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Supporting Information

An Efficient Palladium Catalyst for the *N*-Alkylation of Amines and α-Alkylation of Ketones Using Alcohols

Tuan Thanh Dang, Siah Pei Shan, Balamurugan Ramalingam, Abdul Majeed Seayad*

Institute of Chemical and Engineering Sciences, 8 Biomedical Grove, #07-01 Neuros, Singapore 138665.

Phone: +65-6799 8527

Fax: +65-64642102

E-mail: abdul_seayad@ices.a-star.edu.sg

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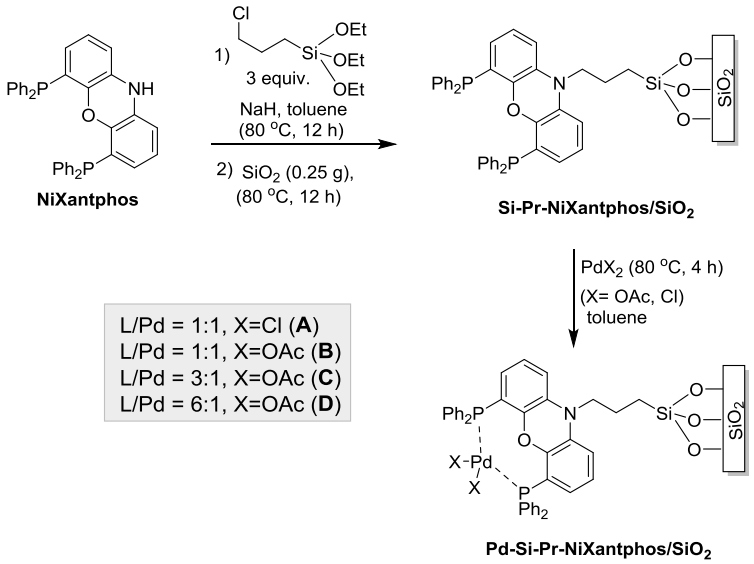
1. General information

Commercially available reagents and solvents were used as received without further purification. Dry solvents were collected from solvent dispenser system. 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 using a cryo-probe on a *Bruker Avance 400* (400 MHz, ^{1}H-NMR; 101MHz, ^{13}C-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.

2. Preparation and characterization of catalysts

General procedure for one-pot preparation of solid catalysts: 10 mL of dry toluene, 55.2 mg of NiXantphos (0.1 mmol), NaH (0.3 mmol) were charged under argon-atmosphere in a Schlenk tube followed by additions of (3-chloropropyl)triethoxysilane (0.3 mmol). The reaction tube was closed with the Teflon stopper and was heated to 80 ^{o}C under stirring for12h. 250 mg of dry SiO_2 was introduced in to the reaction mixture and stirring continued at 80 ^{o}C for another 12h. The reaction mixture was cooled to room temperature and the calculated amount of Pd precursor ($Pd(OAc)_2$) was introduced under argon and the reaction was stirring continued at 80 ^{o}C for another 4h. The reaction mixture was allowed to cool to RT and the brown solid catalyst was collected by filtration and washing with toluene (3 times, 20 mL) under argon atmosphere. The solid catalyst was dried in vacuum oven at 50 ^{o}C overnight, collected and stored under argon atmosphere.



Scheme S1: One-pot synthesis of Pd-Si-Pr-NiXantphos/SiO_2 catalyst.

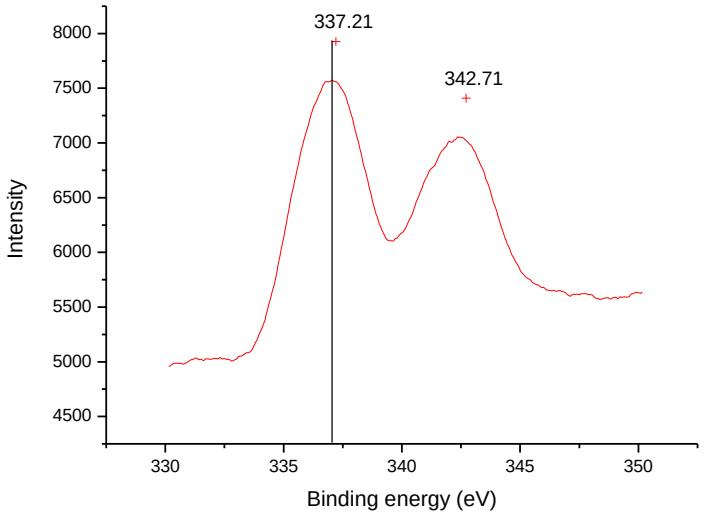


Figure S1: XPS spectra of Pd-Si-Pr-NiXantphos/SiO_2 catalyst B.

Evaluation of Pd loading on catalysts by ICP analysis

Catalyst	Pd loading (wt.%)
A	2.31
B	2.23
C	0.95
D	0.52

3. General procedure for the *N*-alkylation of amines and α-alkylation of ketones with alcohols

General procedure 1: Catalyst **B** (2-20 mg), LiOH (20.0 mol%), alcohol (6.0 mmol), and amine (2.0 mmol) were charged under argon-atmosphere in a Radleys carrousel reaction tube. The reaction tube was closed with the Teflon stopper and was heated to the desired temperature under stirring. After the desired reaction time, the reaction mixture was allowed to cool to room temperature and diluted with toluene (10 mL). The SiO_2 (400mg) was added into the crude mixture. The organic solvent was removed under vacuum and then the product was purified by column chromatography.

General procedure 2: Catalyst **B** (20 mg), LiOH (20.0 mol%), alcohol (6.0 mmol), and ketone (2.0 mmol) were charged under argon-atmosphere in a Radleys carrousel reaction tube. The reaction tube was closed with the Teflon stopper and was heated to the desired temperature under stirring. After the desired reaction time, the reaction mixture was allowed to cool to room temperature and diluted with toluene (10 mL). The SiO_2 (400mg) was added into the crude mixture. The organic solvent was removed under vacuum and then the product was purified by column chromatography.

4. Recycle studies

The recyclability of the silica supported palladium Ni-Xantphos catalysts B, C and D were investigated by taking *N*-alkylation of aniline using benzyl alcohol at 120 ^{o}C for 24 h as the representative reaction. 4 mg, 10mg and 17.2 mg of catalysts B, C and D, (0.042 mol% Pd) respectively were used for easy handling and the catalyst was recovered by simple filtration

under argon and reused for subsequent reactions. In order to estimate the Pd leaching, ICP analysis was carried out using the filtrate of each reaction. Results showed that after each runs, Pd leaching is less than 0.01 ppm.

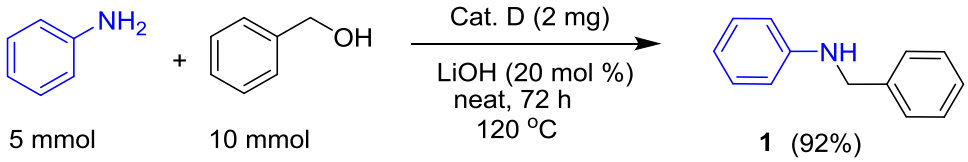
Pd leaching studies by ICP AES:

Entry	**Pd leaching of catalyst D**	
	µg	**ppm**
Run 1	0.0019	0.002
Run 2	0.0032	0.004
Run 3	0.0022	0.003
Run 4	0.0031	0.004
Run 5	0.0008	0.001
Run 6	n.d.[a]	n.d.[a]

[a] Below detection limit

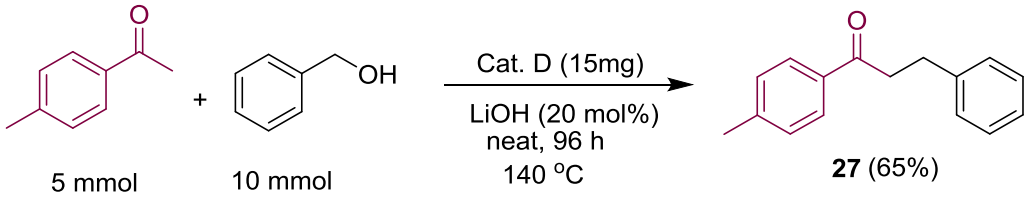
5. High TON reactions

N-alkylation of aniline using benzyl alcohol:



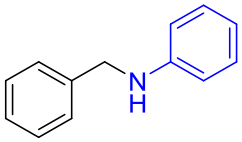
Aniline (5.0 mmol), benzyl alcohol (10 mmol), catalyst **D** (2 mg, 0.00196 mol % of Pd), and LiOH (20 mol %) were charged under argon-atmosphere in a Radleys carrousel reaction tube. The reaction tube was closed with the Teflon stopper and was heated to 120 ^{o}C under stirring. After 72h, the reaction mixture was allowed to cool to room temperature and diluted with toluene (10 mL). Then, 1 mmol of mesiltylene was introduced into the reaction mixture as an internal standard for analysis. *N*-benzylaniline was achieved with 92% yield which was calculated using ^{1}H-NMR spectra of the crude mixture. The total amount of *N*-benzylaniline formed was 4.6 mmol (92% yield) using 0.00196 mol % of palladium corresponding to a TON of 46939.

α-alkylation of 4-methyl acetophenone:

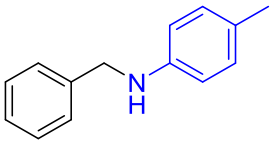


4-methylacetophenone (5.0 mmol), benzyl alcohol (10 mmol), catalyst **D** (15 mg, 0.0146 mol % of Pd), and LiOH (20 mol %), were charged under argon-atmosphere in a Radleys carrousel reaction tube. The reaction tube was closed with the Teflon stopper and was heated to 140 ^{o}C under stirring. After 4 days, the reaction mixture was allowed to cool to room temperature and diluted with toluene (10 mL). Then, 1 mmol of mesiltylene was introduced into the reaction mixture as an internal standard. The product 3-phenyl-1-(p-tolyl)propan-1-one (**27**) was formed in 65% yield as calculated using ^{1}H-NMR spectra of the crude reaction mixture. The total amount of ketone **27** formed was 3.25 mmol (65% yield), using 0.0146 mol % of Pd that gave a TON of 4452.

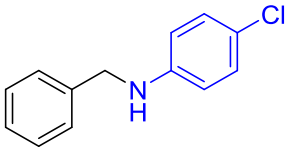
6. Characterization data of compounds 1-37.



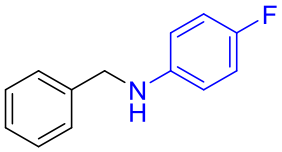
***N*-benzylaniline (1)**:[1] Followed the general procedure 1 using 2 mg of catalyst B, aniline (182 µL, 2.0 mmol) and benzyl alcohol (6.0 mmol) for 24h at 120 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 348 mg (95%) *N*-benzylaniline as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 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.



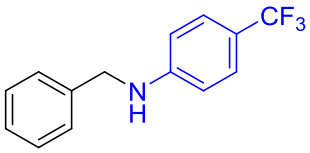
***N*-benzyl-4-methylaniline (15)**:[1] Followed the general procedure 1 using 8 mg of catalyst B, *p*-toluidine (220 µL, 2.0 mmol) and benzyl alcohol (6.0 mmol) for 24h at 120 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 386 mg (98%) *N*-benzyl-4-methylaniline as yellow oil. ^{1}H 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.



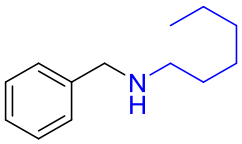
***N*-benzyl-4-chloroaniline (3)**:[3] Followed the general procedure 1, using 2 mg of catalyst **B**, 4-chloroaniline (178 µL, 2.0 mmol) and benzyl alcohol (6.0 mmol) for 24h at 130 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 422 mg (97%) *N*-benzyl-4-chloroaniline as yellow oil. ^{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.



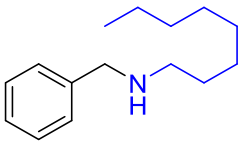
***N*-benzyl-4-fluoroaniline (4)**:[3] Followed the general procedure 1 using 8 mg of catalyst B, 4-fluroaniline (222 µL, 2.0 mmol) and benzyl alcohol (6.0 mmol) for 24 h at 120 °C. Purification by flash chromatography (15% EtOAc/Hexane) gave 400 mg (99%) *N*-benzyl-4-fluoroaniline as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.45 – 7.27 (m, 6H), 6.99 – 6.84 (m, 2H), 6.69 – 6.57 (m, 2H), 4.32 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.13 (d, *J* = 235.6 Hz), 144.0, 138.9, 128.7, 127.6, 127.4, 115.68 (d, *J* = 22.3 Hz), 114.05 (d, *J* = 7.4 Hz), 49.2.



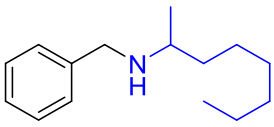
***N*-benzyl-4-(trifluoromethyl)aniline (5)**:[4] Followed the general procedure 1 using 8mg of catalyst B with 4-(trifluromethyl)aniline (251 µL, 2.0 mmol) and benzyl alcohol (6.0 mmol) for 24 h at 120 °C. Purification by flash chromatography (15% EtOAc/Hexane) gave 473 mg (86%) *N*-benzyl-4-(trifluoromethyl)aniline as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.49 – 7.29 (m, 7H), 6.70 (d, *J* = 8.4 Hz, 2H), 4.40 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 149.9, 138.1, 128.8, 127.6, 127.5, 126.8 (q, *J* = 3.8 Hz), 125.0 (q, *J* = 270 Hz), 112.5, 48.2.



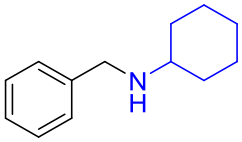
***N*-benzylhexan-1-amine (6)**:[5] Followed the general procedure 1 using 8 mg of catalyst B, 1-hexylamine (264 µL, 2.0 mmol) and benzyl alcohol (6.0 mmol) for 24h at 120 °C. Purification by flash chromatography (45% EtOAc/Hexane) gave 360 mg (94%) *N*-benzylhexan-1-amine as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 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.



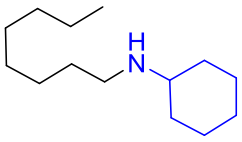
***N*-benzyloctan-1-amine (7)**:[6] Followed the general procedure 1 using 8 mg of catalyst B, 1-octylamine (331 µL, 2.0 mmol) and benzyl alcohol (6.0 mmol) for 24 h at 120 °C. Purification by flash chromatography (15% EtOAc/Hexane) gave 376 mg (86%) *N*-benzyloctan-1-amine as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.38 – 7.20 (m, 5H), 3.86 (d, *J* = 13.0 Hz, 1H), 3.77 (d, *J* = 13.0 Hz, 1H), 2.77 – 2.65 (m, 1H), 1.51 (dd, *J* = 7.1, 5.4 Hz, 1H), 1.41 – 1.27 (m, 9H), 1.11 (d, *J* = 6.3 Hz, 3H), 0.96 – 0.88 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.85, 128.36, 128.12, 126.79, 52.53, 51.37, 37.09, 31.86, 29.51, 25.95, 22.62, 20.30, 14.06.



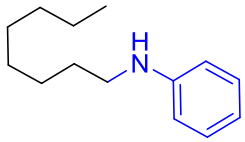
***N*-benzyloctan-2-amine (8)**:[7] Followed the general procedure 1 using 8 mg of catalyst B, 2-aminooctane (335 µL, 2.0 mmol) and benzyl alcohol (6.0 mmol) for 24 h at 120 °C. Purification by flash chromatography (15% EtOAc/Hexane) gave 360 mg (82%) *N*-benzyloctan-1-amine as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.38 – 7.20 (m, 5H), 3.86 (d, *J* = 13.0 Hz, 1H), 3.77 (d, *J* = 13.0 Hz, 1H), 2.77 – 2.65 (m, 1H), 1.51 (dd, *J* = 7.1, 5.4 Hz, 1H), 1.41 – 1.27 (m, 9H), 1.11 (d, *J* = 6.3 Hz, 3H), 0.96 – 0.88 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= ^{13}C NMR (101 MHz, $CDCl_3$) δ= 140.85, 128.36, 128.12, 126.79, 52.53, 51.37, 37.09, 31.86, 29.51, 25.95, 22.62, 20.30, 14.06.



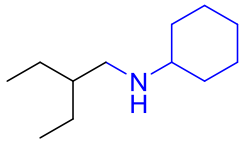
***N*-benzylcyclohexanamine (9)**:[8] Followed the general procedure 1 using 8 mg of catalyst B, cyclohexylamine (229 µL, 2.0 mmol) and benzyl alcohol (6.0 mmol) for 24 h at 120 °C. Purification by flash chromatography (15% EtOAc/Hexane) gave 335 mg (88%) *N*-benzylcyclohexanamine as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.25 – 7.14 (m, 5H), 3.74 (s, 2H), 2.49 – 2.33 (m, 1H), 1.92 – 1.77 (m, 2H), 1.74 – 1.59 (m, 2H), 1.59 – 1.47 (m, 1H), 1.39 (s, 2H), 1.27 – 0.95 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ= 140.99, 128.36, 128.07, 126.75, 56.18, 51.03, 33.56, 26.20, 25.00.



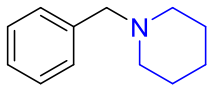
***N*-octylcyclohexanamine** (10)[9] Followed the general procedure 1 using 20 mg of catalyst B, cyclohexylamine (2.0 mmol) and 1-octanol (6 mmol) for 48h at 140 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 351 mg (83%) *N*-octylcyclohexanamine as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 2.60 (t, *J* = 7.3 Hz, 2H), 2.40 (m, 1H), 1.71 (m, 2H), 1.60 (m, 1H), 1.46 (m, 2H), 1.38 – 0.97 (m, 15H), 0.92 – 0.73 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 57.1, 47.2, 33.7, 32.0, 30.6, 29.7, 29.4, 27.6, 26.3, 25.3, 22.8 14.2.



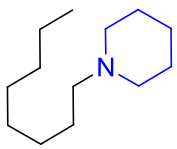
***N*-octylaniline (11):** [10] Followed the general procedure 1 using 20 mg of catalyst B, aniline (2.0 mmol) and 1-octanol (6 mmol) for 48h at 140 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 316 mg (77%) *N*-octylaniline as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.16 – 7.04 (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.



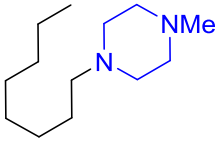
***N*-(2-ethylbutyl)cyclohexanamine(12)**[11] Followed the general procedure 1 using 20 mg of catalyst B, cyclohexyl amine (2 mmol) and 2-ethylbutanol (6 mmol) for 48h at 140 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 274 mg (75%) of **12** as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 2.53 – 2.43 (m, 2H), 2.36 (m, 1H), 1.90 – 1.79 (m, 2H), 1.75 – 1.65 (m, 2H), 1.59 (m, 1H), 1.39 – 0.96 (m, 10H), 0.85 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 57.3, 49.9, 41.2, 33.8, 26.4, 25.3, 24.2, 11.0.



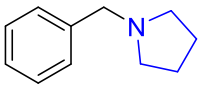
1-benzylpiperidine (13):[12] Followed the general procedure 1 using 20 mg of catalyst B, piperidine (198 µL, 2.0 mmol) and benzyl alcohol (6.0 mmol) for 24h at 130 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 288 mg (82%) 1-benzylpiperdine as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 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.



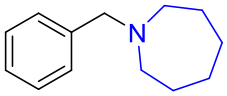
1-octylpiperidine (14):[13] Followed the general procedure 1 using 20 mg of catalyst B, piperidine (2.0 mmol) and 1-octanol (6.0 mmol) for 48h at 140 °C. After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound was isolated as a yellow liquid (327 mg, 1.66 mmol, 83 %). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 2.31-2.47 (m, 3H), 2.22-2.31 (m, 2H), 1.59 (m, 3H), 1.34-1.53 (m, 3H), 1.15-1.34 (m, 12H), 0.86 (t, 3H, CH_3, J = 6.4 Hz). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 59.8, 54.6, 32.0, 29.7, 29.4, 27.9, 26.9, 26.0, 24.6, 22.8, 14.2.



1-methyl-4-octylpiperazine (15):[14] Followed the general procedure 1 using 20 mg of catalyst B, N-methylpiperazine (2.0 mmol) and 1-octanol (6.0 mmol). After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound was isolated as a yellow liquid 350 mg (83 %). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 2.62 – 2.34 (m, 8H), 2.34 – 2.25 (m, 2H), 2.25 (s, 3H), 1.51 – 1.38 (m, 2H), 1.33 – 1.15 (m, 10H), 1.33 – 1.15 (m, 3H). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 58.9, 55.3, 53.4, 46.2, 31.9, 29.7, 29.3, 27.7, 27.0, 22.7, 14.2.

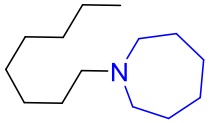


1-benzylpyrrolidine (16): [12] Followed the general procedure 1 using 8 mg of catalyst B, pyrrolidine (164 µL, 2.0 mmol) and benzyl alcohol (6.0 mmol) for 24h at 130 °C. Purification by flash chromatography (2% MeOH/DCM) gave 298 mg (92%) 1-benzylpyrrolidine as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 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.

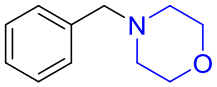


1-benzylazepane (17):[15] Followed the general procedure 1 using 8 mg of catalyst B, azepane (226 µL, 2.0 mmol) and benzyl alcohol (6.0 mmol) for 24 h at 120 °C. Purification by flash chromatography (5% MeOH/DCM) gave 336 mg (89%) 1-benzylazepane as yellow oil. ^{1}H

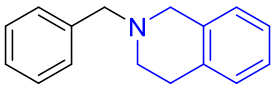
NMR ($CDCl_3$, 400 MHz): δ= 7.33 – 7.10 (m, 5H), 3.57 (s, 2H), 2.55 (dd, *J* = 6.3, 3.9 Hz, 4H), 1.55 (d, *J* = 4.1 Hz, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 27.0, 28.2, 55.6, 62.7, 126.7, 128.1, 128.8, 140.1



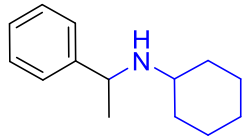
1-octylazepane (18):[16] Followed the general procedure 1 using 20 mg of catalyst B, azepane (2.0 mmol) and 1-octanol (6.0 mmol) for 48h at 140 °C. After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound was isolated as a yellow liquid (332 mg, 79%). ^1H-NMR ($CDCl_3$, 400 MHz): *δ* = 2.62 (m, 4H), 2.44 (m, 2H), 1.50-1.72 (m, 8H), 1.34-1.53 (m, 2H), 1.15-1.34 (m, 10H), 0.88 (t, 3H, CH_3, *J* = 6.4 Hz). ^{13}C-NMR ($CDCl_3$, 101 MHz): *δ* = 57.6, 54.7, 31.0, 28.6, 28.5, 27.0, 26.8, 26.7, 26.2, 21.8, 13.2.



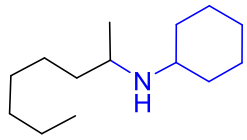
4-benzylmorpholine (19):[12] Followed the general procedure 1 using 8 mg of catalyst B, morpholine (174 µL, 2.0 mmol) and benzyl alcohol (6.0 mmol) for 24h at 140 °C. Purification by flash chromatography (5% MeOH/DCM) gave 322 mg (91%) 4-benzylmorpholine as yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ= 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.



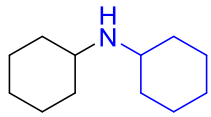
2-benzyl-1,2,3,4-tetrahydroisoquinoline (20):[17] Followed the general procedure 1 using 8 mg of catalyst B, 1,2,3,4-tetrahydroisoquinoline (250 µL, 0.0 mmol) and benzyl alcohol (6.0 mmol) for 24h at 140 °C. Purification by flash chromatography (3% EtOAc/Hexane) gave 378 mg (85%) 2-benzyl-1,2,3,4-tetrahydroisoquinoline as yellow oil. ^1H 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.



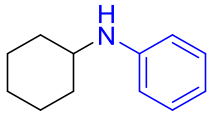
***N*-(1-phenylethyl)cyclohexanamine (21)**[18] Followed the general procedure 1 using 20 mg of catalyst B, cyclohexylamine (2.0 mmol) and 1-methylbenzyl alcohol (6.0 mmol). After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound **21** was isolated as a yellow liquid (329 mg, 81%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.38 – 6.87 (m, 5H), 3.87 (q, J = 6.6 Hz, 1H), 2.26 – 2.09 (m, 1H), 1.93 – 1.81 (m, 1H), 1.70 – 1.50 (m, 3H), 1.50 – 1.39 (m, 1H), 1.25 (d, J = 6.6 Hz, 3H), 1.12 – 0.84 (m, 5H). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 146.2, 128.5, 126.9, 126.7, 54.7, 53.9, 34.6, 33.2, 26.3, 25.4, 25.1, 25.0.



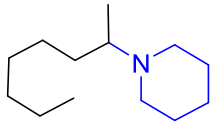
***N*,*N*-cyclohexyl-2-octylamine (22)**:[19] Followed the general procedure 1 using 20 mg of catalyst B, cyclohexylamine (2.0 mmol) and 2-octanol (6.0 mmol). After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound **22** was isolated as a yellow liquid (367 mg, 87%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 2.65-2.79 (m, 1H), 2.38-2.55 (m, 1H), 1.79-1.93 (m, 2H), 1.64-1.77 (m, 2H), 1.52-1.63 (m, 1H), 0.99 (d, 3H, J = 6.2 Hz), 0.88-1.50 (m, 15 H), 0.86 (m, 3H). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 53.7, 49.5, 37.8, 34.7, 34.1, 32.0, 29.7, 26.3, 25.5, 25.4, 22.8, 21.2, 14.2.



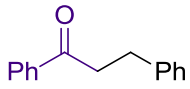
Dicyclohexylamine (23):[9] Followed the general procedure 1 using 20 mg of catalyst B, cyclohexylamine (2.0 mmol) and cyclohexanol (6.0 mmol). After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound **23** was isolated as a yellow liquid (304 mg, 84%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 2.51 (tt, J = 10.5, 3.8 Hz, 1H), 1.88 – 1.74 (m, 2H), 1.67 (m, 2H), 1.61 – 1.51 (m, 1H), 1.37 – 1.06 (m, 4H), 1.05 – 0.92 (m, 2H). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 53.2, 34.4, 26.3, 25.4.



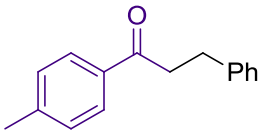
***N*-cyclohexylaniline (24):**[9] Followed the general procedure 1 using 20 mg of catalyst B, aniline (2.0 mmol) and cyclohexanol (2.0 mmol). After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound **24** was isolated as a yellow liquid (185 mg, 53%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.21 (m, 1H), 6.53-6.76 (m, 3 H), 3.28 (m, 1H), 2.08 (dt, J = 12.3, 3.7 Hz, 2H), 1.61 – 1.85 (m, 3H), 1.05 – 1.5 (m, 5H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 147.5, 129.4, 117.0, 113.3, 51.9, 33.6, 26.1, 25.2.



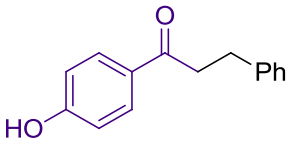
***N*-2-octylpiperidine (25):**[16] Followed the general procedure 1 using 20 mg of catalyst B, piperidine (2.0 mmol) and 2-octanol (6.0 mmol). After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound **25** was isolated as a yellow liquid (256 mg, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.32-2.53 (m, 5H). 1.59 – 1.45 (m, 5H), 1.39 (m, 2H), 1.34 – 1.13 (m, 9H), 0.93 (d, J = 6.6 Hz, 3H), 0.89 – 0.81 (m, 3H). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 59.9, 49.6, 33.6, 32.0, 29.7, 27.3, 26.7, 25.1, 22.8, 14.2, 14.2.



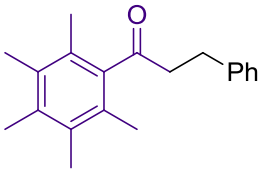
1,3-diphenylpropan-1-one(26):[21] Followed the general procedure 2 using 20 mg of catalyst B, acetophenone (2.0 mmol) and benzyl alcohol (6.0 mmol). After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound **26** was isolated as a colorless liquid (349 mg, 83%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.02 (m, 2H), 7.61 (m, 5H), 7.51 (m, 2H), 7.42 – 7.22 (m, 5H), 3.36 (m, 2H), 3.13 (m, 2H). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 199.3, 141.4, 137.1, 133.2, 128.7, 128.6, 128.5, 128.2, 126.3, 40.6, 30.3.



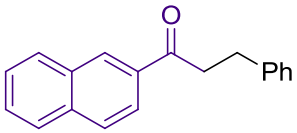
3-phenyl-1-(p-tolyl)propan-1-one (27):[22] Followed the general procedure 2 using 20 mg of catalyst B, 1-(p-tolyl)ethan-1-one (2.0 mmol) and benzyl alcohol (6.0 mmol). After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound **27** was isolated as a colorless liquid (439 mg, 98%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.91 (d, J = 8.3 Hz, 2H), 7.50 – 6.91 (m, 5H), 3.31 (m, 2H), 3.11 (m, 2H), 2.45 (s, 3H). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 198.9, 143.9, 141.5, 134.6, 129.4, 128.6, 128.5, 128.3, 126.2, 40.4, 30.3, 21.7.



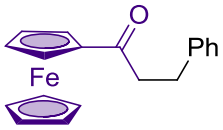
1-(4-hydroxyphenyl)-3-phenylpropan-1-one (28)[23] Followed the general procedure 2 using 20 mg of catalyst B, 1-(4-hydroxyphenyl)ethan-1-one (2.0 mmol) and benzyl alcohol (6.0 mmol). After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound **28** was isolated as a colorless liquid (366 mg, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.91 (d, J = 8.8 Hz, 2H), 7.35 – 7.14 (m, 5H), 6.91 (d, J = 8.8 Hz, 2H), 3.27 (m, 1H), 3.07 (m, 2H). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 199.4, 161.0, 141.3, 131.0, 129.7, 128.7, 128.5, 126.3, 115.7, 40.3, 30.7.



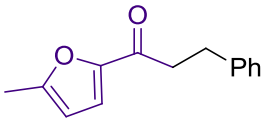
1-(2,3,4,5,6-pentamethylphenyl)-3-phenylpropan-1-one (29): Followed the general procedure 2 using 20 mg of catalyst B, 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (2.0 mmol) and benzyl alcohol (6.0 mmol). After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound **29** was isolated as a colorless liquid (538 mg, 96%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.18 (s, 6H), 2.30 (s, 6H), 2.35 (s, 3H), 3.14 (m, 2H), 3.20 (m, 5H), 7.49 – 7.21 (m, 5H). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 16.0, 16.8, 17.2, 47.2, 126.2, 127.5, 128.5, 128.6, 133.2, 135.5, 140.6, 141.2, 210.9. HR-MS (ESI) $(M+H)^+$ m/z Calcd for $C_{20}H_{25}O$: 281.1905. Found: 281.1896.



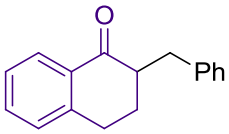
1-(naphthalen-2-yl)-3-phenylpropan-1-one (30):[7] Followed the general procedure 2 using 20 mg of catalyst B, 1-(naphthalen-2-yl)ethan-1-one (2.0 mmol) and benzyl alcohol (6.0 mmol). After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound **30** was isolated as a colorless liquid (405 mg, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.48 – 8.44 (m, 1H), 8.04 (dd, J = 8.6, 1.8 Hz, 1H), 7.97 – 7.85 (m, 3H), 7.57 (m, 2H), 7.36 – 7.12 (m, 5H), 3.45 (m, 2H), 3.14 (m, 2H). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 199.3, 141.5, 135.8, 134.4, 132.7, 129.8, 129.7, 128.7, 128.6, 128.6, 127.9, 126.9, 126.3, 124.0, 40.7, 30.5.



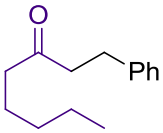
1-(ferrocenyl)-3-phenylpropan-1-one (31):[22] Followed the general procedure 2 using 20 mg of catalyst B, acetylferrocene (2.0 mmol) and benzyl alcohol (6.0 mmol). After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound **31** was isolated as a red solid (623 mg, 98%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.14 – 7.45 (m, 5H), 4.80 (s, 2H), 4.51 (s, 2H), 4.11 (s, 5H), 3.07 (s, 4H). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 203.1, 141.7, 128.7, 128.6, 126.2, 79.1, 72.3, 69.8, 69.4, 41.6, 30.2.



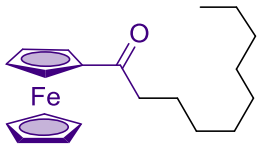
1-(5-methylfuran-2-yl)-3-phenylpropan-1-one (32):[25] Followed the general procedure 2 using 20 mg of catalyst B, 1-(5-methylfuran-2-yl)ethan-1-one (2.0 mmol) and benzyl alcohol (6.0 mmol). After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound **32** was isolated as a colorless liquid (316 mg, 74%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.41 – 7.14 (m, 1H), 7.09 (d, J = 3.5 Hz, 1H), 6.15 (dd, J = 3.4, 1.0 Hz, 1H), 3.34 – 2.67 (m, 4H), 2.39 (s, 3H). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 187.8, 157.7, 151.5, 141.2, 128.5, 128.4, 126.2, 119.1, 108.9, 39.9, 30.3, 14.1.



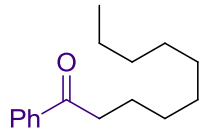
2-benzyl-3,4-dihydronaphthalen-1(2H)-one (33):[7] Followed the general procedure 2 using 20 mg of catalyst B, 3,4-dihydronaphthalen-1(2H)-one (2.0 mmol) and benzyl alcohol (6.0 mmol). After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound **33** was isolated as a colorless liquid (387 mg, 82%). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.83 (m, 1H), 2.15 (m, 1H), 2.69 (m, 1H), 2.78 (m, 1H), 3.05 – 2.87 (m, 2H), 3.53 (dd, *J* = 13.6, 3.9 Hz, 1H), 7.30 – 7.19 (m, 4H), 7.39 – 7.30 (m, 3H), 7.49 (td, *J* = 7.5, 1.5 Hz, 1H), 8.11 (dd, *J* = 7.9, 1.5 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 199.6, 144.3, 140.3, 133.5, 132.7, 129.5, 128.9, 128.6, 127.8, 126.9, 126.4, 49.7, 35.9, 28.9, 27.9.



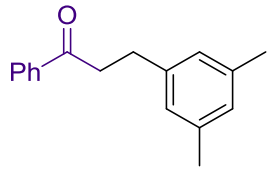
1-phenyloctan-3-one (34): [24] Followed the general procedure 2 using 20 mg of catalyst B, heptan-2-one (2.0 mmol) and benzyl alcohol (6.0 mmol). After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound **34** was isolated as a colorless liquid (396 mg, 97%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.23 – 7.15 (m, 2H), 7.09 (m, 3H), 2.81 (t, *J* = 7.6 Hz, 2H), 2.63 (d, *J* = 8.1 Hz, 2H), 2.28 (t, *J* = 7.4 Hz, 2H), 1.56 – 1.33 (m, 2H), 1.31 – 1.04 (m, 4H), 0.80 (t, *J* = 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 210.3, 141.3, 128.6, 128.4, 126.2, 44.3, 43.1, 31.5, 29.9, 23.6, 22.5, 14.0.



Compound (35):[26] Followed the general procedure 2 using 20 mg of catalyst B, acetylferrocene (2.0 mmol) (2.0 mmol) and 1-octanol (6.0 mmol). After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound **35** was isolated as a dark red solid (453 mg, 67%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.78 (t, *J* = 1.9 Hz, 2H), 4.48 (t, *J* = 1.9 Hz, 2H), 4.19 (s, 5H), 2.69 (t, *J* = 7.5 Hz, 2H), 1.90 – 1.10 (m, 14H), 0.88 (t, *J* = 6.1 Hz, 5H). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 79.5, 72.2, 69.9, 69.5, 39.9, 32.0, 29.7, 29.7, 29.7, 29.5, 24.8, 22.8, 14.2.

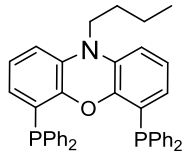


1-phenyldecan-1-one (36):[27] Followed the general procedure 2 using 20 mg of catalyst B, acetophenone (2.0 mmol) and 1-octanol (6.0 mmol). After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound **36** was isolated as a colorless liquid (339 mg, 73%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.99 – 7.91 (m, 2H), 7.59 – 7.51 (m, 1H), 7.48 – 7.41 (m, 2H), 2.96 (t, J = 7.5 Hz, 2H), 1.74 (q, J = 7.3 Hz, 2H), 1.45 – 1.17 (m, 12H), 0.88 (t, J = 6.1 Hz, 5H). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 200.7, 137.3, 132.9, 128.7, 128.2, 38.8, 32.0, 29.6, 29.6, 29.5, 29.4, 24.6, 22.8, 14.2.



3-(3,5-dimethylphenyl)-1-phenylpropan-1-one (37):[28] Followed the general procedure 2 using 20 mg of catalyst B, acetophenone (2.0 mmol) and (3,5-dimethylphenyl)methanol (6.0 mmol). After purification by column chromatography (silica, petroleum ether/EtOAc = 15:1-1:1) the desired compound **37** was isolated as a colorless liquid (357 mg, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.35 (s, 6H), 3.04 (dd, J = 8.5, 7.0 Hz, 2H), 3.32 (dd, J = 8.7, 6.8 Hz, 2H), 6.90 (s, 2H), 6.92 (s, 2H), 7.49 (dd, J = 8.3, 7.0 Hz, 2H), 7.64 – 7.55 (m, 1H), 8.01 (dd, J = 8.4, 1.4 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 21.4, 30.2, 40.7, 126.4, 127.9, 128.2, 128.7, 133.1, 137.1, 138.1, 141.3.

The preparation of BuNiXantphos



BuNiXantphos:10 mL of dry toluene, 55.2 mg of NiXantphos (0.1 mmol), NaH (0.3 mmol) were charged under argon-atmosphere in a schlenk tube followed by additions of 2 mmol of *n*-BuBr. The reaction mixture was heated at 80 ^{o}C overnight under stirring. Crude mixture was purified by flash chromatography (Hexane) gave 48 mg (79%) N-BuNiXantphos as white

solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.39 – 7.01 (m, 20H), 6.66 (t, J = 7.8 Hz, 2H), 6.45 (d, J = 7.9 Hz, 2H), 6.00 (dd, J = 8.0, 2.1 Hz, 2H), 3.49 (dd, J = 9.6, 6.5 Hz, 2H), 1.76 – 1.60 (m, 2H), 1.45 (q, J = 7.4 Hz, 2H), 1.02 (t, J = 7.3 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 147.4, 147.3, 147.2, 137.2, 137.1, 137.1, 134.1, 134.0, 134.0, 133.9, 133.4, 133.4, 133.3, 128.3, 128.3, 128.2, 125.3, 123.8, 111.9, 44.7, 27.0, 20.3, 14.0. HR-MS (ESI) $(M+H)^+$ m/z Calcd for $C_{40}H_{36}NOP_2$: 608.2272. Found: 608.2275.

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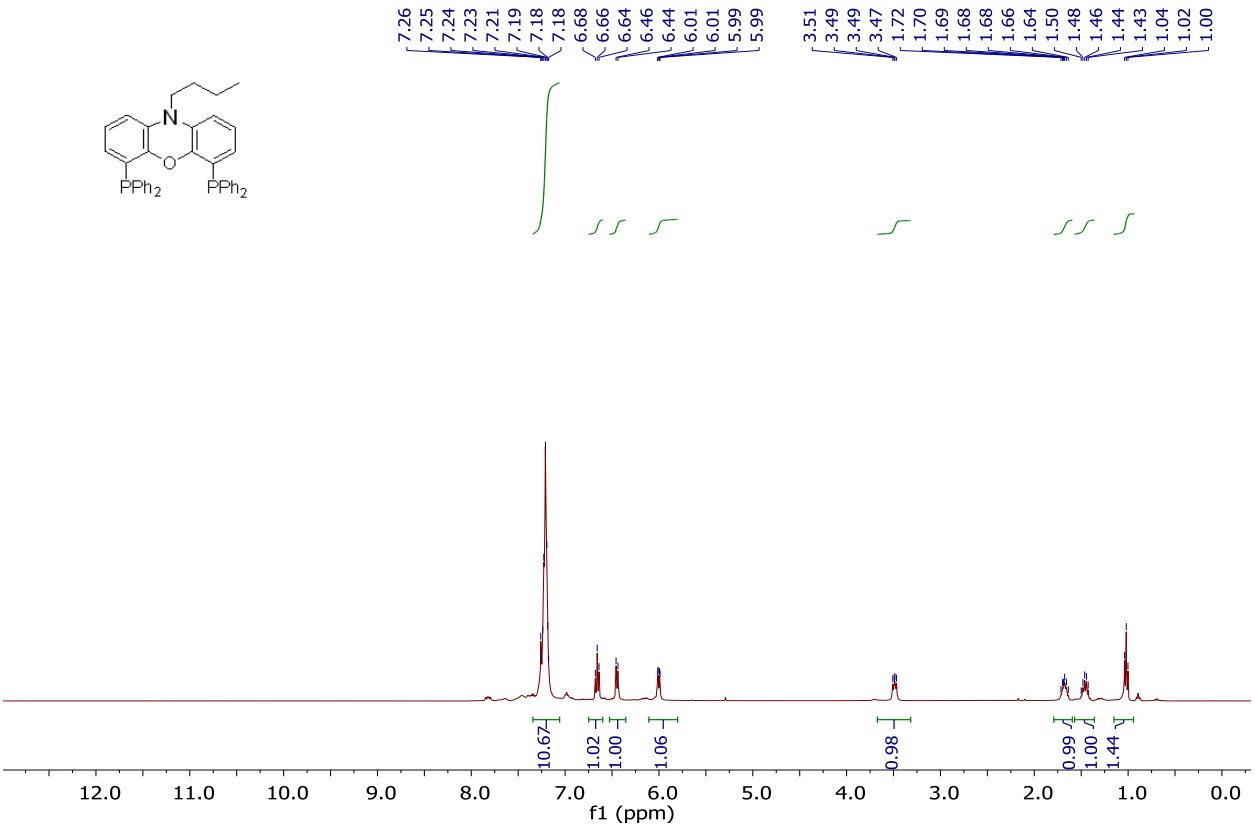
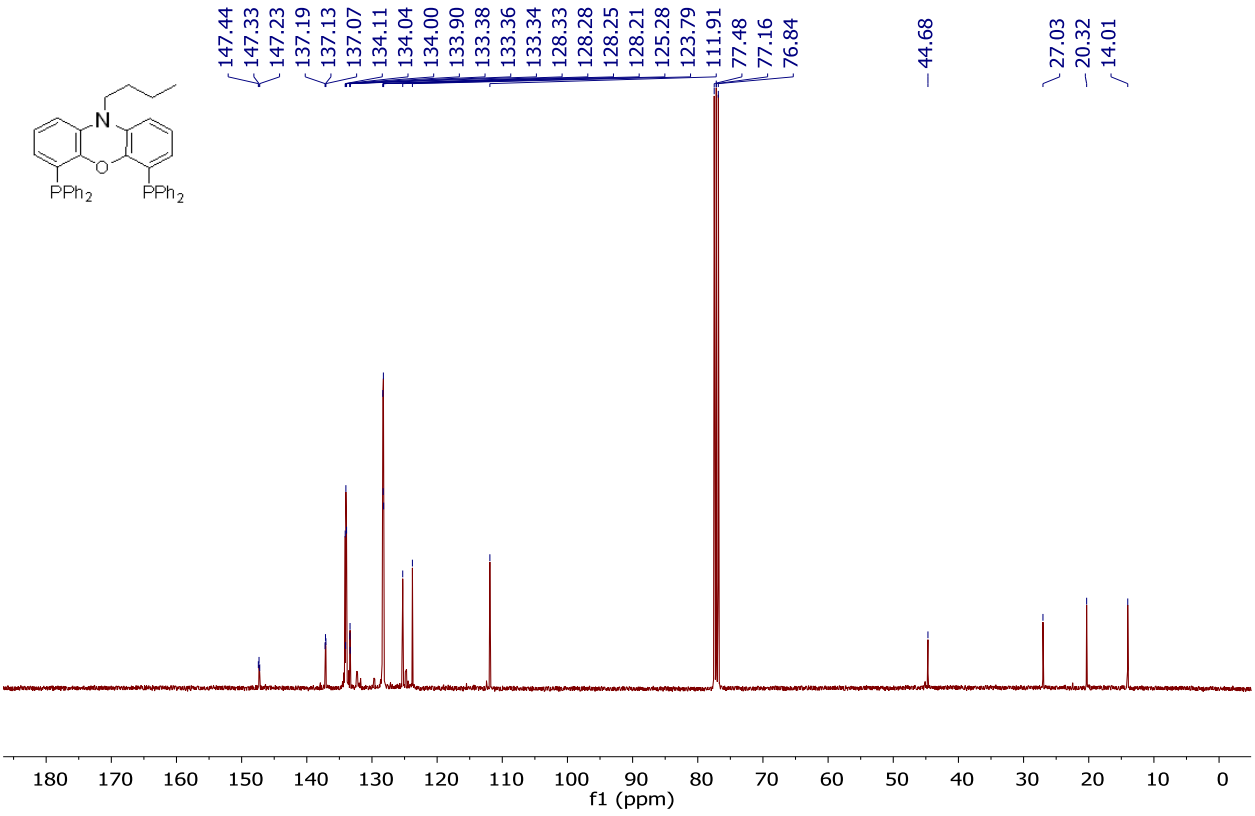
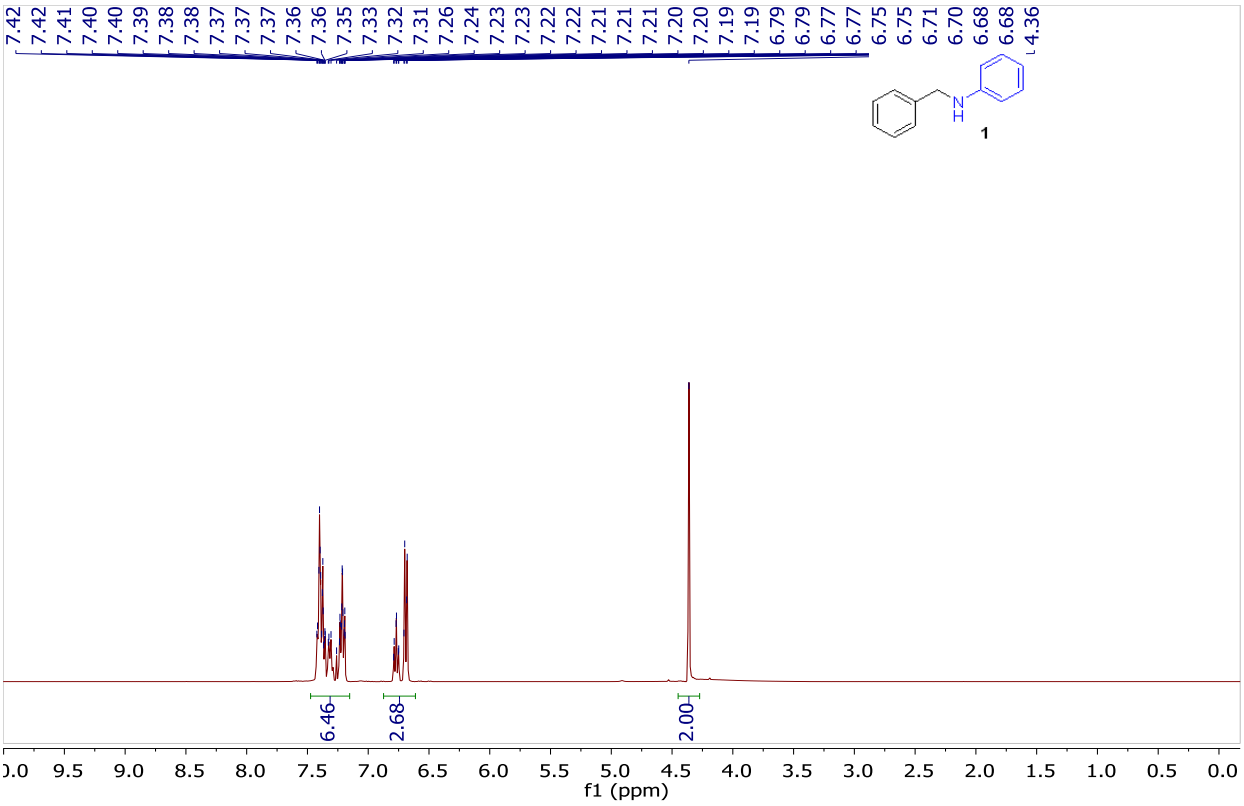
8. NMR Spectra of compounds



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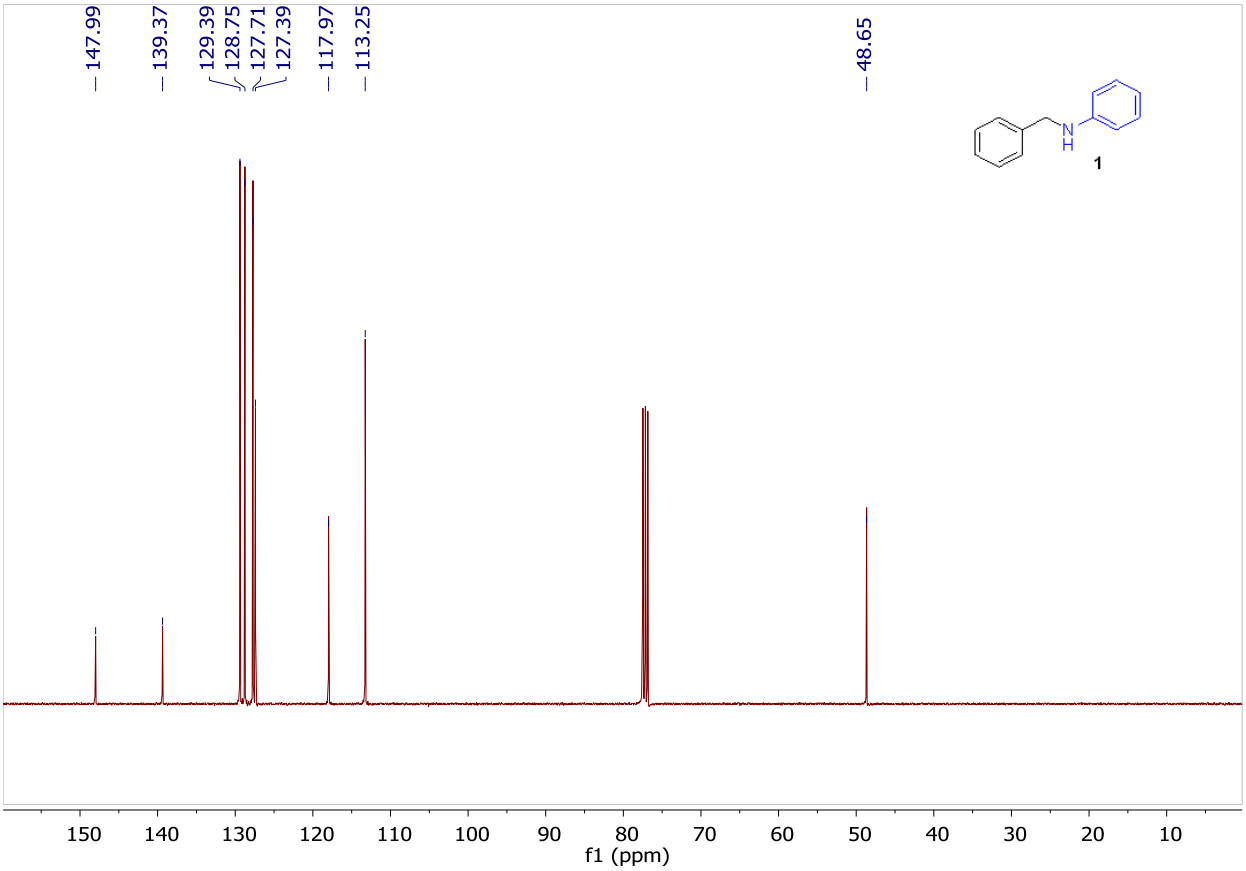
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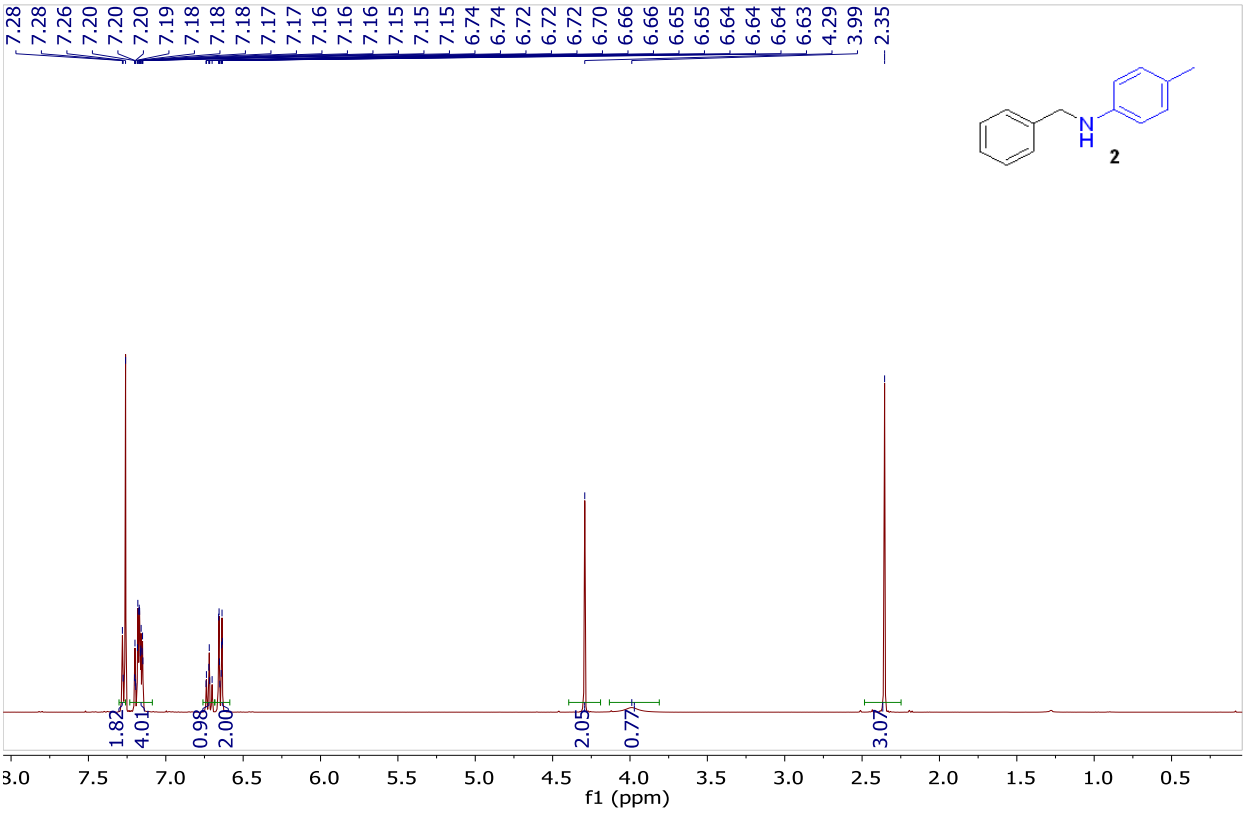
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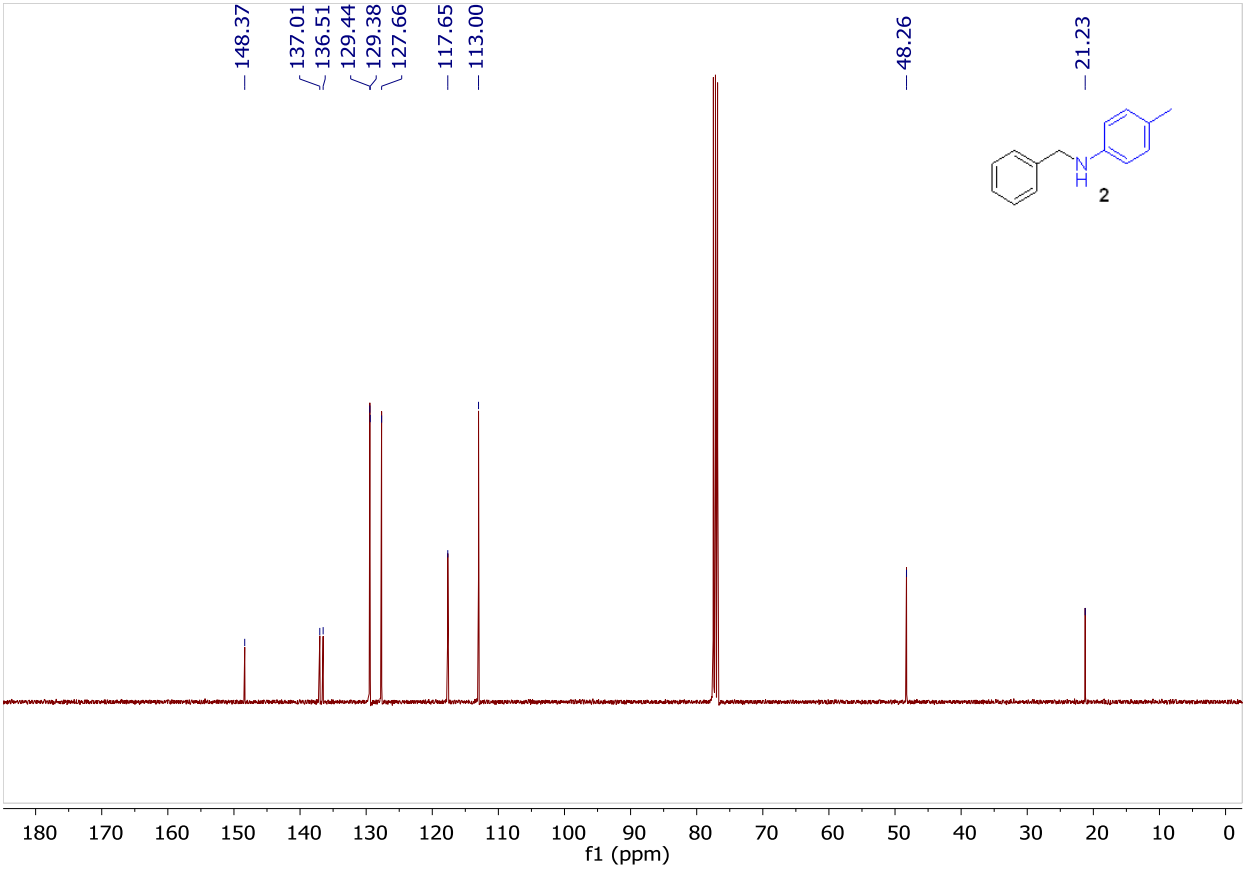
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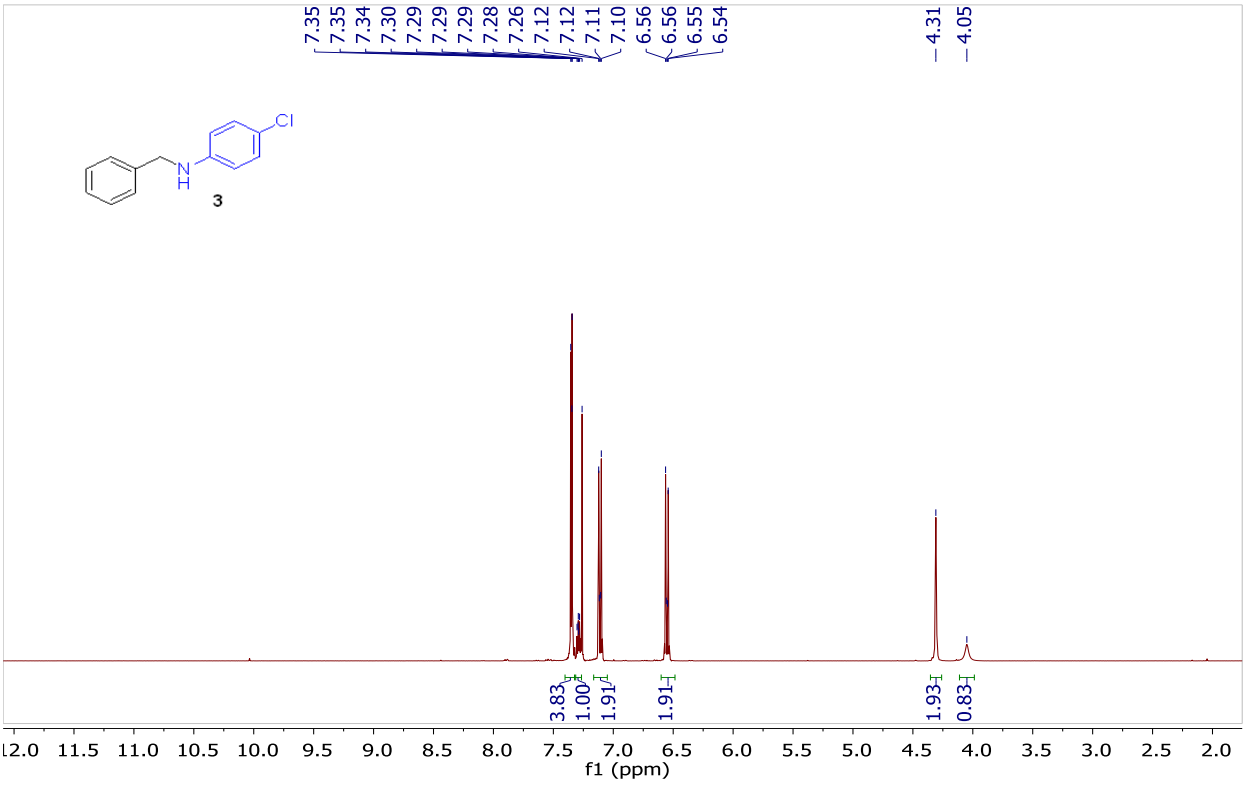
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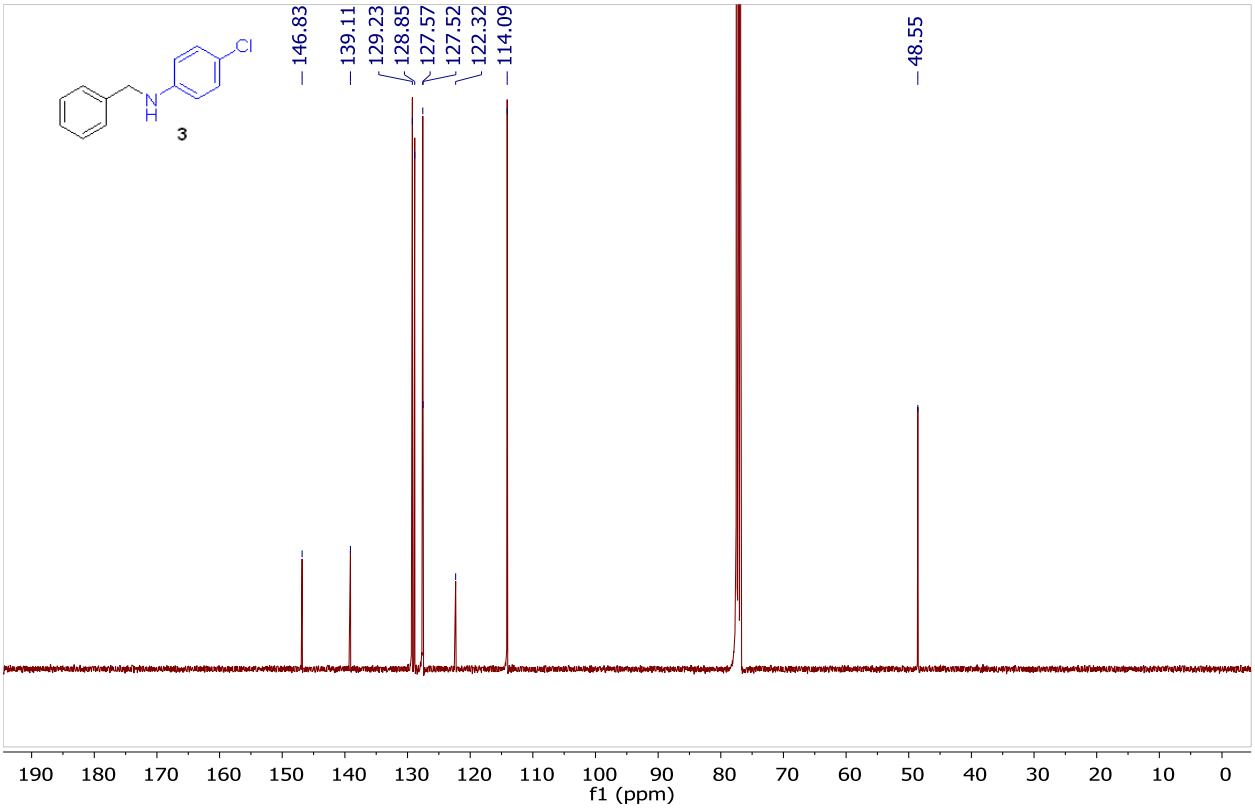
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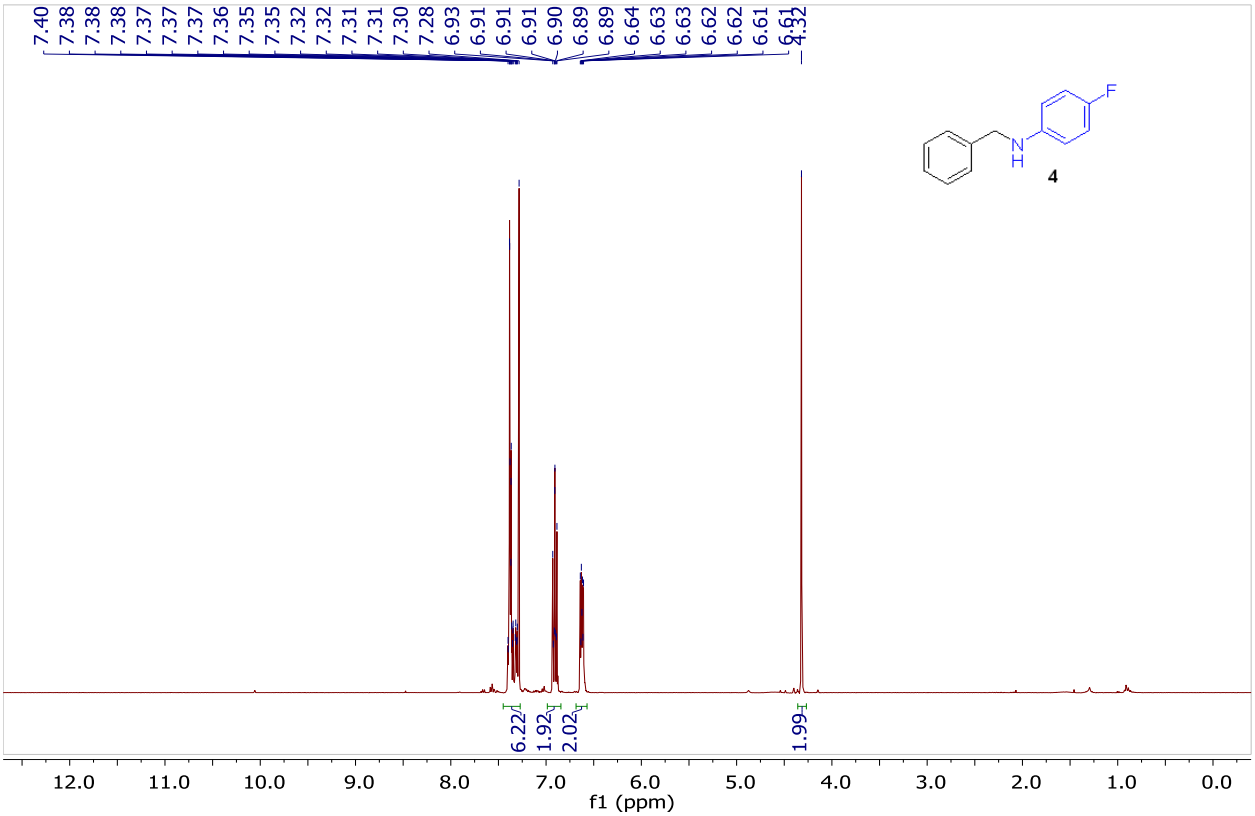
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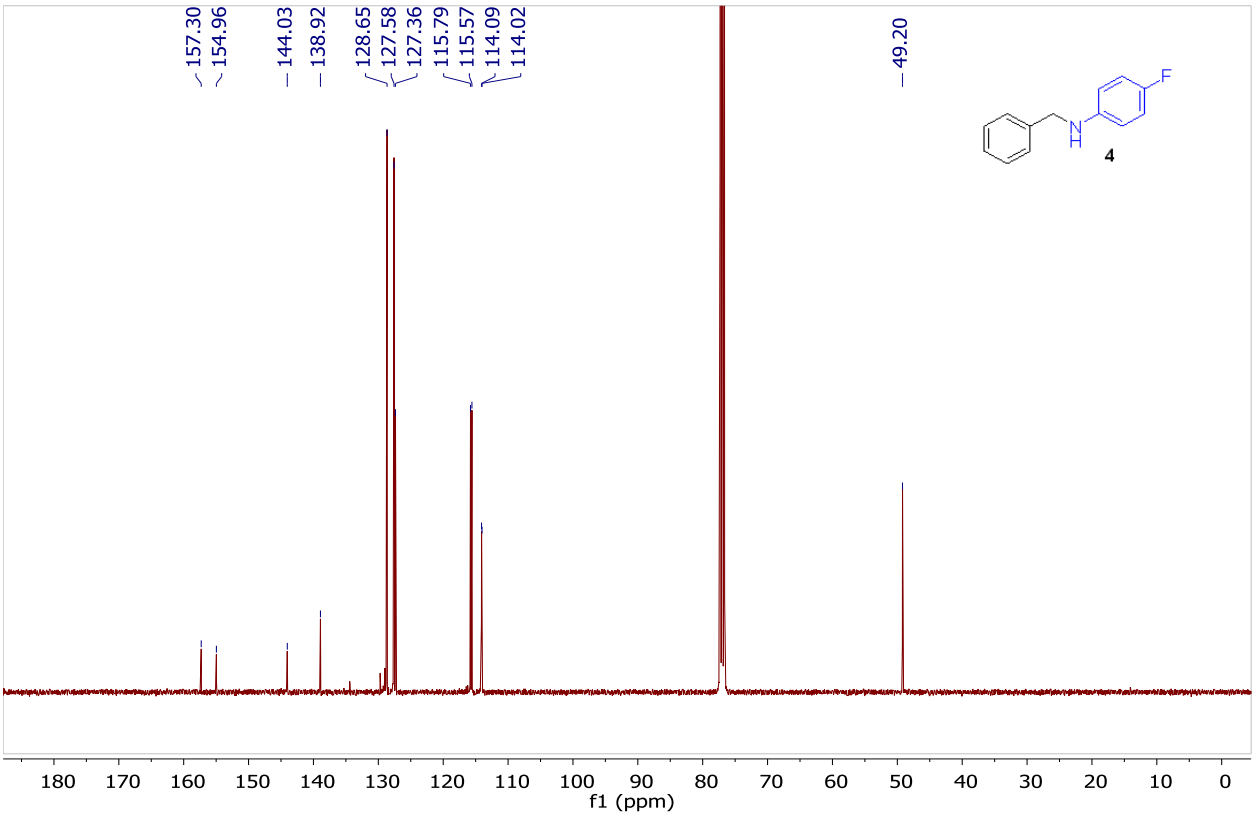
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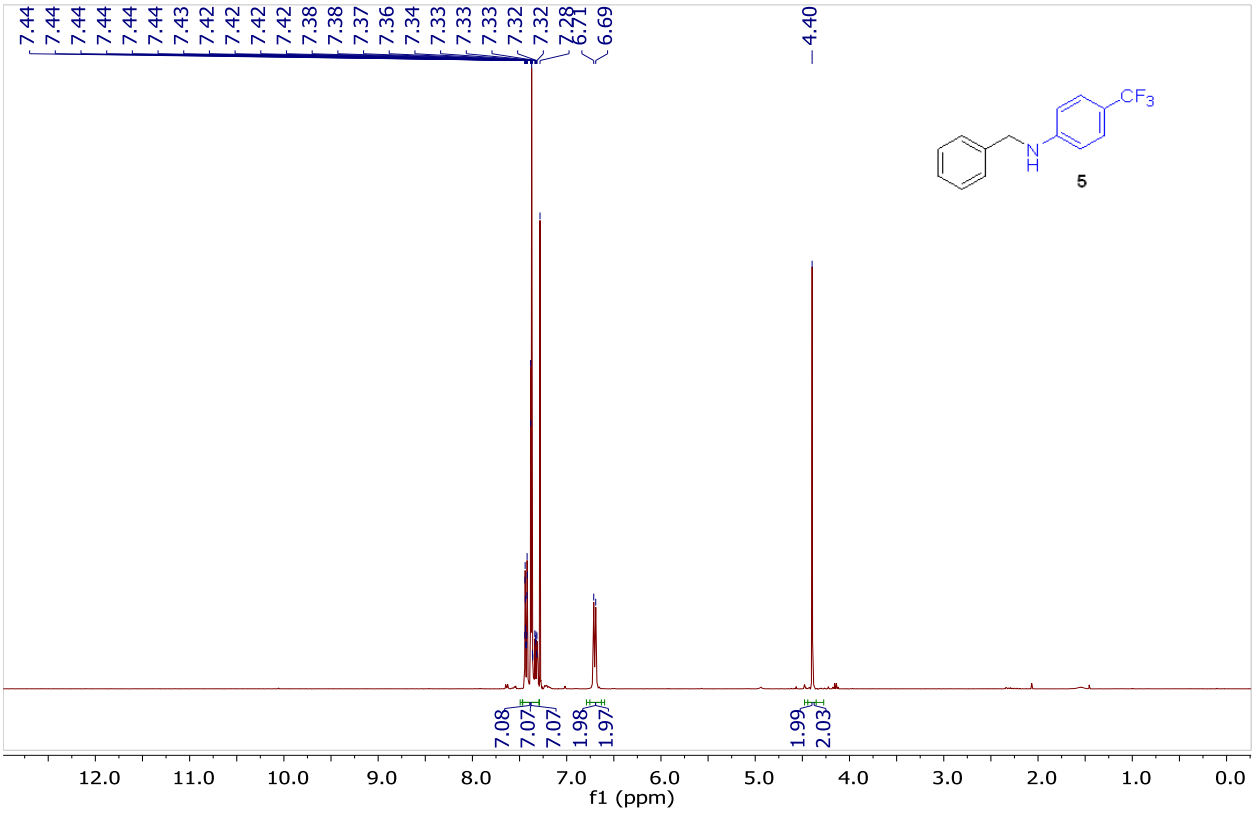
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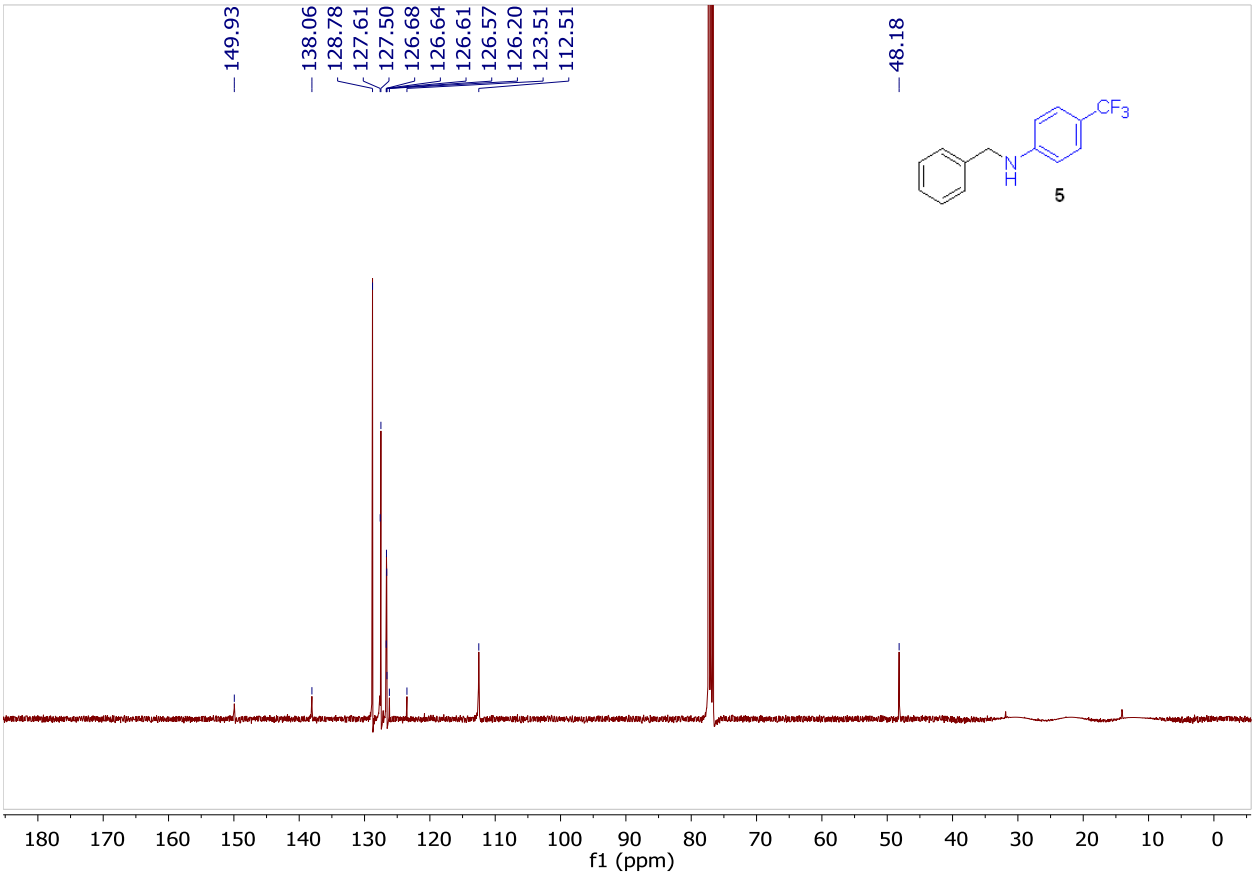
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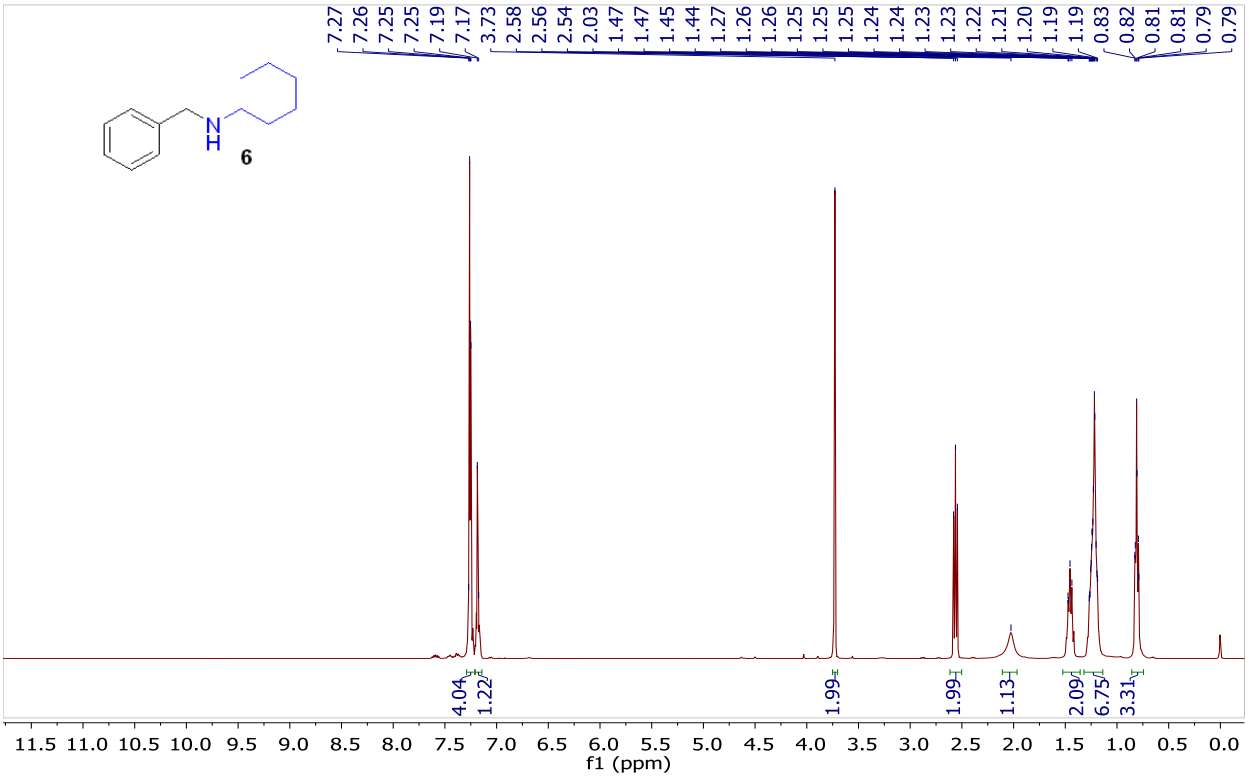
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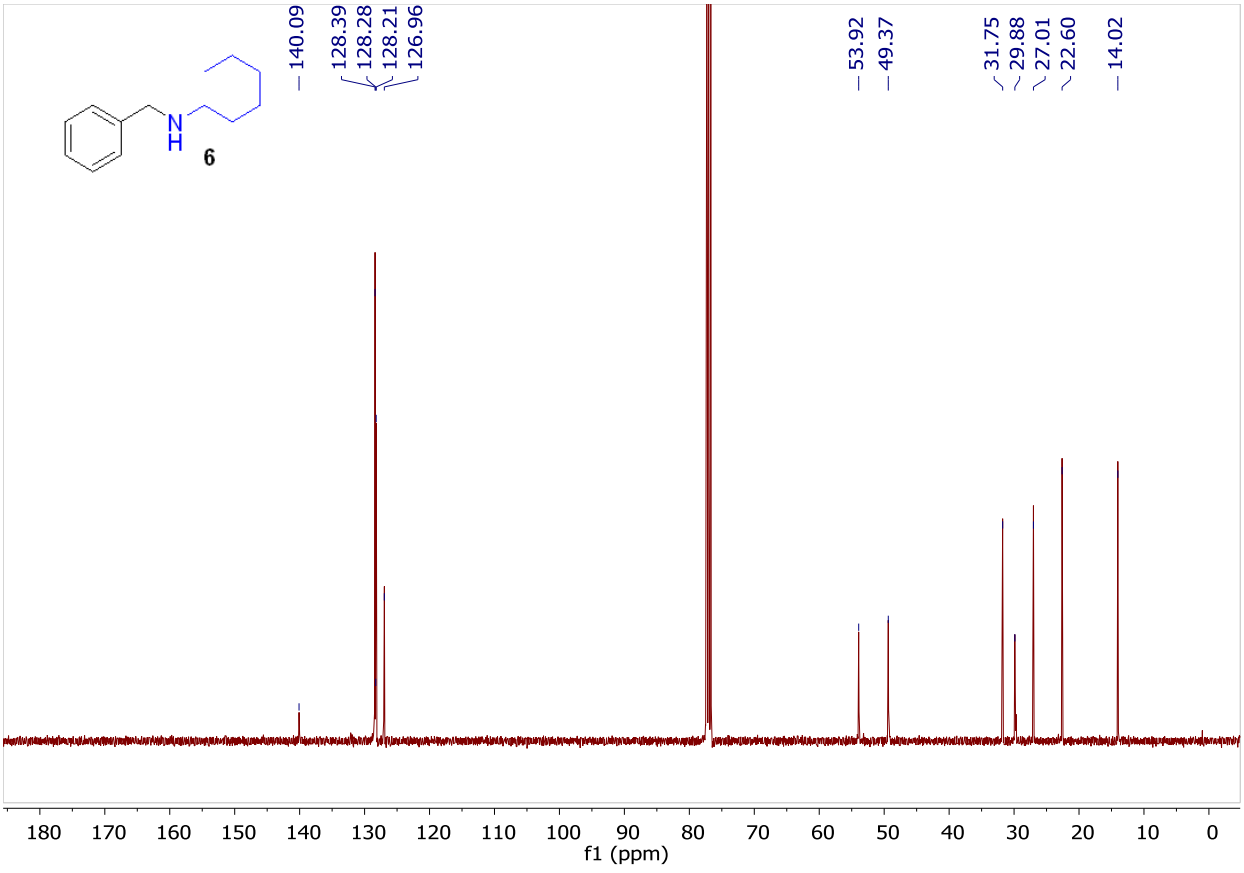
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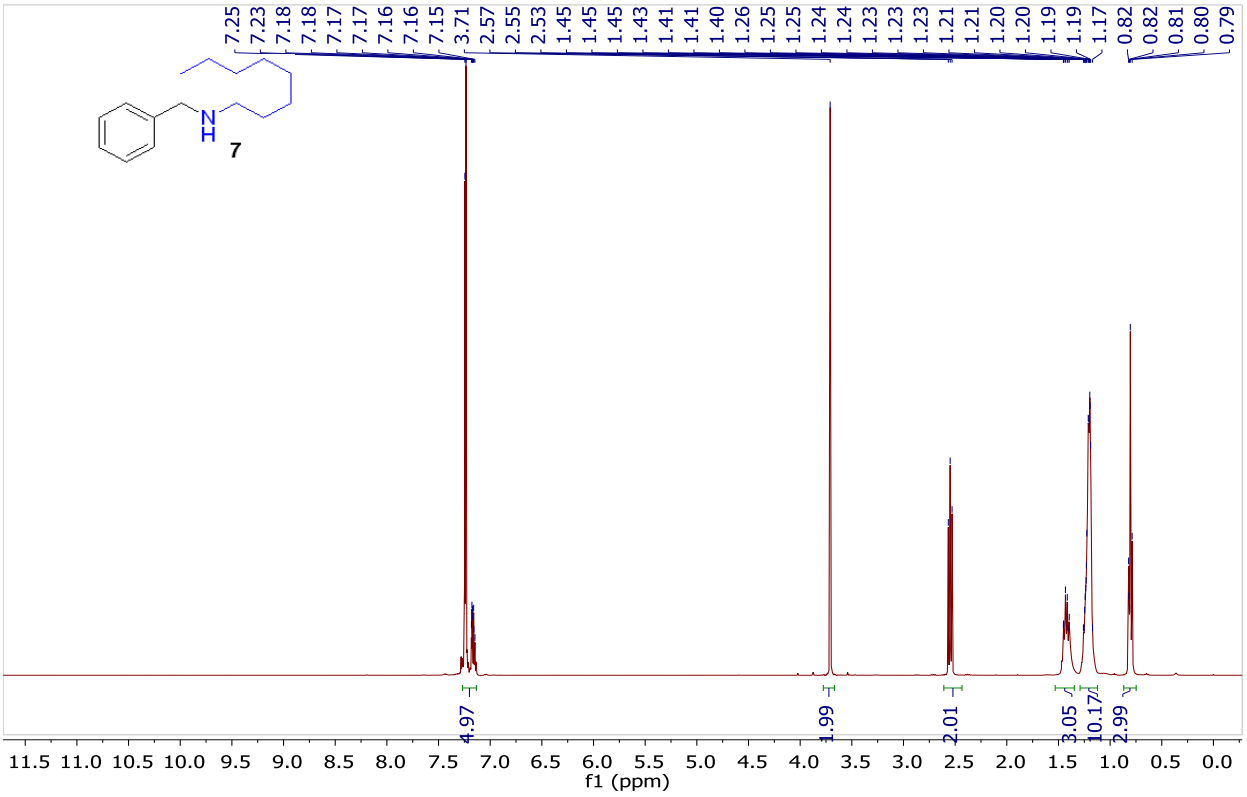
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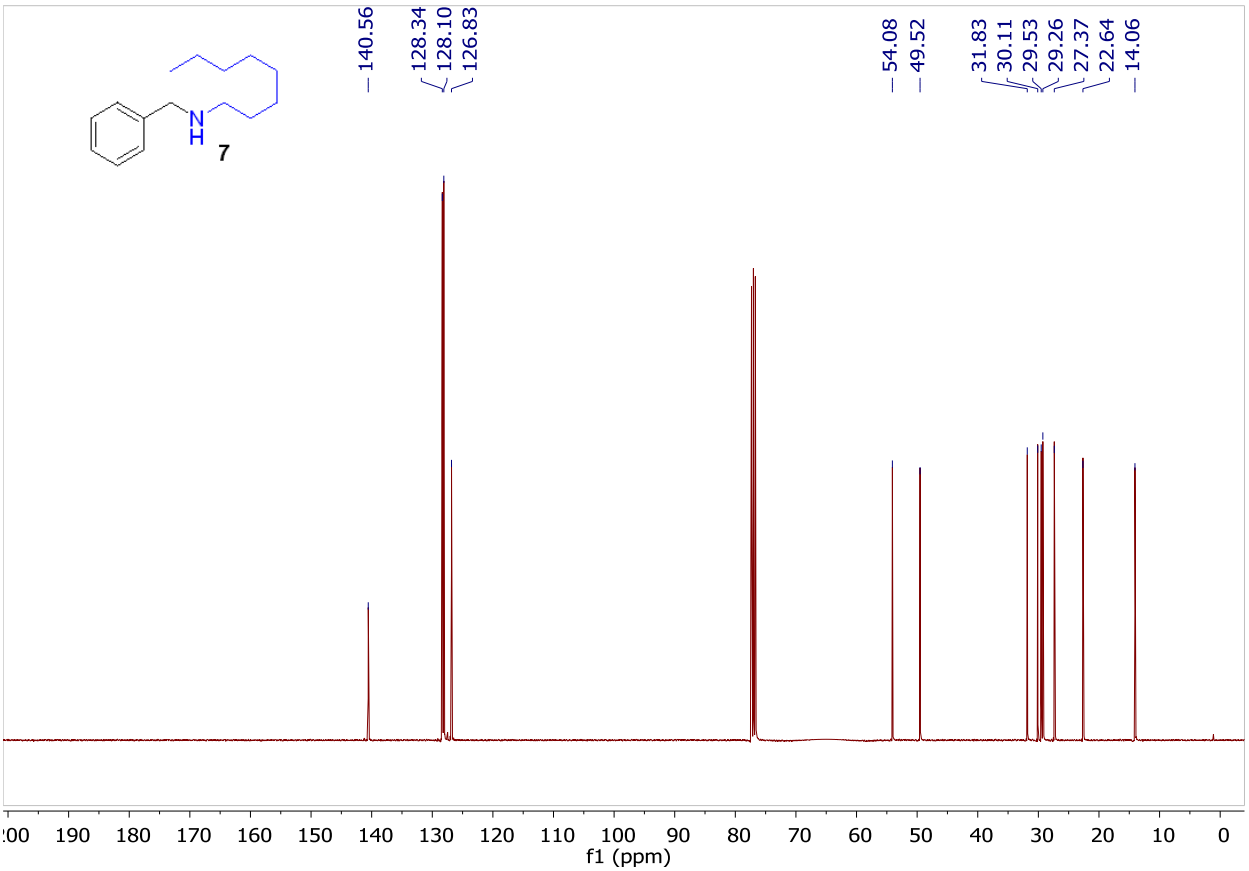
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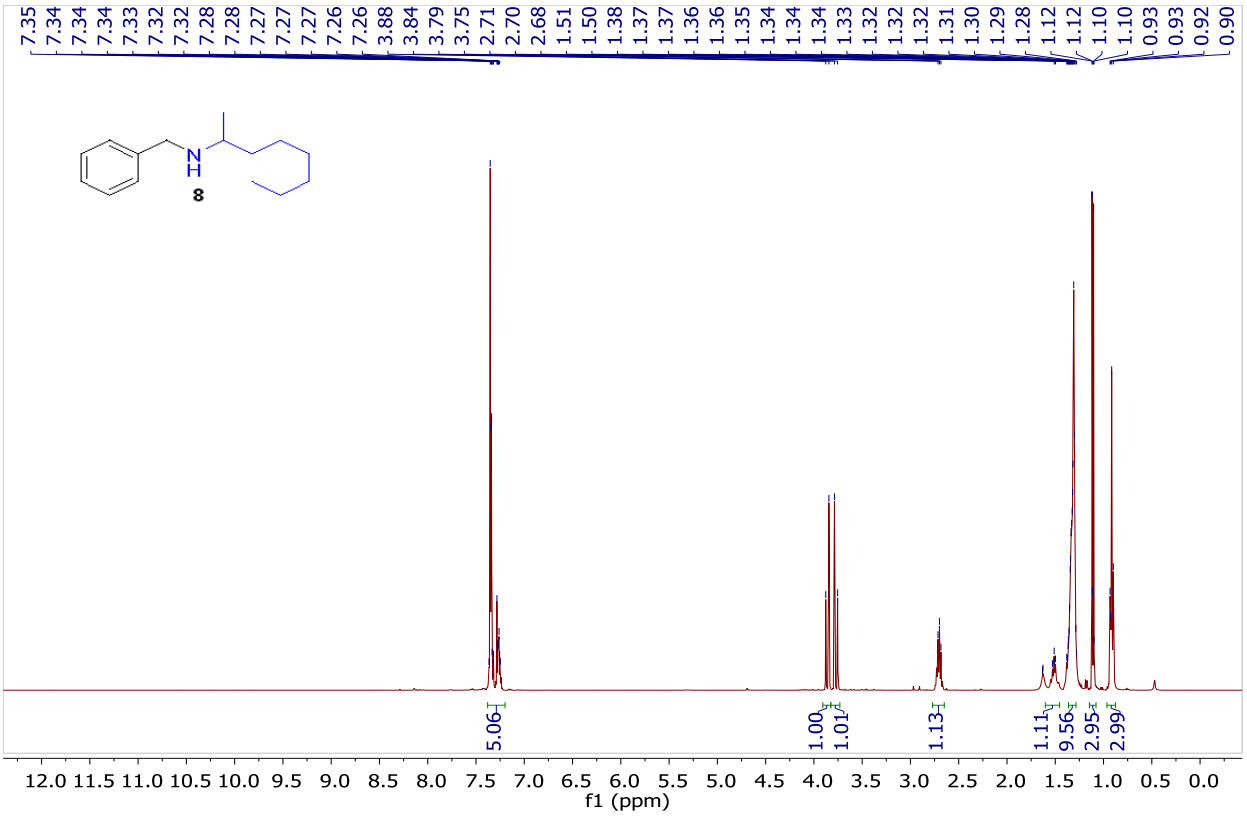
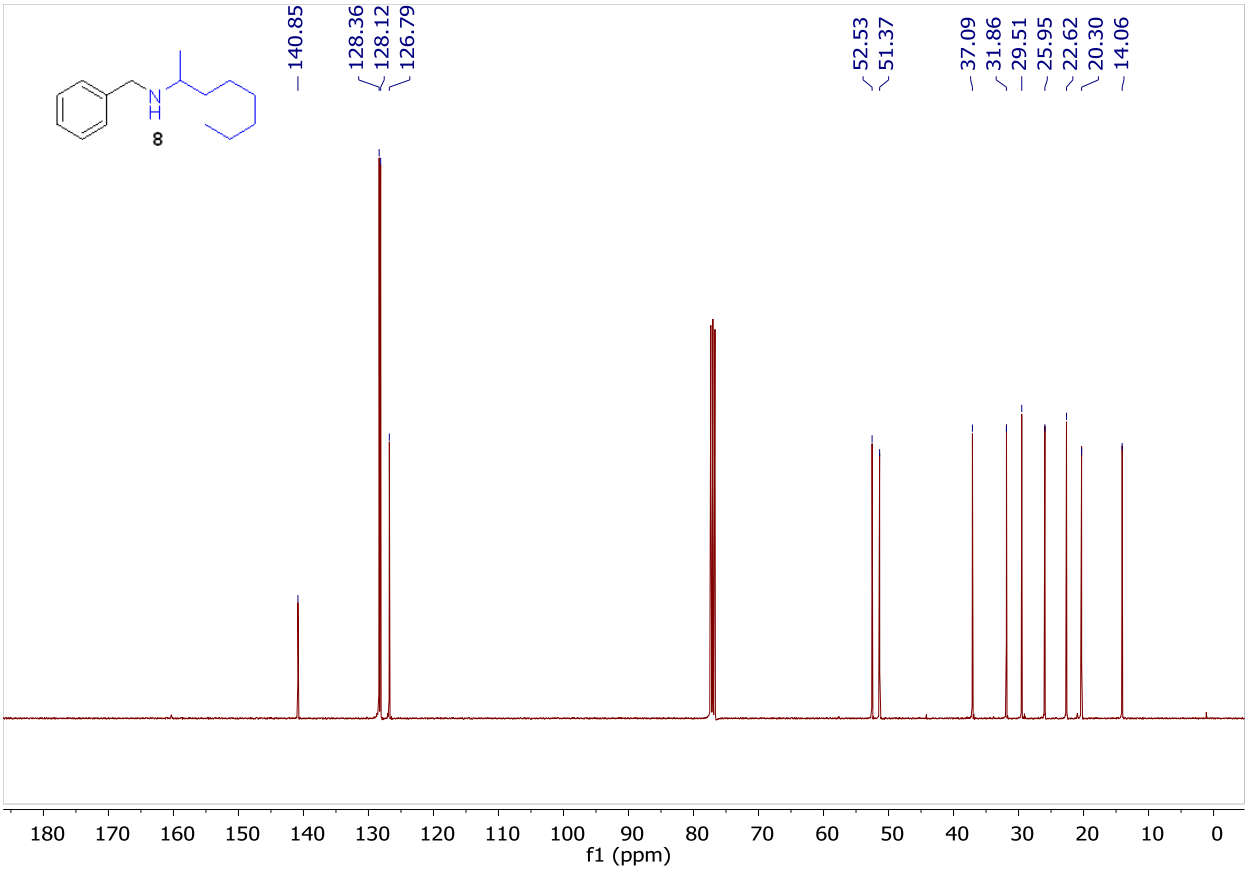
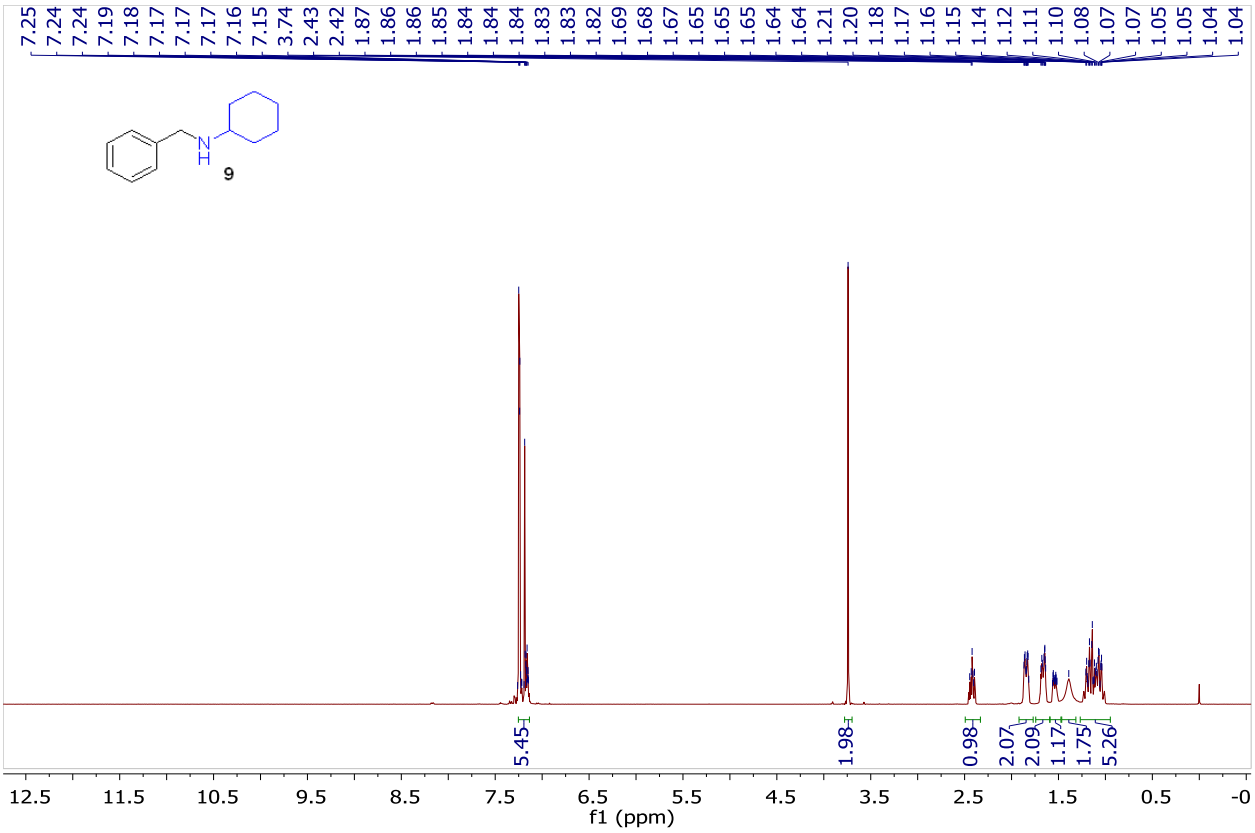
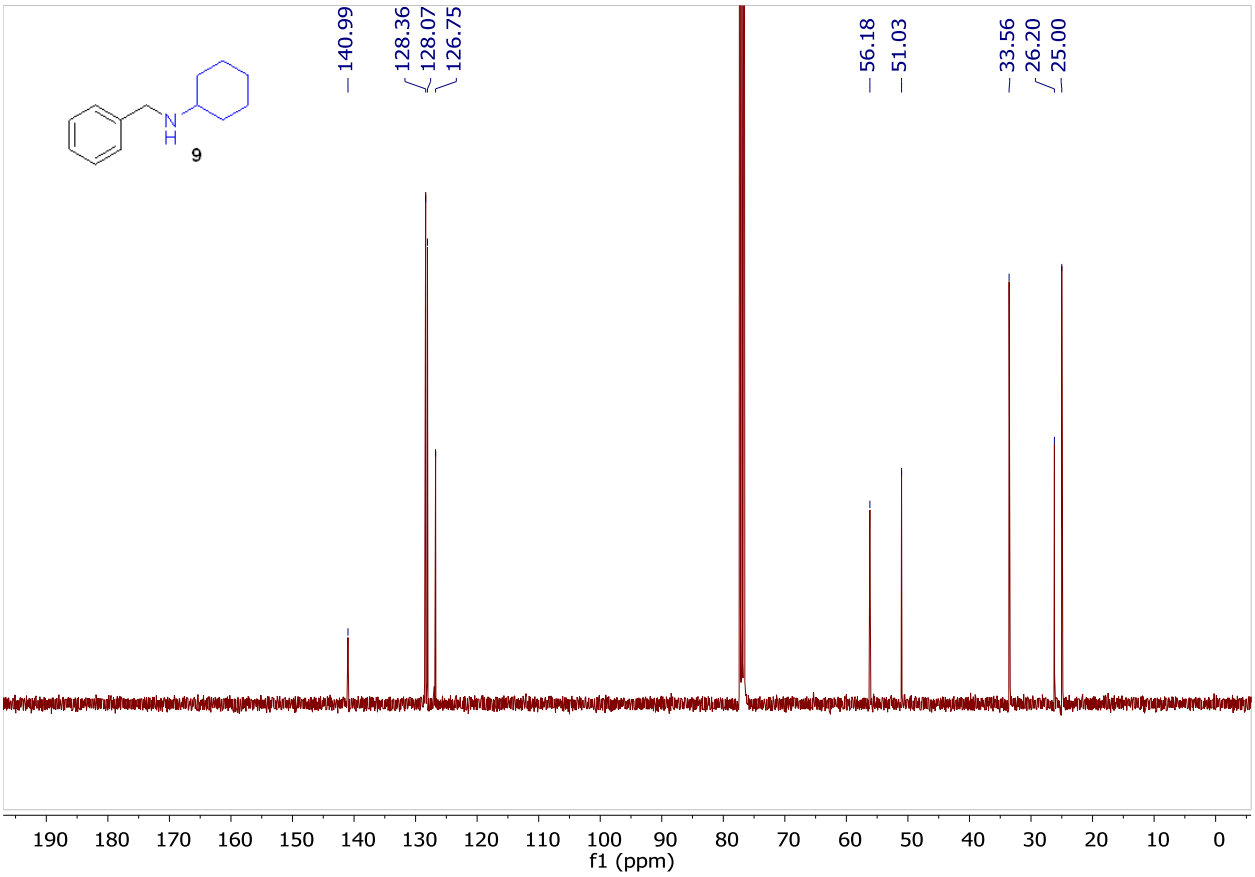
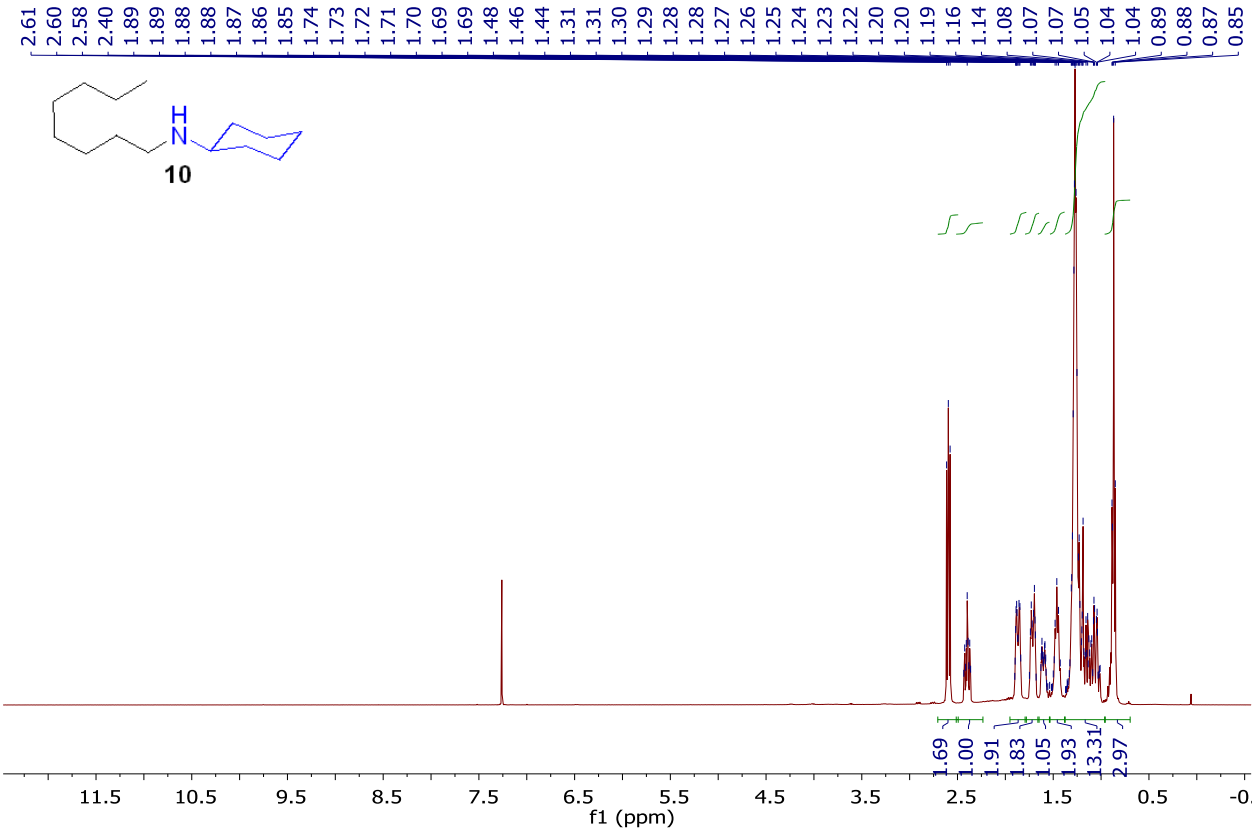
49.52
31.83
30.11
29.53
29.26
27.37
22.64
14.06
7
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

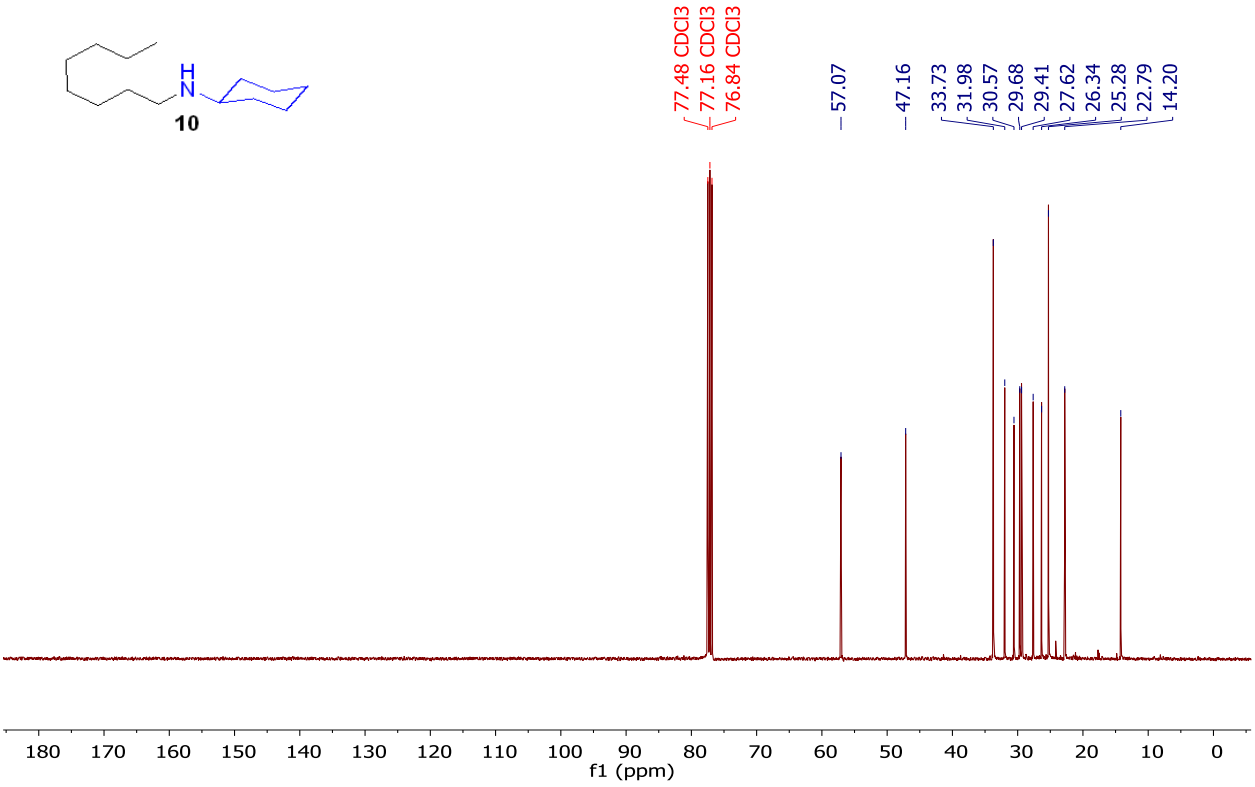

7.35 7.34 7.34 7.34 7.33 7.32 7.32 7.28 7.28 7.27 7.27 7.27 7.26 7.26 3.88 3.84 3.79 3.75 2.71 2.70 2.68 1.51 1.50 1.38 1.37 1.37 1.36 1.36 1.35 1.34 1.34 1.34 1.33 1.32 1.32 1.32 1.31 1.30 1.29 1.28 1.12 1.12 1.10 1.10 0.93 0.93 0.92 0.90
8
5.06
1.00
1.01
1.13
1.11
9.56
2.95
2.99
12.0 11.5 11.0 10.5 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)

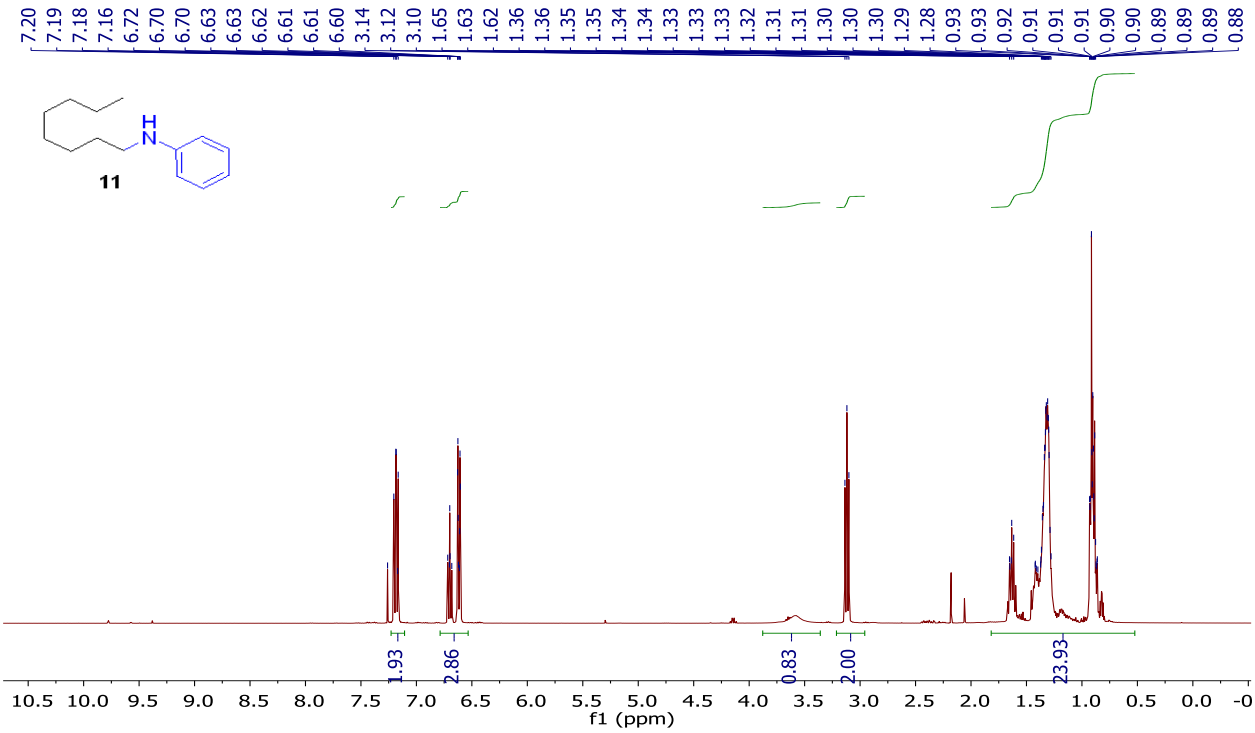

140.85
128.36
128.12
126.79
52.53
51.37
37.09
31.86
29.51
25.95
22.62
20.30
14.06
8
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

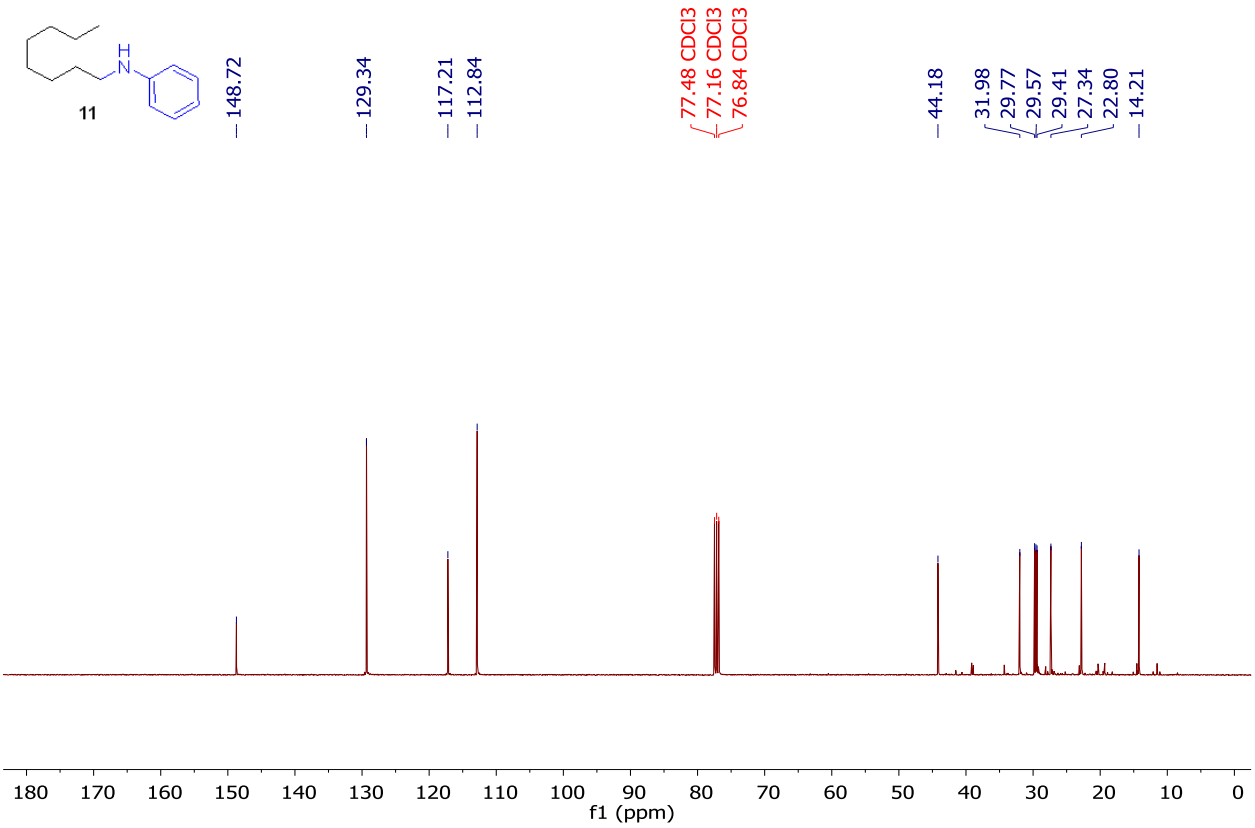

7.25 7.24 7.24 7.19 7.18 7.17 7.17 7.17 7.16 7.15 3.74 2.43 2.42 1.87 1.86 1.86 1.85 1.84 1.84 1.84 1.83 1.83 1.82 1.69 1.68 1.67 1.65 1.65 1.65 1.64 1.64 1.21 1.20 1.18 1.17 1.16 1.15 1.14 1.12 1.11 1.10 1.08 1.07 1.07 1.05 1.05 1.04 1.04
9
5.45 1.98 0.98 2.07 2.09 1.17 1.75 5.26
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0
f1 (ppm)

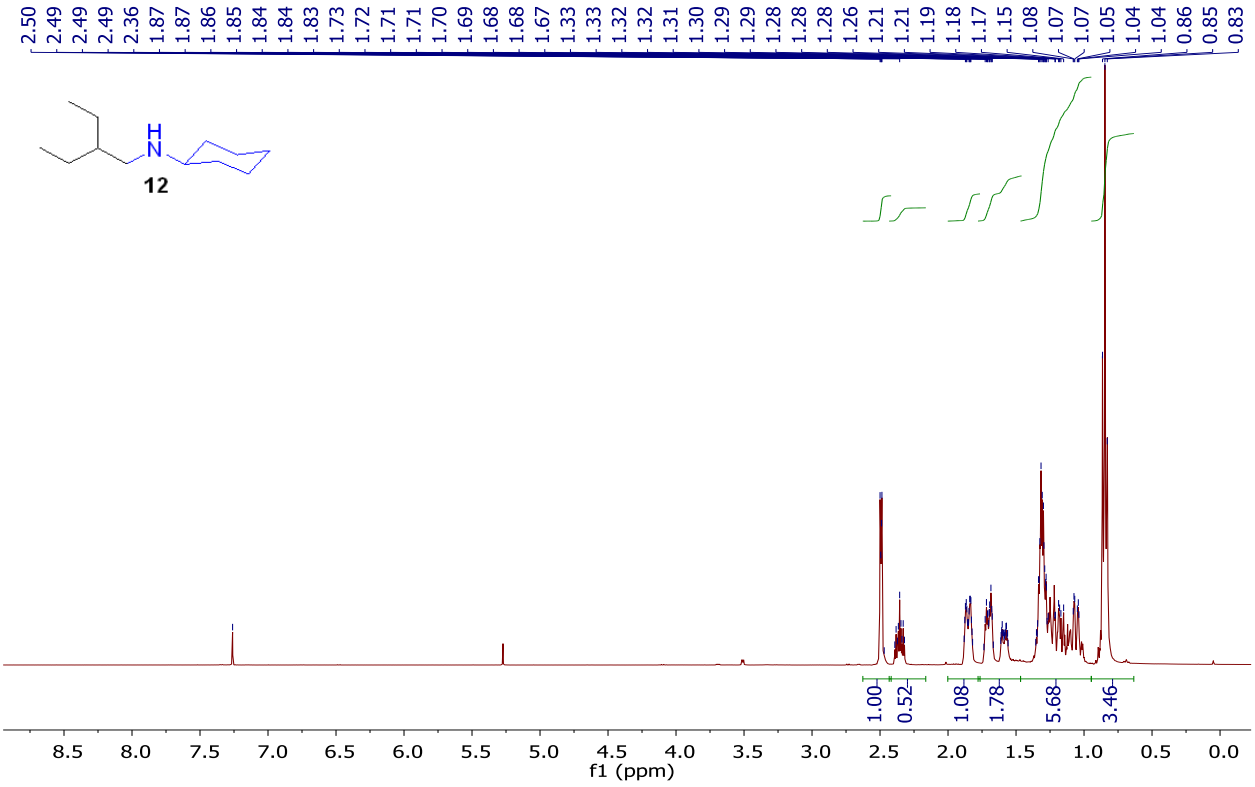

140.99
128.36
128.07
126.75
56.18
51.03
33.56
26.20
25.00
9
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

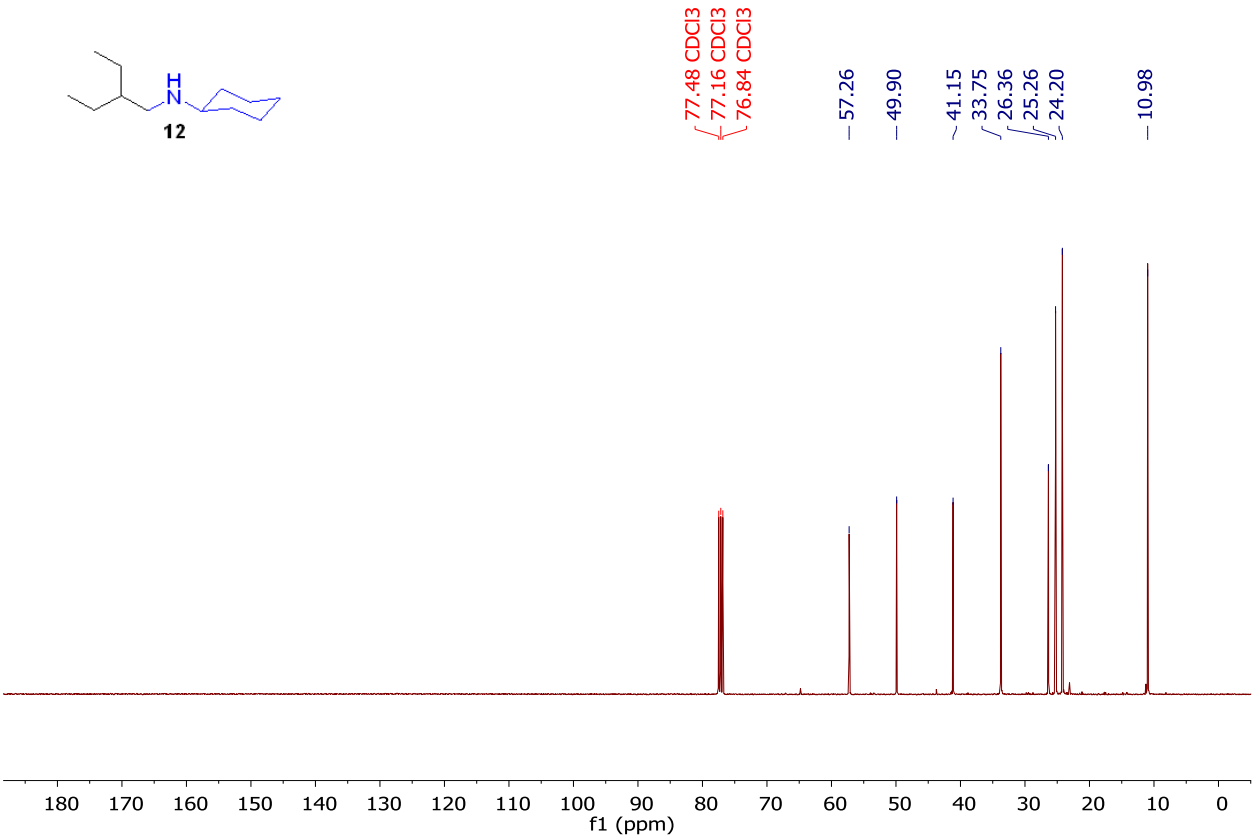

2.61 2.60 2.58 2.40 1.89 1.89 1.88 1.88 1.87 1.86 1.85 1.74 1.73 1.72 1.71 1.70 1.69 1.69 1.48 1.46 1.44 1.31 1.31 1.30 1.29 1.28 1.28 1.27 1.26 1.25 1.24 1.23 1.22 1.20 1.20 1.19 1.16 1.14 1.08 1.07 1.07 1.05 1.04 1.04 0.89 0.88 0.87 0.85
H
N
10
1.69 1.00 1.91 1.83 1.05 1.93 13.31 2.97
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

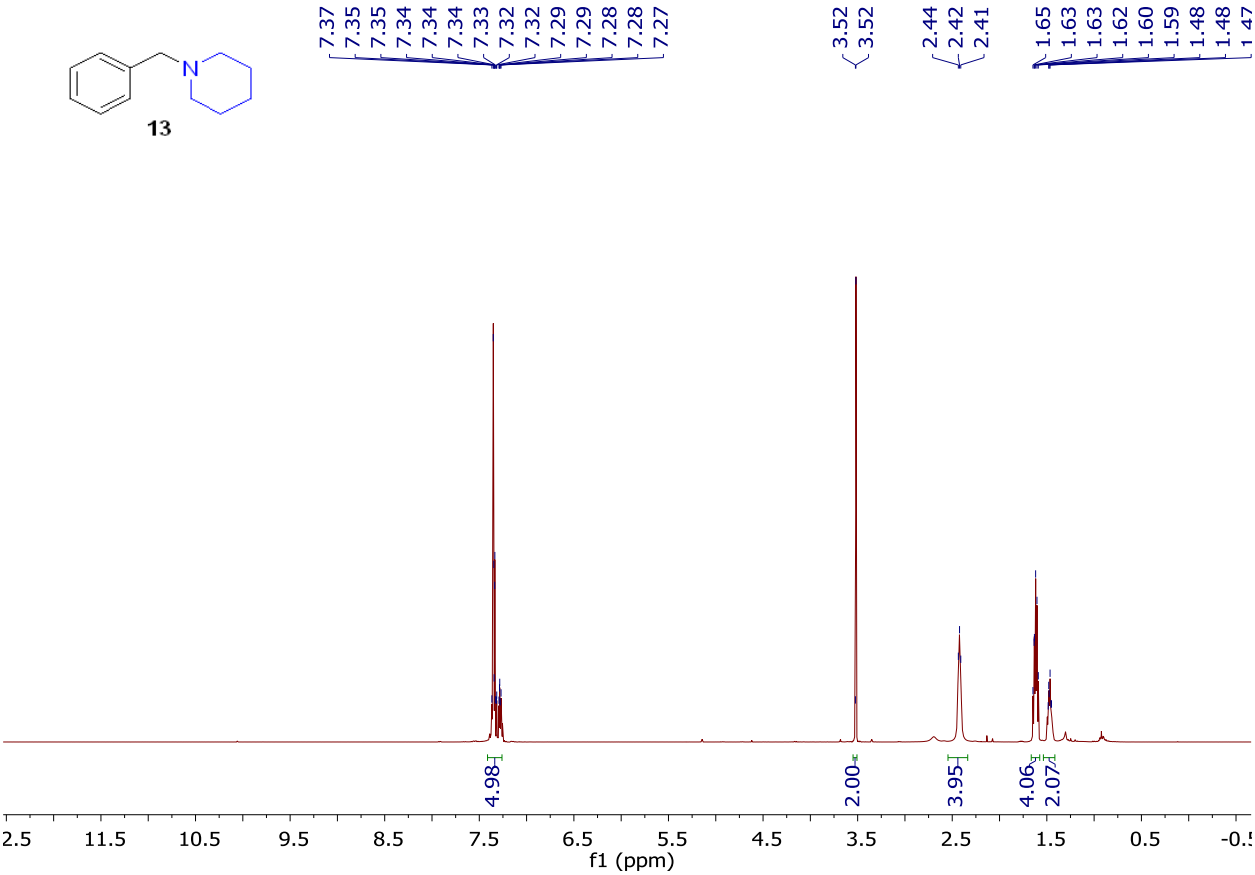

H
N
10
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
57.07
47.16
33.73
31.98
30.57
29.68
29.41
27.62
26.34
25.28
22.79
14.20
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

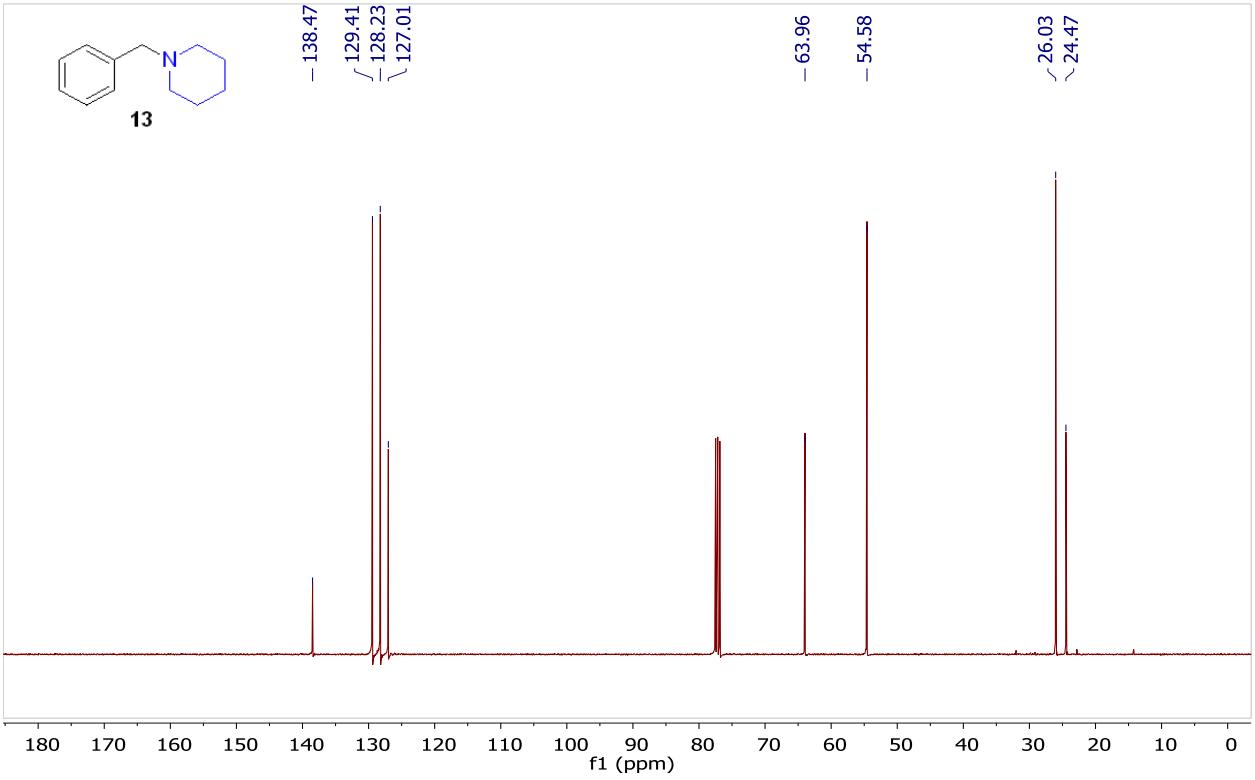

7.20 7.19 7.18 7.16 6.72 6.70 6.70 6.63 6.63 6.62 6.61 6.61 6.60 3.14 3.12 3.10 1.65 1.63 1.62 1.36 1.36 1.35 1.35 1.34 1.34 1.33 1.33 1.33 1.32 1.31 1.31 1.30 1.30 1.29 1.28 0.93 0.93 0.92 0.91 0.91 0.91 0.90 0.90 0.89 0.89 0.89 0.88
11
1.93
2.86
0.83
2.00
23.93
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 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)

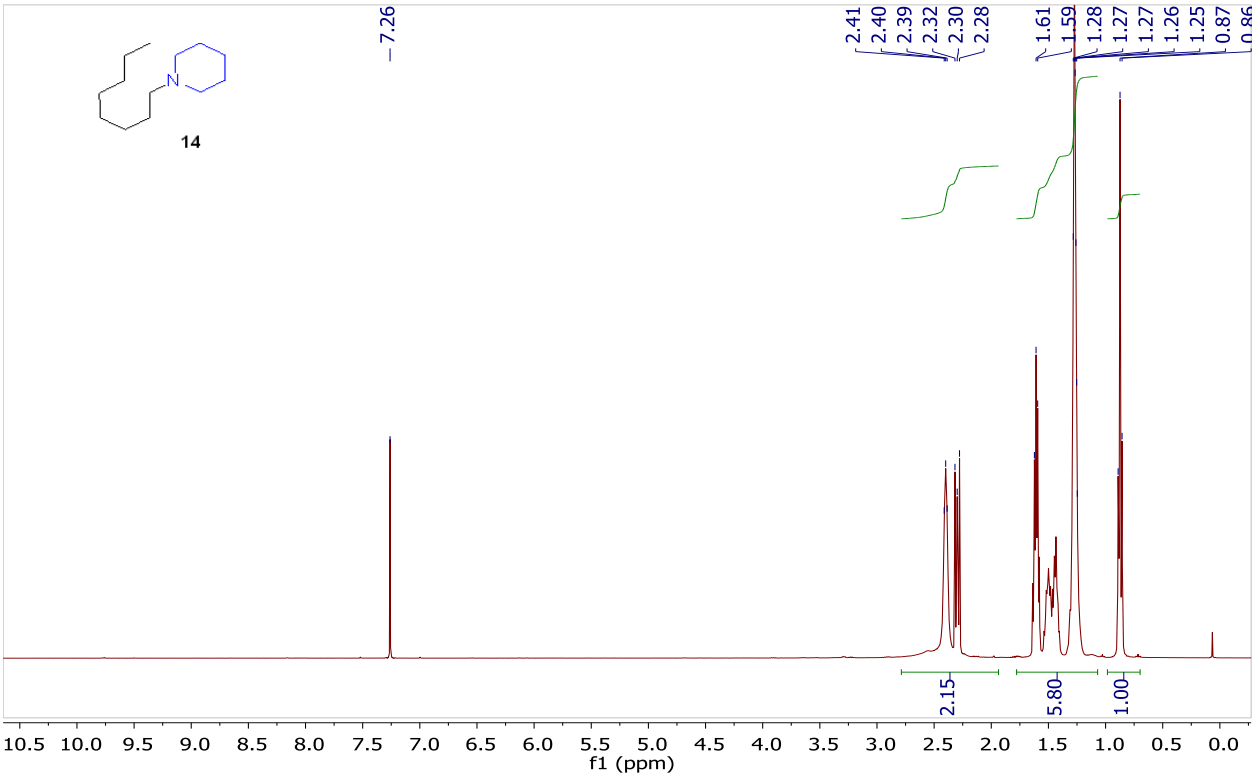

11
148.72
129.34
117.21
112.84
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
44.18
31.98
29.77
29.57
29.41
27.34
22.80
14.21
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

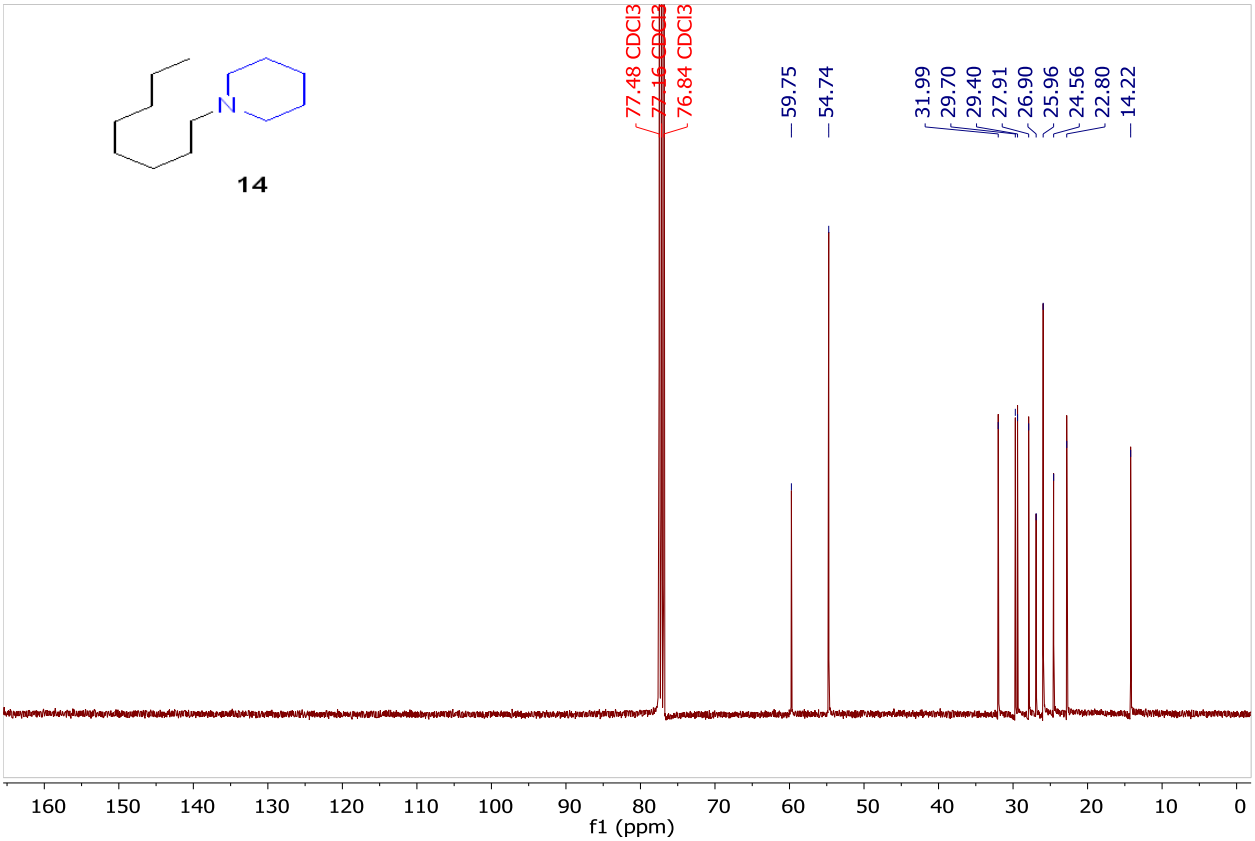

2.50 2.49 2.49 2.49 2.36 1.87 1.87 1.86 1.85 1.84 1.84 1.83 1.73 1.72 1.71 1.71 1.70 1.69 1.68 1.68 1.67 1.33 1.33 1.32 1.32 1.31 1.30 1.29 1.29 1.28 1.28 1.28 1.26 1.21 1.21 1.19 1.18 1.17 1.15 1.08 1.07 1.07 1.05 1.04 1.04 0.86 0.85 0.83
H
N
12
1.00 0.52 1.08 1.78 5.68 3.46
8.5 8.0 7.5 7.0 6.5 6.0 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)

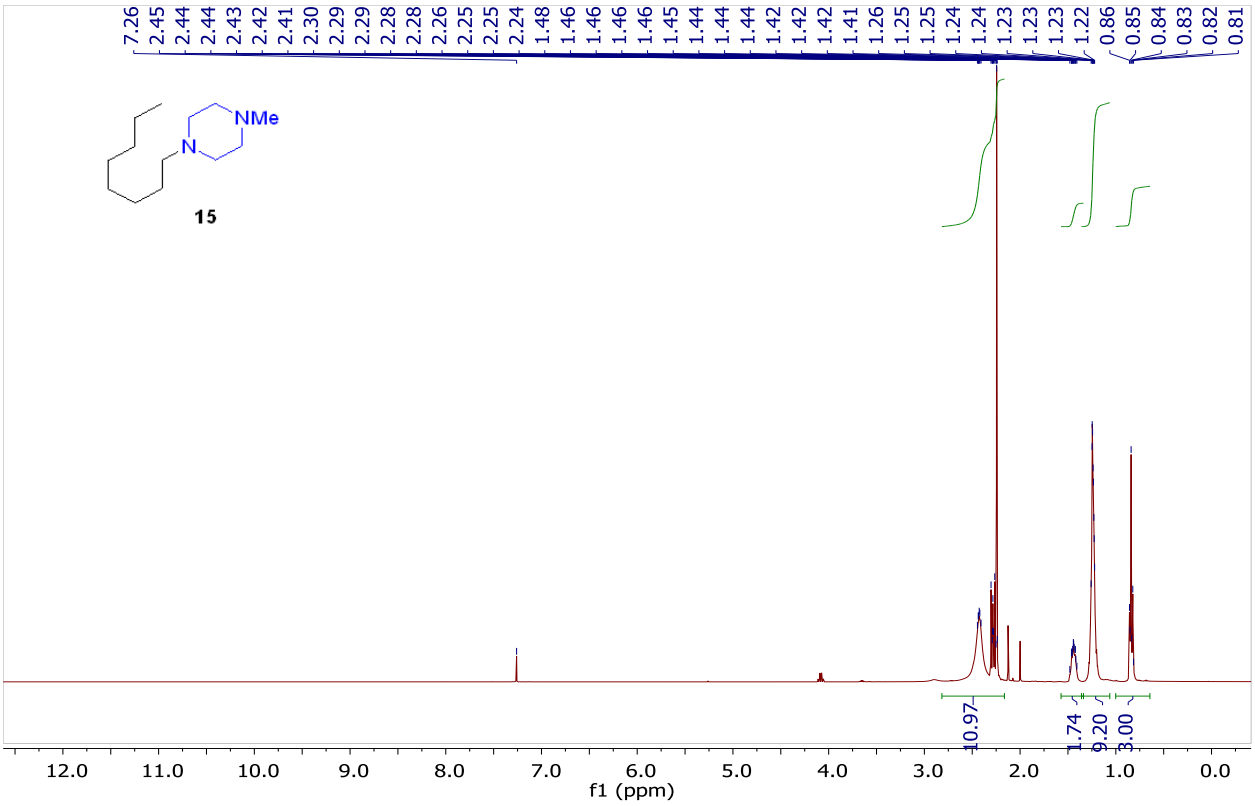

H
N
12
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
57.26
49.90
41.15
33.75
26.36
25.26
24.20
10.98
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

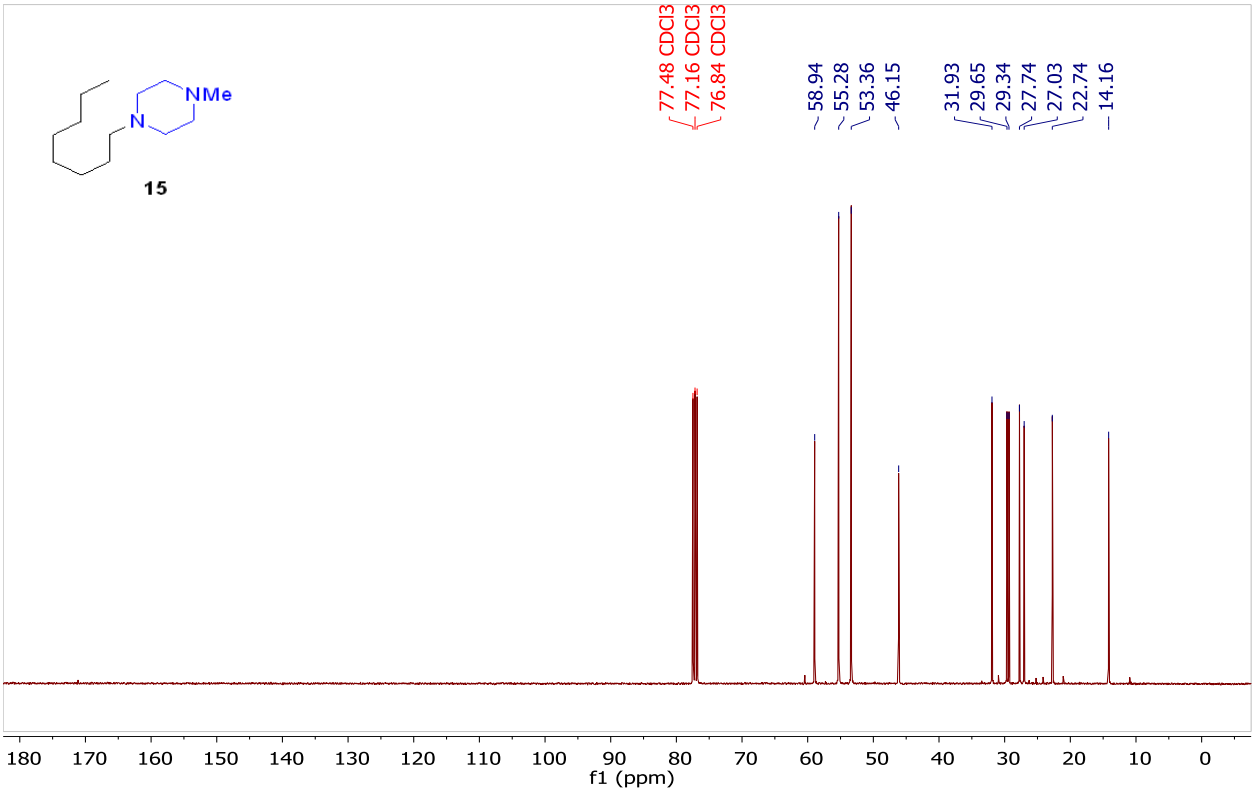

13
7.37
7.35
7.35
7.34
7.34
7.34
7.33
7.32
7.32
7.29
7.29
7.28
7.28
7.27
3.52
3.52
2.44
2.42
2.41
1.65
1.63
1.63
1.62
1.60
1.59
1.48
1.48
4.98
2.00
3.95
4.06
2.07
f1 (ppm)

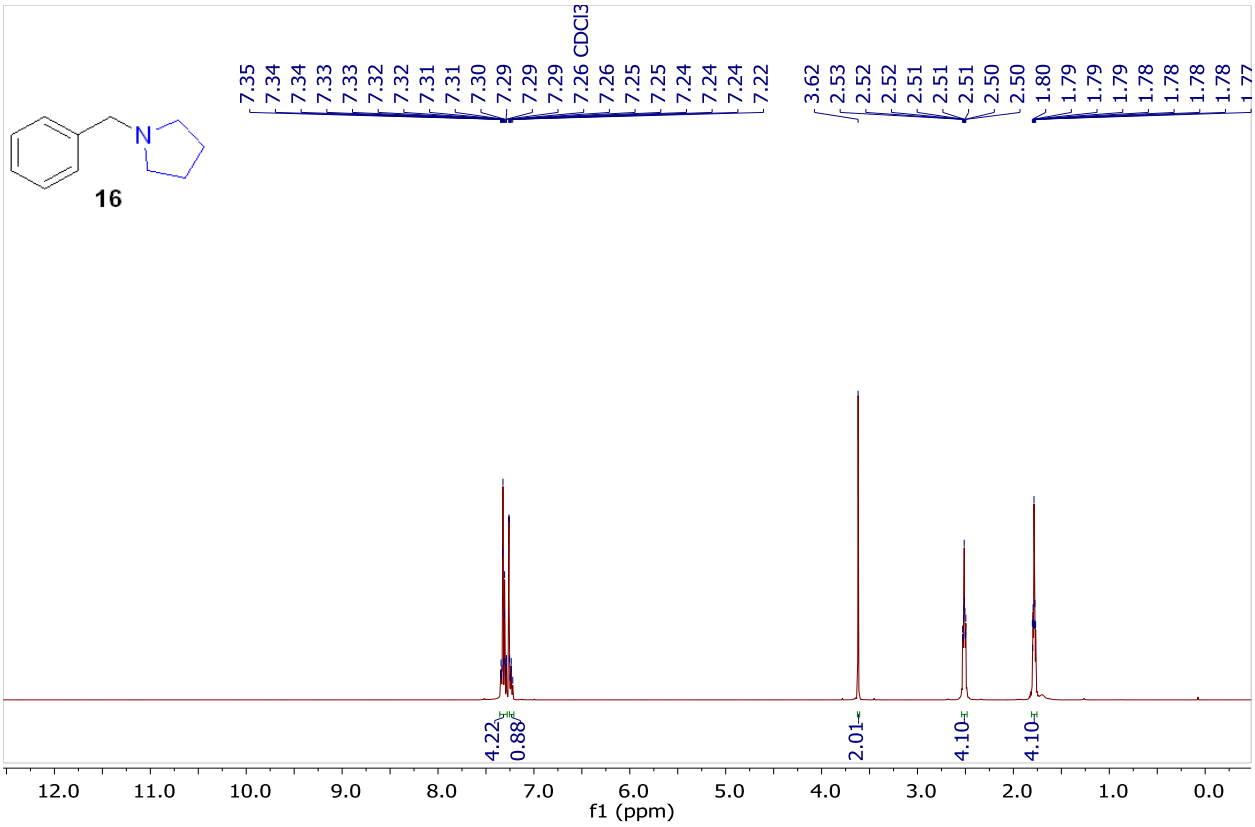

13
138.47
129.41
128.23
127.01
63.96
54.58
26.03
24.47
f1 (ppm)

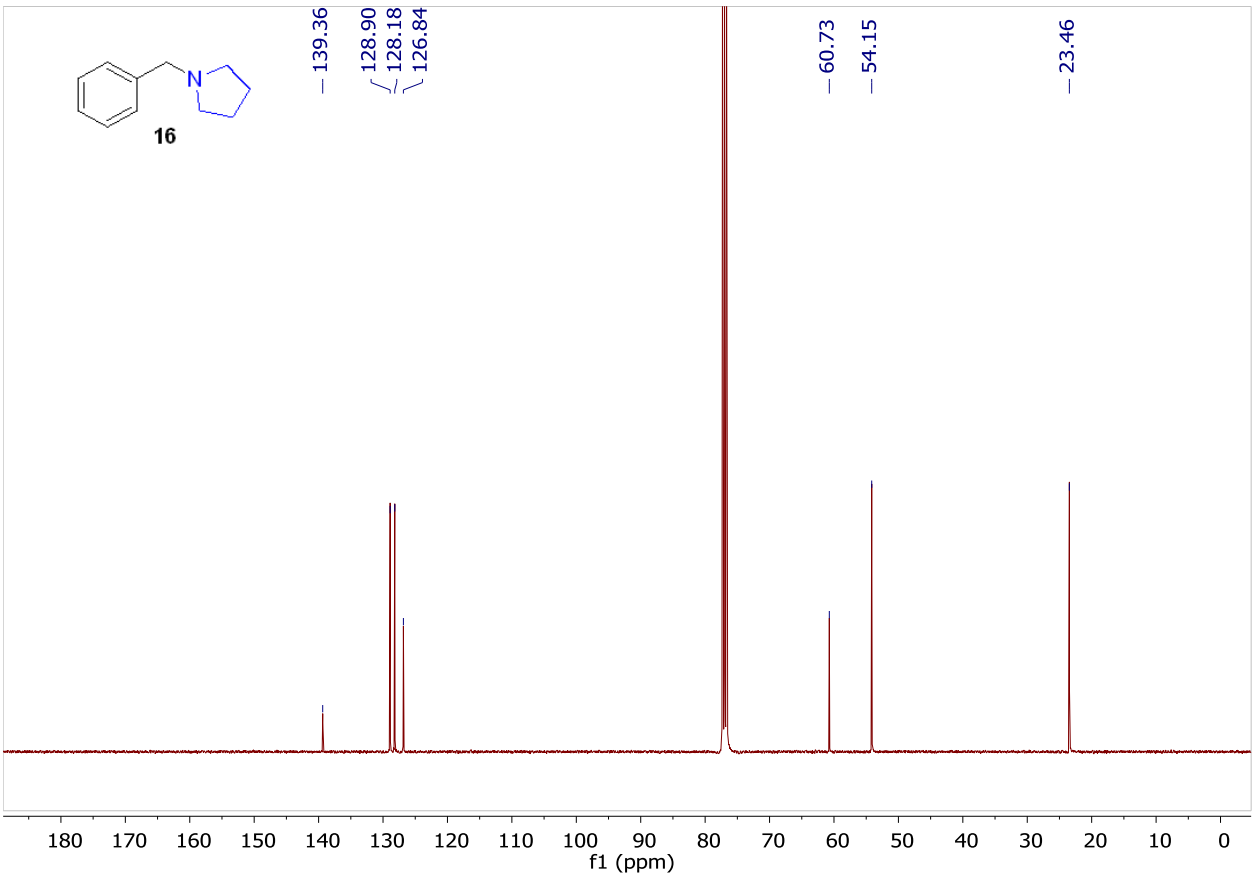

14
7.26
2.41
2.40
2.39
2.32
2.30
2.28
1.61
1.59
1.28
1.27
1.27
1.26
1.25
0.87
2.15
5.80
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


14
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
59.75
54.74
31.99
29.70
29.40
27.91
26.90
25.96
24.56
22.80
14.22
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26 2.45 2.44 2.44 2.43 2.42 2.41 2.30 2.29 2.29 2.28 2.28 2.26 2.25 2.25 2.24 1.48 1.46 1.46 1.46 1.46 1.45 1.44 1.44 1.44 1.42 1.42 1.42 1.41 1.26 1.25 1.25 1.24 1.24 1.23 1.23 1.23 1.22 0.86 0.85 0.84 0.83 0.82 0.81
NMe
N
15
10.97
1.74
9.20
3.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
58.94
55.28
53.36
46.15
31.93
29.65
29.34
27.74
27.03
22.74
14.16
NMe
N
15
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.29 7.29 CDCl3 7.26 7.26 7.25 7.25 7.24 7.24 7.24 7.22
3.62 2.53 2.52 2.52 2.51 2.51 2.51 2.50 2.50 1.80 1.79 1.79 1.79 1.78 1.78 1.78 1.78
N
16
4.22 0.88 2.01 4.10 4.10
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


139.36 128.90 128.18 126.84 60.73 54.15 23.46
N
16
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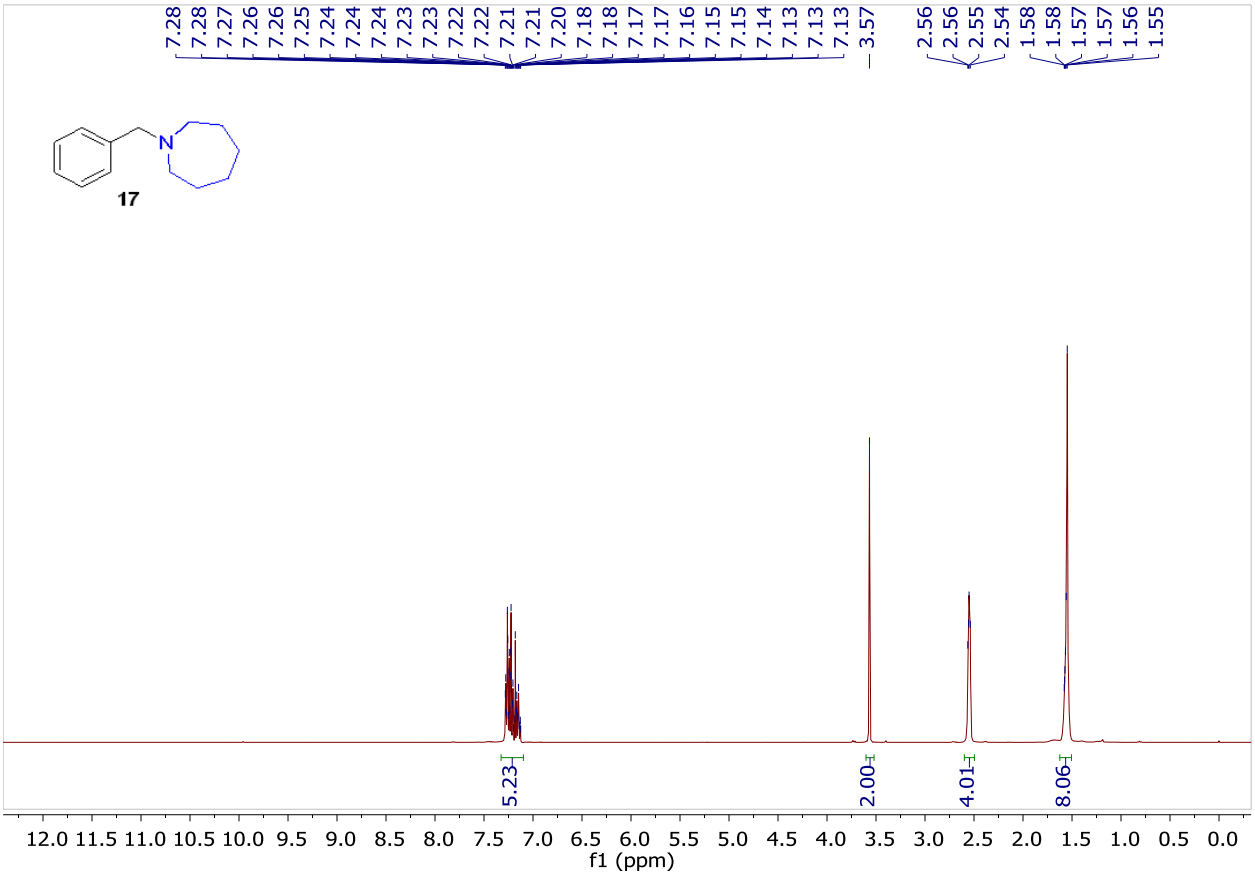
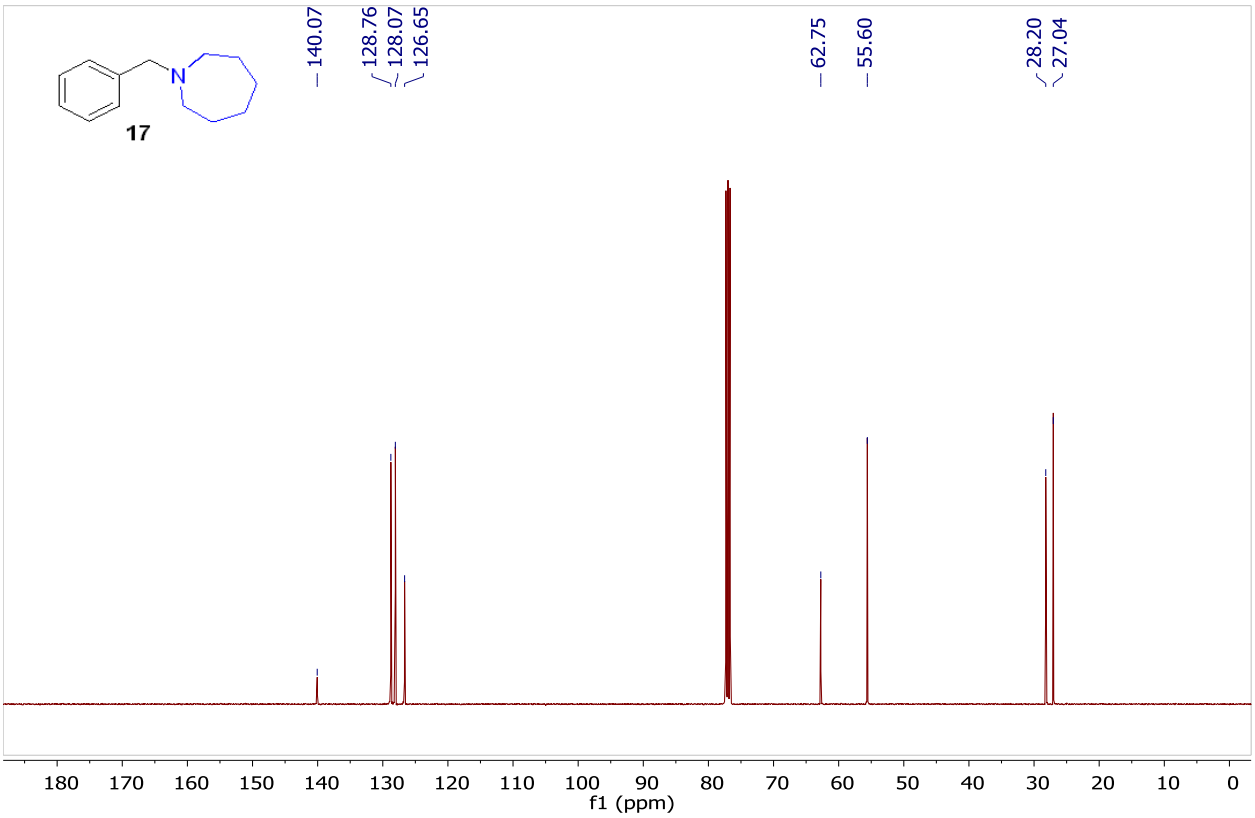
f1 (ppm)


7.28 7.28 7.27 7.26 7.26 7.25 7.24 7.24 7.24 7.23 7.23 7.22 7.22 7.21 7.21 7.20 7.18 7.18 7.17 7.17 7.16 7.15 7.15 7.14 7.13 7.13 7.13 3.57 2.56 2.56 2.55 2.54 1.58 1.58 1.57 1.57 1.56 1.55
N
17
5.23
2.00
4.01
8.06
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
f1 (ppm)


140.07
128.76
128.07
126.65
62.75
55.60
28.20
27.04
N
17
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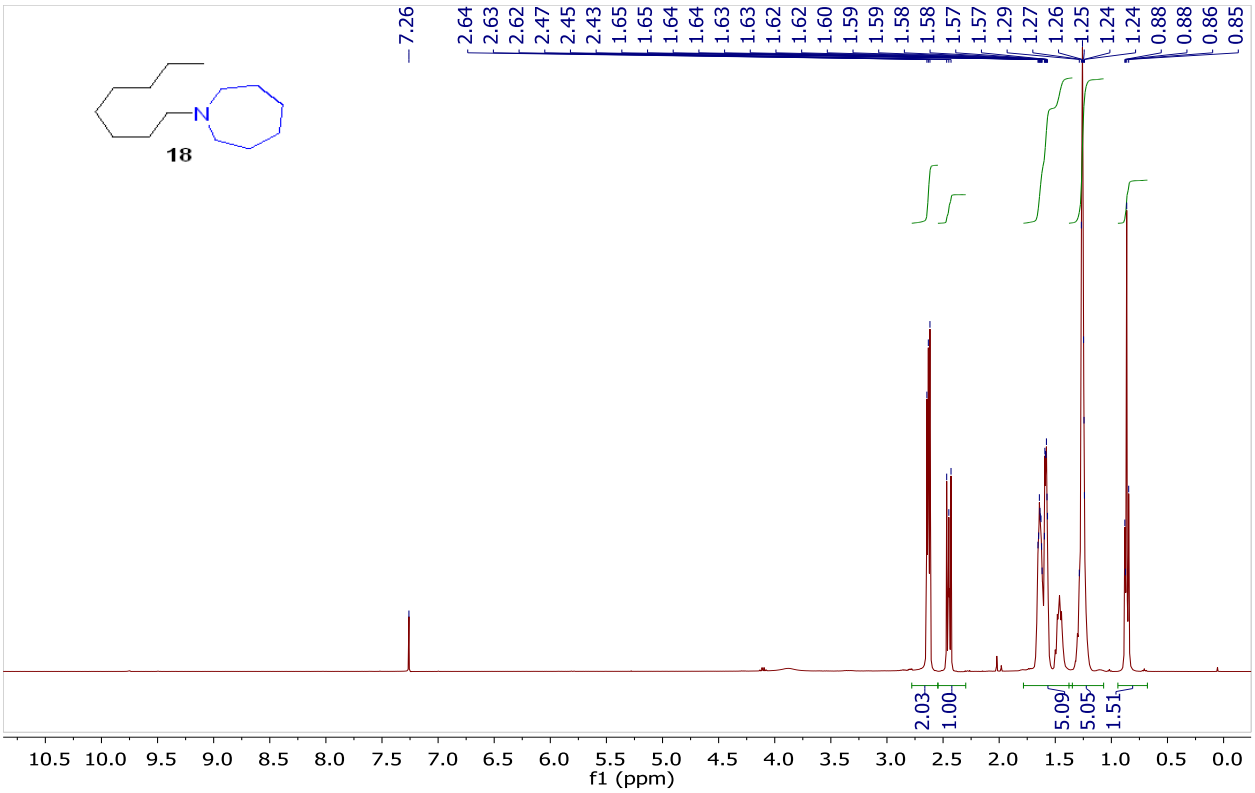
f1 (ppm)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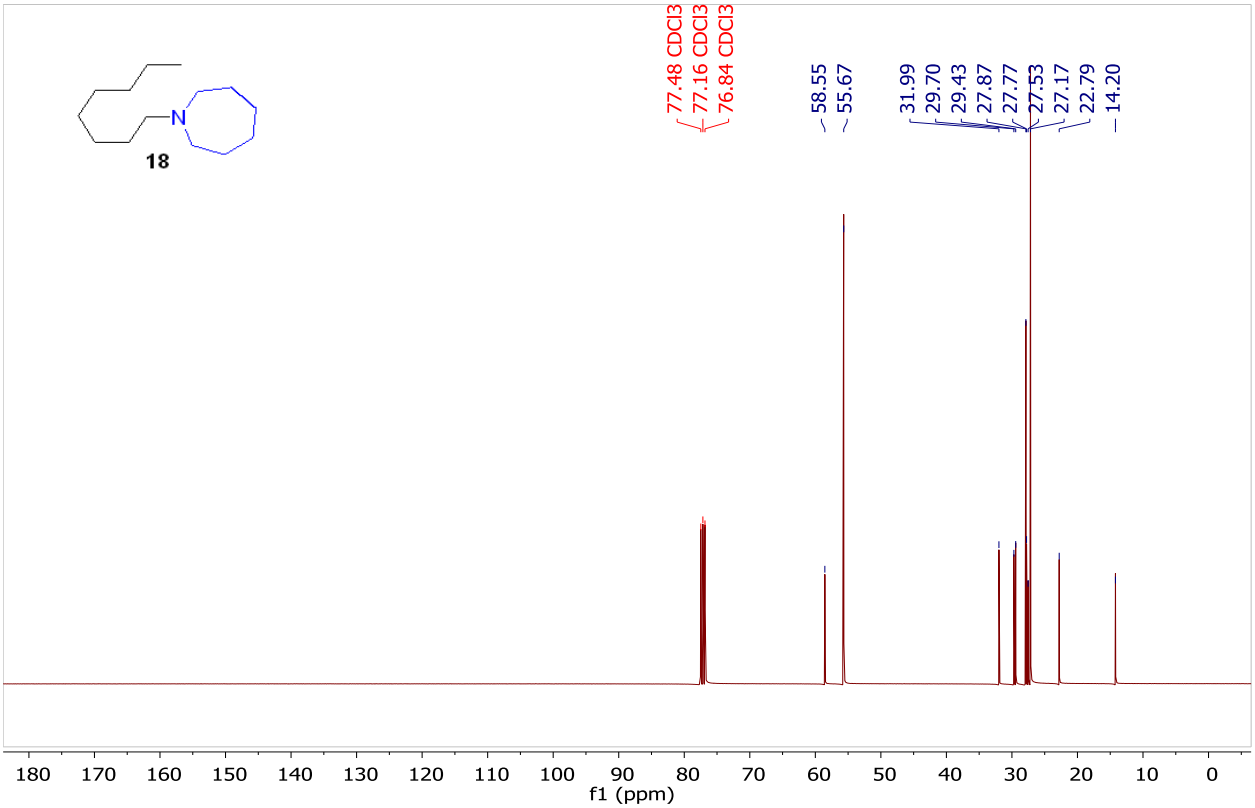
2.64
2.63
2.62
2.47
2.45
2.43
1.65
1.65
1.64
1.64
1.63
1.63
1.62
1.62
1.60
1.59
1.59
1.58
1.58
1.57
1.57
1.29
1.27
1.26
1.25
1.24
1.24
0.88
0.88
0.86
0.85
18
2.03
1.00
5.09
5.05
1.51
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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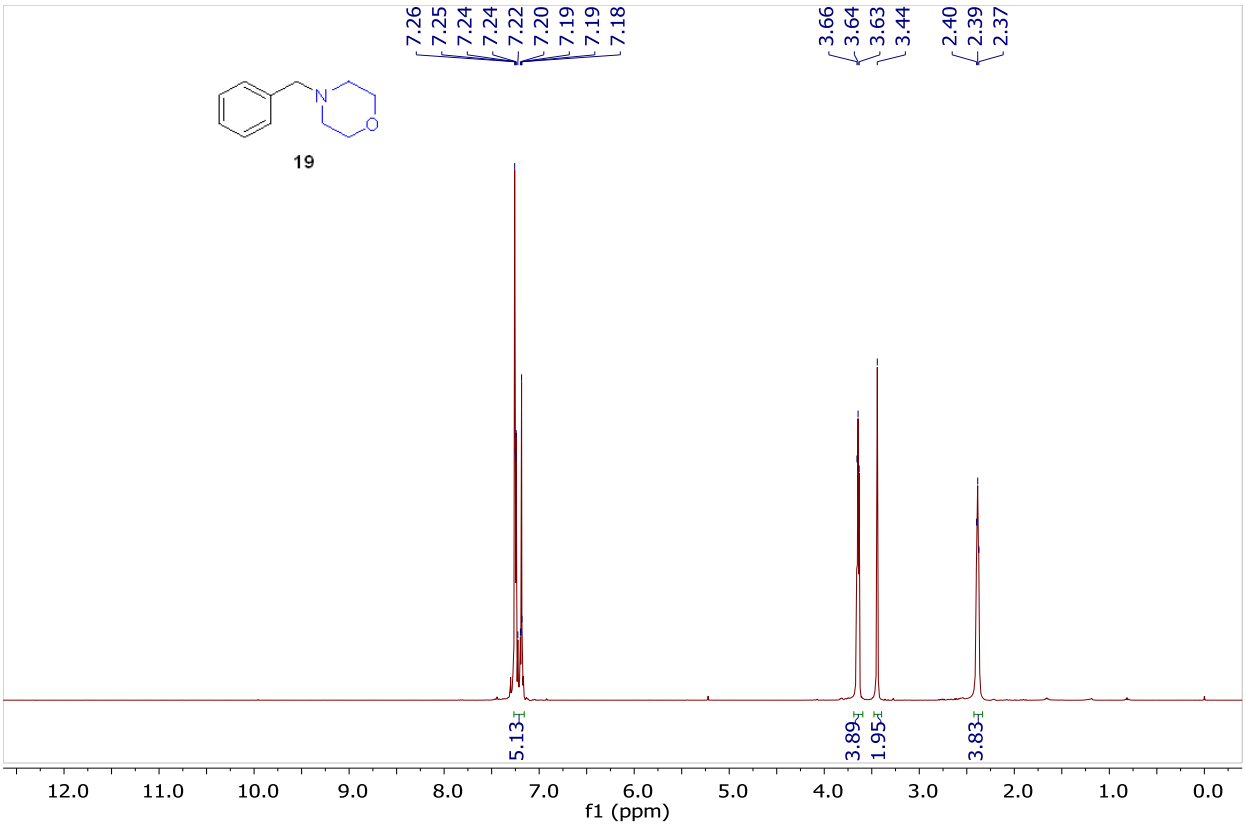
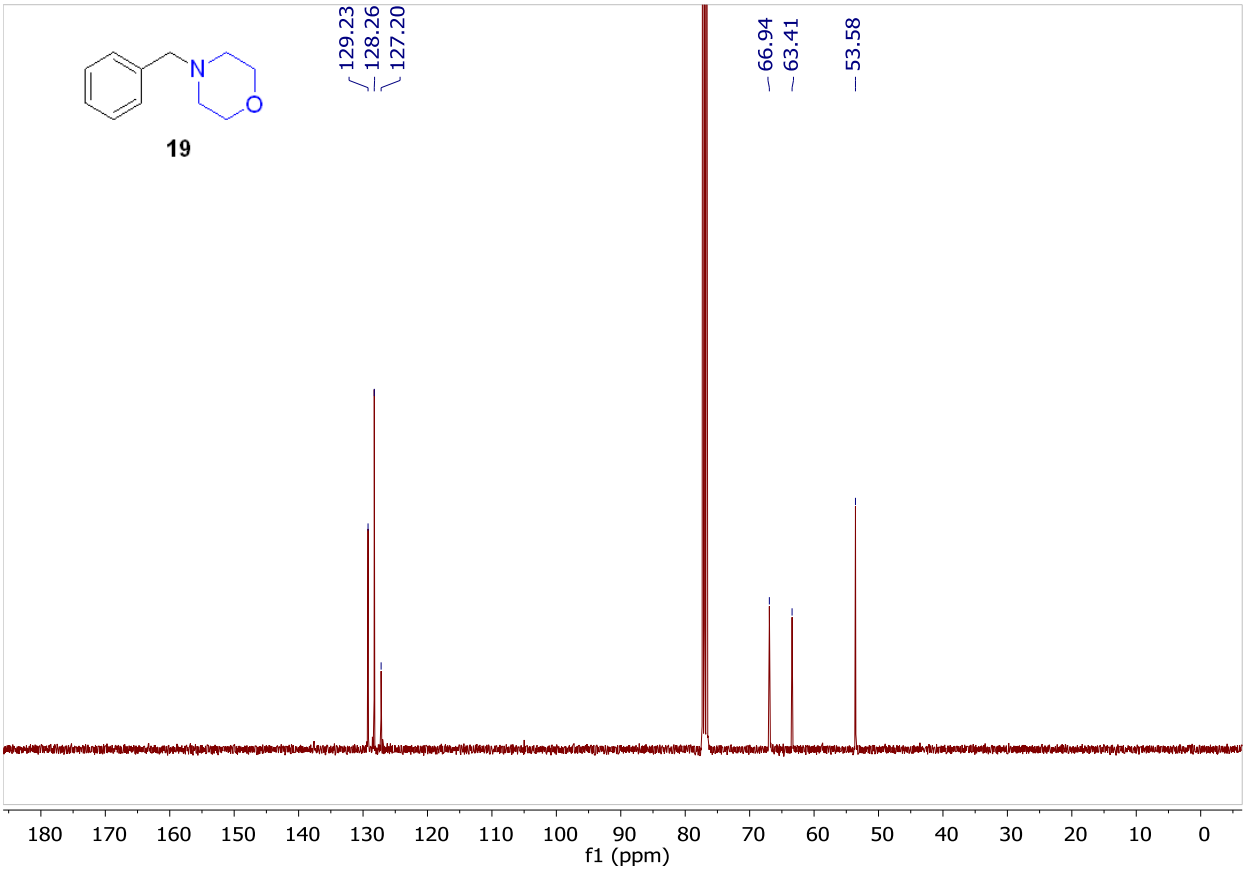
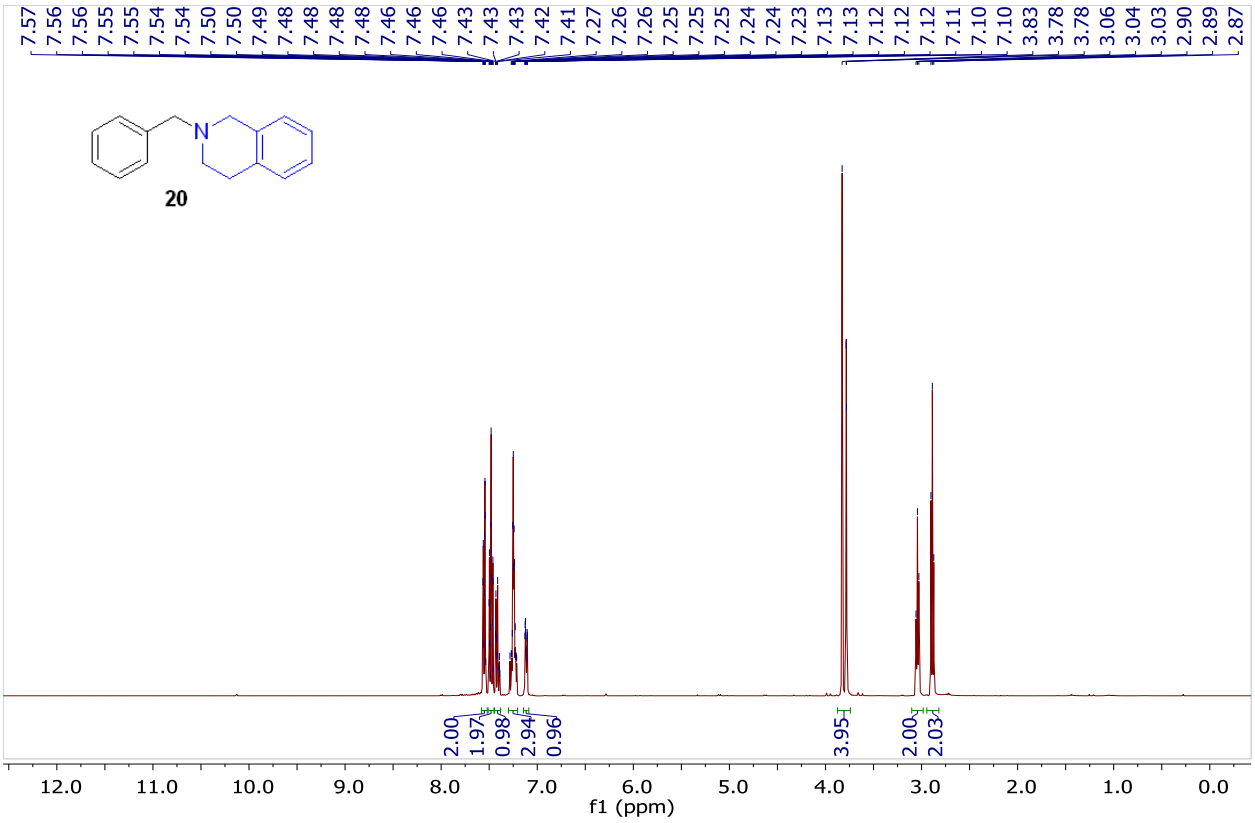
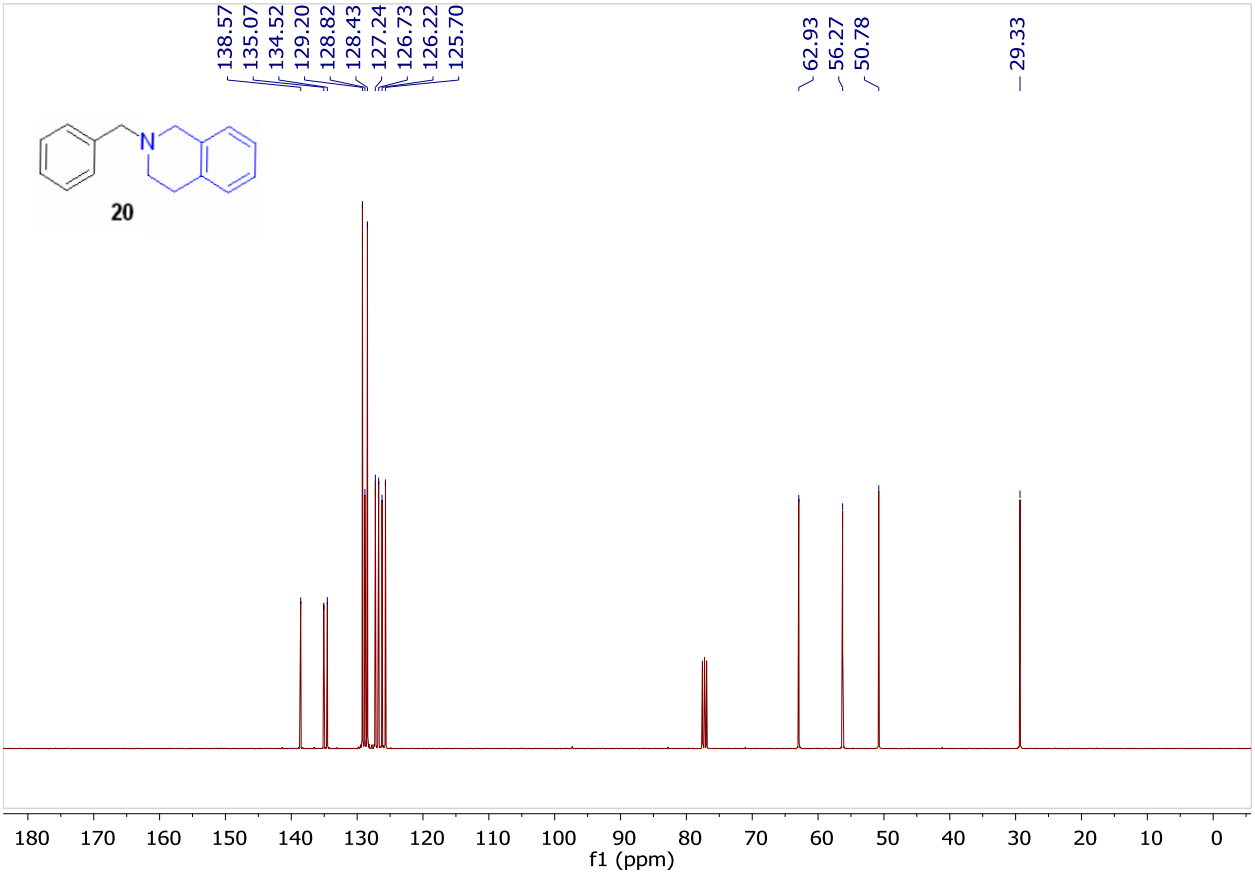
77.16 CDCl3
76.84 CDCl3
58.55
55.67
31.99
29.70
29.43
27.87
27.77
27.53
27.17
22.79
14.20
18
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26
7.25
7.24
7.24
7.22
7.20
7.19
7.19
7.18
3.66
3.64
3.63
3.44
2.40
2.39
2.37
19
5.13
3.89
1.95
3.83
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


129.23
128.26
127.20
66.94
63.41
53.58
19
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 7.50 7.50 7.49 7.48 7.48 7.48 7.48 7.46 7.46 7.46 7.43 7.43 7.43 7.42 7.41 7.27 7.26 7.26 7.25 7.25 7.25 7.24 7.24 7.23 7.13 7.13 7.12 7.12 7.12 7.11 7.10 7.10 3.83 3.78 3.78 3.06 3.04 3.03 2.90 2.89 2.87
N
20
2.00 1.97 0.98 2.94 0.96 3.95 2.00 2.03
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


138.57 135.07 134.52 129.20 128.82 128.43 127.24 126.73 126.22 125.70
62.93 56.27 50.78 29.33
N
20
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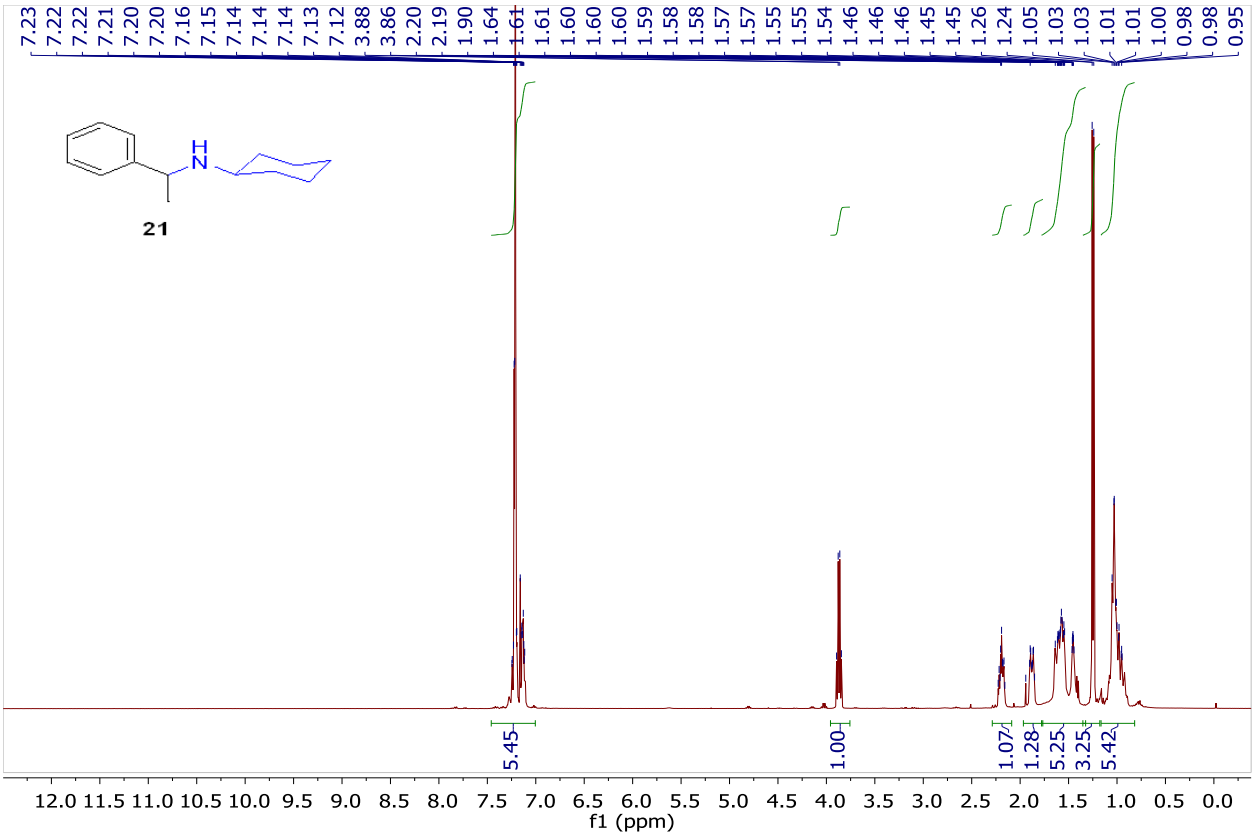
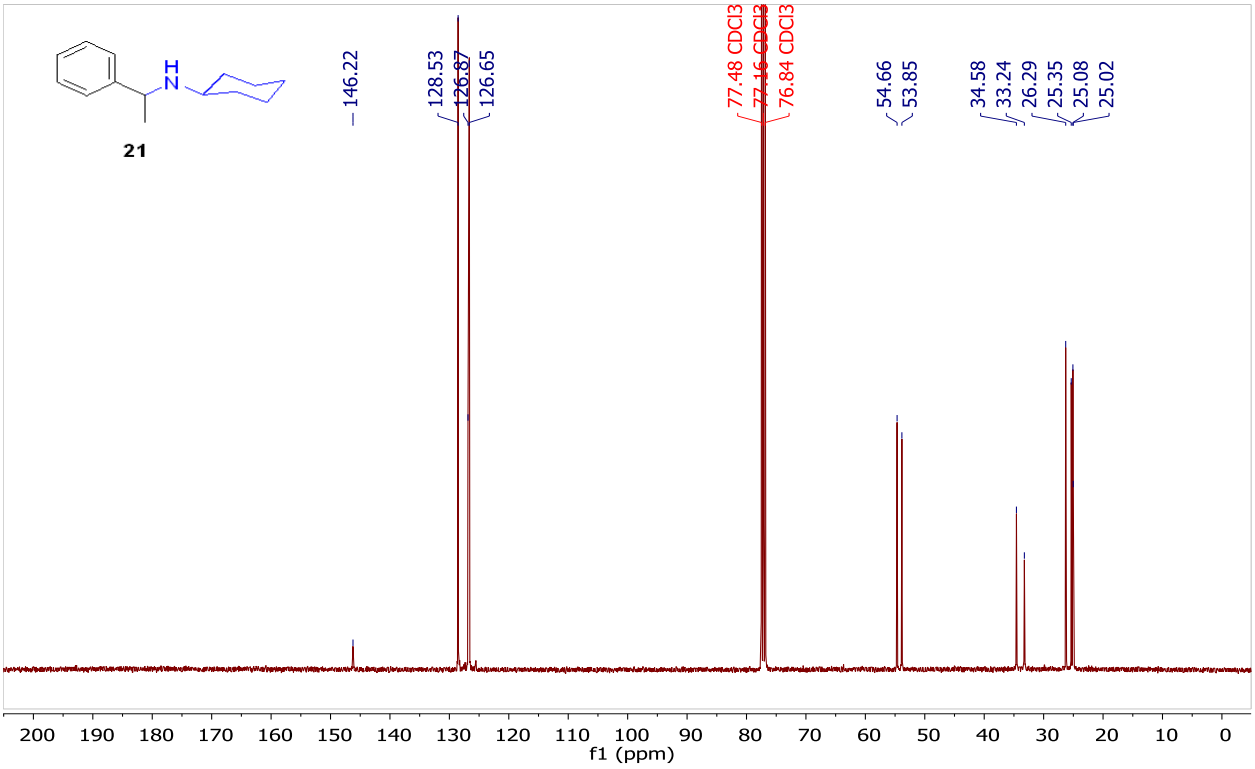
f1 (ppm)


7.23 7.22 7.22 7.21 7.20 7.20 7.16 7.15 7.14 7.14 7.14 7.13 7.12 3.88 3.86 2.20 2.19 1.90 1.64 1.61 1.61 1.60 1.60 1.60 1.59 1.58 1.58 1.57 1.57 1.55 1.55 1.54 1.46 1.46 1.46 1.45 1.45 1.26 1.24 1.05 1.03 1.03 1.01 1.01 1.00 0.98 0.98 0.95
21
5.45
1.00
1.07
1.28
5.25
3.25
5.42
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)


21
146.22
128.53
126.87
126.65
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
54.66
53.85
34.58
33.24
26.29
25.35
25.08
25.02
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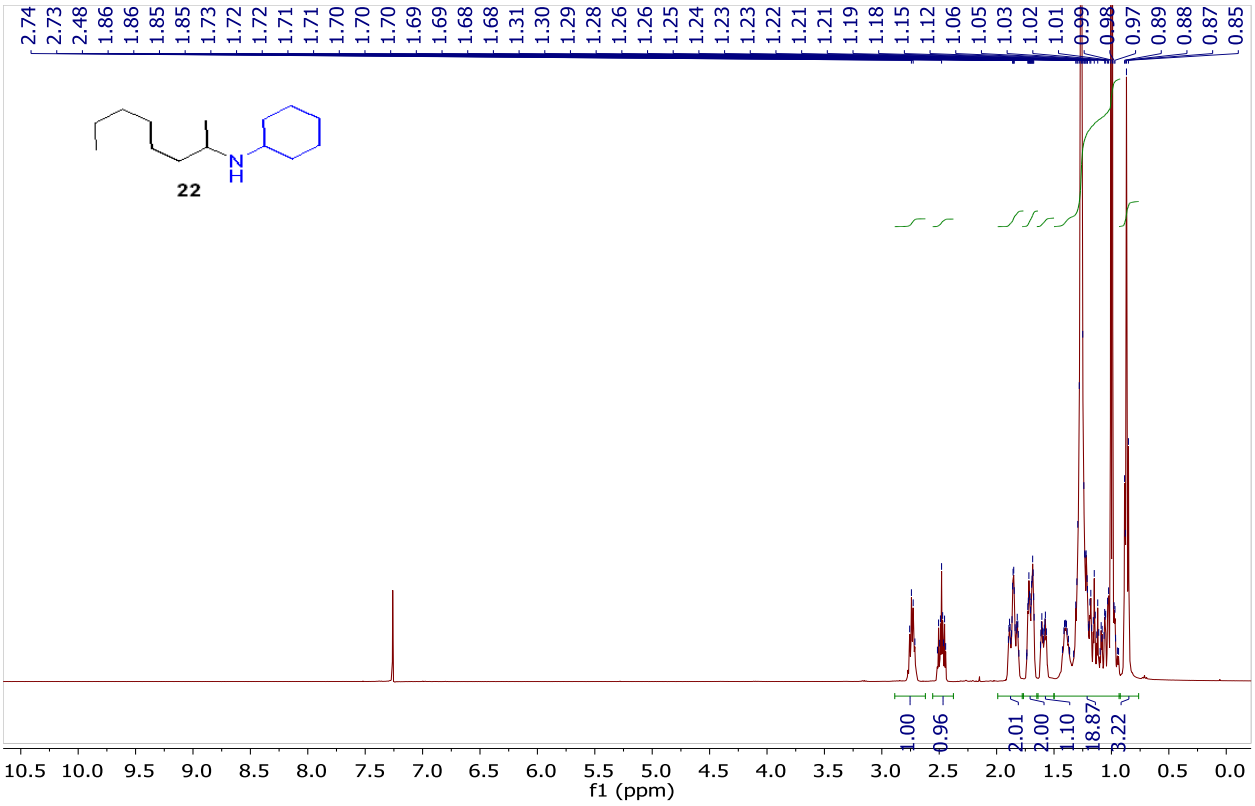
f1 (ppm)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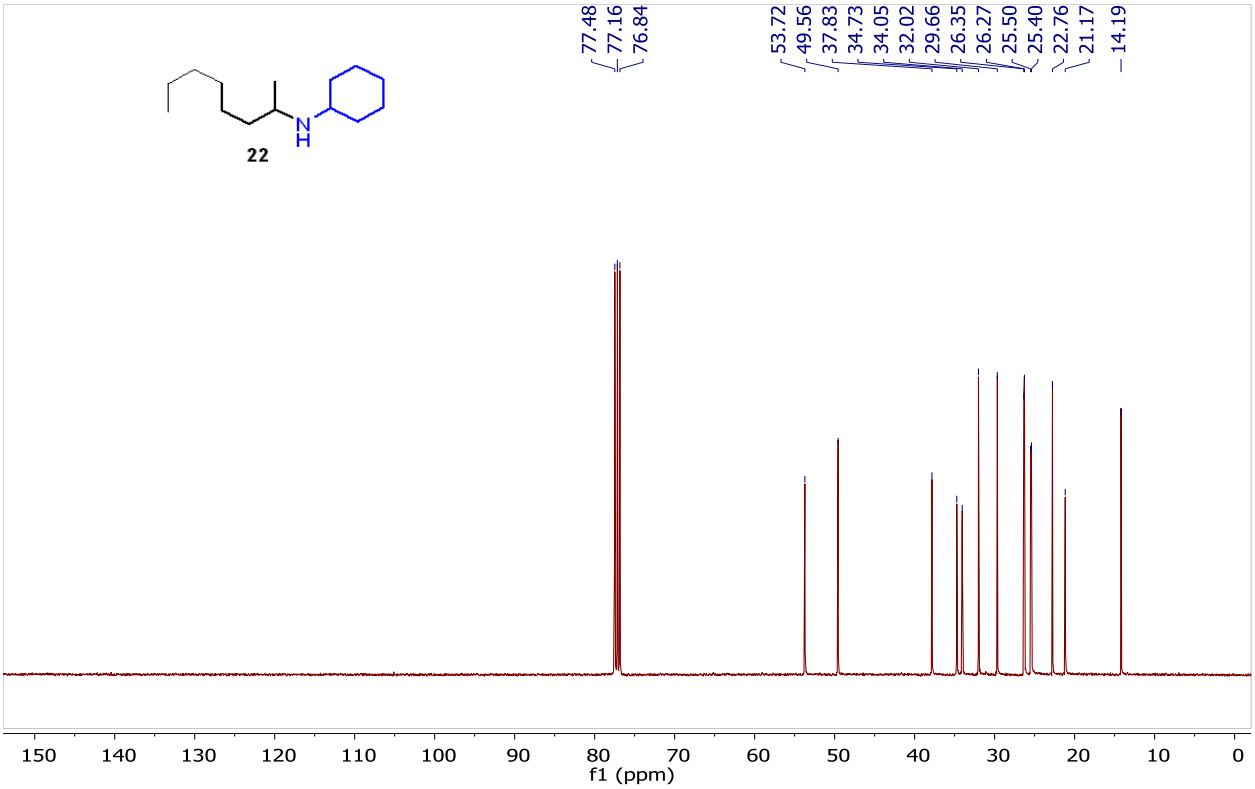
22
1.00 0.96 2.01 2.00 1.10 18.87 3.22
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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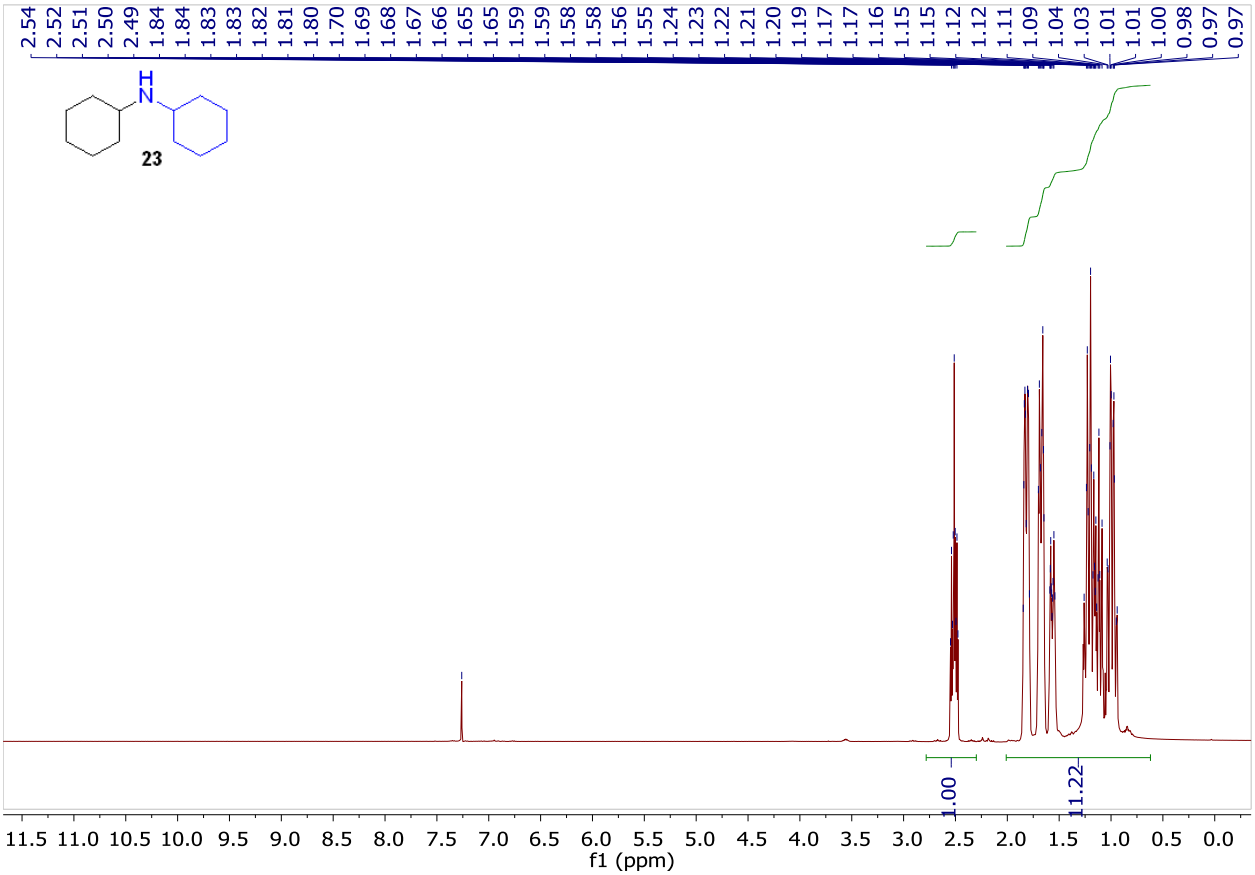
53.72 49.56 37.83 34.73 34.05 32.02 29.66 26.35 26.27 25.50 25.40 22.76 21.17 14.19
22
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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23
1.00
11.22
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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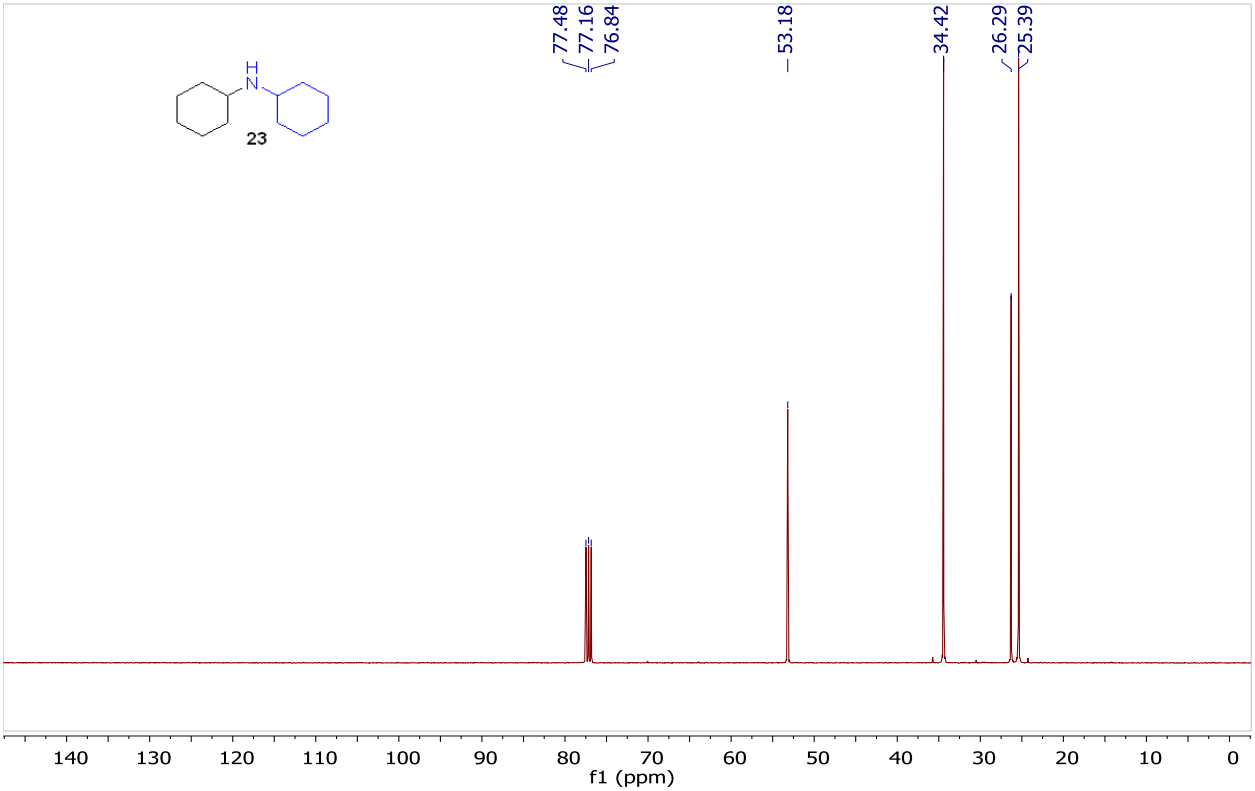
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77.16
76.84
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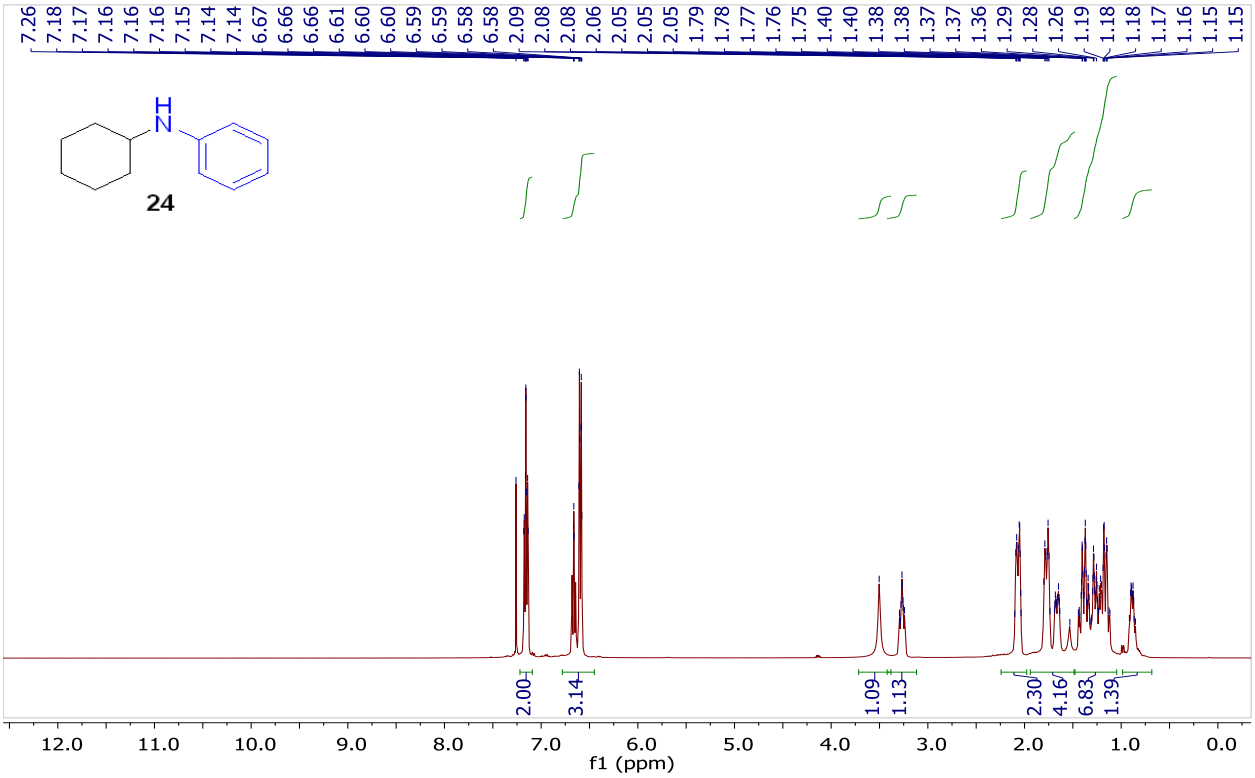
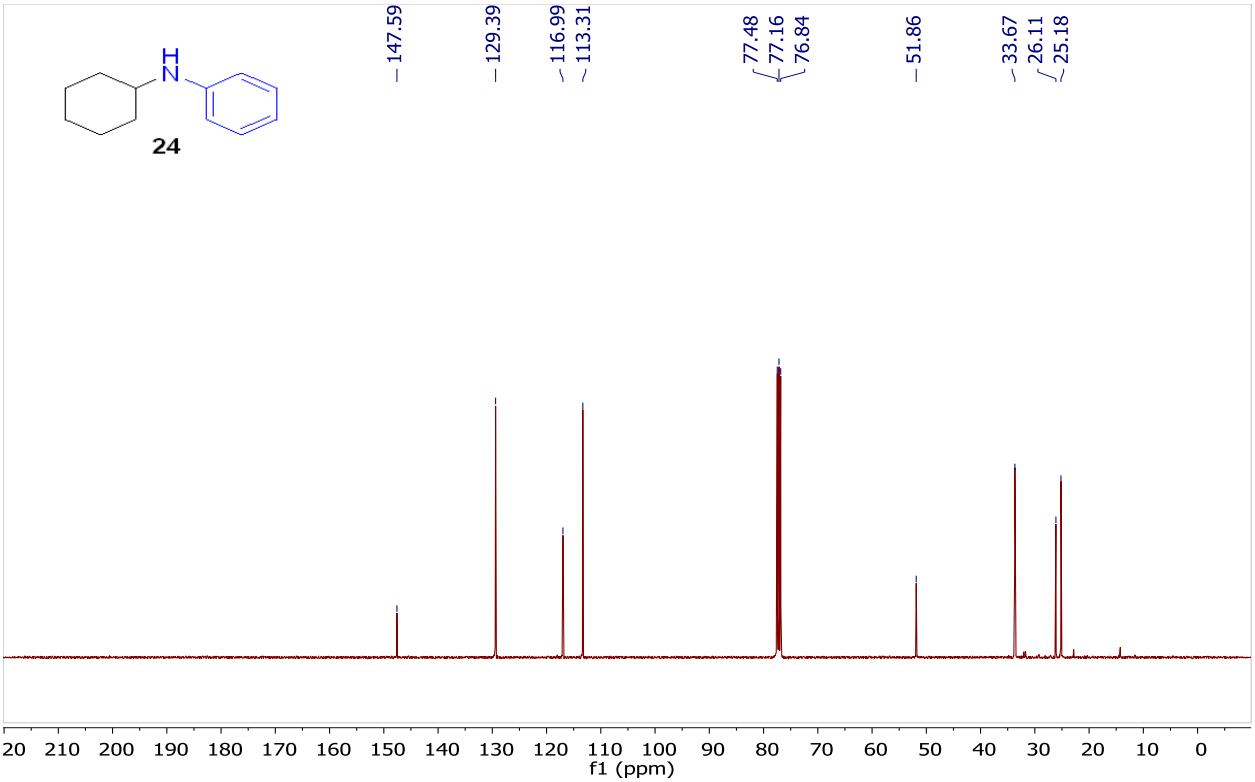
34.42
26.29
25.39
23
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26 7.18 7.17 7.16 7.16 7.16 7.15 7.14 7.14 6.67 6.66 6.66 6.61 6.60 6.60 6.59 6.59 6.58 6.58 2.09 2.08 2.08 2.06 2.05 2.05 2.05 1.79 1.78 1.77 1.76 1.75 1.40 1.38 1.38 1.37 1.37 1.36 1.29 1.28 1.26 1.19 1.18 1.18 1.17 1.16 1.15 1.15
H
N
24
2.00 3.14 1.09 1.13 2.30 4.16 6.83 1.39
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


147.59 129.39 116.99 113.31 77.48 77.16 76.84 51.86 33.67 26.11 25.18
H
N
24
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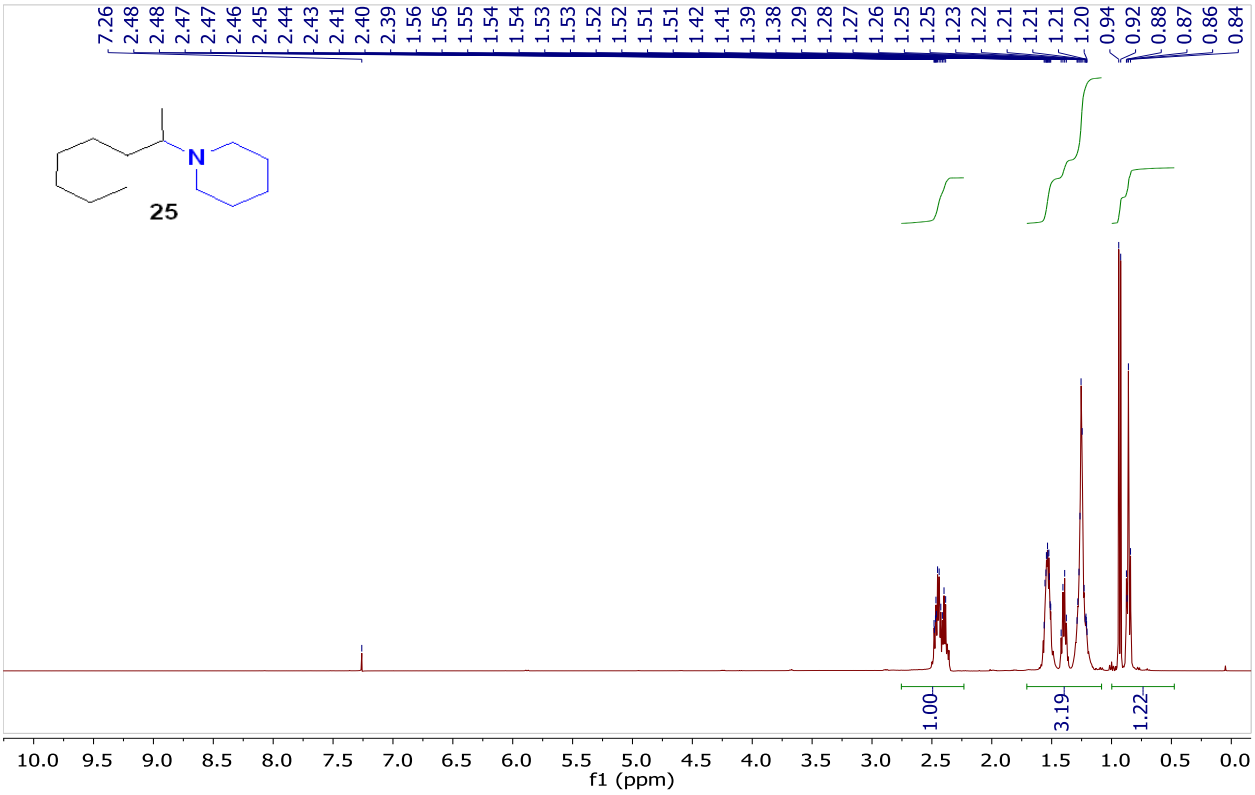
f1 (ppm)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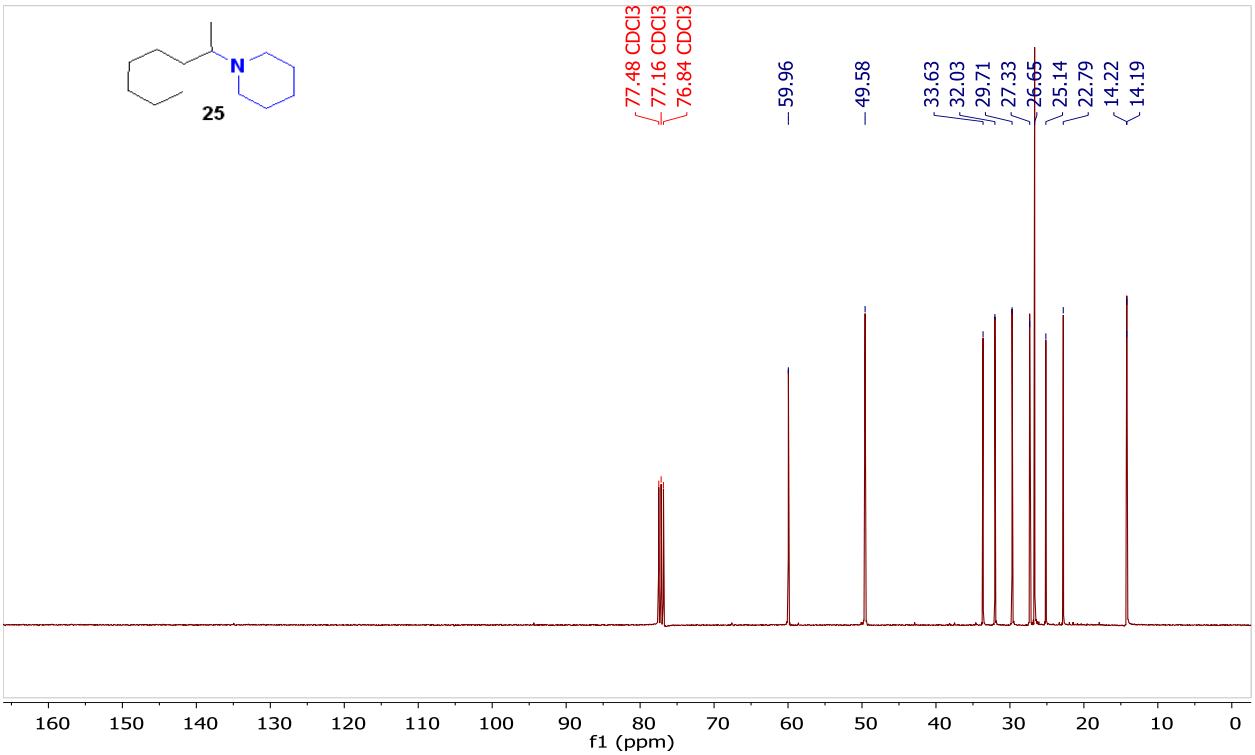
N
25
1.00
3.19
1.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


N
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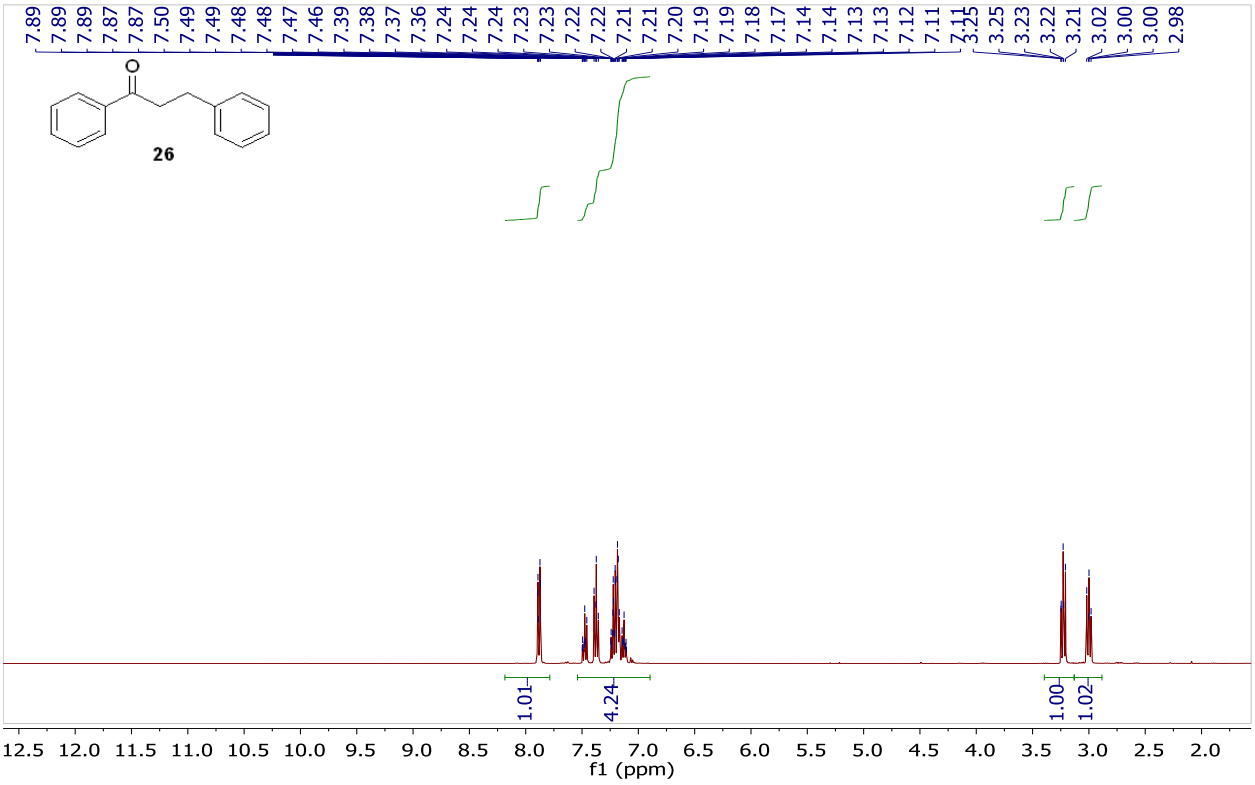
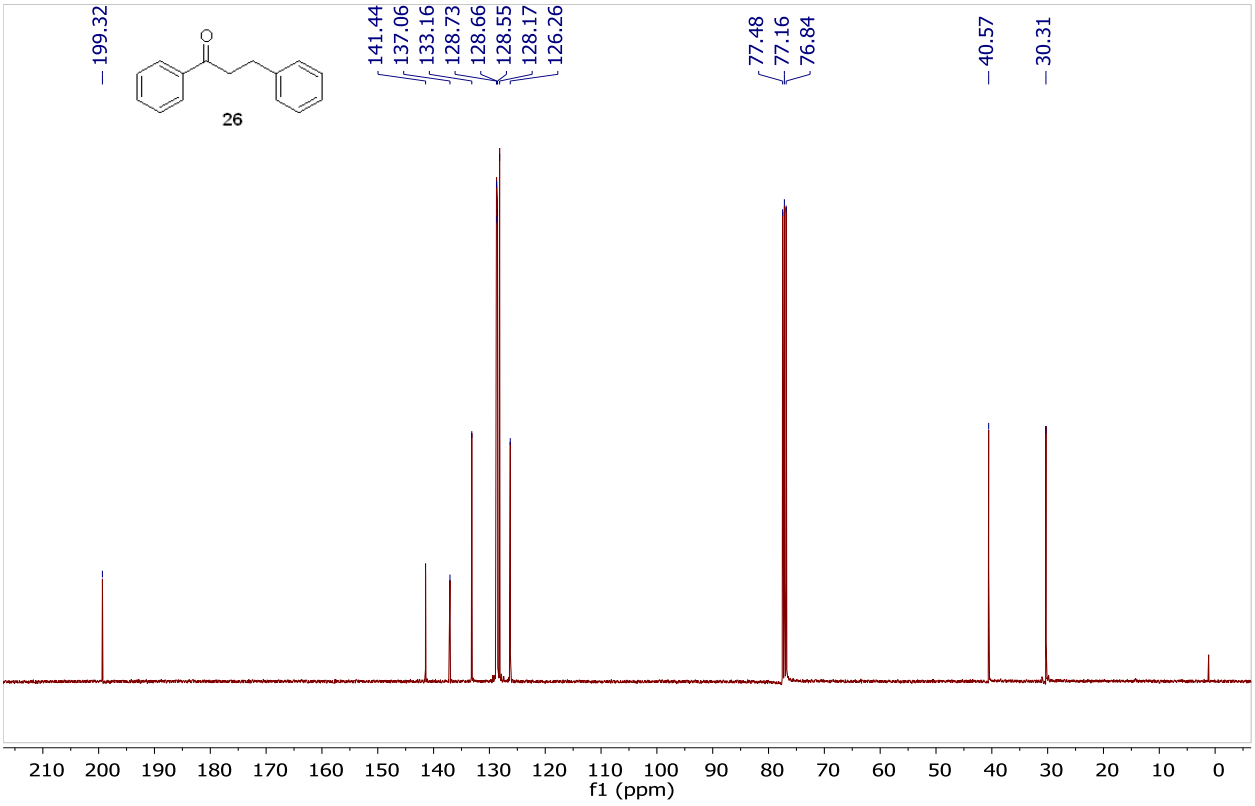
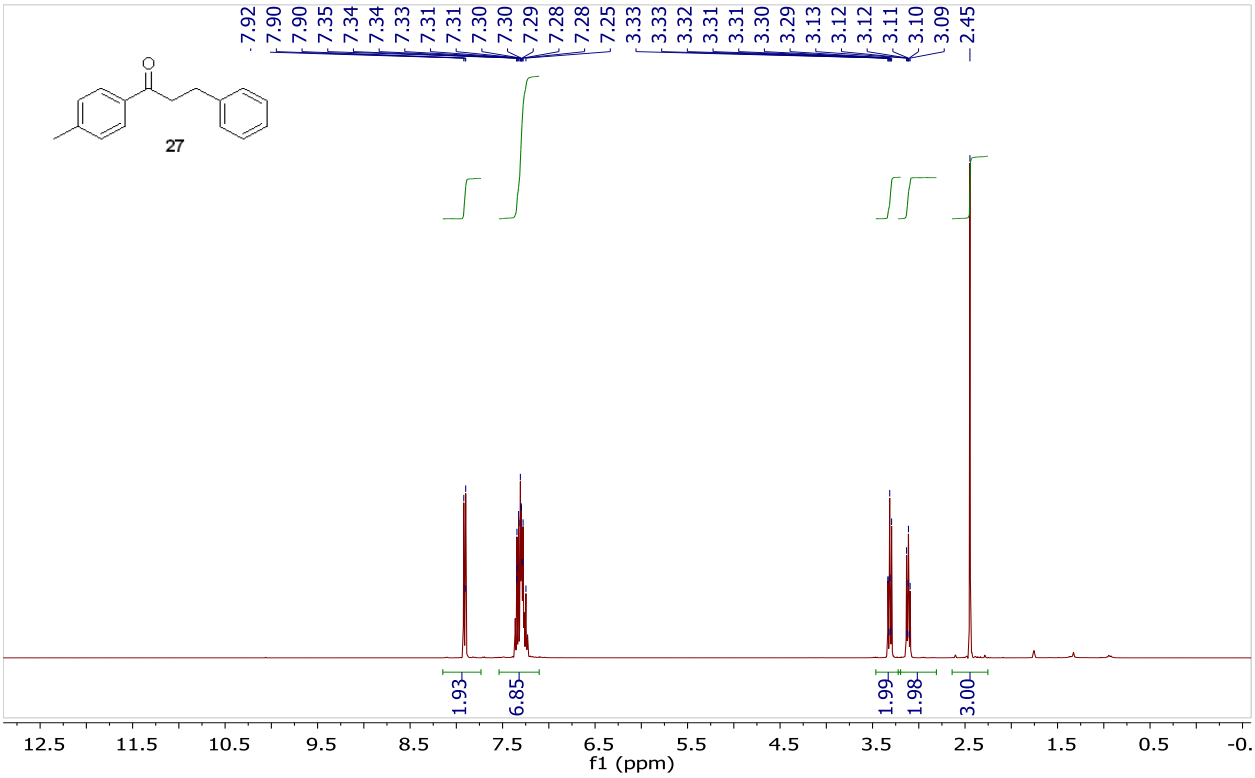
77.16 CDCl3
76.84 CDCl3
59.96
49.58
33.63
32.03
29.71
27.33
26.65
25.14
22.79
14.22
14.19
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.89 7.89 7.89 7.87 7.87 7.50 7.49 7.49 7.48 7.48 7.47 7.46 7.39 7.38 7.37 7.36 7.24 7.24 7.24 7.23 7.23 7.22 7.22 7.21 7.21 7.20 7.19 7.19 7.18 7.17 7.14 7.14 7.13 7.13 7.12 7.11 7.11 3.25 3.25 3.23 3.22 3.21 3.02 3.00 3.00 2.98
26
1.01
4.24
1.00
1.02
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
f1 (ppm)


199.32
141.44 137.06 133.16 128.73 128.66 128.55 128.17 126.26
77.48 77.16 76.84
40.57
30.31
26
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.90
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7.33
7.31
7.31
7.30
7.30
7.29
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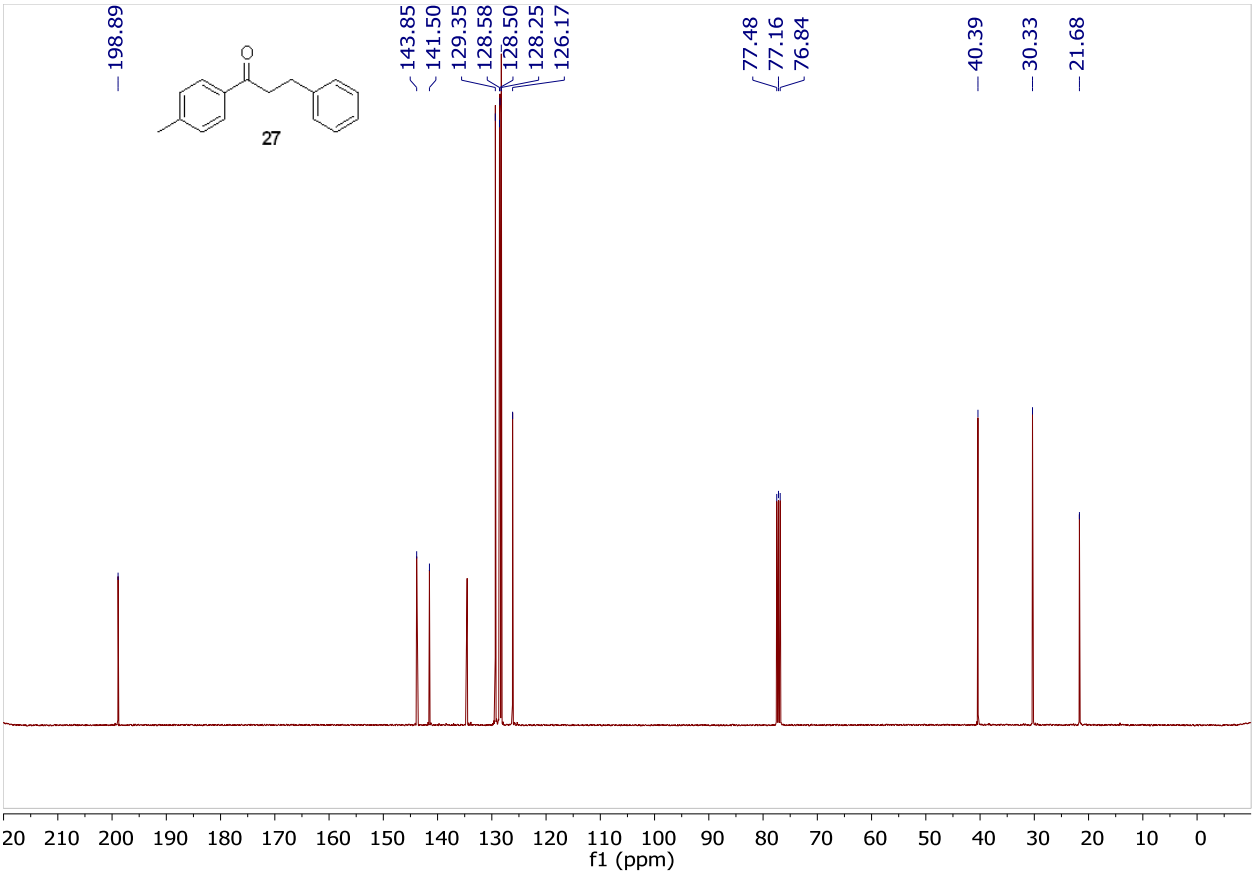
7.28
7.25
3.33
3.33
3.32
3.31
3.31
3.30
3.29
3.13
3.12
3.12
3.11
3.10
3.09
2.45
27
1.93
6.85
1.99
1.98
3.00
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.
f1 (ppm)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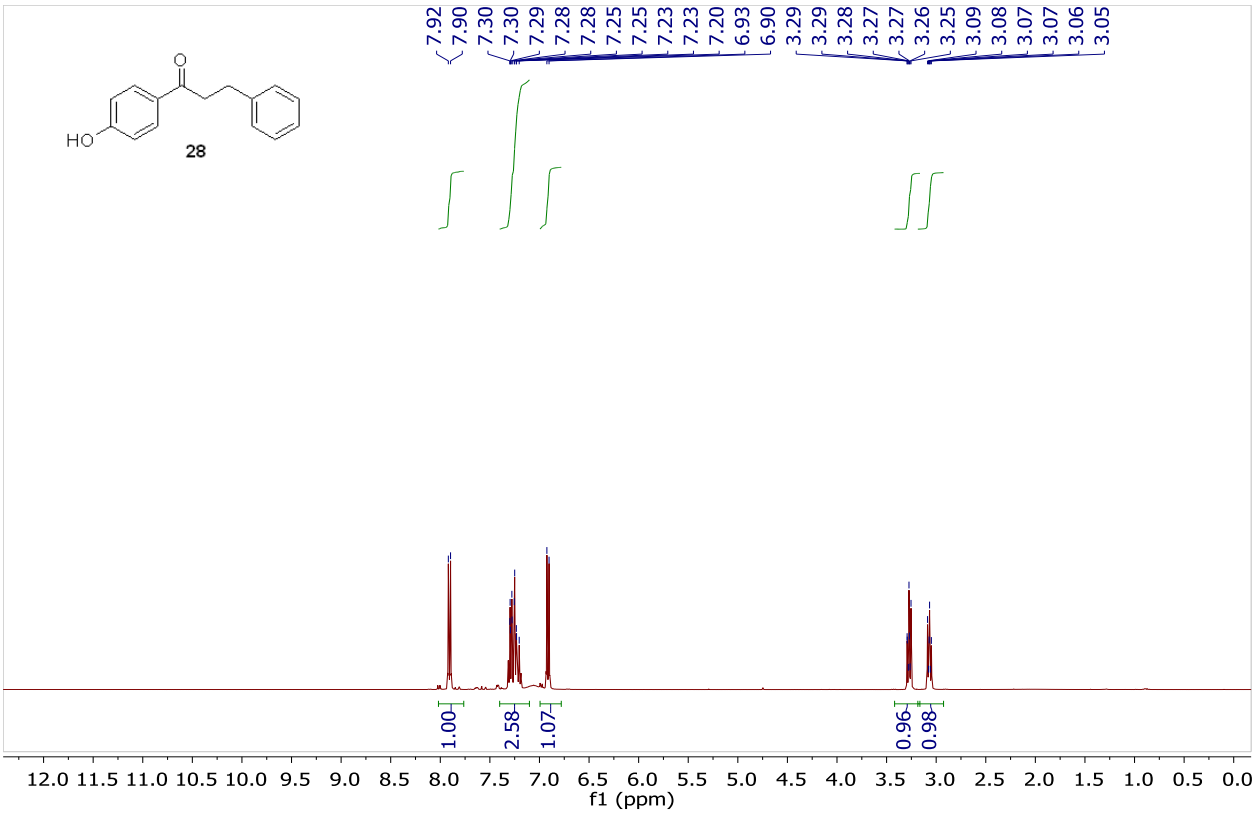
128.50
128.25
126.17
77.48
77.16
76.84
40.39
30.33
21.68
27
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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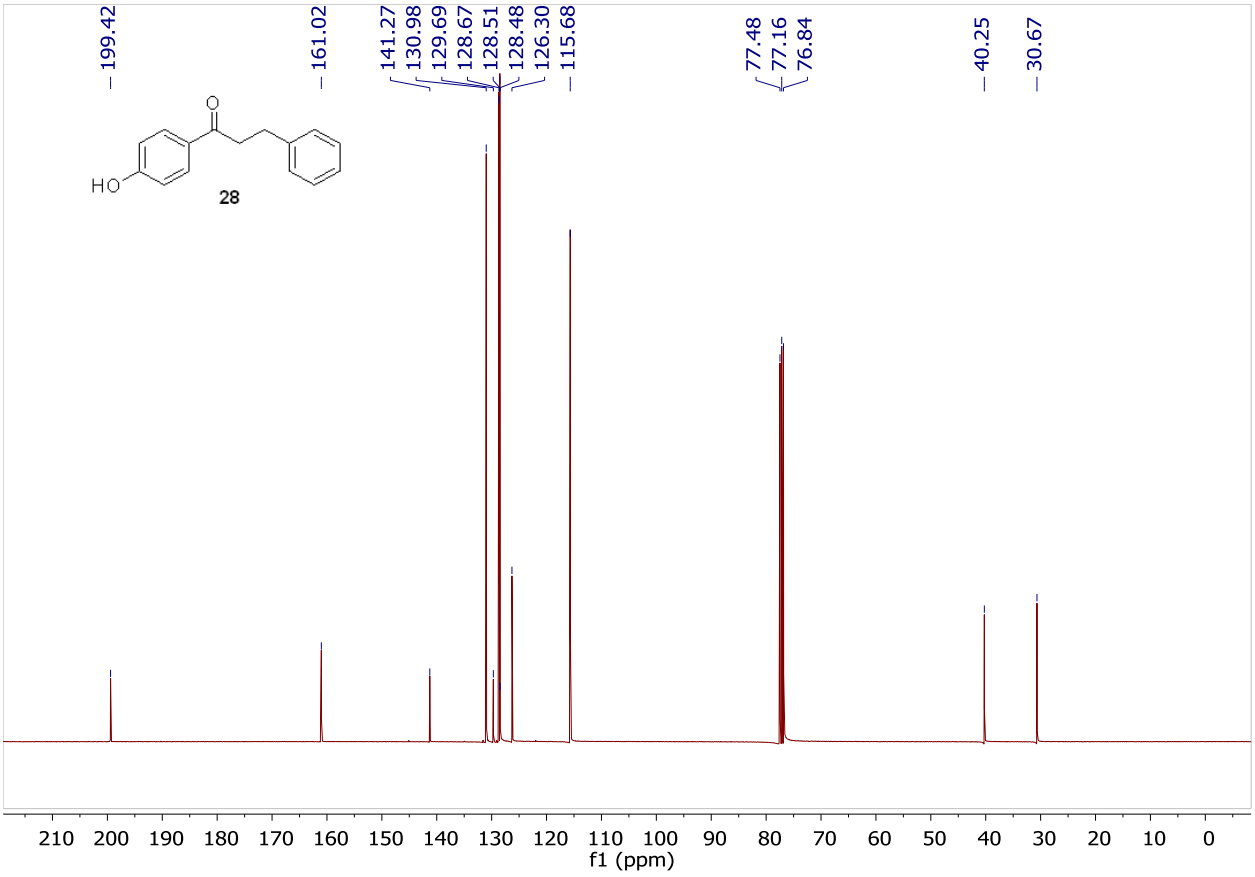
7.30
7.30
7.29
7.28
7.28
7.25
7.25
7.23
7.23
7.20
6.93
6.90
3.29
3.29
3.28
3.27
3.27
3.26
3.25
3.09
3.08
3.07
3.07
3.06
3.05
HO
28
1.00
2.58
1.07
0.96
0.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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161.02
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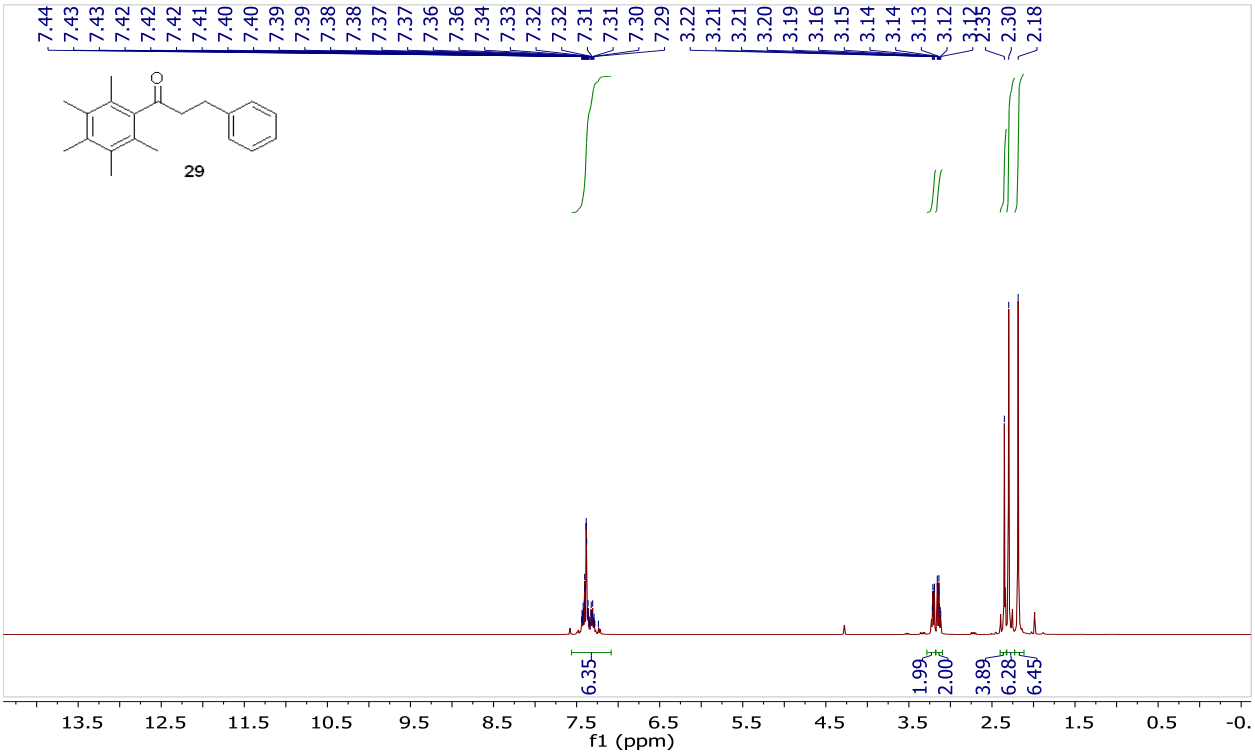
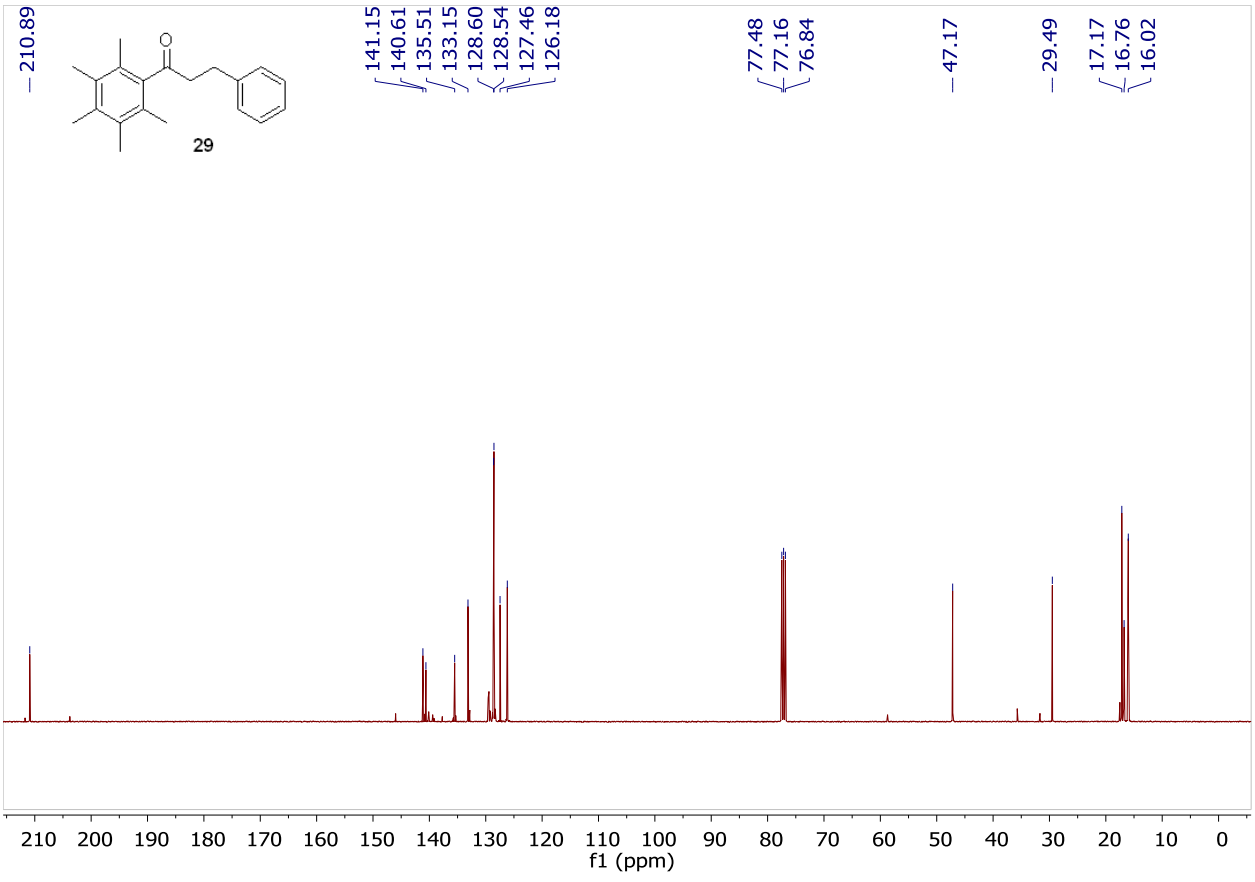
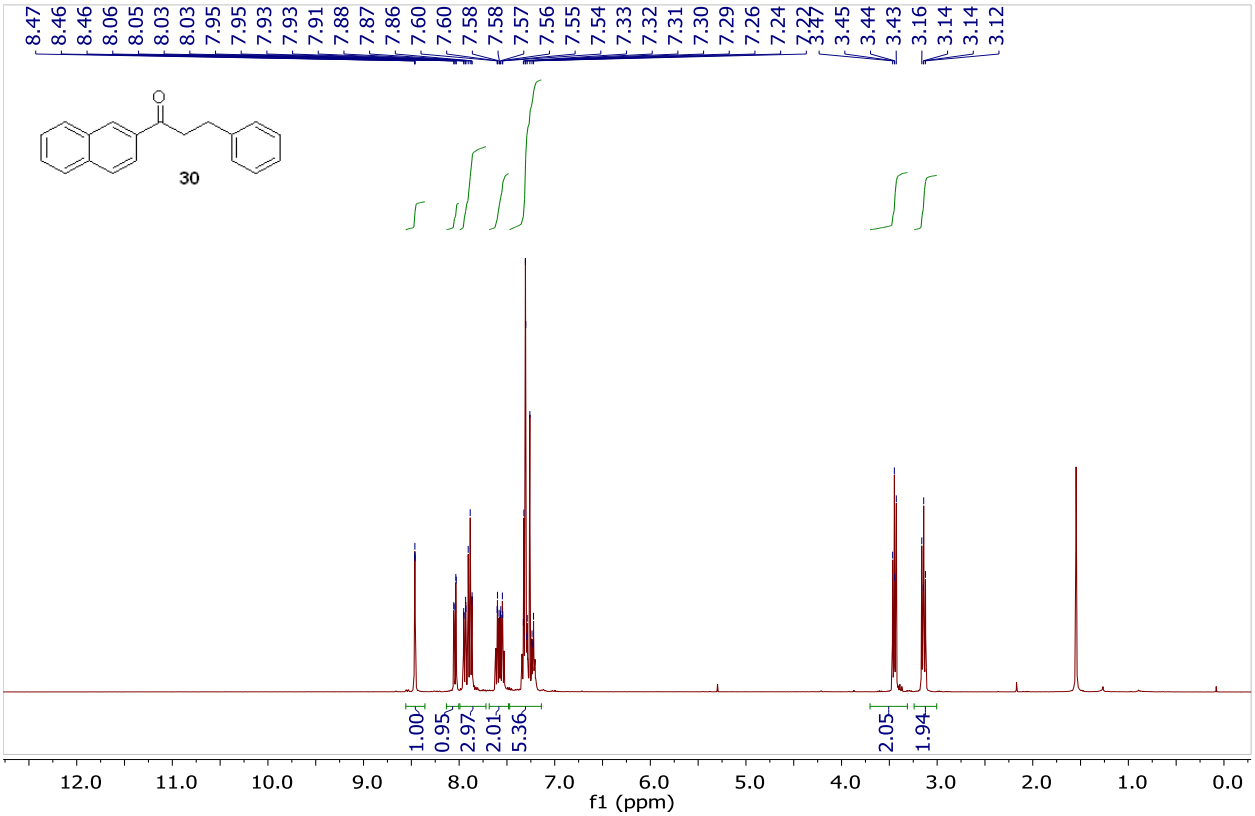
128.67
128.51
128.48
126.30
115.68
77.48
77.16
76.84
40.25
30.67
HO
28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.44 7.43 7.43 7.42 7.42 7.42 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.36 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.29 3.22 3.21 3.21 3.20 3.19 3.16 3.15 3.14 3.14 3.13 3.12 2.35 2.30 2.18
29
6.35 1.99 2.00 3.89 6.28 6.45
13.5 12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.
f1 (ppm)


210.89
141.15 140.61 135.51 133.15 128.60 128.54 127.46 126.18
77.48 77.16 76.84
47.17
29.49
17.17 16.76 16.02
29
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.46
8.46
8.06
8.05
8.03
8.03
7.95
7.95
7.93
7.93
7.91
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7.87
7.86
7.60
7.60
7.58
7.58
7.57
7.56
7.55
7.54
7.33
7.32
7.31
7.30
7.29
7.26
7.24
7.22
3.47
3.45
3.44
3.43
3.16
3.14
3.14
3.12
30
1.00
0.95
2.97
2.01
5.36
2.05
1.94
12.0
11.0
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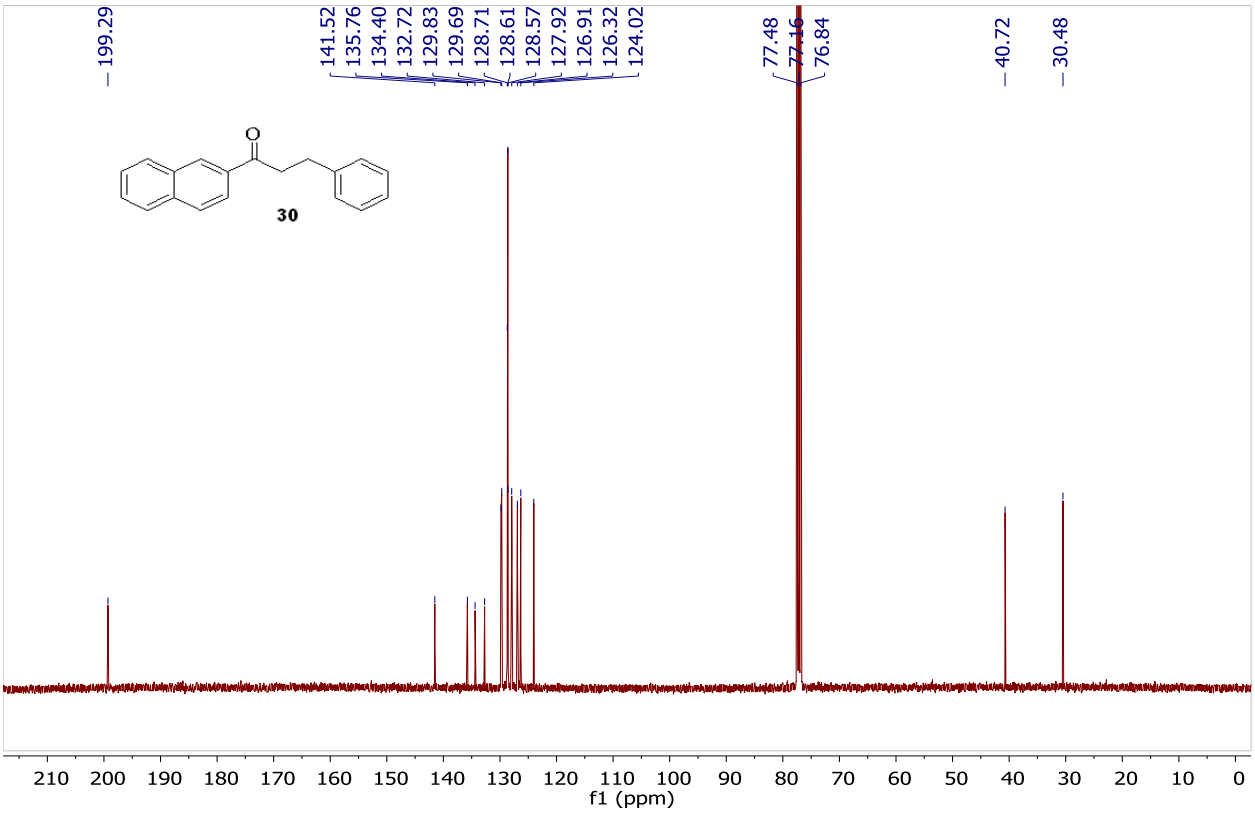
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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127.92
126.91
126.32
124.02
77.48
77.16
76.84
40.72
30.48
30
210
200
190
180
170
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130
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110
100
90
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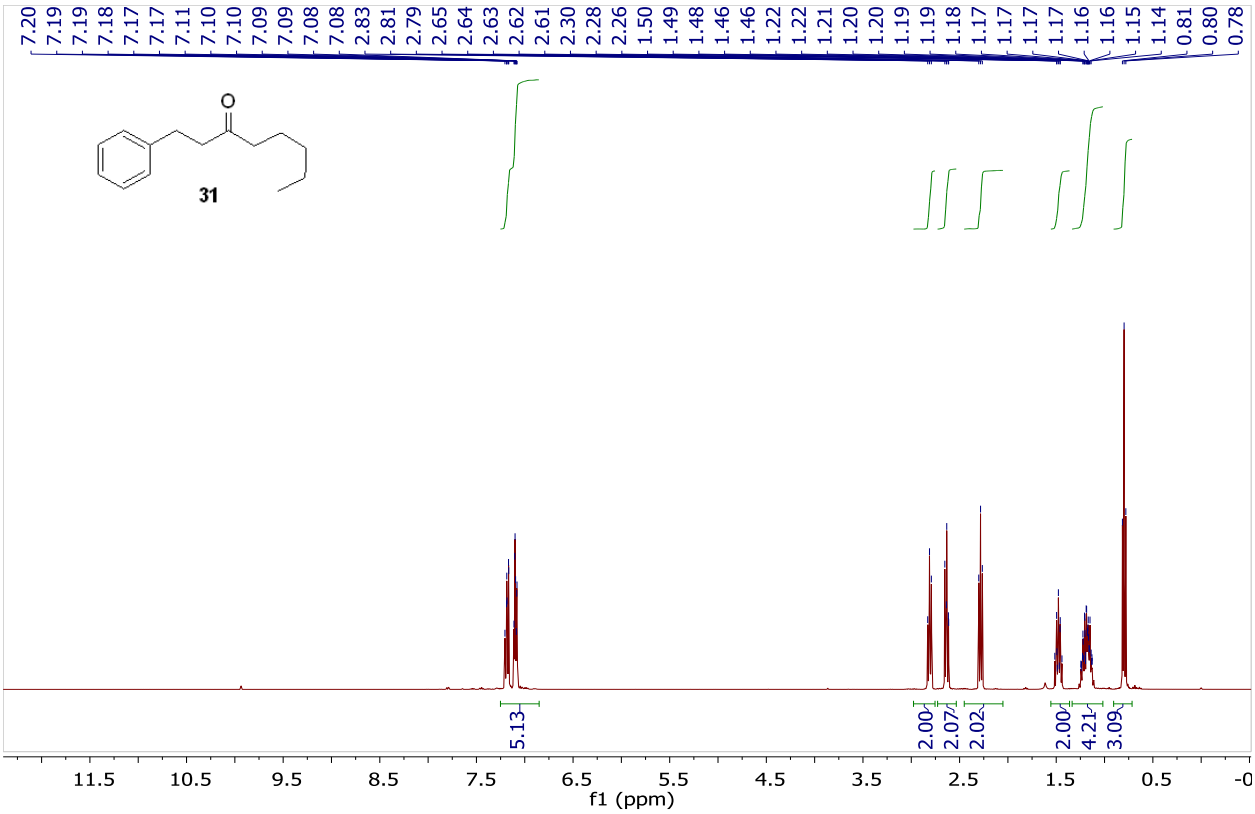
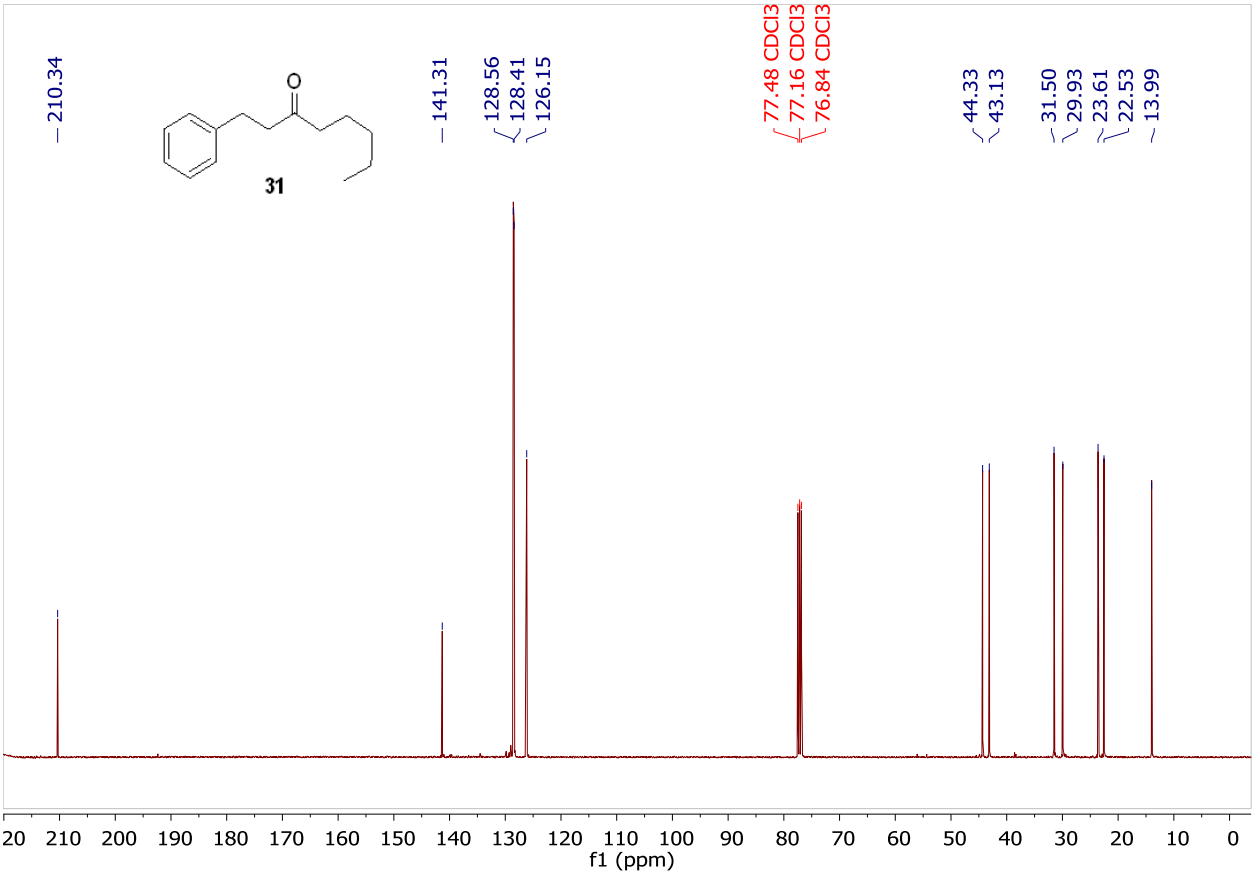
70
60
50
40
30
20
10
0
f1 (ppm)


7.20 7.19 7.19 7.18 7.17 7.17 7.11 7.10 7.10 7.09 7.09 7.08 7.08 2.83 2.81 2.79 2.65 2.64 2.63 2.62 2.61 2.30 2.28 2.26 1.50 1.49 1.48 1.46 1.46 1.22 1.22 1.21 1.20 1.20 1.19 1.19 1.18 1.17 1.17 1.17 1.17 1.16 1.16 1.15 1.14 0.81 0.80 0.78
O
31
5.13
2.00
2.07
2.02
2.00
4.21
3.09
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0
f1 (ppm)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O
31
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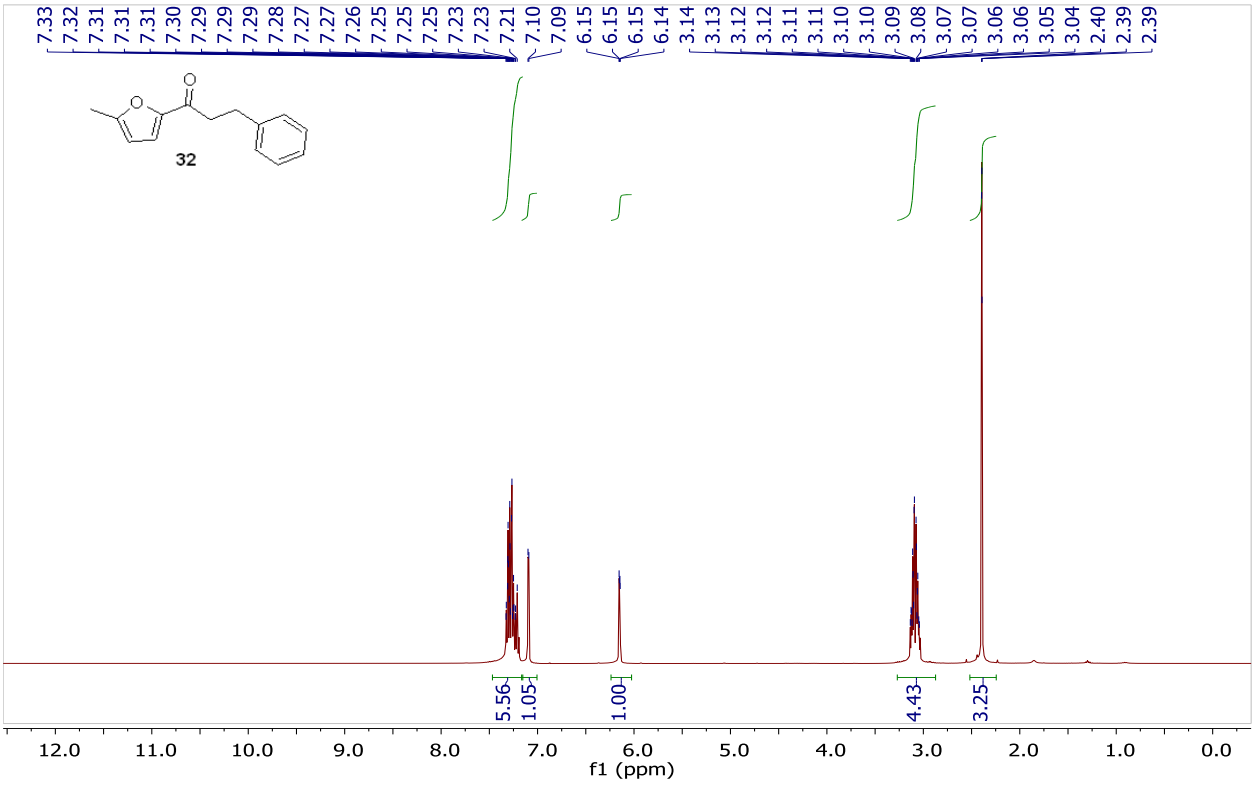
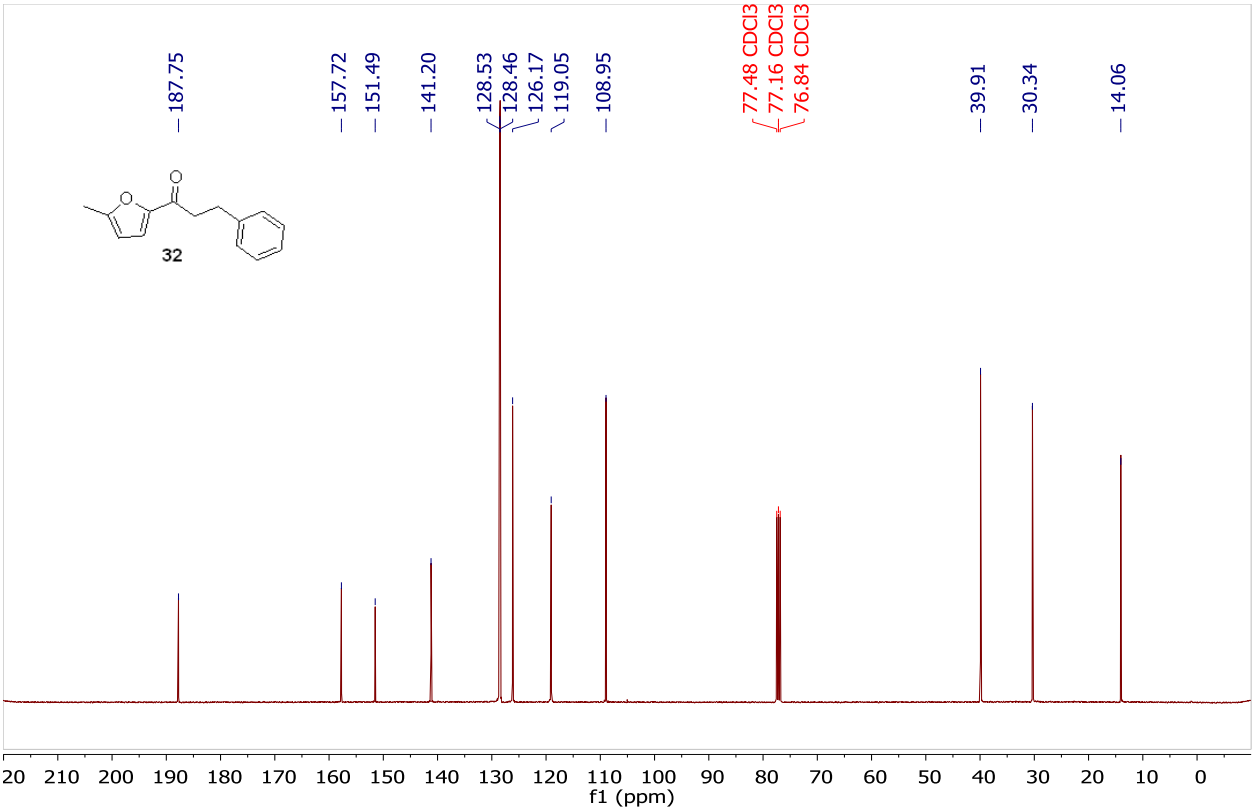
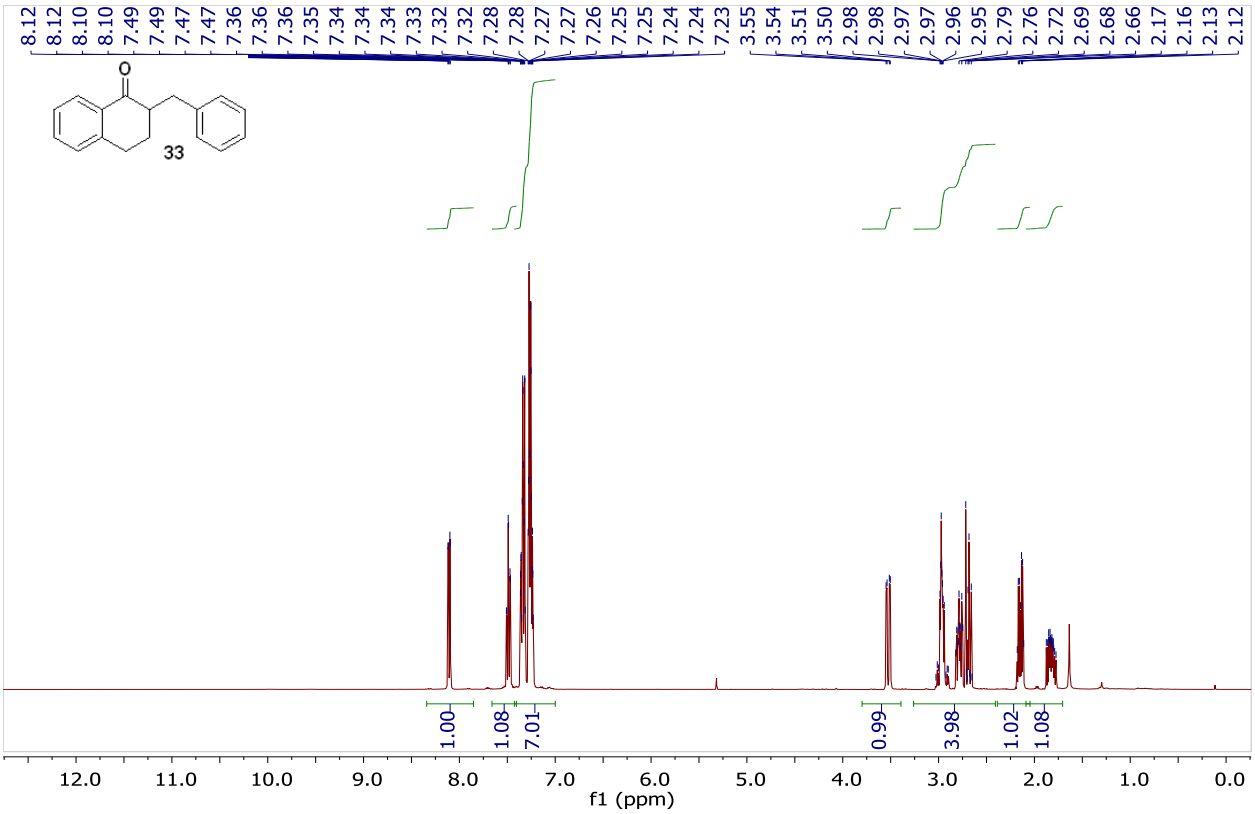
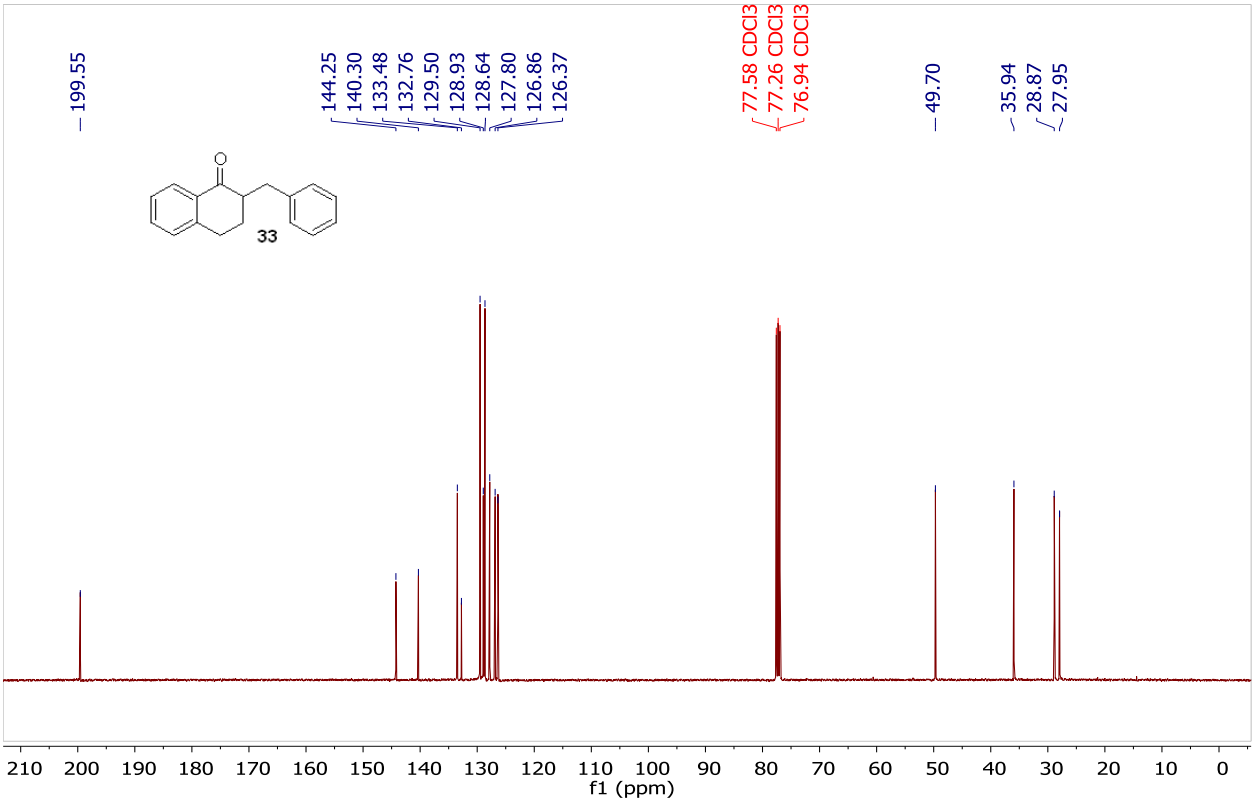
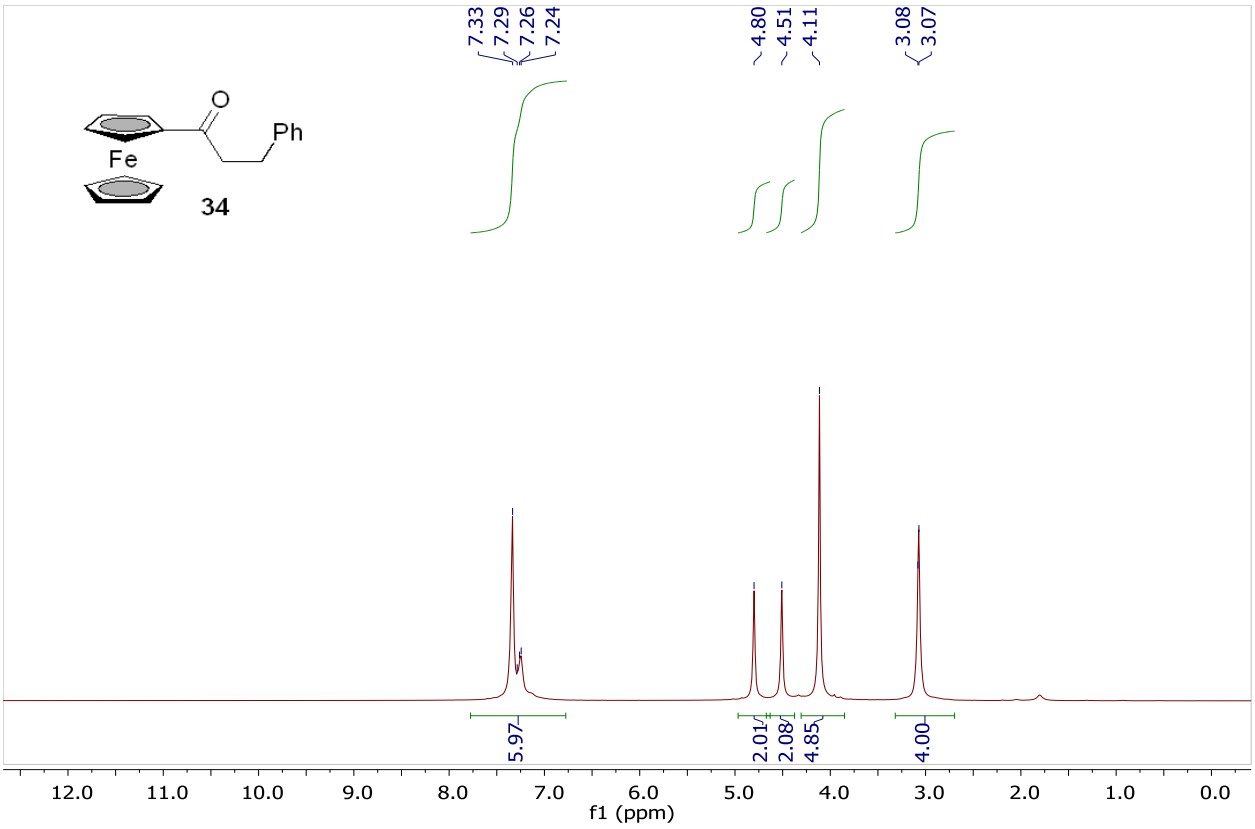
128.41
126.15
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
44.33
43.13
31.50
29.93
23.61
22.53
13.99
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.33 7.32 7.31 7.31 7.31 7.30 7.29 7.29 7.29 7.28 7.27 7.27 7.26 7.25 7.25 7.25 7.23 7.23 7.21 7.10 7.09 6.15 6.15 6.15 6.14 3.14 3.13 3.12 3.12 3.11 3.11 3.10 3.10 3.09 3.08 3.07 3.07 3.06 3.06 3.05 3.04 2.40 2.39 2.39
32
5.56 1.05 1.00 4.43 3.25
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


187.75 157.72 151.49 141.20 128.53 128.46 126.17 119.05 108.95 77.48 CDCl3 77.16 CDCl3 76.84 CDCl3 39.91 30.34 14.06
32
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.12 8.12 8.10 8.10 7.49 7.49 7.47 7.47 7.36 7.36 7.36 7.35 7.34 7.34 7.34 7.33 7.32 7.32 7.28 7.28 7.27 7.27 7.26 7.25 7.25 7.24 7.24 7.23 3.55 3.54 3.51 3.50 2.98 2.98 2.97 2.97 2.96 2.95 2.79 2.76 2.72 2.69 2.68 2.66 2.17 2.16 2.13 2.12
O
33
1.00 1.08 7.01 0.99 3.98 1.02 1.08
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


199.55
144.25 140.30 133.48 132.76 129.50 128.93 128.64 127.80 126.86 126.37
77.58 CDCl3 77.26 CDCl3 76.94 CDCl3
49.70
35.94 28.87 27.95
O
33
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.33
7.29
7.26
7.24
4.80
4.51
4.11
3.08
3.07
O
Ph
Fe
34
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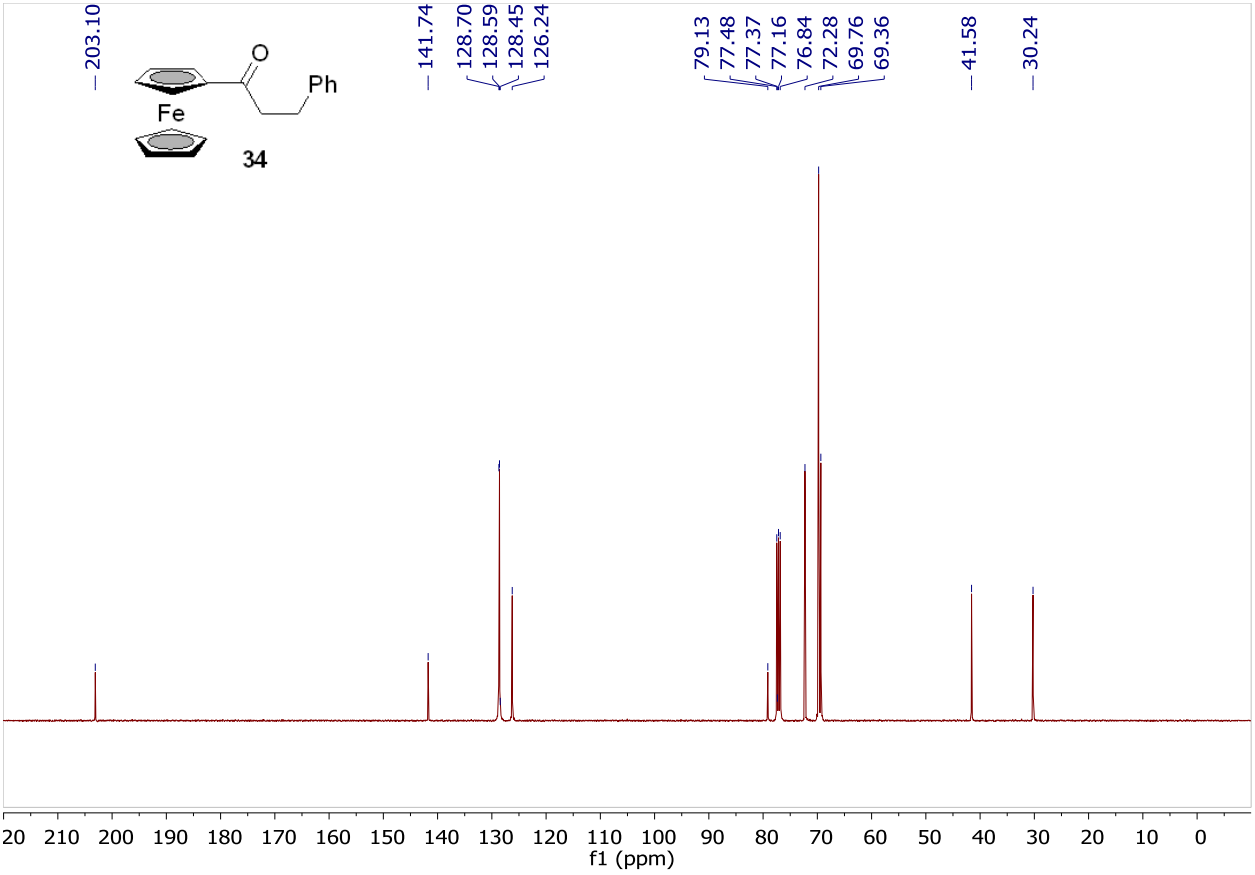
2.01
2.08
4.85
4.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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128.45
126.24
79.13
77.48
77.37
77.16
76.84
72.28
69.76
69.36
41.58
30.24
O
Ph
Fe
34
20
210
200
190
180
170
160
150
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130
120
110
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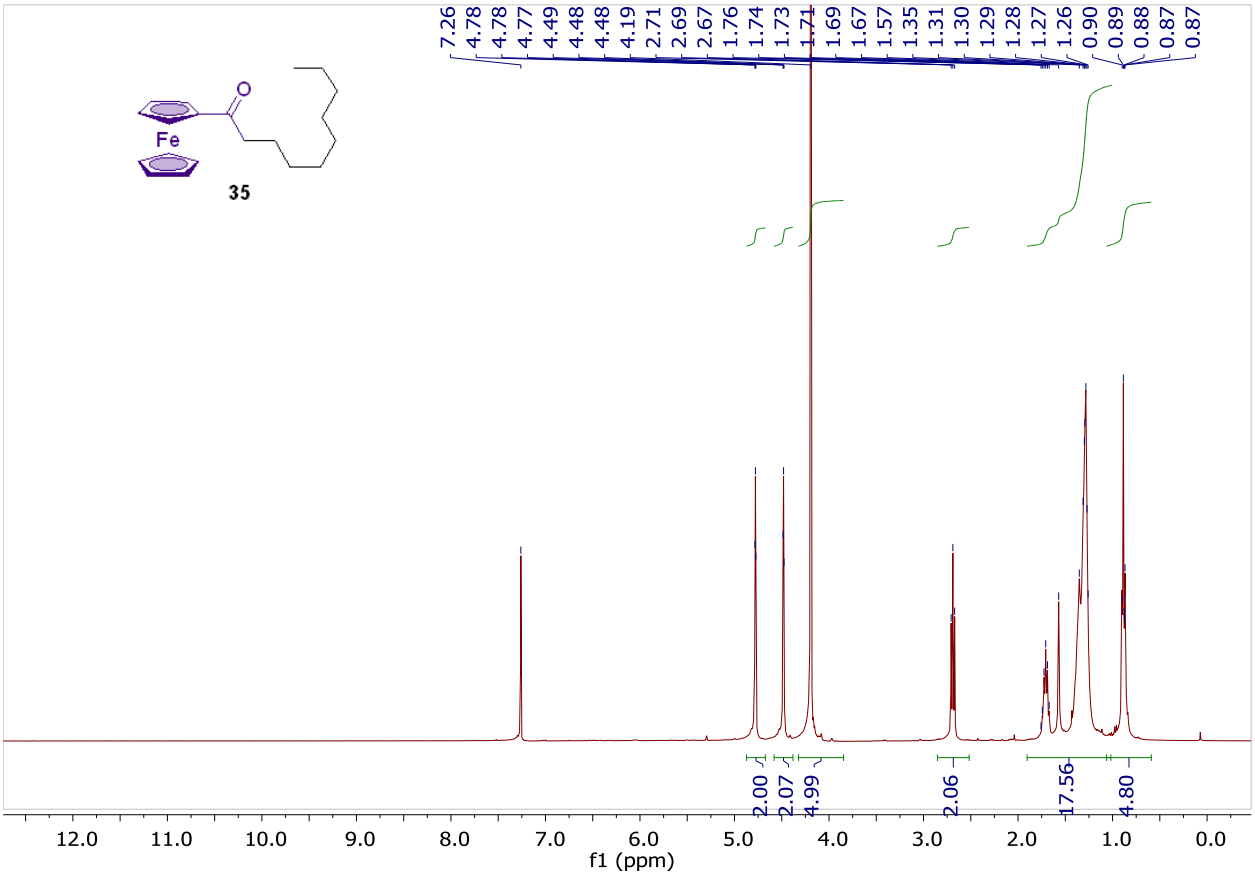
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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4.78
4.77
4.49
4.48
4.48
4.19
2.71
2.69
2.67
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1.73
1.71
1.69
1.67
1.57
1.35
1.31
1.30
1.29
1.28
1.27
1.26
0.90
0.89
0.88
0.87
0.87
Fe
O
35
2.00
2.07
4.99
2.06
17.56
4.80
12.0
11.0
10.0
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5.0
4.0
3.0
2.0
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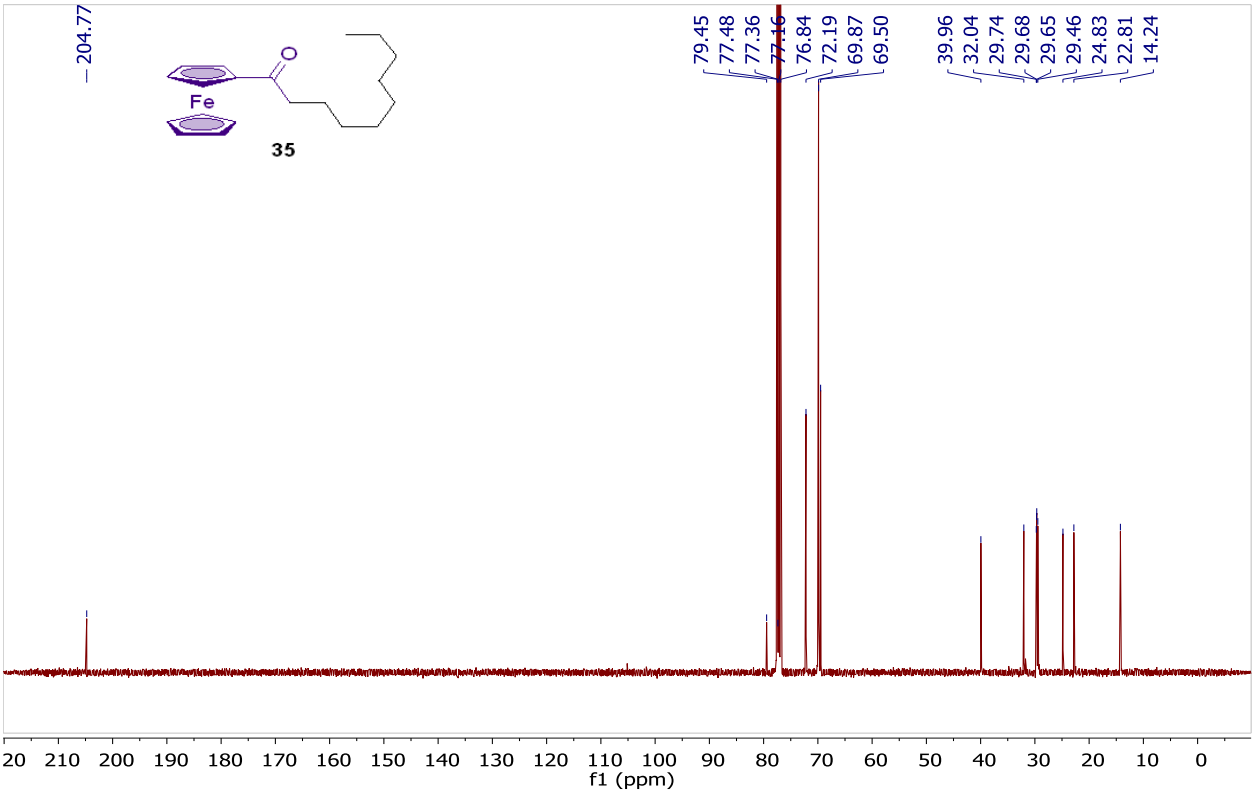
0.0
f1 (ppm)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77.48
77.36
77.16
76.84
72.19
69.87
69.50
39.96
32.04
29.74
29.68
29.65
29.46
24.83
22.81
14.24
Fe
O
35
20
210
200
190
180
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140
130
120
110
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90
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50
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30
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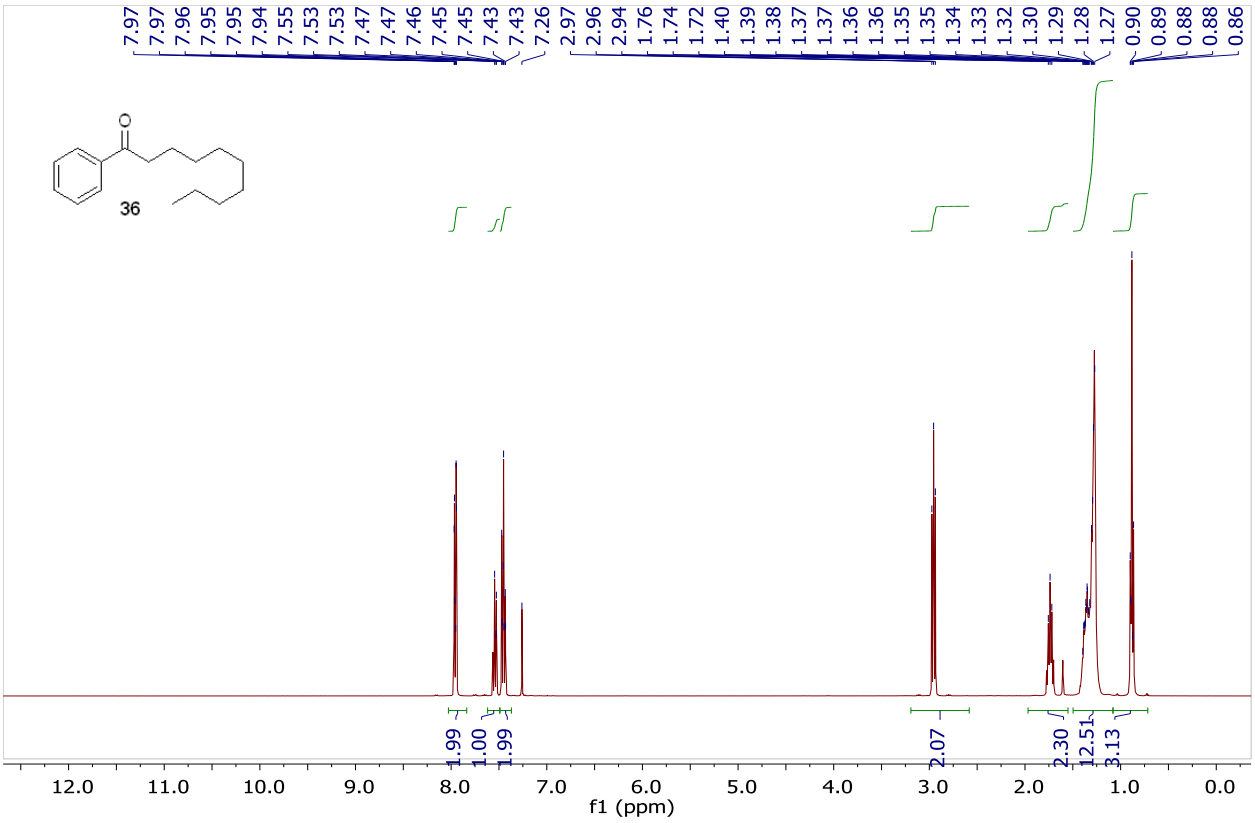
f1 (ppm)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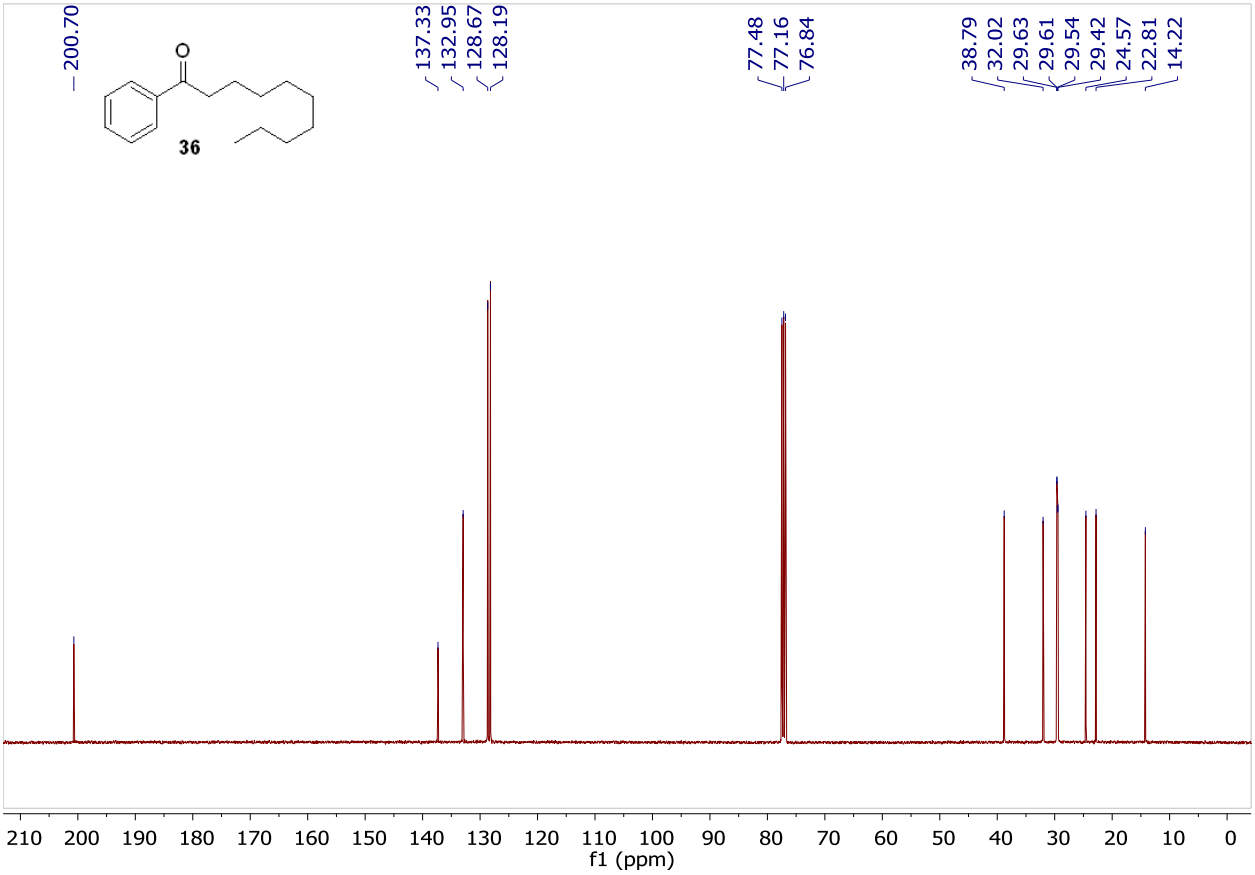
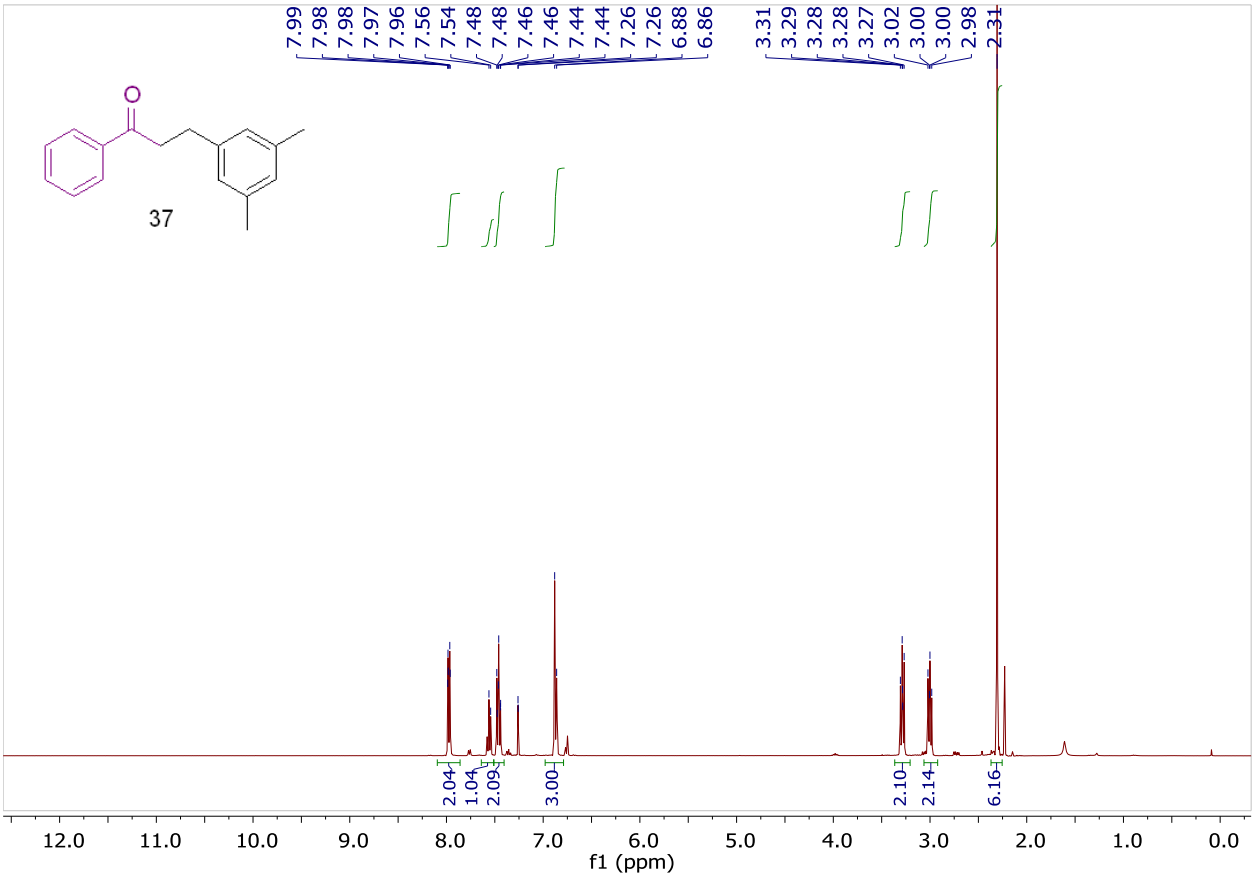
2.97 2.96 2.94 1.76 1.74 1.72 1.40 1.39 1.38 1.37 1.37 1.36 1.36 1.35 1.35 1.34 1.33 1.32 1.30 1.29 1.28 1.27 0.90 0.89 0.88 0.88 0.86
O
36
1.99 1.00 1.99 2.07 2.30 12.51 3.13
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


200.70
137.33 132.95 128.67 128.19
77.48 77.16 76.84
38.79 32.02 29.63 29.61 29.54 29.42 24.57 22.81 14.22
O
36
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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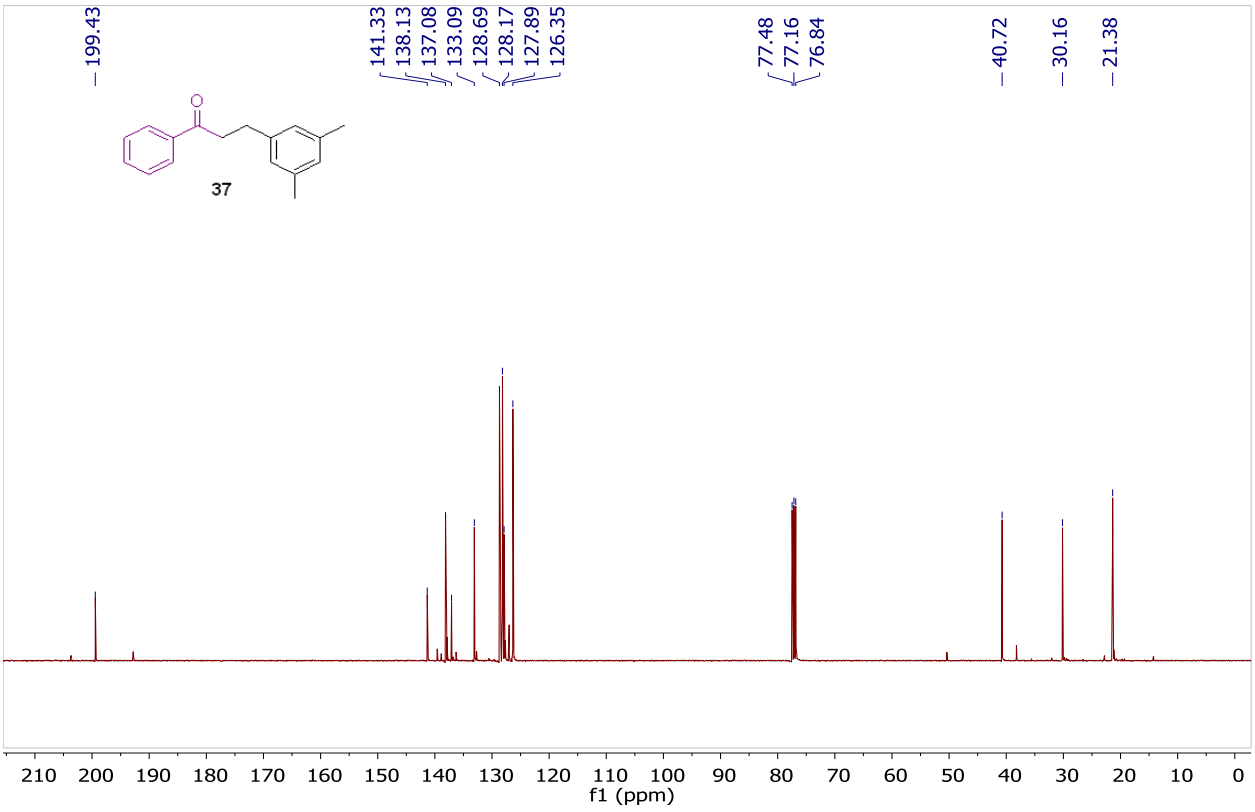
7.98
7.98
7.97
7.96
7.56
7.54
7.48
7.48
7.46
7.46
7.44
7.44
7.26
7.26
6.88
6.86
3.31
3.29
3.28
3.28
3.27
3.02
3.00
3.00
2.98
2.31
37
2.04
1.04
2.09
3.00
2.10
2.14
6.16
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


199.43
141.33
138.13
137.08
133.09
128.69
128.17
127.89
126.35
77.48
77.16
76.84
40.72
30.16
21.38
37
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)