

## Supporting Information

# Alkyl Lithium-Catalyzed Benzylic C–H Bond Addition of Alkyl Pyridines to $\alpha$ -Alkenes

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## Contents

1. General Information.....	1
2. X-ray Crystallographic Studies.....	1
3. General Procedure and Analytical Data for Compounds 3.....	2
4. H–D Exchange Experiments.....	8
5. References.....	9
6. <sup>1</sup> H NMR and <sup>13</sup> C NMR Spectral Charts .....	10
7. X-ray Diffraction Data of 3ai•3,5-dinitrobenzoate .....	33

## 1. General Information

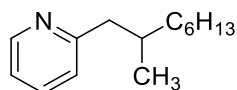
All manipulations of air- and moisture-sensitive compounds were performed under an argon atmosphere by use of standard Schlenk techniques or a nitrogen atmosphere in a Mikrouna glovebox. THF and Et<sub>2</sub>O were dried by distillation over sodium/benzophenone. TMEDA, THF-d<sup>8</sup>, benzene-d<sup>6</sup>, most alkylpyridines and olefins purchased from J&K and TCI were dried over CaH<sub>2</sub>, degassed and kept in a glovebox prior to use. Li[N(SiMe<sub>3</sub>)<sub>2</sub>] (1.0 M in THF), LiCH<sub>2</sub>SiMe<sub>3</sub> (0.55 M in hexane) and LiN<sup>i</sup>Pr<sub>2</sub> (LDA) (2.0 M solution in THF/ hexane) were purchased from J&K. After a process for removing the solvents in vacuum, the metal amides were kept as solids under -30 °C in a glove box. NaDA<sup>[1]</sup>, KDA<sup>[1]</sup>, LiTMP<sup>[2]</sup>, 2-methyl-6-phenylpyridine **1j**<sup>[3]</sup>, 2-methyl-5-phenylpyridine **1k**<sup>[3]</sup>, **1a-Li**<sup>[4]</sup> and **1k-d**<sup>[5]</sup> were prepared according to procedures described in the literatures. TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching ( $\lambda_{\text{max}}=254$  nm). Flash chromatography was performed using Silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co., China. <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded on a Bruker AV 400 (400 MHz for <sup>1</sup>H, 101 MHz for <sup>13</sup>C) instrument in CDCl<sub>3</sub> with tetramethylsilane as an internal standard. Data were reported as follows: chemical shift in ppm ( $\delta$ ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration. High resolution mass spectra (HR MS) were recorded on an Agilent 6520 Q-TOF LC/ MS with Electron Spray Ionization (ESI) resource.

## 2. X-ray Crystallographic Studies

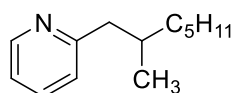
Data collections for **3ai** was performed at 113 K on a Rigaku Saturn CCD diffractometer using graphite-monochromated Cu K $\alpha$  radiation ( $\lambda = 1.54184$  Å). Its structure was solved by direct methods and refined by full-matrix least squares on  $F^2$ . All non-hydrogen atoms were refined anisotropically. The Mercury (3.10) program was utilized to draw the molecule. Crystal data and processing parameters are summarized in table (see Table s1). CCDC 1922302 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### 3. General Procedure and Analytical Data for Compounds 3

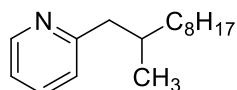
**A typical procedure:** In a glovebox, to a 25-mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added 2-methylpyridine **1a** (1.0 mmol, 93.1 mg), 1-octene **2a** (7.0 mmol, 785.5 mg), LiCH<sub>2</sub>TMS (28.2 mg, 0.30 mmol), TMEDA (0.2 mL) and THF (0.2 mL). The tube was sealed, removed from the glovebox and heated at 125 °C for 48 h. The mixture was cooled to room temperature and purified directly by silica gel column chromatography (hexane/ EtOAc = 20/1) to afford compound **3aa** as a colorless oil (156.8 mg, 76%).



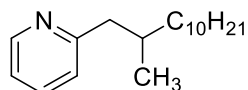
**2-(2-methyloctyl) pyridine (3aa).** Colorless oil, 156.8 mg (76% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.54-8.52 (m, 1H), 7.58-7.52 (m, 1H), 7.10-7.03 (m, 2H), 2.81-2.76 (m, 1H), 2.54-2.49 (m, 1H), 1.97-1.89 (m, 1H), 1.38-1.18 (m, 10H), 0.89-0.86 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.80, 149.27, 136.06, 123.67, 120.90, 46.18, 37.04, 34.09, 32.00, 29.67, 27.12, 22.77, 19.51, 14.21. HR MS (ESI): Found 206.1906 [M+H]<sup>+</sup>, Calcd. for C<sub>14</sub>H<sub>24</sub>N<sup>+</sup>: 206.1903.



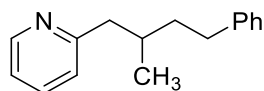
**2-(2-methylheptyl) pyridine (3ab).**<sup>[6]</sup> Colorless oil, 111.0 mg (58% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.54-8.52 (m, 1H), 7.59-7.55 (m, 1H), 7.17-7.06 (m, 2H), 2.81-2.76 (m, 1H), 2.54-2.49 (m, 1H), 2.02-1.87 (m, 1H), 1.37-1.22 (m, 8H), 0.89-0.85 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.78, 149.26, 136.08, 123.69, 120.91, 46.17, 36.99, 34.11, 32.22, 26.83, 22.79, 19.50, 14.21.



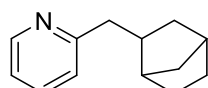
**2-(2-methyldecyl) pyridine (3ac).** Colorless oil, 163.2 mg (70% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.55-8.52 (m, 1H), 7.61-7.57 (m, 1H), 7.15-7.09 (m, 2H), 2.82-2.77 (m, 1H), 2.55-2.50 (m, 1H), 2.00-1.92 (m, 1H), 1.31-1.24 (m, 14H), 0.91-0.86 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.82, 149.29, 136.11, 123.72, 120.94, 46.20, 37.05, 34.13, 32.05, 30.03, 29.76, 29.46, 27.18, 22.82, 19.54, 14.27. HR MS (ESI): Found 234.2220 [M+H]<sup>+</sup>, Calcd. for C<sub>16</sub>H<sub>28</sub>N<sup>+</sup>: 234.2216.



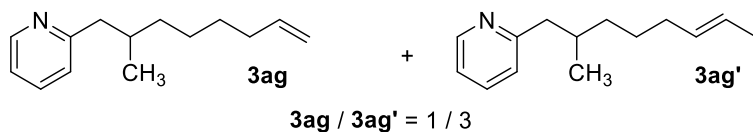
**2-(2-methyldodecyl) pyridine (3ad).** Colorless oil, 182.5 mg (70% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.53-8.51 (m, 1H), 7.58-7.53 (m, 1H), 7.12-7.05 (m, 2H), 2.82-2.77 (m, 1H), 2.55-2.50 (m, 1H), 1.96-1.91 (m, 1H), 1.24-1.23 (m, 18H), 0.88-0.84 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.81, 149.30, 136.08, 123.69, 120.92, 46.21, 37.04, 34.12, 32.05, 30.02, 29.84, 29.78, 29.49, 27.17, 22.82, 19.53, 14.26. HR MS (ESI): Found 262.2533 [M+H]<sup>+</sup>, Calcd. for C<sub>18</sub>H<sub>32</sub>N<sup>+</sup>: 262.2529.



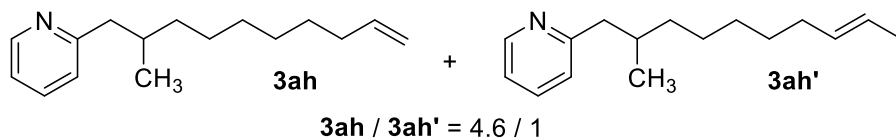
**2-(2-methyl-4-phenylbutyl) pyridine (3ae).** Colorless oil, 174.6 mg (78% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.57-8.55 (m, 1H), 7.60-7.56 (m, 1H), 7.30-7.26 (m, 2H), 7.21-7.16 (m, 3H), 7.13-7.09 (m, 2H), 2.83-2.71 (m, 2H), 2.66-2.57 (m, 2H), 2.26-2.19 (m, 1H), 1.33-1.28 (m, 2H), 0.96-0.92 (m, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.62, 149.31, 141.21, 136.15, 129.35, 128.25, 125.80, 123.76, 120.99, 42.35, 42.06, 39.84, 25.44, 10.89. HR MS (ESI): Found 226.1599  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{16}\text{H}_{20}\text{N}^+$ : 226.1590.



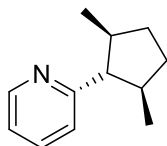
**2-(bicyclo[2.2.1]heptan-2-ylmethyl) pyridine (3af).** Colorless oil, 171.0 mg (91% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.50-8.48 (m, 1H), 7.56-7.52 (m, 1H), 7.10-7.04 (m, 2H), 2.74-2.69 (m, 1H), 2.59-2.53 (m, 1H), 2.20-2.18 (m, 1H), 2.00-1.95 (m, 1H), 1.94-1.86 (m, 1H), 1.45-1.41 (m, 3H), 1.39-1.33 (m, 1H), 1.16-1.07 (m, 4H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.63, 149.24, 136.15, 123.28, 120.93, 45.19, 42.55, 40.70, 37.80, 36.91, 35.34, 30.03, 28.88. HR MS (ESI): Found 188.1345  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{13}\text{H}_{18}\text{N}^+$ : 188.1434.



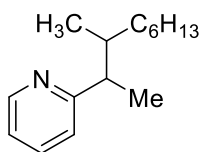
**3ag + 3ag' (3ag/ 3ag' = 1 / 3).** Colorless oil, 111.8 mg (55% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.51-8.49 (m, 1H), 7.56-7.52 (m, 1H), 7.08-7.04 (m, 2H), 5.81-5.71 (m, 0.25H), 5.45-5.28 (m, 1.5H), 4.99-4.86 (m, 0.5H), 2.80-2.75 (m, 1H), 2.54-2.78 (m, 1H), 2.02-1.89 (m, 3H), 1.60-1.59 (m, 1H), 1.56-1.54 (m, 1H), 1.42-1.27 (m, 3.75H), 1.21-1.15 (m, 1H), 0.86-0.83 (m, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.67, 149.25, 139.17, 136.06, 131.57, 130.79, 124.75, 123.80, 123.65, 120.91, 114.27, 46.11, 36.75, 36.62, 36.44, 34.02, 33.98, 33.85, 32.85, 29.19, 27.13, 27.08, 26.58, 19.48, 19.46, 18.01, 12.85. HR MS (ESI): Found 204.1751  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{14}\text{H}_{22}\text{N}^+$ : 204.1747.



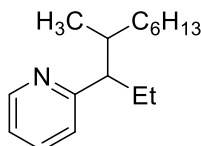
**3ah + 3ah' (3ah/ 3ah' = 4.6 / 1).** Colorless oil, 131.8 mg (57% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.53-8.51 (m, 1H), 7.58-7.54 (m, 1H), 7.10-7.06 (m, 2H), 5.84-5.74 (m, 0.82H), 5.44-5.32 (m, 0.36H), 5.02-4.89 (m, 1.64H), 2.81-2.76 (m, 1H), 2.55-2.49 (m, 1H), 2.04-1.09 (m, 2H), 1.38-1.24 (m, 11.18H), 0.86-0.84 (m, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.77, 149.30, 139.34, 136.09, 123.69, 120.93, 114.22, 46.19, 36.99, 34.10, 33.94, 29.83, 29.25, 29.03, 27.09, 19.52. HR MS (ESI): Found 232.2069  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{16}\text{H}_{26}\text{N}^+$ : 232.2060.



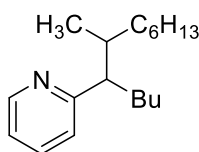
**2-(2,5-dimethylcyclopentyl) pyridine (3ai).** Colorless oil, 52.5 mg (30% yield), a mixture of two diastereoisomers (ratio 12 :1 determined by  $^1\text{H}$  NMR, GC and GC-MS); 82.3 mg (47% yield, 50 mol%  $\text{LiCH}_2\text{TMS}$  as catalyst).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.57-8.55 (m, 1H), 7.59-7.55 (m, 1H), 7.10-7.07 (m, 2H), 2.28-2.24 (m, 2H), 2.14-2.08 (m, 1H), 2.01-1.97 (m, 2H), 1.39-1.28 (m, 2H), 0.87 (d,  $J = 6.6$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.82, 149.62, 136.11, 123.29, 121.20, 64.94, 42.39, 33.21, 19.39. HR MS (ESI): Found 176.1436  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{12}\text{H}_{18}\text{N}^+$ : 176.1434. A single crystal suitable for X-ray study was obtained from the solution of **3ai** and 3,5-dinitrobenzoic acid in toluene and dichloromethane (see page 34).



**2-(3-methylnonan-2-yl) pyridine (3ba).** Colorless oil, 142.9 mg, (65% yield), a mixture of two regioisomer (ratio 1 :1.1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.53-8.51 (m, 2H), 7.58-7.53 (m, 2H), 7.11-7.03 (m, 4H), 2.78-2.66 (m, 2H), 1.86-1.79 (m, 2H), 1.33-1.14 (m, 25H), 0.92-0.82 (m, 10H), 0.74-0.72 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.38, 166.15, 148.92, 135.89, 135.86, 122.30, 122.04, 120.82, 120.77, 47.30, 46.72, 38.32, 38.24, 35.14, 33.35, 31.88, 31.81, 29.61, 29.49, 27.12, 26.80, 22.65, 22.60, 17.68, 17.38, 15.84, 15.72, 14.06, 14.04. HR MS (ESI): Found 220.2063  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{15}\text{H}_{26}\text{N}^+$ : 220.2060.

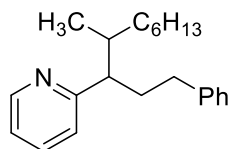


**2-(4-methyldecan-3-yl) pyridine (3ca).** Colorless oil, 92.9 mg (40% yield), a mixture of two regioisomer (ratio 1 :1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.58-8.53 (m, 2H), 7.60-7.52 (m, 2H), 7.09-7.04 (m, 4H), 2.50-2.44 (m, 2H), 1.82-1.75 (m, 4H), 1.37-1.10 (m, 21H), 0.92-0.81 (m, 10H), 0.72-0.67 (m, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.84, 164.53, 149.24, 135.74, 135.68, 123.85, 123.60, 120.97, 120.94, 100.13, 55.47, 55.21, 37.85, 37.57, 34.92, 34.44, 32.08, 31.97, 29.81, 29.64, 27.13, 27.00, 25.10, 24.01, 22.85, 22.77, 17.49, 16.92, 14.27, 14.24, 12.59, 12.53. HR MS (ESI): Found 234.2220  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{16}\text{H}_{28}\text{N}^+$ : 234.2216.

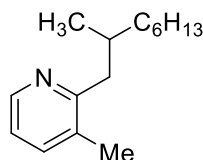


**2-(6-methyldodecan-5-yl) pyridine (3da).** Colorless oil, 116.1 mg (45% yield), a mixture of two regioisomer (ratio 1 :1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.56-8.54 (m, 2H), 7.59-7.52 (m, 2H), 7.08-7.04 (m, 4H), 2.58-2.52 (m, 2H), 1.83-1.69 (m, 6H), 1.32-1.18 (m, 27H), 0.92-0.77 (m, 16H),

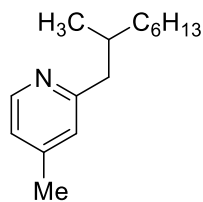
0.70-0.68 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.11, 164.78, 149.20, 149.16, 135.75, 135.68, 123.72, 123.48, 120.93, 120.90, 53.61, 53.34, 38.03, 37.79, 34.87, 34.45, 32.07, 31.96, 30.83, 30.30, 30.25, 29.79, 29.62, 27.16, 27.02, 23.02, 22.96, 22.83, 22.76, 17.45, 16.91, 14.26, 14.23, 14.17. HR MS (ESI): Found 262.2533  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{18}\text{H}_{32}\text{N}^+$ : 262.2529.



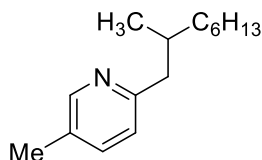
**2-(4-methyl-1-phenyldecan-3-yl) pyridine (3ea).** Colorless oil, 107.9 mg (35% yield), a mixture of two regioisomer (ratio 1 :1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.61-8.59 (m, 2H), 7.62-7.59 (m, 2H), 7.26-7.22 (m, 4H), 7.17-7.07 (m, 10H), 2.66-2.59 (m, 2H), 2.43-2.27 (m, 4H), 2.19-2.00 (m, 4H), 1.82-1.79 (m, 2H), 1.30-1.09 (m, 19H), 0.92-0.80 (m, 10H), 0.71 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.49, 164.17, 149.36, 142.86, 142.81, 135.90, 135.82, 128.49, 128.35, 125.72, 124.03, 123.77, 121.15, 121.12, 53.03, 52.86, 38.09, 37.83, 34.81, 34.36, 34.28, 34.25, 34.04, 32.84, 32.05, 31.94, 29.76, 29.59, 27.15, 26.95, 22.81, 22.75, 17.43, 16.85, 14.26, 14.23. HR MS (ESI): Found 310.2533  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{22}\text{H}_{32}\text{N}^+$ : 310.2529.



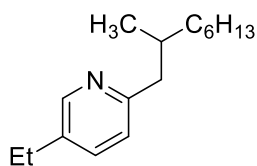
**3-methyl-2-(2-methyloctyl) pyridine (3fa).** Colorless oil, 189.2 mg (86% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.36-8.35 (m, 1H), 7.37-7.35 (m, 1H), 7.04-6.92 (m, 1H), 2.80-2.73 (m, 1H), 2.57-2.52 (m, 1H), 2.28 (s, 3H), 2.01-1.92 (m, 1H), 1.36-1.23 (m, 10H), 0.86-0.84 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.23, 146.61, 137.57, 131.38, 120.93, 42.89, 37.35, 33.46, 32.00, 29.69, 27.22, 22.77, 19.58, 19.21, 14.21. HR MS (ESI): Found 220.2063  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{15}\text{H}_{26}\text{N}^+$ : 220.2060.



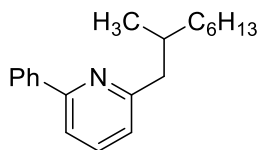
**4-methyl-2-(2-methyloctyl) pyridine (3ga).** Colorless oil, 188.9 mg (86% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.37-8.35 (m, 1H), 6.98-6.84 (m, 2H), 2.76-2.71 (m, 1H), 2.49-2.43 (m, 1H), 2.29 (s, 3H), 1.95-1.89 (m, 1H), 1.35-1.15 (m, 10H), 0.87-0.82 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.52, 149.01, 147.00, 124.55, 121.95, 46.07, 37.08, 34.07, 32.01, 29.68, 27.13, 22.78, 21.10, 19.52, 14.24. HR MS (ESI): Found 220.2067  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{15}\text{H}_{26}\text{N}^+$ : 220.2060.



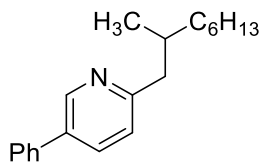
**5-methyl-2-(2-methyloctyl) pyridine (3ha).** Colorless oil, 189.7 mg (87% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.33-8.31(m, 1H), 7.36-7.34 (m, 1H), 6.98-6.96 (m, 1H), 2.76-2.71 (m, 1H), 2.51-2.45 (m, 1H), 2.26 (s, 3H), 1.93-1.85 (m, 1H), 1.34-1.13 (m, 10H), 0.86-0.80 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.70, 149.58, 136.68, 130.01, 123.10, 45.69, 37.00, 34.13, 32.00, 29.68, 27.12, 22.77, 19.47, 18.14, 14.22. HR MS (ESI): Found 220.2064  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{15}\text{H}_{26}\text{N}^+$ : 220.2060.



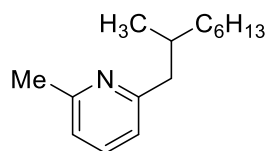
**5-ethyl-2-(2-methyloctyl) pyridine (3ia).** Colorless oil, 214.8 mg (92% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.35-8.34 (m, 1H), 7.39-7.36 (m, 1H), 7.01-6.99 (m, 1H), 2.77-2.72 (m, 1H), 2.62-2.56 (m, 2H), 2.50-2.45 (m, 1H), 1.94-1.86 (m, 1H), 1.35-1.14 (m, 13H), 0.86-0.82 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.98, 148.88, 136.21, 135.47, 123.23, 45.75, 37.03, 34.13, 32.01, 29.68, 27.13, 25.80, 22.78, 19.50, 15.50, 14.23. HR MS (ESI): Found 234.2220  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{16}\text{H}_{28}\text{N}^+$ : 234.2216.



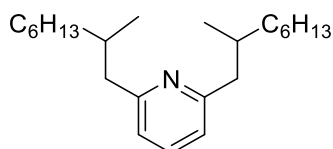
**2-(2-methyloctyl)-6-phenylpyridine (3ja).** Colorless oil, 150.5 mg (54% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.04-8.02 (m, 2H), 7.66-7.62 (m, 1H), 7.55-7.53 (m, 1H), 7.50-7.46 (m, 2H), 7.43-7.37 (m, 1H), 7.07-7.05 (m, 1H), 2.92-2.87 (m, 1H), 2.68-2.63 (m, 1H), 2.16-2.05 (m, 1H), 1.43-1.19 (m, 10H), 0.89-0.95 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.65, 156.81, 140.03, 136.65, 128.74, 127.10, 121.98, 117.68, 46.13, 36.99, 33.80, 32.06, 29.74, 27.15, 22.83, 19.70, 14.26. HR MS (ESI): Found 282.2220  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{20}\text{H}_{28}\text{N}^+$ : 282.2216.



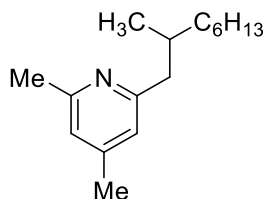
**2-(2-methyloctyl)-5-phenylpyridine (3ka).** Colorless oil, 225.1 mg (80% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.77-8.76(m, 1H), 7.79-7.76 (m, 1H), 7.59-7.57 (m, 2H), 7.48-7.44 (m, 2H), 7.40-7.38 (m, 1H), 7.19-7.17 (m, 1H), 2.88-2.83 (m, 1H), 2.61-2.56 (m, 1H), 2.04-1.92 (m, 1H), 1.39-1.17 (m, 10H), 0.92-0.84 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.69, 147.71, 138.12, 134.54, 133.88, 129.12, 127.86, 127.09, 123.56, 45.86, 37.08, 34.17, 32.04, 29.70, 27.17, 22.80, 19.60, 14.26. HR MS (ESI): Found 282.2220  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{20}\text{H}_{28}\text{N}^+$ : 282.2216.



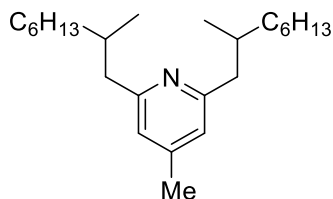
**2-methyl-6-(2-methyloctyl) pyridine (3la).** Colorless oil, 98.6 mg (45% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.45-7.41 (m, 1H), 6.93-6.91 (m, 1H), 6.88-6.87 (m, 1H), 2.76-2.71 (m, 1H), 2.53-2.47 (m, 4H), 1.93-1.89 (m, 1H), 1.33-1.13 (m, 10H), 0.87-0.83 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.13, 157.74, 136.19, 120.48, 120.36, 46.30, 36.98, 34.00, 32.00, 29.68, 27.06, 24.69, 22.77, 19.44, 14.20. HR MS (ESI): Found 220.2063  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{15}\text{H}_{26}\text{N}^+$ : 220.2060.



**2,6-bis(2-methyloctyl) pyridine (3la').** Colorless oil, 109.3 mg (33% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.46-7.42 (m, 1H), 6.90-6.88 (m, 2H), 2.77-2.72 (m, 2H), 2.56-2.51 (m, 2H), 2.00-1.88 (m, 2H), 1.34-1.09 (m, 20H), 0.88-0.82 (m, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.08, 135.89, 120.63, 46.21, 36.92, 34.10, 32.05, 29.74, 27.13, 22.81, 19.51, 14.23. HR MS (ESI): Found 332.3315  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{23}\text{H}_{42}\text{N}^+$ : 332.3312.



**2,4-dimethyl-6-(2-methyloctyl) pyridine (3ma).** Colorless oil, 84.6 mg (36% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.77 (s, 1H), 6.72 (s, 1H), 2.72-2.68 (m, 1H), 2.50-2.43 (m, 4H), 2.26 (s, 3H), 1.94-1.86 (m, 1H), 1.36-1.15 (m, 10H), 0.88-0.83 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.88, 157.43, 147.17, 121.56, 121.51, 46.12, 37.03, 34.02, 32.03, 29.71, 27.09, 24.47, 22.81, 21.00, 19.46, 14.26. HR MS (ESI): Found 234.2221  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{16}\text{H}_{28}\text{N}^+$ : 234.2216.



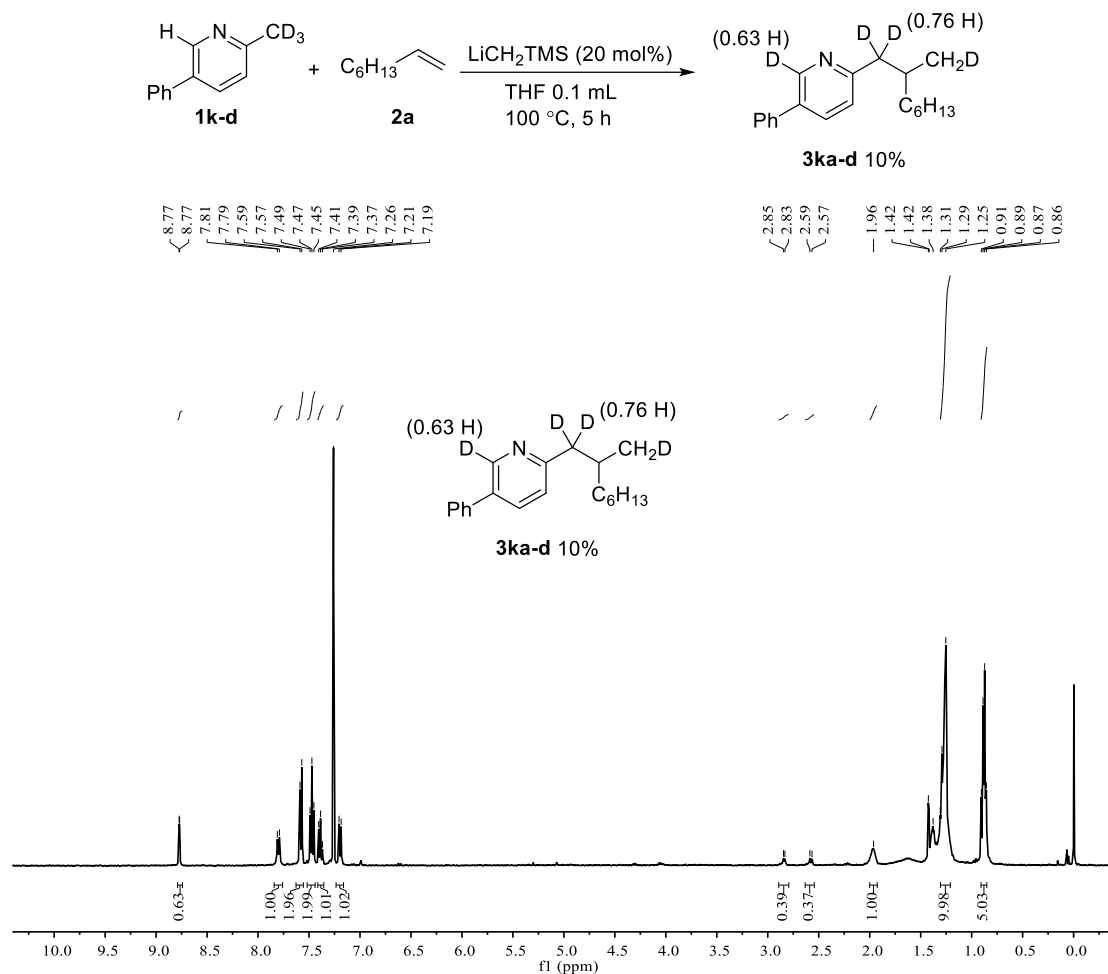
**4-methyl-2,6-bis(2-methyloctyl) pyridine (3ma').** Colorless oil, 163.4 mg (47% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.72 (s, 2H), 2.72-2.68 (m, 2H), 2.51-2.46 (m, 2H), 2.27 (s, 3H), 1.95-1.87 (m, 2H), 1.35-1.16 (m, 20H), 0.91-0.79 (m, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.84, 146.67, 121.68, 46.08, 36.94, 34.07, 32.06, 29.75, 27.13, 22.82, 21.07, 19.50, 14.26. HR MS (ESI): Found 346.3472  $[\text{M}+\text{H}]^+$ , Calcd. for  $\text{C}_{24}\text{H}_{44}\text{N}^+$ : 346.3468.



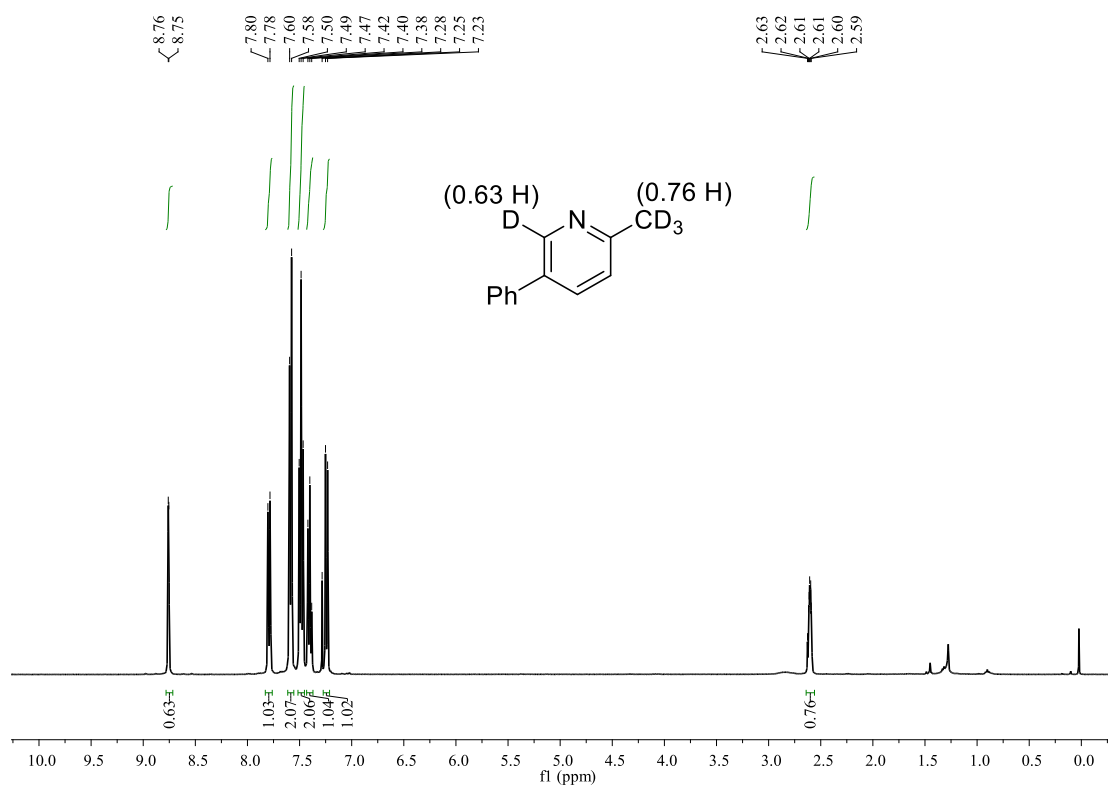
## 4. H–D Exchange Experiments

### The H–D exchange experiment

In a glovebox, to a 25-mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added LiCH<sub>2</sub>TMS (9.4 mg, 0.10 mmol), deuterated 2-methyl-5-phenylpyridine **1k-d** (0.5 mmol, 86.1 mg), 1-octene **2a** (2.50 mmol, 280.5 mg), and THF (0.1 mL). The tube was sealed, removed from the glovebox and stirred at 100 °C for 5 h. The mixture was cooled to room temperature and purified directly by silica gel column chromatography (hexane/ EtOAc = 20/1) to afford the alkylation product **3ka-d** (14 mg, 10%).



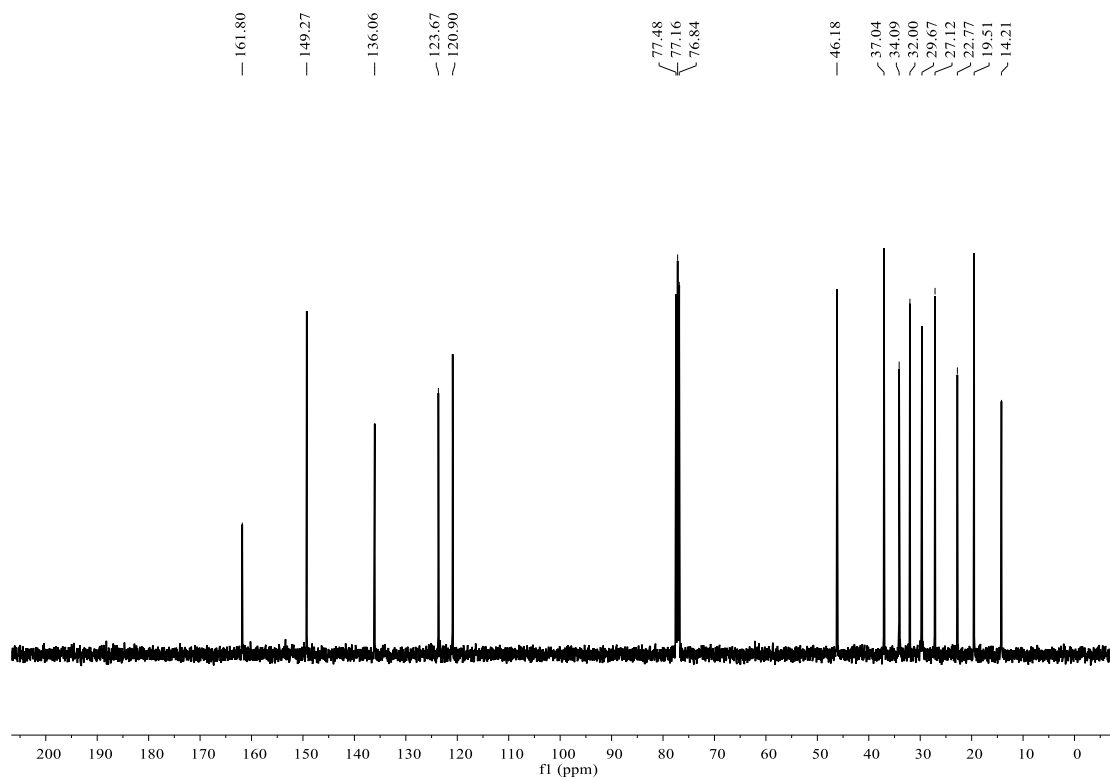
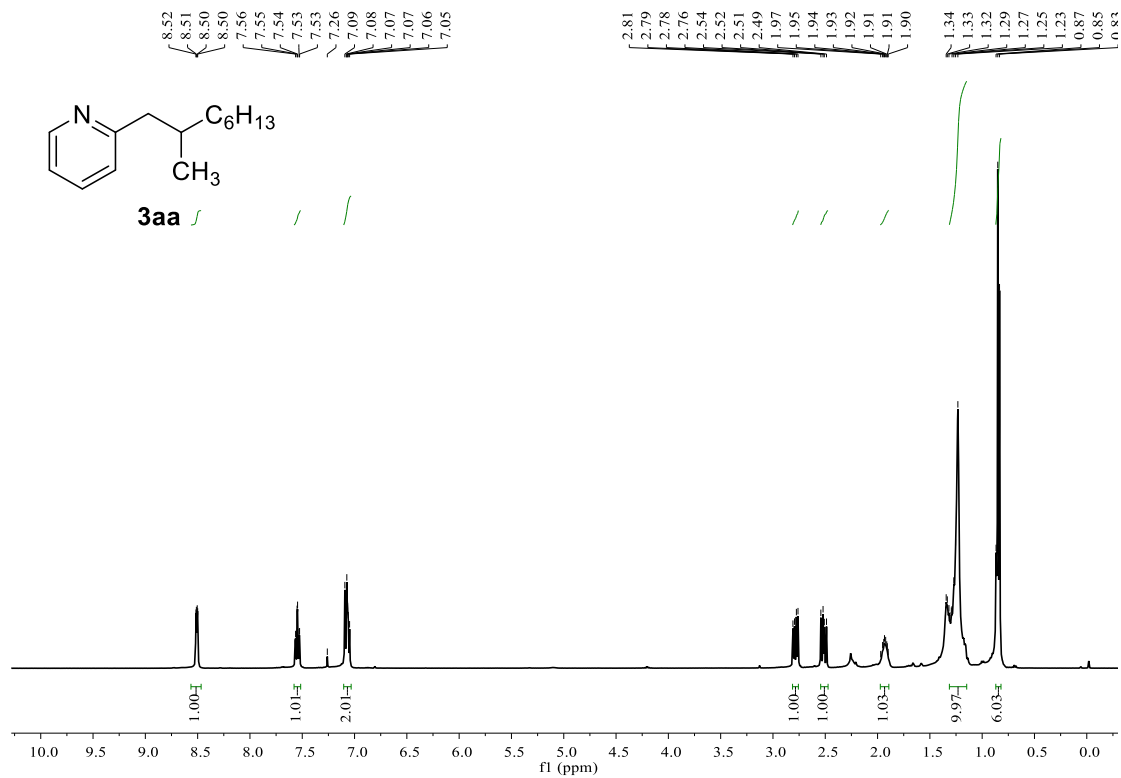
Recovered deuterated 2-methyl-5-phenylpyridine:

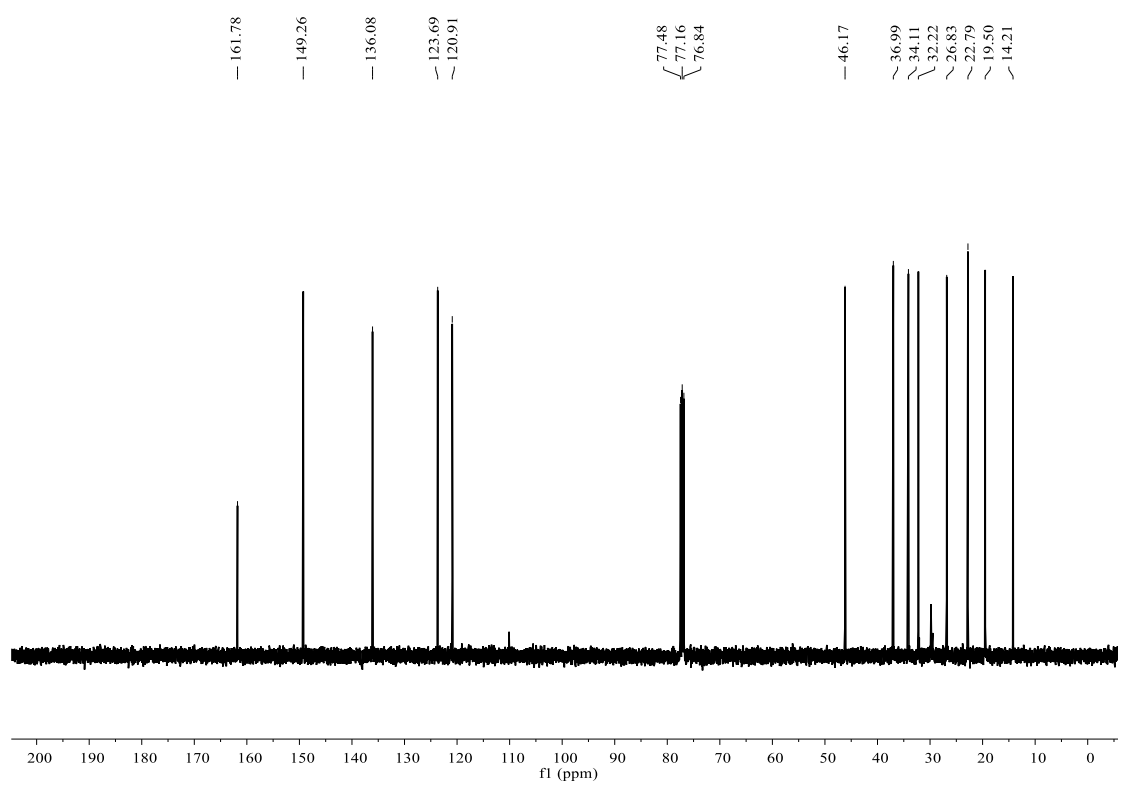
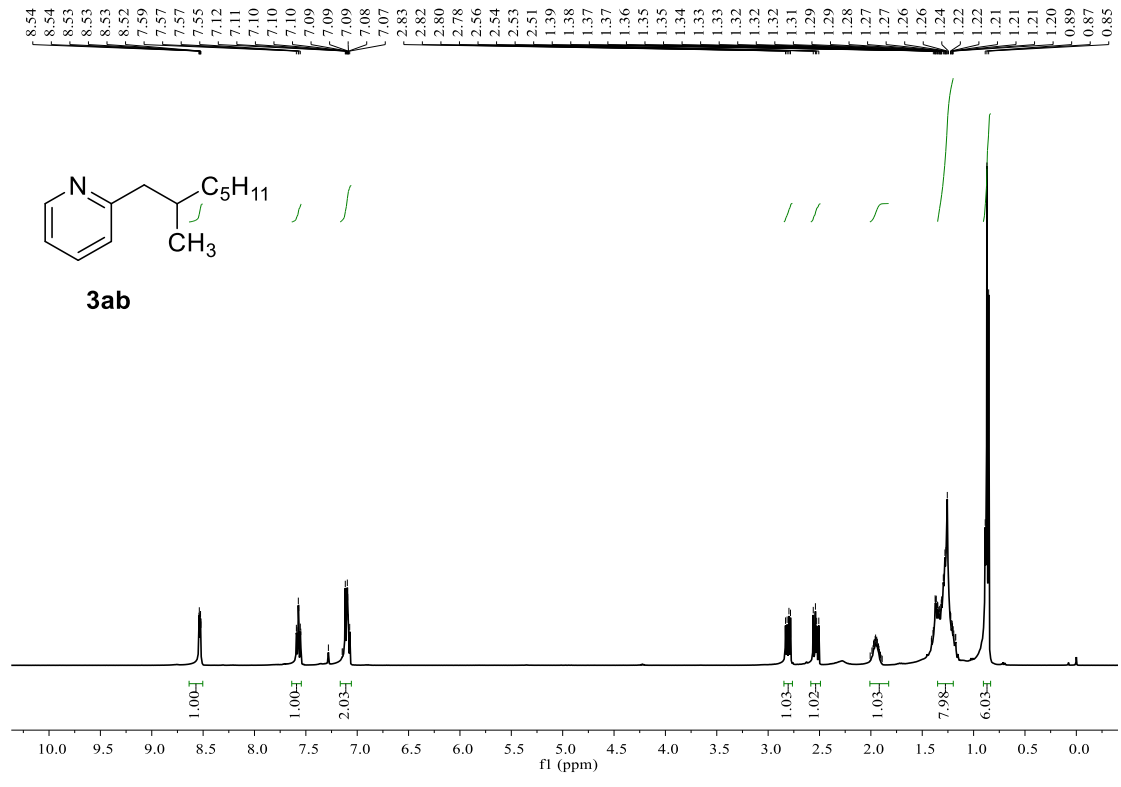


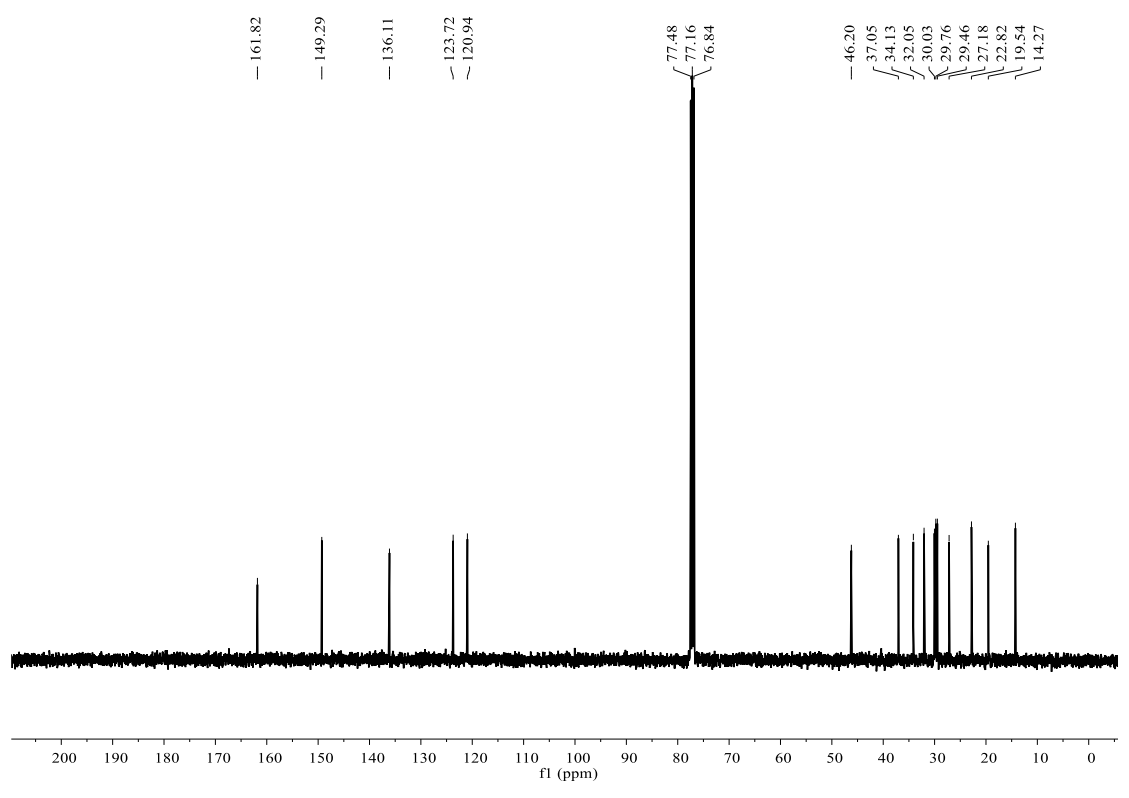
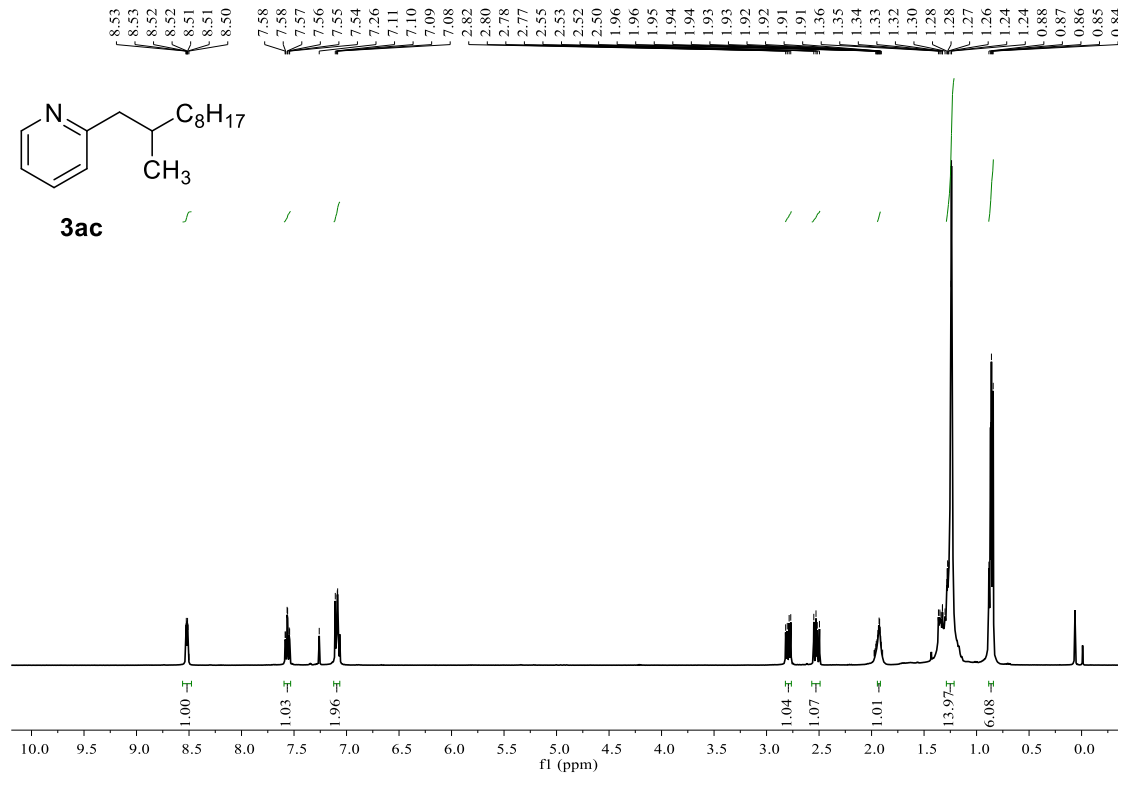
## 5. References

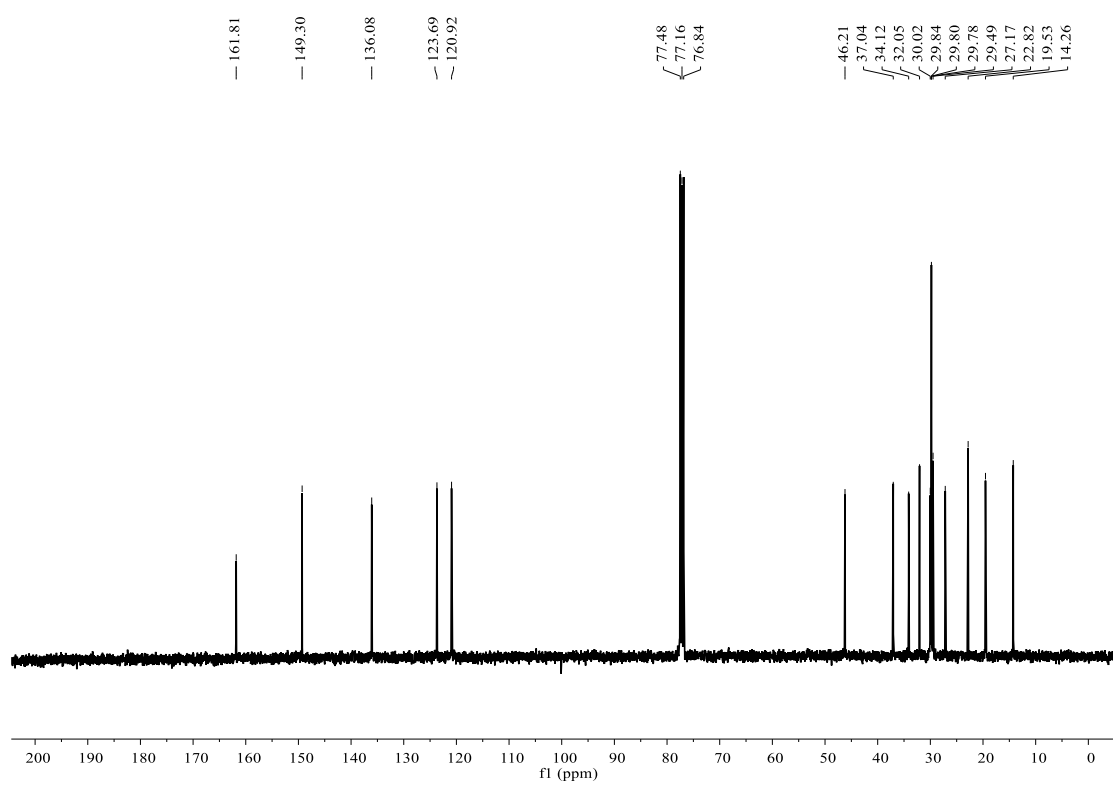
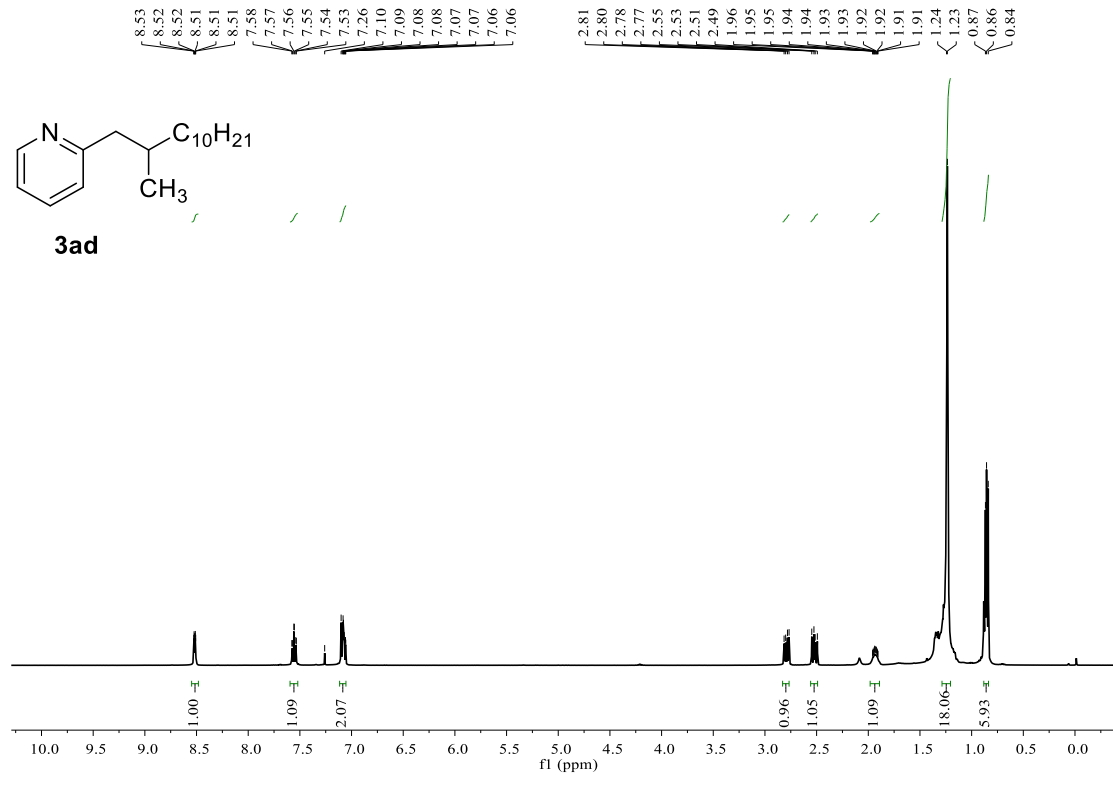
- [1] D. Barr, A. J. Dawson, B. J. Wakefield, *J. Chem. Soc., Chem. Commun.* 1992, 204.
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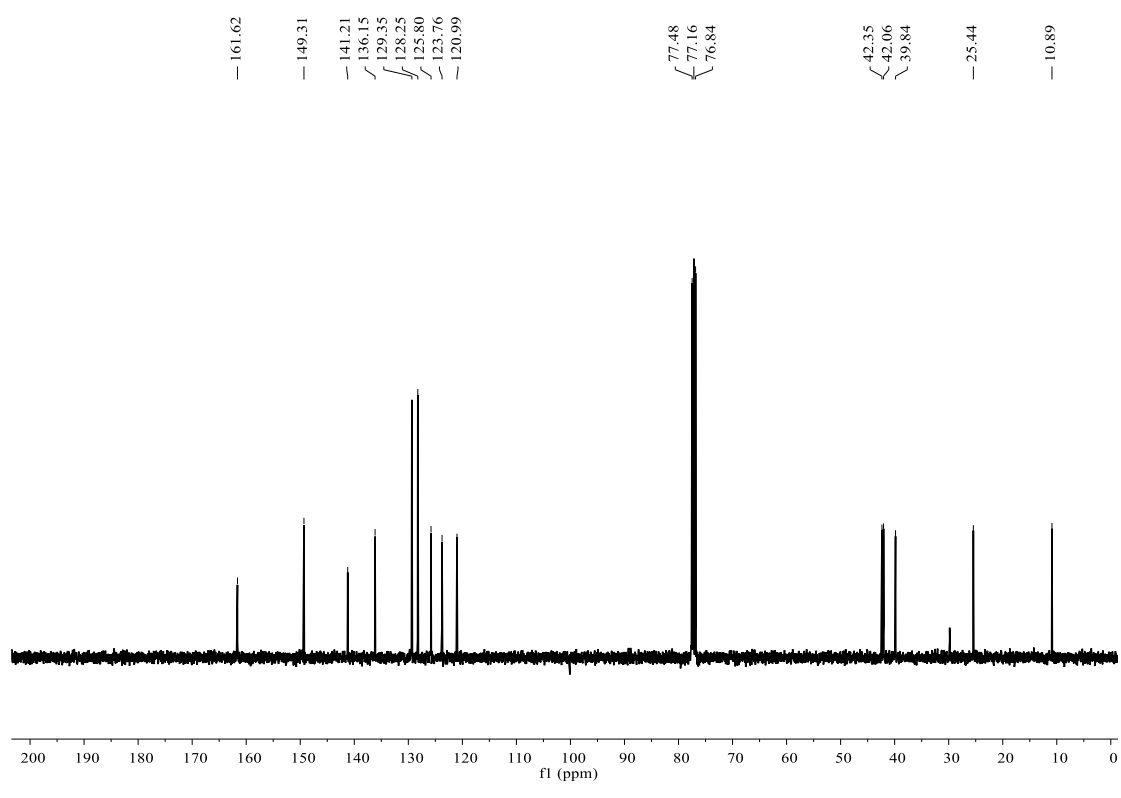
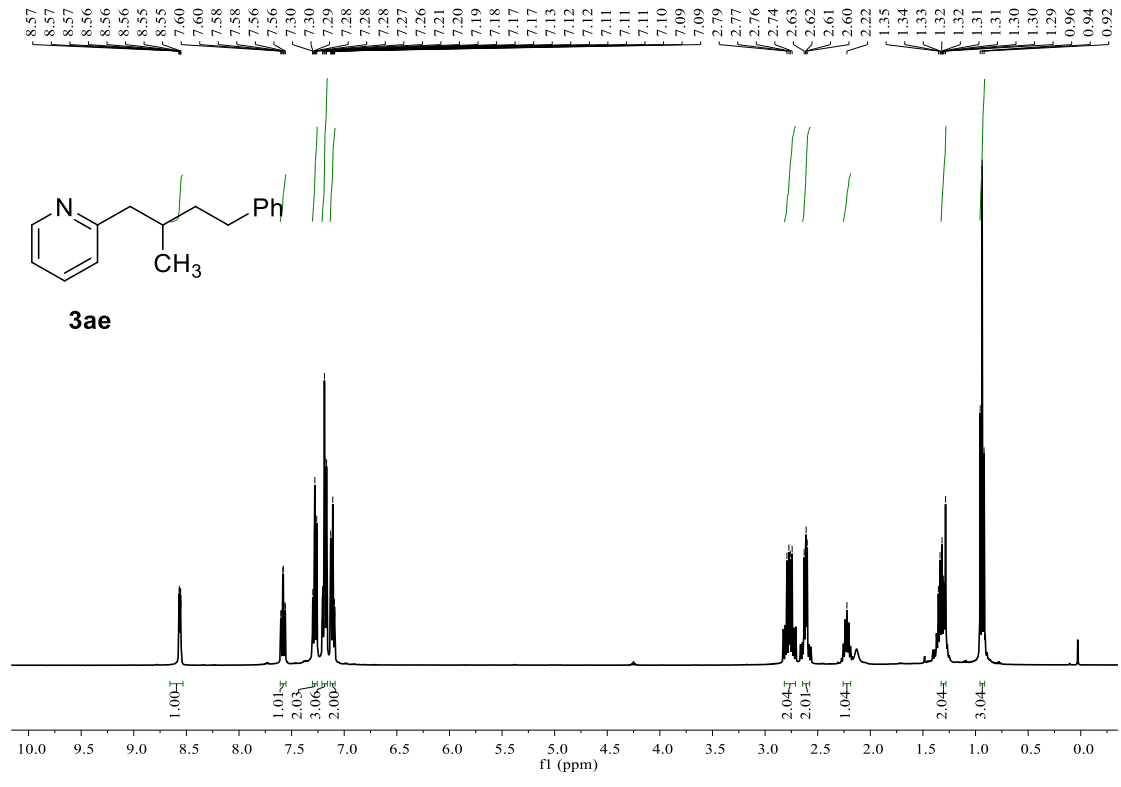
## 6. <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectral Charts

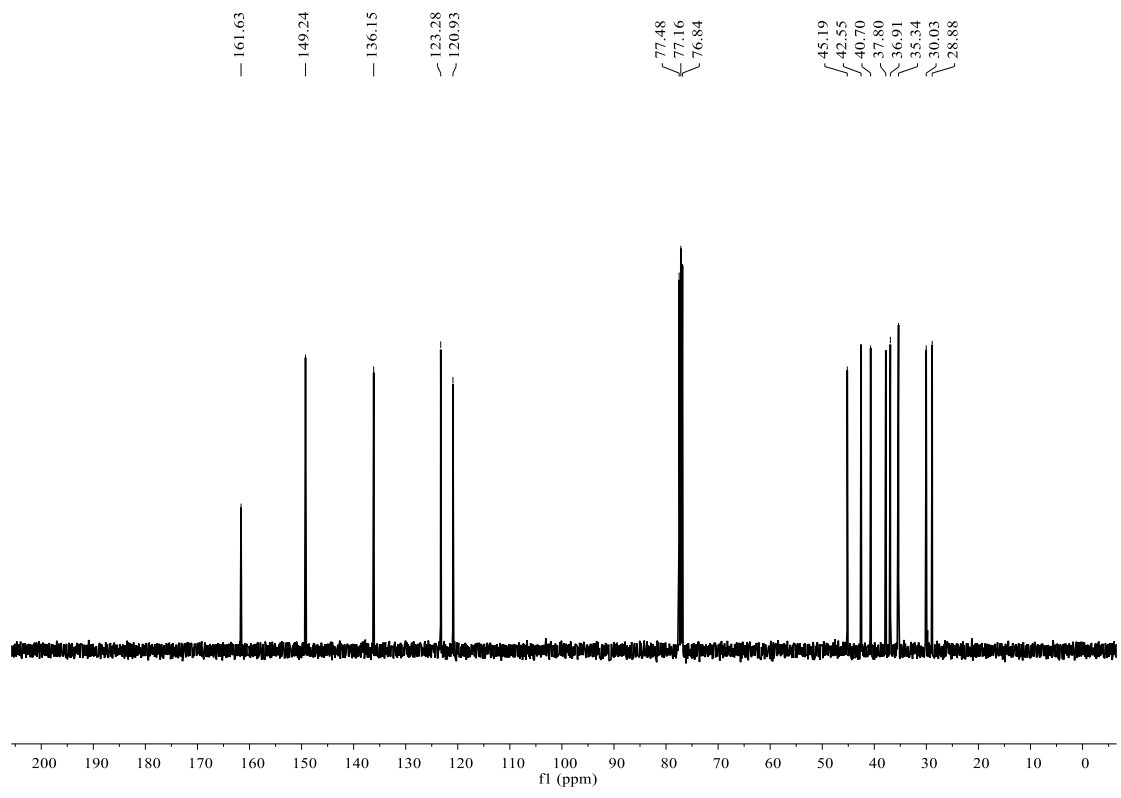
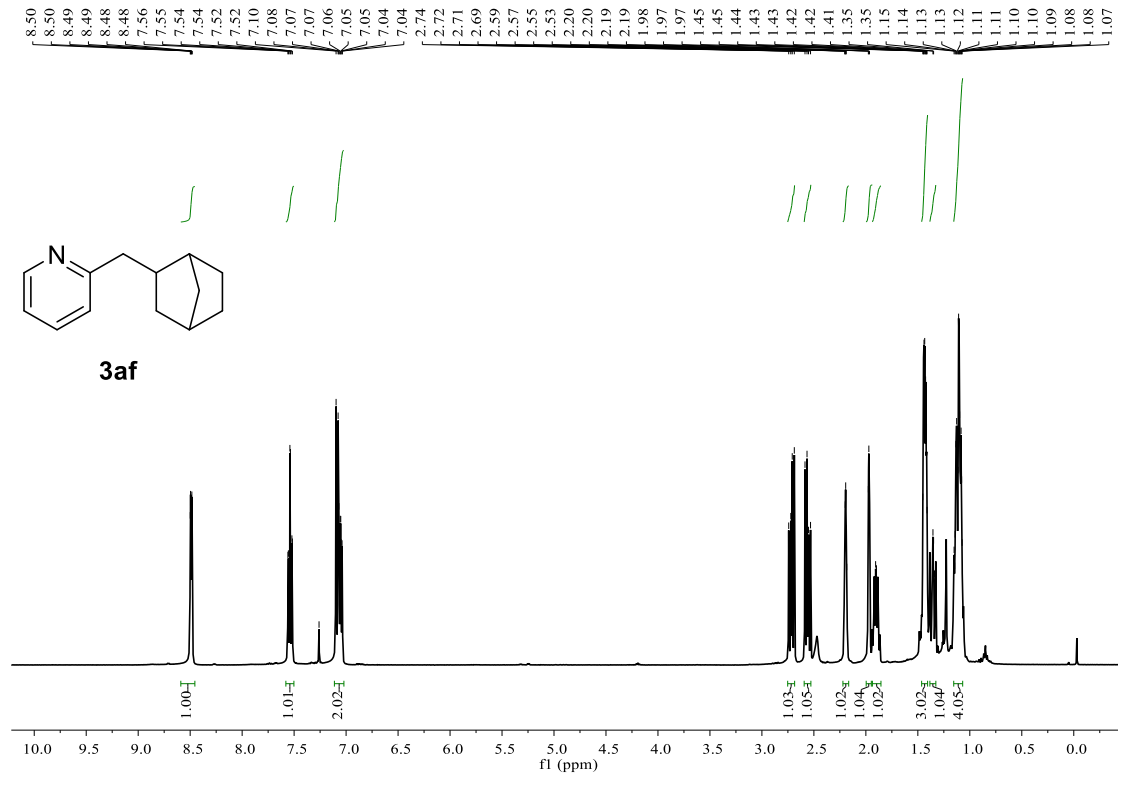




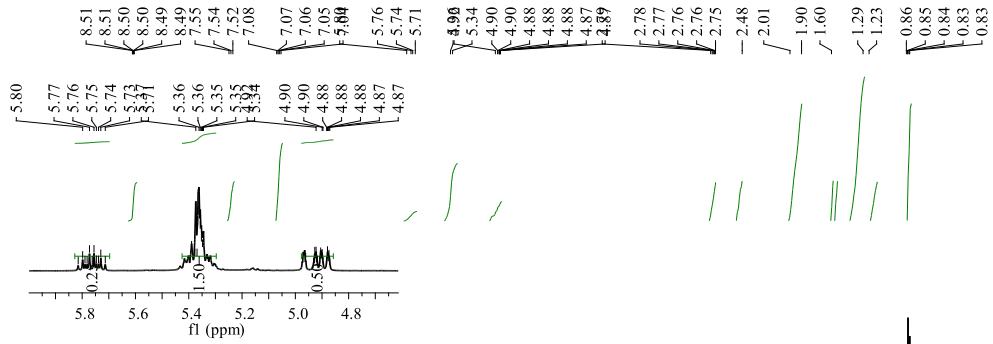




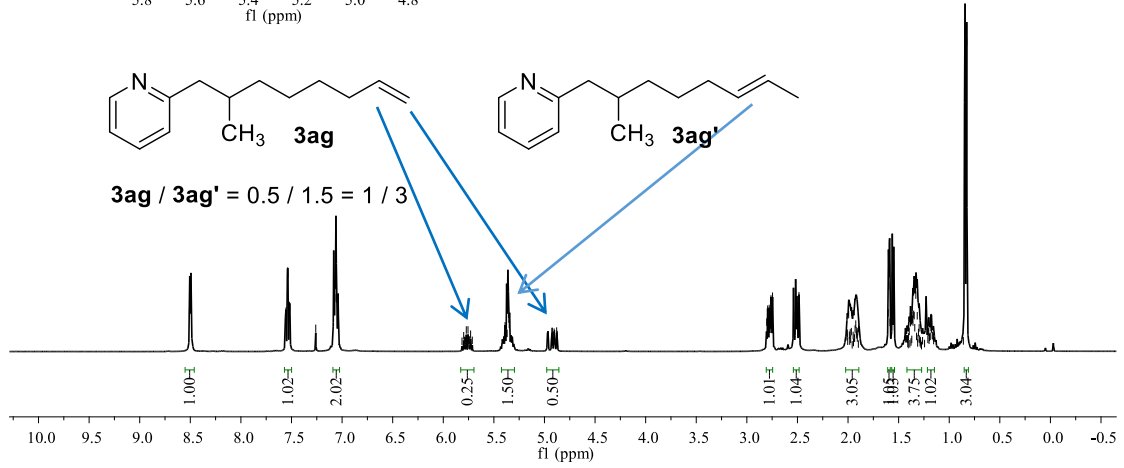




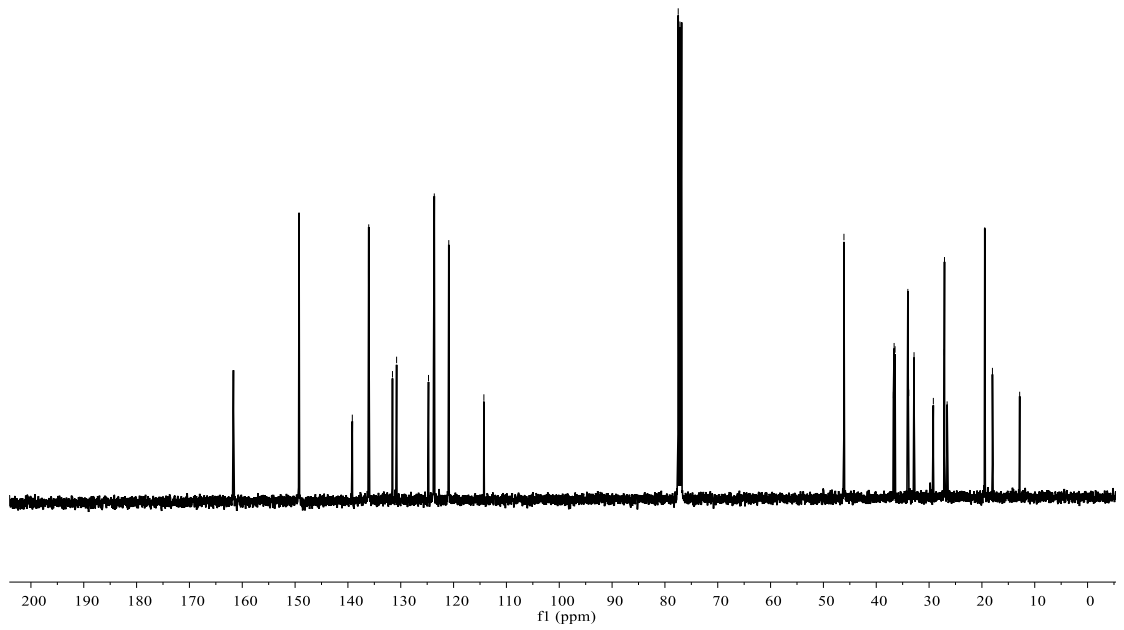


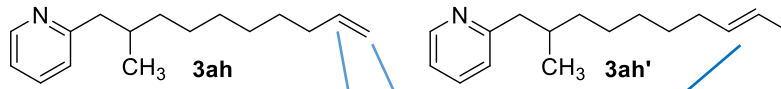
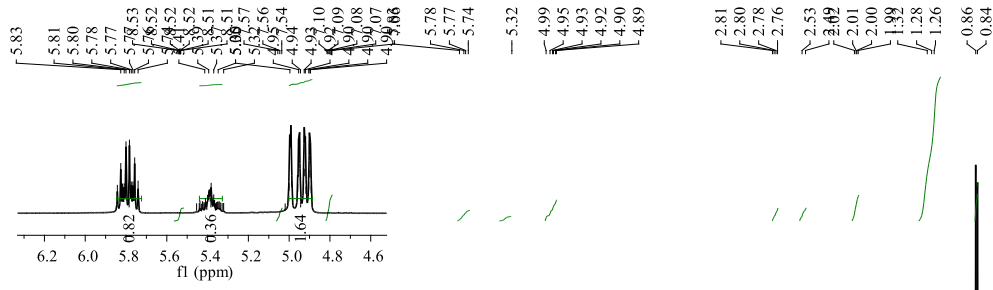


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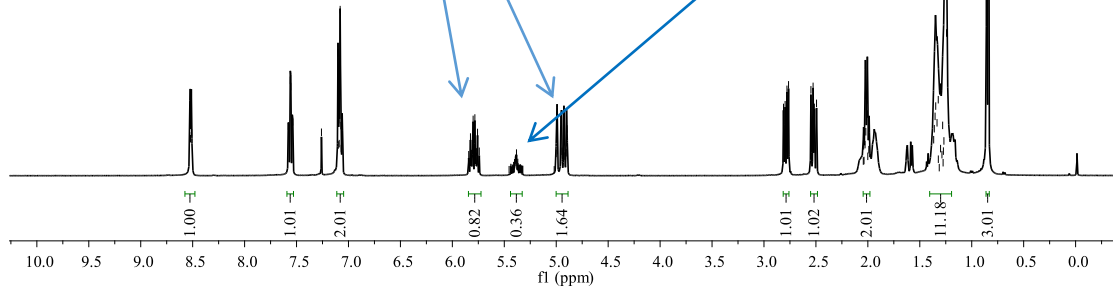


- 161.67  
 - 149.25  
 ✓ 139.17  
 ✓ 136.06  
 ✓ 131.57  
 ✓ 130.79  
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 ✓ 123.65  
 ✓ 120.91  
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 ✓ 36.62  
 ✓ 36.44  
 ✓ 34.02  
 ✓ 33.98  
 ✓ 33.85  
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 ✓ 19.48  
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 ✓ 18.01  
 ✓ 12.85

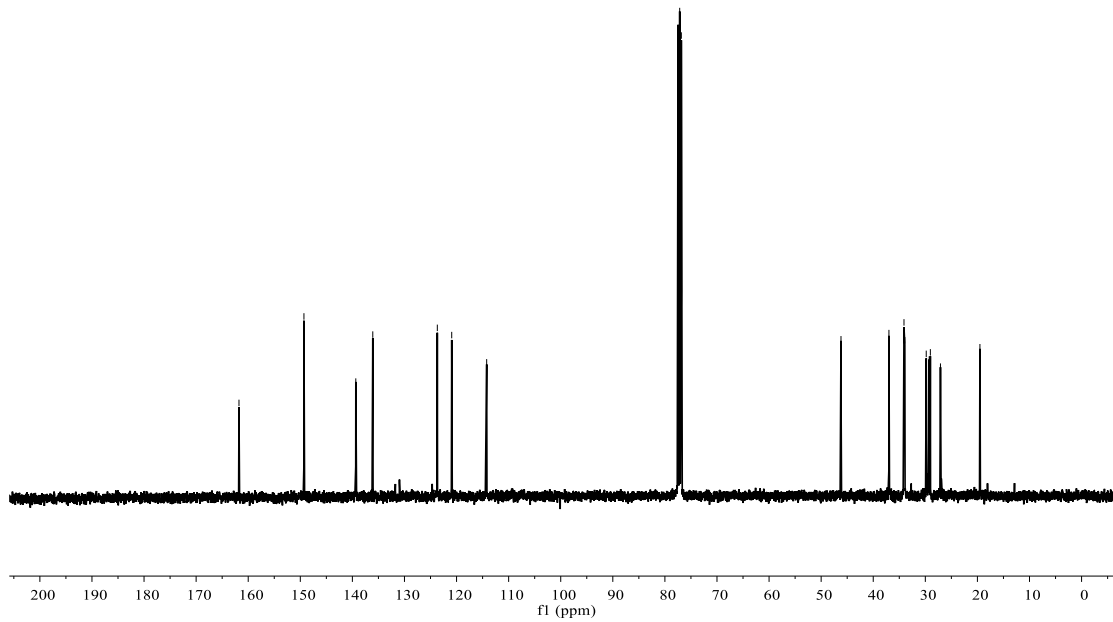


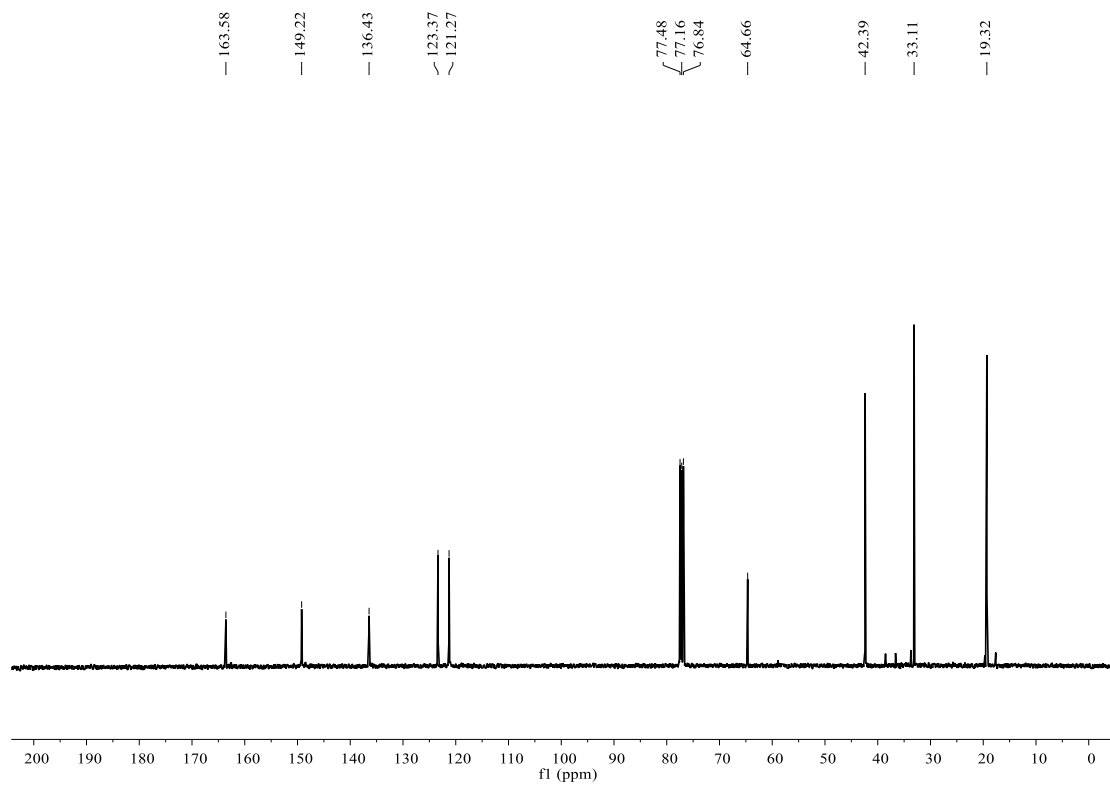
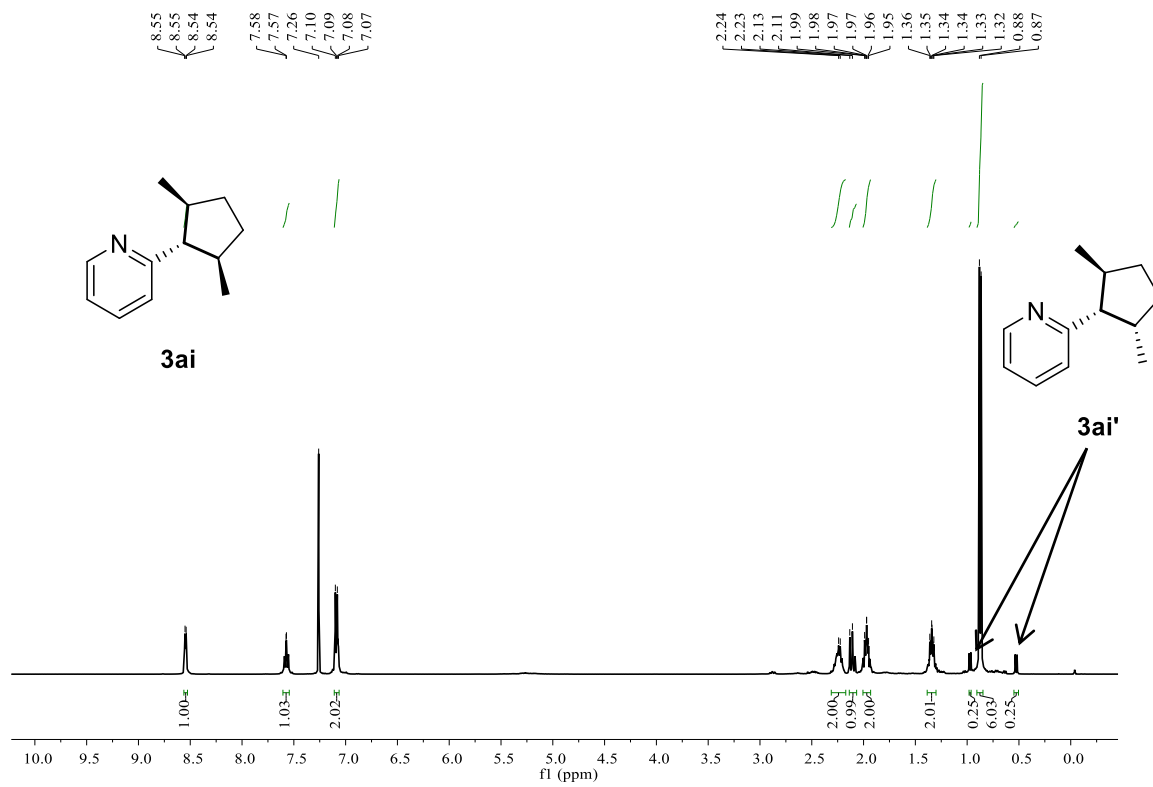


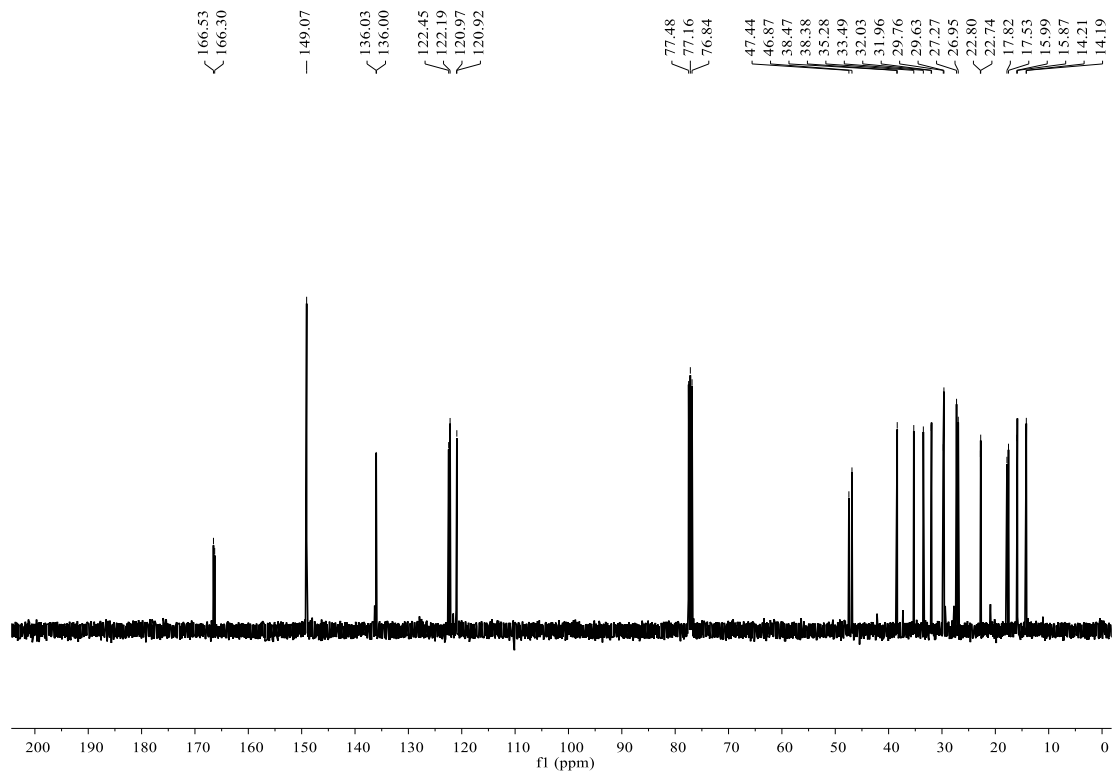
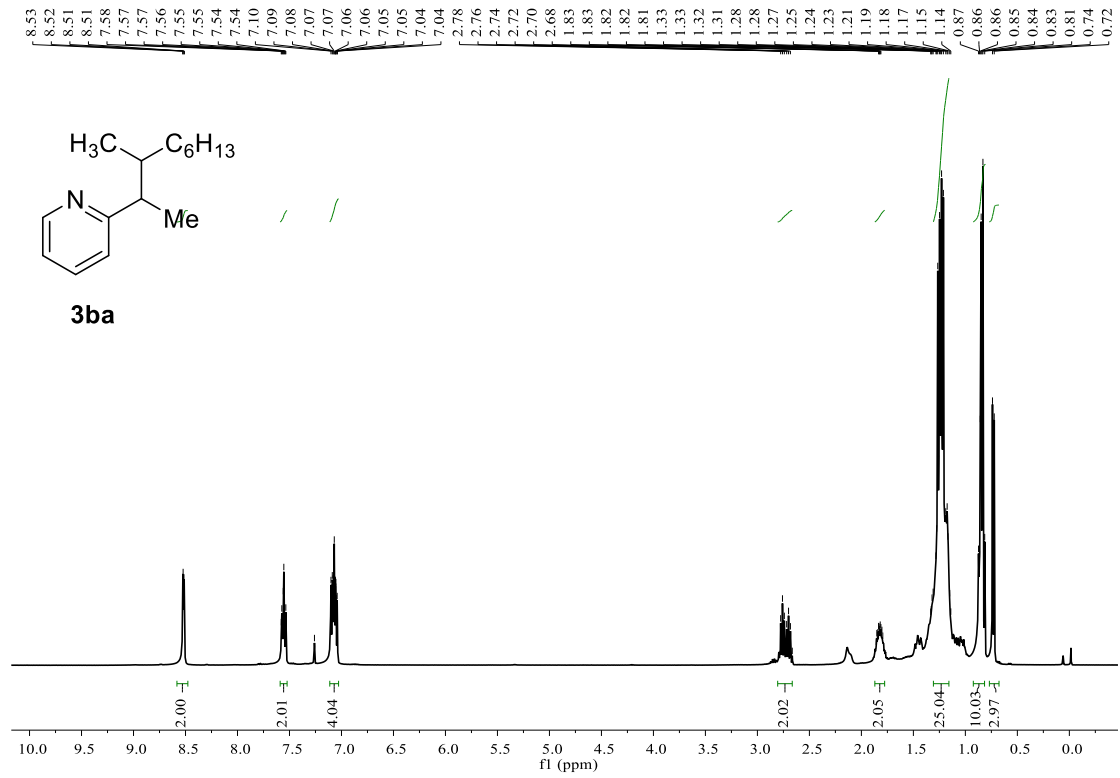
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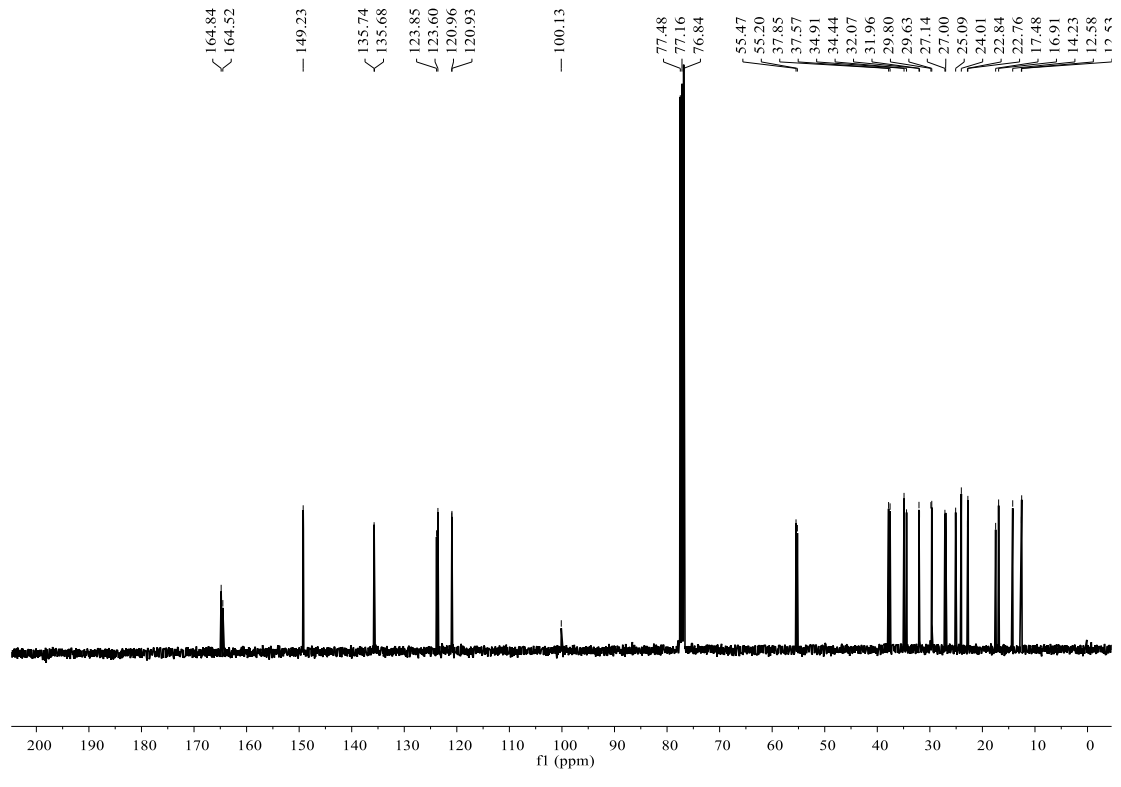
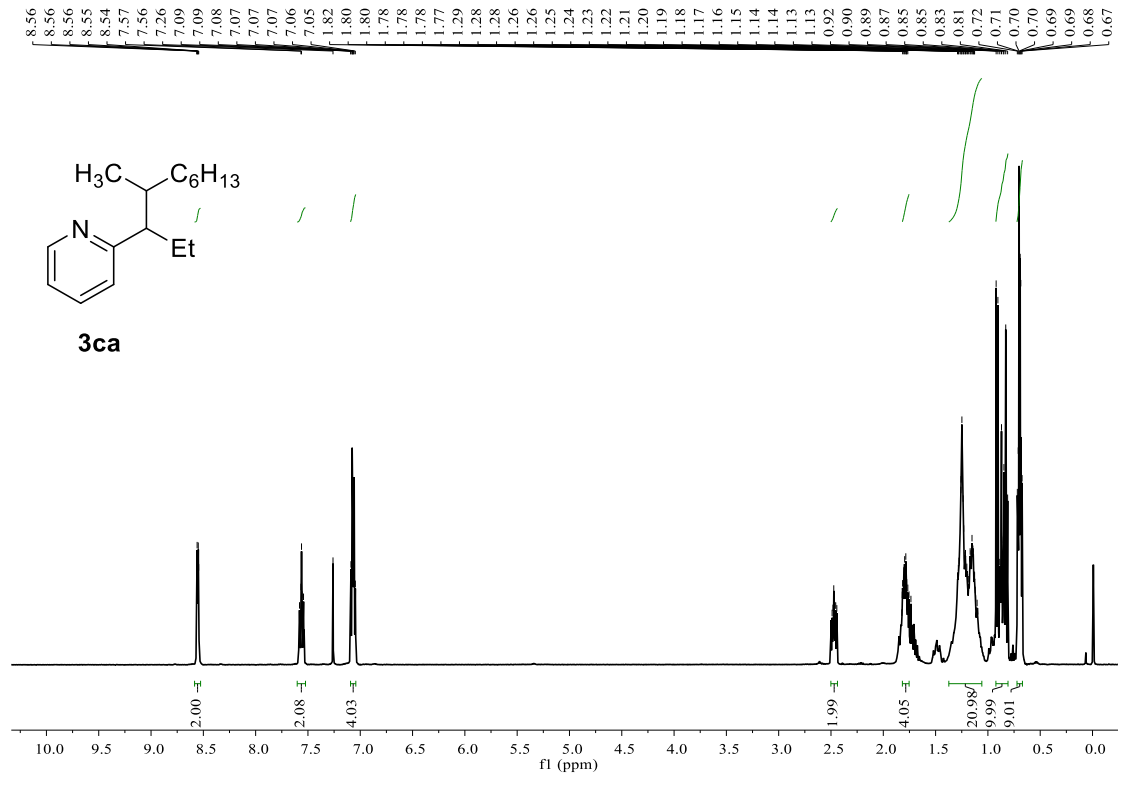


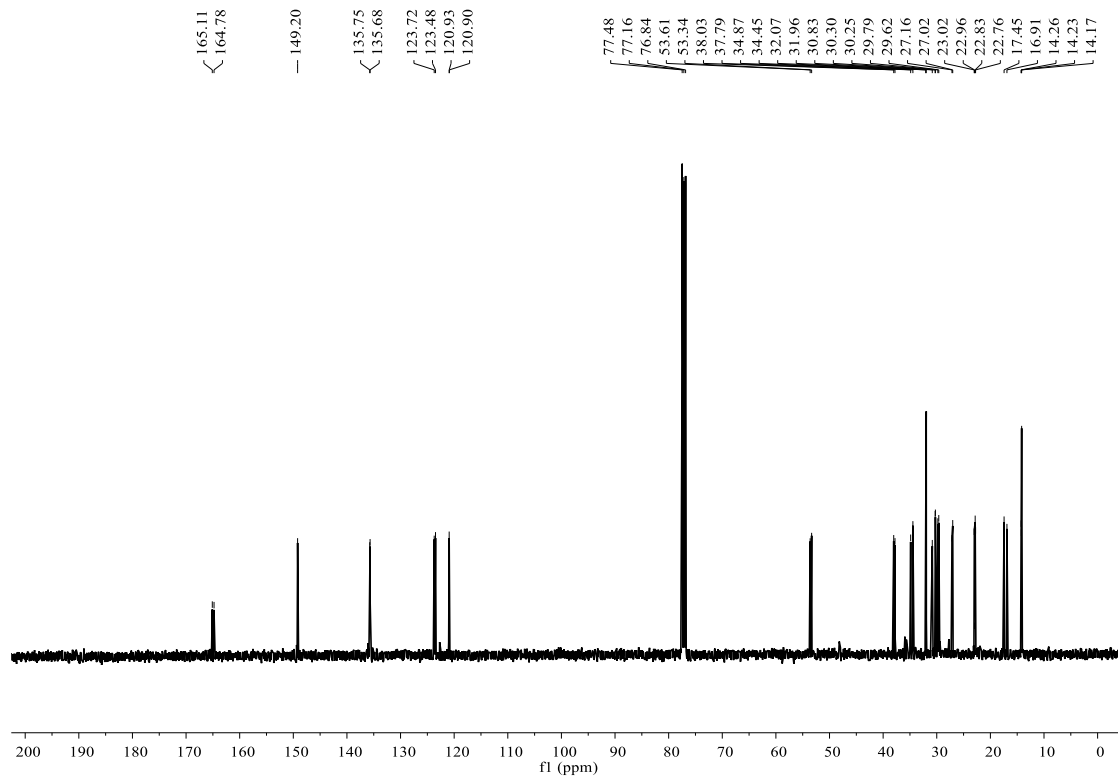
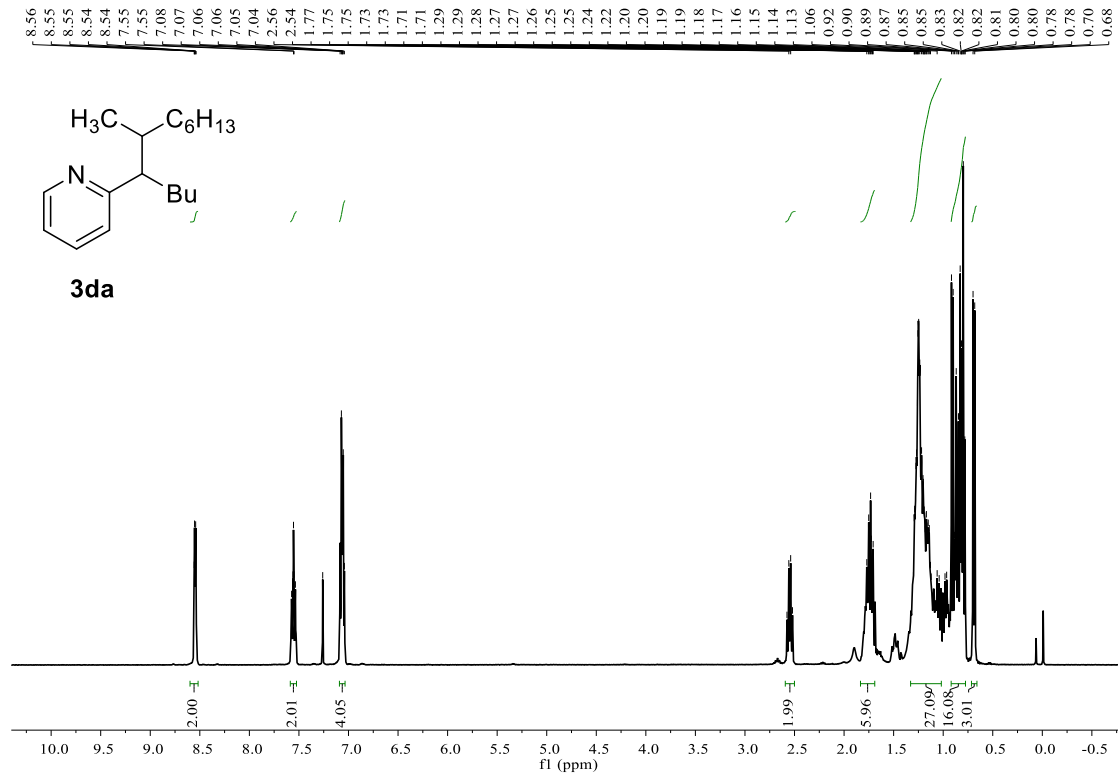
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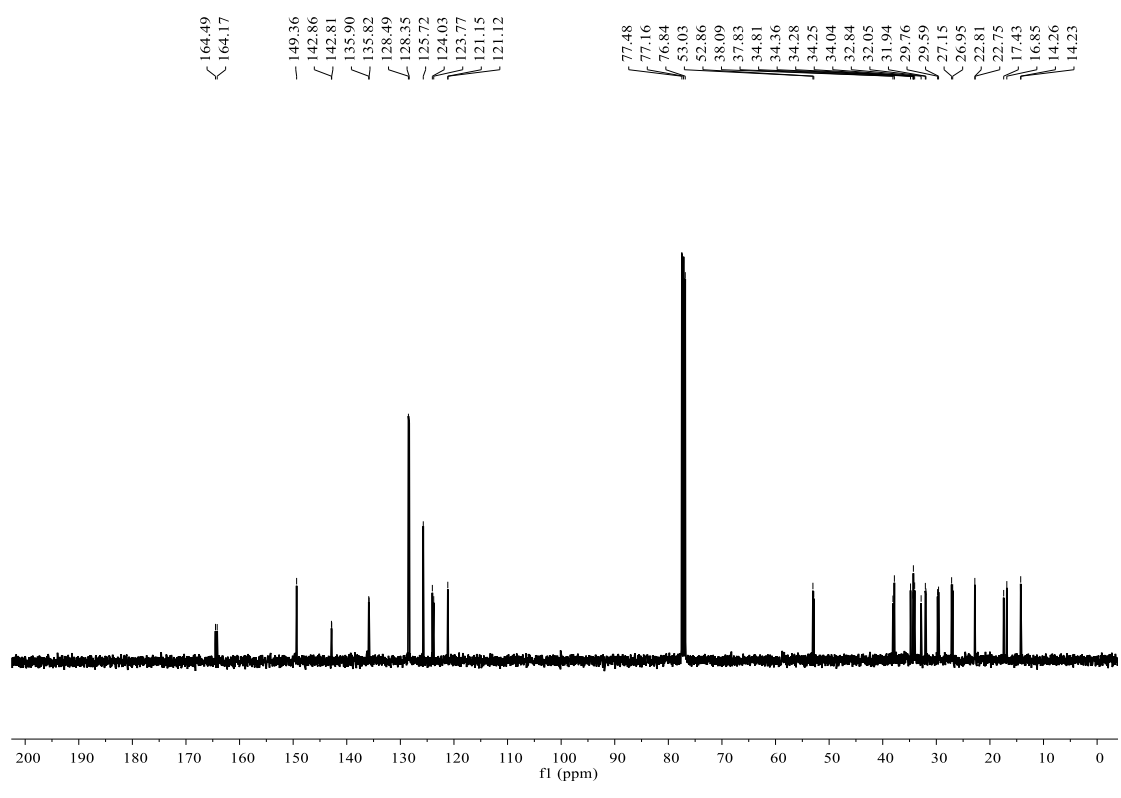
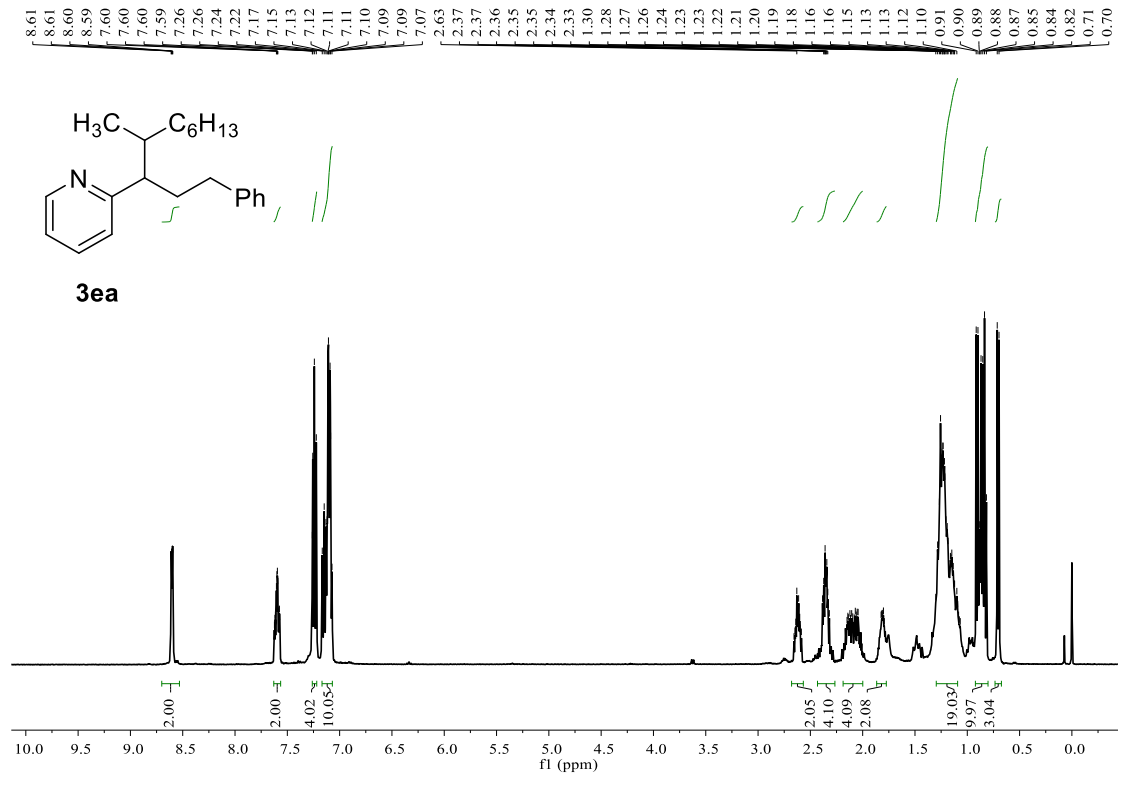


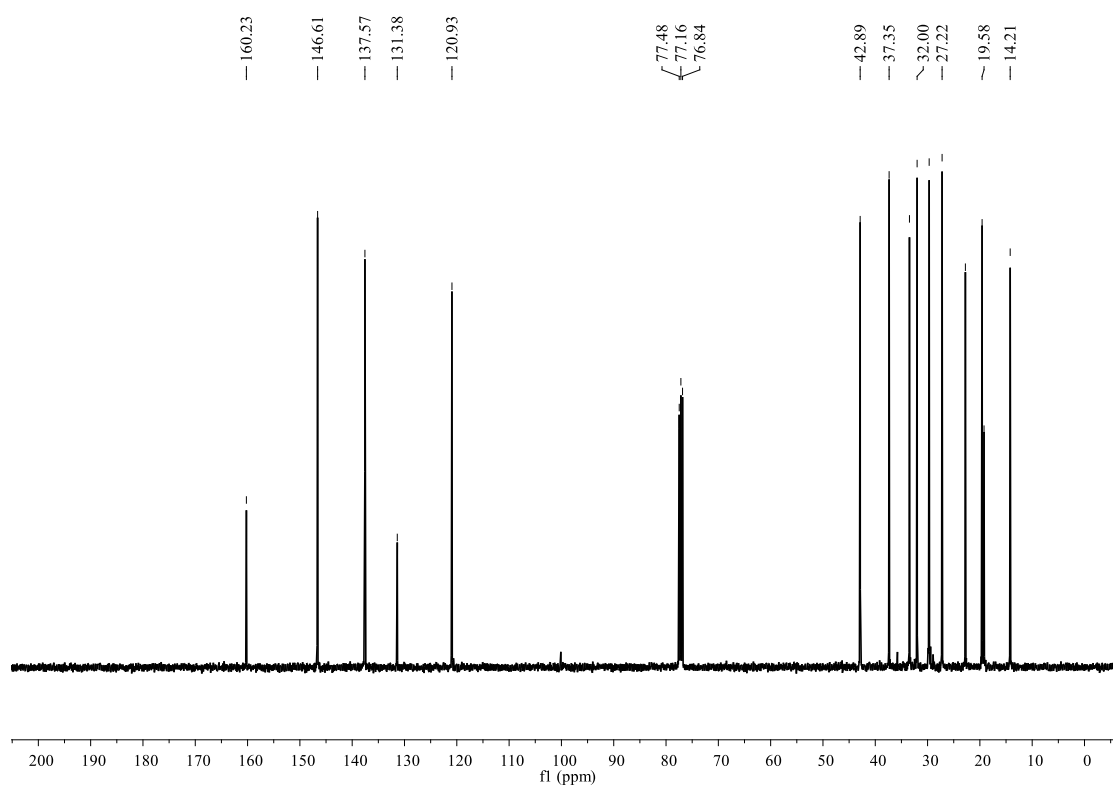
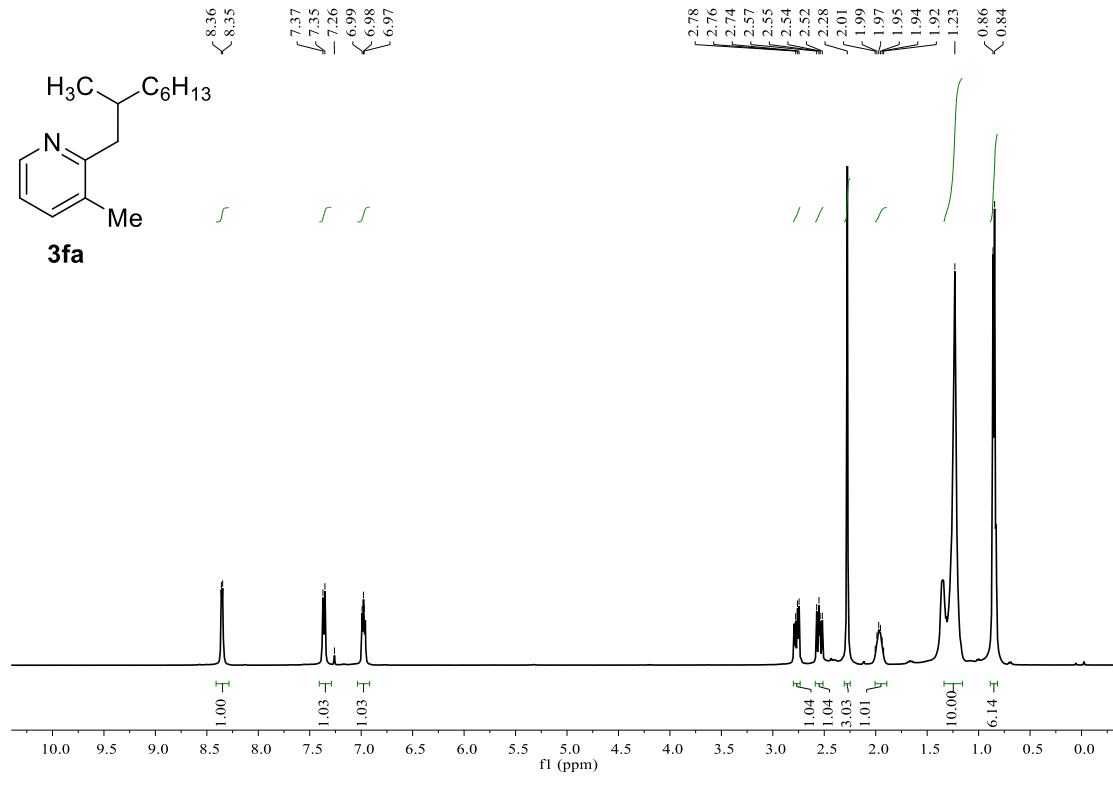




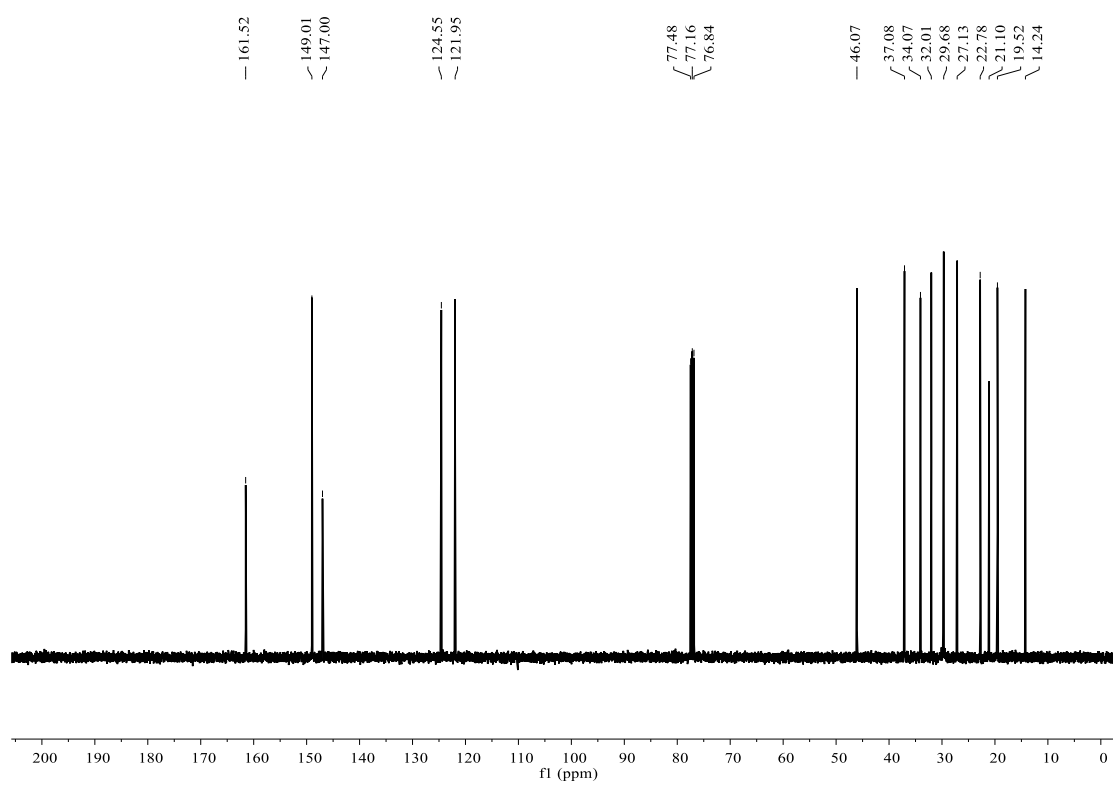
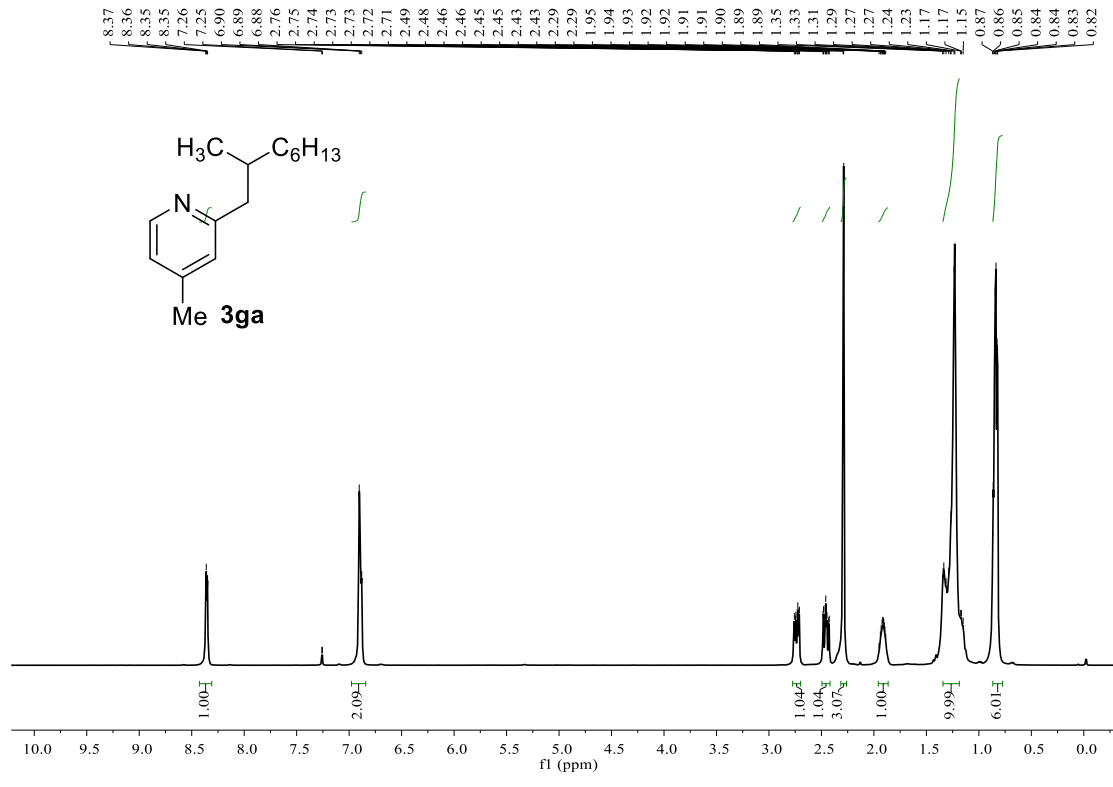


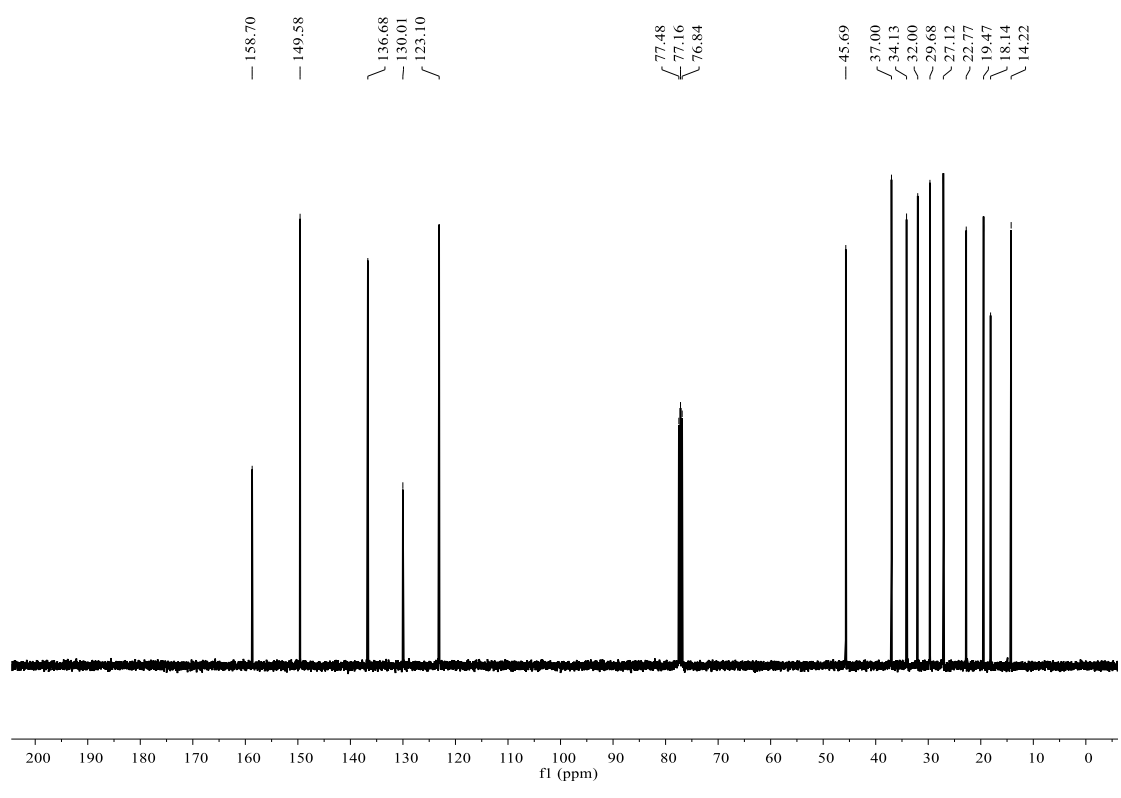
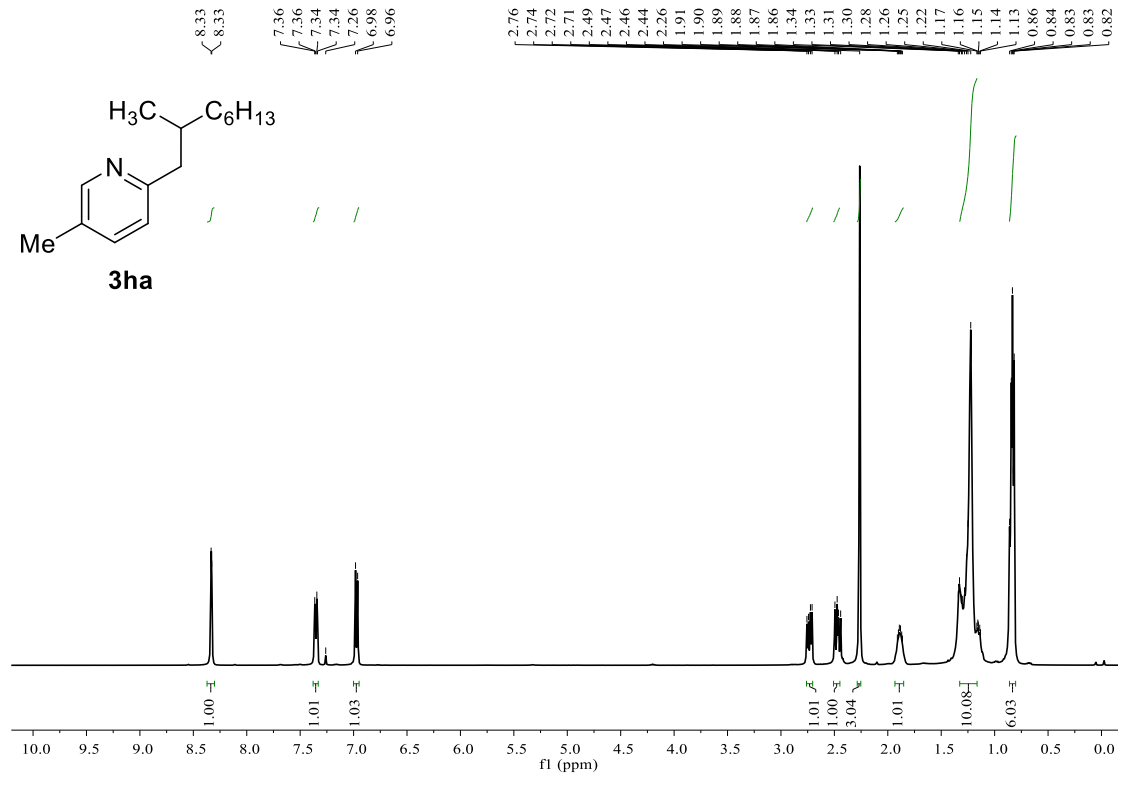


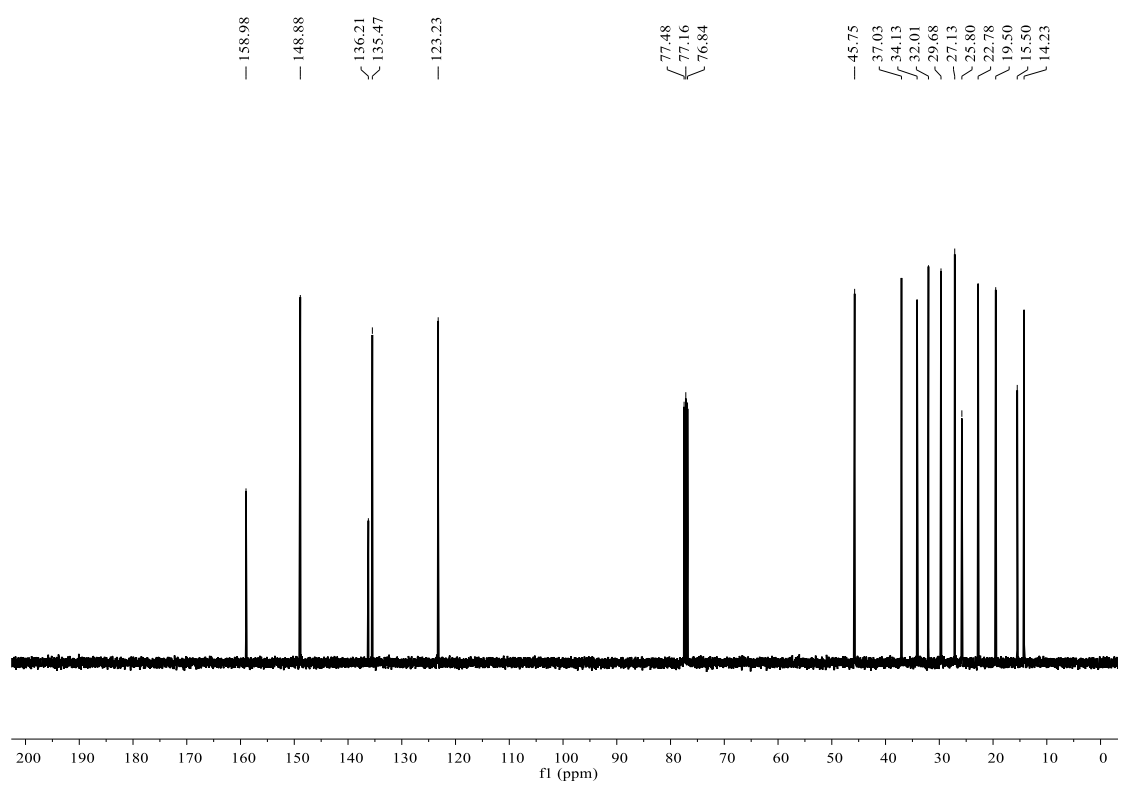
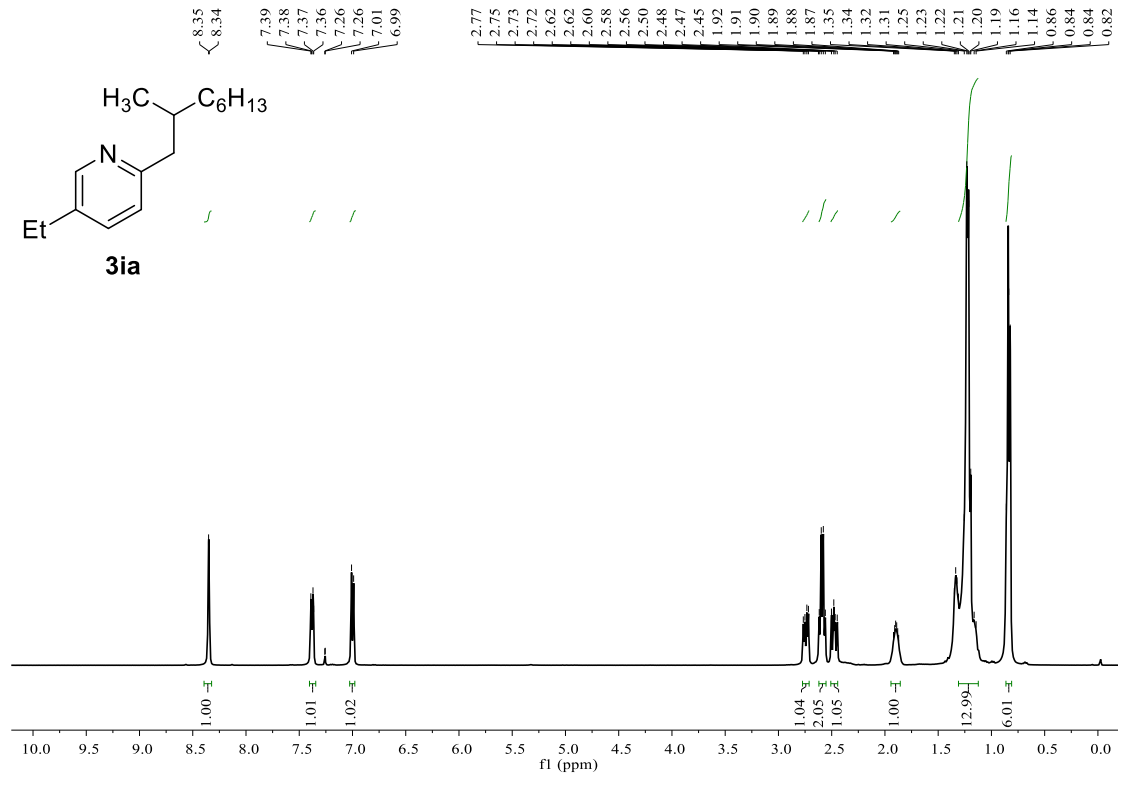


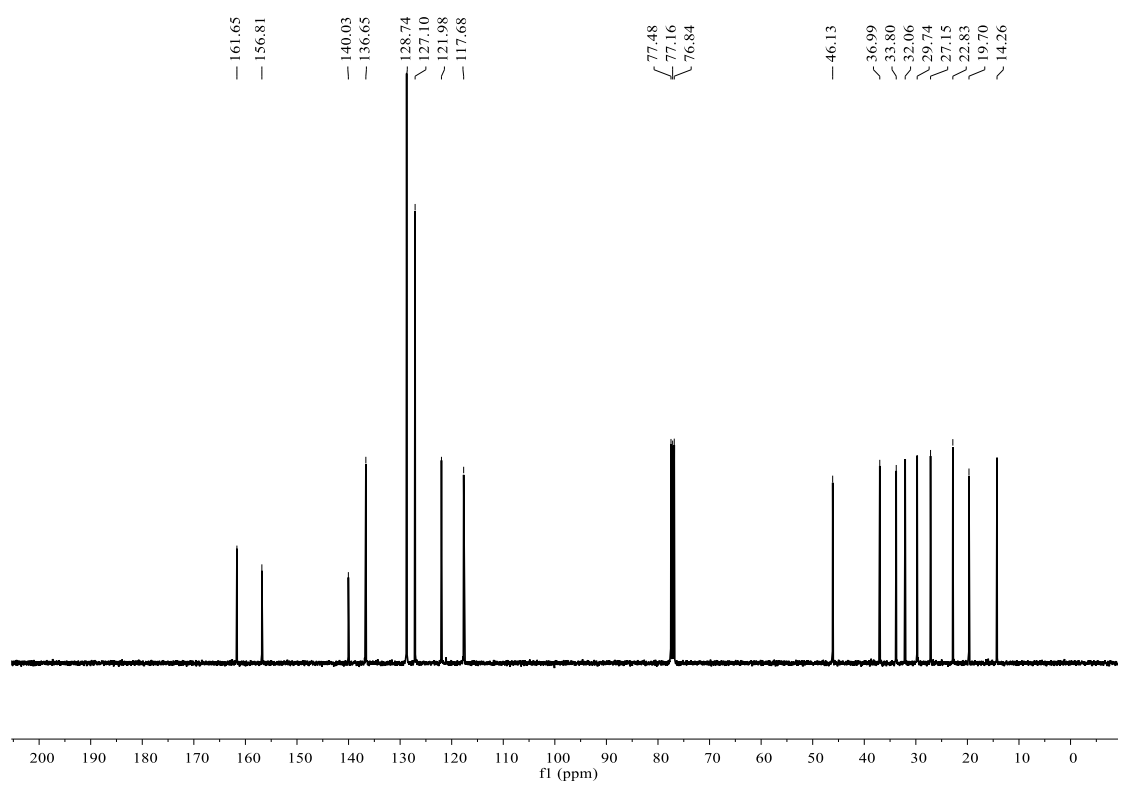
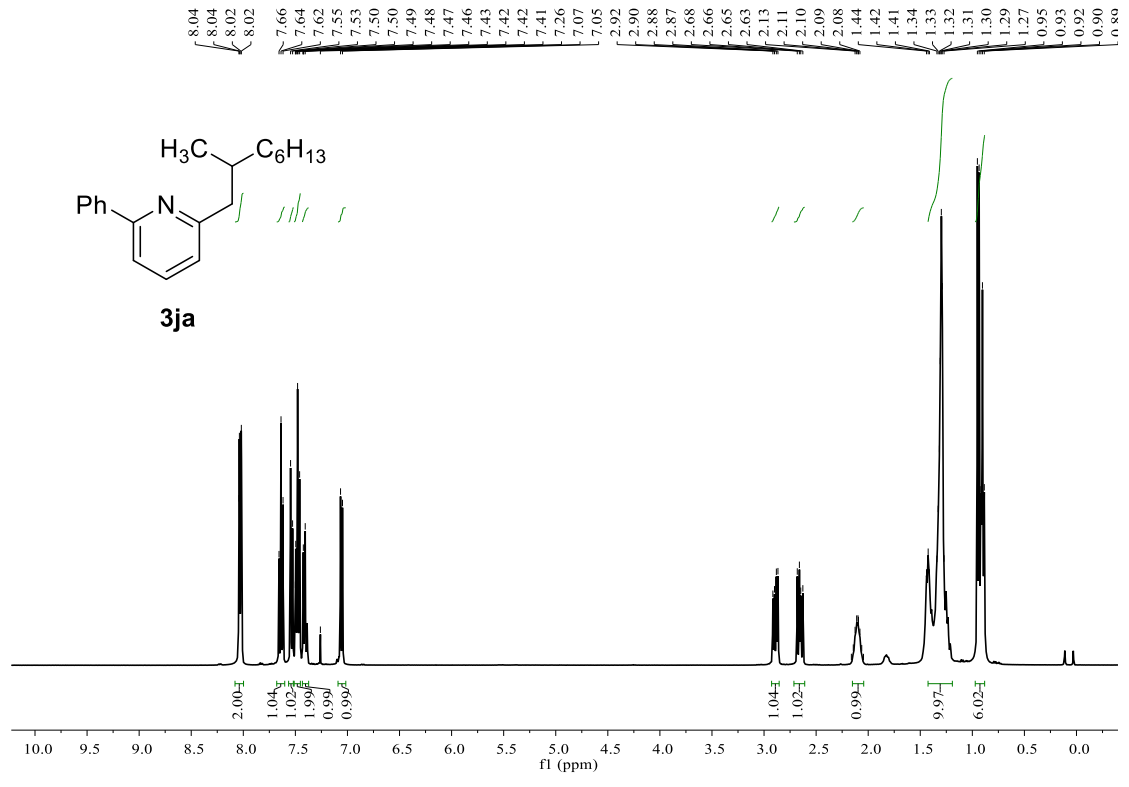


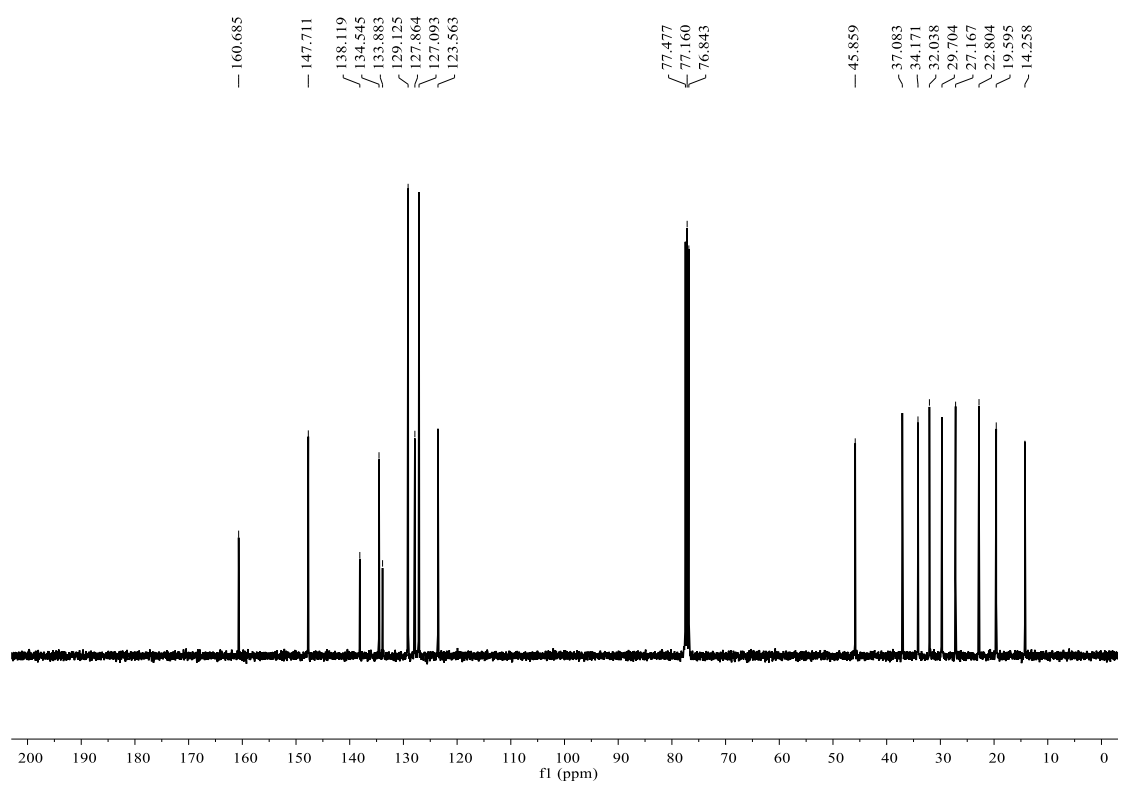
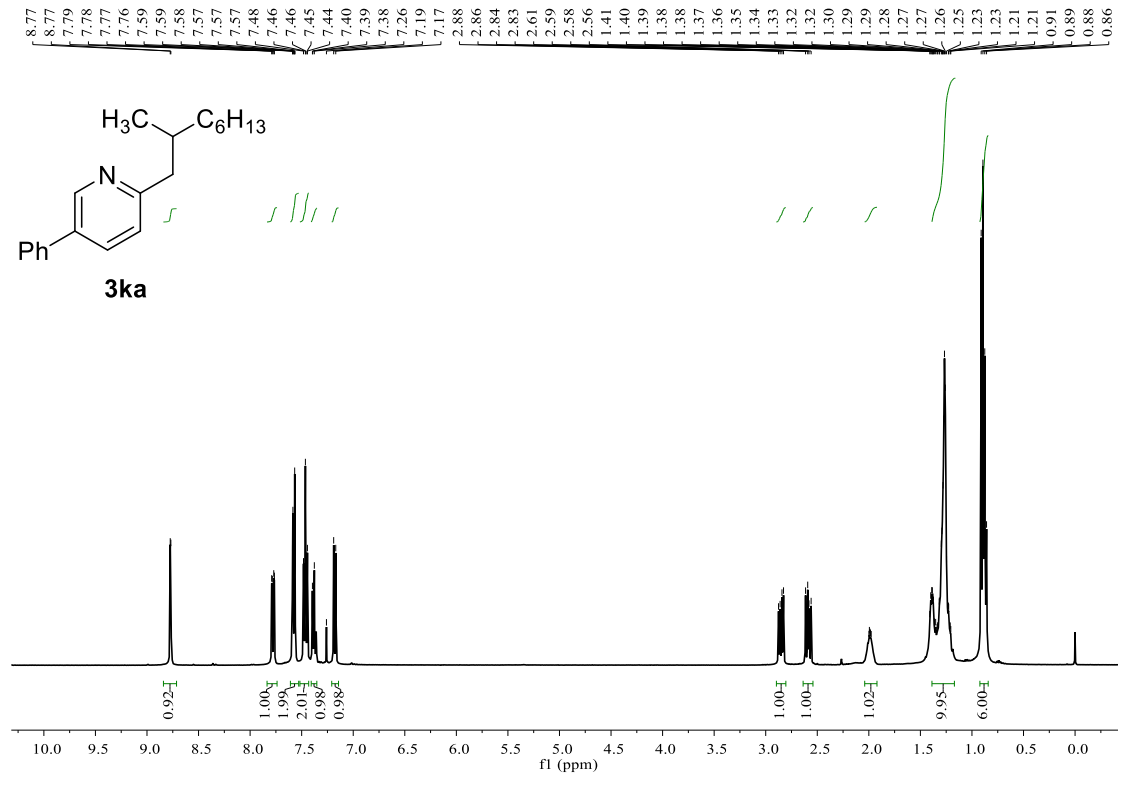


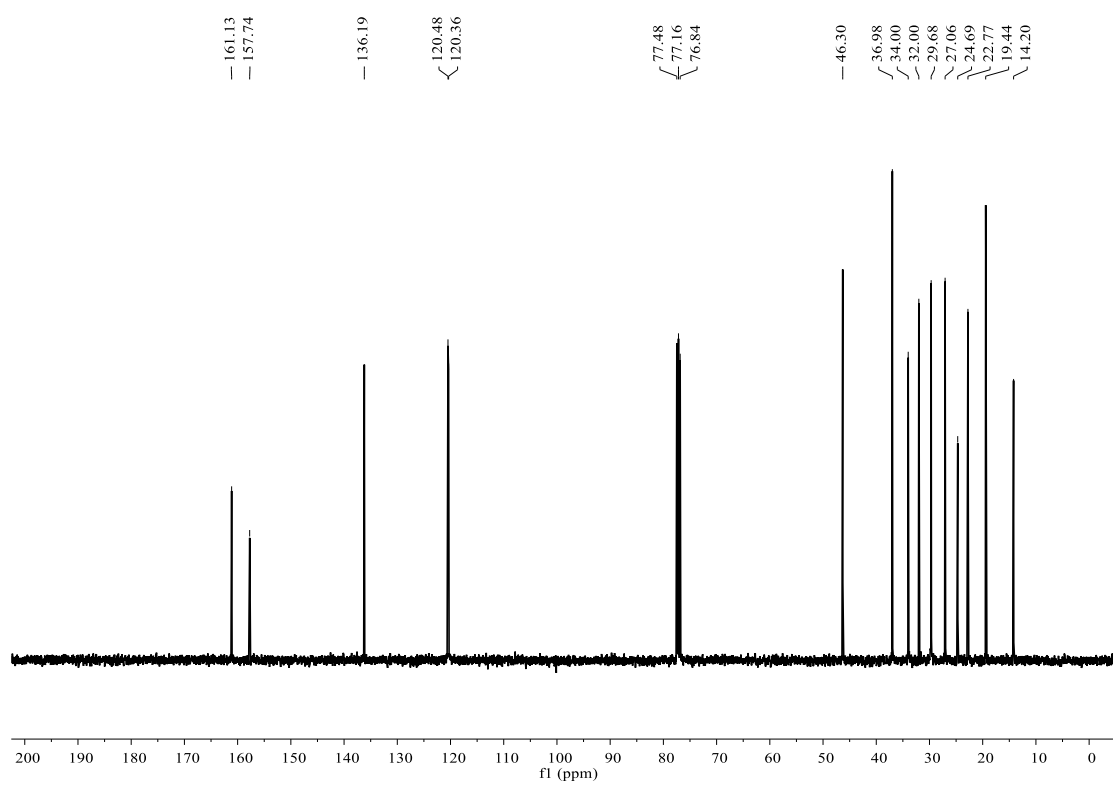
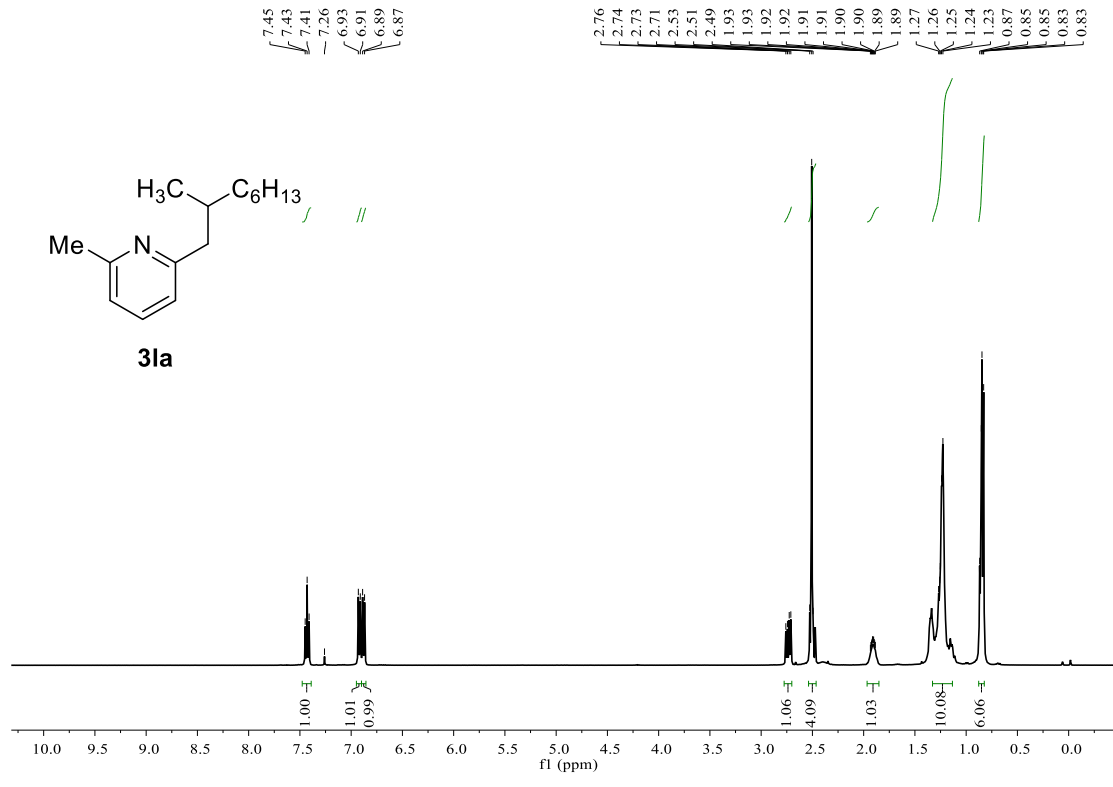


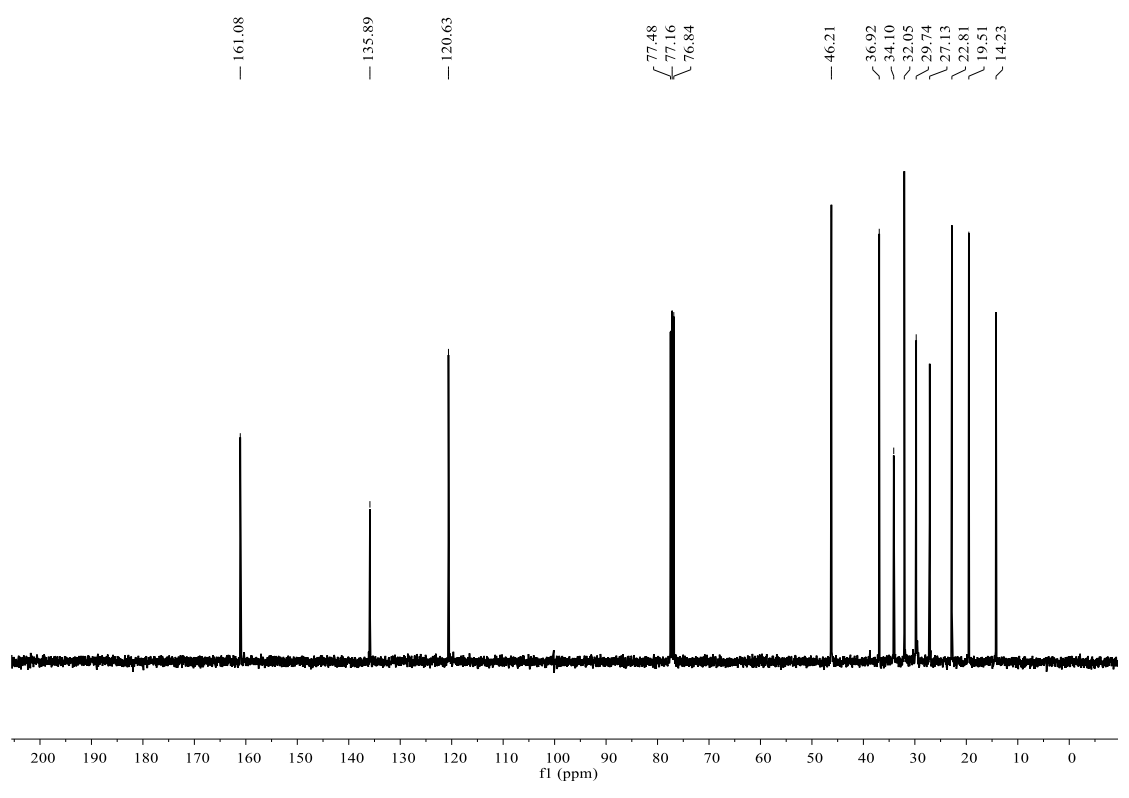
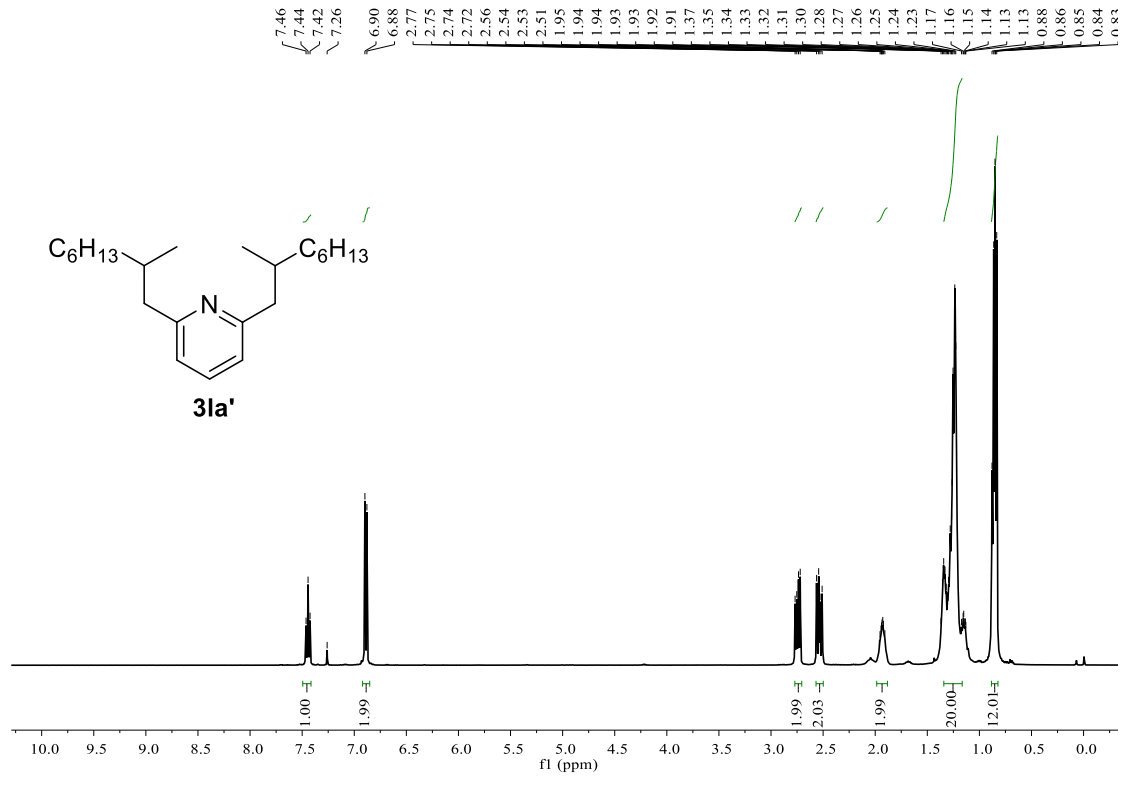


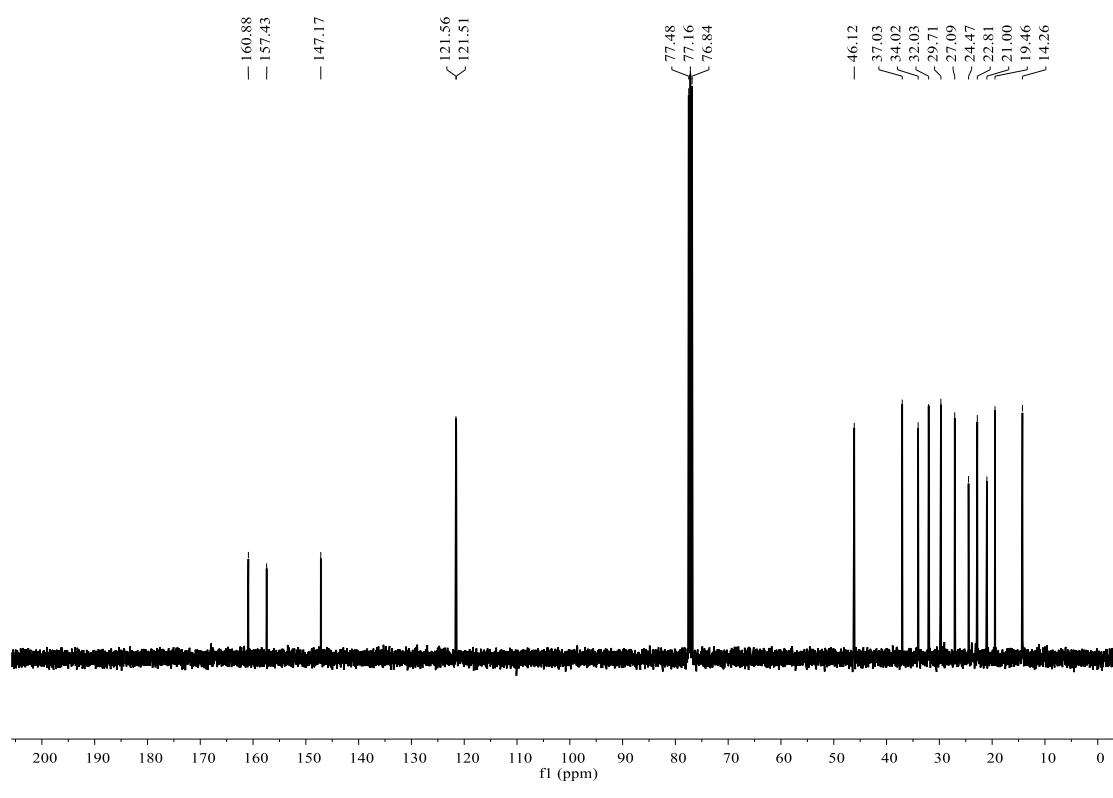
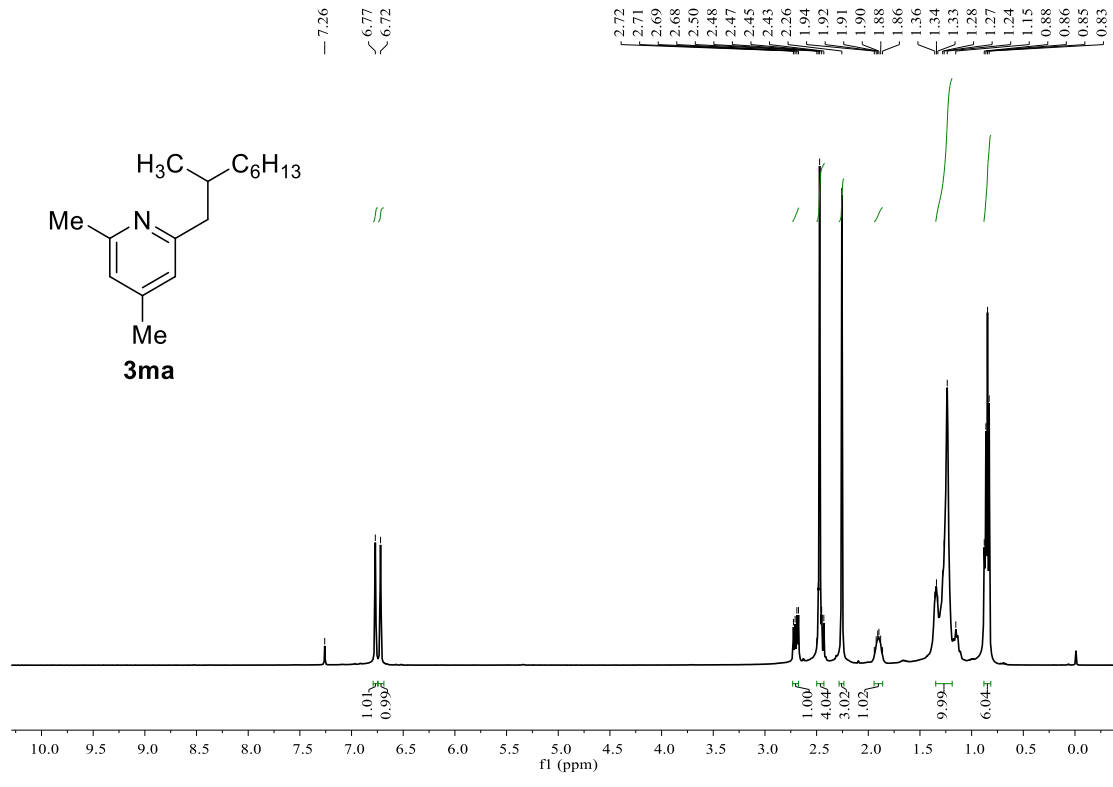




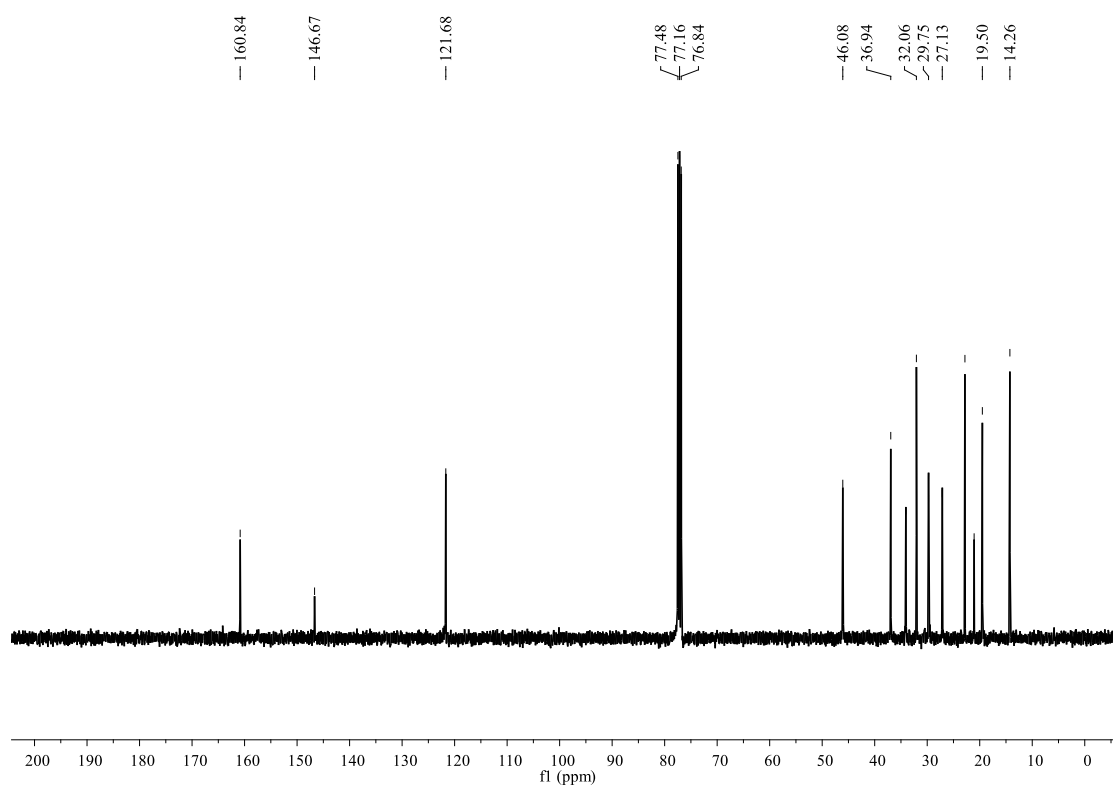
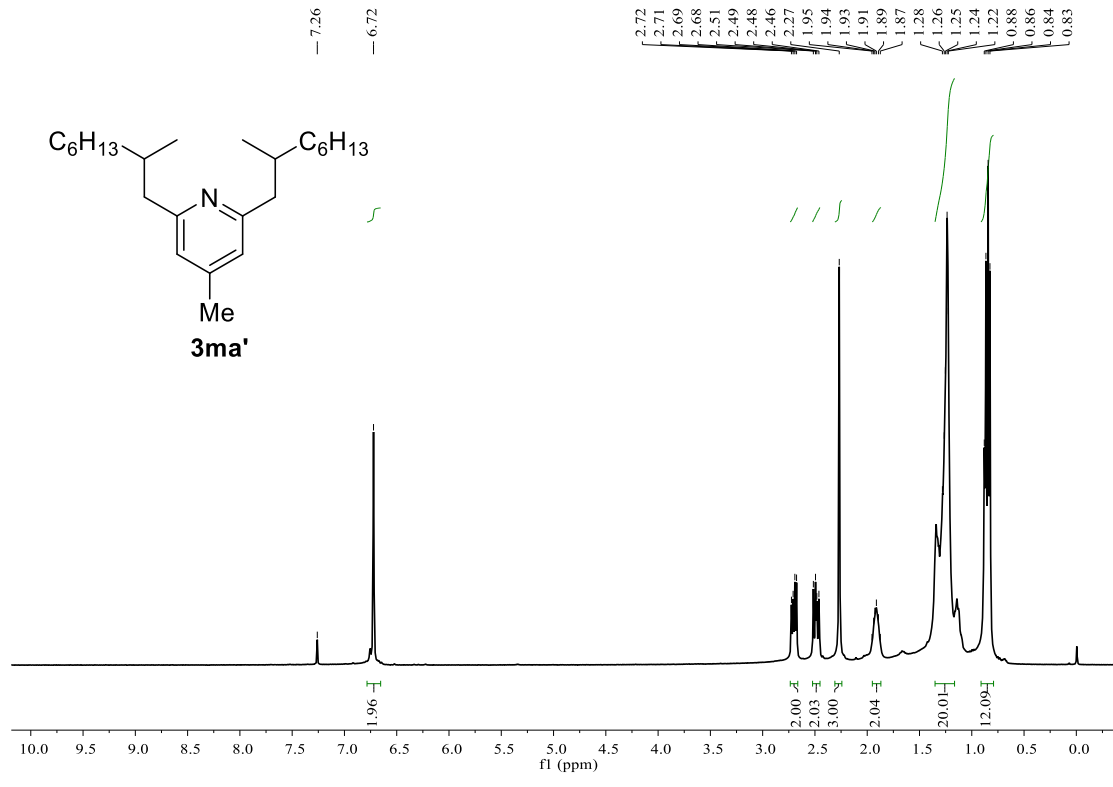




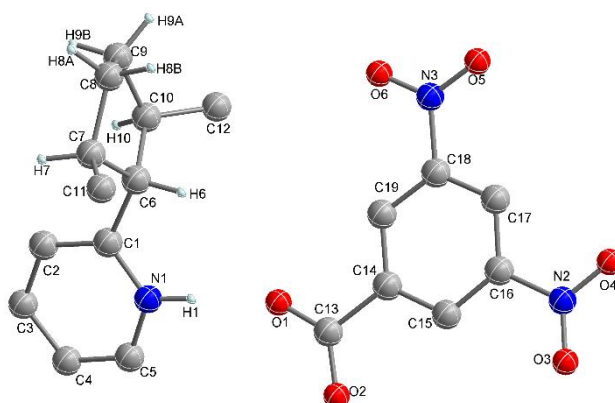








## 7. X-ray Diffraction Data of 3*ai*-3,5-dinitrobenzoate



Crystal structure of **3*ai*-3,5-dinitrobenzoate**

Table s1. Crystal data and structure refinement for P20190605b.

Identification code	P20190605b
Empirical formula	C <sub>19</sub> H <sub>21</sub> N <sub>3</sub> O <sub>6</sub>
Formula weight	387.14
Temperature	294.15 K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 10.03310(10) Å    α = 108.0000(10) deg.
	b = 11.89880(10) Å    β = 99.4130(10) deg.
	c = 13.4124(2) Å    γ = 106.6790(10) deg.
Volume	1401.73(3) Å <sup>3</sup>
Z, Calculated density	2, 1.420 Mg/m <sup>3</sup>
Absorption coefficient	0.980 mm <sup>-1</sup>
F (000)	624.0
Crystal size	0.28 × 0.22 × 0.18 mm
Theta range for data collection	7.212 to 159.084 deg.
Limiting indices	-10 ≤ h ≤ 12, -14 ≤ k ≤ 15, -17 ≤ l ≤ 16
Reflections collected / unique	12153 / 4784 [R(int) = 0.0878]
Completeness to theta = 25.242	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.5682
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	5893 / 0 / 396
Goodness-of-fit on F <sup>2</sup>	1.093
Final R indices [I > 2σ(I)]	R1 = 0.0572, wR2 = 0.1780
R indices (all data)	R1 = 0.0605, wR2 = 0.1816
Extinction coefficient	0.177(10)
Largest diff. peak and hole	0.26 and -0.33 e.Å <sup>-3</sup>