Supporting Information

Scandium-Catalyzed Intermolecular Hydroaminoalkylation of Olefins with Aliphatic Tertiary Amines

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Contents

1. General Methods **S2**

2. Catalyst Screening **S3**

3. Typical Procedure for the Catalytic Alkylation of Amines with Olefins **S4**

4. Analytical Data **S4**

5. Kinetic Isotope Effect Experiments **S9**

6. Dialkylation of 1k to give 3k **S11**

7. References **S12**

8. ^{1}H and ^{13}C NMR Spectra of Products **S13**

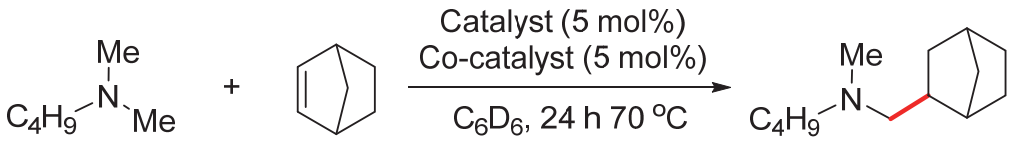
1. General Methods

All manipulations were performed under a nitrogen atmosphere by use of standard Schlenk techniques or in an mBRAUN Labmaster glovebox. Nitrogen was purified by passing through a Dryclean column (4 Å molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). Hexane, THF, toluene and benzene (dehydrated, stabilizer-free) were obtained from Kanto Chemical Co. and purified by use of an MBraun SPS-800 solvent purification system. Silica gel column chromatography was performed with Silica Gel 60 N (spherical, neutral, 40-50 mm) obtained from Kanto Chemical Co. [Ln($CH_2C_6H_4NMe_2$-o)$_3$] (Ln = Sc, Y, Lu, Gd, Sm)[1] and [(C_5Me_5)Sc($CH_2C_6H_4NMe_2$-o)$_2$][2] were prepared according to the literature methods. *N,N*-dimethylbutylamine (**1a**), *N,N*-dimethyloctylamine (**1b**), *N,N*-dimethylcyclohexylamine (**1c**), *N,N*-dibutylmethylamine (**1e**), *N*-methylpyrrolidine (**1f**), d_3-*N*-methylpyrrolidine (**1f$_{d3}$**), *N*-methylpiperidine (**1h**) and tropane (**1j**) were commercially available. *N*-methyl,*N*-ethylbutylamine (**1d**), *N*-methyl,4-methylpiperidine (**1i**), *N*-methylhexamethyleneimine (**1g**), and *N,N*-dimethyladamantylamine (**1k**), were prepared *via* the literature method.[3] All olefins were commercially available, except 4-dimethylaminostyrene (**2e**) which was synthesized *via* the literature method.[4] Amines and olefins were all distilled from appropriate drying agents such as CaH_2 and Na. All ^{1}H NMR and ^{13}C NMR spectra were recorded on either a JEOL AL-400 MHz instrument or a Bruker AVANCE III HD 500 NMR spectrometer in C_6D_6 with tetramethylsilane as an internal standard otherwise mentioned. Data are reported as follows: chemical shift in ppm (d), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, sep = septet, m = multiplet, br = broad signal), coupling constant (Hz), integration. Gas chromatography analysis was performed on Shimadzu GC2014 using a capillary column (Agilent J&W GC columns DB-1, 30m, 0.32 mm i.d., 0.25 mm film thickness. High-resolution MS were obtained on a Bruker microTOF-Q III (ESI+).

2. Catalyst Screening

In a glovebox, [Sc($CH_2C_6H_4NMe_2$-*o*)$_3$] (6 mg, 0.013 mmol) was dissolved in C_6D_6 (1.0 mL). To this solution, ferrocene (19 mg, 0.1 mmol), *N,N*-dimethylbutylamine (25mg, 0.25 mmol), norbornene (26 mg, 0.28 mmol) and [Ph_3C][$B(C_6F_5)_4$] (16 mg, 0.013 mmol) were added sequentially. The biphasic mixture was transferred to a J Young NMR tube, sealed and a baseline ^{1}H NMR spectrum taken. The tube was then heated at 70 °C for 24 hours, and the yield calculated from the internal standard (ferrocene). For entries 5 and 6, the sample was quenched with EtOAc (2 mL) after 24 h at 70 °C, filtered and the volatiles removed *in vacuo* to remove the paramagnetic catalyst.

Table S1. Catalyst Dependant Hydroaminoalkylation of Norbornene with N,N-dimethylbutylamine



1a **2a** **3a**

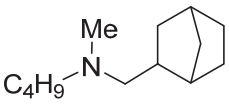
Entry[a]	Catalyst	Co-catalyst	Yield, %[b]
1	[$(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2$-o$)_2$]	[Ph_3C][$B(C_6F_5)_4$]	90
2	[$(C_5H_5)Sc(CH_2C_6H_4NMe_2$-o$)_2$]	[Ph_3C][$B(C_6F_5)_4$]	52
3	[$Y(CH_2C_6H_4NMe_2$-o$)_3$]	[Ph_3C][$B(C_6F_5)_4$]	0
4	[$Lu(CH_2C_6H_4NMe_2$-o$)_3$]	[Ph_3C][$B(C_6F_5)_4$]	0
5	[$Gd(CH_2C_6H_4NMe_2$-o$)_3$]	[Ph_3C][$B(C_6F_5)_4$]	0
6	[$Sm(CH_2C_6H_4NMe_2$-o$)_3$]	[Ph_3C][$B(C_6F_5)_4$]	0
7	[$Sc(CH_2C_6H_4NMe_2$-o$)_3$]	N/A	0
8	N/A	[Ph_3C][$B(C_6F_5)_4$]	0
9[c]	[$Sc(CH_2C_6H_4NMe_2$-o$)_3$]	[Ph_3C][$B(C_6F_5)_4$]	<5

[a] Reactions were carried out with 0.25 mmol amine and 0.275 mmol norbornene in 1 mL of C_6D_6. [b] NMR yield calculated against Cp_2Fe as an internal standard. [c] 10 mol% [Ph_3C][$B(C_6F_5)_4$] used.

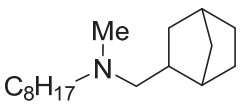
3. Typical Procedure for the Catalytic Alkylation of Amines with Olefins

In a glovebox, [Sc($CH_2C_6H_4NMe_2$-*o*)$_3$] (22 mg, 0.05 mmol) was dissolved in toluene (2.0 mL). To this solution *N*-methylpiperidine (99 mg, 1 mmol), styrene (115 mg, 1.1 mmol) and [Ph_3C][$B(C_6F_5)_4$] (46 mg, 0.05 mmol) were added sequentially. The biphasic mixture was transferred to a Schlenk ampoule, sealed and heated at 70 °C for 24 hours. EtOAc (5 mL) was added to the crude mixture and the volatiles removed *in vacuo.* The compound was purified by silica gel column chromatography (hexane/EtOAc), to afford **4a** as colourless oil (173 mg, 0.851 mmol, 85 % yield).

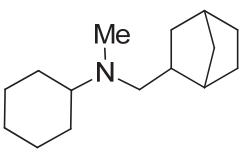
4. Analytical Data



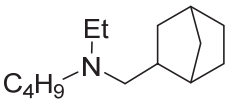
3a: ^{1}H NMR (500 MHz, C_6D_6): δ 2.30 – 2.25 (m, 2H), 2.22 (br, 1H), 2.16 (br, 1H), 2.16 – 2.12 (m, 1H), 2.14 (s, 3H), 1.94 (dd, *J* = 7.5 Hz, 4.5 Hz, 1H), 1.64 – 1.58 (m, 1H), 1.52 – 1.40 (m, 4H), 1.37 – 1.27 (m, 4H), 1.18 – 1.13 (m, 1H), 1.05 (d, *J* = 9.5 Hz, 1H), 0.91 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, C_6D_6): δ 64.3, 58.3, 42.7, 40.7, 39.9, 36.9, 36.5, 35.6, 30.5, 30.2, 29.5, 20.9, 14.3. HR MS (ESI+): Found 196.2066 $[M+H]^+$, calcd. for $C_{13}H_{26}N^+$ 196.2065.



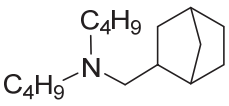
3b: ^{1}H NMR (500 MHz, C_6D_6): δ 2.32 – 2.27 (m, 2H), 2.23 (br, 1H), 2.18 – 2.14 (m, 2H), 2.16 (s, 3H), 1.96 (dd, *J* = 7.0 Hz, 5.0 Hz, 1H), 1.66 – 1.60 (m, 1H), 1.50 – 1.45 (m, 4H), 1.38 – 1.25 (br m, 12H), 1.18 – 1.13 (m, 3H), 1.05 (d, *J* = 9.5 Hz, 1H), 0.90 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (125 MHz, C_6D_6): δ 64.3, 58.7, 42.7, 40.7, 39.9, 37.0, 36.5, 35.6, 32.4, 30.5, 30.1, 29.9, 29.5, 28.1, 27.9, 23.1, 14.4. HR MS (ESI+): Found 252.2692 $[M+H]^+$, calcd. for $C_{17}H_{34}N^+$ 252.2691.



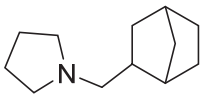
3c: ^{1}H NMR (500 MHz, C_6D_6): δ 2.35 – 2.17 (m, 4H), 2.21 (s, 3H), 2.05 (dd, *J* = 12.3 Hz, 7.2 Hz, 1H), 1.81 – 1.67 (m, 4H), 1.66 – 1.58 (m, 1H), 1.58 – 1.44 (m, 3H), 1.40 – 1.33 (m, 1H), 1.32 – 1.27 (m, 1H), 1.23 – 1.10 (m, 7H), 1.06 (d, *J* = 9.7 Hz, 1H), 1.04 – 0.96 (m, 1H). ^{13}C NMR (125 MHz, C_6D_6): δ 63.7, 59.7, 41.1, 39.9, 38.1, 37.0, 36.3, 35.6, 30.5, 29.6, 29.1, 28.9, 26.9, 26.5. HR MS (ESI+): Found 222.2221 $[M+H]^+$, calcd. for $C_{15}H_{28}N^+$ 222.2222.



3d: ^{1}H NMR (500 MHz, C_6D_6): δ 2.50 – 2.31 (m, 4H), 2.24 (br, 1H), 2.21 – 2.17 (m, 2H), 2.03 (dd, *J* = 12.5 Hz, 7.1 Hz, 1H), 1.65 – 1.58 (m, 1H), 1.55 – 1.27 (m, 8H), 1.20 – 1.12 (m, 3H), 1.06 (d, *J* = 9.7 Hz, 1H), 0.98 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, C_6D_6): δ 60.3, 54.0, 48.2, 41.0, 39.9, 36.9, 36.5, 35.6, 30.5, 30.2, 29.5, 21.0, 14.4, 12.4. HR MS (ESI+): Found: 210.2222 $[M+H]^+$, calcd. for $C_{14}H_{28}N^+$ 210.2222.

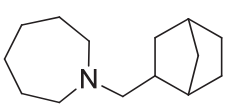


3e: ^{1}H NMR (500 MHz, C_6D_6): δ 2.44 – 2.31 (m, 4H), 2.26 (br, 1H), 2.23 – 2.18 (m, 2H), 2.04 (dd, *J* = 12.5 Hz, 7.0 Hz, 1H), 1.67 – 1.60 (m, 1H), 1.56 – 1.41 (m, 6H), 1.39 – 1.29 (m, 6H), 1.21 – 1.11 (m, 3H), 1.06 (d, *J* = 9.7 Hz, 1H), 0.92 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (125 MHz, C_6D_6): δ 61.0, 54.7, 41.0, 39.9, 36.9, 36.5, 35.5, 30.5, 30.2, 29.5, 21.0, 14.4. HR MS (ESI+): Found 238.2536 $[M+H]^+$, calcd. for $C_{16}H_{32}N^+$ 238.2535.

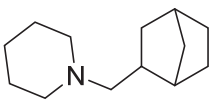


3f: ^{1}H NMR (400 MHz, C_6D_6): δ 2.46 - 2.36 (m, 4H), 2.32 (dd, *J* = 11.6 Hz, 8.8 Hz, 1H), 2.28 (br, 1H), 2.17 (br, 1H), 2.07 (dd, *J* = 11.6 Hz, 7.3 Hz, 1H), 1.67 – 1.60 (m, 5H), 1.51 – 1.44 (m, 2H), 1.41 – 1.35 (m, 1H), 1.30 (ddt, *J* = 9.7 Hz, 3.8 Hz, 1.9 Hz, 1H),

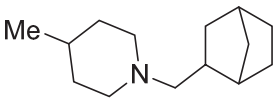
1.22 – 1.10 (m, 3H), 1.07 – 1.03 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6): δ 62.6, 54.6, 41.9, 39.9, 36.9, 36.7, 35.6, 30.5, 29.5, 24.0. HR MS (ESI+): Found 180.1755 $[M+H]^+$, calcd. for $C_{12}H_{22}N^+$ 180.1752.



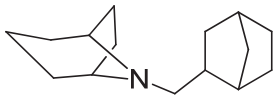
3g: ^{1}H NMR (500 MHz, C_6D_6): δ 2.55 (br, 4H), 2.27 (dd, *J* = 12.1 Hz, 8.5 Hz, 1H), 2.21 – 2.18 (m, 2H), 2.11 (dd, *J* = 12.1 Hz, 7.4 Hz, 1H), 1.57 (br, 9H), 1.51 – 1.44 (m, 2H), 1.37 – 1.30 (m, 1H), 1.28 (d, *J* = 9.5 Hz, 1H), 1.15 (br, 3H), 1.05 (d, *J* = 9.4 Hz, 1H). ^{13}C NMR (125 MHz, C_6D_6): δ 64.5, 56.0, 41.3, 39.9, 37.0, 36.4, 35.7, 30.5, 29.5, 29.3, 27.6. HR MS (ESI+): Found: 208.2066 $[M+H]^+$, calcd. for $C_{14}H_{26}N^+$ 208.2065.



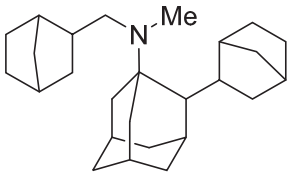
3h: ^{1}H NMR (500 MHz, C_6D_6): δ 2.30 (br, 4H), 2.21 (br, 1H), 2.16 (br, 1H), 2.12 (dd, *J* = 12.2 Hz, 8.6 Hz, 1H), 1.93 (dd, *J* = 12.1 Hz, 7.4 Hz, 1H), 1.66 – 1.61 (m, 1H), 1.56 (s, 2H), 1.56 – 1.51 (m, 4H), 1.48 – 1.44 (m, 1H), 1.35 – 1.27 (m, 4H), 1.18 – 1.10 (m, 3H), 1.03 (d, *J* = 9.7 Hz, 1H). ^{13}C NMR (125 MHz, C_6D_6): δ 65.8, 55.4, 40.0, 37.0, 36.6, 35.6, 30.5, 30.1, 29.5, 26.7, 25.2. HR MS (ESI+): Found 194.1904 $[M+H]^+$, calcd. for $C_{13}H_{24}N^+$ 194.1909.



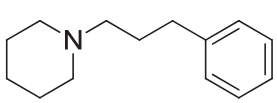
3i: ^{1}H NMR (500 MHz, C_6D_6): δ 2.80 – 2.73 (m, 2H), 2.22 (d, *J* = 9.0 Hz, 1H), 2.17 – 2.12 (m, 2H), 1.99 – 1.91 (m, 1H), 1.77 (m, 1H), 1.71 – 1.63 (m, 2H), 1.61 – 1.42 (m, 7H), 1.40 – 1.27 (m, 2H), 1.20 – 1.10 (m, 3H), 1.05 (d, *J* = 9.7 Hz, 1H), 0.83 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, C_6D_6): δ 65.5 (x2), 63.2, 62.8, 55.0, 54.6, 40.1, 40.0 (x3), 37.0, 36.6 (x2), 35.6 (x2), 33.7, 31.6, 31.5, 30.5, 29.5, 26.1, 20.0. HR MS (ESI+): Found 208.2065 $[M+H]^+$, calcd. for $C_{14}H_{26}N^+$ 208.2065.



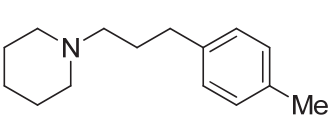
3j: ^{1}H NMR (500 MHz, C_6D_6): δ 3.06 (s, 2H), 2.32 (s, 1H), 2.20 (s, 1H), 2.11 (dd, *J* = 12.1 Hz, 8.5 Hz, 1H), 1.99 (dd, *J* = 12.1 Hz, 7.2 Hz, 1H), 1.85 – 1.78 (m, 4H), 1.58 – 1.47 (m, 3H), 1.44 – 1.35 (m, 5H), 1.32 – 1.30 (m, 1H), 1.22 – 1.13 (m, 5H), 1.07 (d, *J* = 9.1 Hz, 1H). ^{13}C NMR (125 MHz, C_6D_6): δ 57.9, 57.8, 56.7, 39.5, 37.4, 34.5, 34.`, 33.`, 29.1, 29.0, 28.1, 27.1, 24.5, 24.3, 15.0. HR MS (ESI+): Found 220.2065 $[M+H]^+$, calcd. for $C_{15}H_{25}N^+$ 220.2065.



3k: ^{1}H NMR (500 MHz, C_6D_6): δ 2.72 (d, *J* = 3.9 Hz, 1H), 2.53 (t, *J* = 12.5 Hz, 1H), 2.25 (s, 3H), 2.22 – 2.17 (m, 4H), 2.00 (br, 3H), 1.77 (d, *J* = 11.7 Hz, 3H), 1.73 – 1.71 (m, 1H), 1.67 (d, *J* = 11.7 Hz, 3H), 1.61 – 1.45 (m, 12H), 1.43 – 1.40 (m, 1H), 1.35 – 1.17 (m, 5H), 1.15 (d, *J* = 7.5 Hz, 2H), 1.01 (d, *J* = 9.5 Hz, 2H). ^{13}C NMR (125 MHz, C_6D_6): δ 54.0, 52.8, 49.3, 46.0, 43.5, 41.8, 41.4, 41.3, 40.4, 39.3, 37.5, 37.3, 35.4, 34.5, 33.3, 31.8, 30.6, 30.2, 29.7 (x2). HR MS (ESI+): Found 368.3317 $[M+H]^+$, calcd. for $C_{26}H_{42}N^+$ 368.3317.

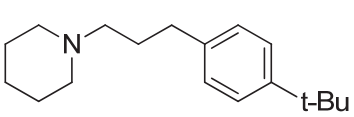


4a: ^{1}H NMR (500 MHz, C_6D_6): δ 7.19 – 7.16 (m, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 2.58 (t, *J* = 7.7 Hz, 2H), 2.25 (br, 4H), 2.20 (t, *J* = 7.1 Hz, 2H), 1.73 (quin, *J* = 7.5 Hz, 2H), 1.52 (quin, *J* = 5.5 Hz, 4H), 1.33 (br, 2H). ^{13}C NMR (125 MHz, C_6D_6): δ 142.9, 128.9, 128.6, 126.0, 58.6, 54.9, 33.3, 29.3, 26.6, 25.1. HR MS (ESI+): Found 204.1753 $[M+H]^+$, calcd. for $C_{14}H_{21}N^+$ 204.1752.

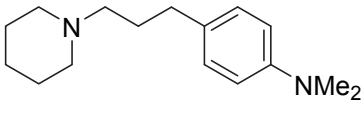


4b: ^{1}H NMR (500 MHz, C_6D_6): δ 7.07 (d, *J* = 7.7 Hz, 2H), 7.02 (d, *J* = 7.7 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.27 (br, 4H), 2.23 (t, *J* = 7.2 Hz, 2H), 2.16 (s, 3H), 1.76 (quin, *J* = 7.5 Hz, 2H), 1.53 (quin, *J* = 6.0 Hz, 4H), 1.33 (br,

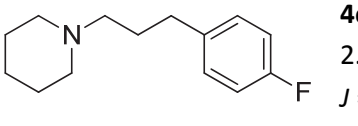
2H). ^{13}C NMR (125 MHz, C_6D_6): δ 139.9, 135.1, 129.3, 128.8, 58.7, 55.0, 33.5, 29.4, 26.7, 25.2, 21.1. HR MS (ESI+): Found 218.1906 $[M+H]^+$, calcd. for $C_{15}H_{24}N^+$ 218.1909.



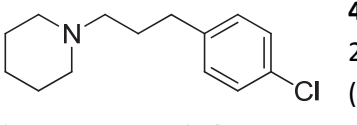
4c: ^{1}H NMR (500 MHz, C_6D_6): δ 7.28 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.27 (br, 4H), 2.24 (t, *J* = 7.0 Hz, 2H), 1.78 (quin, *J* = 7.5 Hz, 2H), 1.53 (quin, *J* = 5.5 Hz, 4H), 1.33 (m, 2H), 1.26 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6): δ 148.1, 139.5, 128.2, 125.1, 58.4, 54.6, 34.0, 33.1, 31.2, 29.0, 26.3, 24.8. HR MS (ESI+): Found 260.2373 $[M+H]^+$, calcd. for $C_{18}H_{30}N^+$ 260.2373.



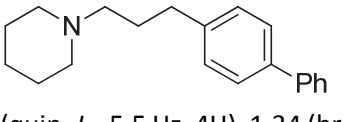
4d: ^{1}H NMR (500 MHz, C_6D_6): δ 7.15 (d, *J* = 8.3 Hz, 2H), 6.67 (d, *J* = 8.5 Hz, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.56 (s, 6H), 2.31 – 2.28 (m, 6H), 1.83 (quin, *J* = 7.5 Hz, 2H), 1.54 (quin, *J* = 6.0 Hz, 4H), 1.34 (br, 2H). ^{13}C NMR (125 MHz, C_6D_6): δ 149.5, 131.1, 129.4, 113.5, 55.8, 55.0, 40.7, 33.1, 29.8, 26.7, 25.2. HR MS (ESI+): Found 247.2177 $[M+H]^+$, calcd. for $C_{16}H_{27}N_2^+$ 247.2174.



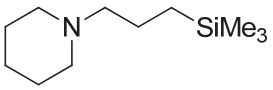
4e: ^{1}H NMR (500 MHz, C_6D_6): δ 6.87 - 6.80 (m, 4H), 2.45 (t, *J* = 7.6 Hz, 2H), 2.24 (br, 4H), 2.14 (t, *J* = 7.0 Hz, 2H), 1.62 (quin, *J* = 7.5 Hz, 2H), 1.52 (quin, *J* = 5.5 Hz, 4H), 1.3 (br, 2H). ^{13}C NMR (125 MHz, C_6D_6): δ 159.8 (*J* = 242.8 Hz), 136.5 (*J* = 3.2 Hz), 128.2 (*J* = 7.7 Hz), 113.3 (*J* = 21.0 Hz), 56.4, 53.0, 31.0, 27.3, 24.7, 23.2. HR MS (ESI+): Found 222.1657 $[M+H]^+$, calcd. for $C_{14}H_{21}FN^+$ 222.1658.



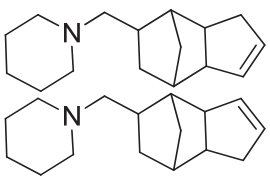
4f: ^{1}H NMR (500 MHz, C_6D_6): δ 7.12 (d, *J* = 8.3 Hz, 2H), 6.79 (d, *J* = 8.3 Hz, 2H), 2.40 (t, *J* = 7.6 Hz, 2H), 2.23 (br, 4H), 2.12 (t, *J* = 7.0 Hz, 2H), 1.58 (quin, *J* = 7.5 Hz, 2H), 1.52 (quin, *J* = 5.5 Hz, 4H), 1.33 (br, 2H). ^{13}C NMR (125 MHz, C_6D_6): δ 141.3, 131.8, 130.2, 128.7, 58.3, 54.9, 37.0, 29.0, 26.6, 25.1HR MS (ESI+): Found 238.1357 $[M+H]^+$, calcd. for $C_{14}H_{21}ClN^+$ 238.1363.



4g: ^{1}H NMR (500 MHz, C_6D_6): δ 7.52 (d, *J* = 7.2 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.17 – 7.12 (m, 3H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.28 (br, 4H), 2.24 (t, *J* = 7.1 Hz, 2H), 1.77 (quin, *J* = 7.0 Hz, 2H), 1.54 (quin, *J* = 5.5 Hz, 4H), 1.34 (br, 2H). ^{13}C NMR (125 MHz, C_6D_6): δ 142.0, 141.8, 139.2, 129.3, 129.0, 127.4 (x2), 127.2, 58.6, 55.0, 33.5, 29.3, 26.7, 25.2. HR MS (ESI+): Found 280.2060 $[M+H]^+$, calcd. for $C_{20}H_{26}N^+$ 280.2065.

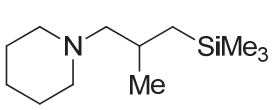


4h: ^{1}H NMR (500 MHz, C_6D_6): δ 2.34 (br, 4H), 2.27 (t, *J* = 7.5 Hz, 2H), 1.58 – 1.50 (m, 6H), 1.35 (br, 2H) 0.53 – 0.49 (m, 2H), 0.01 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6): δ 63.2, 55.1, 26.7, 25.2, 22.1, 14.5 HR MS (ESI+): Found 200.1834 $[M+H]^+$, calcd. for $C_{11}H_{26}NSi^+$ 200.1835.

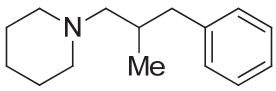


5a: ^{1}H NMR (500 MHz, C_6D_6): **5a** δ 5.64 – 5.59 (m, 1H), 5.53 – 5.51 (m, 1H), 3.01 – 2.95 (m, 1H), 2.48 – 2.41 (m, 1H), 2.38 – 2.23 (br m, 5H), 2.21 – 2.12 (m, 3H), 2.10 (dd, *J* = 7.9 Hz, 4.0Hz, 1H), 2.01 – 1.90 (m, 1H), 1.84 – 1.77 (m, 1H), 1.56 – 1.51 (m, 5H), 1.43 (d, *J* = 9.6 Hz, 1H) 1.36 – 1.25 (m, 3H), 0.931 (dtd, *J* = 12.0 Hz, 5.5Hz, 1.5 Hz, 1H). **5a'** δ 5.64 – 5.59 (m, 1H), 5.53 – 5.51 (m, 1H), 3.08 – 3.02 (m, 1H), 2.48 – 2.41 (m, 1H), 2.38 – 2.23 (br m, 5H), 2.21 – 2.12 (m, 3H), 2.08 – 2.06 (br, 1H), 2.01 – 1.90 (m, 2H), 1.56 – 1.51 (m, 6H), 1.36 – 1.25 (m, 3H), 1.01 (dtd, *J* = 12.9 Hz, 4.4Hz, 1.7 Hz, 1H); ^{13}C NMR (125 MHz, C_6D_6): **5a** δ 132.9, 130.7, 65.9, 55.3, 53.1, 44.7, 42.9, 40.4, 38.7, 32.5, 32.2,

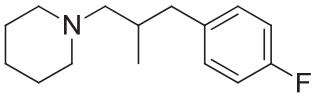
31.3, 26.7, 25.2. **5a'** δ 132.7, 131.4, 65.6, 55.4, 54.1, 43.1, 42.5, 41.5, 38.8, 34.3, 32.7, 29.0, 26.7, 25.2; HR MS (ESI+): Found 232.2070 $[M+H]^+$, calcd. for $C_{16}H_{26}N^+$ 232.2065.



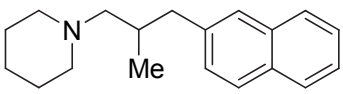
5b: ^{1}H NMR (500 MHz, C_6D_6): δ 2.30 (br, 4H), 2.04 (ddd, *J* = 28.9 Hz, 12.0 Hz, 7.3 Hz, 2H), 1.81 (td, *J* = 13.7 Hz, 6.8 Hz, 1H), 1.53 (quin, *J* = 6.0 Hz, 4H), 1.34 (br, 2H), 1.02 (d, *J* = 6.5 Hz, 3H), 0.84 (dd, *J* = 14.7 Hz, 4.5 Hz, 1H), 0.36 – 0.28 (m, 1H), 0.07 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6): δ 69.8, 55.5, 27.6, 26.7, 25.1, 23.3, 21.8, -0.37. HR MS (ESI+): Found 214.1987 $[M+H]^+$, calcd. for $C_{12}H_{28}NSi^+$ 214.1991.



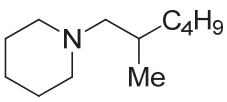
5c: ^{1}H NMR (500 MHz, C_6D_6): δ 7.19 (t, *J* = 7.4 Hz, 2H), 7.13 – 7.08 (m, 3H), 2.84 (dd, *J* = 13.3 Hz, 4.7 Hz, 1H), 2.31 – 2.26 (br m, 5H), 2.09 (dd, *J* = 12.0 Hz, 7.6 Hz, 1H), 1.99 (dd, *J* = 12.0 Hz, 7.1 Hz, 1H), 1.96 – 1.88 (m, 1H), 1.52 (quin, *J* = 6.0 Hz, 4H), 1.33 (br, 2H), 0.87 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, C_6D_6): δ 141.6, 129.7, 128.4 (x2), 126.0, 66.0, 55.3, 41.6, 33.0, 26.7, 25.1, 18.2. HR MS (ESI+): Found 218.1904 $[M+H]^+$, calcd. for $C_{15}H_{24}N^+$ 218.1909.



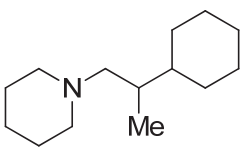
5d: ^{1}H NMR (500 MHz, C_6D_6): δ 6.88 - 6.81 (m, 4H), 2.69 (dd, *J* = 13.4 Hz, 4.7 Hz, 1H), 2.24 (br, 4H), 2.17 (dd, *J* = 13.4 Hz, 8.4 Hz, 1H), 2.02 (dd, *J* = 12.51 Hz, 7.9 Hz, 1H), 1.95 (dd, *J* = 12.2 Hz, 6.9 Hz, 1H), 1.85 – 1.76 (m, 1H), 1.52 (quin, *J* = 5.5 Hz, 4H), 1.33 (br, 2H), 0.80 (d, *J* = 6.6 Hz, 3H).^{13}C NMR (125 MHz, C_6D_6): δ 161.8 (d, *J* = 242.9 Hz), 137.1 (d, *J* = 3.2 Hz), 131.0 (d, *J* = 7.6 Hz), 115.1 (d, *J* = 20.9 Hz), 65.8, 55.3, 40.5, 32.9, 26.6, 25.1, 18.0. HR MS (ESI+): Found 236.1817 $[M+H]^+$, calcd. for $C_{15}H_{23}FN^+$ 236.1815.



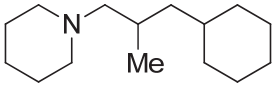
5e: ^{1}H NMR (500 MHz, C_6D_6): δ 8.29 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.23 (d, *J* = 6.9 Hz, 1H), 3.60 (dd, *J* = 13.5 Hz, 8.5 Hz, 1H), 2.46 (dd, *J* = 13.5 Hz, 8.9 Hz, 1H), 2.35 (br, 2H), 2.24 (br, 2H), 2.17 – 1.98 (m, 3H), 1.56 (quin, *J* = 5.5 Hz, 4H), 1.35 (br, 2H), 0.85 (d, *J* = 6.4 Hz, 3H).^{13}C NMR (125 MHz, C_6D_6): δ 138.4, 134.8, 133.0, 129.2, 127.5, 127.0, 125.8, 125.6 (x2), 124.9, 67.0, 55.7, 39.3, 32.8, 26.7, 25.1, 18.7. HR MS (ESI+): Found 268.2063 $[M+H]^+$, calcd. for $C_{19}H_{26}N^+$ 268.2065.



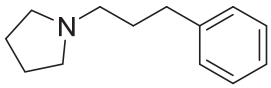
5f: ^{1}H NMR (500 MHz, C_6D_6): δ 2.29 (br, 4H), 2.10 (dd, *J* = 12.1 Hz, 6.7 Hz, 1H), 2.00 (dd, *J* = 12.1 Hz, 7.9 Hz, 1H), 1.68 – 1.59 (m, 1H), 1.54 (quin, *J* = 5.5 Hz, 4H), 1.51 – 1.45 (m, 1H), 1.38 – 1.22 (m, 6H), 1.12 – 1.05 (m, 1H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, C_6D_6): δ 67.0, 55.5, 35.4, 30.9, 29.7, 26.7, 25.2, 23.5, 18.7, 14.4. HR MS (ESI+): Found 184.2064 $[M+H]^+$, calcd. for $C_{12}H_{26}N^+$ 184.2065.



5g: ^{1}H NMR (500 MHz, C_6D_6): δ 2.32 (br m 2H), 2.25 (br, 2H), 2.20 (dd, *J* = 12.1 Hz, 6.2 Hz, 1H), 2.01 (dd, *J* = 12.1 Hz, 8.6 Hz, 1H), 1.75 – 1.72 (m, 2H), 1.68 – 1.65 (m, 1H), 1.60 – 1.51 (m, 7H), 1.36 -1.31 (m, 3H), 1.27 – 1.20 (m, 2H), 1.17 – 1.08 (m, 2H), 1.06 -0.97 (m, 1H), 0.94 (d, *J* = 6.8 Hz, 3H).^{13}C NMR (125 MHz, C_6D_6): δ 64.4, 55.6, 41.3, 35.8, 31.5, 28.7, 27.4, 27.3, 27.2, 26.7, 25.2, 15.1.HR MS (ESI+): Found 210.2224 $[M+H]^+$, calcd. for $C_{14}H_{28}N^+$ 210.2222.

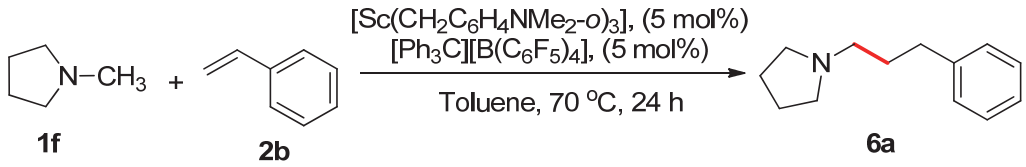


5h: ^{1}H NMR (500 MHz, C_6D_6): δ 2.31 – 2.28 (br, 4H), 2.09 (dd, *J* = 12.0 Hz, 6.7 Hz, 1H), 2.00 (dd, *J* = 12.0 Hz, 7.9 Hz, 1H), 1.89 – 1.64 (m, 6H), 1.54 (quin, *J* = 6.0 Hz, 4H), 1.44 – 1.30 (m, 4H), 1.27 – 1.10 (m, 3H), 0.99 – 0.79 (m, 3H), 0.96 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, C_6D_6): δ 67.4, 55.5, 44.0, 35.4, 34.8, 33.5, 27.7, 27.2, 26.9, 26.8, 26.7, 25.2, 19.2. HR MS (ESI+): Found 224.2378 $[M+H]^+$, calcd. for $C_{15}H_{30}N^+$ 224.2378.



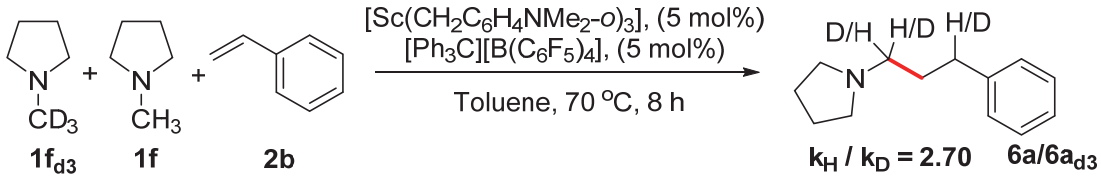
6a: ^{1}H NMR (500 MHz, C_6D_6): δ 7.18 (d, *J* = 7.5 Hz, 2H), 7.11 (d, *J* = 7.3 Hz, 2H) 7.08 (t, *J* = 7.3 Hz, 1H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.35 – 2.32 (m, 6H), 1.74 (quin, *J* = 7.5 Hz, 2H), 1.61 – 1.55 (m, 4H). ^{13}C NMR (125 MHz, C_6D_6): δ 142.7, 128.8, 128.7, 126.1, 55.7, 54.2, 33.9, 30.9, 23.9. HR MS (ESI+): Found 190.1599 $[M+H]^+$, calcd. for $C_{13}H_{20}N^+$ 190.1596.

5. Kinetic Isotope Effect Experiments



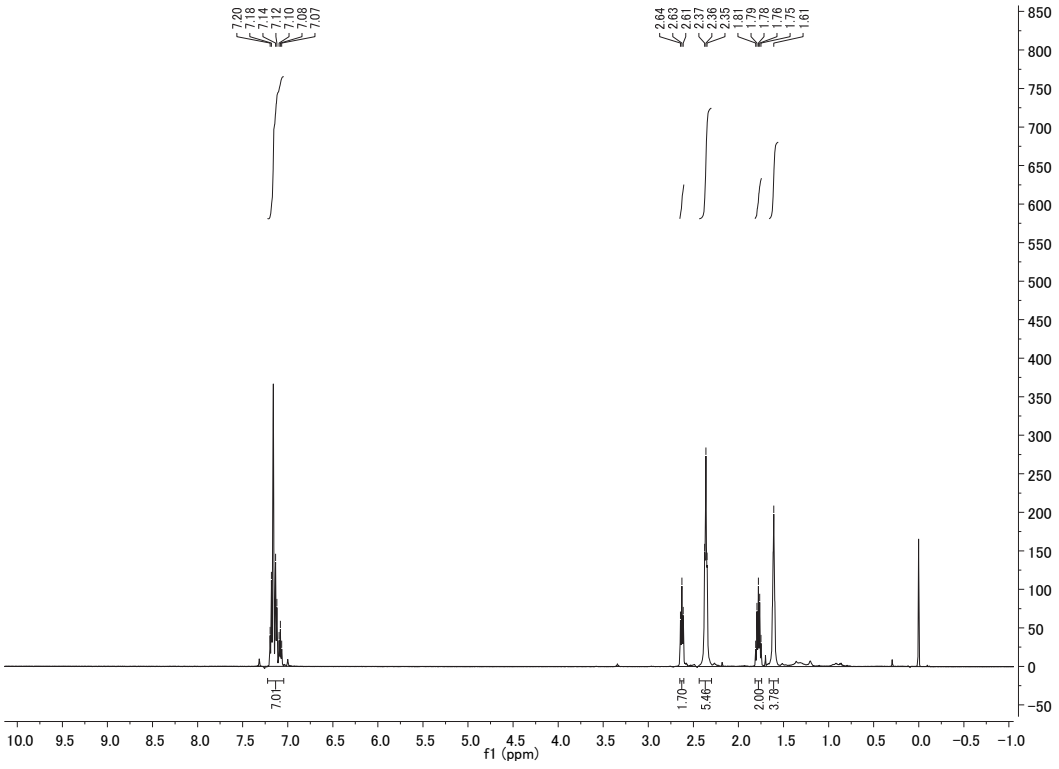
Compound **6a** could be synthesized following the general procedure above in an 81 % isolated yield.

Intermolecular Competition Experiment



In a glovebox, $[Sc(CH_2C_6H_4NMe_2\text{-}o)_3]$ (6 mg, 0.013 mmol) was dissolved in toluene (1.0 mL). To this solution **1f$_{d3}$** (22 mg, 0.25 mmol), **1f** (21 mg, 0.25 mmol), styrene (26 mg, 0.25 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (16 mg, 0.013 mmol) were added sequentially. The biphasic mixture was transferred to a Schlenk ampoule, sealed and heated at 70 °C for 8 hours. EtOAc (5 mL) was added to the crude mixture and the volatiles removed *in vacuo.* The compound was purified by silica gel column chromatography (hexane/EtOAc), to afford a mixture of **6a** and **6a$_{d3}$** as a colorless oil (12 mg, 25 % yield). A k_H/k_D value of 2.70 was found by comparison of the relative ratios of **6a** and **6a$_{d3}$** by ^{1}H NMR spectroscopy using the integration values for the benzylic proton(s). No deuterium scrambling was observed when this mixture of **6a** and **6a$_{d3}$** was exposed to the standard reaction conditions.

Fig. S1. The ^{1}H NMR Spectrum of an Isolated Mixture of 6a and 6a$_{d3}$



Comparison of Initial Rates

In a glovebox, [Sc($CH_2C_6H_4NMe_2$-*o*)$_3$] (6 mg, 0.013 mmol) was dissolved in C_7D_8 (1.0 mL). To this solution, ferrocene (19 mg, 0.1 mmol), *N*-methylpyrrolidine (21mg, 0.25 mmol), styrene (29 mg, 0.28 mmol) and [Ph_3C][$B(C_6F_5)_4$] (16 mg, 0.013 mmol) were added sequentially. The biphasic mixture was transferred to a J Young NMR tube, sealed and the reaction monitored by ^{1}H NMR at 70 °C for 12 h. The reaction with d_3-*N*-methylpyrrolidine was performed and monitored under exactly the same conditions. Initial rates were extracted by comparing the ^{1}H NMR integration of the benzylic proton(s) of **6a** and **6a$_{d3}$** against the internal standard. A k_H/k_D value of 1.97 ± 0.03 was found by comparison of the initial rates of reaction.

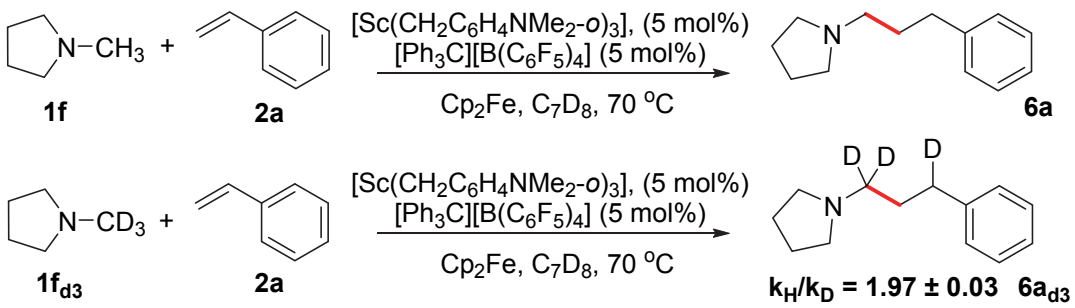
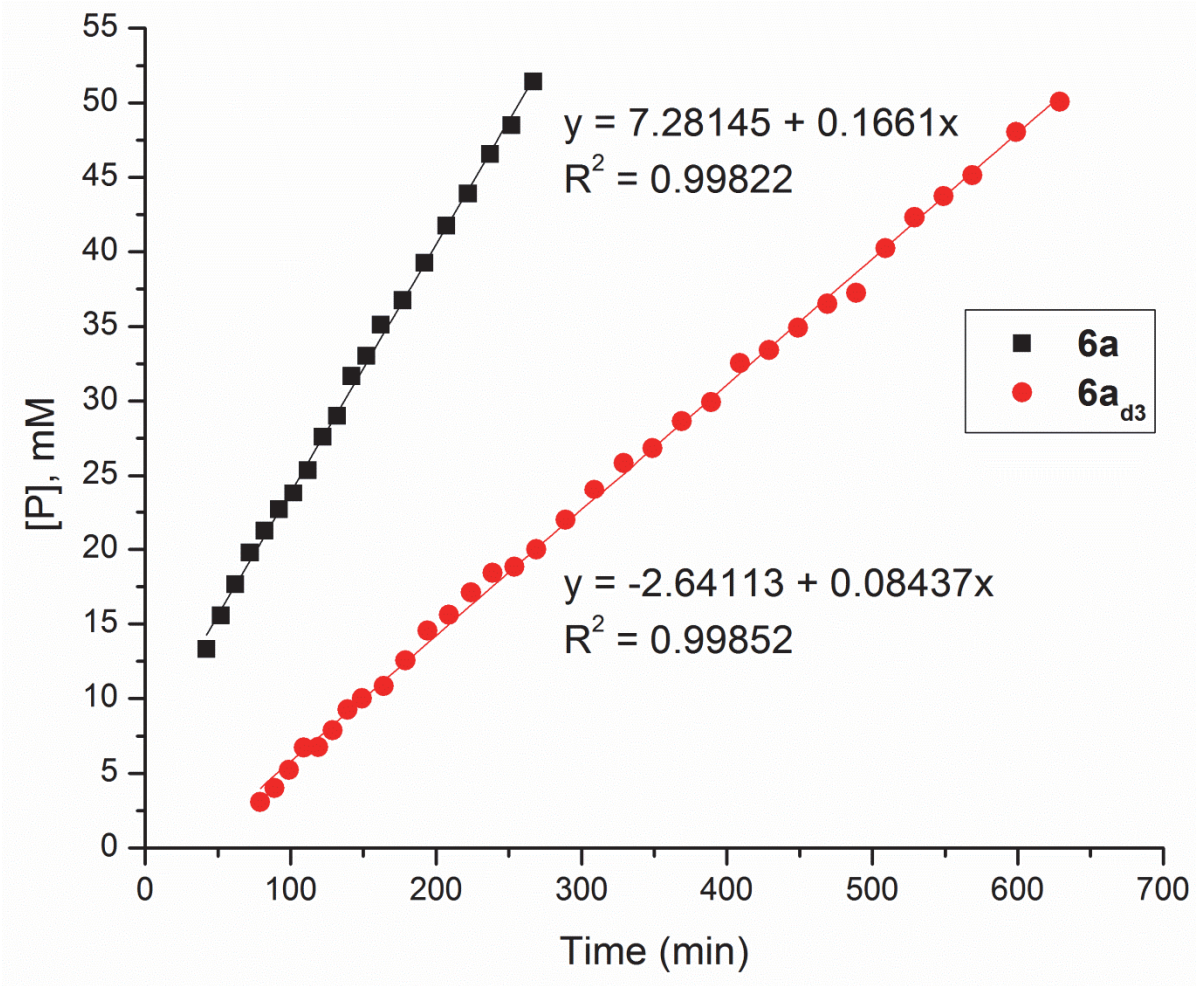
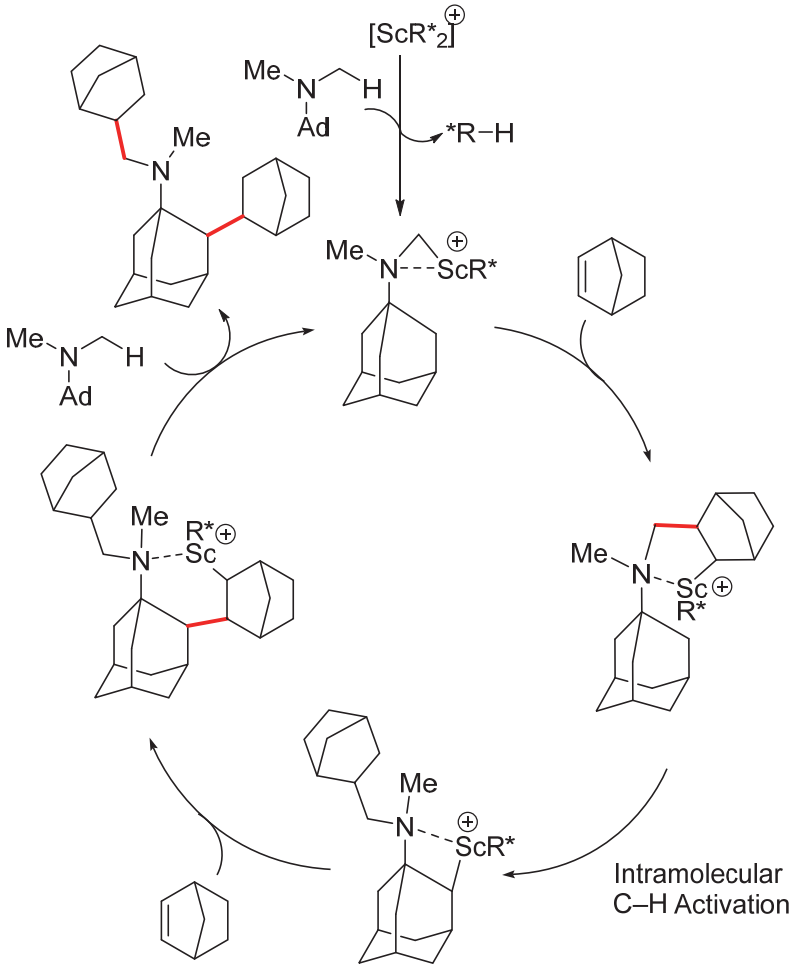


Fig. S2. Initial Rates of C–H/C–D Addition of *N*-methylpyrrolidine to Styrene



6. Dialkylation of 1k to give 3k

Scheme S1. A Plausible Mechanism for the Formation of 3k



7. References

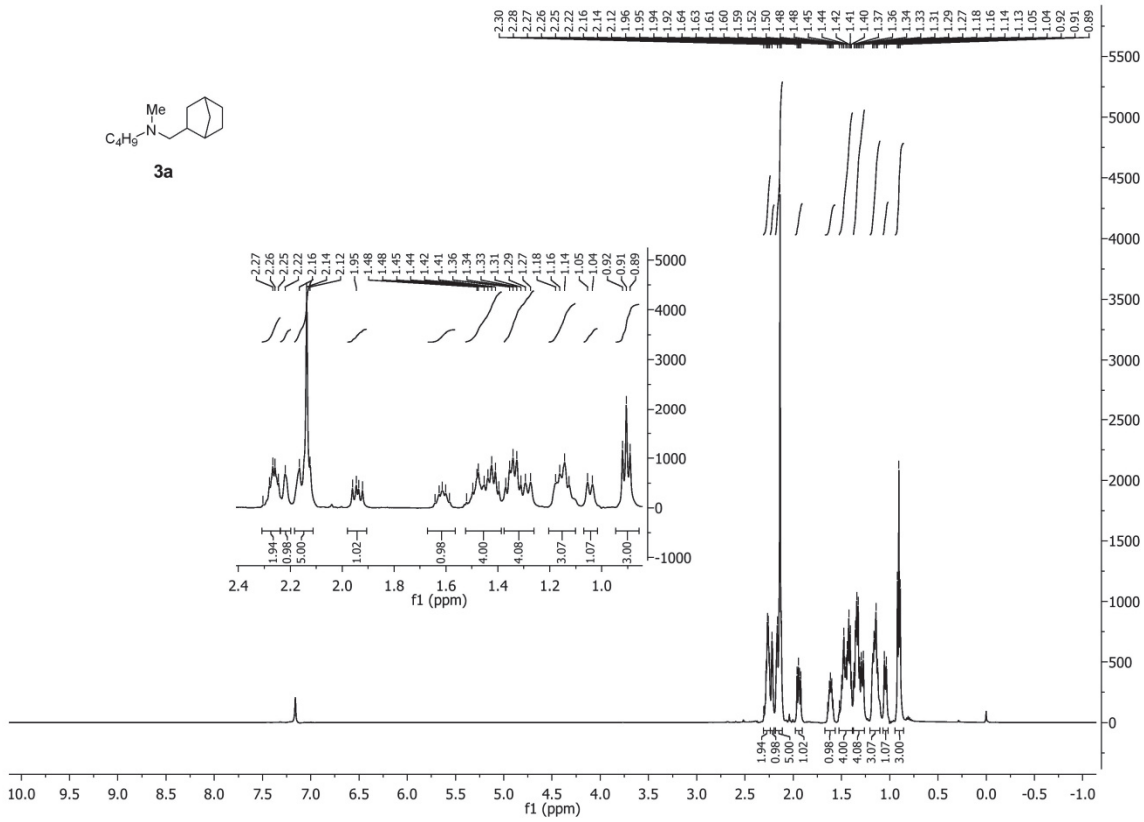
(1) (a) L. E. Manzer, *J. Am. Chem. Soc.*, 1978, **100**, 8068; (b) W. X. Zhang, M. Nishiura, T. Mashiko and Z. Hou, *Chem. Eur. J.*, 2008, **14**, 2167.

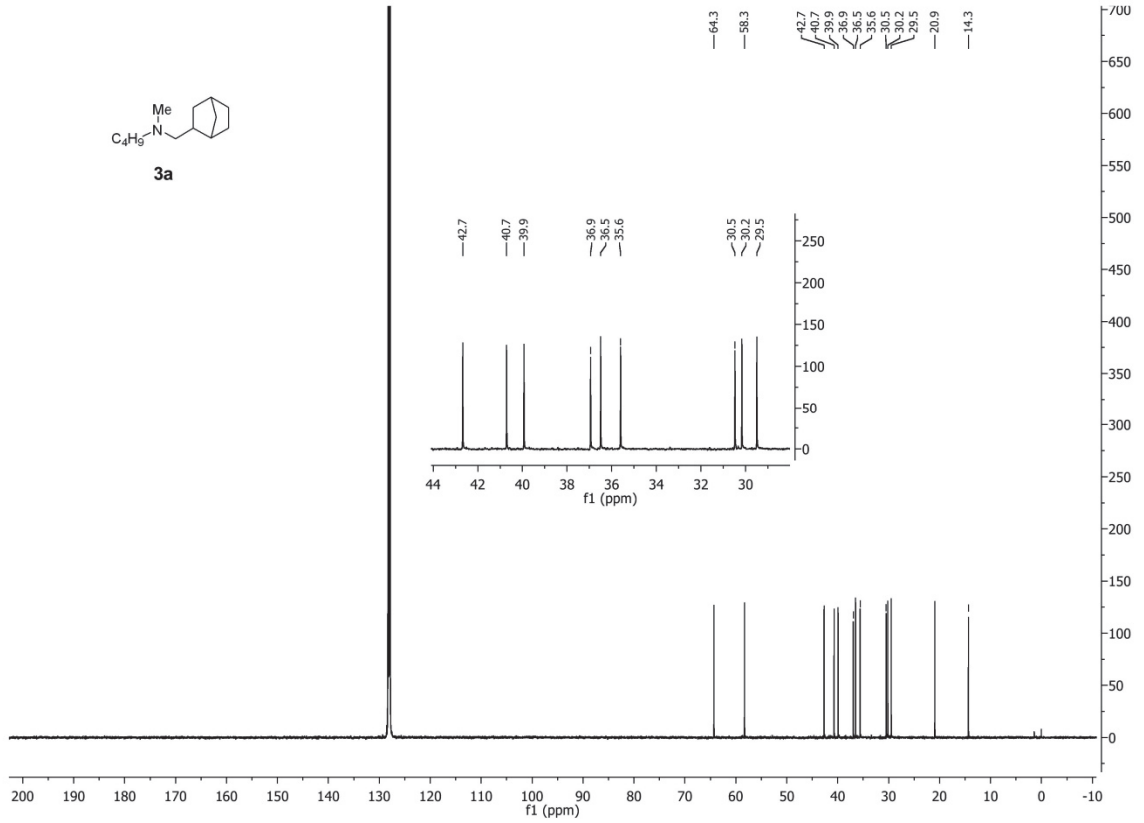
(2) X. Li, M. Nishiura, K. Mori, T. Mashiko and Z. Hou, *Chem. Commun.*, 2007, 4137.

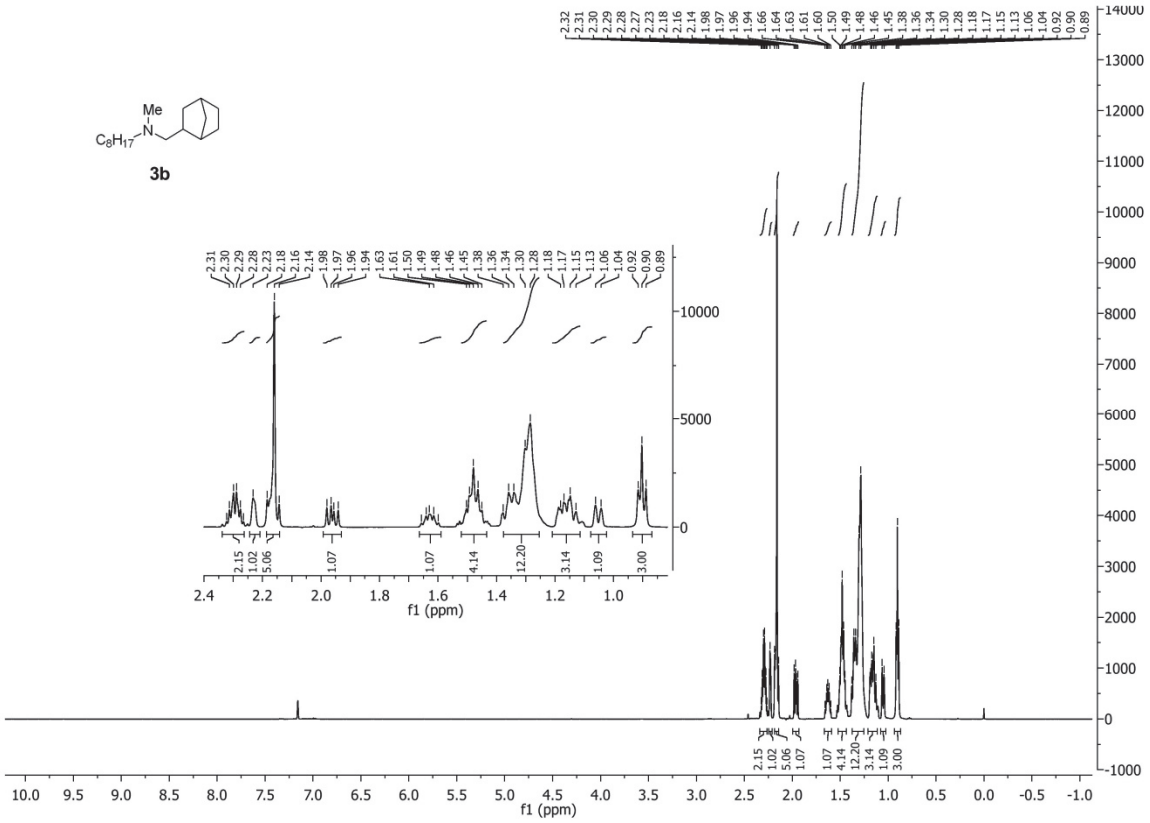
(3) R. N. Icke, B. B. Wisegarver, and G. A. Alles *Org. Synth.*, 1945, **25**, 89.

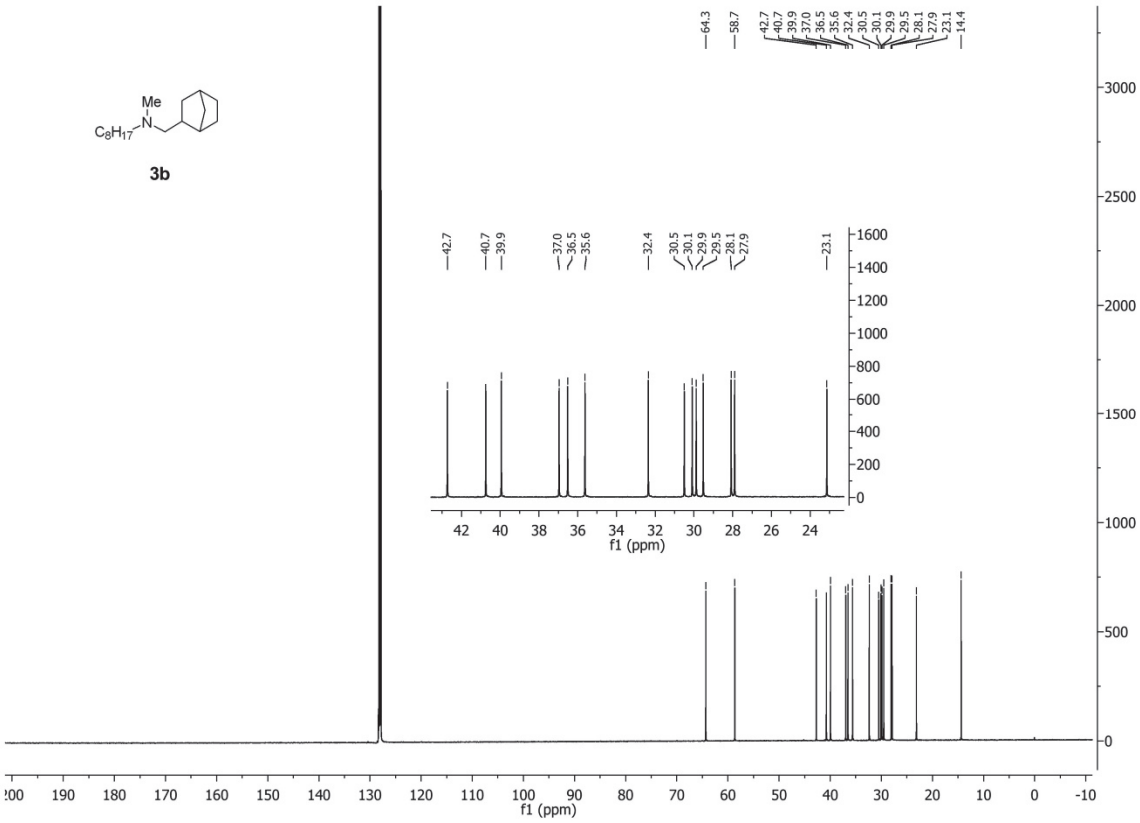
(4) P. Wei, X. Bi, Z. Wu and Z. Xu, *Org. Lett.*, 2005, **7**, 3199.

8. ^{1}H and ^{13}C NMR spectra of products






Me
C8H17
N
3b
f1 (ppm)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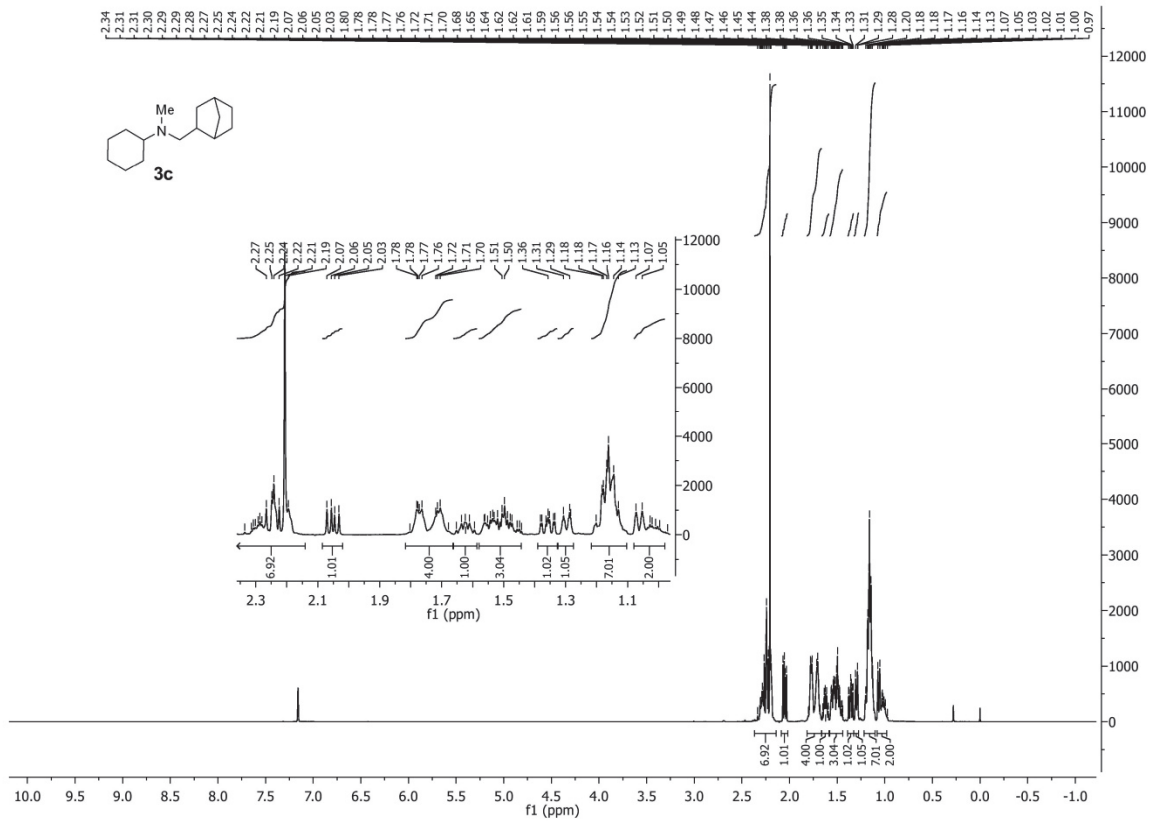
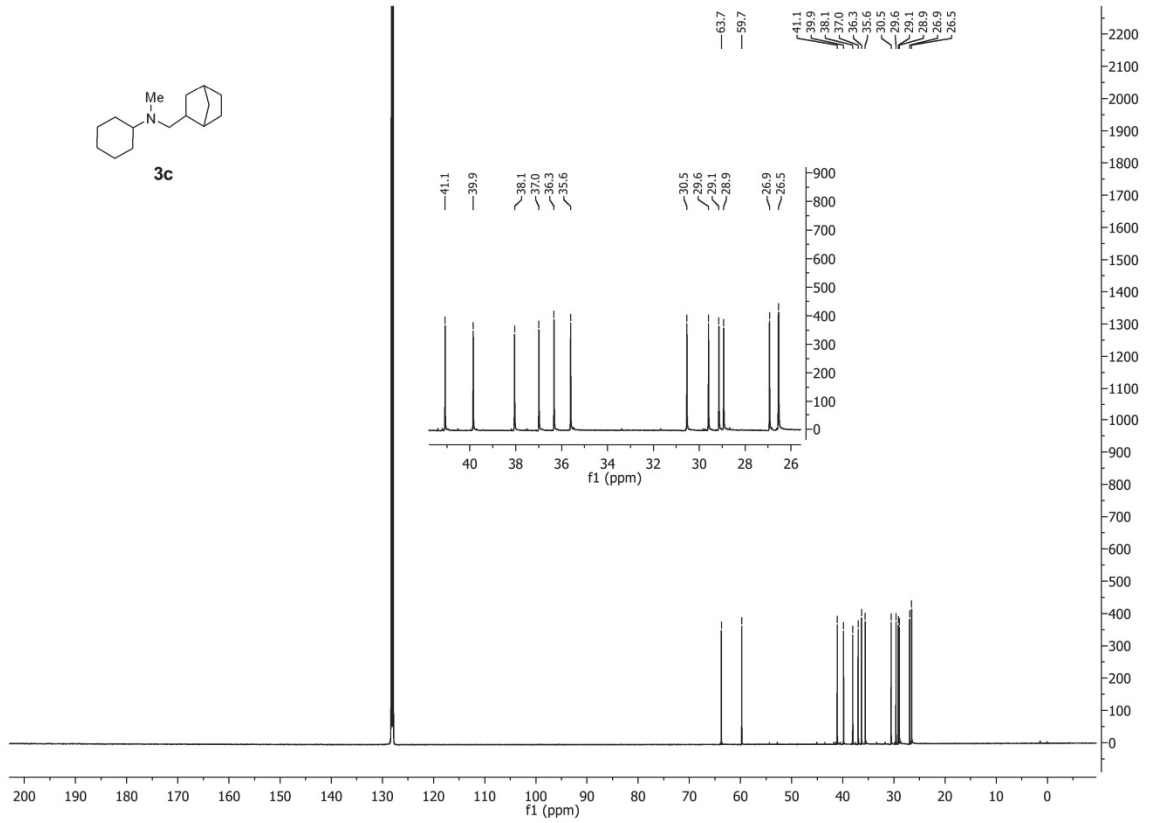
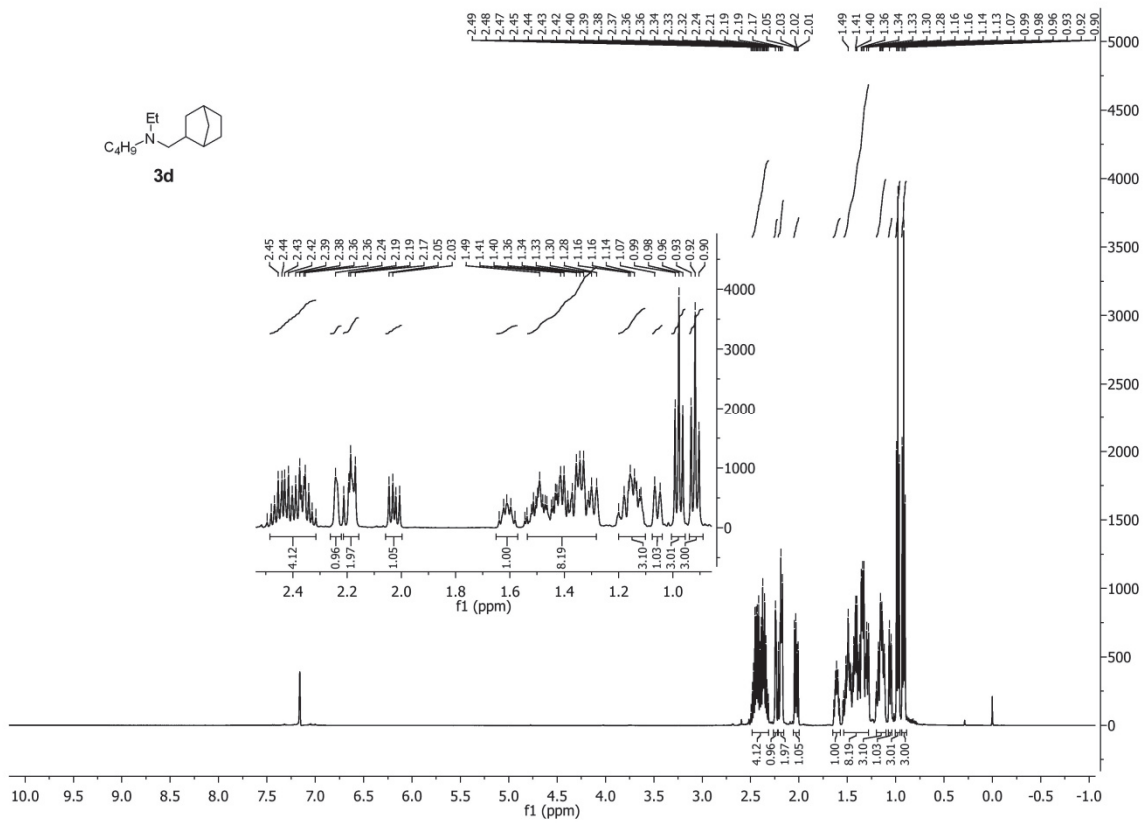
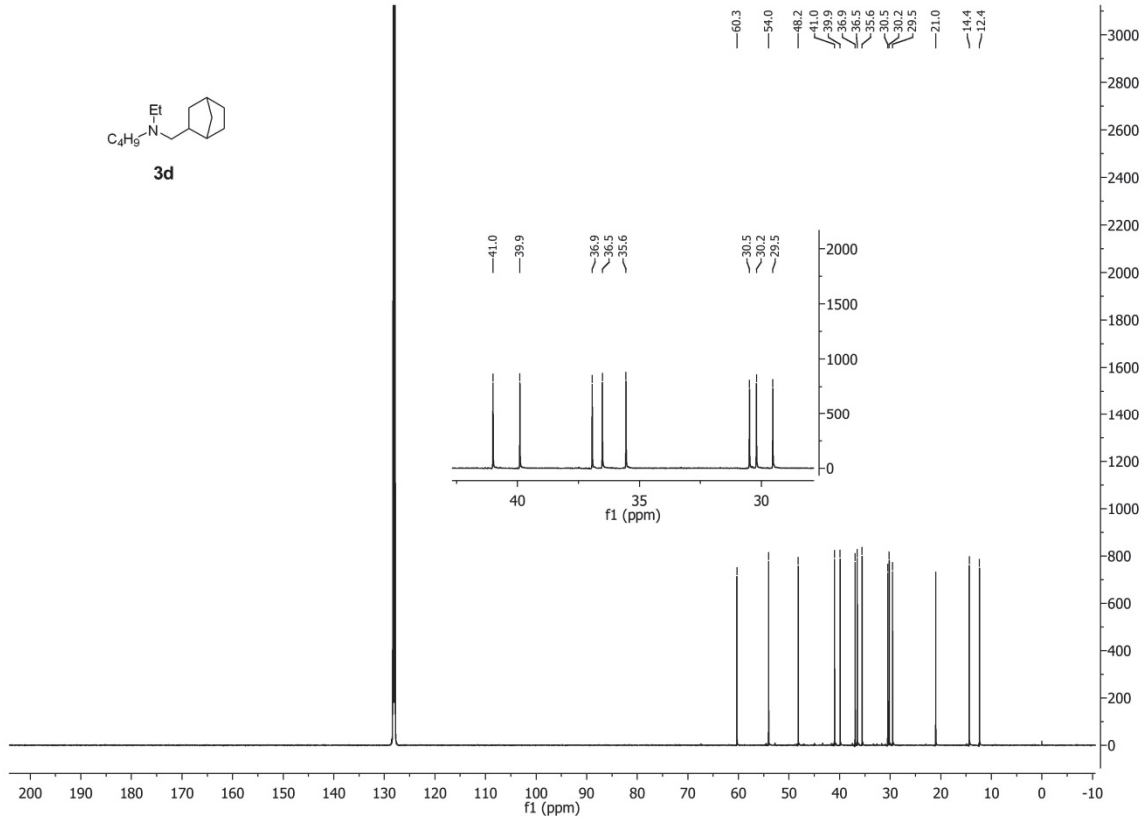
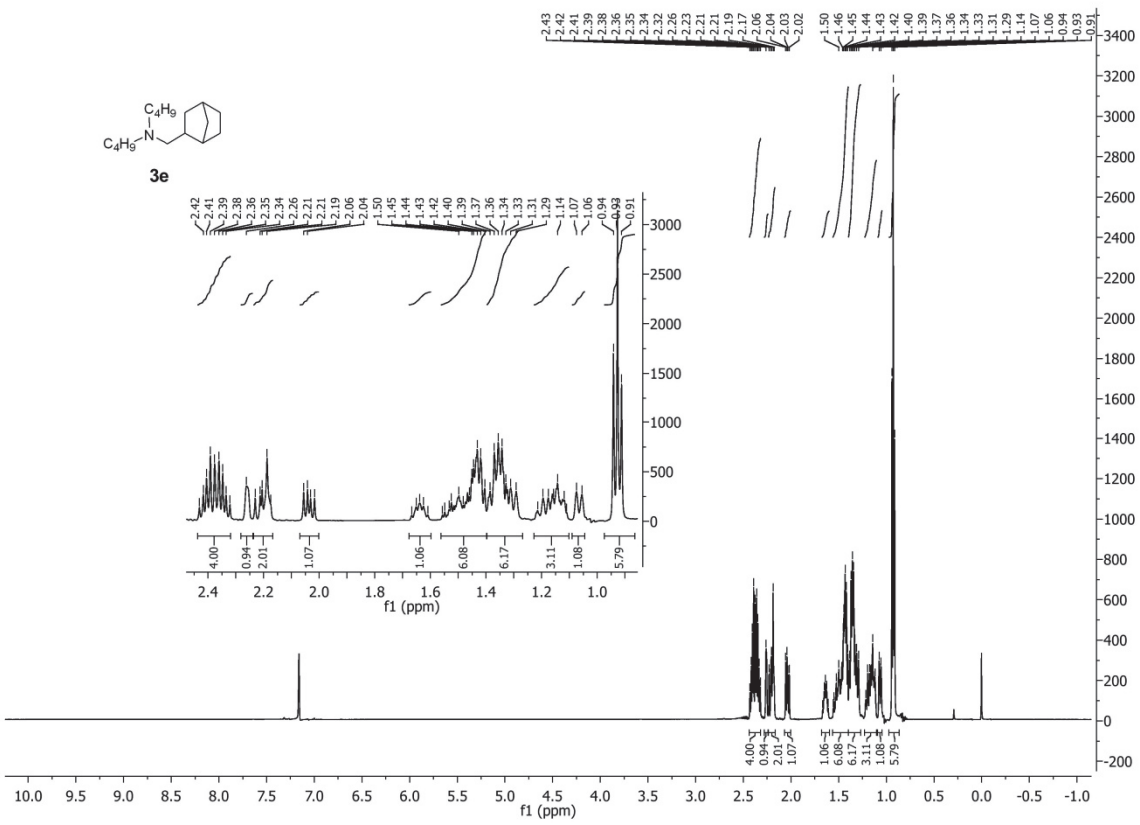
N
3b
f1 (ppm)

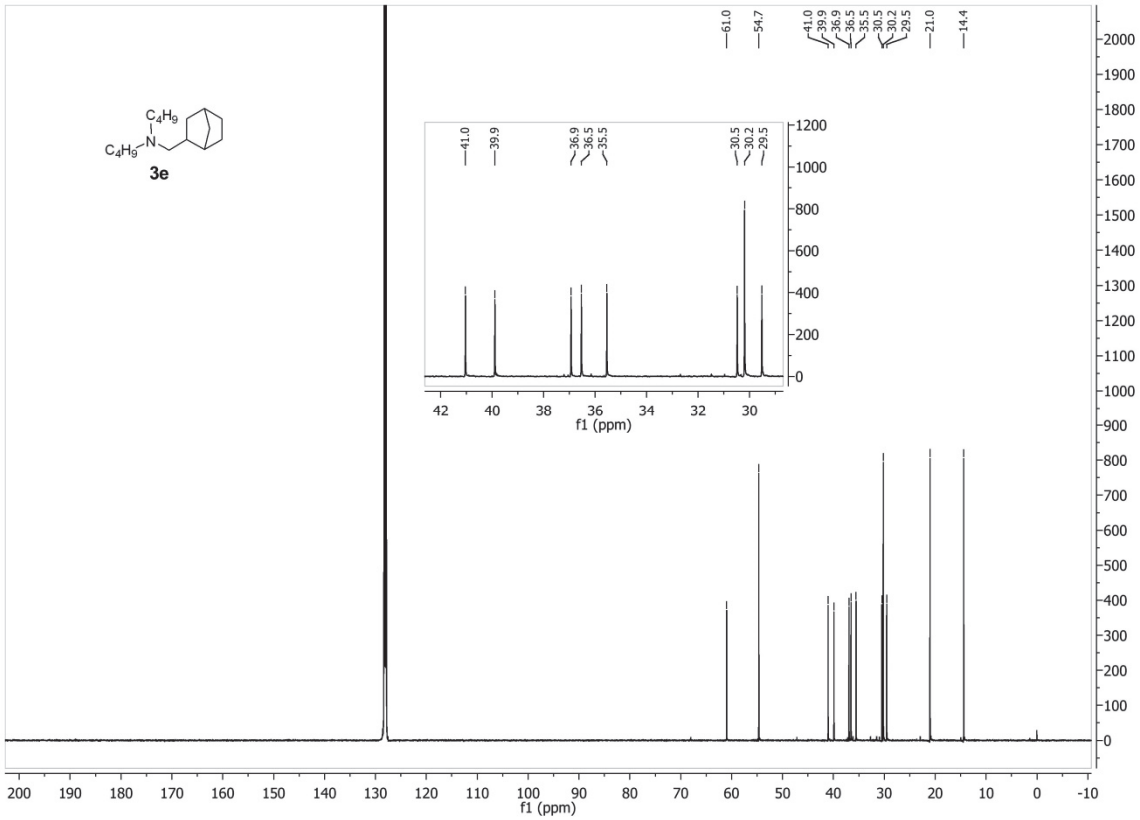

Me
N
3c
f1 (ppm)


Me
N
3c
f1 (ppm)


Et
C4H9
N
3d
f1 (ppm)


Et
C4H9
N
3d
f1 (ppm)


3e
f1 (ppm)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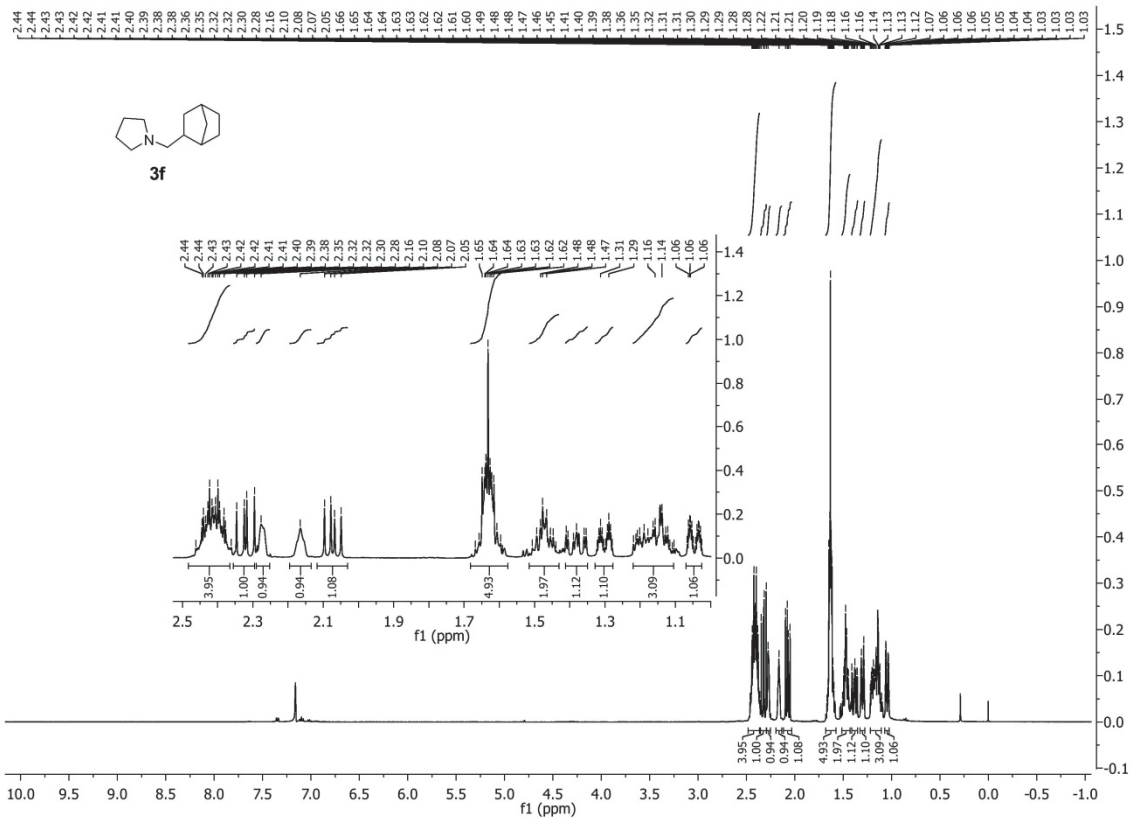
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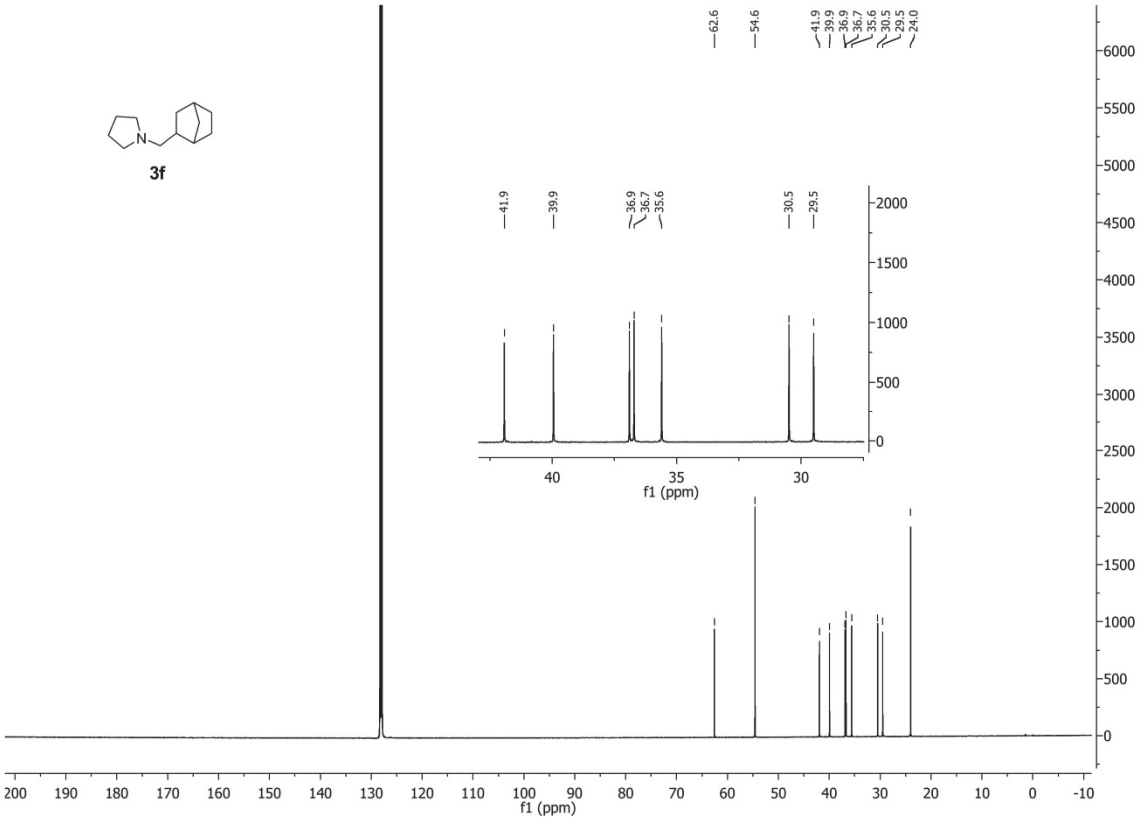
3f
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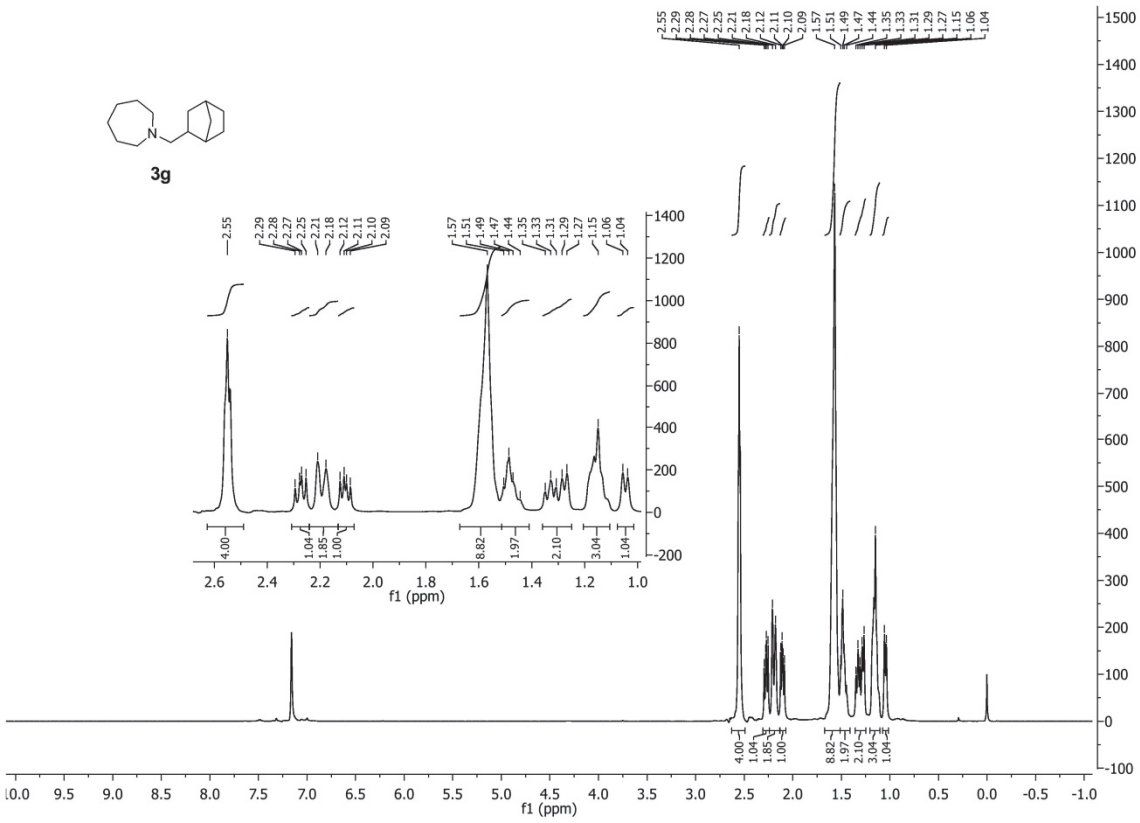
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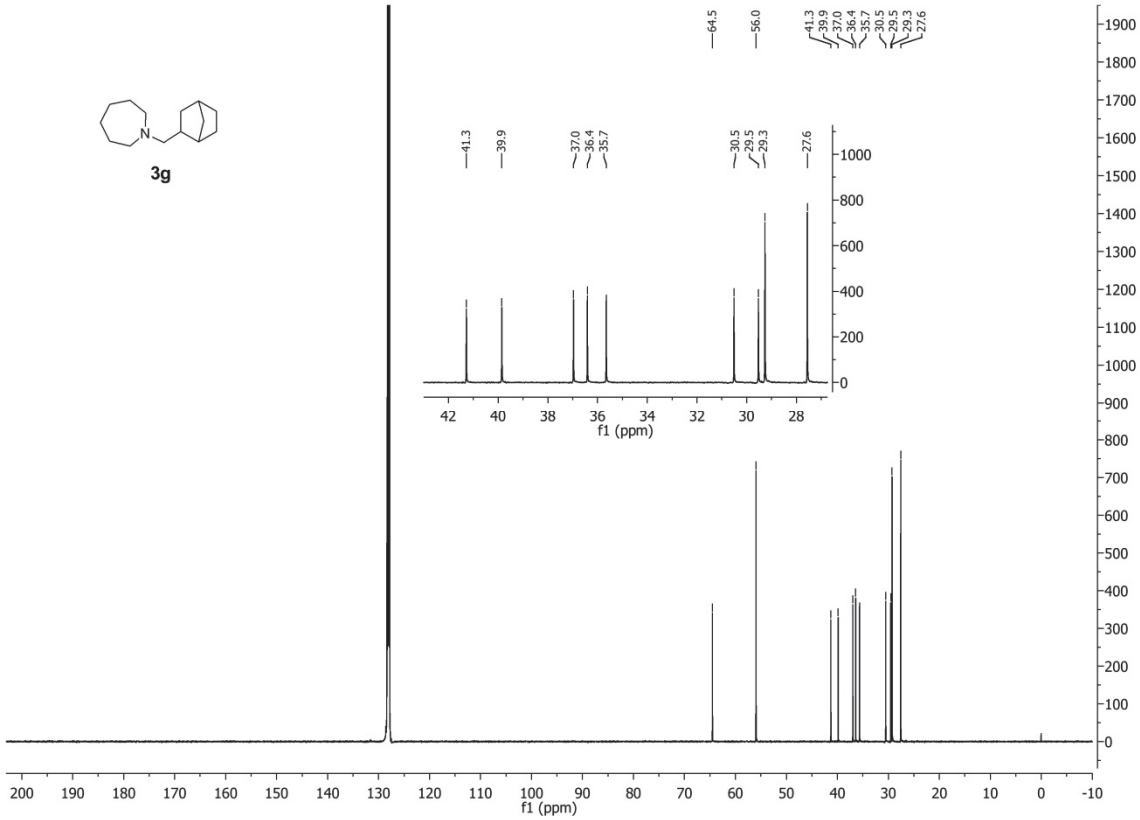
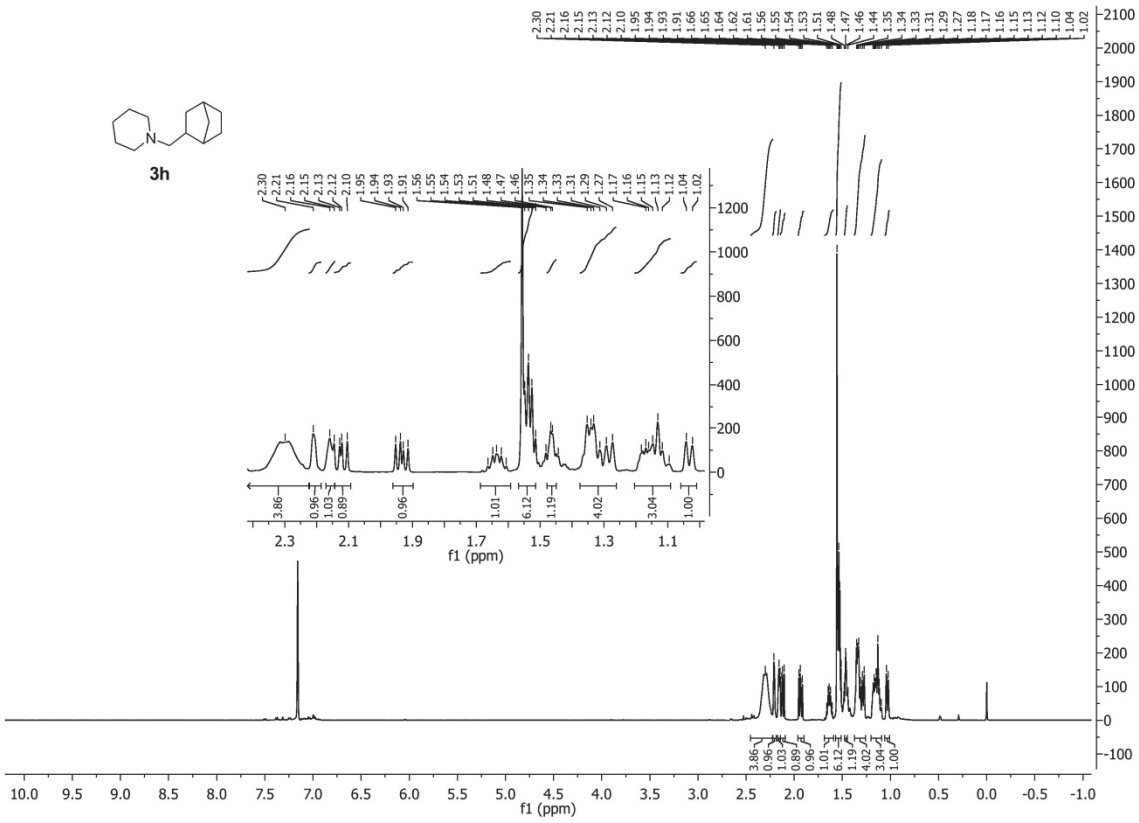
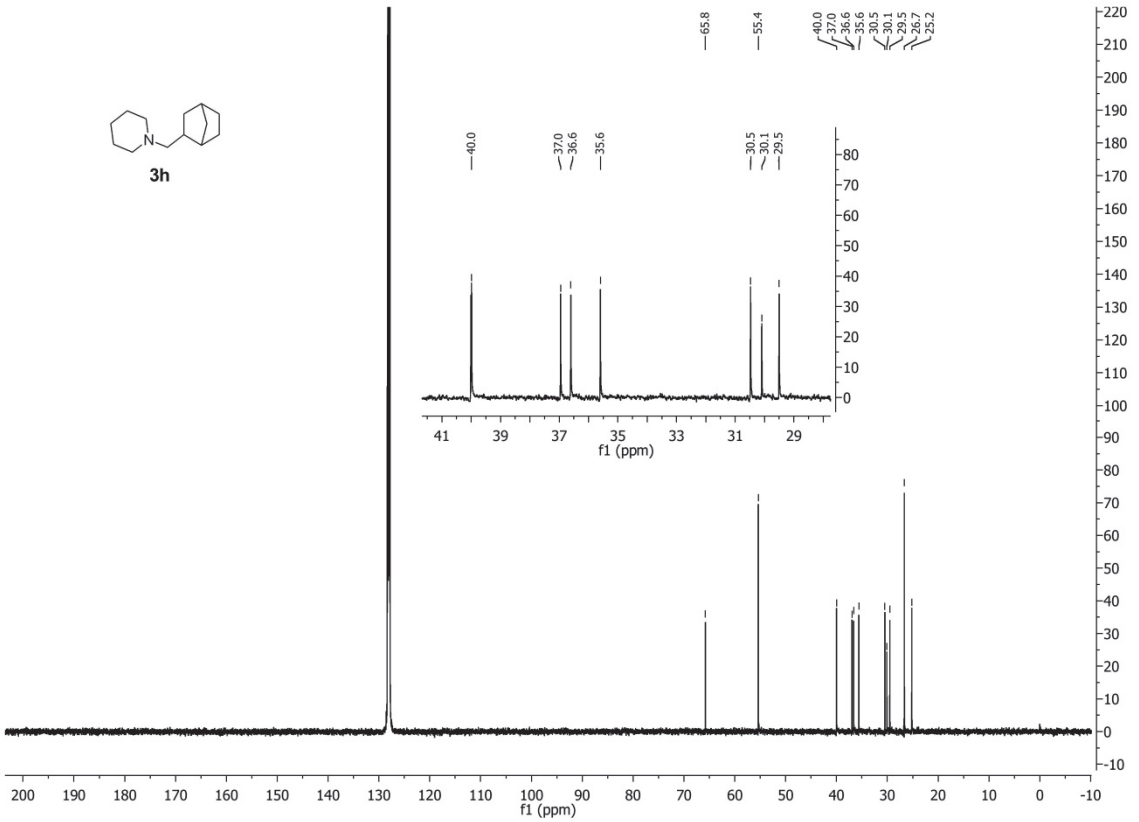
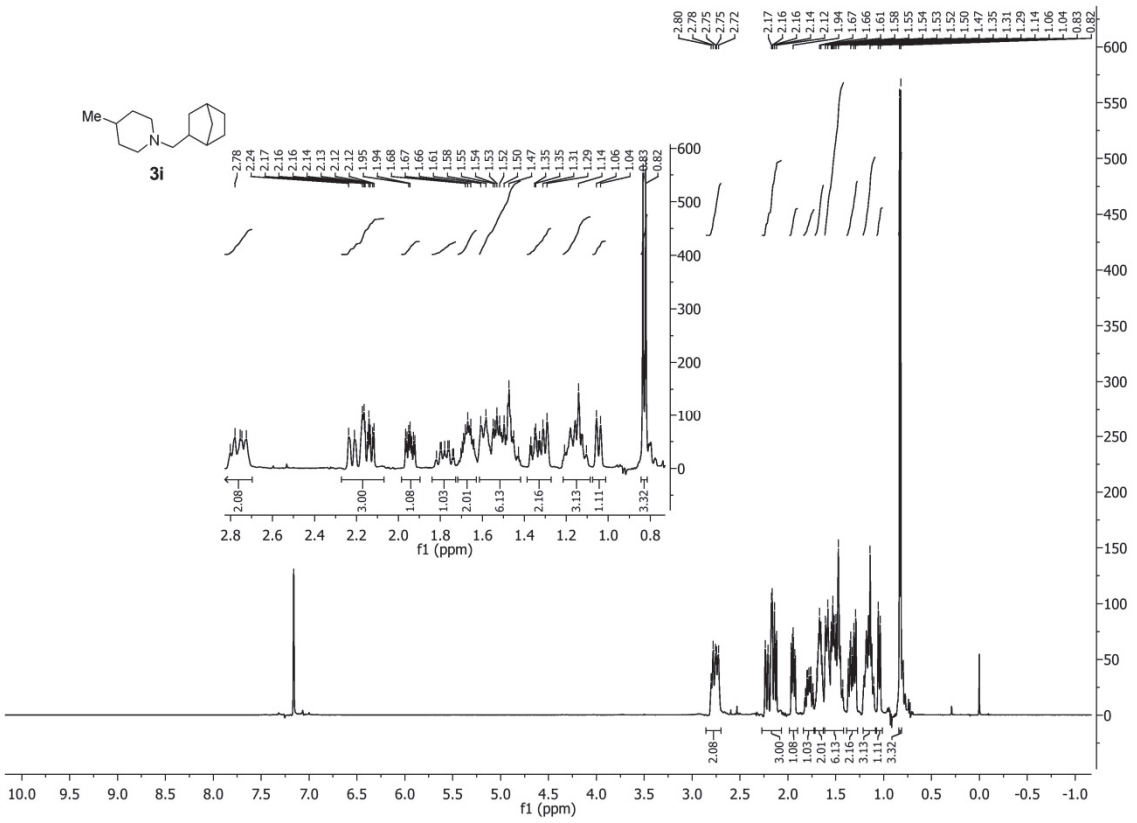
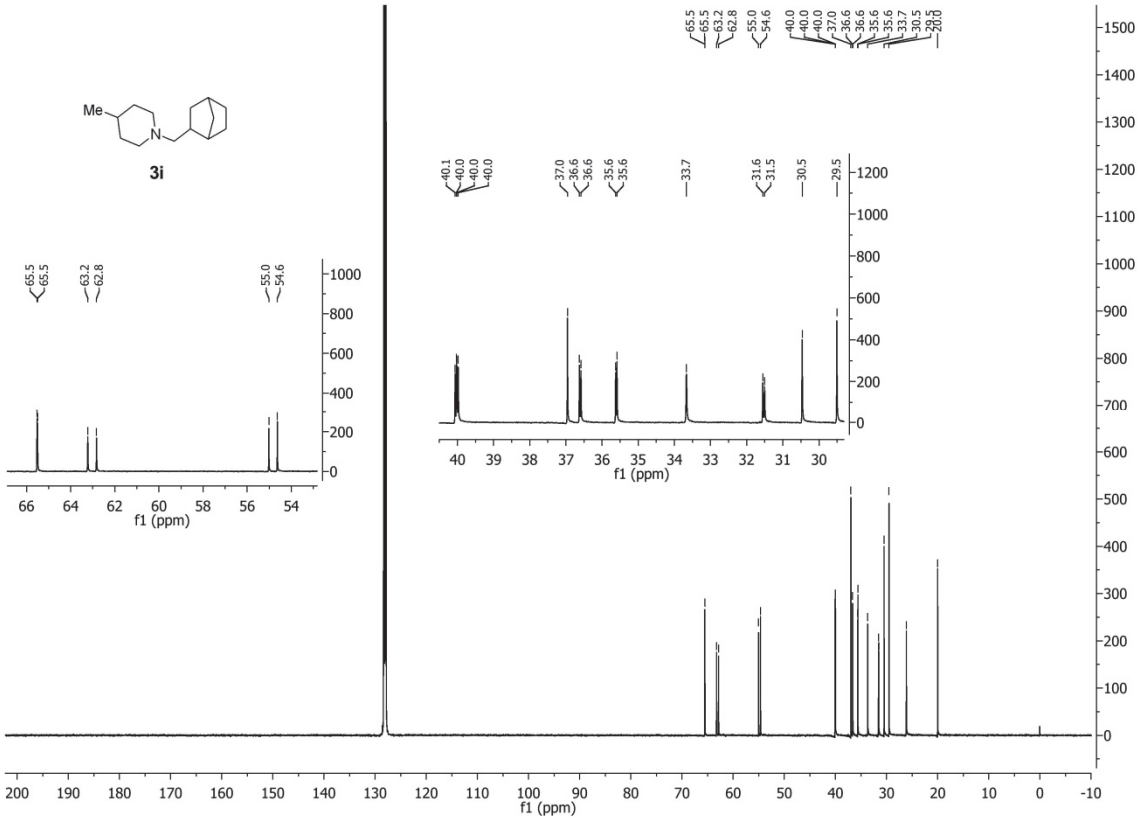
f1 (ppm)

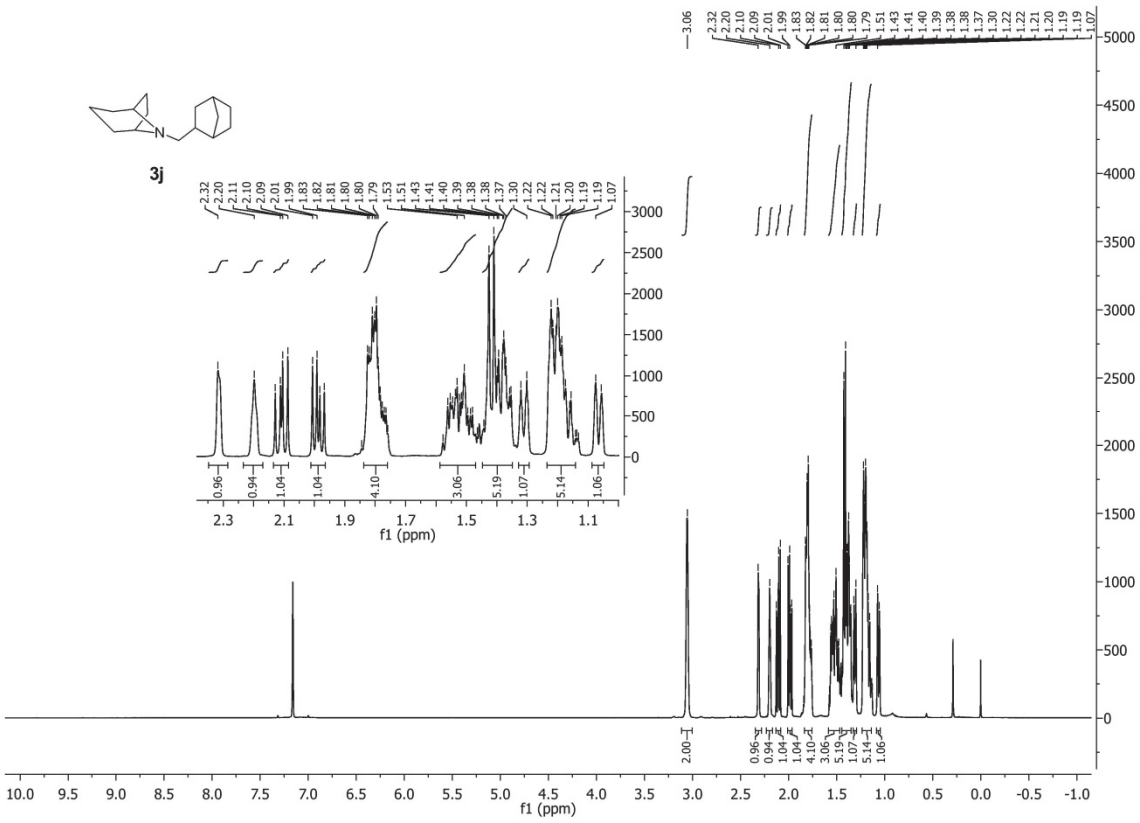

3g
f1 (ppm)


3h
f1 (ppm)


3h
f1 (ppm)


Me
N
3i
f1 (ppm)


Me
N
3i
f1 (ppm)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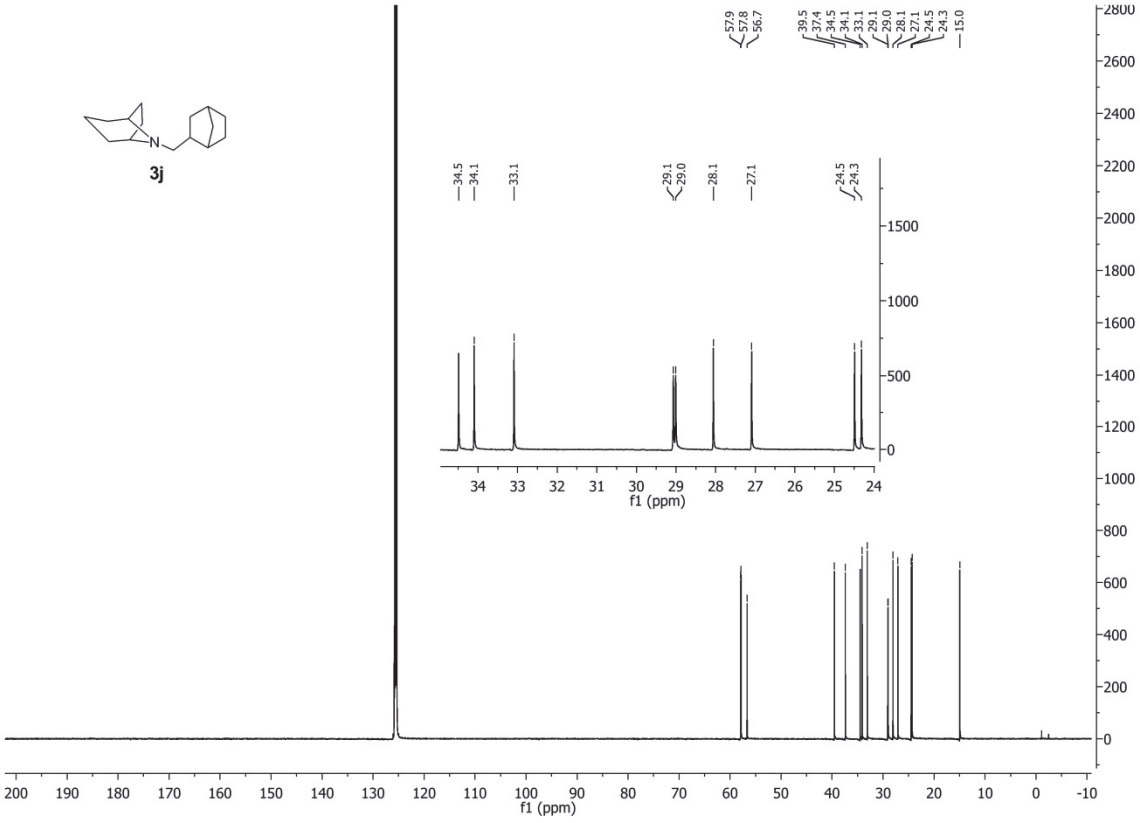
f1 (ppm)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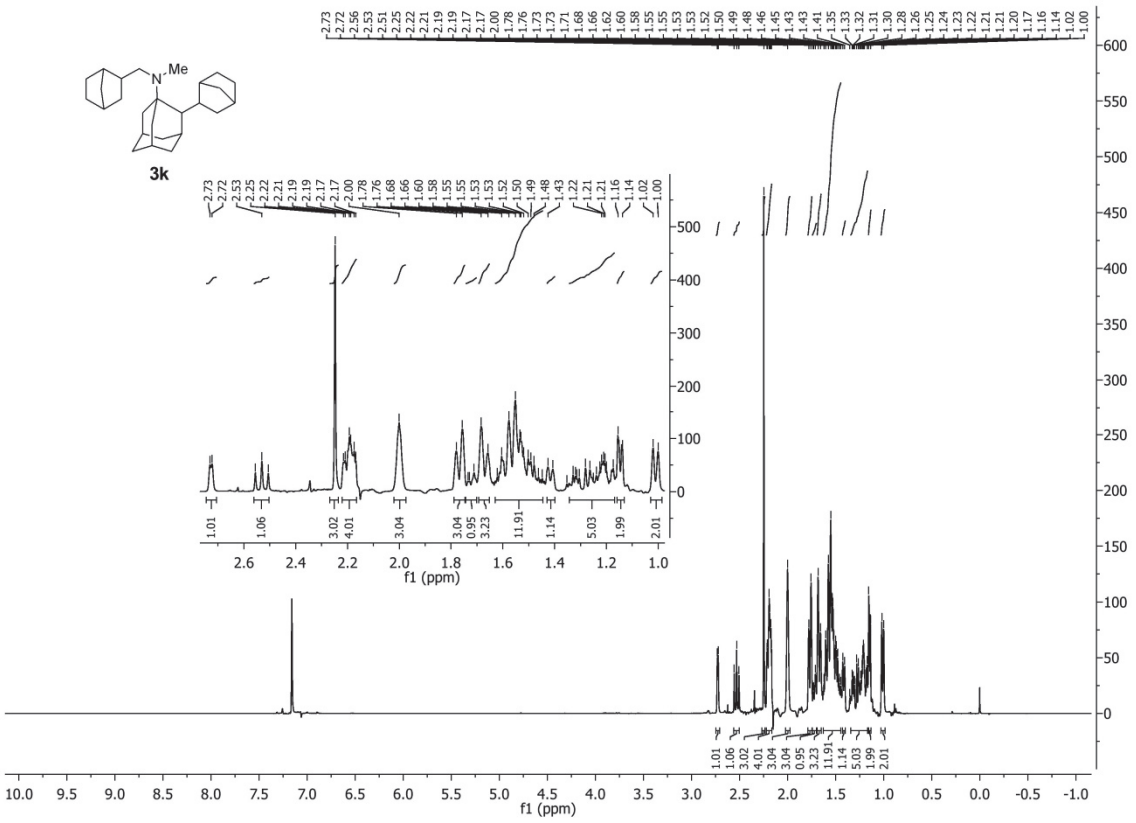
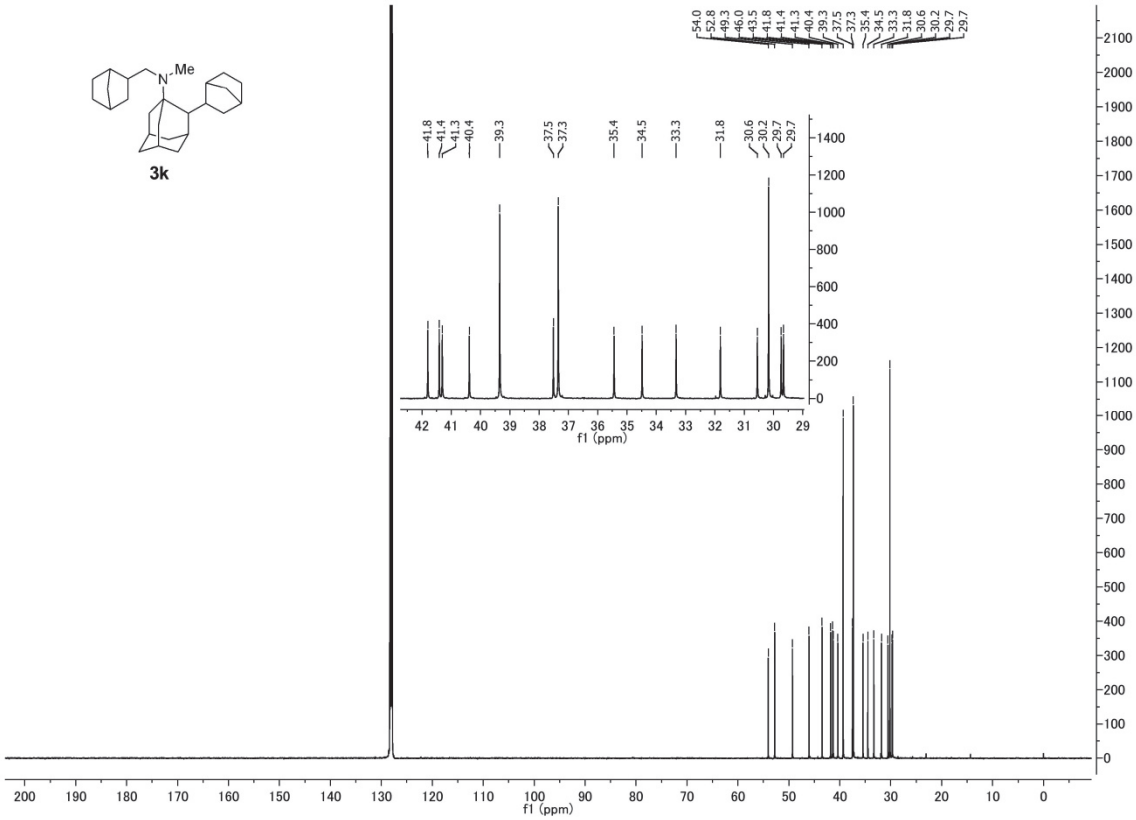
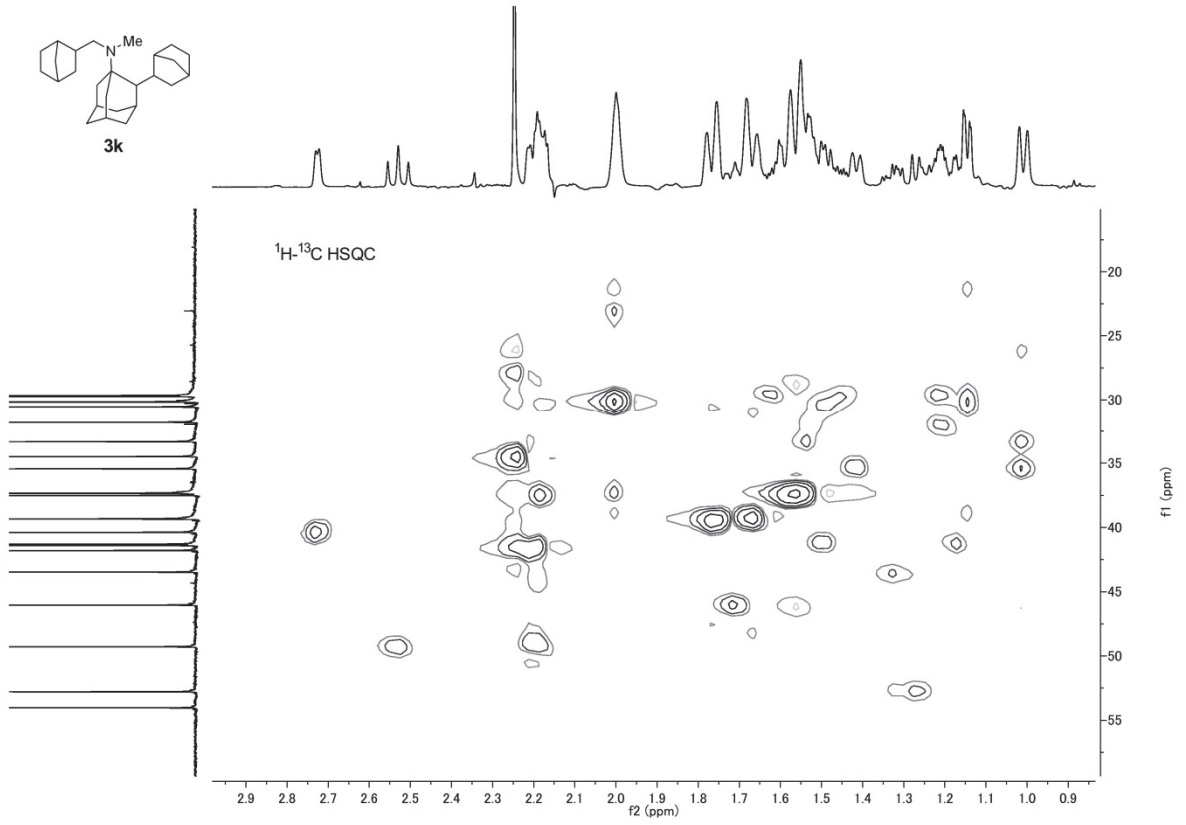
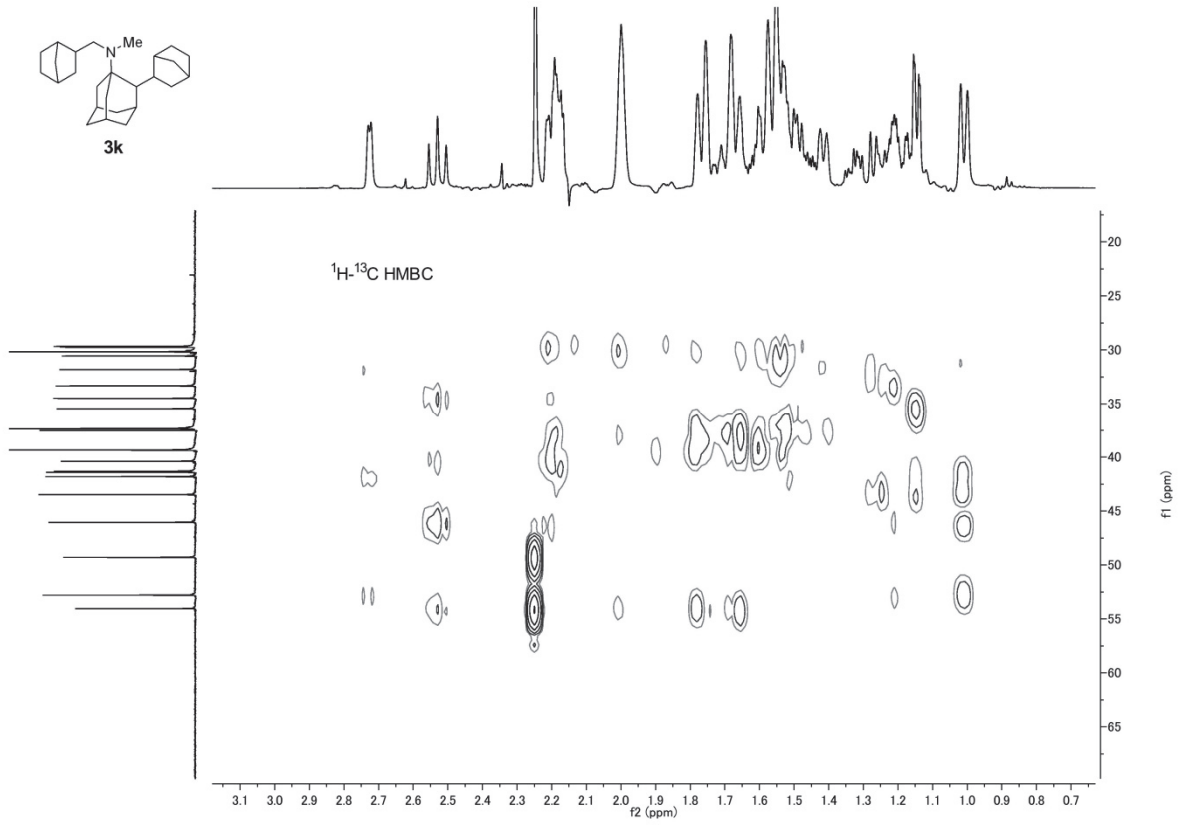
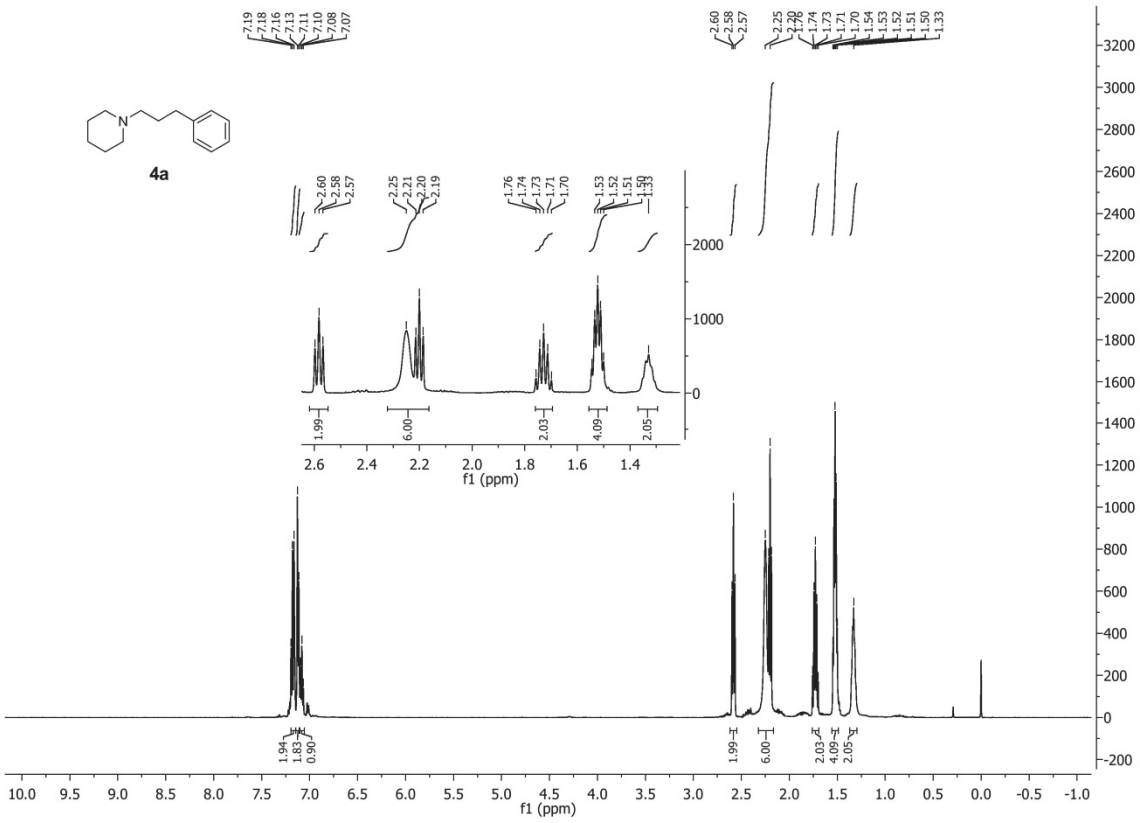
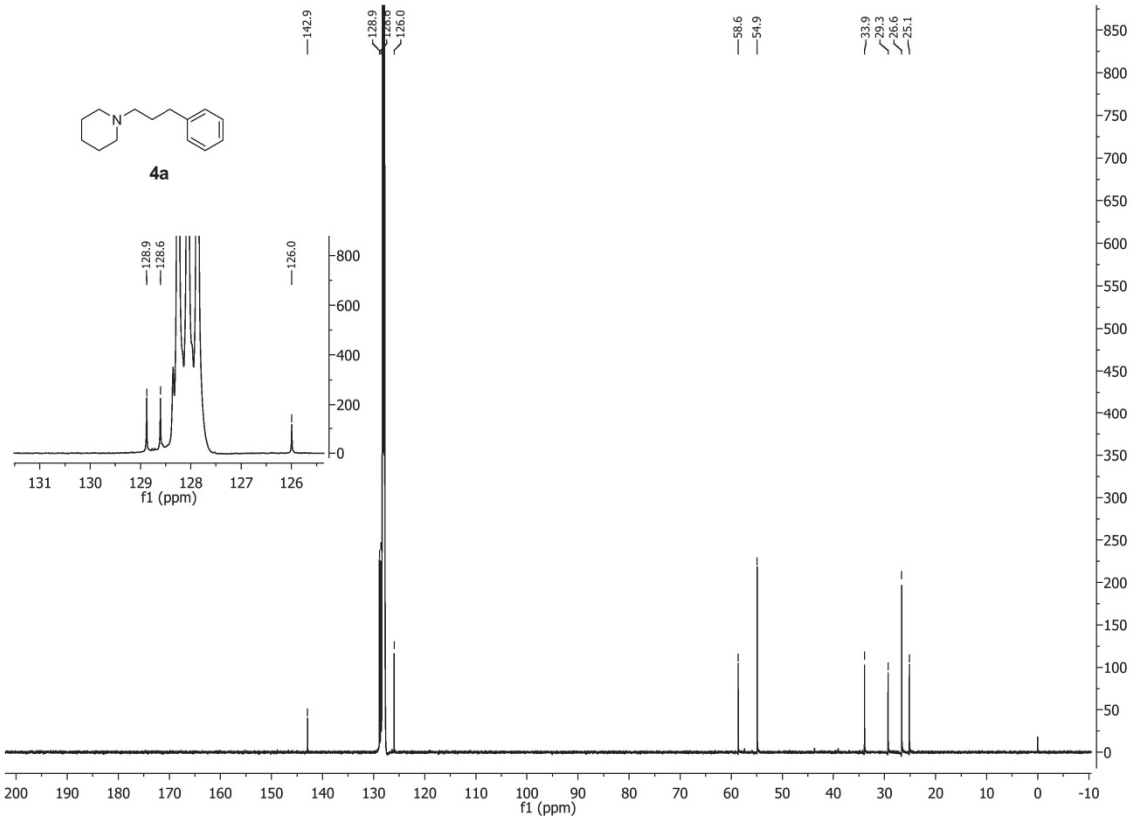

Me
N
3k
f1 (ppm)


Me
N
3k
f1 (ppm)


N
Me
3k
^{1}H-^{13}C HSQC
f2 (ppm)
f1 (ppm)


N
Me
3k
^{1}H-^{13}C HMBC
f2 (ppm)
f1 (ppm)


4a
f1 (ppm)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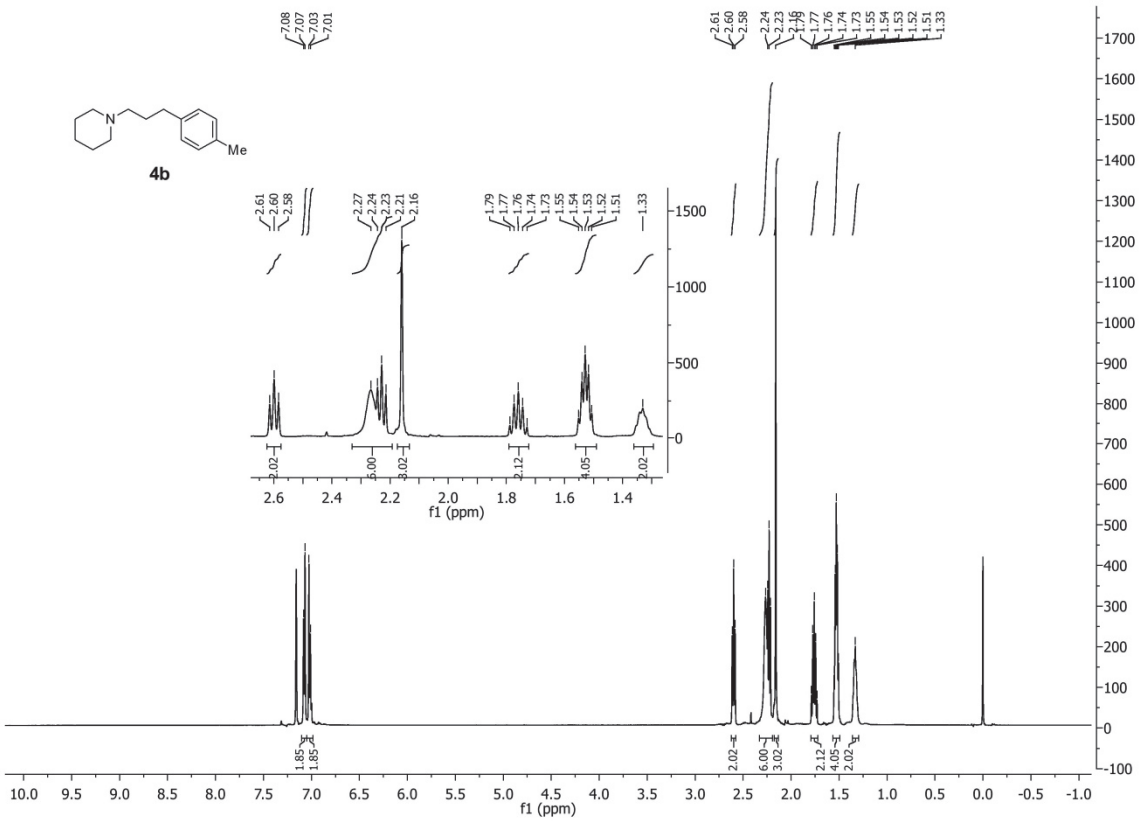
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Me
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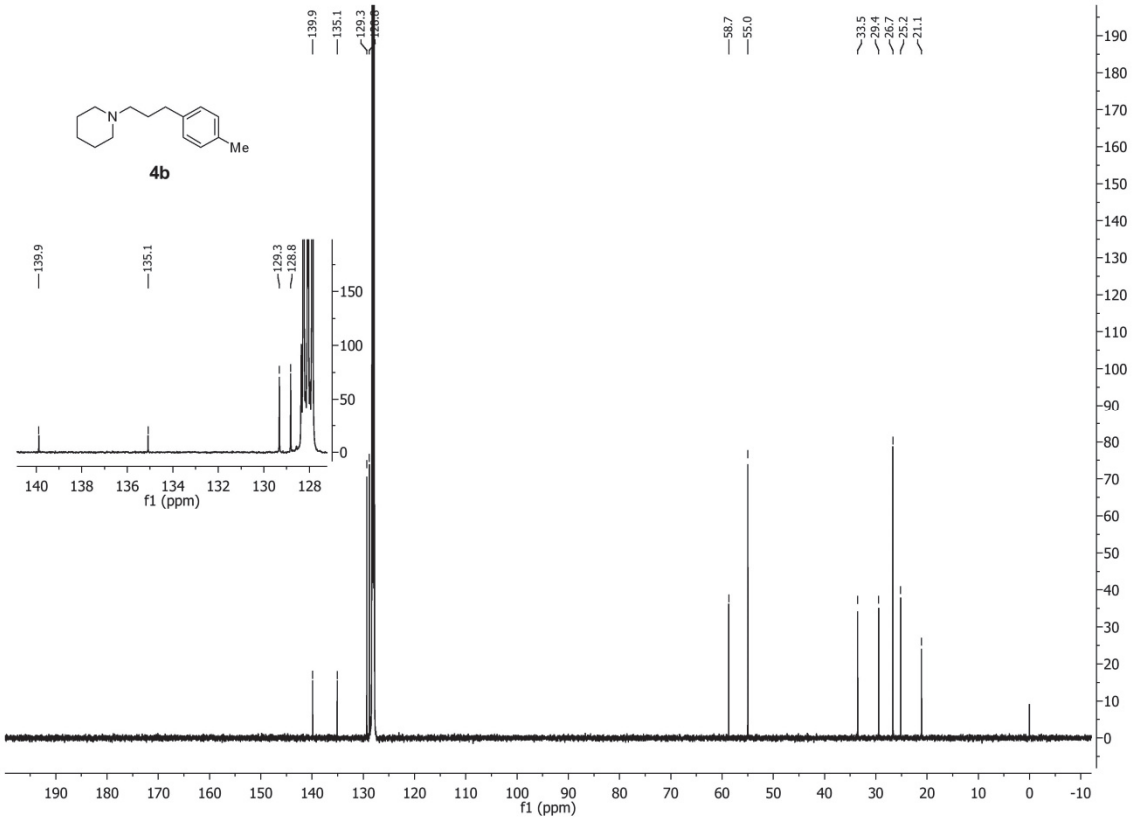
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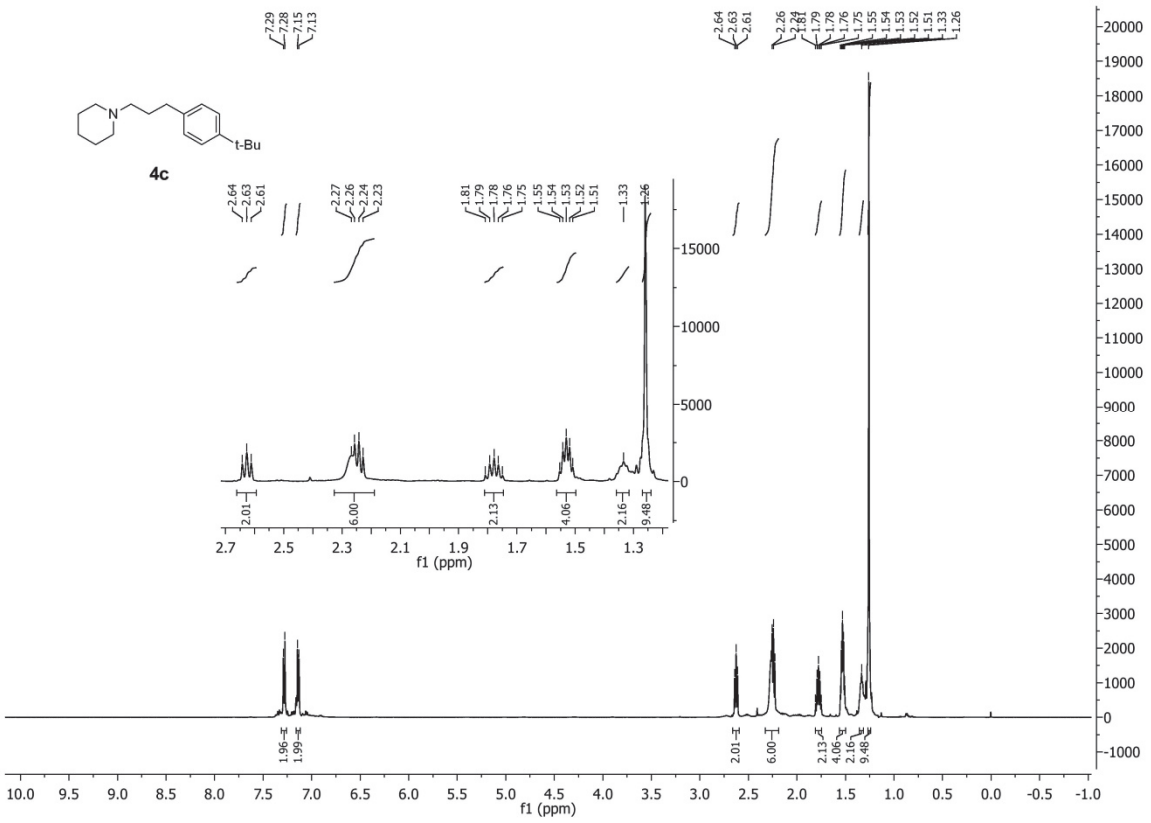
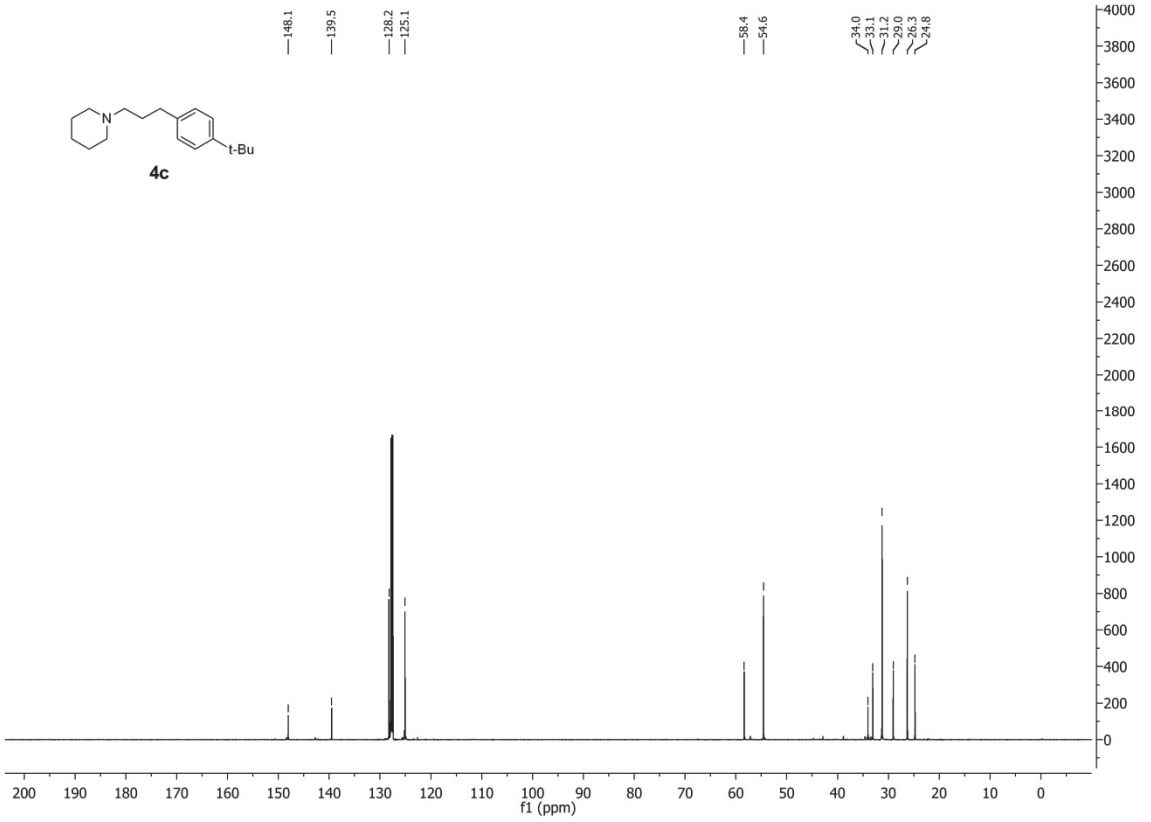
Me
f1 (ppm)


4c
t-Bu
f1 (ppm)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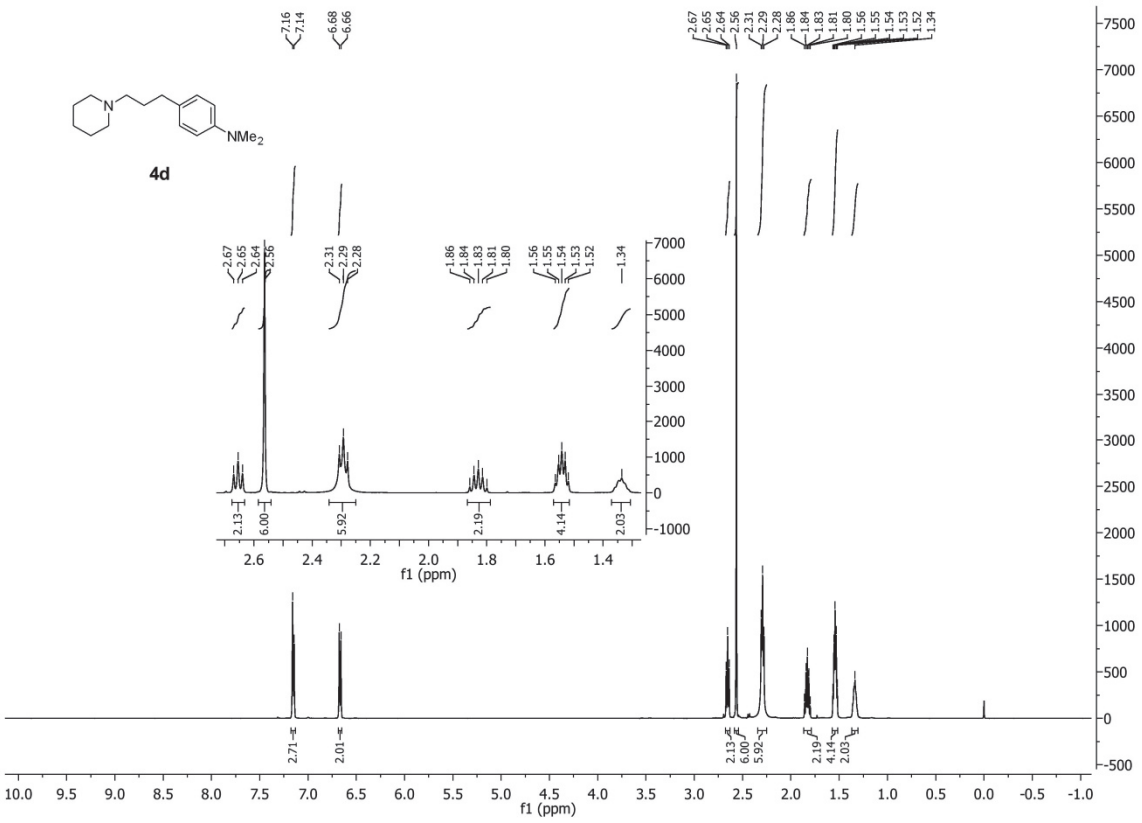
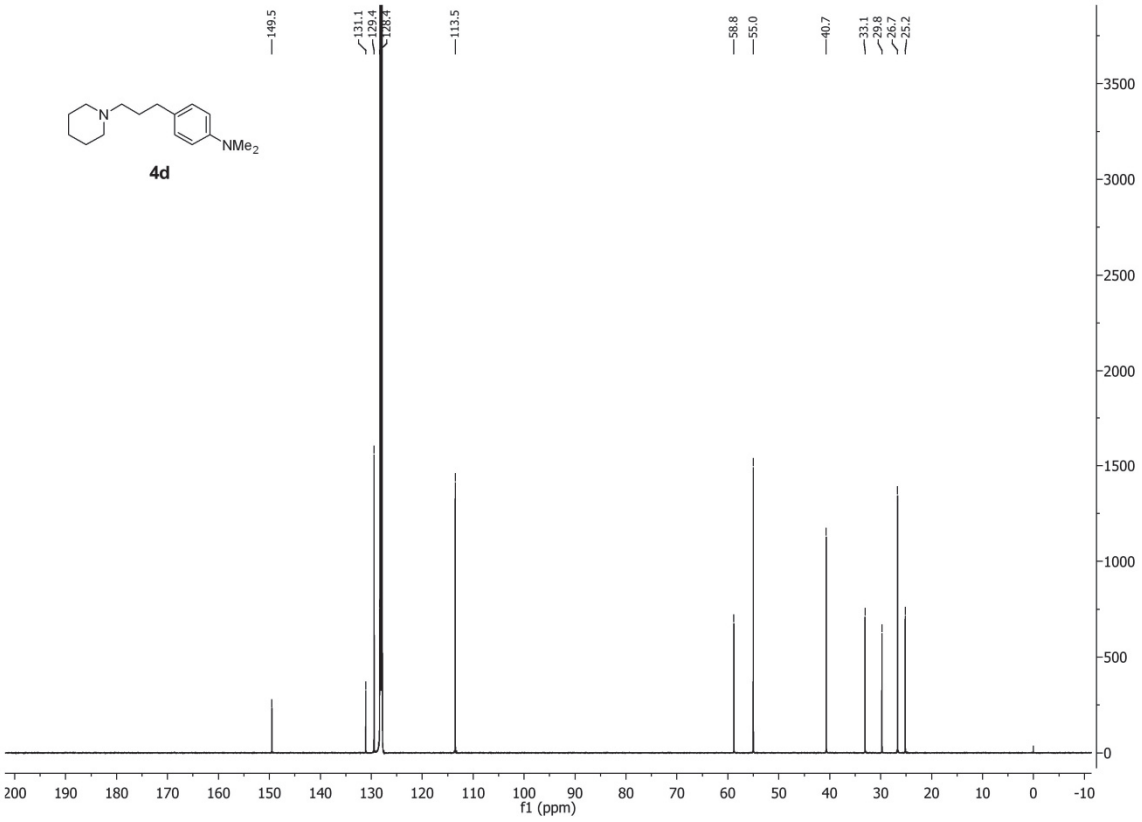
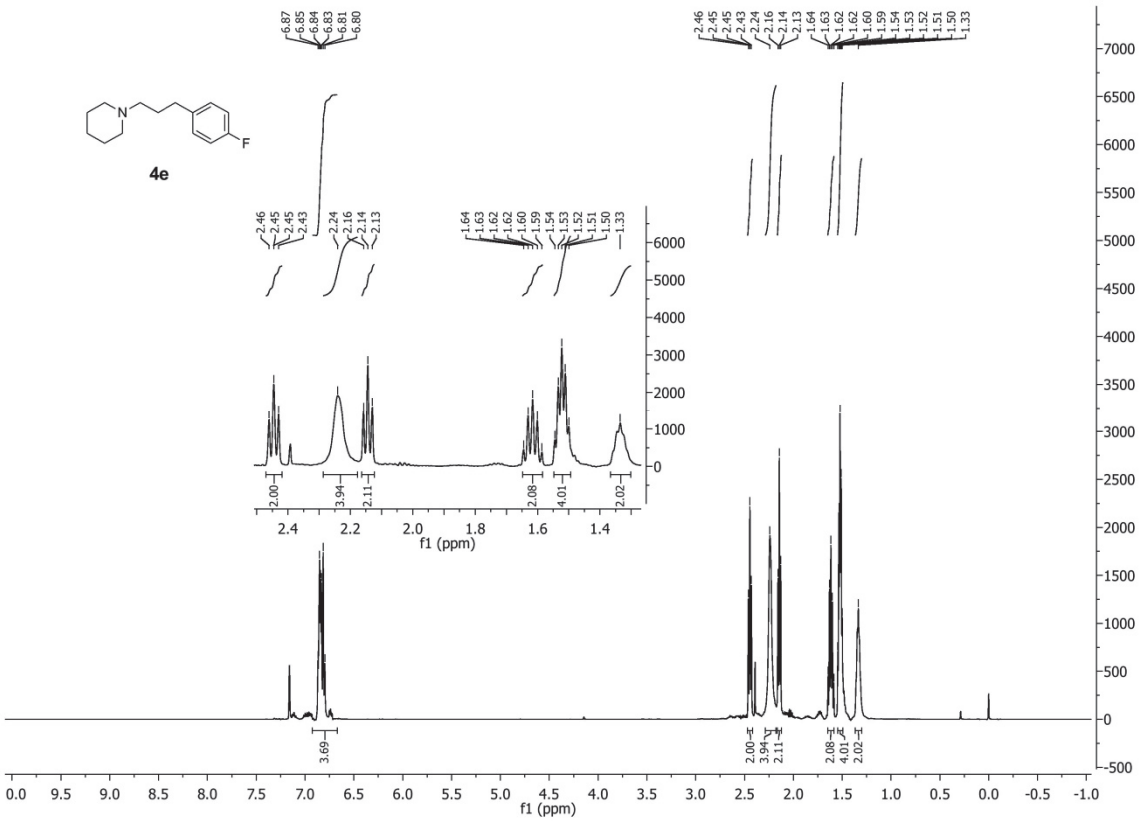
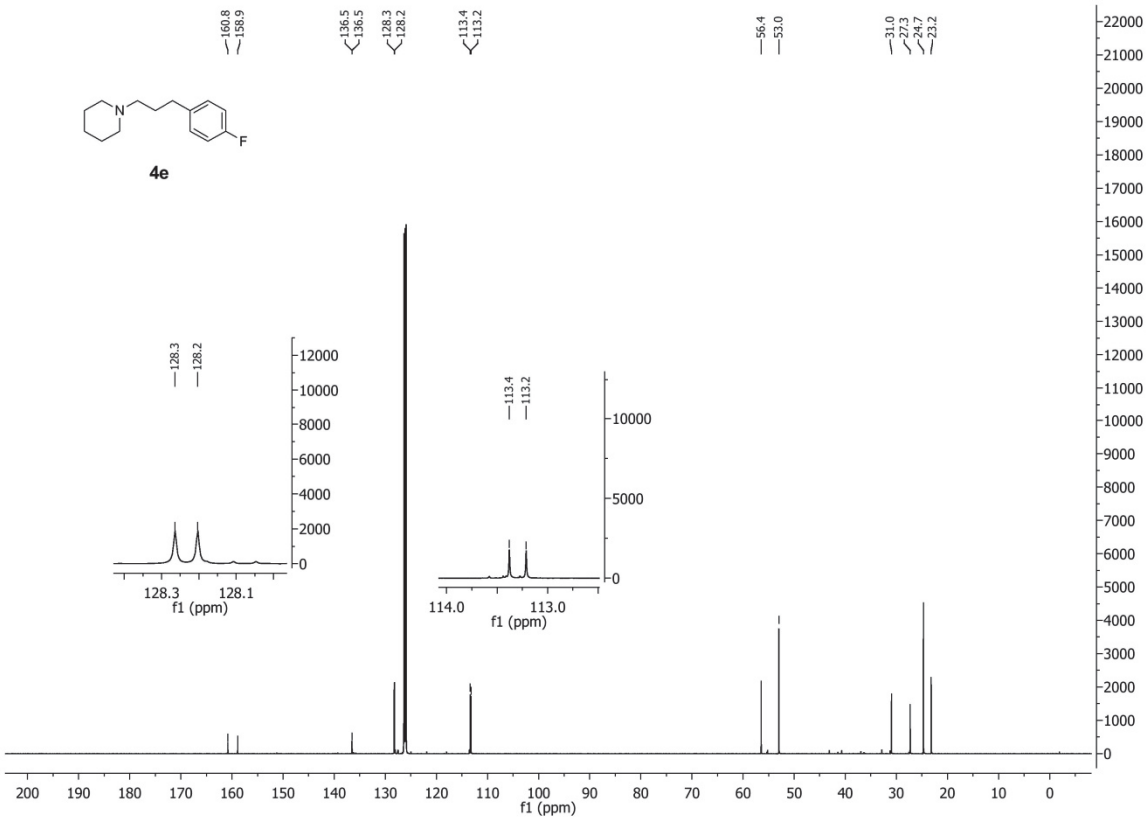
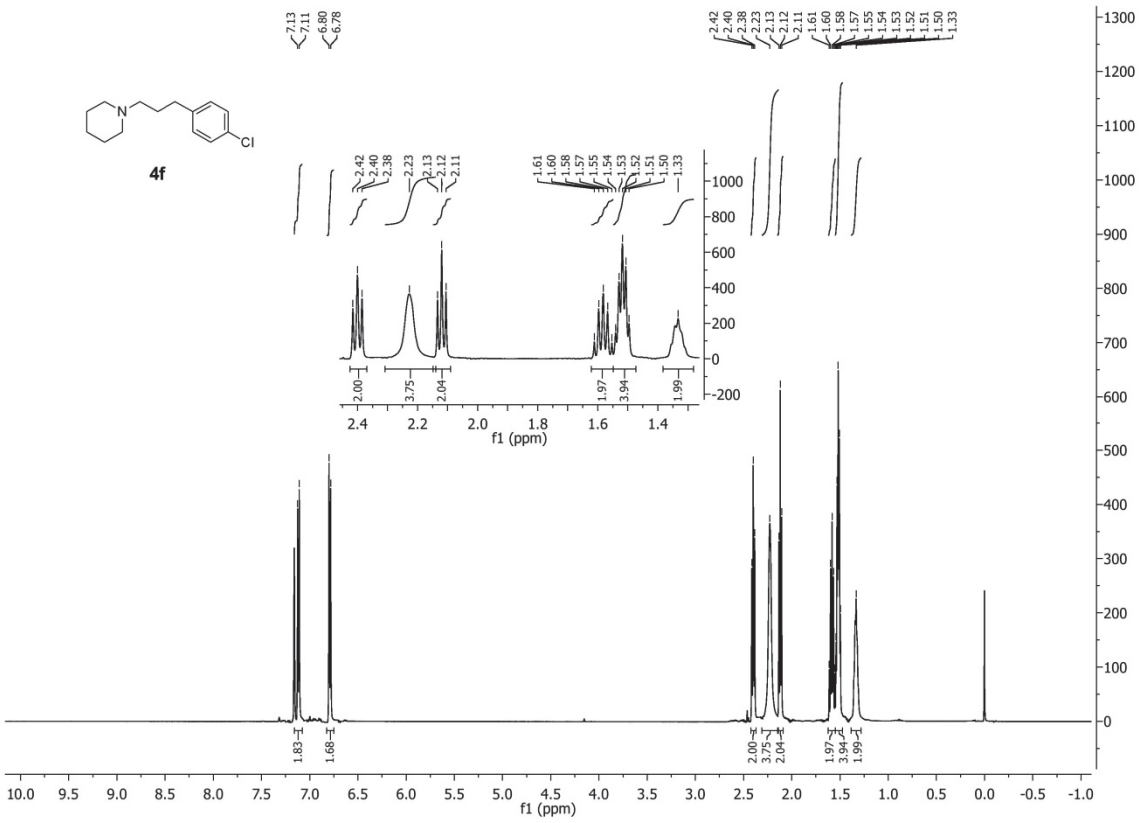

4d
NMe2
f1 (ppm)


4d
NMe2
f1 (ppm)


4e
f1 (ppm)


4e
f1 (ppm)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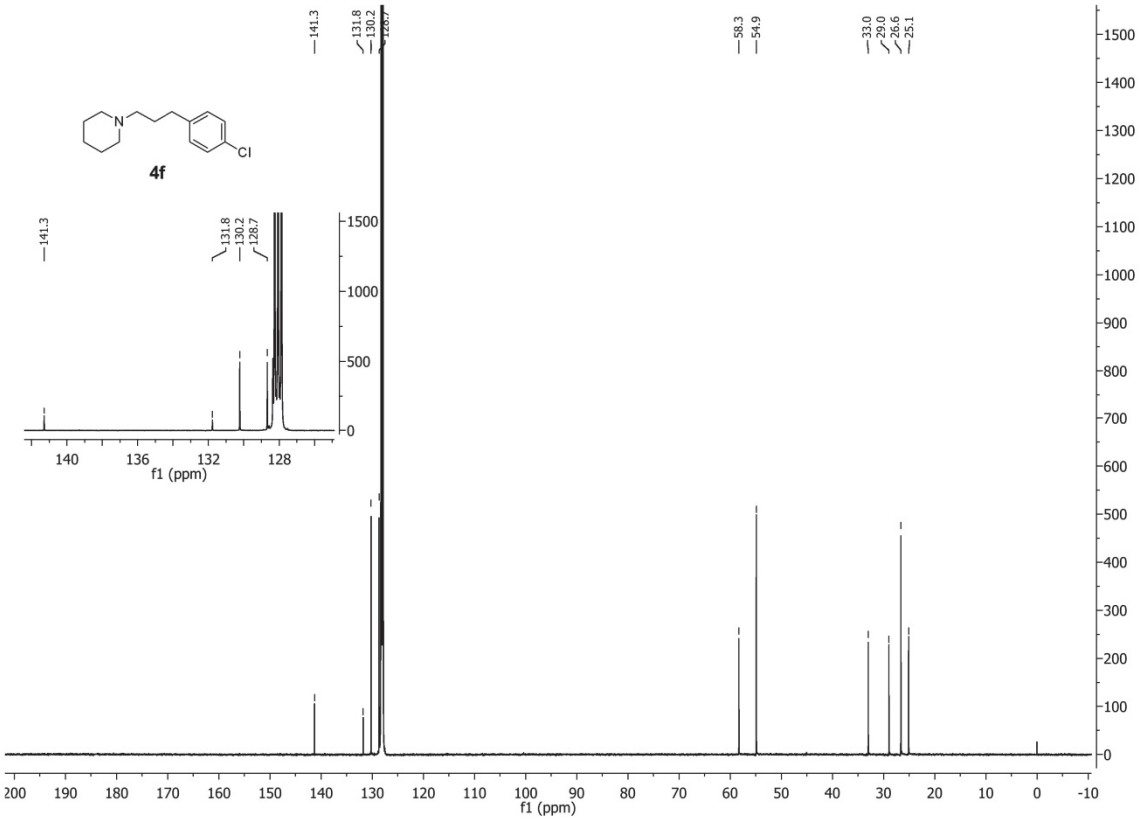
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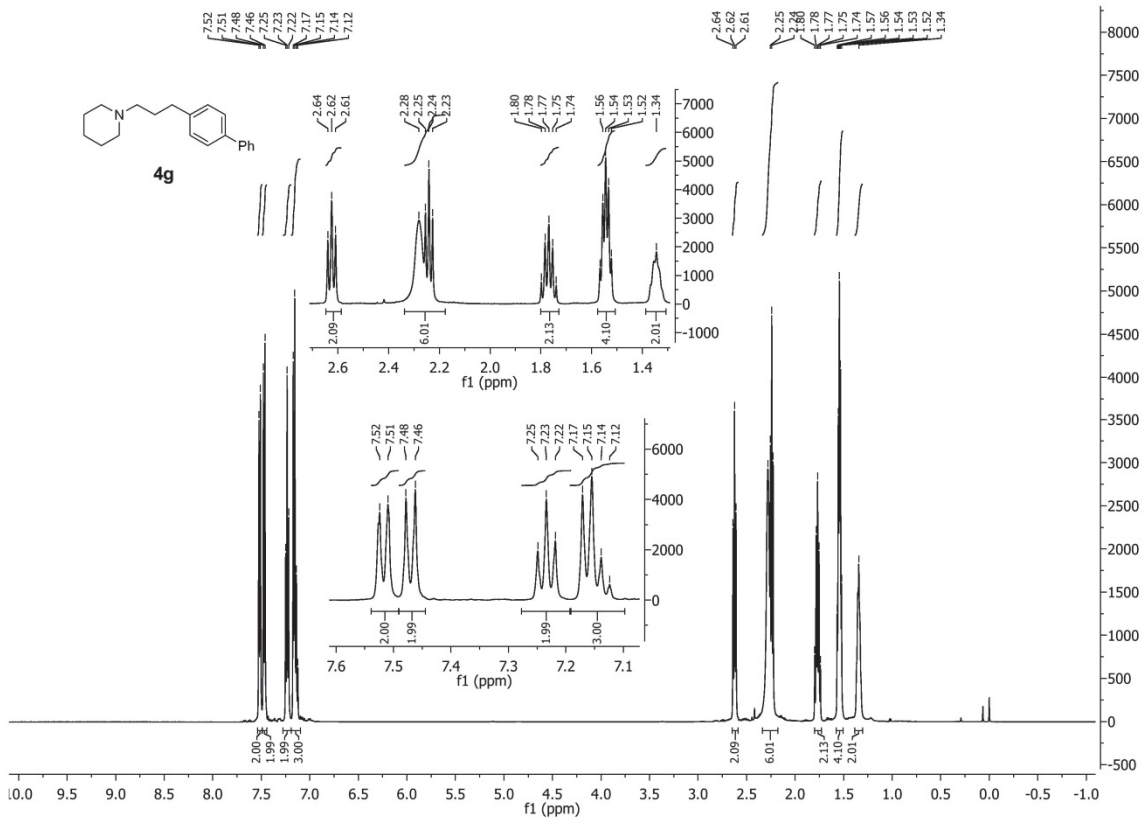
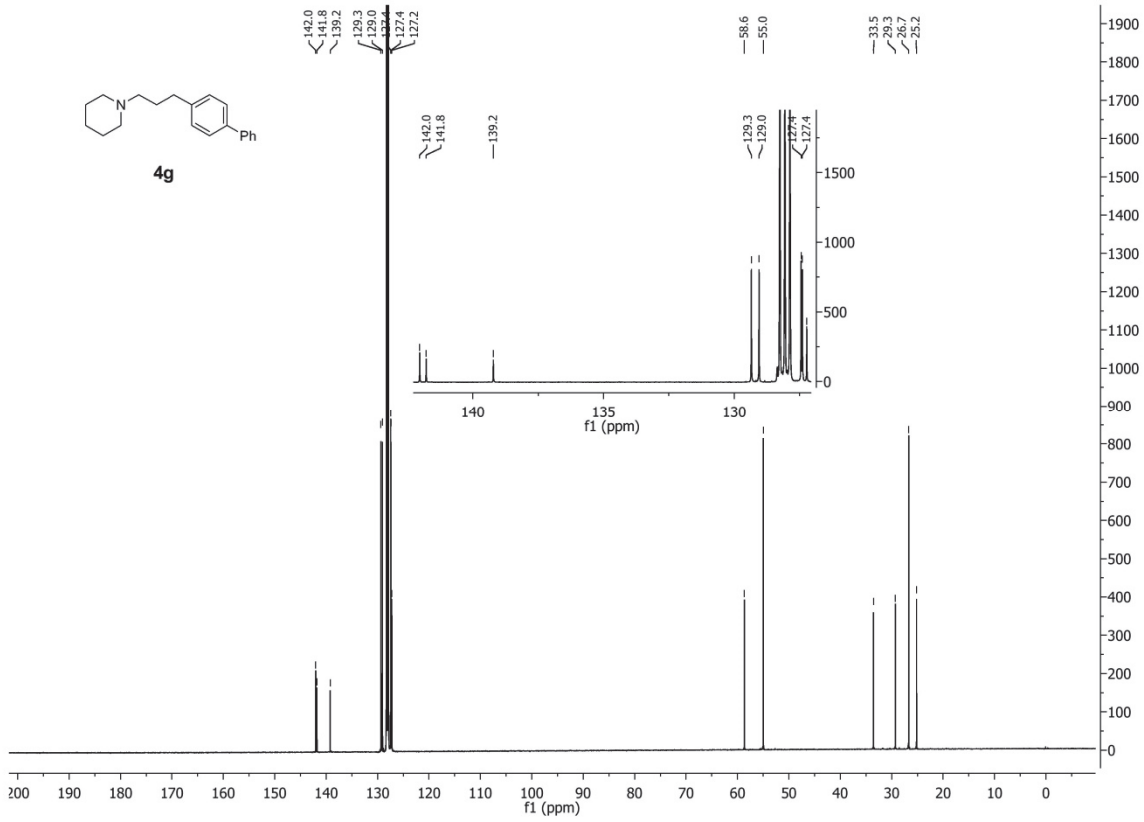
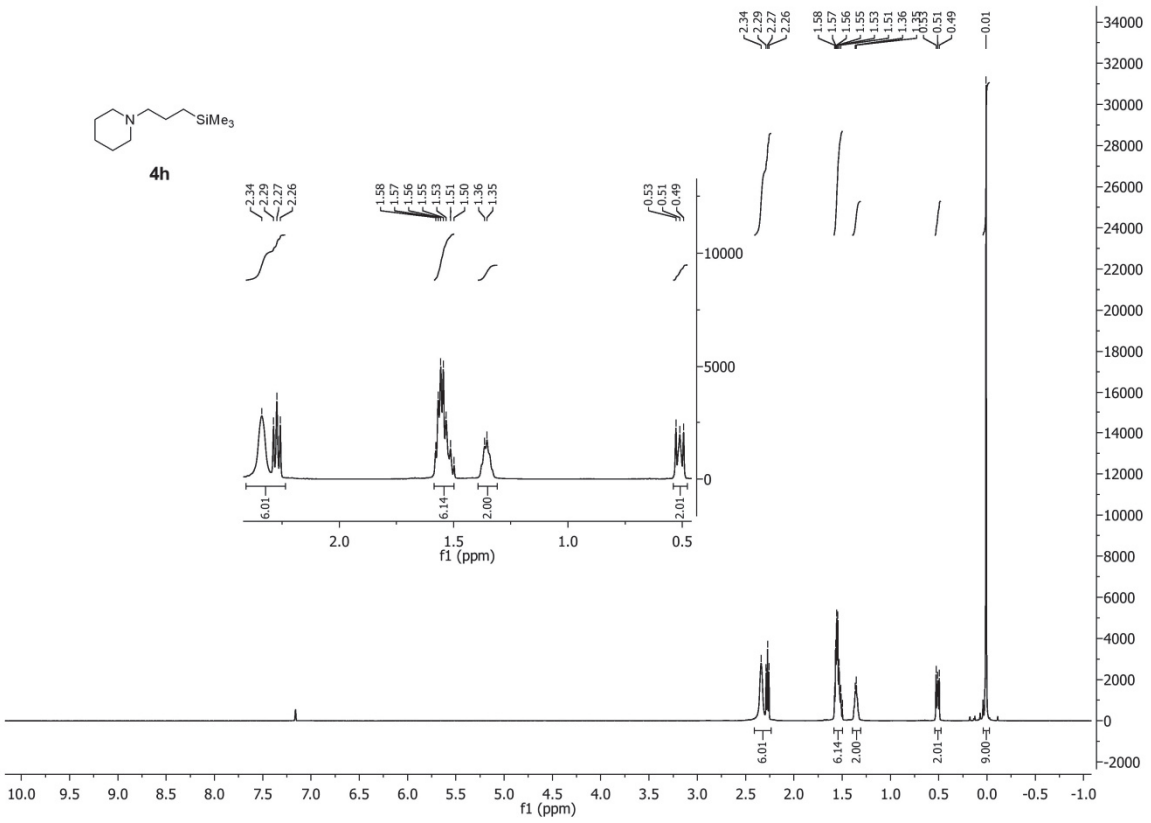
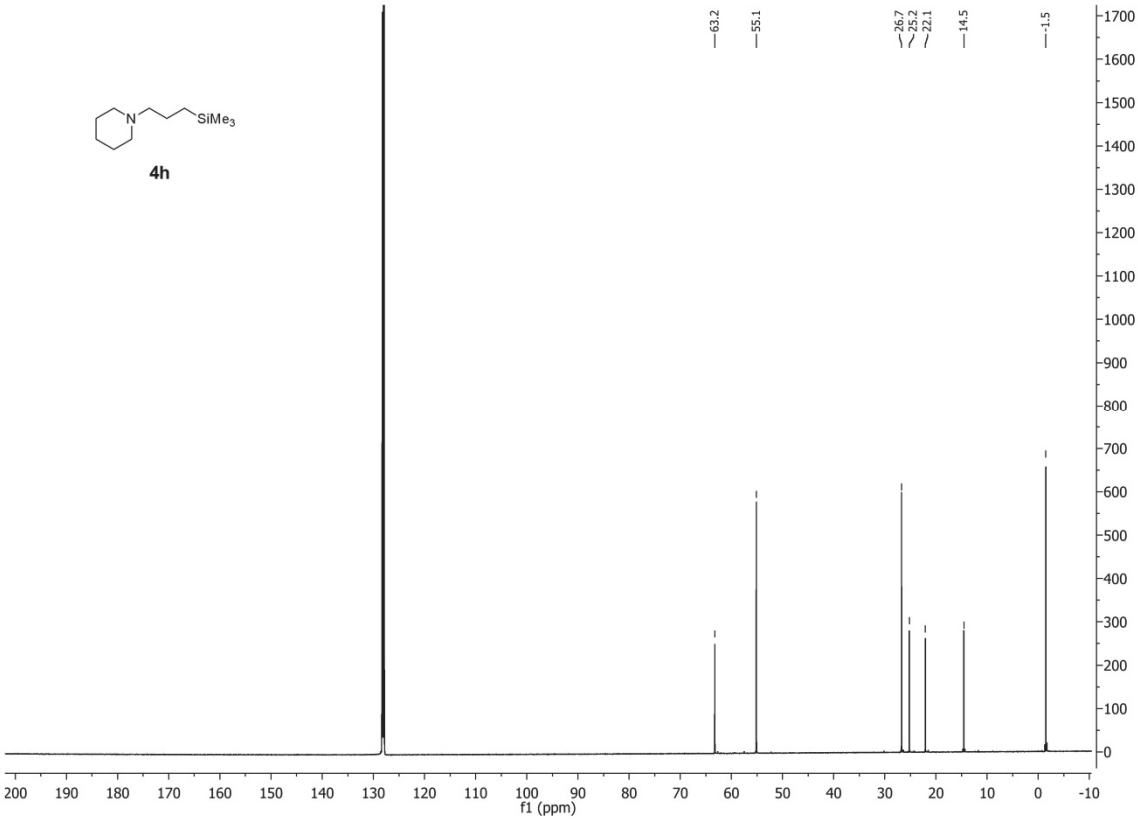
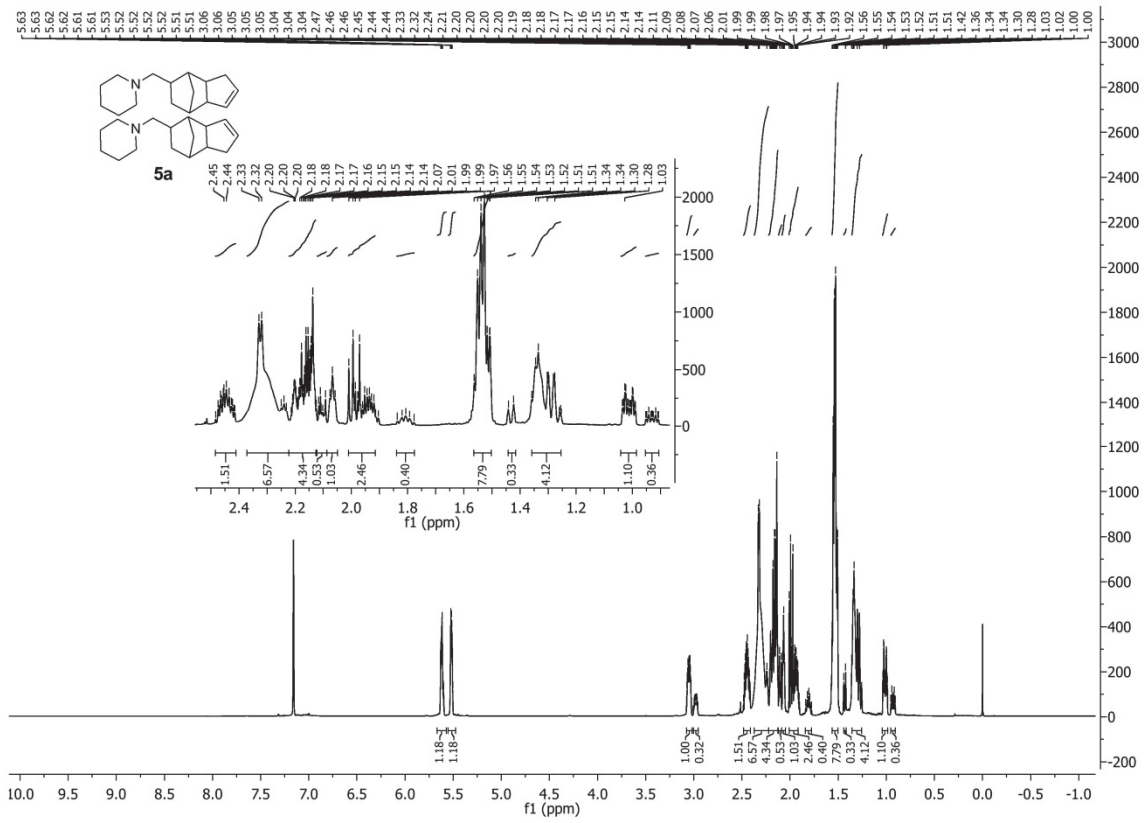
f1 (ppm)

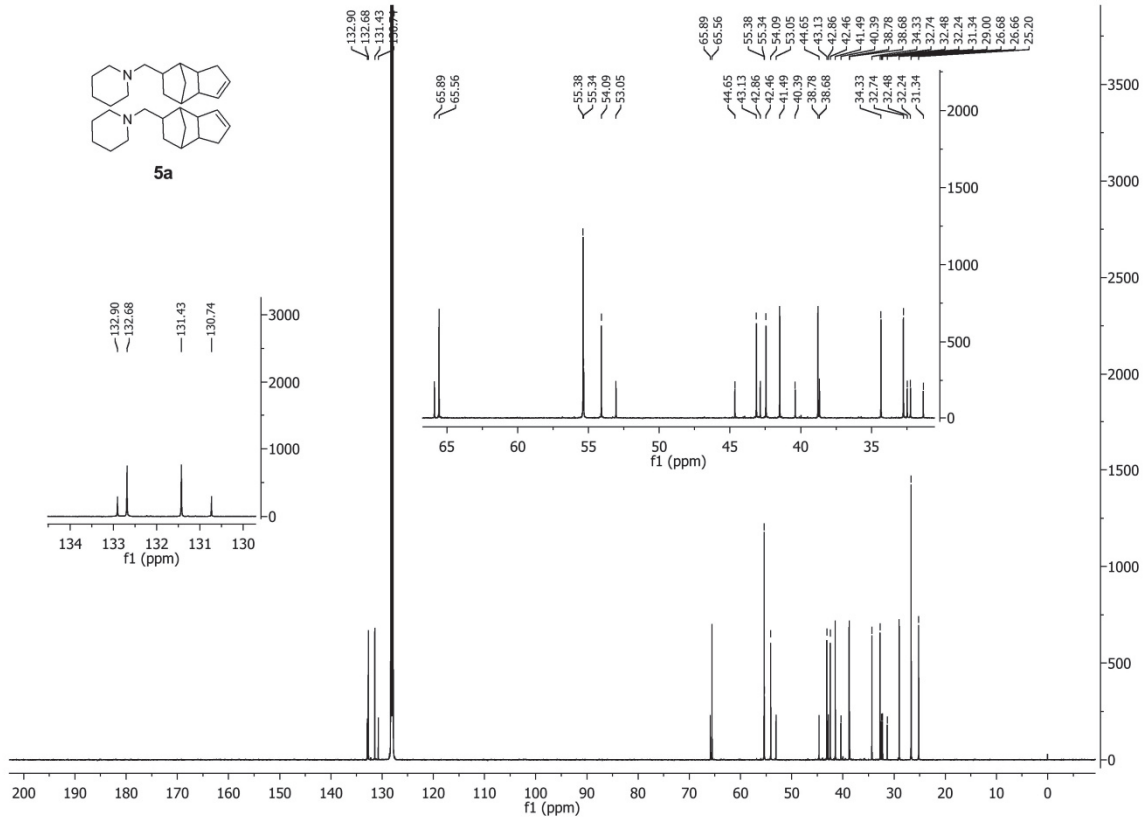

4g
f1 (ppm)


4g
f1 (ppm)


SiMe3
4h
f1 (ppm)


SiMe3
4h
f1 (ppm)


5a
f1 (ppm)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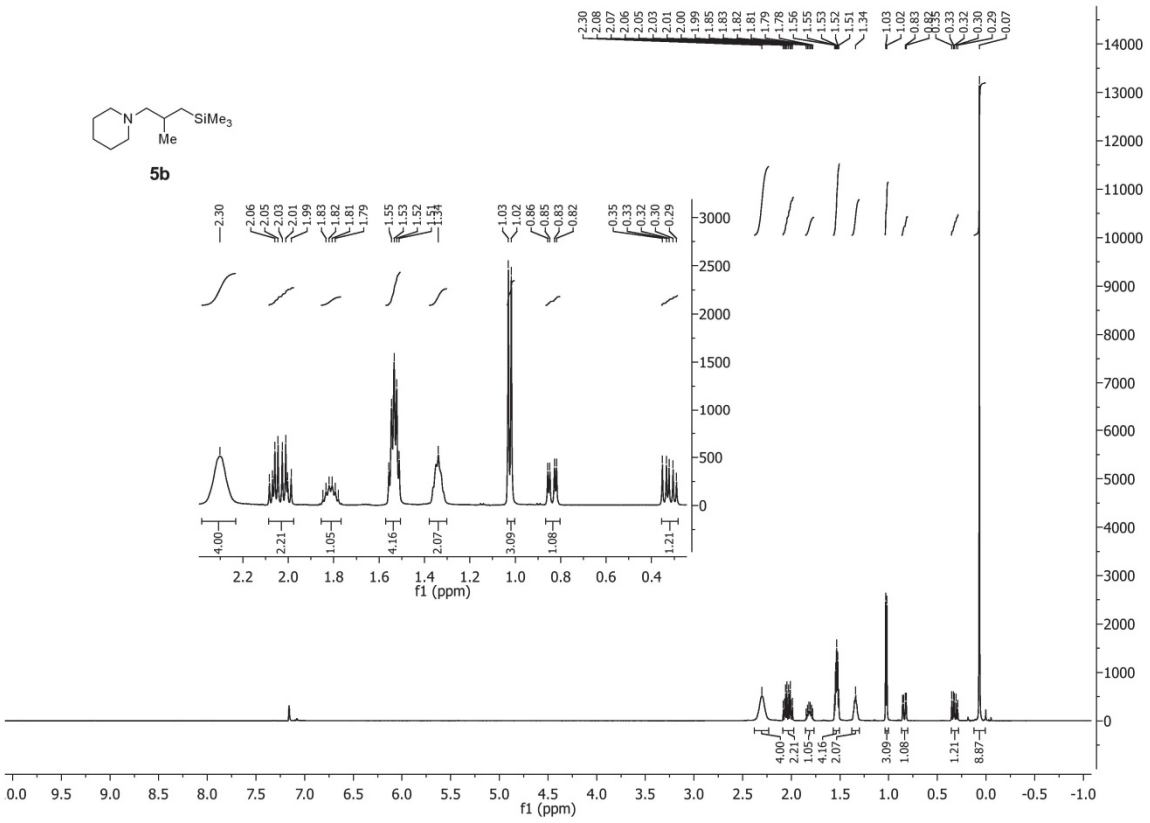
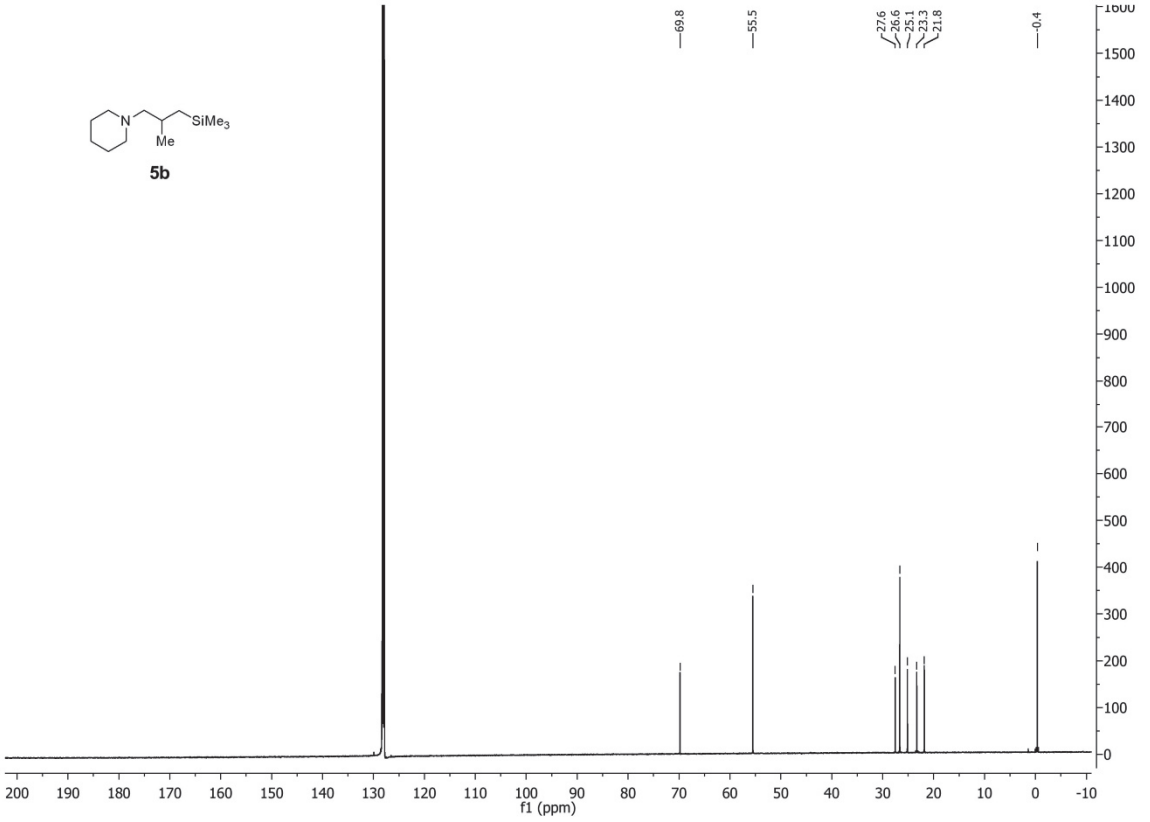
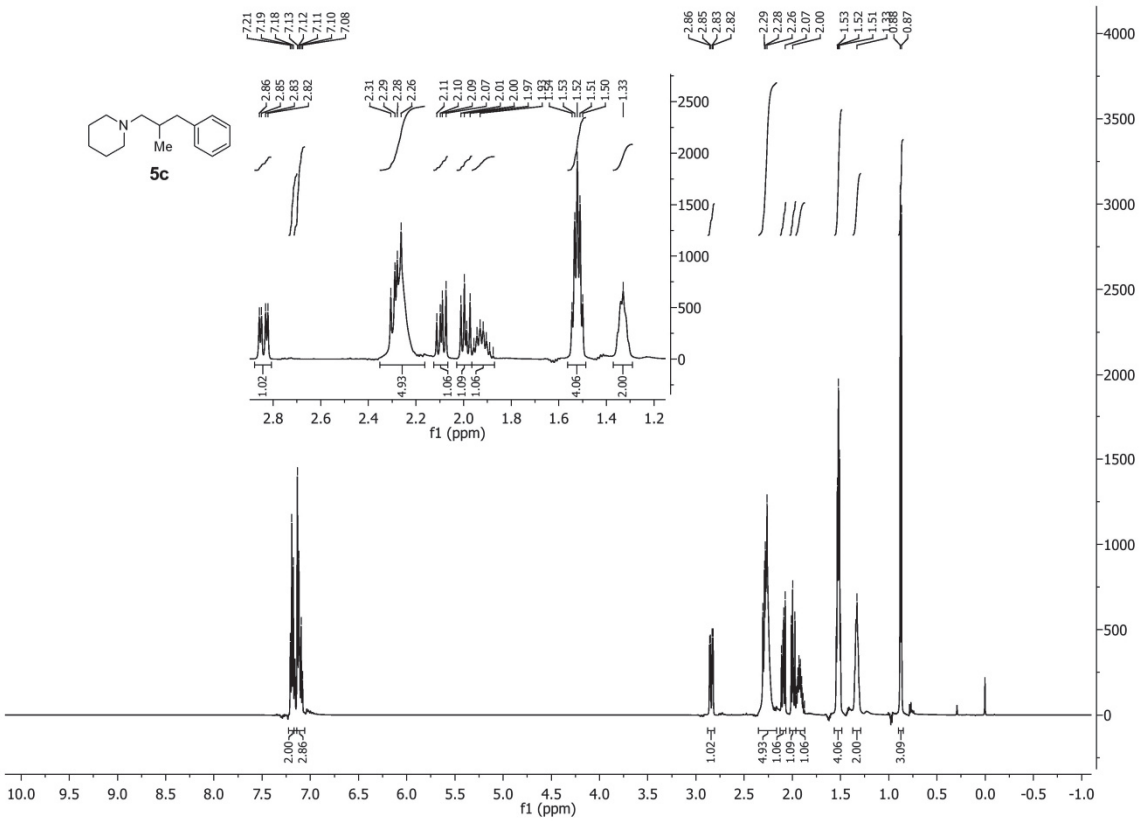
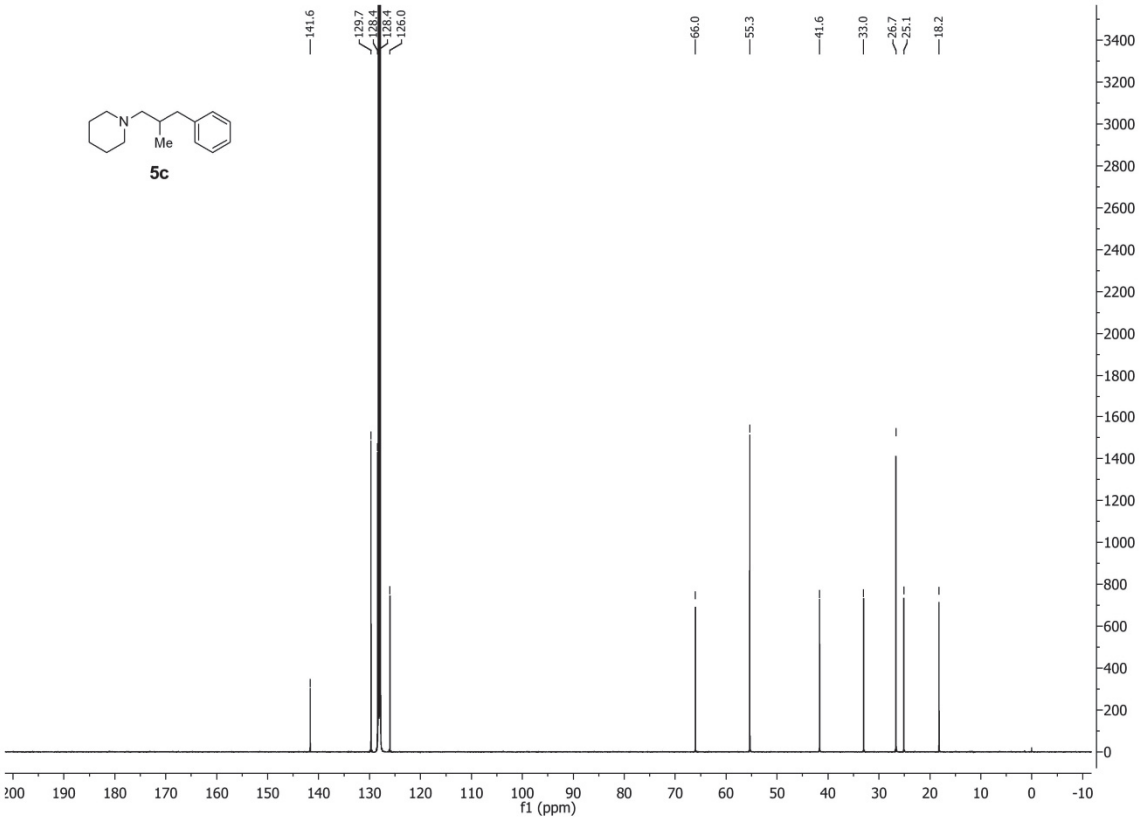

SiMe3
Me
5b
f1 (ppm)


SiMe3
Me
5b
f1 (ppm)


5c
f1 (ppm)


5c
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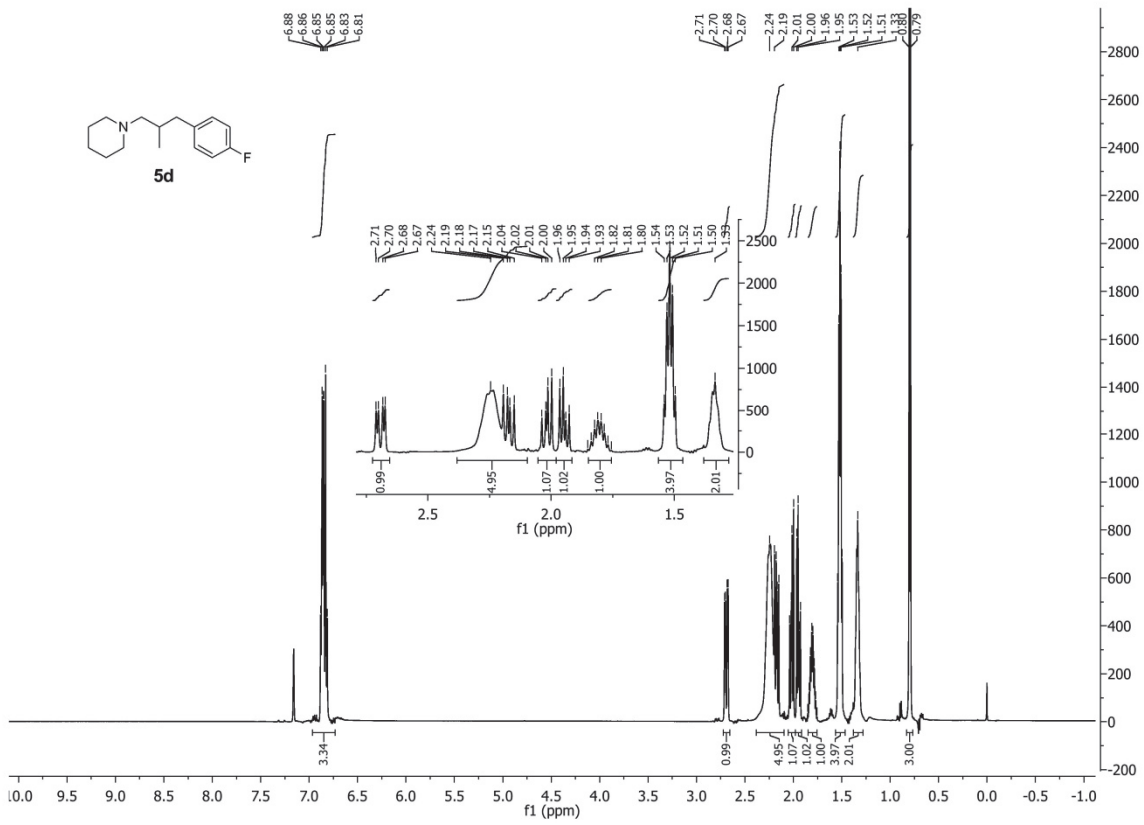
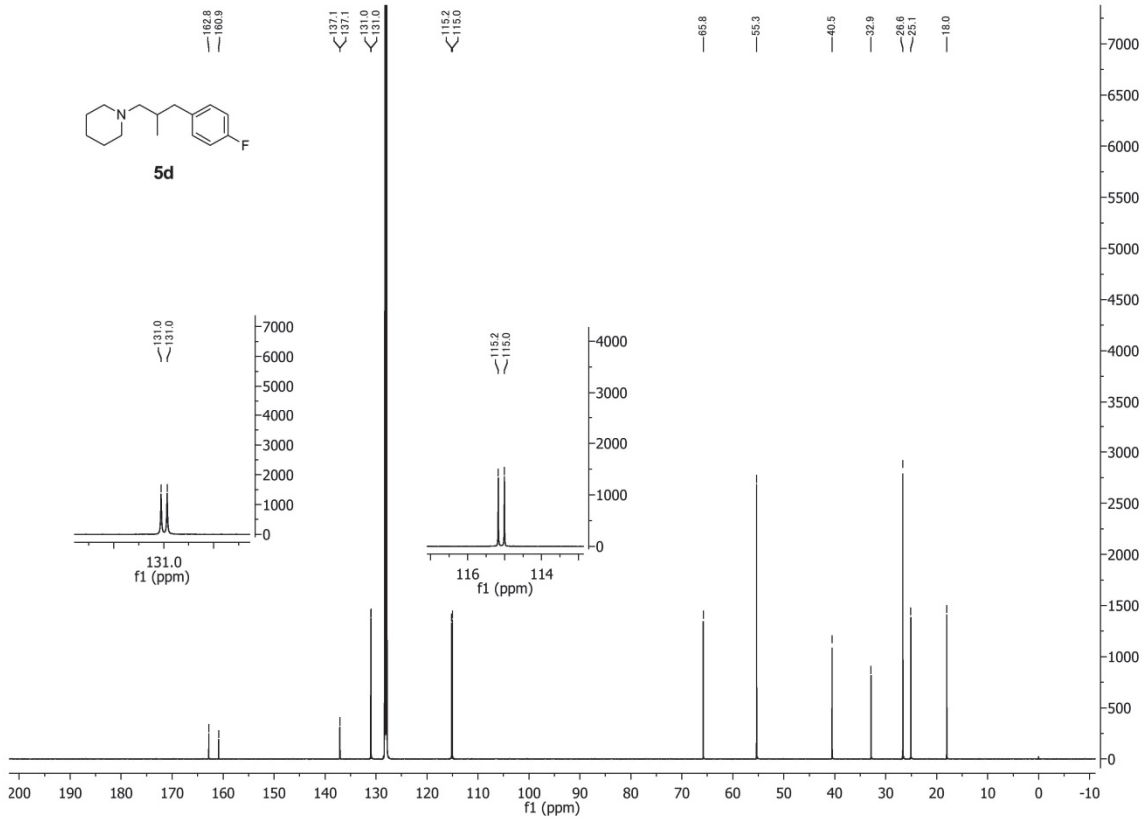
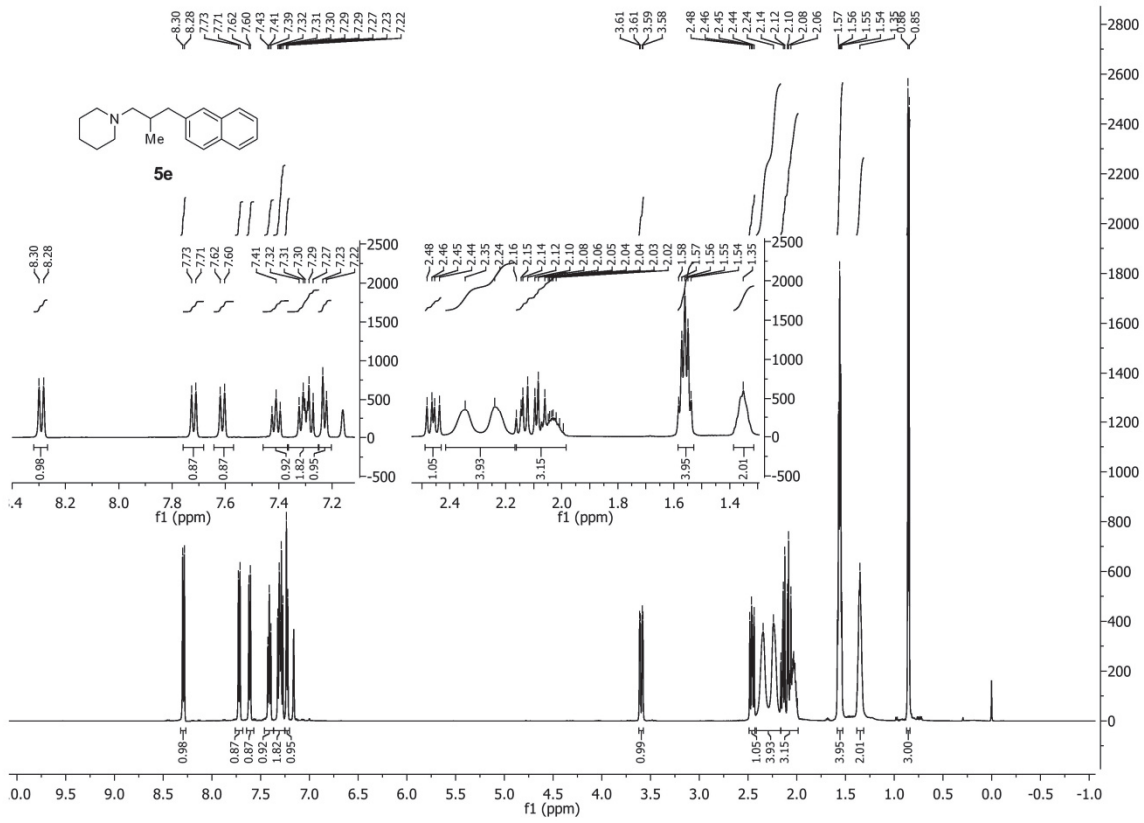

5d
f1 (ppm)


5d
f1 (ppm)


5e
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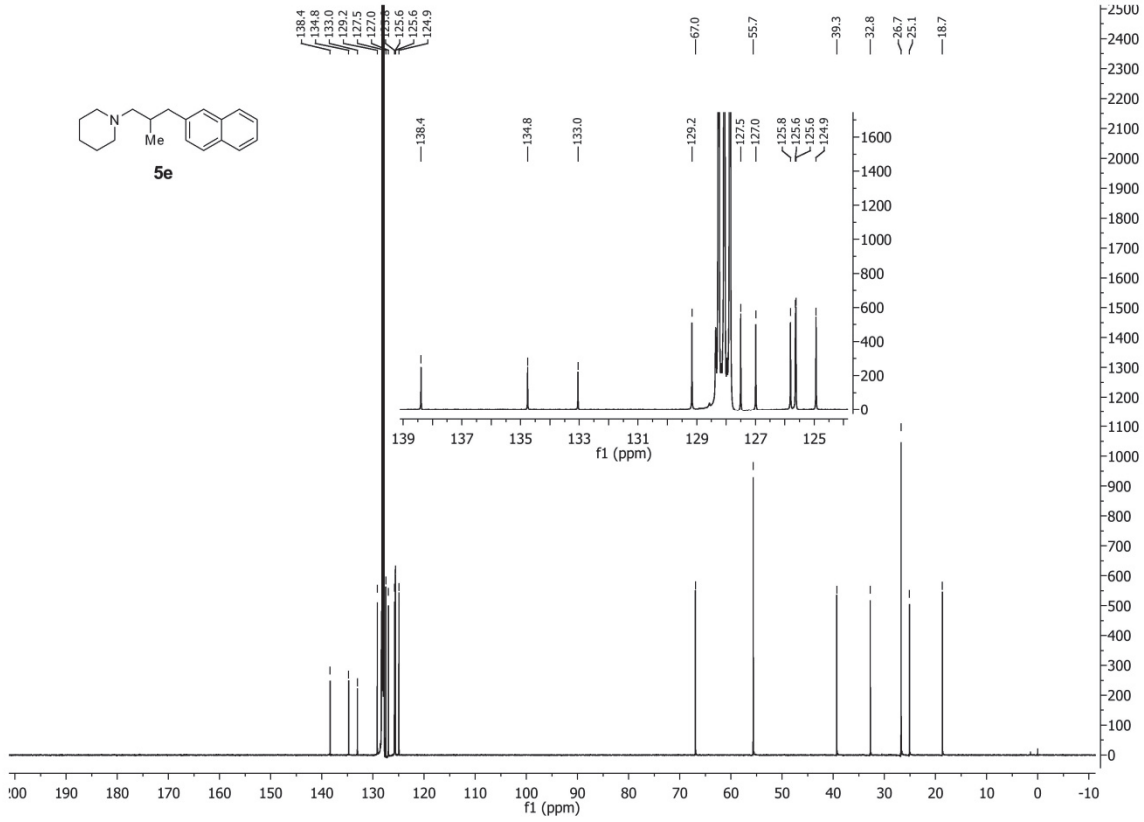
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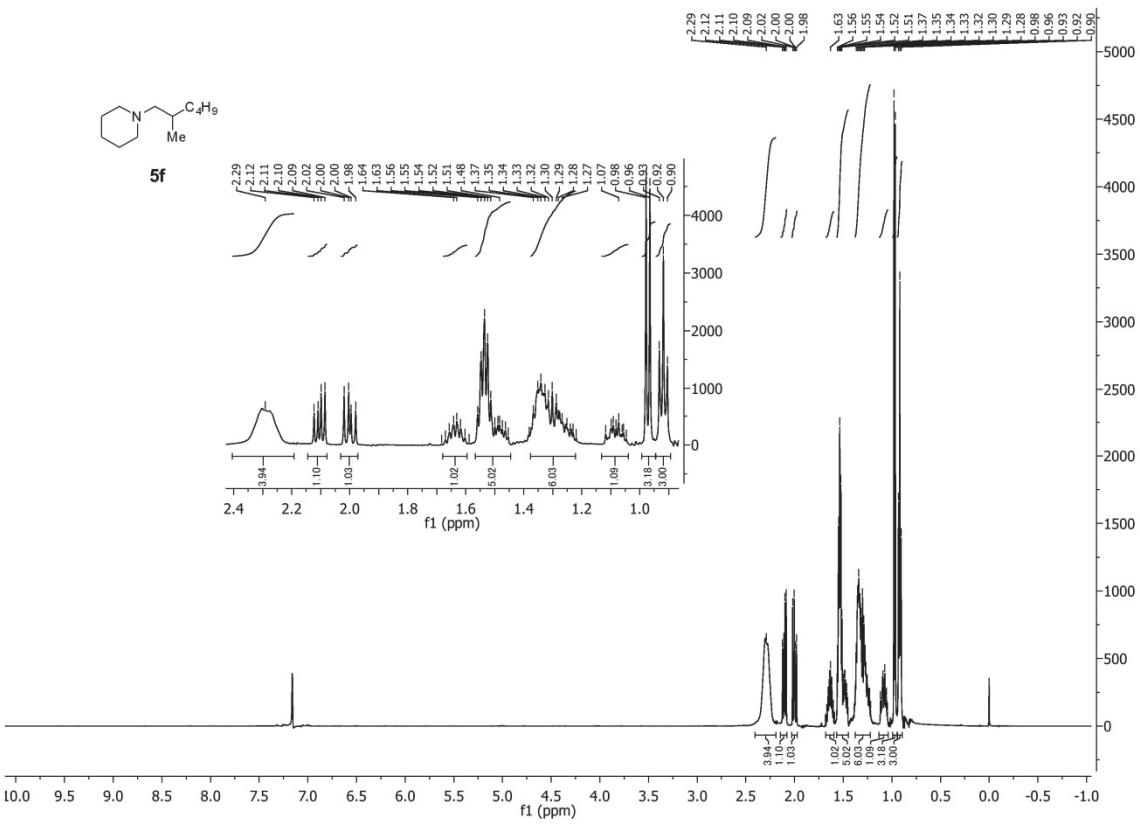
5f
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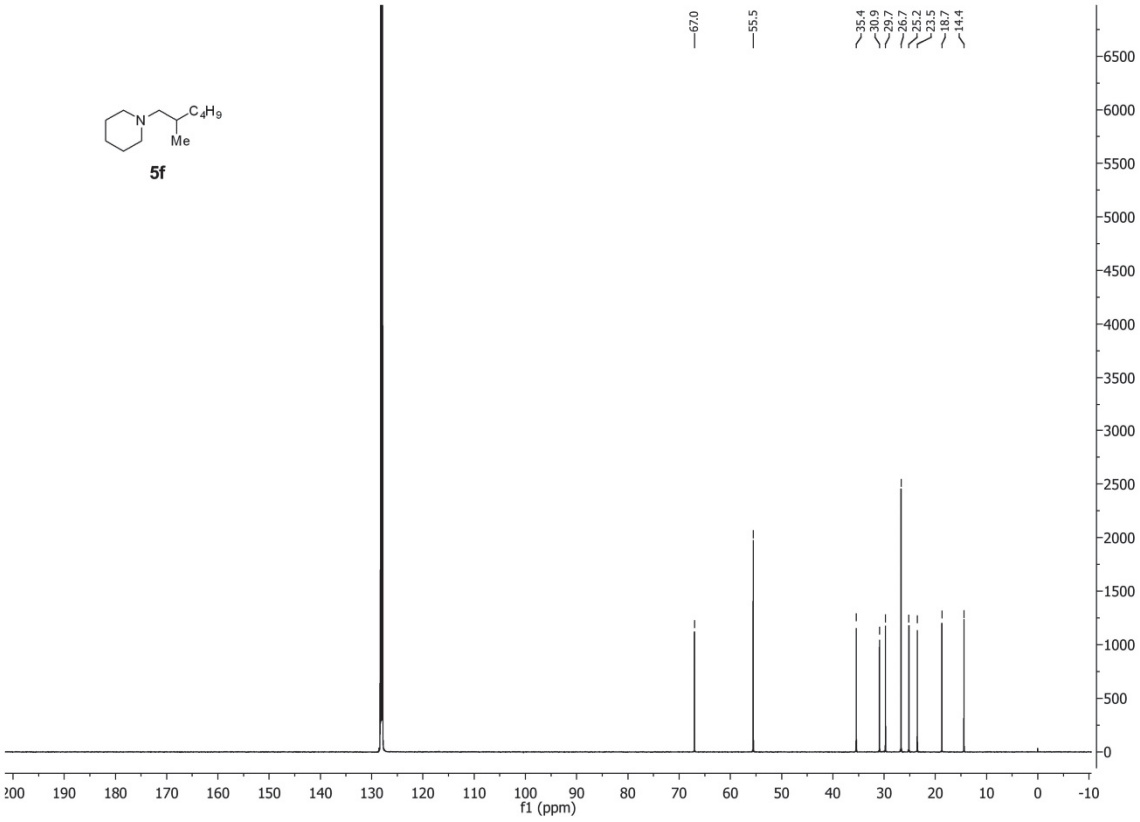
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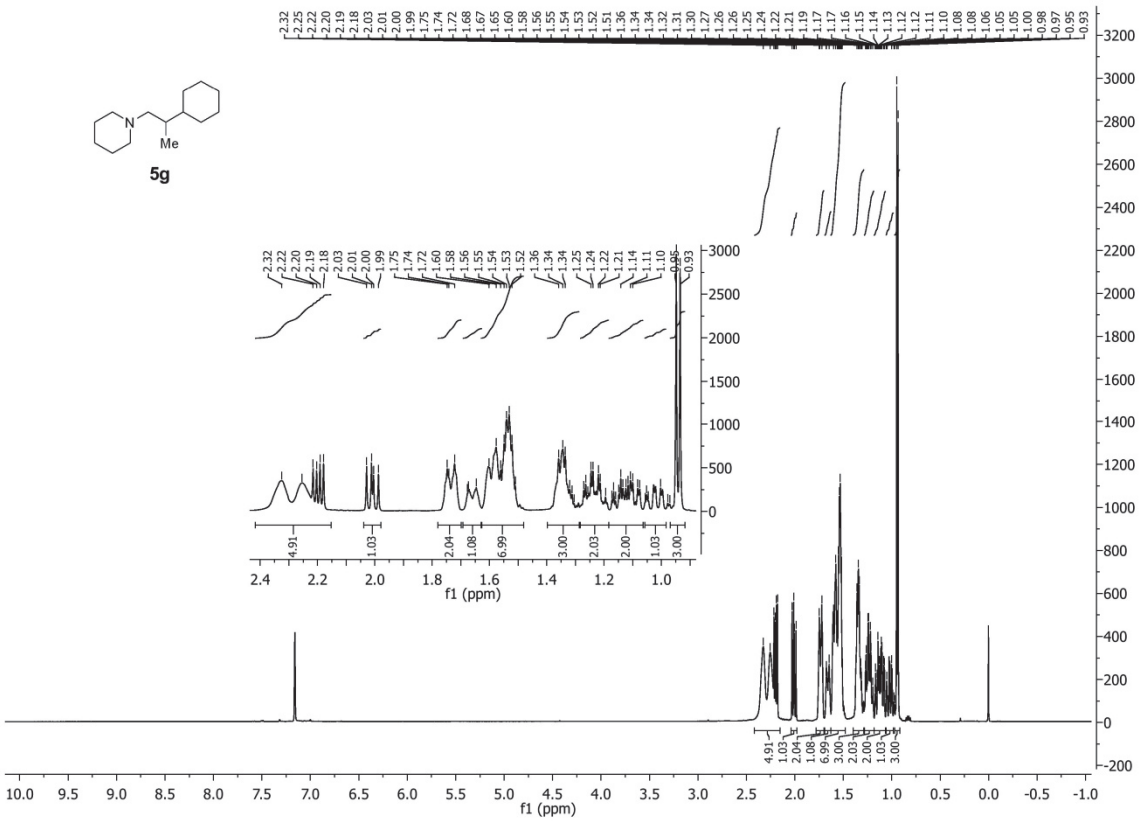
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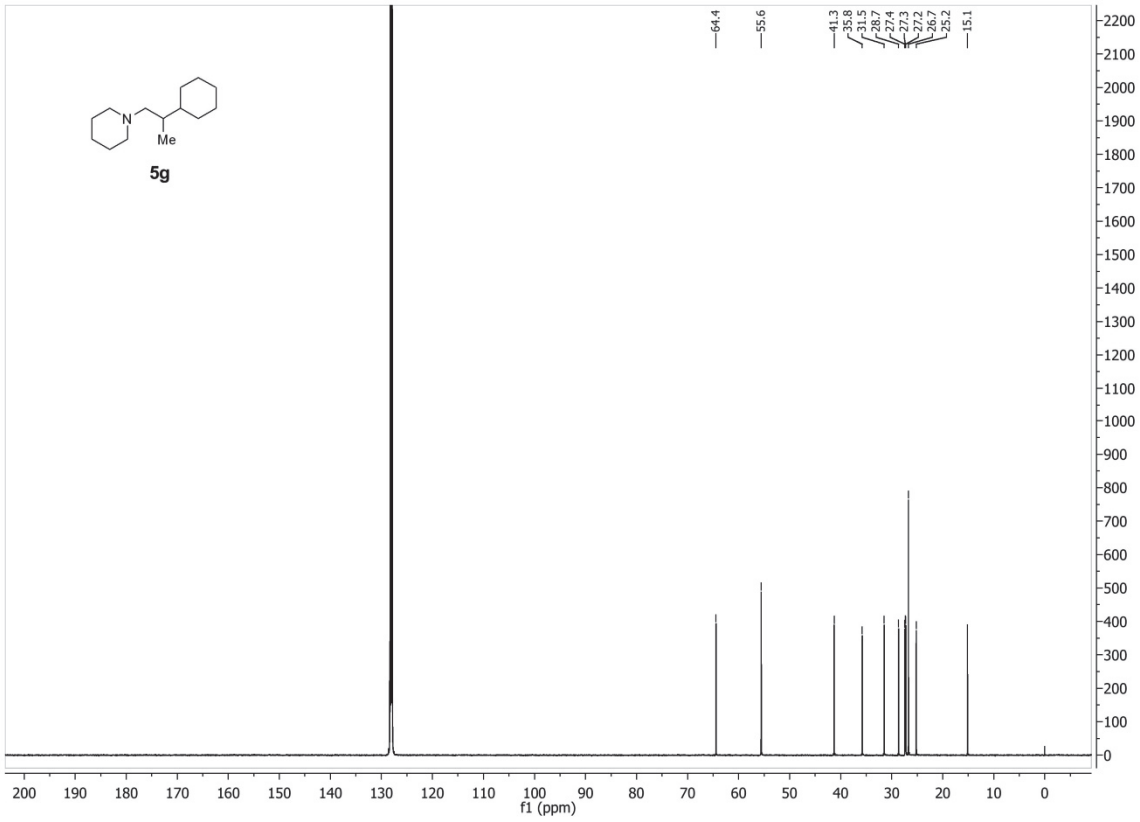
5g
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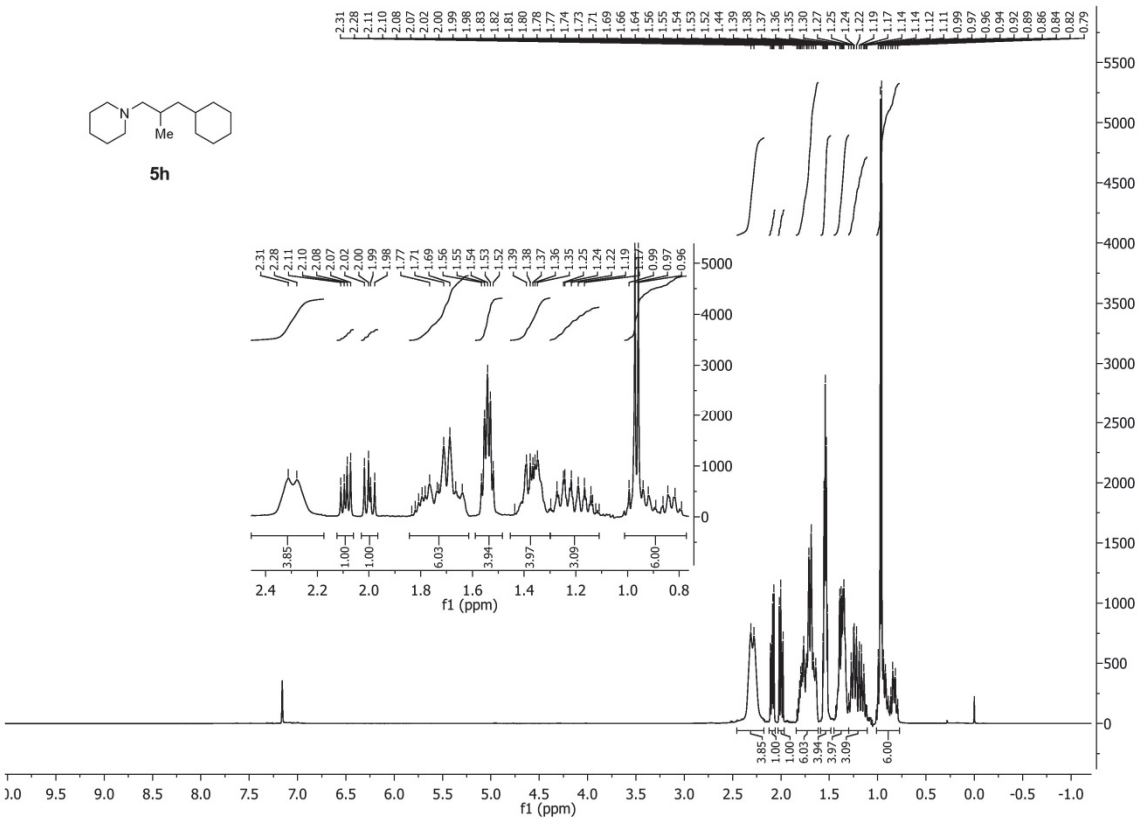
5h
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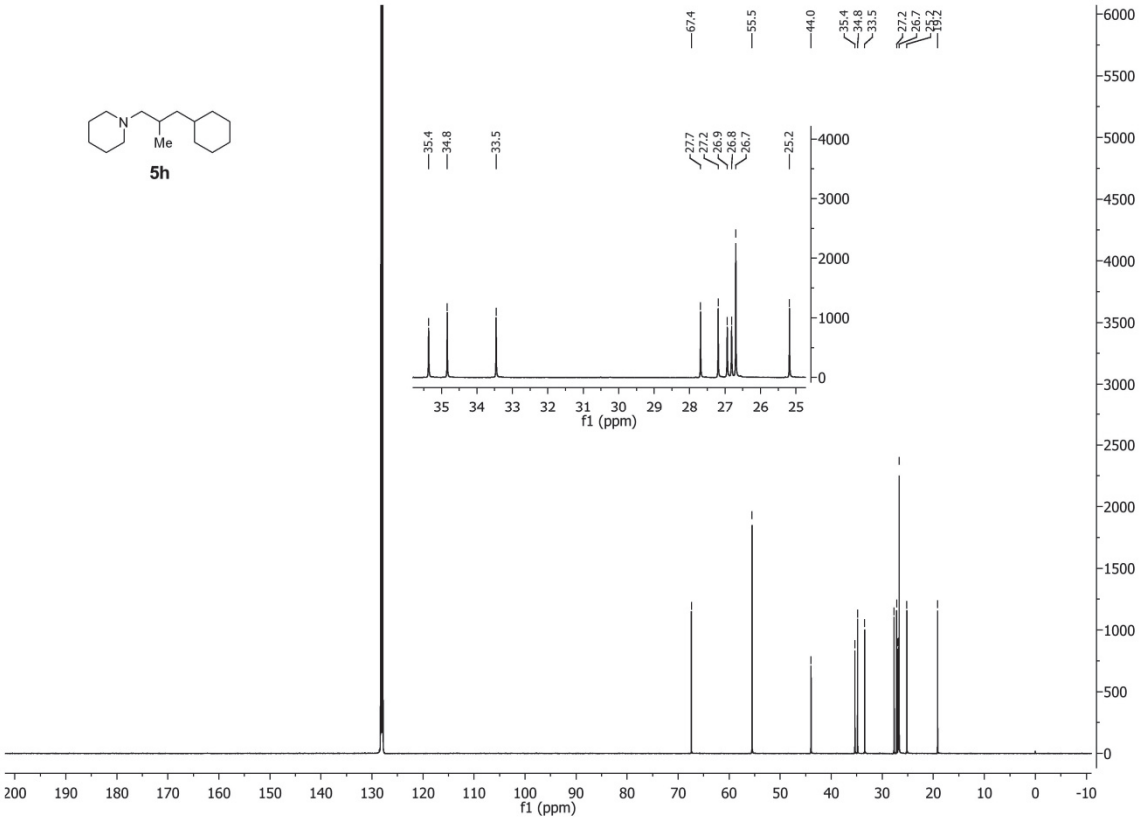
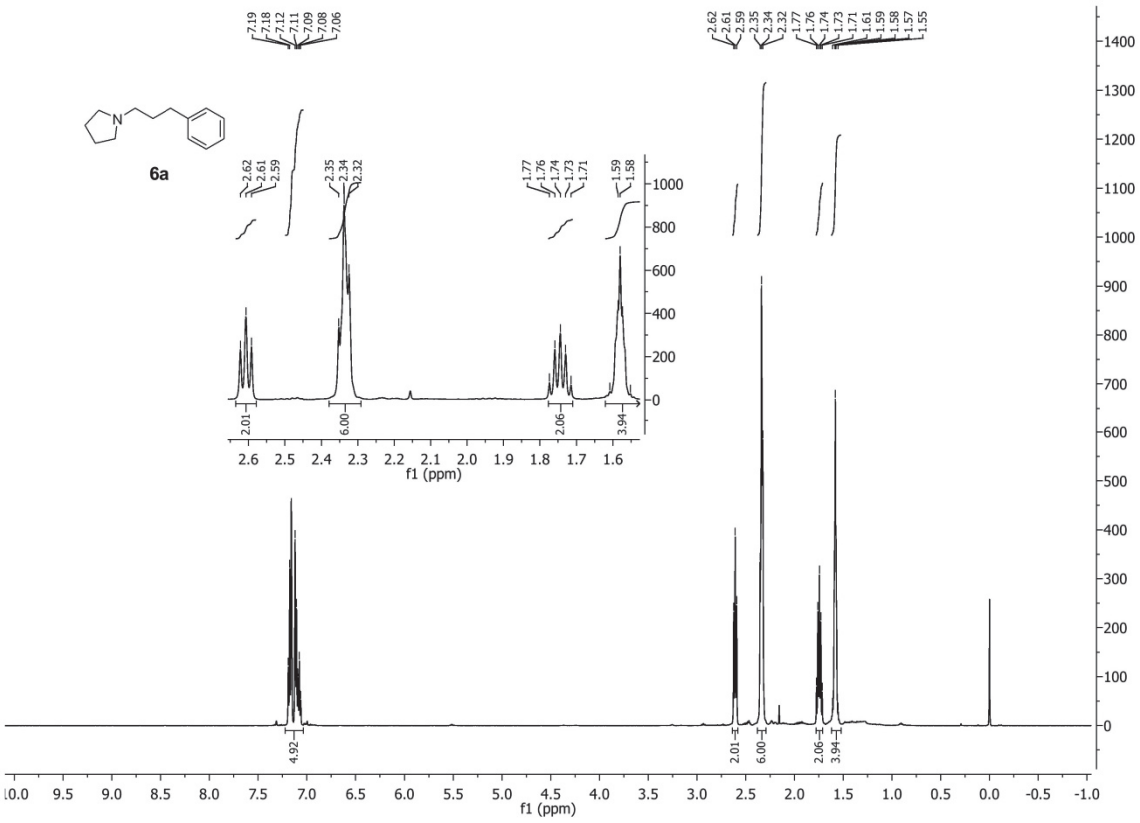
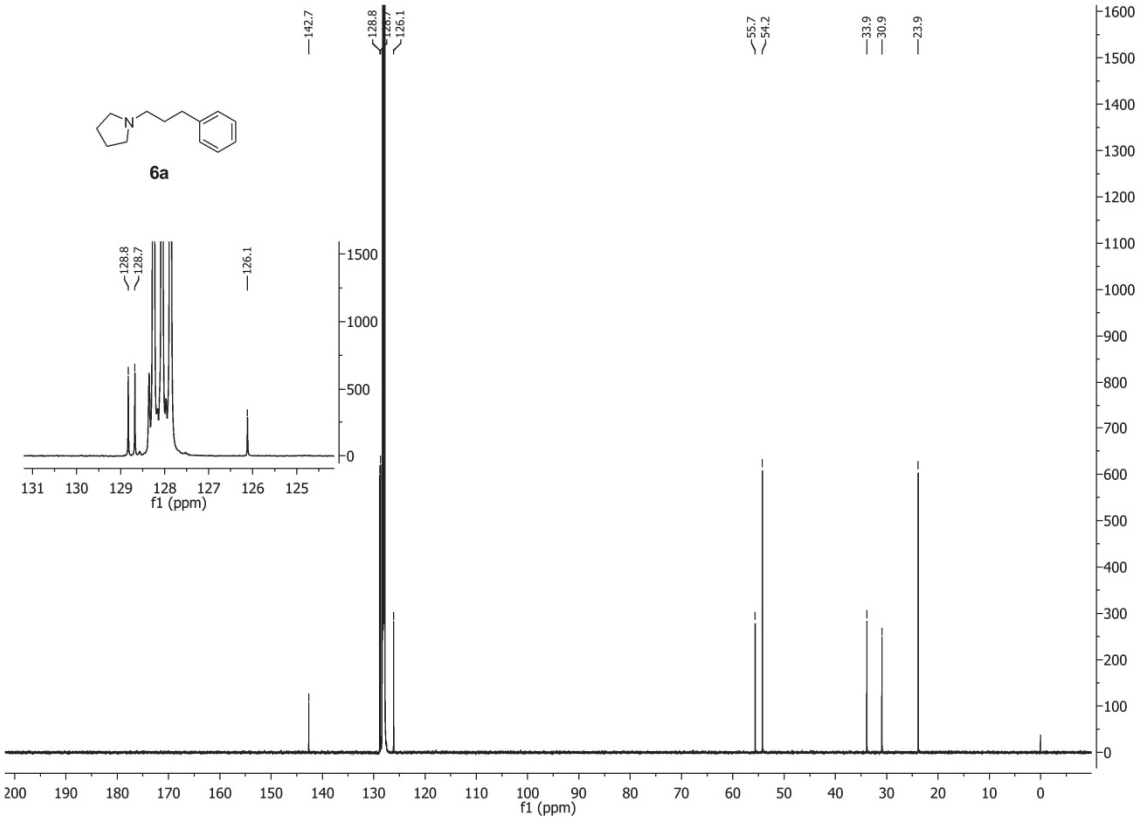

5h
f1 (ppm)


6a
f1 (ppm)


6a
f1 (ppm)