Electronic Supplementary Information for

Acenaphthoimidazolium Chloride Enabled Nickel Catalyzed Amination of Bulky Aryl Tosylates

Jian Jiang, Haibo Zhu, Yajing Shen and Tao Tu *

Department of Chemistry, Fudan University 220 Handan Road, 200433, Shanghai, China

Email: taotu@fudan.edu.cn

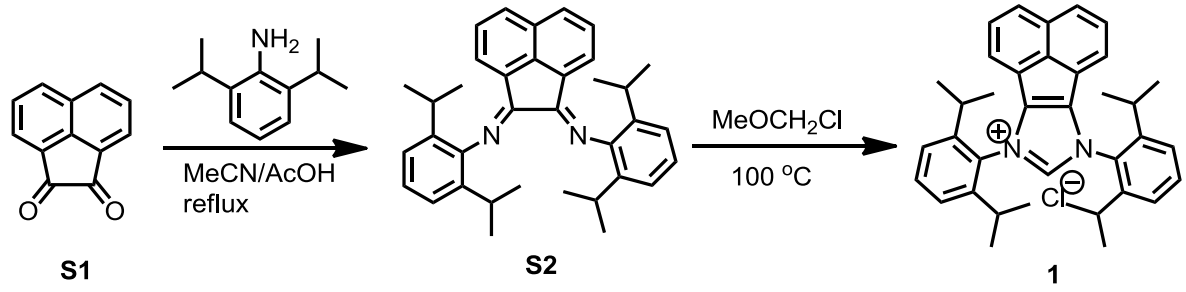
Table of contents:

1. General

All commercial reagents were used directly without further purification, unless otherwise stated. Dry dimethylsulfoxide (DMSO) was purchased from J & K chemical, stored over 4 Å molecular sieves and handled under N_2. Anhydrous methanol (MeOH) was distilled from anhydrous calcium chloride, Dioxane, Tetrahydrofuran (THF), toluene and *m*-Xylene were distilled from sodium/benzophenone, 1,2-Dimethoxyethane (DME) and 1,2-Dichloroethane (DCE) were distilled from calcium hydride prior to use. *t*-BuONa was purchased from J & K chemical. All schlenk tubes and sealed vessels (50 mL) were purchased from Beijing Synthware Glass. $CDCl_3$ was purchased from Cambridge Isotope Laboratories.^{1}H NMR and ^{13}C NMR spectra 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. Experimental sections

2.1 Synthesis of acenaphthoimidazolium chloride



Scheme S1. Synthesis of acenaphthoimidazolium chloride **1**.

Bis[N,N'-(2,6-diisopropylphenyl)imino]acenaphthene (S2):

According to the literature procedure,[S1] acenaphthenequinone (3.5 g, 19.2 mmol) **S1** was suspended in acetonitrile (125 mL) and heated under reflux for 1 hour. After that acetic acid (33 mL) was added, the solid was then completely dissolved. To the hot mixture,

2,6-diisopropylphenylaniline (8.16 g, 46 mmol) was added dropwise over 30 minutes and the obtained solution was continued refluxing for additional 5 hours. The resulting orange-yellow solid was then filtered after cooling to room temperature, washed with *n*-pentane (3 × 40 mL), and dried over under the vacuum. Yield: 8.5 g, 88 %. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.87 (d, J = 8.0 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.27 (bs, 6H), 6.64 (d, J = 7.2 Hz, 2H), 3.06-3.00 (m, 4H), 1.24 (d, J = 6.8 Hz, 12H), 0.97 (d, J = 6.8 Hz, 12H).

Acenaphthoimidazolium chloride (1):

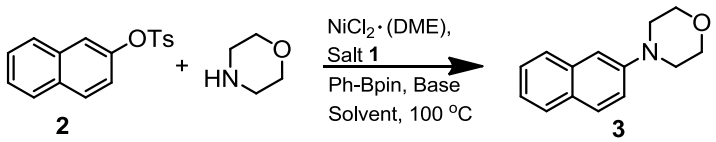
According to the literature procedure,[S1] **S2** (3.00 g, 6 mmol) and methoxy(methyl)chloride (9.66 g, 120 mmol) were added to an nitrogen-flushed thick-walled sealed vessel. Then the reaction mixture was stirred at 100 ^{o}C for 16 hours, during the heating process, the mixture changed from a murky brown suspension to a clear red solution. After cooling to room temperature, a yellow precipitate was formed and 30 mL of diethyl ether was subsequently added. The precipitation was filtered and washed with 100 mL of diethyl ether and over under the vacuum to afford **1** as an analytically pure yellow powder. Yield: 2.3 g, 70%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 12.23 (s, 1H), 8.00 (d, J = 8.0 Hz, 2H), 7.67 (t, J = 7.6 Hz, 2H), 7.58 (t, J = 7.2 Hz, 2H), 7.46 (d, J = 7.6 Hz, 4H), 7.22 (d, J = 7.2 Hz 2H), 2.78-2.68 (m, 4H), 1.40 (d, J= 6.8 Hz, 12H), 1.16 (d, J= 6.8 Hz, 12H).

2.2 General procedure for Ni-NHC catalyzed amination.

To a 50 mL schlenk tube containing base (1.5 mmol), $NiCl_2$•(DME) (2 mol%) and acenaphthoimidazolium chloride **1** (4 mol%), aryl tosylate (0.5 mmol) and Ph-Bpin (1.0 mmol) were added and the tube was purged with N_2 for 3 times. Then dioxane (2.5 mL) and amine (1.25 mmol) were injected via syringe, subsequently (Note, if amine was a solid, it was introduced to the tube before purging with N_2). The resulted mixture was allowed to stir for 1 hour at room temperature, then was heated at 100 ^{o}C for additional 3 hours. After cooling to the room temperature, the reaction mixture was concentrated under the vacuum and directly purified by flash chromatography.

3. Optimization of reaction conditions

Table S1. Base and solvent effects (excluded data in the Table 1)

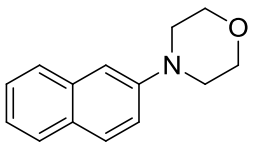


2 **3**

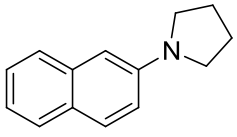
Entry	Solvent	Base (equiv)	Yield (%)[b]
1	Dioxane	Et_3N (3.0)	NR
2	Dioxane	DBU (3.0)	NR
3	Dioxane	Na_2CO_3 (3.0)	NR
4	Dioxane	Cs_2CO_3 (3.0)	NR
5	Dioxane	CsF (3.0)	NR
6	MeOH	*t*-BuONa (3.0)	0
7	DMSO	*t*-BuONa (3.0)	0
8	DCE	*t*-BuONa (3.0)	NR

[a] 0.5 mmol scale for 1 hour at rt, then 3 hours at 100 °C, with 2 mol% $NiCl_2$• (DME), [b] Isolated yield.

4. Data for the amination products

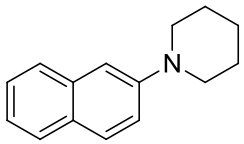
3: [S2] 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.76-7.69 (m, 3H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.27-7.24 (m, 1H), 7.12 (d, *J* = 2.0 Hz, 1H), 3.92 (t, *J* = 4.4 Hz, 4H), 3.27 (t, *J* = 4.4 Hz, 4H); GC-MS: m/z = 213.1 $[M]^+$, 155.1, 127.1.

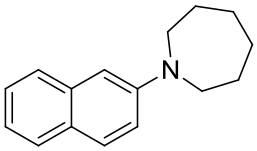
5a: [S2] 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.68 (t, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 1H),

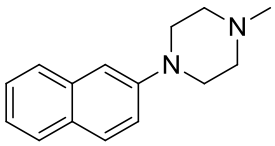
7.34 (t, J = 7.2 Hz, 1H), 7.15 (t, J = 8.4 Hz, 1H), 7.00 (dd, J = 2.4 Hz, J = 8.8 Hz, 1H), 6.75 (s, 1H), 3.41 (t, J = 6.4 Hz, 4H), 2.06 (t, J = 6.4 Hz, 4H); GC-MS: m/z = 196.1 $[M-1]^+$, 141.1, 127.1.

5b: [S2] 

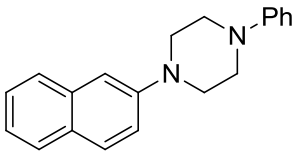
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.71-7.66 (m, 3H), 7.38 (t, J = 7.2 Hz, 1H), 7.30-7.23 (m, 2H), 7.13 (s, 1H), 3.26 (t, J = 6.4 Hz, 4H), 1.80-1.74 (m, 4H), 1.65-1.59 (m, 2H); GC-MS: m/z = 210.2 $[M-1]^+$, 135.9, 127.1.

5c: [S3] 

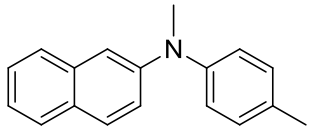
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.66 (t, J = 8.0 Hz, 2H), 7.59 (d, J = 8.4 Hz, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.16-7.09 (m, 2H), 6.86 (d, J = 2.0 Hz, 1H), 3.58 (t, J = 6.0 Hz, 4H), 1.90-1.81 (m, 4H), 1.59-1.56 (m, 4H); GC-MS: m/z = 225.2 $[M]^+$, 196.1, 127.1.

6a: [S4] 

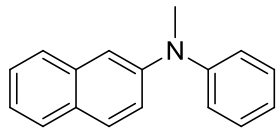
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.75-7.70 (m, 3H), 7.42-7.38 (m, 1H), 7.31-7.26 (m, 2H), 7.13 (d, J = 2.4 Hz, 1H), 3.33 (t, J = 5.0 Hz, 4H), 2.65 (t, J = 5.0 Hz, 4H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 148.98, 134.52, 128.60, 128.43, 127.33, 126.65, 126.17, 123.28, 119.27, 110.17, 55.00, 49.32, 46.02.

6b: [S3] 

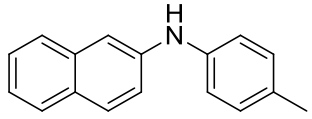
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.77-7.71 (m, 3H), 7.42 (t, J = 7.6 Hz, 1H), 7.34-7.30 (m, 4H), 7.19 (d, J = 2.0 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 6.91 (t, J = 7.6 Hz, 1H), 3.49-3.45 (m, 4H), 3.42-3.40 (m, 4H); GC-MS: m/z = 288.1 $[M]^+$, 155.1, 132.1.

7a: [S5] 

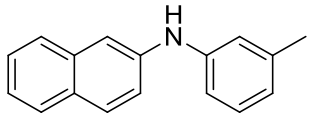
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.72-7.62 (m, 3H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.30-7.28 (m, 1H), 7.22 (d, *J* = 1.6 Hz, 1H), 7.16-7.13 (m, 3H), 7.06 (d, *J* = 8.4 Hz, 2H), 3.40 (s, 3H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 146.92, 146.62, 134.80, 132.76, 130.07, 128.63, 128.46, 127.56, 126.63, 126.29, 123.32, 123.17, 120.71, 112.24, 40.87, 20.85; GC-MS: m/z = 247.1 $[M]^+$, 231.1, 217.1.

7b: [S5] 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.75-7.67 (m, 3H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.33-7.29 (m, 4H), 7.23 (dd, *J* = 2.4 Hz, *J* = 11.2 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.04 (t, *J* = 7.2 Hz, 1H), 3.45 (s, 3H); GC-MS: m/z = 233.1 $[M-1]^+$, 217.1, 127.1.

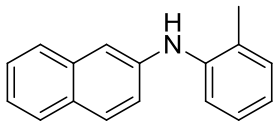
8a: [S5] 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.40-7.35 (m, 2H), 7.29-7.27 (m, 1H), 7.19-7.08 (m, 5H), 5.77 (s, 1H), 2.33 (s, 3H).; ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 141.74, 140.12, 134.76, 131.42, 130.00, 129.18, 128.92, 127.68, 126.45, 126.41, 123.22, 119.62, 119.39, 110.31, 20.81.

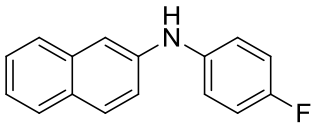
8b: [S5] 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.46-7.41 (m, 2H), 7.35-7.31 (m, 1H), 7.27-7.21 (m, 2H), 7.01 (d, *J* = 6.8 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 1H), 5.86 (s, 1H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 142.83,

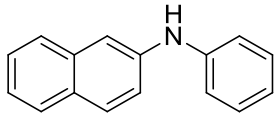
140.94, 139.27, 134.60, 129.20, 129.08, 127.60, 126.44, 126.37, 123.39, 122.26, 120.06, 118.95, 115.33, 111.55, 29.69.

8c: [S2] 

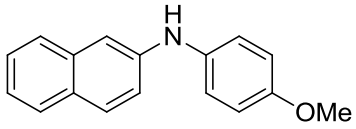
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 6.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.31-7.27 (m, 1H), 7.24-7.18 (m, 4H), 7.00 (t, *J* = 7.2 Hz, 1H), 5.56 (bs, 1H), 2.30 (s, 3H); GC-MS: m/z = 233.1 [M]+, 217.1, 135.9.

9a: [S6] 

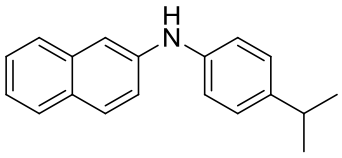
^{1}H NMR (DMSO, 400 MHz, 298 K): δ 8.35 (s, 1H), 7.77-7.72 (m, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.38-7.34 (m, 2H), 7.25-7.19 (m, 4H), 7.13 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 159.42, 157.02, 141.63, 138.68, 134.61, 129.23, 128.93, 127.62, 126.48, 126.34, 123.33, 121.02, 120.94, 119.32, 116.09, 115.87, 110.29. ^{19}F NMR ($CDCl_3$, 400 MHz, 298 K): δ = -121.25.

9b: [S5] 

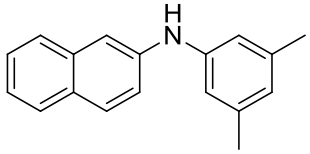
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.79-7.77 (m, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.48-7.41 (m, 2H), 7.36-7.31 (m, 3H), 7.26 (dd, *J* = 2.4 Hz, *J* = 8.8 Hz, 1H), 7.21-7.19 (m, 2H), 7.03-6.99 (m, 1H), 5.91 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 143.03, 140.96, 134.75, 129.54, 129.28, 127.77, 126.61, 126. 57, 123.61, 121.51, 120.16, 118.38, 111.71.

9c: [S5] 

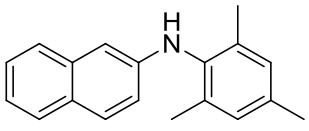
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.71 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.39-7.35 (m, 1H), 7.25-7.21 (m, 2H), 7.19-7.15 (m, 2H), 7.12 (dd, *J* = 2.4 Hz, *J* = 8.8 Hz, 2H), 6.93-6.89 (m, 2H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 155.42, 142.85, 135.44, 134.75, 129.06, 128.46, 127.57, 126.33, 126.16, 122.79, 122.46, 118.82, 114.67, 108.66, 55.49.

10: [S7] 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.40-7.36 (m, 2H), 7.29-7.27 (m, 1H), 7.20-7.18 (m, 3H), 7.14-7.11 (m, 2H), 5.80 (s, 1H), 2.95-2.85 (m, 1H), 1.26 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 142.34, 141.50, 140.36, 134.68, 129.04, 128.85, 127.58, 127.23, 126.33, 123.13, 119.62, 118.99, 110.43, 33.42, 24.11.

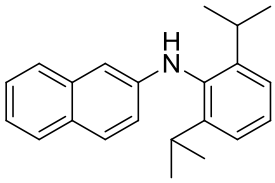
11: [S8] 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.40-7.37 (m, 2H), 7.30-7.27 (m, 1H), 7.24-7.19 (m, 1H), 6.78 (s, 2H), 6.63 (s, 1H), 5.76 (s, 1H), 2.29 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 142.85, 141.09, 139.09, 134.63, 129.05, 127.61, 126.44, 126.35, 123.35, 123.30, 120.15, 116.10, 111.65.

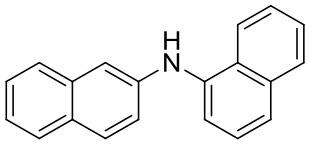
12: [S2] 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.70-7.66 (m, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.00 (s, 2H), 6.95 (dd, *J* = 2.0 Hz, *J* = 8.8 Hz, 1H),

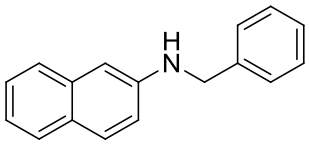
6.55 (d, J = 2.0 Hz, 1H), 5.26 (s, 1H), 2.35 (s, 3H), 2.21 (s, 6H); GC-MS: m/z = 261.3 $[M]^+$, 246.3, 231.2.

13: [S5] 

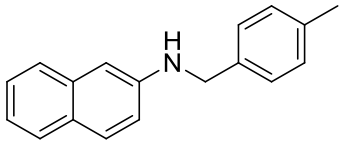
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.69-7.66 (m, 2H), 7.49 (d, J = 8.0 Hz, 1H), 7.37-7.30 (m, 2H), 7.28-7.26 (m, 2H), 7.19 (t, J = 7.6 Hz, 1H), 6.95 (dd, J = 2.0 Hz, J = 8.8 Hz, 1H), 6.56 (s, 1H), 5.29 (s, 1H), 3.29-3.19 (m, 2H), 1.15 (d, J = 6.4 Hz, 12H); GC-MS: m/z = 303.1 $[M]^+$, 288.1, 218.1.

14: [S5] 

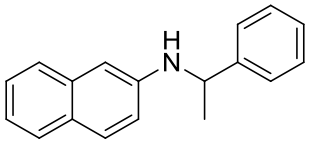
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.08 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.76 (dd, J = 2.8 Hz, J = 8.4 Hz, 2H), 7.63 (dd, J = 2.8 Hz, J = 6.8 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.55-7.44 (m, 4H), 7.41-7.37 (m, 1H), 7.32-7.24 (m, 3H), 6.12 (s, 1H). GC-MS: m/z = 269.3 $[M]^+$, 133.8, 127.2.

15: [S9] 

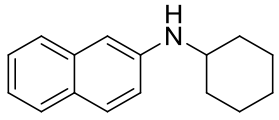
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.66-7.56 (m, 3H), 7.40-7.25 (m, 6H), 7.18 (t, J = 7.2 Hz, 1H), 6.87 (d, J = 8.8 Hz, 1H), 6.81 (s, 1H), 4.39 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 145.72, 139.12, 135.12, 128.91, 128.64, 127.56, 127.28, 126.28, 125.95, 122.01, 117.81, 104.58, 48.28.

16: [S10] 

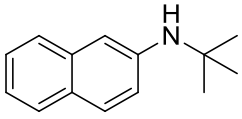
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.69-7.60 (m, 3H), 7.38-7.31 (m, 3H), 7.22-7.17 (m, 3H), 6.91 (dd, *J* = 2.4 Hz, *J* = 8.8 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 4.40 (s, 2H), 4.16 (s, 1H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 145.82, 136.96, 136.08, 135.17, 129.33, 128.90, 127.60, 126.27, 125.96, 121.97, 117.85, 104.58, 48.10, 21.08.

17: [S3] 

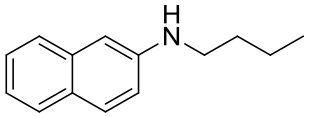
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.63-7.57 (m, 2H), 7.48-7.46 (m, 1H), 7.41-7.39 (m, 2H), 7.33-7.28 (m, 3H),7.24-7.21 (m, 1H), 7.16-7.12 (m, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 6.62 (s, 1H), 4.63-4.58 (m, 1H), 4.18 (s, 1H), 1.55 (dd, *J* = 1.2 Hz, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 144.87, 144.77, 135.00, 128.76, 128.64, 127.51, 127.33, 126.91, 126.12, 125.94, 125.83, 121.87, 117.93, 105.62, 53.40, 24.80.

18: [S5] 

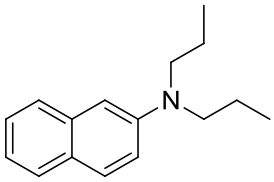
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.66-7.58 (m, 3H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.85 (dd, *J* = 2.4 Hz, *J* = 8.8 Hz, 1H), 6.80 (s, 1H), 3.72 (bs, 1H), 3.44-3.37 (m, 1H), 2.15-2.12 (m, 2H), 1.83-1.77 (m, 2H), 1.71-1.67 (m, 1H), 1.48-1.38 (m, 2H), 1.31-1.20 (m, 3H); GC-MS: m/z = 225.1 $[M]^+$, 182.1, 135.9.

19: [S8] 

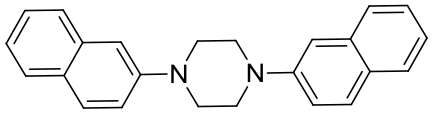
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.65 (d, *J* = 8.4 Hz, 1H), 7.61-7.58 (m, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 2.0 Hz, 1H), 6.88 (dd, *J* = 2.4 Hz, *J* = 8.8 Hz, 1H), 3.45 (bs, 1H), 1.41 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 144.33, 134.83, 128.53, 127.45, 126.10, 126.07, 122.19, 120.92, 109.34, 51.50, 29.87.

20: [S5] 

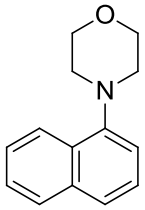
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.57-7.49 (m, 3H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.0 Hz, 1H), 6.74-6.68 (m, 2H), 3.08 (t, *J* = 6.8 Hz, 2H), 1.55-1.52 (m, 2H), 1.38-1.33 (m, 2H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 146.26, 135.41, 128.91, 127.72, 127.49, 126.35, 125.95, 121.86, 118.08, 104.24, 43.78, 31.62, 20.47, 14.04.

21: [S11] 

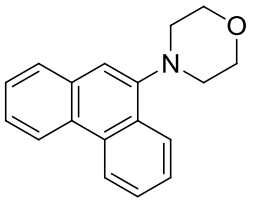
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.68-7.60 (m, 3H), 7.34 (t, *J* = 6.8 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.83 (s, 1H), 3.35 (t, *J* = 7.6 Hz, 4H), 1.73-1.64 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 146.22, 135.27, 128.71, 127.35, 126.07, 125.84, 121.38, 115.89, 105.25, 53.03, 20.55, 11.49.

22: [S5] 

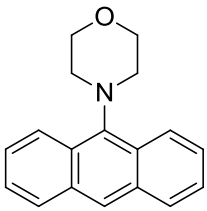
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.79-7.73 (m, 6H), 7.43 (td, *J* = 0.8 Hz, *J* = 7.6 Hz, 2H), 7.37-7.30 (m, 4H), 7.21 (d, *J* = 1.6 Hz, 2H), 3.51 (s, 8H); GC-MS: m/z = 228.3 $[M]^+$, 182.1, 155.2, 135.9.

23: [S12] 

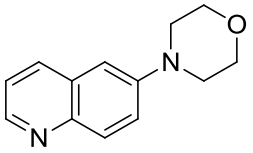
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.23-8.21 (m, 1H), 7.83 (t, *J* = 4.4 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.51-7.46 (m, 2H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 3.99 (t, *J* = 4.4 Hz, 4H), 3.12 (t, *J* = 4.0 Hz, 4H); GC-MS: *m/z* = 263.0 $[M]^+$, 204.0, 176.0.

24: [S12] 

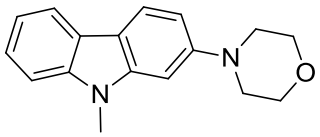
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.70 (d, *J* = 8.4 Hz, 1H), 8.63-8.60 (m, 1H), 8.32 (d, *J* = 7.6 Hz, 1H), 7.82-7.80 (m, 1H), 7.68-7.61 (m, 2H), 7.58-7.54 (m, 2H), 7.30 (s, 1H), 4.03 (t, *J* = 4.4 Hz, 4H), 3.19 (bs, 4H); GC-MS: m/z = 263.1 $[M]^+$, 204.2, 176.2.

25: [S13] 

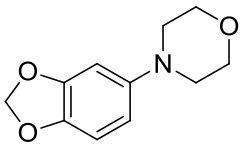
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.54 (d, *J* = 8.4 Hz, 2H), 8.34 (s, 1H), 8.02 (d, *J* = 7.6 Hz, 2H), 7.51-7.44 (m, 4H), 4.05 (t, *J* = 4.4 Hz, 4H), 3.54 (t, *J* = 4.4 Hz, 4H); GC-MS: *m/z* = 263.0 $[M]^+$, 204.0, 176.0.

26: [S14] 

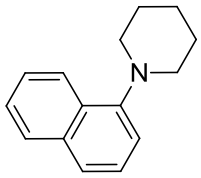
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.73 (d, *J* = 2.4 Hz, 1H), 8.01-7.98 (m, 2H), 7.48 (dd, *J* = 9.6 Hz, *J* = 2.4 Hz, 1H), 7.34-7.31 (m, 1H), 7.03 (d, *J* = 2.4 Hz, 1H), 3.92 (t, *J* = 4.8 Hz, 4H), 3.29 (t, *J* = 4.8 Hz, 4H); GC-MS: m/z = 214.1 $[M]^+$, 156.0, 128.0.

27: [S12] 

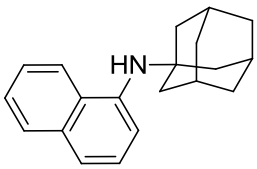
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.97 (t, *J* = 8.8 Hz, 2H), 7.42-7.34 (m, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.84 (s, 1H), 3.94 (t, *J* = 4.8 Hz, 4H), 3.81 (s, 3H), 3.30 (t, *J* = 4.8 Hz, 4H); GC-MS: m/z = 266.3 $[M]^+$, 208.2, 180.2.

28: [S12] 

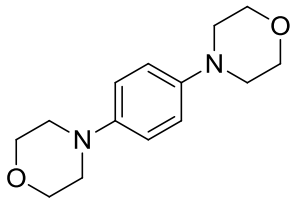
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 6.73 (d, *J* = 8.4 Hz, 1H), 6.55 (s, 1H), 6.35 (d, *J* = 8.0 Hz, 1H), 5.91 (s, 2H), 3.85 (t, *J* = 4.4 Hz, 4H), 3.04 (t, *J* = 4.4 Hz, 4H); GC-MS: m/z = 207.2 $[M]^+$, 149.2.

29: [S15] 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.19 (d, *J* = 7.2 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.47-7.43 (m, 2H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 3.06-3.03 (m, 4H), 1.86-1.83 (m, 4H), 1.68-1.64 (m, 2H); GC-MS: m/z = 210.2 $[M-1]^+$, 154.1, 127.1.

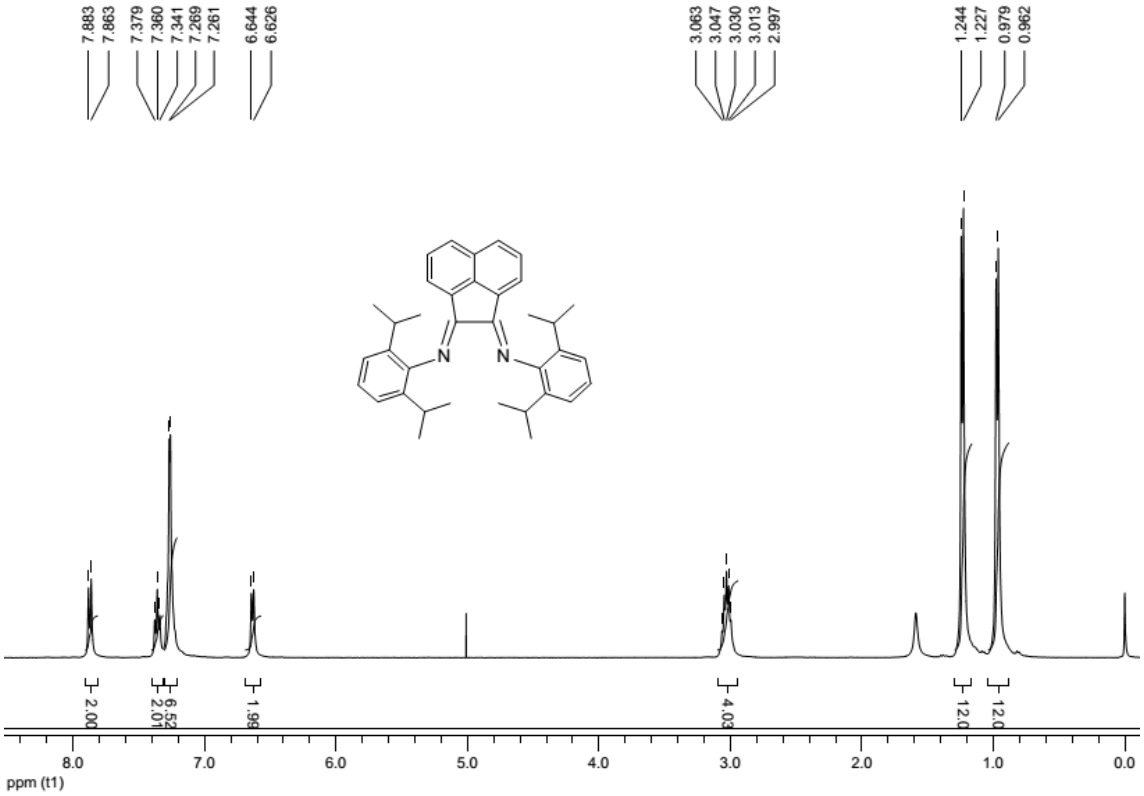
30:[S16] 

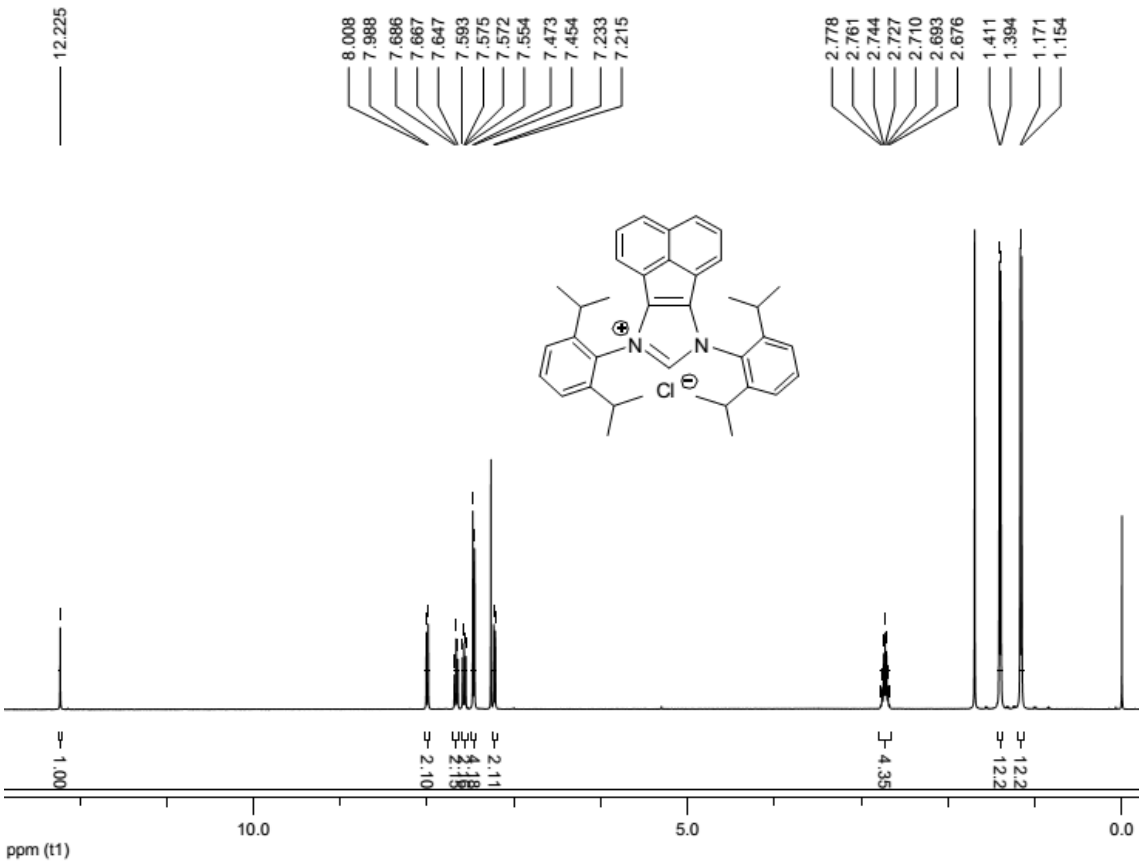
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.90-7.88 (m, 1H), 7.80-7.76 (m, 1H), 7.44-7.41 (m, 2H), 7.32 (d, *J* = 4.4 Hz, 2H), 7.05 (t, *J* = 4.0 Hz, 1H), 4.04 (bs, 1H), 2.14 (s, 3H), 2.03 (s, 6H), 1.71 (s, 6H); GC-MS: m/z = 277.1 $[M]^+$, 220.1, 135.1.

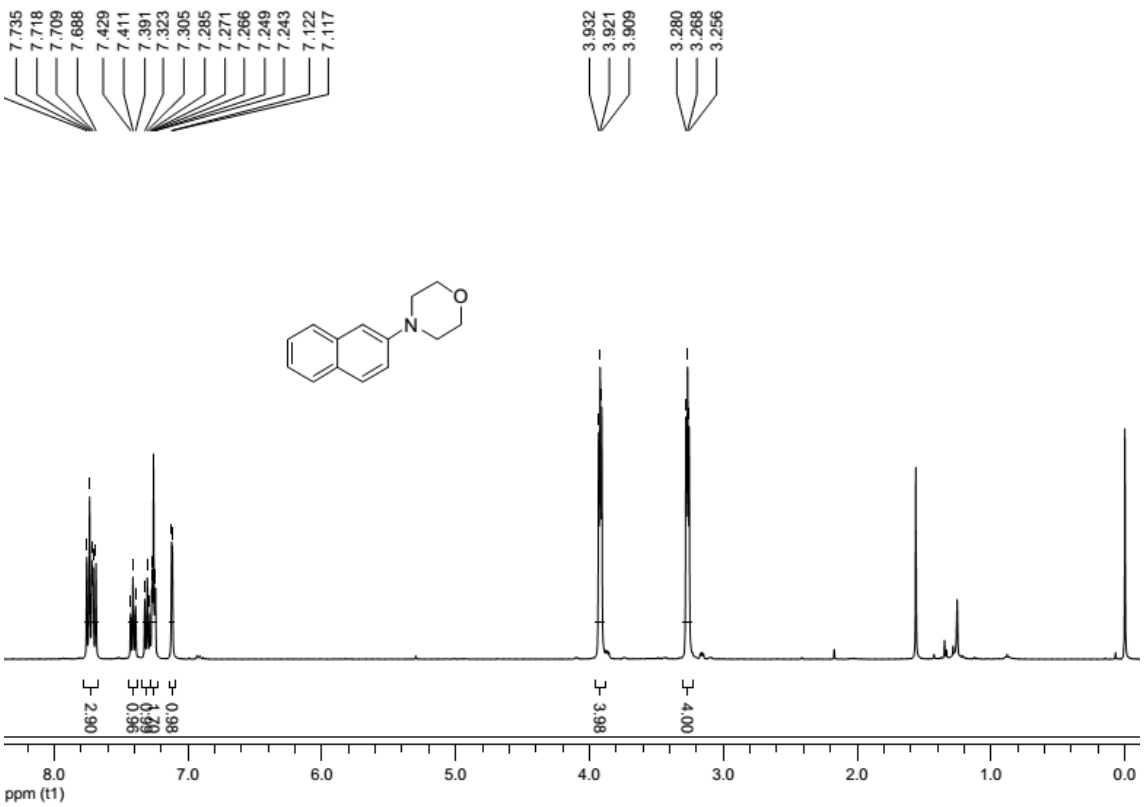
31: [S17] 

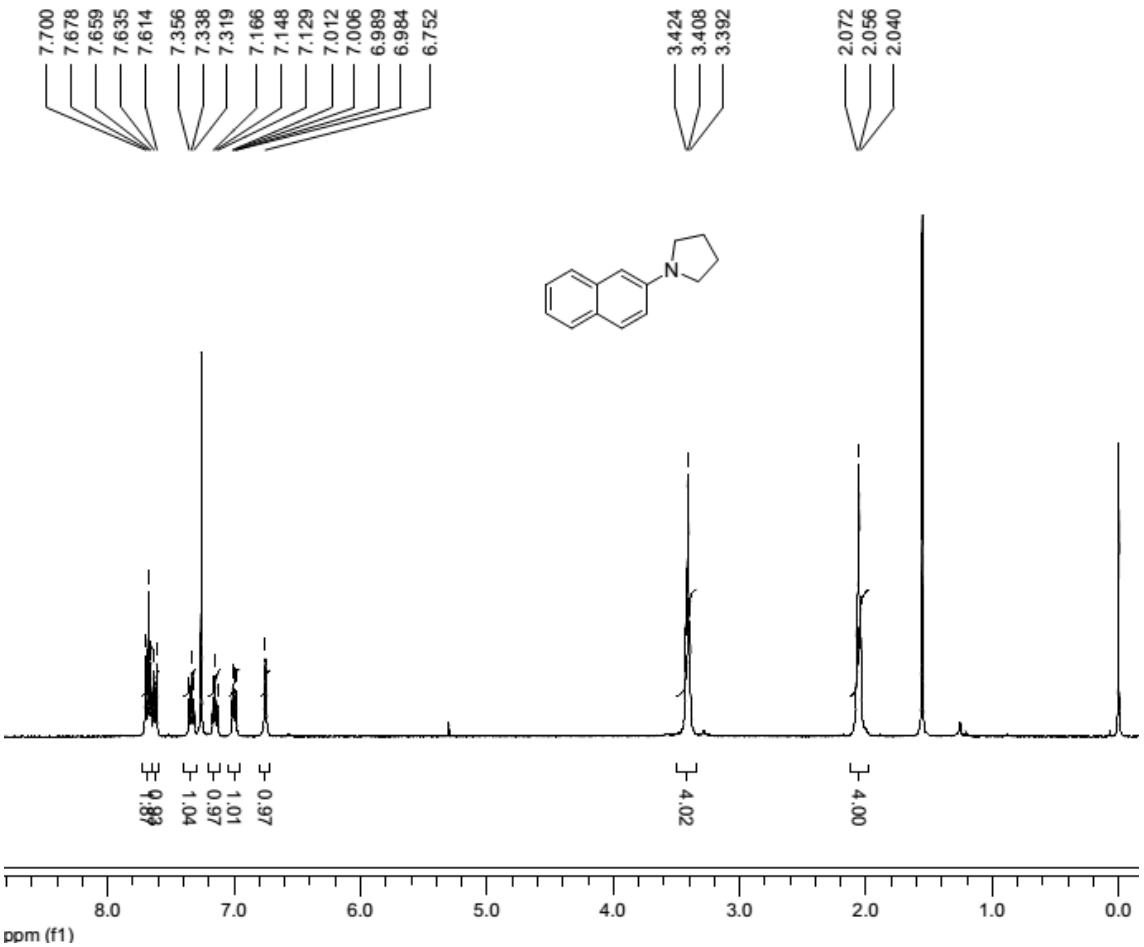
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 6.90 (s, 4H), 3.86 (t, *J* = 4.8 Hz, 8H), 3.07 (t, *J* = 4.8 Hz, 8H); GC-MS: m/z = 248.2 $[M]^+$, 190.1, 132.1.

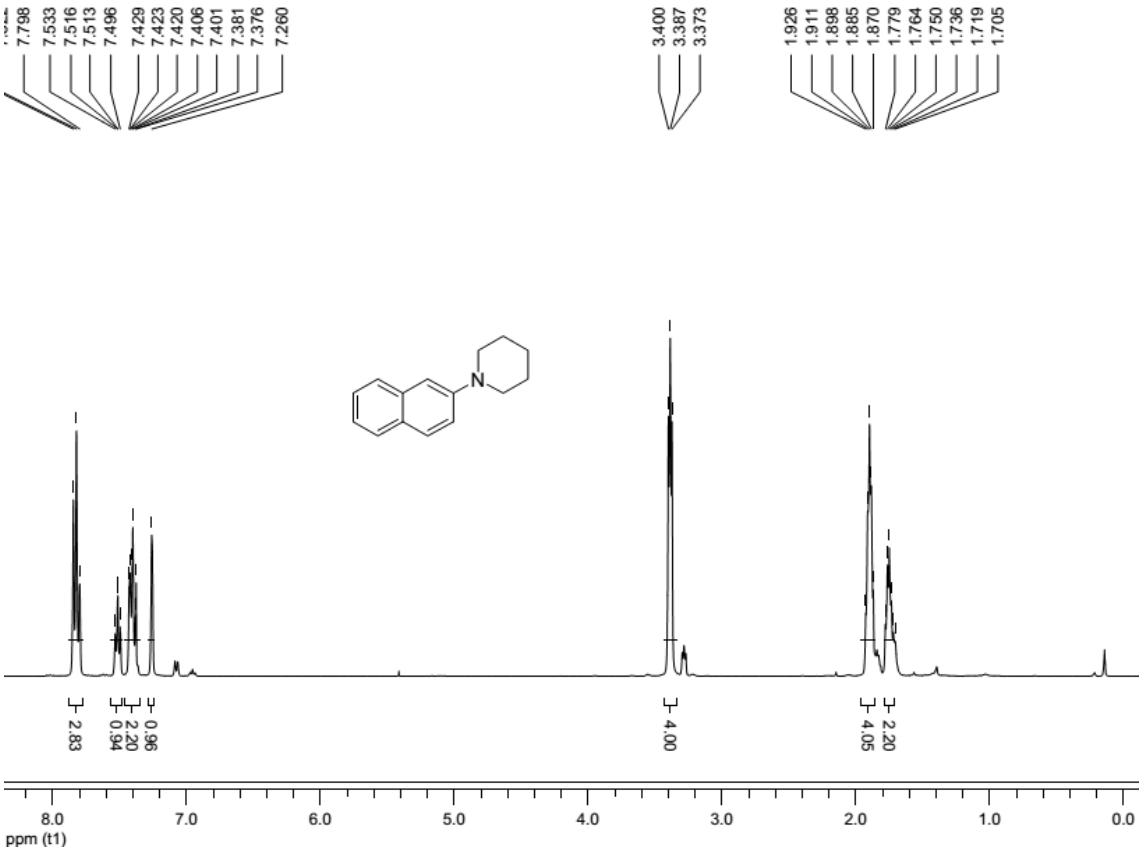
5. ^{1}H NMR, ^{13}C NMR and MS spectra for important compounds

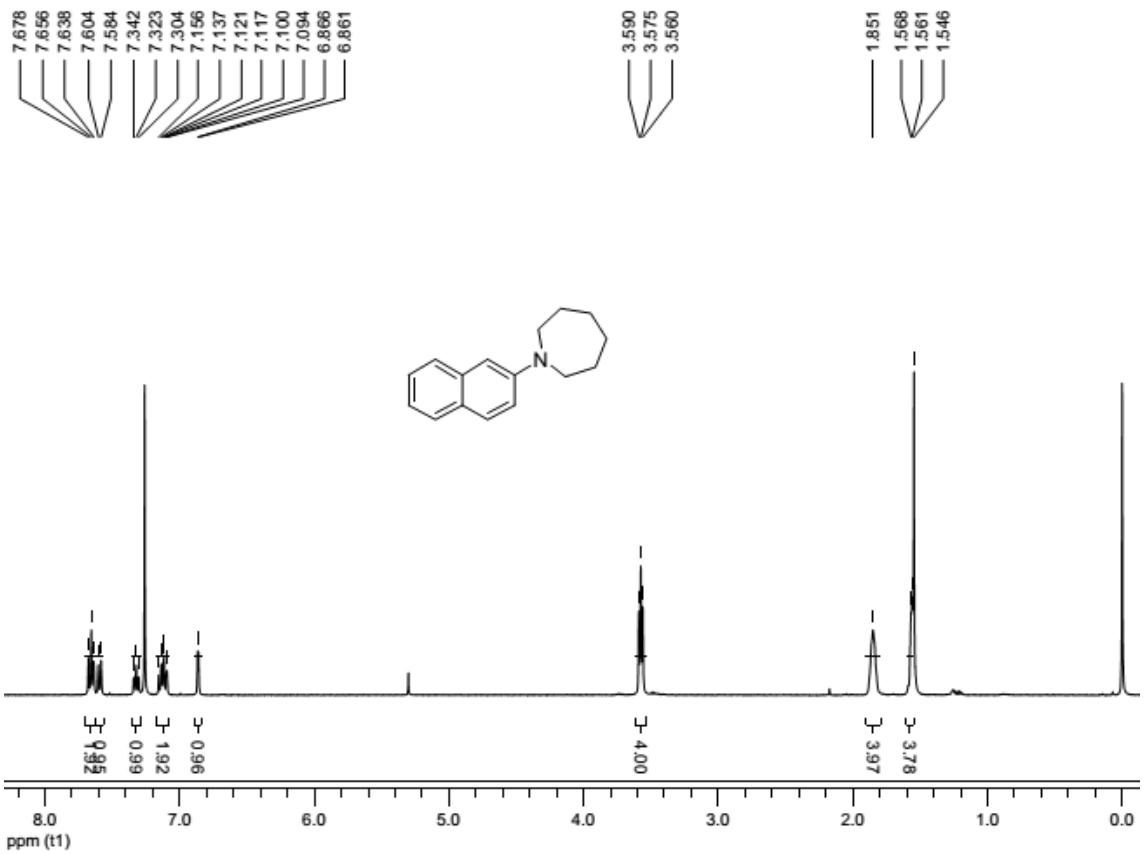


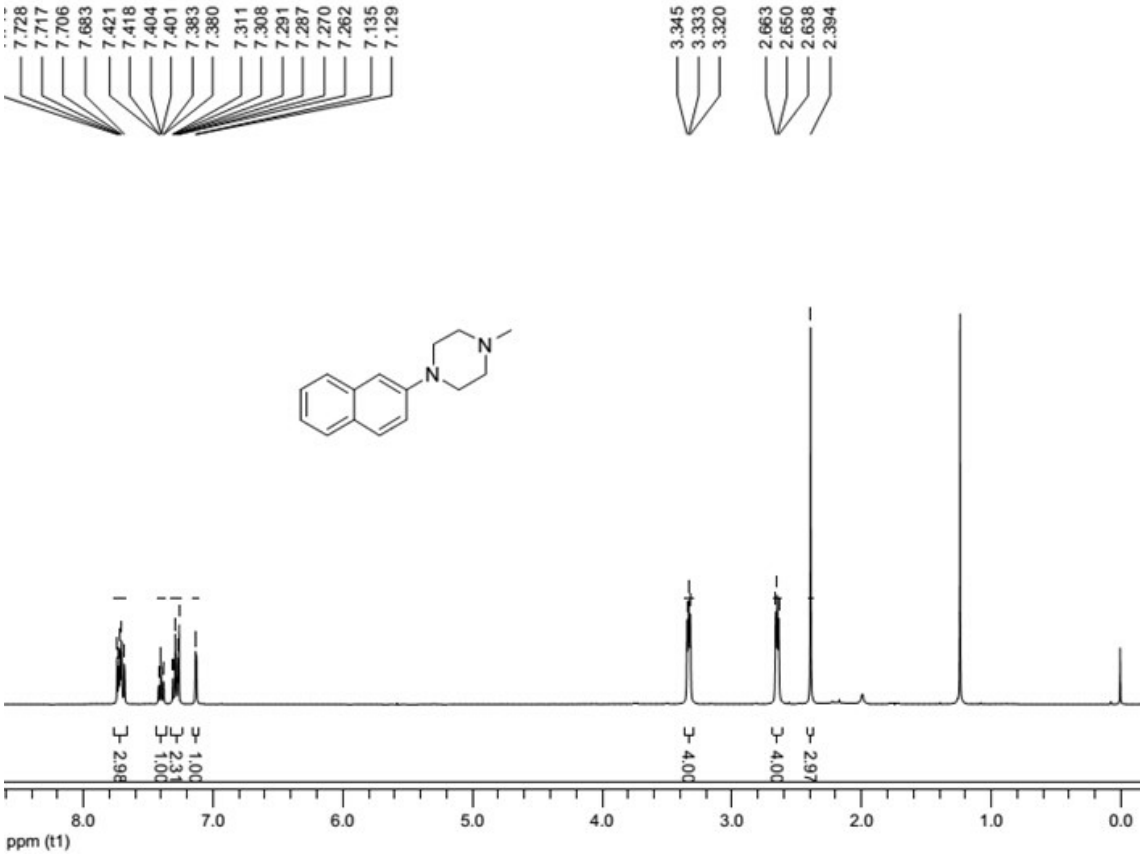


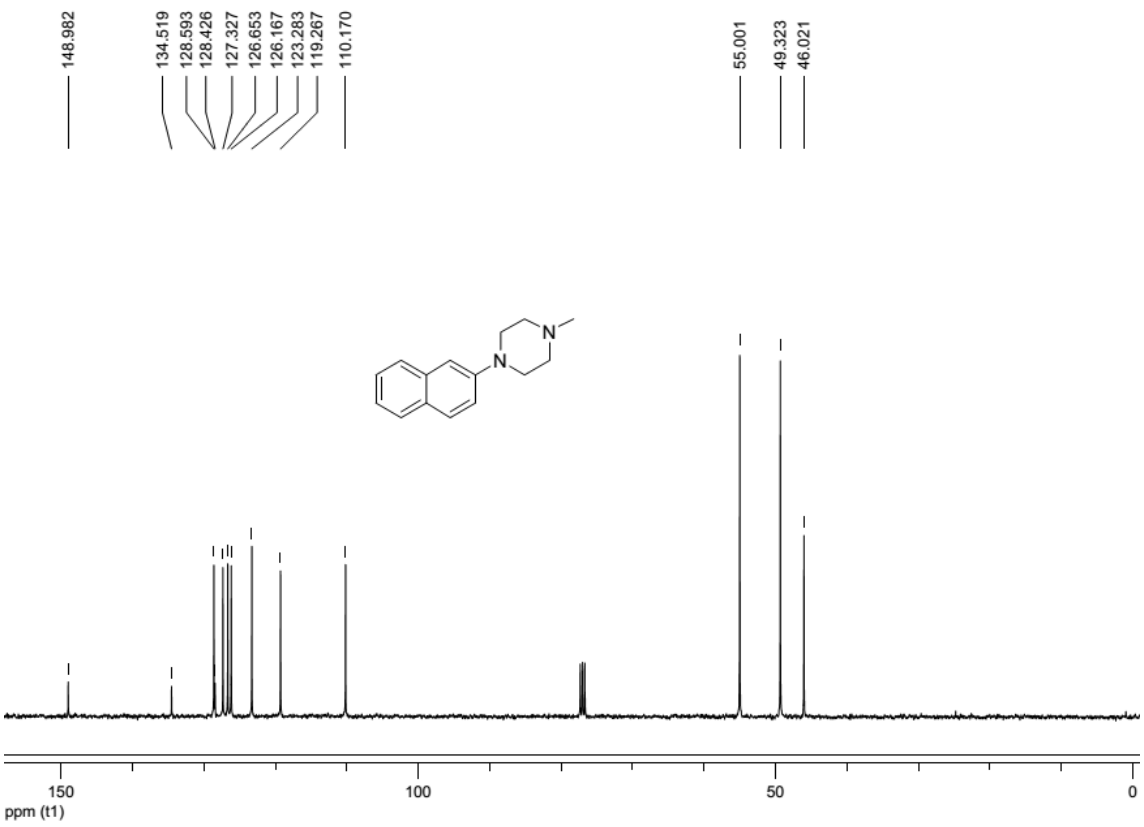

7.735
7.718
7.709
7.688
7.429
7.411
7.391
7.323
7.305
7.285
7.271
7.266
7.249
7.243
7.122
7.117
3.932
3.921
3.909
3.280
3.268
3.256
O
N
2.90
0.98
3.98
4.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

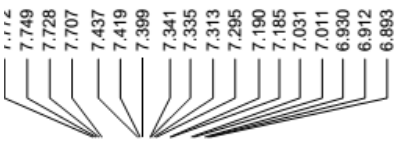

7.700
7.678
7.659
7.635
7.614
7.356
7.338
7.319
7.166
7.148
7.129
7.012
7.006
6.989
6.984
6.752
3.424
3.408
3.392
2.072
2.056
2.040
N
1.04
0.97
1.01
0.97
4.02
4.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

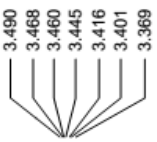

7.798
7.533
7.516
7.513
7.496
7.429
7.423
7.420
7.406
7.401
7.381
7.376
7.260
3.400
3.387
3.373
1.926
1.911
1.898
1.885
1.870
1.779
1.764
1.750
1.736
1.719
1.705
N
2.83
0.94
2.20
0.96
4.00
4.05
2.20
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

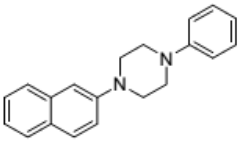

7.678
7.656
7.638
7.604
7.584
7.342
7.323
7.304
7.156
7.137
7.121
7.117
7.100
7.094
6.866
6.861
3.590
3.575
3.560
1.851
1.568
1.561
1.546
N
0.95
0.99
1.92
0.96
4.00
3.97
3.78
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

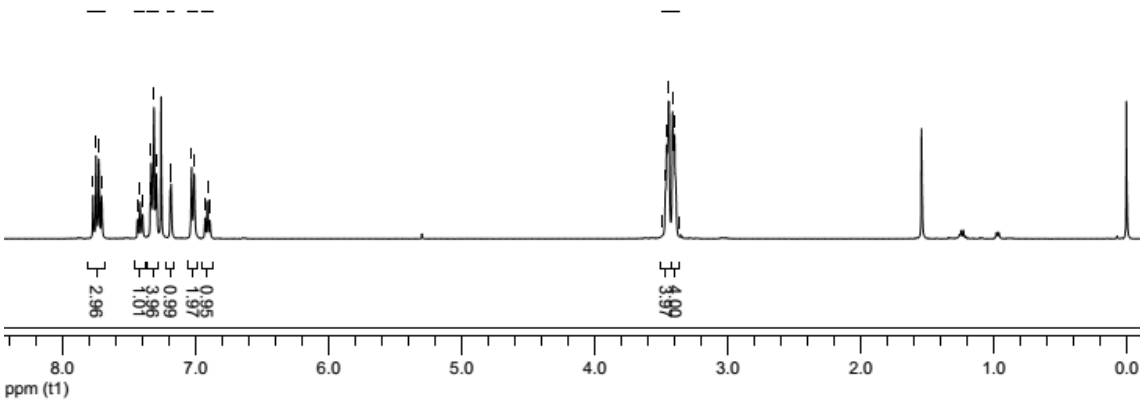

7.728
7.717
7.706
7.683
7.421
7.418
7.404
7.401
7.383
7.380
7.311
7.308
7.291
7.287
7.270
7.262
7.135
7.129
3.345
3.333
3.320
2.663
2.650
2.638
2.394
2.98
2.13
1.00
4.00
4.00
2.97
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

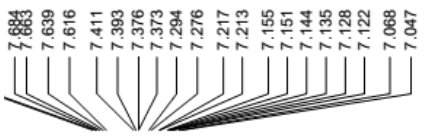

148.982
134.519
128.593
128.426
127.327
126.653
126.167
123.283
119.267
110.170
55.001
49.323
46.021
150
100
50
0
ppm (t1)


7.749
7.728
7.707
7.437
7.419
7.399
7.341
7.335
7.313
7.295
7.190
7.185
7.031
7.011
6.930
6.912
6.893

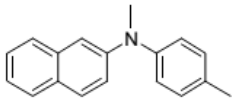

3.490
3.468
3.460
3.445
3.416
3.401
3.369

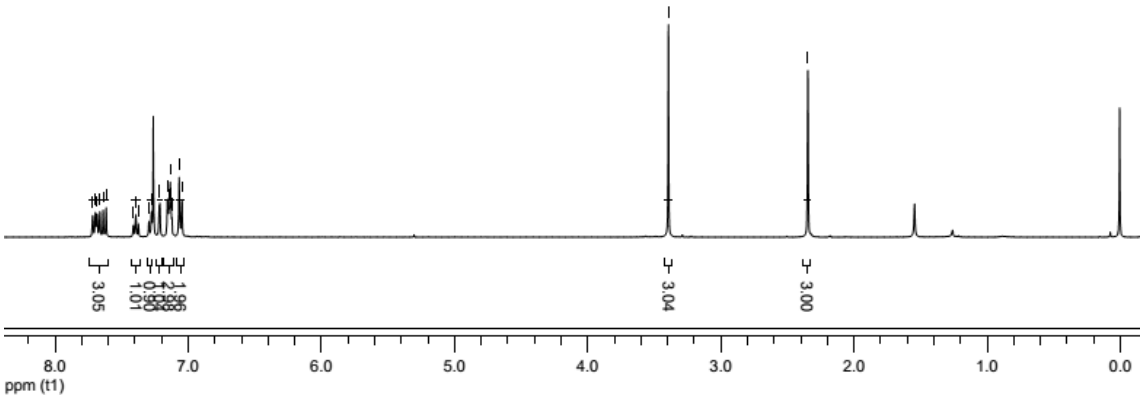

N
N

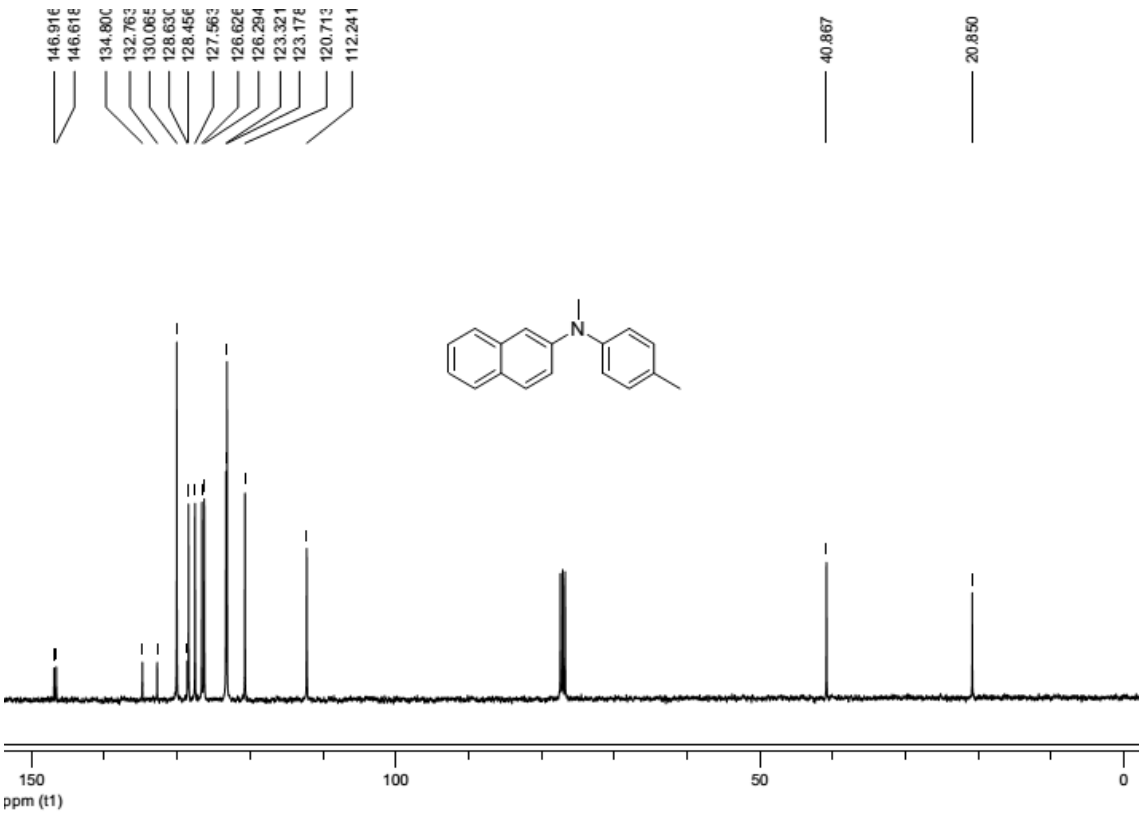

2.96
3.96
0.99
1.97
0.95
4.09
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

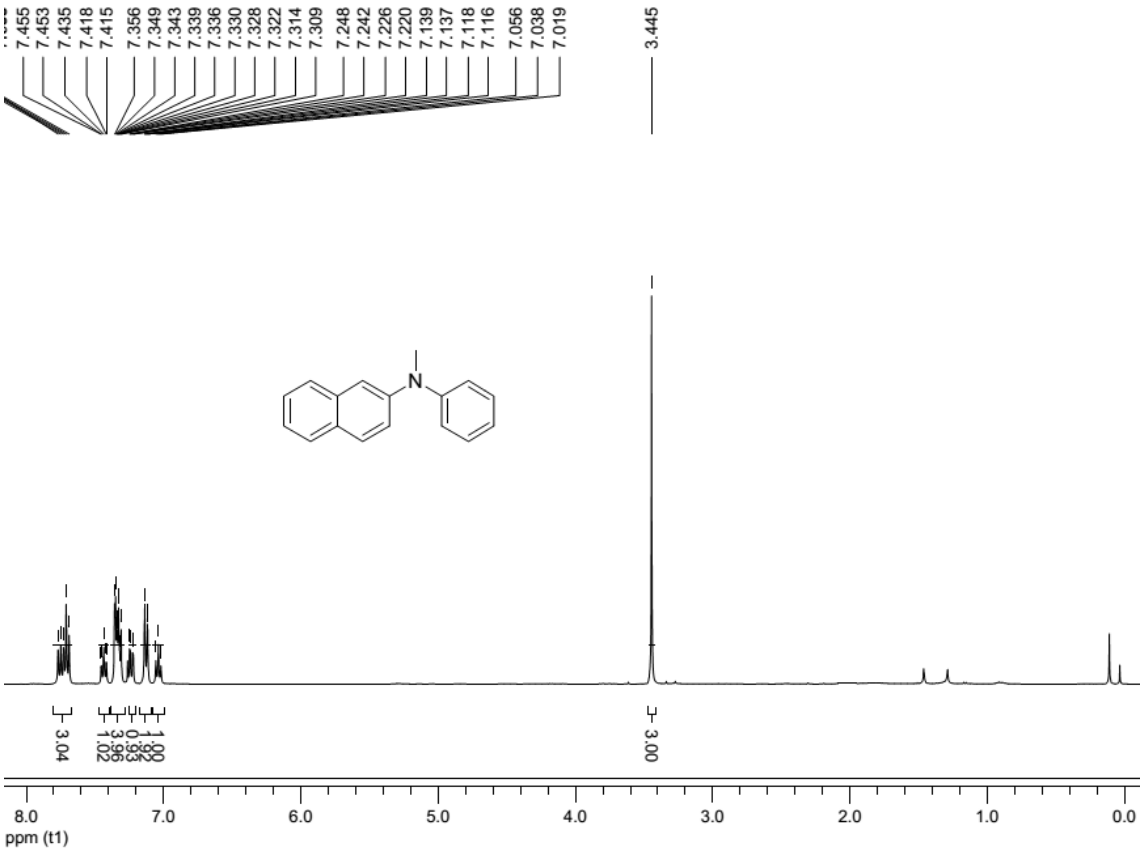

7.684
7.663
7.639
7.616
7.411
7.393
7.376
7.373
7.294
7.276
7.217
7.213
7.155
7.151
7.144
7.135
7.128
7.122
7.068
7.047

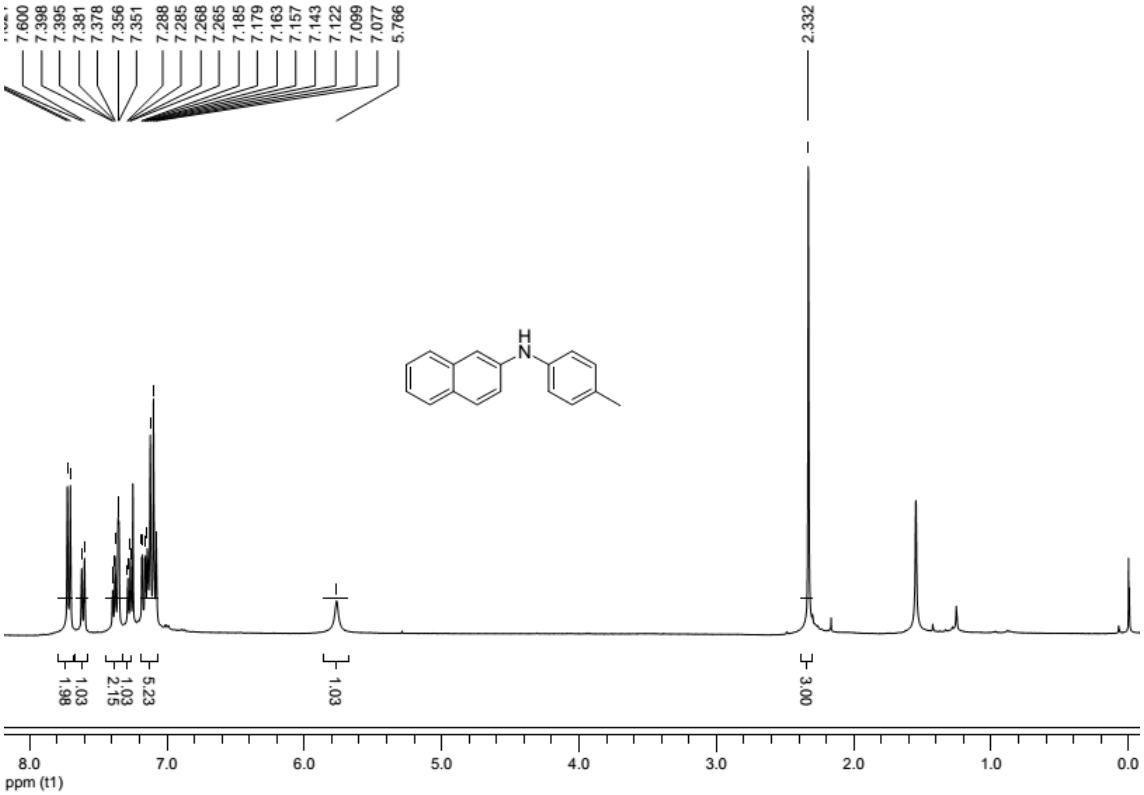

3.394
2.346

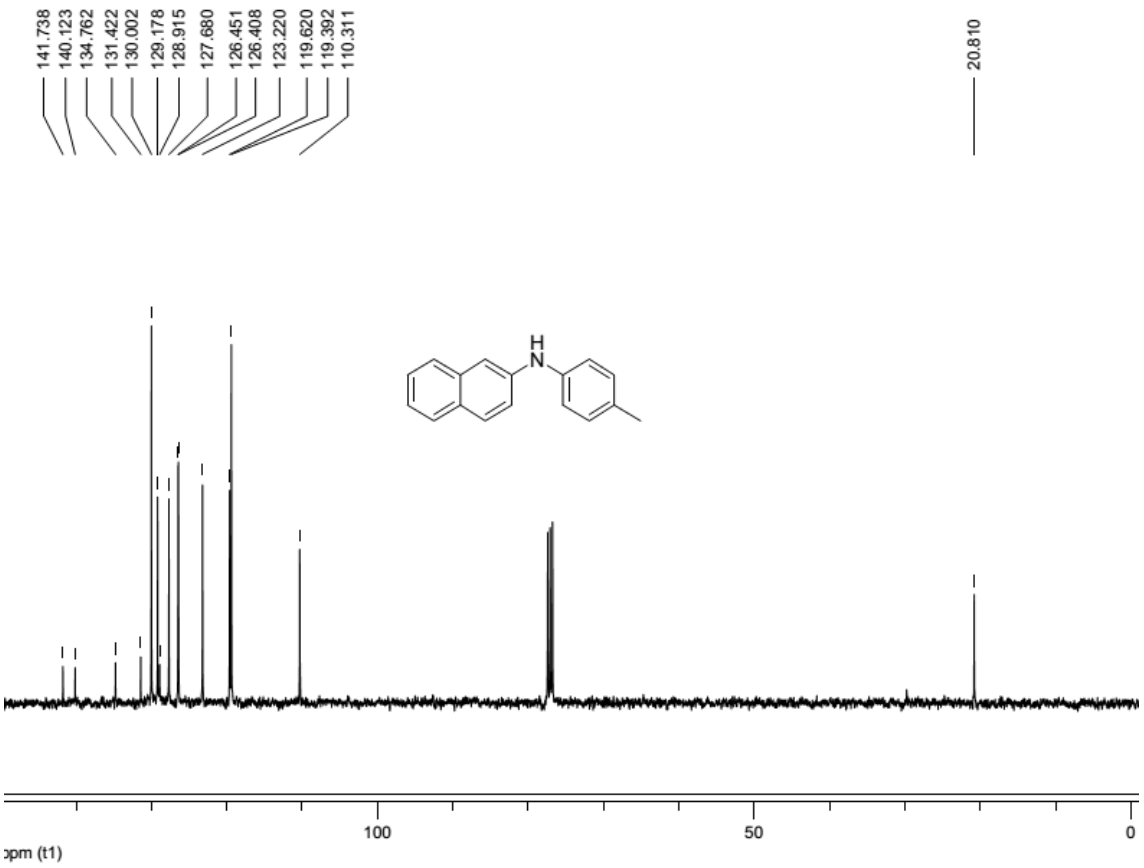

N

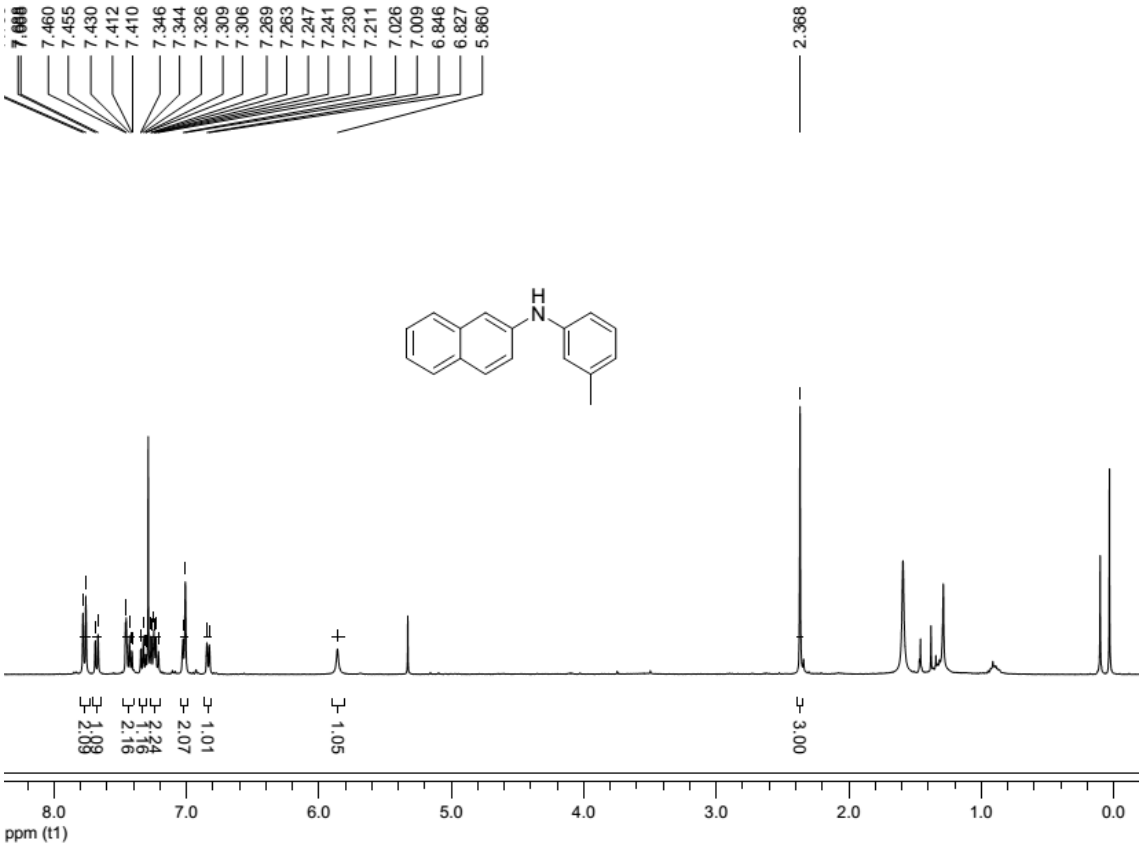

3.05
3.04
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

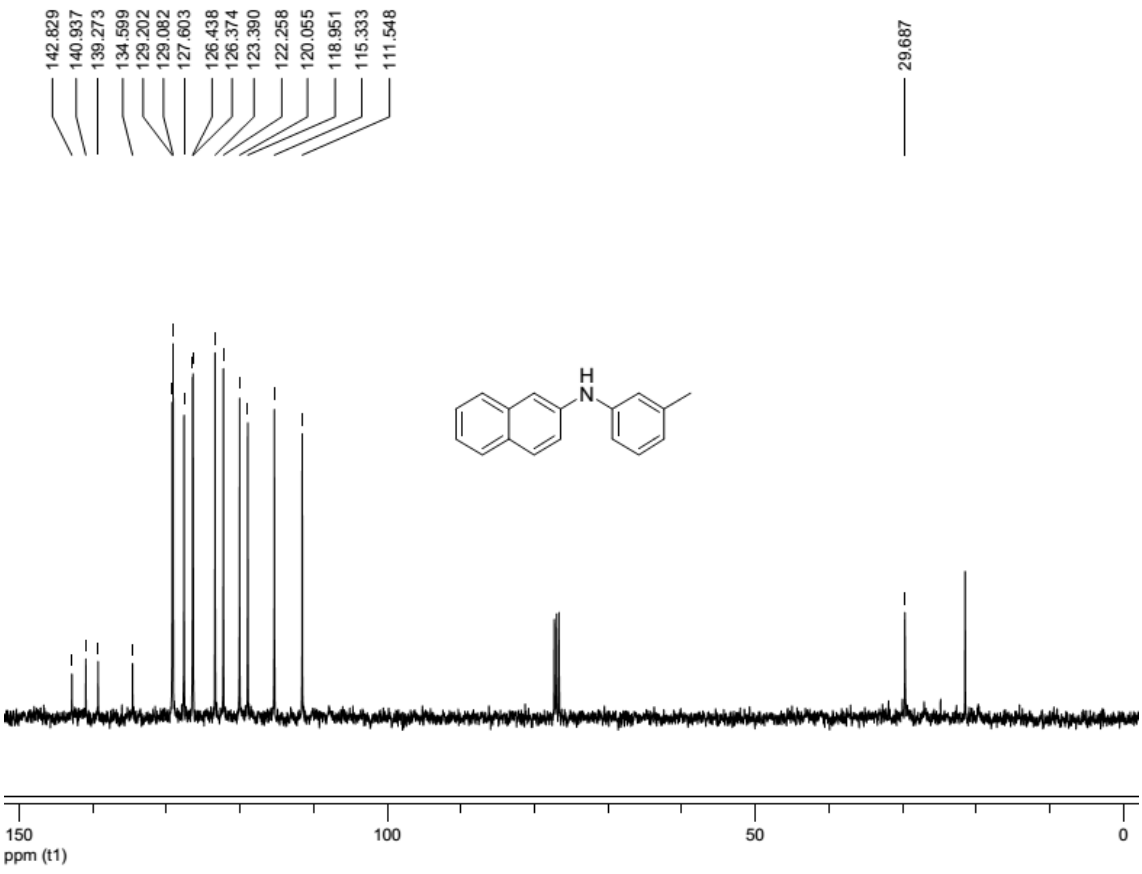

146.916
146.618
134.800
132.763
130.065
128.630
128.456
127.563
126.628
126.294
123.321
123.178
120.713
112.241
40.867
20.850
150
100
50
0
ppm (t1)

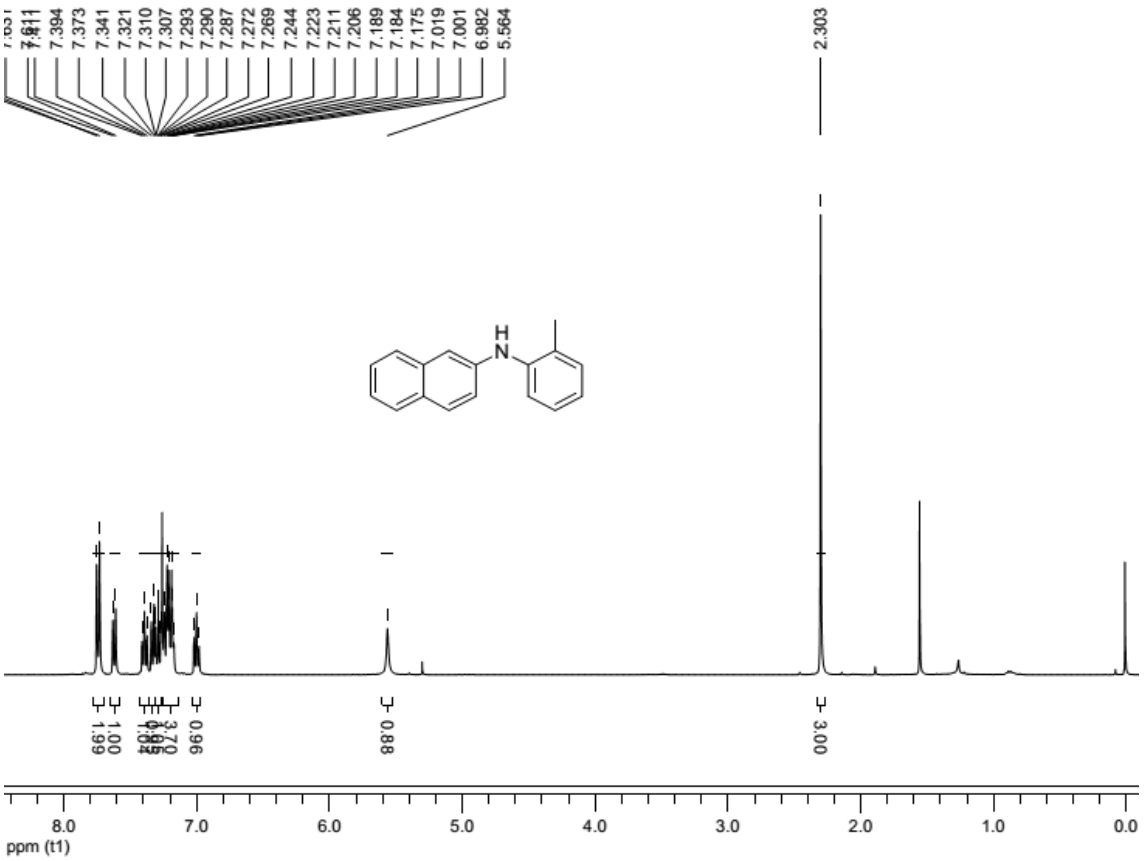

7.455
7.453
7.435
7.418
7.415
7.356
7.349
7.343
7.339
7.336
7.330
7.328
7.322
7.314
7.309
7.248
7.242
7.226
7.220
7.139
7.137
7.118
7.116
7.056
7.038
7.019
3.445
3.04
1.02
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

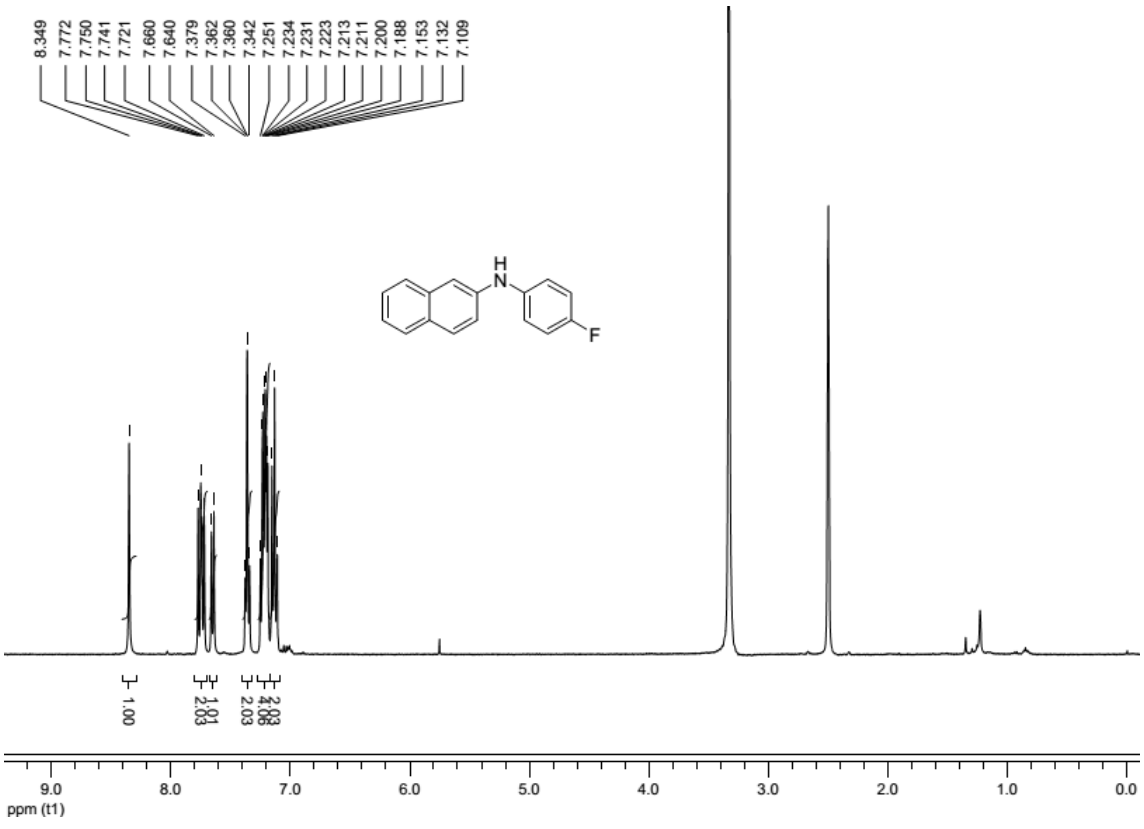

7.600
7.398
7.395
7.381
7.378
7.356
7.351
7.288
7.285
7.268
7.265
7.185
7.179
7.163
7.157
7.143
7.122
7.099
7.077
5.766
2.332
1.98
1.03
2.15
1.03
5.23
1.03
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

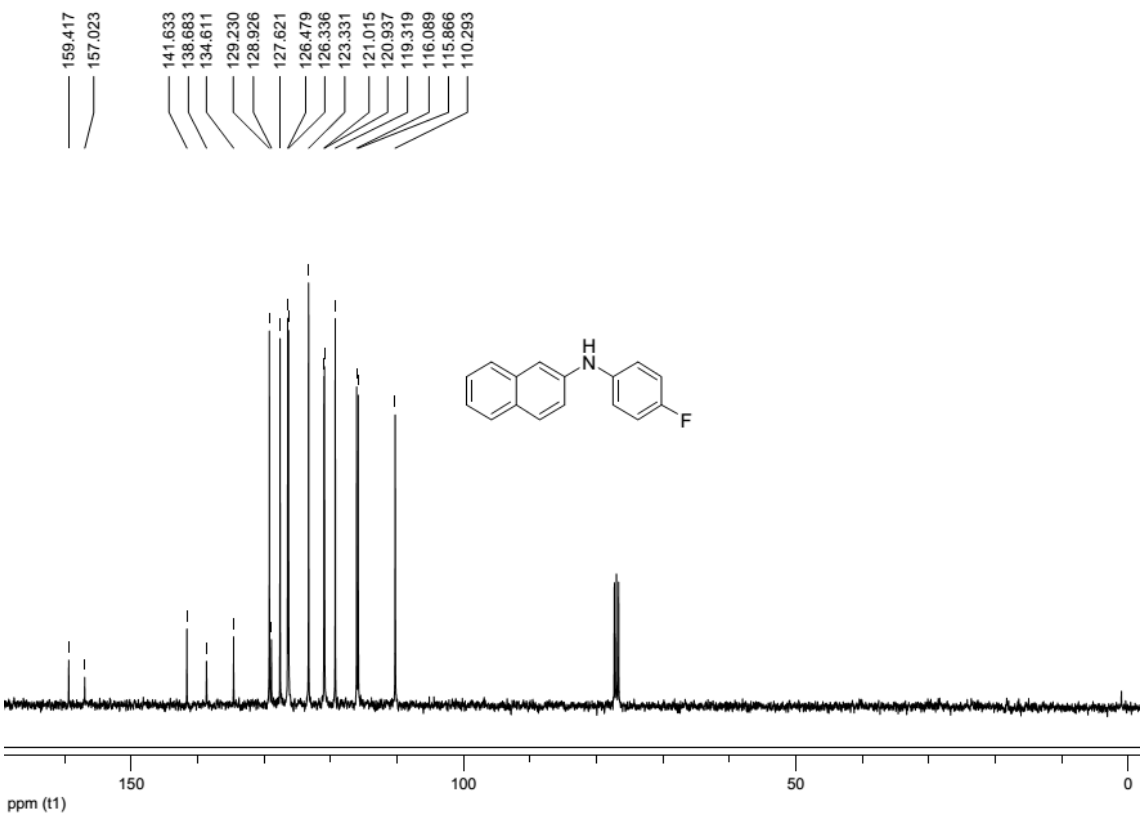

141.738
140.123
134.762
131.422
130.002
129.178
128.915
127.680
126.451
126.408
123.220
119.620
119.392
110.311
20.810
100
50
0
ppm (t1)

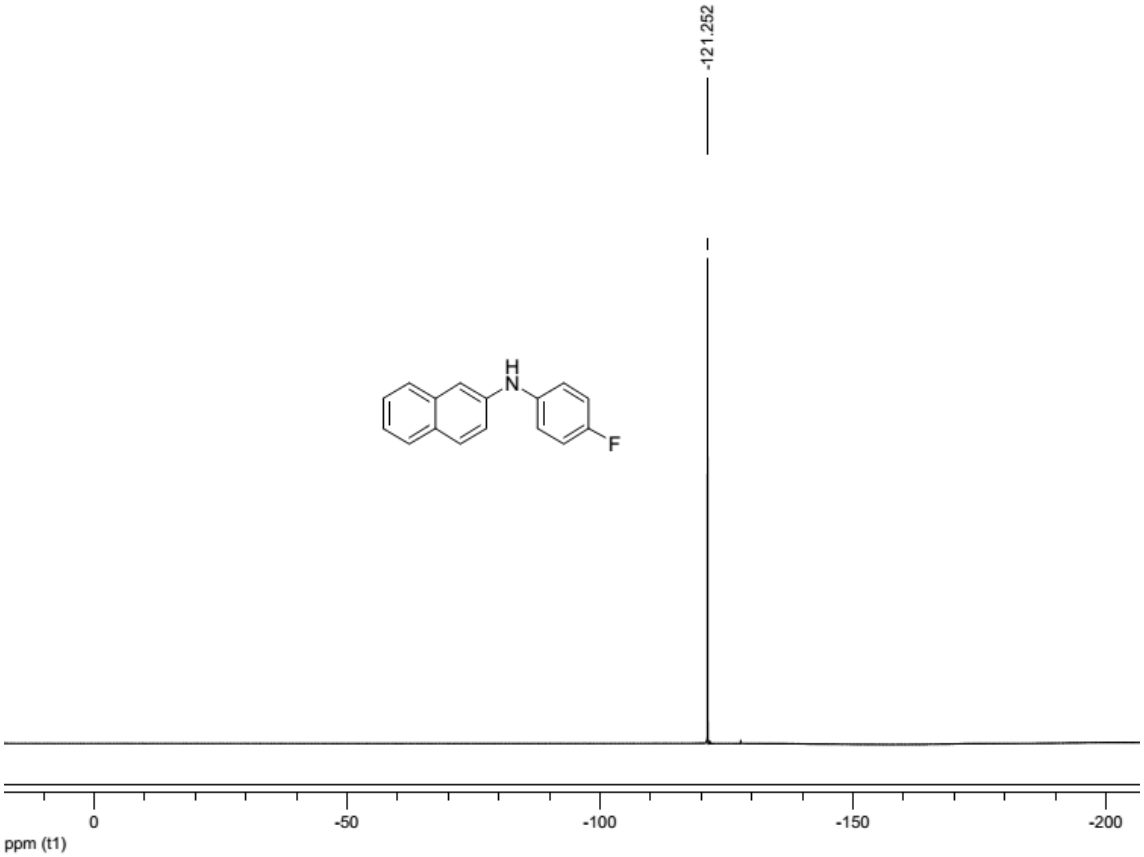

7.460
7.455
7.430
7.412
7.410
7.346
7.344
7.326
7.309
7.306
7.269
7.263
7.247
7.241
7.230
7.211
7.026
7.009
6.846
6.827
5.860
2.368
H
N
2.09
2.16
2.24
2.07
1.01
1.05
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

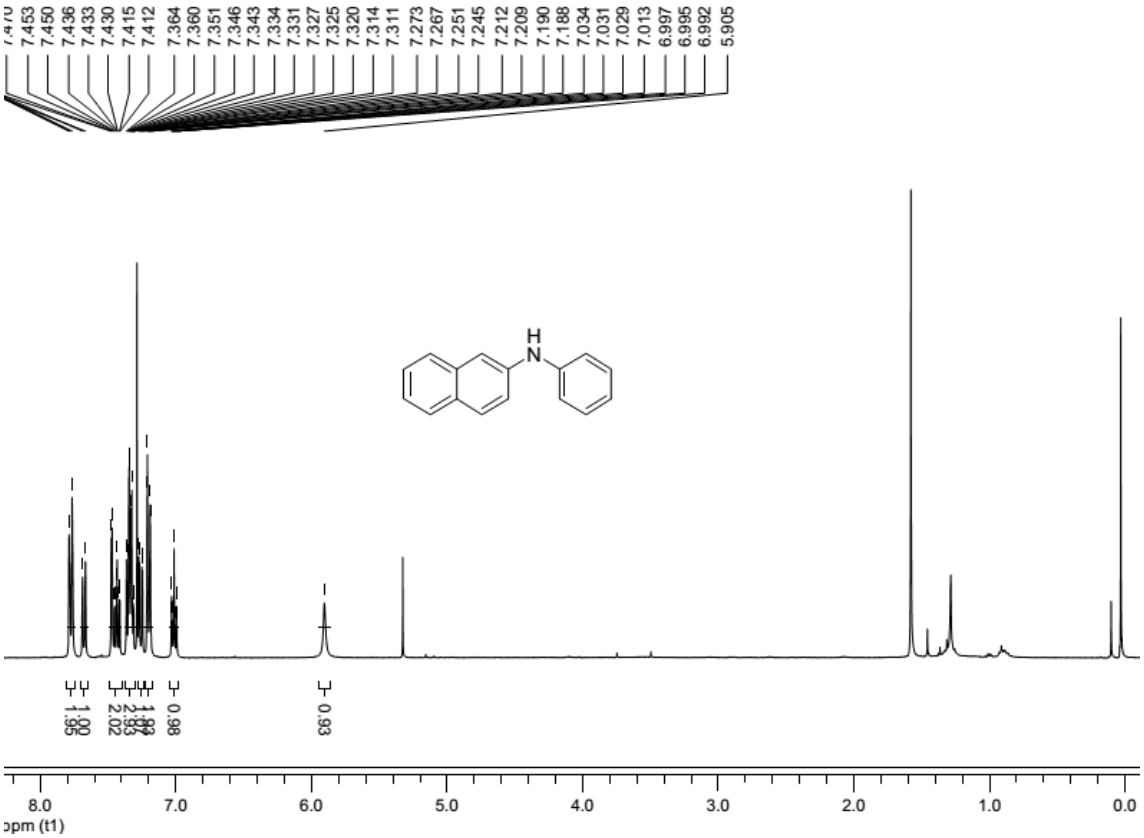

142.829
140.937
139.273
134.599
129.202
129.082
127.603
126.438
126.374
123.390
122.258
120.055
118.951
115.333
111.548
29.687
H
N
150
100
50
0
ppm (t1)

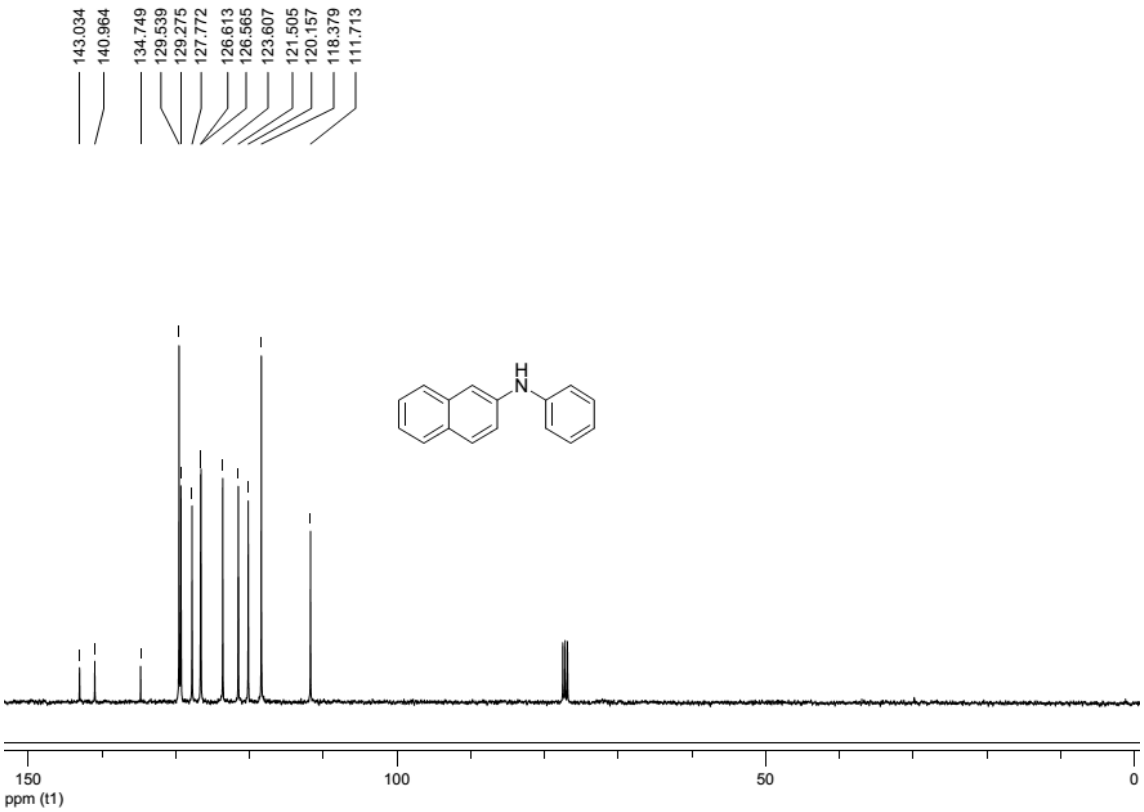

7.394
7.373
7.341
7.321
7.310
7.307
7.293
7.290
7.287
7.272
7.269
7.244
7.223
7.211
7.206
7.189
7.184
7.175
7.019
7.001
6.982
5.564
2.303
1.99
1.00
0.96
0.88
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

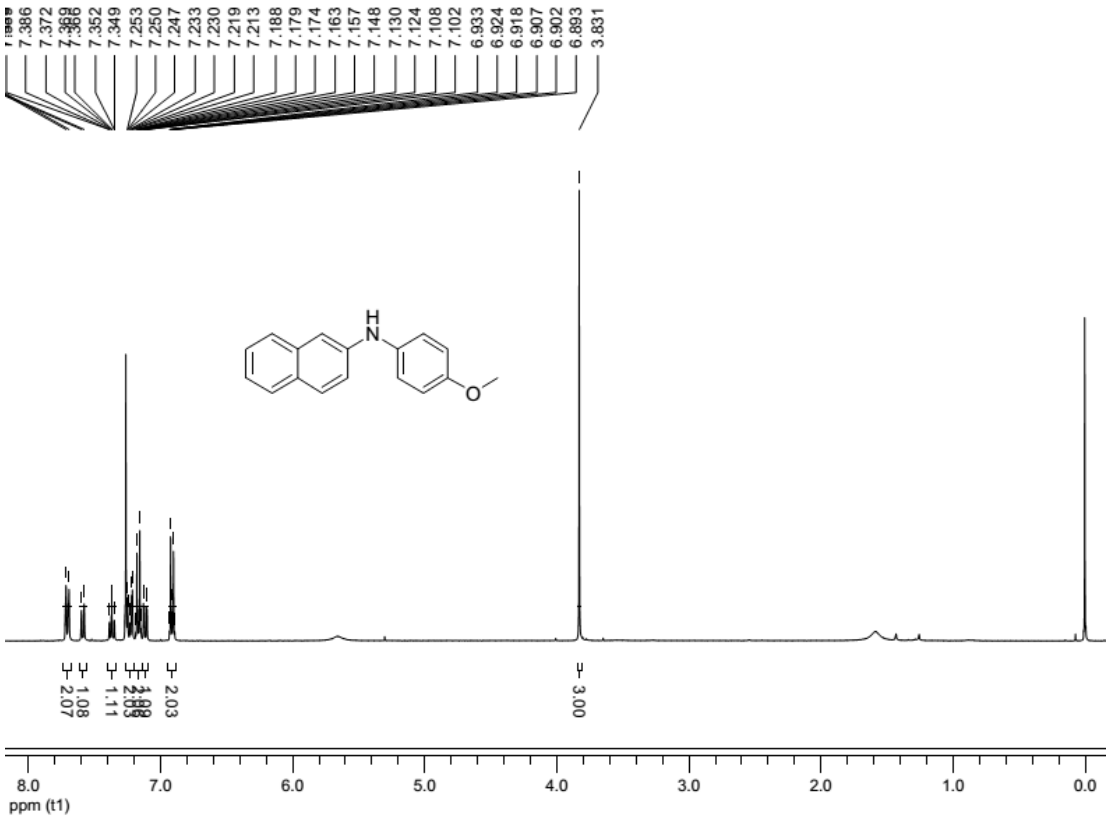

8.349
7.772
7.750
7.741
7.721
7.660
7.640
7.379
7.362
7.360
7.342
7.251
7.234
7.231
7.223
7.213
7.211
7.200
7.188
7.153
7.132
7.109
1.00
2.01
2.03
2.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

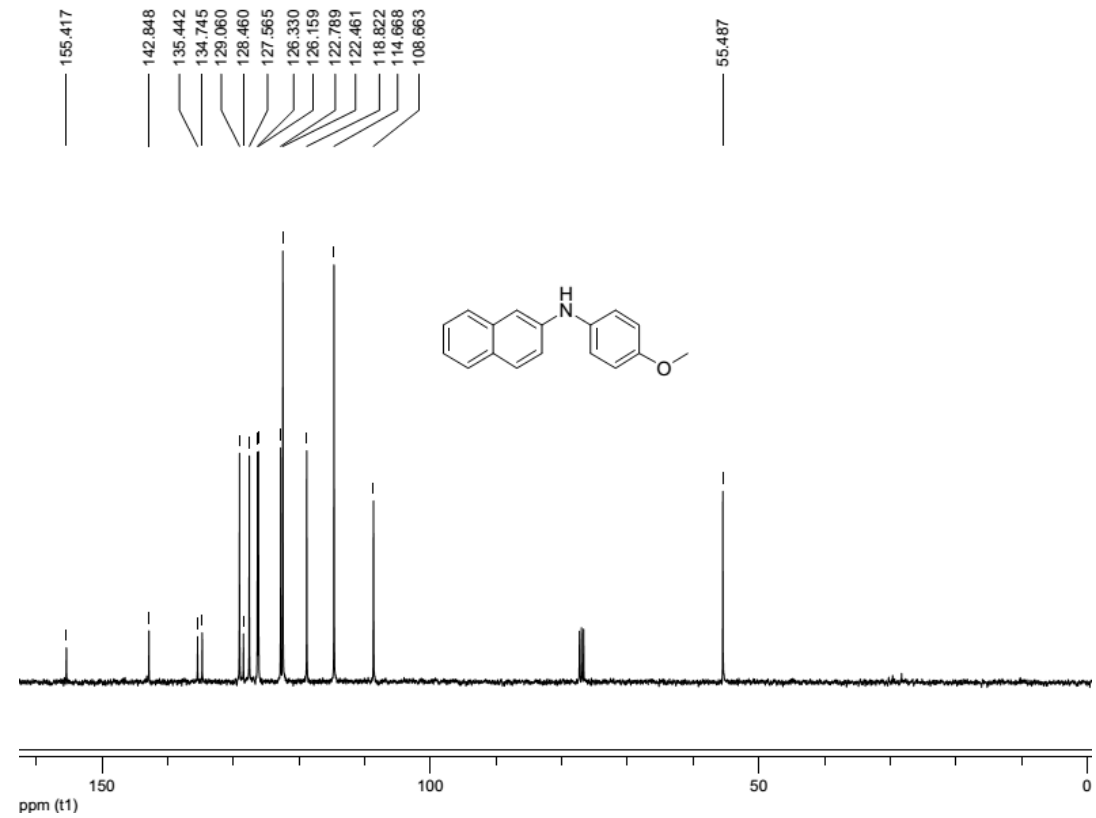

159.417
157.023
141.633
138.683
134.611
129.230
128.926
127.621
126.479
126.336
123.331
121.015
120.937
119.319
116.089
115.866
110.293
H
N
F
150
100
50
0
ppm (t1)

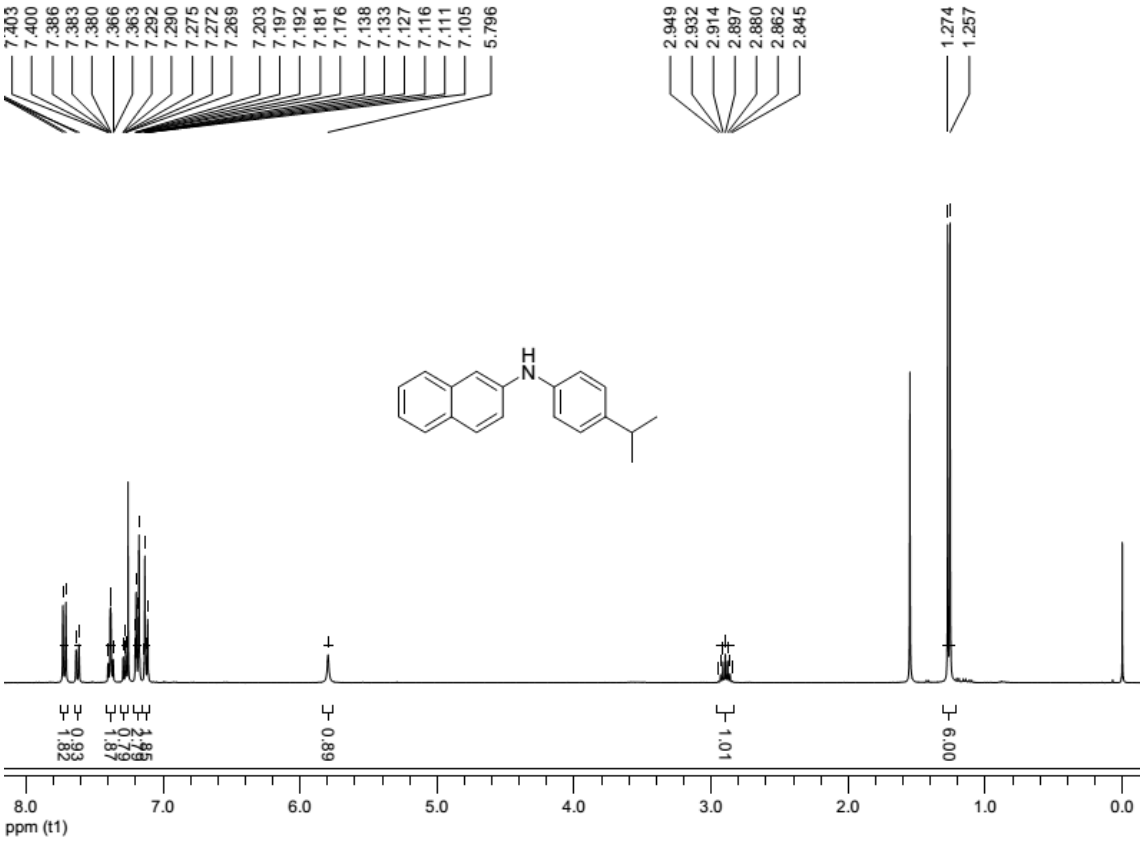

-121.252
H
N
F
0
-50
-100
-150
-200
ppm (t1)

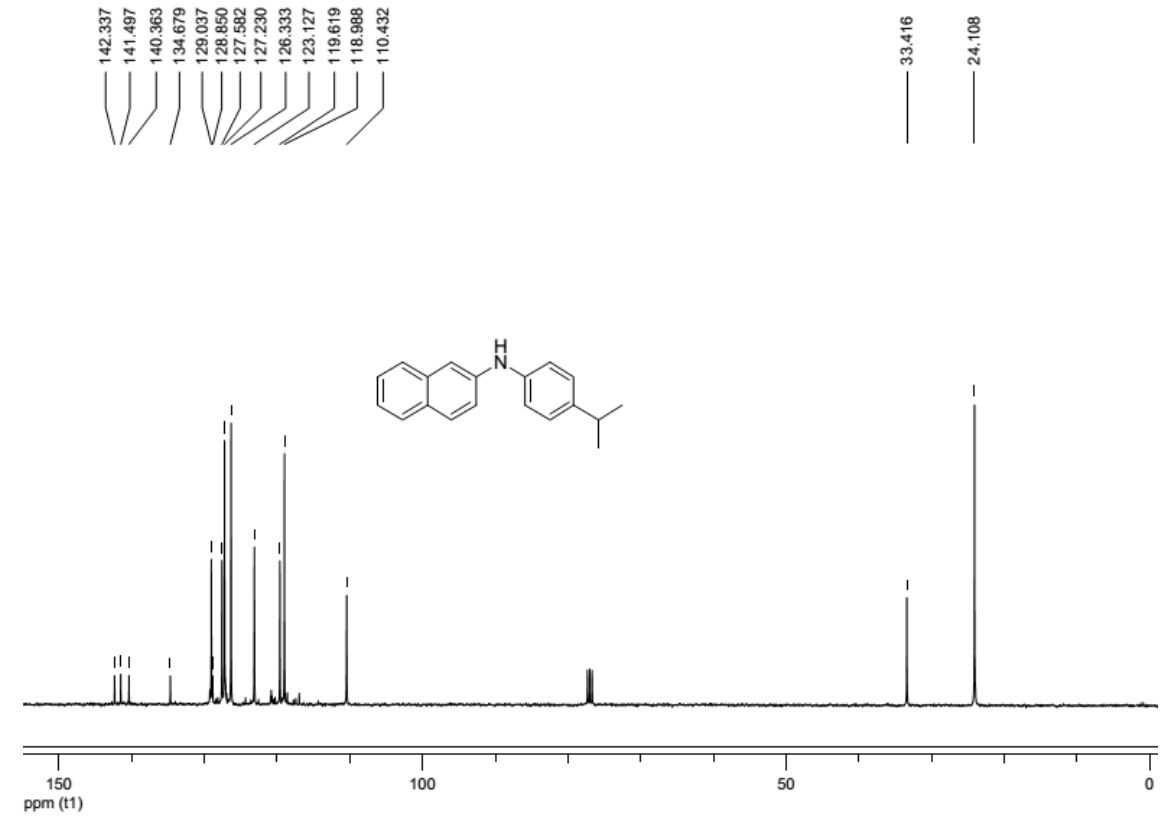

7.453
7.450
7.436
7.433
7.430
7.415
7.412
7.364
7.360
7.351
7.346
7.343
7.334
7.331
7.327
7.325
7.320
7.314
7.311
7.273
7.267
7.251
7.245
7.212
7.209
7.190
7.188
7.034
7.031
7.029
7.013
6.997
6.995
6.992
5.905
H
N
1.00
2.02
0.98
0.93
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

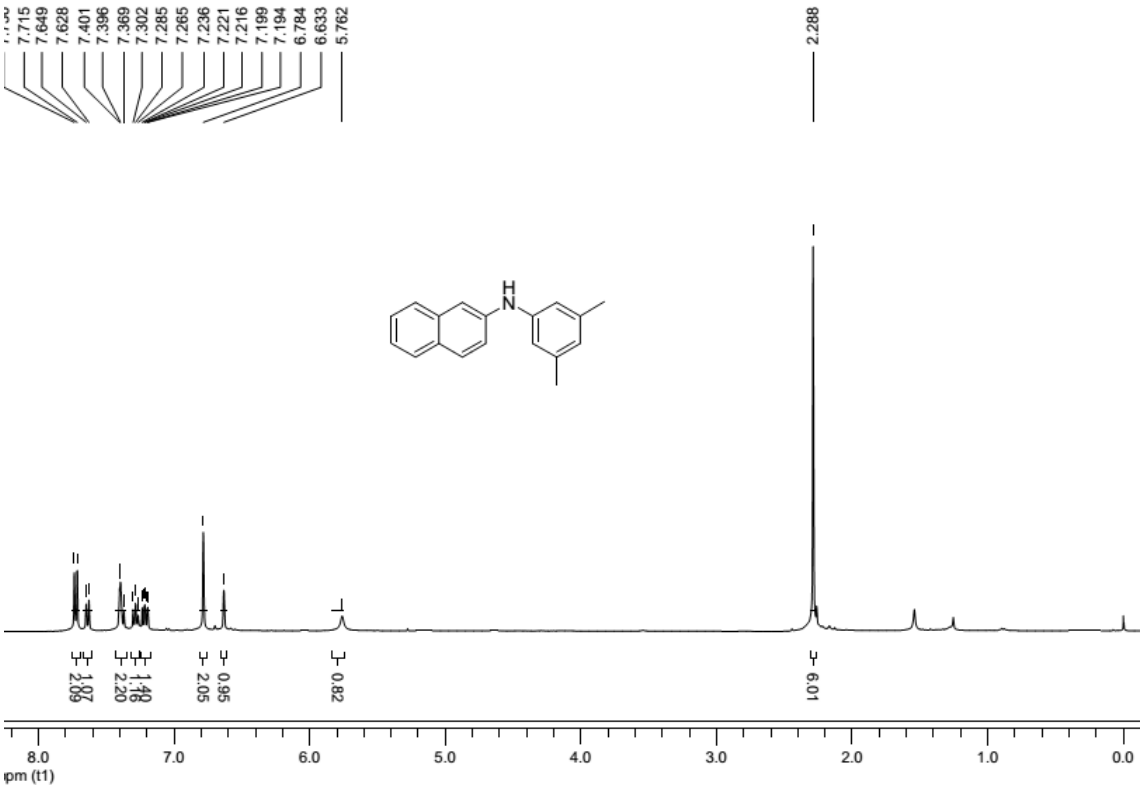

143.034
140.964
134.749
129.539
129.275
127.772
126.613
126.565
123.607
121.505
120.157
118.379
111.713
H
N
150
100
50
0
ppm (t1)

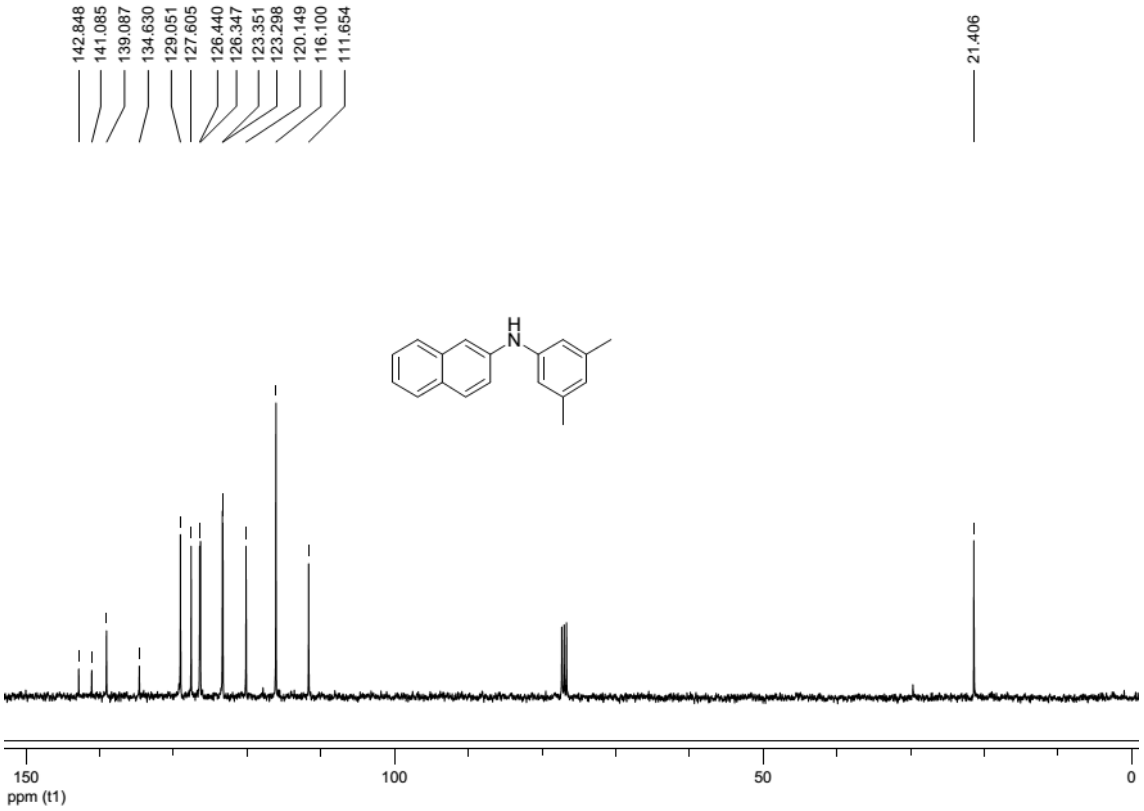

7.386
7.372
7.352
7.349
7.253
7.250
7.247
7.233
7.230
7.219
7.213
7.188
7.179
7.174
7.163
7.157
7.148
7.130
7.124
7.108
7.102
6.933
6.924
6.918
6.907
6.902
6.893
3.831
2.07
1.08
1.11
2.03
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

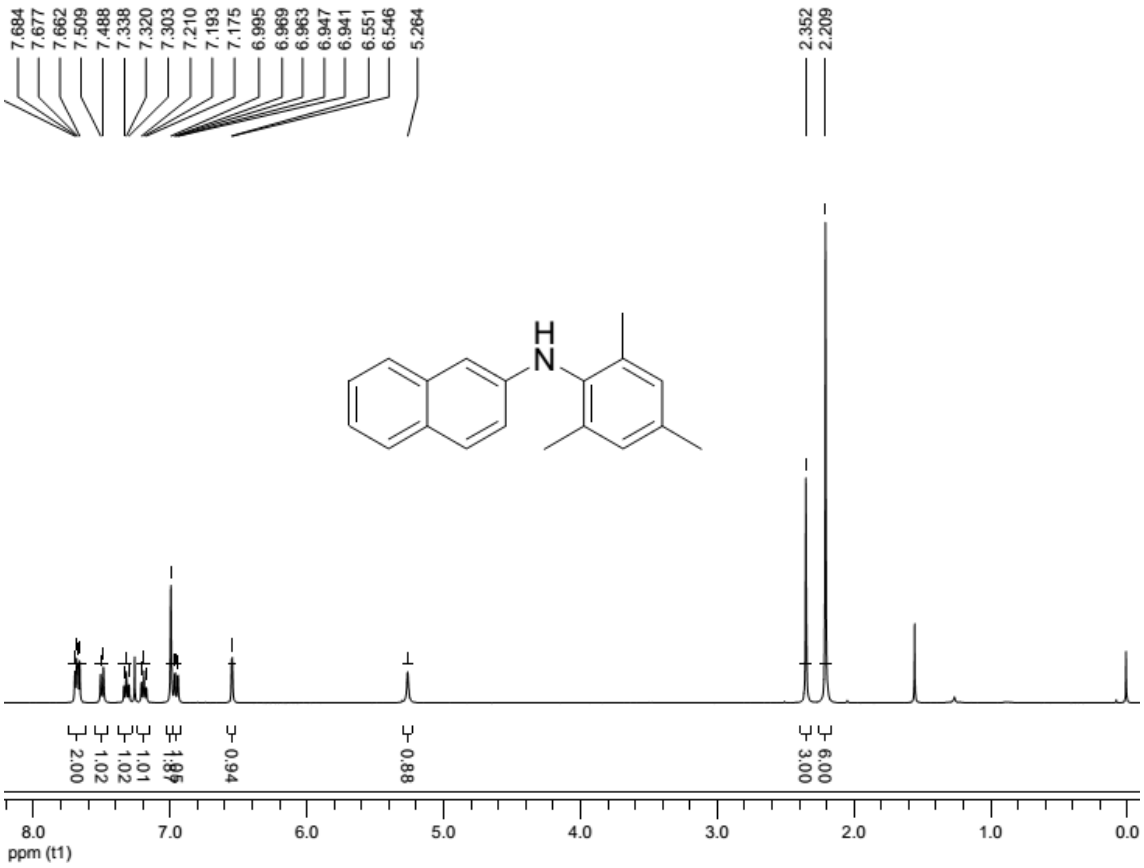

155.417
142.848
135.442
134.745
129.060
128.460
127.565
126.330
126.159
122.789
122.461
118.822
114.668
108.663
55.487
150
100
50
0
ppm (t1)

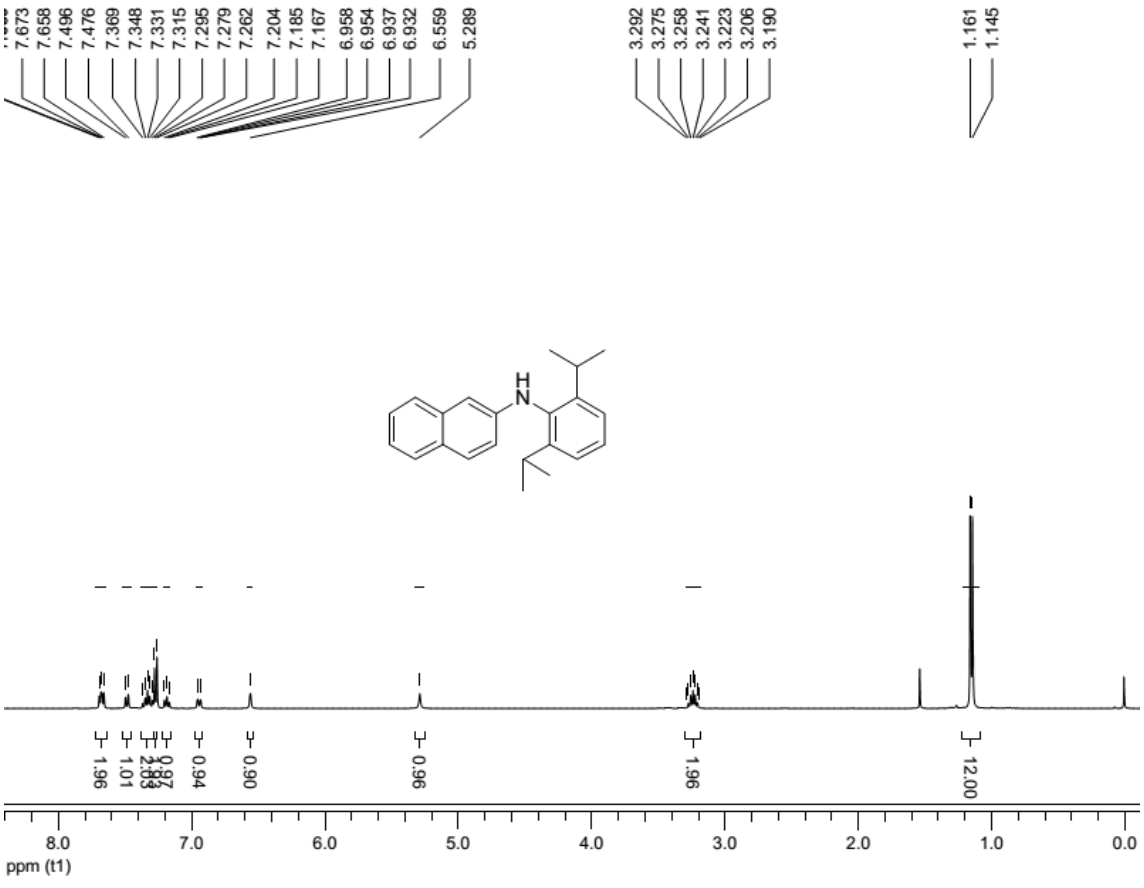

7.403
7.400
7.386
7.383
7.380
7.366
7.363
7.292
7.290
7.275
7.272
7.269
7.203
7.197
7.192
7.181
7.176
7.138
7.133
7.127
7.116
7.111
7.105
5.796
2.949
2.932
2.914
2.897
2.880
2.862
2.845
1.274
1.257
0.93
1.82
1.87
0.89
1.01
6.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

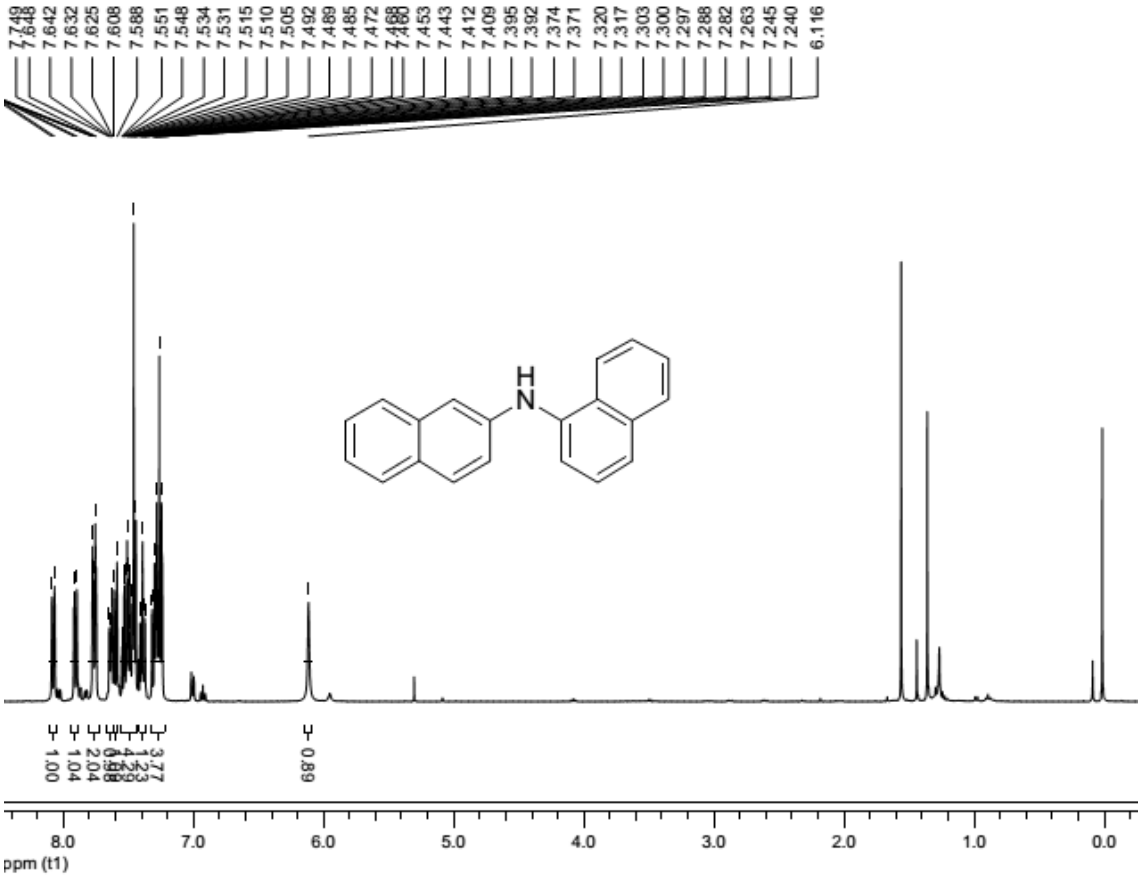

142.337
141.497
140.363
134.679
129.037
128.850
127.582
127.230
126.333
123.127
119.619
118.988
110.432
33.416
24.108
150
100
50
0
ppm (t1)

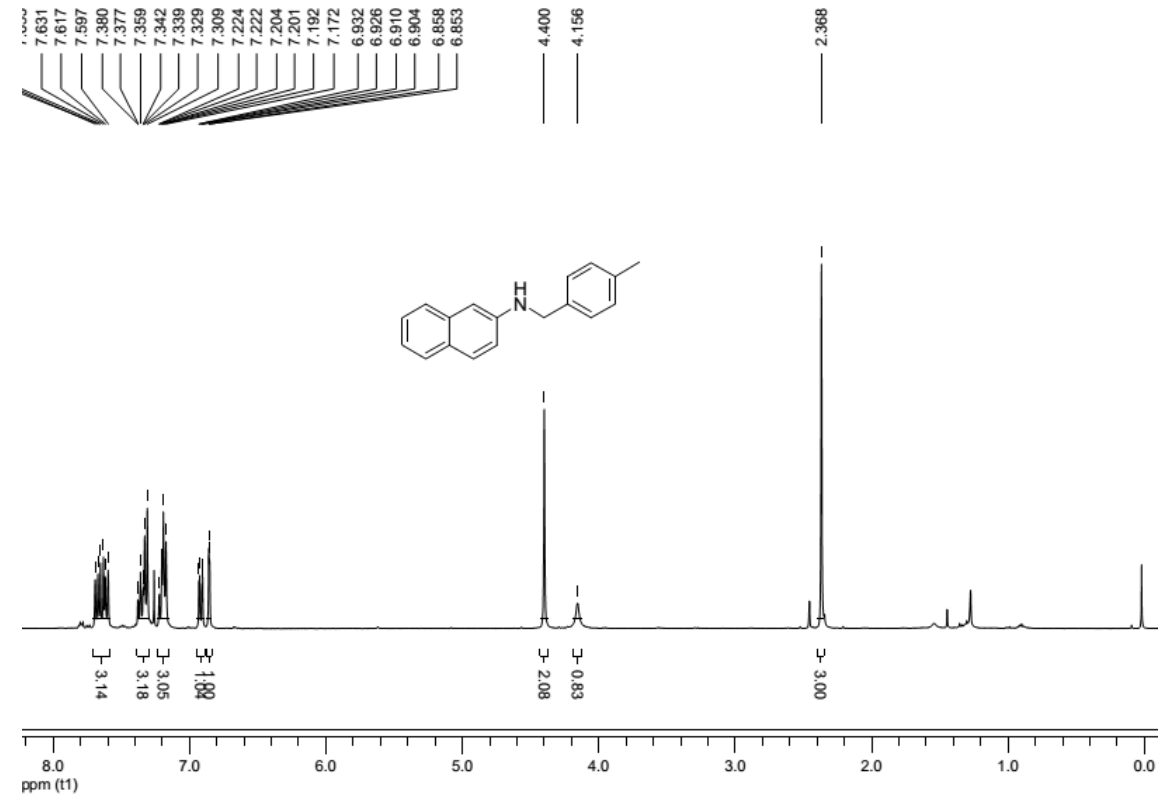

7.715
7.649
7.628
7.401
7.396
7.369
7.302
7.285
7.265
7.236
7.221
7.216
7.199
7.194
6.784
6.633
5.762
2.288
2.07
2.20
1.18
1.40
2.05
0.95
0.82
6.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

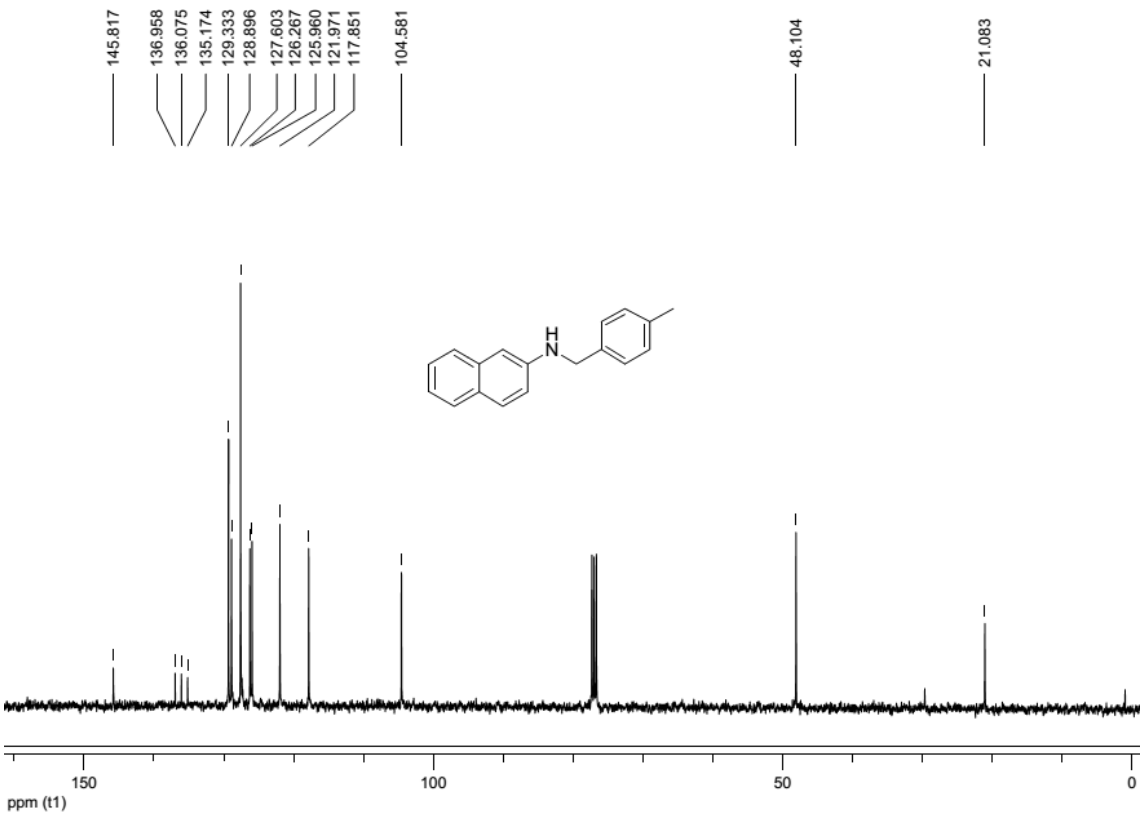

142.848
141.085
139.087
134.630
129.051
127.605
126.440
126.347
123.351
123.298
120.149
116.100
111.654
21.406
150
100
50
0
ppm (t1)

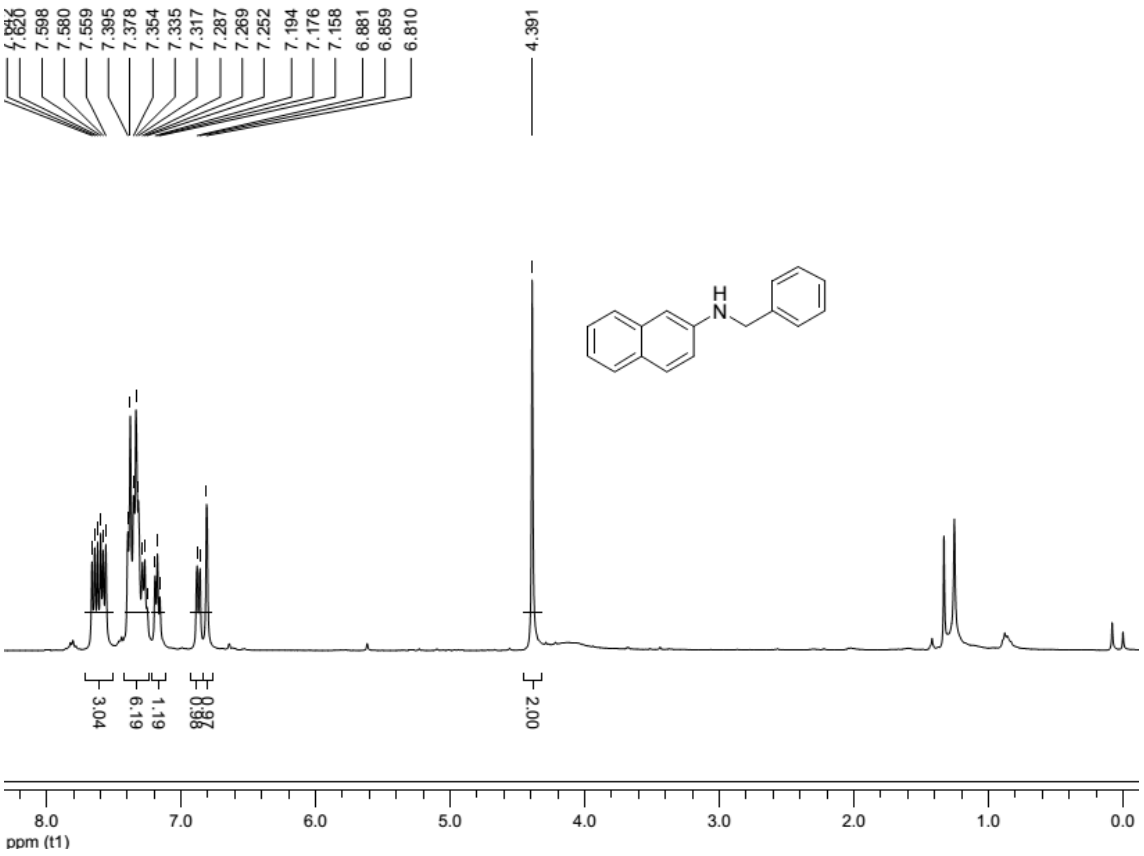

7.684
7.677
7.662
7.509
7.488
7.338
7.320
7.303
7.210
7.193
7.175
6.995
6.969
6.963
6.947
6.941
6.551
6.546
5.264
2.352
2.209
H
N
2.00
1.02
1.01
1.89
0.94
0.88
3.00
6.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

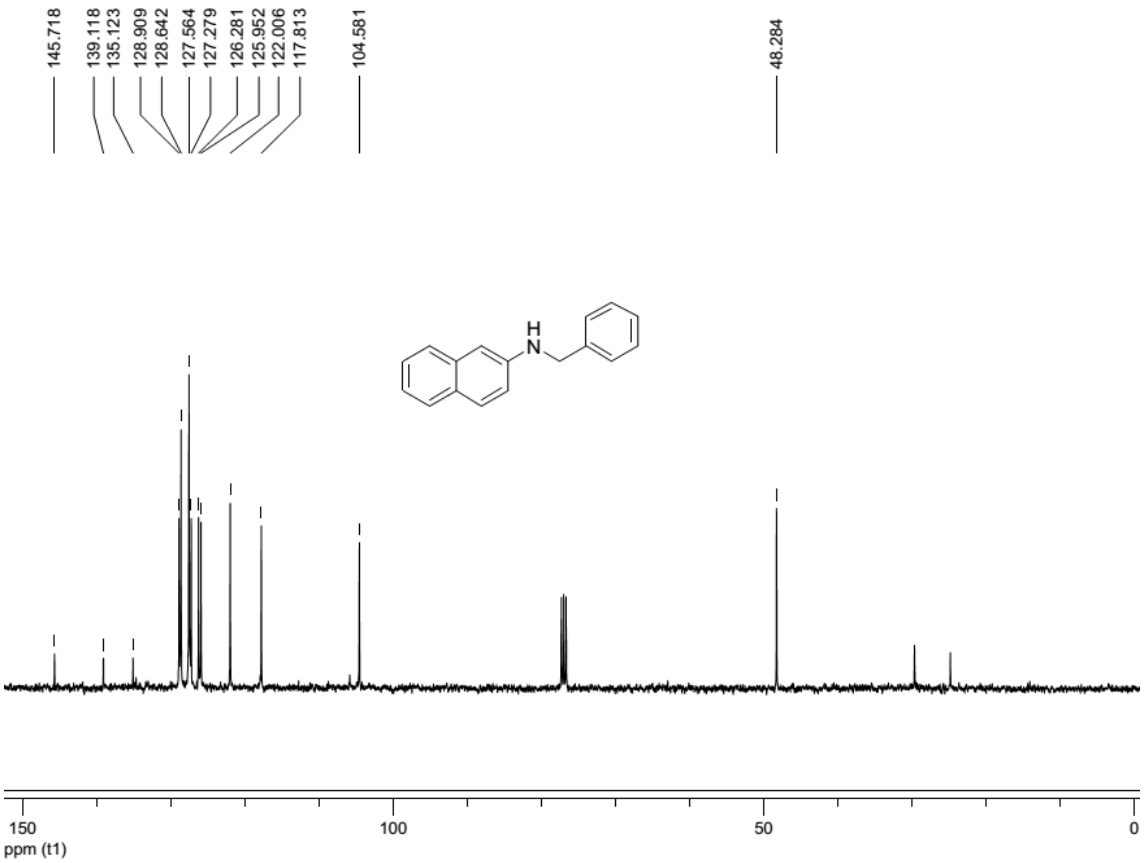

7.673
7.658
7.496
7.476
7.369
7.348
7.331
7.315
7.295
7.279
7.262
7.204
7.185
7.167
6.958
6.954
6.937
6.932
6.559
5.289
3.292
3.275
3.258
3.241
3.223
3.206
3.190
1.161
1.145
H
N
1.96
1.01
0.94
0.90
0.96
1.96
12.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

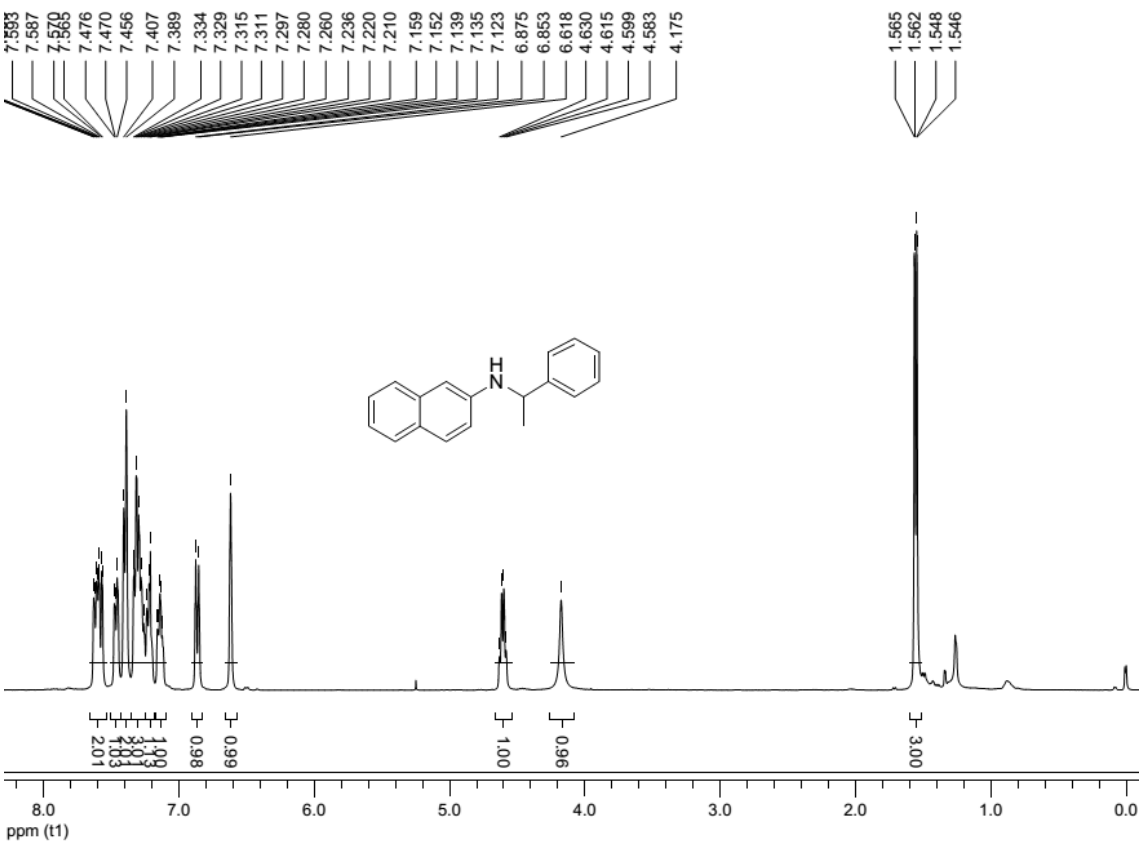

7.749
7.648
7.642
7.632
7.625
7.608
7.588
7.551
7.548
7.534
7.531
7.515
7.510
7.505
7.492
7.489
7.485
7.472
7.453
7.443
7.412
7.409
7.395
7.392
7.374
7.371
7.320
7.317
7.303
7.300
7.297
7.288
7.282
7.263
7.245
7.240
6.116
H
N
1.00
1.04
2.04
3.27
0.89
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

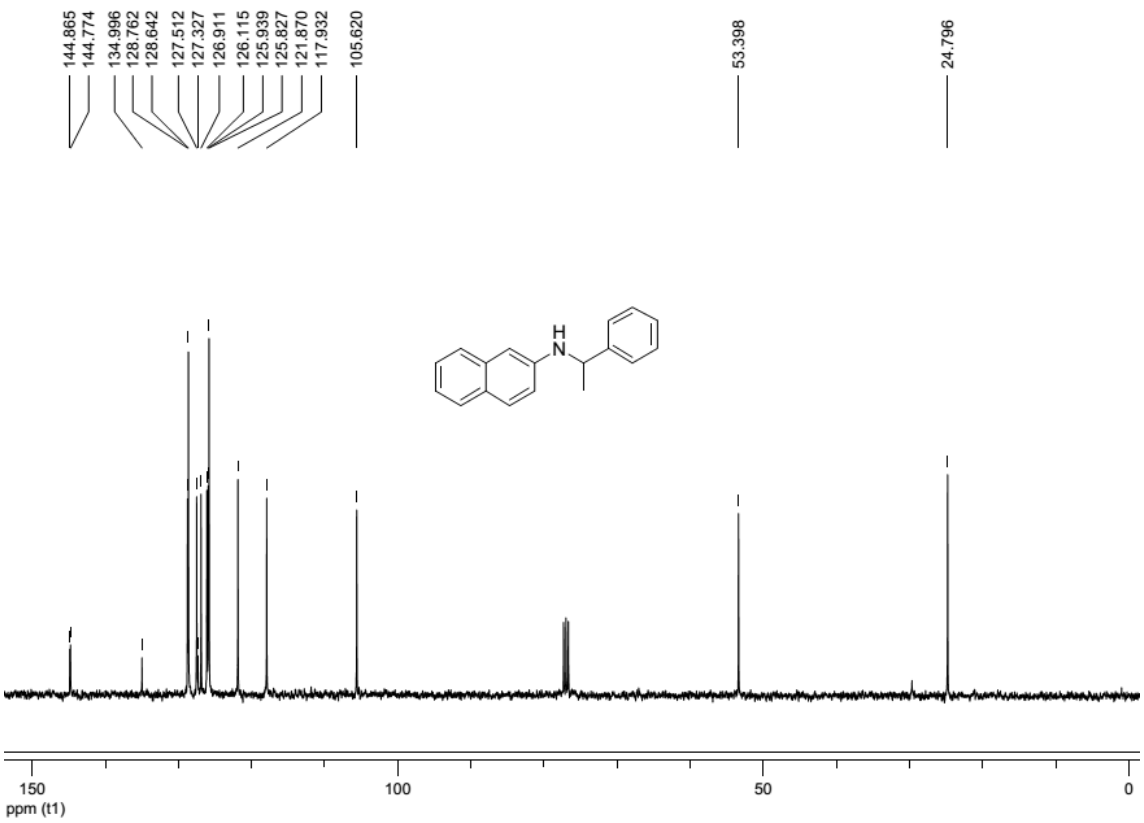

7.631
7.617
7.597
7.380
7.377
7.359
7.342
7.339
7.329
7.309
7.224
7.222
7.204
7.201
7.192
7.172
6.932
6.926
6.910
6.904
6.858
6.853
4.400
4.156
2.368
H
N
3.14
3.18
3.05
2.08
0.83
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

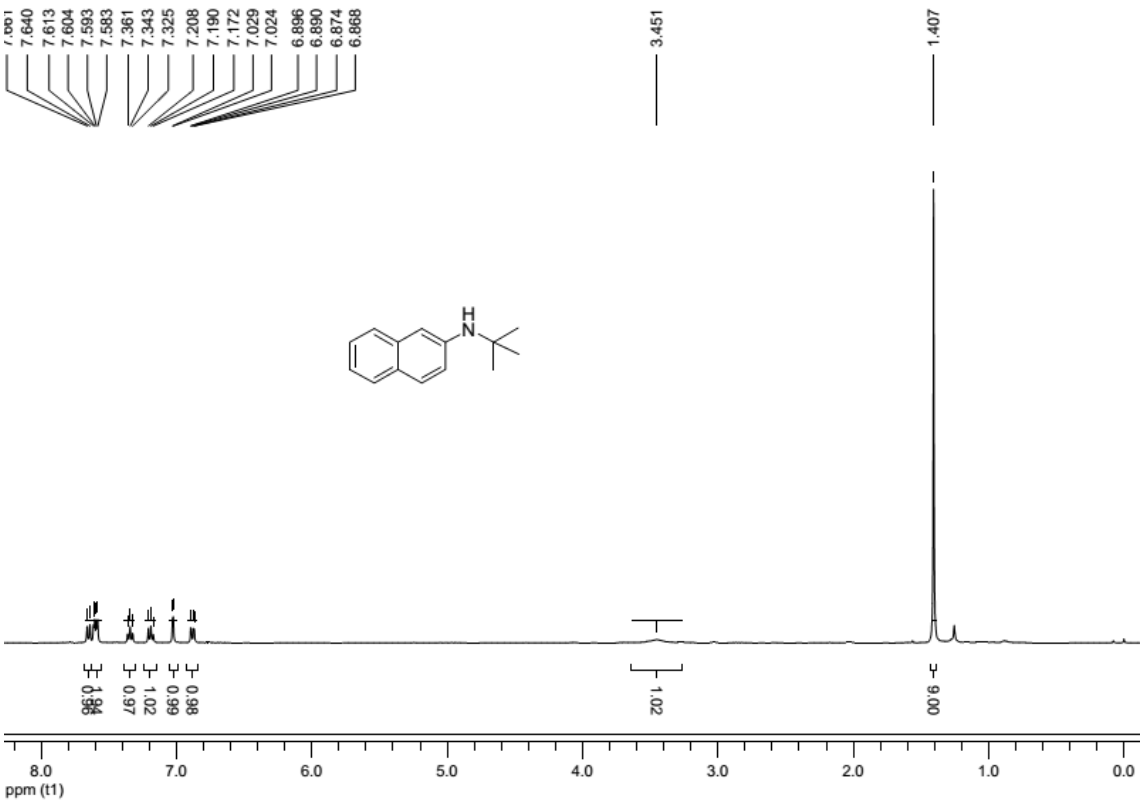

145.817
136.958
136.075
135.174
129.333
128.896
127.603
126.267
125.960
121.971
117.851
104.581
48.104
21.083
H
N
150
100
50
0
ppm (t1)

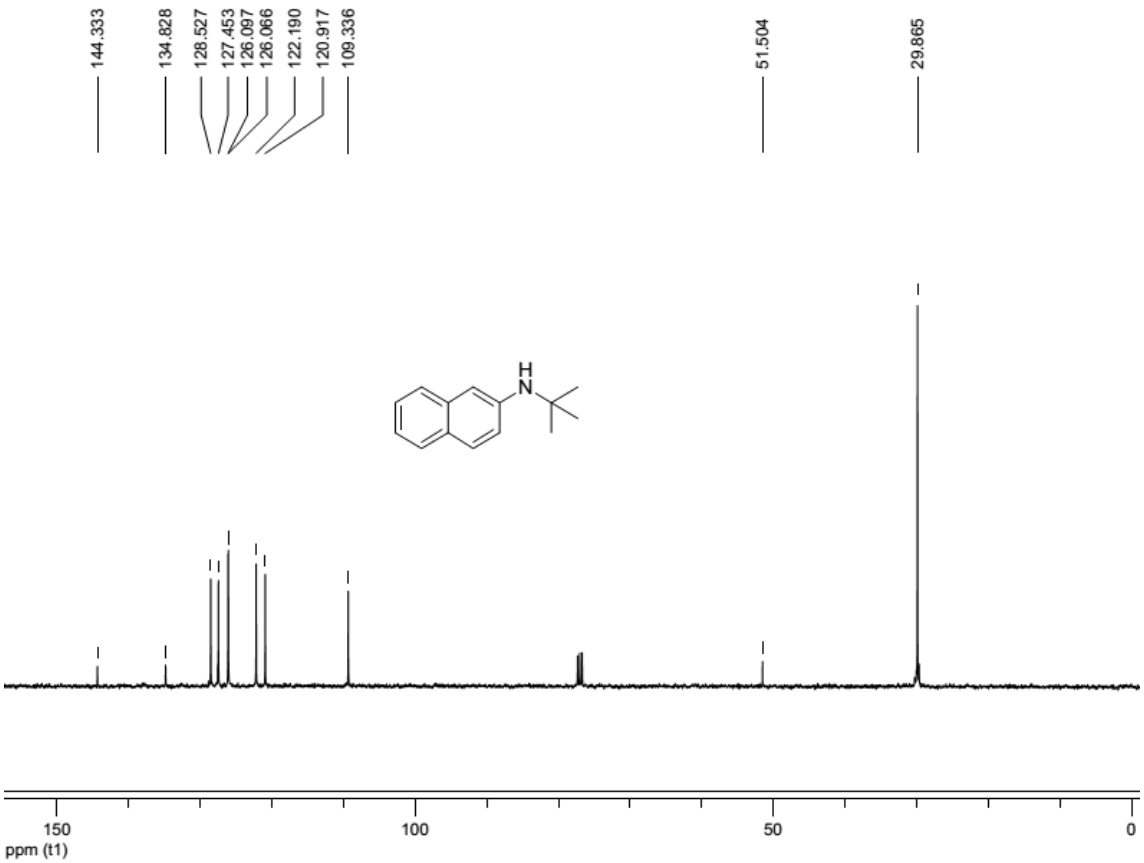

7.620
7.598
7.580
7.559
7.395
7.378
7.354
7.335
7.317
7.287
7.269
7.252
7.194
7.176
7.158
6.881
6.859
6.810
4.391
H
N
3.04
6.19
1.19
0.98
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

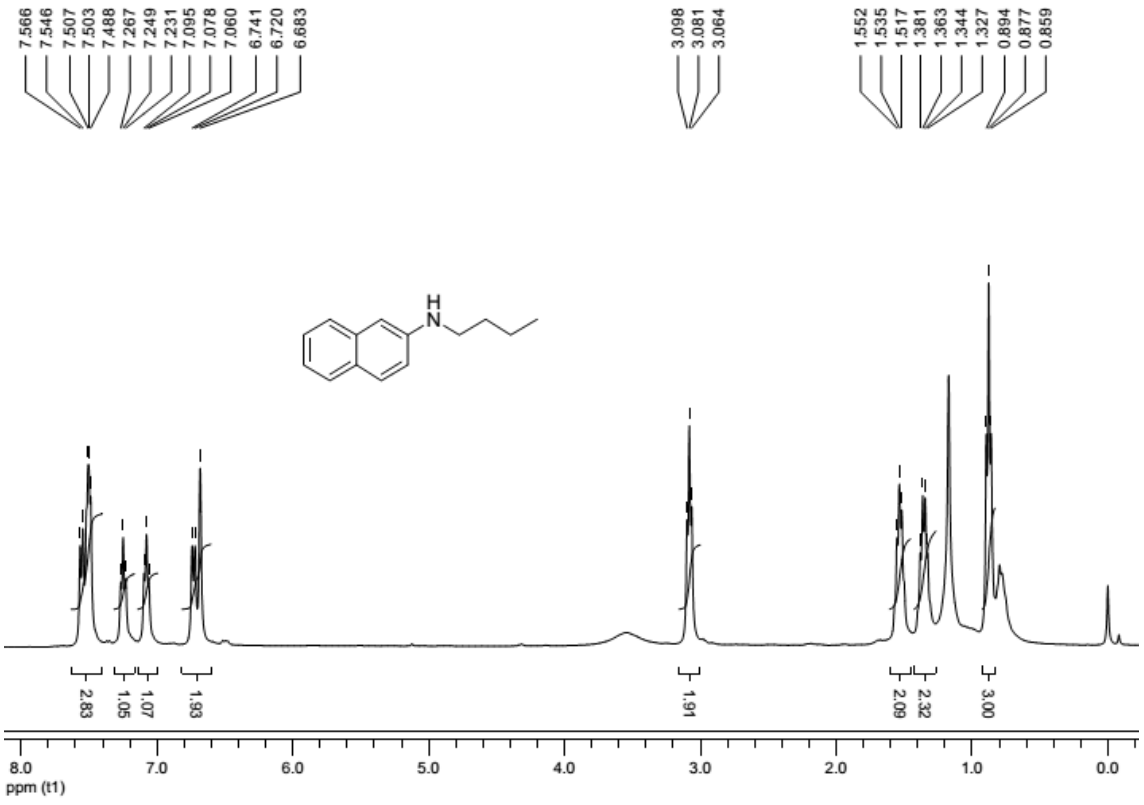

145.718
139.118
135.123
128.909
128.642
127.564
127.279
126.281
125.952
122.006
117.813
104.581
48.284
150
100
50
0
ppm (t1)

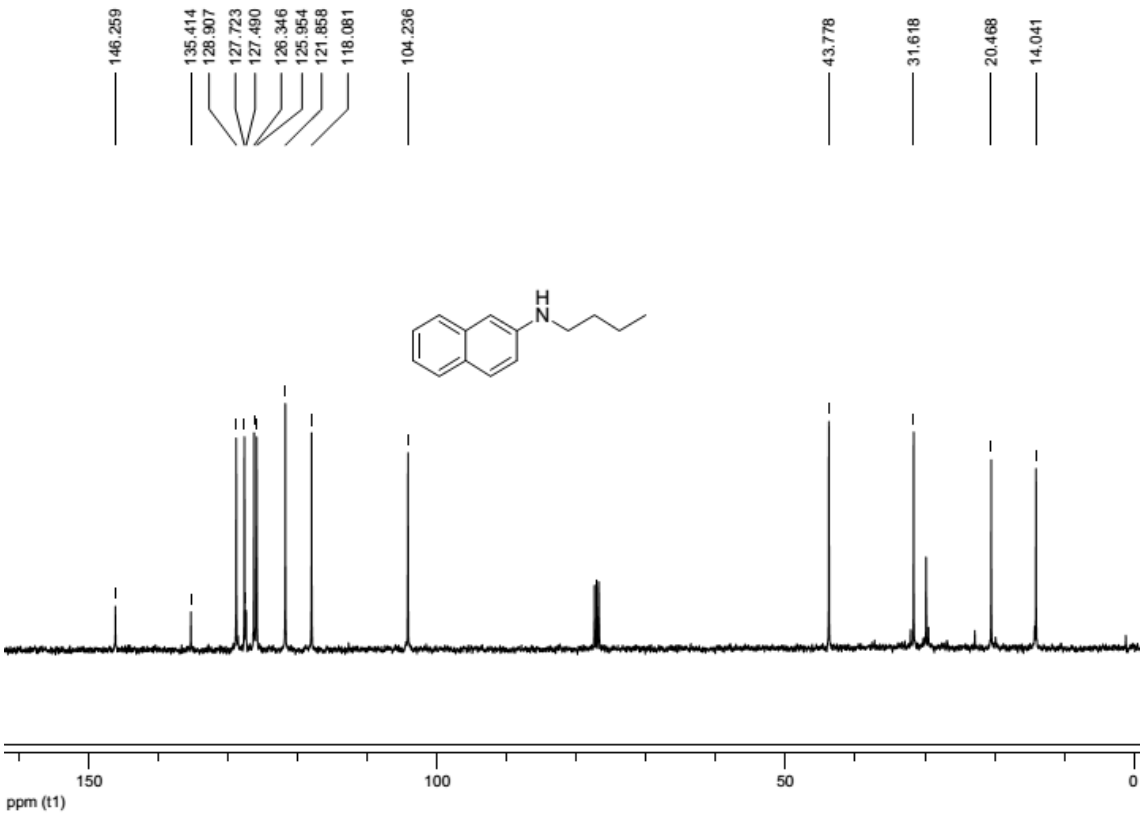

7.587
7.476
7.470
7.456
7.407
7.389
7.334
7.329
7.315
7.311
7.297
7.280
7.260
7.236
7.220
7.210
7.159
7.152
7.139
7.135
7.123
6.875
6.853
6.618
4.630
4.615
4.599
4.583
4.175
1.565
1.562
1.548
1.546
2.01
0.98
0.99
1.00
0.96
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

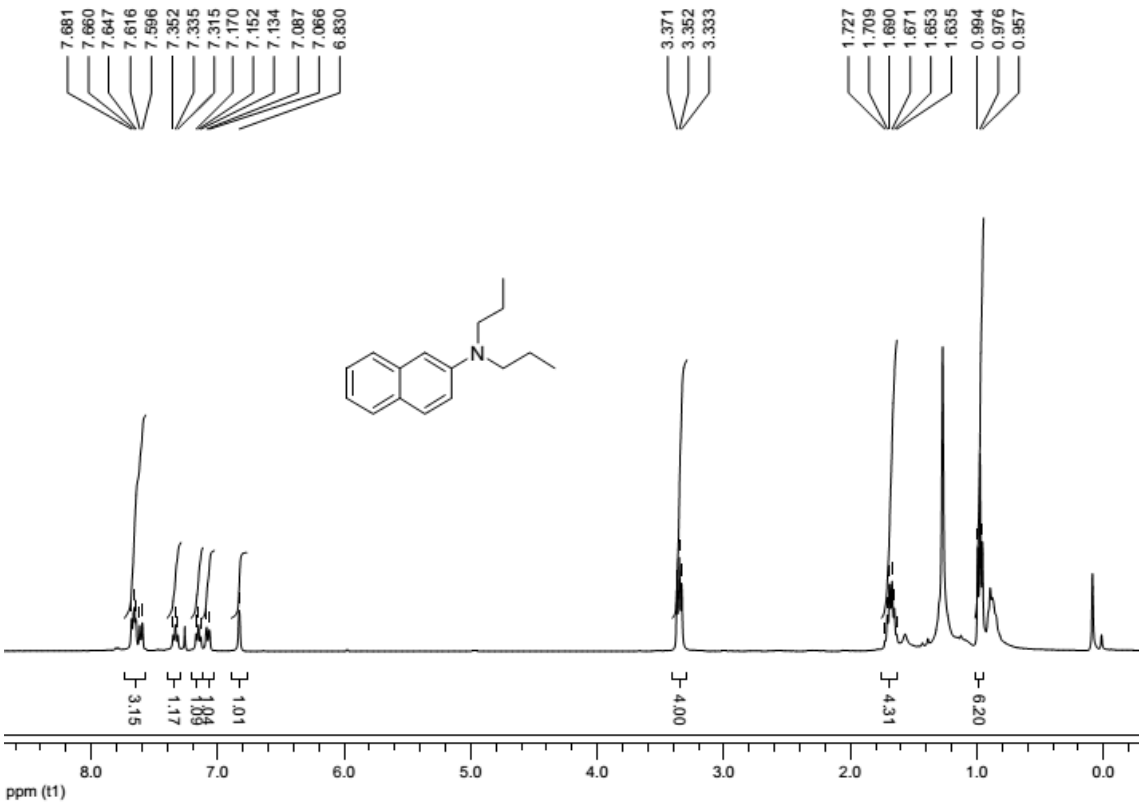

144.865
144.774
134.996
128.762
128.642
127.512
127.327
126.911
126.115
125.939
125.827
121.870
117.932
105.620
53.398
24.796
H
N
150
100
50
0
ppm (t1)

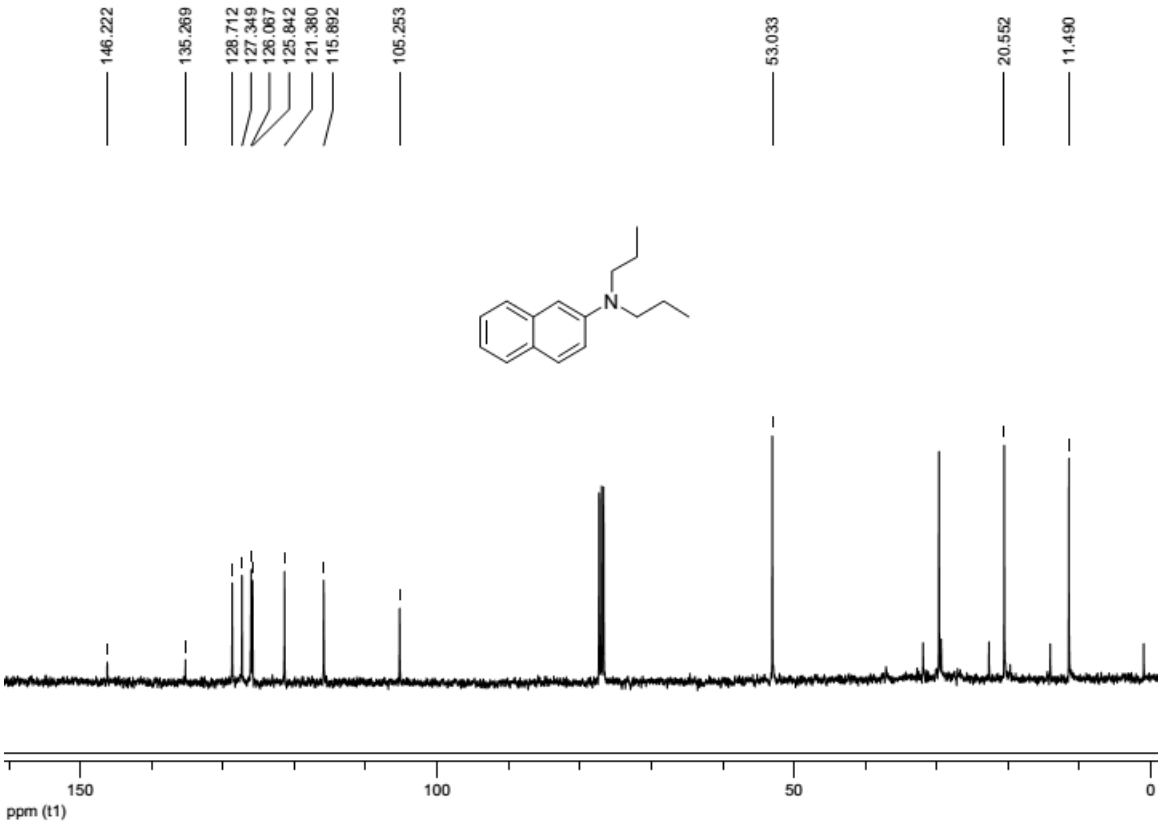

7.640
7.613
7.604
7.593
7.583
7.361
7.343
7.325
7.208
7.190
7.172
7.029
7.024
6.896
6.890
6.874
6.868
3.451
1.407
H
N
0.96
0.97
1.02
0.99
0.98
1.02
9.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

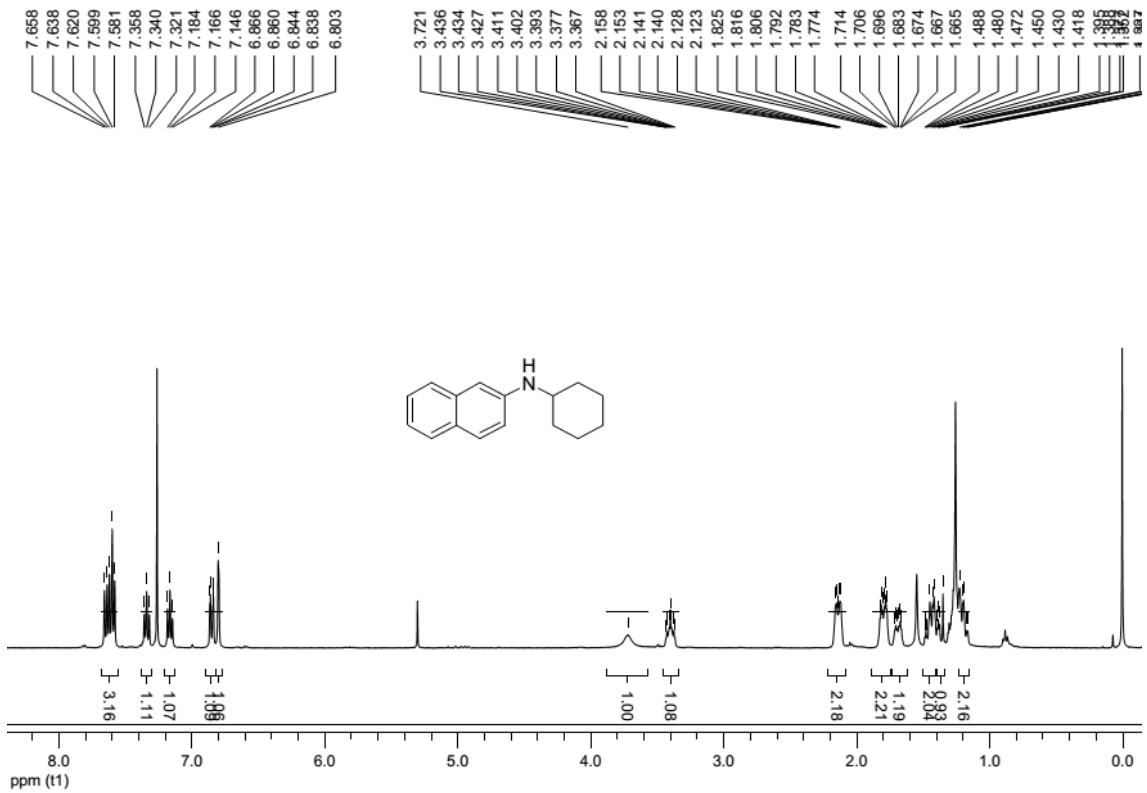

144.333
134.828
128.527
127.453
126.097
126.066
122.190
120.917
109.336
51.504
29.865
H
N
150
100
50
0
ppm (t1)

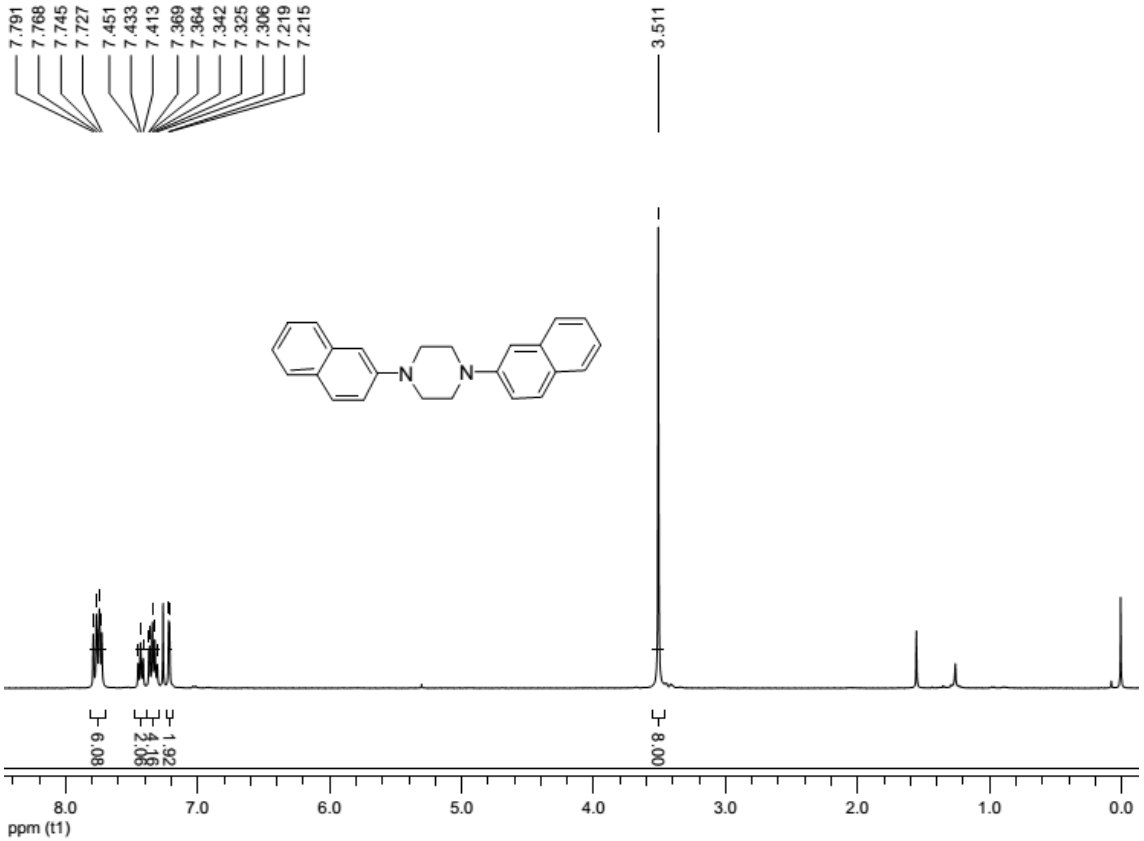

7.566
7.546
7.507
7.503
7.488
7.267
7.249
7.231
7.095
7.078
7.060
6.741
6.720
6.683
3.098
3.081
3.064
1.552
1.535
1.517
1.381
1.363
1.344
1.327
0.894
0.877
0.859
H
N
2.83
1.06
1.07
1.93
1.91
2.09
2.32
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

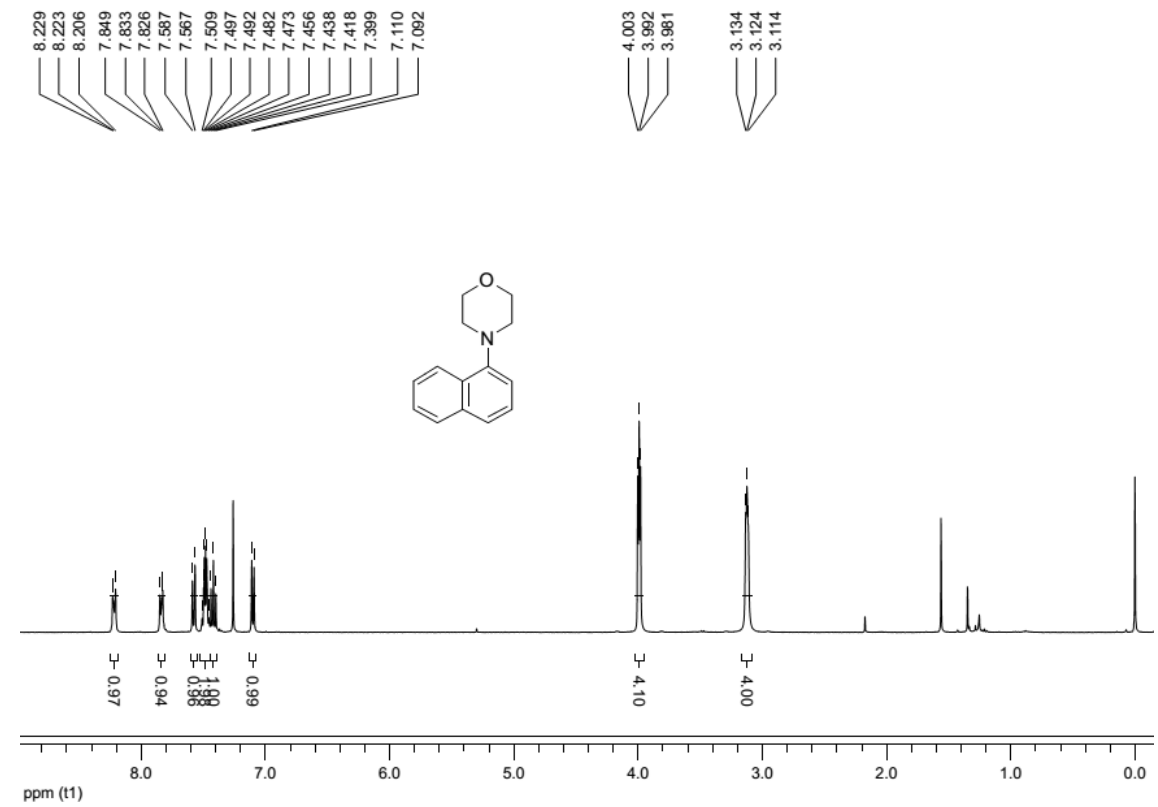

146.259
135.414
128.907
127.723
127.490
126.346
125.954
121.858
118.081
104.236
43.778
31.618
20.468
14.041
H
N
150
100
50
0
ppm (t1)

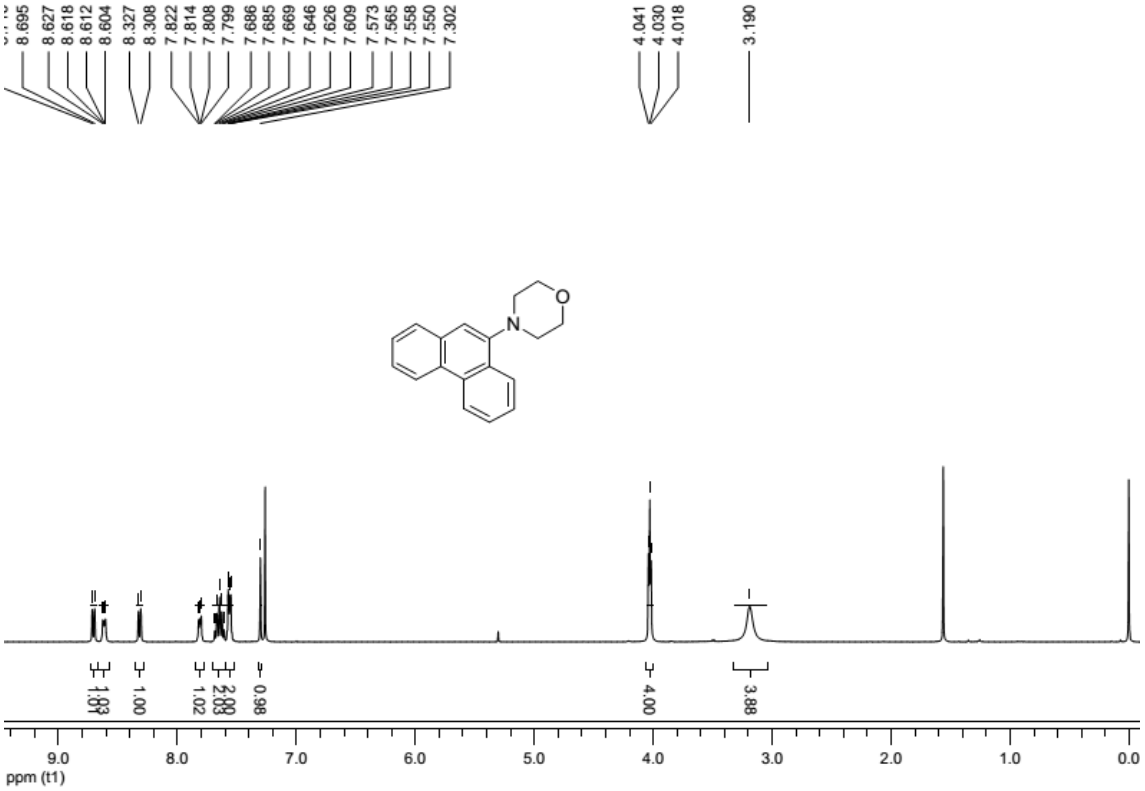

7.681
7.660
7.647
7.616
7.596
7.352
7.335
7.315
7.170
7.152
7.134
7.087
7.066
6.830
3.371
3.352
3.333
1.727
1.709
1.690
1.671
1.653
1.635
0.994
0.976
0.957
N
3.15
1.17
1.09
1.04
1.01
4.00
4.31
6.20
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

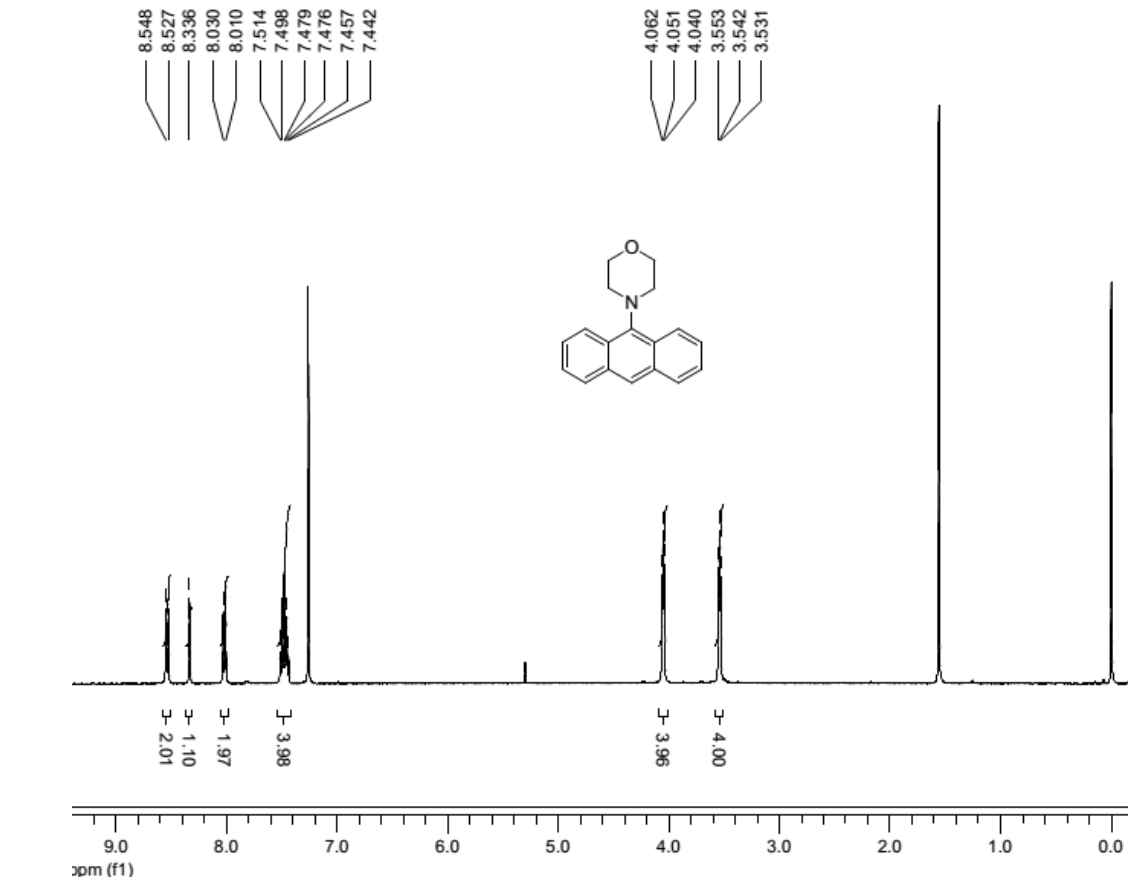

146.222
135.269
128.712
127.349
126.067
125.842
121.380
115.892
105.253
53.033
20.552
11.490
N
150
100
50
0
ppm (t1)

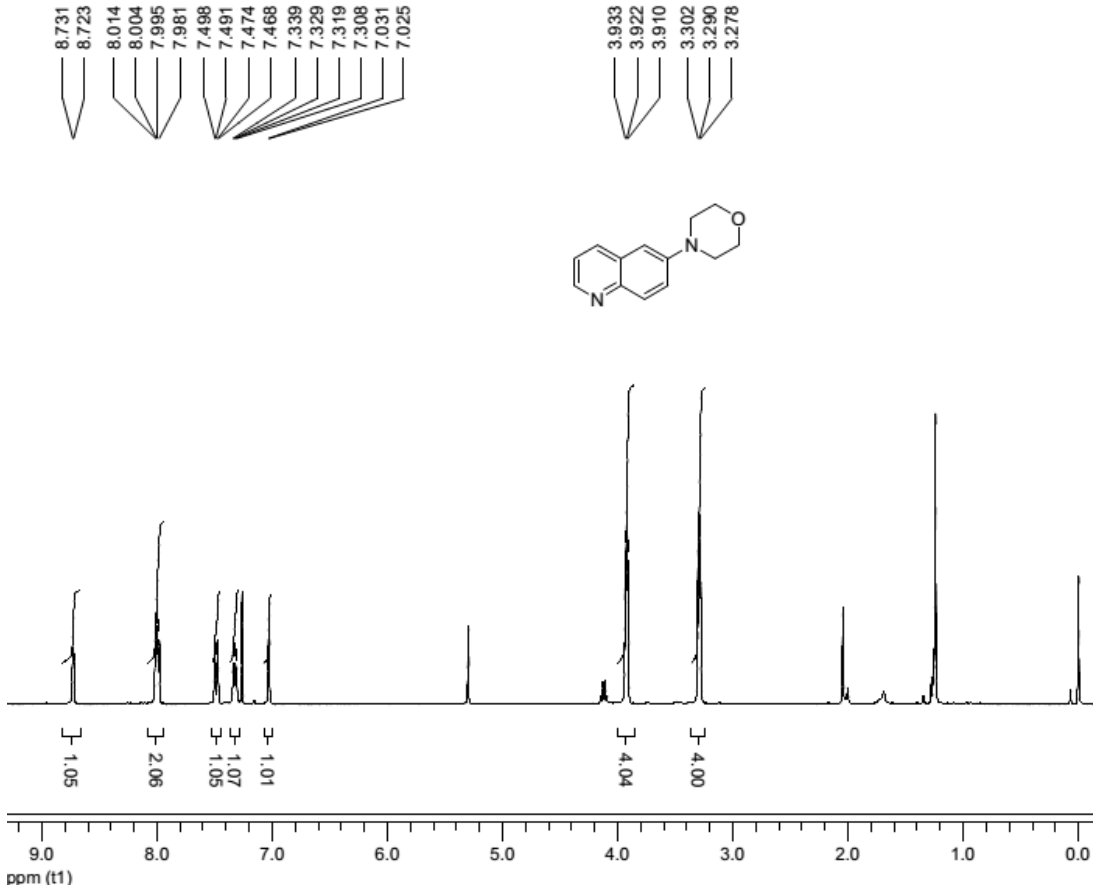

7.658
7.638
7.620
7.599
7.581
7.358
7.340
7.321
7.184
7.166
7.146
6.866
6.860
6.844
6.838
6.803
3.721
3.436
3.434
3.427
3.411
3.402
3.393
3.377
3.367
2.158
2.153
2.141
2.140
2.128
2.123
1.825
1.816
1.806
1.792
1.783
1.774
1.714
1.706
1.696
1.683
1.674
1.667
1.665
1.488
1.480
1.472
1.450
1.430
1.418
H
N
3.16
1.11
1.07
1.00
1.08
2.18
2.21
1.19
2.16
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

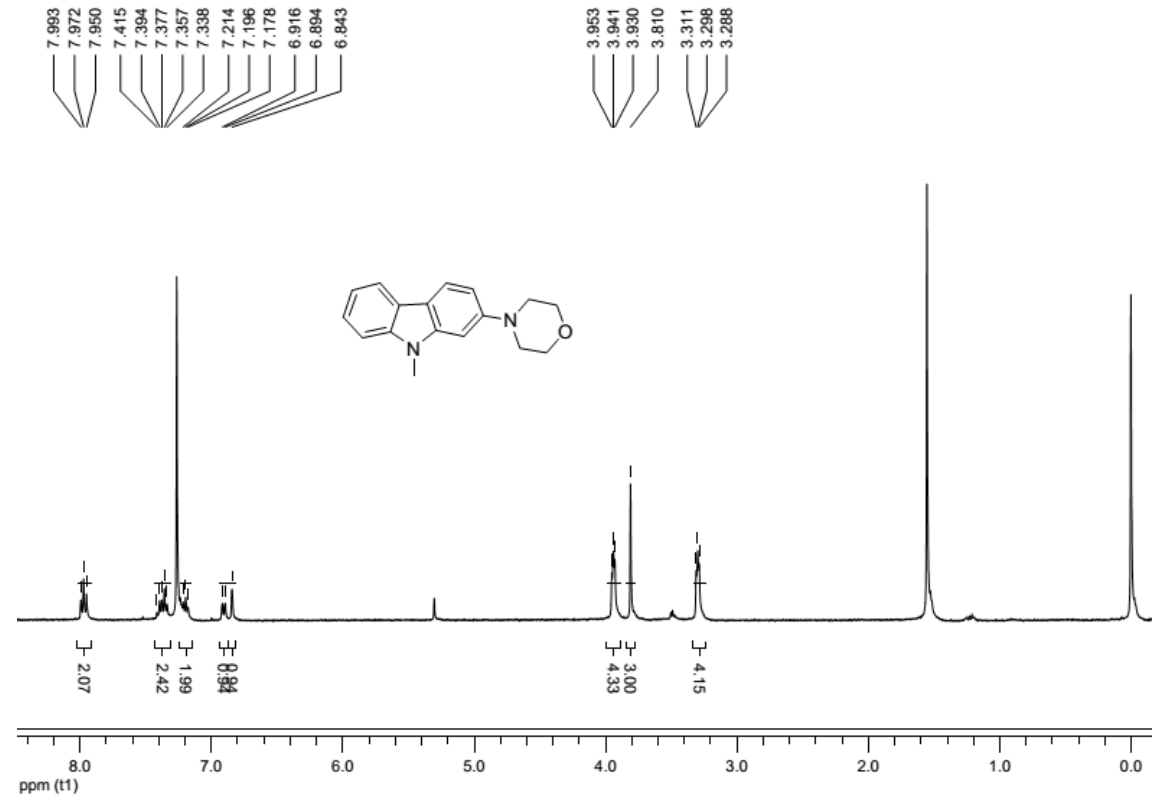

7.791
7.768
7.745
7.727
7.451
7.433
7.413
7.369
7.364
7.342
7.325
7.306
7.219
7.215
3.511
6.08
2.06
1.92
8.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

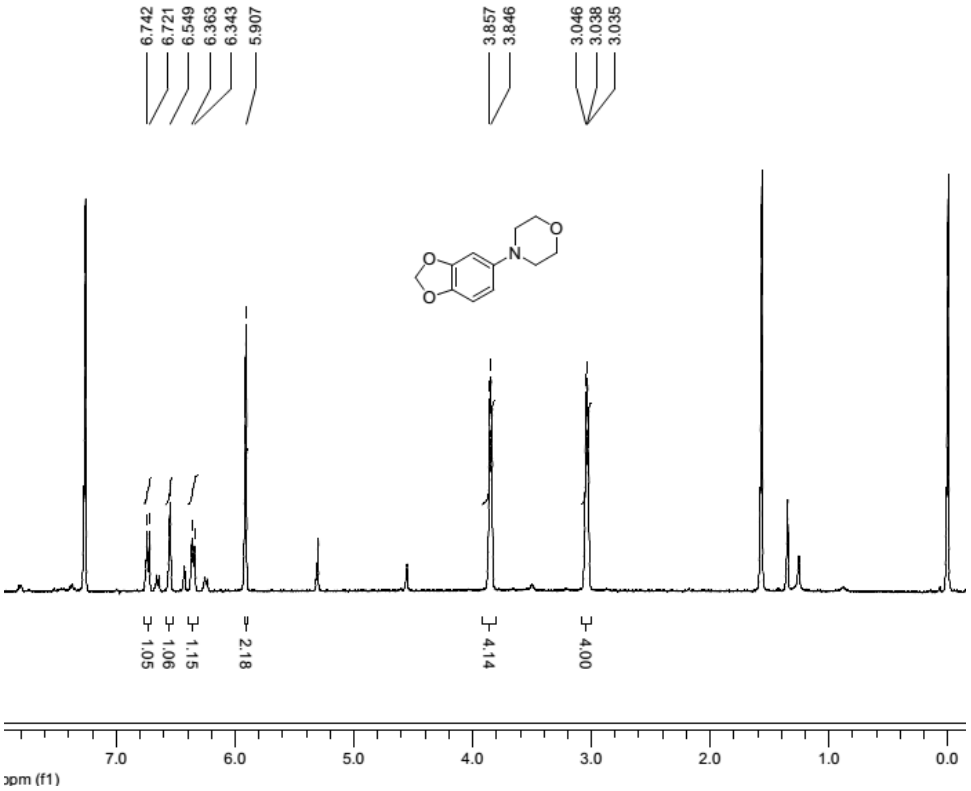

8.229
8.223
8.206
7.849
7.833
7.826
7.587
7.567
7.509
7.497
7.492
7.482
7.473
7.456
7.438
7.418
7.399
7.110
7.092
4.003
3.992
3.981
3.134
3.124
3.114
0.97
0.94
0.99
4.10
4.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

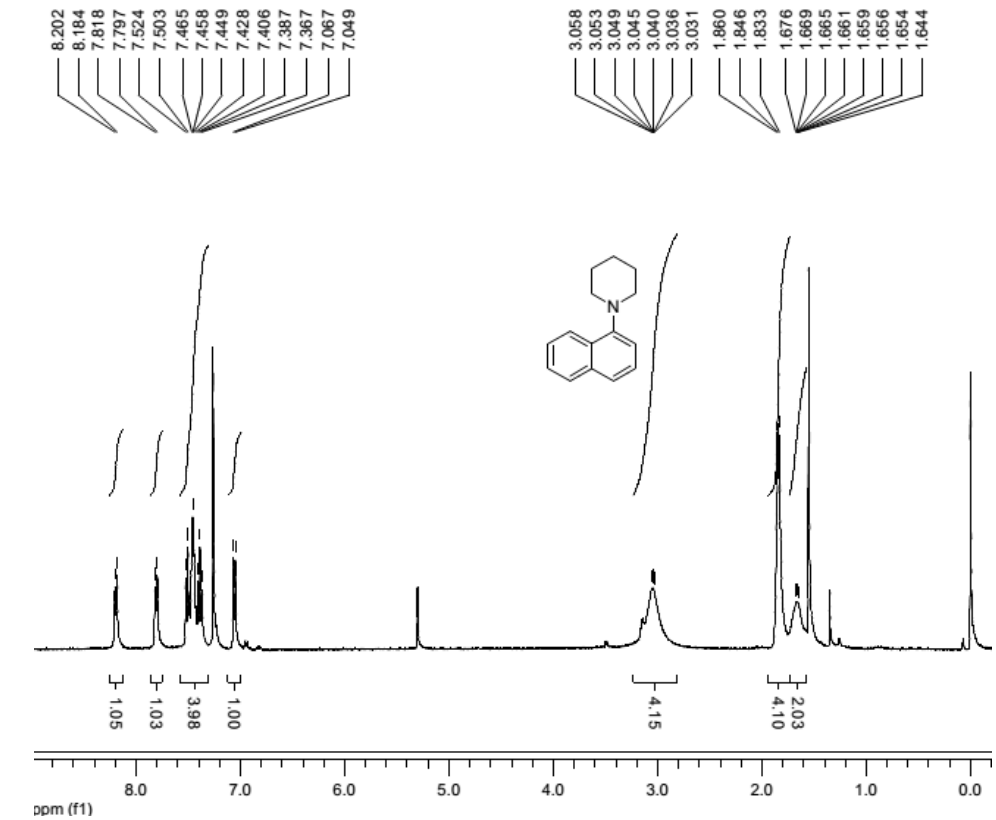

8.695
8.627
8.618
8.612
8.604
8.327
8.308
7.822
7.814
7.808
7.799
7.686
7.685
7.669
7.646
7.626
7.609
7.573
7.565
7.558
7.550
7.302
4.041
4.030
4.018
3.190
O
N
1.03
1.00
1.02
2.03
2.00
0.98
4.00
3.88
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

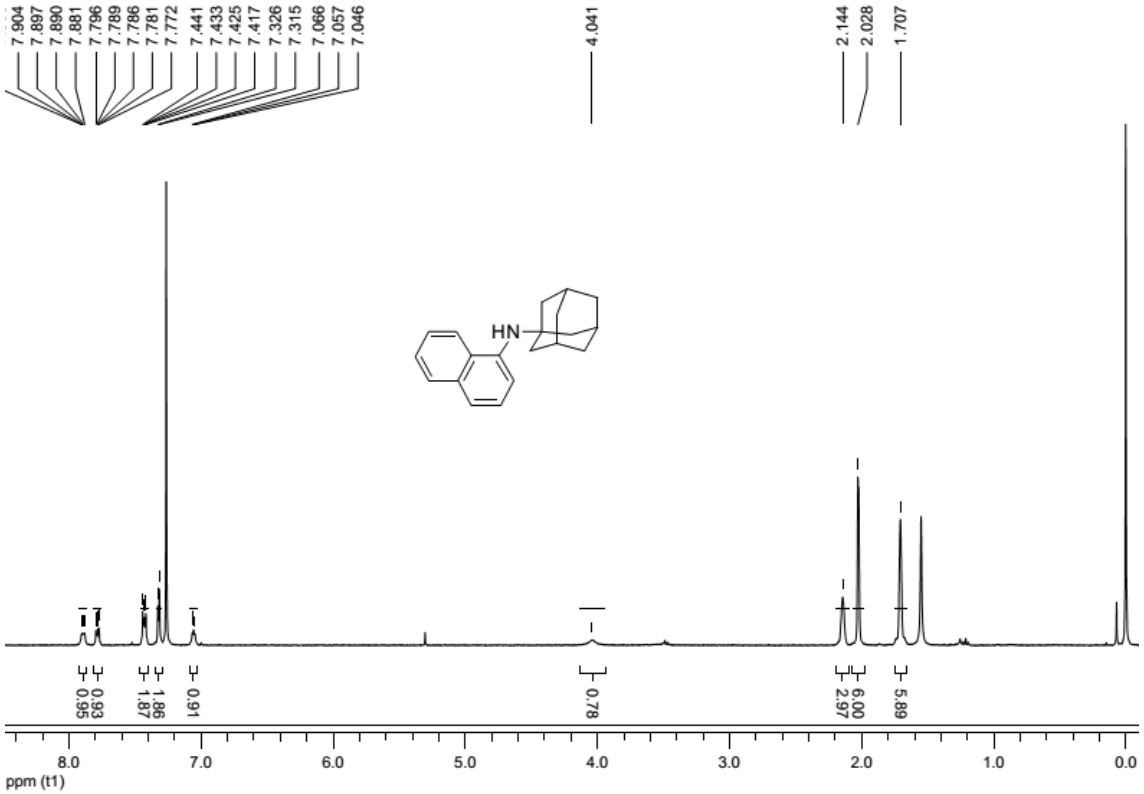

8.548
8.527
8.336
8.030
8.010
7.514
7.498
7.479
7.476
7.457
7.442
4.062
4.051
4.040
3.553
3.542
3.531
O
N
2.01
1.10
1.97
3.98
3.96
4.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

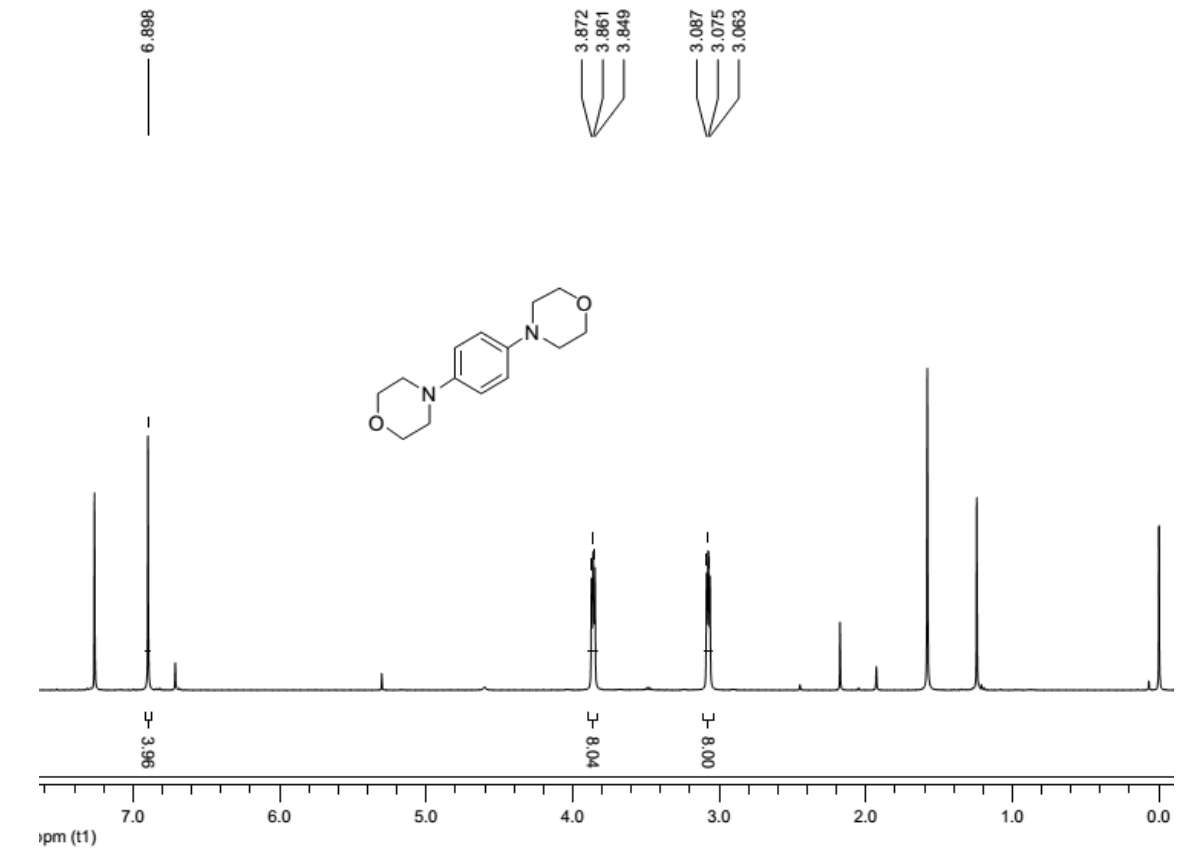

8.731
8.723
8.014
8.004
7.995
7.981
7.498
7.491
7.474
7.468
7.339
7.329
7.319
7.308
7.031
7.025
3.933
3.922
3.910
3.302
3.290
3.278
O
N
N
1.05
2.06
1.05
1.07
1.01
4.04
4.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


7.993
7.972
7.950
7.415
7.394
7.377
7.357
7.338
7.214
7.196
7.178
6.916
6.894
6.843
3.953
3.941
3.930
3.810
3.311
3.298
3.288
N
O
N
2.07
2.42
1.99
4.33
3.00
4.15
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


6.742
6.721
6.549
6.363
6.343
5.907
3.857
3.846
3.046
3.038
3.035
1.05
1.06
1.15
2.18
4.14
4.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


8.202
8.184
7.818
7.797
7.524
7.503
7.465
7.458
7.449
7.428
7.406
7.387
7.367
7.067
7.049
3.058
3.053
3.049
3.045
3.040
3.036
3.031
1.860
1.846
1.833
1.676
1.669
1.665
1.661
1.659
1.656
1.654
1.644
1.05
1.03
3.98
1.00
4.15
2.03
4.10
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


7.904
7.897
7.890
7.881
7.796
7.789
7.786
7.781
7.772
7.441
7.433
7.425
7.417
7.326
7.315
7.066
7.057
7.046
4.041
2.144
2.028
1.707
HN
0.95
0.93
1.87
1.86
0.91
0.78
2.97
6.00
5.89
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


6.898
3.872
3.861
3.849
3.087
3.075
3.063
O
N
N
O
3.96
8.04
8.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

6. References

S1 T. Tu, W. Fang and J. Jiang, *Chem. Commun.*, 2011, **47**, 12358.

S2 M. J. Iglesias, J. F. Blandez, M. R. Fructos, A. Prieto, E. Álvarez, T. R. Belderrain and M. C. Nicasio, *Organometallics*, 2012, **31**, 6312.

S3 M. Tobisu, T. Shimasaki and N. Chatani, *Chem. Lett.*, 2009, **38**, 710.

S4 N. P. Reddy and M. Tanaka, *Tetrahedron Lett.*, 1997, **38**, 4807.

S5 J.-H. Huang and L.-M. Yang, *Org. Lett.*, 2011, **13**, 3750.

S6 X.-L. Li, J.-H. Huang and L.-M. Yang, *Org. Lett.*, 2011, **13**, 4950.

S7 H. Sandra, Z. Mike, D. Sascha and W. Jens, *Ger.*, 2013, DE102012005215 B3 20130411.

S8 S. B. Cortright, J. C. Huffman, R. A. Yoder, J. N. Coalter and J. N. Johnston, *Organometallics*, 2004, **23**, 2238.

S9 Y. Zhang, X. Yang, Q. Yao and D. Ma, *Org. Lett.*, 2012, **14**, 3056.

S10 S. Singh, A. K. Trehan and V. K. Sharma, *Tetrahedron Lett.*, 1978, **50**, 5029.

S11 K. H. Slotta and W. Franke, *Berichte der Deutschen Chemischen Gesellschaft [Abteilung] B: Abhandlungen*, 1930, **63B**, 678.

S12 T. Shimasaki, M. Tobisu and N. Chatani, *Angew. Chem. Int. Ed.*, 2010, **49**, 2929.

S13 R. Pereira and J. Cvengroš, *Eur. J. Org. Chem.*, 2013, 4233.

S14 Z. Dong and G. Dong, *J. Am. Chem. Soc*., 2013, **135**, 18350.

S15 N. Marion, O. Navarro, J. Mei, E. D. Stevens, N. M. Scott and S. P. Nolan, *J. Am. Chem. Soc.*, 2006, **128**, 4101.

S16 B. G. Rarog, V. A. Topchii and A. G. Yurchenko, *Vestnik Kievskogo Politekhnicheskogo Instituta, Khimicheskoe Mashinostroenie i Tekhnologiya,* 1981, **18**, 25-7.

S17 X.-H. Fan, G. Li and L.-M. Yang, *J. Organomet. Chem.*, 2011, **696**, 2482.