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Supporting Information

Benzimidazolin-2-ylidene N-heterocyclic Carbene complexes of Ruthenium as a Simple Catalyst for the N-alkylation of Amines using Alcohols and Diols

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CONTENTS

1. General information

Commercially available reagents were used as received without further purification. For chromatographic purifications, technical-grade solvents were used. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) using *Merck Silica Gel 60 F254* plates. GC analysis was carried out using Agilent 6890N GC controlled by Chemstation software. The chromatographic purification of the products was performed on *silica gel*. NMR-spectra were measured in the given solvent at room temperature on a *Bruker Avance 400* (400 MHz, ^{1}H-NMR *(cryoprobe)*; 101MHz, ^{13}C-NMR, *(cryoprobe)* and 161MHz, ^{31}P-NMR). Chemical shifts δ are given in parts per million (ppm) relative to tetramethylsilane (TMS) for ^{1}H- and ^{13}C-NMR spectra and also calibrated against the solvent residual peak. Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal or as a combination of them. Coupling constants (*J*) are given in Hertz (Hz).

High-resolution mass spectrometry was run by the electrospray ionization time-of-flight (ESI-TOF) mode on an Agilent 6210 mass spectrometer.

GC analysis method:

- *Oven:* Initial temp.: 140 ^{o}C; Initial hold time: 11.00 min; Rate 25 ^{o}C/min; Final temp.: 200 ^{o}C; Final hold time: 16.60 min.
- *Injector:* Mode: Split; temp.: 200 ^{o}C; Gas: Helium, Pressure: 1.52 bar; Split ratio: 66.7:1; Split flow: 100.0 mL/min.
- *Column:* ZB-WaxPlus Capillary column (30m x 0.25 mm); Nominal film thickness: 0.250 µm;; Initial Flow: 1.5 mL/min; Average velocity: 38 cm/sec, Pressure: 1.52 bar.
- *Detector (FID):* Temp.: 255 ^{o}C; Hydrogen flow: 30.0 mL/min; Air flow: 350.0 mL/min.

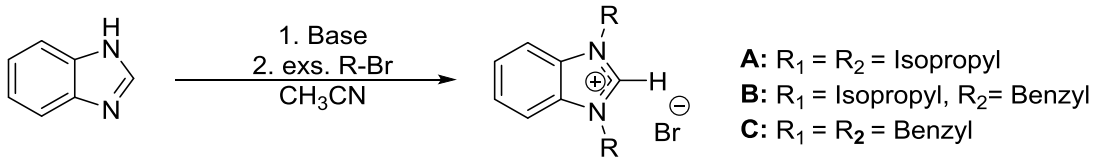
Preparation of GC sample:

Dilute the crude reaction mixture with 5 mL of toluene, added hexadecane as the internal standard, filtered through syringe filter and collected in GC vials for analysis.

Retention times: Benzaldehyde: 3.25 min; Hexadecane: 3.60 min; Aniline: 6.05; Benzyl alcohol: 9.24 min; N-1-diphenylmethanimine: 20.73; N,N-benzylphenylamine: 24.82 min.

2. Preparation and Characterization of Catalysts

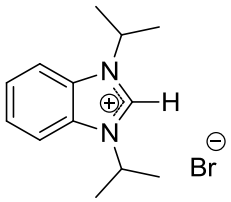
2.1. Synthesis of Benzimidazolium Salts



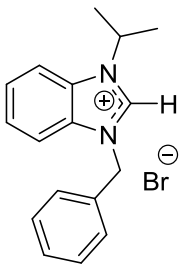
Benzimidazolium salt

General Procedure:

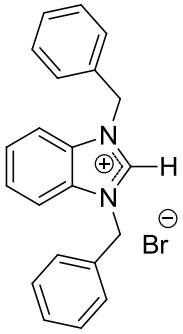
Benzimidazole (1.182 g, 10 mmol) was suspended in CH_3CN (20 mL), a suitable base (11 mmol) was added, and the reaction mixture was stirred for an hour. After adding R-Br (10 mmol) the reaction mixture was stirred overnight under reflux condition. The second portion of R-Br (10 mmol) was added and the reaction mixture was further stirred overnight under reflux condition. The formed precipitate was filtered and washed several times with solvents and dried under vacuum.



Benzimidazolium salt (A):[1] The general procedure was followed using potassium carbonate (1.52 g) and 2-bromopropane (2.8 mL). The volatile solvent was removed in vacuum, dichloromethane was added to the residue and filtered over celite. The solvent was removed under vacuum and gave a spongy solid and was then washed with ethyl acetate to produce 1.43 g benzimidazolium salt **A** as a white solid.

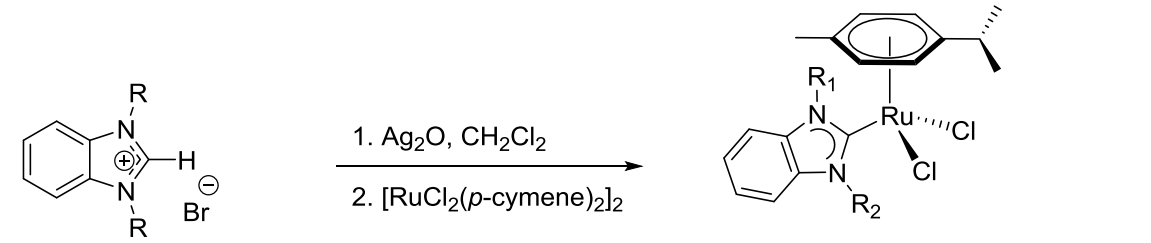


Benzimidazolium salt (B):[1] The general procedure was followed using sodium hydroxide (0.4 g), 2-bromopropane (1.4 mL) and benzyl bromide (2.8 mL). The reaction mixture was filtered and washed with toluene and diethyl ether to afford 2.64 g benzimidazolium salt **B** as white solid.



Benzimidazolium salt (C):[1] The general procedure was followed using, sodium hydroxide (0.4 g) and benzyl bromide (1.2 mL). The reaction mixture was filtered and washed with toluene and diethyl ether to afford 2.64 g benzimidazolium salt **C** as white solid.

2.2. Synthesis of Ru – NHC catalysts

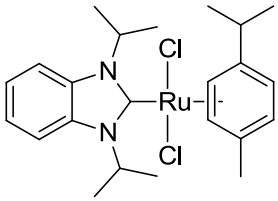


Benzimidazolium salt

1: $R_1 = R_2$ = Isopropyl (58%)
2: R_1 = Isopropyl, R_2= Benzyl (70%)
3: $R_1 = R_2$ = Benzyl (81%)

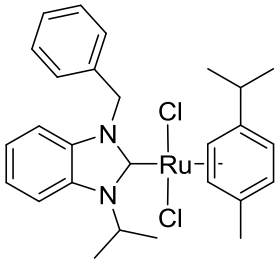
General Procedure:

In aluminum wrapped flask, benzimidazole salt (1.5 mmol) was dissolved in dichloromethane (3 mL) and methanol (0.5 mL) before adding silver oxide (1.2 mmol). After stirring about 2 hours, a solution of [Ru(*p*-cymene)Cl_2] (1 mmol) in dichloromethane was added into the reaction mixture and the reaction mixture was stirred overnight. Then the organic solvent was removed by evaporation and the crude product was purified by column chromatography.



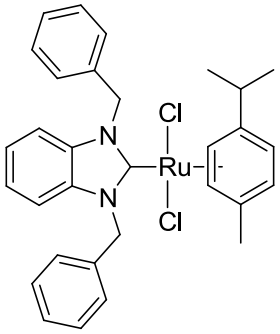
(1,3-diisopropyl-2,3-dihydrobenzoimidazol-2-yl)ruthenium(II)(p-cymene)chloride / Ru – NHC catalyst (1):

Following the general procedure, benzimidazole salt **A** (1.43 g), silver oxide (0.69 g) and [Ru(*p*-cymene)Cl_2] (1.53 g) were added. After purification by flash chromatography (5% MeOH/DCM) gave 1.49 g (58%) Ru-NHC catalyst **1** as a red powder solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.73 – 7.62 (m, 2H), 7.21 – 7.26 (m, 2H), 5.82 (hept, *J* = 7.0 Hz, 2H), 5.64 (d, *J* = 5.9 Hz, 2H), 5.26 (d, *J* = 5.9 Hz, 2H), 3.01 (hept, *J* = 7.0 Hz, 1H), 2.15 (s, 3H), 1.77 (d, *J* = 6.8 Hz, 6H), 1.73 (s, 6H), 1.41 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 187.6, 134.2, 121.9, 110.0, 106.9, 97.5, 86.7, 83.6, 53.8, 31.1, 23.0, 22.7, 22.3, 18.8. Anal. Calcd for $C_{23}H_{32}Cl_2N_2Ru$: C, 54.33; H, 6.34; N, 5.51; Found: C, 53.96; H, 6.46; N, 5.30. MS (ESI): *m/z* 496 [M − 2Cl + OH + MeCN]$^+$.

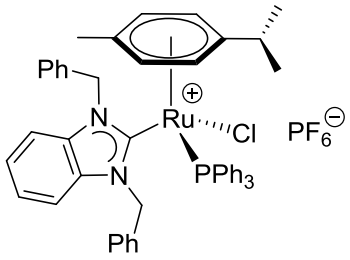


(1-benzyl-3-isopropy-2,3-dihydrobenzoimidazol-2-yl)ruthenium(II)(p-cymene)chloride / Ru – NHC catalyst (2): Following the general procedure, benzimidazole salt **B** (1.43 g), silver oxide (0.69 g) and [Ru(*p*-cymene)Cl_2] (1.53 g) were added. Purification by flash chromatography (5% MeOH/DCM) gave 1.97 g (70%) Ru-NHC catalyst **2** as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.72 (d, 1H), 7.37−7.21 (m, 4H), 7.14−7.02 (m, 4H), 6.54 (d, *J* = 15 Hz, 1H), 5.92−5.86 (m, 1H), 5.76 (d, *J* = 15 Hz, 1H), 5.55−5.14 (m, 4H), 2.89 (m, 1H), 2.07 (s, 3H), 1.86 (d, *J* = 7 Hz, 3H), 1.80 (d, *J* = 7 Hz, 3H), 1.35 (d, *J* = 7 Hz, 3H), 1.26 (d, *J* = 7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 189.7 (NCN), 137.7, 136.5, 133.4, 128.9, 127.5, 125.9, 122.8, 122.5, 112.7, 112.2, 107.7, 97.4, 85.9, 85.5 (Ar−C), 84.5, 84.4 (Ar−NH$(CH_3)_2$), 54.0

(NCH_2Ph), 53.1 ($NCH(CH_3)_2$), 30.9, 22.8, 22.7 ($Ar{-}CH(CH_3)_2$), 18.7 ($Ar{-}CH_3$). Anal. Calcd for $C_{27}H_{32}Cl_2N_2Ru$: C, 44.84; H, 4.80; N, 5.23. Found: C, 45.01; H, 4.98; N, 5.61. MS (ESI): *m/z* 545 $[M - 2Cl + OH + MeCN]^+$.



(1,3-dibenzyl-2,3-dihydrobenzoimidazol-2-yl)ruthenium(II)(*p*-cymene)chloride /Ru – NHC catalyst (3): Following the general procedure, benzimidazole salt **C** (2.64 g), silver oxide (0.97 g) and [Ru(*p*-cymene)Cl_2] (2.13 g) were added. Purification by flash chromatography (5% MeOH/DCM) gave 3.4 g (81%) Ru-NHC catalyst **3** as a red powdery solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.46 – 7.29 (m, 6H), 7.24 – 6.98 (m, 8H), 6.58 (d, *J* = 17.1 Hz, 2H), 5.87 (d, *J* = 17.2 Hz, 2H), 5.38 (d, *J* = 6.1 Hz, 2H), 5.08 (d, *J* = 6.1 Hz, 2H), 2.77 (hept, *J* = 7.0 Hz, 1H), 1.92 (s, 3H), 1.20 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 191.7, 137.5, 135.6, 128.9, 127.5, 126.0, 123.1, 111.7, 108.1, 97.3, 85.5, 84.6, 53.0, 30.6, 22.5, 18.3. Anal. Calcd for $C_{31}H_{32}Cl_2N_2Ru$: C, 61.59; H, 5.34; N, 4.63. Found: C, 61.63; H, 5.48; N, 4.85. MS (ESI): *m/z* 592 $[M - 2Cl + OH + MeCN]^+$.



3a

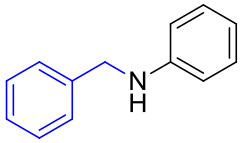
[(1,3-dibenzylbenzimidazolin-2-ylidene)ruthenium(II)(η^6-*p*-cymene)(triphenylphosphene)(chloro)]hexafluorate (3a). A solution of Ru complex **1** (604 mg, 1 mmol, 1.0 equiv) in acetone (30 mL) was added KPF_6 (183 mg, 1 mmol, 1.0 equiv) and triphenylphosphine (262 mg, 1 mmol, 1.0 equiv). The resulting solution was stirred at room temperature for 5 hr. Solvent was removed *in vacuo* and the residue was washed with water (10

mL × 3) and diethyl ether (10 mL × 3) to give **2** as yellow solid (930 mg, 0.95 mmol, 95%). ^{1}HNMR (300 MHz, DMSO-d_6): δ 7.55−7.13 (m, 27H, Ar−H), 6.72−6.62 (m, 3H, Ar−H), 6.31 (s, 1H, Ar−H), 6.19 (s, 1H, Ar−H), 6.04−5.92 (s, 2H, Ar−H), 5.40 (d, ^{3}J (H,H) = 15 Hz,1H, Ar−H), 4.95 (d, ^{3}J (H,H) = 15 Hz, 1H, Ar−H), 2.48−2.53 (m, 1H, Ar−CH(CH_3)$_2$), 1.14 (d, ^{3}J (H,H) = 6 Hz, 1H, NCH(CH_3)$_2$), 1.09 (d, ^{3}J (H,H) = 6 Hz, 1H, NCH(CH_3)$_2$), 0.97 (s, 1H, CH_3Ar). ^{13}C{^{1}H} NMR (75.43 MHz, DMSO-d_6): δ 187.3, 138.0, 137.8, 134.8, 134.6, 134.4, 133.7, 133.4, 129.3, 129.1, 129.0, 128.9, 128.4, 128.0, 127.5, 126.7, 126.1, 123.7, 123.6, 112.6, 112.5, 100.3 (Ar−H), 54.2 (NCH_2Ph), 30.3, 22.3, 21.6, 15.5 (CH_3Ar, CH(CH_3)$_2$Ar & (CH_3)$_2$CHAr).). 31P{^{1}H} NMR (121.44 MHz, DMSO-d_6): δ 32.32 (s, PPh_3), –143.5 (sept, ^{2}J(P,F) = 712 Hz, PF_6^-). No correct elemental analysis could be obtained for this compound, despite several attempts. MS (ESI): m/z 831 [M −PF_6]$^{+}$.

3. General Procedure for the N-alkylation of Amines with Alcohols or Diols

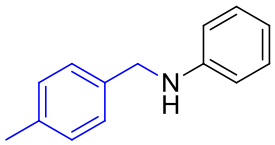
A mixture of amine (1 mmol), alcohol (1.2 mmol) and NHC – Ru catalyst (0.05 mmol) were added into a pressure-glass tube. Then the mixture was purged with argon. The reaction tube was sealed and heated at the desired temperature (130 ^{o}C) for the stipulated reaction time (18 h) under stirring at 500 rpm. After the reaction, the mixture was cooled to room temperature and the product was isolated by column chromatography. In the case of diols as alkylating agent, 2 mmol each of the primary amine and diols were used in the presence of 2.5 mol% Ru-NHC catalyst for 24 h at 130-150^{o}C.

4. Characterization of products

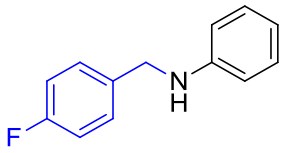


N-benzylaniline (8):[2] General procedure was followed using aniline (91 µL, 1.0 mmol) and benzyl alcohol (124 µL, 1.2 mmol) for 6h at 130 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 152 mg (85%) N-benzylaniline as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.26 (s, 5H), 7.21 – 7.10 (m, 2H), 6.69 (tt, J = 7.3, 1.2 Hz, 1H), 6.65 – 6.55 (m, 2H), 4.29 (s,

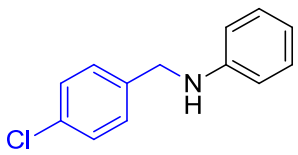
2H), 3.97 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 148.2, 139.5, 129.3, 128.7, 127.6, 127.3, 117.6, 112.9, 48.4. HR-MS $(M+H)^+$ m/z Calcd for $C_{13}H_{13}N$: 183.1048. Found: 184.1123.



N-(4-methylbenzyl)aniline (9):[2] General procedure was followed using aniline (91 µL, 1.0 mmol) and 4-methylbenzyl alcohol (150 µL, 1.2 mmol) for 18h at 130 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 187 mg (95%) N-(4-methylbenzyl)aniline as white solid, m.p. 42-44 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.28 (s, 1H), 7.22 – 7.13 (m, 4H), 6.74 (s, 1H), 6.70 – 6.64 (m, 2H), 4.29 (s, 2H), 2.35 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 147.8, 136.9, 136.0, 129.3, 129.2, 127.6, 117.9, 113.2, 48.4, 21.1. HR-MS $(M+H)^+$ m/z Calcd for $C_{14}H_{15}N$: 197.1208. Found: 198.1281.

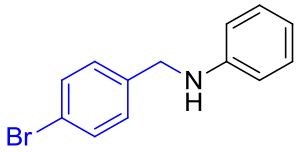


N-(4-fluorobenzyl)aniline (10):[3] General procedure was followed using aniline (91 µL, 1.0 mmol) and 4-fluorobenzyl alcohol (94 µL, 1.2 mmol) for 18h at 130 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 189 mg (91%) N-(4-fluorobenzyl)aniline as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.42 (dq, *J* = 10.2, 4.6, 3.2 Hz, 2H), 7.34 – 7.21 (m, 2H), 7.12 (tdd, *J* = 6.6, 4.7, 2.1 Hz, 2H), 6.84 (q, *J* = 7.5 Hz, 1H), 6.77 – 6.67 (m, 2H), 4.38 (d, *J* = 3.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 163.4, 163.3, 160.9, 160.9, 148.1, 148.0, 135.3, 135.3, 135.2, 129.4, 129.4, 129.1, 129.1, 129.0, 129.0, 117.8, 115.6, 115.4, 113.0, 113.0, 47.7. HR-MS $(M+H)^+$ m/z Calcd for $C_{13}H_{12}FN$: 201.0957. Found: 201.0954.

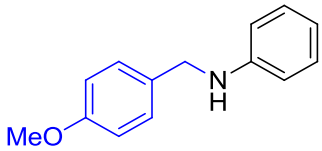


N-(4-chlorobenzyl)aniline (11):[4] General procedure was followed using aniline (91 µL, 1.0 mmol) and 4-chlorobenzyl alcohol (171 µL, 1.2 mmol) for 18h at 130 °C. Purification by flash

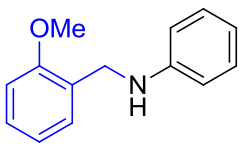
chromatography (3% EtOAc/Hexane) gave 132 mg (61%) N-(4-chlorobenzyl)aniline as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.26 (s, 4H), 7.21 – 7.09 (m, 2H), 6.70 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.64 – 6.52 (m, 2H), 4.25 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 147.9, 138.1, 132.9, 129.4, 129.3, 128.8, 128.7, 128.7, 117.9, 113.0, 112.9, 47.7. HR-MS $(M+H)^+$ m/z Calcd for $C_{13}H_{12}ClN$: 217.0661. Found: 217.0658.



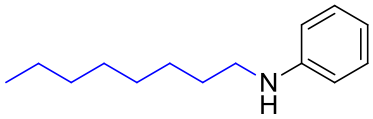
N-(4-bromobenzyl)aniline (12):[5] General procedure was followed using aniline (91 µL, 1.0 mmol) and 4-bromobenzyl alcohol (224 mg, 1.2 mmol) for 18h at 130 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 63 mg (25%) N-(4-bromobenzyl)aniline as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.41 – 7.32 (m, 2H), 7.16 (d, *J* = 2.4 Hz, 2H), 7.13 – 7.04 (m, 2H), 6.65 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.57 – 6.48 (m, 2H), 4.20 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 147.7, 138.5, 131.7, 129.3, 129.3, 129.1, 121.0, 118.0, 113.0, 47.8. HR-MS $(M+H)^+$ m/z Calcd for $C_{13}H_{12}BrN$: 261.0156. Found: 261.0153.



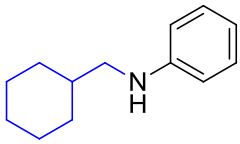
N-(4-methoxybenzyl)aniline (13):[2] General procedure was followed using aniline (91 µL, 1.0 mmol) and 4-methoxybenzyl alcohol (149 µL, 1.2 mmol) for 18h at 130 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 170 mg (80%) N-(4-methoxybenzyl)aniline as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.18 – 7.09 (m, 2H), 7.04 (dddd, *J* = 8.6, 6.8, 4.0, 2.2 Hz, 3H), 6.78 – 6.71 (m, 2H), 6.59 (tq, *J* = 7.3, 1.9, 1.5 Hz, 1H), 6.49 (ddt, *J* = 8.5, 2.5, 1.1 Hz, 2H), 4.10 (s, 2H), 3.65 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 159.0, 148.3, 131.6, 130.7, 129.3, 129.3, 128.9, 128.0, 117.6, 114.1, 113.0, 112.8, 55.4, 55.3, 53.6, 47.9. HR-MS $(M+H)^+$ m/z Calcd for $C_{14}H_{15}NO$: 213.116. Found: 213.1154.



N-(2-methoxybenzyl)aniline (14):[6] General procedure was followed using aniline (91 µL, 1.0 mmol) and 2-methoxybenzyl alcohol (160 µL, 1.2 mmol) for 18h at 130 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 149 mg (70%) N-(2-methoxybenzyl)aniline as white solid m.p. 93-94 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.26 (s, 3H), 7.20 – 7.13 (m, 2H), 6.96 – 6.85 (m, 2H), 6.70 (dd, *J* = 15.9, 7.5 Hz, 3H), 4.34 (s, 2H), 3.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 157.4, 148.3, 148.2, 129.2, 129.0, 128.3, 127.3, 127.2, 120.5, 117.5, 117.5, 113.2, 113.2, 110.3, 55.3, 43.6, 43.6. HR-MS $(M+H)^+$ m/z Calcd for $C_{14}H_{15}NO$: 213.1156. Found: 213.1154. Anal. Calcld. for. $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.84; H, 6.81; N 6.32.

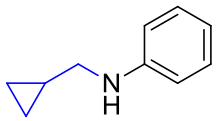


N-octylaniline (15):[7] General procedure was followed using aniline (91 µL, 1.0 mmol) and 1-octanol (193 µL, 1.2 mmol) for 18h at 130 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 150 mg (73%) N-octylaniline as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.16 – 7.04 (m, 2H), 6.61 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.56 – 6.48 (m, 2H), 3.50 (s, 1H), 3.03 (t, *J* = 7.1 Hz, 2H), 1.60 – 1.49 (m, 2H), 1.40 – 1.14 (m, 11H), 0.88 – 0.75 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 148.6, 129.2, 117.1, 112.7, 44.0, 31.8, 29.6, 29.4, 29.3, 29.3, 27.2, 22.7, 14.1, 14.1. HR-MS $(M+H)^+$ m/z Calcd for $C_{14}H_{23}N$: 205.1836. Found: 205.1830.

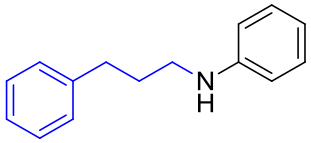


N-(cyclohexylmethyl)aniline (16):[2] General procedure was followed using aniline (91 µL, 1.0 mmol) and cyclohexanemethanol (148 µL, 1.2 mmol) for 18h at 130 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 130 mg (66%) N-(cyclohexylmethyl)aniline as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.24 – 7.14 (m, 2H), 6.70 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.62 (dq, *J* = 7.2, 1.2 Hz, 2H), 3.70 (s, 1H), 2.99 (d, *J* = 6.7 Hz, 2H), 1.93 – 1.68 (m, 5H), 1.68 – 1.53 (m, 1H), 1.27 (dqd, *J* = 15.5, 12.1, 9.0 Hz, 3H), 1.02 (qd, *J* = 11.9, 3.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 148.7, 129.2, 116.9, 112.7, 50.6, 37.6, 31.4, 26.6, 26.0. HR-MS $(M+H)^+$

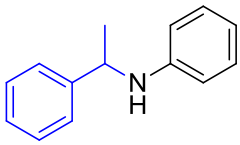
m/z Calcd for $C_{13}H_{19}N$: 189.1521. Found: 189.1517. Anal. Calcld. for. $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.28; H, 9.82; N 7.12.



N-(cyclopropylmethyl)aniline (17):[8] General procedure was followed using aniline (91 µL, 1.0 mmol) and cyclopropylmethanol (87 µL, 1.2 mmol) for 18h at 130 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 103 mg (70%) N-(cyclopropylmethyl)aniline as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.02 – 6.93 (m, 2H), 6.50 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.41 (dq, *J* = 7.6, 1.1 Hz, 2H), 2.76 (d, *J* = 6.9 Hz, 2H), 0.98 – 0.81 (m, 1H), 0.41 – 0.26 (m, 2H), 0.06 (d, *J* = 4.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 148.5, 129.2, 117.3, 112.8, 49.1, 10.9, 3.4. HR-MS $(M+H)^+$ m/z Calcd for $C_{10}H_{13}N$: 147.1052. Found: 147.1048.

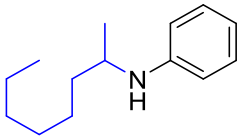


N-(3-phenylpropyl)aniline (18):[9] General procedure was followed using aniline (91 µL, 1.0 mmol) and 3-phenyl-1-propanol (163 µL, 1.2 mmol) for 24h at 130 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 94 mg (45%) N-(3-phenylpropyl)aniline as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.33 – 7.27 (m, 2H), 7.24 – 7.15 (m, 5H), 6.73 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.67 – 6.61 (m, 2H), 3.16 (t, *J* = 7.1 Hz, 2H), 2.78 – 2.71 (m, 2H), 2.04 – 1.91 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 147.7, 141.6, 129.3, 128.5, 128.4, 128.4, 126.0, 117.9, 113.3, 43.9, 33.4, 30.9. HR-MS $(M+H)^+$ m/z Calcd for $C_{15}H_{17}N$: 211.1362. Found: 211.1361.

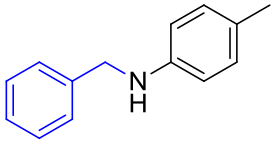


N-(1-phenylethyl)aniline (19):[10] General procedure was followed using aniline (91 µL, 1.0 mmol) and 1-phenylethanol (145 µL, 1.2 mmol) for 30h at 150 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 102 mg (52%) N-(1-phenylethyl)aniline as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.42 – 7.21 (m, 4H), 7.20 – 7.10 (m, 1H), 7.07 – 6.95 (m, 2H),

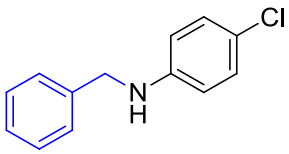
6.62 – 6.50 (m, 1H), 6.49 – 6.38 (m, 2H), 4.40 (q, *J* = 6.7 Hz, 1H), 1.43 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 147.2, 145.2, 129.1, 129.0, 128.6, 128.4, 127.2, 126.9, 125.9, 119.4, 117.3, 113.4, 53.5, 25.0.



N-(octan-2-yl)aniline (20):[9] General procedure was followed using aniline (91 µL, 1.0 mmol) and 2-octanol (191 µL, 1.2 mmol) for 30h at 150 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 26 mg (49%) N-(octan-2-yl)anilineas yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.20 – 7.10 (m, 2H), 6.81 – 6.73 (m, 1H), 6.73 – 6.63 (m, 2H), 3.79 (h, *J* = 6.2 Hz, 3H), 3.64 (s, 2H), 1.56 (s, 6H), 1.50 – 1.22 (m, 37H), 1.19 (d, *J* = 6.2 Hz, 10H), 0.94 – 0.84 (m, 11H).^{13}C NMR ($CDCl_3$, 100 MHz) δ= 129.3, 118.6, 115.1, 68.2, 39.4, 31.8, 29.3, 25.7, 23.5, 22.6, 14.1.

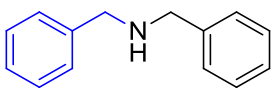


N-benzyl-4-methylaniline (21):[11] General procedure was followed using *p*-toluidine (110 µL, 1.0 mmol) and benzyl alcohol (124 µL, 1.2 mmol) for 18h at 130 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 122 mg (62%) N-benzyl-4-methylaniline as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.46 – 7.27 (m, 5H), 7.11 – 6.95 (m, 2H), 6.71 – 6.49 (m, 2H), 4.35 (s, 2H), 2.29 (d, *J* = 2.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 145.9, 145.9, 139.7, 139.7, 129.8, 128.6, 127.6, 127.2, 126.9, 113.1, 48.7, 20.4. HR-MS $(M+H)^+$ m/z Calcd for $C_{14}H_{15}N$: 197.1210. Found: 197.1204.

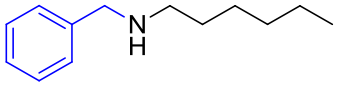


N-benzyl-4-chloroaniline (22):[12] General procedure was followed using 4-chloroaniline (89 µL, 1.0 mmol) and benzyl alcohol (124 µL, 1.2 mmol) for 18h at 130 °C. Purification by flash

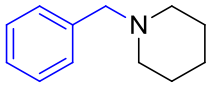
chromatography (3% EtOAc/Hexane) gave 187 mg (86%) N-benzyl-4-chloroanilineas yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.42 – 7.28 (m, 5H), 7.18 – 7.10 (m, 2H), 6.63 – 6.52 (m, 2H), 4.32 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 146.6, 146.6, 138.9, 138.9, 129.1, 128.7, 127.5, 127.4, 122.2, 114.0, 48.4. HR-MS $(M+H)^+$ m/z Calcd for $C_{13}H_{12}ClN$: 217.0657. Found: 217.0658. Anal. Calcld. for. $C_{13}H_{12}ClN$: C, 71.72; H, 5.56; N, 6.43. Found: C, 71.37; H, 5.33; N 6.26.



Dibenzylamine (23):[6] General procedure was followed using benzylamine (109 µL, 1.0 mmol) and benzyl alcohol (124 µL, 1.2 mmol) for 24h at 140 °C. Purification by flash chromatography (5% MeOH/DCM) gave 160 mg (81%) dibenzylamine as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.26 – 7.11 (m, 11H), 4.54 (s, 1H), 3.71 (s, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 140.2, 128.4, 128.2, 127.0, 53.2. HR-MS $(M+H)^+$ m/z Calcd for $C_{14}H_{15}N$: 197.1206. Found: 197.1204.

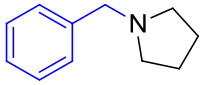


N-benzylhexan-1-amine (24):[13] General procedure was followed using 1-hexylamine (132 µL, 1.0 mmol) and benzyl alcohol (124 µL, 1.2 mmol) for 18h at 130 °C. Purification by flash chromatography (45% EtOAc/Hexane) gave 90 mg (47%) N-benzylhexan-1-amine as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.21 (m, 4H), 7.18 (d, *J* = 5.0 Hz, 1H), 3.73 (s, 2H), 2.62 – 2.50 (m, 2H), 2.03 (s, 1H), 1.45 (t, *J* = 7.5 Hz, 2H), 1.32 – 1.14 (m, 7H), 0.86 – 0.74 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= ^{13}C NMR (101 MHz, $CDCl_3$) δ 128.4, 128.3, 128.2, 127.0, 53.9, 49.4, 31.8, 29.9, 27.0, 22.6, 14.0. HR-MS $(M+H)^+$ m/z Calcd for $C_{13}H_{21}N$: 191.1681. Found: 191.1674.

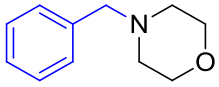


1-benzylpiperidine (25):[14] General procedure was followed using piperidine (99 µL, 1.0 mmol) and benzyl alcohol (124 µL, 1.2 mmol) for 5h at 120 °C. Purification by flash chromatography (3%

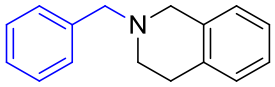
EtOAc/Hexane) gave 172 mg (98%) 1-benzylpiperdine as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.26 (s, 5H), 3.48 (s, 2H), 2.49 – 2.31 (m, 4H), 1.59 (p, *J* = 5.8 Hz, 4H), 1.49 – 1.40 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 138.6, 129.2, 128.1, 126.8, 63.9, 54.5, 26.0, 24.4. HR-MS $(M+H)^+$ m/z Calcd for $C_{12}H_{17}N$: 175.1360. Found: 175.1361.



1-benzylpyrrolidine (26):[14] General procedure was followed using pyrrolidine (82 µL, 1.0 mmol) and benzyl alcohol (124 µL, 1.2 mmol) for 24h at 120 °C. Purification by flash chromatography (2% MeOH/DCM) gave 118 mg (73%) 1-benzylpyrrolidine as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.28 – 7.14 (m, 6H), 3.55 (s, 2H), 2.44 (ddd, *J* = 6.7, 3.9, 1.6 Hz, 4H), 1.71 (p, *J* = 3.2 Hz, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 139.1, 129.0, 128.5, 128.2, 128.2, 126.9, 60.7, 54.1, 23.4. HR-MS $(M+H)^+$ m/z Calcd for $C_{11}H_{15}N$: 161.1207. Found: 161.1204.

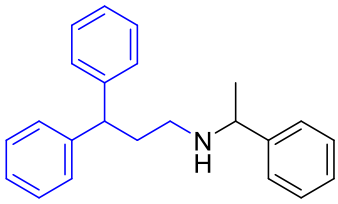


4-benzylmorpholine (27):[14] General procedure was followed using morpholine (87 µL, 1.0 mmol) and benzyl alcohol (124 µL, 1.2 mmol) for 17h at 120 °C. Purification by flash chromatography (5% MeOH/DCM) gave 126 mg (71%) 4-benzylmorpholine as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.40 – 7.28 (m, 5H), 3.76 – 3.67 (m, 4H), 3.50 (d, *J* = 1.1 Hz, 2H), 2.50 – 2.41 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 137.7, 129.2, 128.3, 127.1, 67.0, 63.5, 53.6. HR-MS $(M+H)^+$ m/z Calcd for $C_{11}H_{15}NO$: 177.116. Found: 177.1154.

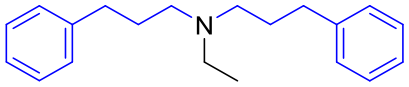


2-benzyl-1,2,3,4-tetrahydroisoquinoline (28):[15] General procedure was followed using 1,2,3,4-tetrahydroisoquinoline (125 µL, 1.0 mmol) and benzyl alcohol (124 µL, 1.2 mmol) for 24h at 120 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 156 mg (70%) 2-benzyl-1,2,3,4-tetrahydroisoquinoline as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.33 – 7.12 (m, 5H), 7.06 – 6.82 (m, 4H), 3.59 (d, *J* = 2.7 Hz, 2H), 3.56 – 3.50 (m, 2H), 2.79 (dd, *J* = 5.8, 3.2 Hz, 2H), 2.65 (dt, *J* = 8.4, 4.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 137.3, 137.3, 133.8,

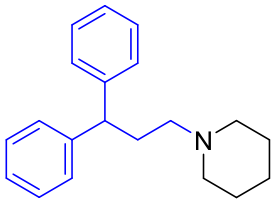
133.8, 133.3, 133.3, 128.0, 127.6, 127.2, 126.1, 125.5, 125.0, 124.5, 61.7, 61.7, 55.1, 55.0, 49.6, 49.6, 28.1, 28.1. HR-MS $(M+H)^+$ m/z Calcd for $C_{16}H_{17}N$: 223.1370. Found: 223.1361.



Fendiline (29):[16] General procedure was followed using methylbenzylamine (129 µL, 1.0 mmol) and 3,3-diphenyl-1-propanol (239 µL, 1.2 mmol) using 2.5mol% catalyst **3a** for 24h at 130 °C. Purification by flash chromatography (8% EtOAc/Hexane) gave 232 mg (74%) Fendiline as yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.04 (m, 15H), 3.90 (t, *J* = 7.8 Hz, 1H), 3.60 (q, *J* = 6.6 Hz, 1H), 2.44 – 2.33 (m, 2H), 2.22 – 2.06 (m, 2H), 1.21 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.76, 144.98, 144.73, 128.38, 128.32, 127.85, 127.75, 126.74, 126.48, 126.08, 58.13, 49.04, 45.99, 36.10, 24.28.

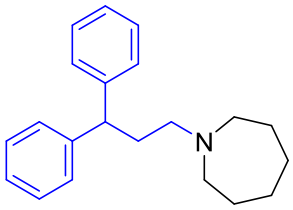


Alverine (30):[17] General procedure was followed using ethylamine (65 µL, 1.0 mmol) and 3-phenyl-1-propanol (324 µL, 2.4 mmol) for 24h at 130 °C. Purification by flash chromatography (20% EtOAc/Hexane) gave 197 mg (70%) Alverine as yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.09 (m, 10H), 2.64 – 2.35 (m, 10H), 1.82 – 1.60 (m, 4H), 0.94 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.15, 128.35, 128.30, 128.24, 125.75, 52.85, 47.47, 33.71, 28.41, 11.43.

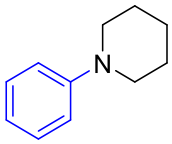


Fenpiprane (31):[17] General procedure was followed using piperidine (99 µL, 1.0 mmol) and 3,3-diphenyl-1-propanol (239 µL, 1.2 mmol) in the presence of 2.5 mol% **3a** for 24h at 130 °C. Purification by flash chromatography (10% EtOAc/Hexane) gave 173 mg (62%) Fenpiprane as

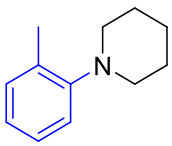
yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.06 (m, 10H), 3.89 (tq, *J* = 4.5, 2.5 Hz, 1H), 2.39 – 2.17 (m, 7H), 1.44 – 1.31 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.78, 128.42, 127.87, 127.84, 126.13, 57.67, 54.58, 49.36, 32.50, 25.73, 24.29.



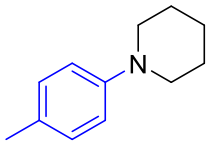
Prozapine (32):[17] General procedure was followed using hexamethyleneimine (113 µL, 1.0 mmol) and 3,3-diphenyl-1-propanol (239 µL, 1.2 mmol) in the presence of 2.5 mol% **3a** for 24h at 130 °C. Purification by flash chromatography (10% EtOAc/Hexane) gave 199 mg (68%) Prozapine as yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.01 (m, 11H), 3.95 (t, *J* = 7.7 Hz, 1H), 2.50 (t, *J* = 5.1 Hz, 4H), 2.42 – 2.26 (m, 2H), 2.22 – 2.02 (m, 2H), 1.51 (s, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.13, 128.35, 127.91, 126.00, 56.41, 55.56, 49.01, 33.65, 28.25, 27.03.



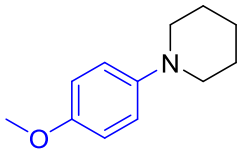
1-phenylpiperidine (33):[18] General procedure was followed using aniline (183 µL, 2.0 mmol) and 1,5-pentanediol (210 µL, 2.0 mmol) in the presence of 2.5 mol% **3a** for 24 h at 150 °C. Purification by flash chromatography (1% EtOAc/Hexane) gave 288 mg (89%) 1-phenylpiperidine as yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.13 (m, 2H), 6.88 (d, *J* = 8.1 Hz, 2H), 6.75 (tt, *J* = 7.3, 1.2 Hz, 1H), 3.13 – 3.04 (m, 4H), 1.71 – 1.59 (m, 4H), 1.55 – 1.47 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.05, 129.01, 119.34, 116.61, 50.80, 25.82, 24.29.



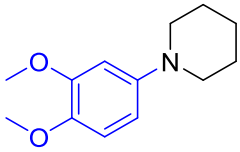
1-(*o*-tolyl)piperidine (35):[19] General procedure was followed using *o*-toluidine (212 µL, 2.0 mmol) and 1,5-pentanediol (210 µL, 2.0 mmol) in the presence of 2.5 mol% **3a** for 24 h at 150 °C. Purification by flash chromatography (1% EtOAc/Hexane) gave 266 mg (76%) 1-(*o*-tolyl)piperidine as yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.07 (ddd, *J* = 9.4, 8.0, 1.8 Hz, 2H), 6.98 – 6.83 (m, 2H), 2.81 – 2.71 (m, 4H), 2.23 (s, 3H), 1.63 (p, *J* = 5.8 Hz, 4H), 1.50 (ddt, *J* = 7.2, 3.9, 2.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.95, 132.69, 130.88, 126.37, 122.57, 118.96, 53.37, 26.64, 24.45, 17.81.



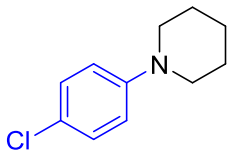
1-(*p*-tolyl)piperidine (36):[20] General procedure was followed using *p*-toluidine (214 mg, 2.0 mmol) and 1,5-pentanediol (210 µL, 2.0 mmol) in the presence of 2.5 mol% **3a** for 24 h at 150 °C. Purification by flash chromatography (1% EtOAc/Hexane) gave 308 mg (88%) 1-(*p*-tolyl)piperidine as yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.03 – 6.94 (m, 2H), 6.82 – 6.74 (m, 2H), 3.08 – 2.95 (m, 4H), 2.19 (s, 3H), 1.63 (tt, *J* = 7.2, 5.0 Hz, 4H), 1.54 – 1.43 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 150.30, 129.50, 128.69, 116.92, 51.30, 25.96, 24.31, 20.38.



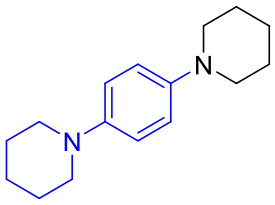
1-(4-methoxyphenyl)piperidine (37):[21] General procedure was followed using *p*-anisidine (246 mg, 2.0 mmol) and 1,5-pentanediol (210 µL, 2.0 mmol) in the presence of 2.5 mol% **3a** for 24 h at 150 °C. Purification by flash chromatography (1% EtOAc/Hexane) gave 374 mg (98%) 1-(4-methoxyphenyl)piperidine as yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.88 – 6.80 (m, 2H), 6.80 – 6.72 (m, 2H), 3.69 (s, 3H), 3.02 – 2.89 (m, 4H), 1.71 – 1.59 (m, 4H), 1.50 – 1.42 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.56, 146.96, 118.71, 114.35, 55.57, 52.27, 26.14, 24.21.



1-(3,4-dimethoxyphenyl)piperidine (38):[21] General procedure was followed using with 3,4-dimethoxyamine (306 mg, 2.0 mmol) and 1,5-pentanediol (210 µL, 2.0 mmol) in the presence of 2.5 mol% **3a** for 24 h at 150 °C. Purification by flash chromatography (1% EtOAc/Hexane) gave 411 mg (93%) 1-(3,4-dimethoxyphenyl)piperidine as yellow oil[1.] H NMR (400 MHz, Chloroform-*d*) δ 6.71 (d, *J* = 8.7 Hz, 1H), 6.52 (d, *J* = 2.7 Hz, 1H), 6.39 (dd, *J* = 8.7, 2.7 Hz, 1H), 3.77 (d, *J* = 14.9 Hz, 6H), 3.04 – 2.92 (m, 4H), 1.72 – 1.59 (m, 4H), 1.51 – 1.46 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.47, 147.57, 143.32, 112.12, 108.42, 103.63, 56.34, 55.82, 52.34, 26.15, 24.23.

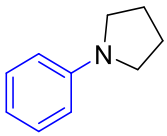


1-(4-chlorophenyl)piperidine (39):[20] General procedure was followed using 4-chloroaniline (255 µL, 2.0 mmol) and 1,5-pentanediol (210 µL, 2.0 mmol) in the presence of 2.5 mol% **3a** for 24 h at 150 °C. Purification by flash chromatography (1% EtOAc/Hexane) gave 246 mg (63%) 1-(4-chlorophenyl)piperidine as white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 – 7.07 (m, 2H), 6.82 – 6.69 (m, 2H), 3.10 – 3.00 (m, 4H), 1.68 – 1.55 (m, 5H), 1.55 – 1.45 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.81, 128.81, 123.86, 117.60, 50.63, 25.71, 24.18.

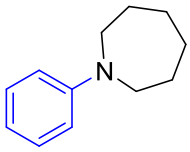


1,4-di(piperidin-1-yl)benzene (40):[22] General procedure was followed using N-(4-aminophenyl)piperine (353 mg, 2.0 mmol) and 1,5-pentanediol (210 µL, 2.0 mmol) in the presence of 2.5 mol% **3a** for 24 h at 150 °C. Purification by flash chromatography (1% EtOAc/Hexane) gave 352 mg (72%) 1,4-di(piperidin-1-yl)benzene as white solid. ^{1}H NMR (400

MHz, Chloroform-*d*) δ 6.81 (s, 4H), 3.04 – 2.86 (m, 8H), 1.63 (q, *J* = 5.6 Hz, 8H), 1.50 – 1.37 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.30, 118.14, 51.97, 26.13, 24.26.



1-phenylpyrrolidine (41):[23] General procedure was followed using aniline (183 µL, 2.0 mmol) and 1,4-butanediol (177 µL, 2.0 mmol) in the presence of 2.5 mol% **3a** for 24 h at 150 °C. Purification by flash chromatography (1% EtOAc/Hexane) gave 210 mg (71%) 1-phenylpyrrolidine as yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.09 (m, 2H), 6.64 – 6.55 (m, 1H), 6.49 (dt, *J* = 7.8, 1.1 Hz, 2H), 3.27 – 3.15 (m, 4H), 1.98 – 1.87 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.01, 129.10, 115.37, 111.65, 47.56, 25.45.



1-phenylazepane (42):[18] General procedure was followed using aniline (183 µL, 2.0 mmol) and 1,6-hexanediol (236 µL, 2.0 mmol) in the presence of 2.5 mol% **3a** for 24 h at 150 °C. Purification by flash chromatography (1% EtOAc/Hexane) gave 264 mg (76%) 1-phenylazepane as yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 – 7.07 (m, 2H), 6.66 – 6.59 (m, 2H), 6.59 – 6.47 (m, 1H), 3.47 – 3.27 (m, 4H), 1.71 (dh, *J* = 8.8, 3.1 Hz, 5H), 1.52 – 1.42 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.92, 129.22, 115.13, 111.17, 49.07, 27.82, 27.18.

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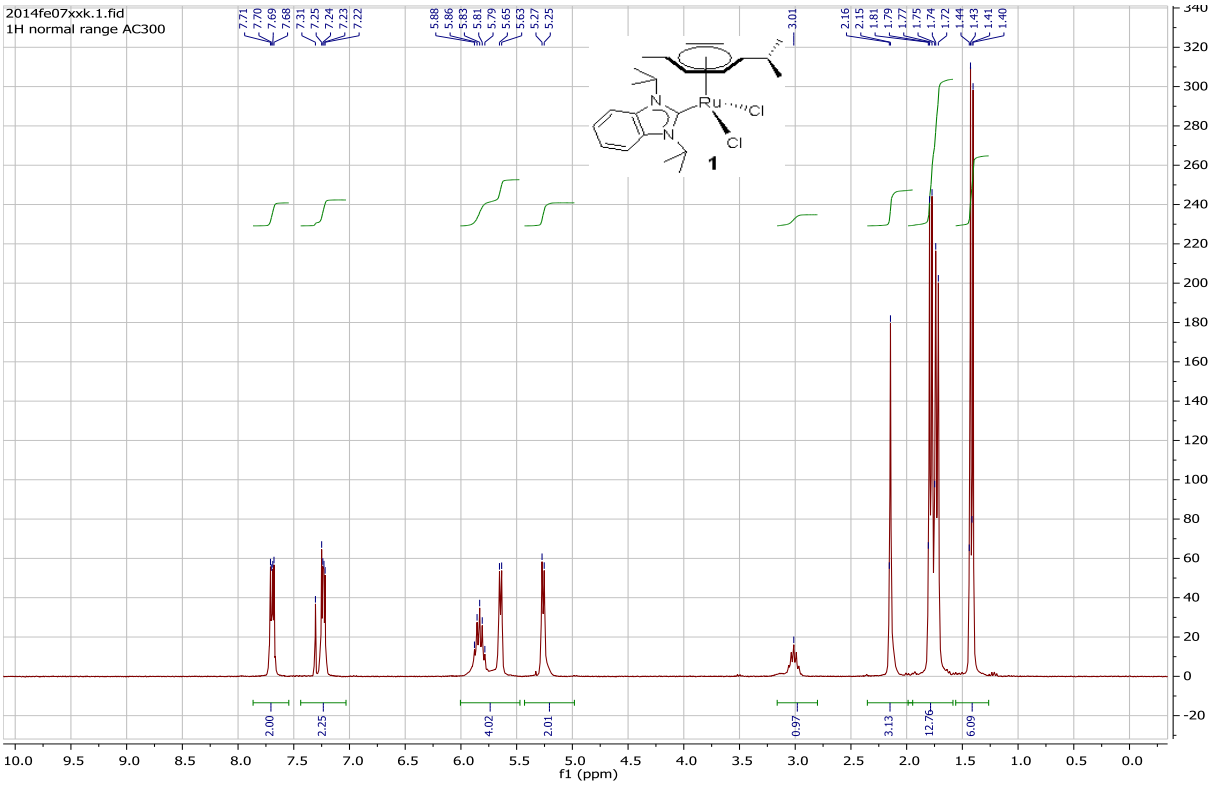
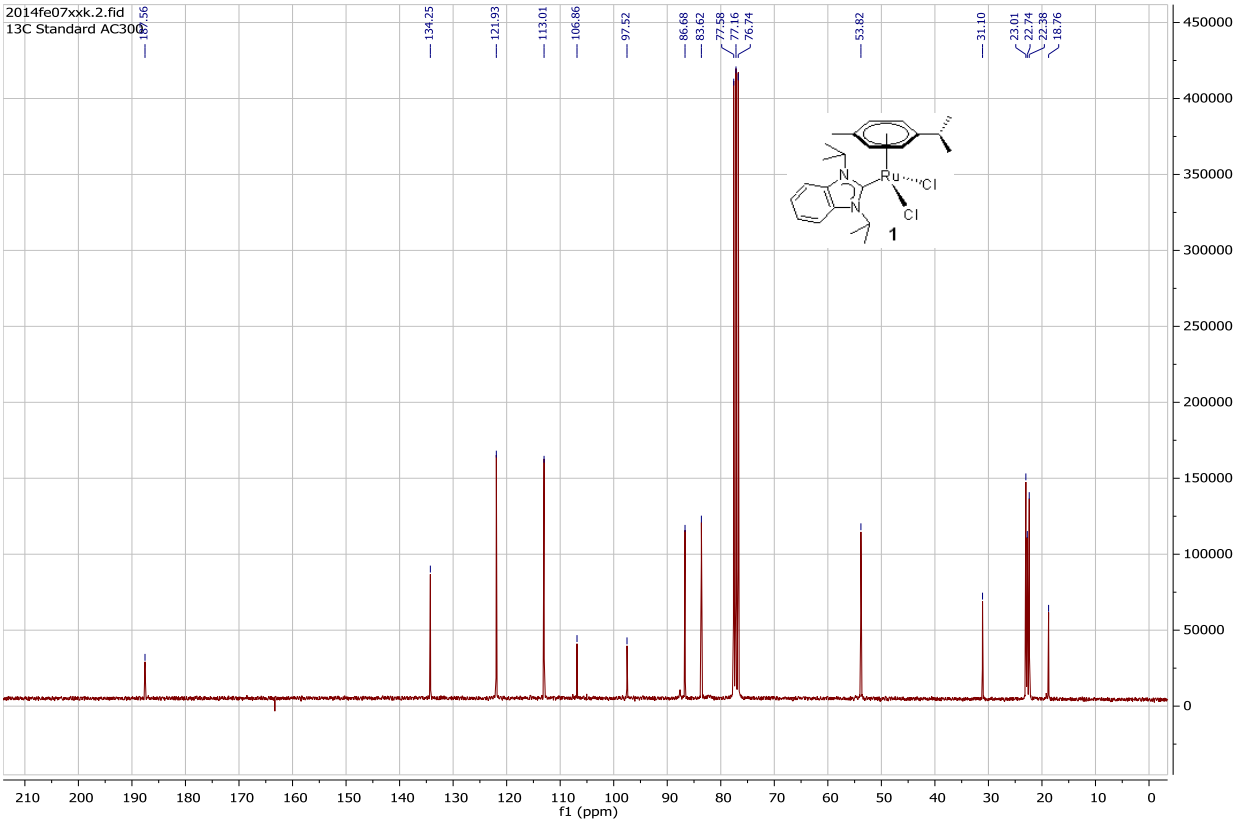
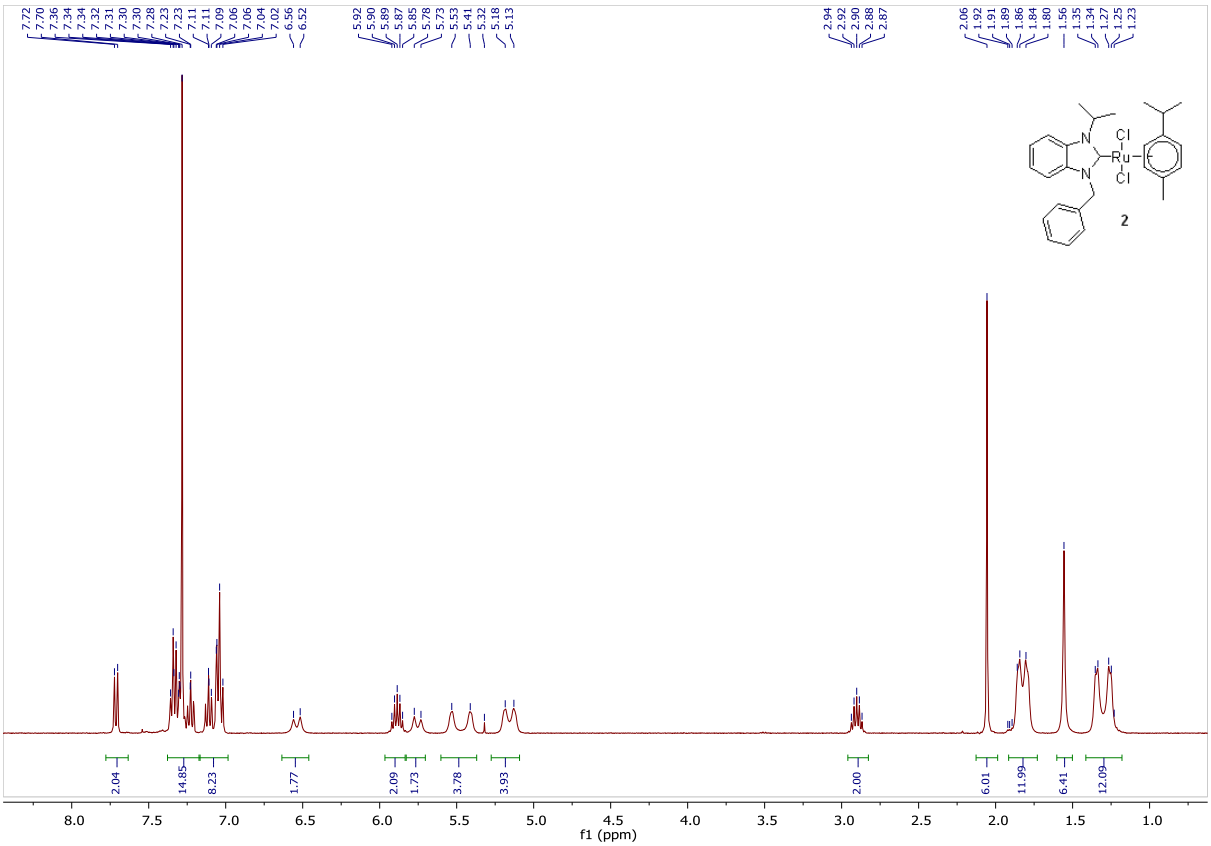
6. NMR Spectra of complexes and compounds



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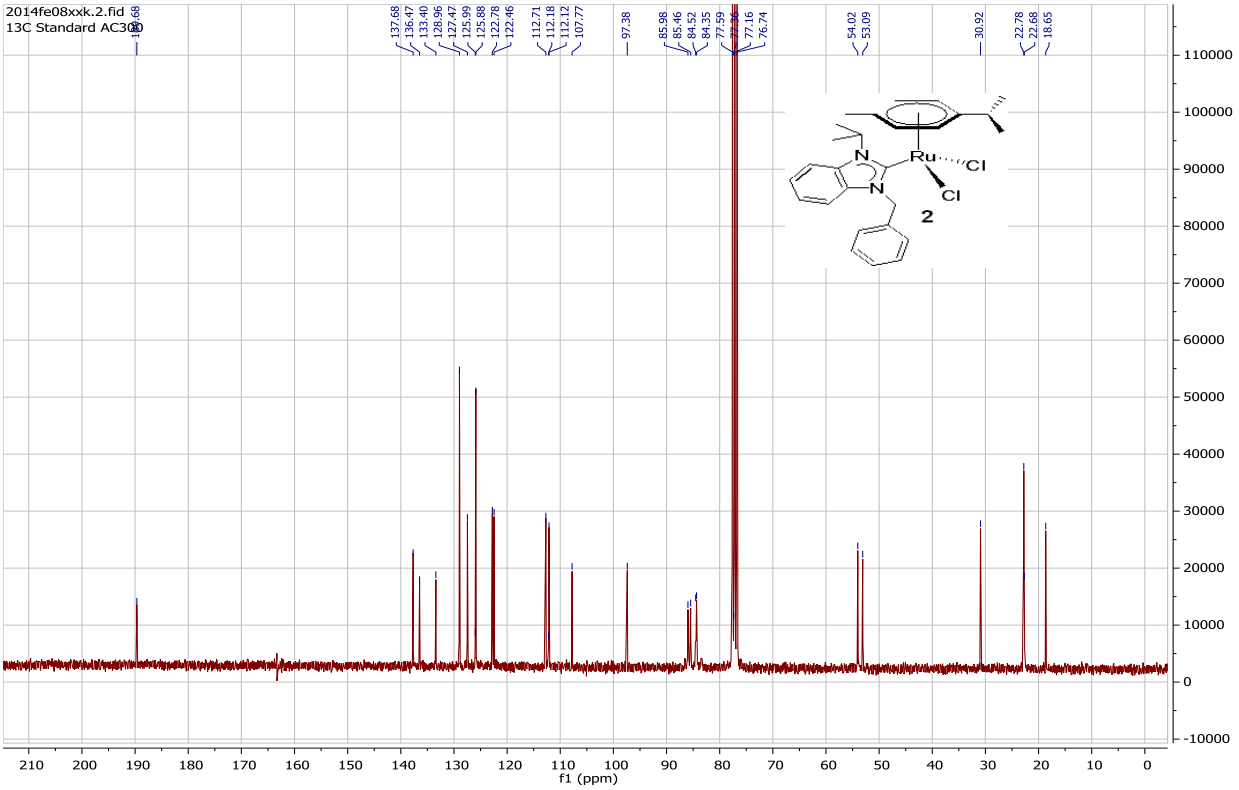
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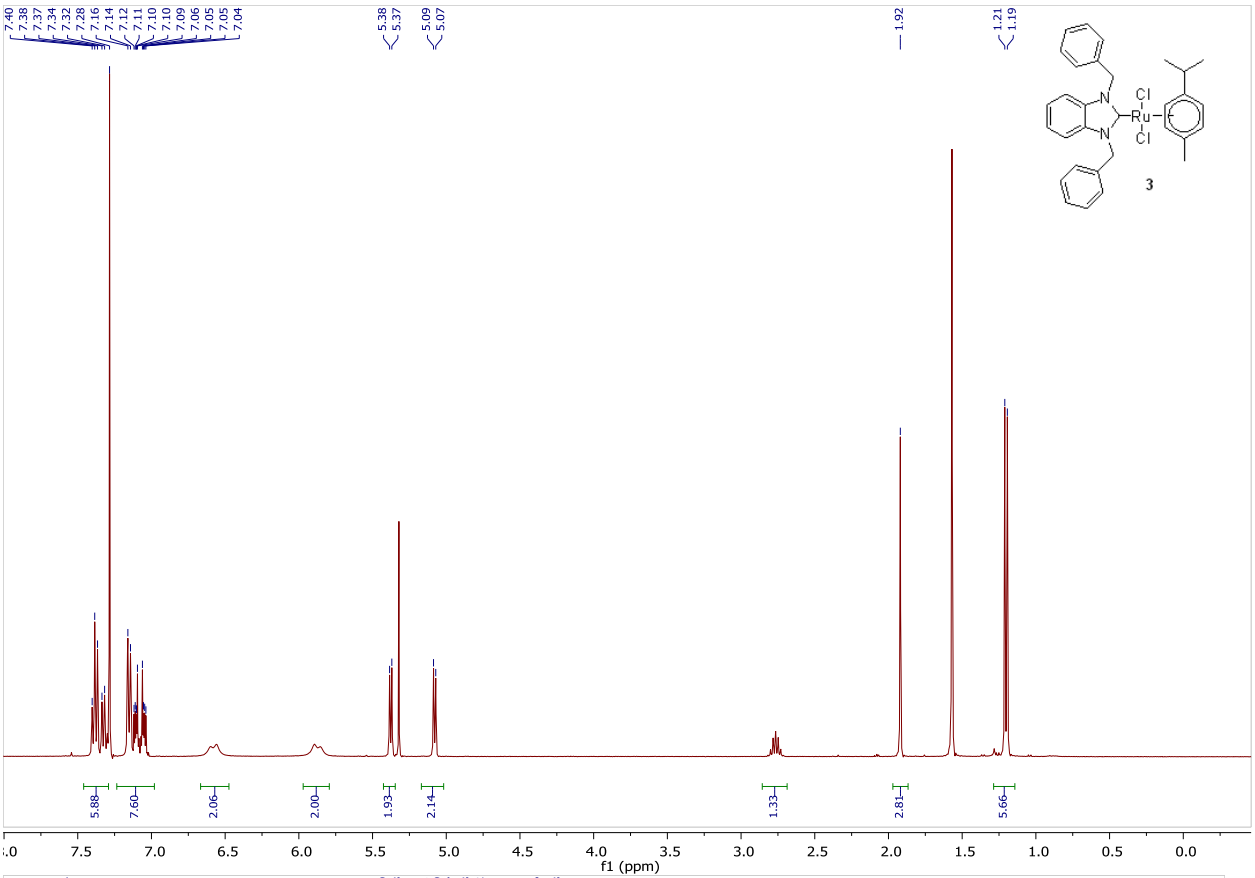
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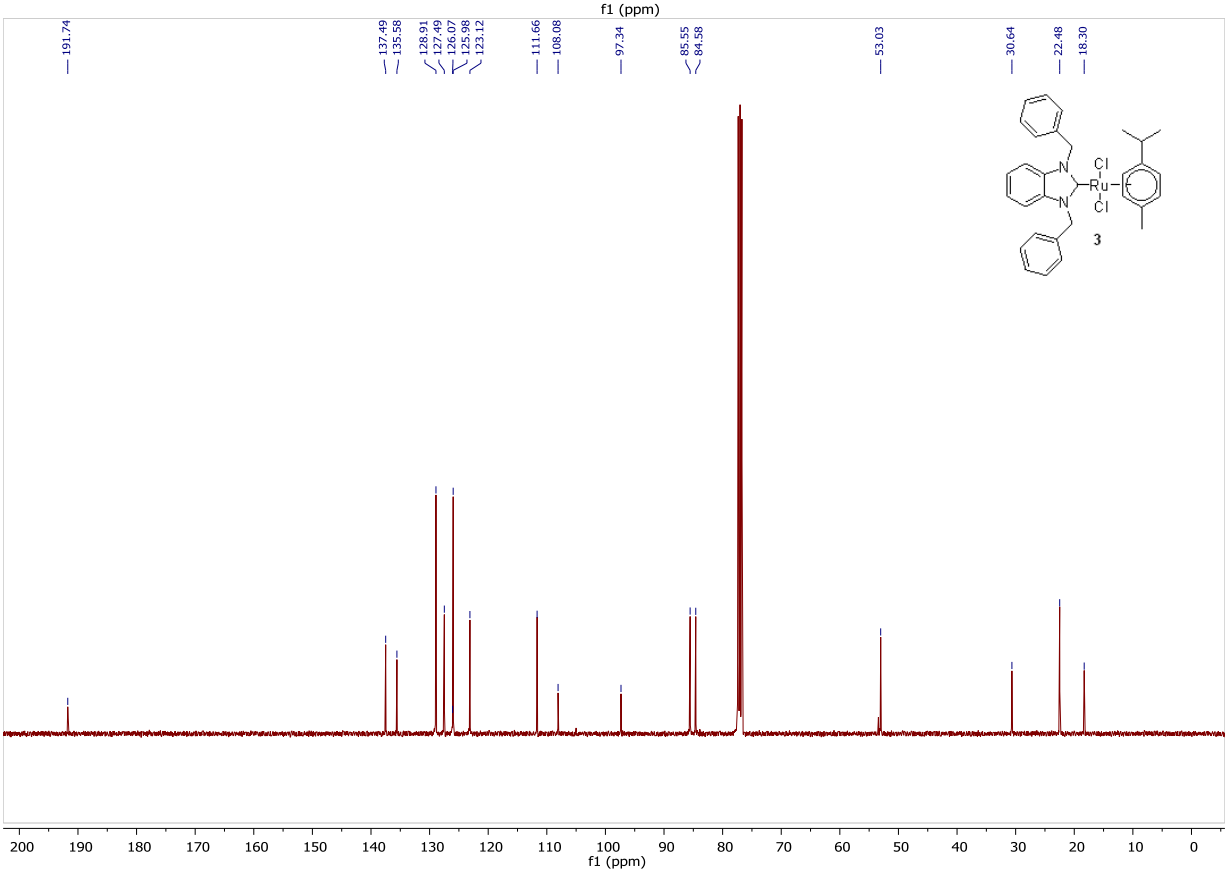
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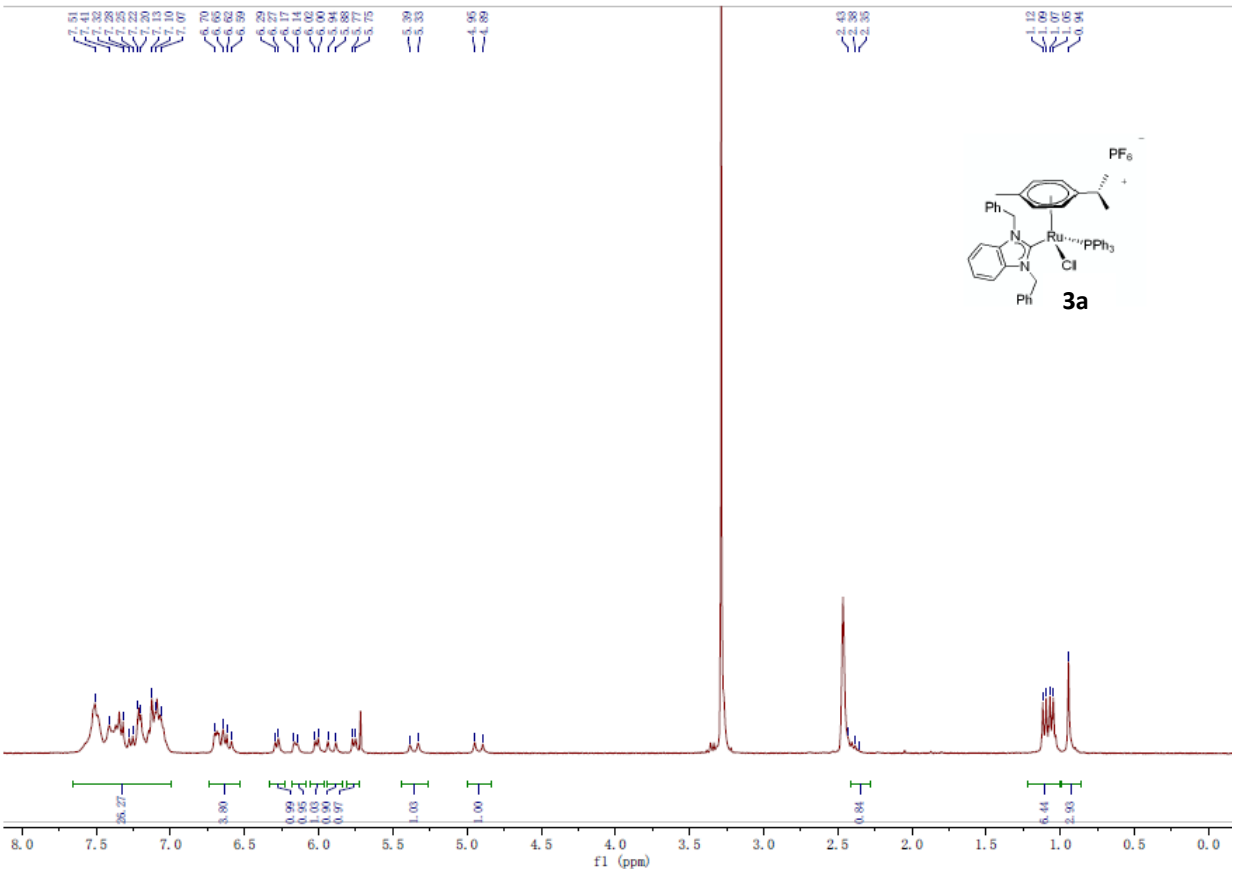
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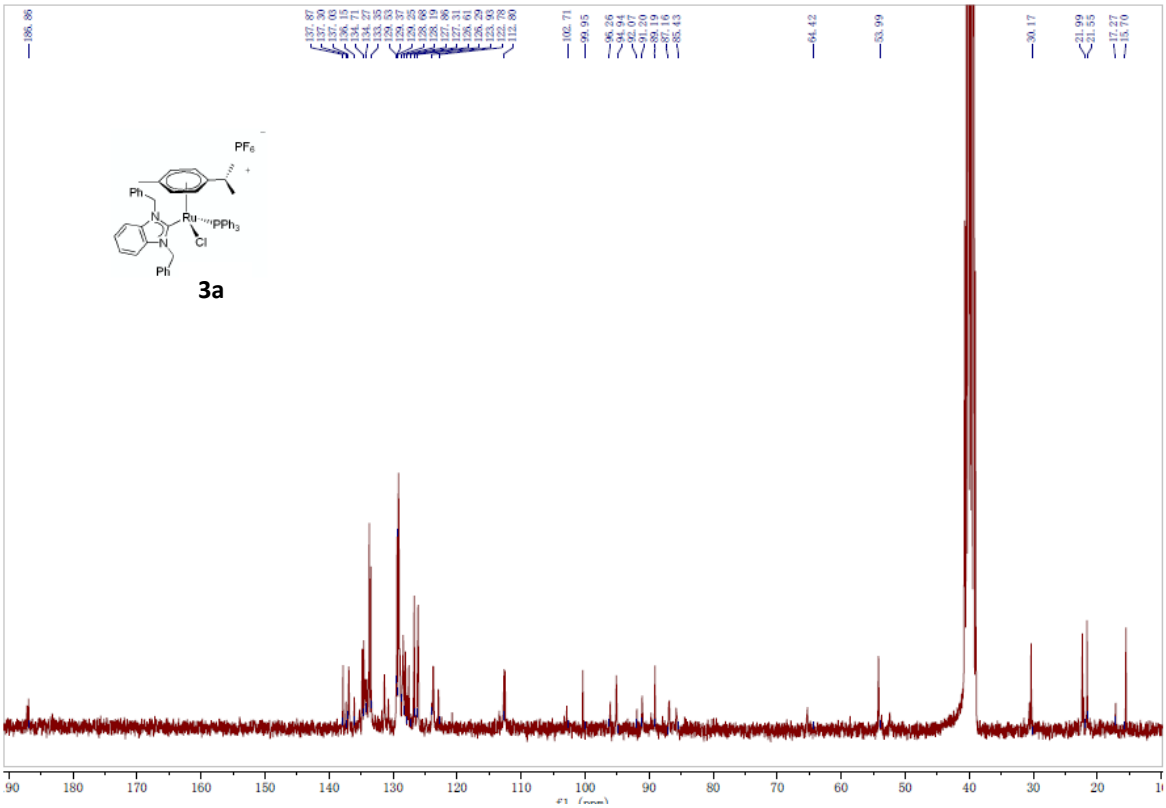
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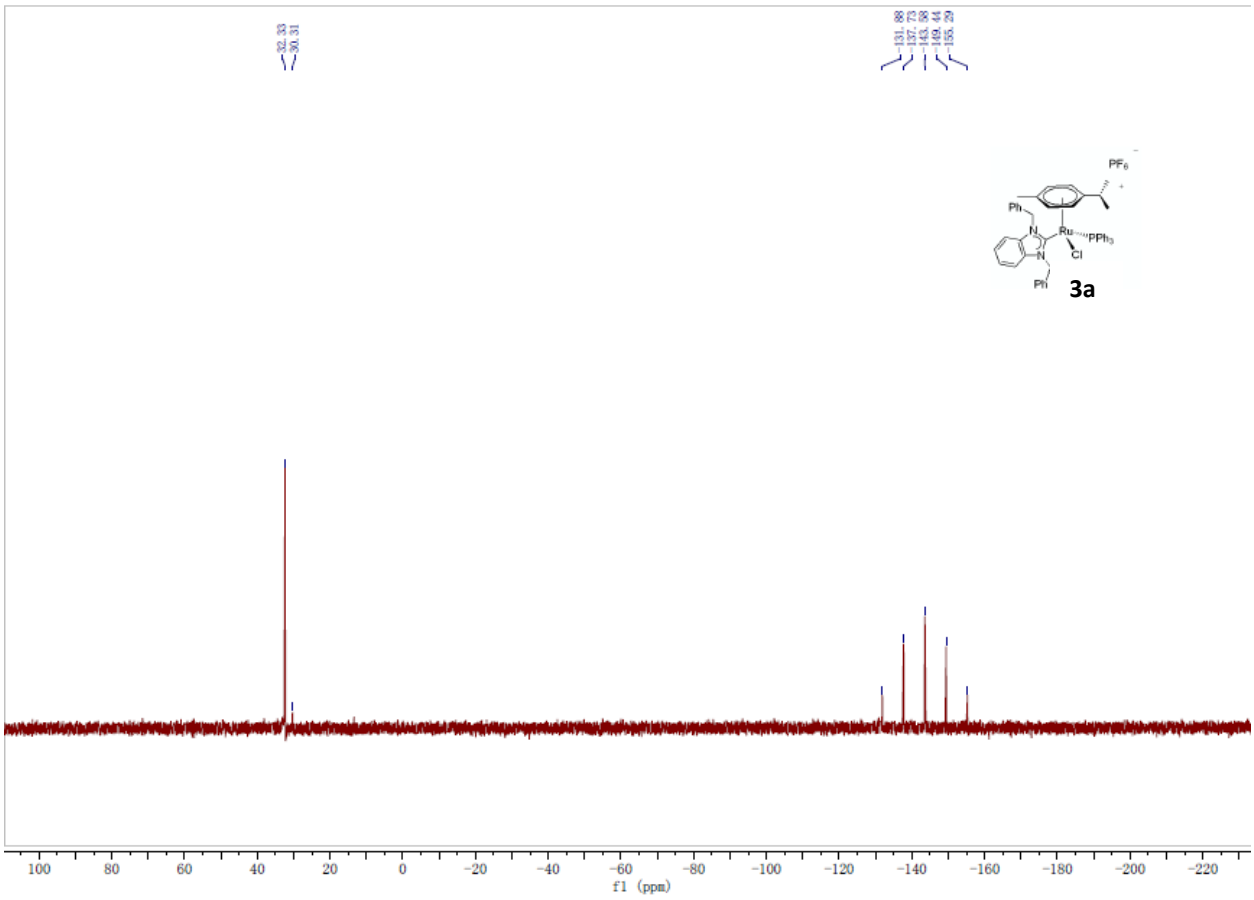
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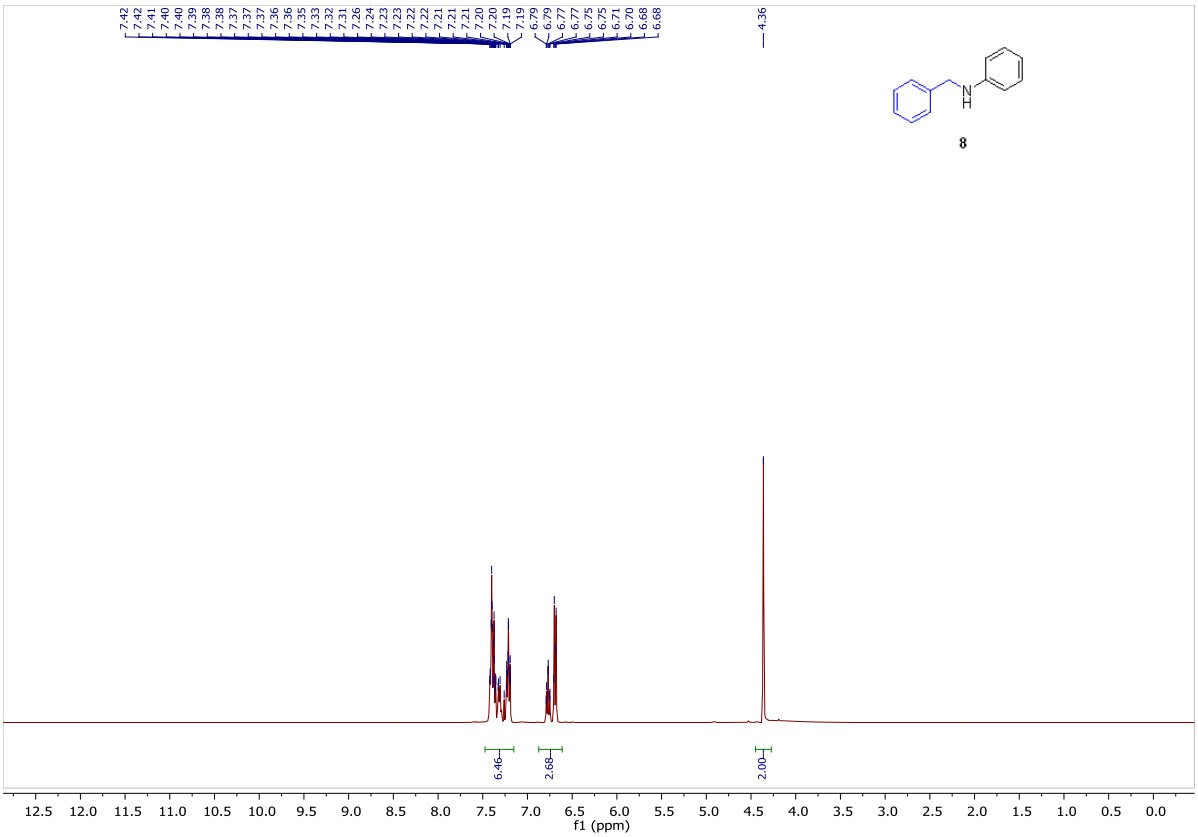
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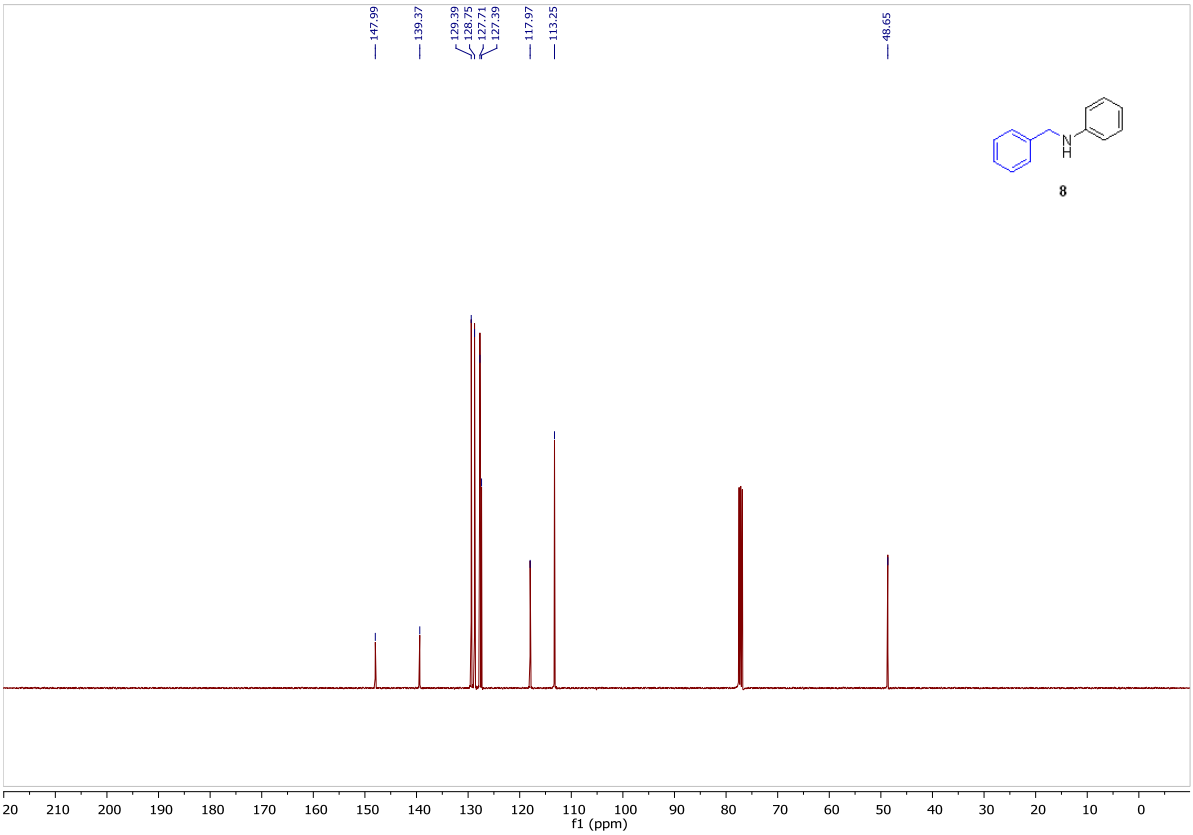
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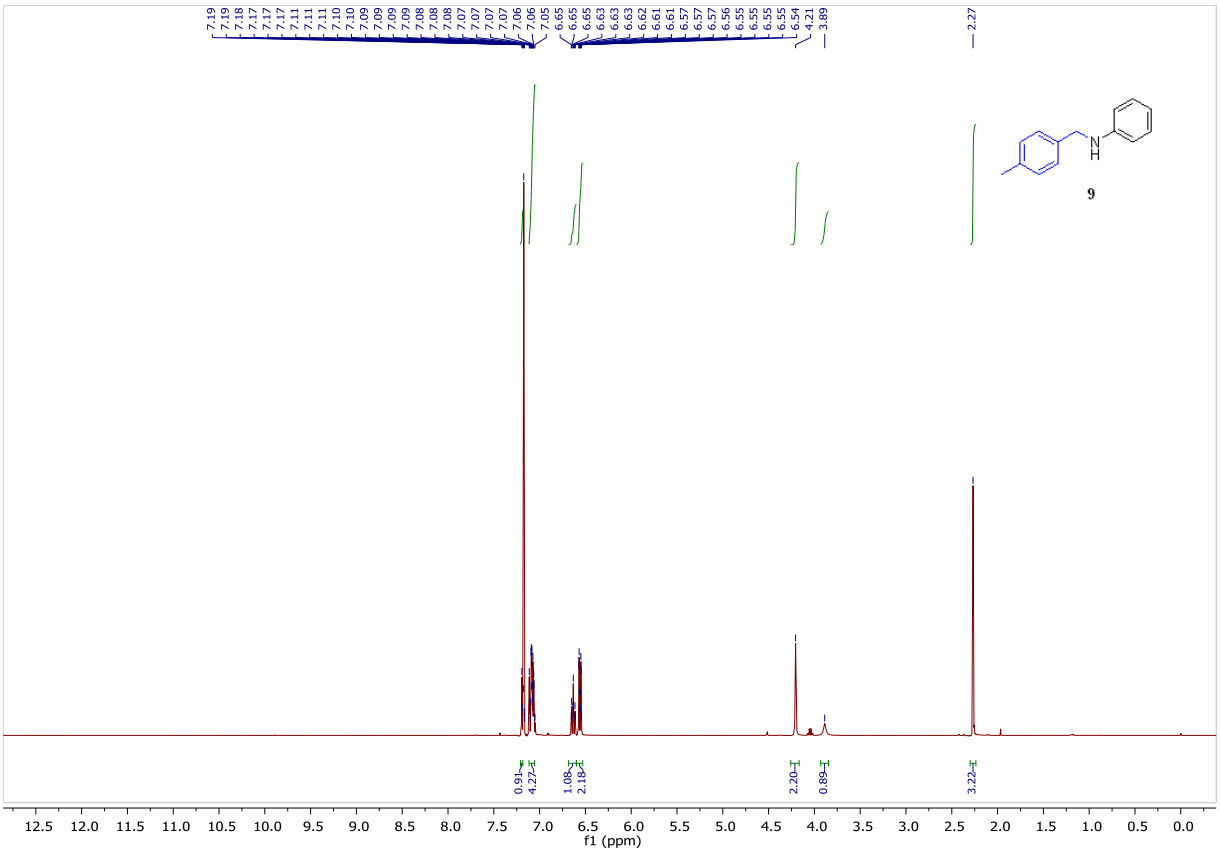
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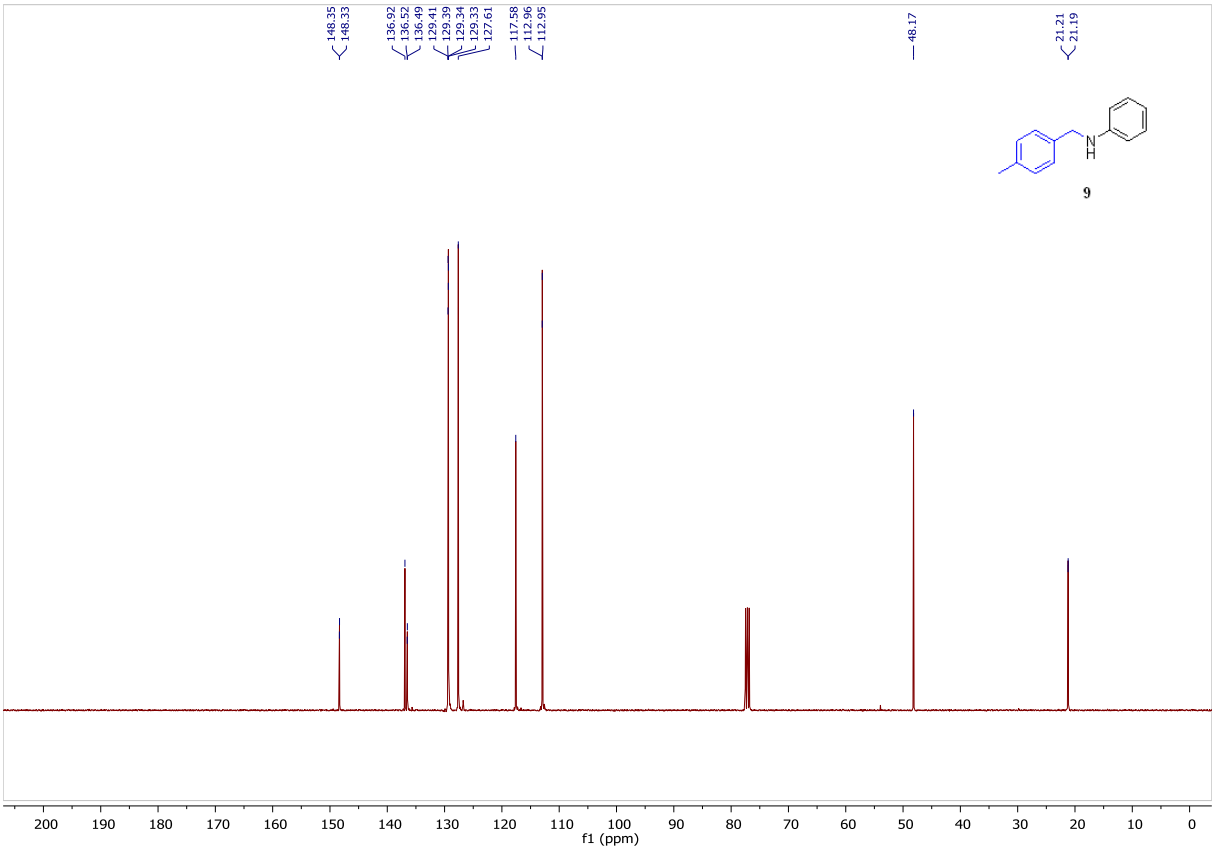
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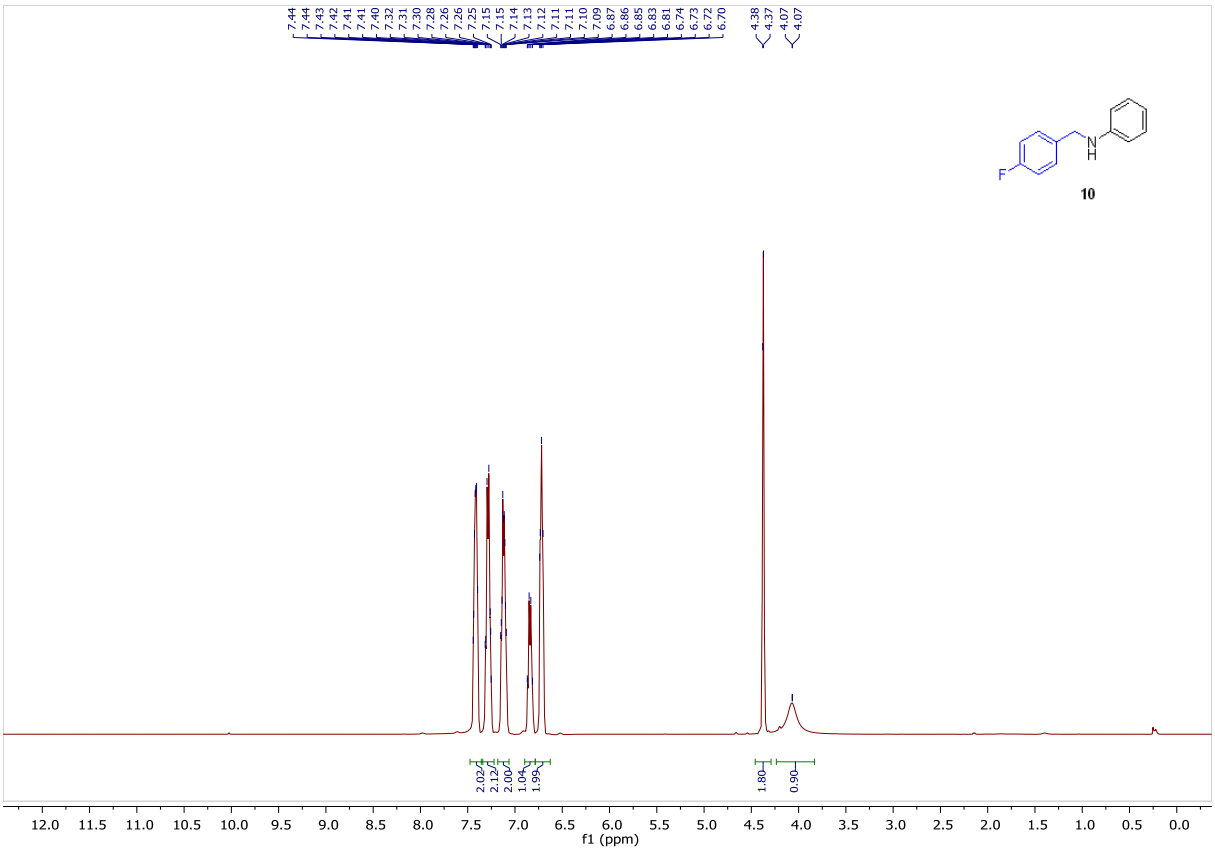
f1 (ppm)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7.15
7.14
7.13
7.12
7.11
7.11
7.10
7.09
6.87
6.86
6.85
6.83
6.81
6.74
6.73
6.72
6.70
4.38
4.37
4.07
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F
N
H
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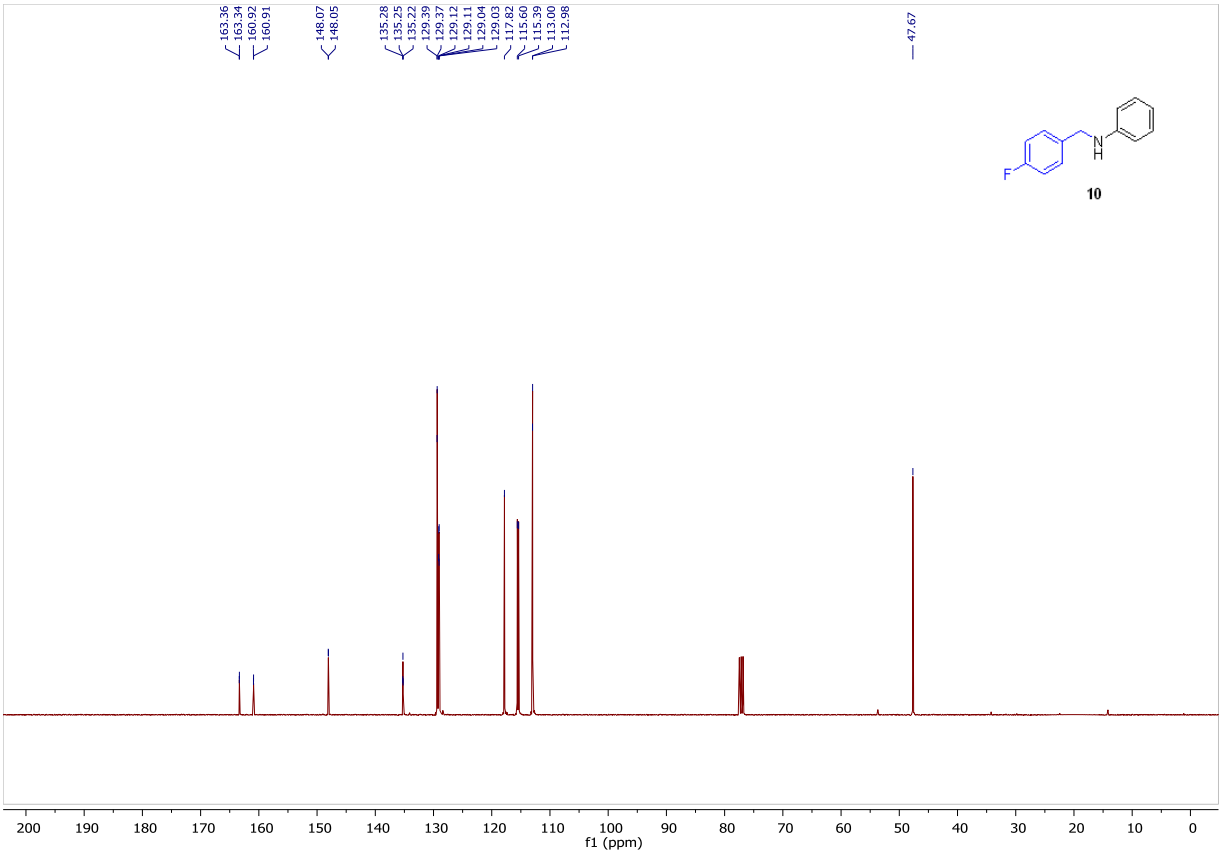
2.12
2.00
1.04
1.99
1.80
0.90
f1 (ppm)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135.25
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129.11
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113.00
112.98
47.67
F
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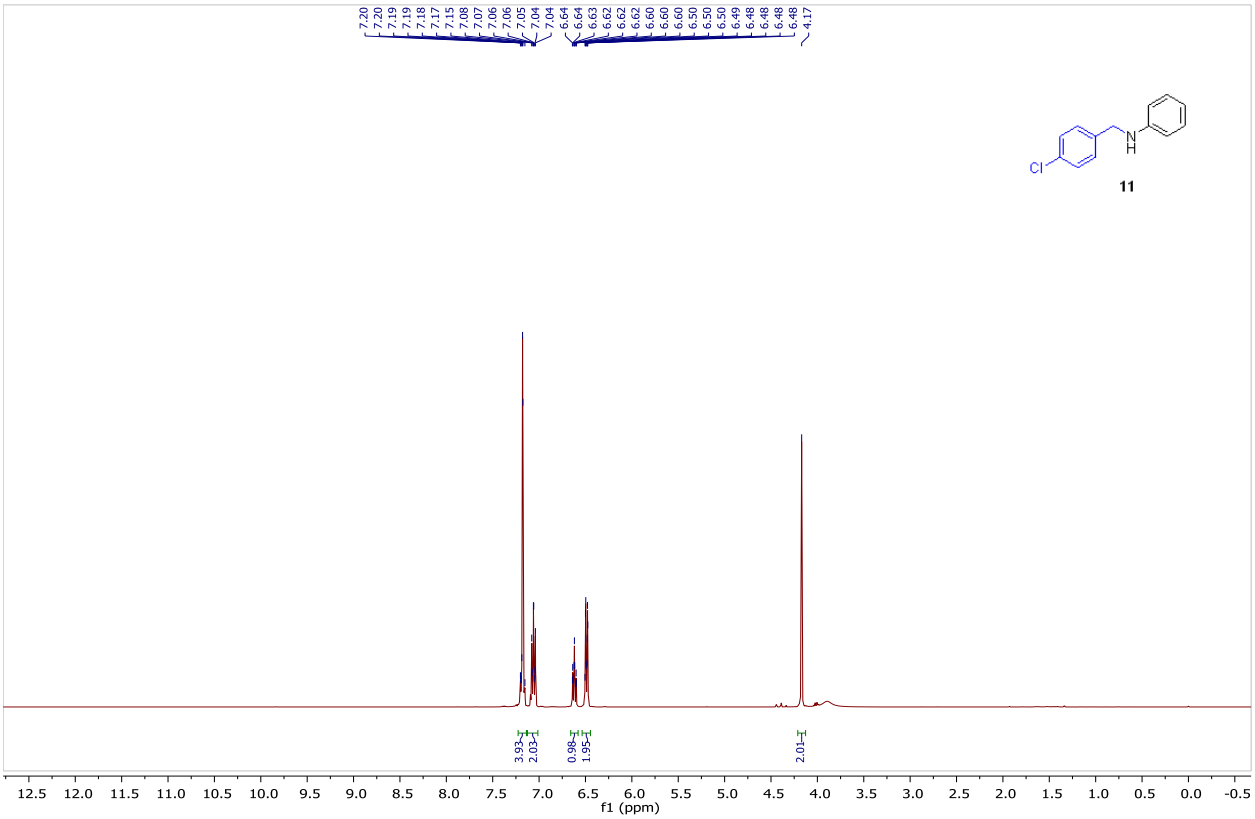
H
10
f1 (ppm)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7.04
7.04
6.64
6.64
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6.62
6.62
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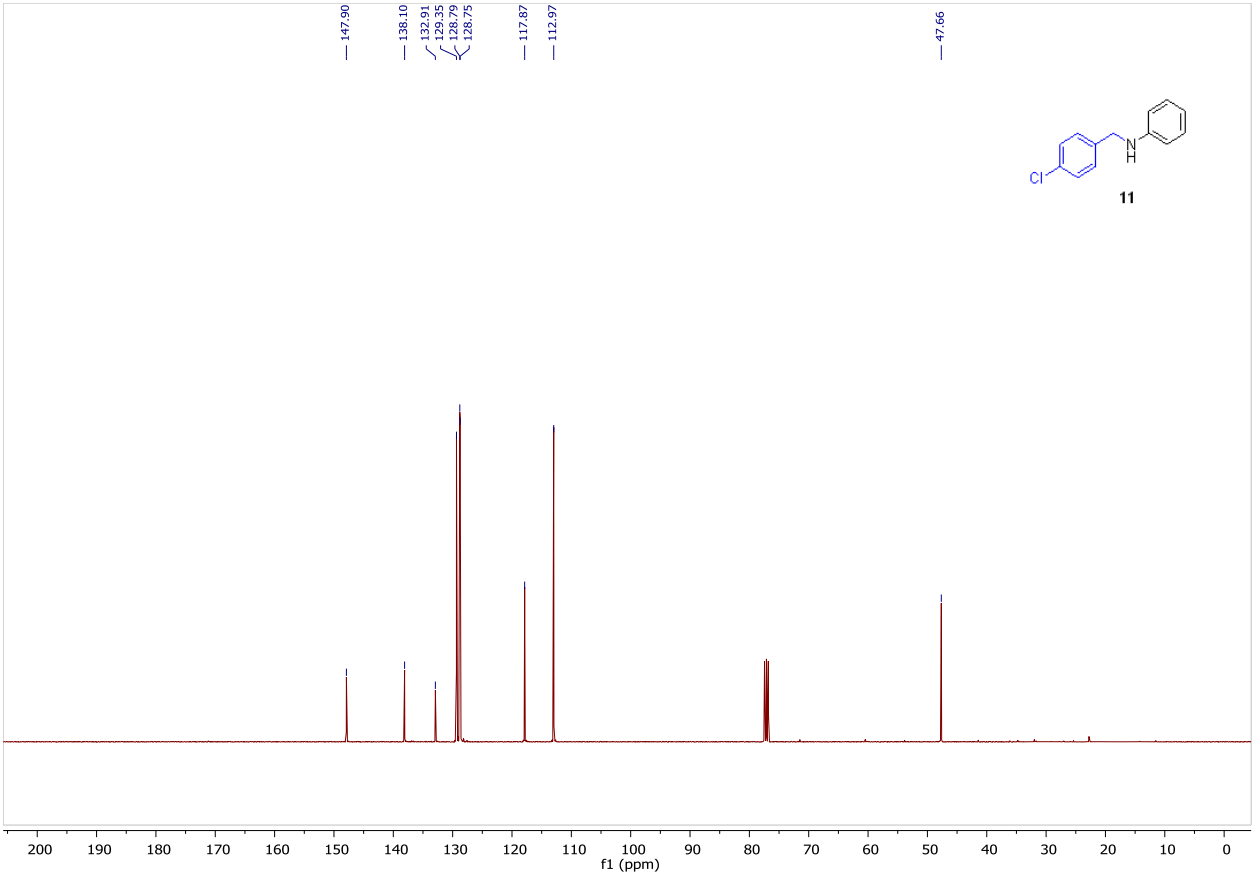
6.60
6.50
6.50
6.50
6.49
6.48
6.48
6.48
6.48
4.17
Cl
N
H
11
3.93
2.03
0.98
1.95
2.01
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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N
H
11
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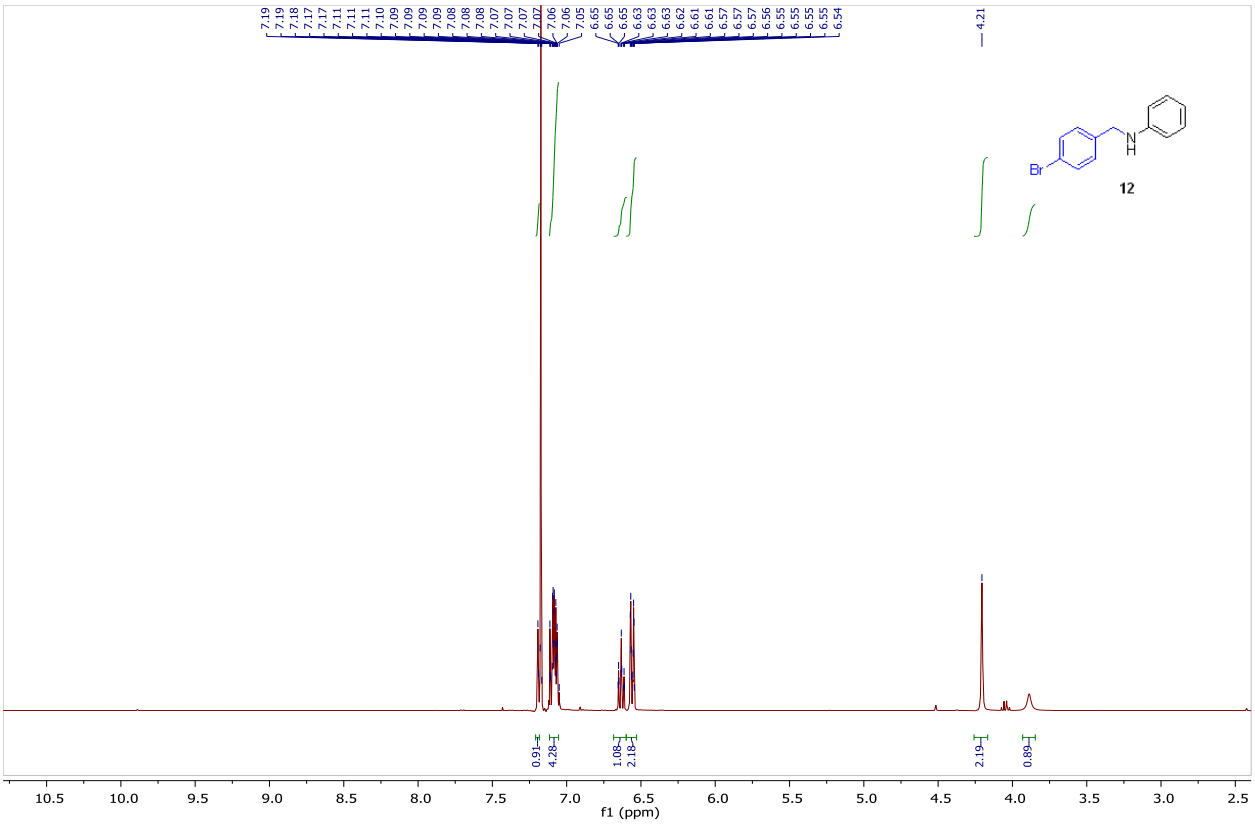
f1 (ppm)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7.09
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7.08
7.08
7.07
7.07
7.07
7.02
7.06
7.06
7.05
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6.57
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6.57
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6.55
6.55
6.55
6.55
6.54
4.21
Br
N
H
12
0.91
4.28
1.08
2.18
2.19
0.89
10.5
10.0
9.5
9.0
8.5
8.0
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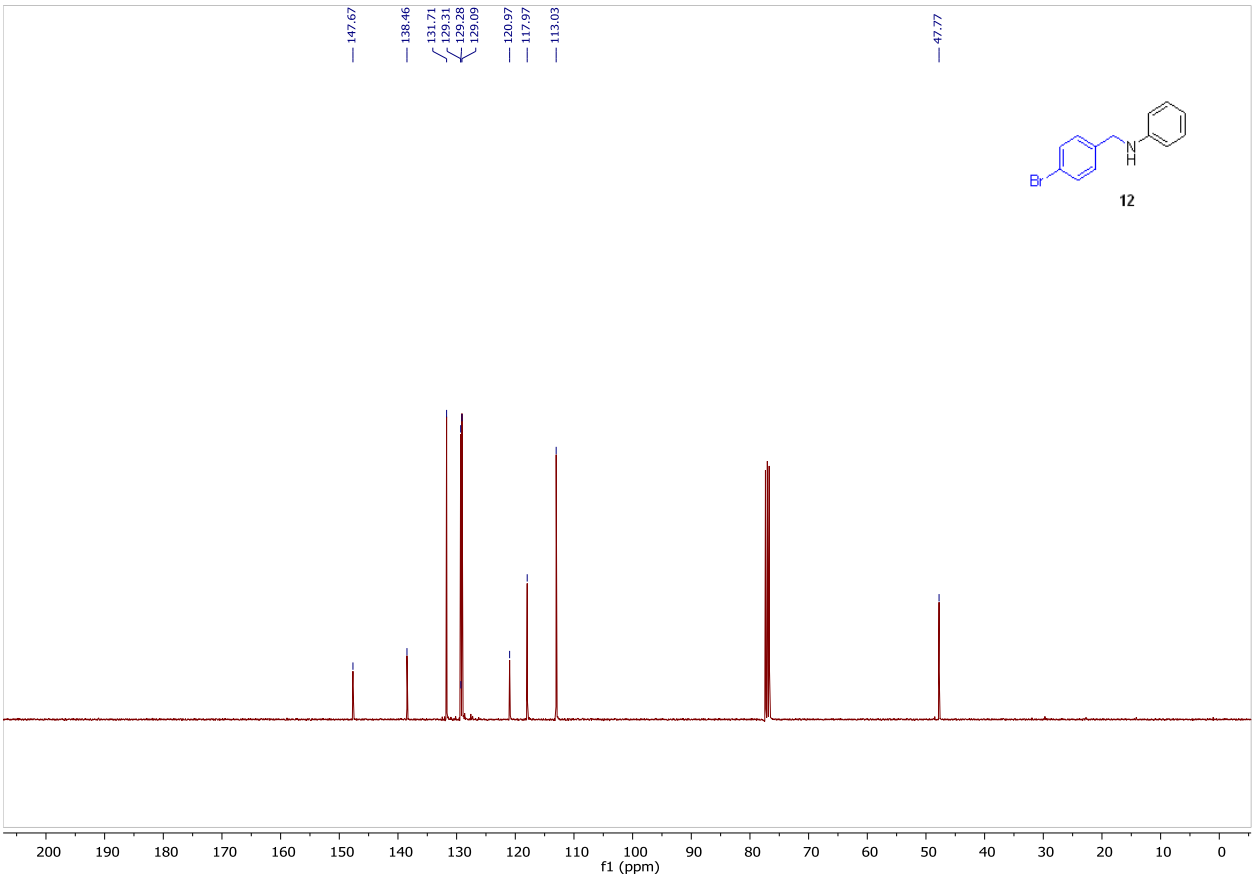
3.5
3.0
2.5
f1 (ppm)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117.97
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47.77
Br
N
H
12
200
190
180
170
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150
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130
120
110
100
90
80
70
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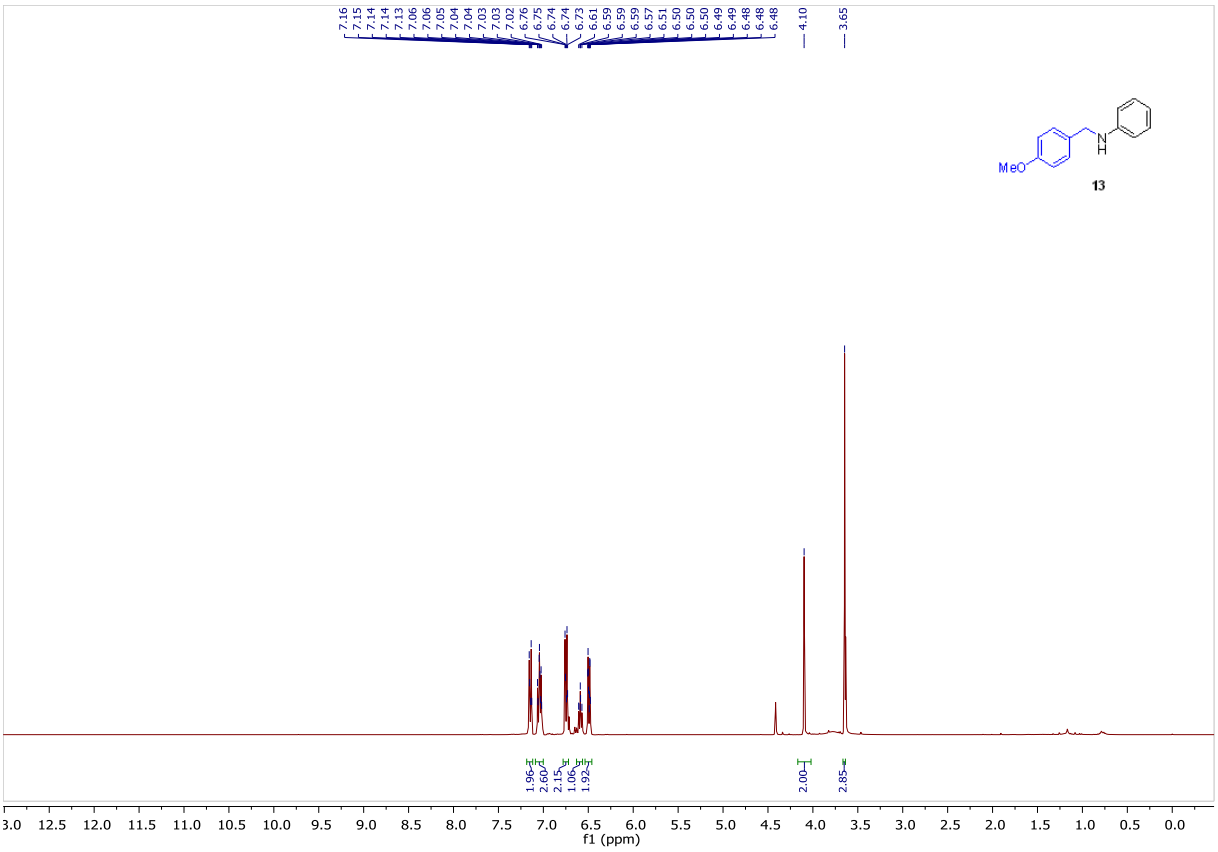
50
40
30
20
10
0
f1 (ppm)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7.05
7.04
7.04
7.03
7.03
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6.75
6.74
6.74
6.73
6.61
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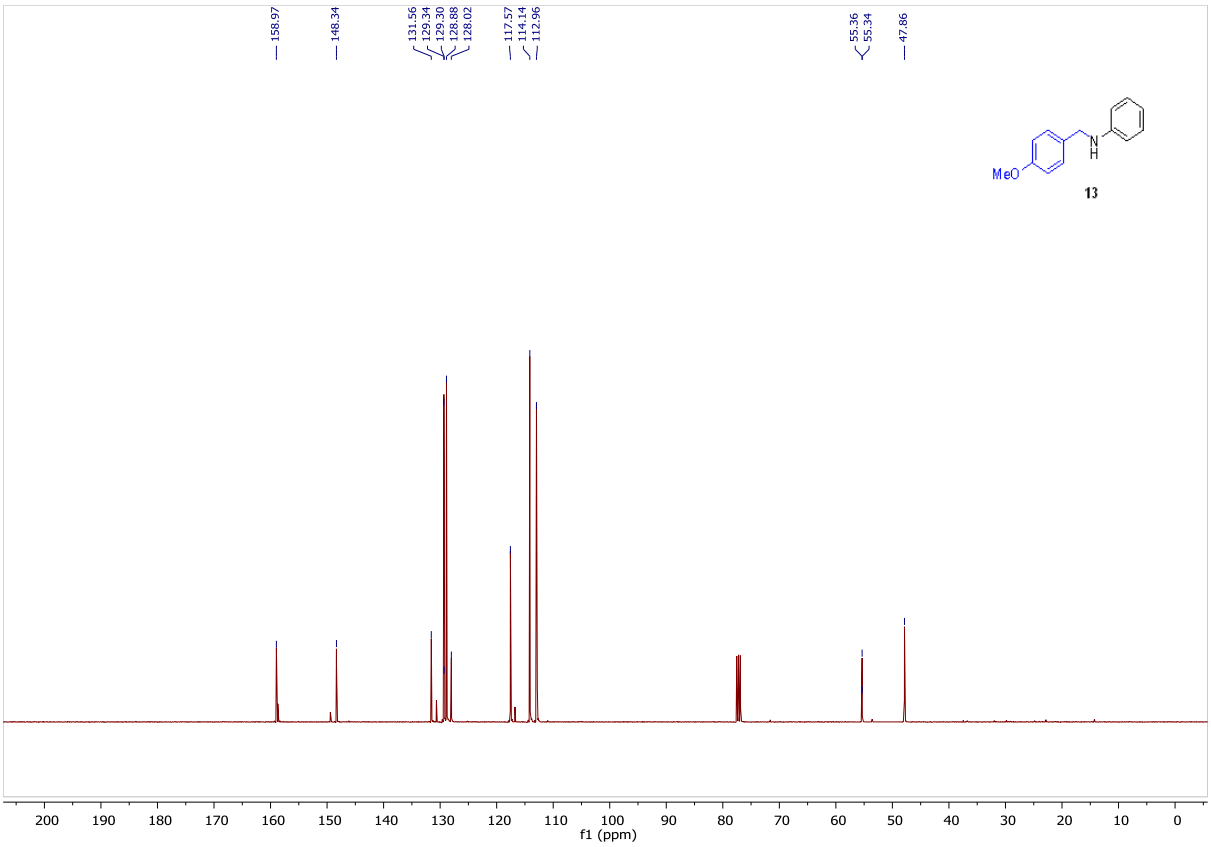
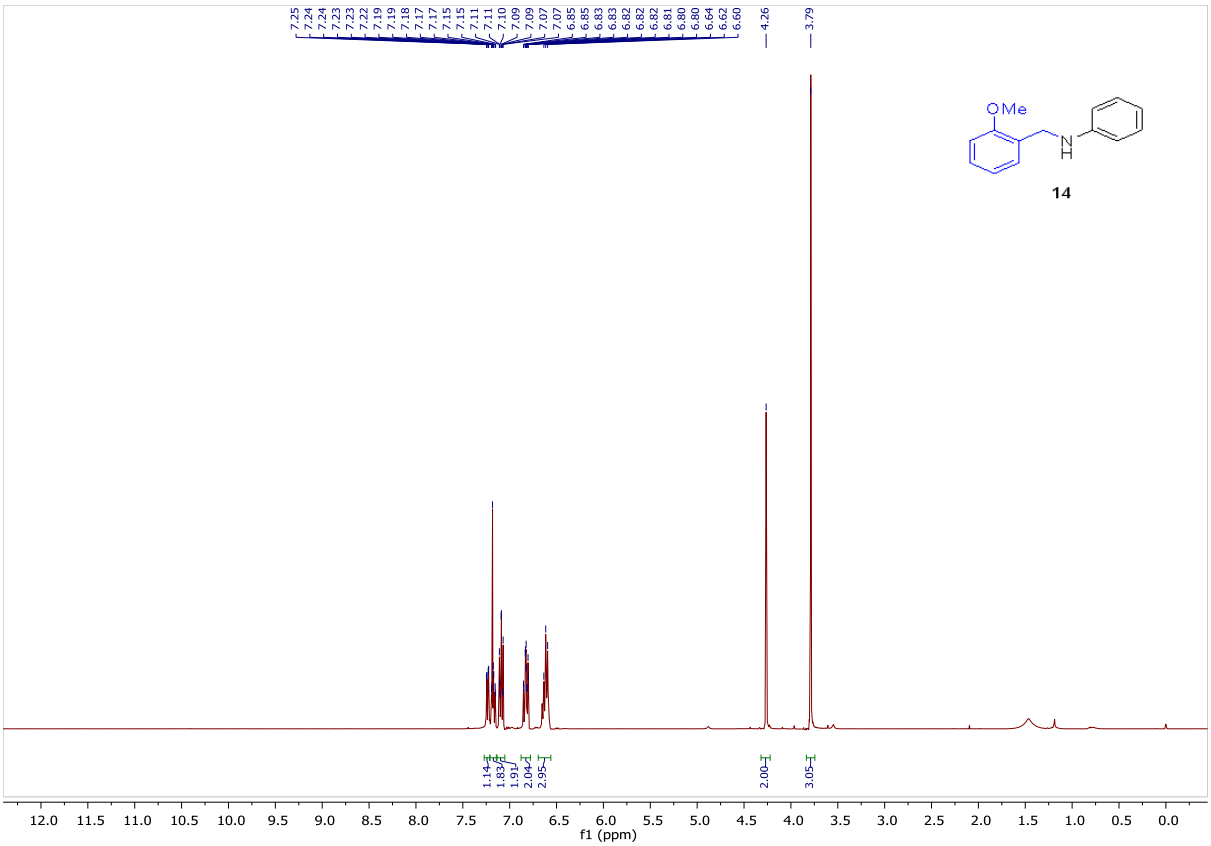
6.59
6.57
6.51
6.50
6.50
6.50
6.49
6.49
6.48
6.48
6.48
4.10
3.65
MeO
13
1.96
2.60
2.15
1.06
1.92
2.00
2.85
f1 (ppm)


158.97
148.34
131.56
129.34
129.30
128.88
128.02
117.57
114.14
112.96
55.36
55.34
47.86
MeO
13
f1 (ppm)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7.10
7.09
7.09
7.07
7.07
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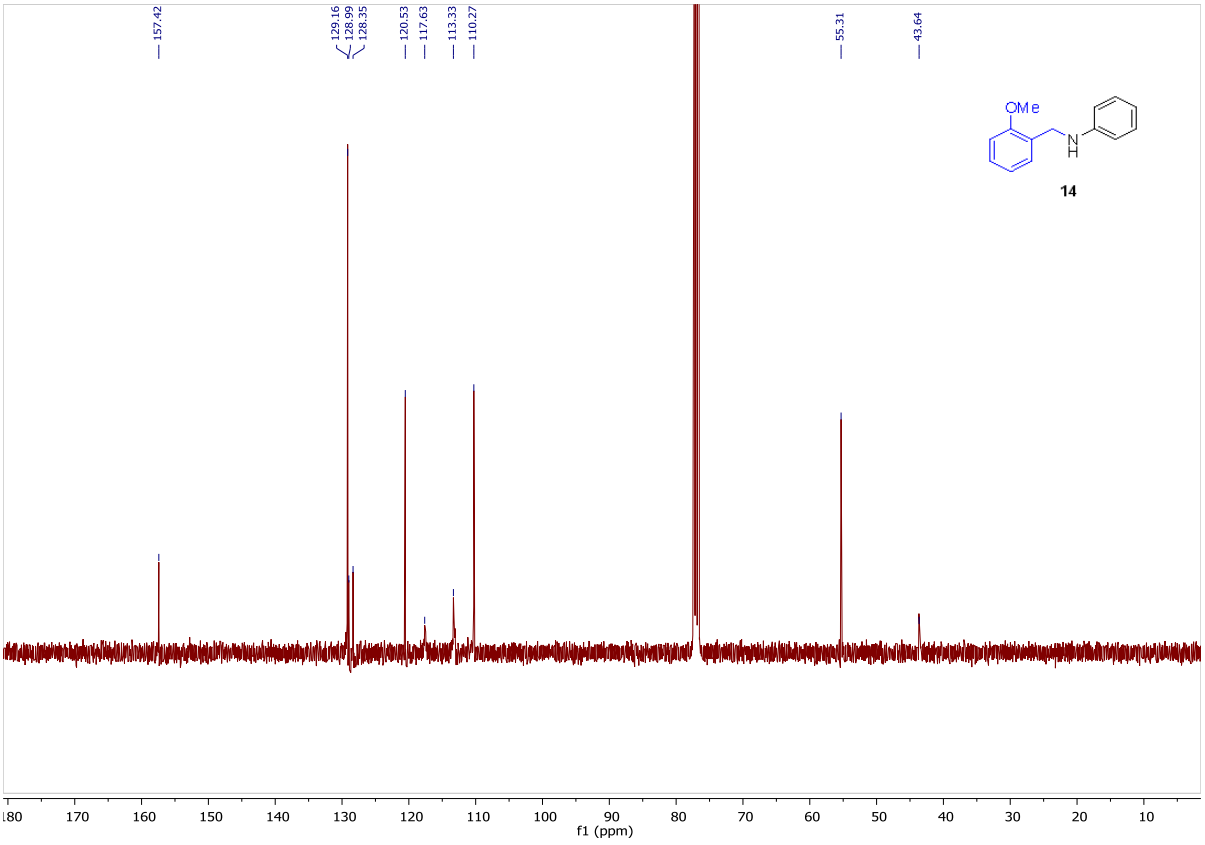
6.85
6.83
6.83
6.82
6.82
6.82
6.81
6.80
6.80
6.64
6.62
6.60
4.26
3.79
OMe
N
H
14
1.14
1.83
1.91
2.04
2.95
2.00
3.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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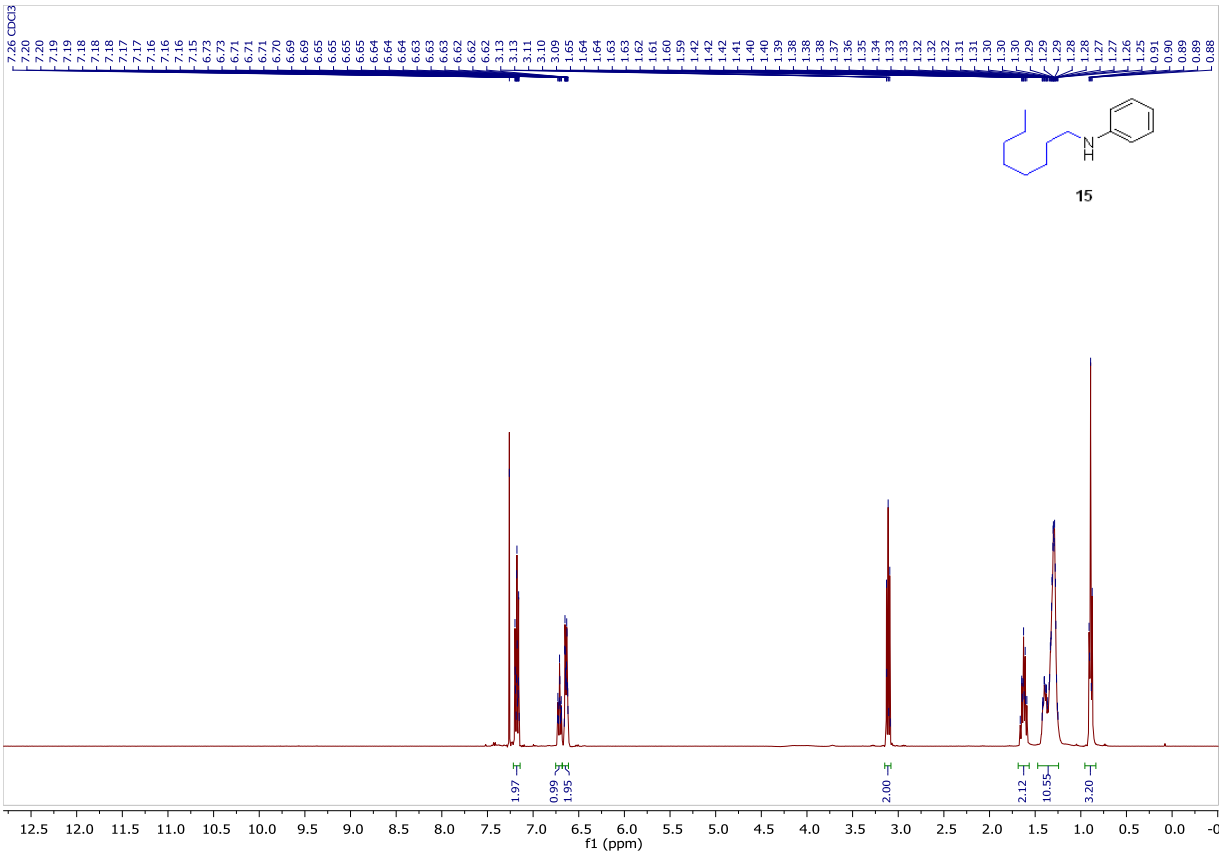
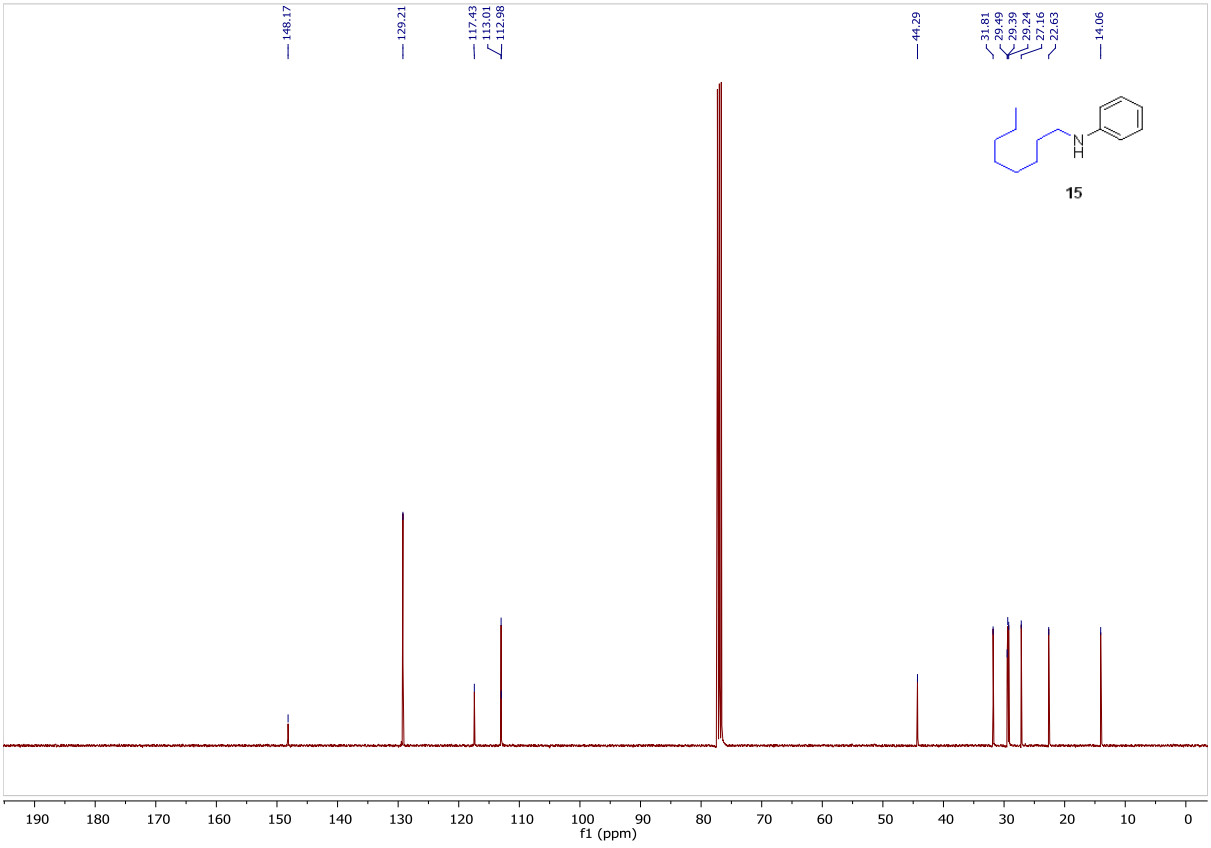
120.53
117.63
113.33
110.27
55.31
43.64
OMe
N
H
14
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.26 CDCl3
15
1.97
0.99
1.95
2.00
2.12
10.55
3.20
f1 (ppm)


148.17
129.21
117.43
113.01
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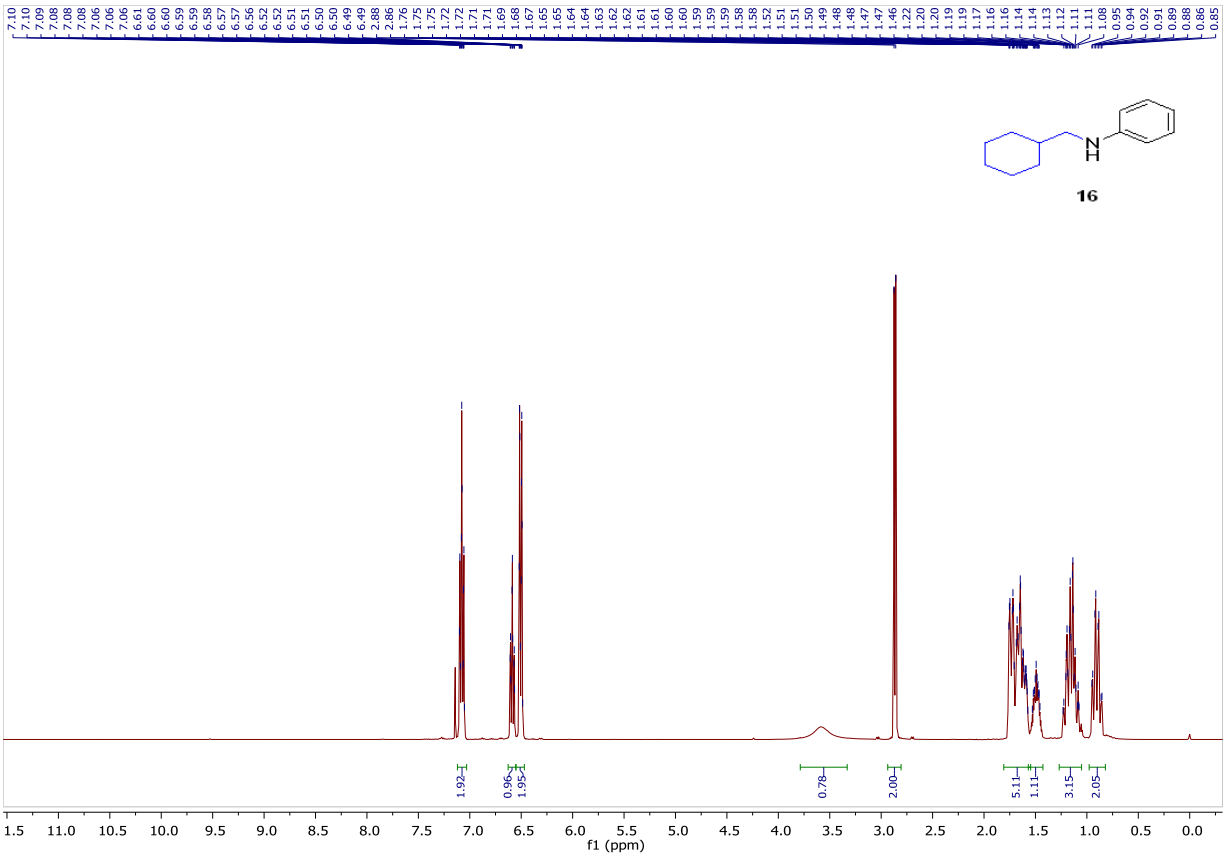
44.29
31.81
29.49
29.39
29.24
27.16
22.63
14.06
15
f1 (ppm)


16
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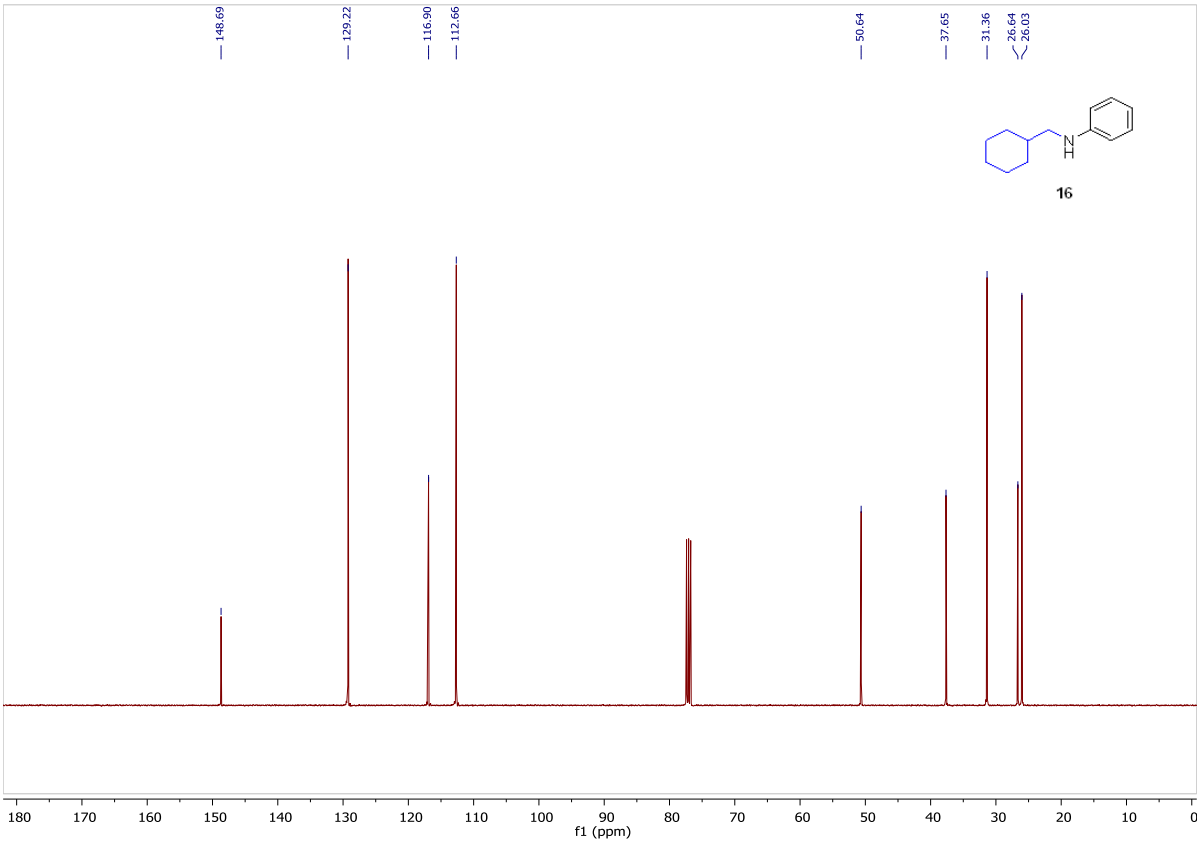
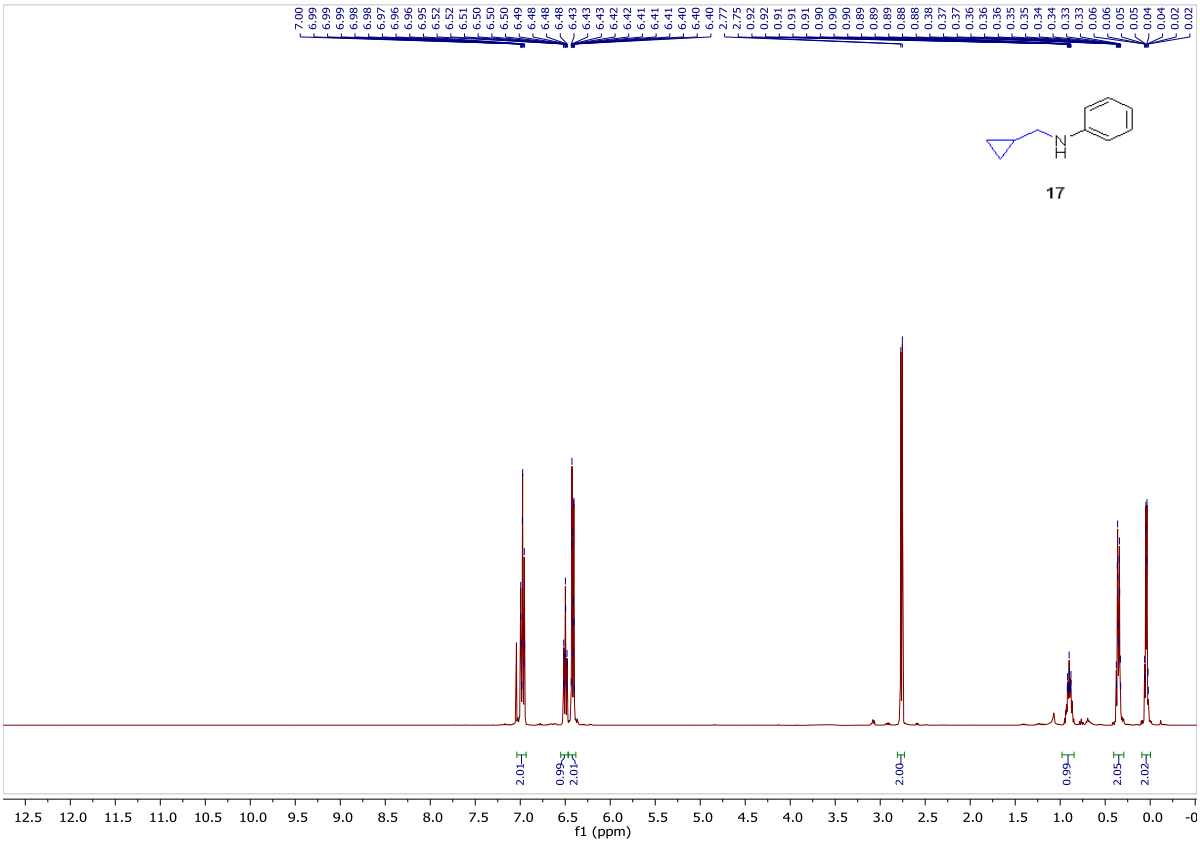
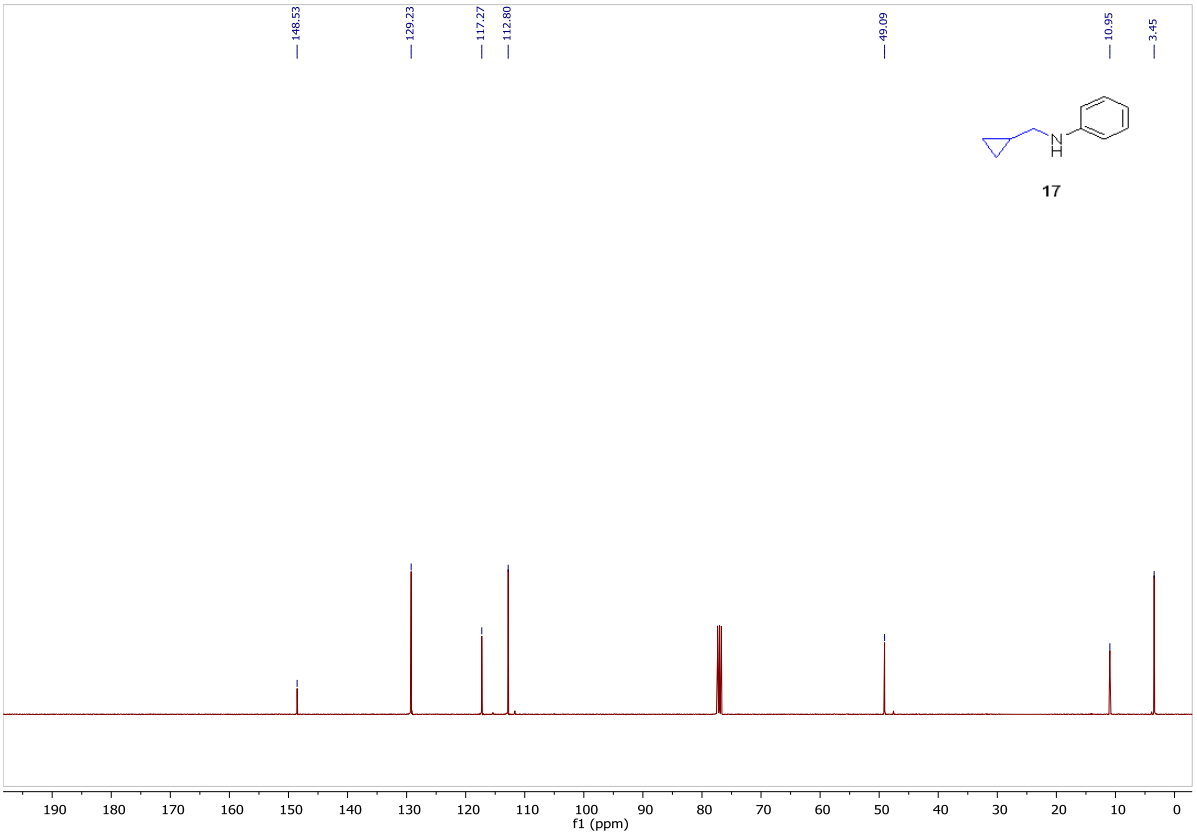
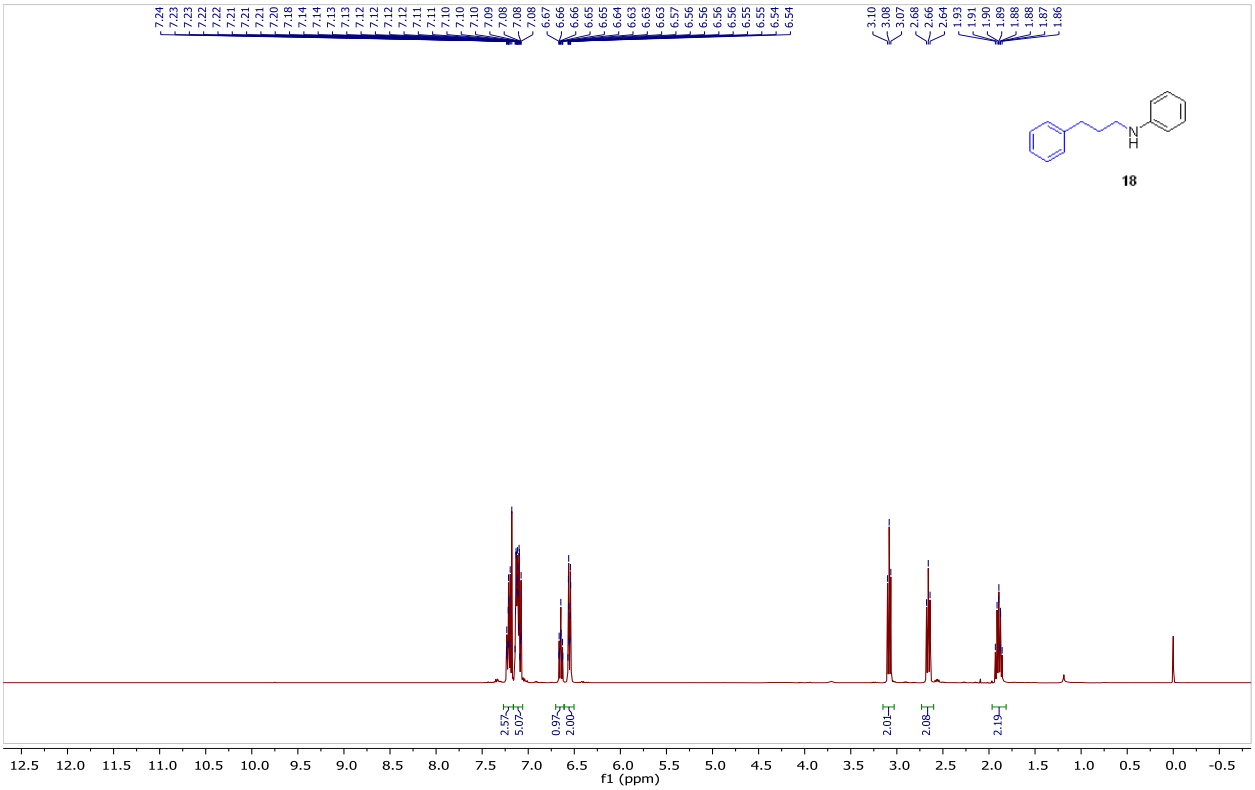
0.96
1.95
0.78
2.00
5.11
1.11
3.15
2.05
f1 (ppm)


148.69
129.22
116.90
112.66
50.64
37.65
31.36
26.64
26.03
16
f1 (ppm)


7.00 6.99 6.99 6.99 6.98 6.98 6.98 6.97 6.96 6.96 6.95 6.52 6.52 6.51 6.50 6.50 6.50 6.49 6.48 6.48 6.48 6.43 6.43 6.43 6.42 6.42 6.41 6.41 6.41 6.40 6.40 6.40 2.77 2.75 0.92 0.92 0.91 0.91 0.91 0.90 0.90 0.90 0.89 0.89 0.89 0.88 0.88 0.38 0.37 0.37 0.36 0.36 0.35 0.35 0.34 0.34 0.33 0.33 0.06 0.06 0.05 0.05 0.04 0.04 0.02 0.02
17
2.01 0.95 2.01 2.00 0.99 2.05 2.02
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


148.53 129.23 117.27 112.80 49.09 10.95 3.45
17
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.10
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7.08
7.08
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3.08
3.07
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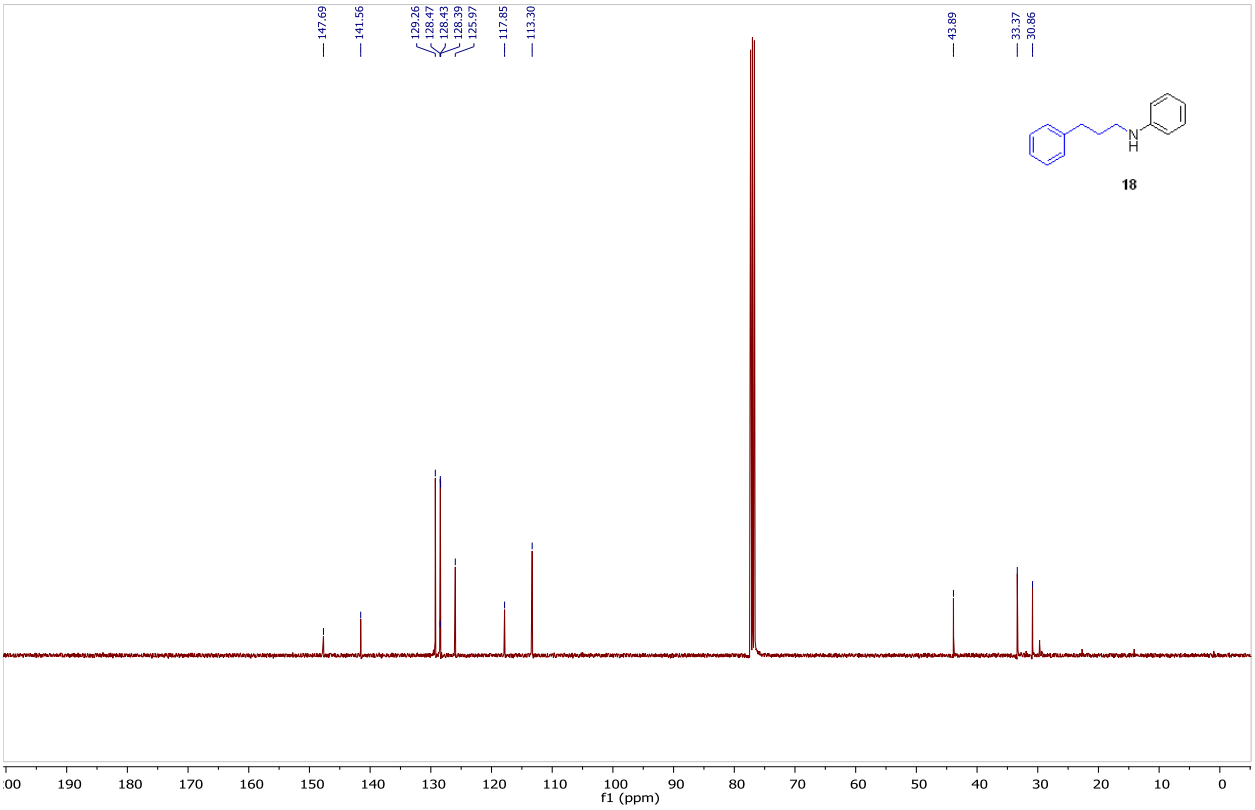
2.66
2.64
1.93
1.91
1.90
1.89
1.88
1.88
1.87
1.86
N
H
18
2.57
5.07
0.97
2.00
2.01
2.08
2.19
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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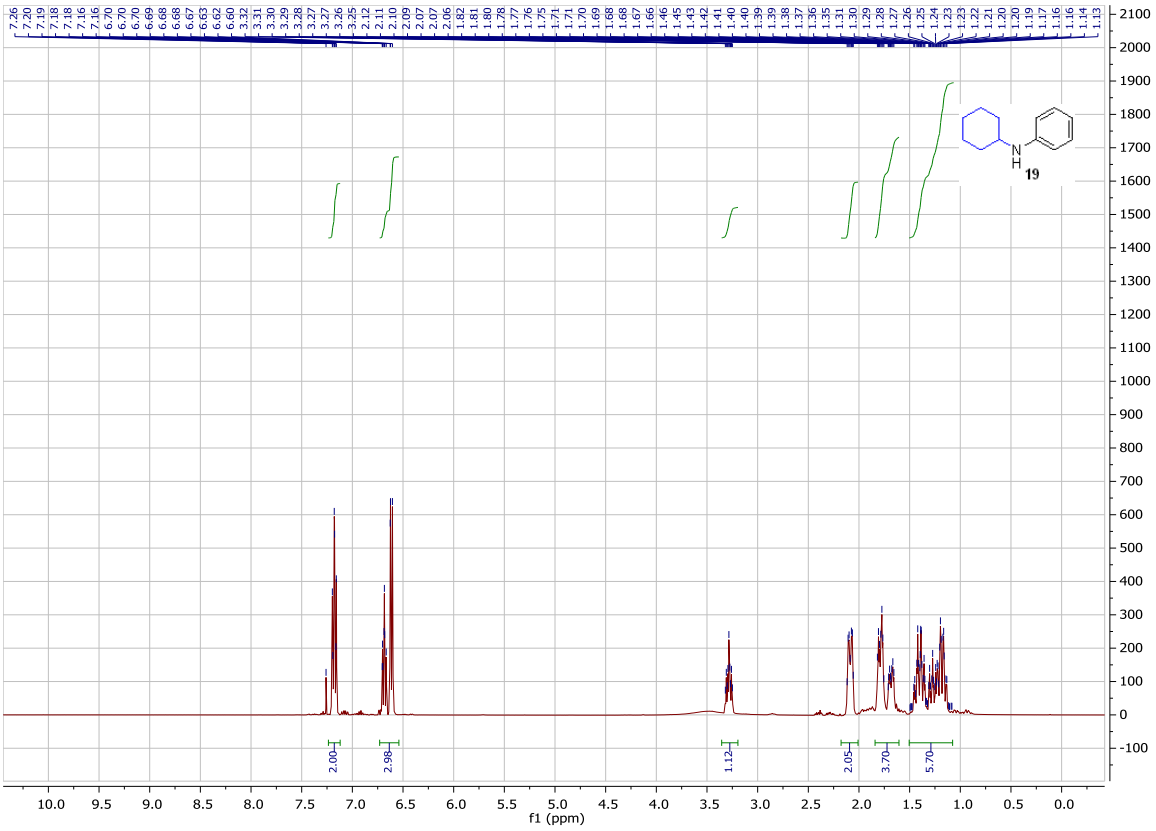
128.39
125.97
117.85
113.30
43.89
33.37
30.86
N
H
18
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


19
2.00
2.98
1.12
2.05
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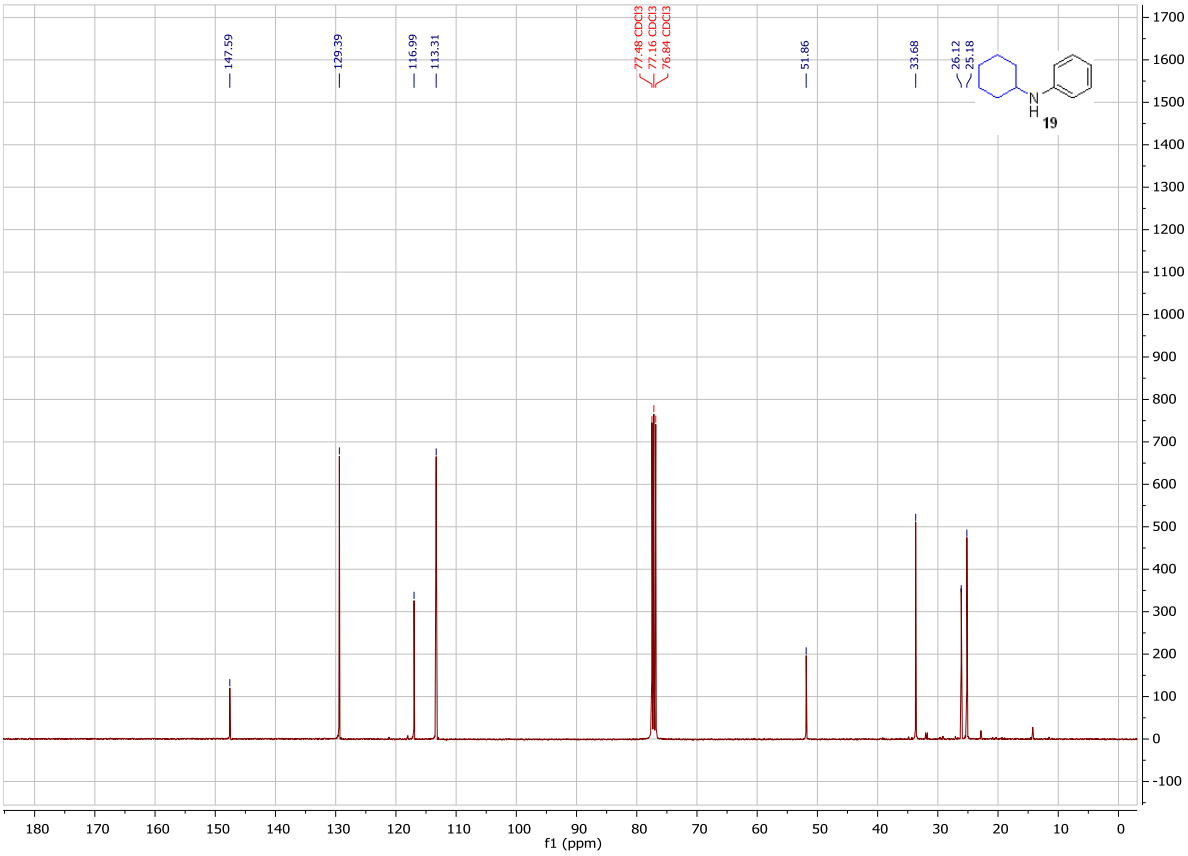
5.70
f1 (ppm)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129.39
116.99
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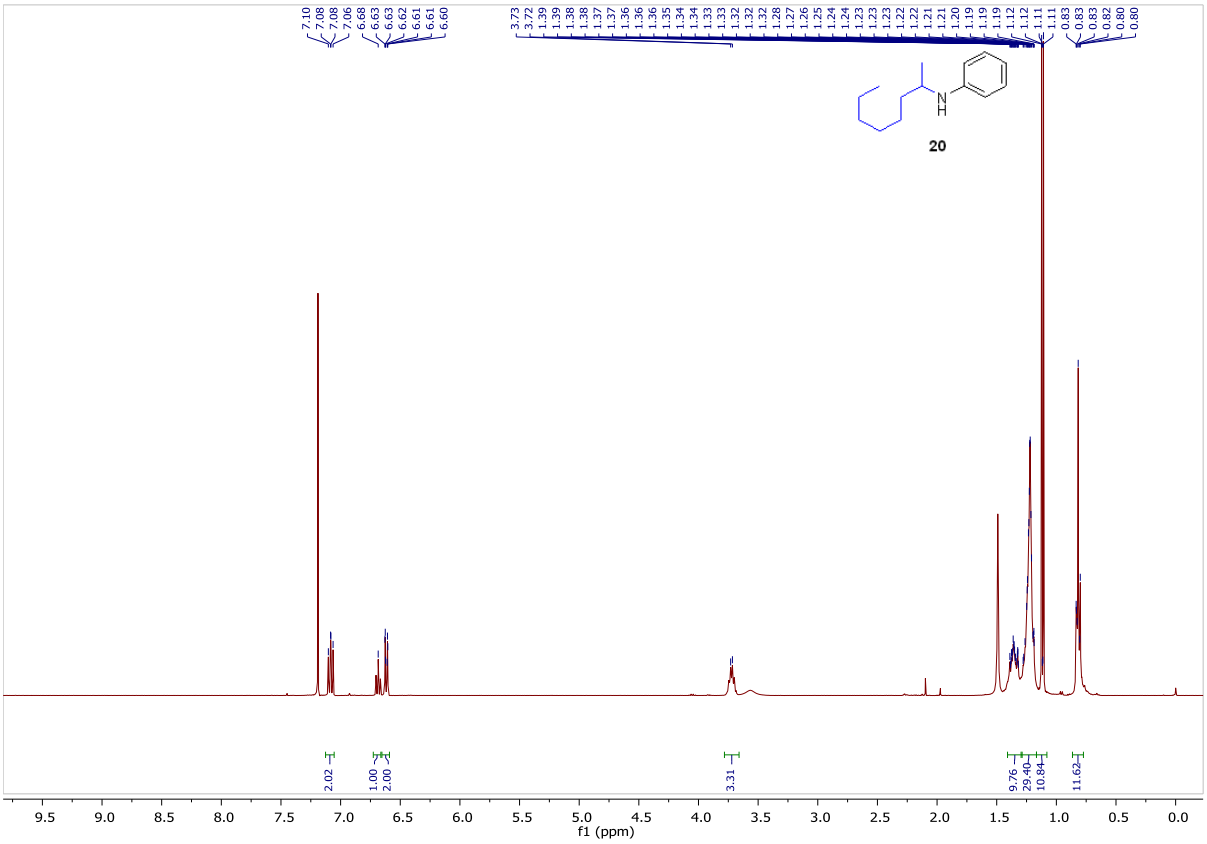
77.16 CDCl3
76.84 CDCl3
51.86
33.68
26.12
25.18
19
f1 (ppm)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1.12
1.11
1.11
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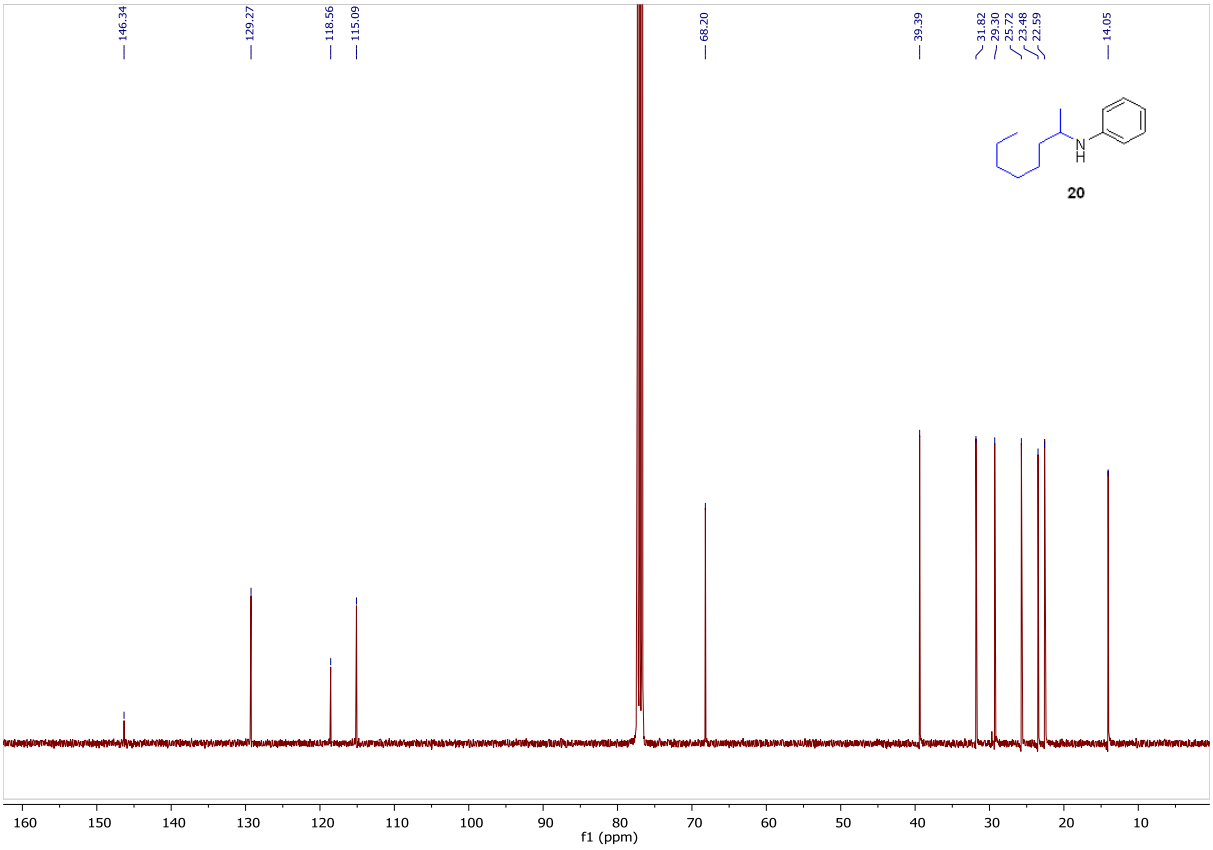
0.83
0.83
0.82
0.80
0.80
N
H
20
2.02
1.00
2.00
3.31
9.76
29.40
10.84
11.62
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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115.09
68.20
39.39
31.82
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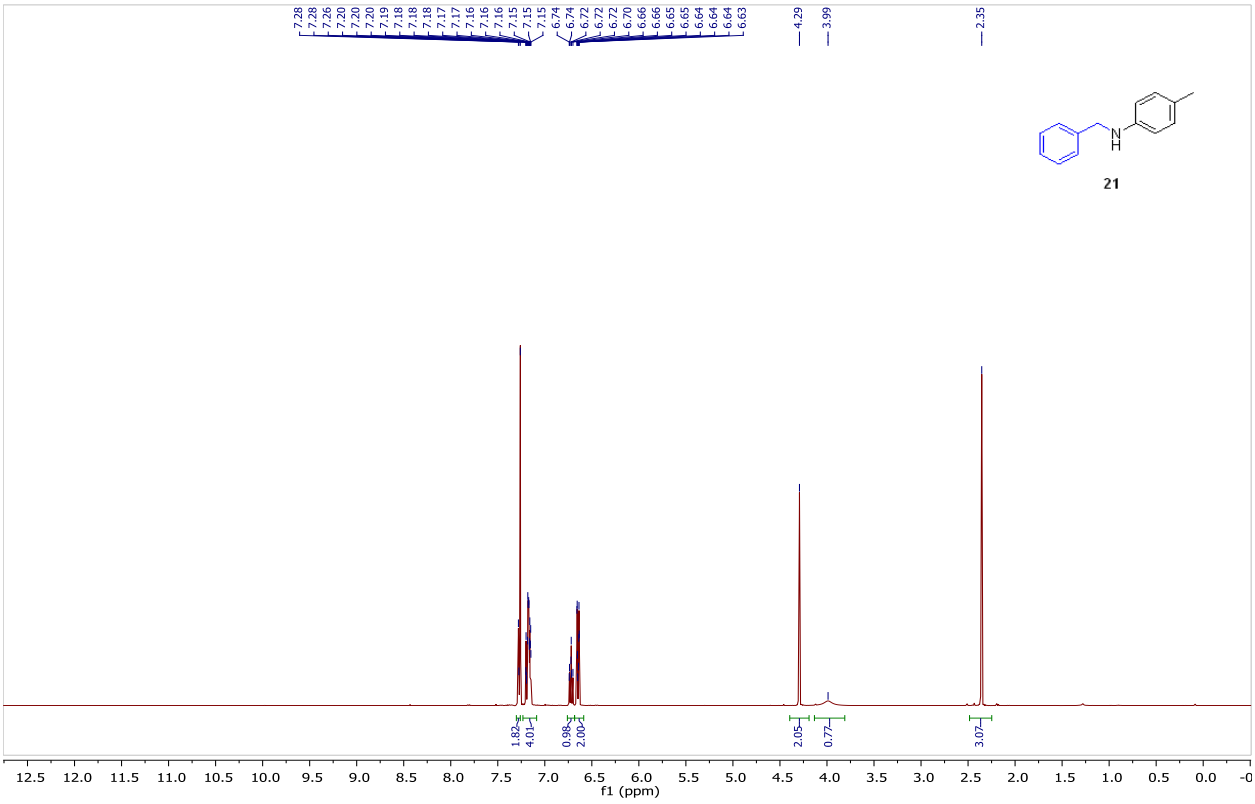
25.72
23.48
22.59
14.05
N
H
20
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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6.66
6.65
6.65
6.64
6.64
6.64
6.63
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0.98
2.00
2.05
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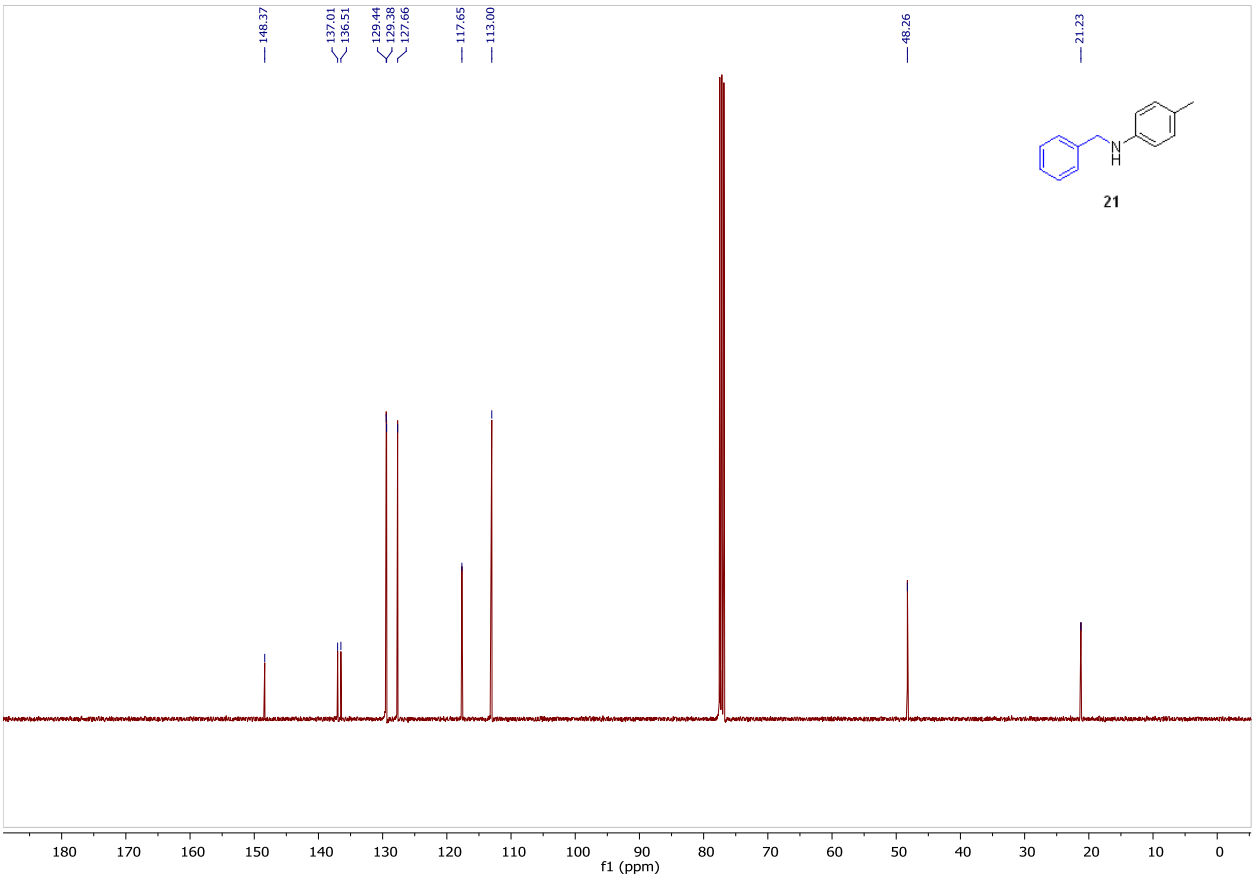
3.07
21
f1 (ppm)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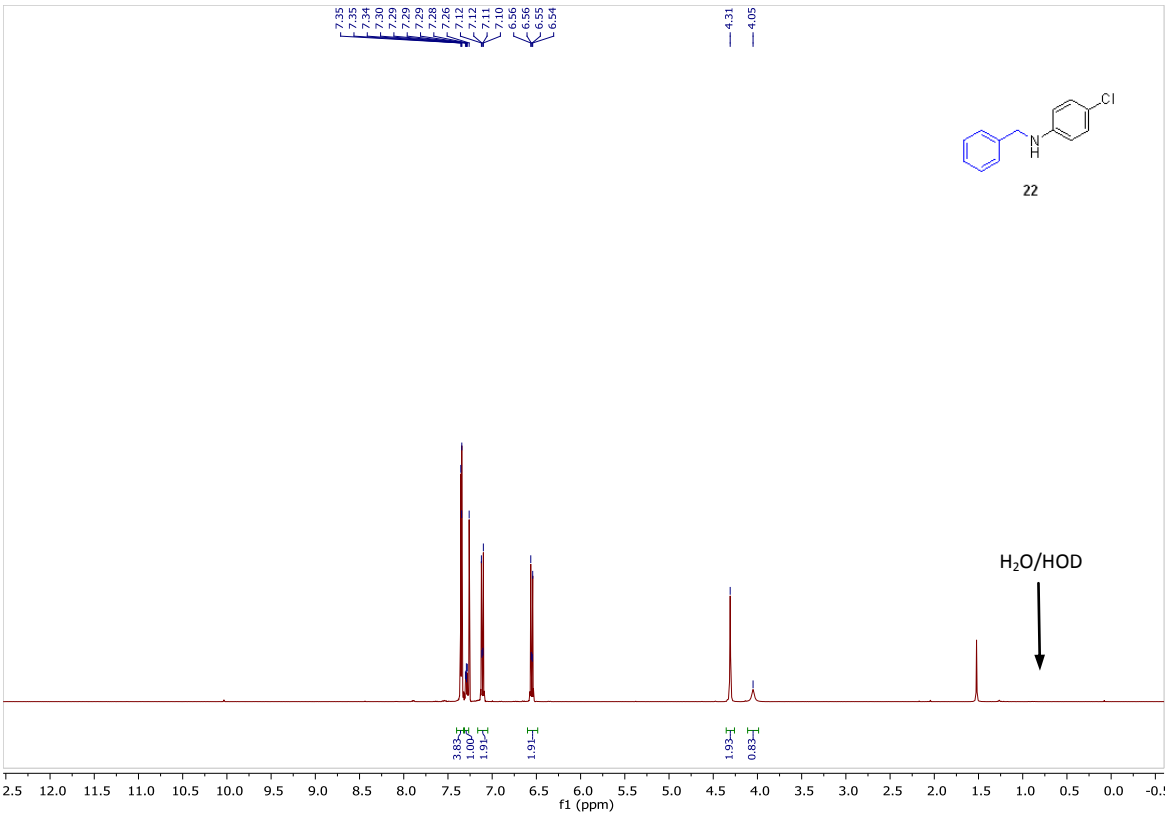
113.00
48.26
21.23
21
f1 (ppm)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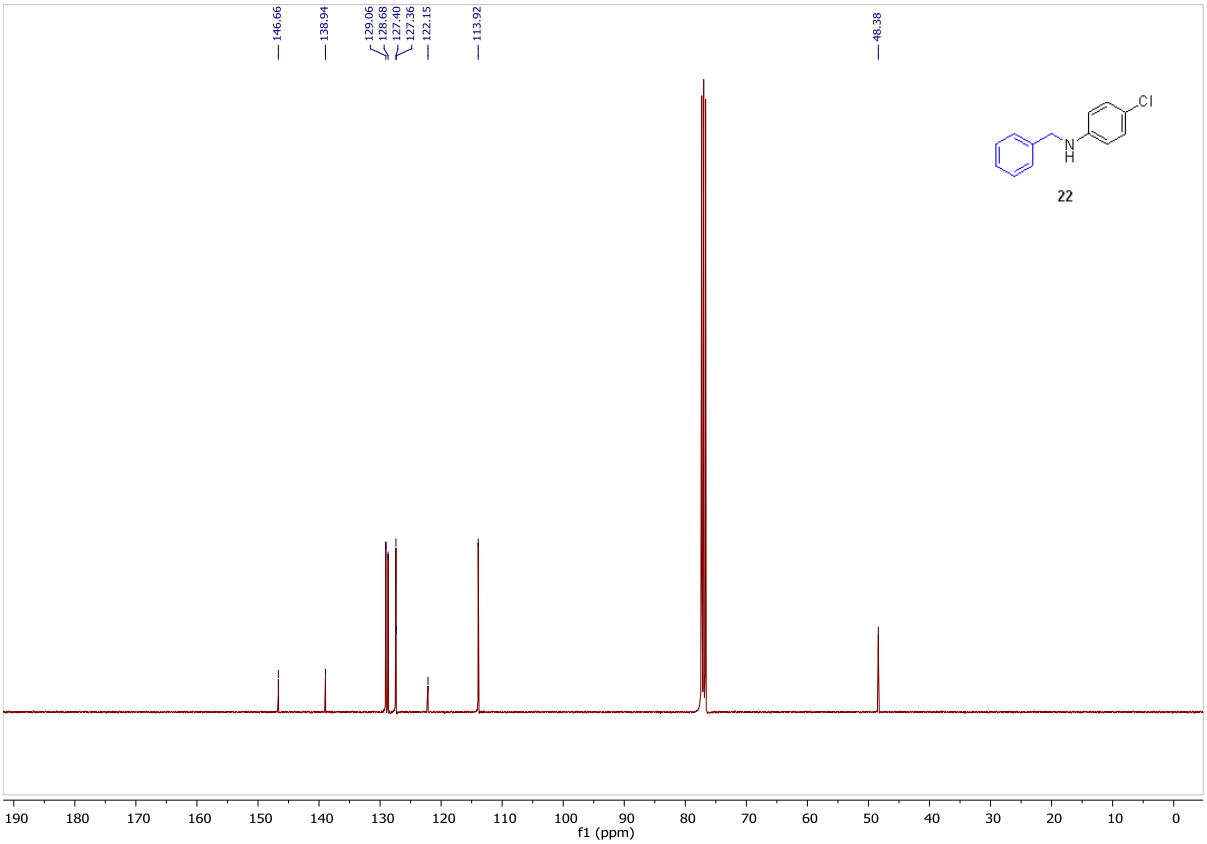
7.11
7.10
6.56
6.56
6.55
6.54
4.31
4.05
Cl
N
H
22
H2O/HOD
3.83
1.00
1.91
1.91
1.93
0.83
f1 (ppm)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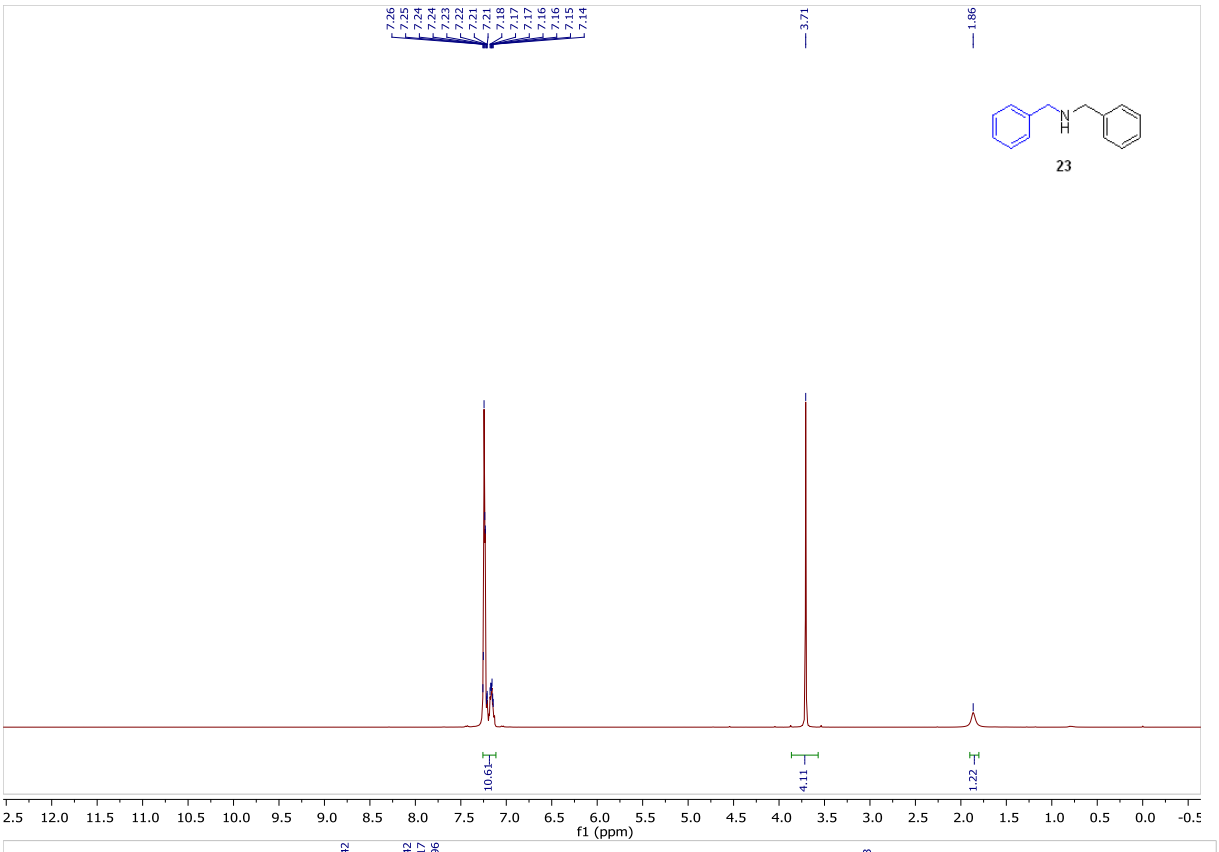
127.36
122.15
113.92
48.38
Cl
N
H
22
f1 (ppm)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7.17
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7.15
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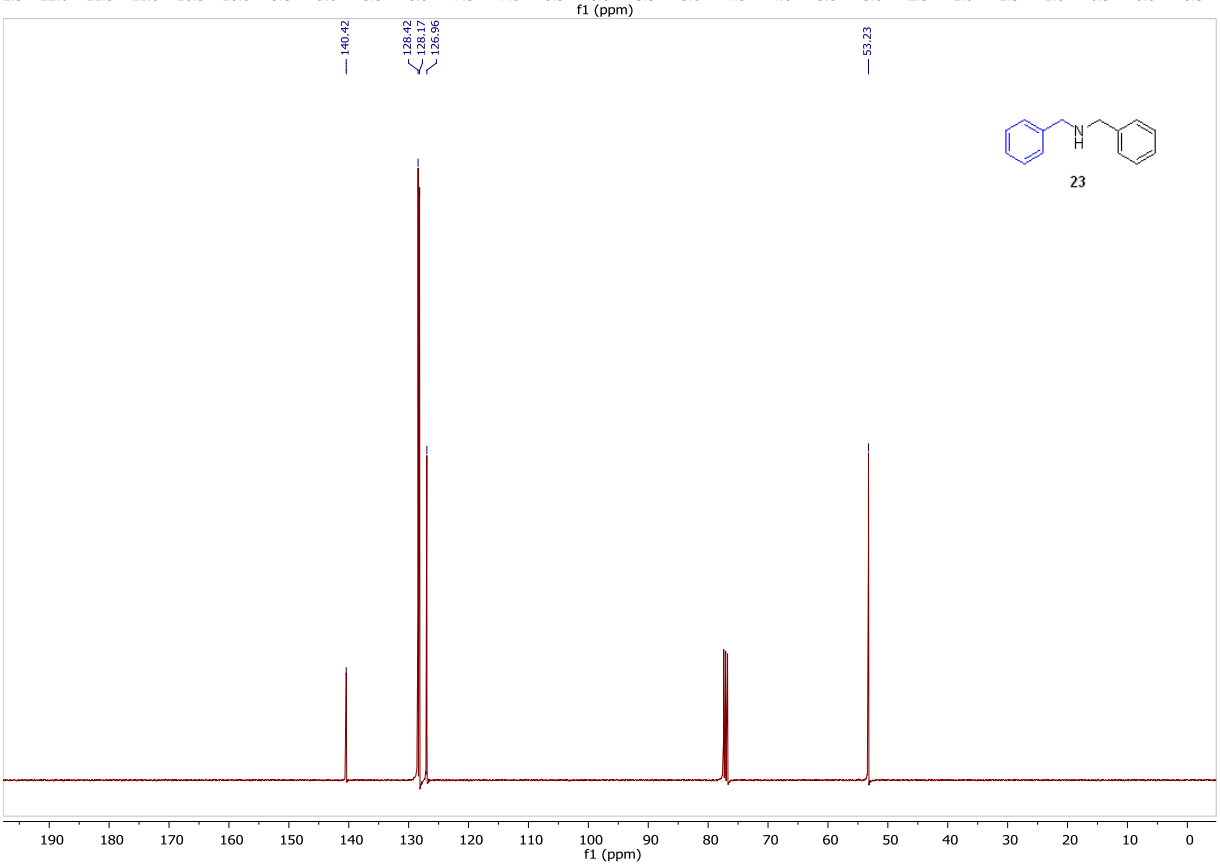
1.86
23
10.61
4.11
1.22
f1 (ppm)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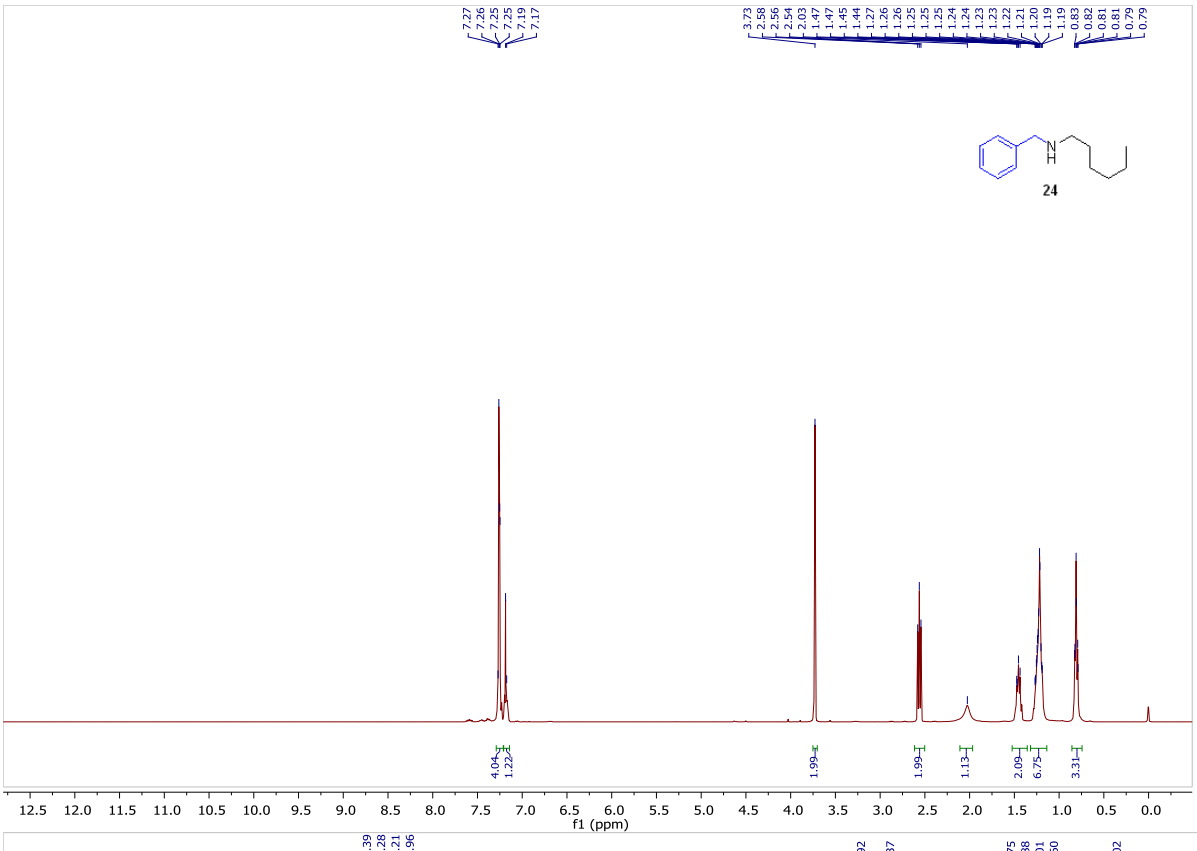
23
f1 (ppm)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2.54
2.03
1.47
1.45
1.44
1.27
1.26
1.26
1.25
1.25
1.24
1.24
1.23
1.23
1.22
1.21
1.20
1.19
1.19
0.83
0.82
0.81
0.81
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0.79
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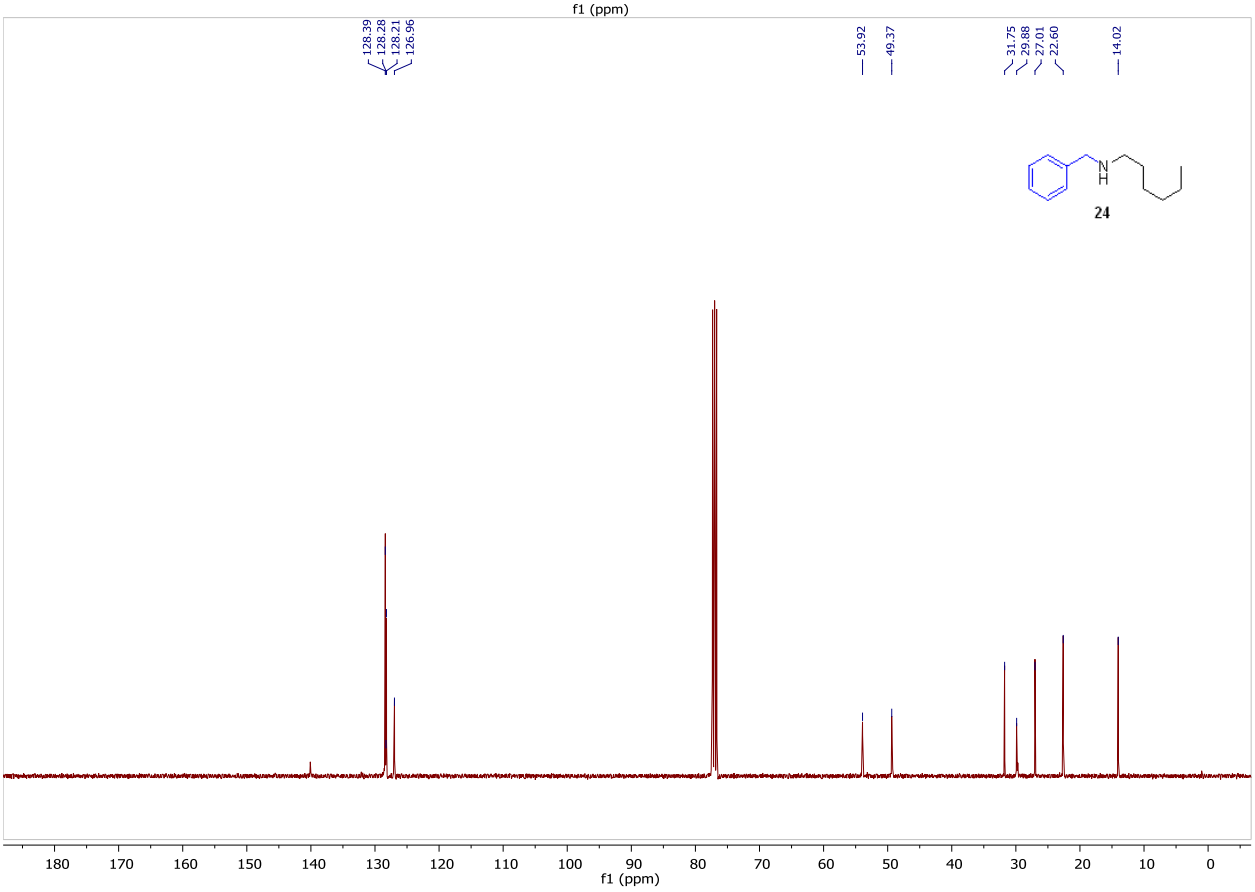
4.04
1.22
1.99
1.99
1.13
2.09
6.75
3.31
f1 (ppm)


128.39
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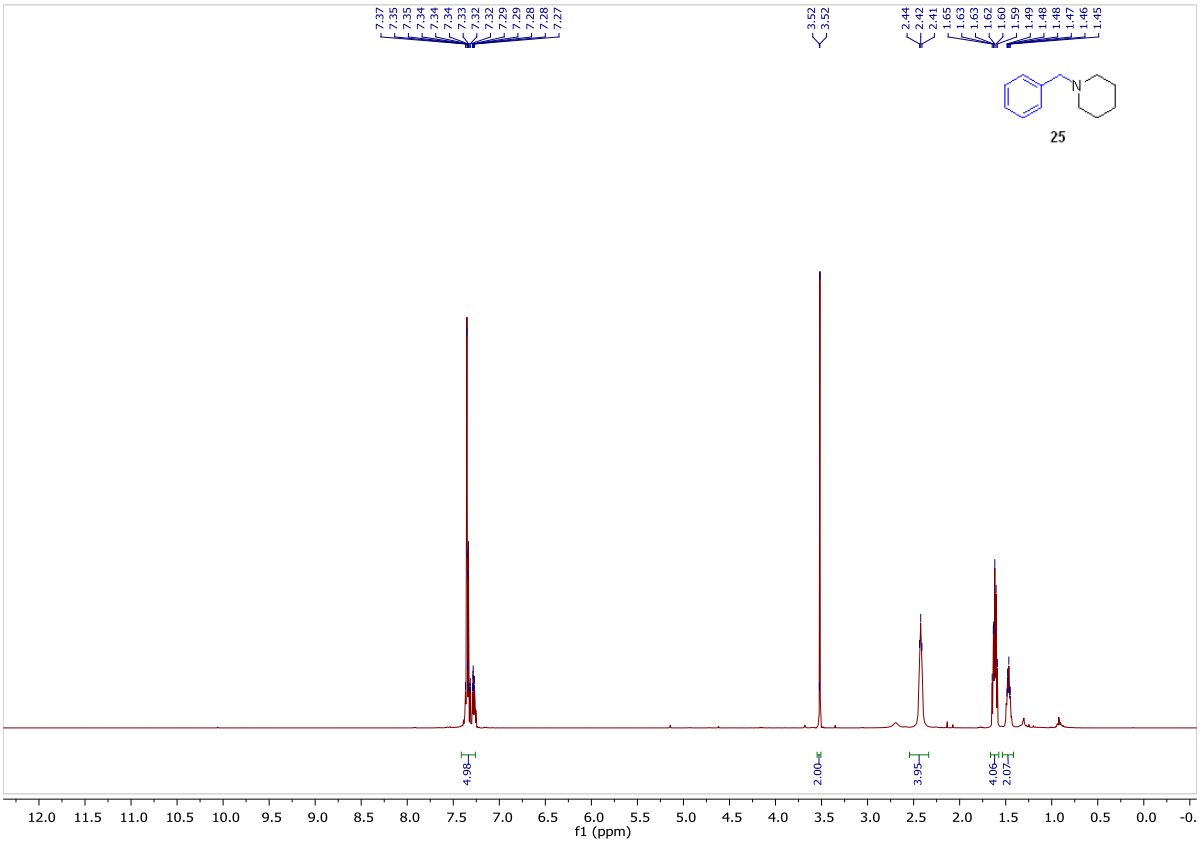
31.75
29.88
27.01
22.60
14.02
24
f1 (ppm)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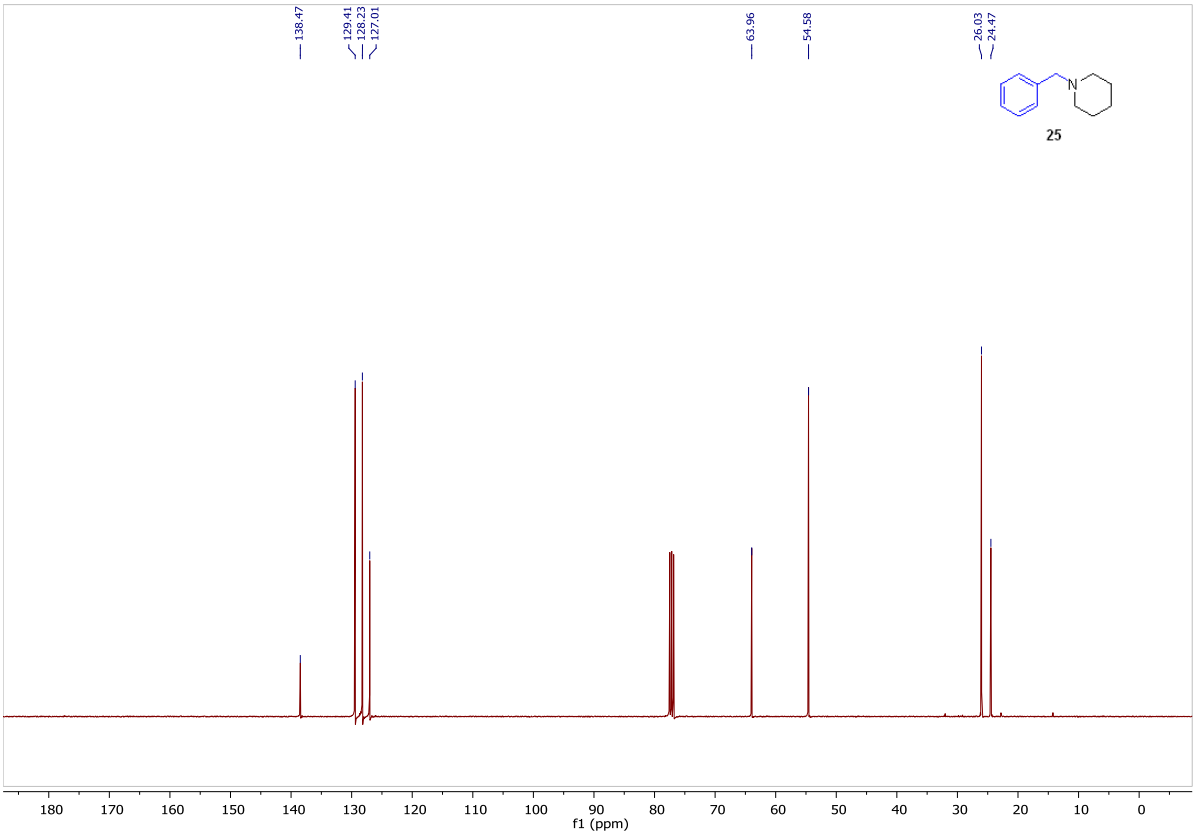
3.52
3.52
2.44
2.42
2.41
1.65
1.63
1.63
1.62
1.60
1.59
1.49
1.48
1.48
1.47
1.46
1.45
N
25
4.98
2.00
3.95
4.06
2.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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54.58
26.03
24.47
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25
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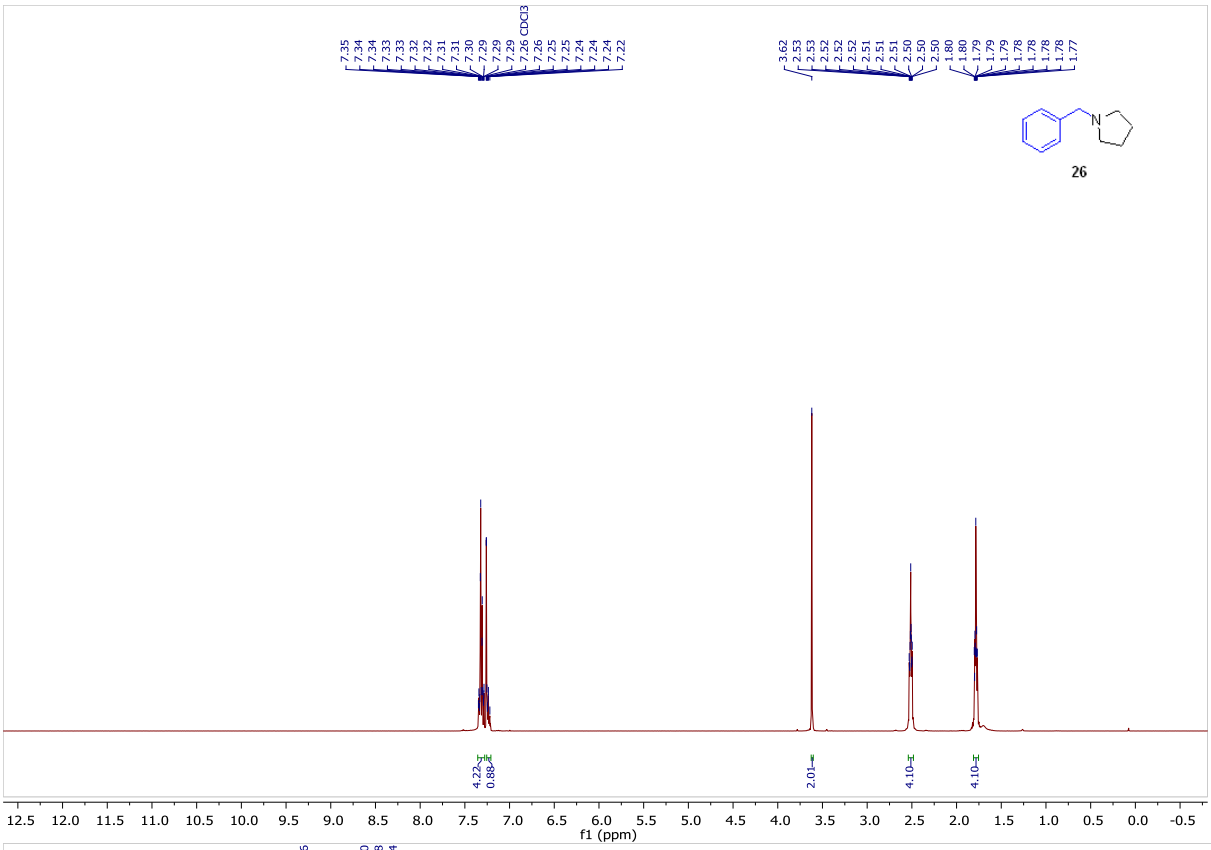
f1 (ppm)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7.29
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CDCl3
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7.24
7.22
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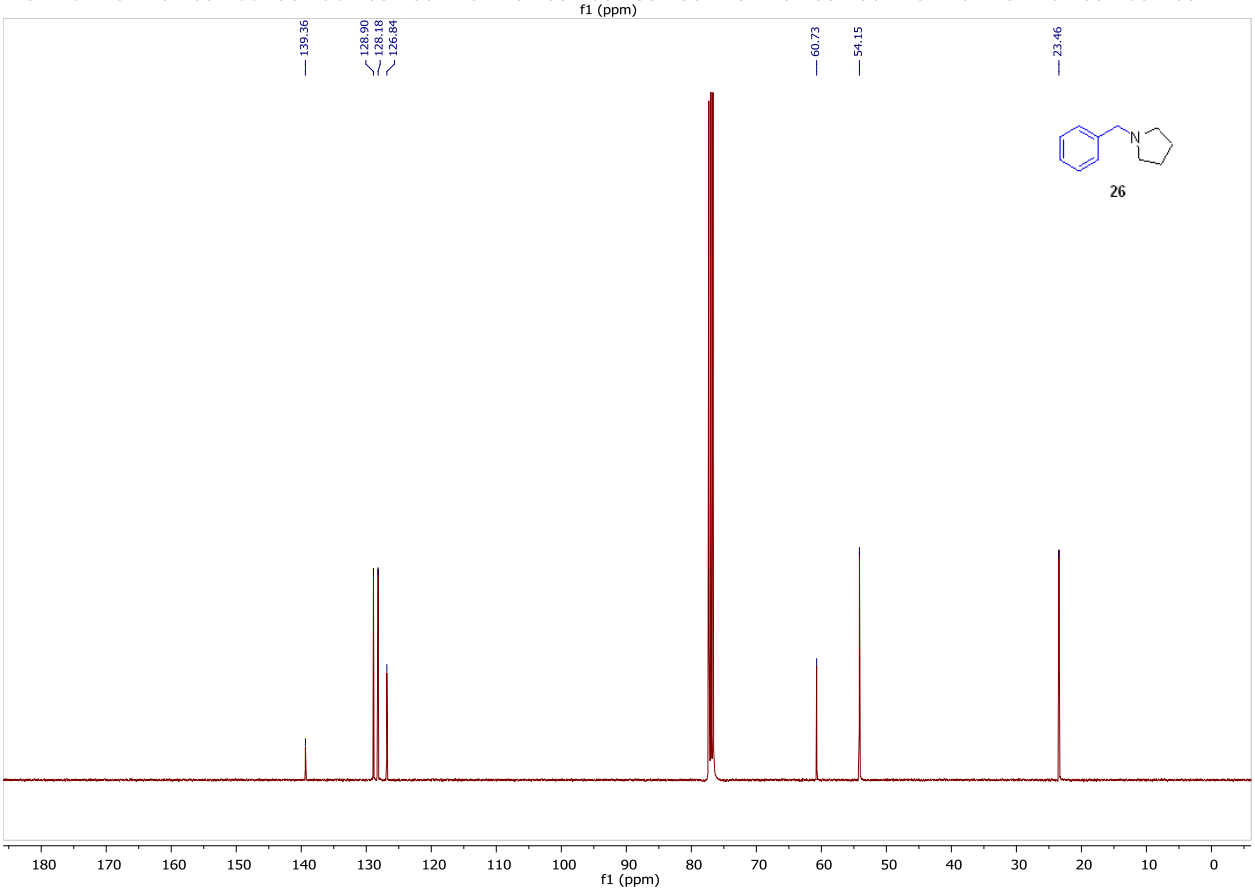
1.80
1.80
1.79
1.79
1.79
1.78
1.78
1.78
1.78
1.77
N
26
4.22
0.88
2.01
4.10
4.10
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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23.46
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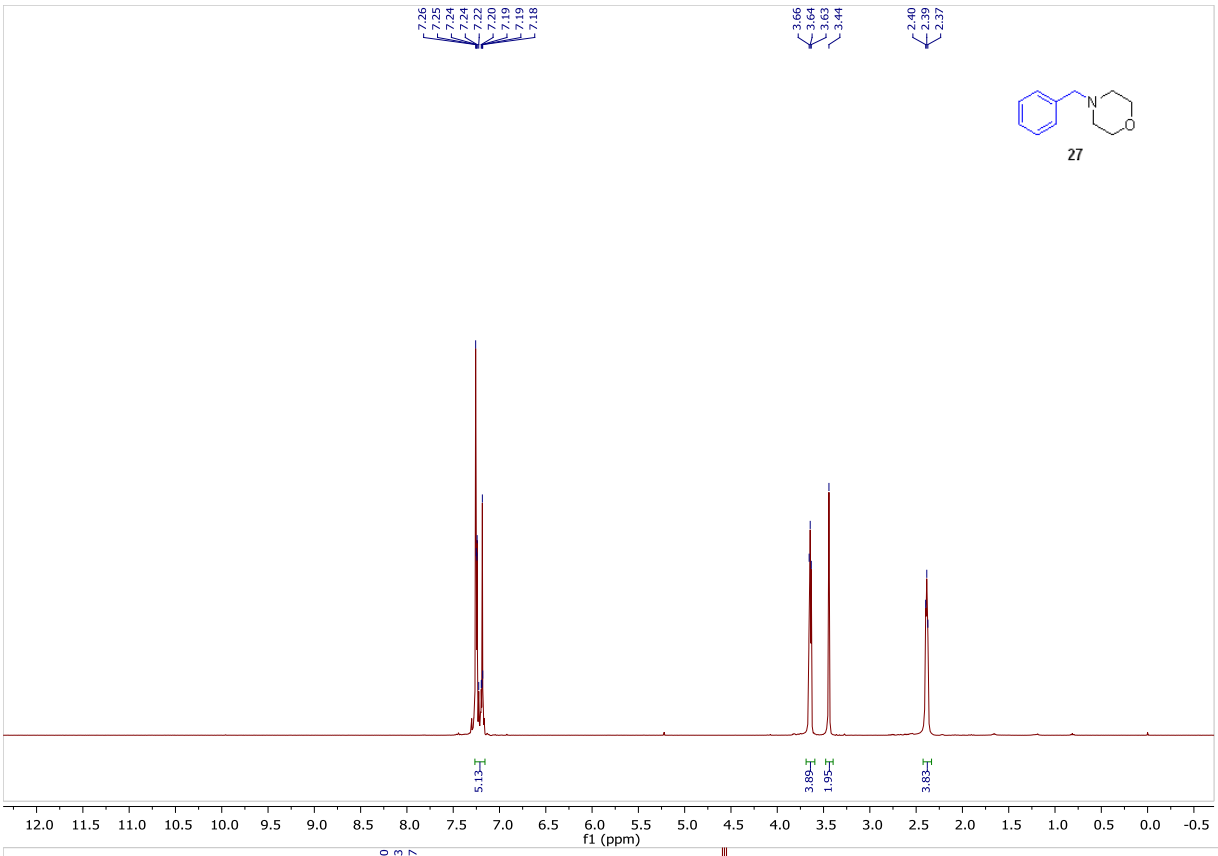
f1 (ppm)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7.24
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7.19
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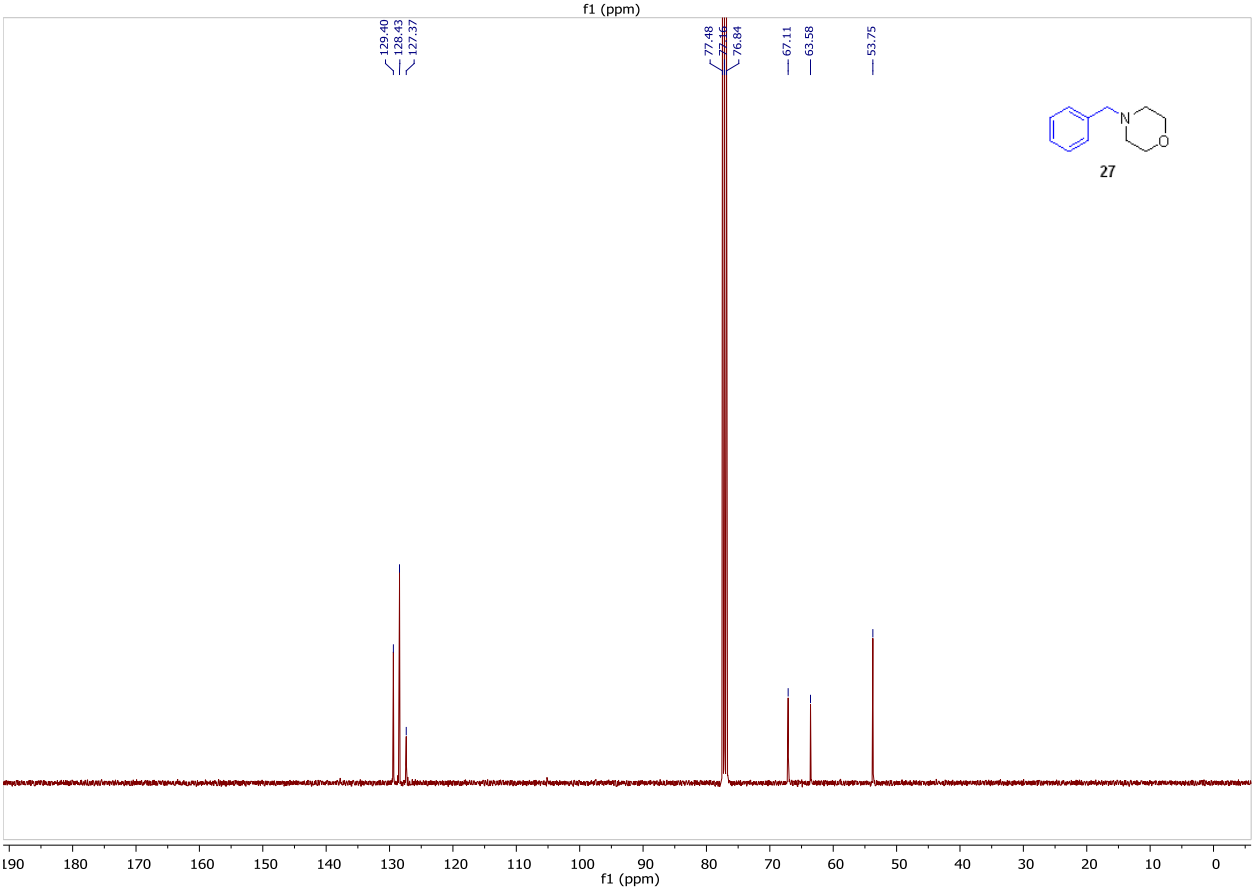
7.18
3.66
3.64
3.63
3.44
2.40
2.39
2.37
N
O
27
5.13
3.89
1.95
3.83
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


129.40
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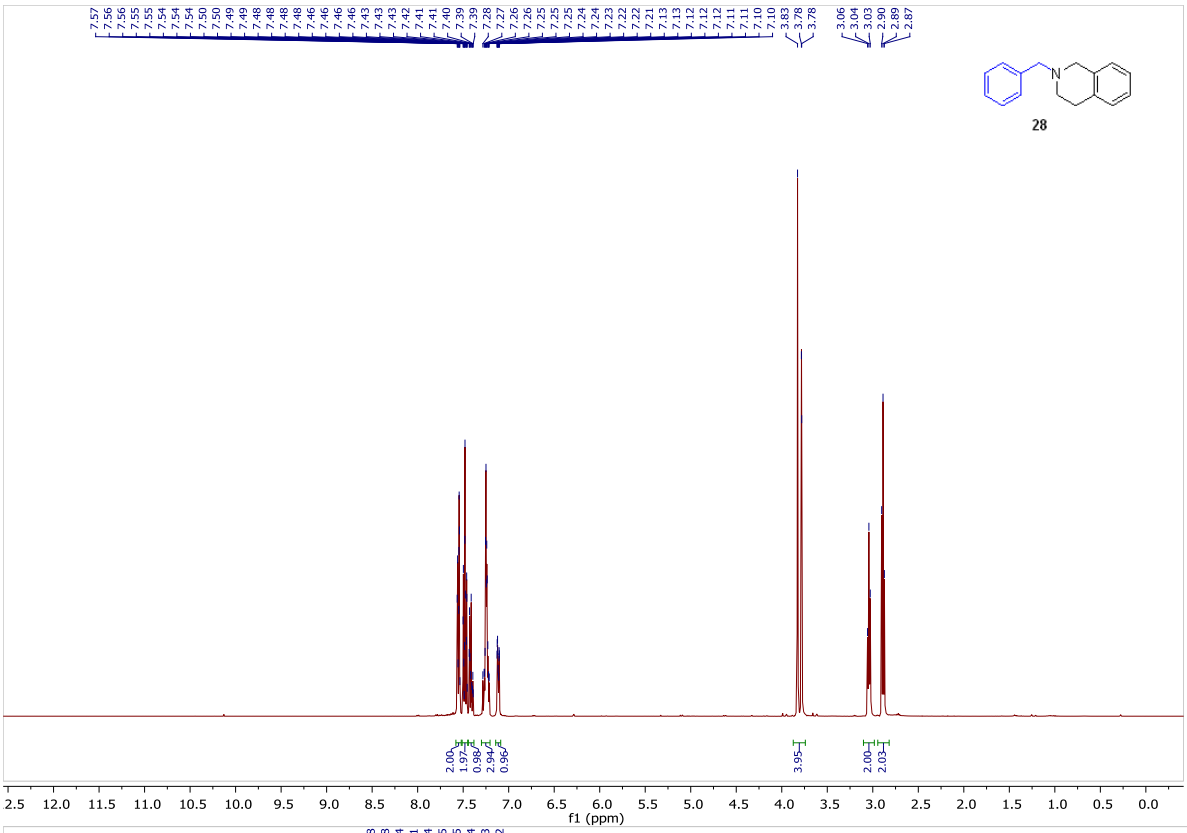
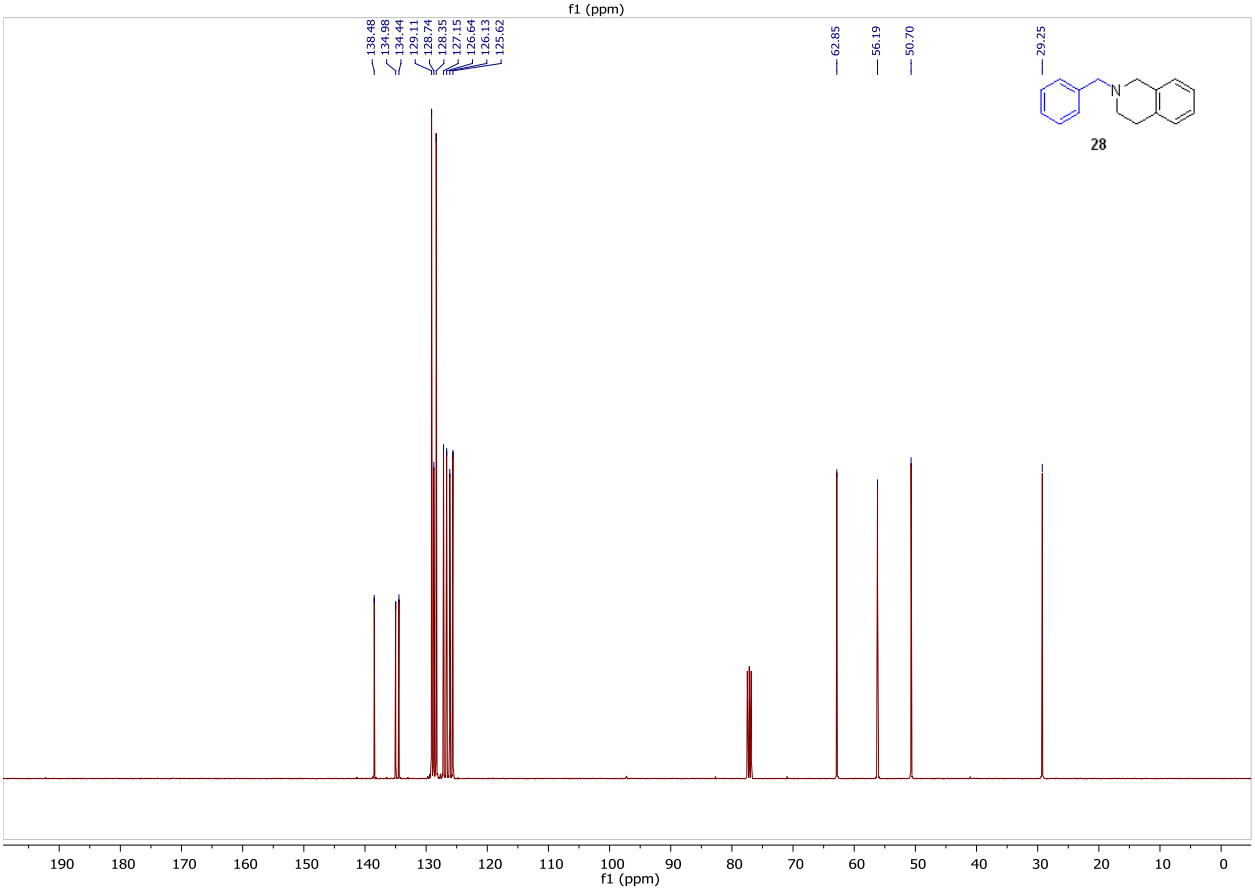
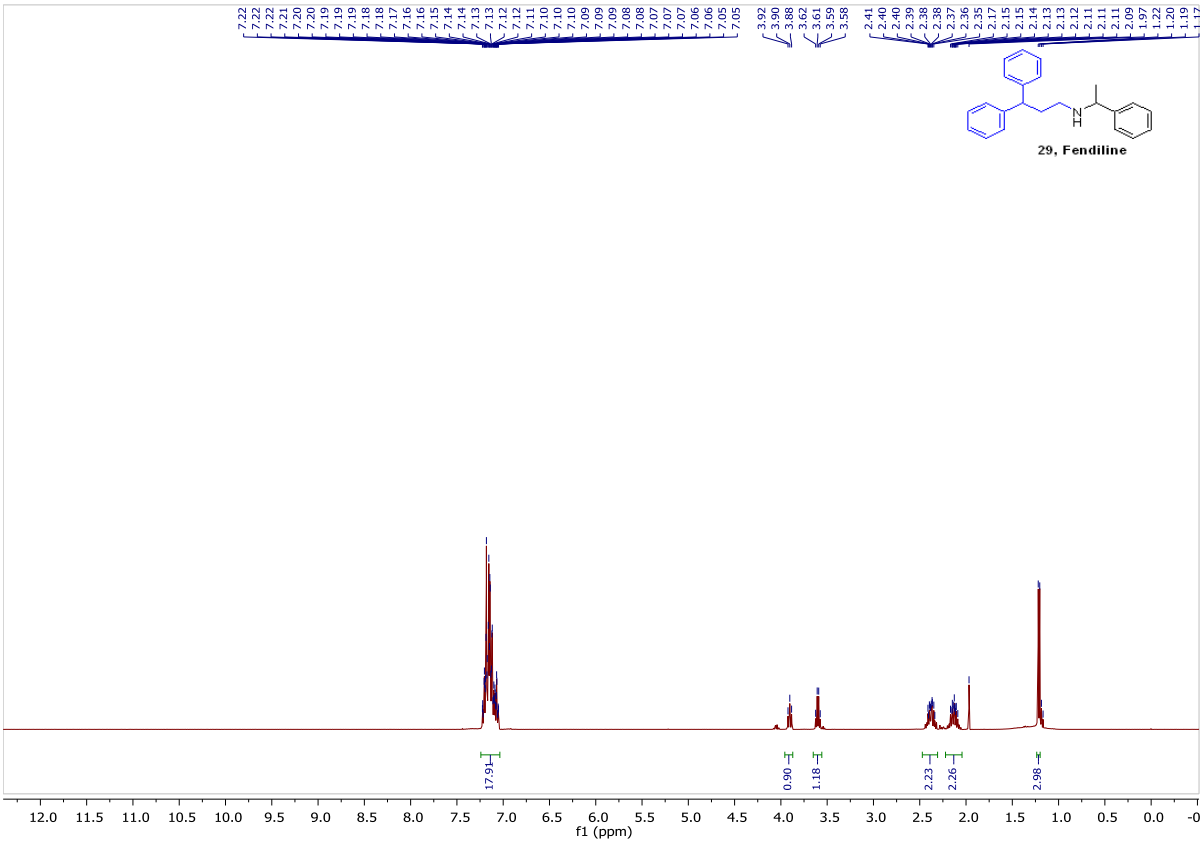
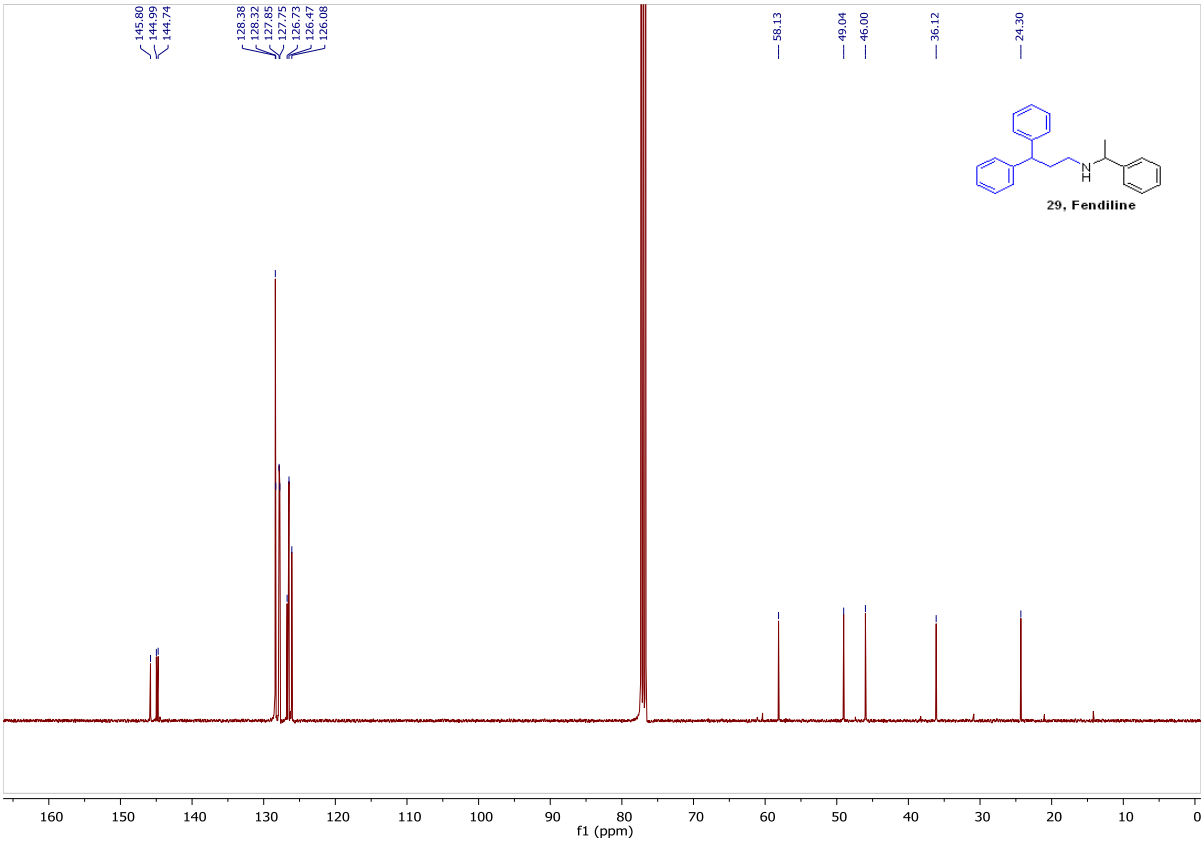
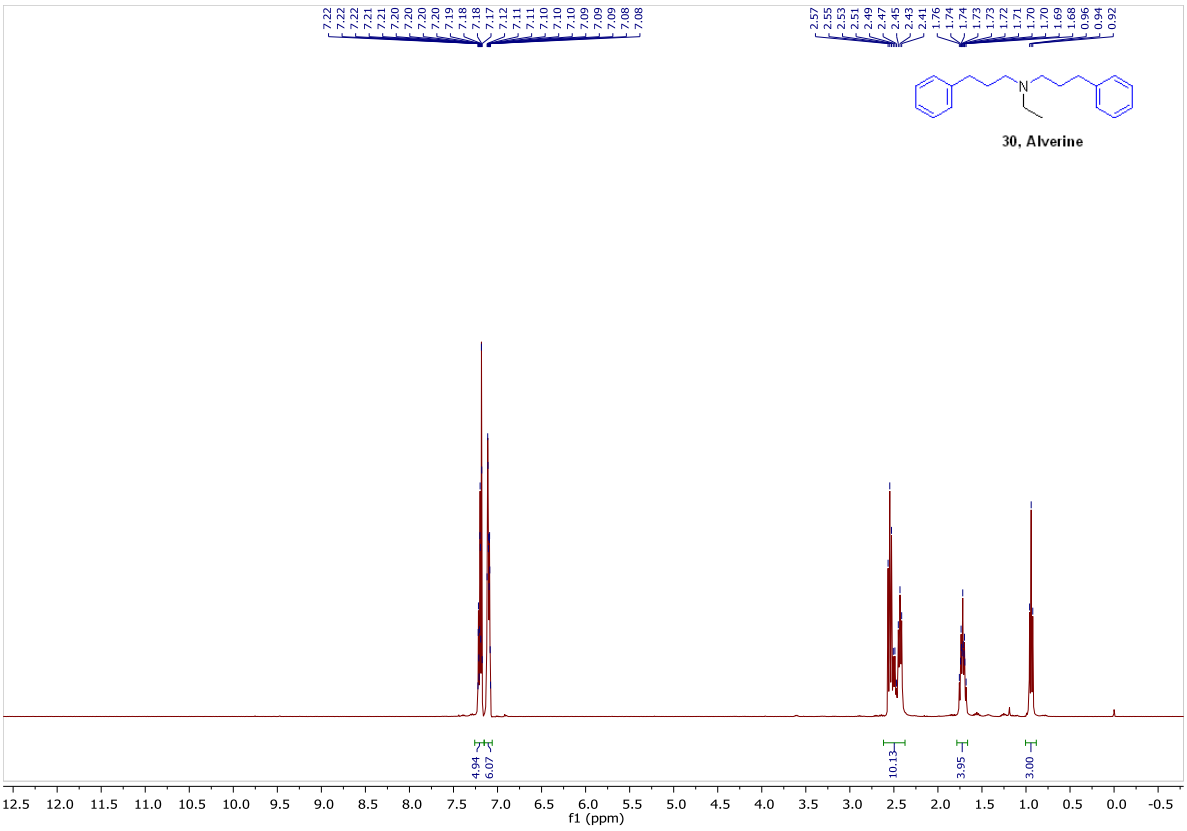
76.84
67.11
63.58
53.75
N
O
27
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.57 7.56 7.56 7.55 7.55 7.54 7.54 7.54 7.50 7.50 7.49 7.49 7.48 7.48 7.48 7.48 7.46 7.46 7.46 7.46 7.43 7.43 7.43 7.42 7.41 7.41 7.40 7.40 7.39 7.39 7.28 7.27 7.26 7.26 7.25 7.25 7.25 7.24 7.24 7.23 7.22 7.22 7.21 7.13 7.12 7.12 7.12 7.11 7.11 7.10 7.10 3.83 3.78 3.78 3.06 3.04 3.03 2.90 2.89 2.87
28
2.00 1.97 0.98 2.94 0.96 3.95 2.00 2.03
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


138.48 134.98 134.44 129.11 128.74 128.35 127.15 126.64 126.13 125.62
62.85 56.19 50.70 29.25
28
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


29, Fendiline
f1 (ppm)


29, Fendiline
f1 (ppm)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7.18
7.18
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7.12
7.11
7.11
7.10
7.10
7.09
7.09
7.09
7.08
7.08
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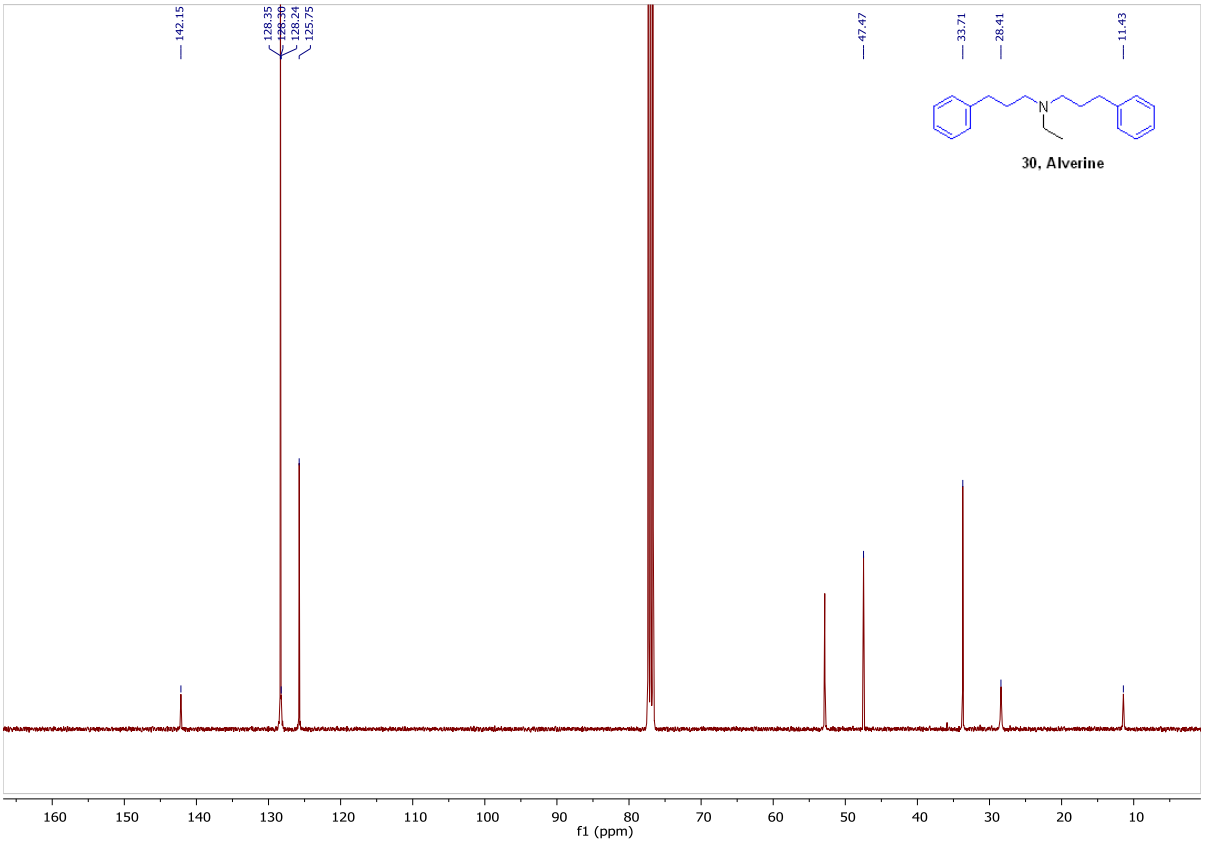
2.55
2.53
2.51
2.49
2.47
2.45
2.43
2.41
1.76
1.74
1.74
1.73
1.73
1.72
1.71
1.70
1.70
1.69
1.68
0.96
0.94
0.92
N
30, Alverine
4.94
6.07
10.13
3.95
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


142.15
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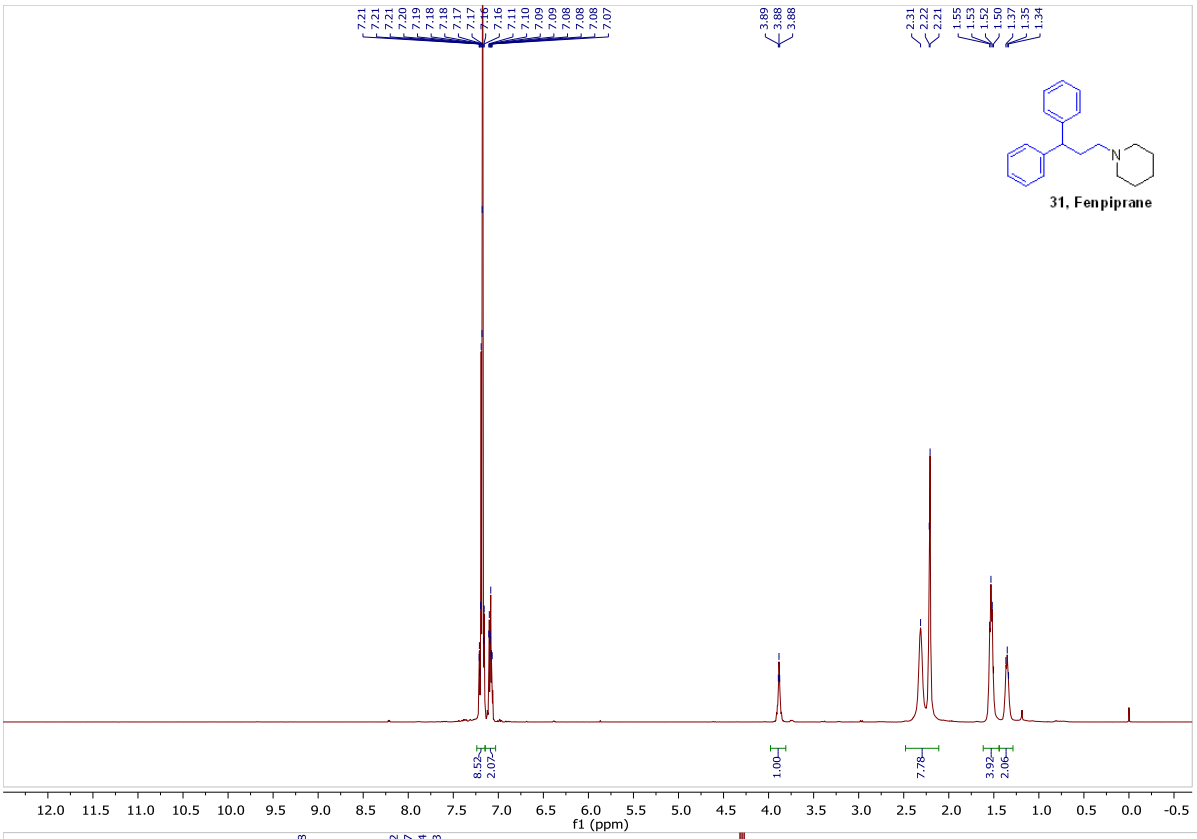
128.30
128.24
125.75
47.47
33.71
28.41
11.43
N
30, Alverine
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.17
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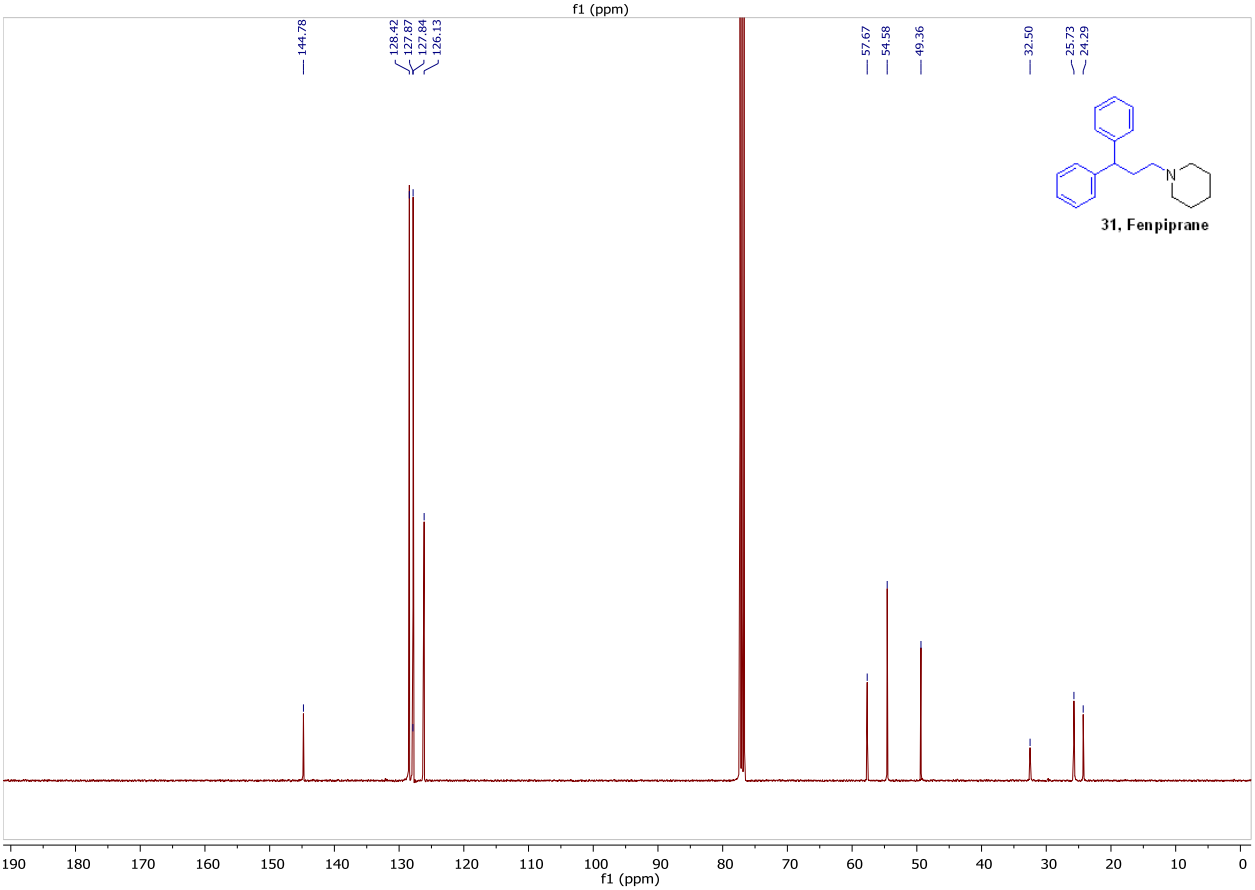
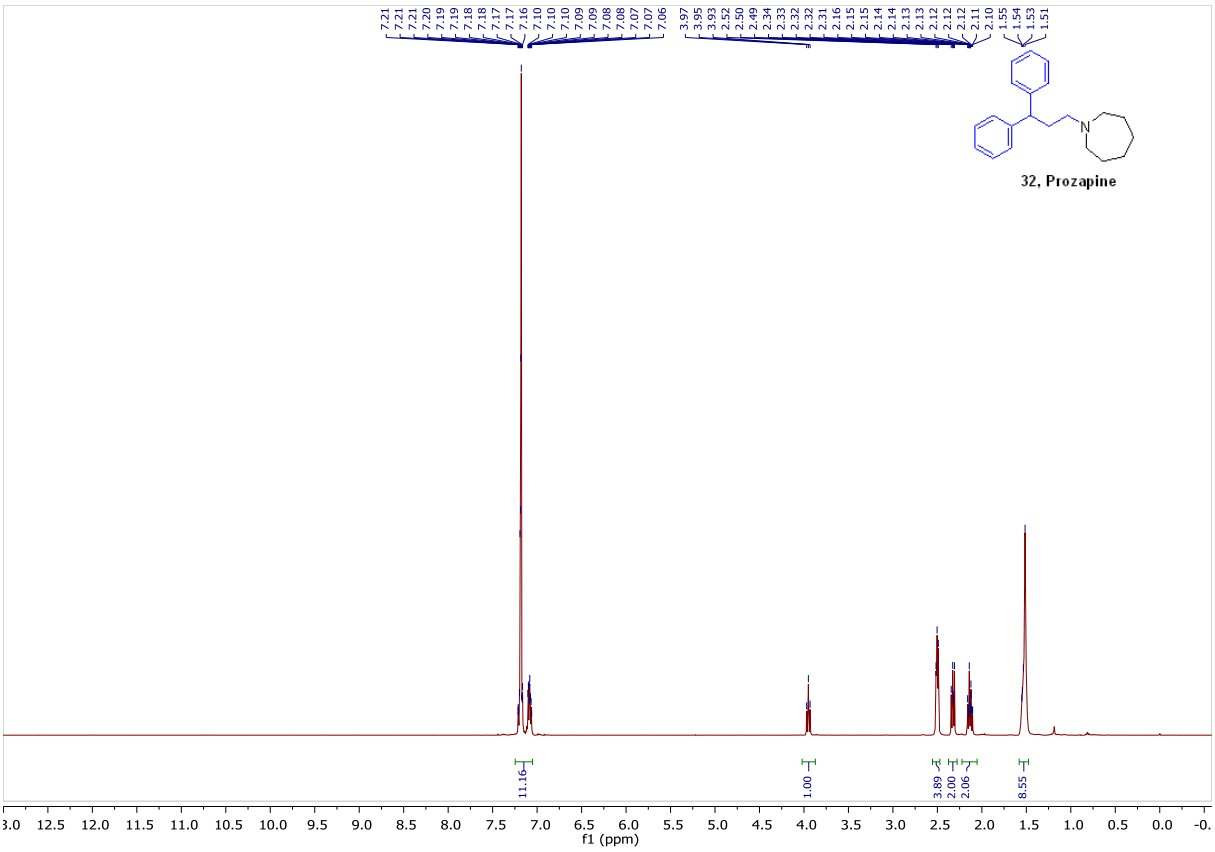
7.16
7.16
7.11
7.10
7.09
7.09
7.08
7.08
7.08
7.07
3.89
3.88
3.88
2.31
2.22
2.21
1.55
1.53
1.52
1.50
1.37
1.35
1.34
N
31, Fenpiprane
8.52
2.07
1.00
7.78
3.92
2.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


144.78
128.42
127.87
127.84
126.13
57.67
54.58
49.36
32.50
25.73
24.29
N
31, Fenpiprane
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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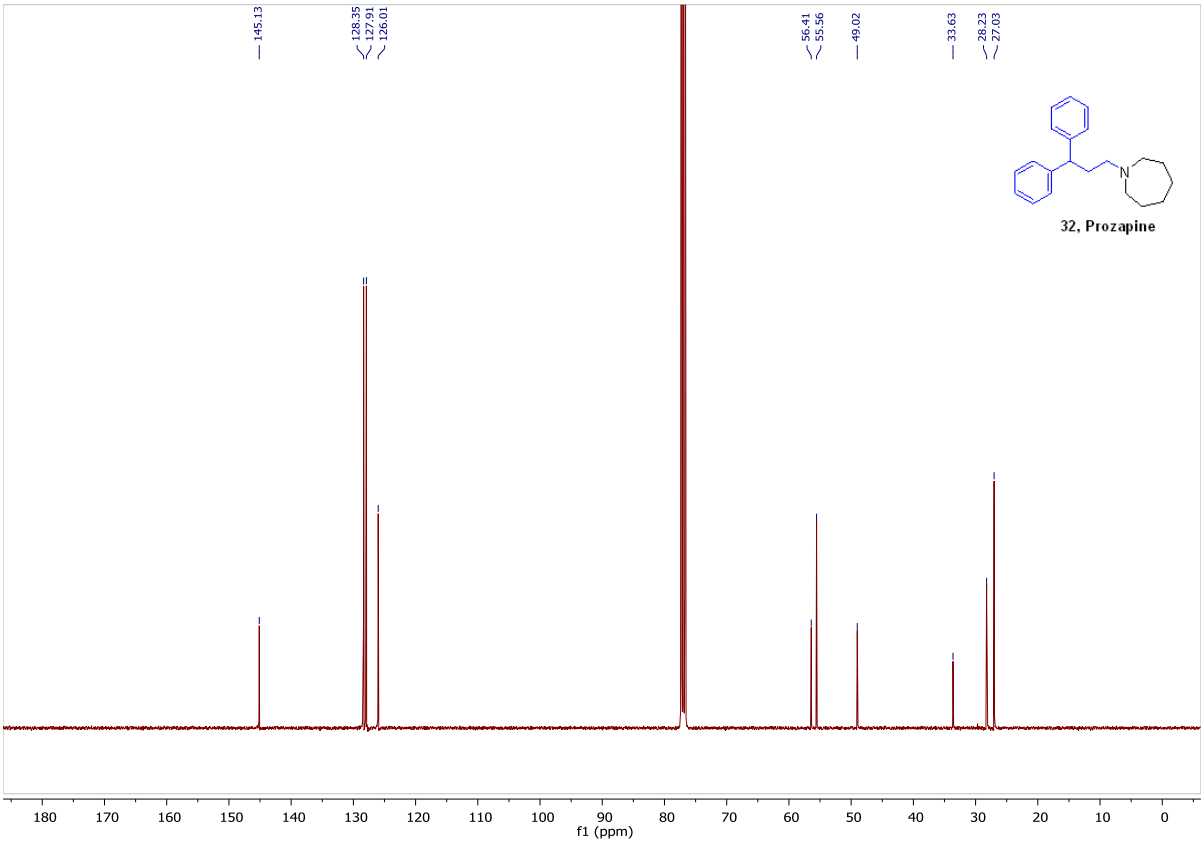
3.97 3.95 3.93 2.52 2.50 2.49 2.34 2.33 2.32 2.32 2.31 2.16 2.15 2.15 2.14 2.14 2.13 2.13 2.12 2.12 2.12 2.11 2.10 1.55 1.54 1.53 1.51
32, Prozapine
11.16
1.00
3.89
2.00
2.06
8.55
f1 (ppm)


145.13
128.35
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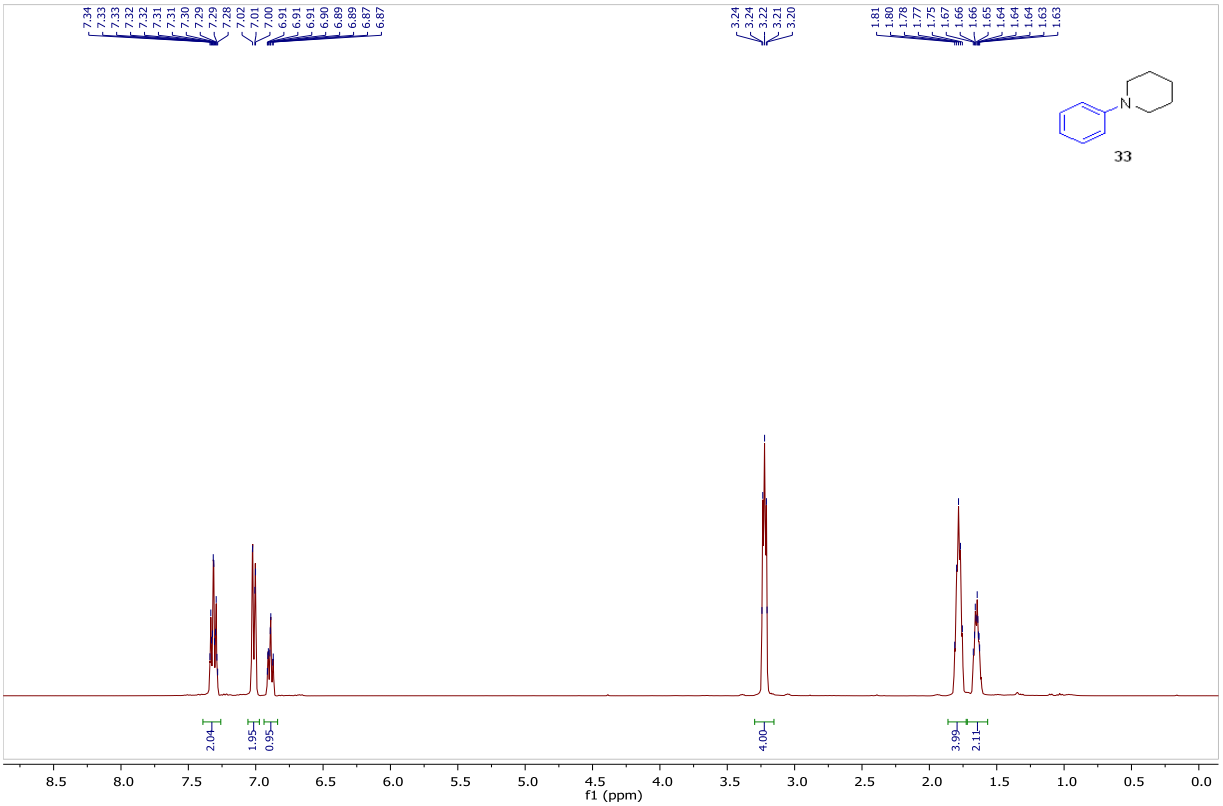
56.41
55.56
49.02
33.63
28.23
27.03
32, Prozapine
f1 (ppm)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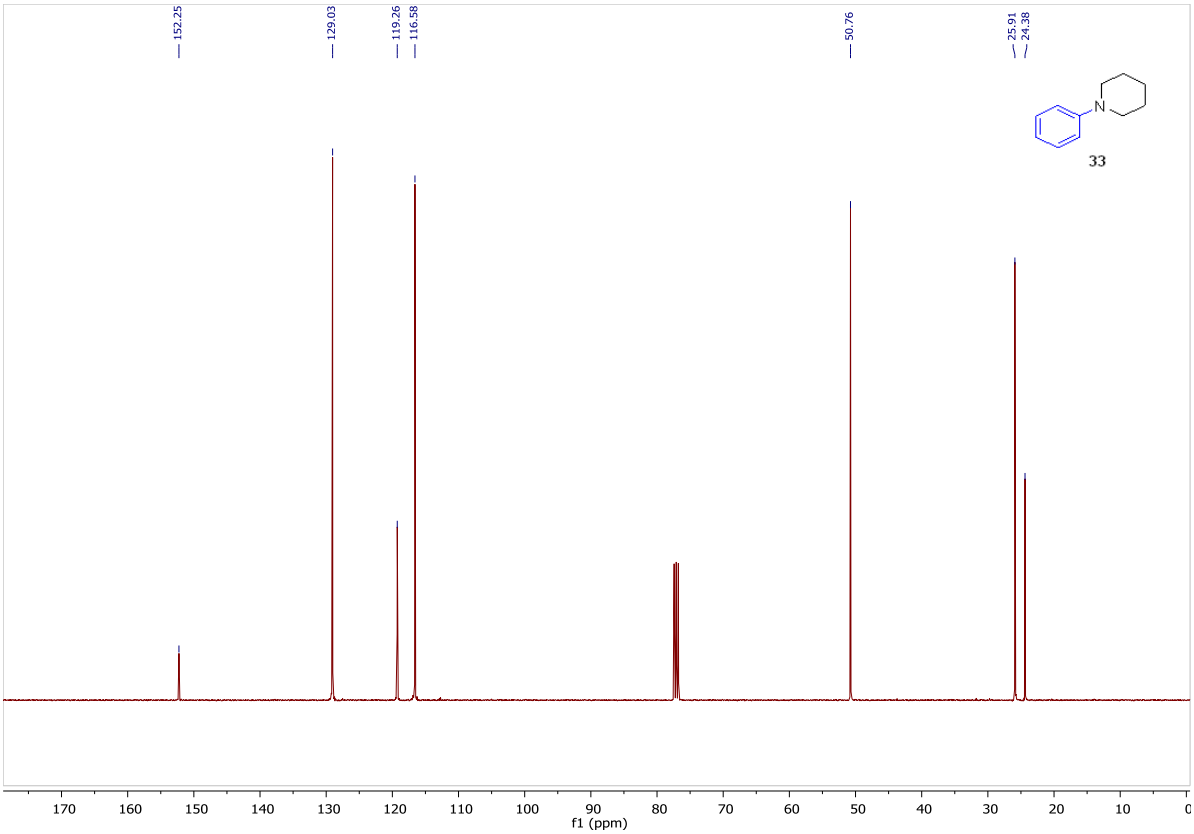
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.02
7.01
7.00
6.91
6.91
6.91
6.90
6.89
6.89
6.87
6.87
3.24
3.24
3.22
3.21
3.21
3.20
1.81
1.80
1.78
1.77
1.75
1.67
1.66
1.66
1.65
1.64
1.64
1.64
1.63
1.63
N
33
2.04
1.95
0.95
4.00
3.99
2.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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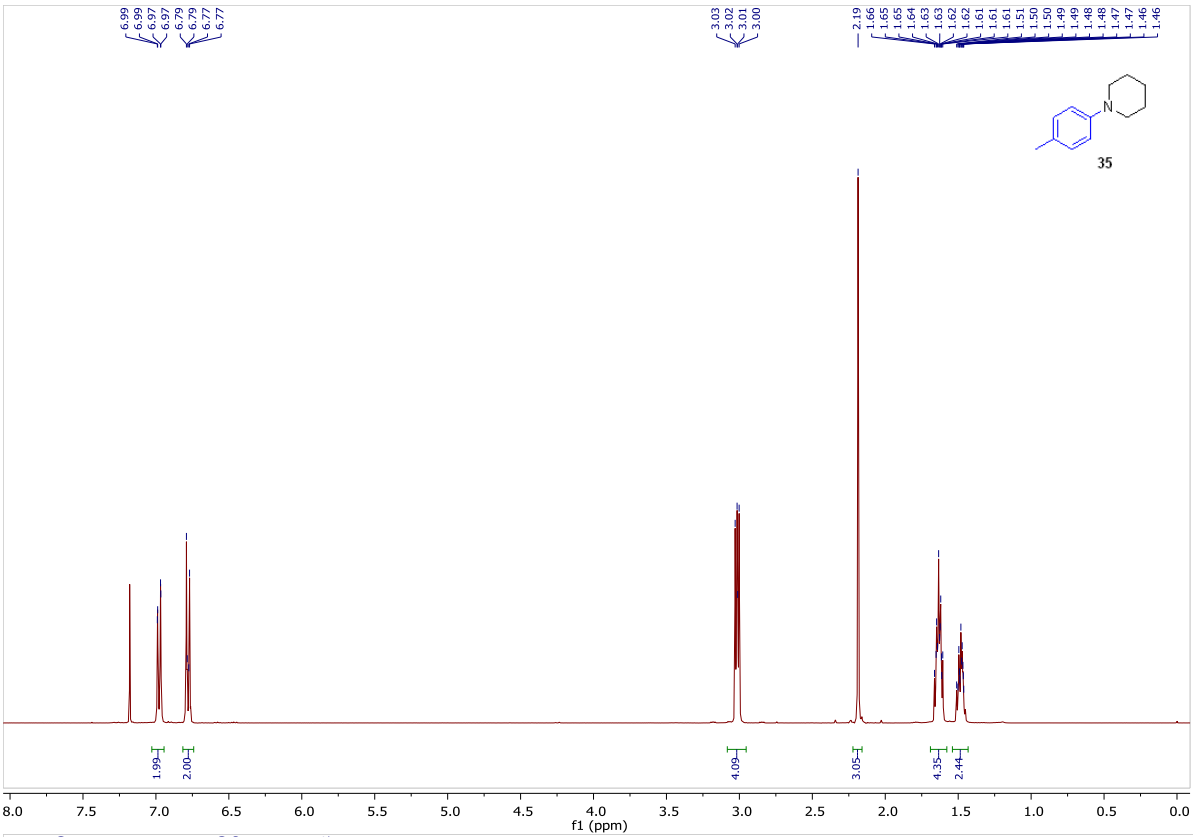
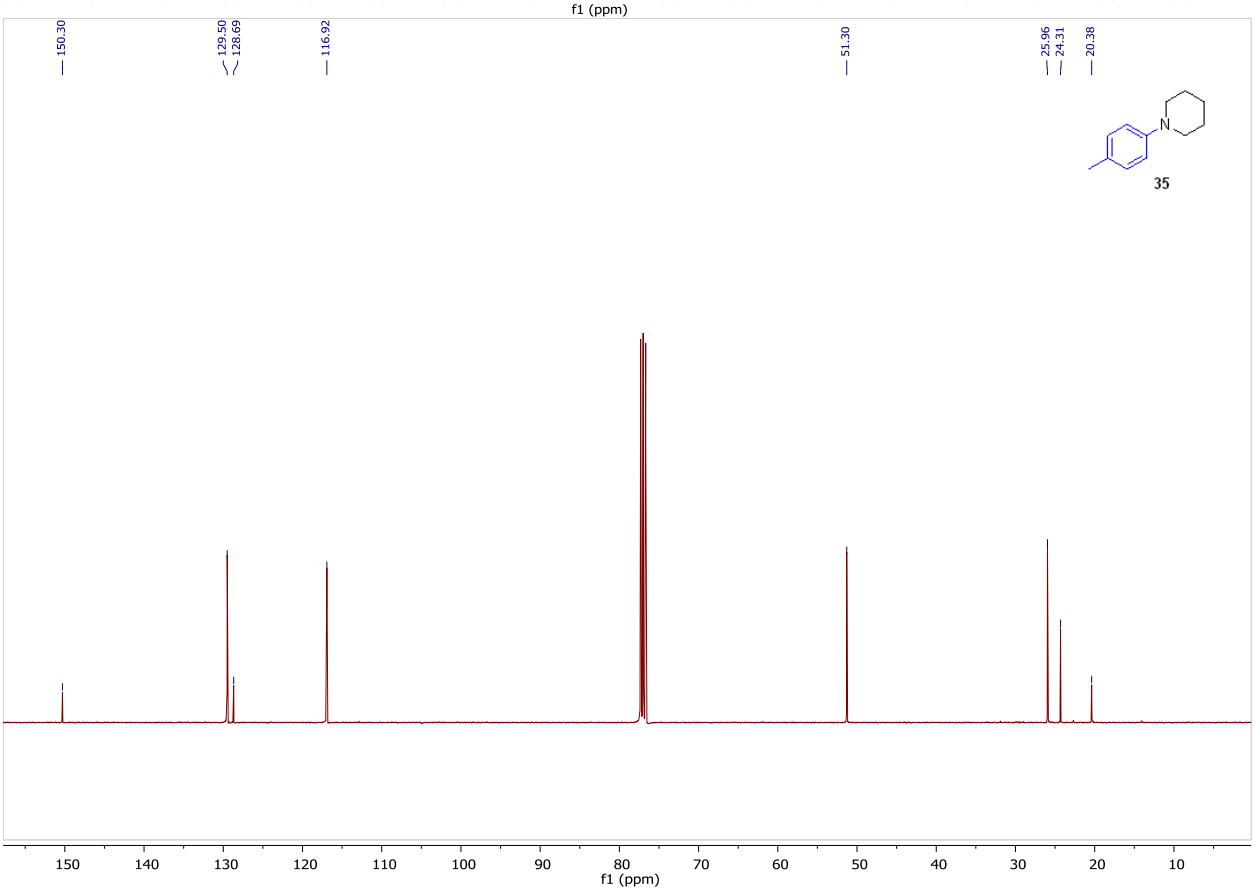
129.03
119.26
116.58
50.76
25.91
24.38
N
33
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


6.99
6.99
6.97
6.97
6.79
6.79
6.77
6.77
3.03
3.02
3.01
3.00
2.19
1.66
1.65
1.65
1.64
1.63
1.63
1.62
1.62
1.61
1.61
1.61
1.51
1.50
1.50
1.49
1.49
1.48
1.48
1.47
1.47
1.46
1.46
35
1.99
2.00
4.09
3.05
4.35
2.44
f1 (ppm)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129.50
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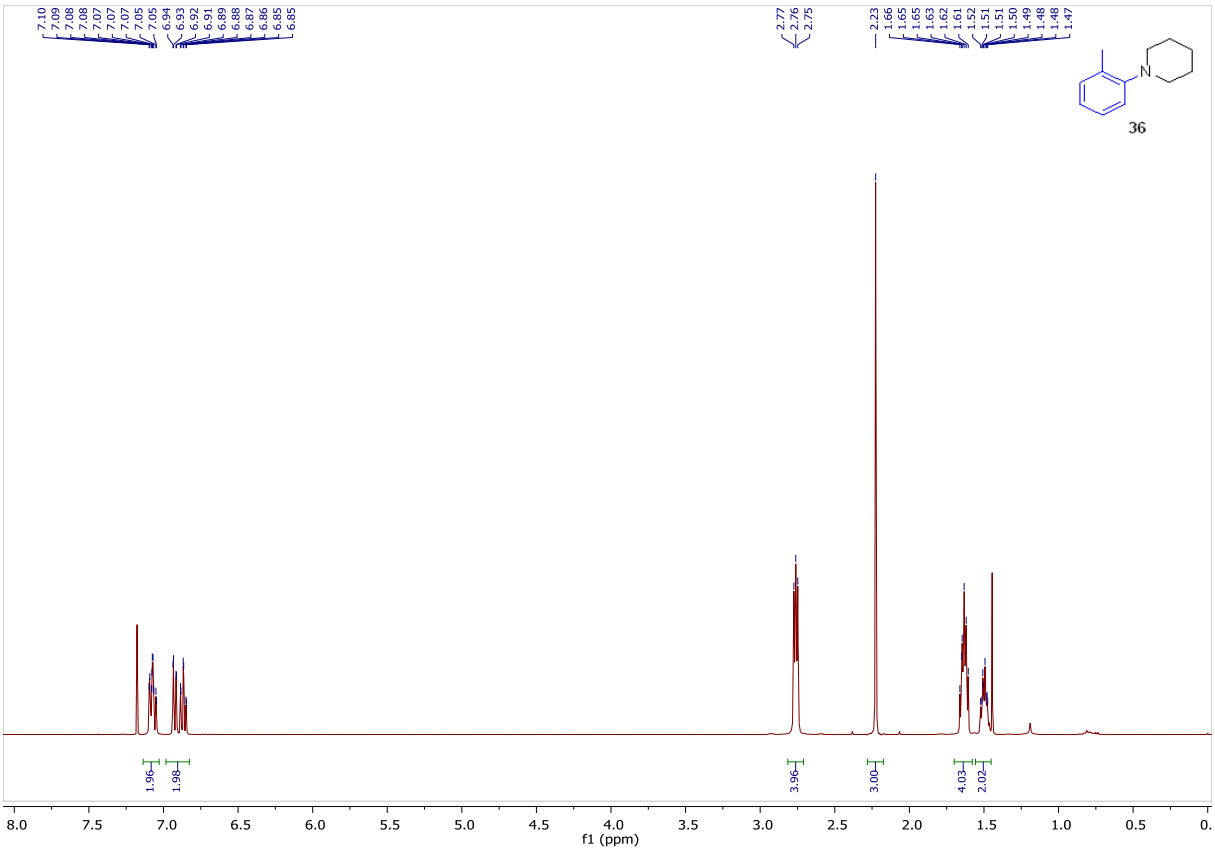
116.92
51.30
25.96
24.31
20.38
35
f1 (ppm)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7.09
7.08
7.08
7.07
7.07
7.07
7.05
7.05
6.94
6.93
6.92
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6.89
6.88
6.87
6.86
6.85
6.85
2.77
2.76
2.75
2.23
1.66
1.65
1.65
1.63
1.62
1.61
1.52
1.51
1.51
1.50
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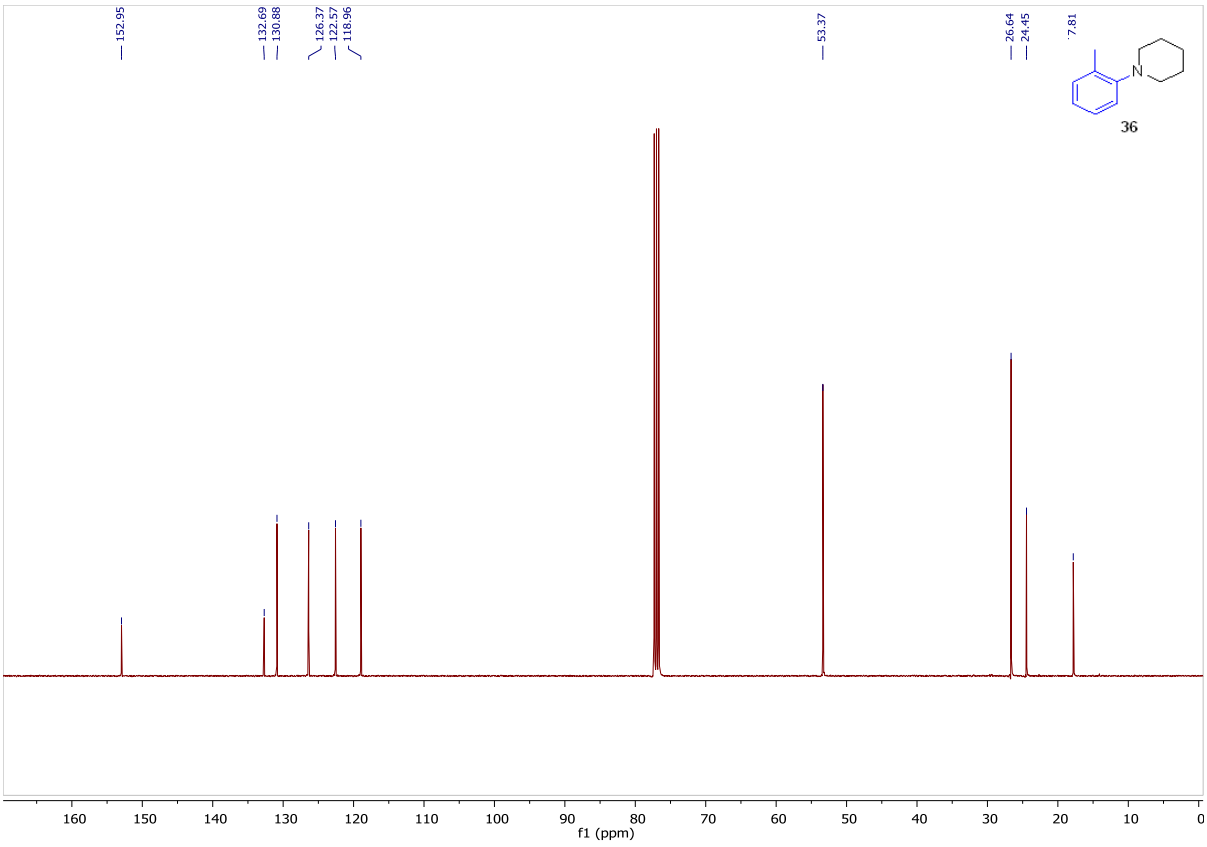
1.98
3.96
3.00
4.03
2.02
f1 (ppm)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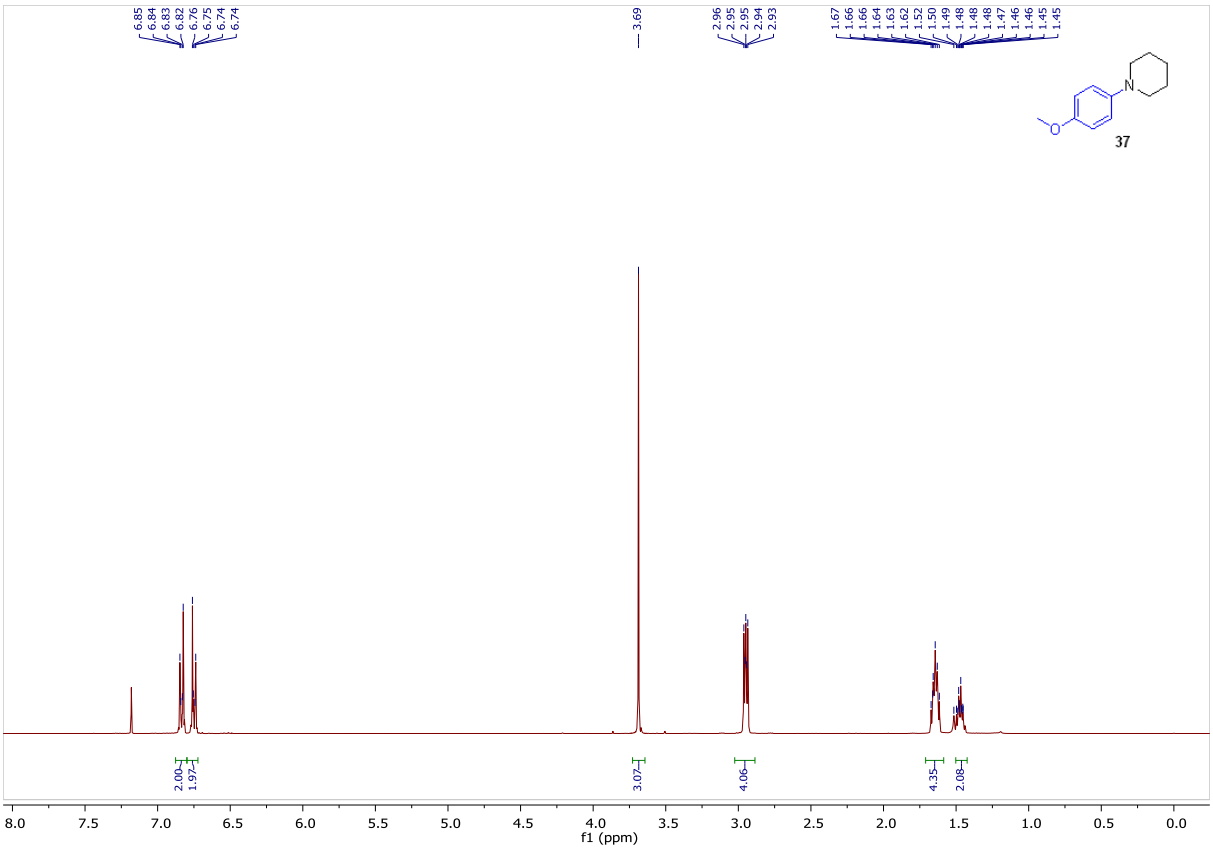
130.88
126.37
122.57
118.96
53.37
26.64
24.45
7.81
36
f1 (ppm)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6.74
3.69
2.96
2.95
2.95
2.94
2.93
1.67
1.66
1.66
1.64
1.63
1.62
1.52
1.50
1.49
1.48
1.48
1.48
1.47
1.46
1.46
1.45
1.45
37
2.00
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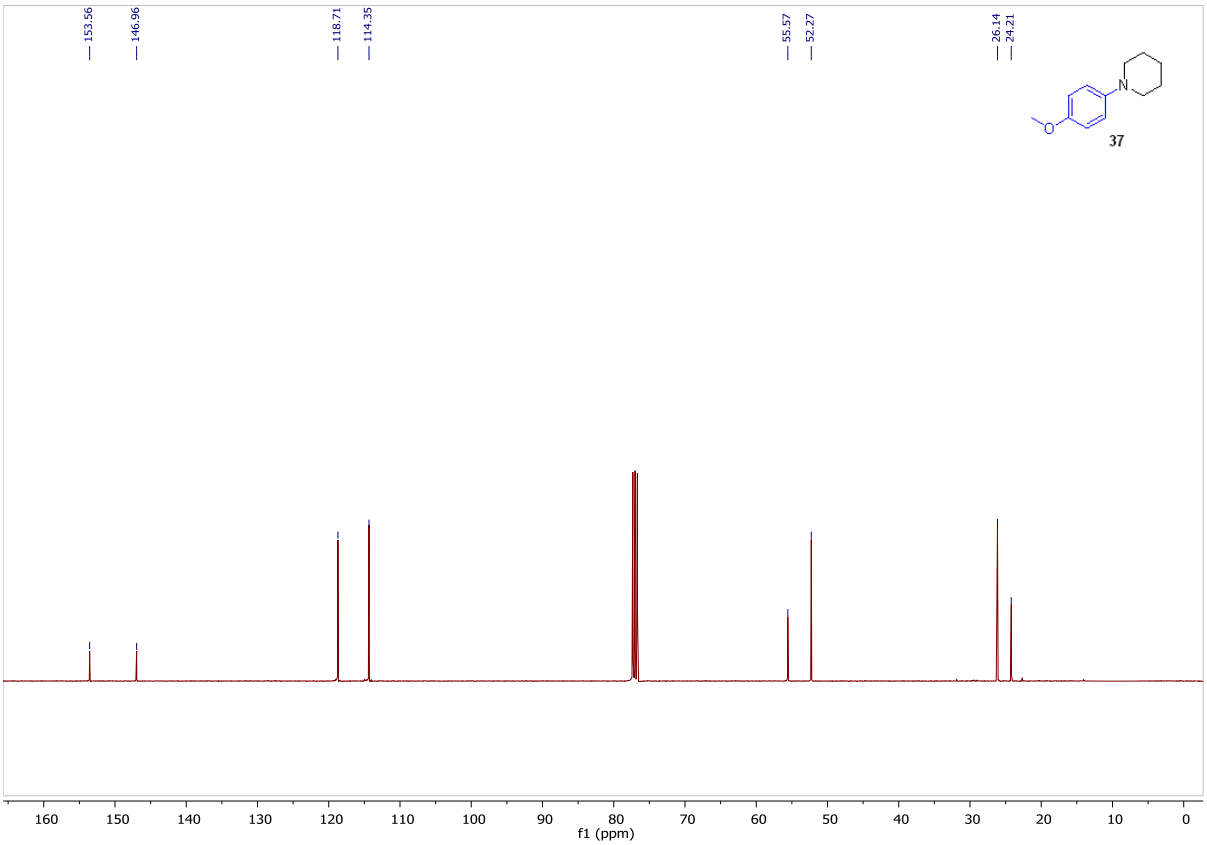
3.07
4.06
4.35
2.08
f1 (ppm)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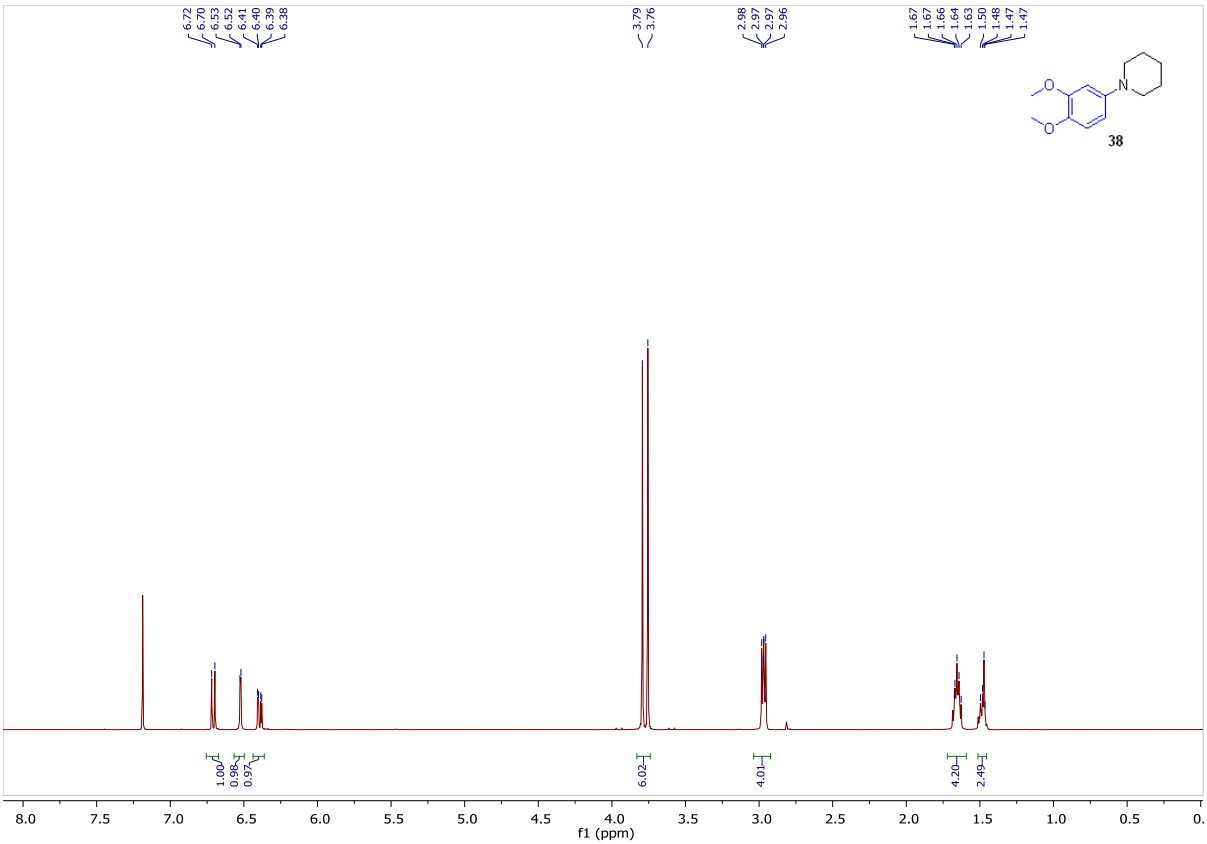
114.35
55.57
52.27
26.14
24.21
37
f1 (ppm)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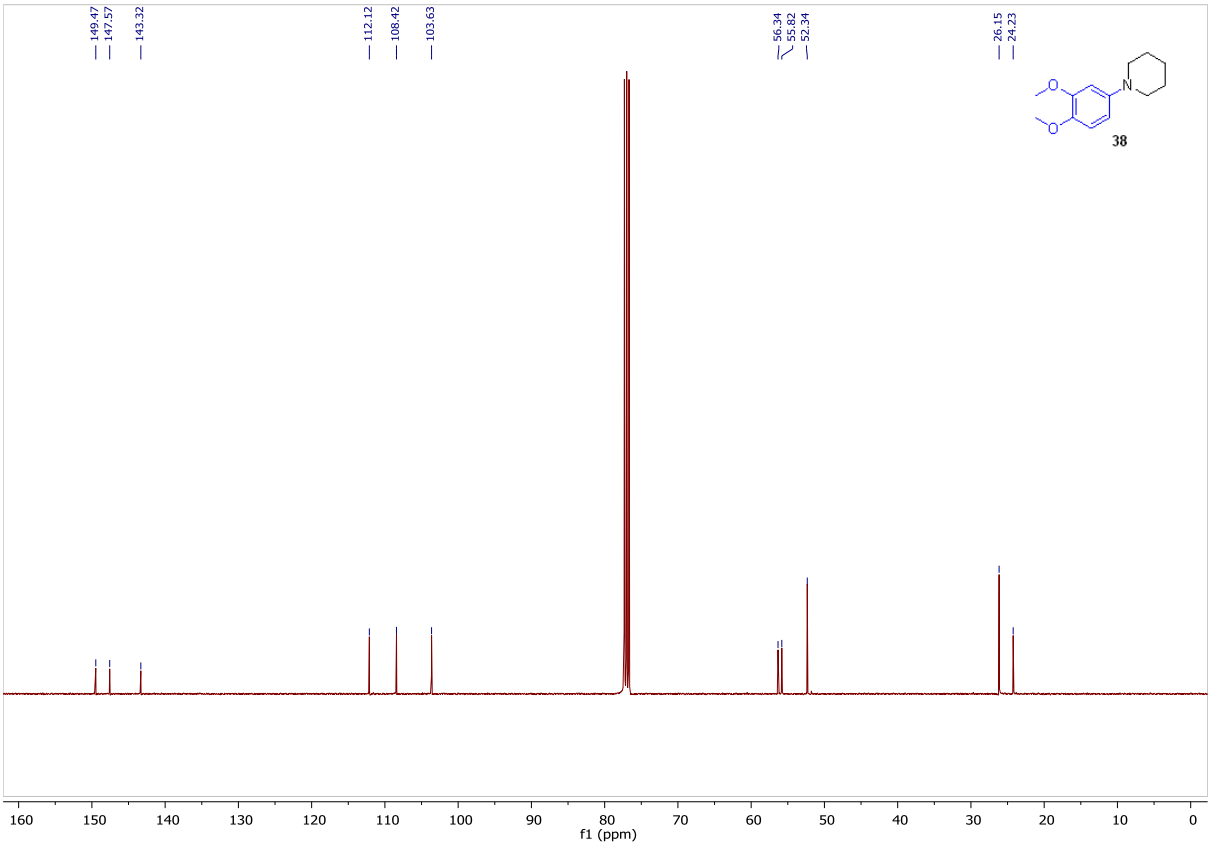
3.76
2.98
2.97
2.97
2.96
1.67
1.67
1.66
1.64
1.63
1.50
1.48
1.47
1.47
38
1.00
0.98
0.97
6.02
4.01
4.20
2.49
f1 (ppm)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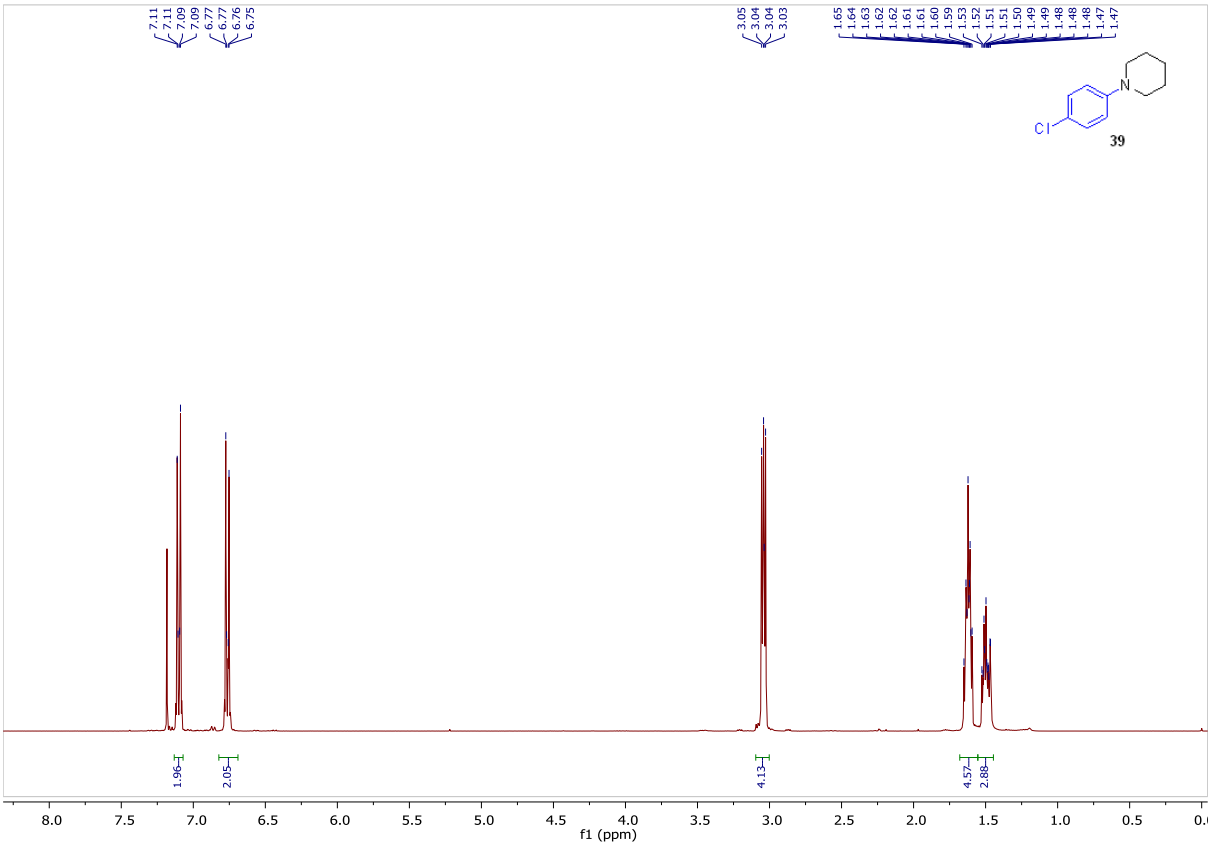
56.34
55.82
52.34
26.15
24.23
38
f1 (ppm)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7.11
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7.09
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3.04
3.04
3.03
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1.53
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1.48
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1.46
1.47
1.47
Cl
N
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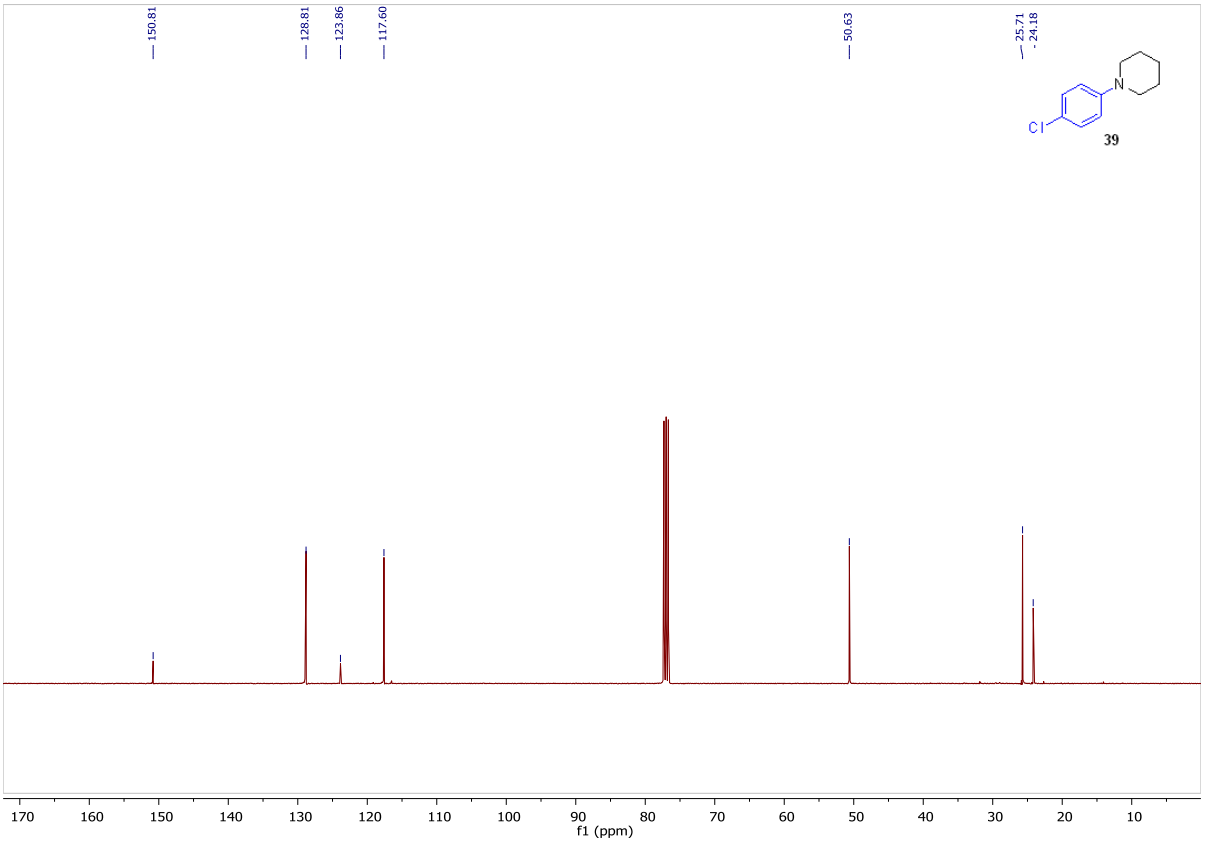
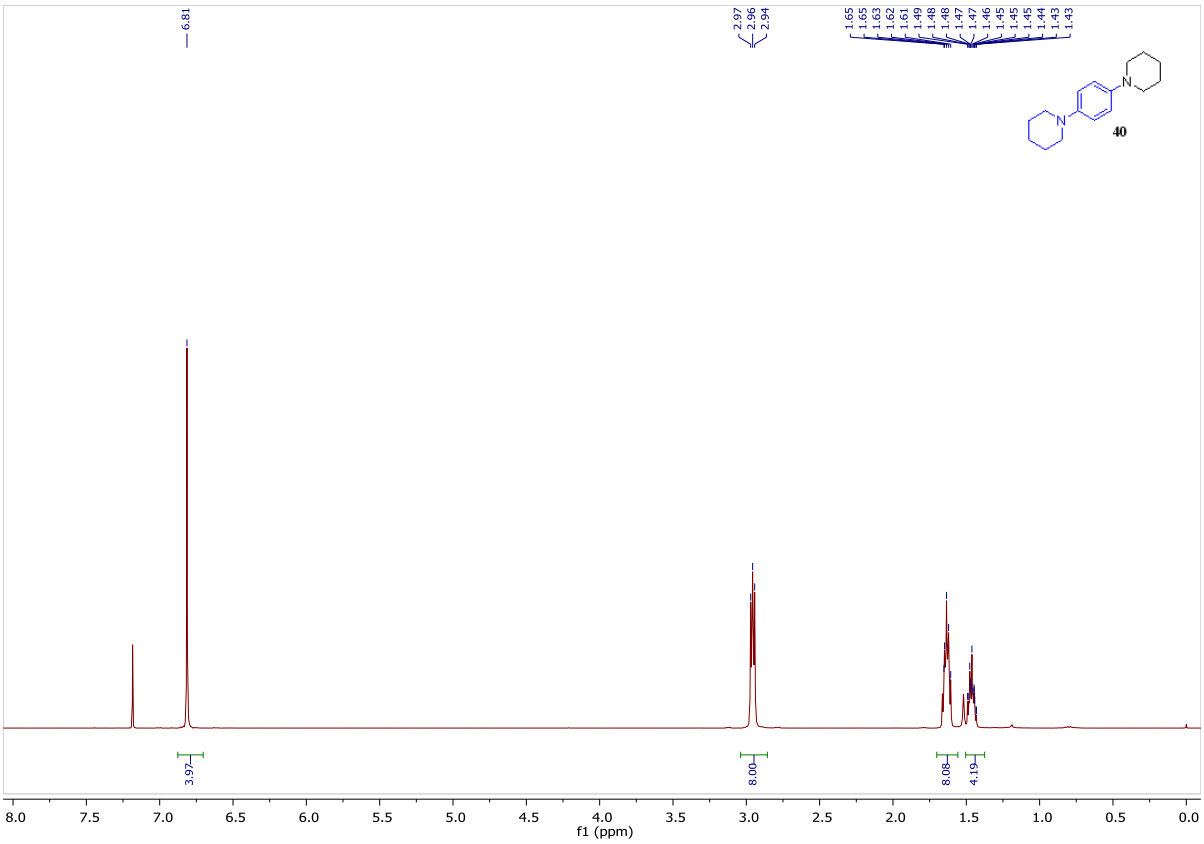
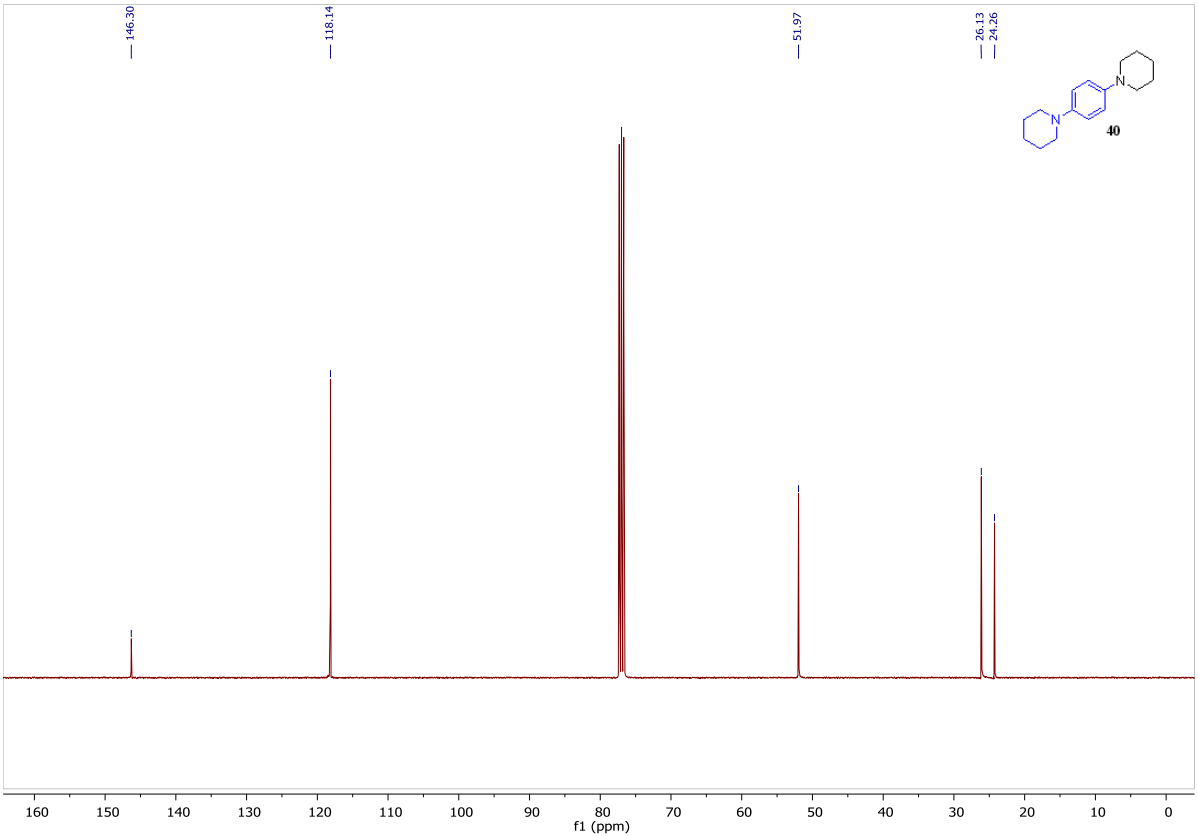
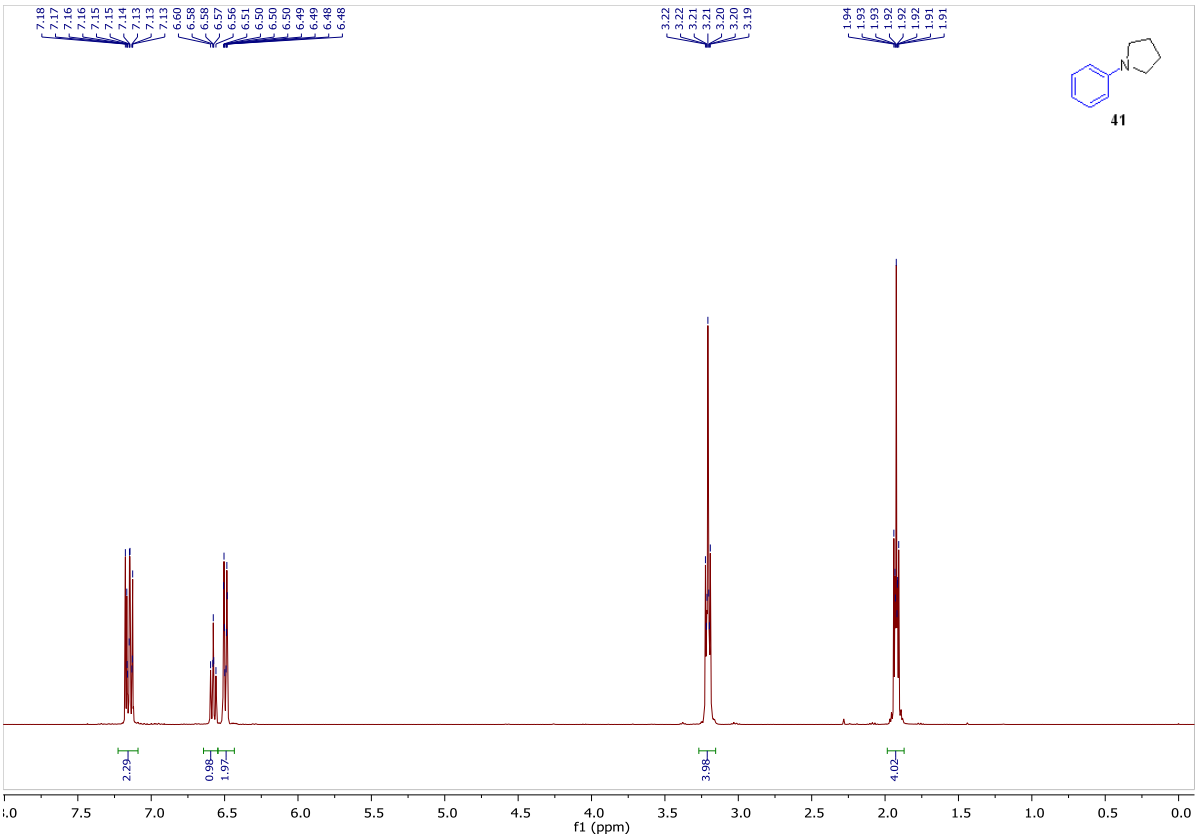
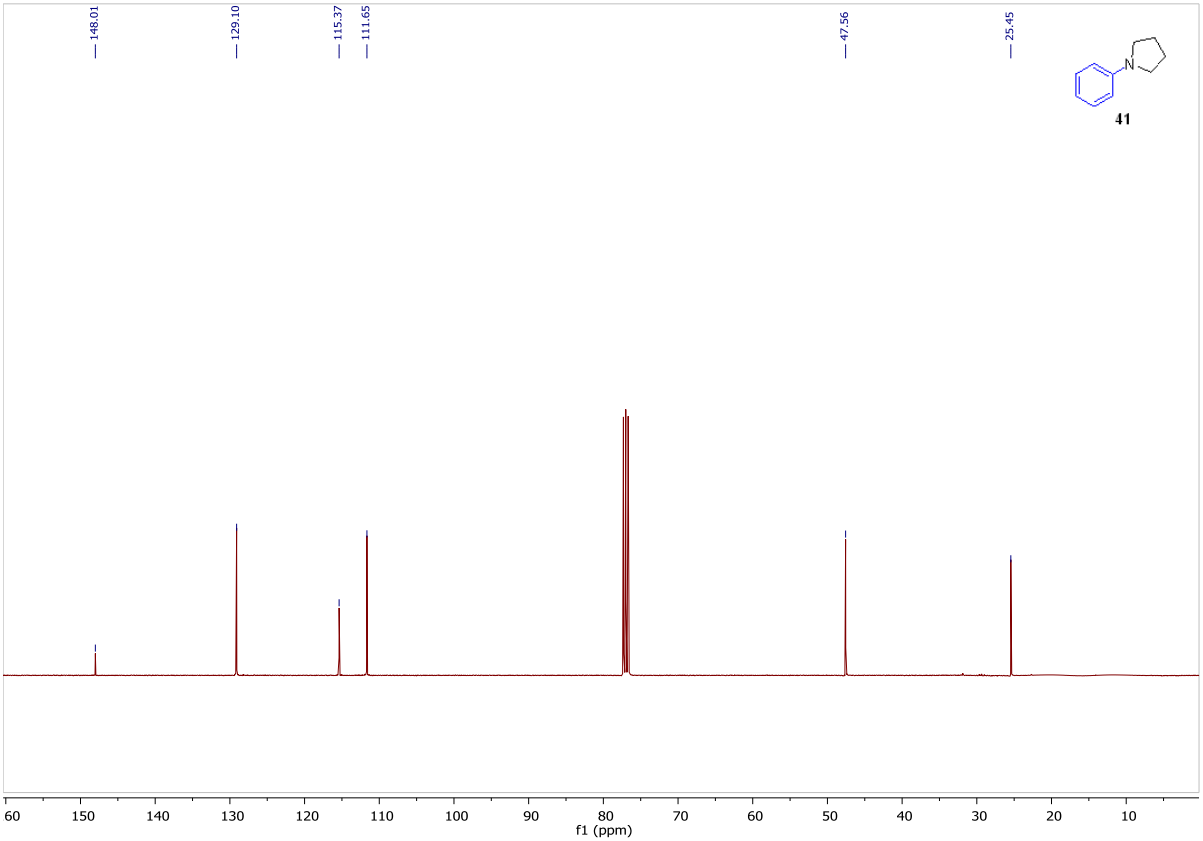
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

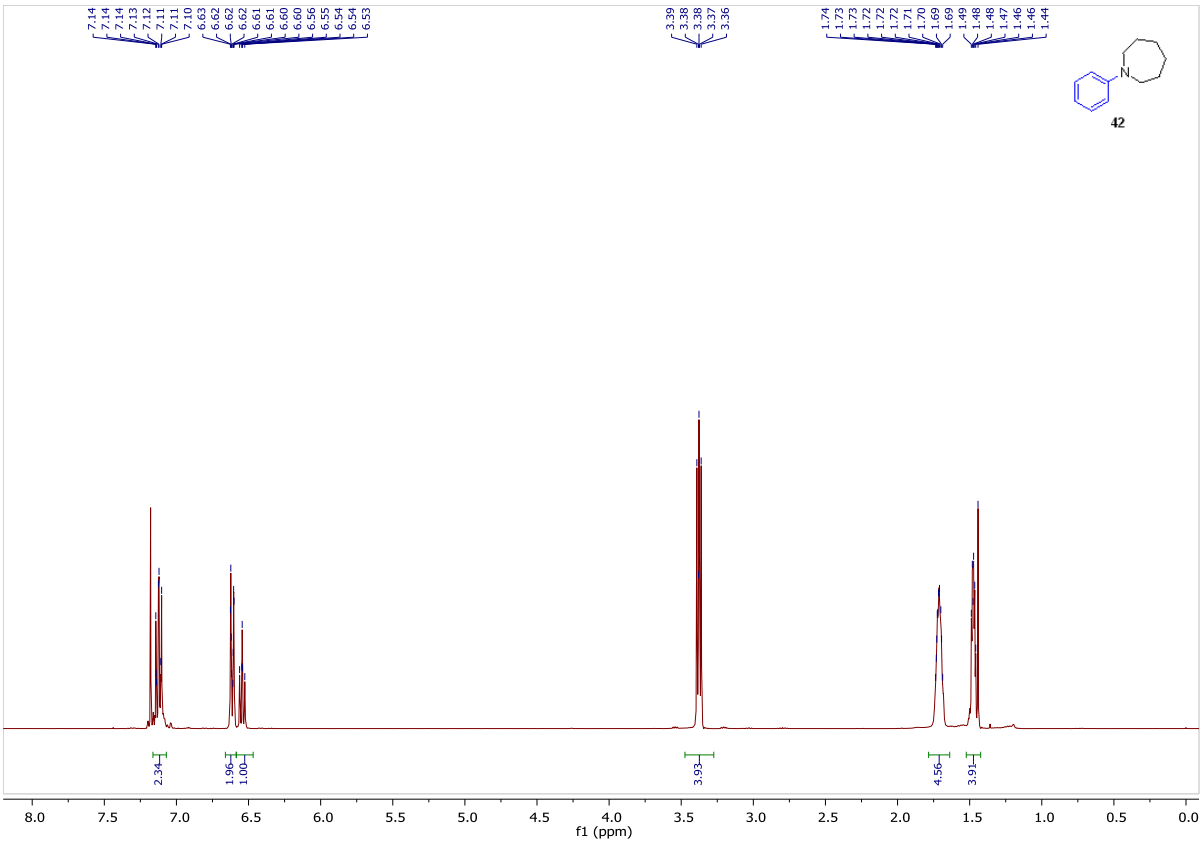

150.81
128.81
123.86
117.60
50.63
25.71
24.18
Cl
N
39
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

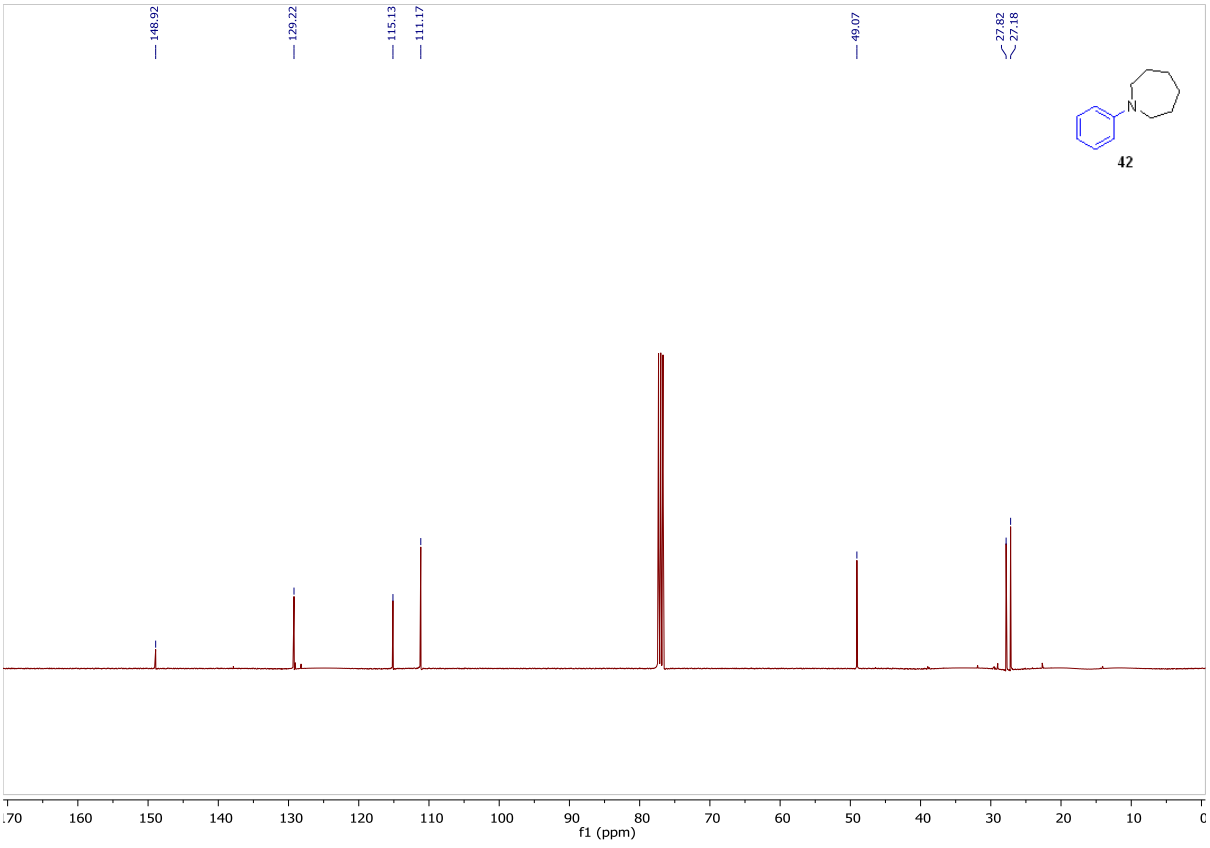

6.81
2.97
2.96
2.94
1.65
1.65
1.63
1.62
1.61
1.49
1.48
1.48
1.47
1.47
1.46
1.45
1.45
1.45
1.44
1.43
1.43
40
3.97
8.00
8.08
4.19
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


146.30
118.14
51.97
26.13
24.26
40
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.18
7.17
7.16
7.16
7.15
7.15
7.14
7.13
7.13
7.13
6.60
6.58
6.58
6.57
6.56
6.51
6.50
6.50
6.50
6.49
6.49
6.48
6.48
3.22
3.22
3.21
3.21
3.20
3.20
3.19
1.94
1.93
1.93
1.92
1.92
1.92
1.91
1.91
41
2.29
0.98
1.97
3.98
4.02
f1 (ppm)


148.01
129.10
115.37
111.65
47.56
25.45
41
f1 (ppm)


7.14
7.14
7.14
7.13
7.12
7.11
7.11
7.10
6.63
6.62
6.62
6.62
6.61
6.61
6.60
6.60
6.56
6.55
6.54
6.54
6.53
3.39
3.38
3.38
3.37
3.36
1.74
1.73
1.73
1.72
1.72
1.72
1.71
1.70
1.69
1.69
1.49
1.48
1.48
1.47
1.46
1.46
1.44
42
2.34
1.96
1.00
3.93
4.56
3.91
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


148.92
129.22
115.13
111.17
49.07
27.82
27.18
42
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

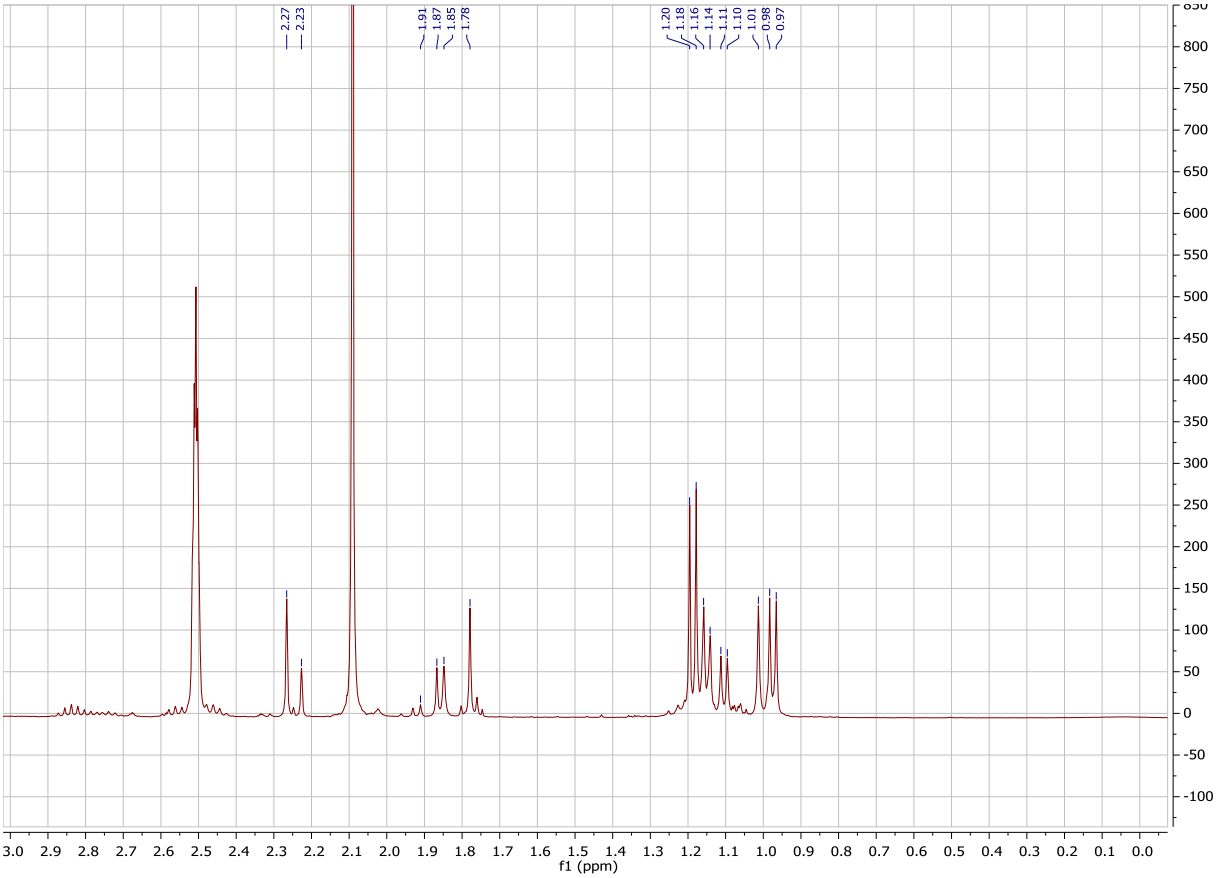
7. NMR Experiments to detect Ru-H Species

General procedure:

Ru complex **1** or **3** or **3a** (0.1 mmol), aniline (0.1 mmol) and benzyl alcohol (1 mmol) were added into a small reaction tube, degassed using argon and closed using a cap. The reaction mixture was heated to 100 ^{o}C under stirring. The reaction is performed at 100 ^{o}C to have a slow reaction so that we could identify intermediate Ru-species. After 1 h of reaction, 5 µL of sample was taken for NMR measurement. All NMRs (^{1}H and ^{31}P) were measured in $CDCl_3$ at room temperature except for complex **3a**, which was measured in DMSO-d_6 due to solubility issues.

Reaction procedure in the presence of added PPh_3 :

Ru complex **1** or **3** (0.1 mmol), PPh_3 (0.1 mmol), aniline (0.1 mmol) and benzyl alcohol (1 mmol) were added into a small microware tube, degassed using argon and closed using a cap. The reaction mixture was heated to 100 ^{o}C under stirring. After 1h reaction, 5 µL sample was taken and dissolved in $CDCl_3$ for NMR (^{1}H and ^{31}P) measurement.



^{1}H NMR spectra of **3a,** following the above general procedure, in the range of 0-3 ppm showed evidences for the presence of different sets of *p*-cymene containing Ru-species.