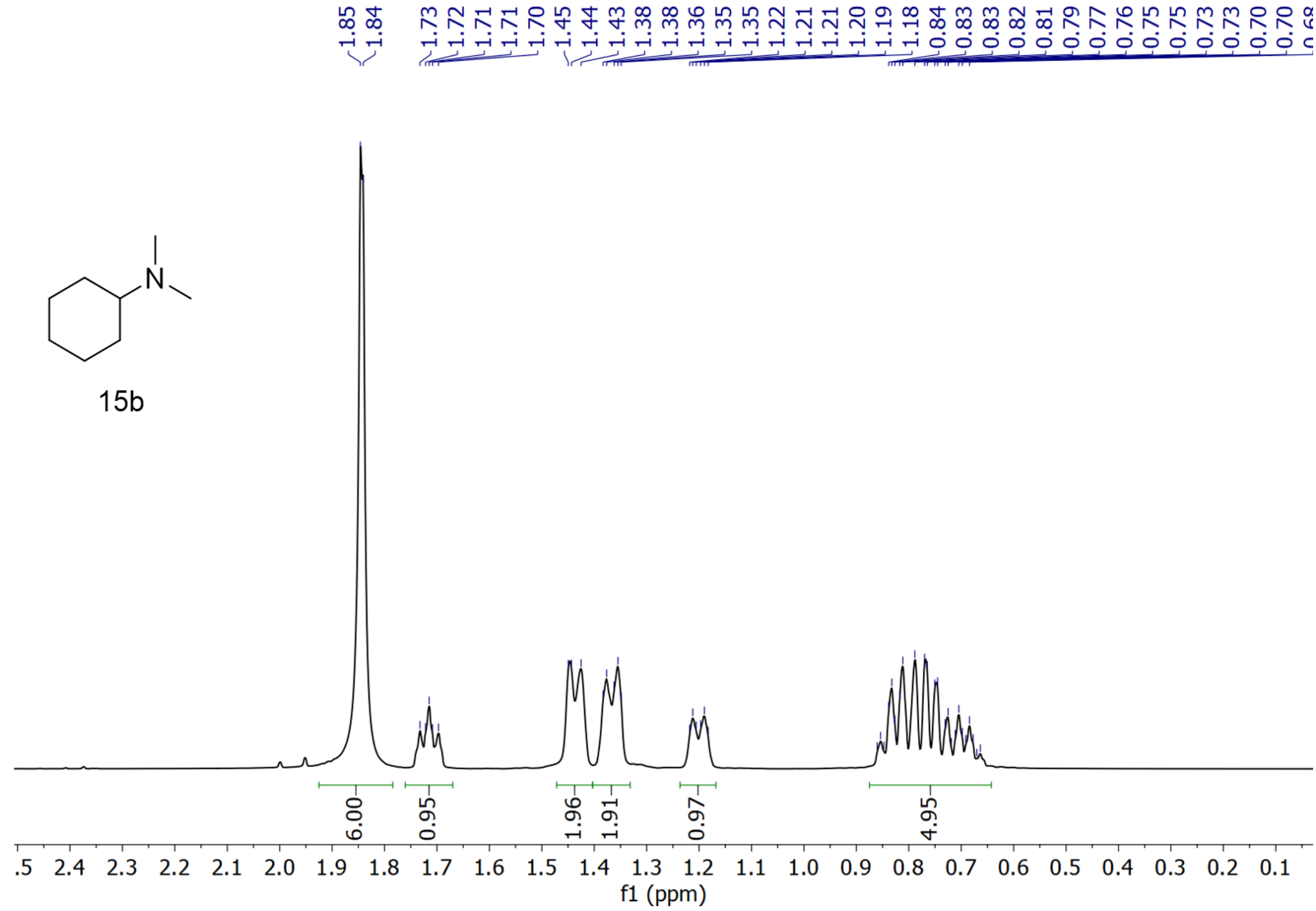
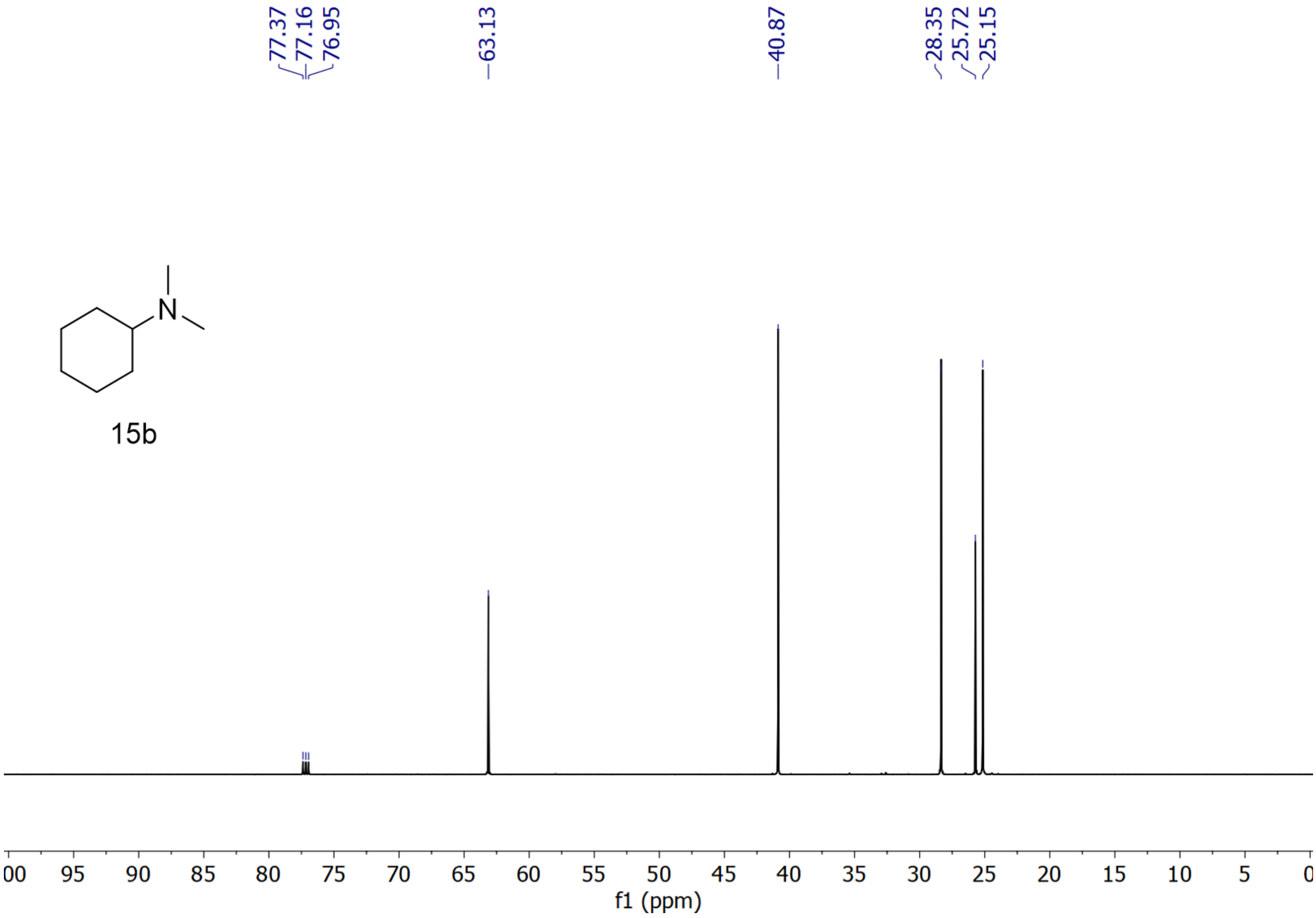
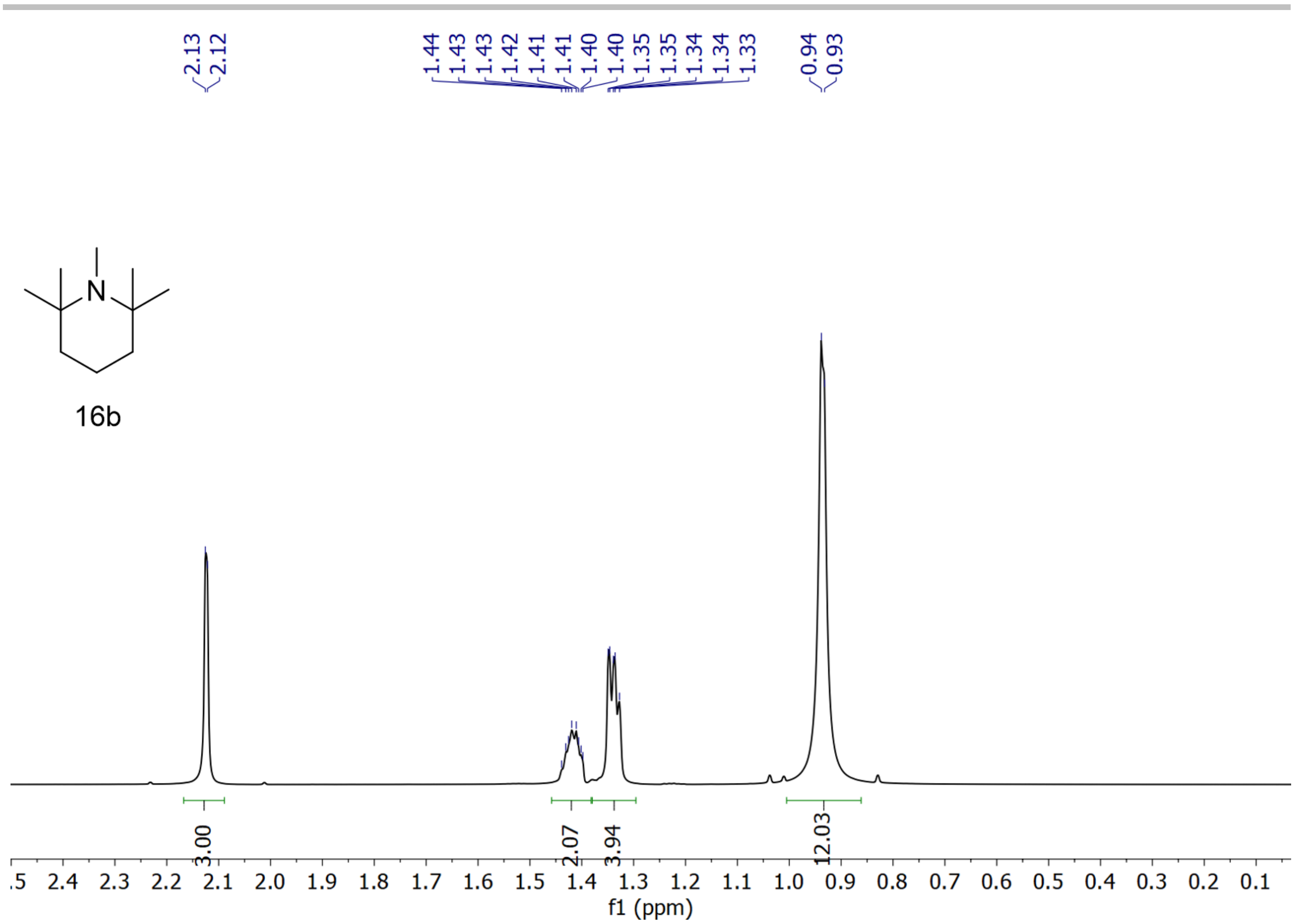
128.96
128.27
126.98
77.37
77.16
76.95
61.92
42.28
N
14b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

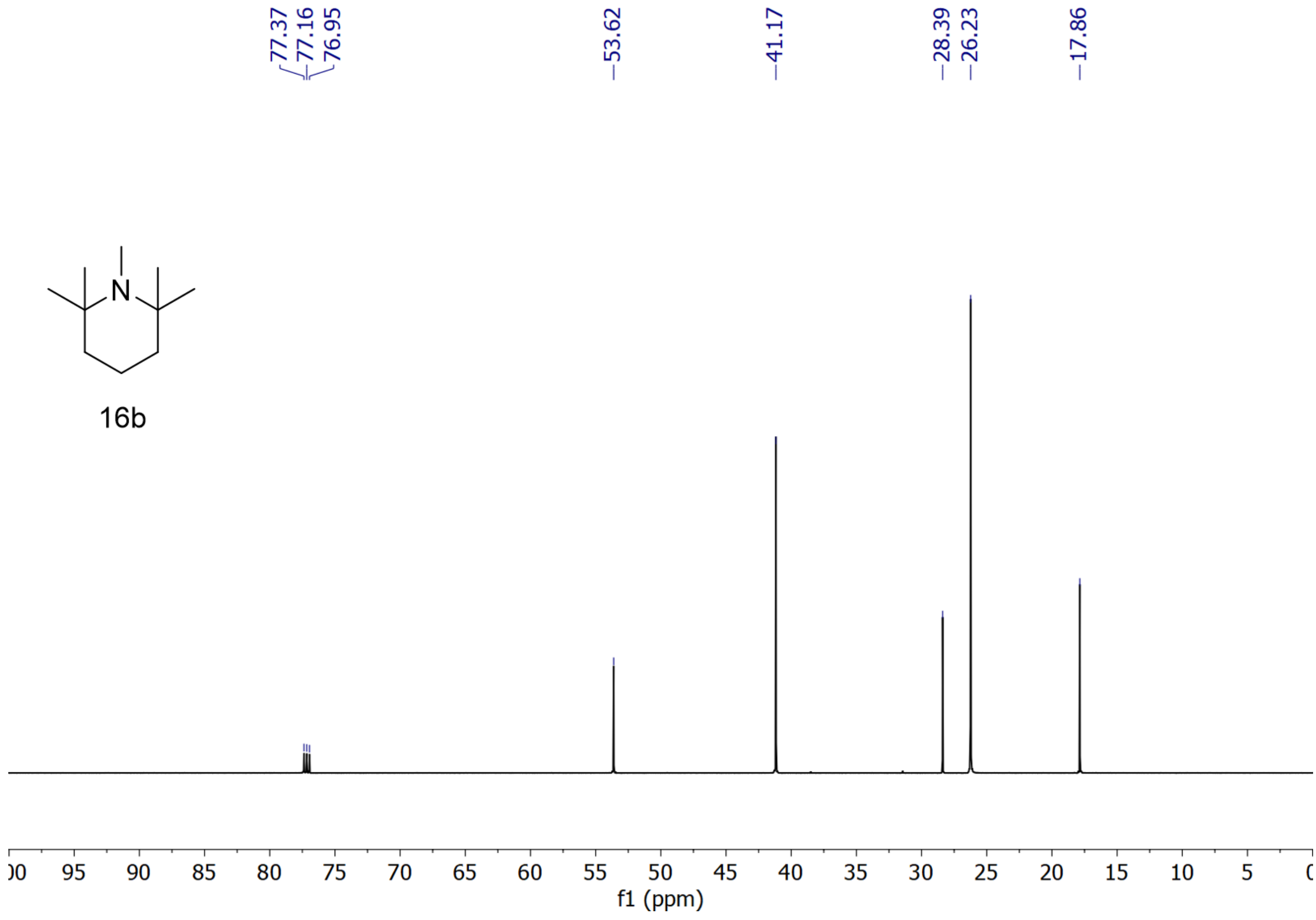


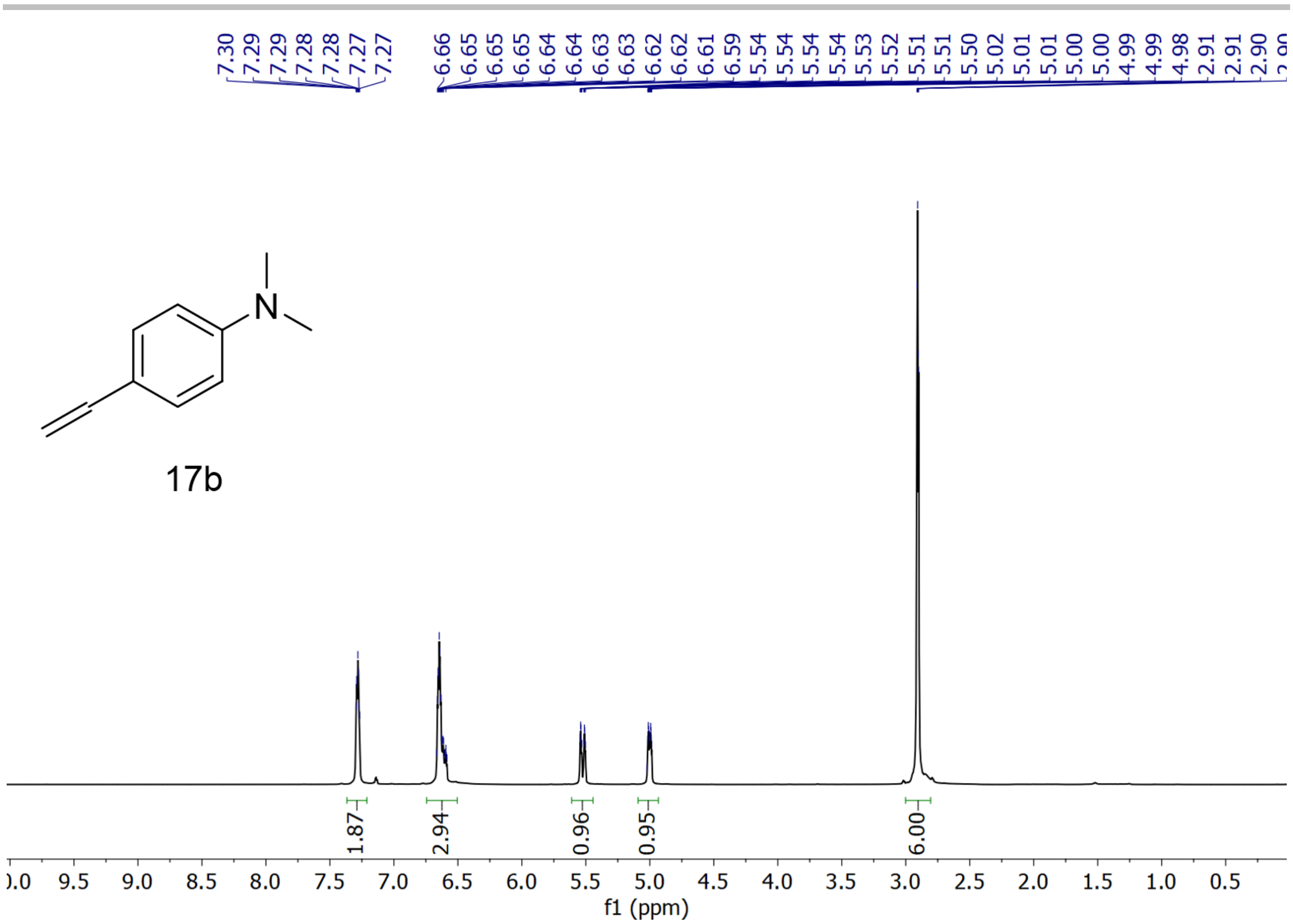
15b
1.85
1.84
1.73
1.72
1.71
1.71
1.70
1.45
1.44
1.43
1.38
1.38
1.36
1.35
1.35
1.22
1.21
1.21
1.20
1.19
1.18
0.84
0.83
0.83
0.82
0.81
0.79
0.77
0.76
0.75
0.75
0.73
0.73
0.70
0.70
6.00
0.95
1.96
1.91
0.97
4.95
.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1
f1 (ppm)



77.37
77.16
76.95
63.13
40.87
28.35
25.72
25.15
15b
00 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


2.13
2.12
1.44
1.43
1.43
1.42
1.41
1.41
1.40
1.40
1.35
1.35
1.34
1.34
1.33
0.94
0.93
N
16b
3.00
2.07
3.94
12.03
2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1
f1 (ppm)


77.37
77.16
76.95
53.62
41.17
28.39
26.23
17.86
N
16b
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)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6.65
6.65
6.65
6.64
6.64
6.63
6.63
6.62
6.62
6.61
6.59
5.54
5.54
5.54
5.54
5.53
5.52
5.51
5.51
5.50
5.02
5.01
5.01
5.00
5.00
4.99
4.99
4.98
2.91
2.91
2.90
N
17b
1.87
2.94
0.96
0.95
6.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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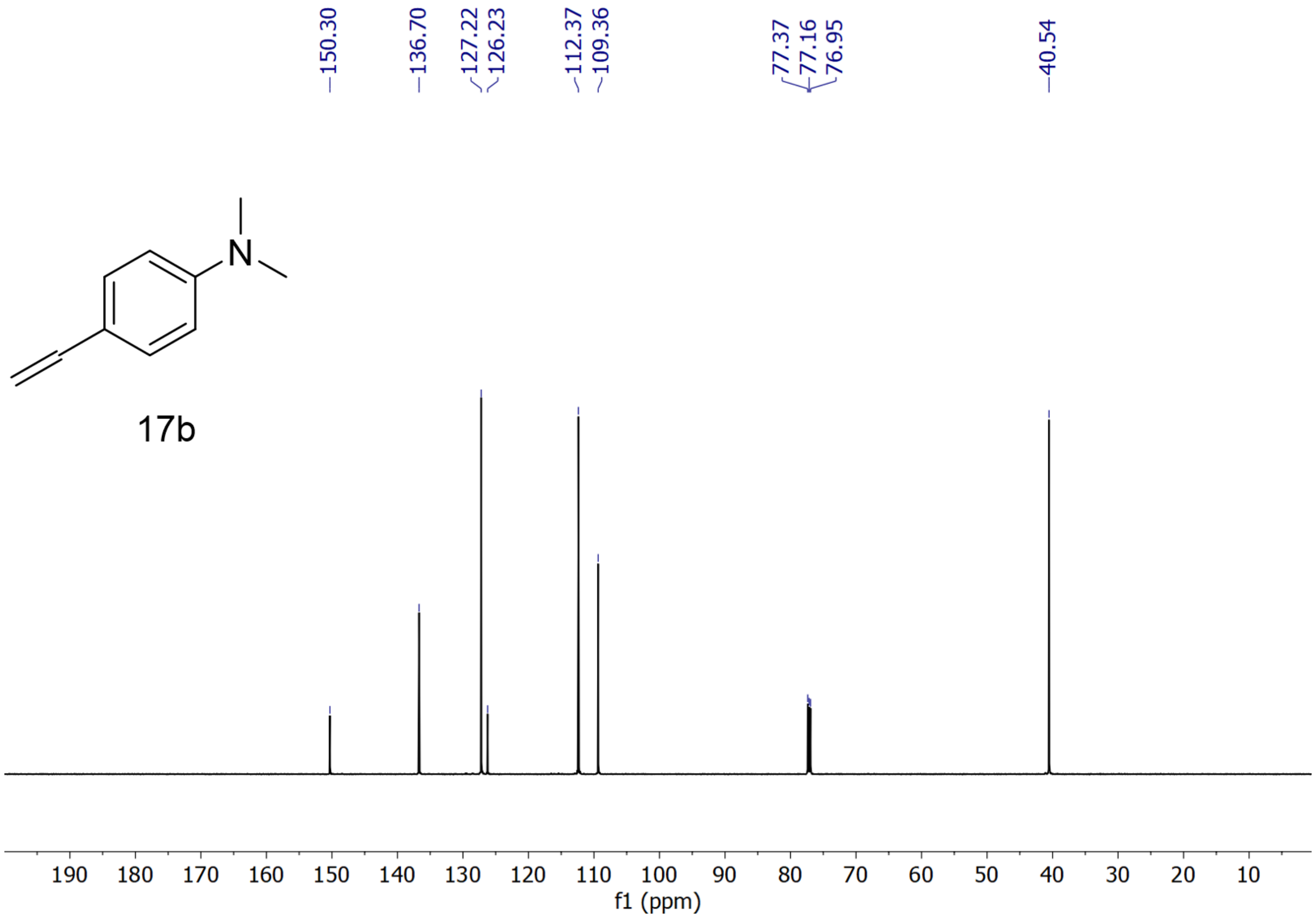
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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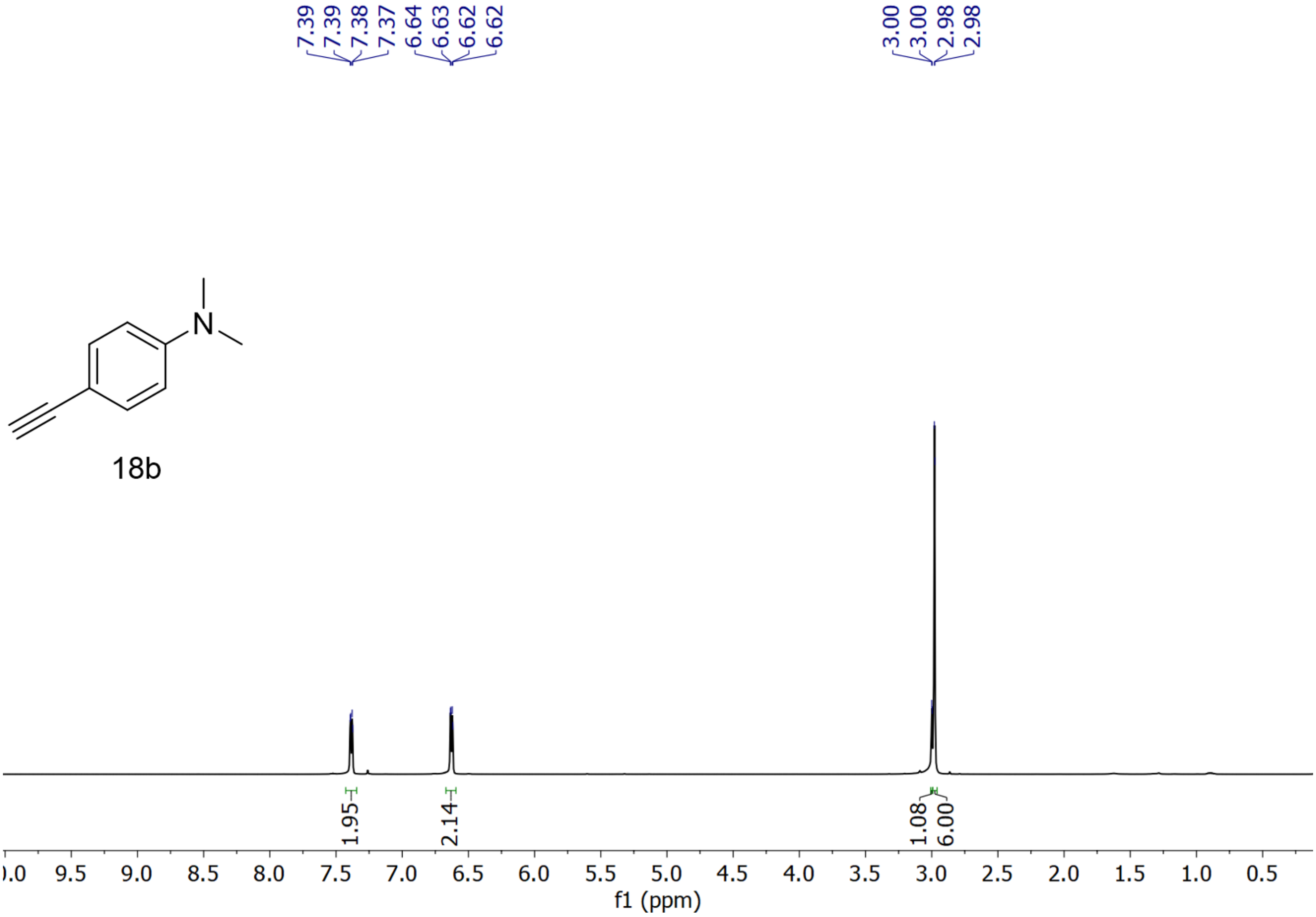
136.70
127.22
126.23
112.37
109.36
77.37
77.16
76.95
40.54
N
17b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.39
7.38
7.37
6.64
6.63
6.62
6.62
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3.00
2.98
2.98
N
18b
1.95
2.14
1.08
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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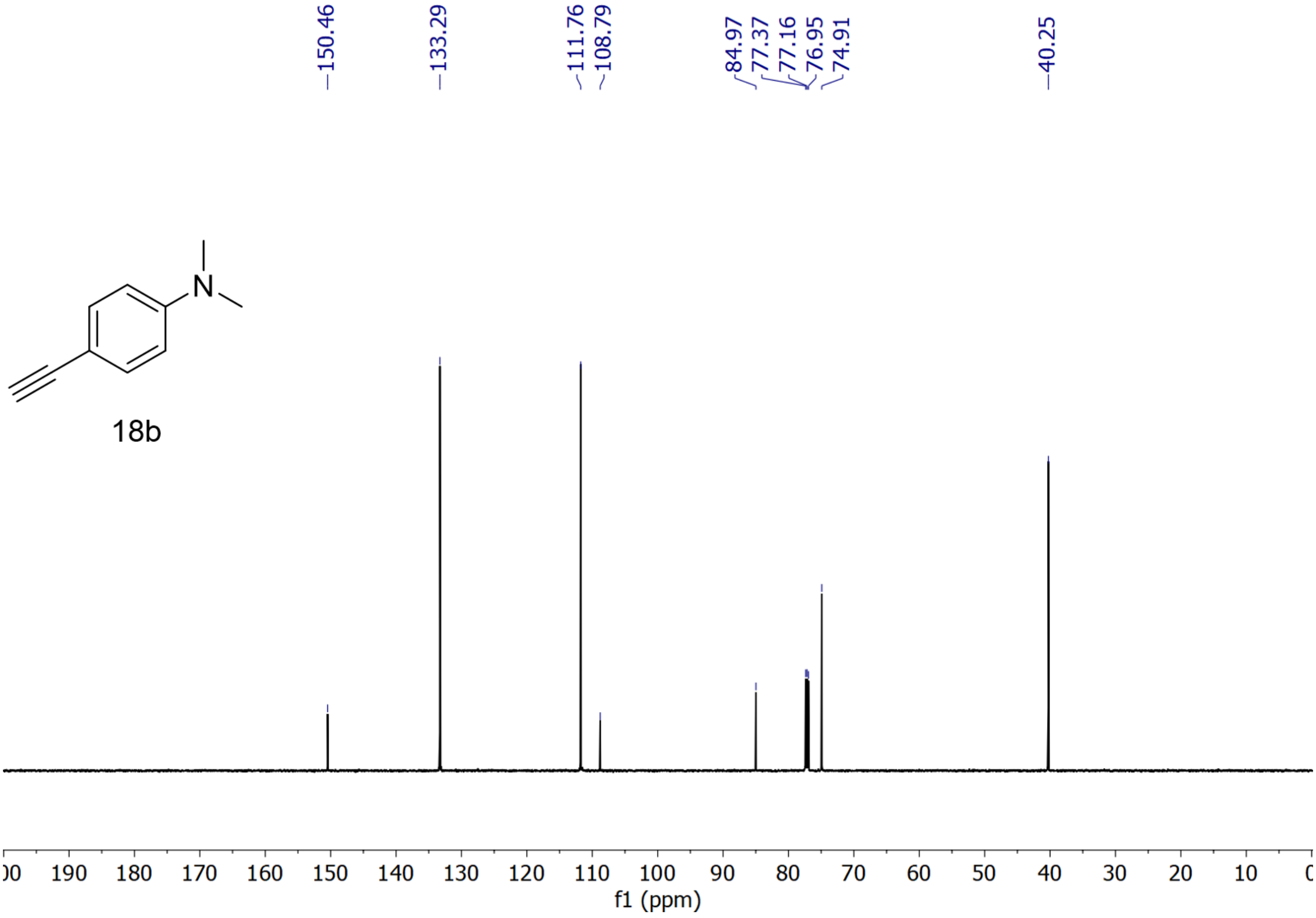
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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108.79
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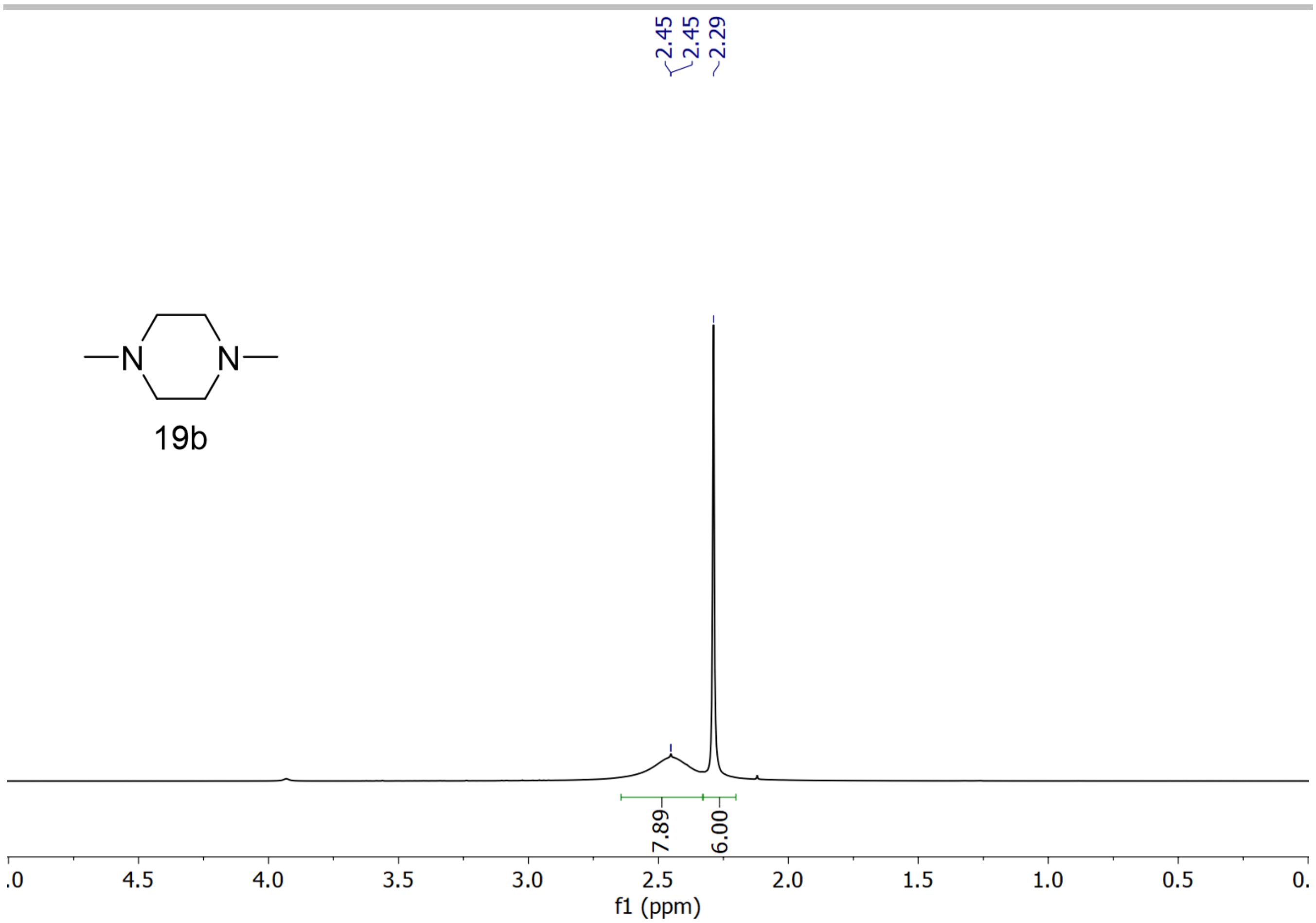
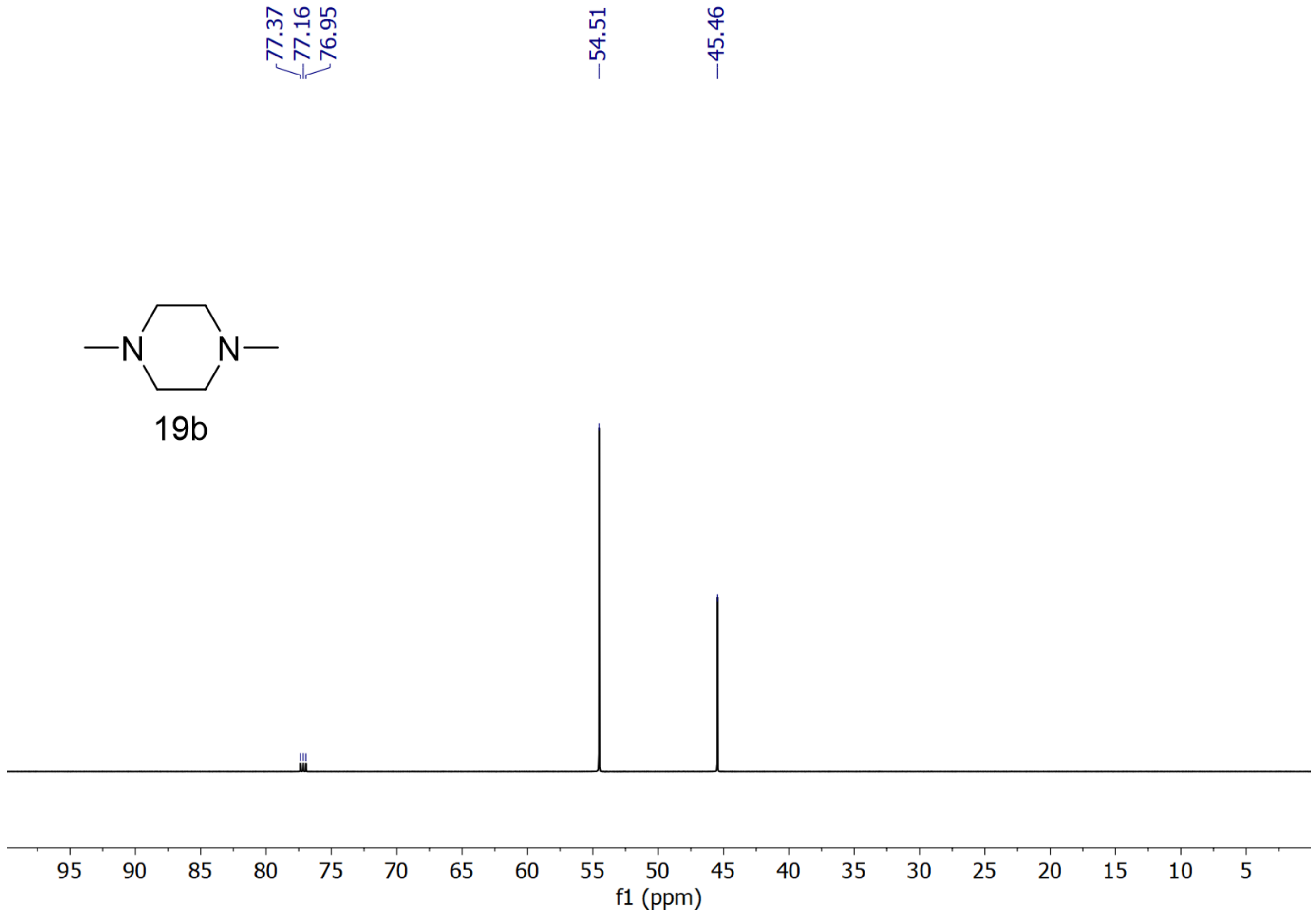
77.37
77.16
76.95
74.91
40.25
N
18b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


19b
2.45
2.45
2.29
7.89
6.00
.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


19b
77.37
77.16
76.95
54.51
45.46
95
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85
80
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70
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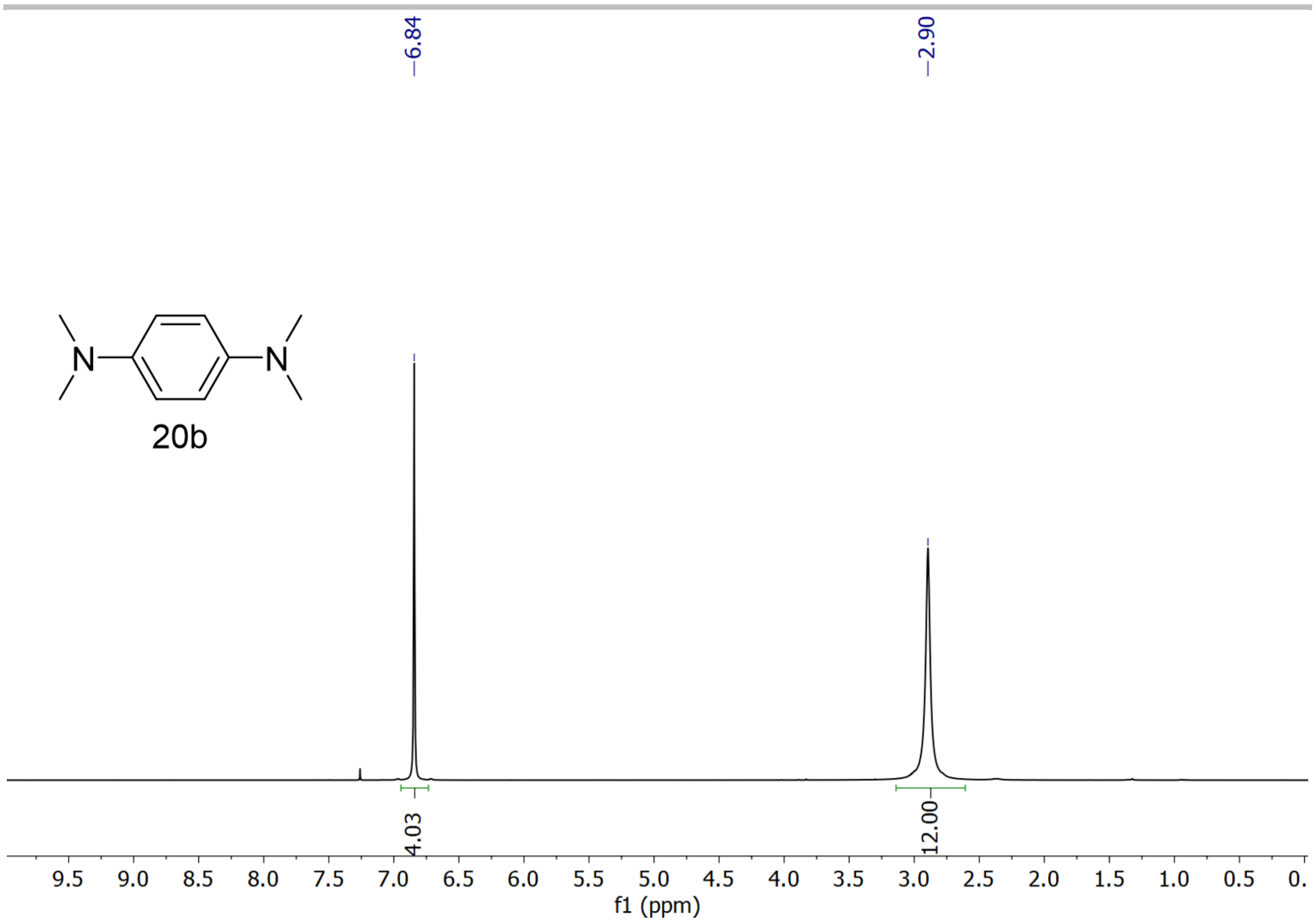
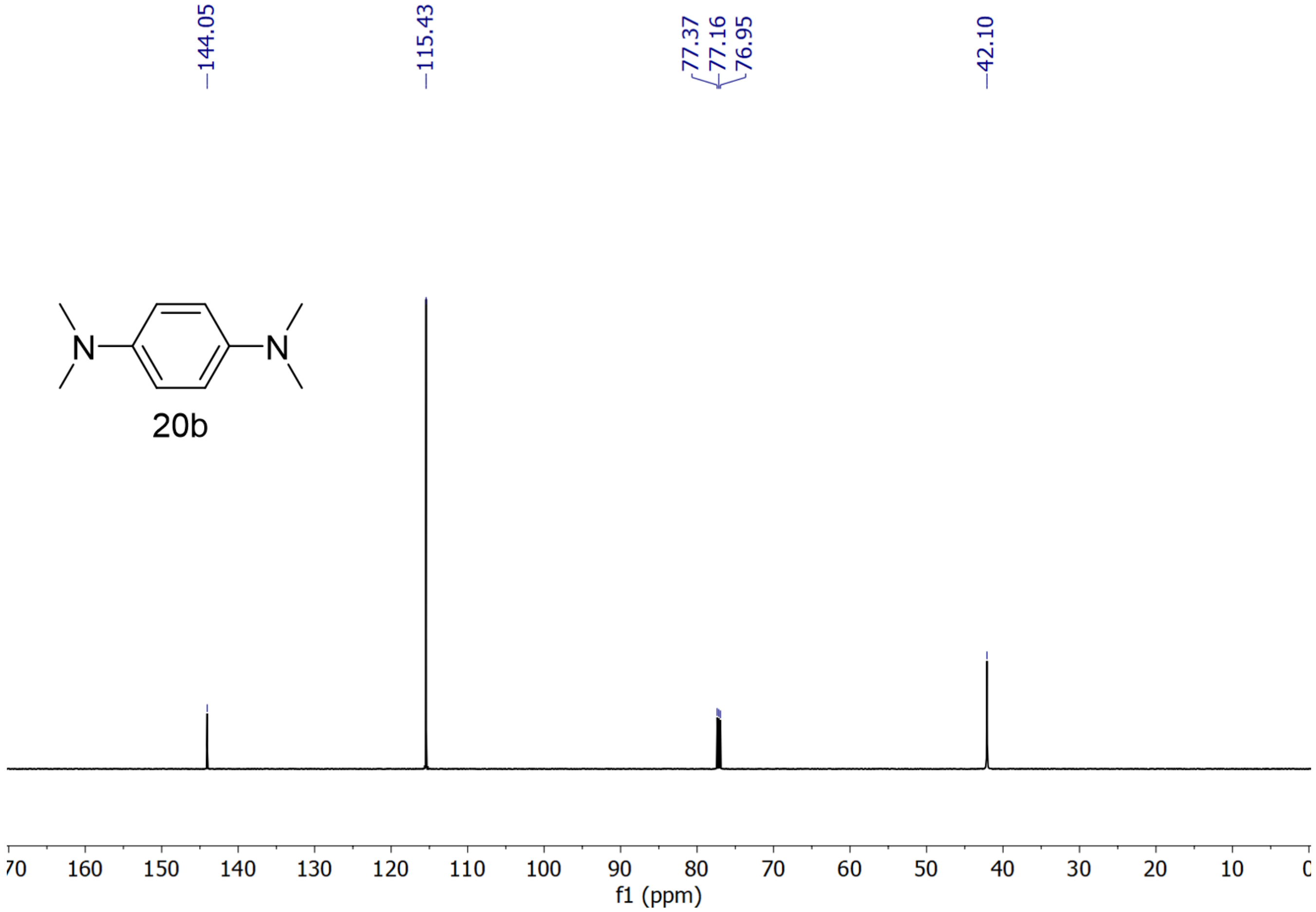
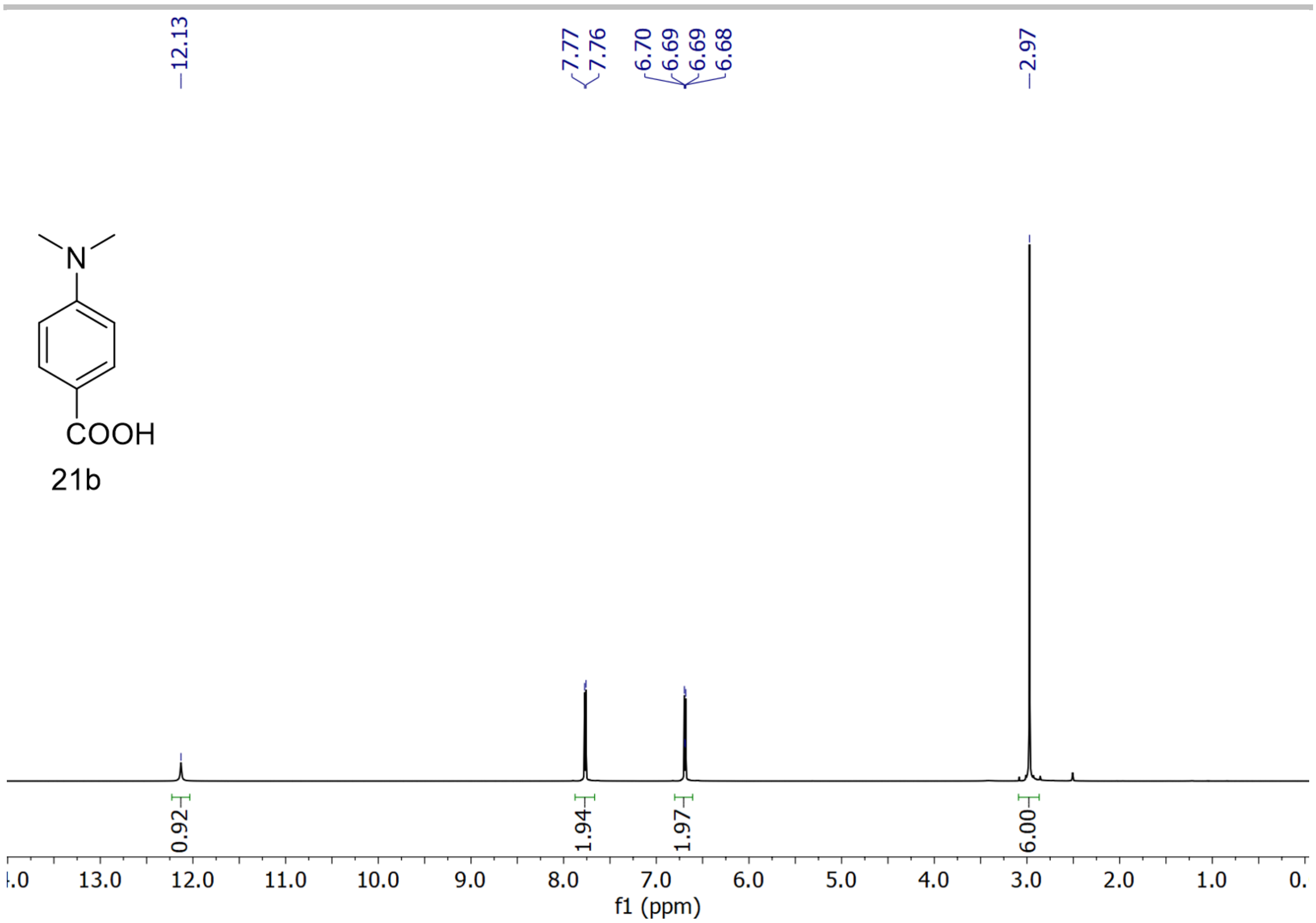
20
15
10
5
f1 (ppm)


20b
6.84
2.90
4.03
12.00
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.
f1 (ppm)


20b
144.05
115.43
77.37
77.16
76.95
42.10
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
C
f1 (ppm)


12.13
7.77
7.76
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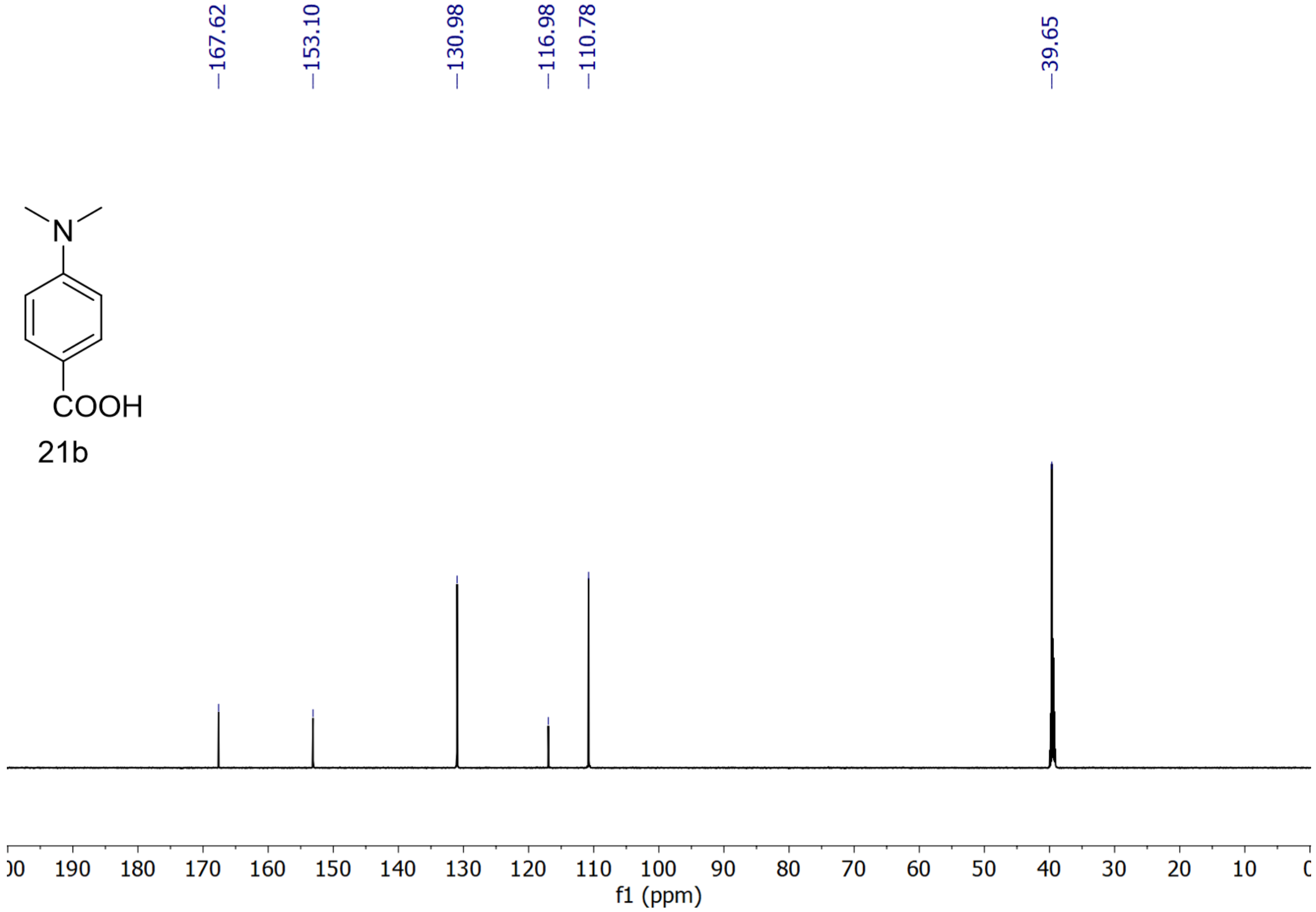
6.69
6.69
6.68
2.97
N
COOH
21b
0.92
1.94
1.97
6.00
.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.
f1 (ppm)


167.62
153.10
130.98
116.98
110.78
39.65
N
COOH
21b
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(
f1 (ppm)