



## Supporting Information

for

### **A sustainable strategy for the straightforward preparation of 2*H*-azirines and highly functionalized *NH*-aziridines from vinyl azides using a single solvent flow-batch approach**

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**Description of general methods, general procedures,  
characterization data for all compounds and copies of  
<sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, NOESY spectra**

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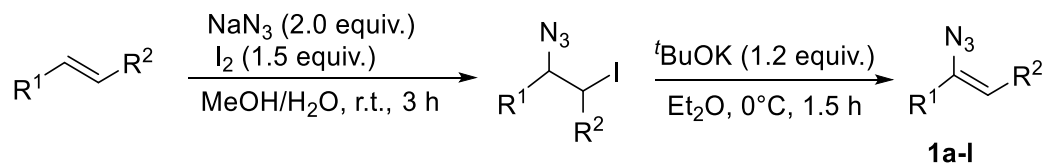
## 1. General methods

All reagents were purchased from Sigma-Aldrich, TCI, Alfa Aesar and Fluorochem, and used without previous purification. Tin-layer chromatography (TLC) was performed on a 0.25 mm precoated silica gel thick plates 60F254 (Merck); the spots were visualized under UV light ( $\lambda = 254$  nm) and/or  $\text{KMnO}_4$  (aq). Flash chromatography was performed using 230–400 mesh silica and a mobile phase as indicated for each entry, according to standard techniques. HRMS spectra were recorded on Agilent 6530 accurate mass Q-TOF instrument using electrospray ion source (ESI), operating in positive and negative ion mode, as described for each entry. Infrared spectra ( $\nu_{\text{max}}$ , FT-IR/ATR) were recorded in reciprocal centimeters ( $\text{cm}^{-1}$ ) using a PerkinElmer 283 Spectrometer (FT-IR) or a PerkinElmer Spectrum Two Spectrometer with a  $2 \times 2$  mm diamond crystal (ATR). Nuclear magnetic resonance spectra were recorded using an Agilent 500 spectrometer (500 MHz for  $^1\text{H}$ , 125 MHz for  $^{13}\text{C}$ , 470 MHz for  $^{19}\text{F}$ ), and a Varian Mercury 300 spectrometer (300 MHz for  $^1\text{H}$ , 75 MHz for  $^{13}\text{C}$ , 282 MHz for  $^{19}\text{F}$ ). The peak of the (residual) solvent signal was used as an internal standard, related to TMS, with  $\delta$  7.26 ppm ( $^1\text{H}$  in  $\text{CDCl}_3$ ),  $\delta$  77.00 ppm ( $^{13}\text{C}$  in  $\text{CDCl}_3$ ). For  $^{19}\text{F}$  spectra, absolute referencing was used. Spin-spin coupling constants ( $J$ ) are given in Hz. Assignment of the resonances was performed by combined application of standard NMR techniques (HSQC, COSY). Assignment of relative stereochemistry for compounds **3k** and **3l** was performed by NOESY experiments.

**Flow equipment:** Solutions of the reagents were introduced into the flow microreactor system using a Harvard PHD 2000 syringe pump, equipped with gastight syringe purchased from SGE (Harvard PHD 2000). A Volcano reactor (Syrris, stainless steel tubular reactor, 4mL) was employed. Connections were obtained using stainless steel and PTFE microtubes with an inner diameter of 500 $\mu\text{L}$ . Microtubes were connected to the reactor by with stainless steel fittings (GL Sciences, 1/16 OUW).

## 2. General Procedure A for the preparation of vinyl azides

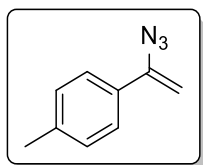
Vinyl azides **1a–l** were prepared according to the reported procedures with slight modification, starting from alkenes.<sup>1,2</sup>



To a solution of alkene (8.5 mmol, 1.0 equiv) in 18 mL of solvent (MeOH/H<sub>2</sub>O = 5:1), sodium azide (17.0 mmol, 2.0 equiv) was added in one portion at 25 °C, then iodine (12.8 mmol, 1.5 equiv) was added, and the solution was stirred for 3 h. Subsequently, CH<sub>2</sub>Cl<sub>2</sub> (90 mL) and H<sub>2</sub>O (50 mL) were added, the organic layer separated and washed with an aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (5%) until the organic phase appeared colourless. The organic layer was washed twice with H<sub>2</sub>O (2 × 35 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated under reduced pressure and the product was immediately used for the next synthetic step without further purification. To a solution of the obtained beta-iodo azide in Et<sub>2</sub>O (17 mL), *t*-BuOK (10.2 mmol, 1.2 equiv) was added at 0 °C and the reaction mixture was stirred at the same temperature for 1.5 h. Subsequently, the mixture was filtered through a pad of diatomaceous earth, and the solvent evaporated under reduced pressure. Purification by column chromatography afforded vinyl azides **1a–l** as reported for each entry.

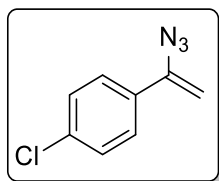
### Characterization data for vinyl azides **1a–l**

#### 1-(1-Azidovinyl)-4-methylbenzene (**1a**)



Prepared according General Procedure A. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.9, Hexane) to afford vinyl azide **1a** as a pale yellow oil (812 mg, 60%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 7.51 (d, *J* = 8.0 Hz, 2H, Ar–H), 7.21 (d, *J* = 8.0 Hz, 2H, Ar–H), 5.43 (d, *J* = 2.2 Hz, 1H), 4.96 (d, *J* = 2.2 Hz, 1H), 2.41 (s, 3H, CH<sub>3</sub>). Analytical data (NMR) in agreement with those reported in the literature.<sup>3</sup>

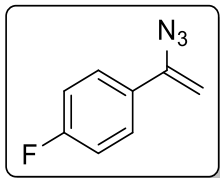
#### 1-(1-Azidovinyl)-4-chlorobenzene (**1b**)



Prepared according General Procedure A. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.9, Hexane) to afford vinyl azide **1b** as a pale yellow oil (1068

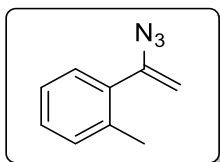
mg, 70%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.50–7.48 (m, 2H, Ar–H), 7.34–7.31 (m, 2H, Ar–H), 5.43 (d,  $J = 2.6$  Hz, 1H), 4.97 (d,  $J = 2.6$  Hz, 1H). Analytical data (NMR) in agreement with those reported in the literature.<sup>3</sup>

#### 1-(1-Azidovinyl)-4-fluorobenzene (1c)



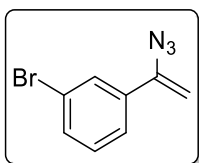
Prepared according General Procedure A. The product was purified by column chromatography ( $\text{SiO}_2$ ,  $R_f$  0.9, Hexane) to afford vinyl azide **1c** as a pale yellow oil (651 mg, 47%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.57–7.50 (m, 2H, Ar–H), 7.08–7.00 (m, 2H, Ar–H), 5.37 (d,  $J = 2.6$  Hz, 1H), 4.94 (d,  $J = 2.6$  Hz, 1H).  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -112.31 (ddd,  $J = 13.6, 8.5, 5.3$  Hz). Analytical data (NMR) in agreement with those reported in the literature.<sup>3</sup>

#### 1-(1-Azidovinyl)-2-methylbenzene (1d)



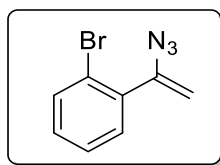
Prepared according General Procedure A. The product was purified by column chromatography ( $\text{SiO}_2$ ,  $R_f$  0.9, Hexane) to afford vinyl azide **1f** as a pale yellow oil (730 mg, 54%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.28–7.18 (m, 4H, Ar–H), 5.05 (s, 1H), 4.74 (s, 1H), 2.39 (s, 3H,  $\text{CH}_3$ ). Analytical data (NMR) in agreement with those reported in the literature.<sup>3</sup>

#### 1-(1-Azidovinyl)-3-bromobenzene (1e)



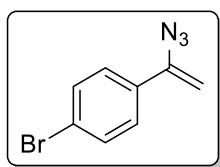
Prepared according General Procedure A. The product was purified by column chromatography ( $\text{SiO}_2$ ,  $R_f$  0.9, Hexane) to afford vinyl azide **1d** as a brown oil (952 mg, 50%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.72–7.70 (m, 1H, Ar–H), 7.50–7.45 (m, 2H, Ar–H), 7.22 (t,  $J = 7.9$  Hz, 1H, Ar–H), 5.45 (d,  $J = 2.7$  Hz, 1H), 4.98 (d,  $J = 2.7$  Hz, 1H). Analytical data (NMR) in agreement with those reported in the literature.<sup>4</sup>

### 1-(1-Azidovinyl)-2-bromobenzene (**1f**)



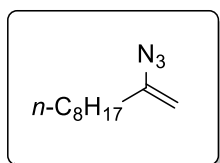
Prepared according General Procedure A. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.9, Hexane) to afford vinyl azide **1f** as a brown oil (1257 mg, 66%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 7.62 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.36–7.32 (m, 2H, Ar-H), 7.26–7.23 (m, 1H, Ar-H), 5.12 (d, *J* = 1.2 Hz, 1H), 4.85 (d, *J* = 1.2 Hz, 1H). Analytical data (NMR) in agreement with those reported in the literature.<sup>3</sup>

### 1-(1-Azidovinyl)-4-bromobenzene (**1g**)



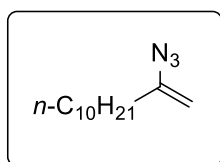
Prepared according General Procedure A. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.9, Hexane) to afford vinyl azide **1g** as a brown oil (1714 mg, 90%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 7.49–7.47 (m, 2H, Ar-H), 7.44–7.42 (m, 2H, Ar-H), 5.44 (d, *J* = 2.4 Hz, 1H), 4.98 (d, *J* = 2.4 Hz, 1H). Analytical data (NMR) in agreement with those reported in the literature.<sup>3</sup>

### 2-Azidodec-1-ene (**1h**)



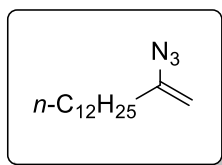
Prepared according General Procedure A. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.95, Hexane) to afford azide **1i** as a colourless oil (478 mg, 31%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 4.62 (broad signal, 2H, C=CH<sub>2</sub>), 2.07 (t, *J* = 7.5 Hz, 2H), 1.51–1.42 (m, 2H), 1.37–1.26 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H). Analytical data (NMR) in agreement with those reported in the literature.<sup>5</sup>

### 2-Azidododec-1-ene (**1i**)



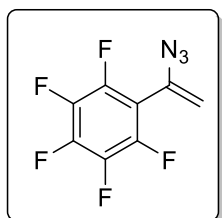
Prepared according General Procedure A. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.95, Hexane) to afford azide **1j** as a colourless oil (961 mg, 54%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 4.62 (broad signal, 2H, C=CH<sub>2</sub>), 2.06 (t, *J* = 7.5 Hz, 2H), 1.49–1.44 (m, 2H), 1.38–1.23 (m, 14H), 0.88 (t, *J* = 6.8 Hz, 3H). Analytical data (NMR) in agreement with those reported in the literature.<sup>6</sup>

## 2-Azidotetradec-1-ene (1j)



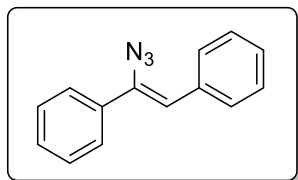
Prepared according General Procedure A. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.95, Hexane) to afford azide **1k** as a colourless oil (1190 mg, 59%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 4.62 (d, *J* = 0.8 Hz, 2H, C=CH<sub>2</sub>), 2.06 (t, *J* = 7.5 Hz, 2H), 1.49–1.43 (m, 2H), 1.36–1.24 (broad signal, 18H), 0.88 (t, *J* = 6.6 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm) δ 147.0 (N<sub>3</sub>C=CH<sub>2</sub>), 98.1 (N<sub>3</sub>C=CH<sub>2</sub>), 33.8 (CH<sub>2</sub>), 32.1 (CH<sub>2</sub>), 29.8 (3 × CH<sub>2</sub>), 29.7 (CH<sub>2</sub>), 29.5 (2 × CH<sub>2</sub>), 29.0 (CH<sub>2</sub>), 27.5 (CH<sub>2</sub>), 22.8 (CH<sub>2</sub>), 14.2 (CH<sub>3</sub>). IR (ATR, neat)/cm<sup>-1</sup> 2955, 2853, 2104, 1626, 1466, 1274. HRMS (ESITOF) *m/z* (M–H)<sup>–</sup> calcd for C<sub>14</sub>H<sub>27</sub>N<sub>3</sub> 236,2132; found 236,2125.

## 1-(1-Azidovinyl)-2,3,4,5,6-pentafluorobenzene (1k)



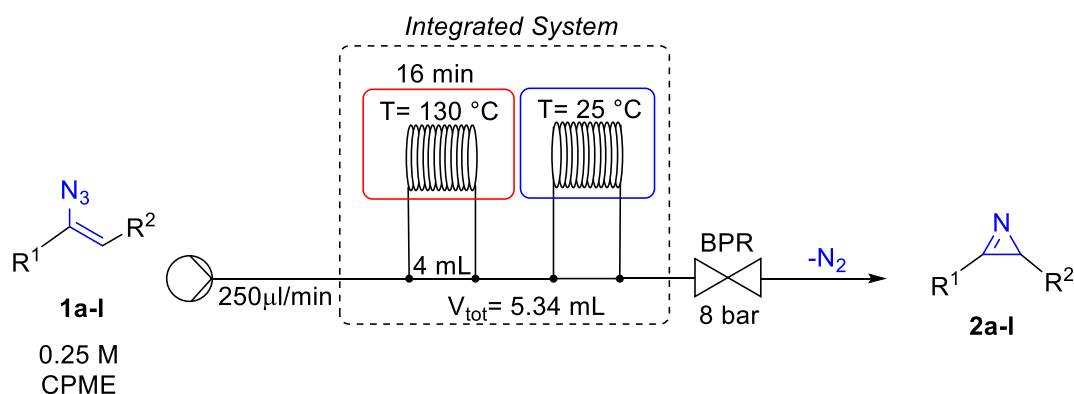
Prepared according General Procedure A. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.9, Hexane) to afford vinyl azide **1l** as a pale yellow oil (700 mg, 35%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 5.40 (d, *J* = 2.3 Hz, 1H), 5.12 (d, *J* = 2.3 Hz, 1H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>, ppm) δ -138.69 – -141.44 (m), -152.16 (tt, *J* = 21.0, 2.4 Hz), -158.59 – -162.86 (m). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm) δ 144.6 (m, C–F), 141.8 (m, C–F), 137.8 (m, C–F), 132.0 (N<sub>3</sub>C=CH<sub>2</sub>), 110.5 (m, Ar–C<sub>q</sub>), 108.3 (N<sub>3</sub>C=CH<sub>2</sub>). IR (ATR, neat)/cm<sup>-1</sup> 2151, 2102, 1493, 1327, 989, 707. HRMS (ESITOF) *m/z* (M–H)<sup>–</sup> calcd for C<sub>8</sub>HF<sub>5</sub>N<sub>3</sub> 234,0096; found 234,0110.

## (Z)-(1-Azidoethene-1,2-diyl)dibenzene (1l)



Prepared according General Procedure A. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.9, Hexane) to afford azide **1m** as a colourless oil (564 mg, 30%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 7.72 (d, *J* = 7.8 Hz, 2H), 7.54–7.42 (m, 7H), 7.28–7.26 (m, 1H), 6.03 (s, 1H). Analytical data (NMR) in agreement with those reported in the literature.<sup>6</sup>

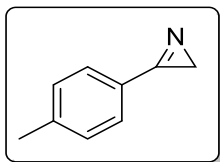
### 3. General Procedure B



The process can be executed using a PHD ULTRA™ Syringe Pump (Harvard Apparatus), a Volcano reactor (4 mL, Syrris) and a back-pressure regulator of 8 bar. A solution of vinyl azide (1.0 mmol) in CPME (4 mL, 0.25 M) was introduced by syringe pump into the pre-heated reactor (130 °C, probe feedback control) with a flow rate of 250 µL/min. Subsequently, fresh solvent (CPME) was fluxed in the reactor upon the same conditions, and the outgoing solution was collected in a round bottom flask. The solvent was evaporated under reduced pressure and the products were obtained after chromatography or without any further purification as indicated for each entry.

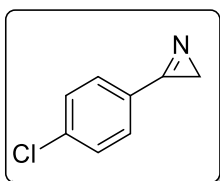
#### Characterization data for azirines 2a–l

##### 3-(*p*-Tolyl)-2*H*-azirine (2a)



Prepared according General Procedure B using vinyl azide **1a** (159 mg). The product was obtained without any further purification as a yellow oil (131 mg, 99%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 7.80 (d, *J* = 8.0 Hz, 2H, Ar–H), 7.36 (d, *J* = 8.0 Hz, 2H, Ar–H), 2.46 (s, 3H, Ar–CH<sub>3</sub>), 1.76 (s, 2H, NCH<sub>2</sub>). Analytical data (NMR) in agreement with those reported in the literature.<sup>7</sup>

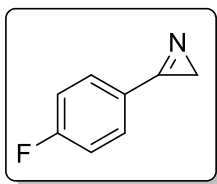
##### 3-(4-Chlorophenyl)-2*H*-azirine (2b)



Prepared according General Procedure B using vinyl azide **1b** (180 mg). The product was obtained without further purification as a yellow oil (150 mg, 99%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 7.86–7.83 (m, 2H, Ar–H), 7.56–7.53 (m, 2H, Ar–H), 1.75 (s, 2H, NCH<sub>2</sub>). Analytical data (NMR) in agreement with those reported in the literature.<sup>7</sup>

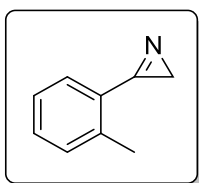


### 3-(4-Fluorophenyl)-2*H*-azirine (2c)



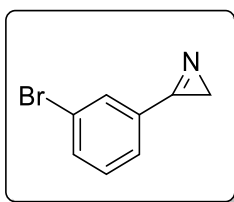
Prepared according General Procedure B using vinyl azide **1c** (163 mg). The product was obtained without further purification as a yellow oil (134 mg, 99%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 7.94–7.90 (m, 2H, Ar–H), 7.28–7.24 (m overlapping CDCl<sub>3</sub>, 2H, Ar–H), 1.80 (s, 2H, NCH<sub>2</sub>). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>, ppm) δ -104.79 (m, 1F) Analytical data (NMR) in agreement with those reported in the literature.<sup>7</sup>

### 3-(*o*-Tolyl)-2*H*-azirine (2d)



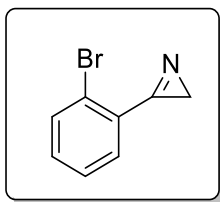
Prepared according General Procedure B using vinyl azide **1d** (159 mg). The product was obtained without further purification as a yellow oil (131 mg, 99%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 7.75 (d, *J* = 7.5 Hz, 1H, Ar–H), 7.47 (t, *J* = 7.5 Hz, 1H, Ar–H), 7.39 (t, *J* = 7.5 Hz, 1H, Ar–H), 7.35 (d, *J* = 7.6 Hz, 1H, Ar–H) 2.70 (s, 3H, Ar–CH<sub>3</sub>), 1.69 (s, 2H, NCH<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm) δ 165.1 (C=N), 140.9 (Ar), 132.5 (Ar), 132.3 (Ar), 130.9 (Ar), 126.3 (Ar), 124.0 (Ar), 19.9 (NCH<sub>2</sub>), 17.9 (Ar–CH<sub>3</sub>). IR (ATR, neat)/cm<sup>-1</sup> 3042, 2976, 2924, 1734, 1488, 981, 759, 669. HRMS (ESITOF) *m/z* (M+H)<sup>+</sup> calcd for C<sub>9</sub>H<sub>10</sub>N 132,0813; found 132,0807.

### 3-(3-Bromophenyl)-2*H*-azirine (2e)



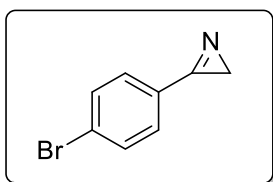
Prepared according General Procedure B using vinyl azide **1e** (224 mg). The product was obtained without further purification as a brown oil (195 mg, 99%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 8.05 (t, *J* = 1.7 Hz, 1H, Ar–H), 7.90–7.81 (m, 1H, Ar–H), 7.72 (ddd, *J* = 8.0, 1.7, 1.0 Hz, 1H, Ar–H), 7.44 (t, *J* = 8.0 Hz, 1H, Ar–H), 1.82 (s, 2H, C=NCH<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm) δ 165.5 (C=N), 135.9 (Ar), 132.5 (Ar), 130.77 (Ar), 128.1 (Ar), 127.6 (Ar), 123.2 (Ar), 20.4 (NCH<sub>2</sub>). IR (film)/cm<sup>-1</sup> 3052, 2978, 2101, 1742, 1566, 1291, 993, 787. HRMS (ESITOF) *m/z* (M+H)<sup>+</sup> calcd for C<sub>8</sub>H<sub>7</sub>BrN 195,9762; found 195,9753.

### 3-(2-Bromophenyl)-2*H*-azirine (2f)



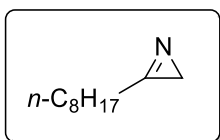
Prepared according General Procedure B using vinyl azide **1f** (224 mg). The product was obtained without further purification as a brown oil (195 mg, 99%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 7.84(dd, *J* = 8.0, 2.0 Hz, 1H, Ar-H), 7.73 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar-H), 7.50 (td, *J* = 8.0, 1.0 Hz, 1H), 7.43 (td, *J* = 8.0, 2.0 Hz, 1H), 1.88 (s, 2H, C=NCH<sub>2</sub>). Analytical data (NMR) in agreement with those reported in the literature.<sup>8</sup>

### 3-(4-Bromophenyl)-2*H*-azirine (2g)



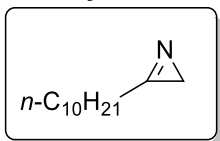
Prepared according General Procedure B using vinyl azide **1g** (224 mg). The product was obtained without further purification as a brown oil (192 mg, 98%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 7.77 (d, *J* = 8.4 Hz, 2H, 2 × Ar-H), 7.71 (d, *J* = 8.4 Hz, 2H, 2 × Ar-H), 1.81 (s, 2H, C=NCH<sub>2</sub>). Analytical data (NMR) in agreement with those reported in the literature.<sup>7</sup>

### 3-Octyl-2*H*-azirine (2h)



Prepared according General Procedure B (twice) using vinyl azide **1i** (181 mg). The product was obtained without further purification as a yellow oil (150 mg, 98%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 2.78 (t, *J* = 7.3 Hz, 2H, CH<sub>2</sub>C=N), 1.74 (q, *J* = 7.3 Hz, 2H), 1.43–1.39 (m, 2H), 1.36 (s, 2H, C=NCH<sub>2</sub>), 1.35–1.21 (broad signal, 8H), 0.88 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm) δ 169.8 (CH<sub>2</sub>C=N), 31.8, 29.2 (2 × CH<sub>2</sub>), 29.1, 28.4, 24.1, 22.6, 18.8, 14.0 (CH<sub>3</sub>). IR (ATR, neat)/cm<sup>-1</sup> 2955, 2925, 2856, 1466, 1260, 725. HRMS (ESI-TOF) *m/z* (M+H)<sup>+</sup> calcd for C<sub>10</sub>H<sub>20</sub>N 154,1596; found 154,1591.

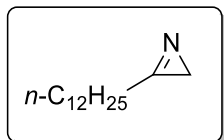
### 3-Decyl-2*H*-azirine (2i)



Prepared according General Procedure B using vinyl azide **1j** (209 mg). The product was obtained without further purification as a brown oil (175 mg, 97%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 2.78 (t, *J* = 7.3 Hz, 2H, CH<sub>2</sub>C=N), 1.74 (q, *J* = 7.3 Hz, 2H), 1.43–1.20 (broad signal, 16H), 0.88 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (125

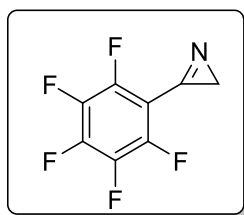
MHz, CDCl<sub>3</sub>, ppm)  $\delta$  169.9 (CH<sub>2</sub>C=N), 32.0, 29.7, 29.6, 29.4 (3  $\times$  CH<sub>2</sub>), 28.6, 24.3, 22.8, 18.9, 14.3 (CH<sub>3</sub>). IR (ATR, neat)/cm<sup>-1</sup> 2956, 2926, 2856, 1672, 1460, 1378, 1261, 1035. HRMS (ESITOF) *m/z* (M+H)<sup>+</sup> calcd for C<sub>12</sub>H<sub>24</sub>N 182,1909; found 182,1909.

### 3-Dodecyl-2*H*-azirine (2j)



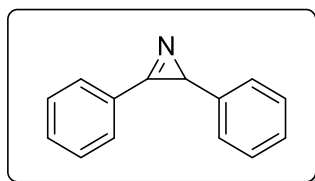
Prepared according General Procedure B using vinyl azide **1k** (237 mg). The product was obtained without further purification as a brown oil (203 mg, 97%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  2.78 (t, *J* = 7.3 Hz, 2H, CH<sub>2</sub>C=N), 1.74 (q, *J* = 7.3 Hz, 2H), 1.36–1.18 (broad signal, 20H), 0.88 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  169.9 (CH<sub>2</sub>C=N), 34.0, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 29.1, 28.6, 24.3, 22.8, 18.9, 14.2. IR (ATR, neat)/cm<sup>-1</sup> 2954, 2924, 2854, 1458, 986. HRMS (ESITOF) *m/z* (M+H)<sup>+</sup> calcd for C<sub>14</sub>H<sub>28</sub>N 210,2222; found 210,2218.

### 3-(Perfluorophenyl)-2*H*-azirine (2k)



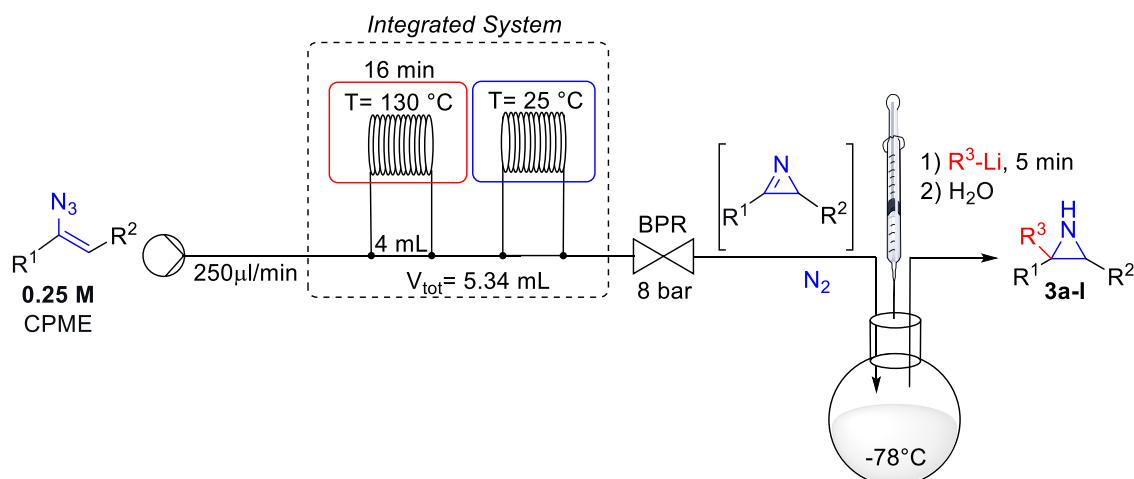
Prepared according General Procedure B. The product was obtained in mixture with vinyl azide **1l** (**1l**:**2l** = 20:80). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  1.85 (s, 2H, NCH<sub>2</sub>). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  -136.90 – -137.06 (m, 2F), -144.63 (tt, *J* = 20.6, 5.1 Hz, 1F), -159.71 – -159.97 (m, 2F).

### 2,3-Diphenyl-2*H*-azirine (2l)



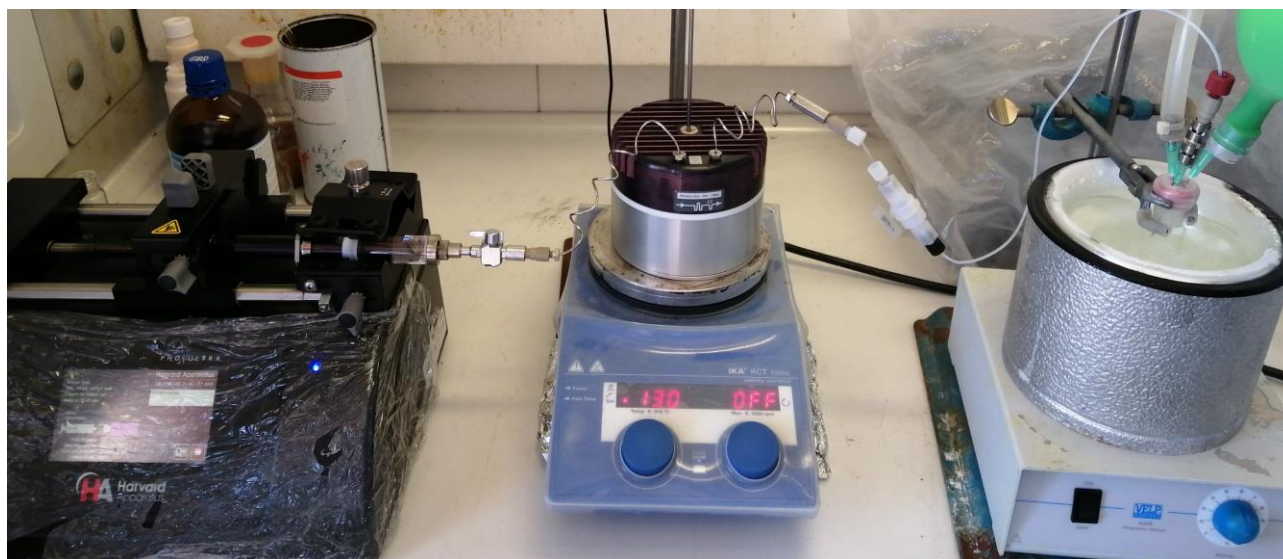
Prepared according General Procedure B. The product was obtained without any further purification as a yellow oil (192 mg, 99%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  7.72–7.69 (m, 2H, Ar-H), 7.63–7.51 (m, 3H, Ar-H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.30–7.27 (m, 2H, Ar-H), 7.17–7.15 (m, 2H, Ar-H), 3.33 (s, 1H, C=NCHPh). Analytical data (NMR) in agreement with those reported in the literature.<sup>7</sup>

#### 4. General Procedure C



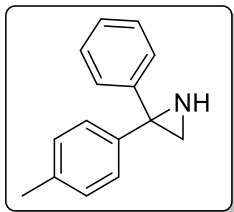
The process can be executed using a PHD ULTRA™ Syringe Pump (Harvard Apparatus), a Volcano reactor (4 mL, Syrris) and a back-pressure regulator of 8 bar. A solution of vinyl azide (1.0 mmol) in CPME (4 mL, 0.25 M) was introduced by syringe pump into the pre-heated reactor (130  $^{\circ}\text{C}$ , probe feedback control) with a flow rate of 250  $\mu\text{L}/\text{min}$ . Subsequently, fresh solvent (CPME) was fluxed in the reactor upon the same conditions. The outgoing solution was collected in a closed round bottom flask with nitrogen atmosphere for 16 min, since the formation of nitrogen was observed. The stirred solution was cooled to -78  $^{\circ}\text{C}$  and organolithium (1.2 equiv) was added in one portion. After 5 min,  $\text{H}_2\text{O}$  (100  $\mu\text{L}$ ) was added, and the reaction mixture was stirred at room temperature. The solution was filtered on a  $\text{Na}_2\text{SO}_4$  pad, the solvent was evaporated under reduced pressure, and the products were isolated through silica gel chromatography as described for each entry.

#### Combined flow-batch system



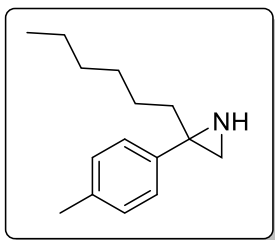
## Characterization data for aziridines 3a–l

### 2-Phenyl-2-(*p*-tolyl)aziridine (3a)



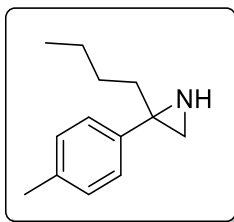
Prepared according General Procedure C using vinyl azide **1a**. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.30, Hexane/Ethyl Acetate/ Triethylamine 80:19:1) to afford aziridine **3a** as a brown waxy solid (102 mg, 49%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 7.37–7.28 (m, 5H, Ar–H), 7.24 (d, *J* = 8.0 Hz, 2H, Ar–H), 7.13 (d, *J* = 8.0 Hz, 2H, Ar–H), 2.38 and 2.34 (2 × s, 2H, 2 × C=NCHH), 2.34 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm) δ 143.0 (Ar–C<sub>q</sub>), 139.8 (Ar–C<sub>q</sub>), 137.0 (Ar–C<sub>q</sub>), 129.2 (Ar), 127.8 (2 × Ar), 127.8 (Ar), 127.2 (Ar), 43.9 (C<sub>q</sub>), 35.5 (NCH<sub>2</sub>), 21.2 (Ar–CH<sub>3</sub>). IR (ATR, neat)/cm<sup>-1</sup> 3293, 3026, 2920, 1657, 1446, 808, 698. HRMS (ESITOF) *m/z* (M+H)<sup>+</sup> calcd for C<sub>15</sub>H<sub>16</sub>N 210,1283; found 210,1286.

### 2-Hexyl-2-(*p*-tolyl)aziridine (3b)



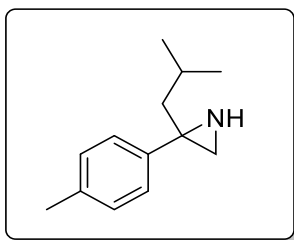
Prepared according General Procedure C using vinyl azide **1a**. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.45 Hexane/Ethyl Acetate/Triethylamine 70:29:1) to afford aziridine **3b** as a brown waxy solid (109 mg, 50%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 7.25 (d, *J* = 8.0 Hz, 2H, Ar–H), 7.12 (d, *J* = 8.0 Hz, 2H, Ar–H), 2.33 (s, 3H, Ar–CH<sub>3</sub>), 1.91 and 1.85 (2 × s, 2H, 2 × C=NCHH), 1.81–1.75 (m, 1H), 1.72–1.67 (m, 1H), 1.29–1.21 (m, 8H), 0.84 (t, *J* = 6.9 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm) δ 139.7 (Ar–C<sub>q</sub>), 136.7 (Ar–C<sub>q</sub>), 129.1 (2 × Ar), 127.6 (2 × Ar), 41.7 (C<sub>q</sub>), 39.6 (CH<sub>2</sub>C=NCH<sub>2</sub>), 33.1 (CH<sub>2</sub>C=NCH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 21.2 (Ar–CH<sub>3</sub>), 14.2 (CH<sub>3</sub>). IR (ATR, neat)/cm<sup>-1</sup> 3291, 2954, 2856, 1676, 1464, 815. HRMS (ESITOF) *m/z* (M+H)<sup>+</sup> calcd for C<sub>15</sub>H<sub>24</sub>N 218,1909; found 218,1914.

### 2-Butyl-2-(*p*-tolyl)aziridine (3c)



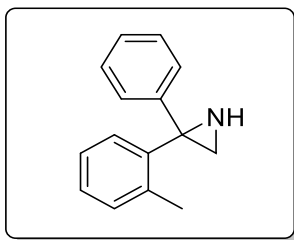
Prepared according General Procedure C using vinyl azide **1a**. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.30 Hexane/Ethyl Acetate/Triethylamine 70:29:1) to afford aziridine **3c** as a brown waxy solid (87 mg, 46%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 7.26(d, *J* = 7.6 Hz, 2H, Ar-H), 7.12 (d, *J* = 7.6 Hz, 2H, Ar-H), 2.33 (s, 3H, Ar-CH<sub>3</sub>), 1.92 and 1.85 (2 × s, 2H, 2 × C=NCHH), 1.80–1.77 (m, 1H), 1.73–1.69(m, 1H), 1.28–1.26 (m, 4H), 0.84 (t, *J* = 6.9 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm) δ 139.7 (Ar-C<sub>q</sub>), 136.7 (Ar-C<sub>q</sub>), 129.1 (2 × Ar), 127.6 (2 × Ar), 41.7 (C<sub>q</sub>), 39.3 (CH<sub>2</sub>C=NCH<sub>2</sub>), 33.0 (CH<sub>2</sub>C=NCH<sub>2</sub>), 28.5 (CH<sub>2</sub>), 22.9 (CH<sub>2</sub>), 21.2 (Ar-CH<sub>3</sub>), 14.2 (CH<sub>3</sub>). IR (ATR, neat)/cm<sup>-1</sup> 3296, 2956, 2928, 2859, 1517, 1458, 817, 561. HRMS (ESITOF) *m/z* (M+H)<sup>+</sup> calcd for C<sub>13</sub>H<sub>20</sub>N 190,1596; found 190,1596.

### 2-Isobutyl-2-(*p*-tolyl)aziridine (**3d**)



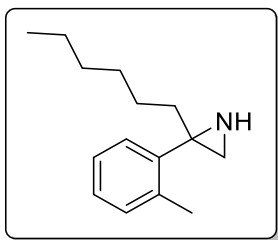
Prepared according General Procedure C using vinyl azide **1a**. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.45 Hexane/Ethyl Acetate/Triethylamine 50:49:1) to afford aziridine **3d** as a brown waxy solid (89 mg, 47%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 7.29(d, *J* = 8.0 Hz, 2H, Ar-H), 7.12 (d, *J* = 8.0 Hz, 2H, Ar-H), 2.33 (s, 3H, Ar-CH<sub>3</sub>), 1.95 and 1.84 (2 × s, 2H, 2 × C=NCHH), 1.69–1.67 (m, 2H), 1.52 (nonet, *J* = 6.7 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.07 (broad signal, 1H, NH), 0.89 and 0.88 (2 × d, *J* = 6.5 Hz, 6H, 2 × CH(CH<sub>3</sub>)). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm) δ 139.6 (Ar-C<sub>q</sub>), 136.6 (Ar-C<sub>q</sub>), 129.1 (2 × Ar), 127.6 (2 × Ar), 48.9 (C<sub>q</sub>), 40.6 (CH<sub>2</sub>C=NCH<sub>2</sub>), 32.8 (CH<sub>2</sub>C=NCH<sub>2</sub>), 26.2 (CH<sub>2</sub>), 23.3 (CHCH<sub>3</sub>), 22.9 (CHCH<sub>3</sub>), 21.2 (Ar-CH<sub>3</sub>). IR (ATR, neat)/cm<sup>-1</sup> 3293, 3052, 2953, 2868, 1517, 1467, 813, 804, 560. HRMS (ESITOF) *m/z* (M+H)<sup>+</sup> calcd for C<sub>13</sub>H<sub>20</sub>N 190,1596; found 190,1596.

### 2-Phenyl-2-(*o*-tolyl)aziridine (**3e**)



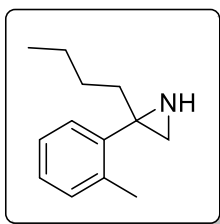
Prepared according General Procedure C using vinyl azide **1d**. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.55 Hexane/Ethyl Acetate/Triethylamine 50:49:1) to afford aziridine **3e** as a brown oil (109 mg, 52%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 7.52–7.51 (m, 1H, Ar-H), 7.27–7.23 (m, 4H, Ar-H), 7.21–7.15 (m, 4H, Ar-H), 2.45 and 2.34 (2 × s, 2H, 2 × C=NCHH), 2.24 (s, 3H, Ar-CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm) δ 142.3 (Ar-C<sub>q</sub>), 140.1 (Ar-C<sub>q</sub>), 138.1 (Ar-C<sub>q</sub>), 130.5 (Ar), 129.5 (Ar), 128.3 (Ar), 127.8 (Ar), 126.6 (Ar), 125.9 (Ar), 125.8 (Ar), 42.8 (C<sub>q</sub>), 36.5, 19.6 (Ar-CH<sub>3</sub>). IR (ATR, neat)/cm<sup>-1</sup> 3280, 3060, 2854, 1639, 1494, 755, 698. HRMS (ESITOF) *m/z* (M+H)<sup>+</sup> calcd for C<sub>15</sub>H<sub>16</sub>N 210,1283; found 210,1281.

### 2-Hexyl-2-(*o*-tolyl)aziridine (3f)



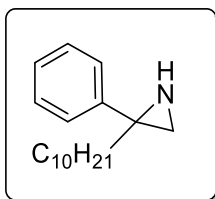
Prepared according General Procedure C using vinyl azide **1d**. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.35 Hexane/Ethyl Acetate/Triethylamine 70:29:1) to afford aziridine **3f** as a brown waxy solid (134 mg, 62%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 7.29–7.26 (m, 1H, Ar–H), 7.18–7.12 (m, 3H, Ar–H), 2.43 (s, 3H, Ar–CH<sub>3</sub>), 1.93 and 1.89 (2 × s, 2H, 2 × C=NCHH), 1.74–1.79 (m, 1H, CHHC=NCH<sub>2</sub>), 1.64–1.59 (m, 1H, CHHC=NCH<sub>2</sub>), 1.31–1.21 (broad signal, 8H), 0.84 (t, *J* = 6.9 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm) δ 140.8 (Ar–C<sub>q</sub>), 136.7 (Ar–C<sub>q</sub>), 130.4 (Ar), 129.4 (Ar), 127.2 (Ar), 125.6 (Ar), 41.7 (C<sub>q</sub>), 38.6 (CH<sub>2</sub>C=NCH<sub>2</sub>), 32.7 (CH<sub>2</sub>C=NCH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 26.2 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 19.3 (Ar–CH<sub>3</sub>), 14.2 (CH<sub>3</sub>). IR (ATR, neat)/cm<sup>−1</sup> 3282, 3058, 2927, 1687, 1457, 878, 760, 729. HRMS (ESITOF) *m/z* (M+H)<sup>+</sup> calcd for C<sub>15</sub>H<sub>24</sub>N 218,1909; found 218,1907.

### 2-Butyl-2-(*o*-tolyl)aziridine (3g)



Prepared according General Procedure C using vinyl azide **1d**. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.35 Hexane/Ethyl Acetate/Triethylamine 60:39:1) to afford aziridine **3g** as a brown waxy solid (97 mg, 51%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 7.30–7.26 (m, 1H, Ar–H), 7.18–7.13 (m, 3H, Ar–H), 2.43 (s, 3H, Ar–CH<sub>3</sub>), 1.93 and 1.89 (2 × s, 2H, 2 × C=NCHH), 1.76–1.62 (m, 2H), 1.33–1.21 (m, 4H), 0.83 (t, *J* = 6.9 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm) δ 140.8 (Ar–C<sub>q</sub>), 136.8 (Ar–C<sub>q</sub>), 130.4 (Ar), 129.5 (Ar), 127.2 (Ar), 125.6 (Ar), 41.7 (C<sub>q</sub>), 38.4 (CH<sub>2</sub>C=NCH<sub>2</sub>), 32.7 (CH<sub>2</sub>C=NCH<sub>2</sub>), 28.4 (CH<sub>2</sub>), 23.0 (CH<sub>2</sub>), 19.3 (Ar–CH<sub>3</sub>), 14.2 (CH<sub>3</sub>). IR (ATR, neat)/cm<sup>−1</sup> 3298, 2956, 2930, 2858, 1491, 1458, 862, 761, 730. HRMS (ESITOF) *m/z* (M+H)<sup>+</sup> calcd for C<sub>13</sub>H<sub>20</sub>N 190,1596; found 190,1591.

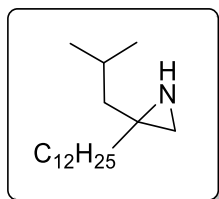
### 2-Decyl-2-phenylaziridine (3h)



Prepared according General Procedure C using vinyl azide **1i**. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.45 Hexane/Ethyl Acetate/Triethylamine 60:39:1) to

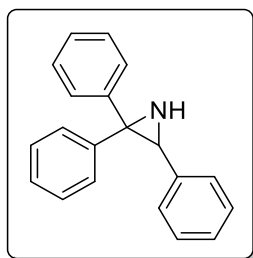
afford aziridine **3h** as a yellow waxy solid (116 mg, 45%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.37 (d,  $J = 7.1$  Hz, 2H, Ar–H), 7.31 (t,  $J = 7.5$  Hz, 2H, Ar–H), 7.24 (t,  $J = 7.3$  Hz, 1H, Ar–H), 1.94 and 1.90 (2  $\times$  s, 2H, 2  $\times$  NCHH), 1.84–1.79 (m, 1H), 1.74–1.68 (m, 1H), 1.29–1.21 (broad signal, 16H), 0.87 (t,  $J = 6.5$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  142.6 (Ar– $\text{C}_q$ ), 128.4 (Ar), 127.7 (Ar), 127.1 (Ar), 42.1 ( $\text{C}_q$ ), 39.6 ( $\text{CH}_2\text{C}_q\text{PhN}$ ), 32.0 ( $\text{C}_q\text{NCH}_2$ ), 29.8 ( $\text{CH}_2$ ), 29.7 (2  $\times$   $\text{CH}_2$ ), 29.6 (2  $\times$   $\text{CH}_2$ ), 29.4 (2  $\times$   $\text{CH}_2$ ), 29.3 ( $\text{CH}_2$ ), 14.3 ( $\text{CH}_3$ ). IR (ATR, neat)/ $\text{cm}^{-1}$  3298, 3059, 2923, 2852, 1465, 867, 698. HRMS (ESITOF)  $m/z$  ( $\text{M}+\text{H}$ ) $^+$  calcd for  $\text{C}_{18}\text{H}_{30}\text{N}$  260,2378; found 260,2380.

## 2-Dodecyl-2-isobutylaziridine (3i)



Prepared according General Procedure C using vinyl azide **1j**. The product was purified by column chromatography ( $\text{SiO}_2$ ,  $R_f$  0.30 Hexane/Ethyl Acetate/Triethylamine 50:49:1) to afford aziridine **3i** as a yellow waxy solid (128 mg, 48%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  1.81–1.73 (m, 1H), 1.52 and 1.51 (2  $\times$  s, 2H, 2  $\times$  NCHH), 1.47 and 1.14 (2  $\times$  dd,  $J = 14.0, 8.0$  Hz, 2H, 2  $\times$  CHHCH( $\text{CH}_3$ ) $_2$ ), 1.34–1.19 (broad signal, 22H), 0.94 and 0.92 (2  $\times$  d,  $J = 6.6$  Hz, 6H, 2  $\times$  CHCH $_3$ ), 0.87 (t,  $J = 6.8$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  45.5, 37.0, 35.7, 32.4, 32.1, 30.0, 29.8 (5  $\times$   $\text{CH}_2$ ), 29.5, 25.9, 25.8, 23.5, 22.9, 22.8, 14.3 ( $\text{CH}_3$ ). IR (ATR, neat)/ $\text{cm}^{-1}$  2954, 2923, 2853, 1466, 1378, 801. HRMS (ESITOF)  $m/z$  ( $\text{M}+\text{H}$ ) $^+$  calcd for  $\text{C}_{18}\text{H}_{37}\text{N}$  268,3004; found 268,3005.

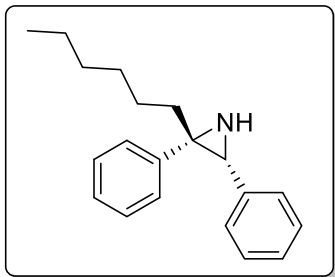
## 2,2,3-Triphenylaziridine (3j)



Prepared according General Procedure C using vinyl azide **1l**. The product was purified by column chromatography ( $\text{SiO}_2$ ,  $R_f$  0.60 Hexane/Ethyl Acetate 90:10) to afford aziridine **3j** as a white solid (168 mg, 62%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.41 (d,  $J = 7.4$  Hz, 2H, Ar–H), 7.35 (t,  $J = 7.5$  Hz, 2H, Ar–H), 7.28 (d,  $J = 7.4$  Hz, 1H, Ar–H), 7.25 (d,  $J = 7.0$  Hz, 2H, Ar–H), 7.16–7.11 (m, 8H, Ar–H), 3.90 (s, 1H, NCHPh), 1.80 (NH).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  144.4 (Ar– $\text{C}_q$ ), 138.5 (Ar– $\text{C}_q$ ), 137.2 (Ar– $\text{C}_q$ ), 129.8 (Ar), 128.8 (Ar), 127.8 (2  $\times$  Ar), 127.6 (Ar), 127.4 (Ar), 127.1 (Ar), 126.8 (2  $\times$  Ar), 52.4, 47.0. Analytical data (NMR) in agreement with those reported in the literature.<sup>9</sup>

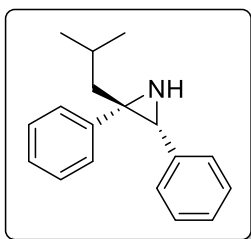


**(2*S*\*,3*R*\*)-2-Hexyl-2,3-diphenylaziridine (3k)**



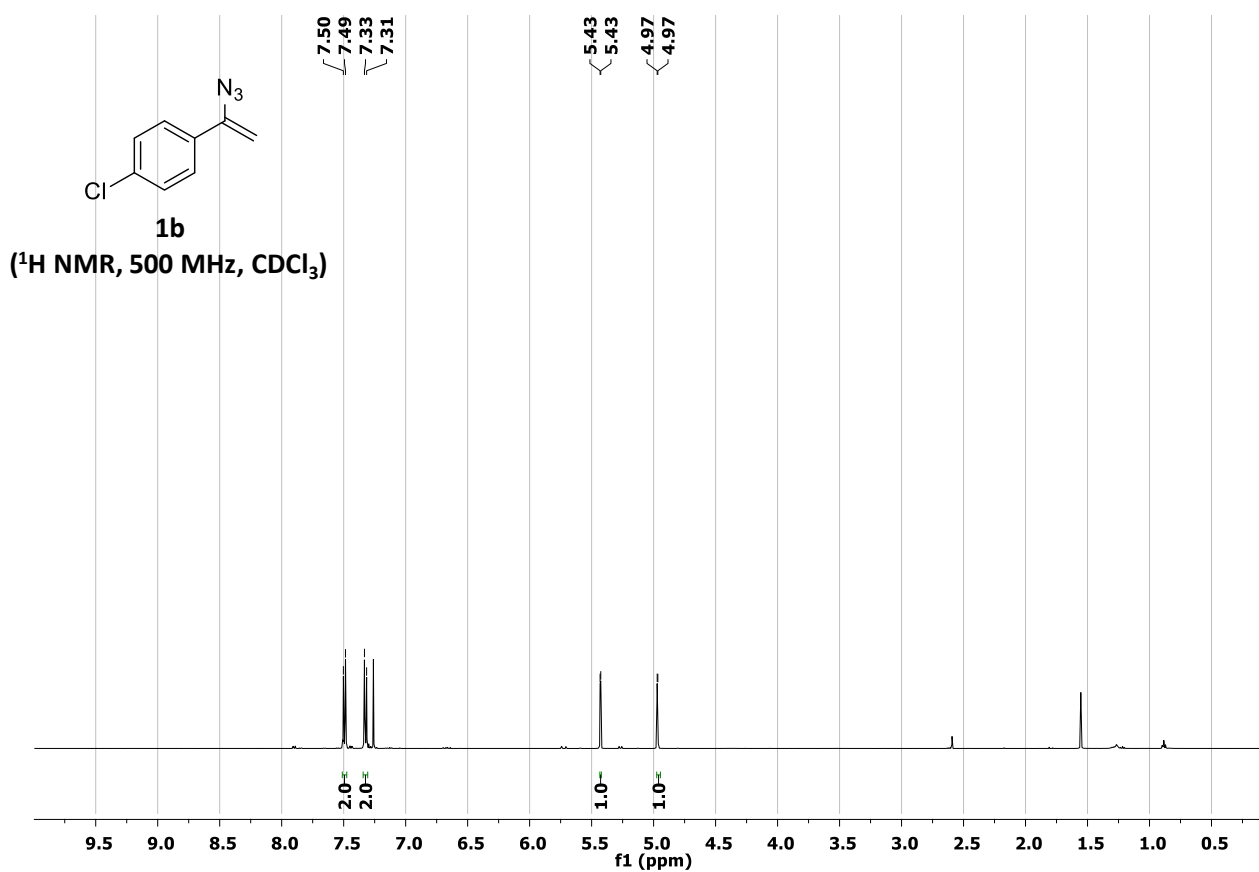
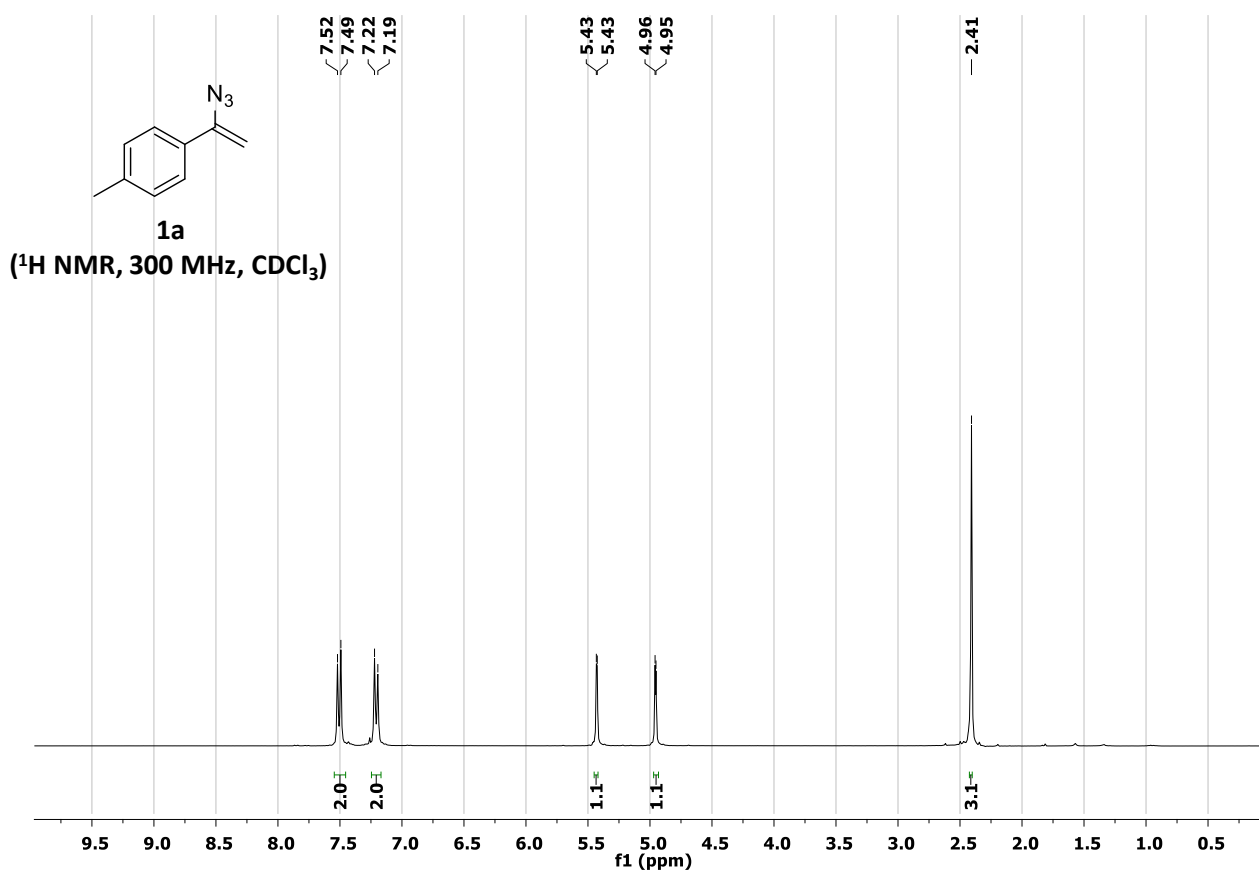
Prepared according General Procedure C using vinyl azide **1l**. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.50 Hexane/Ethyl Acetate 80:20) to afford aziridine **3k** as a pale yellow waxy solid (145 mg, 52%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 7.17–7.12 (m, 4H, Ar–H), 7.10–7.02 (m, 4H, Ar–H), 6.96–6.94 (m, 2H, Ar–H), 3.30 (s, 1H, C=NCHPh), 2.21–2.15 and 1.68–1.62 (2 × m, 2H, 2 × CHHC=N), 1.51 (broad signal, 1H, NH), 1.41–1.19 (broad signal, 8H), 0.86 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm) δ 138.7 (Ar–C<sub>q</sub>), 137.9 (Ar–C<sub>q</sub>), 129.3 (2 × Ar–C), 127.7 (2 × Ar–C), 127.6 (2 × Ar–C), 127.2 (2 × Ar–C), 126.5 (Ar–C), 127.4 (Ar–C), 50.8 (C<sub>q</sub>), 45.6 (NCHPh), 42.9 (PhCCH<sub>2</sub>CH<sub>2</sub>), 31.9, 29.5, 26.2, 22.7, 14.2 (CH<sub>3</sub>). IR (ATR, neat)/cm<sup>–1</sup> 3298, 3028, 2927, 2855, 1603, 1447, 752, 696. HRMS (ESITOF) *m/z* (M+H)<sup>+</sup> calcd for C<sub>20</sub>H<sub>26</sub>N 280,2065; found 280,2053.

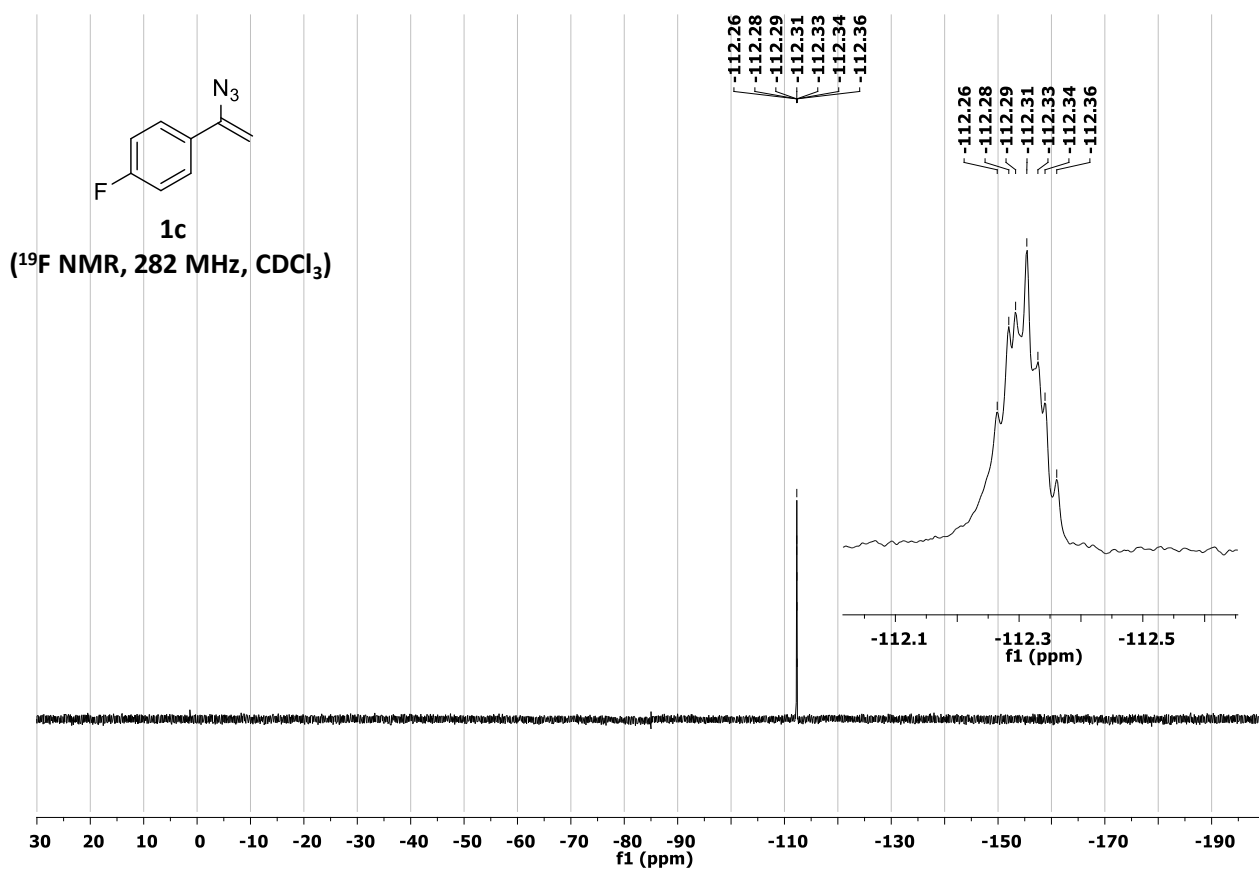
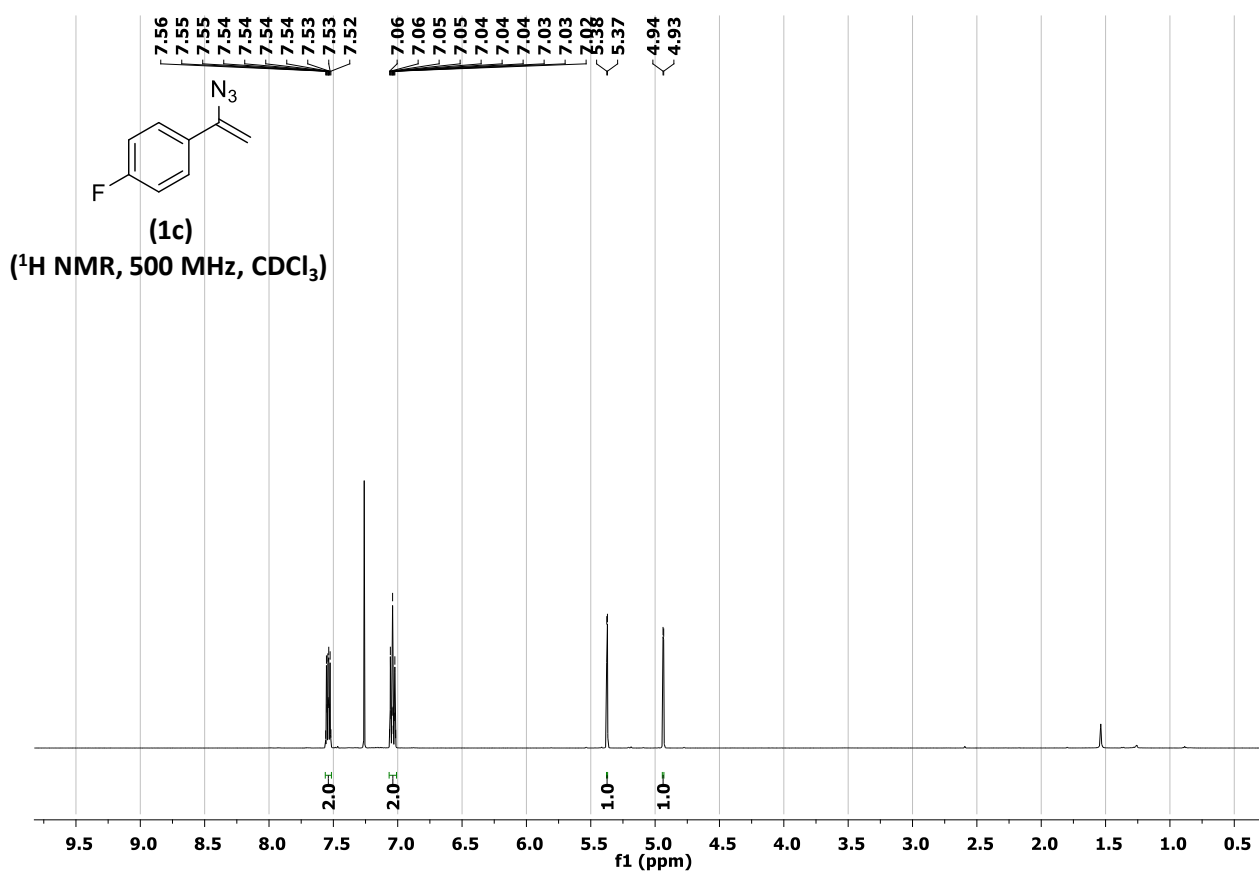
**(2*S*\*,3*R*\*)-2-Isobutyl-2,3-diphenylaziridine (3l)**

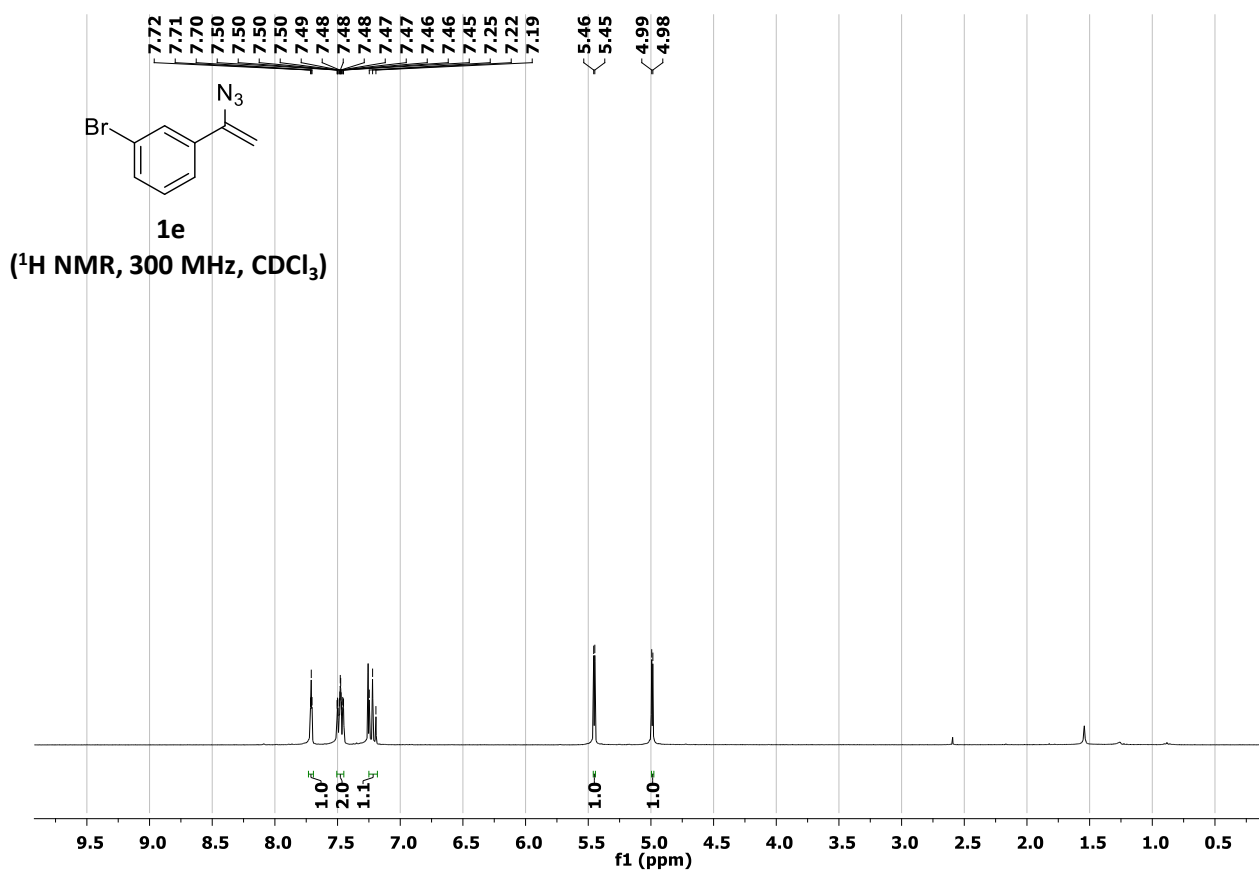
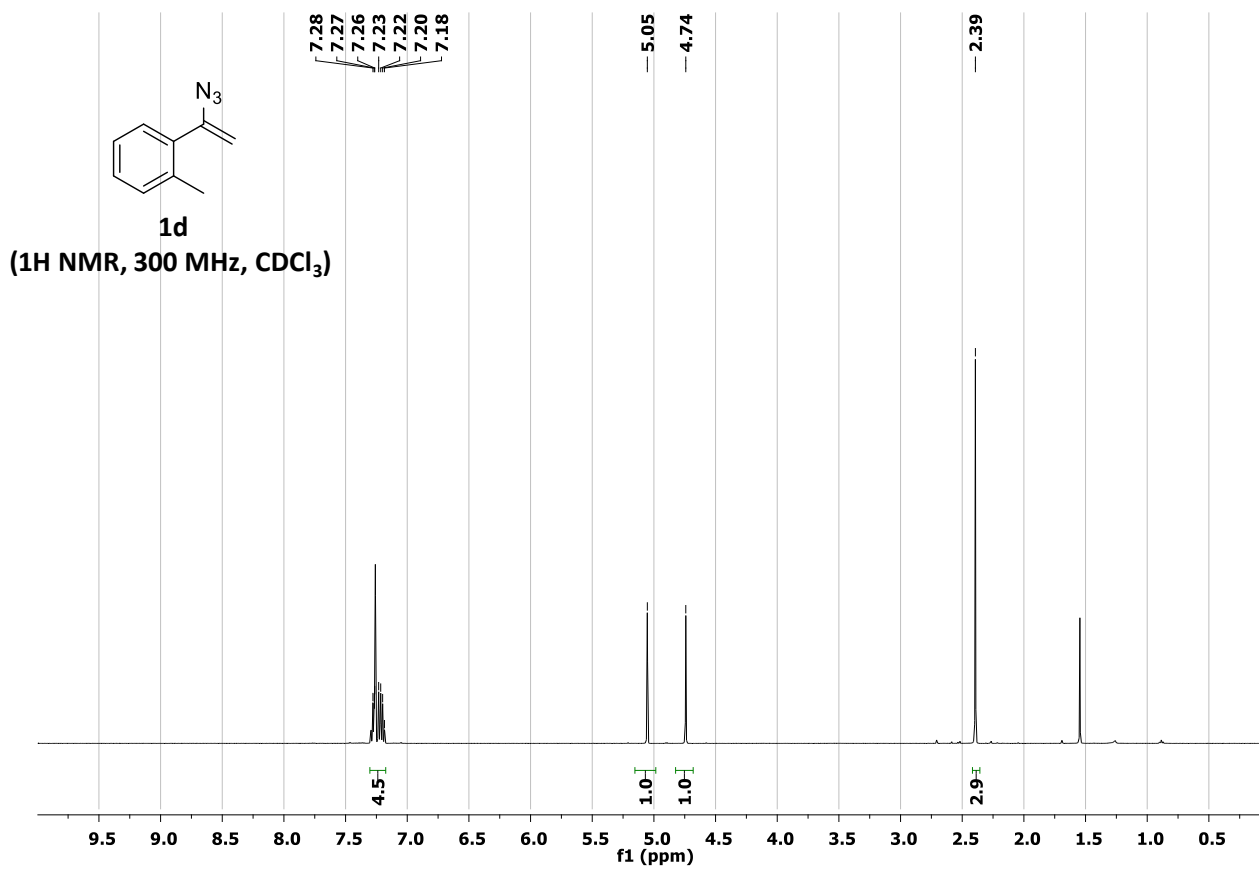


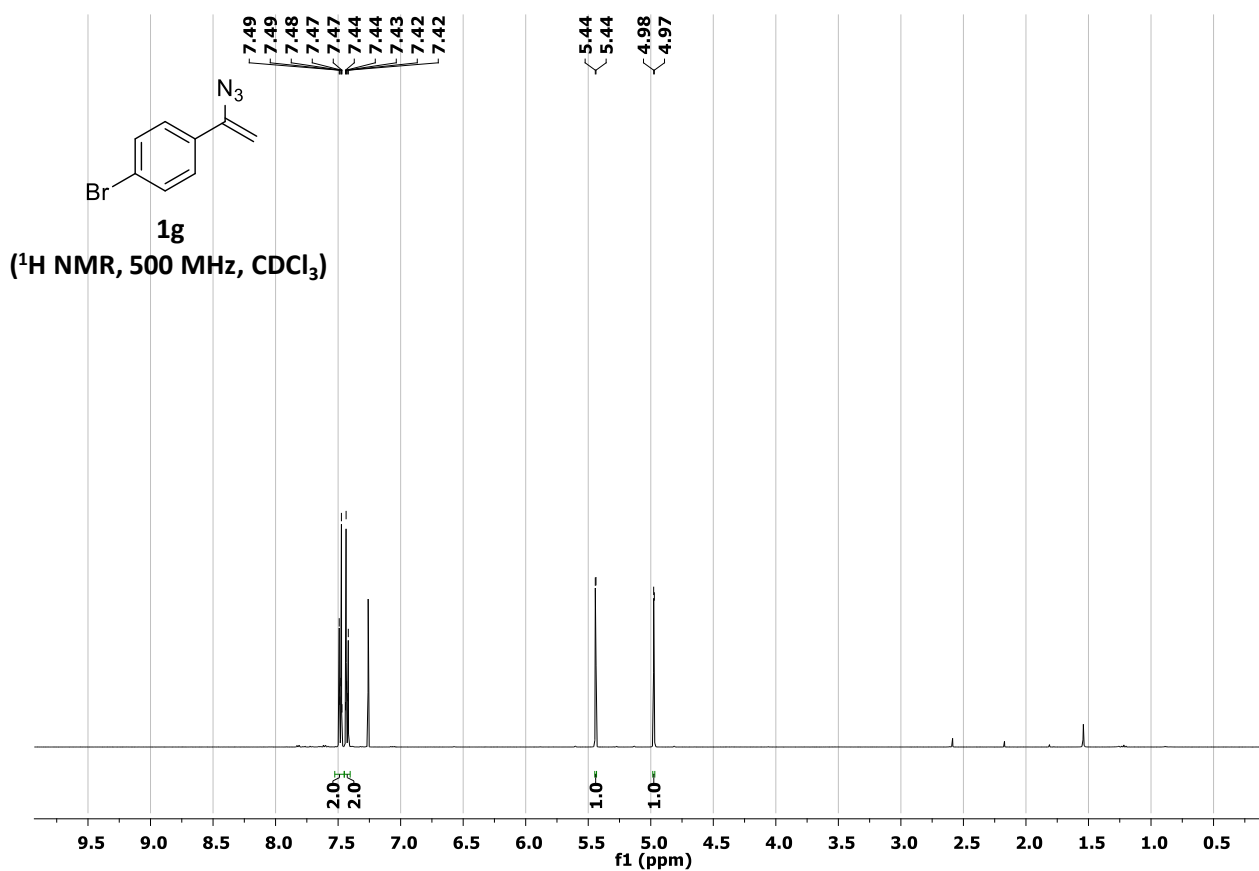
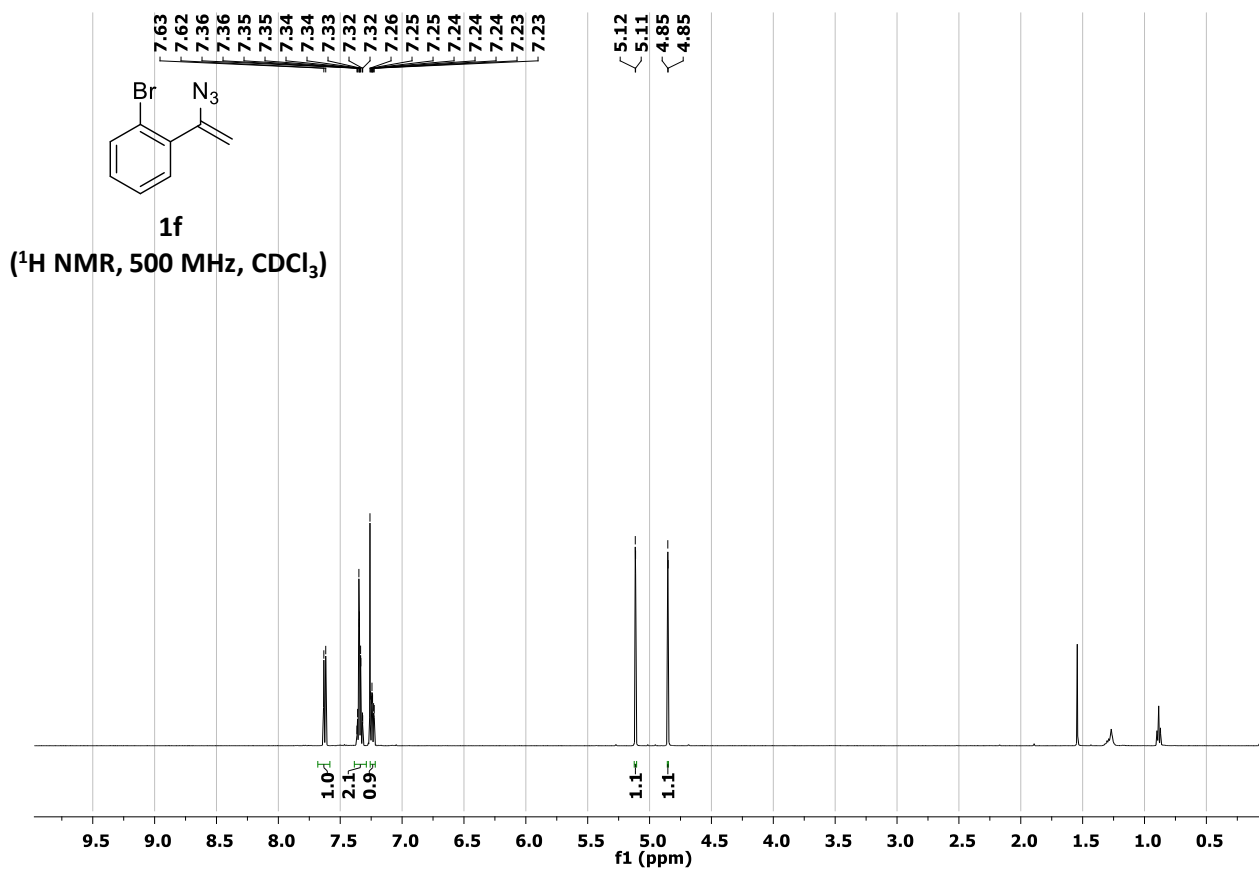
Prepared according General Procedure C using vinyl azide **1l**. The product was purified by column chromatography (SiO<sub>2</sub>, R<sub>f</sub> 0.25 Hexane/AcOEt/Et<sub>3</sub>N 90:9:1) to afford aziridine **3l** as a pale yellow waxy solid (113 mg, 45%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 7.18 (d, *J* = 7.0 Hz, 2H, Ar–H), 7.13 (t, *J* = 7.0 Hz, 2H, Ar–H), 7.09–7.03 (m, 4H, Ar–H), 6.97 (d, *J* = 7.0 Hz, 2H, Ar–H), 3.25 (s, PhCHN, 1H), 2.21 (dd, *J* = 14.0, 6.0 Hz, 1 × PhCCHHCH(CH<sub>3</sub>)<sub>2</sub>, 1H), 1.59–1.47 (m, 2H), 0.98 and 0.94 (2 × d, *J* = 6.5 Hz, 2 × PhCCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm) δ 138.3 (Ar–C<sub>q</sub>), 137.5 (Ar–C<sub>q</sub>), 129.1 (Ar), 127.5 (Ar), 127.4 (Ar), 127.1 (Ar), 126.3 (2 × Ar), 52.0 (PhC<sub>q</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 49.6 (PhC<sub>q</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 45.0 (PhCHN), 26.1 (PhC<sub>q</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 23.2 and 22.7 (2 × CH(CH<sub>3</sub>)<sub>2</sub>). IR (ATR, neat)/cm<sup>–1</sup> 3086, 3028, 2926, 2869, 1683, 1498, 871, 697, 607. HRMS (ESITOF) *m/z* (M+H)<sup>+</sup> calcd for C<sub>18</sub>H<sub>22</sub>N 252,1752; found 252,1756.

## 5. Copies of $^1\text{H}$ , $^{13}\text{C}$ , $^{19}\text{F}$ , NOESY NMR spectra

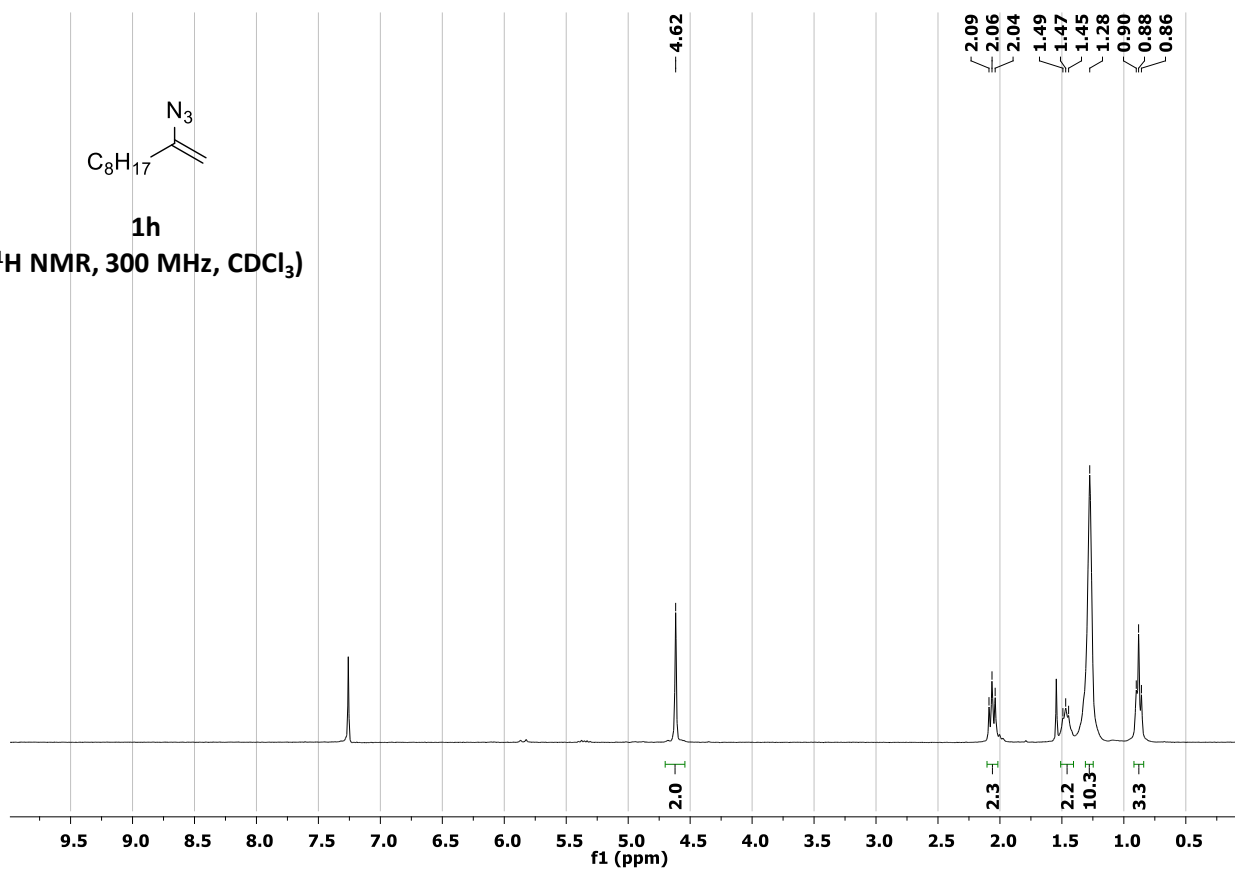




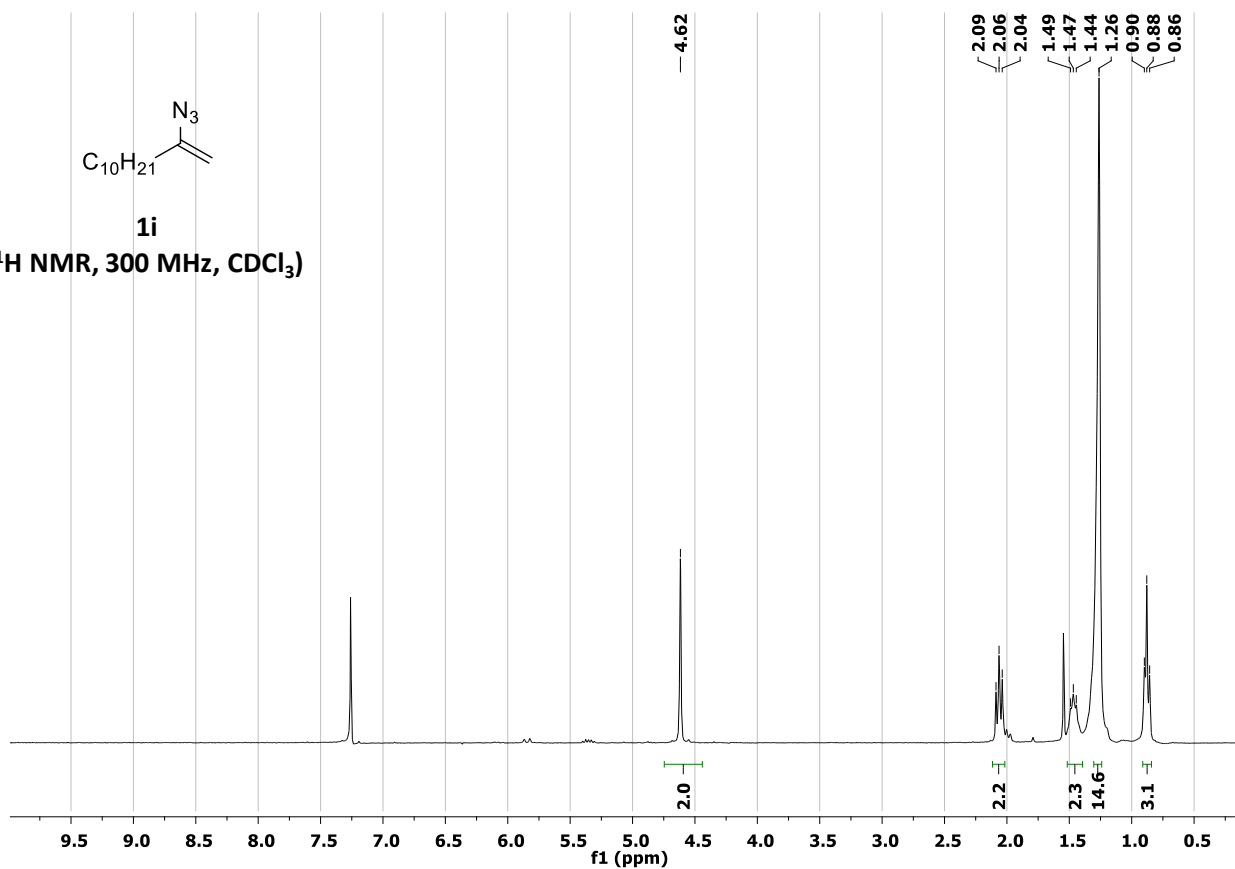


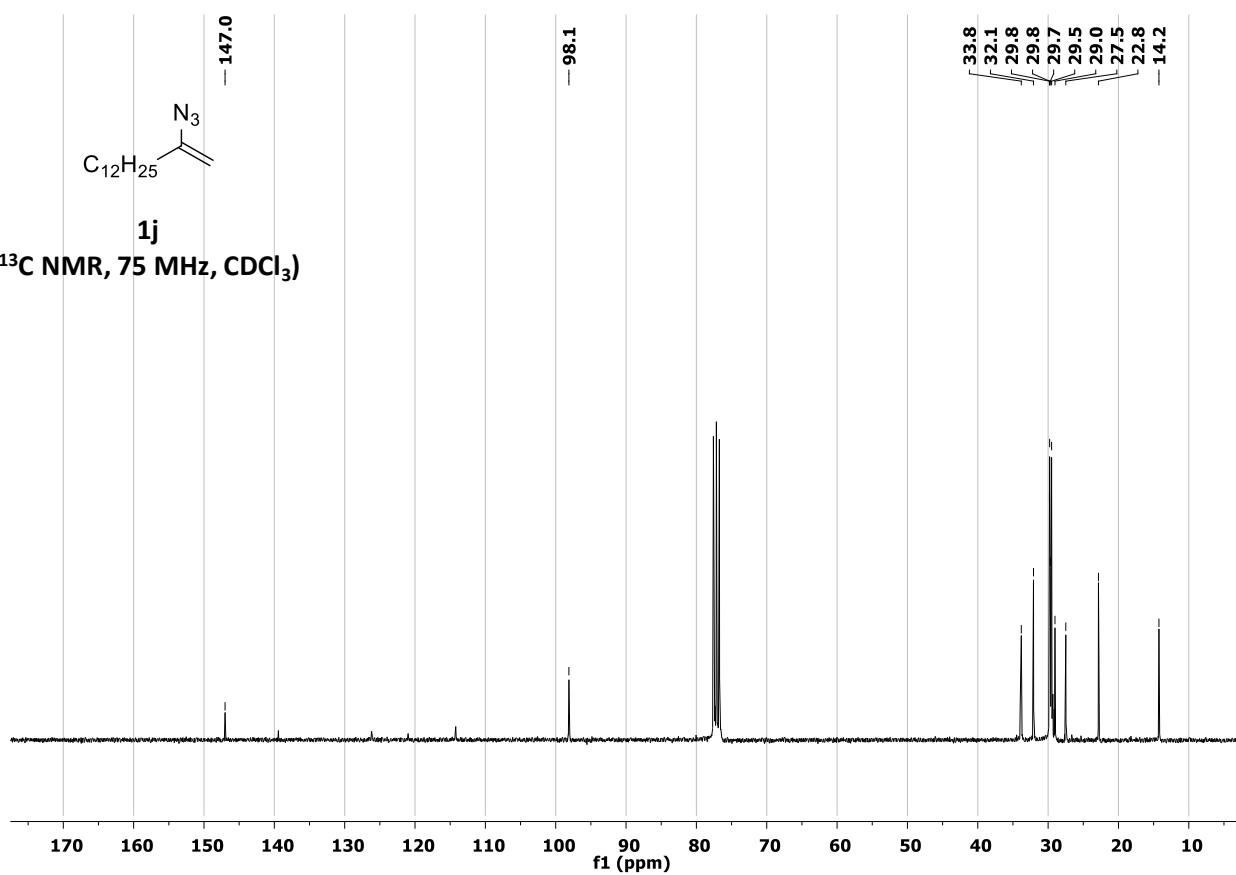
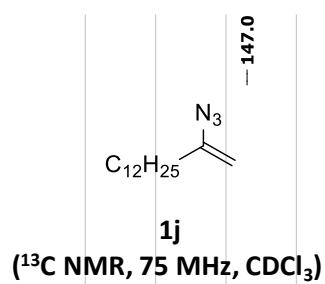
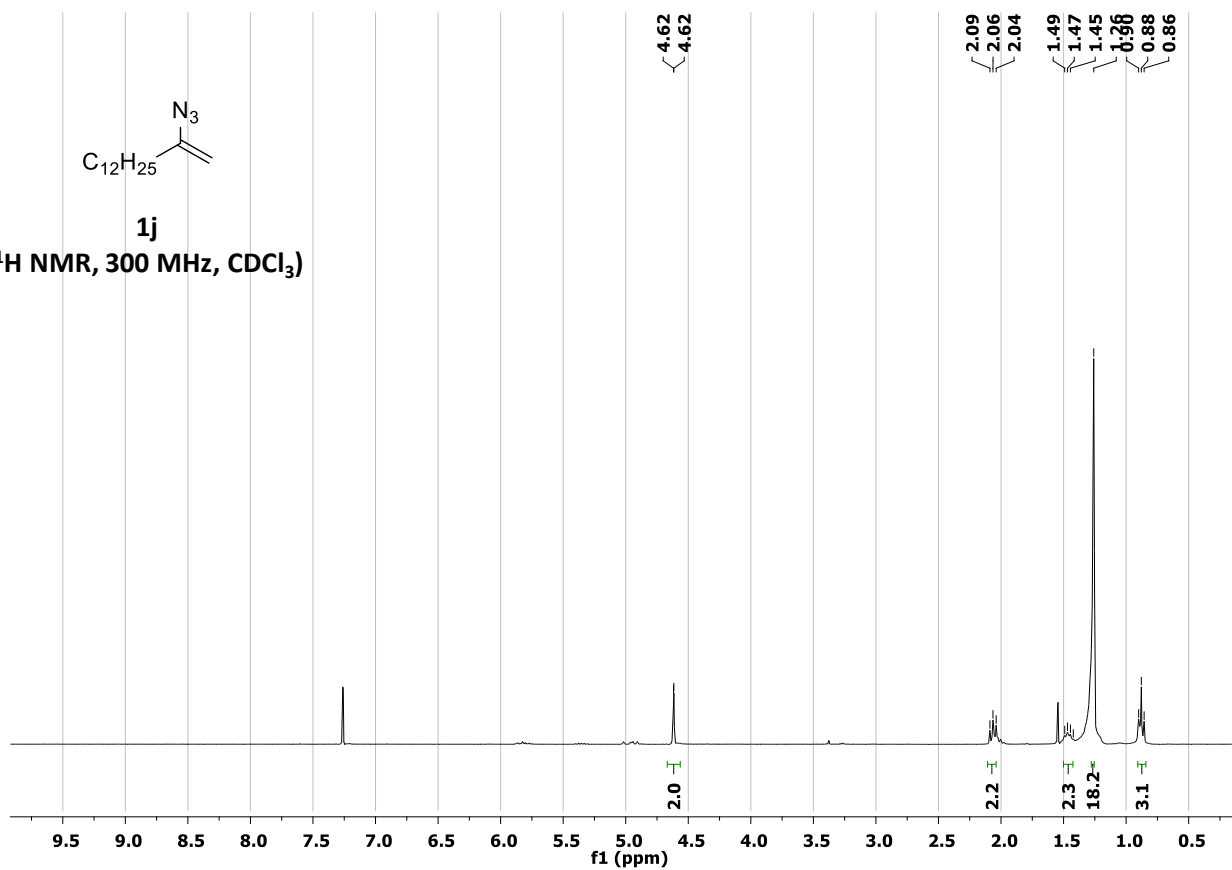
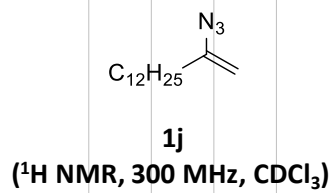


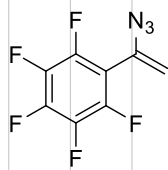
C8H17C(=[N+]=[N-])=C  
**1h**  
 (<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>)



C10H21C(=[N+]=[N-])=C  
**1i**  
 (<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>)

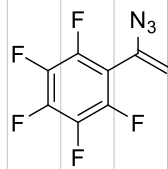
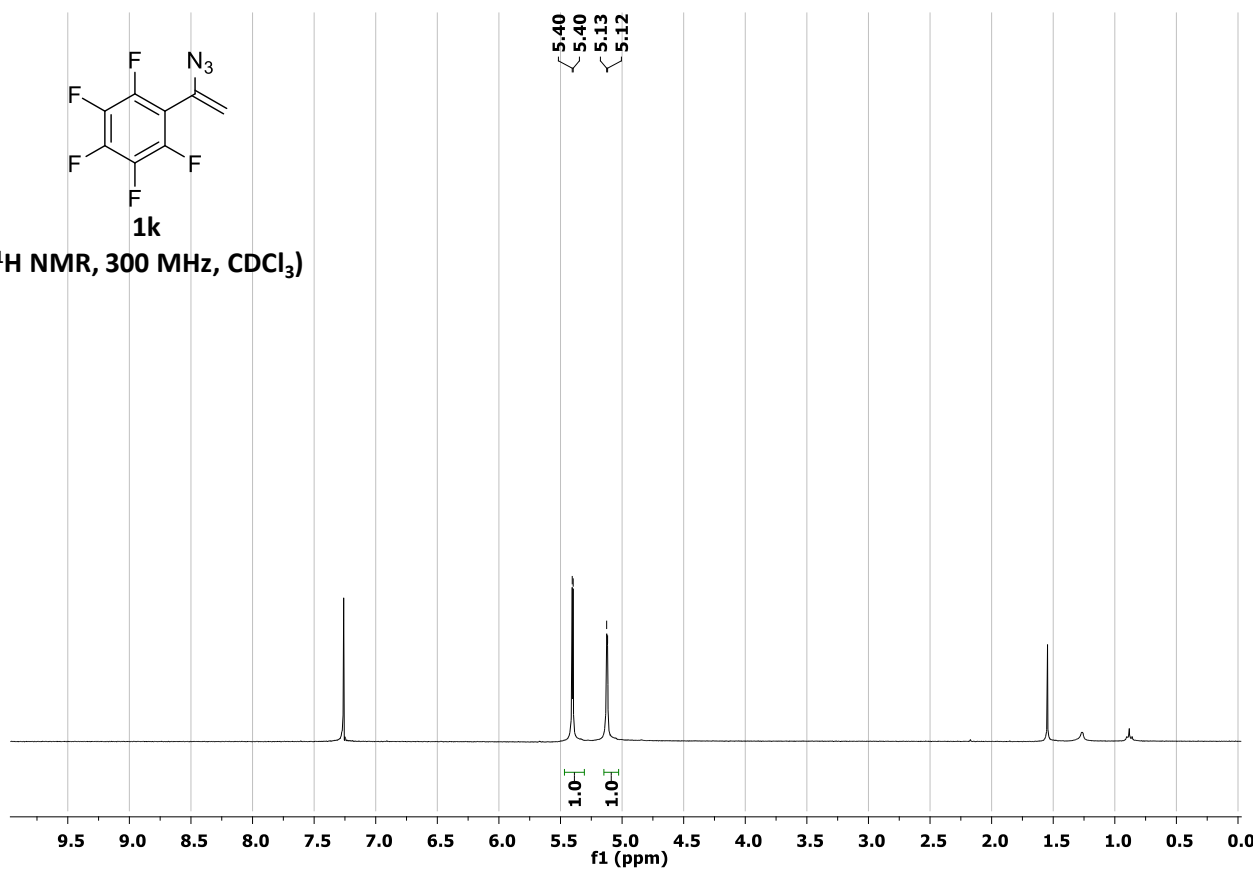






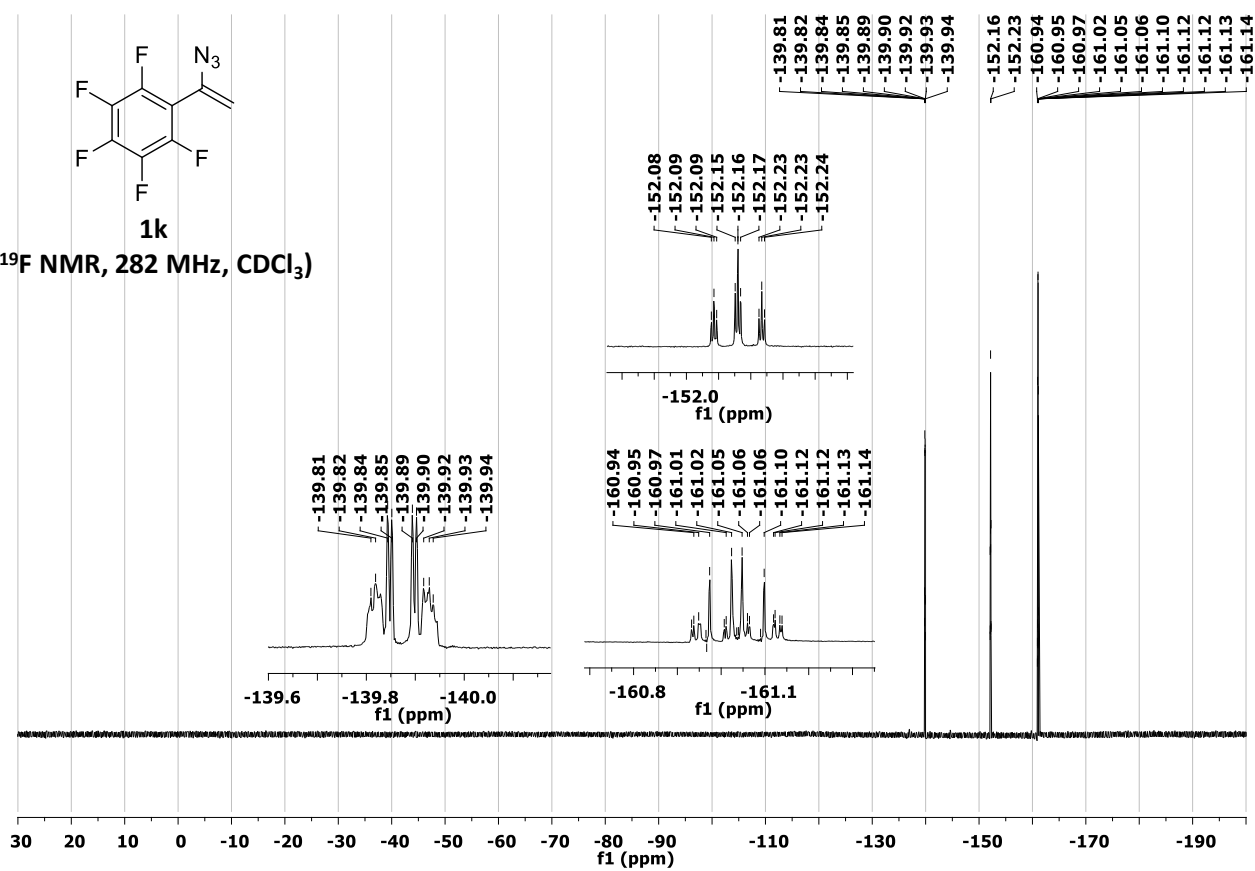
**1k**

(<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>)

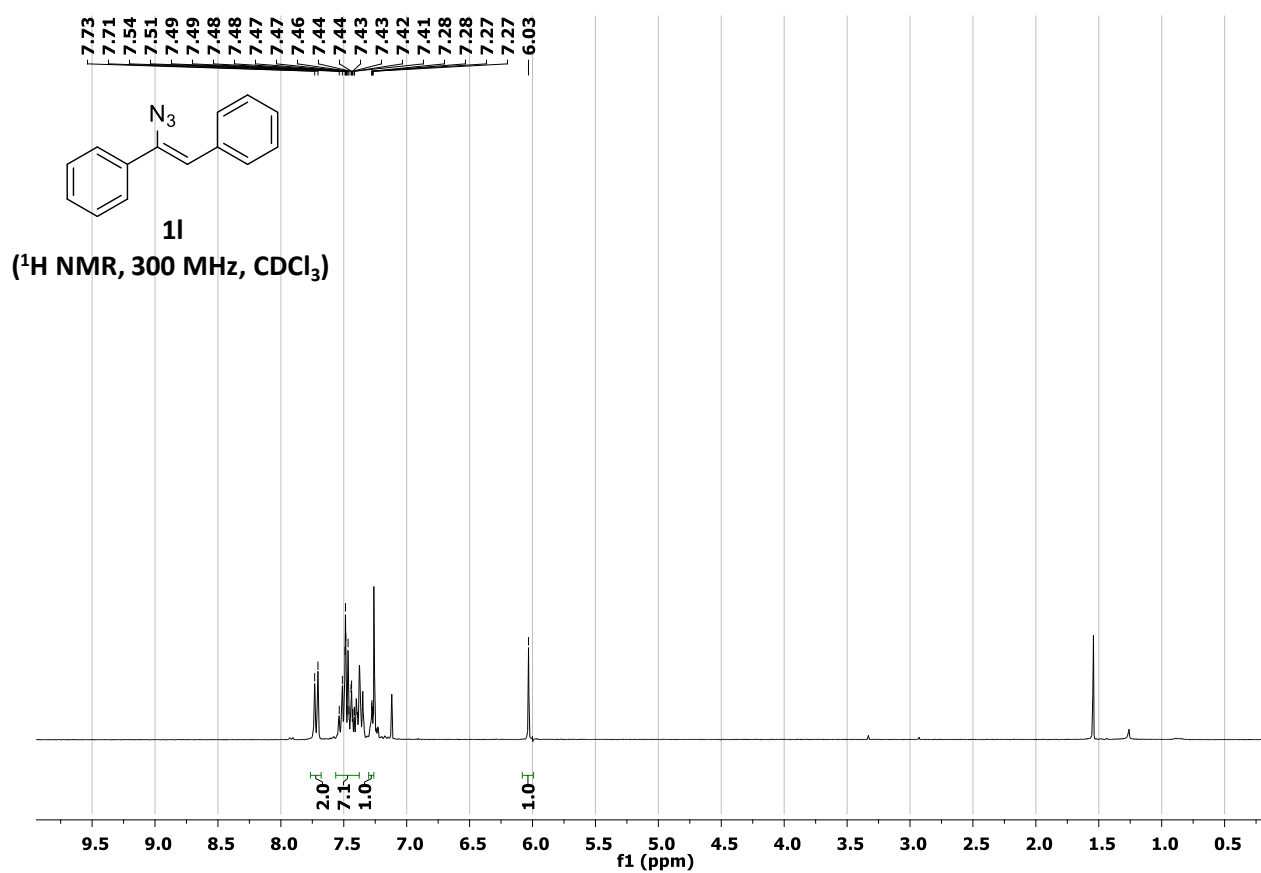
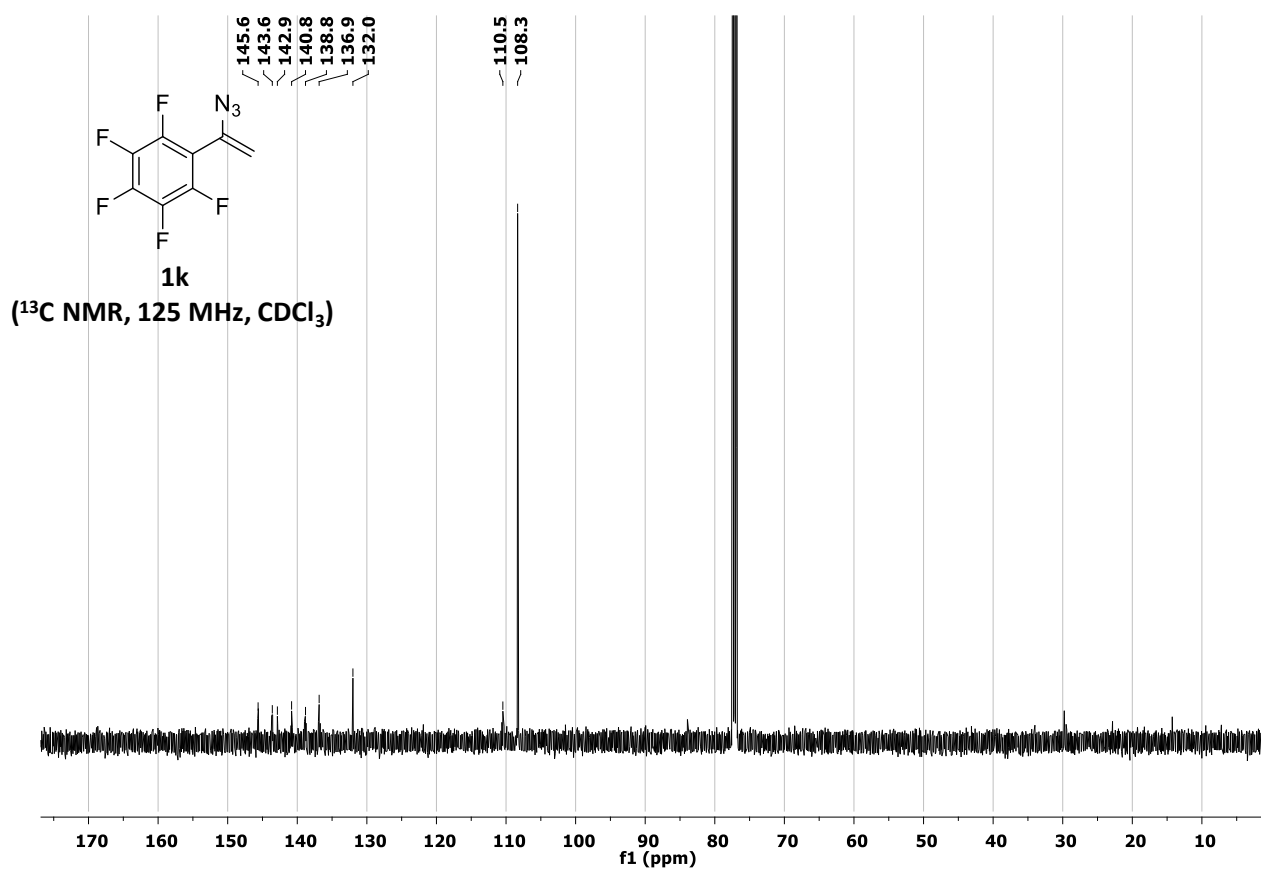


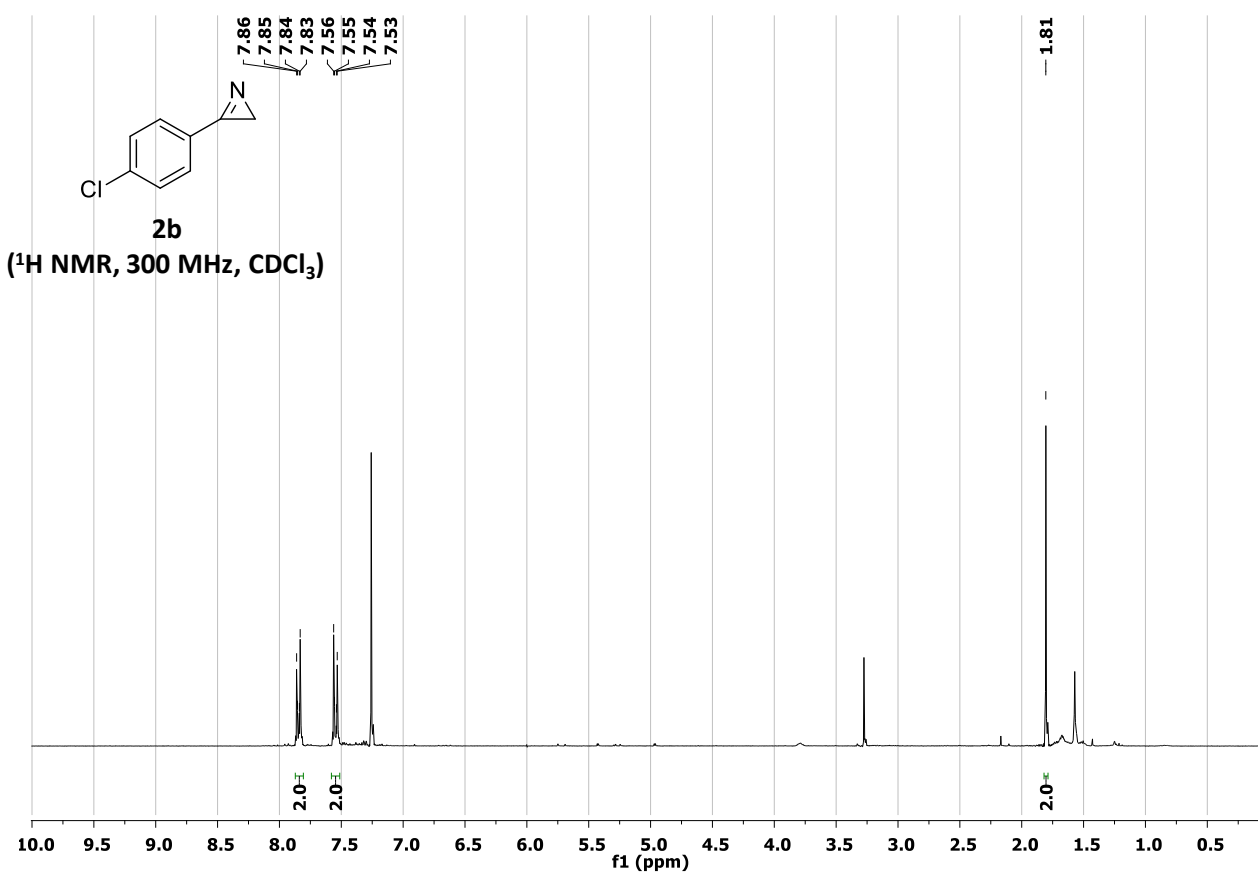
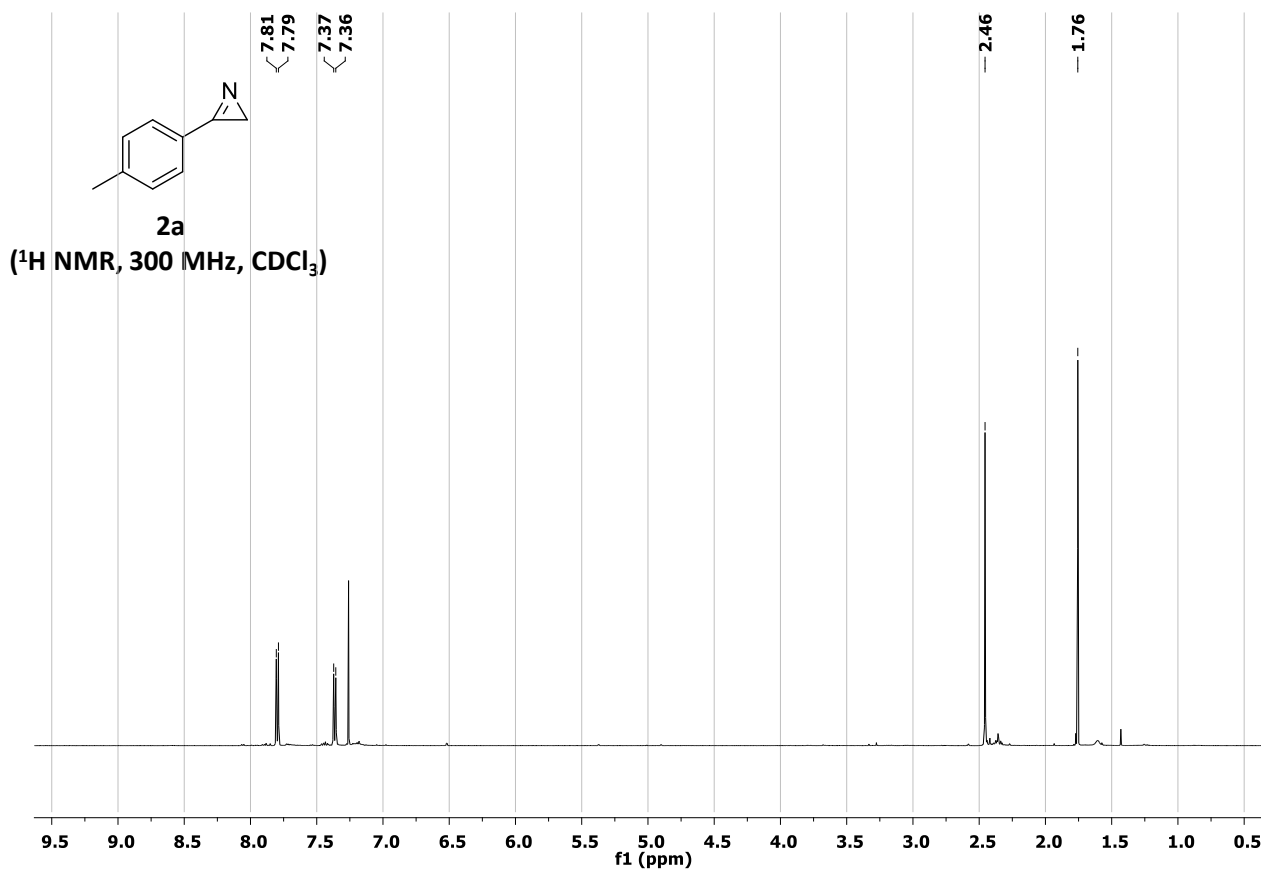
**1k**

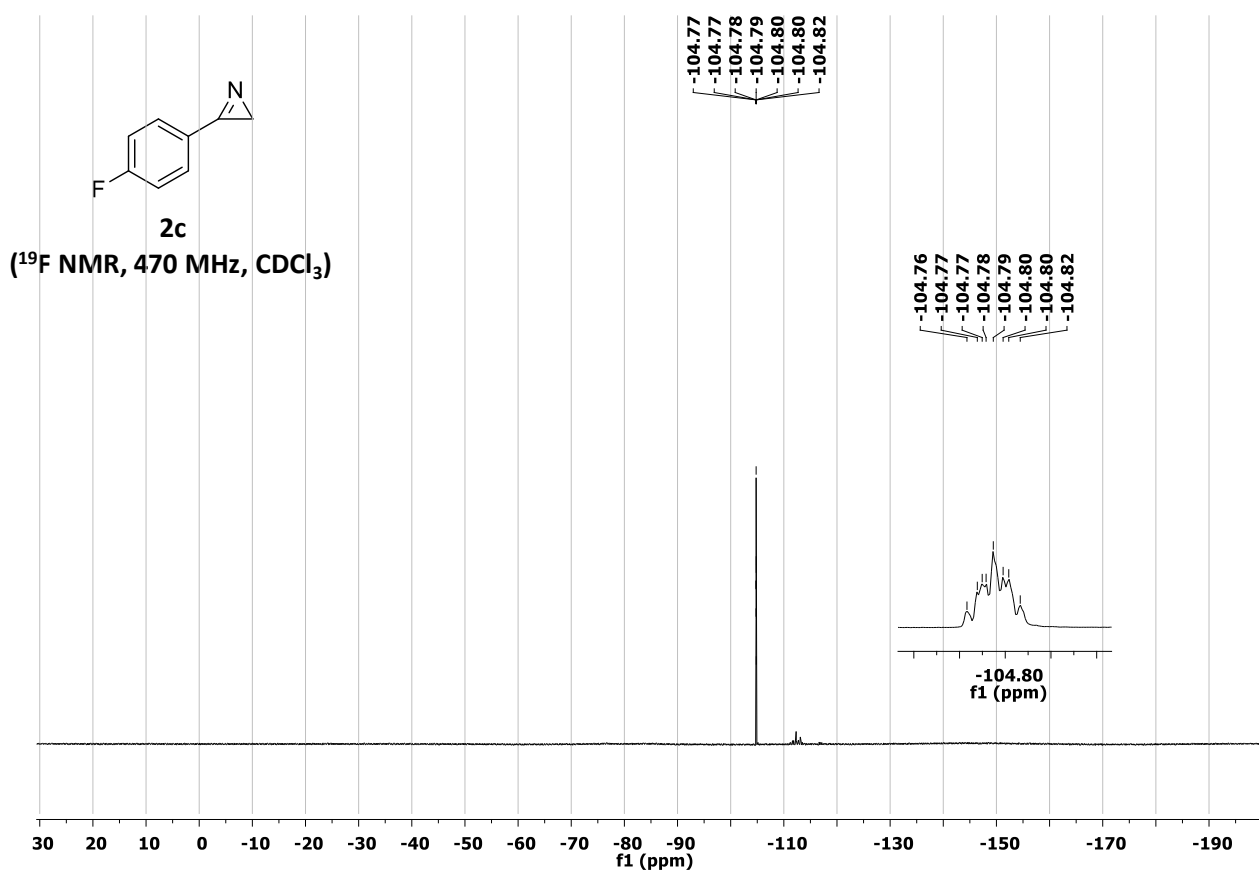
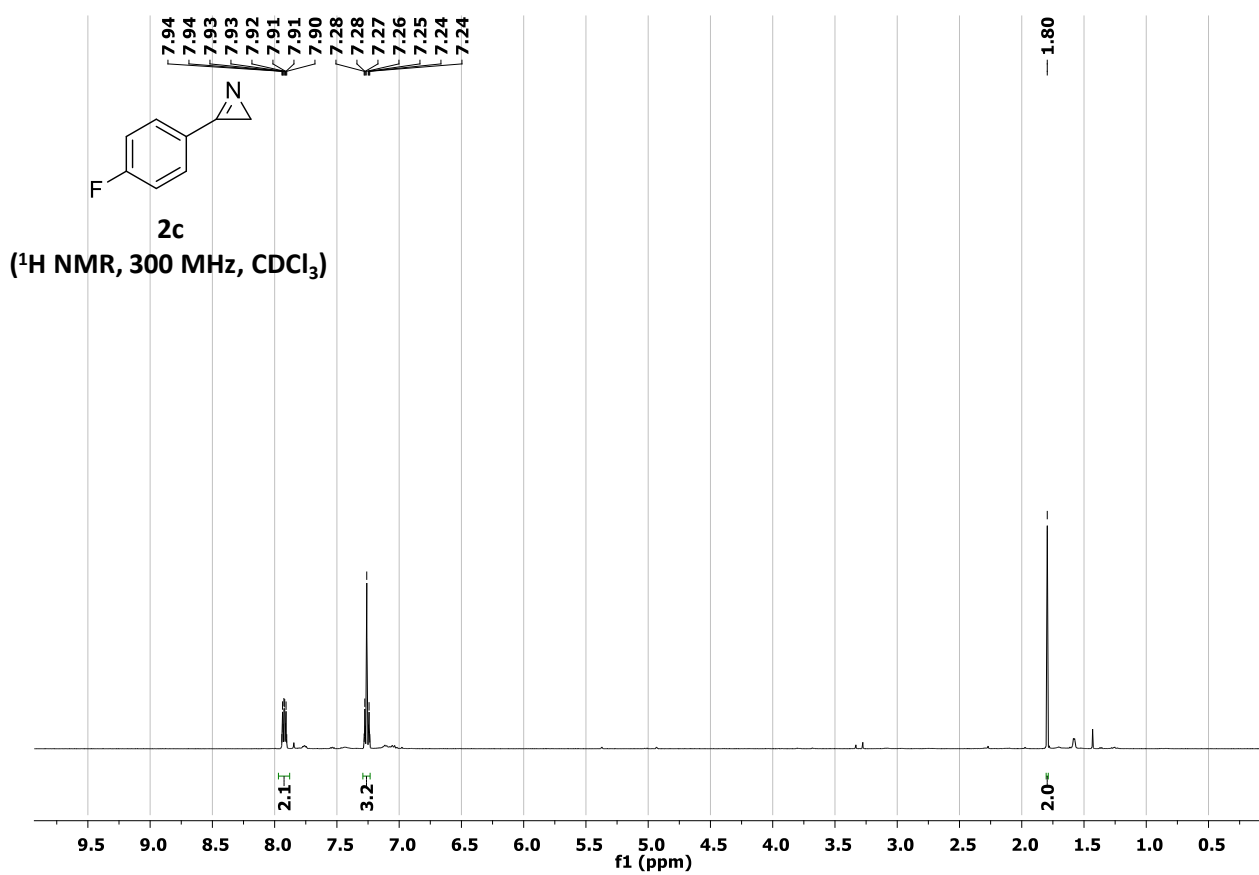
(<sup>19</sup>F NMR, 282 MHz, CDCl<sub>3</sub>)

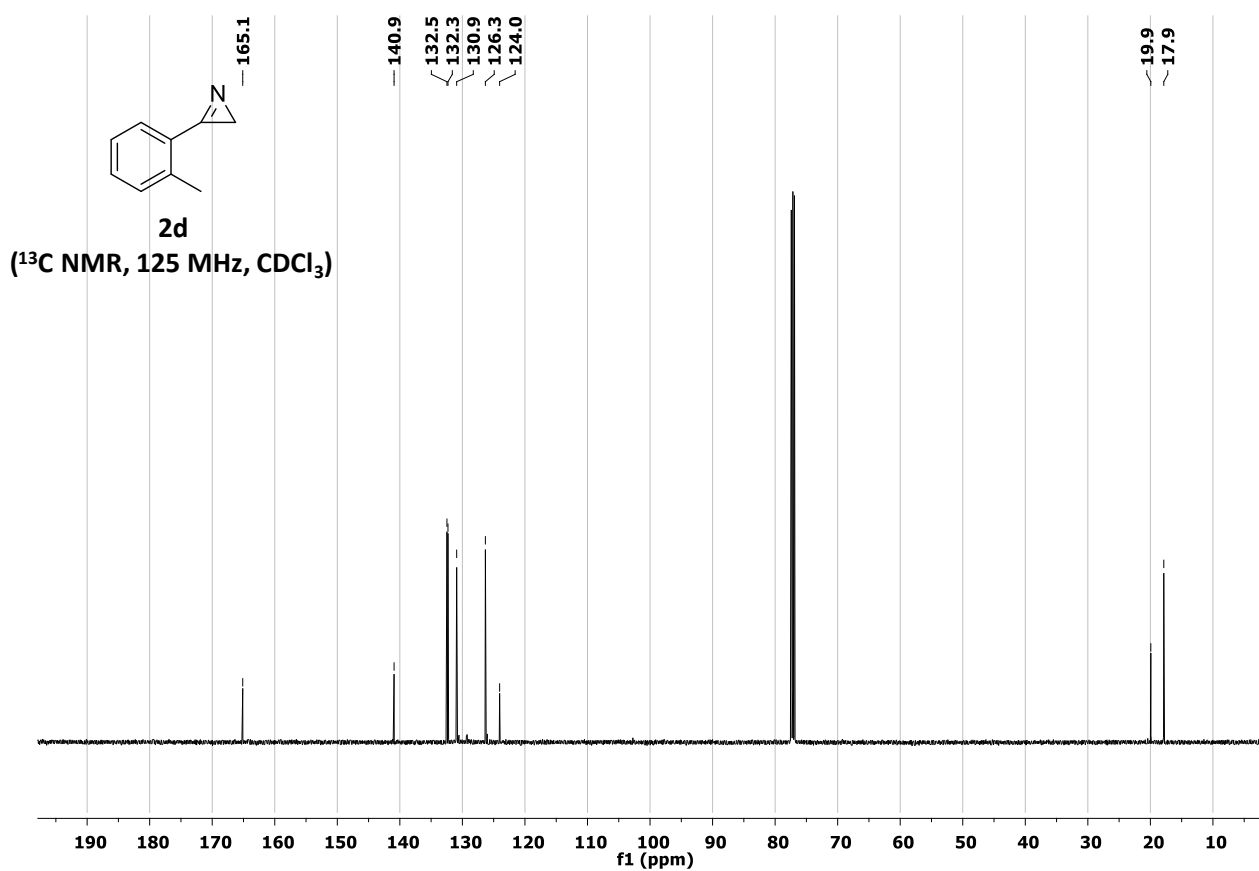
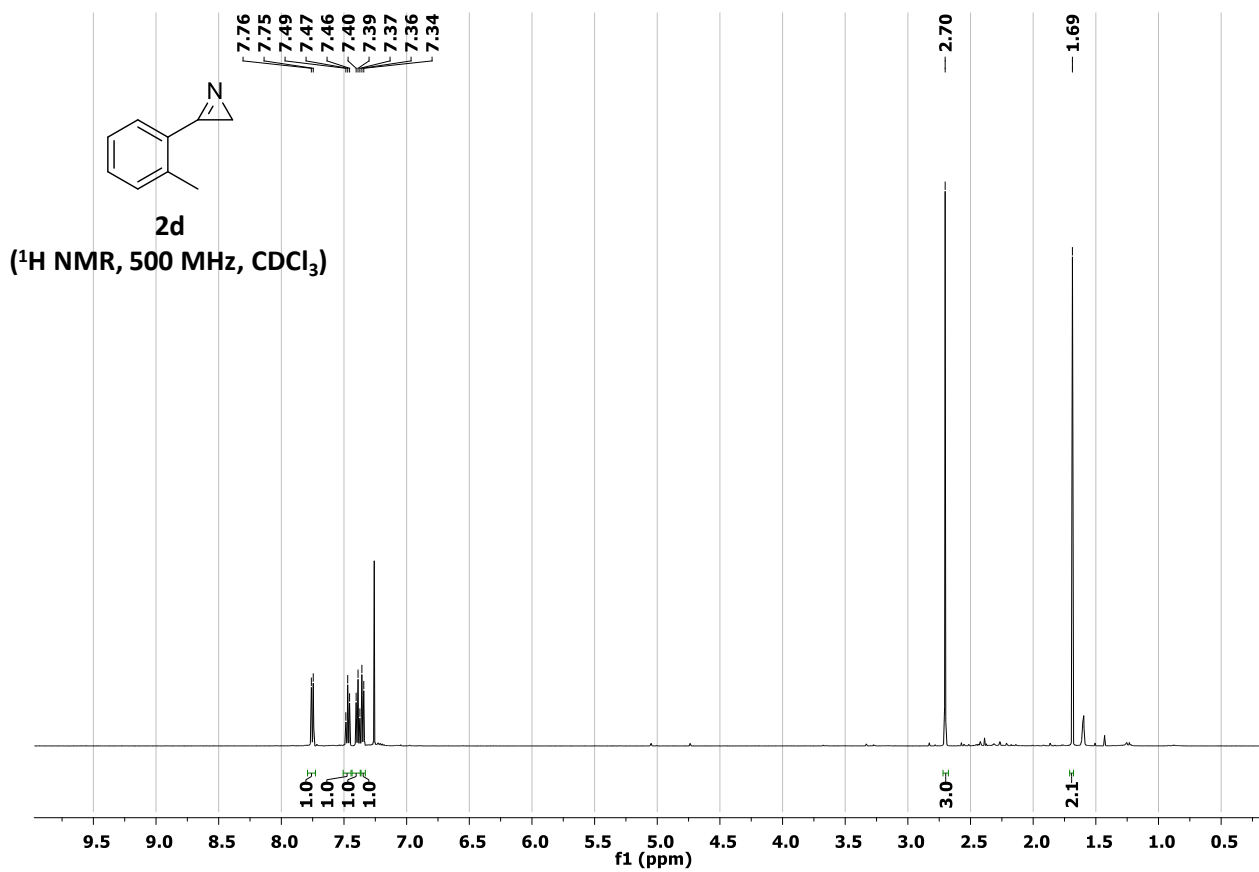


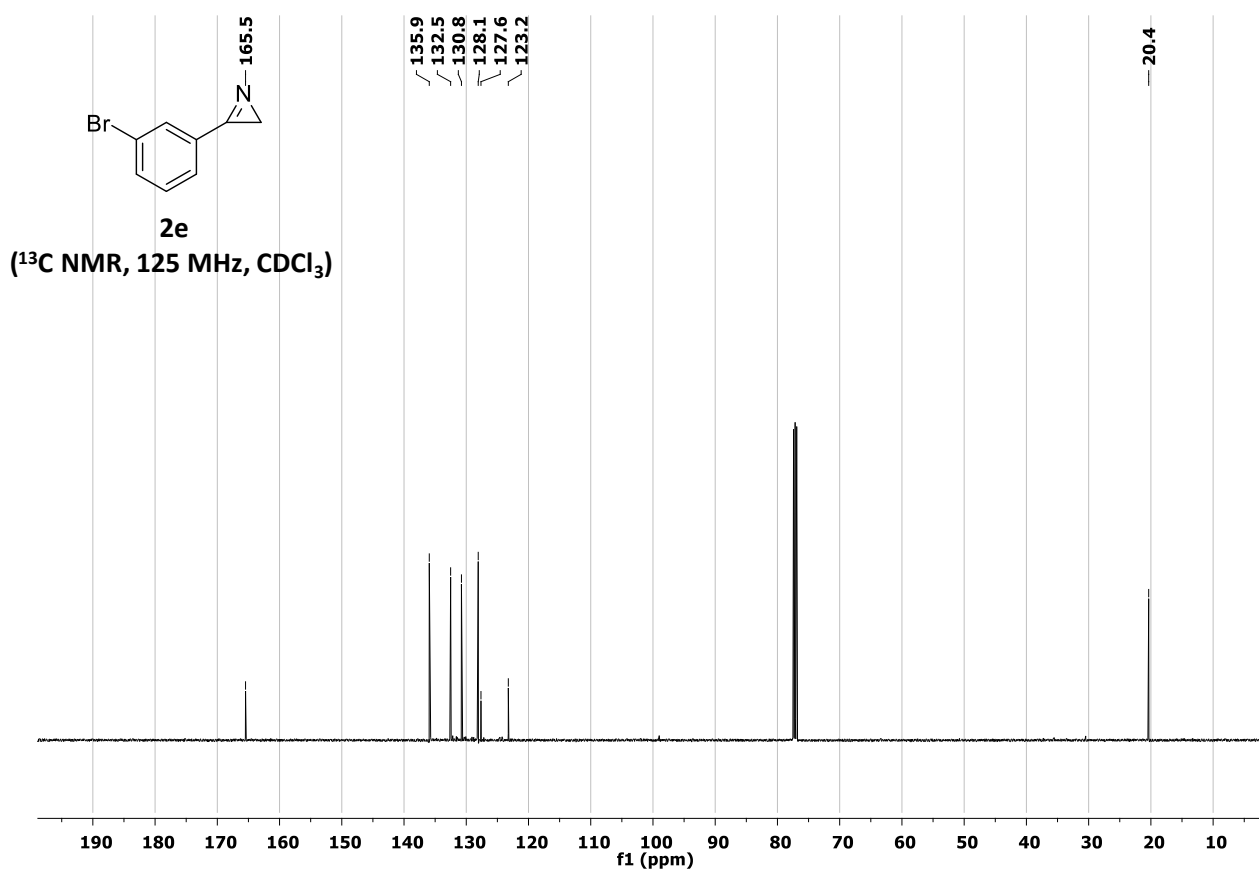
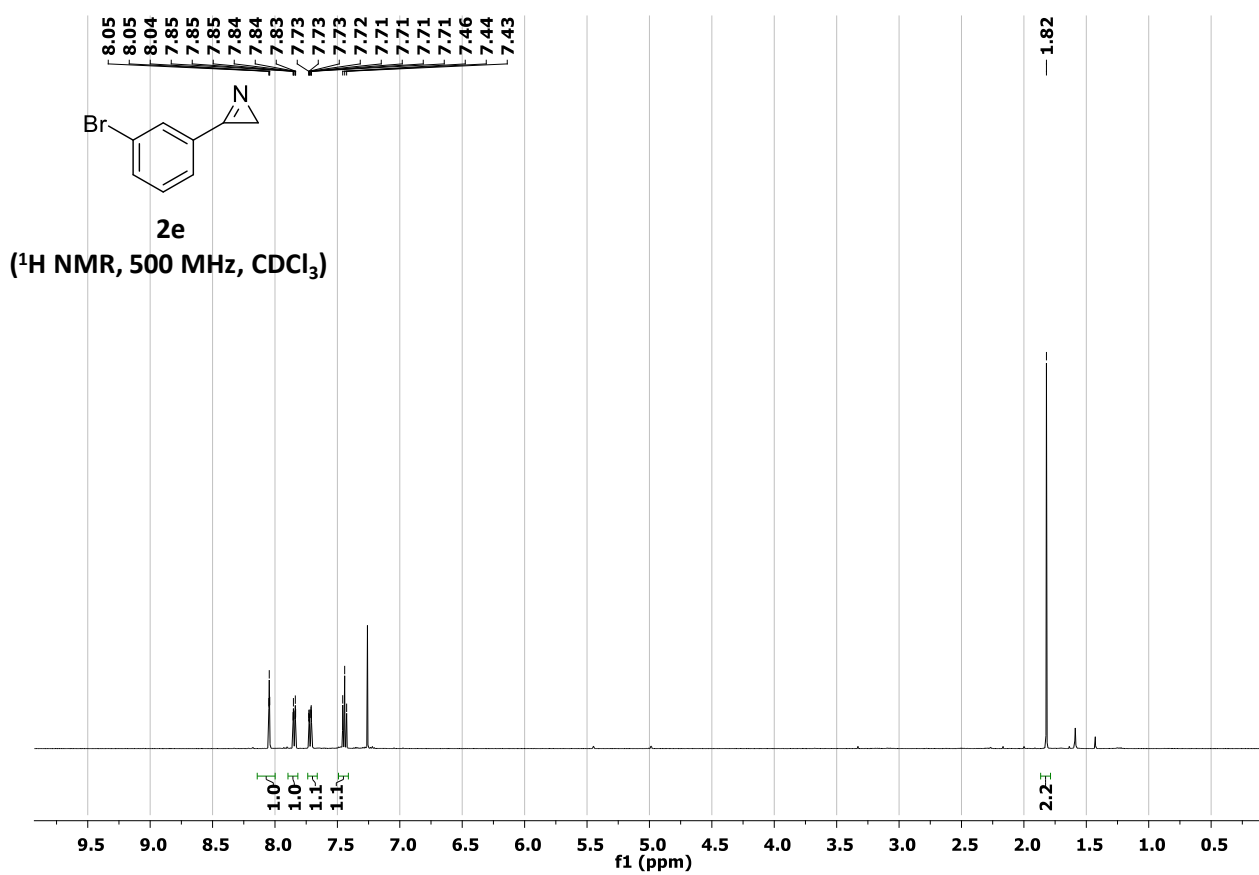


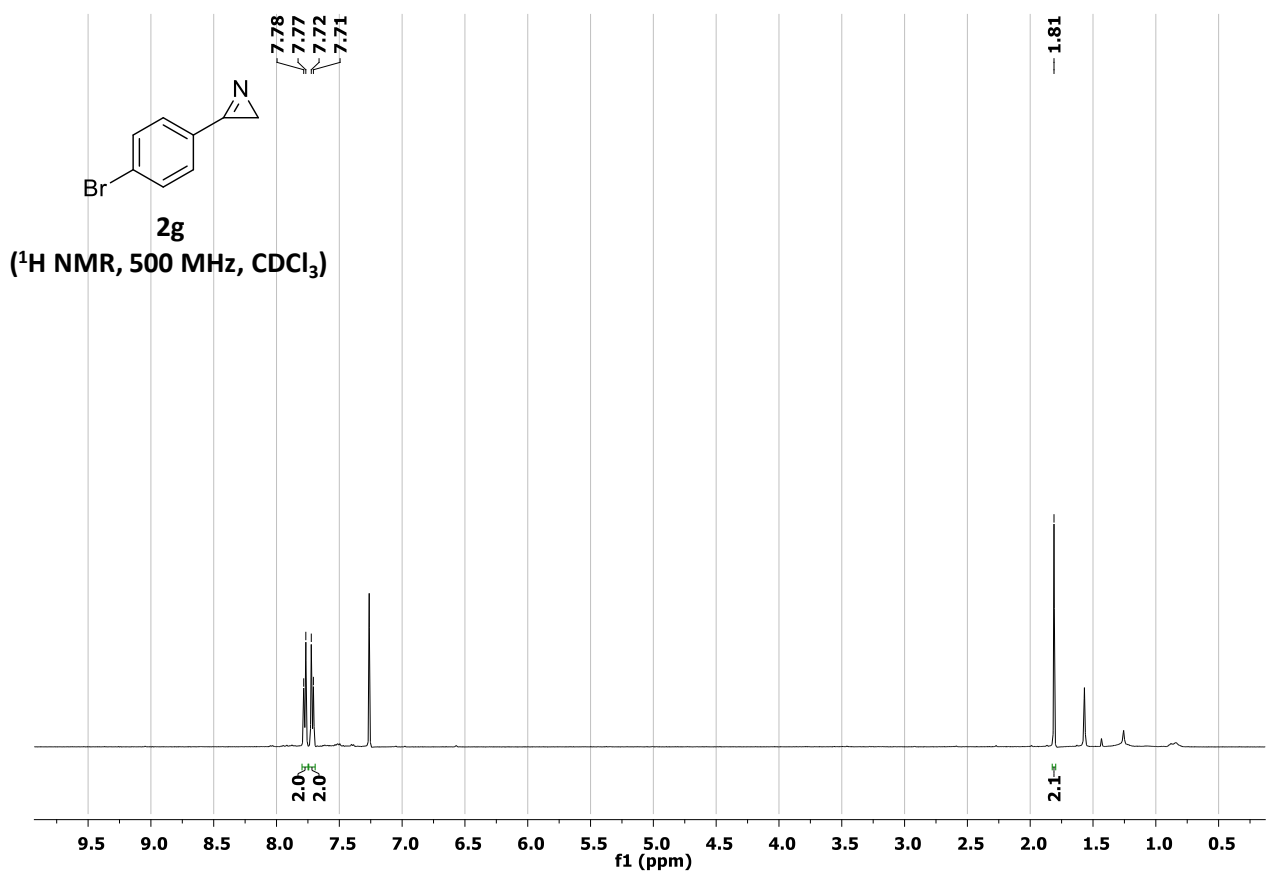
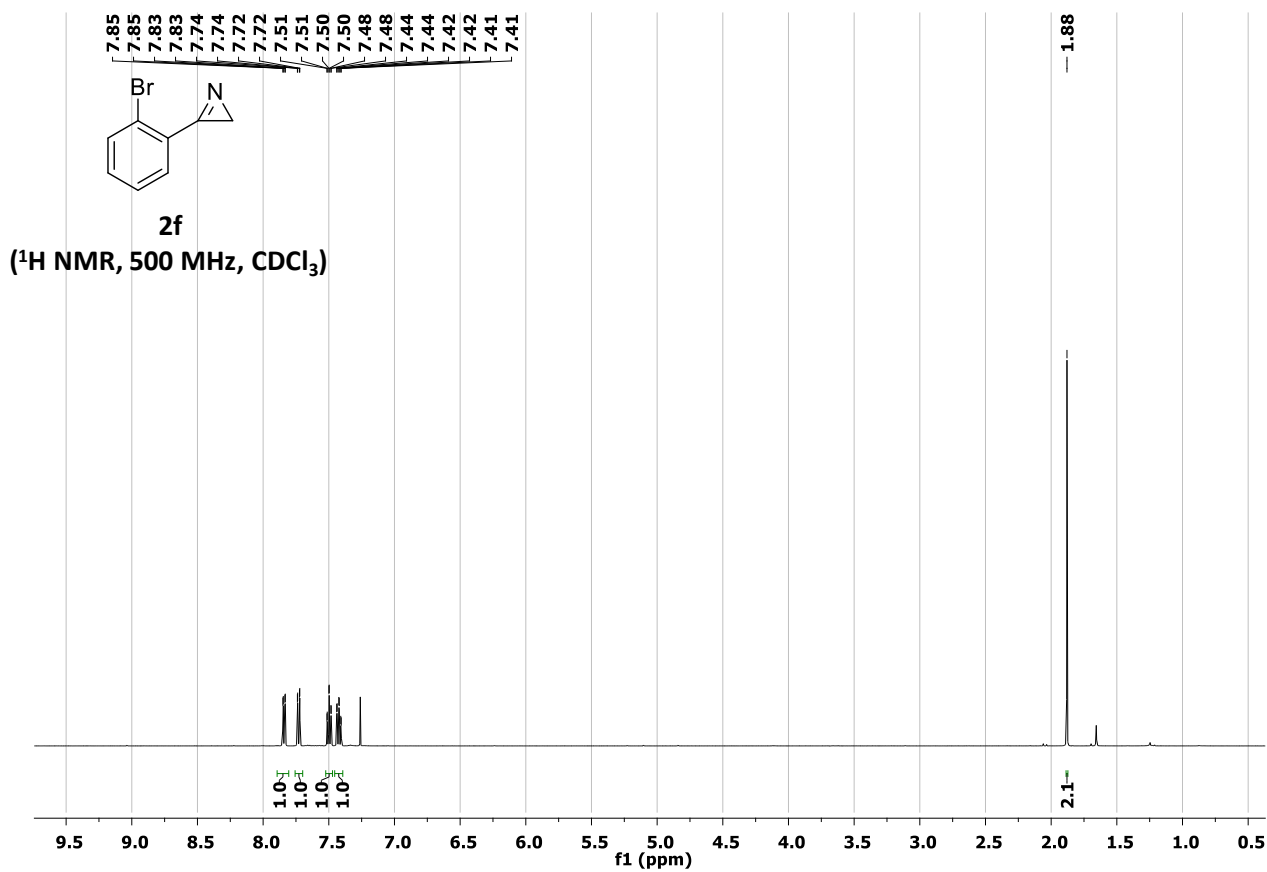




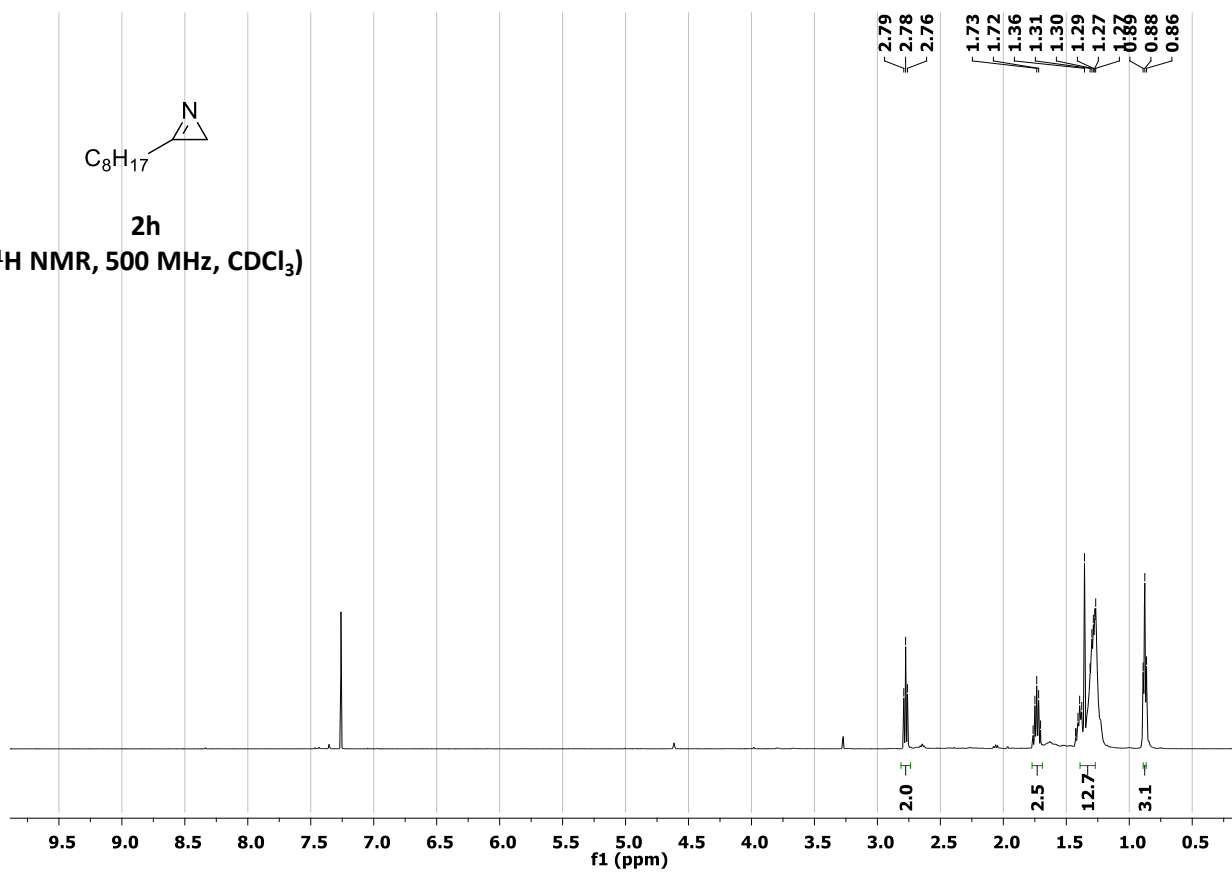




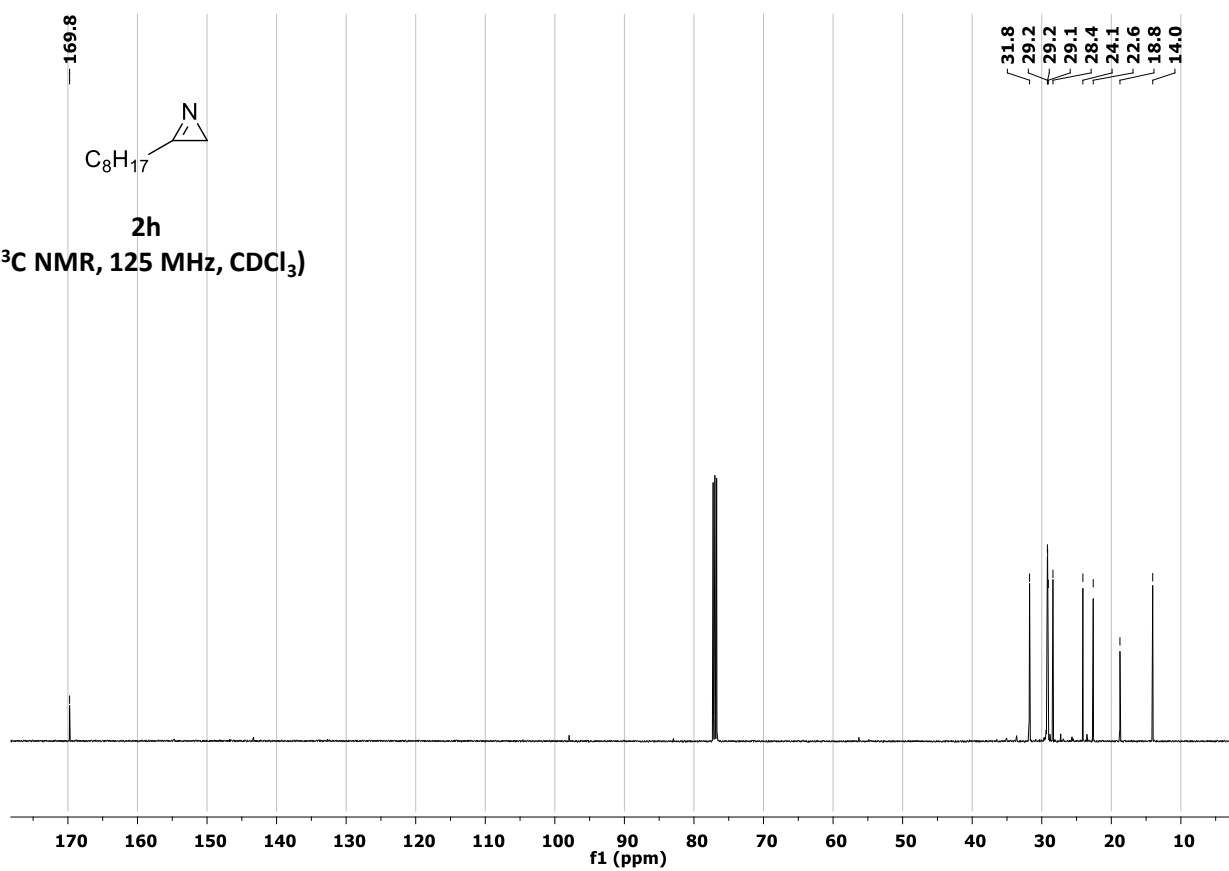


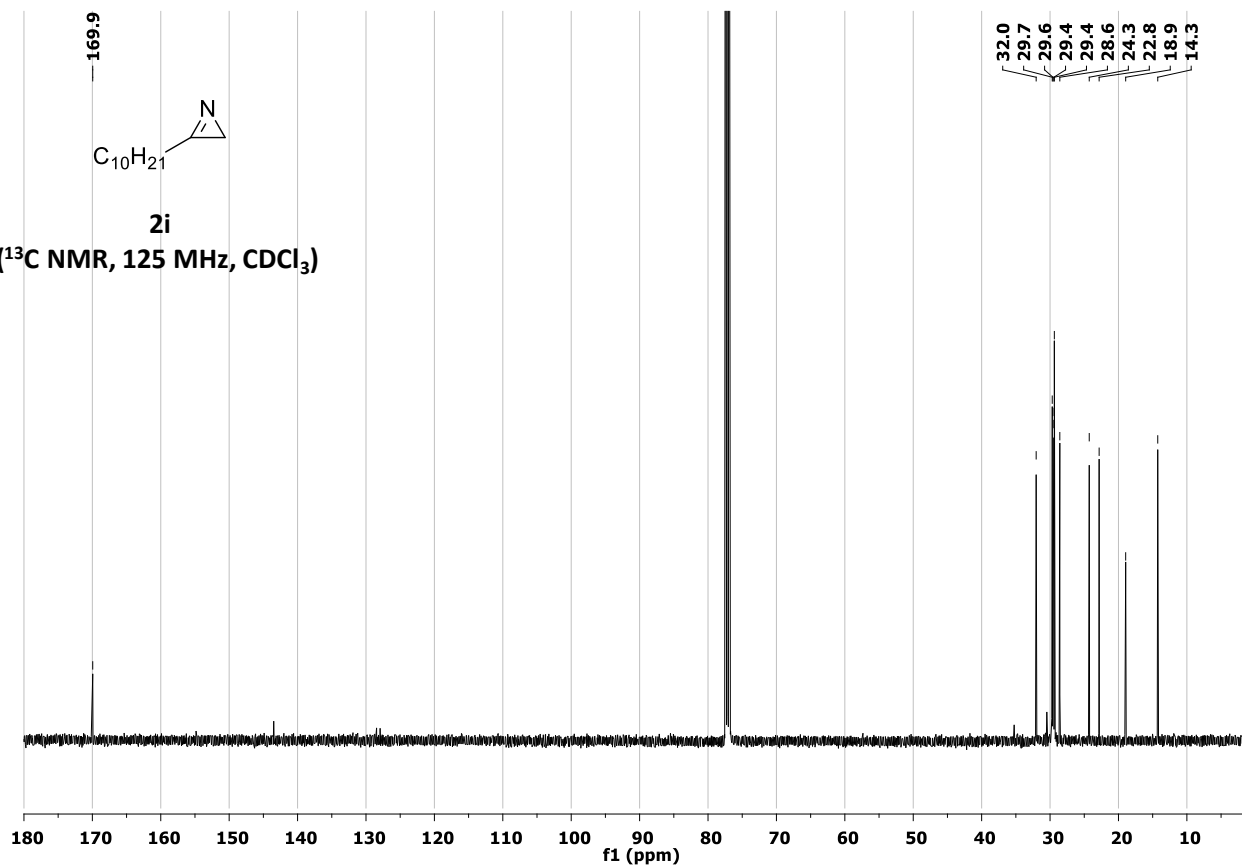
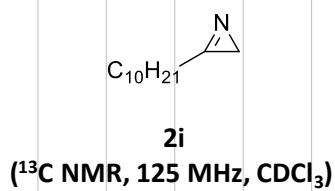
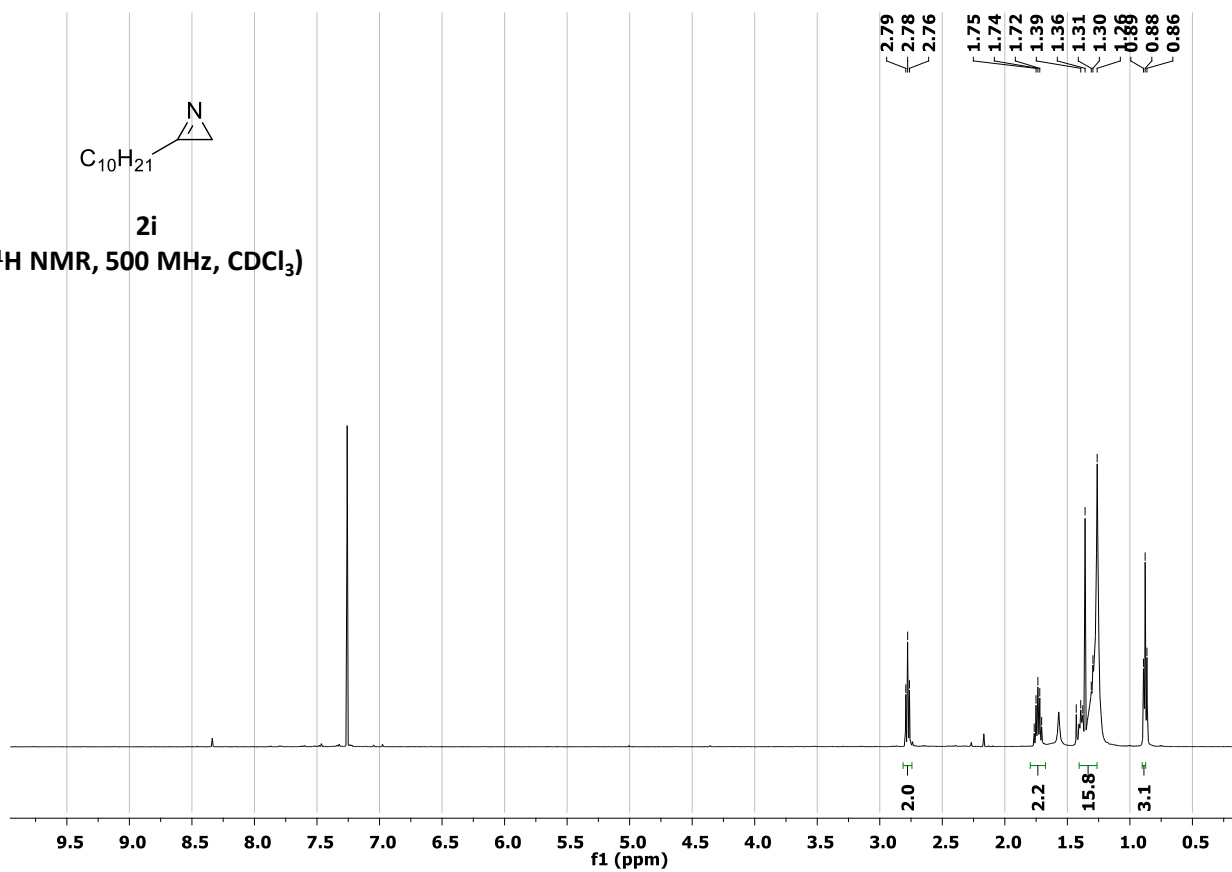
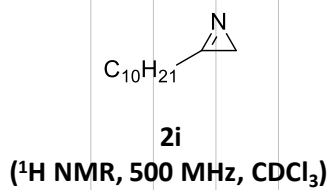


C8H17N1  
**2h**  
 $(^1\text{H NMR, 500 MHz, CDCl}_3)$

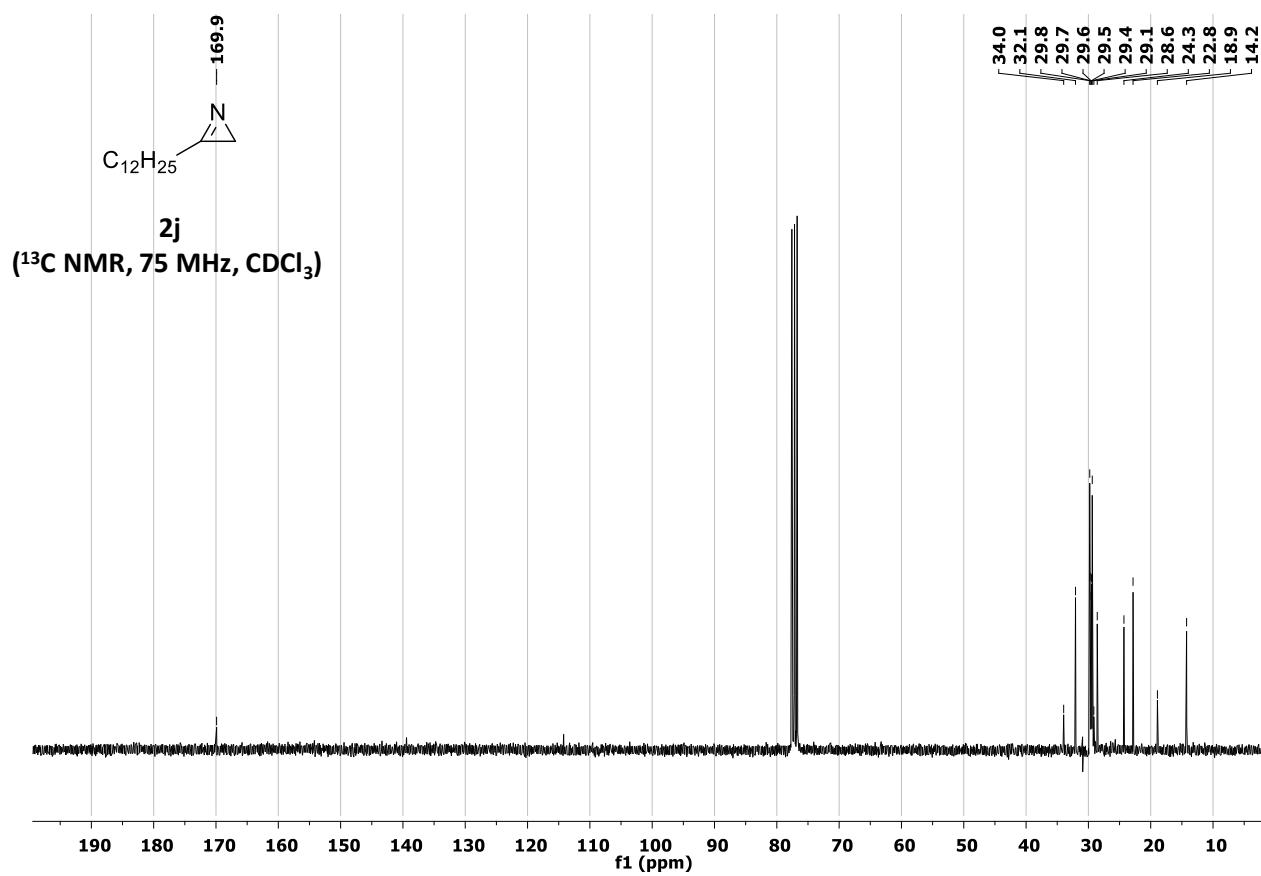
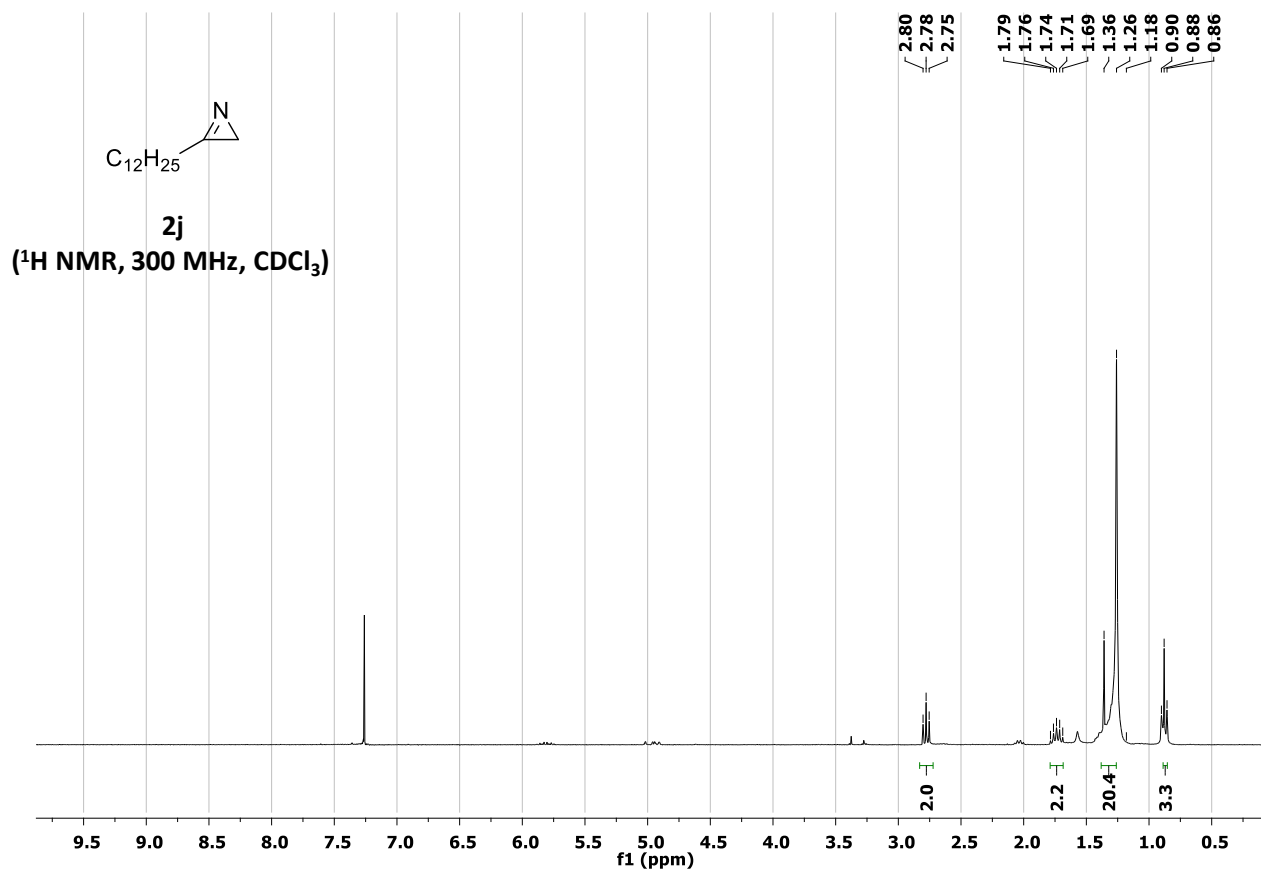


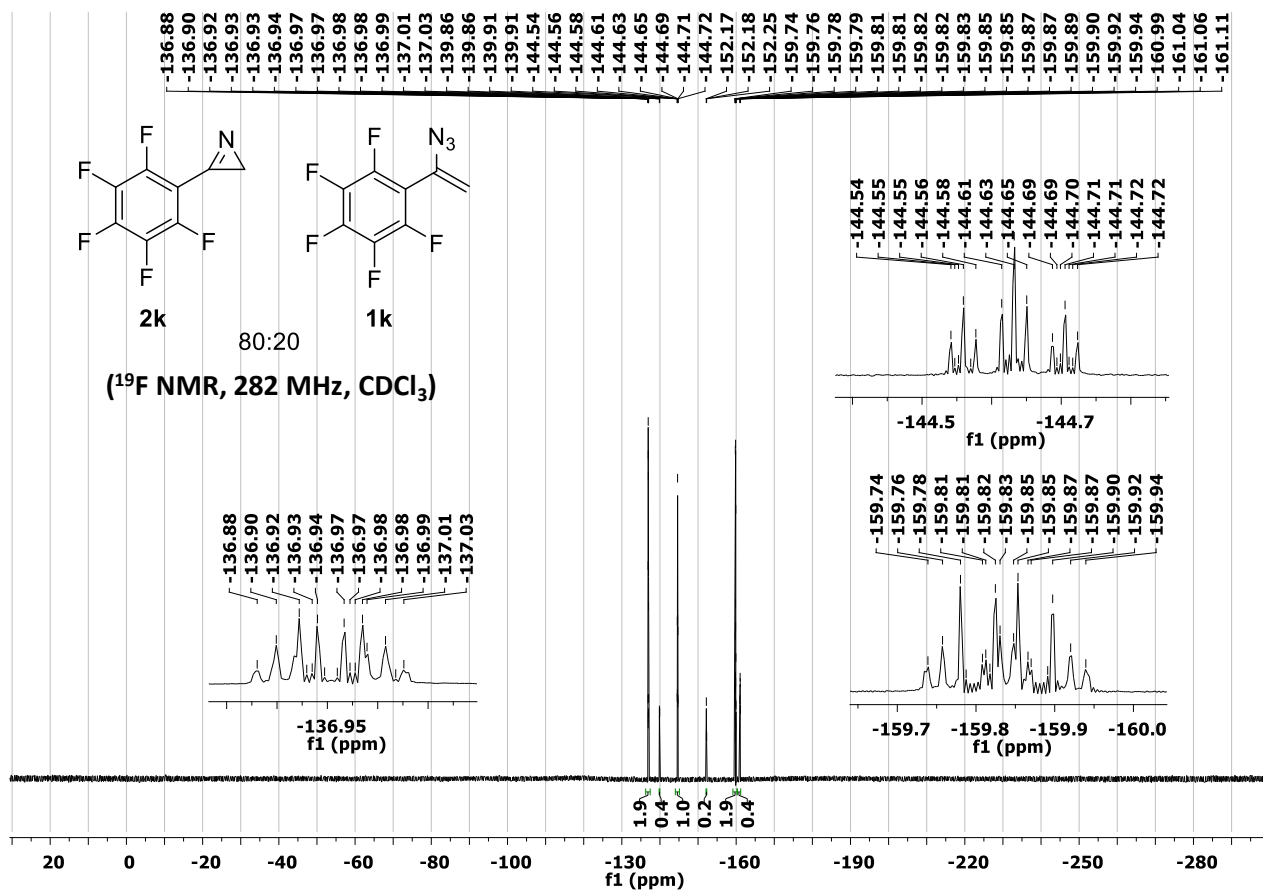
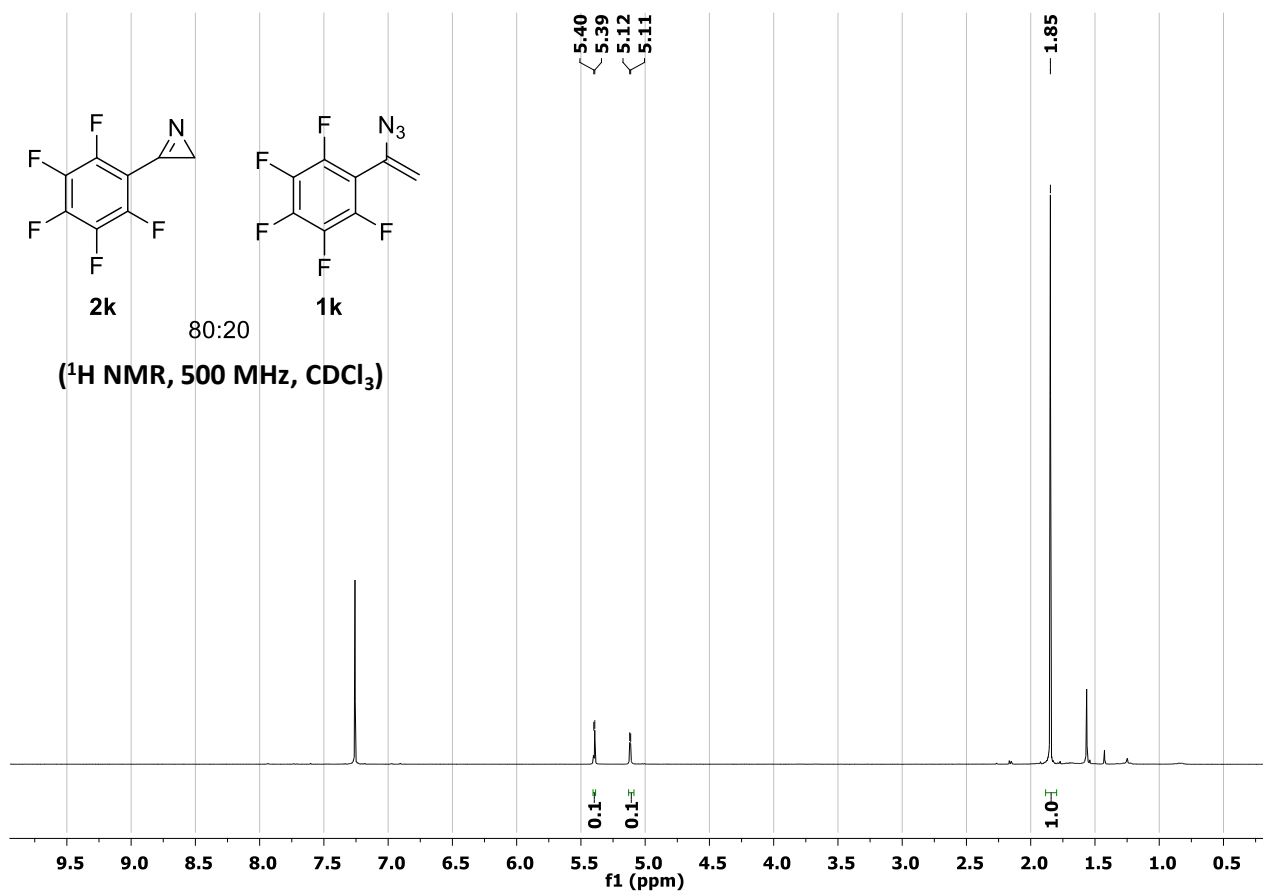
C8H17N1  
**2h**  
 $(^{13}\text{C NMR, 125 MHz, CDCl}_3)$

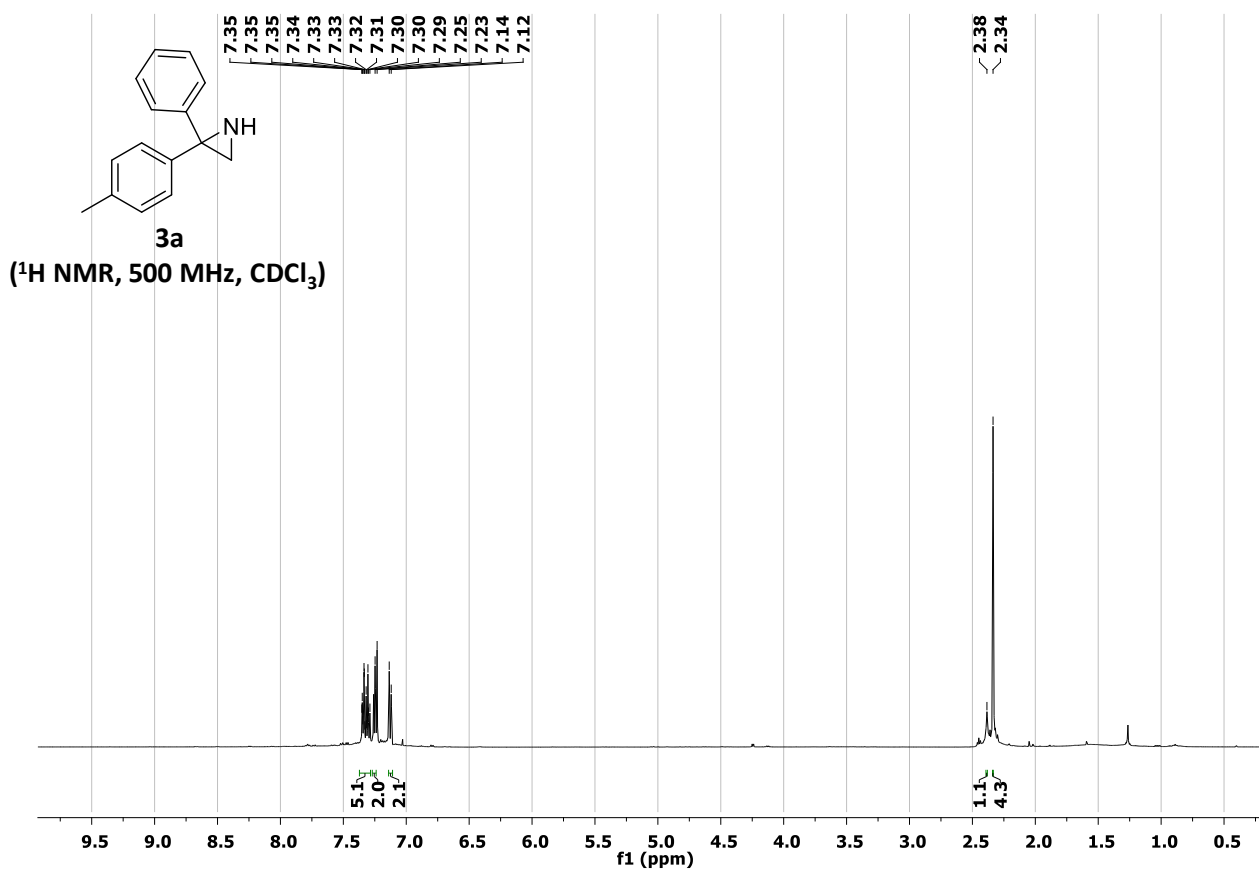
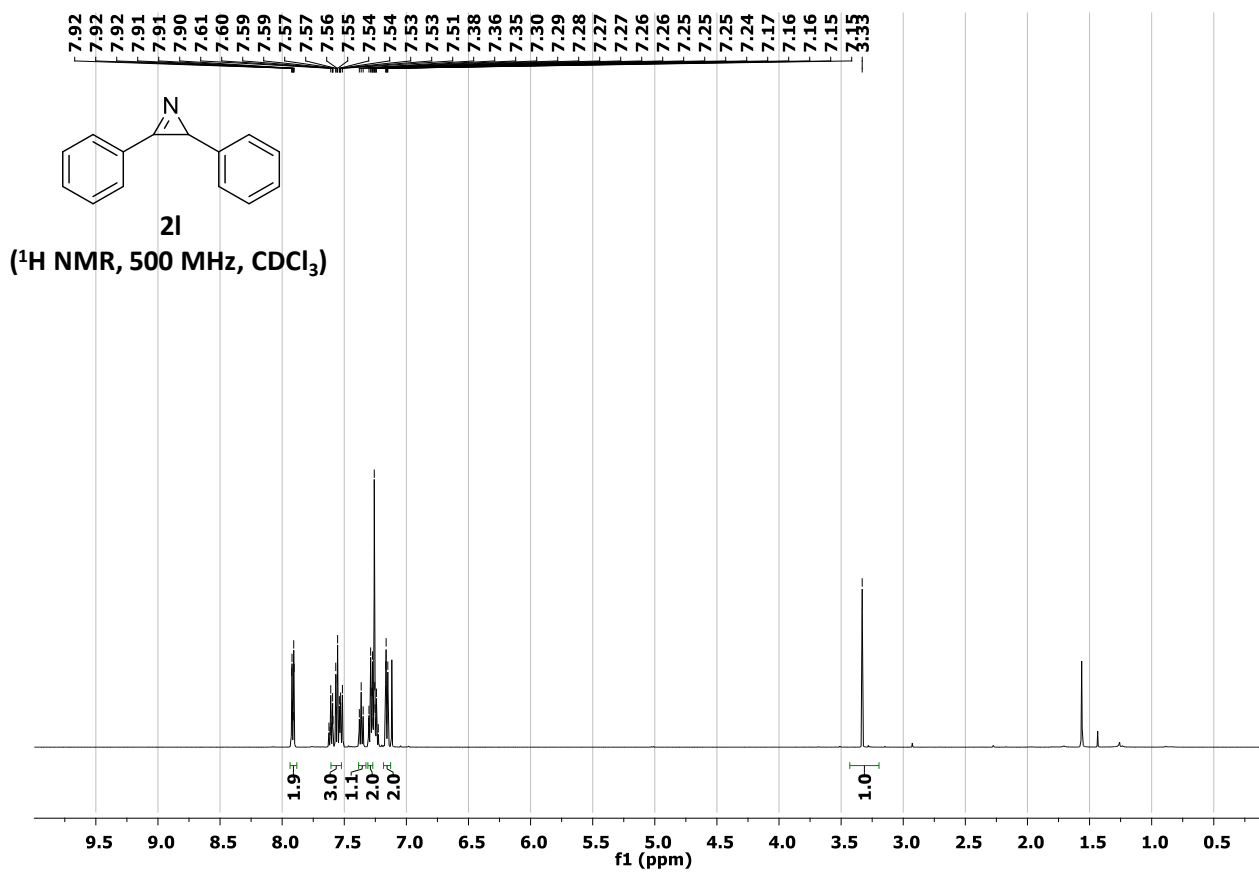


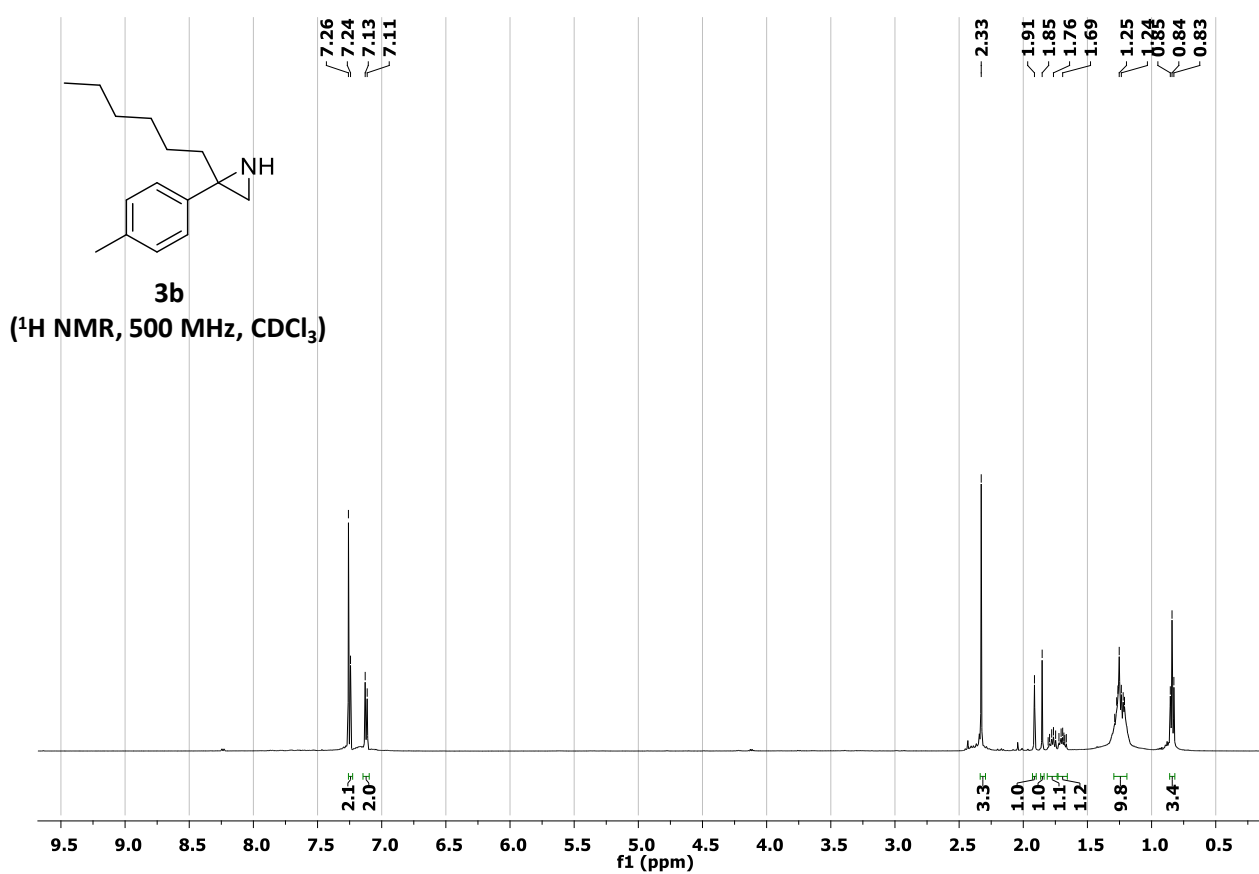
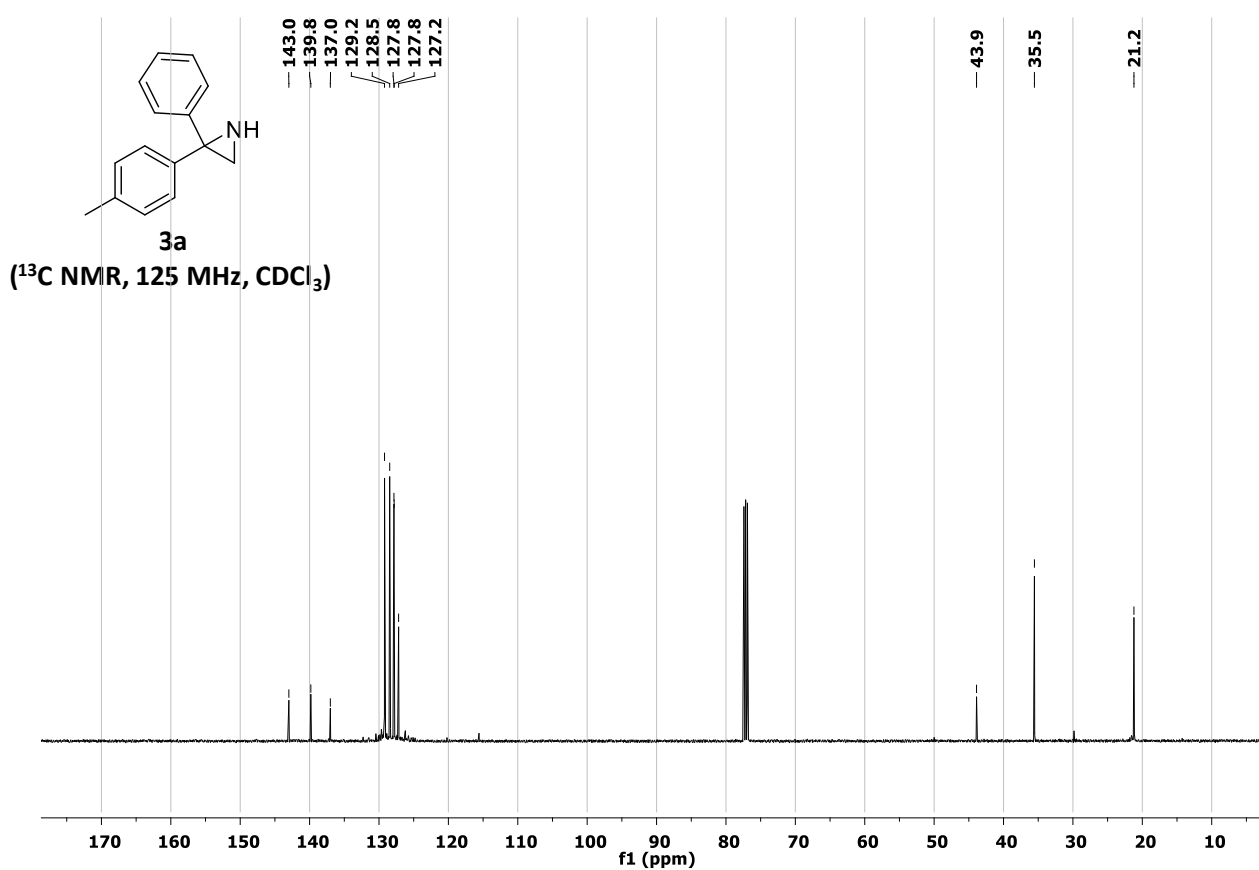


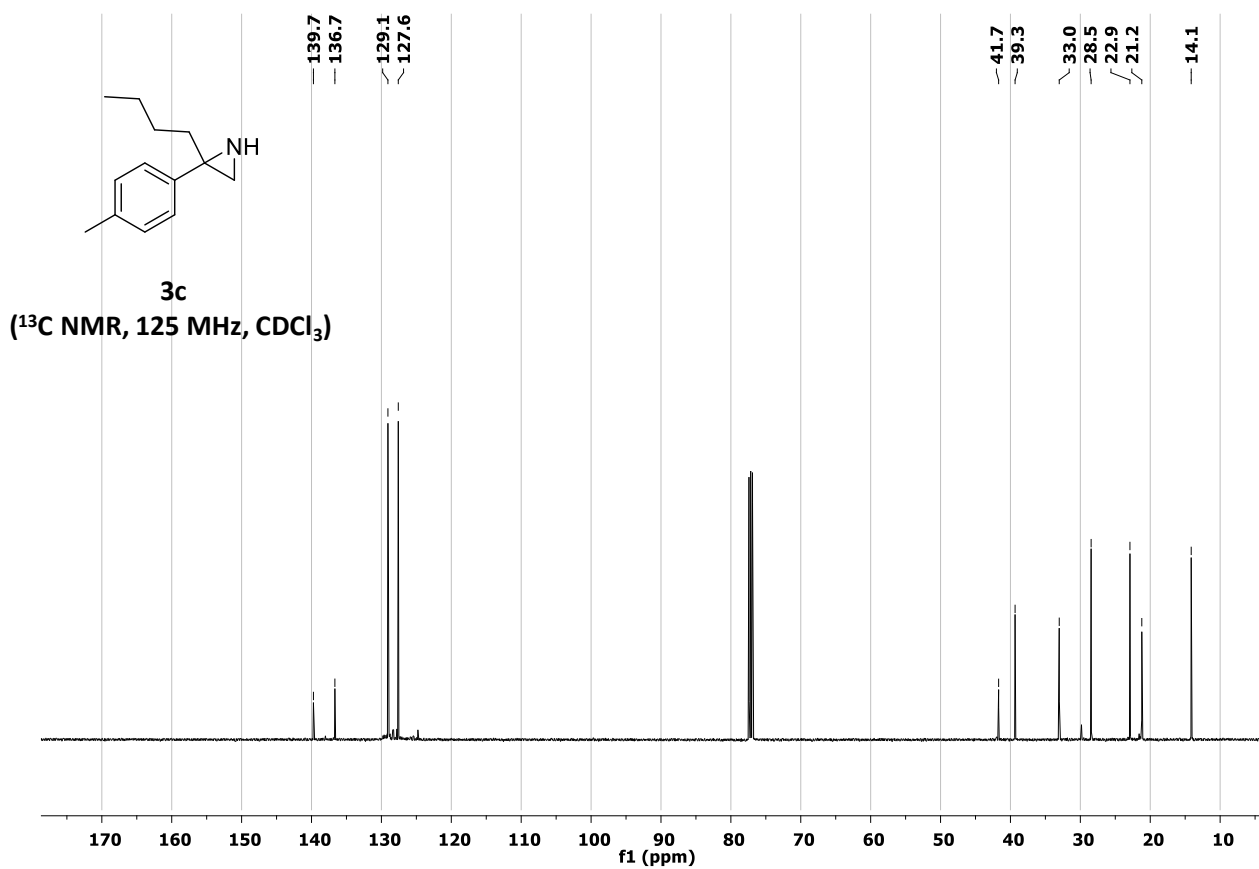
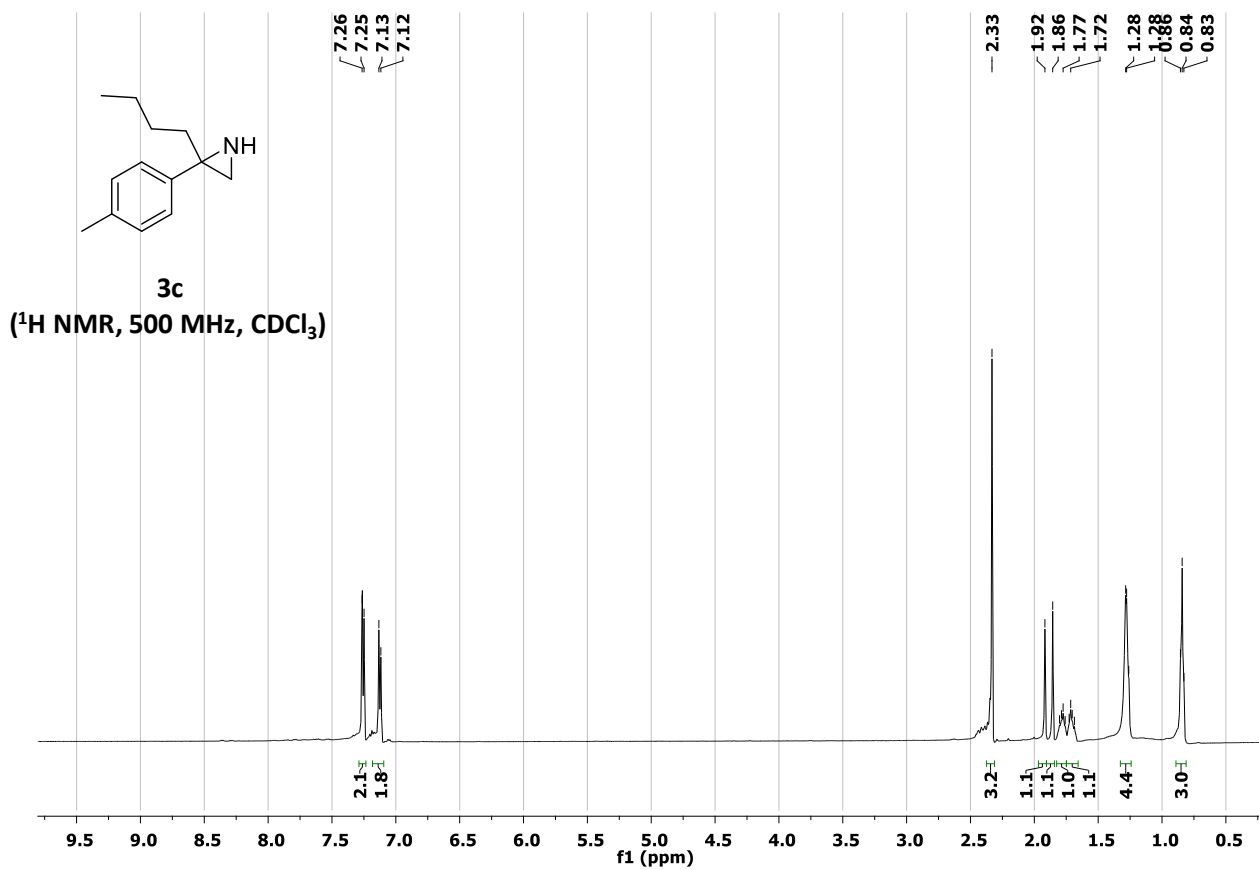


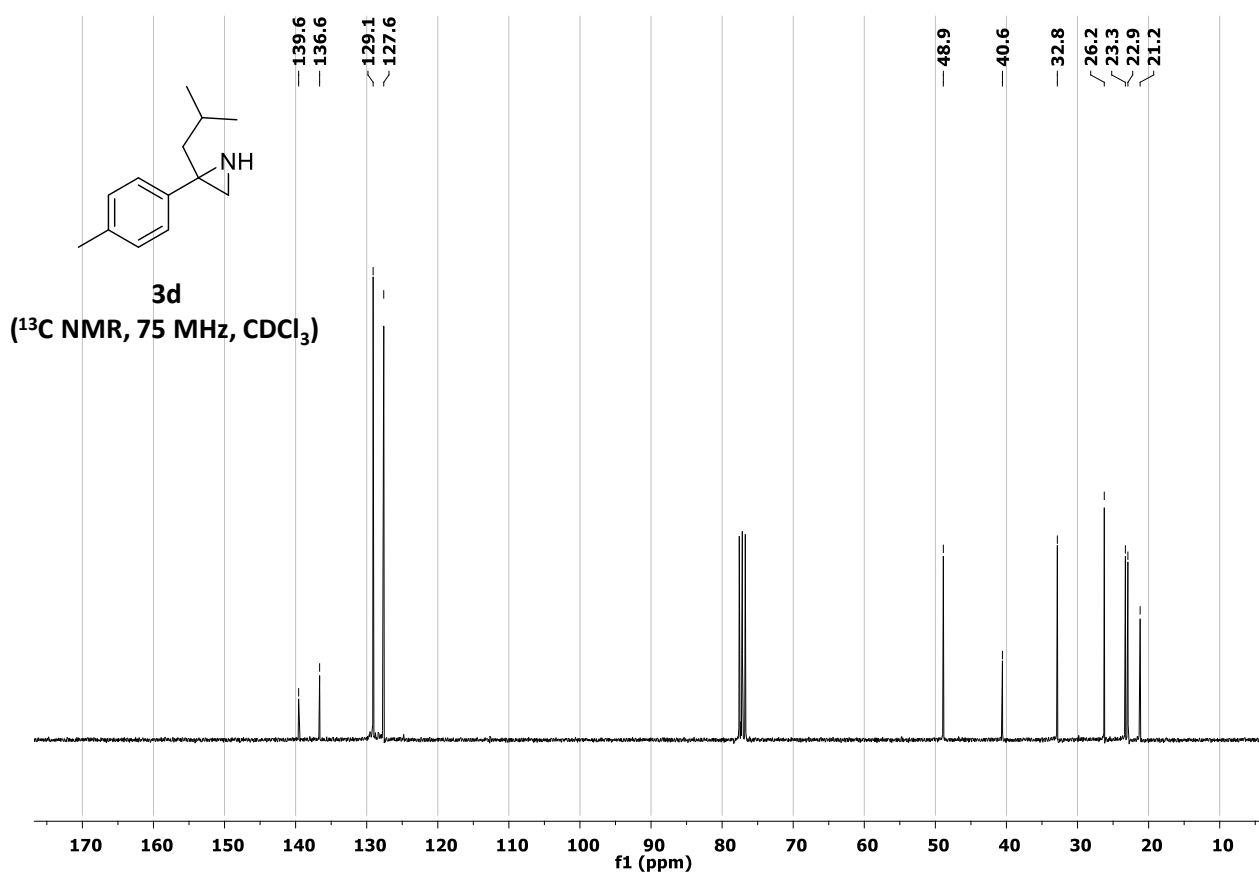
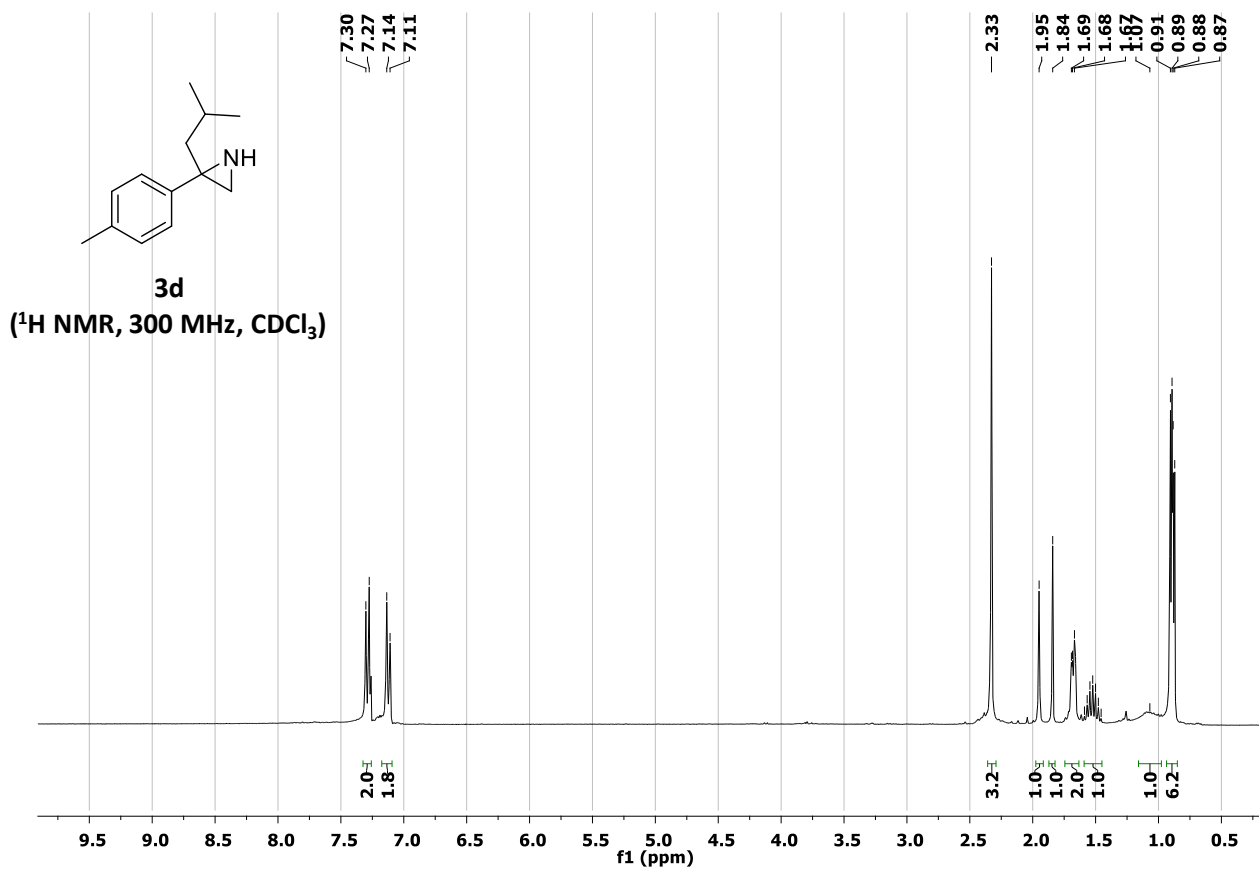


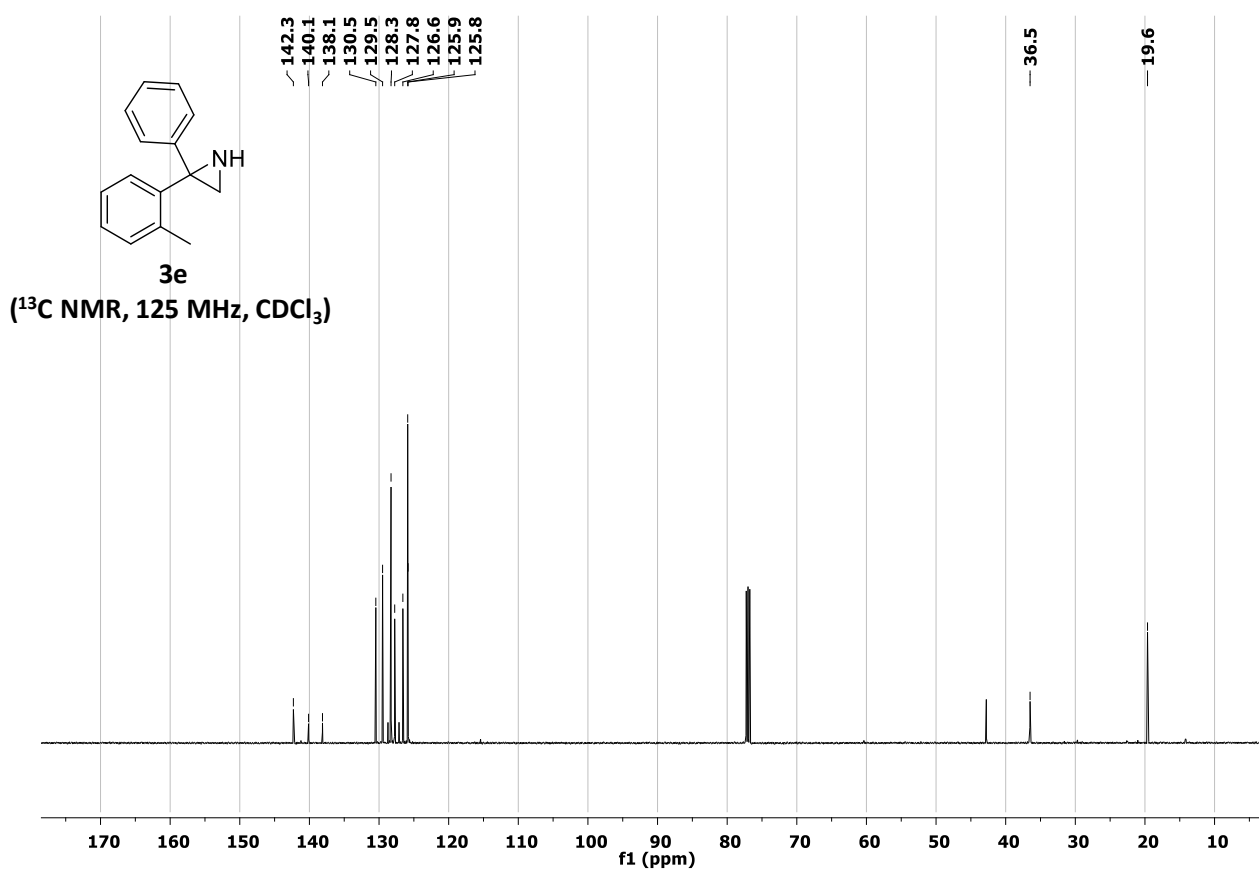
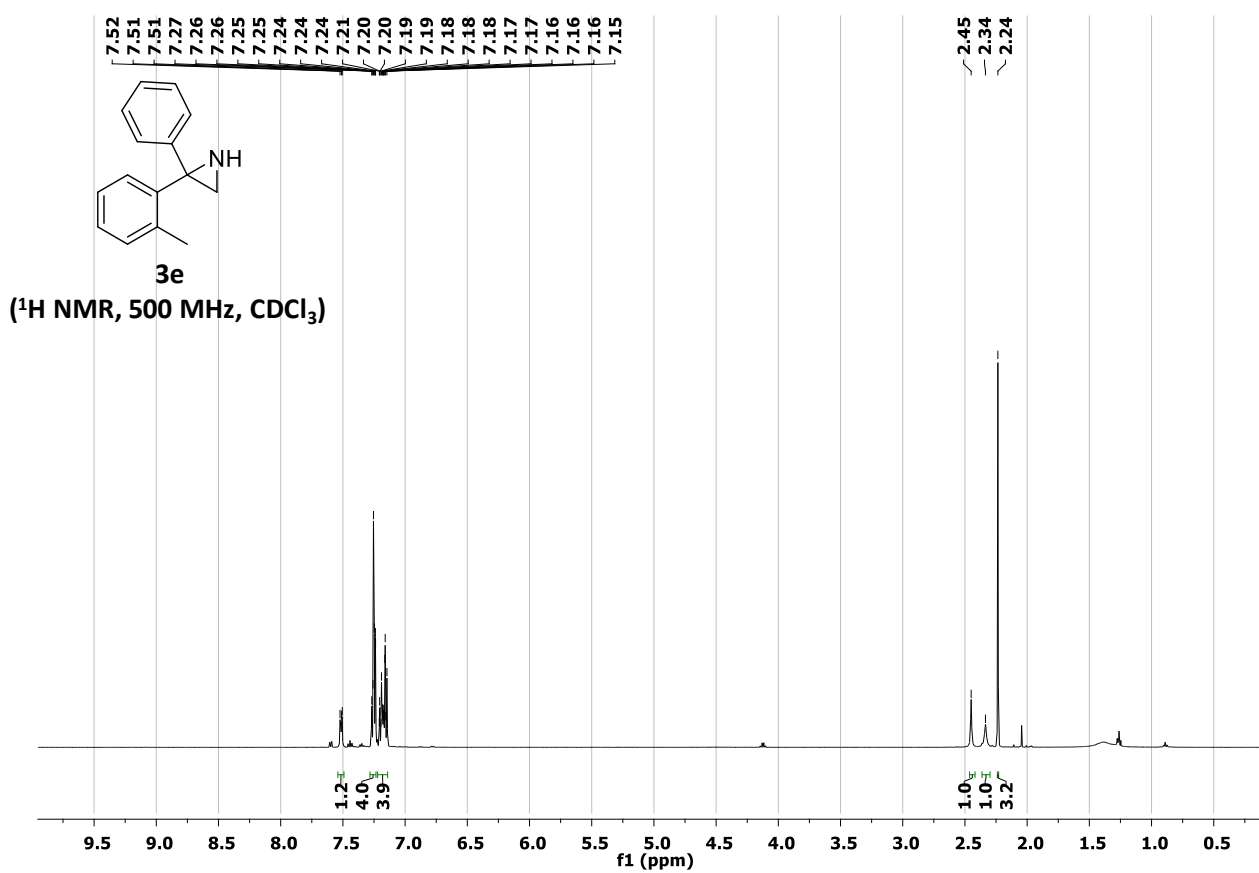


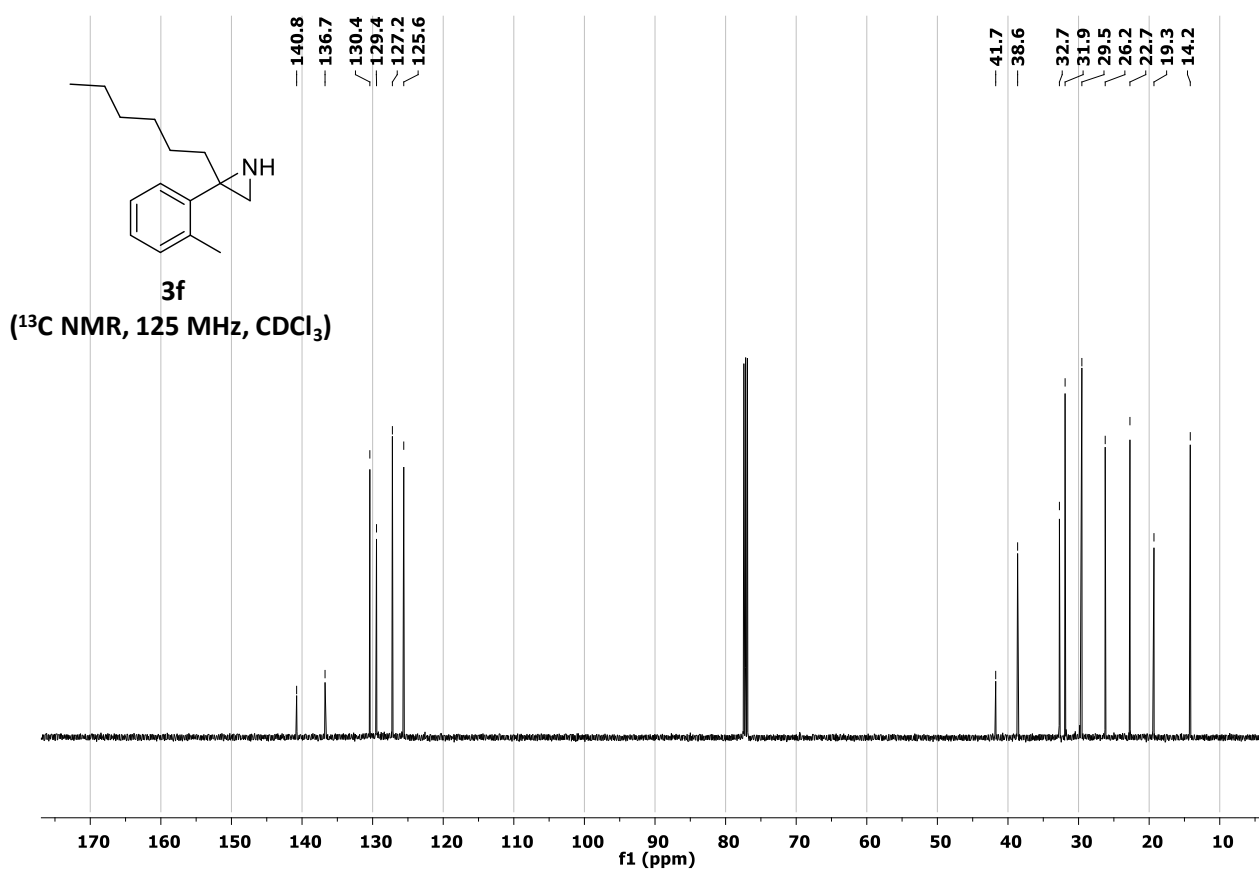
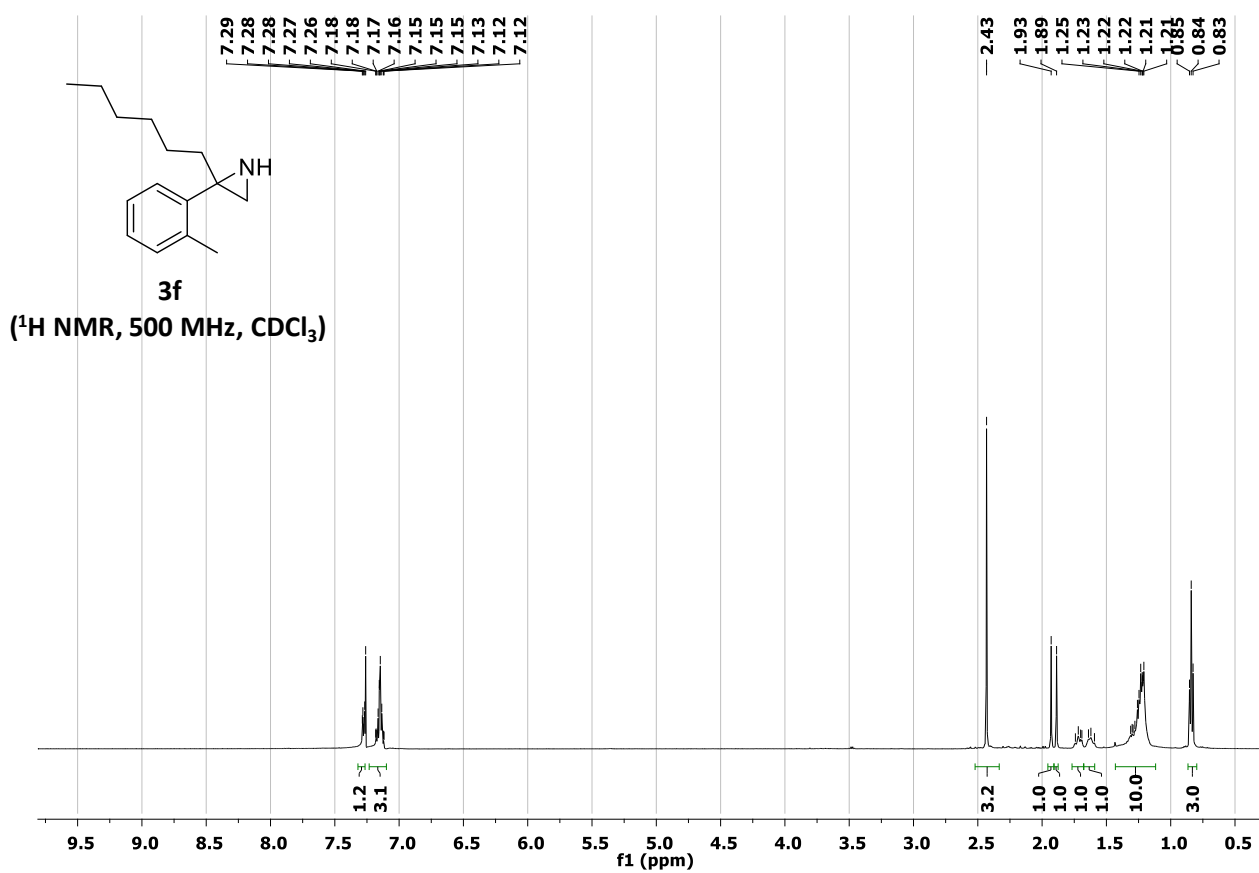




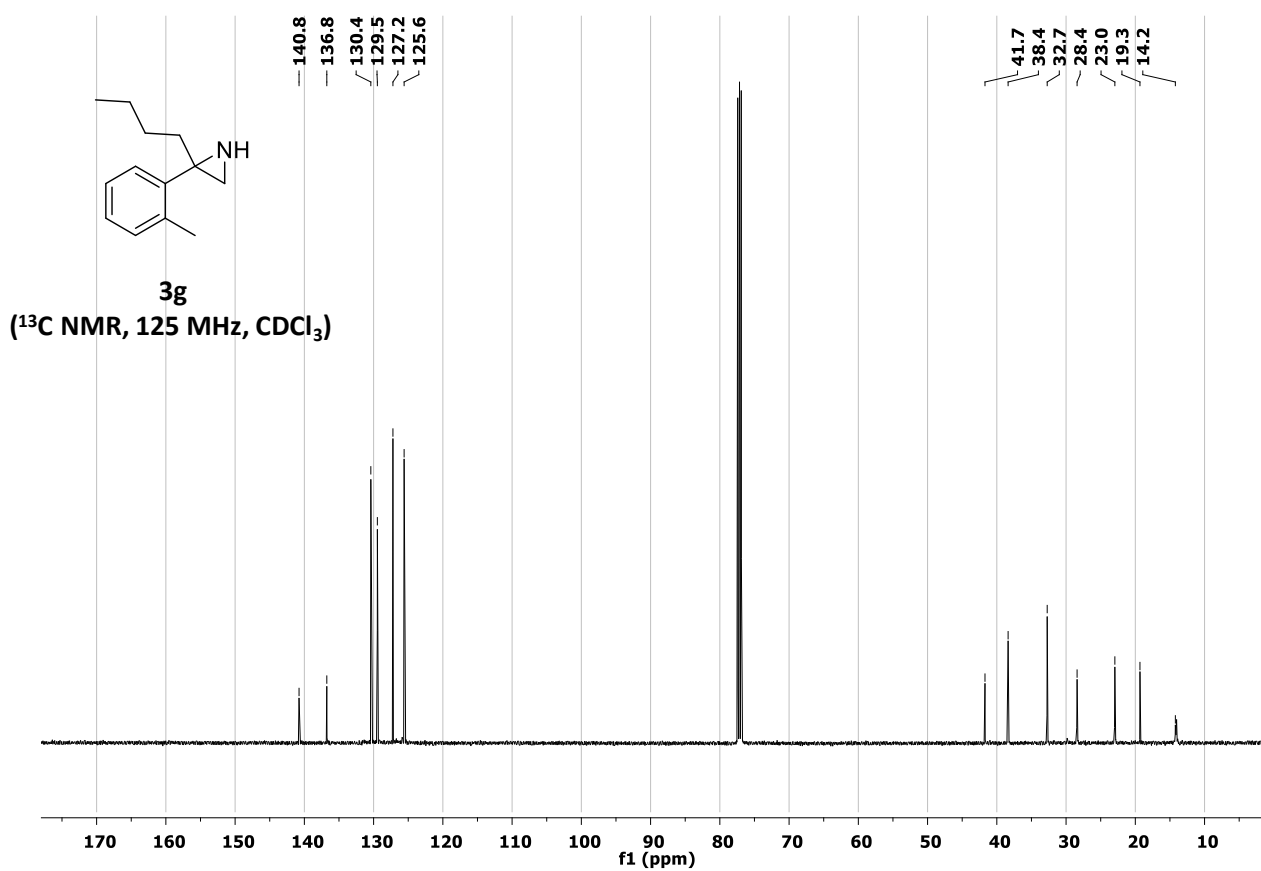
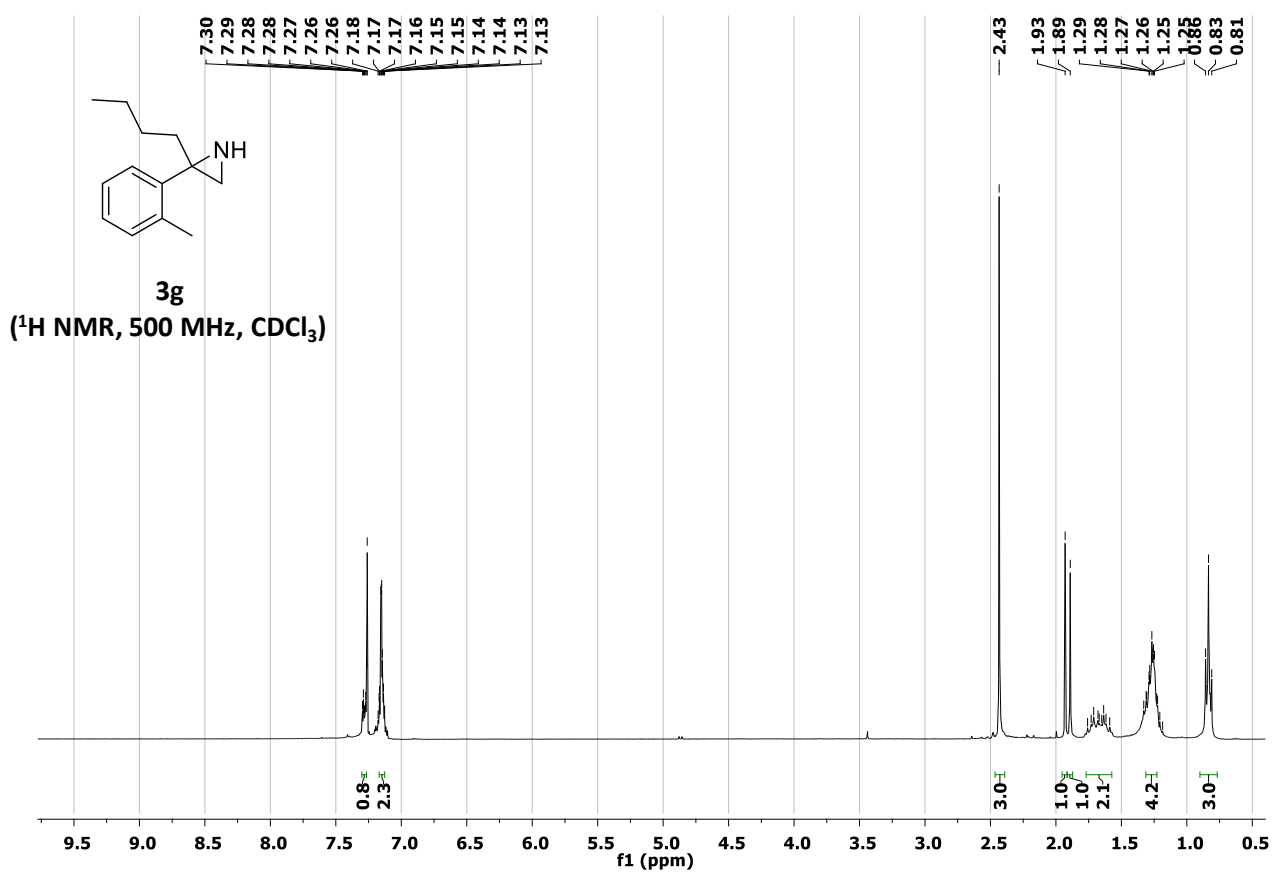


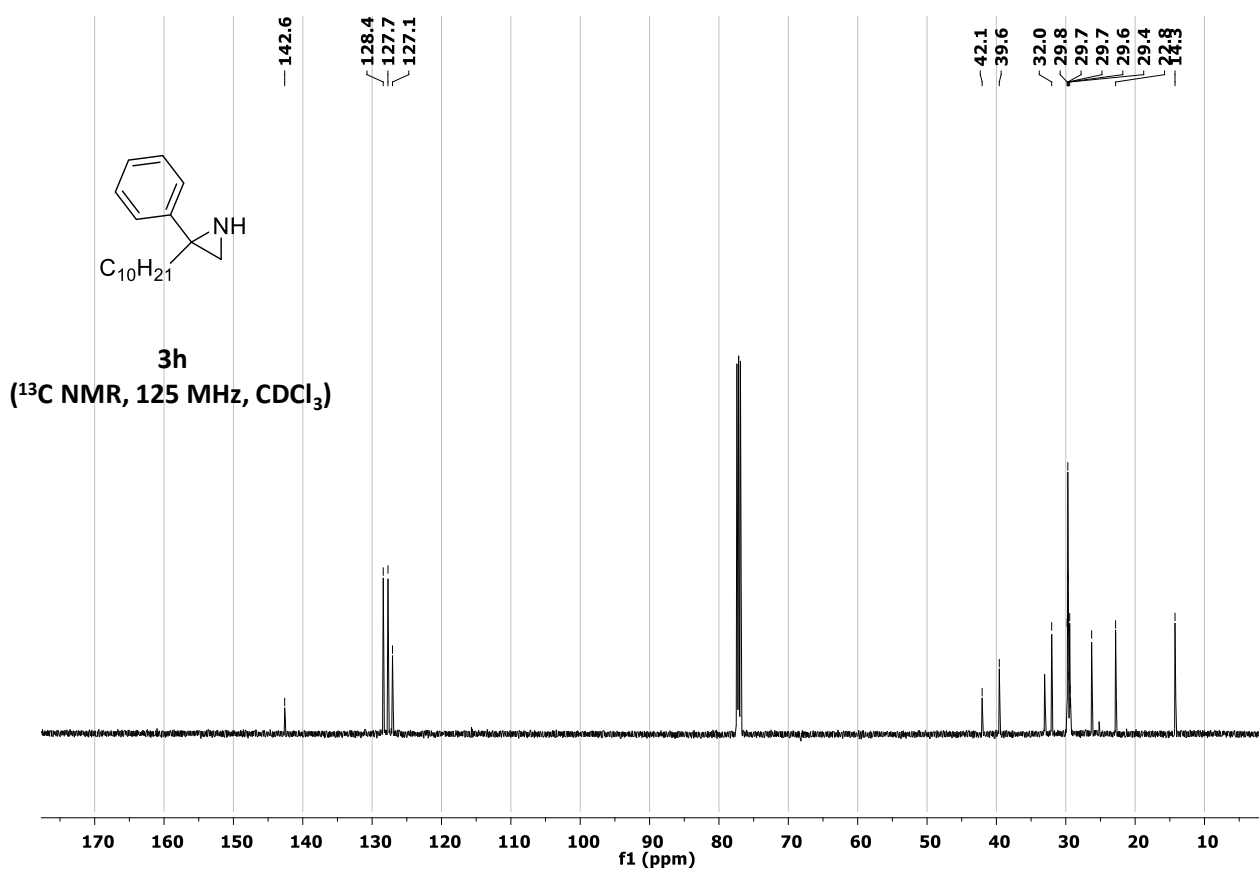
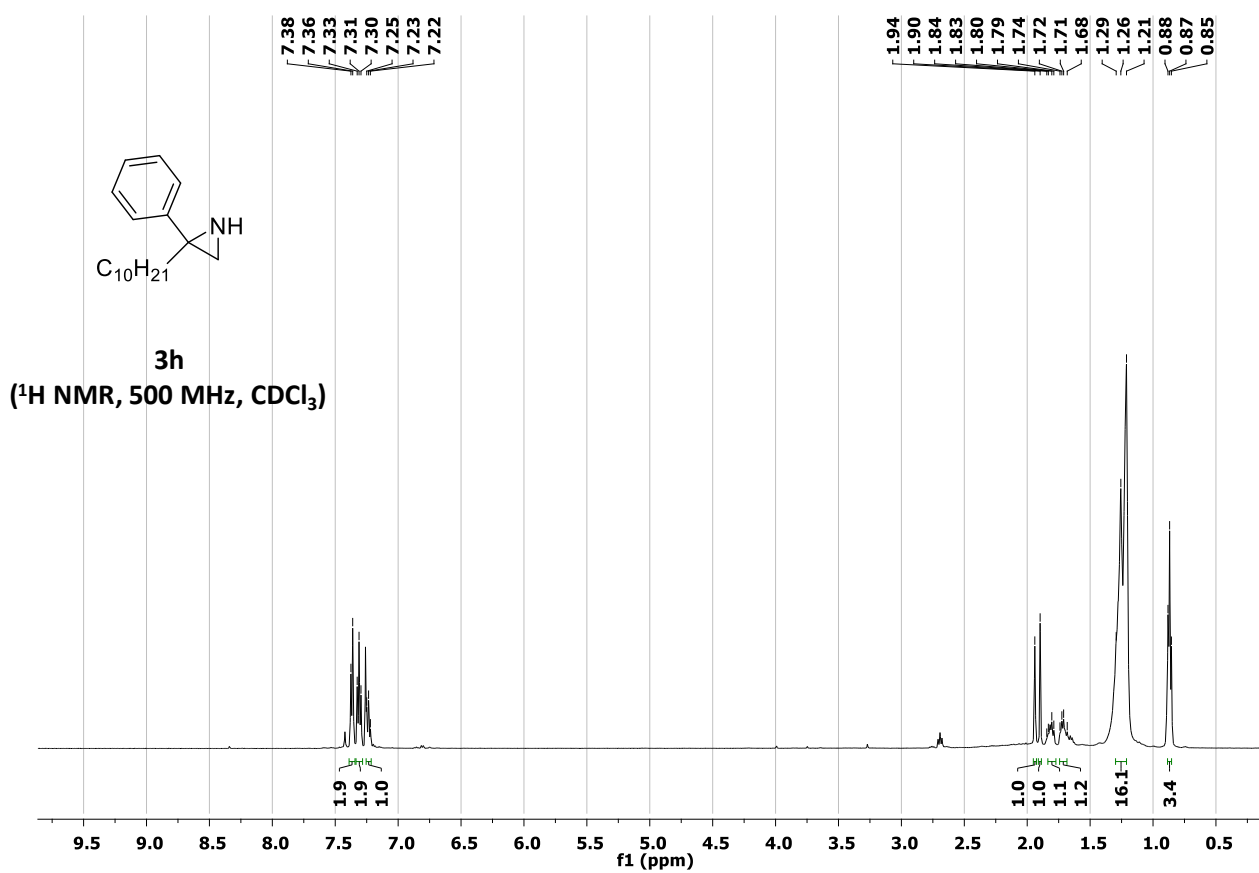


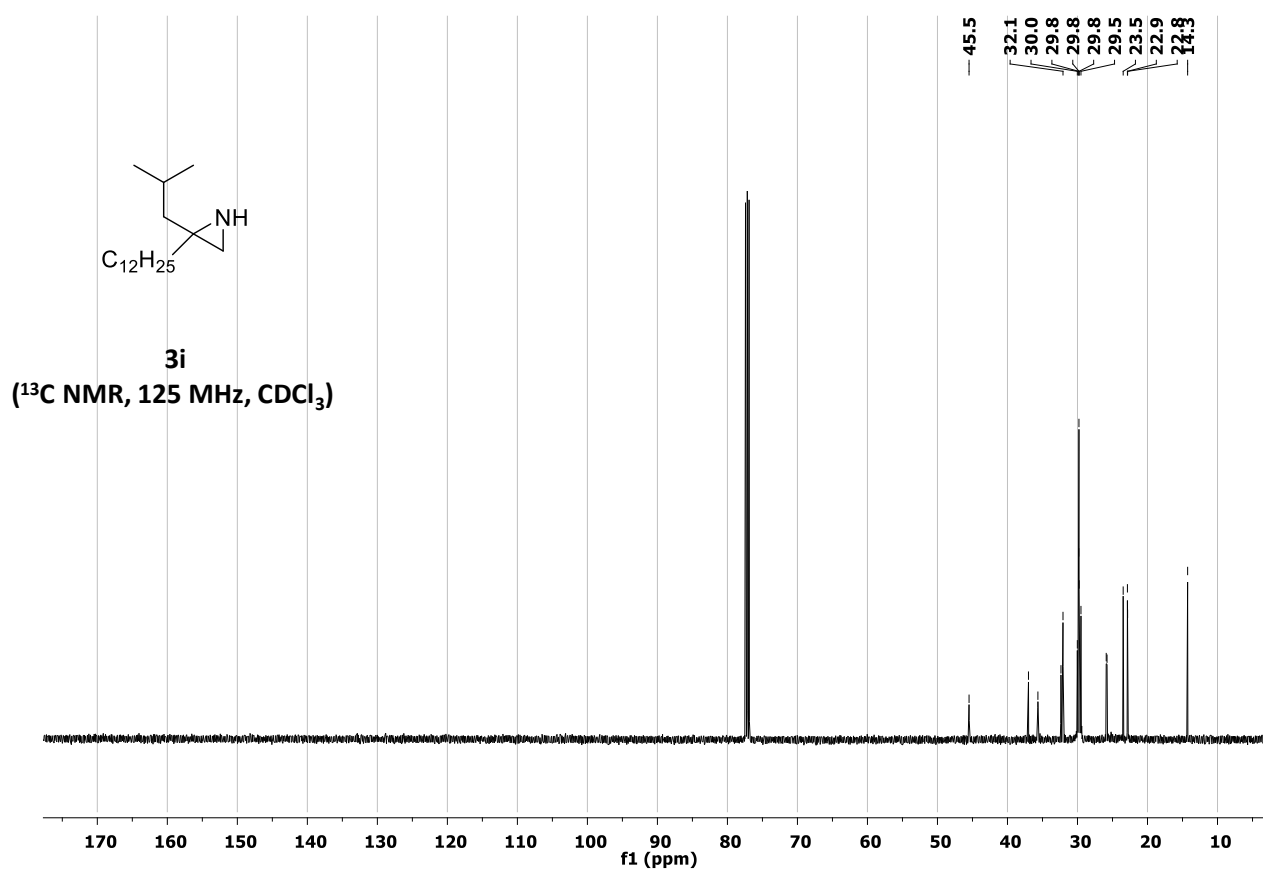
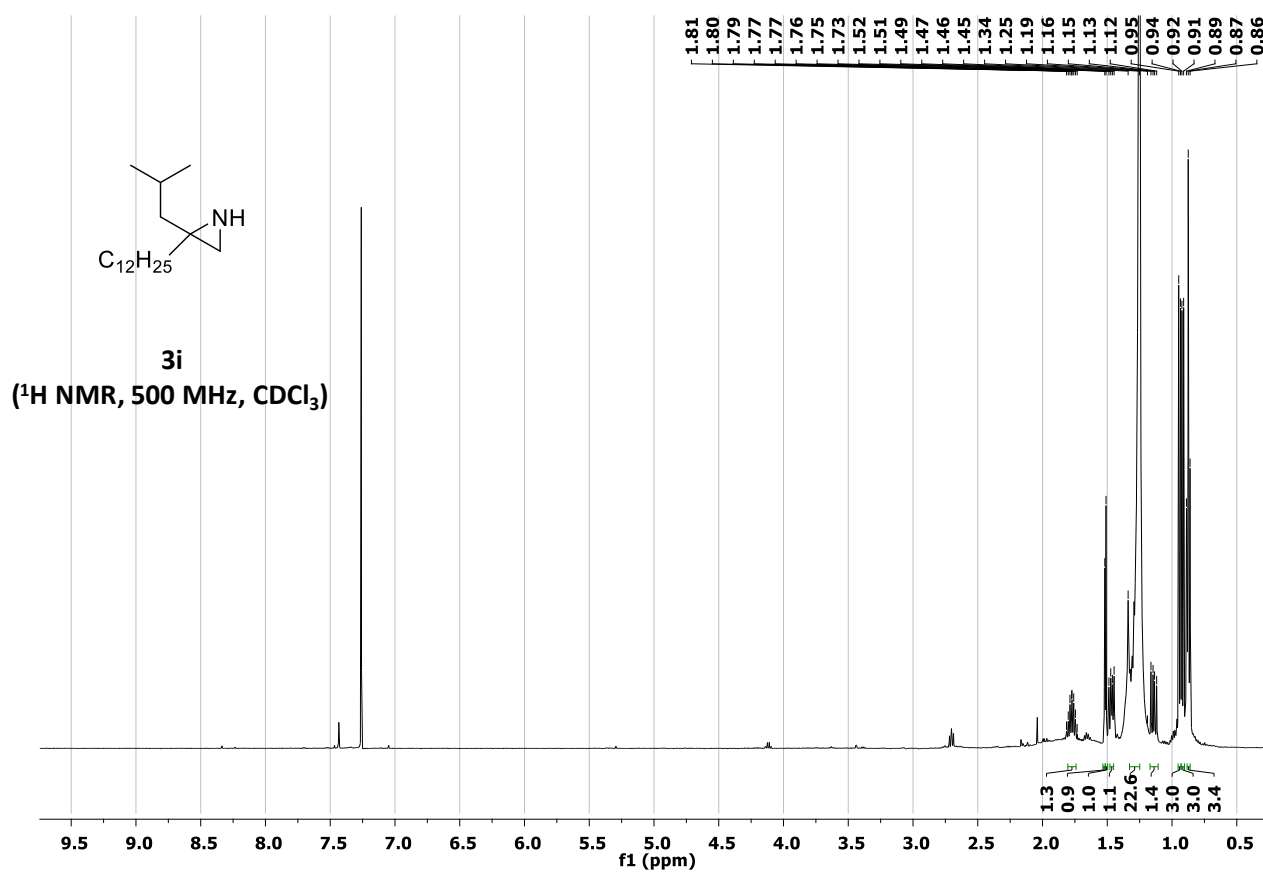


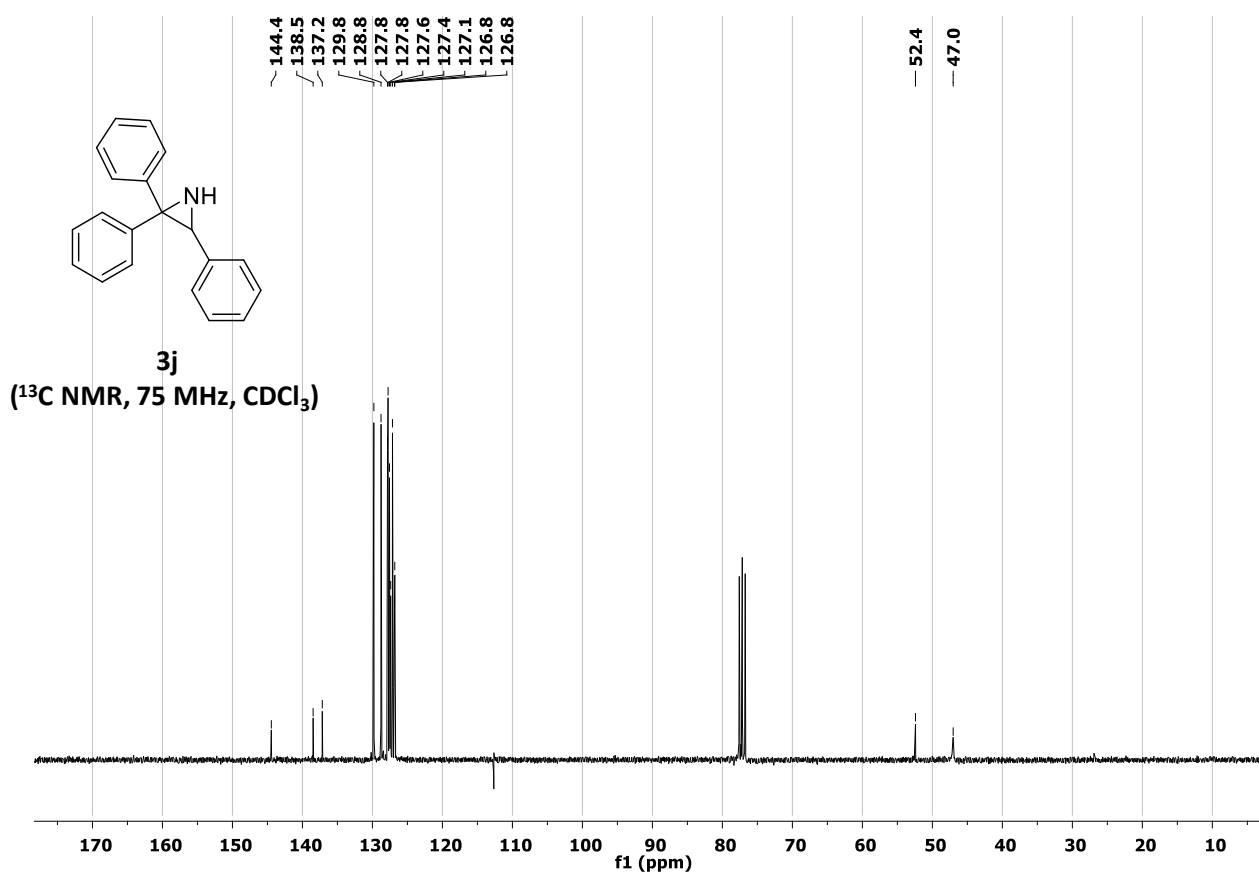
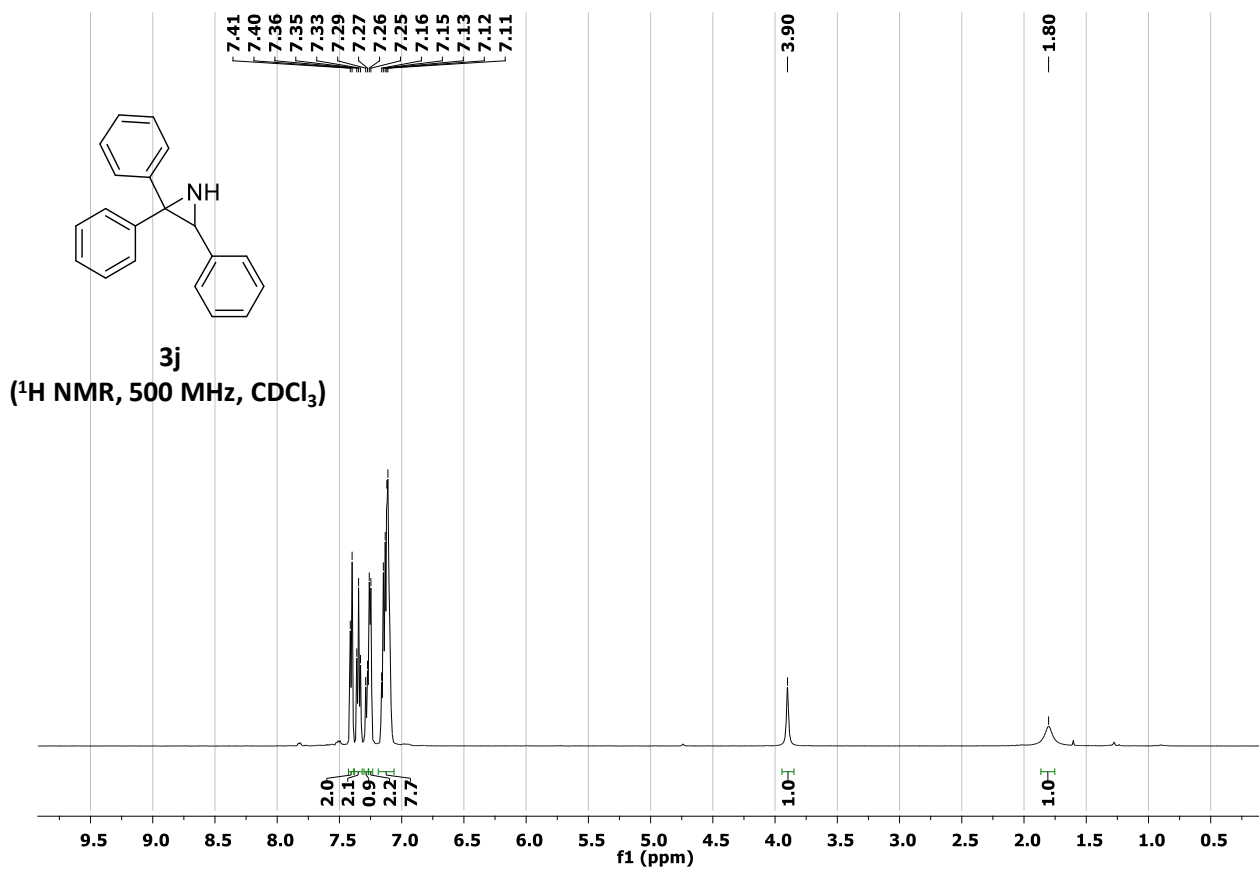


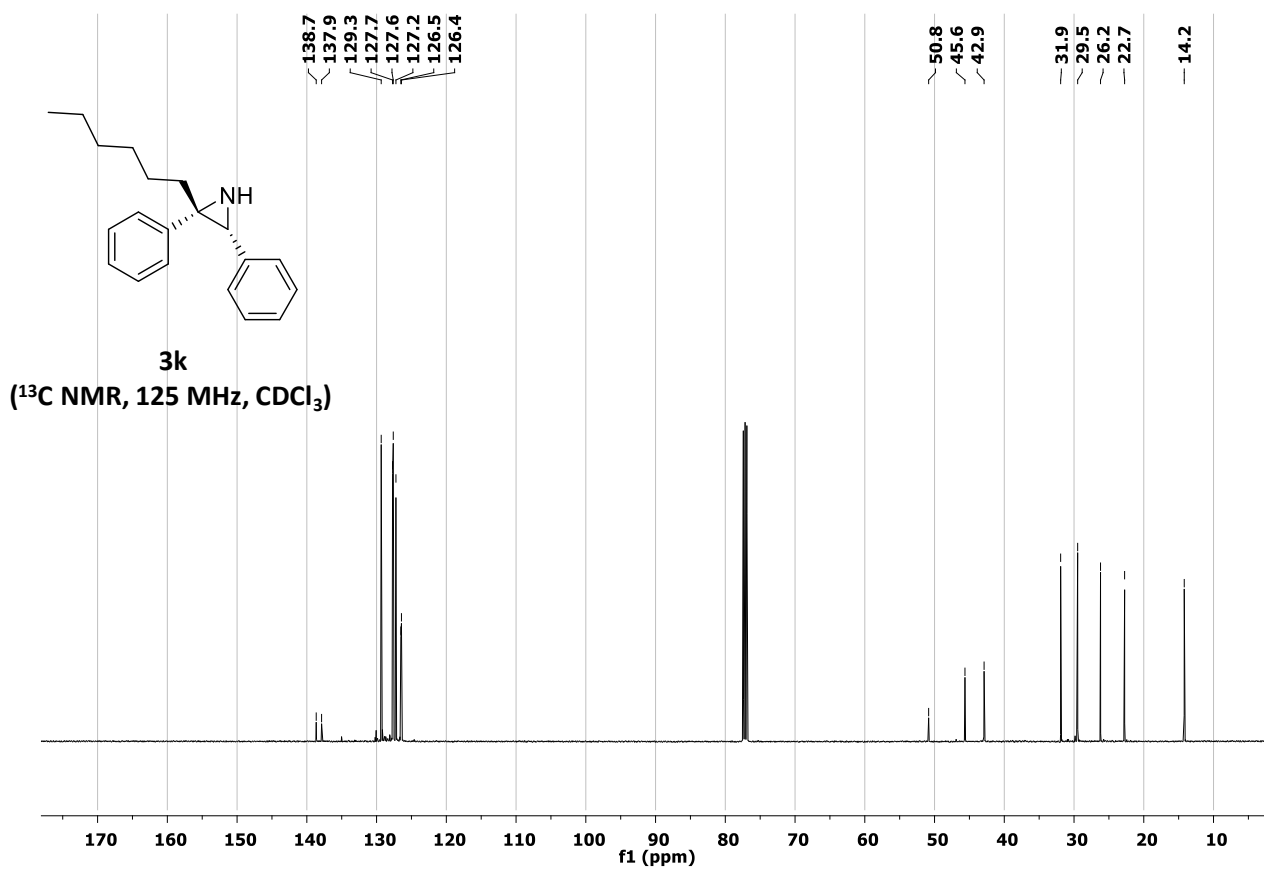
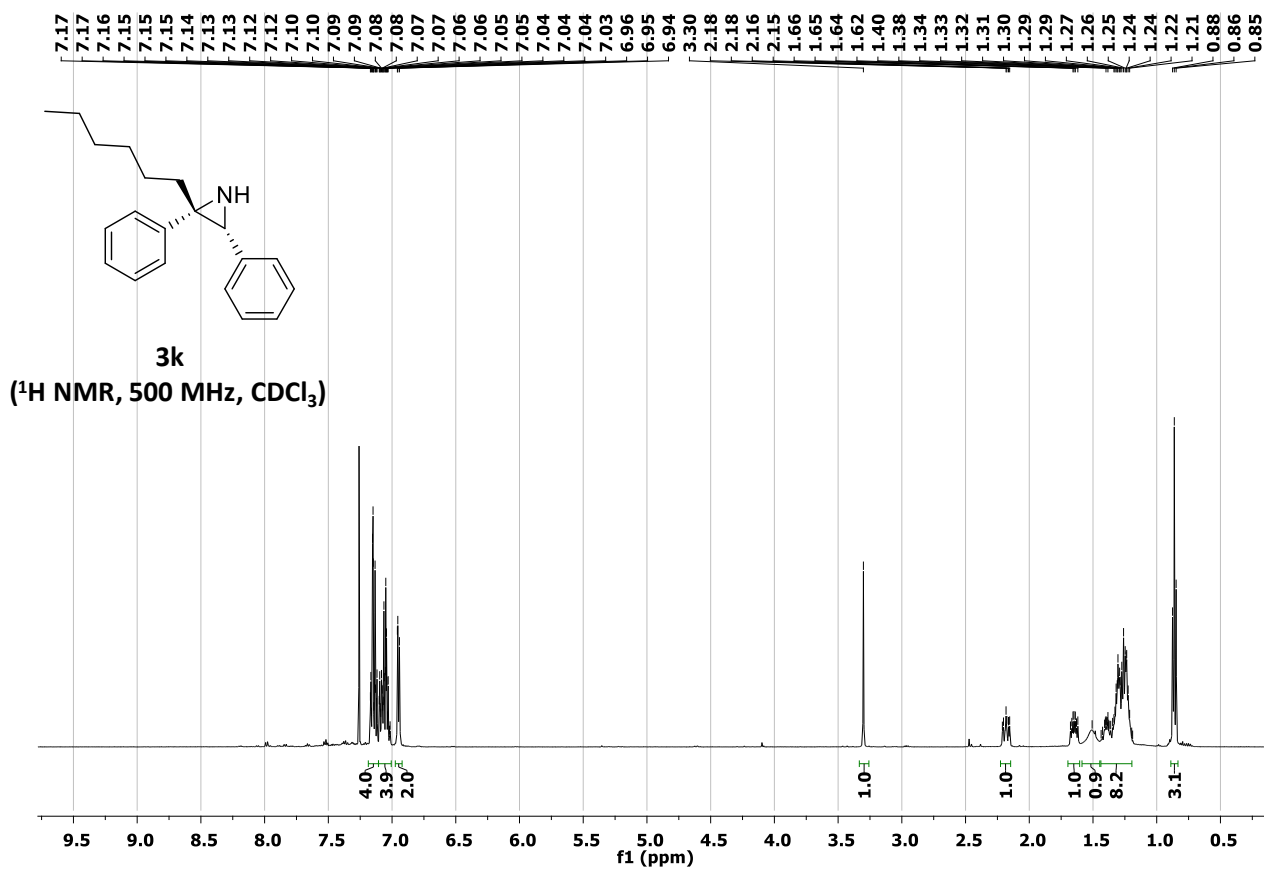


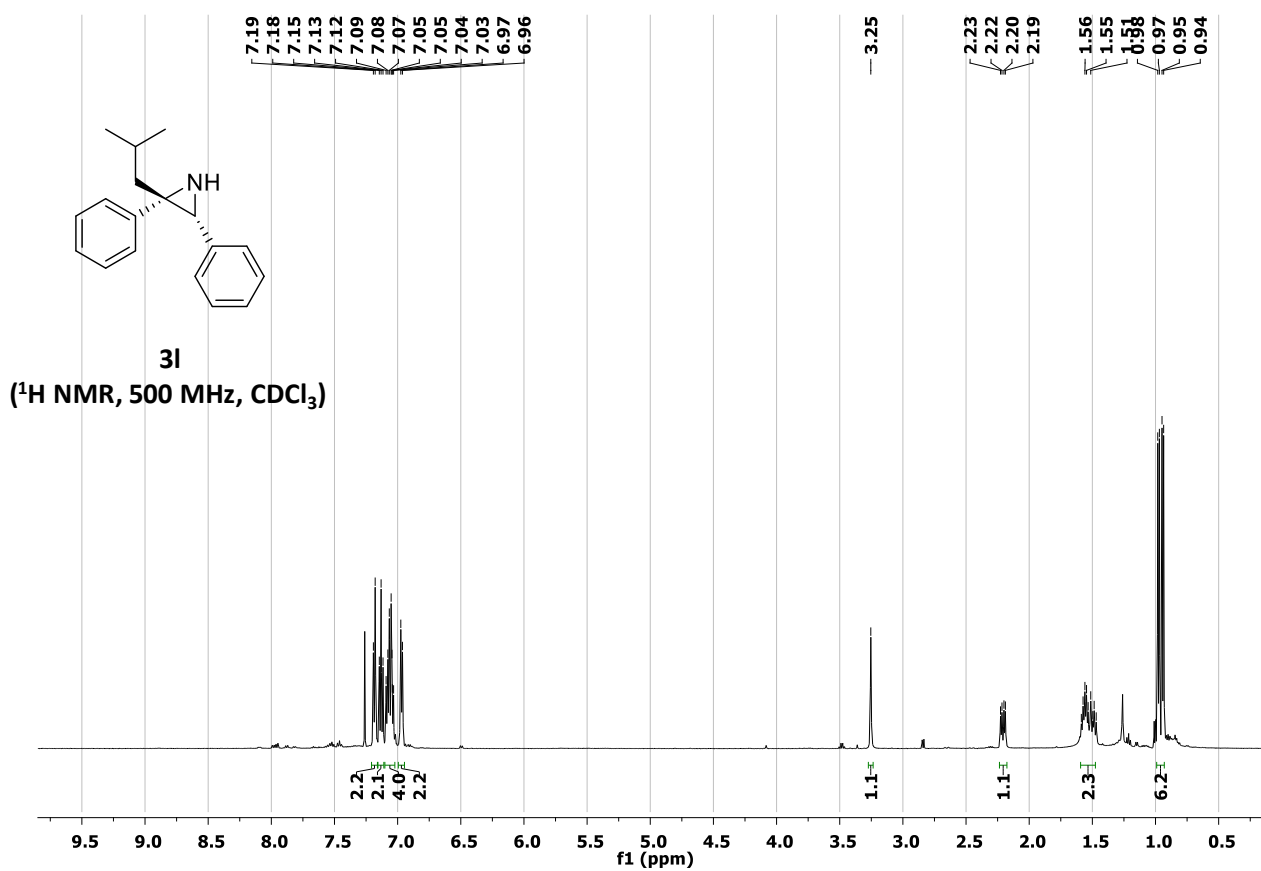
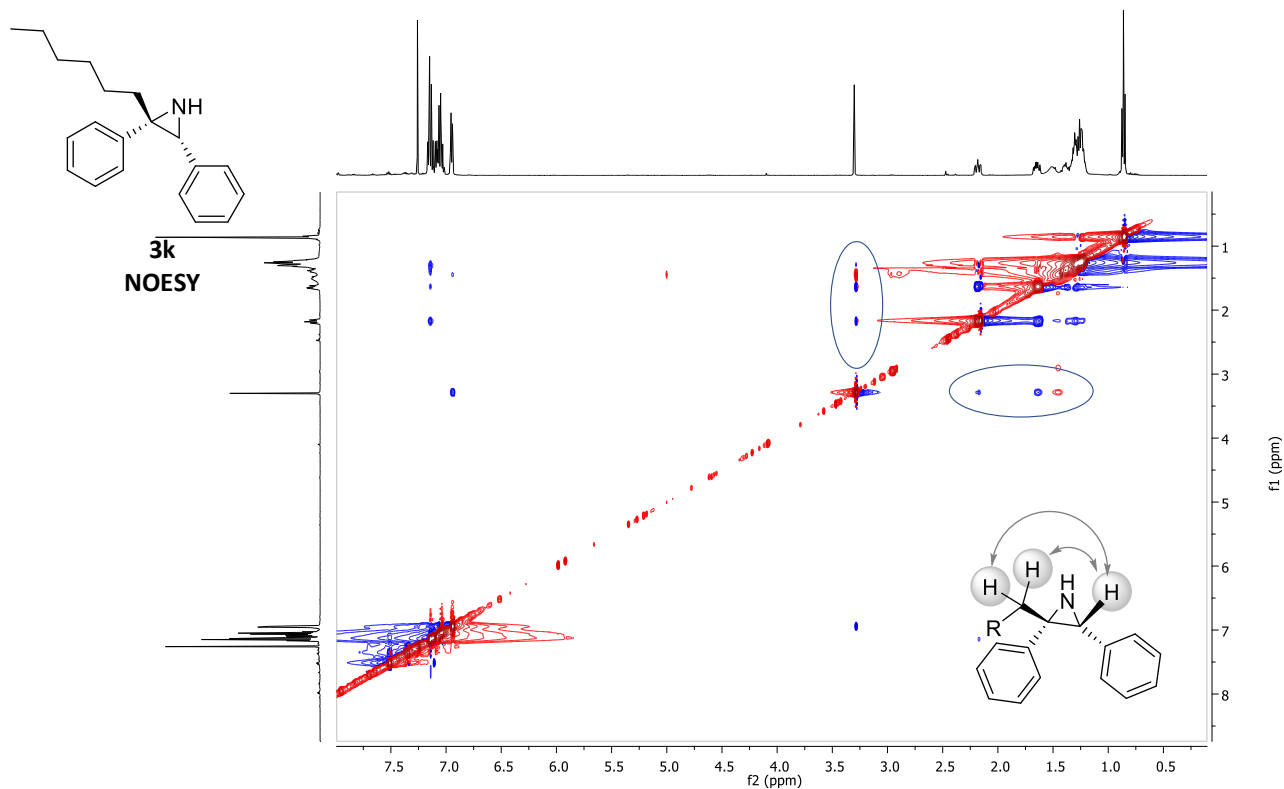


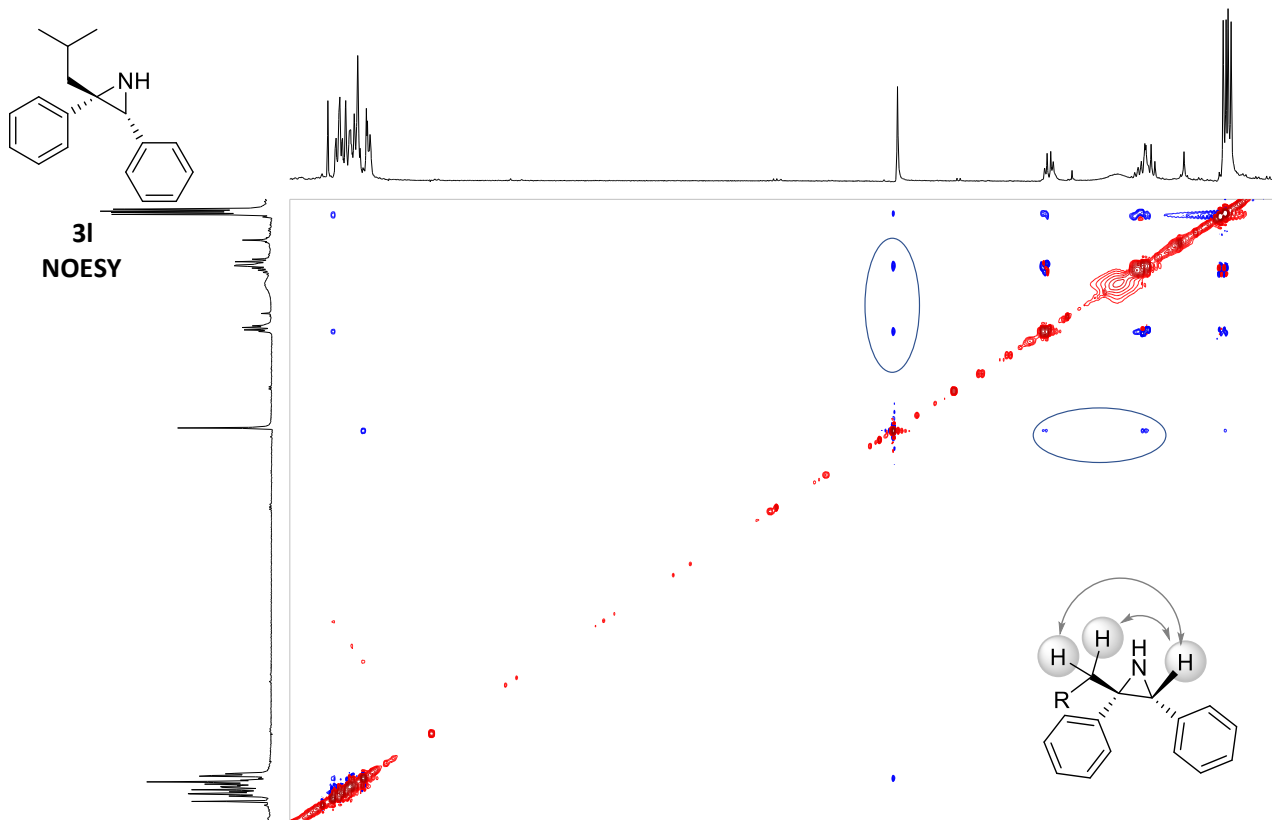
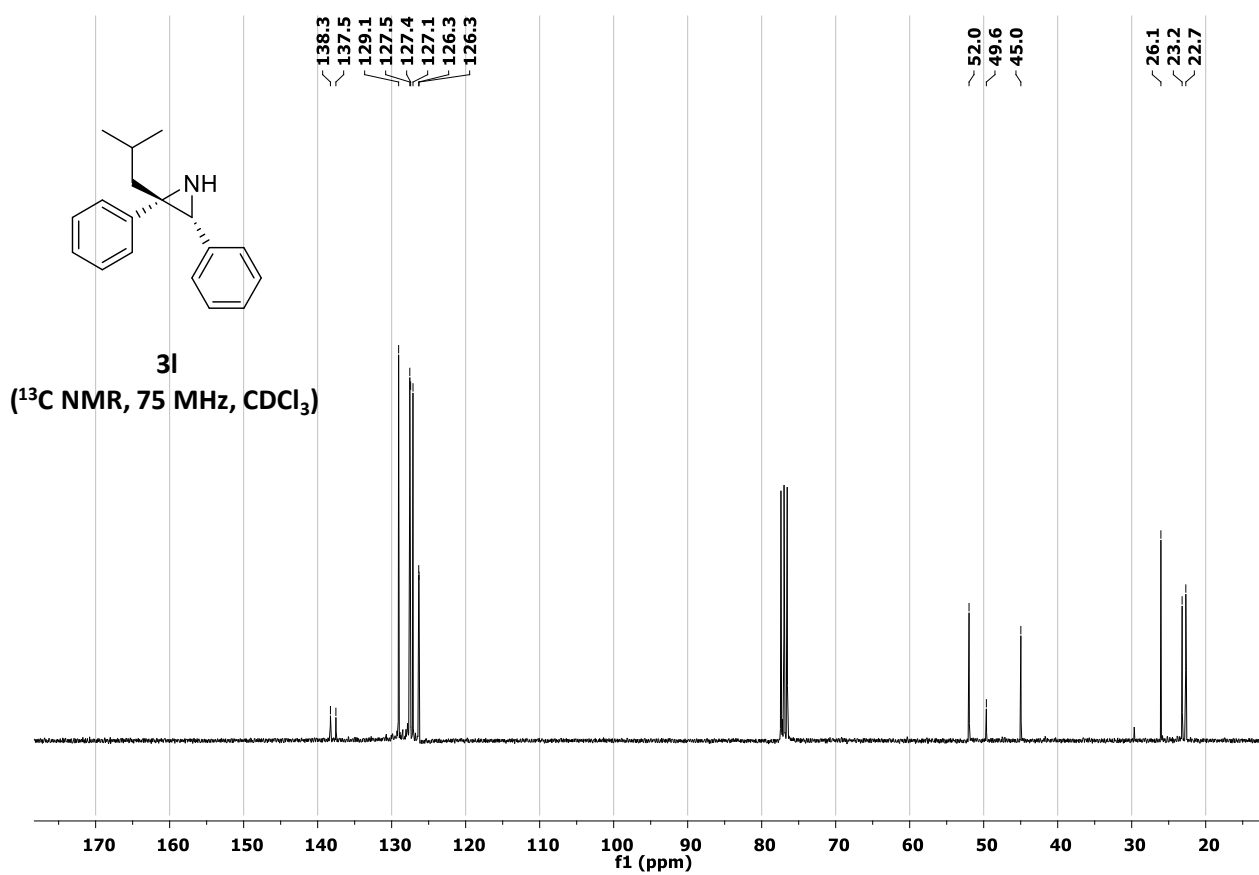


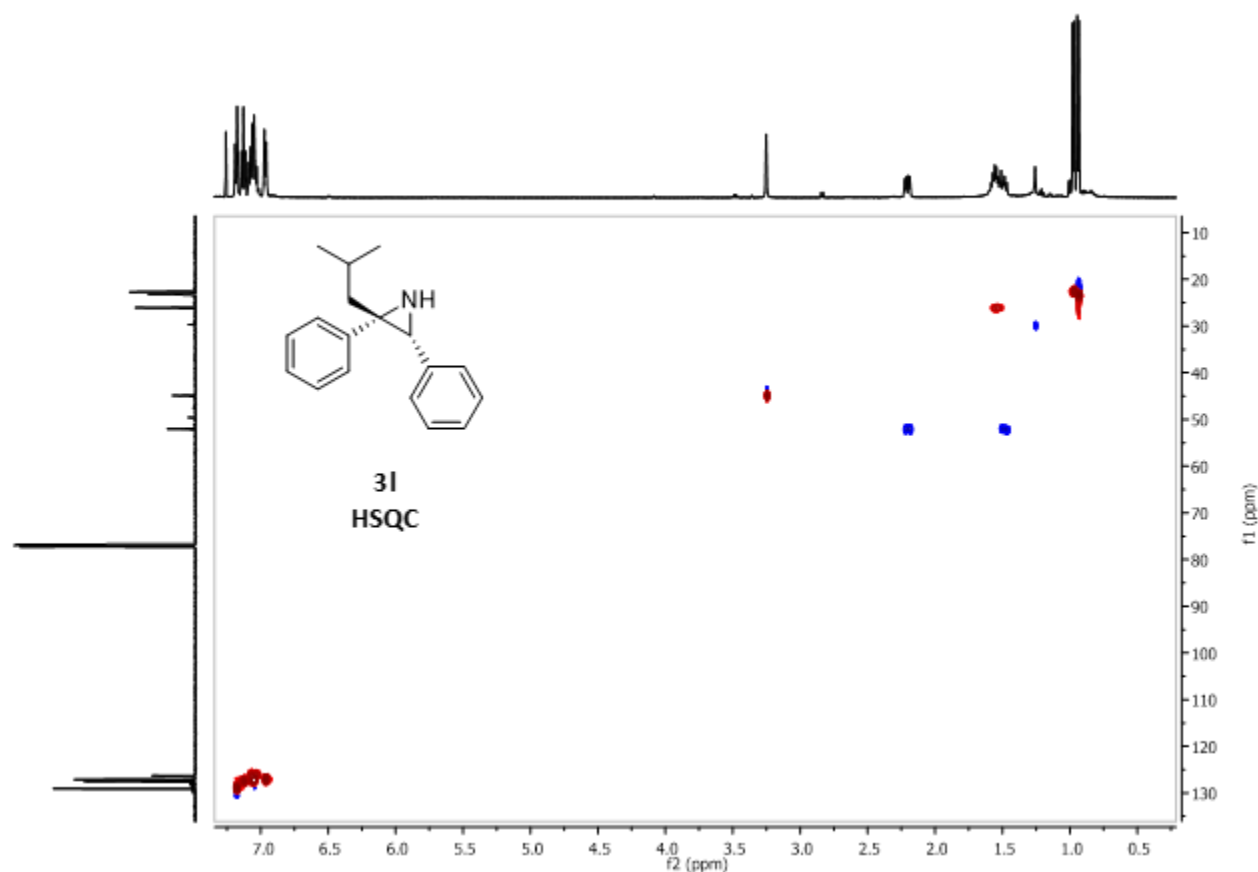












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