

## *Supporting Information*

### **Visible-Light Mediated Remote $\gamma$ -C(sp<sup>3</sup>)-H Functionalization of Alkylimidates: Synthesis of 4-Iodo-3,4-Dihydropyrrole Derivatives**

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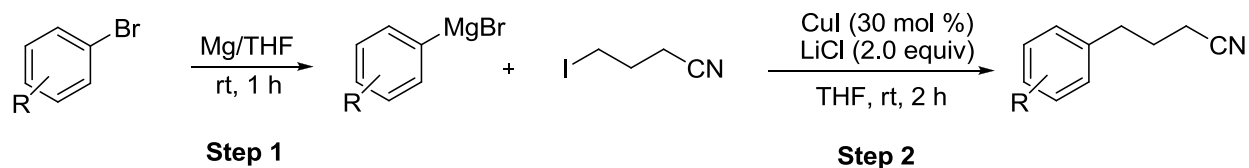
## I. General Information

All reagents and solvents were purchased from commercial sources and were used without purification. Sodium iodide was dried under high vacuum before use. Acetonitrile was distilled over calcium hydride and stored on 4Å molecular sieves before use. All reactions were monitored by TLC, followed by exposure of the TLC plates to UV light and/or an iodine chamber and  $\text{KMnO}_4$  to visualize the reaction spots. Column chromatography was performed using silica gel [ethyl acetate/hexane (in different ratios) solvent system]. FTIR spectra were recorded in ATR mode with the absorption in  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz) and  $^{19}\text{F}$  NMR (376 MHz) spectra were recorded in  $\text{CDCl}_3$  or  $\text{DMSO}-d_6$  as the solvent at 25 °C. Chemical shifts (in ppm) were reported using tetramethylsilane ( $\delta = 0$ ) as an internal standard in  $\text{CDCl}_3$  ( $\delta = 7.26$ ) or  $\text{DMSO}-d_6$  ( $\delta = 2.50$ ) solvent. The following abbreviations were used to define the multiplicities: s = singlet; d = doublet; t = triplet; m = multiplet; dd (doublet of doublets); td (triplet of doublets); br s (broad singlet), coupling constants (J, in Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR data were recorded in terms of the chemical shift (ppm, scale), using the central peak of  $\text{CDCl}_3$  (77.0 ppm) or  $\text{DMSO}-d_6$  ( $\delta = 39.5$  ppm) as the internal standard. HRMS was performed in ESI mode using Q-TOF (positive ion). Melting points were recorded with an automated melting point apparatus without correction.

## II. Substrate Synthesis

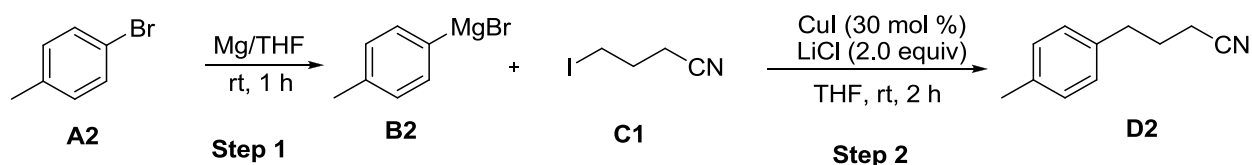
### A) Nitriles Synthesis:

**General Procedure for the Synthesis of 4-Arylbutanenitriles (GP1):** 4-Arylbutanenitriles were prepared according to literature.<sup>1</sup>



**Step 1:** A dried 25 mL round-bottom flask containing a stir bar was charged with magnesium (1.2 equiv.), a small piece of iodine and dry solvent THF (1.0 M) were added under N<sub>2</sub> atmosphere. A solution of aryl bromide (1.0 equiv) in 2 mL of dry THF was added dropwise to the round bottom flask and stirred the reaction for 1 hour. After the formation of Grignard reagent (color indication: brownish-green color appeared), the reaction mixture was cooled to 0 °C under N<sub>2</sub> atmosphere.

**Step 2:** An another dried 25 mL round-bottom flask containing a stir bar was charged with 4-iodobutanenitrile (0.5 equiv), CuI (30 mol %), and LiCl (1.0 equiv). Then 2.0 equiv of the corresponding Grignard reagent (prepared in step 1) was added slowly to the round bottom flask within 20.0 min under N<sub>2</sub> atmosphere and resulting mixture was stirred for 2-3 h at room temperature. After the completion of the reaction (revealed by TLC analysis), the reaction mixture was quenched with a saturated NH<sub>4</sub>Cl solution and extracted with ethyl acetate (3 x 15 mL). The combined organic layer was washed with brine solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was concentrated in vacuo and the crude residue was purified by silica gel column chromatography (hexanes/ethyl acetate) to afford the corresponding nitrile.



#### 4-p-tolylbutanenitrile (D2).

Step 1: Grignard reagent synthesis

Following **GP1**, magnesium (288 mg, 12.0 equiv) was reacted with a small piece of iodine and 1-bromo-4-methylbenzene **A2** (1710 mg, 10.0 mmol) in 10 mL THF at rt for 1 h.

Step 2: Nitrile synthesis

4-iodobutanenitrile **C1** (974 mg, 5.0 mmol), CuI (284 mg, 1.5 equiv), and LiCl (424 mg, 10 mmol) were reacted with **B2** (prepared in step 1) at rt for 2 h. The product was purified by silica gel column chromatography (hexanes/ethyl acetate, 96:04) to afford the corresponding **4-p-tolylbutanenitrile D2** (508 mg, 64%) as a colorless oil.

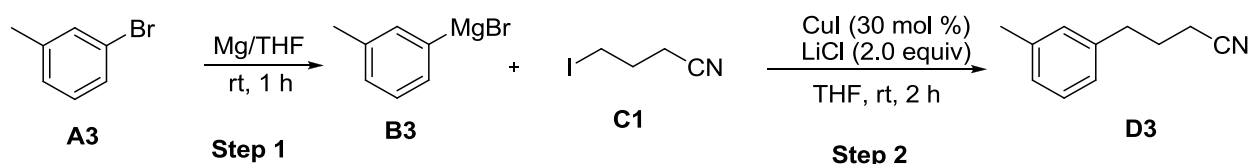
$R_f = 0.50$  (95:05 hexanes/EtOAc).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.13$  (d,  $J = 8.0$  Hz, 2H), 7.08 (d,  $J = 8.0$  Hz, 2H), 2.75 (t,  $J = 8.0$  Hz, 2H), 2.34 (s, 3H), 2.31 (t,  $J = 8.0$  Hz, 2H), 1.97 (quint,  $J = 8.0$  Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 136.6, 136.0, 129.3, 128.3, 119.5, 33.9, 26.9, 20.9, 16.3$ .

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{11}\text{H}_{13}\text{NNa}$   $[\text{M}+\text{H}]^+$  182.0940, found 182.0936.

IR (ATR)  $\text{cm}^{-1}$ : 3018, 2926, 2863, 2247, 1512, 1448, 1426, 802.



#### 4-m-tolylbutanenitrile (D3).

Step 1: Grignard reagent synthesis

Following **GP1**, magnesium (288 mg, 12.0 equiv) was reacted with a small piece of iodine and 1-bromo-3-methylbenzene **A3** (1710 mg, 10.0 mmol) in 10 mL THF at rt for 1 h.

#### Step 2: Nitrile synthesis

4-iodobutanenitrile **C1** (974 mg, 5.0 mmol), CuI (284 mg, 1.5 equiv), and LiCl (424 mg, 10 mmol) were reacted with **B3** (prepared in step 1) at rt for 2 h. The product was purified by silica gel column chromatography (hexanes/ethyl acetate, 96:04) to afford the corresponding **4-m-tolylbutanenitrile D3** (720 mg, 90%) as a colorless oil.

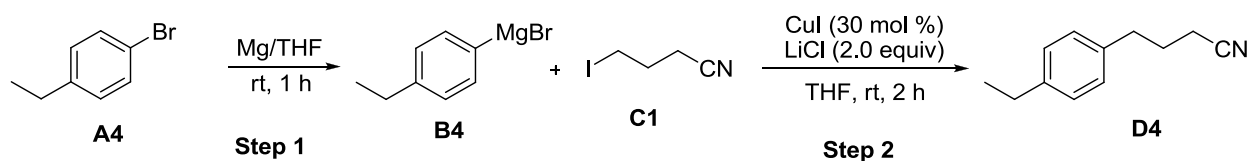
$R_f = 0.50$  (95:05 hexanes/EtOAc).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.21$  (t,  $J = 8.0$  Hz, 1H), 7.05 (d,  $J = 8.0$  Hz, 1H), 7.01-6.98 (m, 2H), 2.75 (t,  $J = 8.0$  Hz, 2H), 2.35 (s, 3H), 2.32 (t,  $J = 8.0$  Hz, 2H), 1.98 (quint,  $J = 8.0$  Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 139.6, 138.2, 129.2, 128.5, 127.2, 125.4, 119.5, 34.2, 26.9, 21.3, 16.3$ .

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{11}\text{H}_{13}\text{NNa}$   $[\text{M}+\text{H}]^+$  182.0940, found 182.0941.

IR (ATR)  $\text{cm}^{-1}$ : 3026, 2932, 2865, 2247, 1606, 1451, 885, 785.



#### 4-(4-ethylphenyl)butanenitrile (**D4**).

##### Step 1: Grignard reagent synthesis

Following **GP1**, magnesium (288 mg, 12.0 equiv) was reacted with a small piece of iodine and 1-bromo-4-ethylbenzene **A4** (1840 mg, 10.0 mmol) in 10 mL THF at rt for 1 h.

##### Step 2: Nitrile synthesis

4-iodobutanenitrile **C1** (974 mg, 5.0 mmol), CuI (284 mg, 1.5 equiv), and LiCl (424 mg, 10 mmol) were reacted with **B4** (prepared in step 1) at rt for 2 h. The product was purified by silica gel column chromatography (hexanes/ethyl acetate, 96:04) to afford the corresponding **4-(4-ethyl phenyl)butanenitrile D4** (720 mg, 83%) as a colorless oil.

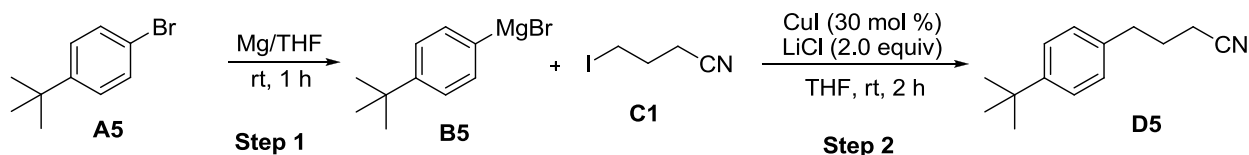
$R_f$  = 0.50 (95:05 hexanes/EtOAc).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.16 (d,  $J$  = 8.0 Hz, 2H), 7.11 (d,  $J$  = 8.0 Hz, 2H), 2.75 (t,  $J$  = 8.0 Hz, 2H), 2.64 (q,  $J$  = 8.0 Hz, 2H), 2.32 (t,  $J$  = 8.0 Hz, 2H), 1.97 (quint,  $J$  = 8.0 Hz, 2H), 1.24 (t,  $J$  = 8.0 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 142.4, 136.8, 128.4, 128.1, 119.6, 33.9, 28.4, 26.9, 16.3, 15.6.

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{12}\text{H}_{15}\text{NNa}$   $[\text{M}+\text{H}]^+$  196.1097, found 196.1088.

IR (ATR)  $\text{cm}^{-1}$ : 3015, 2962, 2871, 2247, 1512, 1454, 833.



#### 4-(4-tert-butylphenyl)butanenitrile (**D5**).

Step 1: Grignard reagent synthesis

Following **GP1**, magnesium (288 mg, 12.0 equiv) was reacted with a small piece of iodine and 1-bromo-4-tert-butylbenzene **A5** (2131 mg, 10.0 mmol) in 10 mL THF at rt for 1 h.

Step 2: Nitrile synthesis

4-iodobutanenitrile **C1** (974 mg, 5.0 mmol), CuI (284 mg, 1.5 equiv), and LiCl (424 mg, 10 mmol) were reacted with **B5** (prepared in step 1) at rt for 2 h. The product was purified by silica gel column chromatography (hexanes/ethyl acetate, 96:04) to afford the corresponding **4-(4-tert-butylphenyl)butanenitrile D5** (900 mg, 89%) as a colorless oil.

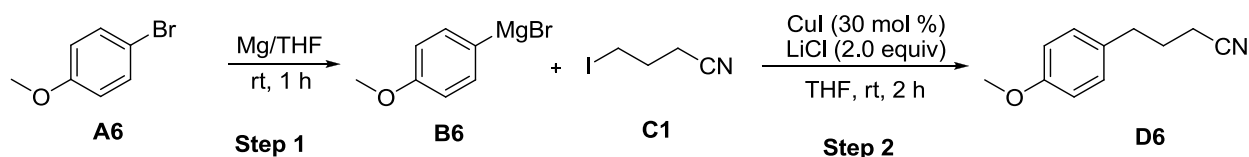
$R_f = 0.50$  (95:05 hexanes/EtOAc).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.34$  (d,  $J = 8.0$  Hz, 2H),  $7.13$  (d,  $J = 8.0$  Hz, 2H),  $2.76$  (t,  $J = 8.0$  Hz, 2H),  $2.33$  (t,  $J = 8.0$  Hz, 2H),  $1.98$  (quint,  $J = 8.0$  Hz, 2H),  $1.32$  (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 149.3, 136.6, 128.1, 125.5, 119.6, 34.4, 33.8, 31.3, 26.9, 16.4$ .

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{14}\text{H}_{19}\text{NNa}$   $[\text{M}+\text{H}]^+$  224.1410, found 224.1409.

IR (ATR)  $\text{cm}^{-1}$ : 2960, 2868, 2247, 1515, 1457, 1362, 1110, 830.



#### 4-(4-methoxyphenyl)butanenitrile (D6).<sup>4</sup>

Step 1: Grignard reagent synthesis

Following **GP1**, magnesium (288 mg, 12.0 equiv) was reacted with a small piece of iodine and 1-bromo-4-methoxybenzene **A6** (1870 mg, 10.0 mmol) in 10 mL THF at rt for 1 h.

Step 2: Nitrile synthesis

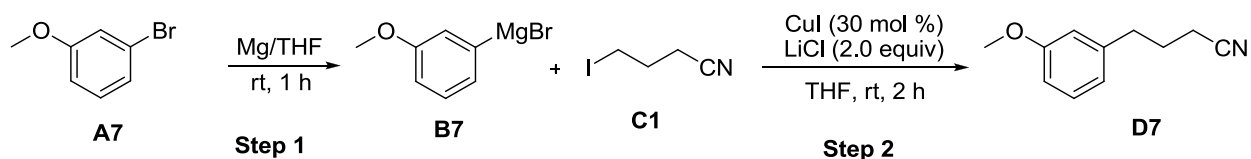
4-iodobutanenitrile **C1** (974 mg, 5.0 mmol), CuI (284 mg, 1.5 equiv), and LiCl (424 mg, 10 mmol) were reacted with **B6** (prepared in step 1) at rt for 2 h. The product was purified by silica gel column chromatography (hexanes/ethyl acetate, 96:04) to afford the corresponding **4-(4-methoxyphenyl)butanenitrile D6** (690 mg, 79%) as a colorless oil.

$R_f = 0.30$  (95:05 hexanes/EtOAc).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.10$  (d,  $J = 8.0$  Hz, 2H),  $6.85$  (d,  $J = 8.0$  Hz, 2H),  $3.79$  (s, 3H),  $2.72$  (t,  $J = 8.0$  Hz, 2H),  $2.30$  (t,  $J = 8.0$  Hz, 2H),  $1.94$  (quint,  $J = 8.0$  Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 158.2, 131.7, 129.4, 119.5, 114.0, 55.2, 33.4, 27.1, 16.2$ .

IR (ATR)  $\text{cm}^{-1}$ : 3004, 2943, 2838, 2244, 1609, 1509, 1240, 1032, 833.



#### 4-(3-methoxyphenyl)butanenitrile (D7).

Step 1: Grignard reagent synthesis

Following **GP1**, magnesium (288 mg, 12.0 equiv) was reacted with a small piece of iodine and 1-bromo-3-methoxybenzene **A7** (1870 mg, 10.0 mmol) in 10 mL THF at rt for 1 h.

Step 2: Nitrile synthesis

4-iodobutanenitrile **C1** (974 mg, 5.0 mmol), CuI (284 mg, 1.5 equiv), and LiCl (424 mg, 10 mmol) were reacted with **B7** (prepared in step 1) at rt for 3 h. The product was purified by silica gel column chromatography (hexanes/ethyl acetate, 96:04) to afford the corresponding **4-(3-methoxyphenyl)butanenitrile D7** (690 mg, 79%) as a colorless oil.

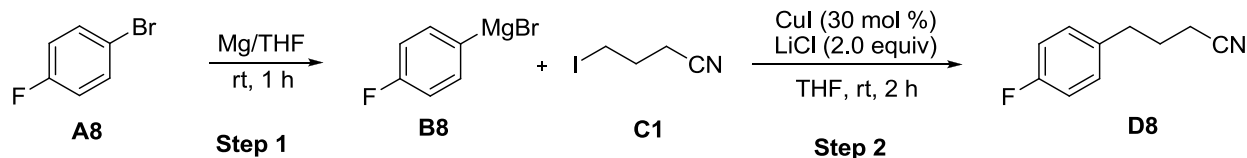
$R_f$  = 0.30 (95:05 hexanes/EtOAc).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.23 (t,  $J$  = 8.0 Hz, 1H), 6.78 (dd,  $J$  = 8.0, 4.0 Hz, 2H), 6.73 (s, 1H), 3.80 (s, 3H), 2.75 (t,  $J$  = 8.0 Hz, 2H), 2.32 (t,  $J$  = 8.0 Hz, 2H), 1.98 (quint,  $J$  = 8.0 Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.8, 141.3, 129.6, 120.8, 119.5, 114.2, 111.7, 55.1, 34.3, 26.8, 16.3.

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{11}\text{H}_{13}\text{NNaO}$   $[\text{M}+\text{H}]^+$  198.0889, found 198.0887.

IR (ATR)  $\text{cm}^{-1}$ : 3001, 2940, 2840, 2244, 1592, 1454, 1257, 1152, 1041, 780.



#### 4-(4-fluorophenyl)butanenitrile (D8).

Step 1: Grignard reagent synthesis

Following **GP1**, magnesium (288 mg, 12.0 equiv) was reacted with a small piece of iodine and 1-bromo-4-fluorobenzene **A8** (1750 mg, 10.0 mmol) in 10 mL THF at rt for 1 h.

Step 2: Nitrile synthesis

4-iodobutanenitrile **C1** (974 mg, 5.0 mmol), CuI (284 mg, 1.5 equiv), and LiCl (424 mg, 10 mmol) were reacted with **B8** (prepared in step 1) at rt for 3 h. The product was purified by silica gel column chromatography (hexanes/ethyl acetate, 96:04) to afford the corresponding **4-(4-fluorophenyl)butanenitrile D8** (740 mg, 91%) as a colorless oil.

$R_f = 0.40$  (95:05 hexanes/EtOAc).

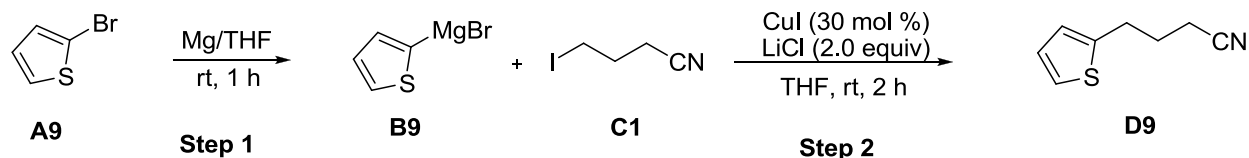
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.16\text{--}7.13$  (m, 2H), 6.99 (t,  $J = 8.0$  Hz, 2H), 2.76 (t,  $J = 8.0$  Hz, 2H), 2.32 (t,  $J = 8.0$  Hz, 2H), 1.96 (quint,  $J = 8.0$  Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 162.79$  and  $160.36$  (d,  $J_{\text{C-F}} = 243.0$  Hz), 135.31 and 135.28 (d,  $J_{\text{C-F}} = 3.0$  Hz), 129.85 and 129.77 (d,  $J_{\text{C-F}} = 8.0$  Hz), 119.3, 115.54 and 115.33 (d,  $J_{\text{C-F}} = 21.0$  Hz), 33.5, 26.9, 16.3.

$^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -116.6$ .

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{10}\text{H}_{10}\text{FNNa}$   $[\text{M}+\text{H}]^+$  186.0689, found 186.0687.

IR (ATR)  $\text{cm}^{-1}$ : 3003, 2937, 2871, 2244, 1601, 1509, 1218, 824.



**4-(thiophen-2-yl)butanenitrile (D9).**<sup>5</sup>

Step 1: Grignard reagent synthesis

Following **GP1**, magnesium (288 mg, 12.0 equiv) was reacted with a small piece of iodine and 2-bromothiophene **A9** (1630 mg, 10.0 mmol) in 10 mL THF at rt for 1 h.

## Step 2: Nitrile synthesis

4-iodobutanenitrile **C1** (974 mg, 5.0 mmol), CuI (284 mg, 1.5 equiv), and LiCl (424 mg, 10 mmol) were reacted with **B9** (prepared in step 1) at rt for 2 h. The product was purified by silica gel column chromatography (hexanes/ethyl acetate, 96:04) to afford the corresponding **4-(thiophen-2-yl)butanenitrile D9** (150 mg, 20%) as a brown oil.

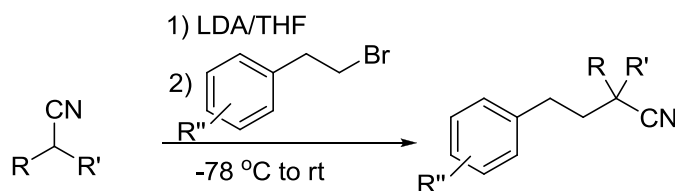
$R_f = 0.50$  (95:05 hexanes/EtOAc).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.17$  (dd,  $J = 4.0, 1.0$  Hz, 1H), 6.94 (dd,  $J = 4.0, 1.0$  Hz, 1H), 6.85 (d,  $J = 4.0$  Hz, 1H), 3.01 (t,  $J = 8.0$  Hz, 2H), 2.37 (t,  $J = 8.0$  Hz, 2H), 2.03 (quint,  $J = 8.0$  Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 142.0, 127.0, 125.2, 123.9, 119.2, 28.4, 27.2, 16.2$ .

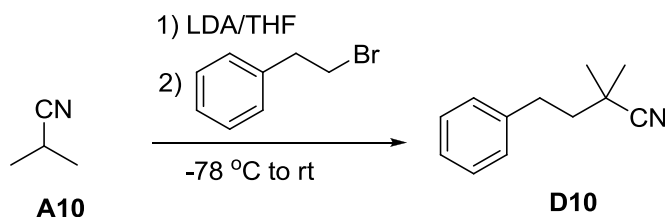
IR (ATR)  $\text{cm}^{-1}$ : 3112, 2937, 2857, 2247, 1440, 1240, 697.

**B) General Procedure for the Synthesis of 2,2-dialkyl-4-arylbutanenitriles (GP2):** 2,2-dialkyl-4-arylbutanenitriles were prepared according to literature.<sup>2</sup>



A dried 25 mL round-bottom flask containing a stir bar was charged with nitrile (1.0 equiv) and dry THF (2 M) was added under N<sub>2</sub> atmosphere. Then, the reaction mixture was cooled to -78 °C at which temperature LDA (2 M, 1.2 equiv) was added dropwise and the further reaction was stirred for a period of 30 min. Next, the corresponding 2-aryl ethyl bromide (1.2 equiv) in 1 mL of dry THF was added dropwise to the stirring solution at -78 °C and reaction was stirred at the same temperature for 1 hour. Further, the reaction was allowed to warm to room temperature while being stirred for 12 h. After the completion of the reaction (revealed by TLC analysis), the

reaction mixture was quenched with a saturated  $\text{NH}_4\text{Cl}$  solution and extracted with ethyl acetate (3 x 15 mL). The combined organic layer was washed with brine solution, dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The organic layer was then concentrated in vacuo and the crude residue was purified by silica gel column chromatography (hexanes/ethyl acetate) to afford the corresponding nitrile.



#### 2,2-dimethyl-4-phenylbutanenitrile (D10).<sup>6</sup>

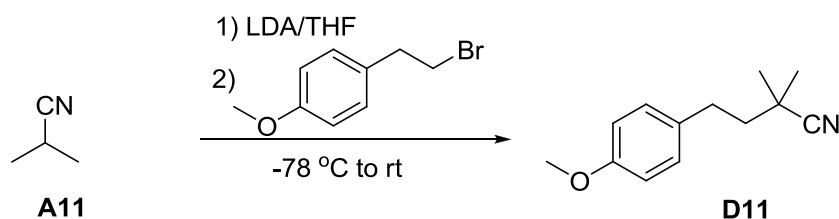
Following **GP2**, Nitrile (345 mg, 5.0 mmol) was reacted with LDA (3 mL, 2 M in THF) and 2-(2-bromoethyl)benzene (1110 mg, 6.0 mmol) in 10 mL of dry THF for 12 h. The product was purified by silica gel column chromatography (hexanes/ethyl acetate) to afford the corresponding **2,2-dimethyl-4-phenylbutanenitrile D10** (406 mg, 47%) as a colorless oil.

$R_f$  = 0.60 (95:05 hexanes/EtOAc).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.31 (t,  $J$  = 8.0 Hz, 2H), 7.22 (t,  $J$  = 8.0 Hz, 3H), 2.83-2.79 (m, 2H), 1.85-1.81 (m, 2H), 1.42 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 140.8, 128.6, 128.3, 126.2, 124.8, 43.1, 32.4, 31.8, 26.7.

IR (ATR)  $\text{cm}^{-1}$ : 3112, 2937, 2857, 2247, 1440, 1240, 697.



#### 4-(4-Methoxyphenyl)-2,2-dimethylbutanenitrile (D11).<sup>2</sup>

Following **GP2**, Nitrile (173 mg, 2.5 mmol) was reacted with LDA (1.5 mL, 2 M in THF) and 1-(2-bromoethyl)-4-methoxybenzene (645 mg, 3.0 mmol) in 5 mL of dry THF for 12 h. The

product was purified by silica gel column chromatography (hexanes/ethyl acetate) to afford the corresponding **4-(4-methoxyphenyl)-2,2-dimethyl butanenitrile D11** (360 mg, 71%) as a colorless oil.

$R_f = 0.50$  (95:05 hexanes/EtOAc).

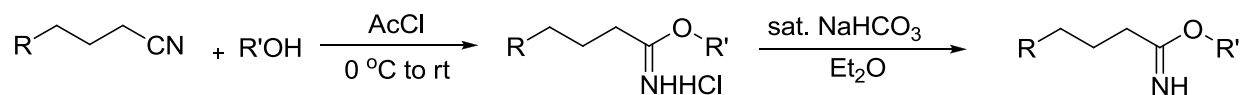
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.12$  (d,  $J = 8.0$  Hz, 2H), 6.84 (d,  $J = 8.0$  Hz, 2H), 3.79 (s, 3H), 2.77-2.72 (m, 2H), 1.81-1.77 (m, 2H), 1.40 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 158.1, 132.9, 129.2, 124.8, 114.0, 55.3, 43.3, 32.4, 30.9, 26.7$ .

IR (ATR)  $\text{cm}^{-1}$ : 2979, 2935, 2838, 2230, 1512, 1457, 1246, 1032, 821.

## B) Imidates Synthesis

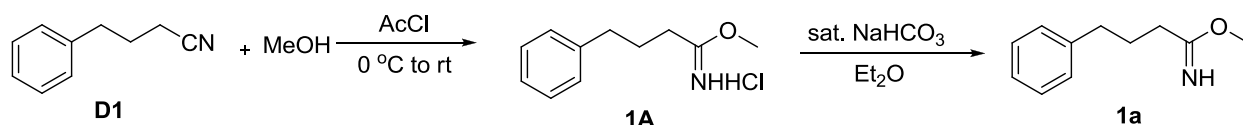
**General Procedure for the Preparation of Imidates (GP3):** Imidates were prepared according to literature.<sup>3</sup>



R = Aryl, alkyl, heteroaryl

A 50 mL flask containing a solution of a nitrile (1.0 mmol) and an alcohol (12.0 mmol) were sealed with the rubber septum at 0 °C under  $\text{N}_2$  and AcCl (0.57 mL, 8.0 mmol) was added slowly to the solution using a glass syringe. The reaction was stirred at room temperature for 12 h (Warning: Excess HCl gas will be released during this process). Upon completion of the reaction (revealed by TLC), the volatile solvents were removed under reduced pressure. The crude product was dried under high vacuum to isolate the imidate hydrochloride salt. Further, imidate hydrochloride salts were dissolved in 20 mL of diethyl ether, and the solution was cooled in ice-water. Then cooled saturated  $\text{NaHCO}_3$  solution was added slowly until  $\text{CO}_2$  gas evolution

ceased. The product was extracted with Et<sub>2</sub>O (2 × 10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to obtain the free imidate.



### Methyl 4-phenylbutanimidate (**1a**).<sup>7</sup>

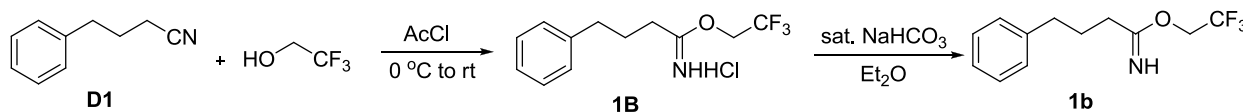
Following **GP3**, nitrile **D1** (725 mg, 5.0 mmol) was reacted with MeOH (1.90 g, 2.42 mL, 60.0 mmol) and AcCl (3.14 g, 2.84 mL, 40.0 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate the **methyl 4-phenylbutanimidate hydrochloride 1A** (970 mg, 91%) as a white solid. Further, Imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated NaHCO<sub>3</sub> solution to obtain the **Methyl 4-phenylbutanimidate (1a)** as a colorless oil.

**R<sub>f</sub>** = 0.40 (90:10 hexanes/EtOAc).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.31 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 3H), 6.98 (br s, 1H), 3.73 (s, 3H), 2.67 (t, *J* = 8.0 Hz, 2H), 2.31 (t, *J* = 8.0 Hz, 2H), 1.92 (quint, *J* = 8.0 Hz, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):** δ = 173.1, 141.3, 128.4, 126.0, 52.9, 35.1, 34.9, 27.7.

**IR (ATR) cm<sup>-1</sup>:** 3323, 3029, 2943, 1648, 1440, 1085, 744.



### 2,2,2-trifluoroethyl 4-phenylbutanimidate (**1b**).

Following **GP3**, nitrile **D1** (1.45 g, 10.0 mmol) was reacted with CF<sub>3</sub>CH<sub>2</sub>OH (12.0 g, 9.2 mL, 120.0 mmol) and AcCl (6.28 g, 5.8 mL, 80.0 mmol) was added in one portion mL pressure tube and the tube was immediately sealed. The reaction was stirred at 50 °C for 48 h (Warning:

Excess HCl gas will be released during this process). The product was dried under high vacuum to isolate **2,2,2-trifluoroethyl 4-phenylbutanimidate hydrochloride 1B** (1305 mg, 93%) as a white solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated NaHCO<sub>3</sub> solution to obtain the **2,2,2-trifluoroethyl 4-phenylbutanimidate (1b)** as a colorless oil.

**R<sub>f</sub>** = 0.50 (90:10 hexanes/EtOAc).

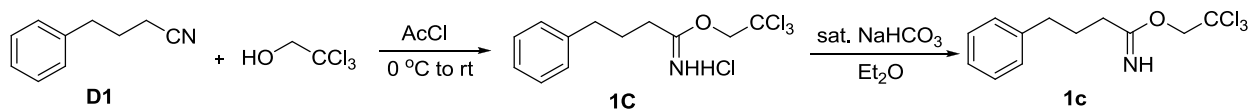
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.31 (d, *J* = 8.0 Hz, 2H), 7.23-7.17 (m, 3H), 4.50 (q, *J* = 8.0 Hz, 2H), 2.66 (t, *J* = 8.0, 2H), 2.34 (t, *J* = 8.0, 2H), 1.92 (quint, *J* = 8.0 Hz, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 171.3, 141.0, 128.5, 128.4, 126.2, 123.6 (q, *J*<sub>(c-f)</sub> = 276.0 Hz), 61.8 (q, *J*<sub>(c-f)</sub> = 35.0 Hz), 34.9, 34.3, 27.4.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -73.8.

**HRMS (ESI-TOF) *m/z*:** calc'd for C<sub>12</sub>H<sub>15</sub>F<sub>3</sub>NO [M+H]<sup>+</sup> 246.1100, found 246.1094.

**IR (ATR) cm<sup>-1</sup>:** 3340, 3026, 2929, 1665, 1412, 1271, 1163, 1096.



#### **2,2,2-trichloroethyl 4-phenylbutanimidate (1c).**

Following **GP3**, nitrile **D1** (725 mg, 5.0 mmol) was reacted with CCl<sub>3</sub>CH<sub>2</sub>OH (9.0 g, 5.8 mL, 60.0 mmol) and AcCl (3.14 g, 2.84 mL, 40.0 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate **2,2,2-trichloroethyl 4-phenylbutanimidate hydrochloride 1C** (450 mg, 31%) as a white solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated NaHCO<sub>3</sub> solution to obtain the **2,2,2-trichloroethyl 4-phenylbutanimidate (1c)** as a colorless oil.

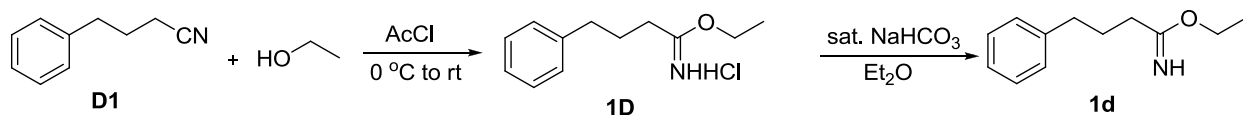
**R<sub>f</sub>** = 0.60 (90:10 hexanes/EtOAc).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 7.29 (d,  $J$  = 8.0 Hz, 2H), 7.20 (t,  $J$  = 8.0 Hz, 3H), 4.79 (s, 2H), 2.69 (t,  $J$  = 8.0 Hz, 2H), 2.40 (t,  $J$  = 8.0 Hz, 2H), 1.97 (quint,  $J$  = 8.0 Hz, 2H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 171.4, 141.1, 128.5, 128.4, 126.1, 95.6, 75.8, 34.9, 34.6, 27.4.

**HRMS (ESI-TOF)  $m/z$ :** calc'd for  $\text{C}_{12}\text{H}_{15}\text{Cl}_3\text{NO}$   $[\text{M}+\text{H}]^+$  294.0214, found 294.0204.

**IR (ATR)  $\text{cm}^{-1}$ :** 3353, 3023, 2932, 2860, 1667, 1448, 1096, 805, 705.



**Ethyl 4-phenylbutanimidate (1d).**<sup>8</sup>

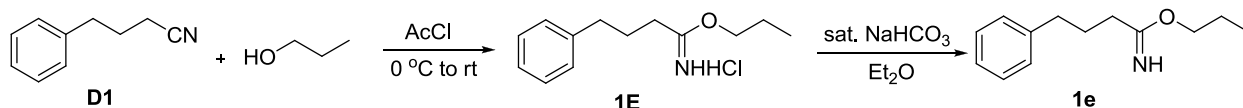
Following **GP3**, nitrile **D1** (1.45 g, 10.0 mmol) was reacted with  $\text{CH}_3\text{CH}_2\text{OH}$  (5.5 g, 7.0 mL, 120.0 mmol) and AcCl (6.28 g, 6.68 mL, 80.0 mmol) for 12 h at rt in 250 mL round bottom flask. The product was dried under high vacuum to isolate **ethyl 4-phenylbutanimidate hydrochloride 1D** (912 mg, 80%) as a white solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated  $\text{NaHCO}_3$  solution to obtain the **Ethyl 4-phenylbutanimidate (1d)** as a colorless oil.

**$R_f$**  = 0.40 (90:10 hexanes/ $\text{EtOAc}$ ).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 7.28 (d,  $J$  = 8.0 Hz, 2H), 7.19 (t,  $J$  = 8.0 Hz, 3H), 5.38 (br s, 1H), 4.12 (q,  $J$  = 8.0 Hz, 2H), 2.65 (t,  $J$  = 8.0 Hz, 2H), 2.27 (t,  $J$  = 8.0 Hz, 2H), 1.90 (quint,  $J$  = 8.0 Hz, 2H), 1.29 (t,  $J$  = 7.1 Hz, 3H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 172.9, 141.4, 128.5, 128.4, 126.0, 61.4, 35.2, 35.1, 27.7, 14.2.

**IR (ATR)  $\text{cm}^{-1}$ :** 3323, 3026, 2935, 1645, 1454, 1085, 741.



#### Propyl 4-phenylbutanimidate (1e).

Following **GP3**, nitrile **D1** (362 mg, 2.5 mmol) was reacted with  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  (1.8 g, 2.3 mL, 30 mmol) and AcCl (1.57g, 1.4 mL, 20 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate **propyl 4-phenylbutanimidate hydrochloride 1E** (540 mg, 90%) as a white solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated  $\text{NaHCO}_3$  solution to obtain the **propyl 4-phenylbutanimidate (1e)** as a colorless oil.

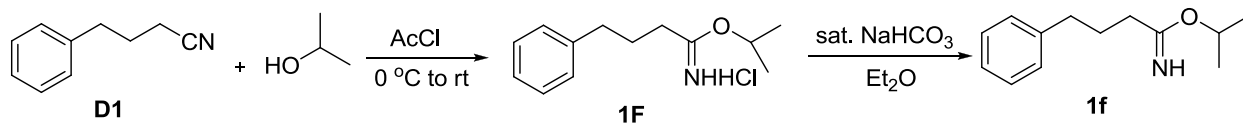
$R_f = 0.40$  (90:10 hexanes/EtOAc).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.29$  (d,  $J = 8.0$  Hz, 2H), 7.22-7.17 (m, 3H), 4.01 (t,  $J = 8.0$  Hz, 2H), 2.65 (t,  $J = 8.0$ , 2H), 2.27 (t,  $J = 8.0$ , 2H), 1.90 (quint,  $J = 8.0$  Hz, 2H), 1.70 (quint,  $J = 8.0$  Hz, 2H), 0.97 (t,  $J = 8.0$  Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 172.8, 141.4, 128.4, 128.3, 126.0, 67.0, 35.2, 35.1, 27.7, 21.9, 10.5$ .

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{13}\text{H}_{20}\text{NO}$   $[\text{M}+\text{H}]^+$  206.1539, found 206.1530.

IR (ATR)  $\text{cm}^{-1}$ : 3320, 2970, 1642, 1380, 1106, 754.



#### Isopropyl 4-phenylbutanimidate (1f).

Following **GP3**, nitrile **D1** (362 mg, 2.5 mmol) was reacted with  $\text{CH}_3\text{CHOHCH}_3$  (1.8 g, 2.29 mL, 30.0 mmol) and AcCl (1.57 g, 1.4 mL, 20.0 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate **isopropyl 4-phenylbutanimidate**

**hydrochloride 1F** (580 mg, 96%) as a white solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated  $\text{NaHCO}_3$  solution to obtain the **isopropyl 4-phenylbutanimidate (1f)** as a colorless oil.

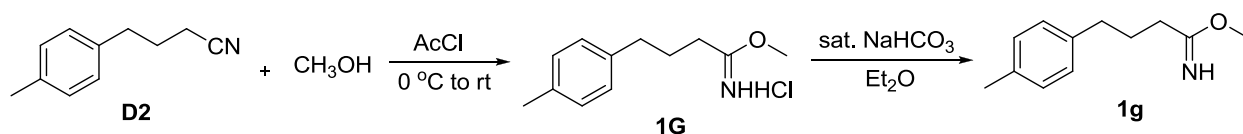
$R_f = 0.40$  (90:10 hexanes/EtOAc).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.28$  (d,  $J = 8.0$  Hz, 2H), 7.19 (t,  $J = 8.0$  Hz, 3H), 5.37 (br s, 1H), 5.09-5.01 (m, 1H), 2.64 (t,  $J = 8.0$ , 2H), 2.23 (t,  $J = 8.0$ , 2H), 1.89 (quint,  $J = 8.0$  Hz, 2H), 1.26 (d,  $J = 8.0$  Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 172.1$ , 141.4, 128.5, 128.4, 126.0, 67.8, 35.0, 27.8, 21.7.

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{13}\text{H}_{20}\text{NO}$   $[\text{M}+\text{H}]^+$  206.1539, found 206.1535.

IR (ATR)  $\text{cm}^{-1}$ : 3317, 2972, 1640, 1376, 1102, 744.



**Methyl 4-p-tolylbutanimidate (1g).**

Following **GP3**, nitrile **D2** (477 mg, 3.0 mmol) was reacted with  $\text{CH}_3\text{OH}$  (1.15 g, 1.45 mL, 36.0 mmol) and  $\text{AcCl}$  (1.88 g, 1.7 mL, 24.0 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate **methyl 4-p-tolylbutanimidate hydrochloride 1G** (600 mg, 88%) as a white solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated  $\text{NaHCO}_3$  solution to obtain the **methyl 4-p-tolylbutanimidate (1g)** as a colorless oil.

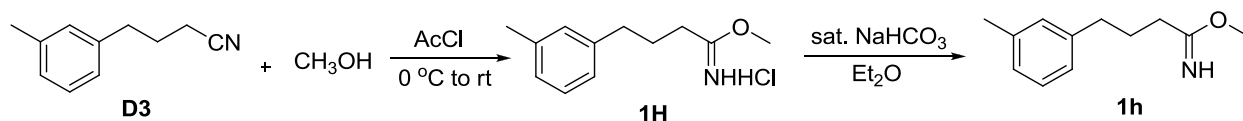
$R_f = 0.50$  (90:10 hexanes/EtOAc).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.10$  (d,  $J = 8.0$  Hz, 2H), 7.06 (d,  $J = 8.0$  Hz, 2H), 6.96 (br s, 1H), 3.70 (s, 3H), 2.60 (t,  $J = 8.0$  Hz, 2H), 2.32 (s, 3H), 2.26 (t,  $J = 8.0$  Hz, 2H), 1.87 (quint,  $J = 8.0$  Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 173.2, 138.2, 135.5, 129.1, 128.3, 52.8, 34.8, 34.6, 27.8, 20.9.

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{12}\text{H}_{18}\text{NO}$   $[\text{M}+\text{H}]^+$  192.1383, found 192.1396.

IR (ATR)  $\text{cm}^{-1}$ : 3326, 2937, 2863, 1648, 1446, 1368, 1088, 808.



#### Methyl 4-m-tolylbutanimidate (1h).

Following **GP3**, nitrile **D3** (477 mg, 3.0 mmol) was reacted with  $\text{CH}_3\text{OH}$  (1.15 g, 1.45 mL, 36.0 mmol) and  $\text{AcCl}$  (1.88 g, 1.7 mL, 24.0 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate **methyl 4-m-tolylbutanimidate hydrochloride 1H** (650 mg, 95%) as a white solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated  $\text{NaHCO}_3$  solution to obtain the **methyl 4-p-tolylbutanimidate (1g)** as a colorless oil.

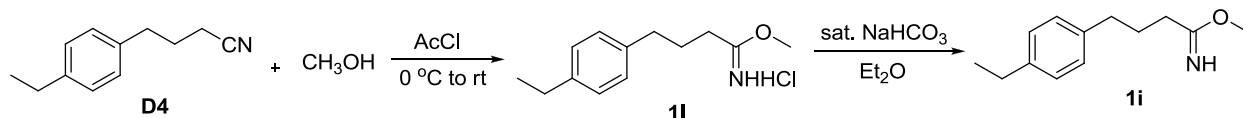
$R_f$  = 0.50 (90:10 hexanes/ $\text{EtOAc}$ ).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.18 (t,  $J$  = 8.0 Hz, 1H), 7.02-6.99 (m, 3H), 6.97 (br s, 1H), 3.71 (s, 3H), 2.61 (t,  $J$  = 8.0 Hz, 2H), 2.33 (s, 3H), 2.27 (t,  $J$  = 8.0 Hz, 2H), 1.88 (quint,  $J$  = 8.0 Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 173.2, 141.2, 137.9, 129.2, 128.3, 126.7, 125.4, 52.8, 34.9, 34.8, 27.7, 21.4.

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{12}\text{H}_{18}\text{NO}$   $[\text{M}+\text{H}]^+$  192.1383, found 192.1387.

IR (ATR)  $\text{cm}^{-1}$ : 3323, 2940, 2857, 1648, 1443, 1368, 1091, 783.



#### Methyl 4-(4-ethylphenyl)butanimidate (**1i**).

Following **GP3**, nitrile **D4** (519 mg, 3.0 mmol) was reacted with CH<sub>3</sub>OH (1.15 g, 1.45 mL, 36.0 mmol) and AcCl (1.88 g, 1.7 mL, 24.0 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate **methyl 4-(4-ethylphenyl)butanimidate hydrochloride 1I** (700 mg, 97%) as a white solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated NaHCO<sub>3</sub> solution to obtain the **methyl 4-(4-ethylphenyl)butanimidate (1i)** as a colorless oil.

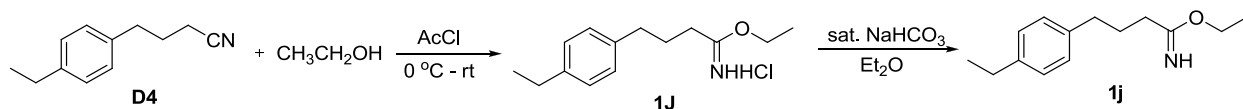
**R<sub>f</sub>** = 0.50 (90:10 hexanes/EtOAc).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.13 (d,  $J$  = 8.0 Hz, 2H), 7.09 (d,  $J$  = 8.0 Hz, 2H), 6.95 (br s, 1H), 3.70 (s, 3H), 2.62 (q,  $J$  = 8.0 Hz, 4H), 2.27 (t,  $J$  = 8.0 Hz, 2H), 1.88 (quint,  $J$  = 8.0 Hz, 2H), 1.23 (t,  $J$  = 8.0 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 173.2, 141.9, 138.5, 128.3, 127.9, 52.8, 34.9, 34.6, 28.4, 27.7, 15.6.

**HRMS (ESI-TOF)  $m/z$ :** calc'd for C<sub>13</sub>H<sub>20</sub>NO [M+H]<sup>+</sup> 206.1539, found 206.1558.

**IR (ATR) cm<sup>-1</sup>:** 3326, 2940, 2868, 1648, 1446, 1368, 1085, 830.



#### Ethyl 4-(4-ethylphenyl)butanimidate (**1j**)

Following **GP3**, nitrile **D4** (160 mg, 0.8 mmol) was reacted with CH<sub>3</sub>CH<sub>2</sub>OH (442 mg, 0.557 mL, 9.6 mmol) and AcCl (502 mg, 0.46 mL, 6.4 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate **ethyl 4-(4-ethylphenyl)butanimidate**

**hydrochloride 1J** (160 mg, 78%) as a white solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated  $\text{NaHCO}_3$  solution to obtain the **ethyl 4-(4-ethylphenyl)butanimidate (1j)** as a colorless oil.

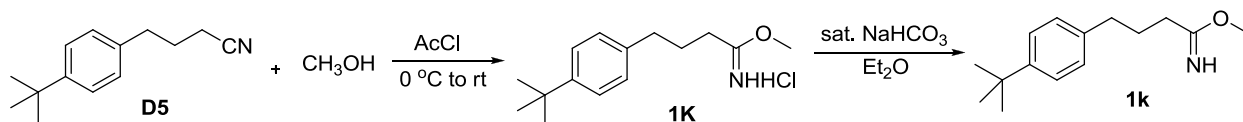
$R_f = 0.50$  (90:10 hexanes/EtOAc).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.13$  (d,  $J = 8.2$  Hz, 2H), 7.09 (d,  $J = 8.2$  Hz, 2H), 6.91 (br s, 1H), 4.11 (q,  $J = 7.2$  Hz, 2H), 2.61 (t,  $J = 7.8$  Hz, 4H), 2.26 (t,  $J = 7.8$  Hz, 2H), 1.88 (quint,  $J = 8.0$  Hz, 2H), 1.29 (t,  $J = 7.2$  Hz, 3H), 1.22 (t,  $J = 7.6$  Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 172.7, 141.9, 138.6, 128.3, 127.9, 61.1, 35.2, 34.6, 28.4, 27.8, 15.6, 14.2$ .

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{12}\text{H}_{22}\text{NO}$   $[\text{M}+\text{H}]^+$  220.1696, found 220.1687.

IR (ATR)  $\text{cm}^{-1}$ : 3324, 2964, 2933, 1649, 1379, 1337, 1089, 830.



#### Methyl 4-(4-tert-butylphenyl)butanimidate (1k).

Following **GP3**, nitrile **D5** (603 mg, 3.0 mmol) was reacted with  $\text{CH}_3\text{OH}$  (1.15 g, 1.45 mL, 36.0 mmol) and  $\text{AcCl}$  (1.88 g, 1.7 mL, 24.0 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate **methyl 4-(4-tert-butylphenyl)butanimidate hydrochloride 1K** (680 mg, 84%) as a white solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated  $\text{NaHCO}_3$  solution to obtain the **methyl 4-(4-tert-butylphenyl)butanimidate (1k)** as a colorless oil.

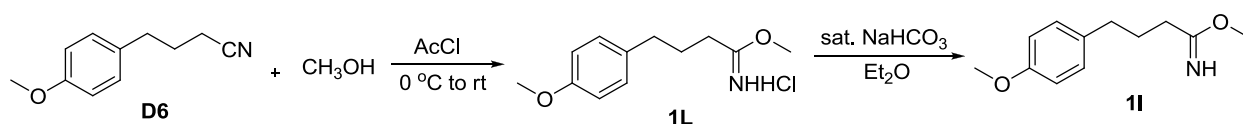
$R_f = 0.50$  (90:10 hexanes/EtOAc).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.31 (d,  $J$  = 8.0 Hz, 2H), 7.11 (d,  $J$  = 8.0 Hz, 2H), 6.96 (br s, 1H), 3.71 (s, 3H), 2.61 (t,  $J$  = 8.0 Hz, 2H), 2.28 (t,  $J$  = 8.0 Hz, 2H), 1.89 (quint,  $J$  = 8.0 Hz, 2H), 1.31 (s, 9H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 173.2, 148.8, 138.2, 128.1, 125.3, 52.8, 34.9, 34.5, 34.3, 31.4, 27.6.

**HRMS (ESI-TOF)  $m/z$ :** calc'd for C<sub>15</sub>H<sub>24</sub>NO [M+H]<sup>+</sup> 234.1852, found 234.1873.

**IR (ATR) cm<sup>-1</sup>:** 3323, 2957, 2868, 1648, 1443, 1362, 1085, 833.



#### **Methyl 4-(4-methoxyphenyl)butanimidate (1I).**

Following **GP3**, nitrile **D6** (525 mg, 3.0 mmol) was reacted with CH<sub>3</sub>OH (1.15 g, 1.45 mL, 36.0 mmol) and AcCl (1.88 g, 1.7 mL, 24.0 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate **methyl 4-(4-methoxyphenyl)butanimidate hydrochloride 1L** (680 mg, 93%) as a white solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated NaHCO<sub>3</sub> solution to obtain the **methyl 4-(4-methoxyphenyl)butanimidate (1I)** as a colorless oil.

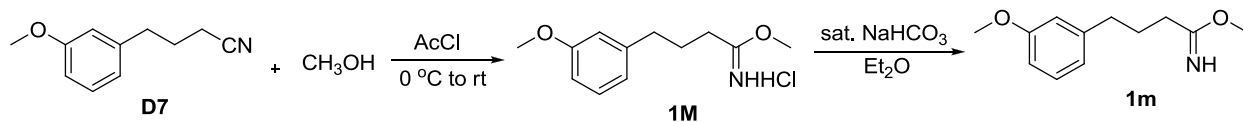
**R<sub>f</sub>** = 0.50 (90:10 hexanes/EtOAc).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.08 (d,  $J$  = 8.0 Hz, 2H), 6.83 (d,  $J$  = 8.0 Hz, 2H), 5.45 (br s, 1H), 3.78 (s, 3H), 3.70 (s, 3H), 2.58 (t,  $J$  = 8.0 Hz, 2H), 2.25 (t,  $J$  = 8.0 Hz, 2H), 1.85 (quint,  $J$  = 8.0 Hz, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 173.3, 157.9, 133.4, 129.3, 113.8, 55.2, 52.8, 34.8, 34.1, 27.9.

**HRMS (ESI-TOF)  $m/z$ :** calc'd for C<sub>15</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 208.1332, found 208.1334.

**IR (ATR)  $\text{cm}^{-1}$ :** 3323, 3004, 2943, 1648, 1512, 1243, 1093, 833.



**Methyl 4-(3-methoxyphenyl)butanimidate (1m).**

Following **GP3**, nitrile **D7** (525 mg, 3.0 mmol) was reacted with  $\text{CH}_3\text{OH}$  (1.15 g, 1.45 mL, 36.0 mmol) and  $\text{AcCl}$  (1.88 g, 1.7 mL, 24.0 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate **methyl 4-(3-methoxyphenyl)butanimidate hydrochloride 1M** (600 mg, 82%) as a white solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated  $\text{NaHCO}_3$  solution to obtain the **methyl 4-(3-methoxyphenyl)butanimidate (1m)** as a colorless oil.

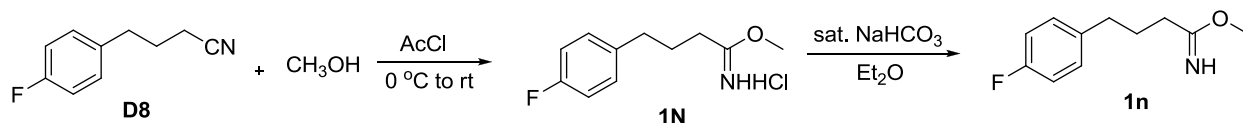
$R_f = 0.50$  (90:10 hexanes/ $\text{EtOAc}$ ).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.20$  (t,  $J = 8.0$  Hz, 1H), 6.77-6.72 (m, 3H), 5.52 (br s, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 2.61 (t,  $J = 7.6$  Hz, 2H), 2.26 (t,  $J = 8.0$  Hz, 2H), 1.88 (quint,  $J = 8.0$  Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 173.2, 159.7, 142.9, 129.4, 120.8, 114.2, 111.2, 55.1, 52.8, 35.0, 34.8, 27.5$ .

**HRMS (ESI-TOF)  $m/z$ :** calc'd for  $\text{C}_{15}\text{H}_{18}\text{NO}_2$   $[\text{M}+\text{H}]^+$  208.1332, found 208.1331.

**IR (ATR)  $\text{cm}^{-1}$ :** 3320, 2943, 2854, 1651, 1443, 1260, 1088, 852.



**Methyl 4-(4-fluorophenyl)butanimidate (1n).**

Following **GP3**, nitrile **D8** (489 mg, 3.0 mmol) was reacted with CH<sub>3</sub>OH (1.15 g, 1.45 mL, 36.0 mmol) and AcCl (1.88 g, 1.7 mL, 24.0 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate **methyl 4-(4-fluorophenyl)butanimidate hydrochloride 1N** (650 mg, 94%) as a white solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated NaHCO<sub>3</sub> solution to obtain the **methyl 4-(4-fluorophenyl)butanimidate (1n)** as a colorless oil.

**R<sub>f</sub>** = 0.50 (90:10 hexanes/EtOAc).

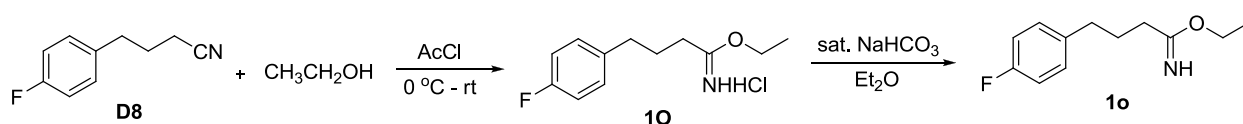
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.11 (dd,  $J$  = 8.0, 4.0 Hz, 2H), 6.96 (t,  $J$  = 8.0 Hz, 2H), 5.50 (br s, 1H), 3.70 (s, 3H), 2.61 (t,  $J$  = 8.0 Hz, 2H), 2.25 (t,  $J$  = 8.0 Hz, 2H), 1.86 (quint,  $J$  = 8.0 Hz, 2H);

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 173.1, 162.55 and 160.12 (d,  $J_{(C-F)}$  = 243 Hz), 136.87 and 136.84 (d,  $J_{(C-F)}$  = 3.0 Hz), 129.74 and 129.67 (d,  $J_{(C-F)}$  = 7.0 Hz), 115.23 and 115.02 (d,  $J_{(C-F)}$  = 21.0 Hz), 52.9, 34.8, 34.2, 27.8;

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  = -117.41.

**HRMS (ESI-TOF)  $m/z$ :** calc'd for C<sub>11</sub>H<sub>15</sub>FNO [M+H]<sup>+</sup> 196.1132, found 196.1131.

**IR (ATR) cm<sup>-1</sup>:** 3320, 2946, 2863, 1651, 1512, 1443, 1218, 1091, 830.



#### **Ethyl 4-(4-fluorophenyl)butanimidate (1o)**

Following **GP3**, nitrile **D8** (220 mg, 1.35 mmol) was reacted with CH<sub>3</sub>CH<sub>2</sub>OH (0.75 g, 0.94 mL, 16.2 mmol) and AcCl (0.85 g, 0.77 mL, 10.80 mmol) for 12 h at rt in 50 mL round bottom flask. The product was dried under high vacuum to isolate **ethyl 4-(4-fluorophenyl) butanimidate 1O** (310 mg, 94%) as a white solid. Further, Imidate hydrochloride salt (0.5 mmol) was hydrolyzed

with a cooled saturated NaHCO<sub>3</sub> solution to obtain the **ethyl 4-(4-fluorophenyl)butanimidate (1o)** as a colorless oil.

**R<sub>f</sub>** = 0.50 (90:10 hexanes/EtOAc).

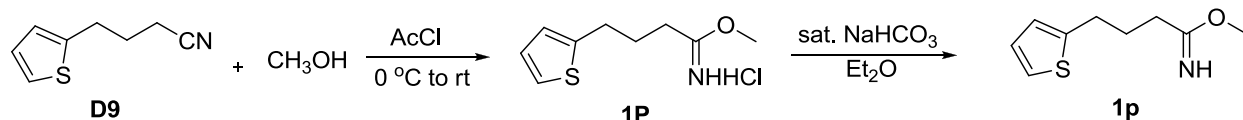
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.14-7.10 (m, 2H), 6.97 (t, *J* = 8.8 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.24 (t, *J* = 7.8 Hz, 2H), 1.86 (quint, *J* = 8.0 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):** δ = 172.6, 162.56 and 160.13 (d, *J*<sub>(C-F)</sub> = 243 Hz), 136.97 and 136.94 (d, *J*<sub>(C-F)</sub> = 3.0 Hz), 129.77 and 129.69 (d, *J*<sub>(C-F)</sub> = 8.0 Hz), 115.24 and 115.03 (d, *J*<sub>(C-F)</sub> = 21.0 Hz), 61.2, 35.1, 34.2, 27.8, 14.2.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ = -117.44.

**HRMS (ESI-TOF) *m/z*:** calc'd for C<sub>12</sub>H<sub>17</sub>FNO [M+H]<sup>+</sup> 210.1289, found 210.1290.

**IR (ATR) cm<sup>-1</sup>:** 3324, 2978, 2939, 1644, 1512, 1222, 1092, 830.



**Methyl 4-(thiophen-2-yl)butanimidate (1p).**

Following **GP3**, nitrile **D9** (375 mg, 2.5 mmol) was reacted with CH<sub>3</sub>OH (960 mg, 1.21 mL, 30.0 mmol) and AcCl (1.57 g, 1.4 mL, 20.0 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate the **methyl 4-(thiophen-2-yl)butanimidate hydrochloride 1P** (450 mg, 82%) as brown solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated NaHCO<sub>3</sub> solution to obtain the **methyl 4-(thiophen-2-yl)butanimidate (1p)** as a brown oil.

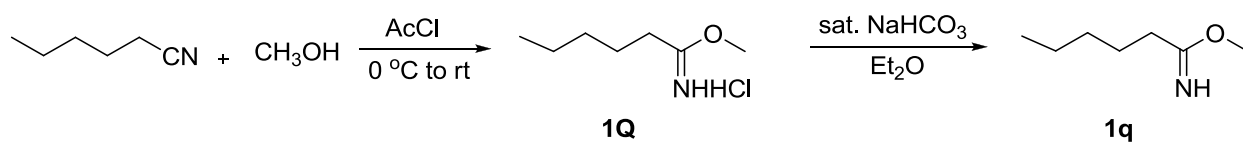
**R<sub>f</sub>** = 0.60 (90:10 hexanes/EtOAc).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.13 (d, *J* = 8.0 Hz, 1H), 6.93-6.91 (m, 1H), 6.80 (d, *J* = 4.0 Hz, 1H), 3.70 (s, 3H), 2.86 (t, *J* = 8.0 Hz, 2H), 2.31 (t, *J* = 8.0 Hz, 2H), 1.94 (quint, *J* = 8.0 Hz, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):** δ = 172.8, 144.0, 126.8, 124.5, 123.3, 52.8, 34.7, 29.0, 28.0.

**HRMS (ESI-TOF) *m/z*:** calc'd for C<sub>9</sub>H<sub>14</sub>NOS [M+H]<sup>+</sup> 184.0791, found 184.0796.

**IR (ATR) cm<sup>-1</sup>:** 3320, 2943, 2860, 1648, 1440, 1362, 1091, 841.



#### Methyl hexanimidate (1q).

Following **GP3**, nitrile (243 mg, 2.5 mmol) was reacted with CH<sub>3</sub>OH (960 mg, 1.21 mL, 30.0 mmol) and AcCl (1.57 g, 1.43 mL, 20.0 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate **methyl hexanimidate hydrochloride 1Q** (386 mg, 94%) as a white solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated NaHCO<sub>3</sub> solution to obtain the **methyl hexanimidate (1o)** as a colorless oil.

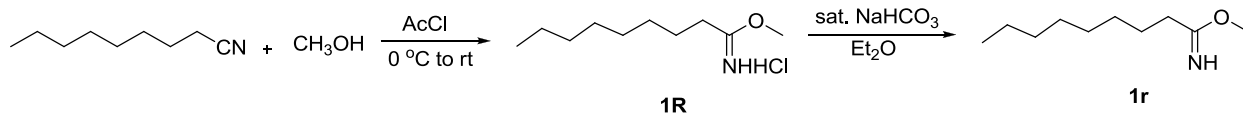
**R<sub>f</sub>** = 0.50 (90:10 hexanes/EtOAc).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 3.69 (s, 3H), 2.22 (t, *J* = 8.0 Hz, 2H), 1.58-1.51 (m, 2H), 1.34 – 1.26 (m, 4H), 0.89 (t, *J* = 8.0 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):** δ = 173.7, 52.8, 35.3, 31.1, 25.7, 22.3, 13.9.

**HRMS (ESI-TOF) *m/z*:** calc'd for C<sub>7</sub>H<sub>16</sub>NO [M+H]<sup>+</sup> 130.1226, found 130.1229.

**IR (ATR) cm<sup>-1</sup>:** 3312, 2937, 2865, 1653, 1446, 1371, 1088.



#### Methyl nonanimidate (1r).

Following **GP3**, nitrile (695 mg, 5.0 mmol) was reacted with CH<sub>3</sub>OH (1.92 g, 2.42 mL, 60.0 mmol) and AcCl (3.14 g, 2.84 mL, 40.0 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate **methyl nonanimidate hydrochloride 1R** (625 mg, 60%) as a white solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated NaHCO<sub>3</sub> solution to obtain the **methyl nonanimidate (1r)** as a colorless oil.

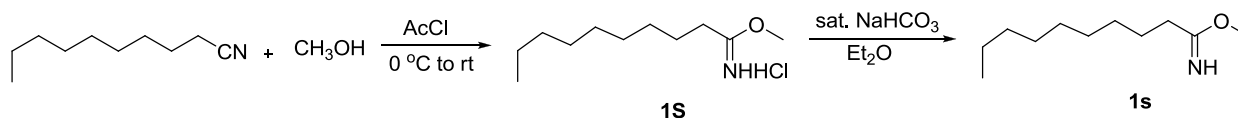
**R<sub>f</sub>** = 0.40 (90:10 hexanes/EtOAc).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 3.70 (s, 3H), 2.23 (t, *J* = 8.0 Hz, 2H), 1.58-1.50 (m, 2H), 1.29-1.26 (m, 10H), 0.87 (t, *J* = 8.0 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):** δ = 173.8, 52.8, 35.3, 31.8, 29.2, 29.1, 29.0, 26.0, 22.6, 14.0.

**HRMS (ESI-TOF) *m/z*:** calc'd for C<sub>10</sub>H<sub>22</sub>NO [M+H]<sup>+</sup> 172.1696, found 172.1700.

**IR (ATR) cm<sup>-1</sup>:** 3392, 2926, 2854, 1651, 1443, 1371, 1085.



**Methyl decanimidate (1s).**

Following **GP3**, nitrile (460 mg, 3.0 mmol) was reacted with CH<sub>3</sub>OH (1.15 g, 1.45 mL, 36.0 mmol) and AcCl (1.88 g, 1.70 mL, 24.0 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate the imidate hydrochloride salt **methyl decanimidate hydrochloride 1S** (450 mg, 68%) as a white solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated NaHCO<sub>3</sub> solution to obtain the **methyl decanimidate (1s)** as a colorless oil.

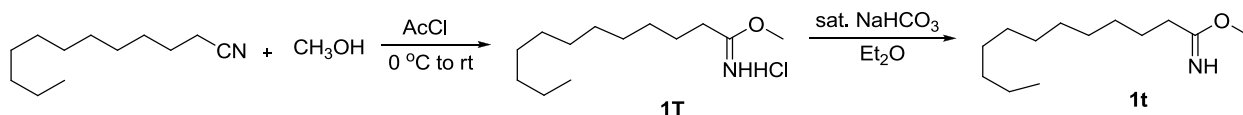
**R<sub>f</sub>** = 0.60 (90:10 hexanes/EtOAc).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 5.75 (br s, 1H), 3.64 (s, 3H), 2.18 (t, *J* = 8.0 Hz, 2H), 1.51-1.49 (m, 2H), 1.25-1.21 (m, 12H), 0.83 (t, *J* = 8.0 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 173.6, 52.7, 35.2, 31.7, 29.3, 29.2, 29.1, 28.9, 25.9, 22.5, 13.9.

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{11}\text{H}_{24}\text{NO}$   $[\text{M}+\text{H}]^+$  186.1852, found 186.1851.

IR (ATR)  $\text{cm}^{-1}$ : 3331, 2926, 2854, 1642, 1382, 1082, 905, 727.



### Methyl dodecanimide (1t).

Following **GP3**, nitrile (906 mg, 5.0 mmol) was reacted with  $\text{CH}_3\text{OH}$  (1.92 g, 2.42 mL, 60.0 mmol) and  $\text{AcCl}$  (3.14 g, 2.84 mL, 40.0 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate **methyl dodecanimide hydrochloride 1T** (1050 mg, 84%) as a white solid. Further, imide hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated  $\text{NaHCO}_3$  solution to obtain the **methyl dodecanimide (1t)** as a colorless oil.

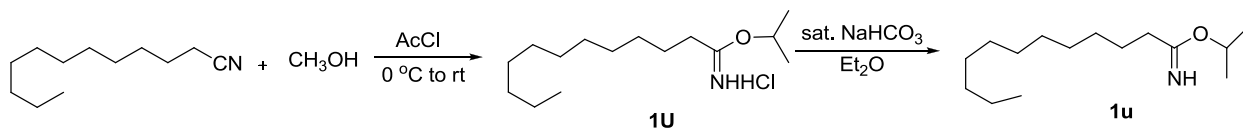
$R_f$  = 0.60 (90:10 hexanes/ $\text{EtOAc}$ ).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.69 (s, 3H), 2.22 (t,  $J$  = 8.0 Hz, 2H), 1.55-1.50 (m, 2H), 1.29-1.25 (m, 16H), 0.87 (t,  $J$  = 8.0 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 173.7, 52.8, 35.3, 31.9, 29.6, 29.4, 29.3, 29.2, 29.0, 26.0, 22.7, 14.1.

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{13}\text{H}_{28}\text{NO}$   $[\text{M}+\text{H}]^+$  214.2165, found 214.2171.

IR (ATR)  $\text{cm}^{-1}$ : 3328, 2924, 2852, 1656, 1537, 1443, 1085, 833.



### Isopropyl dodecanimide (1u).

Following **GP3**, nitrile (452 mg, 2.5 mmol) was reacted with  $\text{CH}_3\text{CHOHCH}_3$  (1.8 g, 2.29 mL, 30.0 mmol) and  $\text{AcCl}$  (1.57 g, 1.42 mL, 20.0 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate **isopropyl dodecanimide hydrochloride 1U** (692 mg, 84%) as a white solid. Further, imide hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated  $\text{NaHCO}_3$  solution to obtain the **isopropyl dodecanimide (1u)** as a colorless oil.

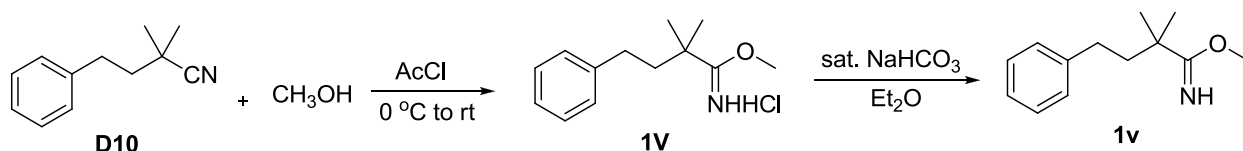
$R_f = 0.60$  (90:10 hexanes/EtOAc).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 6.30$  (br s, 1H), 5.03-4.94 (m, 1H), 2.13 (t,  $J = 8.0$  Hz, 2H), 1.52-1.45 (m, 2H), 1.25-1.22 (m, 16H), 1.20 (d,  $J = 8.0$  Hz, 6H), 0.83 (t,  $J = 8.0$  Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 172.3, 67.1, 36.1, 31.8, 29.5, 29.4, 29.3, 29.2, 28.9, 26.0, 22.6, 21.6, 14.0$ .

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{15}\text{H}_{32}\text{NO}$   $[\text{M}+\text{H}]^+$  242.2478, found 242.2477.

IR (ATR)  $\text{cm}^{-1}$ : 3390, 2924, 2854, 1642, 1373, 1074, 821.



### Methyl 2,2-dimethyl-4-phenylbutanimide (1v).

Following **GP3**, nitrile **D9** (480 mg, 2.17 mmol) was reacted with  $\text{CH}_3\text{OH}$  (833 mg, 1.05 mL, 26.04 mmol) and  $\text{AcCl}$  (1.36 g, 1.23 mL, 17.4 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate **methyl 2,2-dimethyl-4-phenylbutanimide hydrochloride 1V** (350 mg, 52%) as a white solid. Further, imide hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated  $\text{NaHCO}_3$  solution to obtain the **methyl 2,2-dimethyl-4-phenylbutanimide (1v)** as a colorless oil.

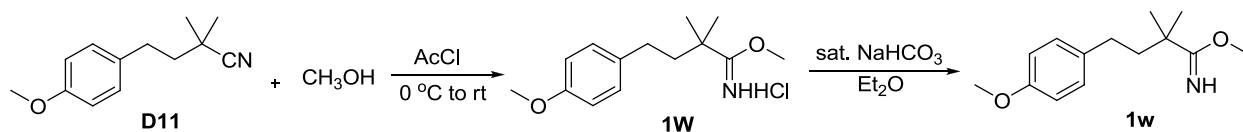
$R_f = 0.60$  (90:10 hexanes/EtOAc).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.28$  (t,  $J = 8.0$  Hz, 2H), 7.20-7.15 (m, 3H), 3.73 (s, 3H), 2.49-2.45 (m, 2H), 1.81-1.77 (m, 2H), 1.22 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 178.0, 142.3, 128.3, 128.2, 125.8, 53.1, 42.7, 41.3, 31.5, 25.8$ .

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{13}\text{H}_{20}\text{NO}$   $[\text{M}+\text{H}]^+$  206.1539, found 206.1544.

IR (ATR)  $\text{cm}^{-1}$ : 3351, 3023, 2949, 2863, 1637, 1457, 1337, 1077, 836.



#### Methyl 4-(4-methoxyphenyl)-2,2-dimethylbutanimidate (1w).

Following **GP3**, nitrile **D11** (350 mg, 1.72 mmol) was reacted with  $\text{CH}_3\text{OH}$  (660 mg, 833  $\mu\text{L}$ , 20.64 mmol) and  $\text{AcCl}$  (1.08 g, 978  $\mu\text{L}$ , 13.76 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate **methyl 4-(4-methoxyphenyl)-2,2-dimethylbutanimidate hydrochloride 1W** (330mg, 71%) as a white solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated  $\text{NaHCO}_3$  solution to obtain the **methyl 4-(4-methoxyphenyl)-2,2-dimethylbutanimidate (1w)** as a colorless oil.

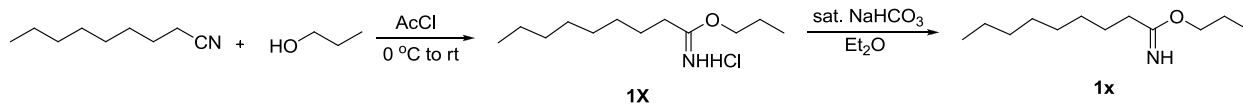
$R_f = 0.50$  (90:10 hexanes/EtOAc).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.07$  (d,  $J = 8.6$  Hz, 2H), 6.82 (d,  $J = 8.6$  Hz, 2H), 3.78 (s, 3H), 3.72 (s, 3H), 2.42-2.38 (m, 2H), 1.77-1.72 (m, 2H), 1.20 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 178.1, 157.7, 134.4, 129.1, 113.8, 55.2, 53.1, 42.9, 41.3, 30.5, 25.8$ .

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{14}\text{H}_{22}\text{NO}_2$   $[\text{M}+\text{H}]^+$  236.1645, found 236.1659.

IR (ATR)  $\text{cm}^{-1}$ : 3345, 2949, 2840, 1642, 1509, 1243, 1082, 821.



### Propyl nonanimidate (**1x**).

Following **GP3**, nitrile (695 mg, 5.0 mmol) was reacted with  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  (3.60 g, 4.5 mL, 60.0 mmol), and  $\text{AcCl}$  (3.14 g, 2.84 mL, 40.0 mmol) for 12 h at rt in 100 mL round bottom flask. The product was dried under high vacuum to isolate **propyl nonanimidate hydrochloride 1X** (950 mg, 81%) as a white solid. Further, imidate hydrochloride salt (0.5 mmol) was hydrolyzed with a cooled saturated  $\text{NaHCO}_3$  solution to obtain the **propyl nonanimidate (1x)** as a colorless oil.

$R_f = 0.40$  (90:10 hexanes/EtOAc).

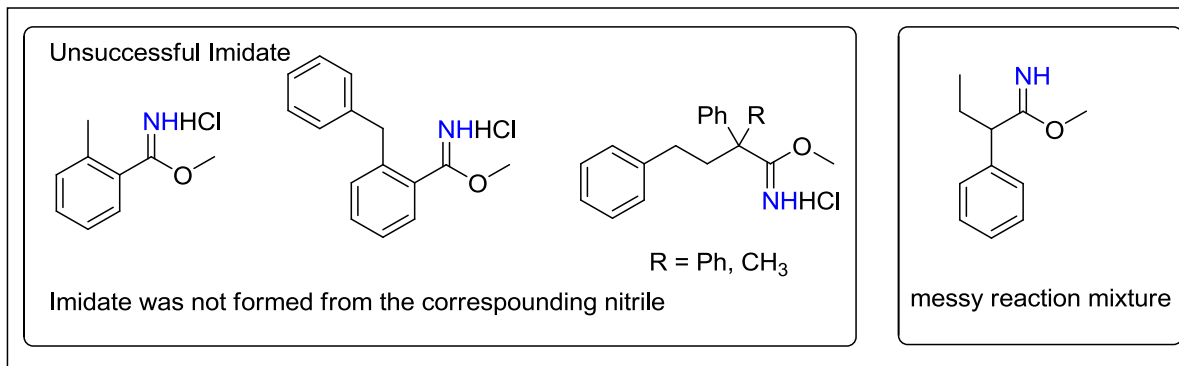
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta = 6.82$  (s, 1H), 3.99 (t,  $J = 6.8$  Hz, 2H), 2.22 (t,  $J = 7.8$  Hz, 2H), 1.73-1.64 (m, 2H), 1.58-1.51 (m, 2H), 1.28-1.22 (m, 10H), 0.96 (t,  $J = 7.4$  Hz, 3H), 0.87 (t,  $J = 6.7$  Hz, 3H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta = 173.4, 66.9, 35.7, 31.8, 29.3, 29.1, 29.0, 26.1, 22.6, 22.0, 14.1, 10.5$ .

**HRMS (ESI-TOF)  $m/z$ :** calc'd for  $\text{C}_{12}\text{H}_{26}\text{NO}$   $[\text{M}+\text{H}]^+$  200.2009, found 200.2010.

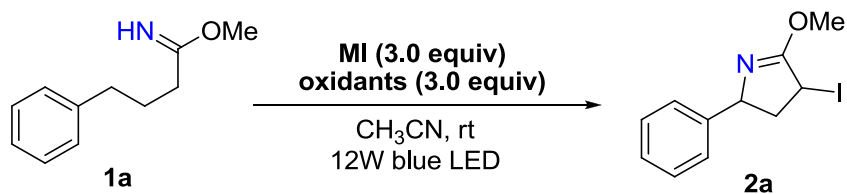
**IR (ATR)  $\text{cm}^{-1}$ :** 3394, 2928, 2856, 1650, 1445, 1372, 1084.

### c) Unsuccessful Substrates



### III. Optimization Tables for the $\gamma$ -C(sp<sup>3</sup>)-H Functionalization

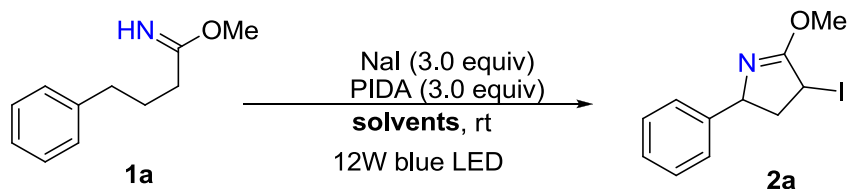
**Table 1:** Optimization of iodide source and oxidants<sup>a</sup>



S.No.	MI (3.0 equiv)	Oxidants (3.0 equiv)	Isolated yield of <b>2a</b> (%) <sup>b</sup>
1	NaI	PIDA	64
2	-	PIDA	0
3	NaI	-	0
4	KI	PIDA	48
5	TBAI	PIDA	41
6	NH <sub>4</sub> I	PIDA	0
7	I <sub>2</sub>	PIDA	trace
8	NaI	PIFA	0
9	NaI	HTIB	0
10	NaI	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0
11	NaI	KHSO <sub>5</sub>	0
12	NaI	TBHP in decane	0

<sup>a</sup>Reaction conditions: **1a** (0.30 mmol), MI (3.0 equiv), oxidant (3.0 equiv) in CH<sub>3</sub>CN (3.0 mL) at a distance of ~8 cm from a 12W blue LED at rt for 18 h. <sup>b</sup>Isolated yield of the product after column chromatography.

**Table 2:** Optimization of solvents<sup>a</sup>

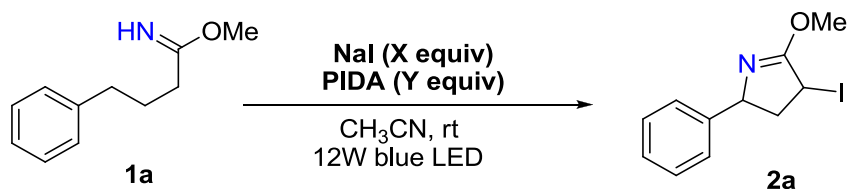


S.No.	Solvents	Isolated yield of <b>2a</b> (%) <sup>b</sup>
1	CH <sub>3</sub> CN	64
2	DCE	0
3	DCM	trace
4	Toluene	Trace
5	Acetone	0
6	1,4-Dioxane	46

7	DMF	37
8	DMSO	0
9 <sup>c</sup>	MeCN/HFIP	65
10 <sup>c</sup>	MeCN /TFE	67
11 <sup>c</sup>	MeCN /PhCF <sub>3</sub>	63

<sup>a</sup>Reaction conditions: **1a** (0.30 mmol), NaI (3.0 equiv), PIDA (3.0 equiv) in solvent (3.0 mL) at a distance of ~8 cm from a 12W blue LED at rt for 18 h. <sup>b</sup>Isolated yield of the product after column chromatography. <sup>c</sup>Solvent ratio (1:1, 3.0 mL), **HFIP**: 1,1,1,3,3,3-Hexafluoro-2-propanol, **TFE**: 2,2,2-Trifluoroethanol-1-ol.

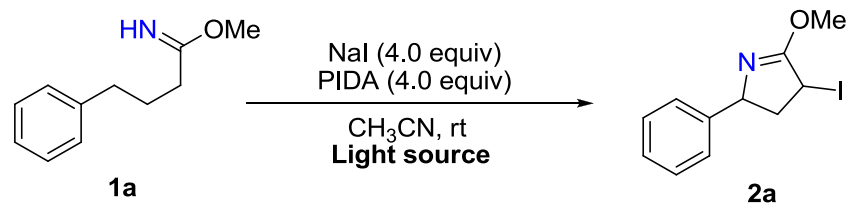
**Table 3:** Optimization of oxidants equivalents and ratios



S.No.	NaI (X Equiv)	PIDA (Y Equiv)	Isolated yield of 2a (%) <sup>b</sup>
1	1.5	3.0	48
2	2.5	3.0	62
3	3.0	3.0	67
4	3.5	3.0	65
5	4.0	4.0	71
6	5.0	5.0	62
7	6.0	6.0	45

<sup>a</sup>Reaction conditions: **1a** (0.30 mmol), NaI (X equiv), PIDA (Y equiv) in CH<sub>3</sub>CN (3.0 mL) at a distance of ~8 cm from a 12W blue LED at rt for 18 h. <sup>b</sup>Isolated yield of the product after column chromatography.

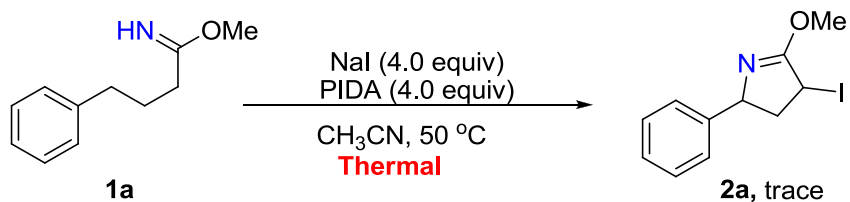
**Table 4:** Optimization of light source<sup>a</sup>



S.No.	Light Source	Isolated yield of 2a (%) <sup>b</sup>
1	under dark	0
2	7 W white LED	51
3	12 W blue LED	71
4	12 W white LED	54
5	12 W green LED	30

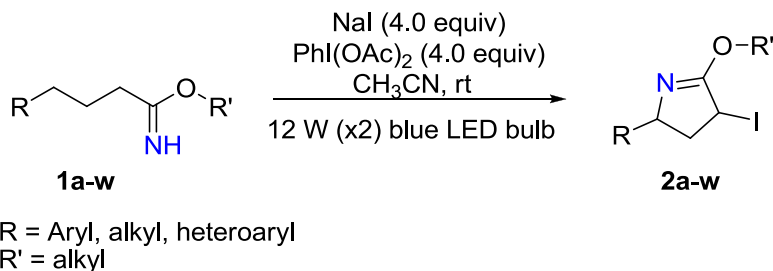
<sup>a</sup> Reaction conditions: **1a** (0.30 mmol), NaI (4.0 equiv), PIDA (4.0 equiv) in CH<sub>3</sub>CN (3.0 mL) at a distance of ~8 cm from a light source at rt for 18 h. <sup>b</sup> Isolated yield of the product after column chromatography.

**Table 5:** Reaction under thermal condition

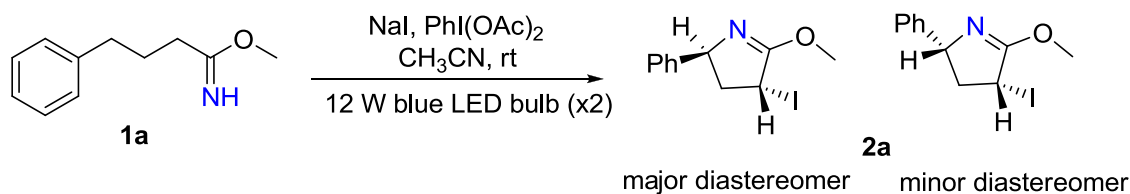


#### IV. Product (3,4-dihydro-2H-pyrrole) Synthesis:

##### General Procedure for the Preparation of 3,4-dihydro-2H-pyrroles (GP4):



To a 10 mL dram vial equipped with a magnetic stir bar was charged with imidate (0.3 mmol), PhI(OAc)<sub>2</sub> (1.2 mmol, 4.0 equiv) and NaI (1.2 mmol, 4.0 equiv). Dry acetonitrile (3 mL) was added to the reaction vial by using a glass syringe under N<sub>2</sub> and evacuated and backfilled with N<sub>2</sub> (x3). Further, the reaction vial was irradiated at a distance of ~8 cm from a 12 W blue LED (x2) at room temperature about 18 h until the reaction was completed, as monitored by TLC analysis. Upon completion, the reaction mixture was poured over 20% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (10 mL) and extracted with ethyl acetate (3 x 15 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was then concentrated in vacuo and the crude residue was purified by silica gel column chromatography (hexanes/ethyl acetate) to afford the corresponding 3,4-dihydro-2H-pyrrole.



#### 4-Iodo-5-methoxy-2-phenyl-3,4-dihydro-2H-pyrrole (**2a**)

Following **GP4**, imidate **1a** (53.1 mg, 0.3 mmol) was reacted with  $\text{PhI(OAc)}_2$  (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3 mL) for 16 hours. The product was purified via silica gel column chromatography (2% ethyl acetate/hexanes) to yield 3,4-dihydro-2H-pyrrole **2a** (68 mg, 75%, dr 3.2:1) as a colorless liquid.

$R_f$  = 0.6 (5% ethyl acetate/hexanes).

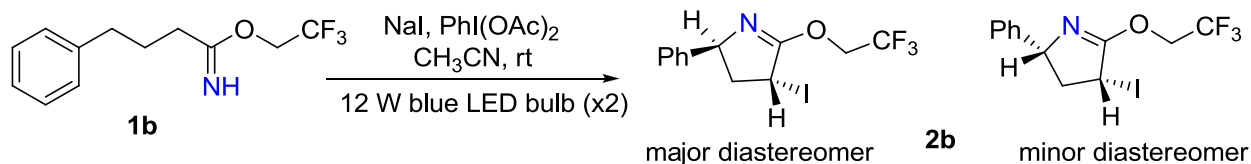
Relative stereochemistry determined by NOESY analysis.

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):** *Major diastereomer (trans)*  $\delta$  = 7.36-7.26 (m, 5H), 4.91-4.87 (m, 1H), 4.74 (d,  $J$  = 7.4 Hz, 1H), 3.97 (s, 3H), 2.80 (dd,  $J$  = 14.6, 5.8 Hz, 1H), 2.26-2.18 (m, 1H). *Minor diastereomer (cis)*  $\delta$  = 7.36-7.26 (m, 5H), 5.13-5.10 (m, 1H), 4.85-4.82 (m, 1H), 3.98 (s, 3H), 3.32-3.24 (m, 1H), 2.55-2.48 (m, 1H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):** *Major diastereomer (trans)*  $\delta$  = 173.1, 142.3, 128.5, 127.2, 126.4, 68.1, 56.6, 47.5, 18.2. *Minor diastereomer (cis)*  $\delta$  = 171.7, 143.3, 128.5, 127.2, 126.3, 69.5, 56.8, 45.5, 14.7.

**HRMS (ESI-TOF)  $m/z$ :** calc'd for  $\text{C}_{11}\text{H}_{13}\text{INO}$   $[\text{M}+\text{H}]^+$  302.0036, found 302.0046.

**IR (ATR)  $\text{cm}^{-1}$ :** 3029, 2940, 1631, 1440, 1332, 985.



#### 4-Iodo-2-phenyl-5-(2,2,2-trichloroethoxy)-3,4-dihydro-2H-pyrrole (**2b**)

Following **GP4**, imidate **1b** (74.0 mg, 0.3 mmol) was reacted with  $\text{PhI}(\text{OAc})_2$  (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3 mL) for 18 hours. Product was purified via silica gel column chromatography (2% ethyl acetate/hexanes) to yield 3,4-dihydro-2H-pyrrole **2b** (67 mg, 61%, dr 4.2:1) as a colorless liquid.

$R_f = 0.6$  (5% ethyl acetate/hexanes).

Relative stereochemistry determined by NOESY analysis.

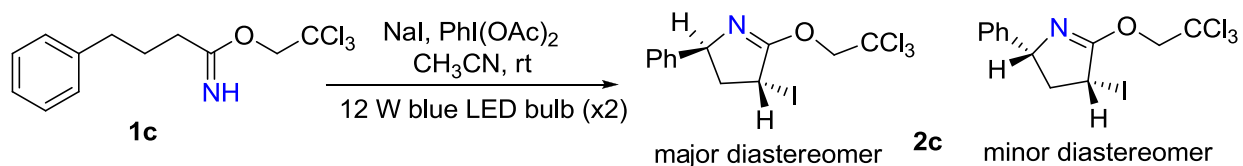
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):** *Major diastereomer (trans)*  $\delta = 7.38\text{--}7.34$  (m, 2H),  $7.30\text{--}7.28$  (m, 3H),  $4.93\text{--}4.88$  (m, 1H),  $4.83\text{--}4.73$  (m, 2H),  $4.69\text{--}4.60$  (m, 1H), 2.85 (dd,  $J = 14.7, 5.9$  Hz, 1H),  $2.35\text{--}2.27$  (m, 1H). *Minor diastereomer (cis):*  $\delta = 7.38\text{--}7.34$  (m, 2H),  $7.30\text{--}7.28$  (m, 3H),  $5.18\text{--}5.14$  (m, 1H),  $4.88\text{--}4.73$  (m, 1H),  $4.73\text{--}4.69$  (m, 2H),  $3.39\text{--}3.31$  (m, 1H),  $2.62\text{--}2.55$  (m, 1H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):** *Major diastereomer (trans)*  $\delta = 171.4, 141.5, 128.7, 127.5, 126.3, 123.0$  (q,  $J_{\text{C-F}} = 276$  Hz),  $68.0, 65.5$  (q,  $J_{\text{C-F}} = 36$  Hz),  $47.6, 16.4$ . *Minor diastereomer (cis):*  $\delta = 170.0, 142.5, 128.6, 127.4, 126.2, 123.0$  (q,  $J_{\text{C-F}} = 276$  Hz),  $69.5, 65.5$  (q,  $J_{\text{C-F}} = 36$  Hz),  $45.5, 12.7$ .

**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):** *Major diastereomer (trans)*  $\delta = -73.83$ , *Minor diastereomer (cis):*  $\delta = -73.85$ .

**HRMS (ESI-TOF)  $m/z$ :** calc'd for  $\text{C}_{12}\text{H}_{12}\text{F}_3\text{INO}$   $[\text{M}+\text{H}]^+$  369.9910, found 369.9935.

**IR (ATR)  $\text{cm}^{-1}$ :** 3035, 2965, 1640, 1340, 1265, 1163, 1038.



#### 4-Iodo-2-phenyl-5-(2,2,2-trichloroethoxy)-3,4-dihydro-2H-pyrrole (**2c**)

Following **GP4**, imidate **1c** (88.0 mg, 0.3 mmol) was reacted with  $\text{PhI}(\text{OAc})_2$  (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3 mL) for 15 hours. Product was purified via

silica gel column chromatography (2% ethyl acetate/hexanes) to yield 3,4-dihydro-2H-pyrrole **2c** (68 mg, 55%, dr 3.2:1) as a colorless liquid.

$R_f$  = 0.6 (5% ethyl acetate/hexanes).

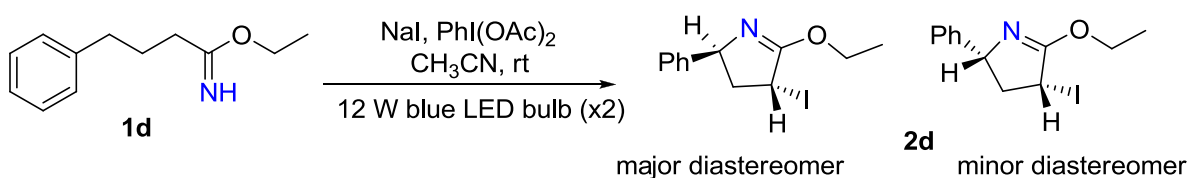
Relative stereochemistry determined by NOESY analysis.

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):** Major diastereomer (*trans*)  $\delta$  = 7.37-7.28 (m, 5H), 5.08-4.96 (m, 2H), 4.93- 4.90 (m, 1H), 4.85 (d,  $J$  = 7.5 Hz, 1H), 2.89 (dd,  $J$  = 14.7, 6.7 Hz, 1H), 2.36-2.28 (m, 1H). Minor diastereomer (*cis*):  $\delta$  = 7.37-7.28 (m, 5H), 5.19-5.16 (m, 1H), 5.08-4.96 (m, 2H), 4.94-4.92 (m, 1H), 3.40-3.32 (m, 1H), 2.63-2.56 (m, 1H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):** Major diastereomer (*trans*)  $\delta$  = 171.4, 141.6, 128.7, 127.5, 126.4, 94.8, 78.5, 68.2, 47.5, 16.9. Minor diastereomer (*cis*):  $\delta$  = 171.4, 141.6, 128.6, 127.4, 126.3, 94.8, 78.7, 69.8, 45.4, 13.2.

**HRMS (ESI-TOF)  $m/z$ :** calc'd for  $\text{C}_{12}\text{H}_{12}\text{Cl}_3\text{INO}$   $[\text{M}+\text{H}]^+$  417.9024, found 417.9020.

**IR (ATR)  $\text{cm}^{-1}$ :** 2921, 2852, 1629, 1384, 1318, 1027, 808.



### 5-Ethoxy-4-iodo-2-phenyl-3,4-dihydro-2H-pyrrole (**2d**)

Following **GP4**, imidate **1d** (76.0 mg, 0.3 mmol) was reacted with  $\text{PhI}(\text{OAc})_2$  (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3 mL) for 15 hours. Product was purified via silica gel column chromatography (2% ethyl acetate/hexanes) to yield 3,4-dihydro-2H-pyrrole **2d** (51 mg, 54%, dr 3.5:1) as a colorless liquid.

$R_f$  = 0.6 (5% ethyl acetate/hexanes).

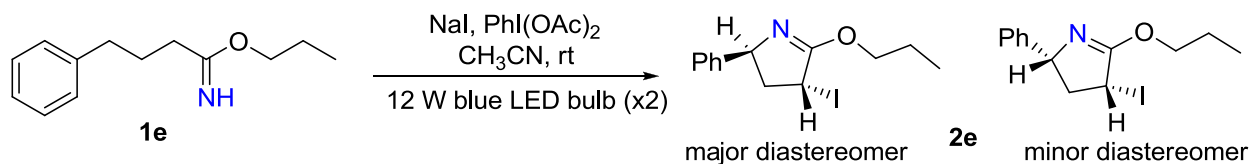
Relative stereochemistry determined by NOESY analysis.

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):** Major diastereomer (*trans*)  $\delta$  = 7.36-7.24 (m, 5H), 4.89-4.86 (m, 1H), 4.72 (d,  $J$  = 7.3 Hz, 1H), 4.43- 4.31 (m, 2H), 2.78 (dd,  $J$  = 15.1, 6.3 Hz, 1H), 2.22-2.14 (m, 1H), 1.38 (t,  $J$  = 7.2 Hz, 3H). Minor diastereomer (*cis*):  $\delta$  = 7.36-7.24 (m, 5H), 5.14-5.10 (m, 1H), 4.84-4.80 (m, 1H), 4.43-4.431 (m, 2H), 3.29-3.21 (m, 1H), 2.53-2.56 (m, 1H), 1.41 (t,  $J$  = 7.2 Hz, 3H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):** Major diastereomer (*trans*):  $\delta$  = 172.5, 142.5, 128.5, 127.2, 126.4, 68.2, 65.3, 47.3, 19.1, 14.1. Minor diastereomer (*cis*):  $\delta$  = 171.1, 143.5, 128.4, 127.1, 126.3, 69.7, 65.5, 45.1, 15.4, 14.2.

**HRMS (ESI-TOF)  $m/z$ :** calc'd for  $\text{C}_{12}\text{H}_{15}\text{INO}$   $[\text{M}+\text{H}]^+$  316.0193, found 316.0221.

**IR (ATR)  $\text{cm}^{-1}$ :** 2976, 1623, 1446, 1323, 1171, 1024.



#### 4-Iodo-2-phenyl-5-propoxy-3,4-dihydro-2H-pyrrole (**2e**)

Following **GP4**, imidate **1e** (61.5 mg, 0.3 mmol) was reacted with PhI(OAc)<sub>2</sub> (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3 mL) for 17 hours. Product was purified via silica gel column chromatography (2% ethyl acetate/hexanes) to yield 3,4-dihydro-2H-pyrrole **2e** (55.0 mg, 56%, dr 3.2:1) as colorless liquid.

**R<sub>f</sub>** = 0.6 (5% ethyl acetate/hexanes).

Relative stereochemistry determined by NOESY analysis.

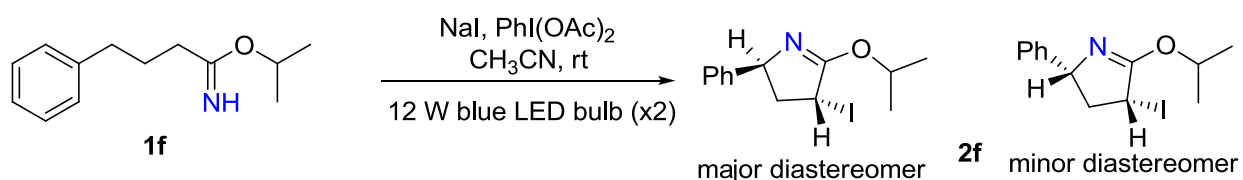
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):** Major diastereomer (*trans*)  $\delta$  = 7.34-7.24 (m, 5H), 4.89-4.85 (m, 1H), 4.74 (d,  $J$  = 7.3 Hz, 1H), 4.29-4.24 (m, 2H), 2.78 (dd,  $J$  = 14.2, 6.3 Hz, 1H), 2.22-2.14 (m, 1H), 1.80-1.76 (m, 2H), 1.02 (t,  $J$  = 7.2 Hz, 3H). Minor diastereomer (*cis*):  $\delta$  = 7.34-7.24 (m,

5H), 5.13-5.10 (m, 1H), 4.84-4.81 (m, 1H), 4.29-4.24 (m, 2H), 3.29-3.21 (m, 1H), 2.53-2.46 (m, 1H), 1.80-1.76 (m, 2H), 1.02 (t,  $J = 7.2$  Hz, 3H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):** *Major diastereomer (trans):*  $\delta = 172.7, 142.5, 128.5, 127.2, 126.4, 71.0, 68.2, 47.3, 22.0, 19.1, 10.4$ . *Minor diastereomer (cis):*  $\delta = 171.2, 143.5, 128.5, 127.1, 126.3, 71.2, 69.7, 45.2, 22.7, 15.4, 14.1$ .

**HRMS (ESI-TOF)  $m/z$ :** calc'd for  $\text{C}_{13}\text{H}_{17}\text{INO}$   $[\text{M}+\text{H}]^+$  330.0349, found 330.0373.

**IR (ATR)  $\text{cm}^{-1}$ :** 2921, 1629, 1451, 1323, 1262, 957.



#### 4-Iodo-5-isopropoxy-2-phenyl-3,4-dihydro-2H-pyrrole (**2f**)

Following **GP4**, imidate **1f** (61.5 mg, 0.3 mmol) was reacted with  $\text{PhI}(\text{OAc})_2$  (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3 mL) for 18 hours. Product was purified via silica gel column chromatography (2% ethyl acetate/hexanes) to yield 3,4-dihydro-2H-pyrrole **2f** (57 mg, 58%, dr 4.3:1) as a colorless liquid.

**$R_f$**  = 0.6 (5% ethyl acetate/hexanes).

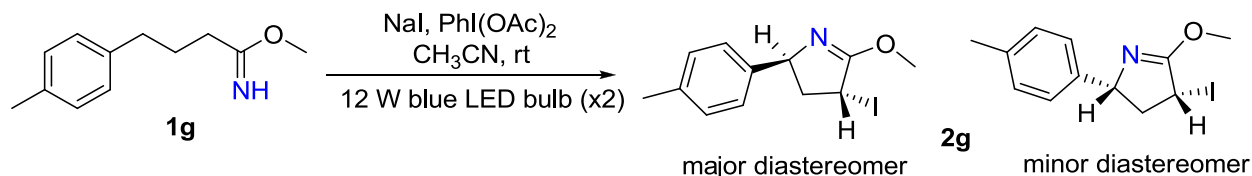
Relative stereochemistry determined by NOESY analysis.

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):** *Major diastereomer (trans)*  $\delta = 7.34\text{--}7.25$  (m, 5H), 5.17-5.11 (m, 1H), 4.86 (dd,  $J = 8.0, 5.8$  Hz, 1H), 4.69 (d,  $J = 7.3$  Hz, 1H), 2.76 (dd,  $J = 13.9, 5.8$  Hz, 1H), 2.17-2.09 (m, 1H), 1.38 (d,  $J = 6.2$  Hz, 3H), 1.33 (d,  $J = 6.2$  Hz, 3H). *Minor diastereomer (cis):*  $\delta = 7.34\text{--}7.25$  (m, 5H), 5.17-5.11 (m, 2H), 4.80-4.76 (m, 1H), 3.27-3.19 (m, 1H), 2.50-2.44 (m, 1H), 1.42 (d,  $J = 6.2$  Hz, 3H), 1.35 (d,  $J = 6.2$  Hz, 3H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):** Major diastereomer (*trans*):  $\delta = 171.8, 142.6, 128.5, 127.1, 126.4, 72.2, 68.3, 47.0, 21.9, 20.9, 20.4$ . Minor diastereomer (*cis*):  $\delta = 170.5, 143.6, 128.4, 127.0, 126.3, 72.5, 69.8, 44.7, 21.2, 16.3$ .

**HRMS (ESI-TOF)  $m/z$ :** calc'd for  $\text{C}_{13}\text{H}_{17}\text{INO}$   $[\text{M}+\text{H}]^+$  330.0349, found 330.0378.

**IR (ATR)  $\text{cm}^{-1}$ :** 2976, 1623, 1371, 1315, 1197, 921.



#### 4-Iodo-5-methoxy-2-p-tolyl-3,4-dihydro-2H-pyrrole (**2g**)

Following **GP4**, imide **1g** (57.1 mg, 0.30 mmol) was reacted with PhI(OAc)<sub>2</sub> (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3.0 mL) for 15 hours. Product was purified via silica gel column chromatography (2% ethyl acetate/hexanes) to yield **3,4-dihydro-2H-pyrrole 2g** (66 mg, 70%, dr 19:1) as a colorless liquid.

**R<sub>f</sub>** = 0.6 (5% ethyl acetate/hexanes).

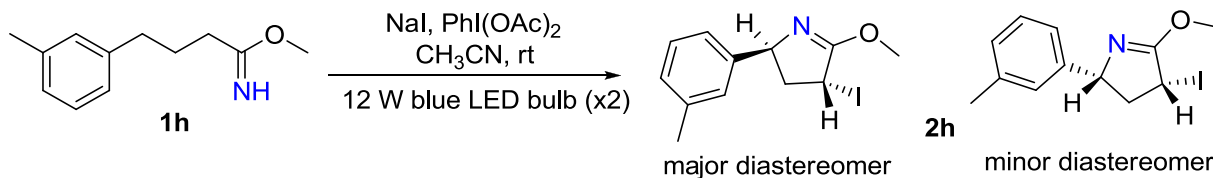
Relative stereochemistry determined by NOESY analysis.

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta = 7.20$  (d,  $J = 8.0$  Hz, 2H),  $7.15$  (d,  $J = 8.0$  Hz, 2H),  $4.85$  (dd,  $J = 7.7, 6.1$  Hz, 1H),  $4.73$  (d,  $J = 7.4$  Hz, 1H),  $3.96$  (s, 3H),  $2.78$  (dd,  $J = 14.6, 5.8$  Hz, 1H),  $2.34$  (s, 3H),  $2.24$ - $2.17$  (m, 1H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta = 173.0, 139.3, 136.8, 129.2, 126.3, 67.9, 56.5, 47.5, 21.1, 18.4$ .

**HRMS (ESI-TOF)  $m/z$ :** calc'd for  $\text{C}_{12}\text{H}_{15}\text{INO}$   $[\text{M}+\text{H}]^+$  316.0193, found 316.0216.

**IR (ATR)  $\text{cm}^{-1}$ :** 2924, 1631, 1440, 1332, 1262, 991.



#### 4-Iodo-5-methoxy-2-m-tolyl-3,4-dihydro-2H-pyrrole (**2h**)

Following **GP4**, imidate **1h** (57.1 mg, 0.30 mmol) was reacted with PhI(OAc)<sub>2</sub> (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3.0 mL) for 15 hours. Product was purified via silica gel column chromatography (2% ethyl acetate/hexanes) to yield **3,4-dihydro-2H-pyrrole 2h** (58 mg, 62%, dr 8.1:1) as a colorless liquid.

**R<sub>f</sub>** = 0.6 (5% ethyl acetate/hexanes).

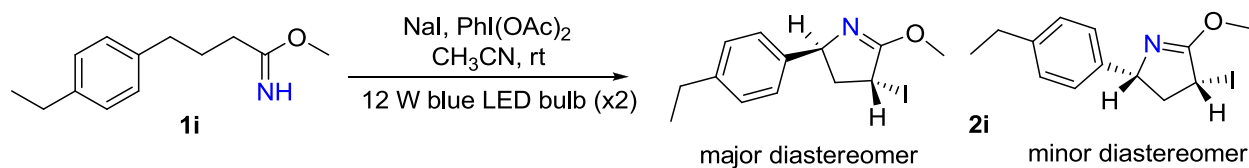
Relative stereochemistry determined by NOESY analysis.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.23 (t,  $J$  = 7.6 Hz, 1H), 7.12-7.06 (m, 3H), 4.85 (dd,  $J$  = 8.0, 6.0 Hz, 1H), 4.73 (d,  $J$  = 7.4 Hz, 1H), 3.97 (s, 3H), 2.78 (dd,  $J$  = 15.1, 5.4 Hz, 1H), 2.35 (s, 3H), 2.25-2.18 (m, 1H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 173.1, 142.2, 138.2, 128.4, 128.0, 127.1, 123.5, 68.1, 56.6, 47.5, 21.4, 18.4.

**HRMS (ESI-TOF)  $m/z$ :** calc'd for C<sub>12</sub>H<sub>15</sub>INO [M+H]<sup>+</sup> 316.0193, found 316.0213.

**IR (ATR) cm<sup>-1</sup>:** 3018, 2918, 1634, 1443, 1323, 1260, 991.



#### 2-(4-Ethylphenyl)-4-iodo-5-methoxy-3,4-dihydro-2H-pyrrole (**2i**)

Following **GP4**, imidate **1i** (61.5 mg, 0.30 mmol) was reacted with PhI(OAc)<sub>2</sub> (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3.0 mL) for 15 hours. Product was purified

via silica gel column chromatography (2% ethyl acetate/hexanes) to yield **3,4-dihydro-2H-pyrrole 2i** (58 mg, 59%, dr 19:1) as a colorless liquid.

$R_f$  = 0.6 (5% ethyl acetate/hexanes).

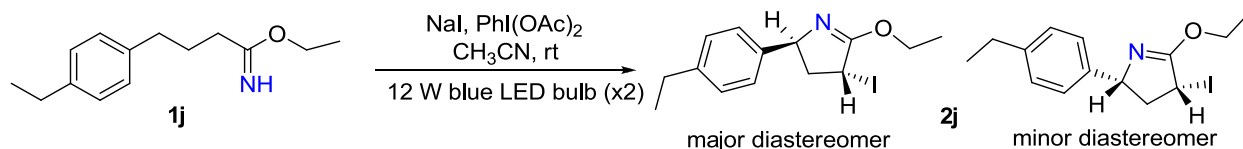
Relative stereochemistry determined by NOESY analysis.

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 7.23 (d,  $J$  = 8.1 Hz, 2H), 7.17 (d,  $J$  = 8.1 Hz, 2H), 4.86 (dd,  $J$  = 7.8, 6.0 Hz, 1H), 4.73 (d,  $J$  = 7.4 Hz, 1H), 3.96 (s, 3H), 2.78 (dd,  $J$  = 14.6, 5.8 Hz, 1H), 2.64 (q,  $J$  = 7.6 Hz, 2H), 2.27-2.19 (m, 1H), 1.22 (t,  $J$  = 7.6 Hz, 3H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 172.9, 143.3, 139.5, 128.0, 126.4, 68.0, 56.6, 47.5, 28.5, 18.4, 15.6.

**HRMS (ESI-TOF)  $m/z$ :** calc'd for  $\text{C}_{13}\text{H}_{17}\text{INO}$   $[\text{M}+\text{H}]^+$  330.0349, found 330.0357.

**IR (ATR)  $\text{cm}^{-1}$ :** 2960, 2871, 1631, 1443, 1329, 1260, 991, 824.



### 5-Ethoxy-2-(4-ethylphenyl)-4-iodo-3,4-dihydro-2H-pyrrole (**2j**)

Following **GP4**, imide **1j** (65.7 mg, 0.30 mmol) was reacted with  $\text{PhI}(\text{OAc})_2$  (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3.0 mL) for 15 hours. Product was purified via silica gel column chromatography (2% ethyl acetate/hexanes) to yield **3,4-dihydro-2H-pyrrole 2j** (52 mg, 50%, dr 10:1) as a colorless liquid.

$R_f$  = 0.7 (5% ethyl acetate/hexanes).

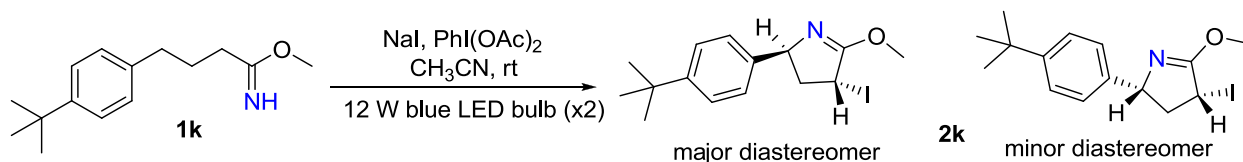
Relative stereochemistry determined by NOESY analysis.

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 7.22 (d,  $J$  = 8.2 Hz, 2H), 7.16 (d,  $J$  = 8.2 Hz, 2H), 4.84 (dd,  $J$  = 7.9, 5.9 Hz, 1H), 4.72 (d,  $J$  = 7.3 Hz, 1H), 4.41-4.31 (m, 2H), 2.76 (dd,  $J$  = 14.6, 5.8 Hz, 1H), 2.63 (q,  $J$  = 7.6 Hz, 2H), 2.22-2.14 (m, 1H), 1.37 (t,  $J$  = 7.2 Hz, 3H), 1.22 (t,  $J$  = 7.6 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 172.3, 143.2, 139.7, 128.0, 126.4, 68.1, 65.2, 47.3, 28.5, 19.3, 15.6, 14.2.

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{14}\text{H}_{19}\text{INO}$   $[\text{M}+\text{H}]^+$  344.0506, found 344.0513.

IR (ATR)  $\text{cm}^{-1}$ : 2967, 2877, 1633, 1326, 1261, 1025, 830.



### 2-(4-tert-butylphenyl)-4-iodo-5-methoxy-3,4-dihydro-2H-pyrrole (**2k**)

Following **GP4**, imidate **1k** (69.9 mg, 0.30 mmol) was reacted with  $\text{PhI}(\text{OAc})_2$  (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3.0 mL) for 18 hours. Product was purified via silica gel column chromatography (2% ethyl acetate/hexanes) to yield **3,4-dihydro-2H-pyrrole 2k** (70 mg, 65%, dr 9:1) as a colorless liquid.

$R_f$  = 0.6 (5% ethyl acetate/hexanes).

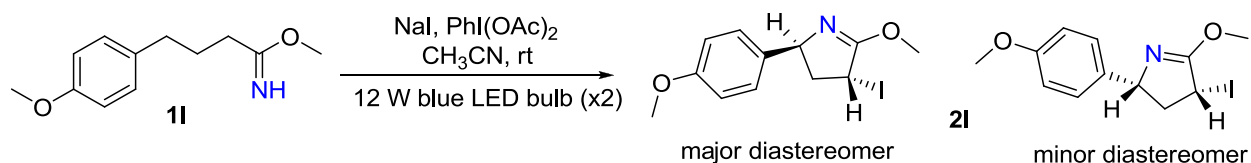
Relative stereochemistry determined by NOESY analysis.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.36 (d,  $J$  = 8.4 Hz, 2H), 7.24 (d,  $J$  = 8.4 Hz, 2H), 4.85 (dd,  $J$  = 7.9, 5.8 Hz, 1H), 4.74 (d,  $J$  = 7.4 Hz, 1H), 3.96 (s, 3H), 2.78 (dd,  $J$  = 14.6, 5.8 Hz, 1H), 2.29-2.21 (m, 1H), 1.31 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 172.9, 150.2, 139.2, 126.2, 125.5, 67.9, 56.6, 47.4, 34.5, 31.4, 18.5.

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{15}\text{H}_{21}\text{INO}$   $[\text{M}+\text{H}]^+$  358.0662, found 358.0662.

IR (ATR)  $\text{cm}^{-1}$ : 2954, 2860, 1629, 1443, 1257, 1107, 991, 824.



#### 4-Iodo-5-methoxy-2-(4-methoxyphenyl)-3,4-dihydro-2H-pyrrole (**2l**)

Following **GP4**, imidate **1l** (61.2 mg, 0.30 mmol) was reacted with PhI(OAc)<sub>2</sub> (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3.0 mL) for 15 hours. Product was purified via silica gel column chromatography (4% ethyl acetate/hexanes) to yield **3,4-dihydro-2H-pyrrole 2l** (62 mg, 63%, dr 4:1) as a colorless liquid.

**R<sub>f</sub>** = 0.4 (5% ethyl acetate/hexanes).

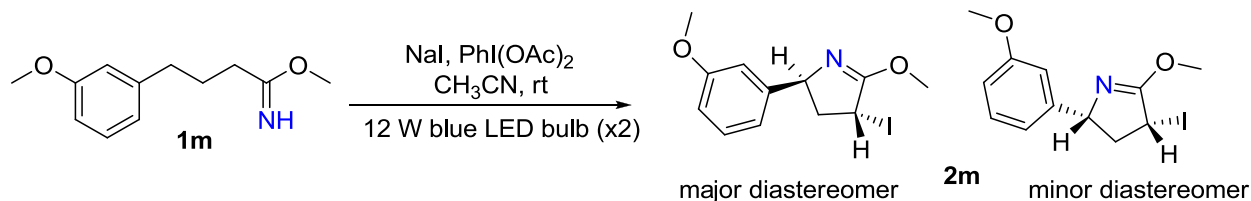
Relative stereochemistry determined by NOESY analysis.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** *Major diastereomer (trans):* δ = 7.23 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.83 (dd, *J* = 7.8, 5.8 Hz, 1H), 4.73 (d, *J* = 7.4 Hz, 1H), 3.95 (s, 3H), 3.80 (s, 3H), 2.76 (dd, *J* = 14.6, 5.8 Hz, 1H), 2.23-2.16 (m, 1H). *Minor diastereomer (cis):* δ = 7.23 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.08-5.05 (m, 1H), 4.83-4.80 (m, 1H), 3.97 (s, 3H), 3.81 (s, 3H), 3.29-3.21 (m, 1H), 2.52-2.46 (m, 1H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):** *Major diastereomer (trans):* δ = 172.9, 158.8, 134.4, 127.6, 113.9, 67.7, 56.6, 55.3, 47.6, 18.4. *Minor diastereomer (cis):* δ = 171.4, 158.7, 135.5, 127.5, 113.8, 69.1, 56.8, 55.3, 45.6, 14.8.

**HRMS (ESI-TOF) *m/z*:** calc'd for C<sub>12</sub>H<sub>15</sub>INO<sub>2</sub> [M+H]<sup>+</sup> 332.0142, found 332.0145.

**IR (ATR) cm<sup>-1</sup>:** 2993, 2946, 2840, 1631, 1509, 1332, 1240, 1174, 1030, 824.



#### 4-Iodo-5-methoxy-2-(3-methoxyphenyl)-3,4-dihydro-2H-pyrrole (2m)

Following **GP4**, imidate **1m** (61.2 mg, 0.30 mmol) was reacted with  $\text{PhI}(\text{OAc})_2$  (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3.0 mL) for 20 hours. Product was purified via silica gel column chromatography (4% ethyl acetate/hexanes) to yield **3,4-dihydro-2H-pyrrole 2m** (58 mg, 60%, dr 3.3:1) as a colorless liquid.

$R_f = 0.4$  (5% ethyl acetate/hexanes).

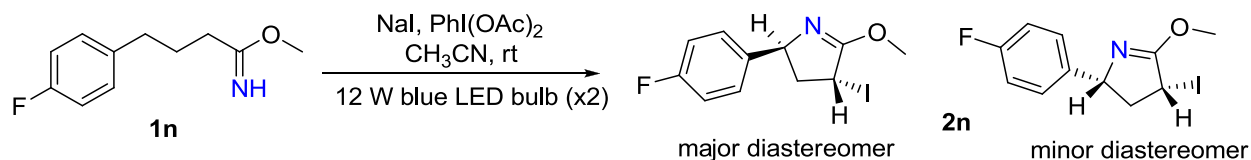
Relative stereochemistry determined by NOESY analysis.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): *Major diastereomer (trans)*:  $\delta = 7.26$  (t,  $J = 8.8$  Hz, 1H), 6.91-6.86 (m, 2H), 6.80 (d,  $J = 8.8$  Hz, 1H), 4.86 (dd,  $J = 7.8, 6.0$  Hz, 1H), 4.73 (d,  $J = 7.4$  Hz, 1H), 3.97 (s, 3H), 3.81 (s, 3H), 2.79 (dd,  $J = 14.6, 5.9$  Hz, 1H), 2.26-2.17 (m, 1H). *Minor diastereomer (cis)*:  $\delta = 7.26$  (t,  $J = 8.8$  Hz, 1H), 6.91-6.86 (m, 2H), 6.80 (d,  $J = 7.2$  Hz, 1H), 5.11-5.07 (m, 1H), 4.83-4.81 (m, 1H), 3.98 (s, 3H), 3.82 (s, 3H), 3.31-3.23 (m, 1H), 2.54-2.48 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ): *Major diastereomer (trans)*:  $\delta = 173.2, 159.8, 144.0, 129.6, 118.7, 112.5, 112.1, 68.0, 56.6, 55.2, 47.4, 18.2$ . *Minor diastereomer (cis)*:  $\delta = 171.8, 159.8, 145.0, 129.5, 118.7, 112.6, 112.0, 69.5, 56.8, 55.3, 45.3, 14.6$ .

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{11}\text{H}_{15}\text{INO}_2$   $[\text{M}+\text{H}]^+$  332.0142, found 332.0139.

IR (ATR)  $\text{cm}^{-1}$ : 2994, 2950, 2848, 1630, 1510, 1336, 1248, 1176, 1035, 832.



#### 2-(4-Fluorophenyl)-4-iodo-5-methoxy-3,4-dihydro-2H-pyrrole (2n)

Following **GP4**, imidate **1n** (58.5 mg, 0.30 mmol) was reacted with  $\text{PhI}(\text{OAc})_2$  (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3.0 mL) for 20 hours. Product was purified

via silica gel column chromatography (2% ethyl acetate/hexanes) to yield **3,4-dihydro-2H-pyrrole 2n** (54 mg, 56%, dr 9:1) as a colorless liquid.

$R_f$  = 0.6 (5% ethyl acetate/hexanes).

Relative stereochemistry determined by NOESY analysis.

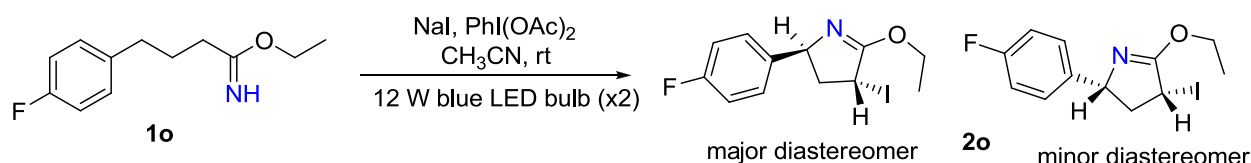
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.28 (dd,  $J$  = 8.8, 5.8 Hz, 2H), 7.02 (t,  $J$  = 8.8 Hz, 2H), 4.86 (dd,  $J$  = 7.8, 6.0 Hz, 1H), 4.72 (d,  $J$  = 7.4 Hz, 1H), 3.96 (s, 3H), 2.78 (dd,  $J$  = 14.6, 5.8 Hz, 1H), 2.21-2.13 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 173.3, 163.29 and 160.85 (d,  $J_{\text{C-F}}$  = 244.0 Hz), 138.1, 128.01 and 127.93 (d,  $J_{\text{C-F}}$  = 8.0 Hz), 115.46 and 115.25 (d,  $J_{\text{C-F}}$  = 21.0 Hz), 67.5, 56.6, 47.6, 18.0.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -115.7

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{11}\text{H}_{12}\text{FINO}$   $[\text{M}+\text{H}]^+$  319.9942, found 319.9935.

IR (ATR)  $\text{cm}^{-1}$ : 2987, 2946, 2857, 1631, 1507, 1329, 1221, 993, 833.



### 5-Ethoxy-2-(4-fluorophenyl)-4-iodo-3,4-dihydro-2H-pyrrole (**2o**)

Following **GP4**, imidate **1o** (62.7 mg, 0.30 mmol) was reacted with PhI(OAc)<sub>2</sub> (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3.0 mL) for 20 hours. Product was purified via silica gel column chromatography (2% ethyl acetate/hexanes) to yield **3,4-dihydro-2H-pyrrole 2o** (49 mg, 49%, dr 10:1) as a colorless liquid.

$R_f$  = 0.6 (5% ethyl acetate/hexanes).

Relative stereochemistry determined by NOESY analysis.

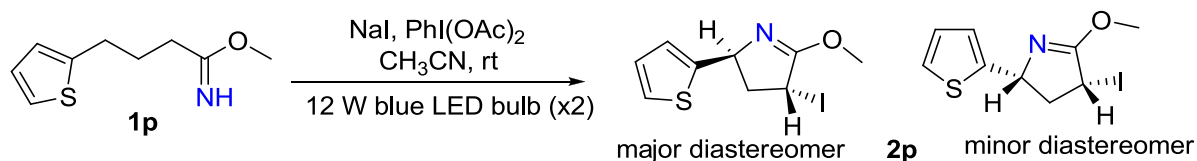
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.29-7.26 (m, 2H), 7.02 (t,  $J$  = 8.8 Hz, 2H), 4.85 (dd,  $J$  = 8.0, 5.8 Hz, 1H), 4.71 (d,  $J$  = 7.4 Hz, 1H), 4.40-4.30 (m, 2H), 2.76 (dd,  $J$  = 15.0, 6.0 Hz, 1H), 2.16-2.09 (m, 1H), 1.38 (t,  $J$  = 7.2 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 172.6, 163.27 and 160.84 (d,  $J_{\text{C-F}}$  = 243.0 Hz), 138.2, 128.02 and 127.94 (d,  $J_{\text{C-F}}$  = 8.0 Hz), 115.44 and 115.22 (d,  $J_{\text{C-F}}$  = 22.0 Hz), 67.6, 65.3, 47.4, 18.9, 14.1.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** *Major diastereomer (trans):*  $\delta$  = -115.8

**HRMS (ESI-TOF)  $m/z$ :** calc'd for C<sub>12</sub>H<sub>14</sub>FINO [M+H]<sup>+</sup> 334.0099, found 334.0109.

**IR (ATR) cm<sup>-1</sup>:** 2981, 2933, 1633, 1514, 1320, 1224, 1022, 830.



#### 4-Iodo-5-methoxy-2-(thiophen-2-yl)-3,4-dihydro-2H-pyrrole (**2p**)

Following **GP4**, imidate **1p** (55.0 mg, 0.30 mmol) was reacted with PhI(OAc)<sub>2</sub> (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3.0 mL) for 20 hours. Product was purified via silica gel column chromatography (2% ethyl acetate/hexanes) to yield **3,4-dihydro-2H-pyrrole 2p** (33 mg, 36%, dr 6.7:1) as a colorless liquid.

**R<sub>f</sub>** = 0.6 (5% ethyl acetate/hexanes).

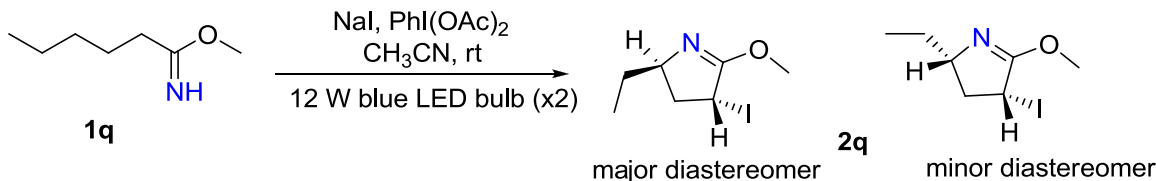
Relative stereochemistry determined by NOESY analysis.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.21 (d,  $J$  = 4.6 Hz, 1H), 6.98-6.96 (m, 2H), 5.17-5.14 (m, 1H), 4.73 (d,  $J$  = 7.6 Hz, 1H), 3.95 (s, 3H), 2.84 (dd,  $J$  = 14.7, 5.8 Hz, 1H), 2.45-2.38 (m, 1H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 173.1, 146.0, 126.8, 124.3, 123.8, 64.3, 56.7, 47.4, 17.4.

**HRMS (ESI-TOF)  $m/z$ :** calc'd for C<sub>9</sub>H<sub>11</sub>INOS [M+H]<sup>+</sup> 307.9601, found 307.9595.

**IR (ATR)  $\text{cm}^{-1}$ :** 2990, 2956, 1634, 1508, 1346, 1250, 1180, 1038, 858.



### 2-Ethyl-4-iodo-5-methoxy-3,4-dihydro-2H-pyrrole (**2q**)

Following **GP4**, imidate **1q** (38.7 mg, 0.30 mmol) was reacted with PhI(OAc)<sub>2</sub> (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3.0 mL) for 16 hours. Product was purified via silica gel column chromatography (2.0% ethyl acetate/hexanes) to yield **3,4-dihydro-2H-pyrrole 2q** (20 mg, 26%, dr 3:1) as colorless liquid.

**R<sub>f</sub>** = 0.6 (5% ethyl acetate/hexanes).

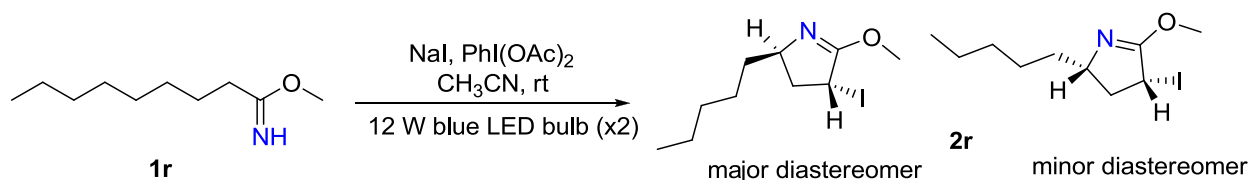
Relative stereochemistry determined by NOESY analysis.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** *Major diastereomer (trans):*  $\delta$  = 4.62 (dd,  $J$  = 9.2, 4.8 Hz, 1H), 3.87 (s, 3H), 3.75-3.67 (m, 1H), 2.48 (dd,  $J$  = 15.8, 5.6 Hz, 1H), 2.00-1.93 (m, 1H), 1.87-1.80 (m, 1H), 1.56-1.49 (m, 1H), 0.97 (t,  $J$  = 7.4 Hz, 3H). *Minor diastereomer (cis):*  $\delta$  = 4.72-4.61 (m, 1H), 4.04-3.97 (m, 1H), 3.88 (s, 3H), 3.15-3.11 (m, 1H), 2.30-2.24 (m, 1H), 1.87-1.80 (m, 1H), 1.68-1.58 (m, 1H), 0.99 (t,  $J$  = 7.4 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):** *diastereomer (trans):*  $\delta$  = 171.7, 66.7, 56.2, 43.6, 28.5, 18.6, 10.5. *Minor diastereomer (cis):*  $\delta$  = 170.5, 68.3, 56.3, 41.4, 28.3, 14.9, 10.9.

**HRMS (ESI-TOF)  $m/z$ :** calc'd for C<sub>7</sub>H<sub>13</sub>INO [M+H]<sup>+</sup> 254.0036, found 254.0034.

**IR (ATR)  $\text{cm}^{-1}$ :** 2960, 2879, 1695, 1637, 1443, 1332, 988.



### 4-Iodo-5-methoxy-2-pentyl-3,4-dihydro-2H-pyrrole (**2r**)

Following **GP4**, imidate **1r** (51.4 mg, 0.30 mmol) was reacted with  $\text{PhI}(\text{OAc})_2$  (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3.0 mL) for 16 hours. Product was purified via silica gel column chromatography (2.0% ethyl acetate/hexanes) to yield **3,4-dihydro-2H-pyrrole 2r** (28 mg, 32%, dr 2.7:1) as colorless liquid.

$R_f = 0.6$  (5% ethyl acetate/hexanes).

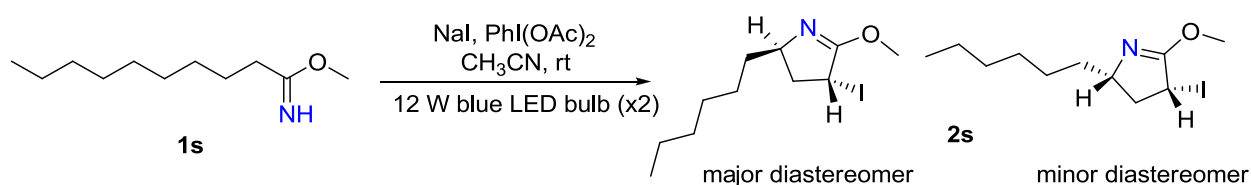
Relative stereochemistry determined by NOESY analysis.

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):** *Major diastereomer (trans):*  $\delta = 4.62$  (d,  $J = 7.6$  Hz, 1H), 3.87 (s, 3H), 3.79-3.72 (m, 1H), 2.48 (dd,  $J = 14.6, 5.5$  Hz, 1H), 1.99-1.92 (m, 1H), 1.47-1.38 (m, 2H), 1.38-1.32 (m, 6H), 0.89 (t,  $J = 3.7$  Hz, 3H). *Minor diastereomer (cis):*  $\delta = 4.71$ -4.67 (m, 1H), 4.09-4.03 (m, 1H), 3.88 (s, 3H), 2.91-2.83 (m, 1H), 2.30-2.24 (m, 1H), 1.85-1.78 (m, 1H), 1.63-1.54 (m, 1H), 1.47-1.32 (m, 6H), 0.89 (t,  $J = 7.4$  Hz, 3H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):** *diastereomer (trans):*  $\delta = 171.6, 65.4, 56.2, 44.1, 35.7, 31.9, 26.0, 22.6, 18.6, 14.0$ . *Minor diastereomer (cis):*  $\delta = 170.4, 66.9, 56.3, 41.8, 35.5, 31.8, 26.4, 22.6, 14.9, 14.0$ .

**HRMS (ESI-TOF)  $m/z$ :** calc'd for  $\text{C}_{10}\text{H}_{19}\text{INO}$   $[\text{M}+\text{H}]^+$  296.0506, found 296.0519.

**IR (ATR)  $\text{cm}^{-1}$ :** 2926, 2857, 1634, 1443, 1329, 988.



### 2-Hexyl-4-iodo-5-methoxy-3,4-dihydro-2H-pyrrole (**2s**)

Following **GP4**, imidate **1s** (55.5 mg, 0.30 mmol) was reacted with  $\text{PhI}(\text{OAc})_2$  (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3.0 mL) for 16 hours. Product was purified

via silica gel column chromatography (2.0% ethyl acetate/hexanes) to yield **3,4-dihydro-2H-pyrrole 2s** (34 mg, 36%, dr 8.1:1) as a colorless liquid.

$R_f$  = 0.6 (5% ethyl acetate/hexanes).

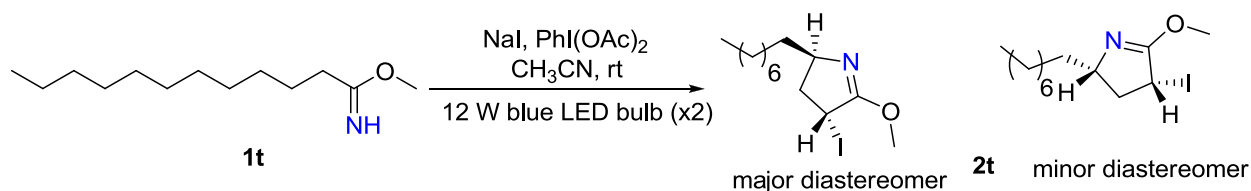
Relative stereochemistry determined by NOESY analysis.

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):** *Major diastereomer (trans):*  $\delta$  = 4.62 (d,  $J$  = 7.6 Hz, 1H), 3.87 (s, 3H), 3.78-3.72 (m, 1H), 2.48 (dd,  $J$  = 14.6, 5.5 Hz, 1H), 1.99-1.92 (m, 1H), 1.33-1.25 (m, 10H), 0.88 (t,  $J$  = 3.7 Hz, 3H). *Minor diastereomer (cis):*  $\delta$  = 4.71-4.67 (m, 1H), 4.09-4.03 (m, 1H), 3.88 (s, 3H), 2.91-2.83 (m, 1H), 2.30-2.24 (m, 1H), 1.85-1.77 (m, 2H), 1.49-1.37 (m, 8H), 0.88 (t,  $J$  = 7.4 Hz, 3H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):** *diastereomer (trans):*  $\delta$  = 171.6, 65.4, 56.2, 44.1, 35.7, 31.8, 29.3, 26.3, 22.6, 18.6, 14.1. *Minor diastereomer (cis):*  $\delta$  = 170.4, 66.9, 56.3, 41.8, 35.5, 31.8, 29.2, 26.6, 22.6, 14.9, 14.1.

**HRMS (ESI-TOF)  $m/z$ :** calc'd for  $\text{C}_{11}\text{H}_{21}\text{INO}$   $[\text{M}+\text{H}]^+$  310.0662, found 310.0663.

**IR (ATR)  $\text{cm}^{-1}$ :** 2924, 2854, 1637, 1443, 1332, 993.



#### 4-Iodo-5-methoxy-2-octyl-3,4-dihydro-2H-pyrrole (**2t**)

Following **GP4**, imidate **1t** (64.0 mg, 0.30 mmol) was reacted with  $\text{PhI}(\text{OAc})_2$  (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3.0 mL) for 16 hours. Product was purified via silica gel column chromatography (2.0% ethyl acetate/hexanes) to yield **3,4-dihydro-2H-pyrrole 2t** (44 mg, 44%, dr 6.7:1) as colorless liquid.

$R_f$  = 0.6 (5% ethyl acetate/hexanes).

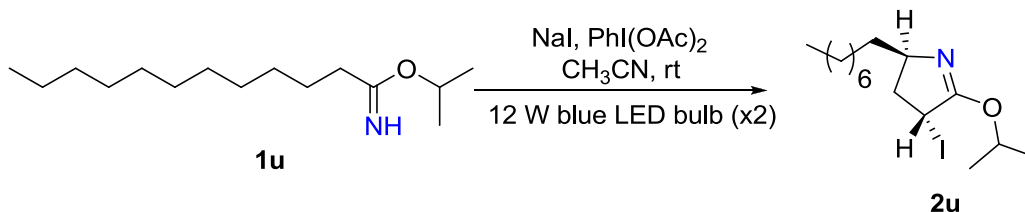
Relative stereochemistry determined by NOESY analysis.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** *Major diastereomer (trans):* δ = 4.61 (d, *J* = 7.6 Hz, 1H), 3.87 (s, 3H), 3.78-3.71 (m, 1H), 2.48 (dd, *J* = 14.6, 5.5 Hz, 1H), 1.99-1.91 (m, 1H), 1.39-1.27 (m, 14H), 0.87 (t, *J* = 3.7 Hz, 3H). *Minor diastereomer (cis):* δ = 4.71-4.67 (m, 1H), 4.09-4.03 (m, 1H), 3.88 (s, 3H), 2.91-2.83 (m, 1H), 2.30-2.24 (m, 1H), 1.85-1.77 (m, 2H), 1.49-1.37 (m, 12H), 0.88 (t, *J* = 7.4 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):** *diastereomer (trans):* δ = 171.6, 65.4, 56.2, 44.1, 35.8, 31.9, 29.6, 29.5, 29.2, 26.3, 22.7, 18.6, 14.1. *Minor diastereomer (cis):* δ = 170.4, 66.9, 56.3, 41.8, 35.5, 31.8, 29.6, 29.5, 29.2, 26.7, 22.7, 14.9, 14.1.

**HRMS (ESI-TOF) *m/z*:** calc'd for C<sub>13</sub>H<sub>25</sub>INO [M+H]<sup>+</sup> 338.0975, found 338.0988.

**IR (ATR) cm<sup>-1</sup>:** 2926, 2854, 1637, 1437, 1329, 991.



#### 4-Iodo-5-isopropoxy-2-octyl-3,4-dihydro-2H-pyrrole (**2u**)

Following **GP4**, imide **1u** (72.4 mg, 0.30 mmol) was reacted with PhI(OAc)<sub>2</sub> (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3.0 mL) for 16 hours. Product was purified via silica gel column chromatography (2.0% ethyl acetate/hexanes) to yield **3,4-dihydro-2H-pyrrole 2u** (42 mg, 38%) as colorless liquid.

**R<sub>f</sub>** = 0.6 (5% ethyl acetate/hexanes).

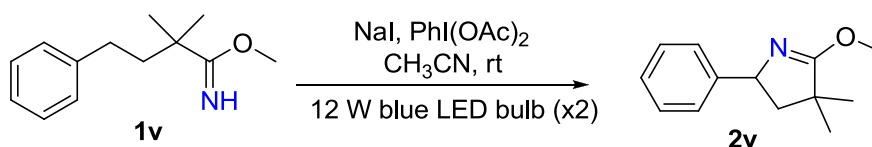
Relative stereochemistry determined by NOESY analysis.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 5.04-4.98 (m, 1H), 4.57 (d, *J* = 7.5 Hz, 1H), 3.75-3.69 (m, 1H), 2.44 (dd, *J* = 14.5, 5.5 Hz, 1H), 1.91-1.84 (m, 1H), 1.84-1.79 (m, 1H), 1.48-1.38 (m, 3H), 1.36-1.28 (m, 16H), 0.87 (t, *J* = 6.9 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):** δ = 170.2, 71.6, 65.5, 43.5, 35.7, 31.9, 29.7, 29.5, 29.2, 26.2, 22.7, 21.8, 20.9, 20.8, 14.1.

**HRMS (ESI-TOF) *m/z*:** calc'd for C<sub>15</sub>H<sub>29</sub>INO [M+H]<sup>+</sup> 366.1288, found 366.1315.

**IR (ATR) cm<sup>-1</sup>:** 2924, 2857, 1631, 1459, 1312, 1107, 921.



**5-Methoxy-4,4-dimethyl-2-phenyl-3,4-dihydro-2H-pyrrole (2v)**

Following **GP4**, imidate **1v** (61.5 mg, 0.30 mmol) was reacted with PhI(OAc)<sub>2</sub> (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3.0 mL) for 20 hours. Product was purified via silica gel column chromatography (10% ethyl acetate/hexanes) to yield **3,4-dihydro-2H-pyrrole 2v** (38 mg, 62%) as a colorless liquid.

**R<sub>f</sub>** = 0.4 (10% ethyl acetate/hexanes).

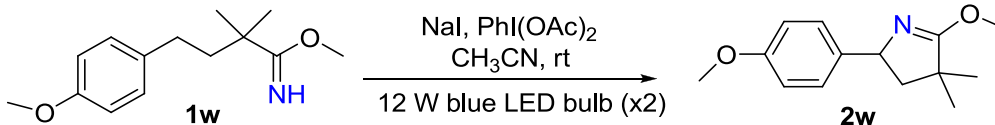
Relative stereochemistry determined by NOESY analysis.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.28-7.21 (m, 4H), 7.19-7.13 (m, 1H), 4.78 (t, *J* = 7.8 Hz, 1H), 3.81 (s, 3H), 2.32 (dd, *J* = 12.7, 7.3 Hz, 1H), 1.71 (dd, *J* = 12.7, 8.1 Hz, 1H), 1.16 (s, 3H), 1.11 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):** δ = 178.0, 145.6, 128.3, 126.6, 126.2, 65.2, 55.7, 49.9, 44.8, 25.7, 24.8.

**HRMS (ESI-TOF) *m/z*:** calc'd for C<sub>13</sub>H<sub>18</sub>NO [M+H]<sup>+</sup> 204.1383, found 204.1381.

**IR (ATR) cm<sup>-1</sup>:** 3026, 2965, 1645, 1454, 1326, 1165, 999, 749.



#### 5-Methoxy-2-(4-methoxyphenyl)-4,4-dimethyl-3,4-dihydro-2H-pyrrole (**2w**)

Following **GP4**, imidate **1w** (70.5 mg, 0.30 mmol) was reacted with PhI(OAc)<sub>2</sub> (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3.0 mL) for 14 hours. Product was purified via silica gel column chromatography (10% ethyl acetate/hexanes) to yield **3,4-dihydro-2H-pyrrole 2w** (43 mg, 61%) as a colorless liquid.

$R_f$  = 0.4 (15% ethyl acetate/hexanes).

Relative stereochemistry determined by NOESY analysis.

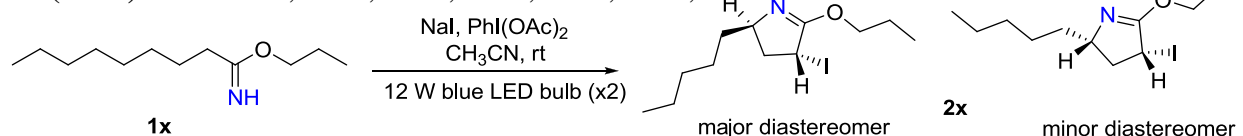
**1**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.21 (d,  $J$  = 8.6 Hz, 2H), 6.86 (d,  $J$  = 8.6 Hz, 2H), 4.80 (t,  $J$  = 7.8 Hz, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 2.35 (dd,  $J$  = 12.7, 7.3 Hz, 1H), 1.75 (dd,  $J$  = 12.7, 8.1 Hz, 1H), 1.22 (s, 3H), 1.18 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 177.8, 158.3, 137.7, 127.2, 113.7, 64.7, 55.7, 55.2, 49.9, 44.7, 25.7, 24.7.

**HRMS (ESI-TOF)  $m/z$ :** calc'd for C<sub>14</sub>H<sub>20</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 234.1489, found 234.1500.

**IR (ATR) cm<sup>-1</sup>:** 3028, 2968, 1644, 1458, 1436, 1168, 978.



#### 4-Iodo-2-pentyl-5-propoxy-3,4-dihydro-2H-pyrrole (**2x**)

Following **GP4**, imidate **1x** (59.8 mg, 0.30 mmol) was reacted with PhI(OAc)<sub>2</sub> (386 mg, 1.2 mmol) and NaI (180 mg, 1.2 mmol) in acetonitrile (3.0 mL) for 16 hours. Product was purified

via silica gel column chromatography (2.0% ethyl acetate/hexanes) to yield **3,4-dihydro-2H-pyrrole 2x** (27 mg, 28%, dr 2.8:1) as a colorless liquid.

$R_f$  = 0.6 (5% ethyl acetate/hexanes).

Relative stereochemistry determined by NOESY analysis.

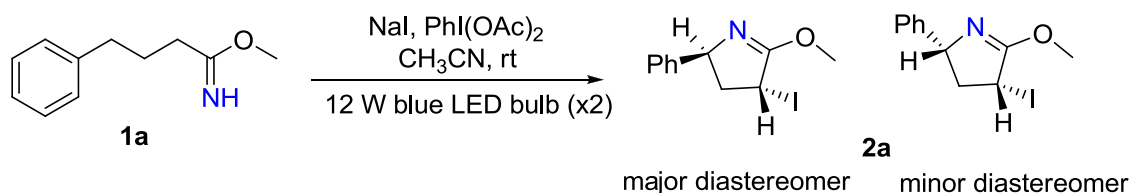
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):** *Major diastereomer (trans):*  $\delta$  = 4.61 (d,  $J$  = 7.6 Hz, 1H), 4.14 (t,  $J$  = 7.6 Hz, 2H), 3.75-3.70 (m, 1H), 2.47 (dd,  $J$  = 14.6, 5.6 Hz, 1H), 1.91 (m, 1H), 1.75-1.69 (m, 2H), 1.32-1.29 (m, 8H), 0.99 (t,  $J$  = 7.4 Hz, 3H), 0.88 (d,  $J$  = 6.0 Hz, 3H). *Minor diastereomer (cis):*  $\delta$  = 4.70-4.67 (m, 1H), 4.31-4.19 (m, 2H), 4.02 (t,  $J$  = 6.8 Hz, 1H), 2.83-2.77 (m, 1H), 2.31-2.27 (m, 1H), 1.65-1.55 (m, 2H), 1.32-1.29 (m, 8H), 0.99 (t,  $J$  = 7.4 Hz, 3H), 0.88 (d,  $J$  = 6.0 Hz, 3H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):** *Major diastereomer (trans):*  $\delta$  = 171.1, 70.5, 65.5, 43.9, 35.7, 31.9, 26.0, 22.6, 22.0, 19.5, 14.0, 10.4. *Minor diastereomer (cis):*  $\delta$  = 169.9, 70.6, 67.0, 41.4, 35.4, 31.8, 26.4, 22.6, 22.0, 15.6, 14.0, 10.4.

**HRMS (ESI-TOF)  $m/z$ :** calc'd for  $\text{C}_{12}\text{H}_{23}\text{INO}$   $[\text{M}+\text{H}]^+$  324.0819, found 324.0824.

**IR (ATR)  $\text{cm}^{-1}$ :** 2928, 2858, 1636, 1444, 1330, 986.

## V. Reaction Procedure for 1.0 mmol Reaction

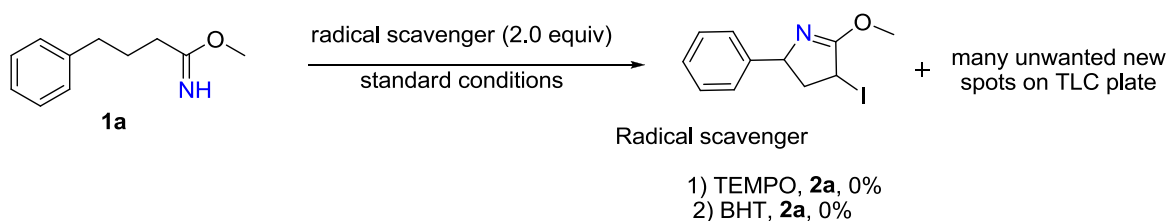


To a 25 mL dram vial equipped with a magnetic stir bar was charged with imide **1a** (1.0 mmol),  $\text{PhI}(\text{OAc})_2$  (1.2 mmol, 1296 mg), and NaI (1.2 mmol, 600 mg). Dry acetonitrile (10 mL) was added to the reaction vial by using a glass syringe under  $\text{N}_2$  and evacuated and backfilled with  $\text{N}_2$  (x3). Further, the reaction vial was irradiated at a distance of ~8 cm from a 12 W blue

LED (×2) at room temperature about 18 h until the reaction was completed, as monitored by TLC analysis. Upon completion, the reaction mixture was poured over 20% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (20 mL) and extracted with ethyl acetate (3 x 25 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was then concentrated in vacuo and the crude residue was purified by silica gel column chromatography (2% ethyl acetate/hexanes) to afford the corresponding 3,4-dihydro-2H-pyrrole **2a** (175 mg, 58%, dr 3.2:1) as a colorless liquid.

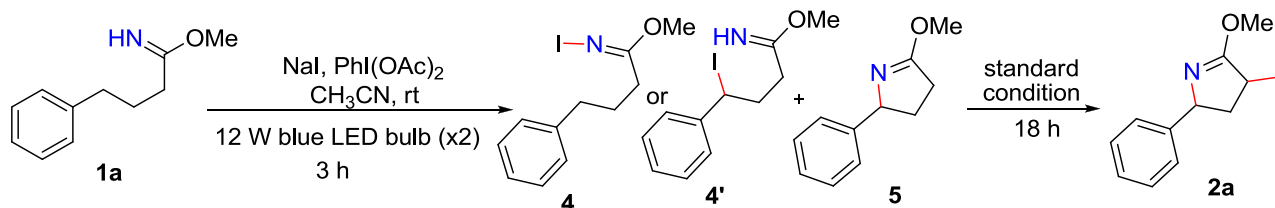
## VI. Miscellaneous Experiments

### A) Experimental Procedure for Radical Capture Experiment with TEMPO and BHT.



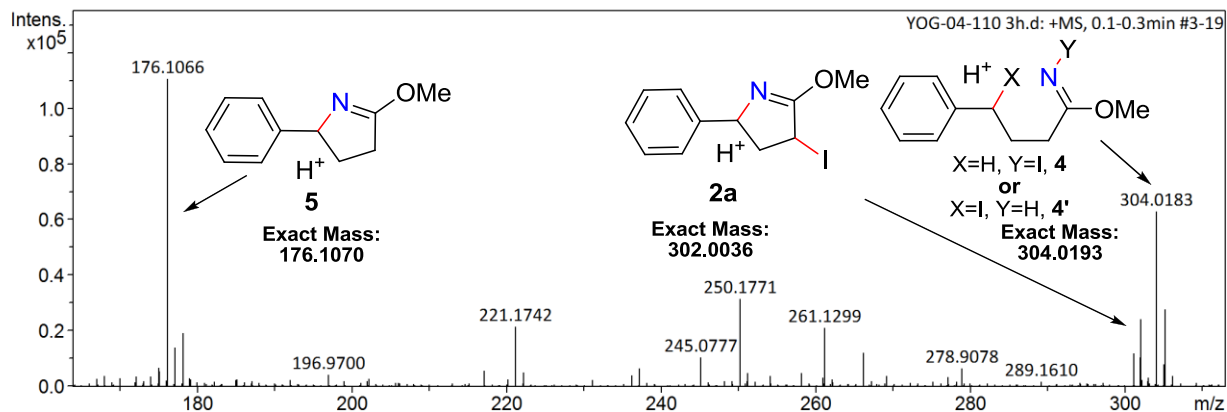
To a 10 mL dram vial equipped with a magnetic stir bar was charged with imidate (0.3 mmol), PhI(OAc)<sub>2</sub> (1.2 mmol), NaI (1.2 mmol) and radical scavenger (TEMPO and BHT). Dry acetonitrile (3 mL) was added to the reaction vial by using a glass syringe under N<sub>2</sub> and evacuated and backfilled with N<sub>2</sub> (x3). Further, the reaction vial was irradiated at a distance of ~8 cm from a 12 W blue LED (×2) at room temperature about 18 h until the reaction was completed, as monitored by TLC analysis. The reaction was monitored by TLC, no desired product was formed along with many new unwanted spots generated on TLC. The results indicate that the radical pathway may be involved in the reaction mechanism.

## B) HRMS of the Crude Reaction Mixture

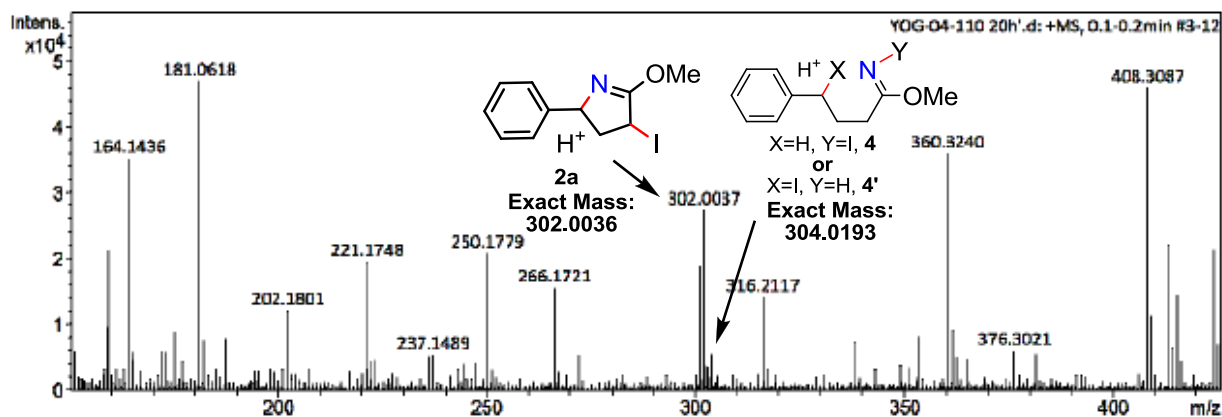


To a 10 mL dram vial equipped with a magnetic stir bar was charged with imidate (0.3 mmol), PhI(OAc)<sub>2</sub> (1.2 mmol), and NaI (1.2 mmol). Dry CH<sub>3</sub>CN (3 mL) was added to the reaction vial by using a glass syringe under N<sub>2</sub> and evacuated and backfilled with N<sub>2</sub> (x3). Further, the reaction vial was irradiated at a distance of ~8 cm from a 12 W blue LED (x2) at room temperature about 3 h. Then, the crude reaction sample was directly subjected for HRMS analysis, and two intermediates **4** or **4'** and **5** were detected by the mass spectrometer. The HRMS analysis showed the [M+H]<sup>+</sup> ion peak at  $m/z = 304.0183$  and  $176.1066$ , which corresponds to either the intermediates **4** or **4'** and **5**, respectively. Further, after 18 h, HRMS data was again recorded for crude reaction mixture, and the major [M+H]<sup>+</sup> ion peak appeared at  $m/z = 302.0037$ , which eventually confirmed the formation of desired product **2a**. The results indicate that *N*-iodobutyrimidate (**4**) or methyl 4-iodo-4-phenylbutanimidate (**4'**) and 1-pyrroline (**5**) could be the possible reaction intermediates in this transformation.

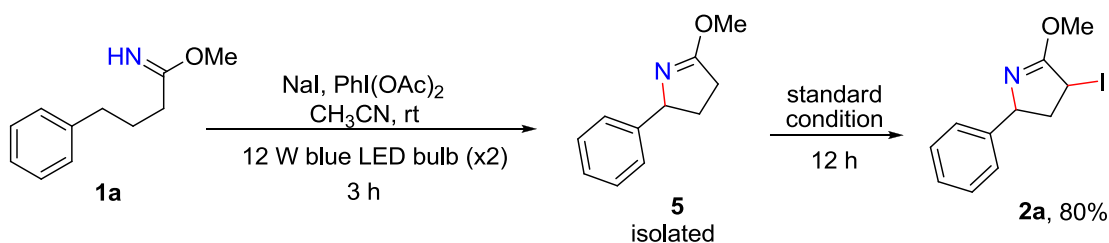
### 1) Crude reaction mixture after 3 h reaction



## 2) Crude reaction mixture after 20 h reaction



## C) Isolation of Reaction Intermediate



To a 25 mL dram vial equipped with a magnetic stir bar was charged with imide **1a** (1.0 mmol), PhI(OAc)<sub>2</sub> (1.2 mmol, 1296 mg), and NaI (1.2 mmol, 600 mg). Dry acetonitrile (10 mL) was added to the reaction vial by using a glass syringe under N<sub>2</sub> and evacuated and backfilled with N<sub>2</sub> (x3). Further, the reaction vial was irradiated at a distance of ~8 cm from a 12 W blue

LED ( $\times 2$ ) at room temperature about 3 h. Then, the reaction mixture was poured over 20%  $\text{Na}_2\text{S}_2\text{O}_3$  (20 mL) and extracted with ethyl acetate (3 x 25 mL) and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The organic layer was then concentrated in *vacuo* and the crude residue was purified by silica gel column chromatography (10% ethyl acetate/hexanes) to afford the corresponding product 5-methoxy-2-phenyl-3,4-dihydro-2H-pyrrole (**5**) (18 mg, 10%) as a colorless liquid. Further, the intermediate 5-methoxy-2-phenyl-3,4-dihydro-2H-pyrrole (**5**) (18 mg, 0.1 mmol) was subjected to the standard reaction conditions and afforded the desired product **2a** (24 mg, 80%) as a colorless liquid.

#### 5-Methoxy-2-phenyl-3,4-dihydro-2H-pyrrole (**5**)

$R_f = 0.3$  (5% ethyl acetate/hexanes).

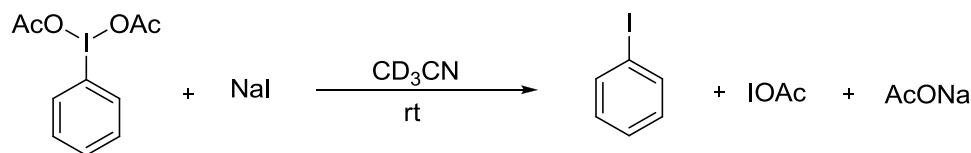
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.26\text{--}7.13$  (m, 5H), 4.90 (t,  $J = 7.6$  Hz, 1H), 3.83 (s, 3H), 2.54–2.49 (m, 2H), 2.47–2.42 (m, 1H), 1.85–1.81 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 174.1, 145.3, 128.3, 126.7, 126.1, 69.7, 55.6, 33.2, 31.5$ .

HRMS (ESI-TOF)  $m/z$ : calc'd for  $\text{C}_{11}\text{H}_{14}\text{NO}$   $[\text{M}+\text{H}]^+$  176.1070, found 176.1098.

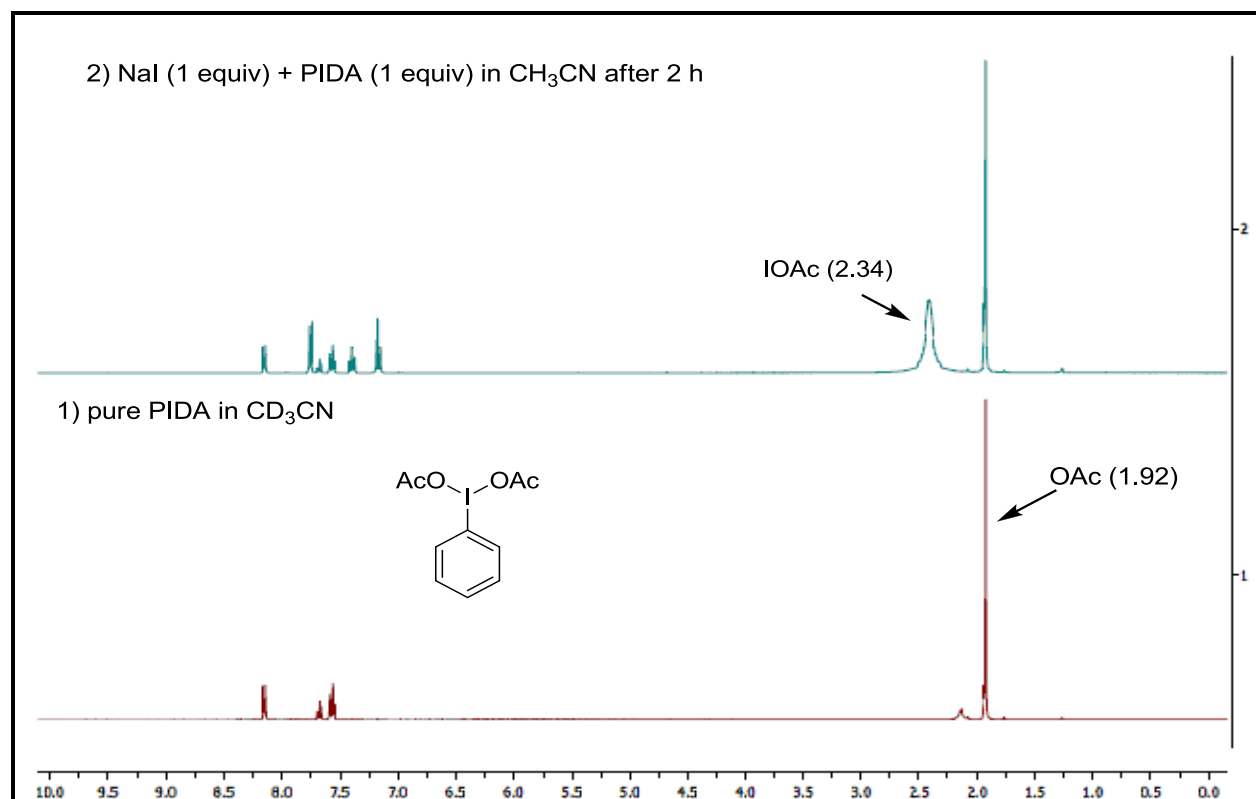
IR (ATR)  $\text{cm}^{-1}$ : 2930, 2854, 1638, 1454, 1332, 988.

#### D) $^1\text{H}$ NMR Experiment for the Generation of IOAc Species



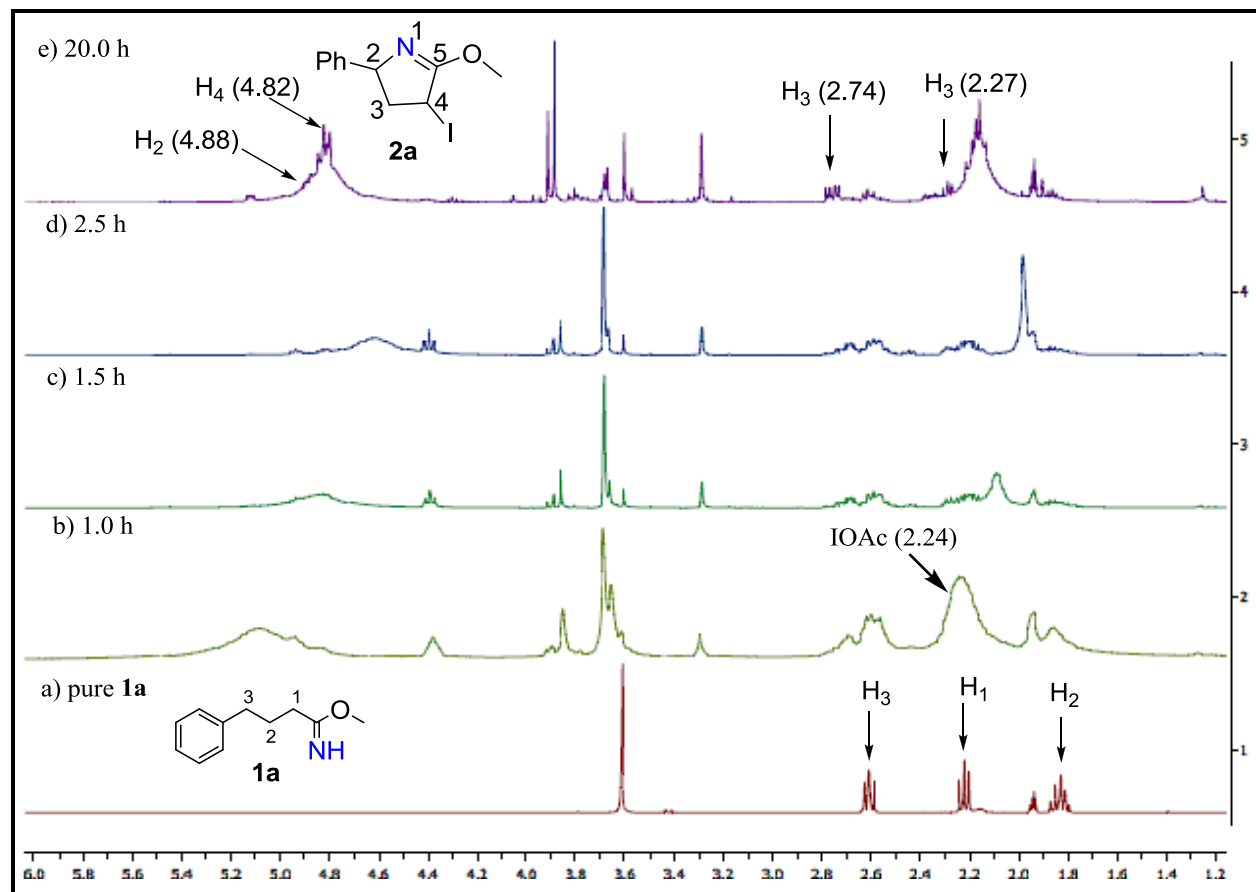
Based on the literature precedence<sup>9</sup>,  $^1\text{H}$  NMR monitoring experiment was conducted to identify iodine monoacetate (IOAc) as an active species in the visible-light-mediated remote  $\gamma\text{-C}(\text{sp}^3)\text{-H}$  functionalization of alkylimidates. Similar to pagé's work<sup>9</sup>,  $^1\text{H}$  NMR monitoring experiment was

used for the investigation for the IOAc species. First, a solution of PIDA (phenyliodine(III) diacetate) (7.0 mg, 0.0217 mmol) in 0.7 mL  $\text{CD}_3\text{CN}$  was placed in the NMR tube and  $^1\text{H}$  NMR spectra were recorded at room temperature. The  $^1\text{H}$  NMR spectrum showed the peak at  $\delta$  1.92 ppm corresponds to acetate group of the PIDA. Further, a solution of PIDA (7.0 mg, 0.0217 mmol) in 0.7 mL  $\text{CD}_3\text{CN}$  was added to NaI (0.0217 mmol, 3.26 mg) and the resulting solution was stirred in a 5 mL dram vial for 2.0 h at room temperature under  $\text{N}_2$  atmosphere. The  $^1\text{H}$  NMR spectrum showed a new peak at  $\delta$  2.34 ppm corresponds to the generation of IOAc species, and match with the literature report<sup>9</sup>.



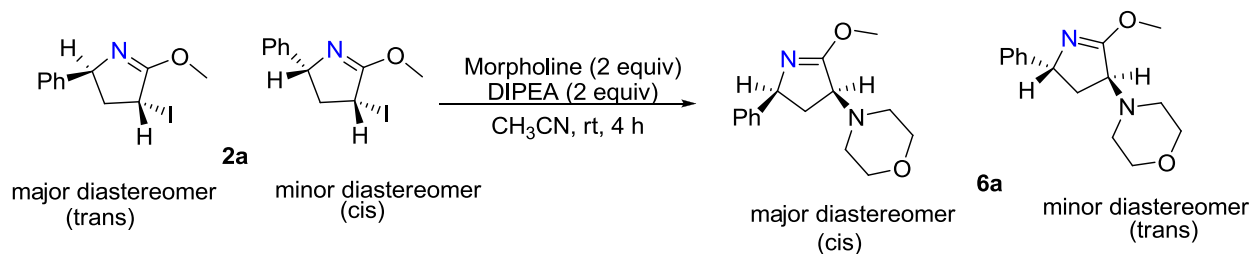
**Figure 1:**  $^1\text{H}$  NMR experiment for the generation of IOAc species

### E) $^1\text{H}$ NMR Experiment for the Reaction Monitoring



**Figure 2:**  $^1\text{H}$  NMR monitoring experiments for the formation of 4-iodo-2,3 dihydropyrrole **2a** in  $\text{CD}_3\text{CN}$ : a)  $^1\text{H}$  NMR spectrum of pure **1a** in  $\text{CD}_3\text{CN}$ , b)  $^1\text{H}$  NMR spectrum of **1a** (0.15 mmol, 26.5 mg), PIDA (0.225 mmol, 72.6 mg), and NaI (0.225 mmol, 33.7 mg) were irradiated by the 12 W (x2) blue light source for 1.0 h in 1.5 mL of  $\text{CD}_3\text{CN}$ , c)  $^1\text{H}$  NMR spectrum of the reaction after 1.5 h in  $\text{CD}_3\text{CN}$ , d)  $^1\text{H}$  NMR spectrum of the reaction after 2.5 h in  $\text{CD}_3\text{CN}$ , e)  $^1\text{H}$  NMR spectrum of the reaction after 20.0 h in  $\text{CD}_3\text{CN}$ .

## VII. Synthetic Manipulations of 3,4-dihydro-2H-pyrrole.



### 4-(5-Methoxy-2-phenyl-3,4-dihydro-2H-pyrrol-4-yl)morpholine (**6a**)

A dried 10 mL dram vial containing a stir bar was charged with 3,4-dihydro-2H-pyrrole **2a** (60.0 mg, 0.2 mmol) in acetonitrile (1 mL) at room temperature. Then, morpholine (35.0 mg, 2.0 equiv) and DIPEA (N,N-diisopropylethylamine) (51.7 mg, 2.0 equiv) were added dropwise to the stirring solution and reaction was allowed to stir at room temperature for 6 h until the reaction was completed, as monitored by TLC analysis. Upon completion, the reaction mixture was extracted with ethyl acetate (3 × 15 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was then concentrated in vacuo and the crude residue was purified by silica gel column chromatography (hexanes/ethyl acetate) to afford the corresponding compound **6a** (45 mg, 86%, dr 3.8:1) as a colorless liquid.

**R<sub>f</sub>** = 0.2 (70% ethyl acetate/hexanes).

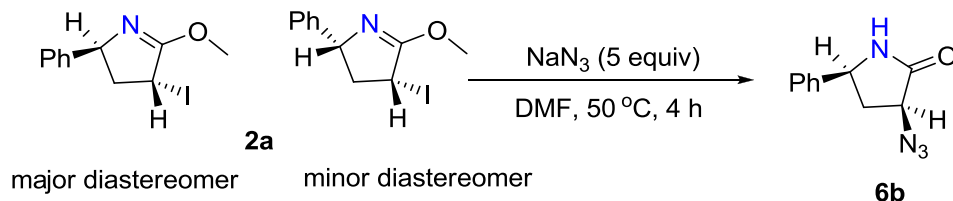
Relative stereochemistry determined by NOESY analysis.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** *Major diastereomer (cis):* δ = 7.34-7.22 (m, 5H), 4.74 (t, *J* = 7.8 Hz, 1H), 3.98 (t, *J* = 9.0 Hz, 1H), 3.94 (s, 3H), 3.74-3.69 (m, 4H), 2.69-2.62 (m, 2H), 2.60-2.55 (m, 1H), 2.46-2.41 (m, 2H), 1.88-1.81 (m, 1H). *Minor diastereomer (trans):* δ = 7.34-7.22 (m, 5H), 4.96 (t, *J* = 7.8 Hz, 1H), 3.94 (s, 3H), 3.92 (t, *J* = 9.0 Hz, 1H), 3.74-3.69 (m, 4H), 2.69-2.62 (m, 2H), 2.51-2.47 (m, 2H), 2.39-2.36 (m, 1H), 2.01-1.93 (m, 1H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):** Major diastereomer (*cis*):  $\delta$  = 172.0, 144.8, 128.4, 126.8, 125.9, 68.5, 66.9, 64.9, 55.7, 49.2, 34.1. Minor diastereomer (*trans*):  $\delta$  = 171.7, 144.8, 128.4, 126.8, 125.9, 68.2, 67.6, 66.9, 55.7, 49.2, 34.6.

**HRMS (ESI-TOF)  $m/z$ :** calc'd for  $\text{C}_{15}\text{H}_{21}\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  261.1598, found 261.1611.

**IR (ATR)  $\text{cm}^{-1}$ :** 2943, 2857, 1648, 1446, 1262, 1110, 910.



### 3-Azido-5-phenylpyrrolidin-2-one (6b)

A dried 10 mL dram vial containing a stir bar was charged with 3,4-dihydro-2H-pyrrole **2a** (36.0 mg, 0.10 mmol), NaN<sub>3</sub> (32.6 mg, 0.5 mmol, 5.0 equiv) in anhydrous DMF (2.0 mL) at room temperature. Then, the reaction vial was allowed to stir at 50 °C for 4 h. Upon completion (monitored by TLC analysis), the reaction solution was cooled to room temperature, and diluted with H<sub>2</sub>O and extracted with ethyl acetate (3 × 15 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was then concentrated in vacuo and the crude residue was purified by silica gel column chromatography (hexanes/ethyl acetate) to afford the corresponding compound **6b** (15.2 mg, 75 %) as a white solid.

**R<sub>f</sub>** = 0.4 (20 % ethyl acetate/hexanes).

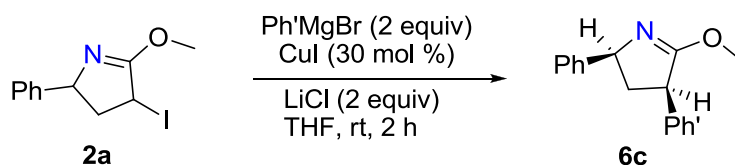
Relative stereochemistry determined by NOESY analysis.

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.33-7.19 (m, 5H), 6.50 (br s, 1H), 4.57 (dd,  $J$  = 8.2, 6.8 Hz, 1H), 4.17 (t,  $J$  = 8.2, 6.8 Hz, 1H), 2.82-2.75 (m, 1H), 1.83-1.75 (m, 1H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 173.6, 140.5, 129.1, 128.5, 126.0, 59.3, 55.0, 37.9.

**HRMS (ESI-TOF)  $m/z$ :** calc'd for  $\text{C}_{10}\text{H}_{10}\text{N}_4\text{NaO}$   $[\text{M}+\text{H}]^+$  225.0747, found 225.0740.

**IR (ATR)  $\text{cm}^{-1}$ :** 3172, 3079, 2908, 2100, 1694, 1250.



### 5-Methoxy-2,4-diphenyl-3,4-dihydro-2H-pyrrole (**6c**)

An dried 10 mL round-bottom flask containing stir bar was charged with 3,4-dihydro-2H-pyrrole **2a** (60.0 mg, 0.2 mmol), CuI (11.4 mg, 30 mol %), LiCl (17 mg, 2.0 equiv). Then, Grignard reagent (0.4 mL, 2.0 equiv) was added slowly to the round bottom flask within 2.0 min under N<sub>2</sub> atmosphere and the resulting mixture was stirred for 3 h at room temperature. After the completion of the reaction (revealed by TLC analysis), the reaction mixture was quenched with a saturated NH<sub>4</sub>Cl solution and extracted with ethyl acetate (3 x 10 mL). The combined organic layer was washed with brine solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was then concentrated in vacuo and the crude residue was purified by silica gel column chromatography (hexanes/ethyl acetate, 90:10) to afford the corresponding product **6c** (31 mg, 62%) as a colorless oil.

**R<sub>f</sub>** = 0.3 (15% ethyl acetate/hexanes).

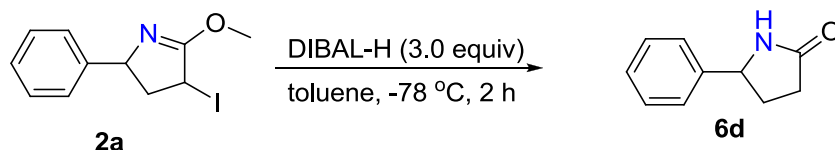
Relative stereochemistry determined by NOESY analysis.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.38-7.30 (m, 8H), 7.22 (d, *J* = 8.2 Hz, 2H), 5.19 (t, *J* = 7.2 Hz, 1H), 4.07 (dd, *J* = 9.8, 5.2 Hz, 1H), 3.94 (s, 3H), 2.62-2.55 (m, 1H), 2.50-2.43 (m, 1H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):** δ = 174.3, 144.9, 140.5, 128.9, 128.5, 127.4, 127.0, 126.9, 126.1, 68.0, 56.1, 50.6, 43.7.

**HRMS (ESI-TOF) *m/z*:** calc'd for C<sub>17</sub>H<sub>18</sub>NO [M+H]<sup>+</sup> 252.1383, found 252.1377.

**IR (ATR) cm<sup>-1</sup>:** 2930, 2854, 1706, 1638, 1447, 1326, 1264, 991.



### 5-Phenylpyrrolidin-2-one (6d)

A dried 10 mL round-bottom flask containing a stir bar was charged with 3,4-dihydro-2H-pyrrole **2a** (36.0 mg, 0.12 mmol) in anhydrous toluene (0.7 mL) at room temperature. Then, the reaction mixture was cooled to -78 °C at which temperature DIBAL-H (1 M in THF, 0.36 mL, 3.0 equiv) was added dropwise and the resulting mixture was stirred for 2 h at -78 °C. After the completion of the reaction (revealed by TLC analysis), the reaction mixture was quenched with a saturated NH<sub>4</sub>Cl solution and extracted with ethyl acetate (3 x 10 mL). The combined organic layer was washed with brine solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was then concentrated in vacuo and the crude residue was purified by silica gel column chromatography (hexanes/ethyl acetate, 60:40) to afford the corresponding product **6d** (16 mg, 84%) as a colorless oil.

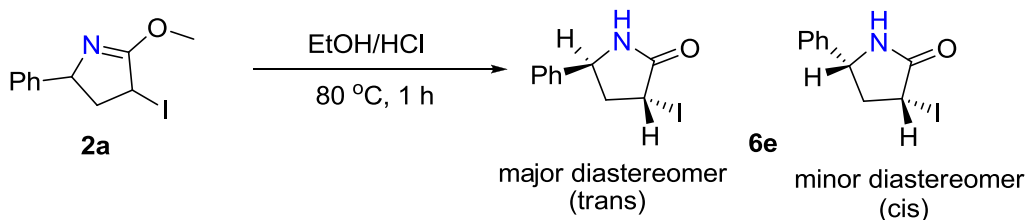
**R<sub>f</sub>** = 0.2 (40 % ethyl acetate/hexanes).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.38-7.34 (m, 2H), 7.30-7.28 (m, 3H), 6.38 (br s, 1H), 4.75 (t, *J* = 7.2 Hz, 1H), 2.61-2.52 (m, 1H), 2.48-2.35 (m, 2H), 1.98-1.93 (m, 1H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):** δ = 178.5, 142.5, 128.9, 127.9, 125.6, 58.0, 31.3, 30.2.

**HRMS (ESI-TOF) *m/z*:** calc'd for C<sub>10</sub>H<sub>12</sub>NO [M+H]<sup>+</sup> 162.0913, found 162.0912.

**IR (ATR) cm<sup>-1</sup>:** 3182, 3068, 2915, 2852, 1687, 1448, 1257, 1179, 760.



### 3-Iodo-5-phenylpyrrolidin-2-one (6e)

A dried 25 mL round bottom flask containing a stir bar was charged with 3,4-dihydro-2H-pyrrole **2a** (60.0 mg, 0.2 mmol) in EtOH (3 mL) at room temperature. Then, HCl (35%, 3 mL) was added dropwise to the stirring solution and reaction was allowed to stir at 80 °C for 1 h. Upon completion (monitored by TLC analysis), the reaction solution was neutralized with 20% NaHCO<sub>3</sub>, extracted with ethyl acetate (3 × 15 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was then concentrated in vacuo and the crude residue was purified by silica gel column chromatography (hexanes/ethyl acetate) to afford the corresponding compound **6e** (40 mg, 70%, dr 2:1) as a colorless liquid.

**R<sub>f</sub>** = 0.2 (40% ethyl acetate/hexanes).

Relative stereochemistry determined by NOESY analysis.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** *Major diastereomer (trans):* δ = 7.41-7.26 (m, 5H), 6.41 (s, 1H), 4.79 (dd, *J* = 8.2, 5.8 Hz, 1H), 4.61 (dd, *J* = 7.0, 1.2 Hz, 1H), 2.68 (dd, *J* = 14.6, 5.8 Hz, 1H), 2.42-2.35 (m, 1H). *Minor diastereomer (cis):* δ = 7.41-7.26 (m, 5H), 6.52 (s, 1H), 4.86 (t, *J* = 7.2 Hz, 1H), 4.73 (t, *J* = 8.4 Hz, 1H), 3.30-3.23 (m, 1H), 2.54-2.47 (m, 1H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):** *Major diastereomer (trans):* δ = 175.6, 139.2, 129.1, 128.5, 126.1, 57.3, 44.5, 18.3. *Minor diastereomer (cis):* δ = 175.6, 139.2, 129.0, 128.4, 125.9, 58.2, 43.5, 15.2.

**HRMS (ESI-TOF) *m/z*:** calc'd for C<sub>10</sub>H<sub>11</sub>INO [M+H]<sup>+</sup> 287.9980, found 287.9891.

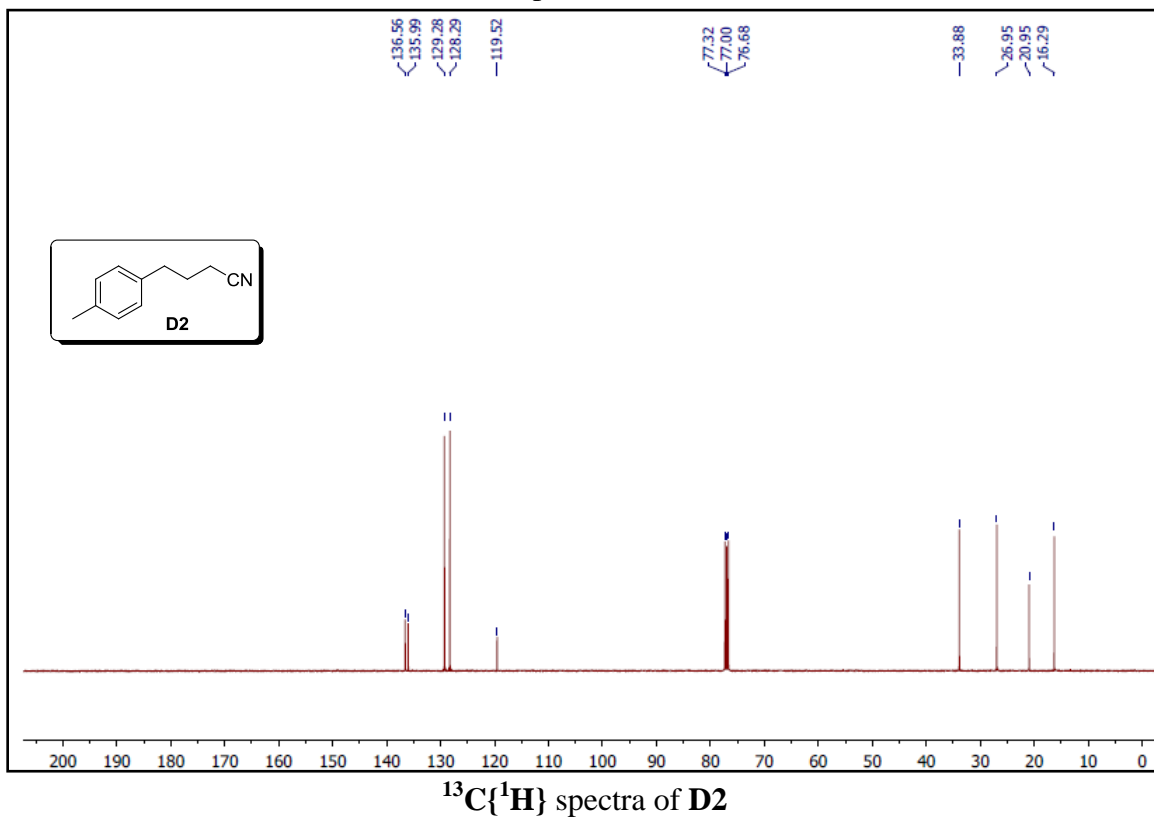
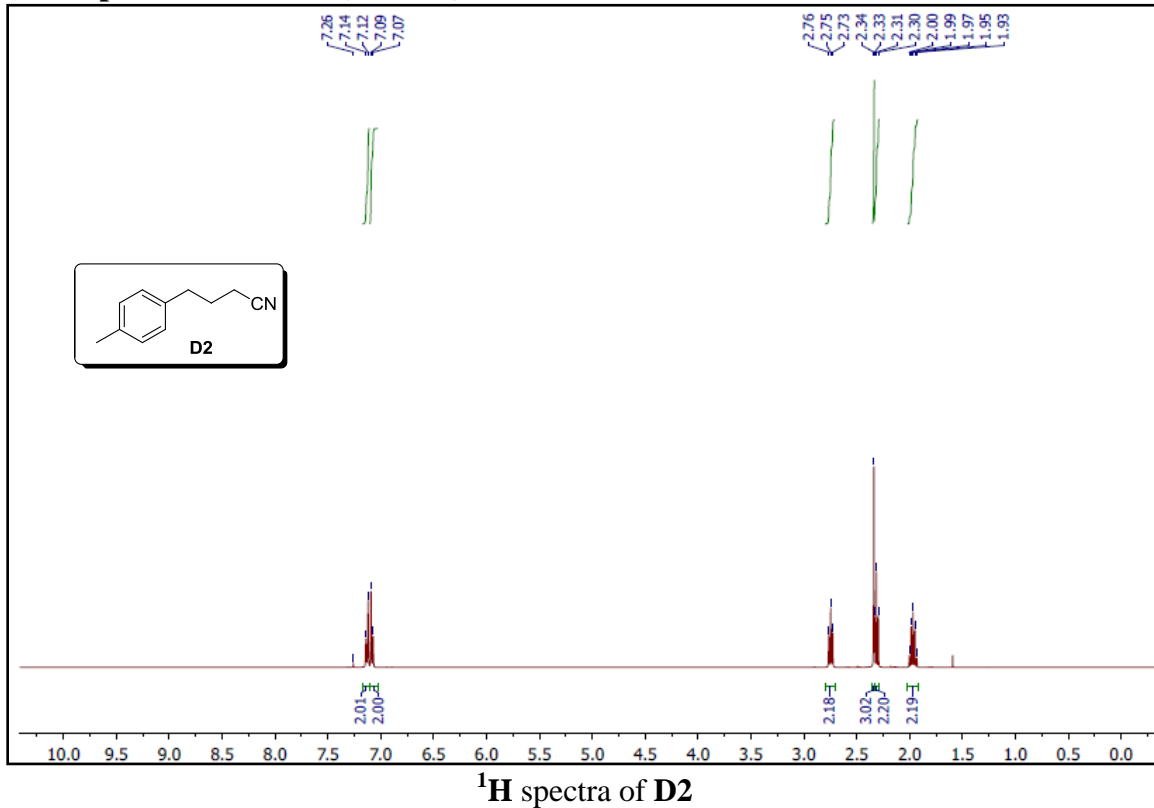
**IR (ATR) cm<sup>-1</sup>:** 3182, 3068, 2915, 2852, 1687, 1448, 1257, 1179, 760.

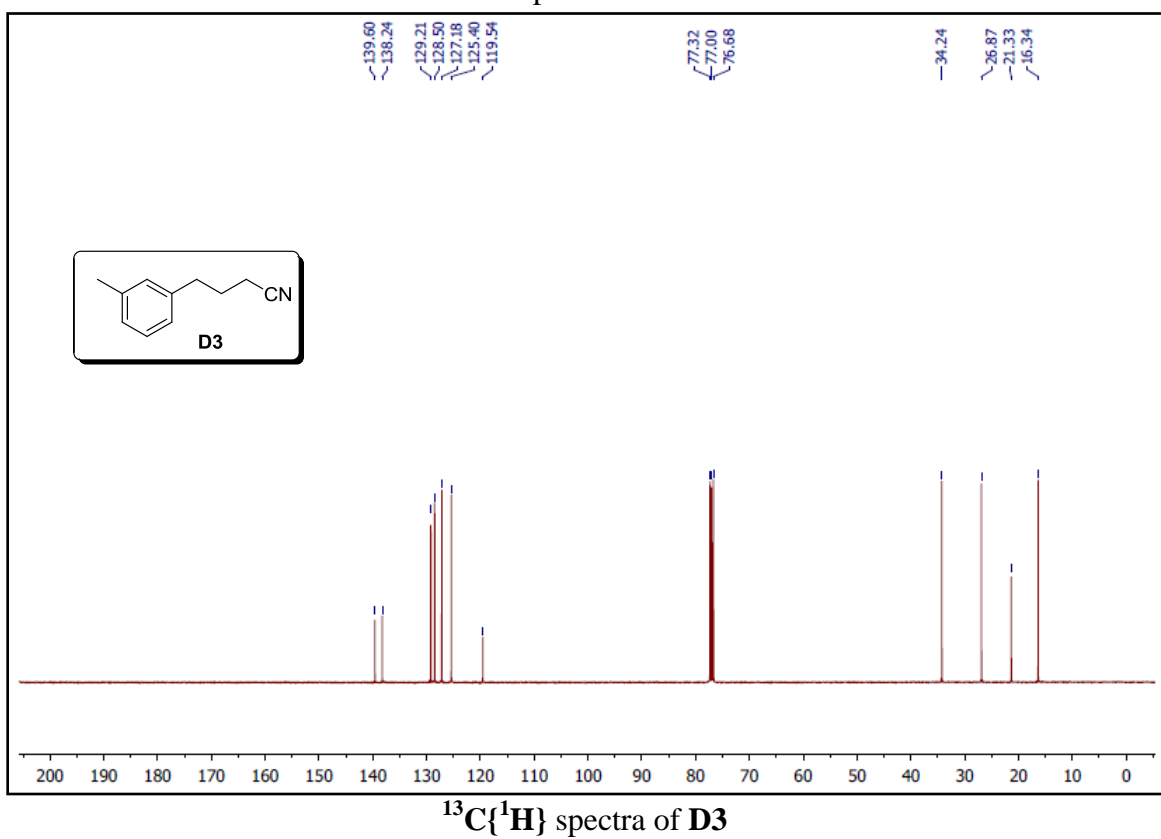
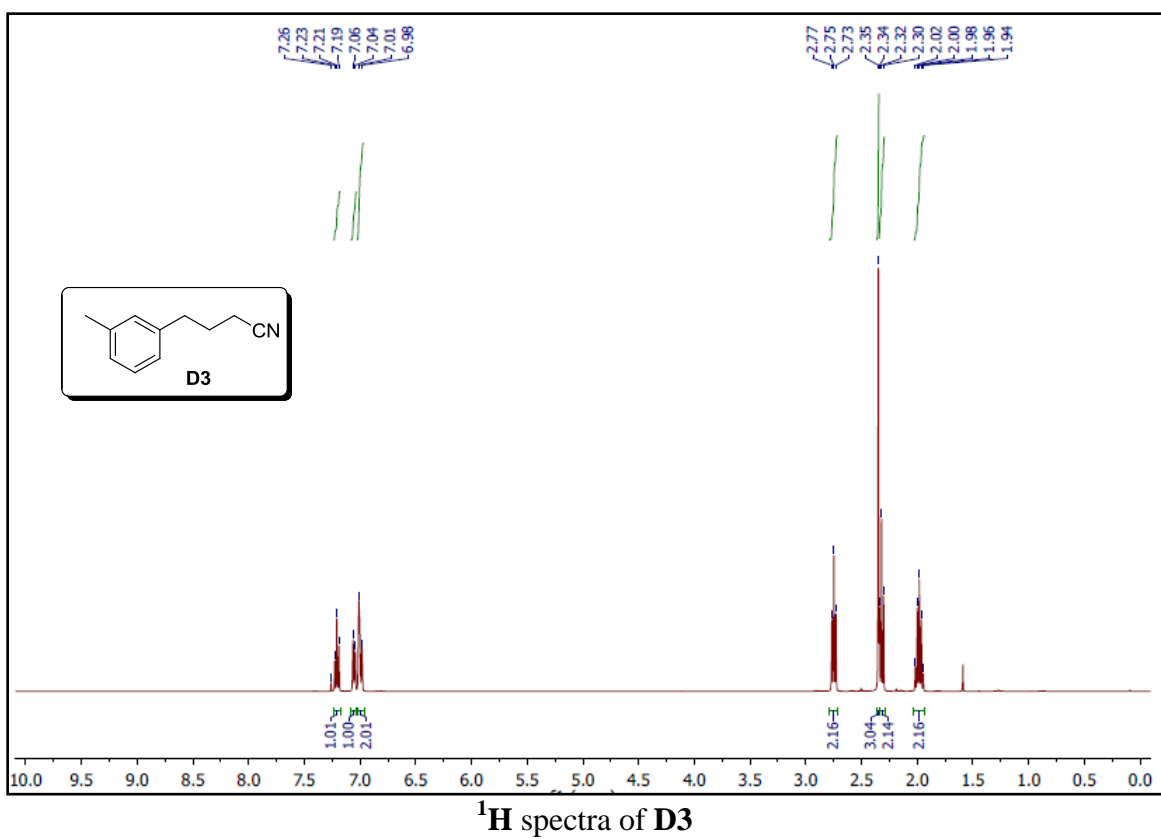
## VIII. References

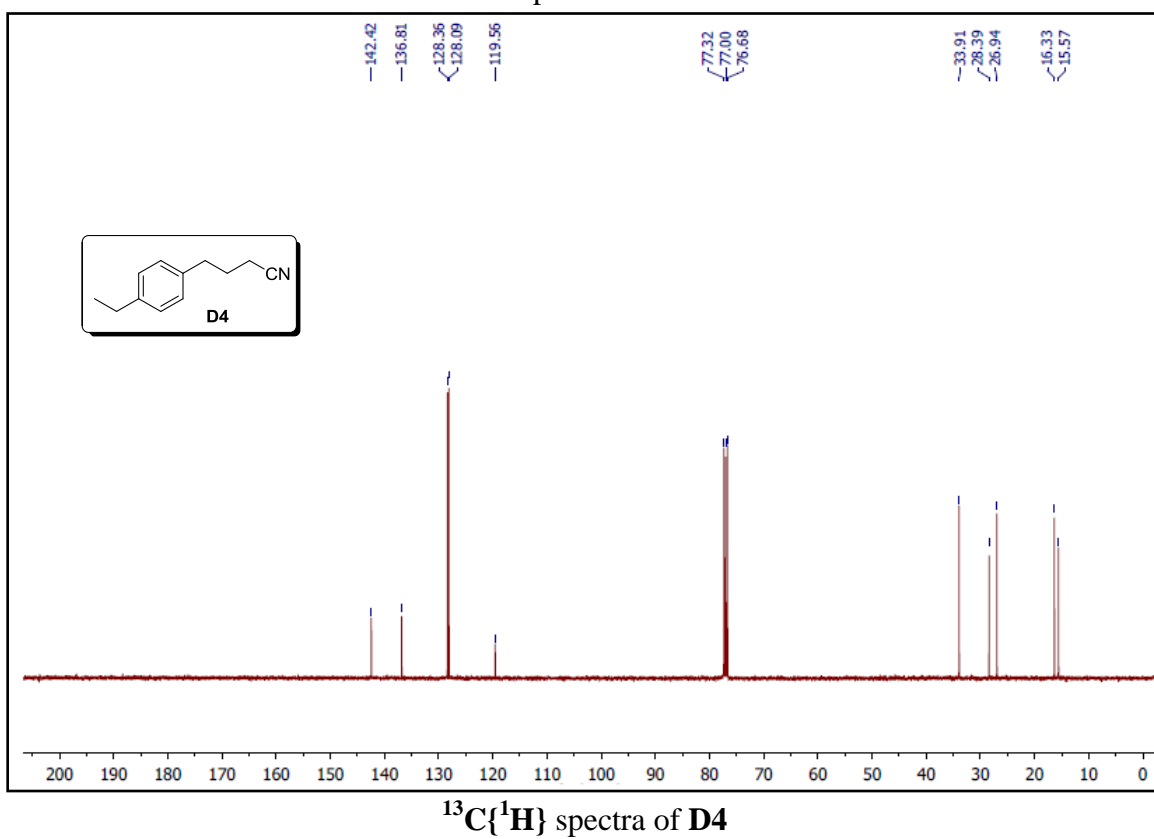
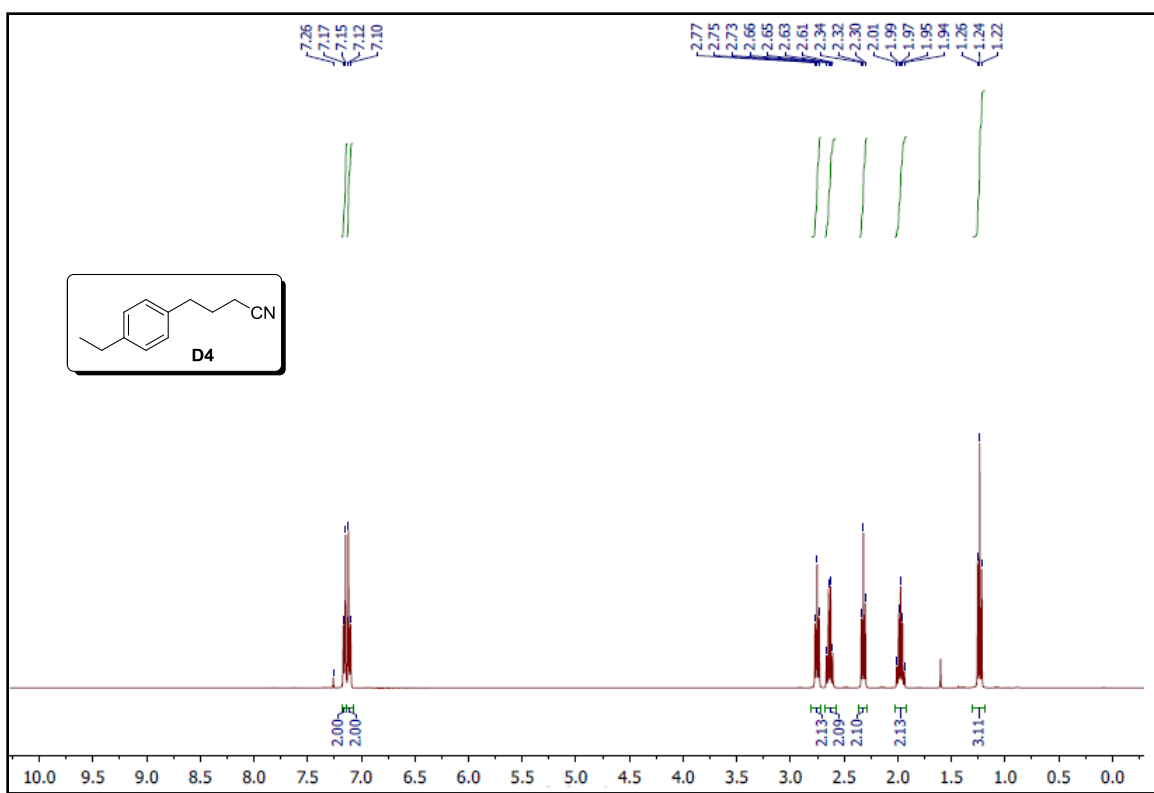
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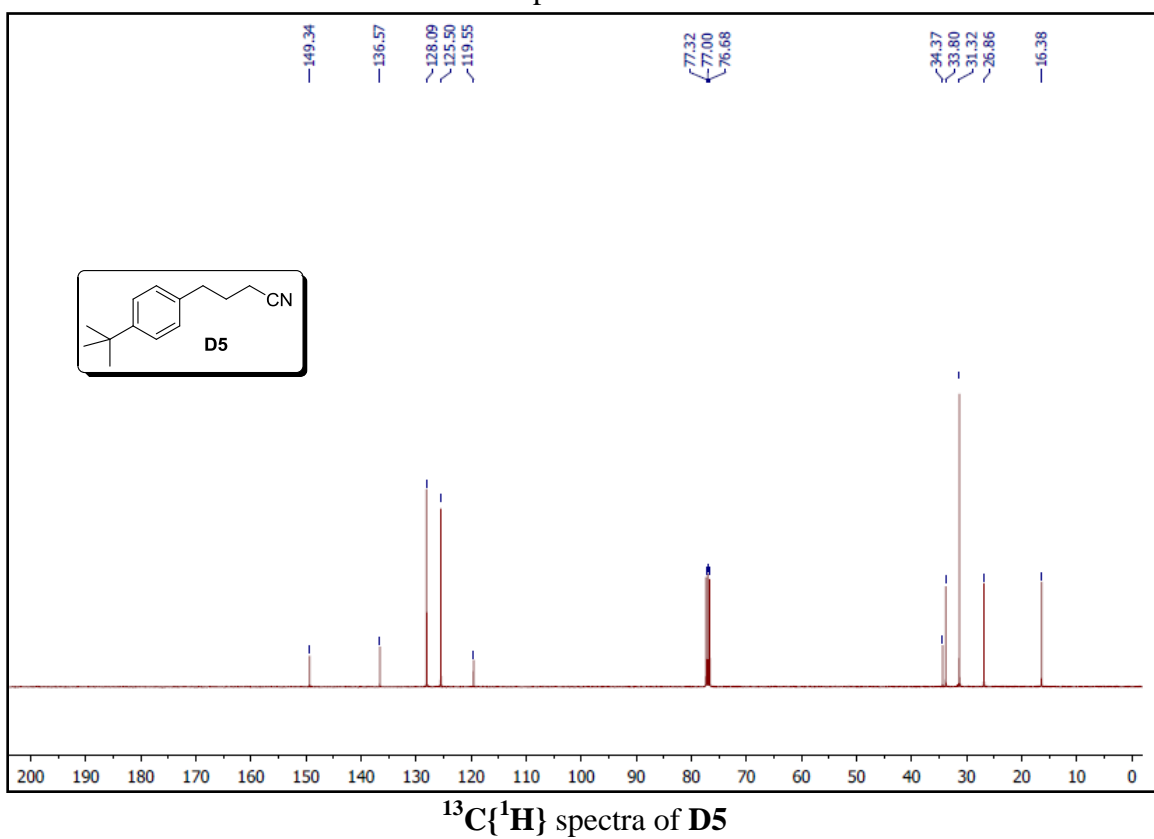
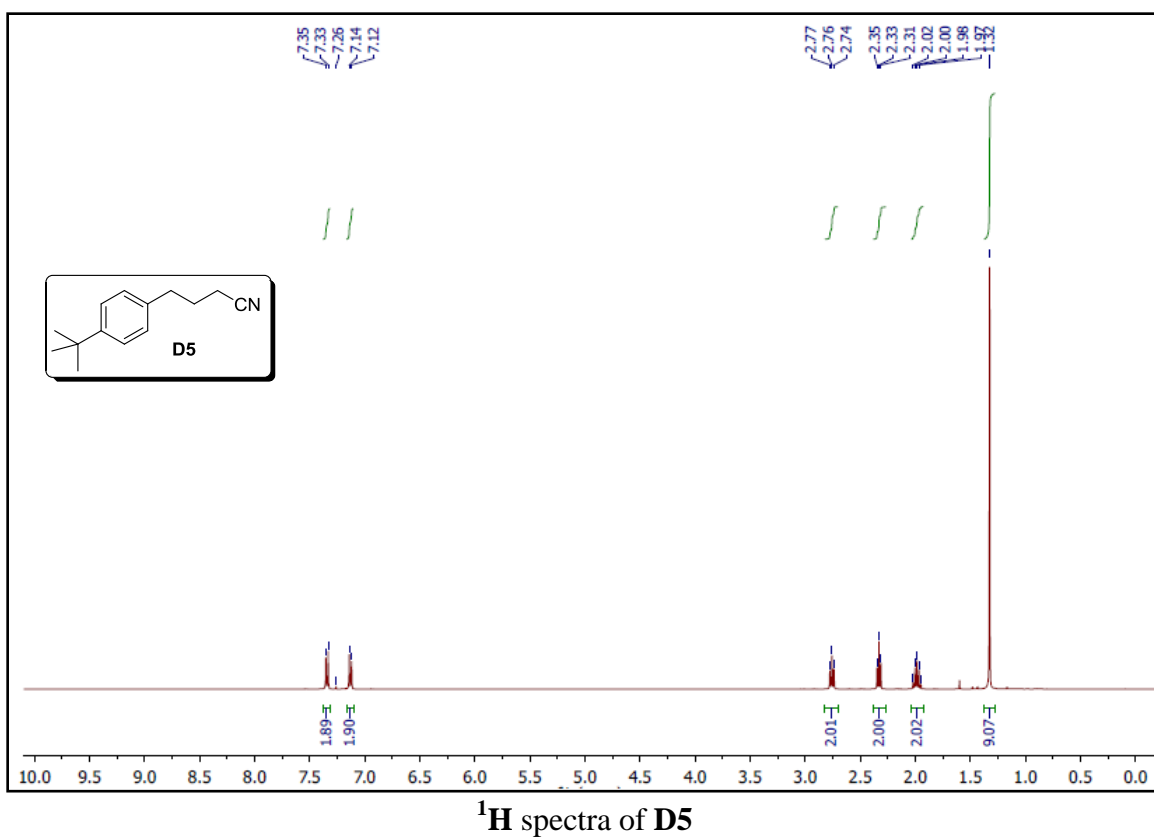
## IX. NMR Spectra

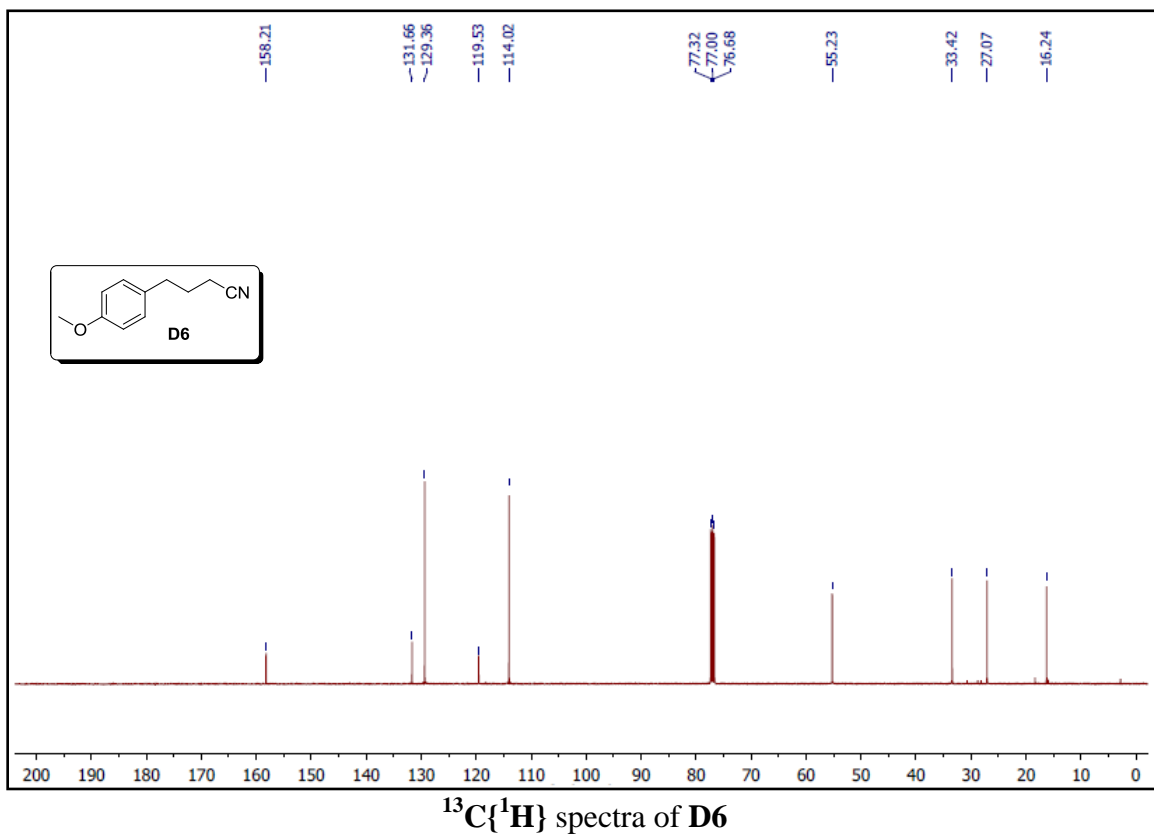
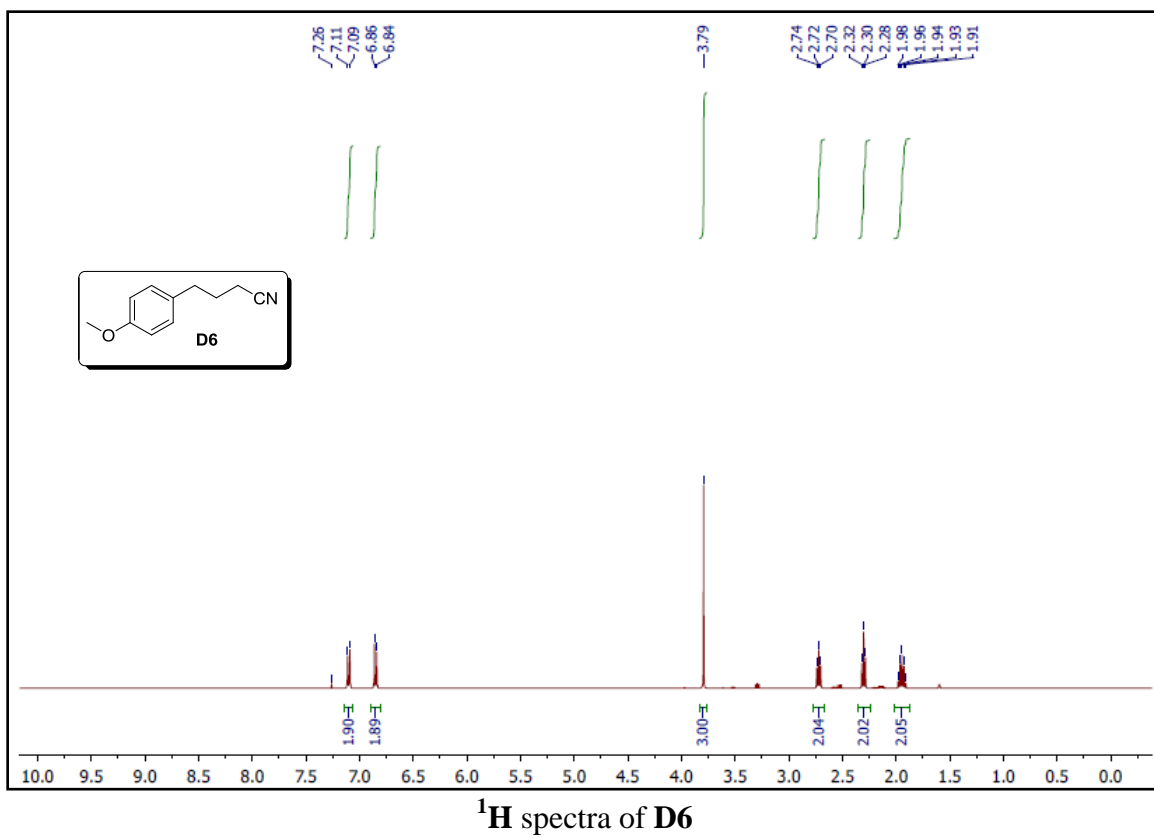
### A) NMR spectra of Nitriles (D2-D11):

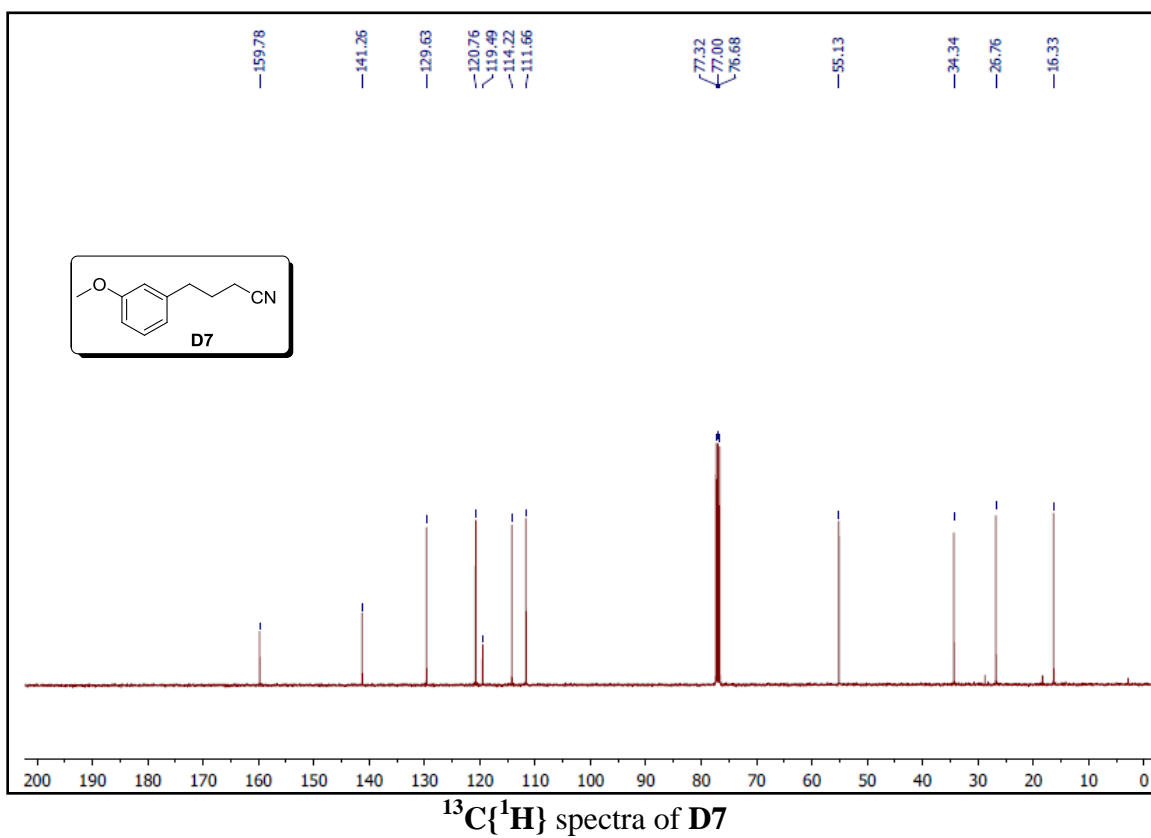
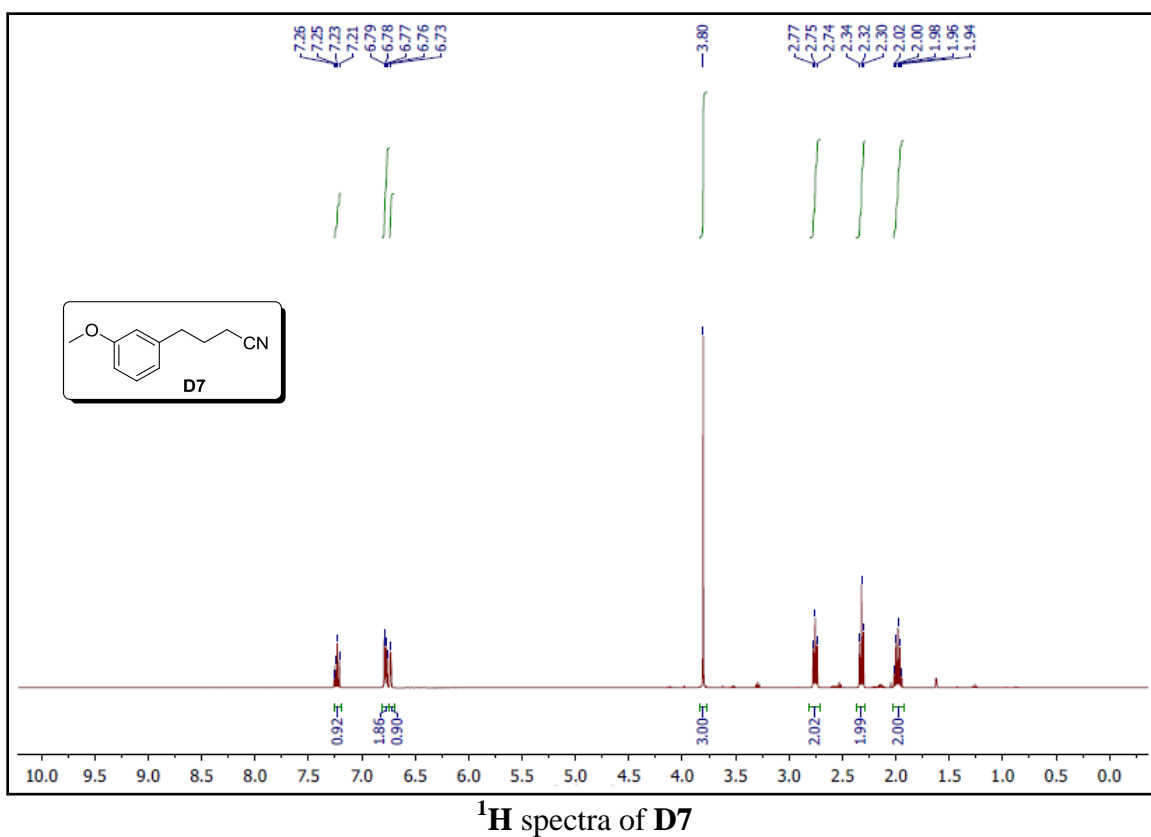


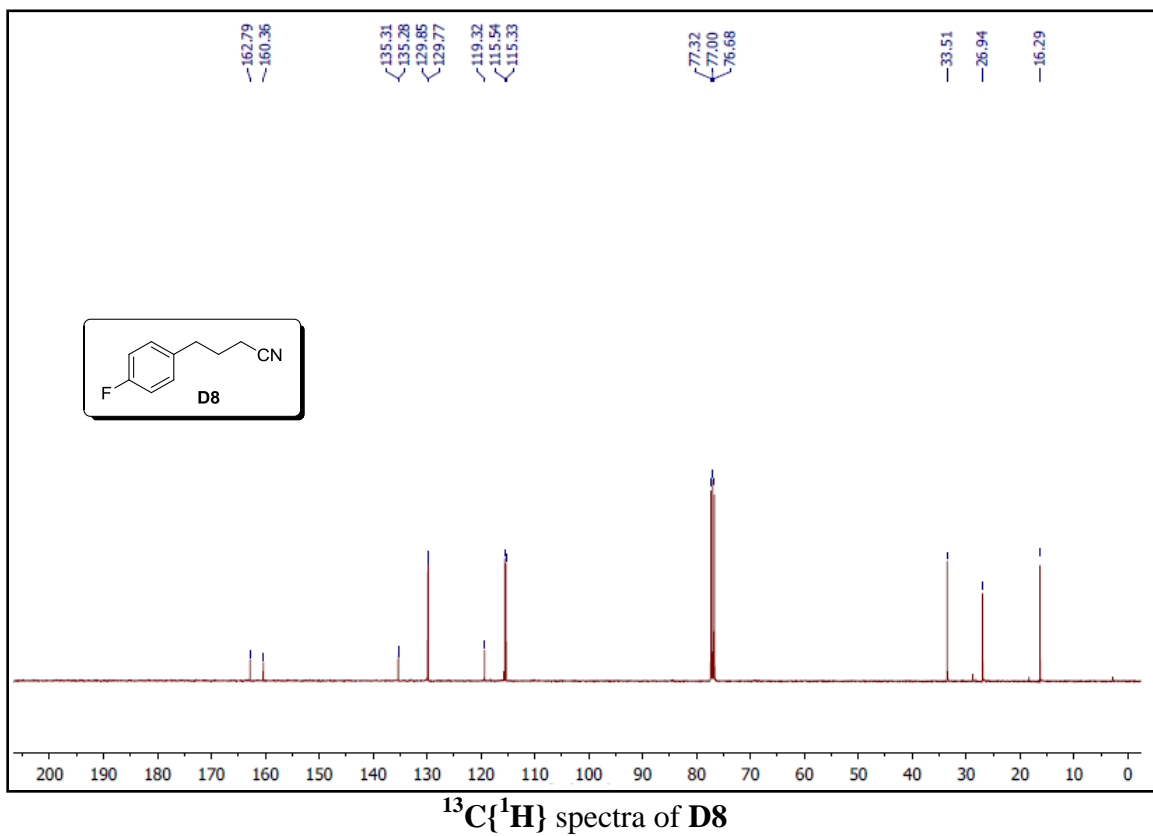
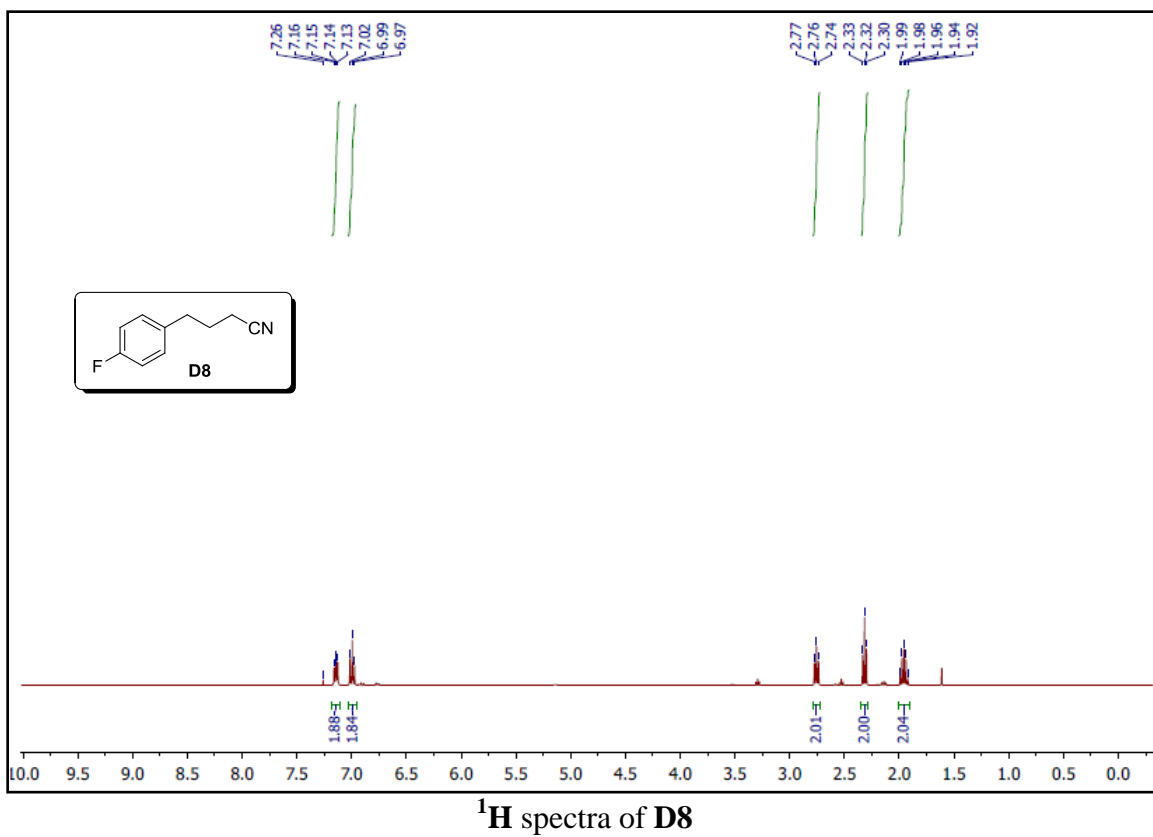


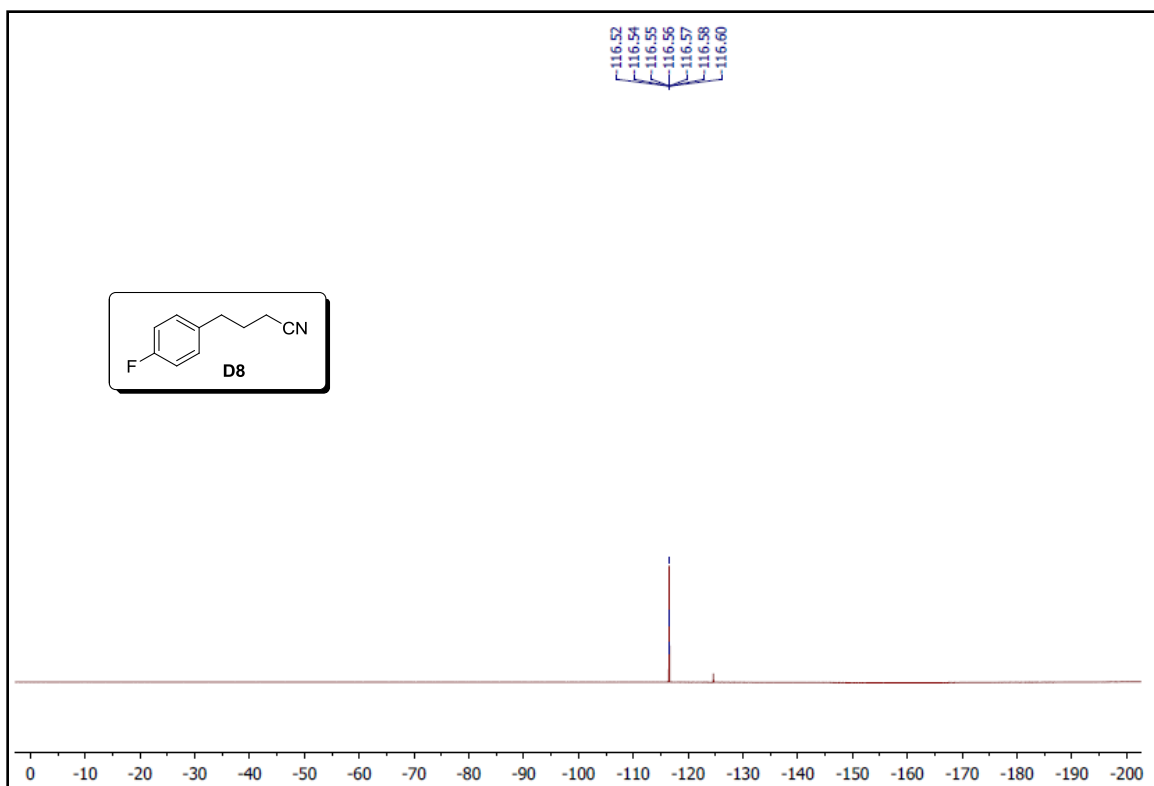




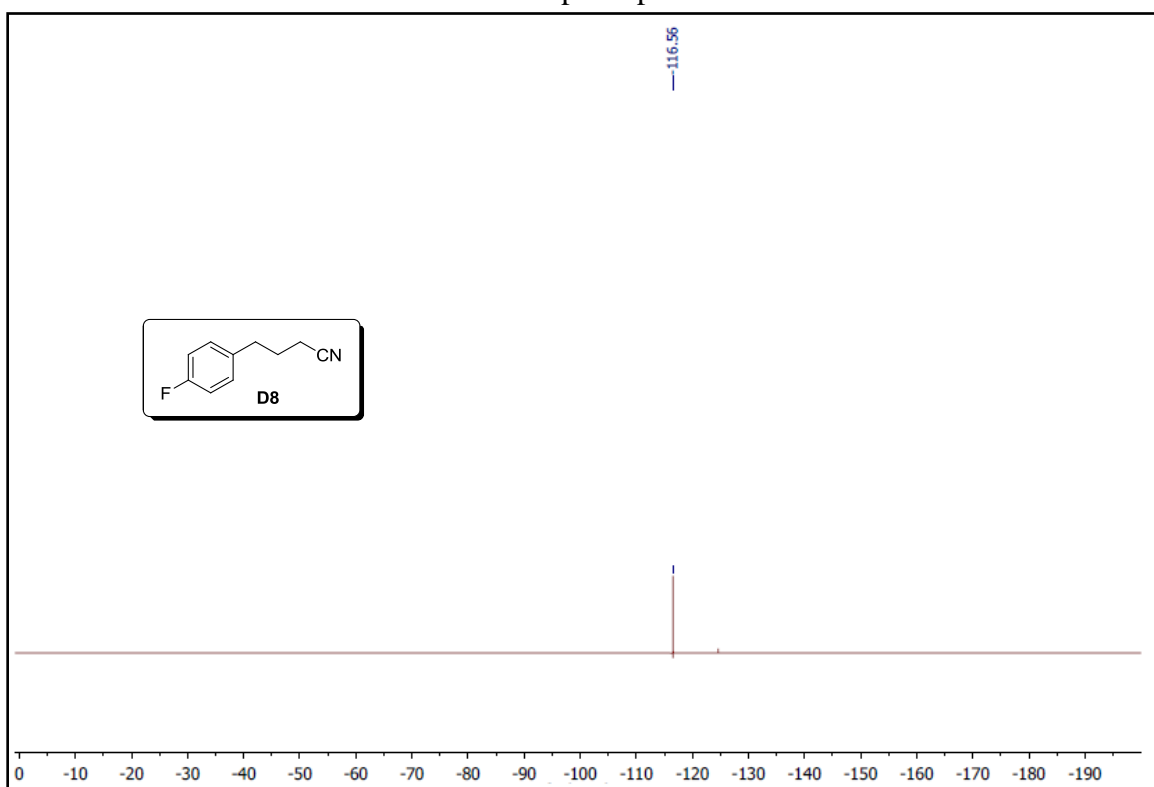




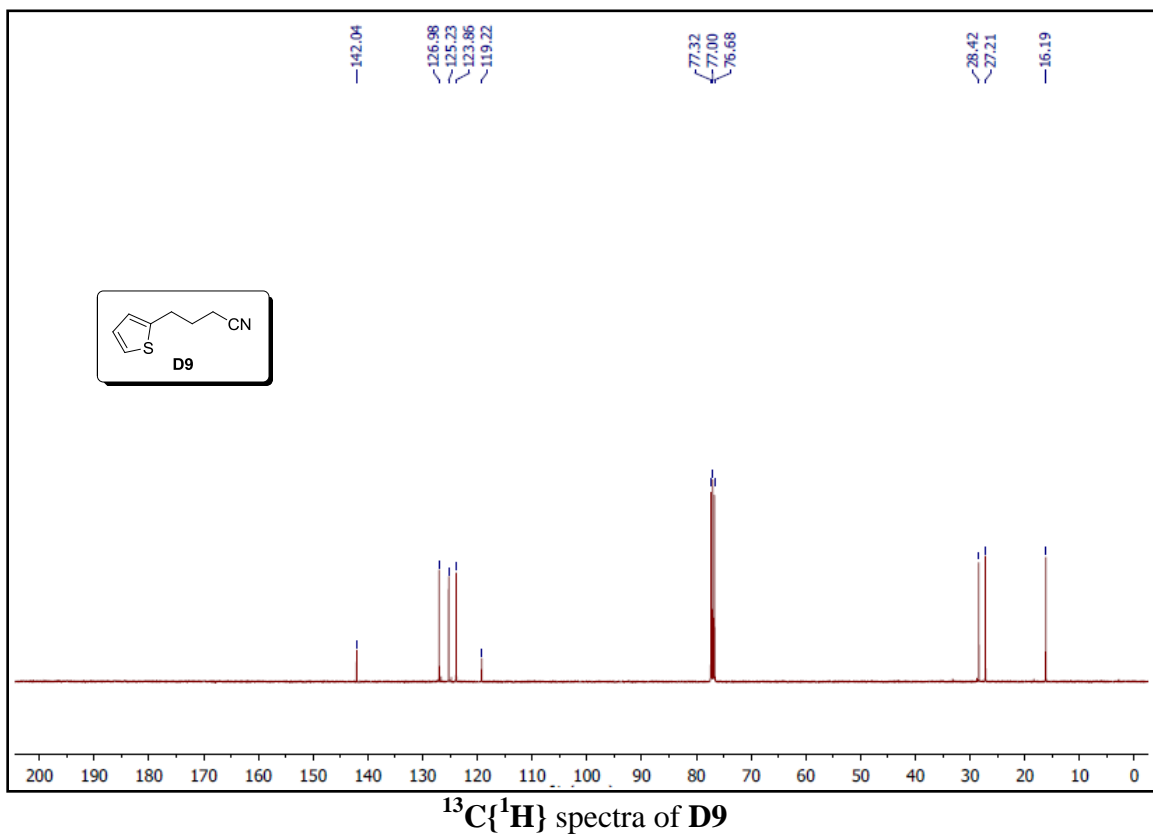
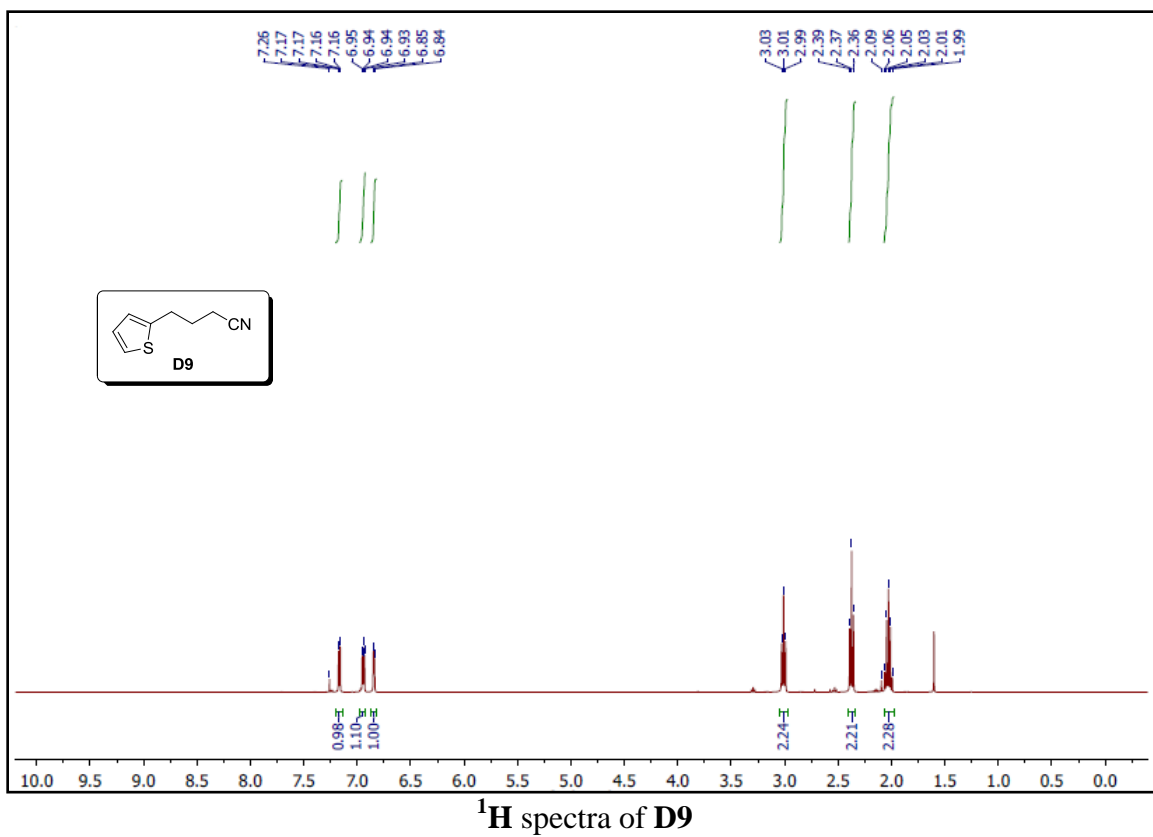


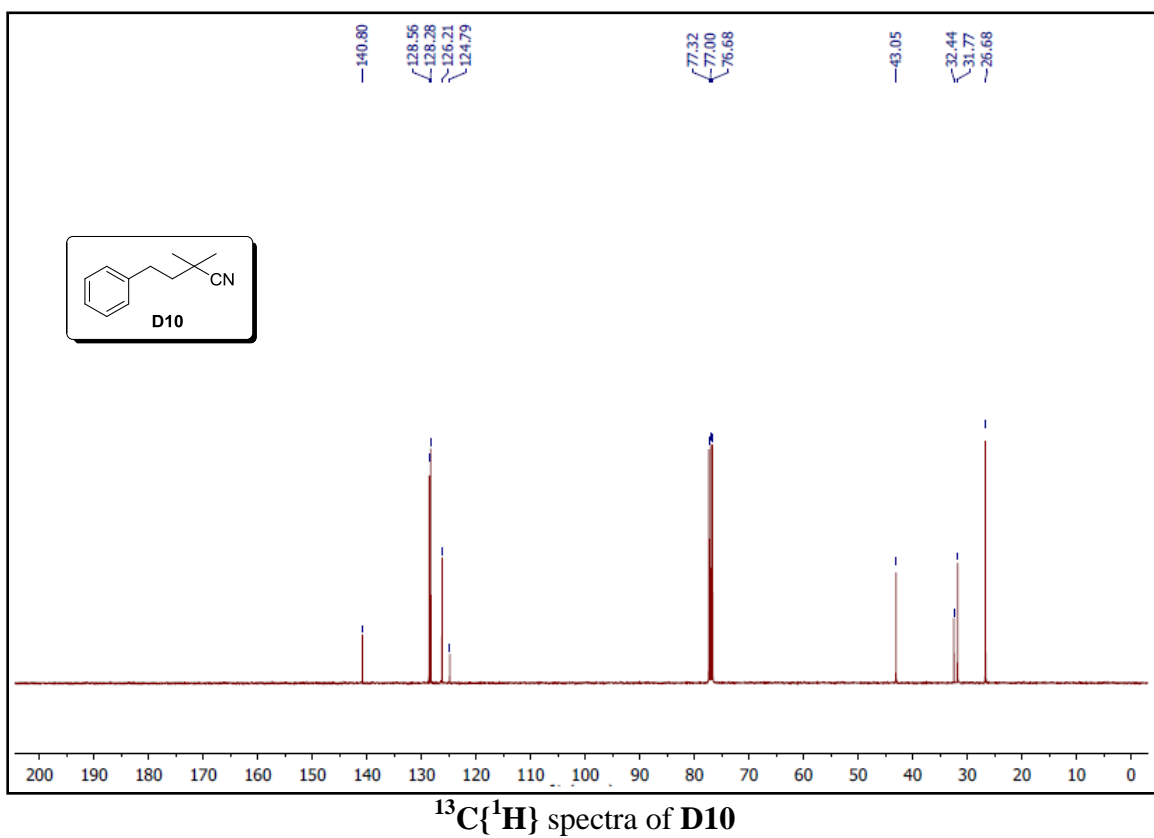
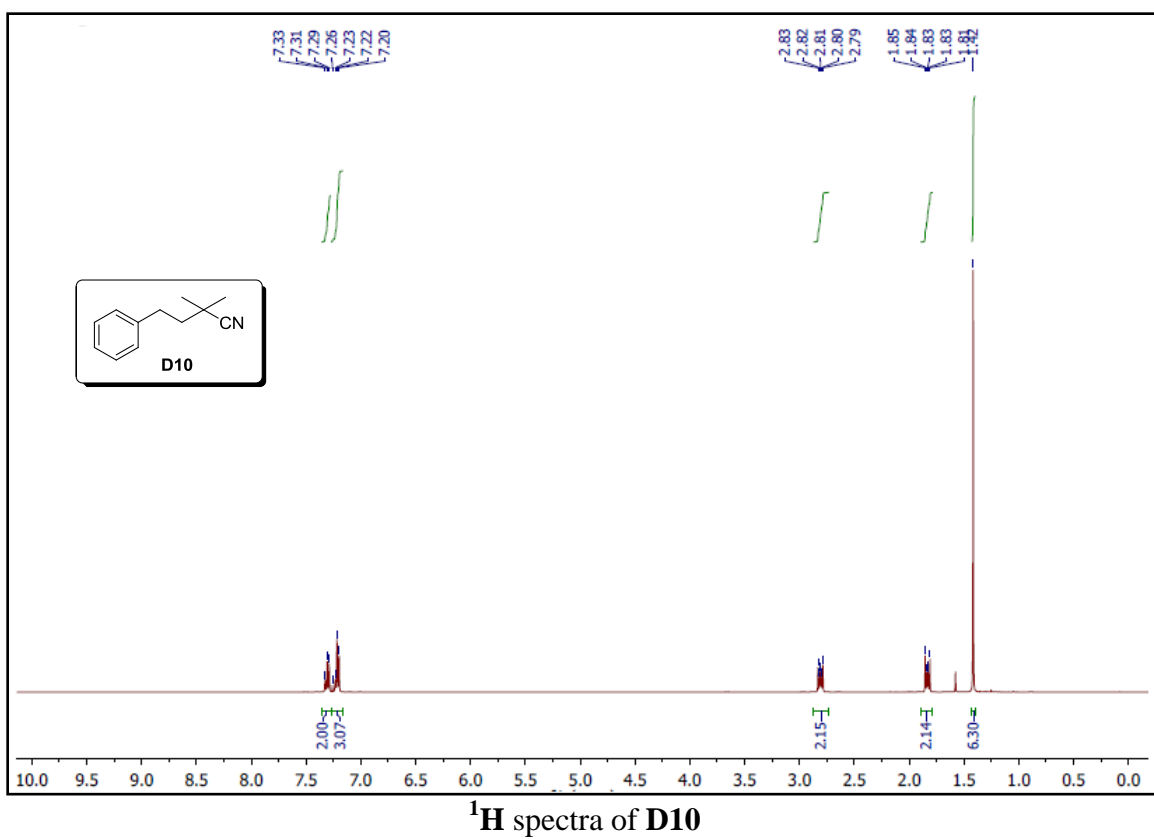


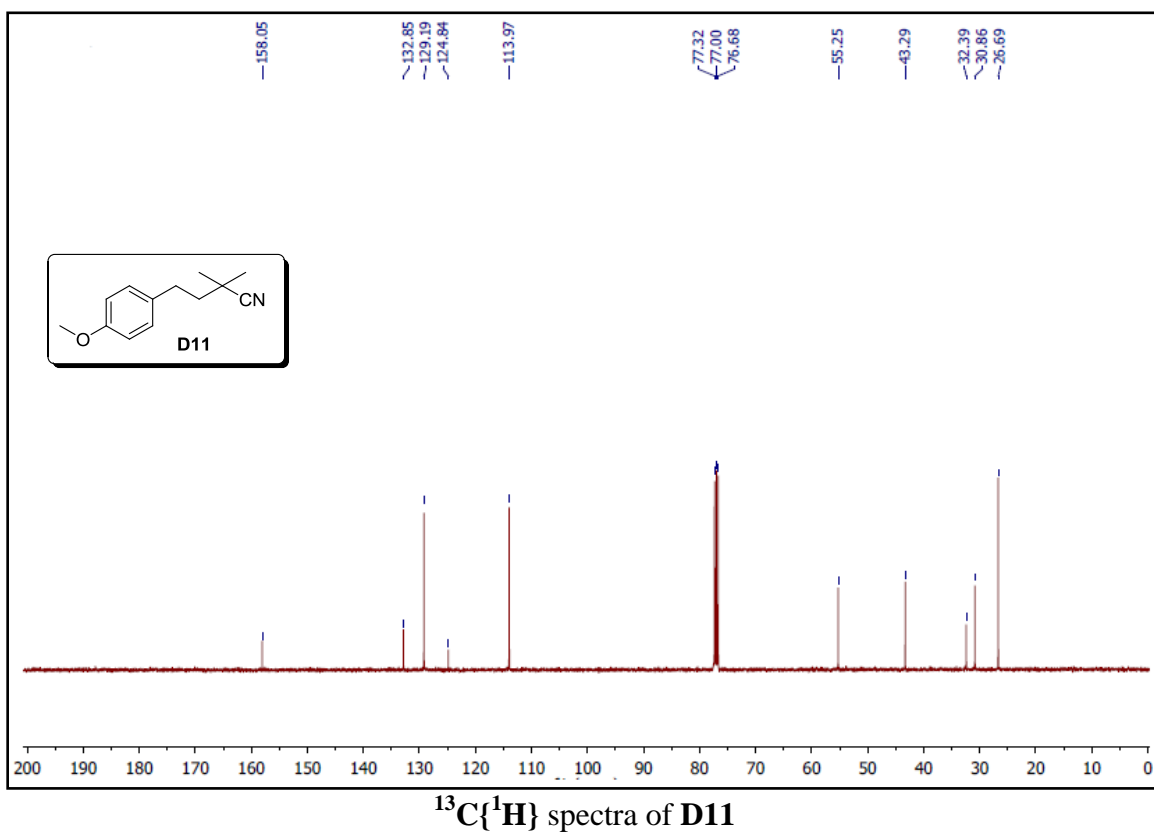
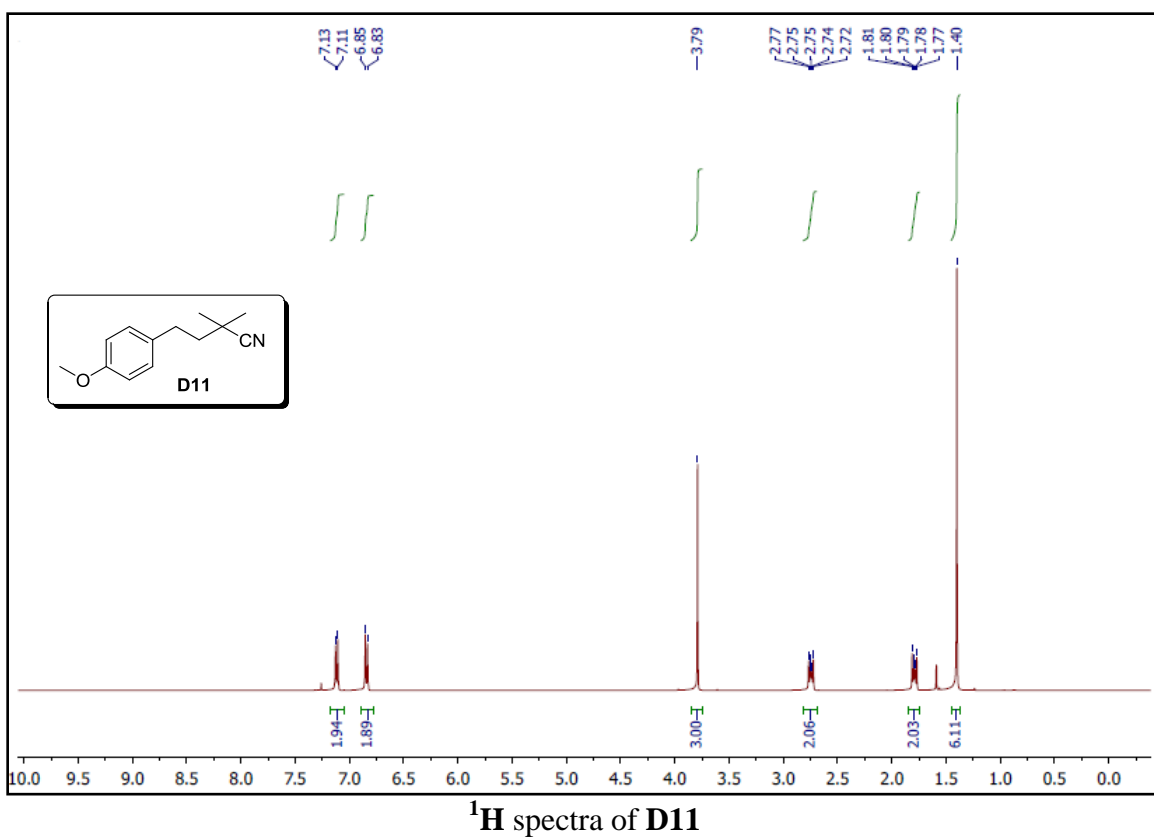
$^{19}\text{F}$  Proton coupled spectra of **D8**



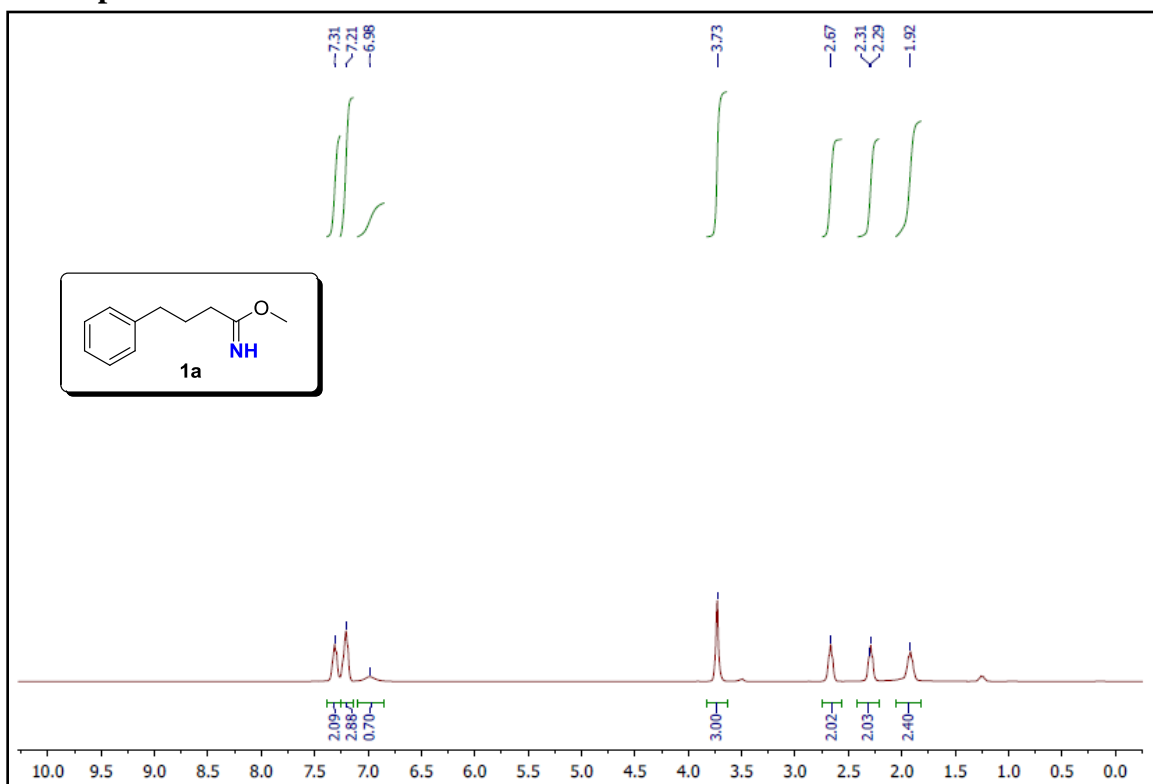
$^{19}\text{F}$  Proton decoupled spectra of **D8**



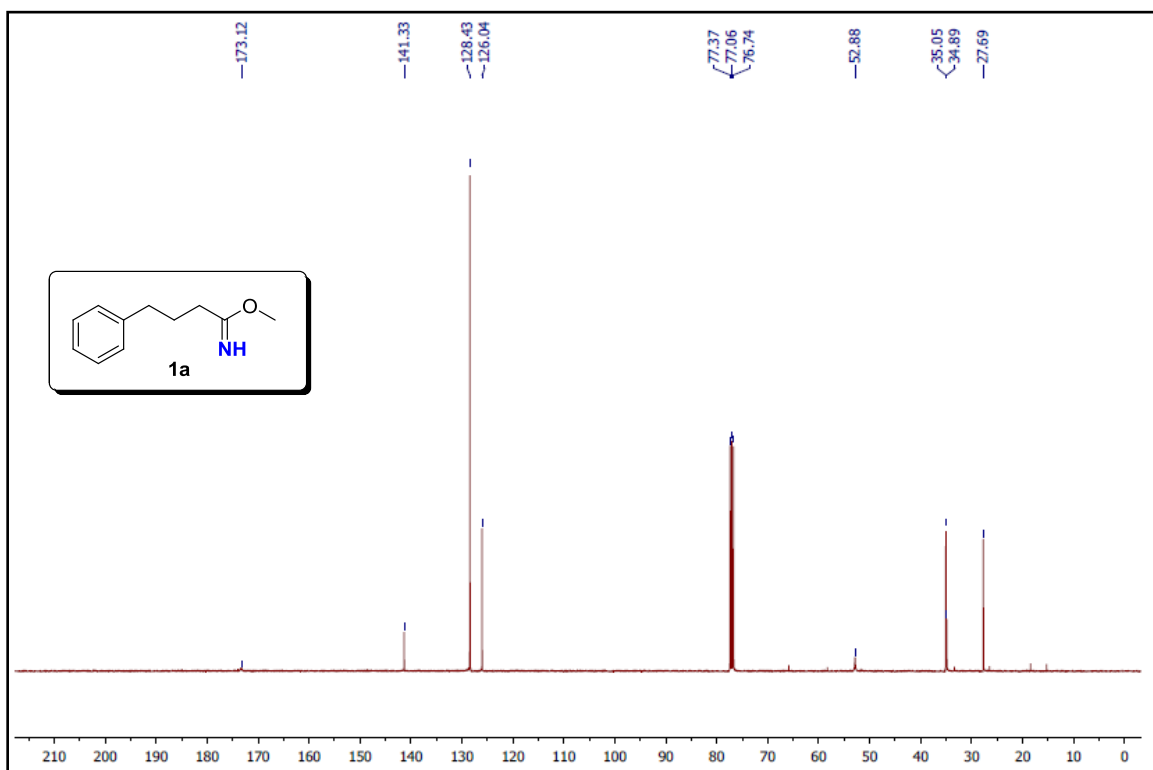




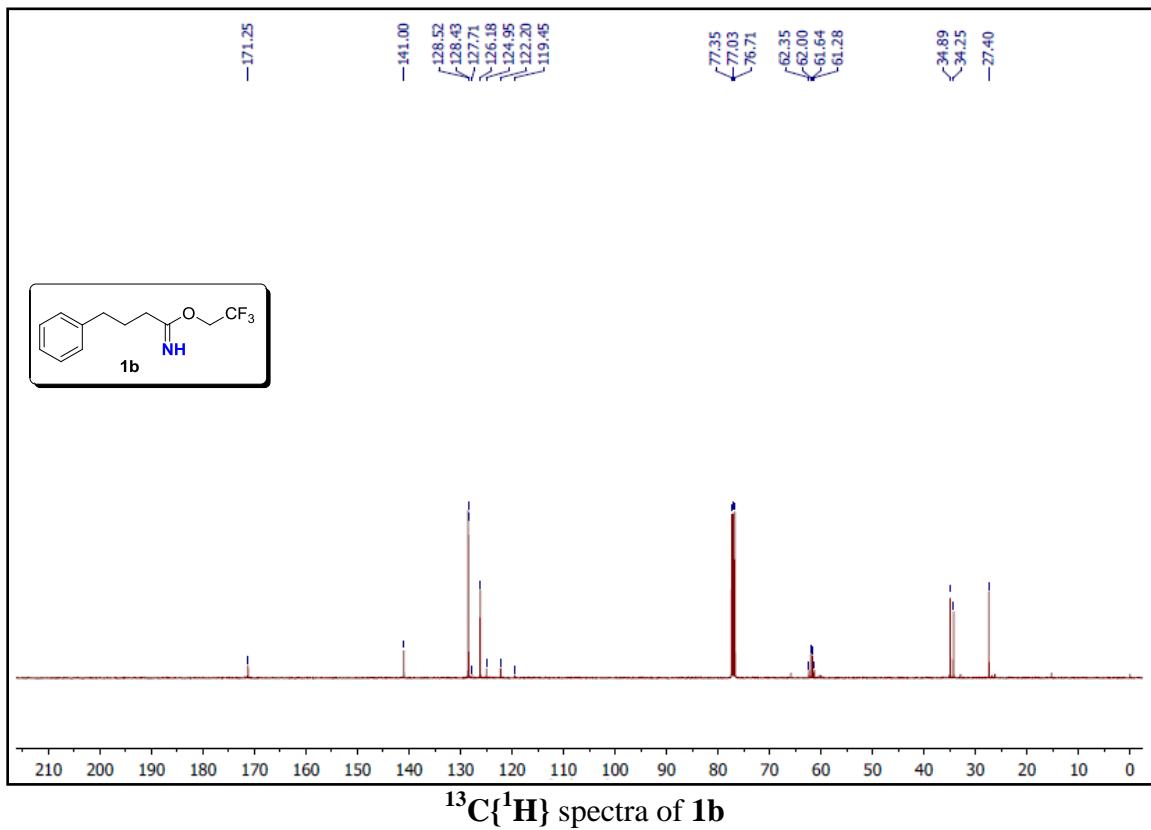
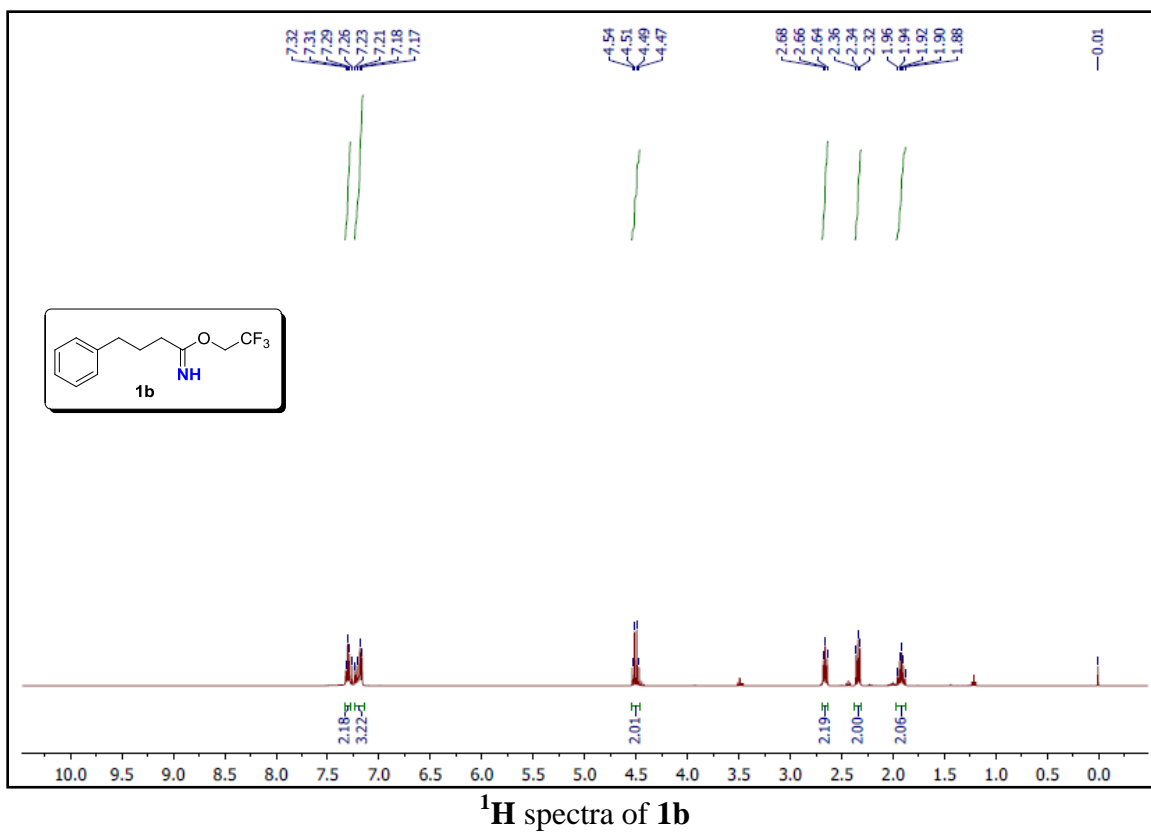
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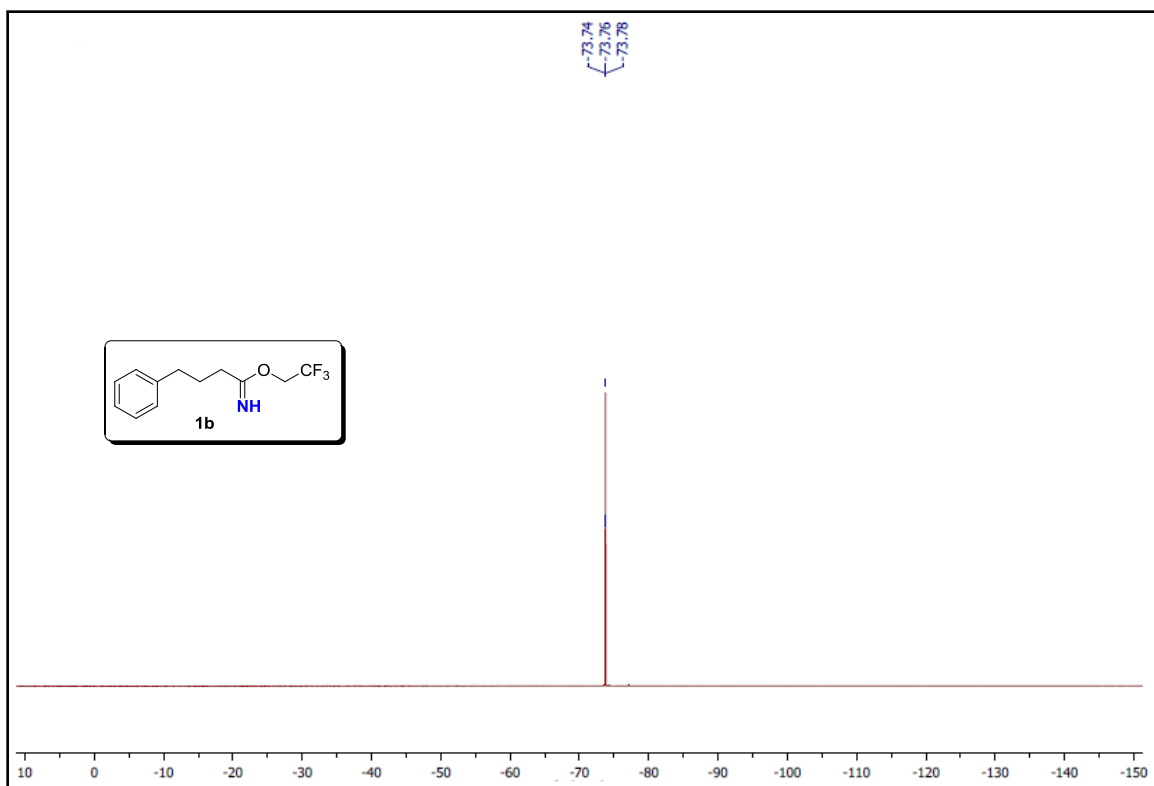


<sup>1</sup>H spectra of **1a**

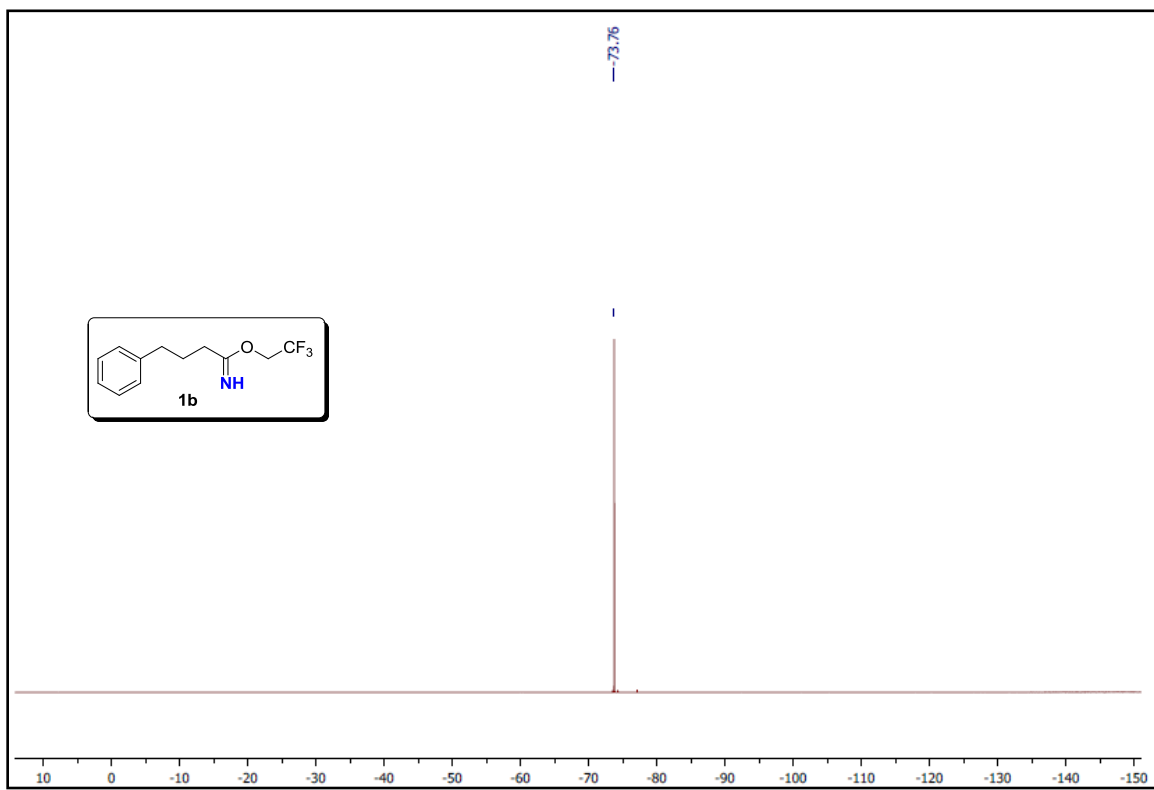


<sup>13</sup>C{<sup>1</sup>H} spectra of **1a**

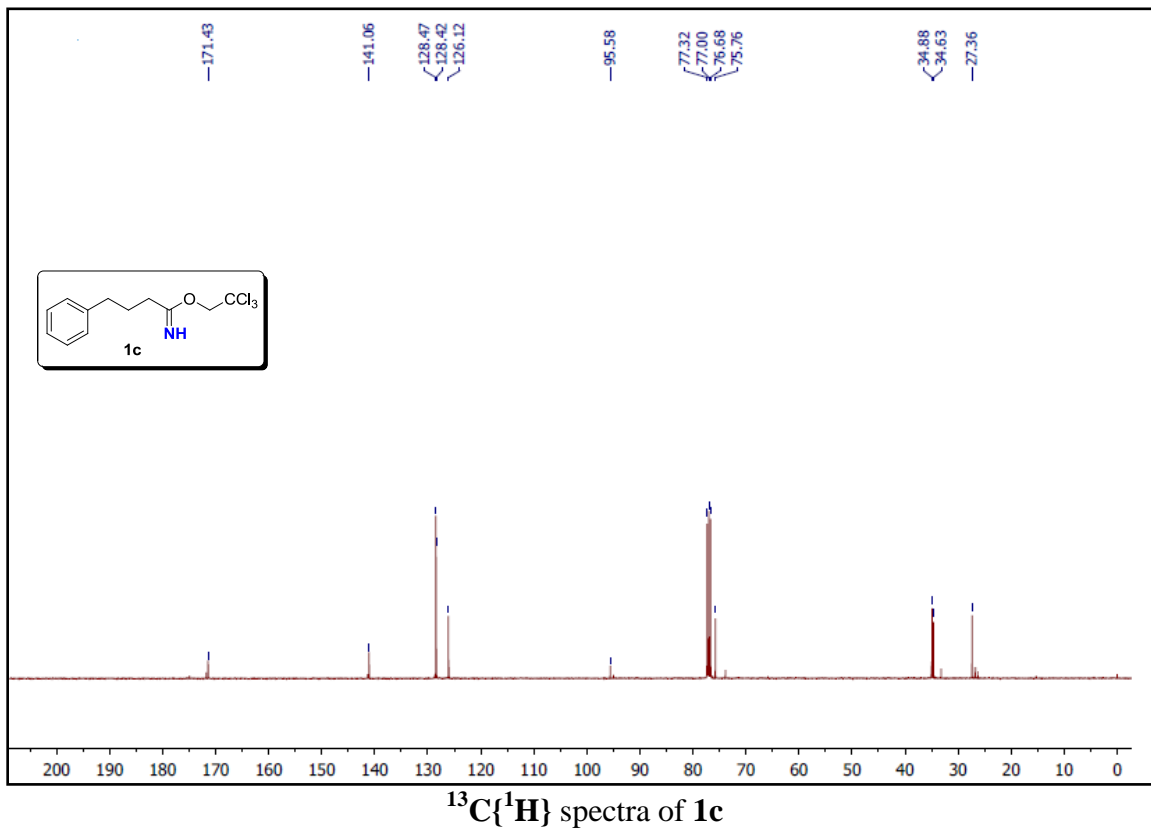
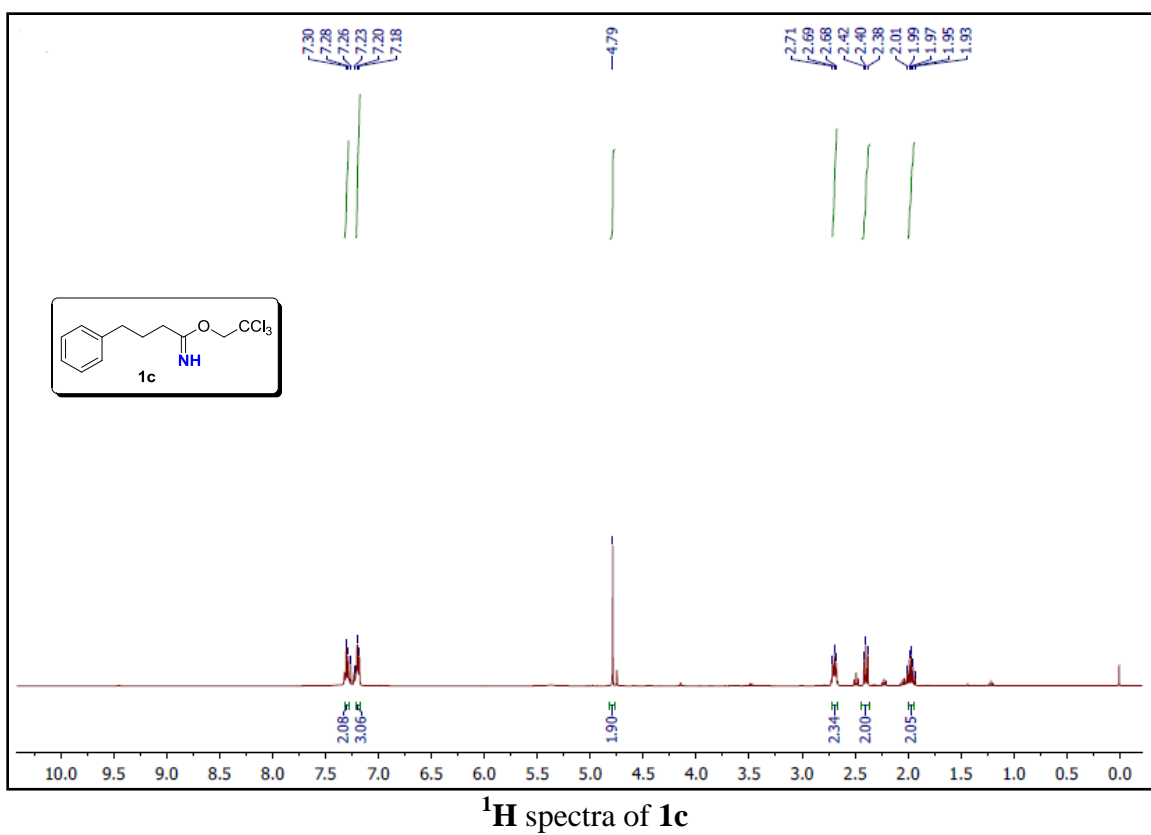


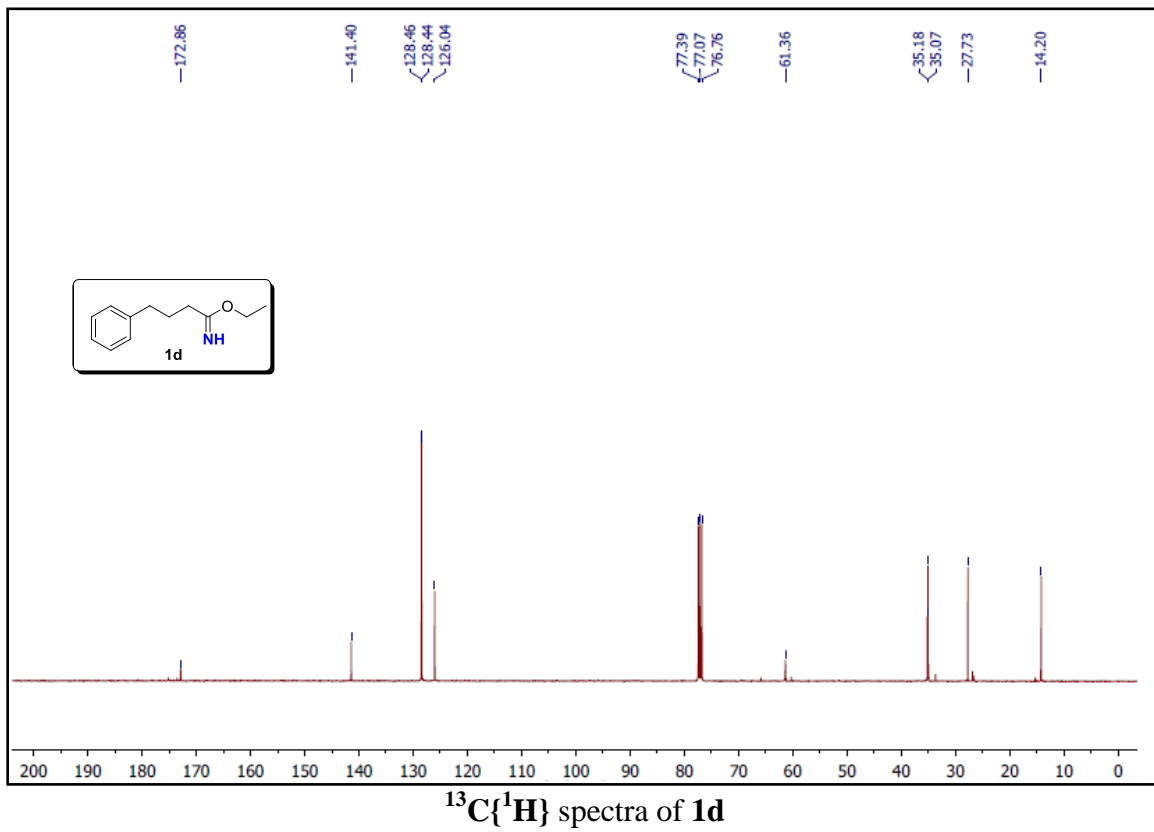
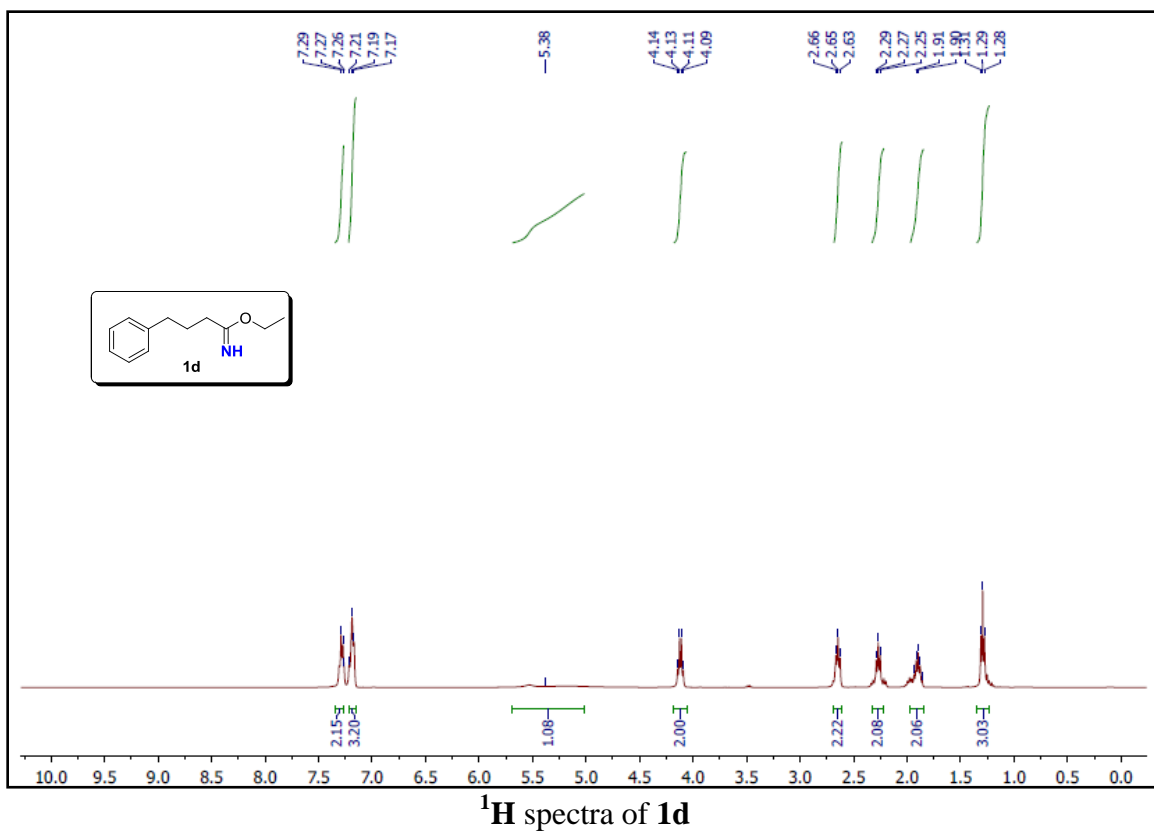


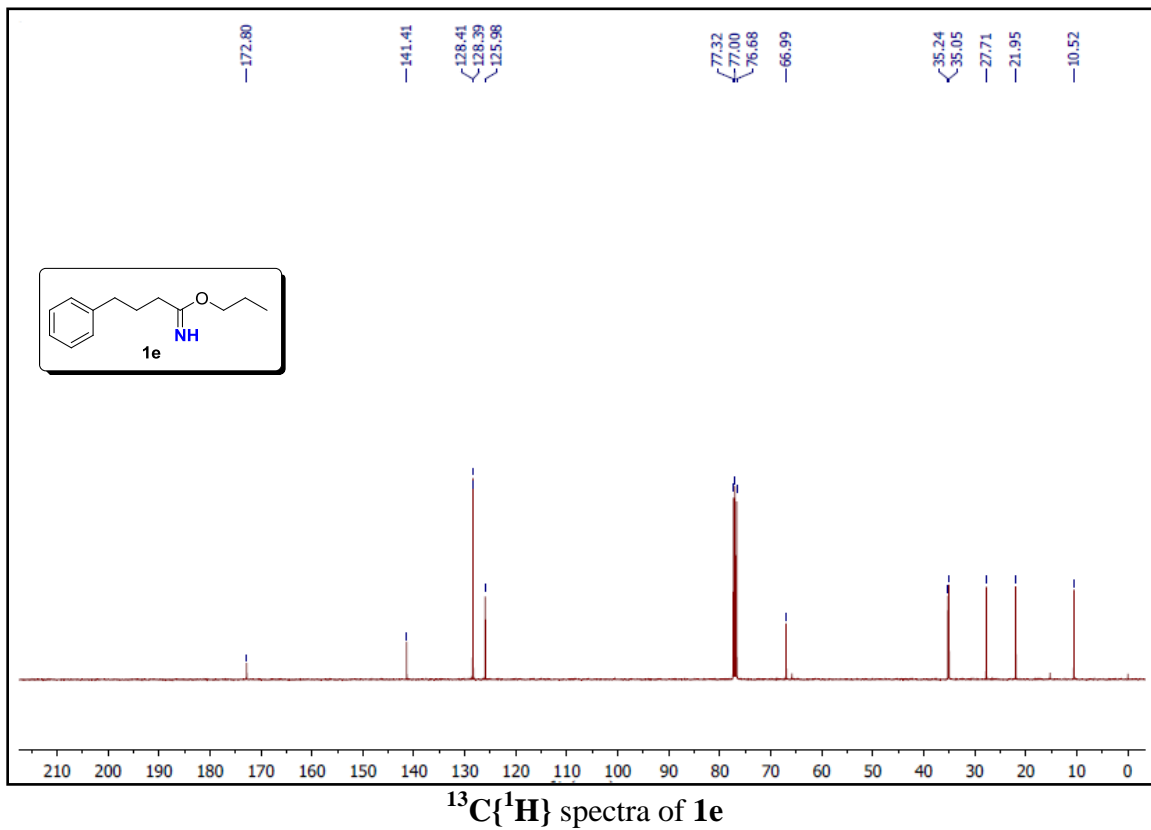
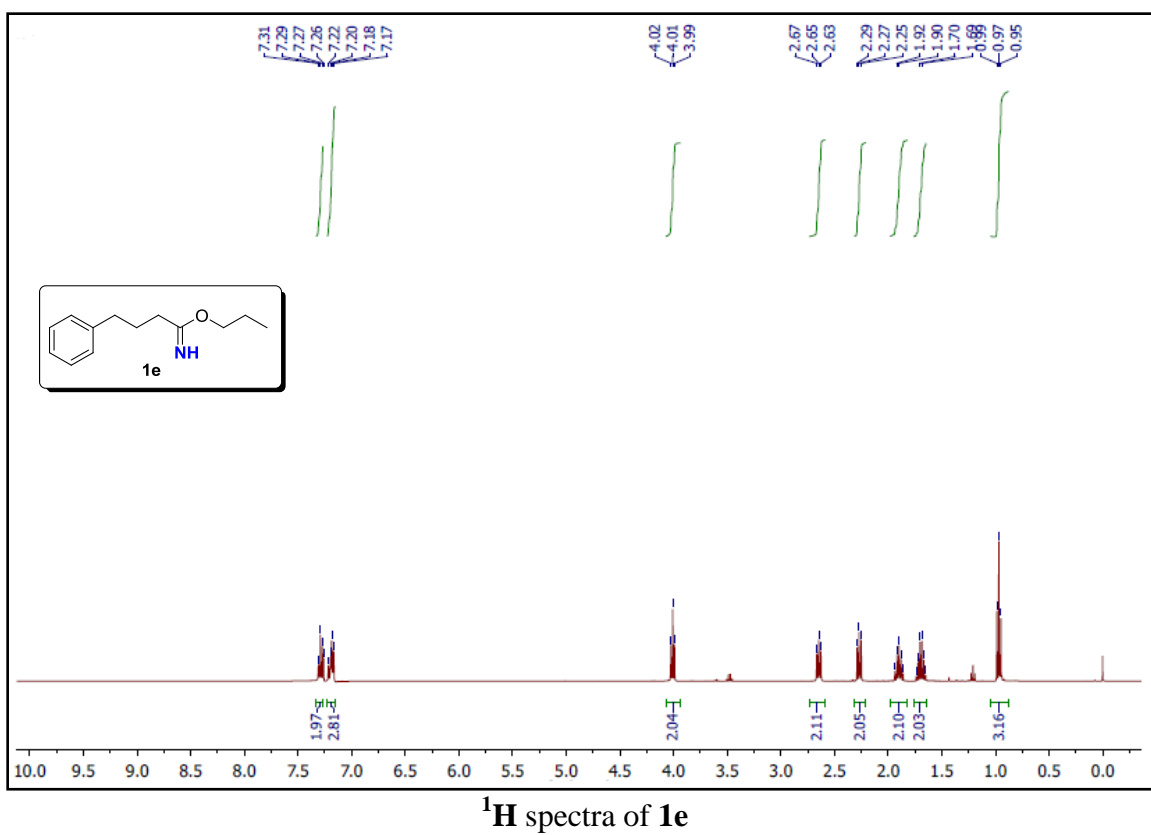
$^{19}\text{F}$  Proton coupled spectra of **1b**

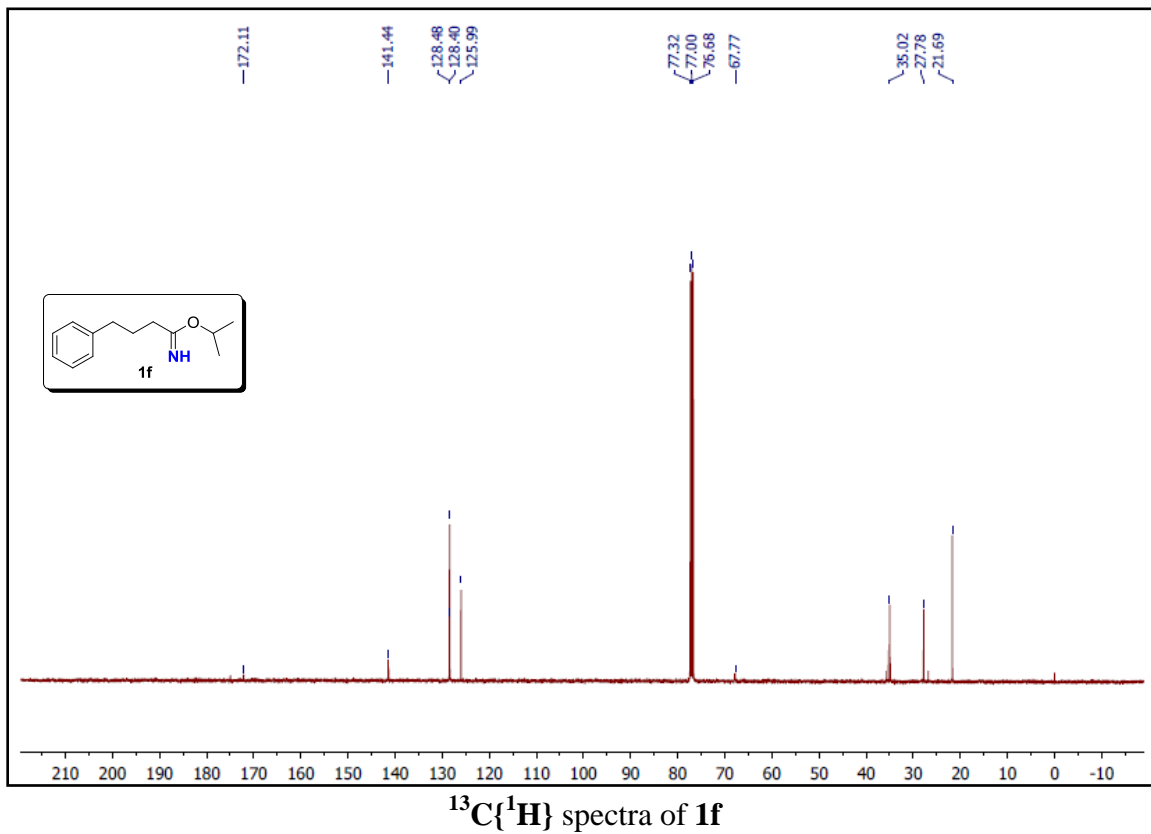
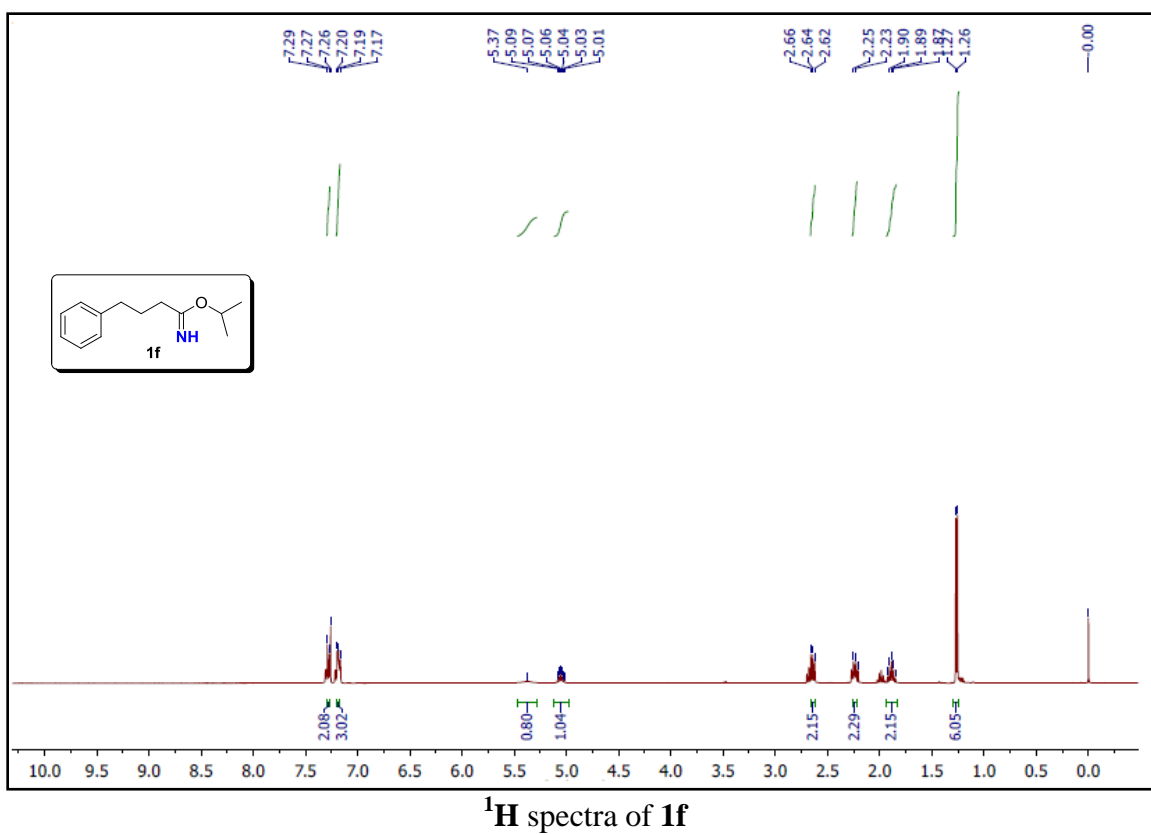


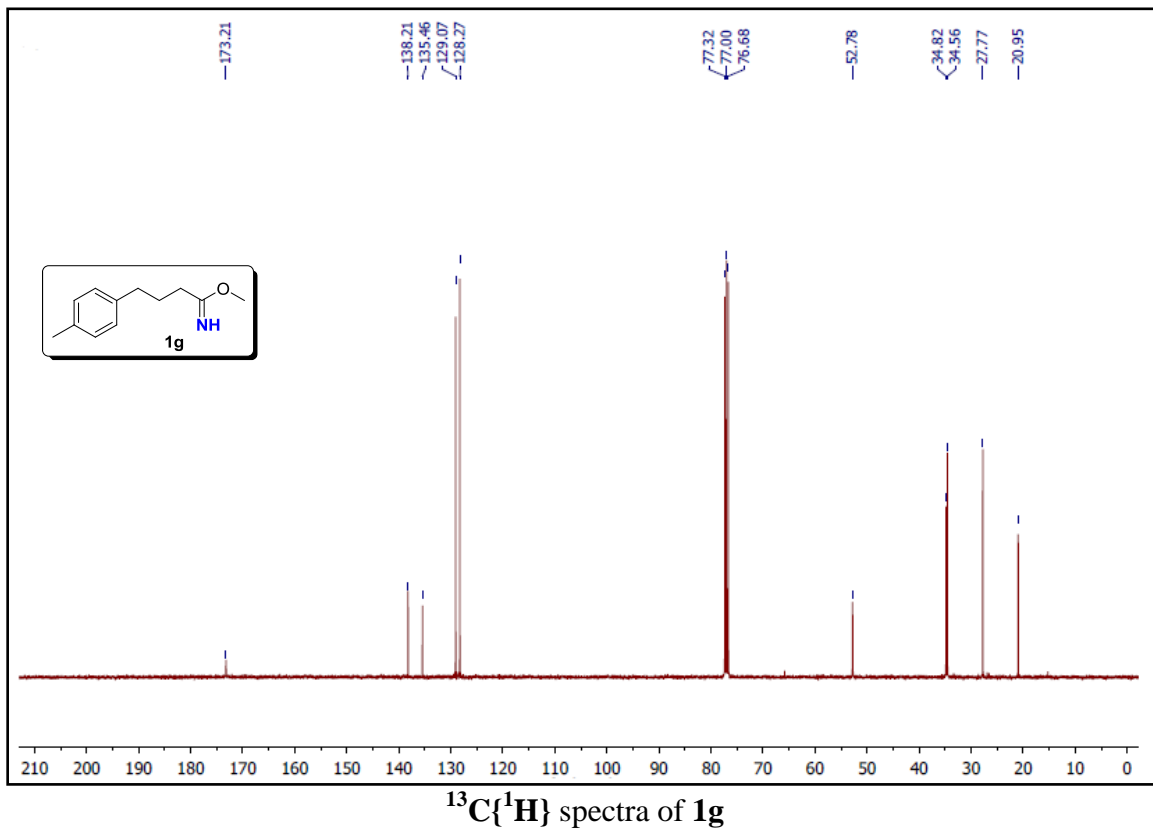
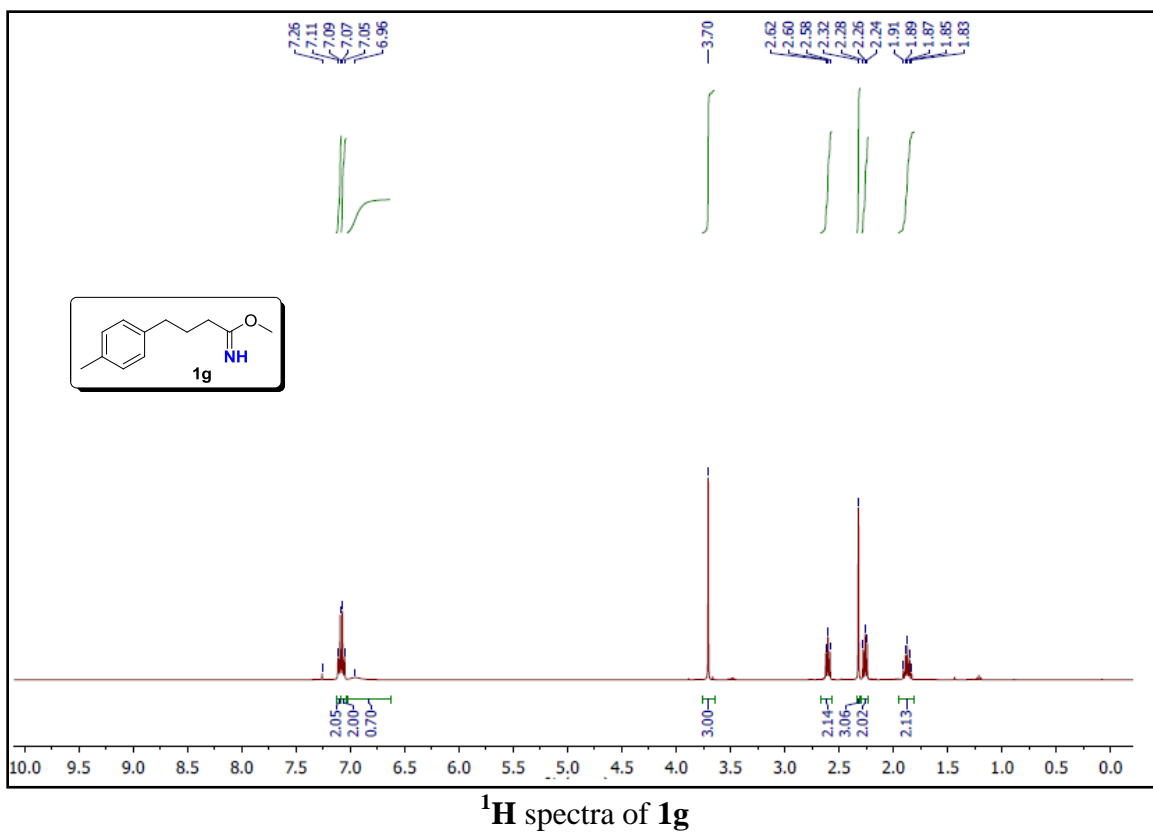
$^{19}\text{F}$  Proton decoupled spectra of **1b**

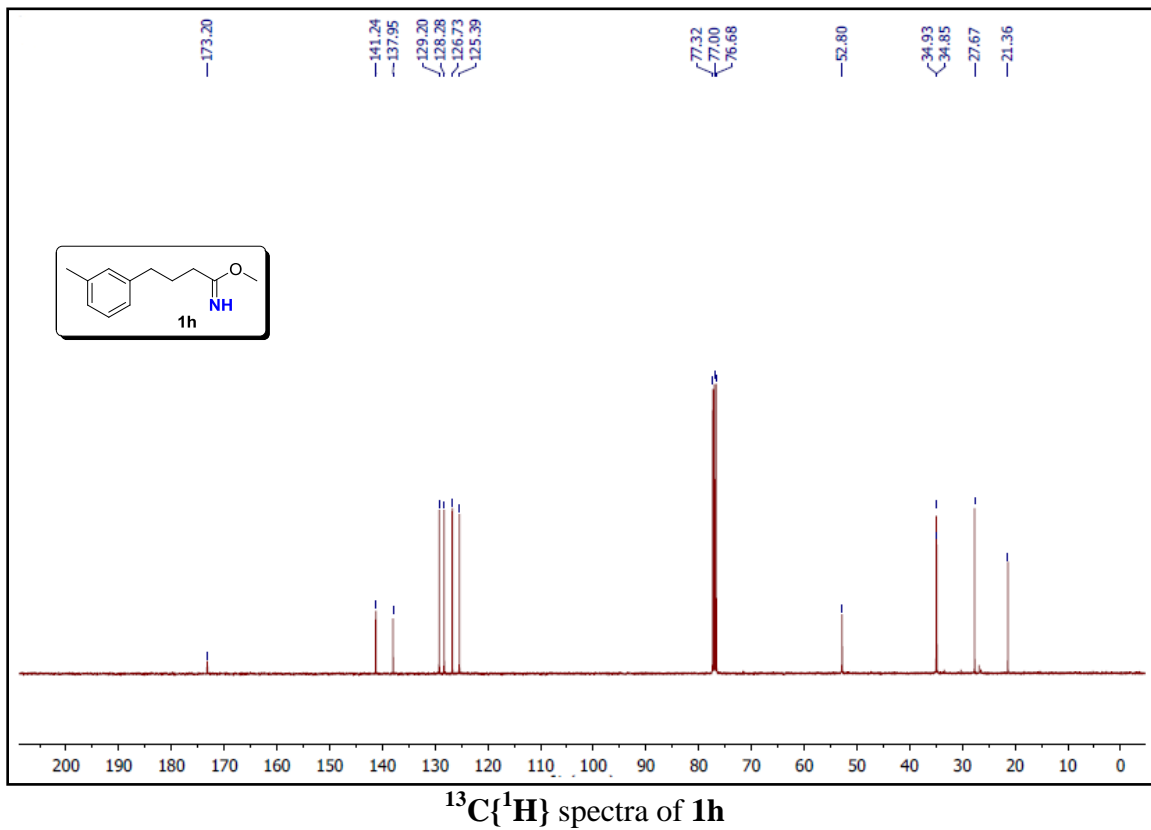
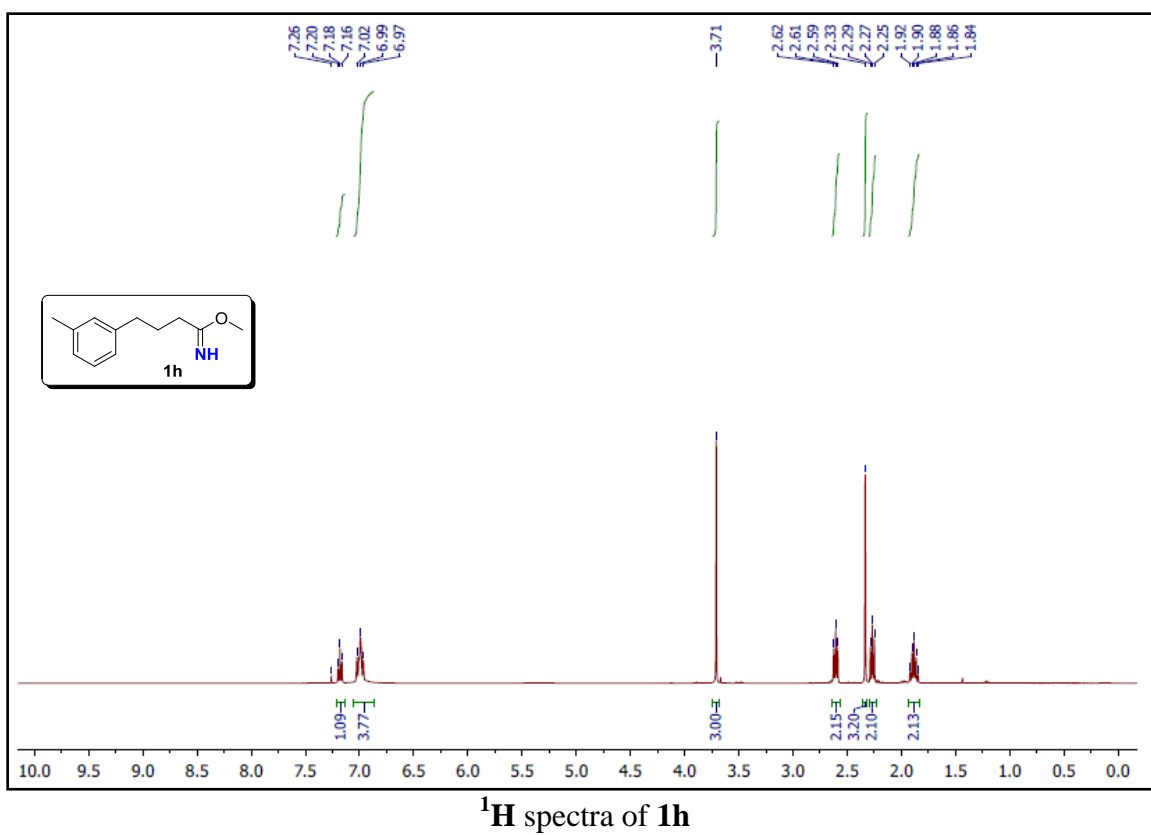


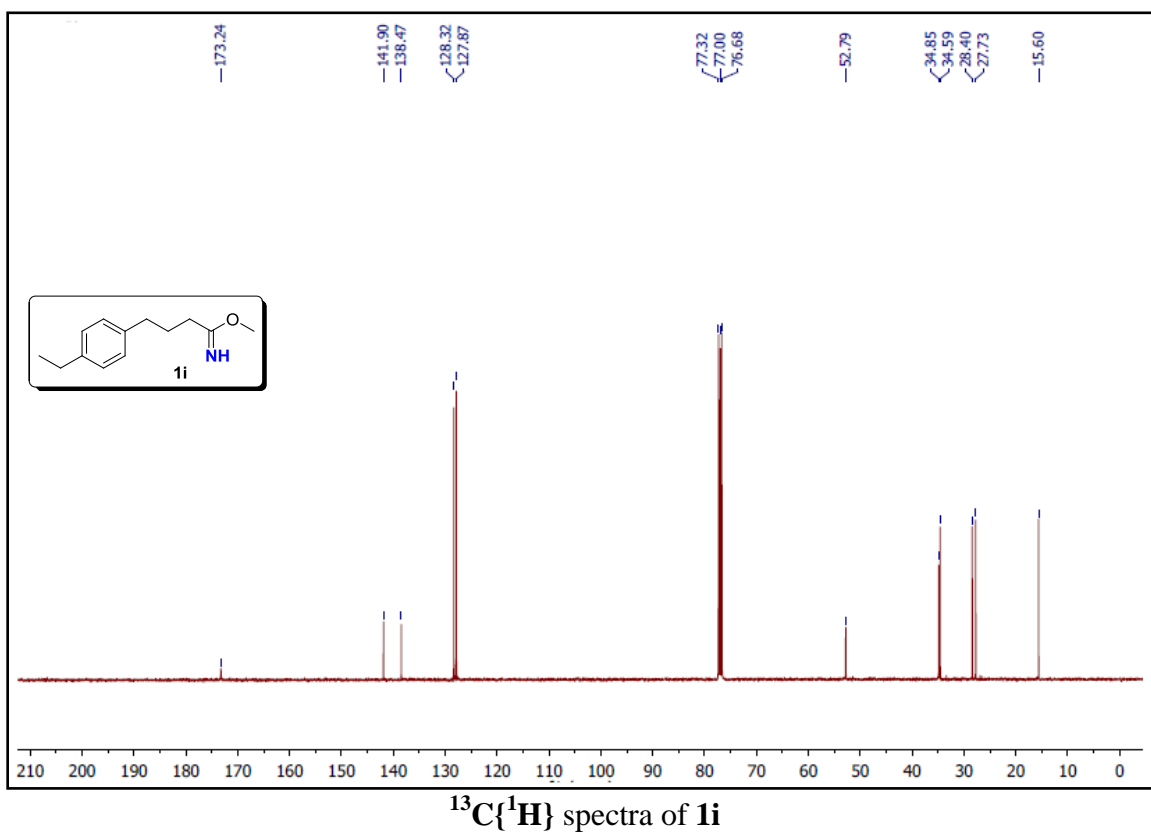
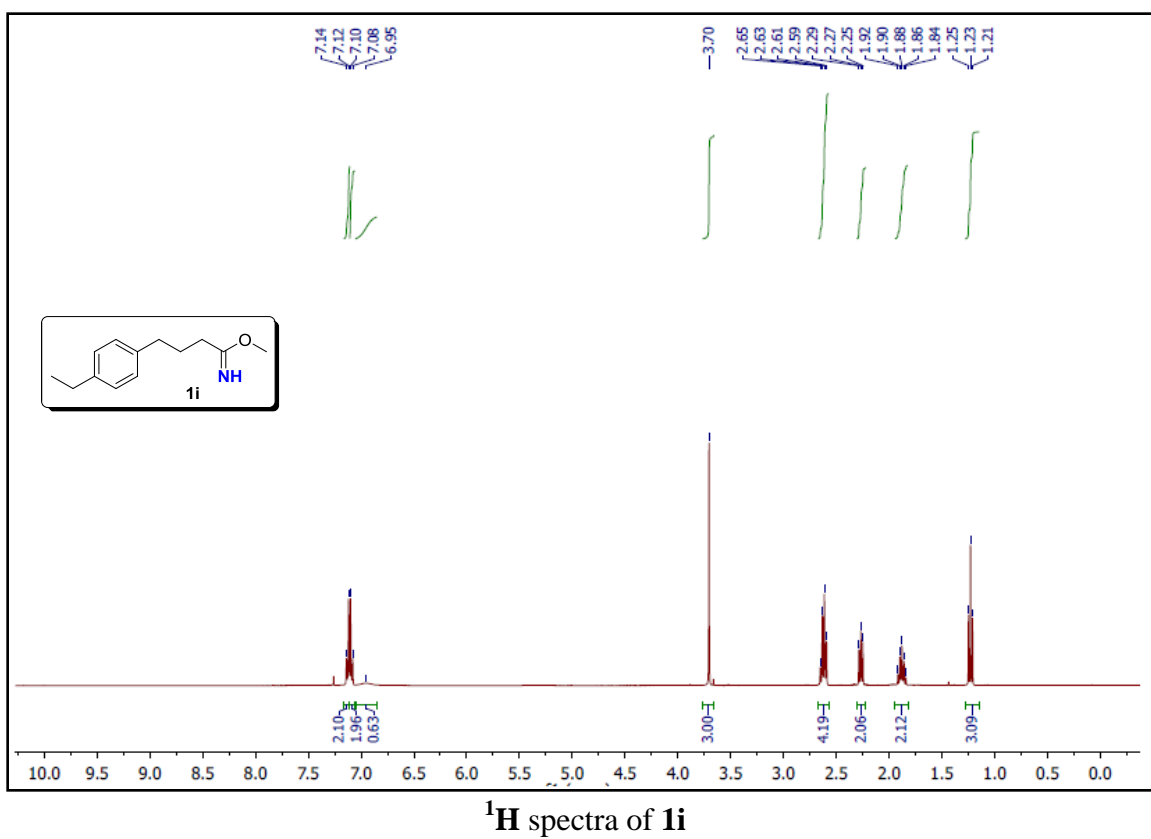


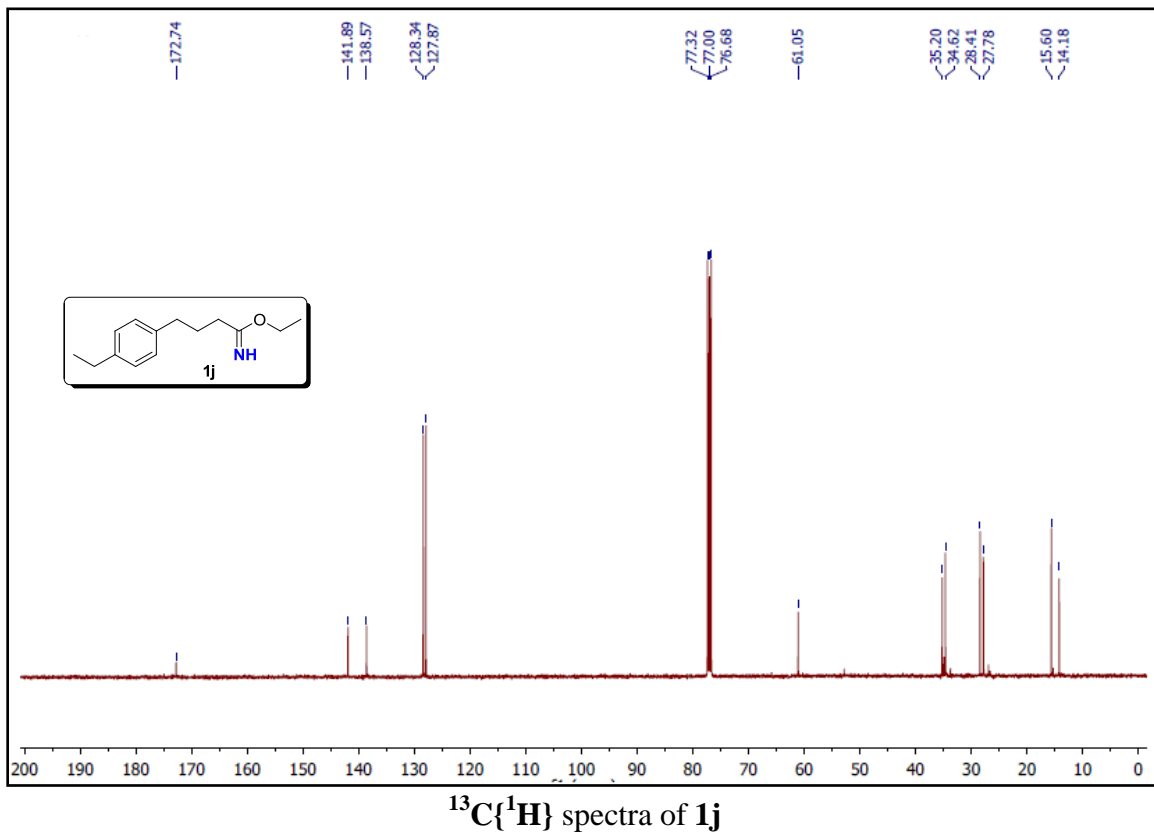
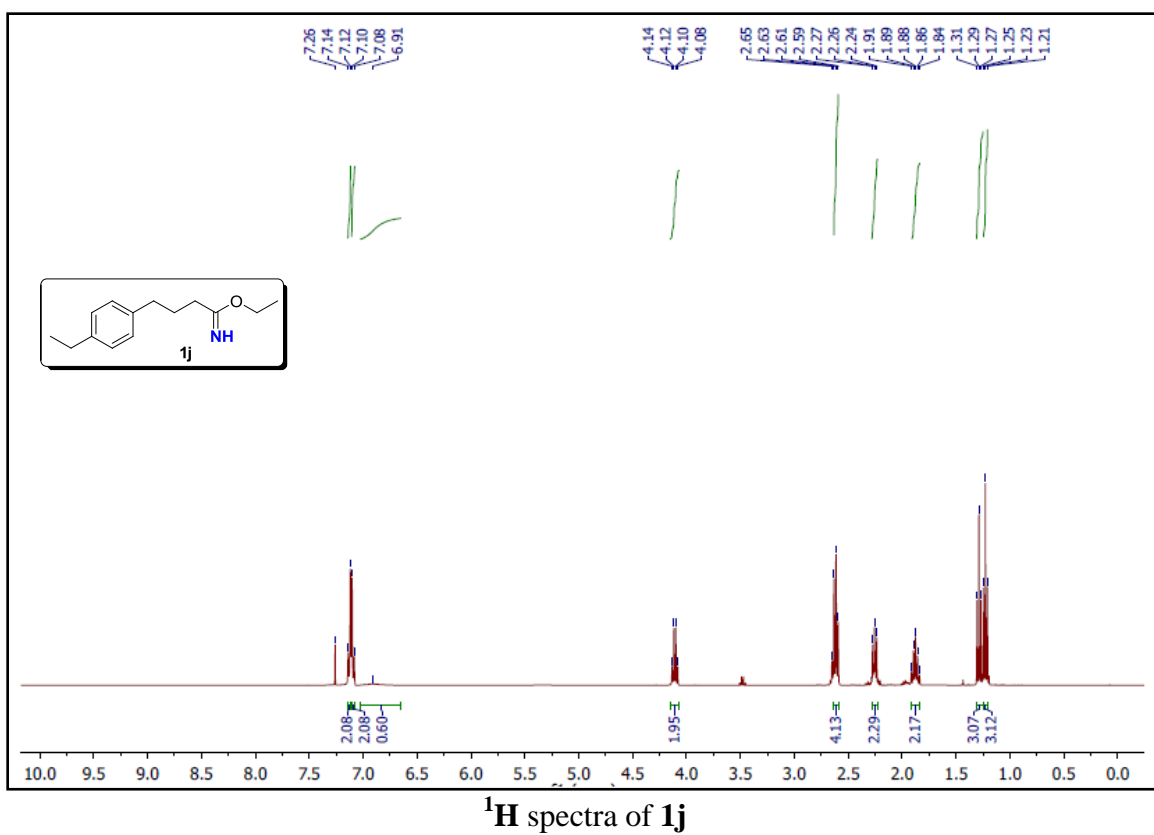


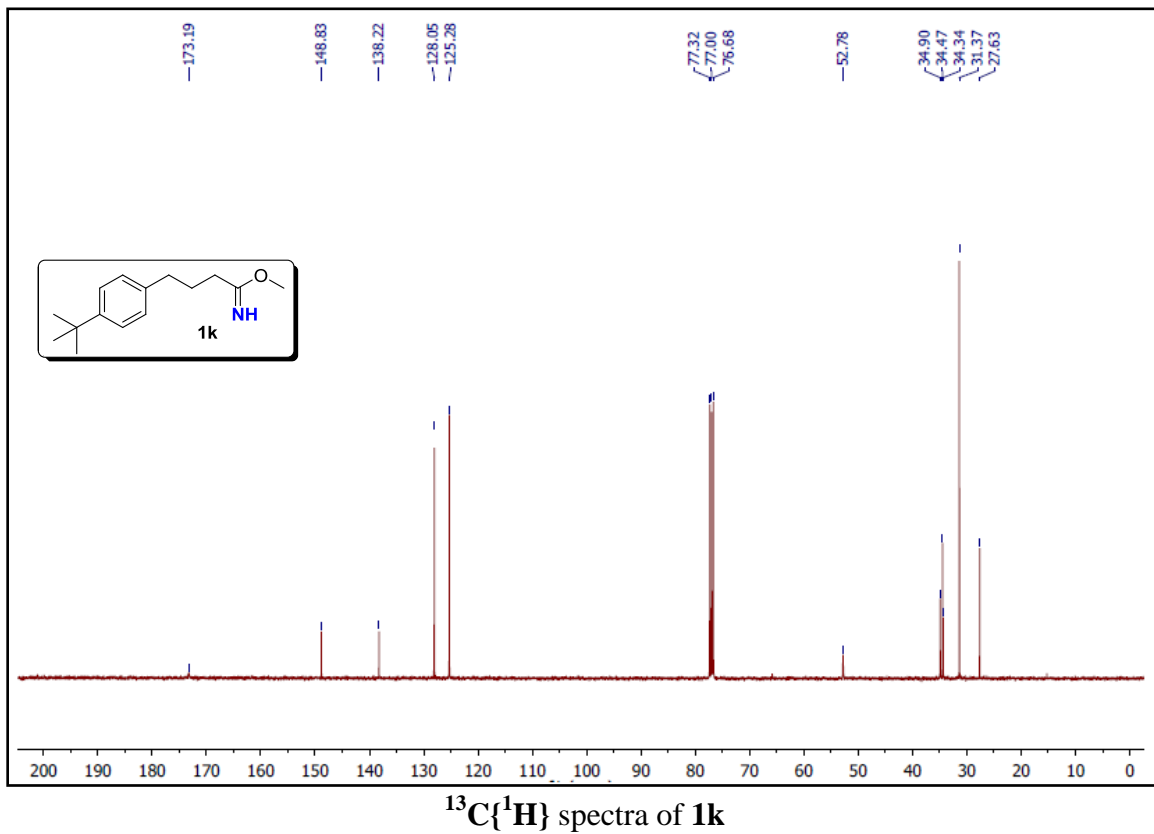
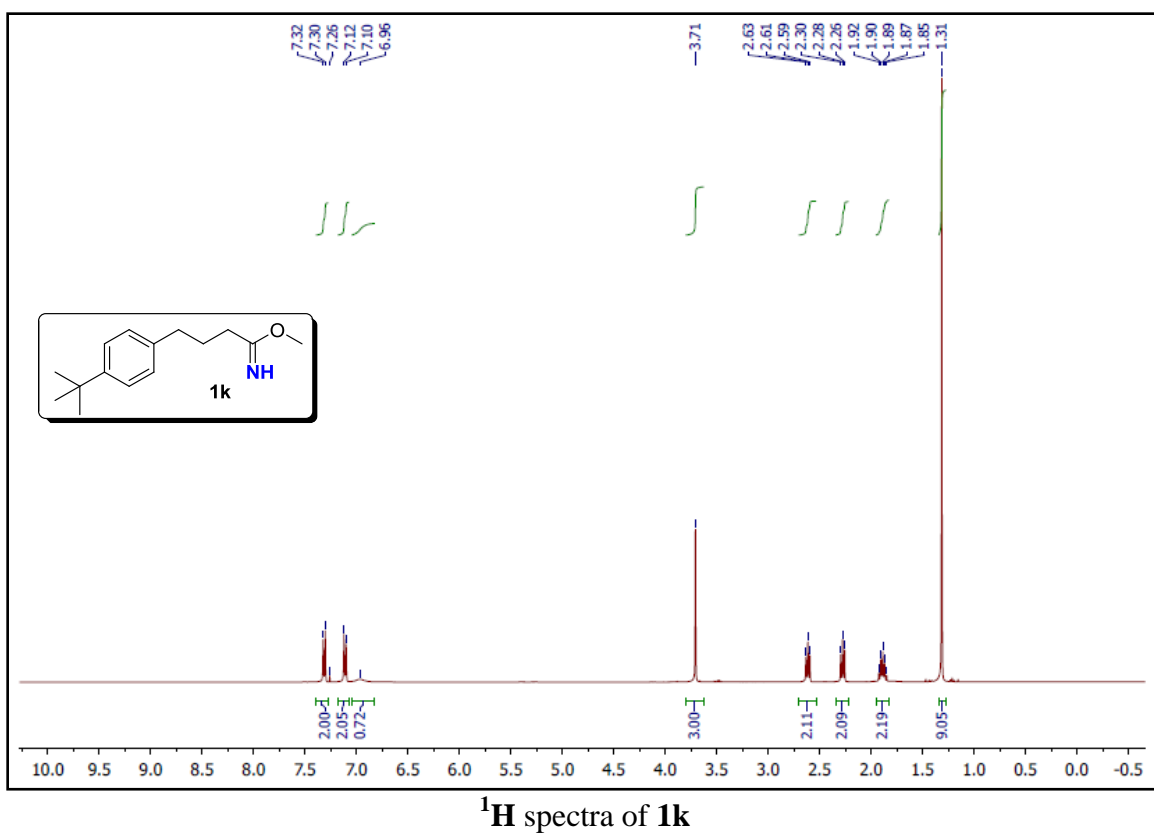


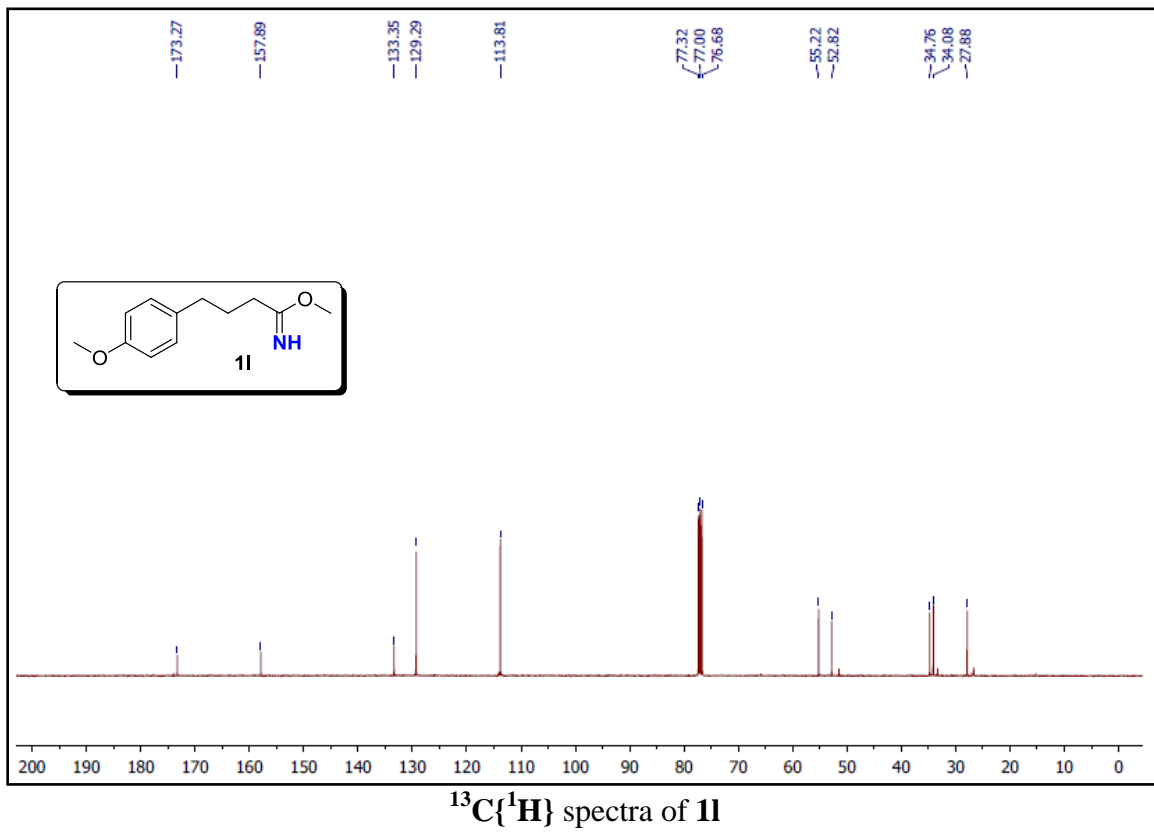
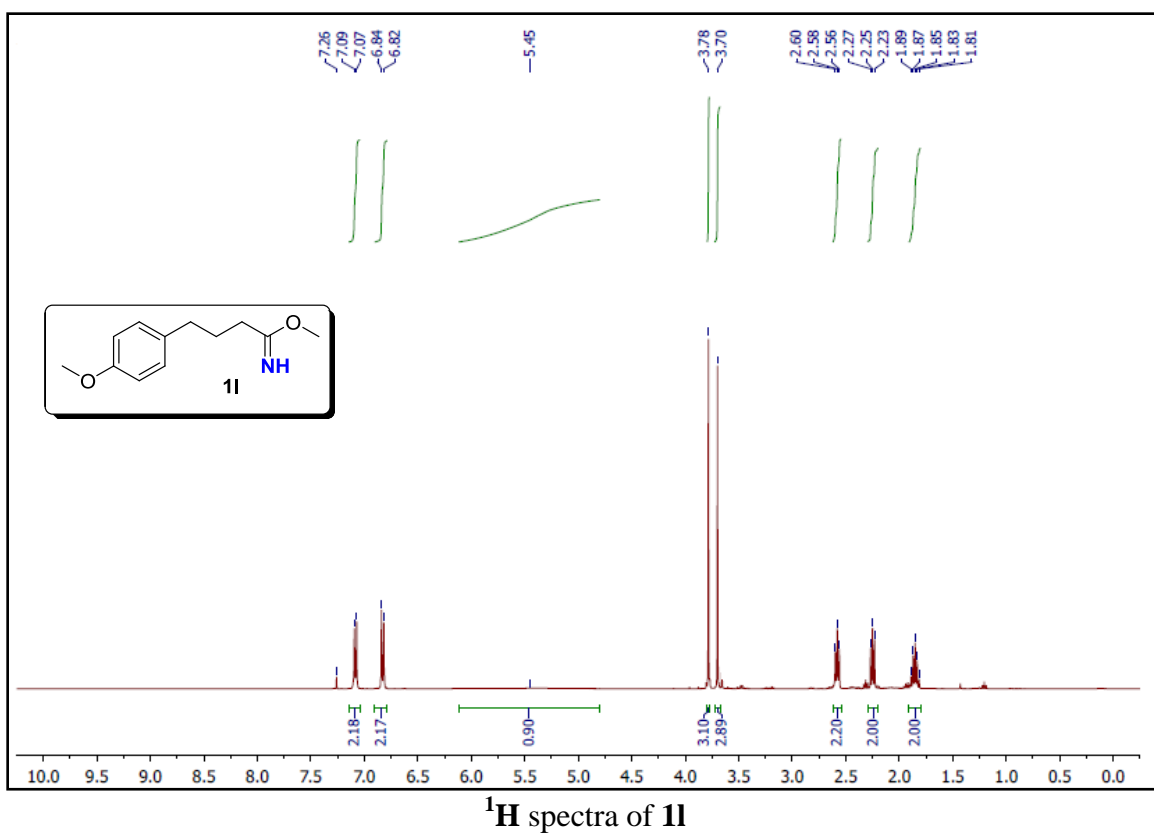


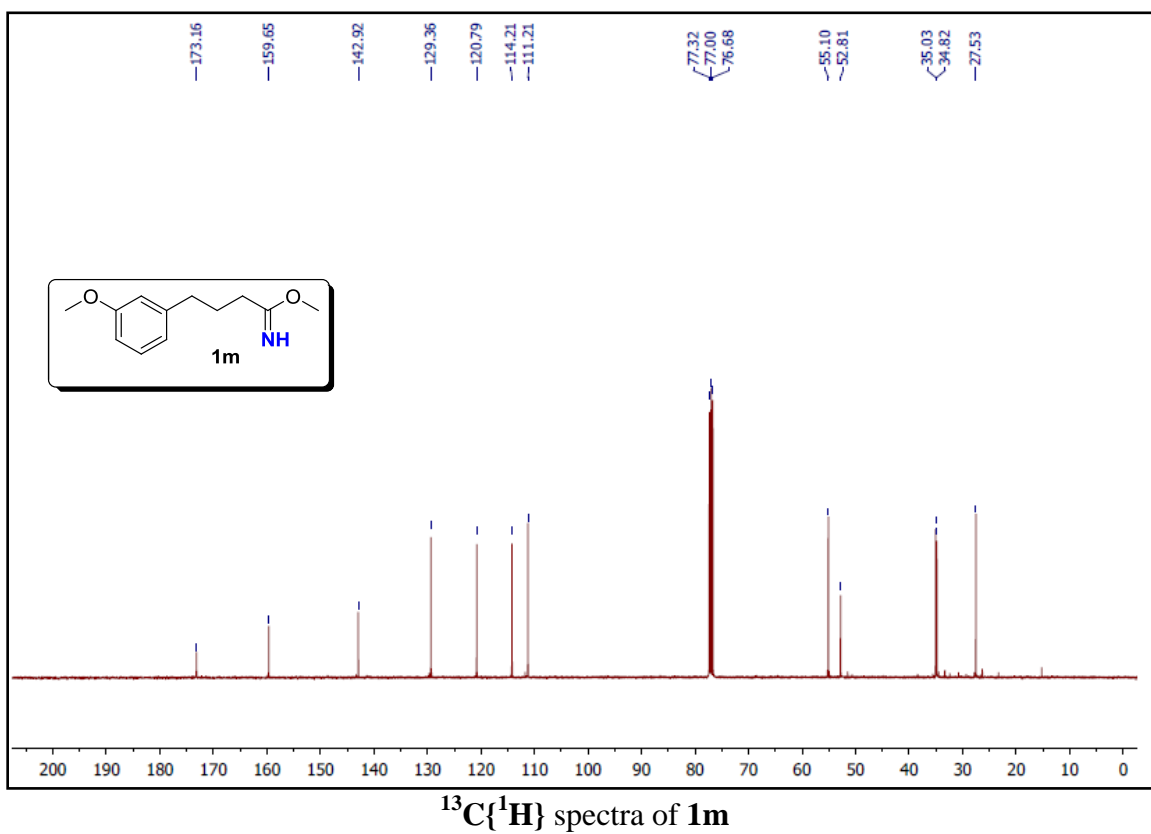
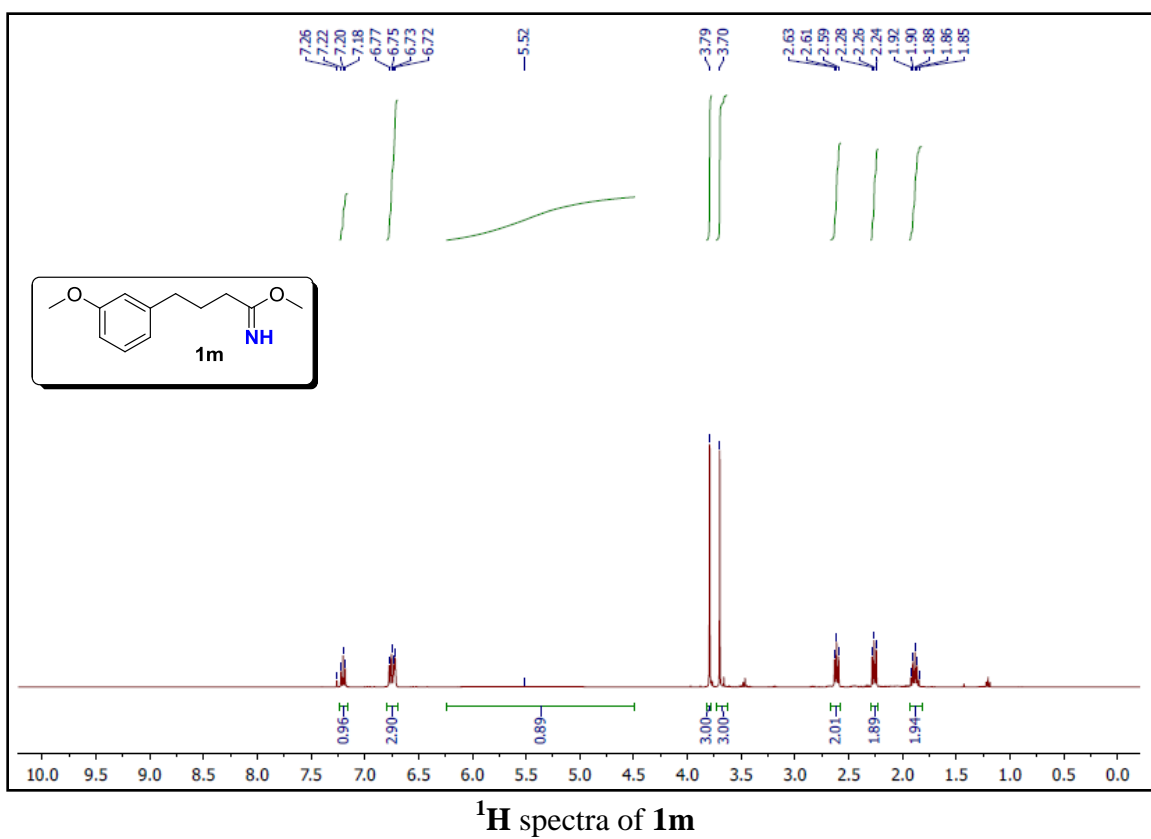


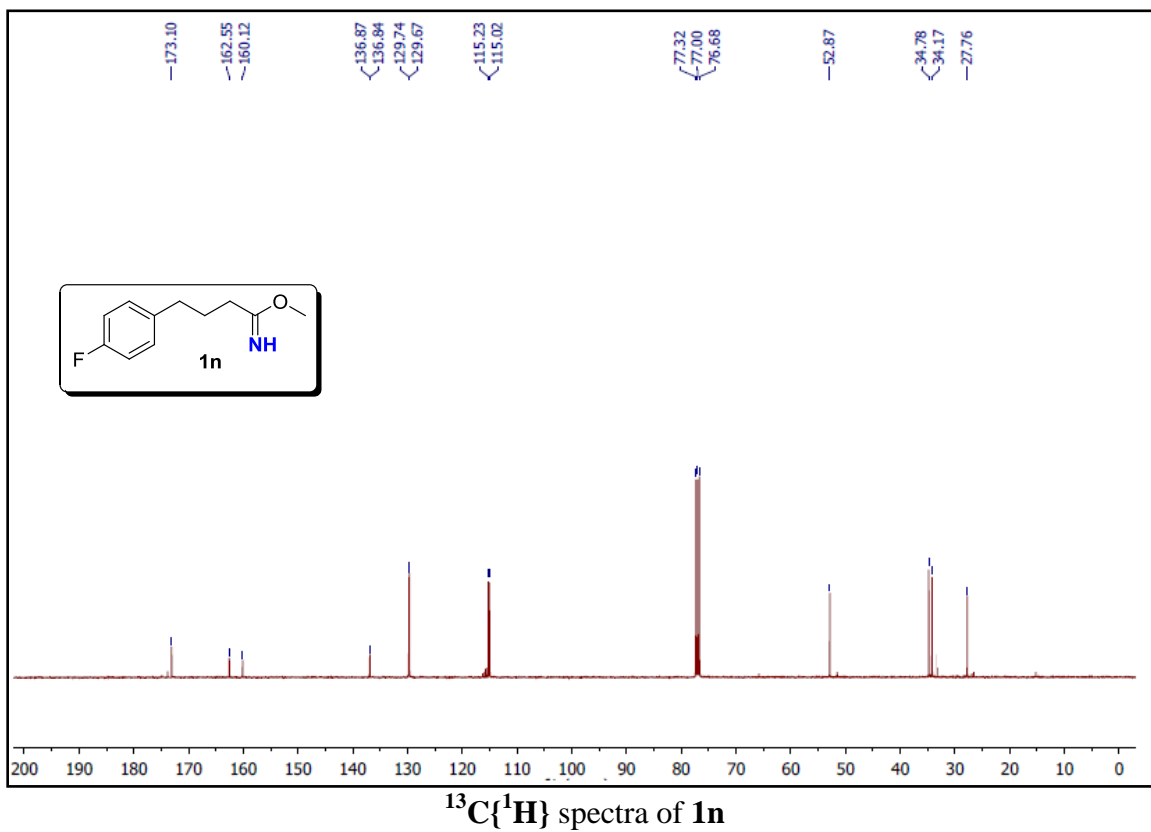
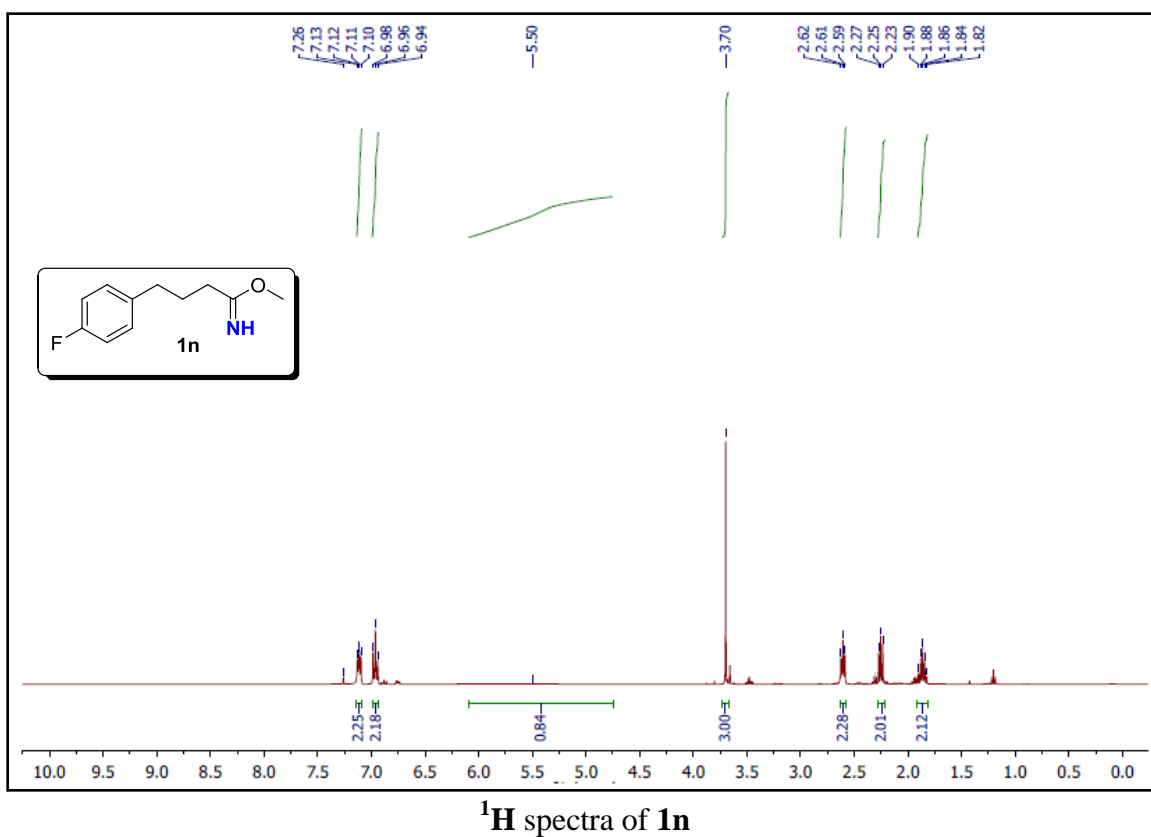


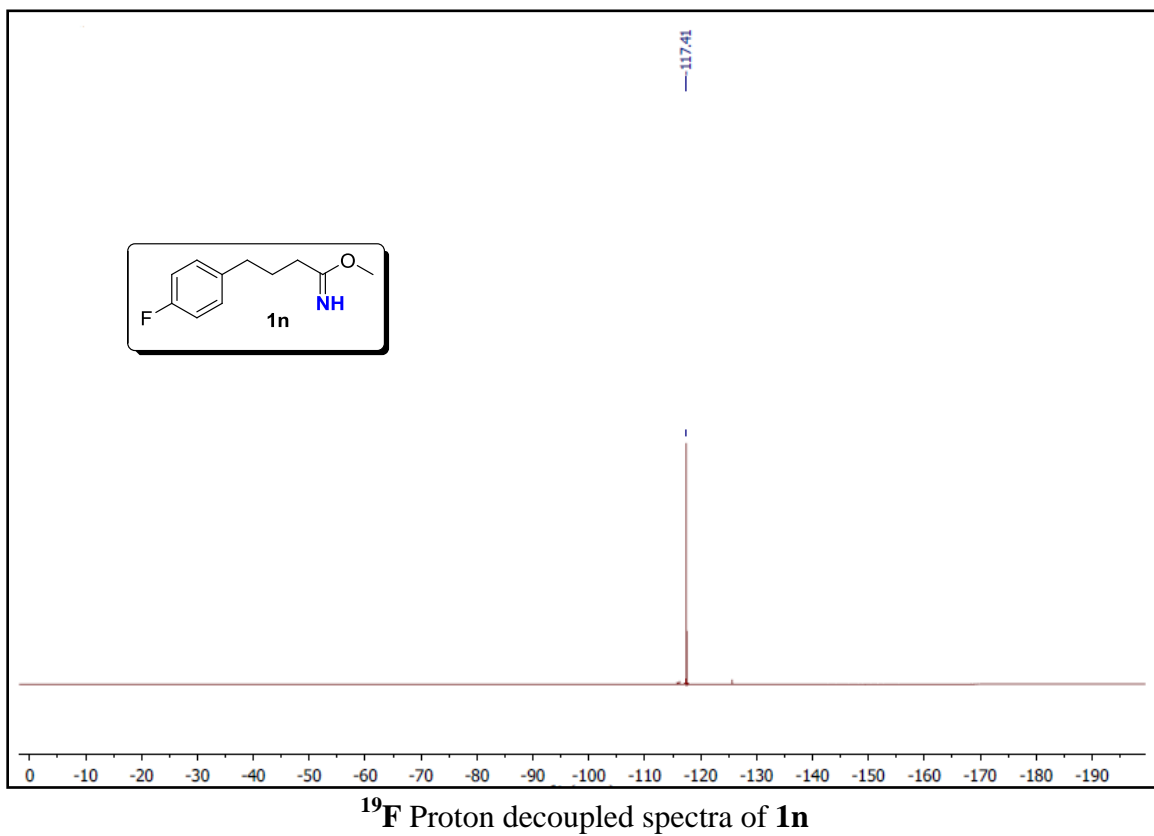
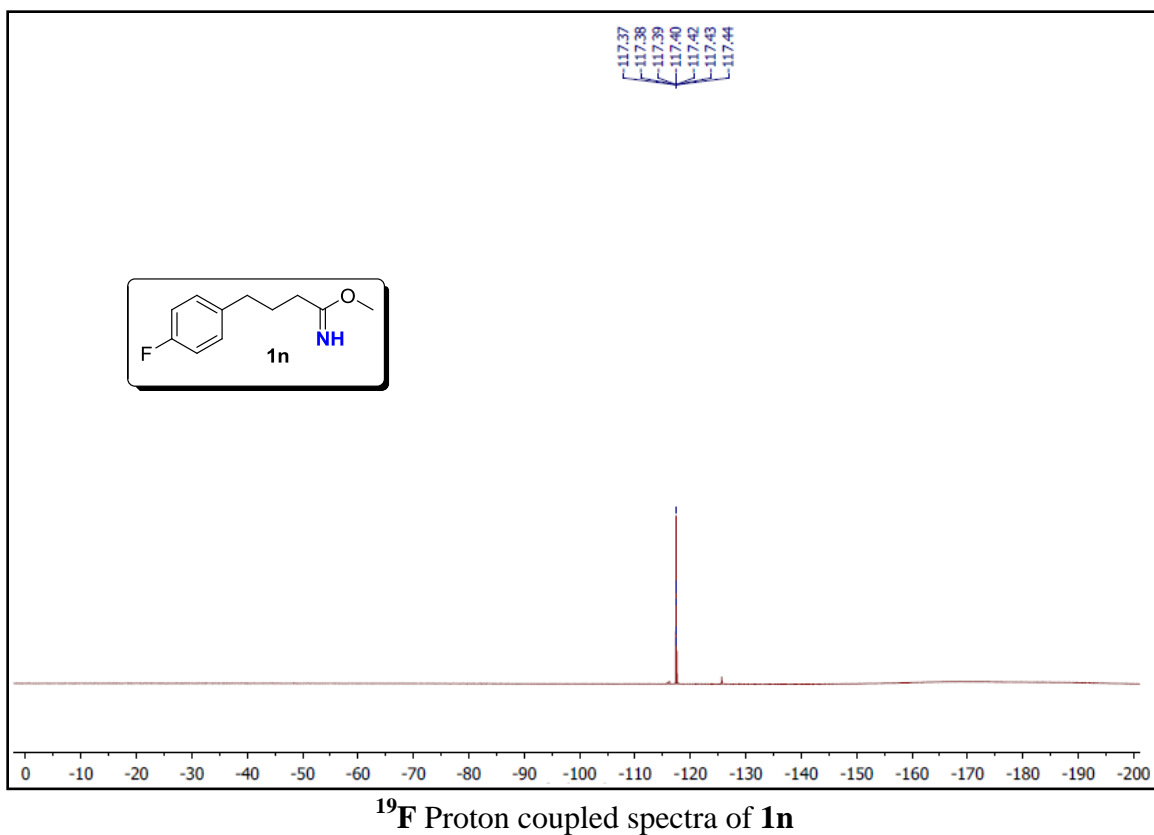


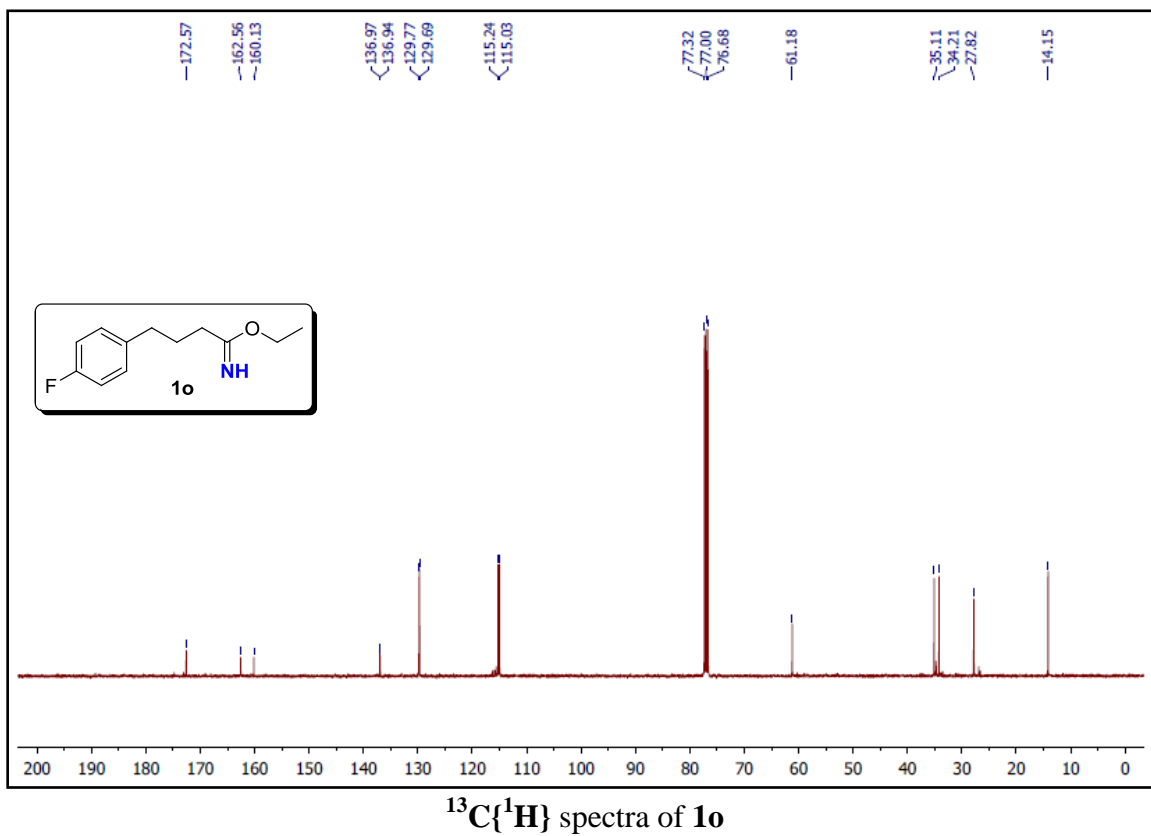
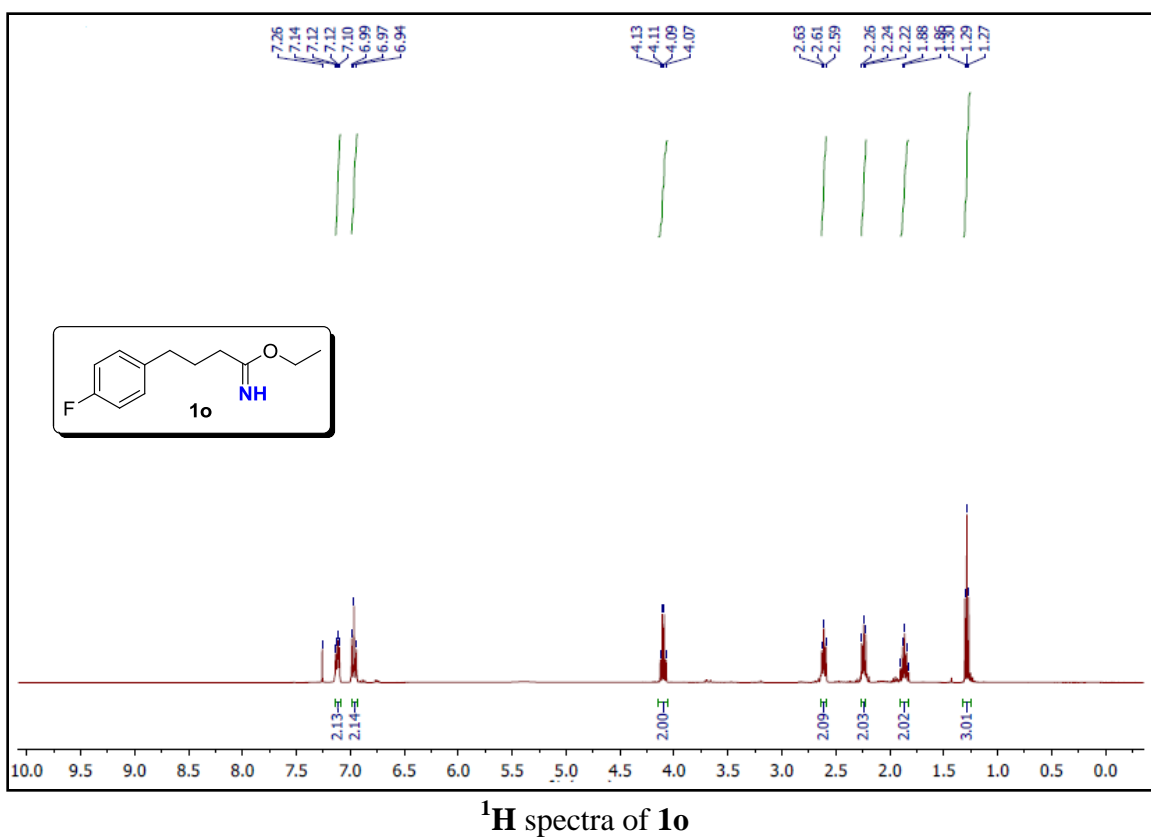


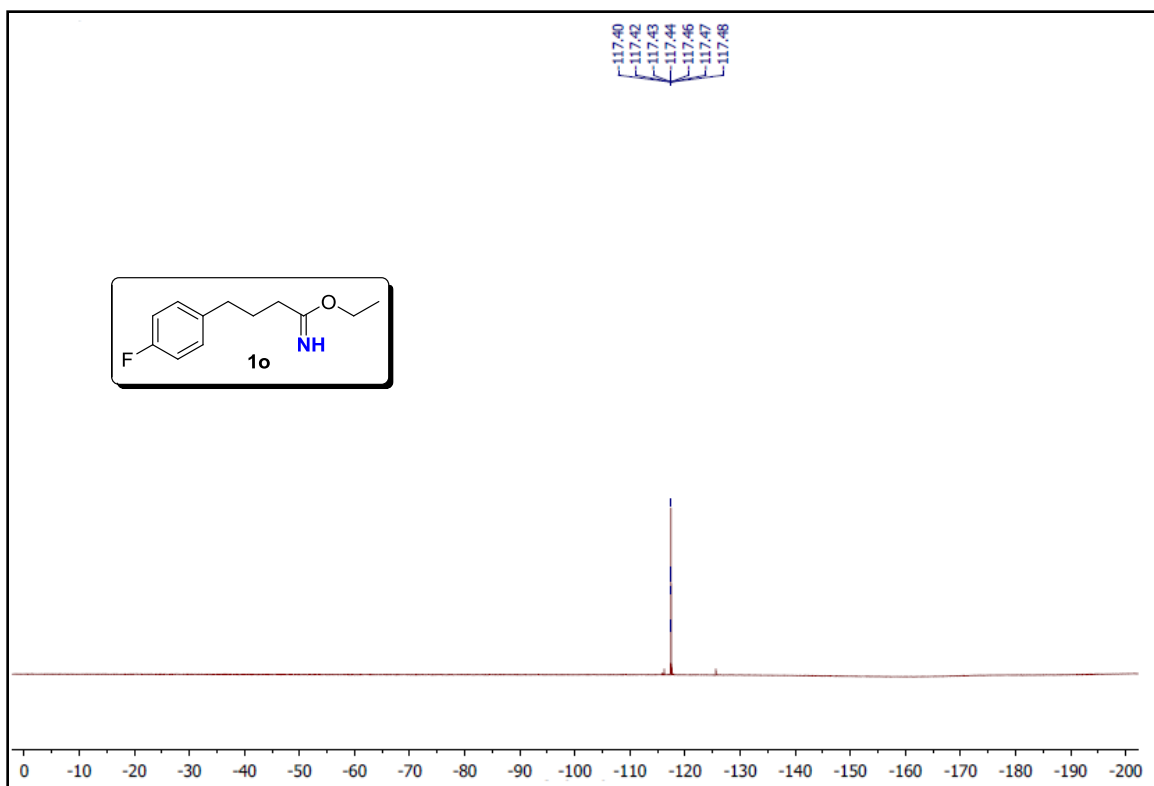




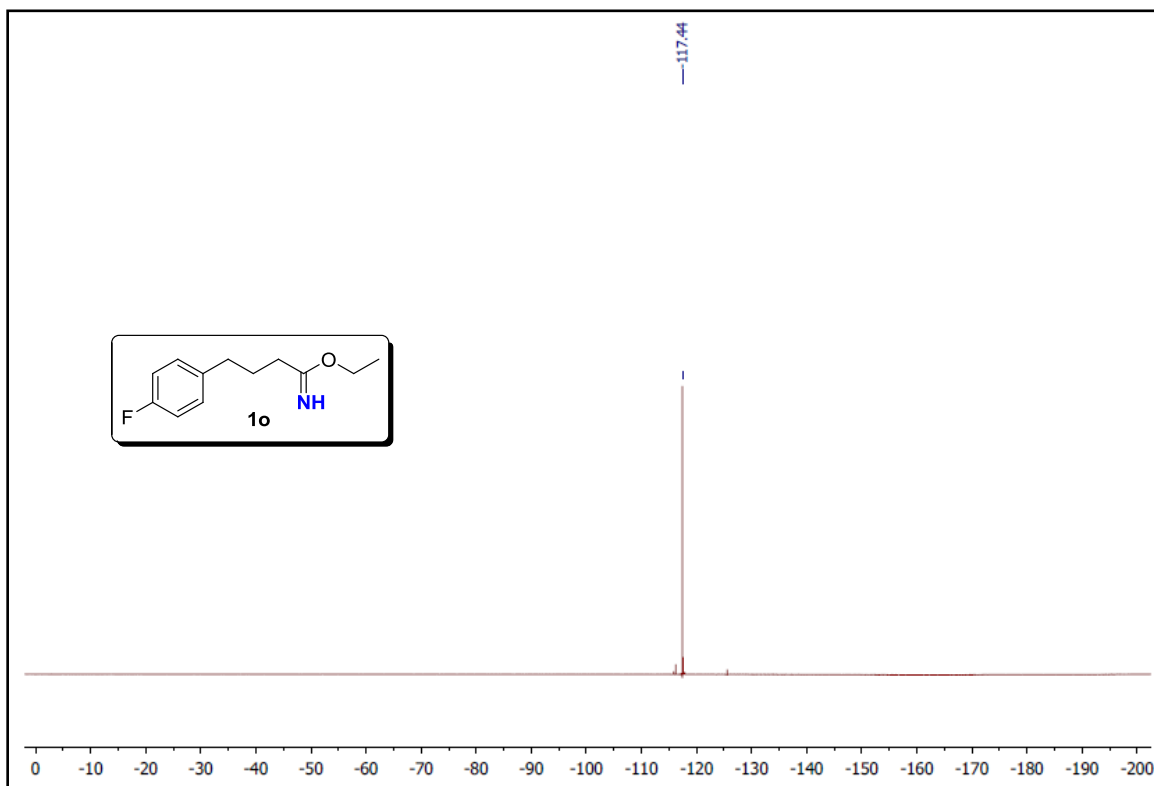




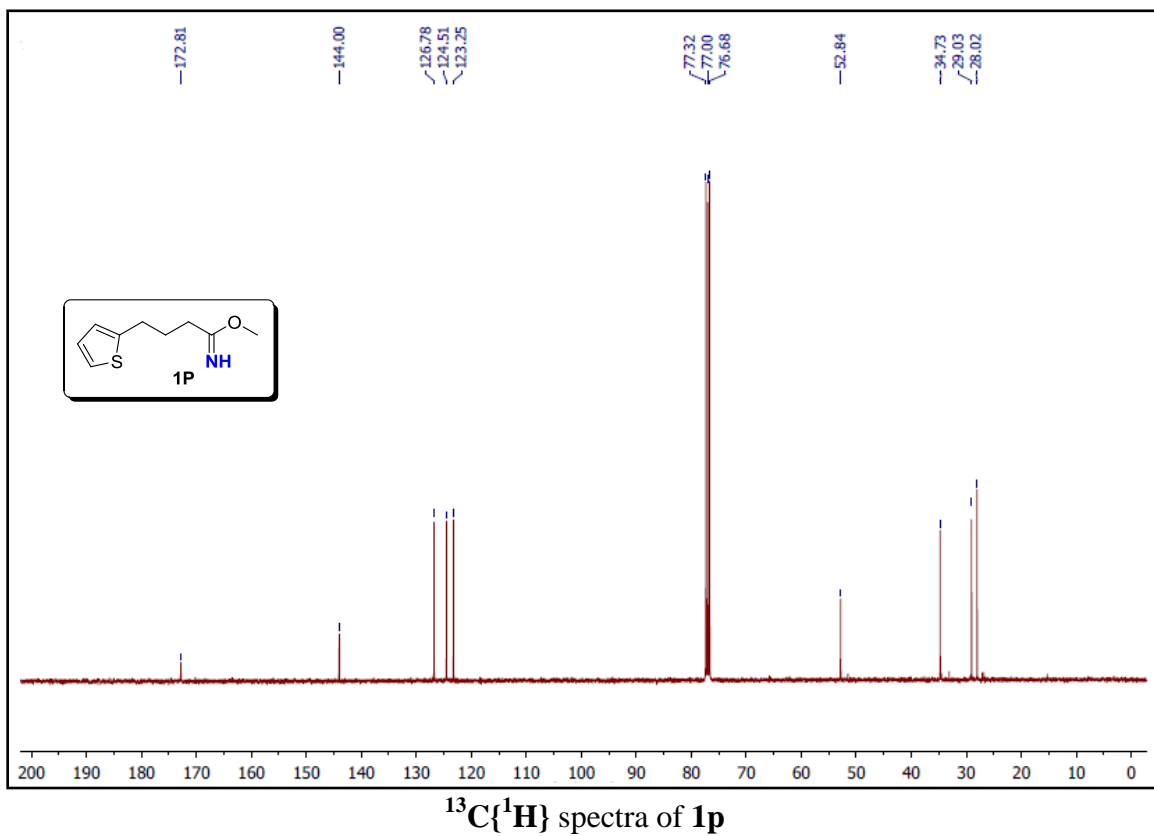
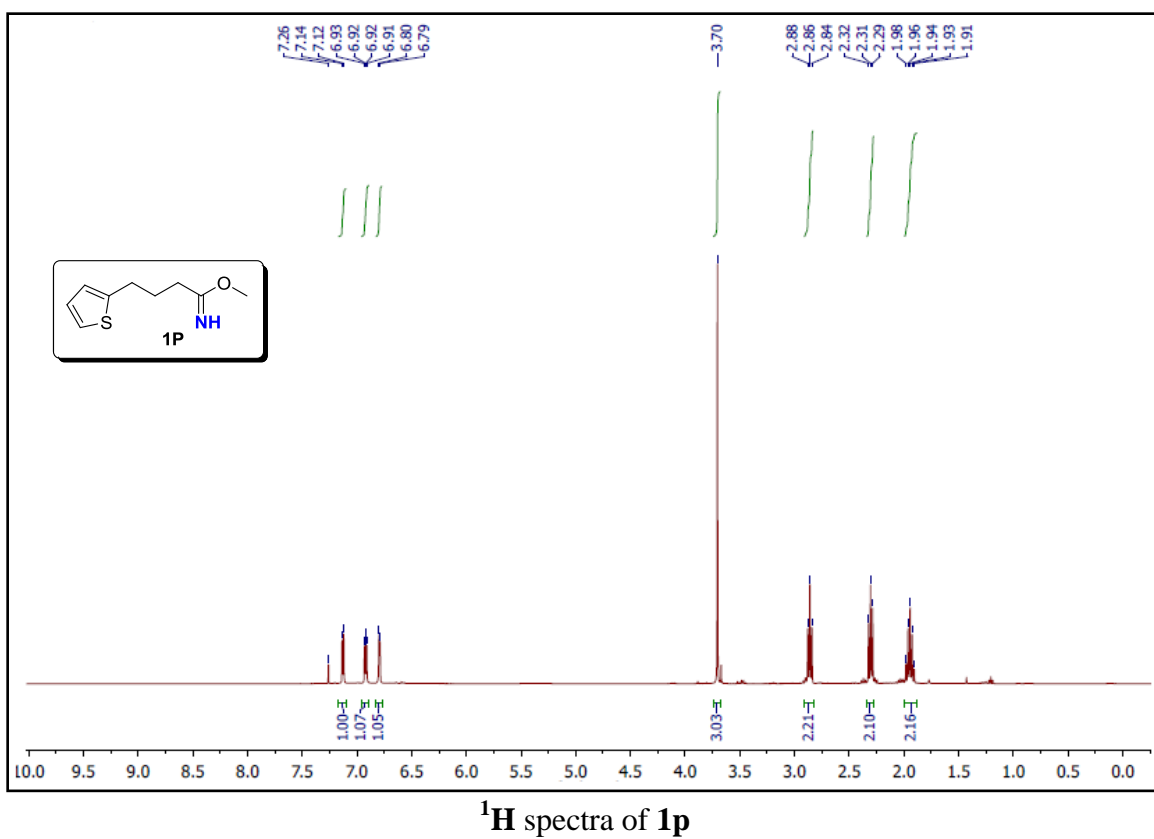


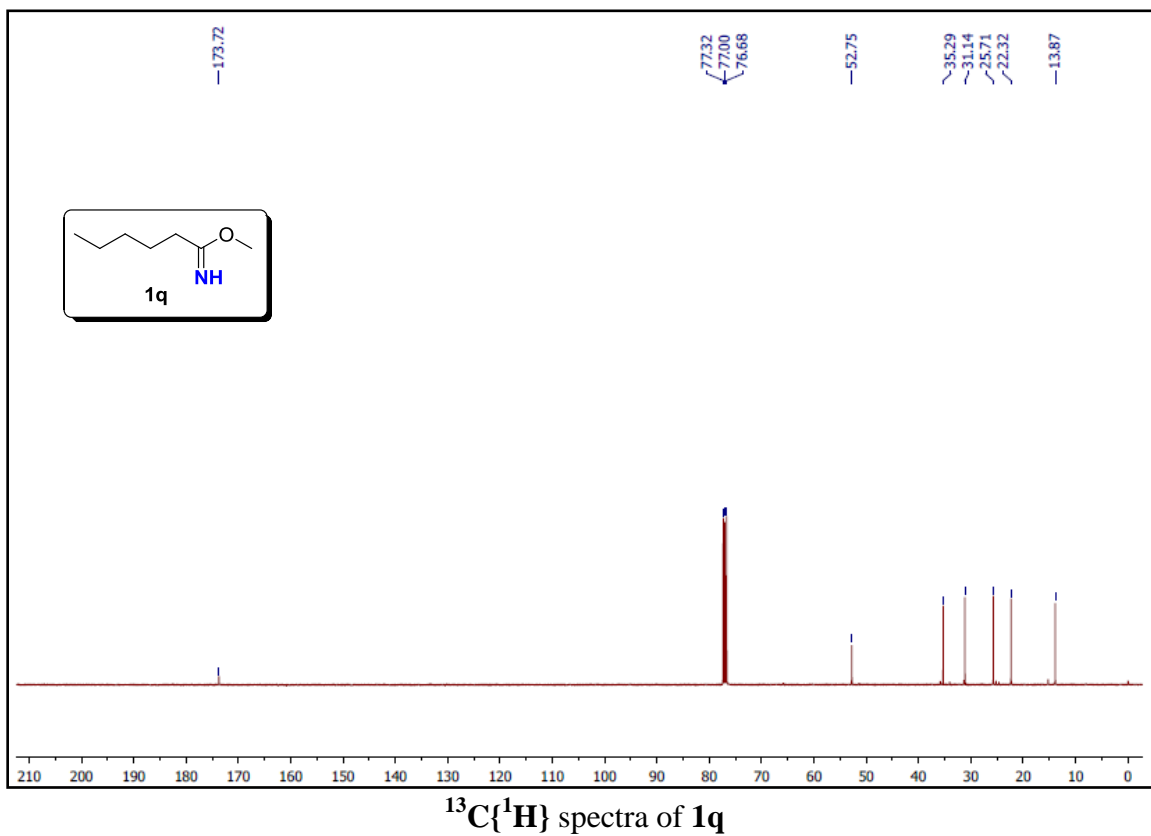
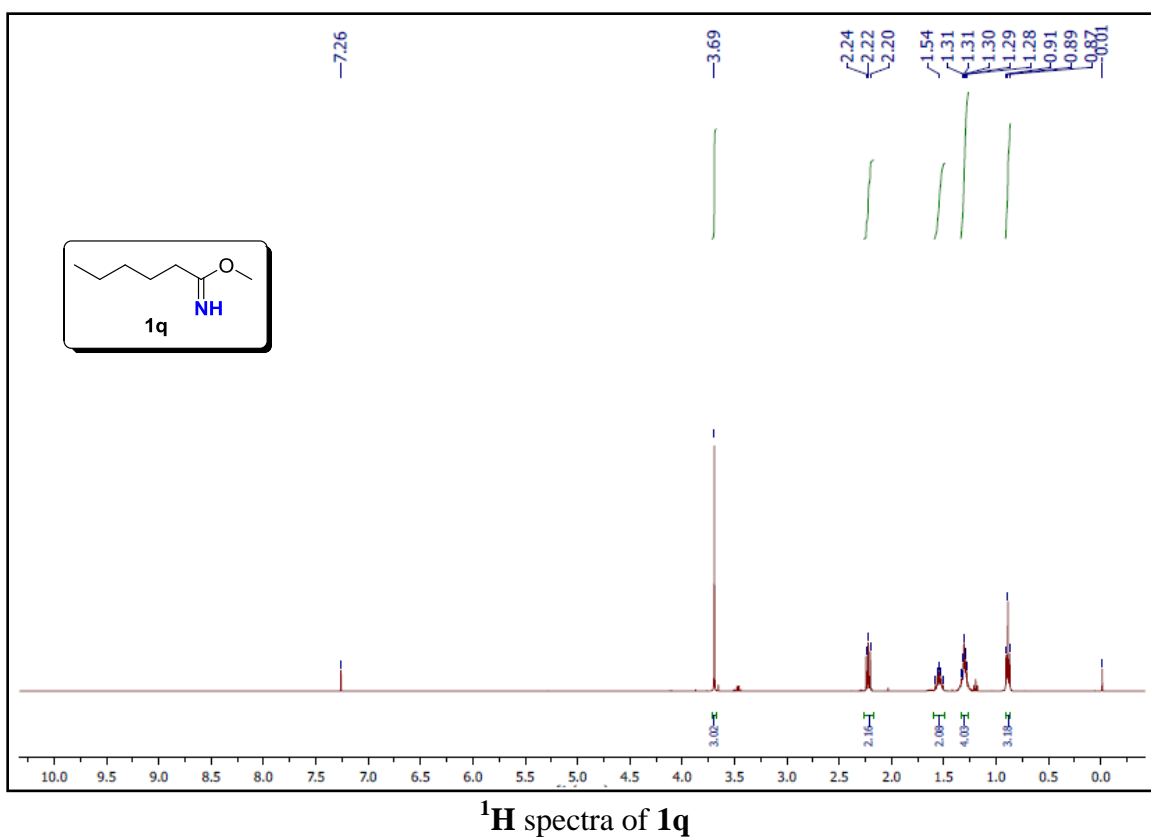


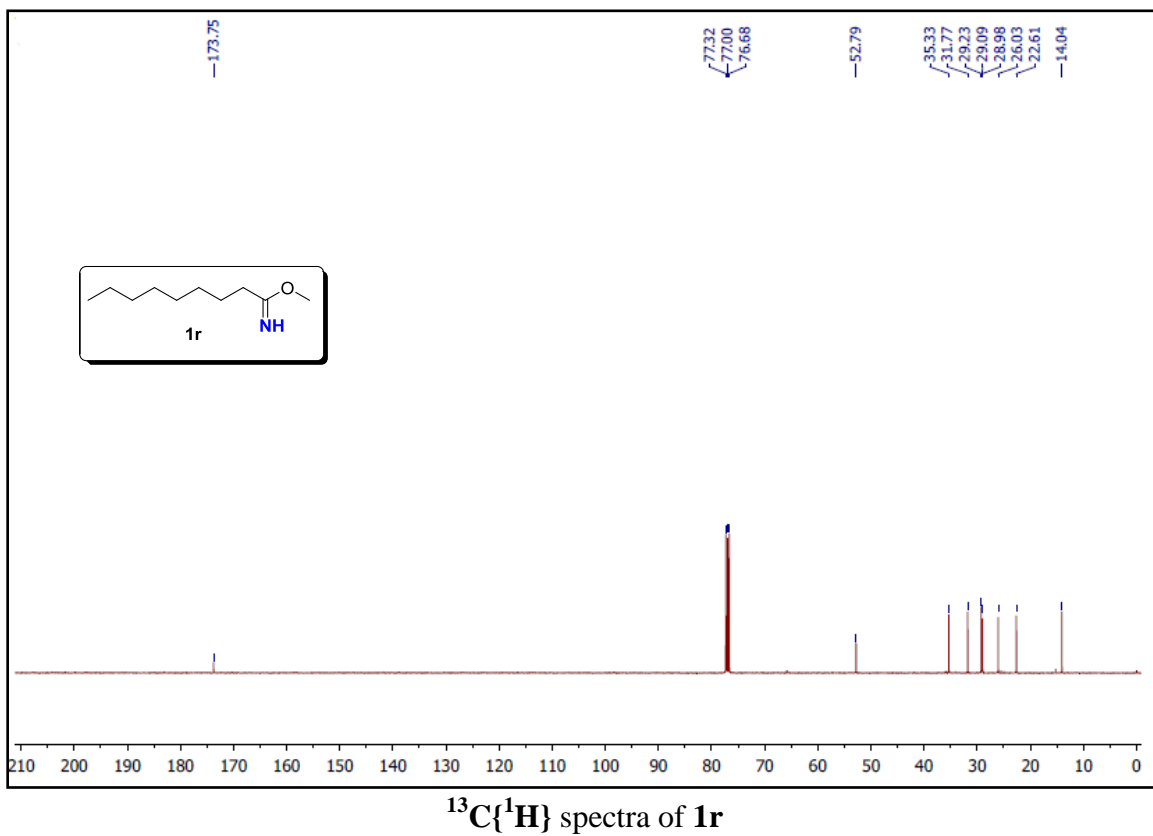
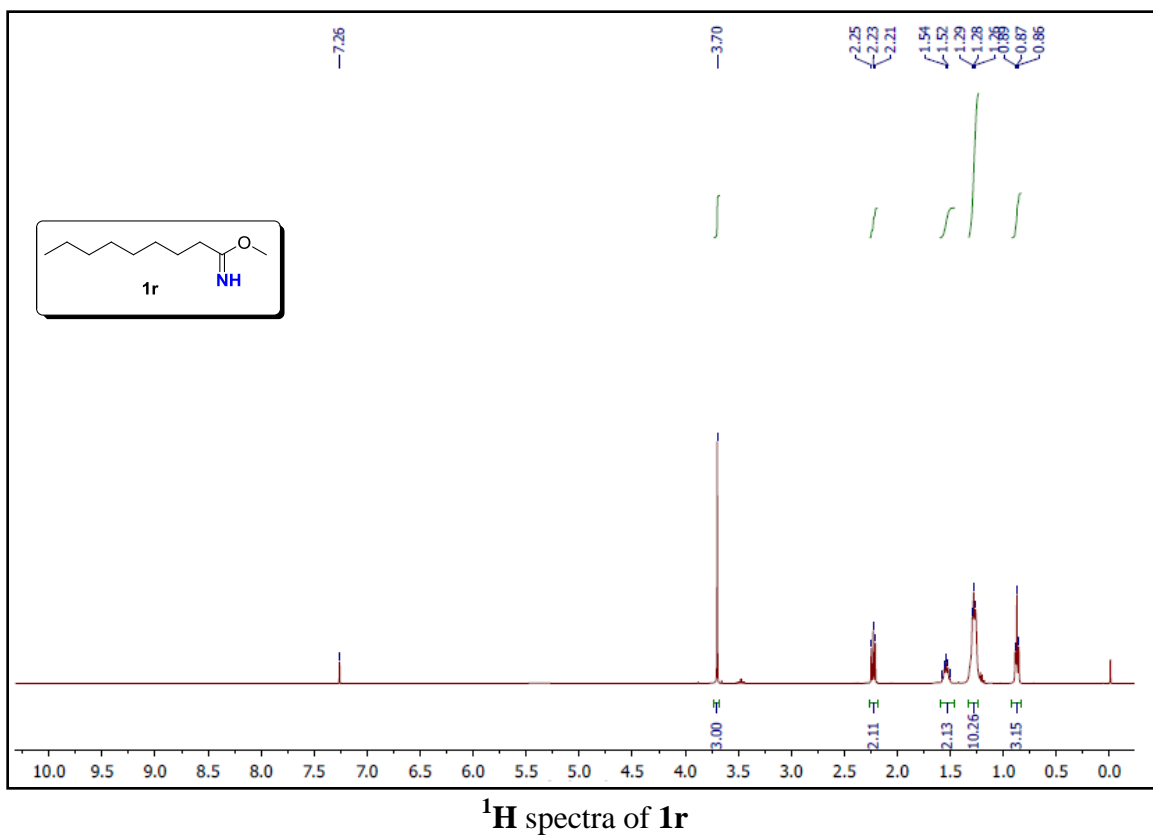
<sup>19</sup>F Proton coupled spectra of **1o**

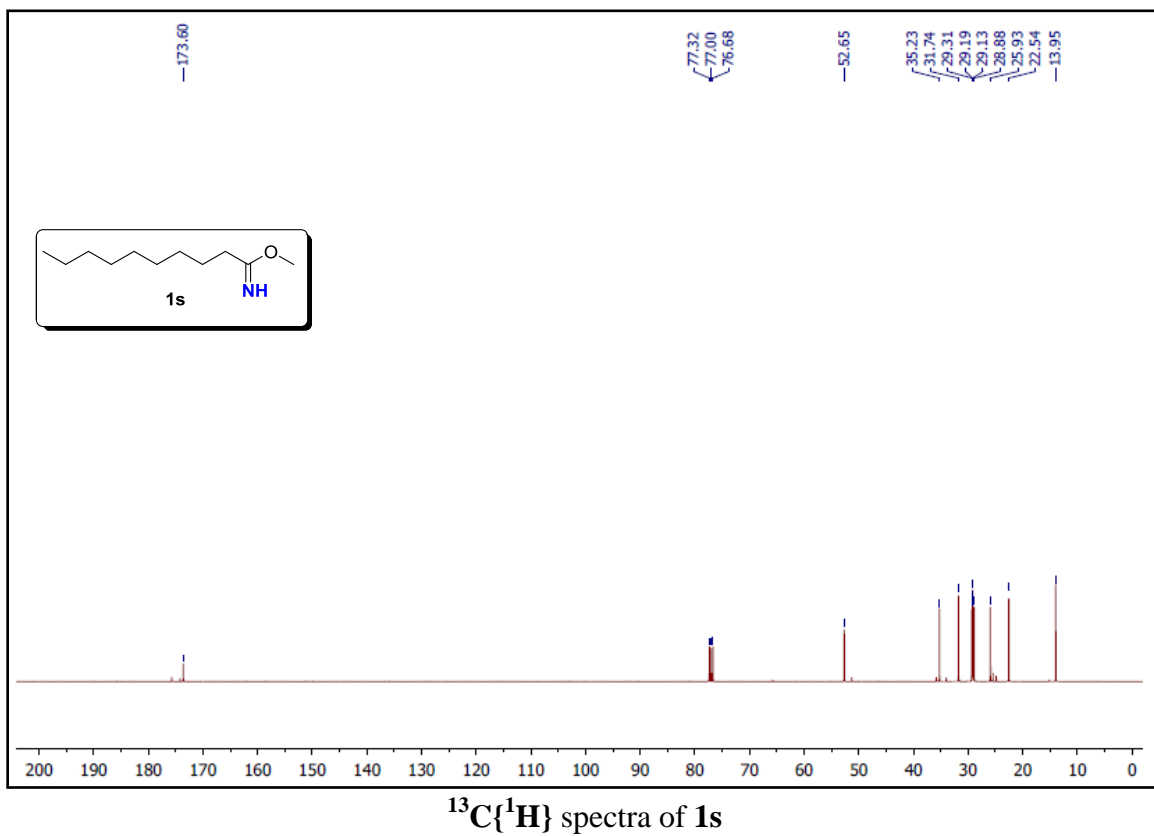
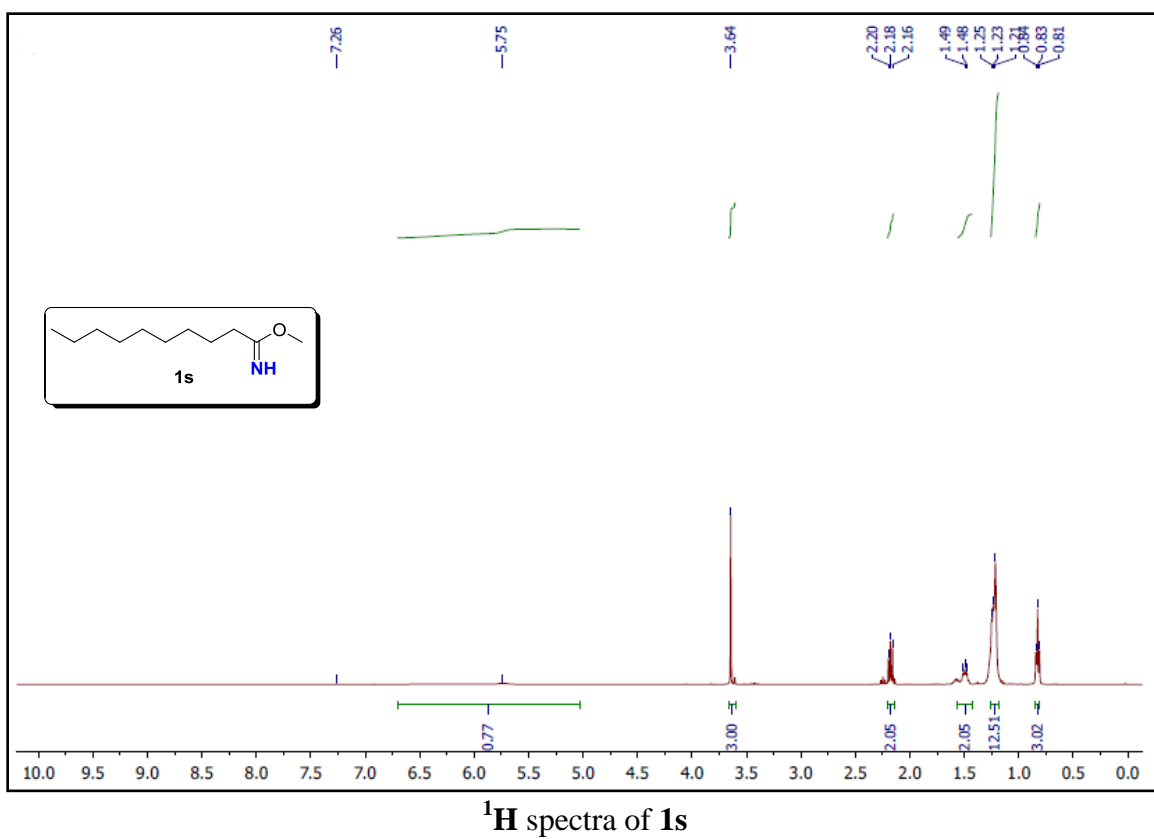


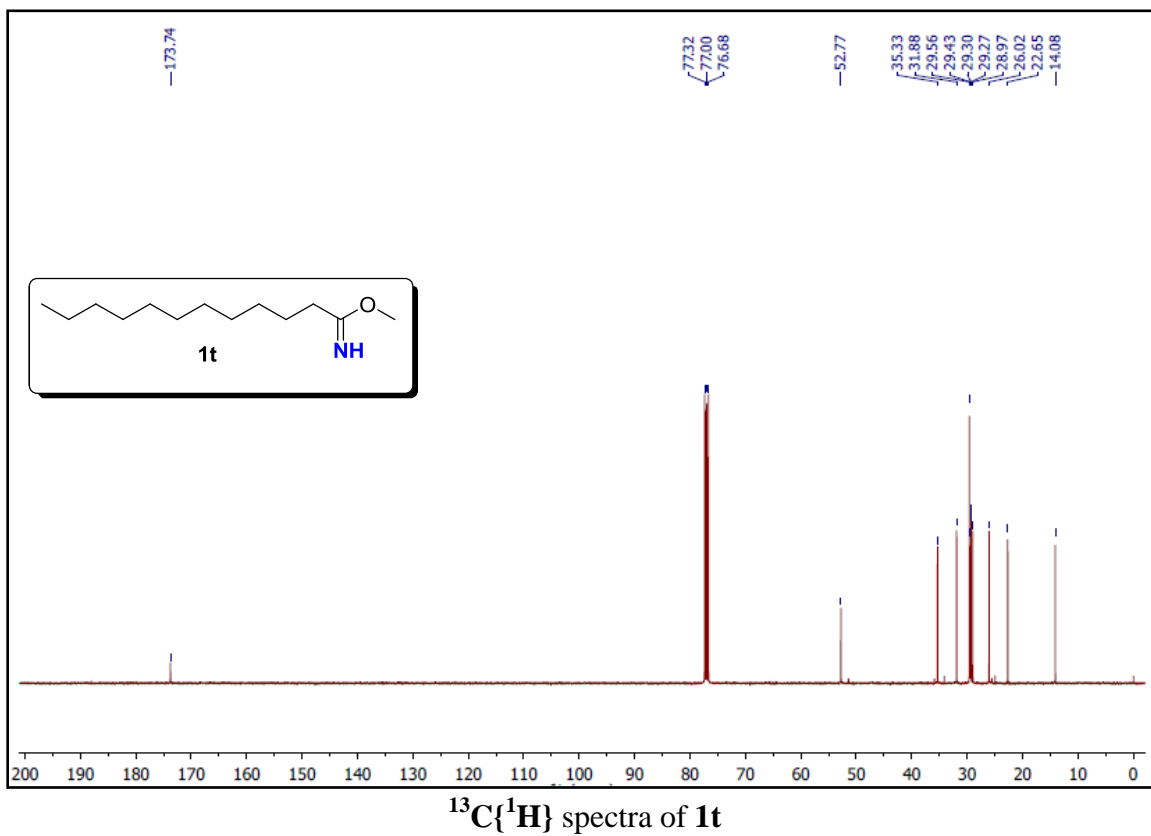
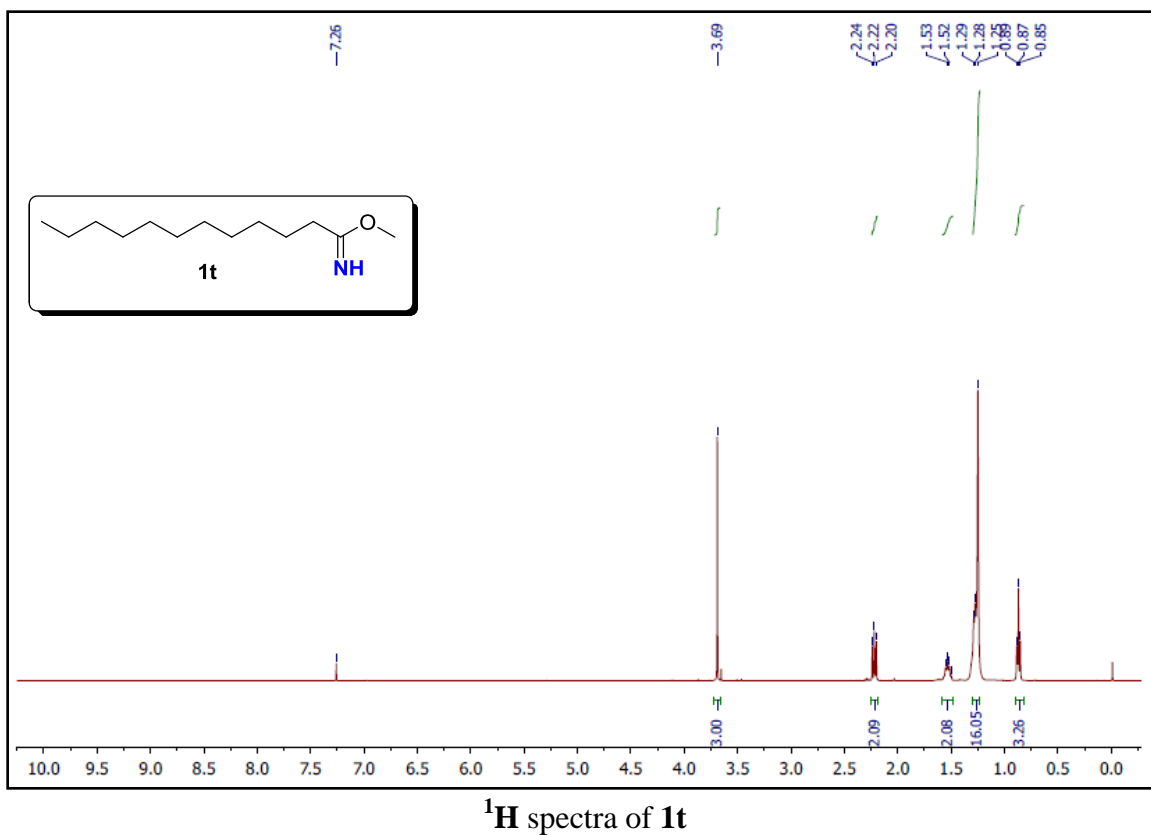
<sup>19</sup>F Proton decoupled spectra of **1o**

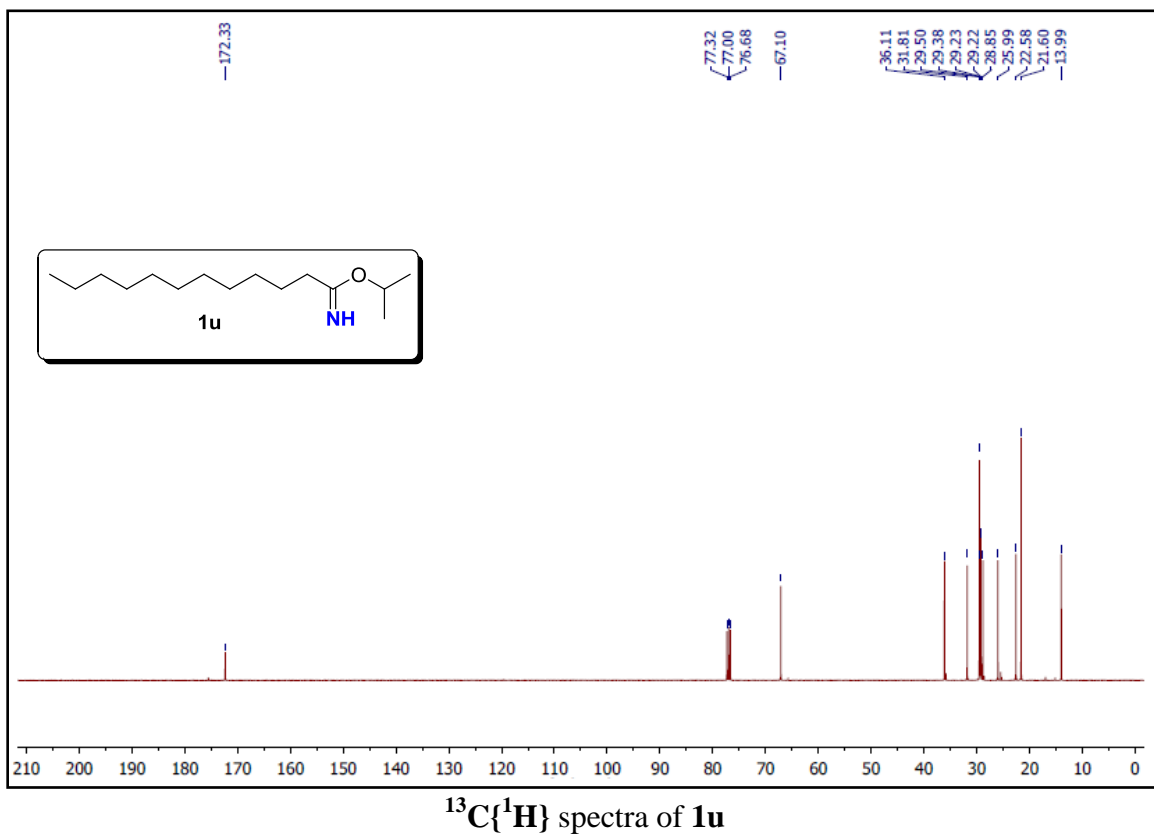
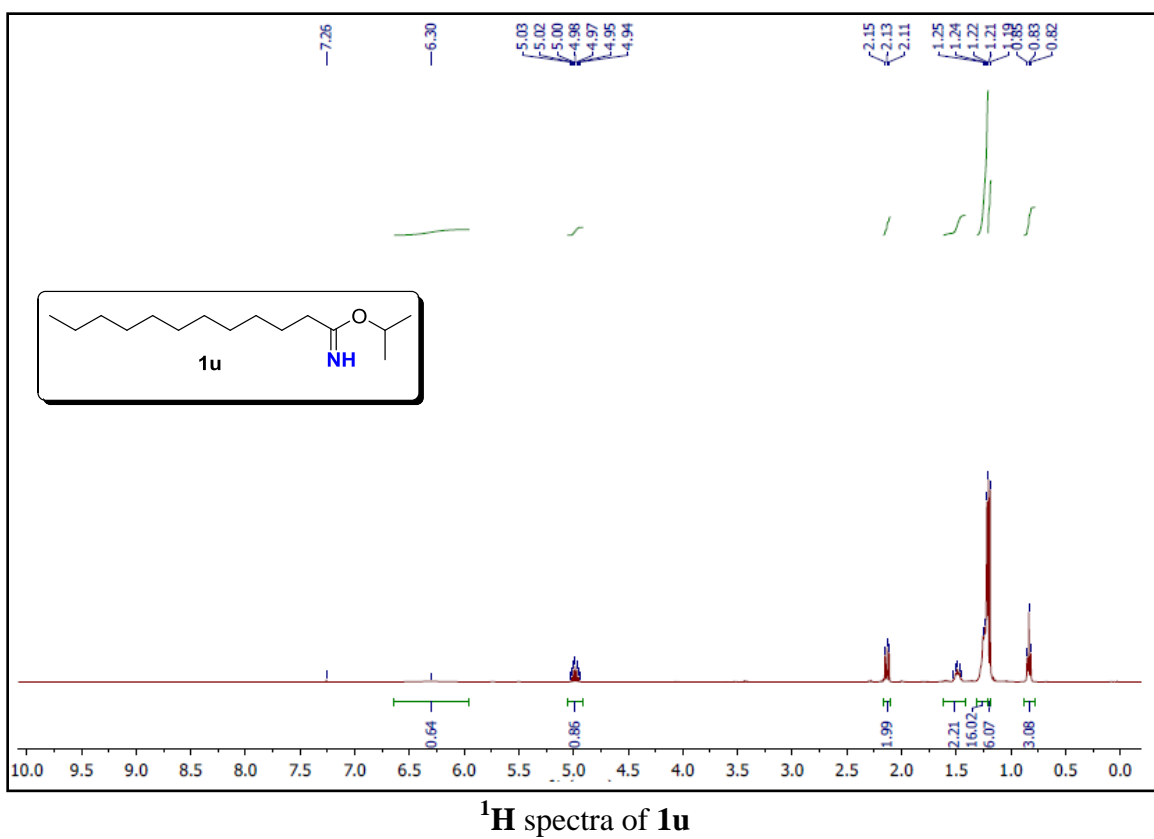


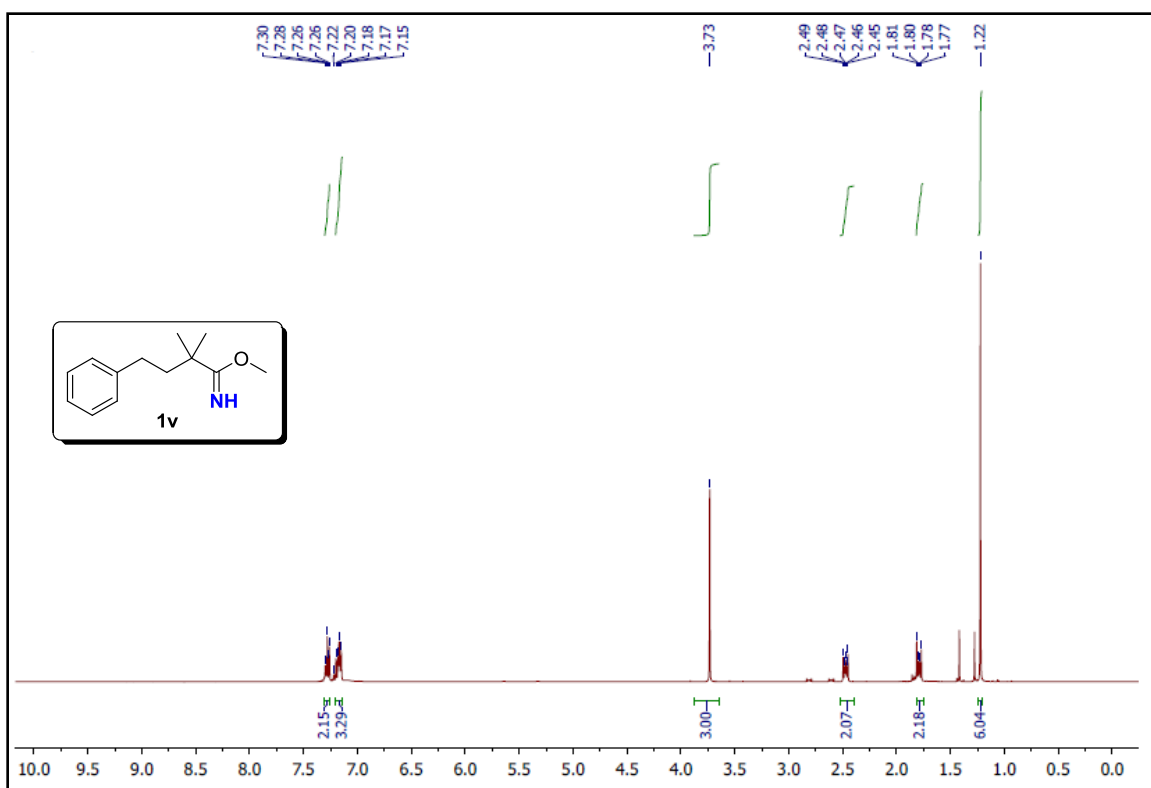




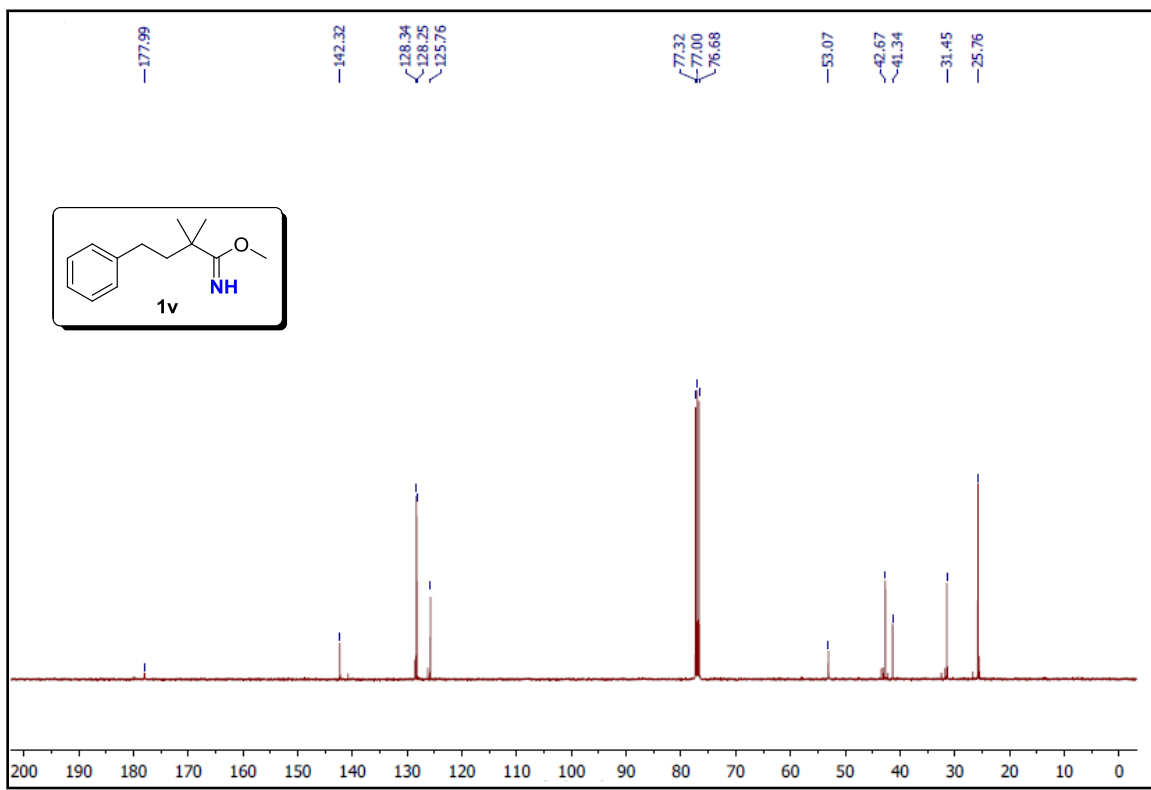




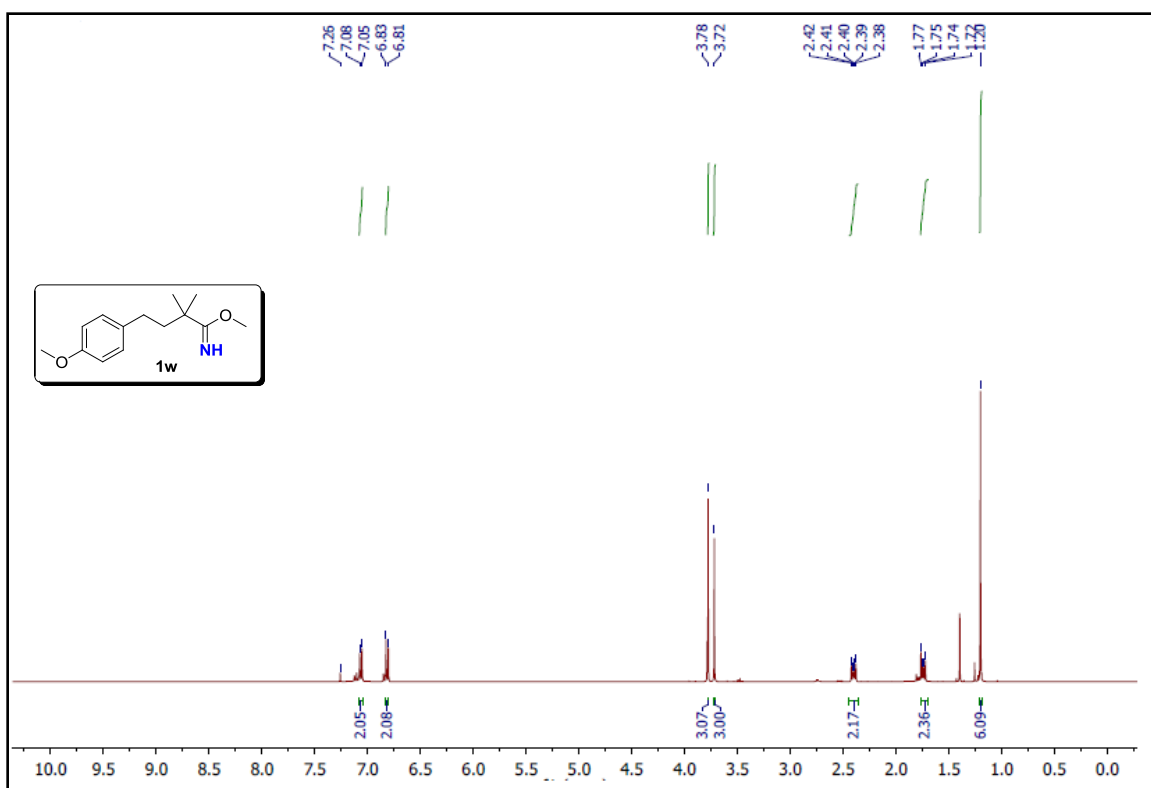




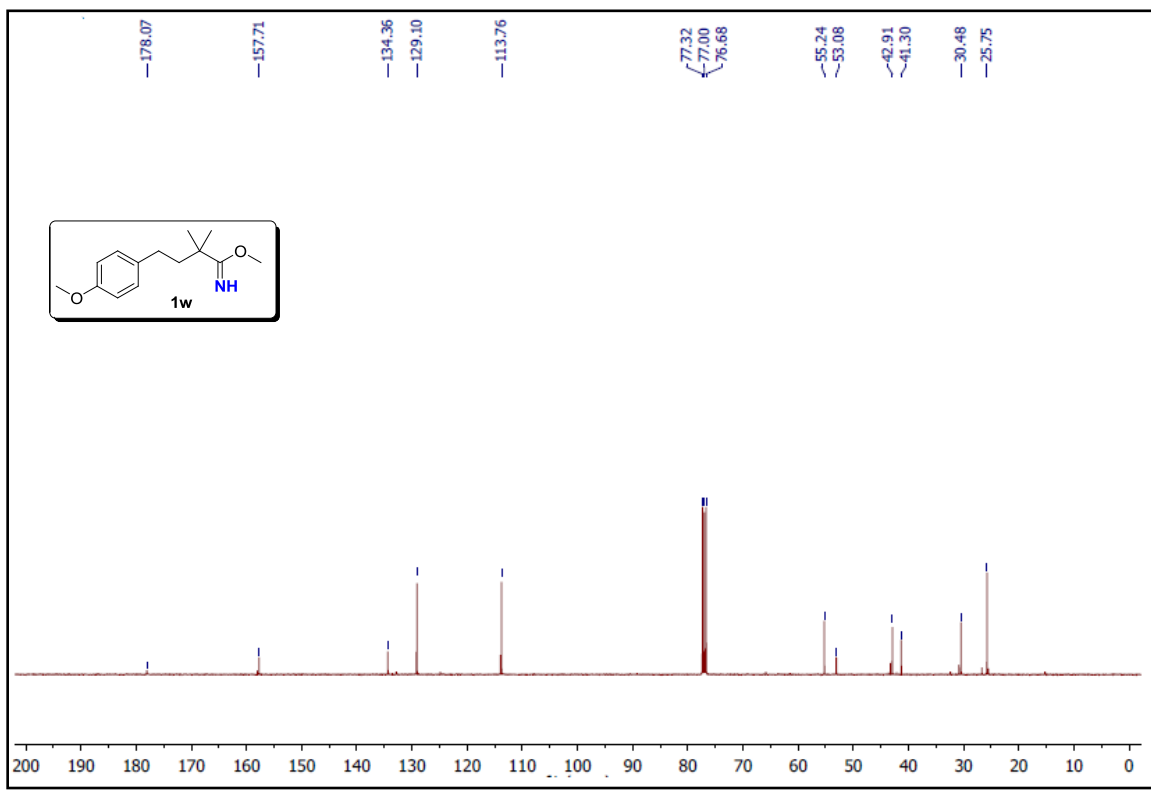
<sup>1</sup>H spectra of 1v



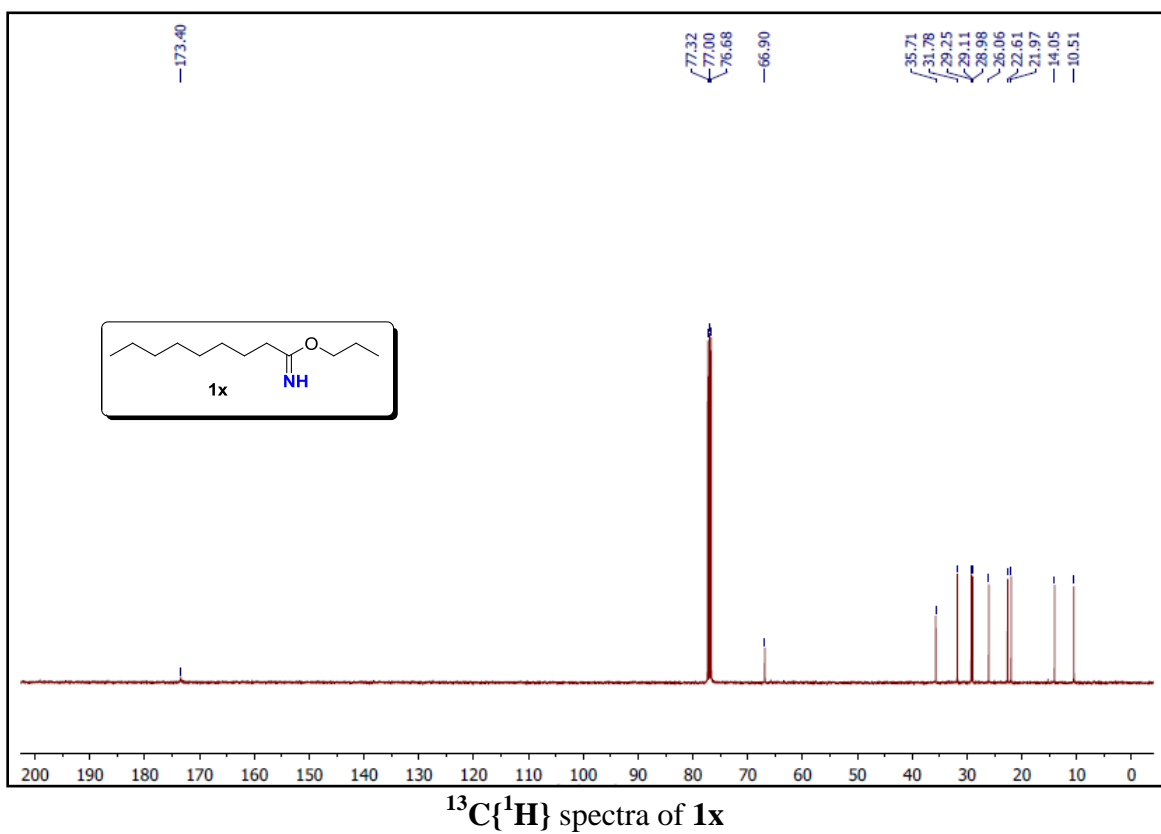
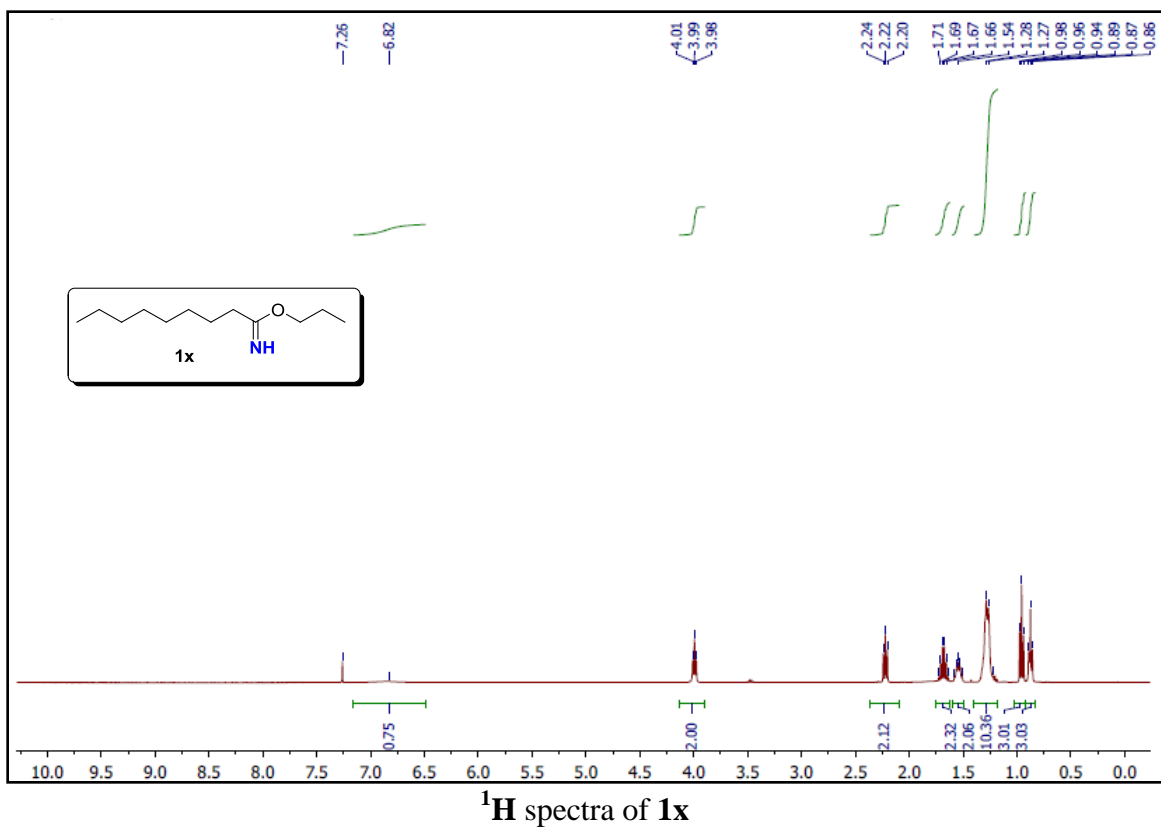
<sup>13</sup>C{<sup>1</sup>H} spectra of 1v



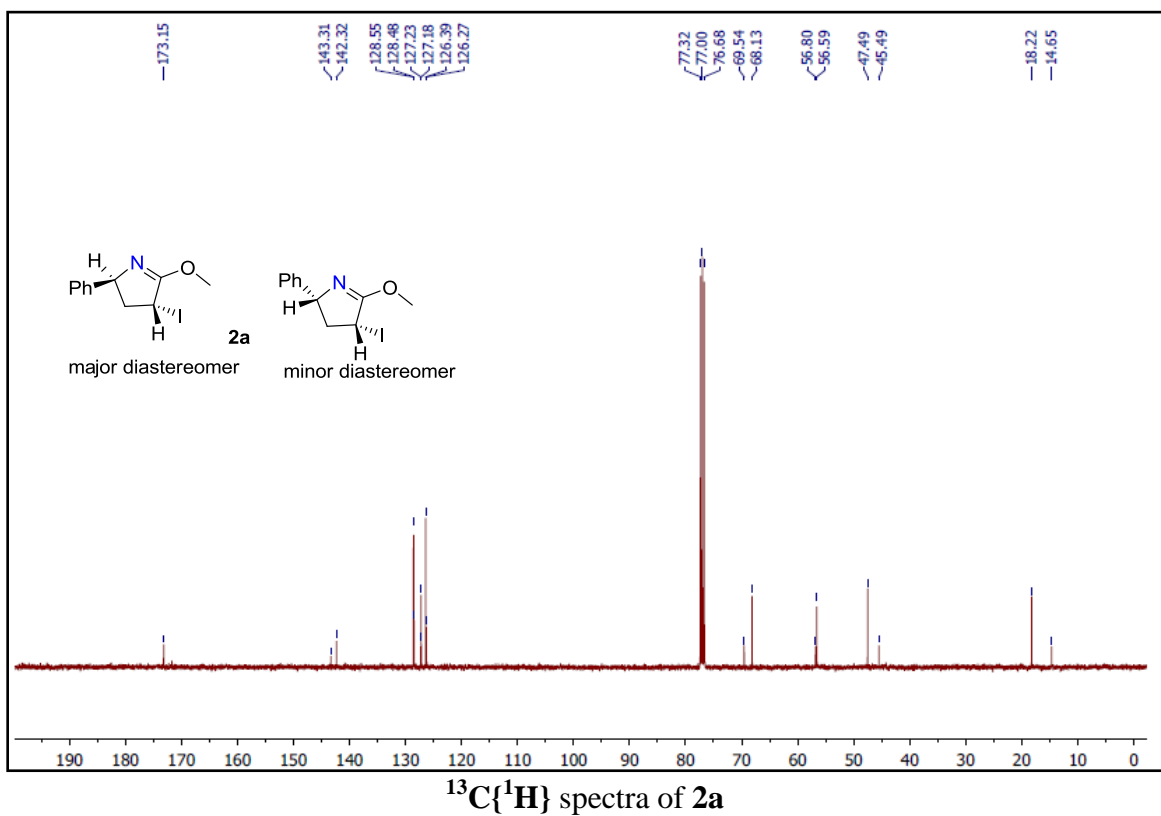
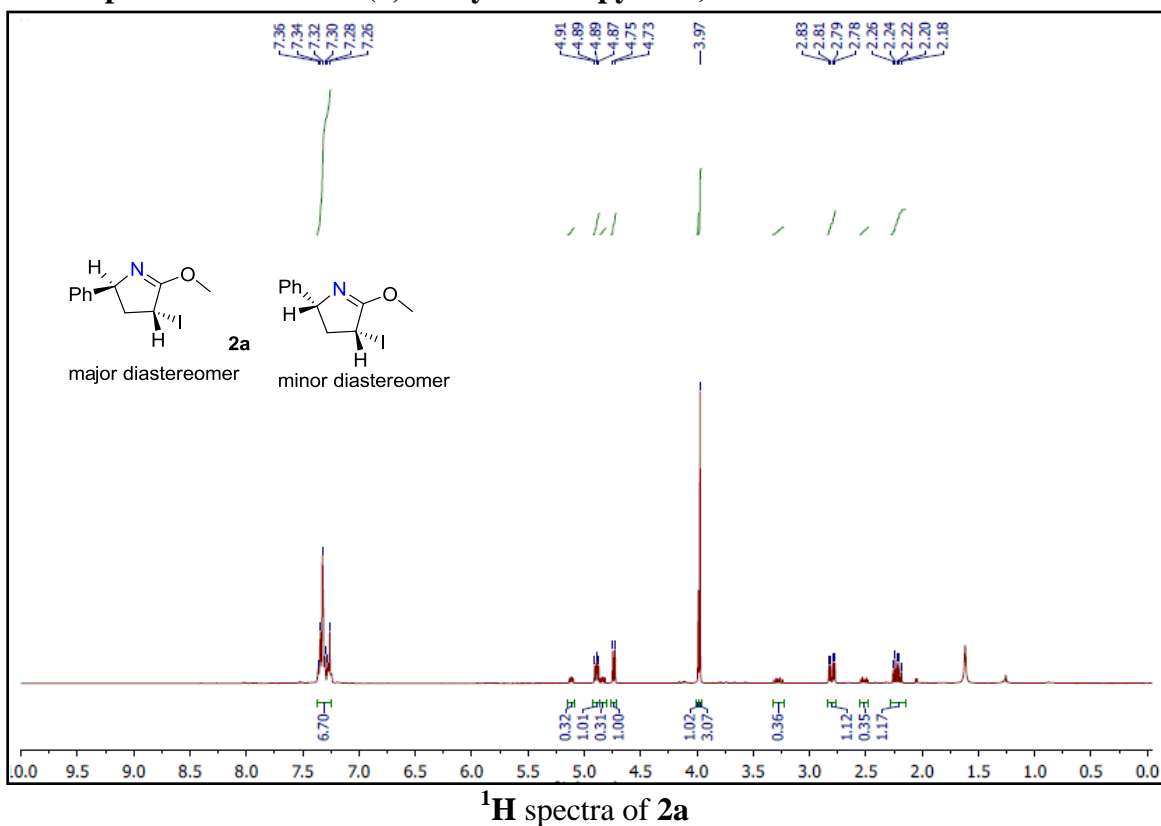
<sup>1</sup>H spectra of 1w

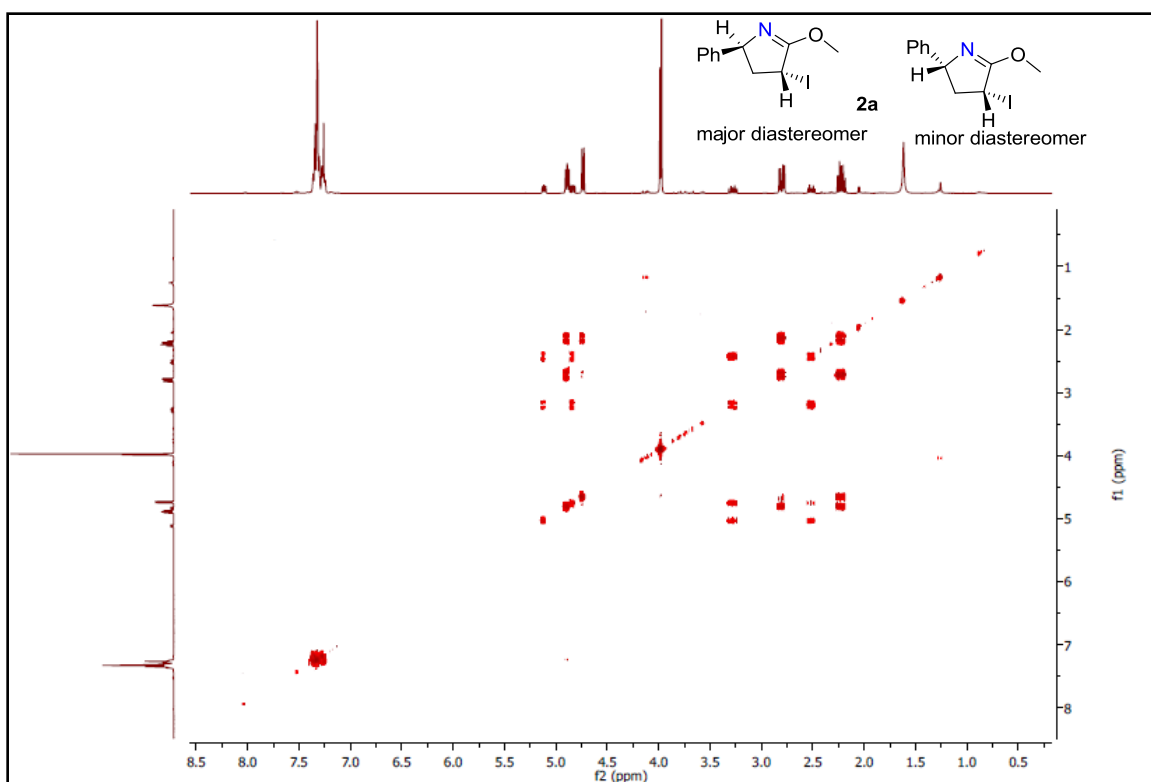


<sup>13</sup>C{<sup>1</sup>H} spectra of 1w

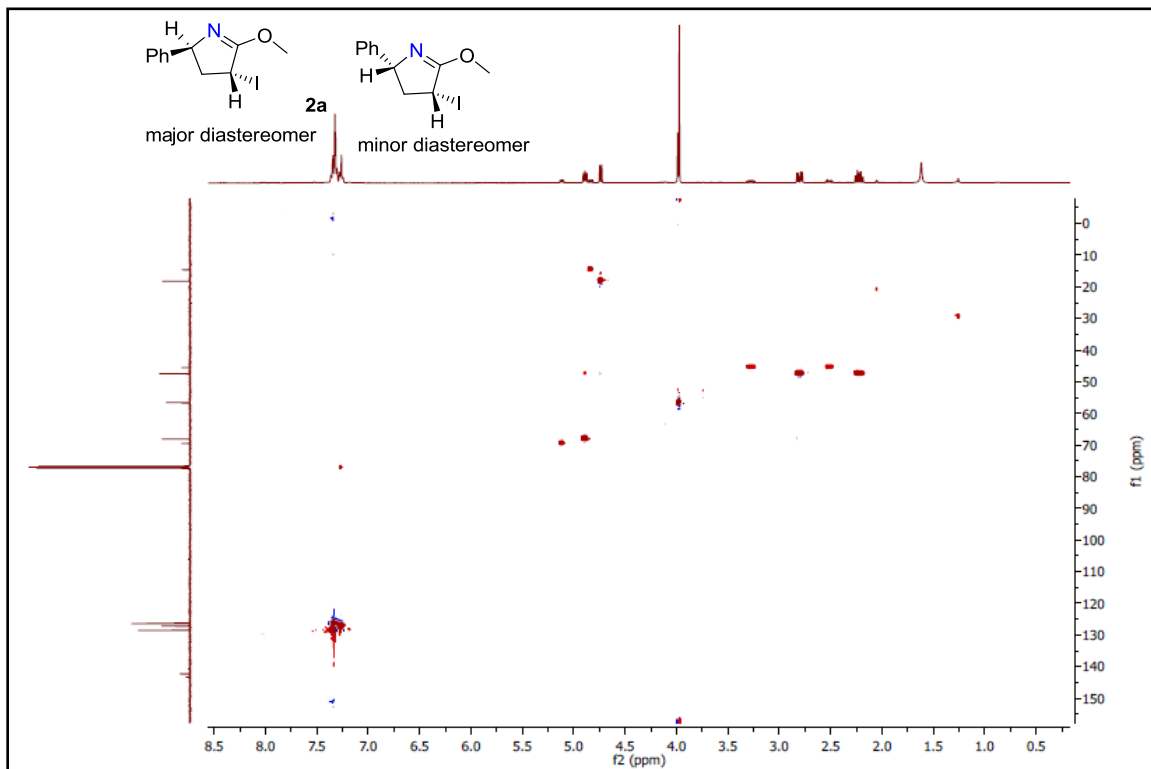


**C) NMR Spectra of Products (3,4-dihydro-2H-pyrrole):**

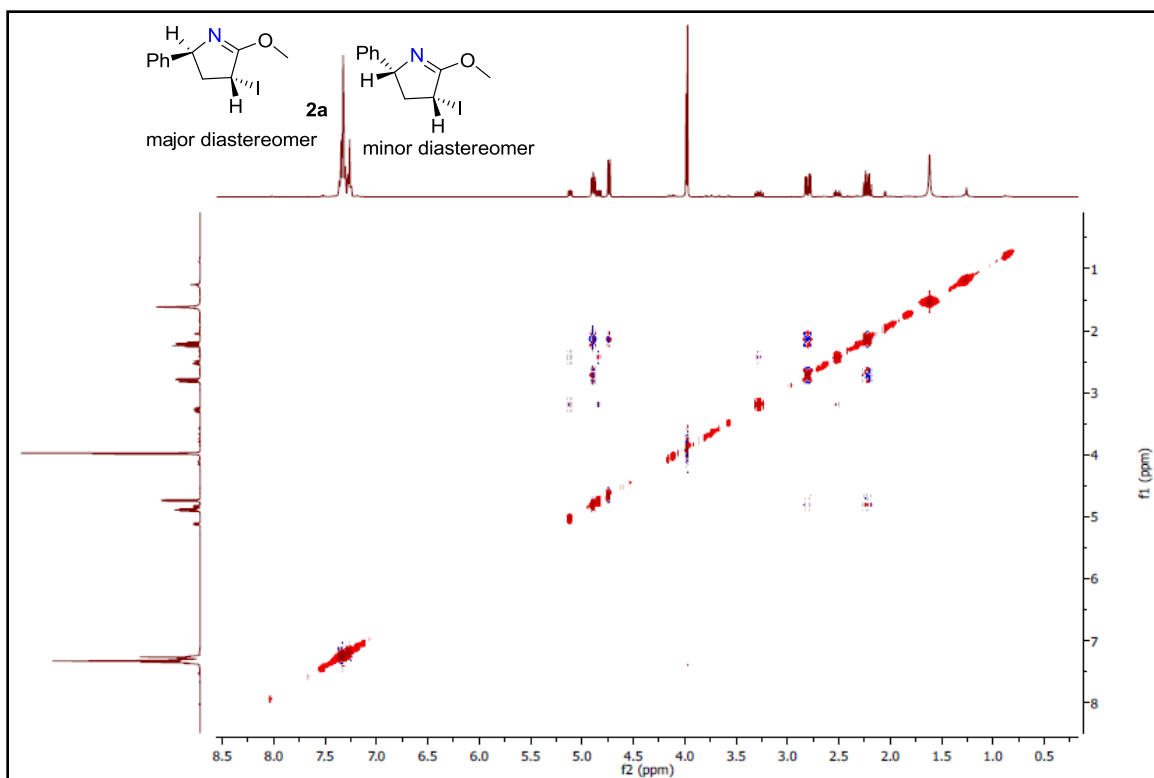




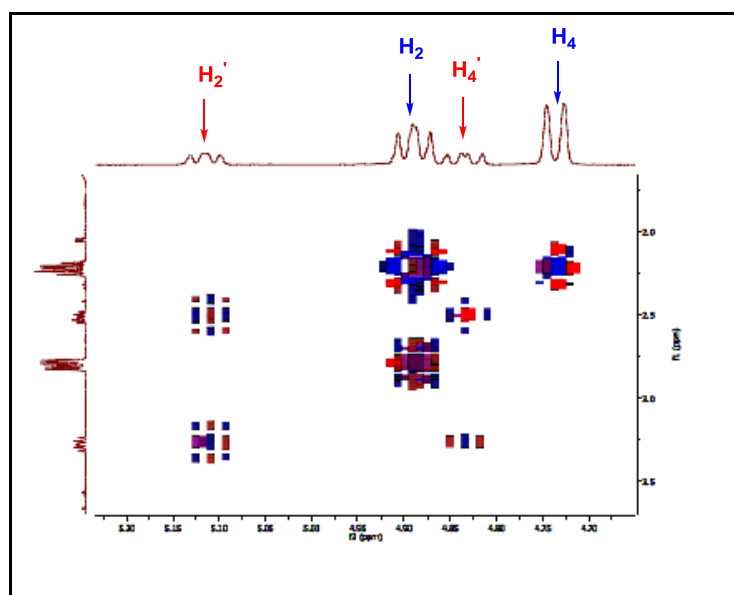
COSY spectra of **2a**



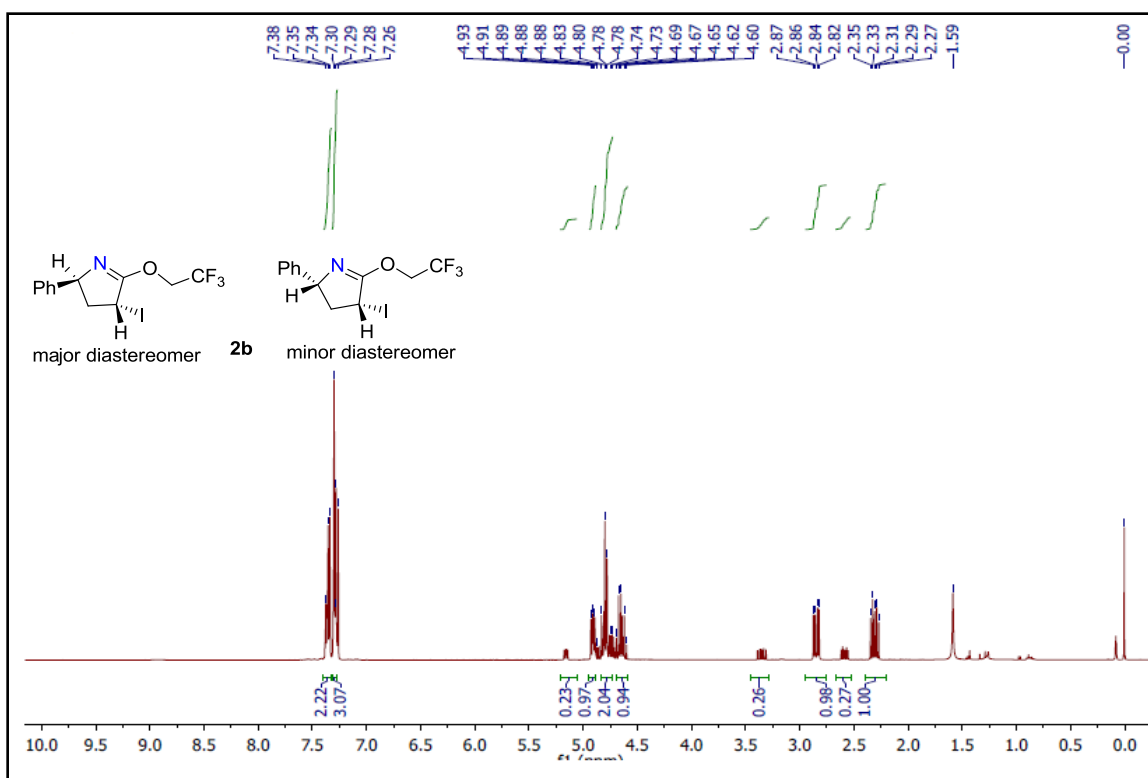
HSQC spectra of **2a**



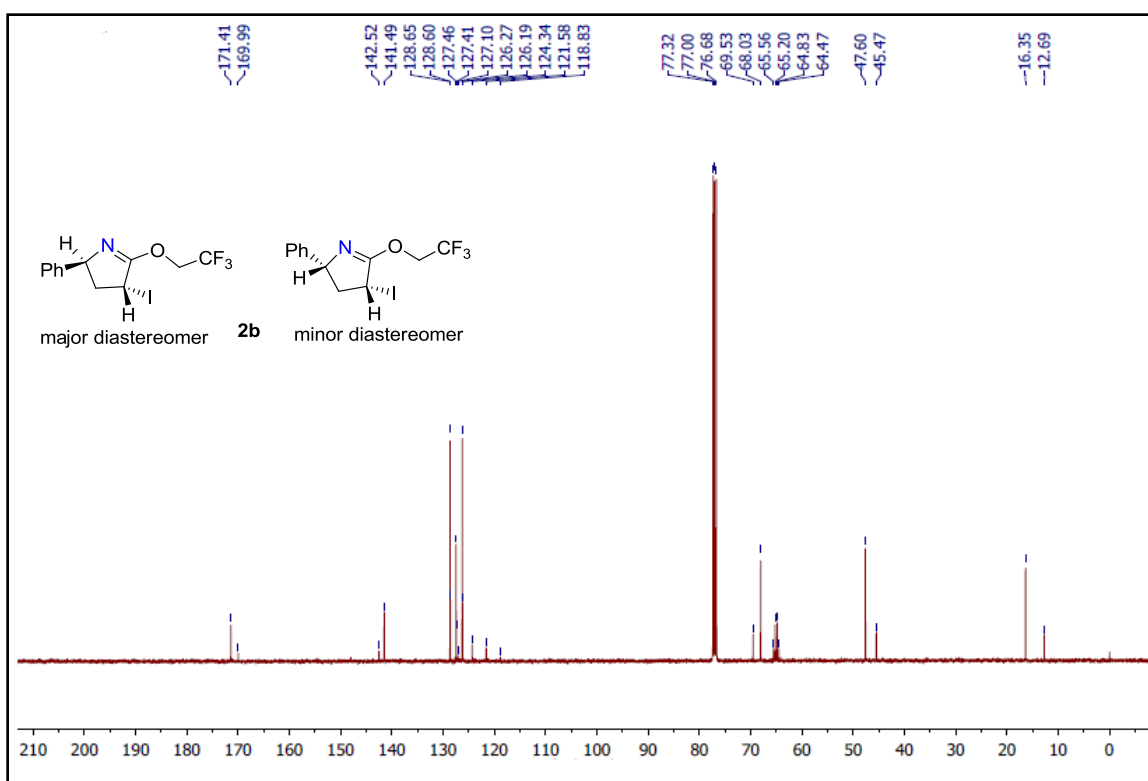
NOESY spectra of **2a**



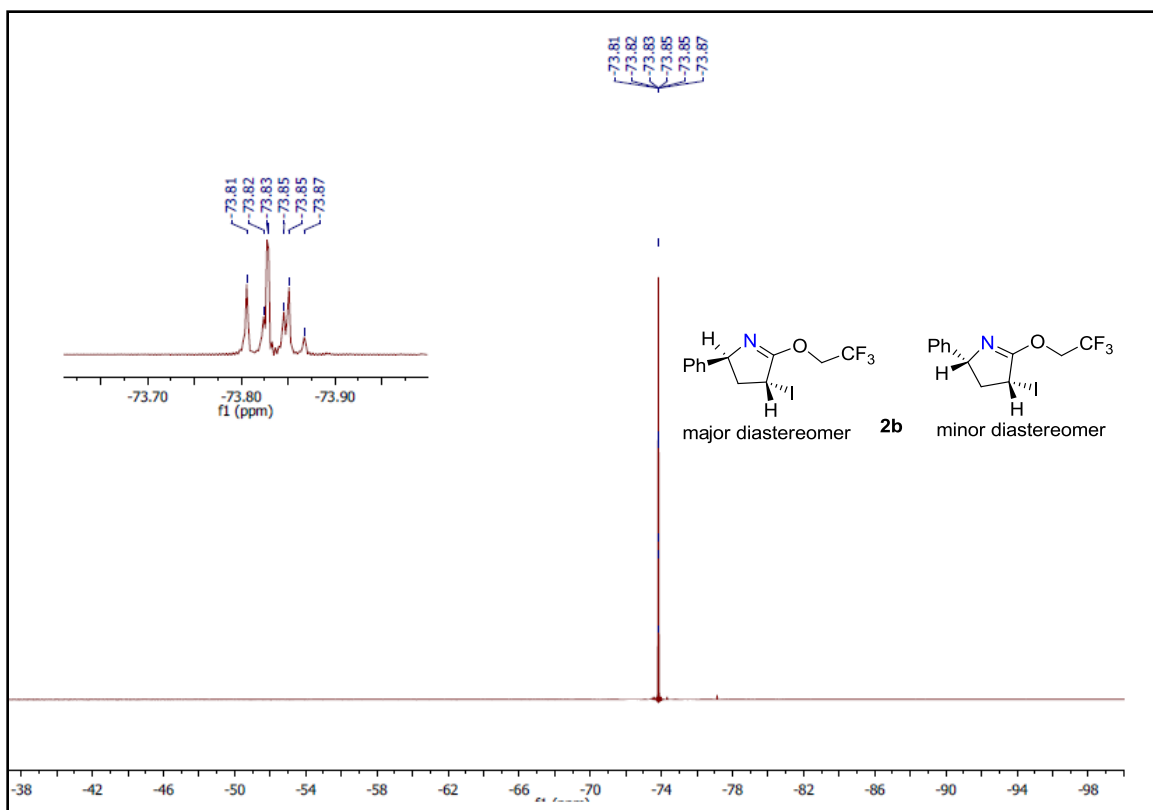
NOESY spectra of **2a**



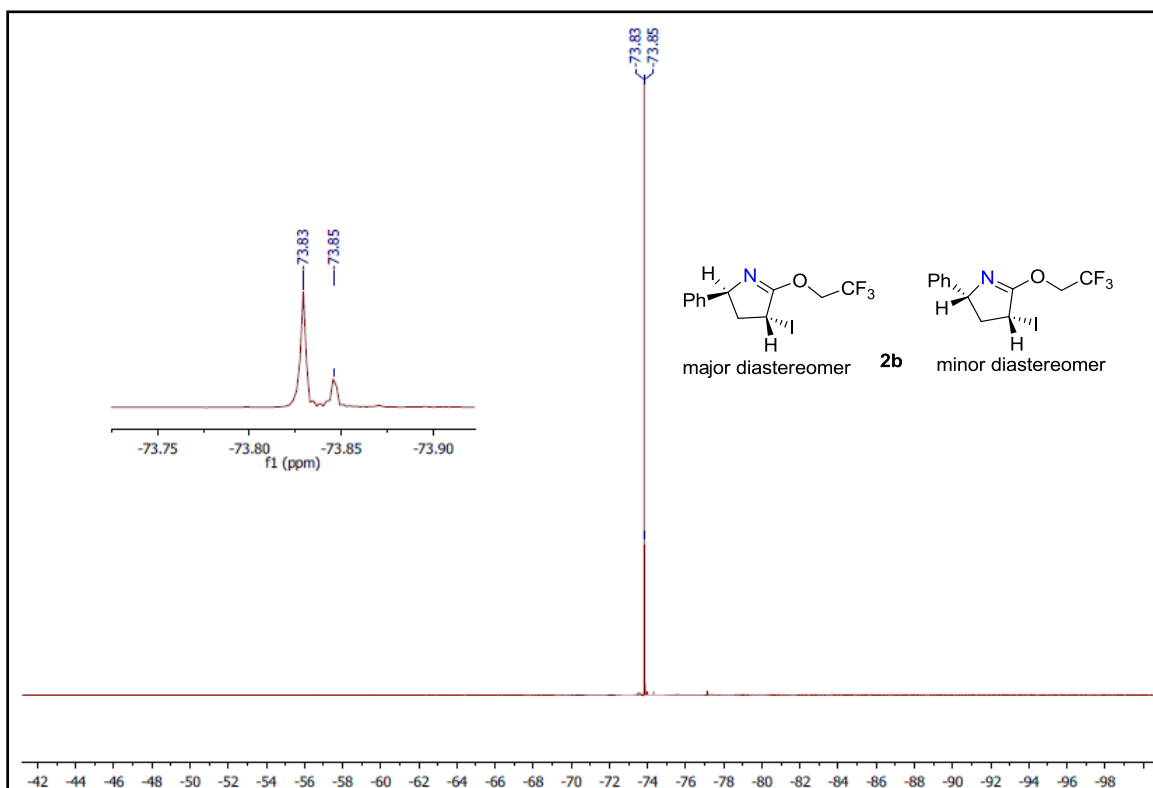
**<sup>1</sup>H spectra of 2b**



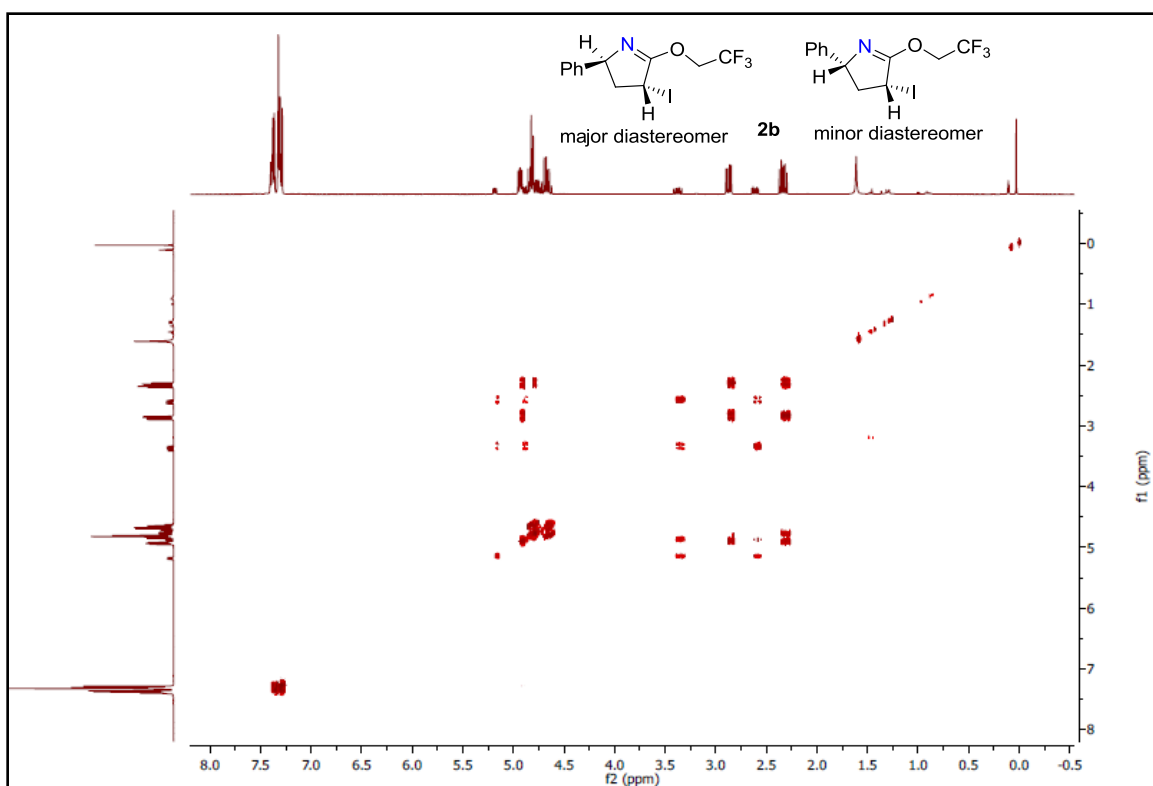
**<sup>13</sup>C{<sup>1</sup>H} spectra of 2b**



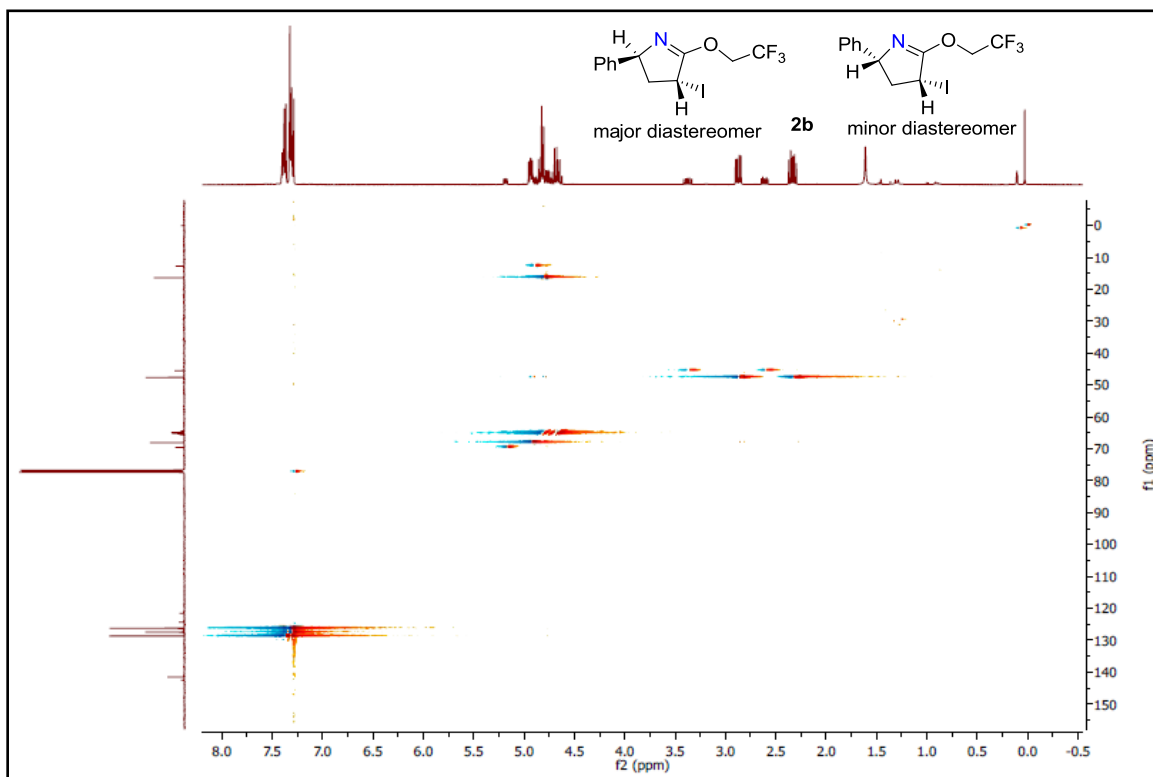
<sup>19</sup>F Proton coupled spectra of **2b**



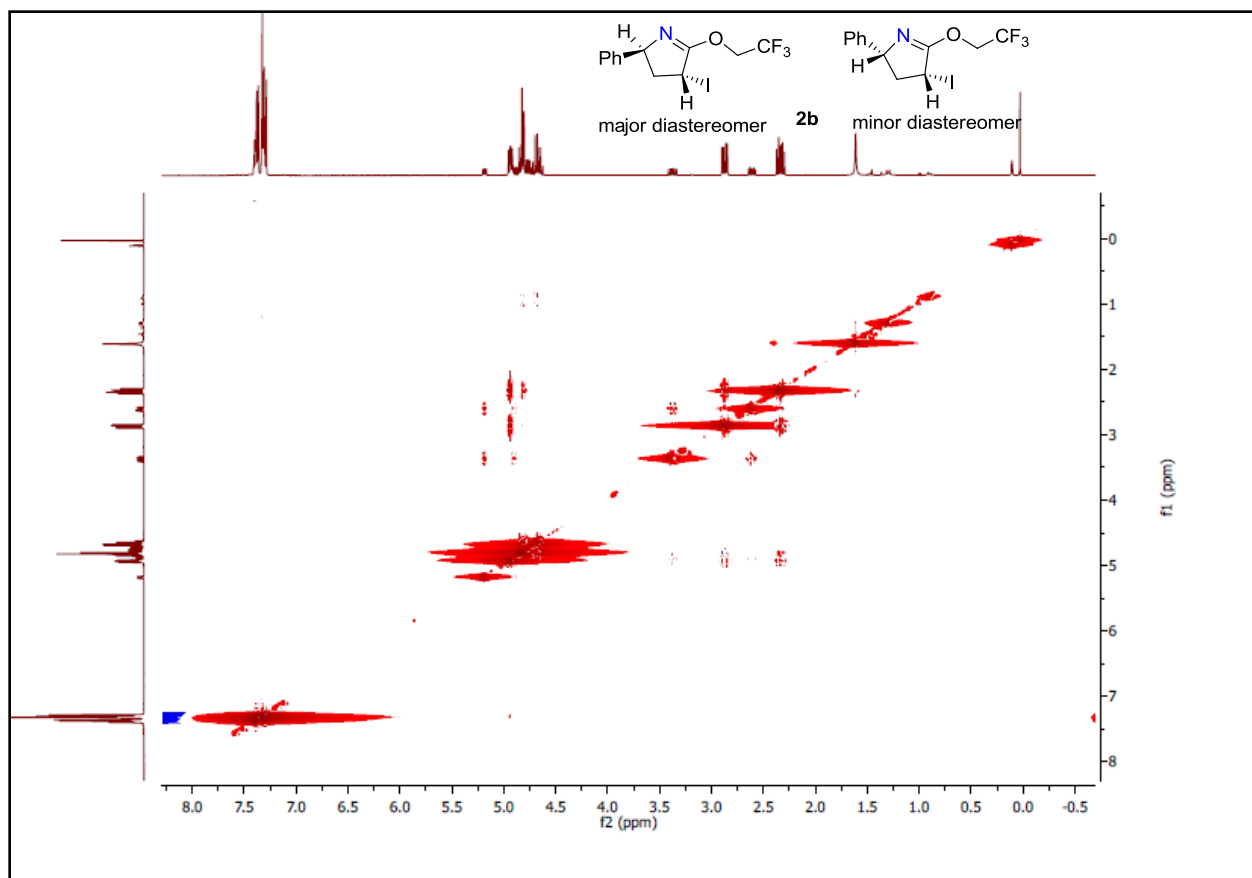
<sup>19</sup>F Proton decoupled spectra of **2b**



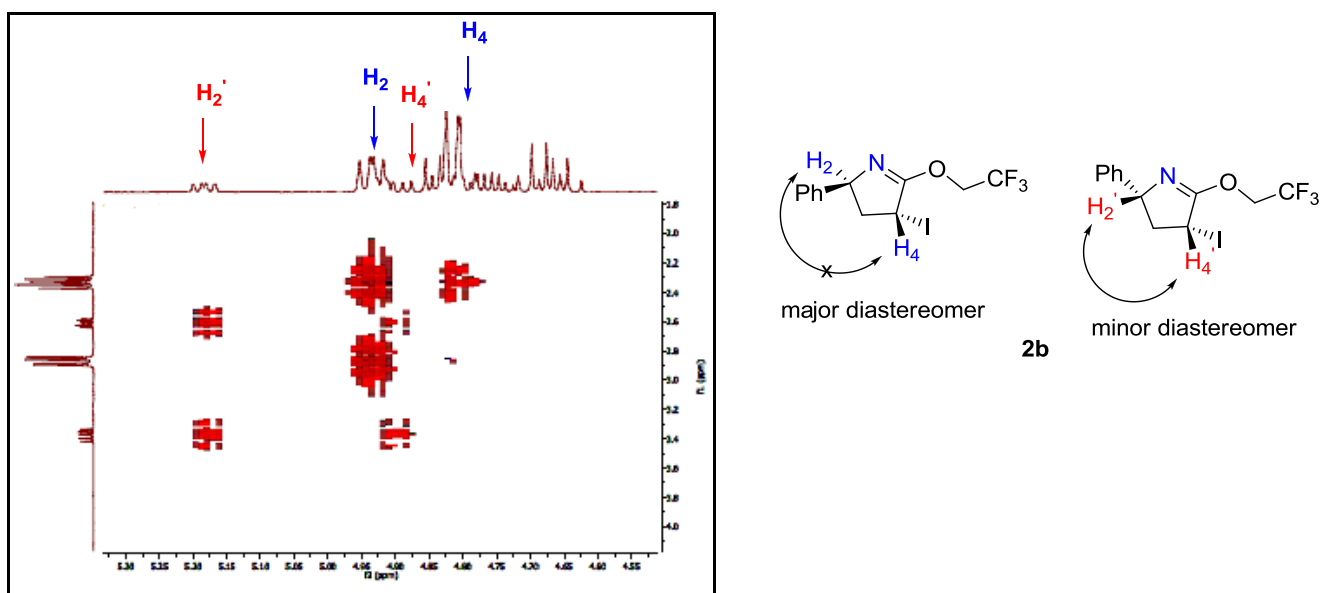
COSY spectra of **2b**



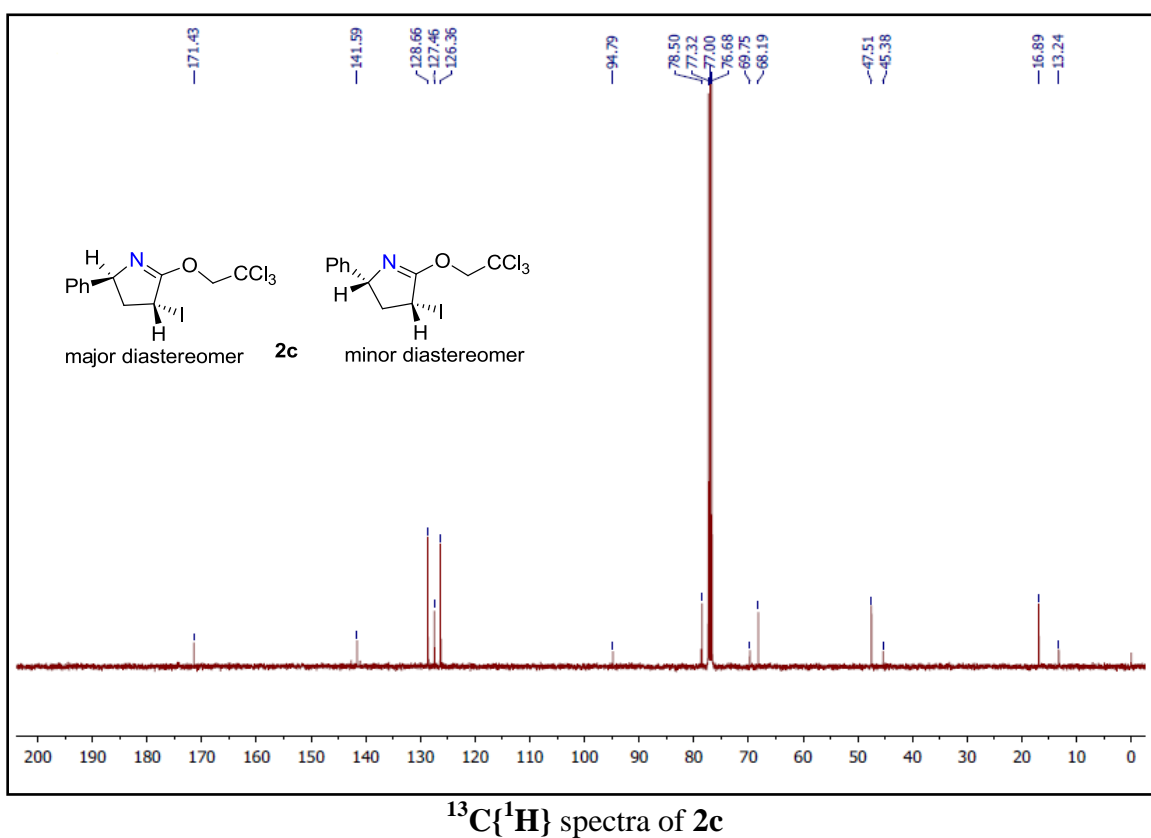
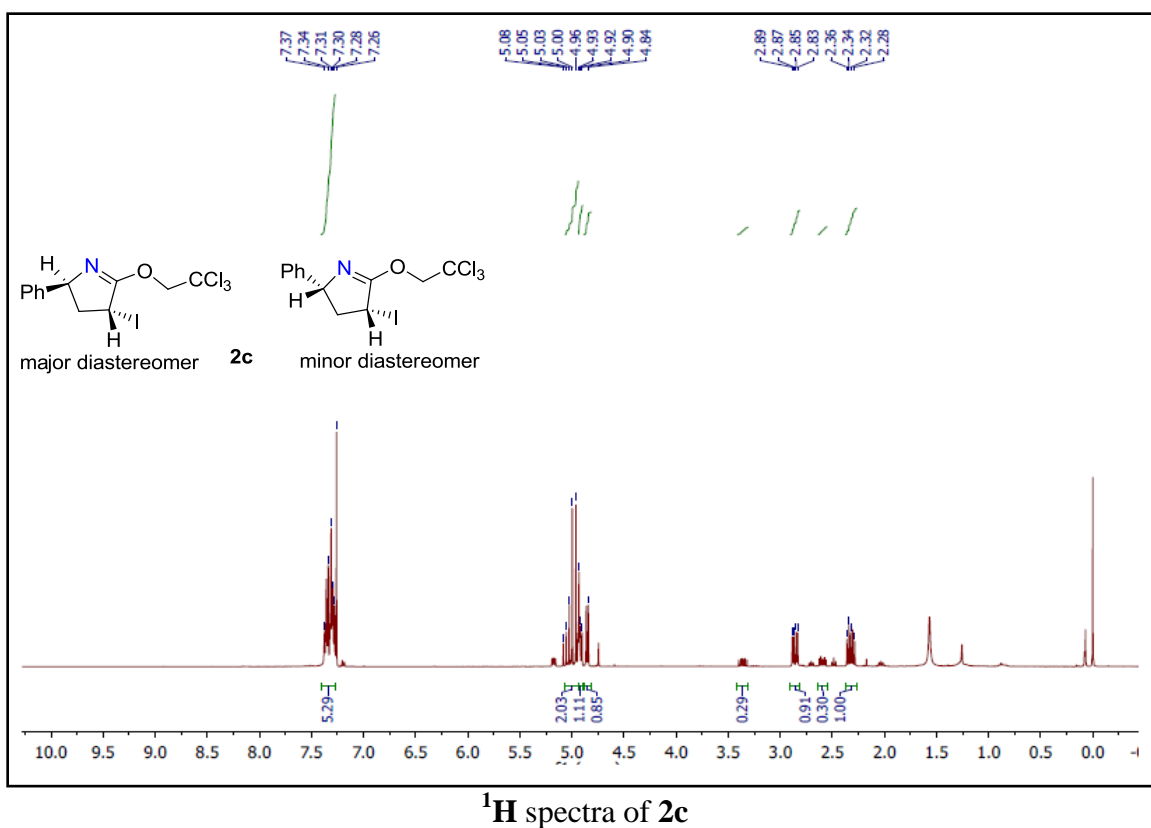
HSQC spectra of **2b**

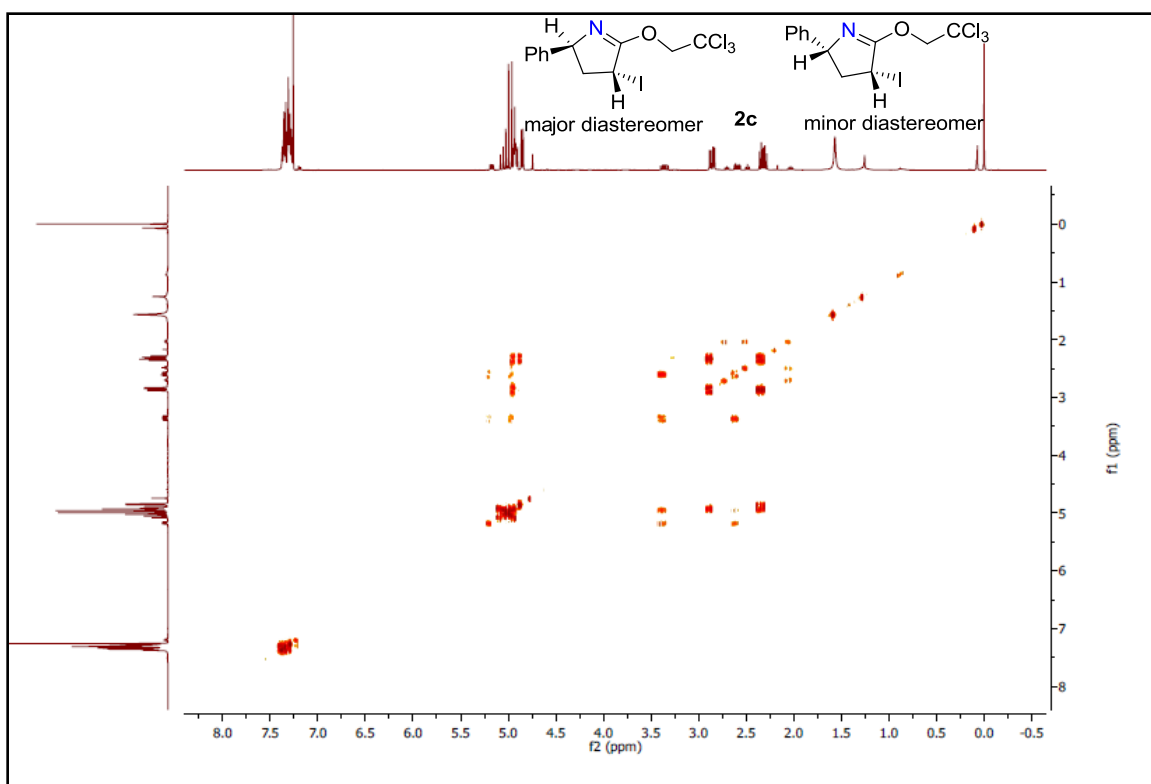


NOESY spectra of **2b**

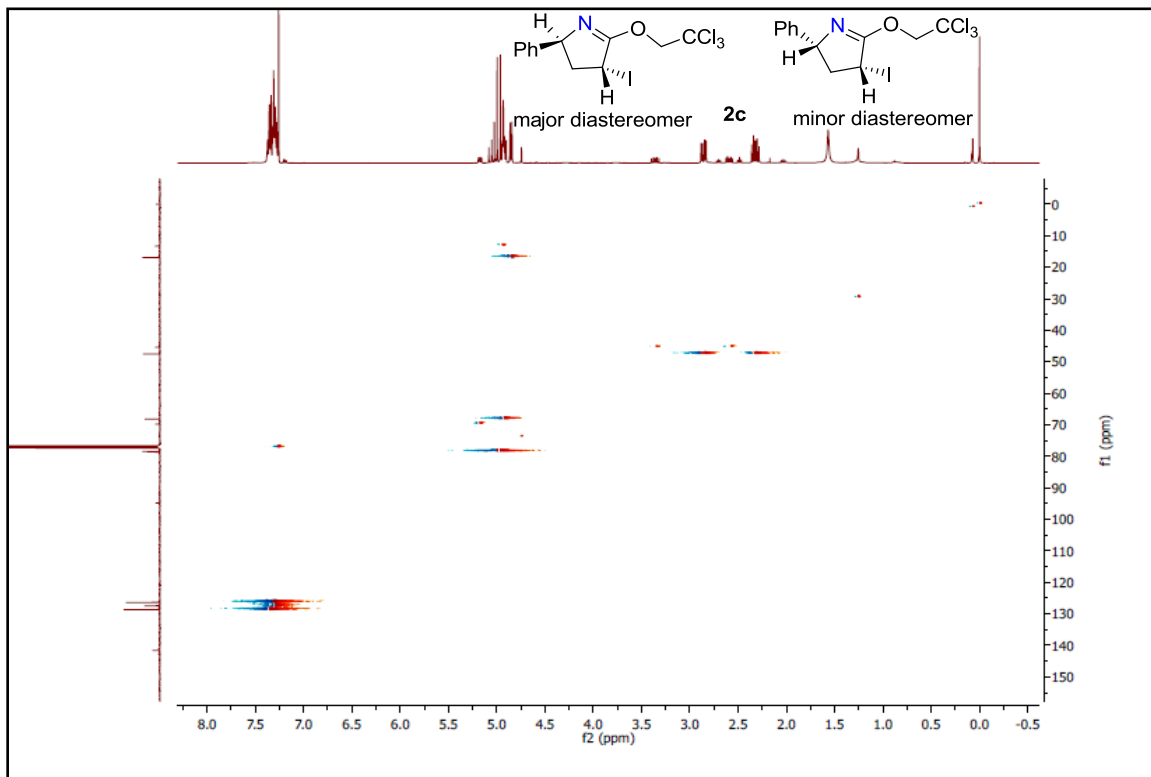


NOESY spectra of **2b**

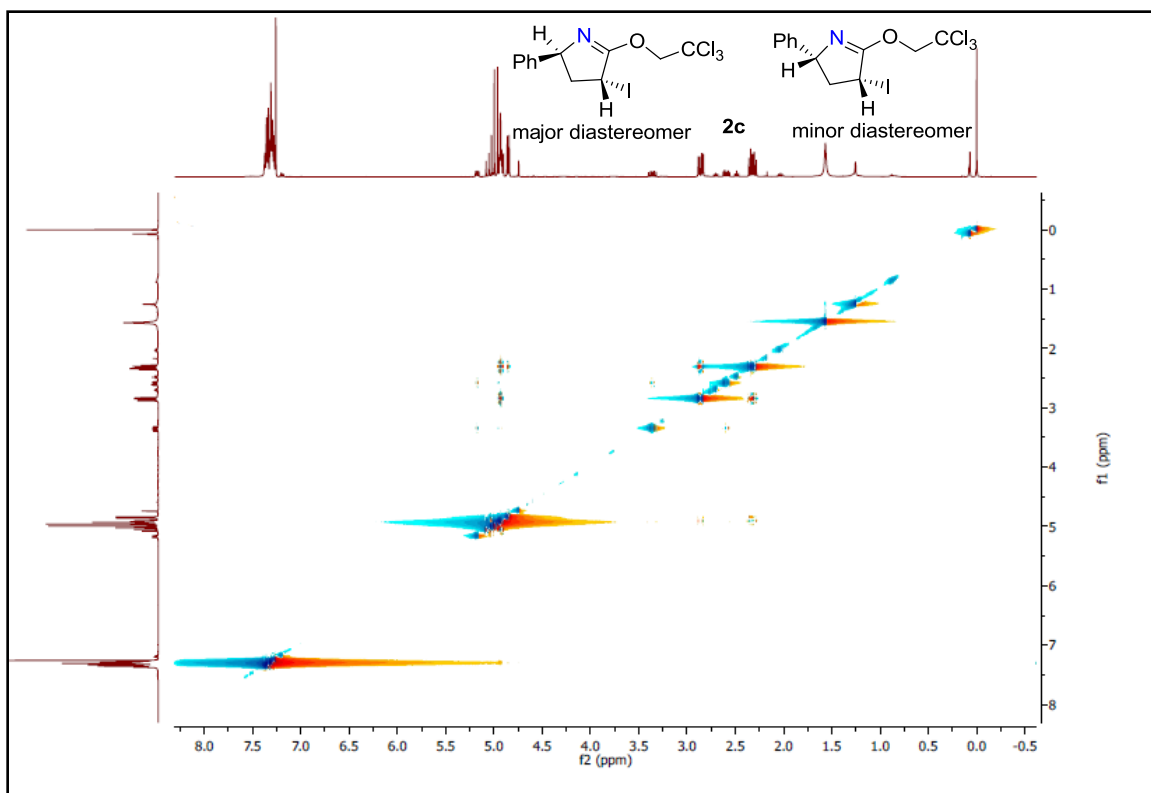




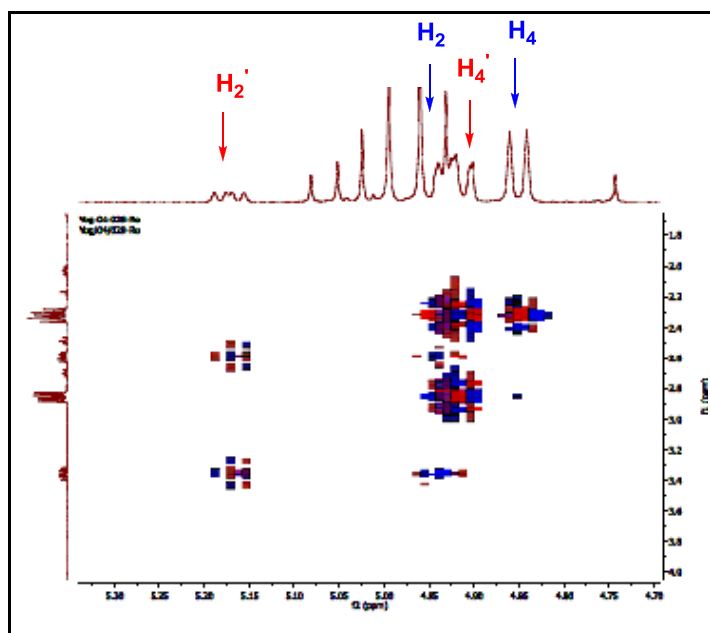
COSY spectra of **2c**



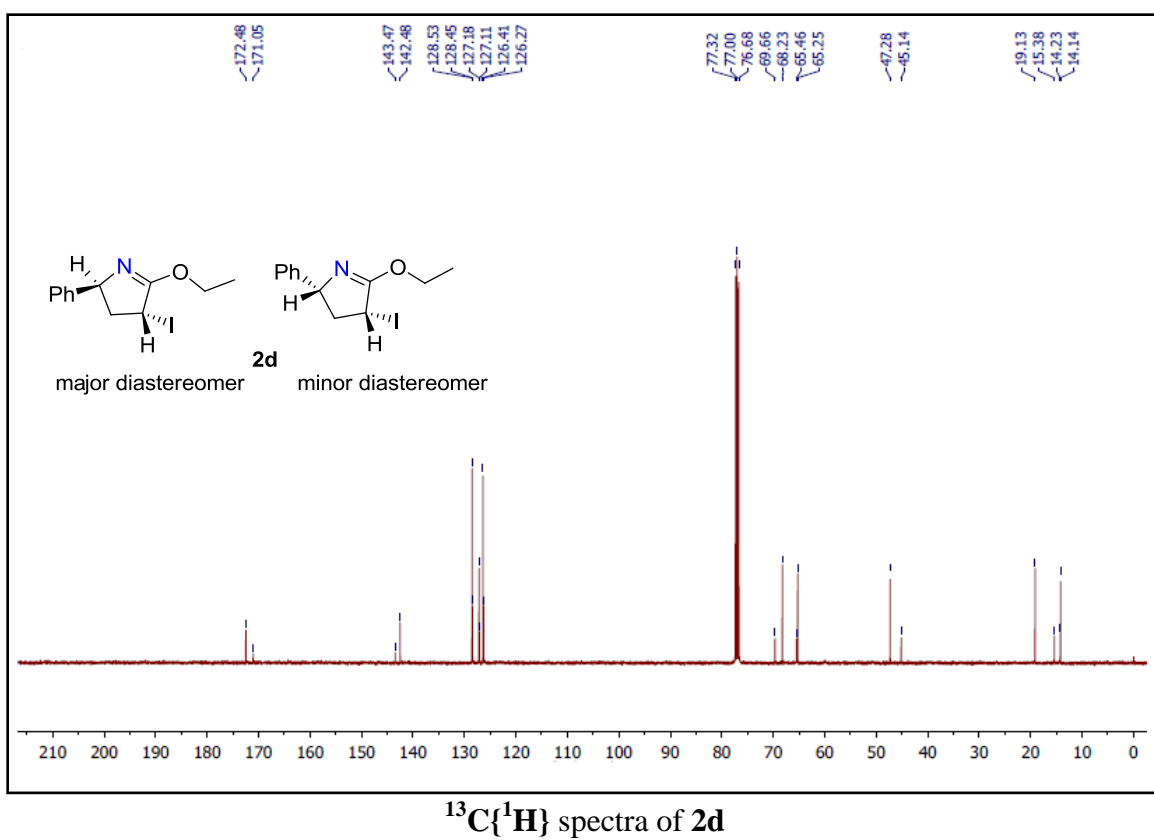
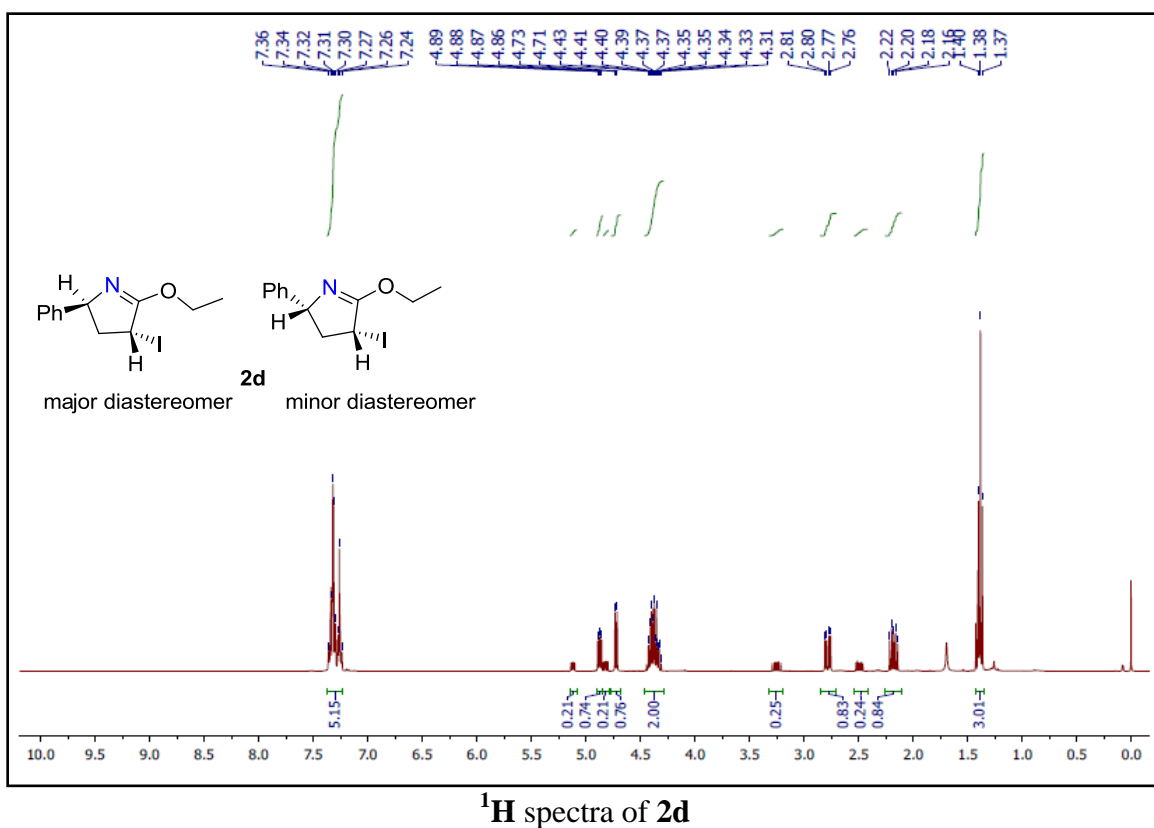
HSQC spectra of **2c**

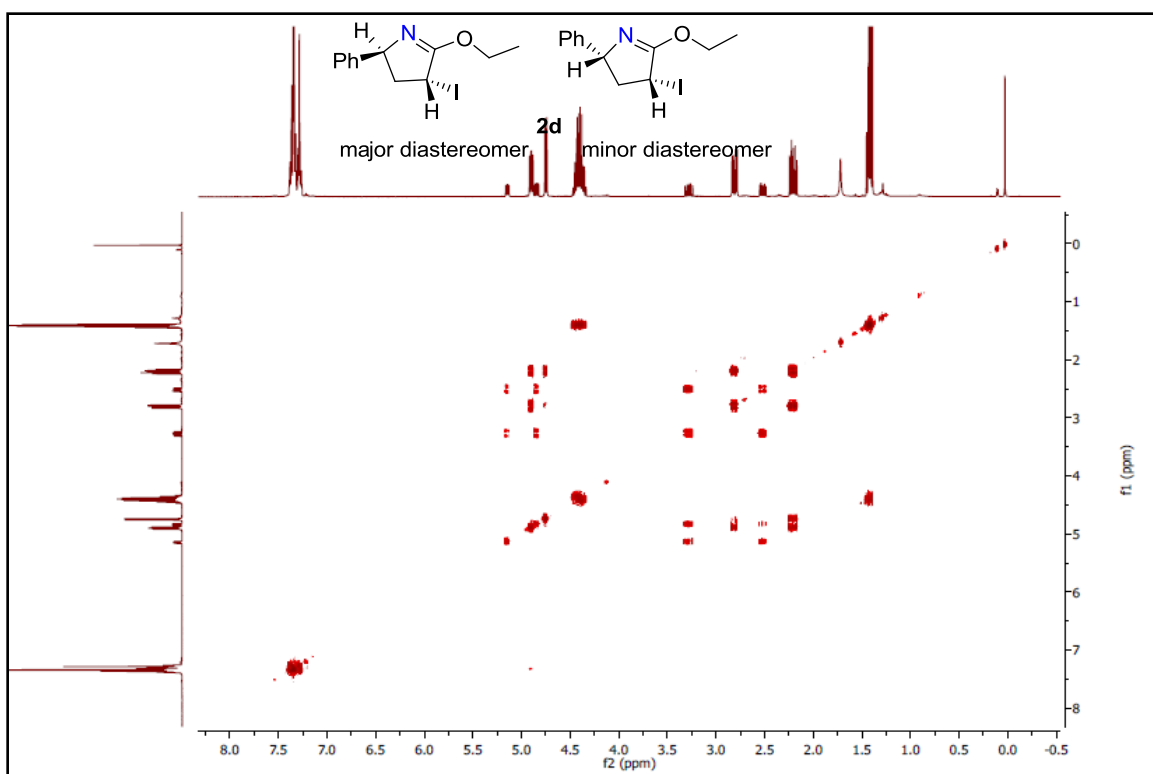


NOESY spectra of **2c**

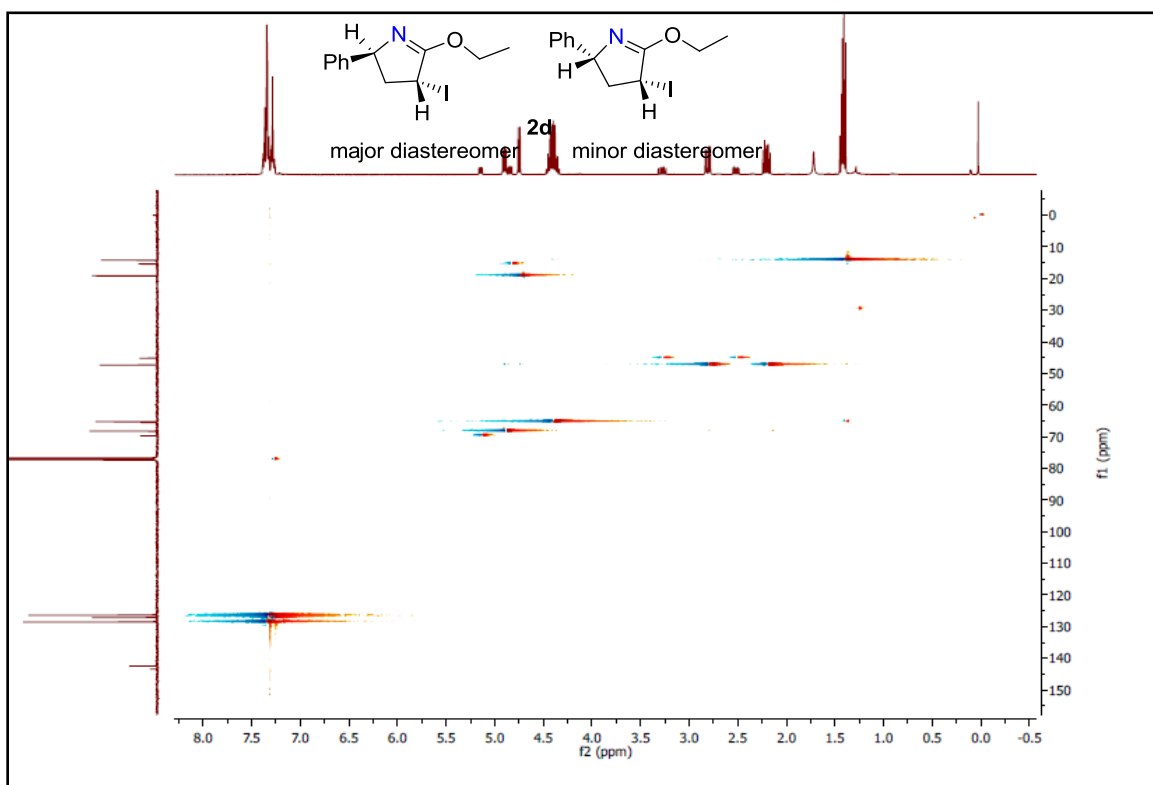


NOESY spectra of **2c**

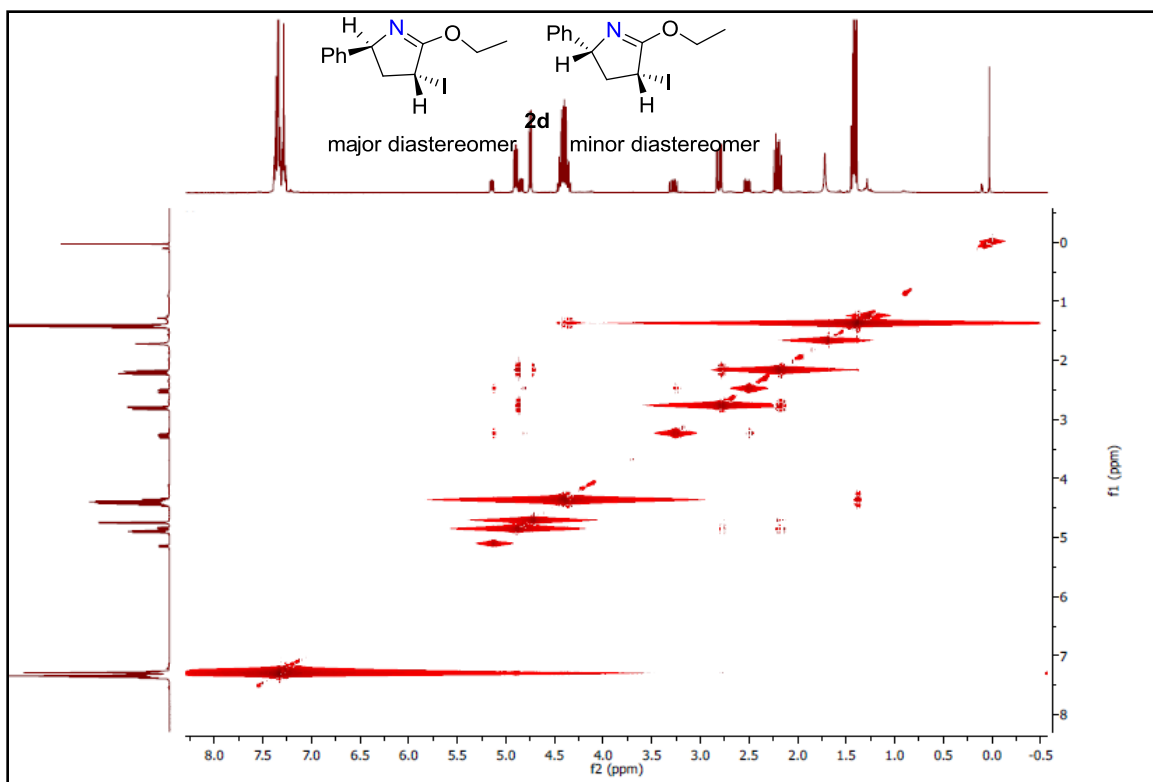




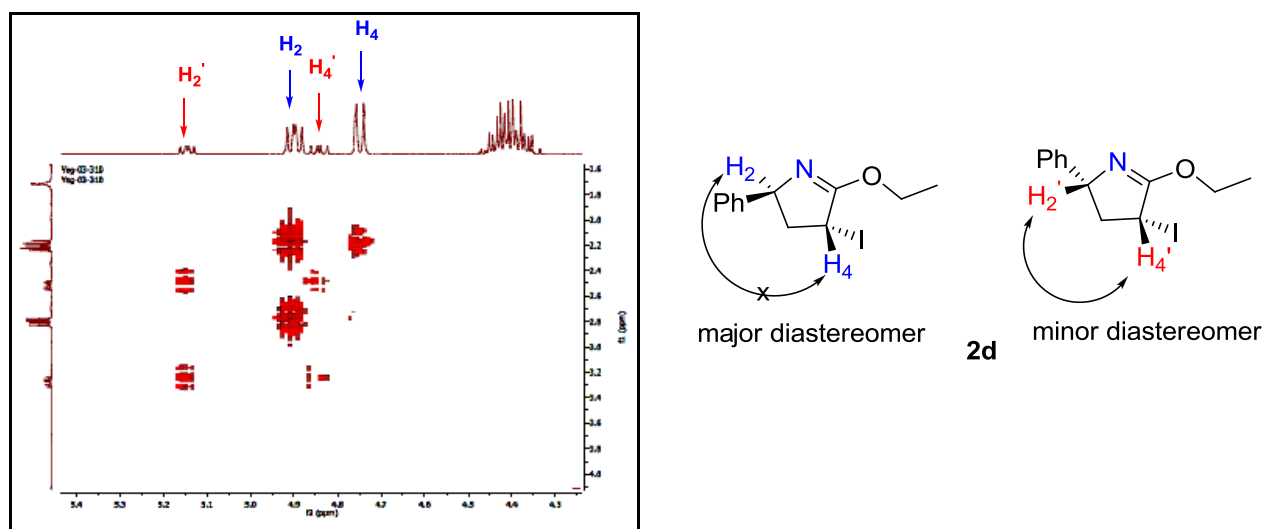
COSY spectra of **2d**



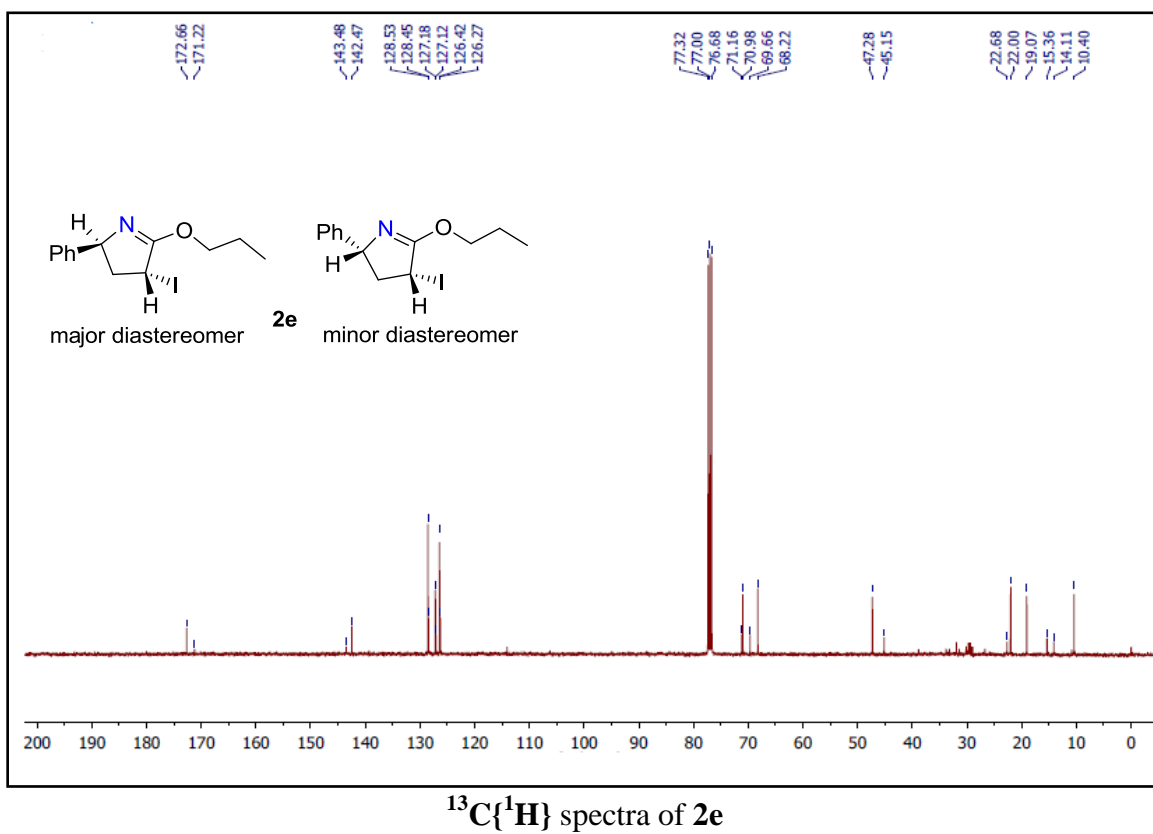
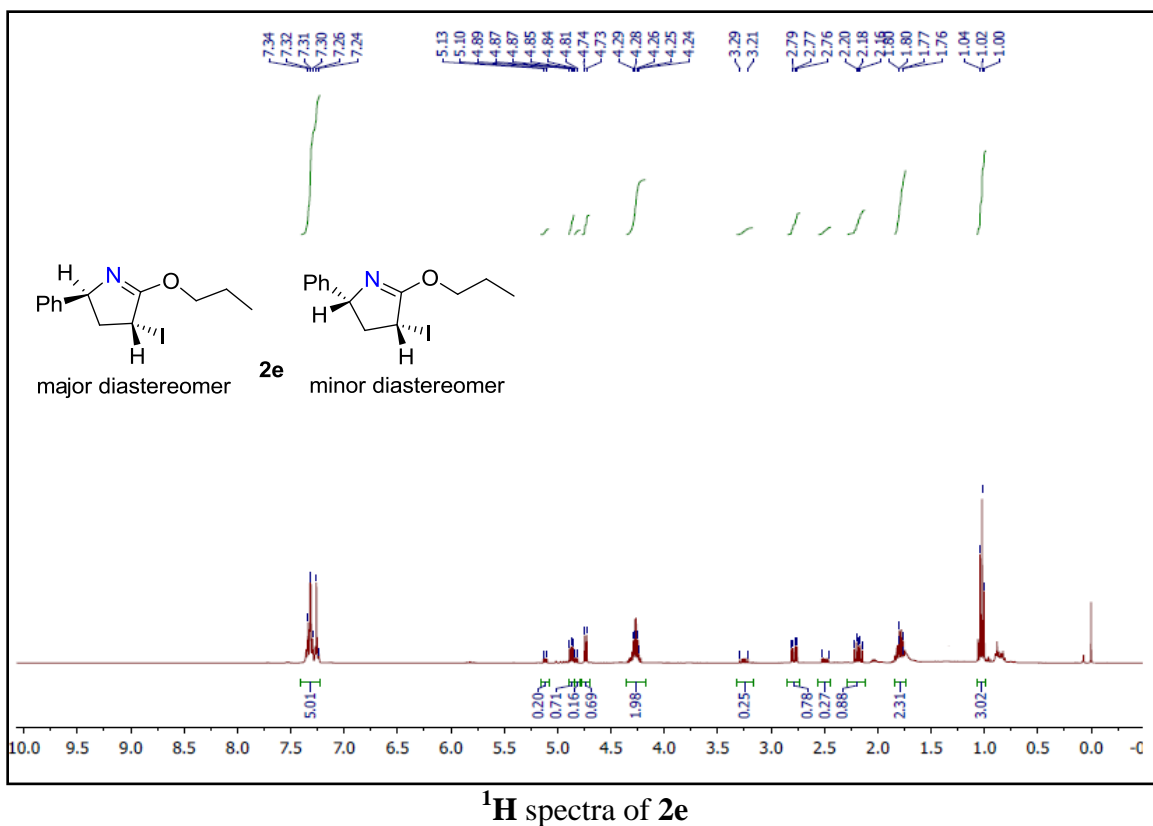
HSQC spectra of **2d**

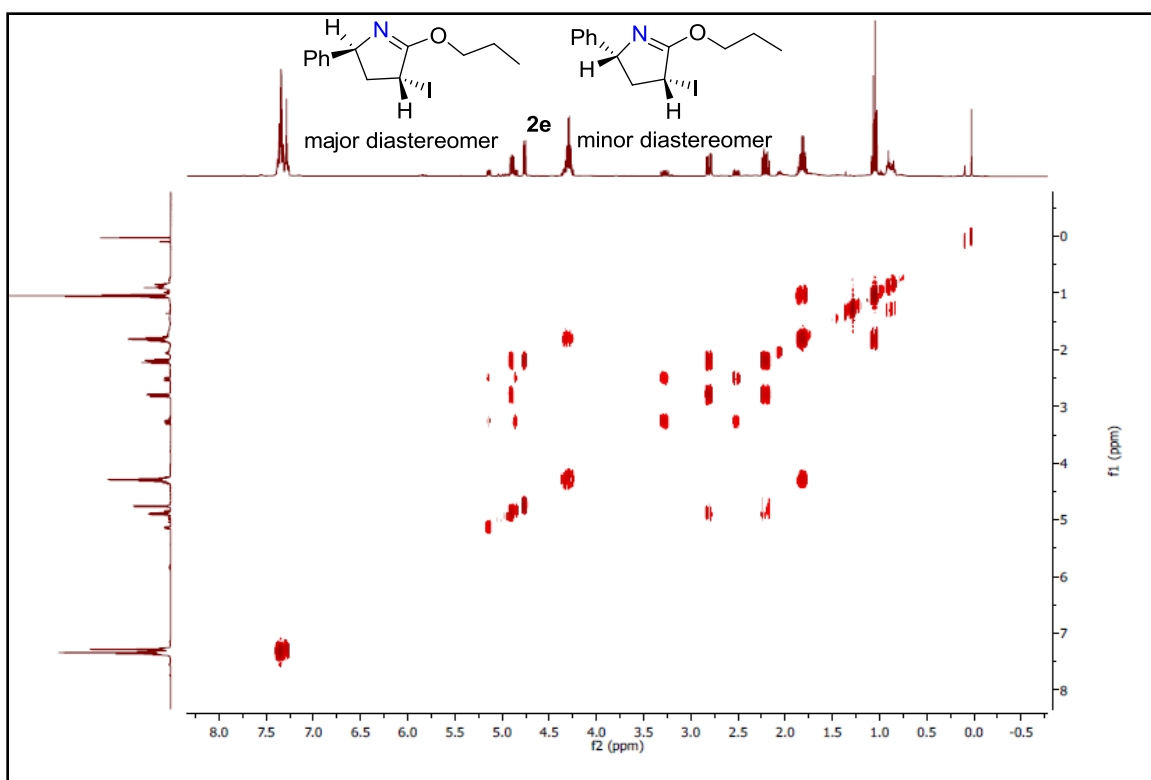


NOESY spectra of **2d**

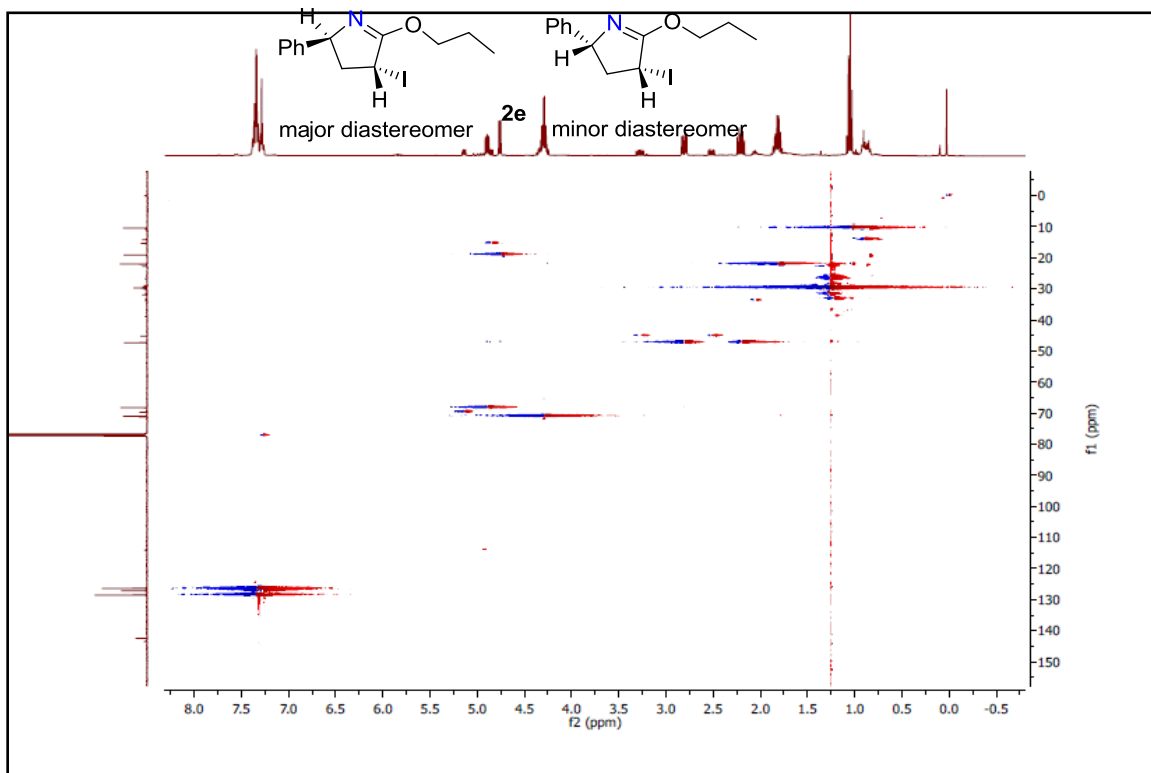


NOESY spectra of **2d**

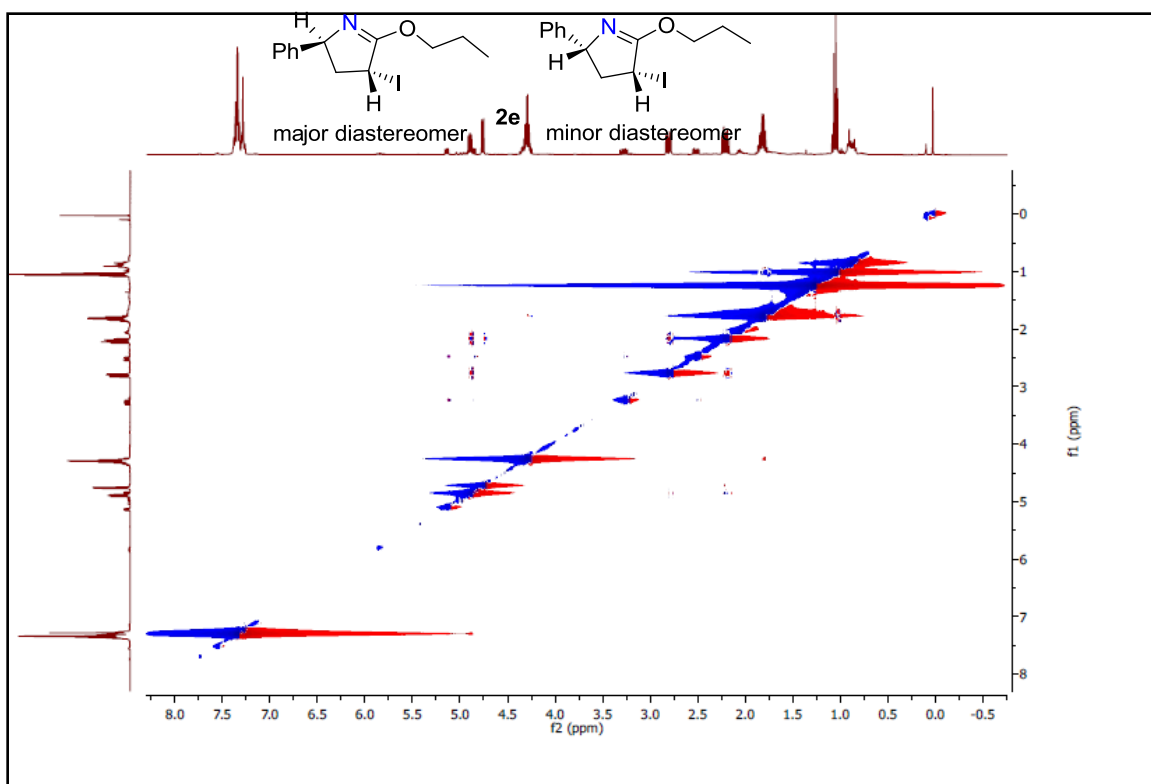




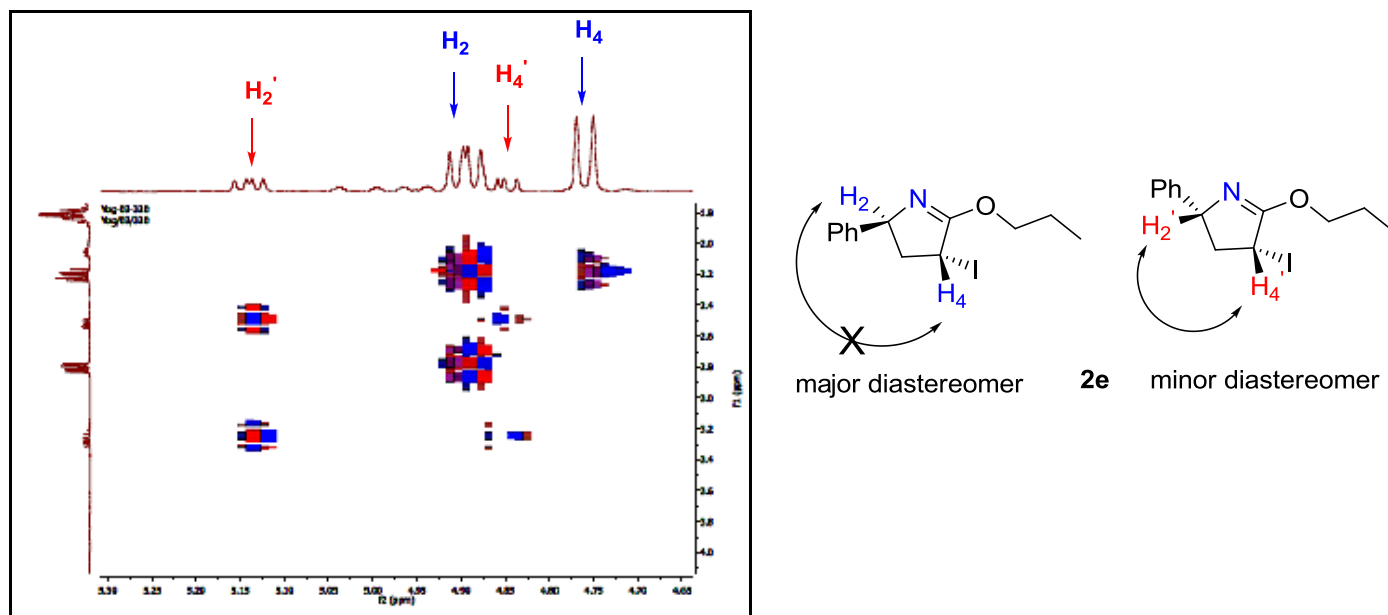
**COSY spectra of 2d**



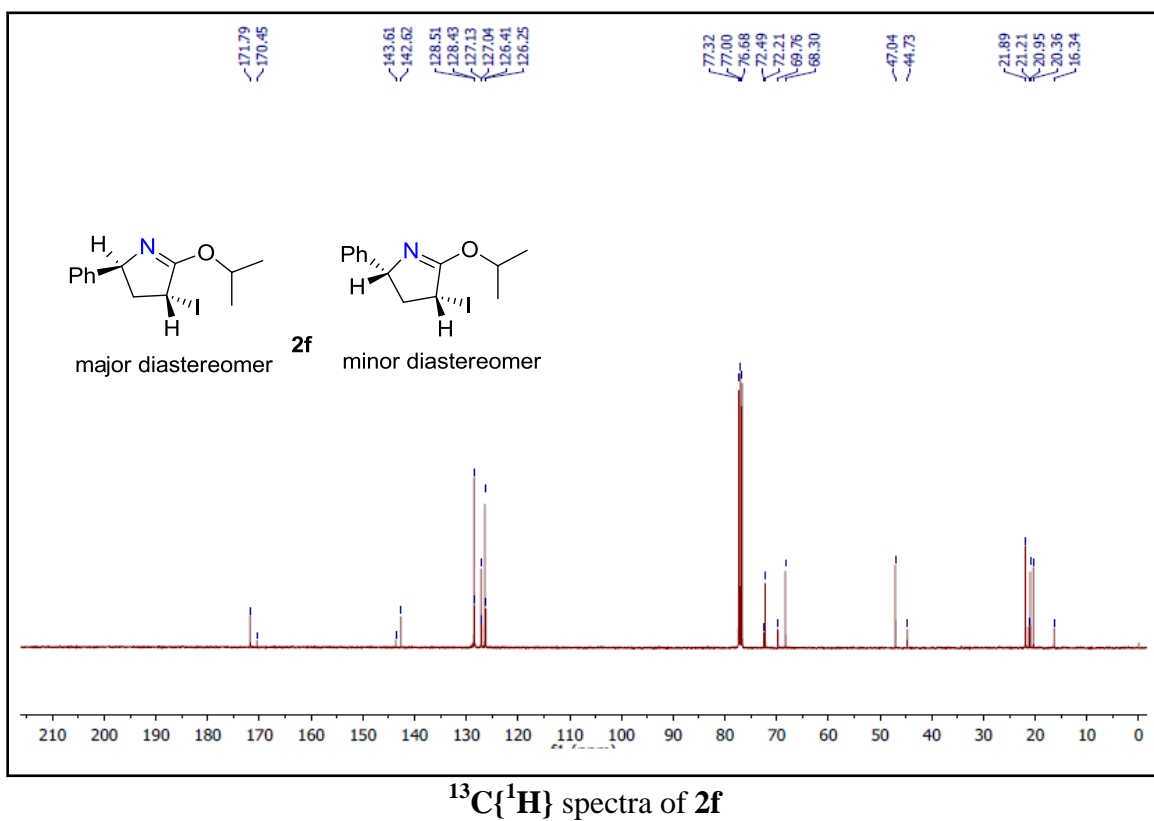
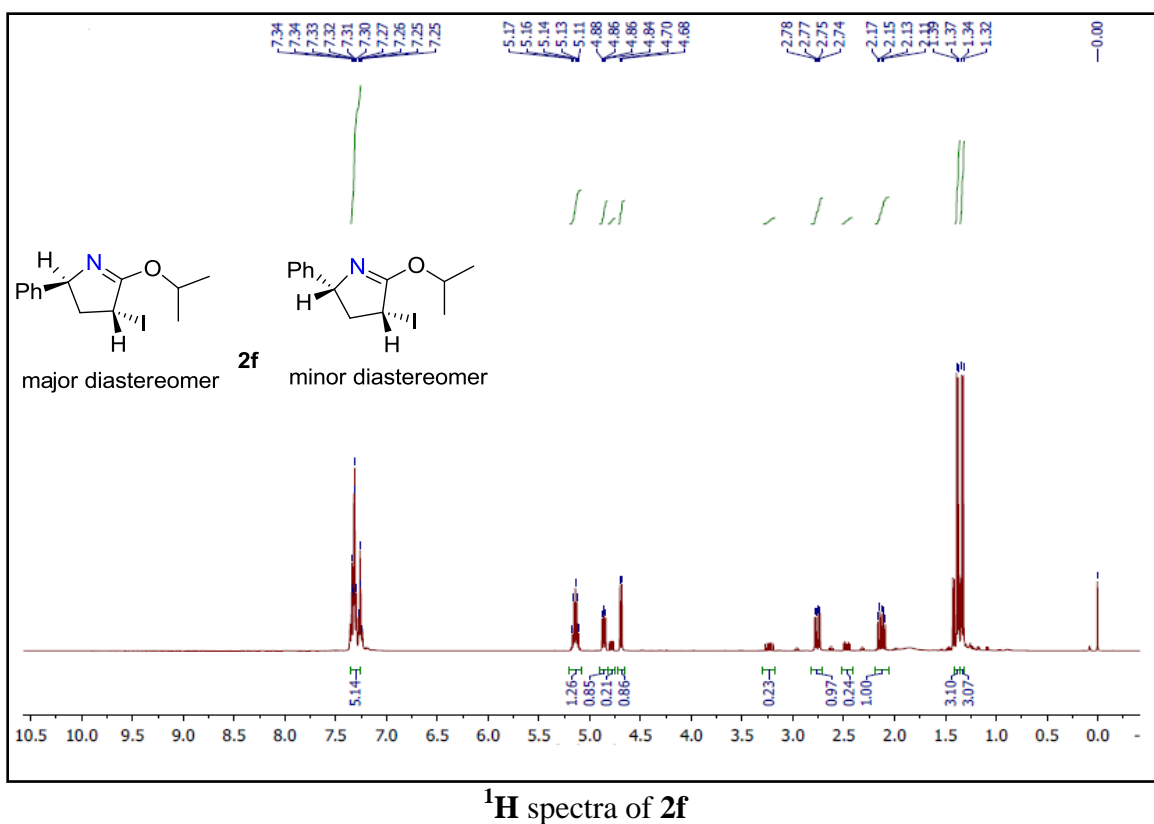
**HSQC spectra of 2e**

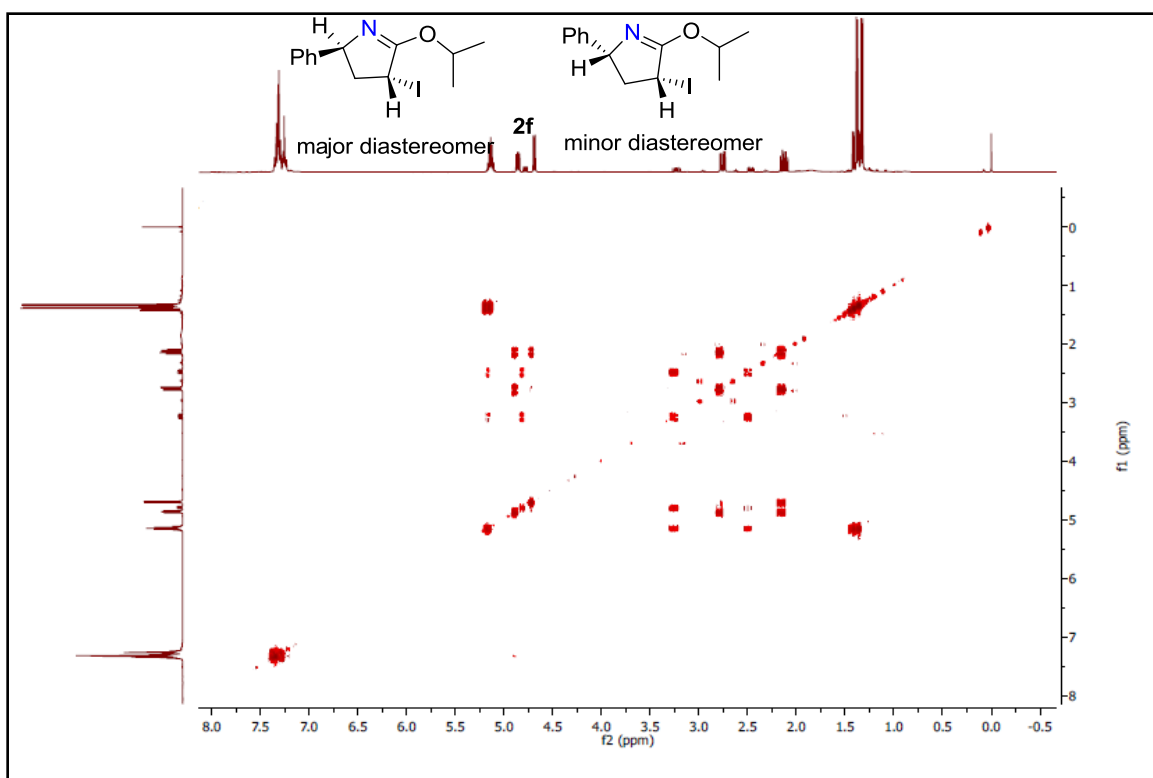


NOESY spectra of **2e**

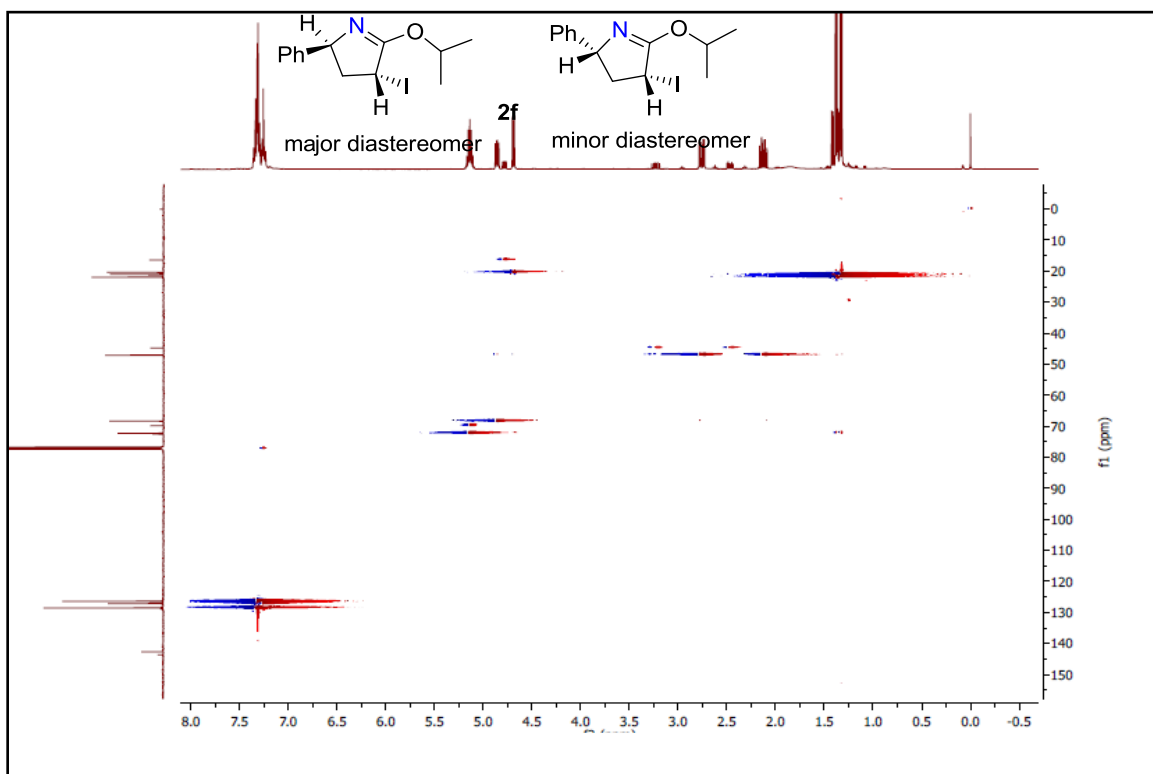


NOESY spectra of **2e**

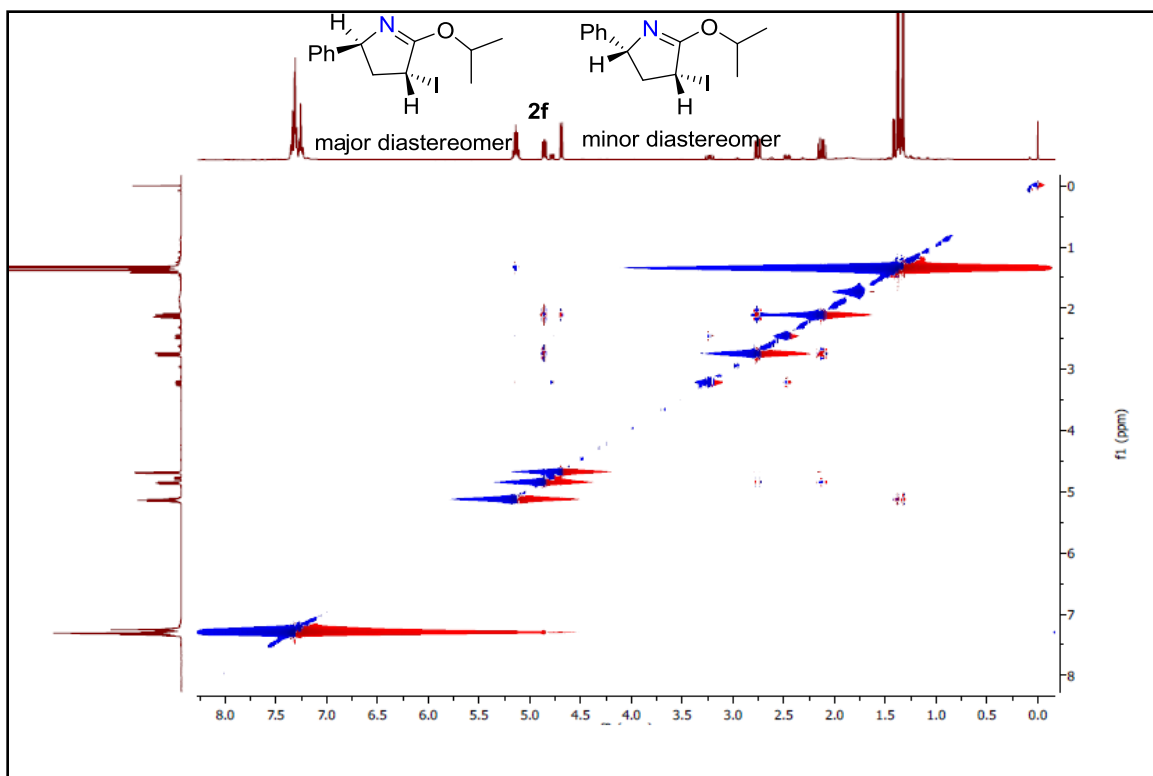




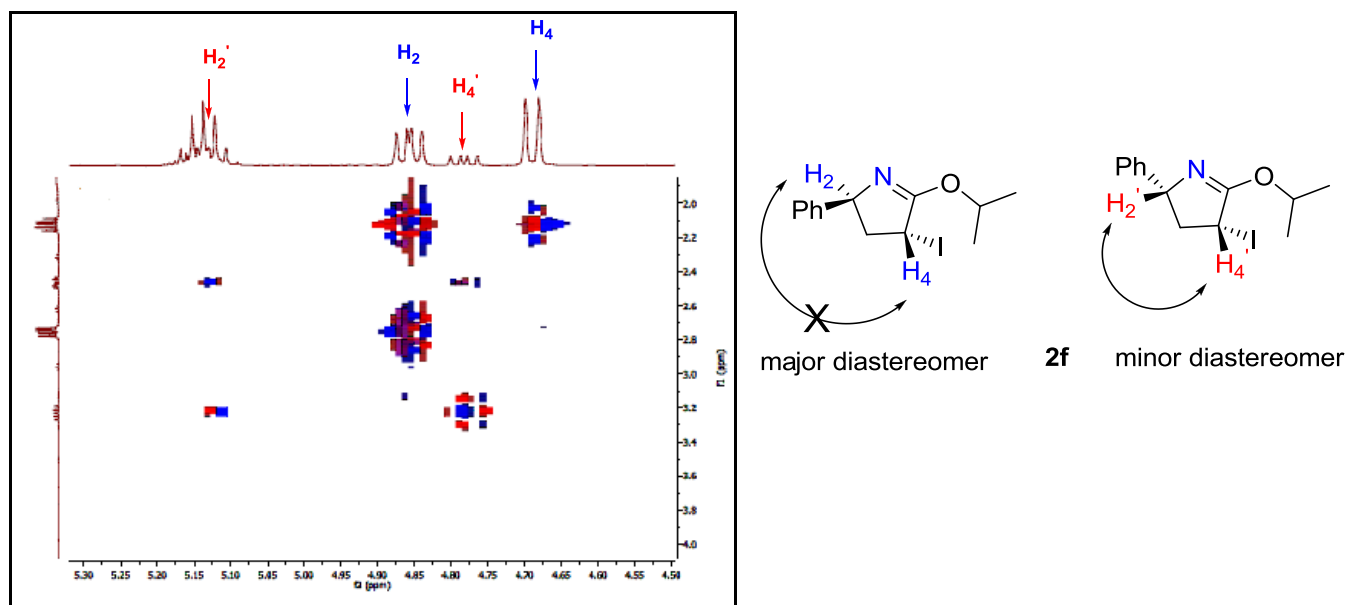
COSY spectra of **2f**



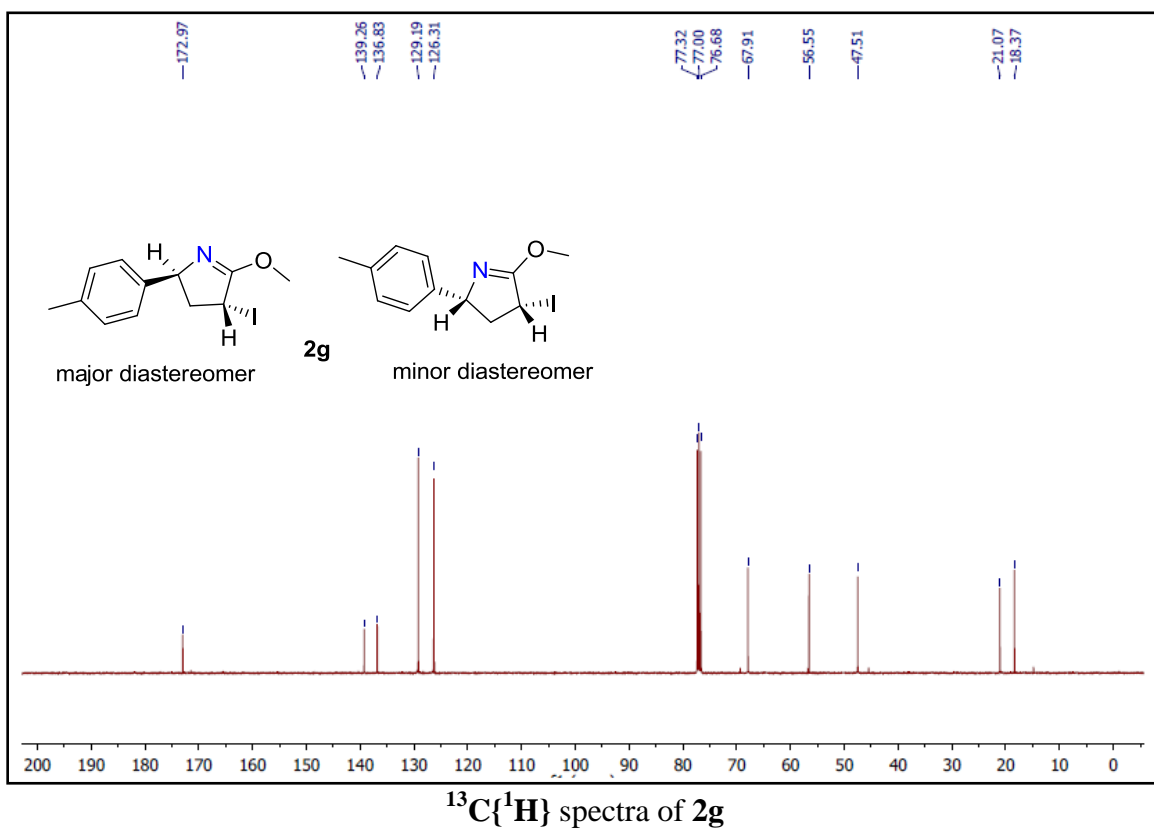
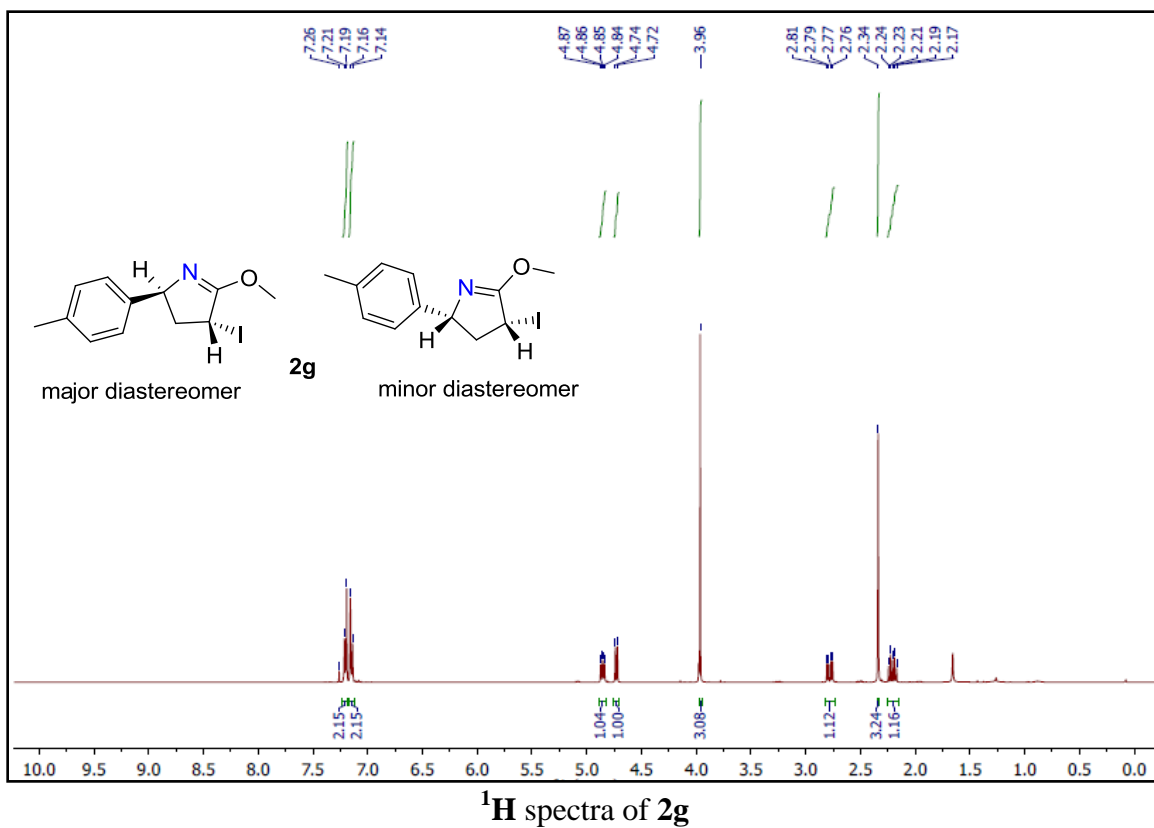
HSQC spectra of **2f**

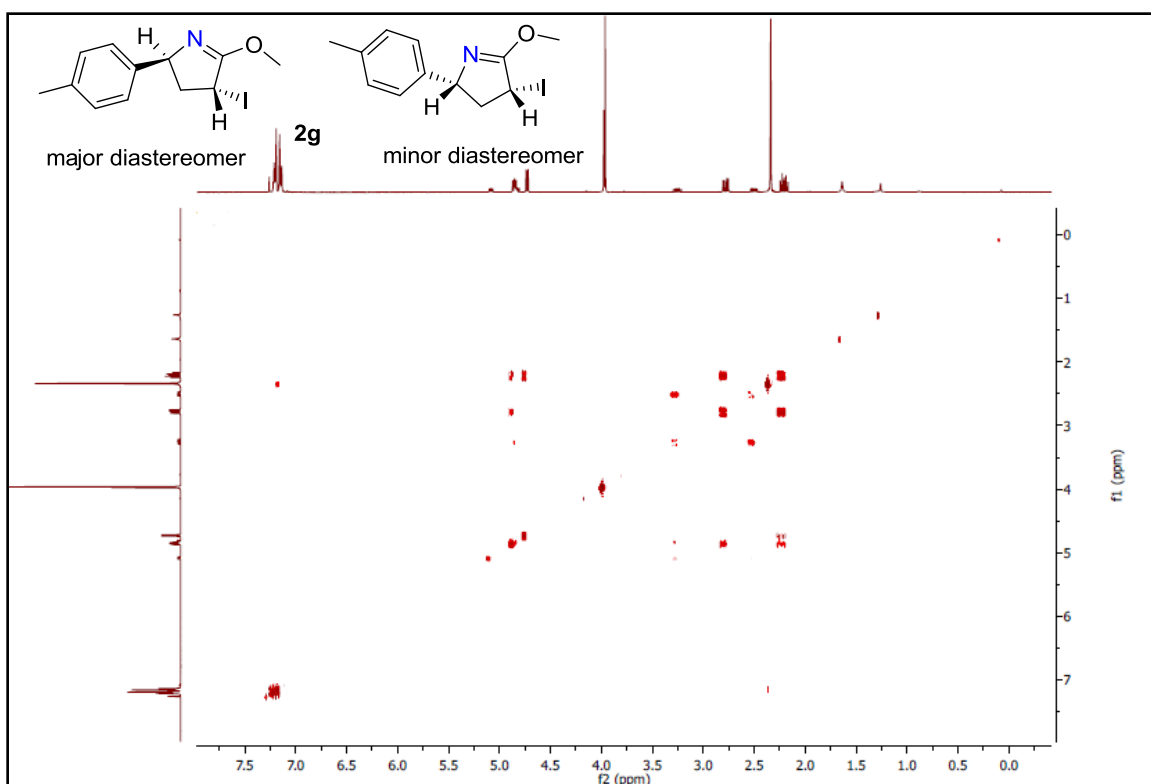


NOESY spectra of **2f**

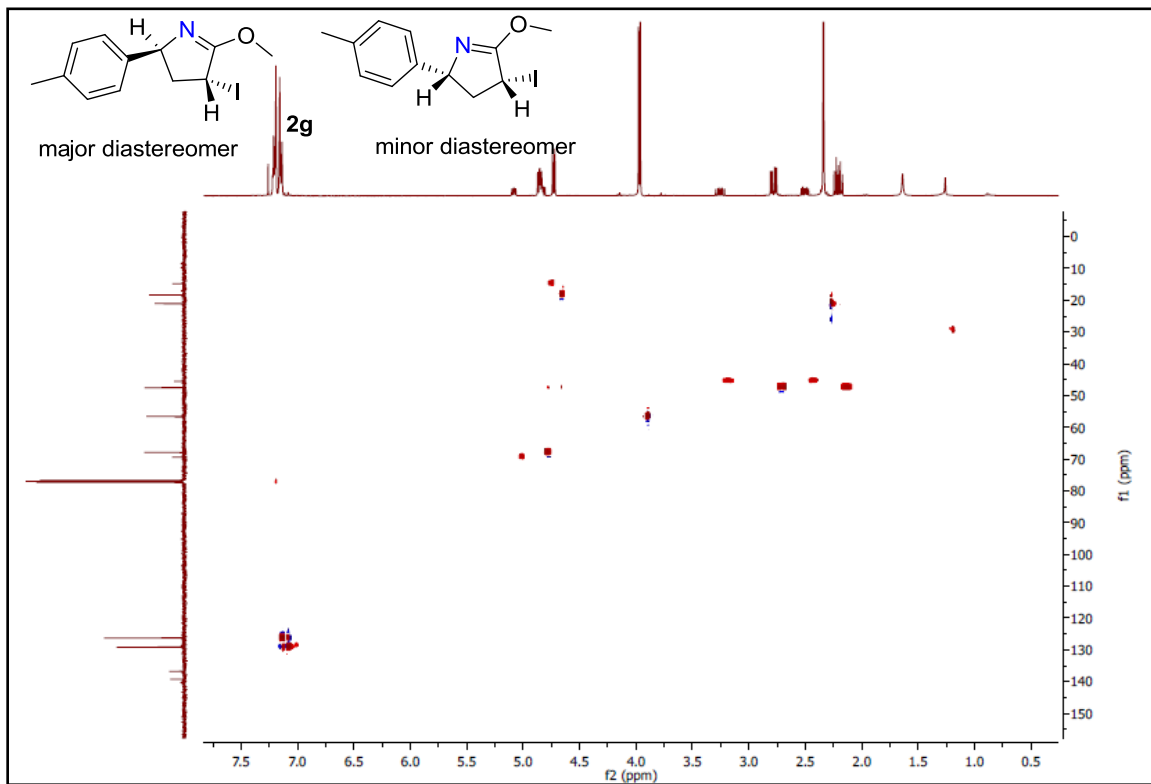


NOESY spectra of **2f**

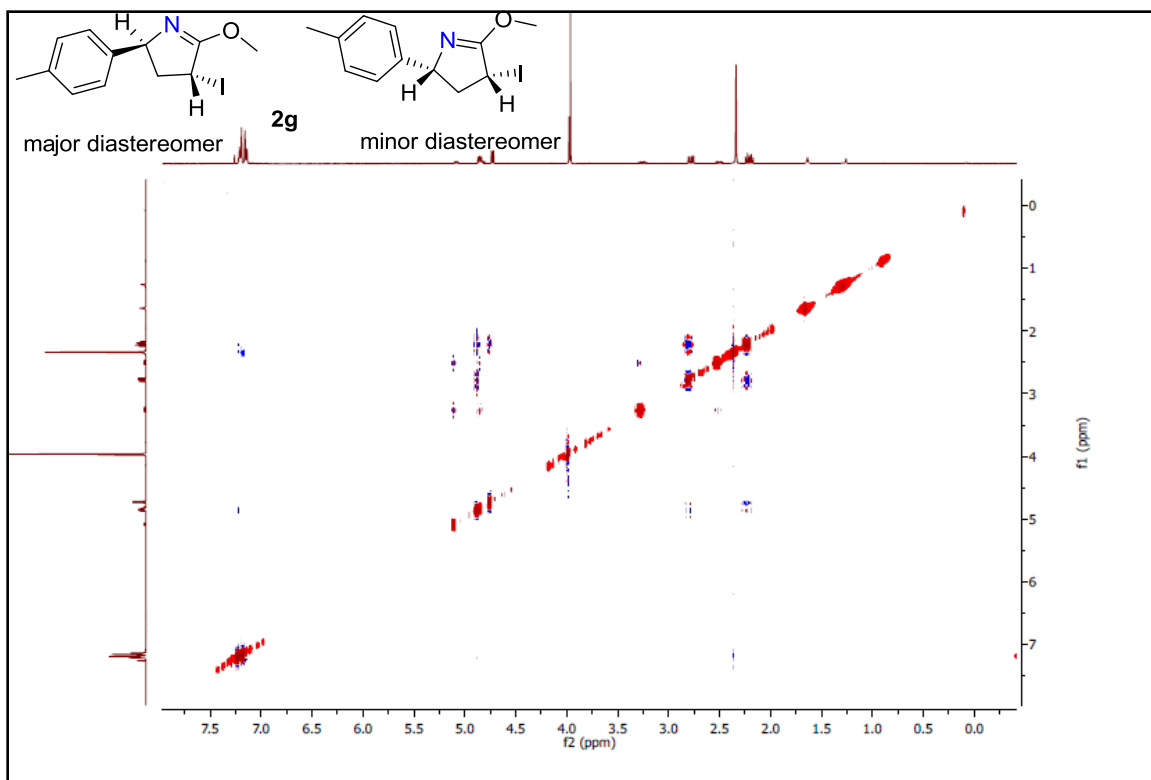




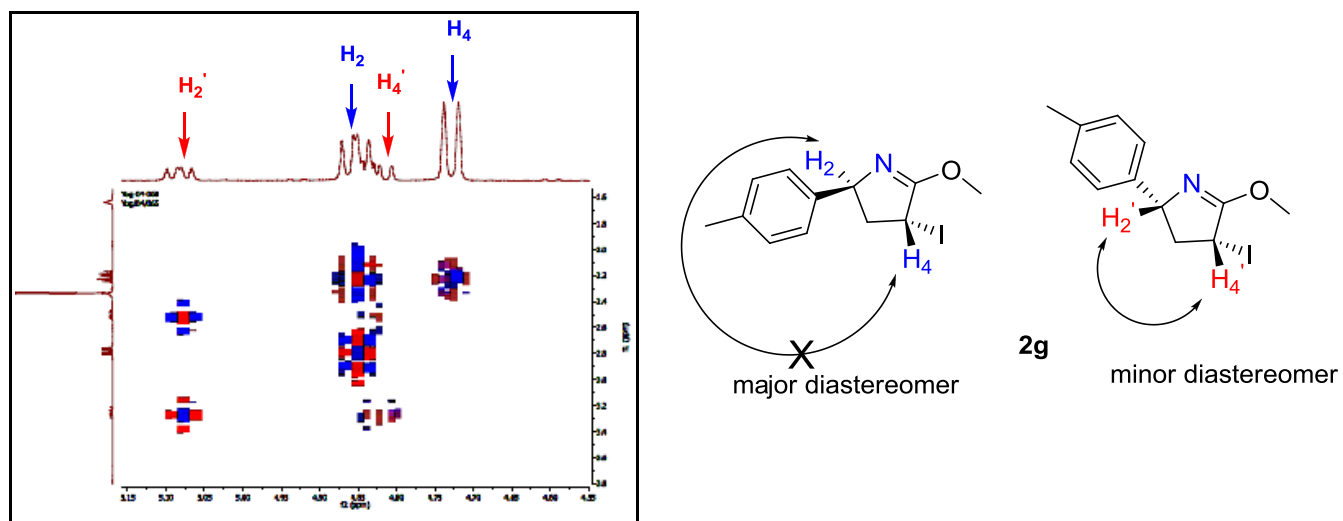
COSY spectra of **2g**



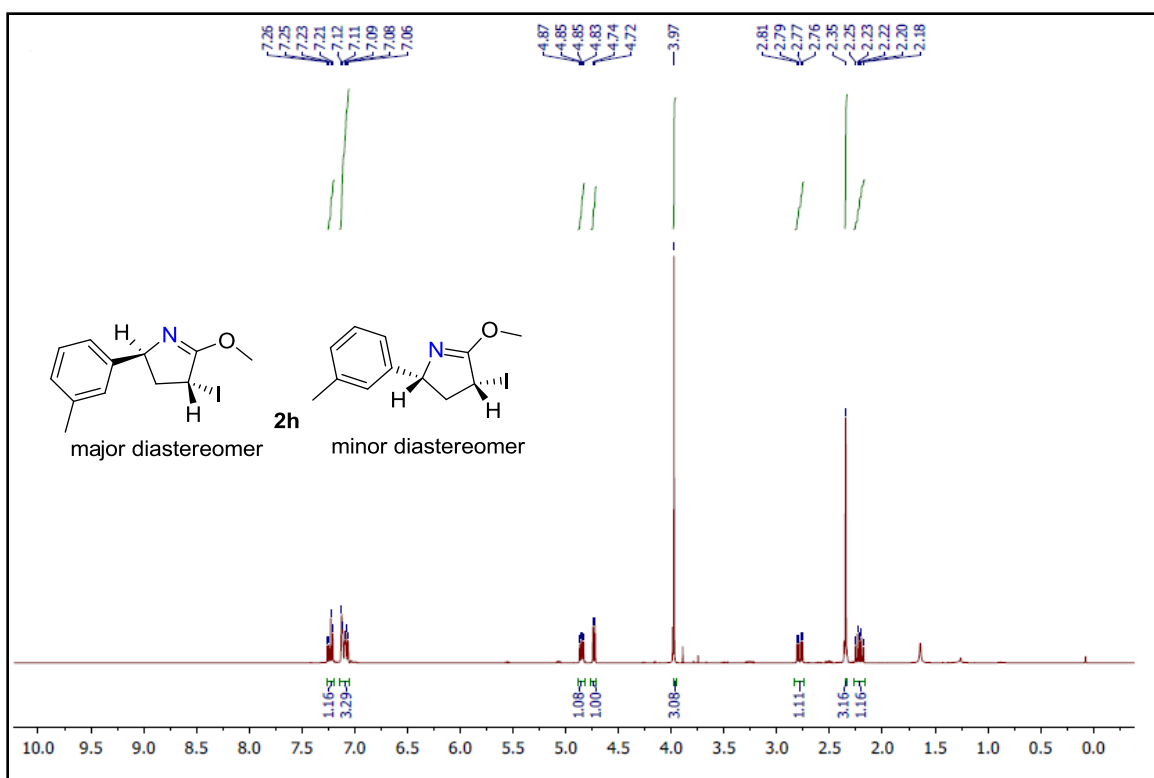
HSQC spectra of **2g**



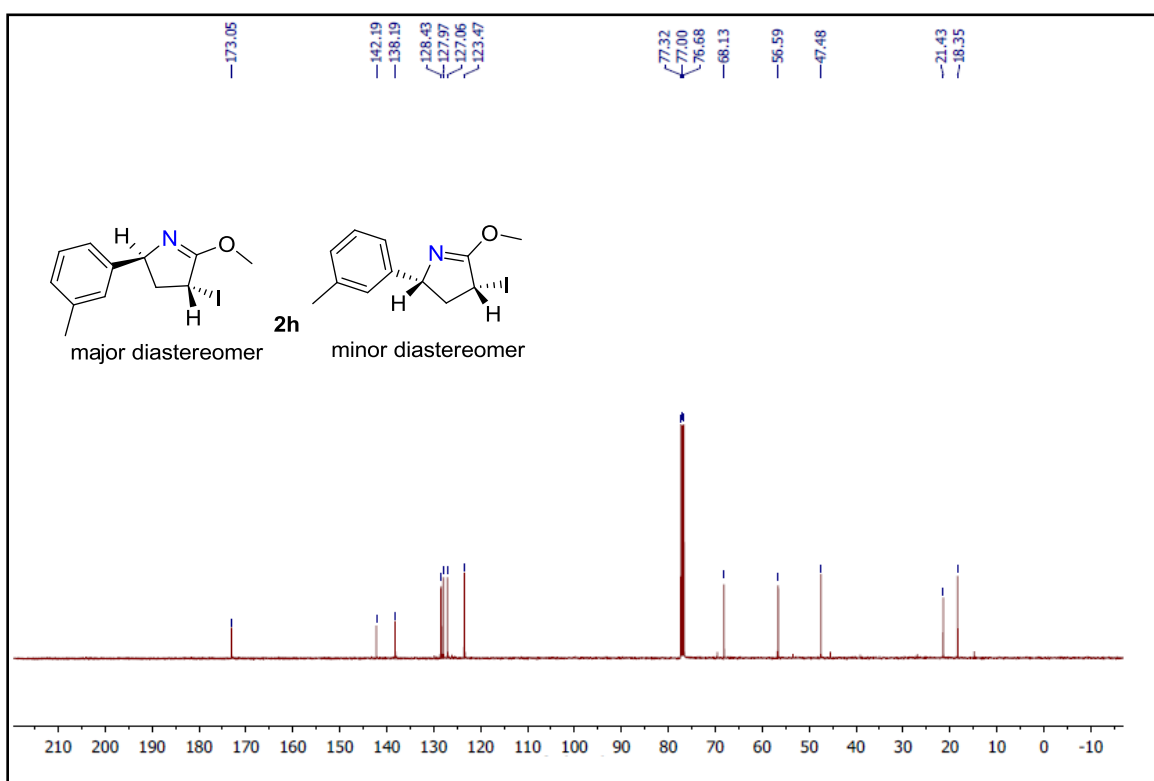
NOESY spectra of **2g**



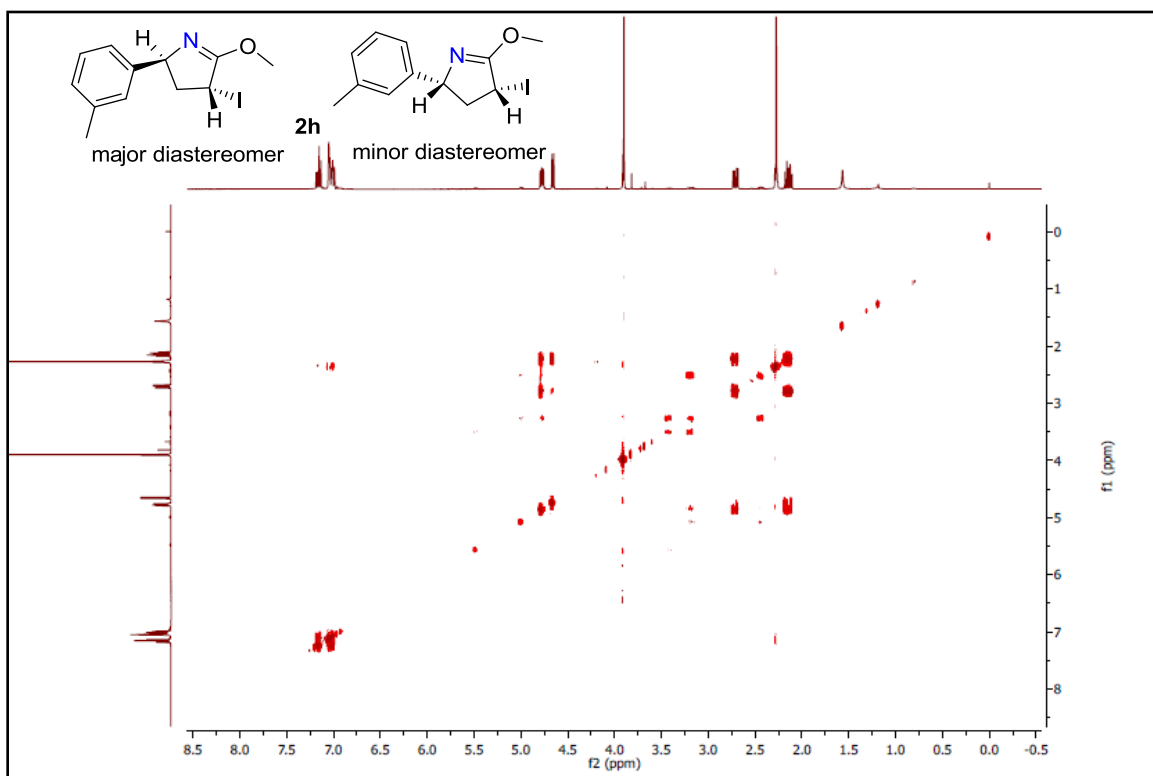
NOESY spectra of **2g**



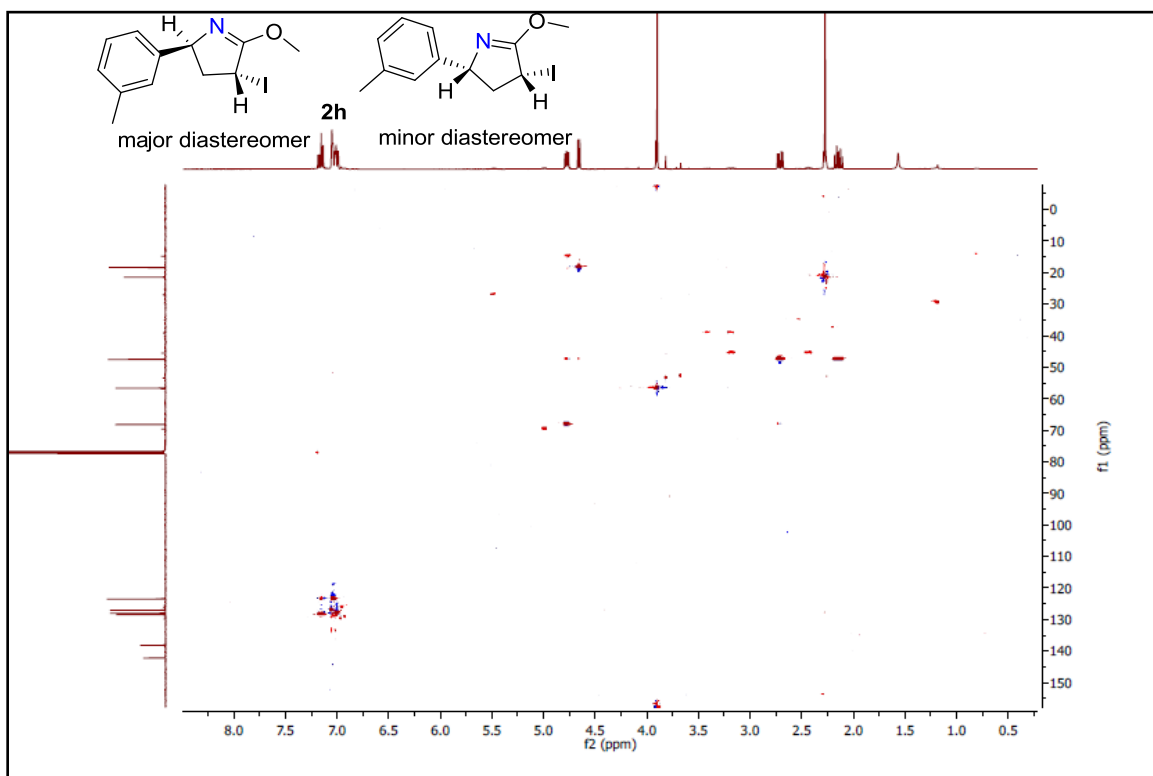
<sup>1</sup>H spectra of 2h



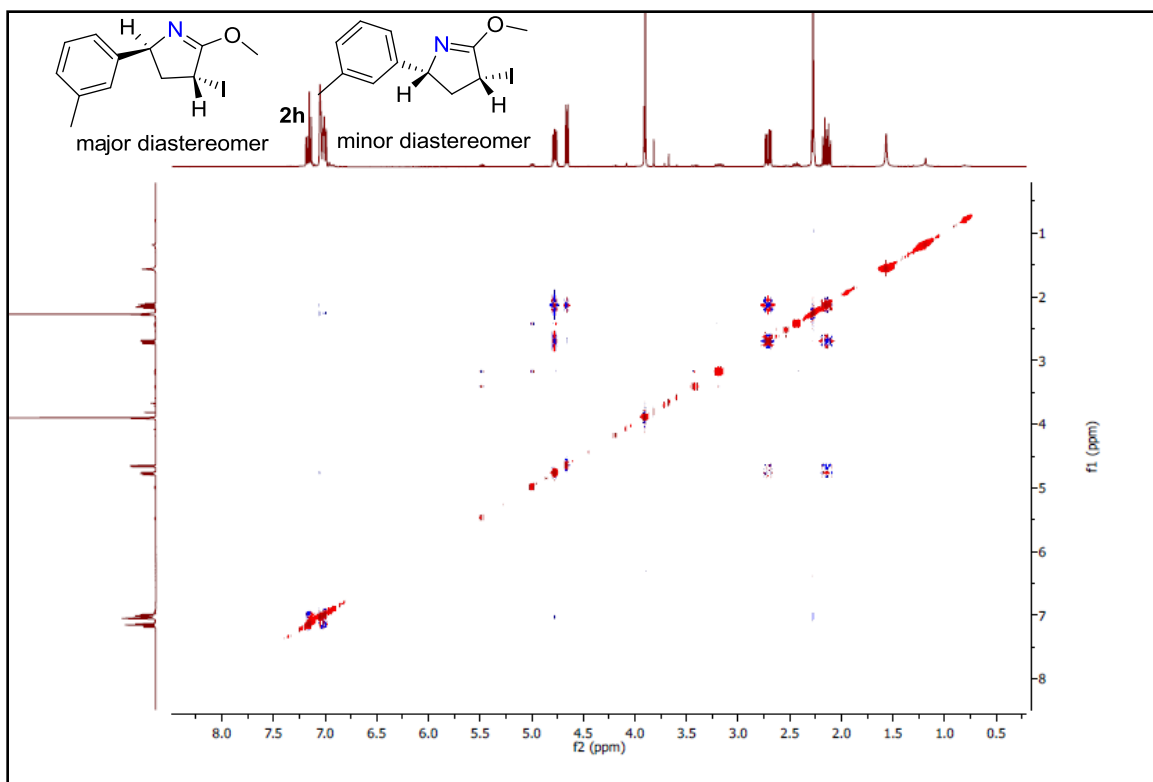
<sup>13</sup>C{<sup>1</sup>H} spectra of 2h



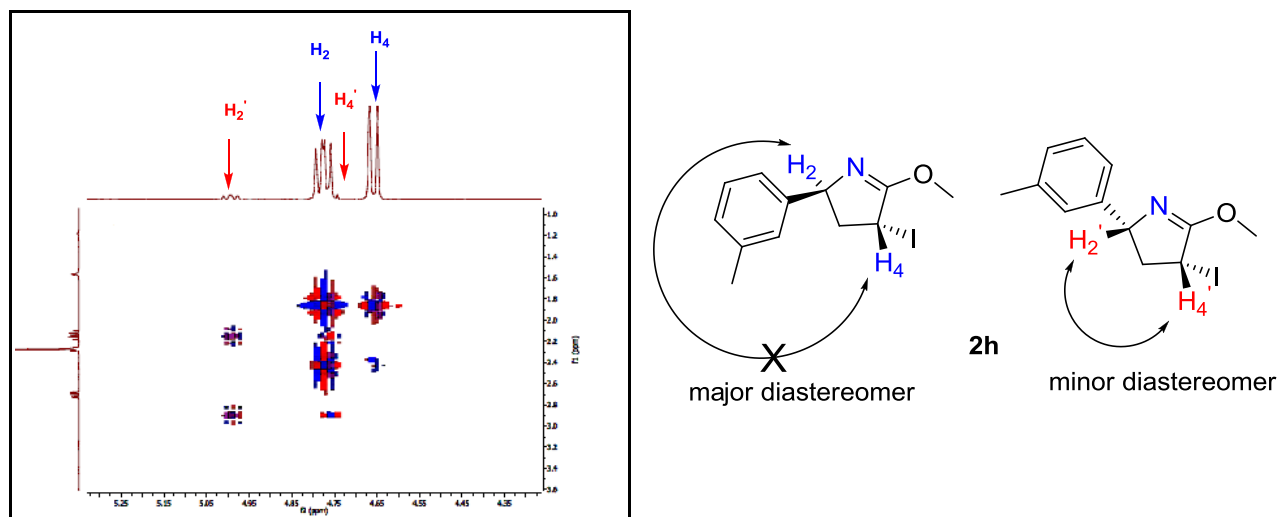
COSY spectra of **2h**



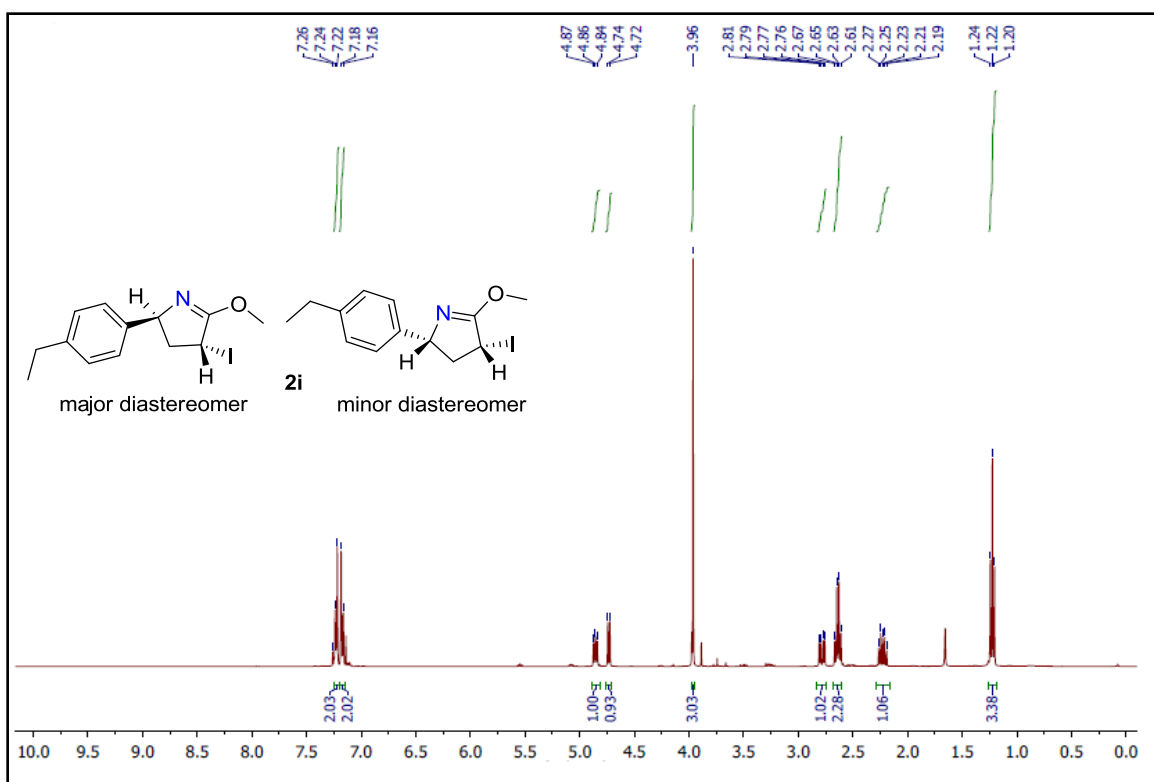
HSQC spectra of **2h**



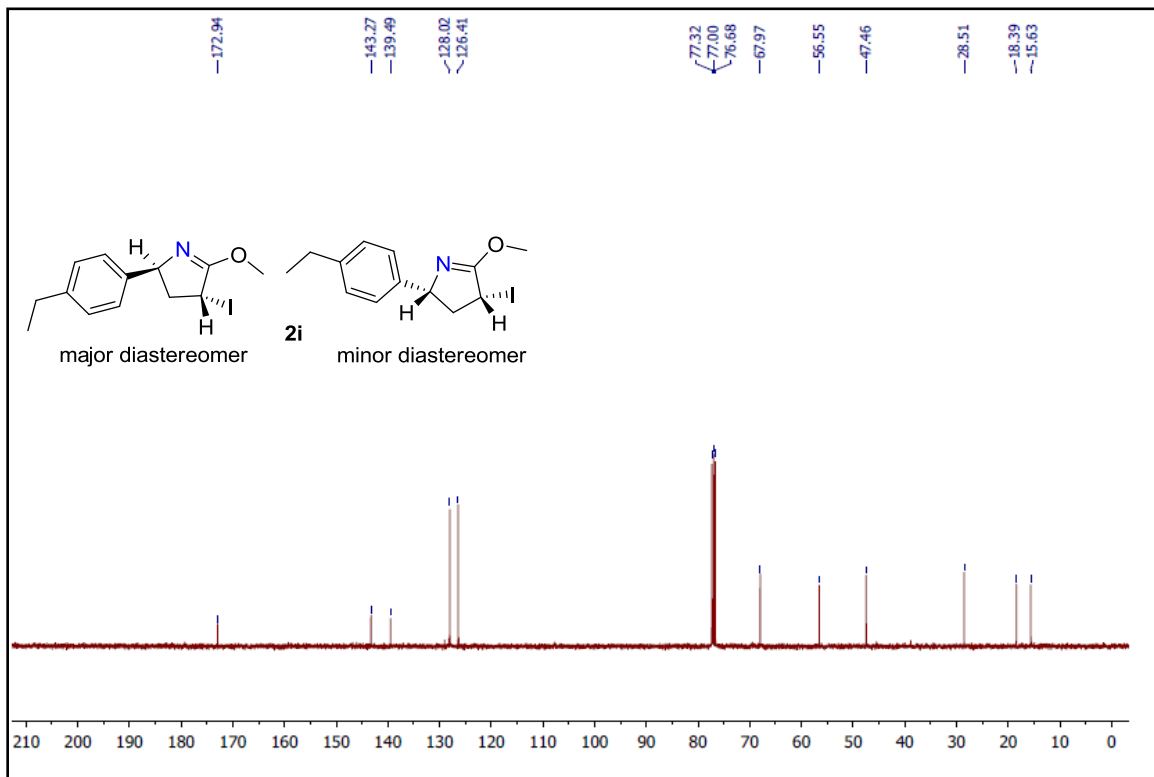
NOESY spectra of **2h**



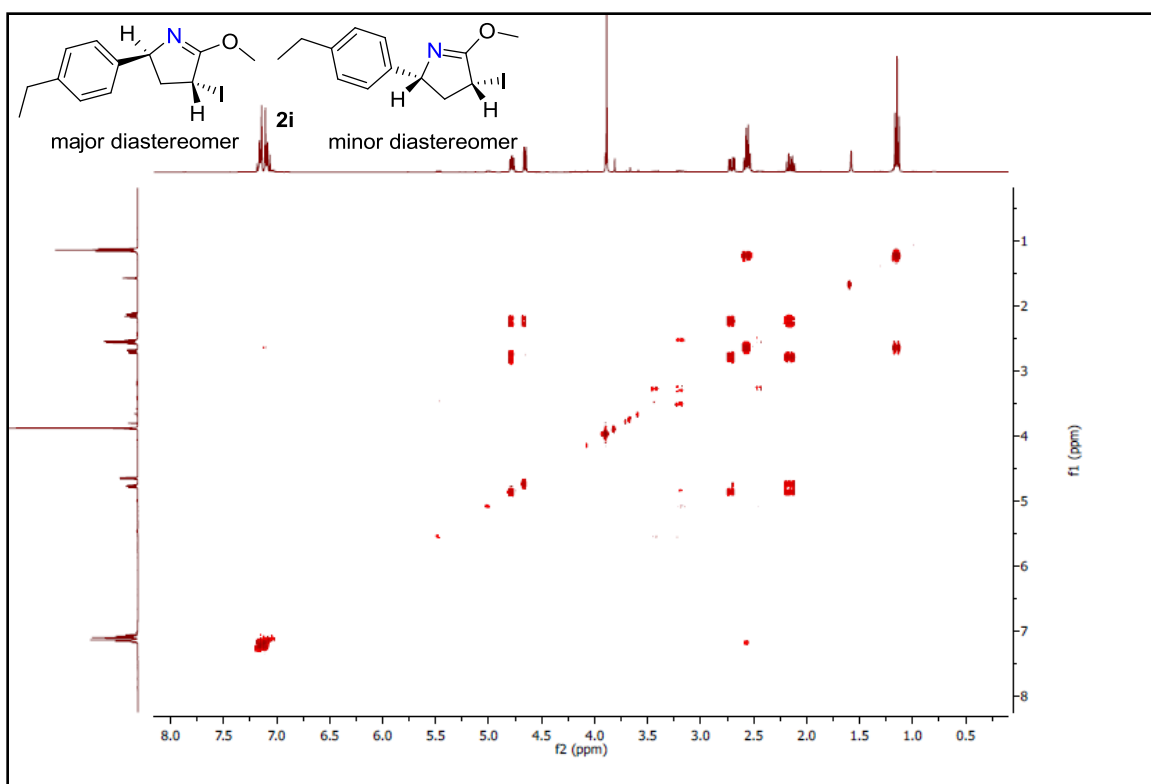
NOESY spectra of **2h**



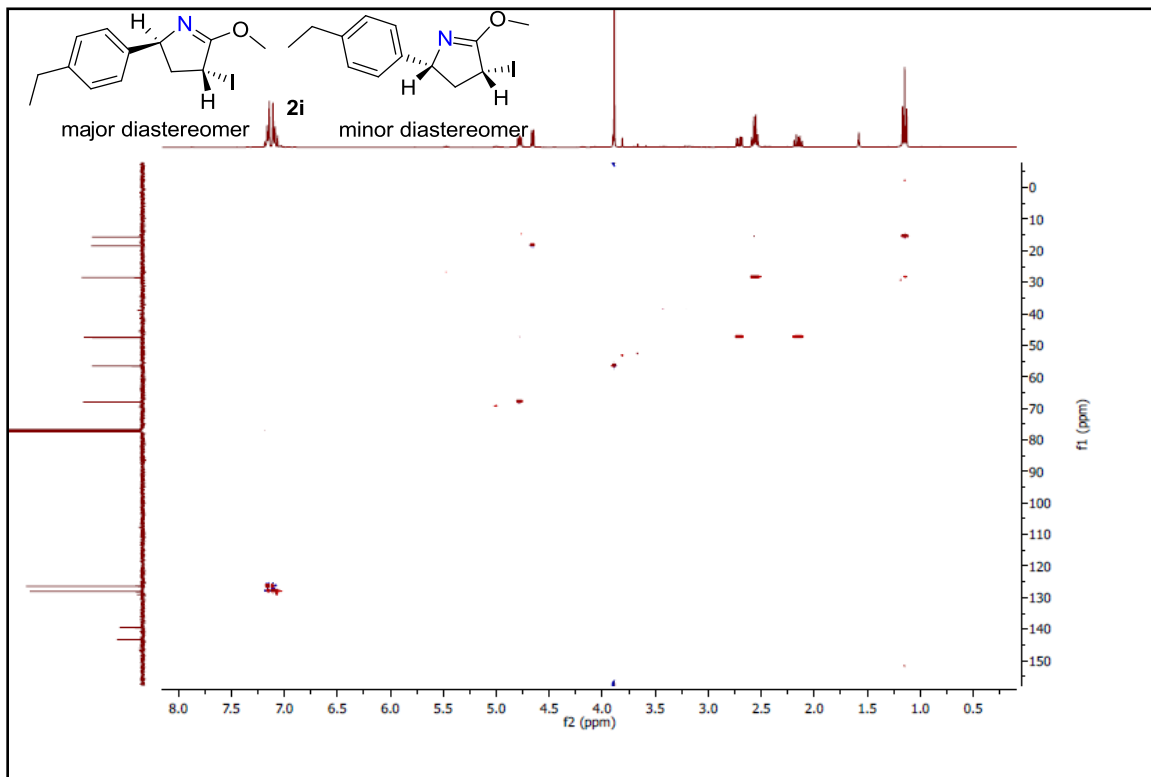
<sup>1</sup>H spectra of 2i



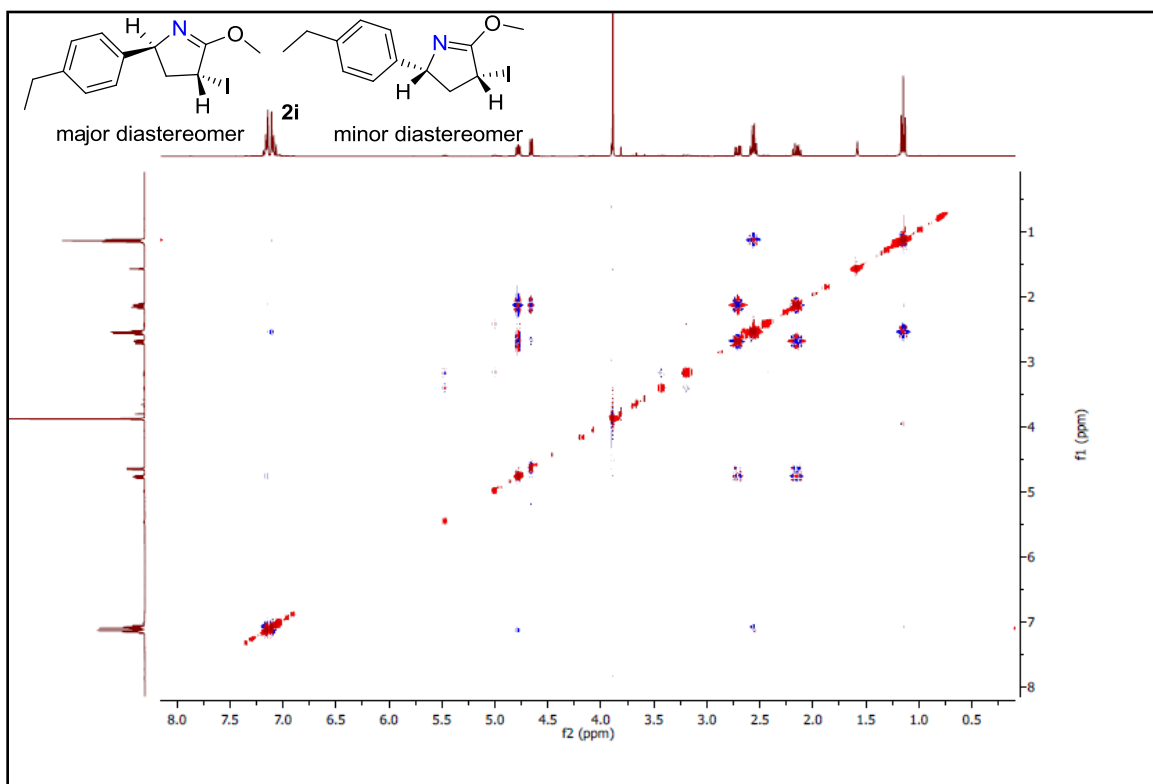
<sup>13</sup>C{<sup>1</sup>H} spectra of 2i



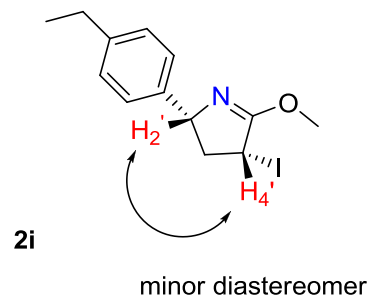
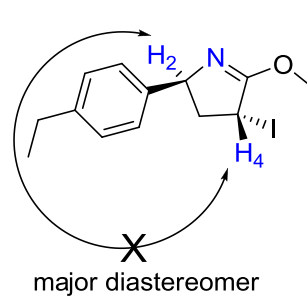
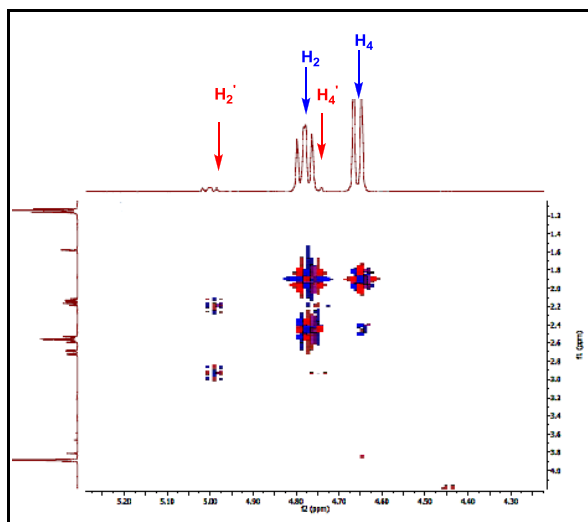
COSY spectra of **2i**



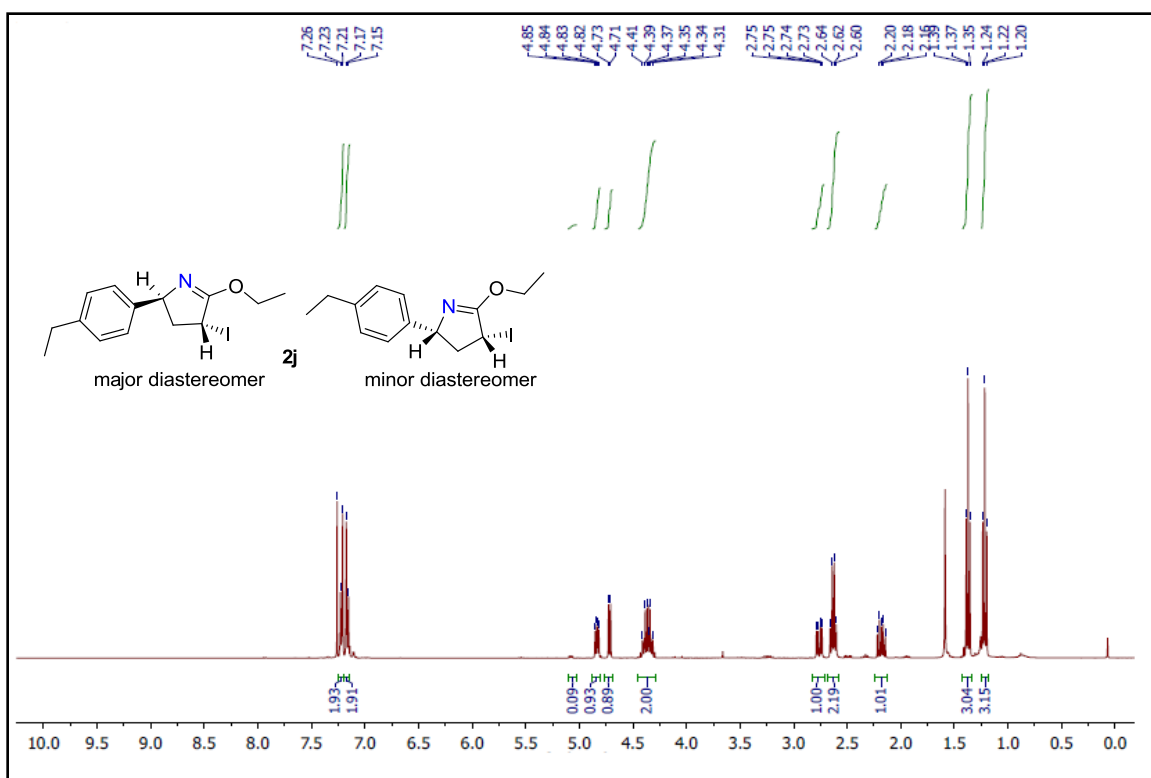
HSQC spectra of **2i**



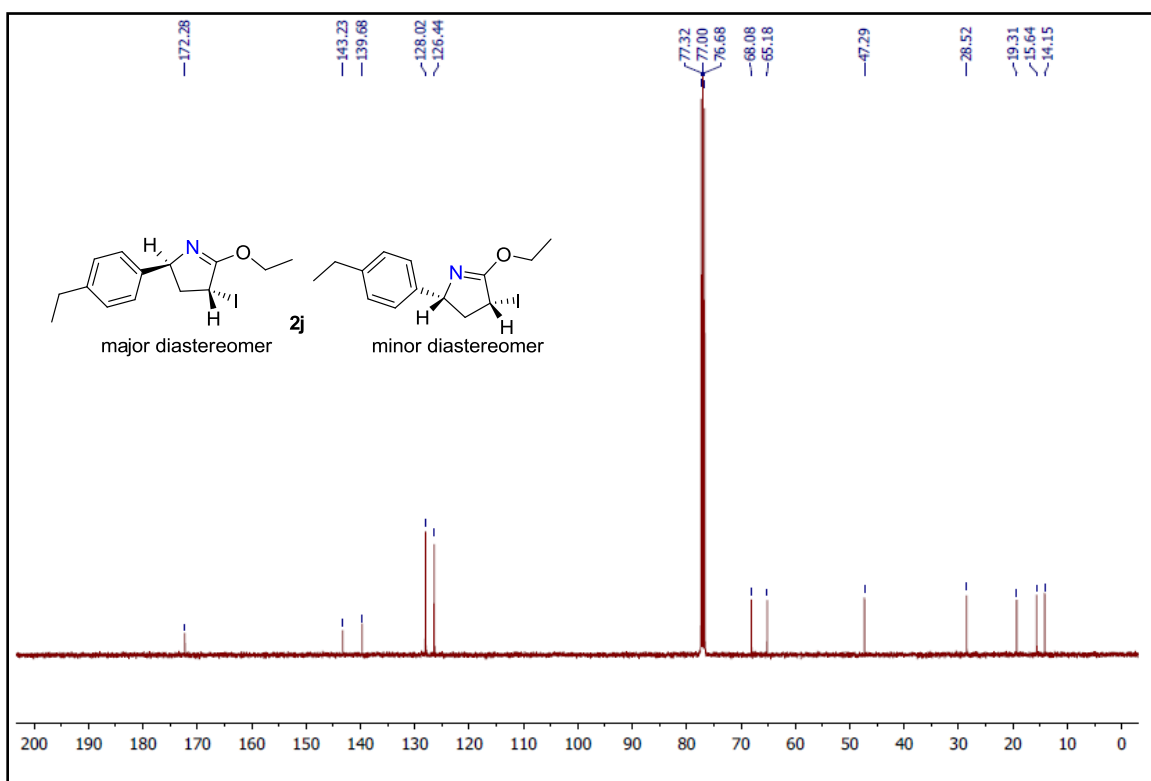
NOESY spectra of **2i**



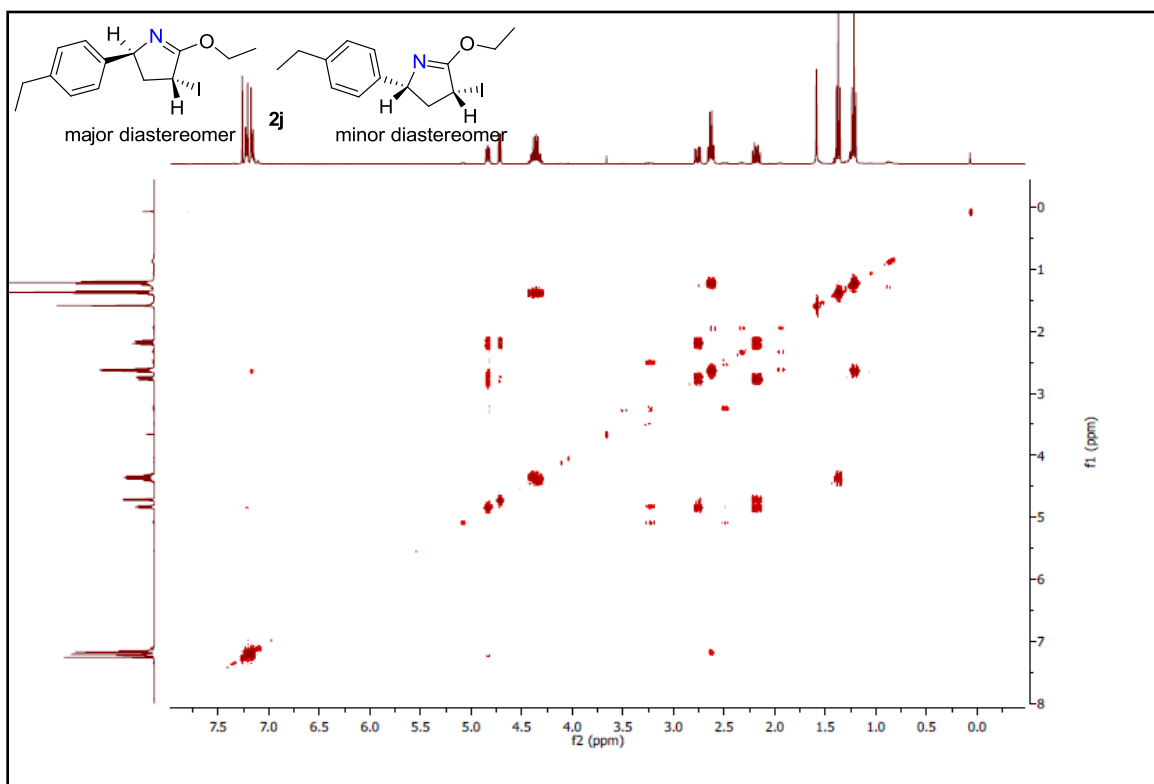
NOESY spectra of **2i**



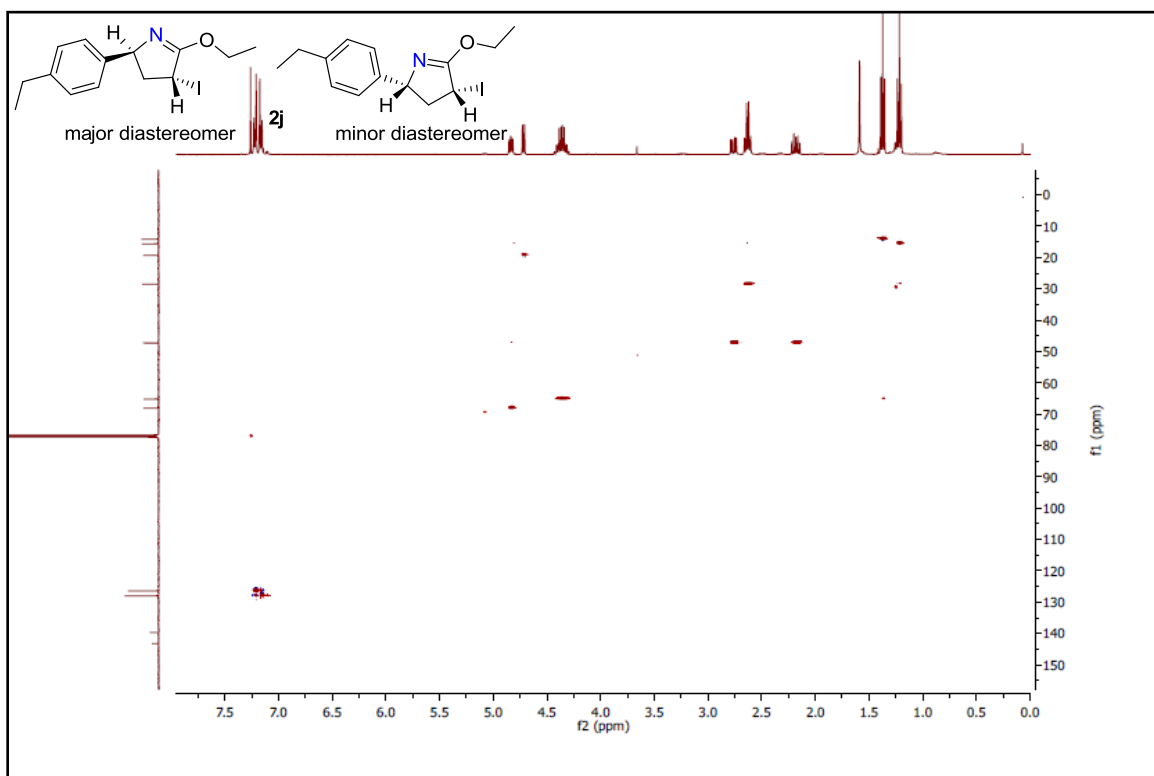
<sup>1</sup>H spectra of 2j



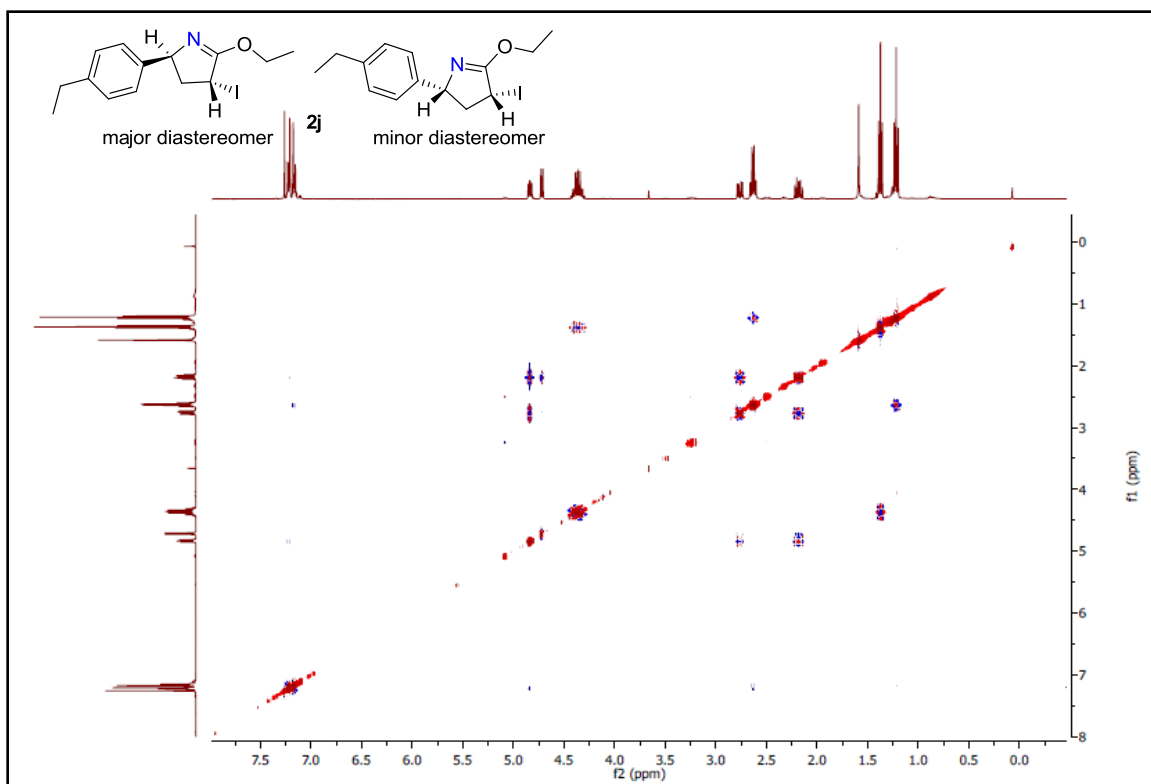
<sup>13</sup>C{<sup>1</sup>H} spectra of 2j



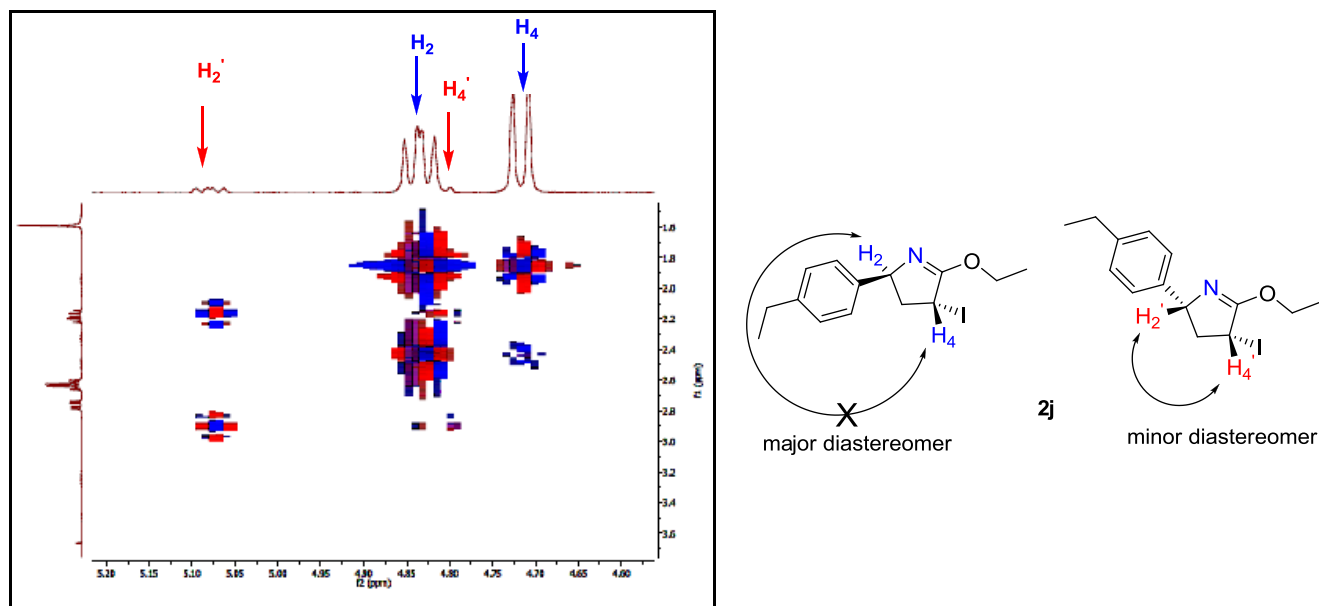
COSY spectra of **2j**



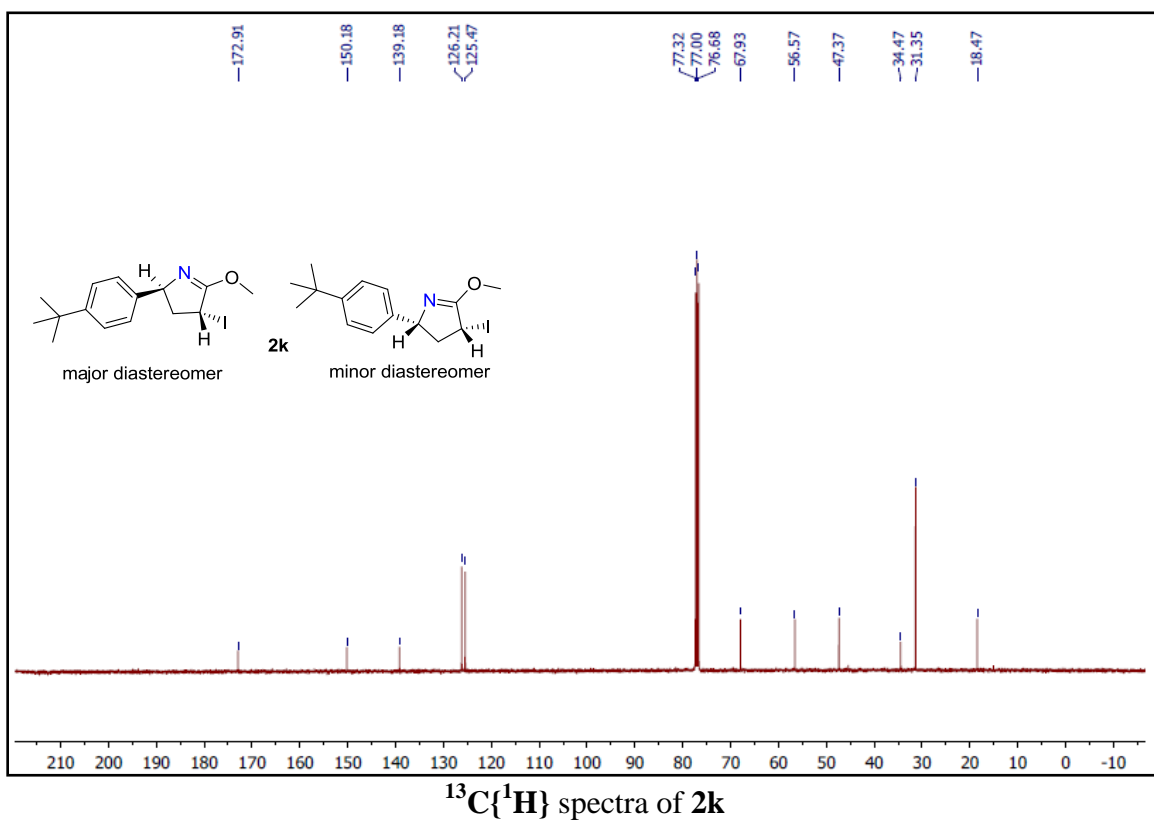
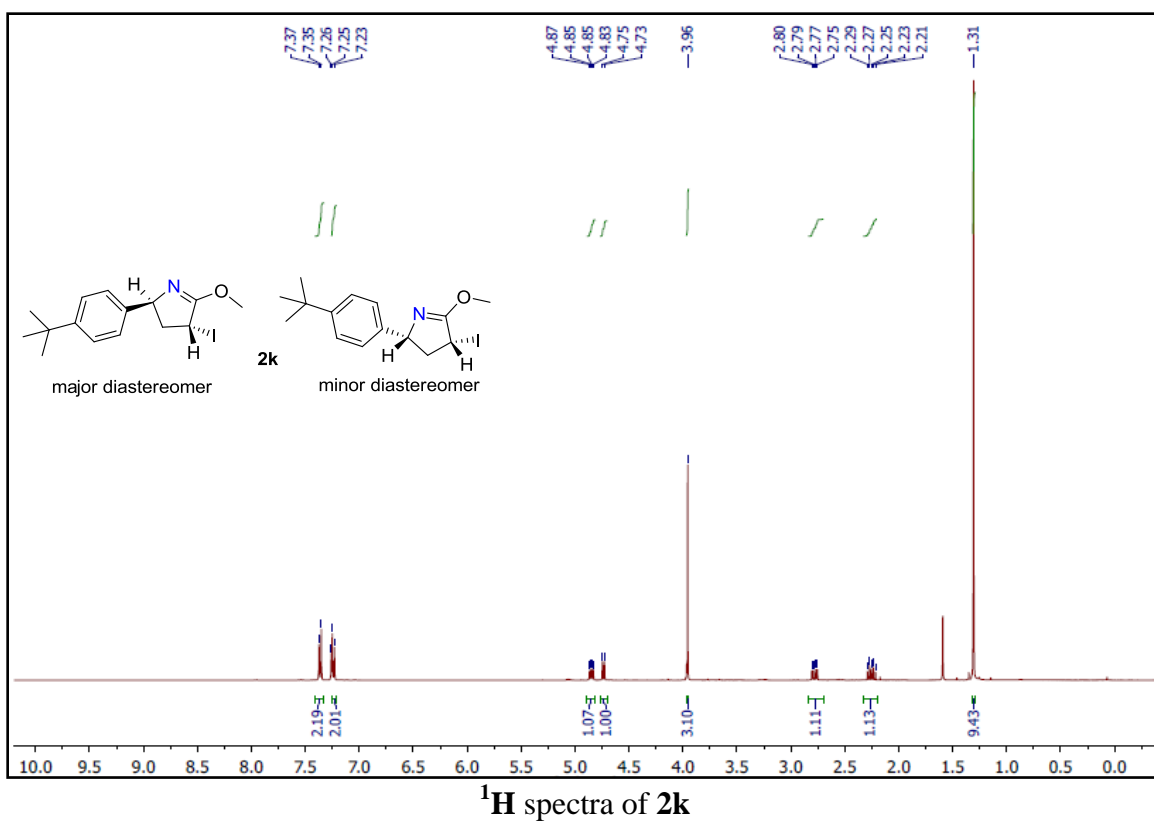
HSQC spectra of **2j**

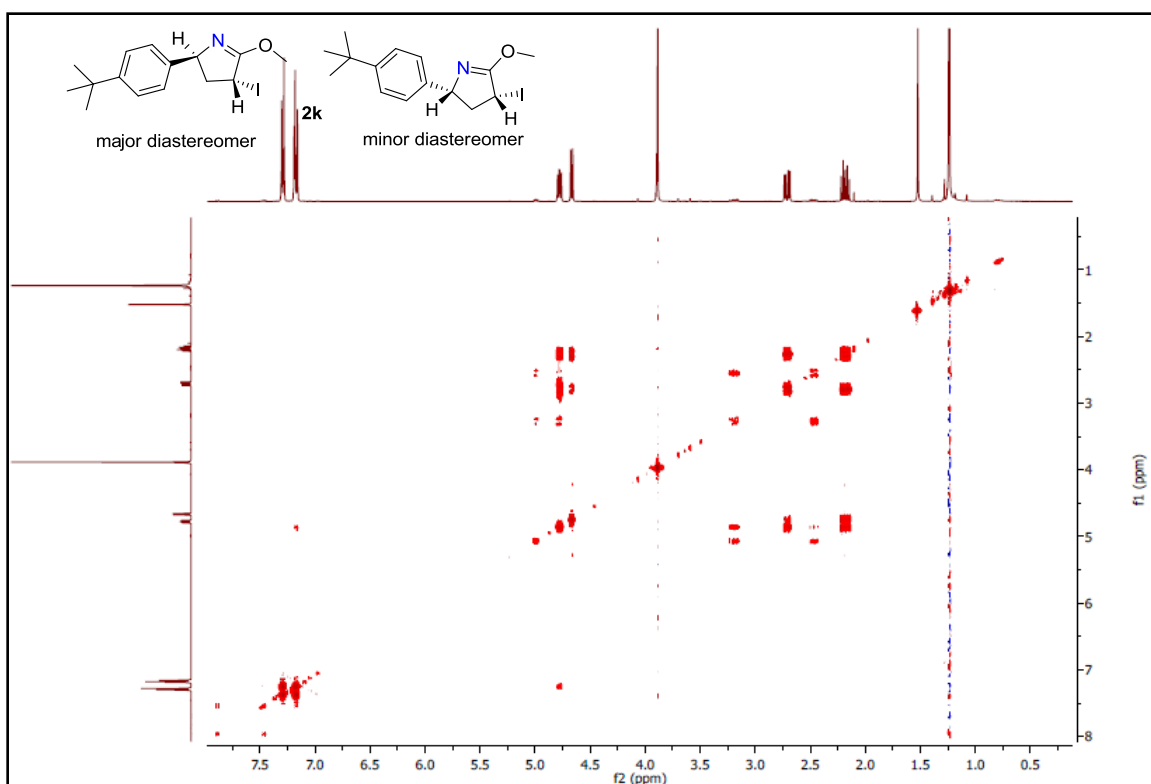


NOESY spectra of **2j**

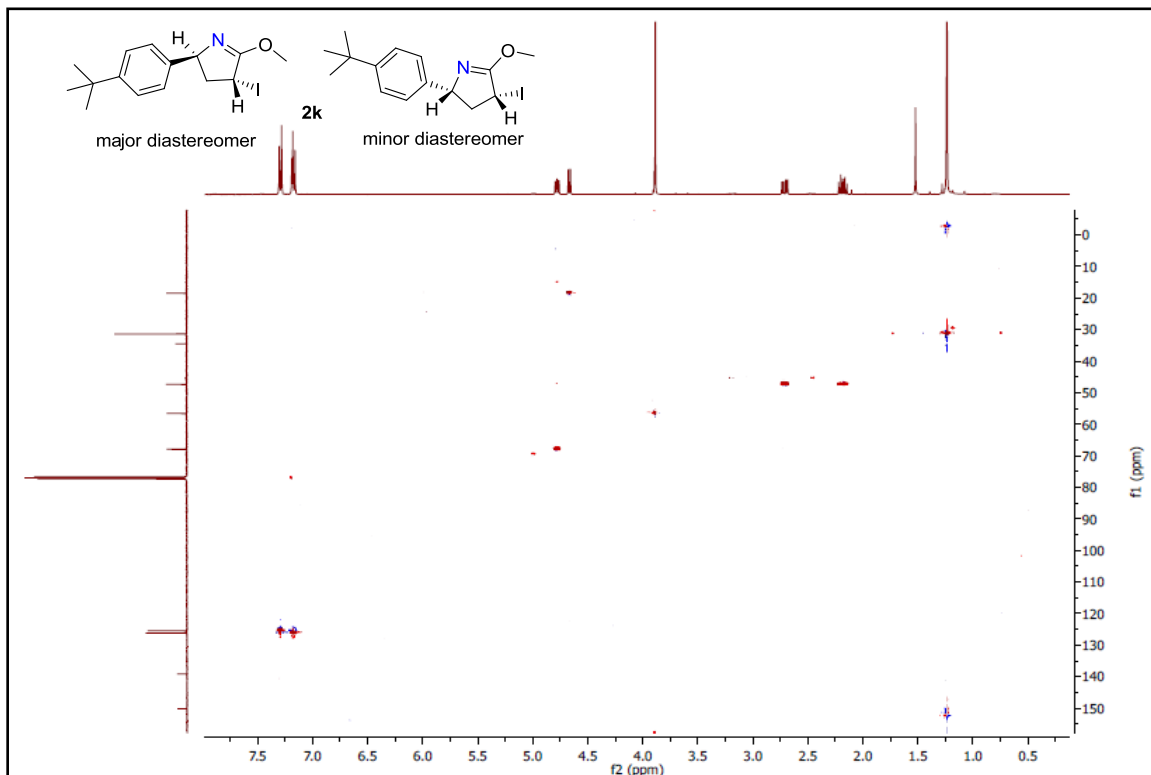


NOESY spectra of **2j**

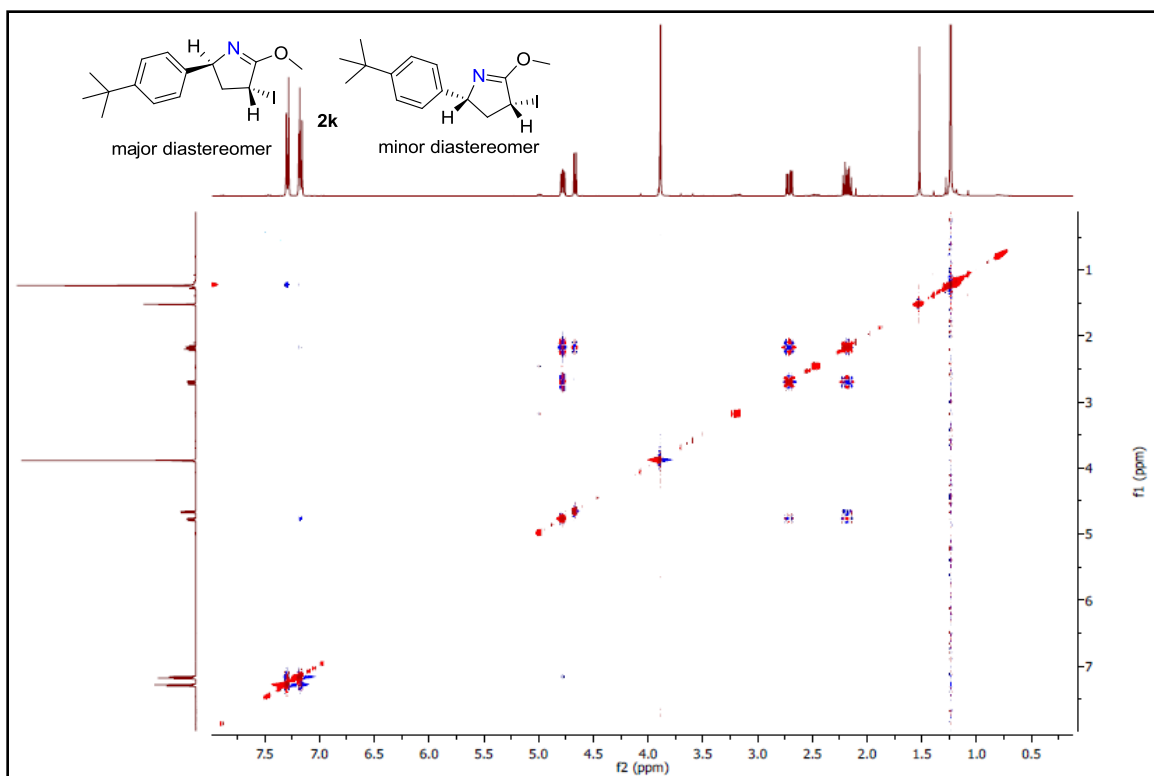




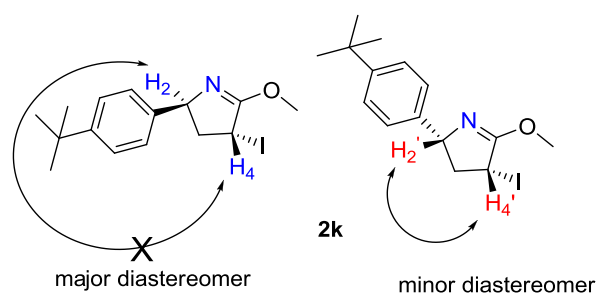
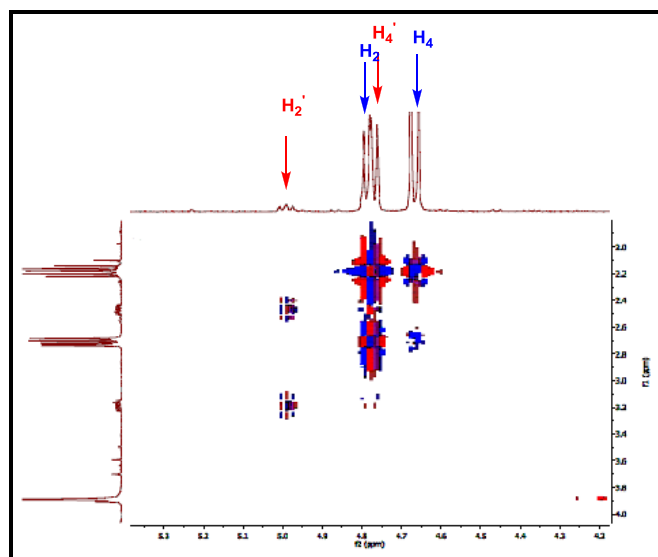
COSY spectra of **2k**



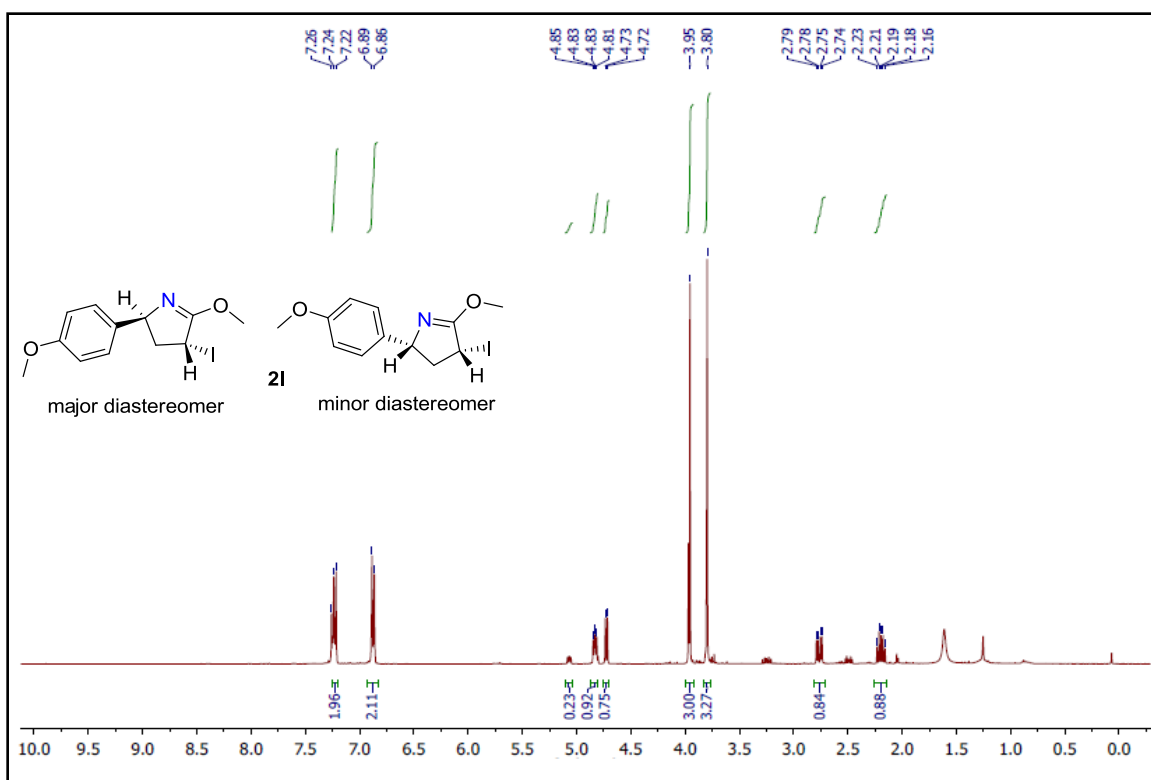
HSQC spectra of **2k**



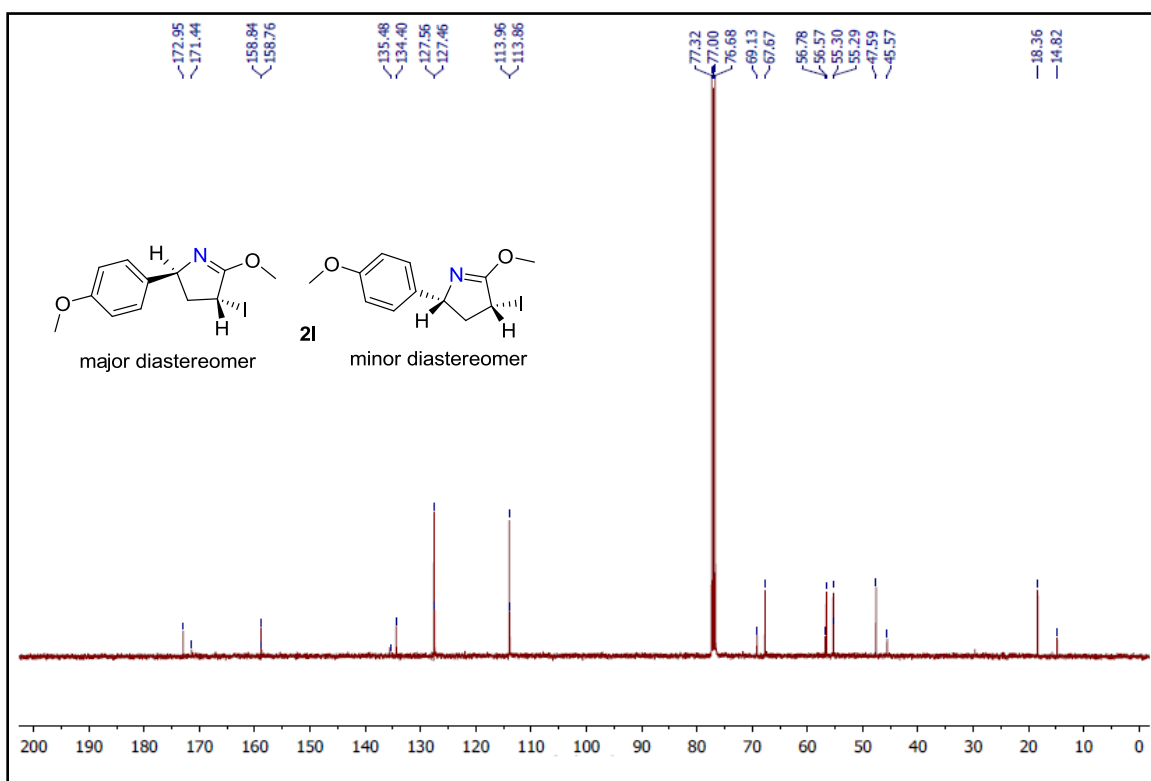
NOESY spectra of **2k**



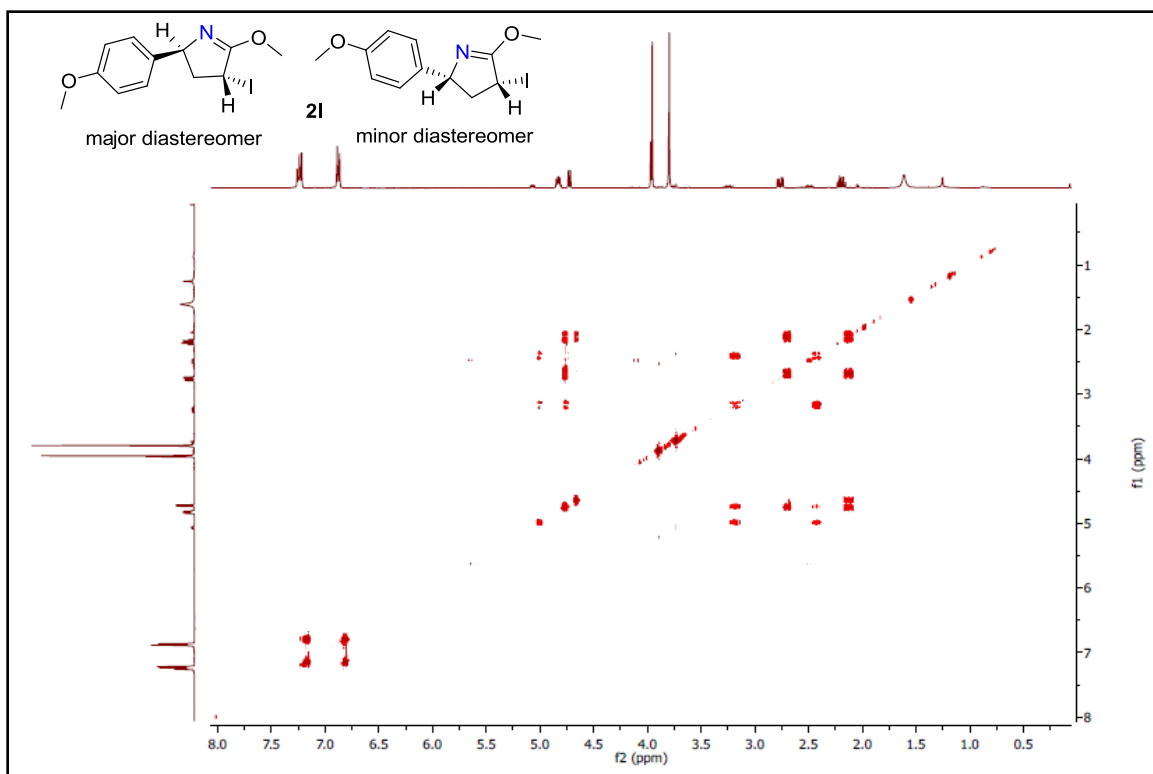
NOESY spectra of **2k**



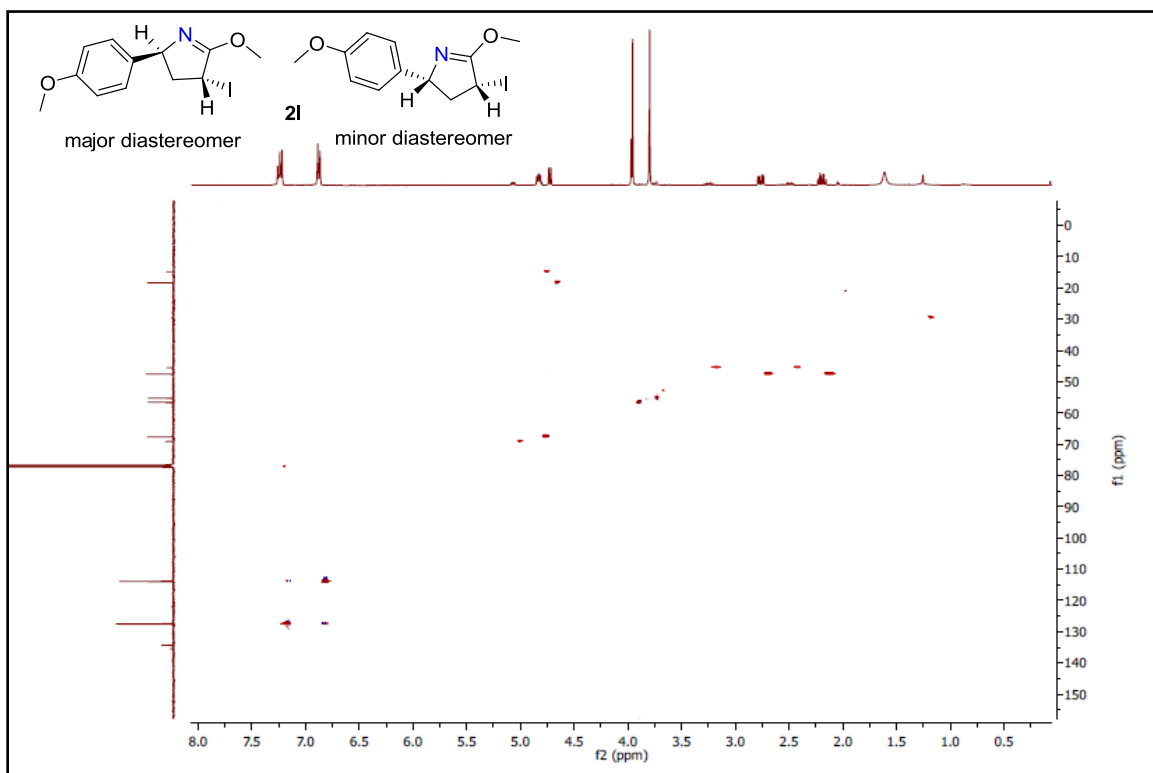
<sup>1</sup>H spectra of 2l



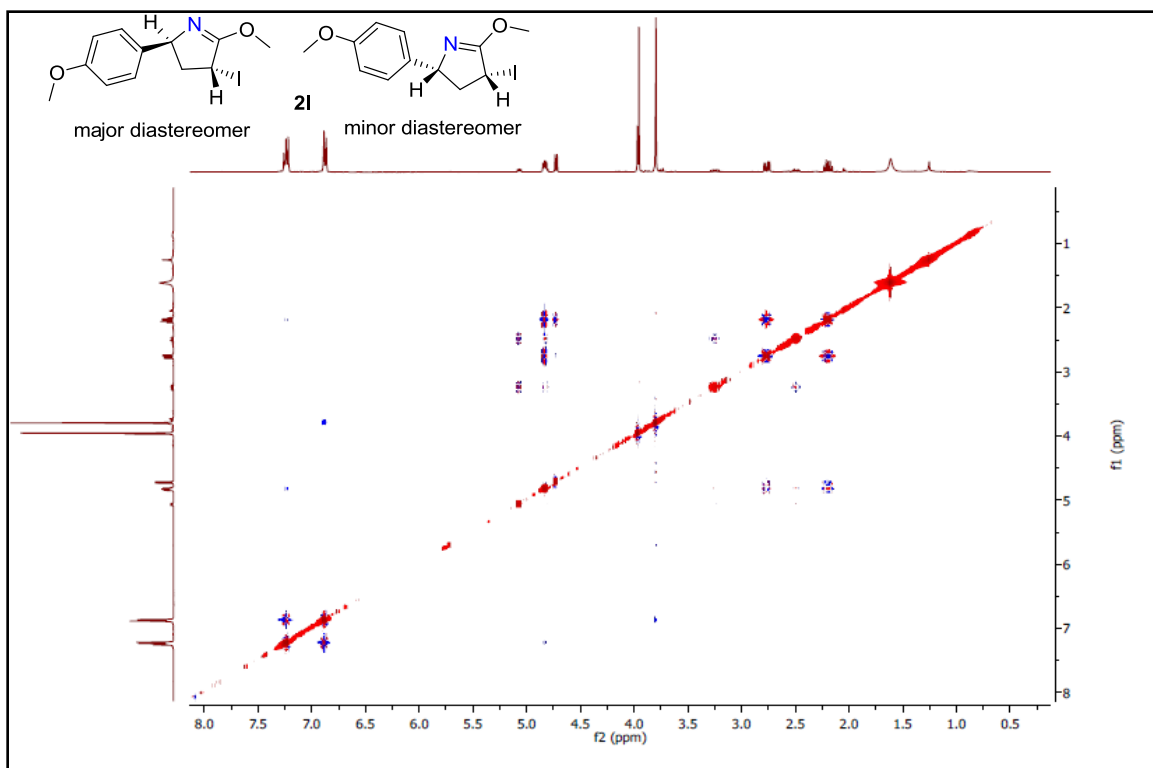
<sup>13</sup>C{<sup>1</sup>H} spectra of 2l



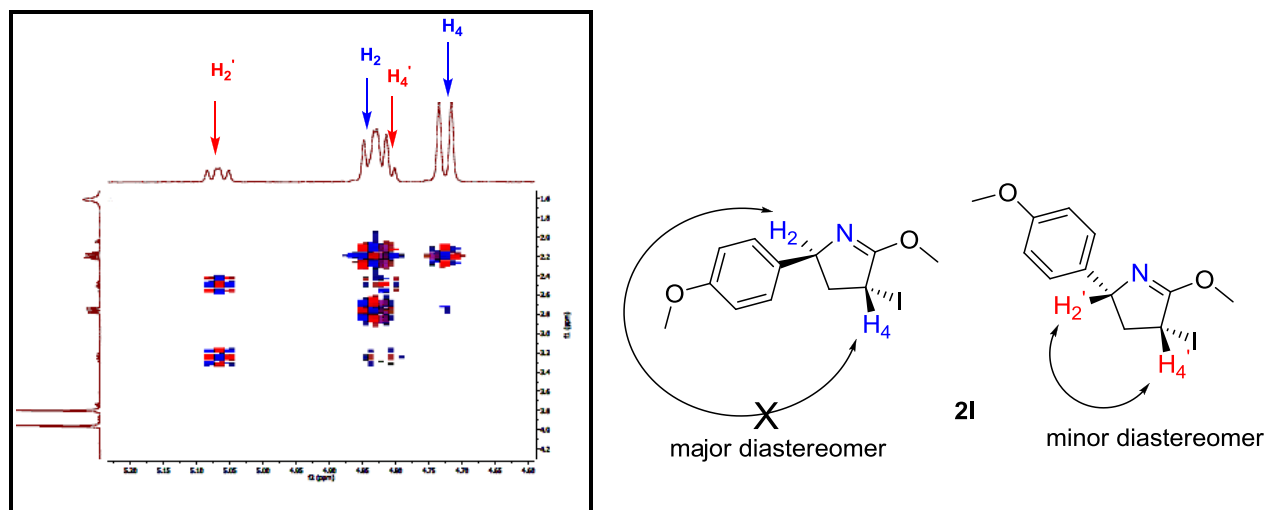
COSY spectra of **2l**



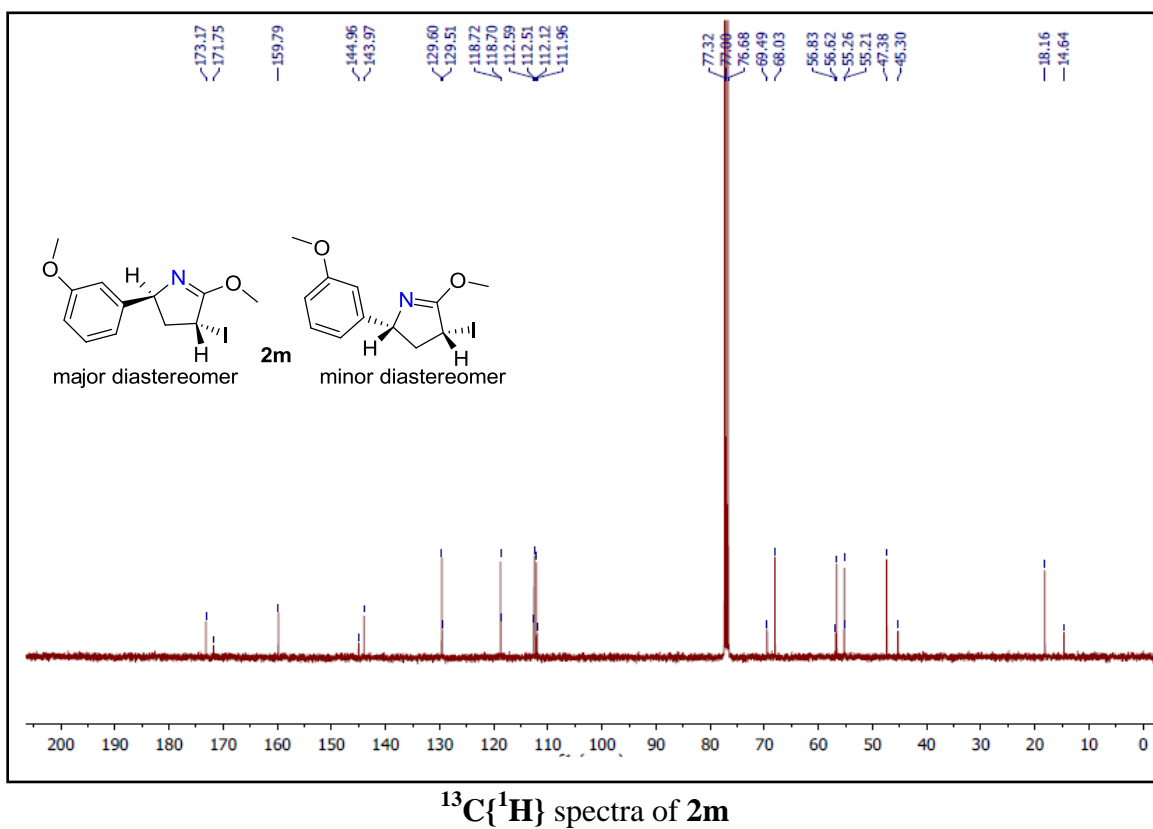
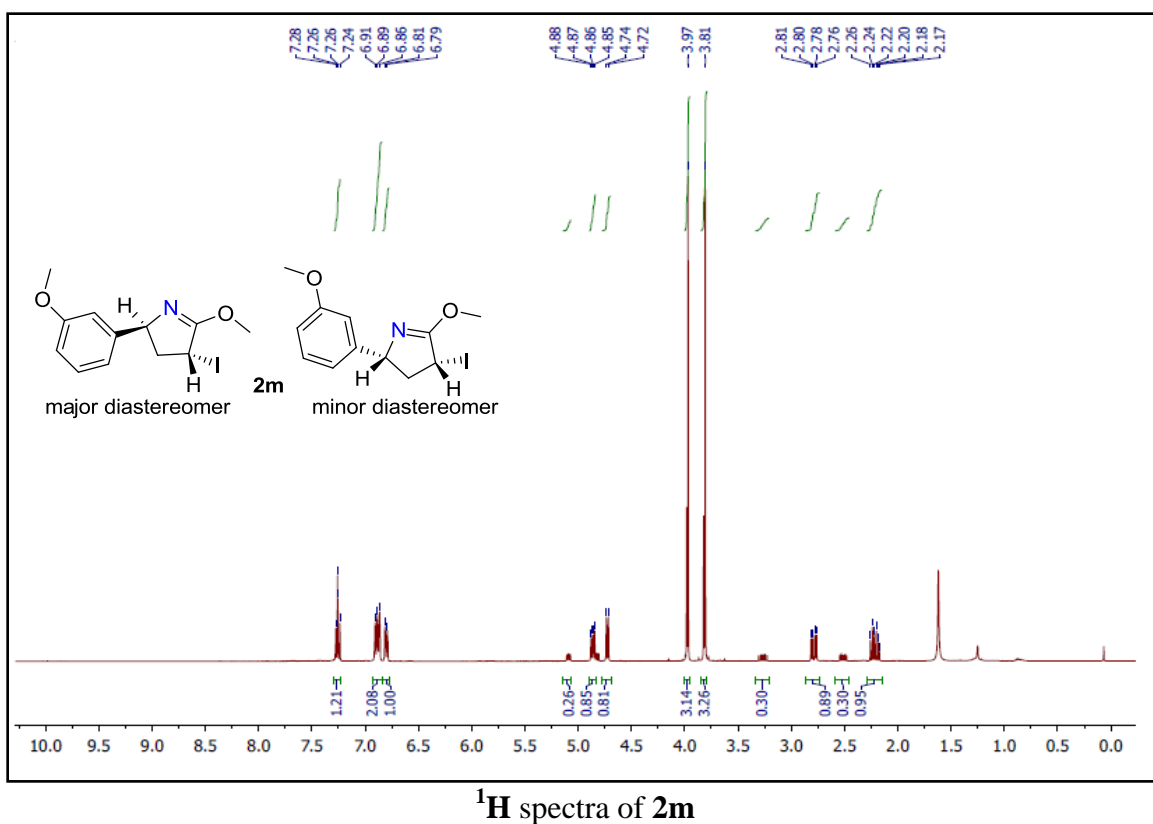
HSQC spectra of **2l**

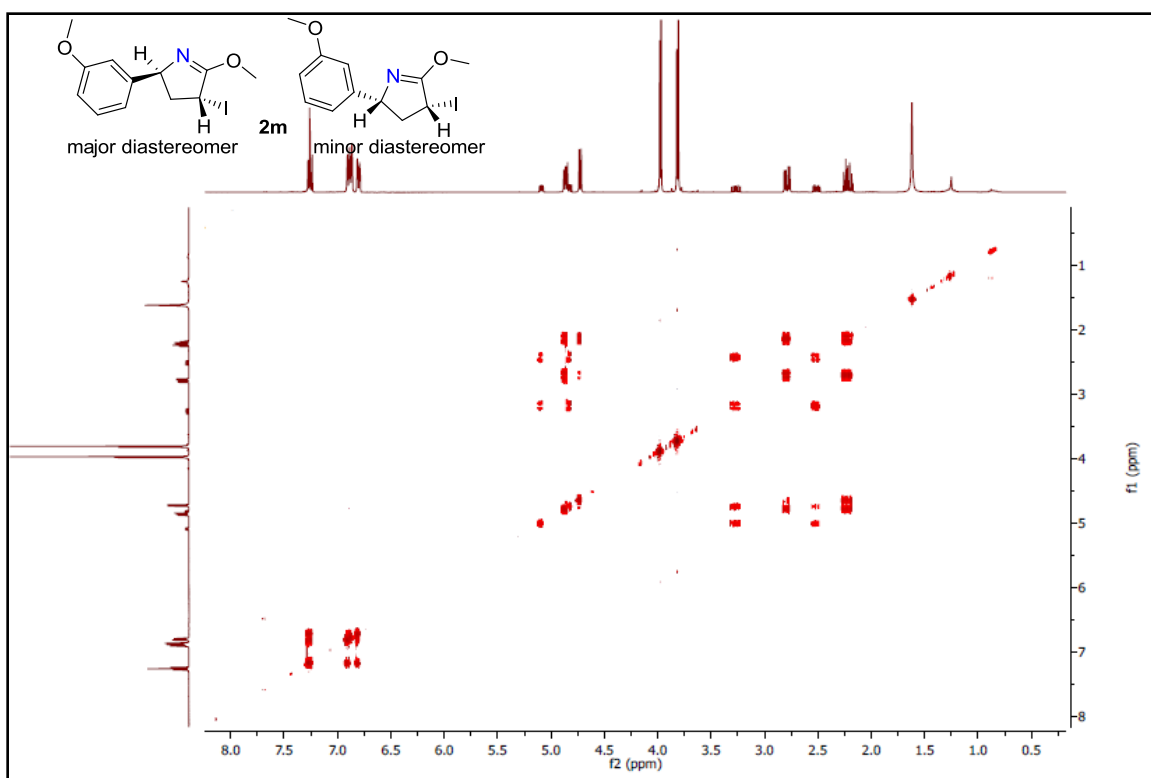


NOESY spectra of **2I**

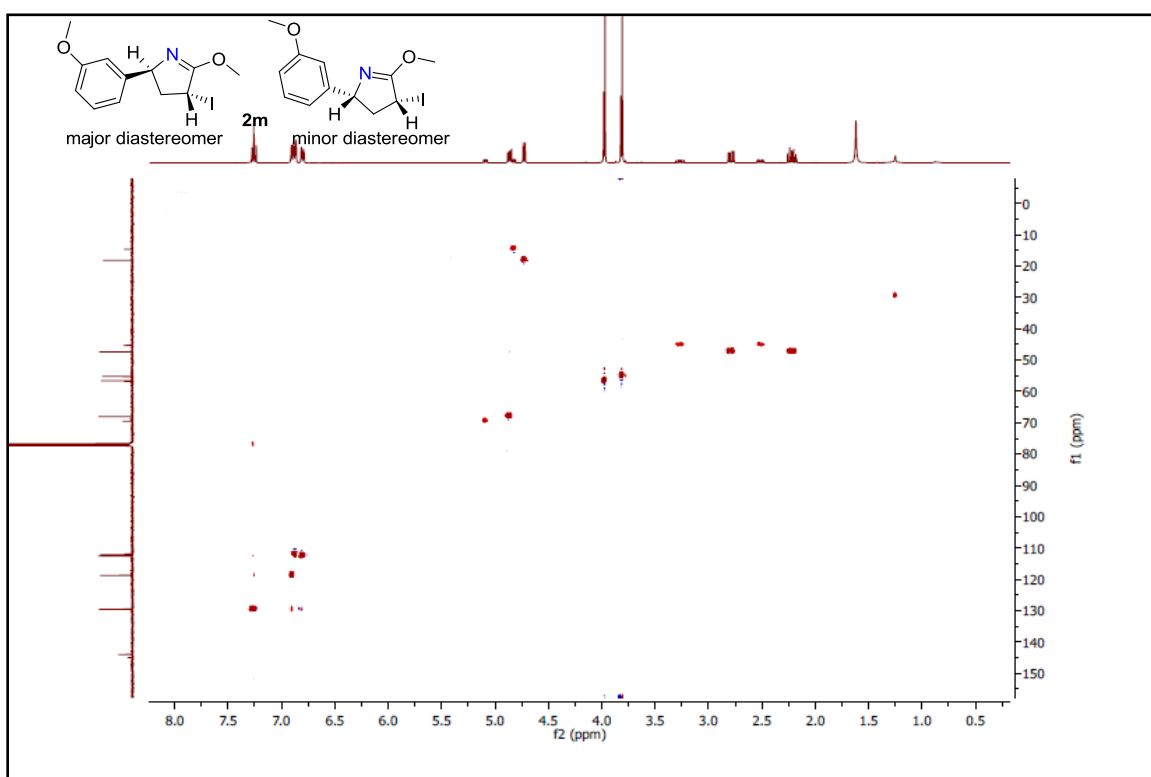


NOESY spectra of **2I**

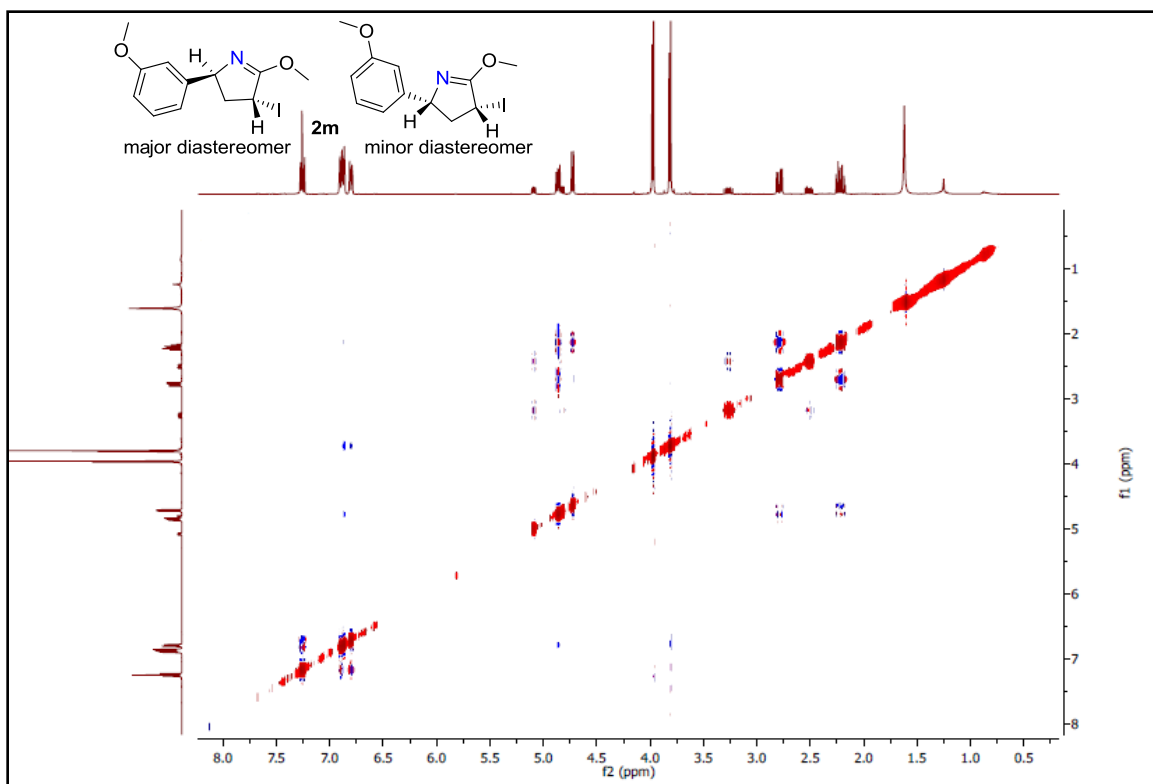




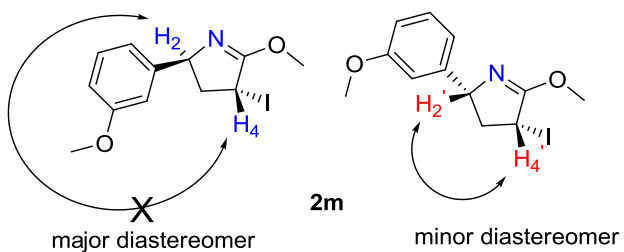
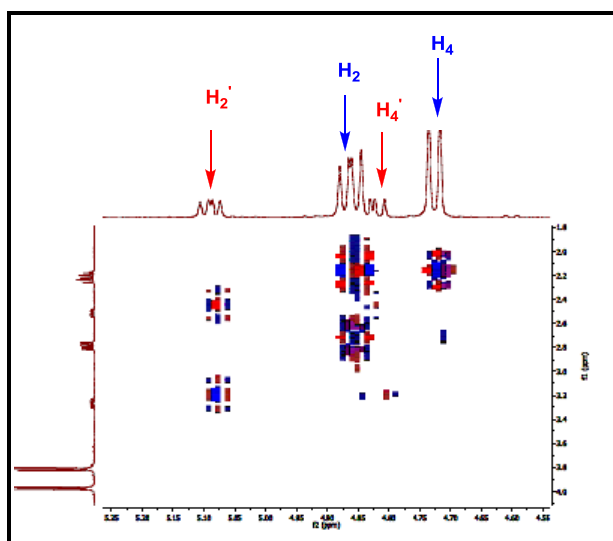
COSY spectra of **2m**



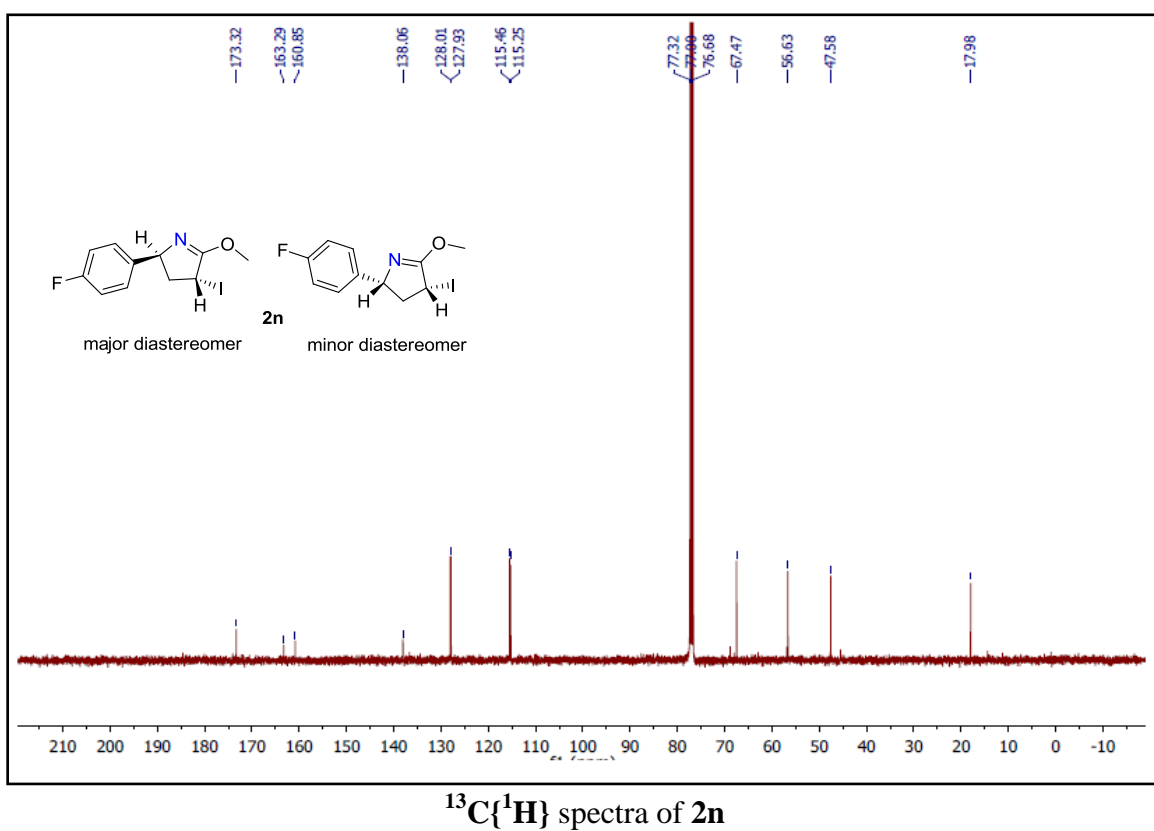
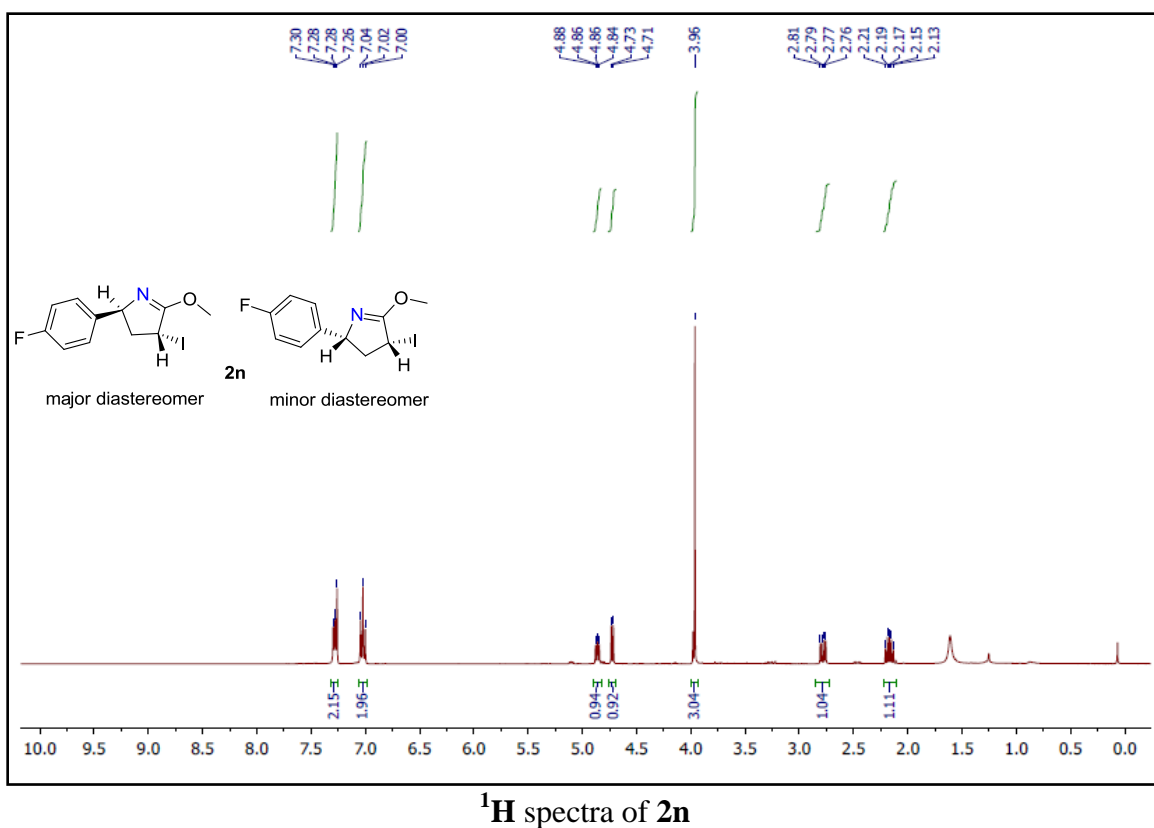
HSQC spectra of **2m**

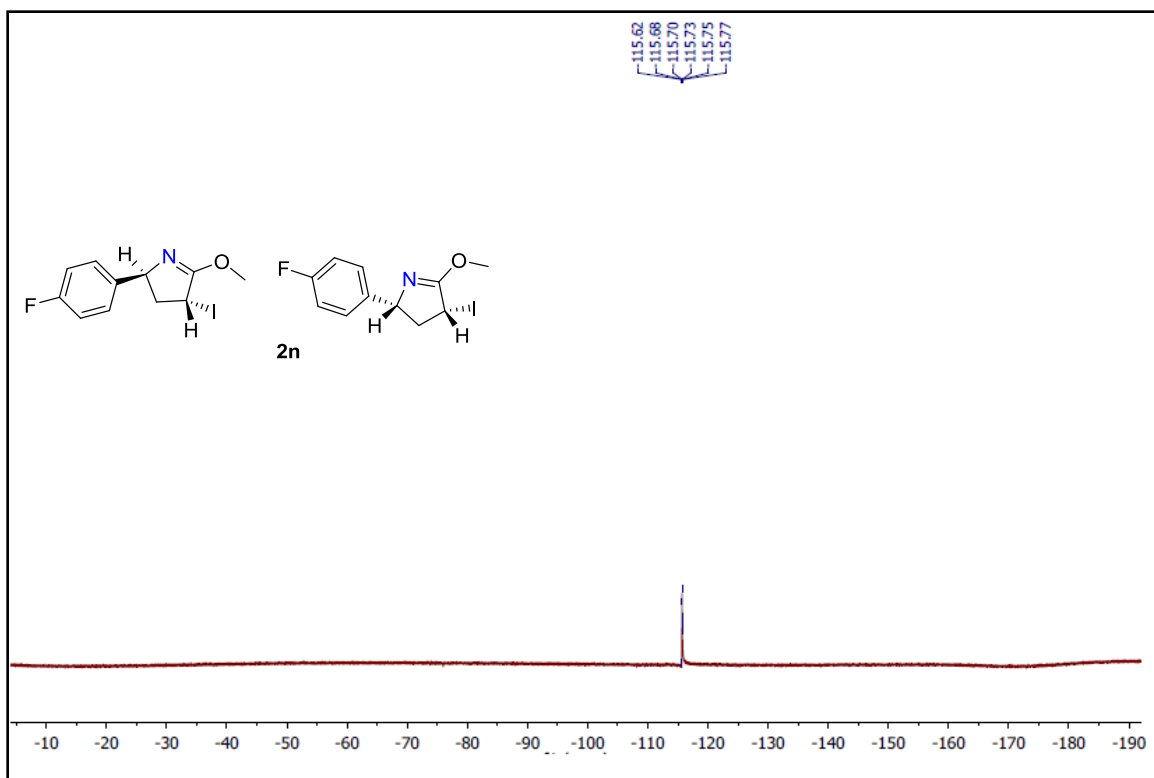


NOESY spectra of **2m**

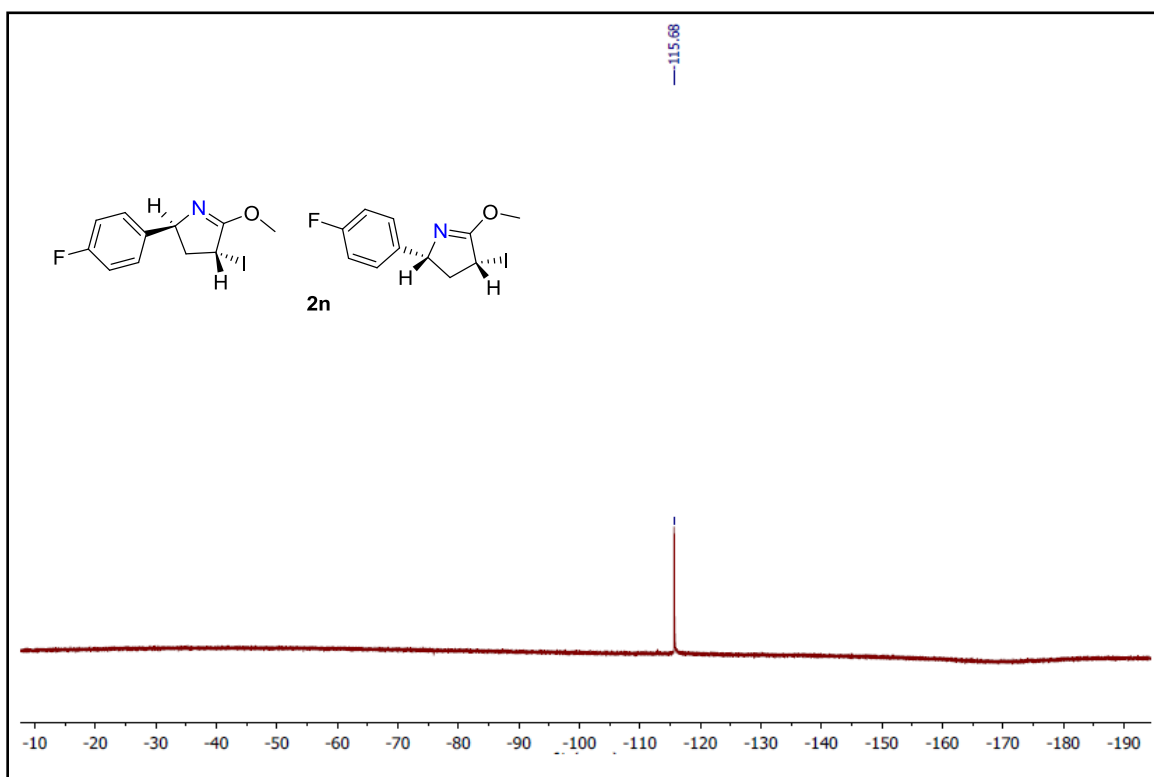


NOESY spectra of **2m**

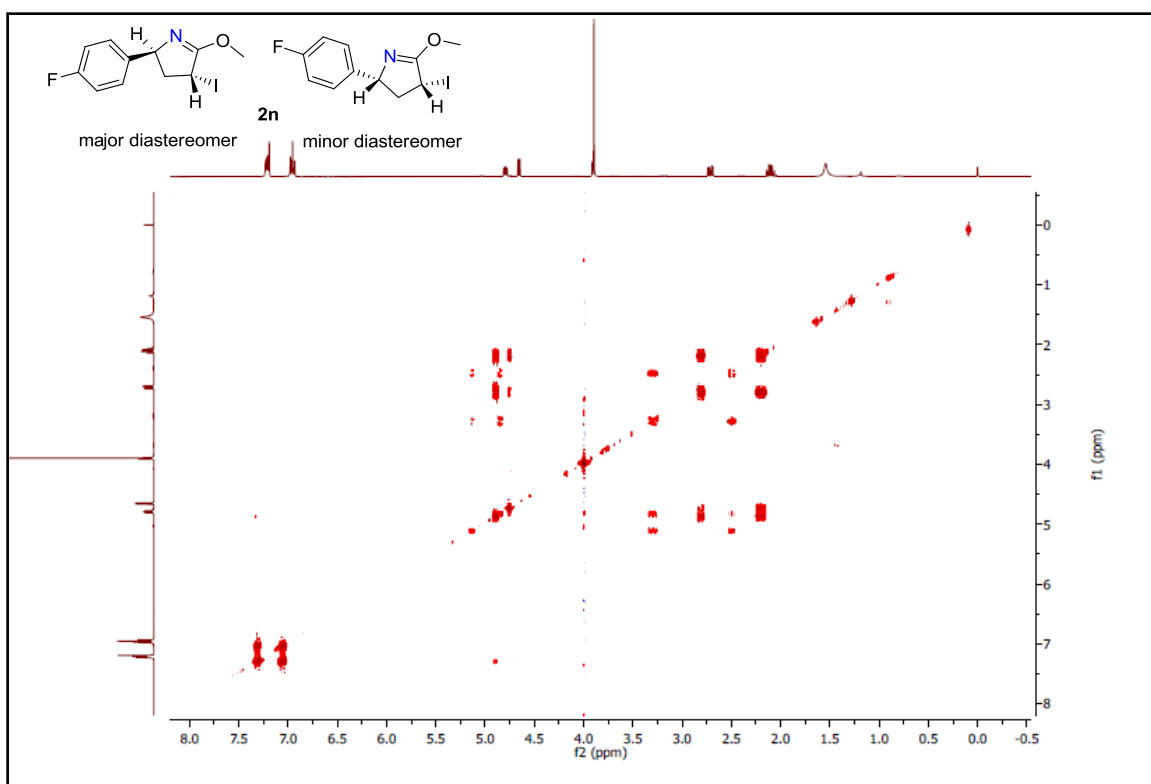




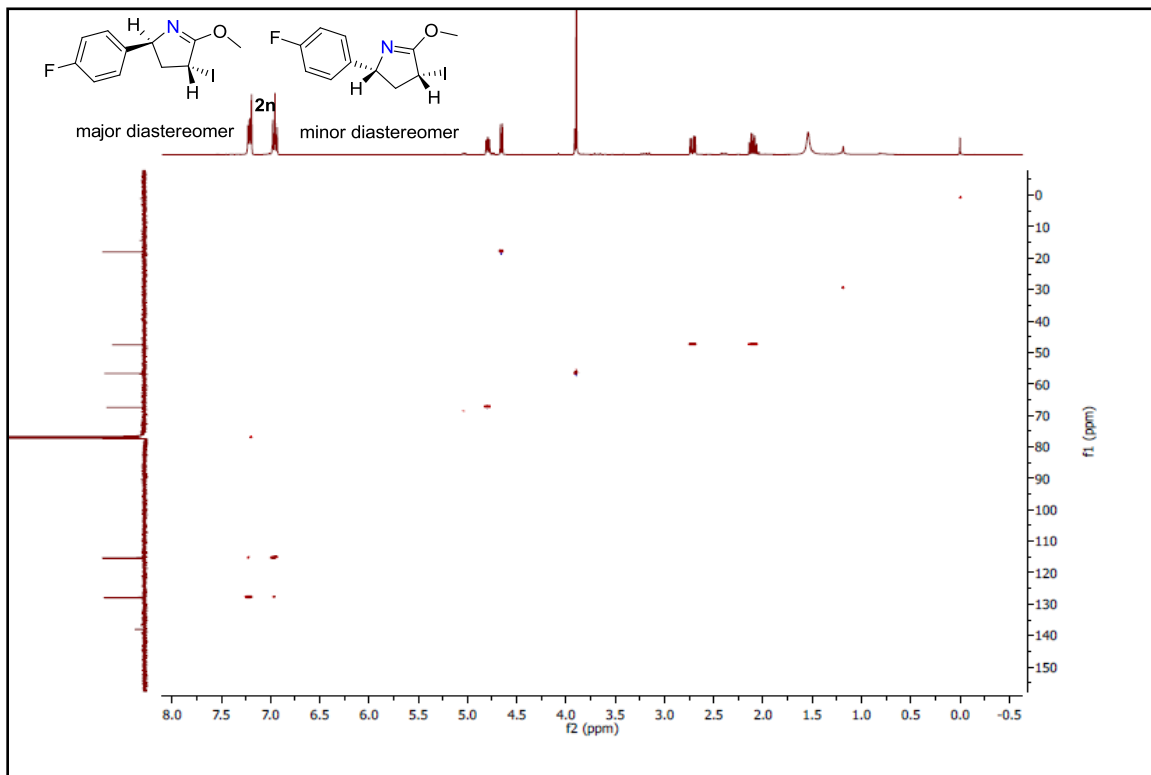
$^{19}\text{F}$  Proton coupled spectra of **2n**



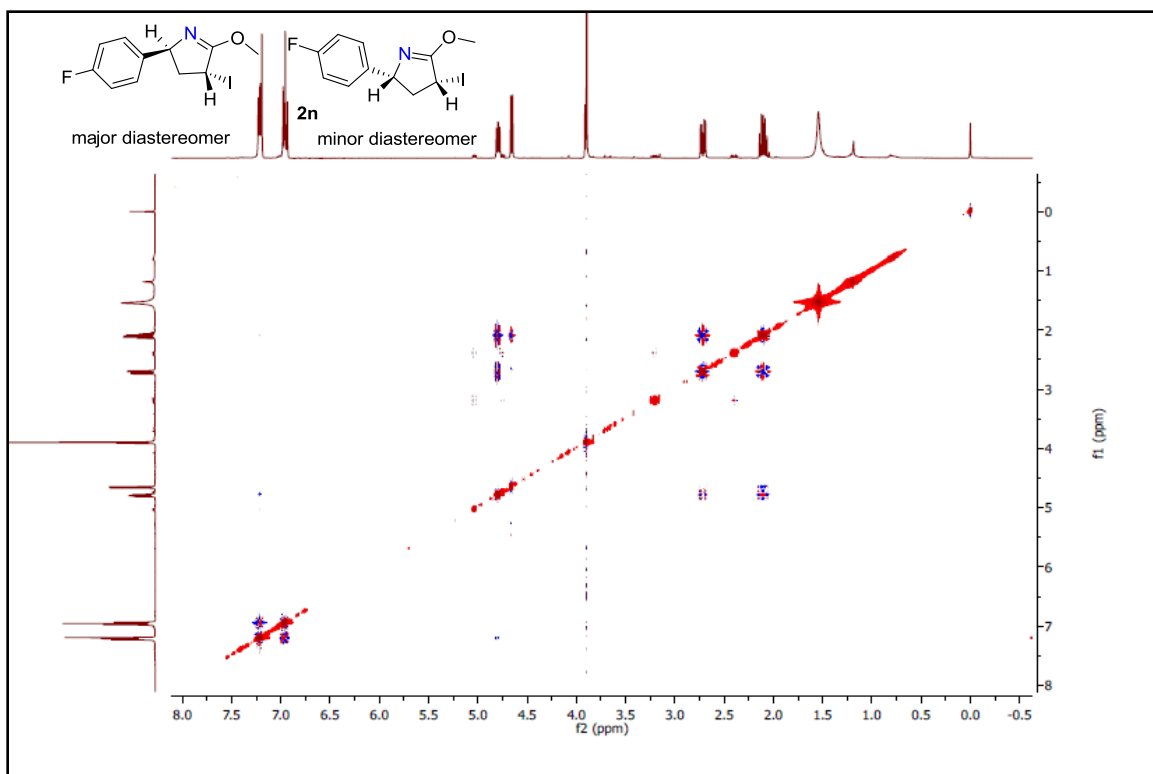
$^{19}\text{F}$  Proton decoupled spectra of **2n**



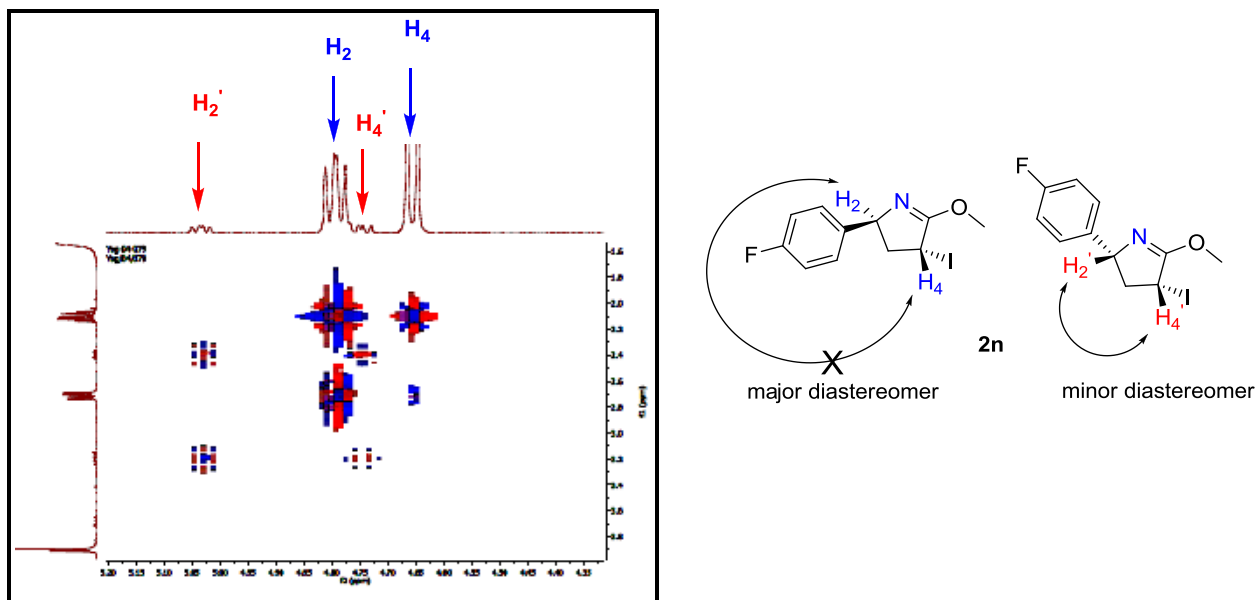
COSY spectra of **2n**



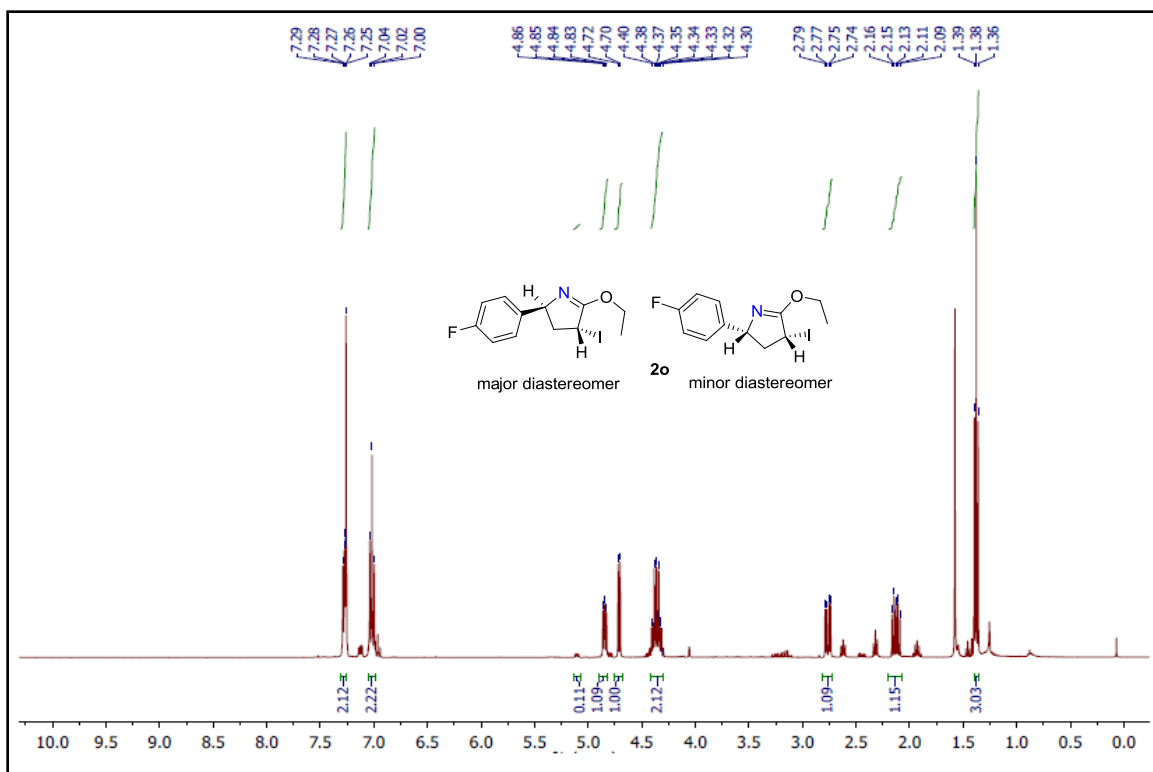
HSQC spectra of **2n**



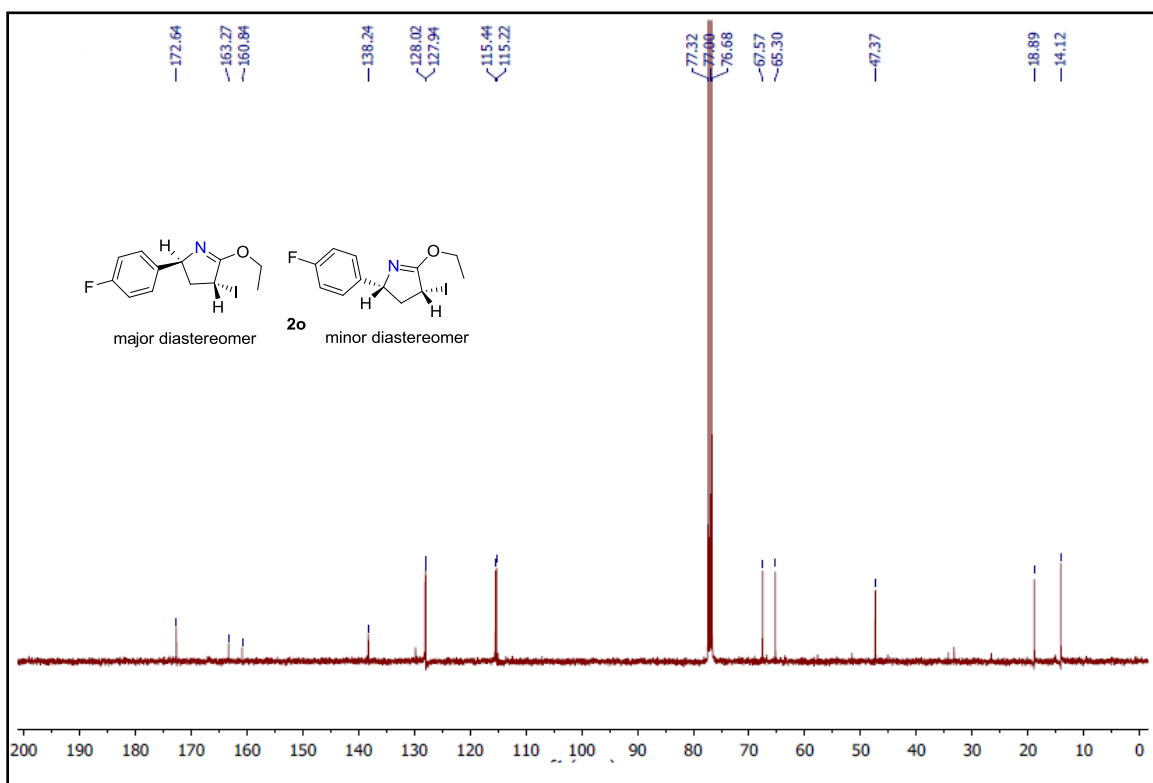
NOESY spectra of **2n**



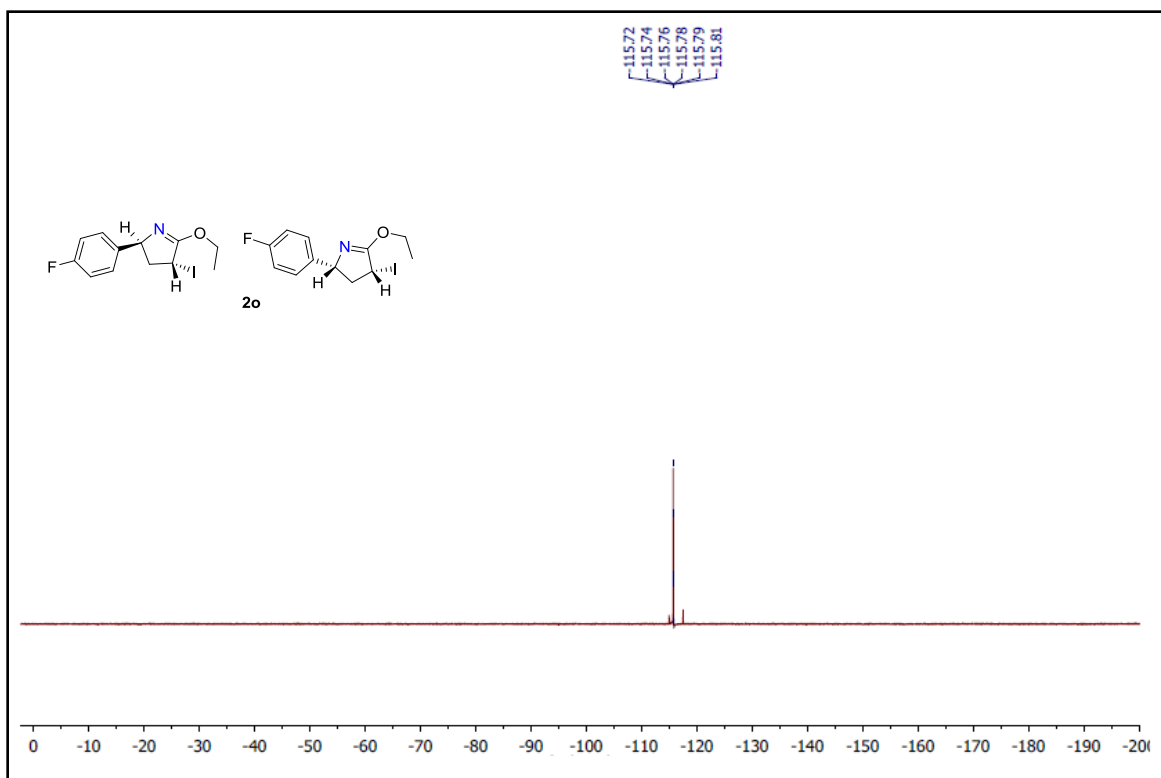
NOESY spectra of **2n**



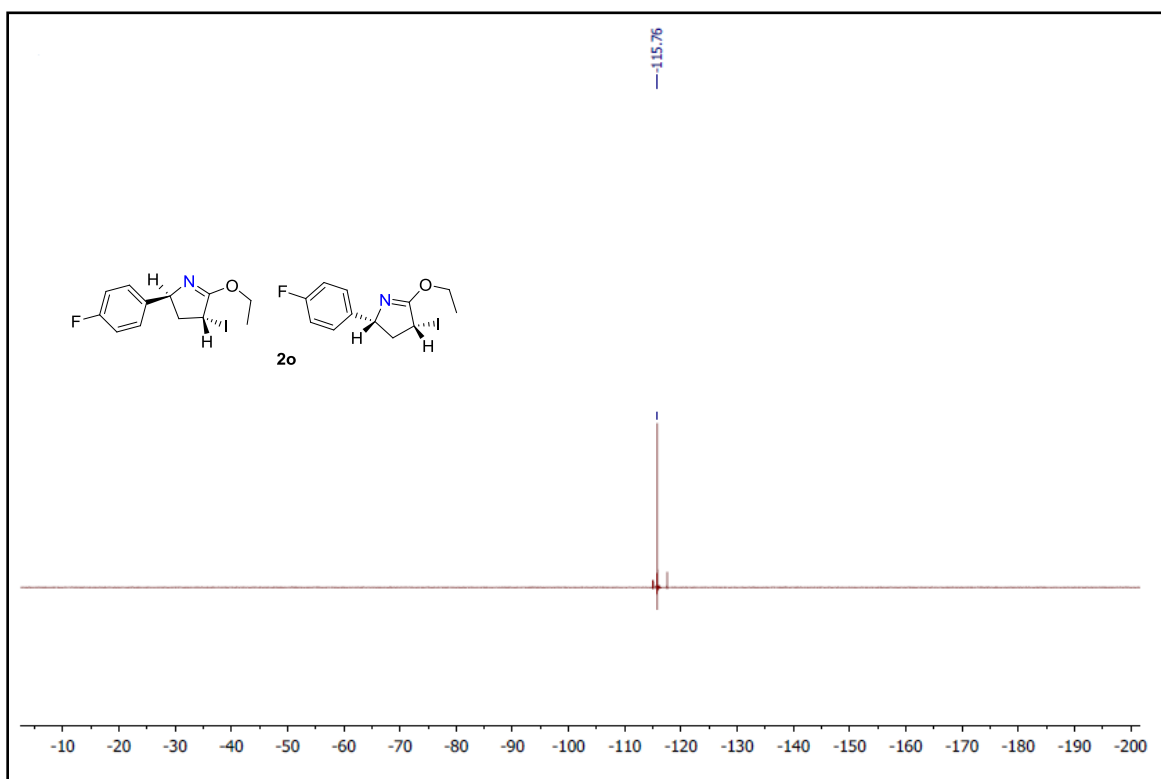
<sup>1</sup>H spectra of **2o**



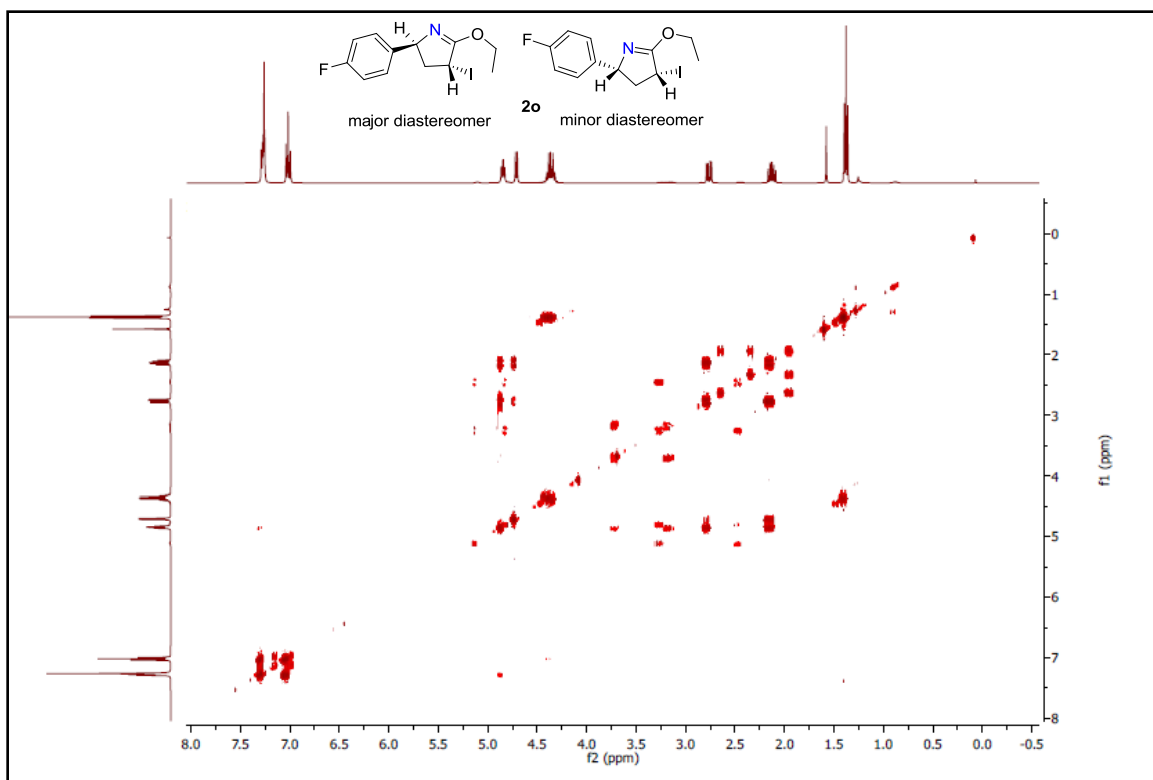
<sup>13</sup>C{<sup>1</sup>H} spectra of **2o**



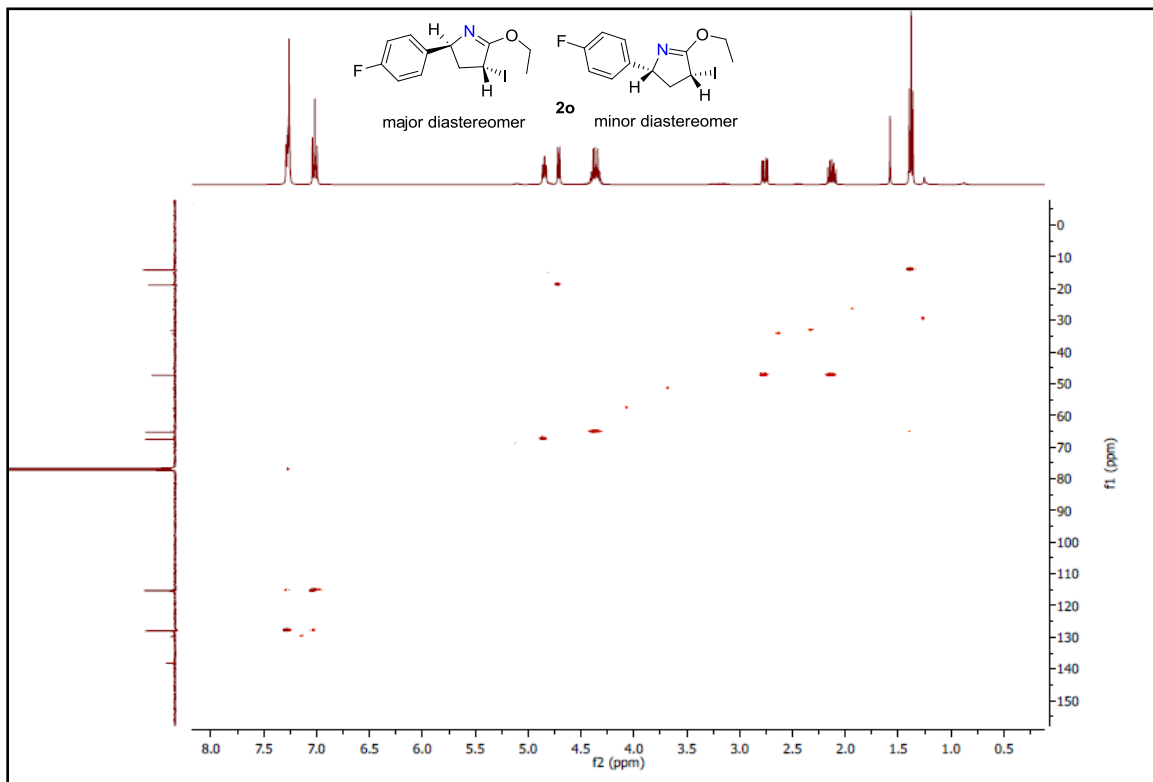
$^{19}\text{F}$  Proton coupled spectra of **2o**



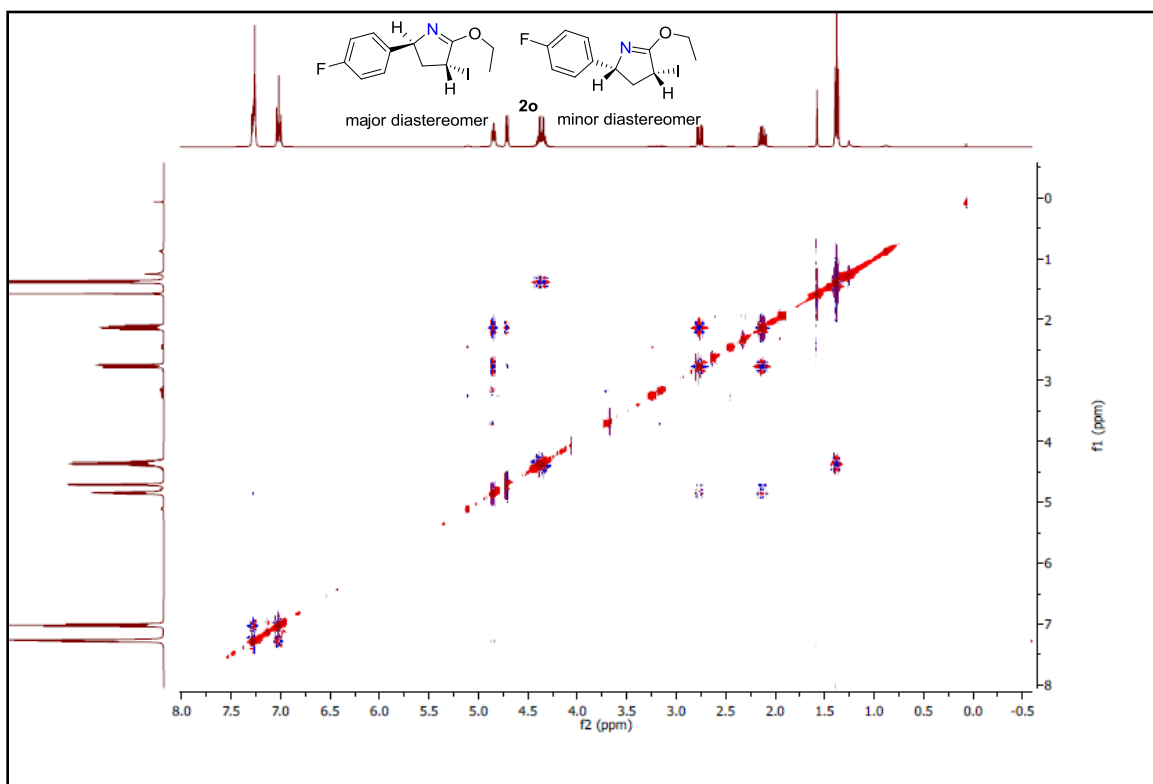
$^{19}\text{F}$  Proton decoupled spectra of **2o**



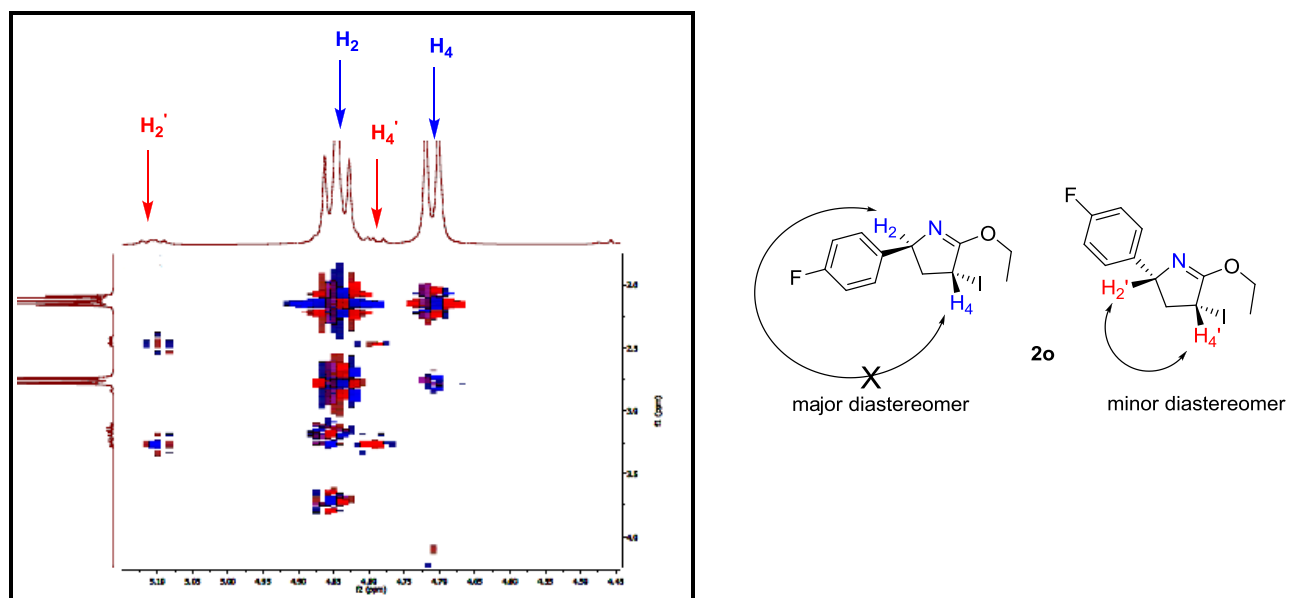
**COSY spectra of **2o****



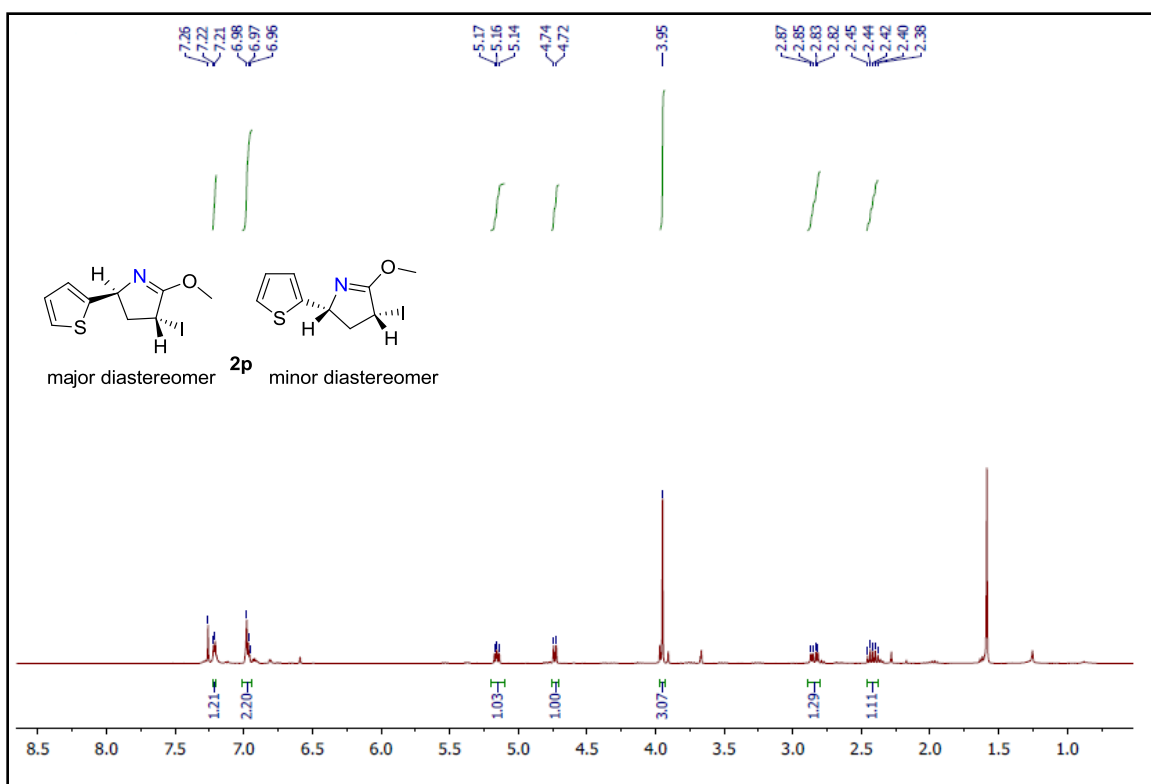
**HSQC spectra of **2o****



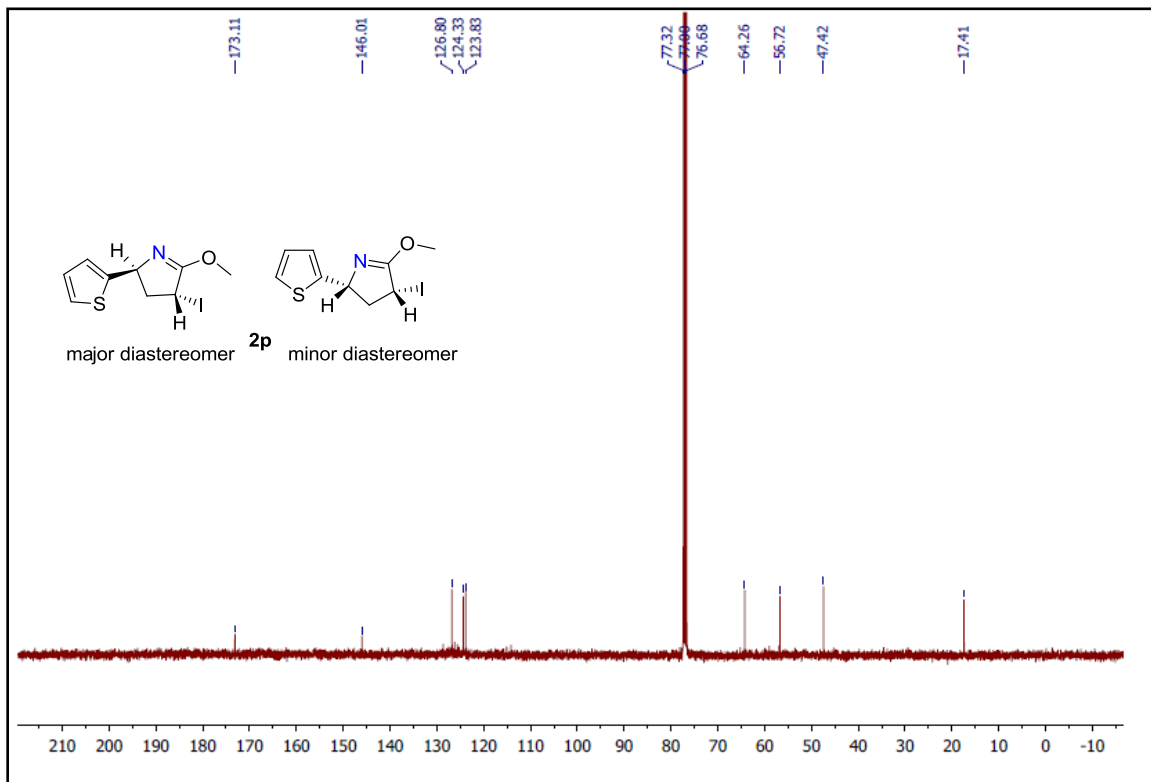
NOESY spectra of **2o**



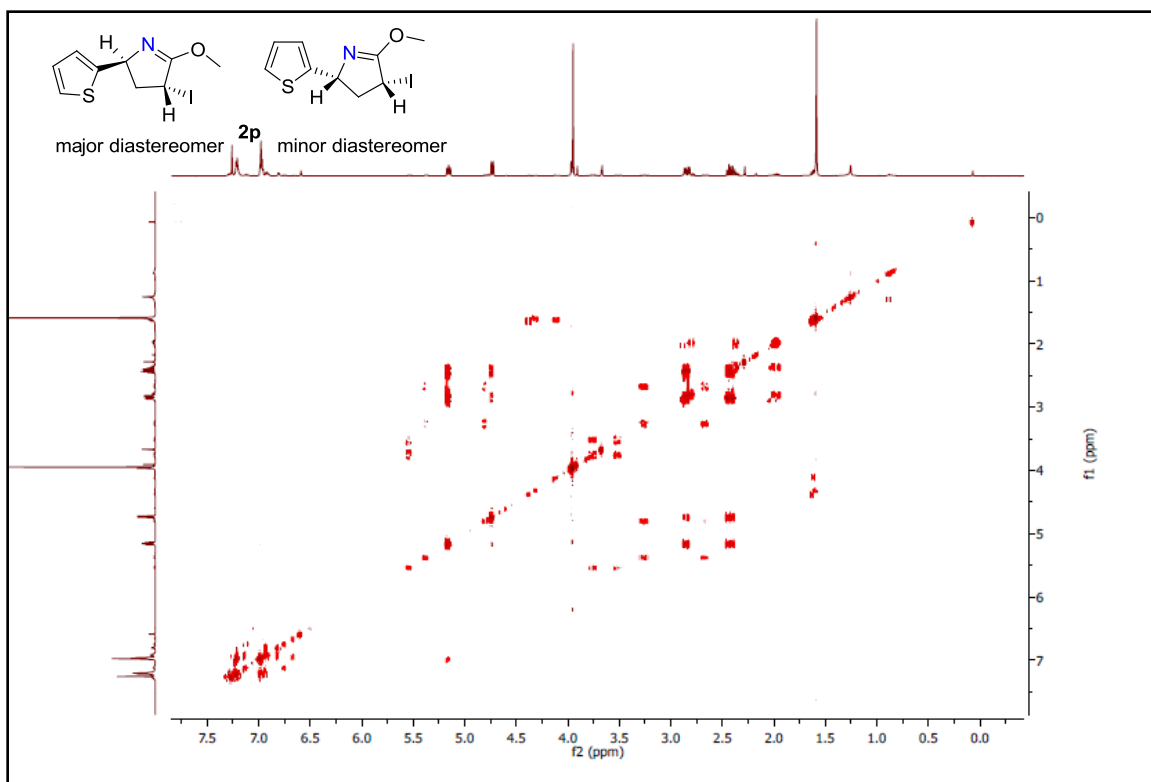
NOESY spectra of **2o**



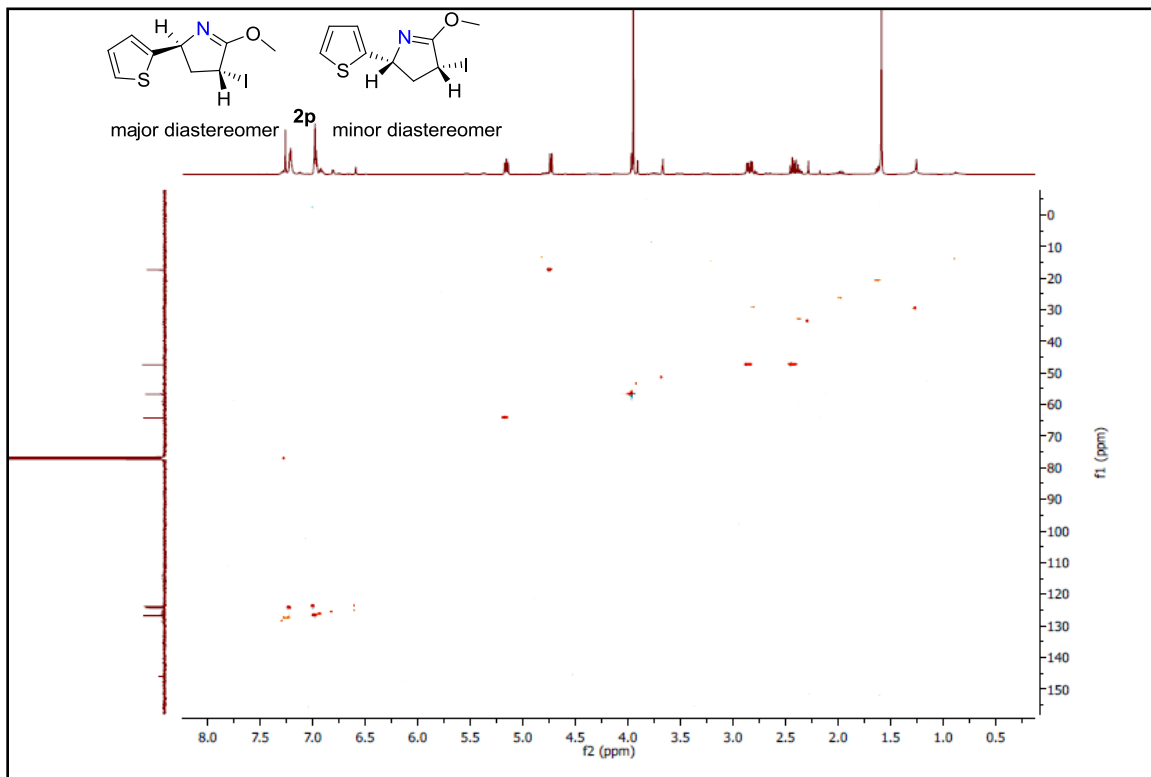
<sup>1</sup>H spectra of 2p



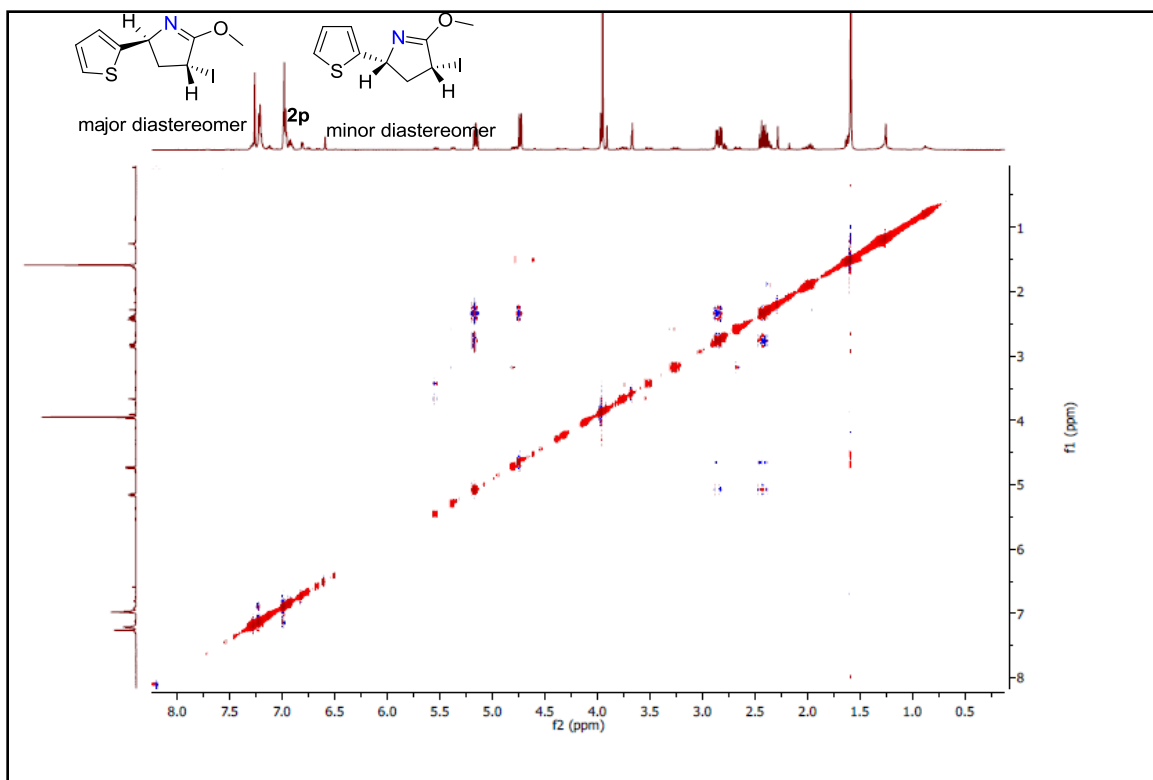
<sup>13</sup>C{<sup>1</sup>H} spectra of 2p



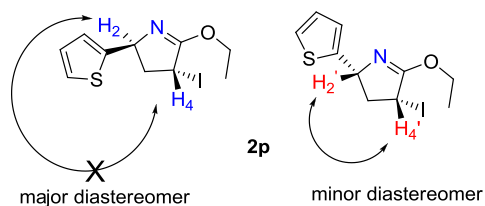
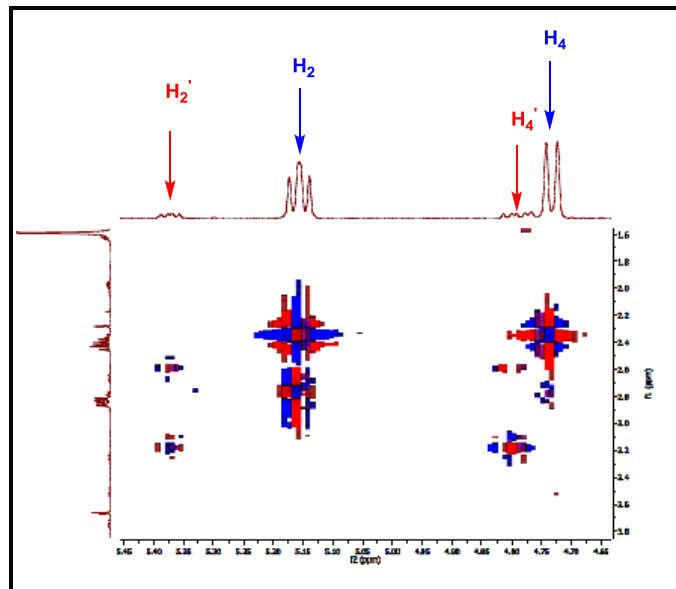
COSY spectra of **2p**



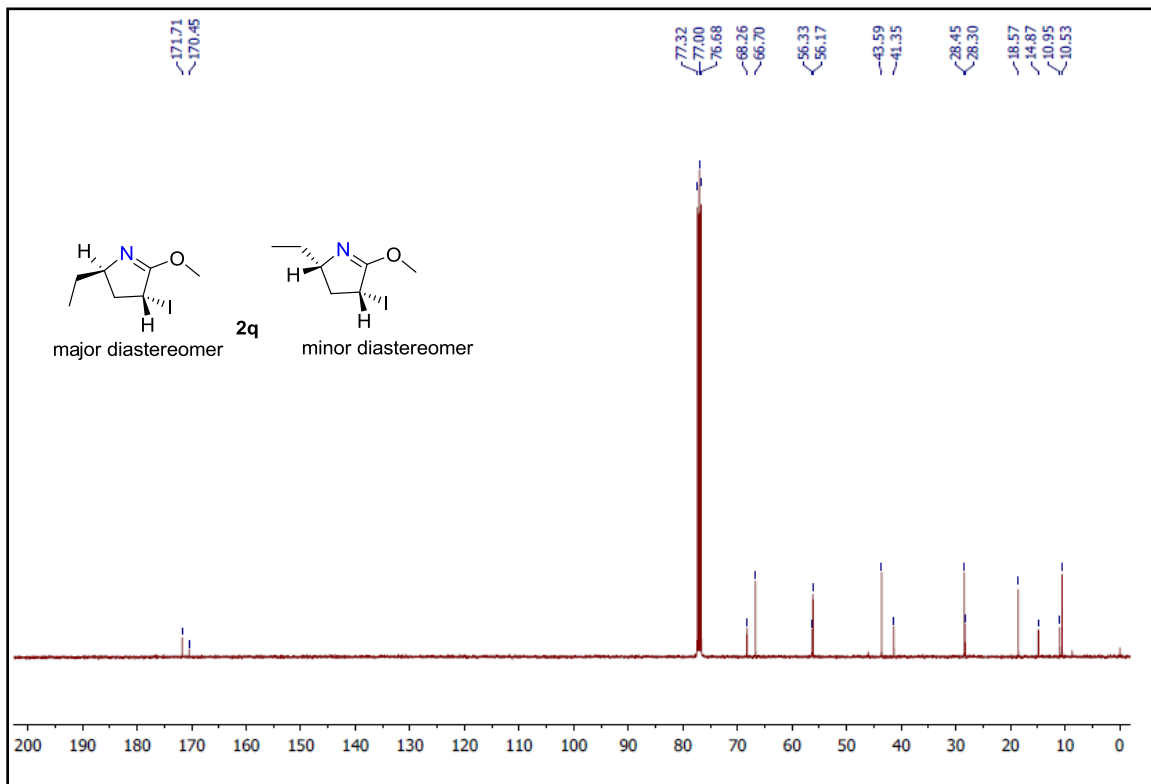
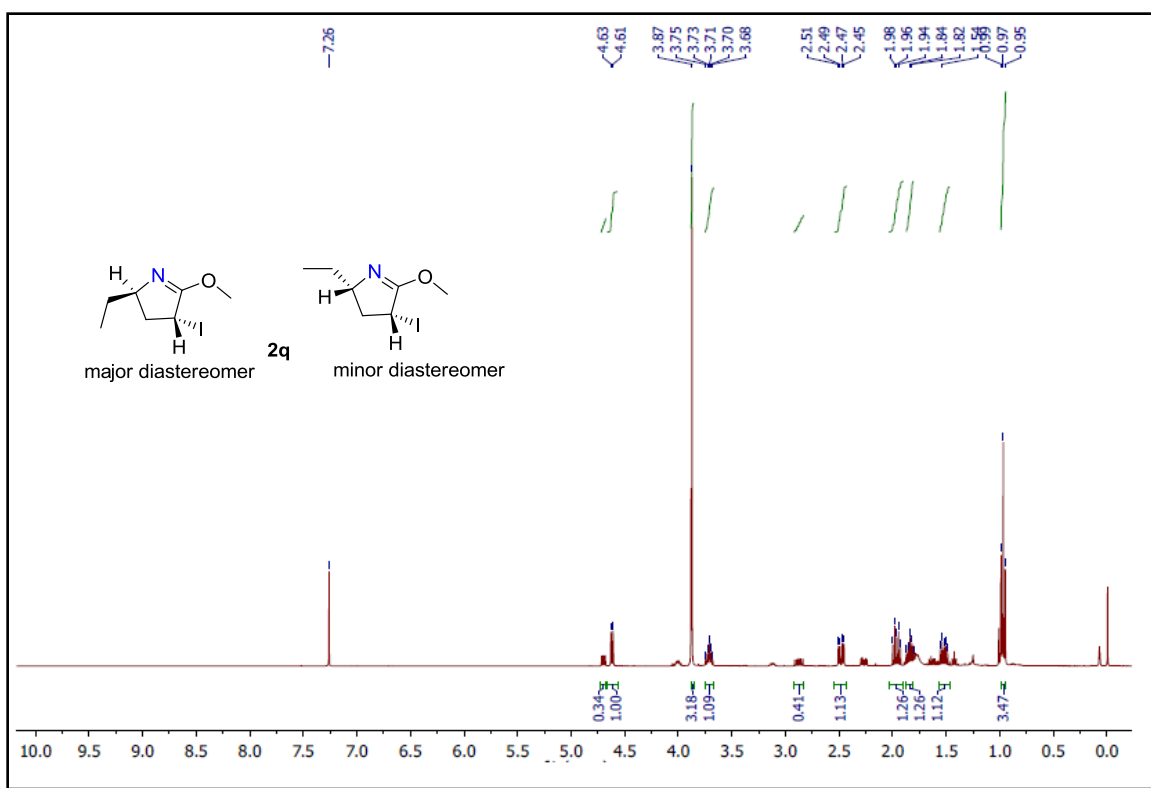
HSQC spectra of **2p**

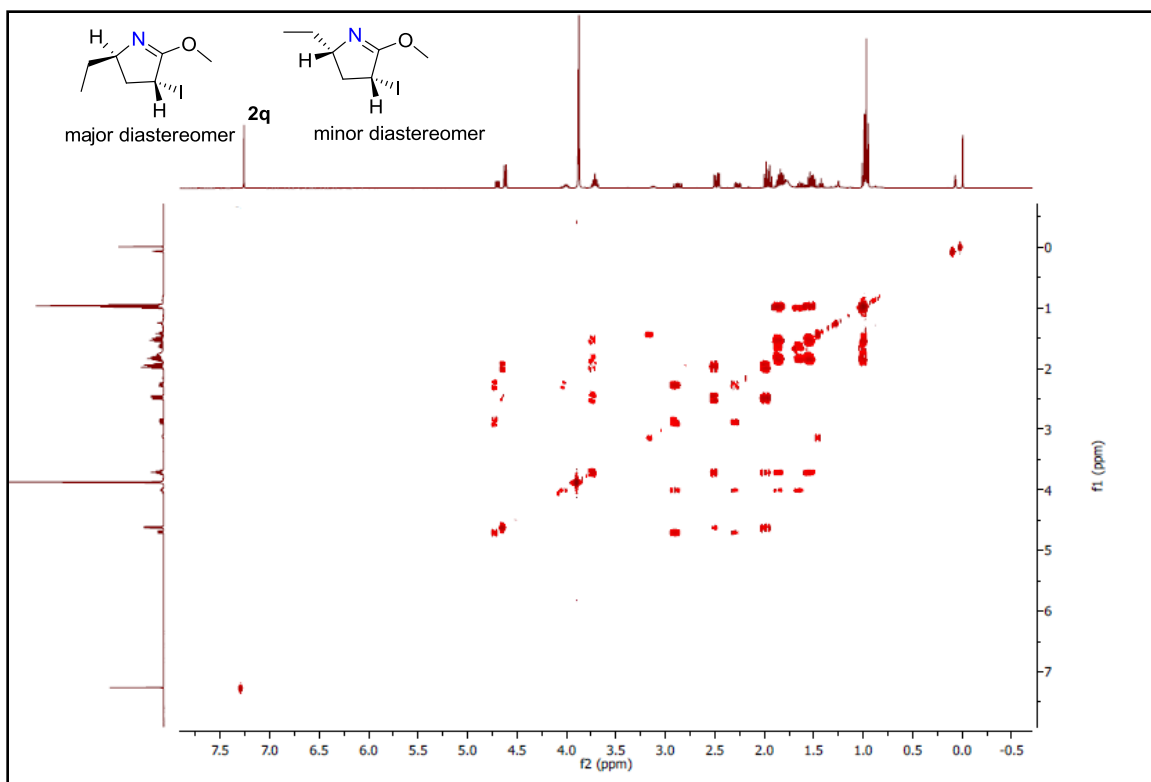


NOESY spectra of **2p**

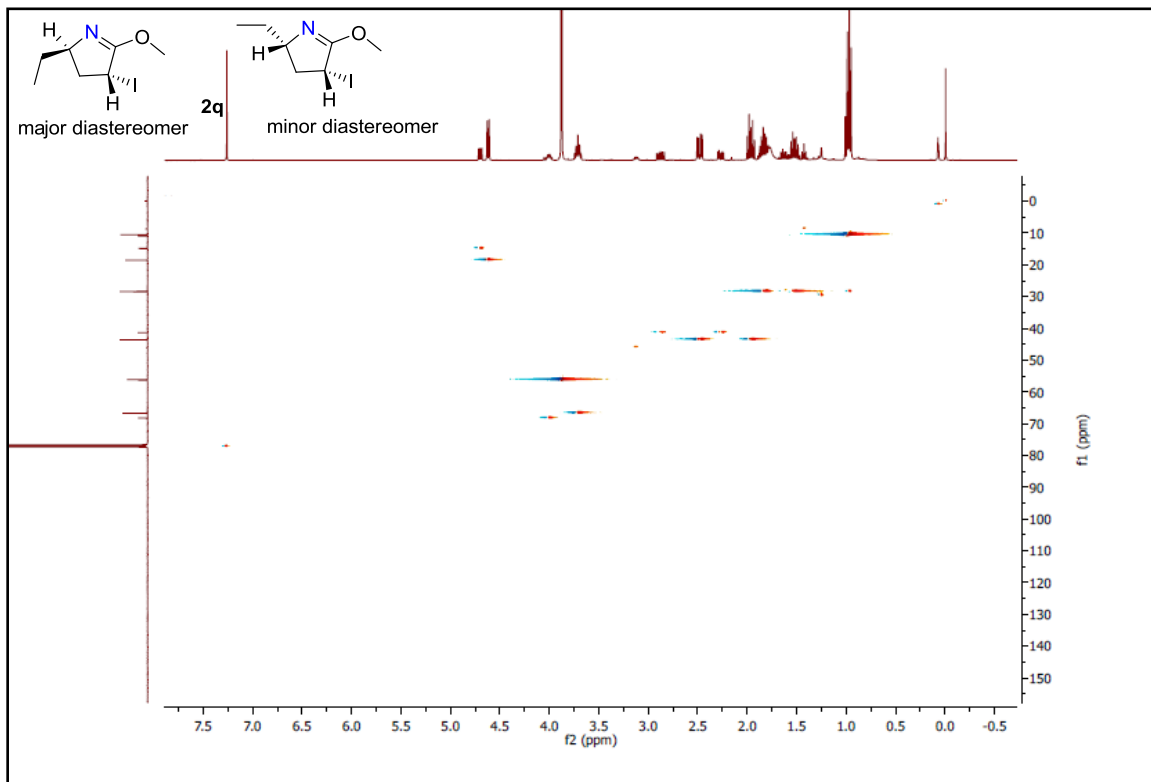


NOESY spectra of **2p**

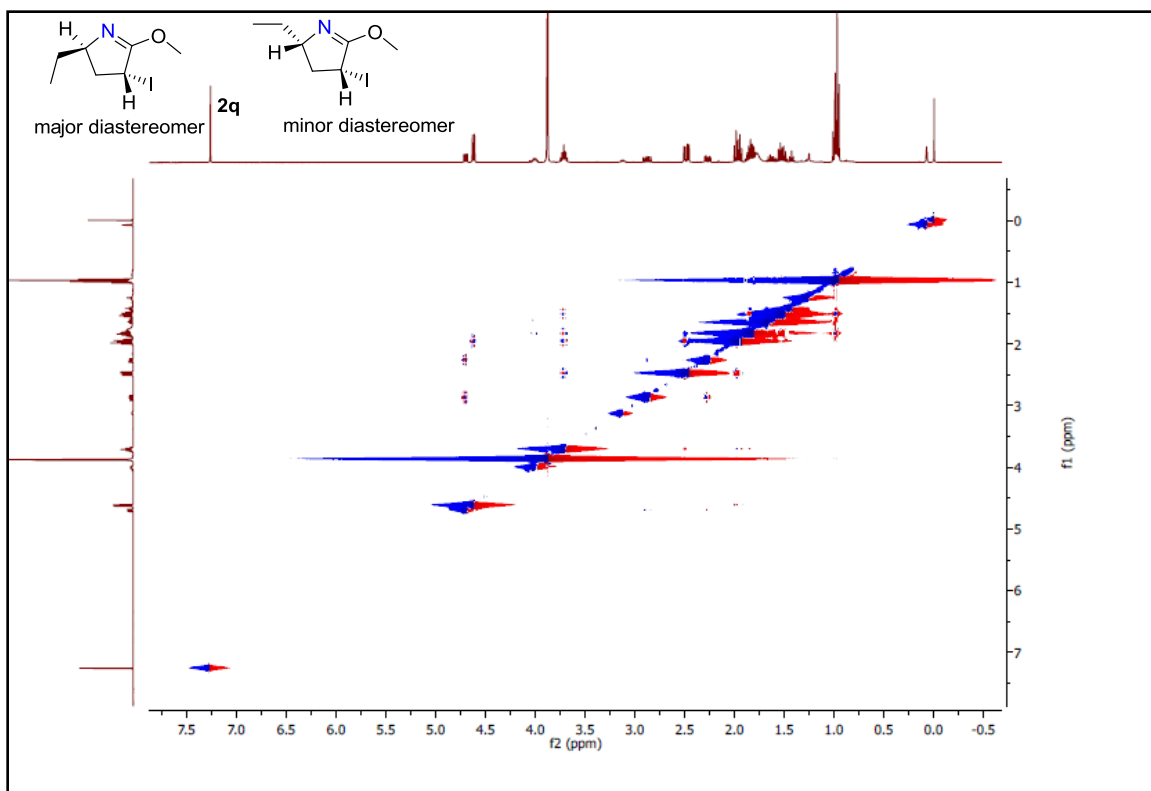




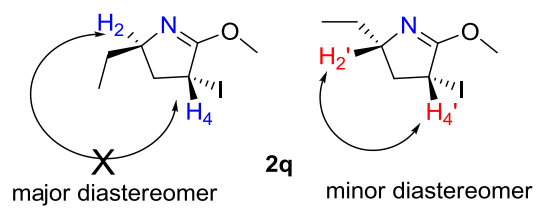
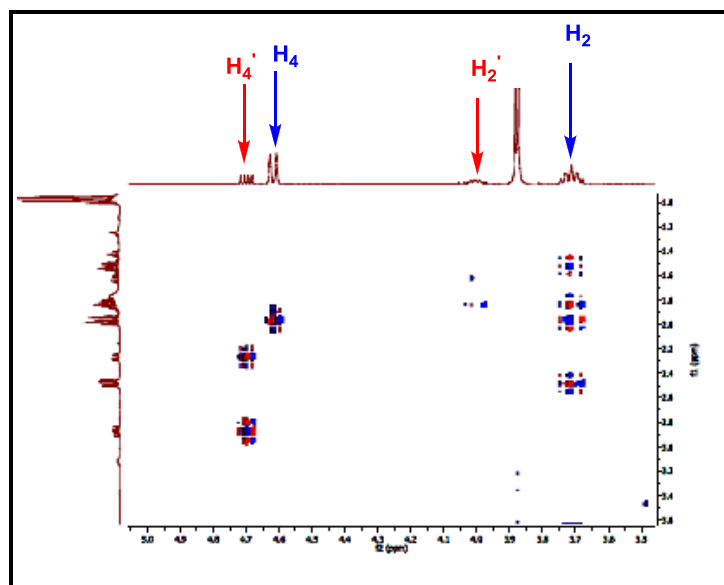
COSY spectra of **2q**



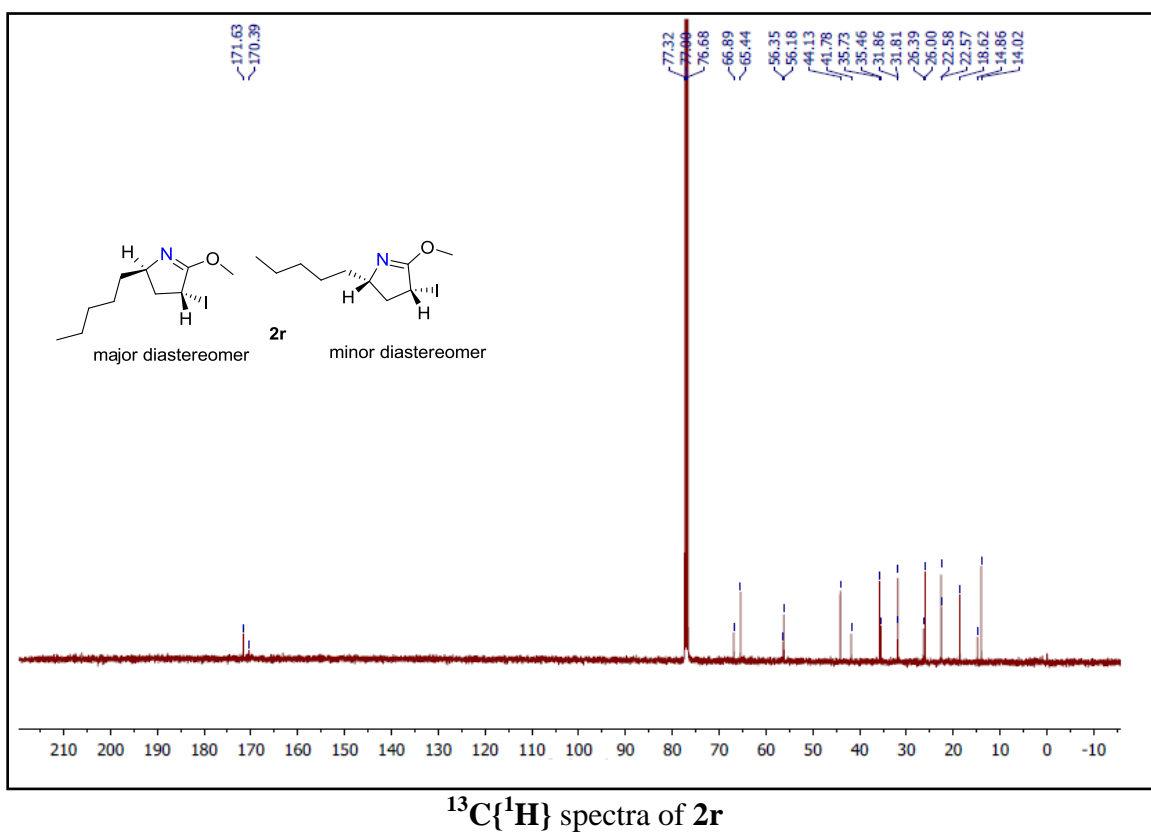
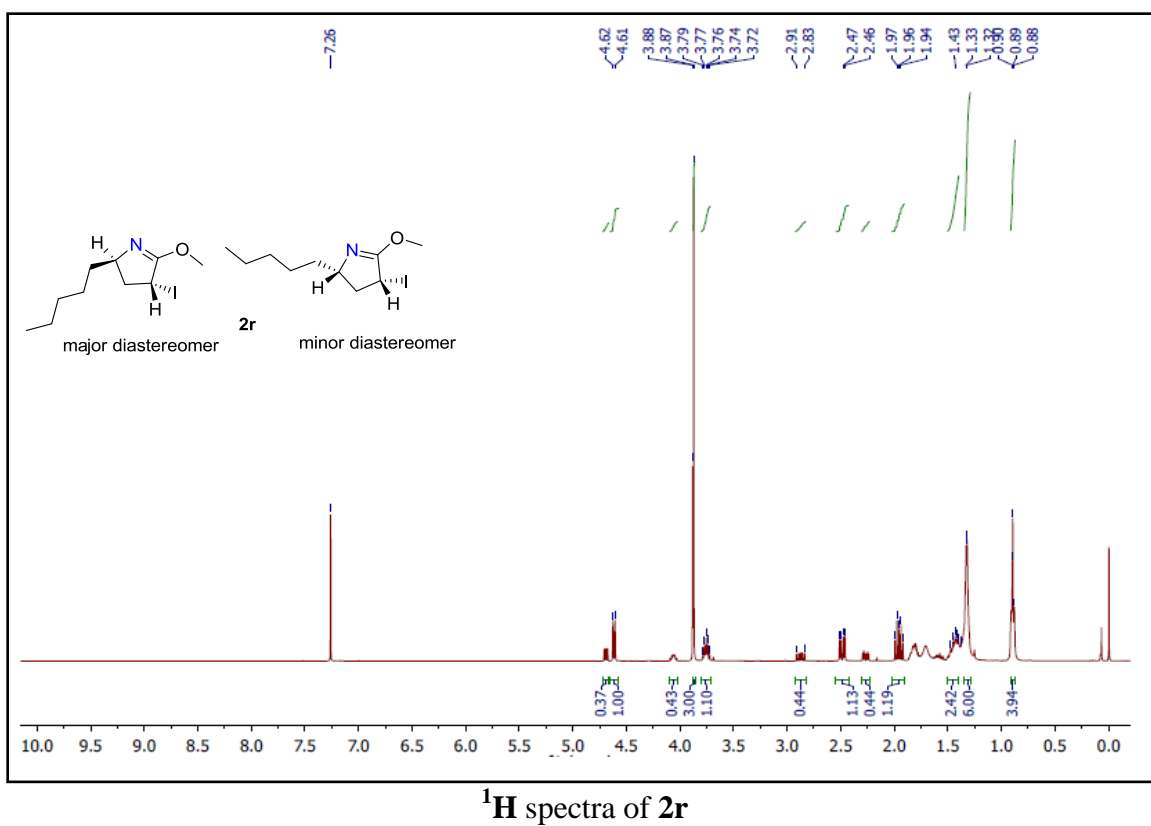
HSQC spectra of **2q**

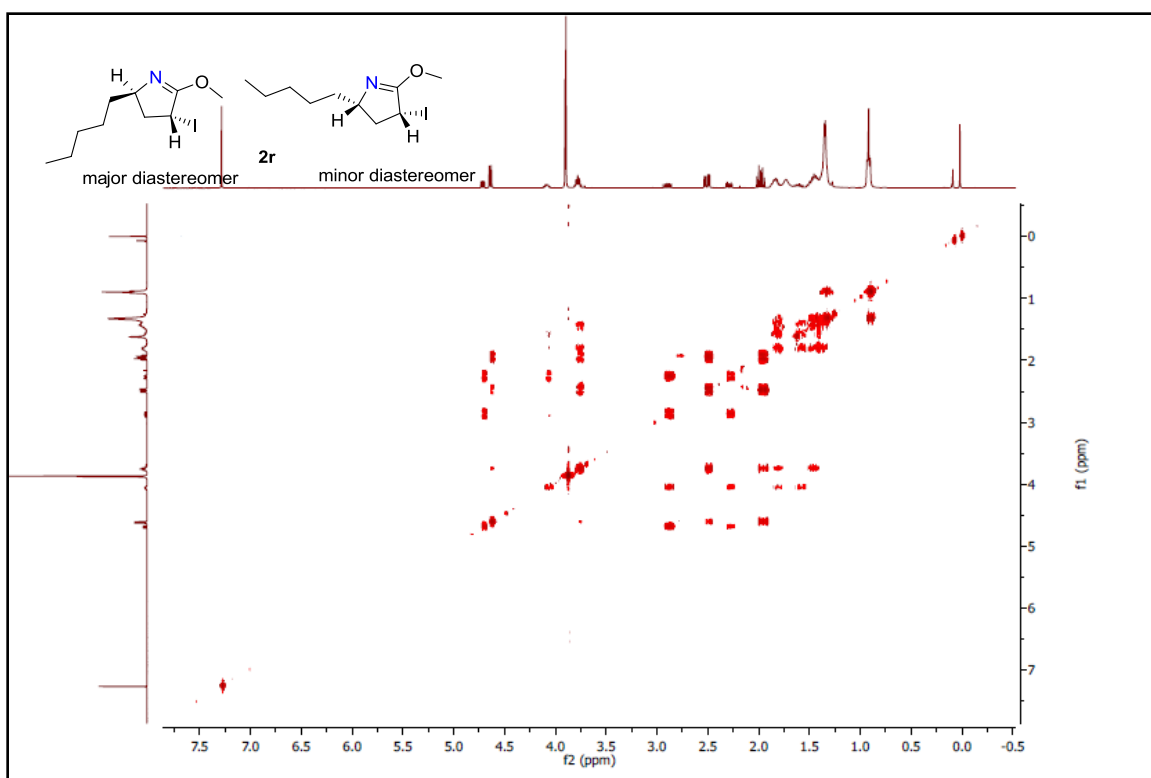


NOESY spectra of **2q**

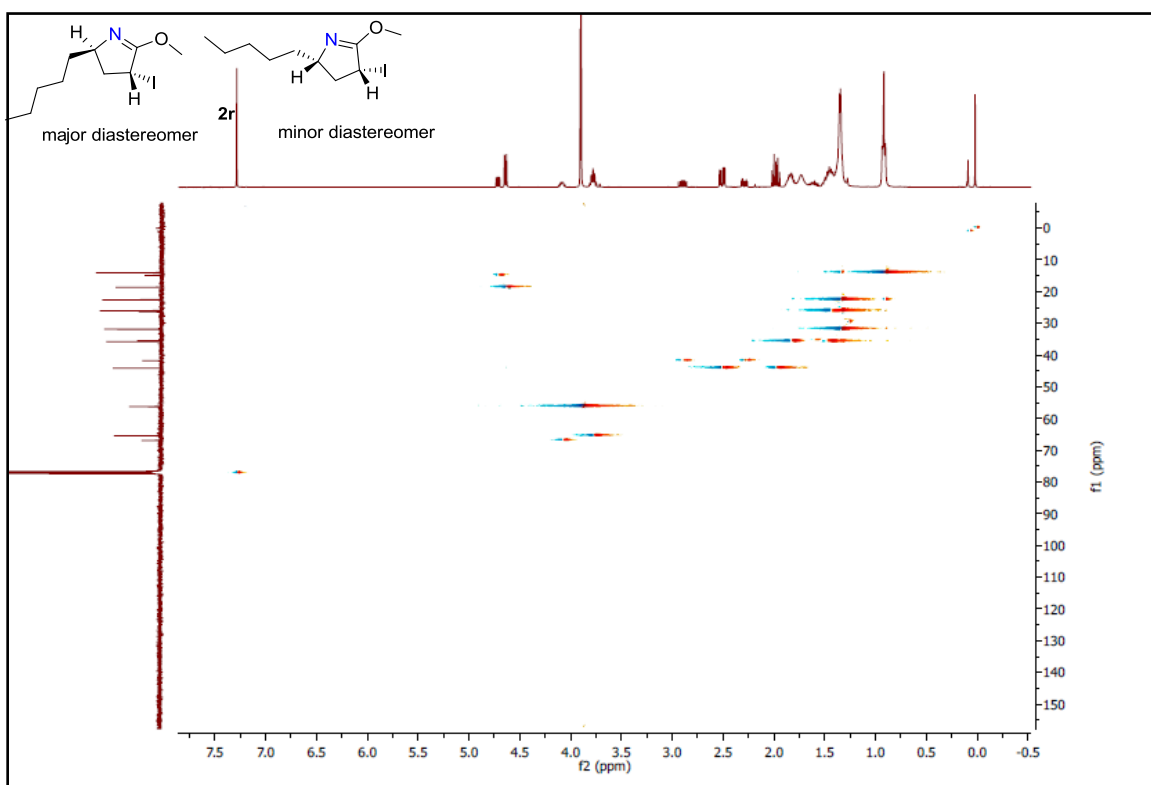


NOESY spectra of **2q**

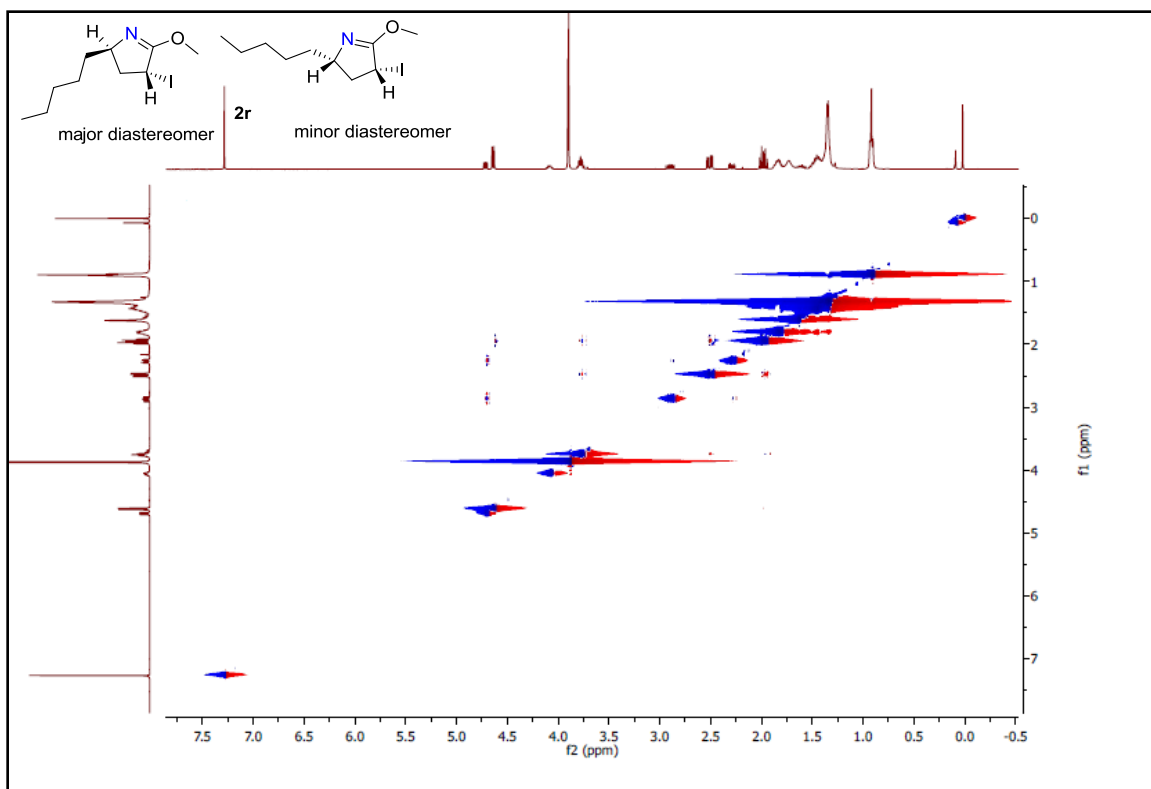




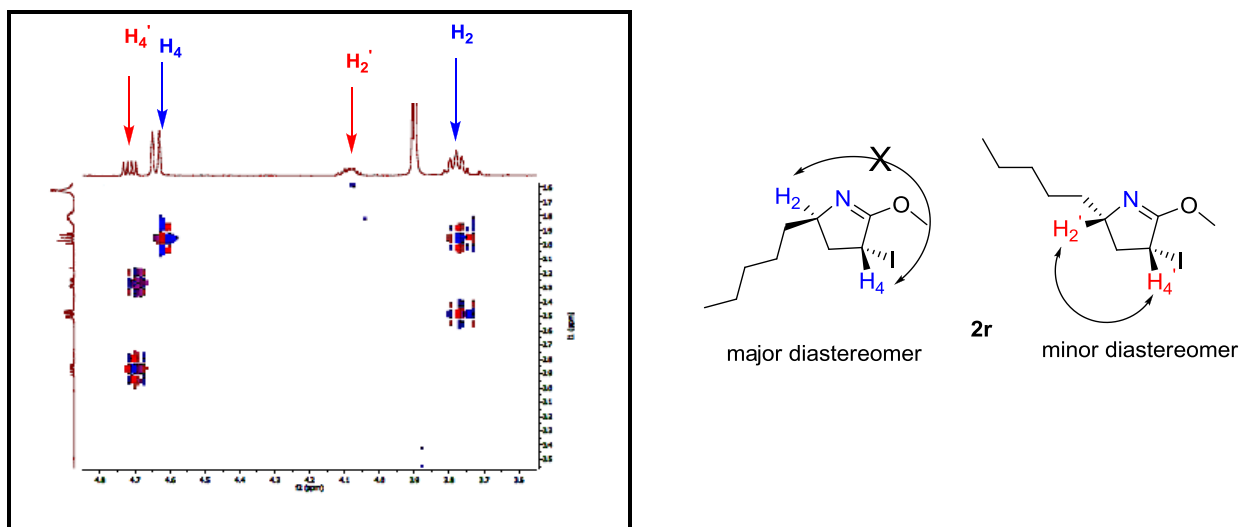
COSY spectra of **2r**



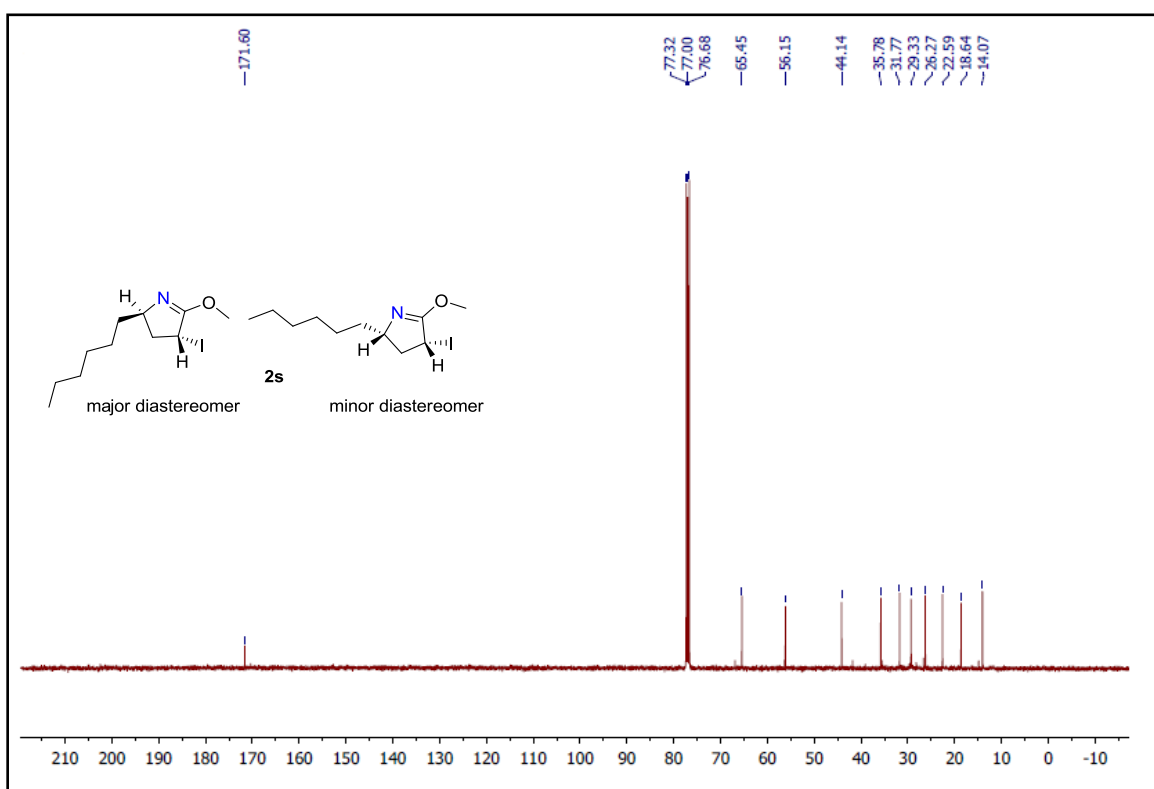
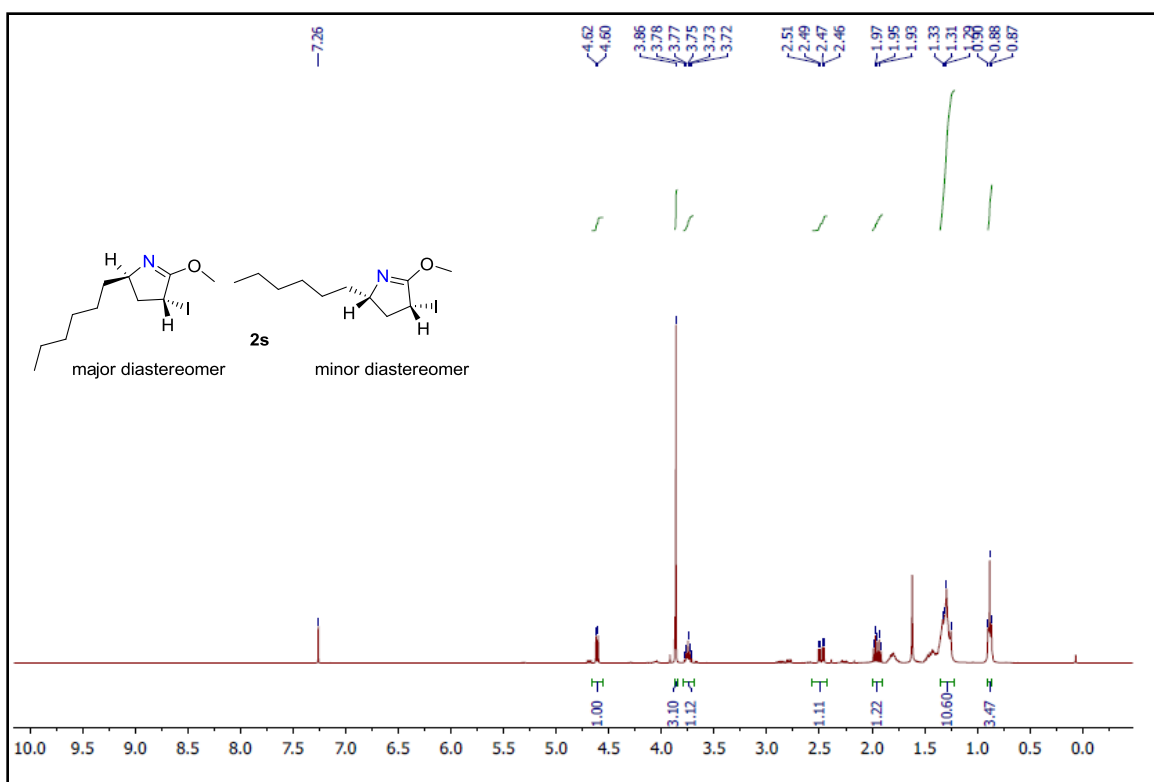
HSQC spectra of **2r**

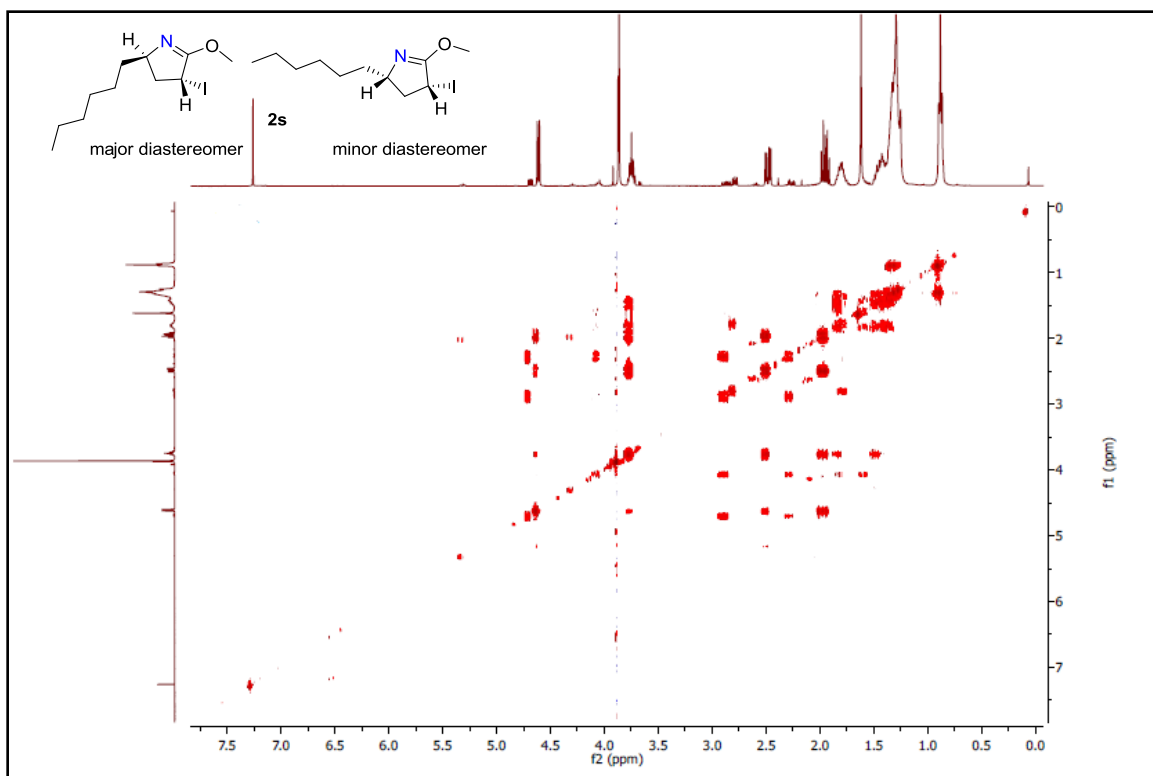


NOESY spectra of **2r**

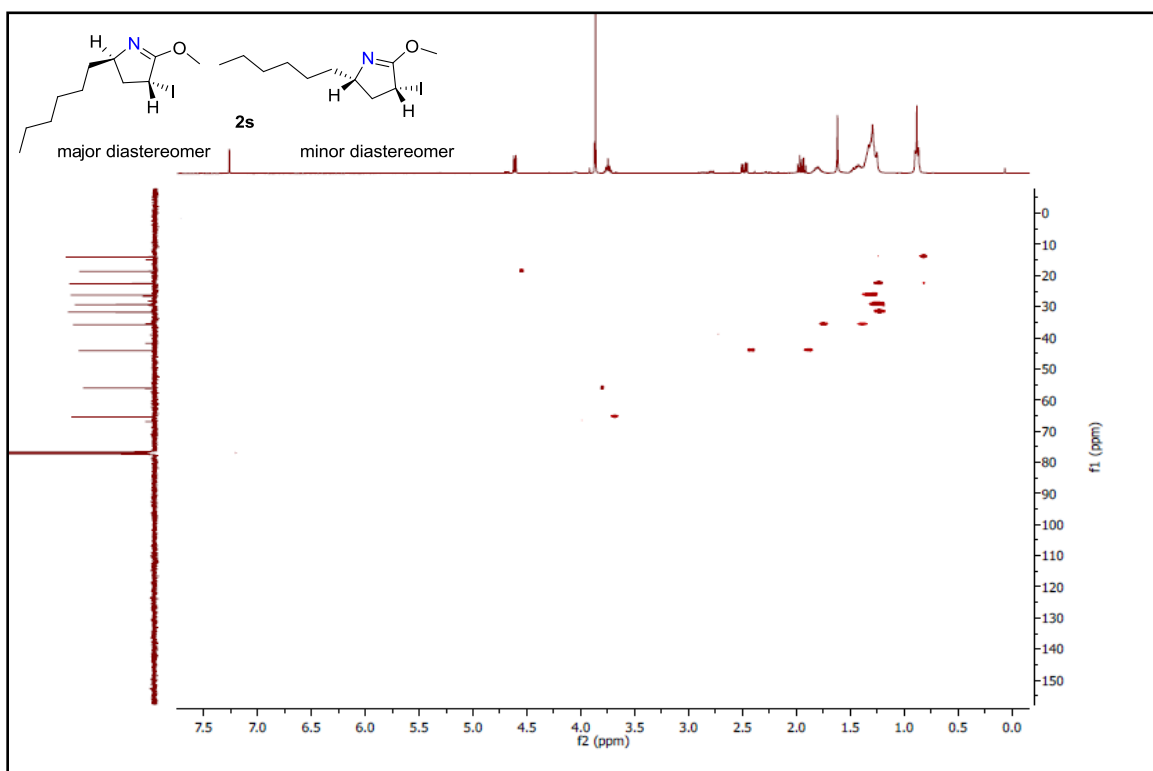


NOESY spectra of **2r**

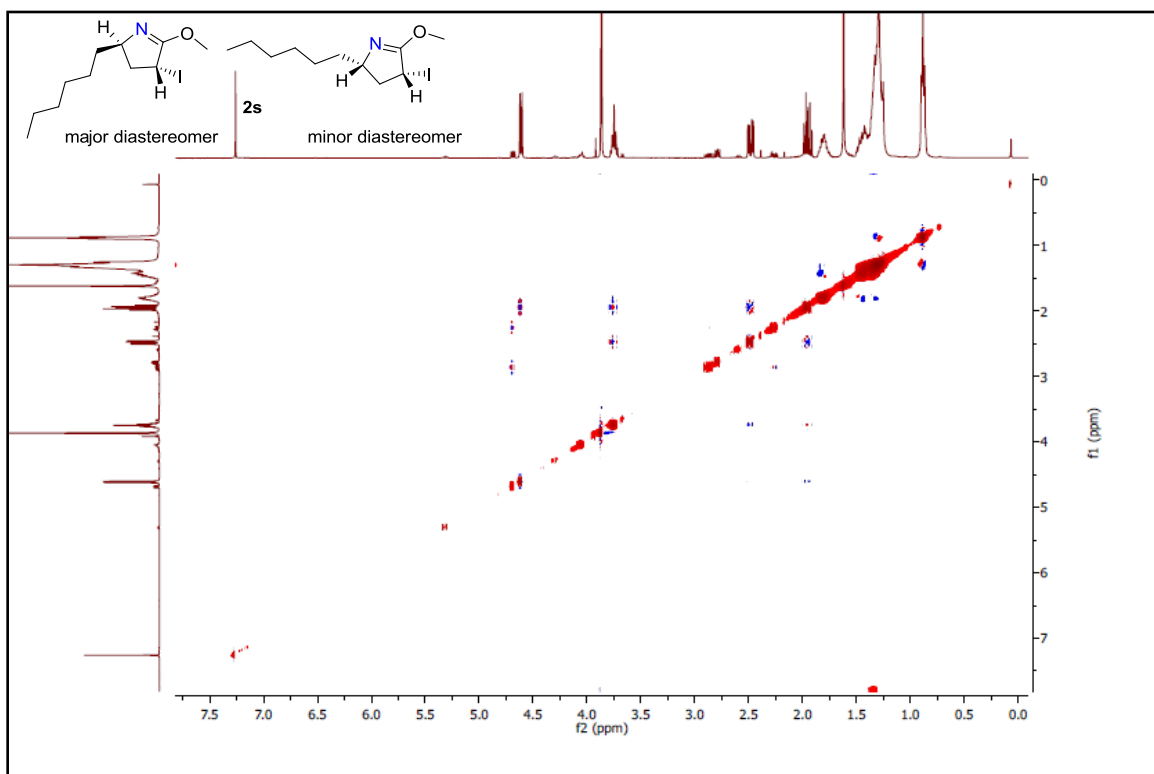




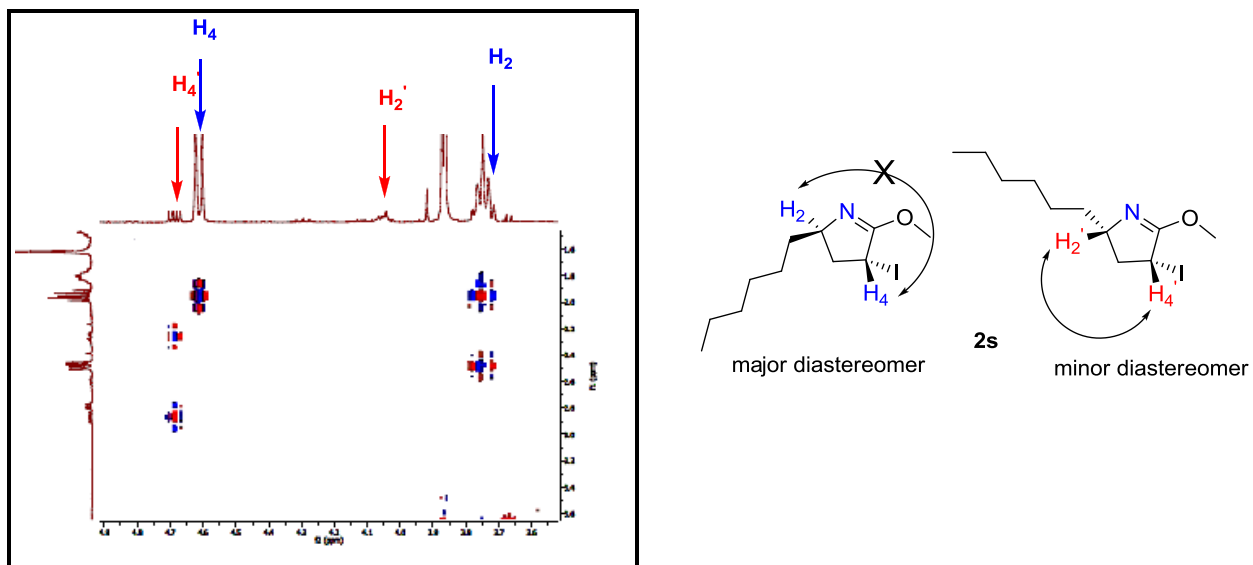
COSY spectra of **2s**



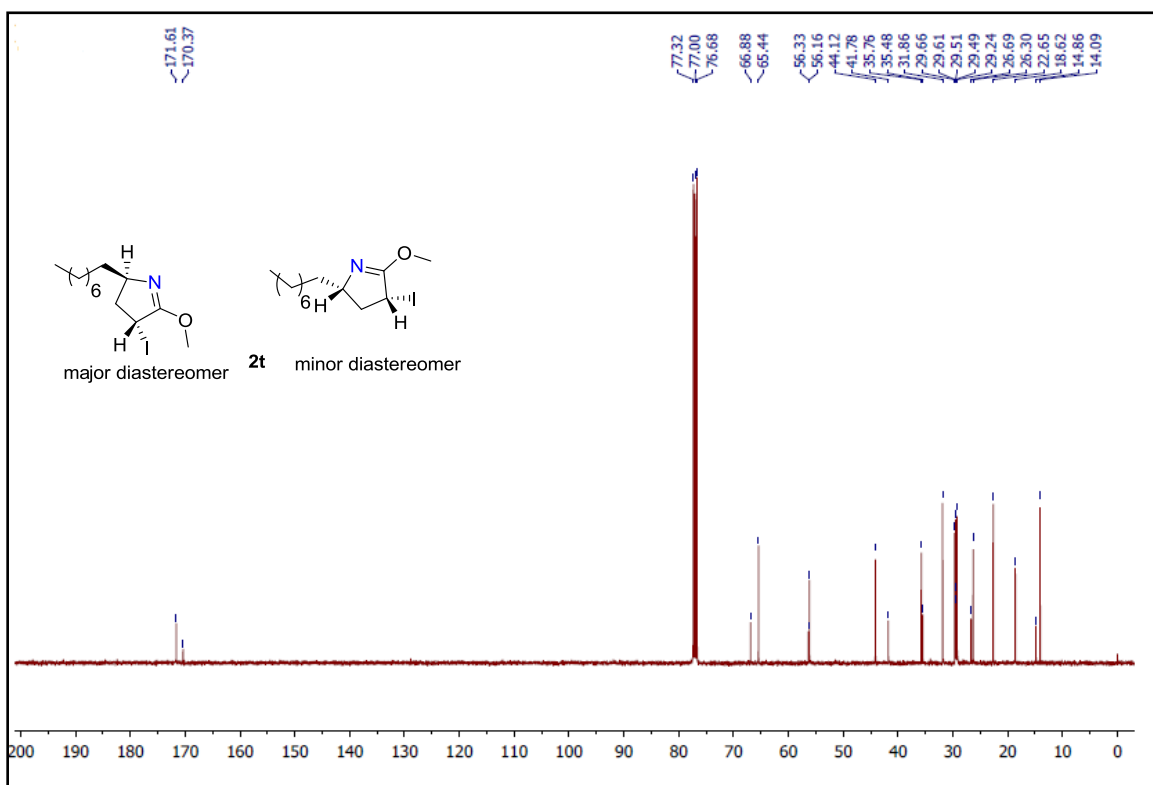
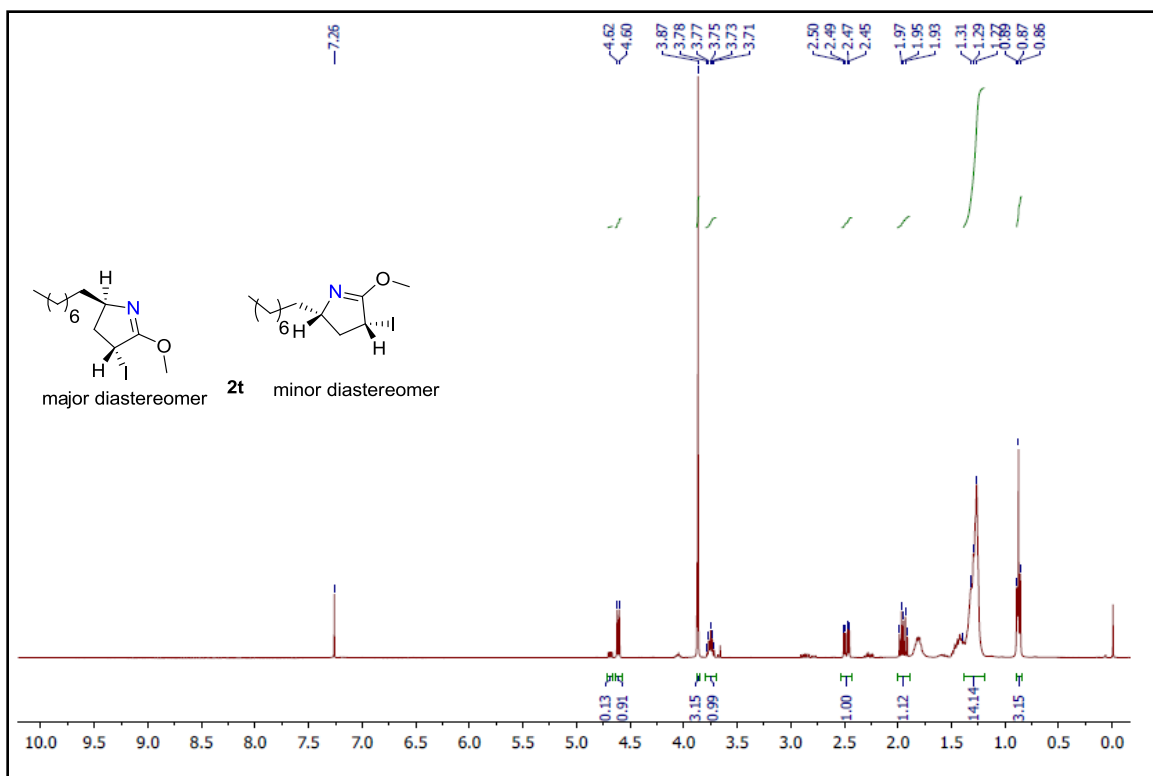
HSQC spectra of **2s**

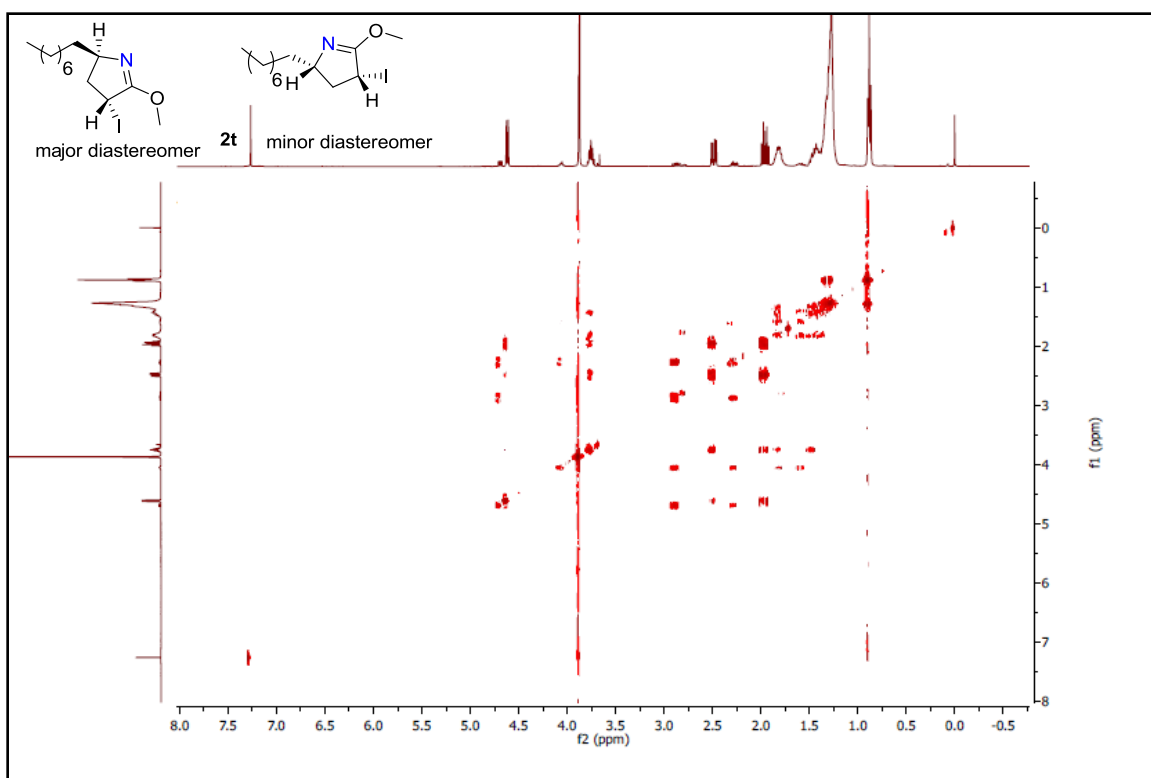


NOESY spectra of **2s**

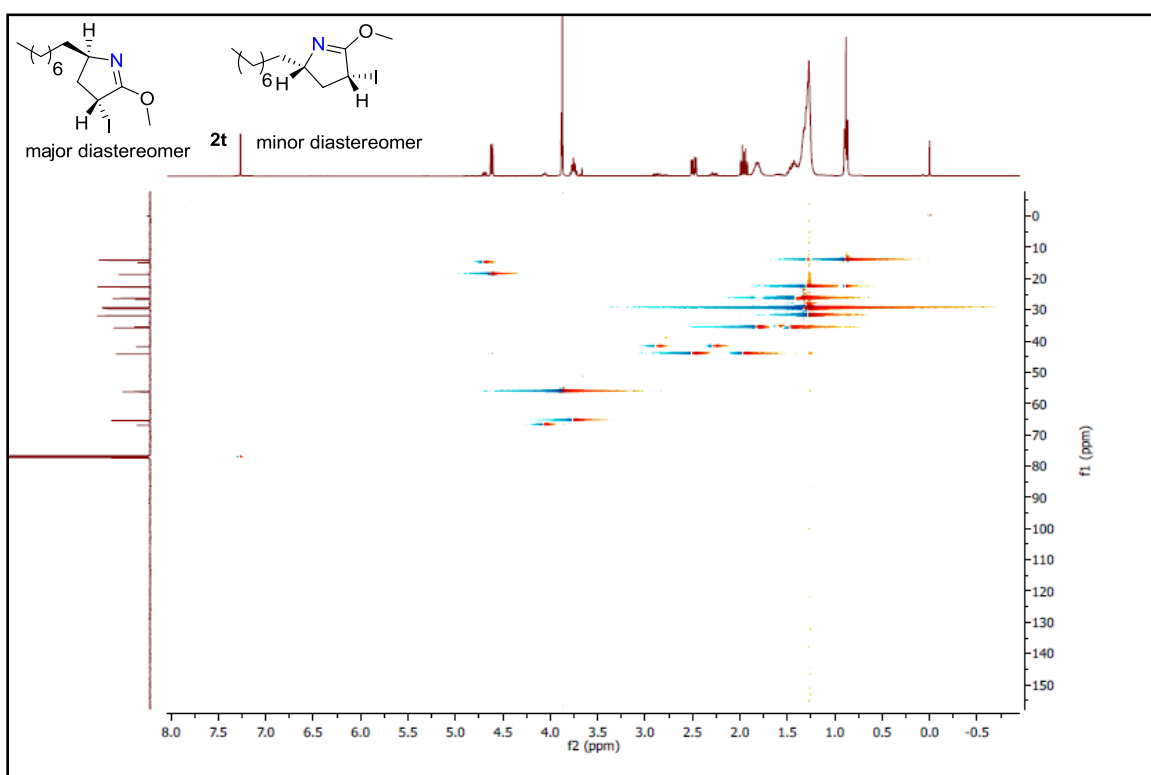


NOESY spectra of **2s**

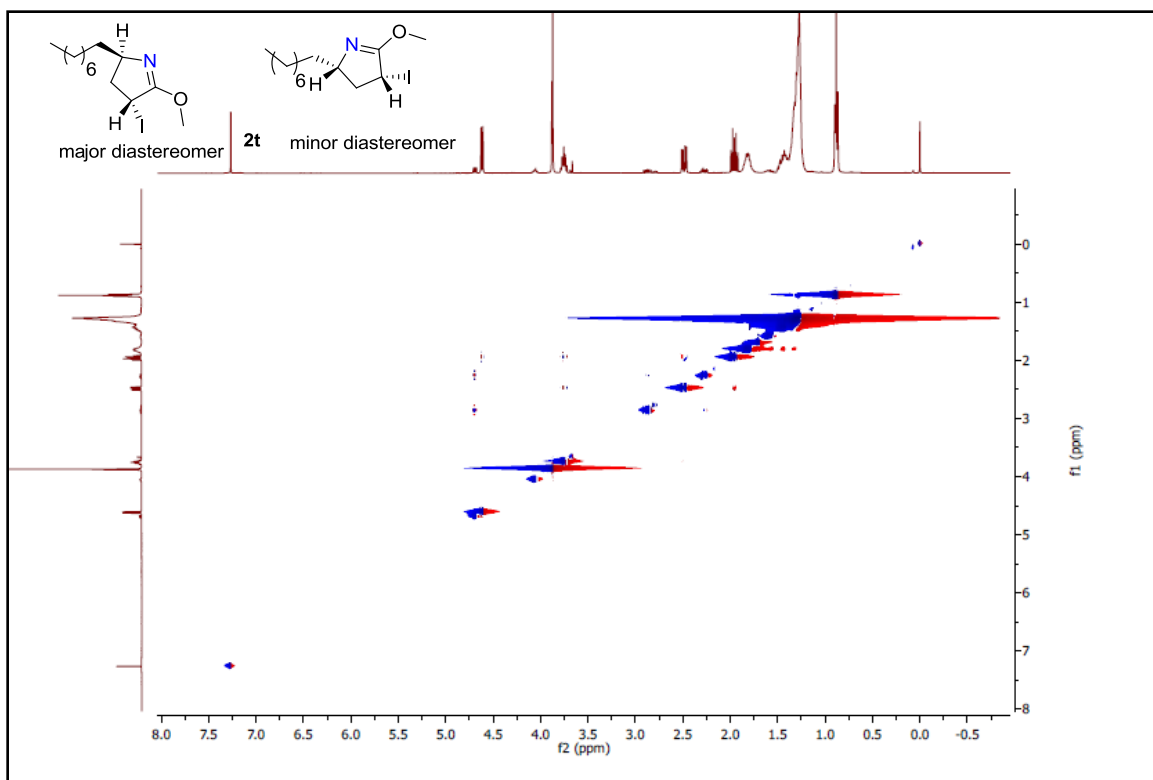




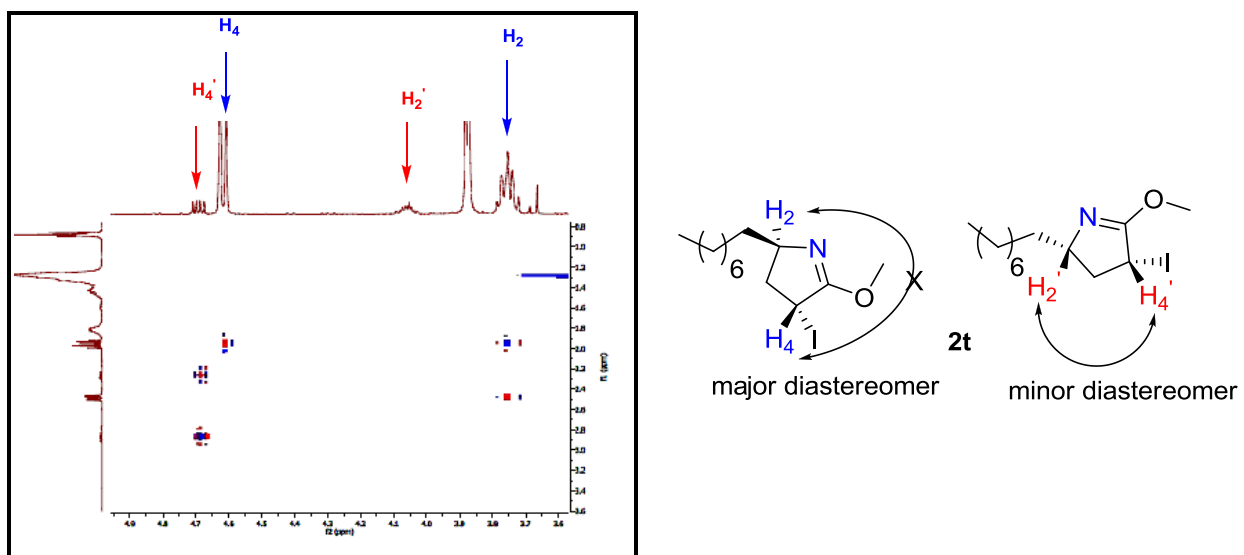
COSY spectra of **2t**



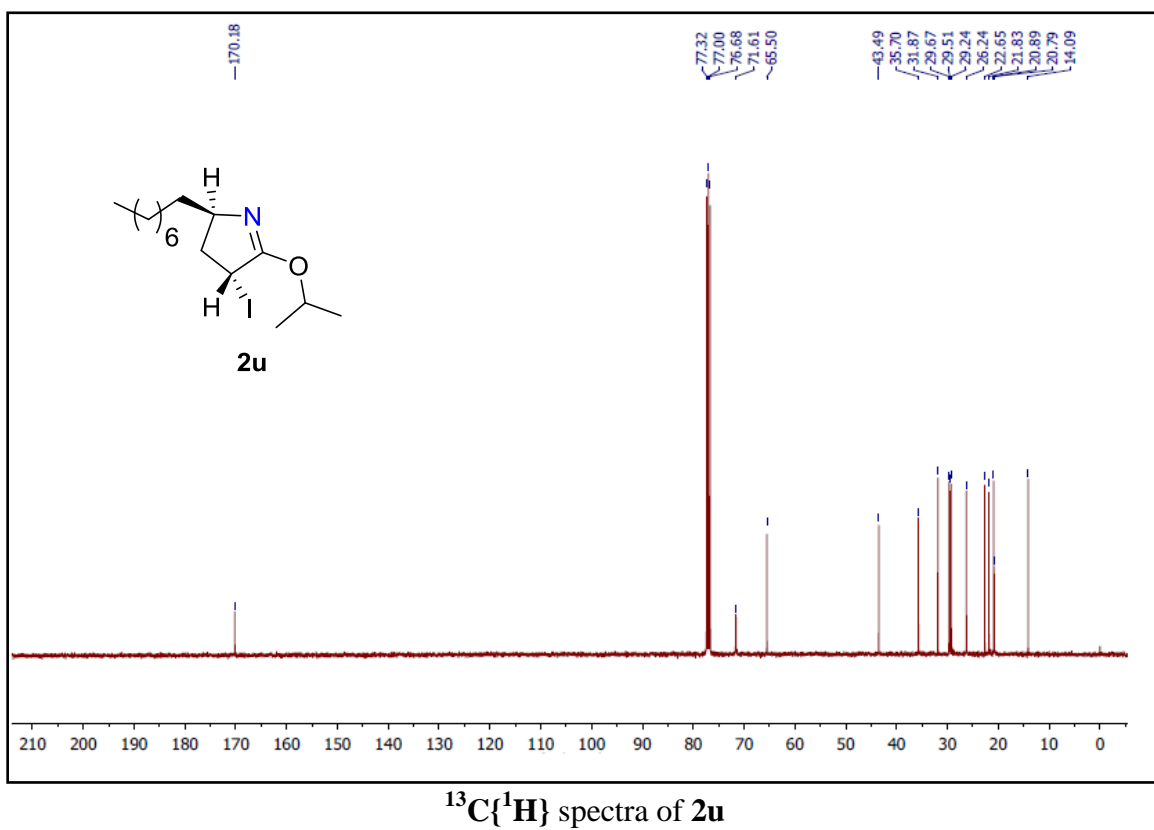
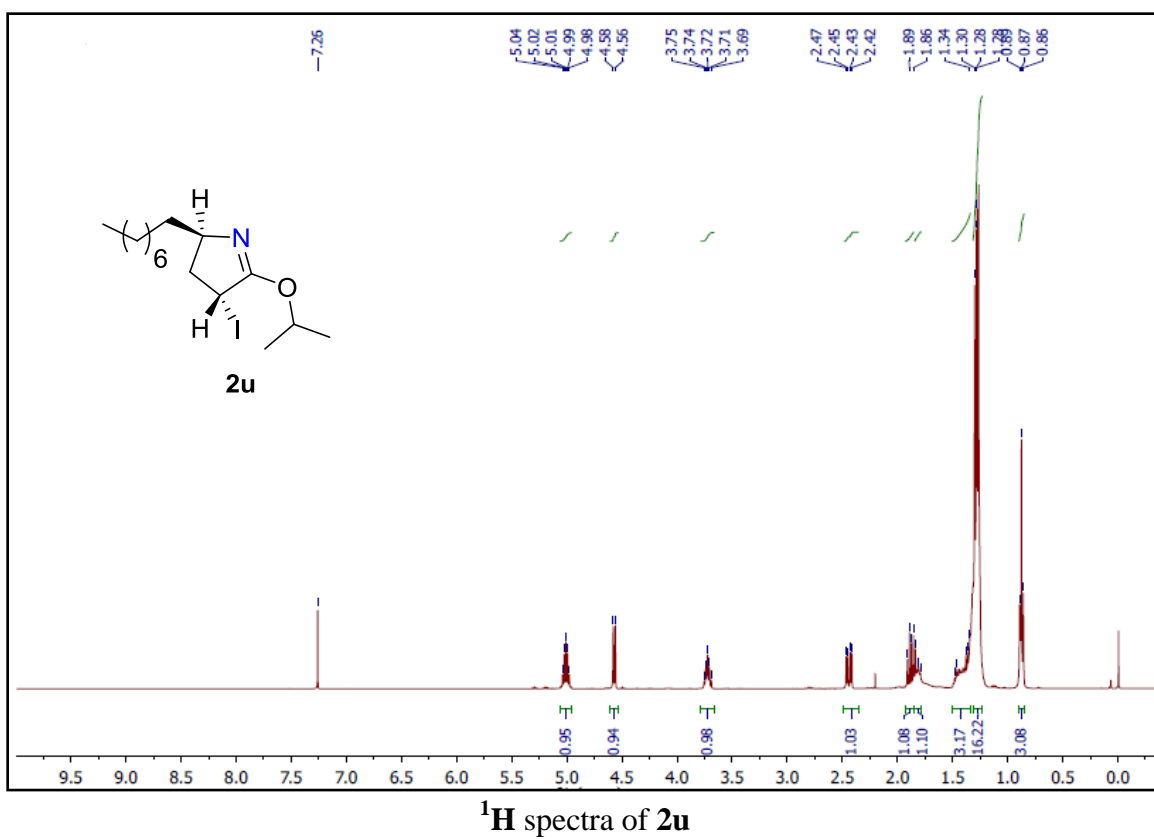
HSQC spectra of **2t**

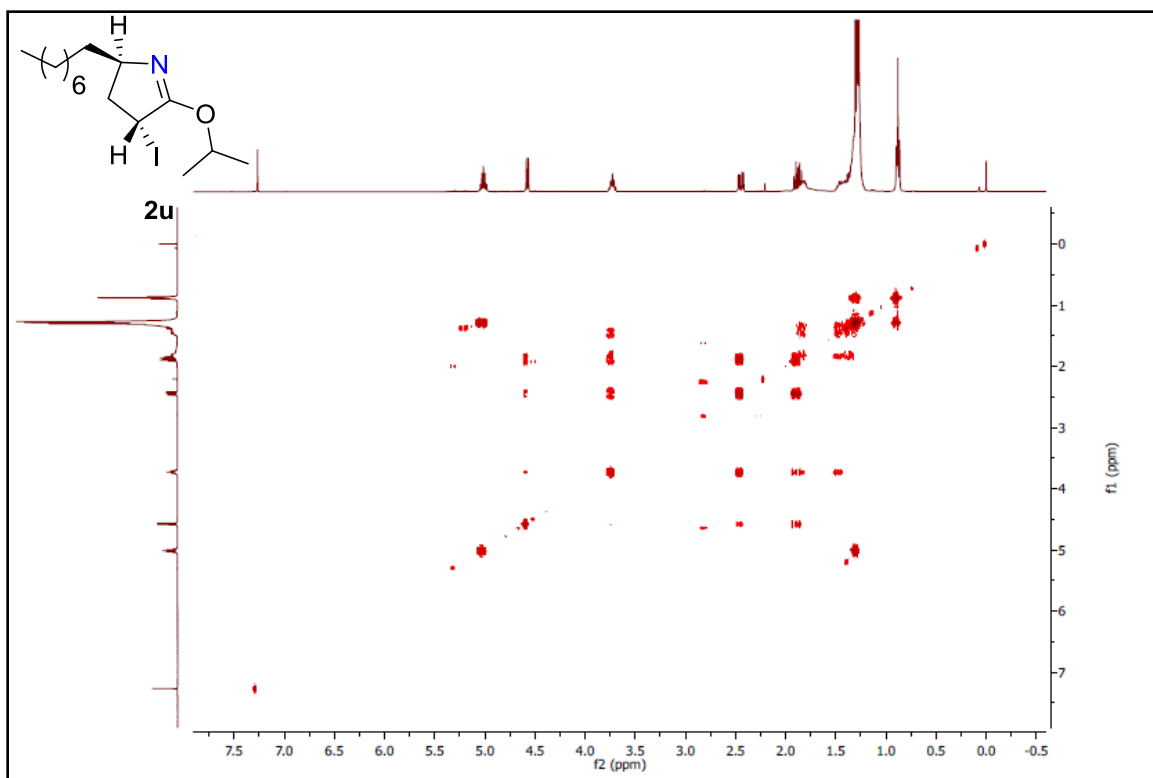


NOESY spectra of **2t**

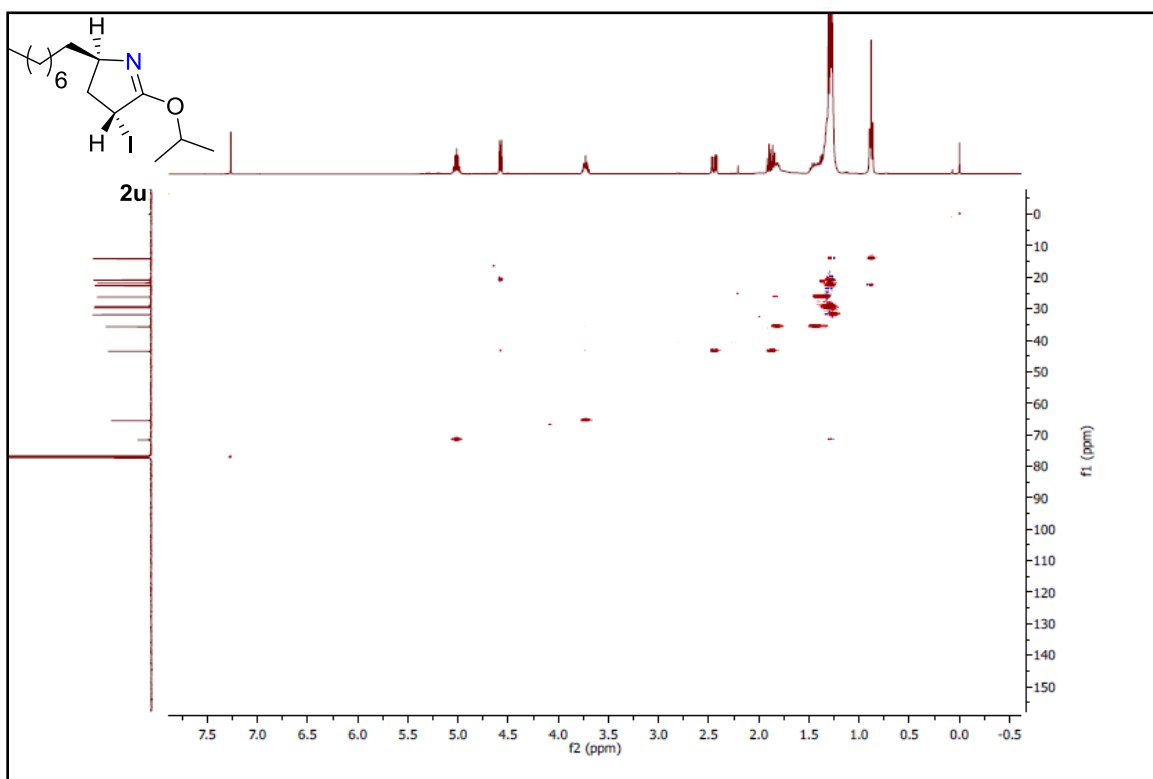


NOESY spectra of **2t**

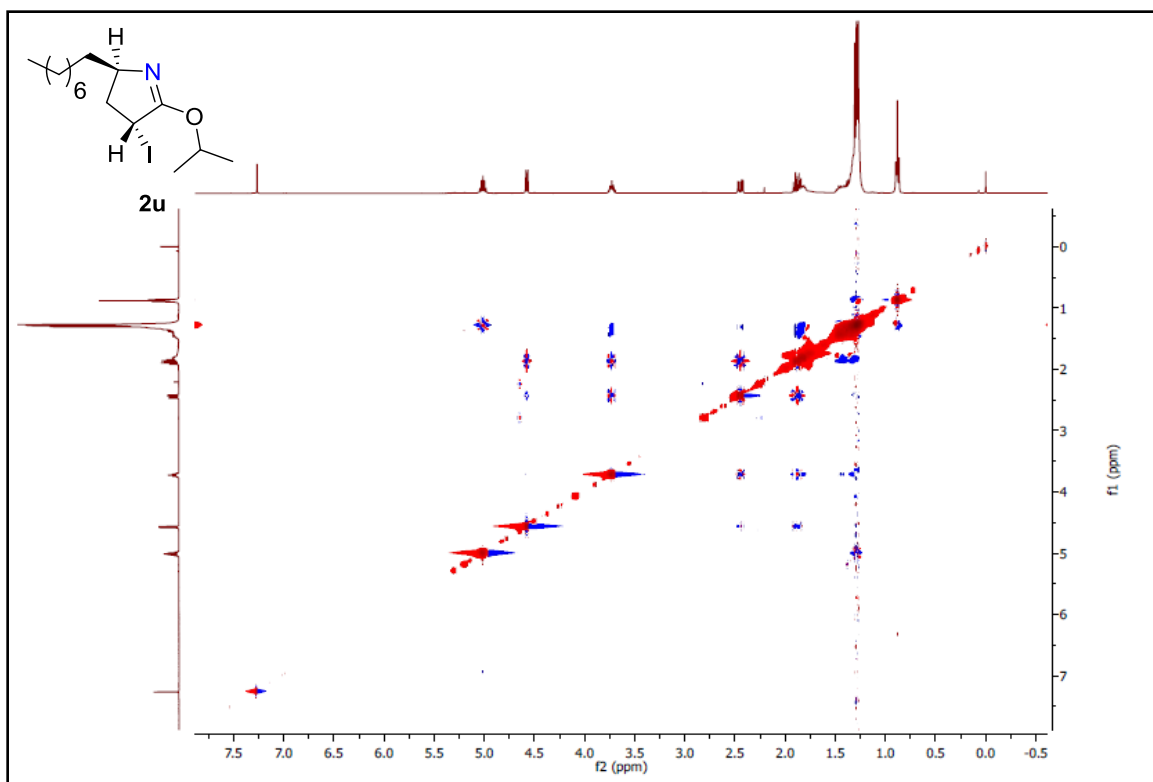




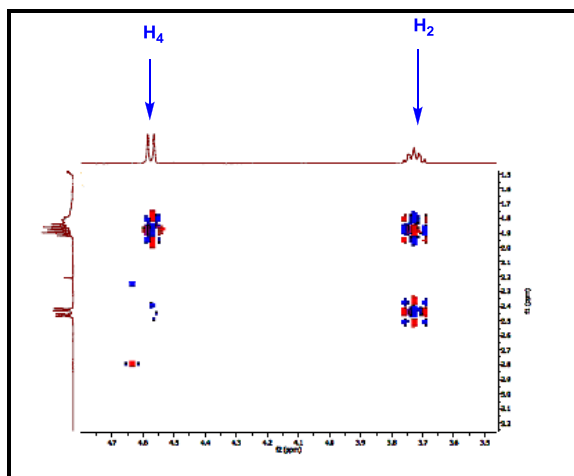
COSY spectra of **2u**



HSQC spectra of **2u**

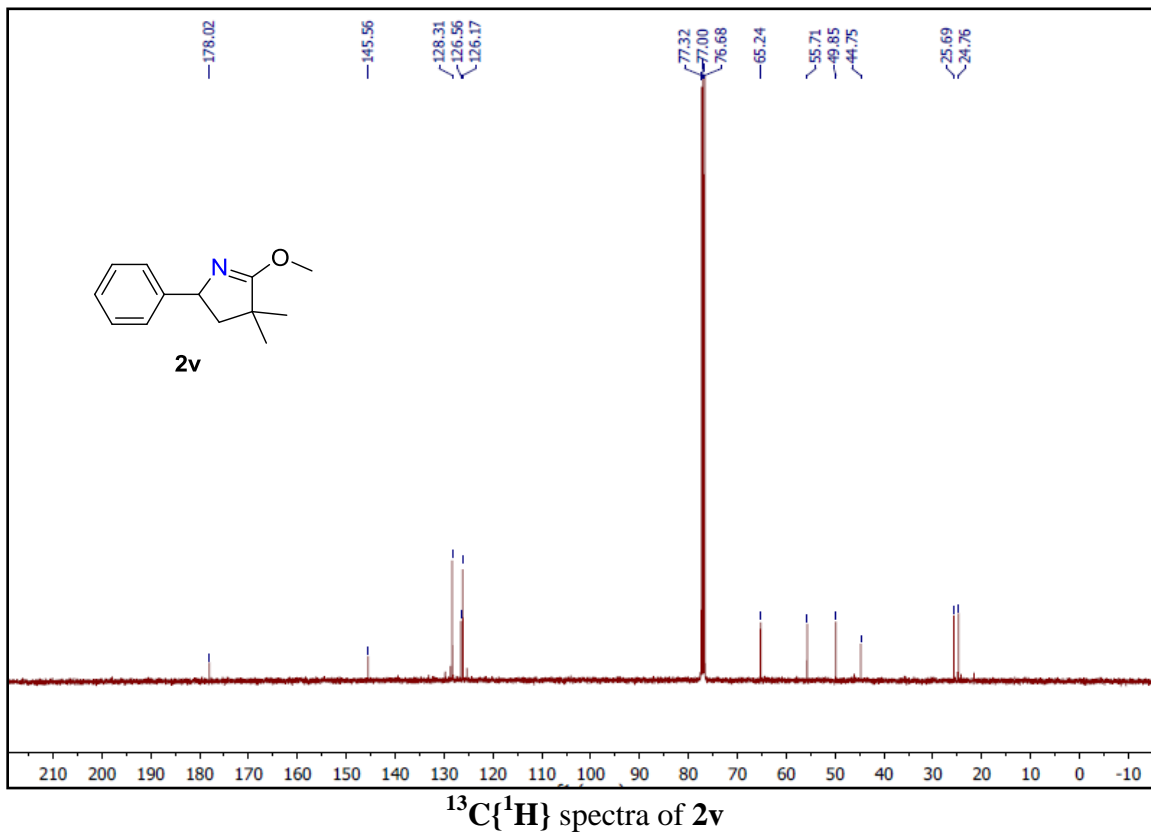
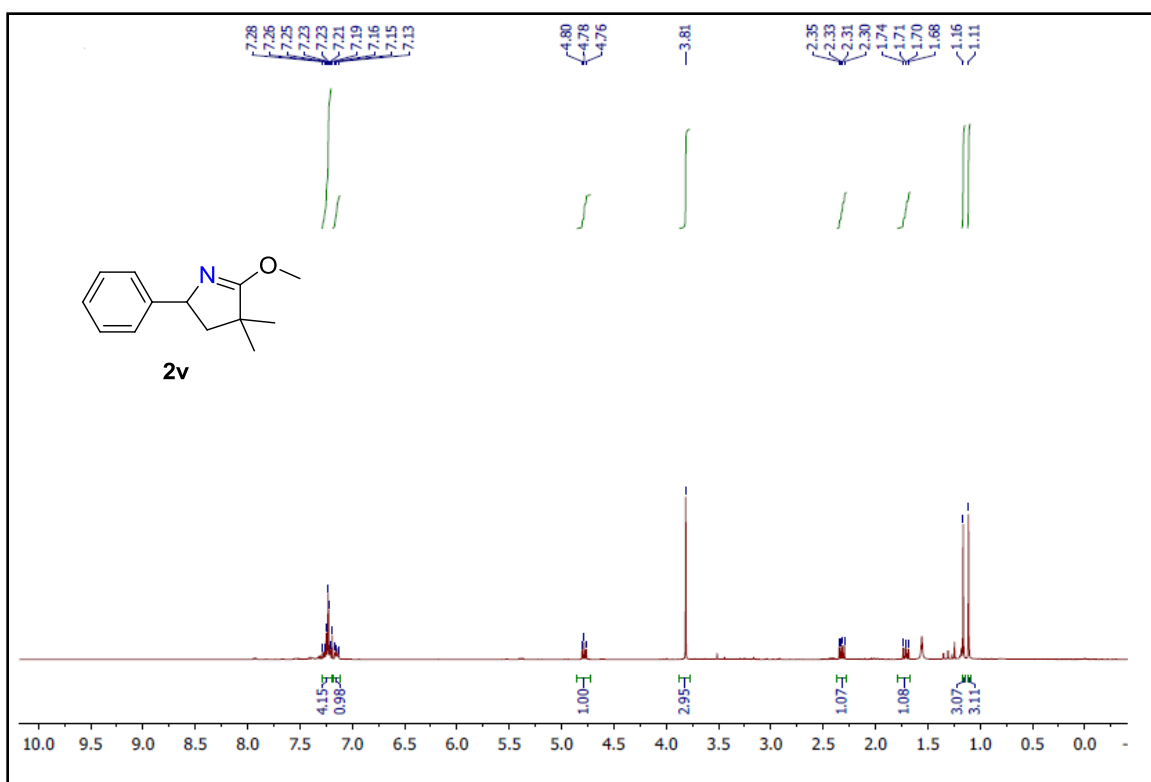


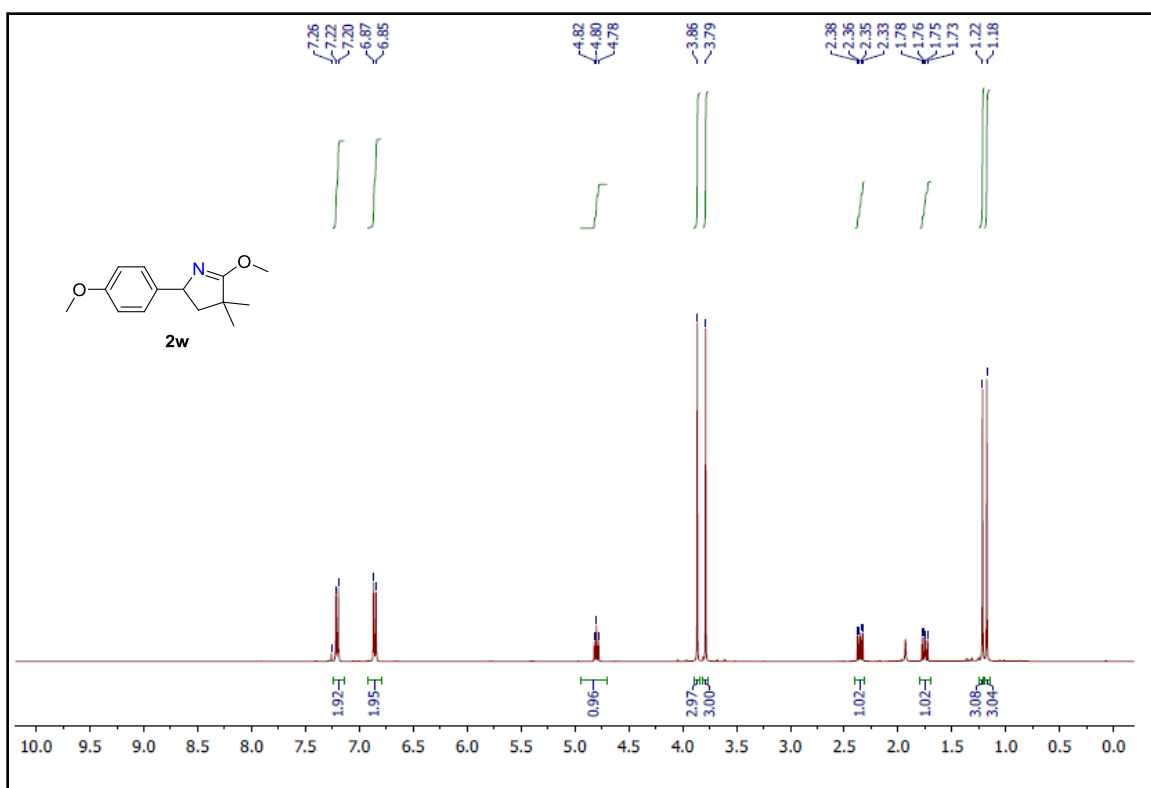
NOESY spectra of **2u**



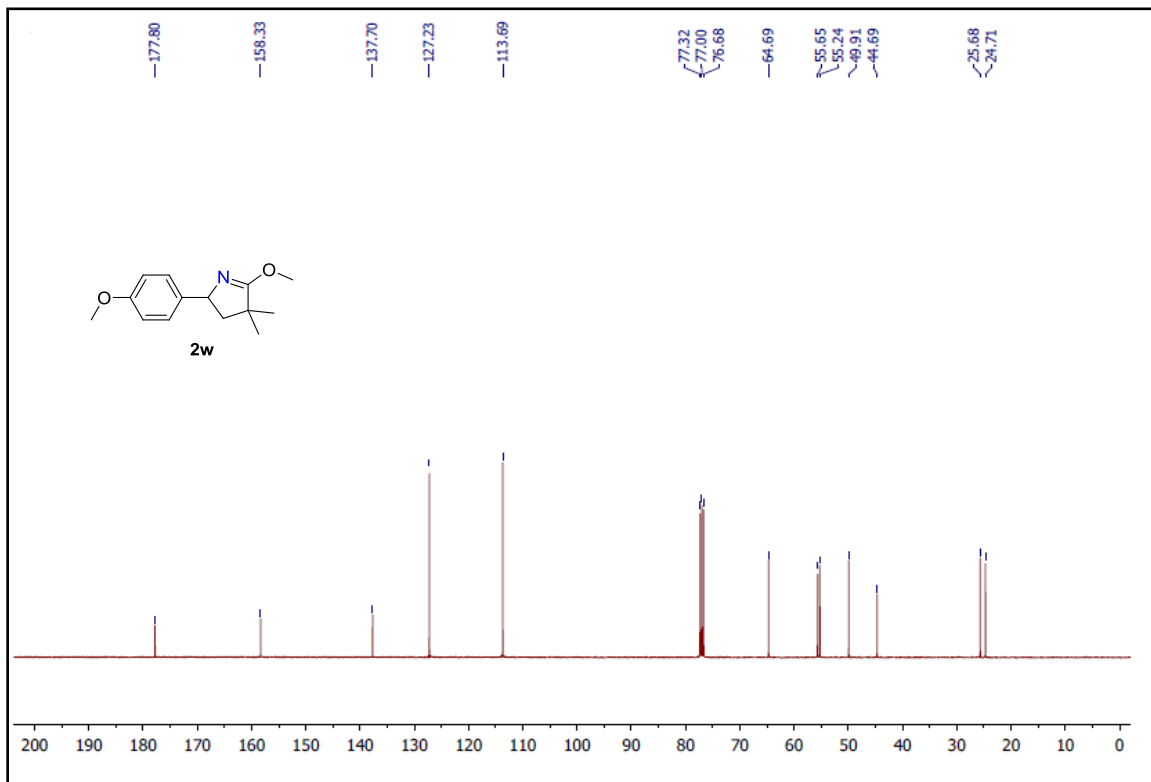
**2u**  
major diastereomer

NOESY spectra of **2u**

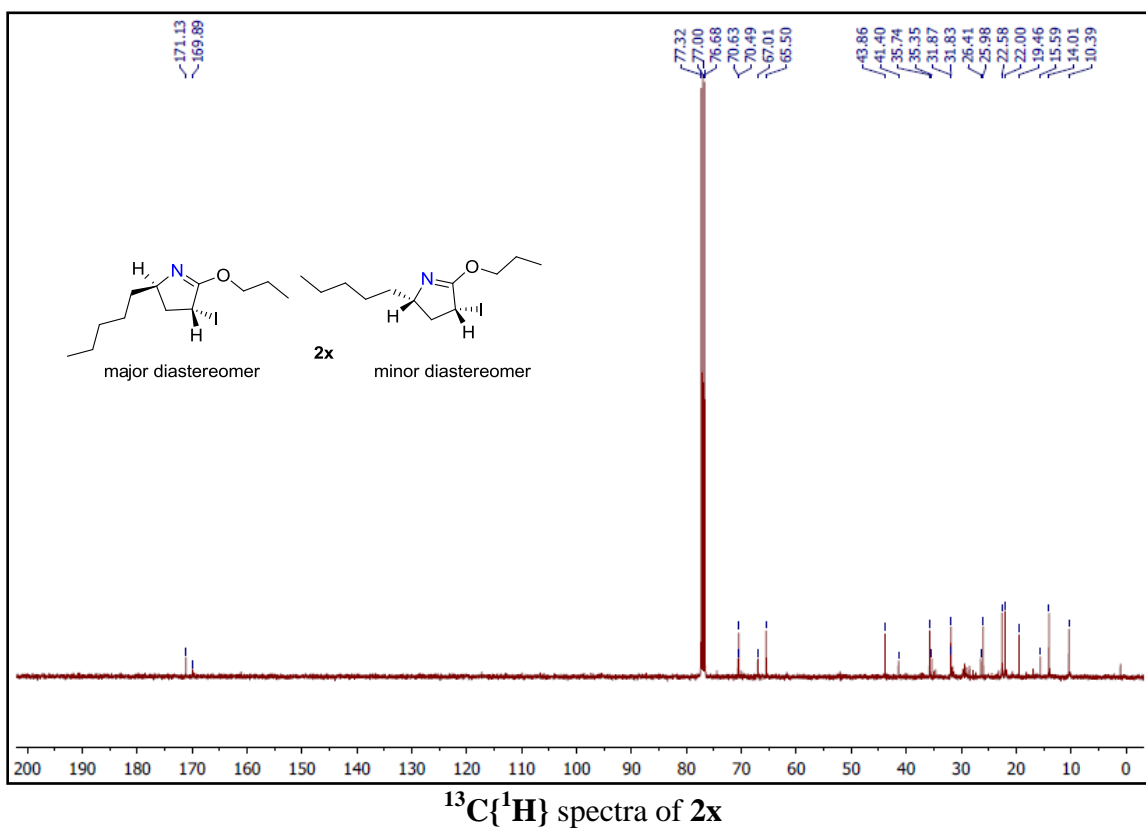
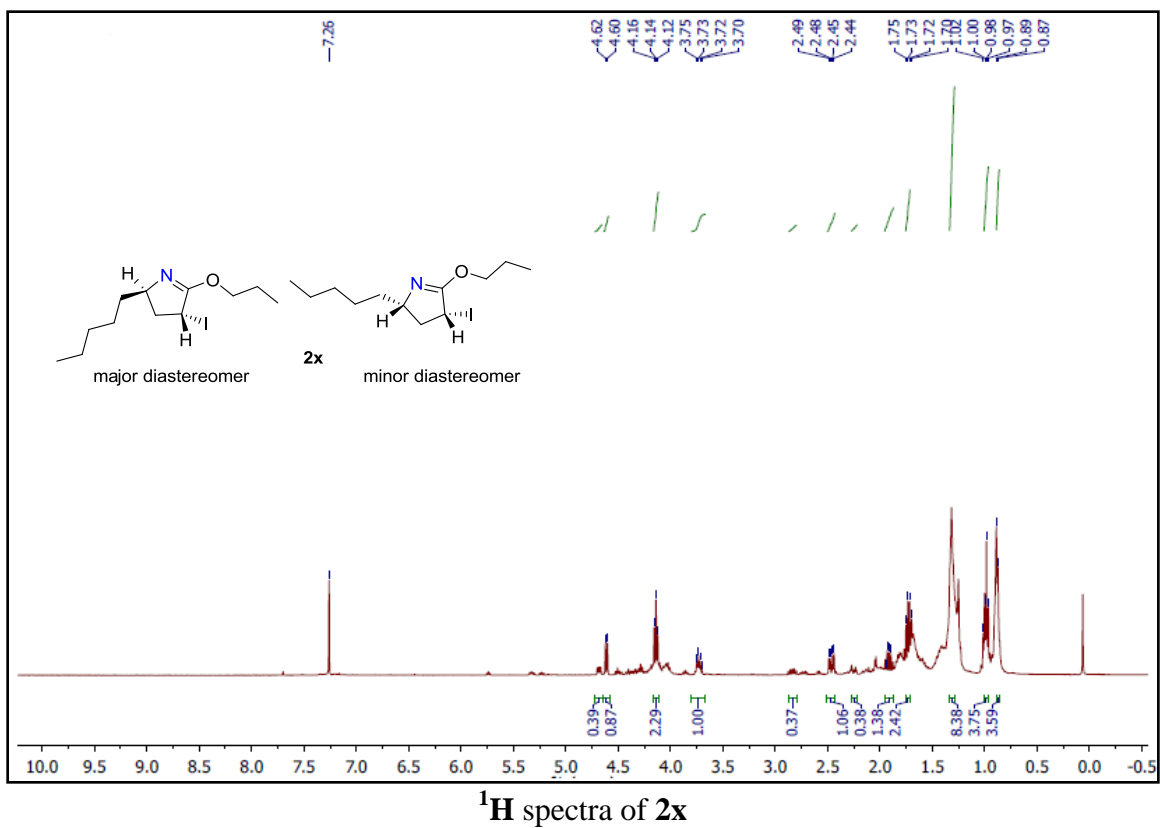


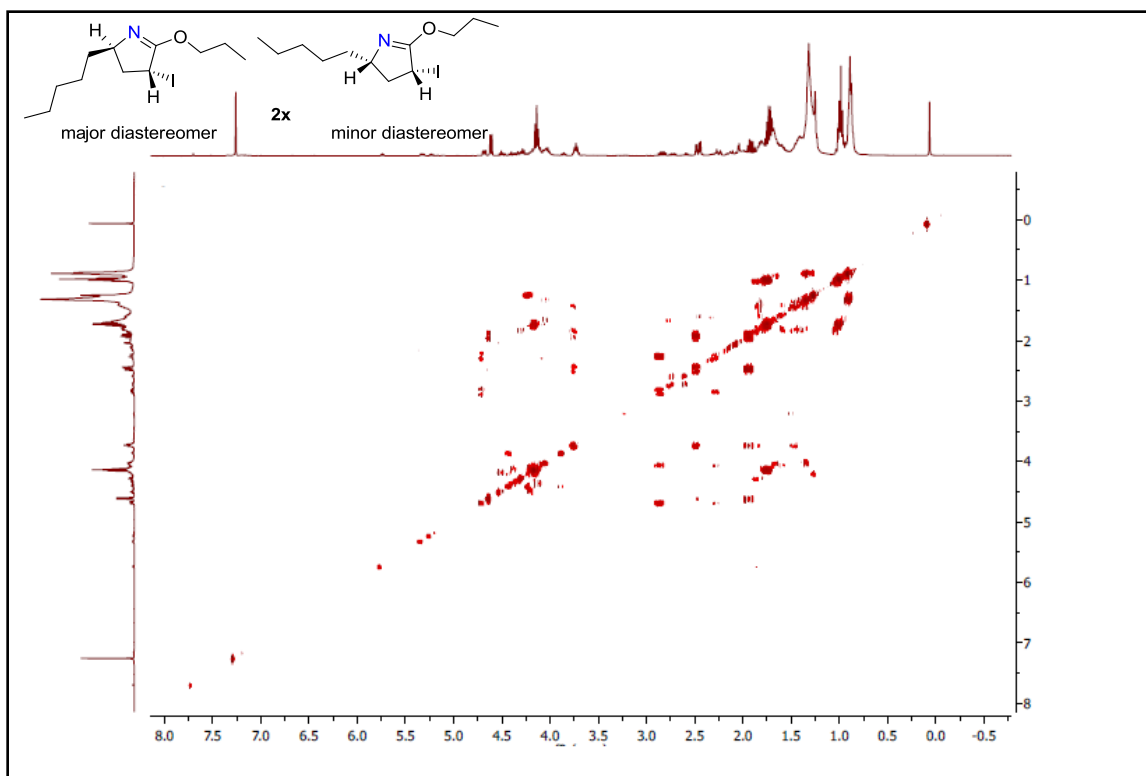


<sup>1</sup>H spectra of 2w

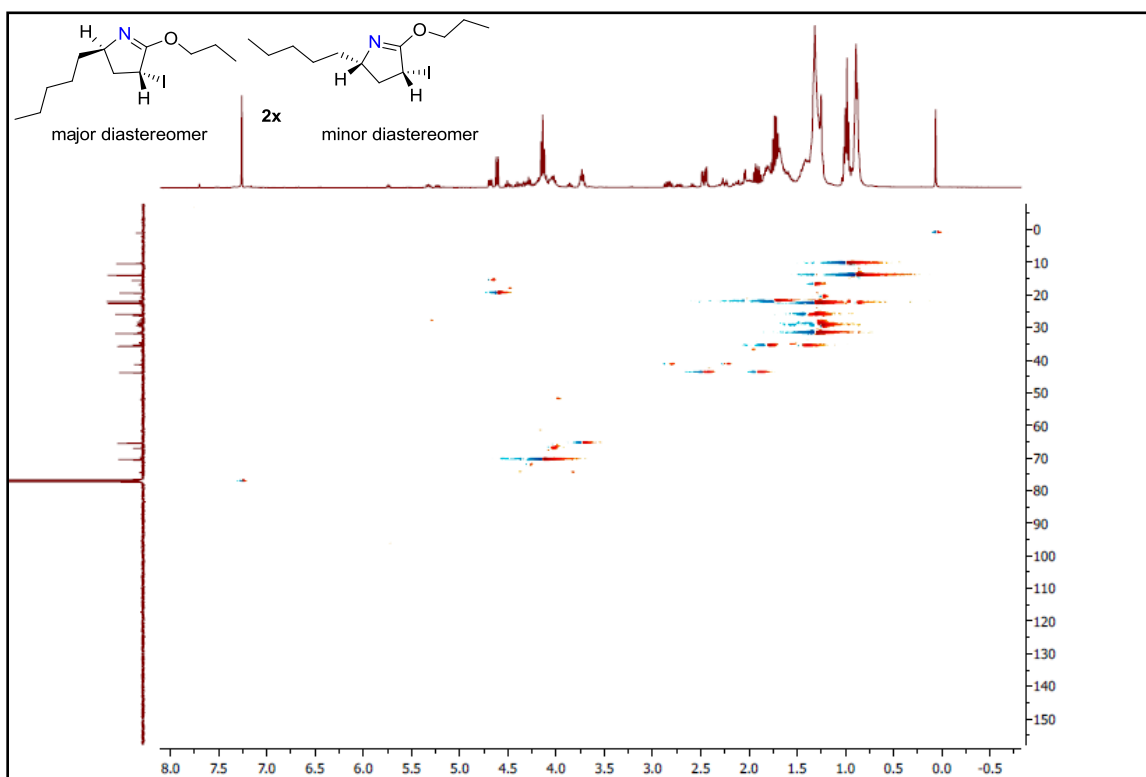


<sup>13</sup>C{<sup>1</sup>H} spectra of 2w

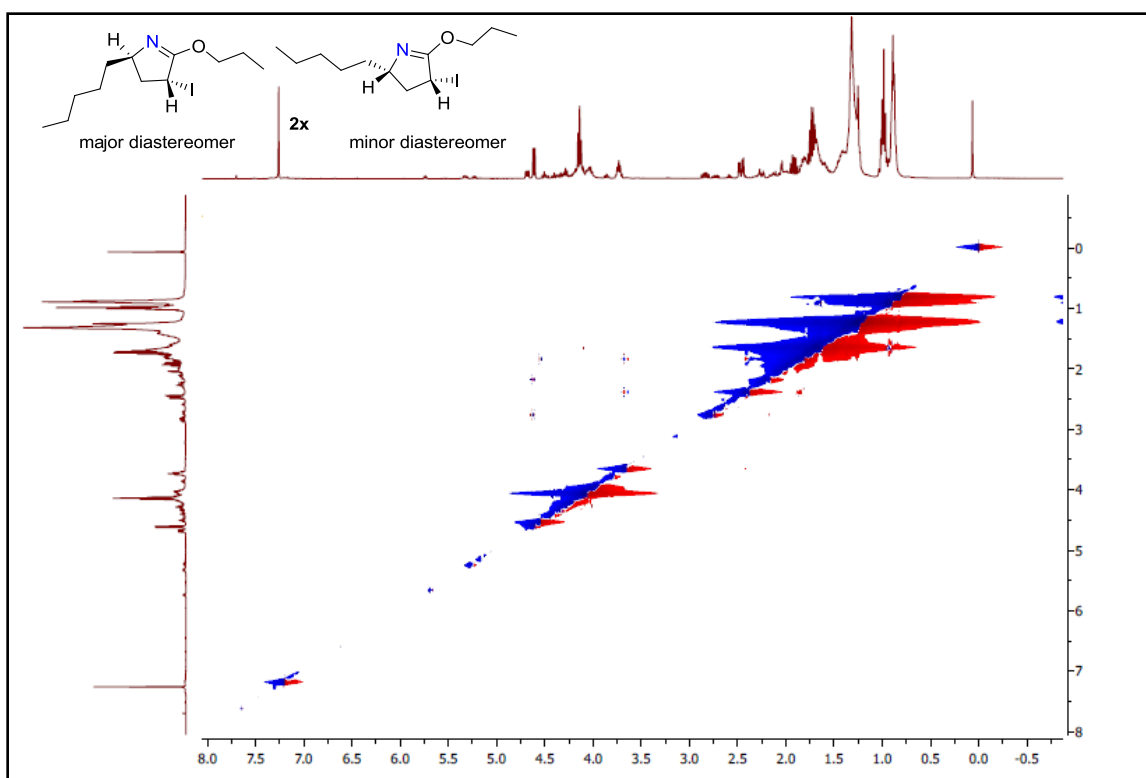




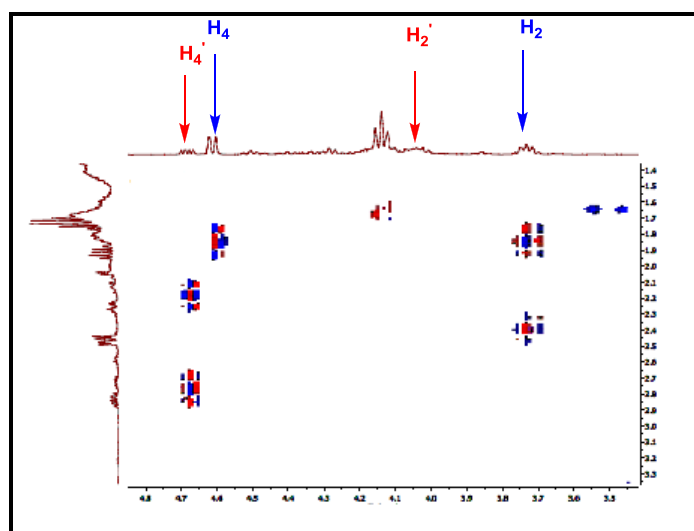
COSY spectra of **2x**



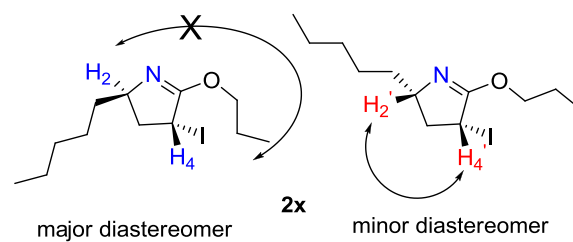
HSQC spectra of **2x**

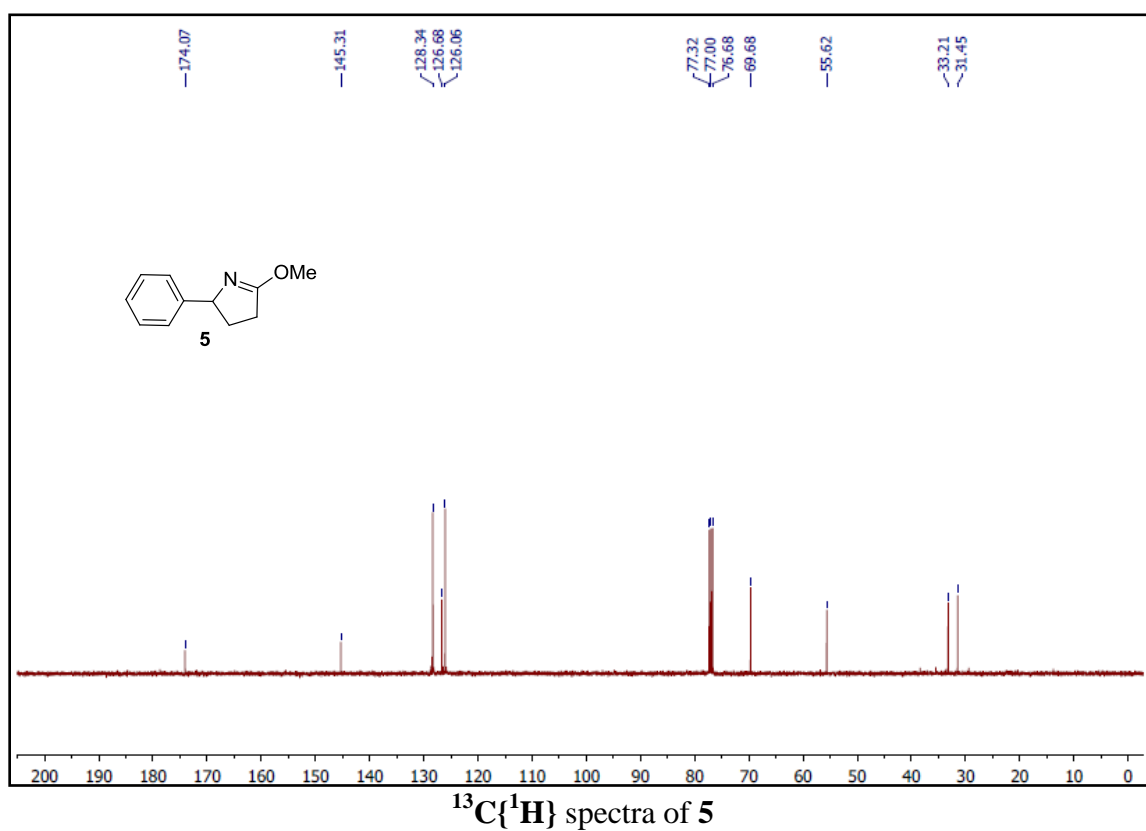
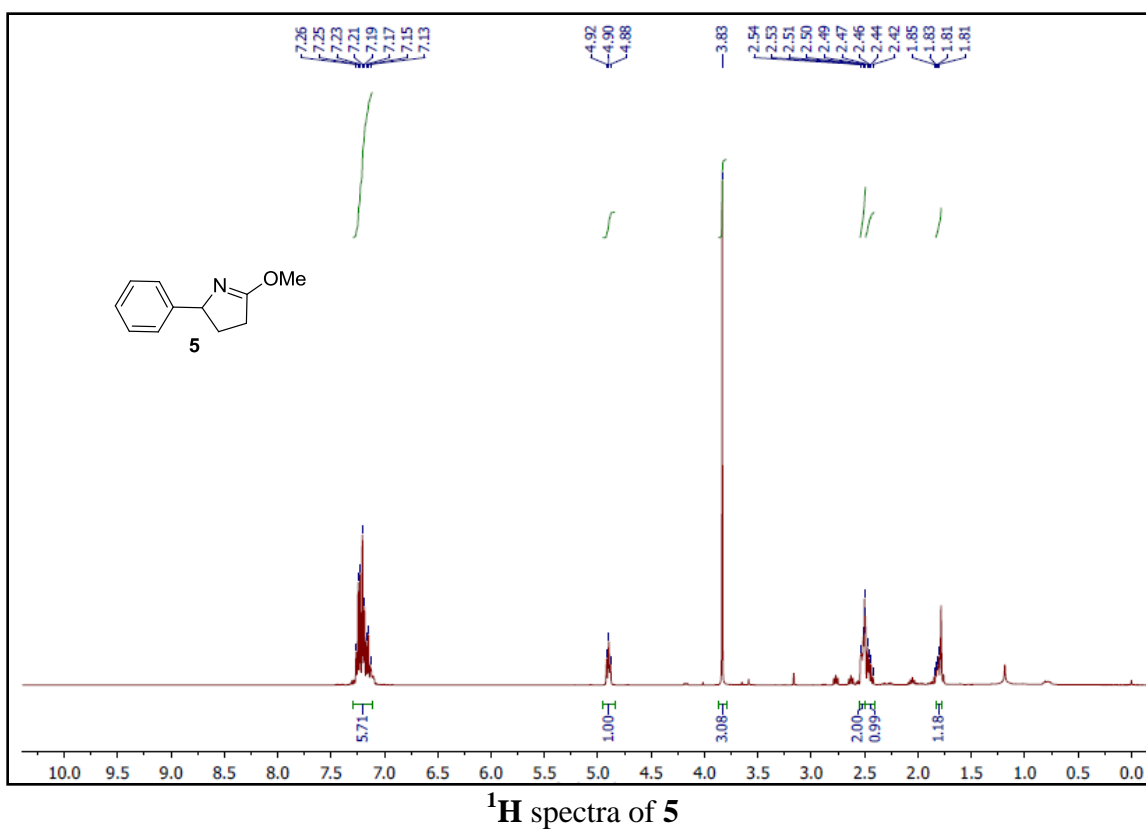


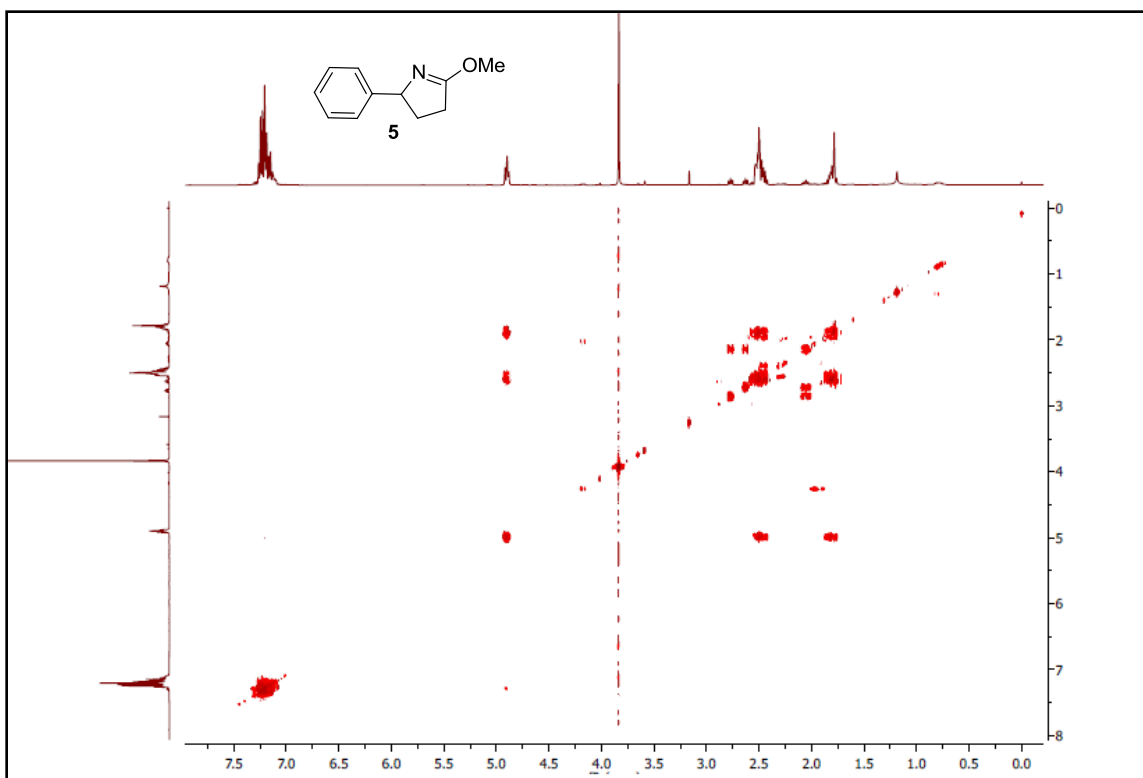
NOESY spectra of **2x**



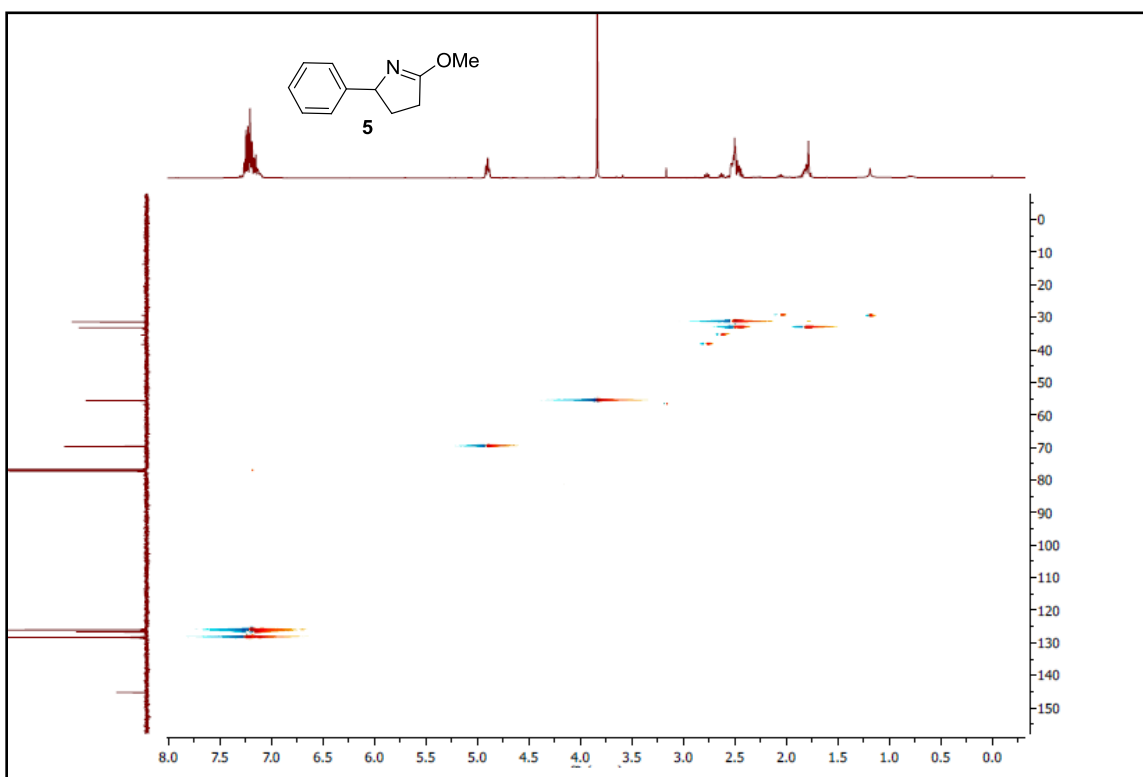
NOESY spectra of **2x**



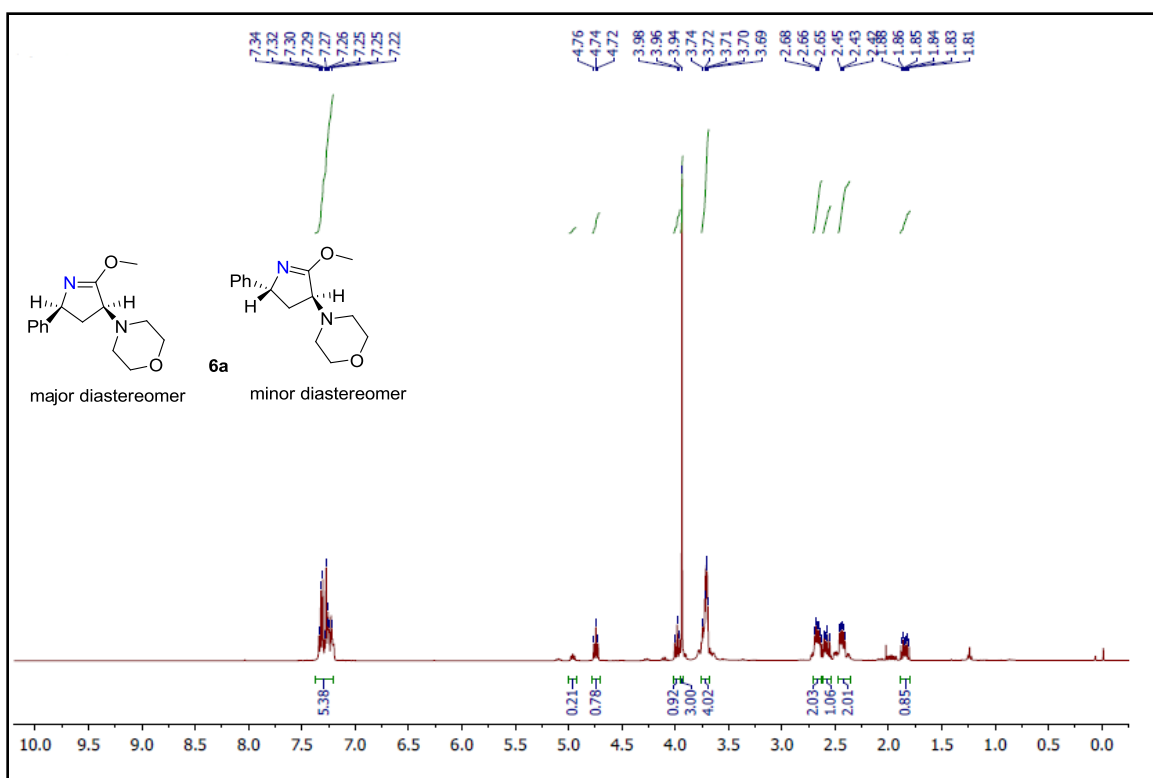




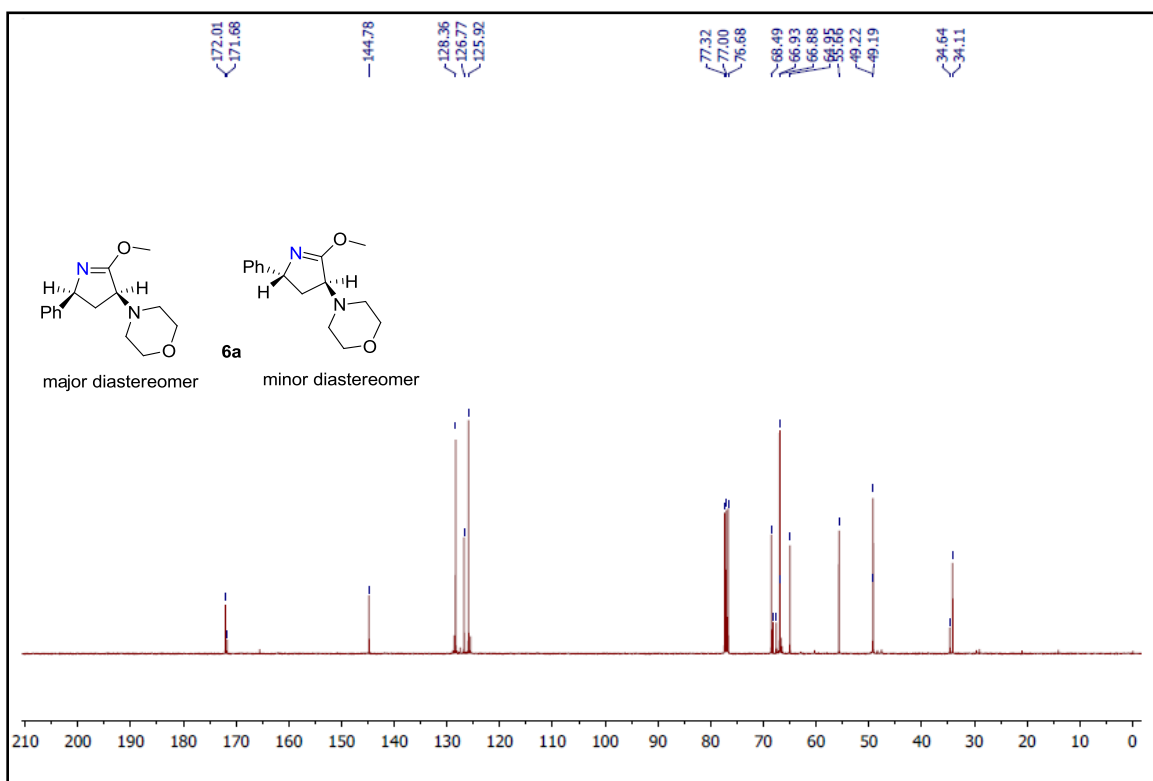
COSY spectra of **5**



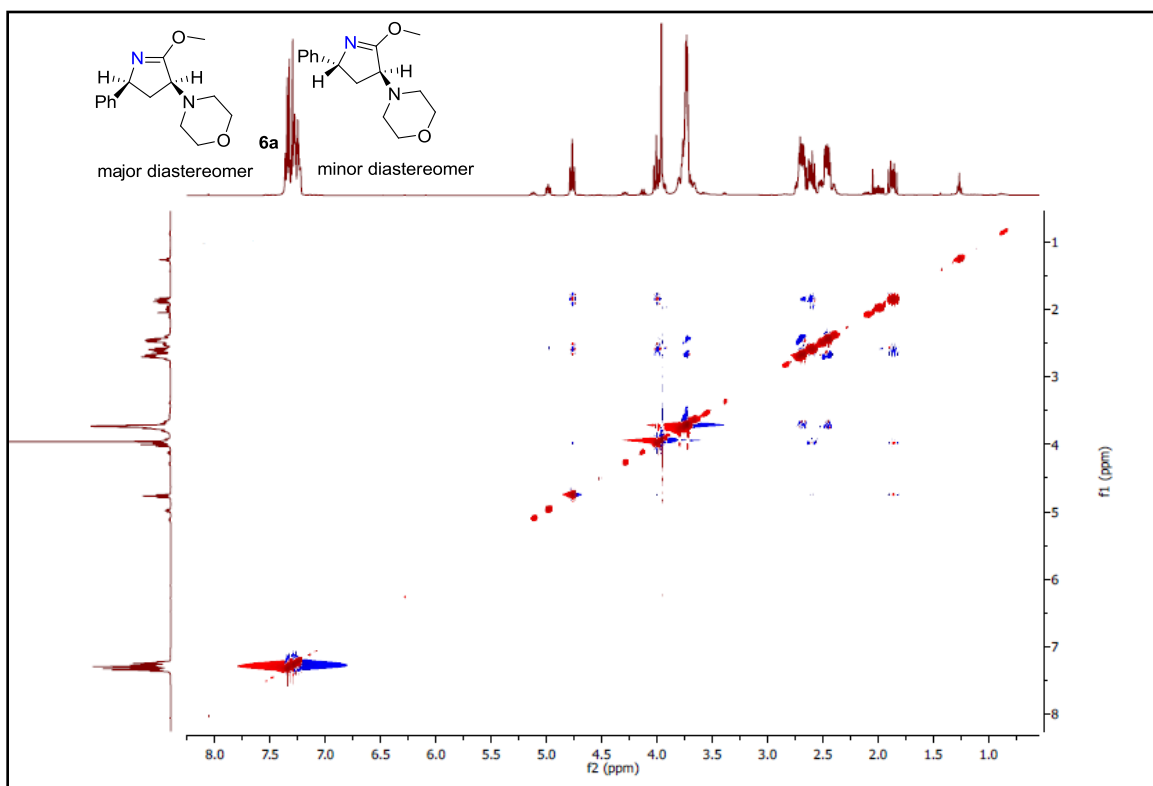
HSQC spectra of **5**



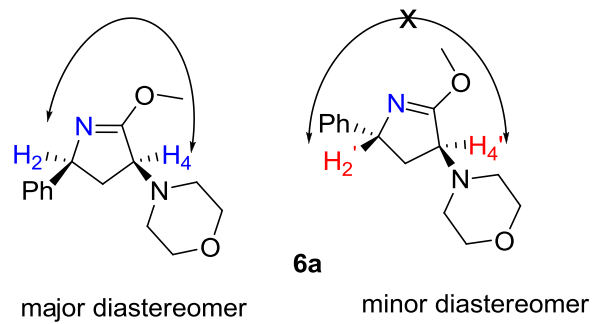
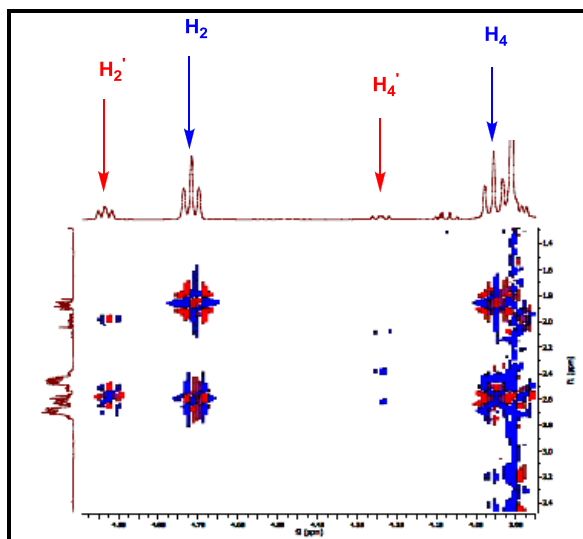
<sup>1</sup>H spectra of 6a



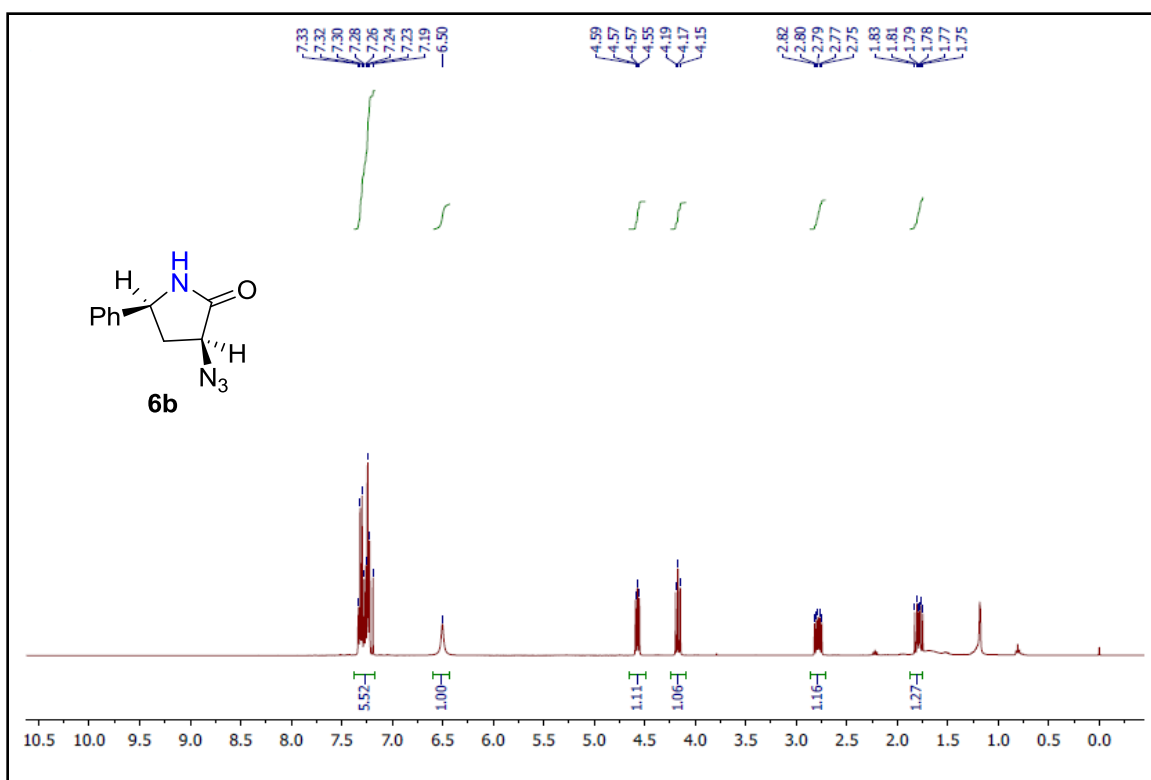
<sup>13</sup>C{<sup>1</sup>H} spectra of 6a



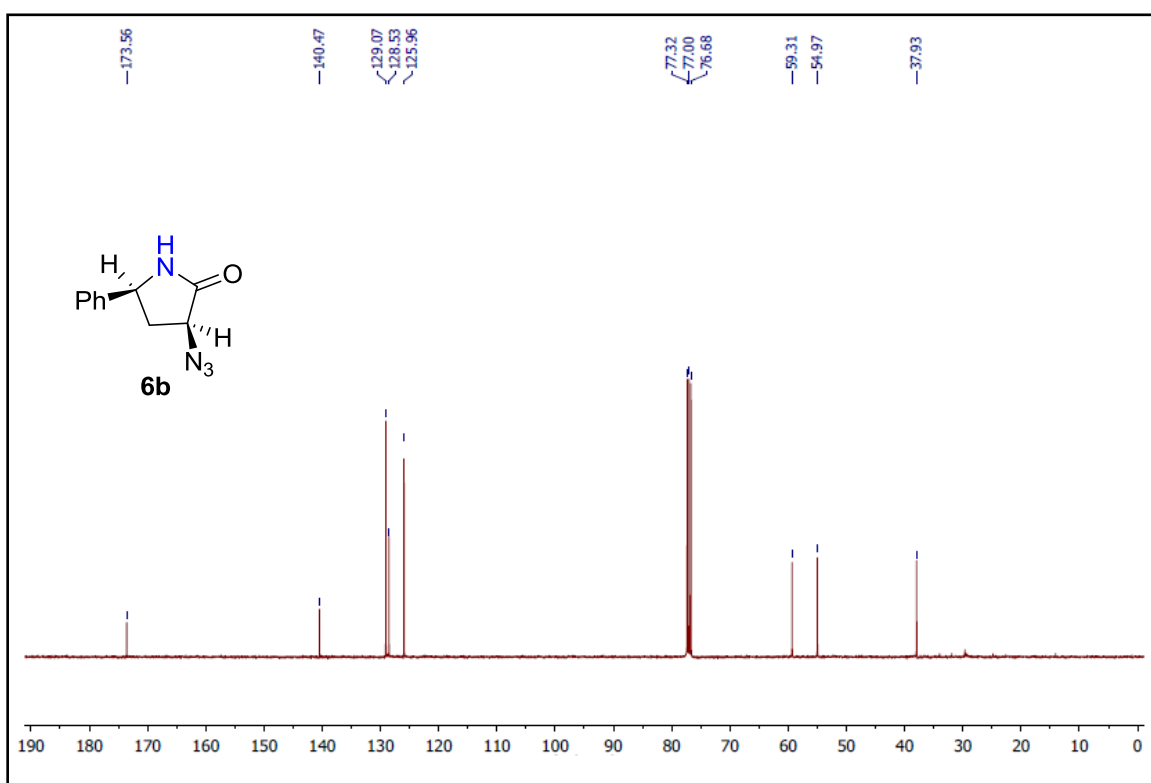
NOESY spectra of **6a**



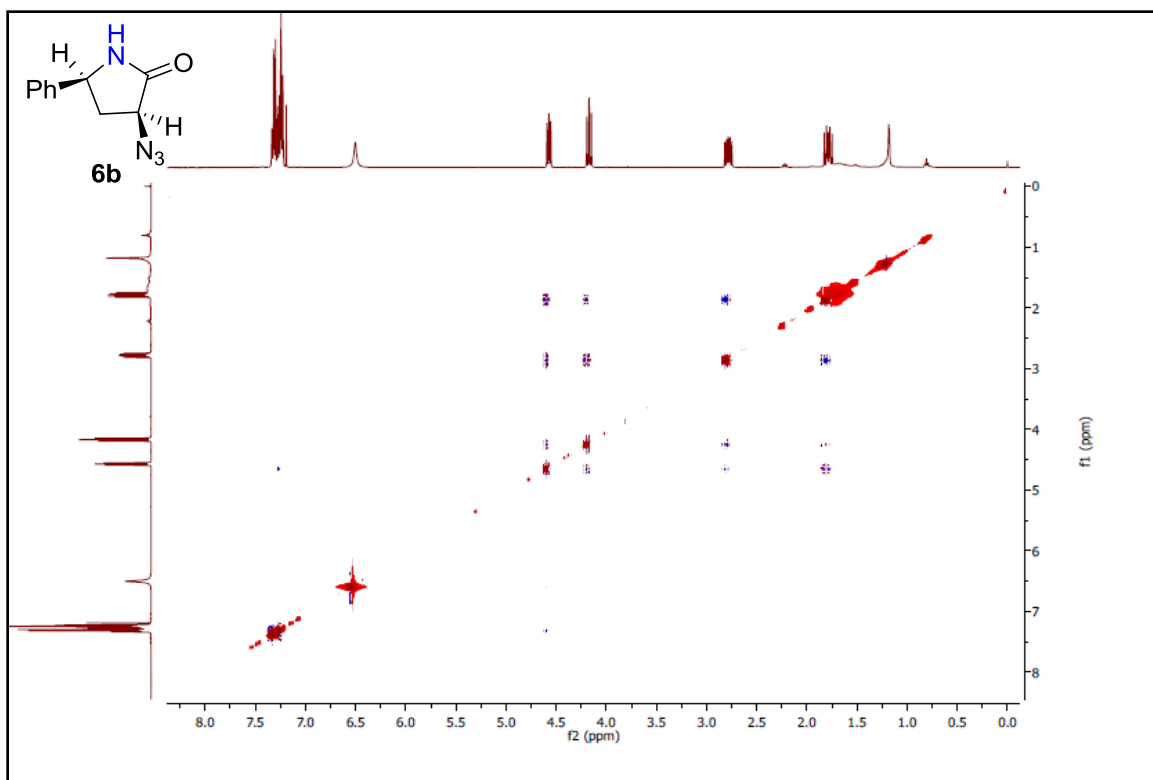
NOESY spectra of **6a**



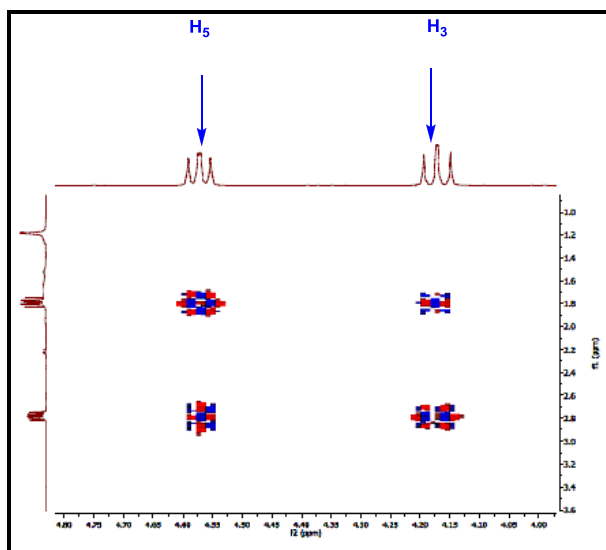
<sup>1</sup>H spectra of **6b**



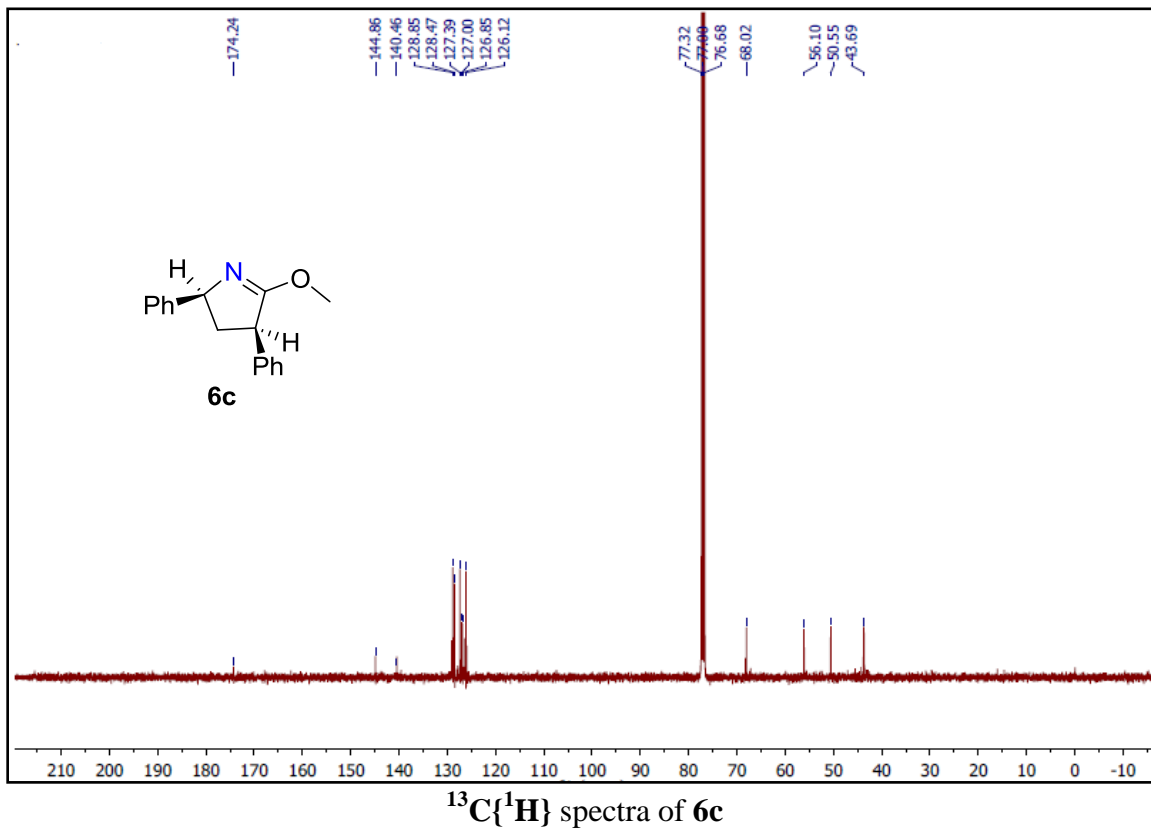
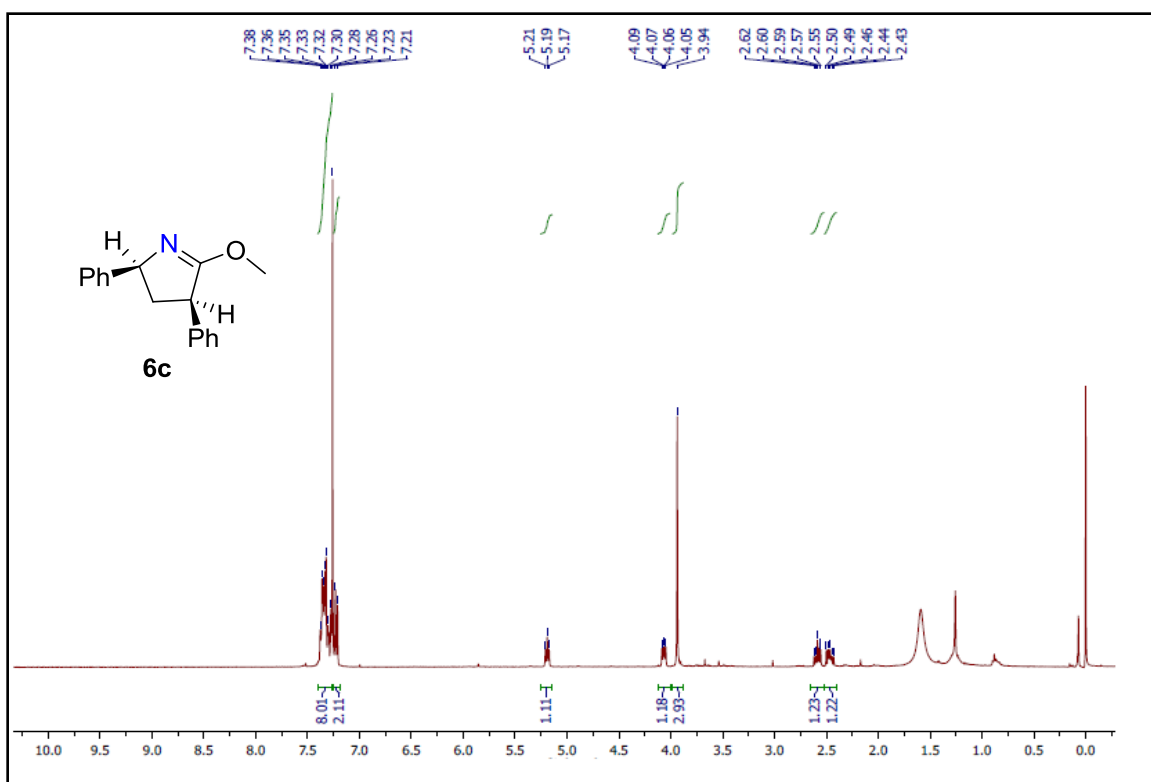
<sup>13</sup>C{<sup>1</sup>H} spectra of **6b**

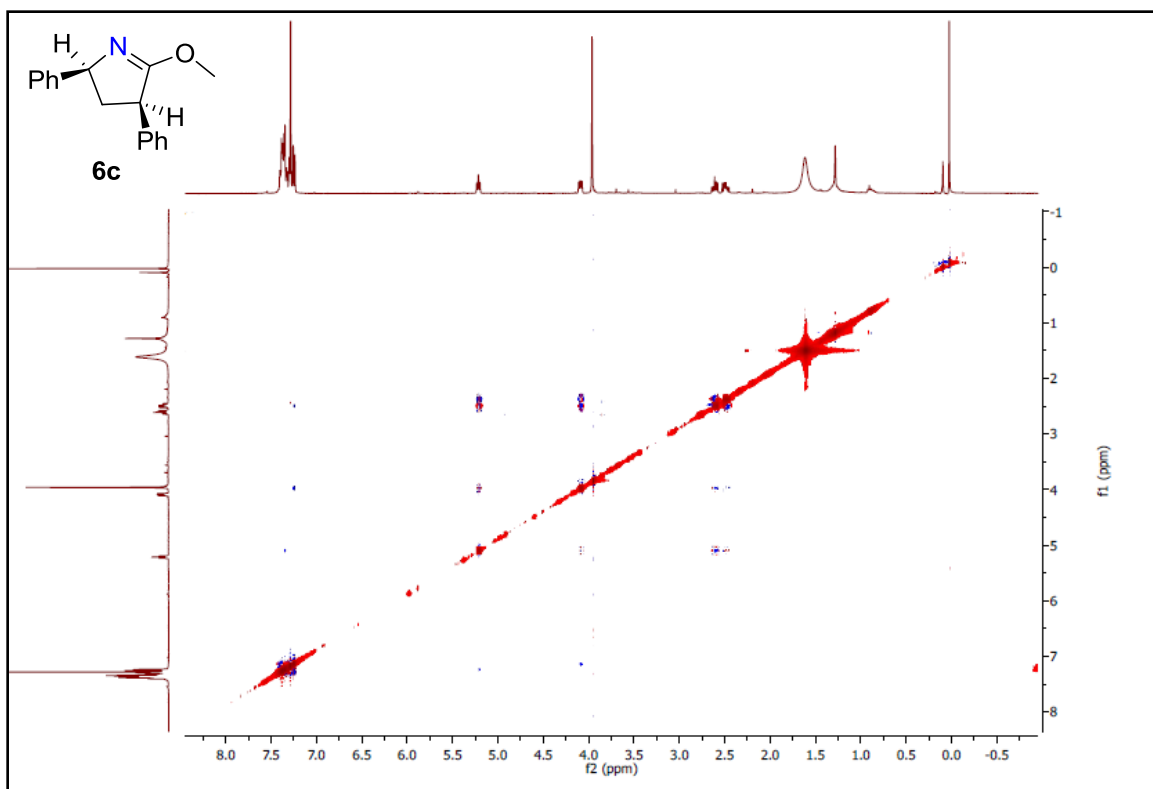


NOESY spectra of **6b**

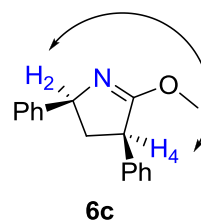
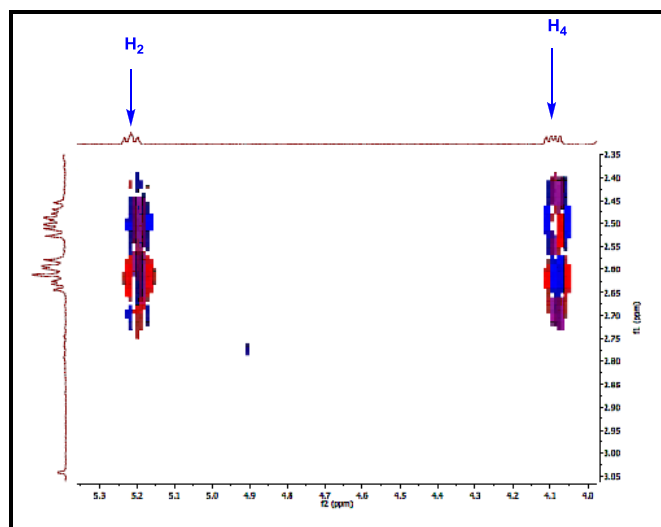


NOESY spectra of **6b**

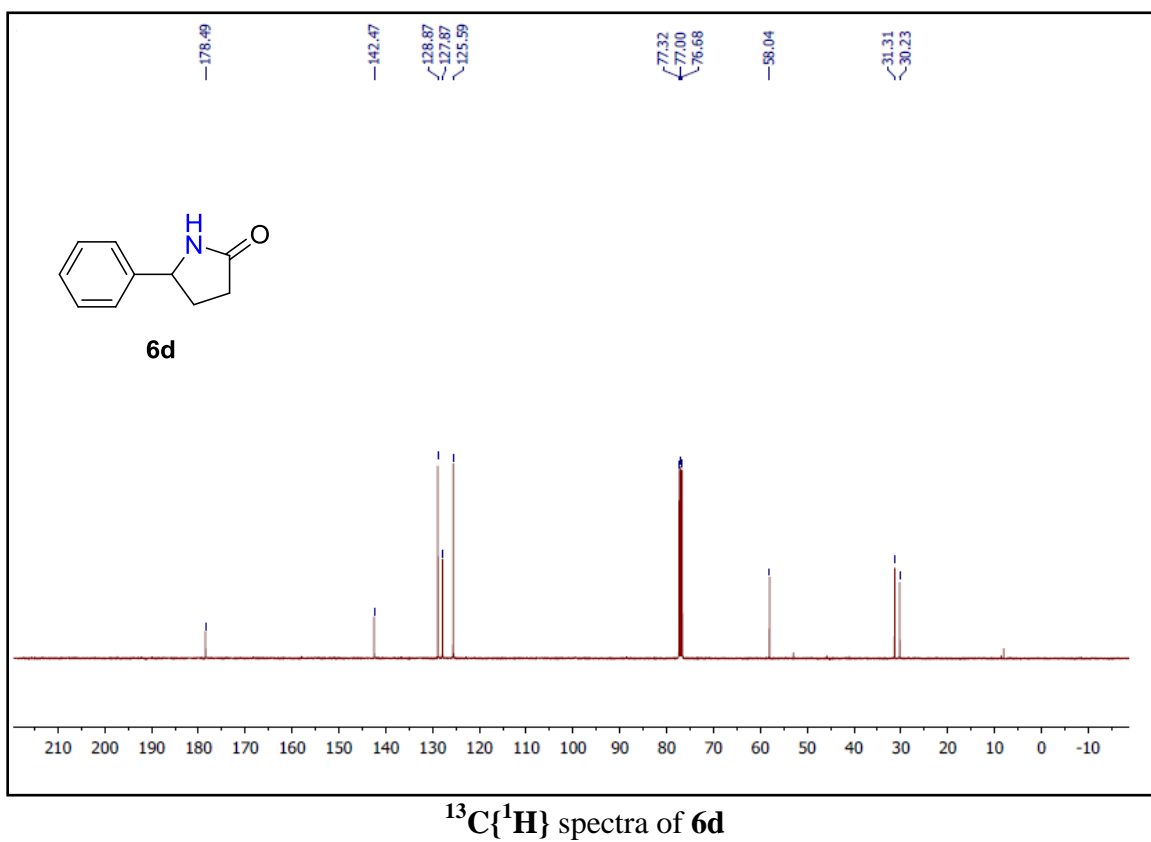
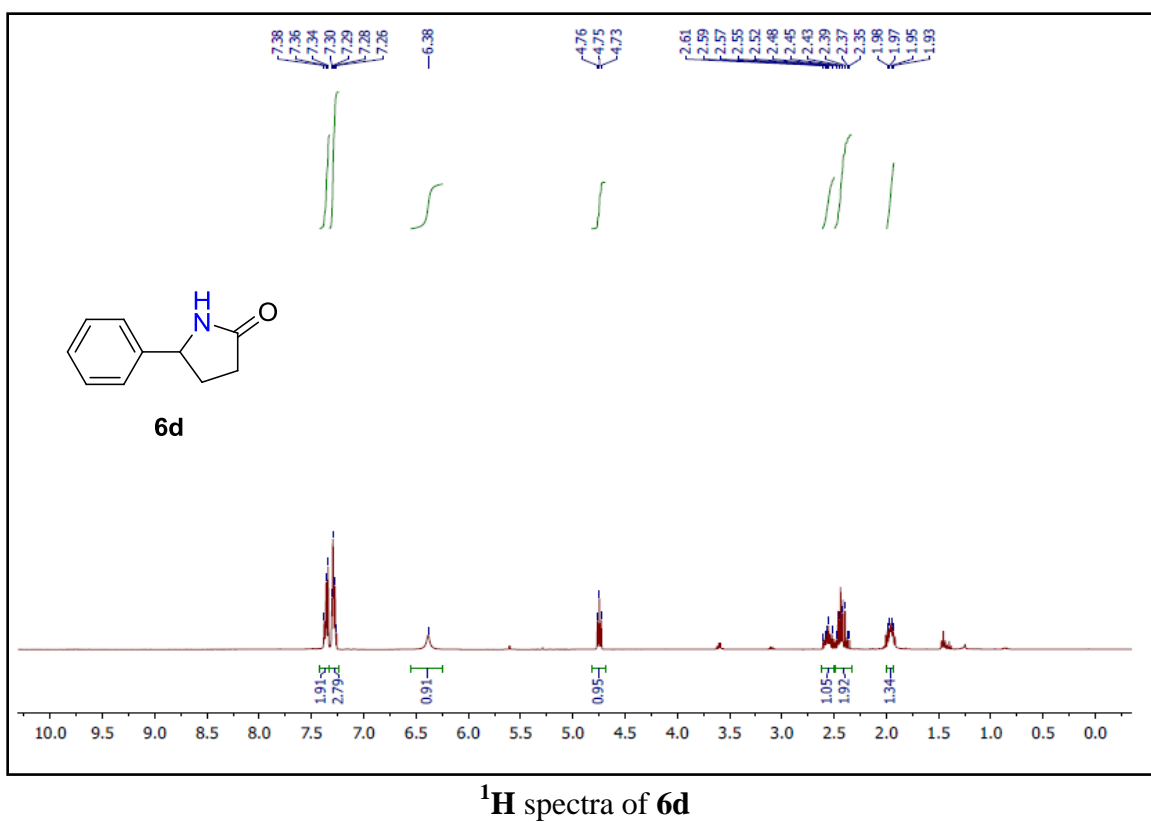


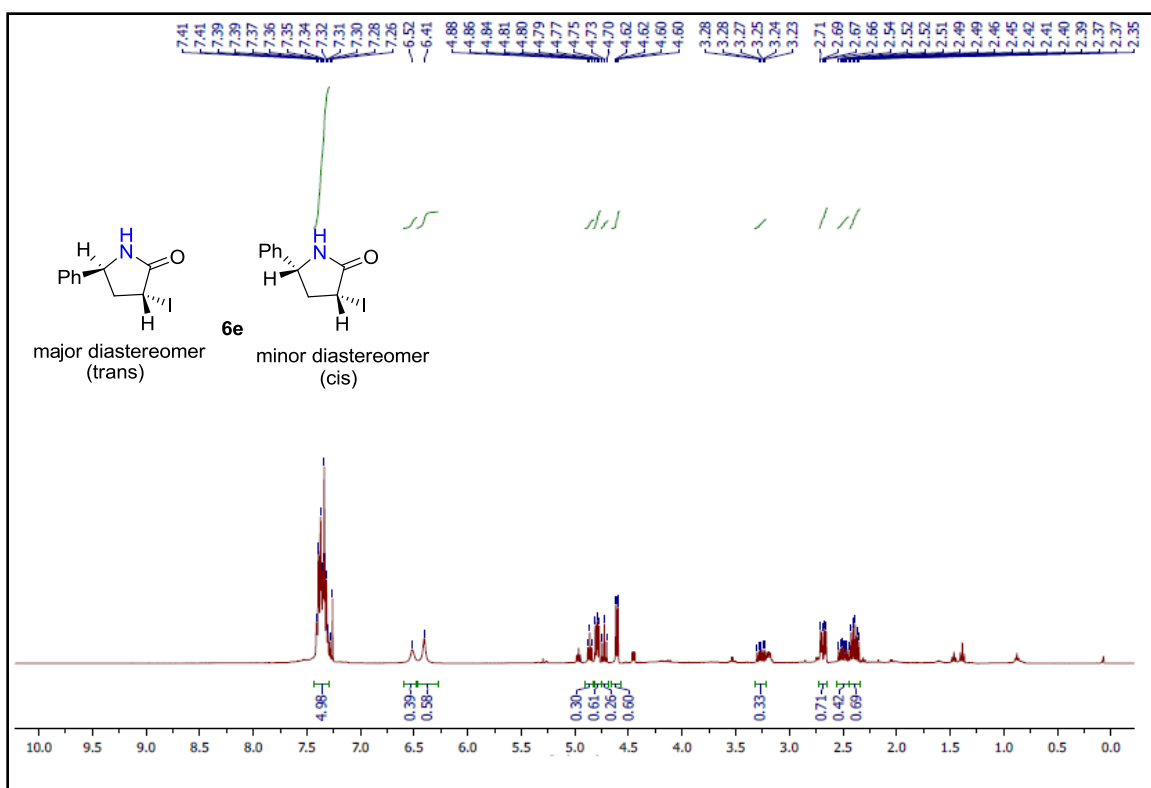


NOESY spectra of **6c**

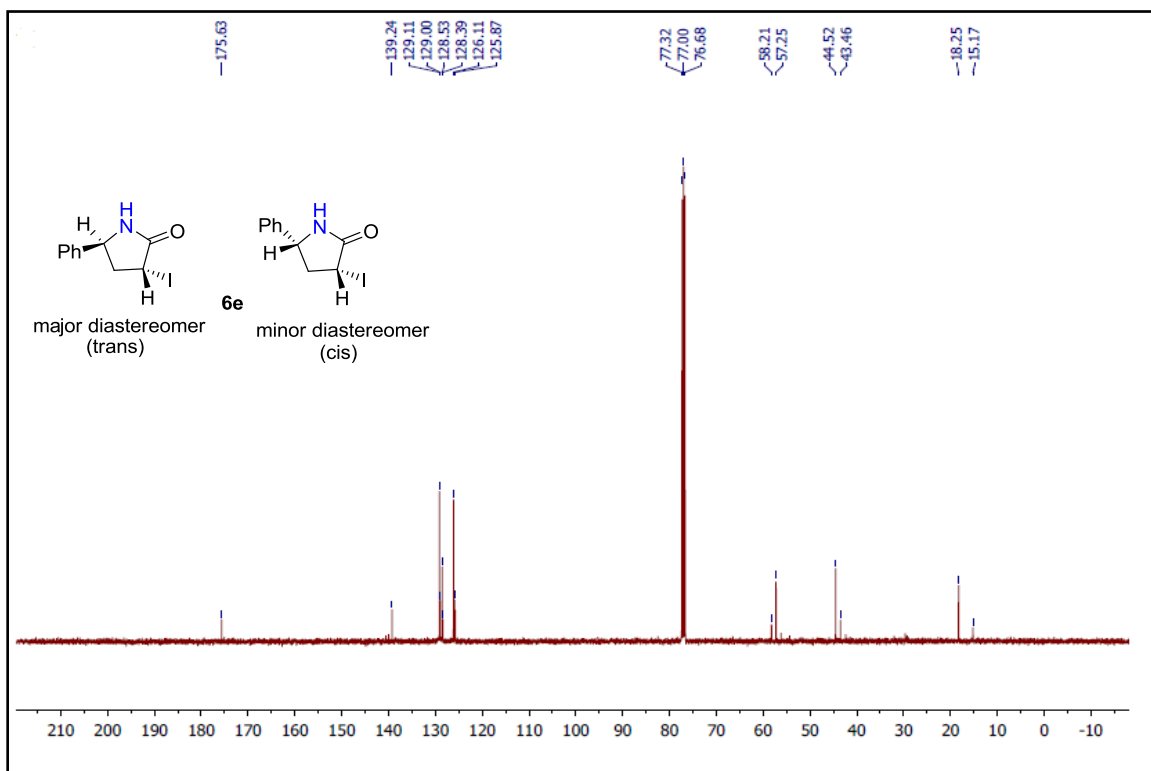


NOESY spectra of **6c**

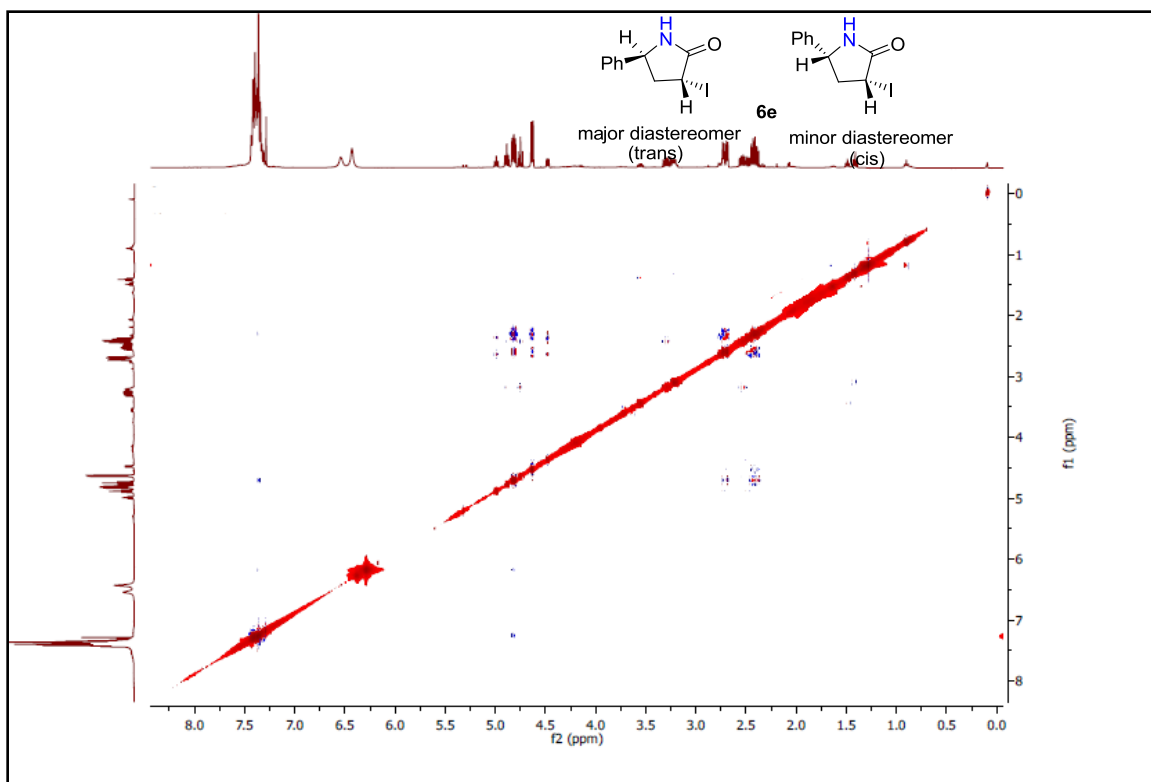




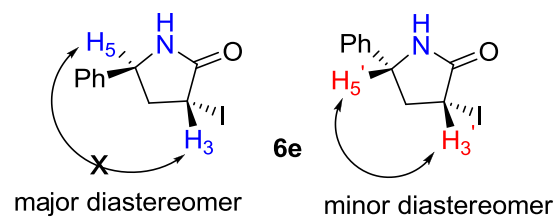
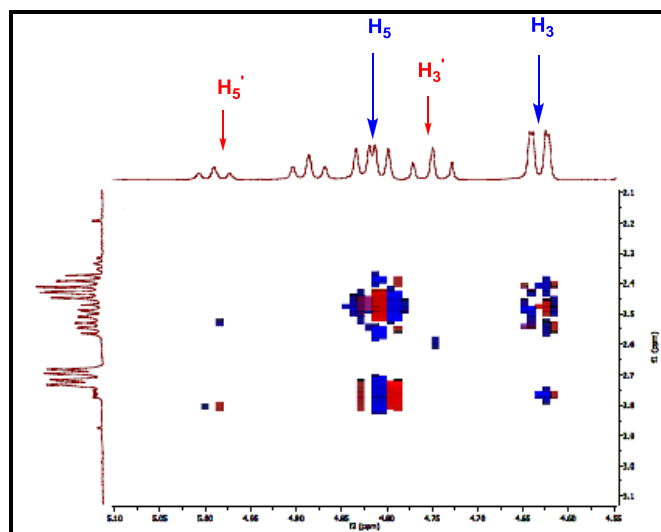
<sup>1</sup>H spectra of 6e



<sup>13</sup>C{<sup>1</sup>H} spectra of 6e



NOESY spectra of **6e**



NOESY spectra of **6e**