

## Supplementary Information

### Nucleophilic aromatic substitution of non-activated aryl fluorides with aliphatic amides

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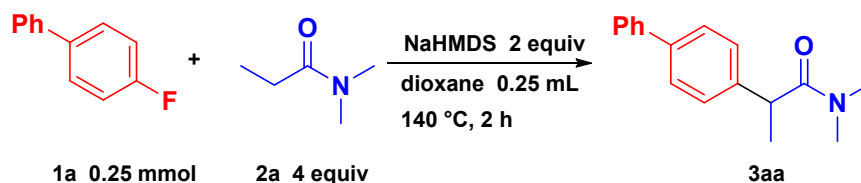
## 1. General Information

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded on a JEOL ECZ-400S spectrometer in  $\text{CDCl}_3$  with tetramethylsilane as an internal reference standard. The chemical shifts in the  $^1\text{H}$  NMR spectra were recorded relative to tetramethylsilane ( $\delta$ : 0.0). The chemical shifts in  $^{13}\text{C}$  NMR spectra were recorded relative to  $\text{CDCl}_3$  ( $\delta$ : 77.0). Data are given as follows: chemical shifts in ppm ( $\delta$ ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, brd = broad doublet, m = multiplet, c = complex), coupling constant (Hz), and integration. Infrared spectra (IR) were recorded on a JASCO FT/IR-4000 spectrometer using the ATR method. Absorption data are reported in reciprocal centimeters from 800 to 3500  $\text{cm}^{-1}$  with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained using SHIMADZU QP-2010 or QP-2020 spectrometers with a quadrupole mass analyzer at 70 eV. Data were recorded as follows: mass/charge ratio and relative intensity to base peak at 100%. High-resolution mass spectra (HRMS) were obtained using a JEOL JMS-T100LP spectrometer with a time-of-flight mass analyzer. Melting points were determined on a Stanford Research Systems MPA100 apparatus equipped with a digital thermometer and are uncorrected. Medium-pressure liquid chromatography (MPLC) was performed with Biotage Isolera<sup>®</sup>.

## 2. Materials

Toluene (super dehydrated), 1,4-dioxane (super dehydrated), DMF (super dehydrated), DME (super dehydrated), NaHMDS, KHMDS, NaO<sup>t</sup>Bu and KO<sup>t</sup>Bu were purchased from commercial sources and were used as received. The aryl fluorides (**1a-1g**, **1m**) and amide (**2d**) were purchased from commercial sources and recrystallized from hexane and EtOAc before use. The aryl fluorides (**1h-1l**), amide (**2a-2c**, **2e-2i**) and alkyl fluorides (**5**) were purchased from commercial sources and used after bubbling with nitrogen.

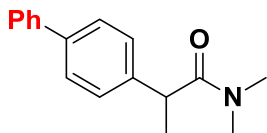
## 3. Nucleophilic Aromatic Substitution of Non-activated Aryl Fluorides with Aliphatic Amides



To an oven-dried 10 mL screw-capped vial in a glove box, NaHMDS (91.7 mg, 0.5 mmol), *N,N*-dimethylpropionamide (**2a**, 101.9 mg, 1.0 mmol), 4-fluorobiphenyl (**1a**, 43.1 mg, 0.25 mmol), and 1,4-dioxane (0.25 mL) were added in sequential order. The mixture was stirred at 100 °C for 18 h

followed by cooling. The resulting mixture was washed with H<sub>2</sub>O (10 mL) and extracted with EtOAc (30 mL). The organic layer filtered through a silica pad. The filtrate was concentrated to dryness in vacuo and the residue was purified by MPLC (hexane/EtOAc = 1/3) to afford the desired product.

**2-[(1,1'-biphenyl)-4-yl]-*N,N*-dimethylpropanamide (3aa) [CAS No. 675840-25-2]**



A white solid. Mp = 102.2-103.5 °C. *R*<sub>f</sub> = 0.50 (hexane/EtOAc = 1/3). Yield = 86%, m = 53.8 mg.

**<sup>1</sup>H NMR** (399.78 MHz, CDCl<sub>3</sub>) δ 1.47 (d, *J* = 6.9 Hz, 3H), 2.93 (s, 3H), 2.97 (s, 3H), 3.93 (q, *J* = 6.9 Hz, 1H), 7.31-7.35 (c, 3H), 7.41-7.44 (m, 2H), 7.53-7.58 (c, 4H).

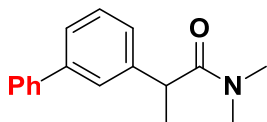
**<sup>13</sup>C NMR** (100.53 MHz, CDCl<sub>3</sub>) δ 20.7, 35.9, 37.2, 42.8, 127.0, 127.2, 127.5, 127.7, 128.7, 139.6, 140.7, 140.9, 173.6.

**IR** (ATR) 2970 w, 2930 w, 1644 s, 1422 m, 1147 m

**MS:** *m/z* (EI, relative intensity, %) 254 (11), 253 (52, M<sup>+</sup>), 182 (16), 181 (100), 179 (1), 166 (23), 165 (24), 72 (70).

**HRMS** ([M+H]<sup>+</sup>) Calcd for C<sub>17</sub>H<sub>20</sub>NO: 254.15394; Found: 254.15399.

**2-[(1,1'-biphenyl)-3-yl]-*N,N*-dimethylpropanamide (3ba)**



A white solid. Mp = 87.2-88.7 °C. *R*<sub>f</sub> = 0.50 (hexane/EtOAc = 1/3). Yield = 69%, m = 41.3 mg.

**<sup>1</sup>H NMR** (399.78 MHz, CDCl<sub>3</sub>) δ 1.48 (d, *J* = 6.9 Hz, 3H), 2.92 (s, 3H), 2.95 (s, 3H), 3.94 (q, *J* = 6.8 Hz, 1H), 7.24-7.26 (m, 1H), 7.32-7.48 (c, 6H), 7.56-7.59 (m, 2H).

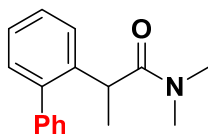
**<sup>13</sup>C NMR** (100.53 MHz, CDCl<sub>3</sub>) δ 20.8, 35.9, 37.2, 43.3, 125.5, 126.1, 126.2, 127.2, 127.3, 128.7, 129.2, 140.9, 141.7, 142.4, 173.5.

**IR** (ATR) 2973 w, 2930 w, 1644 s, 1476 m, 1394 m, 758 m, 704 m.

**MS:** *m/z* (EI, relative intensity, %) 253 (37, M<sup>+</sup>), 181 (22), 166 (11), 165 (14), 72 (100).

**HRMS** ([M+H]<sup>+</sup>) Calcd for C<sub>17</sub>H<sub>20</sub>NO: 254.15394; Found: 254.15407.

### 2-[(1,1'-biphenyl)-2-yl]-*N,N*-dimethylpropanamide (3ca)



A colorless oil.  $R_f = 0.52$  (hexane/EtOAc = 1/3). Yield = 36%,  $m = 22.1$  mg. (**3ba**: Yield = 5%,  $m = 3.0$  mg.)

$^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ )  $\delta$  1.47 (d,  $J = 6.9$  Hz, 3H), 2.48 (s, 3H), 2.85 (s, 3H), 3.87 (q,  $J = 6.8$  Hz, 1H), 7.21-7.49 (c, 9H).

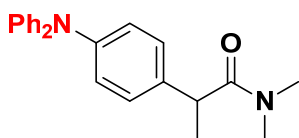
$^{13}\text{C NMR}$  (100.53 MHz,  $\text{CDCl}_3$ )  $\delta$  20.7, 35.9, 36.6, 39.0, 126.6, 127.2, 127.3, 128.2, 128.3, 129.1, 130.0, 139.2, 140.8, 141.3, 174.2.

**IR** (ATR) 2977 w, 2931 w, 1647 s, 1479 m, 1394 m, 758 m, 207 m.

**MS**:  $m/z$  (EI, relative intensity, %) 253 (23,  $\text{M}^+$ ), 208 (13), 182 (12), 181 (74), 179 (13), 166 (30), 165 (39), 72 (100).

**HRMS** ( $[\text{M}+\text{H}]^+$ ) Calcd for  $\text{C}_{17}\text{H}_{20}\text{NO}$ : 254.15394; Found: 254.15383.

### 2-[4-(diphenylamino)phenyl]-*N,N*-dimethylpropanamide (3da)



A yellow solid.  $\text{Mp} = 93.9\text{-}95.2$  °C.  $R_f = 0.53$  (hexane/EtOAc = 1/3). Yield = 69%,  $m = 55.3$  mg.

$^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ )  $\delta$  1.43 (d,  $J = 6.9$  Hz, 3H), 2.95 (s, 3H), 2.97 (s, 3H), 3.85 (q,  $J = 6.9$  Hz, 1H), 6.98-7.02 (c, 4H), 7.05-7.08 (c 4H), 7.11-7.14 (m, 2H), 7.21-7.26 (c, 5H).

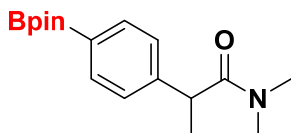
$^{13}\text{C NMR}$  (100.53 MHz,  $\text{CDCl}_3$ )  $\delta$  20.6, 35.9, 37.2, 42.3, 122.6, 124.1, 128.1, 129.1, 135.9, 146.3, 147.7, 173.8. One signal is obscured by overlap with other signals.

**IR** (ATR) 2970 w, 2929 w, 1644 s, 1588, 1489 s, 1275 s, 753 s, 697 s.

**MS**:  $m/z$  (EI, relative intensity, %) 344 (30,  $\text{M}^+$ ), 273 (23), 272 (100).

**HRMS** ( $[\text{M}+\text{H}]^+$ ) Calcd for  $\text{C}_{23}\text{H}_{25}\text{N}_2\text{O}$ : 345.19614; Found: 345.19608.

### *N,N*-dimethyl-2-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]propanamide (3ea)



A white solid.  $\text{Mp} = 158.0\text{-}158.9$  °C.  $R_f = 0.66$  (hexane/EtOAc = 1/3). Yield = 73%,  $m = 60.2$  mg.

$^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ )  $\delta$  1.33 (s, 12H), 1.43 (d,  $J = 6.9$  Hz, 3H), 2.85 (s, 3H), 2.94 (s, 3H), 3.88 (q,  $J = 6.9$  Hz, 1H), 7.27 (d,  $J = 7.3$  Hz, 2H), 7.77 (d,  $J = 7.5$  Hz, 2H).

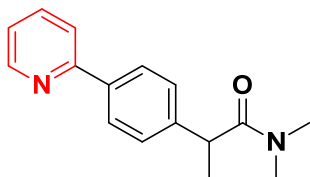
$^{13}\text{C}$  NMR (100.53 MHz,  $\text{CDCl}_3$ )  $\delta$  20.7, 24.8, 24.8, 35.9, 37.1, 43.6, 83.7, 126.7, 135.3, 145.1, 173.3.

IR (ATR) 2978 m, 2931 m, 1648 m, 1360 s, 1145 m, 1092 m.

MS:  $m/z$  (EI, relative intensity, %) 303 (23,  $\text{M}^+$ ), 231 (55), 230 (16), 132 (22), 131 (17), 116 (11), 83 (10), 72 (100).

HRMS ( $[\text{M}+\text{H}]^+$ ) Calcd for  $\text{C}_{17}\text{H}_{27}\text{BNO}_3$ : 304.20785; Found: 304.20824.

### *N,N*-dimethyl-2-[4-(pyridin-2-yl)phenyl]propanamide (3fa)



A white solid. Mp = 103.3-104.1 °C.  $R_f$  = 0.16 (hexane/EtOAc = 1/3). Yield = 90%, m = 56.3 mg.

$^1\text{H}$  NMR (399.78 MHz,  $\text{CDCl}_3$ )  $\delta$  1.47 (d,  $J$  = 6.9 Hz, 3H), 2.90 (s, 3H), 2.97 (s, 3H), 3.94 (q,  $J$  = 6.8 Hz, 1H), 7.21-7.24 (m, 1H), 7.38 (d,  $J$  = 8.0 Hz, 2H), 7.70-7.77 (m, 2H), 7.94 (d,  $J$  = 8.0 Hz, 2H), 8.68 (dt,  $J$  = 4.8, 0.9 Hz, 1H).

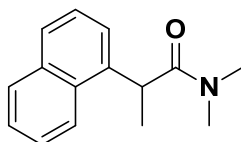
$^{13}\text{C}$  NMR (100.53 MHz,  $\text{CDCl}_3$ )  $\delta$  20.6, 35.9, 37.1, 43.1, 120.4, 122.0, 127.4, 127.7, 136.7, 137.9, 142.7, 149.6, 157.1, 173.4.

IR (ATR) 2975 w, 2930 w, 1643 s, 1466 m, 777 m.

MS:  $m/z$  (EI, relative intensity, %) 255 (10), 256 (54,  $\text{M}^+$ ), 183 (15), 181 (100), 167 (38), 72 (91).

HRMS ( $[\text{M}+\text{H}]^+$ ) Calcd for  $\text{C}_{16}\text{H}_{19}\text{NO}$ : 255.14919; Found: 255.14921.

### *N,N*-dimethyl-2-(naphthalen-2-yl)propanamide (3ga) [CAS No. 169770-80-3]



A white solid. Mp = 103.3-106.4 °C.  $R_f$  = 0.41 (hexane/EtOAc = 1/3). Yield = 92%, m = 67.1 mg.

$^1\text{H}$  NMR (399.78 MHz,  $\text{CDCl}_3$ )  $\delta$  1.54 (d,  $J$  = 6.9 Hz, 3H), 2.67 (s, 3H), 3.00 (s, 3H), 4.59 (q,  $J$  = 6.9 Hz, 1H), 7.37 (dd,  $J$  = 7.2, 1.3 Hz, 1H), 7.42 (t,  $J$  = 7.5 Hz, 1H), 7.49-7.53 (m, 1H), 7.55-7.59 (m, 1H), 7.75 (d,  $J$  = 8.0 Hz, 1H), 7.89 (d,  $J$  = 7.8 Hz, 1H), 8.11 (d,  $J$  = 8.5 Hz, 1H).

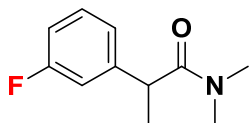
$^{13}\text{C}$  NMR (100.53 MHz,  $\text{CDCl}_3$ )  $\delta$  19.6, 35.9, 37.0, 39.3, 122.3, 124.0, 125.6, 125.9, 126.4, 127.3, 129.2, 130.5, 134.0, 138.1, 174.1.

IR (ATR) 2974 w, 2930 w, 1644 s, 1394 m, 777 s.

MS:  $m/z$  (EI, relative intensity, %) 228 (11), 227 (64,  $\text{M}^+$ ), 156 (15), 155 (100), 153 (26), 152 (13), 128 (12), 127 (10), 72 (99).

HRMS ( $[\text{M}+\text{H}]^+$ ) Calcd for  $\text{C}_{15}\text{H}_{18}\text{NO}$ : 228.13829; Found: 228.13829.

**2-(4-fluorophenyl)-*N,N*-dimethylpropanamide (3ha) [CAS No. 2041088-95-1]**



A yellow oil.  $R_f = 0.51$  (hexane/EtOAc = 1/3). Yield = 71%,  $m = 64.9$  mg.

$^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ )  $\delta$  1.43 (d,  $J = 6.9$  Hz, 3H), 2.91 (s, 3H), 2.96 (s, 3H), 3.90 (q,  $J = 6.9$  Hz, 1H), 6.92 (tq,  $J = 8.5, 1.1$  Hz, 1H), 6.98-7.02 (m, 1H), 7.04 (d,  $J = 7.8$  Hz, 1H), 7.25-7.30 (m, 1H).

$^{13}\text{C NMR}$  (100.53 MHz,  $\text{CDCl}_3$ )  $\delta$  20.5, 35.9, 37.1, 42.8, 113.7 (d,  $J = 21.2$  Hz), 114.2 (d,  $J = 21.2$  Hz), 123.0, 123.0, 130.2, 130.2, 144.3, 144.3, 163.0 (d,  $J = 246.6$  Hz), 173.0.

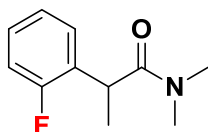
$^{19}\text{F NMR}$  (376.17 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.5.

**IR** (ATR): 2975 w, 2933 w, 1643 s, 1483 m.

**MS**:  $m/z$  (EI, relative intensity, %) 195 (15,  $\text{M}^+$ ), 72 (100).

**HRMS** ( $[\text{M}+\text{H}]^+$ ) Calcd for  $\text{C}_{11}\text{H}_{15}\text{NOF}$ : 196.11322; Found: 196.11310.

**2-(2-fluorophenyl)-*N,N*-dimethylpropanamide (3ia)**



A yellow oil.  $R_f = 0.65$  (hexane/EtOAc = 1/3). Yield = 76%,  $m = 69.9$  mg.

$^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ )  $\delta$  1.39 (d,  $J = 6.9$  Hz, 3H), 2.86 (s, 3H), 2.92 (s, 3H), 4.24 (q,  $J = 6.9$  Hz, 1H), 6.98-7.03 (m, 1H), 7.07 (td,  $J = 7.5, 1.2$  Hz, 1H), 7.15-7.21 (m, 1H), 7.30 (td,  $J = 7.7, 1.8$  Hz, 1H).

$^{13}\text{C NMR}$  (100.53 MHz,  $\text{CDCl}_3$ )  $\delta$  19.0, 34.6, 35.8, 36.8, 115.1 (d,  $J = 22.2$  Hz), 124.6 (d,  $J = 2.9$  Hz), 128.3 (d,  $J = 15.4$  Hz), 128.3 (d,  $J = 2.9$  Hz), 128.5 (d,  $J = 15.4$  Hz), 159.5 (d,  $J = 244.7$  Hz), 173.1.

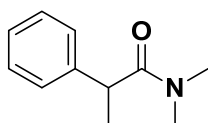
$^{19}\text{F NMR}$  (376.17 MHz,  $\text{CDCl}_3$ )  $\delta$  -120.1.

**IR** (ATR) 2978 w, 2934 w, 1650 s, 1396 m, 760 m.

**MS**:  $m/z$  (EI, relative intensity, %) 195 (31,  $\text{M}^+$ ), 123 (14), 103 (13), 72 (100).

**HRMS** ( $[\text{M}+\text{H}]^+$ ) Calcd for  $\text{C}_{11}\text{H}_{15}\text{NOF}$ : 196.11322; Found: 196.11294.

***N,N*-dimethyl-2-phenylpropanamide (3ja) [CAS No. 41836-85-5]**



To an oven-dried 10 mL screw-capped vial in a glove box, NaHMDS (367.0 mg, 2.0 mmol), *N,N*-dimethylpropanamide (**2a**, 404.8 mg, 4.0 mmol), fluorobenzene (**1j**, 47.6 mg, 1.0 mmol), and 1,4-

dioxane (0.25 mL) were added in sequential order. The mixture was stirred at 140 °C for 18 h.

A colorless oil.  $R_f = 0.66$  (hexane/EtOAc = 1/3). Yield = 28%,  $m = 63.3$  mg.

$^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ )  $\delta$  1.44 (d,  $J = 6.9$  Hz, 3H), 2.89 (s, 3H), 2.95 (s, 3H), 3.88 (q,  $J = 6.9$  Hz, 1H), 7.21-7.33 (c, 5H).

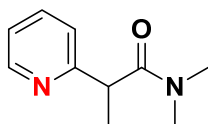
$^{13}\text{C NMR}$  (100.53 MHz,  $\text{CDCl}_3$ )  $\delta$  20.7, 35.8, 37.1, 43.2, 126.6, 127.2, 128.7, 141.8, 173.6.

**IR** (ATR) 2976 w, 2931 w, 1644 s, 1396 m, 1148 m, 759 m.

**MS**:  $m/z$  (EI, relative intensity, %) 177 (28,  $\text{M}^+$ ), 105 (26), 72 (100).

**HRMS** ( $[\text{M}+\text{H}]^+$ ) Calcd for  $\text{C}_{11}\text{H}_{16}\text{NO}$ : 178.12264; Found: 178.12260.

#### ***N,N*-dimethyl-2-(pyridin-2-yl)propanamide (3ka) [CAS No. 886193-93-7]**



A colorless oil.  $R_f = 0.08$  (hexane/EtOAc = 1/3). Yield = 16%,  $m = 7.2$  mg.

$^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ )  $\delta$  1.50 (d,  $J = 7.1$  Hz, 3H), 2.96 (s, 3H), 2.98 (s, 3H), 4.19 (q,  $J = 6.9$  Hz, 1H), 7.16 (ddd,  $J = 7.5, 5.0, 1.1$  Hz, 1H), 7.34 (d,  $J = 7.8$  Hz, 1H), 7.65 (td,  $J = 7.7, 1.8$  Hz, 1H), 8.51 (dq,  $J = 5.0, 0.8$  Hz, 1H).

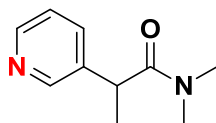
$^{13}\text{C NMR}$  (100.53 MHz,  $\text{CDCl}_3$ )  $\delta$  18.8, 35.9, 37.3, 45.9, 121.3, 121.8, 137.0, 149.1, 161.5, 173.0.

**IR** (ATR) 2931 w, 1646 m, 1472 w, 1397 w, 772 s.

**MS**:  $m/z$  (EI, relative intensity, %) 178 (7,  $\text{M}^+$ ), 134 (15), 133 (12), 121 (50), 107 (37), 106 (100), 93 (18), 78 (17), 72 (66).

**HRMS** ( $[\text{M}+\text{H}]^+$ ) Calcd for  $\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}$ : 179.11789; Found: 179.11768.

#### ***N,N*-dimethyl-2-(pyridin-3-yl)propanamide (3la) [CAS No. 1881981-45-8]**



A colorless oil.  $R_f = 0.16$  (hexane/EtOAc = 1/3). Yield = 13%,  $m = 6.5$  mg.

$^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ )  $\delta$  1.46 (d,  $J = 6.9$  Hz, 3H), 2.95 (s, 3H), 2.96 (s, 3H), 3.95 (q,  $J = 6.9$  Hz, 1H), 7.25-7.28 (c, 2H), 7.68 (dt,  $J = 8.0, 1.9$  Hz, 1H), 8.49-8.52 (c, 2H).

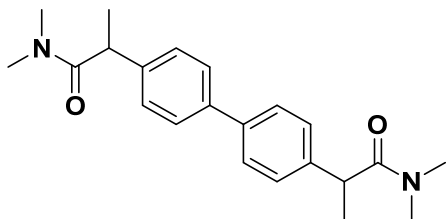
$^{13}\text{C NMR}$  (100.53 MHz,  $\text{CDCl}_3$ )  $\delta$  20.4, 36.0, 37.2, 40.3, 134.8, 148.4, 149.1, 172.8. two signals are obscured by overlap with other signals.

**IR** (ATR) 2975 w, 2929 w, 1643 s, 1398 m.

**MS**:  $m/z$  (EI, relative intensity, %) 178 (33,  $\text{M}^+$ ), 106 (13), 72 (100).

**HRMS** ( $[\text{M}+\text{H}]^+$ ) Calcd for  $\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}$ : 179.11789; Found: 179.11760.

### 2,2'-[(1,1'-biphenyl)-4,4'-diyl]bis(*N,N*-dimethylpropanamide) (**3ma**)



To an oven-dried 10 mL screw-capped vial in a glove box, NaHMDS (183.4 mg, 1.0 mmol), *N,N*-dimethylpropanamide (**2a**, 202.8 mg, 2.0 mmol), 4,4'-difluoro-1,1'-biphenyl (**1m**, 47.6 mg, 0.25 mmol), and 1,4-dioxane (0.25 mL) were added in sequential order.

A white solid. Mp = 156.5-157.8 °C.  $R_f$  = 0.41 (hexane/EtOAc = 0/1). Yield = 87%, m = 76.1 mg.

$^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ )  $\delta$  1.47 (d,  $J$  = 6.9 Hz, 6H), 2.93 (s, 6H), 2.97 (s, 6H), 3.93 (q,  $J$  = 6.9 Hz, 2H), 7.33 (dt,  $J$  = 8.4, 1.8 Hz, 4H), 7.52 (dt,  $J$  = 8.5, 1.9 Hz, 4H).

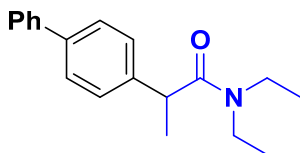
$^{13}\text{C NMR}$  (100.53 MHz,  $\text{CDCl}_3$ )  $\delta$  20.6, 35.9, 37.1, 42.8, 127.3, 127.7, 139.1, 140.8, 173.6.

**IR** (ATR) 2973 w, 2930 w, 1638 s, 1493 m, 1395 m.

**MS**:  $m/z$  (EI, relative intensity, %) 352 (21,  $\text{M}^+$ ), 281 (20), 280 (100), 208 (36), 207 (13), 72 (43).

**HRMS** ( $[\text{M}+\text{H}]^+$ ) Calcd for  $\text{C}_{22}\text{H}_{29}\text{N}_2\text{O}_2$ : 353.22235; Found: 353.22194.

### 2-[(1,1'-biphenyl)-4-yl]-*N,N*-diethylpropanamide (**3ab**)



A colorless oil.  $R_f$  = 0.66 (hexane/EtOAc = 3/1). Yield = 75%, m = 56.5 mg.

$^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ )  $\delta$  1.03 (t,  $J$  = 7.1 Hz, 3H), 1.11 (t,  $J$  = 7.1 Hz, 3H), 1.48 (d,  $J$  = 6.9 Hz, 3H), 3.14 (td,  $J$  = 14.5, 7.3 Hz, 1H), 3.25 (td,  $J$  = 13.8, 6.8 Hz, 1H), 3.32-3.41 (m, 1H), 3.52 (td,  $J$  = 13.8, 7.0 Hz, 1H), 3.87 (q,  $J$  = 6.9 Hz, 1H), 7.30-7.37 (m, 3H), 7.40-7.44 (m, 2H), 7.52-7.59 (m, 4H).

$^{13}\text{C NMR}$  (100.53 MHz,  $\text{CDCl}_3$ )  $\delta$  12.8, 14.3, 20.9, 40.3, 41.6, 42.6, 126.9, 127.1, 127.4, 127.6, 128.7, 139.5, 140.7, 141.4, 172.6.

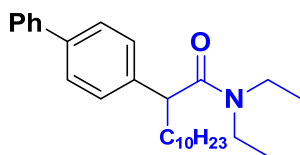
**IR** (ATR): 2972 w, 2931 w, 1639 s, 1484 m, 1458 m, 1429 m, 762 m.

**MS**:  $m/z$  (EI, relative intensity, %): 281 (13,  $\text{M}^+$ ), 180 (15), 100 (100), 72 (33).

**HRMS** ( $[\text{M}+\text{H}]^+$ ) Calcd for  $\text{C}_{19}\text{H}_{24}\text{NO}$ : 282.18524; Found: 282.18560.

### 2-[(1,1'-biphenyl)-4-yl]-*N,N*-diethyldodecanamide (**3ac**)





The mixture was stirred at 140 °C for 2 h.

A colorless oil.  $R_f = 0.75$  (hexane/EtOAc = 1/3). Yield = 69%, m = 70.2 mg.

$^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ )  $\delta$  0.87 (t,  $J = 6.9$  Hz, 3H), 1.04-1.11 (m, 6H), 1.24-1.34 (m, 16H), 1.67-1.76 (m, 1H), 2.07-2.16 (m, 1H), 3.17 (td,  $J = 14.6, 7.3$  Hz, 1H), 3.29 (td,  $J = 13.8, 6.9$  Hz, 1H), 3.36-3.51 (m, 2H), 3.67 (t,  $J = 7.3$  Hz, 1H), 7.30-7.35 (m, 1H), 7.38 (dd,  $J = 6.5, 1.7$  Hz, 2H), 7.40-7.46 (m, 2H), 7.52-7.59 (c, 4H).

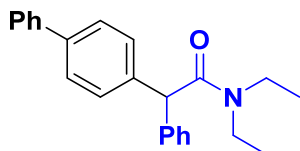
$^{13}\text{C NMR}$  (100.53 MHz,  $\text{CDCl}_3$ )  $\delta$  12.9, 14.1, 14.6, 22.7, 28.0, 29.3, 29.5, 29.6, 29.6, 31.9, 35.5, 40.4, 41.7, 48.5, 126.9, 127.1, 127.2, 128.2, 128.7, 139.5, 140.0, 140.8, 172.2. One signal is obscured by overlap with other signals.

**IR** (ATR) 2924 s, 2853 m, 1641 s, 1484 m, 1458 m, 1429 m, 761 m.

**MS:**  $m/z$  (EI, relative intensity, %) 407 (5,  $\text{M}^+$ ), 267 (41), 167 (44), 100 (100), 72 (25).

**HRMS** ( $[\text{M}+\text{H}]^+$ ) Calcd for  $\text{C}_{28}\text{H}_{42}\text{NO}$ : 408.32609; Found: 408.32582.

### 2-[(1,1'-biphenyl)-4-yl]-*N,N*-diethyl-2-phenylacetamide (3ad)



The mixture was stirred at 140 °C for 4 h.

A white solid.  $\text{Mp} = 99.6\text{-}100.7$  °C.  $R_f = 0.33$  (hexane/EtOAc = 3/1). Yield = 74%, m = 60.4 mg.

$^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ )  $\delta$  1.12-1.25 (m, 6H), 3.28-3.51 (m, 4H), 5.19 (s, 1H), 7.23-7.28 (c, 1H), 7.29-7.36 (m, 7H), 7.39-7.43 (m, 2H), 7.51-7.57 (c, 3H).

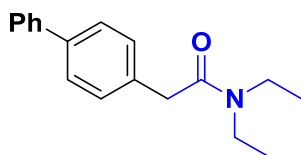
$^{13}\text{C NMR}$  (100.53 MHz,  $\text{CDCl}_3$ )  $\delta$  12.8, 14.7, 40.7, 42.1, 54.2, 127.0, 127.0, 127.1, 127.2, 128.6, 128.7, 128.9, 129.4, 139.0, 139.7, 140.8, 170.6. One signal is obscured by overlap with other signals.

**IR** (ATR) 2974 w, 2932 m, 1641 s, 1485 m, 1454 m, 1428 m, 1131 m, 759 s, 728 m, 697 s.

**MS:**  $m/z$  (EI, relative intensity, %) 343 (5,  $\text{M}^+$ ), 243 (24), 100 (100), 72 (29).

**HRMS** ( $[\text{M}+\text{H}]^+$ ) Calcd for  $\text{C}_{24}\text{H}_{26}\text{NO}$ : 344.20089; Found: 344.20178.

### 2-[(1,1'-biphenyl)-4-yl]-*N,N*-diethylacetamide (3ae) [CAS No. 180728-35-2]



A colorless oil.  $R_f = 0.50$  (hexane/EtOAc = 1/3). Yield = 67%, m = 48.3 mg.

$^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ )  $\delta$  1.13 (td,  $J = 7.1, 5.3$  Hz, 6H), 3.32 (q,  $J = 7.1$  Hz, 2H), 3.40 (q,  $J = 7.1$  Hz, 2H), 3.73 (s, 2H), 7.30-7.34 (m, 3H), 7.42 (td,  $J = 6.7, 1.5$  Hz, 2H), 7.52-7.59 (m, 4H).

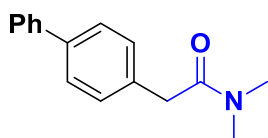
$^{13}\text{C NMR}$  (100.53 MHz,  $\text{CDCl}_3$ )  $\delta$  12.9, 14.2, 40.1, 40.4, 42.3, 127.0, 127.1, 127.3, 128.7, 129.1, 134.5, 139.5, 140.8, 170.0

**IR** (ATR) 2947 w, 2933 w, 1639 s, 1485 m, 1458 m, 1428 m, 755 m.

**MS**:  $m/z$  (EI, relative intensity, %) 267 (22,  $\text{M}^+$ ), 165 (13), 100 (100), 72 (43).

**HRMS** ( $[\text{M}+\text{H}]^+$ ) Calcd for  $\text{C}_{18}\text{H}_{22}\text{NO}$ : 268.16959; Found: 268.16941.

#### 2-[(1,1'-biphenyl)-4-yl]-*N,N*-dimethylacetamide (3af) [CAS No. 180728-36-3]



A white solid.  $\text{Mp} = 90.2\text{-}92.2$  °C.  $R_f = 0.42$  (hexane/EtOAc = 1/3). Yield = 71%, m = 44.6 mg.

$^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ )  $\delta$  2.99 (s, 3H), 3.04 (d,  $J = 0.9$  Hz, 3H), 3.76 (s, 2H), 7.32-7.35 (c, 3H), 7.41-7.45 (m, 2H), 7.54-7.59 (c, 4H).

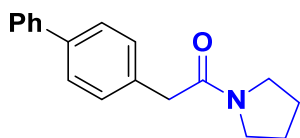
$^{13}\text{C NMR}$  (100.53 MHz,  $\text{CDCl}_3$ )  $\delta$  35.6, 37.7, 40.6, 127.0, 127.2, 127.3, 128.7, 129.2, 134.1, 139.6, 140.8, 170.9.

**IR** (ATR) 3028 w, 2930 w, 1639 s, 1486 m, 1393 m, 1130 m, 756 s, 698 m.

**MS**:  $m/z$  (EI, relative intensity, %) 239 (37,  $\text{M}^+$ ), 167 (25), 165 (16), 72 (100).

**HRMS** ( $[\text{M}+\text{H}]^+$ ) Calcd for  $\text{C}_{16}\text{H}_{18}\text{NO}$ : 240.13829; Found: 240.13818.

#### 2-[(1,1'-biphenyl)-4-yl]-1-(pyrrolidin-1-yl)ethan-1-one (3ag) [CAS No. 903761-18-2]



The mixture was stirred at 140 °C for 2 h.

A white solid.  $\text{Mp} = 88.2\text{-}89.1$  °C.  $R_f = 0.51$  (hexane/EtOAc = 1/3). Yield = 57%, m = 36.5 mg.

$^1\text{H NMR}$  (399.78 MHz,  $\text{CDCl}_3$ )  $\delta$  1.81-1.88 (m, 2H), 1.90-1.97 (m, 2H), 3.46 (t,  $J = 6.7$  Hz, 2H), 3.51 (t,  $J = 6.9$  Hz, 2H), 3.69 (s, 2H), 7.31-7.37 (c, 3H), 7.41-7.44 (m, 2H), 7.51-7.59 (c, 4H).

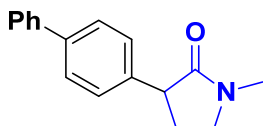
$^{13}\text{C NMR}$  (100.53 MHz,  $\text{CDCl}_3$ )  $\delta$  24.3, 26.1, 41.8, 45.9, 46.9, 127.0, 127.1, 127.3, 128.7, 129.4, 134.0, 139.6, 140.8, 169.4.

**IR** (ATR) 2970 w, 2873 w, 1637 s, 1428 m, 758 m, 698 m.

**MS:**  $m/z$  (EI, relative intensity, %) 265 (28,  $M^+$ ), 167 (10), 165 (14), 98 (100), 179 (15), 56 (12), 55 (36).

**HRMS** ( $[M+H]^+$ ) Calcd for  $C_{18}H_{20}NO$ : 266.15394; Found: 266.15401.

### 3-[(1,1'-biphenyl)-4-yl]-1-methylpyrrolidin-2-one (**3ah**)



A colorless oil.  $R_f$  = 0.33 (hexane/EtOAc = 1/3). Yield = 69%, m = 41.4 mg.

**$^1H$  NMR** (399.78 MHz,  $CDCl_3$ )  $\delta$  2.13-2.22 (m, 1H), 2.51-2.60 (m, 1H), 2.96 (s, 3H), 3.42-3.53 (m, 2H), 3.70 (t,  $J$  = 8.8 Hz, 1H), 7.31-7.35 (c, 3H), 7.43 (t,  $J$  = 7.7 Hz, 2H), 7.53-7.57 (c, 4H)

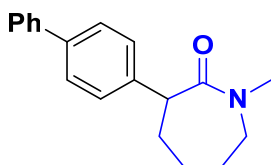
**$^{13}C$  NMR** (100.53 MHz,  $CDCl_3$ )  $\delta$  28.0, 30.1, 47.7, 127.1, 127.1, 127.5, 128.3, 128.7, 139.0, 139.9, 140.9, 174.8. one signal is obscured by overlap with other signals.

**IR** (ATR) 3028 w, 2944 w, 2877 w, 1687 s, 765 m.

**MS:**  $m/z$  (EI, relative intensity, %) 252(19), 251 (100,  $M^+$ ), 195 (10), 194 (60), 193 (25), 179 (21), 178 (26), 165 (16), 117 (11).

**HRMS** ( $[M+H]^+$ ) Calcd for  $C_{17}H_{18}NO$ : 252.13829; Found: 252.13922.

### 3-[(1,1'-biphenyl)-4-yl]-1-methylpiperidin-2-one (**3ai**)



The mixture was stirred at 140 °C for 2 h.

A white solid. Mp = 97.2-102.1 °C.  $R_f$  = 0.58 (hexane/EtOAc = 8/1). Yield = 35%, m = 23.5 mg.

**$^1H$  NMR** (399.78 MHz,  $CDCl_3$ )  $\delta$  1.51-1.88 (c, 3H), 2.02-2.08 (c, 3H), 3.04 (s, 3H), 3.27 (dd,  $J$  = 15.3, 5.0 Hz, 1H), 3.73 (dd,  $J$  = 15.3, 10.7 Hz, 1H), 3.91 (t,  $J$  = 6.1 Hz, 1H), 7.26-7.34 (c, 3H), 7.42 (t,  $J$  = 7.5 Hz, 2H), 7.55 (d,  $J$  = 8.2 Hz, 2H), 7.58 (dd,  $J$  = 8.1, 1.0 Hz, 2H)

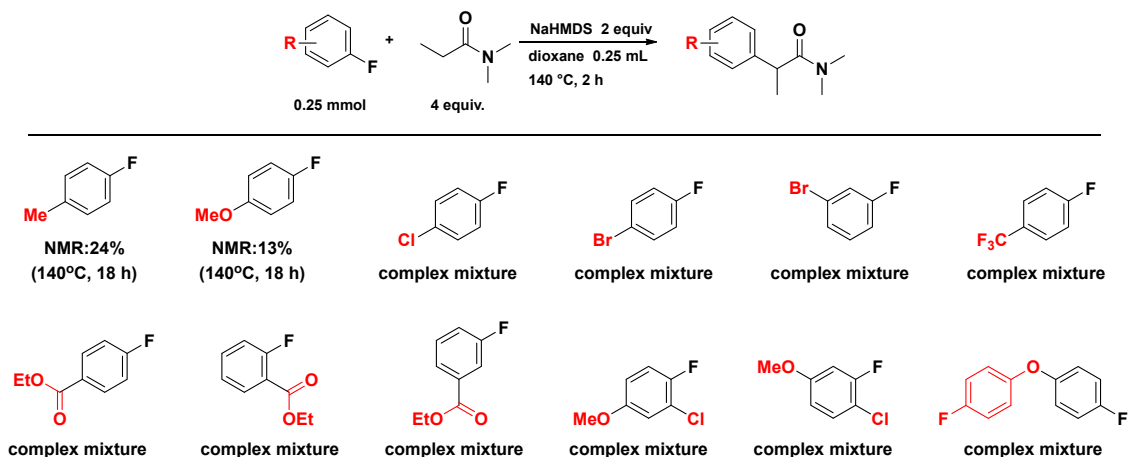
**$^{13}C$  NMR** (100.53 MHz,  $CDCl_3$ )  $\delta$  27.1, 28.9, 31.1, 36.2, 49.9, 50.6, 77.3, 126.9, 126.9, 127.1, 128.6, 128.8, 139.4, 140.8, 141.2, 175.3

**IR** (ATR) 3028 w, 2928 m, 2856 w, 1647 s, 1485 m, 763 m.

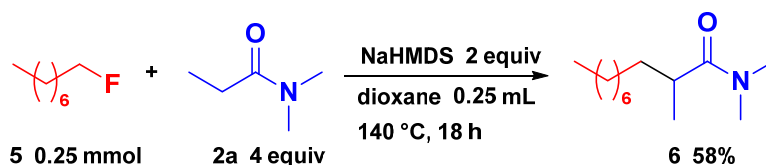
**MS:**  $m/z$  (EI, relative intensity, %) 280 (22), 279 (100,  $M^+$ ), 222 (10), 221 (14), 220 (39), 205 (13), 194 (13), 193 (27), 180 (33), 179 (21), 178 (41), 167 (23), 165 (32), 154 (12), 152 (13), 98 (13), 73 (19), 72 (15), 70<sup>+</sup> (10), 44 (20).

**HRMS** ( $[M+H]^+$ ) Calcd for  $C_{19}H_{22}NO$ : 280.16959; Found: 280.16968.

## Ineffective aryl fluorides



## 4. S<sub>N</sub>2 Reaction of Primary Alkyl Fluoride with Aliphatic Amide



To an oven-dried 10 mL screw-capped vial in a glove box, NaHMDS (91.7 mg, 0.5 mmol), *N,N*-dimethylpropionamide (**2a**, 101.9 mg, 1.0 mmol), 1-fluorooctane (**1a**, 33.1 mg, 0.25 mmol), and 1,4-dioxane (0.25 mL) were added in sequential order. The mixture was stirred at 140 °C for 18 h followed by cooling. The resulting mixture was washed with H<sub>2</sub>O (10 mL) and extracted with EtOAc (30 mL). The organic layer was washed with water and filtered through a silica pad. The filtrate was concentrated to dryness in vacuo and the residue was purified by MPLC (hexane/EtOAc = 1/3) to afford the desired product *N,N*,2-trimethyldecanamide (**6**, 26.3 mg, 58%).

A colorless oil. *R*<sub>f</sub> = 0.25 (hexane/EtOAc = 3/1). Yield = 58%, *m* = 26.3 mg.

<sup>1</sup>H NMR (399.78 MHz, CDCl<sub>3</sub>) δ 0.87 (t, *J* = 6.9 Hz, 3H), 1.09 (d, *J* = 6.9 Hz, 3H), 1.25-1.39 (m, 13H), 1.64-1.70 (m, 1H), 2.65-2.73 (m, 1H), 2.96 (s, 3H), 3.05 (s, 3H)

<sup>13</sup>C NMR (100.53 MHz, CDCl<sub>3</sub>) δ 14.1, 17.4, 22.6, 27.5, 29.3, 29.5, 29.7, 31.8, 34.1, 35.5, 35.6, 37.2, 176.8

IR (ATR) 2928 s, 2855 m, 1646 s, 1464 m, 1397 m, 722 m.

MS: *m/z* (EI, relative intensity, %) 213 (1, M<sup>+</sup>), 114 (14), 101 (100), 72 (35), 57 (14), 45 (23), 43 (14), 41 (11).

HRMS ([M+H]<sup>+</sup>) Calcd for C<sub>13</sub>H<sub>28</sub>ON: 214.21654; Found: 214.21626.

## 5. Computational Studies

### 5.1 General Information

All calculations of the geometry optimizations were performed by Gaussian 16 package.<sup>[1]</sup> The geometry optimizations and frequency calculations of all structures were conducted at the M06-2X functional<sup>[2]</sup> in conjunction with the def2SVP basis set<sup>[3]</sup> in the presence of two Me<sub>2</sub>O models. The self-consistent reaction field (SCRF) method based on conductor-like polarizable continuum model (CPCM)<sup>[4]</sup> was adopted to evaluate the effects of solvent (THF). Each reported minimum has no imaginary frequency and each transition state structure has one imaginary frequency. Intrinsic reaction coordinate (IRC) analyses<sup>[5]</sup> from transition states to minima were used for confirming the reaction pathways. This level is denoted as CPCM(THF)-M06-2X/def2SVP. For describing energy diagram, the relative energies were corrected for the thermal free energies and given in kcal·mol<sup>-1</sup>. The structures of intermediates and transition states were described by GaussView 6.0 package.<sup>[6]</sup>

### 5.2 DFT Studies on the Reaction Pathway

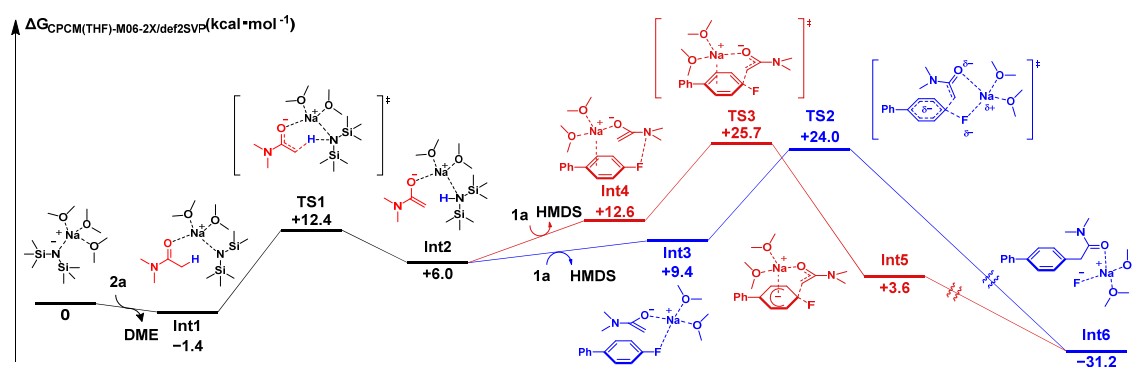
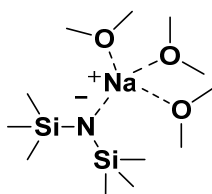


Figure S1. Energy diagram of the reaction pathway at CPCM(THF)-M06-2X/def2SVP level.

### 5.3 Energies and Cartesian Coordinates on the Reaction Pathway

#### NaHMDS



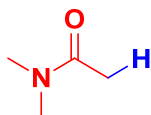
Electronic Energy (EE): - 1499.546695 Hartree

EE + Zero-point Energy: - 1499.074912 Hartree

EE + Thermal Free Energy Correction: - 1499.144443 Hartree

Na	1.02885800	0.22399400	0.23157300	H	-0.39288900	1.31995000	2.50442500
O	1.53567500	2.23814300	-0.70329900	H	-0.27362900	2.58447700	1.25360800
C	2.63504500	3.08727300	-0.48957500	C	-3.19738400	2.21835100	-0.23035200
H	3.36923900	2.54335900	0.11848000	H	-3.76552600	2.87605400	0.44738800
H	3.10372900	3.37643600	-1.44632400	H	-2.57734800	2.85483100	-0.88133400
H	2.32895800	4.00344200	0.04393700	H	-3.92087700	1.69098300	-0.87355200
C	0.52530900	2.81671800	-1.49941700	C	-2.04035400	-0.82664800	-3.02644400
H	-0.29205800	2.08578100	-1.56347800	H	-2.97187100	-0.23843500	-2.99595300
H	0.15005800	3.74771300	-1.03926800	H	-1.26463900	-0.19484800	-3.48910500
H	0.90904700	3.04904500	-2.50788100	H	-2.20868800	-1.69497000	-3.68402900
N	-1.18891000	-0.05024800	-0.23889600	C	-2.87455700	-2.53575800	-0.66573600
Si	-2.12909100	0.96454800	0.72707900	H	-2.96589700	-3.41599200	-1.32262800
Si	-1.51738800	-1.34394100	-1.26992900	H	-2.66123000	-2.89066700	0.35577600
O	1.31239400	-0.91534100	2.17764000	H	-3.85363300	-2.03019800	-0.64275000
C	0.19497600	-1.64045700	2.64124200	C	0.05586800	-2.39572700	-1.49059000
H	-0.20648000	-1.19021400	3.56611800	H	0.40510700	-2.77713000	-0.51578000
H	-0.56881000	-1.59356800	1.85310600	H	-0.10502500	-3.26012100	-2.15429300
H	0.46851200	-2.68985100	2.84670300	H	0.87117900	-1.78864400	-1.91953800
C	2.35530600	-0.83567700	3.11662500	O	2.94282900	-0.66144200	-0.62530000
H	2.71679600	-1.84131400	3.39332700	C	3.46389600	-0.22687800	-1.85861700
H	3.17919900	-0.27237900	2.65992800	H	3.01382000	0.74765900	-2.08288300
H	2.02415300	-0.31594300	4.03198900	H	4.56158800	-0.12442400	-1.80877700
C	-3.34403300	0.07843800	1.89703100	H	3.21185600	-0.93871500	-2.66379700
H	-3.88078700	0.79691600	2.53788200	C	3.40852800	-1.93644200	-0.25253100
H	-4.09384700	-0.49182900	1.32625000	H	2.91673800	-2.20526000	0.69026100
H	-2.81522300	-0.63178100	2.55245600	H	3.15212500	-2.68690500	-1.02000700
C	-0.98214200	1.98891400	1.85358300	H	4.50305400	-1.92943000	-0.11115100
H	-1.54100300	2.68174500	2.50213500				

**2a**



Electronic Energy (EE): – 287.482353 Hartree

EE + Zero-point Energy: – 287.351491 Hartree

EE + Thermal Free Energy Correction: – 287.383851 Hartree

C	0.72357300	-0.29633000	0.00000200	H	-0.23639200	2.15875400	0.00008500
O	1.06213900	-1.47023700	0.00000600	H	-1.68434100	1.63513700	-0.89064600
N	-0.58790300	0.07909100	0.00000100	H	-1.68446100	1.63508100	0.89058300
C	-1.62399700	-0.93252600	-0.00000600	C	1.76539300	0.80723400	-0.00000600
H	-2.26197200	-0.82970700	0.89217500	H	2.74863800	0.32711200	-0.00003500
H	-2.26199400	-0.82967200	-0.89216600	H	1.67428000	1.44583500	-0.88925600
H	-1.15505800	-1.92012100	-0.00003000	H	1.67432100	1.44580500	0.88927000
C	-1.06410400	1.44496100	0.00000400				

**DME**



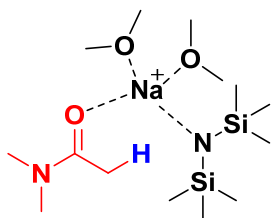
Electronic Energy (EE): - 154.8273547 Hartree

EE + Zero-point Energy: - 154.747075 Hartree

EE + Thermal Free Energy Correction: - 154.772451 Hartree

O	0.0000000	-0.5858440	-0.0000040	C	1.1624260	0.1914200	0.0000000
C	-1.1624260	0.1914200	-0.0000010	H	2.0268770	-0.4842860	0.0002910
H	-2.0268790	-0.4842840	0.0002990	H	1.2189970	0.8393690	-0.8945770
H	-1.2187670	0.8397790	0.8943000	H	1.2187700	0.8397730	0.8943040
H	-1.2189990	0.8393640	-0.8945800				

### Int1



Electronic Energy (EE): - 1632.207195 Hartree

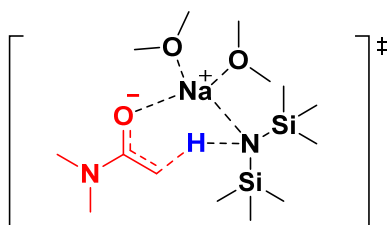
EE + Zero-point Energy: - 1631.684762 Hartree

EE + Thermal Free Energy Correction: - 1631.758080 Hartree

Na	0.6086650	-1.0535340	0.4836740	C	1.3914910	-3.3932560	-1.6092820
O	2.3630330	-0.7612220	1.9032410	H	0.3325780	-3.5156030	-1.3491800
C	3.0831180	-1.7477460	2.5974090	H	1.4761430	-3.0597740	-2.6587540
H	2.7150520	-2.7279910	2.2686750	H	1.9122390	-4.3602130	-1.5016150
H	4.1628790	-1.6768550	2.3775370	C	-1.9357950	-1.0671580	-1.8532660
H	2.9391150	-1.6516460	3.6872400	H	-0.9626050	-1.4594280	-2.1676800
C	2.7623520	0.5531290	2.2176830	H	-2.7041910	-1.3469000	-2.5849020
H	2.1537380	1.2288300	1.6019250	H	-1.8478210	0.0292870	-1.7979580
H	2.5999330	0.7683140	3.2885510	N	0.1385400	1.0882830	-0.1640180
H	3.8315150	0.7018340	1.9846800	Si	-0.8288700	1.8215800	1.0090460
C	-2.2283200	-1.6021280	-0.4706430	Si	0.9570320	1.7411740	-1.4893010
O	-1.3333340	-2.1626680	0.1796740	C	2.7099210	2.3618520	-1.0657530
N	-3.4656210	-1.4315300	0.0327810	H	3.2147690	2.8082140	-1.9379700
C	-3.8071040	-1.9587320	1.3409020	H	2.6754600	3.1192330	-0.2654810
H	-4.0791840	-1.1384440	2.0228420	H	3.3328690	1.5266800	-0.7045290
H	-4.6661590	-2.6418800	1.2569580	C	1.2128750	0.4420470	-2.8590770
H	-2.9484880	-2.5000560	1.7468650	H	0.2748880	0.2487670	-3.4033170
C	-4.5609470	-0.8101730	-0.6881880	H	1.9688710	0.7637240	-3.5933480
H	-5.2450610	-1.5682630	-1.1030530	H	1.5451400	-0.5124460	-2.4176240
H	-5.1291010	-0.1747300	0.0056280	C	0.0744260	3.2083270	-2.3259950
H	-4.1948790	-0.1740950	-1.4990020	H	0.6390490	3.5923470	-3.1910590
O	1.9299780	-2.4318670	-0.7339290	H	-0.9241550	2.9039920	-2.6801040
C	3.2981110	-2.1825810	-0.9453580	H	-0.0653960	4.0407770	-1.6170320
H	3.6025080	-1.4013920	-0.2373240	C	-0.1289400	3.4333750	1.7490300
H	3.8962810	-3.0931790	-0.7682110	H	-0.7983460	3.8608210	2.5131010
H	3.4812410	-1.8320070	-1.9760580	H	0.8517710	3.2554820	2.2192820

H	0.01384200	4.19282200	0.96291300	C	-1.07368300	0.62922800	2.47517100
C	-2.58763200	2.24497000	0.41502000	H	-0.10808600	0.37099600	2.94204400
H	-3.09646200	1.32024400	0.09881800	H	-1.72010800	1.05982900	3.25632200
H	-3.19625800	2.71505100	1.20447800	H	-1.54379200	-0.30733400	2.13011200
H	-2.55939400	2.92718800	-0.44976000				

### TS1



Electronic Energy (EE): - 1632.184892 Hartree

EE + Zero-point Energy: - 1631.666328 Hartree

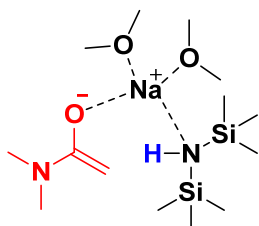
EE + Thermal Free Energy Correction: - 1631.736107 Hartree

Imaginary frequency = - 1321.52 cm<sup>-1</sup>

Na	0.69501200	-0.96048300	0.46483900	H	-0.65943100	-1.26550100	-2.17104800
O	2.44141900	-0.72243800	1.89706700	H	-2.37489800	-0.67212100	-2.26644000
C	3.28783800	-1.79797900	2.22734700	H	-1.00164800	0.15811100	-0.93911700
H	3.10851100	-2.59616100	1.49652200	N	-0.32249800	1.09190300	-0.27023600
H	4.34726500	-1.49199900	2.18123700	Si	-1.37267600	1.83659500	0.87864400
H	3.07116000	-2.17274500	3.24198300	Si	0.81817400	1.92817300	-1.26089500
C	2.56741100	0.37204300	2.77314500	C	2.43220900	2.26403800	-0.32643400
H	1.86122400	1.14456000	2.44389900	H	3.18974200	2.73067000	-0.97596000
H	2.33145900	0.07744700	3.80991500	H	2.25476600	2.93586700	0.52864000
H	3.59020500	0.78484300	2.74252100	H	2.84921700	1.32342100	0.06901300
C	-1.83292700	-1.91754500	-0.55279600	C	1.23690700	0.85728300	-2.76210400
O	-0.90031700	-2.48261500	0.07439000	H	0.35925100	0.73820300	-3.41611900
N	-3.12785000	-2.13599700	-0.15785600	H	2.04859900	1.30970400	-3.35306600
C	-3.41325900	-2.94229300	1.01068100	H	1.55731900	-0.14682500	-2.44378600
H	-3.74917000	-2.32199000	1.86008500	C	0.19289900	3.59059900	-1.92159700
H	-4.20494200	-3.67281600	0.78559500	H	0.94979000	4.06939300	-2.56291800
H	-2.50387400	-3.47503000	1.30143900	H	-0.71989700	3.44630700	-2.52079500
C	-4.23780400	-1.43117200	-0.76529100	H	-0.04756200	4.28994100	-1.10537400
H	-4.26861900	-1.58632500	-1.85308800	C	-0.52211500	3.16959400	1.92249100
H	-5.17344600	-1.81570700	-0.34175400	H	-1.23929000	3.62124800	2.62623600
H	-4.19420900	-0.34568300	-0.57247300	H	0.31100500	2.75656000	2.51167800
O	2.23705900	-1.96110800	-0.88043900	H	-0.11896500	3.97696100	1.29116900
C	3.55983000	-1.53914500	-1.10347400	C	-2.86398000	2.65987800	0.05039600
H	3.80586100	-0.79685200	-0.33365400	H	-3.38260700	1.94585600	-0.60874000
H	4.26101400	-2.38855000	-1.02872200	H	-3.58873300	3.03365300	0.79077000
H	3.66596900	-1.07820700	-2.10119200	H	-2.54005100	3.50924700	-0.57087100
C	1.80150000	-2.94003100	-1.79758500	C	-2.03572800	0.51169100	2.05389600
H	0.77692900	-3.21203300	-1.51550600	H	-1.21878800	0.05285100	2.63537000
H	1.81237500	-2.54261700	-2.82804800	H	-2.76310500	0.92963500	2.76708500
H	2.45265100	-3.82993800	-1.75482900	H	-2.53442700	-0.28795000	1.48332700
C	-1.55204800	-0.96345000	-1.60804000				



## Int2



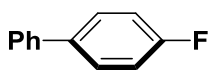
Electronic Energy (EE): - 1632.198085 Hartree

EE + Zero-point Energy: - 1631.675249 Hartree

EE + Thermal Free Energy Correction: - 1631.746289 Hartree

Na	0.67453700	-1.03639400	0.54999600	H	-0.95334400	-1.49557400	-2.28754700
O	2.50999700	-0.65491700	1.83345900	H	-2.74547100	-1.00687100	-2.49996100
C	3.28432300	-1.75742600	2.24664100	H	-0.86602800	0.41619100	-0.86919900
H	3.00746900	-2.61268700	1.61744500	N	-0.23043800	1.05978700	-0.35954200
H	4.36063800	-1.54814400	2.12294800	Si	-1.09127800	1.79611300	0.98996100
H	3.08877200	-2.00138600	3.30435300	Si	0.88394200	1.81167400	-1.49380100
C	2.77440600	0.51310700	2.57246100	C	2.50917700	2.18497800	-0.62191700
H	2.12226800	1.30652900	2.18599200	H	3.24368000	2.58530400	-1.33772600
H	2.56573000	0.35927000	3.64494100	H	2.38413200	2.92622000	0.18171600
H	3.82607700	0.82493500	2.45351800	H	2.92385000	1.26420600	-0.18127100
C	-2.10192800	-1.65679200	-0.51379000	C	1.18255800	0.57171700	-2.87442800
O	-1.17021900	-2.12346000	0.23420300	H	0.26298000	0.41369700	-3.45779100
N	-3.35072300	-1.43476800	0.11915300	H	1.96959900	0.92783800	-3.55667400
C	-3.67637300	-2.25158800	1.26655200	H	1.49038100	-0.39952900	-2.45742000
H	-4.35994900	-1.70842000	1.93750300	C	0.18717900	3.39144200	-2.24967700
H	-4.16911500	-3.20357300	0.98106900	H	0.88056700	3.80263000	-2.99972300
H	-2.75595100	-2.49115900	1.80698900	H	-0.76916500	3.17708200	-2.75139200
C	-4.48546000	-1.06540700	-0.68855600	H	0.00667300	4.17083300	-1.49462300
H	-4.80439900	-1.87153400	-1.38014600	C	-0.18520400	3.34060500	1.57559800
H	-5.33278400	-0.82024400	-0.03231100	H	-0.77188600	3.81143900	2.37958800
H	-4.25704100	-0.17584500	-1.29186300	H	0.80946200	3.11108100	1.98551000
O	2.05955400	-2.18087300	-0.81934900	H	-0.06178300	4.08325900	0.77366500
C	3.40974500	-1.95642400	-1.13805500	C	-2.84041700	2.21969600	0.45569700
H	3.77969700	-1.16186800	-0.47716500	H	-3.34819600	1.28196300	0.17989100
H	4.00950400	-2.86998800	-0.98203800	H	-3.40995100	2.69607700	1.26809000
H	3.52042000	-1.63628400	-2.18898300	H	-2.84156800	2.89193400	-0.41553600
C	1.45053600	-3.18203700	-1.60688400	C	-1.18537600	0.55686700	2.40366500
H	0.40710300	-3.26043000	-1.27446400	H	-0.19270400	0.33842200	2.83101500
H	1.47879400	-2.90604700	-2.67582200	H	-1.82008700	0.93731100	3.21854600
H	1.96767800	-4.14793600	-1.47572000	H	-1.62377500	-0.38126500	2.02588500
C	-1.93416800	-1.31494700	-1.84585000				

## 1a



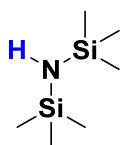
Electronic Energy (EE): - 561.899657 Hartree

EE + Zero-point Energy: - 561.724613 Hartree

EE + Thermal Free Energy Correction: - 561.760415 Hartree

F	-4.43303200	-0.00000400	-0.00004600	C	1.17747200	-0.00000300	0.00001500
C	-3.09669000	0.00000200	-0.00000300	C	1.89555800	1.14466600	0.37709100
C	-2.42098500	-1.15313600	0.37805400	C	1.89554900	-1.14467100	-0.37708300
C	-2.42097700	1.15314300	-0.37803400	C	3.28921000	1.14507200	0.37641400
C	-1.02850500	-1.14456900	0.37553800	H	1.35632200	2.03857600	0.69626500
H	-2.98836200	-2.03484300	0.67661700	C	3.28920100	-1.14507600	-0.37644000
C	-1.02849900	1.14457600	-0.37549400	H	1.35630600	-2.03857900	-0.69625200
H	-2.98834900	2.03486100	-0.67657500	C	3.99177000	-0.00000200	-0.00002100
C	-0.30899100	0.00000100	0.00002400	H	3.82911700	2.04334800	0.67999600
H	-0.49211800	-2.04029500	0.69293100	H	3.82910000	-2.04335100	-0.68004000
H	-0.49210200	2.04030300	-0.69286600	H	5.08270700	-0.00000200	-0.00003700

### HMDS



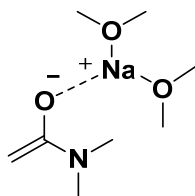
Electronic Energy (EE): - 873.348994 Hartree

EE + Zero-point Energy: - 873.111596 Hartree

EE + Thermal Free Energy Correction: - 873.154281 Hartree

H	-0.00004500	-0.01216000	-1.85083900	H	-1.33179000	-2.20313500	1.06797500
N	0.00012400	-0.00182200	-0.83326500	H	-0.83314700	-0.87275100	2.14187600
Si	1.58281400	0.00890900	-0.09007600	C	1.57052400	1.18064200	1.38353300
Si	-1.58268300	-0.00921900	-0.09011700	H	2.55659100	1.19695700	1.87256100
C	-2.07976800	1.70803900	0.50309400	H	1.32696400	2.20493900	1.06296500
H	-3.08323900	1.69596800	0.95612100	H	0.82999900	0.87592100	2.13947600
H	-1.37020900	2.08357700	1.25591900	C	2.08226200	-1.70632400	0.50731600
H	-2.09028900	2.41973100	-0.33649200	H	2.09430600	-2.42000700	-0.33057300
C	-2.81872700	-0.59889300	-1.37730700	H	3.08543300	-1.69194000	0.96094300
H	-2.57376100	-1.61441700	-1.72262300	H	1.37260700	-2.08099600	1.26050600
H	-3.83722700	-0.61388700	-0.96087700	C	2.81929000	0.59730100	-1.37746000
H	-2.82310400	0.06949000	-2.25216900	H	2.57342100	1.61178500	-1.72513600
C	-1.57385300	-1.17774200	1.38620500	H	3.83743700	0.61421900	-0.96022100
H	-2.56020100	-1.19140200	1.87476200	H	2.82517100	-0.07292100	-2.25091500

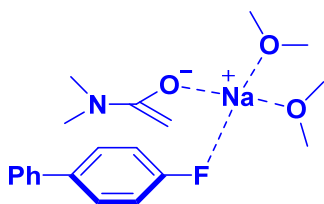
### amide enolate



Electronic Energy (EE): - 758.823820 Hartree  
 EE + Zero-point Energy: - 758.540944 Hartree  
 EE + Thermal Free Energy Correction: - 758.592217 Hartree

Na	-0.52584400	0.55780000	-0.04090900	H	-4.19263100	1.99017900	-1.23385100
O	-2.68256400	1.30371600	0.01067000	H	-3.49914400	3.20901700	-0.11646100
O	-1.51185000	-1.49424400	-0.01577800	C	2.04606500	-0.07685000	-0.08308100
C	-2.69189100	-1.89782200	-0.66108100	C	1.63925000	-0.58630300	-1.31229800
H	-3.38628300	-2.38325600	0.04737100	H	2.28180600	-0.62281700	-2.18778500
H	-3.16830400	-1.00058900	-1.07584400	H	0.71189800	-1.16181500	-1.34387900
H	-2.47313000	-2.60574300	-1.47921900	O	1.31934300	-0.10288900	0.97481100
C	-0.77999000	-2.56591300	0.53849700	N	3.29934500	0.56099100	0.03532500
H	-0.52148300	-3.30390900	-0.24062400	C	3.89723000	0.63706800	1.34766300
H	0.13873800	-2.13778400	0.95925500	H	4.49936000	-0.26099900	1.59558900
H	-1.36686800	-3.07207200	1.32481400	H	4.56233000	1.51222800	1.41152400
C	-3.52174600	0.84016800	1.04286800	H	3.10382400	0.73318800	2.09407100
H	-3.00221600	0.01808100	1.55048100	C	4.22696700	0.50193400	-1.06404000
H	-3.73849900	1.64431600	1.76611200	H	3.76643800	0.89374400	-1.98225400
H	-4.47526600	0.46493700	0.63292300	H	5.10187000	1.12588200	-0.83398200
C	-3.26417100	2.33646400	-0.74894900	H	4.58274500	-0.52598100	-1.27880600
H	-2.54602600	2.63551900	-1.52179900				

### Int3

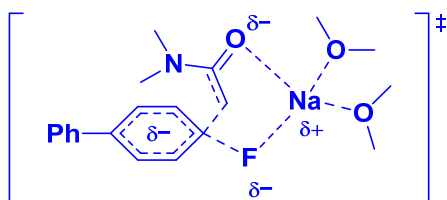


Electronic Energy (EE): - 1320.737890 Hartree  
 EE + Zero-point Energy: - 1320.279126 Hartree  
 EE + Thermal Free Energy Correction: - 1320.347030 Hartree

Na	-2.86577000	-0.07701300	-0.13625400	H	2.83972000	0.16956600	-1.97690600
F	-1.01985100	-1.43626500	-0.32383100	C	4.50540300	-0.52149100	0.06428200
C	0.30775100	-1.20100000	-0.22074500	C	5.07206700	0.65854600	-0.44045900
C	0.97908000	-1.64924800	0.90588000	C	5.35185600	-1.46338000	0.66806500
C	0.94620400	-0.53738700	-1.25564500	C	6.44308400	0.88985600	-0.34444800
C	2.35199400	-1.42638700	0.98931400	H	4.42869000	1.41424900	-0.89561300
H	0.42960200	-2.15357500	1.70069300	C	6.72267100	-1.23217000	0.76481000
C	2.31902500	-0.32848200	-1.15701100	H	4.93477100	-2.39836900	1.04690300
H	0.37197400	-0.19573500	-2.11721700	C	7.27395000	-0.05455800	0.25885700
C	3.04274100	-0.76475000	-0.03678300	H	6.86299300	1.81735400	-0.73672700
H	2.88896000	-1.75219100	1.88142500	H	7.36502400	-1.98065100	1.23141400

H	8.34712400	0.12633700	0.33440000	H	-4.39634600	-3.84244300	0.29434700
O	-4.06133800	-1.96981700	-0.53137200	H	-3.53824000	-3.83354600	-1.28017300
O	-4.81634200	0.74342400	0.68396900	C	-1.18756700	1.91536600	0.10751000
C	-5.79629800	0.08048800	1.43966900	C	-1.45091100	1.58650600	1.43638300
H	-6.80084000	0.22642000	1.00461800	H	-0.71318800	1.68621700	2.22853400
H	-5.55239900	-0.98953400	1.43505200	H	-2.49580100	1.47439000	1.73343100
H	-5.80759900	0.44632000	2.48094200	O	-2.07226400	1.87714000	-0.82375200
C	-4.98358900	2.14394400	0.64367000	N	0.11456700	2.26076200	-0.27102100
H	-4.99148200	2.56388400	1.66452400	C	0.38024700	2.81511500	-1.57066100
H	-4.12834500	2.54733100	0.08600700	H	0.61560600	3.89592600	-1.52938100
H	-5.93174900	2.40896000	0.14415700	H	1.23805100	2.30860900	-2.04966200
C	-5.27905800	-1.86919700	-1.23164600	H	-0.50886700	2.67591900	-2.19342500
H	-5.52865600	-0.80407600	-1.31486900	C	1.17722100	2.27592700	0.69572500
H	-5.19125600	-2.30846700	-2.23972700	H	1.22895700	1.31333600	1.23177400
H	-6.08807100	-2.38774100	-0.68859100	H	2.13598200	2.42356400	0.17885700
C	-3.65711700	-3.30191900	-0.32093000	H	1.06549000	3.07841300	1.45028100
H	-2.69291600	-3.28292800	0.19955800				

## TS2



Electronic Energy (EE):  $-1320.713908$  Hartree

EE + Zero-point Energy:  $-1320.255839$  Hartree

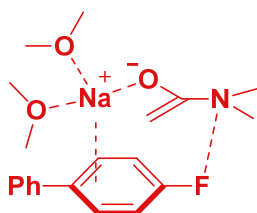
EE + Thermal Free Energy Correction:  $-1320.323675$  Hartree

Imaginary frequency =  $-422.53 \text{ cm}^{-1}$

Na	3.22456400	0.33555400	-0.35159900	C	-5.03228300	1.10289300	1.22025500
F	1.39075300	0.98144200	0.77685800	C	-6.17823300	-0.24928100	-0.92235900
C	0.11271800	0.42666500	0.69836100	H	-4.16498400	-0.74001900	-1.50036800
C	-0.71448300	0.62418300	1.83373900	C	-6.41805000	1.05735600	1.08384800
C	-0.49179900	0.51516300	-0.58149800	H	-4.59586400	1.66082400	2.05065700
C	-2.08913100	0.60883600	1.69333300	C	-7.00172800	0.38337700	0.01002600
H	-0.24897400	0.68718600	2.81871700	H	-6.61864200	-0.78923000	-1.76271300
C	-1.87123600	0.50104300	-0.69592100	H	-7.04770400	1.56359100	1.81800400
H	0.14945200	0.51308900	-1.46618500	H	-8.08679900	0.35054500	-0.09827900
C	-2.71505800	0.51001000	0.43126400	O	3.31162400	2.47806100	-1.11339100
H	-2.70415800	0.66498300	2.59438300	O	4.49781400	-0.72132500	1.20228900
H	-2.31232800	0.52104800	-1.69578900	C	5.19474200	-0.17829600	2.29600900
C	-4.18627100	0.46931000	0.29168500	H	6.26208200	-0.45625200	2.26280900
C	-4.79277600	-0.21136100	-0.78010500	H	5.10719000	0.91411600	2.24755300

H	4.76763100	-0.53191100	3.24977600	C	0.99655200	-1.57084800	0.95639900
C	4.54413100	-2.13096300	1.15869700	H	0.21028500	-2.06824500	1.52018900
H	4.13485600	-2.56218500	2.08821500	H	1.89817500	-1.31353800	1.51517800
H	3.92596600	-2.44766200	0.30970900	O	2.20626700	-1.46816300	-1.06849000
H	5.58244100	-2.48222000	1.03005700	N	0.15302100	-2.44629400	-1.11143300
C	4.47637600	3.05734400	-1.65125800	C	0.19421700	-2.56276300	-2.55098400
H	5.30600600	2.35383300	-1.50725800	H	0.05643800	-3.60975000	-2.86783200
H	4.35643800	3.25717900	-2.72942700	H	-0.59854800	-1.95808200	-3.02447600
H	4.71602300	4.00506900	-1.14025700	H	1.16777300	-2.21031600	-2.90261300
C	2.17747100	3.30558900	-1.24555500	C	-1.04969700	-2.88841500	-0.43924000
H	1.32796800	2.78450200	-0.78925400	H	-1.58190800	-2.05303100	0.04646000
H	2.33510100	4.26722400	-0.72860300	H	-1.72312900	-3.33755300	-1.18012600
H	1.96157400	3.50567100	-2.30869400	H	-0.83004400	-3.65065400	0.32537700
C	1.18852500	-1.86097700	-0.42045800				

#### Int4



Electronic Energy (EE): - 1320.738057 Hartree

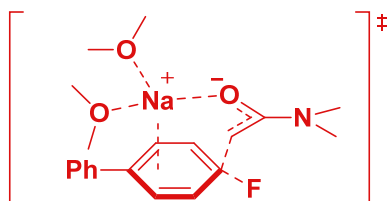
EE + Zero-point Energy: - 1320.278130 Hartree

EE + Thermal Free Energy Correction: - 1320.341875 Hartree

O	-1.80485900	0.69543500	1.30321200	H	5.37214000	-2.29770600	-0.53172300
Na	0.26610300	1.02990500	1.10188200	H	4.55428700	1.92298600	-0.27394400
C	0.95544100	-0.92221500	-1.14055200	H	6.17328300	0.03042600	-0.14425500
C	0.14466300	0.00819800	-1.81165200	F	-2.99093600	-1.77611300	-1.98156800
C	-1.19871100	-0.25591500	-2.07142300	H	-1.42311500	-3.34870200	-0.66788400
C	-1.72929600	-1.47500000	-1.67192200	H	0.57617500	0.94557200	-2.16829700
C	-0.96595700	-2.41076800	-0.98397400	O	1.21041200	-0.68558900	2.21688500
C	0.36754000	-2.12269100	-0.71117300	C	0.19572700	-1.45365100	2.82744500
H	-1.83319400	0.46105100	-2.59344700	C	2.49912100	-1.20999300	2.42072500
H	0.96233600	-2.84735400	-0.15216000	H	0.37176300	-1.53872600	3.91346900
C	2.39755000	-0.65654700	-0.89333000	H	-0.75799400	-0.94195700	2.64121100
C	3.32408300	-1.70872200	-0.83570600	H	0.16103100	-2.46845700	2.39285800
C	2.86831100	0.65136100	-0.69979700	H	3.21865500	-0.56478900	1.90012300
C	4.66947100	-1.46377300	-0.56856800	H	2.74198400	-1.24232800	3.49698300
H	2.99247500	-2.73231000	-1.01738800	H	2.57636200	-2.23180500	2.00941100
C	4.21392900	0.89769500	-0.42940400	O	0.52078100	2.96279700	-0.06331900
H	2.16953300	1.48821900	-0.74994000	C	1.51735200	3.95623200	-0.10380700
C	5.12039700	-0.16028100	-0.35614200	C	-0.60495200	3.27052400	-0.85964200

H	1.11943800	4.92413500	0.24352200	H	-4.93650100	0.50976600	-1.02821800
H	2.33415900	3.64573200	0.56006000	C	-3.39870900	-1.52950300	1.12384300
H	1.90858200	4.08043000	-1.12852800	H	-4.02776000	-1.60580400	2.03627300
H	-1.36044500	2.48937500	-0.69601100	H	-3.62058400	-2.40253500	0.48929800
H	-1.03547600	4.24096300	-0.56023500	H	-2.34670700	-1.57530900	1.42153000
H	-0.32548300	3.32088100	-1.92686800	C	-2.98018100	0.86278200	0.80432600
N	-3.63561000	-0.31945300	0.37868800	C	-3.60369000	2.08215900	0.64550200
C	-4.94275400	-0.22571900	-0.21132400	H	-3.05447200	2.97964700	0.93023300
H	-5.21751100	-1.20239100	-0.63421900	H	-4.62738100	2.19093000	0.29685300
H	-5.73169600	0.07610900	0.50912800				

### TS3



Electronic Energy (EE): - 1320.717150 Hartree

EE + Zero-point Energy: - 1320.258141 Hartree

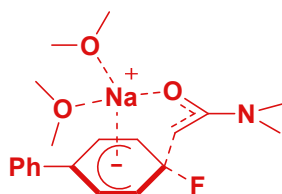
EE + Thermal Free Energy Correction: - 1320.321007 Hartree

Imaginary frequency = - 431.15  $\text{cm}^{-1}$

O	2.09314700	0.82930600	1.31708300	F	3.09241200	-1.68666600	-1.98294000
Na	0.04585000	0.07774600	1.10035200	H	2.25038700	0.79400000	-1.91099300
C	-0.84868300	-0.58843100	-1.35798600	H	-1.15543600	-2.71129700	-1.03040900
C	-0.41371300	-1.92305000	-1.18156700	O	-1.04994500	2.04994500	0.85362100
C	0.91979900	-2.27841600	-1.24918100	C	-0.17945800	3.13184800	0.61128900
C	1.92759500	-1.28271500	-1.38930700	C	-2.39397900	2.44175300	0.99226200
C	1.49337200	0.03458800	-1.70530500	H	-0.23023500	3.86922500	1.43135300
C	0.15039000	0.36400200	-1.65401300	H	0.83849400	2.72522000	0.54754700
H	1.22951600	-3.31948100	-1.14096500	H	-0.44343900	3.63788800	-0.33407400
H	-0.13508000	1.40396000	-1.82684300	H	-3.01360300	1.53514200	1.01797800
C	-2.27390100	-0.21361500	-1.25306300	H	-2.54017300	3.02416300	1.91907400
C	-2.80079700	0.88271100	-1.96014600	H	-2.71268600	3.05426200	0.13222600
C	-3.15441800	-0.93517500	-0.42505100	O	-1.21169000	-1.46745800	2.18121800
C	-4.13955300	1.24628800	-1.83623200	C	-2.33223900	-1.11623600	2.95847800
H	-2.15519700	1.44949200	-2.63325300	C	-0.97528800	-2.85573100	2.15380100
C	-4.49539800	-0.57479800	-0.30509400	H	-2.20124200	-1.44102500	4.00428900
H	-2.77093900	-1.77594400	0.15548700	H	-2.43703900	-0.02444000	2.93072400
C	-4.99752800	0.52276200	-1.00612500	H	-3.25113300	-1.57543100	2.55449600
H	-4.51880000	2.10024400	-2.40084600	H	-0.08436800	-3.03588700	1.53967500
H	-5.15108100	-1.15234500	0.34977600	H	-0.80496600	-3.24442200	3.17173800
H	-6.04622300	0.80764500	-0.91089100	H	-1.83301400	-3.39128200	1.70936000

N	4.10358900	0.87608100	0.26322000	H	4.44712300	2.86145000	-0.35133100
C	5.22699400	0.19838800	-0.34513100	H	3.37958500	2.64691400	1.06818800
H	5.82021300	0.93219000	-0.90705900	C	3.03751400	0.17498000	0.78885500
H	5.89015300	-0.27849000	0.39986300	C	2.94690100	-1.22689900	0.57350100
H	4.87874200	-0.56732800	-1.04882100	H	2.19303800	-1.72505400	1.18745900
C	4.27930500	2.27741900	0.56793500	H	3.83599800	-1.81800200	0.36039000
H	5.14663100	2.43847400	1.23301600				

## Int5



Electronic Energy (EE): - 1320.754307 Hartree

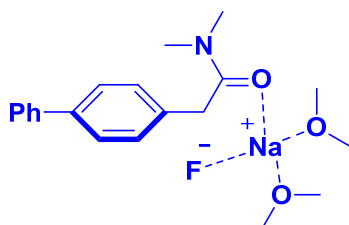
EE + Zero-point Energy: - 1320.292948 Hartree

EE + Thermal Free Energy Correction: - 1320.356289 Hartree

O	2.45822900	0.92800000	-0.04024900	C	-0.00519600	1.74740100	-2.93254500
Na	0.24951800	0.85349200	0.02733400	C	-2.18015200	1.38811300	-2.13034600
C	-1.19489700	-1.37446100	0.18680000	H	-0.31823000	2.58149200	-3.58324400
C	-0.46742900	-1.27165800	1.40300700	H	1.02136700	1.92442800	-2.58696900
C	0.90133200	-1.39520800	1.47258700	H	-0.03085500	0.81088000	-3.51627500
C	1.70342500	-1.85996000	0.31881100	H	-2.75129800	1.29168100	-1.19737700
C	0.96316300	-1.68739200	-0.95015100	H	-2.59880600	2.20655600	-2.74148400
C	-0.40555600	-1.56517300	-0.98114800	H	-2.26756100	0.44141200	-2.69099700
H	1.41266900	-1.27493100	2.43199800	O	-0.91842500	2.08378900	1.52594900
H	-0.89591800	-1.51769300	-1.95900000	C	-1.92057000	3.00534600	1.16798400
C	-2.64217700	-1.14559500	0.11124100	C	-0.78886300	1.91710500	2.91691300
C	-3.41969700	-1.67458500	-0.94071300	H	-1.74307300	3.98275800	1.64802900
C	-3.31791700	-0.34653400	1.05904900	H	-1.88488400	3.12720400	0.07865700
C	-4.77979000	-1.39690300	-1.05479000	H	-2.91838200	2.63649900	1.46327400
H	-2.94517500	-2.32557100	-1.67769900	H	0.02378300	1.20199600	3.09641800
C	-4.68057200	-0.08009100	0.95202500	H	-0.54596100	2.87593200	3.40561900
H	-2.74906100	0.10872600	1.87161200	H	-1.72184000	1.52383500	3.35854600
C	-5.42577100	-0.59543600	-0.11118000	N	4.67047100	0.50184500	-0.09976200
H	-5.34584500	-1.82311500	-1.88589700	C	5.79260600	-0.42106200	-0.08108200
H	-5.16335100	0.55155400	1.70127100	H	6.69660000	0.13852900	0.18907100
H	-6.49176300	-0.38127300	-0.19896800	H	5.65280200	-1.21017000	0.66504400
F	1.95522500	-3.30828200	0.50835200	H	5.95605100	-0.88785300	-1.06590100
H	1.52753600	-1.74720400	-1.88499700	C	4.98589900	1.88144400	-0.42378700
H	-1.01053100	-1.04515600	2.32552800	H	5.68387000	2.29425000	0.31921800
O	-0.83620100	1.65414100	-1.79940000	H	5.45773900	1.94329300	-1.41674300

H	4.06511500	2.46994700	-0.42408700	H	3.62320400	-1.63877800	1.24681500
C	3.38112400	0.11314800	0.03647700	H	3.68652300	-1.94448800	-0.48235700
C	3.15294400	-1.36666000	0.28801100				

## Int6



Electronic Energy (EE): - 1320.807040 Hartree

EE + Zero-point Energy: - 1320.344574 Hartree

EE + Thermal Free Energy Correction: - 1320.411536 Hartree

Na	3.05286800	0.99713700	0.93888300	H	5.05603200	3.80345800	-1.11296100
F	2.57202100	0.43531600	2.84274900	C	4.04123100	1.56647400	-2.11070800
C	-0.07844200	-1.31464100	0.83936600	H	5.08503900	1.72131100	-2.43412600
C	-1.15486300	-1.50274300	1.71554300	H	3.84209100	0.49366600	-2.00313900
C	-0.33169400	-0.69198500	-0.38803800	H	3.36907100	1.99144600	-2.87713100
C	-2.43684700	-1.07504000	1.38389800	C	0.51816300	2.72259600	-0.47291000
H	-0.98312900	-1.99366500	2.67617200	H	1.23565100	2.66253100	-1.30195500
C	-1.61712400	-0.27394200	-0.72687000	H	-0.45018700	2.30211000	-0.79767300
H	0.48930300	-0.50675600	-1.08481600	H	0.36584100	3.78324600	-0.20227300
C	-2.69298400	-0.45079700	0.15387100	C	0.19169600	1.93847000	1.72414900
H	-3.25768400	-1.25076400	2.08184700	H	0.73303500	1.35243700	2.47975100
H	-1.78147300	0.22397100	-1.68483300	H	-0.01928600	2.95565400	2.10189600
C	-4.06071600	0.00760600	-0.20288400	H	-0.76493200	1.45234500	1.45906100
C	-4.52641900	-0.07400100	-1.52393900	C	2.25272000	-1.87618300	0.07634400
C	-4.91804300	0.53478500	0.77483400	C	1.31220500	-1.74085800	1.25700700
C	-5.80896600	0.35789500	-1.85699300	H	1.25456400	-2.68210800	1.82177700
H	-3.88364700	-0.50156000	-2.29574400	H	1.74879400	-0.97198600	1.93289200
C	-6.20090300	0.96604200	0.44246900	O	3.01277300	-0.94922100	-0.22450200
H	-4.56701500	0.62815800	1.80430200	N	2.20995600	-3.01494900	-0.64869500
C	-6.65182300	0.87949000	-0.87507000	C	3.13708800	-3.21488500	-1.74710800
H	-6.15473000	0.27864900	-2.88893300	H	3.61438200	-4.20104000	-1.65139100
H	-6.84920800	1.37951600	1.21667900	H	2.61109100	-3.17512500	-2.71399700
H	-7.65603900	1.21701700	-1.13554100	H	3.90342500	-2.43538200	-1.72059000
O	1.04558800	1.99643200	0.60127800	C	1.28999400	-4.10904300	-0.39292700
O	3.80925400	2.16387400	-0.85764400	H	0.98739000	-4.54470400	-1.35488600
C	4.01160200	3.55454500	-0.85793200	H	1.76059800	-4.90065900	0.21193900
H	3.34369100	4.05163700	-1.58318900	H	0.38410900	-3.75725200	0.11133600
H	3.78762700	3.93076400	0.14826100				



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- [6] GaussView, Version 6.1, R. Dennington, T. A. Keith, J. M. Millam, Semichem Inc., Shawnee Mission, KS, 2016.

## 6. X-ray Crystallographic Data

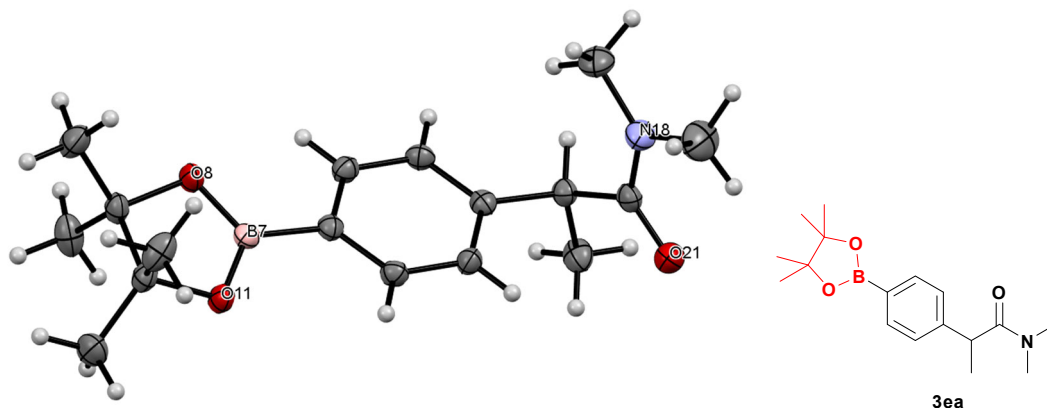


Figure S3. ORTEP plots of 3ea with thermal ellipsoids drawn at 50% probability level.

Table S1. Crystal data and structure refinement for 3ea

Identification code	3ea
Empirical formula	C <sub>17</sub> H <sub>26</sub> BNO <sub>3</sub>
Formula weight	303.20
Temperature/K	123
Crystal system	triclinic
Space group	P-1
a/Å	6.4832(3)
b/Å	11.8496(6)
c/Å	11.9710(5)
α/°	70.722(4)
β/°	85.965(4)
γ/°	89.751(4)
Volume/Å <sup>3</sup>	865.76(7)
Z	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.163
μ/mm <sup>-1</sup>	0.077
F (000)	328.0
Crystal size/mm <sup>3</sup>	0.259 × 0.203 × 0.147

Radiation	Mo K $\alpha$ ( $\lambda = 0.71073$ )
2 $\theta$ range for data collection/ $^{\circ}$	3.642 to 61.328
Index ranges	$-8 \leq h \leq 9$ , $-14 \leq k \leq 16$ , $-17 \leq l \leq 15$
Reflections collected	12100
Independent reflections	4253 [ $R_{\text{int}} = 0.0467$ , $R_{\text{sigma}} = 0.0567$ ]
Data/restraints/parameters	4253/0/206
Goodness-of-fit on $F^2$	1.053
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0544$ , $wR_2 = 0.1331$
Final R indexes [all data]	$R_1 = 0.0812$ , $wR_2 = 0.1454$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.33/-0.21

#### Experimental

Single crystals of  $C_{17}H_{26}BNO_3$  3ea were CCDC-2183954. A suitable crystal was selected and CCDC-2183954 on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Mo-K $\alpha$  radiation. The crystal was kept at 123 K during data collection. Using Olex2<sup>[7]</sup>, the structure was solved with the SHELXT<sup>[8]</sup> structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation.

[7] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K. & Puschmann, H., *J. Appl. Cryst.*, 2009, 42, 339.

[8] Sheldrick, G.M., *Acta Cryst.*, 2015, A71, 3.

## 7. ICP Analysis of Starting Materials and Product

ICP-AES (Inductively Coupled Plasma Emission Spectrometry) of NaHMDS

A sample was prepared by dissolving NaHMDS (1.0 g) neutralized with hydrochloric acid (5.0 mL) in pure water (1 or 5 wt%). An analysis was conducted on ICPS-8100(SHIMADZU). The Contents of Elements are shown in Table S2 and S3.

Table S2. 1wt% NaHMDS aq.

Order	Contents of NaHMDS
< 100 ppm	Na, Si
< 1 ppm	K
< 0.1 ppm	B, Al
0.1 ppm <	Mg, Ca, Fe, Zn, Sr, Ba

Table S3. 5wt% NaHMDS aq.

Order	Contents of NaHMDS
< 100 ppm	Na, Si
< 1 ppm	B, K
< 0.1 ppm	Al, Ca, Ba
0.1 ppm <	Mg, Fe, Zn, Sr

ICP-AES (Inductively Coupled Plasma Emission Spectrometry) of **1a**

A sample was prepared by dissolving **1a** (0.35 g) in EtOH (3.5 wt%). An analysis was conducted on ICPS-8100(SHIMADZU). The Contents of Elements are shown in Table S4.

Table S4. 3.5wt% **1a** aq.

Order	Contents of <b>1a</b>
< 1 ppm	-
< 0.1 ppm	Na, Si
0.1 ppm <	B, Mg, Ca, Cu, Zn

ICP-AES (Inductively Coupled Plasma Emission Spectrometry) of **2a**

A sample was prepared by dissolving **2a** (0.7 g) in EtOH (3.5 wt%). An analysis was conducted on ICPS-8100(SHIMADZU). The Contents of Elements are shown in Table S5.

Table S5. 3.5wt% **2a** aq.

Order	Contents of <b>2a</b>
< 1 ppm	-
< 0.1 ppm	Na, Si
0.1 ppm <	B, Mg, Ca, Cu, Zn

ICP-AES (Inductively Coupled Plasma Emission Spectrometry) of **3aa**

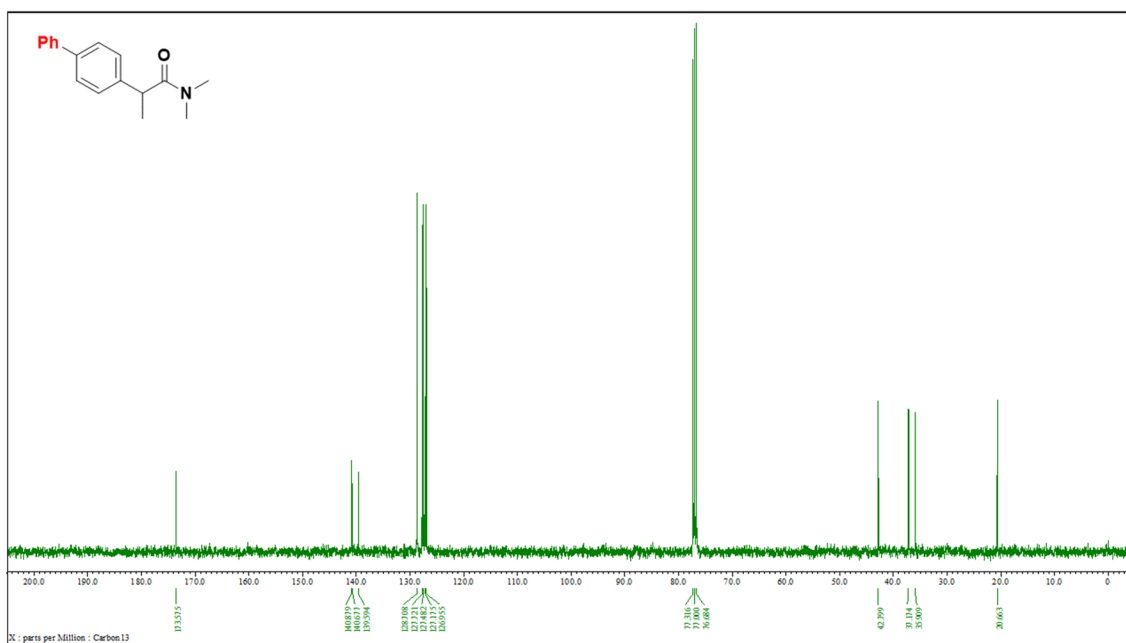
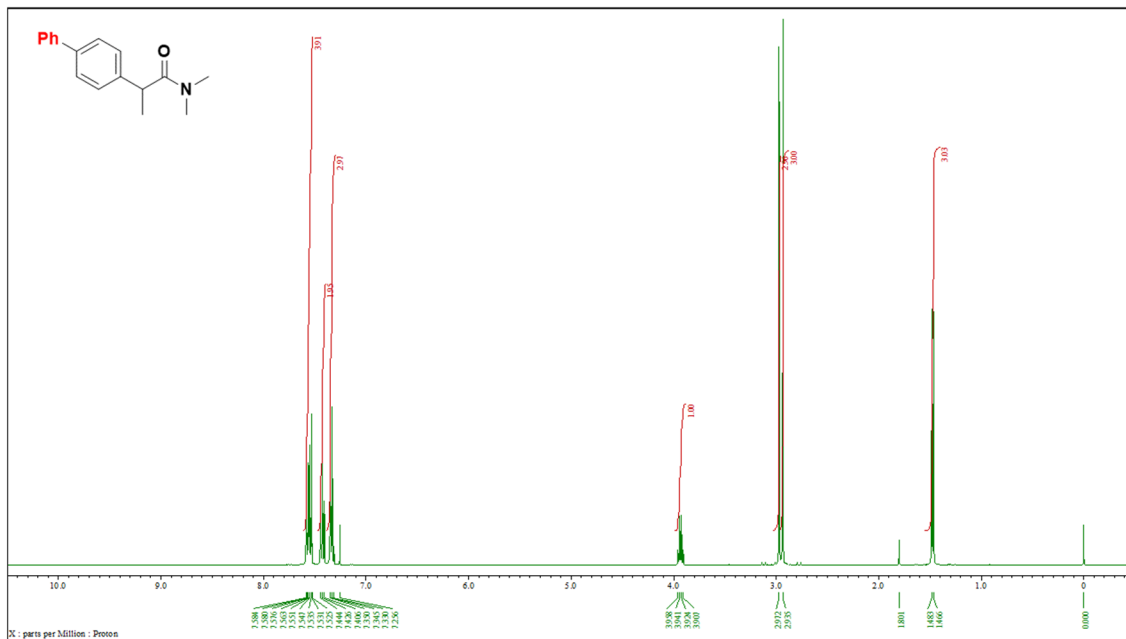
A sample was prepared by dissolving **3aa** (0.35 g) in EtOH (3.5 wt%). An analysis was conducted on ICPS-8100(SHIMADZU). The Contents of Elements are shown in Table S6.

Table S6. 3.5wt% **3aa** aq.

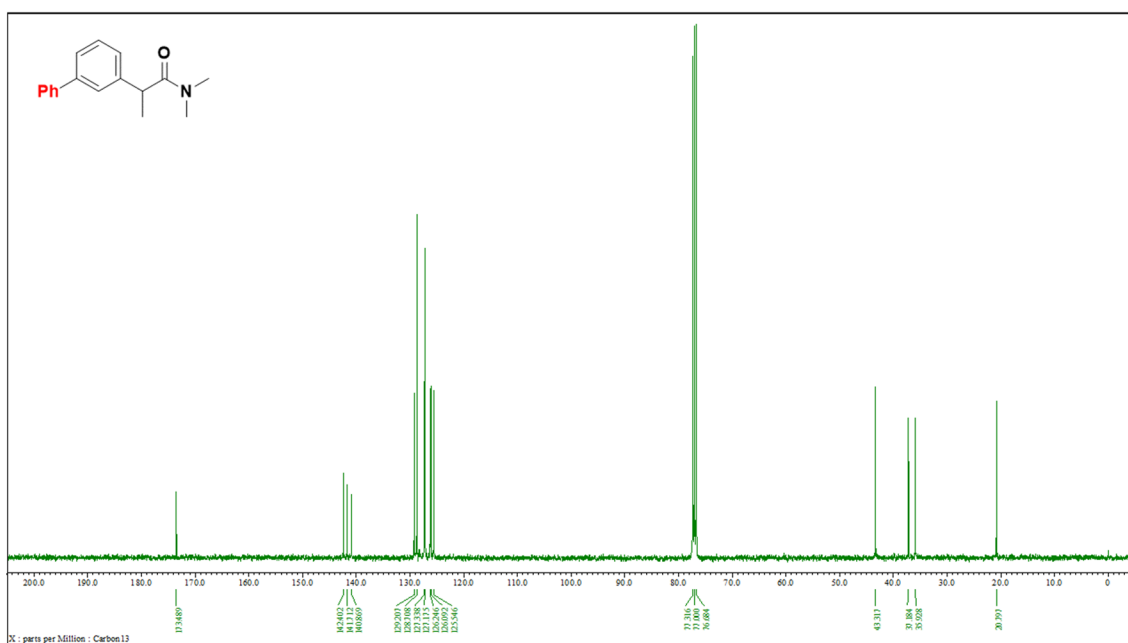
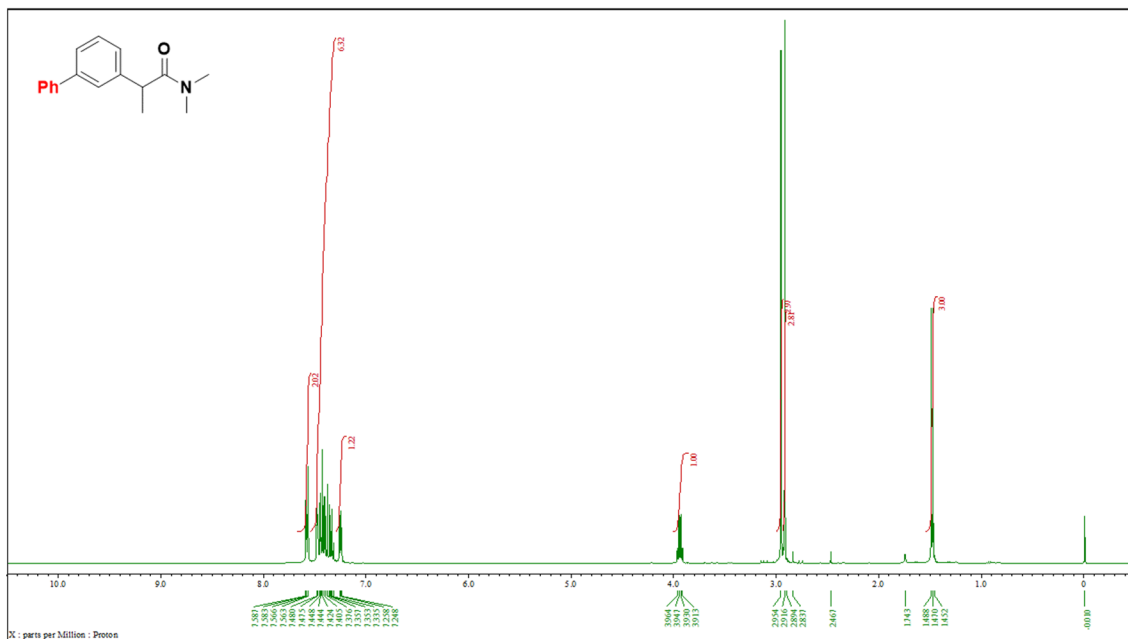
Order	Contents of <b>3aa</b>
< 10 ppm	-
< 1 ppm	Na, Si
< 0.1 ppm	B
0.1 ppm <	Mg, Ca, Cu, Zn

## 8. Copies of $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ NMR Spectra

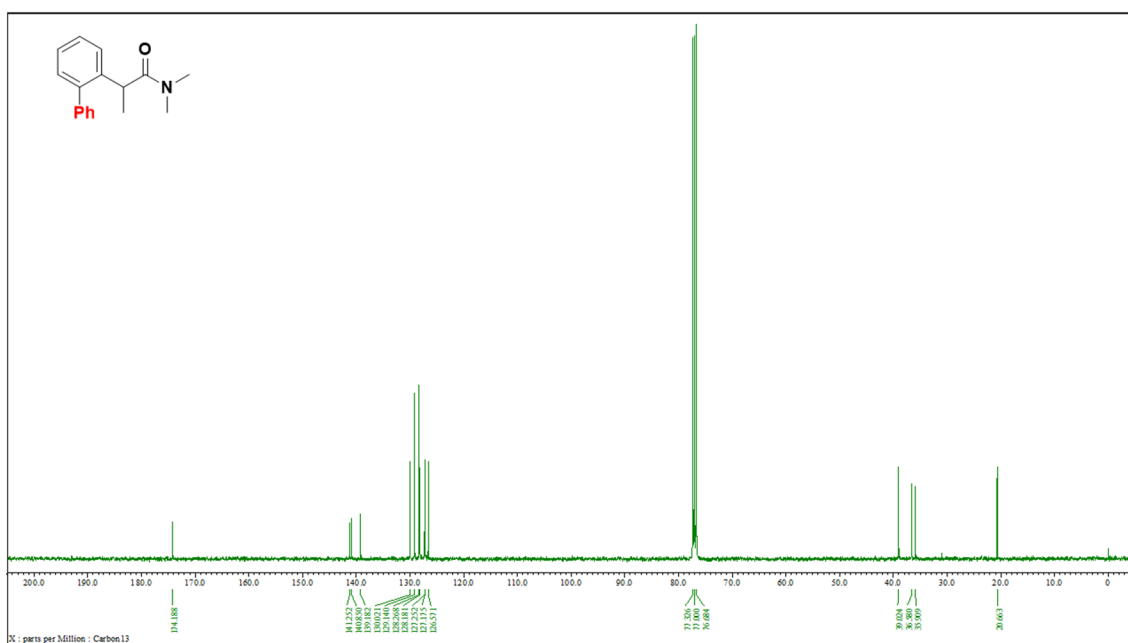
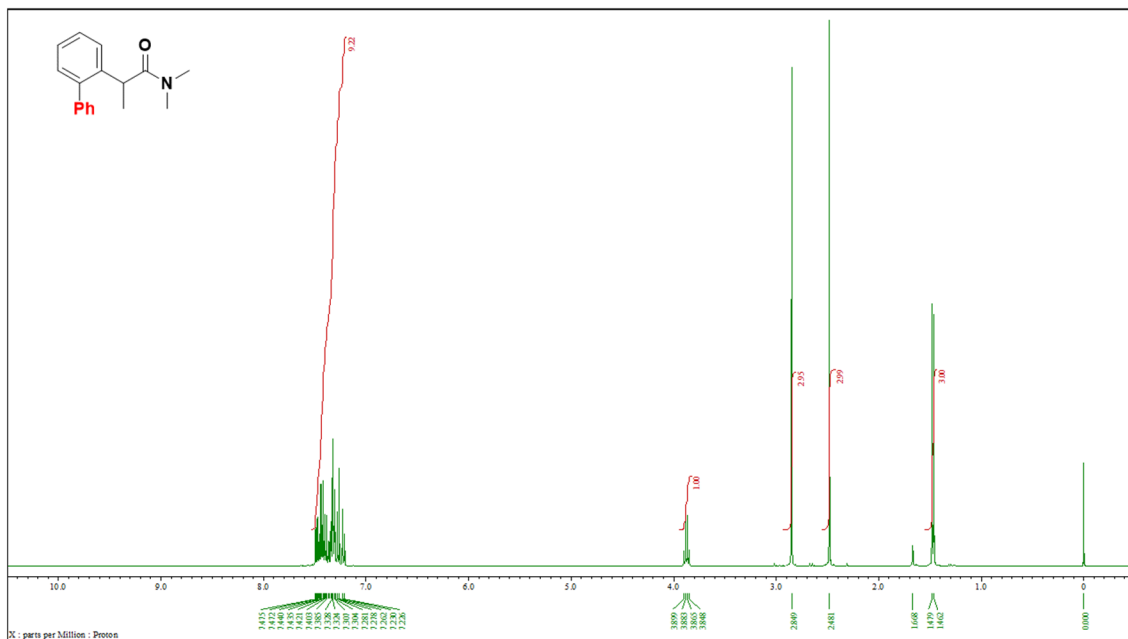
3aa



3ba

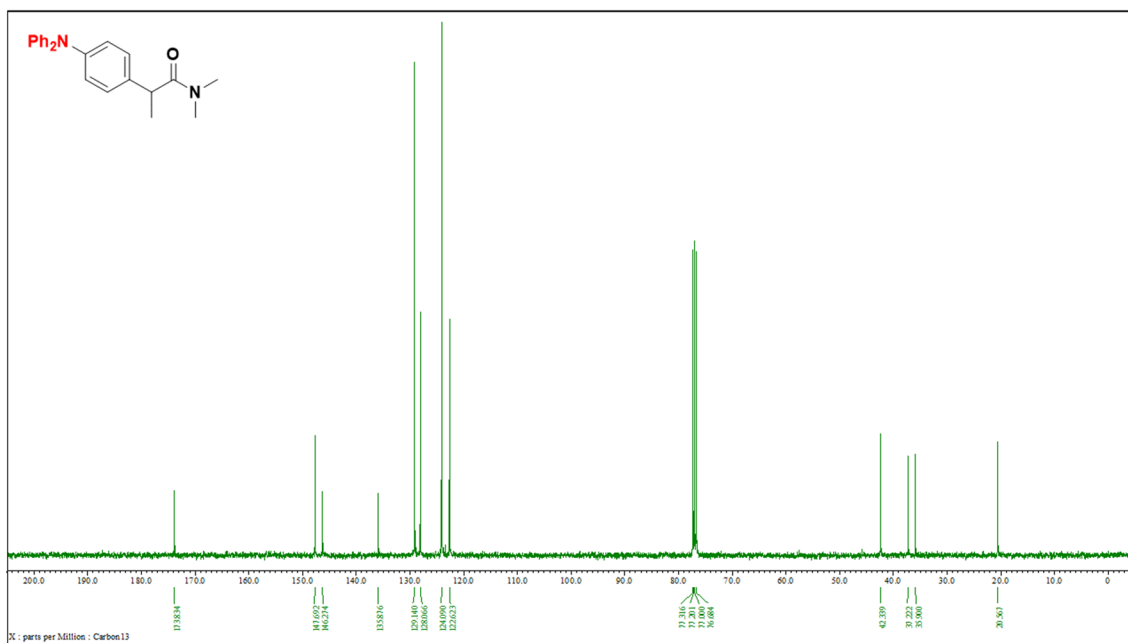
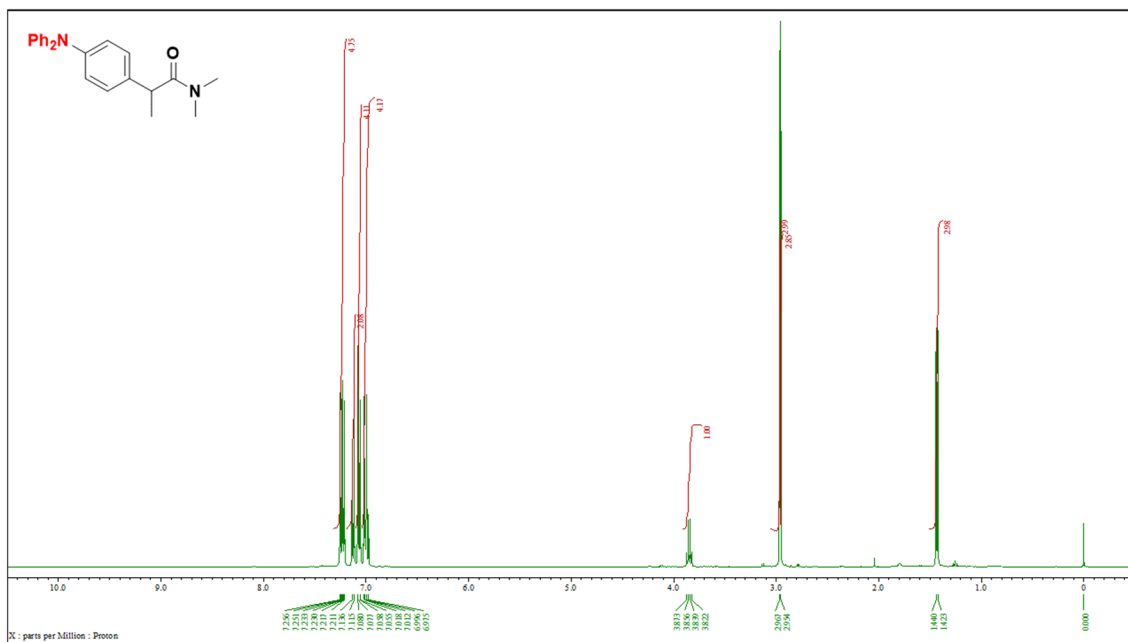


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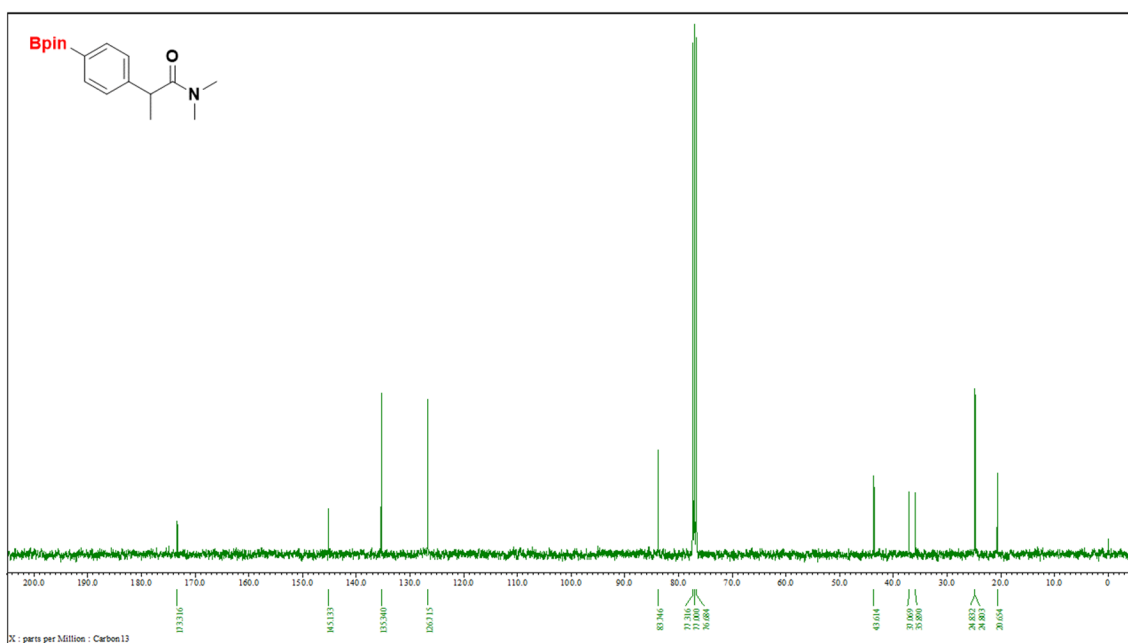
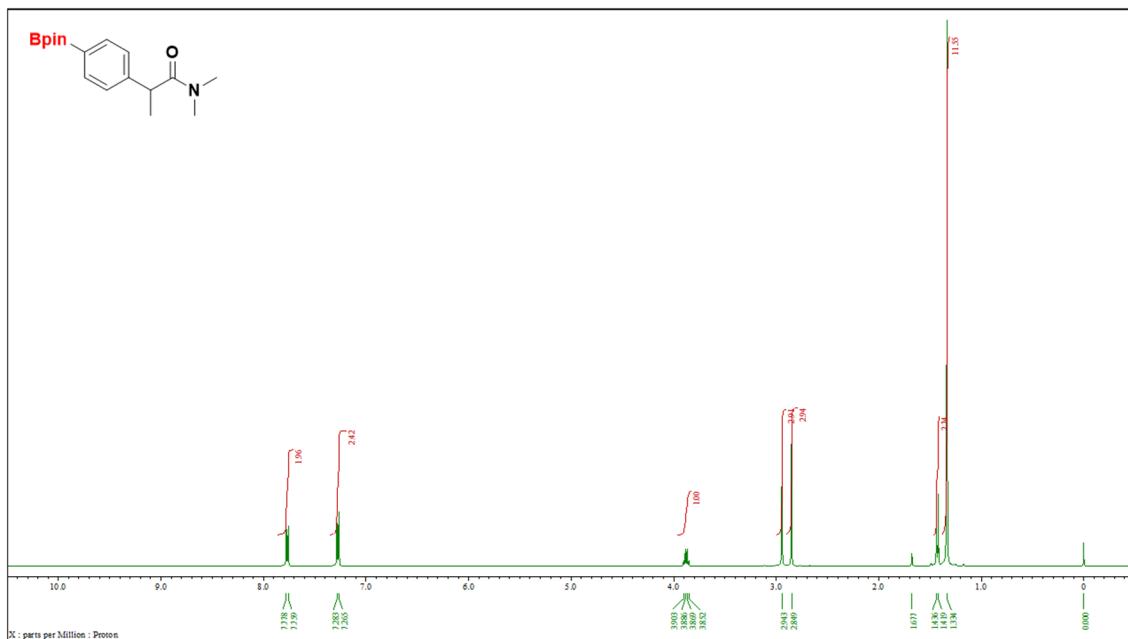




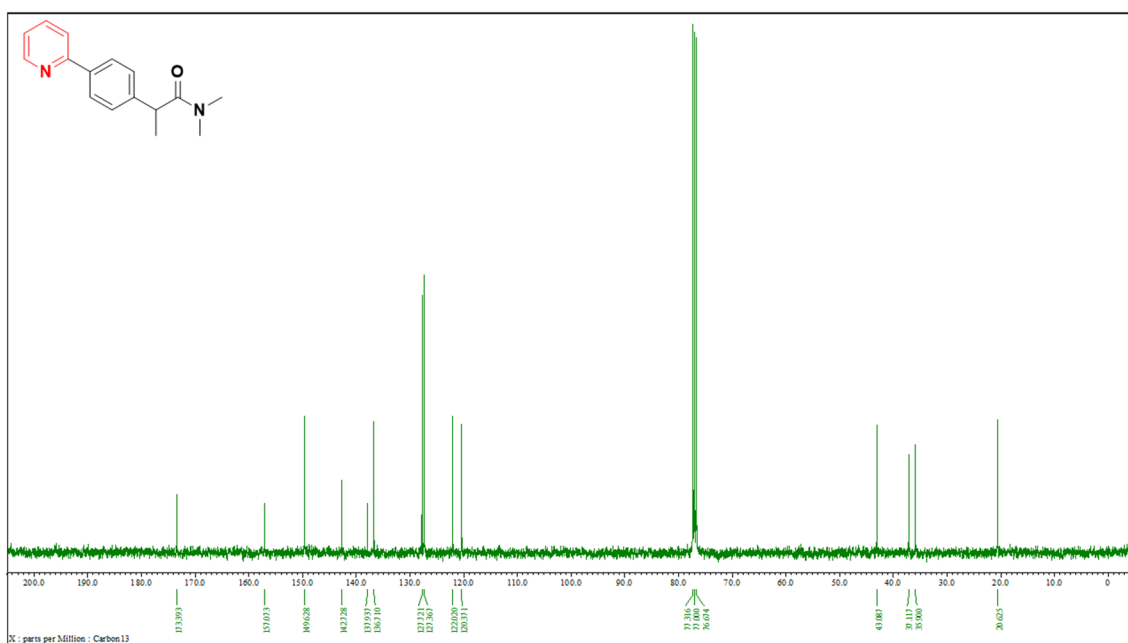
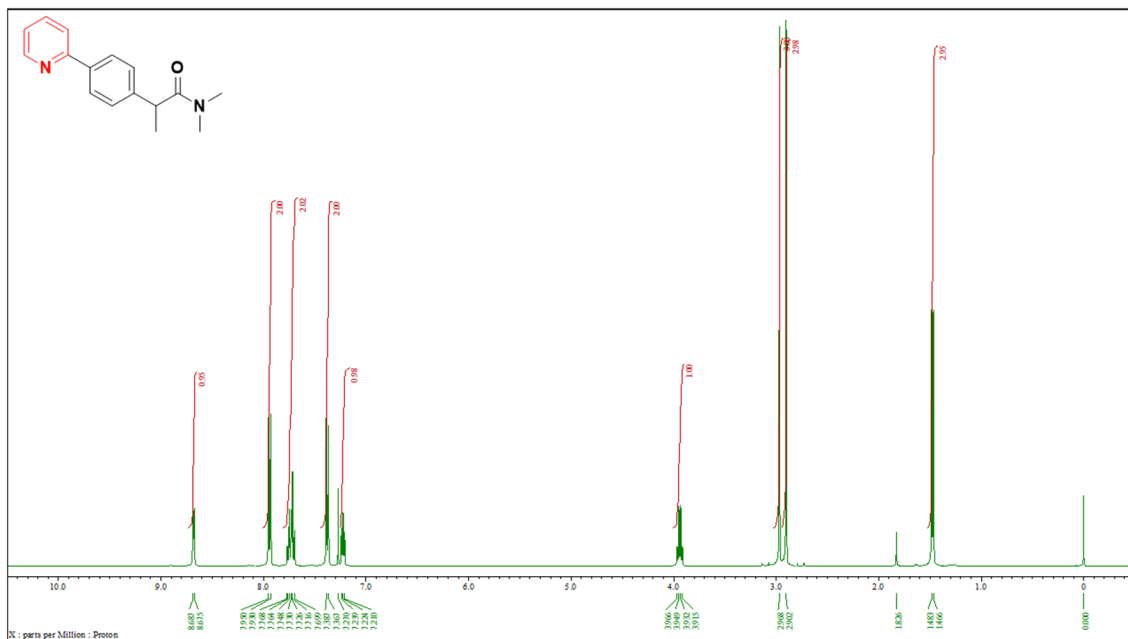
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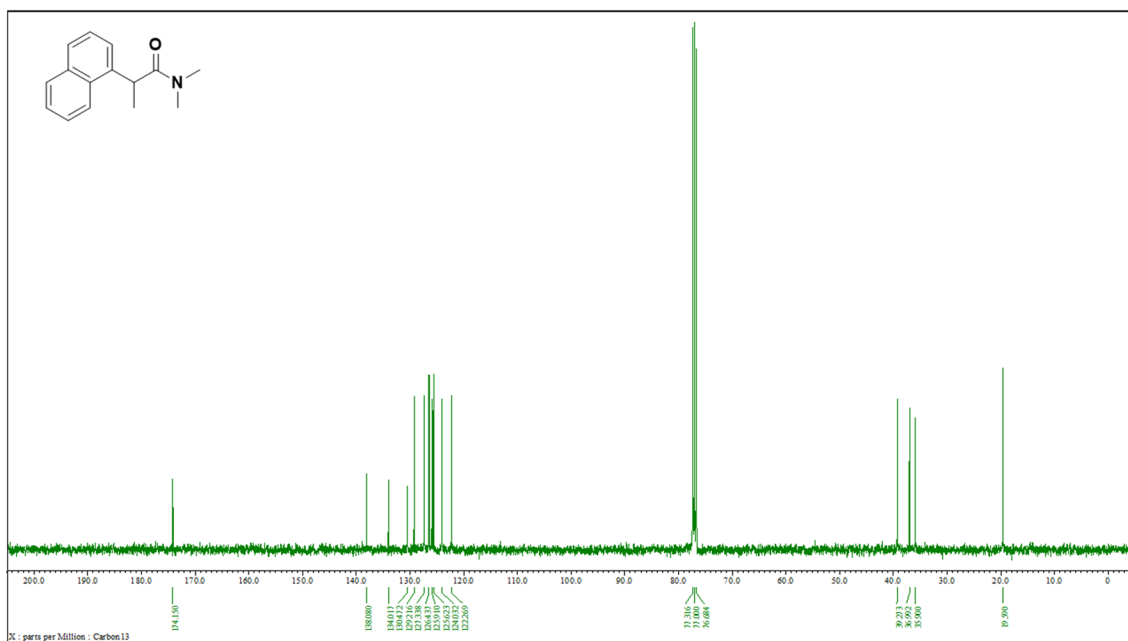
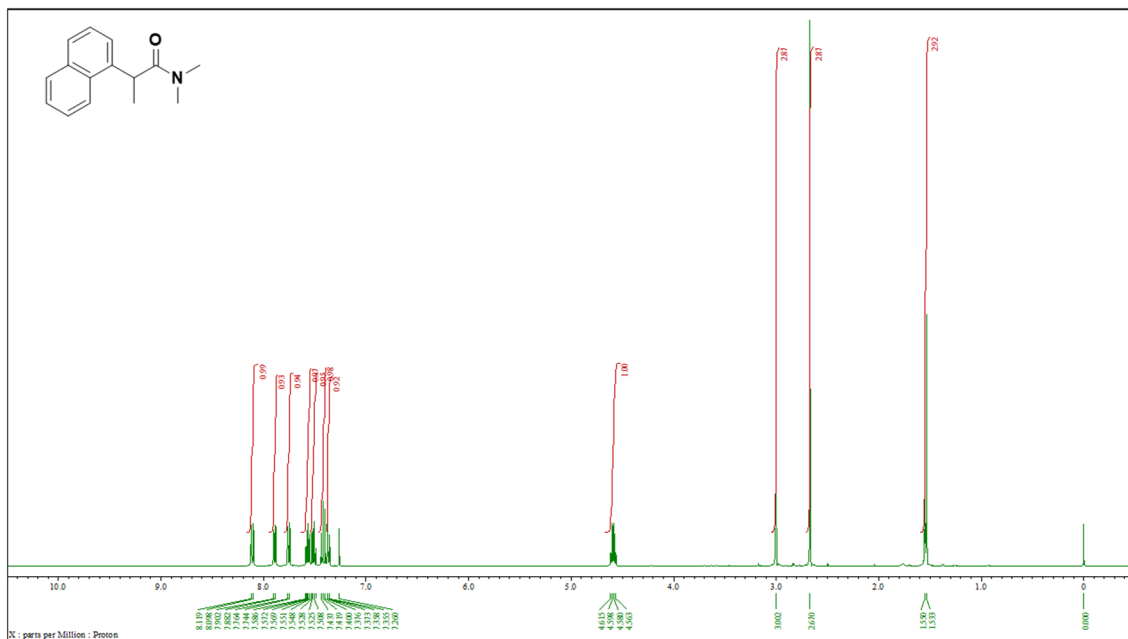
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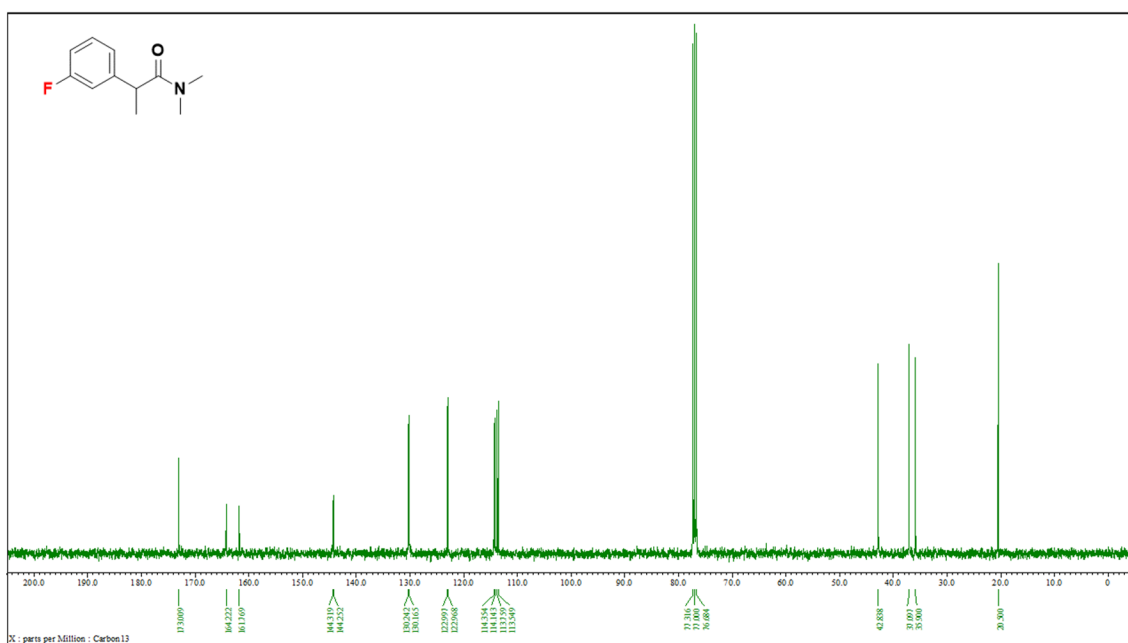
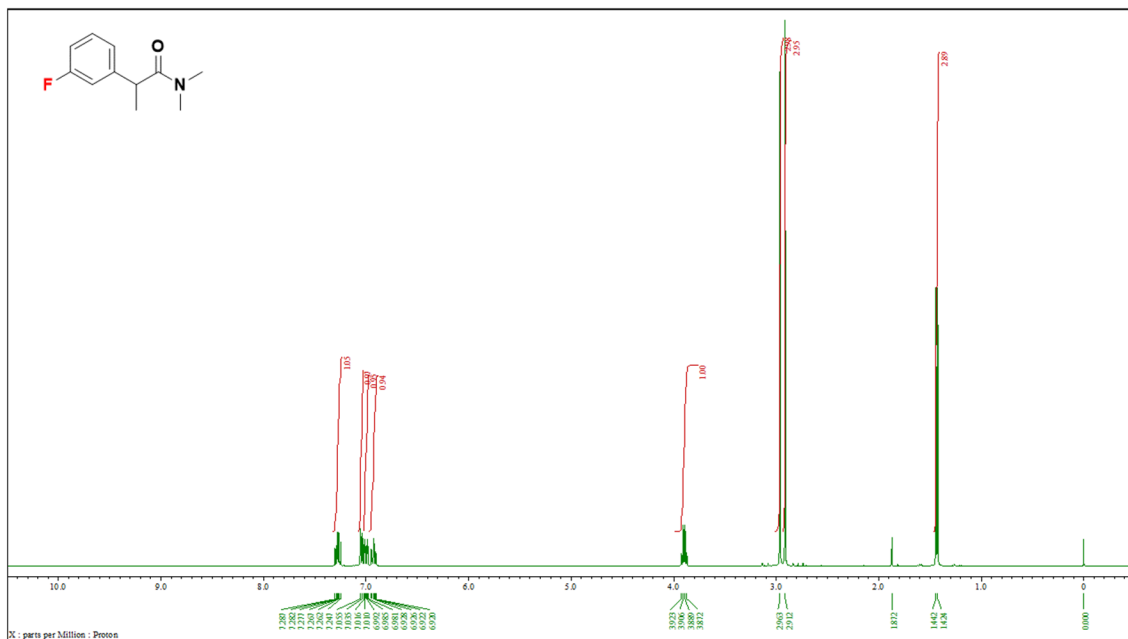
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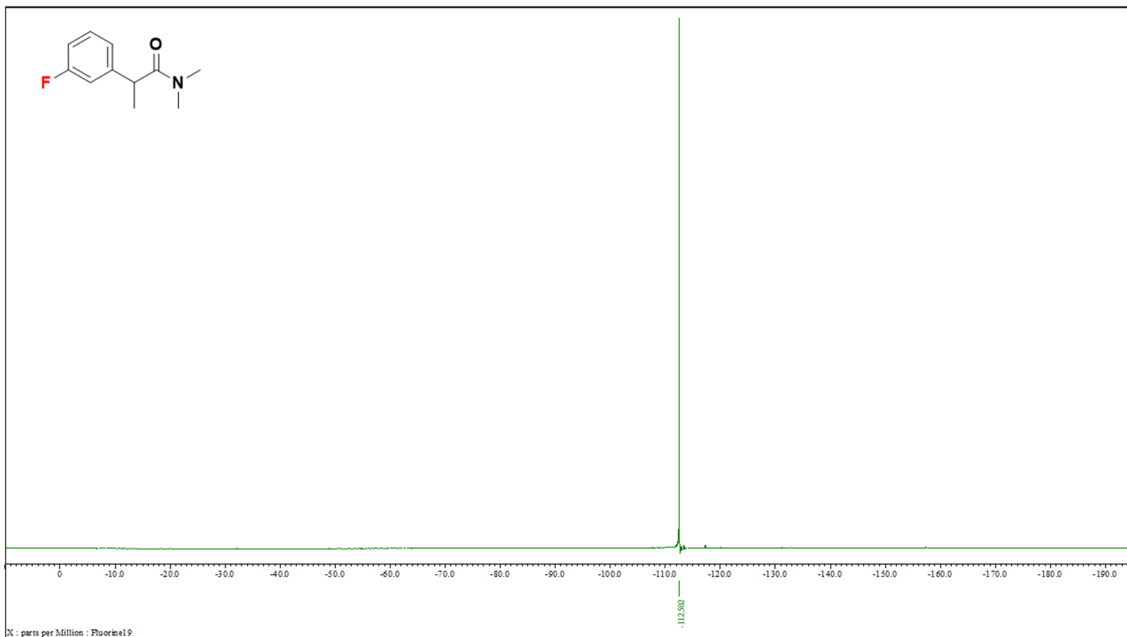


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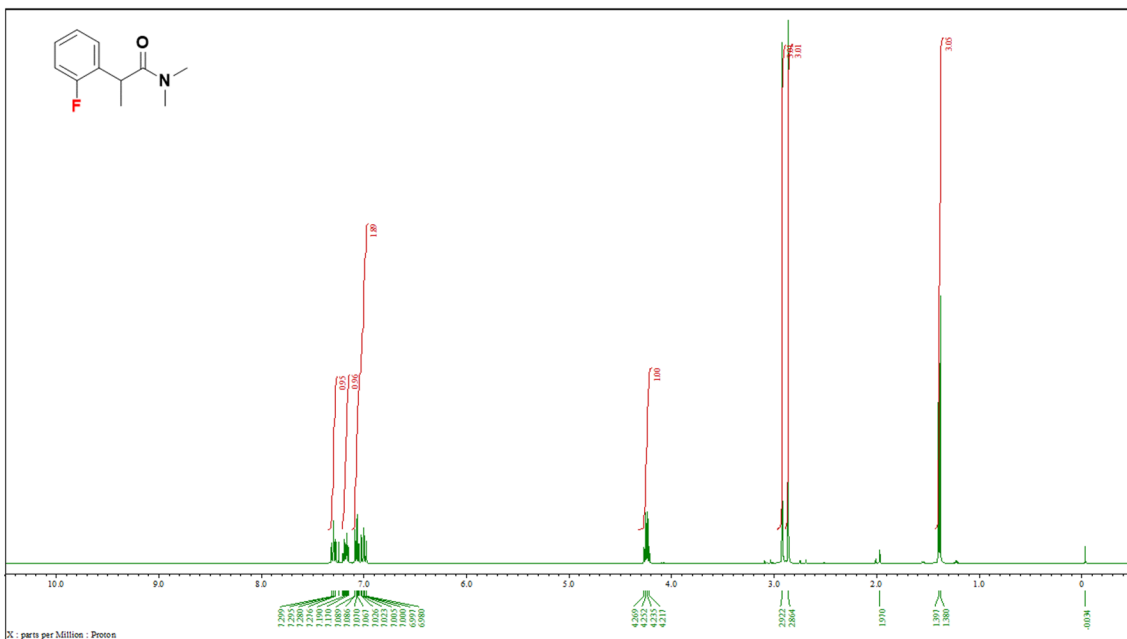


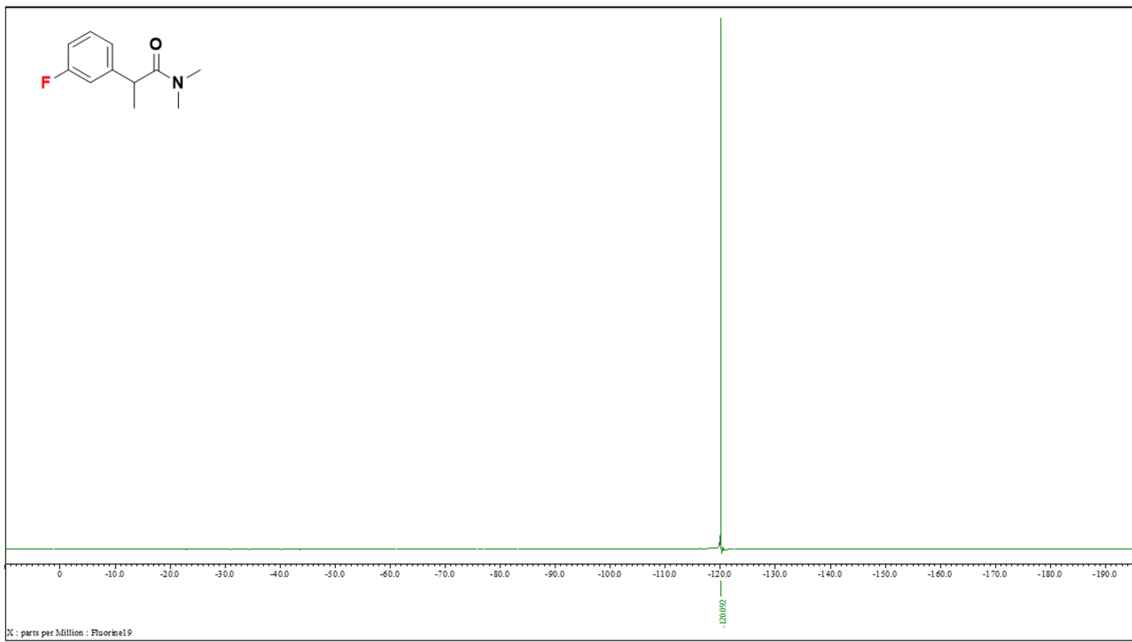
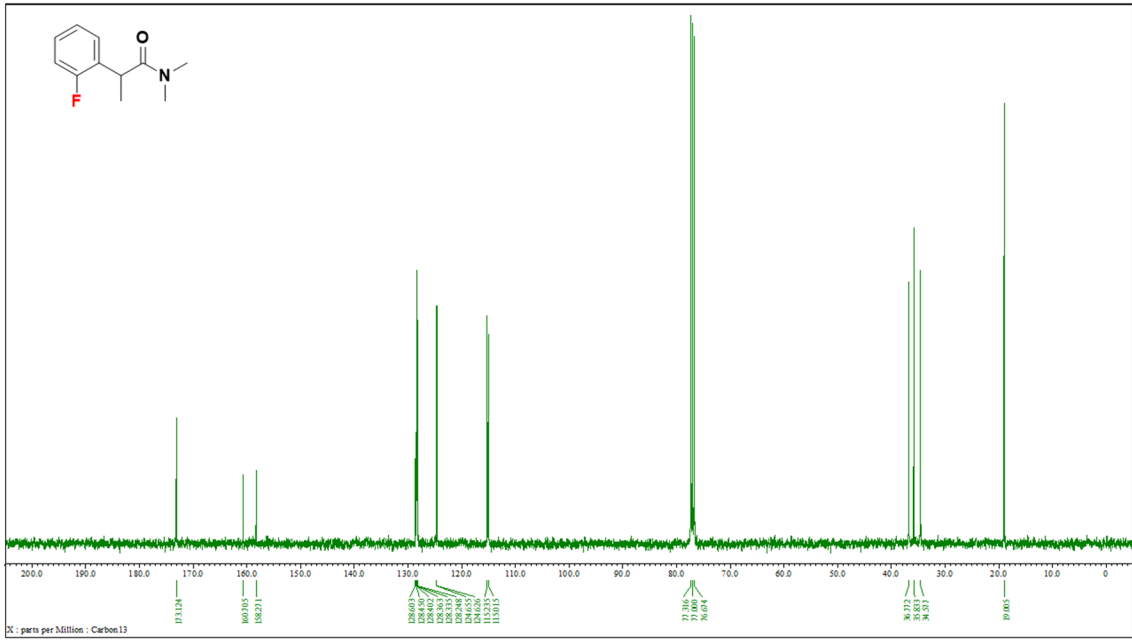
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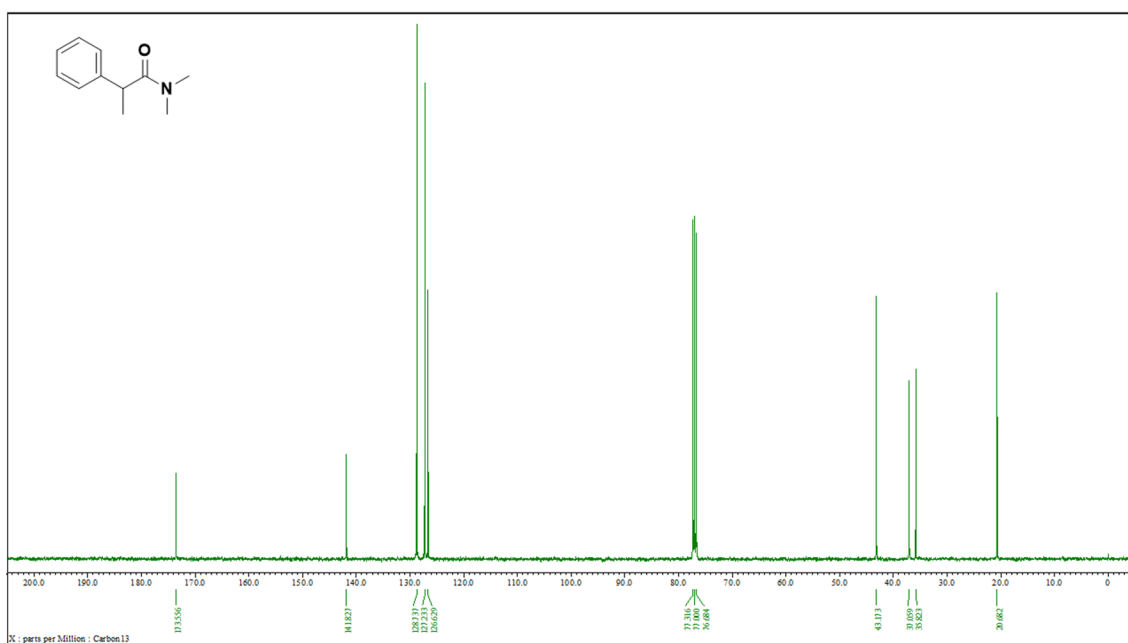
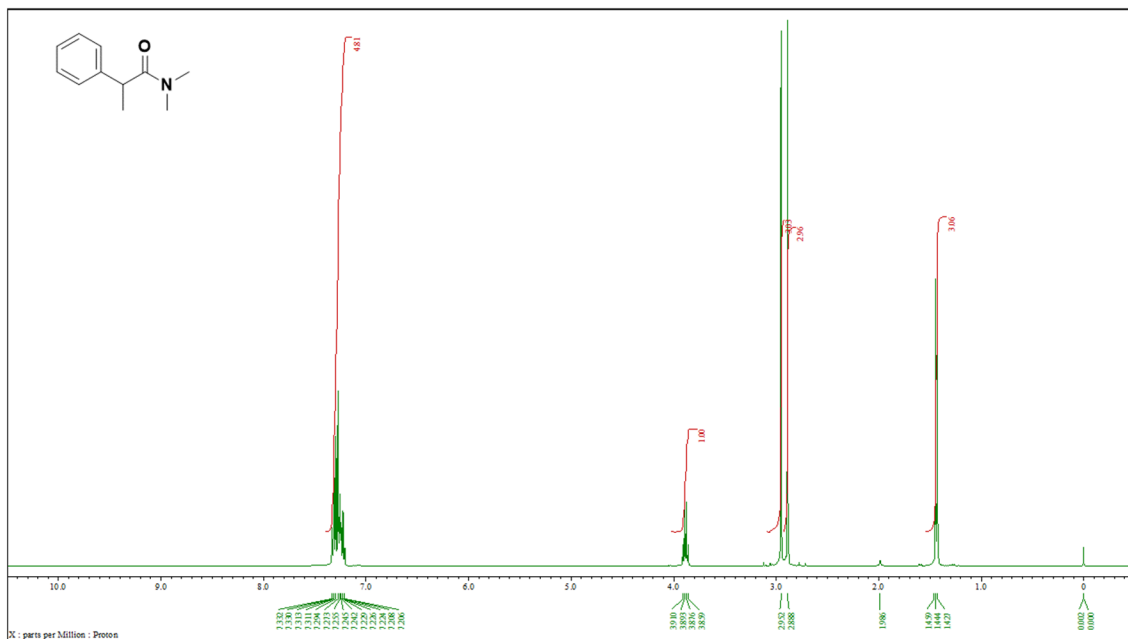


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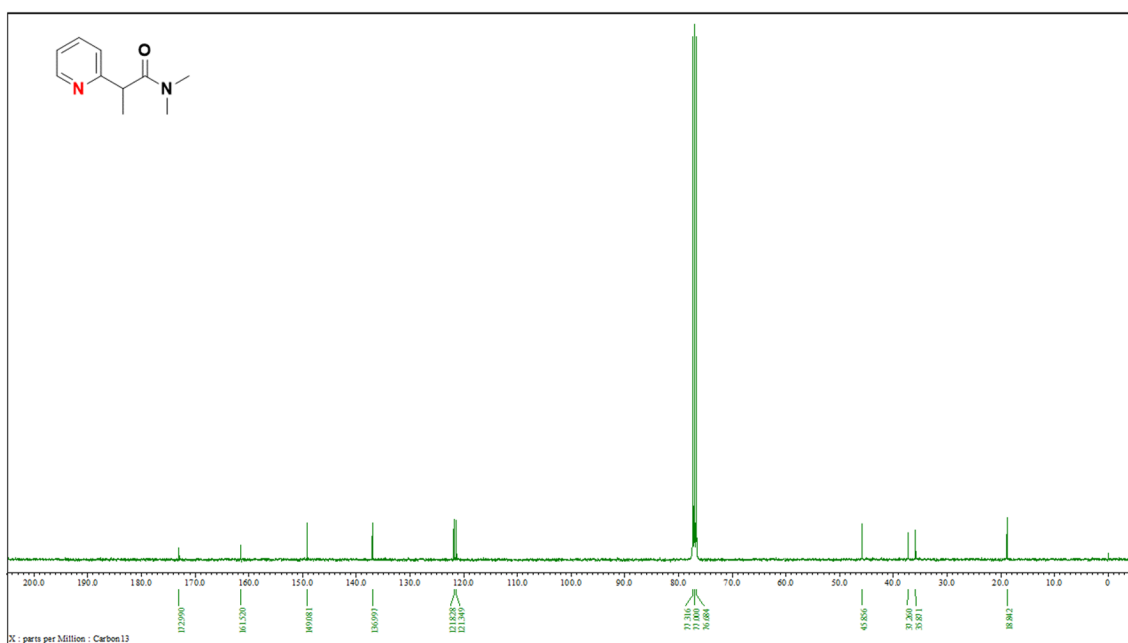
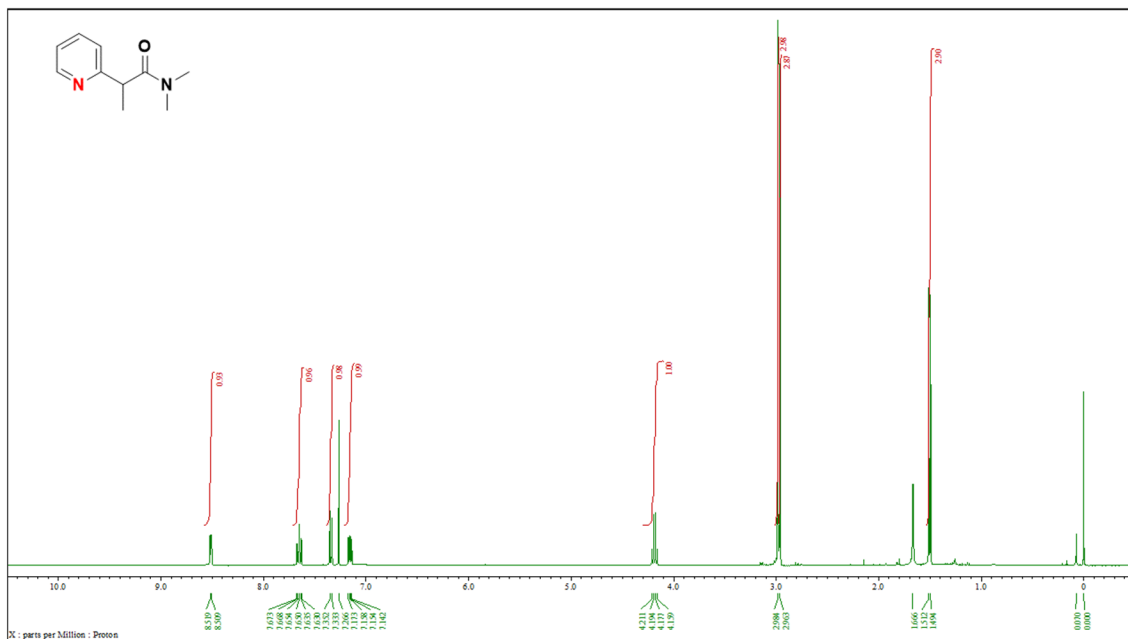


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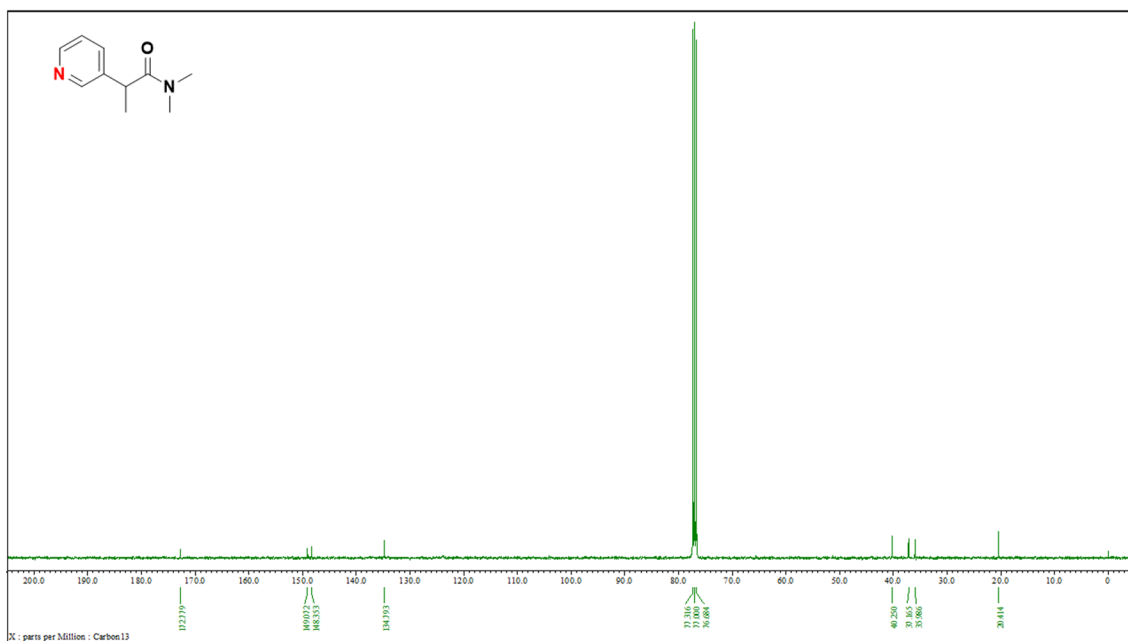
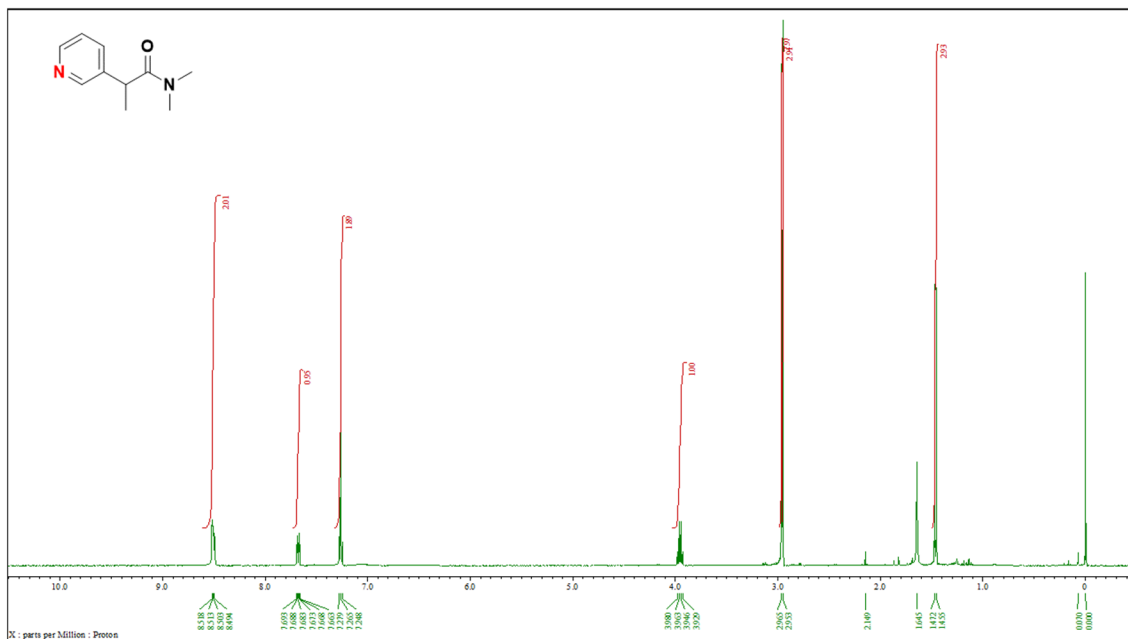




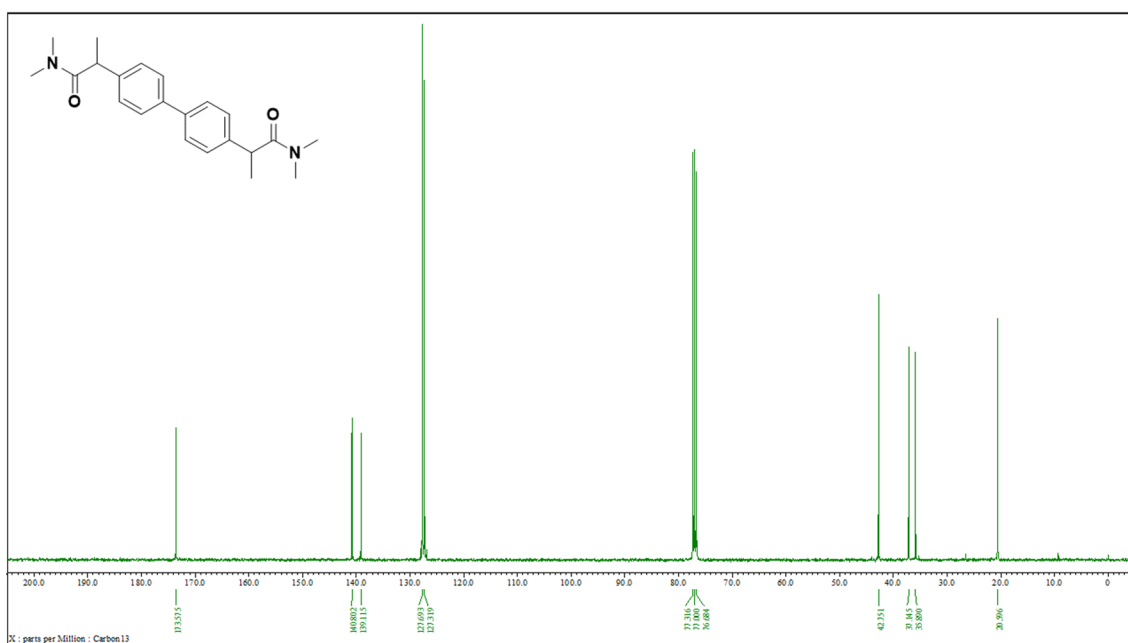
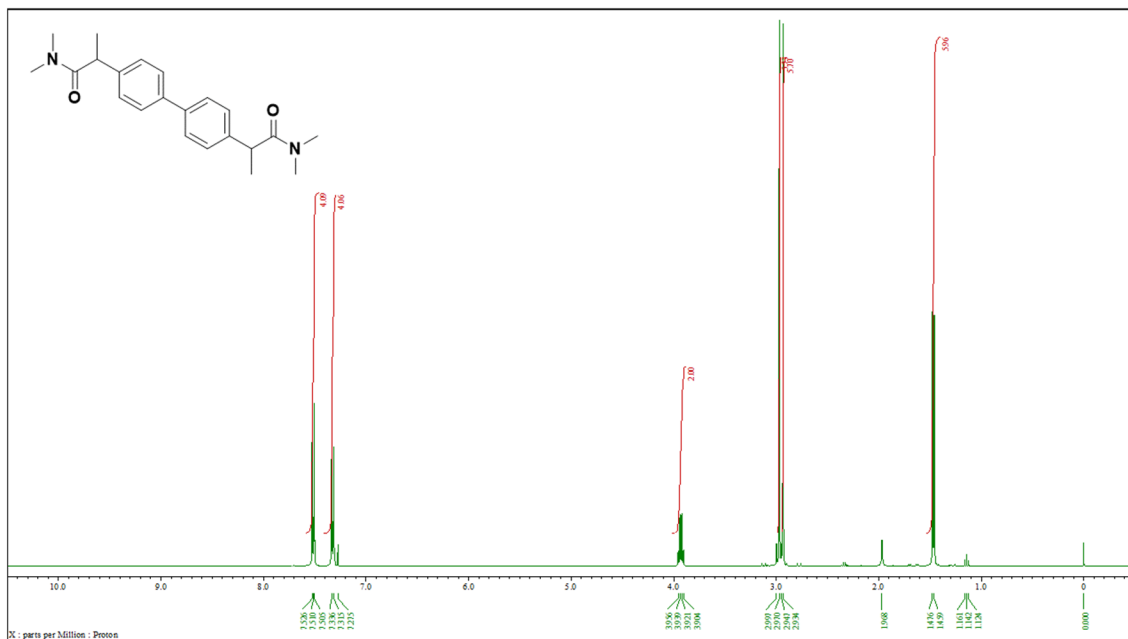
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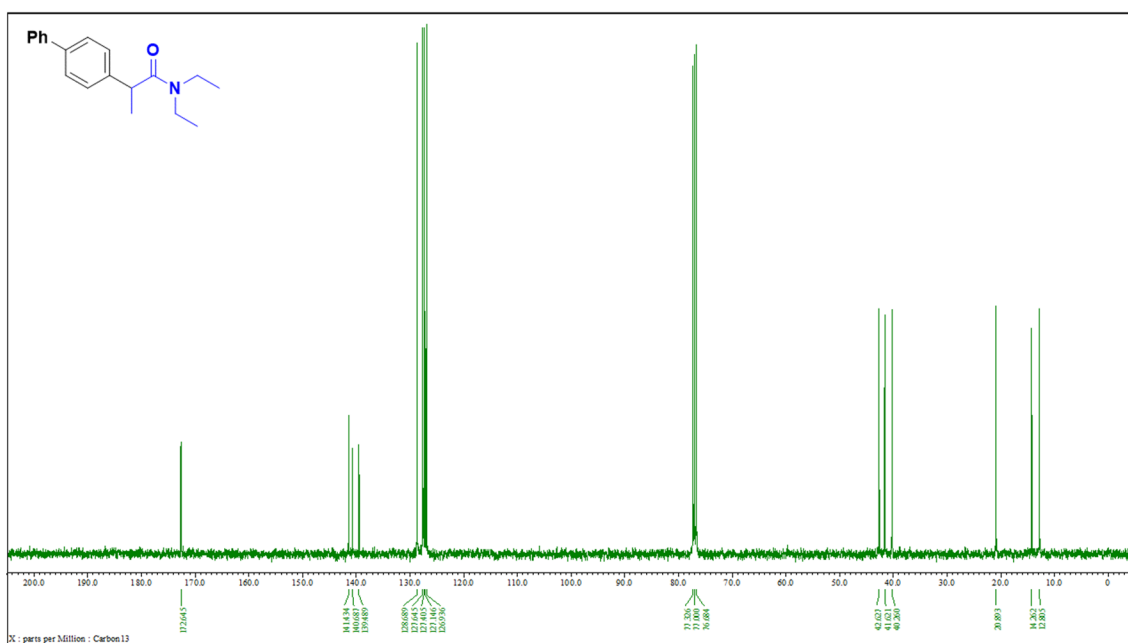
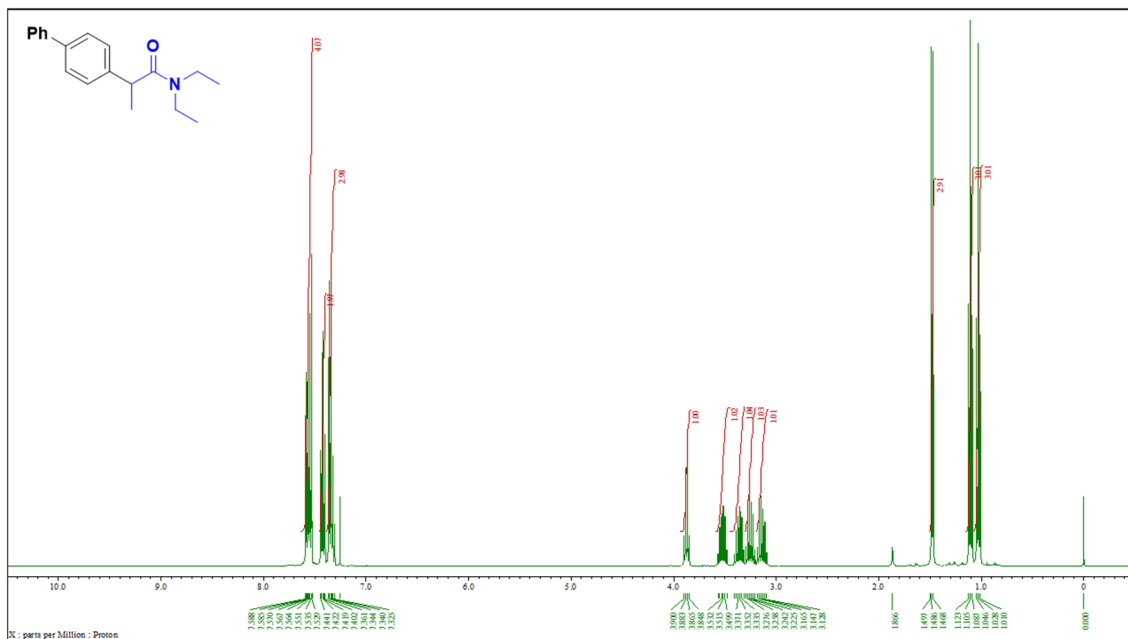
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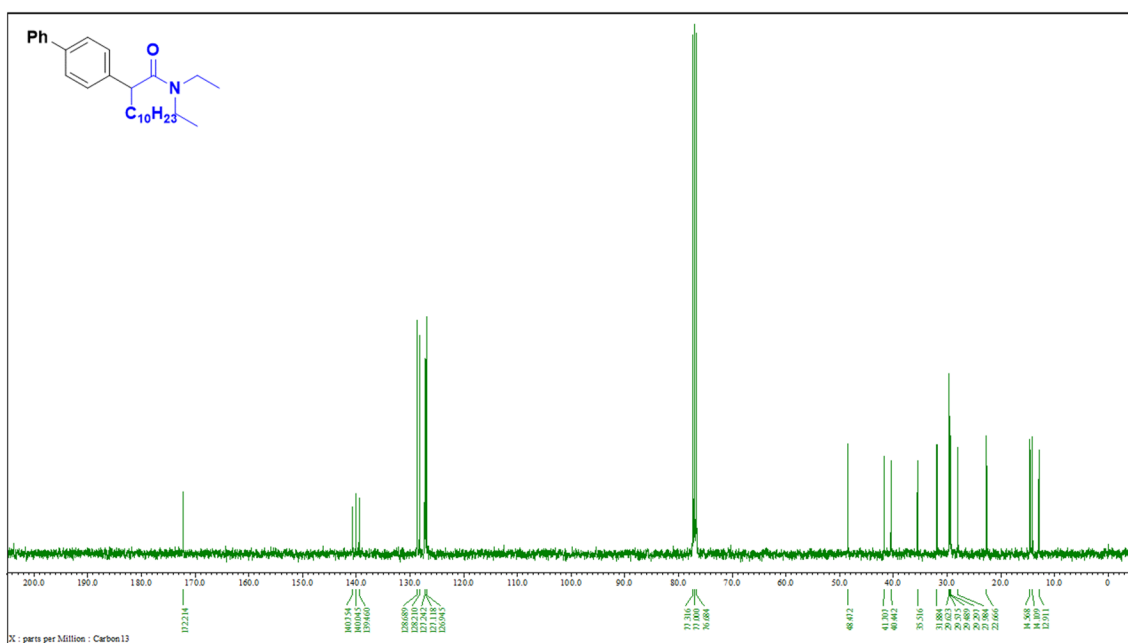
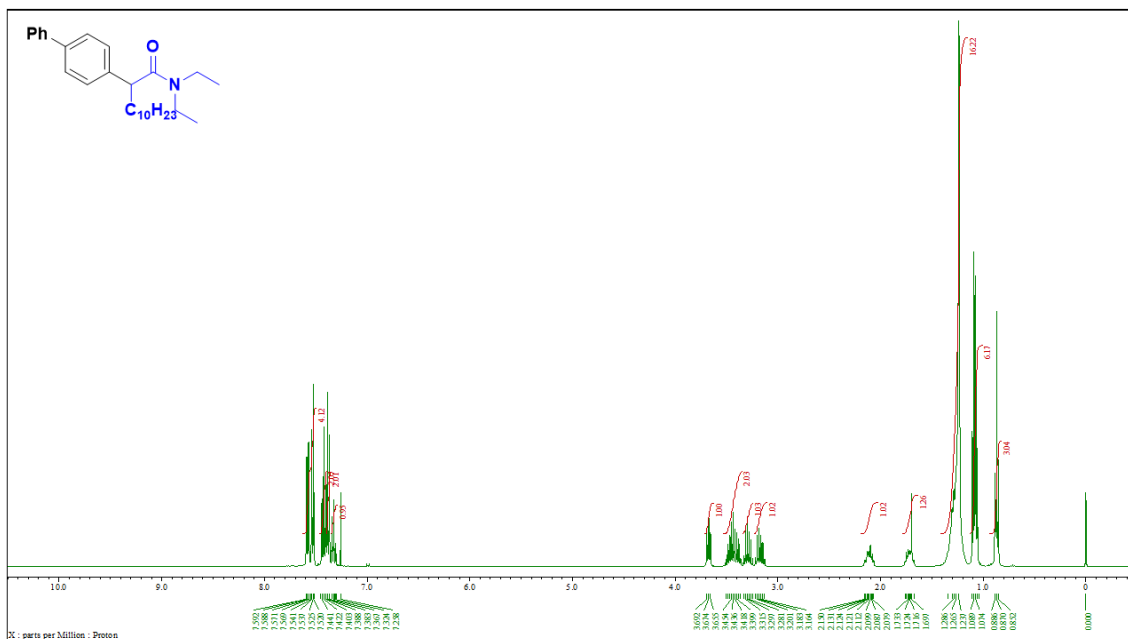
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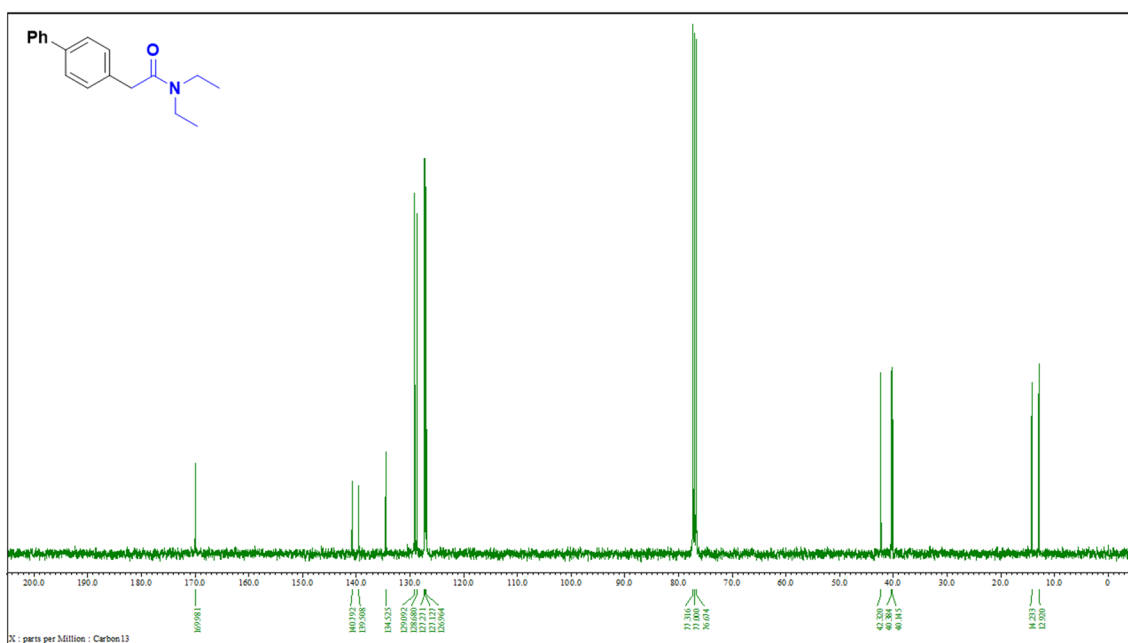
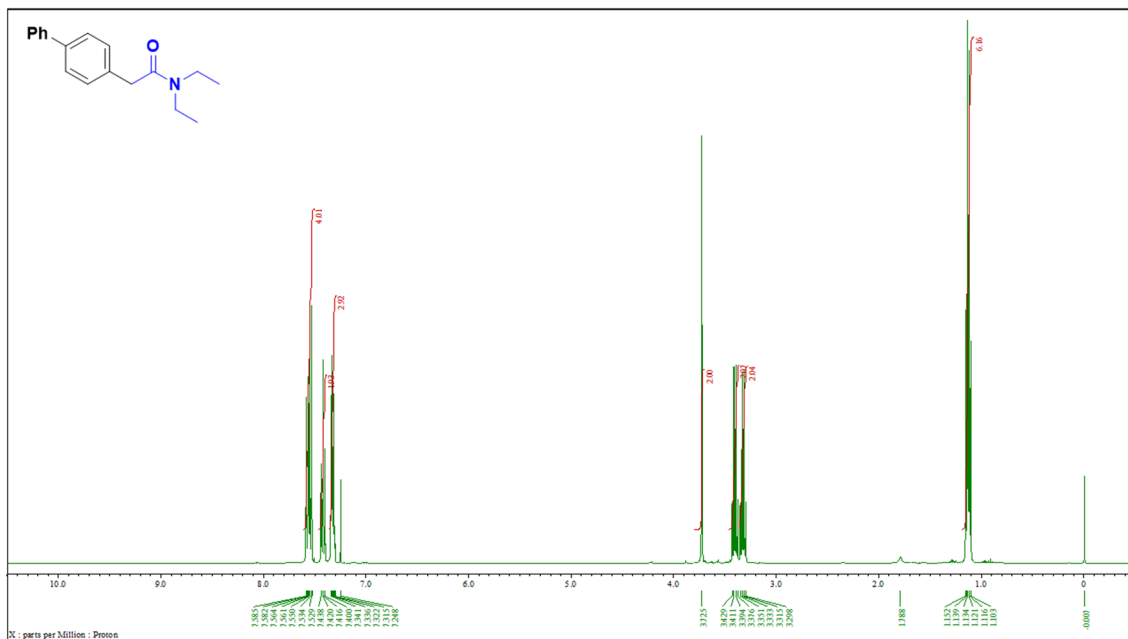


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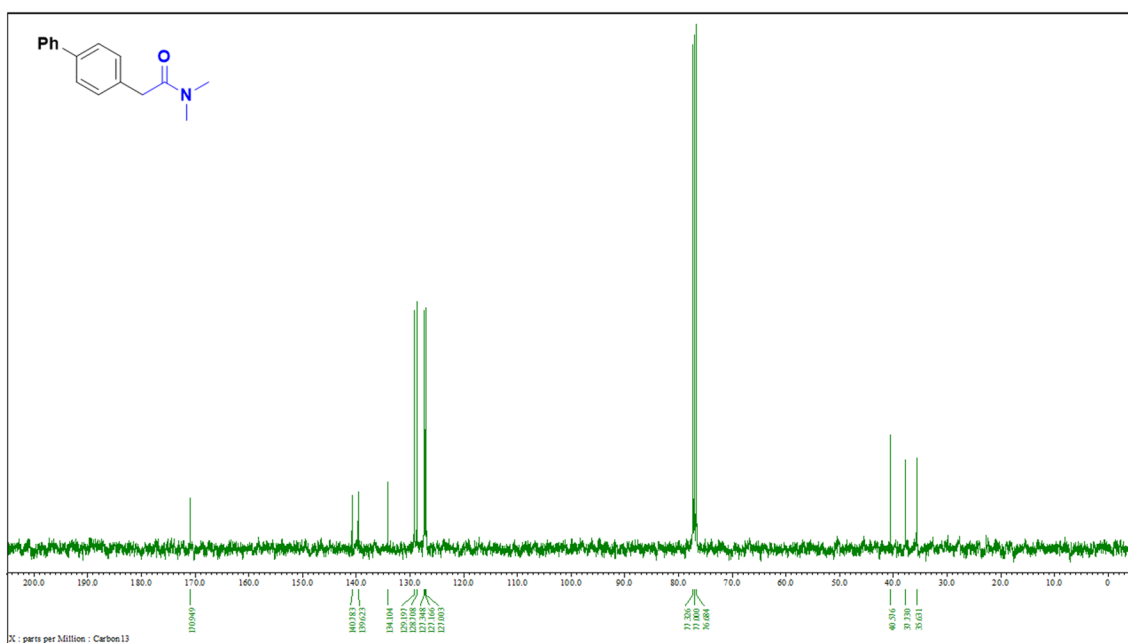
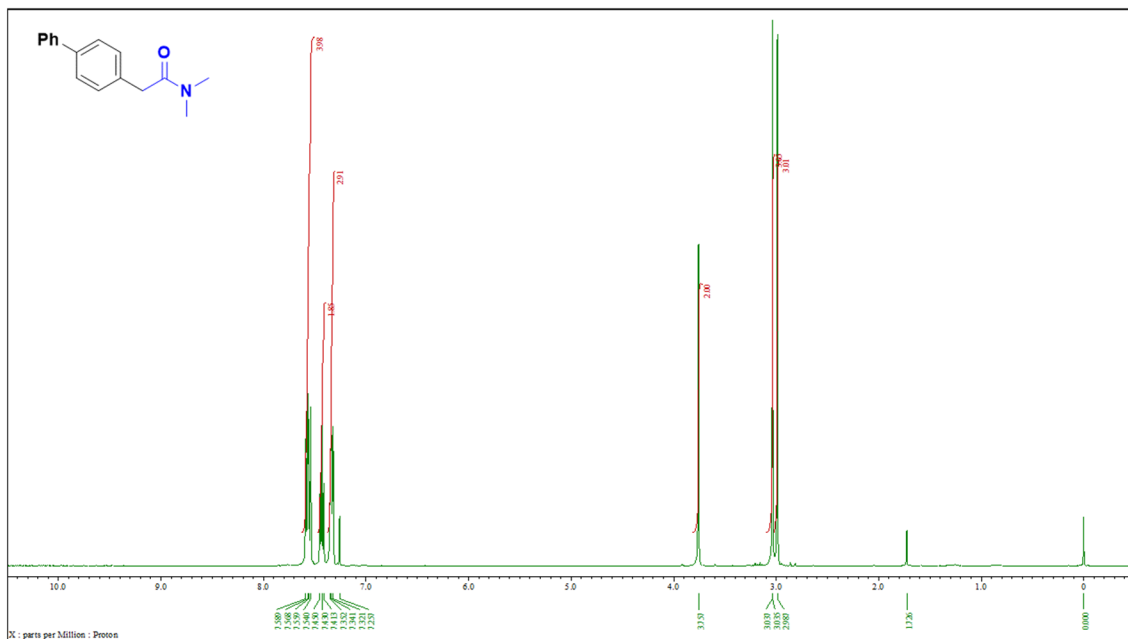




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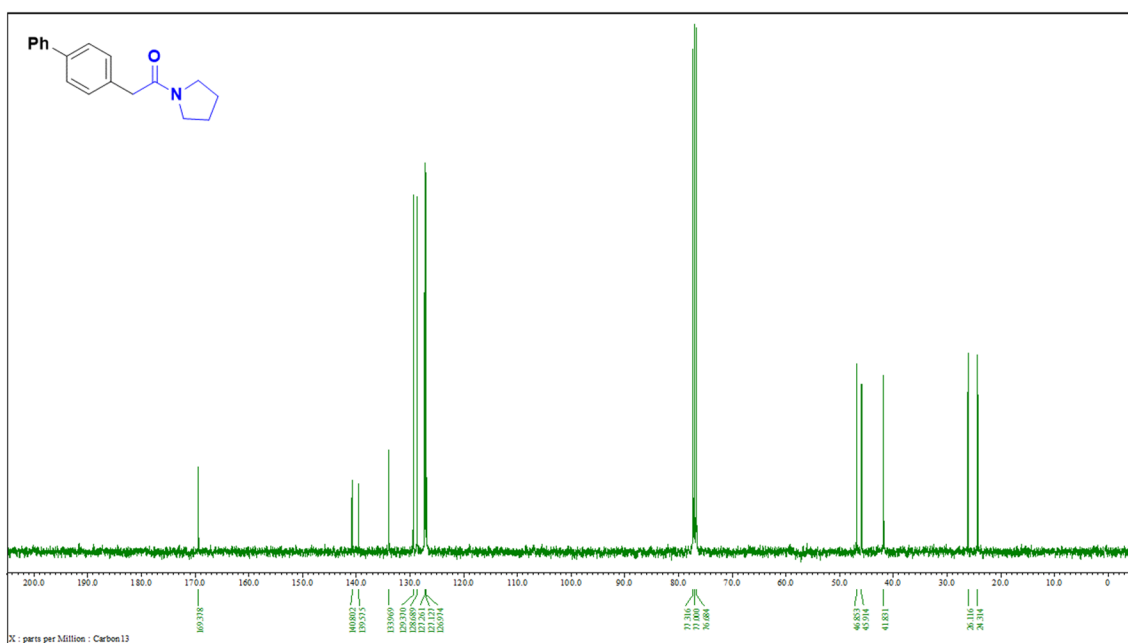
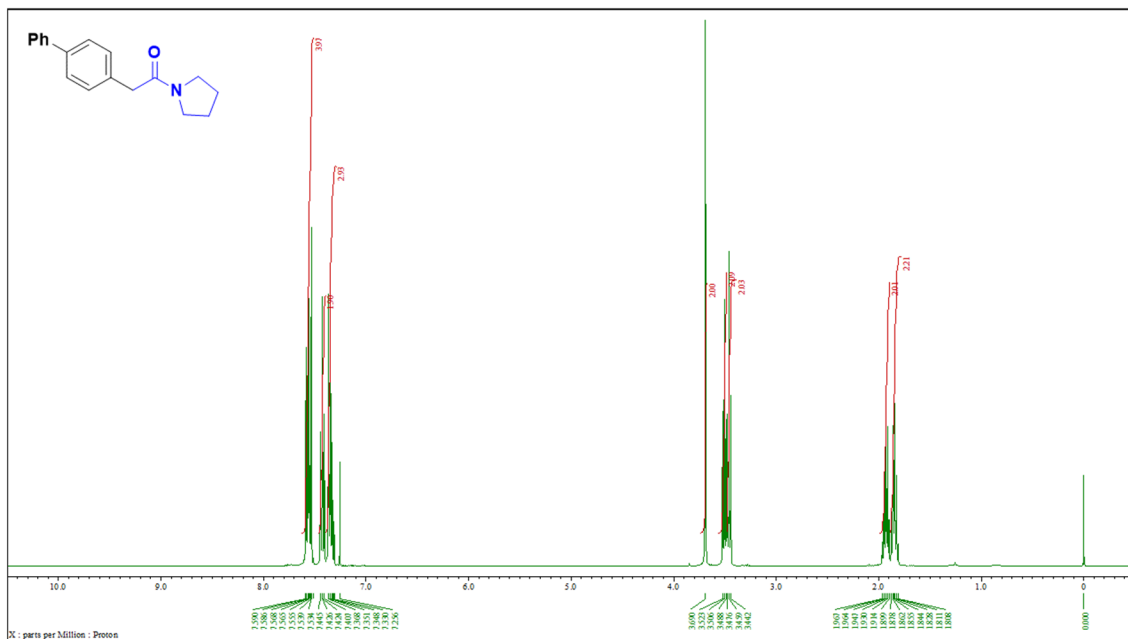


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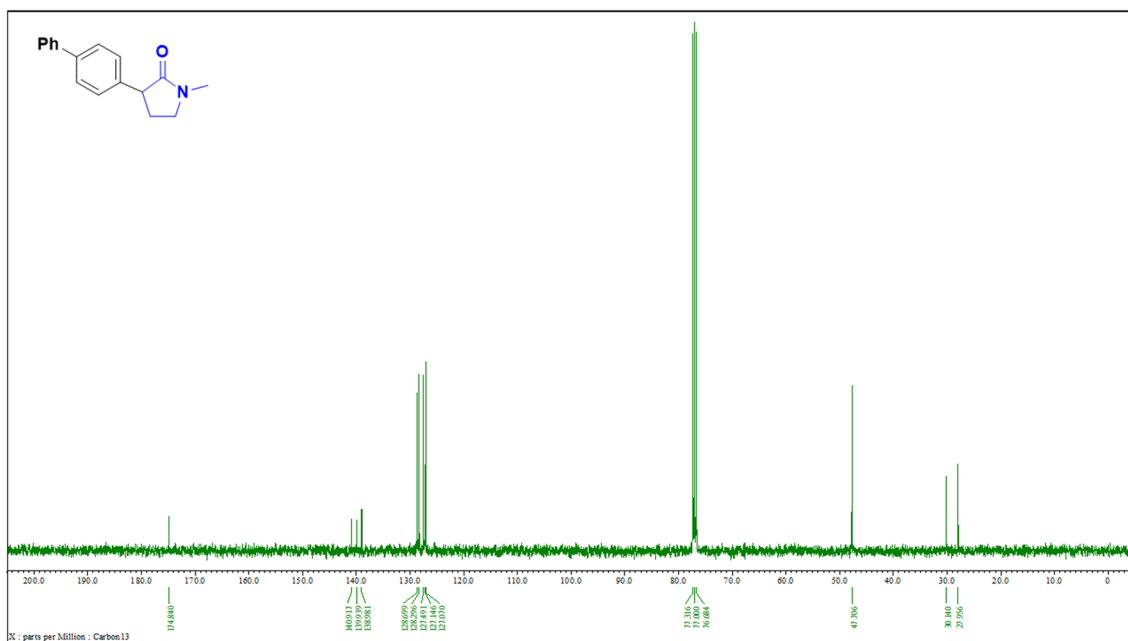
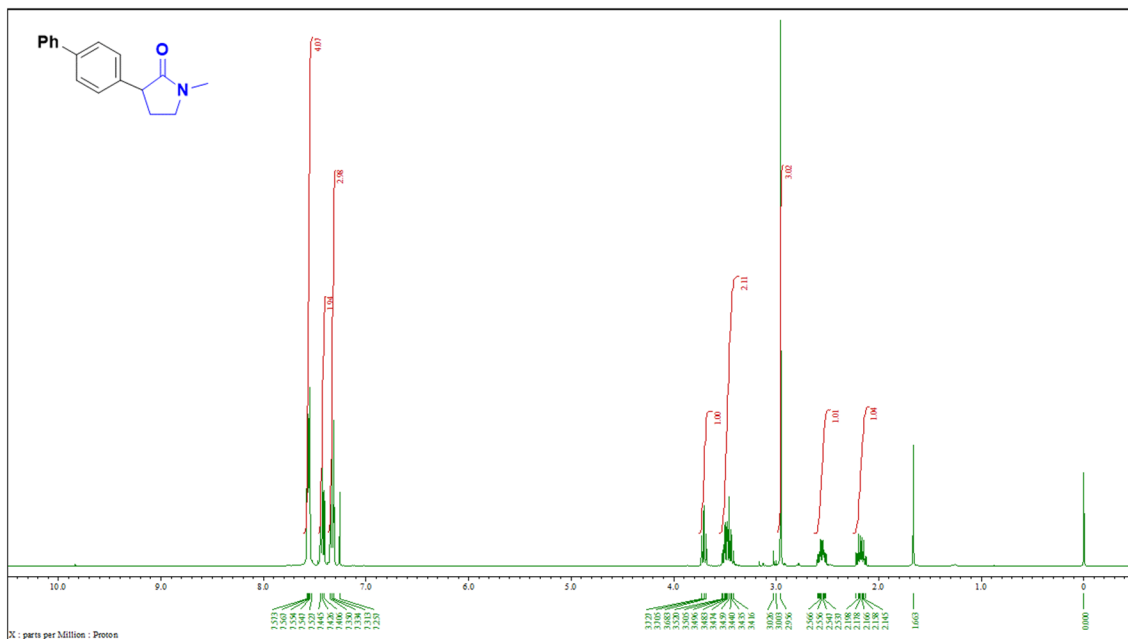




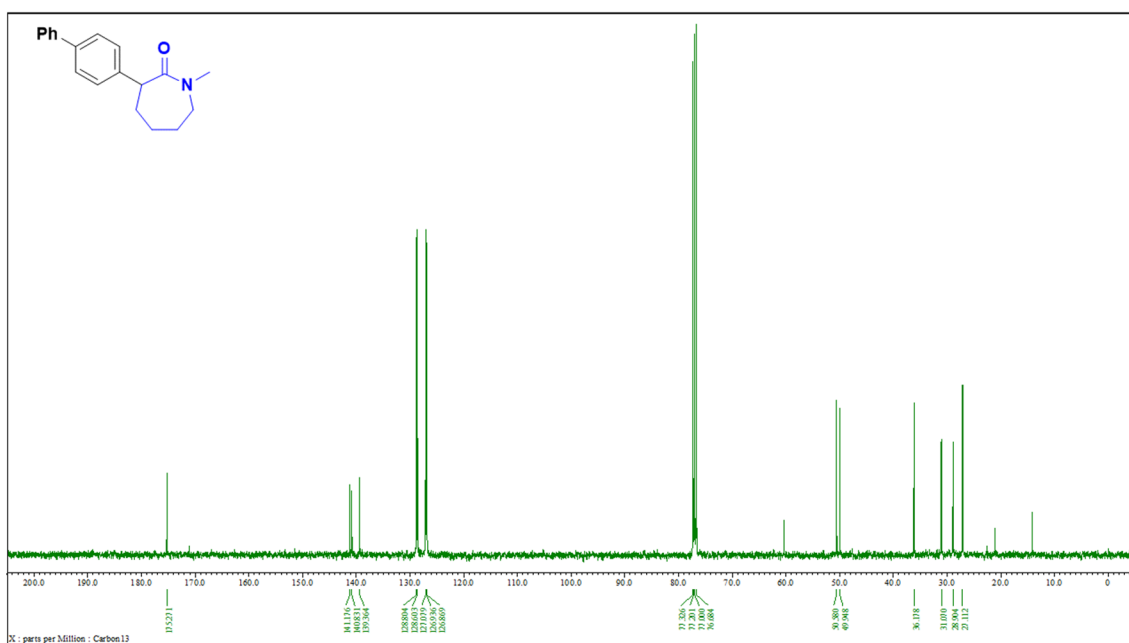
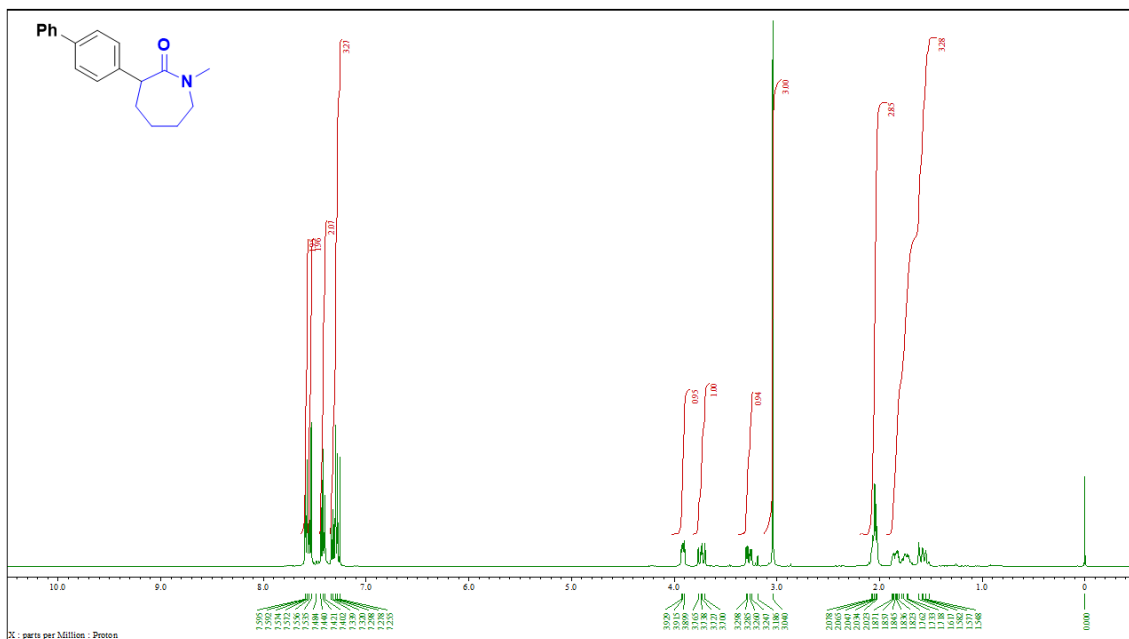
### 3ag



### 3ah



3ai



6

