Supporting Information

for

Enhanced catalytic activity of [CpNi(NHC)Cl] complexes in arylamination

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General considerations:

All aryl halides and amines were used as received. Anhydrous solvents (1,4-dioxane, tetrahydrofuran (THF), dimethoxyethane (DME), and toluene) and the bases (NaO^tBu, KO^tBu) were stored in a glovebox and used as received. KO^tAm, received as a 1.7 M solution in toluene, was dried on a schlenk line, stored in a glovebox and used a white powder. Nickelocene was purchased from STREM chemicals and used as received.

Flash chromatography was performed on silica gel 60 Å pore diameter and 40-63 μm particle size.

^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker- 300 MHz or 400 MHz spectrometer at ambient temperature in CD_2Cl_2 or $CDCl_3$. Chemical shifts (δ) are reported in ppm, relative to the solvent residual peak CD_2Cl_2 (5.32 ppm for ^1H and 54.00 ppm for ^{13}C) and $CDCl_3$ (7.26 ppm for ^1H and 77.16 ppm for ^{13}C). Data for ^1H NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, br = broad signal, m = multiplet), coupling constants (*J*) in Hz and integration.

Elemental analyses were performed at London Metropolitan University 166-220 Holloway Road, London, N7 8DB.

Gas chromatography analyses (GC) were performed on an Agilent 7890A apparatus equipped with a flame ionization detector and a (5%-Phenyl)-methylpolysiloxane column (30 m, 320 μm, film: 0.25 μm). Flow rate 1 mL/min constant flow, inlet temperature 260°C, column temperature 50°C, 20°C/min increase to 300°C (held for 1 min), total time 7.6 min.

Structure Overlay of complexes 1-5:

The overlays of the core molecular structure of **1-5** obtained by X-Ray analysis are shown in Figure S1. The spatial postions of the C1 (carbene carbon), the nickel center and the Cp ligand do not appear significantly different regardless of the nature of the NHC ligand.

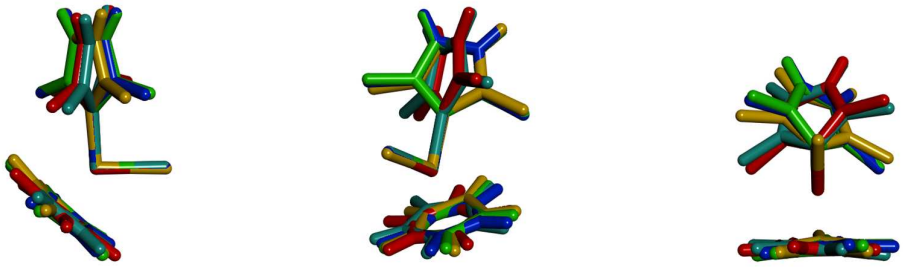
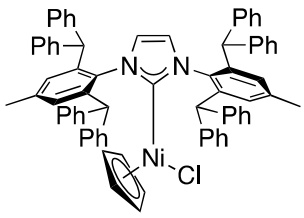


Figure S1. Three views of the overlay of **1-5**. Red (**1**), Green (**2**), Blue (**3**), Teal (**4**), Yellow (**5**). *N*-aryl substituents have been omitted for clarity.

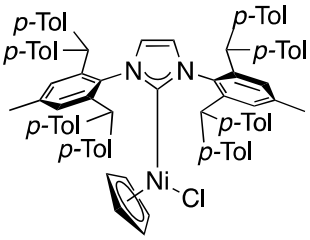
General procedure for the preparation of the complexes 1-4.

In a glovebox, a 50 mL Schlenk flask equipped with a magnetic stirring bar was charged with nickelocene (200 mg, 1.06 mmol) NHC•HCl (1.0 eq., 1.06 mmol) and 20 mL of THF. Outside of the glovebox, the reaction mixture was connected to a Schlenk line and stirred at 70°C for 3-16h. The solvent was eventually evaporated off and the crude residue was dissolved into CH_2Cl_2 (15 mL) before being passed through a bed of Celite® over silica (4 cm of each). The collected filtrate was concentrated until 3 mL of solution remains (excepted for IPent which was concentrated to dryness and did not need further purification). Addition of pentane resulted in the precipitation of the complexes. The supernatant was removed and the residue was washed twice with 25 mL of pentane. The complexes were finally dried overnight under high vacuum at 80°C.

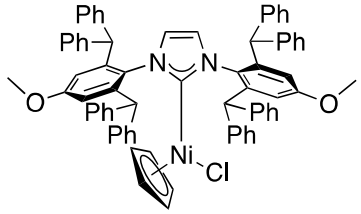


[Ni(IPr*)CpCl] (1). Following the general procedure, using 200 mg of nickelocene and 1.006 g of IPr*•HCl, **1** was isolated as a purple-pink powder (896 mg) in a 79% yield. Suitable crystals for X-Ray diffraction analysis were grown by slow diffusion of pentane into a staurated solution of **1** in chloroform. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 2.34 (s,

6H, CH_3) 4.59 (s, 5H, CH_{Cp}), 5.02 (s, 2H, C$H_{imid.}$), 5.77 (s, 4H, CH(Ph)$_2$), 6.70-6.74 (m, 8H, H_{Ar}), 7.03 (s, 4H, H_{Ar}), 7.07-7.10 (m, 12H, H_{Ar}), 7.22-7.33 (m, 20H, H_{Ar}). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz) δ 22.1 (*C*H_3), 51.7 (*C*H), 93.5 (*C*H_{Cp}), 125.6 (*C*H_{Ar}), 126.8 (*C*H_{Ar}), 127.0 (*C*H_{Ar}), 128.6 (*C*H_{Ar}), 128.7 (*C*H_{Ar}), 129.8 (*C*H_{Ar}), 130.8 (*C*H_{Ar}), 130.9 (*C*H_{Ar}), 137.0 (C_{Ar}), 139.3 (C_{Ar}), 142.6 (C_{Ar}), 143.9 (C_{Ar}), 145.1 (C_{Ar}), 167.9 (C_{Ar}). Anal. Calcd for $C_{74}H_{61}N_2ClNi$: C, 82.88; H, 5.73; N, 2.61; found C, 82.91; H, 5.81; N, 2.74.

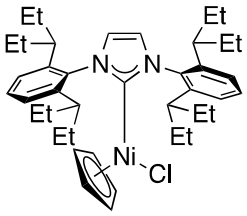


[Ni(IPr*^{Tol})CpCl] (2). Following the general procedure, using 200 mg of nickelocene and 1.124 g of IPr*^{Tol}•HCl, **2** was isolated as a purple-pink powder (839 mg) in a 67% yield. Suitable crystals for X-Ray diffraction analysis were grown by slow diffusion of pentane into a saturated solution of **2** in toluene. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 2.23 (s, 12H, CH_3) 2.32-2.34 (m, 18H, CH_3) 4.59 (s, 5H, CH_{Cp}), 5.12 (s, 2H, C$H_{imid.}$), 5.72 (s, 4H, CH(Ph)$_2$), 6.58 (d, *J* 8.1 Hz, 8H, H_{Ar}), 6.87 (d, *J* 7.9 Hz, 8H, H_{Ar}), 7.02 (s, 4H, H_{Ar}), 7.07 (d, *J* 8.0 Hz, 8H, H_{Ar}), 7.19 (d, *J* 8.1 Hz, 8H, H_{Ar}). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz) δ 21.2 (*C*H_3), 21.3 (*C*H_3), 22.1 (*C*H_3), 51.0 (*C*H), 93.6 (*C*H_{Cp}), 125.6 (*C*H_{Ar}), 129.2 (*C*H_{Ar}), 129.3 (*C*H_{Ar}), 129.6 (*C*H_{Ar}), 130.5 (*C*H_{Ar}), 130.8 (*C*H_{Ar}), 136.3 (C_{Ar}), 136.5 (C_{Ar}), 137.0 (C_{Ar}), 138.9 (C_{Ar}), 141.3 (C_{Ar}), 142.3 (C_{Ar}), 142.6 (C_{Ar}), 166.9 (C_{Ar}). Anal. Calcd for $C_{82}H_{77}N_2ClNi$: C, 83.14; H, 6.55; N, 2.36; found C, 83.12; H, 6.53; N, 2.46.



[Ni(IPr*^{OMe})CpCl] (3). Following the general procedure, using 200 mg of nickelocene and 1.039 g of IPr*^{OMe}•HCl, **3** was isolated as a purple-pink powder (983 mg) in a 84% yield. Suitable crystals for X-Ray diffraction analysis were grown by slow evaporation of a concentrated solution of **3** in dichloromethane. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 3.65 (s, 6H, OCH_3) 4.64 (s, 5H, CH_{Cp}), 4.96 (s, 2H, C$H_{imid.}$), 5.77 (s, 4H, CH(Ph)$_2$), 6.71 (s, 4H, H_{Ar}), 6.73-6.76 (m, 8H, H_{Ar}), 7.07-7.10 (m, 12H, H_{Ar}), 7.22-733

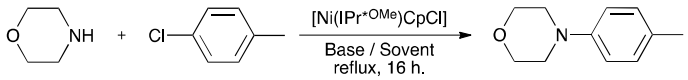
(m, 20H, H_{Ar}). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 75 MHz) δ 52.0 (*C*H), 55,7 (O*C*H_3) 93.4 (*C*H_{Cp}), 115,4 (*C*H_{Ar}), 125.7 (*C*H_{Ar}), 126.9 (*C*H_{Ar}), 127.2 (*C*H_{Ar}), 128.7 (*C*H_{Ar}), 129.7 (*C*H_{Ar}), 130.9 (*C*H_{Ar}), 132.5 (C_{Ar}), 143.7 (C_{Ar}), 144.5 (C_{Ar}), 144.9 (C_{Ar}), 159.7 (C_{Ar}), 168.7. Anal. Calcd for $C_{74}H_{61}N_2O_2ClNi$: C, 80.47; H, 5.57; N, 2.54; found C, 80.53; H, 5.65; N, 2.67.



[Ni(IPent)CpCl] (4). Following the general procedure, using 200 mg of nickelocene and 531 mg of IPent•HCl, **4** was isolated as a purple-pink powder (468 mg) in a 76% yield. Suitable crystals for X-Ray diffraction analysis were grown by slow evaporation of a saturated solution of **4** in pentane. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 0.73 (t, *J* 7.5 Hz, 12H, C*H*$_3$), 1.02 (t, *J* 7.3 Hz, 12H, C*H*$_3$), 1.43-1.58 (m, 8H, C*H*$_2$), 1.83-2.04 (m, 8H, C*H*$_2$), 2.46-2.54 (m, 4H, C*H*), 4.48 (s, 5H, C*H*$_{Cp}$), 7.09 (s, 2H, C*H*$_{imid.}$), 7.32 (d, *J* 7.8 Hz, 4H, H_{Ar}), 7.52 (t, *J* 7.7 Hz, 2H, H_{Ar}). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 75 MHz) δ 10.4 (*C*H_3), 12.9 (*C*H_3), 26.6 (*C*H_2), 27.6 (*C*H_2), 41.3 (*C*H), 92.8 (*C*H_{Cp}), 125.9 (*C*H_{Ar}), 126.4 (*C*H_{Ar}), 129.2 (*C*H_{Ar}), 145.0 (C_{Ar}), 167.5 (C_{Ar}). Anal. Calcd for $C_{40}H_{57}N_2ClNi$: C, 72.79; H, 8.70; N, 4.24; found C, 72.68; H, 8.82; N, 4.33.

Optimization reactions:

Optimization of the solvent/ base combination and catalyst loading[a]



Solvent	Base	Catalyst loading (mol %)	Conversion (%)[b]
Dioxane	KO^{t}Bu	5	89
Dioxane	NaO^{t}Bu	5	39
Dioxane	KO^{t}Am	5	97
Dimethoxyethane (DME)	KO^{t}Bu	5	26
Dimethoxyethane (DME)	NaO^{t}Bu	5	2
Dimethoxyethane (DME)	KO^{t}Am	5	52
THF	KO^{t}Bu	5	48
THF	NaO^{t}Bu	5	0
THF	KO^{t}Am	5	66
Toluene	KO^{t}Bu	5	89
Toluene	NaO^{t}Bu	5	58
Toluene	KO^{t}Am	5	>99
Toluene	KO^{t}Am	2.5	17
Toluene	KO^{t}Am	1	<2

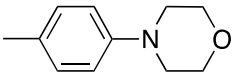
[a] Reaction conditions: 4-chlorotoluene (0.38 mmol), morpholine (0.57 mmol), base (0.76 mmol), solvent (1 mL).

[b] Conversion to *N*-arylated product was determined by GC.

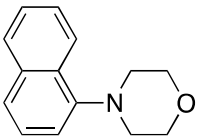
General procedure for the Buchwald-Hartwig amination reaction.

In a glovebox, a vial containing a stir bar was charged with KO^{t}Am (96 mg, 0.76 mmol, 2.0 equiv.), [Ni(IPr*^{OMe})CpCl] **3** (1.90 x 10^{-5} mol, 21 mg, 5 mol%) and sealed with a screw cap fitted with a septum. The amine (0.57 mmol, 1.5 equiv.) and/or the aryl chloride (0.38 mmol, 1.0 equiv.) were added at this point if solids. Outside of the glovebox, the solvent (toluene, 1 mL) was added, followed by the amine and/or the aryl chloride if liquids. Finally, the vial was heated at 110°C for 16 h. The solution was then cooled to room temperature, diluted with 5 mL of dichloromethane and passed through a plug of celite® which was subsequently washed twice with 5 mL of dichloromethane. The collected filtrated was concentrated and adsorbed on silica gel prior to purification via flash column chromatography.

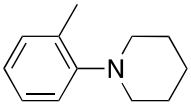
Characterization data of the coupling products.



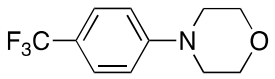
N-(p-tolyl)morpholine[1] *(Table 4,* ***9a****)*. The general procedure yielded, after flash chromatography on silica gel (EtOAc, Pentane), 124 mg (92%) of the title compound as a colourless solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.30 (s, 3H, C*H*$_3$), 3.11-3.14 (m, 4H, N-C*H*$_2$), 3.86-3.90 (m, 4H, O-C*H*$_2$), 6.86 (d, *J* 8.7 Hz, 2H, H_{Ar}), 7.12 (d, *J* 8.7 Hz, 2H, H_{Ar}). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 20.5 (*C*H$_3$), 50.1 (*C*H$_2$), 67.1 (*C*H$_2$), 116.2 (*C*H$_{Ar}$), 129.7 (C_{Ar}), 129.8 (*C*H$_{Ar}$), 149.2 (C_{Ar}).



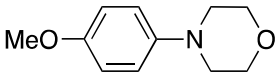
N-naphthalenylmorpholine[2] *(Table 4,* ***9b****)*. The general procedure yielded, after flash chromatography on silica gel (EtOAc, Pentane), 117 mg (72%) of the title compound as a colourless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.13-3.16 (m, 4H, N-C*H*$_2$), 4.01-4.04 (m, 4H, O-C*H*$_2$), 7.12 (dd, *J* 7.4 and 1.1 Hz, 1H, H_{Ar}), 7.46 (dd, *J* 8.2 and 7.4 Hz, 1H, H_{Ar}), 7.49-7.57 (m, 2H, H_{Ar}), 7.62 (d, *J* 8.2 Hz, 1H, H_{Ar}), 7.87-7.90 (m, 1H, H_{Ar}), 8.27-8.30 (m, 1H, H_{Ar}). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 53.5 (*C*H$_2$), 67.5 (*C*H$_2$), 114.7 (*C*H$_{Ar}$), 123.5 (*C*H$_{Ar}$), 123.8 (*C*H$_{Ar}$), 125.5 (*C*H$_{Ar}$), 125.9 (*C*H$_{Ar}$), 128.5 (*C*H$_{Ar}$), 128.8 (C_{Ar}), 134.8 (C_{Ar}), 149.5 (C_{Ar}).



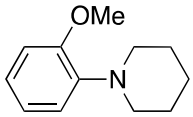
N-(o-tolyl)piperidine[3] *(Table 4,* ***9c****)*. The general procedure yielded, after flash chromatography on silica gel (EtOAc, Pentane), 38 mg (29%) of the title compound as a colourless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.51-1.69 (m, 2H, C*H*$_2$), 1.69-1.76 (m, 4H, C*H*$_2$), 2.32 (s, 3H, C*H*$_3$), 2.84-2.87 (m, 4H, C*H*$_2$), 6.85 (td, *J* 7.4 and 1.3 Hz, 1H, H_{Ar}), 7.02 (d, *J* 8.1 Hz, 1H, H_{Ar}), 7.14-7.20 (m, 2H, H_{Ar}). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 18.0 (*C*H$_3$), 24.6 (*C*H$_2$), 26.8 (*C*H$_2$), 53.5 (*C*H$_2$), 119.1 (*C*H$_{Ar}$), 122.7 (*C*H$_{Ar}$), 126.5 (*C*H$_{Ar}$), 131.0 (*C*H$_{Ar}$), 132.8 (C_{Ar}), 153.1 (C_{Ar}).



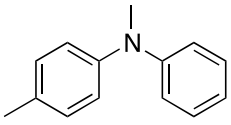
N-(4-trifluoromethylphenyl)morpholine[4] *(Table 4,* ***9e****)*. The general procedure yielded, after flash chromatography on silica gel (EtOAc, Pentane), 163 mg (93%) of the title compound as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.23-3.25 (m, 4H, CH_2), 3.86-3.88 (m, 4H, CH_2), 6.93 (d, *J* 8.6 Hz, 2H, H_{Ar}), 7.50 (d, *J* 8.5 Hz, 2H, H_{Ar}). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 48.3 (*C*H_2), 66.8 (*C*H_2), 114.4 (*C*H_{Ar}), 121.1 (q, $J_{C\text{-}F}$ 32.7 Hz, C_{Ar}), 124.8 (q, $J_{C\text{-}F}$ 270.7 Hz, C_{Ar}), 126.6 (q, $J_{C\text{-}F}$ 3.6 Hz, *C*H_{Ar}), 153.5 (C_{Ar}). ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz) δ -61.93.



N-(4-methoxyphenyl)morpholine[5] *(Table 4,* ***9f****)*. The general procedure yielded, after flash chromatography on silica gel (EtOAc, Pentane), 129 mg (88%) of the title compound as a colourless solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.04-3.07 (m, 4H, CH_2), 3.77 (s, 3H, CH_3), 3.85-3.88 (m, 4H, CH_2), 6.84-6.92 (m, 4H, H_{Ar}). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 50.9 (*C*H_2) 55.7 (*C*H_3), 67.1 (*C*H_2), 114.6 (*C*H_{Ar}), 117.9 (*C*H_{Ar}), 145.7 (C_{Ar}), 154.1 (C_{Ar}).

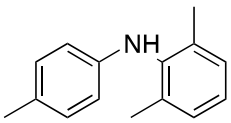


N-(2-methoxyphenyl)piperidine[2] *(Table 4,* ***9g****)*. The general procedure yielded, after flash chromatography on silica gel (EtOAc, Pentane), 97 mg (67%) of the title compound as a colourless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.54-1.60 (m, 2H, CH_2), 1.74-1.79 (m, 4H, CH_2), 2.97-3.00 (m, 4H, CH_2), 3.87 (s, 3H, CH_3), 6.85 (dd, *J* 7.7 and 1.4 Hz, 1H, H_{Ar}), 6.89-7.00 (m, 3H, H_{Ar}). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 24.6 (*C*H_2), 26.5 (*C*H_2), 52.4 (*C*H_2), 55.4 (*C*H_3), 111.2 (*C*H_{Ar}), 118.5 (*C*H_{Ar}), 121.0 (*C*H_{Ar}), 122.6 (*C*H_{Ar}), 142.9 (C_{Ar}), 152.5 (C_{Ar}).

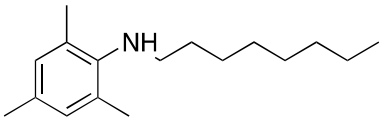


N,4-dimethyl-N-phenylaniline[1] *(Table 4,* ***9h****)*. The general procedure yielded, after flash chromatography on silica gel (EtOAc, Pentane), 127

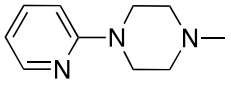
mg (85%) of the title compound as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.38 (s, 3H, CH_3), 3.34 (s, 3H, CH_3), 6.92 (tt, *J* 7.2 and 1.1 Hz, 1H, H_{Ar}), 6.95-7.00 (m, 2H, H_{Ar}), 7.03-7.08 (m, 2H, H_{Ar}), 7.16-7.19 (m, 2H, H_{Ar}), 7.25-7.32 (m, 2H, H_{Ar}). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 20.9 (*C*H_3), 40.4 (*C*H_3), 118.3 (*C*H_{Ar}), 119.9 (*C*H_{Ar}), 122.7 (*C*H_{Ar}), 129.1 (*C*H_{Ar}), 130.0 (*C*H_{Ar}), 131.1 (C_{Ar}), 146.7 (C_{Ar}), 149.5 (C_{Ar}).



N-(p-tolyl)-2,6-dimethylaniline[6] *(Table 4,* ***9i****)*. The general procedure yielded, after flash chromatography on silica gel (EtOAc, Pentane), 117 mg (73%) of the title compound as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.24 (s, 6H, CH_3), 2.28 (s, 3H, CH_3), 5.10 (br, 1H, N*H*), 6.44-6.49 (m, 2H, H_{Ar}), 7.00 (d, *J* 8.5 Hz, 2H, H_{Ar}), 7.07-7.17 (m, 3H, H_{Ar}). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 18.5 (*C*H_3), 20.6 (*C*H_3), 113.8 (*C*H_{Ar}), 125.5 (*C*H_{Ar}), 127.5 (C_{Ar}), 128.6 (*C*H_{Ar}), 129.8 (*C*H_{Ar}), 135.6 (C_{Ar}), 138.8 (C_{Ar}), 144.0 (C_{Ar}).

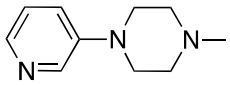


N-octyl-2,4,6-trimethylaniline[7] *(Table 4,* ***9j****)*. The general procedure yielded, after flash chromatography on silica gel (EtOAc, Pentane), 43 mg (23%) of the title compound as a colourless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.91 (t, *J* 7.1 Hz, 3H, CH_3), 1.27-1.42 (m, 10H, CH_2), 1.55-1.64 (m, 2H, CH_2), 2.25 (s, 3H, CH_3), 2.27 (s, 6H, CH_3), 2.85 (br, 1H, N*H*), 2.91-2.96 (m, 2H, CH_2), 6.83 (s, 2H, H_{Ar}). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 14.2 (*C*H_3), 18.5 (*C*H_3), 20.7 (*C*H_3), 22.8 (*C*H_2), 27.4 (*C*H_2), 29.4 (*C*H_2), 29.7 (*C*H_2), 31.3 (*C*H_2), 32.0 (*C*H_2), 49.1 (*C*H_2), 129.5 (*C*H_{Ar}), 129.6 (C_{Ar}), 131.1 (C_{Ar}), 144.0 (C_{Ar}).



2-(4-methylpiperaz-1-yl)pyridine[8] *(Table 4,* ***9k****)*. The general procedure yielded, after flash chromatography on silica gel (MeOH, DCM), 78 mg

(58%) of the title compound as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.33 (s, 3H, C*H*$_3$), 2.49-2.55 (m, 4H, C*H*$_2$), 3.53-3.56 (m, 4H, C*H*$_2$), 6.58-6.65 (m, 2H, H_{Ar}), 7.46 (ddd, *J* 8.7, 7.1 and 2.0 Hz, 1H, H_{Ar}), 8.18 (ddd, *J* 4.9, 2.0 and 0.9 Hz, 1H, H_{Ar}). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 45.3 (*C*H$_2$), 46.4 (*C*H$_3$), 55.1 (*C*H$_2$), 107.2 (*C*H$_{Ar}$), 113.4 (*C*H$_{Ar}$), 137.5 (*C*H$_{Ar}$), 148.1 (*C*H$_{Ar}$), 159.7 (C$_{Ar}$).



3-(4-methylpiperaz-1-yl)pyridine[5] *(Table 4,* ***9l****)*. The general procedure yielded, after flash chromatography on silica gel (MeOH, DCM), 108 mg (80%) of the title compound as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.33 (s, 3H, C*H*$_3$), 2.54-2.57 (m, 4H, C*H*$_2$), 3.18-3.23 (m, 4H, C*H*$_2$), 7.10-7.18 (m, 2H, H_{Ar}), 8.08 (dd, *J* 4.0 and 1.9 Hz, 1H, H_{Ar}), 8.29 (d, *J* 1.8 Hz, 1H, H_{Ar}). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 46.2 (*C*H$_3$), 48.5 (*C*H$_2$), 54.9 (*C*H$_2$), 122.3 (*C*H$_{Ar}$), 123.5 (*C*H$_{Ar}$), 138.7 (*C*H$_{Ar}$), 140.8 (*C*H$_{Ar}$), 147.0 (C$_{Ar}$).

References:

(1) Chartoire, A.; Frogneux, X.; Nolan, S. P. *Adv. Synth. Catal.* **2012**, *354*, 1897–1901.

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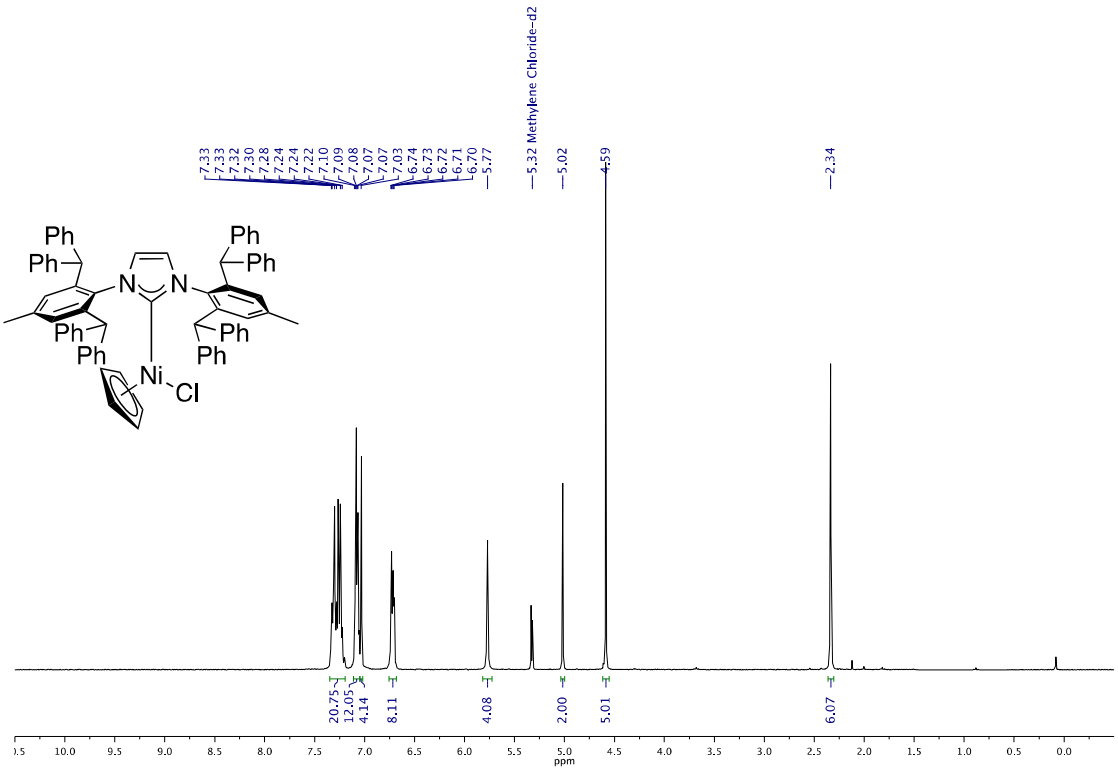
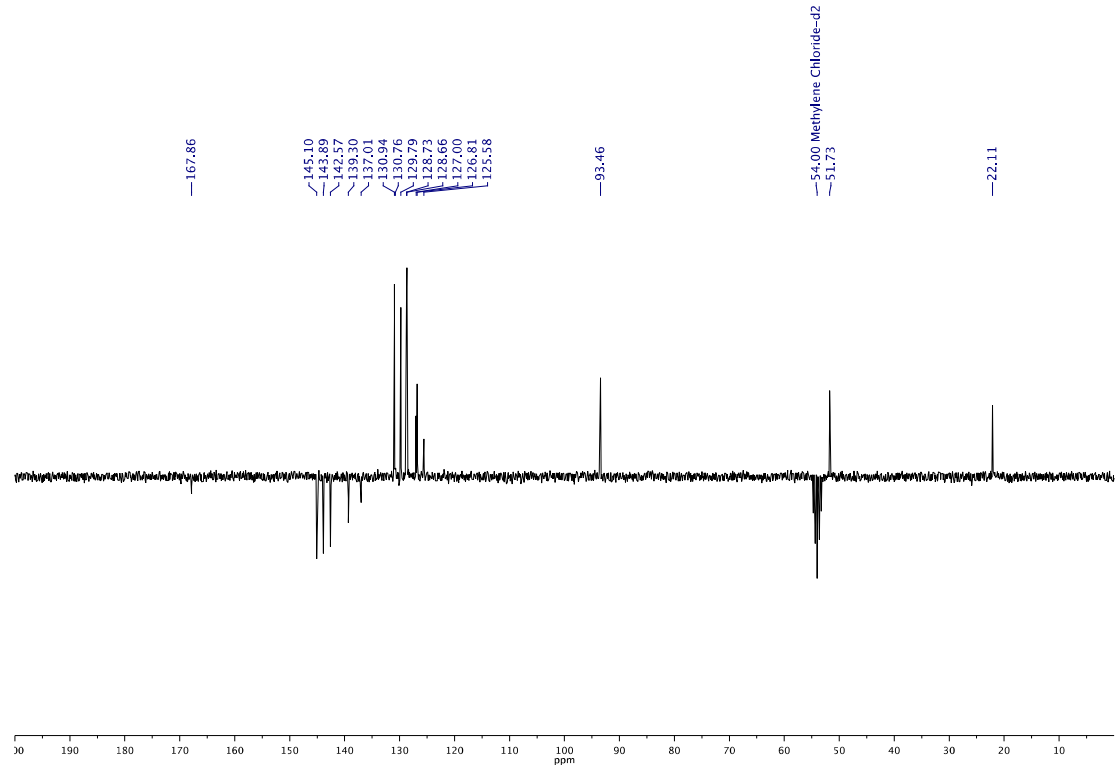
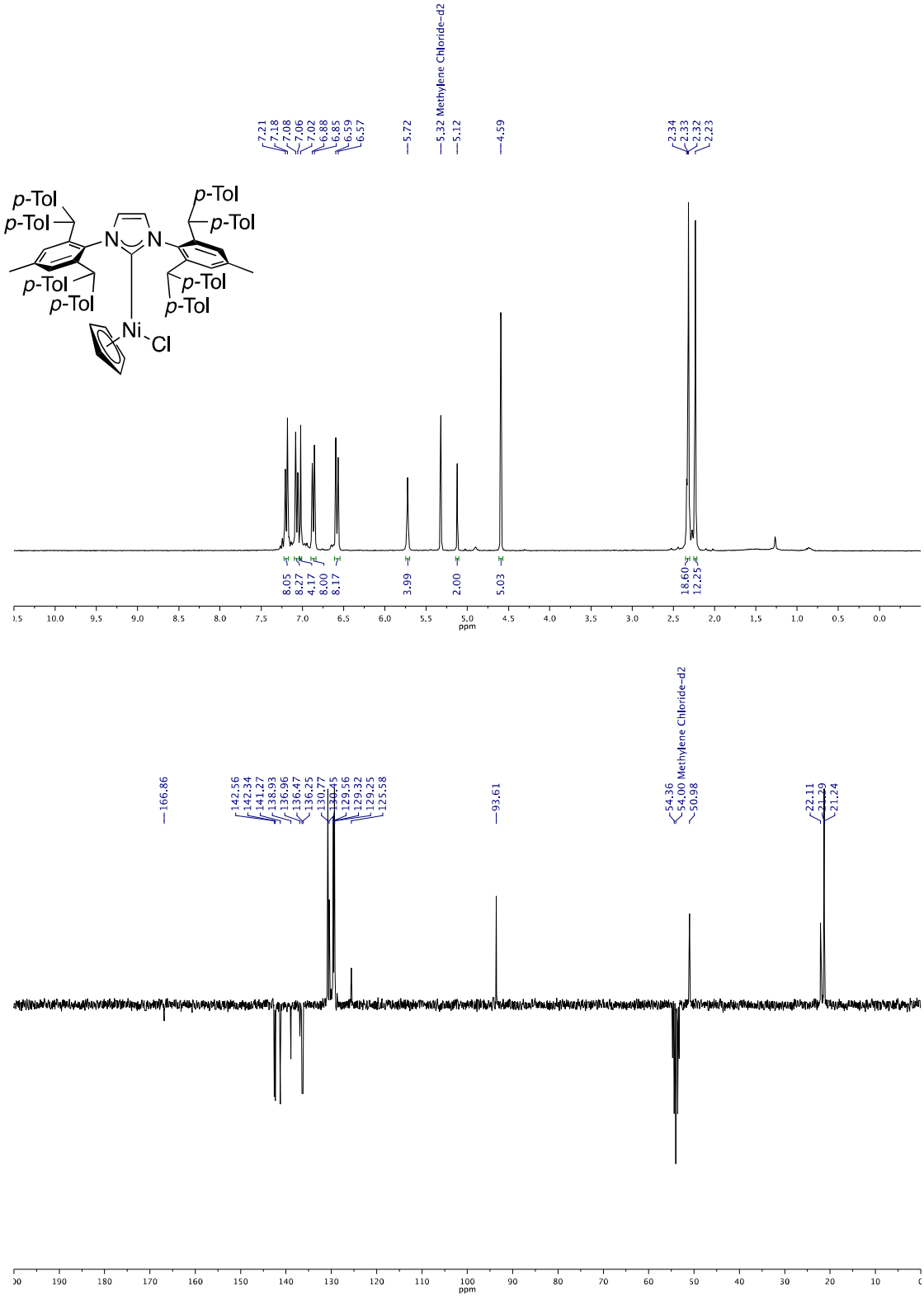
^{1}H and ^{13}C NMR spectra of all compounds



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p-Tol
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N
Ni
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7.18
7.08
7.06
7.02
6.88
6.85
6.59
6.57
5.72
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5.12
4.59
2.34
2.33
2.32
2.23
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4.17
8.00
8.17
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2.00
5.03
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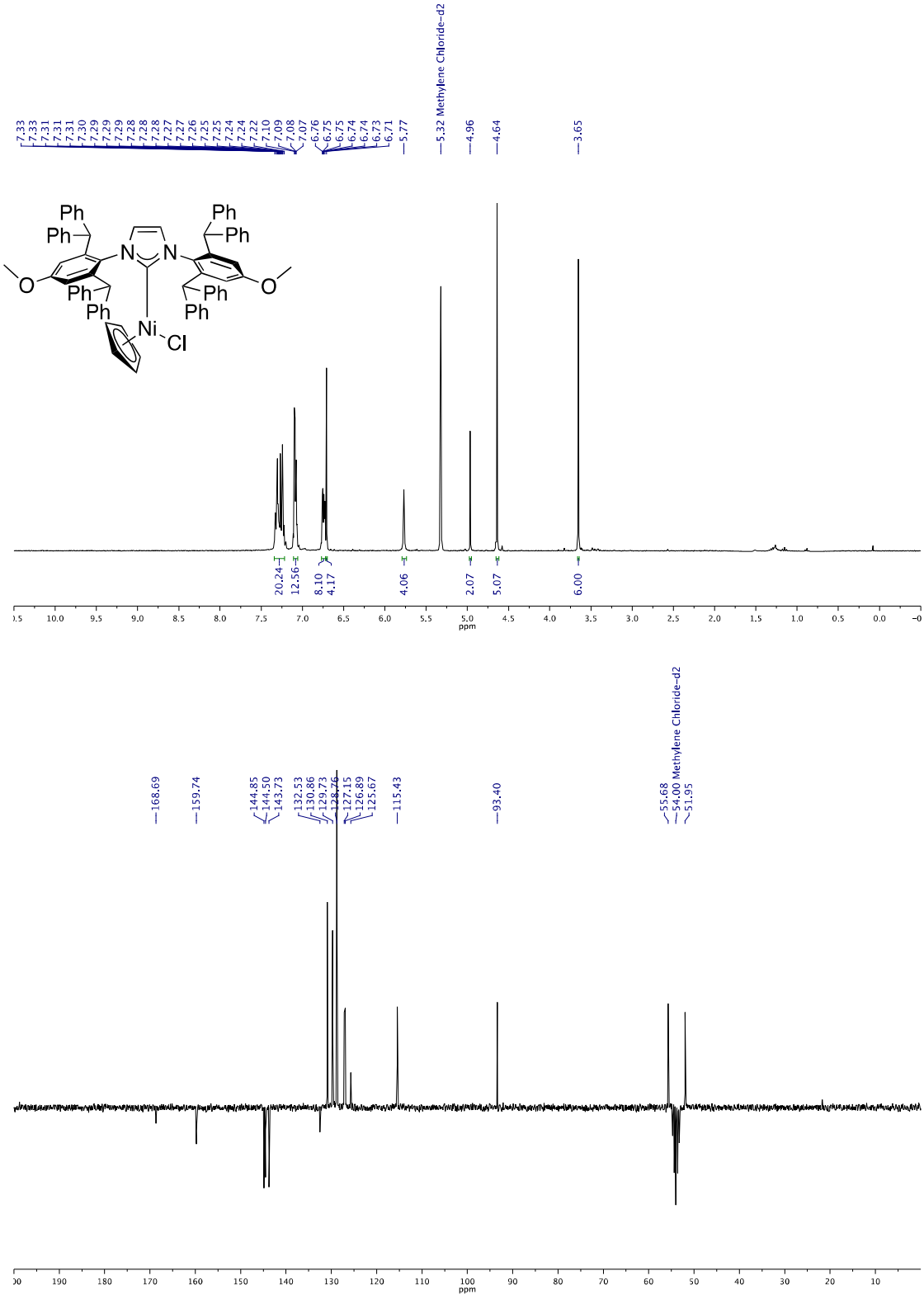
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Ph
Ph
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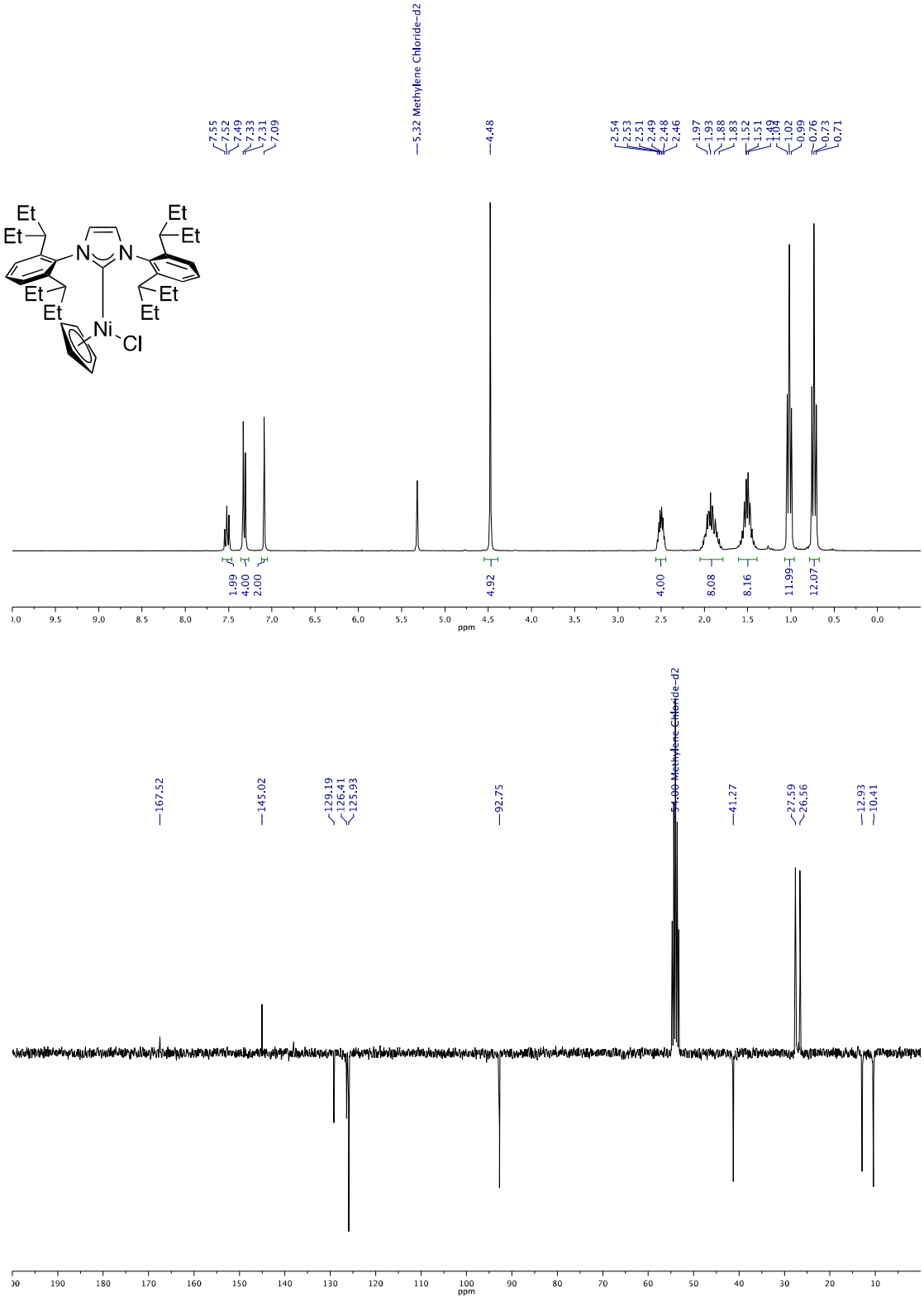
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Et
Et
Et
Et
Et
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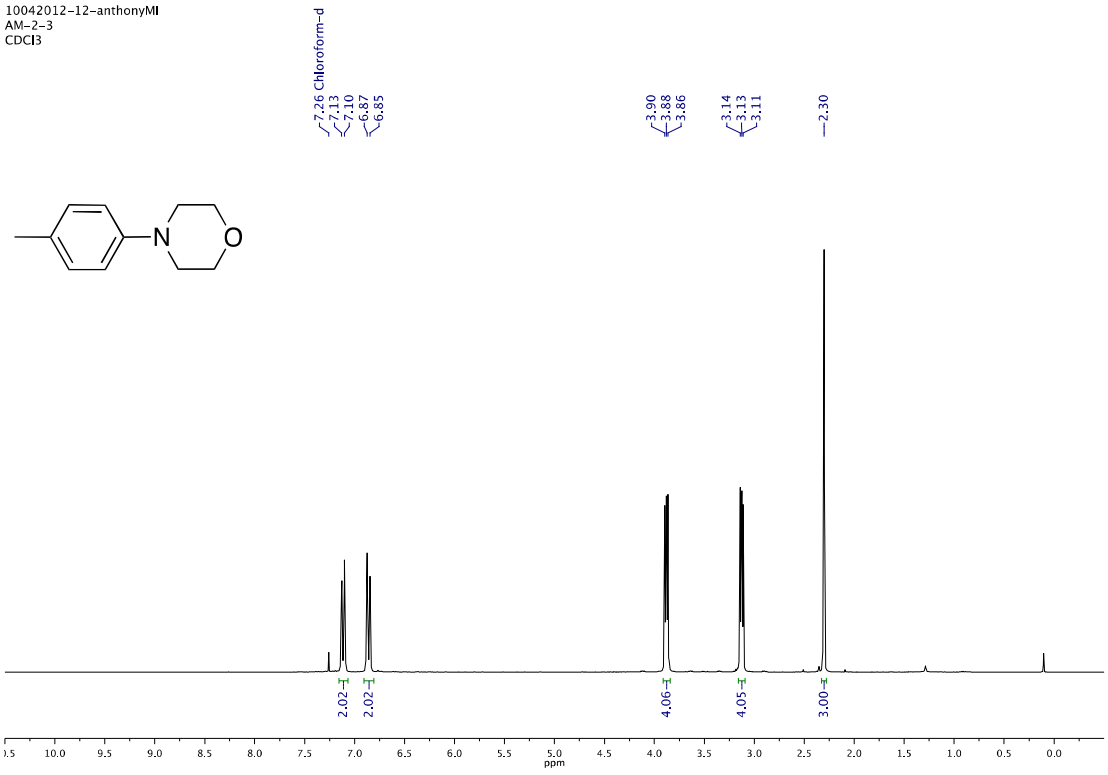
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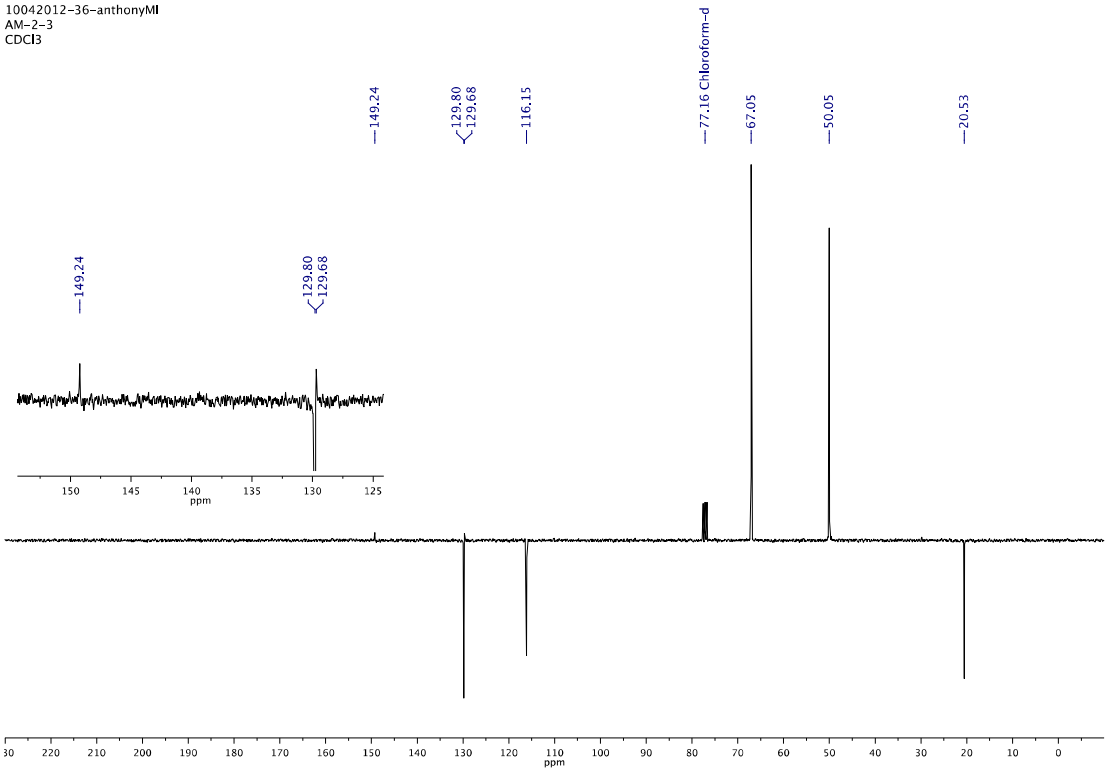
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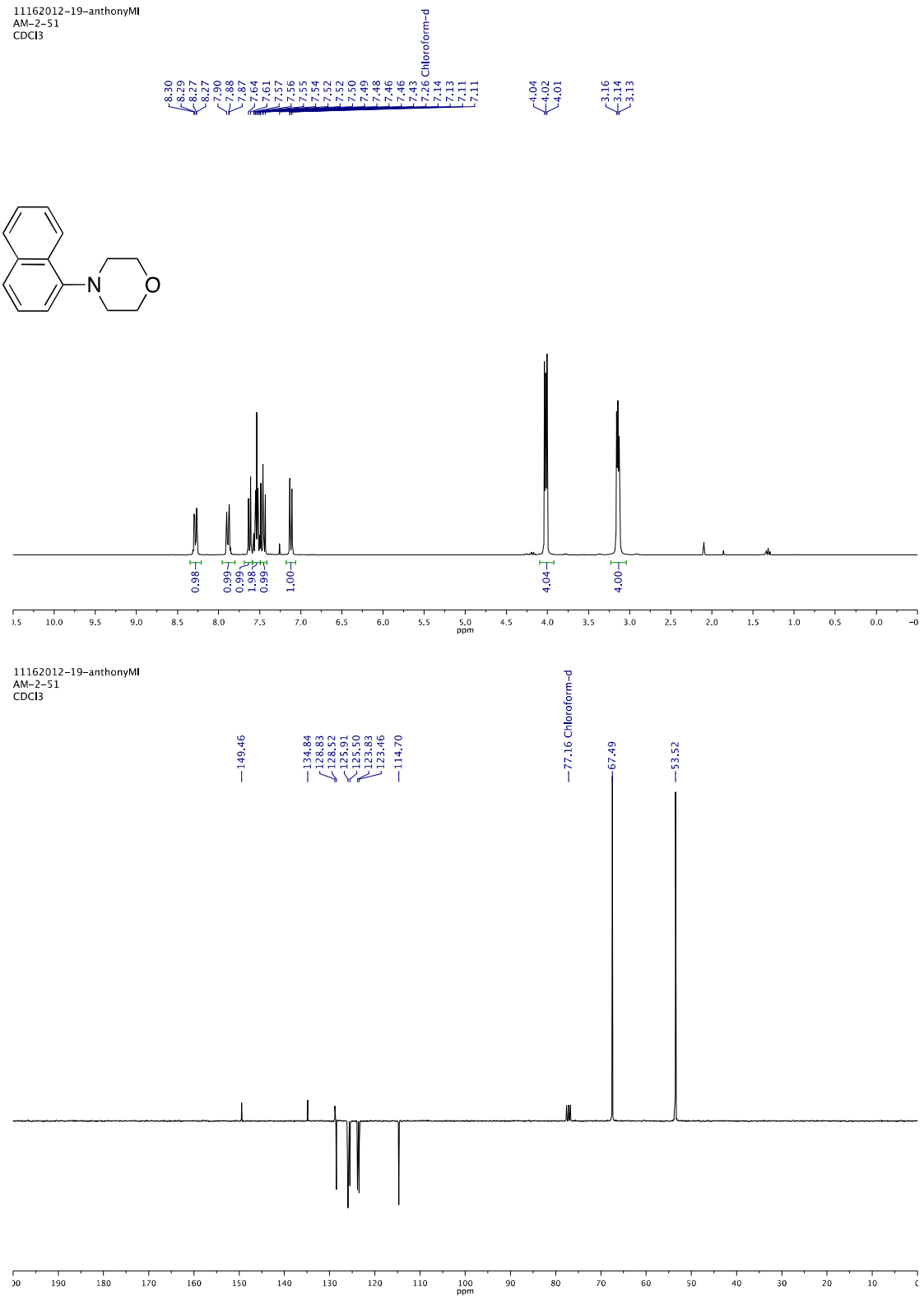
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7.54
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7.52
7.50
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7.48
7.46
7.46
7.43
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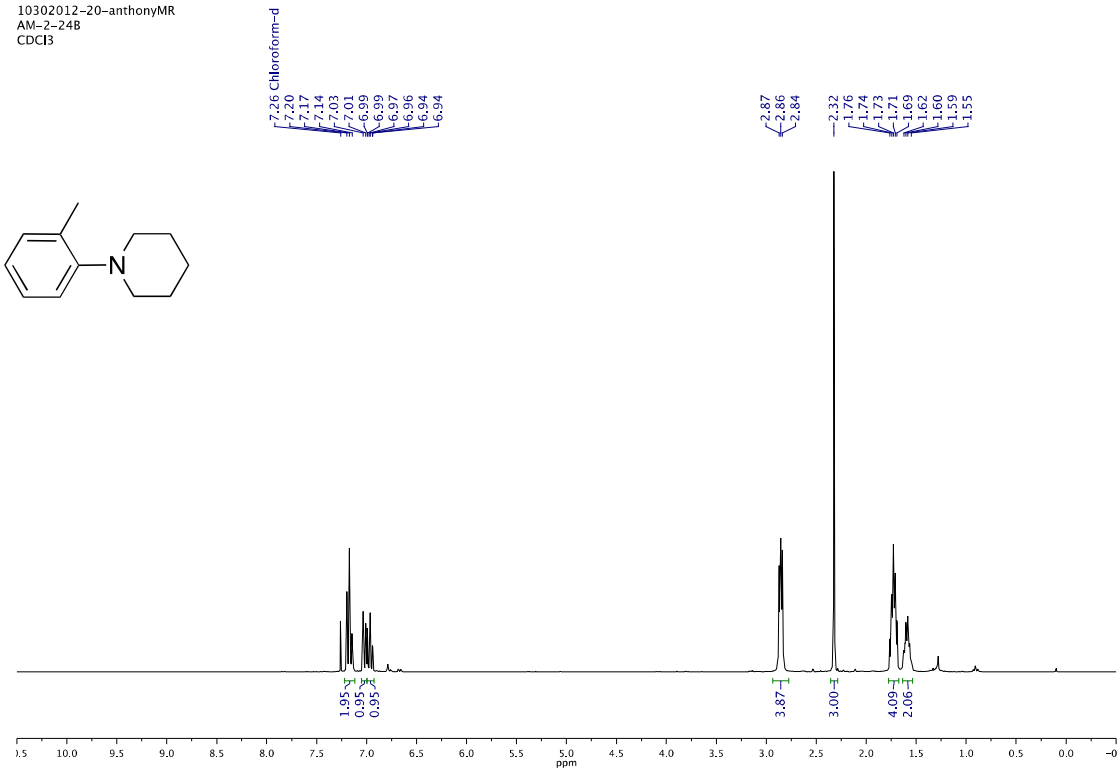
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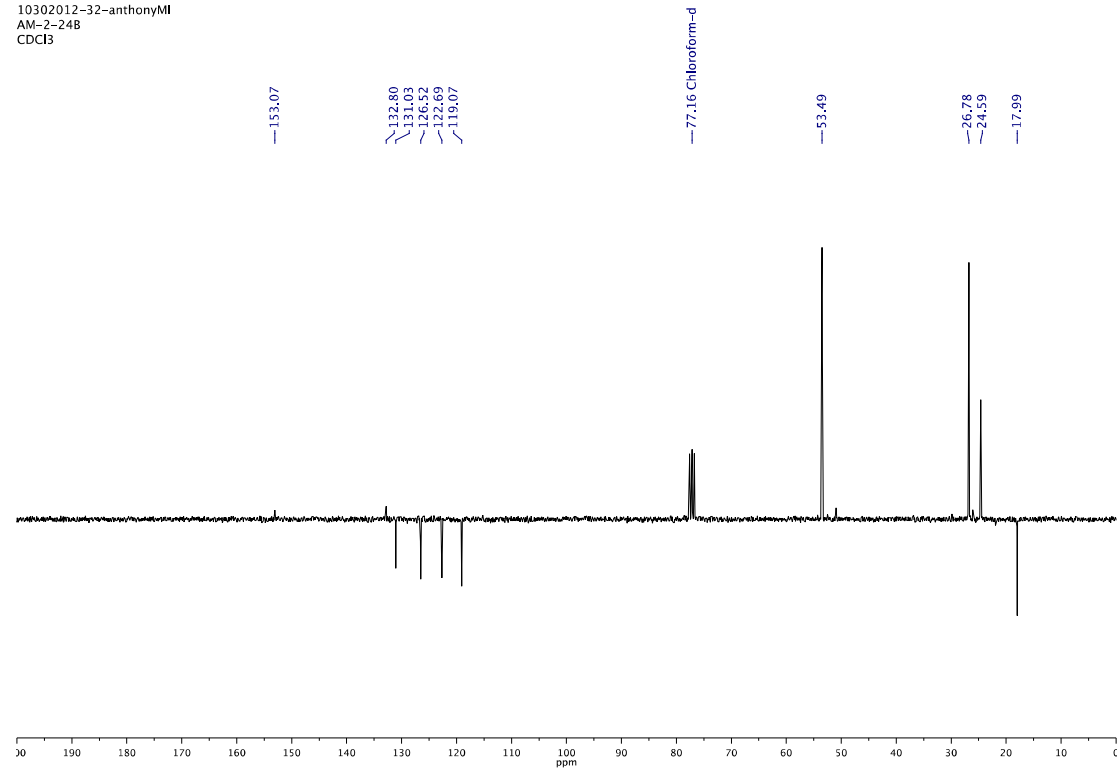
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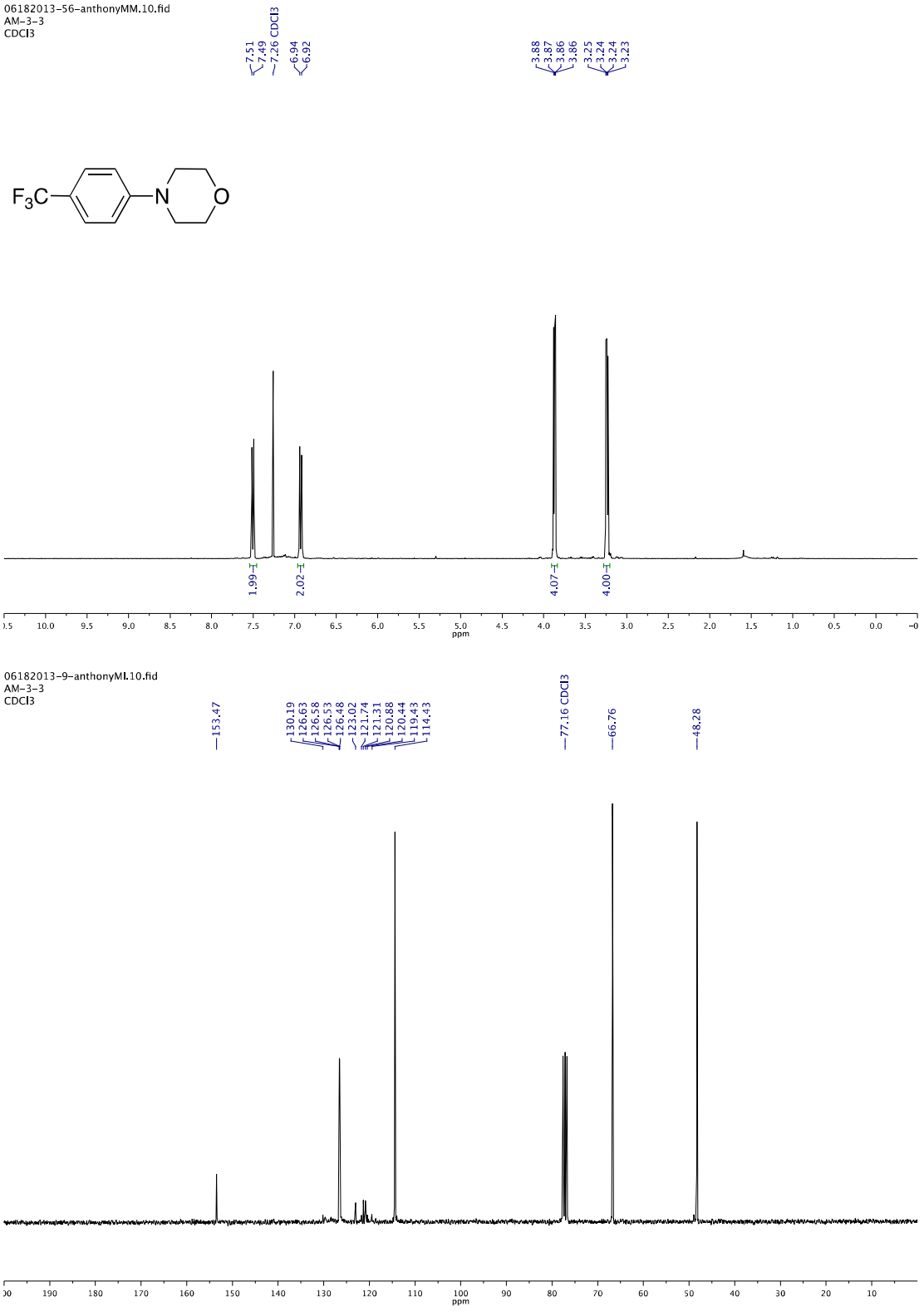
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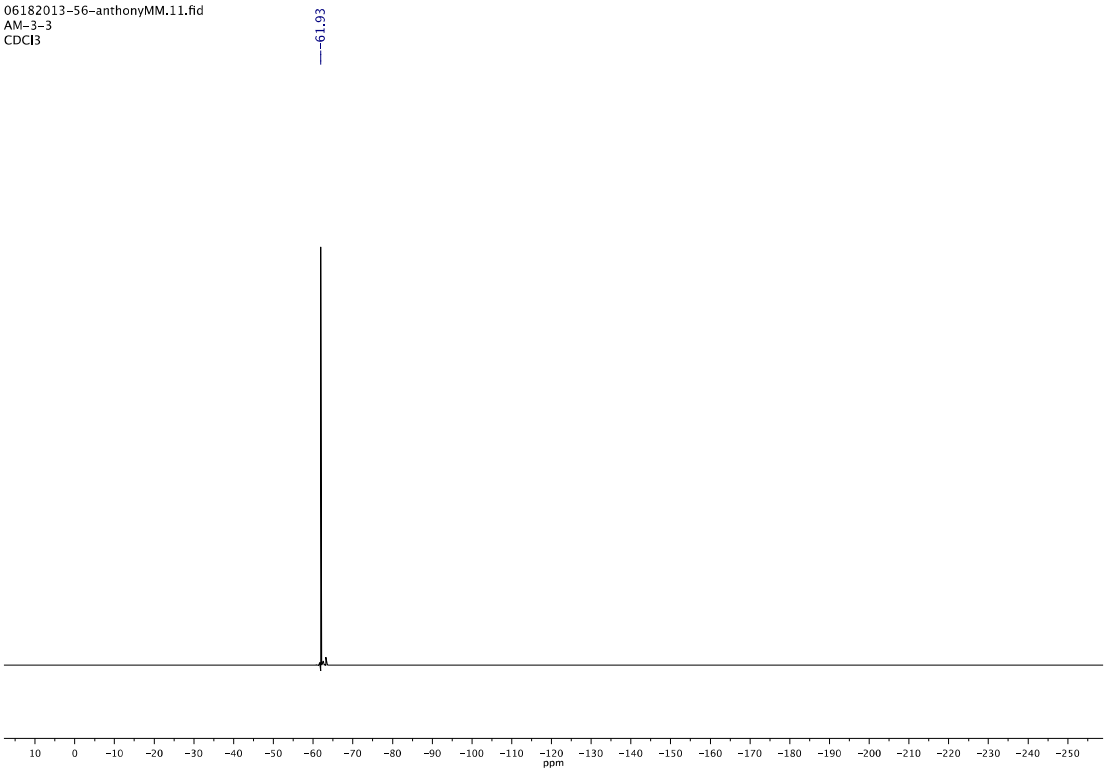
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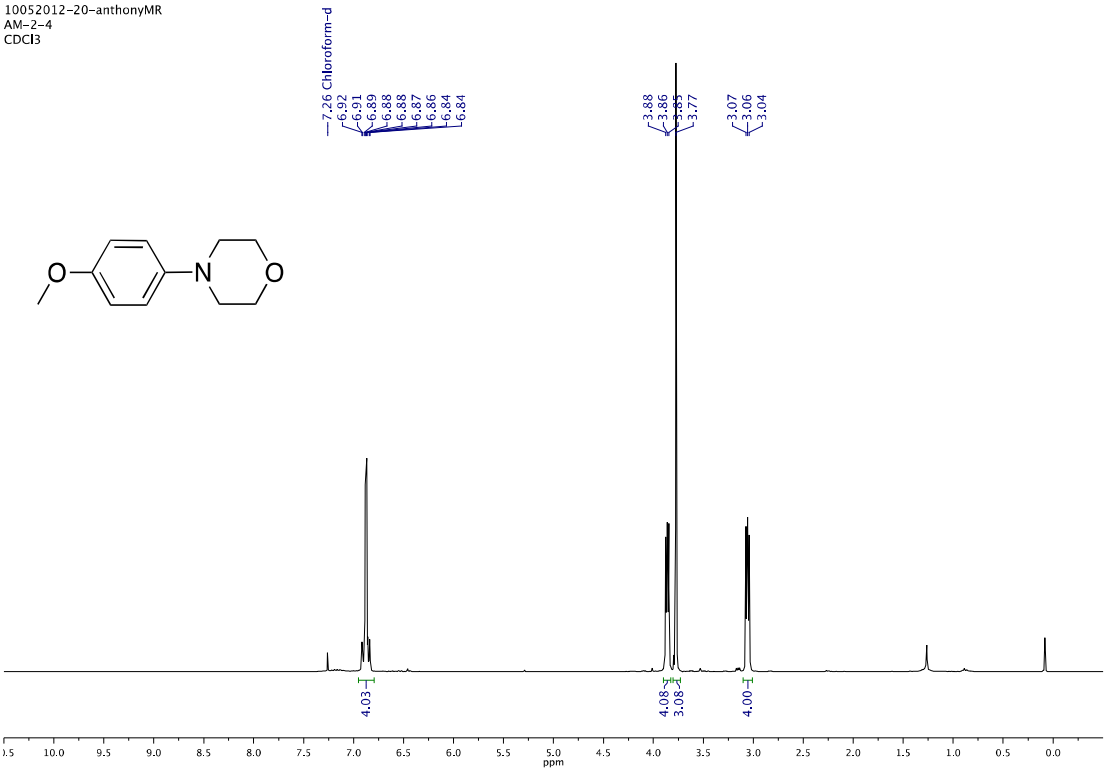
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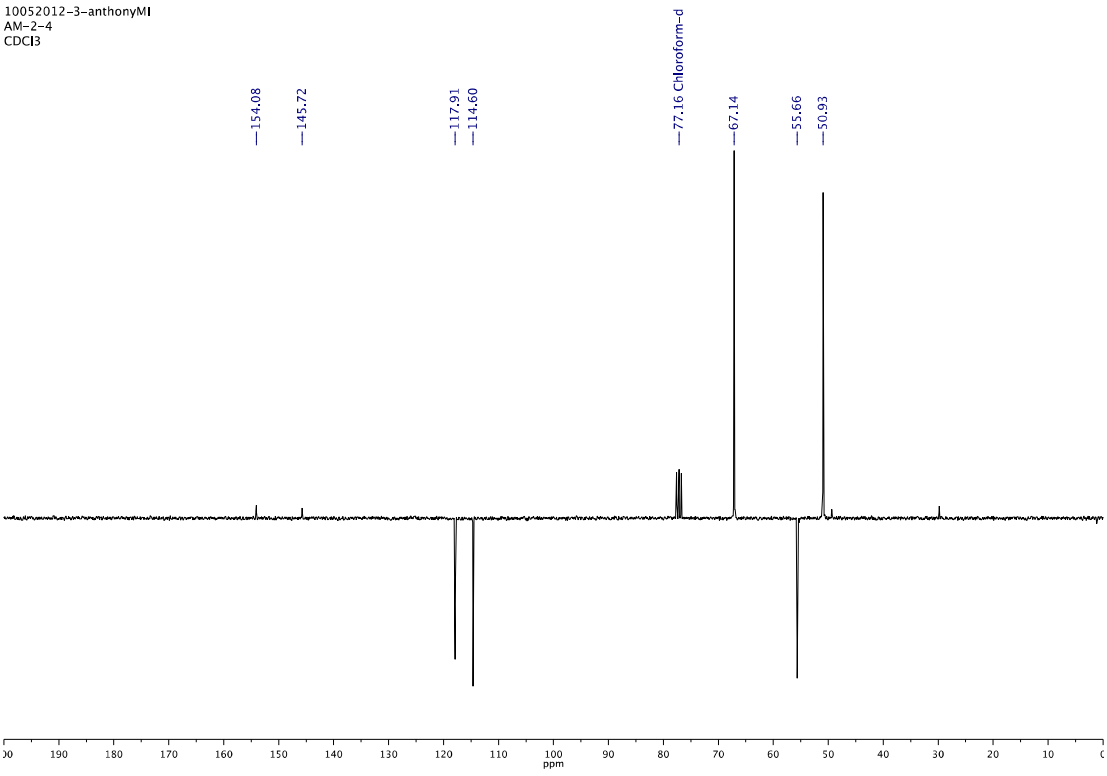
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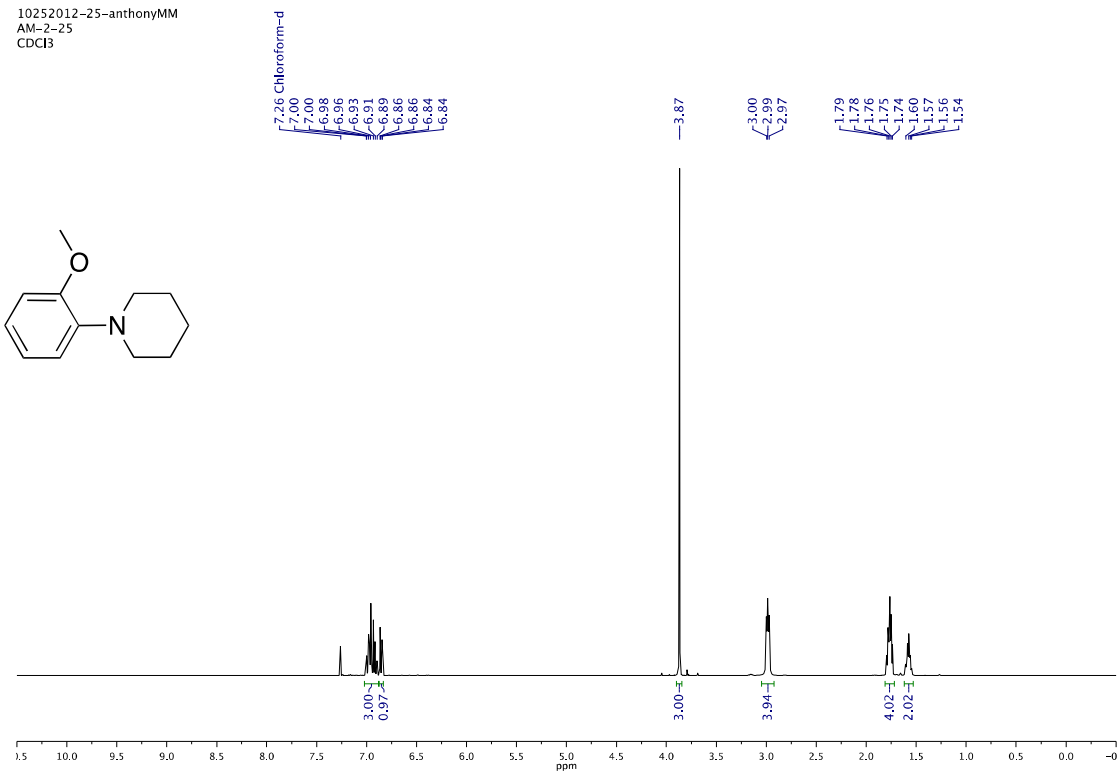
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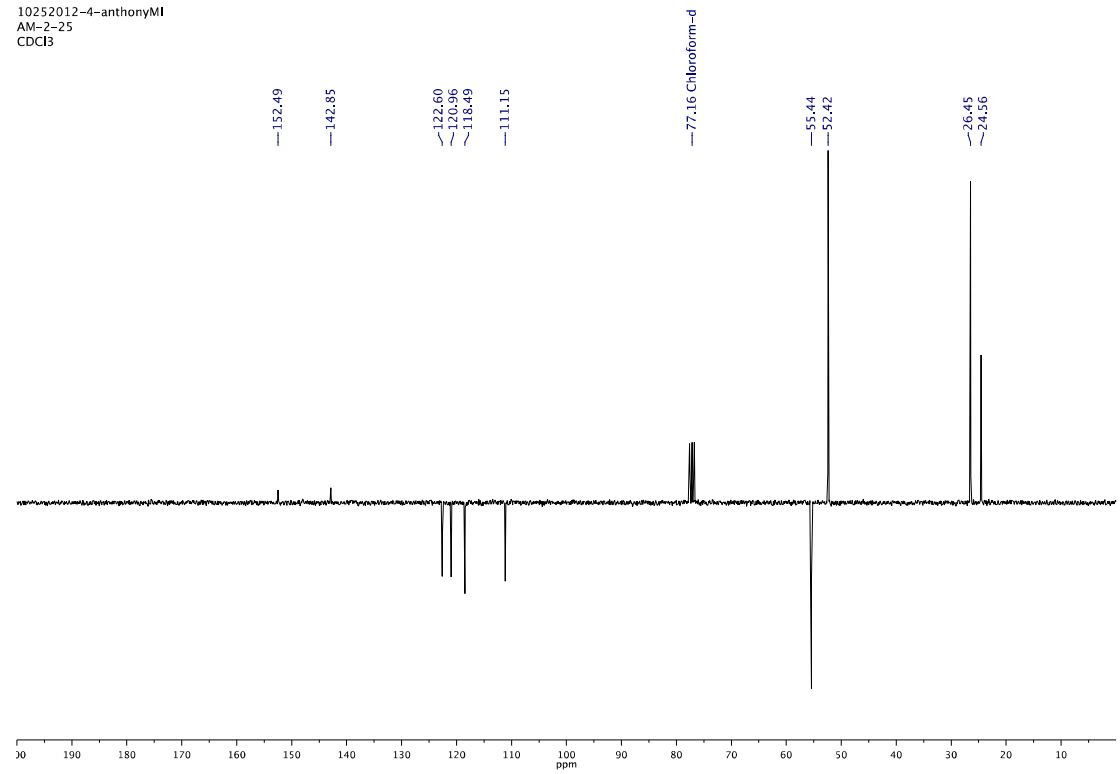
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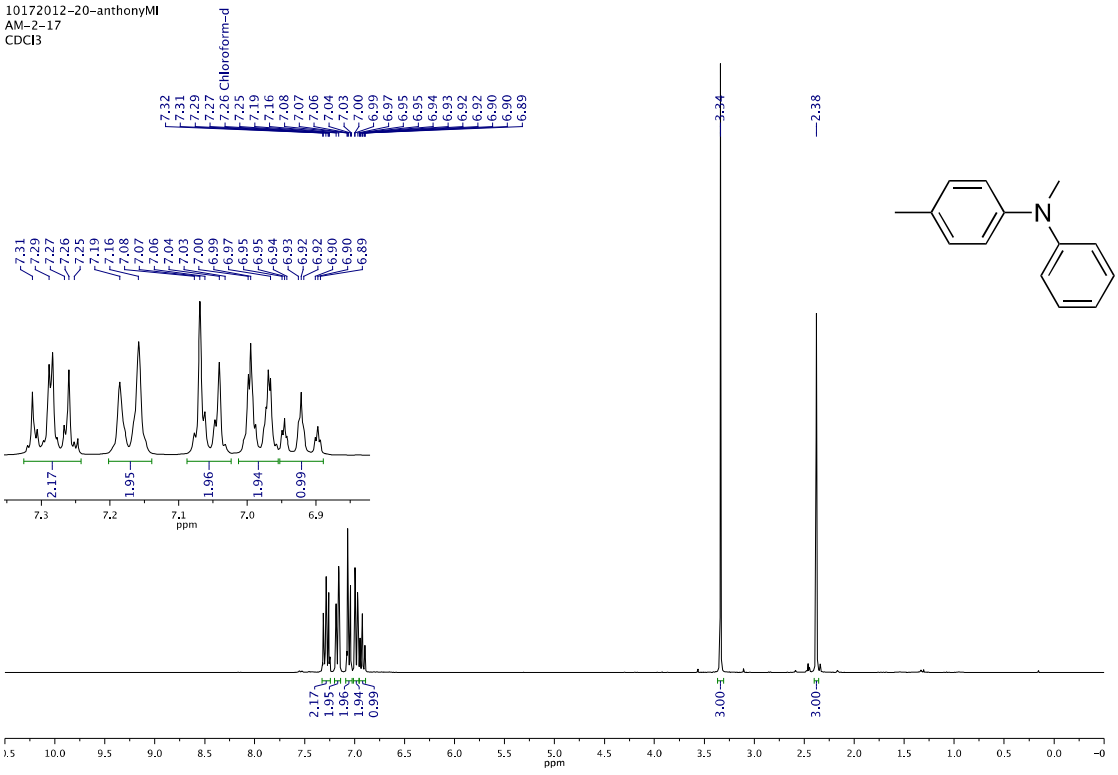
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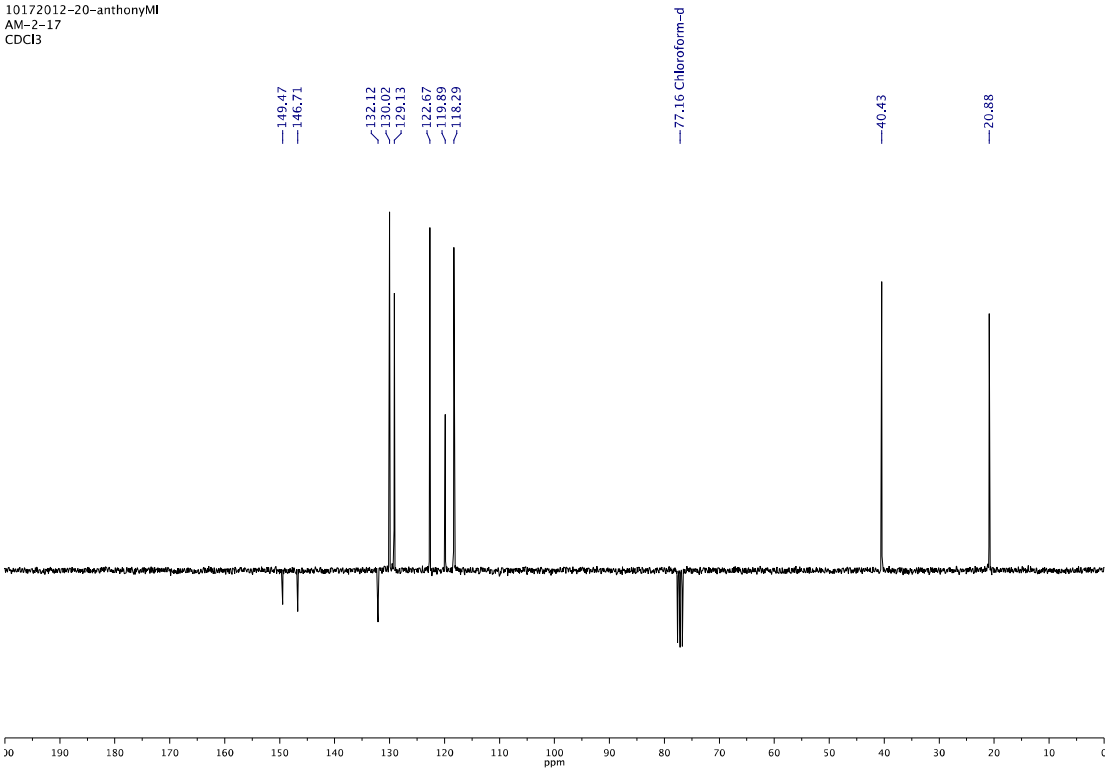
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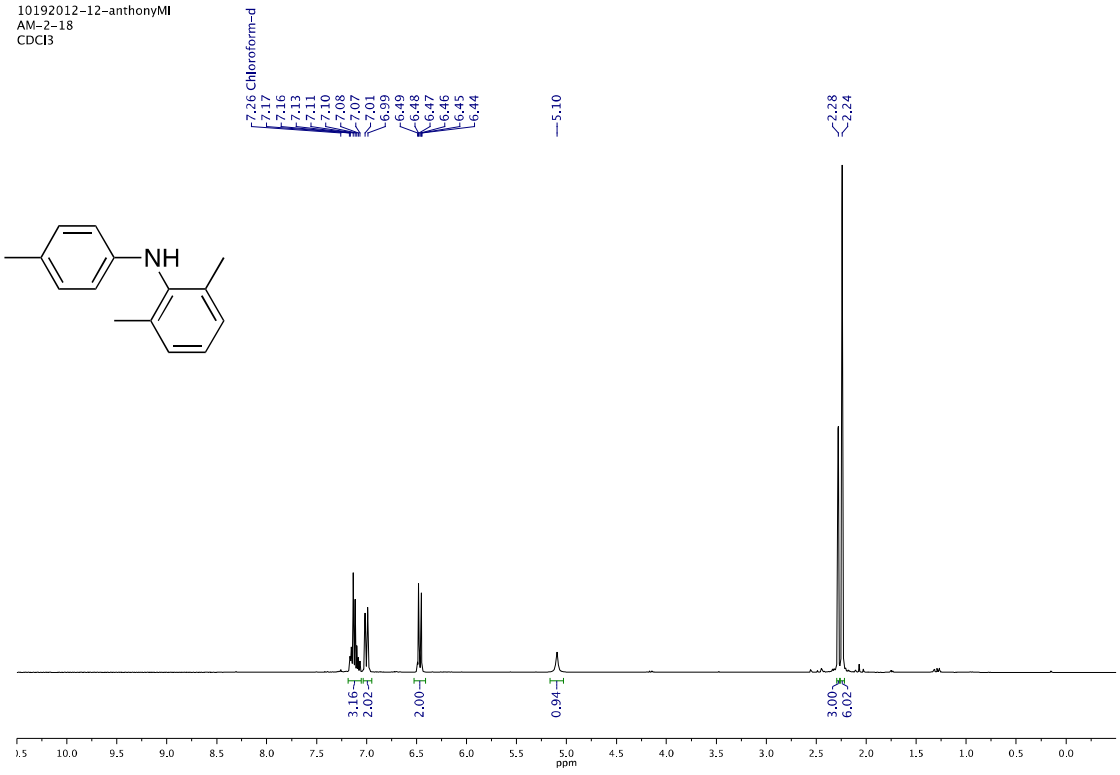
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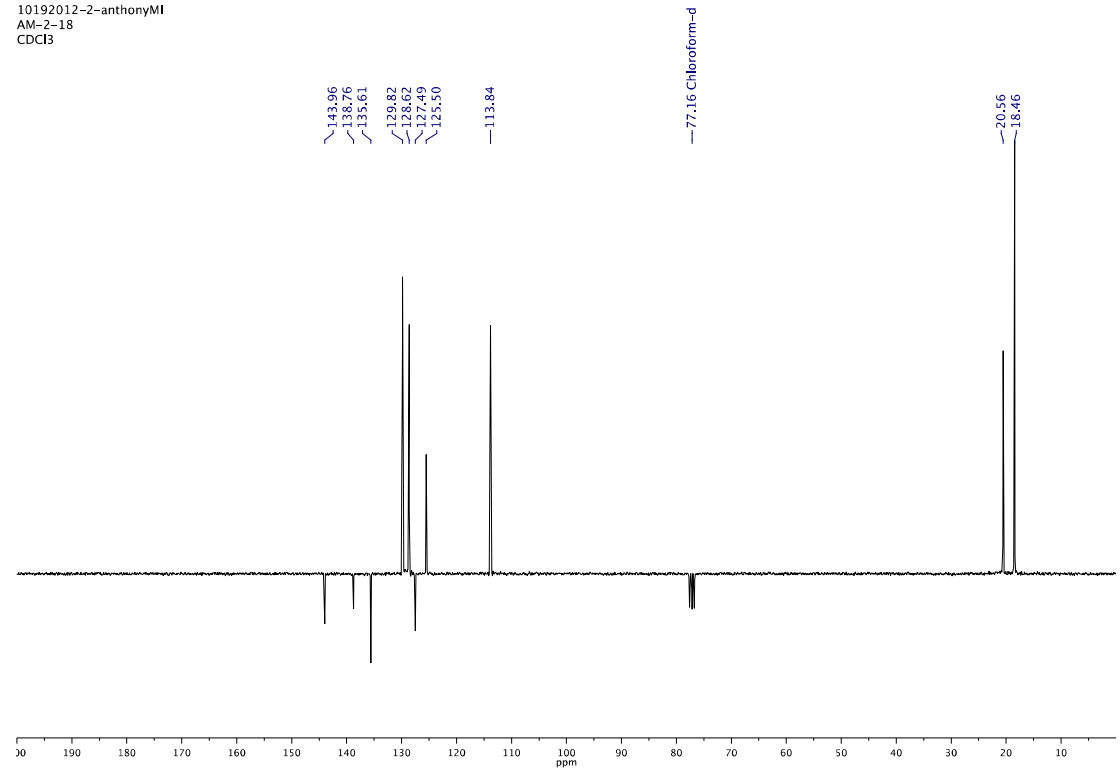
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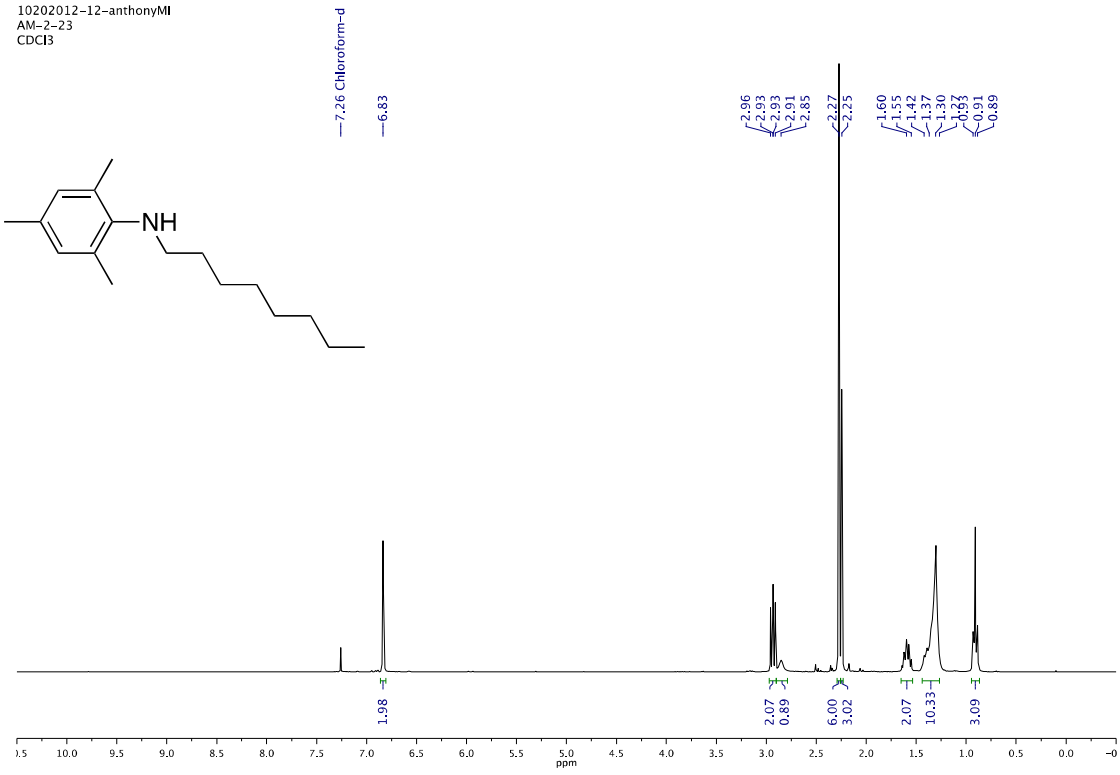
ppm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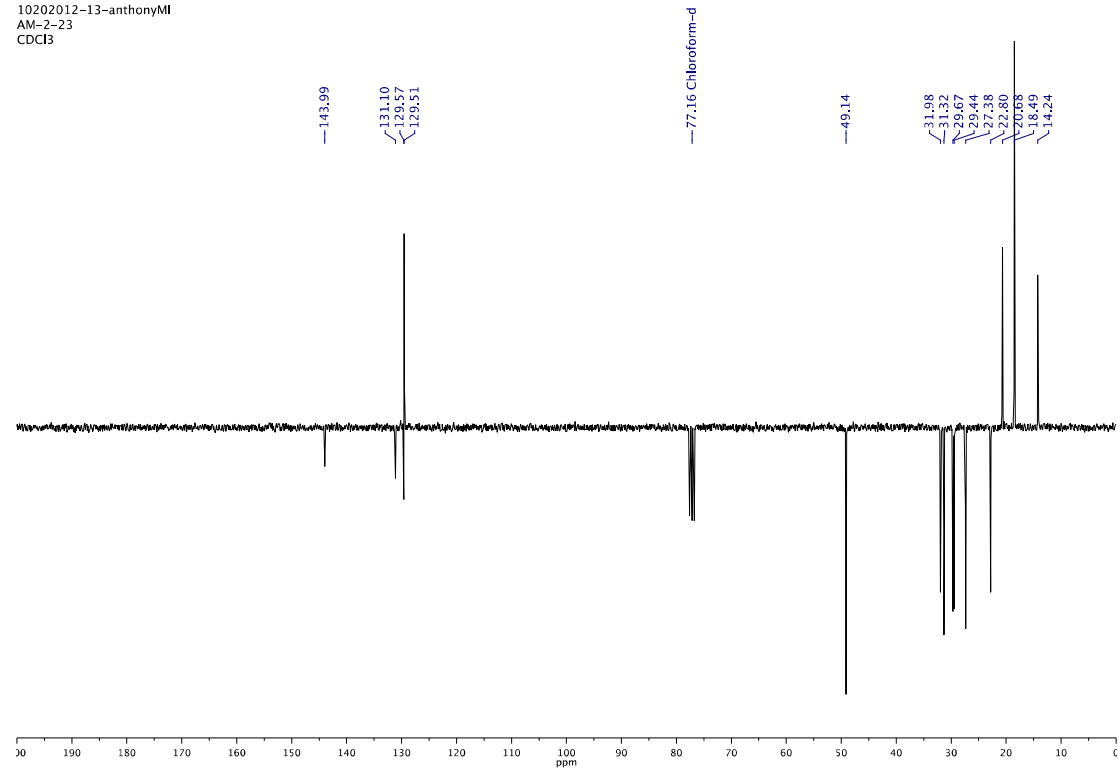
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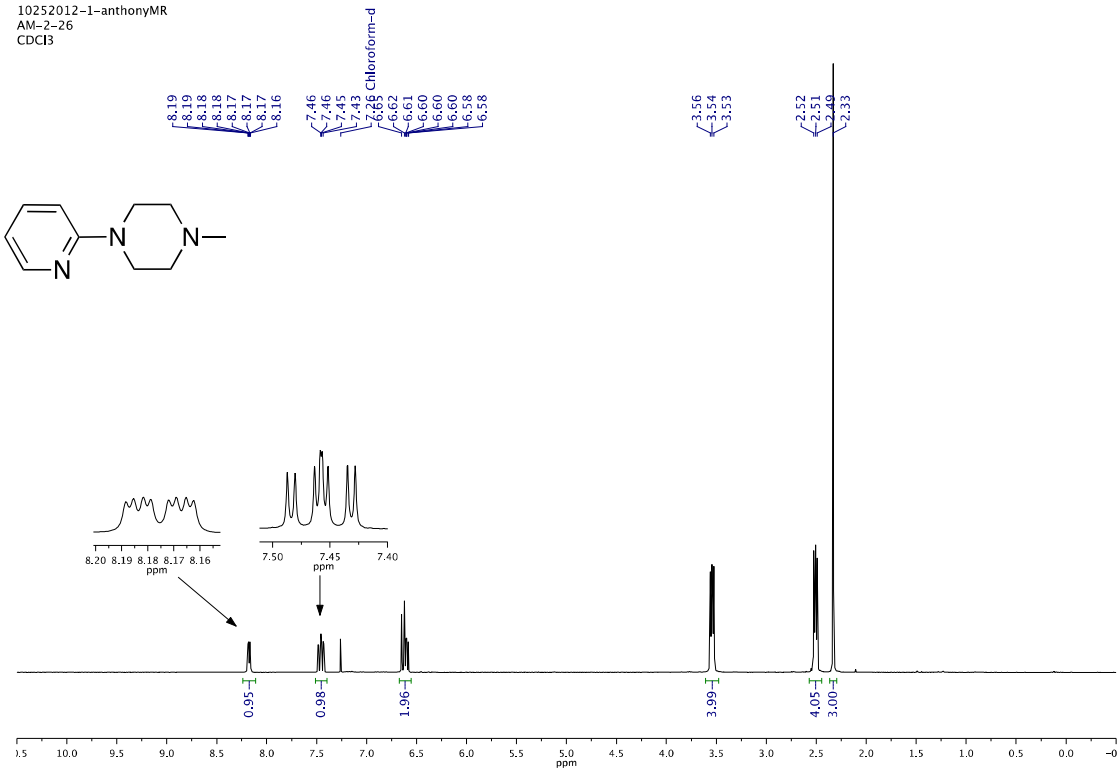
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1.96
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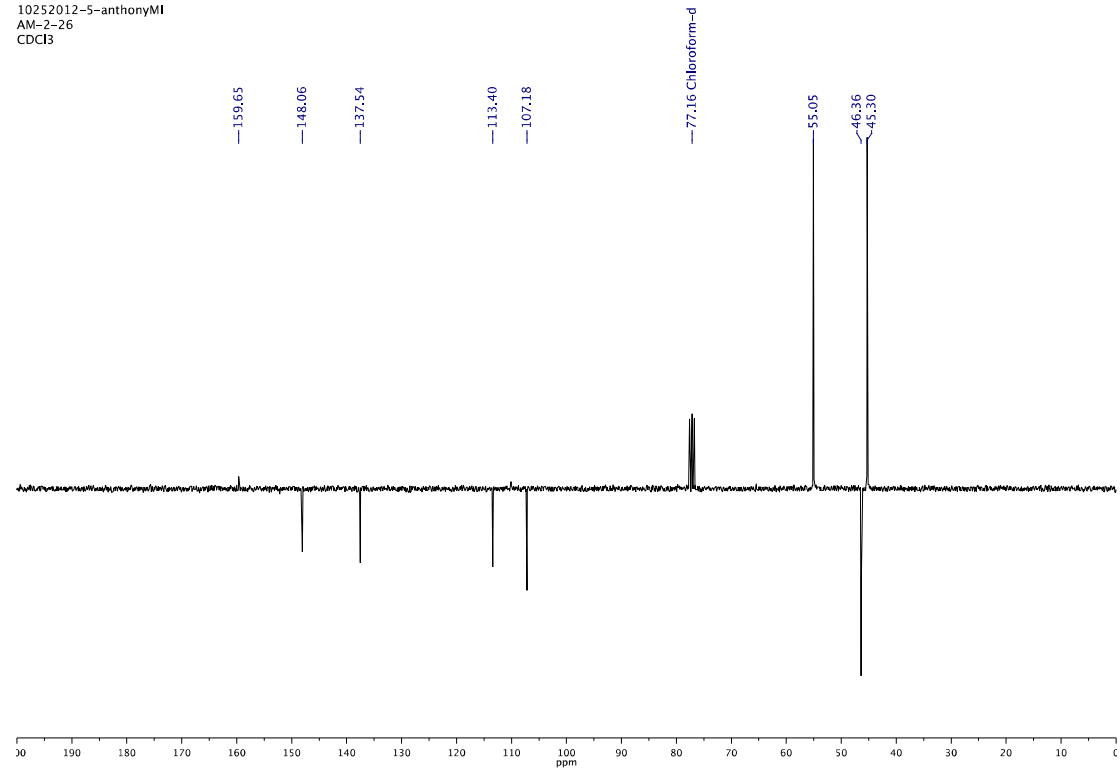
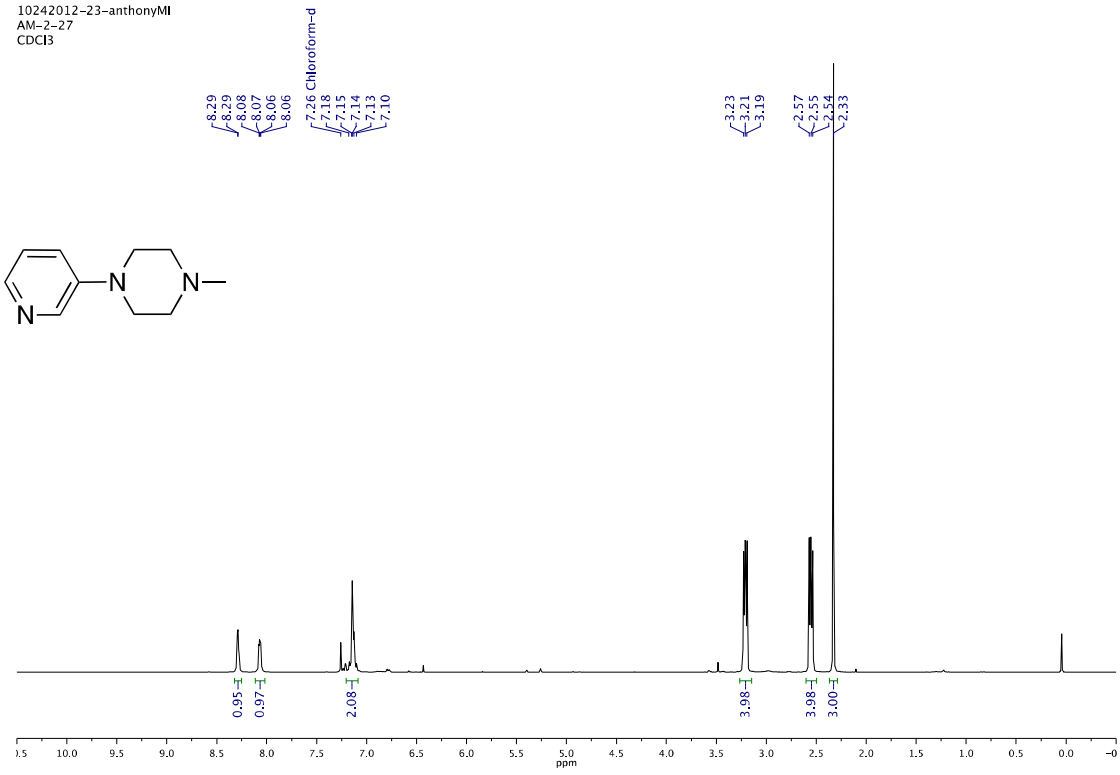
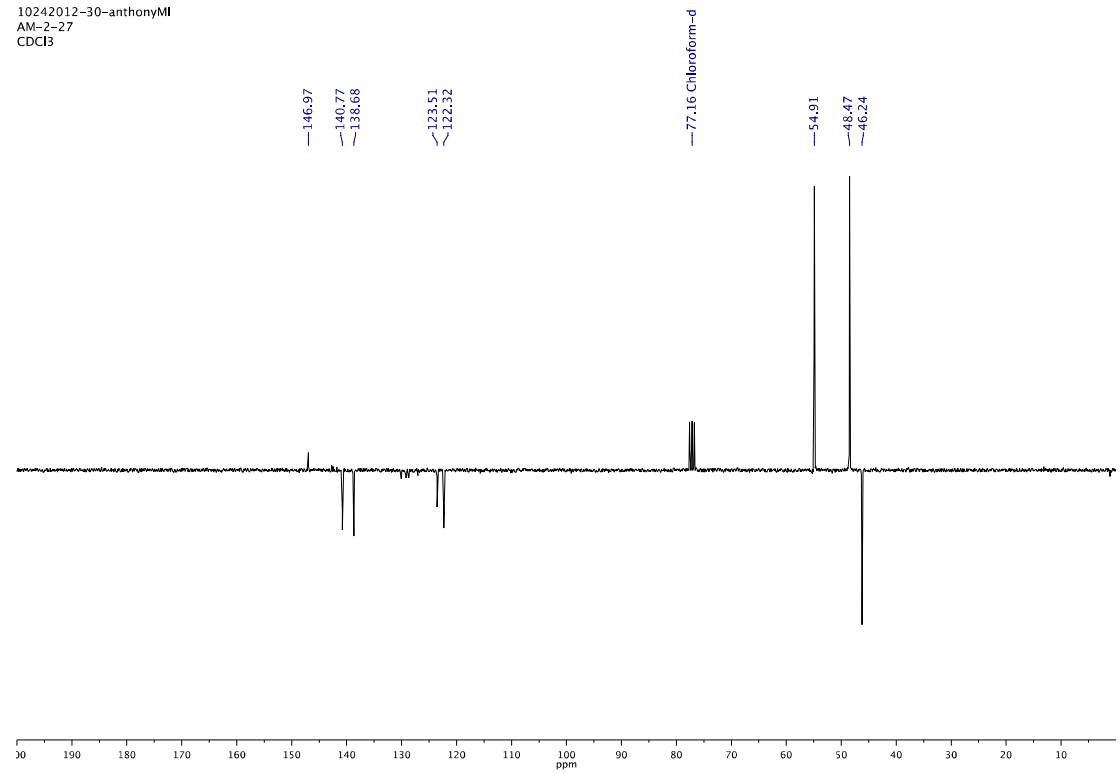
3.00
ppm


10252012-5-anthonyMI
AM-2-26
CDCl3
159.65
148.06
137.54
113.40
107.18
77.16 Chloroform-d
55.05
46.36
45.30
ppm


10242012-23-anthonyMI
AM-2-27
CDCl3
8.29
8.29
8.08
8.07
8.06
8.06
7.26 Chloroform-d
7.18
7.15
7.14
7.13
7.10
3.23
3.21
3.19
2.57
2.55
2.54
2.33
N
N
N
0.95
0.97
2.08
3.98
3.98
3.00
ppm


10242012-30-anthonyMI
AM-2-27
CDCl3
146.97
140.77
138.68
123.51
122.32
77.16 Chloroform-d
54.91
48.47
46.24
ppm