Supplementary Material (ESI) for

A Highly Efficient Precatalyst for Amination of Aryl Chlorides: Synthesis, Structure and Application of a Robust Acenaphthoimidazolylidene Palladium Complex

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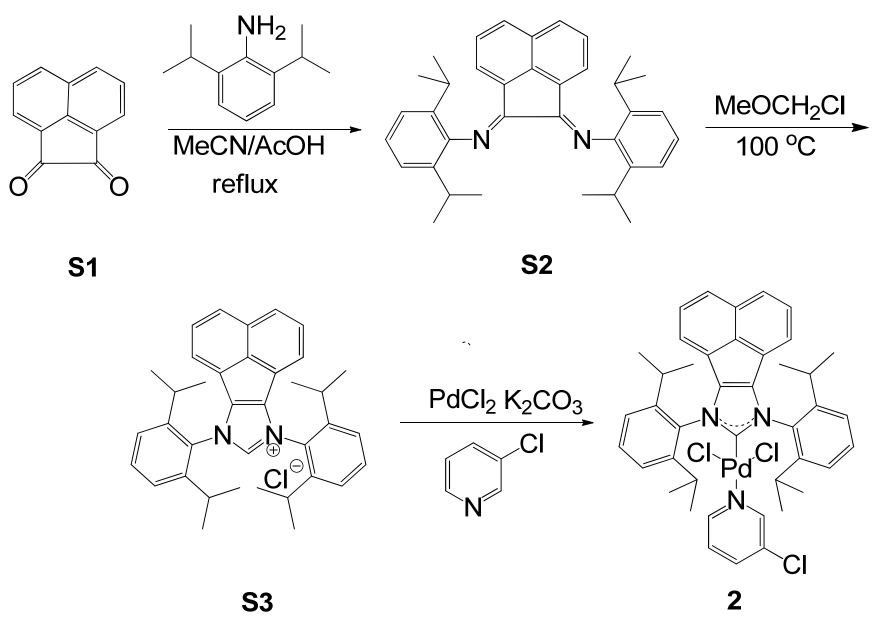
1. General.

All commercial reagents were used directly without further purification, unless otherwise stated. Dry N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO) N,N-Dimethylacetamide (DMA) were purchased from Alfa Aesar and Acros, stored over 4 Å molecular sieves and handled under N_2. Anhydrous methanol (MeOH) and *tert*-butanol (*t*-BuOH) were distilled from anhydrous calcium chloride, Tetrahydrofuran (THF) was distilled from sodium/benzophenone, 1,2-Dimethoxyethane (DME), 1,4-dioxane and toluene were distilled from calcium hydride prior to use. *t*-BuOK was purchased from Acros. All schlenk tubes and sealed vessels (50 mL) were purchased from Beijing Synthware Glass. $CDCl_3$ was purchased from Cambridge Isotope Laboratories. ^{1}H and ^{13}C NMR were recorded on Jeol ECA-400 and Bruker 400 DRX spectrometers. ^{13}C NMR spectra were referenced to the carbon signal of $CDCl_3$ (77.0 ppm). GC-MS spectra were recorded on Agilent Technologies 1890A GC system and 5975C inert MSD with Triple-Axis Detector.

2. Synthetic procedures:

2.1. Synthesis of palladium NHC complex **2**.



Scheme S1. Synthesis of pyridine-stabilized palladium NHC complex **2**.

Bis[N,N'-(2,6-diisopropylphenyl)imino]acenaphthene (S2): According to literature procedure [S1], acenaphthenequinone (0.7 g, 3.84 mmol) was suspended in acetonitrile (25 mL) and heated under reflux condition for 60 min. Then acetic acid (6.5 mL) was added, and the resulting reaction mixture was heated until the acenaphthenequinone had been completely dissolved. To the hot mixture, 2,6-diisopropylphenylaniline (1.63 g, 9.2 mmol) was added dropwise over 30 min, and the solution was heated under reflux condition for another 5 h and then cooled to room temperature. The resulting orange-yellow solid was then filtered, washed with pentane (3 ×20 mL), and dried over under the air. Yield: 1.73 g, 90%.^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.88 (d, *J* = 10.8 Hz, 2H), 7.36 (t, *J* = 10.0 Hz, 2H), 7.27 (bs, 6H), 6.63 (d, *J* = 9.2 Hz, 2H), 3.07-2.98 (m, 4H), 1.24 (d, *J* = 8.8 Hz, 12H), 0.97 (d, *J* = 8.8 Hz, 12H); HR-MS (ESI): *m/z* 500.3191 (calcd.); 501.3258 (found, $[M+1]^+$).

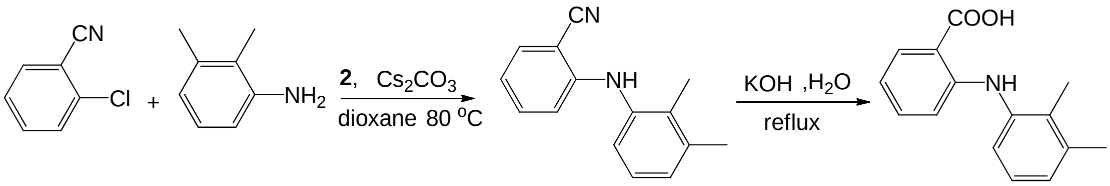
IPr(BIAN) imidazolium chloride (S3): According to literature procedure[S2], S**2** (1.00 g, 2 mmol) and methoxy(methyl)chloride (3.22 g, 40 mmol) were added to an netrogen-flushed thick-walled reaction vessel. After sealed the vessel, the reaction mixture was stirred at 100 ℃ for 16 h, during which time the mixture changed from a murky brown suspension to a clear red solution. After cooling to room temperature, 10 mL of diethyl ether was subsequently added resulting in the formation of a yellow precipitate. The precipitation was filtered off and washed with 50 mL of diethyl ether and dried *in vacuo* to afford S**3** as an analytically pure yellow powder. Yield: 0.89 g, 81%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 11.82 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 4H), 7.23 (d, *J* = 6.8 Hz 2H), 2.77-2.66 (m, 4H), 1.39 (d, *J* = 6.8 Hz, 12H), 1.16 (d, *J* = 6.8 Hz, 12H); HR-MS (ESI): *m/z* 513.3264 (calcd.); 513.3264 (found, $[M-Cl]^+$).

Pd-NHC complex (2): To a schlenk tube containing $PdCl_2$ (0.088 g, 0.5 mmol), **S3** (0.55 mmol), K_2CO_3 (0.345 g, 5.0 mmol) and a stirrer bar, 3-Chloropyridine (2.0 mL) was added. The reaction mixture was heated with vigorous stirring at 90℃ for 24 h. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 and passed through a short pad of silica gel covered with a pad of Celite eluting with CH_2Cl_2 until the product was completely recovered. Most of the CH_2Cl_2 was removed (rotary evaporator) at room temperature and 3-chloropyridine was then vacuum-distilled (water aspirator vacuum) and saved for reuse. The pure pd-NHCcomplex **2** was isolated after triturating with pentane, decanting of the supernatant and drying in high vacuum[S3]. Yield: 0.305 g, 76%.^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.68 (d, *J* = 2.0 Hz, 1H), 8.61 (dd, *J* = 5.2 and 0.8 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.64 (t, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz 1H), 7.48 (d, *J* = 8.0 Hz, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.10 (dd, *J* = 8.0 Hz, 5.6 Hz, 1H), 6.80 (d, *J* = 7.32 Hz, 2H), 3.45 - 3.35 (m, 4H), 1.46 (d, *J* = 6.4 Hz, 12H), 0.92 (d, *J* = 6.4 Hz, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 159.07, 150.49, 149.48, 147.21, 140.39, 137.37, 133.79, 131.78, 130.65, 129.51, 129.05, 128.06, 127.21, 126.02, 124.71, 124.24, 122.13, 28.86, 25.76, 24.24. HR-MS (ESI): *m/z* 617.2226 ([M-Cl-Py-2Cl], calcd.); 617.2163 (found, $[M\text{-}Cl\text{-}Py\text{-}2Cl]^+$).

2.2. General procedure for Pd-catalyzed amination with complex **2**.

To a 50 mL schlenk tube containing base (3.0 mmol) and precatalyst **2** (0.075 mol%, 0.0012 g) purged with N_2 (3 times), amine (2.2 mmol) was added. The resulted mixture was allowed to stir for 2–3 minutes at room temperature before dioxane (2 mL) was injected via syringe. Aryl chloride (2.0 mmol) was added subsequently. (Note, if aryl chloride was a solid, it was introduced before purging with N_2). The result mixture was then heated at 80 ℃ for 24 h. After cooling to the room temperature, the reaction mixture was concentrated in vacuo and directly purified by silica gel flash chromatography.

2.3. Hydration of Mefenamic acid **30**



29 **30**

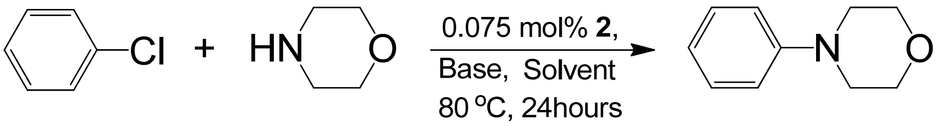
Scheme S2. Synthesis of mefenamic acid **30**.

2-(2,3-dimethylphenylamino)benzonitrile (29): 80% yield.^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.48 (dd, *J* = 7.6 and 1.2 Hz, 1H), 7.30 (td, *J* = 8.0 and 1.2Hz, 1H), 7.17 - 7.09 (m, 3H), 6.77 (t, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 8.4 Hz 1H), 6.15 (s, 1H), 2.35 (s, 3H), 2.17 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 148.88, 138.43, 137.50, 133.84, 132.65, 132.58, 127.69, 126.24, 123.21, 117.91, 117.74, 113.22, 96.65, 20.49, 13.87. GC-MS: *m/z* = 222.2 $[M]^+$, 207.1, 194.1

Mefenamic acid (30): A mixture of **29** (0.10 g, 0.45 mmol), KOH (2.52 g), H_2O (15 mL) and MeOH (10mL) was stirred and heated under reflux condition for 12 h resulting in a clear solution[S4]. After cooling to room temperature, MeOH was removed, the precipitation occurred. The mixture was extracted with EtOAc (5 × 30 mL). The organic phase was combined and dried over Na_2SO_4; the filtrate was concentrated in vacuo affording Mefenamic acid in a 95% yield (0.103 g). The compound was further purified by silica gel flash chromatography. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 12.96 (br s, 1H), 9.46 (br s, 1H), 7.88 (d, J = 7.2 Hz, 1H), 7.29 (t, J = 7.2 Hz, 1H), 7.12 - 7.08 (m, 2H), 7.04 – 6.99 (m, 1H), 6.69 - 6.66 (m, 2H), 2.72 (s, 3H), 2.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 170.10, 148.72, 138.23, 137.78, 134.07, 131.69, 131.14, 126.31, 125.92, 122.09, 116.15, 113.01, 111.16, 20.12, 13.56. GC-MS: m/z = 241.1 $[M]^+$

3. Optimization of the reaction conditions (data not listed in the Table 1)

Table S1. Base and solvent effects on the amination of chlorobenzene with morpholine catalyzed by palladium complex 2.[a]



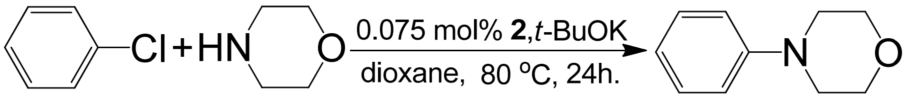
Entry	Solvent	Base	Yield (%)[b]
1	DME	*t*-BuONa	58
2	DME	KOH	8
3	DME	K_3PO_4	3
4	DME	KOAc	N.R.
5	DME	K_2CO_3	<2%
6	DME	Cs_2CO_3	2%
7	DME	Et_3N	N.R.
8	DME	DBU	N.R.
9	*t*-BuOH	*t*-BuOK	13
10	MeOH	*t*-BuOK	N.R.
11	DMF	*t*-BuOK	68
12	DMSO	*t*-BuOK	44
13	DMA	*t*-BuOK	66

[a] Reaction was carried out on a 2 mmol scale (chlorobenzene) with 2.2 mmol morpholine, 3.0 mmol base in 2 mL solvent with Pd-NHC complex **2** for 24 hours.

[b] Isolated yield.

4. Poisoning experiments

Table S2. Poisoning experiments for complex 2 in the aminations. [a]

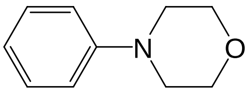


Entry	Aditive	Yield (%)[b]
1	Hg (1 drop after 0 hour)	50
2	Hg (1 drop after 0.5 hours)	91
3	Hg (1 drop after 1 hours)	91
4	Hg (1 drop after 3 hours)	90
5	Hg (1 drop after 6 hours)	94
6	Hg (1 drop after 12 hours)	98
7	PvPy (300 eq. Pd sources after 0 hour)	97

[a] Reaction was carried out on a 2 mmol scale with 0.075 mol% **2** at 80 ℃ for 24 hours.

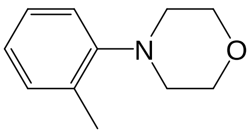
[b] Isolated yield.

5. Data for the products of aminations.



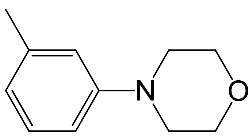
3:

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.316-7.266 (m, 2H), 6.93 (d, J = 8.4 Hz, 2H), 6.89 (t, J = 7.2 Hz, 1H), 3.87 (t, J = 4.8 Hz, 4H), 3.17 (t, J = 4.8 Hz, 4H); GC-MS: m/z = 163.1 $[M]^+$, 132.0, 106.0, 86.0, 77.0.



4a:

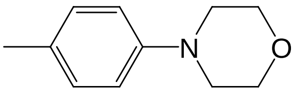
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.20 (t, J = 7.2 Hz, 2H), 7.04 (d, J = 7.2 Hz, 1H), 7.01 (d, J = 7.2 Hz, 1H), 3.86 (t, J = 4.4 Hz, 4H), 2.92 (t, J = 4.4 Hz, 4H), 2.33 (s, 3H); GC-MS: m/z = 177.1 $[M]^+$, 132.0, 119.1, 91.1, 77.0.



4b:

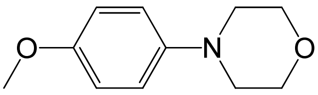
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.19 (t, J = 8.0 Hz, 1H), 6.80-6.71 (m, 3H), 3.87 (t, J = 4.8 Hz, 4H), 3.16 (t, J = 4.8 Hz, 4H), 2.35 (s, 3H); GC-MS: m/z = 177.1 $[M]^+$, 119.1, 91.1, 77.0.

4c:



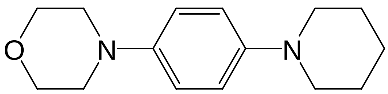
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.10 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 3.86 (t, *J* = 4.4 Hz, 4H), 3.11 (t, *J* = 4.4 Hz, 4H), 2.28 (s, 3 H); GC-MS: *m/z* = 177.0 $[M]^+$, 119.1, 91.1, 65.0.

5a:



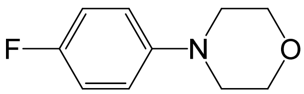
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.10 – 6.82 (m, 4H),, 3.86 (t, *J* = 4.4 Hz, 4H), 3.77 (s, 3 H), 3.06 (t, *J* = 4.4 Hz, 4H); GC-MS: *m/z* = 193.0 $[M]^+$, 135.0, 120.0, 92.0, 77.0.

5b:



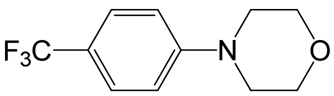
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 6.94-6.85 (m, 4H), 3.85 (t, *J* = 4.8 Hz, 4H), 3.06 (t, *J* = 4.8 Hz, 4H), 3.04 (qn, *J* = 5.6 Hz, 8H), 3.04 (qn, *J* = 5.6 Hz, 2H); GC-MS: *m/z* = 246.2 $[M]^+$, 188.1, 132.0.

6a:



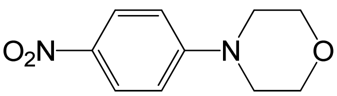
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 6.98 (d, *J* = 8.4 Hz, 2H), 6.90-6.80 (m, 2H), 3.86 (t, *J* = 4.8 Hz, 4H), 3.08 (t, *J* = 4.8 Hz, 4H); GC-MS: *m/z* = 181.0 $[M]^+$, 123.1, 95.0.

6b:

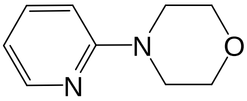


^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.50 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.86 (t, *J* = 4.8 Hz, 4H), 3.24 (t, *J* = 4.8 Hz, 4H); GC-MS: *m/z* = 231.0 $[M]^+$, 172.9, 144.9, 68.9.

6c:

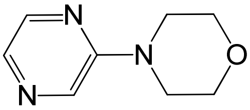


^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.14 (d, *J* = 9.6 Hz, 2H), 6.83 (d, *J* = 9.6 Hz, 2H), 3.86 (t, *J* = 4.8 Hz, 4H), 3.37 (t, *J* = 4.8 Hz, 4H); GC-MS: *m/z* = 207.9 $[M]^+$, 149.9, 119.9, 77.0.



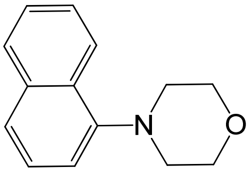
7:

[1]H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.19 (d, *J* = 4.0 Hz, 1H), 7.49 (t, *J* = 8.8 Hz, 1H), 6.70-6.50 (m, 2H), 3.82 (t, *J* = 4.8 Hz, 4H), 3.49 (t, *J* = 4.8 Hz, 4H); GC-MS: *m/z* = 164.0 $[M]^+$, 133.0, 107.0, 77.0.



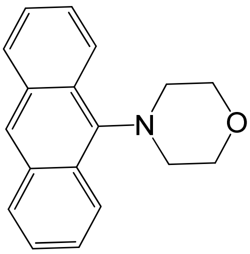
8:

[1]H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.13 (s, 1H), 8.07 (d, *J* = 2.8 Hz, 1H), 7.89 (d, *J* = 2.8 Hz, 1H), 3.83 (t, *J* = 4.8 Hz, 4H), 3.55 (t, *J* = 4.8 Hz, 4H); GC-MS: *m/z* = 165.0 $[M]^+$, 134.0, 108.0, 80.0.



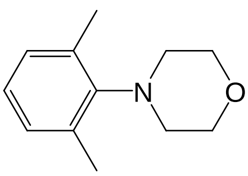
9:

[1]H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.23 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.51-7.46 (m, 2H), 7.42 (t, *J* = 8.0 Hz, 1H) 7.10 (d, *J* = 7.2 Hz, 1H), 3.99 (t, *J* = 4.4 Hz, 4H), 3.13 (t, *J* = 4.4 Hz, 4H); GC-MS: *m/z* = 213.0 $[M]^+$, 153.9, 126.9, 76.9.



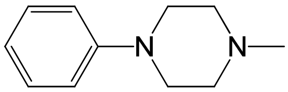
10:

[1]H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.54 (d, *J* = 8.8 Hz, 2H), 8.33 (s, 1H), 8.02 (d, *J* = 7.6 Hz, 2H), 7.52-7.44 (m, 4H), 4.05 (t, *J* = 4.4 Hz, 4H), 3.54 (t, *J* = 4.4 Hz, 4H); GC-MS: *m/z* = 263.0 $[M]^+$, 204.0, 176.0.

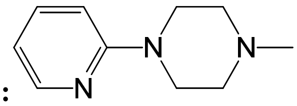


11:

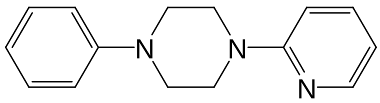
[1]H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.30-6.96 (m, 3H), 3.81 (t, *J* = 4.4 Hz, 4H), 3.11 (t, *J* = 4.4 Hz, 4H), 2.36 (s, 3 H); GC-MS: *m/z* = 191.0 $[M]^+$, 132.0, 77.0.

12a: 

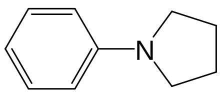
^{1}H NMR (CDCl$_3$, 400 MHz, 298 K): δ = 7.29 – 7.24 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.86 (t, *J* = 7.2 Hz, 1H), 3.22 (t, *J* = 4.8 Hz, 4H), 2.58 (t, *J* = 4.8 Hz, 4H), 2.36 (s, 3H); GC-MS: *m/z* = 176.1 $[M]^+$, 105.1, 77.0.

12b: 

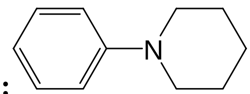
^{1}H NMR (CDCl$_3$, 400 MHz, 298 K): δ = 8.17 (d, *J* = 4.8 Hz, 1H), 7.46 (dt, *J* = 8.8 and 2.0 Hz,, 1H), 6.65 – 6.59 (m, 2H), 3.54 (t, *J* = 5.2 Hz, 4H), 2.51 (t, *J* = 5.2 Hz, 4H), 2.33 (s, 3H); GC-MS: *m/z* = 177.1 $[M]^+$, 107.1, 79.0.

12c: 

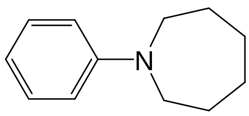
^{1}H NMR (CDCl$_3$, 400 MHz, 298 K): δ = 8.22 (dd, *J* = 4.8 and 1.6 Hz, 1H), 7.46 (dt, *J* = 8.0 and 2.0 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.89 (t, *J* = 7.2 Hz, 1H), 6.71 (d, *J* = 8.8 Hz, 1H), 6.67 – 6.64 (m, 1H), 3.71 (t, *J* = 5.2 Hz, 4H), 3.32 (t, *J* = 5.2 Hz, 4H); GC-MS: *m/z* = 239.0 $[M]^+$, 145.0, 133.0, 107.1, 79.0.

13a: 

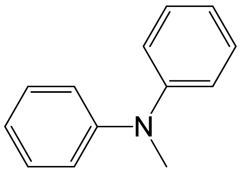
^{1}H NMR (CDCl$_3$, 400 MHz, 298 K): δ = 7.25 (t, *J* = 8.8 Hz, 2H), 6.68 (t, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 2H), 3.30 (t, *J* = 6.4 Hz, 4H), 2.02 (t, *J* = 6.4 Hz, 4H); GC-MS: *m/z* = 147.0 $[M]^+$, 104.0, 91.1, 77.0.

13b: 

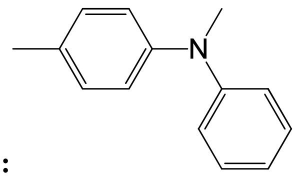
^{1}H NMR (CDCl$_3$, 400 MHz, 298 K): δ = 7.24 (t, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 7.2 Hz, 1H), 3.15 (t, *J* = 5.6 Hz, 4H), 1.74-1.68 (m, 4H), 1.60-1.54 (m, 2H); GC-MS: *m/z* = 161.0 $[M]^+$, 160.1, 105.0, 77.0.

13c: 

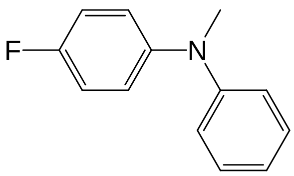
^{1}H NMR (CDCl$_3$, 400 MHz, 298 K): δ = 7.23 (t, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 2H), 6,65 (t, *J* = 7.2 Hz, 1H), 3.47 (t, *J* = 6.0 Hz, 4H), 1.82-1.80 (m, 4H), 1.59-1.54 (m, 4H); GC-MS: *m/z* = 175.1 $[M]^+$, 147.0, 132.1, 104.1, 91.0, 77.0.

14a: 

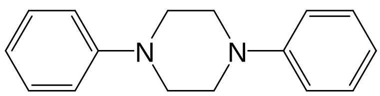
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.29 (t, *J* = 7.2 Hz, 4H), 7.04 (d, *J* = 8.0 Hz, 4H), 6.97 (t, *J* = 7.2 Hz, 2H), 3.33 (s, 3H); GC-MS: *m/z* = 183.0 $[M]^+$, 167.1, 104.0, 77.1.

14b: 

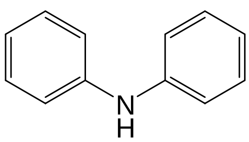
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.27 (t, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.90 (t, *J* = 7.2 Hz, 1H), 2.99 (s, 3H), 2.36 (s, 3H); GC-MS: *m/z* = 197.2 $[M]^+$, 182.1, 167.1, 77.0.

14c: 

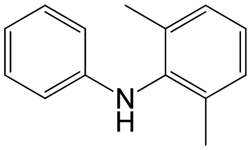
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.25 (t, *J* = 8.0 Hz, 2H), 7.07-6.99 (m, 4H), 6.92-6.70 (m, 3H), 3.28 (s, 3H); GC-MS: *m/z* = 201.0 $[M]^+$, 185.0 122.0, 77.0.

15: 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.31 (d, *J* = 8.4 Hz, 4H), 7.00 (d, *J* = 8.4 Hz, 4H), 6.91 (t, *J* = 7.2 Hz, 2H), 3.36 (s, 8H); GC-MS: *m/z* = 238.1 $[M]^+$, 132.0, 105.0, 77.0.

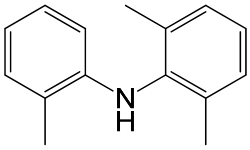
16: 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.28 (t, *J* = 7.6 Hz, 4H), 7.08 (d, *J* = 7.6 Hz, 4H), 6.94 (t, *J* = 7.2 Hz, 2H), 5.70 (s, 1H); GC-MS: *m/z* = 169.1 $[M]^+$.



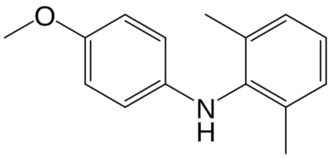
17:

[1]H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.19-7.06 (m, 5H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.51 (d, *J* = 7.2 Hz, 2H), 5.19 (s, 1H), 2.21 (s, 6H); GC-MS: *m/z* = 197.1 $[M]^+$, 182.1, 120.1, 77.0.



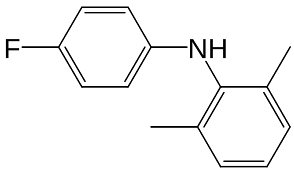
18:

[1]H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.14-7.06 (m, 4H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.71 (t, *J* = 7.6 Hz, 1H), 6.15 (d, *J* = 8.0 Hz, 1H), 4.94 (s, 1H), 2.34 (s, 3H), 2.19 (s, 6H); GC-MS: *m/z* = 211.0 $[M]^+$, 194.0, 180.0, 120.0, 107.0, 77.0.



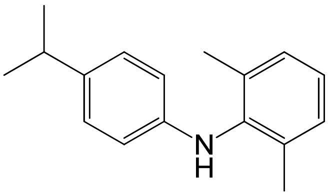
19a:

[1]H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.12 (d, *J* = 7.2 Hz, 2H), 7.05 (dd, *J* = 8.4 Hz, 6.0 Hz, 1H), 6.76 (t, *J* = 9.2 Hz, 2H), 6.50 (t, *J* = 9.2 Hz, 2H), 5.04 (s, 1H), 3.76 (s, 3H), 2.21 (s, 6H); GC-MS: *m/z* = 227.1 $[M]^+$, 212.1, 182.1.



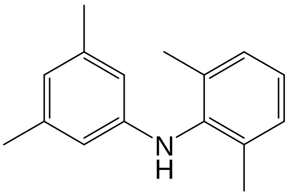
19b:

[1]H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.13 – 7.05 (m, 3H), 6.89 – 6.83 (m, 2H), 6.47 – 6.42 (m, 2H), 5.10 (s, 1H), 2.20 (s, 6H); GC-MS: *m/z* = 215.1 $[M]^+$, 198.1, 120.1, 77.1.



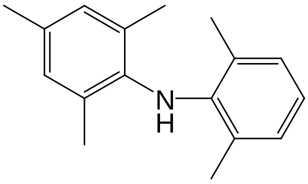
20:

[1]H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.13-7.01 (m, 5H), 6.48 (t, *J* = 3.6 Hz, 1H), 6.46 (t, *J* = 3.6 Hz, 1H), 5.12 (s, 1H), 2.87-2.77 (m, 1H), 2.22 (s, 6H), 1.22 (d, *J* = 6.8 Hz, 6H); GC-MS: *m/z* = 239.1 $[M]^+$, 224.2, 194.1.



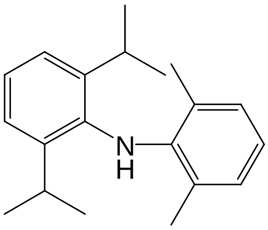
21:

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.14-7.07 (m, 3H), 6.43 (s, 1H), 6.16 (s, 1H), 5.10 (s, 1H), 2.22 (s, 6H), 2.21 (s, 6H); GC-MS: *m/z* = 225.1 $[M]^+$, 210.0, 195.1, 120.1, 77.0.



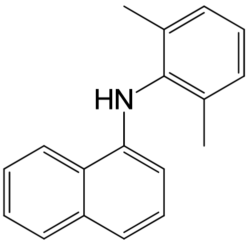
22:

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 6.97 (d, *J* = 7.2 Hz, 2H), 6.83-6.79 (m, 3H), 4.72 (s, 1H), 2.27 (s, 3H), 2.01 (d, *J* = 2.0 Hz, 12H); GC-MS: *m/z* = 239.1 $[M]^+$.



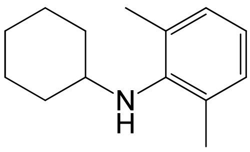
23:

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.18-7.11 (m, 3H), 6.95 (d, *J* = 7.6 Hz, 2H), 6,73 (t, *J* = 8.0 Hz, 1H), 4.80 (s, 1H), 3.21-3.11 (m, 2H), 1.99 (s, 6H), 1.13 (d, *J* = 7.2 Hz, 12H); GC-MS: *m/z* = 281.3 $[M]^+$, 236.2, 208.1.



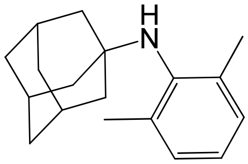
24:

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.10 (d, *J* = 9.2 Hz, 1H), 7.86 (d, *J* = 9.2 Hz, 1H), 7.56 – 7.50 (m, 2 H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.10 (m, 4H), 6.24 (d, *J* = 7.6 Hz, 1H), 5.72 (s, 1H), 2.22 (s, 6H); GC-MS: *m/z* = 247.1 $[M]^+$, 232.1, 217.1.



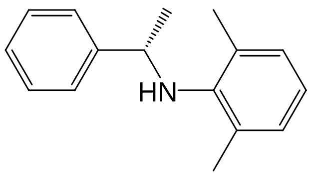
25:

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 6.99 (d, *J* = 7.6 Hz, 2H), 6.80 (t, *J* = 7.6 Hz, 1H), 3.00-2.93 (m, 1H), 2.28 (s, 6 H), 1.99-1.96 (m, 2H), 1.78-1.74 (m, 2H), 1.65-1.62 (m, 1H), 1.32-1.08 (m, 6H), 3.86 (t, *J* = 4.4 Hz, 4H), 3.11 (t, *J* = 4.4 Hz, 4H), 2.28 (s, 3 H); GC-MS: *m/z* = 203.1 $[M]^+$



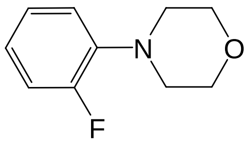
26:

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.01 (d, *J* = 7.2 Hz, 2H), 6.88 (t, *J* = 7.2 Hz, 1H), 2.36 (s, 6 H), 2.04 (s, 3 H), 3.00-2.93 (m, 1H),1.99-1.96 (m, 2H), 1.78-1.74 (m, 2H), 1.65-1.62 (m, 1H), 1.32-1.08 (m, 6H), 1.77 (d, *J* = 2.8 Hz, 6H),1.57 (t, *J* =14.8 Hz, 6H), 3.11 (t, *J* = 4.4 Hz, 4H), 2.28 (s, 3 H); GC-MS: *m/z* = 255.2 $[M]^+$, 198.1, 135.1.



27:

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.33-7.22 (m, 5H), 6.96 (d, *J* = 7.2 Hz, 2H), 6.80 (t, *J* = 7.6 Hz, 1H), 4.33 (q, *J* = 6.8 Hz, 1H), 2.18 (s, 6H), 1.52 (d, *J* = 6.8 Hz, 3H); $[\alpha]_{20}^{D}$ = -100.8° (c = 0.73, $CHCl_3$).[S5] GC-MS: *m/z* = 225.1 $[M]^+$, 210.1, 121.0, 105.0, 77.0.



28:

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.09 – 7.01 (m, 2H), 6.98 – 6.93 (m, 2H), 3.88 (t, *J* = 4.8 Hz, 4H), 3.09 (t, *J* = 4.8 Hz, 4H); GC-MS: *m/z* = 181.1 $[M]^+$, 123.1, 95.0.

6. Crystal data and structure information for the catalyst (2).

Table S3. Crystal data and structure refinement for pd-NHC complex **2**.

Identification code	**2**
Empirical formula	C43 H46 Cl5 N3 Pd
	C42 H44 Cl3 N3 Pd - CH2Cl2
Formula weight	888.48
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 31.83(2) A alpha = 90 deg.
	b = 12.576(8) A beta = 98.962(15) deg.
	c = 23.076(14) A gamma = 90 deg.
Volume	9125(10) A^3
Z, Calculated density	8, 1.293 Mg/m^3
Absorption coefficient	0.730 mm^-1
F(000)	3648
Crystal size	0.30 x 0.25 x 0.10 mm
Theta range for data collection	1.74 to 25.01 deg.
Limiting indices	-37<=h<=28, -14<=k<=14, -27<=l<=27
Reflections collected / unique	18407 / 7994 [R(int) = 0.0654]
Completeness to theta = 25.01	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9305 and 0.8106
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7994 / 0 / 469
Goodness-of-fit on F^2	1.120
Final R indices [I>2sigma(I)]	R1 = 0.0709, wR2 = 0.1879
R indices (all data)	R1 = 0.1046, wR2 = 0.2238
Largest diff. peak and hole	1.666 and -1.049 e.A^-3

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pd(1)	1209(1)	3861(1)	1742(1)	46(1)
Cl(1)	548(1)	4422(2)	1323(1)	81(1)
Cl(2)	1863(1)	3296(2)	2162(1)	66(1)
Cl(3)	1147(1)	1612(4)	3853(1)	165(2)
Cl(4)	823(3)	486(9)	2023(5)	353(5)
N(1)	989(2)	3672(6)	2553(3)	65(2)
N(2)	1630(2)	4956(4)	844(2)	43(1)
N(3)	1329(2)	3484(4)	490(2)	40(1)
C(1)	727(3)	4354(10)	2733(4)	98(3)
C(2)	566(4)	4240(14)	3265(6)	141(5)
C(3)	699(5)	3419(15)	3618(5)	140(6)
C(4)	972(3)	2712(10)	3436(4)	99(3)
C(5)	1117(3)	2846(8)	2899(3)	77(2)
C(6)	1411(2)	4087(5)	992(3)	41(1)
C(7)	1678(2)	4905(5)	261(2)	46(1)
C(8)	1848(2)	5486(5)	-201(3)	52(2)
C(9)	2050(2)	6417(6)	-263(3)	67(2)
C(10)	2158(3)	6674(7)	-817(4)	80(2)
C(11)	2071(3)	6015(7)	-1289(3)	73(2)
C(12)	1859(2)	5046(6)	-1241(3)	59(2)
C(13)	1756(2)	4816(6)	-692(3)	53(2)
C(14)	1545(2)	3859(5)	-571(3)	47(1)
C(15)	1445(2)	3130(6)	-1014(3)	63(2)
C(16)	1555(3)	3376(7)	-1571(3)	71(2)
C(17)	1749(3)	4281(8)	-1682(3)	72(2)

C(18)	1497(2)	3992(5)	44(3)	45(1)
C(19)	1827(2)	5760(5)	1248(2)	44(1)
C(20)	1582(2)	6626(6)	1361(3)	56(2)
C(21)	1785(3)	7378(7)	1755(4)	76(2)
C(22)	2196(3)	7283(7)	2002(3)	76(2)
C(23)	2430(2)	6441(7)	1873(3)	70(2)
C(24)	2253(2)	5644(6)	1485(3)	50(2)
C(25)	2527(2)	4730(7)	1365(4)	71(2)
C(26)	2786(3)	5000(9)	879(4)	98(3)
C(27)	2834(3)	4373(10)	1903(5)	118(4)
C(28)	1134(2)	6802(7)	1063(4)	76(2)
C(29)	1146(4)	7512(9)	519(6)	130(5)
C(30)	846(3)	7214(11)	1482(6)	147(6)
C(31)	1139(2)	2453(5)	406(3)	51(2)
C(32)	732(2)	2366(6)	104(3)	70(2)
C(33)	597(4)	1314(9)	-63(5)	113(4)
C(34)	844(5)	471(9)	102(6)	140(5)
C(35)	1244(4)	584(8)	399(5)	104(3)
C(36)	1402(3)	1572(6)	569(3)	62(2)
C(37)	1846(3)	1679(7)	904(3)	71(2)
C(38)	2167(3)	1622(11)	487(4)	118(4)
C(39)	1952(4)	824(9)	1392(4)	109(4)
C(40)	442(2)	3316(8)	-81(4)	82(2)
C(41)	382(3)	3520(11)	-733(5)	121(4)
C(42)	15(3)	3176(11)	132(5)	115(4)
C(43)	400(10)	1452(19)	1711(15)	450(30)
Cl(5)	60(5)	620(12)	1308(5)	440(8)

Table S5. Bond lengths [A] and angles [deg] for **2**.

Pd(1)-C(6)	1.960(6)
Pd(1)-N(1)	2.113(6)
Pd(1)-Cl(2)	2.271(2)
Pd(1)-Cl(1)	2.286(2)
Cl(3)-C(4)	1.727(12)
Cl(4)-C(43)	1.87(3)
N(1)-C(1)	1.307(11)
N(1)-C(5)	1.334(10)
N(2)-C(6)	1.367(8)
N(2)-C(7)	1.379(7)
N(2)-C(19)	1.449(7)
N(3)-C(6)	1.374(7)
N(3)-C(18)	1.388(7)
N(3)-C(31)	1.430(8)
C(1)-C(2)	1.410(14)
C(1)-H(1A)	0.9300
C(2)-C(3)	1.34(2)
C(2)-H(2A)	0.9300
C(3)-C(4)	1.356(18)
C(3)-H(3A)	0.9300
C(4)-C(5)	1.397(11)
C(5)-H(5A)	0.9300
C(7)-C(18)	1.346(8)
C(7)-C(8)	1.464(8)
C(8)-C(9)	1.354(10)
C(8)-C(13)	1.405(9)
C(9)-C(10)	1.413(10)

C(9)-H(9A)	0.9300
C(10)-C(11)	1.361(12)
C(10)-H(10A)	0.9300
C(11)-C(12)	1.405(11)
C(11)-H(11A)	0.9300
C(12)-C(13)	1.389(9)
C(12)-C(17)	1.405(11)
C(13)-C(14)	1.427(9)
C(14)-C(15)	1.374(9)
C(14)-C(18)	1.460(8)
C(15)-C(16)	1.418(10)
C(15)-H(15A)	0.9300
C(16)-C(17)	1.337(12)
C(16)-H(16A)	0.9300
C(17)-H(17A)	0.9300
C(19)-C(20)	1.387(9)
C(19)-C(24)	1.391(9)
C(20)-C(21)	1.399(10)
C(20)-C(28)	1.499(10)
C(21)-C(22)	1.350(11)
C(21)-H(21A)	0.9300
C(22)-C(23)	1.354(12)
C(22)-H(22A)	0.9300
C(23)-C(24)	1.402(10)
C(23)-H(23A)	0.9300
C(24)-C(25)	1.494(11)
C(25)-C(27)	1.523(12)
C(25)-C(26)	1.529(12)
C(25)-H(25A)	0.9800
C(26)-H(26A)	0.9600

C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600
C(27)-H(27A)	0.9600
C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600
C(28)-C(30)	1.523(13)
C(28)-C(29)	1.547(13)
C(28)-H(28A)	0.9800
C(29)-H(29A)	0.9600
C(29)-H(29B)	0.9600
C(29)-H(29C)	0.9600
C(30)-H(30A)	0.9600
C(30)-H(30B)	0.9600
C(30)-H(30C)	0.9600
C(31)-C(32)	1.378(10)
C(31)-C(36)	1.403(10)
C(32)-C(33)	1.426(12)
C(32)-C(40)	1.530(12)
C(33)-C(34)	1.341(16)
C(33)-H(33A)	0.9300
C(34)-C(35)	1.356(15)
C(34)-H(34A)	0.9300
C(35)-C(36)	1.374(12)
C(35)-H(35A)	0.9300
C(36)-C(37)	1.508(11)
C(37)-C(38)	1.510(12)
C(37)-C(39)	1.556(11)
C(37)-H(37A)	0.9800
C(38)-H(38A)	0.9600
C(38)-H(38B)	0.9600

C(38)-H(38C)	0.9600
C(39)-H(39A)	0.9600
C(39)-H(39B)	0.9600
C(39)-H(39C)	0.9600
C(40)-C(41)	1.508(13)
C(40)-C(42)	1.525(12)
C(40)-H(40A)	0.9800
C(41)-H(41A)	0.9600
C(41)-H(41B)	0.9600
C(41)-H(41C)	0.9600
C(42)-H(42A)	0.9600
C(42)-H(42B)	0.9600
C(42)-H(42C)	0.9600
C(43)-Cl(5)	1.68(2)
C(43)-H(43A)	0.9700
C(43)-H(43B)	0.9700

C(6)-Pd(1)-N(1)	178.1(3)
C(6)-Pd(1)-Cl(2)	90.88(17)
N(1)-Pd(1)-Cl(2)	89.71(18)
C(6)-Pd(1)-Cl(1)	89.45(17)
N(1)-Pd(1)-Cl(1)	89.96(19)
Cl(2)-Pd(1)-Cl(1)	179.61(8)
C(1)-N(1)-C(5)	118.2(8)
C(1)-N(1)-Pd(1)	121.4(7)
C(5)-N(1)-Pd(1)	120.4(5)
C(6)-N(2)-C(7)	110.2(5)
C(6)-N(2)-C(19)	125.7(5)
C(7)-N(2)-C(19)	123.8(5)
C(6)-N(3)-C(18)	109.0(5)

C(6)-N(3)-C(31)	129.5(5)
C(18)-N(3)-C(31)	121.3(5)
N(1)-C(1)-C(2)	123.0(12)
N(1)-C(1)-H(1A)	118.5
C(2)-C(1)-H(1A)	118.5
C(3)-C(2)-C(1)	119.0(12)
C(3)-C(2)-H(2A)	120.5
C(1)-C(2)-H(2A)	120.5
C(2)-C(3)-C(4)	118.2(10)
C(2)-C(3)-H(3A)	120.9
C(4)-C(3)-H(3A)	120.9
C(3)-C(4)-C(5)	120.8(11)
C(3)-C(4)-Cl(3)	121.2(9)
C(5)-C(4)-Cl(3)	118.0(9)
N(1)-C(5)-C(4)	120.8(9)
N(1)-C(5)-H(5A)	119.6
C(4)-C(5)-H(5A)	119.6
N(2)-C(6)-N(3)	105.6(5)
N(2)-C(6)-Pd(1)	125.9(4)
N(3)-C(6)-Pd(1)	128.1(4)
C(18)-C(7)-N(2)	107.2(5)
C(18)-C(7)-C(8)	109.9(5)
N(2)-C(7)-C(8)	142.9(6)
C(9)-C(8)-C(13)	118.4(6)
C(9)-C(8)-C(7)	138.1(6)
C(13)-C(8)-C(7)	103.5(6)
C(8)-C(9)-C(10)	118.8(7)
C(8)-C(9)-H(9A)	120.6
C(10)-C(9)-H(9A)	120.6
C(11)-C(10)-C(9)	122.4(8)

C(11)-C(10)-H(10A)	118.8
C(9)-C(10)-H(10A)	118.8
C(10)-C(11)-C(12)	120.4(7)
C(10)-C(11)-H(11A)	119.8
C(12)-C(11)-H(11A)	119.8
C(13)-C(12)-C(17)	116.8(7)
C(13)-C(12)-C(11)	115.9(7)
C(17)-C(12)-C(11)	127.3(7)
C(12)-C(13)-C(8)	124.1(7)
C(12)-C(13)-C(14)	122.6(6)
C(8)-C(13)-C(14)	113.2(6)
C(15)-C(14)-C(13)	118.6(6)
C(15)-C(14)-C(18)	138.9(6)
C(13)-C(14)-C(18)	102.5(5)
C(14)-C(15)-C(16)	118.0(7)
C(14)-C(15)-H(15A)	121.0
C(16)-C(15)-H(15A)	121.0
C(17)-C(16)-C(15)	123.0(7)
C(17)-C(16)-H(16A)	118.5
C(15)-C(16)-H(16A)	118.5
C(16)-C(17)-C(12)	121.1(7)
C(16)-C(17)-H(17A)	119.5
C(12)-C(17)-H(17A)	119.5
C(7)-C(18)-N(3)	108.0(5)
C(7)-C(18)-C(14)	110.8(5)
N(3)-C(18)-C(14)	141.2(6)
C(20)-C(19)-C(24)	123.4(6)
C(20)-C(19)-N(2)	118.0(5)
C(24)-C(19)-N(2)	118.5(6)
C(19)-C(20)-C(21)	115.9(7)

C(19)-C(20)-C(28)	123.5(6)
C(21)-C(20)-C(28)	120.5(7)
C(22)-C(21)-C(20)	122.3(8)
C(22)-C(21)-H(21A)	118.9
C(20)-C(21)-H(21A)	118.9
C(21)-C(22)-C(23)	120.5(7)
C(21)-C(22)-H(22A)	119.8
C(23)-C(22)-H(22A)	119.8
C(22)-C(23)-C(24)	121.3(7)
C(22)-C(23)-H(23A)	119.3
C(24)-C(23)-H(23A)	119.3
C(19)-C(24)-C(23)	116.5(7)
C(19)-C(24)-C(25)	124.7(6)
C(23)-C(24)-C(25)	118.7(6)
C(24)-C(25)-C(27)	113.2(8)
C(24)-C(25)-C(26)	111.2(7)
C(27)-C(25)-C(26)	108.2(7)
C(24)-C(25)-H(25A)	108.0
C(27)-C(25)-H(25A)	108.0
C(26)-C(25)-H(25A)	108.0
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(25)-C(27)-H(27A)	109.5
C(25)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(25)-C(27)-H(27C)	109.5

H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(20)-C(28)-C(30)	112.5(8)
C(20)-C(28)-C(29)	108.5(7)
C(30)-C(28)-C(29)	114.4(10)
C(20)-C(28)-H(28A)	107.0
C(30)-C(28)-H(28A)	107.0
C(29)-C(28)-H(28A)	107.0
C(28)-C(29)-H(29A)	109.5
C(28)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(28)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(28)-C(30)-H(30A)	109.5
C(28)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(28)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(32)-C(31)-C(36)	123.2(7)
C(32)-C(31)-N(3)	119.0(6)
C(36)-C(31)-N(3)	117.2(6)
C(31)-C(32)-C(33)	115.5(8)
C(31)-C(32)-C(40)	124.0(7)
C(33)-C(32)-C(40)	120.4(8)
C(34)-C(33)-C(32)	121.2(9)
C(34)-C(33)-H(33A)	119.4
C(32)-C(33)-H(33A)	119.4
C(33)-C(34)-C(35)	121.6(10)

C(33)-C(34)-H(34A)	119.2
C(35)-C(34)-H(34A)	119.2
C(34)-C(35)-C(36)	120.8(10)
C(34)-C(35)-H(35A)	119.6
C(36)-C(35)-H(35A)	119.6
C(35)-C(36)-C(31)	117.5(8)
C(35)-C(36)-C(37)	119.9(8)
C(31)-C(36)-C(37)	122.6(7)
C(36)-C(37)-C(38)	110.1(7)
C(36)-C(37)-C(39)	113.0(8)
C(38)-C(37)-C(39)	109.6(8)
C(36)-C(37)-H(37A)	108.0
C(38)-C(37)-H(37A)	108.0
C(39)-C(37)-H(37A)	108.0
C(37)-C(38)-H(38A)	109.5
C(37)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(37)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(37)-C(39)-H(39A)	109.5
C(37)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(37)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(41)-C(40)-C(42)	111.1(8)
C(41)-C(40)-C(32)	112.9(9)
C(42)-C(40)-C(32)	110.4(8)
C(41)-C(40)-H(40A)	107.4

C(42)-C(40)-H(40A)	107.4
C(32)-C(40)-H(40A)	107.4
C(40)-C(41)-H(41A)	109.5
C(40)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
C(40)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
C(40)-C(42)-H(42A)	109.5
C(40)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
C(40)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
Cl(5)-C(43)-Cl(4)	99.9(15)
Cl(5)-C(43)-H(43A)	111.8
Cl(4)-C(43)-H(43A)	111.8
Cl(5)-C(43)-H(43B)	111.8
Cl(4)-C(43)-H(43B)	111.8
H(43A)-C(43)-H(43B)	109.5

Table S6. Anisotropic displacement parameters (A^2 x 10^3) for **2**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Pd(1)	46(1)	60(1)	33(1)	-2(1)	8(1)	1(1)
Cl(1)	48(1)	120(2)	73(1)	9(1)	7(1)	13(1)
Cl(2)	58(1)	108(2)	32(1)	8(1)	5(1)	17(1)
Cl(3)	170(3)	239(4)	90(2)	78(3)	33(2)	-22(3)
Cl(4)	340(12)	317(11)	409(14)	-78(10)	78(10)	-82(10)
N(1)	47(3)	102(5)	49(3)	-13(3)	17(3)	-7(3)
N(2)	45(3)	47(3)	34(3)	-4(2)	0(2)	-4(2)
N(3)	44(3)	44(3)	30(2)	0(2)	2(2)	-2(2)
C(1)	90(6)	137(9)	73(6)	-25(6)	33(5)	11(6)
C(2)	125(10)	209(15)	106(10)	-42(10)	69(9)	5(10)
C(3)	138(11)	238(17)	56(6)	-1(9)	51(7)	-22(12)
C(4)	95(7)	154(10)	54(5)	17(6)	28(5)	-22(7)
C(5)	80(5)	111(7)	43(4)	7(4)	20(4)	-13(5)
C(6)	30(3)	55(4)	37(3)	1(3)	0(2)	2(3)
C(7)	60(4)	50(4)	26(3)	0(3)	5(3)	-6(3)
C(8)	55(4)	62(4)	35(3)	7(3)	0(3)	-5(3)
C(9)	79(5)	74(5)	45(4)	9(3)	3(4)	-20(4)
C(10)	94(6)	83(6)	61(5)	24(4)	8(4)	-25(5)
C(11)	83(5)	97(6)	38(4)	21(4)	12(4)	-3(5)
C(12)	57(4)	85(5)	31(3)	10(3)	1(3)	5(4)
C(13)	53(4)	63(4)	42(4)	6(3)	7(3)	2(3)
C(14)	52(3)	57(4)	30(3)	-3(3)	-1(3)	7(3)
C(15)	69(5)	67(5)	50(4)	-10(3)	2(3)	3(4)
C(16)	87(5)	94(6)	31(4)	-16(4)	3(3)	12(5)
C(17)	70(5)	105(6)	39(4)	0(4)	4(3)	6(5)

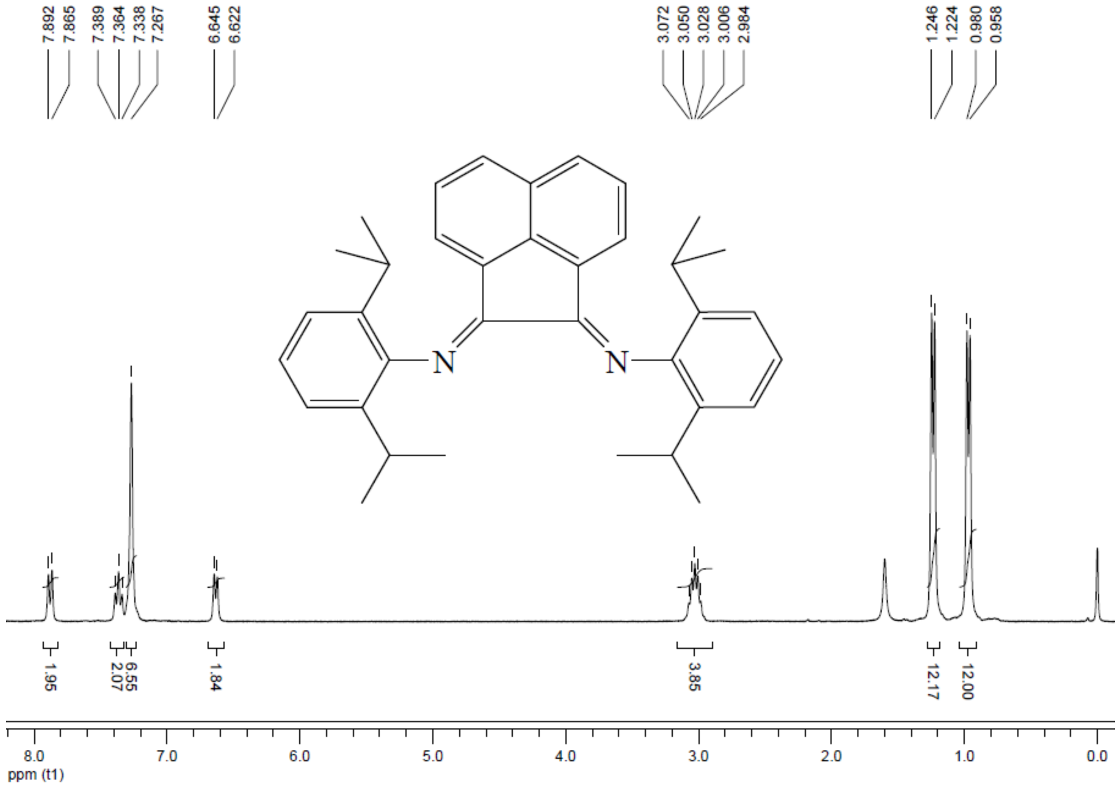
C(18)	48(3)	54(4)	31(3)	-3(3)	1(3)	-1(3)
C(19)	55(4)	51(3)	24(3)	-2(2)	-1(3)	-7(3)
C(20)	60(4)	59(4)	49(4)	-12(3)	12(3)	-12(3)
C(21)	72(5)	73(5)	87(6)	-37(4)	26(5)	-19(4)
C(22)	68(5)	104(7)	57(5)	-37(4)	11(4)	-29(5)
C(23)	58(4)	97(6)	51(4)	-1(4)	-5(3)	-22(4)
C(24)	51(4)	65(4)	33(3)	3(3)	-1(3)	-9(3)
C(25)	61(4)	75(5)	73(5)	8(4)	-6(4)	-4(4)
C(26)	98(7)	131(8)	63(5)	-14(5)	11(5)	41(6)
C(27)	72(6)	132(9)	147(10)	68(8)	5(6)	12(6)
C(28)	60(4)	63(5)	101(7)	-17(4)	3(4)	-2(4)
C(29)	122(9)	103(8)	146(11)	52(8)	-39(8)	-8(7)
C(30)	69(6)	162(12)	213(15)	-87(11)	30(8)	13(7)
C(31)	60(4)	53(4)	38(3)	-5(3)	2(3)	-9(3)
C(32)	65(5)	74(5)	64(5)	1(4)	-7(4)	-23(4)
C(33)	105(8)	100(8)	116(9)	-5(6)	-37(7)	-44(7)
C(34)	182(13)	62(7)	155(12)	6(7)	-37(10)	-40(8)
C(35)	135(9)	62(6)	99(7)	-1(5)	-28(7)	-8(6)
C(36)	86(5)	50(4)	49(4)	-6(3)	4(4)	0(4)
C(37)	87(5)	67(5)	57(5)	4(4)	4(4)	26(4)
C(38)	107(8)	180(11)	68(6)	13(7)	20(6)	59(8)
C(39)	138(9)	104(7)	77(6)	22(6)	-5(6)	41(7)
C(40)	56(4)	104(7)	80(6)	10(5)	-14(4)	-9(5)
C(41)	86(7)	176(11)	94(8)	49(8)	-11(6)	24(7)
C(42)	59(5)	171(11)	114(9)	0(8)	6(5)	-19(6)
C(43)	440(40)	165(18)	600(60)	160(30)	-390(40)	-140(20)
Cl(5)	487(17)	541(19)	283(11)	47(12)	34(11)	-208(16)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **2**.

	x	y	z	U(eq)
H(1A)	643	4942	2498	117
H(2A)	371	4727	3370	169
H(3A)	606	3337	3978	168
H(5A)	1304	2353	2781	92
H(9A)	2116	6878	53	80
H(10A)	2294	7317	-862	96
H(11A)	2152	6207	-1644	87
H(15A)	1310	2495	-951	75
H(16A)	1490	2885	-1873	85
H(17A)	1811	4406	-2057	86
H(21A)	1631	7964	1851	91
H(22A)	2320	7801	2262	92
H(23A)	2714	6390	2045	84
H(25A)	2341	4129	1231	86
H(26A)	2597	5197	530	147
H(26B)	2950	4392	800	147
H(26C)	2974	5582	1003	147
H(27A)	2676	4178	2209	177
H(27B)	3025	4944	2036	177
H(27C)	2994	3771	1803	177
H(28A)	1022	6109	920	91
H(29A)	1328	7195	273	195
H(29B)	1252	8204	642	195
H(29C)	864	7579	303	195
H(30A)	852	6727	1804	221

H(30B)	561	7276	1278	221
H(30C)	945	7898	1630	221
H(33A)	332	1211	-290	135
H(34A)	739	-209	10	168
H(35A)	1413	-14	489	124
H(37A)	1870	2380	1091	85
H(38A)	2103	2157	189	176
H(38B)	2155	933	306	176
H(38C)	2447	1741	699	176
H(39A)	1749	865	1658	163
H(39B)	2233	950	1602	163
H(39C)	1941	131	1217	163
H(40A)	578	3948	114	99
H(41A)	654	3618	-855	182
H(41B)	212	4148	-822	182
H(41C)	240	2923	-937	182
H(42A)	62	3062	548	173
H(42B)	-131	2574	-60	173
H(42C)	-154	3803	42	173
H(43A)	271	1797	2016	542
H(43B)	508	1987	1470	542

7. ^{1}H NMR, ^{13}C NMR and MS spectra for important compounds.



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Comment			

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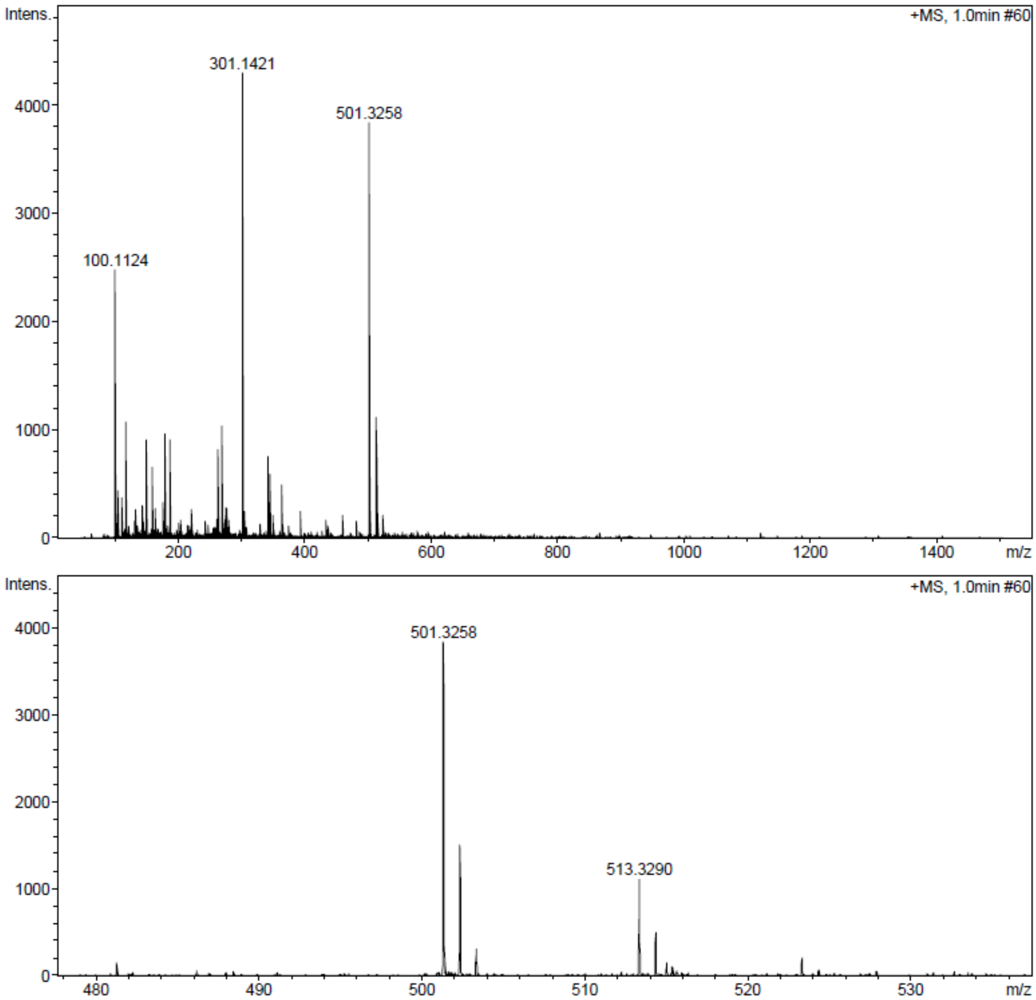

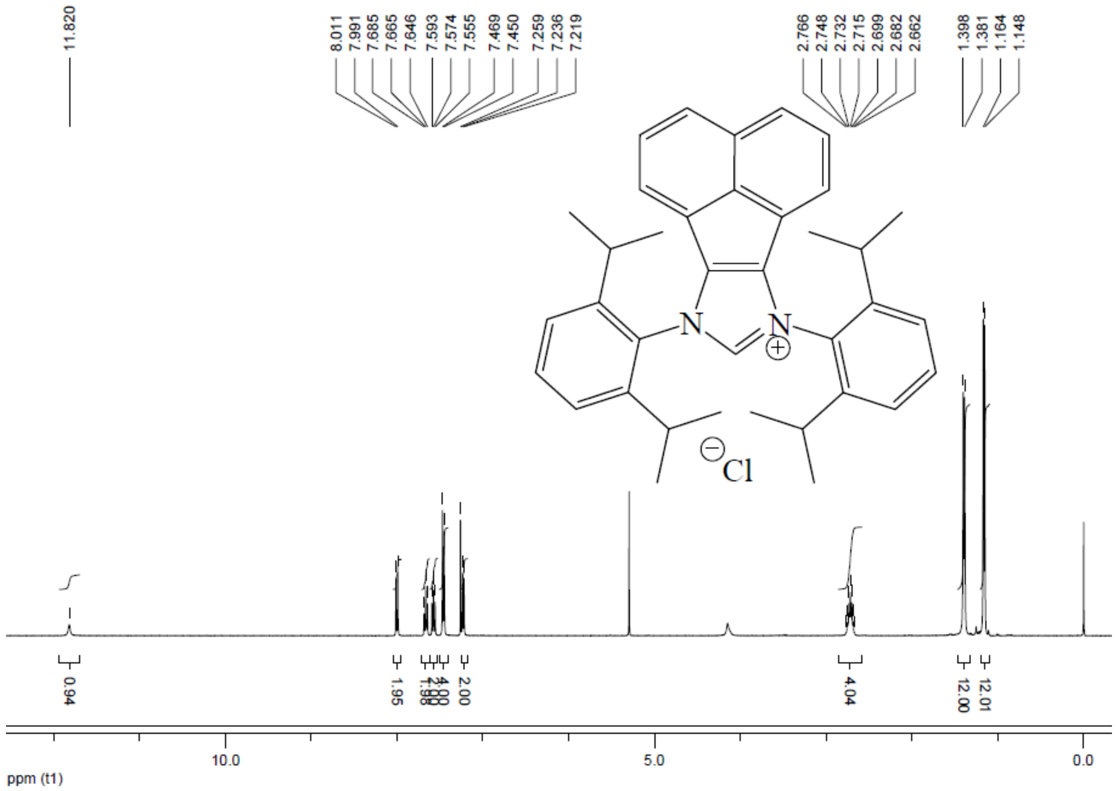
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7.219
2.766
2.748
2.732
2.715
2.699
2.682
2.662
1.398
1.381
1.164
1.148
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N
Cl
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Display Report

Analysis Info

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Focus	Not active			Set Dry Heater	200 °C
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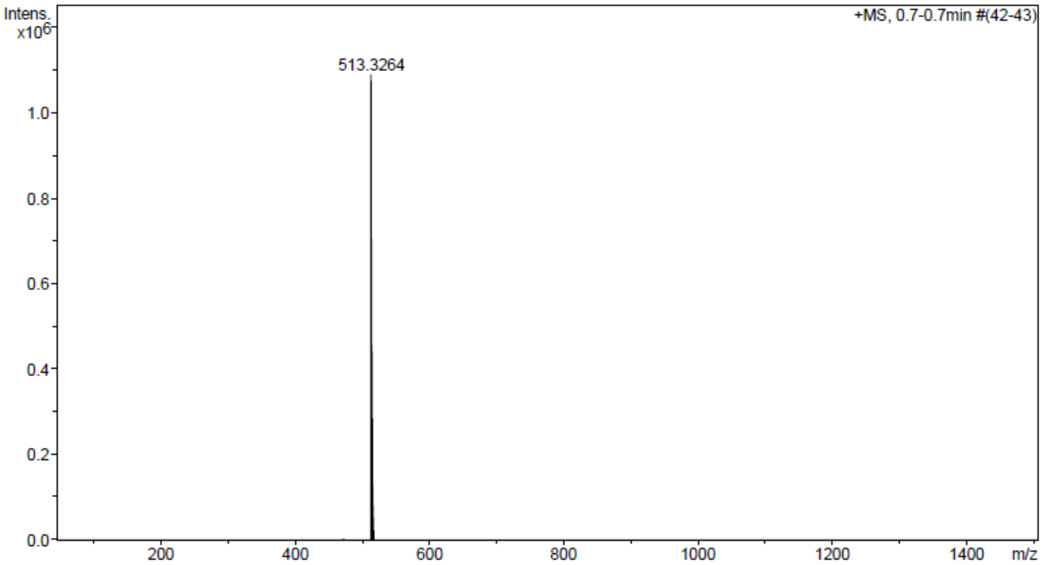
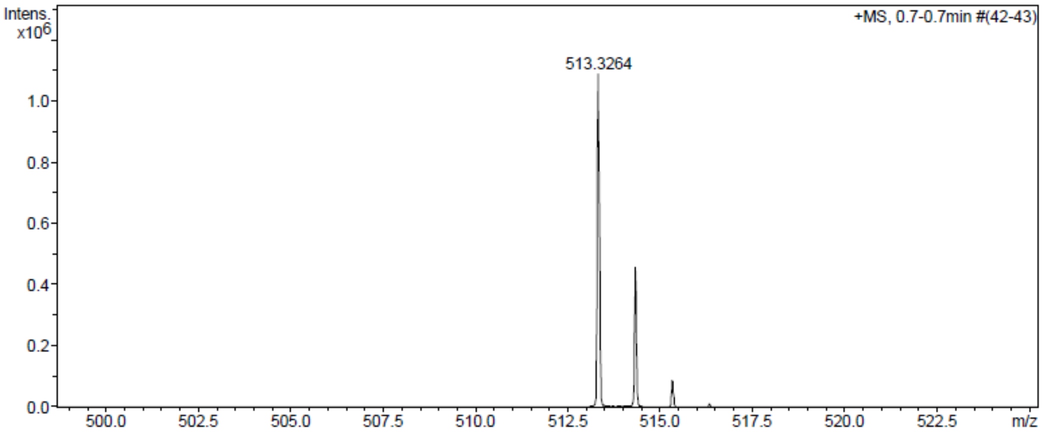
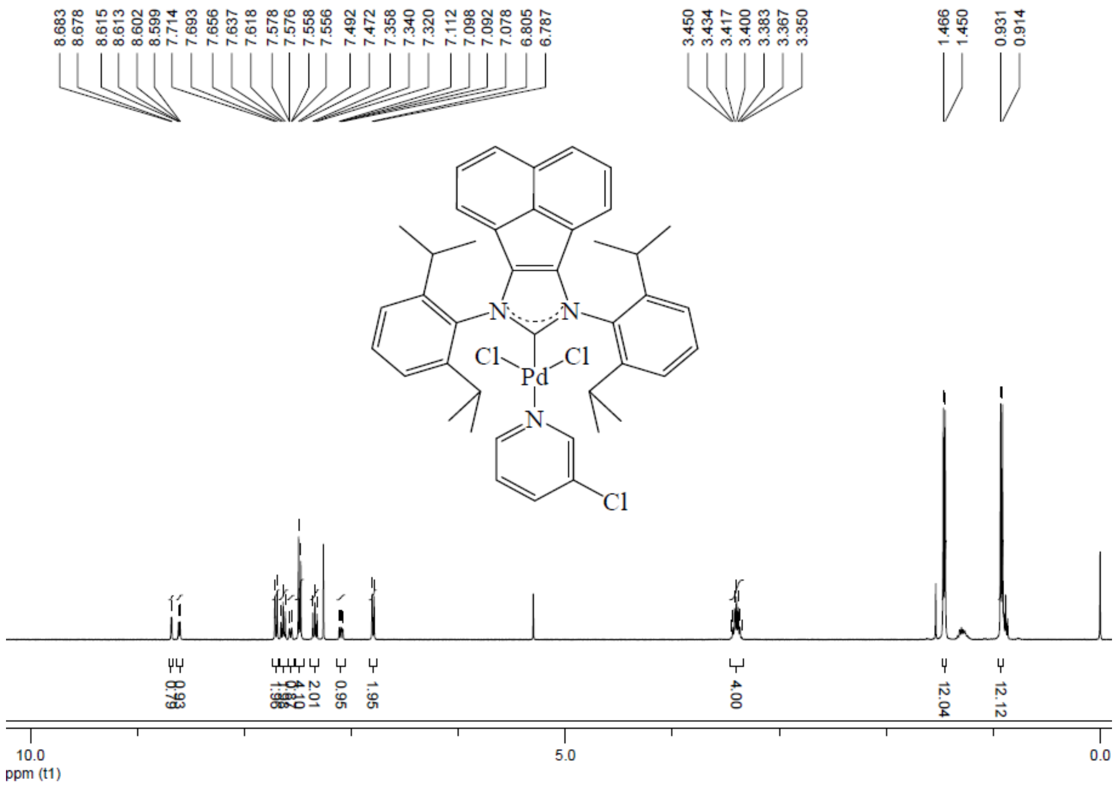
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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7.693
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7.637
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7.578
7.576
7.558
7.556
7.492
7.472
7.358
7.340
7.320
7.112
7.098
7.092
7.078
6.805
6.787
3.450
3.434
3.417
3.400
3.383
3.367
3.350
1.466
1.450
0.931
0.914
N
N
Cl
Cl
Pd
N
Cl
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12.04
12.12
2.01
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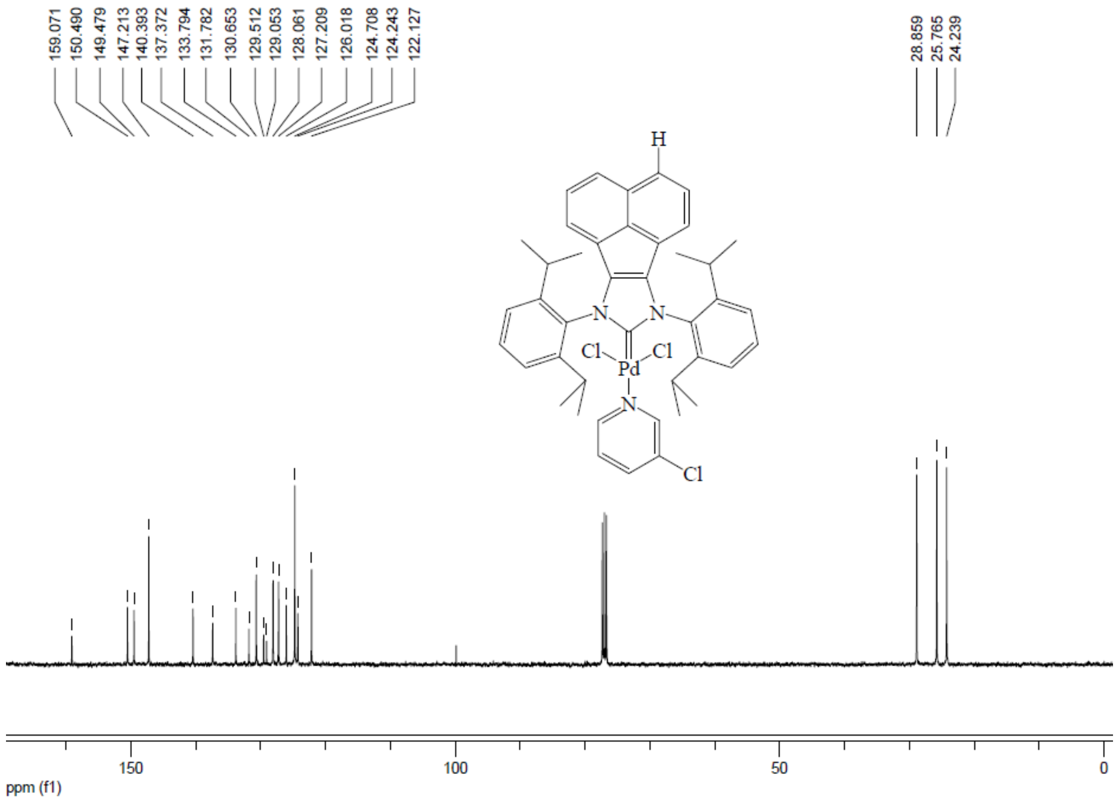
1.95
10.0
5.0
0.0
ppm (t1)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149.479
147.213
140.393
137.372
133.794
131.782
130.653
129.512
129.053
128.061
127.209
126.018
124.708
124.243
122.127
28.859
25.765
24.239
H
N
N
Cl
Cl
Pd
N
Cl
150
100
50
0
ppm (f1)

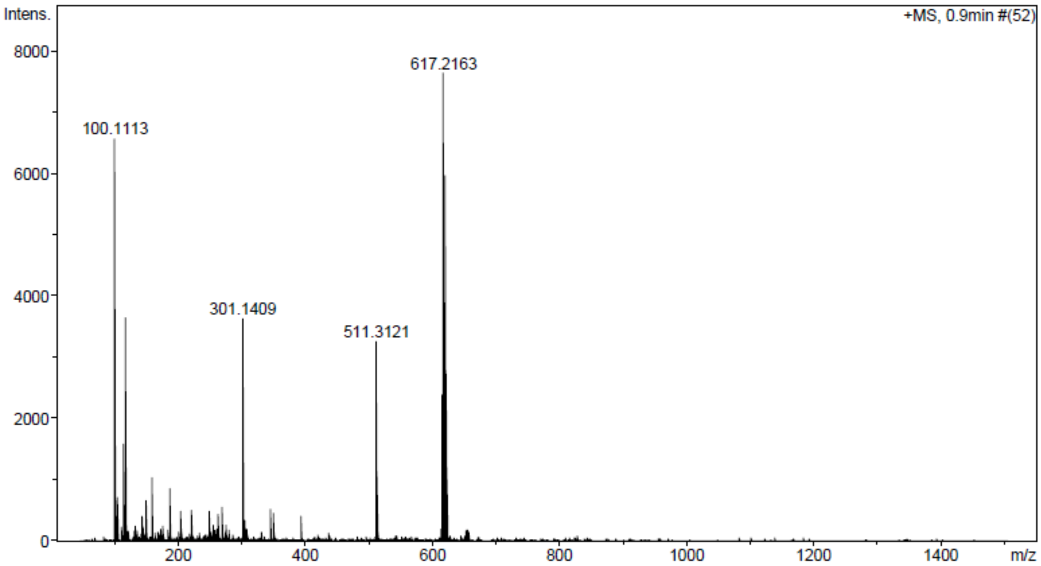
Display Report

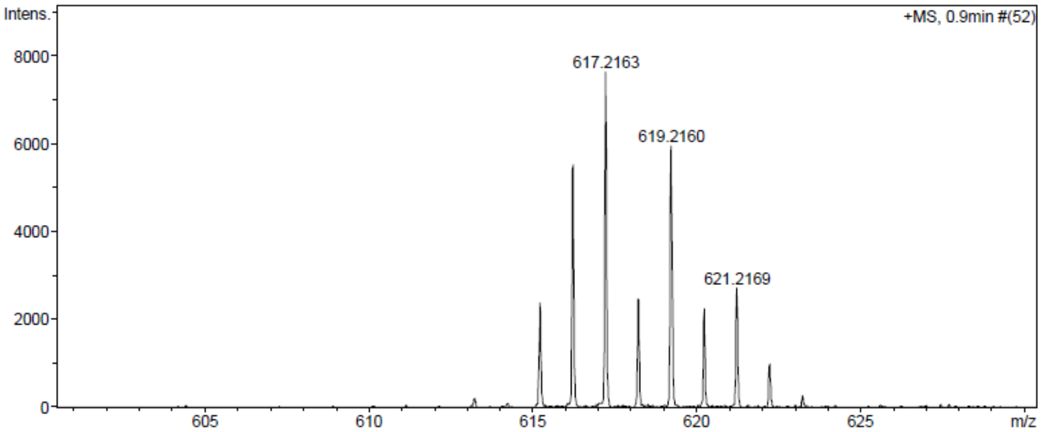
Analysis Info

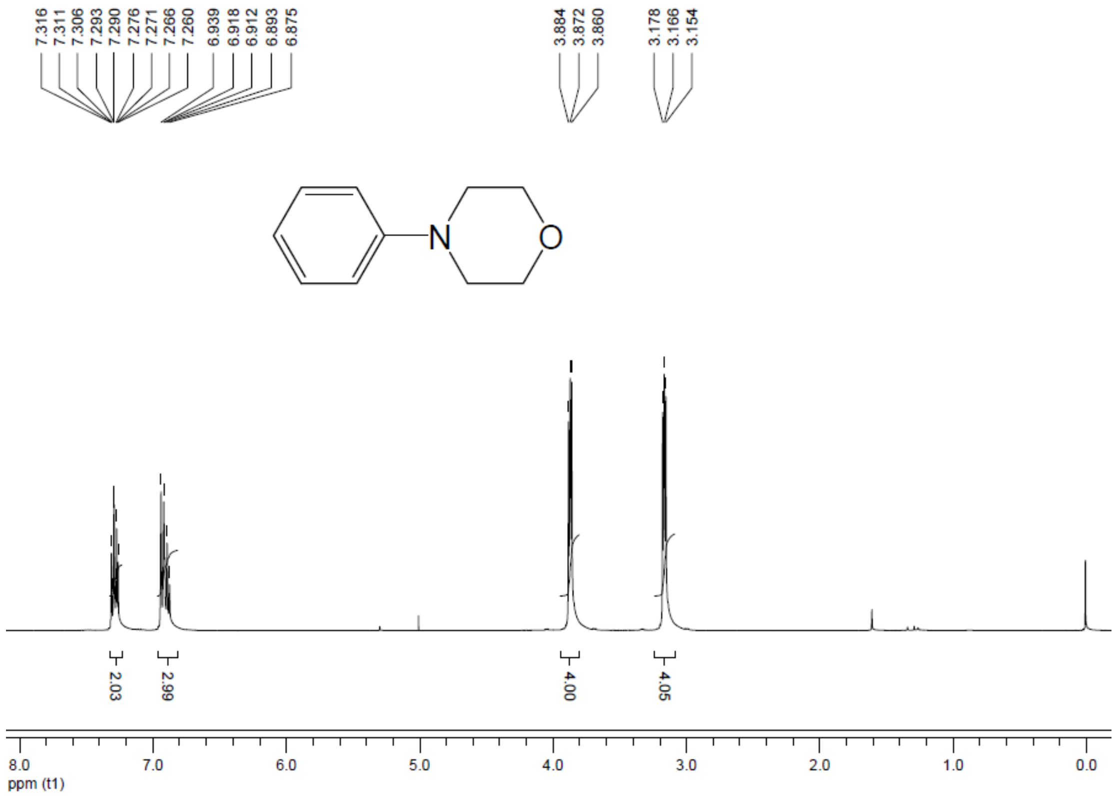
Analysis Name	D:\Data\MS\tt\0708\f110329_GA7_01_515.d	Acquisition Date	7/8/2011 10:09:43 AM
Method	tune_200-800_hcoona-pos_esi.m	Operator	gftang
Sample Name	f110329	Instrument / Ser#	micrOTOF II 10257
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
Focus	Not active			Set Dry Heater	200 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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7.266
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6.918
6.912
6.893
6.875
3.884
3.872
3.860
3.178
3.166
3.154
N
O
2.03
2.99
4.00
4.05
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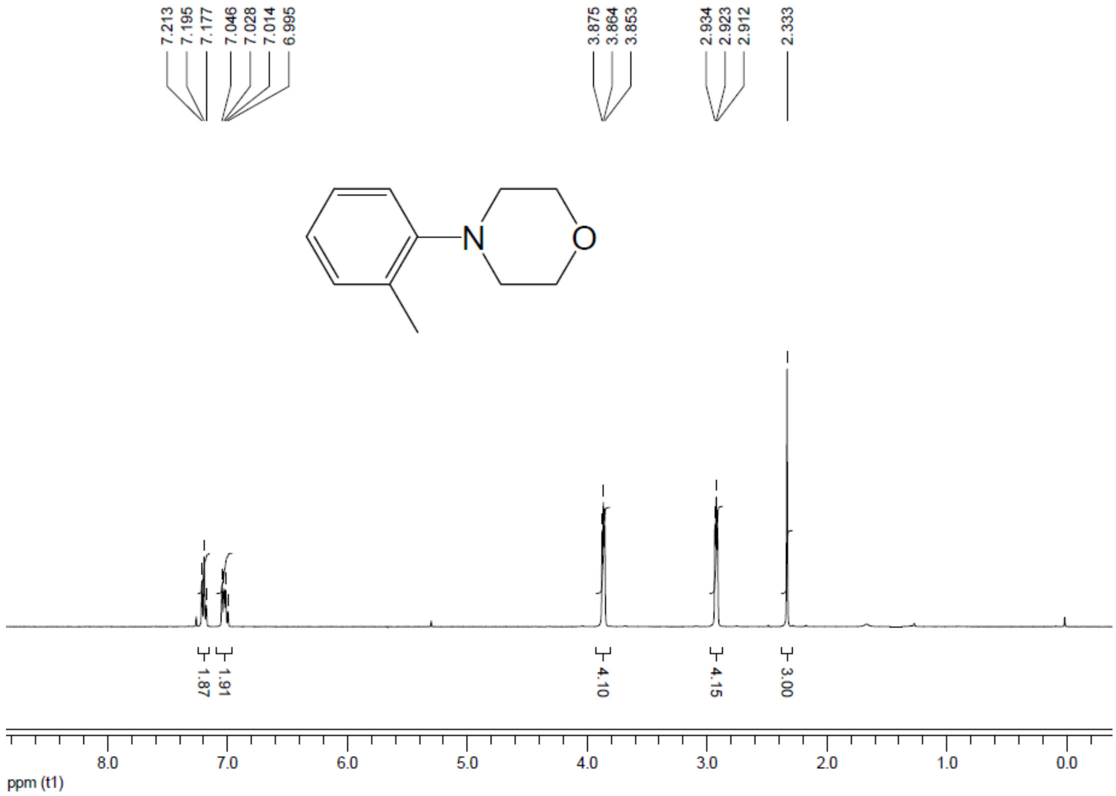
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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7.195
7.177
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7.028
7.014
6.995
3.875
3.864
3.853
2.934
2.923
2.912
2.333
N
O
1.87
1.91
4.10
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3.00
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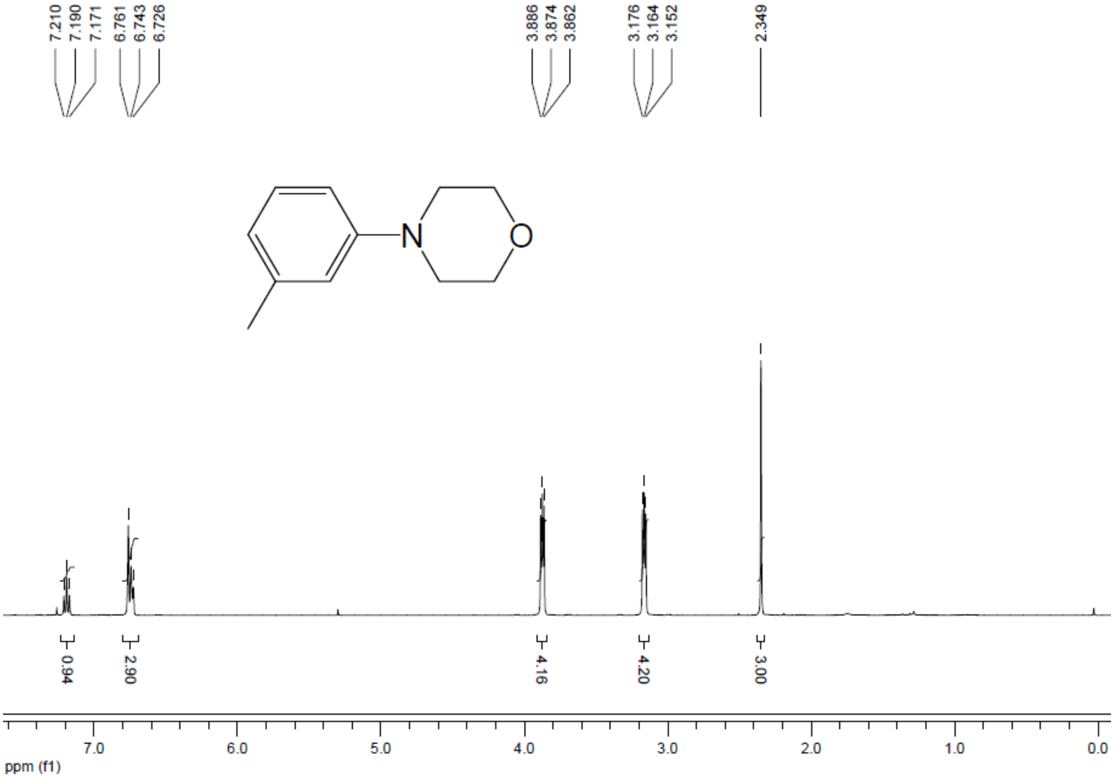
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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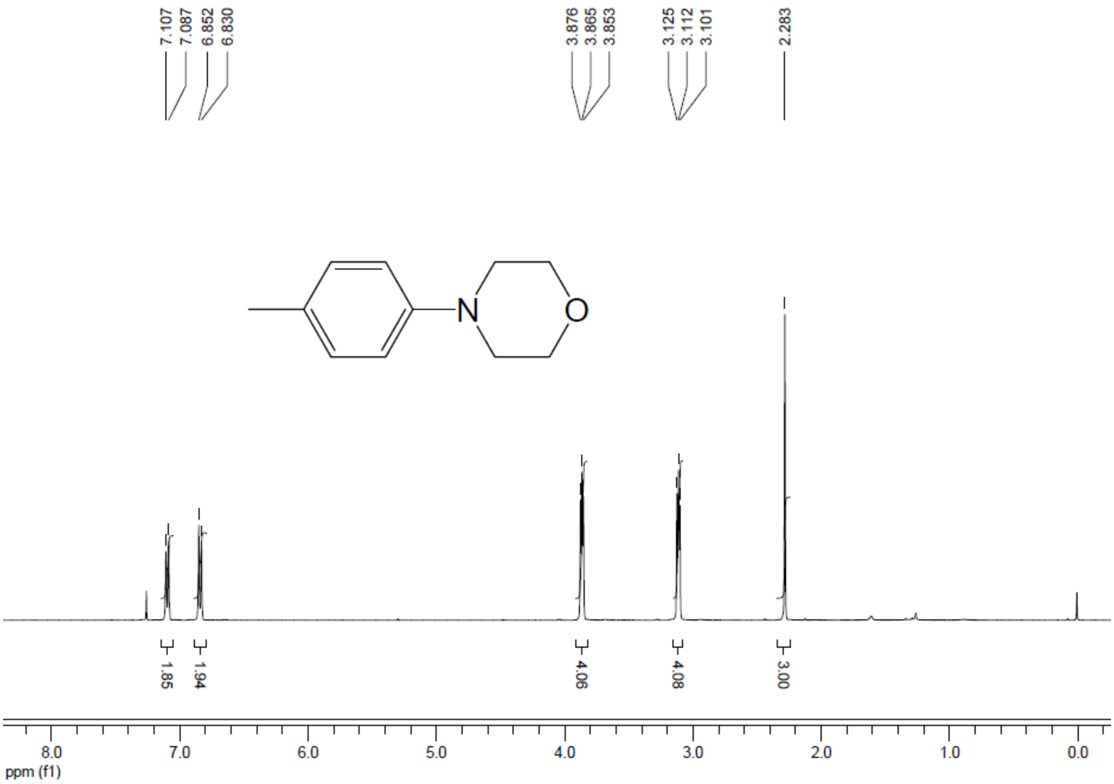
7.190
7.171
6.761
6.743
6.726
3.886
3.874
3.862
3.176
3.164
3.152
2.349
N
O
0.94
2.90
4.16
4.20
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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7.087
6.852
6.830
3.876
3.865
3.853
3.125
3.112
3.101
2.283
N
O
1.85
1.94
4.06
4.08
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7.0
6.0
5.0
4.0
3.0
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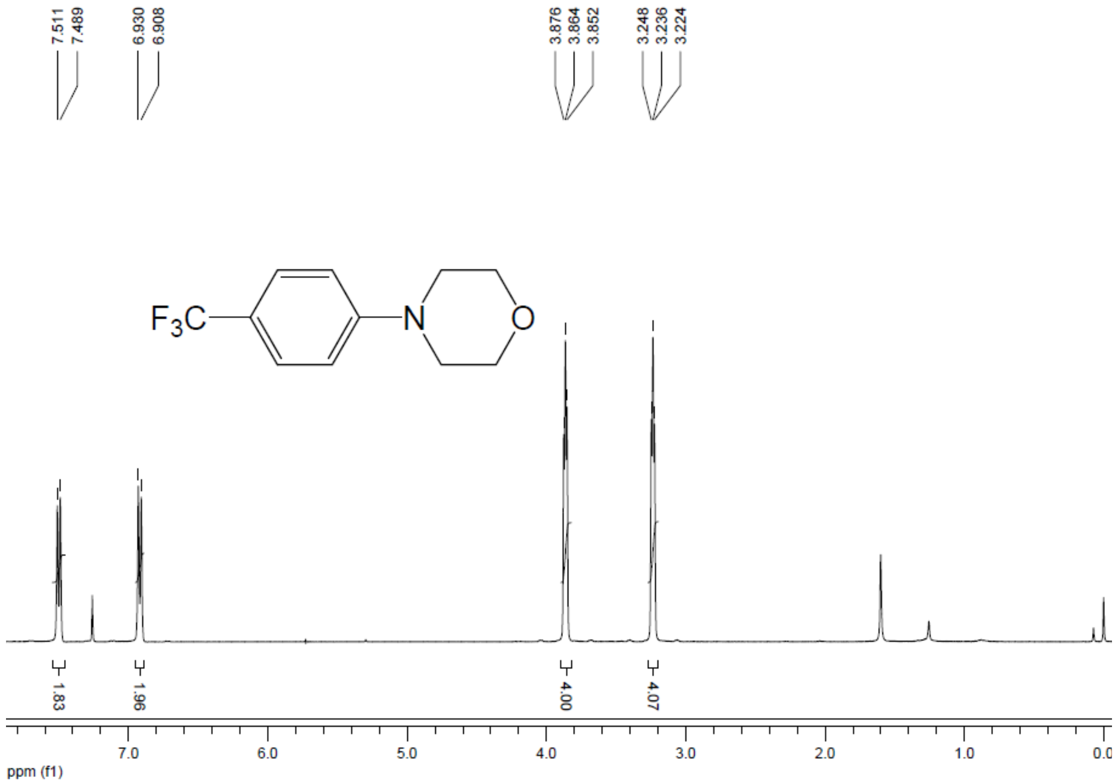
1.0
0.0
ppm (f1)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7.489
6.930
6.908
3.876
3.864
3.852
3.248
3.236
3.224
F3C
N
O
1.83
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6.0
5.0
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2.0
1.0
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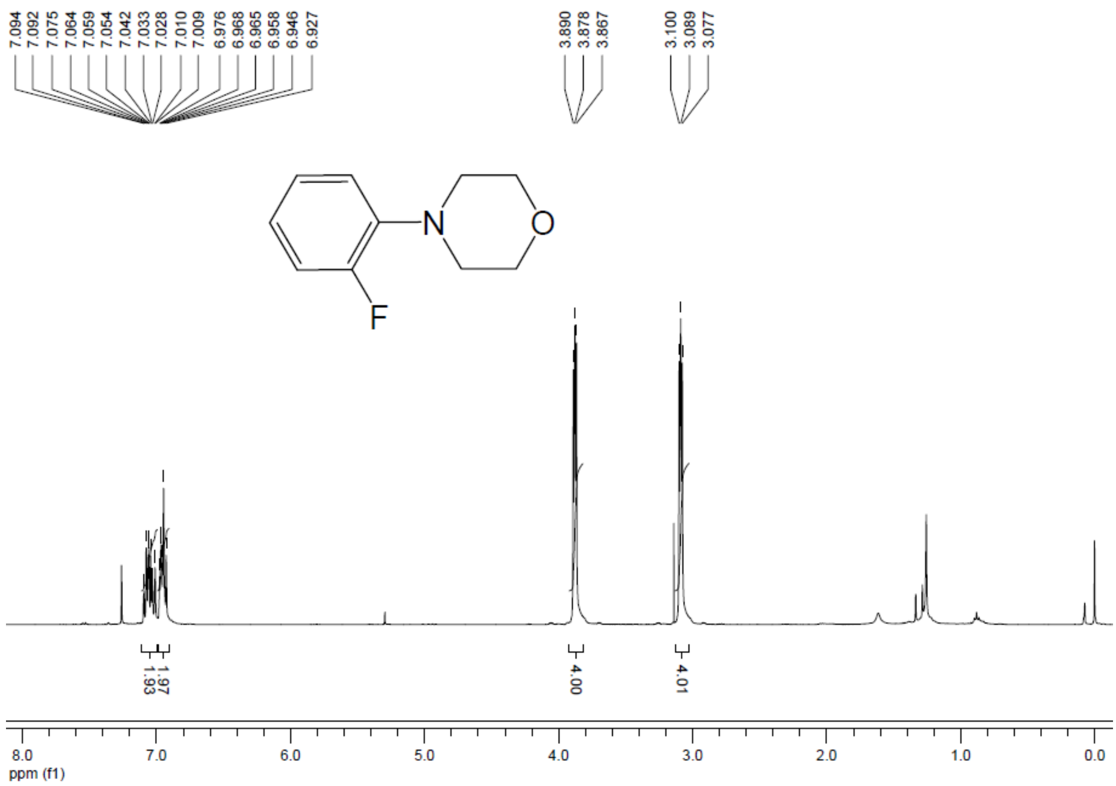
ppm (f1)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7.054
7.042
7.033
7.028
7.010
7.009
6.976
6.968
6.965
6.958
6.946
6.927
3.890
3.878
3.867
3.100
3.089
3.077
N
O
F
1.93
1.97
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4.01
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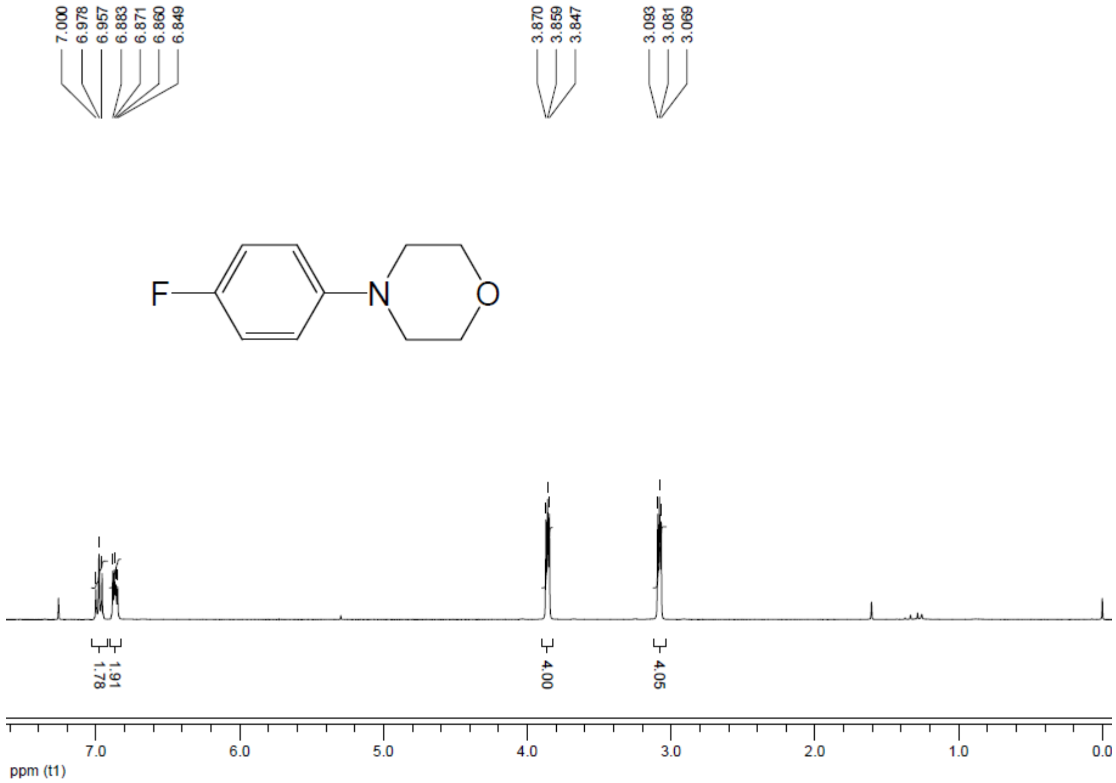
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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6.883
6.871
6.860
6.849
3.870
3.859
3.847
3.093
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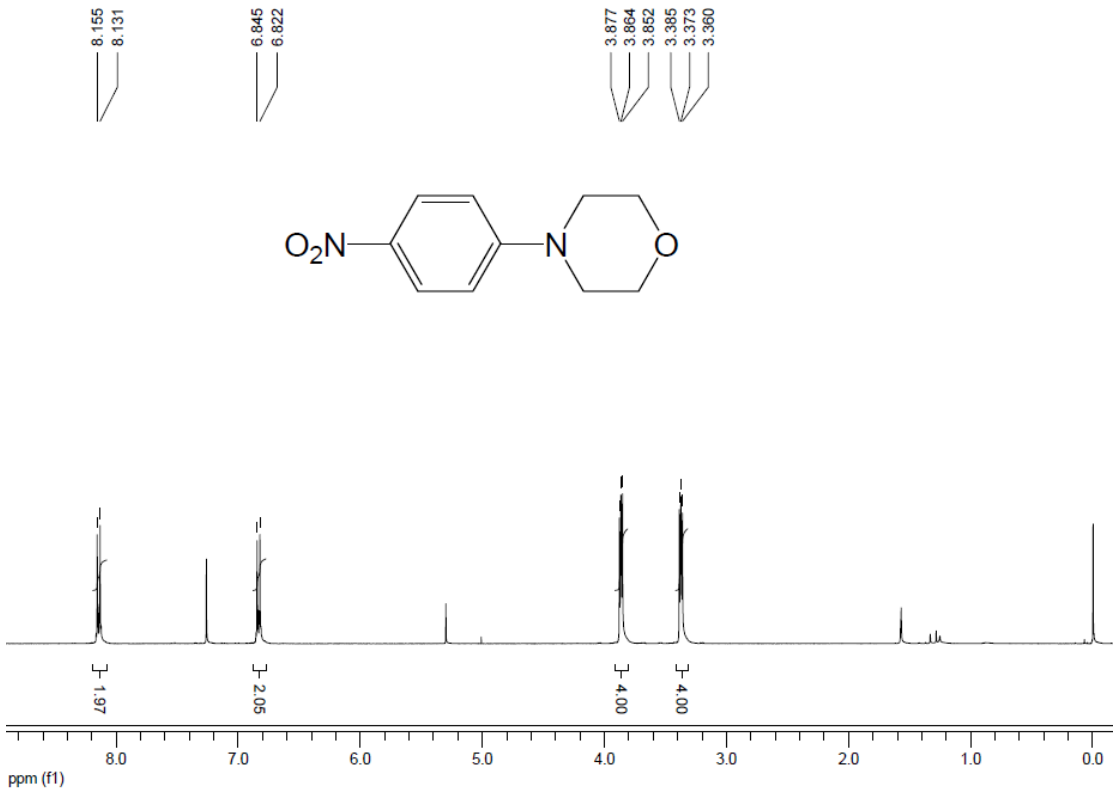
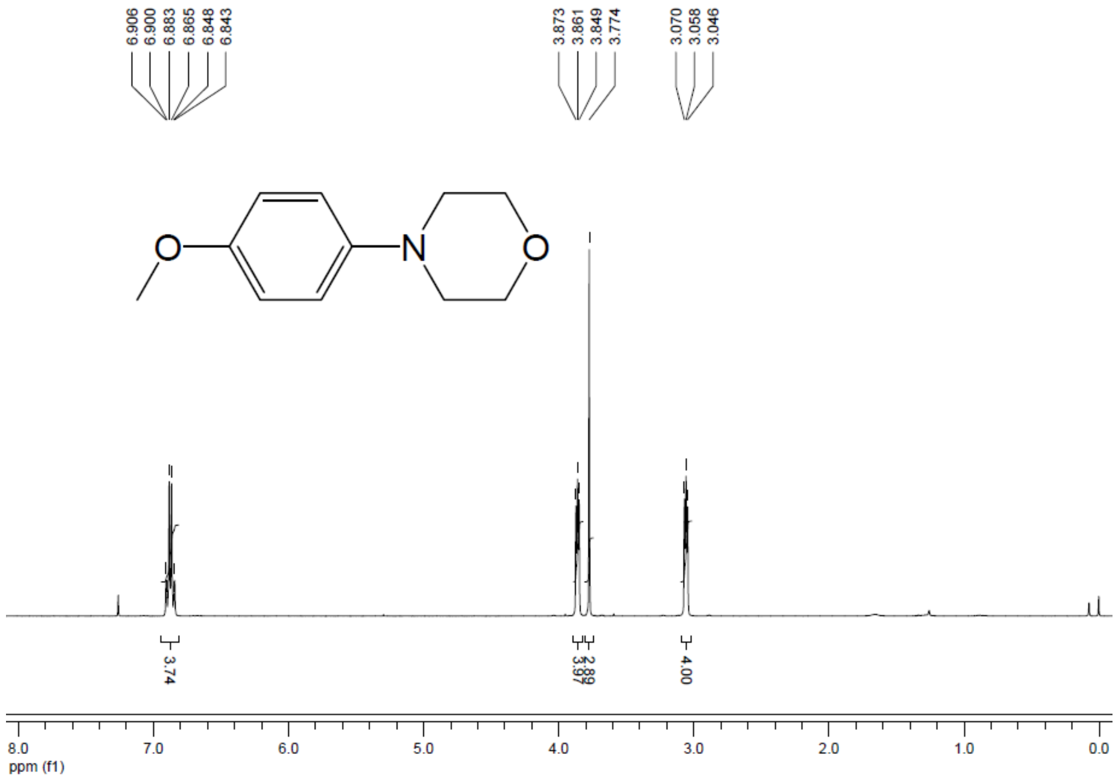
3.069
F
N
O
1.78
1.91
4.00
4.05
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


8.155
8.131
6.845
6.822
3.877
3.864
3.852
3.385
3.373
3.360
O2N
N
O
1.97
2.05
4.00
4.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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6.900
6.883
6.865
6.848
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3.873
3.861
3.849
3.774
3.070
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3.046
O
N
O
3.74
3.97
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7.0
6.0
5.0
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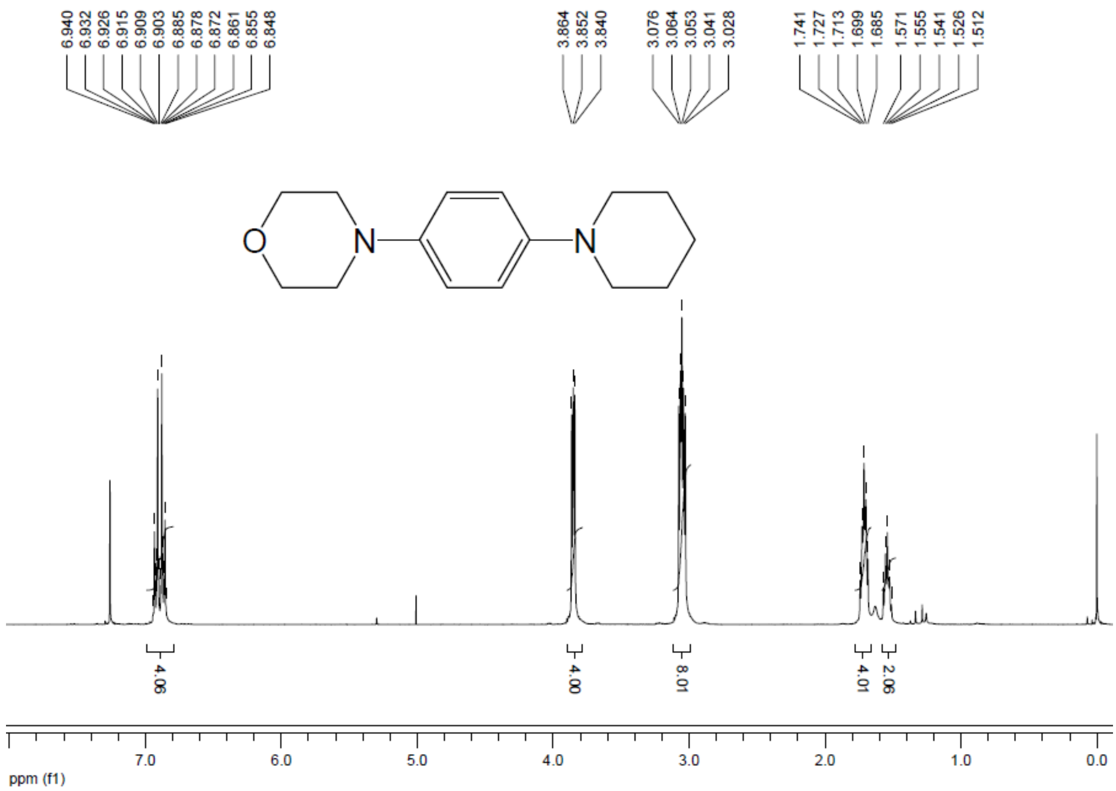
3.0
2.0
1.0
0.0
ppm (f1)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6.926
6.915
6.909
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6.878
6.872
6.861
6.855
6.848
3.864
3.852
3.840
3.076
3.064
3.053
3.041
3.028
1.741
1.727
1.713
1.699
1.685
1.571
1.555
1.541
1.526
1.512
O
N
N
4.06
4.00
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4.01
2.06
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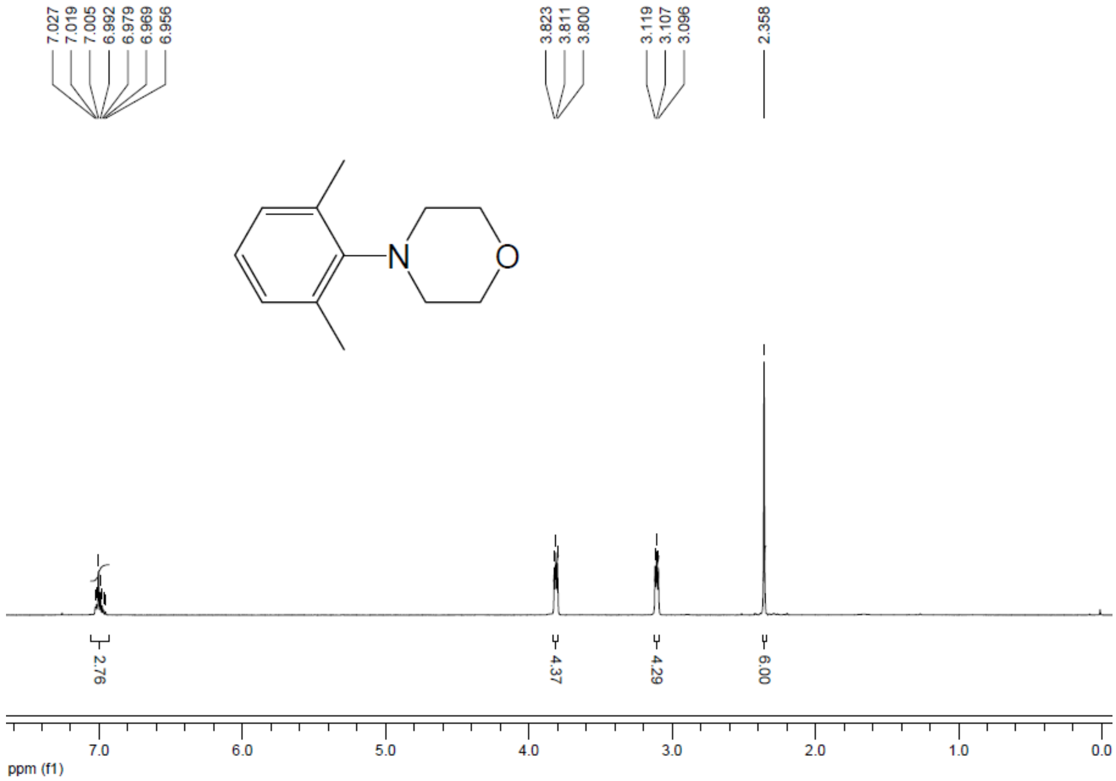
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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7.019
7.005
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6.969
6.956
3.823
3.811
3.800
3.119
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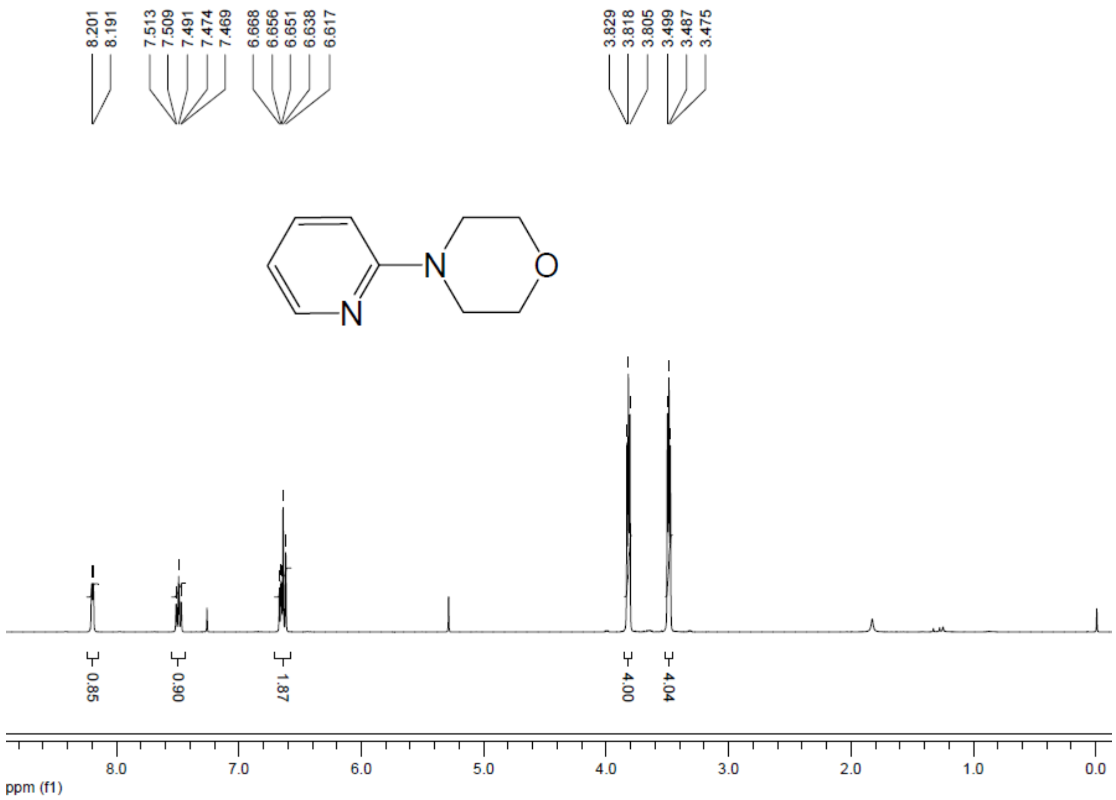
3.096
2.358
N
O
2.76
4.37
4.29
6.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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7.474
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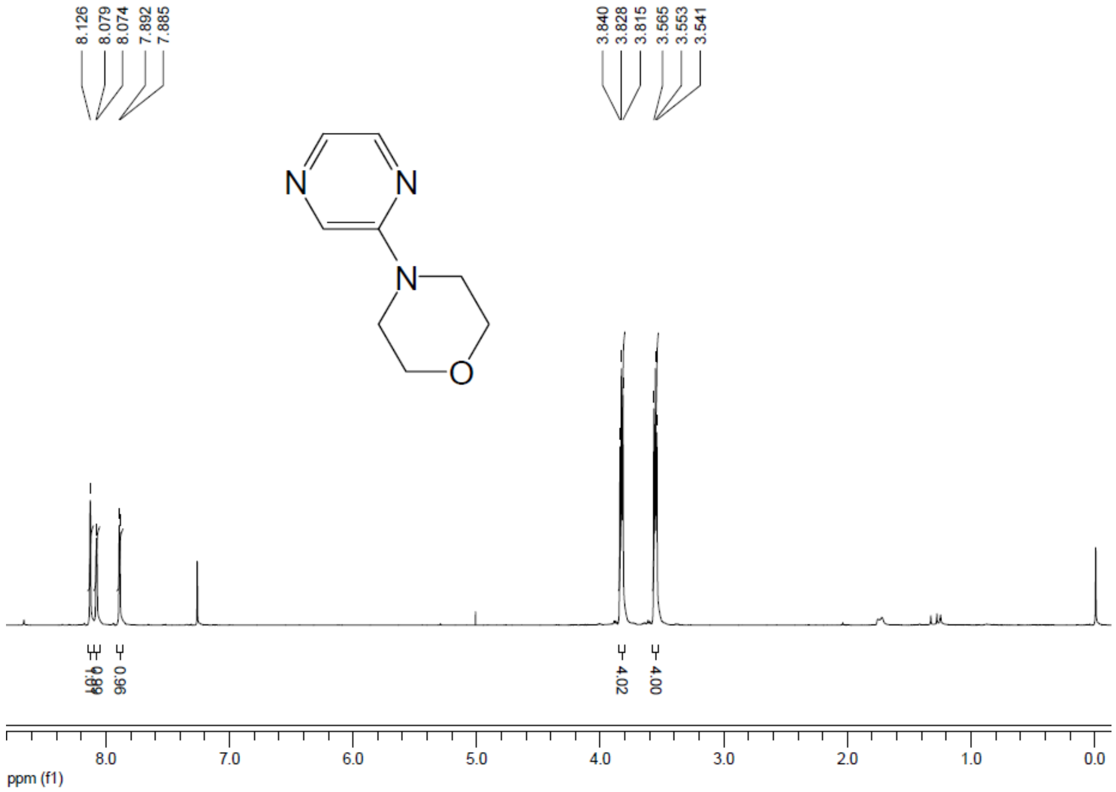
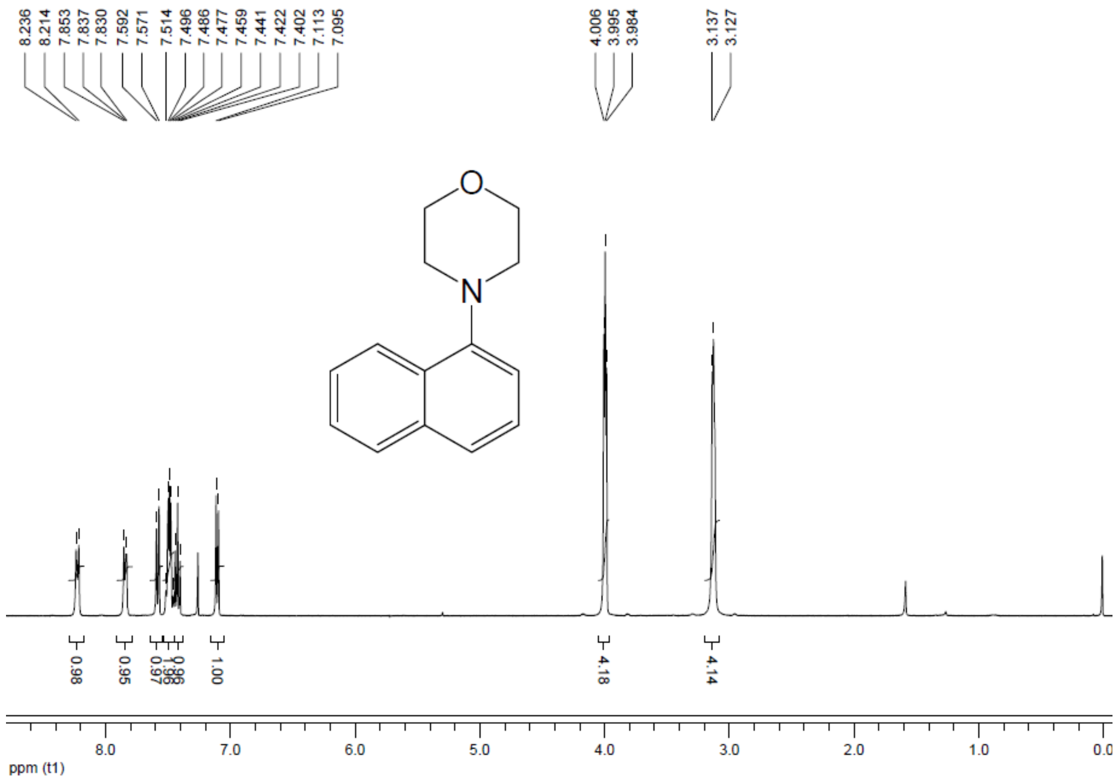
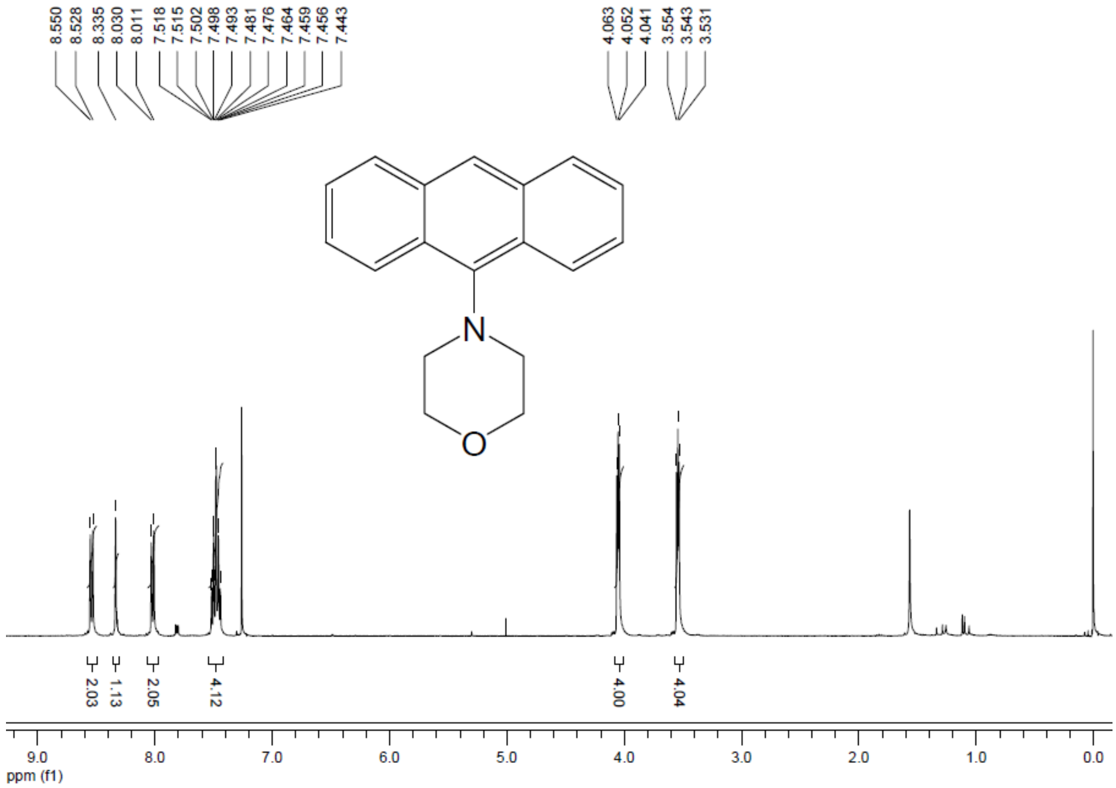
6.668
6.656
6.651
6.638
6.617
3.829
3.818
3.805
3.499
3.487
3.475
N
O
N
0.85
0.90
1.87
4.00
4.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)



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7.476
7.464
7.459
7.456
7.443
4.063
4.052
4.041
3.554
3.543
3.531
N
O
2.03
1.13
2.05
4.12
4.00
4.04
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6.0
5.0
4.0
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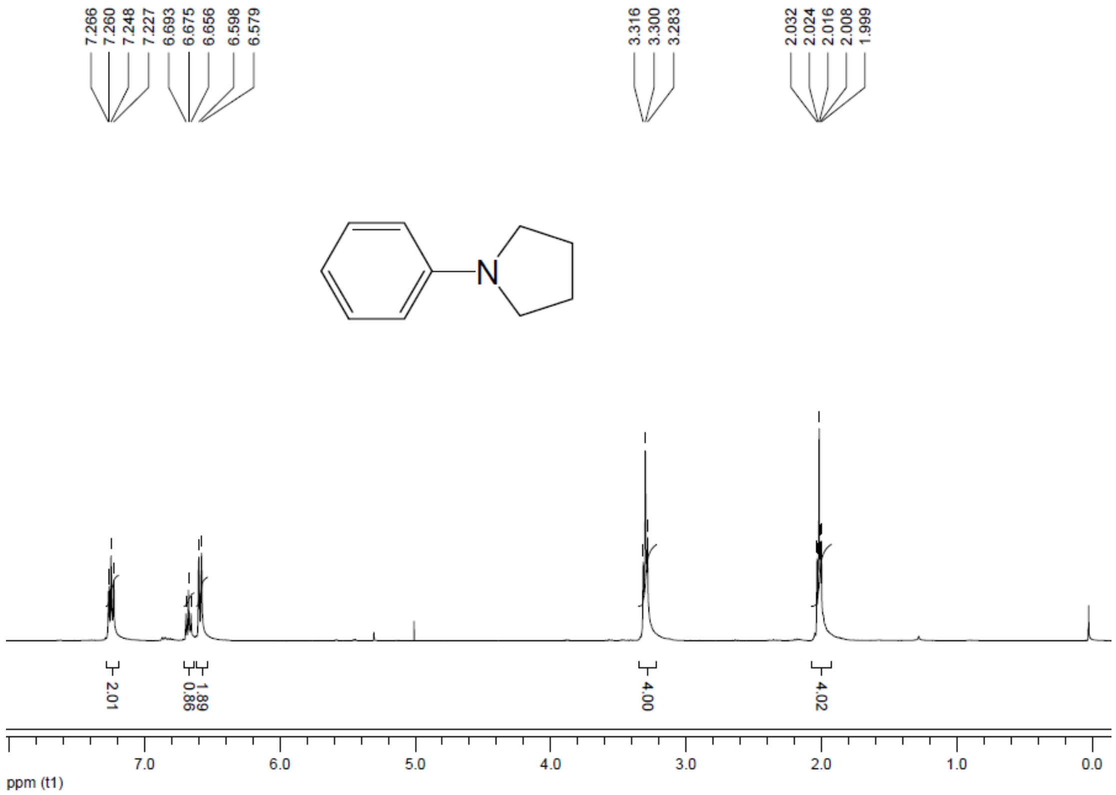
2.0
1.0
0.0
ppm (f1)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6.598
6.579
3.316
3.300
3.283
2.032
2.024
2.016
2.008
1.999
N
2.01
0.86
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4.00
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6.0
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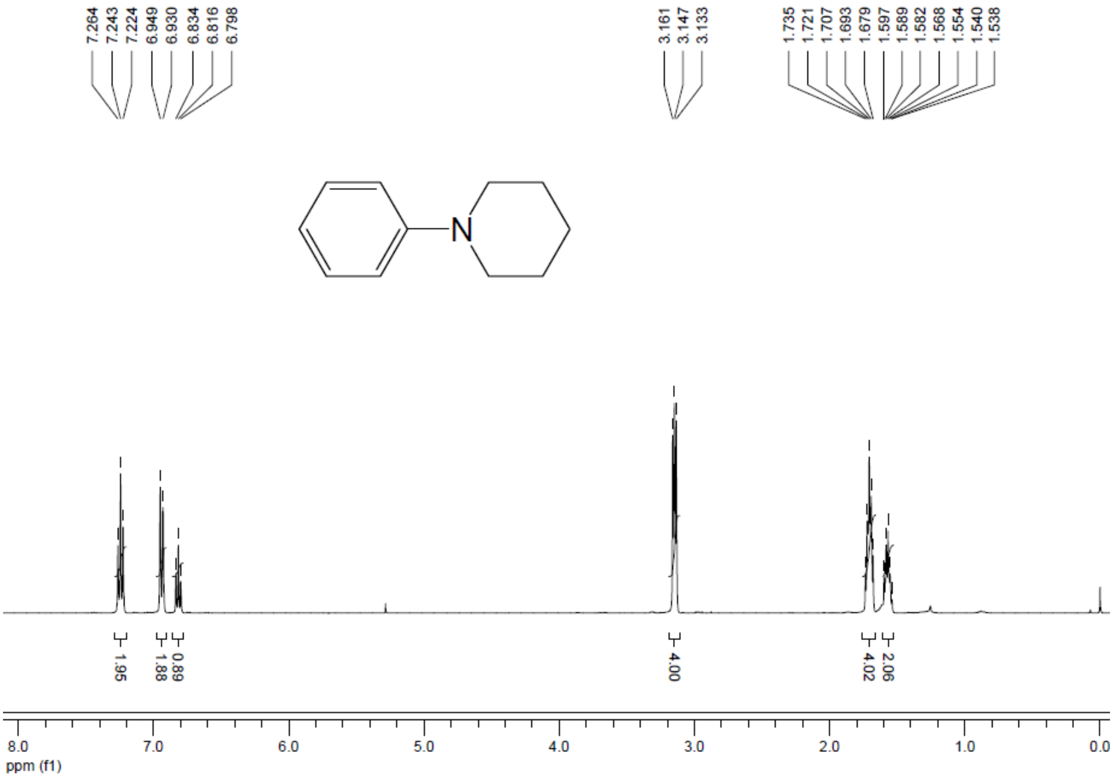
2.0
1.0
0.0
ppm (t1)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3.161 3.147 3.133
1.735 1.721 1.707 1.693 1.679 1.597 1.589 1.582 1.568 1.554 1.540 1.538
N
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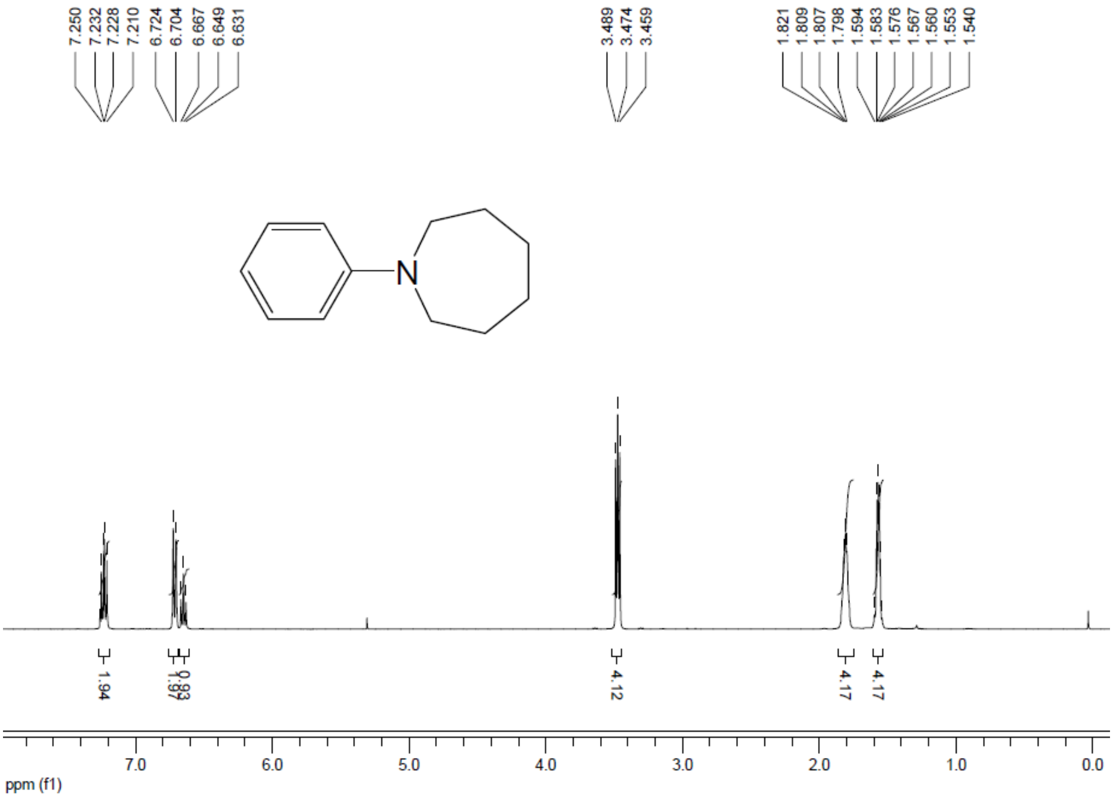
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (f1)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3.489 3.474 3.459
1.821 1.809 1.807 1.798 1.594 1.583 1.576 1.567 1.560 1.553 1.540
N
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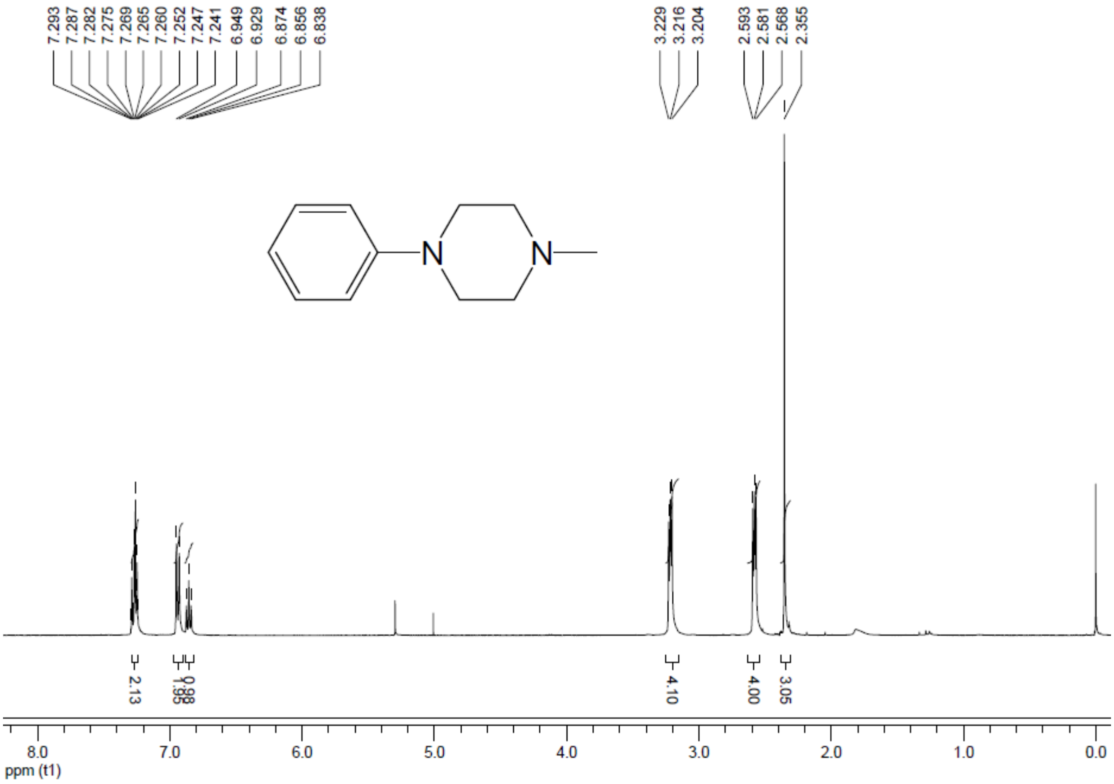
7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (f1)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7.252
7.247
7.241
6.949
6.929
6.874
6.856
6.838
3.229
3.216
3.204
2.593
2.581
2.568
2.355
N
N
2.13
1.95
0.98
4.10
4.00
3.05
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7.0
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5.0
4.0
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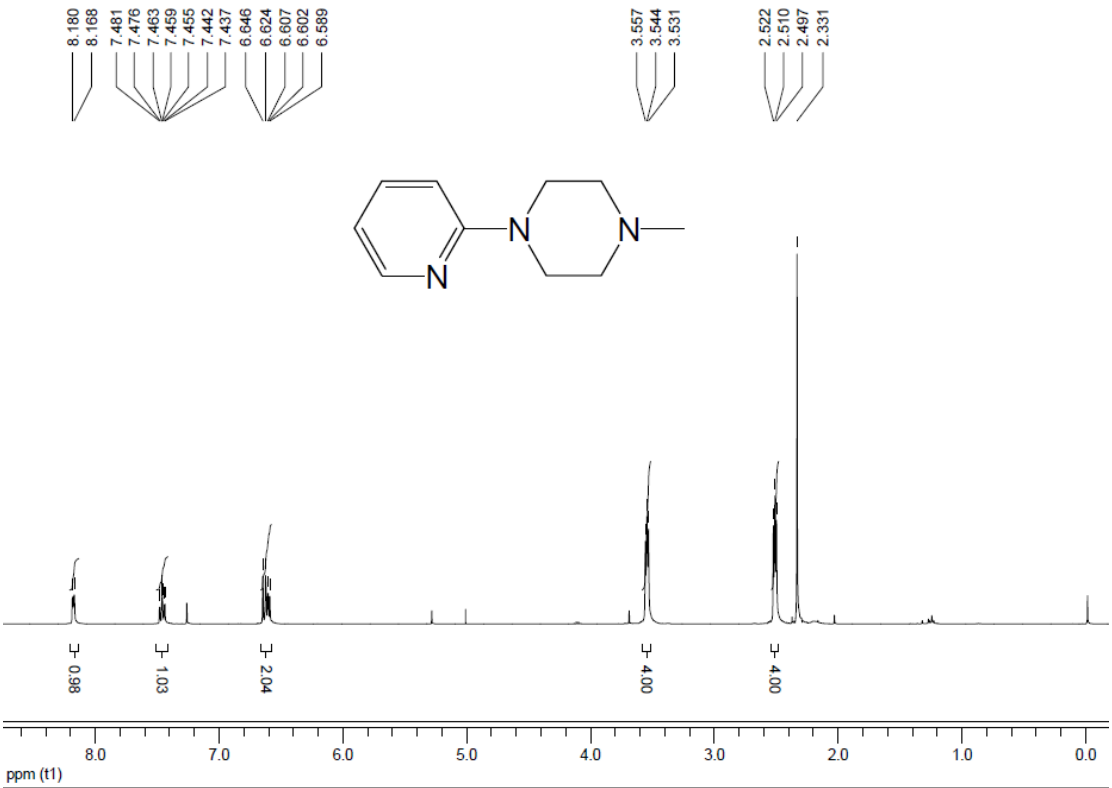
2.0
1.0
0.0
ppm (t1)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6.646
6.624
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6.602
6.589
3.557
3.544
3.531
2.522
2.510
2.497
2.331
N
N
N
0.98
1.03
2.04
4.00
4.00
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7.0
6.0
5.0
4.0
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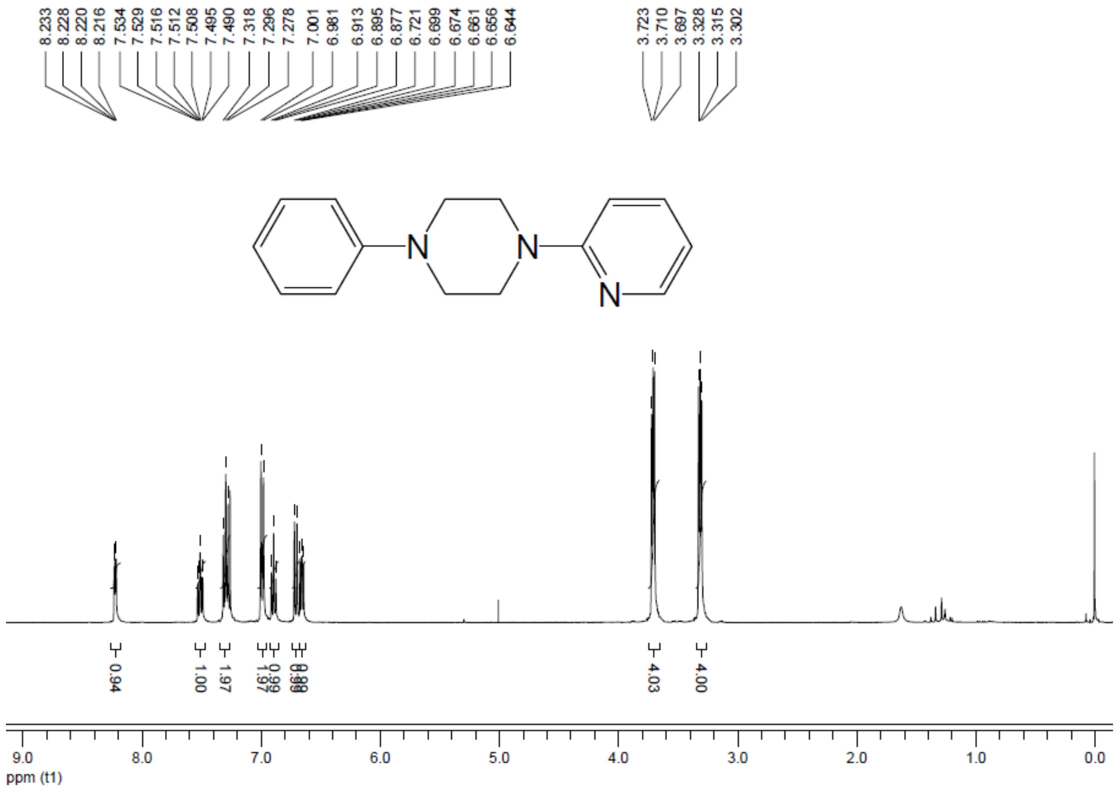
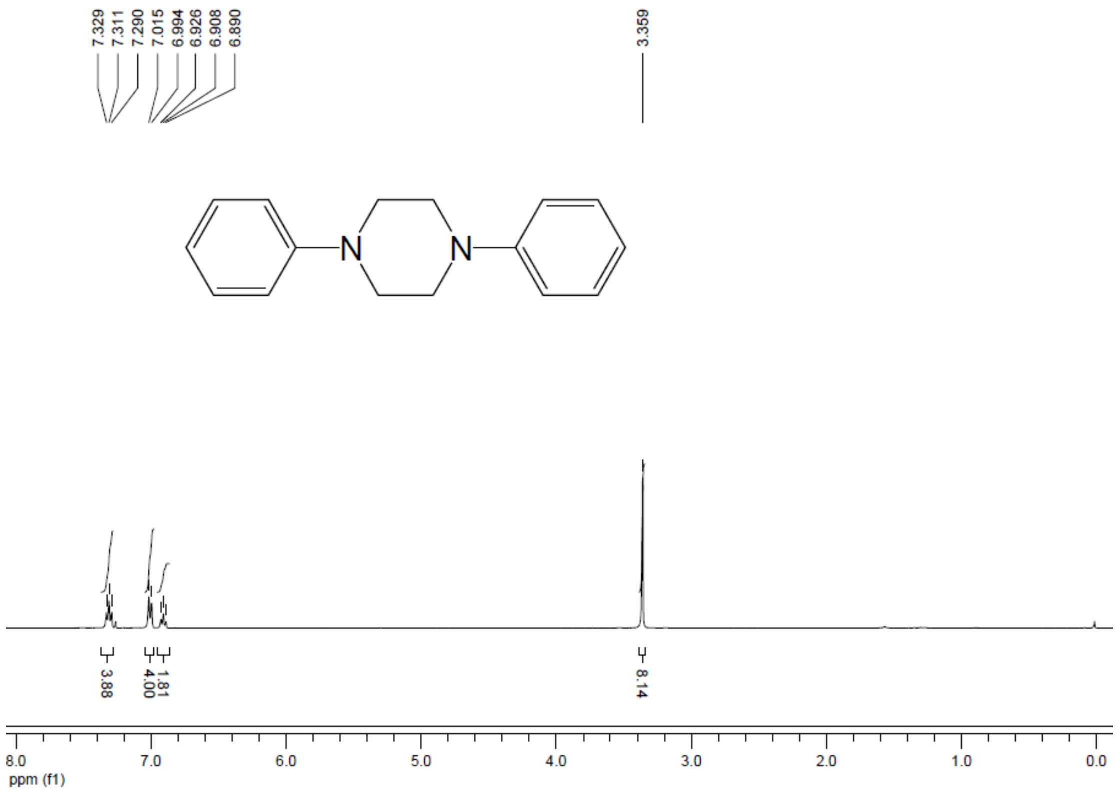
2.0
1.0
0.0
ppm (t1)


8.233 8.228 8.220 8.216 7.534 7.529 7.516 7.512 7.508 7.495 7.490 7.318 7.296 7.278 7.001 6.981 6.913 6.895 6.877 6.721 6.699 6.674 6.661 6.656 6.644
3.723 3.710 3.697 3.328 3.315 3.302
N
N
N
0.94 1.00 1.97 1.97 0.99 4.03 4.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)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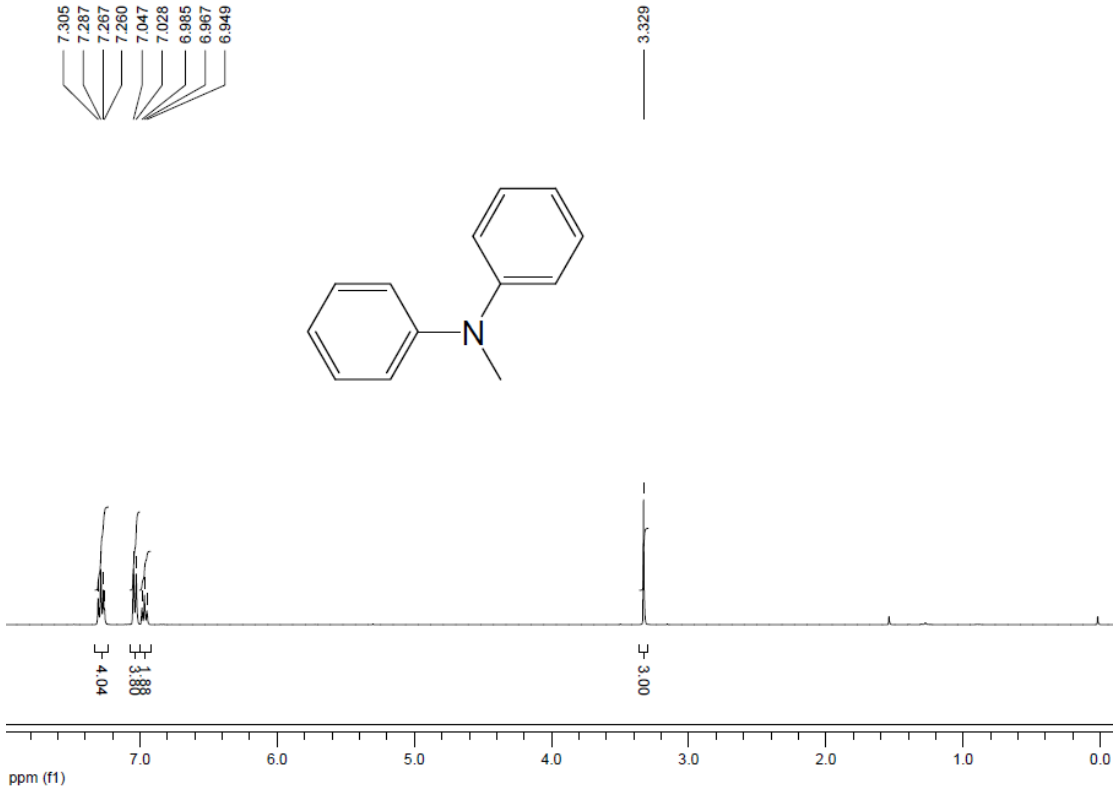
ppm (f1)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6.967
6.949
3.329
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6.0
5.0
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2.0
1.0
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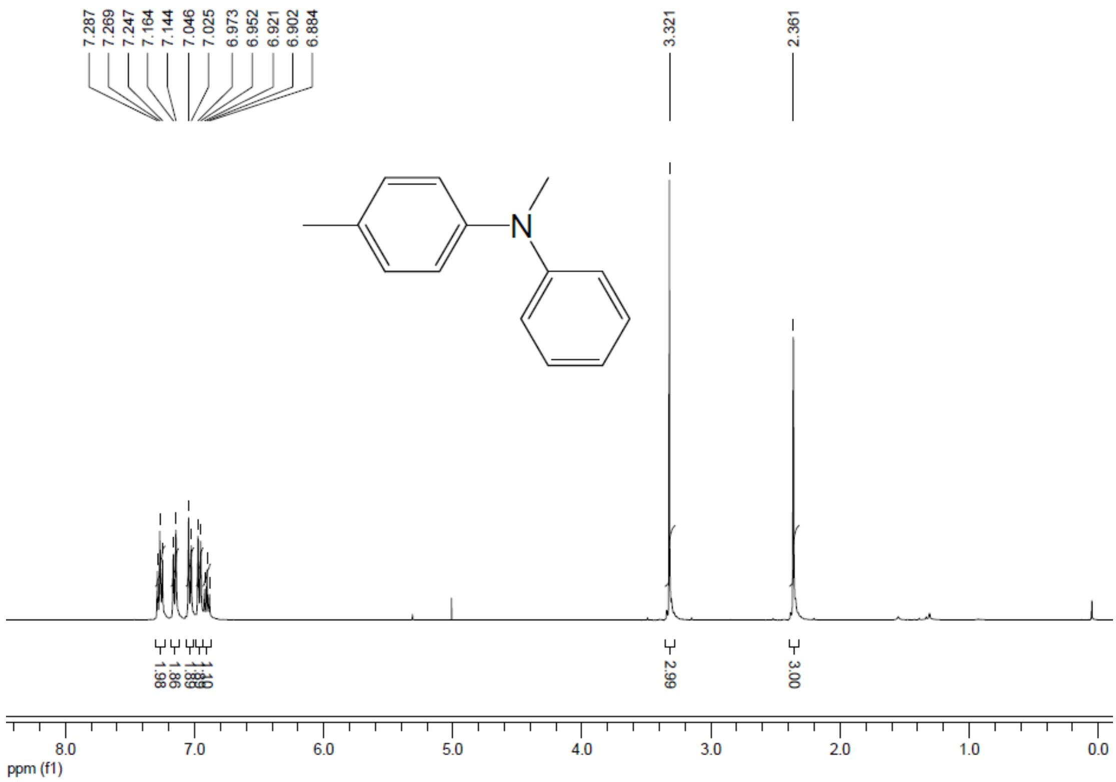
ppm (f1)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6.921
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1.98
1.86
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2.0
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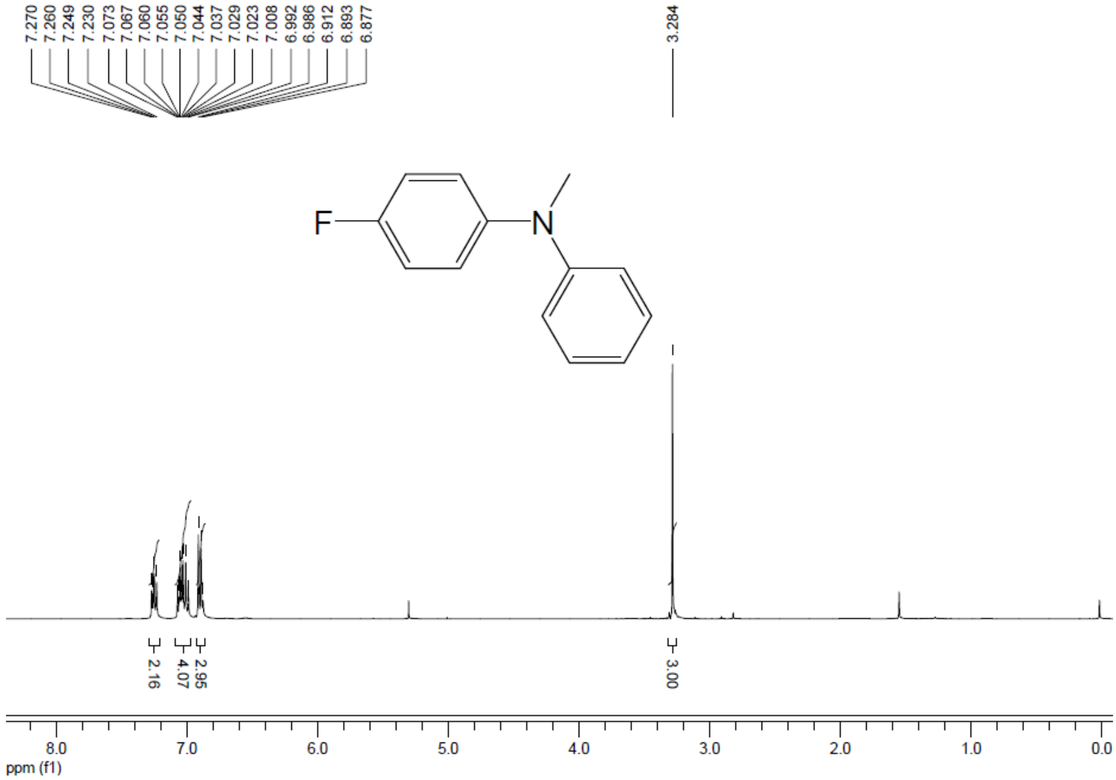
ppm (f1)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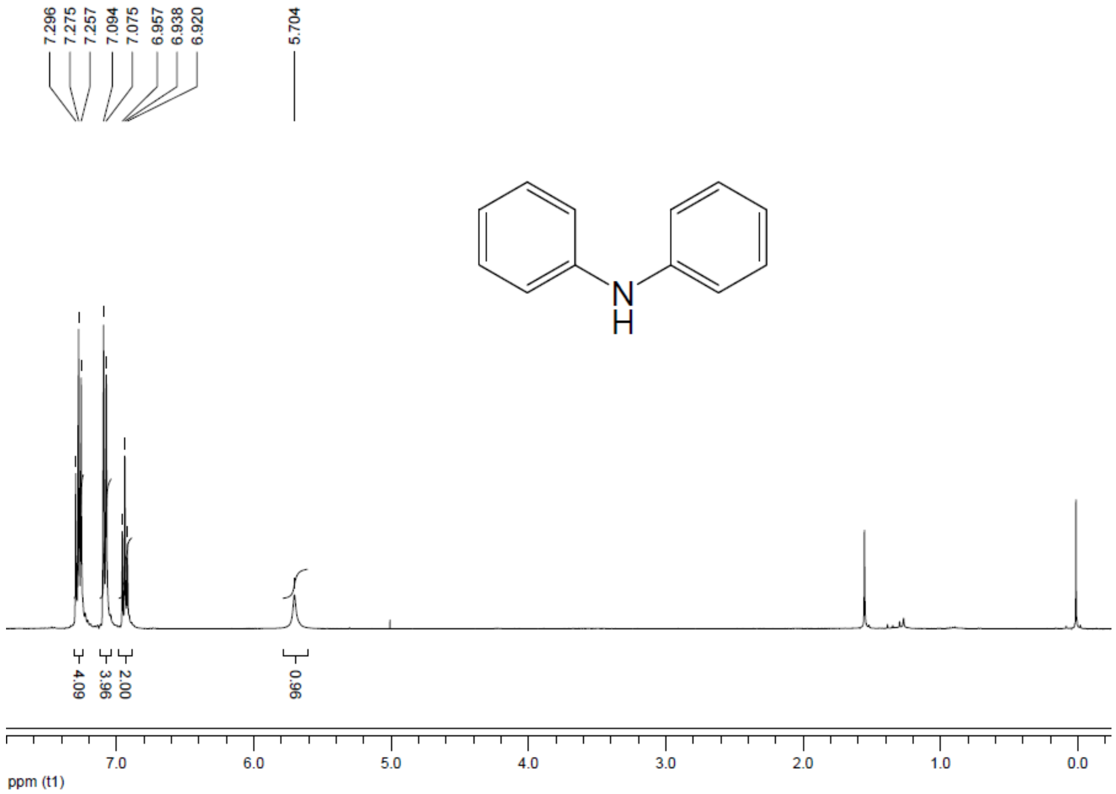
7.067
7.060
7.055
7.050
7.044
7.037
7.029
7.023
7.008
6.992
6.986
6.912
6.893
6.877
3.284
F
N
2.16
4.07
2.95
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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7.075
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6.938
6.920
5.704
N
H
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6.0
5.0
4.0
3.0
2.0
1.0
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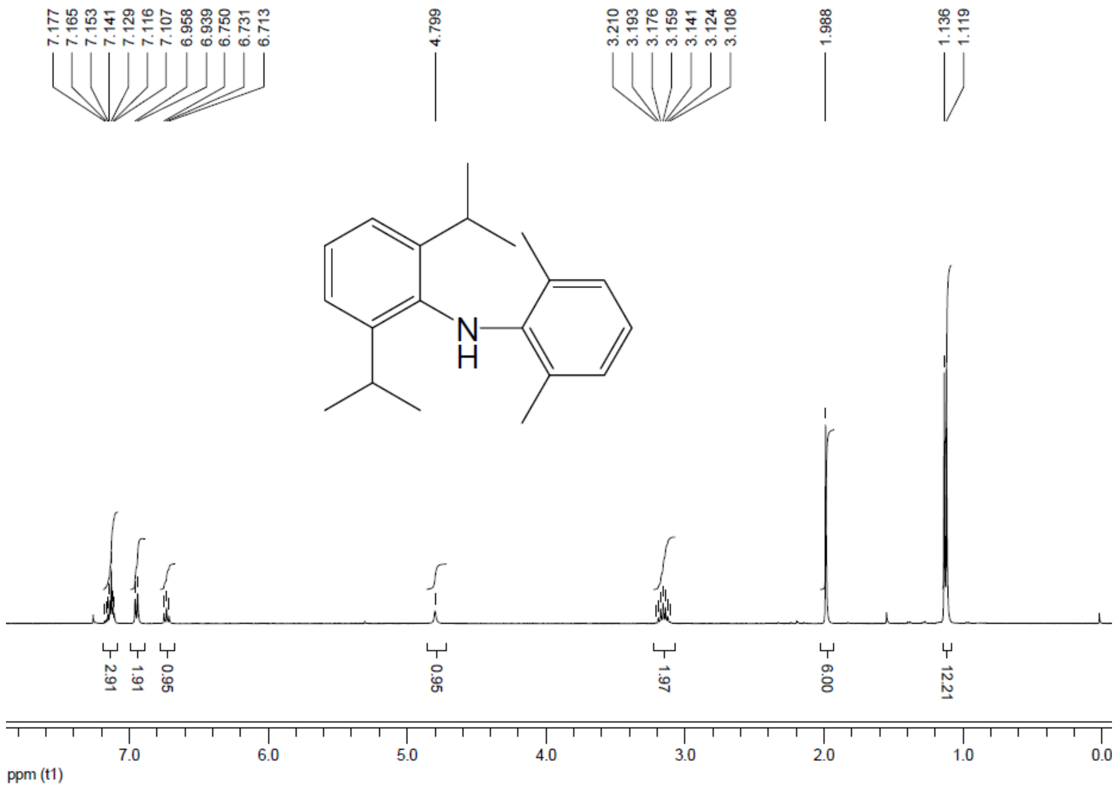
ppm (t1)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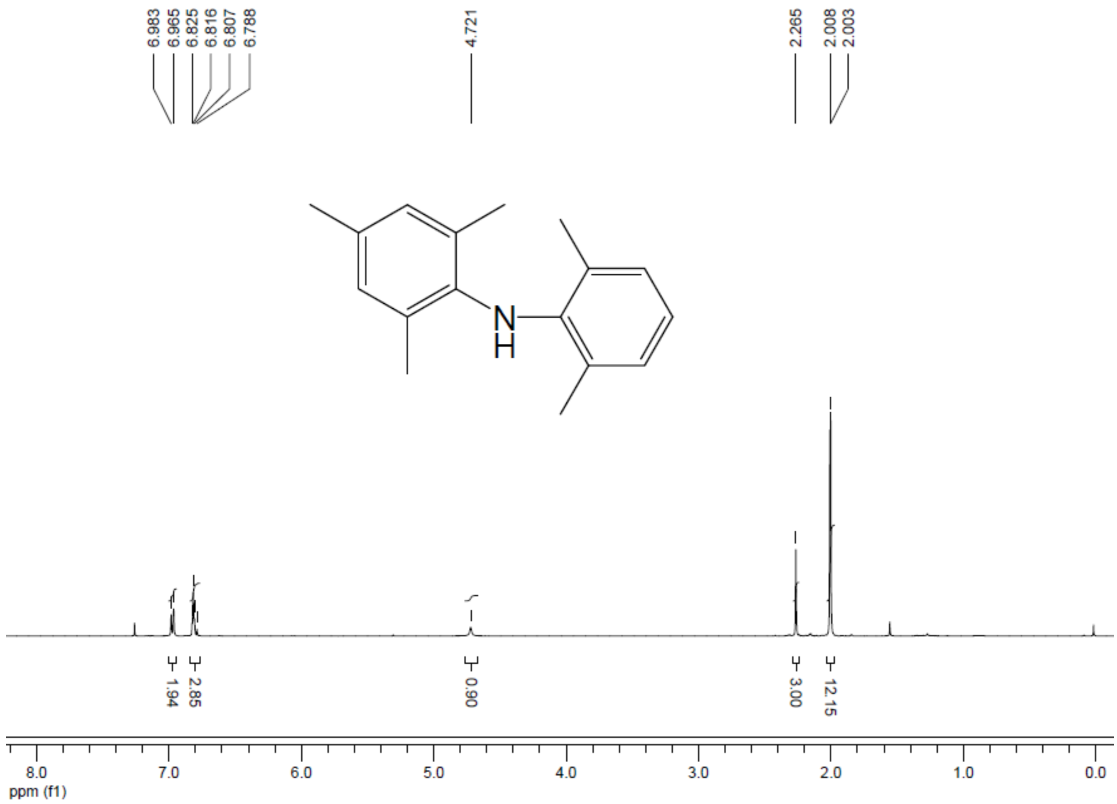
7.165
7.153
7.141
7.129
7.116
7.107
6.958
6.939
6.750
6.731
6.713
4.799
3.210
3.193
3.176
3.159
3.141
3.124
3.108
1.988
1.136
1.119
N
H
2.91
1.91
0.95
0.95
1.97
6.00
12.21
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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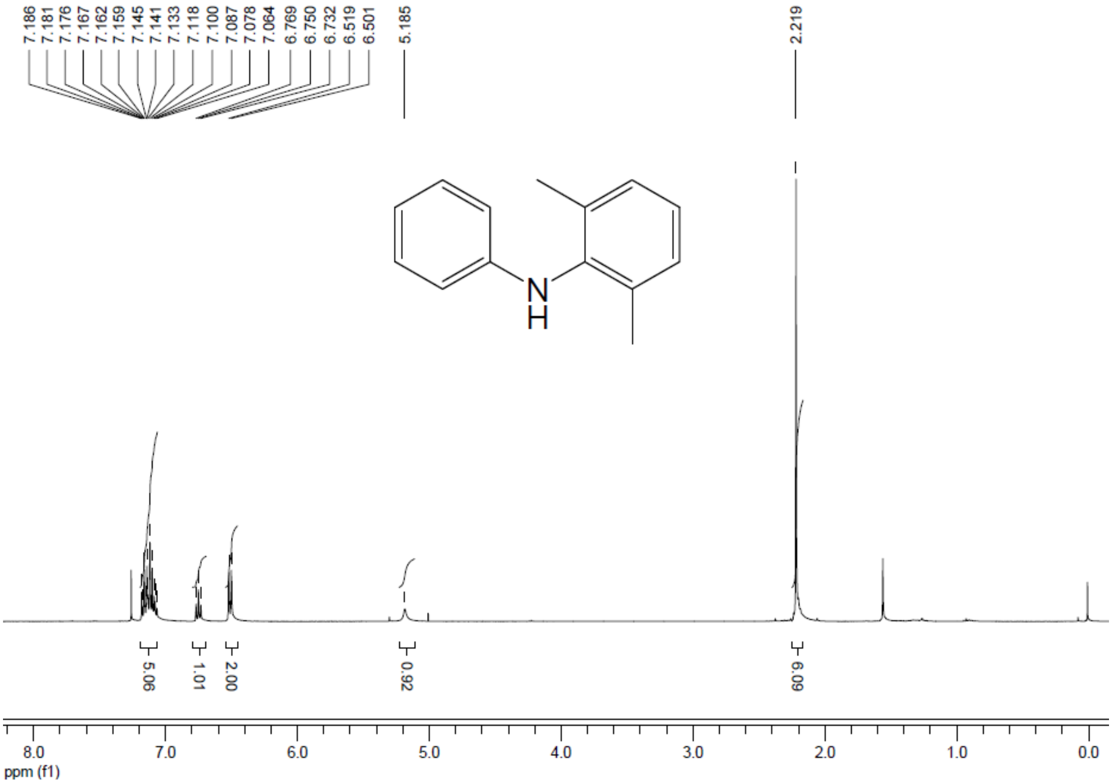
6.965
6.825
6.816
6.807
6.788
4.721
2.265
2.008
2.003
N
H
1.94
2.85
0.90
3.00
12.15
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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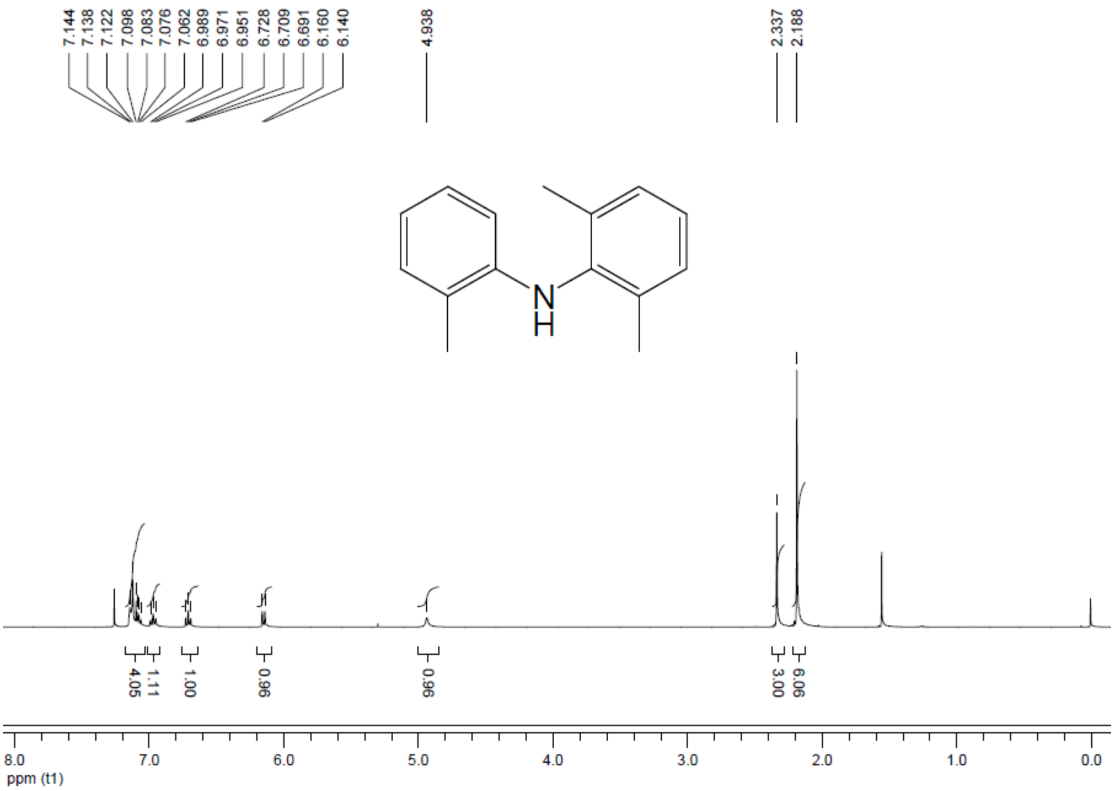
7.181
7.176
7.167
7.162
7.159
7.145
7.141
7.133
7.118
7.100
7.087
7.078
7.064
6.769
6.750
6.732
6.519
6.501
5.185
2.219
N
H
5.06
1.01
2.00
0.92
6.09
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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7.138
7.122
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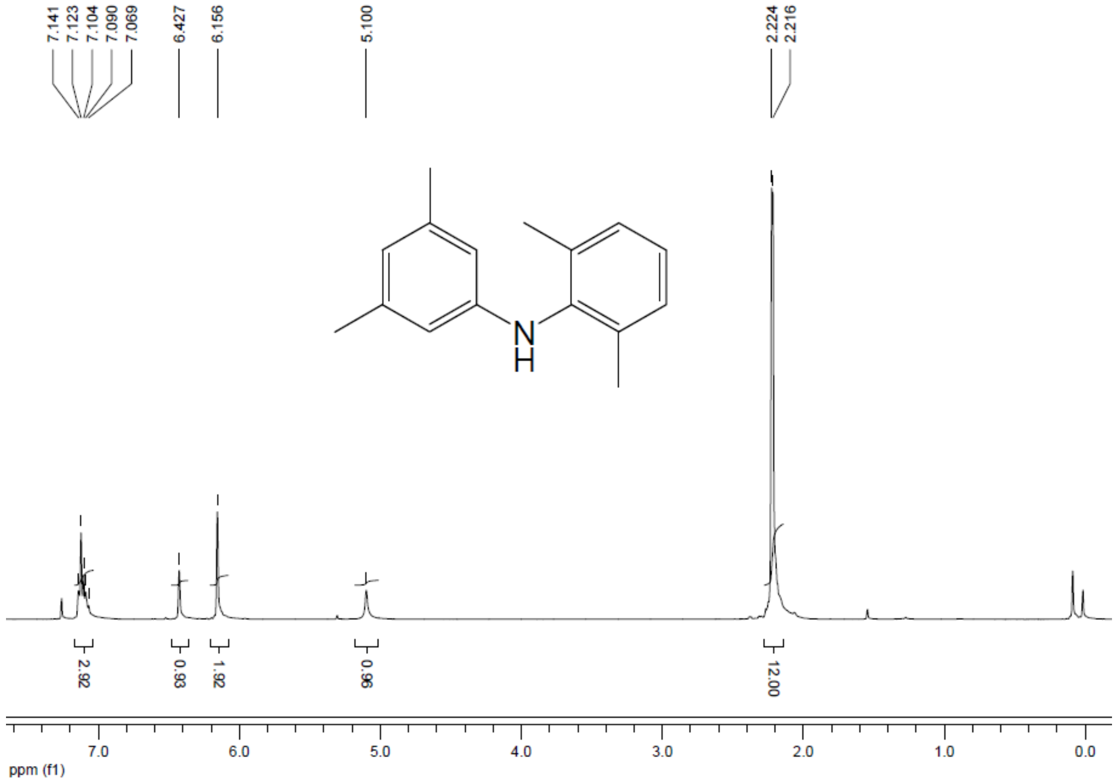
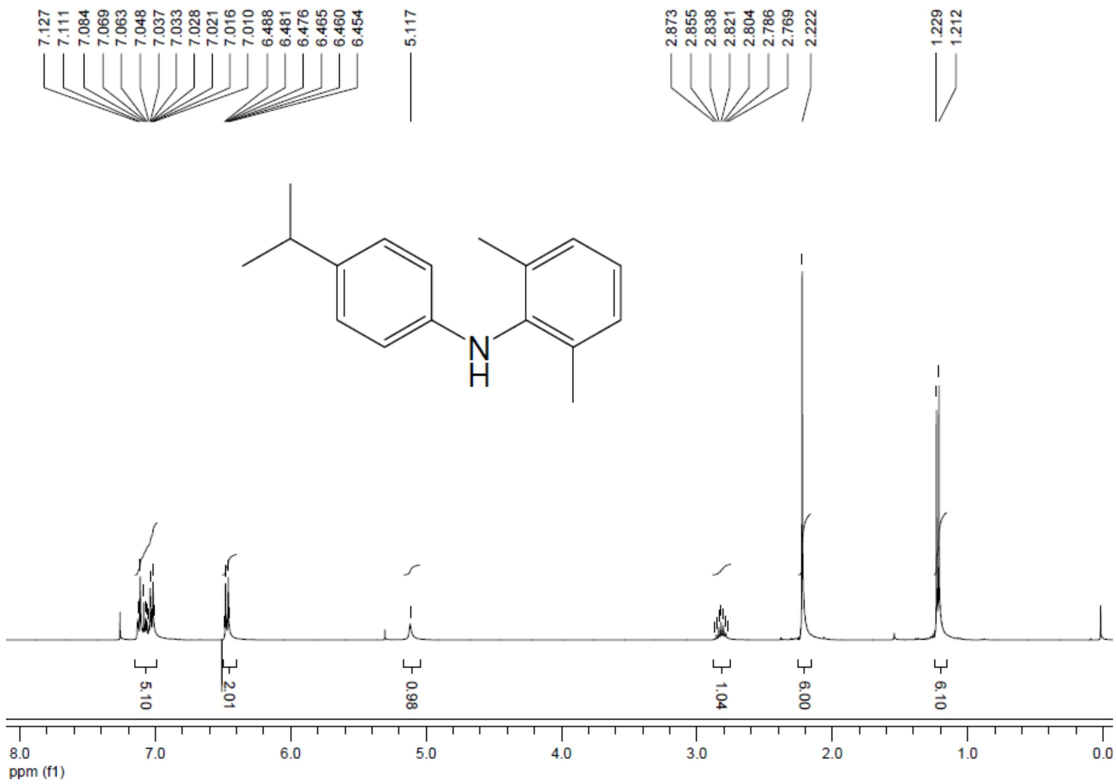
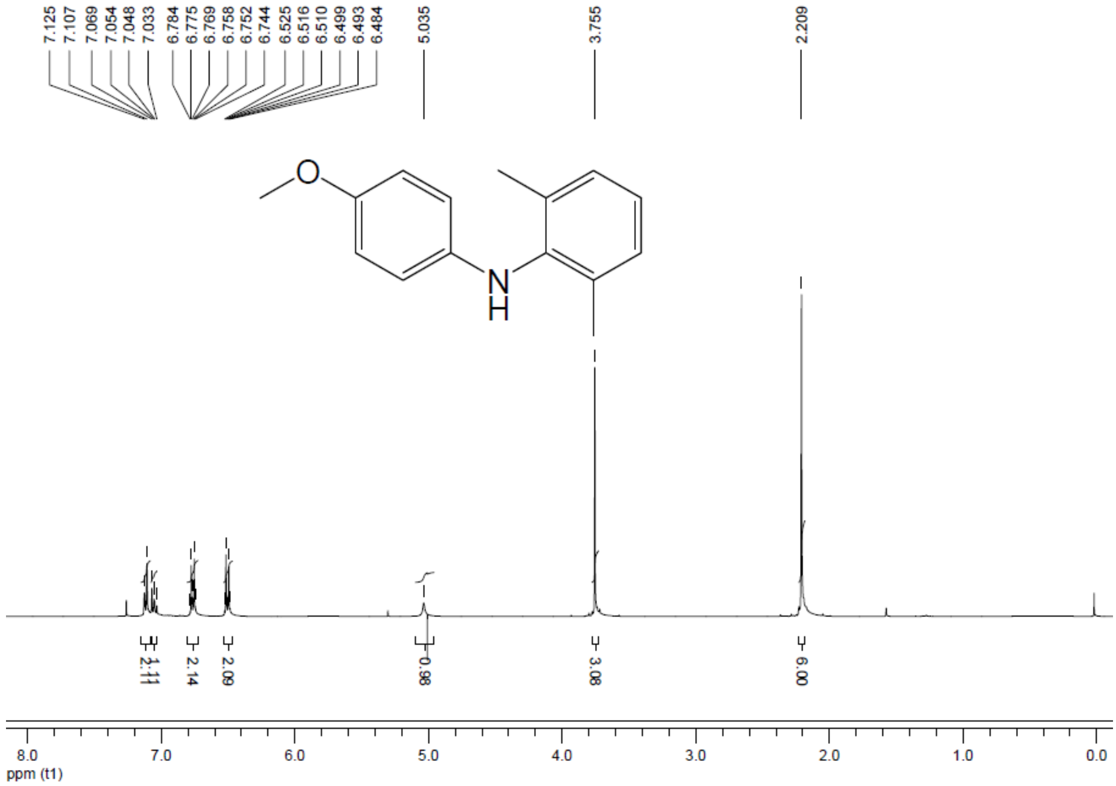
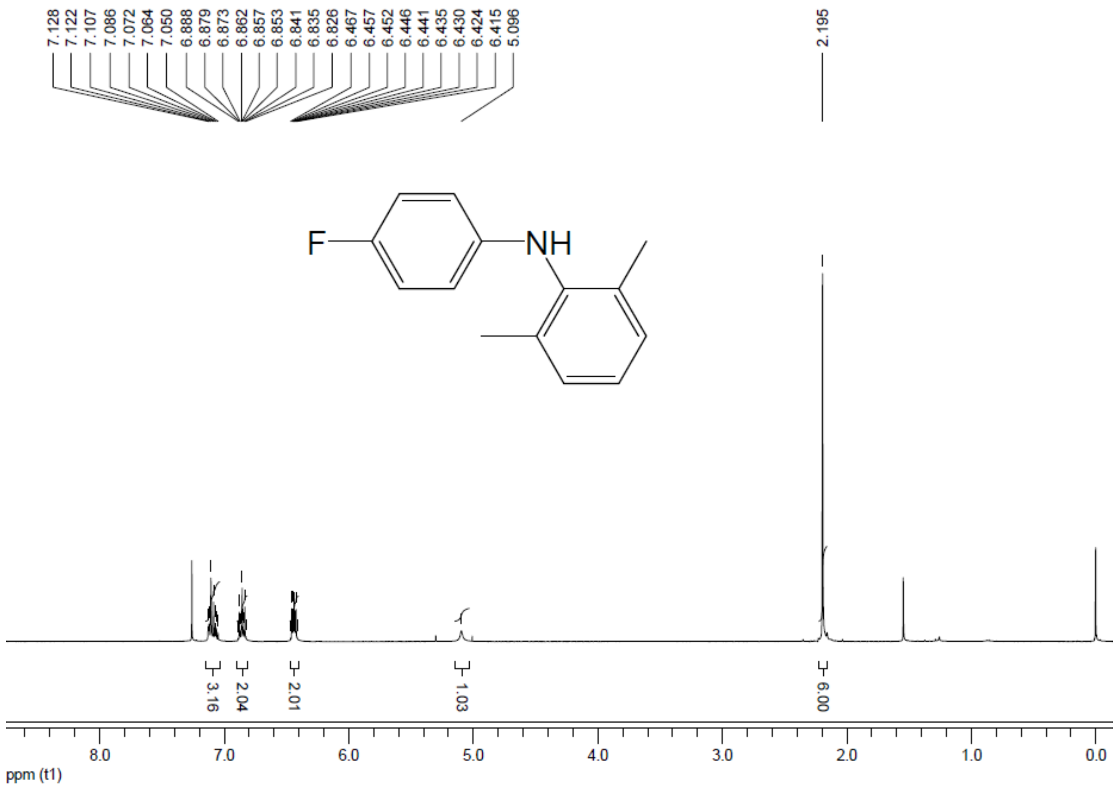
7.083
7.076
7.062
6.989
6.971
6.951
6.728
6.709
6.691
6.160
6.140
4.938
2.337
2.188
N
H
4.05
1.11
1.00
0.96
0.96
3.00
6.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


7.141
7.123
7.104
7.090
7.069
6.427
6.156
5.100
2.224
2.216
N
H
2.92
0.93
1.92
0.96
12.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


7.127
7.111
7.084
7.069
7.063
7.048
7.037
7.033
7.028
7.021
7.016
7.010
6.488
6.481
6.476
6.465
6.460
6.454
5.117
2.873
2.855
2.838
2.821
2.804
2.786
2.769
2.222
1.229
1.212
N
H
5.10
2.01
0.98
1.04
6.00
6.10
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


7.125
7.107
7.069
7.054
7.048
7.033
6.784
6.775
6.769
6.758
6.752
6.744
6.525
6.516
6.510
6.499
6.493
6.484
5.035
3.755
2.209
O
N
H
2.11
2.14
2.09
0.98
3.08
6.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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7.122
7.107
7.086
7.072
7.064
7.050
6.888
6.879
6.873
6.862
6.857
6.853
6.841
6.835
6.826
6.467
6.457
6.452
6.446
6.441
6.435
6.430
6.424
6.415
5.096
2.195
F
NH
3.16
2.04
2.01
1.03
6.00
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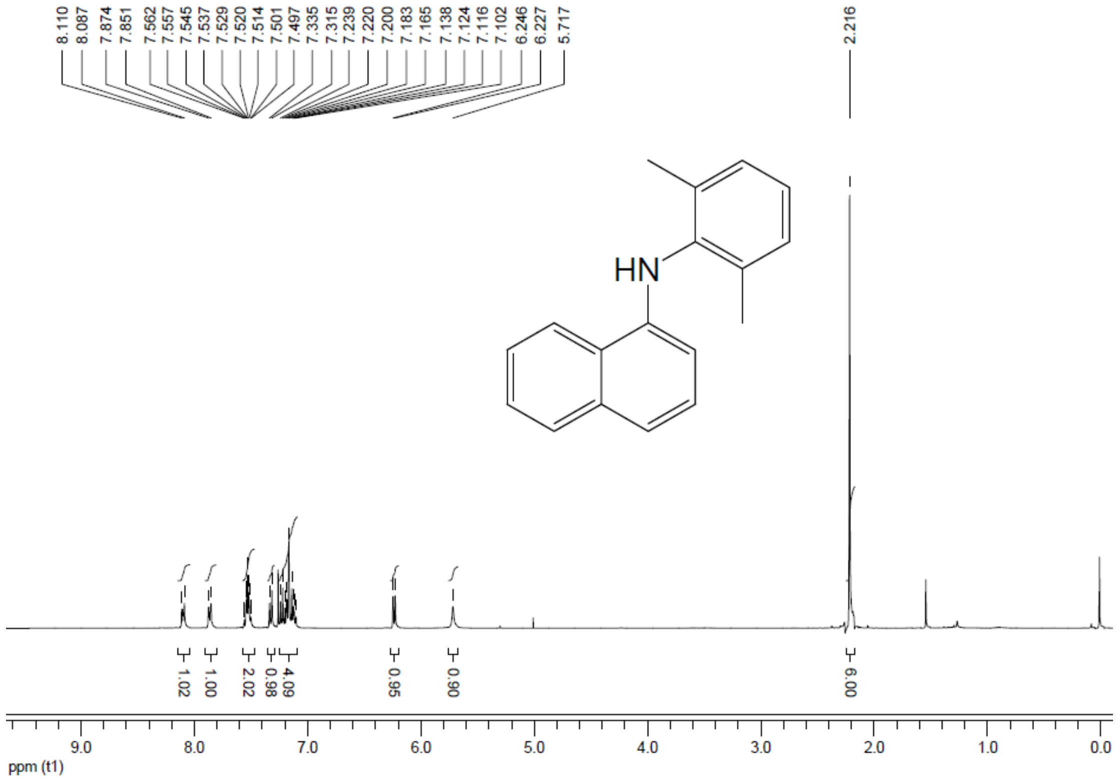
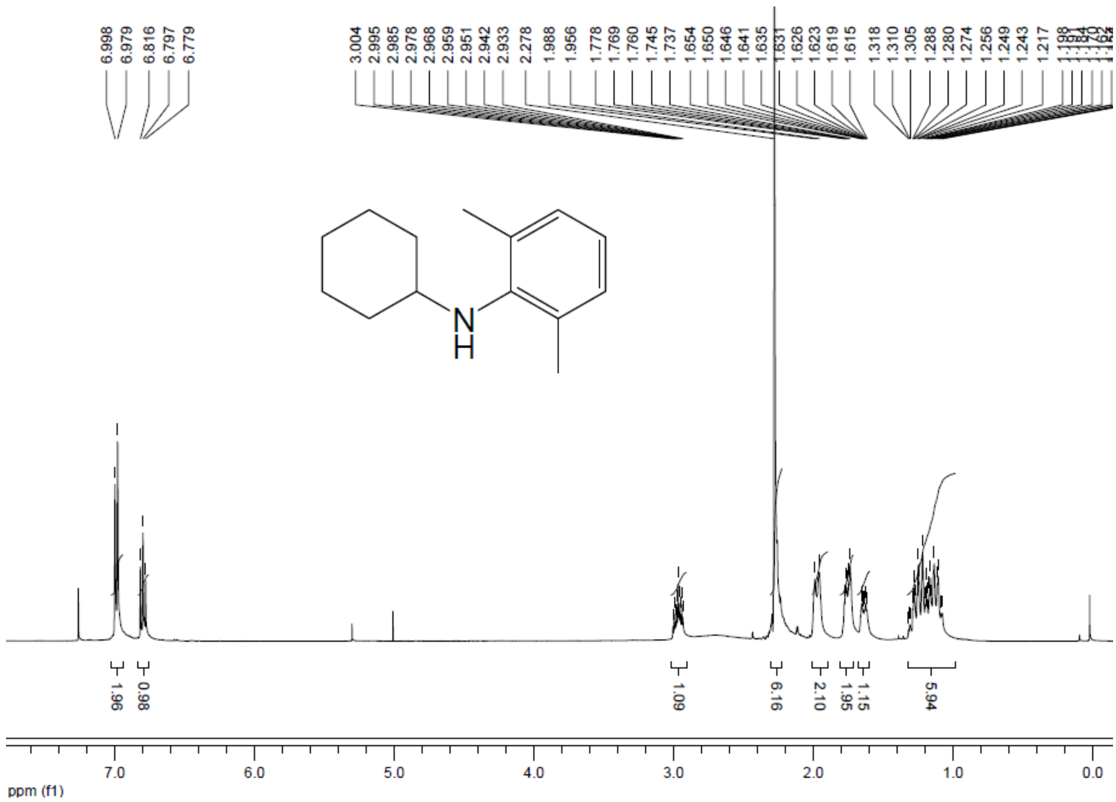
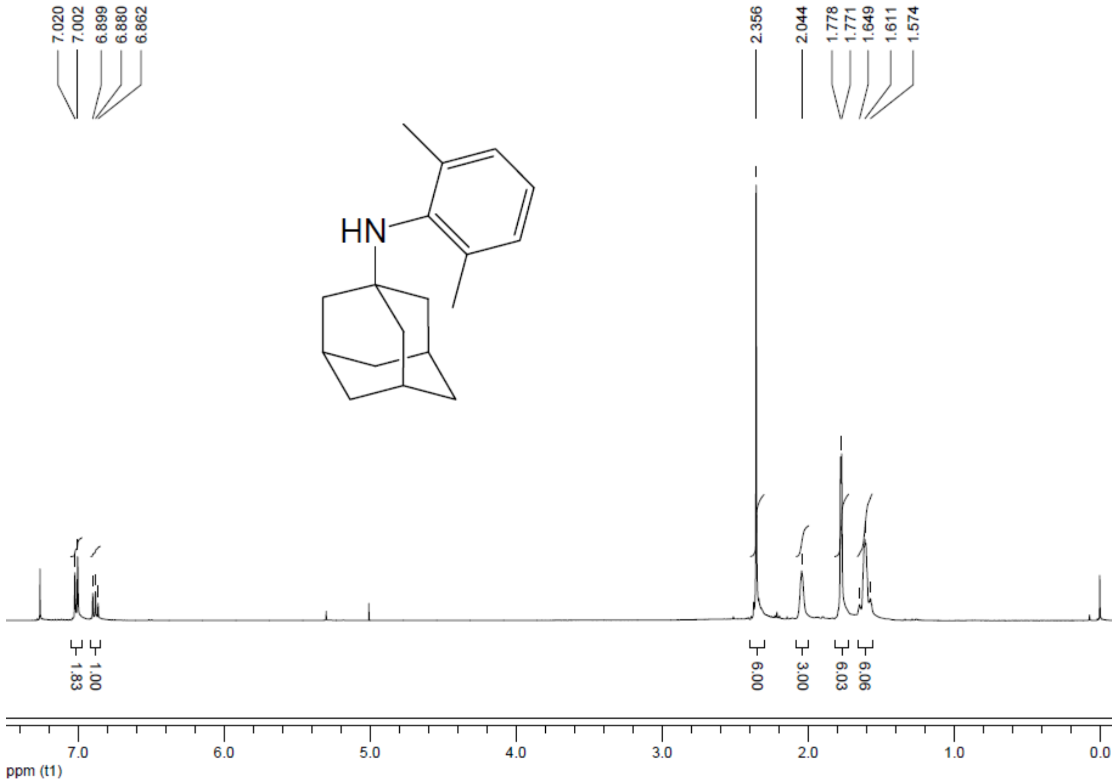
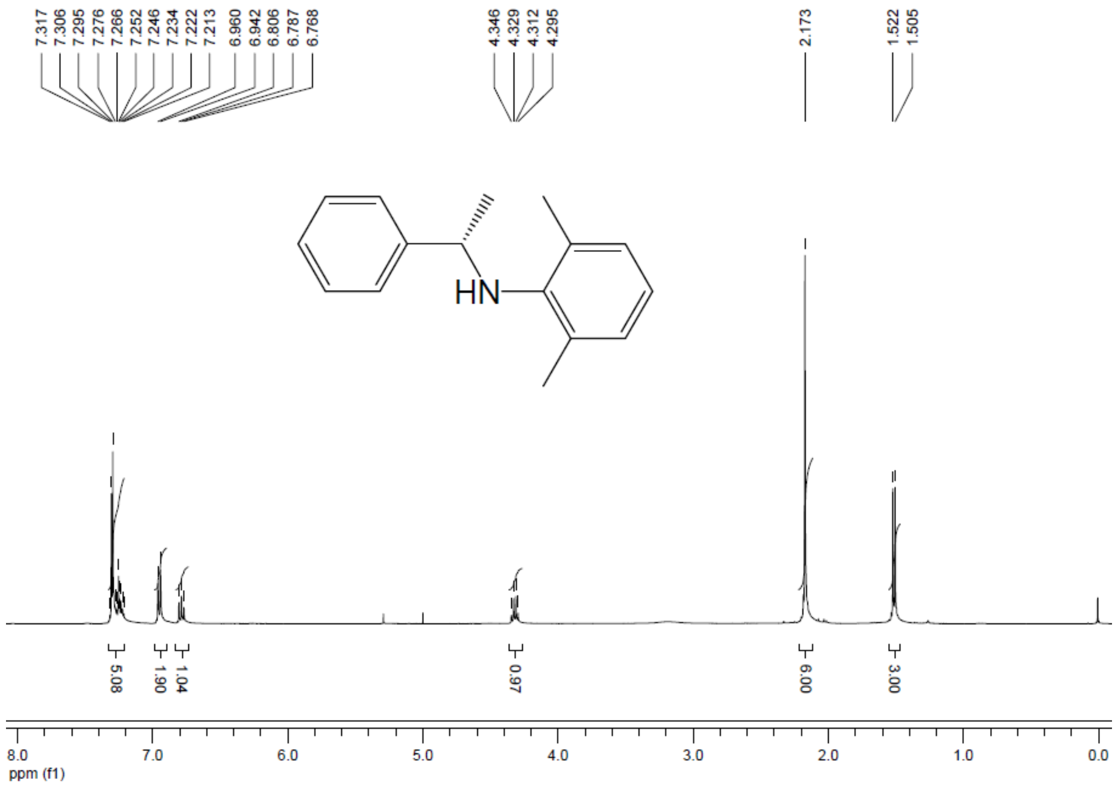
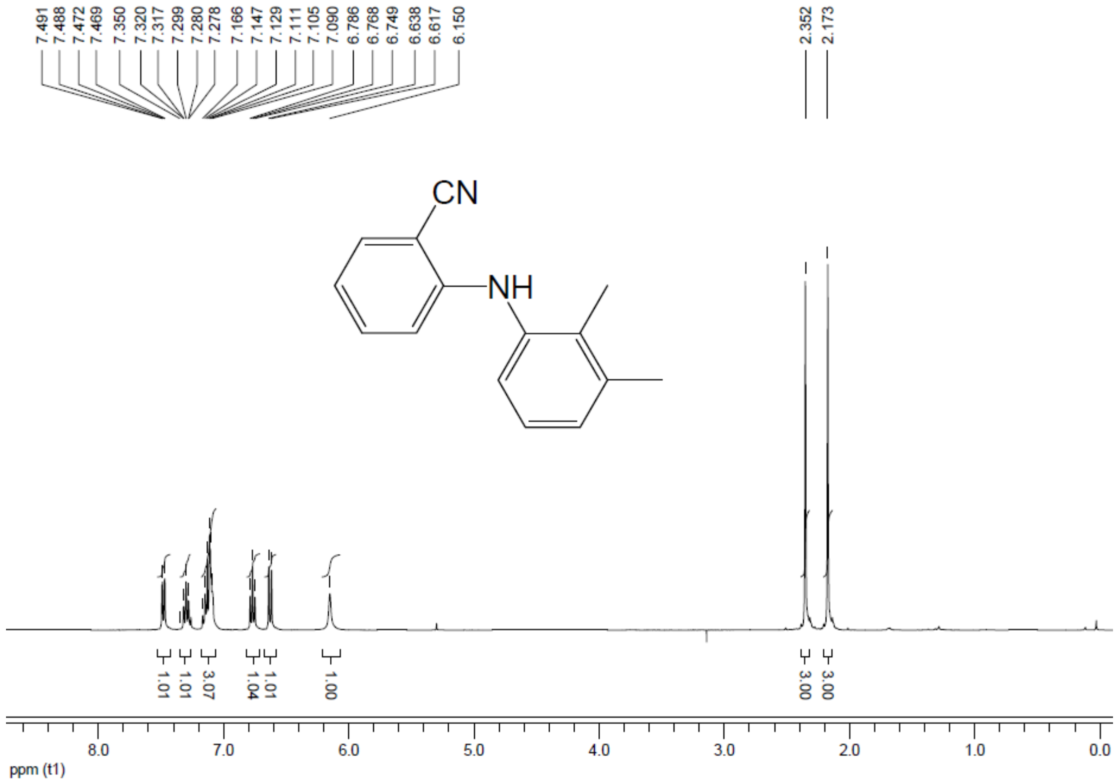
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)







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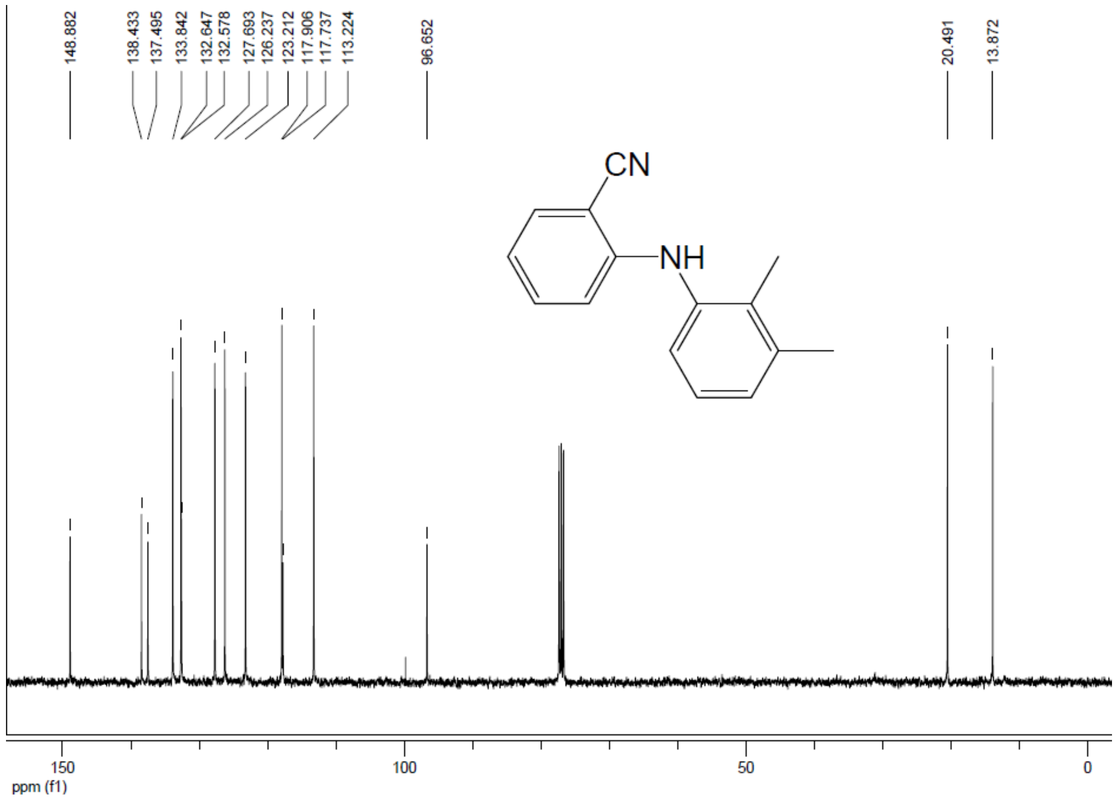
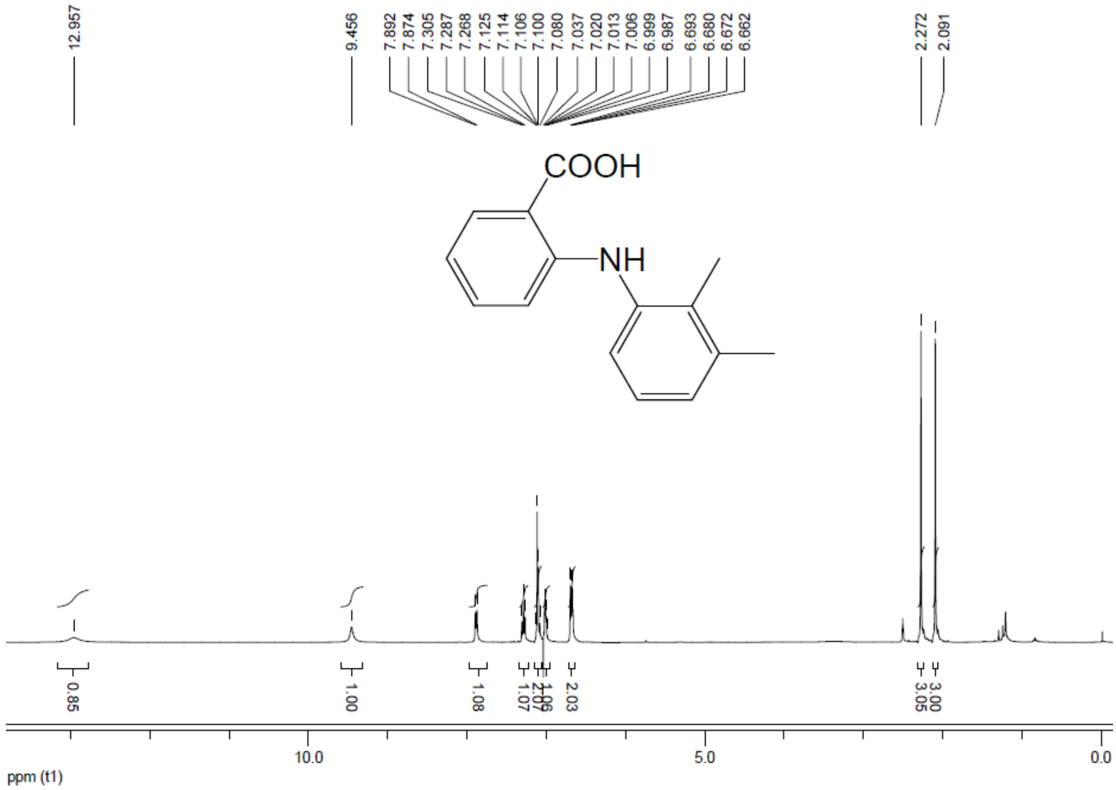
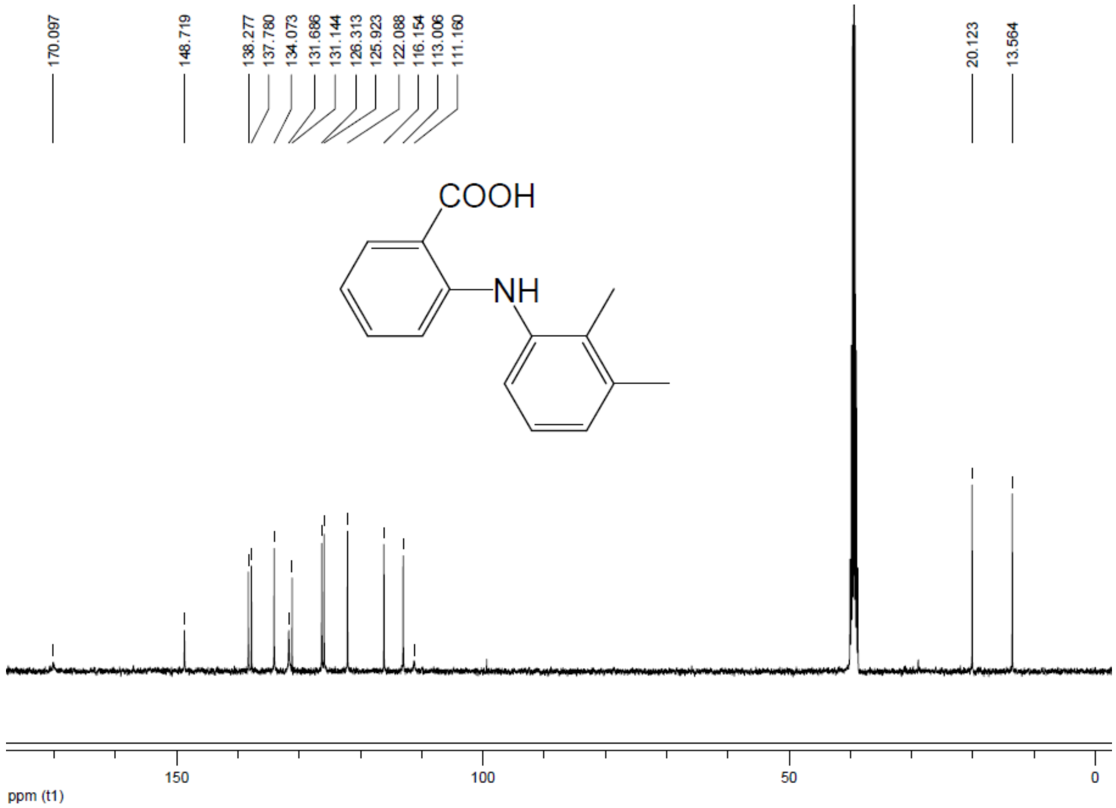
7.488
7.472
7.469
7.350
7.320
7.317
7.299
7.280
7.278
7.166
7.147
7.129
7.111
7.105
7.090
6.786
6.768
6.749
6.638
6.617
6.150
2.352
2.173
CN
NH
1.01
1.01
3.07
1.04
1.01
1.00
3.00
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


148.882
138.433
137.495
133.842
132.647
132.578
127.693
126.237
123.212
117.906
117.737
113.224
96.652
20.491
13.872
CN
NH
150
100
50
0
ppm (f1)


12.957
9.456
7.892
7.874
7.305
7.287
7.268
7.125
7.114
7.106
7.100
7.080
7.037
7.020
7.013
7.006
6.999
6.987
6.693
6.680
6.672
6.662
2.272
2.091
COOH
NH
0.85
1.00
1.08
1.07
2.07
1.06
2.03
3.05
3.00
10.0
5.0
0.0
ppm (t1)


170.097
148.719
138.277
137.780
134.073
131.686
131.144
126.313
125.923
122.088
116.154
113.006
111.160
20.123
13.564
COOH
NH
150
100
50
0
ppm (t1)

8. References.

S1. S. Dastgir, A. K. S. Coleman, R. Cowley and L. H. Green, *Organometallics* 2010, **29**, 4858.

S2. K. V. Vasudevan, R. R. Butorac, C. D. Abernethy and A. H. Cowley, *Dalton Trans.* 2010, **39**, 7401.

S3. C. J. O'Brien, E. A. B. Kantchev, C. Valente, N. Hadei, G. A. Chass, A. Lough, A. C. Hopkinson and M. G. Organ. *Chem. Eur. J.* 2006, **12**, 4743.

S4. N. Saemian, O. K. Arjomandi and G. Shirvani, *J. Label Compd. Radiopharm*, 2009, **52**, 453.

S5. M. G. Organ, M. Abdel-Hadi, S. Avola, I. Dubovyk, N. Hadei, E. A. B. Kantchev, C. J. Sayah, M. O'Brien and C. Valente, *Chem. Eur. J.* 2008, **14**, 2443.