Supporting Information

For

Reductive amination using a combination of CaH_2 and noble metal

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1. General information

All reagents were obtained from commercial sources and used as received. CaH_2 90-95% 2 mm & down (ref: 19106) was purchased from Alfa Aesar®. 5% Pt/SiO_2 (Escat 2351), 5% Pt/C (ref: 78-1600), 5% Pd/C (Escat 1431), 5% Pd/SiO_2 (Escat 1351), 5% Pd/alumina (ref: 46-1950) and 5% Ru/C (ref: 44-4050) were purchased from Strem Chemicals, Inc.. AcroSeal® solvents were used as received.

The complete references of the sealed tubes are: ACE pressure tubes, #15 Ace-Thred, order code (8648-03), length (10.2 cm), body O.D. (25.4 mm), capacity (15 mL), pressure rating (150 PSI or 10.3 bar). The pressure tube was closed by a back seal PTFE plug 5845 associated with an 210 O-ring for #15 Ace-Thred in FETFE™ or silicone.

All reactions were performed under an inert atmosphere of argon. Silica gel (40–63 micron) was used for column chromatography. Thin layer chromatography was performed on precoated silica

gel 60–F 254 plates. UV light, phosphomolybdic acid and ninhydrine were used for analysis of the TLC plates.

All compounds were characterized by spectroscopic data. The nuclear magnetic resonance (NMR) spectra were recorded either on a Bruker ALS 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz), a DRX 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) or a Bruker DRX 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) spectrometer, in $CDCl_3$, CD_3OD or DMSO-d_6 at 293K. Chemical shifts are reported in parts per million (ppm) and are calibrated on residual solvent peaks: $CDCl_3$ 7.26 ppm in ^{1}H and 77.16 ppm in ^{13}C, CD_3OD 3.31 ppm in ^{1}H and 49.00 ppm in ^{13}C or DMSO-d_6 2.50 ppm in ^{1}H and 39.52 ppm in ^{13}C.[1] Spin-spin coupling constants (*J)* are given in Hz. The peak patterns are indicated as follows: (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and br. for broad).

IR spectra were recorded on a Spectro Nicolet IS10 Smart ITR with an ATR diamond. Melting points were recorded on a Heizbank system Kofler Type WME (Wagner & Munz).

High-Resolution Mass Spectra (HRMS) mass spectra were recorded on MicroTOFQ II - Bruker Daltonics spectrometer with an Electrospray Ionization (ESI) ion source.
GC-MS analyses were performed on a DSQ - Thermofinnigan spectrometer equipped with quadrupole analyzer and a DB-5MS capillary column (30.0 m × 0.25mm × 0.25µm). The carrier gas was helium, at a flow rate of 1 mL/min. Column temperature was initially 70 °C for 2 min, then gradually increased to 310 °C at 15 °C/min and finally kept at 310 °C for 10 min. The injector temperature was 220 °C and the transfer line temperature was 280 °C.

GC analyses were performed on a Shimadzu Gas Chromatograph GC-2025 equipped with a ZB-5-MS column (30.0 m × 0.25mm × 0.25µm). The carrier gas was N_2 at a flow rate of 1.27 mL/min. Column temperature was initially 70 °C for 2 min, then gradually increased to 280 °C at 15 °C/min and finally kept at 280 °C for 15 min. The injector temperature was 250 °C and for detection a FID was used at 280 °C.

2. General procedure

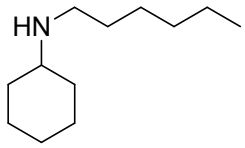
In a sealed tube was introduced dodecane (68 mg, 0.4 mmol, 10 mol%) as internal standard, followed by a carbonyl derivative (4 mmol, 1 equiv.), an amine (4 mmol, 1 equiv.) and toluene (2

[1] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997,** *62,* 7512-7515.

mL, [S] = 2 M) as solvent if one of the starting material was solid. The reaction was inerted under argon, followed by the addition of Pt/C 5% (155 mg, 0,04 mmol, 1 mol%) and CaH_2 90 % (110 mg, 0.6 equiv.). After the addition of CaH_2, the sealed tube was rapidly closed because exothermic gas evolution might appear rapidly. The tube was then introduced in a preheated oil bath at 60 °C and stirred with rpm of 700 at this temperature for 15 h. The reaction was cooled to room temperature, suspended in ethyl acetate, filtered on a pad of celite. The filtrate was introduced in a 250 mL volumetric flask and completed. A sample of the solution was injected in GC. From the relative area of the product and the dodecane, the rate formation of the different products of the reaction could be inferred. The filtrate was evaporated and purified by flash column chromatography using a gradient of dichloromethane / methanol: 100 / 0 to 8 / 2. If necessary the compound was transformed to its hydrochloride salt: after dissolution in ether, addition of excess of HCl (1 M in ether). The suspension was stirred one hour at room temperature, filtrated, washed with ether and dried.

Remark: Considering that 4 mmol of water can be generated, the maximum pressure at 60 °C in the pressure tube of 15 mL is 7 bar which is within the limit of the pressure tube.

3. Characterization

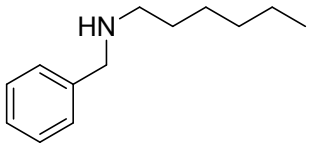


Chemical Formula: $C_{12}H_{25}N$
Molecular Weight: 183,33

***N*-hexyl-cyclohexylamine [4746-28-5] (3)**[2]

3 was obtained following the general procedure starting from cyclohexanone (471 mg, 4.8 mmol) and hexylamine (483 mg, 4.78 mmol, 1.00 equiv.). GC yield was determined by GC using dodecane as internal standard: 63%. Purification by flash column chromatography using a gradient of dichloromethane / methanol: 100 / 0 to 8 / 2 afforded 545 mg (62%) of the desired product as a colorless oil. **^{1}H NMR (300 MHz, CD_3OD):** δ 2.59 (t, *J* = 7.7 Hz, 2 H, C*H*$_2$-NH), 2.43 (tt, 1 H, *J* = 10.8, 3.8 Hz, C*H*-NH), 1.94–1.90 (m, 2 H, C*H*$_2$), 1.79–1.74 (m, 2 H, C*H*$_2$), 1.67–1.63 (m, 1 H, C*H*), 1.54–1.45 (m, 2 H, C*H*$_2$), 1.35–1.02 (m, 11 H, C*H*$_2$), 0.91 (t, *J* = 6.8 Hz, 3 H, CH_2-C*H*$_3$) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 57.0 (CH), 47.2 (CH_2), 33.8 (2 CH_2), 31.9 (CH_2), 30.6 (CH_2), 27.2 (CH_2), 26.3 (CH_2), 25.2 (2 CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm. **IR (neat):** υ max = 2954, 2922, 2852, 1449, 1368, 1259, 1132, 889, 725 cm^{-1}. **HRMS (ESI +):** calcd for $C_{12}H_{26}N$ $[MH]^+$ 184.2060 found 184.2052. **GC:** retention time: 9.4 min. **GC/MS:** retention time: 9.21 min.

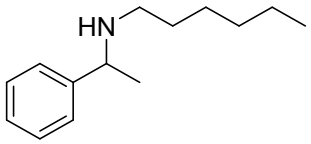
[2] A. Wetzel, S. Wockel, M. Schelwies, M. K. Brinks, F. Rominger, P. Hofmann, M. Limbach, *Org. Lett.* **2013**, *15*, 266-269.



Chemical Formula: $C_{13}H_{21}N$
Molecular Weight: 191,31

***N*-benzyl-*N*-hexylamine [25468-44-4] (11)**[2,3]

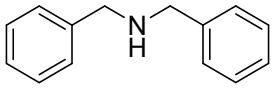
11 was obtained following the general procedure starting from benzaldehyde (425 mg, 4.01 mmol) and hexylamine (410 mg, 4.06 mmol, 1.01 equiv.). GC yield was determined by GC using dodecane as internal standard: 89%. Purification by flash column chromatography using a gradient of dichloromethane / methanol: 100 / 0 to 9 / 1 afforded 671 mg (88%) of the desired product as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.40–7.20 (m, 5 H, 5 CH_{Ar}) 3.80 (s, 2 H, Ar-CH_2), 2.64 (t, *J* = 7.2 Hz, 2 H, CH_2-NH), 1.6–1.4 (m, 2 H + 1 H, NH-CH_2-CH_2 + N*H*), 1.40–1.20 (m, 6 H, 3 CH_2), 0.90 (t, *J* = 5.8 Hz, 3 H, CH_2-CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 140.7 (C_q, C_{Ar}), 128.5 (2 CH, C_{Ar}), 128.2 (2 CH, C_{Ar}), 126.9 (CH, C_{Ar}), 54.2 (CH_2), 49.6 (CH_2), 31.9 (CH_2), 30.2 (CH_2), 27.2 (CH_2), 22.7 (CH_2), 14.2 (CH_3) ppm. **IR (neat):** υ max = 3085, 3063, 3026, 2954, 2924, 2855, 2810, 1604, 1494, 1453, 1378, 1119, 729, 696 cm^{-1}. **HRMS (ESI +):** calcd for $C_{13}H_{22}N$ $[MH]^+$ 192.1747 found 192.1744. **GC:** retention time: 10.4 min. **GC/MS:** retention time: 10.6 min.



Chemical Formula: $C_{14}H_{23}N$
Molecular Weight: 205,34

***N*-(1-phenyl-ethyl)hexylamine [55386-59-9] (13)**[4]

13 was obtained following the general procedure starting from acetophenone (482 mg, 4.02 mmol) and hexylamine (422 mg, 4.18 mmol, 1.04 equiv.). GC yield was determined by GC using dodecane as internal standard: 77%. Purification by flash column chromatography using a gradient of dichloromethane / methanol: 100 / 0 to 8 / 2 afforded 655 mg (80%) of the desired product as a colorless oil. **^{1}H NMR (300 MHz, CD_3OD):** δ 7.32–7.29 (m, 4 H, 4 CH_{Ar}), 7.27–7.20 (m, 1 H, 1 CH_{Ar}), 3.73 (q, *J* = 6.7 Hz, 1 H, C*H*-NH), 2.46–2.29 (m, 2 H, CH_2-NH), 1.53–1.42 (m, 2 H, CH_2), 1.36 (d, *J* = 6.7 Hz, 3 H, CH-CH_3), 1.28–1.23 (m, 6 H, 3 CH_2), 0.88 (t, *J* = 6.7 Hz, 3 H, CH_2-CH_3) ppm. **^{13}C NMR (75 MHz, CD_3OD):** δ 146.0 (C_q, C_{Ar}), 129.5 (2 CH, C_{Ar}), 128.1 (CH, C_{Ar}), 127.8 (2 CH, C_{Ar}), 59.4 (CH), 48.5 (CH_2), 32.9 (CH_2), 30.4 (CH_2), 28.1 (CH_2), 23.8 (CH_3), 23.6 (CH_2), 14.4 (CH_3) ppm. **IR (neat):** υ max = 3083, 3062, 3025, 2957, 2924, 2855, 1451, 1368, 1130, 760, 725, 699 cm^{-1}. **HRMS (ESI +):** calcd for $C_{14}H_{24}N$ $[MH]^+$ 206.1903 found 206.1902. **GC:** retention time: 10.3 min. **GC/MS:** retention time: 10.6 min.



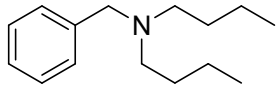
Chemical Formula: $C_{14}H_{15}N$
Molecular Weight: 197,2756

dibenzylamine [103-49-1] (22)[5]

22 was obtained following the general procedure starting from benzaldehyde (425 mg, 4.01 mmol) and *N*-benzylamine (429 mg, 4.21 mmol). GC yield was determined by GC using dodecane as internal standard: 94%. Purification by flash column chromatography using a gradient of dichloromethane / methanol: 100 / 0 to 98 / 2 afforded 688 mg (87%) of the desired product as a colorless oil. **^{1}H NMR (300 MHz, CD_3OD):** δ 7.34–7.22 (m, 10 H, 10 CH_{Ar}), 3.73 (s, 4 H, 2 CH_2) ppm. **^{13}C NMR (75 MHz,**

[3] M. S. Kwon, S. Kim, S. Park, W. Bosco, R. K. Chidrala, J. Park, *J. Org. Chem*. **2009**, *74*, 2877-2879.
[4] a) D. Hollmann, A. Tillack,D. Michalik, R. Jackstell, M. Beller, *Chemistry – An Asian Journal* **2007**, *2*, 403-410; b) A. Johansson, P. Abrahamsson, Ö. Davidsson, *Tetrahedron: Asymmetry* **2003**, *14*, 1261-1266.
[5] K.-I. Fujita, Y. Enoki, R. Yamaguchi, *Tetrahedron* **2008**, *64*, 1943-1954.

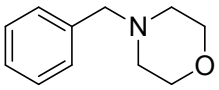
CD_3OD): δ 140.5 (C_q, C_{Ar}), 129.45 (2 CH, C_{Ar}), 129.4 (2 CH, C_{Ar}), 128.1 (CH, C_{Ar}), 53.5 (CH_2) ppm. **IR (neat):** υ max = 3309, 3084, 3061, 3025, 2915, 2811, 2702, 1947, 1873, 1808, 1602, 1494, 1452, 1361, 1198, 1107, 1027, 907, 827, 731 cm^{-1}. **HRMS (ESI +):** calcd for $C_{14}H_{16}N$ $[MH]^+$ 198.1277 found 198.1275. **GC:** retention time: 12.25 min.



Chemical Formula: $C_{15}H_{25}N$
Molecular Weight: 219,37

***N*,*N*-dibutylBenzenemethanamine [4383-27-1] (24)**[5]

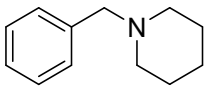
24 was obtained following the general procedure starting from benzaldehyde (420 mg, 4.0 mmol) and *N*,*N*-dibutylamine (530 mg, 4.1 mmol) in toluene (2 mL, 2 M). GC yield was determined by GC using dodecane as internal standard: >99%. Purification by flash column chromatography using a gradient of dichloromethane / methanol: 100 / 0 to 9 / 1 afforded 724 mg (82%) of the desired product as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.33–7.20 (m, 5 H, 5 CH_{Ar}), 3.53 (s, 2 H, Ar-CH_2), 2.39 (t, J = 7.1 Hz, 4 H, 2 CH_2-NH), 1.49–1.39 (m, 4 H, 2 CH_2), 1.34–1.22 (m, 4 H, 2 CH_2), 0.87 (t, J = 7.3 Hz, 6 H, 2 CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 140.5 (C_q, C_{Ar}), 128.9 (2 CH, C_{Ar}), 128.1 (2 CH, C_{Ar}), 126.7 (CH, C_{Ar}), 58.8 (CH_2), 53.7 (CH_2), 29.4 (CH_2), 20.7 (CH_2), 14.2 (CH_3) ppm. **IR (neat):** υ max = 3085, 3063, 3027, 2955, 2929, 2871, 2794, 1602, 1494, 1453, 1376, 1302, 1253, 1176, 1156, 1069, 1028, 946, 908, 806, 729 cm^{-1}. **HRMS (ESI +):** calcd for $C_{15}H_{26}N$ $[MH]^+$ 220.2060 found 220.2058. **GC:** retention time: 10.4 min.



Chemical Formula: $C_{11}H_{15}NO$
Molecular Weight: 177,24

***N*-benzyl-morpholine [10316-00-4] (26)**[6]

26 was obtained following the general procedure starting from benzaldehyde (428 mg, 4.04 mmol) and morpholine (348 mg, 4.04 mmol, 1 equiv.) in toluene (2 mL, 2 M). GC yield was determined by GC using dodecane as internal standard: 87%. Purification by flash column chromatography using a gradient of dichloromethane / methanol: 100 / 0 to 97 / 3 afforded 538 mg (75%) of the desired product as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.33–7.20 (m, 5 H, 5 CH_{Ar}), 3.70–3.67 (m, 4 H, 2 CH_2), 3.48 (s, 2 H, Ar-CH_2), 2.44-2.41 (m, 4 H, 2 CH_2) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 137.8 (C_q, C_{Ar}), 129.2 (2 CH, C_{Ar}), 128.3 (2 CH, C_{Ar}), 127.2 (CH, C_{Ar}), 67.0 (CH_2), 63.5 (CH_2), 53.6 (CH_2) ppm. **IR (neat):** υ max = 3027, 2957, 2852, 2804, 1494, 1453, 1396, 1351, 1285, 1263, 1205, 1115, 1070, 1034, 1007, 914, 865, 803, 737 cm^{-1}. **HRMS (ESI +):** calcd for $C_{11}H_{16}NO$ $[MH]^+$ 178.1226 found 178.1222. **GC:** retention time: 9.58 min.



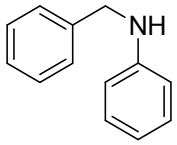
Chemical Formula: $C_{12}H_{17}N$
Molecular Weight: 175,2701

1-benzylpiperidine [2905-56-8] (28)[5]

28 was obtained following the general procedure starting from benzaldehyde (422 mg, 4.00 mmol) and piperidine (348 mg, 4.09 mmol) in toluene (2 mL, 2 M). GC yield was determined by GC using dodecane as internal standard: 48 %. Purification by flash column chromatography: silica gel 50g, gradient of cyclohexane / dichloromethane: 100 / 0 (500 mL), 9 / 1 (500 mL), 1 / 1 (500 mL), 0 / 100 (750 mL) afforded 282 mg (40%) of the desired product as

[6] A. J. A. Watson, A. C. Maxwell, J. M. J. Williams, *J. Org. Chem.* **2011**, *76*, 2328-2331.

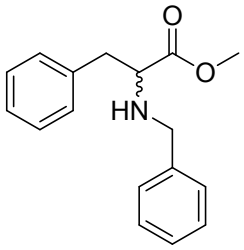
a colorless oil. **^{1}H NMR (300 MHz, CD_3OD):** δ 7.32–7.26 (m, 5 H, 5 CH_{Ar}), 3.49 (s, 2 H, Ar-CH_2), 2.42 (br. s, 4 H, 2 CH_2-N), 1.63–1.56 (m, 4 H, 2 CH_2), 1.49–1.44 (m, 2 H, CH_2) ppm. **^{13}C NMR (75 MHz, CD_3OD):** δ 138.3 (C_q, C_{Ar}), 130.8 (2 CH, C_{Ar}), 129.2 (2 CH, C_{Ar}), 128.3 (CH, C_{Ar}), 64.7 (CH_2), 55.3 (CH_2), 26.4 (CH_2), 25.2 (CH_2) ppm. **IR (neat):** υ max = 3084, 3062, 3026, 2932, 2852, 2792, 2754, 2723, 2685, 1601, 1493, 1467, 1346, 1298, 1153, 1112, 1039, 995 906, 861, 788, 733, 696 cm^{-1}. **HRMS (ESI +):** calcd for $C_{12}H_{18}N$ $[MH]^+$ 176.1434 found 176.1441. **GC:** retention time: 9.38 min.



Chemical Formula: $C_{13}H_{13}N$
Molecular Weight: 183,25

***N*-benzyl-aniline [758640-21-0] (30)**[5]

30 was obtained following the general procedure starting from benzaldehyde (428 mg, 4.04 mmol) and aniline (400 mg, 4.30 mmol) in toluene (2 mL, 2 M). GC yield was determined by GC using dodecane as internal standard: 58 %. Purification by flash column chromatography using a gradient of cyclohexane / dichloromethane: 100 / 0 to 8 / 2 afforded 439 mg (60%) of the desired product as a white solid. **MP**: 37 °C. **^{1}H NMR (300 MHz, CD_3OD):** δ 7.39–7.36 (m, 2 H, 2 CH_{Ar}), 7.33–7.28 (m, 2 H, 2 CH_{Ar}), 7.24–7.18 (m, 1 H, 1 CH_{Ar}), 7.10–7.04 (m, 2 H, 2 CH_{Ar}), 6.65–6.57 (m, 3 H, 3 CH_{Ar}), 4.31 (s, 2 H, CH_2-N) ppm. **^{13}C NMR (75 MHz, CD_3OD):** δ 150.0 (C_q, C_{Ar}), 141.4 (C_q, C_{Ar}), 129.9 (2 CH, C_{Ar}), 129.3 (2 CH, C_{Ar}), 128.3 (2 CH, C_{Ar}), 127.7 (CH, C_{Ar}), 117.9 (CH, C_{Ar}), 114.1 (2 CH, C_{Ar}), 48.7 (CH_2) ppm. **IR (neat):** υ max = 3417, 3080, 3052, 3024, 2926, 1600, 1502, 1460, 1328, 1301, 1276, 1180, 1151, 1044, 1026, 989, 939, 856, 794 cm^{-1}. **HRMS (ESI +):** calcd for $C_{13}H_{14}N$ $[MH]^+$ 184.1121 found 184.1125. **GC:** retention time: 12.22 min.



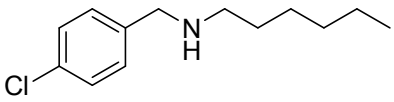
Chemical Formula: $C_{17}H_{19}NO_2$
Molecular Weight: 269,34

***N*-benzylphenylananine methyl ester [200435-16-1] (34)**[7]

31 was obtained following the general procedure starting from benzaldehyde (428 mg, 4.04 mmol), DL-phenylalanine methyl ester hydrochloride (885 mg, 4.10 mmol) and CaH_2 (220 mg, 5.23 mmol, 1.3 equiv.) in toluene (2 mL, 2 M). Purification by flash column chromatography using a gradient of cyclohexane / ethyl acetate: 100 / 0 to 9 / 1 afforded 765 mg (71%) of the desired product as an oil. **^{1}H NMR (300 MHz, CD_3Cl_3):** δ 7.35–7.19 (m, 10 H, 10 CH_{Ar}), 3.86 (d, *J* = 13.3 Hz, 1 H, 1 C*H*), 3.69 (s, 3 H, CO_2CH_3), 3.68 (d, *J* = 13.3 Hz, 1 H, C*H*), 3.59 (t, *J* = 7.1 Hz, 1 H, C*H*), 3.01 (d, *J* = 7.1 Hz, 2 H, CH_2), 1.89 (br. s, 1 H, N*H*) ppm. **^{1}H NMR (300 MHz, CD_3OD):** δ 7.29–7.12 (m, 10 H, 10 CH_{Ar}), 3.75 (d, *J* = 13.0 Hz, 1 H, 1 C*H*), 3.60 (d, *J* = 13.0 Hz, 1 H, C*H*), 3.58 (s, 3 H, CO_2CH_3), 3.51 (t, *J* = 7.1 Hz, 1 H, C*H*), 2.94 (d, *J* = 7.1 Hz, 2 H, CH_2) ppm. **^{13}C NMR (75 MHz, CD_3OD):** δ 175.9 (C_q, CO_2Me), 140.4 (C_q, C_{Ar}), 138.4 (C_q, C_{Ar}), 130.2 (2 CH, C_{Ar}), 129.5 (2 CH, C_{Ar}), 129.4 (2 CH, C_{Ar}), 129.3 (2 CH, C_{Ar}), 128.2 (CH, C_{Ar}), 127.7 (CH, C_{Ar}), 63.2, 52.7, 52.1, 40.3 ppm. **IR (neat):** υ max = 3333, 3062, 3027, 2949, 2844, 1731, 1603, 1494, 1453, 1339, 1272, 1197, 1169, 1129, 1027, 990, 906, 736, 696 cm^{-1}. **HRMS (ESI +):** calcd for $C_{17}H_{20}NO_2$ $[MH]^+$ 270.1493

[7] A. V. Lee, L. L. Schafer, *Synlett* **2006**, 2973-2976.

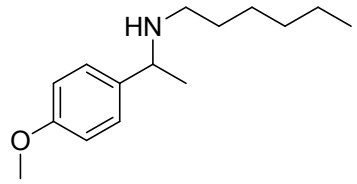
found 270.1489. **GC:** retention time: 14.38 min.



Chemical Formula: $C_{13}H_{20}ClN$
Molecular Weight: 225,76

4-chloro-*N*-hexyl-benzenemethanamine [104868-32-8] (37)

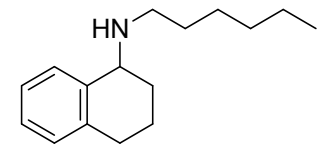
37 was obtained following the general procedure for the reaction starting from 4-chlorobenzaldehyde (562 mg, 4.01 mmol) and *N*-hexylamine (505 mg, 5.00 mmol), toluene (2 mL, 2 M). Purification by flash column chromatography: silica gel 50 g, gradient of dichloromethane / methanol: 100 / 0 to 96 / 4 afforded 605 mg (67%) of the desired product as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.30–7.23 (m, 4 H, 4 CH_{Ar}), 3.75 (s, 2 H, Ar-CH_2), 2.59 (t, *J* = 7.3 Hz, 2 H, CH_2-NH), 1.51–1.47 (m, 2 H, CH_2), 1.43 (br. s, 1 H, N*H*), 1.34–1.25 (m, 6 H, 3 CH_2), 0.88 (t, *J* = 6.7 Hz, 6 H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 138.7 (C_q, C_{Ar}), 132.5 (C_q, C_{Ar}), 129.4 (2 CH, C_{Ar}), 128.4 (2 CH, C_{Ar}), 53.1 (CH_2), 49.3 (CH_2), 31.7 (CH_2), 29.9 (CH_2), 27.0 (CH_2), 22.6 (CH_2), 14.0 (CH_3) ppm. **IR (neat):** υ max = 3306, 3026, 2955, 2924, 2870, 2855, 2820, 1597, 1490, 1456, 1406, 1378, 1354, 1287, 1118, 1088, 1015, 973, 835, 798, 727 cm^{-1}. **HRMS (ESI +):** calcd for $C_{13}H_{21}NCl$ $[MH]^+$ 226.1357 found 226.1355. **GC:** retention time: 12.2 min.



Chemical Formula: $C_{15}H_{25}NO$
Molecular Weight: 235,37

***N*-[1-(4-methoxyphenyl)ethyl]hexan-1-amine [1040343-75-6] (39)**

39 was obtained following the general procedure starting from *p*-methoxyacetophenone (600 mg, 4.00 mmol) and hexylamine (419 mg, 4.15 mmol, 1.04 equiv.). GC yield was determined by GC using dodecane as internal standard: 94%. Purification by flash column chromatography using a gradient of dichloromethane / methanol: 100 / 0 to 8 / 2 afforded 879 mg (81%) of the desired product as a colorless oil. **^{1}H NMR (300 MHz, CD_3OD):** δ 7.22 (d, *J* = 8.6 Hz, 2 H, 2 CH_{Ar}), 6.88 (d, *J* = 8.6 Hz, 2 H, 2 CH_{Ar}), 3.78 (s, 3 H, OCH_3), 3.69 (q, *J* = 6.7 Hz, 1 H, C*H*-NH), 2.44–2.29 (m, 2 H, CH_2-NH), 1.53–1.40 (m, 2 H, CH_2), 1.34 (d, *J* = 6.7 Hz, 3 H, CH_3-CH), 1.31–1.22 (m, 6 H, 3 CH_2), 0.88 (t, *J* = 6.7 Hz, 3 H, CH_2-CH_3) ppm. **^{13}C NMR (75 MHz, CD_3OD):** δ 160.2 (C_q, C_{Ar}), 137.8 (C_q, C_{Ar}), 128.8 (2 CH, C_{Ar}), 114.9 (2 CH, C_{Ar}), 58.7 (CH), 55.6 (CH_3, OCH_3), 48.5 (CH_2), 32.9 (CH_2), 30.4 (CH_2), 28.2 (CH_3), 23.7 (CH_2), 23.6 (CH_3), 14.4 (CH_3) ppm. **IR (neat):** υ max = 3061, 2955, 2925, 2854, 1610, 1510, 1463, 1367, 1241, 1173, 1129, 1037, 830, 726 cm^{-1}. **GC:** retention time: 12.6 min. **GC/MS:** retention time: 12.2 min. **HRMS (ESI +):** calcd for $[MH]^+$ 236.2009 found 236.2009.



Chemical Formula: $C_{16}H_{25}N$
Molecular Weight: 231,38

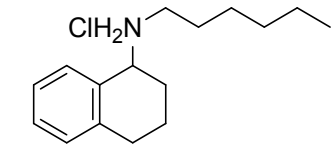
***N*-hexyl-1,2,3,4-tetrahydro-1-naphthalenamine [1040321-04-7] (41)**

41 were obtained following the general procedure starting from α-tetralone (590 mg, 4.04 mmol) and hexylamine (428 mg, 4.24 mmol, 1.05 equiv.). Purification by flash column chromatography: silica gel 50 g, gradient of dichloromethane / methanol: 100 / 0 to 9 / 1 to afford after evaporation a brown oil. The oil in ether was treated with HCl (1 M in ether). The suspension was filtered and washed with ether to afford 585.5 mg (54%) of the corresponding HCl salt as a brownish solid. **^{1}H NMR (300 MHz, CD_3OD):** δ 7.31–7.28 (m, 1 H, 1 CH_{Ar}), 7.15–7.06 (m, 3 H, 3 CH_{Ar}), 3.83 (t, *J* = 4.7 Hz, 1 H, C*H*-NH), 2.87–2.72 (m, 2 H, CH_2), 2.70–2.63 (m, 2 H, CH_2), 2.01–1.88 (m, 3 H, CH_2 + C*H*), 1.76–1.70 (m, 1 H, C*H*), 1.59–1.50 (m,

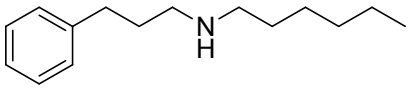
2 H, CH_2), 1.40–1.29 (m, 7 H, 3 CH_2 + N*H*), 0.91 (t, *J* = 6.6 Hz, 3 H, CH_3) ppm. **^{13}C NMR (75 MHz, CD_3OD):** δ 139.2 (C_q, C_{Ar}), 138.7 (C_q, C_{Ar}), 130.3 (CH, C_{Ar}), 129.7 (CH, C_{Ar}), 128.0 (CH, C_{Ar}), 126.9 (CH, C_{Ar}), 56.5 (CH), 47.9 (CH_2), 33.1 (CH_2), 30.8 (CH_2), 30.5 (CH_2), 29.1 (CH_2), 28.4 (CH_2), 23.9 (CH_2), 20.3 (CH_2), 14.7 (CH_3) ppm.

HCl salt:

MP: 118 °C. **^{1}H NMR (300 MHz, DMSO-d_6):** δ 9.04 (br. s, 2 H, NH_2Cl), 7.62 (d, *J* = 7.7 Hz, 1 H, 1 CH_{Ar}), 7.33–7.19 (m, 3 H, 3 CH_{Ar}), 4.44 (t, *J* = 5.2 Hz, 1 H, C*H*-NH), 2.92–2.67 (m, 4 H, 2 CH_2), 2.18–2.09 (m, 1 H, C*H*), 2.05–1.91 (m, 2 H, CH_2), 1.80–1.64 (m, 3 H, CH_2 + C*H*), 1.35–1.23 (m, 6 H, 3 CH_2), 0.87 (t, 3 H, *J* = 6.9 Hz, CH_3) ppm. **^{13}C NMR (75 MHz, DMSO-d_6):** δ 138.3 (C_q, C_{Ar}), 130.7 (C_q, C_{Ar}), 129.7 (CH, C_{Ar}), 129.3 (CH, C_{Ar}), 128.4 (CH, C_{Ar}), 125.6 (CH, C_{Ar}), 53.9 (CH), 43.7 (CH_2), 30.7 (CH_2), 28.1 (CH_2), 25.8 (CH_2), 25.2 (CH_2), 24.4 (CH_2), 21.8 (CH_2), 18.1 (CH_2), 13.8 (CH_3) ppm. **IR (neat):** υ max = 3045, 2933, 2871, 2780, 1571, 1496, 1460, 1443, 1420, 1354, 755, 730 cm^{-1}. **HRMS (ESI +):** calcd for $C_{16}H_{26}N$ $[M\text{-}Cl]^+$ 232.2060 found 232.2063.



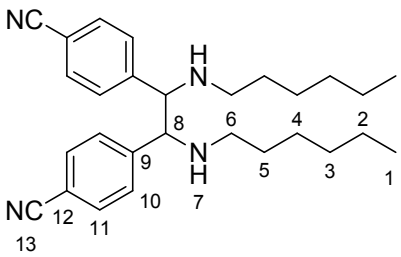
Chemical Formula: $C_{16}H_{26}ClN$
Molecular Weight: 267,84



Chemical Formula: $C_{15}H_{25}N$
Molecular Weight: 219,37

***N*-(3-phenylpropyl)hexan-1-amine [857544-88-8] (43)**

43 was obtained following the general procedure starting from 3-phenylpropionaldehyde (543 mg, 4.05 mmol) and hexylamine (420 mg, 4.11 mmol, 1.01 equiv.). GC yield was determined by GC using dodecane as internal standard: 62%. Purification by flash column chromatography using a gradient of dichloromethane / methanol: 100 / 0 to 9 / 1 afforded 516 mg (58%) of the desired product as a colorless oil. **^{1}H NMR (300 MHz, CD_3OD):** δ 7.30–7.14 (m, 5 H, 5 CH_{Ar}), 2.69–2.57 (m, 6 H, 3 CH_2), 1.91–1.77 (m, 2 H, CH_2), 1.56–1.47 (m, 2 H, 2 CH_2-N), 1.38–1.28 (m, 6 H, 3 CH_2), 0.92 (t, *J* = 6.7 Hz, 3 H, CH_2-CH_3) ppm. **^{13}C NMR (75 MHz, CD_3OD):** δ 143.1 (C_q, C_{Ar}), 129.39 (2 CH, C_{Ar}), 129.37 (2 CH, C_{Ar}), 126.9 (CH, C_{Ar}), 50.6 (CH_2), 50.1 (CH_2), 34.6 (CH_2), 32.9 (CH_2), 31.9 (CH_2), 30.1 (CH_2), 28.1 (CH_2), 23.6 (CH_2), 14.4 (CH_3) ppm. **IR (neat):** υ max = 3287, 3084, 3062, 3026, 2953, 2925, 2855, 2808, 1496, 1453, 1377, 1128, 744, 697 cm^{-1}. **HRMS (ESI +):** calcd for $C_{15}H_{26}N$ $[MH]^+$ 220.2060 found 220.2051. **GC:** retention time: 12.24 min.



Chemical Formula: $C_{28}H_{38}N_4$
Molecular Weight: 430,6281

***N*,*N*'-dihexyl-1,2-di(4-cyanophenyl)-1,2-ethylenediamine (45)**

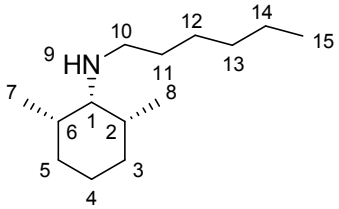
45 were obtained following the general procedure starting from *p*-cyanobenzaldehyde (524 mg, 4.02 mmol) and hexylamine (400 mg, 4.32 mmol, 1.07 equiv.) in toluene (2 mL, 2 M). Purification by flash column chromatography: silica gel 50 g, gradient of dichloromethane / methanol: 100 / 0 (750 mL), 99:1 (1 L), afforded 69 mg (8%) of the diasteroisomer 1 as a white solid and 563 mg (65%) of a mixture of the two diastereoisomers as a yellow solid.

<u>Dia 1</u>

White solid. **MP**: 120 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.54 (d, *J* = 8.2 Hz, 4 H, 4 C*H*$_{Ar}$, H11), 7.24 (d, *J* = 8.2 Hz, 4 H, 4 C*H*$_{Ar}$, H10), 3.86 (s, 2 H, 2 C*H*, H8), 2.32 (t, *J* = 7.0 Hz, 4 H, 2 C*H*$_2$, H6), 1.47 (br. s, 2 H, 2 N*H*, H7), 1.40-1.13 (m, 16 H, 8 C*H*$_2$, H5-2), 0.85 (t, *J* = 6.9 Hz, 6 H, 2 C*H*$_3$, H1) ppm. **^{13}C NMR (300 MHz, $CDCl_3$):** δ 146.3 (2 C_q, C_{Ar}, C12), 131.9 (4 CH, C_{Ar}, C11), 129.1 (4 CH, C_{Ar}, C10), 118.8 (2 C_q, C_{Ar}, C13), 111.4 (2 C_q, C9), 67.9 (2 CH, C8), 47.7 (2 CH_2, C6), 31.7 (2 CH_2, C5 or 4, 3, 2), 29.9 (2 CH_2, C5 or 4, 3, 2), 26.8 (2 CH_2, C5 or 4, 3, 2), 22.6 (2 CH_2, C5 or 4, 3, 2), 14.1 (2 CH_3, C1) ppm. **IR (neat):** υ max = 3306, 3061, 3022, 2950, 2922, 2854, 2808, 2229, 1606, 1503, 1464, 1412, 1340, 1145, 1106, 1016, 901, 870, 847, 828, 790, 741 cm^{-1}. **HRMS (ESI +):** calcd for $C_{28}H_{39}N_4$ $[MH]^+$ 431.3169 found 431. 3158.

Melange

Yellow solid. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.54 (d, *J* = 8.2 Hz, 4 H, 4 C*H*$_{Ar\ dia1}$), 7.45 (d, *J* = 8.3 Hz, 4 H, 4 C*H*$_{Ar\ dia2}$),7.24 (d, *J* = 8.2 Hz, 4 H, 4 C*H*$_{Ar\ dia1}$), 7.10 (d, *J* = 8.3 Hz, 4 H, 4 C*H*$_{Ar\ dia2}$), 3.84 (s, 2 H, 2 C*H*$_{dia1}$), 3.60 (s, 2 H, 2 C*H*$_{dia2}$), 2.36–2.28 (m, 8 H, 2 C*H*$_{2\ dia1}$+ 2 C*H*$_{2\ dia2}$), 1.40–1.30 (m, 4 H, 2 C*H*$_{2\ dia1}$), 1.28–1.13 (m, 14 H, 6 C*H*$_{2\ dia1}$ + 6 C*H*$_{2\ dia2}$ + N*H*$_{dia1}$ + N*H*$_{dia2}$), 0.89–0.82 (m, 12 H, 2 C*H*$_{3\ dia1}$ + 2 C*H*$_{3\ dia2}$) ppm. **^{13}C NMR (300 MHz, $CDCl_3$):** δ 147.2 (2 C_q, $C_{Ar\ dia2}$), 146.3 (2 C_q, $C_{Ar\ dia1}$), 132.0 (4 CH, $C_{Ar\ dia2}$), 131.9 (4 CH, $C_{Ar\ dia1}$), 129.1 (4 CH, $C_{Ar\ dia1}$), 128.6 (4 CH, $C_{Ar\ dia2}$), 118.9 (2 C_q, CN_{dia1}), 118.8 (2 C_q, CN_{dia2}), 111.4 (2 C_q, $C_{Ar\ dia1}$), 111.39 (2 C_q, $C_{Ar\ dia2}$), 69.2 (2 CH_{dia2}), 67.9 (2 CH_{dia1}), 47.8 (2 $CH_{2\ dia2}$), 47.7 (2 $CH_{2\ dia1}$), 31.74 (2 $CH_{2\ dia2}$), 31.67 (2 $CH_{2\ dia1}$), 30.1 (2 $CH_{2\ dia2}$), 29.9 (2 $CH_{2\ dia1}$), 26.9 (2 $CH_{2\ dia2}$), 26.8 (2 $CH_{2\ dia1}$), 22.7 (2 $CH_{2\ dia2}$), 22.6 (2 $CH_{2\ dia1}$), overlapping 14.11 (2 $CH_{3\ dia2}$), 14.09 (2 $CH_{3\ dia1}$) ppm. **IR (neat):** υ max = 3306, 3061, 2952, 2924, 2855, 2227, 1606, 1503, 1465, 1412, 1340, 1145, 1106, 1016, 901, 870, 847, 828, 790, 741 cm^{-1}. **Reference describing structurally close compounds.**[8]

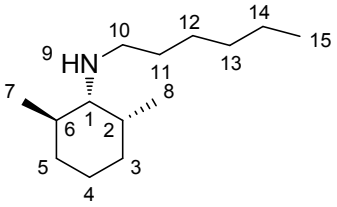


Chemical Formula: $C_{14}H_{29}N$
Molecular Weight: 211,39

***N*-hexyl-2,6-dimethylcyclohexanamine (47A)**

47A was obtained following the general procedure starting from 2,6-dimethylcyclohexanone (514 mg, 4.08 mmol) and hexylamine (418 mg, 4.14 mmol, 1 equiv.). Purification by flash column chromatography using a gradient of dichloromethane / methanol: 100 / 0 to 9 / 1 afforded 198 mg (23%) of the desired product as an oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.56 (t, *J* = 7.2 Hz, 2 H, C*H*$_2$, H10), 2.29 (t, *J* = 3.2 Hz, 1 H, C*H*, H1), 1.59-1.54 (m, 1 H, C*H*), 1.50-1.44 (m, 2 H, C*H*$_2$, H2 and H6), 1.42-1.34 (m, 2 H, C*H*$_2$, H11), 1.35-1.21 (m, 9 H), 1.20-1.03 (m, 3 H), 0.91 (d, 6 H, 2 C*H*$_3$, H7 and H8), 0.86 (t, *J* = 6.8 Hz, C*H*$_3$, H15) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 63.5 (CH, C1), 52.9 (CH_2, C10), 37.9 (2 CH, C2 and C6), 32.0 (CH_2, C13), 30.9 (CH_2, C11), 28.7 (CH_2, C3 and C5), 27.2 (CH_2, C12), 26.0 (CH_2, C4), 22.8 (CH_2, C14), 19.4 (2 CH_3, C7 and 8), 14.2 (CH_3, C15) ppm. **HRMS (ESI +):** calcd for $C_{14}H_{30}N$ $[MH]^+$ 212. 2373 found 212.2368. **GC:** retention time: 10.02 min. **GC/MS:** retention time: 9.71 min. **Related reference.**[9]

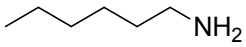
[8] D. H. R. Barton, L. Bohé, X. Lusinchi, *Tetrahedron Lett.* **1988**, *29*, 2571-2574.
[9] a) C. L. Barney, E. W. Huber, J. R. McCarthy, *Tetrahedron Lett.* **1990**, *31*, 5547-5550; b) G. Bellucci, F. Macchia,



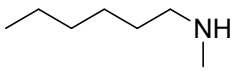
Chemical Formula: $C_{14}H_{29}N$
Molecular Weight: 211,3868

_N_-hexyl-2,6-dimethylcyclohexanamine (47C)

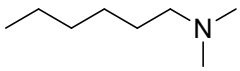
47C was obtained following the general procedure starting from 2,6-dimethylcyclohexanone (514 mg, 4.08 mmol) and hexylamine (418 mg, 4.14 mmol, 1.01 equiv.). Purification by flash column chromatography using a gradient of dichloromethane / methanol: 100 / 0 to 9 / 1 afforded 215 mg (25%) of the desired product as an oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.64 (dt, *J* = 11.3, 7.2 Hz, 1 H, C*H*, H10), 2.46 (dt, *J* = 11.3, 7.2 Hz, 1 H, C*H*, H10), 2.17 (dd, *J* = 9.0, 4.2 Hz, 1 H, C*H*-NH, H1), 2.09–2.01 (m, 1 H, C*H*, H2), 1.67–1.35 (m, 9 H), 1.34–1.29 (m, 6 H, 3 CH_2, H12, H13 and H14), 1.06–0.96 (m, 1 H, C*H*), 0.93 (d, *J* = 6.5 Hz, 3 H, CH_3, H7), 0.90–0.87 (m, 6 H, 2 CH_3, H15 and H8) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 65.3 (CH, C1), 47.4 (CH_2, C10), 33.9 (CH_2, C5), 31.9 (CH_2, C13), 31.8 (CH_2, C3), 31.6 (CH, C6), 30.3 (CH_2, C11), 29.8 (CH, C2), 27.2 (CH_2, C12), 22.8 (CH_2, C14), 20.3 (CH_2, C4), 19.4 (CH_3, C7), 14.2 (CH_3, C15), 13.0 (CH_3, C8) ppm. **IR (neat):** υ max = 2954, 2922, 2852, 1714, 1560, 1456, 1378, 1303, 1132, 974, 787, 724, 689 cm^{-1}. **HRMS (ESI +):** calcd for $C_{14}H_{30}N$ $[MH]^+$ 212. 2373 found 212.2368. **GC:** retention time: 10.3 min. **GC/MS:** retention time: 9.89 min. **Related reference.**[9]



Chemical Formula: $C_6H_{15}N$
Molecular Weight: 101,19



Chemical Formula: $C_7H_{17}N$
Molecular Weight: 115,22



Chemical Formula: $C_8H_{19}N$
Molecular Weight: 129,24

Monomethylation of hexylamine

The reaction was carried out following the general procedure starting from paraformaldehyde (122 mg, 3.90 mmol) and hexylamine (429 mg, 4.25 mmol, 1.09 equiv.) in toluene (4 mL). RMN aliquot was made after opening of the sealed tube. The reaction was diluted with ethylacetate, filtrated on a pad of celite and washed with ethyl acetate. The filtrate was injected in GC. To the filtrate was added 6 mL of HCl (1 M in ether) and the solvent was evaporated to afford 687 mg (> 95% yield) of a white solid.

Proportions

Proportions	NMR before filtration	GC after filtration
Hexylamine	11	11
N-methylhexylamine	73	67
N,*N*-dimethylhexylamine	16	22

The attribution of GC peaks was confirmed by GC/MS.

Compounds characteristics

hexylamine [111-26-2][10]
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.71–2.65 (m, 2 H, CH_2, CH_2-NH_2), 1.50–1.26 (m, 8 H, 4 CH_2), 0.91–0.86 (m, 3 H, CH_3) ppm. **GC:** retention time: 3.25 min.
***N*-methylhexylamine [35161-70-7] (49)**

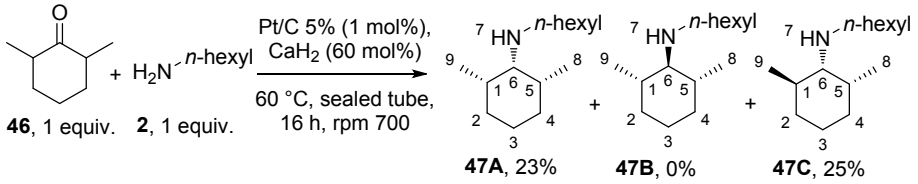
Franco; M. Poggianti, *Gazz. Chim. Ital.* **1969**, *99*, 1217-1235.
[10] J. Z. Saavedra, A. Resendez, A. Rovira, S. Eagon, D. Haddenham, B. Singaram, *J. Org. Chem.* **2012**, *77*, 221-228.

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.58–2.53 (m, 2 H, CH_2-NH_2), 2.42 (s, 3 H, NH-CH_3), 1.50–1.26 (m, 8 H, 4 CH_2), 0.91–0.86 (m, 3 H, CH_3) ppm. **GC:** retention time: 3.81 min. **Associated reference.**[11]

***N*,*N*-dimethylhexylamine [4385-04-0] (50)**
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.26–2.21 (m, 2 H, CH_2-N), 2.21 (s, 6 H, 2 CH_3, N(CH_3)$_2$), 1.50–1.26 (m, 8 H, 4 CH_2), 0.91–0.86 (m, 3 H, CH_3) ppm. **GC:** retention time: 3.87 min. **Associated reference.**[12]

5. Assignment by NMR of the reductive amination of 2,6-dimethylcyclohexane with hexylamine

From 2,6-dimethylcyclohexanone **46** (83/17 *cis/trans* mixture) two diastereoisomers **47A** and **47C** were isolated respectively in 23% and 25% yield (Scheme 4). Three different products can be obtained: two diastereoisomers (**47A** and **47B**) and one pair of enantiomers (**47C**).



Reductive amination of the 2,6-dimethylcyclohexanone with hexylamine

47C has been assigned thanks to the carbon RMN. In fact, **47C** possess 14 different peaks of carbons in ^{13}C RMN against 11 for **47A** and **47B** having a plane of symmetry. In the case of a plane of symmetry the carbons 1 and 5, 2 and 4, 9 and 8 are equivalent two by two.
The second product isolated has 11 carbons differentiated in ^{13}C RMN and consequently has a plane of symmetry. It remains to determine if the amine is *cis* or *trans* of the methyles so respectively **47A** or **47B**. The proton 6 is a triplet at 2.36 ppm with a coupling constant of 3.2 Hz characteristic of *cis* protons. The NOESY spectrum shows a coupling in the space between the protons 1, 5 and 6 (Fig.). Consequently, protons 1, 5 and 6 are on the same side of the plane. Hence, the second product isolated is **47A**. Analysis of this product is in agreement with the literature.[13]

[11] T. Cohen, A. Onopchenko, *J. Org. Chem.* **1983**, *48*, 4531-4537.
[12] S. H. Pine, B. A. Catto, F. G. Yamagis, *J. Org. Chem.* **1970**, *35*, 3663-3665.
[13] C. L. Barney, E. W. Huber, J. R. McCarthy, *Tetrahedron Lett.* **1990**, *31*, 5547-5550.

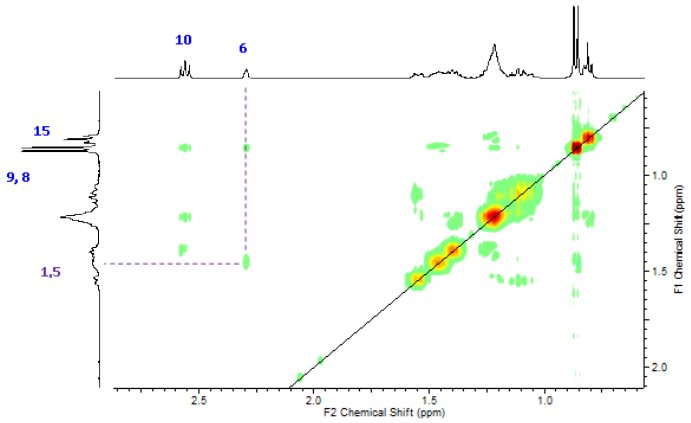


Fig. NOESY of **47A**

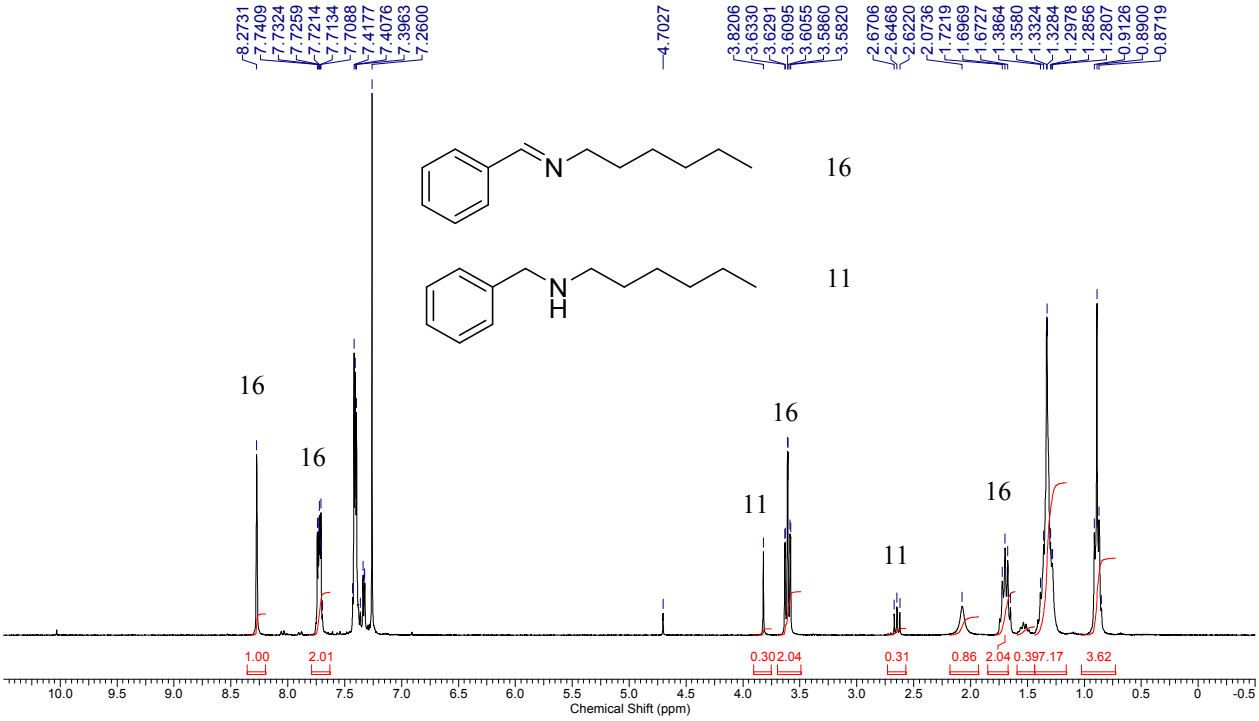
5. Mechanism investigation

Preparation of the imine

A batch of imine has been prepared in the following manner: hexylamine (2.02 g, 2.64 mL, 20 mmol), benzaldehyde (2.12 g, 2.03 mL, 20 mmol) in the presence of $MgSO_4$ (0.212 g, 10 wt%) was stirred for 1 h at room temperature. The imine was used without further purification by withdrawal from the supernatant of the mixture.

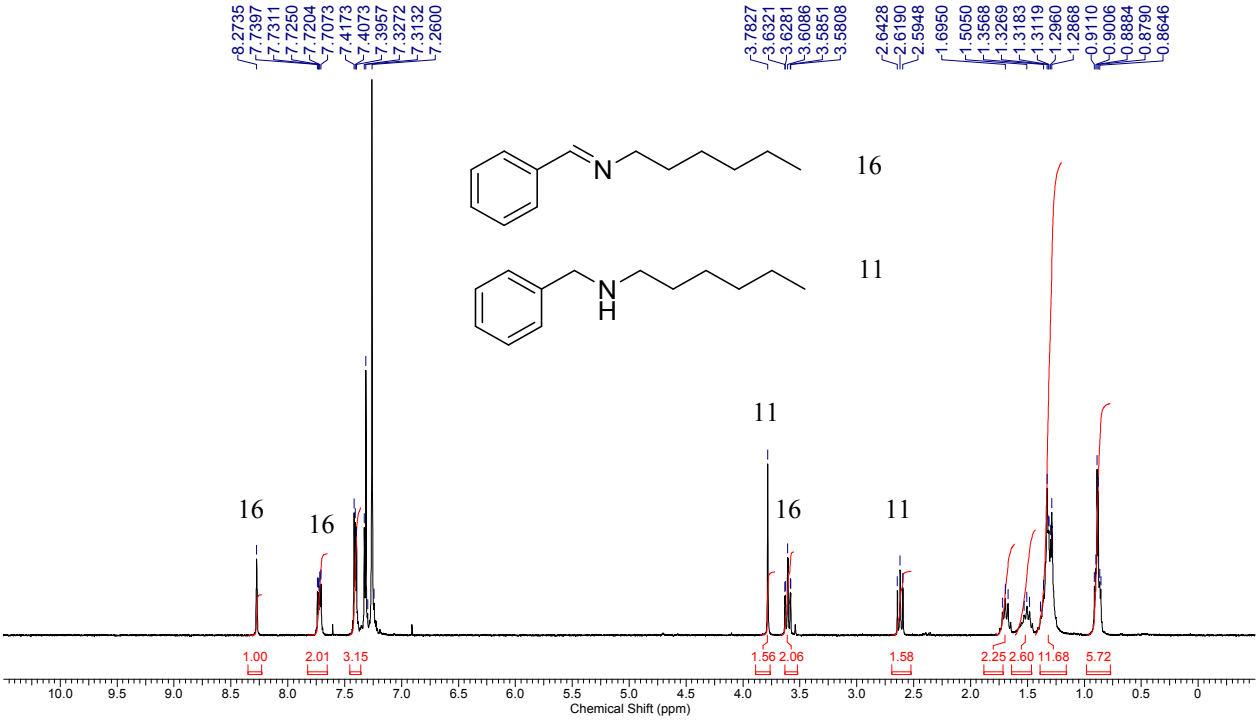
Hydrogenation of the imine

In a round bottom flask, the previously prepared imine (451 mg, 2.4 mmol) was submitted to hydrogenation in the presence of Pt/C (0.8 mol%), hydrogen (1 bar), at room temperature (20 °C) without additional solvent. Only 13% of amine was then observed after 16 h of reaction, determined by NMR of the reaction before filtration and confirmed by GC of the filtrate.

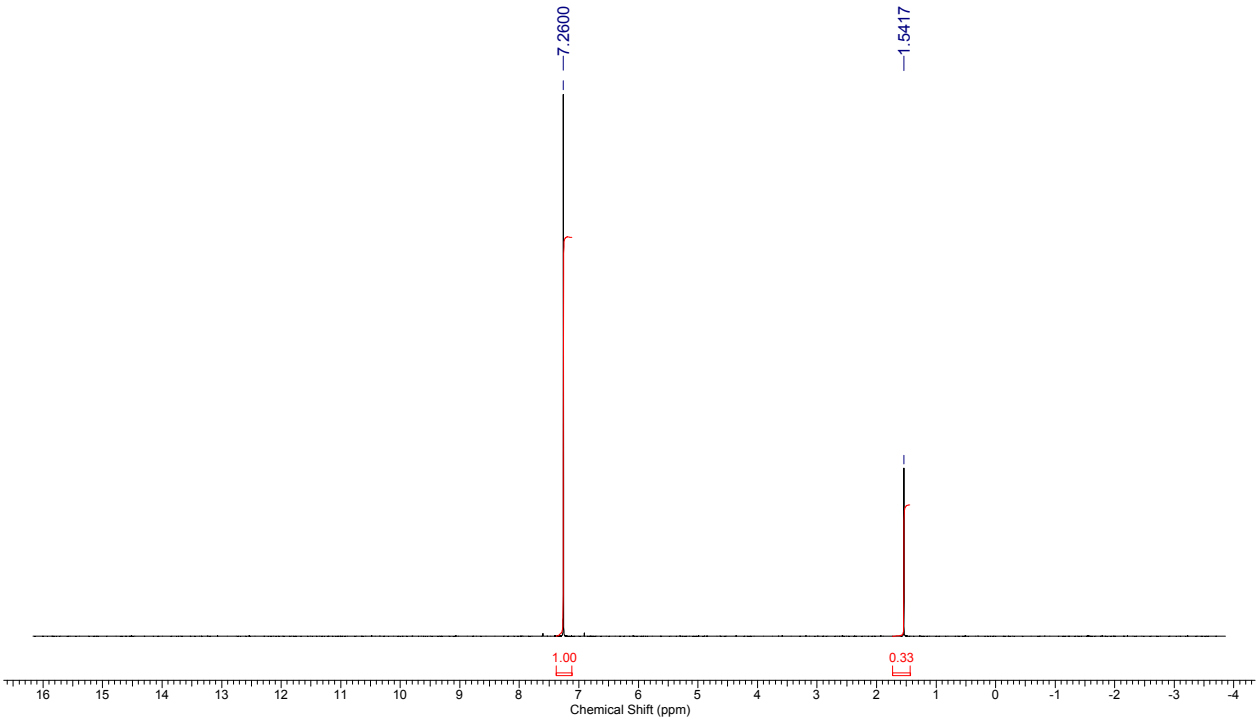


Reduction of the imine with CaH_2 and Pt/C in the absence of H_2O

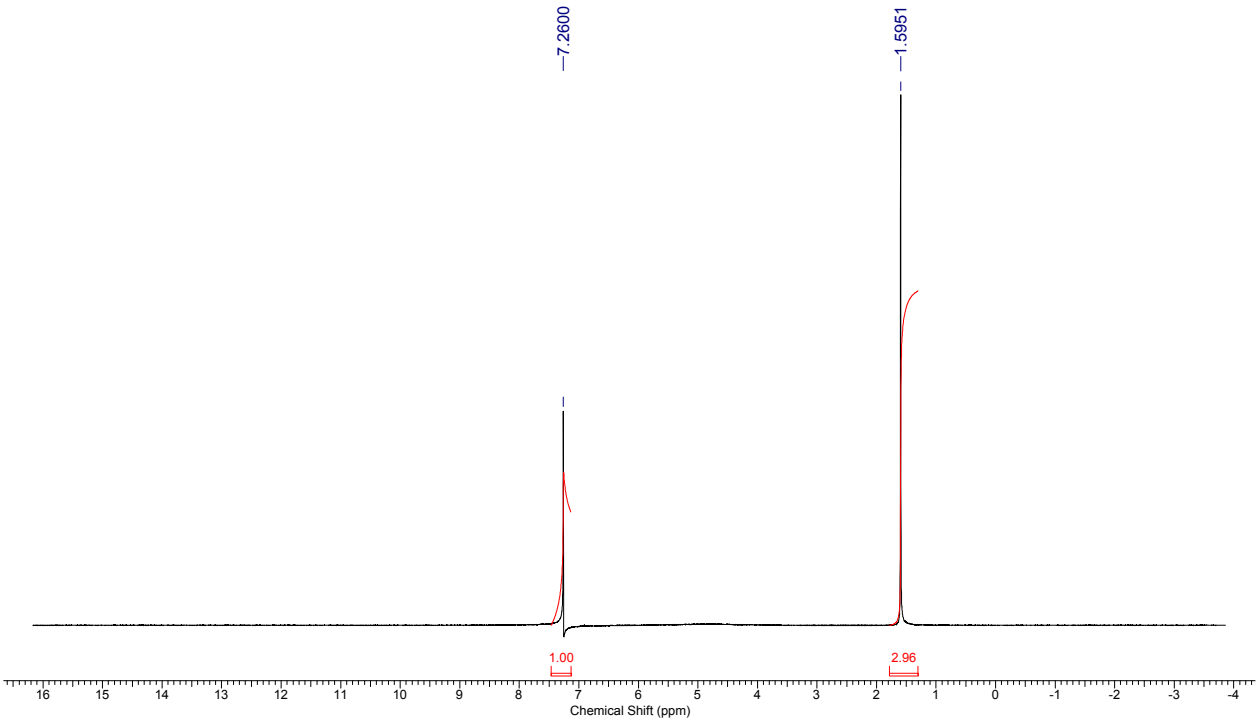
In a flame dried sealed tube under argon was introduced the previously prepared imine (405 mg, 2.14 mmol), the Pt/C (1 mol%) followed by CaH_2 (59 mg, 0.6 mol%). The sealed tube was closed and the reaction was stirred at 700 rpm. The imine was reduced at 44% determined by NMR of the reaction before filtration and confirmed by GC of the filtrate. This could be attributed to the presence of water in the catalyst. This was confirmed by the NMR of 8 mg of Pt/C in $CDCl_3$ and compared with the NMR of the $CDCl_3$ measured at 10 minutes of intervals.



NMR of the $CDCl_3$

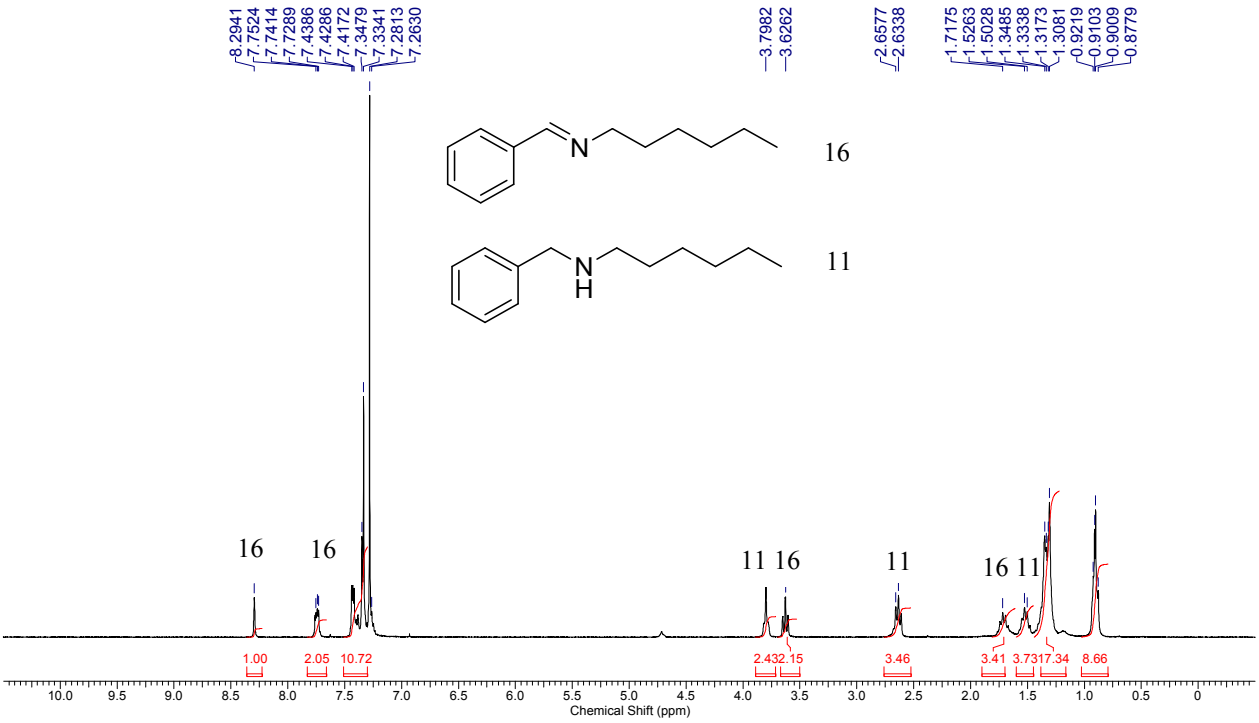


NMR of the $CDCl_3$ in the presence of 8 mg of Pt/C



Reduction of the imine with CaH_2 and Pt/C in the presence of D_2O

In a flame dried sealed tube under argon was introduced the previously prepared imine (401 mg, 2.12 mmol), the Pt/C (75 mg, 0.9 mol%) followed by CaH_2 (70 mg, 0.7 mol%) and D_2O (approximately 36 mg, 1.8 mmol, 0.86 equiv.). The imine was reduced at 63% determined by NMR of the reaction before filtration and confirmed by GC of the filtrate. It was noticed that a part of the formed amine was deuterated (30% of the benzylic protons).

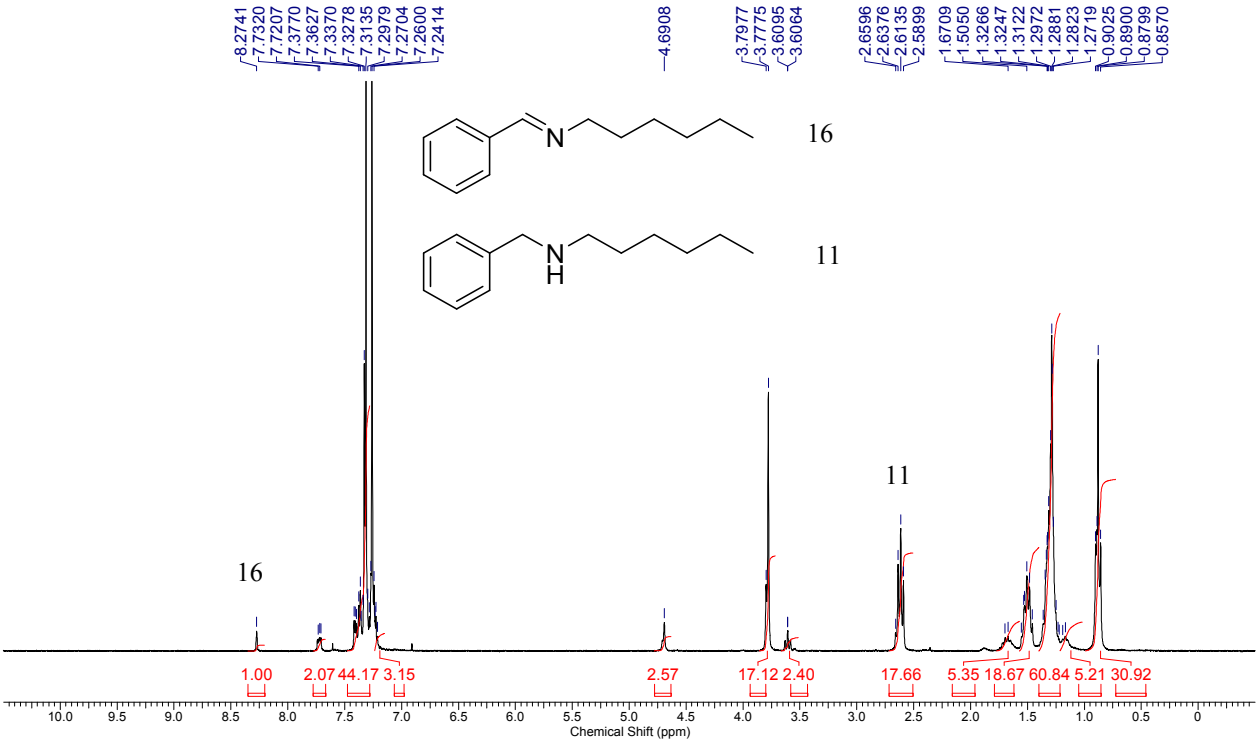


Homogeneity of the catalyst

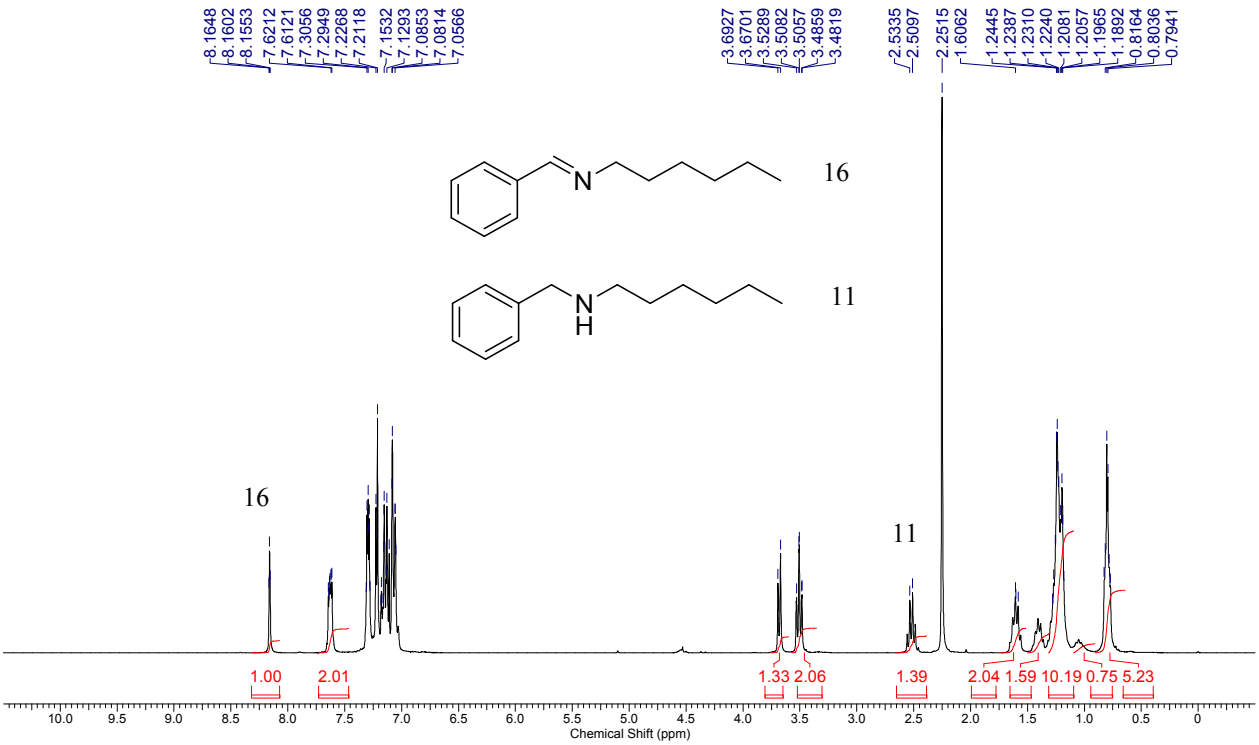
In order to check the heterogeneity of the catalyst, the reaction under the optimized conditions was carried out: In a flame dried sealed tube under argon was introduced benzaldehyde (0.403 mL, 4 mmol, 1 equiv.) and hexylamine (0.527 mL, 4 mmol, 1 equiv.) followed by the addition of Pt/C 5% (155 mg, 0,04 mmol, 1 mol%) and CaH_2 90% (110 mg, 0.6 equiv.). After the addition of CaH_2, the sealed tube was rapidly closed. The tube was then introduced in a preheated oil bath at 60 °C and stirred with rpm of 700 at this temperature for 15 h. ^{1}H NMR of the reaction showed complete conversion of the starting material and a mixture of imine and amine of 11/89. The reaction was filtrated on Millipore and washed with 2 mL of toluene straight in another sealed tube.

To this crude was added under argon benzaldehyde (427 mg, 4.03 mmol, 1.01 equiv), hexylamine (402 mg, 3.98 mmol) followed by CaH_2 (110 mg). The tube was sealed, heated, introduced in an oil bath preheated at 60 °C and stirred at rpm 700 for 15 h. After reaction, an ^{1}H NMR of the reaction showed a mixture of amine and imine of 40/60. After filtration and evaporation of the solvent 1.434g was recovered corresponding to 95% of the total expected mass. ^{1}H NMR of the crude showed the same proportion than before filtration. Hence, the yield of imine is 57% and of amine 38%. The quantity of imine observed in the reaction corresponds to the 10% remaining of the first reaction followed by the only formation of imine in the second reaction. Consequently, it seems that the filtrate of the first reaction does not contain any active catalyst. These observations let us think that the reaction is heterogeneously catalysed.

[1]H NRM of the first reaction before filtration

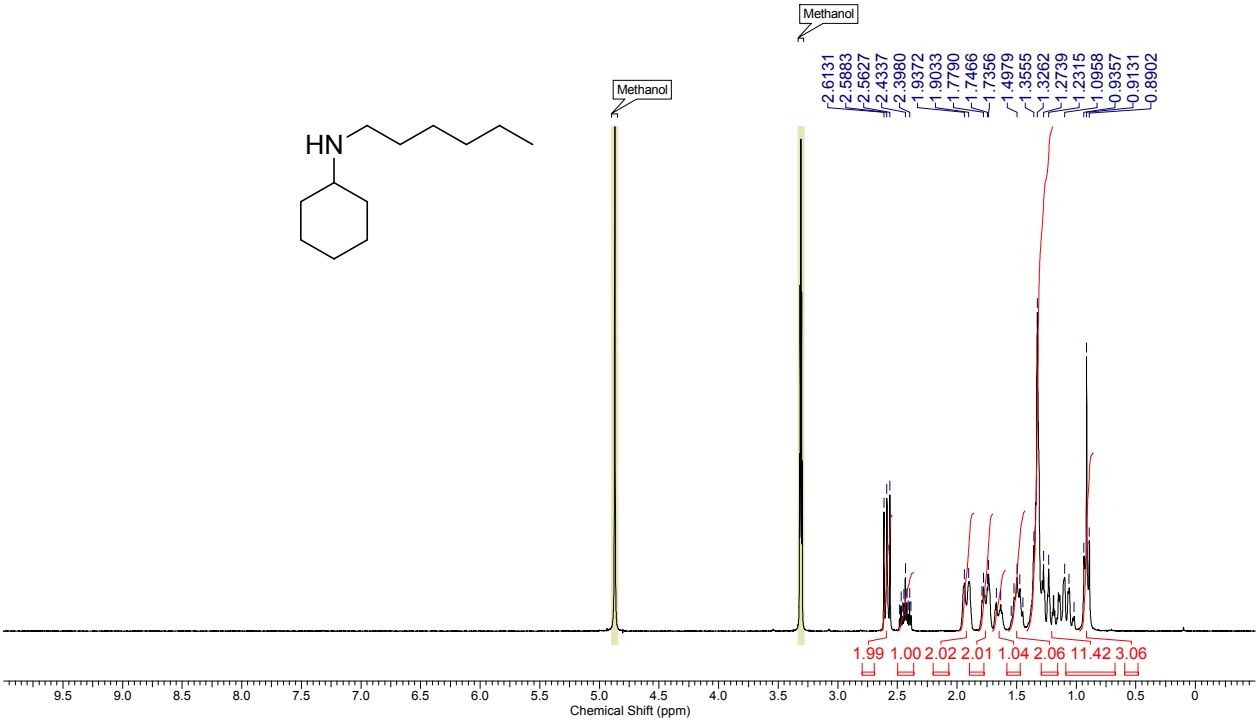


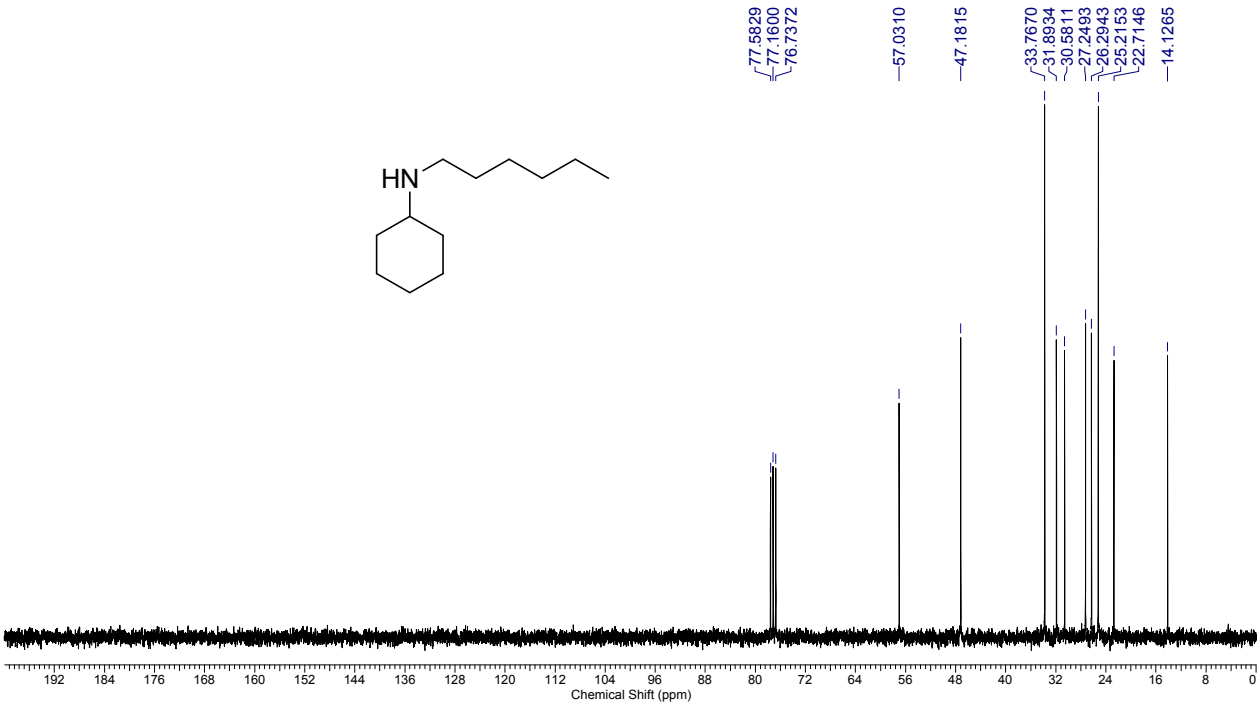
[1]H NRM of the second reaction before filtration

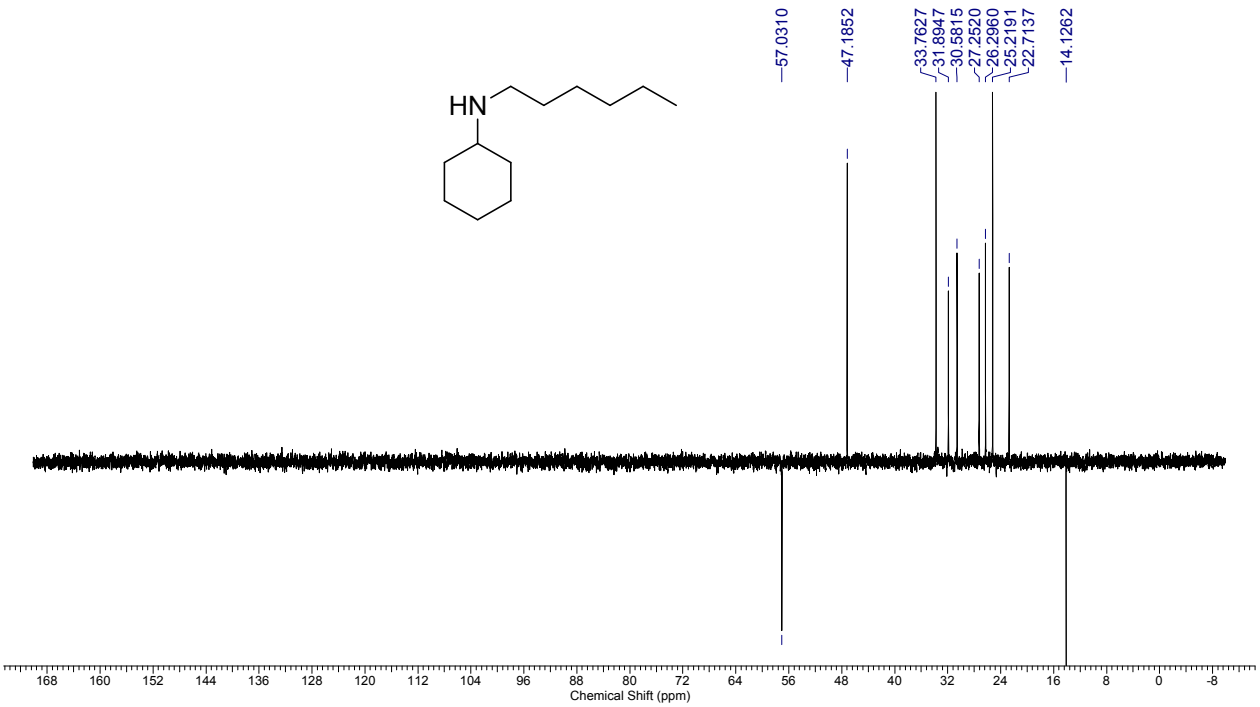


6. Spectra

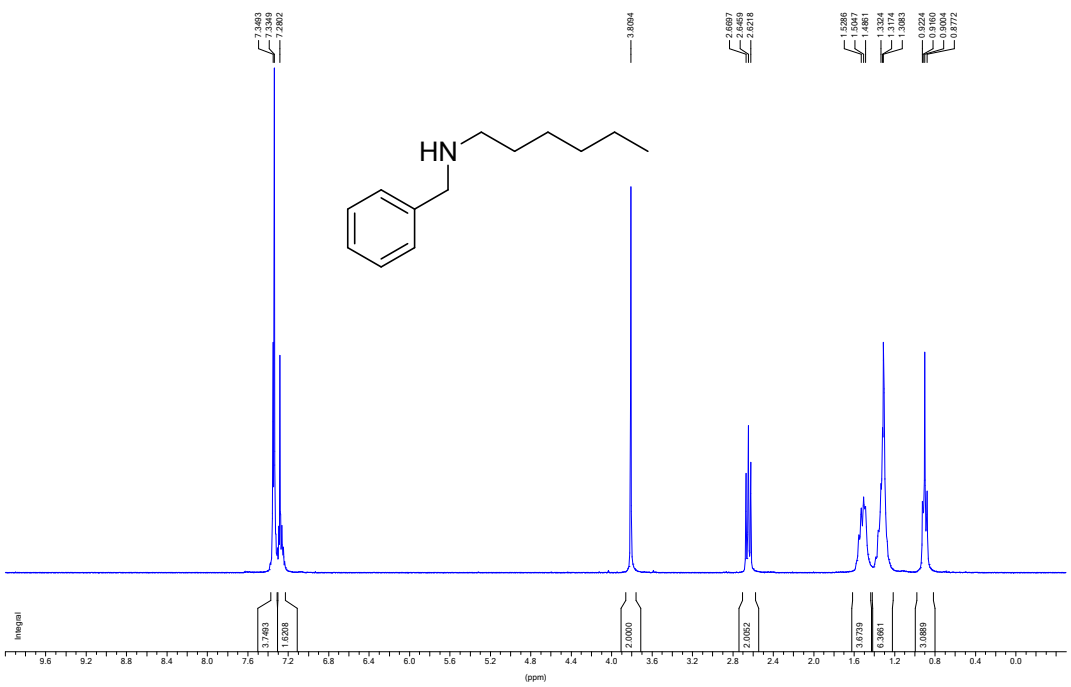
N-hexyl-cyclohexylamine (3)

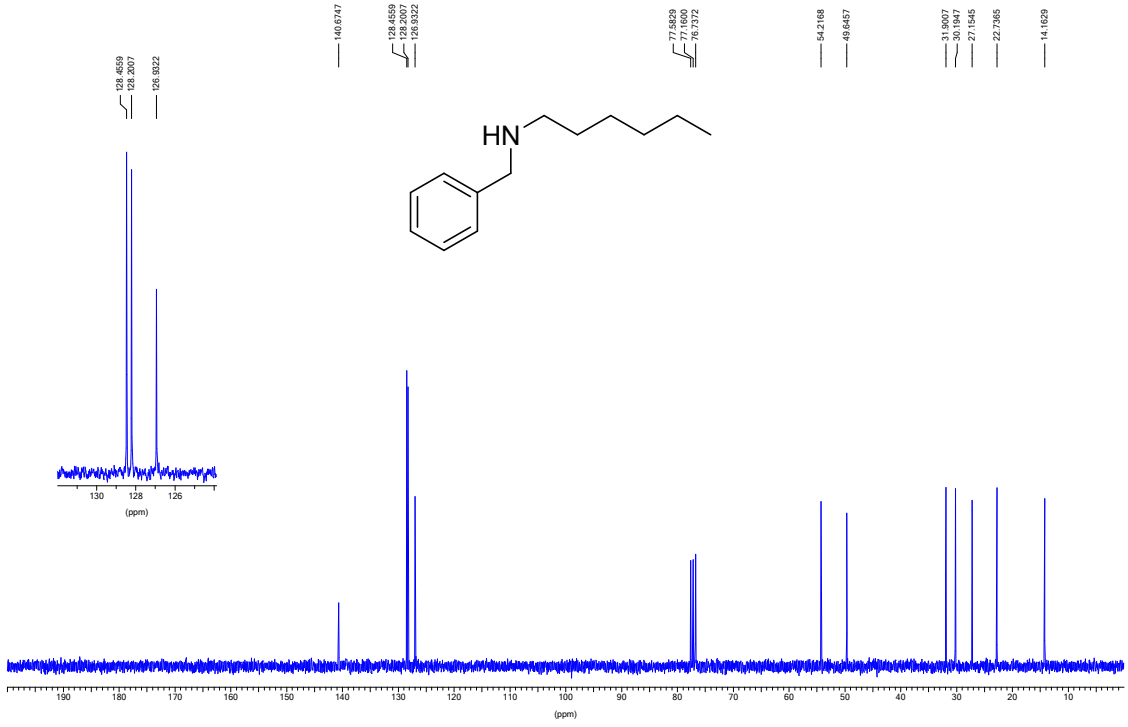


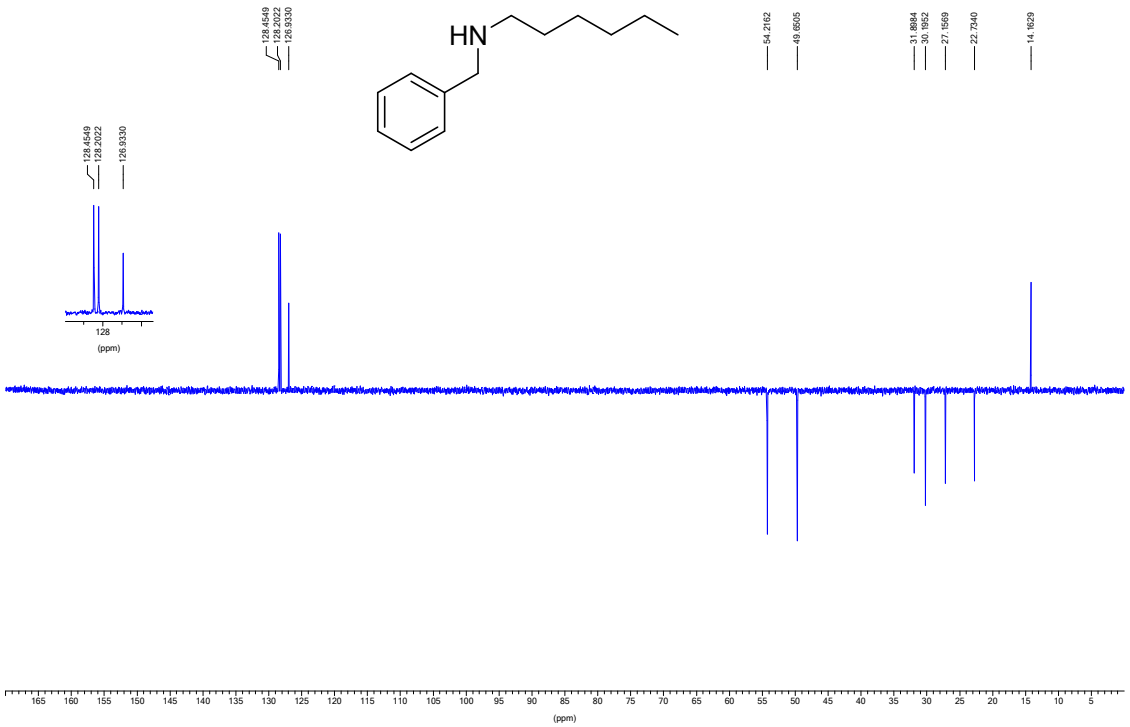




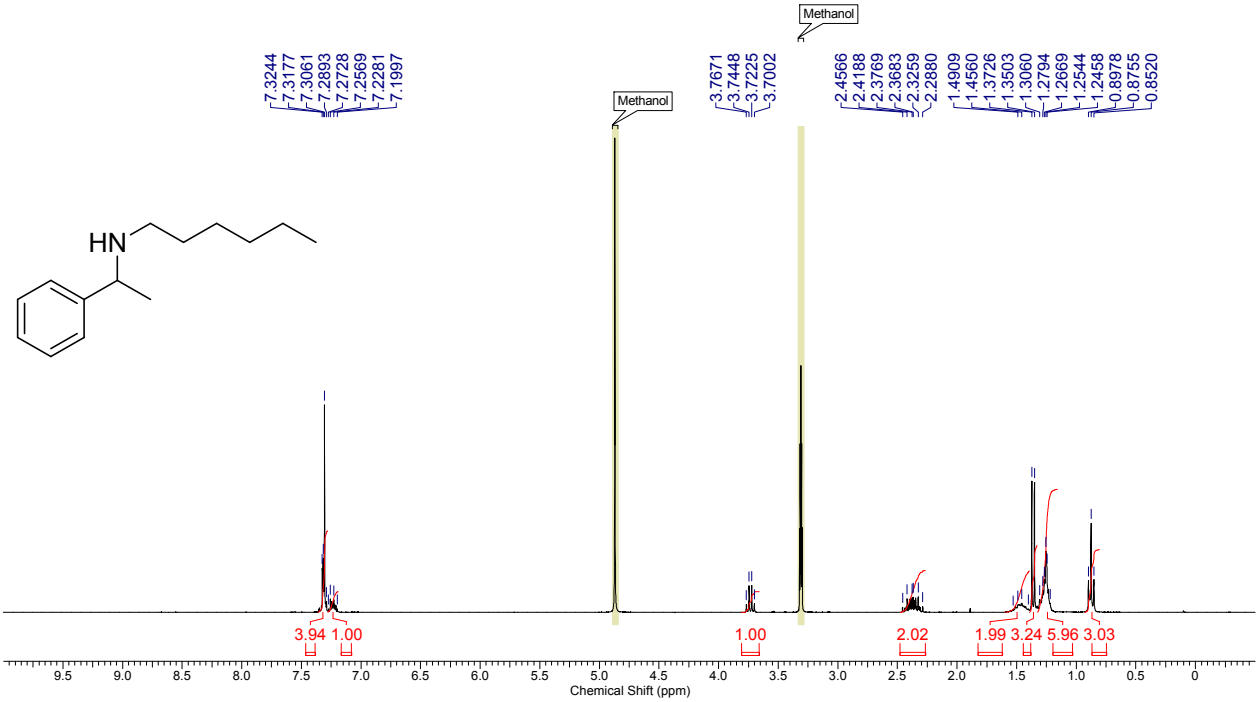
***N*-benzyl-*N*-hexylamine (11)**

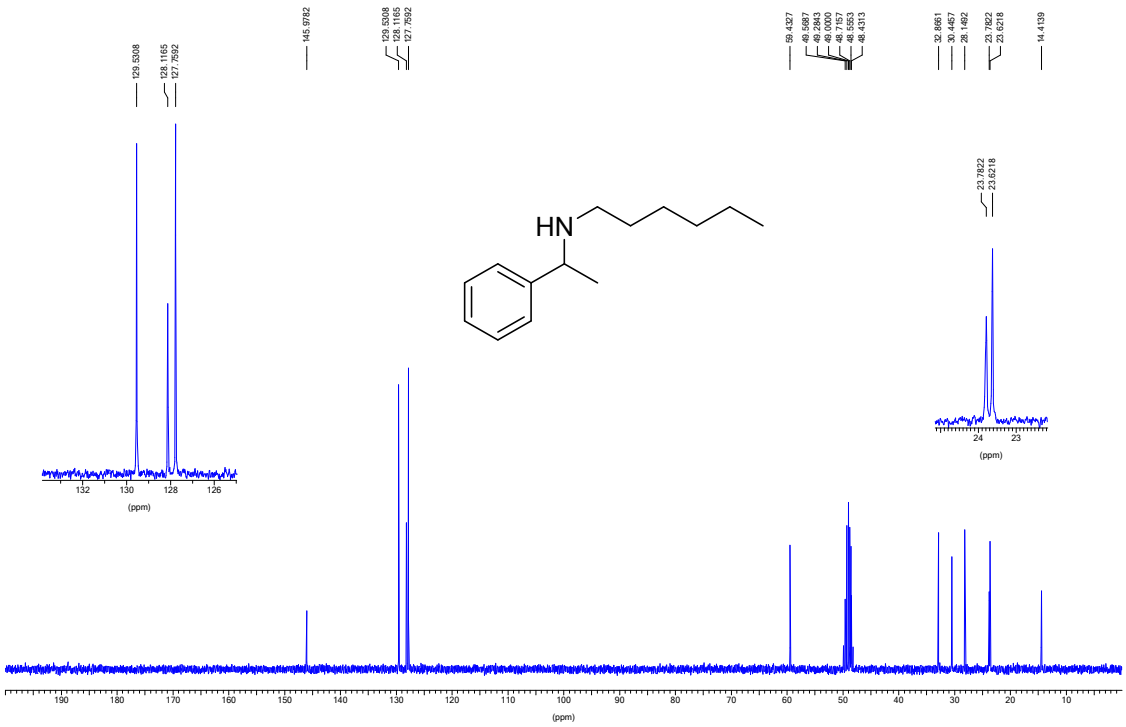

7.3483
7.3349
7.2802
3.8084
2.6697
2.6459
2.6218
1.5286
1.5067
1.4861
1.3324
1.3174
1.3083
0.9224
0.9160
0.9004
0.8772
HN
Integral
3.7483
1.6208
2.0000
2.0052
3.6739
6.3961
3.0889
(ppm)

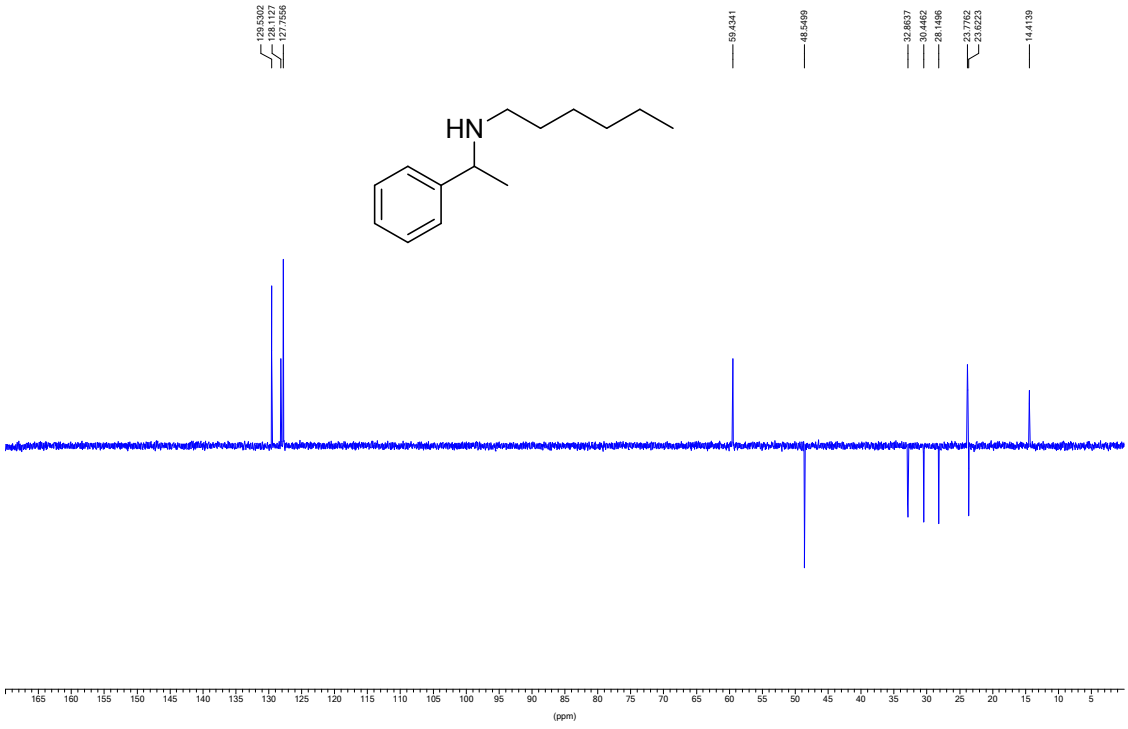

140.6747
128.4559
128.2007
128.9322
77.5829
77.1600
76.7372
54.2168
49.8457
31.9007
30.1947
27.1545
22.7365
14.1629
HN
(ppm)



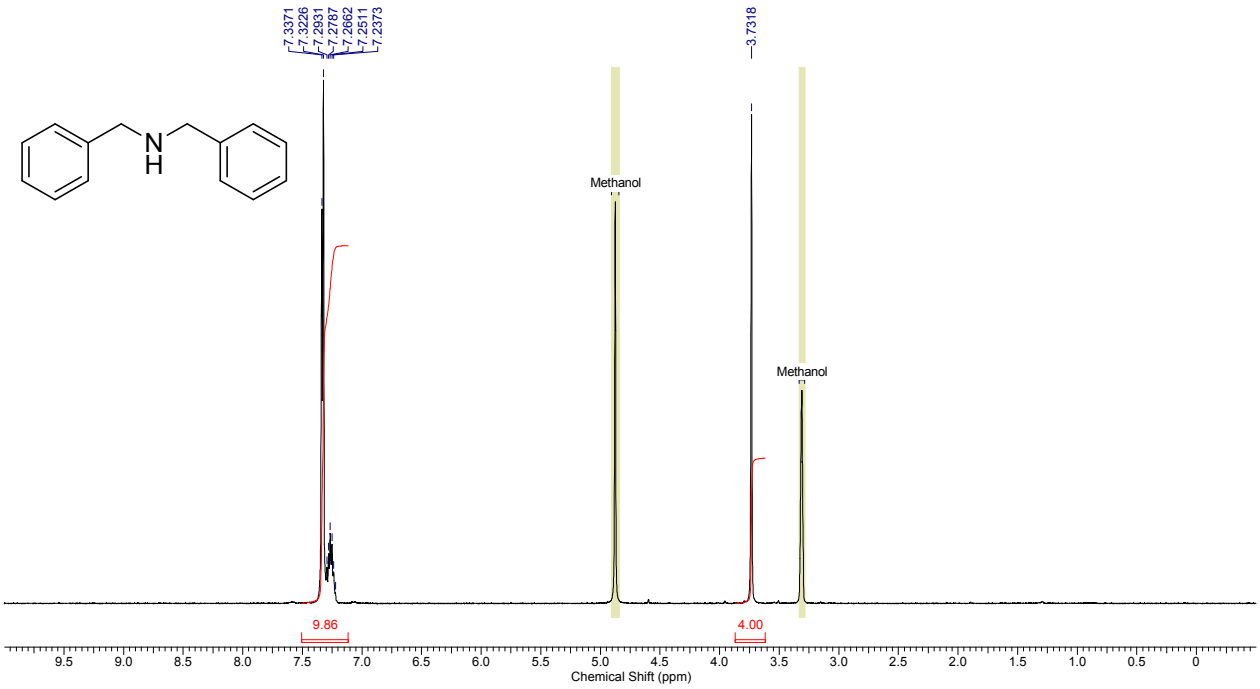
N-(1-phenyl-ethyl)hexylamine (13)

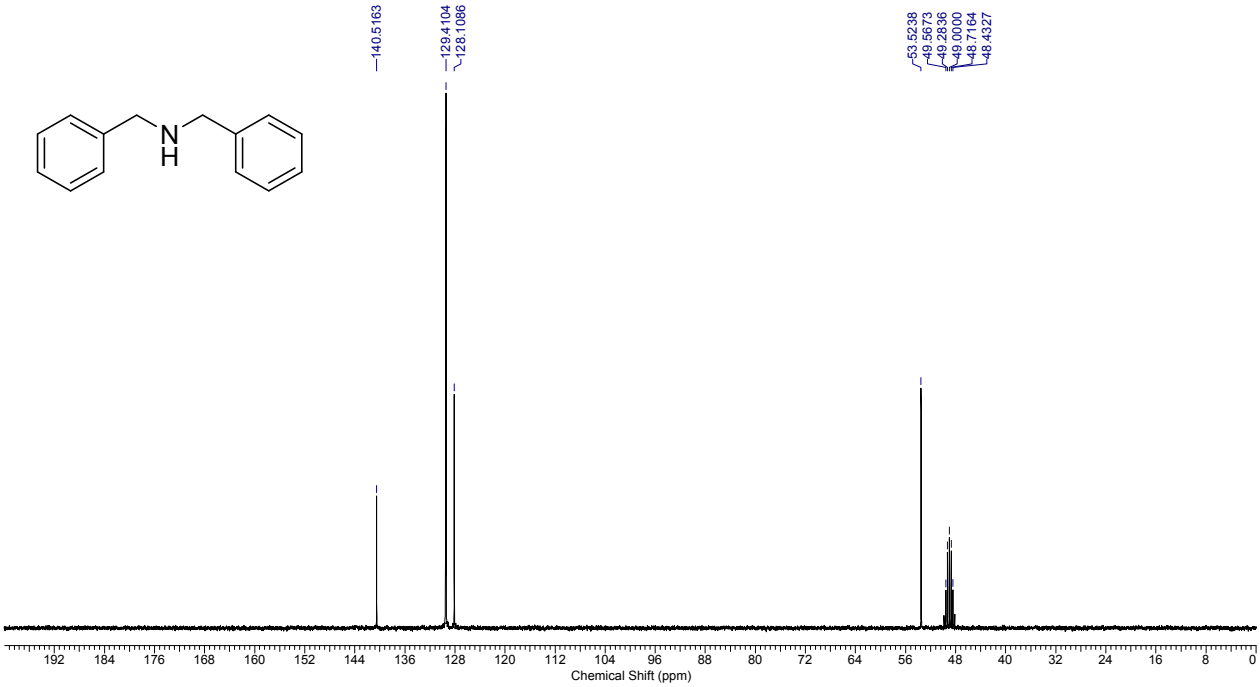



129.5308
128.1165
127.7692
145.9782
129.5308
128.1165
127.7692
59.4327
49.5687
49.2843
49.0000
48.7157
48.5553
48.4313
32.8651
30.4457
28.1492
23.7822
23.6218
14.4139
HN
(ppm)
(ppm)

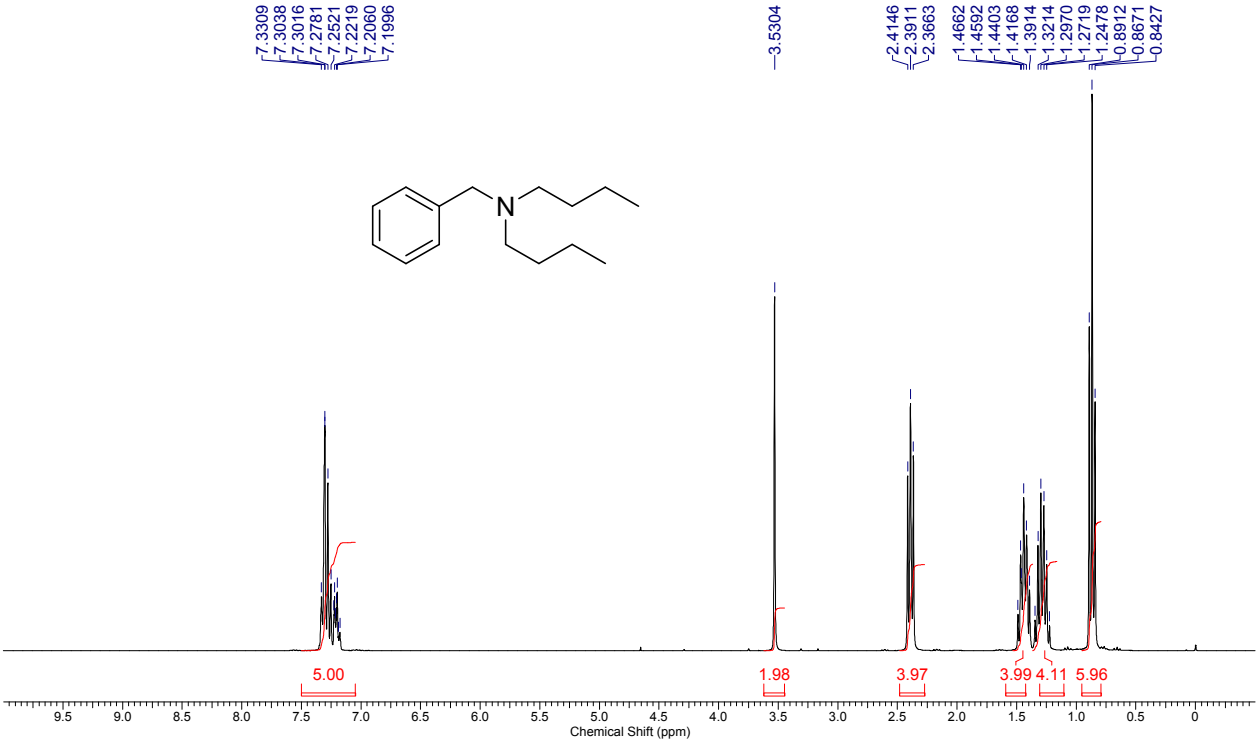

129.5302
128.1127
127.7556
59.4341
48.5499
32.8637
30.4462
28.1496
23.7752
23.6223
14.4139
HN
(ppm)

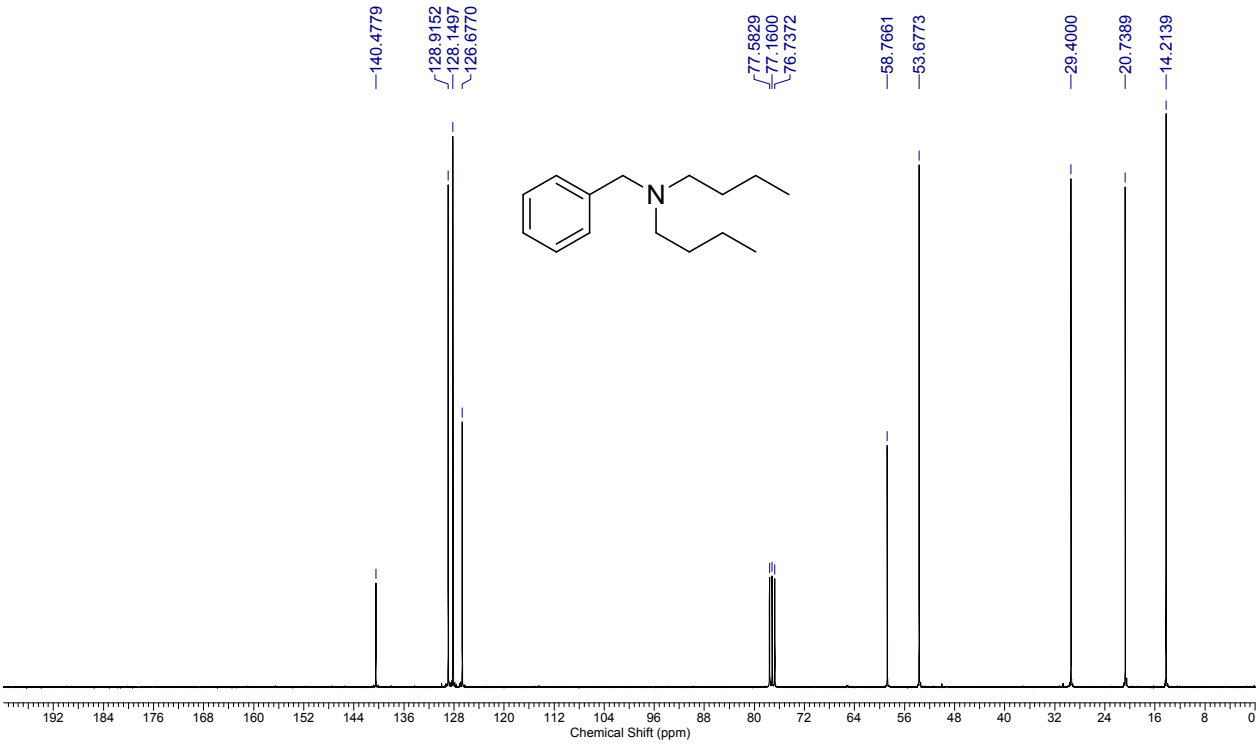
Dibenzylamine (22)

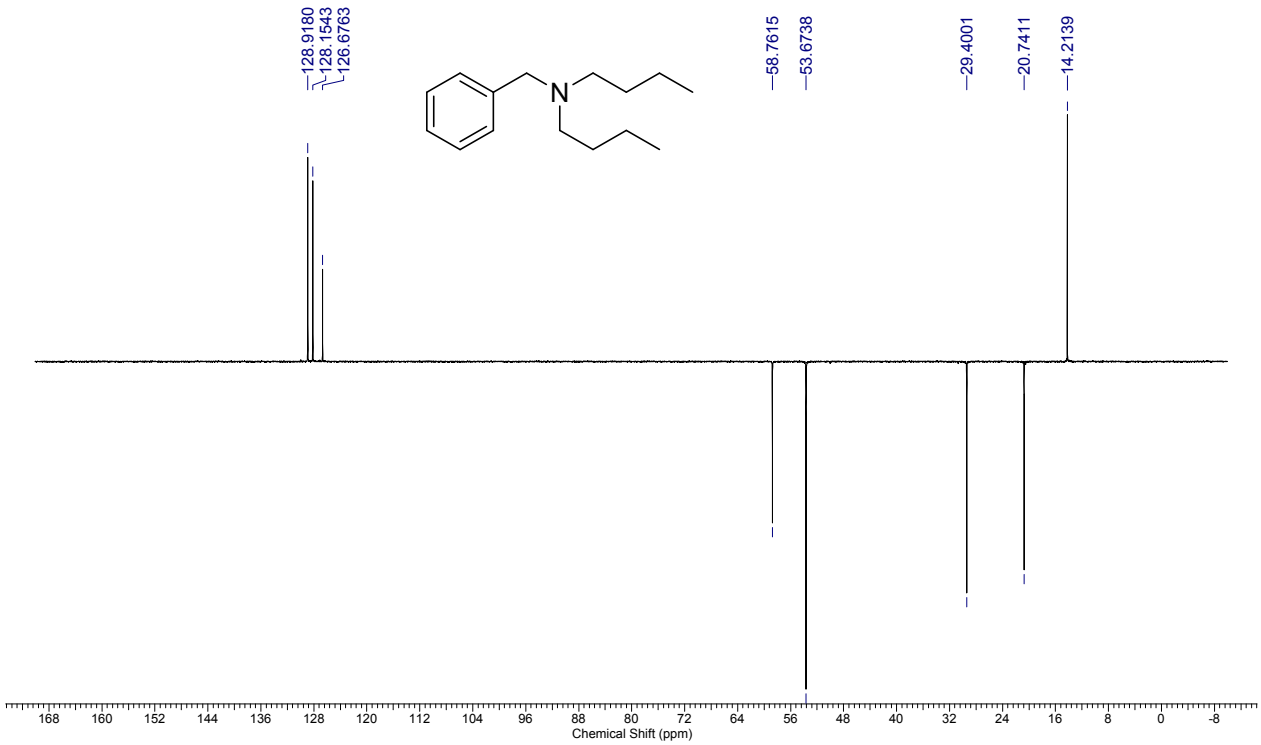




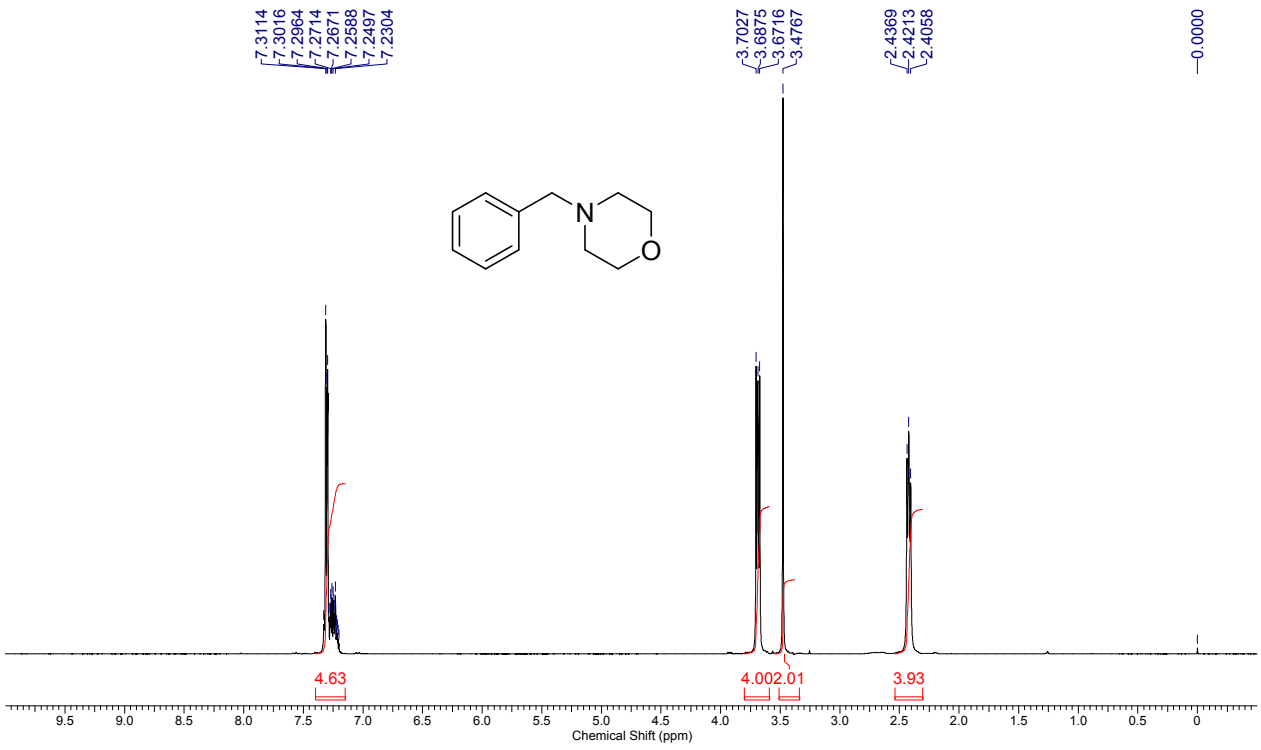
N,*N*-dibutylBenzenemethanamine (24)

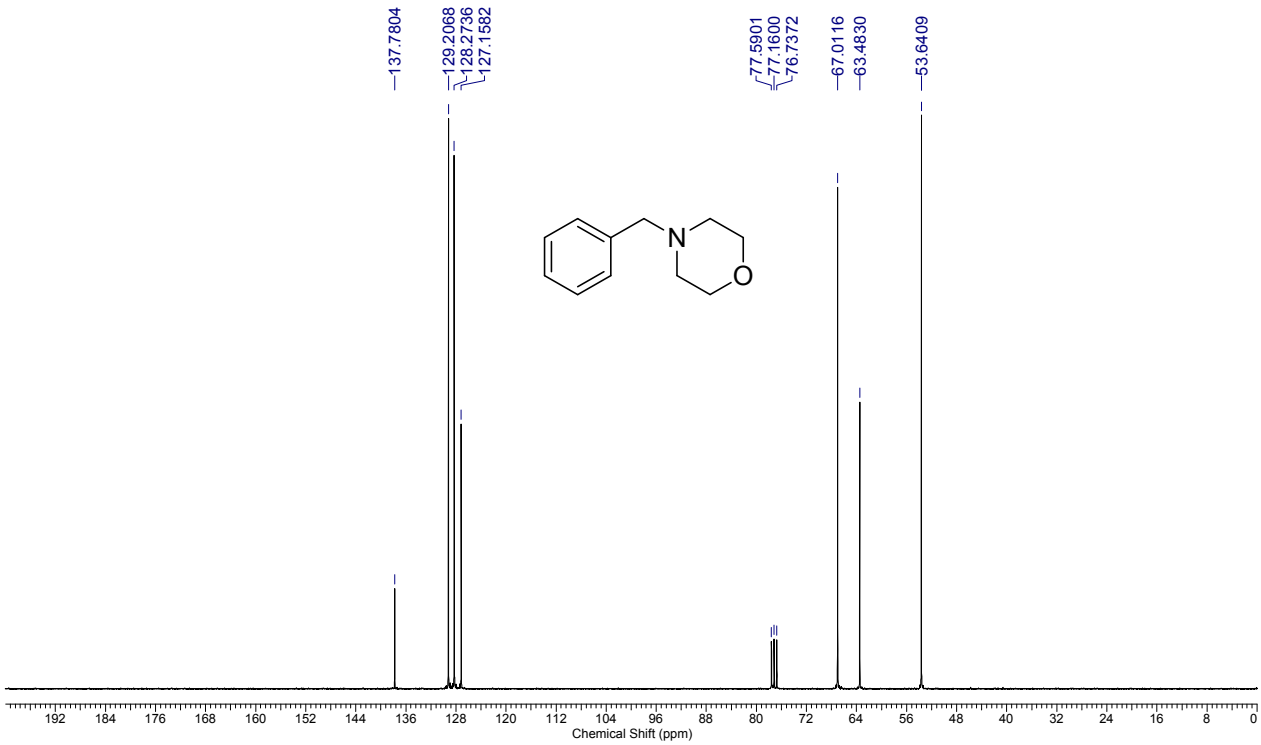




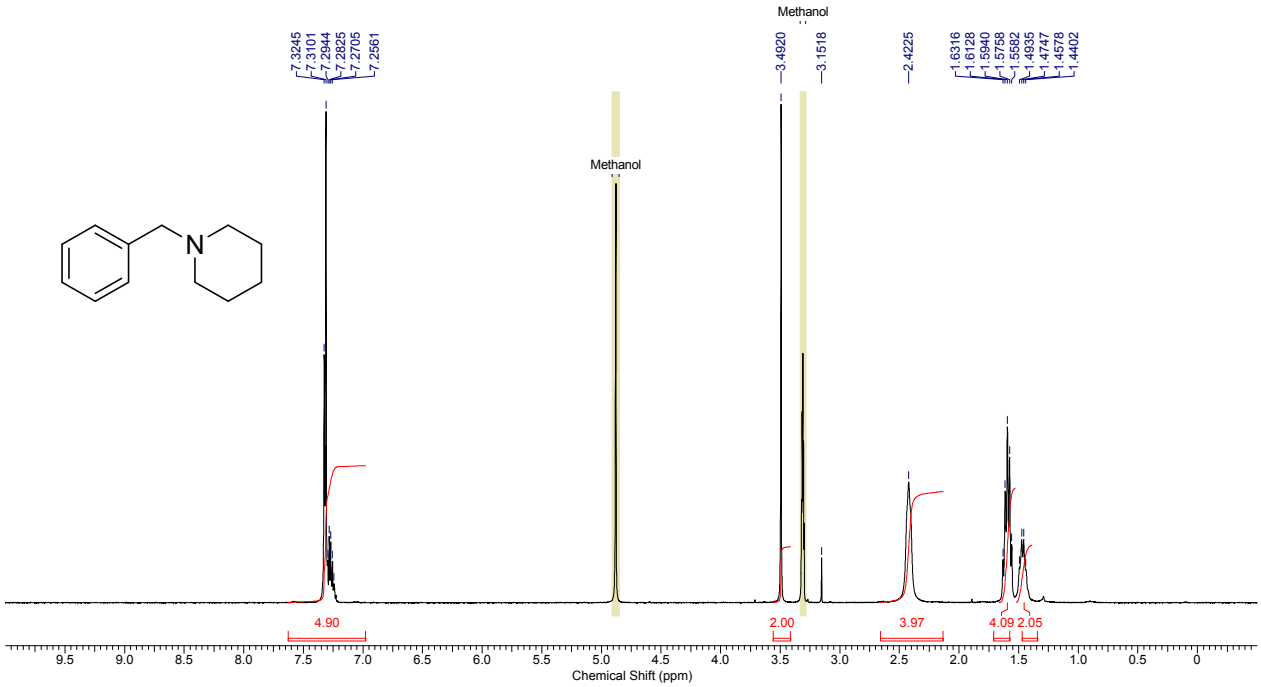


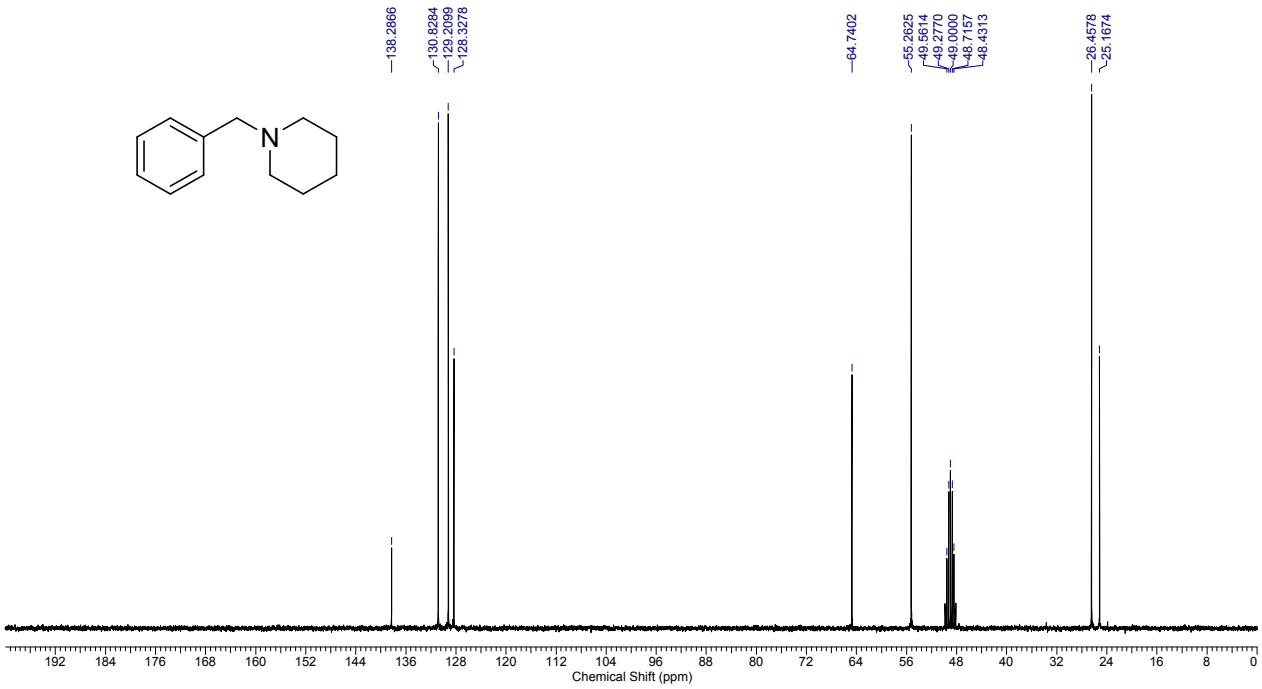
N-benzyl-morpholine (26)

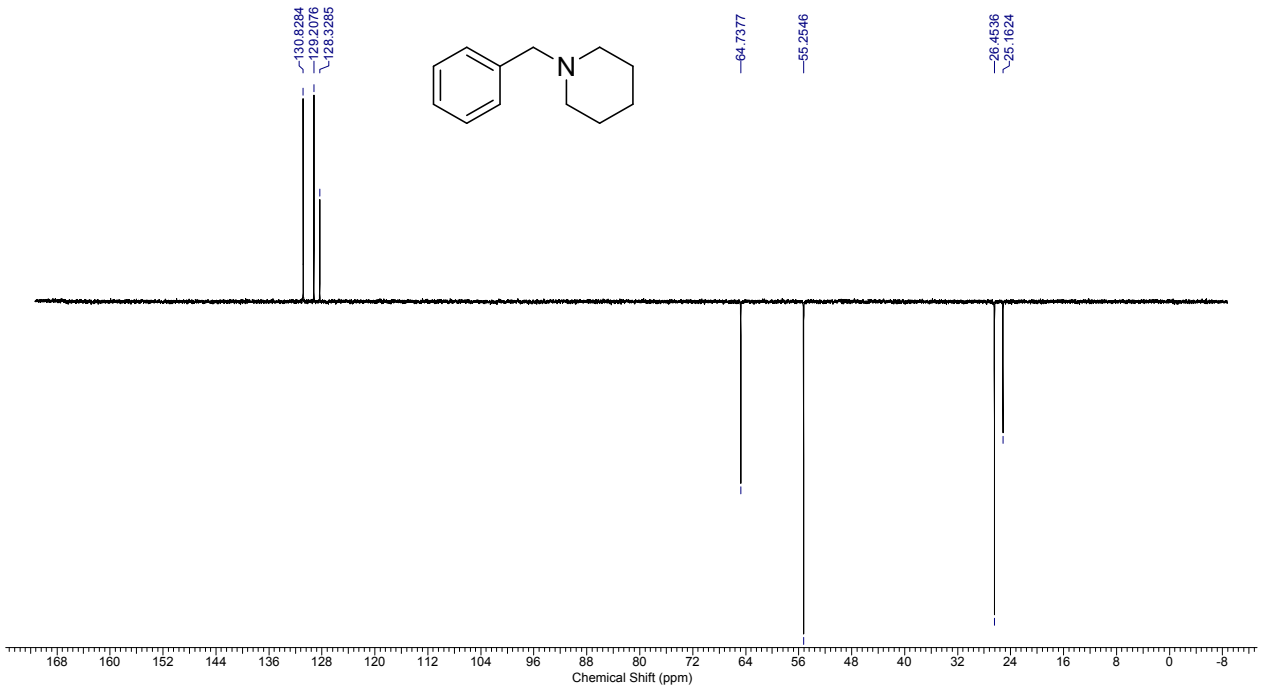




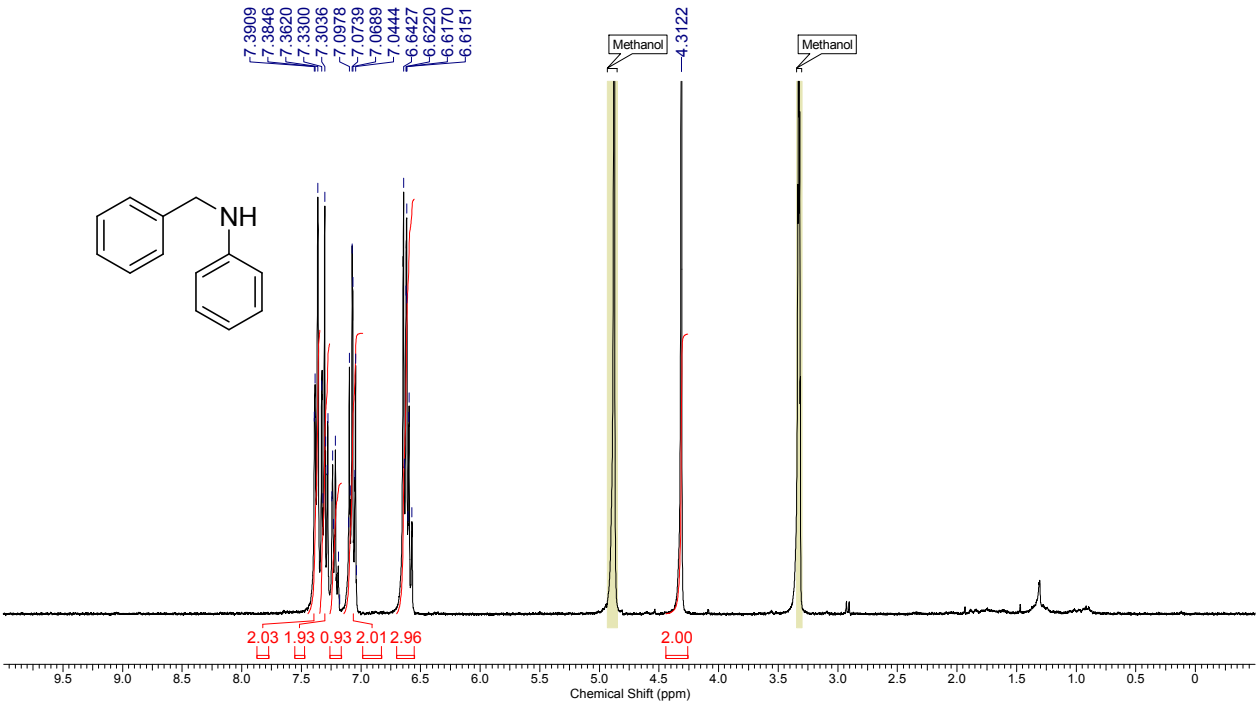
1-Benzylpiperidine (28)

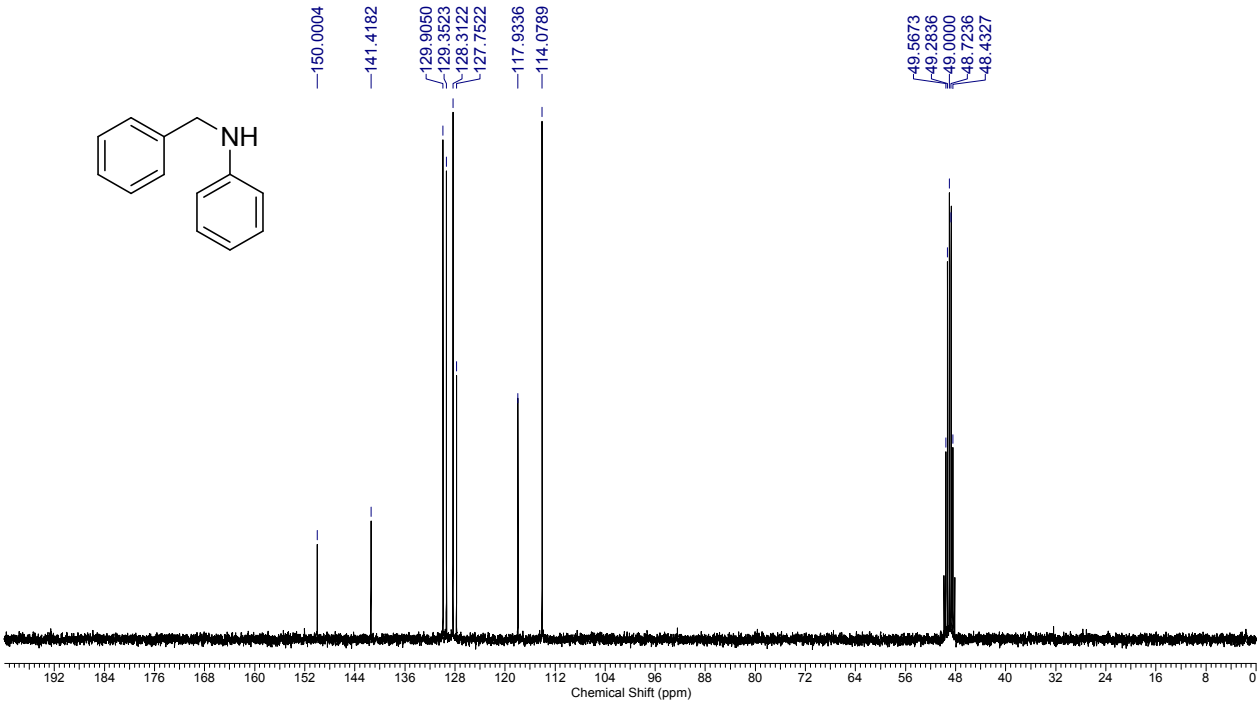


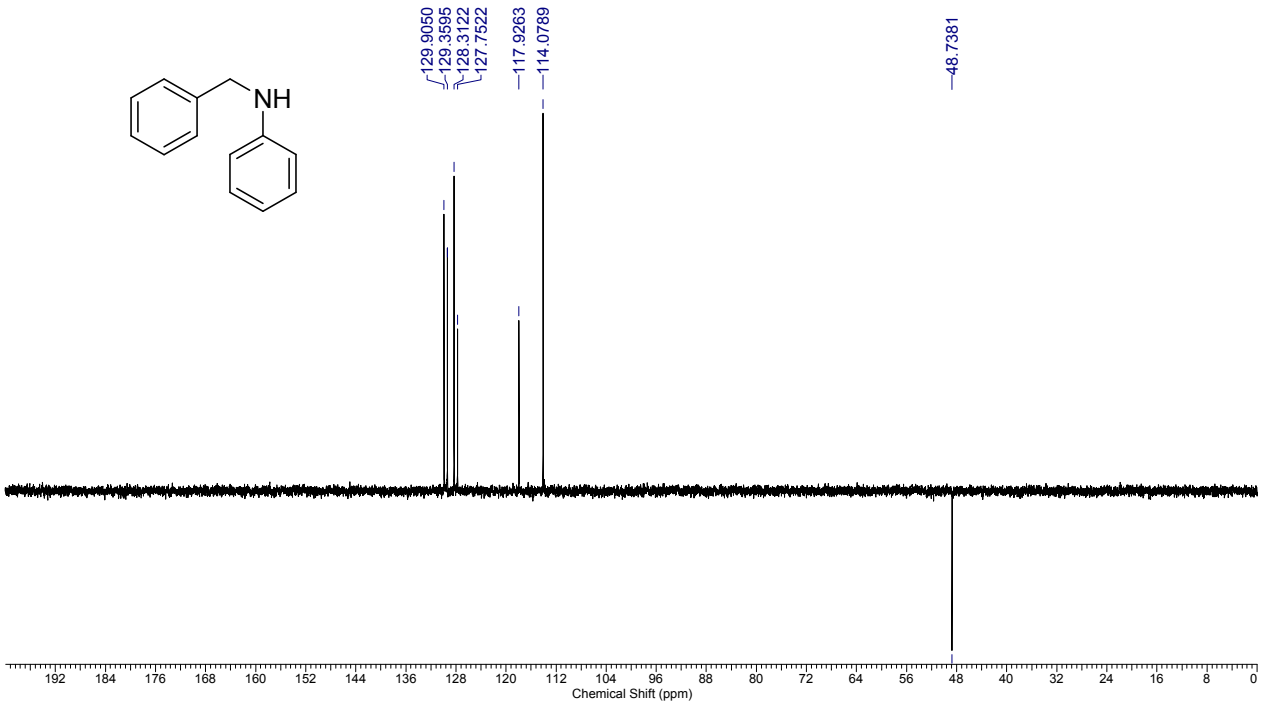

138.2866
130.8284
129.2099
128.3278
64.7402
55.2625
49.5614
49.2770
49.0000
48.7157
48.4313
26.4578
25.1674
N
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


130.8284
129.2076
128.3285
64.7377
55.2546
26.4536
25.1624
N
168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)

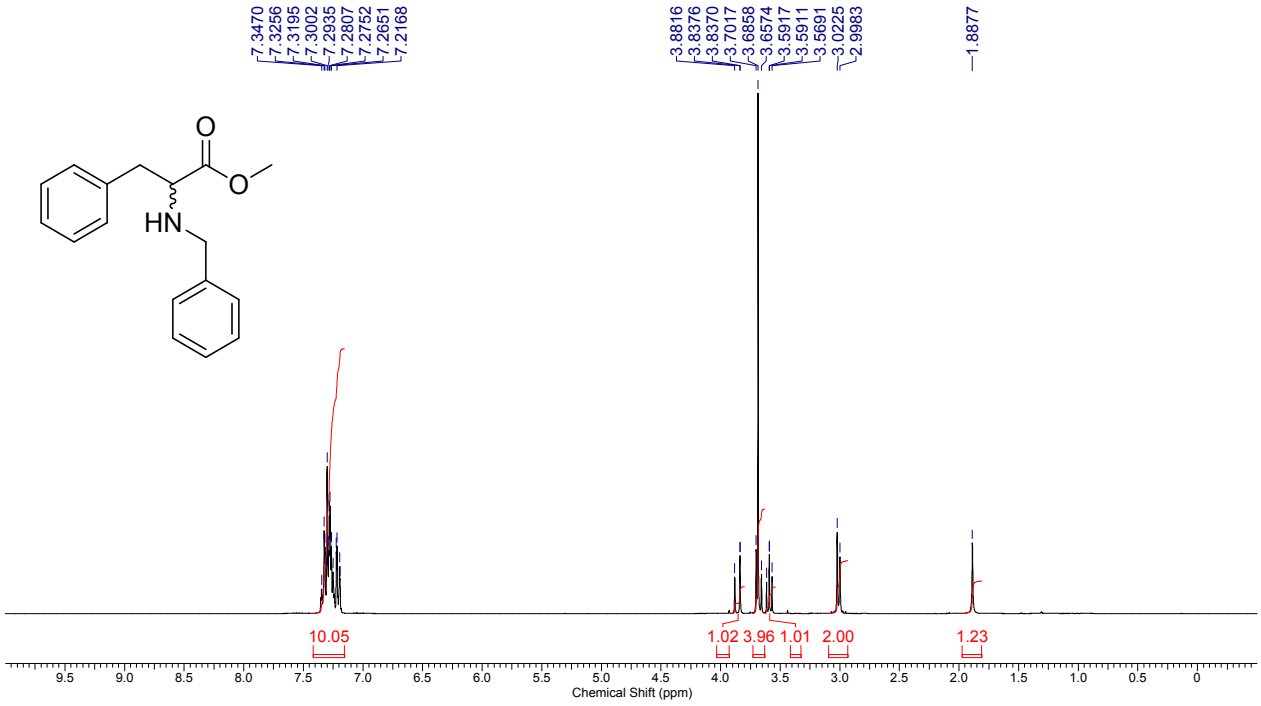
N-benzyl-aniline (30)

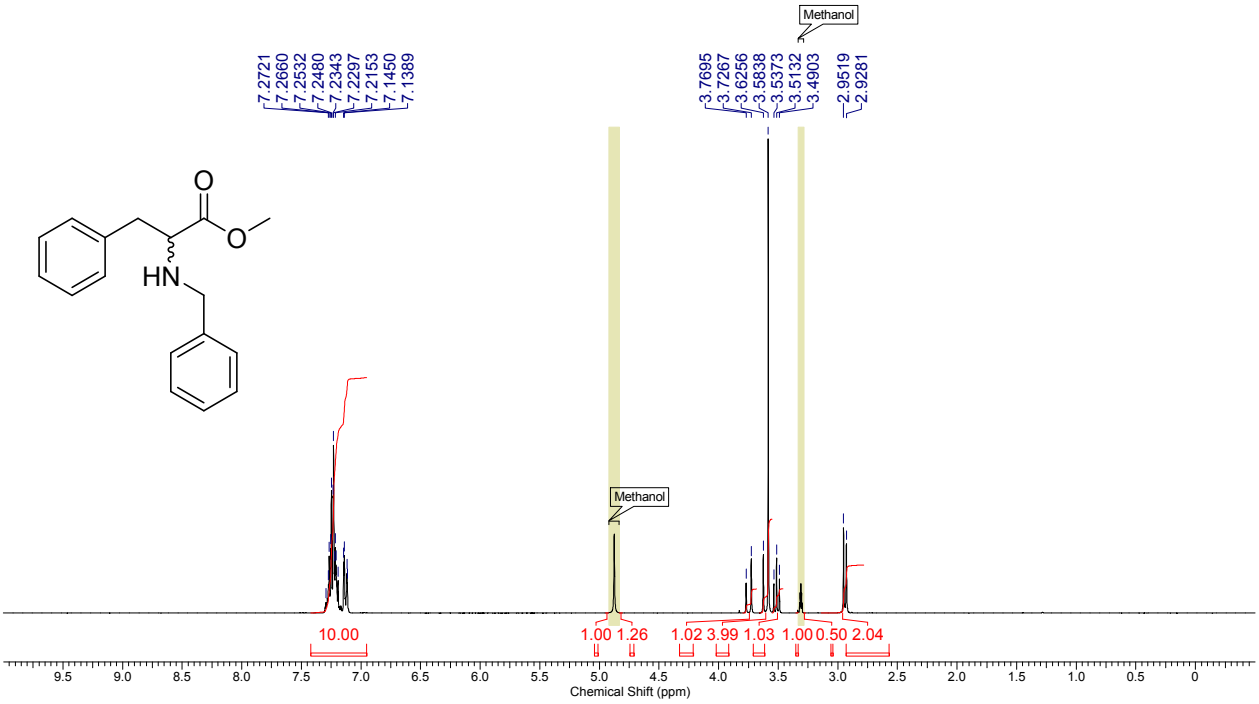


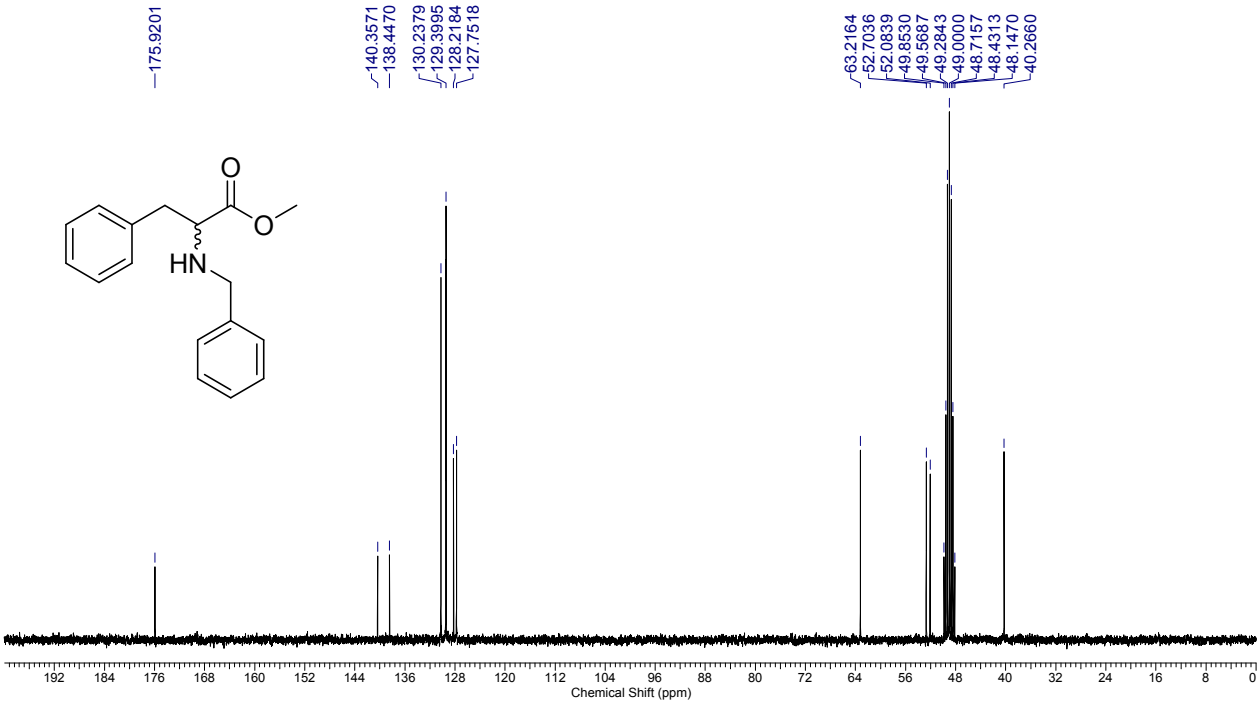




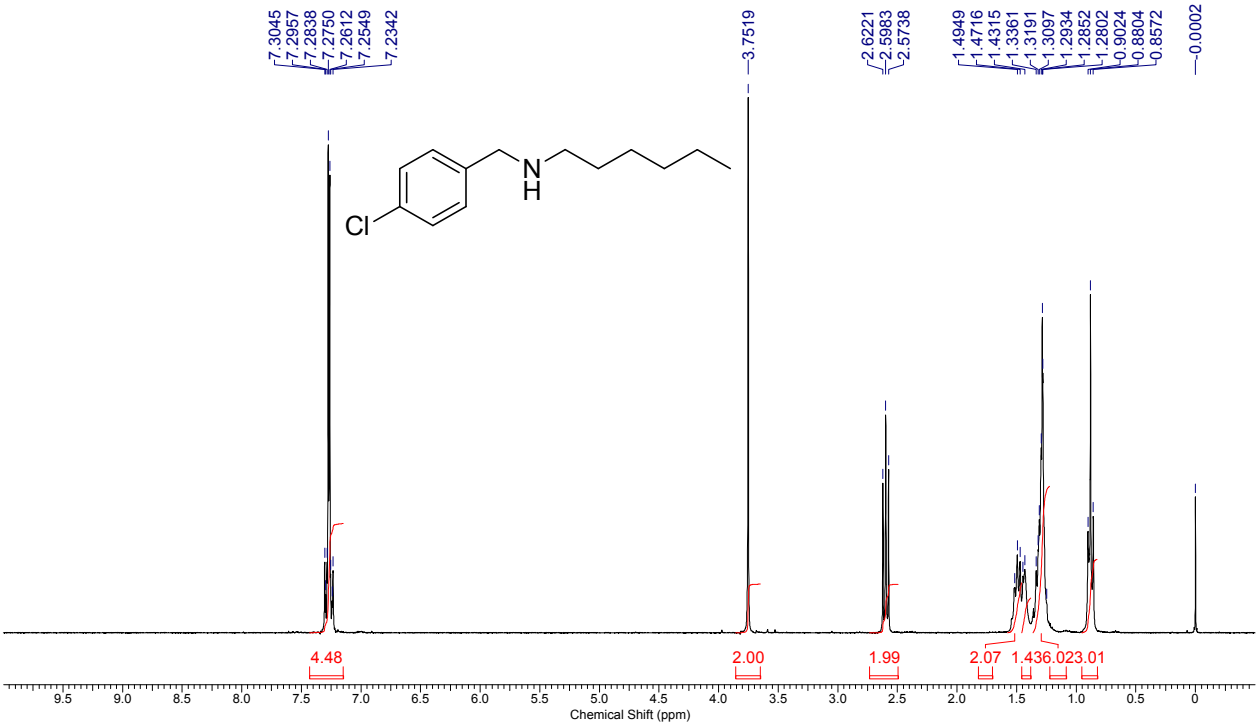
N-benzylphenylananine methyl ester (34)

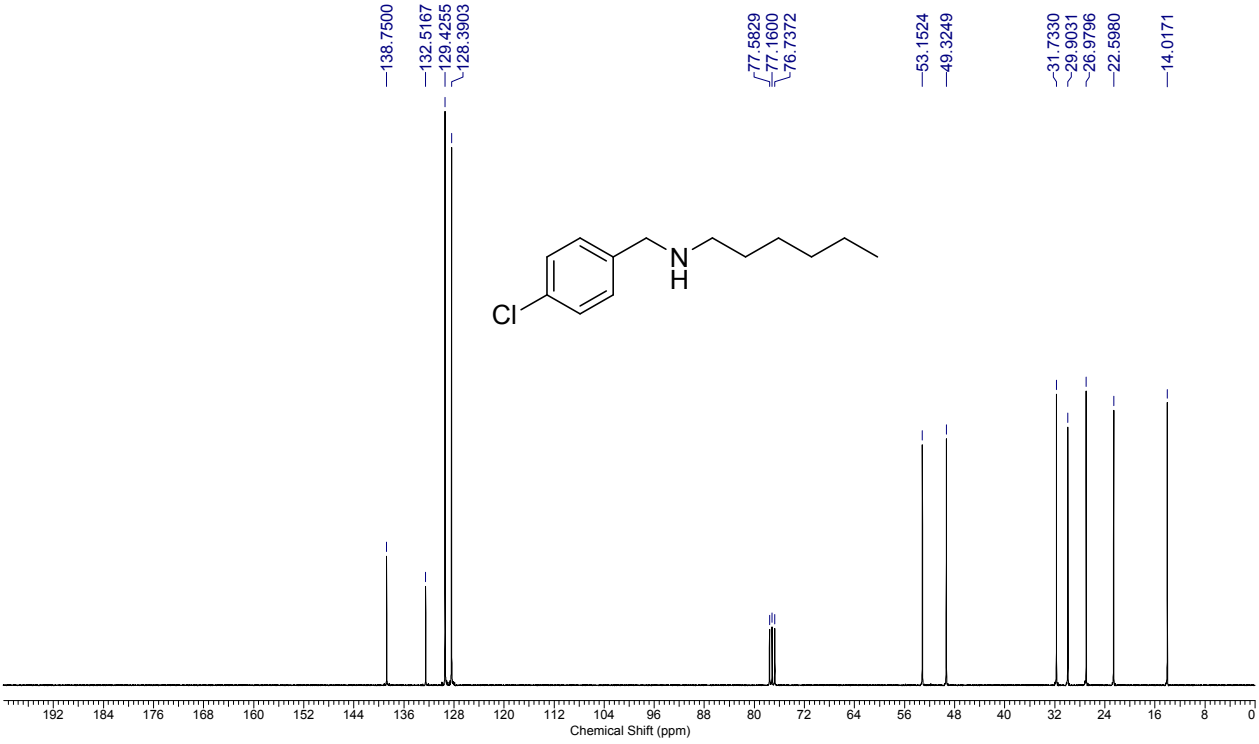



Methanol
7.2721
7.2660
7.2532
7.2480
7.2343
7.2297
7.2153
7.1450
7.1389
3.7695
3.7267
3.6256
3.5838
3.5373
3.5132
3.4903
2.9519
2.9281
O
O
HN
Methanol
10.00
1.00
1.26
1.02
3.99
1.03
1.00
0.50
2.04
Chemical Shift (ppm)

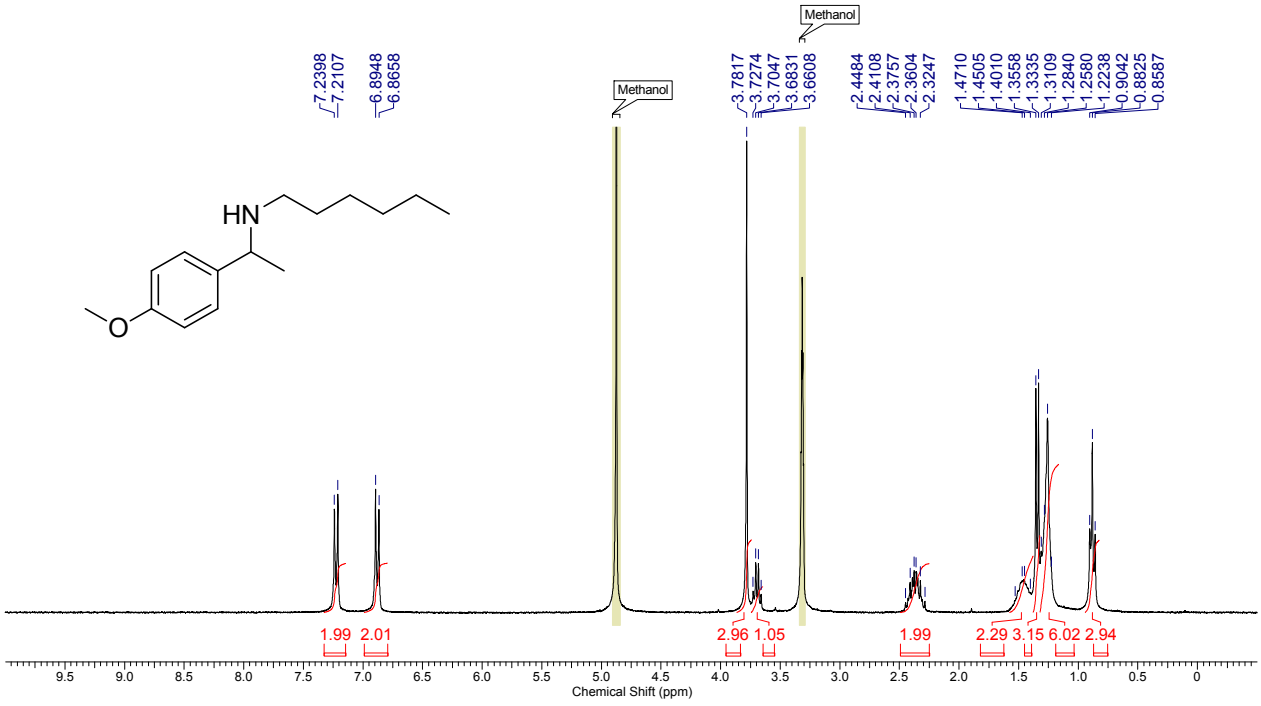

175.9201
140.3571
138.4470
130.2379
129.3995
128.2184
127.7518
63.2164
52.7036
52.0839
49.8530
49.5687
49.2843
49.0000
48.7157
48.4313
48.1470
40.2660
O
O
HN
Chemical Shift (ppm)

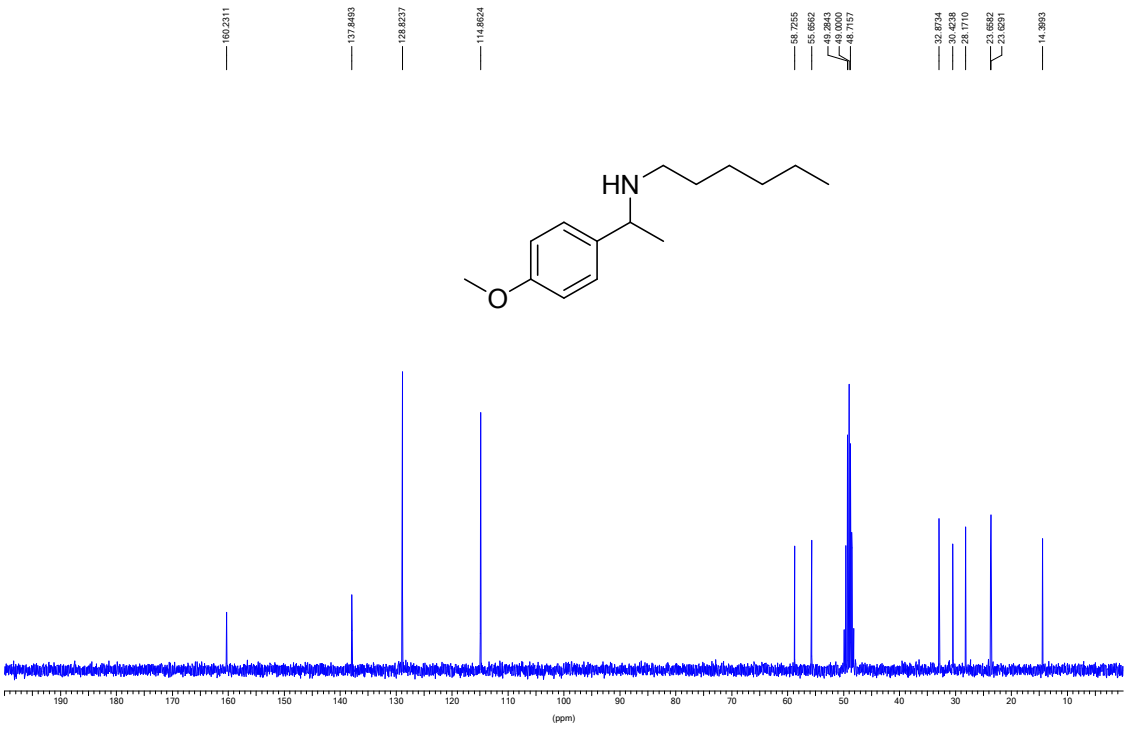
4-chloro-*N*-hexyl-Benzenemethanamine (37)

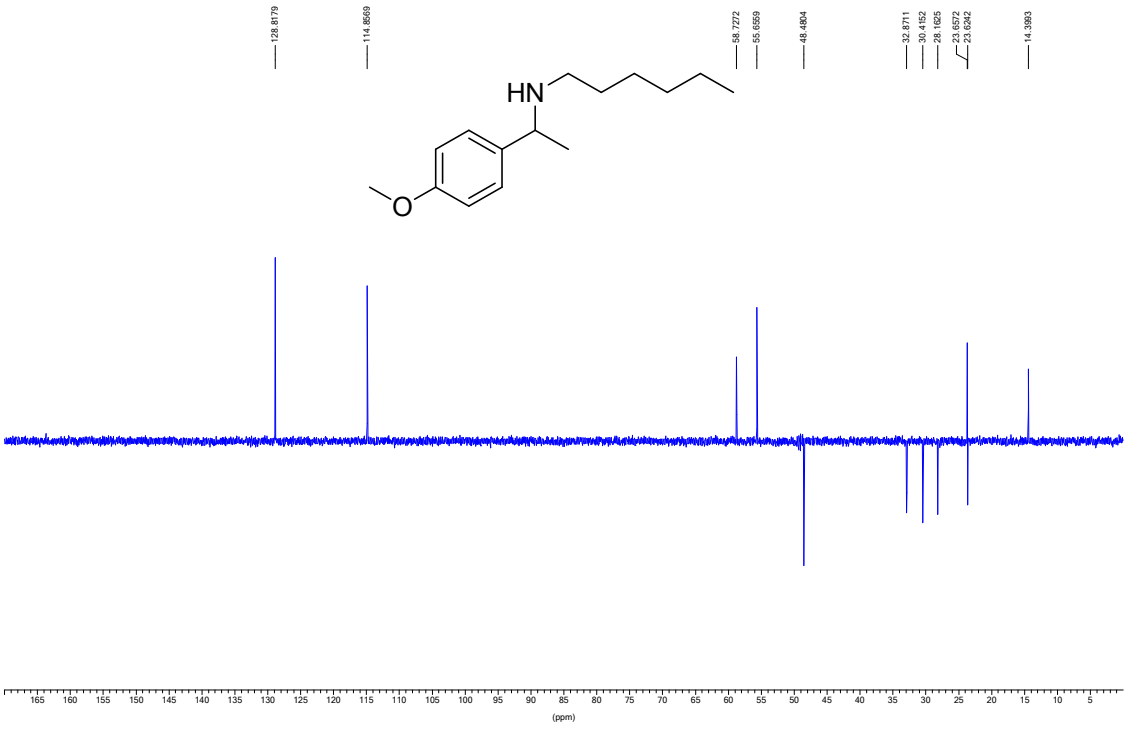




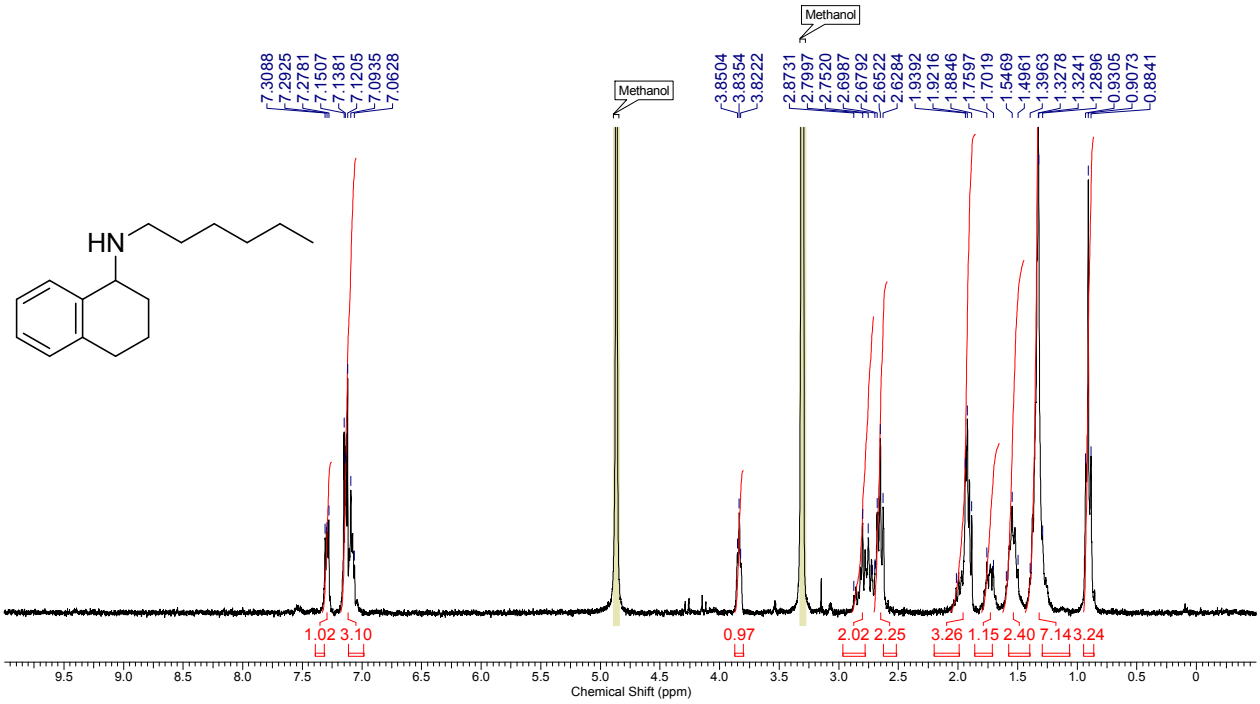
N-[1-(4-methoxyphenyl)ethyl]hexan-1-amine (39)

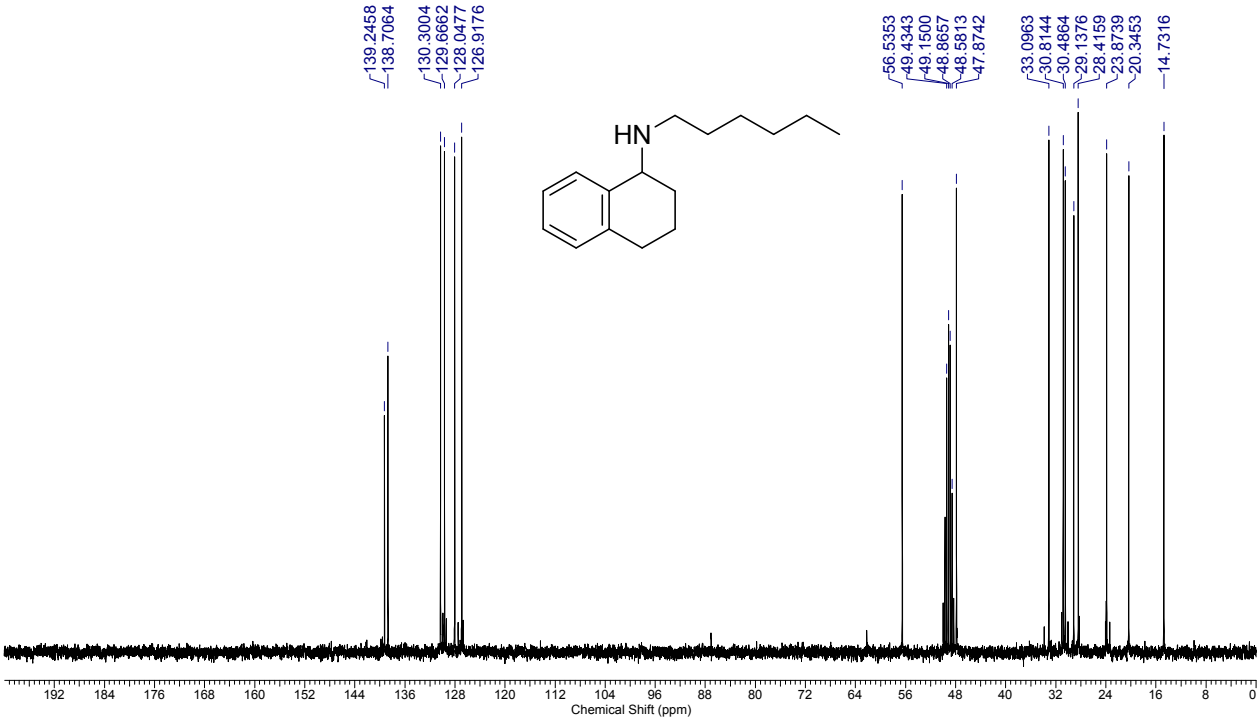


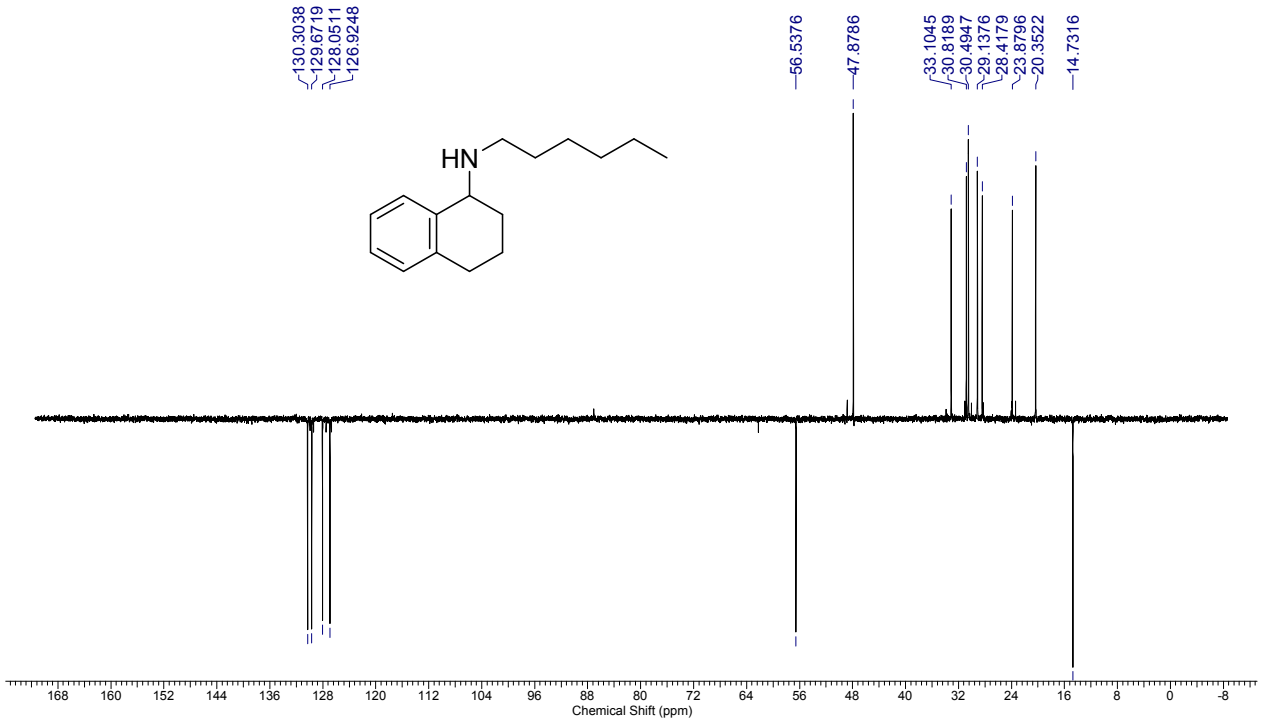

160.2311
137.8493
128.8237
114.8624
58.7255
55.6562
49.2843
49.0030
48.7157
32.8734
30.4238
28.1710
23.6582
23.6291
14.3993
HN
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

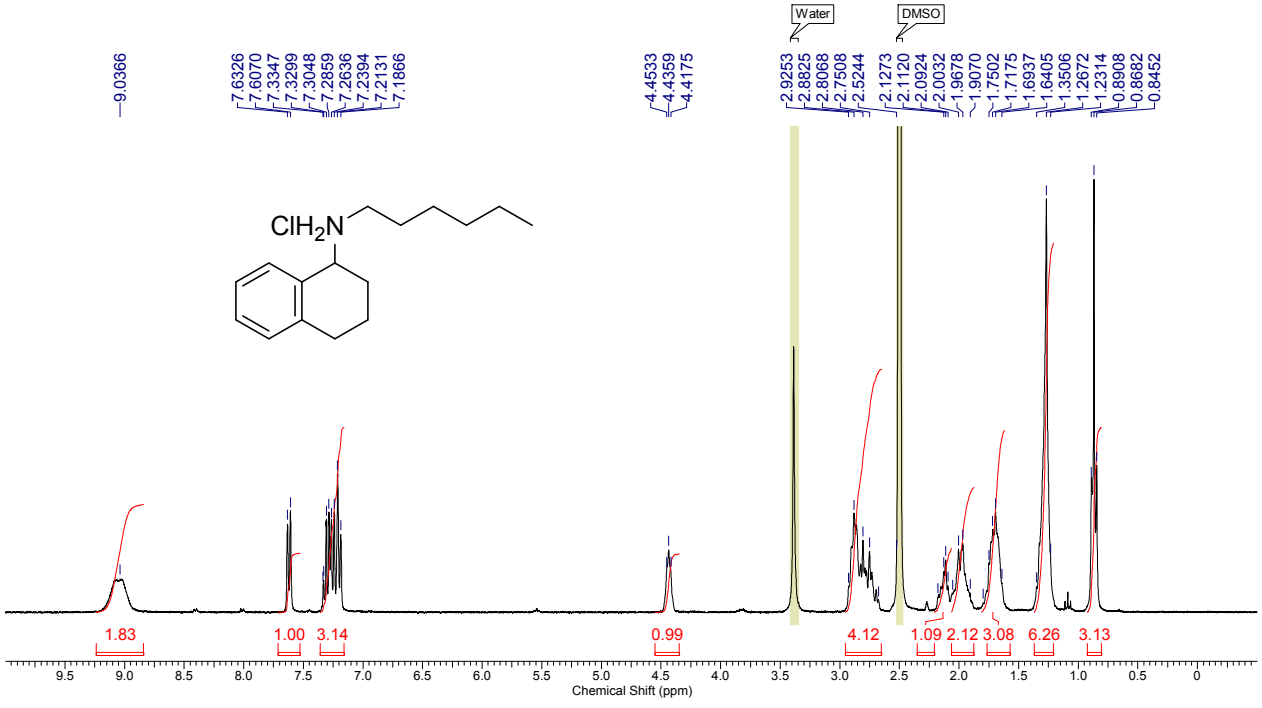

128.8179
114.8569
58.7272
55.6559
48.4804
32.8711
30.4152
28.1625
23.6572
23.6242
14.3993
HN
O
165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
(ppm)

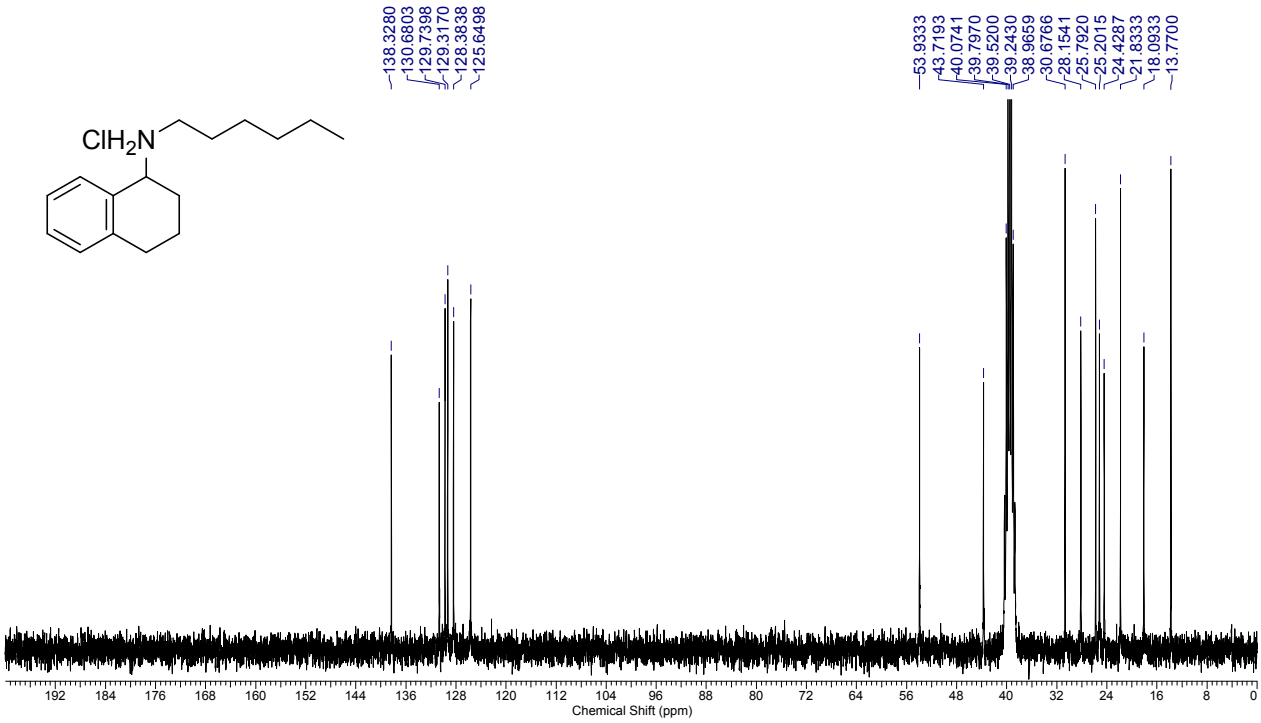
N-hexyl-1,2,3,4-tetrahydro 1-Naphthalenamine (41)

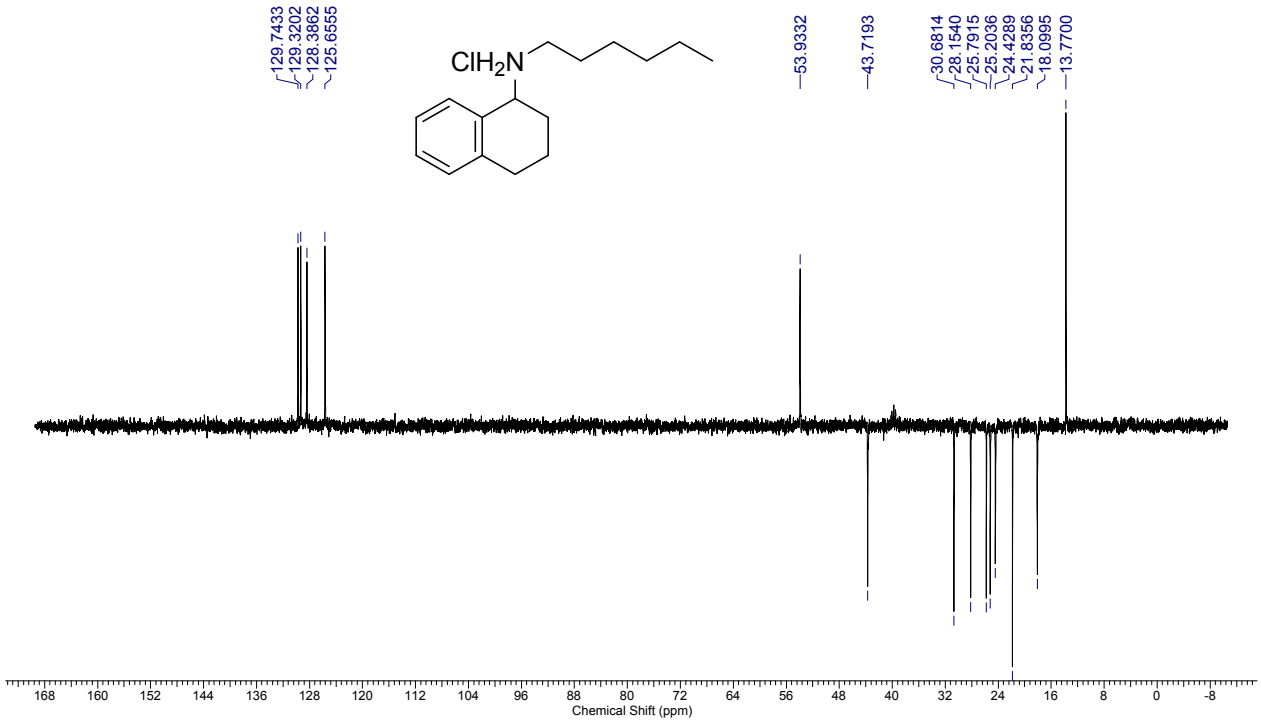




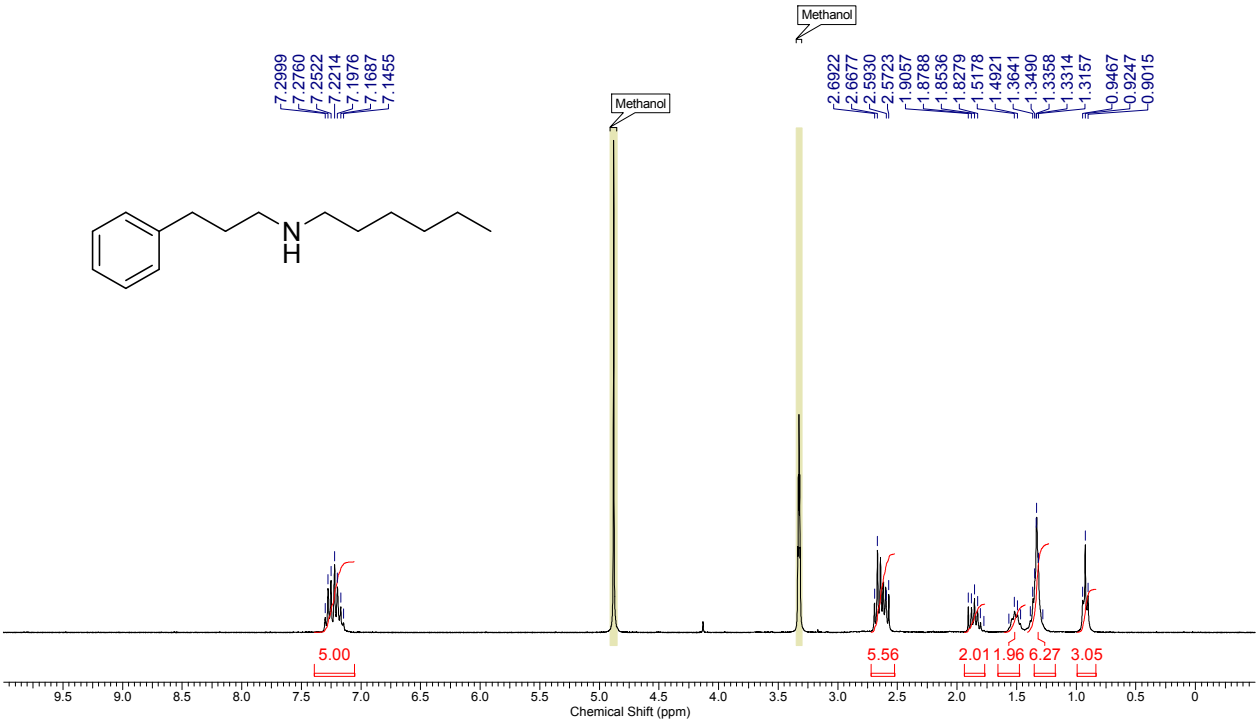

130.3038
129.6719
128.0511
126.9248
56.5376
47.8786
33.1045
30.8189
30.4947
29.1376
28.4179
23.8796
20.3522
14.7316
HN
Chemical Shift (ppm)

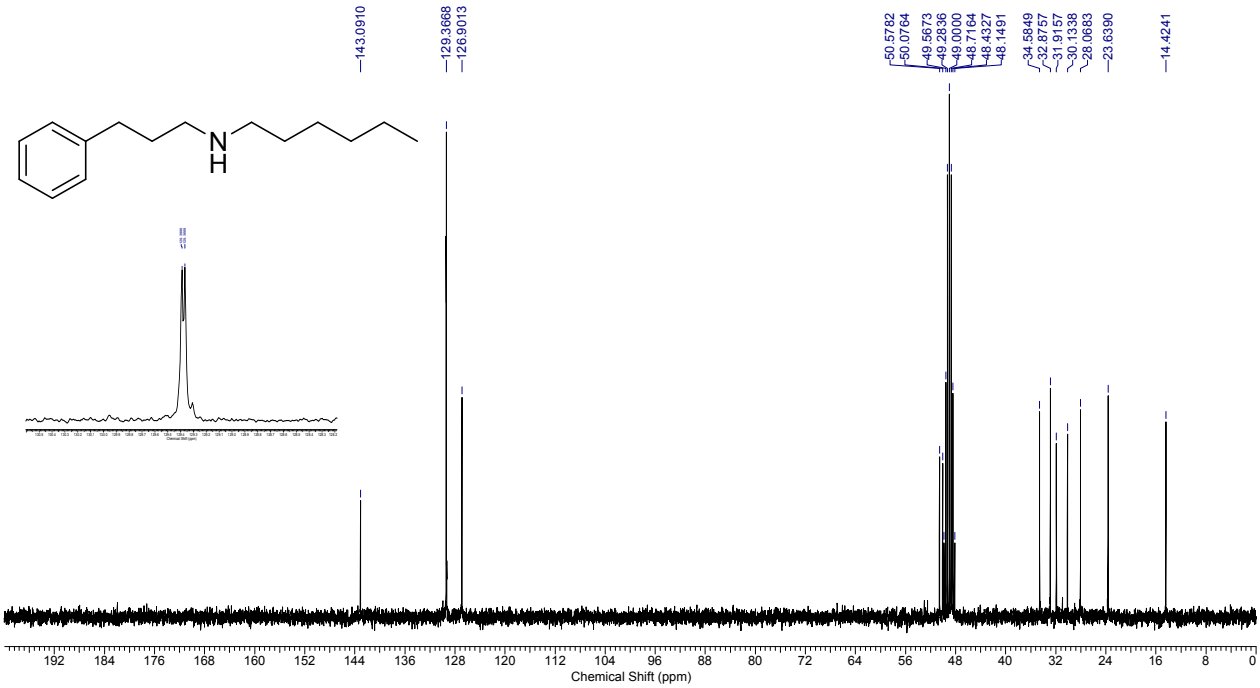

Water
DMSO
9.0366
7.6326
7.6070
7.3347
7.3299
7.3048
7.2859
7.2636
7.2394
7.2131
7.1866
4.4533
4.4359
4.4175
2.9253
2.8825
2.8068
2.7508
2.5244
2.1273
2.1120
2.0924
2.0032
1.9678
1.9070
1.7502
1.7175
1.6937
1.6405
1.3506
1.2672
1.2314
0.8908
0.8682
0.8452
ClH2N
1.83
1.00
3.14
0.99
4.12
1.09
2.12
3.08
6.26
3.13
Chemical Shift (ppm)

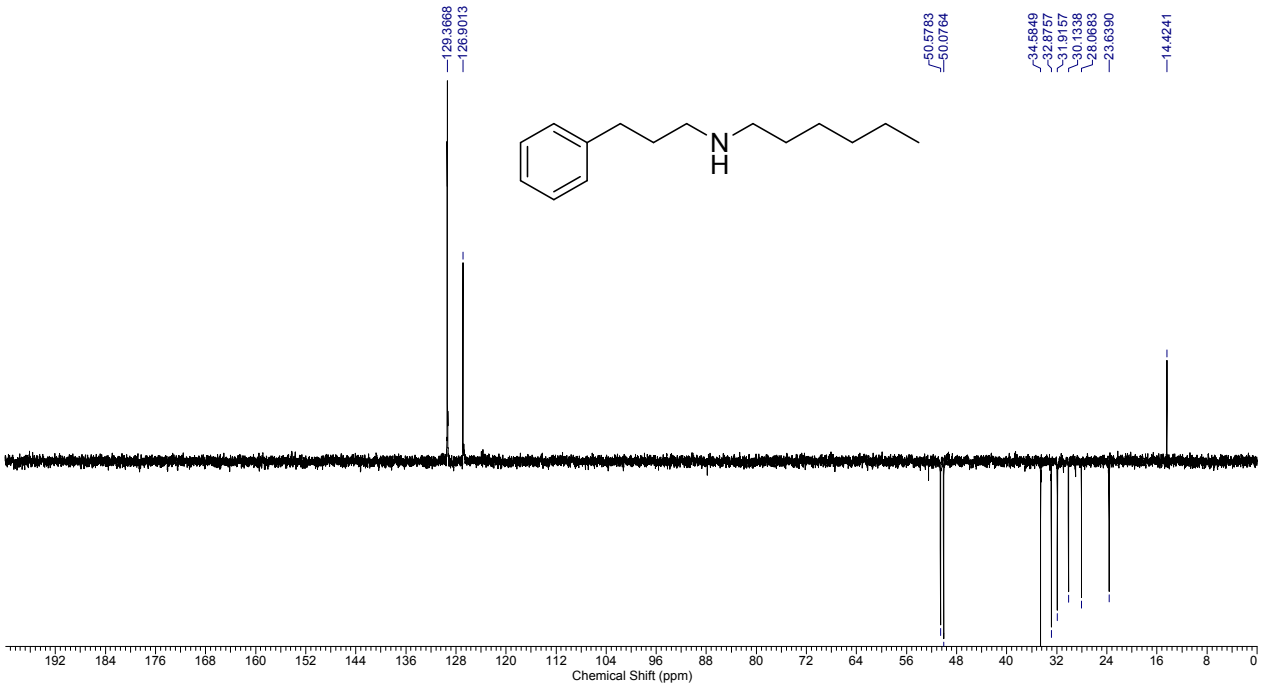

ClH2N
138.3280
130.6803
129.7398
129.3170
128.3838
125.6498
53.9333
43.7193
40.0741
39.7970
39.5200
39.2430
38.9659
30.6766
28.1541
25.7920
25.2015
24.4287
21.8333
18.0933
13.7700
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


ClH2N
129.7433
129.3202
128.3862
125.6555
53.9332
43.7193
30.6814
28.1540
25.7915
25.2036
24.4289
21.8356
18.0995
13.7700
168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)

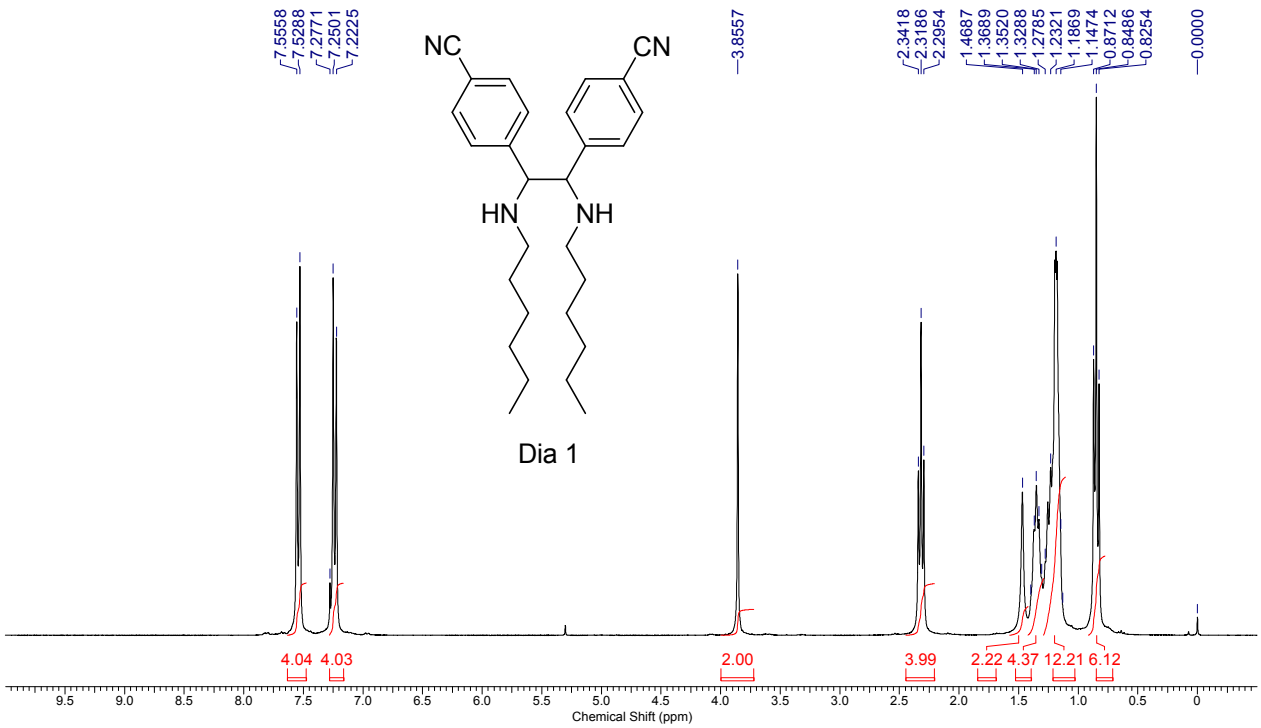
N-(3-phenylpropyl)hexan-1-amine (43)

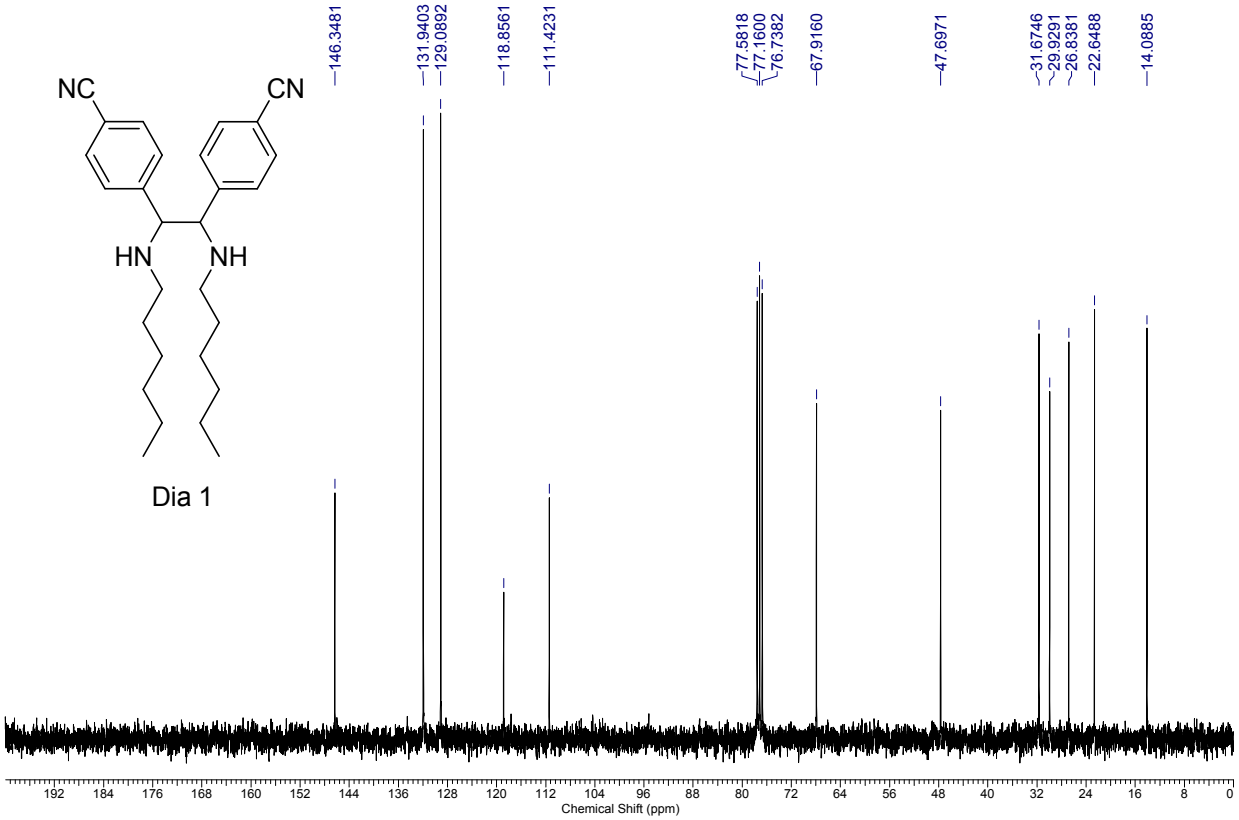


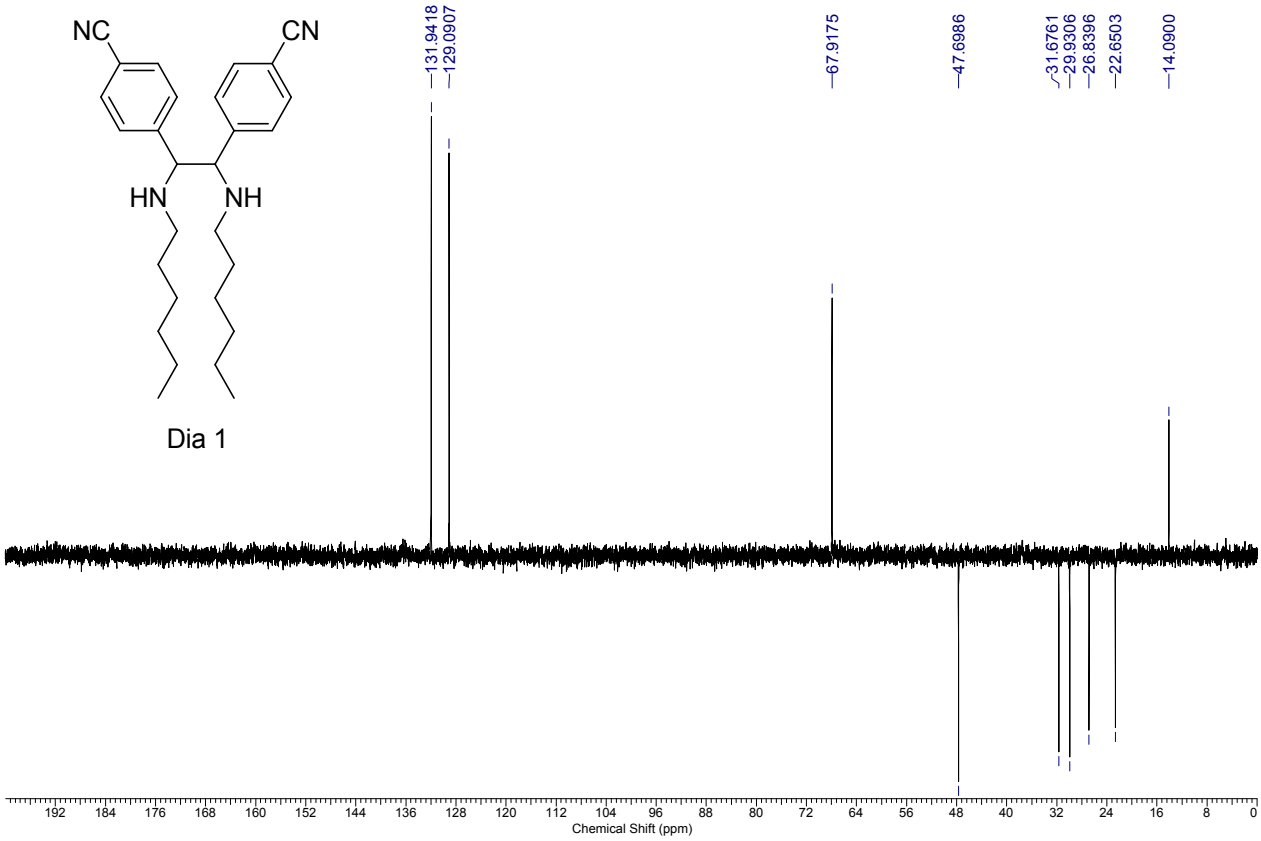


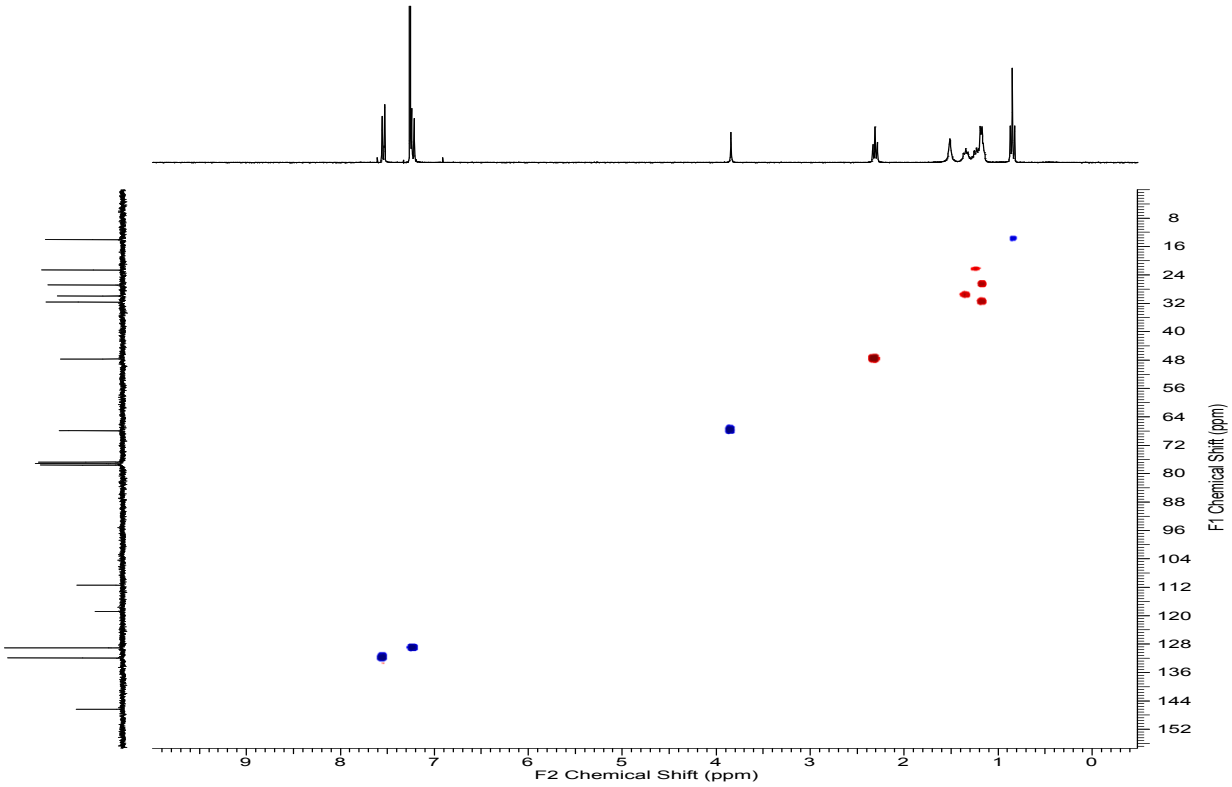


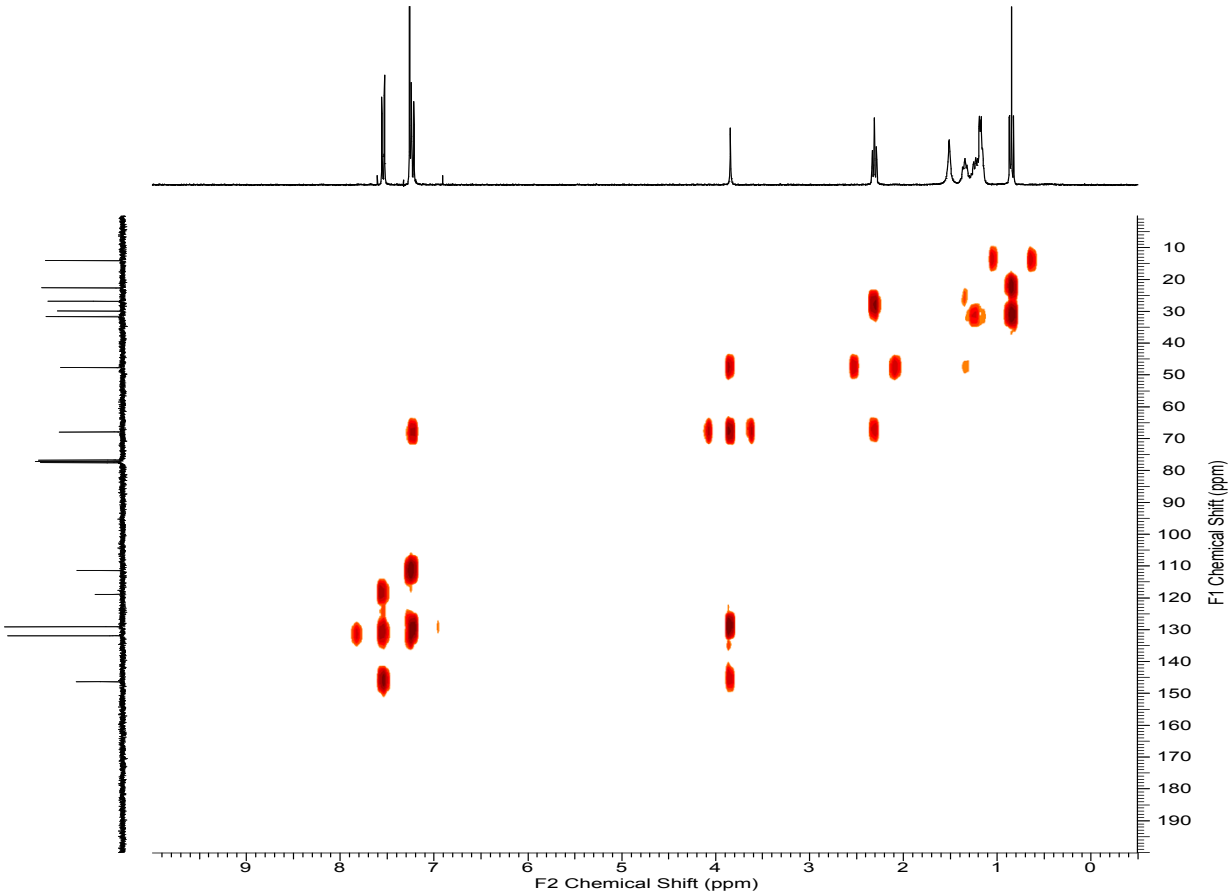
_N_,_N_'-dihexyl-1,2-di(4-cyanophenyl)-1,2-ethylenediamine (45)

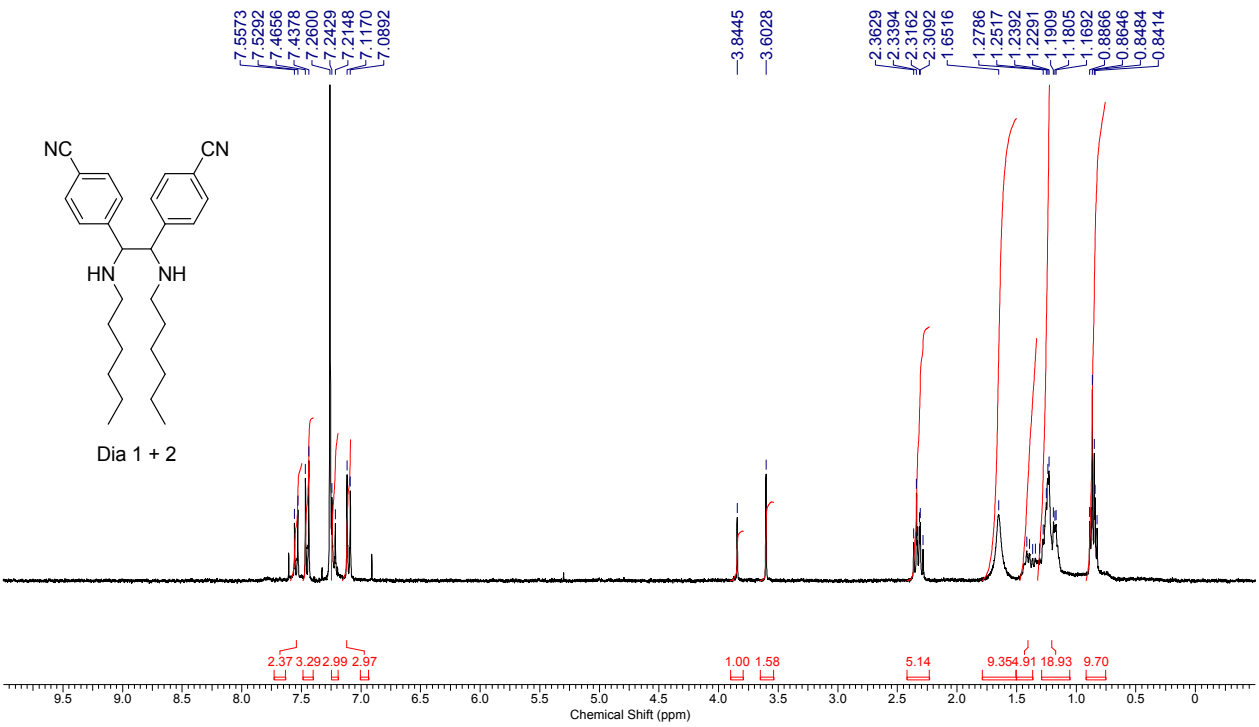


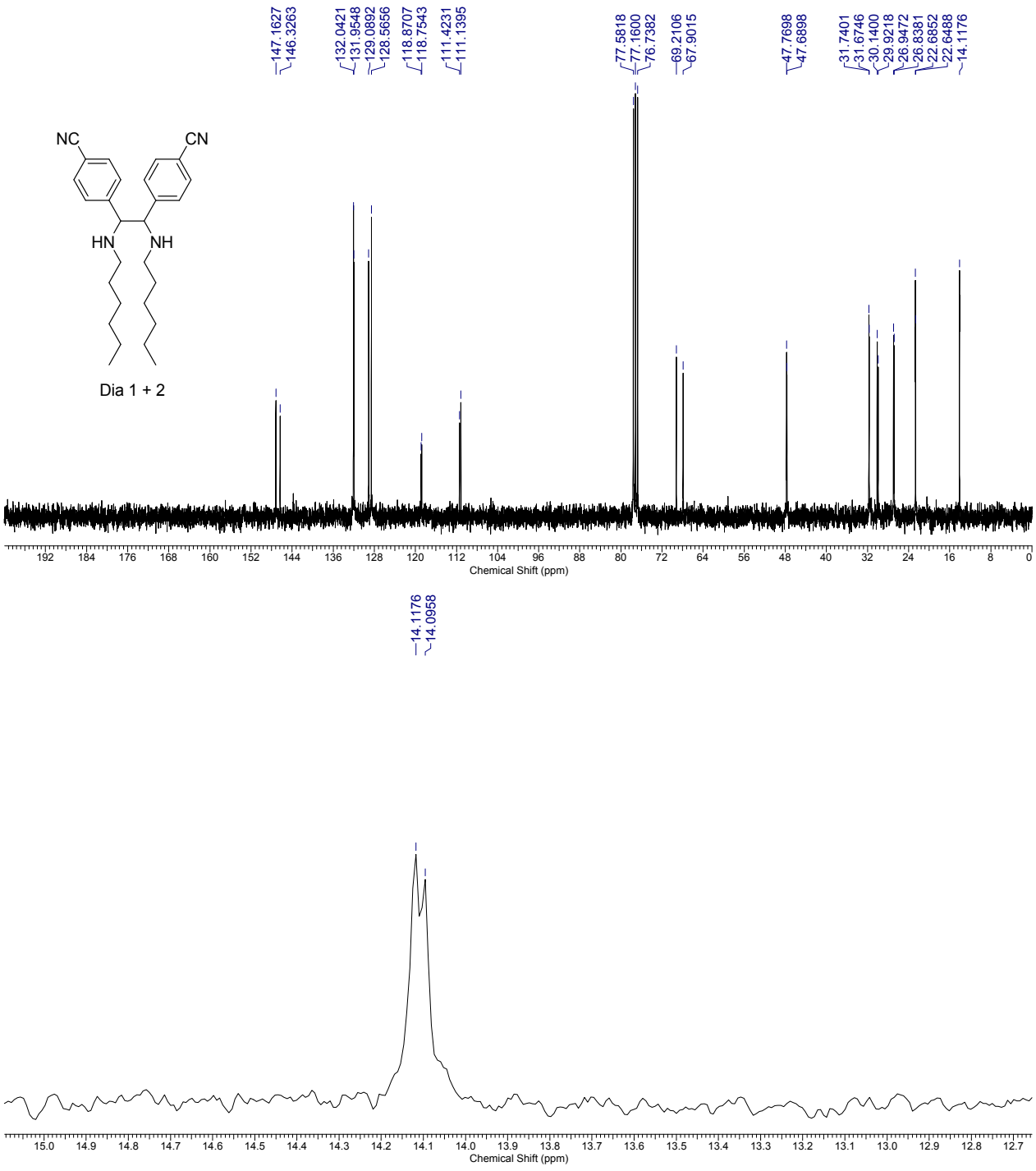

NC
CN
HN
NH
Dia 1
146.3481
131.9403
129.0892
118.8561
111.4231
77.5818
77.1600
76.7382
67.9160
47.6971
31.6746
29.9291
26.8381
22.6488
14.0885
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


NC
CN
HN
NH
Dia 1
131.9418
129.0907
67.9175
47.6986
31.6761
29.9306
26.8396
22.6503
14.0900
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

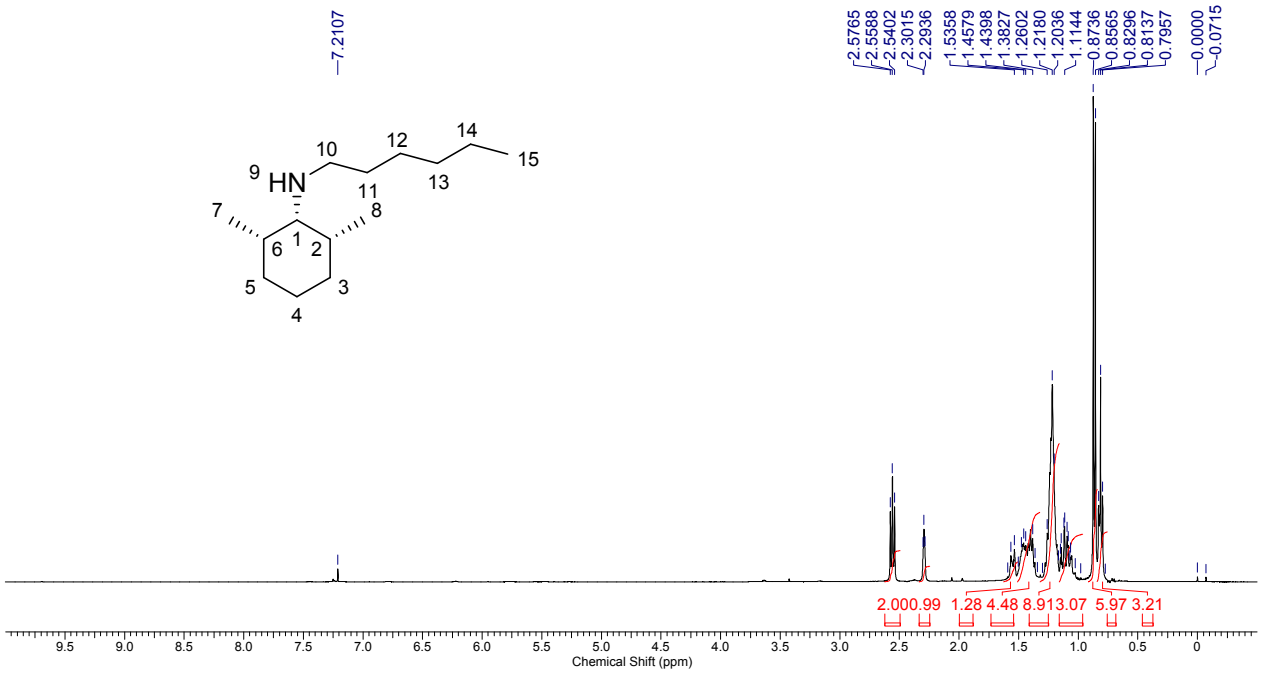

F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)

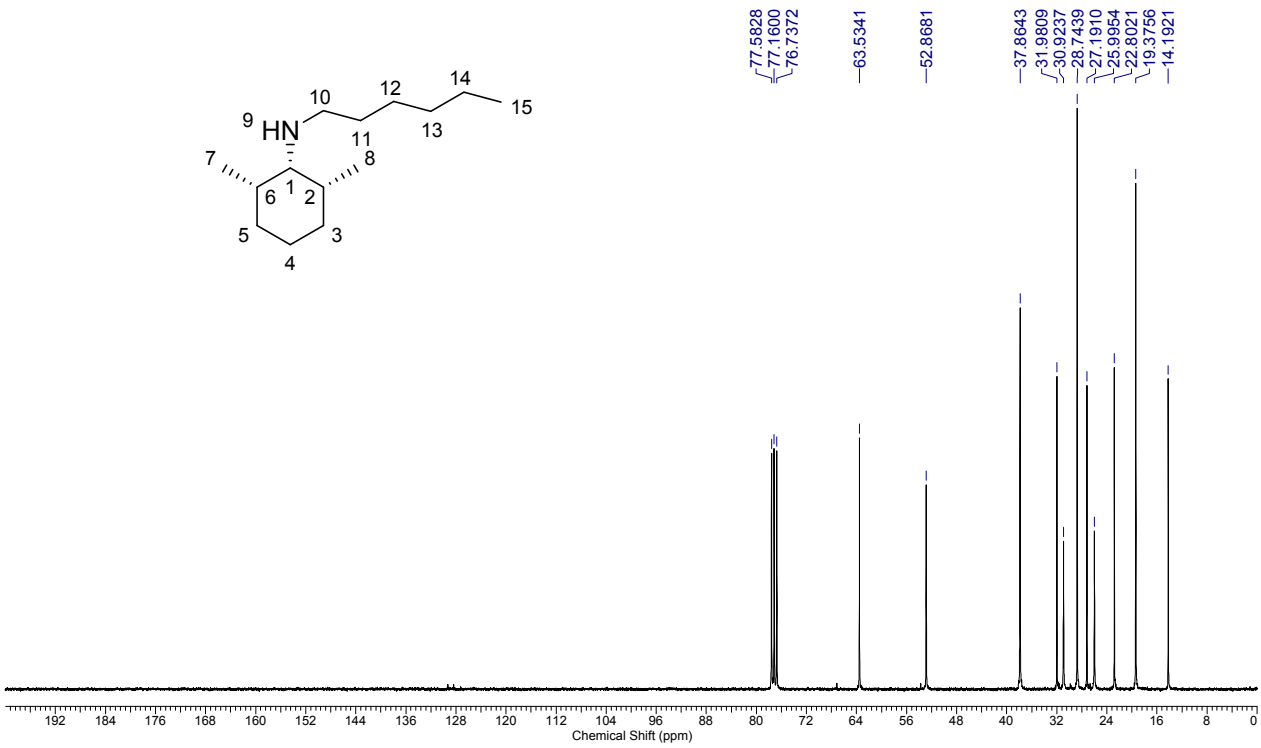

F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)


7.5573
7.5292
7.4656
7.4378
7.2600
7.2429
7.2148
7.1170
7.0892
3.8445
3.6028
2.3629
2.3394
2.3162
2.3092
1.6516
1.2786
1.2517
1.2392
1.2291
1.1909
1.1805
1.1692
0.8866
0.8646
0.8484
0.8414
NC
CN
HN
NH
Dia 1 + 2
2.37 3.29 2.99 2.97
1.00 1.58
5.14
9.35 4.91 18.93 9.70
Chemical Shift (ppm)

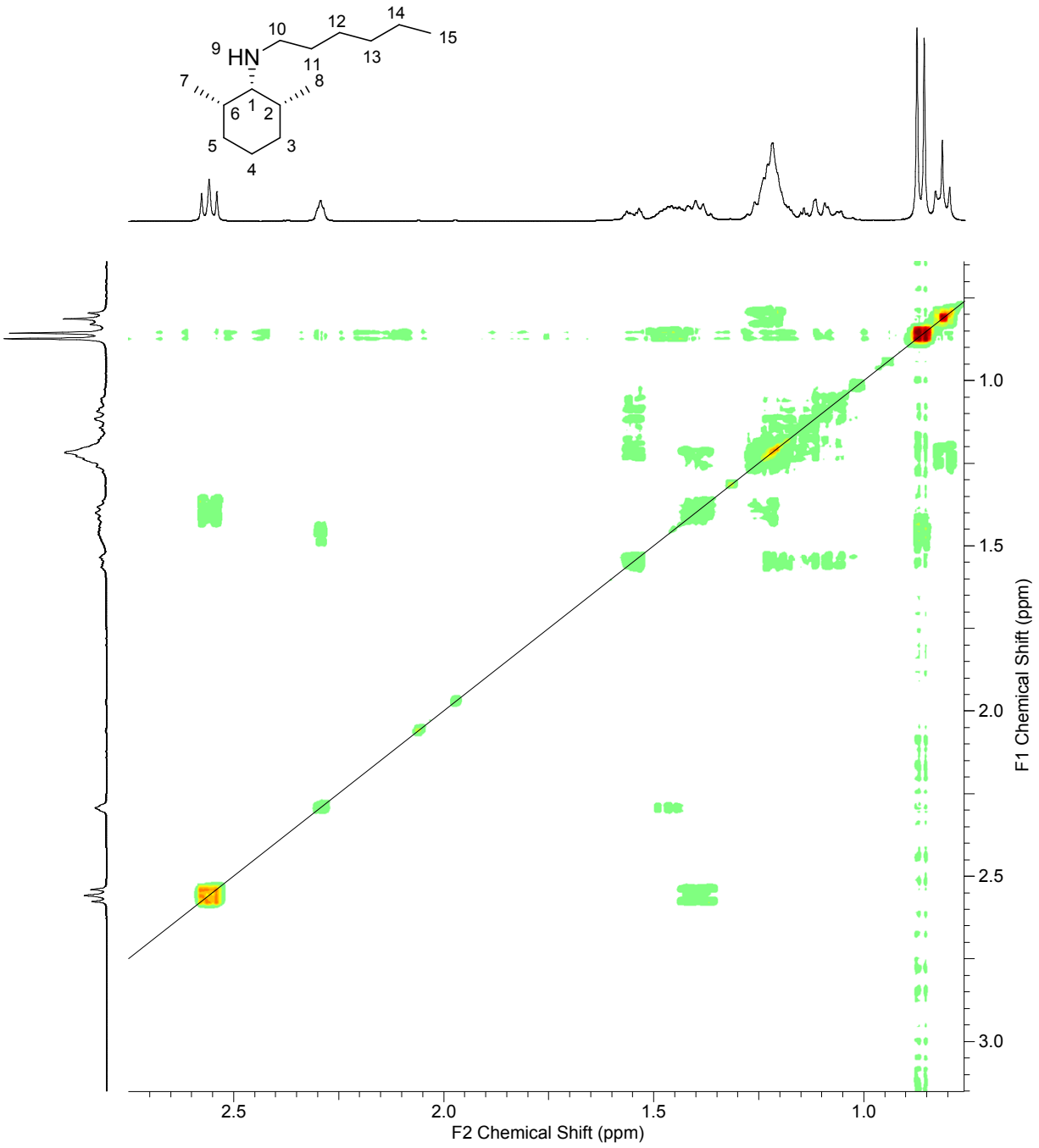


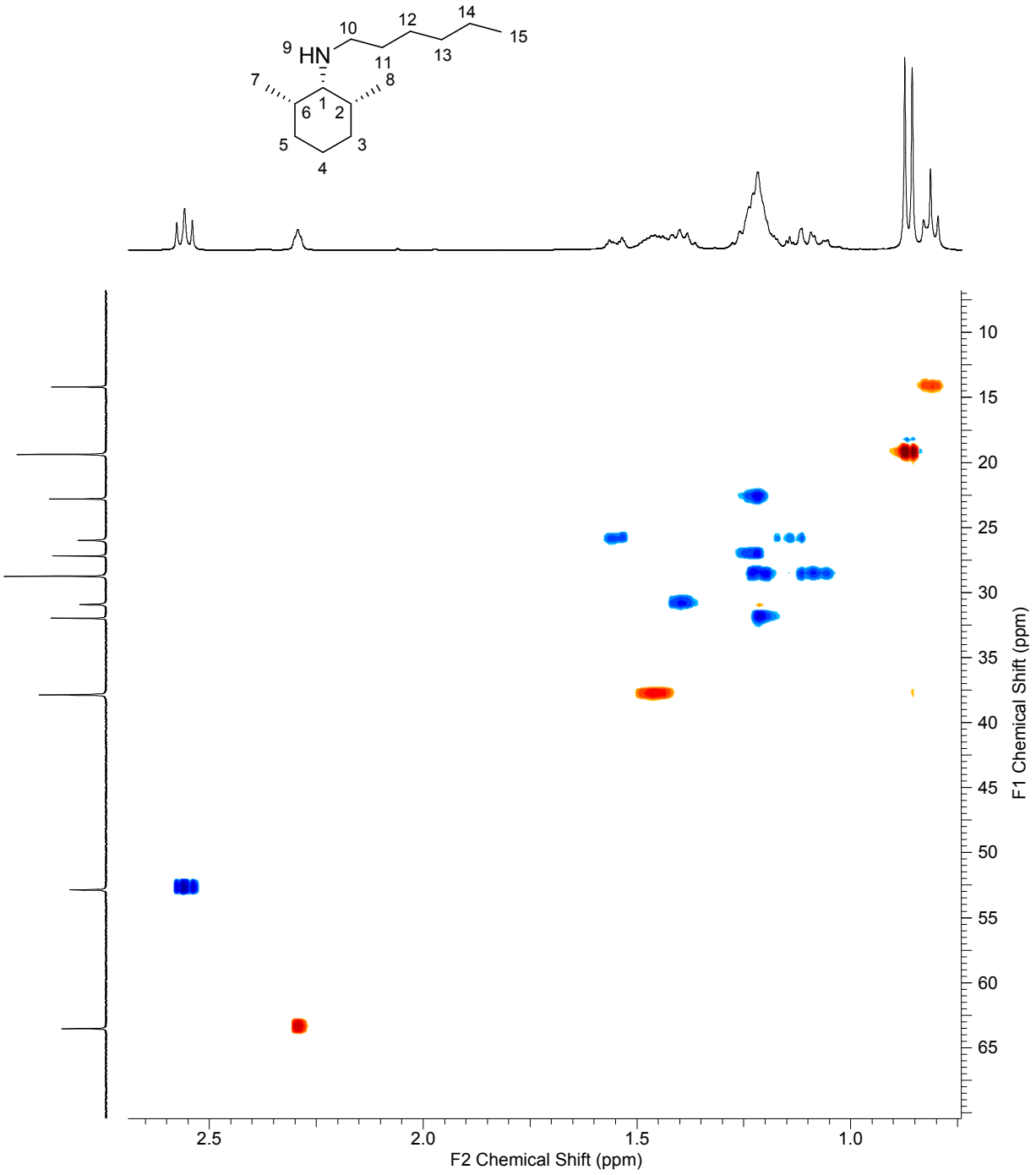
_N_-hexyl-2,6-dimethylcyclohexanamine (47A)

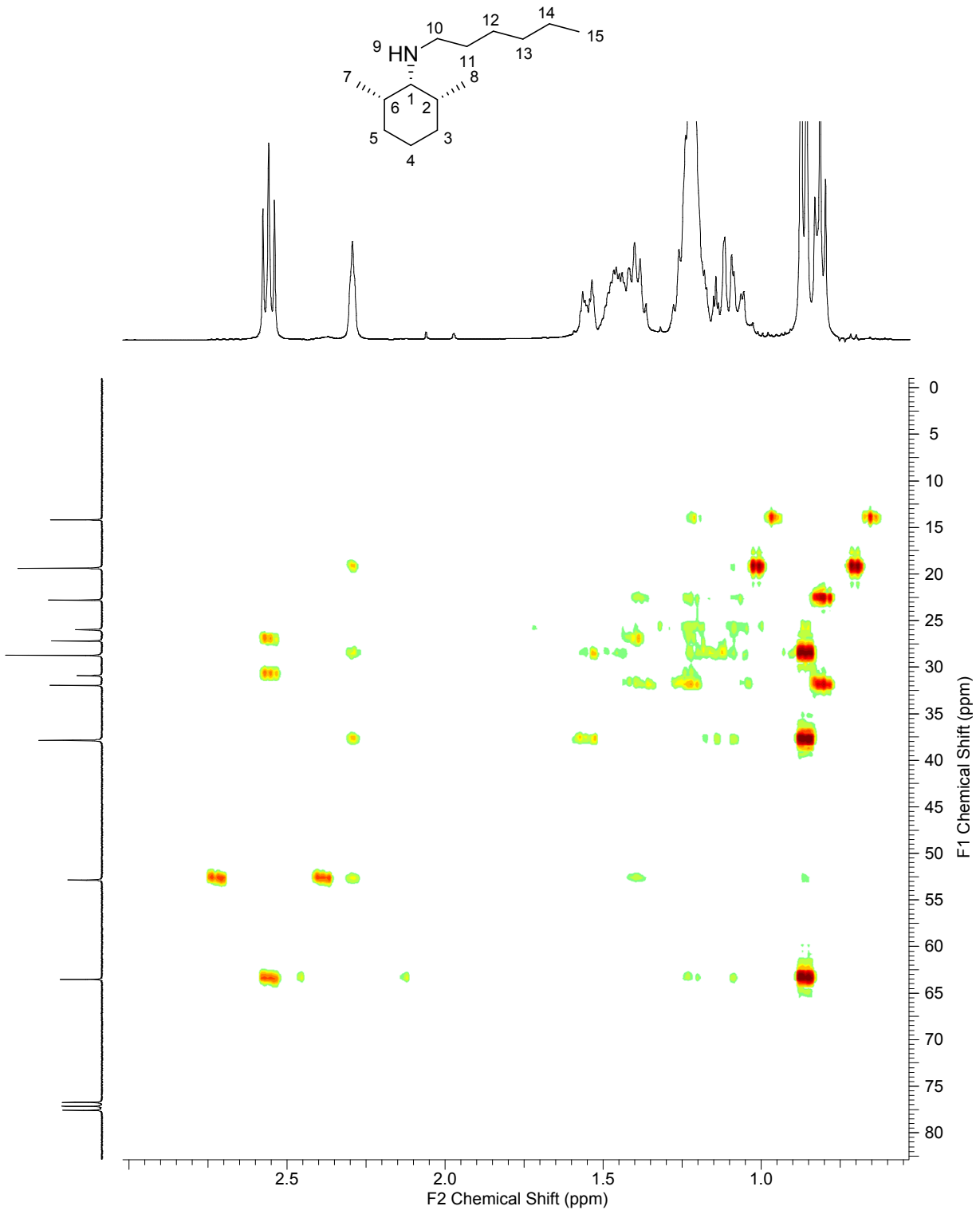

7.2107
2.5765
2.5588
2.5402
2.3015
2.2936
1.5358
1.4579
1.4398
1.3827
1.2602
1.2180
1.2036
1.1144
0.8736
0.8565
0.8296
0.8137
0.7957
0.0000
-0.0715
2.00 0.99 1.28 4.48 8.91 3.07 5.97 3.21
Chemical Shift (ppm)

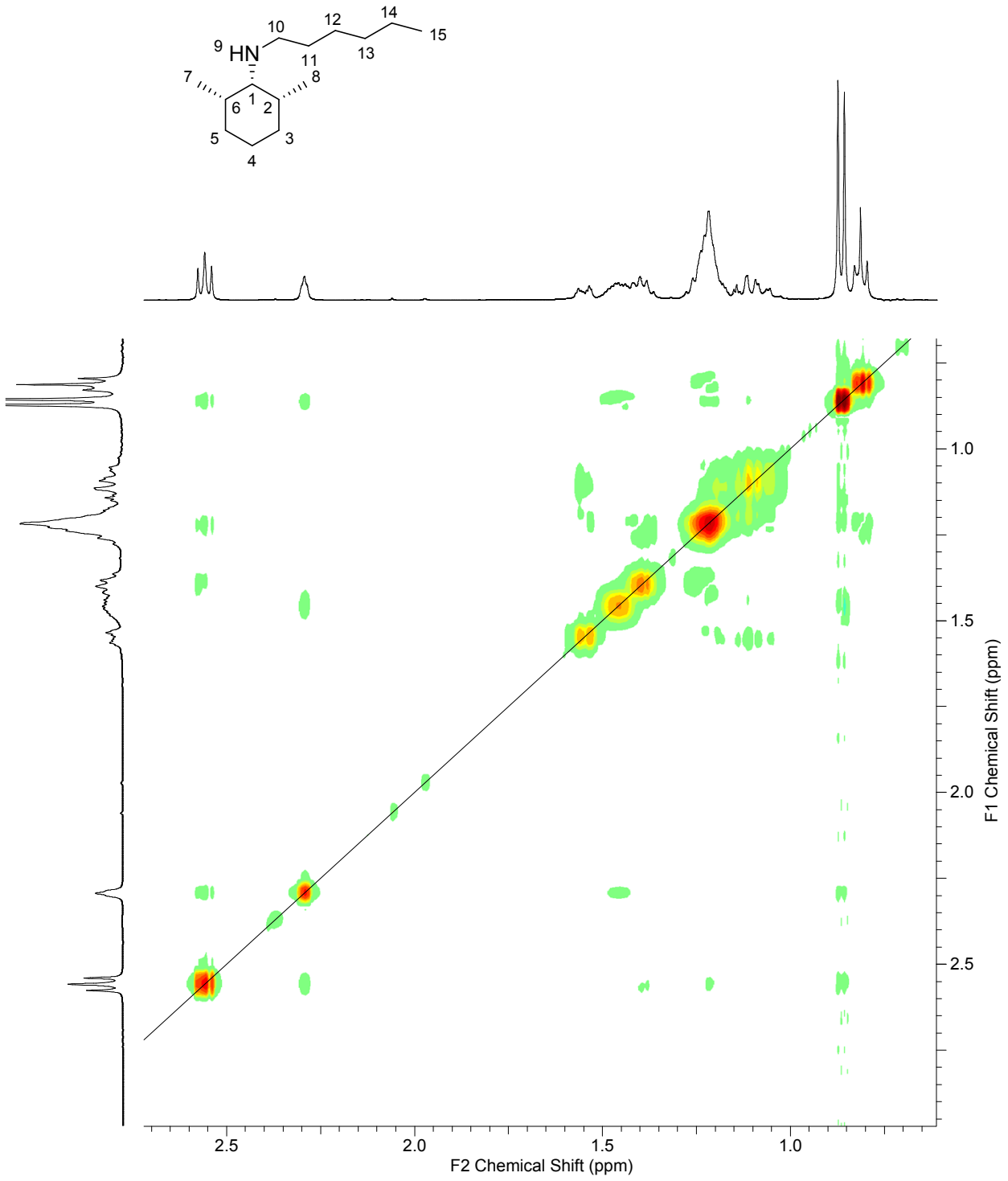

77.5828
77.1600
76.7372
63.5341
52.8681
37.8643
31.9809
30.9237
28.7439
27.1910
25.9954
22.8021
19.3756
14.1921
Chemical Shift (ppm)


63.5307
52.8663
37.8670
31.9771
30.9222
28.7410
27.1861
25.9938
22.8016
19.3787
14.1921
HN
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)

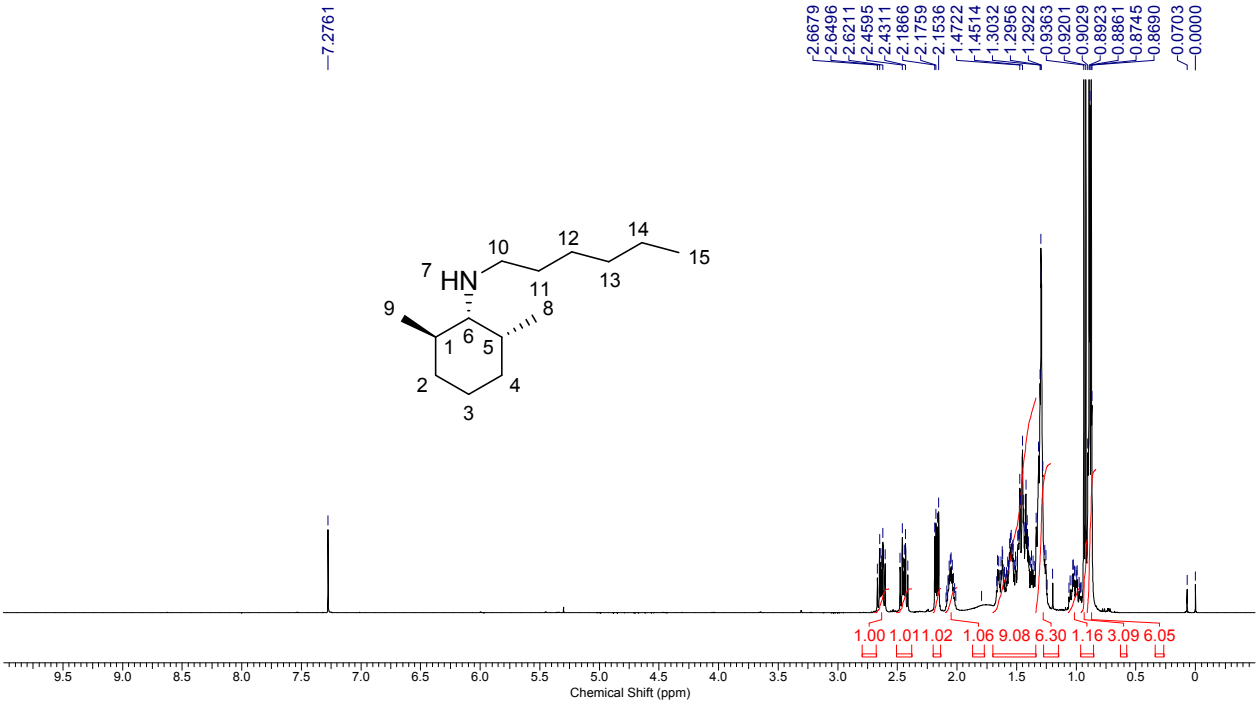

HN
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
2.5
2.0
1.5
1.0
F2 Chemical Shift (ppm)
1.0
1.5
2.0
2.5
3.0
F1 Chemical Shift (ppm)

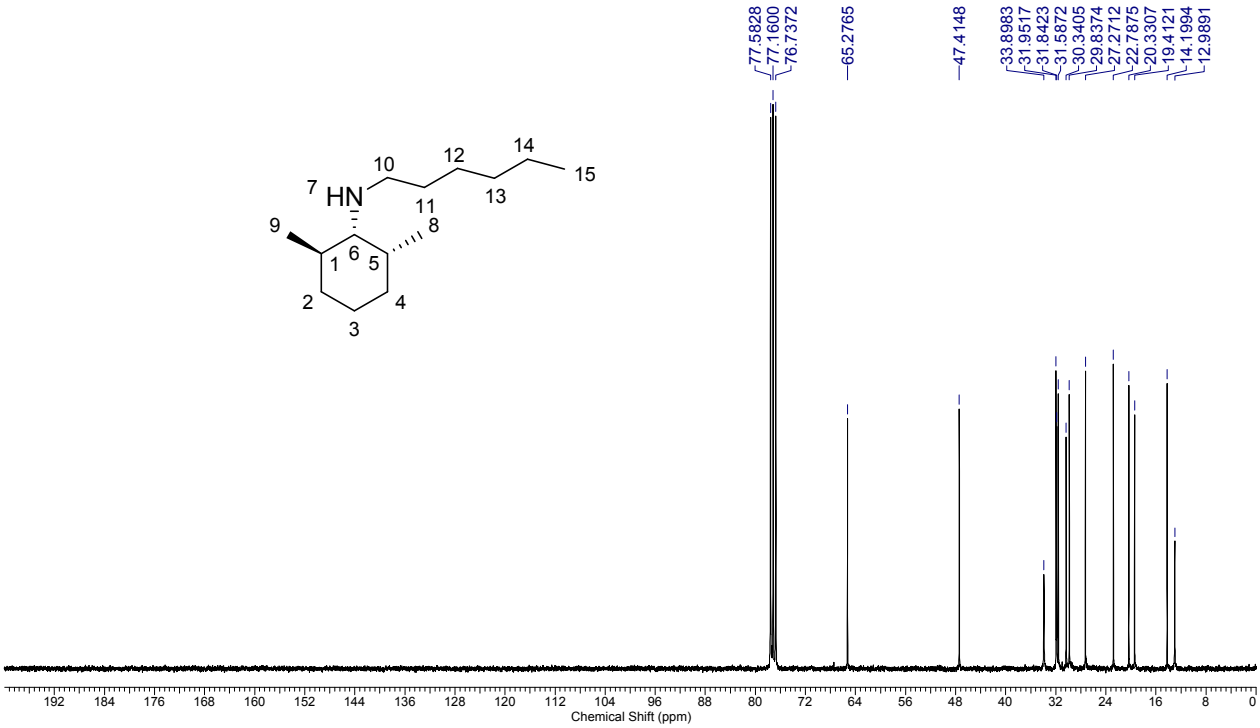

HN
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
2.5
2.0
1.5
1.0
F2 Chemical Shift (ppm)
10
15
20
25
30
35
40
45
50
55
60
65
F1 Chemical Shift (ppm)

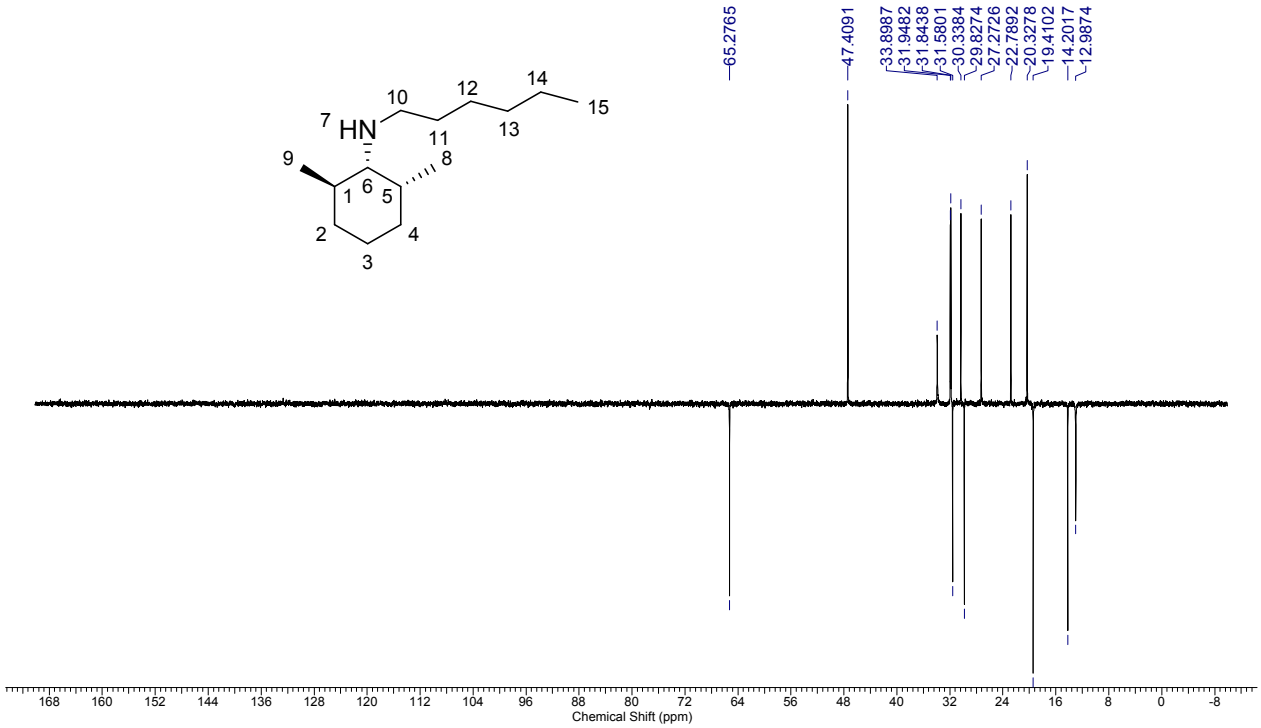

HN
9
10
11
12
13
14
15
7
8
6
1
2
5
3
4
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)
2.5
2.0
1.5
1.0
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80


9
HN
10
12
14
15
11
13
7
8
1
6
2
5
3
4
1.0
1.5
2.0
2.5
F1 Chemical Shift (ppm)
2.5
2.0
1.5
1.0
F2 Chemical Shift (ppm)

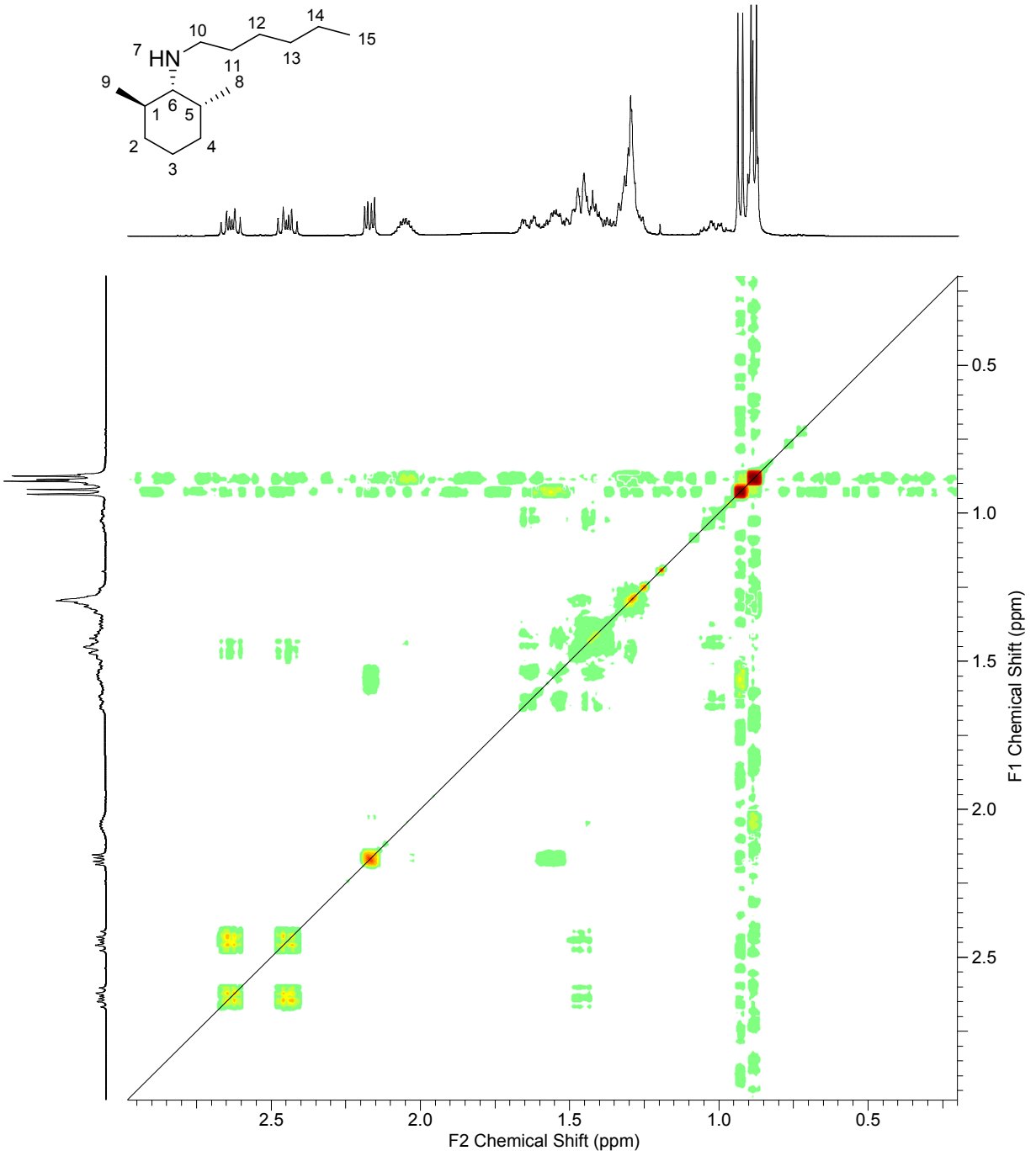
N-hexyl-2,6-dimethylcyclohexanamine (47C)



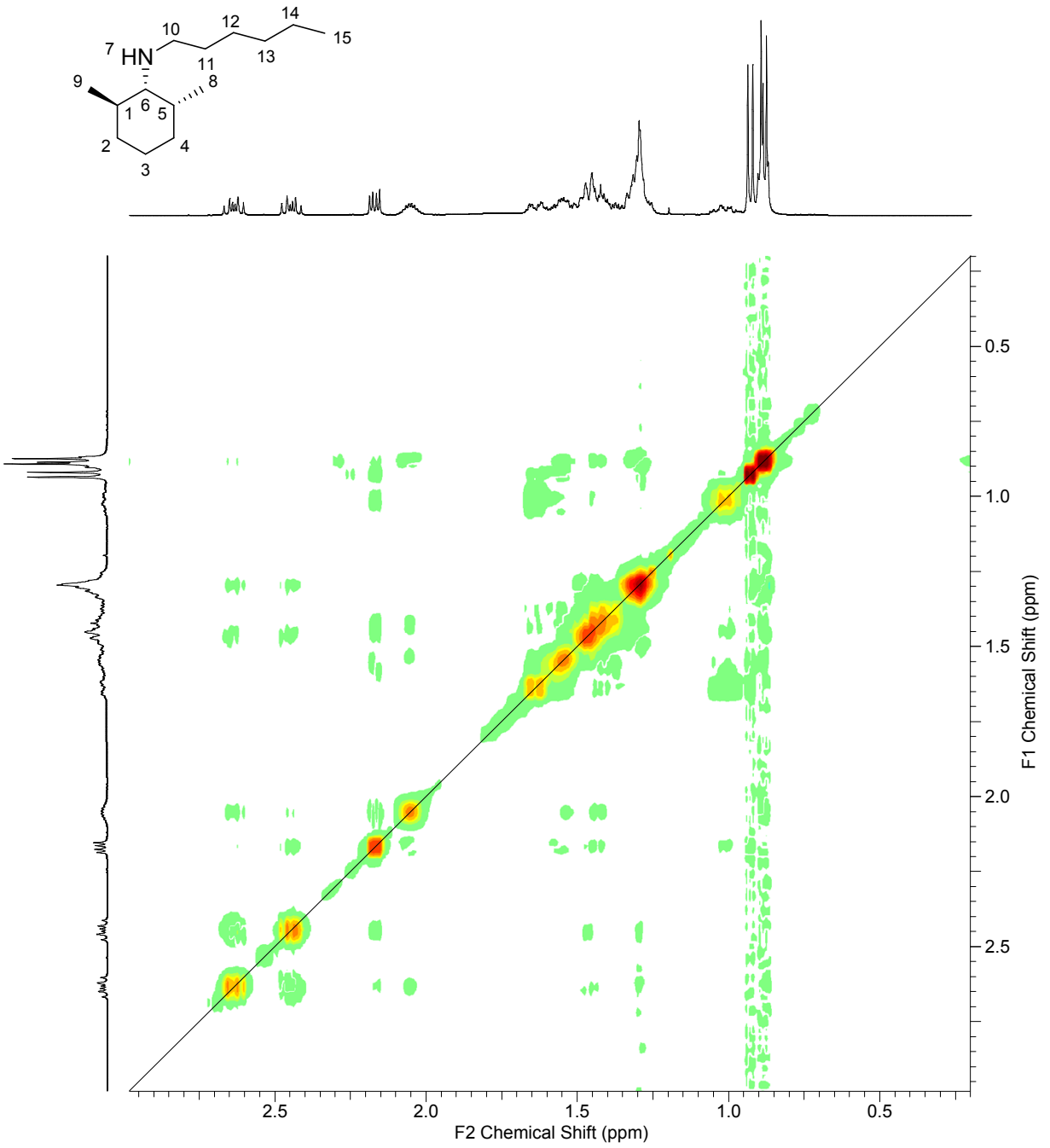


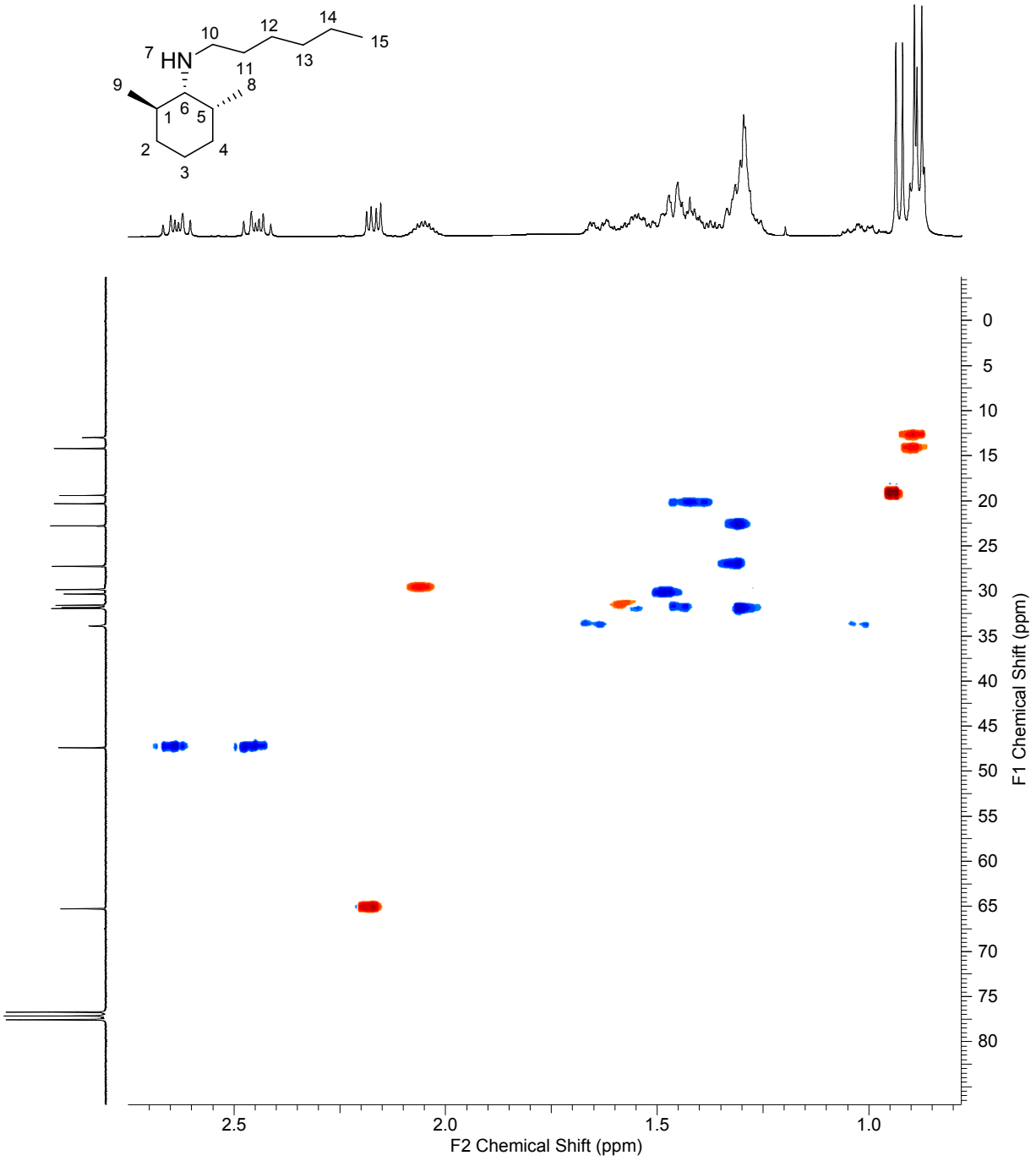

65.2765
47.4091
33.8987
31.9482
31.8438
31.5801
30.3384
29.8274
27.2726
22.7892
20.3278
19.4102
14.2017
12.9874
HN
Chemical Shift (ppm)

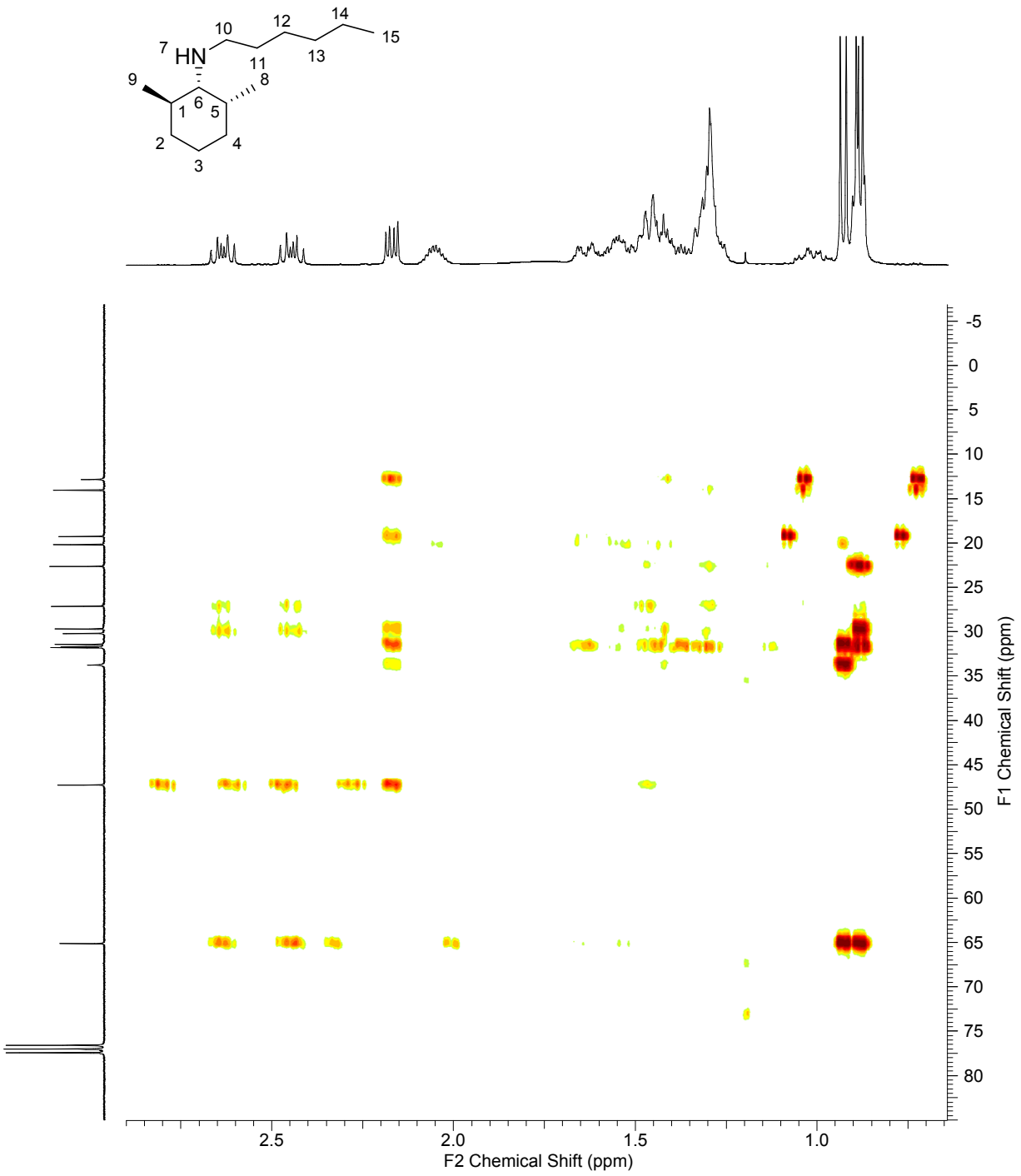
COSY


7 HN
9
10
11
12
13
14
15
8
1
6
5
2
4
3
0.5
1.0
1.5
2.0
2.5
F1 Chemical Shift (ppm)
2.5
2.0
1.5
1.0
0.5
F2 Chemical Shift (ppm)

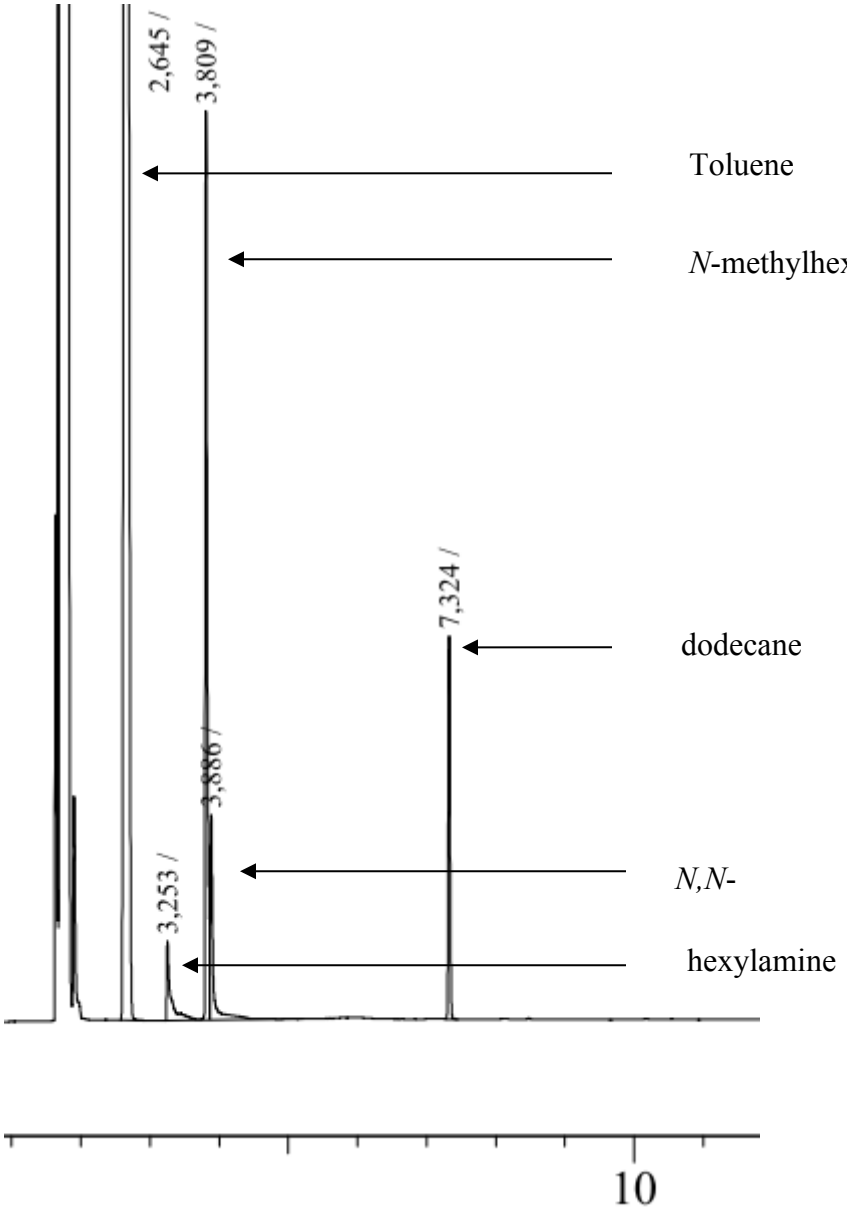
NOESY


7 HN
10
12
14
15
11
13
9
8
1
6
5
2
4
3
0.5
1.0
1.5
2.0
2.5
F1 Chemical Shift (ppm)
2.5
2.0
1.5
1.0
0.5
F2 Chemical Shift (ppm)


HN
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
2.5
2.0
1.5
1.0
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80

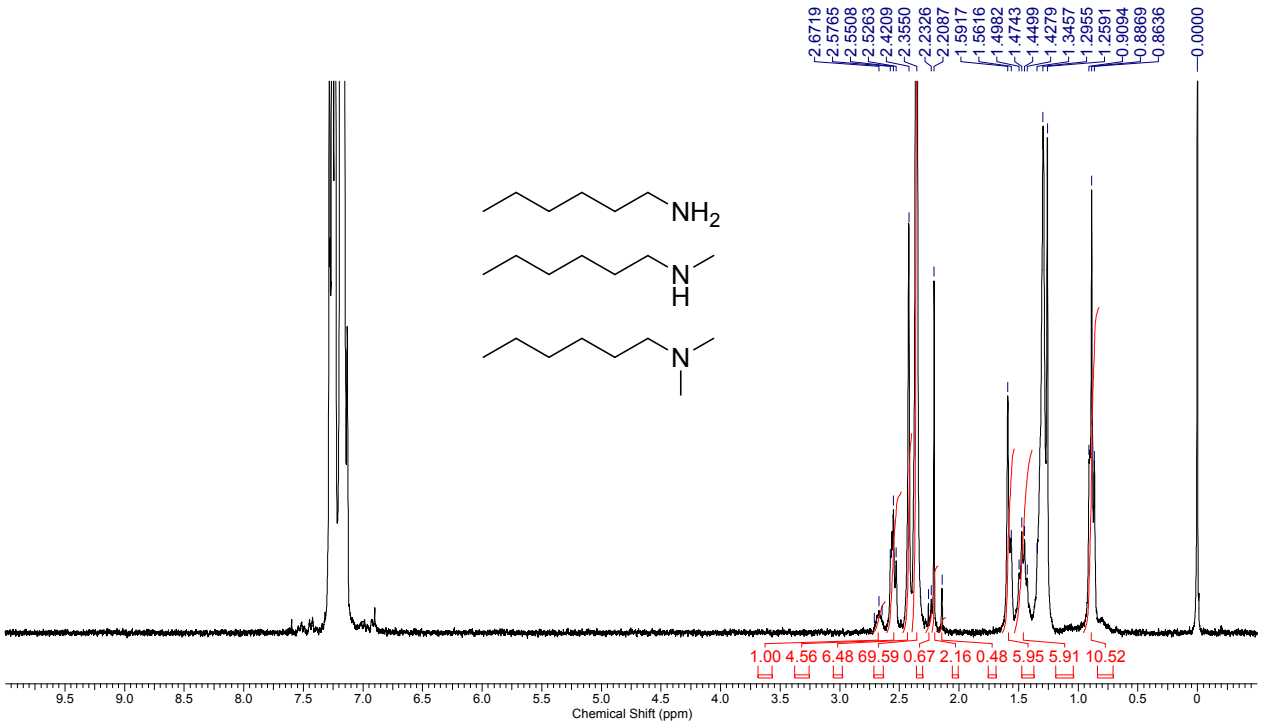

HN
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)

Monoalkylation of hexylamine



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Area%
1	2,645	15244816	7698886	0,000	89,8437
2	3,253	161841	39451	0,000	0,9538
3	3,809	933692	444837	0,000	5,5026
4	3,886	301360	101935	0,000	1,7760
5	7,324	326450	189011	0,000	1,9239
Total		16968159	8474120		100,0000


2.6719
2.5765
2.5508
2.5263
2.4209
2.3550
2.2326
2.2087
1.5917
1.5616
1.4982
1.4743
1.4499
1.4279
1.3457
1.2955
1.2591
0.9094
0.8869
0.8636
0.0000
NH2
N
H
N
1.00 4.56 6.48 69.59 0.67 2.16 0.48 5.95 5.91 10.52
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
Chemical Shift (ppm)