

## Supporting Information

### **DABSO-Mediated Pummerer Reaction-Enables One-Pot Synthesis of Pyrroloquinolines for Accessing Marinoquinolines: Mechanistic and Photophysical Investigations**

Rahimuddin Khan,<sup>a</sup> Dipun Kumar Penthi,<sup>a</sup> Aditi Chatterjee,<sup>b</sup> Chandrakanta Sahoo,<sup>a</sup> Shanti Gopal Patra,<sup>c</sup> Viswanathan Arun Nagraj,<sup>b</sup> and Tabrez Khan<sup>\*a</sup>

<sup>a</sup>*Organic Synthesis Laboratory, School of Basic Sciences, Indian Institute of Technology Bhubaneswar, Odisha-752050, India.*

<sup>b</sup>*Institute of Life Sciences, Nalco Square, Bhubaneswar-751023, Odisha, India*

<sup>c</sup>*Department of Chemistry, National Institute of Technology Silchar, Assam-788010, India.*

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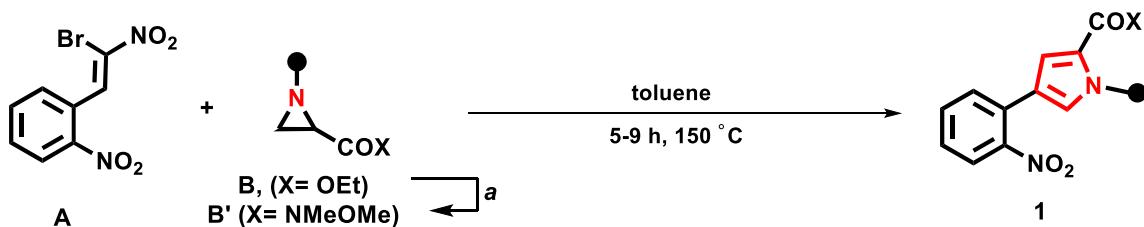
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## 1. General Method:

All the reagents were purchased from commercial suppliers and used without further purification, while most of the desired solvents supplied by commercial suppliers were dried using the standard drying procedures. All the moisture- and air-sensitive reactions were performed under a flow of nitrogen or argon atmosphere using flame-dried or oven-dried glassware with magnetic stirring. All purifications were done using column chromatography with 100–200 mesh size SiO<sub>2</sub> gel as the stationary phase. Distilled ethyl acetate (EtOAc) and petroleum (pet) ether were typically used for column chromatography. The <sup>1</sup>H, <sup>13</sup>C {1H}, <sup>19</sup>F (Decoupled) NMR spectra were recorded on 400 MHz Bruker spectrometer using CDCl<sub>3</sub> with residual solvent peaks (H: δ = 7.26 and C: δ = 77.0 ppm) or tetramethylsilane (TMS) (δ = 0.0) as internal standard. The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, p = quintet/pentet, sept = septet, dd = doublet of doublet, ddd = doublet of doublet of doublet, ddt = doublet of doublet of triplet, td = triplet of doublet, dq = doublet of quartet, and m = multiplet. The chemical shifts are reported as δ values (ppm) and the coupling constant (J) values are reported in hertz. High-resolution mass spectra (HRMS) were obtained using electron spray ionization (ESI) technique and Orbitrap mass analyzer. Melting points were determined on a Buchi M-560 apparatus and are uncorrected. The emission spectra were recorded on Horiba Scientific's FluoroMax-4 spectrofluorometer. Progress of the reactions was monitored using precoated SiO<sub>2</sub> gel GF<sub>254</sub> thin-layer chromatography (TLC) plates, while spot visualizations were done under UV light and using spot-developing stains like p-anisaldehyde, ceric ammonium molybdate or KMnO<sub>4</sub>.

## 2. Preparation of Starting Materials

### I General procedure for preparation of PNDs (1a-1n)

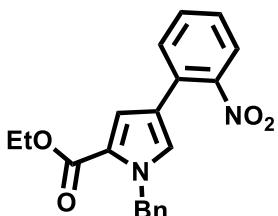


In an oven-dried seal tube, under a nitrogen atmosphere,  $\beta$ -bromo- $\beta$ -nitrostyrene (2 mmol) was taken. After that aziridine (2 mmol, 1 equiv.) dissolved in toluene (2 mL) was added. The reaction was then sealed while maintaining the N<sub>2</sub> atmosphere and then stirred in a preheated

oil bath at 150 °C for 6 h. After completion, the solvent was removed under reduced pressure and the crude residue was purified by SiO<sub>2</sub>-gel flash column chromatography to access 1,2,4-trisubstituted pyrrole (PNDs).

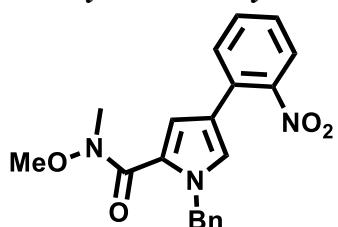
**Note:**  $\beta$ -bromo- $\beta$ -nitrostyrene **A** and aziridine **B** were prepared according to the reported procedure.<sup>1</sup> The characterization data of the known PNDs **1g** and **1h** were found to be in accordance with the reported data<sup>1</sup> while those for new derivatives are documented below.

**ethyl 1-benzyl-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (1a):** Following the general



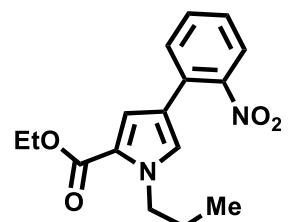
procedure **I**, **1a** was obtained as a yellow oil (500 mg, 70%).  $R_f = 0.5$  (hexane: EtOAc = 9:1). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.68 (dd,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.55 – 7.46 (m, 2H), 7.40 – 7.28 (m, 4H), 7.18 – 7.12 (m, 2H), 7.10 (d,  $J = 2$  Hz, 1H), 7.04 (d,  $J = 2$  Hz, 1H), 5.58 (s, 2H), 4.25 (q,  $J = 7$  Hz, 2H), 1.31 (t,  $J = 7$  Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 160.8, 149.0, 137.6, 131.9, 131.1, 128.7 (2C), 127.6, 127.3, 127.2, 127.0 (2C), 123.7 (2C), 123.1, 118.8, 117.5, 60.2, 52.4, 14.3. **HRMS** (ESI) m/z calcd for C<sub>20</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub> (M+H)<sup>+</sup> : 351.1339; found: 351.1337.

**1-benzyl-N-methoxy-N-methyl-4-(2-nitrophenyl)-1H-pyrrole-2-carboxamide (1a'):**



Following the general procedure **A**, **1a'** was obtained as yellow oil (460 mg, 65%).  $R_f = 0.5$  (hexane: EtOAc = 7:3). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.66 (dd,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.54 – 7.46 (m, 2H), 7.37 – 7.32 (m, 1H), 7.32 – 7.28 (m, 2H), 7.27 – 7.23 (m, 1H), 7.16 – 7.10 (m, 2H), 7.03 (d,  $J = 2$  Hz, 1H), 7.00 (d,  $J = 2$  Hz, 1H), 5.54 (s, 2H), 3.54 (s, 3H), 3.25 (s, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 161.8, 149.1, 138.1, 131.7, 130.9, 128.9, 128.6 (2C), 127.5, 127.0, 126.9 (2C), 125.9, 124.0, 123.5, 118.2, 115.9, 61.0, 52.5, 33.6. **HRMS** (ESI) m/z calcd for C<sub>20</sub>H<sub>20</sub>N<sub>3</sub>O<sub>4</sub> (M+H)<sup>+</sup> : 366.1448; found: 366.1440.

**ethyl 4-(2-nitrophenyl)-1-propyl-1H-pyrrole-2-carboxylate (1b):** Following the general



procedure **A**, **1** was obtained as a yellow oil (510 mg, 74%).  $R_f = 0.5$  (hexane: EtOAc = 19:1). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.20 (dd,  $J_1 = 7$  Hz,  $J_2 = 2$  Hz, 1H), 7.16 (d,  $J = 2$  Hz, 1H), 7.09 (td,  $J_1 = 8$  Hz,  $J_2 = 2$  Hz, 1H), 7.05 (d,  $J = 2$  Hz, 1H), 6.83 – 6.72 (m, 2H), 4.30 (q,  $J = 7$  Hz, 4H), 1.84 (sext,  $J = 7$  Hz, 2H), 1.37 (t,  $J = 7$  Hz, 3H), 0.94 (t,  $J = 7$  Hz, 3H). **13C{1H} NMR**

(100 MHz, CDCl<sub>3</sub>) δ 161.1, 143.7, 129.8, 127.6, 127.2 (2C), 122.2, 121.1, 118.8, 117.4, 115.7, 59.9, 50.9, 24.9, 14.4, 11.2. **HRMS** (ESI) m/z calcd for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub> (M+H)<sup>+</sup> : 303.1339; found: 303.1337.

**ethyl 1-isobutyl-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (1c):** Following the general

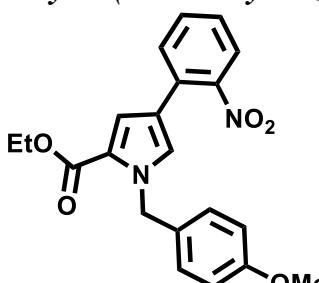
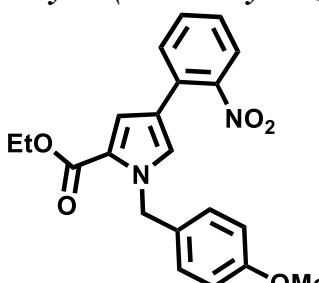
procedure **A**, **1c** was obtained as a yellow oil (438 mg, 62%).  $R_f = 0.5$  (hexane:EtOAc = 19:1). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.66 (dd,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.55 – 7.46 (m, 2H), 7.35 (ddd,  $J_1 = 8$  Hz,  $J_2 = 7$  Hz,  $J_3 = 2$  Hz, 1H), 7.06 (d,  $J = 2$  Hz, 1H), 6.94 (d,  $J = 2$  Hz, 1H), 4.29 (q,  $J = 7$  Hz, 2H), 4.12 (d,  $J = 7$  Hz, 2H), 2.11 (hept,  $J = 7$  Hz, 1H), 1.36 (t,  $J = 7$  Hz, 3H), 0.91 (d,  $J = 7$  Hz, 6H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 160.9, 149.1, 131.8, 131.0, 128.8, 127.6, 127.0, 123.6, 122.8, 117.8, 117.4, 60.0, 56.8, 30.0, 19.8 (2C), 14.4. **HRMS** (ESI) m/z calcd for C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>O<sub>4</sub> (M+H)<sup>+</sup> : 317.1496; found: 317.1505.

**ethyl 1-(cyclopropylmethyl)-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (1d):** Following the

general procedure **A**, **1d** was obtained as a yellow oil (500 mg, 70%).  $R_f = 0.5$  (hexane: EtOAc = 9:1). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.68 – 7.62 (m, 1H), 7.54 – 7.48 (m, 2H), 7.34 (ddd,  $J_1 = 8$  Hz,  $J_2 = 6$  Hz,  $J_3 = 2$  Hz, 1H), 7.11 (d,  $J = 2$  Hz, 1H), 7.06 (d,  $J = 2$  Hz, 1H), 4.29 (q,  $J = 7$  Hz, 2H), 4.20 (d,  $J = 7$  Hz, 2H), 1.35 (t,  $J = 7$  Hz, 3H), 0.64 – 0.55 (m, 2H), 0.36 (dt,  $J = 6.0, 4.7$  Hz, 2H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 161.0, 149.0, 131.8, 131.0, 128.8, 126.9, 126.5, 123.6, 122.8, 118.1, 117.2, 60.1, 53.7, 14.4, 11.9, 3.9 (2C). **HRMS** (ESI) m/z calcd for C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub> (M+H)<sup>+</sup> : 315.1339; found: 315.1337.

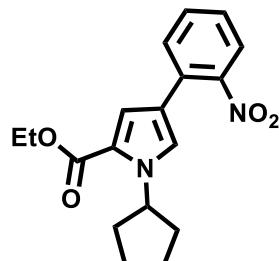
**ethyl 1-(4-methoxybenzyl)-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (1e):** Following the

general procedure **A**, **1e** was obtained as yellow oil (445 mg, 63%).  $R_f = 0.5$  (hexane: EtOAc = 9:1). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.67 (dt,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.55 – 7.44 (m, 2H), 7.38 – 7.30 (m, 1H), 7.16 – 7.11 (m, 2H), 7.08 (dd,  $J_1 = 2$  Hz,  $J_2 = 1$  Hz, 1H), 7.01 (dd,  $J_1 = 2$  Hz,  $J_2 = 1$  Hz, 1H), 6.89 – 6.82 (m, 2H), 5.50 (s, 2H), 4.26 (q,  $J = 7$  Hz, 2H), 3.78 (s, 3H), 1.32 (t,  $J = 7$  Hz, 3H). **13C{1H}**



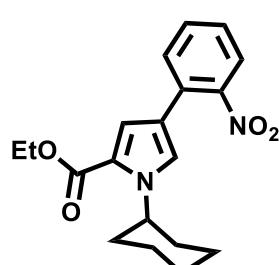
**NMR** (100 MHz, CDCl<sub>3</sub>) δ 160.8, 159.2, 149.0, 131.8, 131.1, 129.6, 128.8, 128.7 (2C), 127.1, 123.6, 123.0, 118.6, 117.5, 114.1 (2C), 60.1, 55.3, 51.8, 14.4. **HRMS** (ESI) m/z calcd for C<sub>21</sub>H<sub>21</sub>N<sub>2</sub>O<sub>5</sub> (M+H)<sup>+</sup> : 381.1445; found: 381.1442.

**ethyl 1-cyclopentyl-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (1i):** Following the general



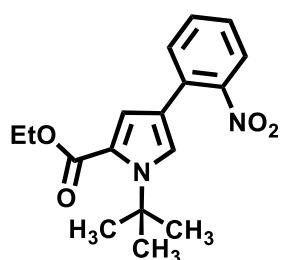
procedure A, **1** was obtained as a yellow oil (530 mg, 75%).  $R_f = 0.5$  (hexane:EtOAc = 19:1). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.66 (dd,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.55 – 7.46 (m, 2H), 7.38 – 7.31 (m, 1H), 7.14 (d,  $J = 2$  Hz, 1H), 7.05 (d,  $J = 2$  Hz, 1H), 5.54 (p,  $J = 7$  Hz, 1H), 4.29 (q,  $J = 7$  Hz, 2H), 2.29 – 2.15 (m, 2H), 1.90 – 1.70 (m, 6H), 1.36 (t,  $J = 7$  Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 161.0, 149.0, 131.8, 131.0, 129.0, 126.9, 123.6, 123.4, 123.1, 118.2, 117.3, 60.0, 58.8, 33.8 (2C), 23.9 (2C), 14.4. **HRMS** (ESI) m/z calcd for C<sub>18</sub>H<sub>21</sub>N<sub>2</sub>O<sub>4</sub> (M+H)<sup>+</sup> : 329.1496; found: 329.1490.

**ethyl 1-cyclohexyl-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (1j):** Following the general



procedure A, **1** was obtained as a yellow oil (340 mg, 48%).  $R_f = 0.5$  (hexane: EtOAc = 19:1). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.65 (dd,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.54 – 7.46 (m, 2H), 7.33 (ddd,  $J_1 = 9$  Hz,  $J_2 = 7$  Hz,  $J_3 = 2$  Hz, 1H), 7.17 (d,  $J = 2$  Hz, 1H), 7.05 (d,  $J = 2$  Hz, 1H), 5.03 (tt,  $J_1 = 11$  Hz,  $J_2 = 3$  Hz, 1H), 4.29 (q,  $J = 7$  Hz, 2H), 2.18 – 2.10 (m, 2H), 1.92 – 1.84 (m, 2H), 1.78 – 1.71 (m, 1H), 1.62 – 1.41 (m, 5H), 1.35 (t,  $J = 7$  Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 160.9, 149.0, 131.7, 131.0, 129.0, 126.8, 123.6, 123.0, 122.6, 118.2, 117.2, 60.0, 56.8, 34.6 (2C), 25.9 (2C), 25.5, 14.4. **HRMS** (ESI) m/z calcd for C<sub>19</sub>H<sub>23</sub>N<sub>2</sub>O<sub>4</sub> (M+H)<sup>+</sup> : 343.1652; found: 343.1657.

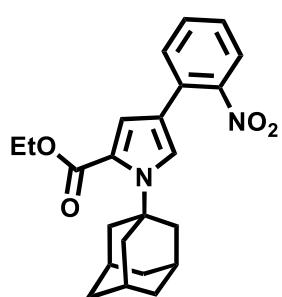
*ethyl 1-(tert-butyl)-4-(2-nitrophenyl)-1*H*-pyrrole-2-carboxylate (1k)* : Following the general



procedure A, **1** was obtained as a yellow oil (530 mg, 75%).  $R_f = 0.5$  (hexane: EtOAc = 19:1). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.66 (dd,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.55 – 7.47 (m, 2H), 7.34 (ddd,  $J_1 = 8$  Hz,  $J_2 = 7$  Hz,  $J_3 = 2$  Hz, 1H), 7.25 (d,  $J = 2$  Hz, 1H), 7.21 (d,  $J = 2$  Hz, 1H), 4.27 (q,  $J = 7$  Hz, 2H), 1.74 (s, 9H), 1.35 (t,  $J = 7$  Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.9, 149.0, 131.7, 131.0, 129.0, 126.8, 125.0, 124.0, 123.6, 121.0, 116.5, 60.2, 59.0, 30.3 (3C), 14.4. **HRMS** (ESI) m/z calcd for C<sub>20</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub> (M+H)<sup>+</sup> : 351.1339; found: 351.1337.

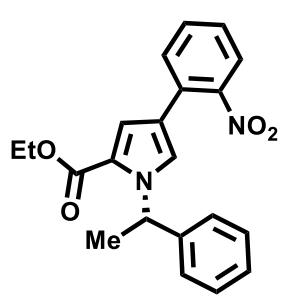
*ethyl 1-((3s,5s,7s)-adamantan-1-yl)-4-(2-nitrophenyl)-1*H*-pyrrole-2-carboxylate (1l)*:

Following the general procedure A, **1** was obtained as a yellow oil 530 mg, 75%).  $R_f = 0.5$



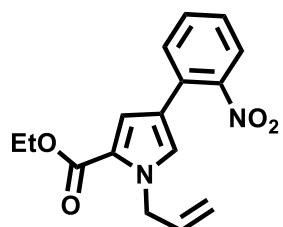
(hexane: EtOAc = 19:1). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.68 – 7.63 (m, 1H), 7.53 – 7.48 (m, 2H), 7.33 (ddd,  $J_1 = 8$  Hz,  $J_2 = 6$  Hz,  $J_3 = 3$  Hz, 1H), 7.30 (d,  $J = 2$  Hz, 1H), 7.25 (d,  $J = 2$  Hz, 1H), 4.27 (q,  $J = 7$  Hz, 2H), 2.39 (d,  $J = 3$  Hz, 6H), 2.23 (br s, 3H), 1.85 – 1.70 (m, 6H), 1.36 (t,  $J = 7$  Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.0, 149.0, 131.7, 131.0, 129.0, 126.7, 124.4, 123.9, 123.6, 121.3, 116.6, 60.2, 59.8, 42.9, 41.9 (2C), 36.0 (2C), 35.8, 30.5, 30.2 (2C), 14.4. **HRMS** (ESI) m/z calcd for C<sub>23</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub> (M+H)<sup>+</sup> : 395.1965; found: 395.1960.

*ethyl (S)-4-(2-nitrophenyl)-1-(1-phenylethyl)-1*H*-pyrrole-2-carboxylate (1m)*: Following the



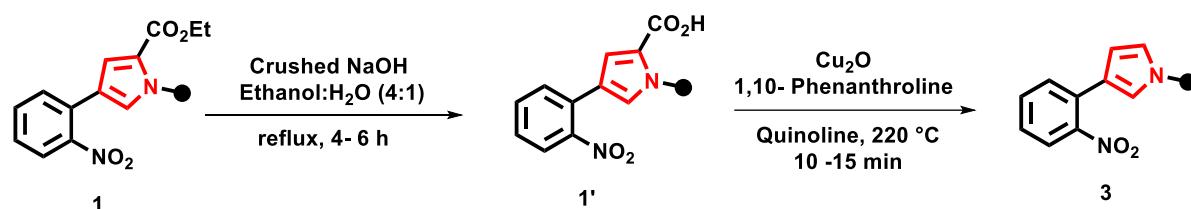
general procedure A, **1** was obtained as a yellow oil (340 mg, 48%).  $R_f = 0.5$  (hexane: EtOAc = 19:1).  $[\alpha]_D^{25} = -35.7$  ( $c = 0.05$ , CHCl<sub>3</sub>). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.68 (dd,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.57 – 7.44 (m, 3H), 7.37 – 7.30 (m, 3H), 7.29 – 7.23 (m, 1H), 7.21 – 7.14 (m, 3H), 7.10 (dd,  $J_1 = 2.1$  Hz,  $J_2 = 1.2$  Hz, 1H), 6.60 (q,  $J = 7$  Hz, 1H), 4.38 (q,  $J = 7$  Hz, 1H), 4.32 – 4.17 (m, 2H), 1.83 (d,  $J = 7$  Hz, 3H), 1.31 (t,  $J = 7$  Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.9, 149.0, 142.4, 131.8, 131.1, 128.7 (2C), 127.5, 127.1, 126.2 (2C), 124.0, 123.7, 117.7, 60.1, 55.9, 22.2, 14.4. **HRMS** (ESI) m/z calcd for C<sub>21</sub>H<sub>21</sub>N<sub>2</sub>O<sub>4</sub> (M+H)<sup>+</sup> : 365.1496; found: 365.1505.

**ethyl 1-allyl-4-(2-nitrophenyl)-1*H*-pyrrole-2-carboxylate (1o):** Following the general



procedure A, **1o** was obtained as a yellow oil (500 mg, 70%).  $R_f = 0.5$  (hexane: EtOAc = 9:1). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.66 (dd,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.55 – 7.45 (m, 2H), 7.34 (ddd,  $J_1 = 8$  Hz,  $J_2 = 7$ ,  $J_3 = 2$  Hz, 1H), 7.05 (d,  $J = 2$  Hz, 1H), 7.00 (d,  $J = 2$  Hz, 1H), 6.02 (ddt,  $J_1 = 17$  Hz,  $J_2 = 11$  Hz,  $J_3 = 5$  Hz, 1H), 5.18 (dq,  $J_1 = 10$  Hz,  $J_2 = 1$  Hz, 1H), 5.03 (dq,  $J_1 = 17$  Hz,  $J_2 = 1$  Hz, 1H), 4.97 (dt,  $J_1 = 5$  Hz,  $J_2 = 2$  Hz, 2H), 4.28 (q,  $J = 7$  Hz, 2H), 1.34 (t,  $J = 7$  Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.8, 149.0, 134.1, 131., 131.0, 128.7, 127.1, 126.8, 123.6, 122.9, 118.6, 117.2, 117.1, 60.2, 51.2, 14.4. **HRMS** (ESI) m/z calcd for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O<sub>4</sub> (M+H)<sup>+</sup> : 301.1183; found: 301.1196.

## II General procedure for preparation of PNDs (3a-3m)

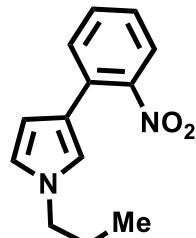


To a solution of the **1a-m** (0.57 mmol, 1 equiv.) in ethanol : water (4:1, 12 mL), crushed NaOH pellets (2.85 mmol, 5 equiv.) were added at rt and the reaction was then allowed to reflux for 3 h, until completion of the saponification process was indicated by TLC analysis. The reaction was worked up by removing the volatiles under reduced pressure and then neutralization of the resultant residue by 1N HCl. The aqueous phase was subjected to extraction with EtOAc ( $4 \times 20$  mL). Then the solvent was removed under reduced pressure and the crude residue was purified by SiO<sub>2</sub>-gel flash column chromatography to access pyrrole-2-carboxylic acid **1'**.

To an oven-dried sealed tube, compound **1'a-m** (0.4 mmol, 1 equiv.) was added along with 1 mL of quinoline, followed by copper (I) oxide (0.4 mmol, 1 equiv.) and 1,10-phenanthroline (0.4 mmol, 1 equiv.). The reaction vessel was then sealed and subjected to heating at 220 °C for 10-15 min until complete decarboxylation was indicated by TLC analysis. Upon reaction completion the volatiles were removed under vacuum and the crude residue was subjected to SiO<sub>2</sub>-gel column chromatography to access decarboxylated product **3a-m**.

**Note:** PNDs (**3a-m**) were prepared according to the reported procedure.<sup>1</sup> The characterization data of the known PNDs **3a** was found to be in accordance with the reported data<sup>1</sup> while those for new derivatives are documented below.

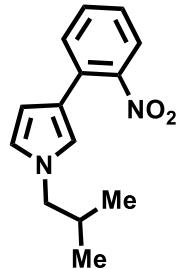
**3-(2-nitrophenyl)-1-propyl-1H-pyrrole (3b):** Following the general procedure II, **3b** was



obtained as a yellow oil (118 mg, 77%).  $R_f = 0.5$  (hexane: EtOAc = 19:1).

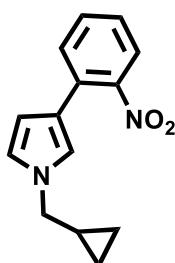
**1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (dd,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.54 – 7.44 (m, 2H), 7.30 – 7.23 (m, 1H), 6.83 (t,  $J = 2$  Hz, 1H), 6.67 (t,  $J = 2$  Hz, 1H), 6.25 (dd,  $J_1 = 3$  Hz,  $J_2 = 2$  Hz, 1H), 3.84 (t,  $J = 7$  Hz, 2H), 1.81 (sext,  $J = 7$  Hz, 2H), 0.93 (t,  $J = 7$  Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  149.0, 131.4, 130.6, 129.8, 125.9, 123.2, 121.6, 119.5, 118.4, 107.9, 51.6, 24.7, 11.2. **HRMS** (ESI) m/z calcd for C<sub>13</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 231.1128; found: 231.1331.

**1-isobutyl-3-(2-nitrophenyl)-1H-pyrrole (3c):** Following the general procedure II, **3c** was



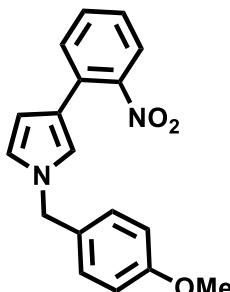
obtained as a yellow oil (96 mg, 62%).  $R_f = 0.5$  (hexane:EtOAc = 19:1) **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (dd,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.52 (dd,  $J_1 = 8$  Hz,  $J_2 = 2$  Hz, 1H), 7.47 (td,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.27 (ddd,  $J_1 = 8$  Hz,  $J_2 = 7$  Hz,  $J_3 = 2$  Hz, 1H), 6.81 (t,  $J = 2.0$  Hz, 1H), 6.65 (t,  $J = 3$  Hz, 1H), 6.26 (dd,  $J_1 = 3$  Hz,  $J_2 = 2$  Hz, 1H), 3.67 (d,  $J = 7$  Hz, 2H), 2.09–1.99 (m, 1H), 0.92 (d,  $J = 7$  Hz, 6H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  149.0, 131.4, 130.6, 129.8, 126.0, 123.2, 122.0, 119.9, 118.3, 107.8, 57.7, 30.5, 20.0 (2C). **HRMS** (ESI) m/z calcd for C<sub>14</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 245.1285; found: 245.1298.

**1-(cyclopropylmethyl)-3-(2-nitrophenyl)-1H-pyrrole (3d):** Following the general procedure



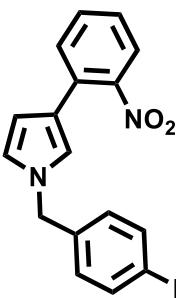
II, **3d** was obtained as a yellow oil (108 mg, 70%).  $R_f = 0.5$  (hexane: EtOAc = 19:1). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.58 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1$  Hz, 1H), 7.55 – 7.45 (m, 2H), 7.31 – 7.24 (m, 2H), 6.92 (t,  $J = 2$  Hz, 1H), 6.76 (t,  $J = 3$  Hz, 1H), 6.26 (dd,  $J_1 = 3$  Hz,  $J_2 = 2$  Hz, 1H), 3.75 (d,  $J = 7$  Hz, 2H), 0.92 – 0.82 (m, 1H), 0.71 – 0.61 (m, 2H), 0.35 (q,  $J = 5$  Hz, 2H). **13C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  149.1, 131.4, 130.7, 129.8, 126.0, 123.3, 121.5, 119.4, 118.5, 107.9, 54.4, 11.8, 4.0 (2C). **HRMS** (ESI) m/z calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 243.1128; found: 243.1125.

**1-(4-methoxybenzyl)-3-(2-nitrophenyl)-1H-pyrrole (3e):** Following the general procedure II,



**3d** was obtained as yellow oil (115 mg, 70%).  $R_f = 0.5$  (hexane: EtOAc = 19:1). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.58 (dd,  $J_1 = 8.1$  Hz,  $J_2 = 1.3$  Hz, 1H), 7.53 – 7.42 (m, 2H), 7.30 – 7.23 (m, 1H), 7.16 – 7.07 (m, 2H), 6.92 – 6.83 (m, 3H), 6.68 (t,  $J = 2.5$  Hz, 1H), 6.28 (dd,  $J_1 = 2.8$  Hz,  $J_2 = 1.8$  Hz, 1H), 5.00 (s, 2H), 3.80 (s, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 159.35, 149.02, 131.45, 130.72, 129.75, 129.34, 128.70, 126.12, 123.29, 121.99, 119.91, 119.01, 114.23, 108.49, 55.32, 53.13. **HRMS** (ESI) m/z calcd for C<sub>18</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub> (M+H)<sup>+</sup> : 309.1234; found: 309.1229.

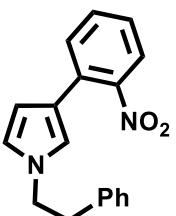
**1-(4-fluorobenzyl)-3-(2-nitrophenyl)-1H-pyrrole (3f):** Following the general procedure II, **3f** was obtained as yellow oil (116 mg, 72%).  $R_f = 0.5$  (hexane: EtOAc = 7:3). **1H NMR** (400



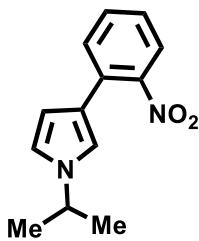
MHz, CDCl<sub>3</sub>) δ 7.61 – 7.55 (m, 1H), 7.53 – 7.45 (m, 2H), 7.32 – 7.26 (m, 1H), 7.13 (ddd,  $J_1 = 8$  Hz,  $J_2 = 5$  Hz,  $J_3 = 3$  Hz, 2H), 7.07 – 7.00 (m, 2H), 6.86 (t,  $J = 2$  Hz, 1H), 6.68 (t,  $J = 3$  Hz, 1H), 6.29 (dd,  $J_1 = 3$  Hz,  $J_2 = 3$  Hz, 1H), 5.04 (s, 2H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 162.4 (d,  $J = 240$  Hz, 1C), 149.1, 133.2 (d,  $J = 4$  Hz, 1C), 131.5, 130.7, 129.6, 128.9 (d,  $J = 18$  Hz, 2C), 126.3, 123.3, 122.0, 119.9, 119.3, 115.8 (d,  $J = 22$  Hz, 2C), 108.8, 52.9.

**<sup>19</sup>F NMR** (377 MHz, CDCl<sub>3</sub>) δ -113.5. **HRMS** (ESI) m/z calcd for C<sub>17</sub>H<sub>14</sub>FN<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup> : 297.1034; found: 297.1033.

**3-(2-nitrophenyl)-1-phenethyl-1H-pyrrole (3g):** Following the general procedure II, **3f** was obtained as yellow oil (110 mg, 76%).  $R_f = 0.6$  (hexane: EtOAc = 9:1). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.56 (m, 1H), 7.49 – 7.46 (m, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.26 (m, 3H), 7.14 – 7.09 (m, 3H), 6.77 (t,  $J = 2.1$  Hz, 1H), 6.61 (t,  $J = 2.5$  Hz, 1H), 6.24 (dd,  $J_1 = 2.8$  Hz,  $J_2 = 1.8$  Hz, 1H), 4.11 (t,  $J = 7.4$  Hz, 3H), 3.08 (t,  $J = 7.3$  Hz, 2H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 149.07, 138.12, 131.45, 130.74, 129.85, 128.75 (2C), 128.68 (2C), 128.37, 126.78, 126.10, 123.28, 121.71, 119.50, 118.75, 108.13, 51.51, 38.24. **HRMS** (ESI) m/z calcd for C<sub>18</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 293.1285; found: 293.1297.

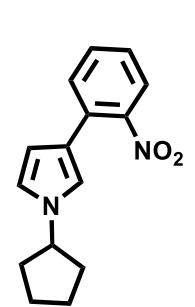


**1-isopropyl-3-(2-nitrophenyl)-1H-pyrrole (3h):** Following the general procedure II, **3h** was



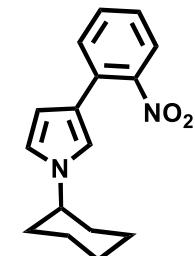
obtained as a yellow oil (110 mg, 70%).  $R_f = 0.5$  (hexane:EtOAc = 7:3). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.57 (dd,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.53 (dd,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.47 (td,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.26 (ddd,  $J_1 = 8$  Hz,  $J_2 = 7$  Hz,  $J_3 = 2$  Hz, 1H), 6.91 (t,  $J = 2$  Hz, 1H), 6.75 (t,  $J = 3$  Hz, 1H), 6.26 (dd,  $J_1 = 3$  Hz,  $J_2 = 2$  Hz, 1H), 4.24 (hept,  $J = 7$  Hz, 1H), 1.48 (d,  $J = 7$  Hz, 6H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 149.0, 131.4, 130.6, 129.9, 125.9, 123.2, 119.2, 118.2, 117.4, 107.7, 51.2, 23.8 (2C). **HRMS** (ESI) m/z calcd for C<sub>13</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup> : 231.1128; found: 231.1125.

**1-cyclopentyl-3-(2-nitrophenyl)-1H-pyrrole (3i):** Following the general procedure II, **3i** was



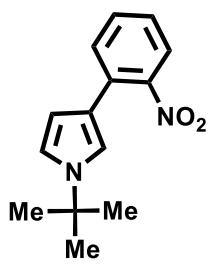
obtained as a yellow oil (114 mg, 73%).  $R_f = 0.5$  (hexane:EtOAc = 7:3). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.57 (dd,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.52 (dd,  $J_1 = 8$  Hz,  $J_2 = 2$  Hz, 1H), 7.47 (td,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.26 (td,  $J_1 = 8$  Hz,  $J_2 = 2$  Hz, 1H), 6.90 (t,  $J = 2$  Hz, 1H), 6.74 (t,  $J = 3$  Hz, 1H), 6.24 (t,  $J = 2$  Hz, 1H), 4.39 (p,  $J = 7$  Hz, 1H), 2.22-2.14 (m, 2H), 1.93 – 1.79 (m, 4H), 1.76-1.67 (m, 2H). **13C NMR** (101 MHz, CDCl<sub>3</sub>) δ 149.0, 131.4, 130.6, 129.9, 125.9, 123.3, 120.1, 118.2, 118.2, 107.8, 60.6, 33.7 (2C), 23.9 (2C). **HRMS** (ESI) m/z calcd for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup> : 257.1285; found: 257.1279.

**1-cyclohexyl-3-(2-nitrophenyl)-1H-pyrrole (3j):** Following the general procedure II, **3j** was obtained as a yellow oil (76 mg, 48%).  $R_f = 0.5$  (hexane:EtOAc = 7:3). **1H NMR** (400 MHz,



CDCl<sub>3</sub>) δ 7.56 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1$  Hz, 1H), 7.53 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1$  Hz, 1H), 7.47 (td,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.26 (ddd,  $J_1 = 8$  Hz,  $J_2 = 6$  Hz,  $J_3 = 1$  Hz, 1H), 6.92 (t,  $J = 2$  Hz, 1H), 6.75 (t,  $J = 3$  Hz, 1H), 6.26 (dd,  $J_1 = 3$  Hz,  $J_2 = 2$  Hz, 1H), 3.81 (tt,  $J_1 = 12$  Hz,  $J_2 = 4$  Hz, 1H), 2.17 – 2.09 (m, 2H), 1.90 (dp,  $J_1 = 14$  Hz,  $J_2 = 4$  Hz, 2H), 1.78 -1.71 (m, 1H), 1.64 (qd,  $J_1 = 12$  Hz,  $J_2 = 3$  Hz, 2H), 1.41 (qt,  $J_1 = 13$  Hz,  $J_2 = 3$  Hz, 2H), 1.31 – 1.21 (m, 1H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 148.9, 131.4, 130.5, 129.9, 125.8, 123.2, 119.5, 117.9, 117.7, 107.5, 59.0, 34.5 (2C), 25.6 (2C), 25.4. **HRMS** (ESI) m/z calcd for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 271.1441; found: 271.1438.

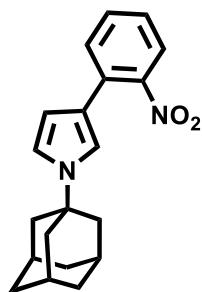
**1-(*tert*-butyl)-3-(2-nitrophenyl)-1*H*-pyrrole (3k):** Following the general procedure II, **3k** was



obtained as yellow oil (105 mg, 68%).  $R_f = 0.5$  (hexane: EtOAc = 7:3). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (dd,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.53 (dd,  $J_1 = 8$  Hz,  $J_2 = 2$  Hz, 1H), 7.47 (td,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.30 – 7.20 (m, 1H), 7.01 (t,  $J = 2$  Hz, 1H), 6.85 (t,  $J = 3$  Hz, 1H), 6.26 (dd,  $J_1 = 3$  Hz,  $J_2 = 2$  Hz, 1H), 1.56 (s, 9H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  149.0, 131.4, 130.6, 130.0, 125.8, 123.27, 118.7, 118.1, 116.8, 107.6, 55.3, 30.7 (3C).

**HRMS** (ESI) m/z calcd for C<sub>14</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 245.1285; found: 245.1294.

**1-((3s,5s,7s)-adamantan-1-yl)-3-(2-nitrophenyl)-1*H*-pyrrole (3l):** Following the general procedure II, **3l** was obtained as yellow oil (128 mg, 78%).  $R_f = 0.5$  (hexane: EtOAc = 7:3).



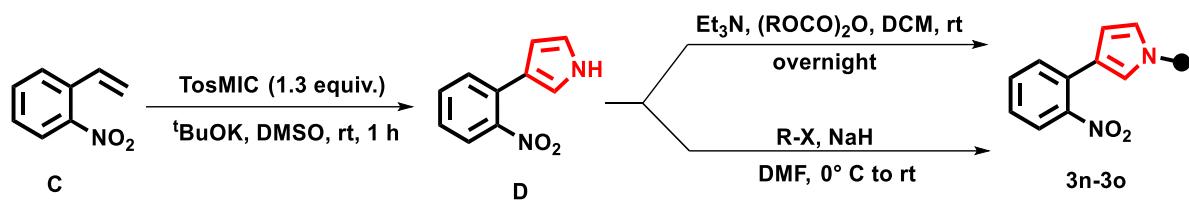
**1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.60 – 7.50 (m, 2H), 7.47 (t,  $J = 8$  Hz, 1H), 7.29 – 7.21 (m, 1H), 7.06 (t,  $J = 2$  Hz, 1H), 6.90 (t,  $J = 3$  Hz, 1H), 6.28 (t,  $J = 3$  Hz, 1H), 2.23 (br s, 3H), 2.10 (d,  $J = 3$  Hz, 6H), 1.77 (dd,  $J_1 = 7$  Hz,  $J_2 = 3$  Hz, 6H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  148.9, 131.4, 130.6, 130.1, 125.8, 123.2, 117.72, 117.68, 115.8, 107.3, 55.6, 43.8 (2C), 36.1 (2C), 29.7 (2C). **HRMS** (ESI) m/z calcd for C<sub>20</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>:

323.1754; found: 323.1755.

**(S)-3-(2-nitrophenyl)-1-(1-phenylethyl)-1*H*-pyrrole (3m):** Following the general procedure II,

**3m** was obtained as yellow oil (77 mg, 48%).  $R_f = 0.5$  (hexane: EtOAc = 7:3). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.59 (dd,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.53 (dd,  $J_1 = 8$  Hz,  $J_2 = 2$  Hz, 1H), 7.48 (td,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 1H), 7.39 – 7.32 (m, 2H), 7.32 – 7.24 (m, 2H), 7.18 – 7.12 (m, 2H), 6.97 (t,  $J = 2$  Hz, 1H), 6.78 (t,  $J = 3$  Hz, 1H), 6.32 (dd,  $J_1 = 3$  Hz,  $J_2 = 2$  Hz, 1H), 5.29 (q,  $J = 7$  Hz, 1H), 1.86 (d,  $J = 7$  Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  149.0, 142.88, 131.5, 130.7, 129.9, 128.8 (2C), 127.7, 126.1, 125.9 (2C), 123.3, 120.7, 118.7, 118.6, 108.2, 58.5, 22.1. **HRMS** (ESI) m/z calcd for C<sub>18</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 293.1285; found: 293.1297.

### III General procedure for preparation of PNDs (3n and 3o)



To a suspension of *t*BuOK (384 mg, 4 mmol) in dry DMSO (10 mL) at room temperature was added a solution of styrene (208 mg, 2 mmol) and tosylmethylisocyanide (508 mg, 2.6 mmol) in DMSO (10 mL) dropwise and the reaction mixture was stirred under nitrogen atmosphere for 1 h. On completion of the reaction, the reaction mixture was diluted with EtOAc (50 mL) and brine (50 mL) and shaken. The aqueous layer was washed with EtOAc (3 x 50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo onto silica gel. The reaction mixture was purified by SiO<sub>2</sub>-gel column chromatography (Hexane/EtOAc = 1/0 to 1/1) to 3-(phenyl)-1*H*-pyrrole as a pale yellow oil (134 mg, 47%).

**Note:** PNDs (3n-3o) were prepared according to the reported procedure.<sup>2</sup> The characterization data of these derivatives are documented below.

**3-(2-nitrophenyl)-1-tosyl-1*H*-pyrrole (3o):** Following the general procedure III, 1 was obtained as a yellow oil (-- mg, --%). *R*<sub>f</sub> = 0.5 (hexane: EtOAc = 19:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 8 Hz, 2H), 7.72 (dd, *J*<sub>1</sub> = 8 Hz, *J*<sub>2</sub> = 1 Hz, 1H), 7.54 (td, *J*<sub>1</sub> = 8 Hz, *J*<sub>2</sub> = 1 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.35 – 7.31 (m, 3H), 7.18 (dd, *J*<sub>1</sub> = 3 Hz, *J*<sub>2</sub> = 2 Hz, 1H), 6.35 (dd, *J*<sub>1</sub> = 3 Hz, *J*<sub>2</sub> = 2 Hz, 1H), 2.43 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 149.1, 145.4, 135.8, 132.1, 131.3, 130.2 (2C), 128.1, 128.0, 126.9 (2C), 124.2, 123.8, 121.3, 118.9, 113.7, 21.7. HRMS (ESI) m/z calcd for C<sub>17</sub>H<sub>15</sub>N<sub>2</sub>O<sub>4</sub>S (M+H)<sup>+</sup> : 343.0747; found: 343.0743.

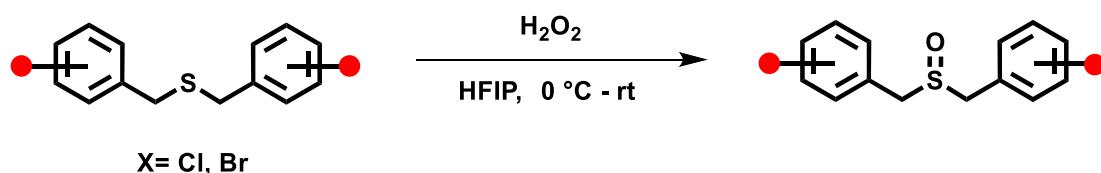
**tert-butyl 3-(2-nitrophenyl)-1*H*-pyrrole-1-carboxylate (3p):** Following the general procedure III, 1 was obtained as a yellow oil (– mg, 75%). *R*<sub>f</sub> = 0.5 (hexane: EtOAc = 19:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 (dd, *J*<sub>1</sub> = 8 Hz, *J*<sub>2</sub> = 1 Hz, 1H), 7.55 (td, *J*<sub>1</sub> = 8 Hz, *J*<sub>2</sub> = 1 Hz, 1H), 7.50 (dd, *J*<sub>1</sub> = 8 Hz, *J*<sub>2</sub> = 2 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.30 – 7.25 (m, 1H), 6.27 (dd, *J*<sub>1</sub> = 3 Hz, *J*<sub>2</sub> = 2 Hz, 1H), 1.62 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 149.1, 148.4, 132.0, 131.2, 128.9, 127.6, 123.8, 122.8,

120.8, 118.2, 111.8, 84.3, 28.0 (3C). **HRMS** (ESI) m/z calcd for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O<sub>4</sub> (M+H)<sup>+</sup> : 289.1183; found: 289.1179.

#### IV. General procedure for preparation of symmetric sulfoxides



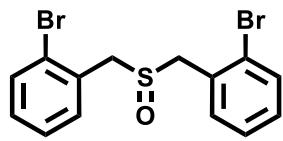
The synthesis was adapted from the reported literature. To a stirred solution of benzylic chloride (1 gm, 7.94 mmol) in <sup>t</sup>BuOH (6 mL) at rt was added an aqueous solution (4 mL) of Na<sub>2</sub>S (8 mmol) in one portion, the mixture was stirred for overnight at room temperature. Upon the completion of the reaction as monitored by TLC analysis, the mixture was diluted with H<sub>2</sub>O and extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated to give the corresponding bis-benzylic sulfide, which was directly involved into the next step without further purification.



The synthesis was adapted from the reported literature. To a stirred solution of the bis-benzylic sulfide (1 mmol) in HFIP (sometimes with CH<sub>2</sub>Cl<sub>2</sub>/CHCl<sub>3</sub> to increase the solubility of sulfide) at 0 °C was added 30% aq. H<sub>2</sub>O<sub>2</sub> (1.1 mmol) in one portion. The mixture was stirred at 0 °C or allowed to warm to rt for 0.5-24 h. Upon the completion of the reaction as monitored by TLC analysis, the mixture was quenched by adding Na<sub>2</sub>SO<sub>3</sub> and reaction for 30 min. The mixture was then filtered and washed with CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was concentrated and purified by column chromatography on silica gel (Petroleum Ether/EtOAc 4/1 to pure EtOAc) to afford the desired symmetric bis-benzylic sulfoxides in 50-90% total yield (over two steps).

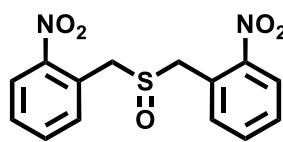
**Note:** Sulfoxides (**5a-g**) were prepared according to the reported procedure.<sup>3</sup> The characterization data of the known sulfoxides **5a**, **5b** and **5e** was found to be in accordance with the reported data, while those for new derivatives are documented below.

**2,2'-(sulfinylbis(methylene))bis(bromobenzene) (5c):** Following the general procedure IV, **5c**



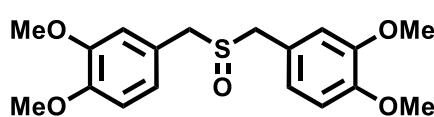
was obtained as a white solid (1.25 gm, 80%).  $R_f = 0.6$  (EtOAc).  **$^1\text{H}$  NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 (dd,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 2H), 7.43 (dd,  $J_1 = 8$  Hz,  $J_2 = 2$  Hz, 2H), 7.33 (td,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 2H), 7.22 (td,  $J_1 = 8$  Hz,  $J_2 = 2$  Hz, 2H), 4.38 (d,  $J = 13$  Hz, 2H), 4.07 (d,  $J = 13$  Hz, 2H).  **$^{13}\text{C}\{\text{H}\}$  NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  133.2 (2C), 132.6 (2C), 130.6 (2C), 130.1 (2C), 127.9 (2C), 125.1 (2C), 58.7 (2C). **HRMS** (ESI) m/z calcd for C<sub>14</sub>H<sub>13</sub>Br<sub>2</sub>OS (M+H)<sup>+</sup> : 386.9048; found: 386.9040.

**2,2'-(sulfinylbis(methylene))bis(nitrobenzene) (5d):** Following the general procedure IV, **5d**



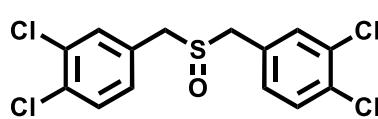
was obtained as a light yellow solid (0.86 gm, 68%).  $R_f = 0.6$  (EtOAc).  **$^1\text{H}$  NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 (dd,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 2H), 7.67 (td,  $J_1 = 8$  Hz,  $J_2 = 1$  Hz, 2H), 7.58-7.52 (m, 4H), 4.75 (d,  $J = 13$  Hz, 2H), 4.19 (d,  $J = 3$  Hz, 2H).  **$^{13}\text{C}\{\text{H}\}$  NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  148.8 (2C), 134.0 (2C), 133.8(2C), 129.8 (2C), 126.2 (2C), 125.8 (2C), 56.7 (2C). **HRMS** (ESI) m/z calcd for C<sub>14</sub>H<sub>13</sub>N<sub>2</sub>O<sub>5</sub>S (M+H)<sup>+</sup>: 321.0540; found: 321.0536.

**4,4'-(sulfinylbis(methylene))bis(1,2-dimethoxybenzene) (5f):** Following the general



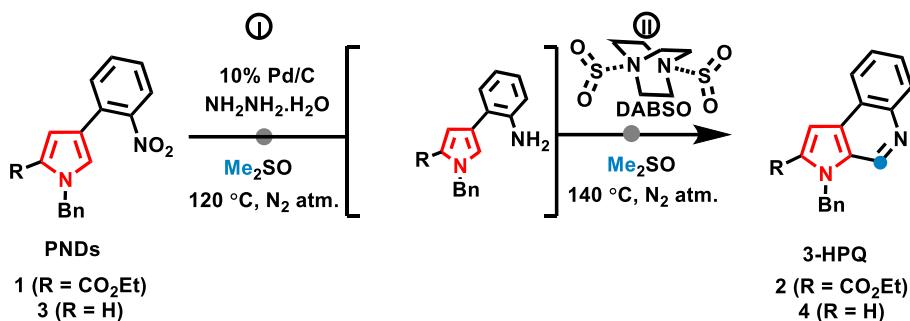
procedure IV, **5f** was obtained as a white solid (0.71 gm, 74%).  $R_f = 0.6$  (EtOAc).  **$^1\text{H}$  NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.95 (dd,  $J_1 = 2$  Hz,  $J_2 = 1$  Hz, 2H), 6.87 – 6.81 (m, 4H), 4.64 (s, 4H), 3.84 (s, 6H), 3.79 (s, 6H).  **$^{13}\text{C}\{\text{H}\}$  NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.5 (2C), 151.5 (2C), 126.7 (2C), 116.2 (2C), 114.7 (2C), 112.0 (2C), 56.2 (2C), 55.8 (2C), 41.5 (2C). **HRMS** (ESI) m/z calcd for C<sub>18</sub>H<sub>23</sub>O<sub>5</sub>S (M+H)<sup>+</sup>: 351.1261; found: 351.1254.

**4,4'-(sulfinylbis(methylene))bis(1,2-dichlorobenzene) (5g):** Following the general procedure



IV, **5g** was obtained as a yellow solid (0.65 gm, 69%).  $R_f = 0.6$  (EtOAc).  **$^1\text{H}$  NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 (s, 1H), 7.37 (s, 1H), 7.34 (d,  $J = 2$  Hz, 2H), 7.10 (d,  $J = 2$  Hz, 1H), 7.08 (d,  $J = 2$  Hz, 1H), 3.53 (s, 4H).  **$^{13}\text{C}\{\text{H}\}$  NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.9 (2C), 132.6 (2C), 131.2 (2C), 130.8 (2C), 130.5 (2C), 128.2 (2C), 34.7 (2C). **HRMS** (ESI) m/z calcd for C<sub>14</sub>H<sub>11</sub>Cl<sub>4</sub>OS (M+H)<sup>+</sup>: 366.9279; found:366.9278.

**A. Procedure for the one-pot synthesis of 3-HPQ scaffold 2/4**



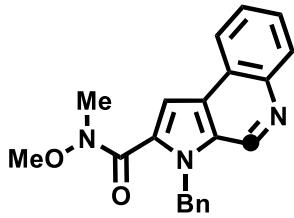
To a stirred solution of substituted PNDs **1/3** (0.1 mmol, 1 equiv.) in DMSO (2 mL) was added 10% Pd/C (5% w/w) followed by the addition of NH<sub>2</sub>NH<sub>2</sub>.H<sub>2</sub>O (5 equiv.) and the reaction mixture was allowed to stir at 120 °C for 7-8 h under inert condition until complete reduction of -NO<sub>2</sub> was indicated by TLC analysis. After completion of the reaction, DABSO was added to the same reaction mixture and the stirring was continued at 140° C for the next 4-5 h. After that, extraction was done with EtOAc (5 mL) and water (5 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3×5 mL). The combined organic layer dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo and the resultant residue was subjected to purification using SiO<sub>2</sub>-gel column chromatography to arrive at the desired tricyclic product.

**ethyl 3-benzyl-3*H*-pyrrolo[2,3-*c*]quinoline-2-carboxylate (2a):** Following the general

procedure A, using **1a** (35 mg, 0.1 mmol), **2a** was obtained as a pale yellow semi-solid (24 mg, 74%).  $R_f$  = 0.4 (hexane:EtOAc = 7:3). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.09 (s, 1H), 8.26 – 8.13 (m, 2H), 7.82 (d, *J* = 1 Hz, 1H), 7.68 – 7.58 (m, 2H), 7.32 – 7.18 (m, 4H), 7.09 (dd, *J*<sub>1</sub> = 8 Hz, *J*<sub>2</sub> = 2 Hz, 2H), 6.04 (s, 2H), 4.40 (q, *J* = 7 Hz, 2H), 1.42 (t, *J* = 7 Hz, 3H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 161.4, 142.7, 137.6, 137.5, 132.3, 129.8, 129.0, 128.8 (2C), 127.7, 127.1, 126.8, 126.6, 126.3 (2C), 123.4, 122.8, 108.7, 61.2, 48.5, 14.3. **HRMS (ESI)** m/z calcd for C<sub>21</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 331.1441; found: 331.1433.

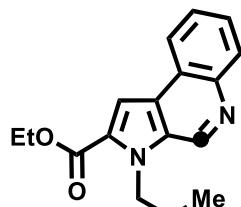
**3-benzyl-N-methoxy-N-methyl-3*H*-pyrrolo[2,3-*c*]quinoline-2-carboxamide (2a'): Following**

the general procedure A, using **1a'** (37 mg, 0.1 mmol), **2a'** was obtained as a yellow semi-solid (16 mg, 43%).  $R_f$  = 0.4 (hexane: EtOAc = 6:4). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.11 (s, 1H), 8.25 – 8.14 (m, 2H), 7.67 – 7.59 (m, 2H), 7.57 (d, *J* = 1 Hz, 1H), 7.26 – 7.20



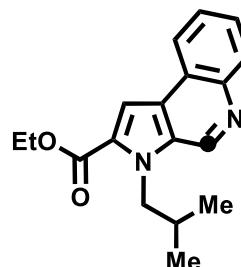
(m, 3H), 7.10 (dd,  $J_1$  = 8 Hz,  $J_2$  = 2 Hz, 2H), 5.88 (s, 2H), 3.47 (s, 3H), 3.35 (s, 3H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) δ 161.98, 142.6, 137.6, 137.2, 131.2, 131.0, 129.8, 128.8 (2C), 127.8, 127.1, 126.81, 126.77 (2C), 126.6, 123.5, 122.8, 105.8, 61.5, 48.6, 29.7. HRMS (ESI) m/z calcd for  $\text{C}_{21}\text{H}_{20}\text{N}_3\text{O}_2$  ( $\text{M}+\text{H}$ )<sup>+</sup>: 346.1550; found: 346.1545.

*ethyl 3-propyl-3*H*-pyrrolo[2,3-*c*]quinoline-2-carboxylate (2b):* Following the general



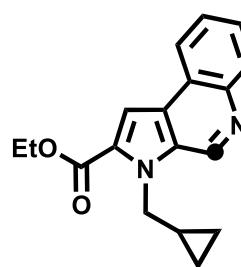
procedure A, using **1c** (30 mg, 0.1 mmol), **2c** was obtained as a yellow solid (18 mg, 68%), m.p. 175–176 °C.  $R_f$  = 0.4 (hexane:EtOAc = 6:4).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) δ 9.13 (d,  $J$  = 0.9 Hz, 1H), 8.24 – 8.15 (m, 2H), 7.75 (d,  $J$  = 0.9 Hz, 1H), 7.67 – 7.58 (m, 2H), 4.79 – 4.72 (m, 2H), 4.45 (q,  $J$  = 7.1 Hz, 2H), 2.01 – 1.87 (m, 2H), 1.47 (t,  $J$  = 7.1 Hz, 3H), 0.98 (t,  $J$  = 7.4 Hz, 3H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) δ 161.46, 142.67, 137.55, 132.14, 129.93, 128.78, 126.97, 126.55, 126.13, 123.47, 122.81, 108.24, 61.07, 46.88, 24.70, 14.37, 11.25. HRMS (ESI) m/z calcd for  $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_2$  ( $\text{M}+\text{H}$ )<sup>+</sup>: 283.1441; found: 283.1457.

*ethyl 3-isobutyl-3*H*-pyrrolo[2,3-*c*]quinoline-2-carboxylate (2c):* Following the general



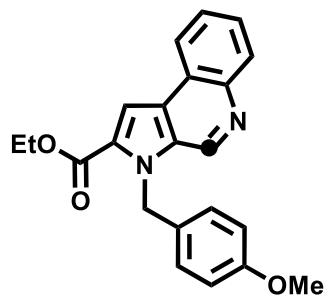
procedure A, using **1c** (32 mg, 0.1 mmol), **2c** was obtained as a yellow semi-solid (16.5 mg, 54%).  $R_f$  = 0.4 (hexane:EtOAc = 6:4).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) δ 9.12 (s, 1H), 8.23 – 8.16 (m, 2H), 7.76 (d,  $J$  = 1 Hz, 1H), 7.67 – 7.57 (m, 2H), 4.60 (d,  $J$  = 7 Hz, 2H), 4.44 (q,  $J$  = 7 Hz, 2H), 2.27 (hept,  $J$  = 7 Hz, 1H), 1.46 (t,  $J$  = 7 Hz, 3H), 0.94 (d,  $J$  = 7 Hz, 6H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) δ 161.5, 142.3, 137.6, 132.4, 129.7, 129.2, 127.1, 126.7, 126.2, 123.4, 122.8, 108.4, 61.1, 52.4, 30.7, 20.0 (2C), 14.3. HRMS (ESI) m/z calcd for  $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_2$  ( $\text{M}+\text{H}$ )<sup>+</sup>: 297.1598; found: 297.1616.

*ethyl 3-(cyclopropylmethyl)-3*H*-pyrrolo[2,3-*c*]quinoline-2-carboxylate (2d):* Following the



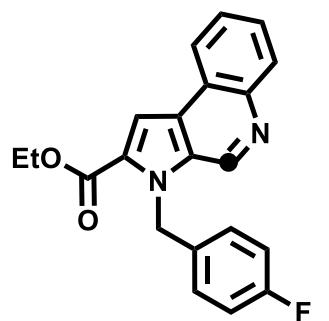
general procedure A, using **1d** (32 mg, 0.1 mmol), **2d** was obtained as a colourless semi-solid (21 mg, 70%).  $R_f$  = 0.4 (hexane: EtOAc = 6:4).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) δ 9.13 (s, 1H), 8.25 – 8.14 (m, 2H), 7.76 (d,  $J$  = 1 Hz, 1H), 7.67 – 7.58 (m, 2H), 4.72 (d,  $J$  = 7 Hz, 2H), 4.45 (q,  $J$  = 7 Hz, 2H), 1.47 (t,  $J$  = 7 Hz, 3H), 0.57-0.51 (m, 2H), 0.50-0.46 (m, 2H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) δ 161.6, 142.6, 137.6, 132.2, 129.8, 128.7, 127.0, 126.6, 126.3, 123.5, 122.8, 108.4, 61.1, 49.2, 14.4, 12.6, 3.9 (2C). HRMS (ESI) m/z calcd for  $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_2$  ( $\text{M}+\text{H}$ )<sup>+</sup>: 295.1441; found: 295.1437.

*ethyl 3-(4-methoxybenzyl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (2e):* Following the



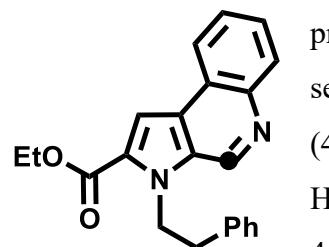
general procedure A, using **1e** (38 mg, 0.1 mmol), **2e** was obtained as a yellow semi-solid (20 mg, 55%).  $R_f = 0.4$  (hexane:EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.12 (s, 1H), 8.23–8.20 (m, 1H), 8.20 – 8.16 (m, 1H), 7.80 (d,  $J$  = 1 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.08 (d,  $J$  = 9 Hz, 2H), 6.79 (d,  $J$  = 9 Hz, 2H), 5.98 (s, 2H), 4.42 (q,  $J$  = 7 Hz, 2H), 3.74 (s, 3H), 1.43 (t,  $J$  = 7 Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.4, 159.1, 142.7, 137.7, 132.3, 129.9, 129.5, 128.9, 127.8 (2C), 127.1, 126.7, 126.5, 123.4, 122.8, 114.2 (2C), 108.7, 61.2, 55.2, 48.0, 14.3. **HRMS** (ESI) m/z calcd for C<sub>22</sub>H<sub>21</sub>N<sub>2</sub>O<sub>3</sub> (M+H)<sup>+</sup>: 361.1547; found: 361.1555.

*ethyl 3-(4-fluorobenzyl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (2f):* Following the



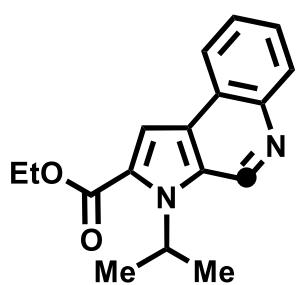
general procedure A, using **1f** (38 mg, 0.1 mmol), **2f** was obtained as a yellow semi-solid (22 mg, 60%).  $R_f = 0.4$  (hexane:EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.08 (s, 1H), 8.26 – 8.20 (m, 1H), 8.20 – 8.15 (m, 1H), 7.81 (d,  $J$  = 1 Hz, 1H), 7.68 – 7.60 (m, 2H), 7.09 (dd,  $J_1$  = 9 Hz,  $J_2$  = 5 Hz, 2H), 6.96 (t,  $J$  = 9 Hz, 2H), 6.00 (s, 2H), 4.41 (q,  $J$  = 7 Hz, 2H), 1.43 (t,  $J$  = 7 Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.4 (d,  $J$  = 204 Hz, 1C), 161.4, 142.8, 137.4, 133.2 (d,  $J$  = 3 Hz, 1C), 132.2, 130.0, 128.8, 128.2, 128.1 (d,  $J$  = 8 Hz, 2C), 127.2, 126.8, 126.6, 123.3, 122.8, 115.7 (d,  $J$  = 22 Hz, 2C), 108.9, 61.2, 47.8, 14.3. **19F NMR** (377 MHz, CDCl<sub>3</sub>)  $\delta$  -114.3. **HRMS** (ESI) m/z calcd for C<sub>21</sub>H<sub>18</sub>FN<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 349.1374; found: 349.1369.

*ethyl 3-phenethyl-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (2g):* Following the general



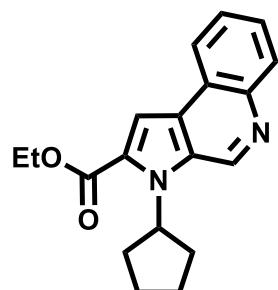
procedure A, using **1g** (37 mg, 0.1 mmol), **2g** was obtained as a yellow semi-solid (21 mg, 60%).  $R_f = 0.4$  (hexane:EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.83 (s, 1H), 8.35 – 8.30 (m, 1H), 8.00 (d,  $J$  = 9 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.22–7.18 (m, 3H), 7.12 – 7.05 (m, 2H), 4.98 (t,  $J$  = 7 Hz, 2H), 4.43 (q,  $J$  = 7 Hz, 2H), 3.16 (t,  $J$  = 7 Hz, 2H), 1.46 (t,  $J$  = 7 Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.2, 141.1, 137.7, 137.5, 132.1, 131.5, 129.9, 128.9, 128.9 (2C), 128.7 (2C), 126.9, 125.4, 125.0, 124.7, 120.9, 108.3, 61.2, 47.1, 37.8, 14.4. **HRMS** (ESI) m/z calcd for C<sub>22</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub> (M+H): 345.1598; found: 345.1605.

*ethyl 3-isopropyl-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (2h):* Following the general



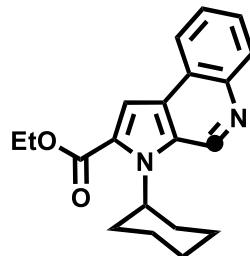
procedure A, using **1h** (32 mg, 0.1 mmol), **2h** was obtained as a white semi-solid (22 mg, 72%).  $R_f = 0.6$  (hexane:EtOAc = 7:3). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.40 (s, 1H), 8.19 (td,  $J_1 = 7$  Hz,  $J_2 = 3$  Hz, 2H), 7.73 (d,  $J = 1$  Hz, 1H), 7.67 – 7.56 (m, 2H), 6.01 (hept,  $J = 7$  Hz, 1H), 4.44 (q,  $J = 7$  Hz, 2H), 1.77 (d,  $J = 7$  Hz, 6H), 1.47 (t,  $J = 7$  Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.7, 141.6, 138.9, 131.2, 129.4, 129.3, 127.4, 126.9, 126.7, 123.7, 122.7, 108.4, 61.2, 48.9, 22.7 (2C), 14.3. **HRMS** (ESI) m/z calcd for C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 283.1441; found: 283.1457.

*ethyl 3-cyclopentyl-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (2i):* Following the general



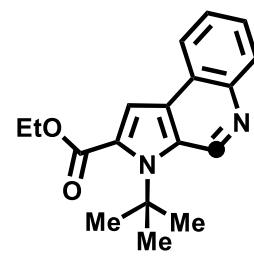
procedure A, using **1i** (33 mg, 0.1 mmol), **2i** was obtained as an orange semi-solid (17 mg, 52%).  $R_f = 0.4$  (hexane:EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.27 (s, 1H), 8.26 – 8.11 (m, 2H), 7.72 (d,  $J = 1$  Hz, 1H), 7.68 – 7.55 (m, 2H), 6.14 (p,  $J = 9$  Hz, 1H), 4.43 (q,  $J = 7$  Hz, 2H), 2.41 – 2.18 (m, 4H), 2.20 – 2.05 (m, 2H), 1.95 – 1.79 (m, 2H), 1.47 (t,  $J = 7$  Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.9, 142.1, 138.8, 130.8, 129.8 (2C), 127.2, 126.8, 126.6, 123.7, 122.7, 108.3, 61.1, 57.2, 32.2 (2C), 25.4 (2C), 14.3. **HRMS** (ESI) m/z calcd for C<sub>19</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 309.1598; found: 309.1594.

*ethyl 3-cyclohexyl-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (2j):* Following the general

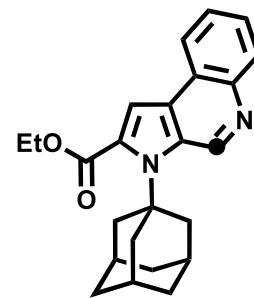


procedure A, using **1j** (34 mg, 0.1 mmol), **2j** was obtained as an orange semi-solid (19 mg, 60%).  $R_f = 0.4$  (hexane:EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.43 (s, 1H), 8.24 – 8.12 (m, 2H), 7.73 (d,  $J = 1$  Hz, 1H), 7.66 – 7.56 (m, 2H), 5.58 (tt,  $J_1 = 12$  Hz,  $J_2 = 4$  Hz, 1H), 4.43 (q,  $J = 7$  Hz, 2H), 2.35 (qd,  $J_1 = 13$  Hz,  $J_2 = 4$  Hz, 2H), 2.10 (dd,  $J_1 = 13$  Hz,  $J_2 = 3$  Hz, 2H), 2.00 (dt,  $J_1 = 15$  Hz,  $J_2 = 3$  Hz, 2H), 1.84 (dt,  $J_1 = 13$  Hz,  $J_2 = 3$  Hz, 1H), 1.64 – 1.48 (m, 2H), 1.47 (t,  $J = 7.1$  Hz, 3H), 1.42–1.33 (m, 1H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.8, 141.8, 139.5, 131.6, 129.6, 129.2, 127.1, 126.8, 126.6, 123.6, 122.6, 108.4, 61.2, 57.1, 32.8 (2C), 26.4 (2C), 25.5, 14.4. **HRMS** (ESI) m/z calcd for C<sub>20</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 323.1754; found: 323.1255.

*ethyl 3-(tert-butyl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (2k):* Following the general procedure A, using **1j** (32 mg, 0.1 mmol), **2j** was obtained as a yellow semi-solid (20 mg, 64%).  $R_f = 0.5$  (hexane: EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.45 (s, 1H), 8.15 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.60 (pd,  $J_1 = 7.0$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.38 (d,  $J = 0.8$  Hz, 1H), 4.43 (q,  $J = 7.1$  Hz, 2H), 1.93 (s, 9H), 1.45 (t,  $J = 7.2$  Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 164.23, 141.59, 140.02, 133.78, 132.10, 129.27, 128.30, 126.66, 126.63, 123.36, 122.62, 107.40, 61.94, 60.50, 31.72, 14.15. **HRMS** (ESI) m/z calcd for C<sub>18</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 297.1598; found: 297.1614.

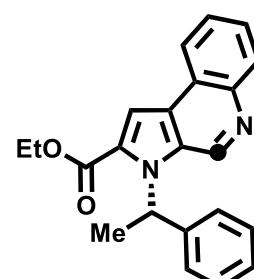


*ethyl 3-((3s,5s,7s)-adamantan-1-yl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (2l):*

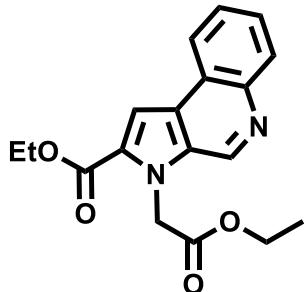


Following the general procedure A, using **1l** (40 mg, 0.1 mmol), **2l** was obtained as an orange semi-solid (23 mg, 62%).  $R_f = 0.4$  (hexane:EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.57 (s, 1H), 8.26 – 8.19 (m, 1H), 8.19 – 8.13 (m, 1H), 7.63 (dqd,  $J_1 = 8.4$  Hz,  $J_2 = 7.1$  Hz,  $J_3 = 1.6$  Hz, 2H), 7.35 (d,  $J = 0.8$  Hz, 1H), 4.45 (q,  $J = 7.1$  Hz, 2H), 2.57 (d,  $J = 3.0$  Hz, 6H), 2.31 (d,  $J = 3.5$  Hz, 4H), 1.90 – 1.77 (m, 7H), 1.46 (t,  $J = 7.1$  Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 164.87, 148.81, 141.55, 140.52, 133.49, 131.51, 129.22, 128.70, 126.62, 126.59, 126.52, 123.49, 122.64, 107.16, 62.34, 62.01, 42.95, 36.04, 30.30, 14.15. **HRMS** (ESI) m/z calcd for C<sub>24</sub>H<sub>27</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 375.2067; found: 375.2058.

*ethyl (S)-3-(1-phenylethyl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (2m):* Following the general procedure A, using **1m** (37 mg, 0.1 mmol), **2m** was obtained as a yellow semi-solid (10 mg, 27%).  $R_f = 0.4$  (hexane:EtOAc = 6:4). (*c* = 0.05, CHCl<sub>3</sub>). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.68 (s, 1H), 8.25 – 8.16 (m, 1H), 8.10 – 8.02 (m, 1H), 7.82 (d,  $J = 1$  Hz, 1H), 7.63 – 7.55 (m, 2H), 7.35 – 7.25 (m, 5H), 7.22 (q,  $J = 7$  Hz, 1H), 4.47 (q,  $J = 7$  Hz, 2H), 2.09 (d,  $J = 7$  Hz, 3H), 1.49 (t,  $J = 7$  Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 161.9, 142.1, 140.8, 139.5, 131.2, 129.7, 129.3, 128.8 (2C), 127.6, 127.2, 126.8, 126.7, 126.2 (2C), 123.5, 122.6, 108.7, 61.3, 54.0, 19.5, 14.3. **HRMS** (ESI) m/z calcd for C<sub>22</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 345.1598; found: 345.1601.

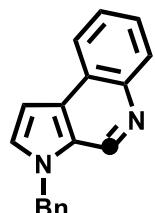


*ethyl 3-(2-ethoxy-2-oxoethyl)-3H-pyrrolo[2,3-*c*]quinoline-2-carboxylate (2n):* Following the



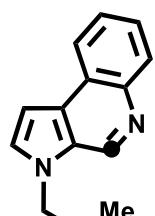
general procedure A, using **1n** (35 mg, 0.1 mmol), **2n** was obtained as a colourless semi-solid (19 mg, 56%).  $R_f = 0.4$  (hexane:EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.04 (s, 1H), 8.29 – 8.15 (m, 2H), 7.82 (d,  $J = 1$  Hz, 1H), 7.70 – 7.60 (m, 2H), 5.52 (s, 2H), 4.43 (q,  $J = 7$  Hz, 2H), 4.26 (q,  $J = 7$  Hz, 2H), 1.45 (t,  $J = 7$  Hz, 3H), 1.29 (t,  $J = 7$  Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.14, 161.57, 142.94, 136.50, 132.27, 129.96, 129.10, 127.20, 126.85, 126.73, 123.33, 122.89, 108.86, 61.94, 61.32, 46.73, 14.31, 14.14. **HRMS** (ESI) m/z calcd for C<sub>18</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub> (M+H)<sup>+</sup>: 327.1339; found: 327.1341.

*3-benzyl-3H-pyrrolo[2,3-*c*]quinoline (4a):* Following the general procedure A, using **3a** (30



mg, 0.1 mmol), **4a** was obtained as a yellow semi-solid (17 mg, 60%).  $R_f = 0.4$  (hexane:EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.99 (s, 1H), 8.25 – 8.20 (m, 1H), 8.20 – 8.14 (m, 1H), 7.64 – 7.56 (m, 2H), 7.37 (d,  $J = 3$  Hz, 1H), 7.35 – 7.28 (m, 3H), 7.18 – 7.12 (m, 2H), 7.07 (dd,  $J_1 = 3$  Hz,  $J_2 = 1$  Hz, 1H), 5.54 (s, 2H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.2, 136.6, 136.3, 130.4, 129.43, 129.40, 129.3, 129.0 (2C), 128.2, 126.8 (2C), 126.2, 126.1, 123.5 123.0, 100.8, 50.9. **HRMS** (ESI) m/z calcd for C<sub>18</sub>H<sub>15</sub>N<sub>2</sub> (M+H)<sup>+</sup>: 259.1230; found: 259.1233.

*3-propyl-3H-pyrrolo[2,3-*c*]quinoline (4b):* Following the general procedure A, using **3b** (25

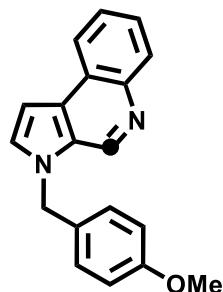
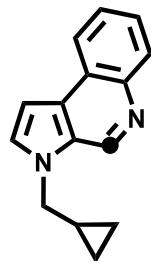
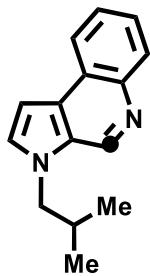


mg, 0.1 mmol), **4b** was obtained as a yellow solid (14 mg, 60%), m.p. 165–167 °C.  $R_f = 0.4$  (hexane: EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.06 (s, 1H), 8.26 – 8.17 (m, 2H), 7.65 – 7.57 (m, 2H), 7.36 (d,  $J = 3.0$  Hz, 1H), 7.03 (dd,  $J_1 = 2.9$  Hz,  $J_2 = 0.8$  Hz, 1H), 4.32 (t,  $J = 7.0$  Hz, 2H), 1.98 (q,  $J = 7.2$  Hz, 2H), 0.96 (t,  $J = 7.4$  Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.5, 135.5, 130.6, 129.5, 129.0, 128.9, 126.3, 126.3, 123.5, 123.0, 100.4, 48.8, 24.3, 11.4. **HRMS** (ESI) m/z calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub> (M+H)<sup>+</sup>: 211.1230; found: 211.1224.

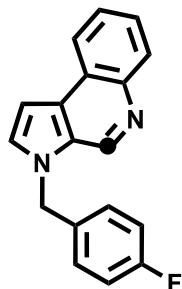
**3-isobutyl-3H-pyrrolo[2,3-*c*]quinoline (4c):** Following the general procedure A, using **3c** (25 mg, 0.1 mmol), **4c** was obtained as a yellow semi-solid (14 mg, 60%).  $R_f = 0.4$  (hexane: EtOAc = 6:4).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.27 (s, 1H), 8.09 (d,  $J = 8$  Hz, 1H), 7.45 (d,  $J = 8$  Hz, 1H), 7.38 (t,  $J = 8$  Hz, 1H), 7.32 – 7.26 (m, 2H), 6.37 (t,  $J = 6.0$  Hz, 1H), 3.43 (t,  $J = 6$  Hz, 2H), 2.03 – 1.94 (m, 1H), 1.04 (d,  $J = 7$  Hz, 6H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.7, 136.7, 126.8, 124.4, 123.2, 121.8, 121.2, 113.5, 112.5, 106.3, 47.3, 28.6, 20.3. HRMS (ESI) m/z calcd for  $\text{C}_{15}\text{H}_{17}\text{N}_2$  ( $\text{M}+\text{H})^+$ : 225.1386; found: 225.1380.

**3-(cyclopropylmethyl)-3H-pyrrolo[2,3-*c*]quinoline (4d):** Following the general procedure A, using **3d** (24 mg, 0.1 mmol), **4d** was obtained as a colourless semi-solid (17 mg, 75%).  $R_f = 0.4$  (hexane:EtOAc = 6:4).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.12 (s, 1H), 8.33 – 8.26 (m, 1H), 8.26 – 8.20 (m, 1H), 7.68 – 7.61 (m, 2H), 7.57 (d,  $J = 2.9$  Hz, 1H), 7.08 (d,  $J = 2.9$  Hz, 1H), 4.23 (d,  $J = 6.9$  Hz, 2H), 1.35 (dddt,  $J_1 = 11.9$  Hz,  $J_2 = 7.0$  Hz,  $J_3 = 3.3$  Hz,  $J_4 = 1.6$  Hz, 1H), 0.76 – 0.68 (m, 2H), 0.49 – 0.42 (m, 2H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.3, 135.4, 130.4, 129.6, 129.1, 128.7, 126.3 (2C), 123.5, 123.1, 100.5, 51.5, 11.7, 4.3 (2C). HRMS (ESI) m/z calcd for  $\text{C}_{15}\text{H}_{15}\text{N}_2$  ( $\text{M}+\text{H})^+$ : 223.1230; found: 223.1227.

**3-(4-methoxybenzyl)-3H-pyrrolo[2,3-*c*]quinoline (4e):** Following the general procedure A, using **3e** (31 mg, 0.1 mmol), **4e** was obtained as a yellow semi-solid (16 mg, 52%).  $R_f = 0.4$  (hexane: EtOAc = 6:4).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.04 – 8.97 (m, 1H), 8.25 – 8.17 (m, 2H), 7.66 – 7.55 (m, 2H), 7.37 (d,  $J = 2.9$  Hz, 1H), 7.17 – 7.08 (m, 2H), 7.05 (dd,  $J_1 = 3.0$  Hz,  $J_2 = 0.8$  Hz, 1H), 6.88 – 6.80 (m, 2H), 5.46 (s, 2H), 3.78 (s, 3H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 141.8, 135.9, 130.7, 129.7, 129.2, 129.1, 128.4, 126.3, 123.5, 123.0, 114.45, 100.8, 55.3, 50.5. HRMS (ESI) m/z calcd for  $\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}$  ( $\text{M}+\text{H})^+$ : 289.1335; found: 289.1339.

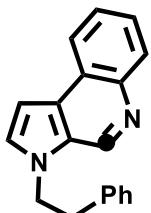


**3-(4-fluorobenzyl)-3H-pyrrolo[2,3-c]quinoline (4f):** Following the general procedure A,



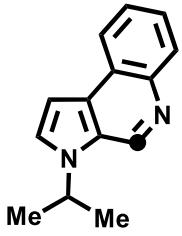
using **3f** (30 mg, 0.1 mmol), **4f** was obtained as a yellow semi-solid (15 mg, 52%).  $R_f = 0.4$  (hexane: EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.01 (s, 1H), 8.31 – 8.20 (m, 2H), 7.67 (tdd,  $J_1 = 5.7$  Hz,  $J_2 = 4.1$  Hz,  $J_3 = 1.8$  Hz, 2H), 7.42 – 7.36 (m, 1H), 7.18 (dd,  $J_1 = 7.8$  Hz,  $J_2 = 4.8$  Hz, 2H), 7.14 – 7.10 (m, 1H), 7.07 (td,  $J_1 = 8.6$  Hz,  $J_2 = 1.7$  Hz, 2H), 5.54 (s, 2H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 163.7, 161.3, 142.5, 136.2, 132.4, 132.4, 130.1, 129.6, 129.43, 129.3, 128.6, 128.5, 126.2, 126.2, 123.5, 123.0, 116.1, 115.9, 101.0, 50.2. **19F NMR** (377 MHz, CDCl<sub>3</sub>) δ -113.8. **HRMS** (ESI) m/z calcd for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>F (M+H)<sup>+</sup>: 277.1136; found: 277.1133.

**3-phenethyl-3H-pyrrolo[2,3-c]quinoline (4g):** Following the general procedure A, using **3g**



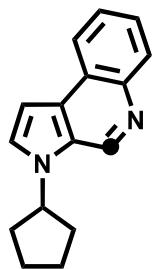
(30 mg, 0.1 mmol), **4g** was obtained as a yellow semi-solid (18 mg, 66 %).  $R_f = 0.4$  (hexane: EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.04 (s, 1H), 8.20 (tt,  $J_1 = 9.6$  Hz,  $J_2 = 3.2$  Hz, 2H), 7.60 (qd,  $J_1 = 7.3$  Hz,  $J_2 = 3.3$  Hz, 2H), 7.28 – 7.19 (m, 4H), 7.11 (d,  $J = 3.0$  Hz, 1H), 7.01 (dd,  $J_1 = 7.2$  Hz,  $J_2 = 2.3$  Hz, 2H), 6.94 (d,  $J = 2.9$  Hz, 1H), 4.58 (t,  $J = 6.9$  Hz, 2H), 3.20 (t,  $J = 6.9$  Hz, 2H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 141.2, 137.7, 135.3, 130.9, 129.7, 128.8 (2C), 128.7, 128.7 (2C), 128.4, 127.0, 126.3, 126.3, 123.5, 123.1, 100.4, 48.9, 37.6. **HRMS** (ESI) m/z calcd for C<sub>19</sub>H<sub>17</sub>N<sub>2</sub> (M+H)<sup>+</sup>: 273.1386; found: 273.1383.

**3-isopropyl-3H-pyrrolo[2,3-c]quinoline (4h):** Following the general procedure A, using **3h**



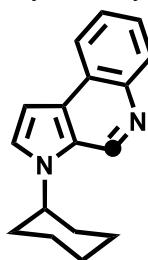
(33 mg, 0.1 mmol), **4h** was obtained as an orange semi-solid (19 mg, 67 %).  $R_f = 0.4$  (hexane: EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.10 (s, 1H), 8.25 – 8.13 (m, 2H), 7.64 – 7.54 (m, 2H), 7.44 (d,  $J = 3.0$  Hz, 1H), 7.03 (d,  $J = 3.0$  Hz, 1H), 4.94 (h,  $J = 6.7$  Hz, 1H), 1.64 (d,  $J = 6.6$  Hz, 6H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 142.36, 136.14, 129.43, 129.09, 128.69, 126.02, 125.93, 125.85, 123.68, 122.95, 100.35, 48.26, 23.37 (2C). **HRMS** (ESI) m/z calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub> (M+H)<sup>+</sup>: 211.1230; found: 211.1235.

**3-cyclopentyl-3H-pyrrolo[2,3-c]quinoline (4i):** Following the general procedure A, using **3i**



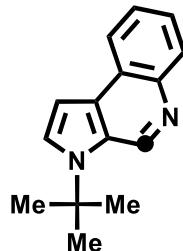
(26 mg, 0.1 mmol), **4i** was obtained as an orange semi-solid (14 mg, 56%).  $R_f = 0.4$  (hexane: EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.16 (s, 1H), 8.22–8.19 (m, 2H), 7.64 – 7.54 (m, 2H), 7.45 (d,  $J$  = 3 Hz, 1H), 7.02 (d,  $J$  = 3 Hz, 1H), 5.05 (p,  $J$  = 7 Hz, 1H), 2.42–2.28 (m, 2H), 2.08 – 1.92 (m, 4H), 1.88–1.83 (m, 2H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.6, 135.9, 129.6, 129.2, 128.8, 127.3, 126.2 (2C), 123.6, 123.0, 100.3, 57.9, 33.3 (2C), 24.1 (2C). **HRMS** (ESI) m/z calcd for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub> (M+H)<sup>+</sup>: 237.1386; found: 237.1391.

**3-cyclohexyl-3H-pyrrolo[2,3-c]quinoline (4j):** Following the general procedure A, using **3j**



(27 mg, 0.1 mmol), **4j** was obtained as a yellow semi-solid (12 mg, 45%).  $R_f = 0.4$  (hexane:EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.10 (s, 1H), 8.19 (ddd,  $J_1$  = 7.2 Hz,  $J_2$  = 3.4 Hz,  $J_3$  = 2.2 Hz, 2H), 7.61 – 7.54 (m, 2H), 7.43 (d,  $J$  = 3.0 Hz, 1H), 7.01 (dd,  $J_1$  = 3.0 Hz,  $J_2$  = 0.8 Hz, 1H), 4.46 (tt,  $J_1$  = 11.9 Hz,  $J_2$  = 3.8 Hz, 1H), 2.22 (ddt,  $J_1$  = 10.1 Hz,  $J_2$  = 3.9 Hz,  $J_3$  = 1.8 Hz, 2H), 2.02 – 1.93 (m, 2H), 1.87 – 1.75 (m, 4H), 1.63 – 1.49 (m, 3H), 1.38 – 1.29 (m, 1H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.15, 136.00, 129.18, 129.03, 128.68, 126.47, 126.03, 125.94, 123.69, 122.96, 100.25, 77.39, 77.07, 76.76, 56.13, 34.15, 25.81, 25.48. **HRMS** (ESI) m/z calcd for C<sub>17</sub>H<sub>19</sub>N<sub>2</sub> (M+H)<sup>+</sup>: 251.1543; found: 251.1539.

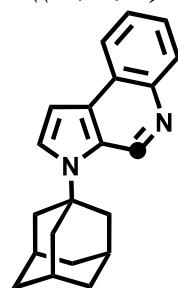
**3-(tert-butyl)-3H-pyrrolo[2,3-c]quinoline (4k):** Following the general procedure A, using **3k**



(25 mg, 0.1 mmol), **4k** was obtained as a yellow semi-solid (14 mg, 60%).  $R_f = 0.4$  (hexane: EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.40 (s, 1H), 8.24 – 8.14 (m, 2H), 7.64 – 7.54 (m, 2H), 7.52 (d,  $J$  = 3 Hz, 1H), 6.99 (dd,  $J_1$  = 3 Hz,  $J_2$  = 1 Hz, 1H), 1.84 (s, 9H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.8, 138.2, 131.3, 128.5, 128.4, 128.0, 126.3, 126.1, 123.6, 122.9, 99.2, 57.1, 30.7.

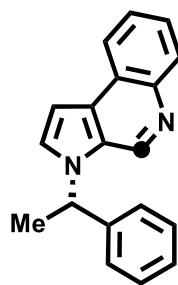
**HRMS** (ESI) m/z calcd for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub> (M+H)<sup>+</sup> : 225.1386; found: 225.1399.

**3-((3s,5s,7s)-adamantan-1-yl)-3H-pyrrolo[2,3-c]quinoline (4l):** Following the general



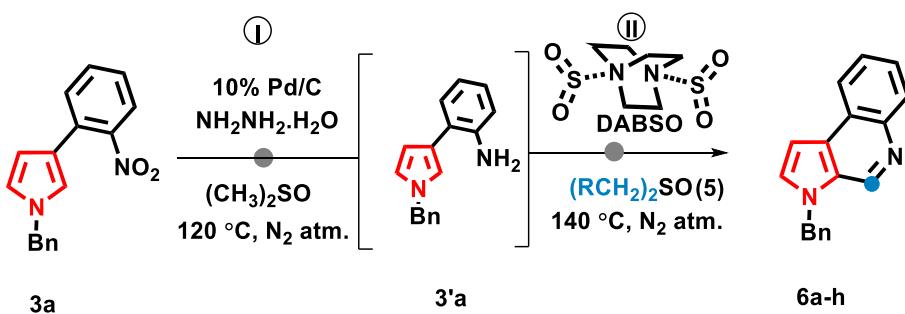
procedure A, using **3l** (32 mg, 0.1 mmol), **4l** was obtained as an orange semi-solid (19 mg, 60%).  $R_f = 0.4$  (hexane: EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.48 (s, 1H), 8.24 – 8.10 (m, 2H), 7.61–7.55 (m, 2H), 7.53 (d,  $J = 3$  Hz, 1H), 6.99 (d,  $J = 3$  Hz, 1H), 2.44 (d,  $J = 3.0$  Hz, 6H), 2.34 (br s, 3H), 1.87 (t,  $J = 3$  Hz, 6H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 138.9, 129.1, 126.5, 126.0, 125.8, 122.9, 99.1, 57.9, 43.3 (3C), 36.2 (3C), 29.8 (3C). **HRMS** (ESI) m/z calcd for C<sub>21</sub>H<sub>23</sub>N<sub>2</sub> (M+H)<sup>+</sup>: 303.1856; found: 303.1259.

**(S)-3-(1-phenylethyl)-3H-pyrrolo[2,3-c]quinoline (4m):** Following the general procedure



A, using **3m** (29 mg, 0.1 mmol), **4m** was obtained as a yellow semi-solid (5 mg, 18%).  $R_f = 0.4$  (hexane: EtOAc = 6:4). ( $c = 0.05$ , CHCl<sub>3</sub>). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.21 (s, 1H), 9.51 – 9.42 (m, 1H), 8.96 (s, 1H), 8.21 – 8.11 (m, 2H), 7.74 – 7.65 (m, 2H), 7.40 – 7.29 (m, 3H), 7.24 – 7.16 (m, 2H), 5.96 (q,  $J = 7$  Hz, 1H), 2.09 (d,  $J = 7$  Hz, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 144.3, 140.1, 138.1, 136.6, 130.9, 129.5, 129.4 (2C), 128.7, 127.8, 127.6, 127.0, 126.9, 125.8 (2C), 123.5, 120.7, 53.4, 21.9. **HRMS** (ESI) m/z calcd for C<sub>19</sub>H<sub>17</sub>N<sub>2</sub> (M+H)<sup>+</sup>: 273.1386; found: 273.1381.

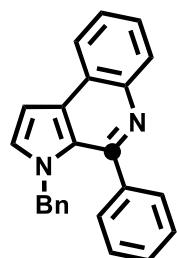
B. Procedure for the DABSO-facilitated formal [5+1] heteroannulation of PNDs with substituted sulfoxides



To a stirred solution of **3a** (0.1 mmol, 1 equiv.) in DMSO (2 mL) was added 10% Pd/C (5% w/w<sub>1a</sub>) followed by the addition of NH<sub>2</sub>NH<sub>2</sub>.H<sub>2</sub>O (5 equiv.) and the reaction mixture was allowed to stir at 120 °C for 7-8 h under inert condition until complete reduction of -NO<sub>2</sub> was indicated by TLC analysis. After completion of the reaction, DMSO was removed under high vacuum at 80-100 °C. Then resultant residue was then dissolved in appropriate substituted sulfoxide followed by DABSO and the reaction mixture was allowed to stir at 140 °C for 4-5 h

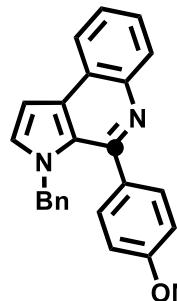
under inert condition. After completion of the reaction, the extraction was done and the combined organic layer dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo and the resultant residue was subjected to purification using  $\text{SiO}_2$ -gel column chromatography to arrive at the desired substituted tricyclic product **6a-h**.

**3-benzyl-4-phenyl-3H-pyrrolo[2,3-c]quinoline (6a):** Following the general procedure B,



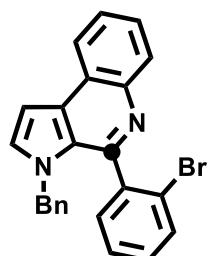
using **3a** (28 mg, 0.1 mmol) and sulfoxide **5a**, **6a** was obtained as a yellow semi-solid (25 mg, 72%).  $R_f = 0.4$  (hexane:EtOAc = 6:4).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 – 8.25 (m, 1H), 8.25 – 8.19 (m, 1H), 7.67 – 7.58 (m, 2H), 7.46 – 7.34 (m, 5H), 7.33 (d,  $J = 3$  Hz, 1H), 7.19 (d,  $J = 3$  Hz, 1H), 7.17 – 7.10 (m, 3H), 6.48 (dd,  $J_1 = 8$  Hz,  $J_2 = 2$  Hz, 2H), 5.07 (s, 2H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.3, 142.0, 139.7, 137.8, 132.5, 131.1, 129.6, 129.0 (2C), 128.6, 128.5, 128.4 (2C), 128.2 (2C), 127.6, 127.4, 126.4, 126.0, 125.8 (2C), 123.2, 122.7, 101.0, 52.4.  $\text{HRMS}$  (ESI) m/z calcd for  $\text{C}_{24}\text{H}_{19}\text{N}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 335.1543; found: 335.1545.

**3-benzyl-4-(4-methoxyphenyl)-3H-pyrrolo[2,3-c]quinoline (6b):** Following the general



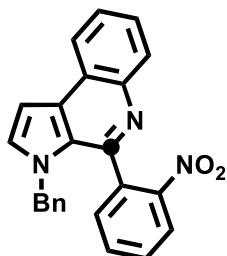
procedure B, using **3a** (28 mg, 0.1 mmol) and sulfoxide **5b**, **6b** was obtained as a white semi-solid (20 mg, 52%).  $R_f = 0.4$  (hexane:EtOAc = 6:4).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30 – 8.23 (m, 1H), 8.23 – 8.18 (m, 1H), 7.66 – 7.55 (m, 2H), 7.36 – 7.28 (m, 3H), 7.20 – 7.09 (m, 4H), 6.89 (d,  $J = 8$  Hz, 2H), 6.59 – 6.49 (m, 2H), 5.11 (s, 2H), 3.86 (s, 3H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 148.1, 142.1, 137.8, 132.4, 132.2, 131.1, 130.3 (2C), 129.5, 128.4 (2C), 127.9, 127.4, 126.3, 125.9 (2C), 125.8, 123.1, 122.6, 113.6 (2C), 55.4, 52.3.  $\text{HRMS}$  (ESI) m/z calcd for  $\text{C}_{25}\text{H}_{21}\text{N}_2\text{O}$  ( $\text{M}+\text{H}$ ) $^+$ : 365.1648; found: 365.1643.

**3-benzyl-4-(2-bromophenyl)-3H-pyrrolo[2,3-c]quinoline (6c):** Following the general



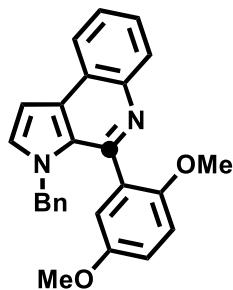
procedure B, using **3a** (28 mg, 0.1 mmol) and sulfoxide **5c**, **6c** was obtained as a yellow semi-solid (19 mg, 45%).  $R_f = 0.4$  (hexane: EtOAc = 6:4).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.33 – 8.27 (m, 1H), 8.22-8.20 (m, 1H), 7.64 (m, 3H), 7.35 – 7.29 (m, 2H), 7.21 – 7.09 (m, 6H), 6.56 – 6.49 (m, 2H), 5.12 (d,  $J = 16$  Hz, 1H), 4.98 (d,  $J = 16$  Hz, 1H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.5, 132.3, 131.3, 128.5 (2C), 127.5, 127.7, 126.3, 125.9 (2C), 123.4, 122.7, 100.9, 51.9.  $\text{HRMS}$  (ESI) m/z calcd for  $\text{C}_{24}\text{H}_{18}\text{BrN}_2$  ( $\text{M}+\text{H}$ ) $^+$  : 413.0648; found: 413.0651.

**3-benzyl-4-(2-nitrophenyl)-3H-pyrrolo[2,3-c]quinoline (6d):** Following the general



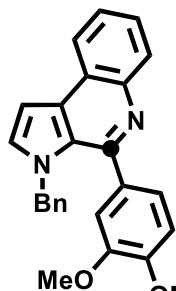
procedure B, using **3a** (28 mg, 0.1 mmol) and sulfoxide **5d**, **6d** was obtained as a yellow semi-solid (19 mg, 48%).  $R_f = 0.4$  (hexane:EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.39 – 8.26 (m, 1H), 8.19 (d,  $J$  = 8 Hz, 2H), 7.69–7.34 (m, 6H), 7.25–7.12 (m, 4H), 6.50 (d,  $J$  = 8 Hz, 2H), 5.09 (d,  $J$  = 17 Hz, 1H), 4.95 (d,  $J$  = 17 Hz, 1H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.05, 148.64, 140.90, 137.49, 133.64, 131.73, 130.06, 129.99, 128.57, 128.43, 127.69, 127.54, 127.43, 126.86, 126.12, 125.93, 123.04, 122.80, 116.42, 101.12, 52.47. **HRMS** (ESI) m/z calcd for C<sub>24</sub>H<sub>18</sub>N<sub>3</sub>O<sub>2</sub> (M+H)<sup>+</sup> : 380.1394; found: 380.1399.

**3-benzyl-4-(2,5-dimethoxyphenyl)-3H-pyrrolo[2,3-c]quinoline (6e):** Following the general



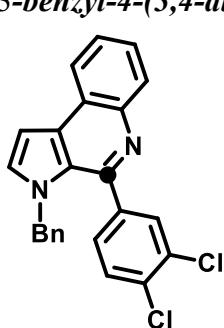
procedure B, using **3a** (28 mg, 0.1 mmol) and sulfoxide **5e**, **6e** was obtained as a white semi-solid (33 mg, 81%).  $R_f = 0.4$  (hexane: EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.29–8.25 (m, 1H), 8.25 – 8.17 (m, 1H), 7.64 – 7.55 (m, 2H), 7.29 (d,  $J$  = 3 Hz, 1H), 7.21 – 7.09 (m, 4H), 6.94 (dd,  $J_1$  = 9 Hz,  $J_2$  = 3 Hz, 1H), 6.84 (d,  $J$  = 9 Hz, 1H), 6.63 (d,  $J$  = 3 Hz, 1H), 6.59 – 6.50 (m, 2H), 5.11 (d,  $J$  = 17 Hz, 1H), 5.05 (d,  $J$  = 17 Hz, 1H), 3.57 (s, 3H), 3.46 (s, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.5, 151.4, 145.4, 142.2, 138.3, 131.9, 130.4, 129.6, 129.2, 128.3 (2C), 128.2, 127.1, 126.1, 125.9, 125.7 (2C), 123.4, 122.6, 116.1, 115.5, 112.3, 100.6, 56.0, 55.5, 51.5. **HRMS** (ESI) m/z calcd for C<sub>26</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 395.1754; found: 395.1758.

**3-benzyl-4-(3,4-dimethoxyphenyl)-3H-pyrrolo[2,3-c]quinoline (6f):** Following the general

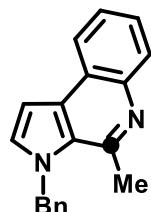


procedure B, using **3a** (28 mg, 0.1 mmol) and sulfoxide **5f**, **6f** was obtained as a white semi-solid (21 mg, 52%).  $R_f = 0.4$  (hexane: EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.30 – 8.19 (m, 2H), 7.62 (td,  $J_1$  = 6.6 Hz,  $J_2$  = 6.0 Hz,  $J_3$  = 3.5 Hz, 2H), 7.35 (d,  $J$  = 3.0 Hz, 1H), 7.19 (d,  $J$  = 3.1 Hz, 1H), 7.18 – 7.10 (m, 3H), 6.99 (dd,  $J_1$  = 8.1 Hz,  $J_2$  = 1.9 Hz, 1H), 6.90 (d,  $J$  = 8.1 Hz, 1H), 6.76 (d,  $J$  = 1.9 Hz, 1H), 6.54 – 6.46 (m, 2H), 5.12 (s, 2H), 3.95 (s, 3H), 3.57 (s, 3H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  149.4, 148.6, 147.9, 141.8, 138.1, 132.8, 131.2, 129.3, 128.5, 127.7, 127.3, 126.5, 126.0, 125.6, 123.1, 122.6, 121.5, 112.0, 110.8, 101.1,

56.14, 55.5, 52.2. **HRMS** (ESI) m/z calcd for C<sub>26</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup> : 395.1754; found: 395.1758.

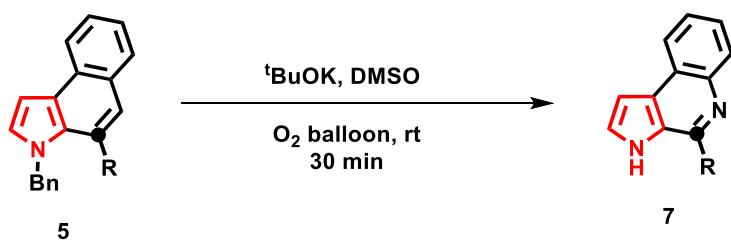


**3-benzyl-4-(3,4-dichlorophenyl)-3H-pyrrolo[2,3-c]quinoline (6g):** Following the general procedure B, using **3a** (28 mg, 0.1 mmol) and sulfoxide **5g**, **6g** was obtained as a yellow solid (21 mg, 52%), m.p. 171–172 °C.  $R_f = 0.4$  (hexane: EtOAc = 6:4). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.43 (s, 1H), 8.39 – 8.32 (m, 1H), 7.79 (d,  $J = 7.6$  Hz, 3H), 7.46 (d,  $J = 7.6$  Hz, 1H), 7.43 – 7.37 (m, 2H), 7.22 (d,  $J = 7.1$  Hz, 1H), 7.17 (t,  $J = 7.4$  Hz, 2H), 6.43 (d,  $J = 7.4$  Hz, 2H), 5.21 (s, 2H). **13C{1H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 142.46, 139.66, 135.74, 135.43, 133.02, 131.28, 130.40, 129.78, 129.03, 128.75, 128.55, 128.38, 125.24, 123.19, 122.35, 102.74, 53.54. **HRMS** (ESI) m/z calcd for C<sub>24</sub>H<sub>17</sub>Cl<sub>2</sub>N<sub>2</sub> (M+H)<sup>+</sup>: 403.0763; found: 403.0769.



using **3a** (28 mg, 0.1 mmol) and sulfoxide **5h**, **6h** was obtained as a brown semi-solid (18 mg, 65%).  $R_f$  = 0.4 (hexane:EtOAc = 6:4). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.23 – 8.14 (m, 1H), 8.07 (dd,  $J_1$  = 8 Hz,  $J_2$  = 2 Hz, 1H), 7.58 (td,  $J_1$  = 7.0 Hz,  $J_2$  = 2 Hz, 1H), 7.53 (td,  $J_1$  = 7.0 Hz,  $J_2$  = 2 Hz, 1H), 7.34 – 7.21 (m, 4H), 7.09 (1H), 6.95 – 6.83 (m, 2H), 5.71 (s, 2H), 2.85 (s, 3H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) 5.7, 142.2, 138.4, 131.9, 130.3, 129.1 (2C), 128.8, 128.6, 127.8, 126.1, 125.4, 123.2, 122.5, 100.8, 52.9, 23.9. **HRMS** (ESI) m/z calcd for C<sub>19</sub>H<sub>17</sub>N<sub>2</sub> (M+H)<sup>+</sup>: found: 273.1392.

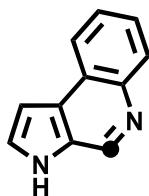
### C. Procedure for accessing some natural and unnatural Marinoquinolines



To the stirred solution of **5** (0.1 mmol, 1 equiv.) in DMSO (2 mL) was added <sup>t</sup>BuOK ( 0.6 mmol, 6 equiv.) portion wise and the reaction mixture was allowed to stir at room temperature for 30 min under oxygen condition. Upon complete consumption of starting material and

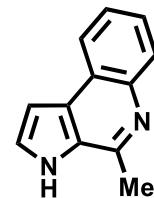
indication of new spot by TLC analysis, the reaction was quenched with water (5 mL) and extracted with EtOAc (5 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc ( $3 \times 5$  mL). The combined organic layer dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo and the resultant residue was subjected to purification using SiO<sub>2</sub>-gel column chromatography to arrive at the desired debenzylated product.

**3H-pyrrolo[2,3-c]quinoline (MQ K):** Following the general procedure C, using **4a** (26 mg, 0.1



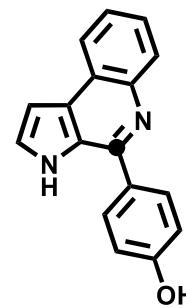
mmol), **MQ K** was obtained as a yellow solid (15 mg, 89%). m.p. 226–227 °C.  $R_f = 0.4$  (hexane: EtOAc = 6:4). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.66 (s, 1H), 8.36 (d,  $J = 8$  Hz, 1H), 8.33 – 8.25 (m, 1H), 7.90 (d,  $J = 3$  Hz, 1H), 7.79 – 7.66 (m, 2H), 7.18 (d,  $J = 3$  Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 135.2, 134.0, 133.4, 132.5, 128.4, 128.0, 127.7, 123.8, 123.7, 122.8, 102.6. HRMS (ESI) m/z calcd for C<sub>11</sub>H<sub>9</sub>N<sub>2</sub> (M+H)<sup>+</sup>: 169.0760; found: 169.0755.

**4-methyl-3H-pyrrolo[2,3-c]quinoline (MQ A):** Following the general procedure C, using **6h**



(27 mg, 0.1 mmol), **MQ A** was obtained as a white solid (10 mg, 52%), m.p. 234–235 °C.  $R_f = 0.4$  (hexane:EtOAc = 6:4). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.24 – 8.10 (m, 2H), 7.63 – 7.51 (m, 2H), 7.49 (d,  $J = 3.0$  Hz, 1H), 7.10 (d,  $J = 3.0$  Hz, 1H), 2.92 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 145.4, 141.9, 128.5, 128.5, 128.0, 126.6, 126.3, 125.6, 123.1, 122.9, 102.2, 20.52. HRMS (ESI) m/z calcd for C<sub>12</sub>H<sub>11</sub>N<sub>2</sub> (M+H)<sup>+</sup>: 183.0917; found: 183.0929.

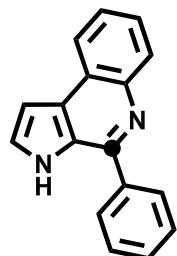
**4-(3H-pyrrolo[2,3-c]quinolin-4-yl)phenol (MQ H):** Following the general procedure C, using



**6b** (36 mg, 0.1 mmol), **7a** was obtained as a brown solid (12 mg, 44%), m.p. 173–174 °C.  $R_f = 0.4$  (hexane:EtOAc = 6:4). Then boron tribromide (500 μL of a 1 M solution in dichloromethane, 0.5 mmol) was added, dropwise, to a magnetically stirred solution of compound **7a** (60 mg, 0.2 mmol) in dichloromethane, maintained at -78 °C. After that, the reaction mixture was allowed to warm to room temperature over 2 h. After completion of the reaction, reaction mixture was quenched by adding NaHCO<sub>3</sub> and extraction was done with EtOAc (5 mL) and water (5 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc ( $3 \times 5$  mL). The combined organic layer dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo and the resultant residue was subjected to purification using SiO<sub>2</sub>-gel column chromatography to arrive at the desired debenzylated product.

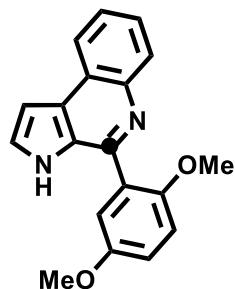
gel column chromatography (DCM:Methanol = 9:1,  $R_f$  = 0.3) to afford, **MQ-H** as a white, crystalline solid, m.p. 220-221 °C. **<sup>1</sup>H NMR** (400 MHz, MeOD) δ 8.47 (dd,  $J_1$  = 8 Hz,  $J_2$  = 2 Hz, 1H), 8.19 (d,  $J$  = 8 Hz, 1H), 8.06 (d,  $J$  = 3 Hz, 1H), 7.90 (d,  $J$  = 8 Hz, 2H), 7.83-7.73 (m, 2H), 7.45 (d,  $J$  = 3 Hz, 1H), 7.16 (d,  $J$  = 9 Hz, 2H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, MeOD) δ 161.3, 144.7, 135.8, 134.8, 133.6, 131.0 (2C), 128.8, 127.3, 123.8, 121.3, 116.3 (2C), 103.1. **HRMS** (ESI) m/z calcd for C<sub>17</sub>H<sub>13</sub>N<sub>2</sub>O (M+H)<sup>+</sup>: 261.1022; found: 261.1019.

**4-phenyl-3H-pyrrolo[2,3-c]quinoline (7b):** Following the general procedure C, using **6a** (33



mg, 0.1 mmol), **7b** was obtained as a white solid (16 mg, 65%), m.p. 213-214 °C.  $R_f$  = 0.4 (hexane:EtOAc = 6:4). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.01 (br s, 1H), 8.25 (td,  $J_1$  = 8 Hz,  $J_2$  = 2 Hz, 2H), 8.01 – 7.92 (m, 2H), 7.69 – 7.55 (m, 4H), 7.55 – 7.49 (m, 1H), 7.45 (d,  $J$  = 3 Hz, 1H), 7.16 (d,  $J$  = 3 Hz, 1H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 146.8, 143.1, 138.4, 129.8, 129.3 (2C), 129.3, 128.4 (2C), 127.5, 126.3, 126.2, 125.9, 123.2, 122.9, 102.2. **HRMS** (ESI) m/z calcd for C<sub>17</sub>H<sub>13</sub>N<sub>2</sub> (M+H)<sup>+</sup>: 245.1073; found: 245.1086.

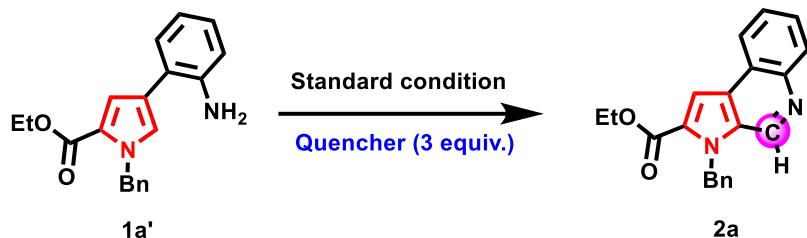
**4-(2,5-dimethoxyphenyl)-3H-pyrrolo[2,3-c]quinoline (7c):** Following the general procedure



C, using **6e** (39 mg, 0.1 mmol), **7c** was obtained as a yellow solid (24 mg, 80%), m.p. 185-186 °C.  $R_f$  = 0.4 (hexane:EtOAc = 6:4). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.12 (br s, 1H), 8.27 (dd,  $J_1$  = 7 Hz,  $J_2$  = 2 Hz, 1H), 8.25 (dd,  $J_1$  = 7 Hz,  $J_2$  = 2 Hz, 1H), 7.63 (td,  $J_1$  = 8 Hz,  $J_2$  = 2 Hz, 1H), 7.59 (td,  $J_1$  = 8 Hz,  $J_2$  = 2 Hz, 1H), 7.43 (t,  $J$  = 3 Hz, 1H), 7.40 (d,  $J$  = 3 Hz, 1H), 7.12 (dd,  $J_1$  = 3 Hz,  $J_2$  = 2 Hz, 1H), 7.10 – 7.01 (m, 2H), 3.86 (s, 3H), 3.75 (s, 3H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 154.8, 151.1, 144.7, 142.9, 129.9, 128.9, 128.7, 128.3, 126.0, 125.9, 125.9, 123.3, 122.8, 116.9, 116.8, 114.9, 101.4, 57.8, 55.9. **HRMS** (ESI) m/z calcd for C<sub>19</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 305.1285; found: 305.1301.

### 3. Mechanism Studies

#### (a) Radical quenching experiment

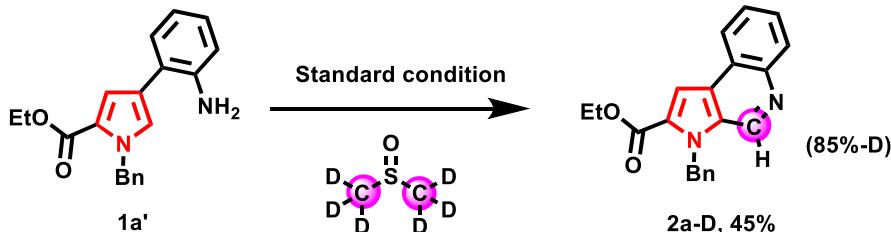


To a stirred solution of **1a'** (0.1 mmol, 1 equiv.) in DMSO (2 mL) was added DABSO followed by a radical scavenger, TEMPO/BHT (---. 3 equiv.), and the reaction mixture was allowed to stir at 140 °C for 4-5 h under inert condition. After completion of the reaction, extraction was done with EtOAc (5 mL) and water (5 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3×5 mL). The combined organic layer dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo and the resultant residue was subjected to purification using SiO<sub>2</sub>-gel column chromatography (hexane: EtOAc = 4: 1) to arrive **2a** (Table 1).

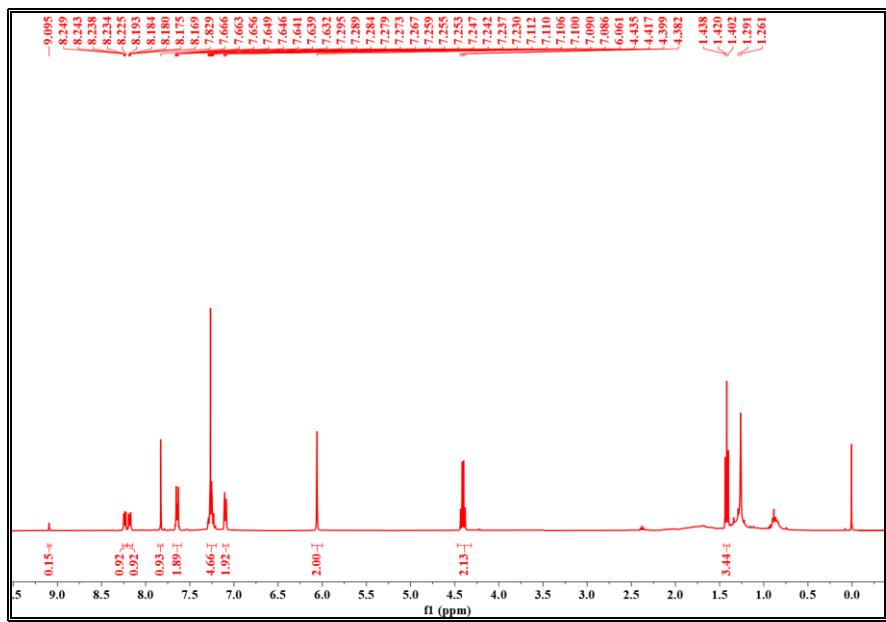
Table 1:

Sr. No.	Quencher	Yield (%) of <b>2a</b>
1	TEMPO	56
2	BHT	68

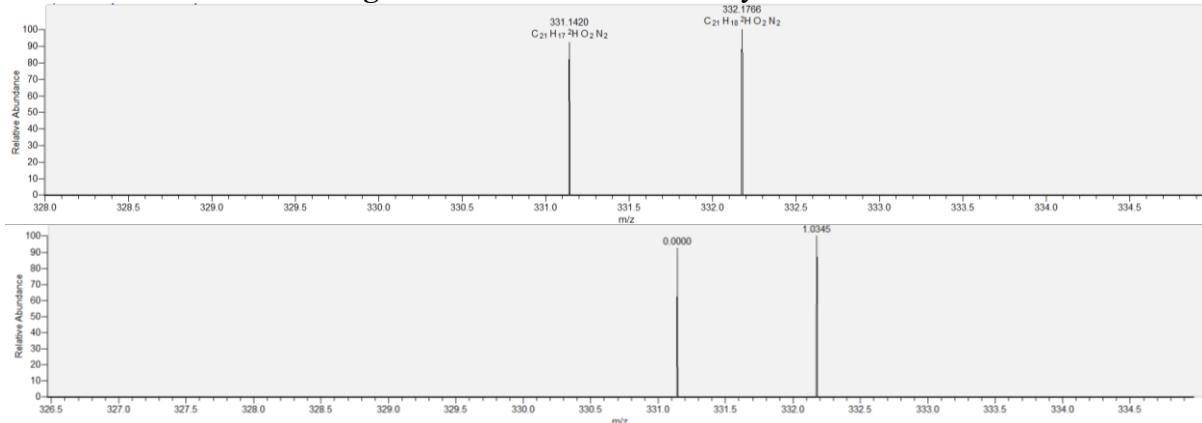
#### (b) Deuterated DMSO experiment



To a stirred solution of **1a'** (0.1 mmol, 1 equiv.) in DMSO-d<sub>6</sub> (2 mL) was added DABSO and the reaction mixture was allowed to stir at 140 °C for 4-5 h under inert condition. After completion of the reaction, extraction was done with EtOAc (5 mL) and water (5 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3×5 mL). The combined organic layer dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo and the resultant residue was subjected to purification using SiO<sub>2</sub>-gel column chromatography (hexane: EtOAc = 4: 1) to arrive **2a-D** in 45% yield. The product was analyzed by <sup>1</sup>H NMR (Figure S1) and HRMS (Figure S2).

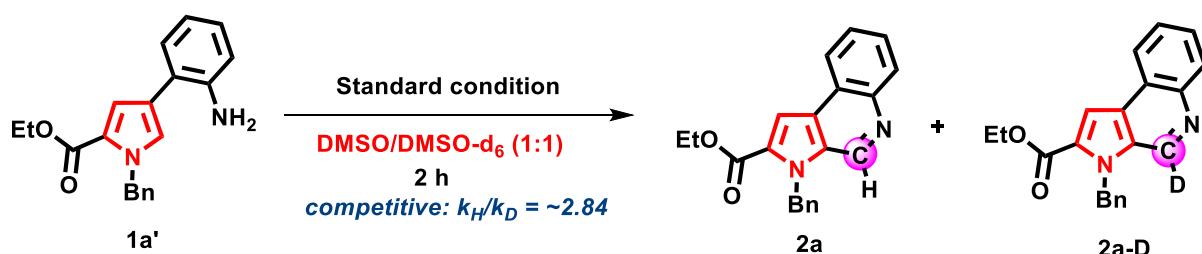


**Figure S1:** Detection of 2a-D by  $^1\text{H}$  NMR



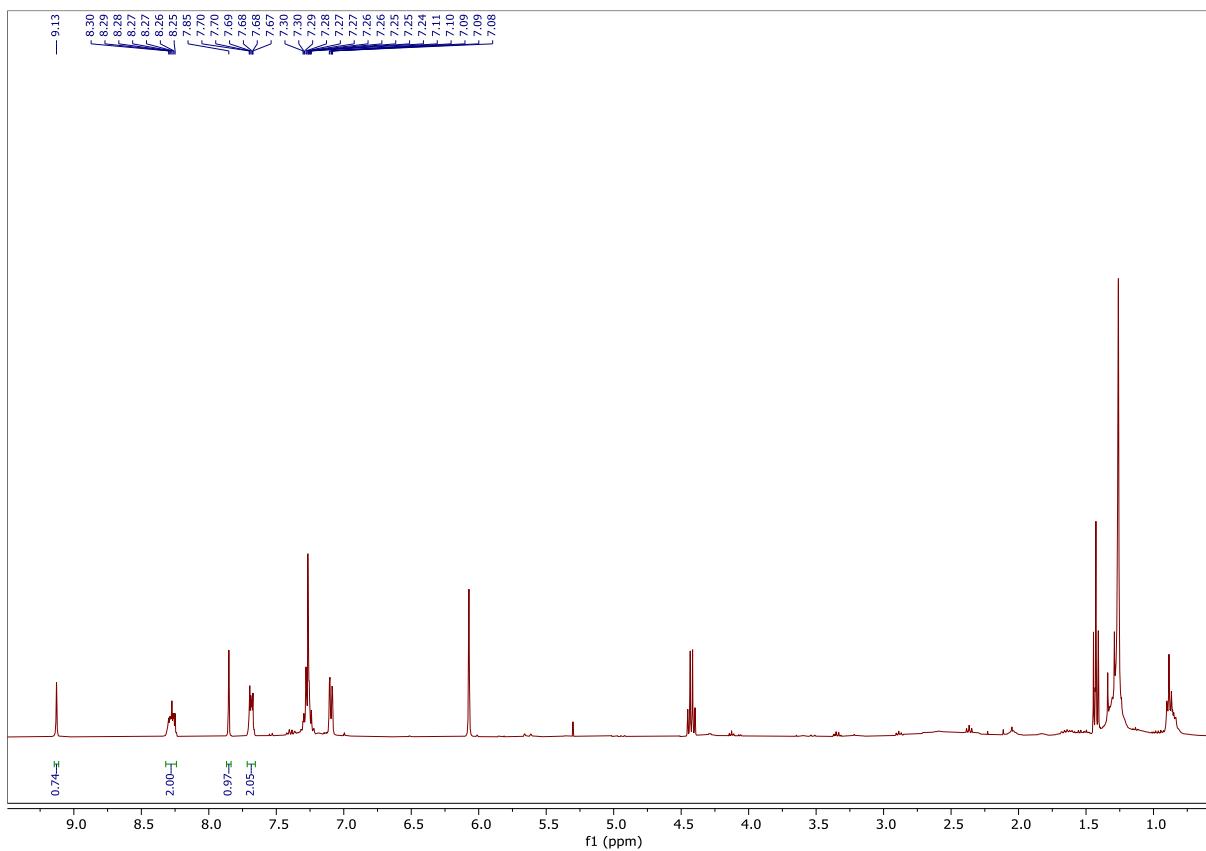
**Figure S2:** Detection of 2a-D by HRMS

### (c) KIE Experiment

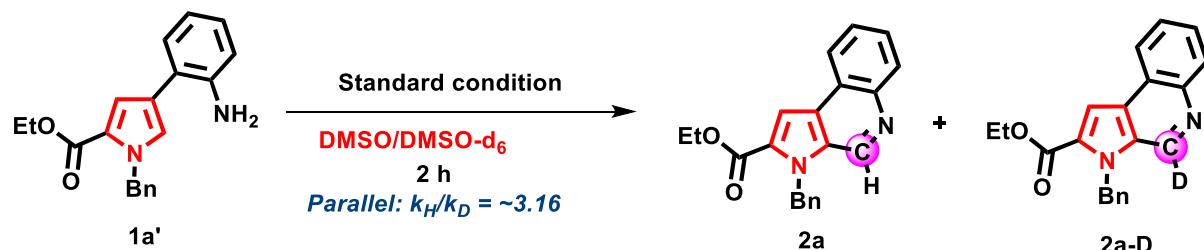


To a stirred solution of **1a'** (0.1 mmol, 1 equiv.) in DMSO and DMSO-d<sub>6</sub> (equimolar quantity) were added DABSO and the reaction mixture was allowed to stir at 140 °C for 2 h under inert condition. After completion of the reaction, extraction was done with EtOAc (5 mL) and water (5 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3×5 mL). The combined organic layer dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo and

the resultant residue was subjected to purification using SiO<sub>2</sub>-gel column chromatography (hexane: EtOAc = 4: 1) to arrive **2a-H/D**. The mixture of the product was analyzed by <sup>1</sup>H NMR (Figure S3).

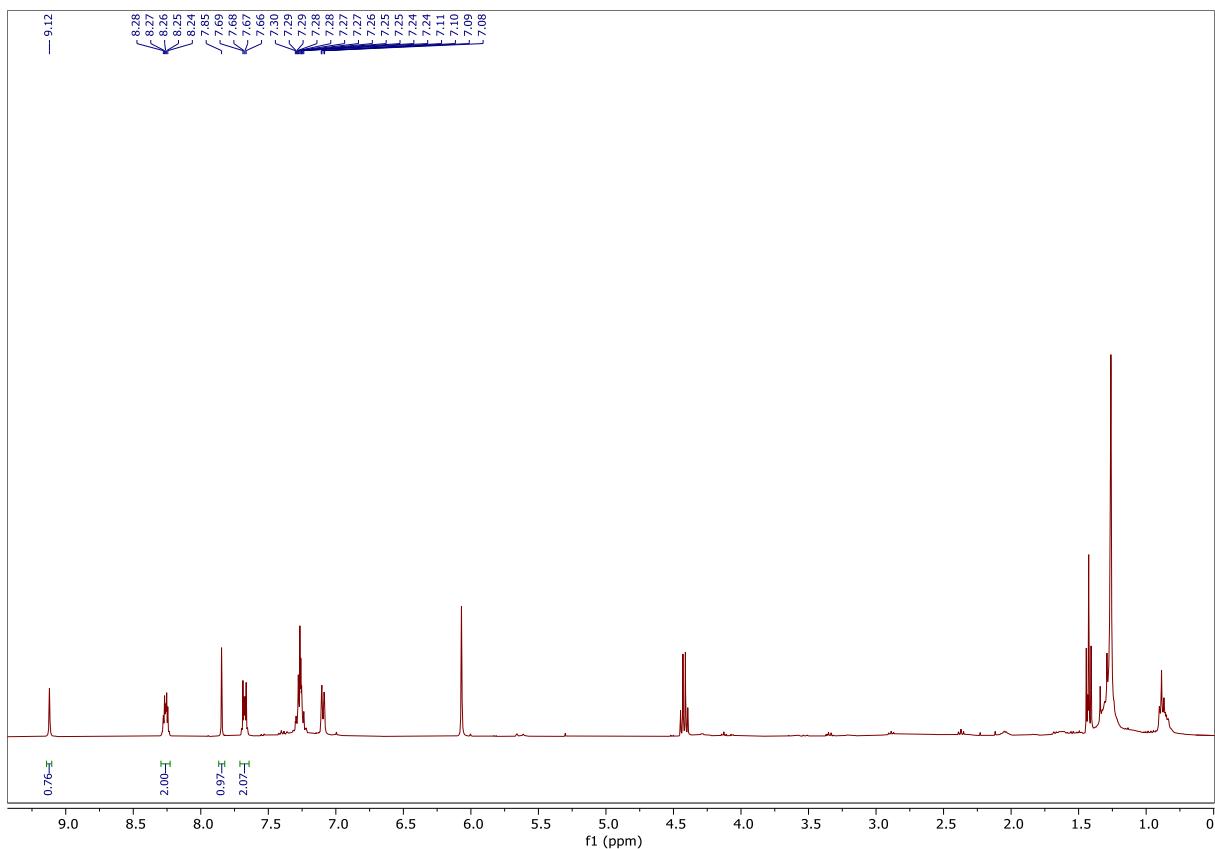


**Figure S3:** Detection of **2a-H/D** by <sup>1</sup>H NMR



To a stirred solution of **1a'** (0.1 mmol, 1 equiv.) in DMSO were added DABSO and the reaction mixture was allowed to stir at 140 °C for 2 h under inert condition. The same analysis was repeated with deuterated DMSO. After that, both the reaction mixture are mixed and extraction was done with EtOAc (5 mL) and water (5 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3×5 mL). The combined organic layer dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo and the resultant residue was subjected to

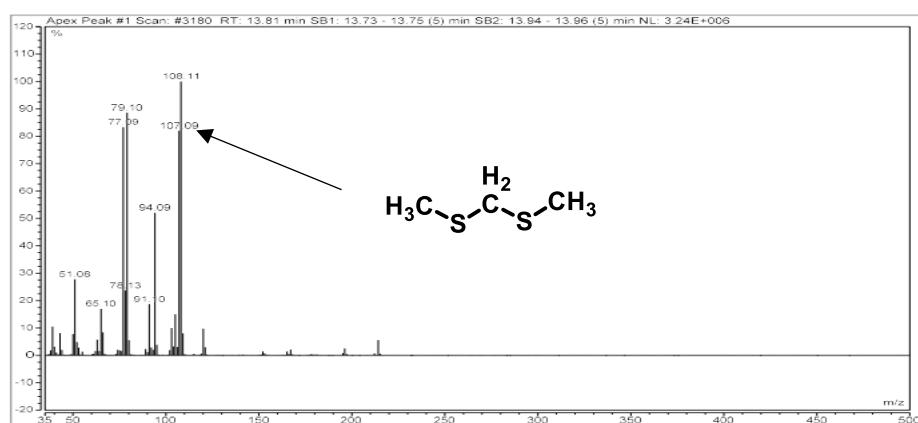
purification using SiO<sub>2</sub>-gel column chromatography (hexane: EtOAc = 4: 1) to arrive **2a-H/D**. The mixture of the product was analyzed by <sup>1</sup>H NMR (Figure S4).



**Figure S4:** Detection of **2a-H/D** by <sup>1</sup>H NMR

#### (d) Detection Of Bis(methylthio)methane ( $\text{CH}_3\text{SCH}_2\text{SCH}_3$ )

The Molecular weight of  $\text{CH}_3\text{SCH}_2\text{SCH}_3$  is 108 and was confirmed by GC-MS as shown in figure S5.



**Figure S5:** Detection of Bis(methylthio)methane by GC-MS.

#### 4. Spectral comparisons of the presently synthesized Marinoquinolines with the reported data

**Table 3:**  $^1\text{H}$  &  $^{13}\text{C}$  NMR comparison of presently synthesized **MQ K** with the reported data

$^1\text{H}$ NMR ((CD <sub>3</sub> ) <sub>2</sub> CO) [reported] <sup>4</sup>	$^1\text{H}$ NMR (400 MHz, (CD <sub>3</sub> ) <sub>2</sub> CO) (Our report)	$^{13}\text{C}$ NMR (CD <sub>3</sub> ) <sub>2</sub> CO [reported] <sup>4</sup>	$^{13}\text{C}$ NMR (100 MHz, (CD <sub>3</sub> ) <sub>2</sub> CO (Our report)
11.22 (broad s, 1H)	11.29 (broad s, 1H)	143.7	143.4
9.09 (s, 1H)	9.1 (s, 1H)	139.0	138.9
8.29 (m, 1H)	8.32-8.27 (m, 1H)	130.6	130.3
8.09 (m, 1H)	8.13-8.08 (m, 1H)	128.6	128.8
7.65 (d, <i>J</i> = 2.8 Hz, 1H)	7.66 (d, <i>J</i> = 3 Hz, 1H)	127.8	128.1
7.56 (m, 2H)	7.59-7.54 (m, 2H)	127.7	127.4
7.15 (d, <i>J</i> = 2.8 Hz, 1H)	7.15 (d, <i>J</i> = 3 Hz, 1H)	126.4	126.5
		126.1	126.2
		124.7	124.7
		123.9	124.0
		101.5	101.6

**Table 4:**  $^1\text{H}$  &  $^{13}\text{C}$  NMR comparison of presently synthesized **MQ A** with the reported data

$^1\text{H}$ NMR ((CD <sub>3</sub> ) <sub>2</sub> CO) [reported] <sup>4</sup>	$^1\text{H}$ NMR ((CD <sub>3</sub> ) <sub>2</sub> CO) [Our report]	$^{13}\text{C}$ NMR (CD <sub>3</sub> ) <sub>2</sub> CO [reported] <sup>4</sup>	$^{13}\text{C}$ NMR (100 MHz, (CD <sub>3</sub> ) <sub>2</sub> CO) [Our report]
11.39 (broad s, 1H),	11.40 (s, 1H)	146.8	146.8
8.24 (m, 1H),	δ 8.26 – 8.19 (m, 1H)	143.0	143.1
8.05 (m, 1H),	8.07 – 8.00 (m, 1H),	129.6	129.7
7.63 (d, <i>J</i> = 3.0 Hz, 1H),	7.60 (d, <i>J</i> = 3.0 Hz, 1H),	129.2	129.4
7.52 (m, 2H),	7.55-7.49 (m, 2H),	128.7	128.5
7.14 (d, <i>J</i> = 2.9 Hz, 1H),	7.13 (d, <i>J</i> = 3.0 Hz, 1H).	127.8	127.5
2.87 (s, 3H)	2.85 (s, 3H)	126.3	126.2
		125.9	125.7
		124.0	124.1
		123.8	123.7
		102.1	102.0
		20.9	20.9

**Table 4:**  $^1\text{H}$  &  $^{13}\text{C}$  NMR comparison of presently synthesized **MQ H** with the reported data

$^1\text{H}$ NMR (CD <sub>3</sub> OD ) [reported] <sup>5</sup>	$^1\text{H}$ NMR (400 MHz, CD <sub>3</sub> OD) (Our report)	$^{13}\text{C}$ NMR (CD <sub>3</sub> OD ) [reported] <sup>5</sup>	$^{13}\text{C}$ NMR (100 MHz, (CD <sub>3</sub> OD) (Our report)
8.54, d (7.4 Hz)	8.47 (dd, $J_1 = 8$ Hz, $J_2 = 2$ Hz, 1H)	162.5	161.3
8.20, d (7.4 Hz)	8.19 (d, $J = 8$ Hz, 1H)	144.0	144.6
8.17, d (2.4 Hz)	8.06 (d, $J = 3$ Hz, 1H)	137.5	135.8
7.86, dd (7.4 Hz, 7.4 Hz)	7.90 (d, $J = 8$ Hz, 2H)	134.6	134.8
7.85, dd (7.4 Hz, 7.4 Hz)	7.82-7.75 (m, 2H)	133.2	133.6
7.53, d (2.4 Hz )	7.45 (d, $J = 3$ Hz, 1H)	129.4	131.0
7.17, d (7.6 Hz)	7.16 (d, $J = 8$ Hz, 2H)	128.1	128.8
		125.6	127.3
		124.2	123.8
		121.5	121.3
		116.0	116.3
		103.7	103.1

## 5. Photoluminescence quantum yield measurements

2-Aminopyridine in 0.1 M H<sub>2</sub>SO<sub>4</sub> (quantum yield  $0.60 \pm 0.05$  at 285 nm)<sup>6</sup> was chosen as a standard for the fluorescence quantum yield measurement. The values are calculated using the standard reference sample that has a fixed and known fluorescence quantum yield value, according to the following equation:

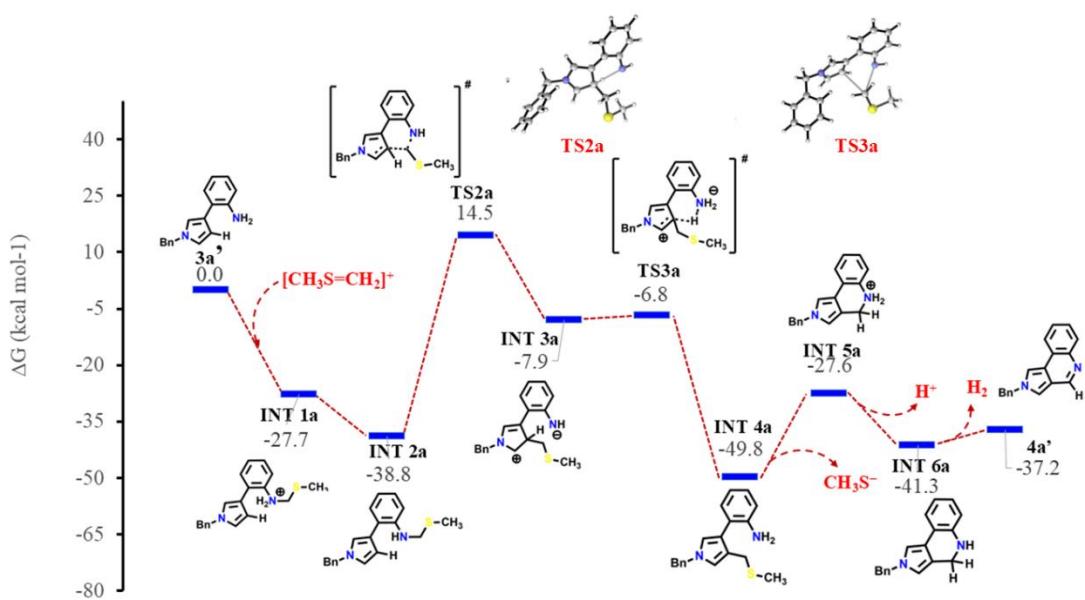
$$Q = Q_R \frac{I}{I_R} \frac{OD_R}{OD} \frac{\eta^2}{\eta_R^2}$$

where QY is the quantum yield,  $I$  is the measured integrated emission intensity, and OD is the optical density, and  $\eta$  is the refractive index. The subscript “R” refers to the reference fluorophore 2-aminopyridine of known quantum yield.

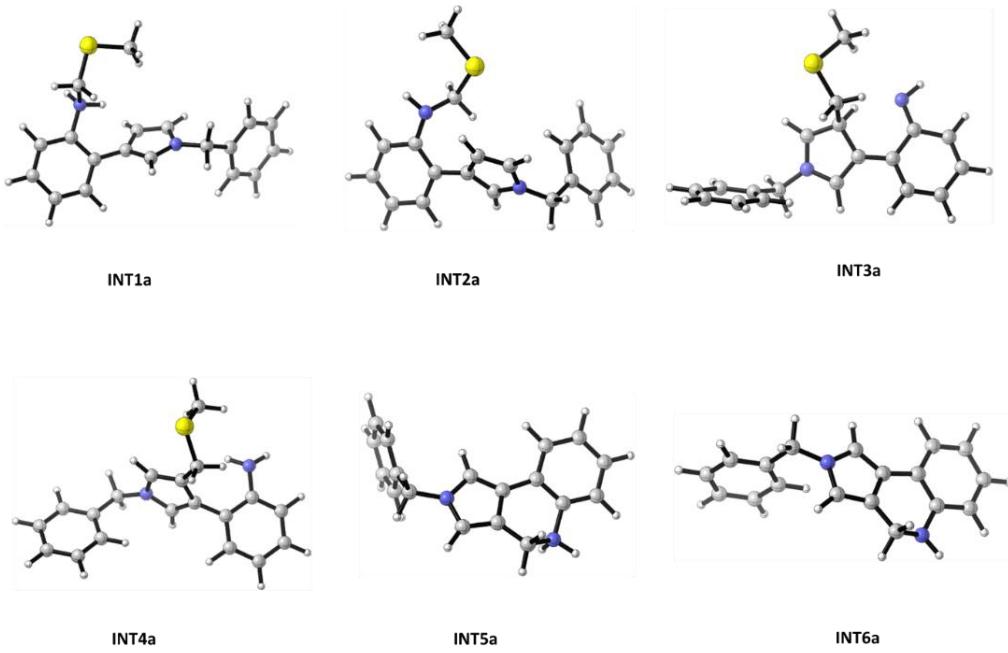
## 6. DFT calculations

Geometry optimization, transition state search, and intrinsic reaction coordinate (IRC) calculations are performed using the Gaussian 16 program package. Frequency calculations are performed at the optimized geometry to confirm the presence of true minima via the absence of any imaginary frequency. However, the imaginary frequency with less than  $-200\text{ cm}^{-1}$  confirms the transition state structure (TSs). Further IRC calculations were performed to check whether the TSs go backward and forward to form the desired reactants and products. PBE functional was used to perform all the calculations. For the geometry optimization and frequency calculations, the Pople's basis set 6-31G(d,p) was used. Single-point calculations were performed using the 6-311+G(d,p) basis set. To account for the dispersion effect the Grimme's dispersion correction (GD3), including the parameters of Becke-Johnson,<sup>38</sup> was utilized. Further, with a higher basis set, the solvation effect was incorporated by employing the solvent model based on density (SMD) in DMSO solvent. In the solvation process, molecules are transformed from the gas phase (1 atm) to the condensed phase (1 M), and hence, a concentration correction of  $\Delta G^{0 \rightarrow *}=1.89\text{ kcal mol}^{-1}$  was applied to the free energy values. In this work, the nucleus-independent chemical shift (NICS) was calculated using the gauge-independent atomic orbitals (GIAO) method. NICS, as defined by Schleyer, refers to the negative of the shielding constant obtained for a ghost atom placed at specific locations within a cyclic molecule.

DFT calculations were also done to check the feasibility of attack at the C-4 of the pyrrole ring. It was found that the formation of **TS2a** requires 53.3 kcal/mol compared to 36.9 kcal/mol for **C-2** attack (**Figure S6**). Since the activation energy for the **C-4** attack is 16.4 kcal/mol higher than that for **C-2** attack and hence product formation via **C-2** attack is energetically more favourable which corroborate well with the experimental data. The structures of the intermediates are shown in **Figures S7**.



**Figure S6.** The energy profile diagram of the formation of the product via **C-4** attack starting from **INT1a**. The values in the parenthesis represent the relative energy (in kcal mol<sup>-1</sup>).



**Figure S7.** The optimized structures of **INT1a-INT6a** at the PBE/6-31G(d,p) level of theory.

## **Coordinates of the optimized structures**

### **INT1**

C	1.710346000	-1.696290000	0.090400000
C	2.836190000	-0.963840000	-0.346016000
C	4.100194000	-1.530663000	-0.533358000
C	4.266422000	-2.896439000	-0.273368000
C	3.177279000	-3.654140000	0.185286000
C	1.920155000	-3.064785000	0.362415000
H	4.944531000	-0.924822000	-0.878895000
H	5.241976000	-3.363552000	-0.427020000
H	3.307545000	-4.719044000	0.395136000
H	1.069649000	-3.664446000	0.696930000
C	-0.406047000	-1.052743000	1.453683000
C	-1.551233000	-0.321059000	1.175588000
H	-0.160440000	-1.528015000	2.401563000
H	-2.413404000	-0.086903000	1.795680000
C	0.399510000	-1.045834000	0.273316000
N	2.661227000	0.498935000	-0.509065000
H	3.065150000	0.836473000	-1.395946000
C	3.222113000	1.335657000	0.655705000
H	2.656154000	1.011753000	1.541202000
H	4.279454000	1.056147000	0.773392000
S	2.980855000	3.103809000	0.422802000
C	4.458267000	3.543094000	-0.567075000
H	4.421642000	4.636766000	-0.677135000
H	5.381597000	3.277054000	-0.031834000
H	4.447705000	3.100487000	-1.574578000
C	-0.296291000	-0.283031000	-0.686337000
H	-0.128581000	-0.173809000	-1.758388000
C	-2.494794000	0.974330000	-0.791902000
H	-2.328227000	2.026346000	-0.501681000
H	-2.297717000	0.894218000	-1.873897000
C	-3.914294000	0.562260000	-0.467952000

C	-4.432110000	-0.656137000	-0.948204000
C	-4.730992000	1.395593000	0.315981000
C	-5.745571000	-1.032463000	-0.646561000
H	-3.803136000	-1.310801000	-1.561007000
C	-6.048606000	1.019935000	0.615866000
H	-4.337025000	2.348407000	0.686370000
C	-6.555945000	-0.194450000	0.135896000
H	-6.141755000	-1.978032000	-1.027240000
H	-6.677383000	1.677825000	1.222141000
H	-7.583763000	-0.488053000	0.366666000
N	-1.482041000	0.131168000	-0.121224000
H	1.620487000	0.666387000	-0.544438000

### INT2

C	2.010459000	-1.457736000	0.198472000
C	2.904845000	-0.589331000	-0.498348000
C	4.091427000	-1.110413000	-1.050074000
C	4.430860000	-2.461791000	-0.923001000
C	3.582769000	-3.314733000	-0.205674000
C	2.397196000	-2.809557000	0.337977000
H	4.765478000	-0.426780000	-1.580321000
H	5.357539000	-2.836908000	-1.367220000
H	3.830418000	-4.373321000	-0.085436000
H	1.712246000	-3.490292000	0.851823000
C	-0.031168000	-1.676293000	1.788020000
C	-1.234713000	-1.011952000	1.936446000
H	0.307733000	-2.512544000	2.397217000
H	-2.065049000	-1.175541000	2.619872000
C	0.703840000	-1.032922000	0.731667000
N	2.599730000	0.790291000	-0.692672000
H	3.228182000	1.180825000	-1.398511000
C	2.601538000	1.640683000	0.498412000
H	2.083727000	1.111090000	1.311042000
H	3.623014000	1.894149000	0.848341000

S	1.669438000	3.209213000	0.294971000
C	2.782595000	4.095894000	-0.850723000
H	2.379880000	5.113305000	-0.962002000
H	3.802642000	4.167376000	-0.439425000
H	2.808340000	3.626591000	-1.846962000
C	-0.106827000	0.014858000	0.280241000
H	0.068545000	0.750793000	-0.500752000
C	-2.391667000	0.925123000	0.802863000
H	-2.724495000	1.316102000	1.780474000
H	-2.000190000	1.789406000	0.237766000
C	-3.571521000	0.302390000	0.069025000
C	-3.389606000	-0.740282000	-0.855937000
C	-4.867060000	0.802552000	0.289074000
C	-4.485820000	-1.268240000	-1.551225000
H	-2.385081000	-1.141992000	-1.022066000
C	-5.962617000	0.278739000	-0.410199000
H	-5.019442000	1.608230000	1.016376000
C	-5.774378000	-0.759698000	-1.333198000
H	-4.331747000	-2.082713000	-2.265587000
H	-6.965453000	0.676213000	-0.226396000
H	-6.629044000	-1.174673000	-1.875711000
N	-1.271038000	0.019643000	1.016247000

### INT3

C	-2.510112000	-0.603882000	-0.181119000
C	-2.586364000	0.009896000	1.166162000
C	-3.808930000	-0.253863000	1.914900000
C	-4.864586000	-0.956267000	1.391872000
C	-4.797286000	-1.499008000	0.068929000
C	-3.649658000	-1.329362000	-0.670732000
H	-3.870175000	0.168144000	2.924988000
H	-5.771718000	-1.101118000	1.988452000
H	-5.650668000	-2.042389000	-0.345308000
H	-3.601459000	-1.740562000	-1.683735000

C	-0.987009000	-1.411593000	-2.061325000
C	0.337501000	-1.164440000	-2.401013000
H	-1.609471000	-2.170940000	-2.530022000
H	0.941357000	-1.668574000	-3.159001000
C	-1.321394000	-0.597053000	-0.945758000
N	-1.590769000	0.737184000	1.651345000
H	-1.821859000	0.985364000	2.626134000
C	-0.546763000	1.779918000	-1.067826000
H	-0.747990000	1.829202000	-2.149844000
H	-1.472521000	2.018501000	-0.525973000
S	0.685360000	3.094222000	-0.714713000
C	0.307468000	3.433064000	1.046428000
H	-0.502270000	4.173576000	1.131612000
H	-0.001912000	2.496639000	1.536726000
H	1.217821000	3.833757000	1.515722000
C	-0.131855000	0.321041000	-0.707531000
H	0.200042000	0.283295000	0.348241000
C	2.323237000	0.078277000	-1.522510000
H	2.794997000	-0.312111000	-2.440710000
H	2.475193000	1.169214000	-1.494356000
C	2.945513000	-0.559770000	-0.289857000
C	3.166045000	-1.948447000	-0.231622000
C	3.290783000	0.233033000	0.818778000
C	3.724144000	-2.533194000	0.911407000
H	2.898536000	-2.576467000	-1.088921000
C	3.849926000	-0.350703000	1.964838000
H	3.115476000	1.313411000	0.776191000
C	4.067583000	-1.734078000	2.012938000
H	3.895038000	-3.613470000	0.942989000
H	4.114957000	0.276839000	2.821059000
H	4.504337000	-2.190837000	2.906010000
N	0.887494000	-0.182959000	-1.646572000

#### INT4

C	-2.719404000	-0.931568000	0.030511000
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C	-3.368084000	0.140342000	0.713960000
C	-4.771975000	0.106183000	0.873188000
C	-5.533301000	-0.957850000	0.385700000
C	-4.906872000	-2.021981000	-0.279758000
C	-3.518649000	-1.993494000	-0.446091000
H	-5.260768000	0.934792000	1.398309000
H	-6.618279000	-0.954724000	0.529227000
H	-5.491736000	-2.859944000	-0.668722000
H	-3.014875000	-2.812002000	-0.970092000
C	-0.492206000	-2.215878000	0.118853000
C	0.823149000	-1.966240000	-0.222270000
H	-0.882987000	-3.137908000	0.545746000
H	1.713815000	-2.586278000	-0.150451000
C	-1.251464000	-1.027220000	-0.138359000
N	-2.653031000	1.241513000	1.192357000
H	-3.083895000	1.712903000	1.985417000
C	-0.603791000	1.295595000	-1.162725000
H	-0.237109000	1.440837000	-2.194261000
H	-1.689141000	1.475896000	-1.147655000
S	0.179651000	2.602289000	-0.081927000
C	-0.834767000	4.038494000	-0.573030000
H	-0.731268000	4.255785000	-1.647513000
H	-1.890916000	3.851954000	-0.322413000
H	-0.471194000	4.905018000	-0.001263000
C	-0.347174000	-0.079081000	-0.651615000
H	-1.651748000	1.092888000	1.331463000
C	2.130211000	-0.087493000	-1.260567000
H	2.309489000	-0.517455000	-2.263396000
H	1.948313000	0.992819000	-1.389725000
C	3.354847000	-0.293819000	-0.388331000
C	4.497225000	-0.928832000	-0.903064000
C	3.371468000	0.170435000	0.941162000
C	5.642581000	-1.093456000	-0.109569000
H	4.489772000	-1.296180000	-1.935321000

C	4.511694000	0.003501000	1.734974000
H	2.481924000	0.661026000	1.349742000
C	5.651303000	-0.627998000	1.211410000
H	6.524899000	-1.590376000	-0.524022000
H	4.513557000	0.369335000	2.766202000
H	6.541803000	-0.757364000	1.833761000
N	0.912630000	-0.669438000	-0.686711000

### INT5

C	-2.521472000	0.307021000	-0.114078000
C	-2.451755000	-0.976065000	0.473296000
C	-3.465462000	-1.927915000	0.387748000
C	-4.622758000	-1.600729000	-0.333315000
C	-4.734400000	-0.334596000	-0.929534000
C	-3.701872000	0.604284000	-0.826571000
H	-3.368688000	-2.907268000	0.869210000
H	-5.428861000	-2.331840000	-0.425038000
H	-5.638003000	-0.078944000	-1.488990000
H	-3.795111000	1.579009000	-1.312186000
C	-1.172301000	2.580999000	-0.242590000
C	0.164554000	2.844497000	0.005354000
H	-1.914971000	3.308648000	-0.562514000
H	0.724933000	3.774654000	-0.059664000
C	-1.372283000	1.193081000	0.022535000
C	-0.139059000	0.673921000	0.438599000
C	2.212376000	1.577235000	0.796842000
H	2.680386000	2.529187000	0.495362000
H	2.289991000	1.518695000	1.897429000
C	2.924286000	0.399099000	0.157440000
C	2.805449000	0.145930000	-1.223510000
C	3.738957000	-0.437268000	0.942395000
C	3.489137000	-0.930004000	-1.804609000
H	2.181474000	0.797489000	-1.844491000
C	4.429473000	-1.509079000	0.357462000
H	3.847040000	-0.239224000	2.014879000

C	4.302668000	-1.758690000	-1.015851000
H	3.396325000	-1.115208000	-2.878521000
H	5.067436000	-2.146752000	0.975785000
H	4.840913000	-2.593330000	-1.473391000
N	0.795606000	1.681011000	0.413760000
C	0.069035000	-0.777655000	0.704670000
N	-1.246347000	-1.265157000	1.312247000
H	0.225914000	-1.380244000	-0.209193000
H	0.874772000	-1.007622000	1.417093000
H	-1.356688000	-0.783285000	2.224906000
H	-1.199115000	-2.279337000	1.499577000

#### INT6

C	2.569034000	0.309598000	0.174947000
C	2.628530000	-0.990498000	-0.413343000
C	3.790200000	-1.769017000	-0.246485000
C	4.879667000	-1.278684000	0.484906000
C	4.825280000	-0.005570000	1.070015000
C	3.671955000	0.774496000	0.910204000
H	3.837045000	-2.765772000	-0.700491000
H	5.771059000	-1.902430000	0.602257000
H	5.671937000	0.376758000	1.646713000
H	3.616269000	1.768032000	1.366862000
C	0.965928000	2.423083000	0.224951000
C	-0.341165000	2.576823000	-0.204648000
H	1.585980000	3.203843000	0.661733000
H	-0.999363000	3.443328000	-0.201765000
C	1.343509000	1.068870000	-0.048963000
C	0.245566000	0.452357000	-0.643270000
C	-2.122043000	1.108498000	-1.233487000
H	-2.602375000	2.091049000	-1.386563000
H	-2.057932000	0.637649000	-2.231178000
C	-2.974111000	0.244935000	-0.312433000
C	-2.789669000	0.266566000	1.081327000
C	-3.988049000	-0.563410000	-0.856041000

C	-3.610330000	-0.505086000	1.915132000
H	-1.993521000	0.884775000	1.508228000
C	-4.813190000	-1.329572000	-0.021859000
H	-4.131649000	-0.594272000	-1.942220000
C	-4.625502000	-1.302587000	1.367355000
H	-3.454099000	-0.483855000	2.997894000
H	-5.597045000	-1.955664000	-0.458757000
H	-5.263941000	-1.905412000	2.019903000
N	-0.779074000	1.370774000	-0.738536000
C	0.194401000	-0.996745000	-1.010533000
N	1.575374000	-1.445517000	-1.215198000
H	-0.338908000	-1.585841000	-0.224529000
H	-0.366305000	-1.161419000	-1.951251000
H	1.648688000	-2.431915000	-1.457363000

### TS1

S	-1.676904000	-0.039428000	0.339136000
O	-2.260574000	-1.071096000	-0.575030000
O	-1.525236000	1.355820000	-0.219379000
O	-0.132121000	-0.466015000	0.758005000
S	1.252169000	-0.067416000	-0.579225000
C	2.429004000	-1.198458000	0.209448000
H	2.332421000	-1.126982000	1.301879000
H	2.165708000	-2.212620000	-0.120902000
H	3.451553000	-0.952552000	-0.115630000
C	1.713768000	1.525194000	0.154937000
H	1.769365000	1.413907000	1.246718000
H	2.671303000	1.869043000	-0.265241000
H	0.892228000	2.208627000	-0.100482000

### TS2

C	2.292625000	-1.343257000	0.076259000
C	3.012142000	-0.413167000	-0.787629000
C	4.393460000	-0.716819000	-1.065714000
C	4.998733000	-1.878649000	-0.620652000
C	4.274339000	-2.794443000	0.181669000

C	2.957542000	-2.510745000	0.526979000
H	4.951402000	-0.008001000	-1.689800000
H	6.039553000	-2.089700000	-0.887176000
H	4.748779000	-3.715212000	0.532632000
H	2.404032000	-3.218066000	1.152598000
C	0.252654000	-1.627346000	1.641621000
C	-0.968116000	-0.995655000	1.752308000
H	0.619988000	-2.405240000	2.308133000
H	-1.785154000	-1.142532000	2.456368000
C	0.961140000	-1.034757000	0.534597000
N	2.381572000	0.672596000	-1.283843000
H	3.103049000	1.239954000	-1.763544000
C	1.565193000	1.892067000	0.920482000
H	1.076377000	1.422959000	1.776602000
H	2.648618000	1.795626000	0.870267000
S	0.829717000	3.386710000	0.467985000
C	1.922298000	3.959164000	-0.871801000
H	1.486335000	4.881426000	-1.280910000
H	2.932879000	4.169260000	-0.491236000
H	1.957375000	3.176359000	-1.642720000
C	0.105463000	-0.017780000	0.028323000
H	0.225243000	0.560206000	-0.881817000
C	-2.227112000	0.809110000	0.503965000
H	-2.494678000	1.349872000	1.429884000
H	-1.907968000	1.576949000	-0.222140000
C	-3.440648000	0.052307000	-0.015507000
C	-3.296372000	-1.061778000	-0.861440000
C	-4.732910000	0.492691000	0.319624000
C	-4.426537000	-1.718270000	-1.365924000
H	-2.293181000	-1.418308000	-1.115348000
C	-5.863917000	-0.160088000	-0.189303000
H	-4.854174000	1.353841000	0.986630000
C	-5.713011000	-1.268674000	-1.033915000
H	-4.301104000	-2.586188000	-2.020327000

H	-6.863559000	0.192317000	0.082472000
H	-6.594270000	-1.784083000	-1.427167000
N	-1.063972000	-0.032918000	0.754582000

### TS3

C	-2.532625000	0.669546000	0.285857000
C	-2.421113000	0.156638000	-1.080774000
C	-3.478058000	0.522749000	-1.984277000
C	-4.611452000	1.190816000	-1.555678000
C	-4.742283000	1.617135000	-0.208418000
C	-3.701033000	1.380318000	0.674647000
H	-3.394632000	0.193036000	-3.025979000
H	-5.418661000	1.391306000	-2.268079000
H	-5.644462000	2.139177000	0.121076000
H	-3.768859000	1.731609000	1.709931000
C	-0.888562000	1.644737000	2.008779000
C	0.460216000	1.379083000	2.246097000
H	-1.427910000	2.521922000	2.362357000
H	1.178975000	1.970855000	2.815456000
C	-1.351020000	0.669363000	1.096068000
N	-1.363456000	-0.599929000	-1.451774000
H	-1.247200000	-0.578214000	-2.474157000
C	-0.595391000	-1.747092000	1.213627000
H	-0.611124000	-1.836819000	2.312002000
H	-1.609487000	-1.956662000	0.844054000
S	0.505889000	-3.090092000	0.592993000
C	-0.475049000	-3.715883000	-0.821377000
H	-1.291143000	-4.366208000	-0.470653000
H	-0.881830000	-2.858104000	-1.380614000
H	0.205567000	-4.302094000	-1.456337000
C	-0.244643000	-0.281602000	0.839175000
H	-0.287801000	-0.326696000	-0.404650000
C	2.261240000	-0.176304000	1.479603000
H	2.776230000	0.138025000	2.402677000
H	2.271747000	-1.276972000	1.440932000

C	2.964920000	0.394321000	0.259041000
C	3.679598000	1.602439000	0.345132000
C	2.886918000	-0.269053000	-0.979363000
C	4.303269000	2.143975000	-0.786745000
H	3.754804000	2.120159000	1.308351000
C	3.509330000	0.272573000	-2.112071000
H	2.335761000	-1.213795000	-1.042795000
C	4.217094000	1.479745000	-2.018774000
H	4.860796000	3.082010000	-0.705946000
H	3.445338000	-0.252125000	-3.070202000
H	4.705049000	1.900170000	-2.903246000
N	0.864381000	0.259909000	1.593866000

### INT1a

C	-2.008192000	-1.513516000	-0.064753000
C	-3.133090000	-0.743032000	-0.436168000
C	-4.437939000	-1.243356000	-0.453563000
C	-4.650705000	-2.575222000	-0.077275000
C	-3.561955000	-3.366769000	0.320837000
C	-2.262561000	-2.846922000	0.321314000
H	-5.279180000	-0.611430000	-0.757174000
H	-5.661026000	-2.990243000	-0.097202000
H	-3.726537000	-4.406069000	0.617143000
H	-1.414690000	-3.479485000	0.596912000
C	-0.053625000	-0.157529000	-1.141983000
C	1.217952000	0.209034000	-0.710764000
H	-0.411398000	-0.062150000	-2.169350000
H	2.022881000	0.728164000	-1.225747000
C	-0.655160000	-0.932874000	-0.082147000
N	-2.903679000	0.692120000	-0.728654000
H	-1.868690000	0.802831000	-0.881246000
C	-3.317539000	1.649447000	0.402792000
H	-4.390137000	1.486906000	0.579458000
H	-2.746907000	1.331997000	1.288323000
S	-3.054644000	3.374418000	-0.035802000

C	-1.268298000	3.561563000	0.326225000
H	-1.020400000	4.596962000	0.050711000
H	-1.075308000	3.425355000	1.400359000
H	-0.641286000	2.881324000	-0.270903000
C	0.282533000	-0.981300000	0.950170000
H	0.214282000	-1.422436000	1.942703000
C	2.601625000	-0.070020000	1.397611000
H	2.496395000	0.901770000	1.910187000
H	2.584826000	-0.856170000	2.169952000
C	3.892505000	-0.110117000	0.609554000
C	4.359238000	-1.322603000	0.065617000
C	4.640278000	1.064338000	0.414790000
C	5.554384000	-1.356100000	-0.661339000
H	3.784539000	-2.242854000	0.215417000
C	5.839980000	1.030180000	-0.310994000
H	4.288510000	2.008908000	0.844218000
C	6.296645000	-0.179452000	-0.850404000
H	5.912950000	-2.302628000	-1.075358000
H	6.418101000	1.947824000	-0.450544000
H	7.233448000	-0.208727000	-1.413762000
N	1.405639000	-0.293691000	0.553955000
H	-3.376261000	0.995968000	-1.595501000

### INT2a

C	-1.956814000	-1.448423000	0.024872000
C	-2.997040000	-0.517478000	-0.273379000
C	-4.193693000	-0.985119000	-0.855221000
C	-4.379081000	-2.335188000	-1.169553000
C	-3.345509000	-3.248904000	-0.925714000
C	-2.161415000	-2.798947000	-0.331525000
H	-4.985799000	-0.260341000	-1.078750000
H	-5.321445000	-2.664846000	-1.617251000
H	-3.467919000	-4.307560000	-1.171360000
H	-1.373758000	-3.516725000	-0.081862000
C	-0.549776000	-0.149787000	1.812907000

C	0.779329000	-0.183747000	2.194645000
H	-1.335841000	0.453993000	2.260121000
H	1.312005000	0.345854000	2.982222000
C	-0.710717000	-1.069444000	0.718760000
N	-2.878898000	0.860049000	0.044799000
H	-3.776919000	1.329270000	-0.087293000
C	-1.802338000	1.628812000	-0.574916000
H	-0.890417000	1.015664000	-0.583225000
H	-2.028912000	1.921830000	-1.620733000
S	-1.340162000	3.150050000	0.341223000
C	-2.752774000	4.224903000	-0.093985000
H	-2.525317000	5.225345000	0.302684000
H	-2.875113000	4.302271000	-1.186695000
H	-3.692699000	3.880855000	0.366390000
C	0.550422000	-1.620630000	0.479793000
H	0.882202000	-2.322503000	-0.282718000
C	2.884487000	-1.300481000	1.362962000
H	3.268756000	-1.001436000	2.354632000
H	3.082420000	-2.382261000	1.265490000
C	3.618060000	-0.541543000	0.264427000
C	3.148397000	0.697233000	-0.206246000
C	4.808567000	-1.067774000	-0.266872000
C	3.861744000	1.397284000	-1.188390000
H	2.217162000	1.109287000	0.196307000
C	5.525405000	-0.365121000	-1.244889000
H	5.176224000	-2.038136000	0.086093000
C	5.052790000	0.870541000	-1.708778000
H	3.482876000	2.358429000	-1.548835000
H	6.448826000	-0.788707000	-1.651437000
H	5.607374000	1.417955000	-2.476713000
N	1.444416000	-1.088071000	1.383769000

### INT3a

C	2.373712000	-1.100108000	0.068925000
C	3.552404000	-0.231831000	-0.102111000

C	4.840386000	-0.891971000	0.026583000
C	4.967186000	-2.208501000	0.408727000
C	3.814425000	-3.013378000	0.644858000
C	2.561599000	-2.460810000	0.455328000
H	5.732884000	-0.277584000	-0.141552000
H	5.964865000	-2.642510000	0.536725000
H	3.922405000	-4.053085000	0.965064000
H	1.671384000	-3.076089000	0.628655000
C	0.690162000	0.812618000	-0.528866000
C	-0.652712000	0.726826000	-1.141717000
H	1.521116000	1.272393000	-1.136347000
H	-1.332423000	1.529494000	-1.417644000
C	1.073674000	-0.642531000	-0.302912000
N	3.421182000	1.068673000	-0.358821000
H	4.351197000	1.454564000	-0.582710000
C	0.677874000	1.644129000	0.794127000
H	-0.058251000	1.221520000	1.495879000
H	1.684525000	1.581925000	1.232498000
S	0.216136000	3.402280000	0.580551000
C	1.794331000	4.097896000	-0.027938000
H	1.600402000	5.156783000	-0.255048000
H	2.575938000	4.025280000	0.742297000
H	2.137469000	3.582565000	-0.936031000
C	-0.039268000	-1.404389000	-0.662032000
H	-0.171638000	-2.480886000	-0.741395000
C	-2.343790000	-1.034717000	-1.612531000
H	-2.602143000	-0.492979000	-2.536153000
H	-2.222850000	-2.098116000	-1.879426000
C	-3.432236000	-0.849046000	-0.569315000
C	-3.227179000	-1.232172000	0.769240000
C	-4.676279000	-0.316707000	-0.947798000
C	-4.251970000	-1.081122000	1.710965000
H	-2.256004000	-1.636604000	1.074081000
C	-5.705414000	-0.174802000	-0.006250000

H	-4.841015000	-0.009657000	-1.986446000
C	-5.494678000	-0.555725000	1.325349000
H	-4.079860000	-1.375649000	2.750363000
H	-6.668568000	0.242911000	-0.313609000
H	-6.294214000	-0.439993000	2.062779000
N	-1.025007000	-0.557632000	-1.164980000

#### INT4a

C	-2.191585000	-1.230384000	0.049009000
C	-3.457751000	-0.726722000	0.467173000
C	-4.613788000	-1.510117000	0.266094000
C	-4.529797000	-2.776725000	-0.319703000
C	-3.287365000	-3.291008000	-0.717302000
C	-2.138026000	-2.512856000	-0.530175000
H	-5.585079000	-1.115758000	0.585341000
H	-5.441960000	-3.364694000	-0.461158000
H	-3.214584000	-4.281610000	-1.174356000
H	-1.159878000	-2.890629000	-0.844896000
C	-0.588351000	0.839909000	-0.273890000
C	0.688367000	1.132106000	0.190759000
H	-2.687539000	0.866669000	1.469188000
H	1.320106000	1.997302000	0.001161000
C	-0.948316000	-0.452958000	0.265139000
N	-3.556449000	0.548139000	1.037889000
H	-4.360004000	0.672767000	1.651292000
C	-1.399679000	1.649222000	-1.249368000
H	-1.117007000	1.415537000	-2.291327000
H	-2.472002000	1.418213000	-1.145019000
S	-1.177495000	3.474529000	-1.137402000
C	-1.854708000	3.764377000	0.532727000
H	-1.813221000	4.848184000	0.715312000
H	-2.900529000	3.424823000	0.593668000
H	-1.248168000	3.247905000	1.293956000
C	0.139513000	-0.881308000	1.025551000
H	0.267587000	-1.784245000	1.619990000

C	2.432601000	-0.009480000	1.605907000
H	2.654198000	0.941210000	2.121823000
H	2.360846000	-0.782294000	2.391895000
C	3.561875000	-0.346699000	0.641166000
C	3.328804000	-1.094150000	-0.525925000
C	4.872961000	0.063361000	0.940550000
C	4.391964000	-1.428905000	-1.375339000
H	2.307982000	-1.404153000	-0.770784000
C	5.937037000	-0.276215000	0.094504000
H	5.062036000	0.656779000	1.842415000
C	5.698643000	-1.024115000	-1.067179000
H	4.197226000	-2.006522000	-2.284036000
H	6.951713000	0.052878000	0.338220000
H	6.526814000	-1.284492000	-1.732871000
N	1.118875000	0.088386000	0.985028000

### INT5a

C	2.164254000	-0.561229000	-0.179299000
C	3.343854000	-0.033485000	0.394045000
C	4.524173000	-0.759053000	0.549697000
C	4.549374000	-2.090247000	0.112769000
C	3.396253000	-2.655575000	-0.455807000
C	2.225701000	-1.905309000	-0.605973000
H	5.412312000	-0.307066000	1.005054000
H	5.464126000	-2.677849000	0.216125000
H	3.415313000	-3.694176000	-0.796134000
H	1.344447000	-2.352163000	-1.073564000
C	1.166928000	1.744050000	-0.188915000
C	-0.084285000	2.317714000	-0.346203000
H	-0.405975000	3.357010000	-0.349123000
C	1.014723000	0.322162000	-0.312521000
C	-0.340682000	0.082313000	-0.536479000
C	-2.427121000	1.491446000	-0.841096000
H	-2.691075000	2.480004000	-0.431801000
H	-2.560745000	1.536648000	-1.935513000

C	-3.299080000	0.407443000	-0.247967000
C	-3.536617000	0.360187000	1.139434000
C	-3.881978000	-0.565632000	-1.079260000
C	-4.342997000	-0.645505000	1.684132000
H	-3.093304000	1.119370000	1.792879000
C	-4.691566000	-1.572582000	-0.533635000
H	-3.712201000	-0.526890000	-2.160850000
C	-4.921256000	-1.613722000	0.847941000
H	-4.529894000	-0.669960000	2.761392000
H	-5.147144000	-2.319553000	-1.189561000
H	-5.556990000	-2.394740000	1.274241000
N	-0.986459000	1.294648000	-0.555667000
N	3.275812000	1.363789000	0.924657000
H	2.777818000	1.354970000	1.834076000
H	4.234058000	1.704720000	1.101589000
C	2.519741000	2.331803000	0.005200000
H	2.525229000	3.320619000	0.488246000
H	3.123550000	2.374944000	-0.918964000
H	-0.901500000	-0.843612000	-0.637403000

### INT6a

C	-2.502495000	0.417076000	-0.255082000
C	-3.305012000	-0.438177000	0.560679000
C	-4.594242000	-0.012170000	0.941316000
C	-5.087999000	1.230566000	0.529454000
C	-4.308801000	2.070277000	-0.281371000
C	-3.027866000	1.655217000	-0.665137000
H	-5.209009000	-0.666865000	1.569986000
H	-6.092787000	1.537273000	0.835755000
H	-4.696559000	3.037117000	-0.613625000
H	-2.414832000	2.299728000	-1.304050000
C	-0.784758000	-1.417378000	-0.296516000
C	0.527980000	-1.582393000	-0.699689000
H	1.193859000	-2.442215000	-0.661616000
C	-1.163770000	-0.064000000	-0.577938000

C	-0.051193000	0.556934000	-1.141849000
C	2.333345000	-0.089374000	-1.624545000
H	2.701813000	-0.927447000	-2.242407000
H	2.300072000	0.792704000	-2.288785000
C	3.296427000	0.160982000	-0.469845000
C	2.836473000	0.520429000	0.807980000
C	4.680997000	0.058723000	-0.695982000
C	3.749489000	0.777966000	1.840594000
H	1.760191000	0.591432000	0.992900000
C	5.592763000	0.320742000	0.334529000
H	5.048399000	-0.230701000	-1.687377000
C	5.128336000	0.681658000	1.607824000
H	3.378847000	1.053504000	2.832570000
H	6.667074000	0.235298000	0.144787000
H	5.838606000	0.881760000	2.415524000
N	0.965256000	-0.376200000	-1.224460000
N	-2.783224000	-1.645391000	1.035001000
H	-3.486518000	-2.242997000	1.466695000
C	-1.787275000	-2.389427000	0.252324000
H	-1.308467000	-3.130621000	0.916565000
H	-2.262491000	-2.963138000	-0.578639000
H	0.113196000	1.580407000	-1.472535000

### TS2a

C	2.288801000	-1.233646000	-0.056057000
C	3.321845000	-0.226730000	-0.293337000
C	4.597653000	-0.442591000	0.346429000
C	4.868412000	-1.555834000	1.123038000
C	3.864087000	-2.529456000	1.329892000
C	2.610209000	-2.352690000	0.747088000
H	5.374179000	0.314572000	0.181129000
H	5.858331000	-1.682986000	1.573488000
H	4.068910000	-3.418184000	1.933472000
H	1.849704000	-3.126713000	0.892808000
C	0.489174000	-0.209487000	-1.656991000

C	-0.851956000	-0.473754000	-1.882899000
H	1.140788000	0.481000000	-2.184814000
H	-1.567139000	-0.028211000	-2.570789000
C	0.948543000	-1.100978000	-0.609958000
N	3.073104000	0.836880000	-1.088886000
H	3.952446000	1.383790000	-1.120000000
C	0.620297000	1.801845000	0.387548000
H	-0.342810000	1.292933000	0.380667000
H	1.479175000	1.353641000	0.884142000
S	0.597471000	3.440239000	-0.044806000
C	2.362385000	3.851374000	0.041144000
H	2.516481000	4.816849000	-0.459842000
H	2.699055000	3.911658000	1.086213000
H	2.886299000	3.028147000	-0.479649000
C	-0.179377000	-1.852828000	-0.230864000
H	-0.305277000	-2.625930000	0.524112000
C	-2.617615000	-1.938760000	-0.839422000
H	-3.043354000	-2.147635000	-1.835737000
H	-2.567201000	-2.903987000	-0.305864000
C	-3.512388000	-0.961028000	-0.090688000
C	-3.062565000	-0.321779000	1.079622000
C	-4.816771000	-0.707925000	-0.546778000
C	-3.903359000	0.553917000	1.777501000
H	-2.044524000	-0.511136000	1.437651000
C	-5.662279000	0.163850000	0.154720000
H	-5.173227000	-1.195408000	-1.461105000
C	-5.206904000	0.797832000	1.318151000
H	-3.540540000	1.047074000	2.684417000
H	-6.674544000	0.353560000	-0.214706000
H	-5.862691000	1.482558000	1.863886000
N	-1.246355000	-1.470795000	-1.008460000

### TS3a

C	-2.370281000	-1.122488000	-0.141788000
C	-3.522998000	-0.259609000	0.146651000

C	-4.815543000	-0.909599000	0.110955000
C	-4.977054000	-2.216467000	-0.303270000
C	-3.853959000	-3.015610000	-0.652105000
C	-2.585191000	-2.470255000	-0.542520000
H	-5.690489000	-0.301067000	0.367975000
H	-5.984453000	-2.642218000	-0.365727000
H	-3.990993000	-4.045612000	-0.991859000
H	-1.709207000	-3.080310000	-0.791632000
C	-0.699700000	0.793584000	0.398477000
C	0.627364000	0.743975000	1.021843000
H	-1.618977000	1.195085000	0.983282000
H	1.294728000	1.563247000	1.279624000
C	-1.054627000	-0.661590000	0.188779000
N	-3.360637000	1.040103000	0.426296000
H	-4.238409000	1.419629000	0.809872000
C	-0.746791000	1.665696000	-0.892883000
H	-0.033583000	1.278244000	-1.637415000
H	-1.768796000	1.605605000	-1.295394000
S	-0.291328000	3.422147000	-0.653369000
C	-1.797823000	4.069172000	0.156199000
H	-1.643363000	5.152071000	0.274631000
H	-2.683443000	3.888852000	-0.469734000
H	-1.956805000	3.614443000	1.144454000
C	0.047174000	-1.407069000	0.600474000
H	0.175509000	-2.480261000	0.723572000
C	2.322607000	-0.984797000	1.605717000
H	2.546161000	-0.413480000	2.520638000
H	2.204511000	-2.040947000	1.901677000
C	3.444765000	-0.821539000	0.594484000
C	3.278818000	-1.219485000	-0.745006000
C	4.681686000	-0.297278000	1.006209000
C	4.335263000	-1.091951000	-1.654792000
H	2.313651000	-1.617509000	-1.076080000
C	5.742190000	-0.178481000	0.096872000

H	4.816075000	0.021807000	2.045625000
C	5.570570000	-0.574778000	-1.235901000
H	4.193530000	-1.398168000	-2.695415000
H	6.699304000	0.233433000	0.429908000
H	6.394730000	-0.477100000	-1.948423000
N	1.015317000	-0.537057000	1.101411000

## 7. Biological Assay

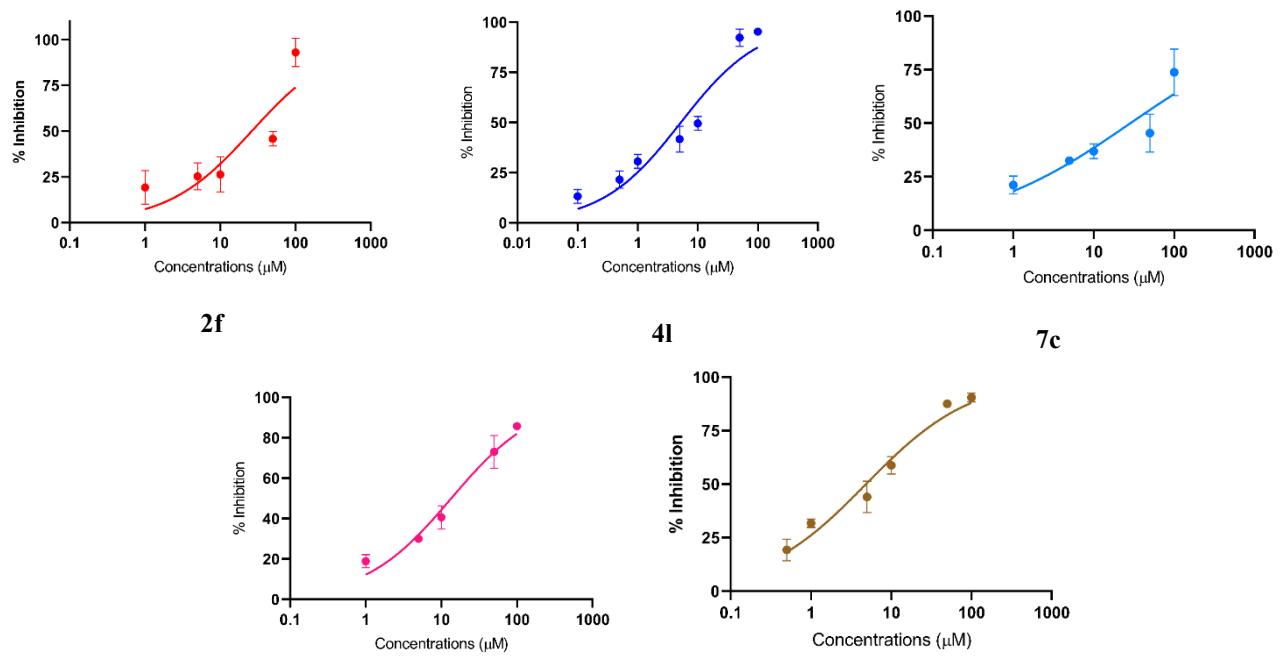
### *In vitro culture maintenance of Plasmodium falciparum (Pf)*

*In vitro Pf3D7* culture was maintained following the standard procedures with minor modifications.<sup>7</sup> The parasites were cultured in sterile tissue culture flasks using O<sup>+ve</sup> human RBCs (5% haematocrit) in RPMI-1640 medium supplemented with 50 mg/L hypoxanthine, 1% albumax II, and 50 µg/L gentamicin. The cultures were maintained under the gas mixture of 5% CO<sub>2</sub>, 5% O<sub>2</sub>, and 90% N<sub>2</sub> at 37°C. Giemsa-stained smears were prepared to monitor the parasite growth and the cultures were synchronized using 5% (w/v) D-sorbitol to select the ring stage parasites.

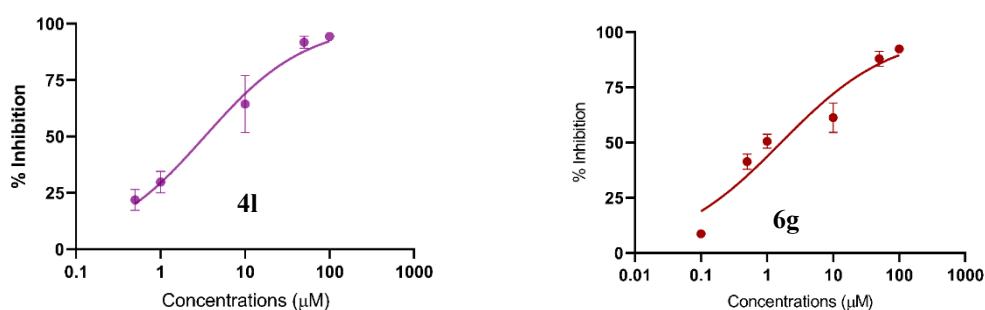
### *In vitro growth inhibition assays*

*In vitro* antiplasmodial activity of the compounds was examined by performing growth assays using radiolabeled [<sup>3</sup>H]-hypoxanthine.<sup>8</sup> Incorporation of [<sup>3</sup>H]-hypoxanthine in *Pf3D7* cultures treated with different concentrations of compounds (0.5, 1.0, 10, 50 and 100 µM) was determined by measuring the radioactive counts using MicroBeta Counter (PerkinElmer), and the parasite morphology and % parasitemia were assessed by examining the Giemsa-stained smears. The compounds were added to the synchronized cultures having ring stages followed by [<sup>3</sup>H]-hypoxanthine addition after 2 h at a concentration of 5 µCi/ml of culture volume. 100 µl of the parasite cultures was collected at different time points and lysed in water. The lysates were harvested on glass fiber filters (PerkinElmer) and dried for 2-3 h at 60 °C. The radioactive counts were measured by adding 150 µl of Ultima Gold XR scintillation cocktail. For solvent control, DMSO was used and for positive control, 25 nM CQ was used. The growth inhibition assays were carried out in triplicates to calculate the IC<sub>50</sub> values.

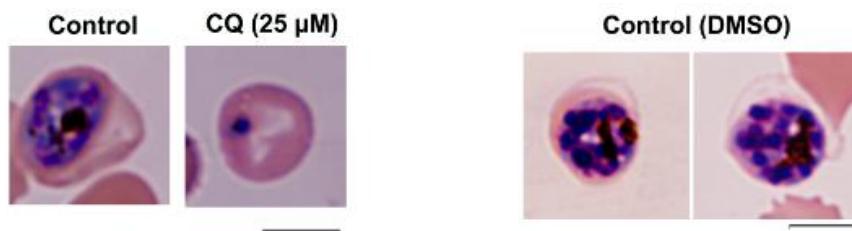
a) Growth inhibition against blood stages of *Pf3D7* culture treated with compound 1,2, 3,4,5 and 6 (24 Hours)



b) Growth inhibition against blood stages of *Pf3D7* culture treated with compound 2, compound 3 and compound 6 (48 Hours)



**Figure S8:** Growth inhibition against blood stages of *Pf3D7*.



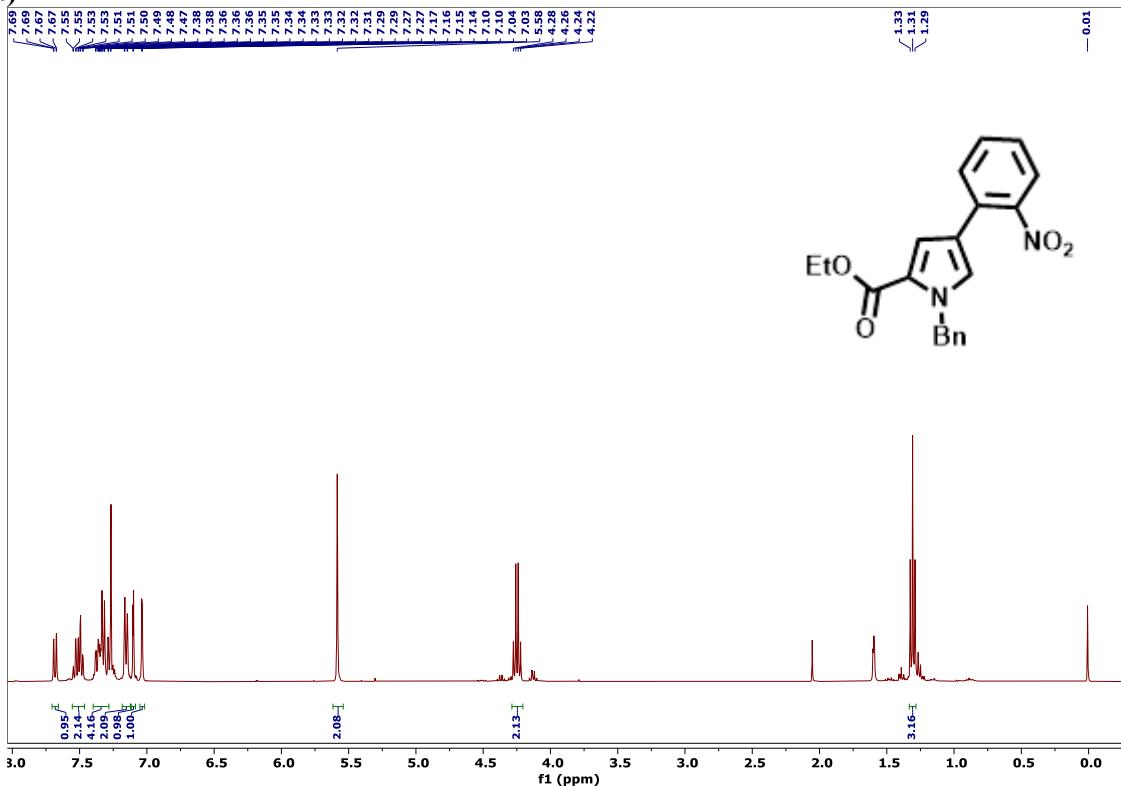
**Figure S9:** Giemsa-stained images of *Pf3D7* cultures treated with 25 nM chloroquine (CQ) and DMSO.

## 8. References

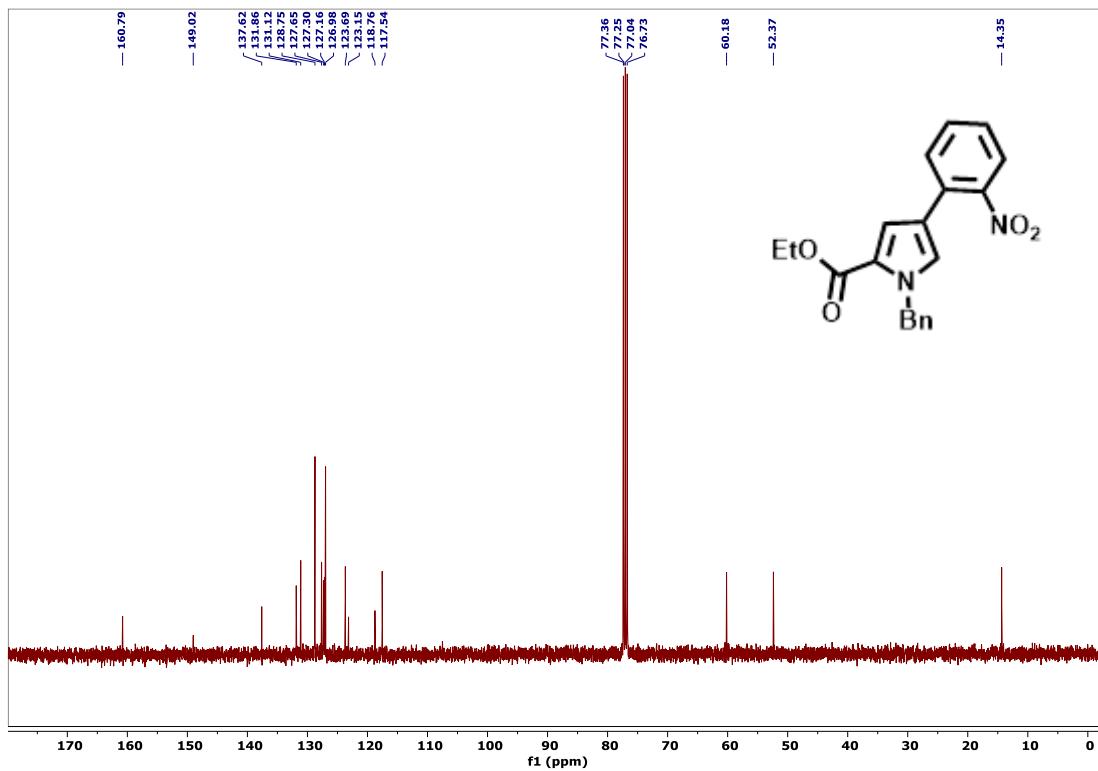
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## **9. Copies of the NMR Spectra**

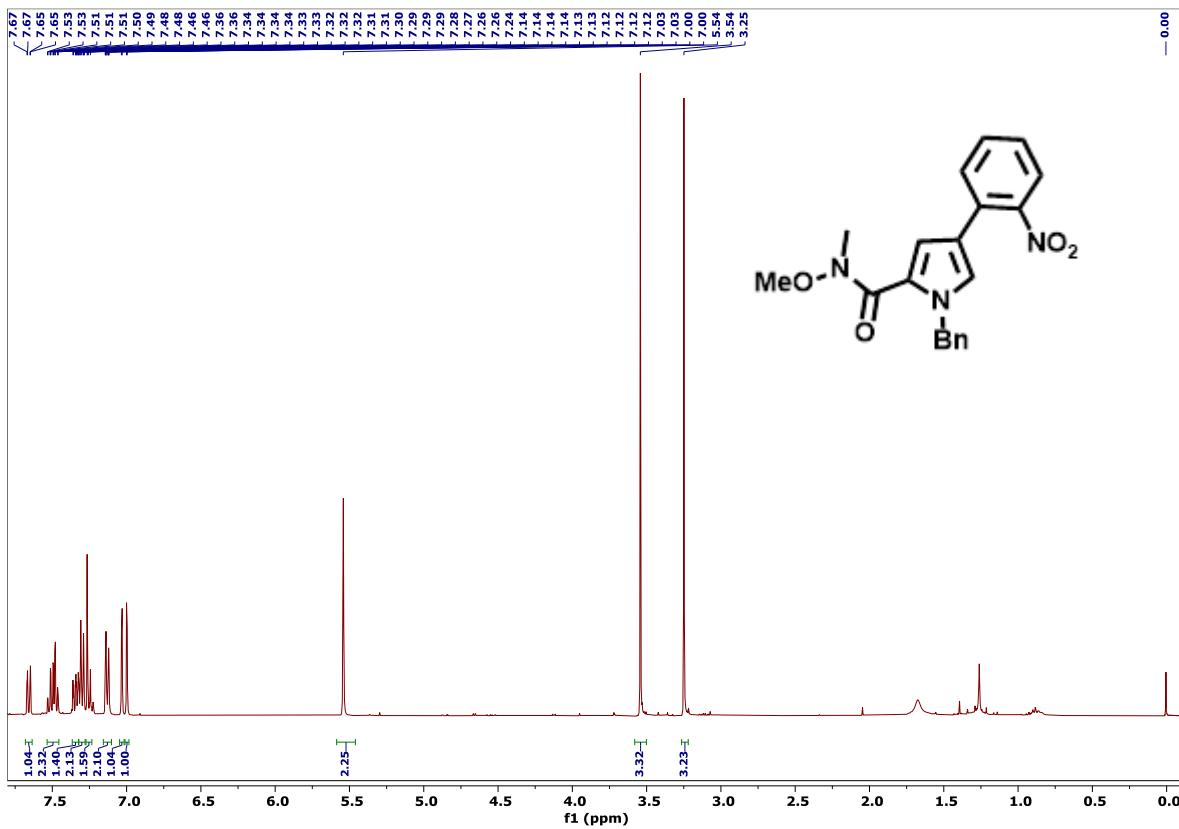
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 1-benzyl-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (**1a**)



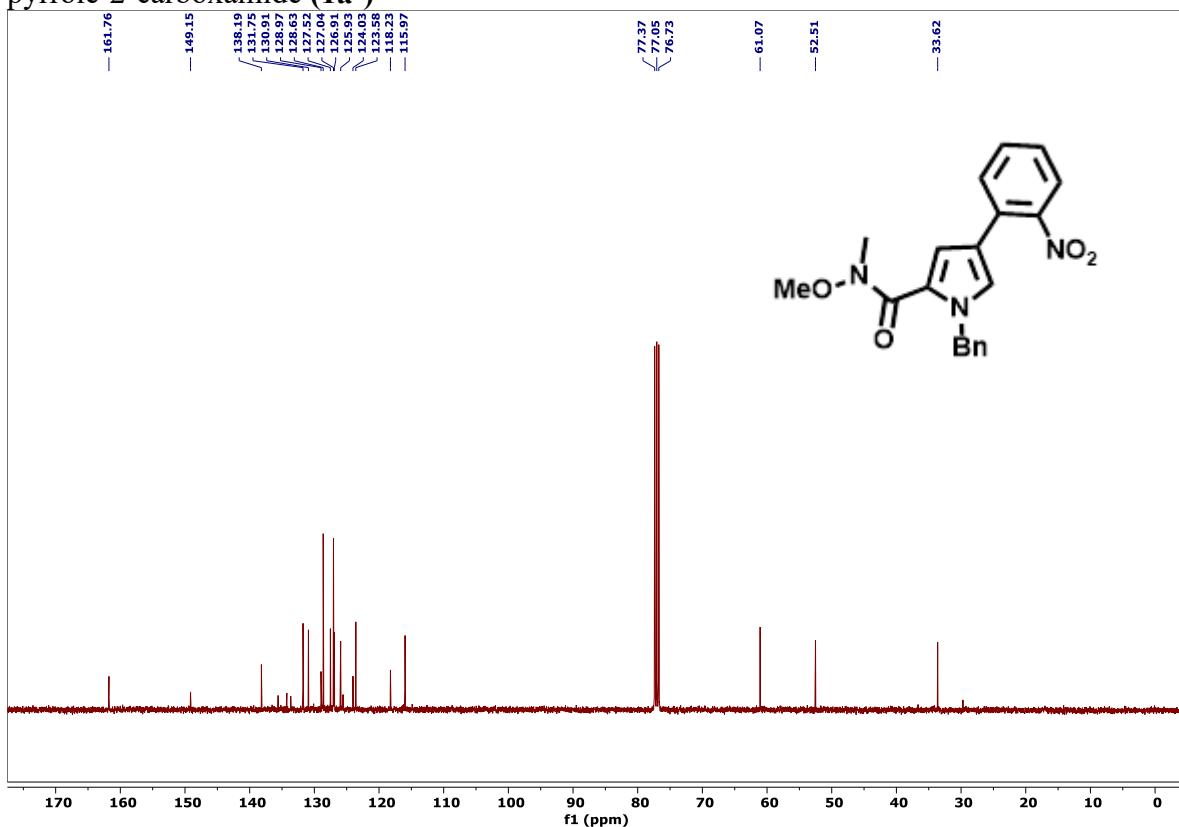
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of ethyl 1-benzyl-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (**1a**)



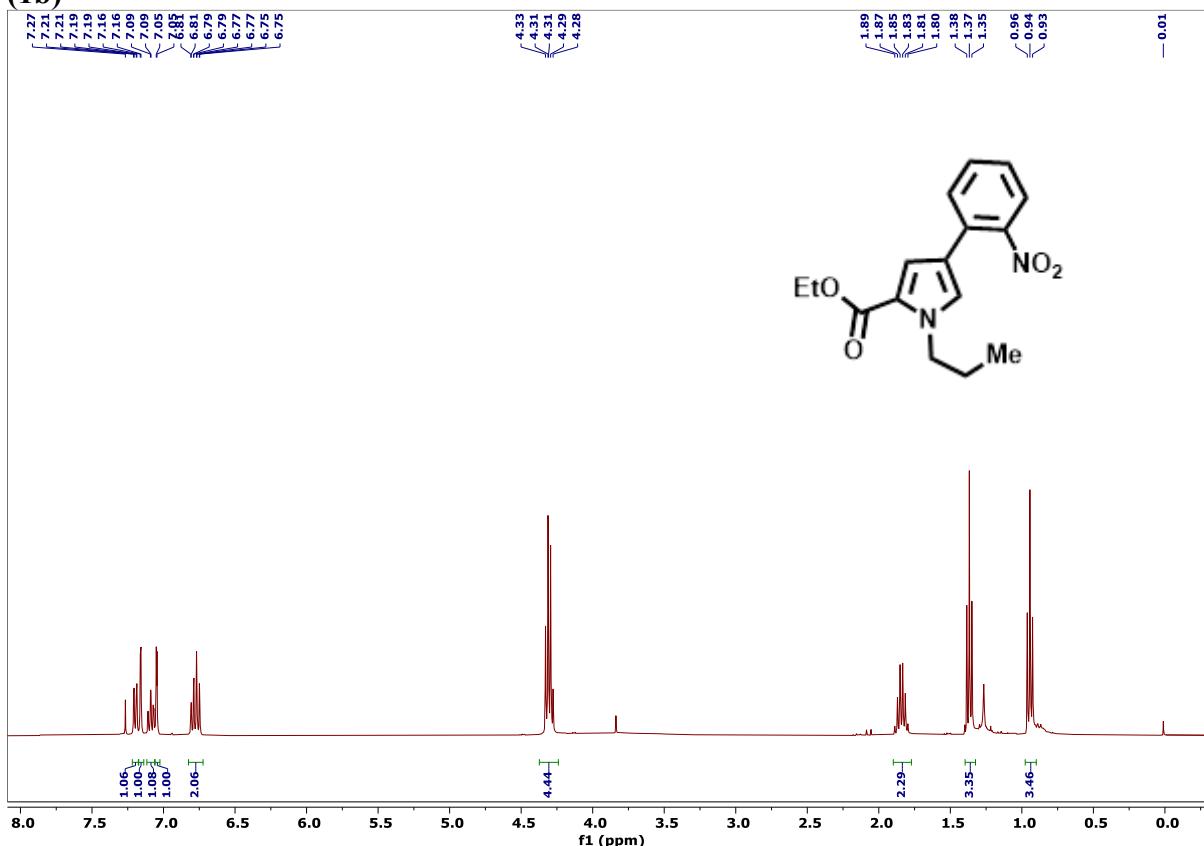
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 1-benzyl-N-methoxy-N-methyl-4-(2-nitrophenyl)-1H-pyrrole-2-carboxamide (**1a'**)



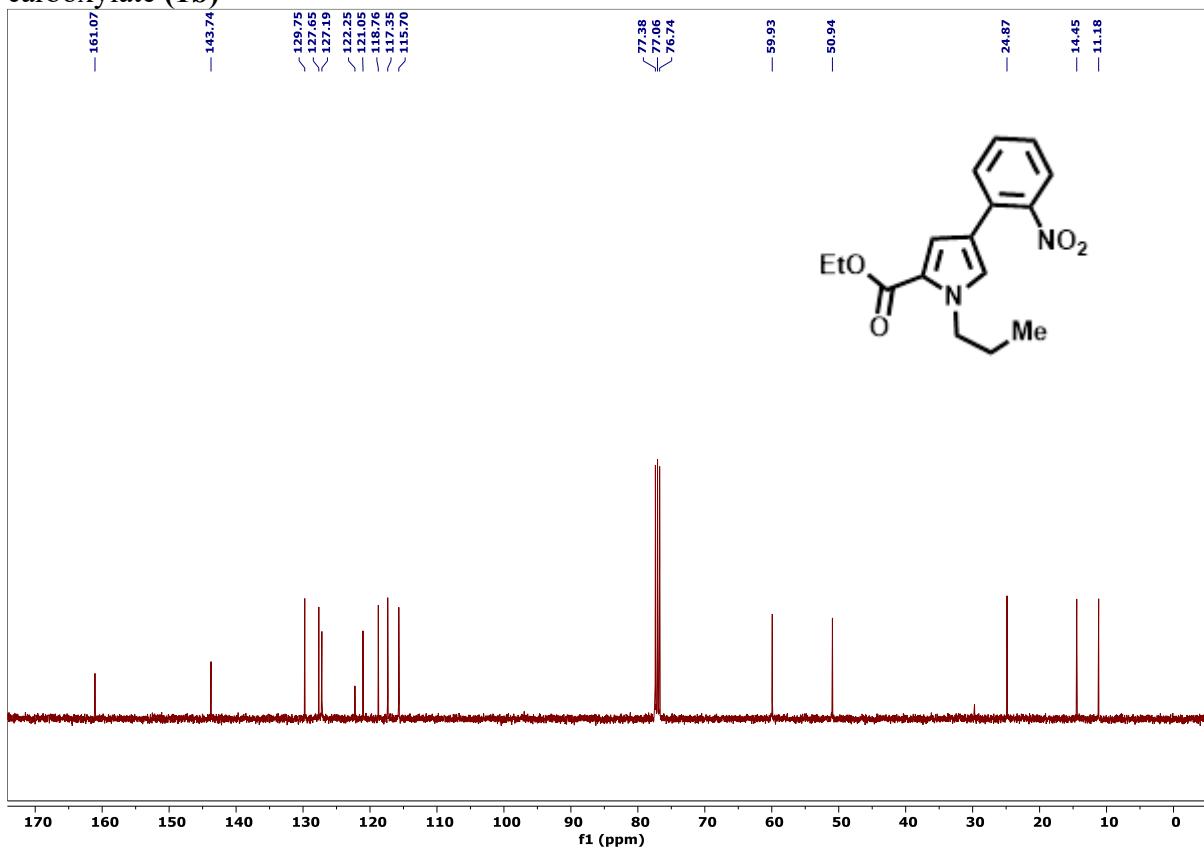
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of 1-benzyl-N-methoxy-N-methyl-4-(2-nitrophenyl)-1H-pyrrole-2-carboxamide (**1a'**)



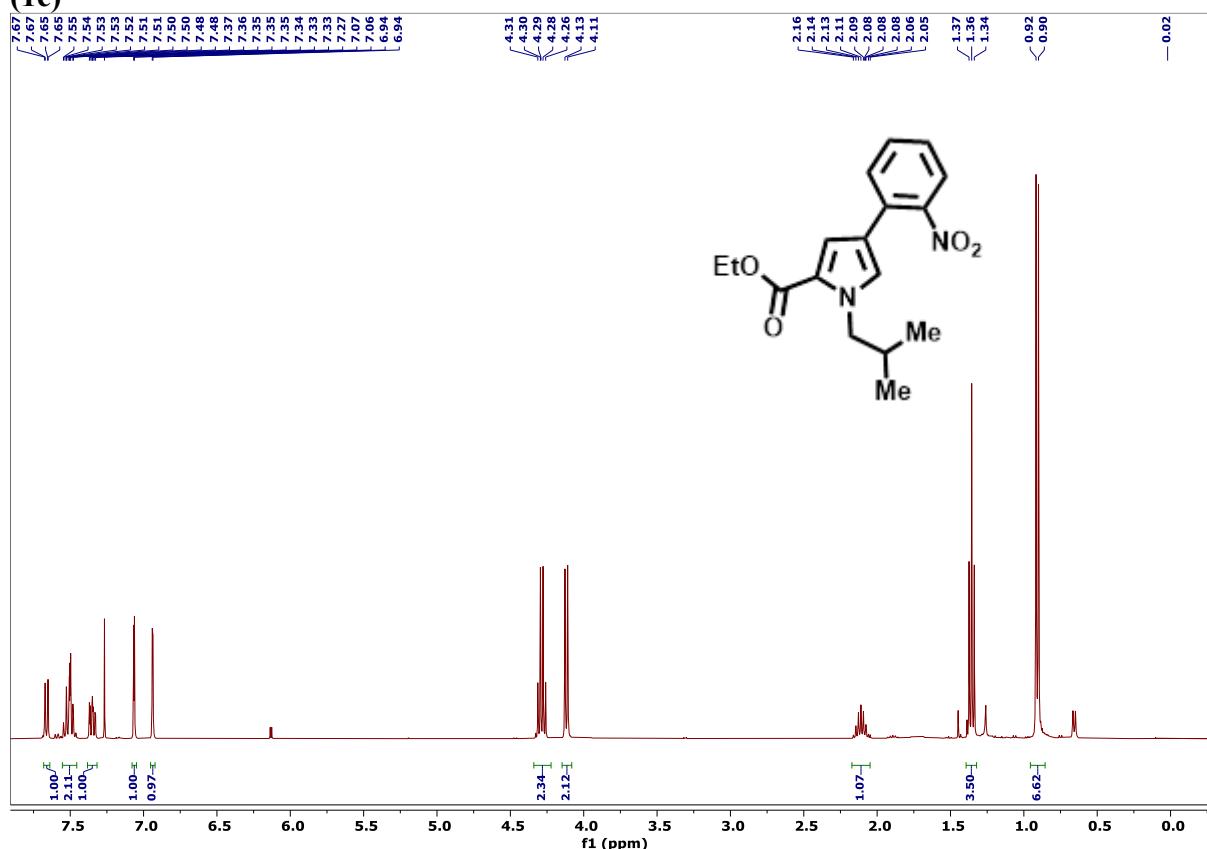
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 4-(2-nitrophenyl)-1-propyl-1H-pyrrole-2-carboxylate (**1b**)



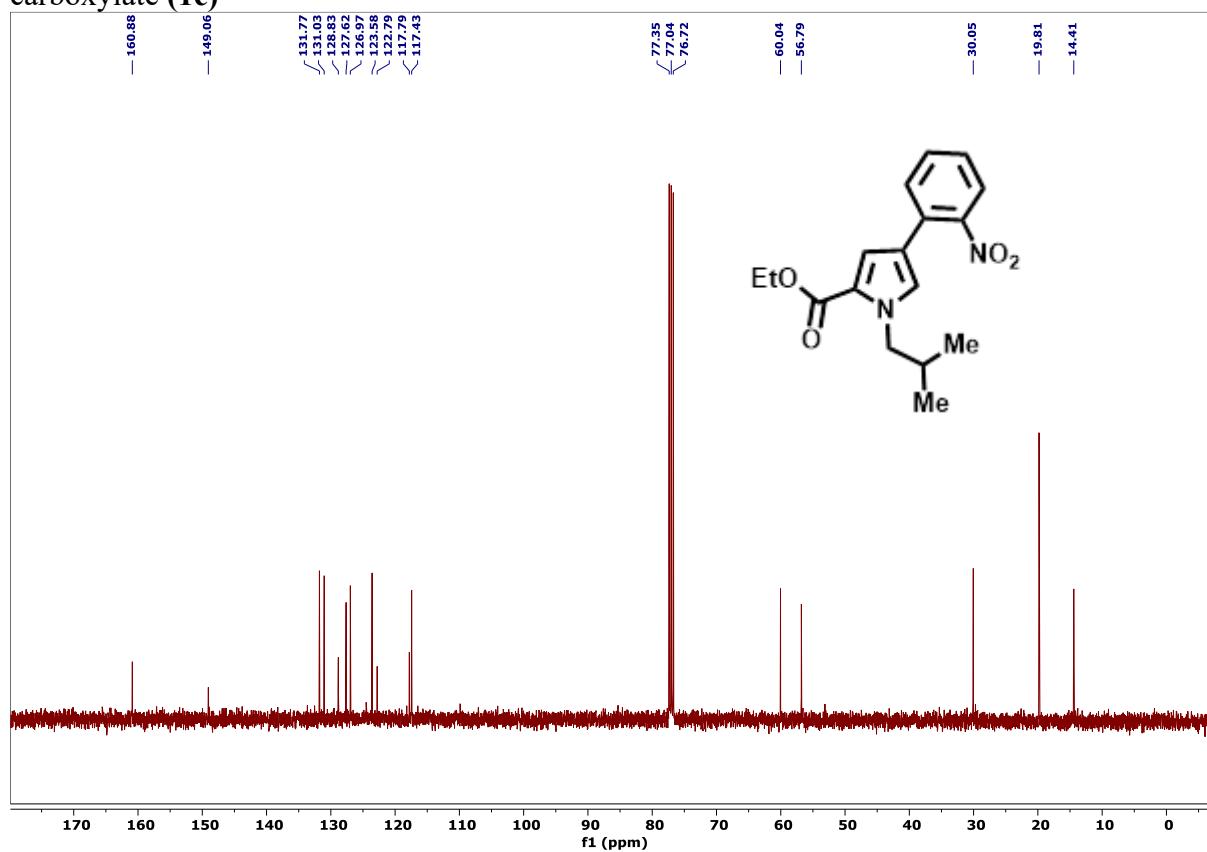
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of ethyl 4-(2-nitrophenyl)-1-propyl-1H-pyrrole-2-carboxylate (**1b**)



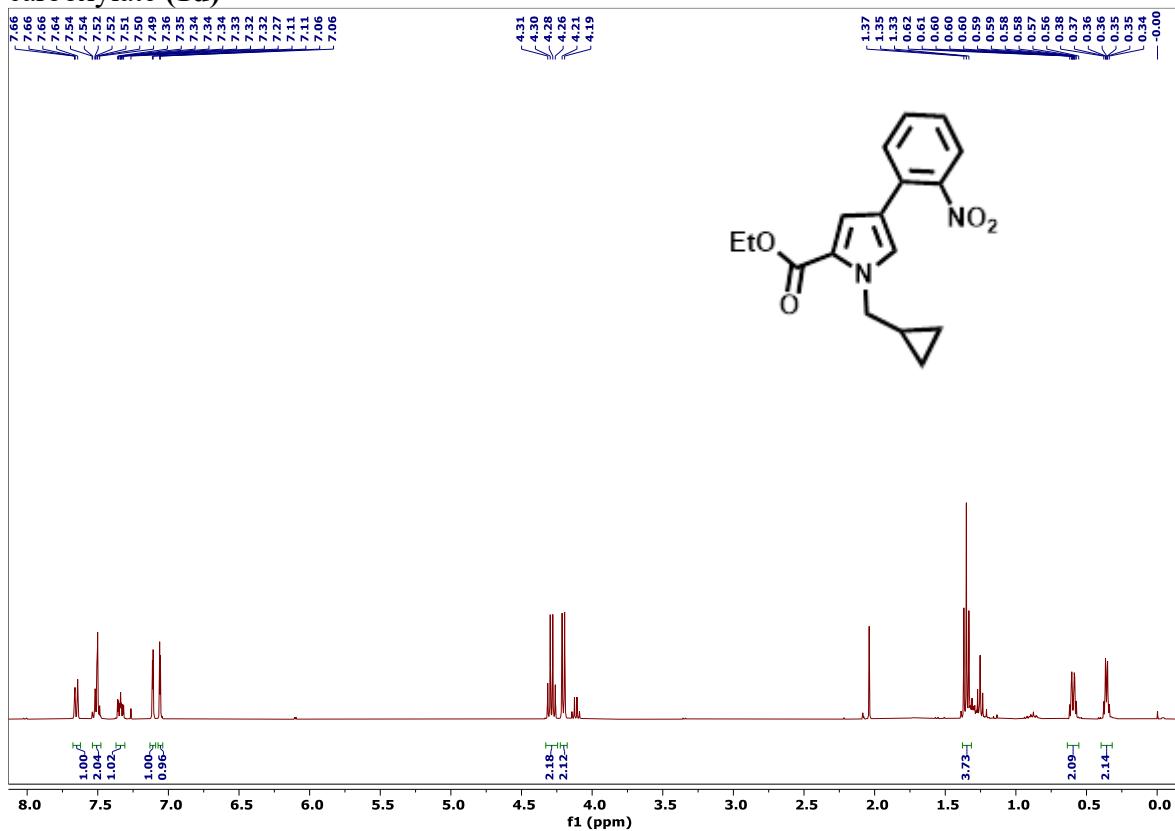
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 1-isobutyl-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (1c)



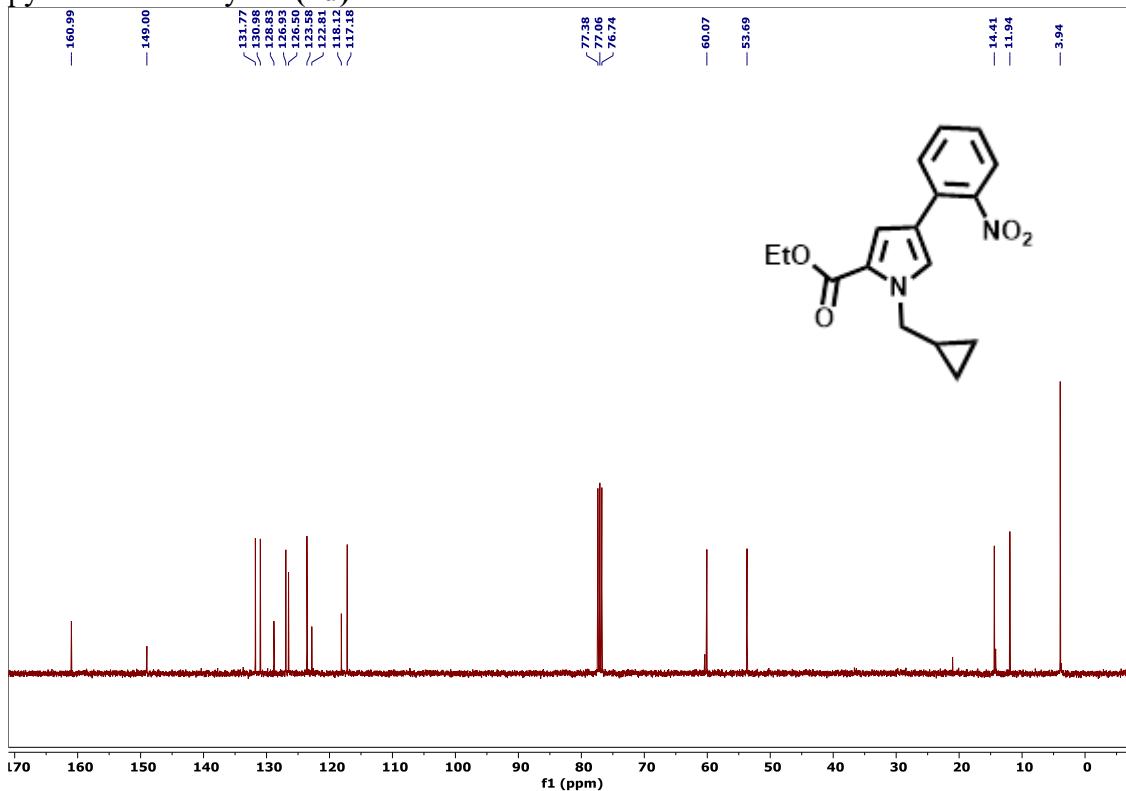
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of ethyl 1-isobutyl-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (**1c**)



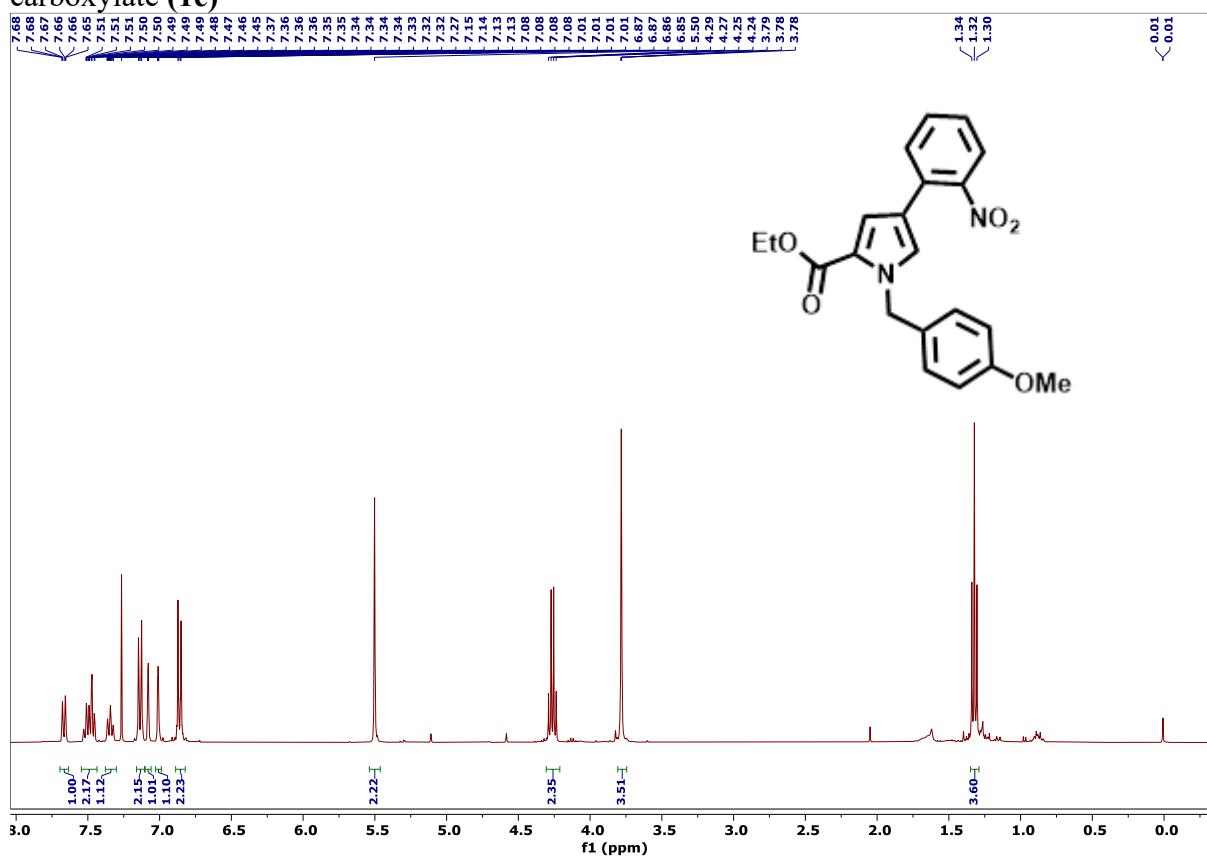
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 1-(cyclopropylmethyl)-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (**1d**)



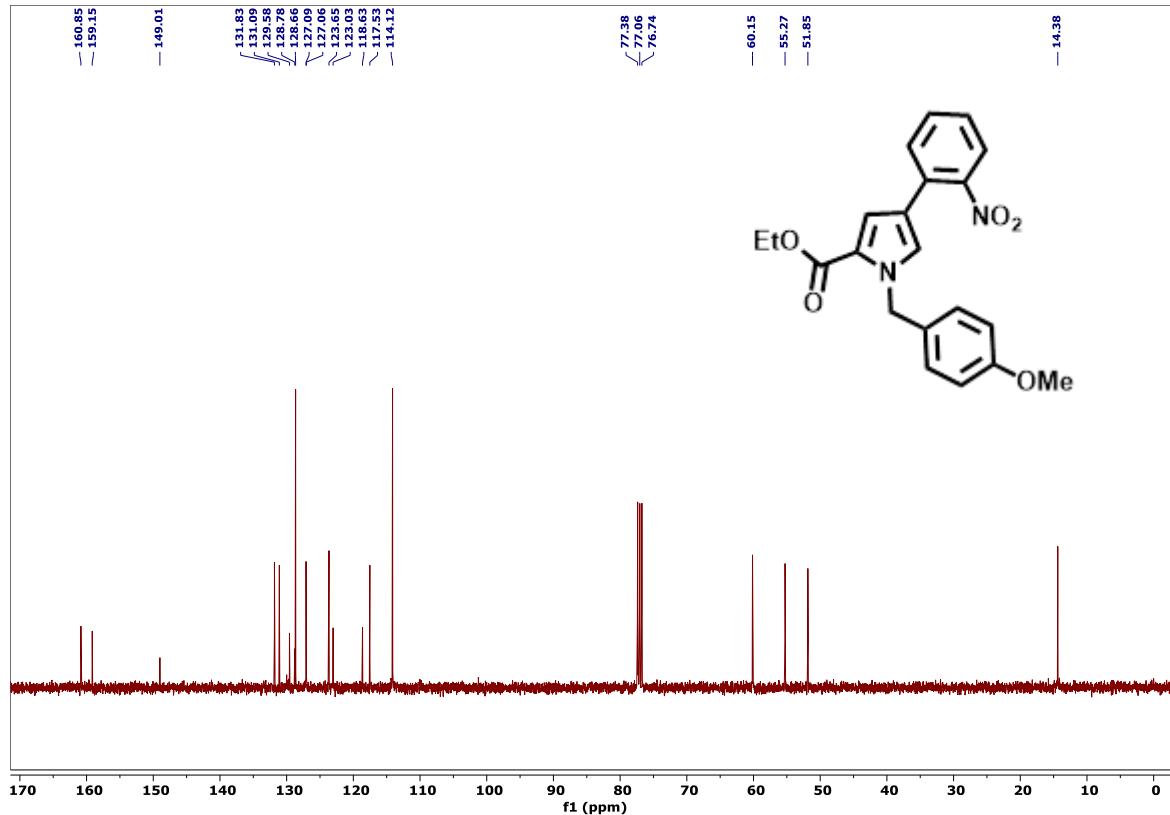
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of ethyl 1-(cyclopropylmethyl)-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (**1d**)



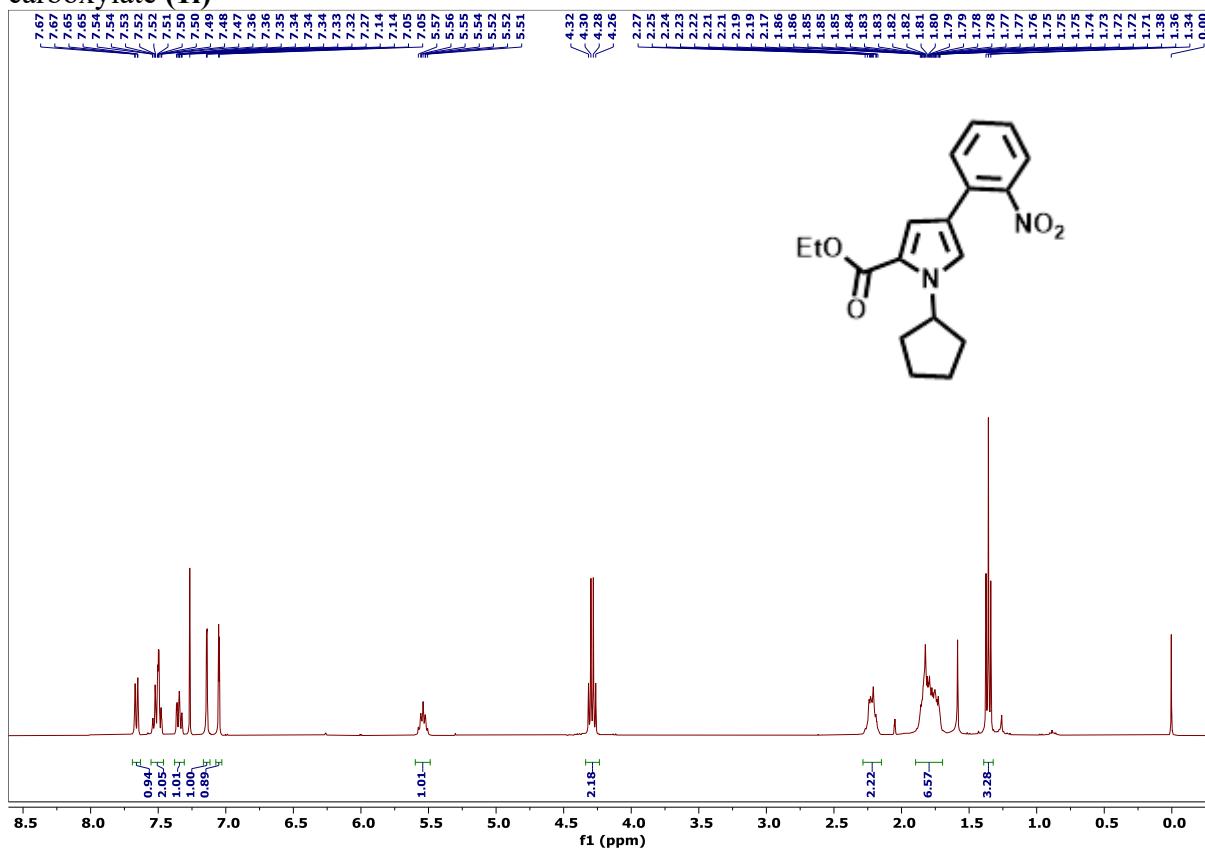
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 1-(4-methoxybenzyl)-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (**1e**)



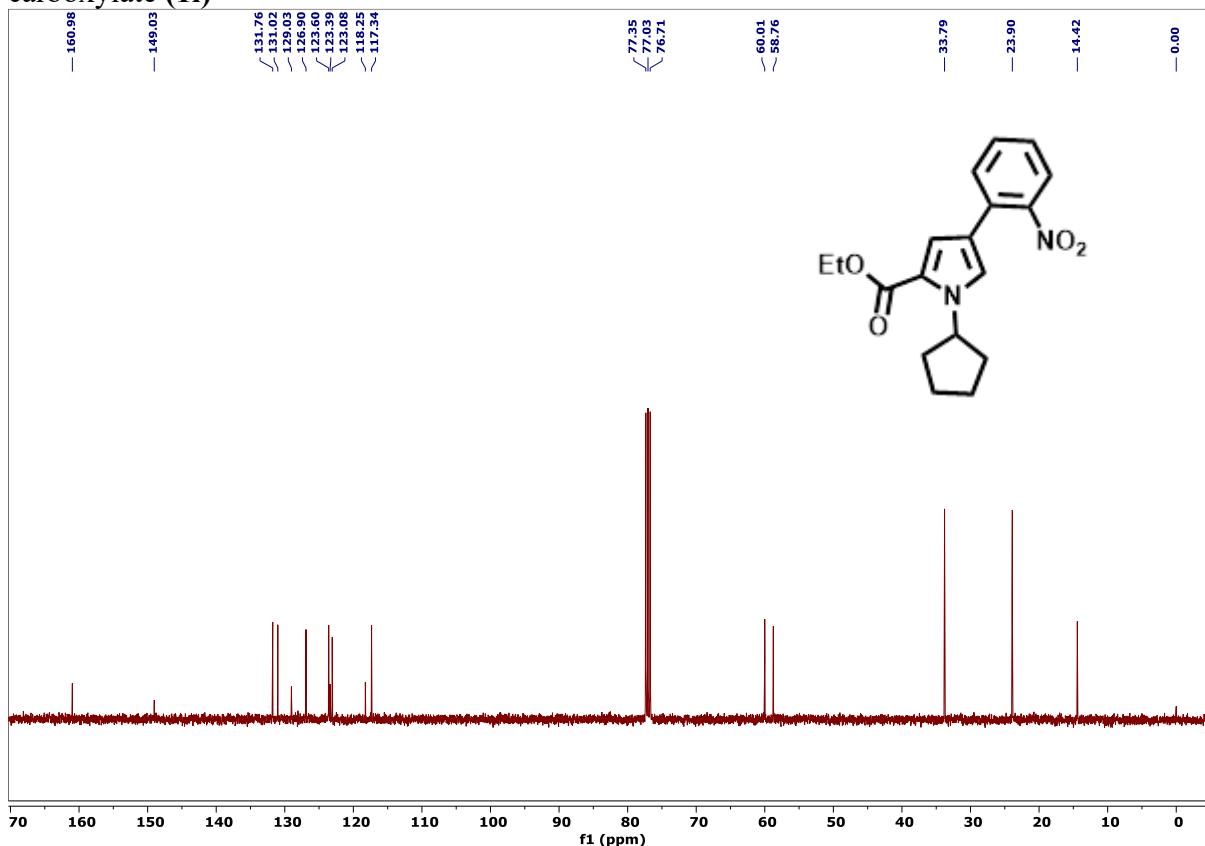
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of ethyl 1-(4-methoxybenzyl)-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (**1e**)



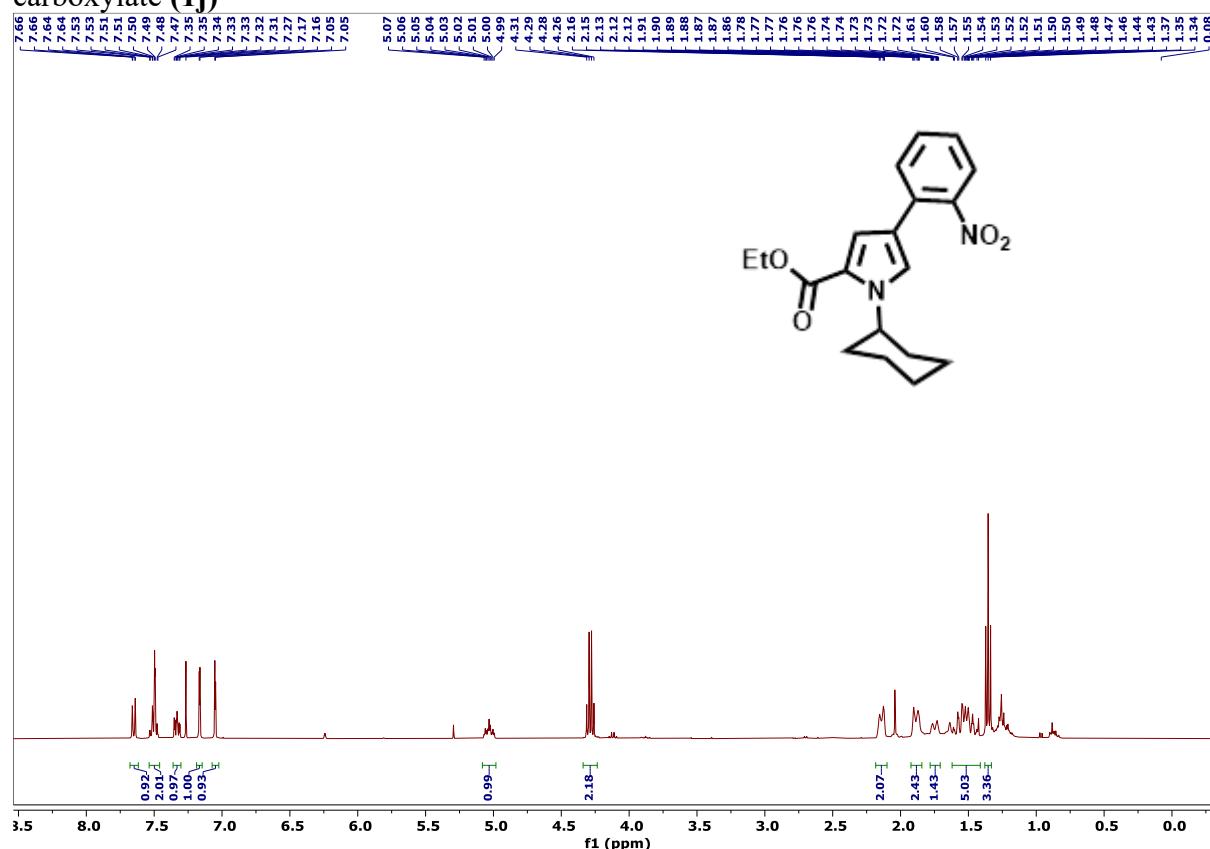
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 1-cyclopentyl-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (**1i**)



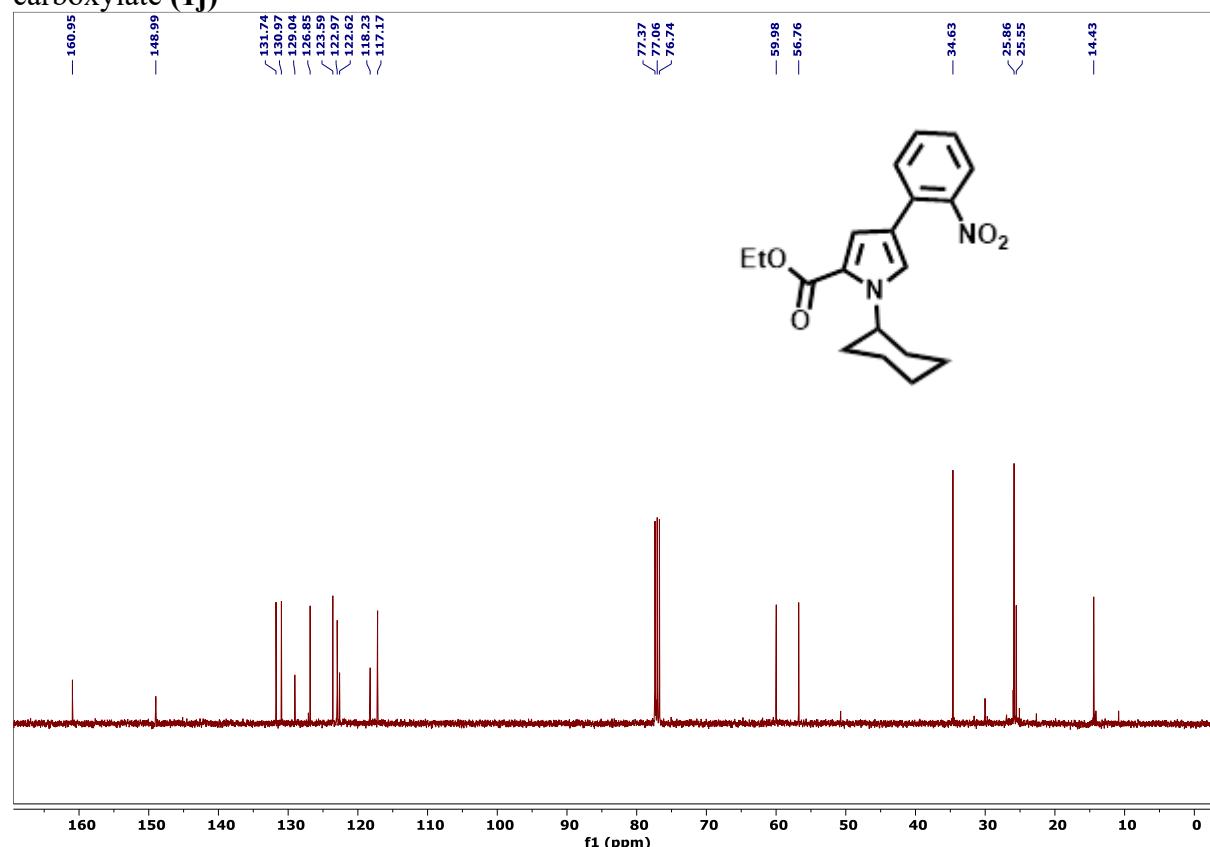
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of ethyl 1-cyclopentyl-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (**1i**)



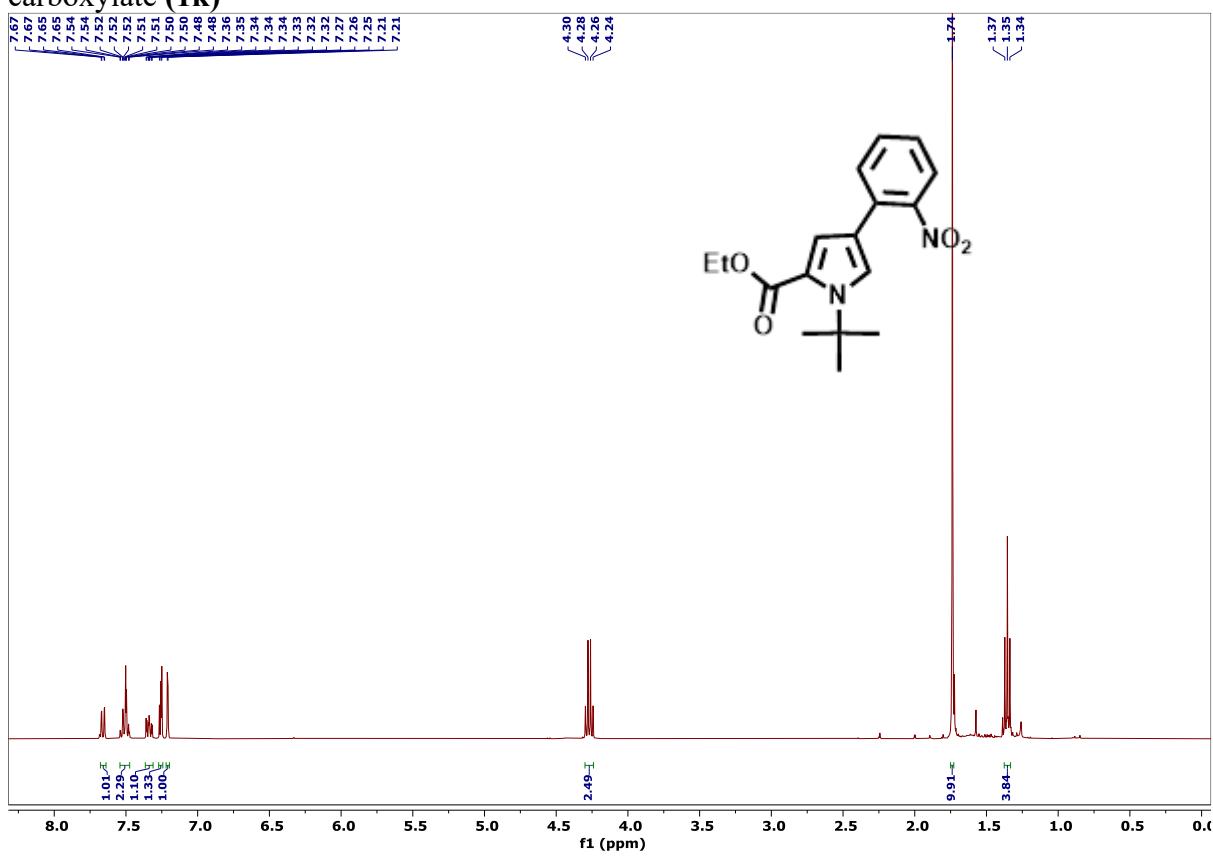
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 1-cyclohexyl-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (**1j**)



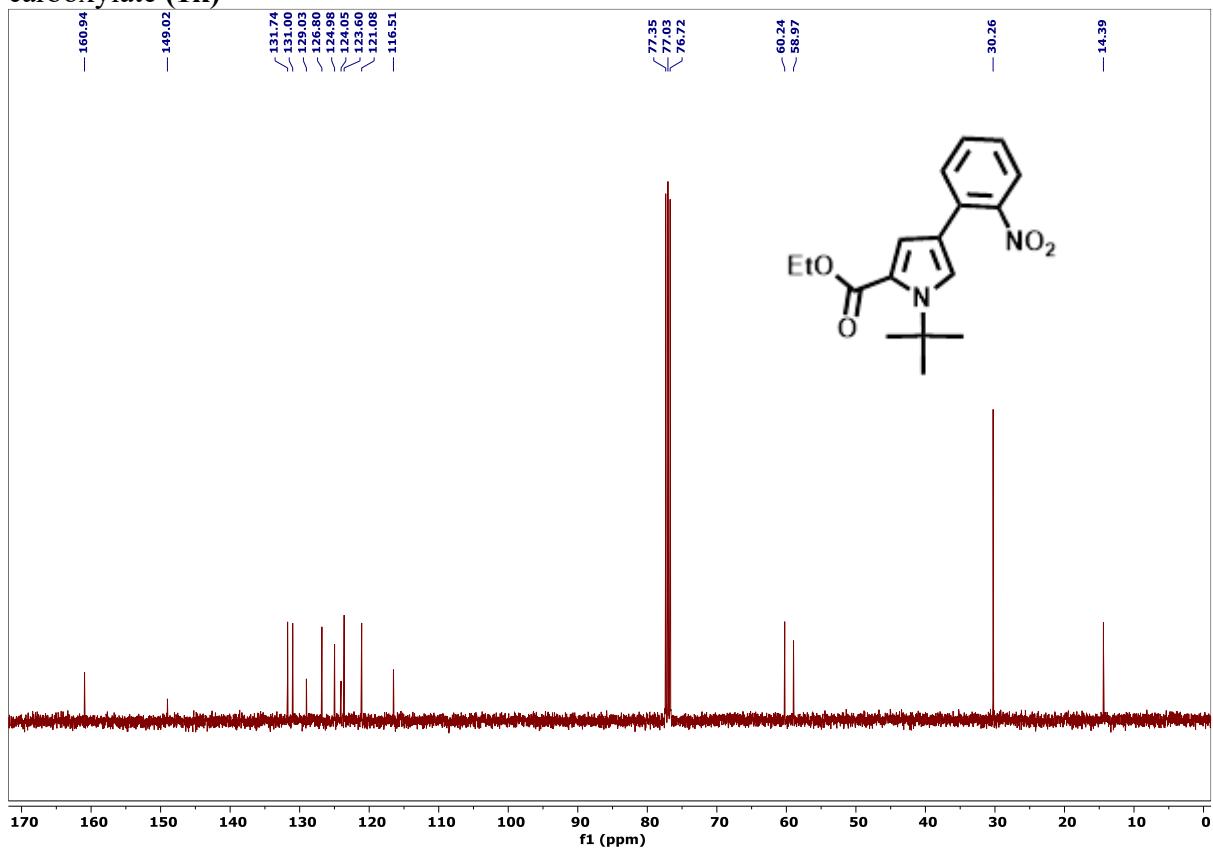
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of ethyl 1-cyclohexyl-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (**1j**)



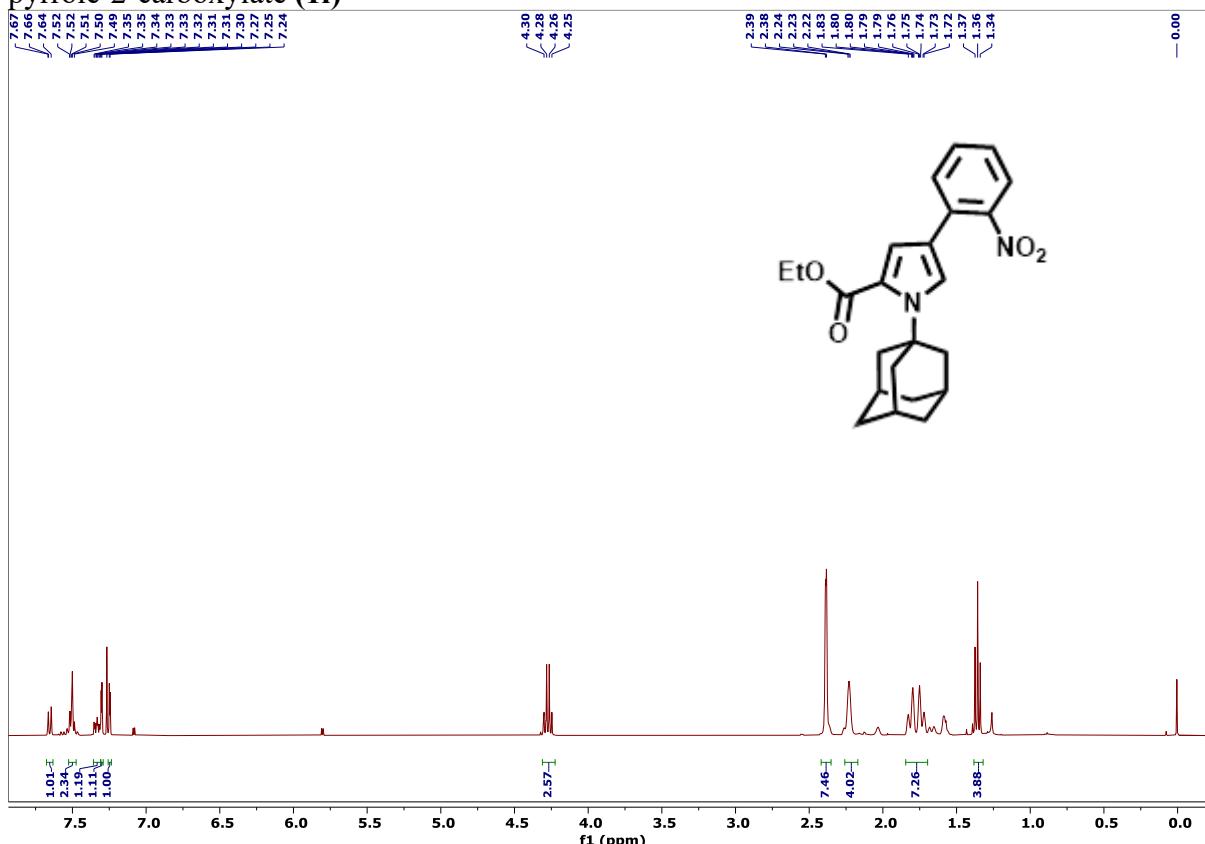
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 1-(tert-butyl)-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (**1k**)



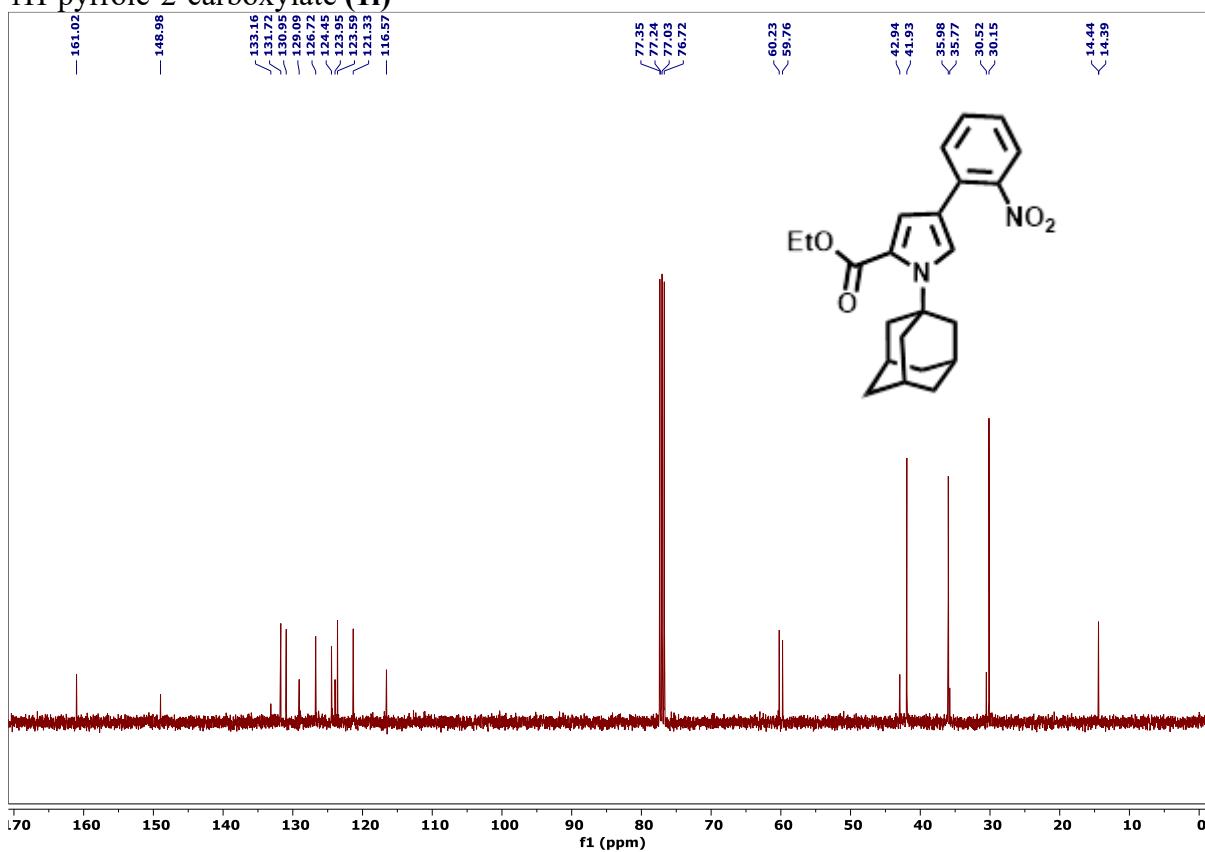
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of ethyl 1-(tert-butyl)-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (**1k**)



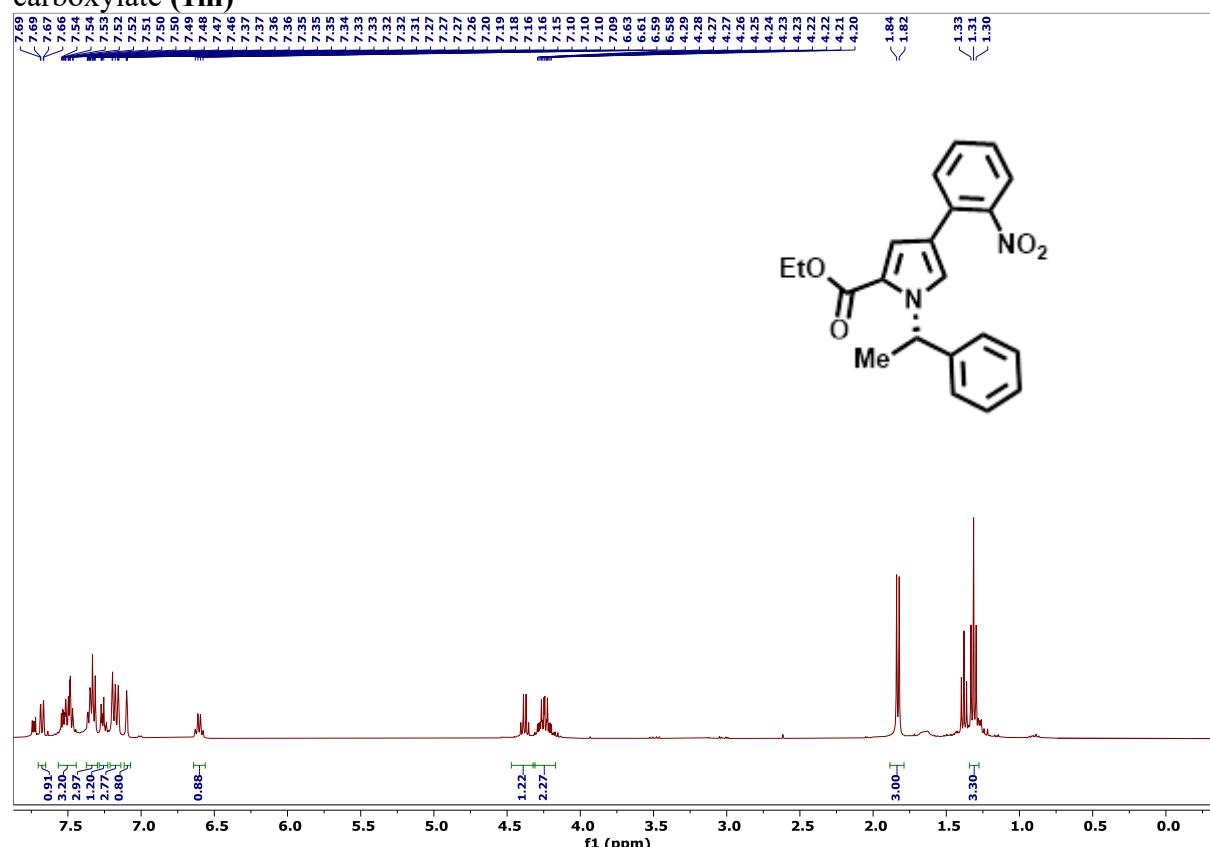
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 1-((3s,5s,7s)-adamantan-1-yl)-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (**1l**)



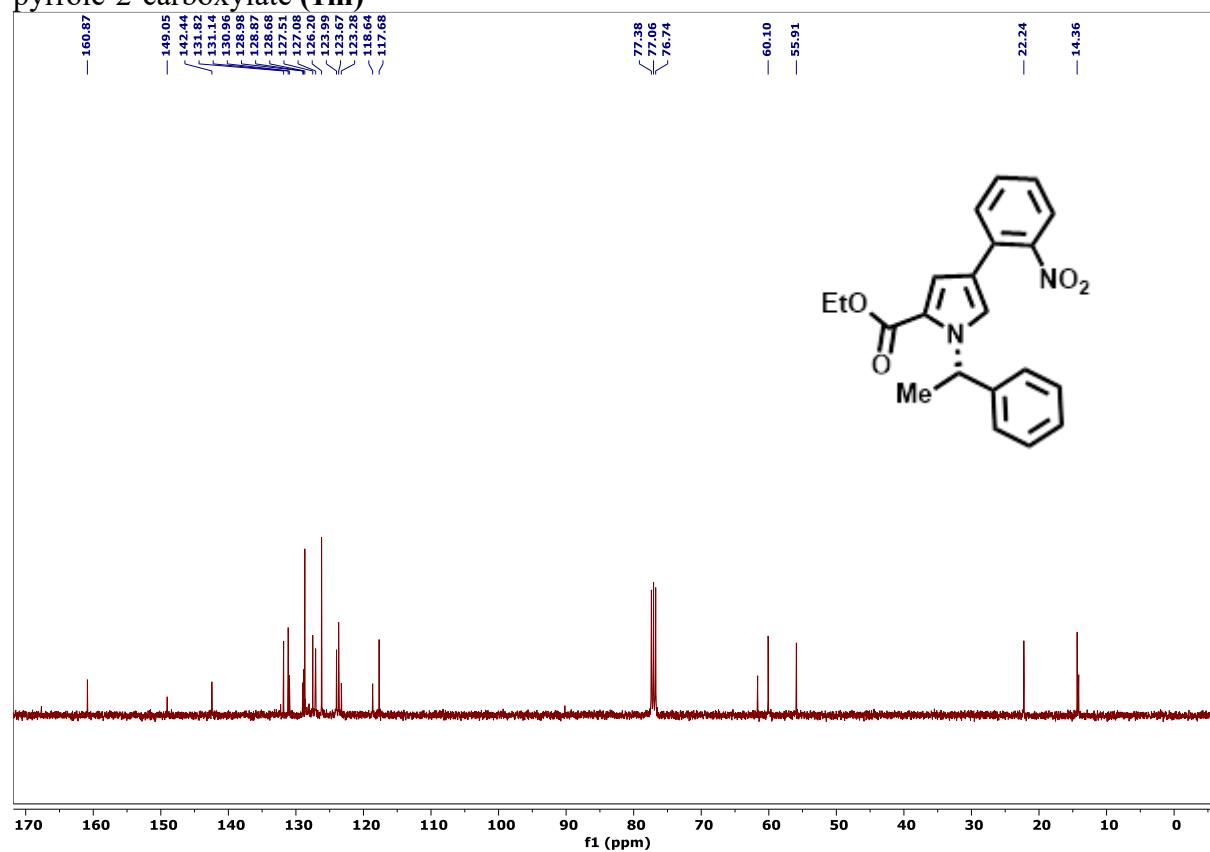
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of ethyl 1-((3s,5s,7s)-adamantan-1-yl)-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (**1l**)



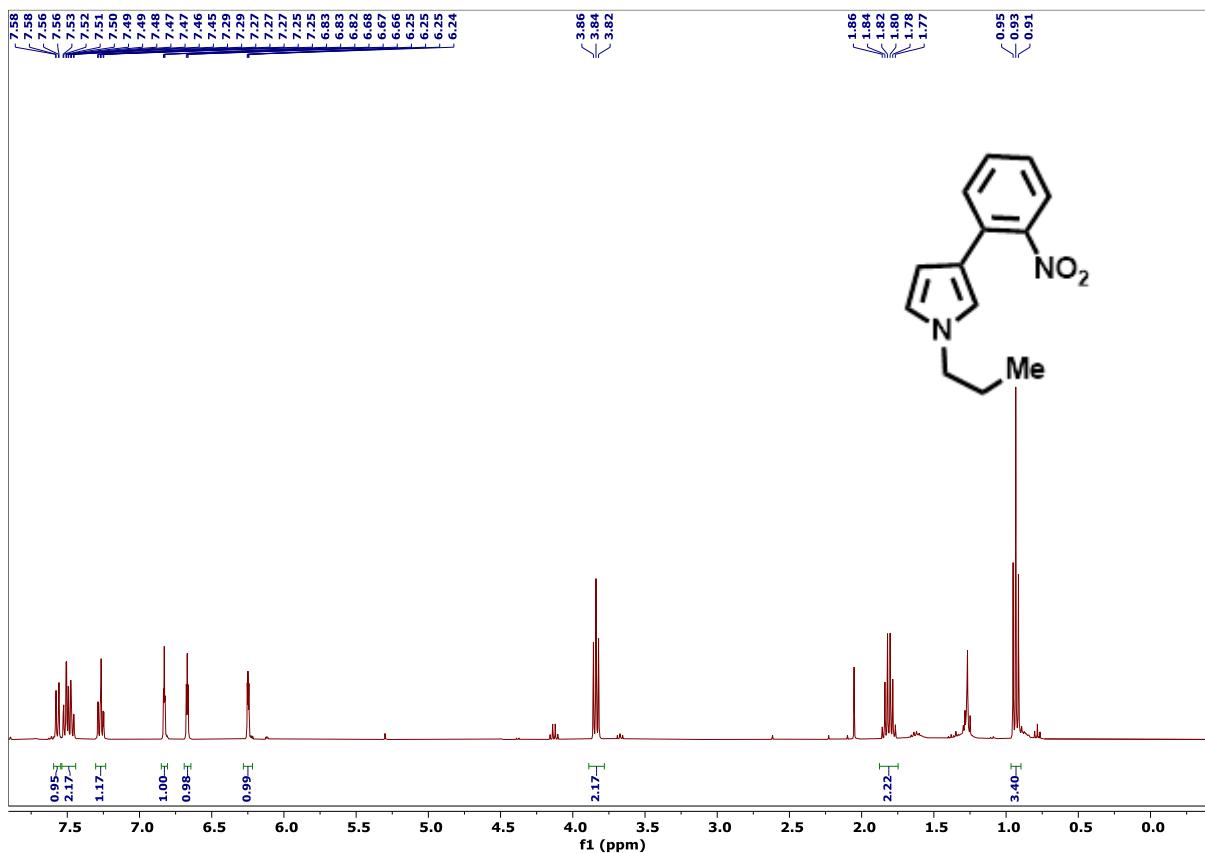
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl (S)-4-(2-nitrophenyl)-1-(1-phenylethyl)-1H-pyrrole-2-carboxylate (**1m**)



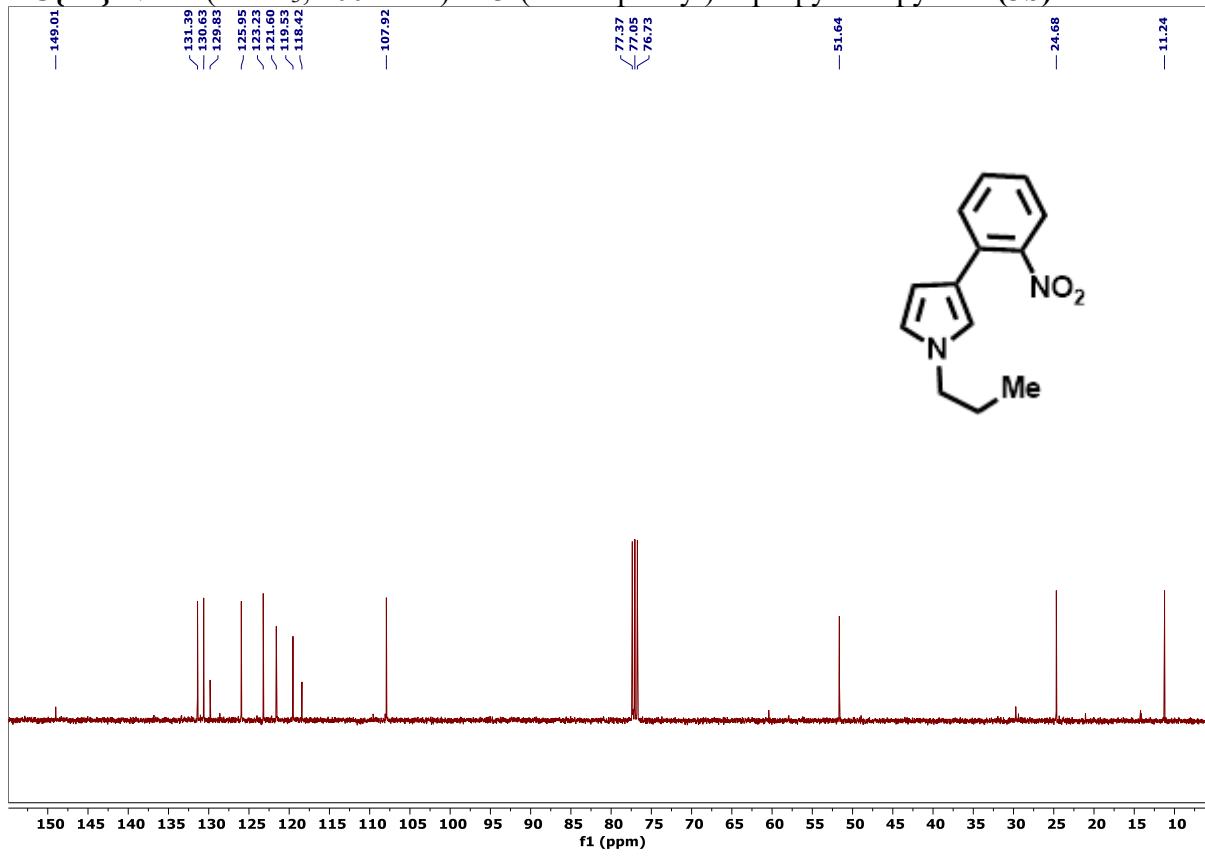
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of ethyl (S)-4-(2-nitrophenyl)-1-(1-phenylethyl)-1H-pyrrole-2-carboxylate (**1m**)



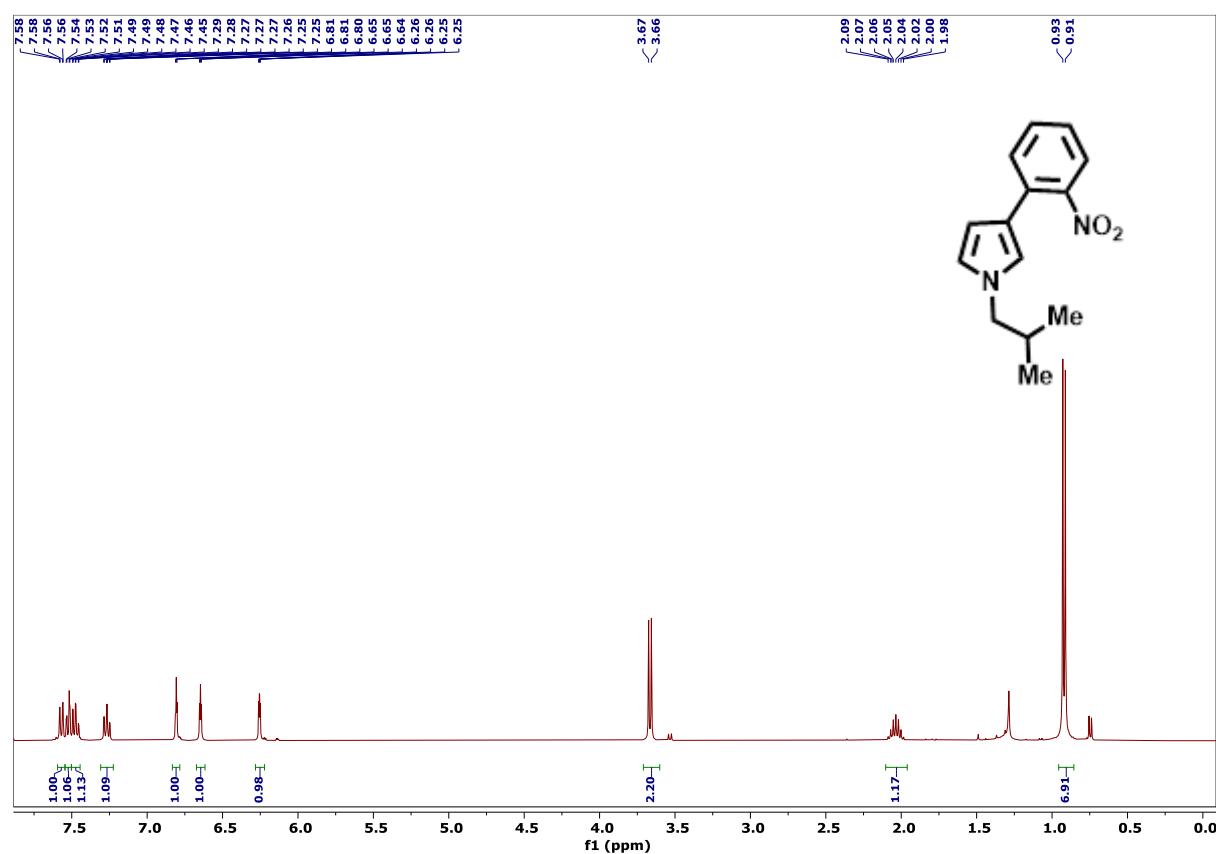
<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz) of 3-(2-nitrophenyl)-1-propyl-1H-pyrrole (**3b**)



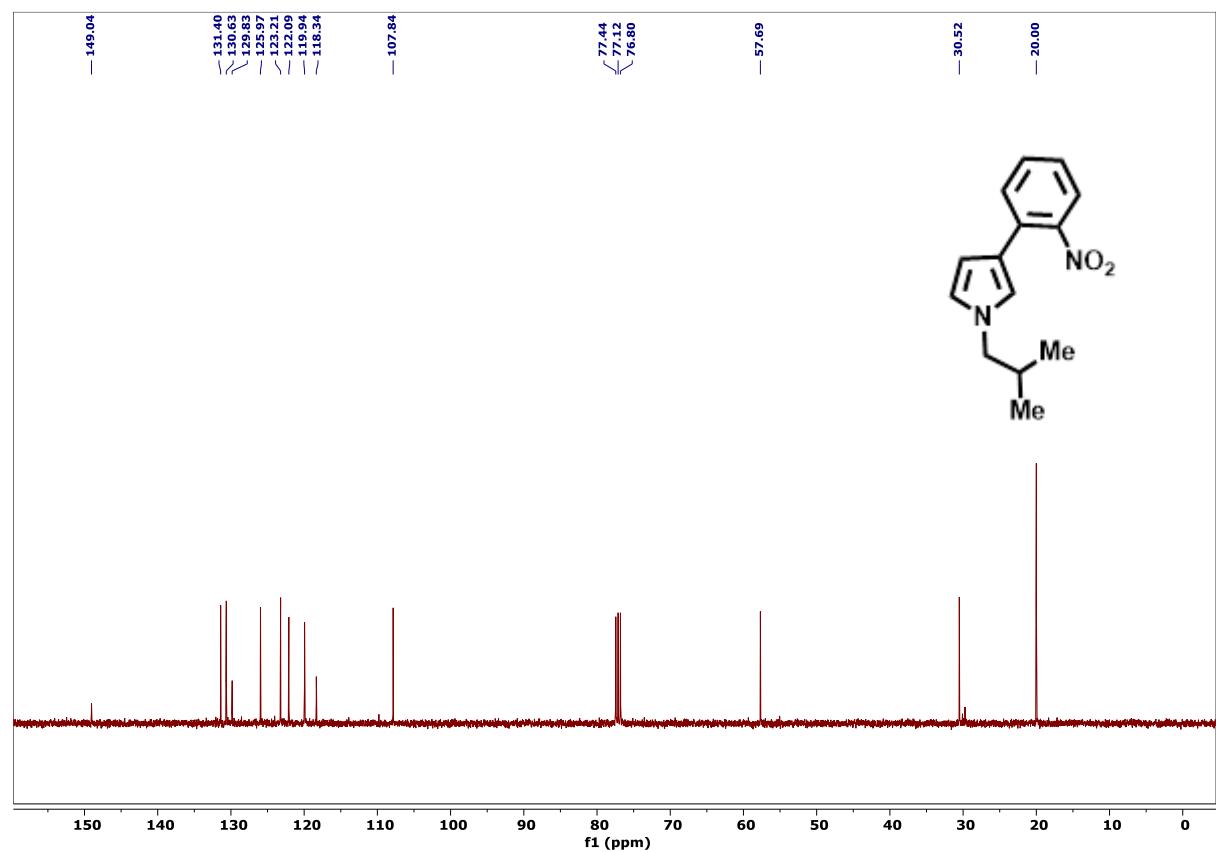
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of 3-(2-nitrophenyl)-1-propyl-1H-pyrrole (**3b**)



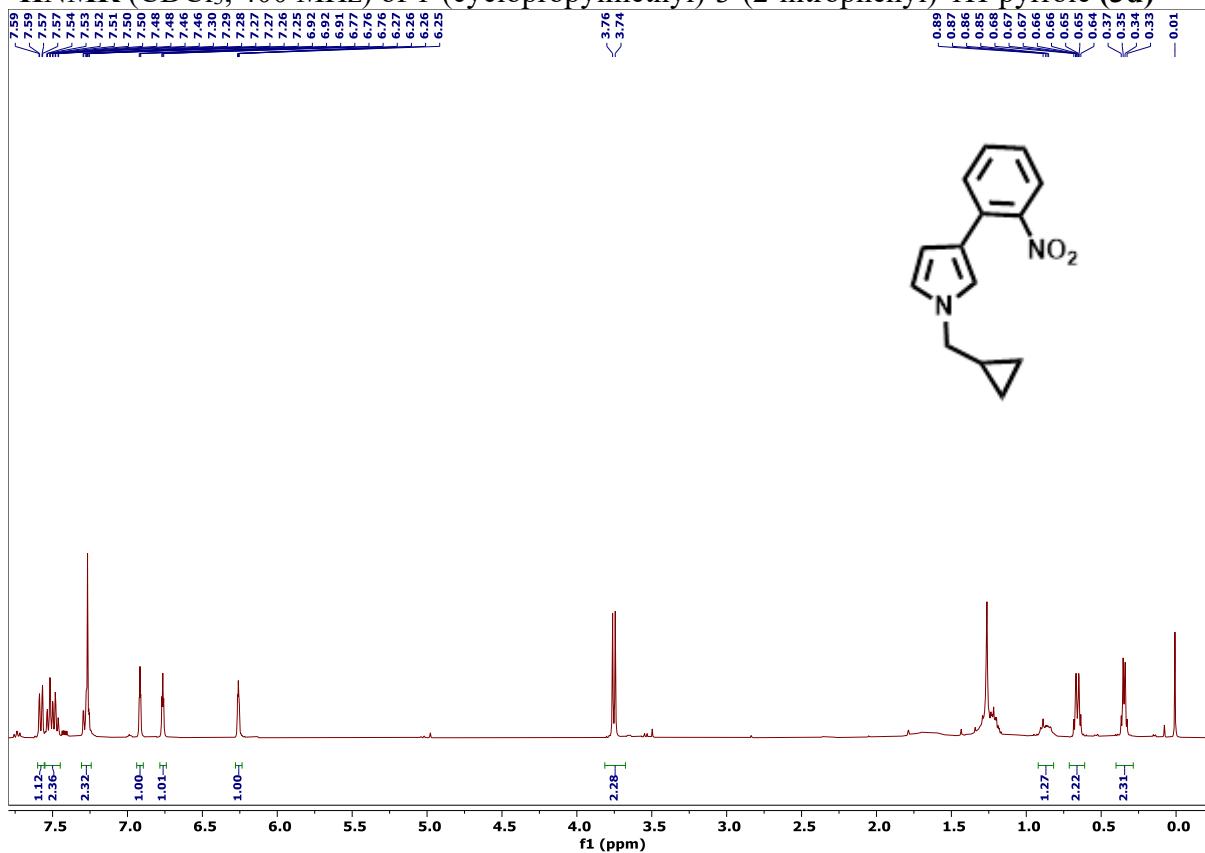
**$^1\text{H}$ NMR** ( $\text{CDCl}_3$ , 400 MHz) of 1-isobutyl-3-(2-nitrophenyl)-1H-pyrrole (**3c**)



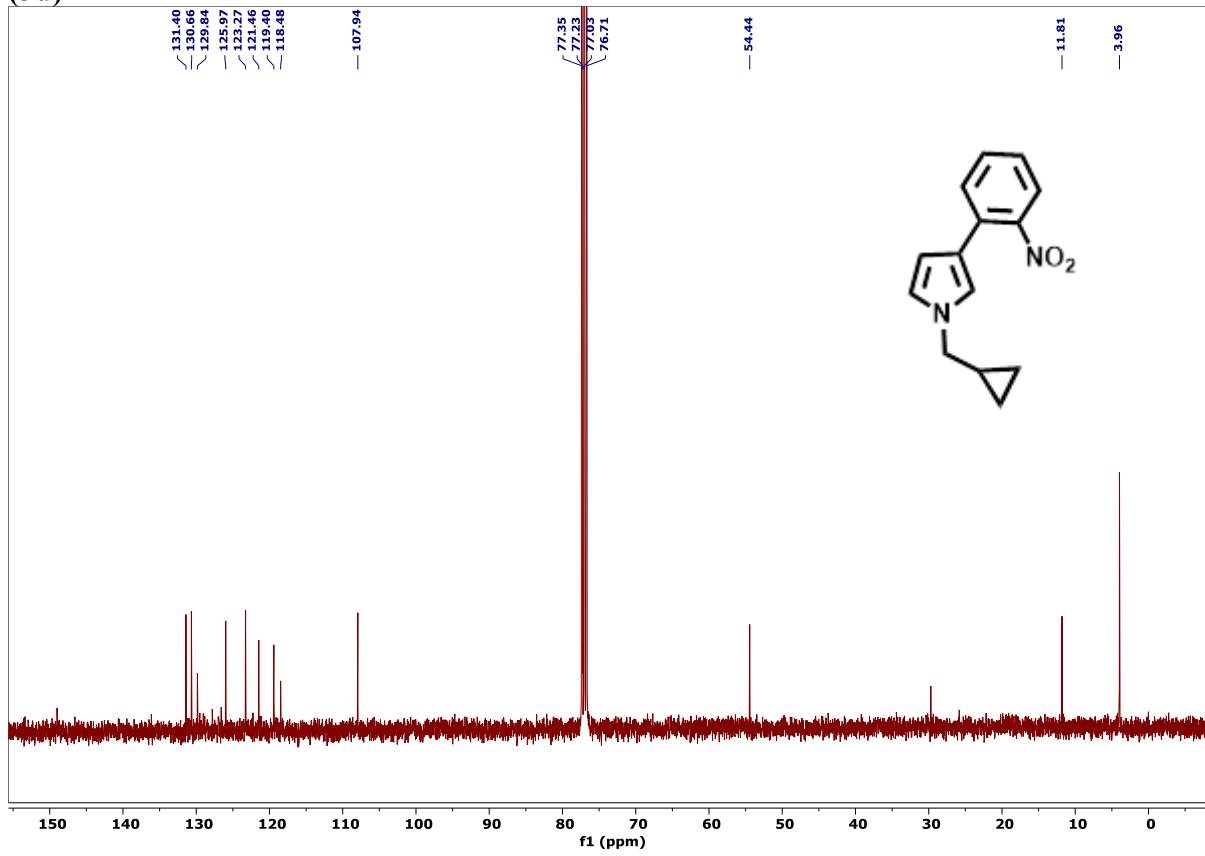
**$^{13}\text{C}\{\text{H}\}$  NMR** ( $\text{CDCl}_3$ , 100 MHz) of 1-isobutyl-3-(2-nitrophenyl)-1H-pyrrole (**3c**)



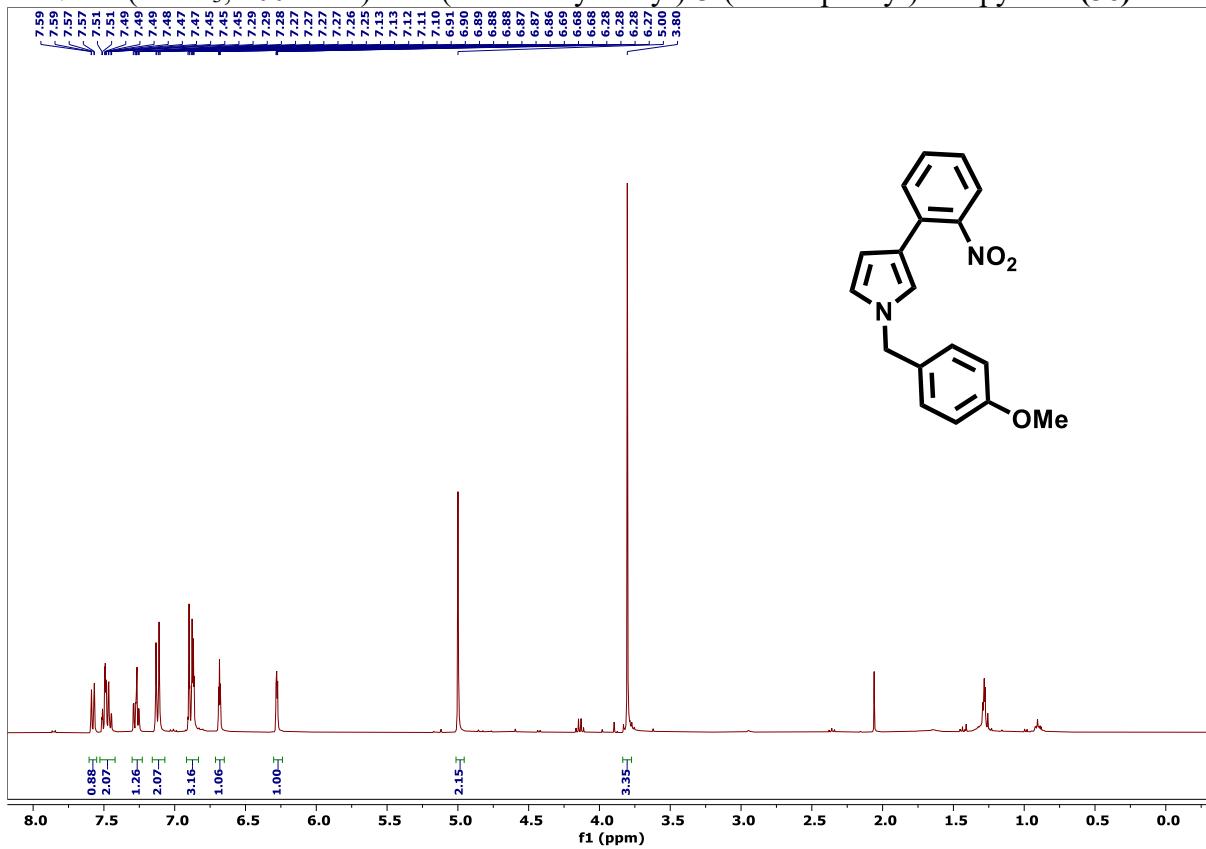
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 1-(cyclopropylmethyl)-3-(2-nitrophenyl)-1H-pyrrole (**3d**)



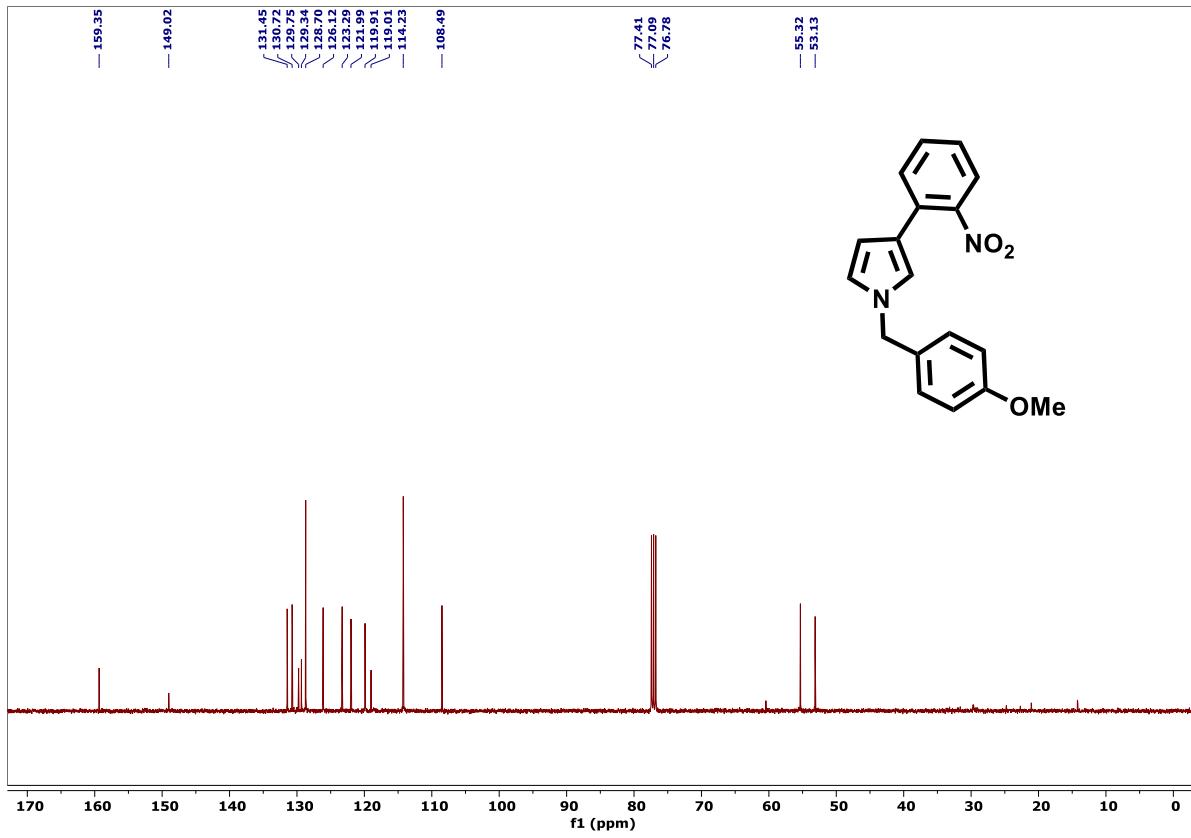
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 1-(cyclopropylmethyl)-3-(2-nitrophenyl)-1H-pyrrole (**3d**)



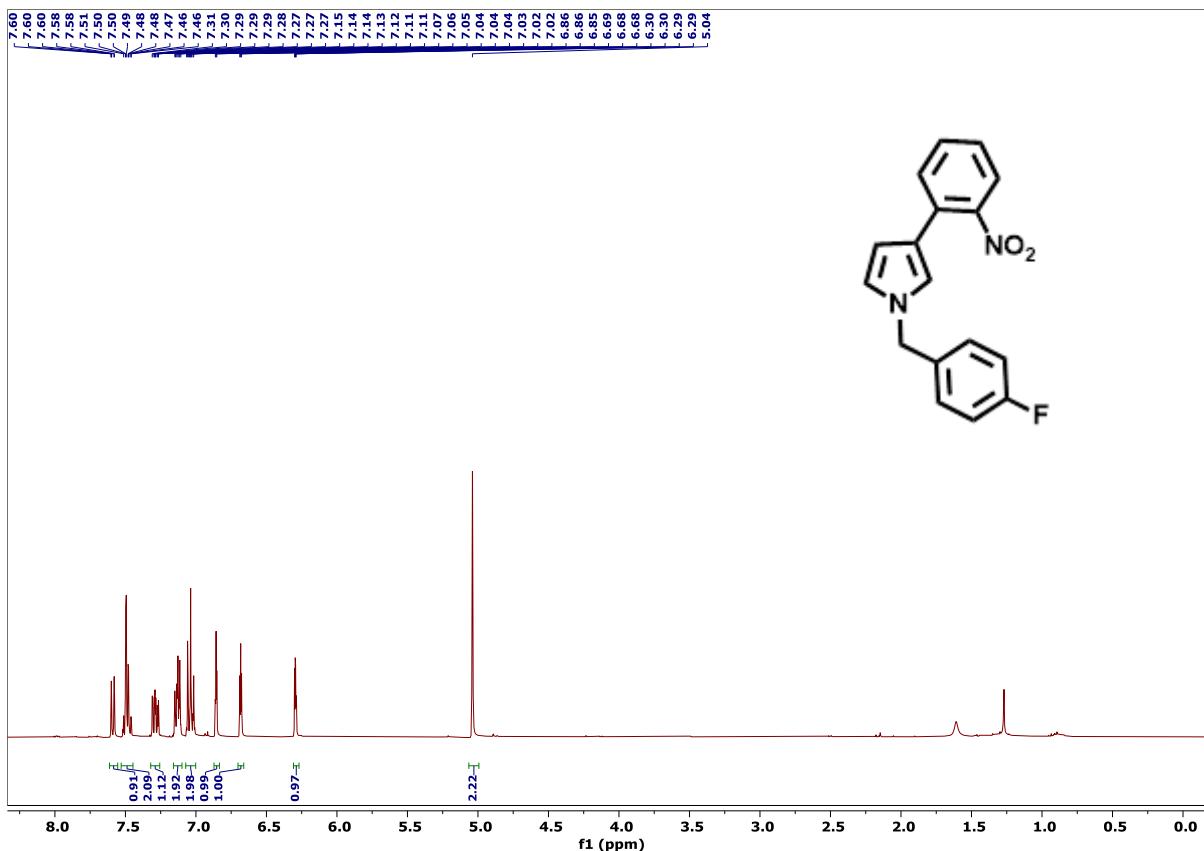
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of 1-(4-methoxybenzyl)-3-(2-nitrophenyl)-1H-pyrrole (**3e**)



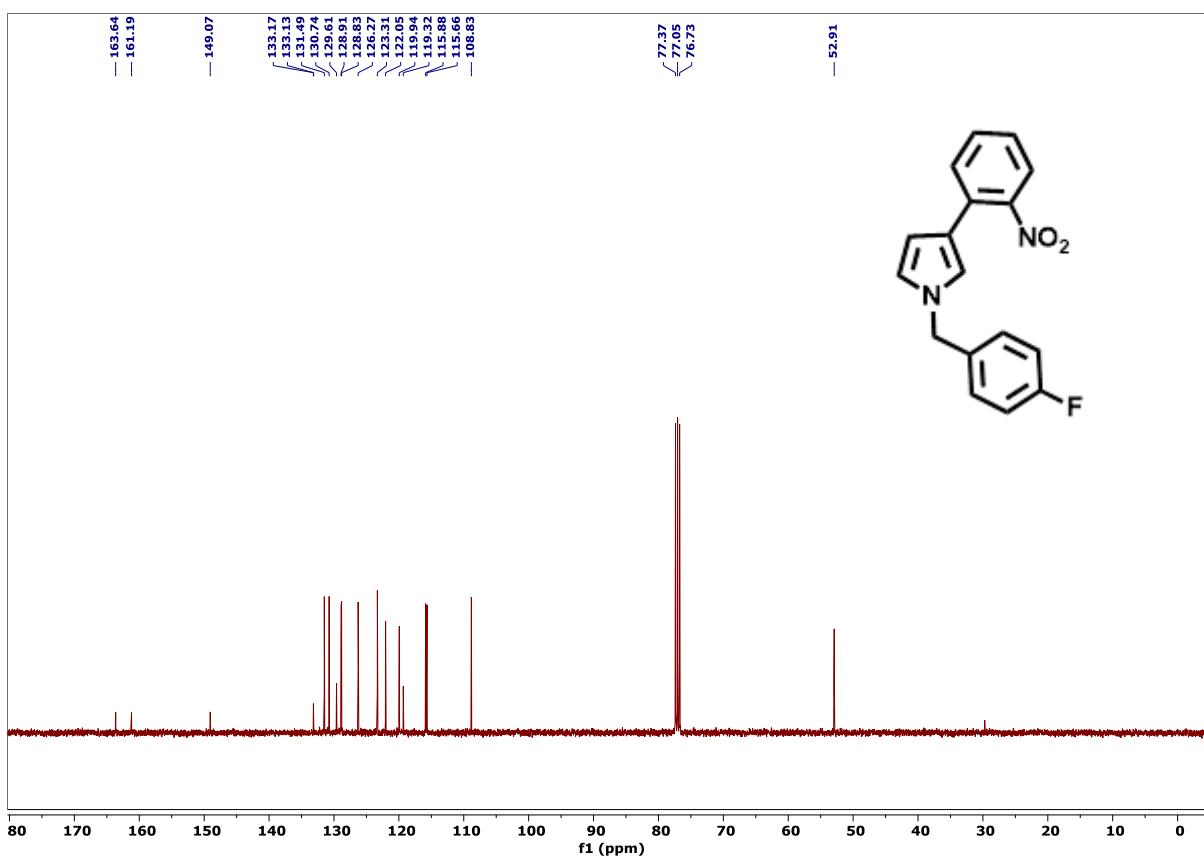
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of 1-(4-methoxybenzyl)-3-(2-nitrophenyl)-1H-pyrrole (**3e**)



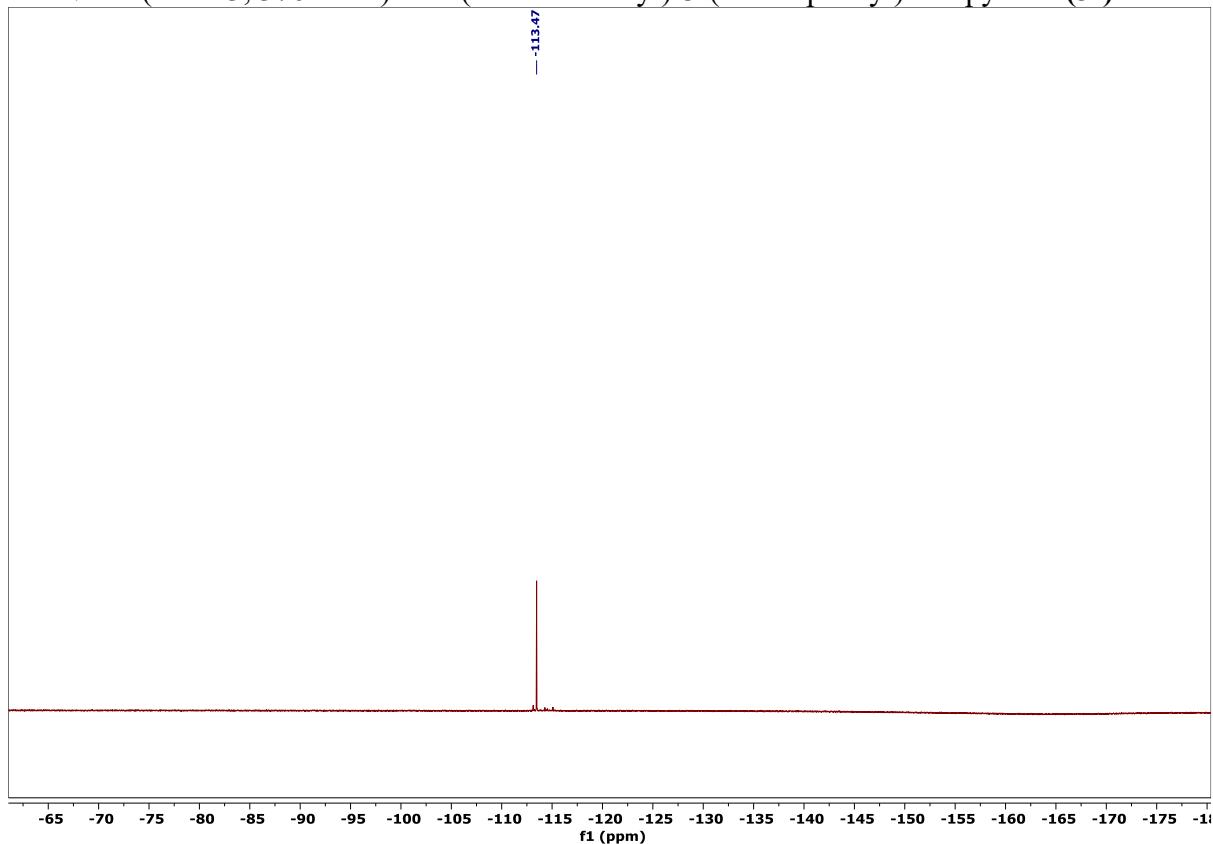
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 1-(4-fluorobenzyl)-3-(2-nitrophenyl)-1H-pyrrole (**3f**)



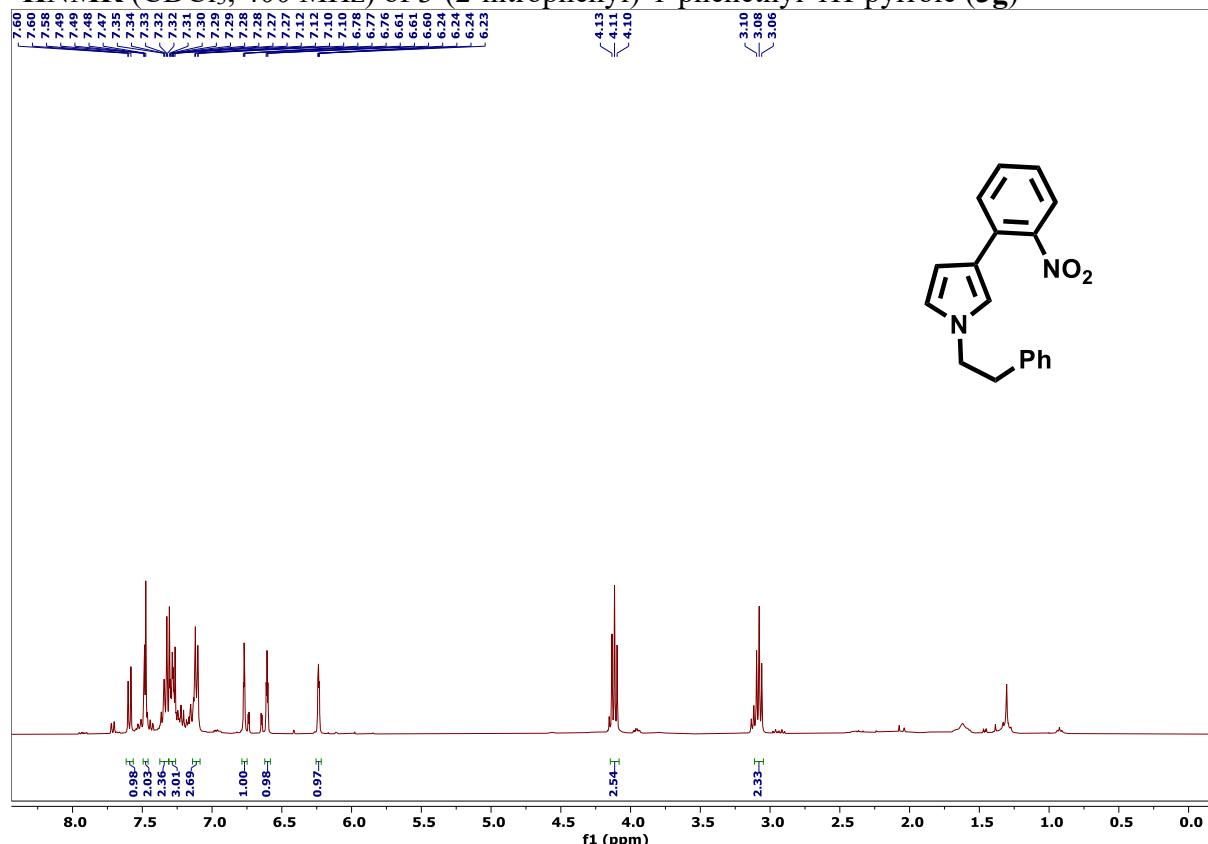
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 1-(4-fluorobenzyl)-3-(2-nitrophenyl)-1H-pyrrole (**3f**)



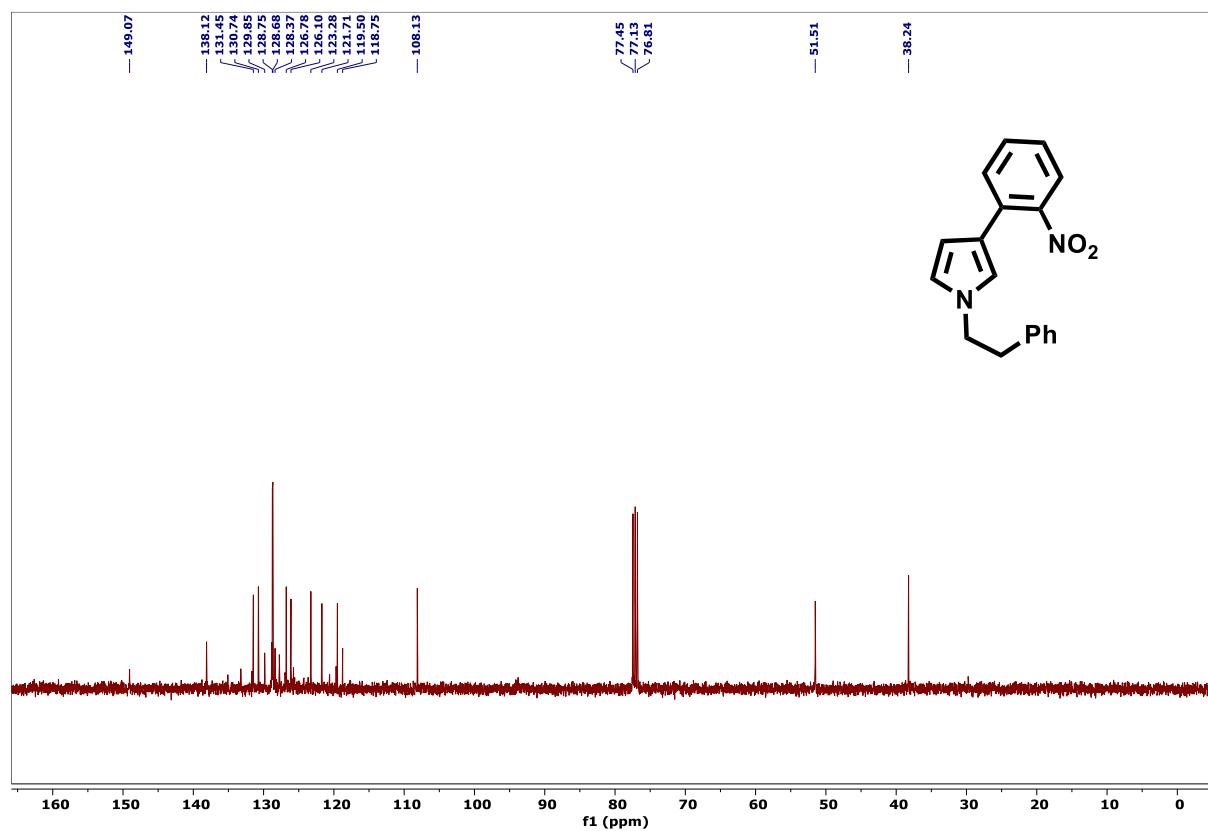
**<sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz) of 1-(4-fluorobenzyl)-3-(2-nitrophenyl)-1H-pyrrole (**3f**)**



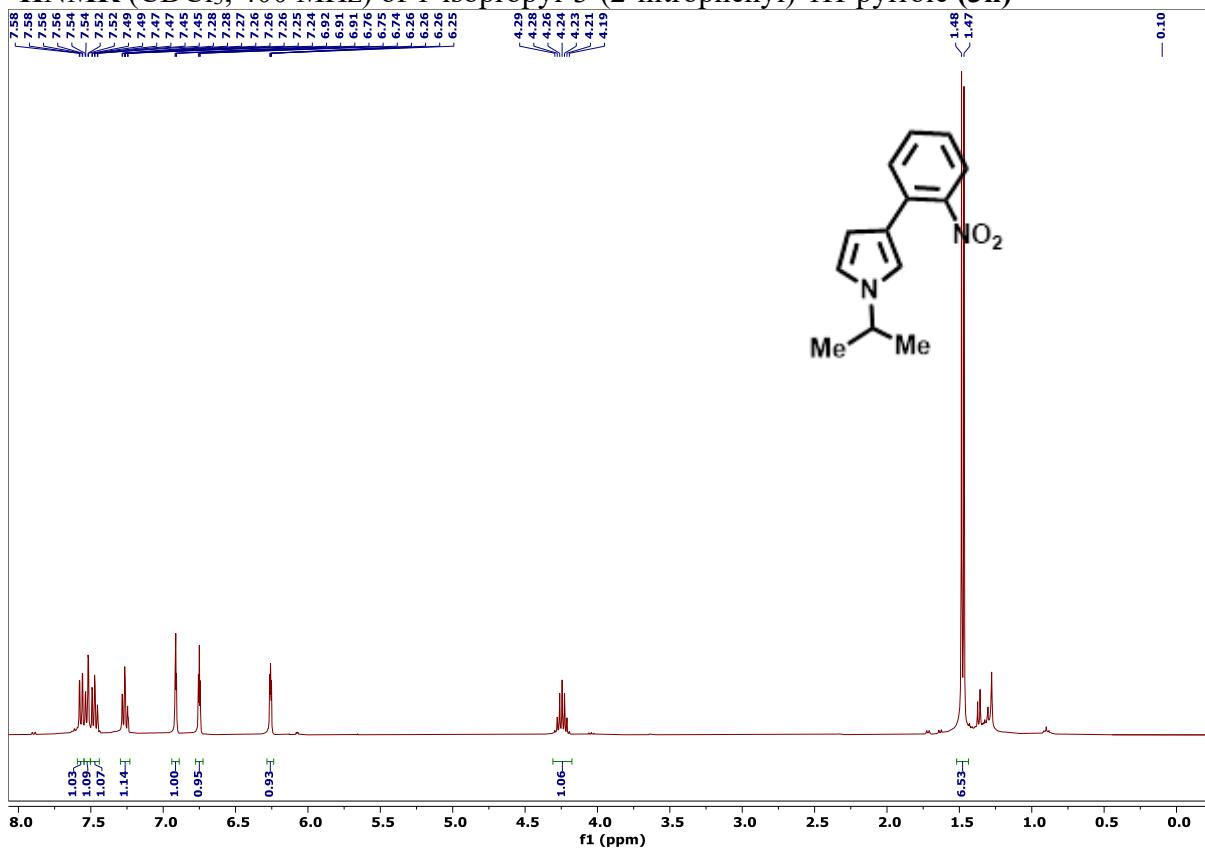
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of 3-(2-nitrophenyl)-1-phenethyl-1H-pyrrole (3g)**



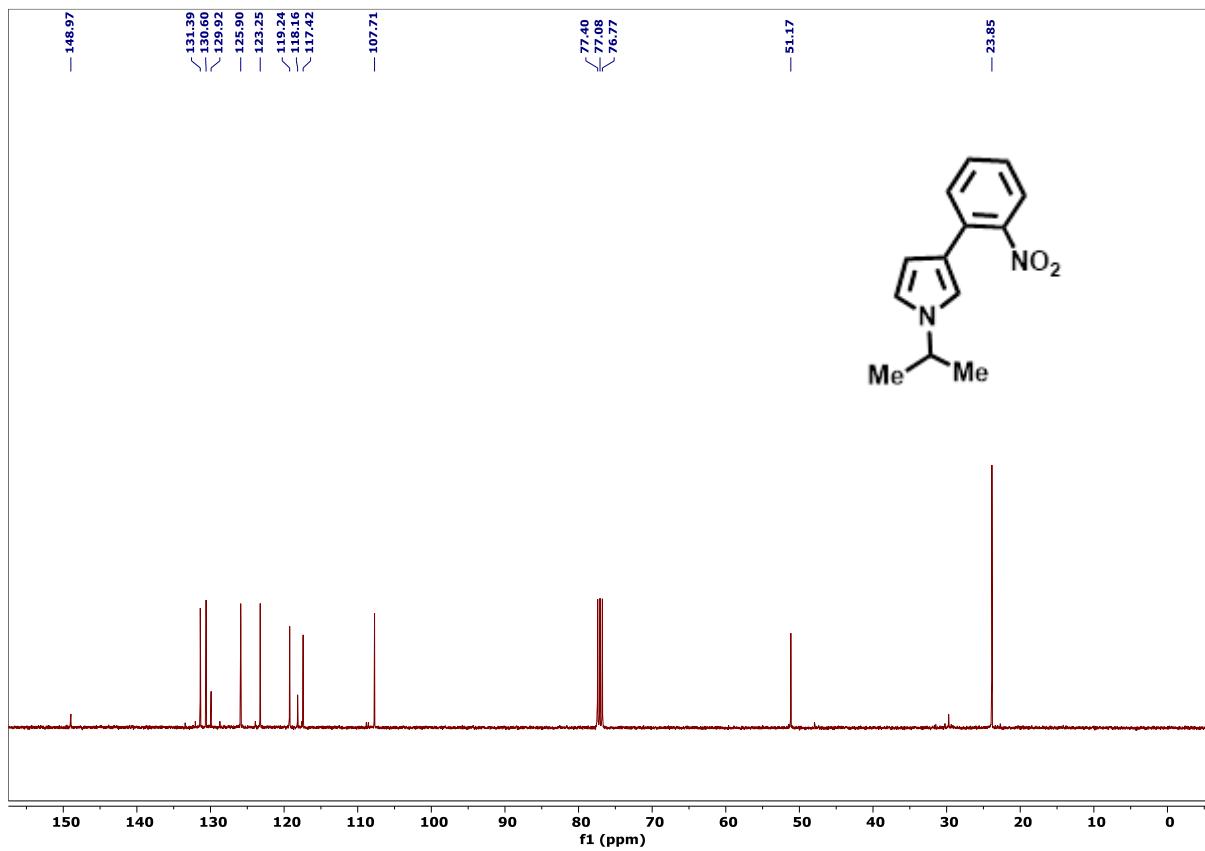
**<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of 3-(2-nitrophenyl)-1-phenethyl-1H-pyrrole (3g)**



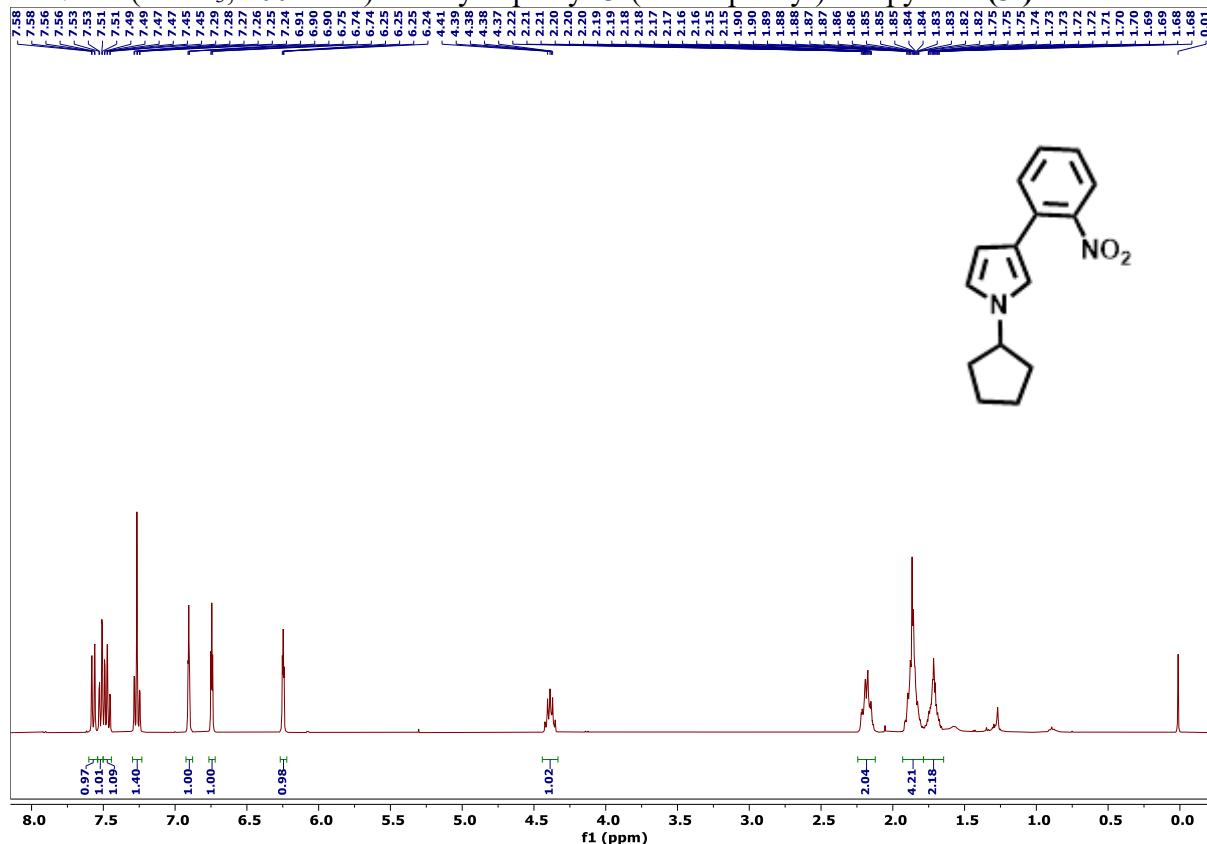
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 1-isopropyl-3-(2-nitrophenyl)-1H-pyrrole (**3h**)



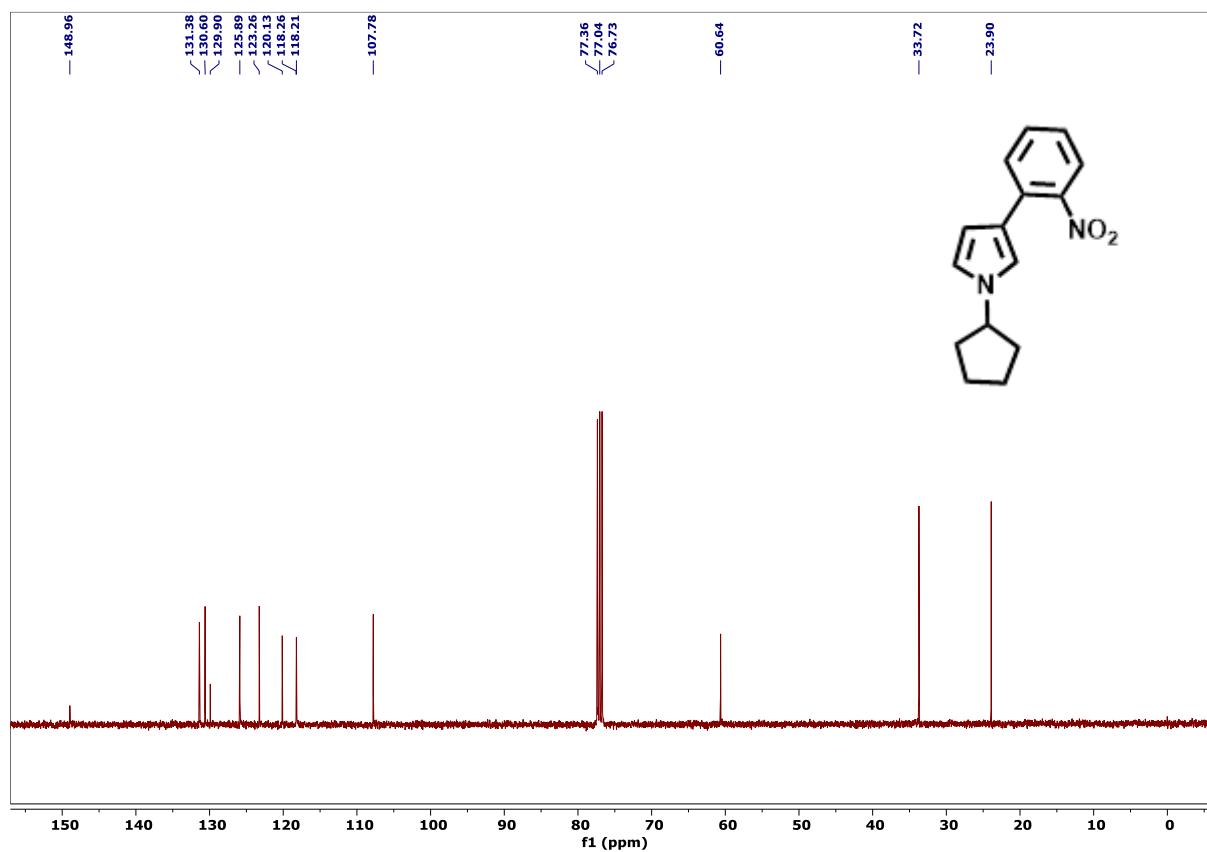
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 1-isopropyl-3-(2-nitrophenyl)-1H-pyrrole (**3h**)



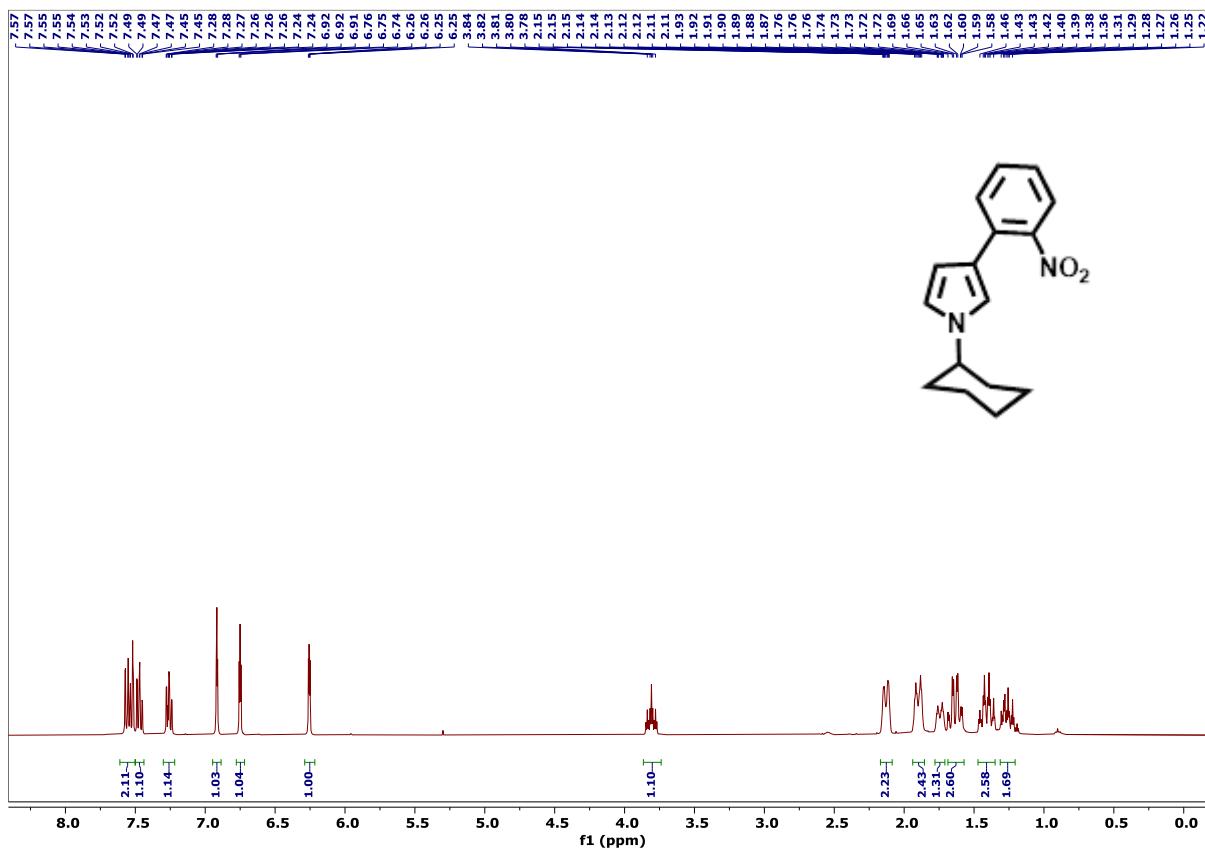
<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz) of 1-cyclopentyl-3-(2-nitrophenyl)-1H-pyrrole (3i)



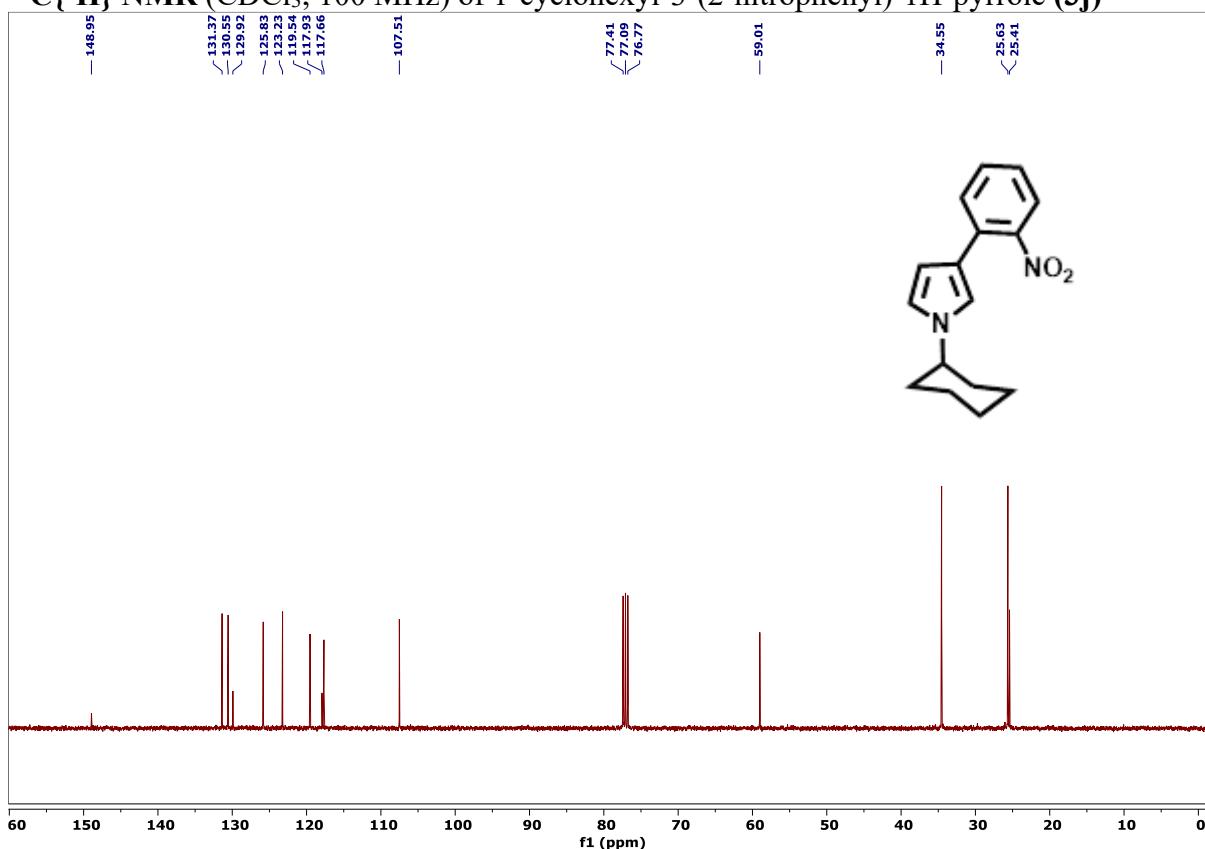
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of 1-cyclopentyl-3-(2-nitrophenyl)-1H-pyrrole (**3i**)



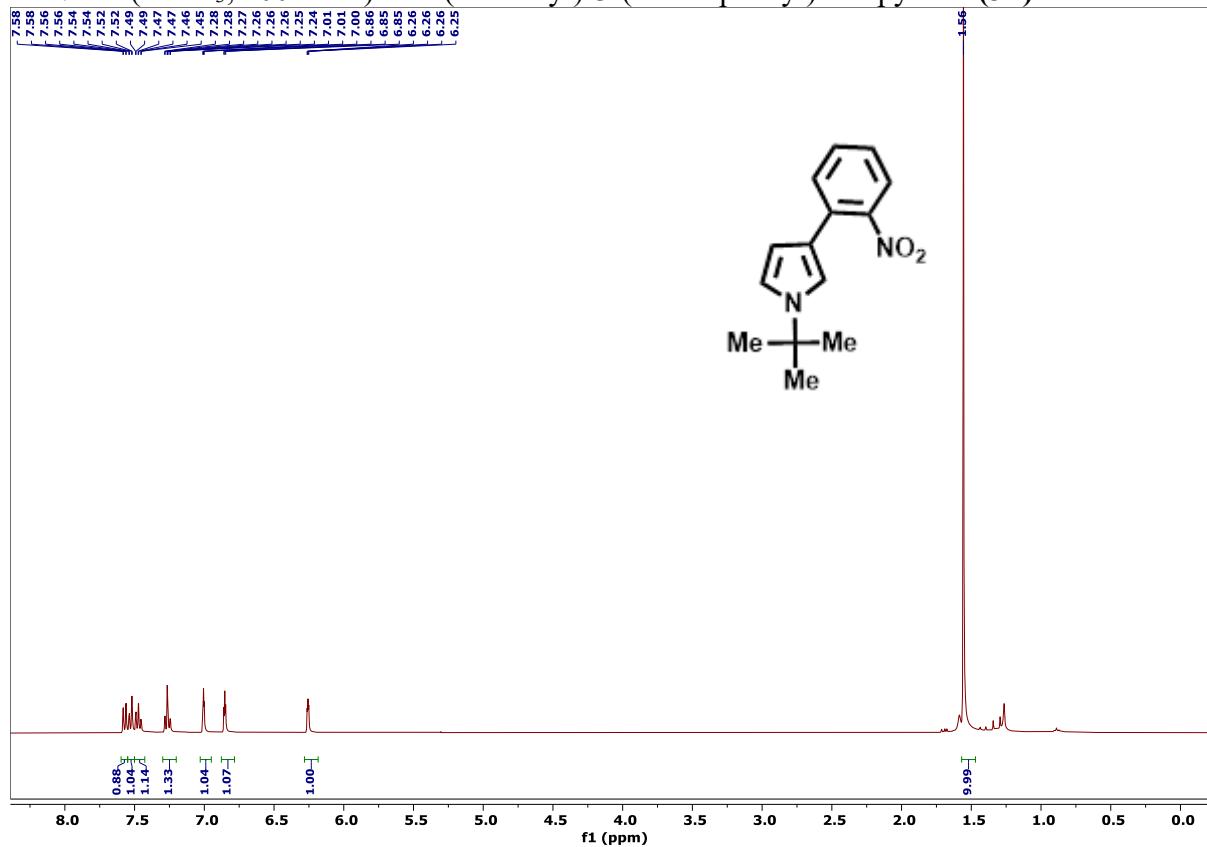
**$^1\text{H}$ NMR** ( $\text{CDCl}_3$ , 400 MHz) of 1-cyclohexyl-3-(2-nitrophenyl)-1H-pyrrole (**3j**)



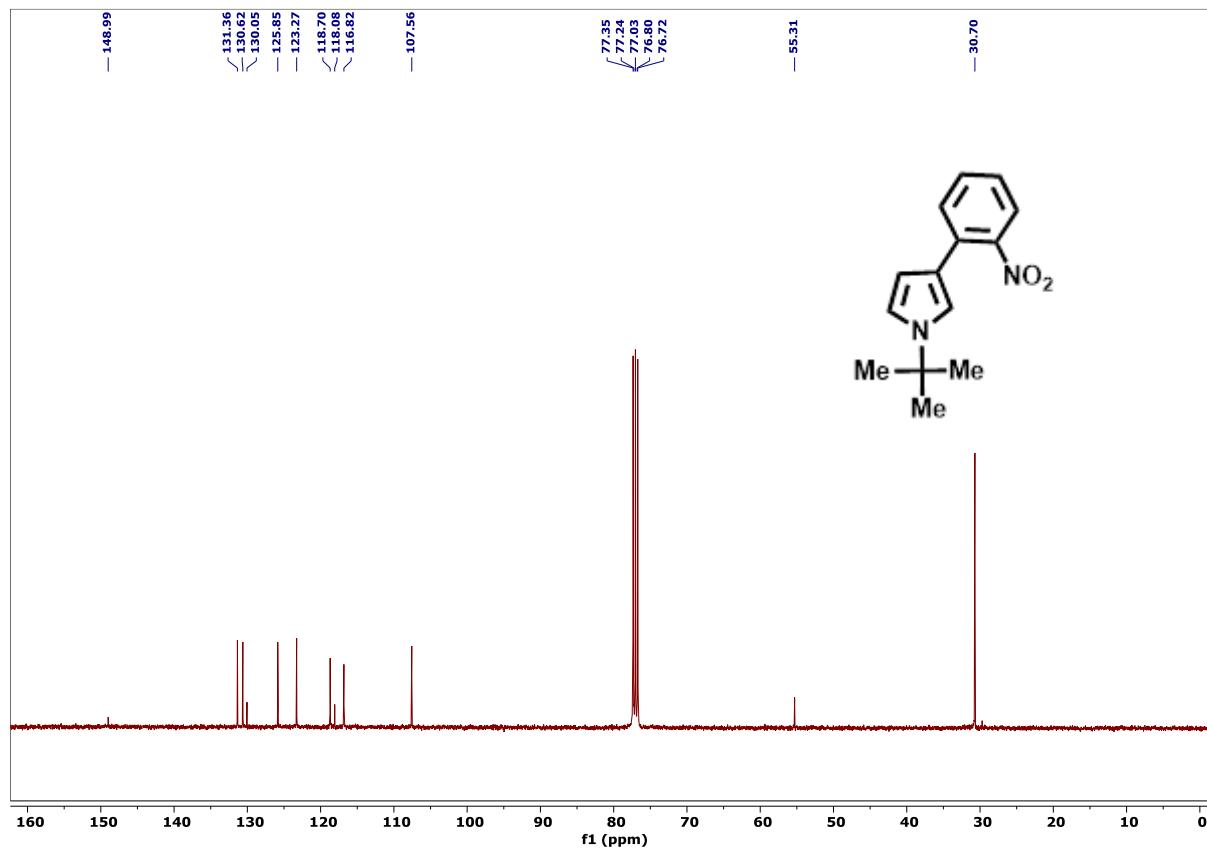
**$^{13}\text{C}\{^1\text{H}\}$  NMR** ( $\text{CDCl}_3$ , 100 MHz) of 1-cyclohexyl-3-(2-nitrophenyl)-1H-pyrrole (**3j**)



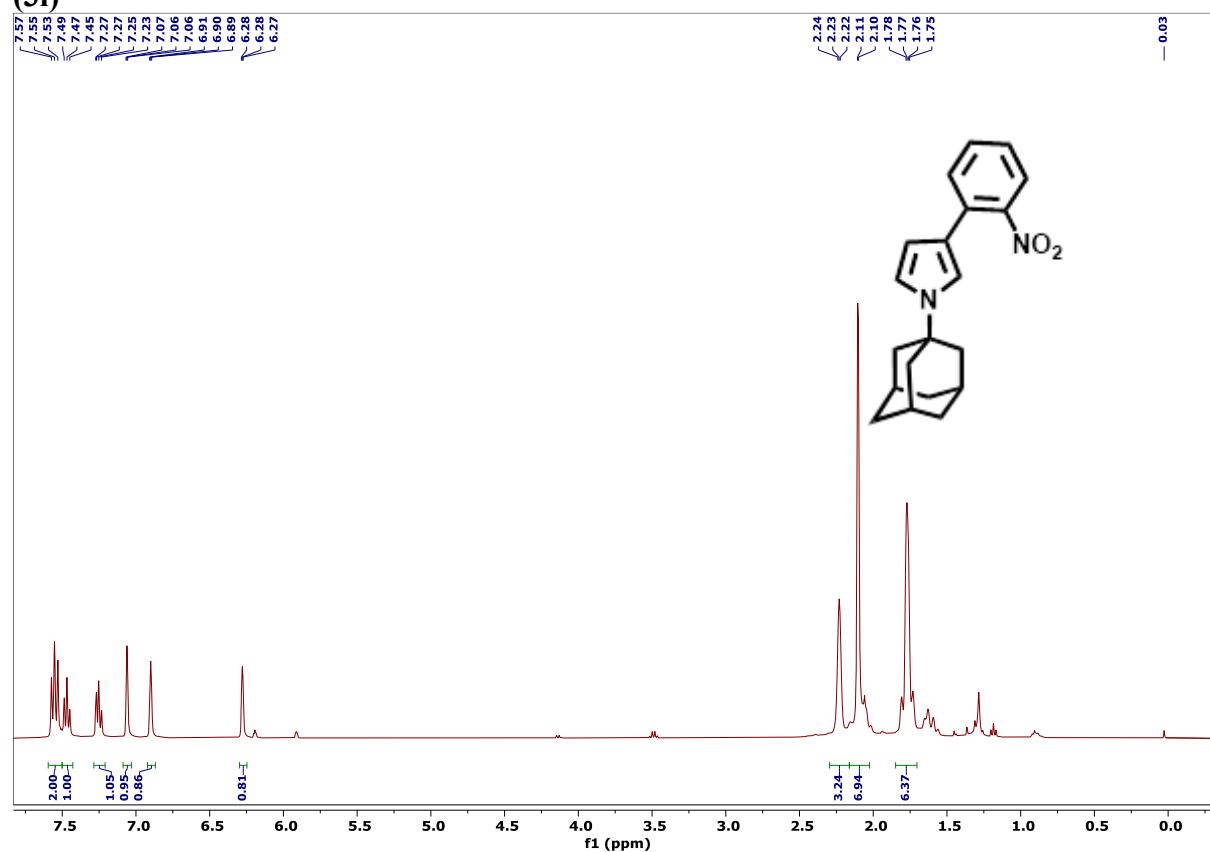
<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz) of 1-(tert-butyl)-3-(2-nitrophenyl)-1H-pyrrole (3k)



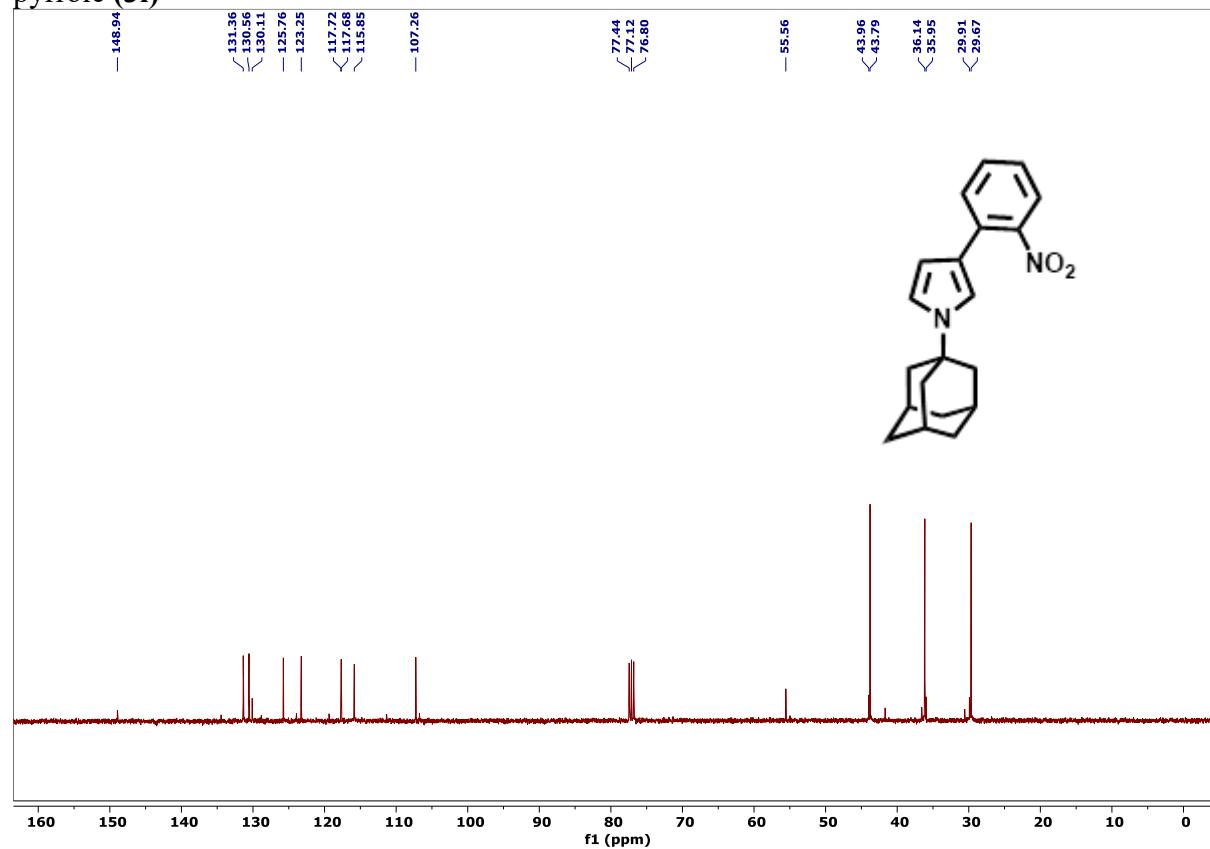
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of 1-(tert-butyl)-3-(2-nitrophenyl)-1H-pyrrole (**3k**)



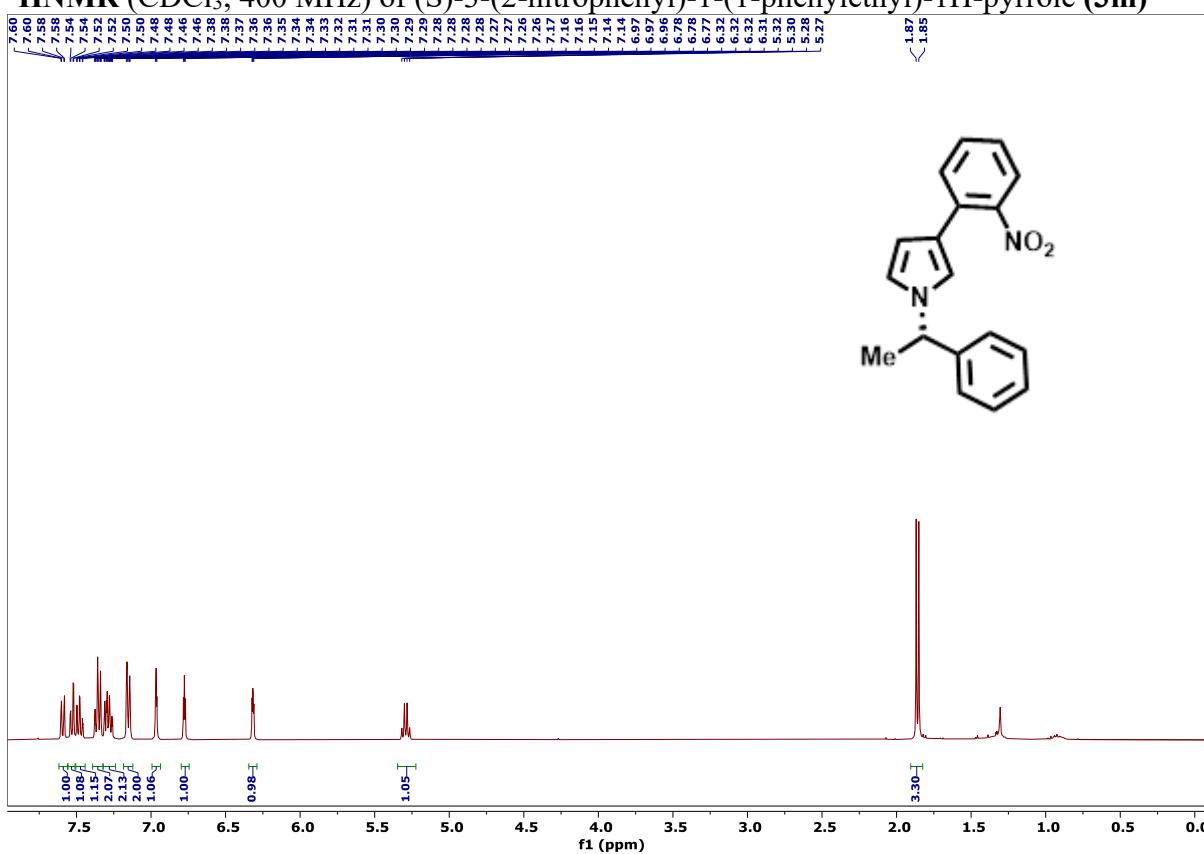
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 1-((3s,5s,7s)-adamantan-1-yl)-3-(2-nitrophenyl)-1H-pyrrole (**3l**)



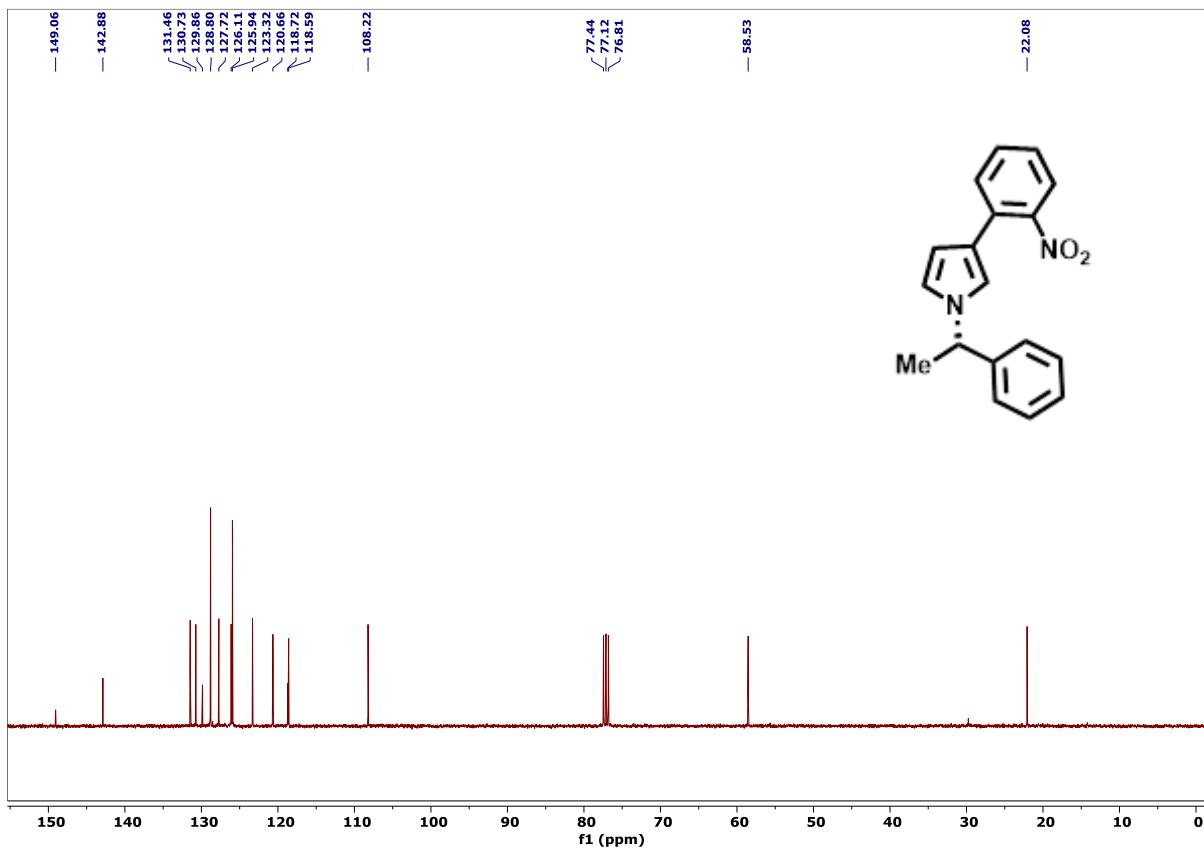
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 1-((3s,5s,7s)-adamantan-1-yl)-3-(2-nitrophenyl)-1H-pyrrole (**3l**)



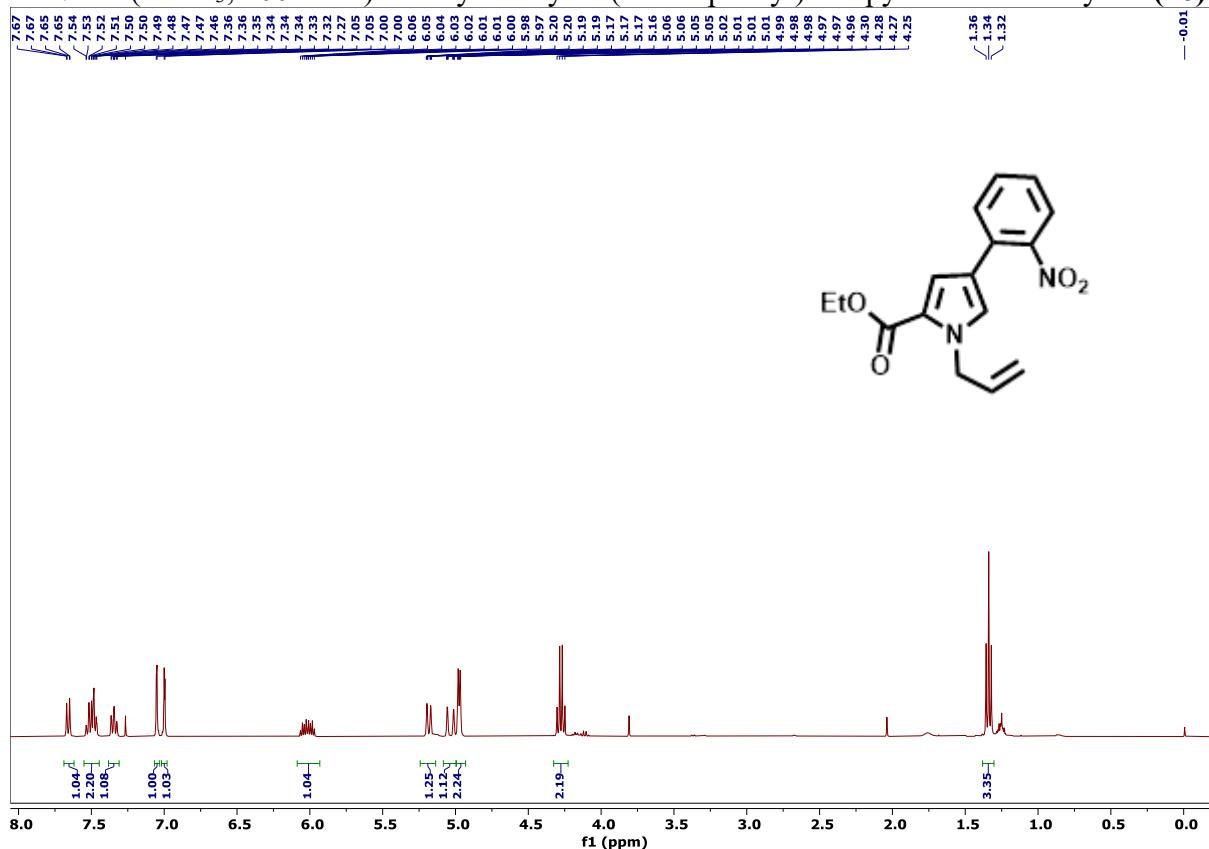
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of (S)-3-(2-nitrophenyl)-1-(1-phenylethyl)-1H-pyrrole (**3m**)**



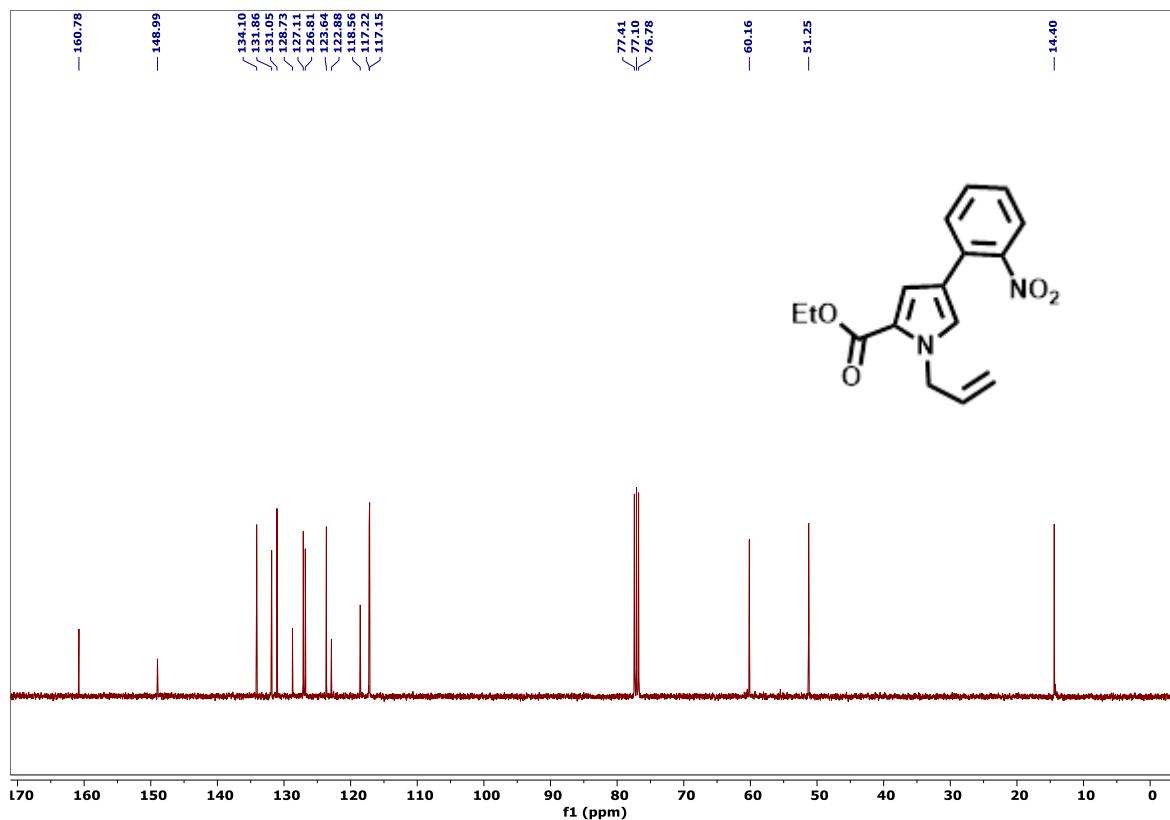
**<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of (S)-3-(2-nitrophenyl)-1-(1-phenylethyl)-1H-pyrrole (**3m**)**



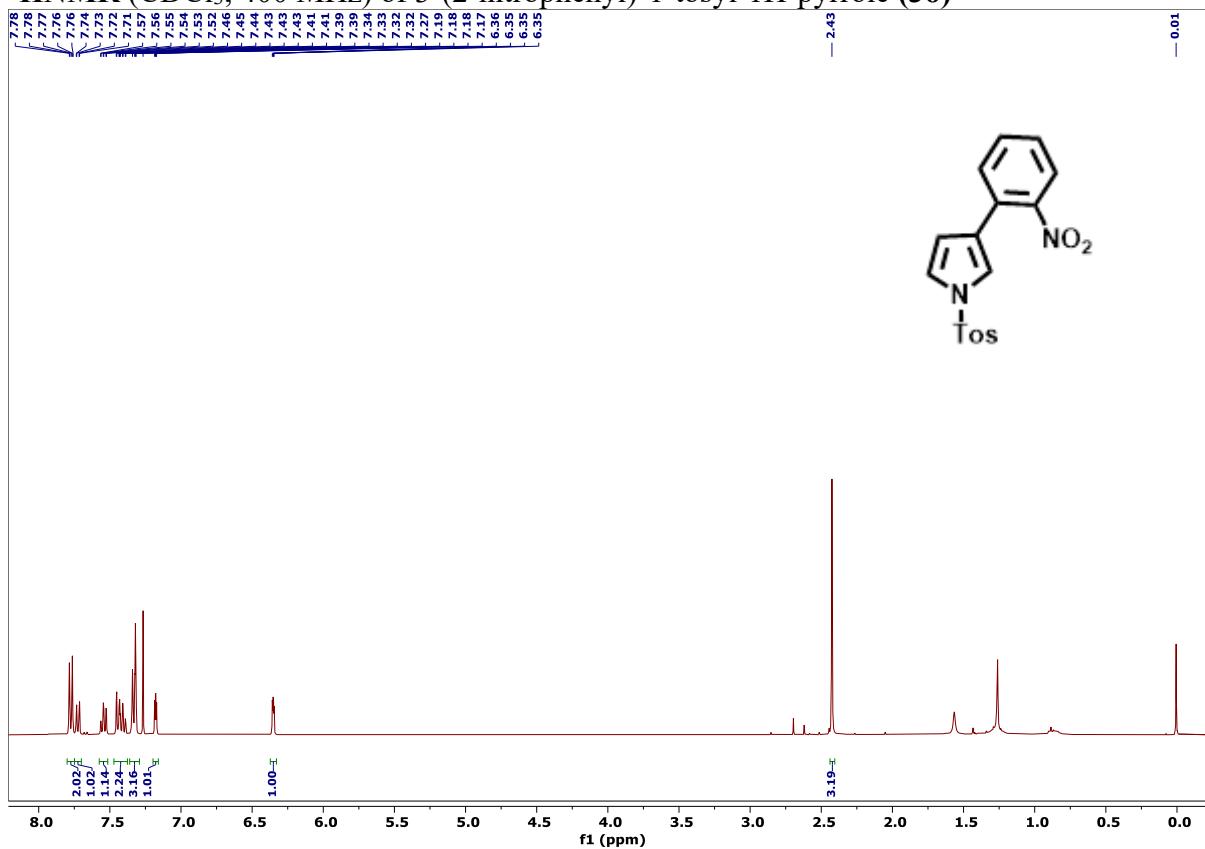
<sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz) of ethyl 1-allyl-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (**10**)



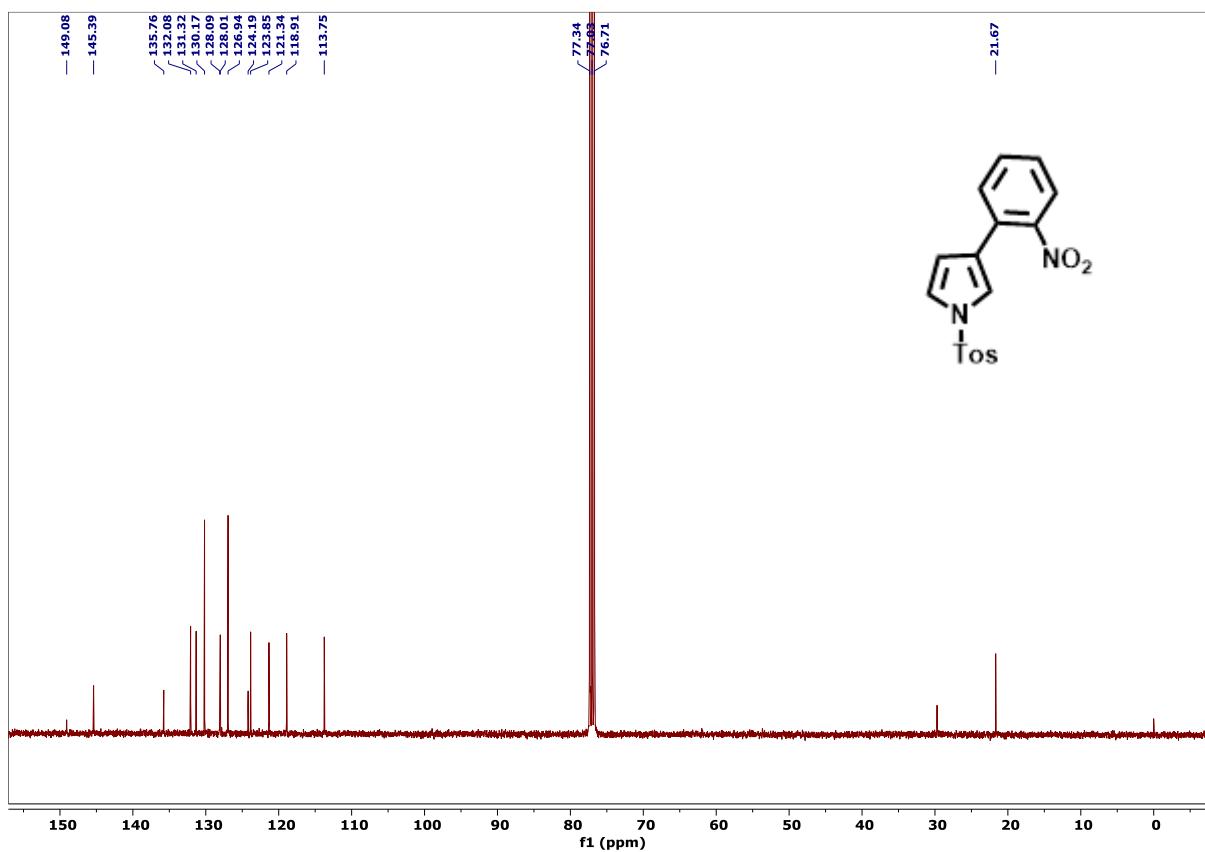
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of ethyl 1-allyl-4-(2-nitrophenyl)-1H-pyrrole-2-carboxylate (**10**)



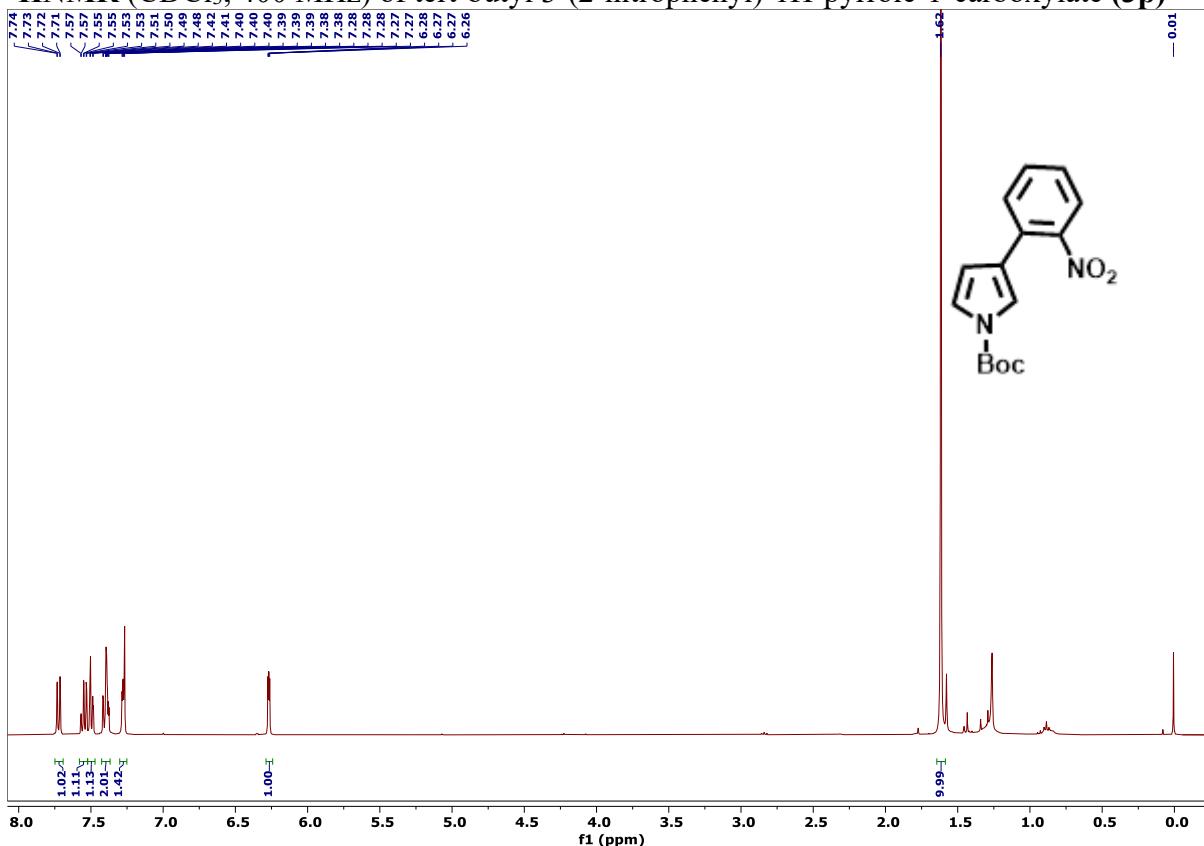
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of 3-(2-nitrophenyl)-1-tosyl-1H-pyrrole (**3o**)**



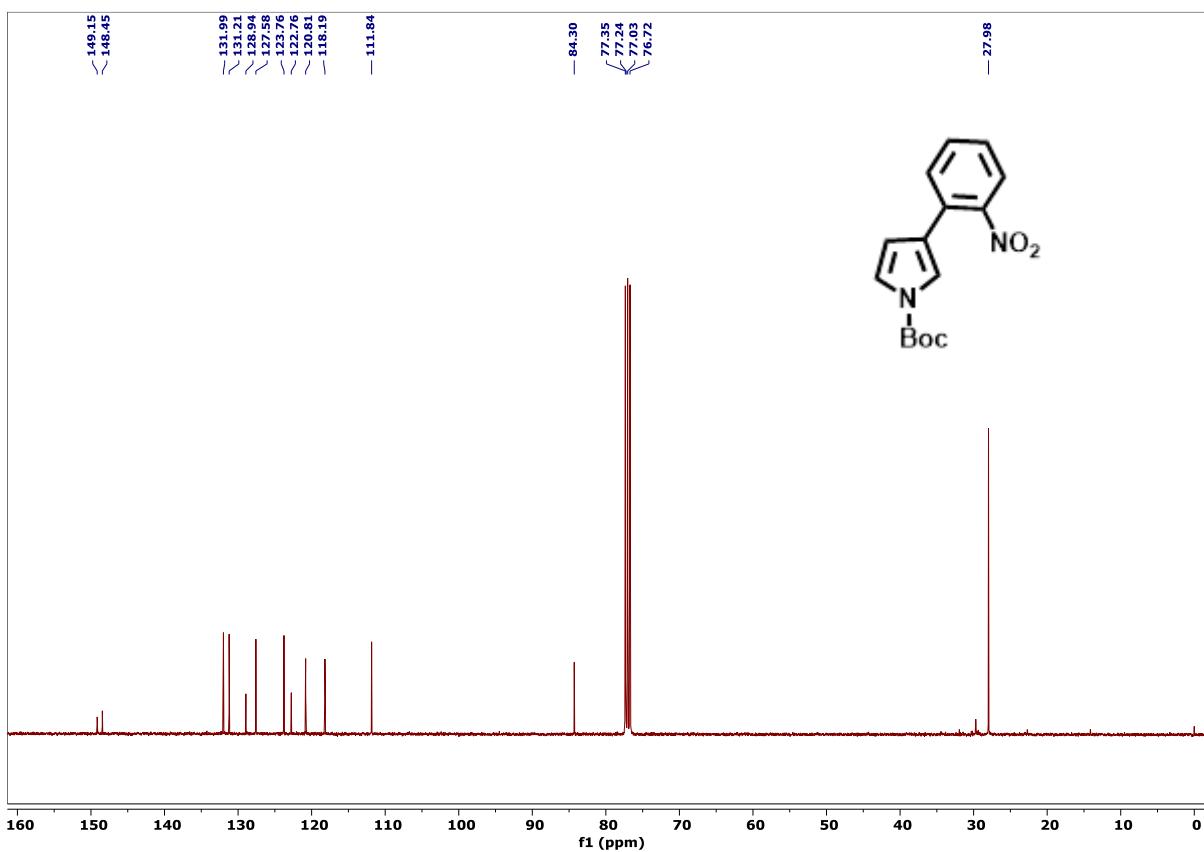
**<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of 3-(2-nitrophenyl)-1-tosyl-1H-pyrrole (**3o**)**



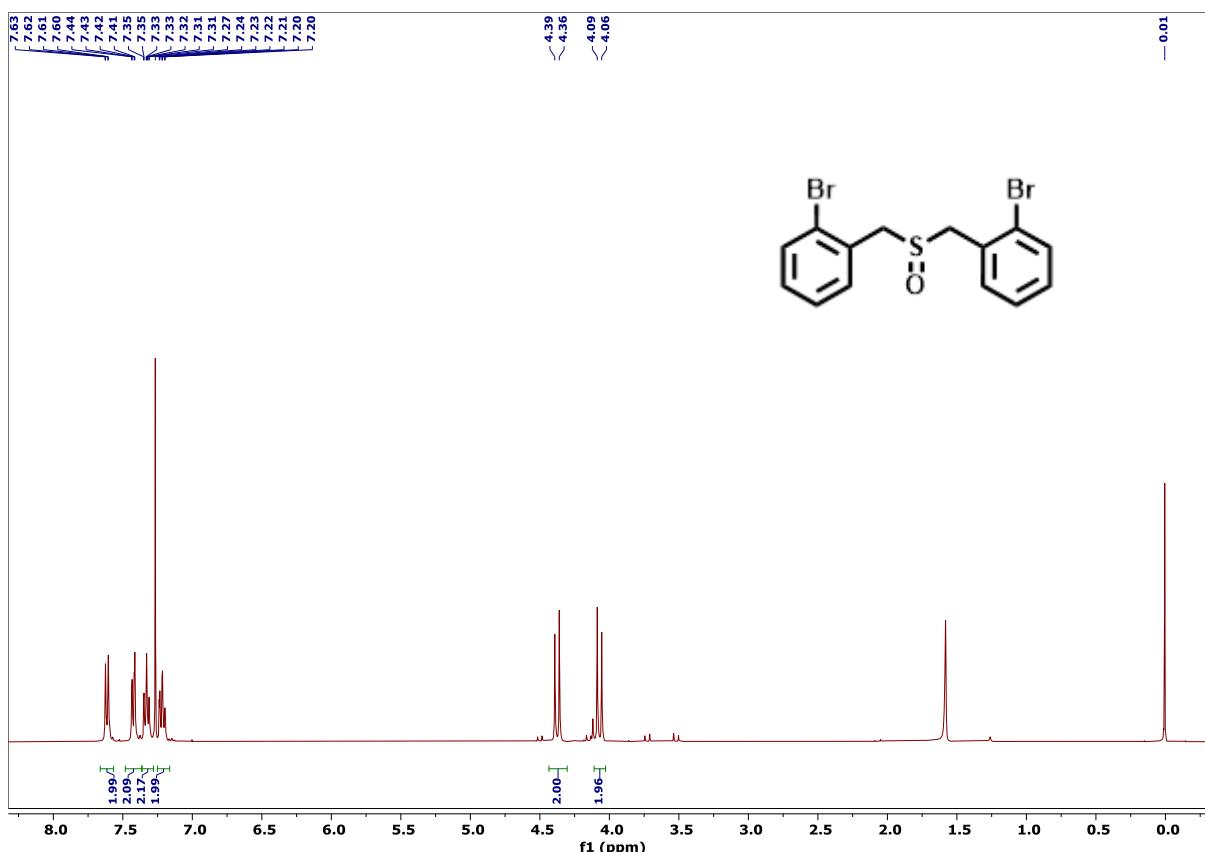
**$^1\text{H}$ NMR (CDCl<sub>3</sub>, 400 MHz) of tert-butyl 3-(2-nitrophenyl)-1H-pyrrole-1-carboxylate (**3p**)**



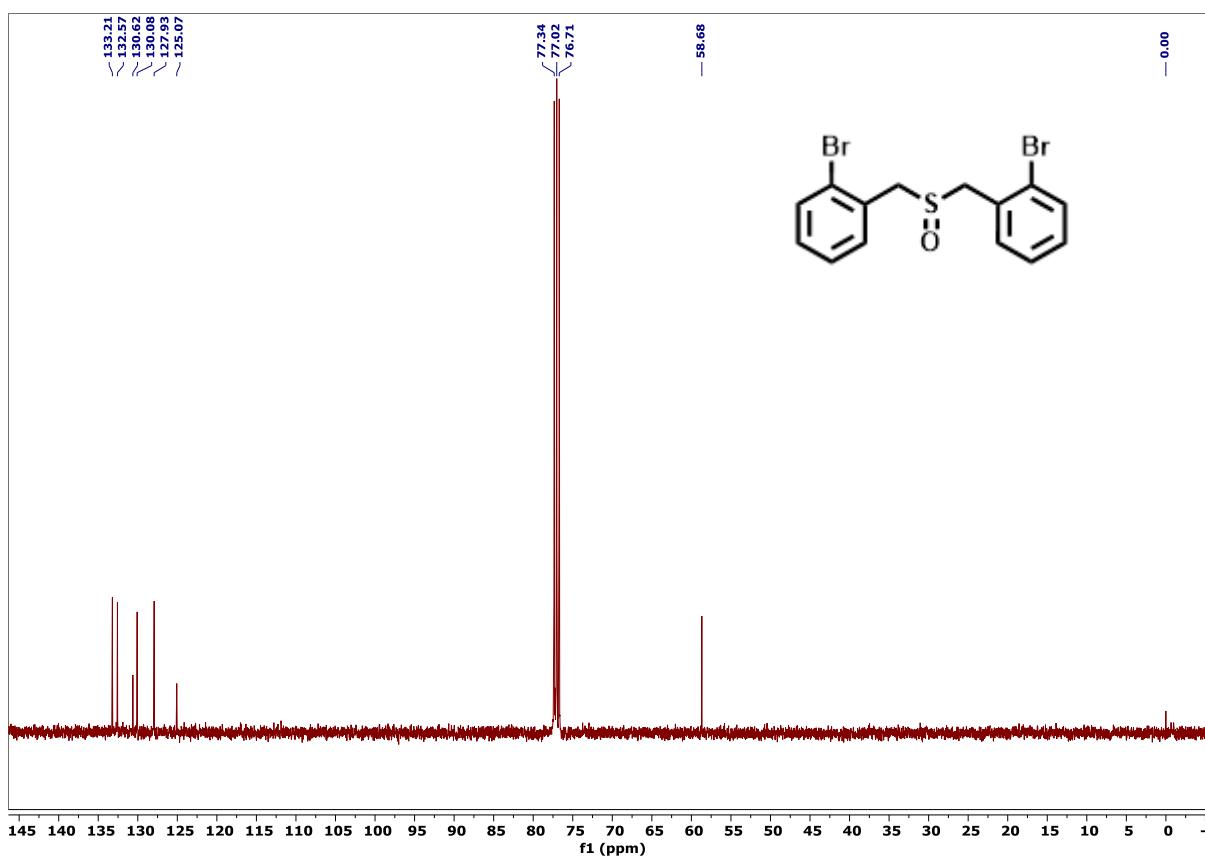
**$^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 100 MHz) of tert-butyl 3-(2-nitrophenyl)-1H-pyrrole-1-carboxylate (**3p**)**



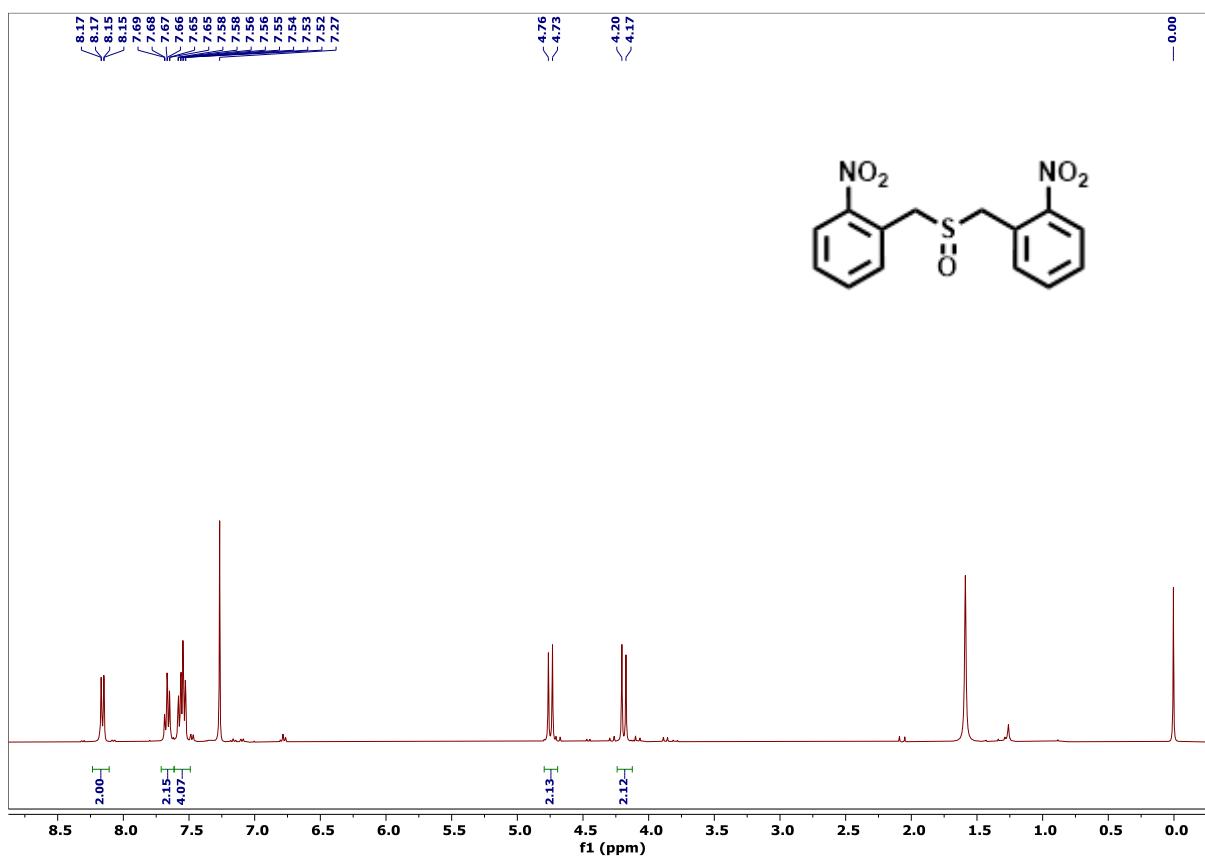
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 2,2'-(sulfinylbis(methylene))bis(bromobenzene) (**5c**)



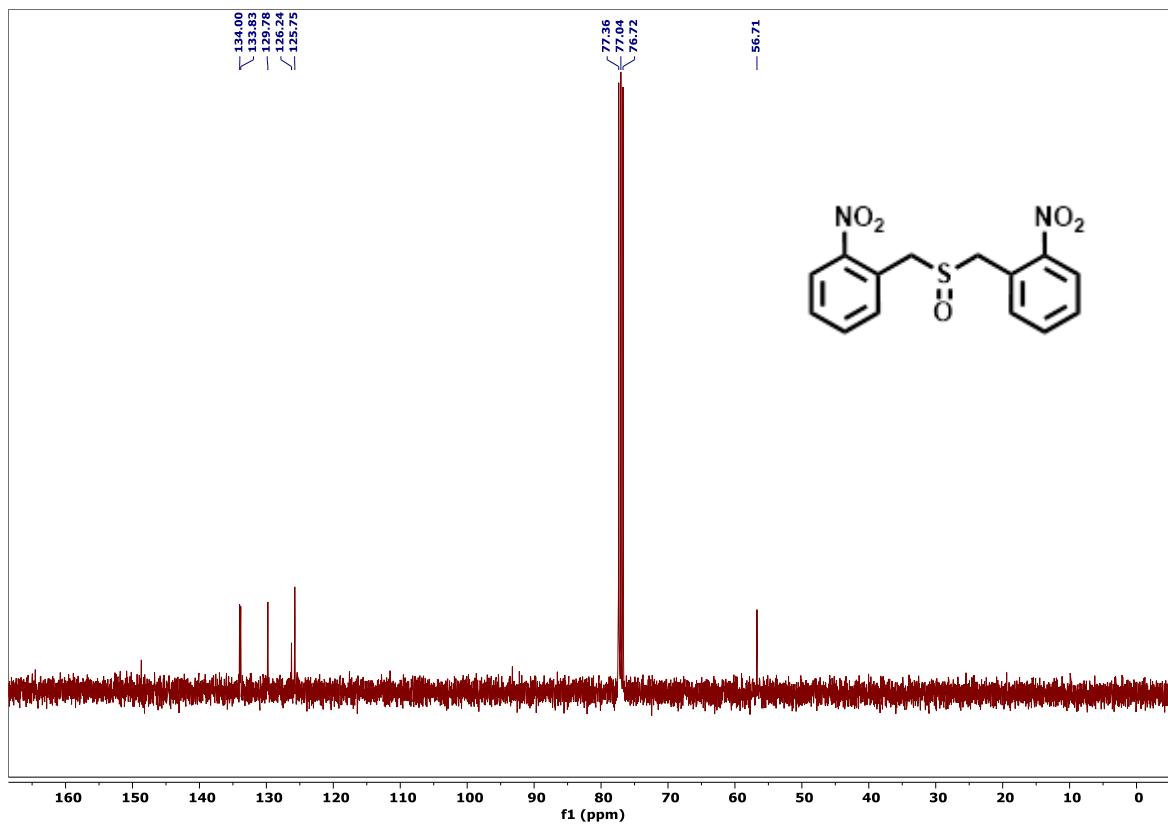
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 2,2'-(sulfinylbis(methylene))bis(bromobenzene) (**5c**)



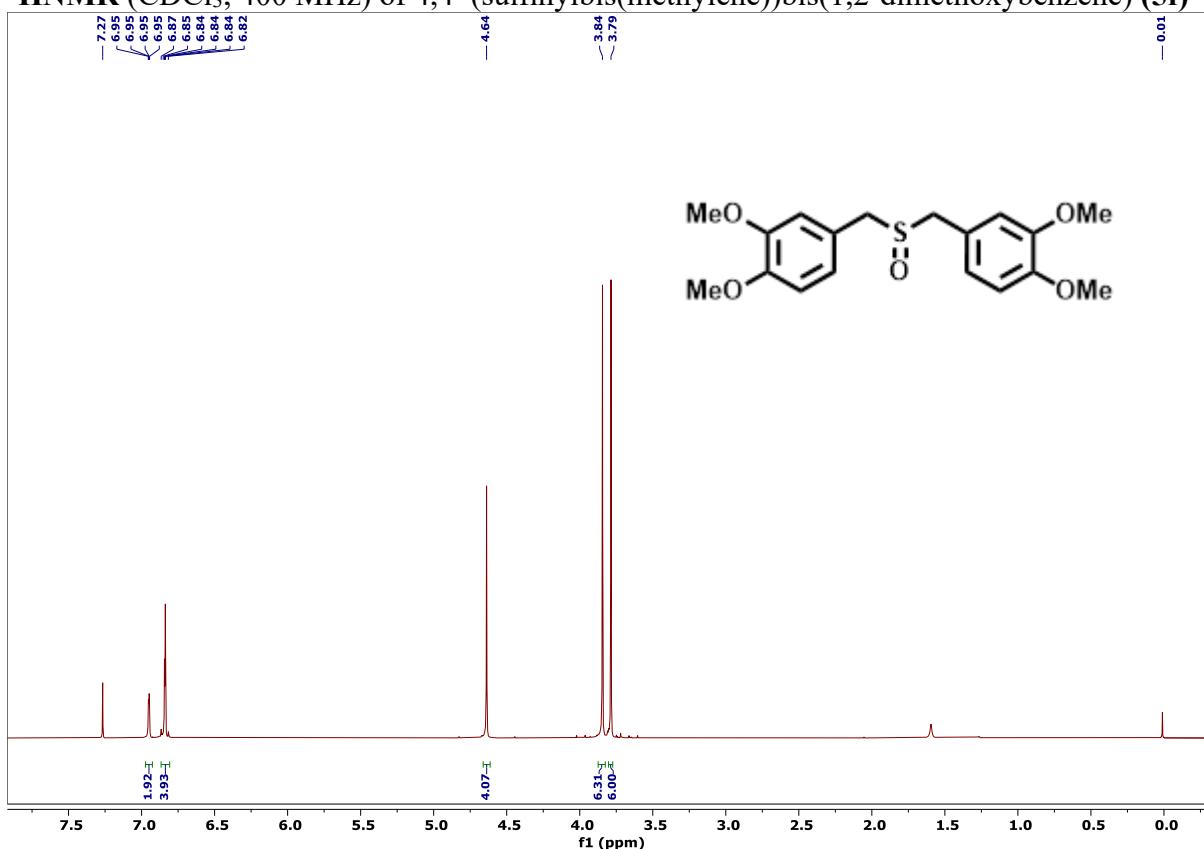
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 2,2'-(sulfinylbis(methylene))bis(nitrobenzene) (**5d**)



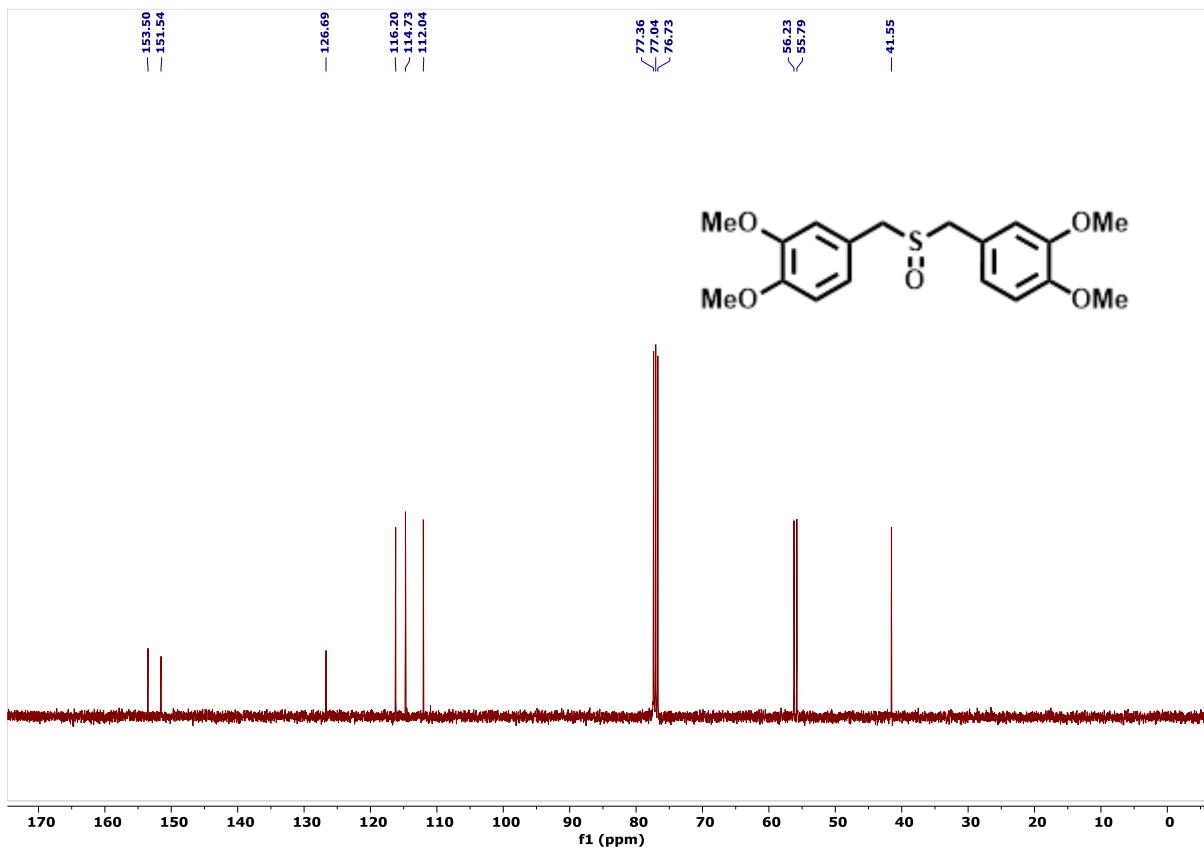
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 2,2'-(sulfinylbis(methylene))bis(nitrobenzene) (**5d**)



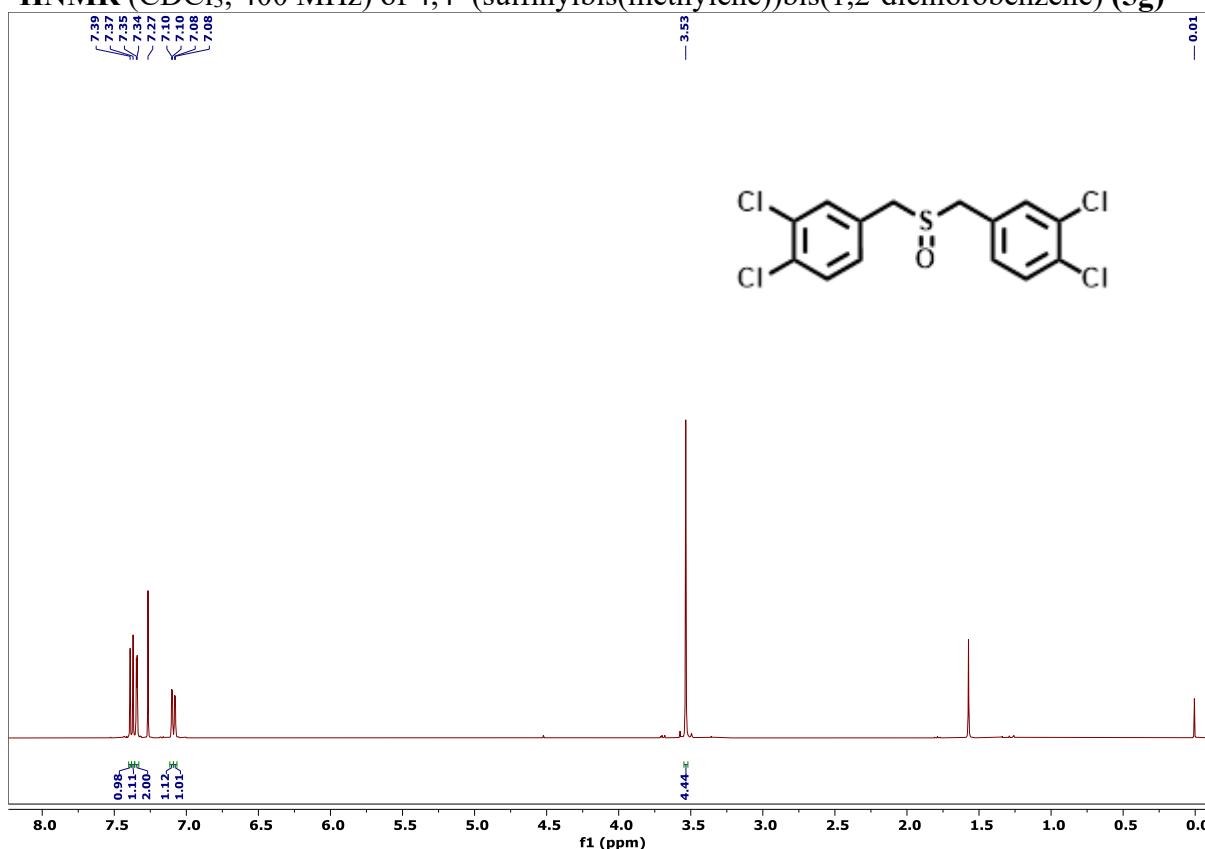
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 4,4'-(sulfinylbis(methylene))bis(1,2-dimethoxybenzene) (**5f**)



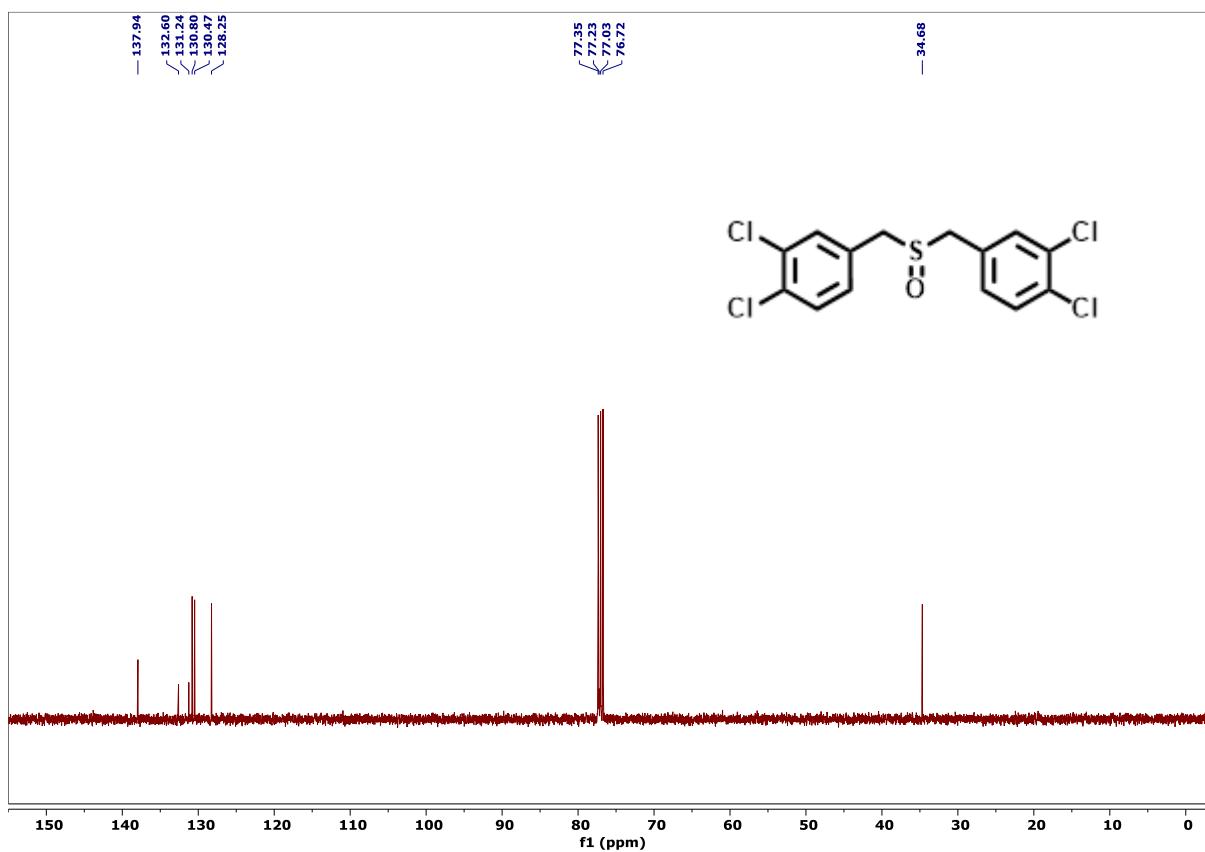
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 4,4'-(sulfinylbis(methylene))bis(1,2-dimethoxybenzene) (**5f**)



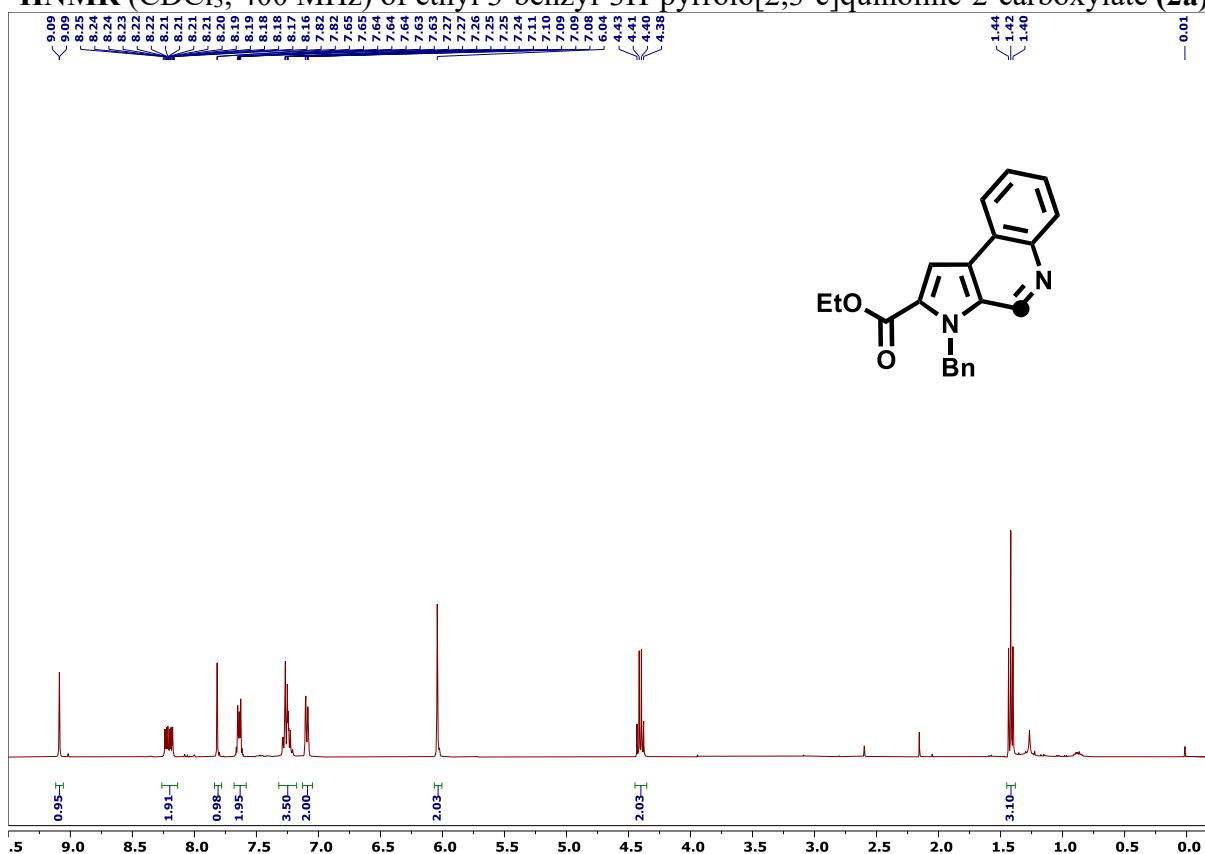
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 4,4'-(sulfinylbis(methylene))bis(1,2-dichlorobenzene) (**5g**)



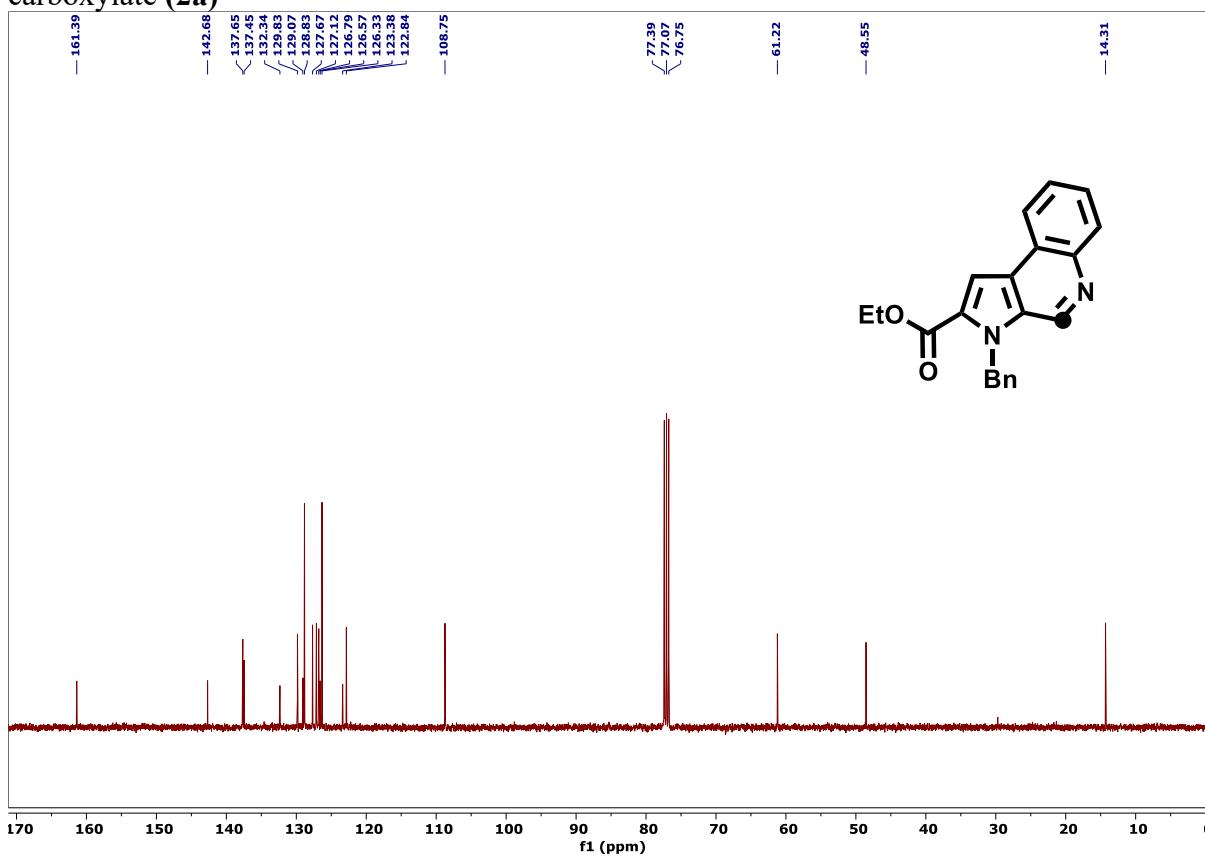
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 4,4'-(sulfinylbis(methylene))bis(1,2-dichlorobenzene) (**5g**)



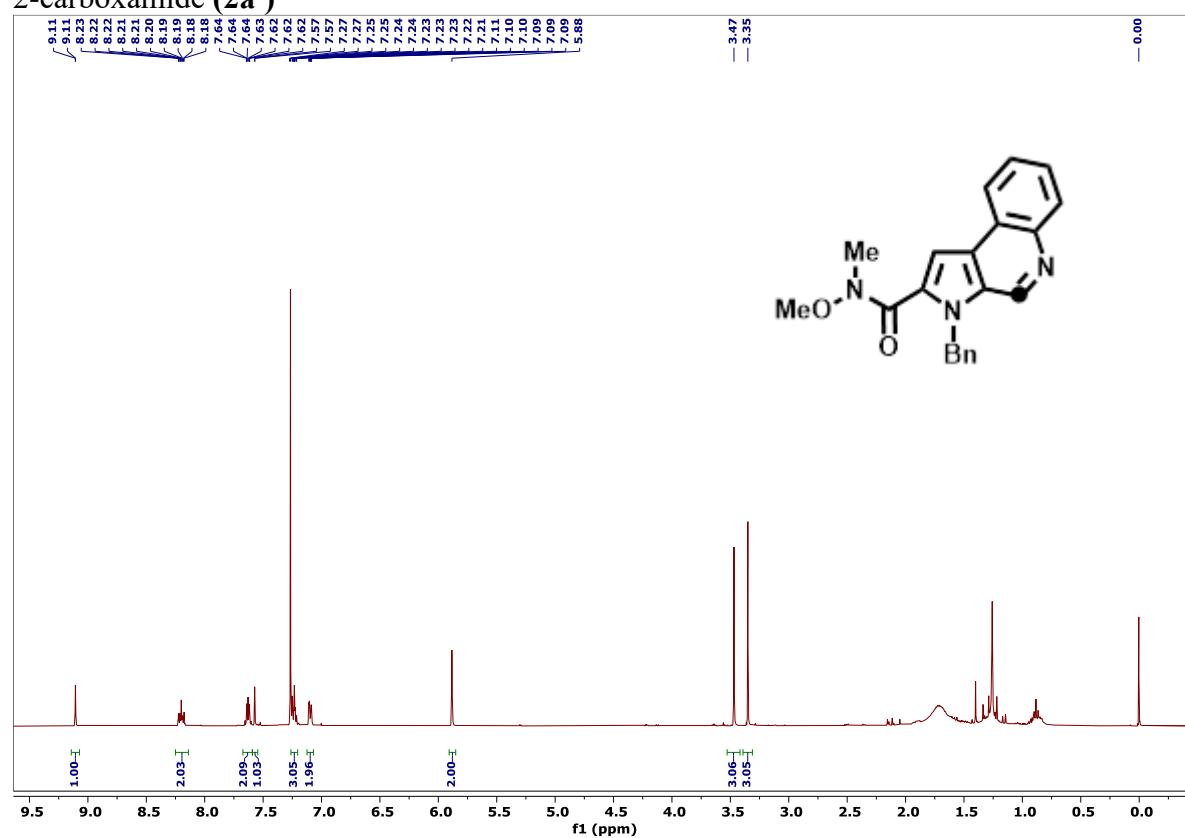
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of ethyl 3-benzyl-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2a**)**



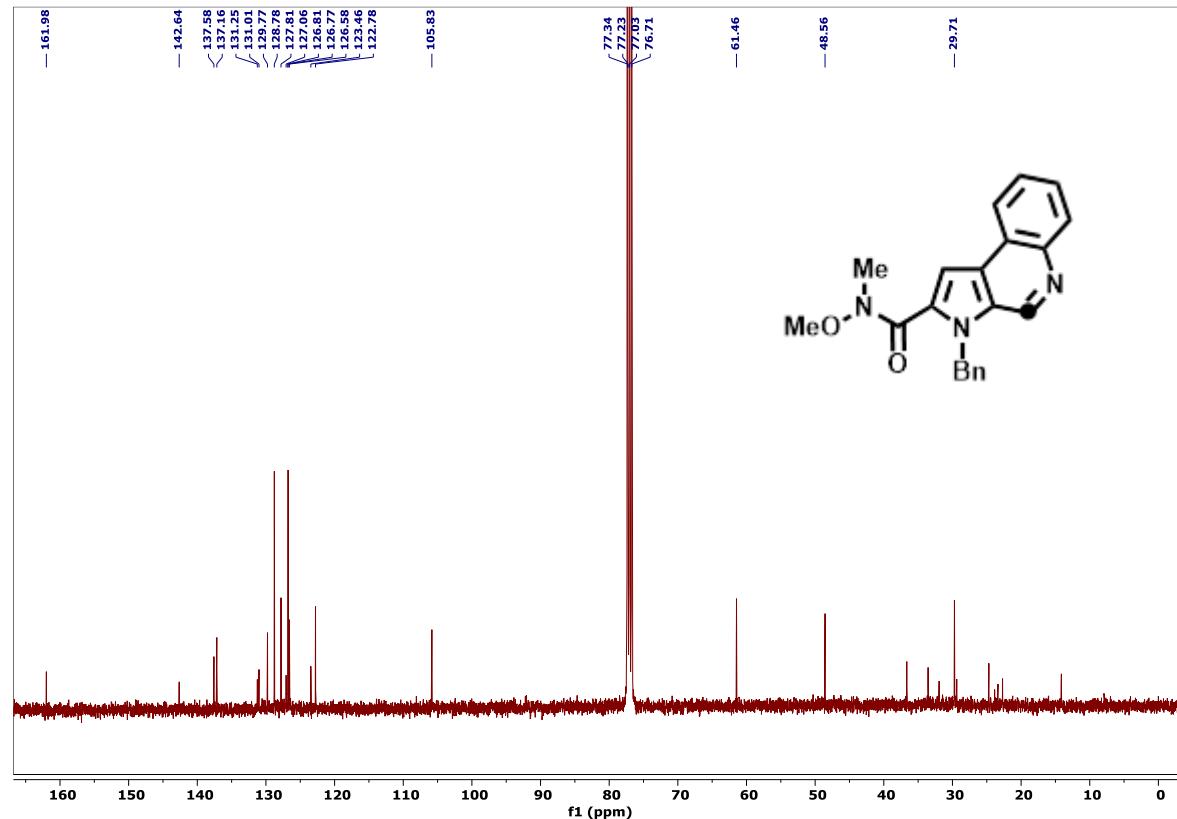
**<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of ethyl 3-benzyl-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2a**)**



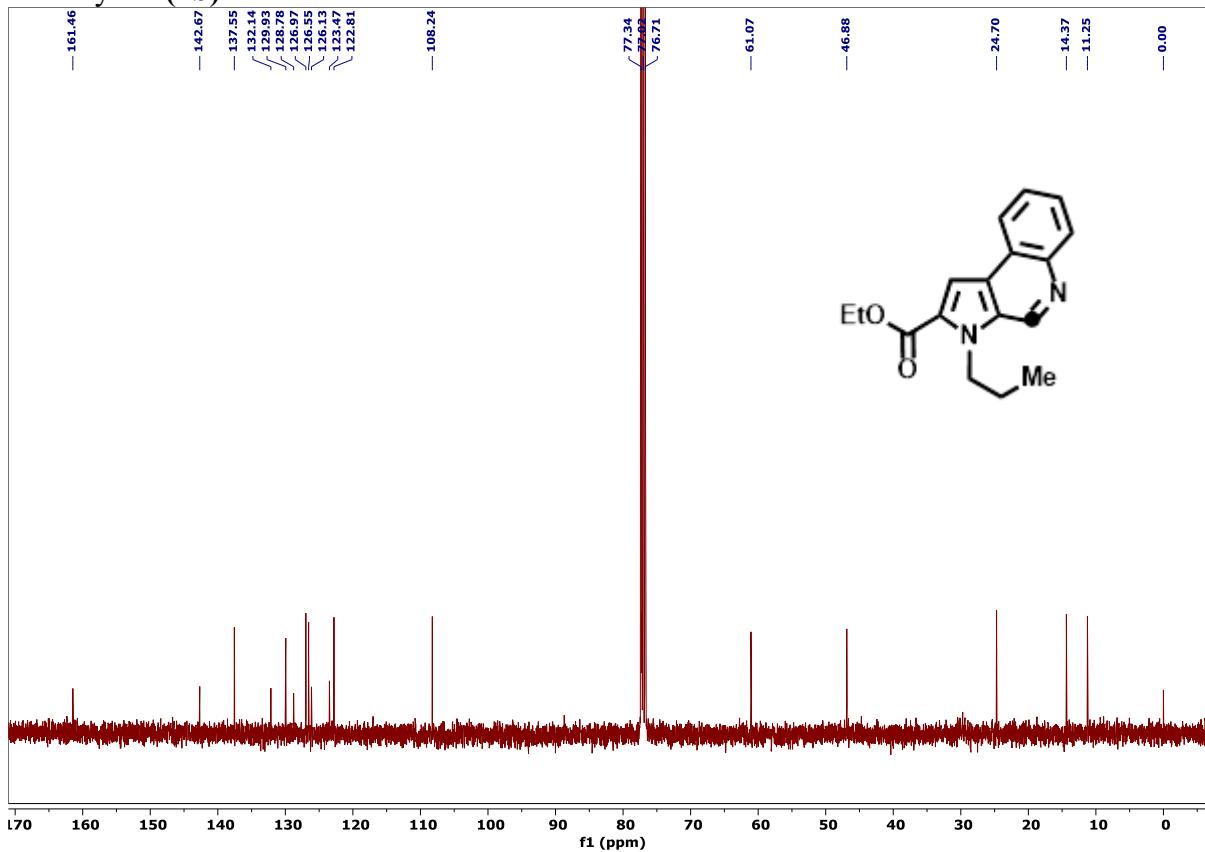
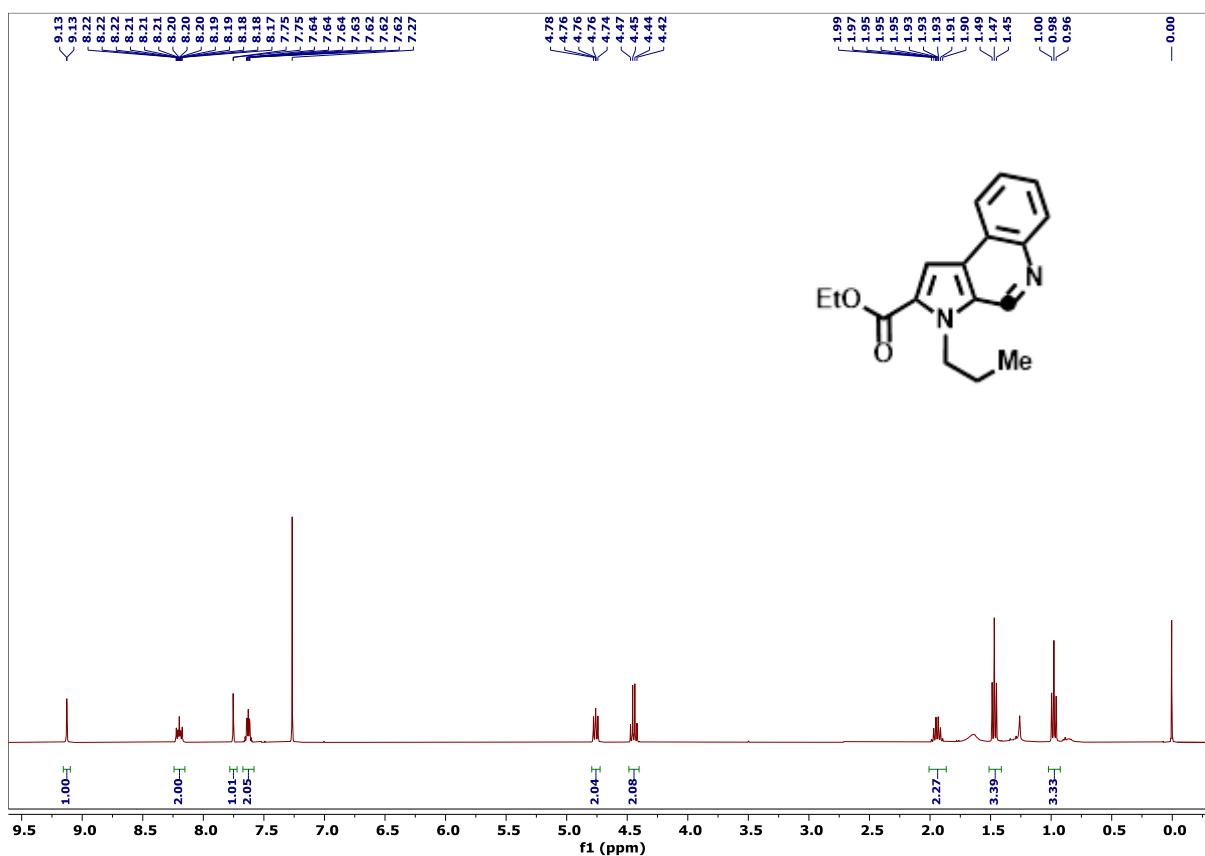
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 3-benzyl-N-methoxy-N-methyl-3H-pyrrolo[2,3-c]quinoline-2-carboxamide (**2a'**)



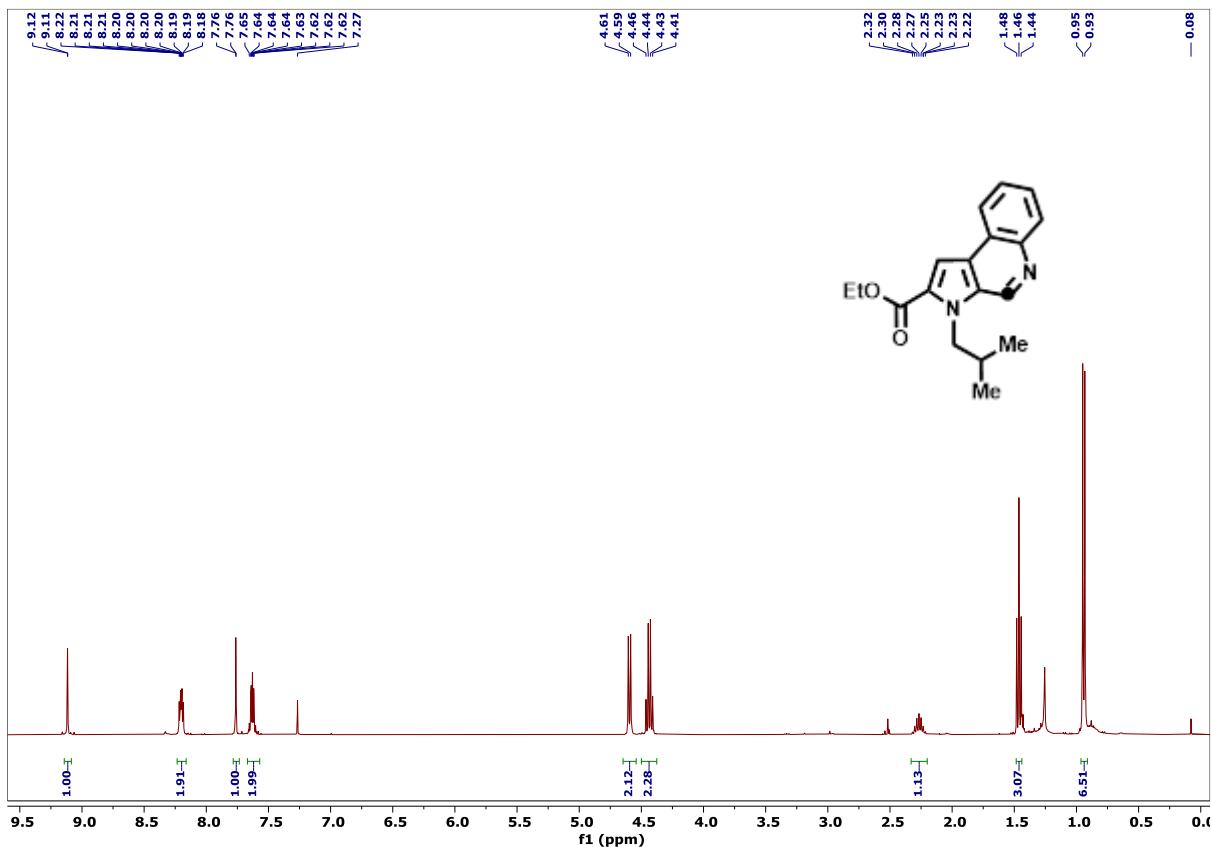
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 3-benzyl-N-methoxy-N-methyl-3H-pyrrolo[2,3-c]quinoline-2-carboxamide (**2a'**)



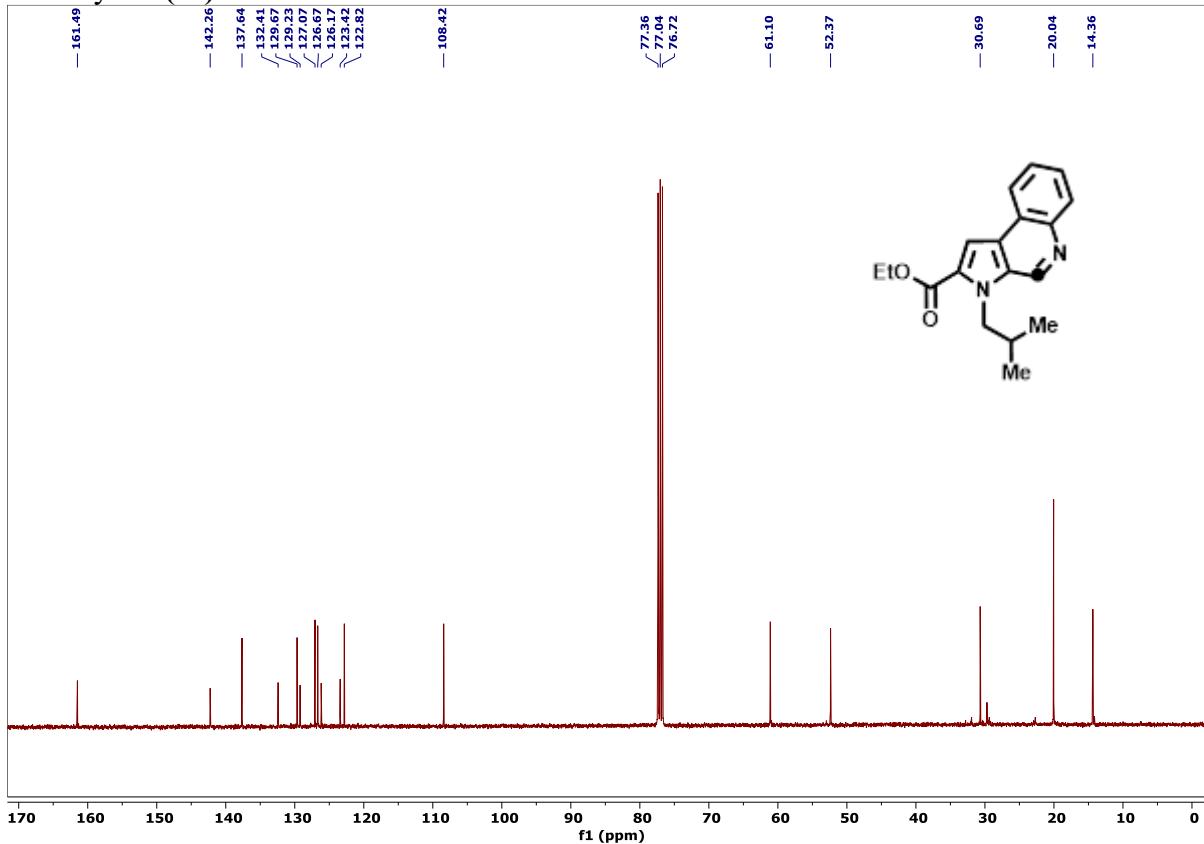
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 3-propyl-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2b**)



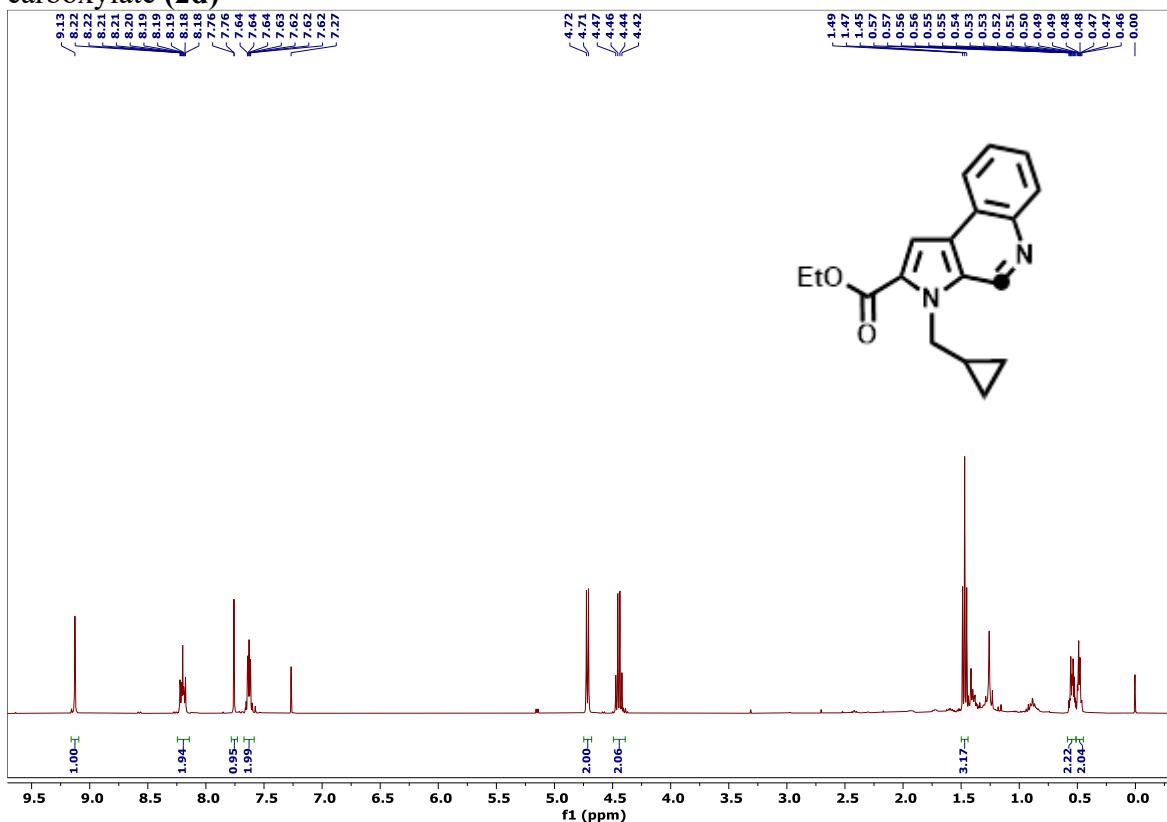
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 3-isobutyl-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (2c)



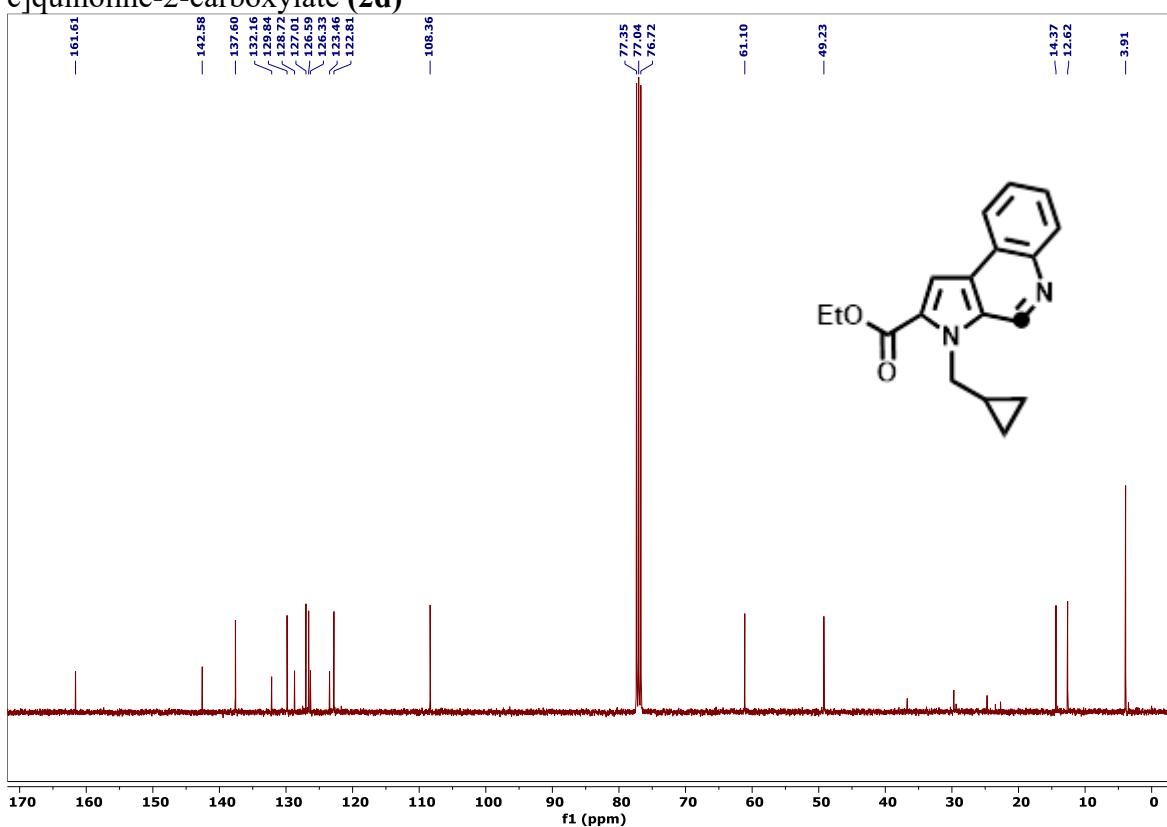
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of ethyl 3-isobutyl-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2c**)



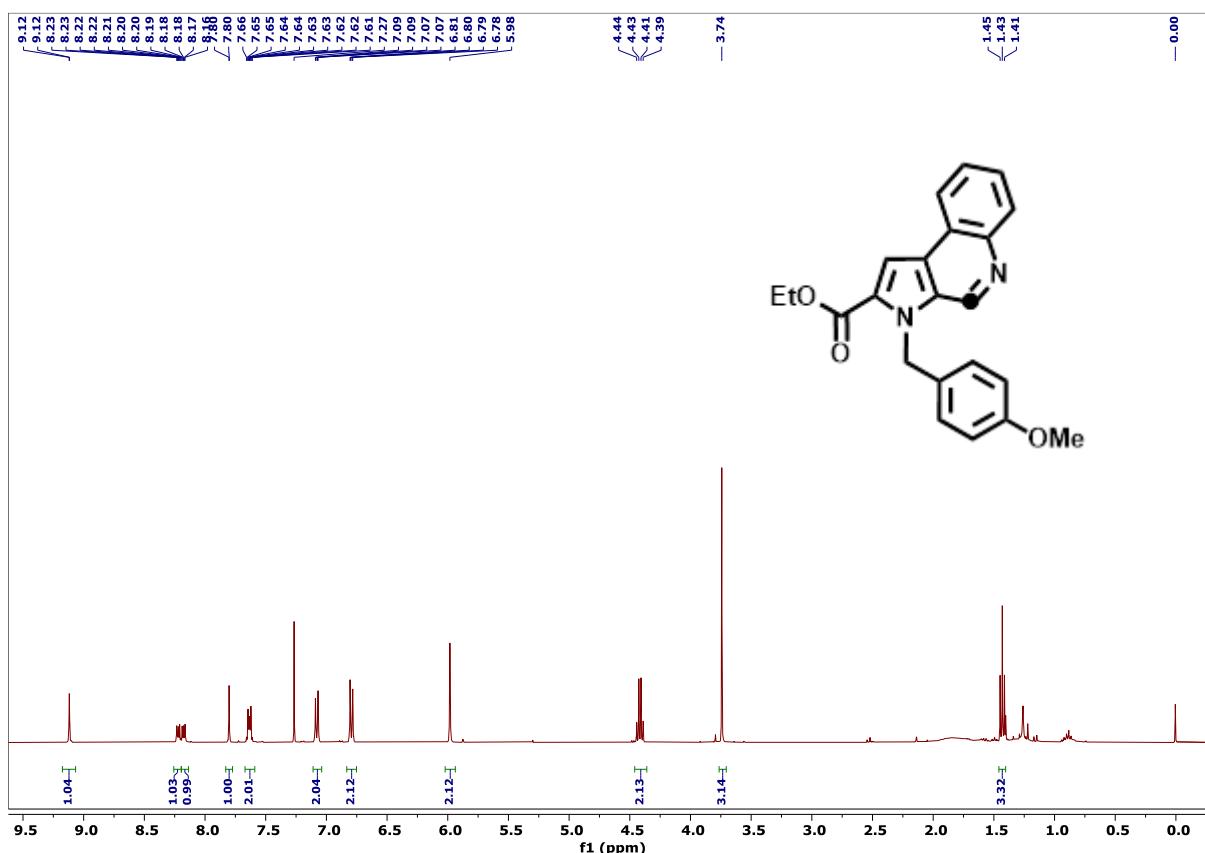
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 3-(cyclopropylmethyl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2d**)



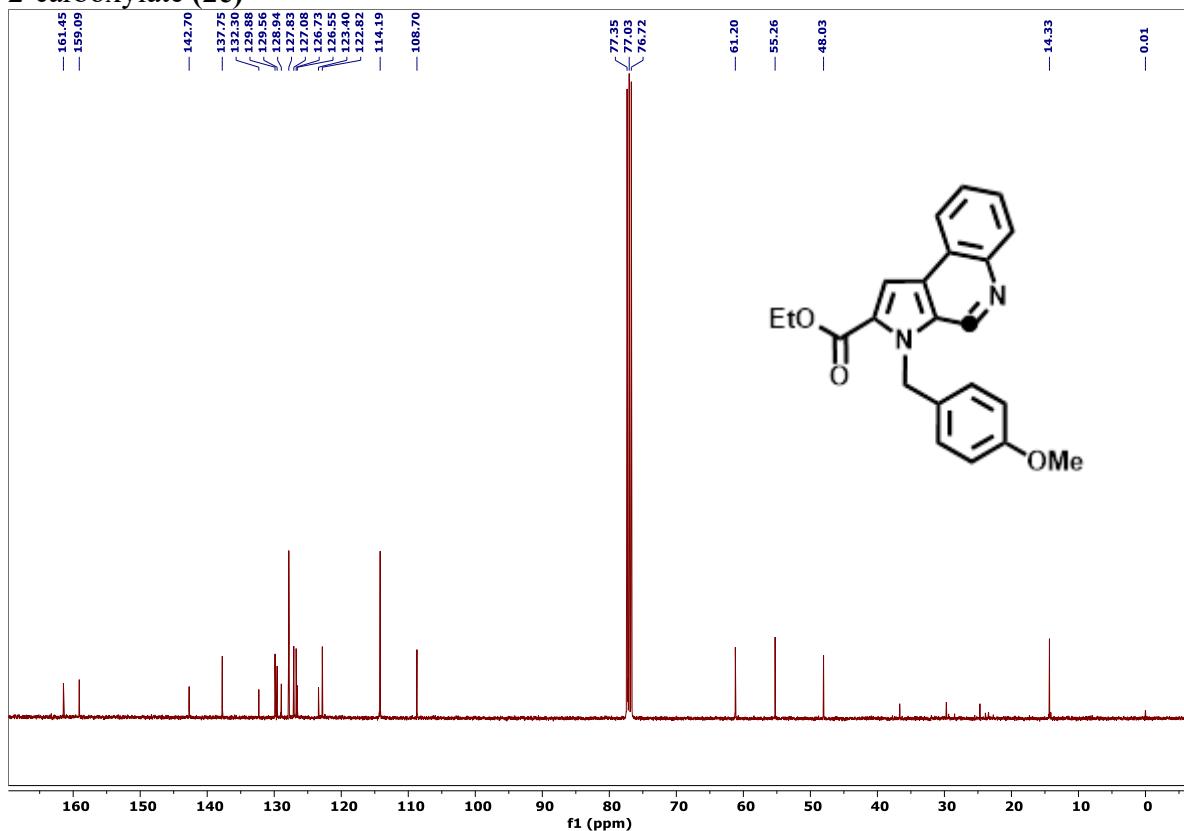
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of ethyl 3-(cyclopropylmethyl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2d**)



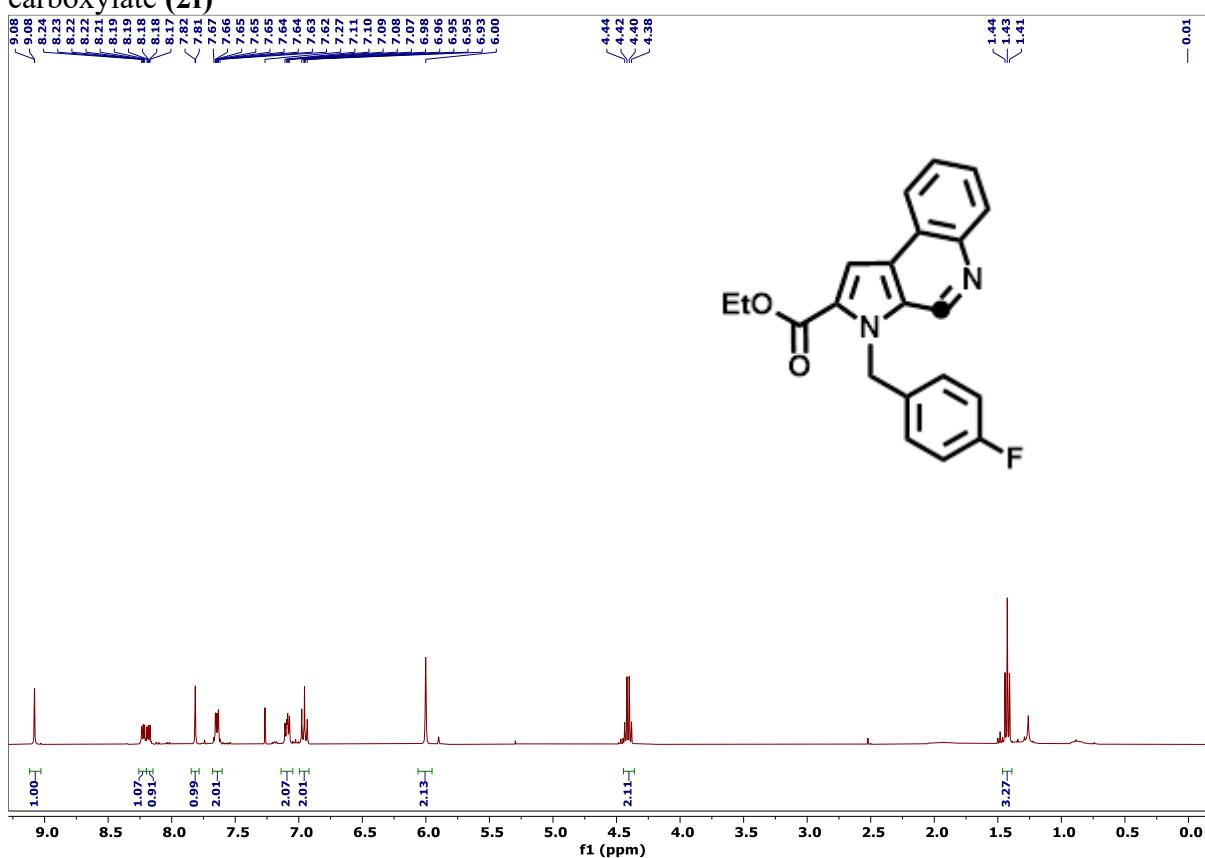
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 3-(4-methoxybenzyl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2e**)



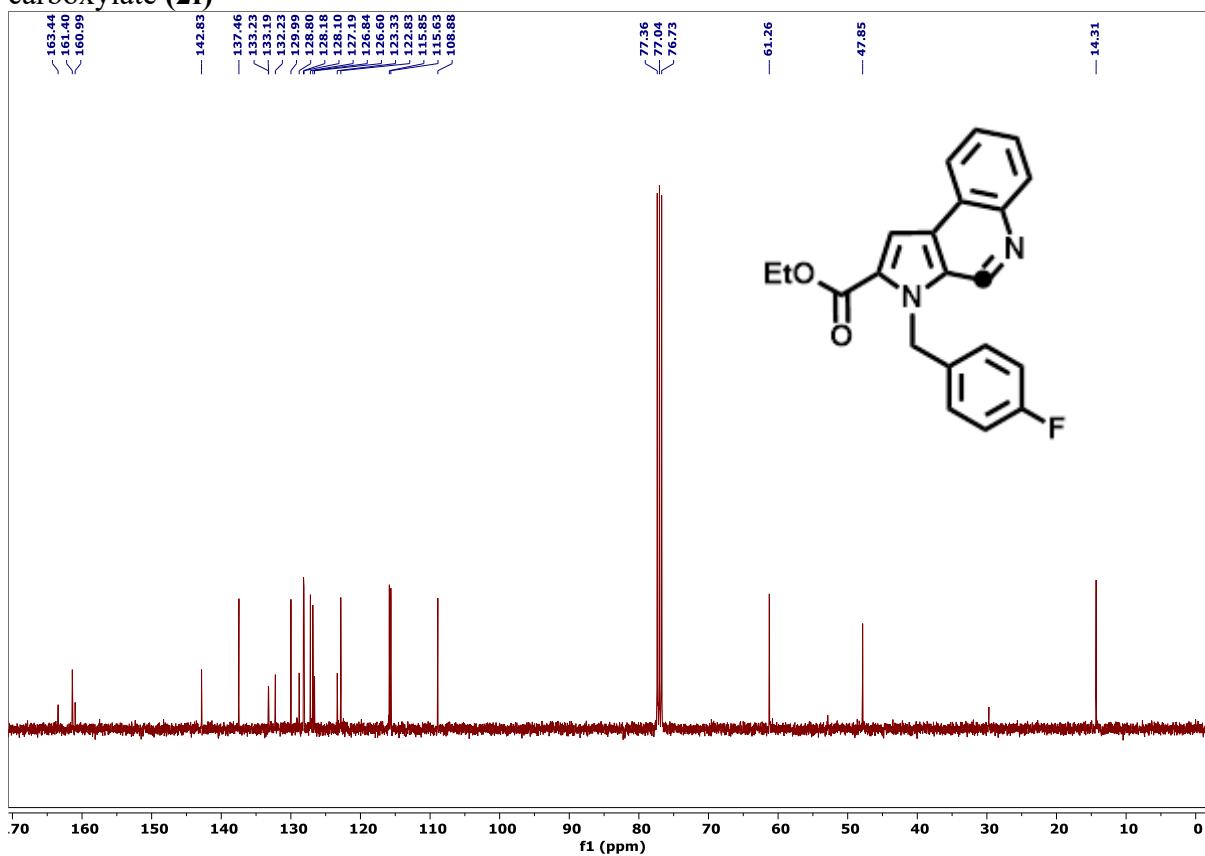
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of ethyl 3-(4-methoxybenzyl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2e**)



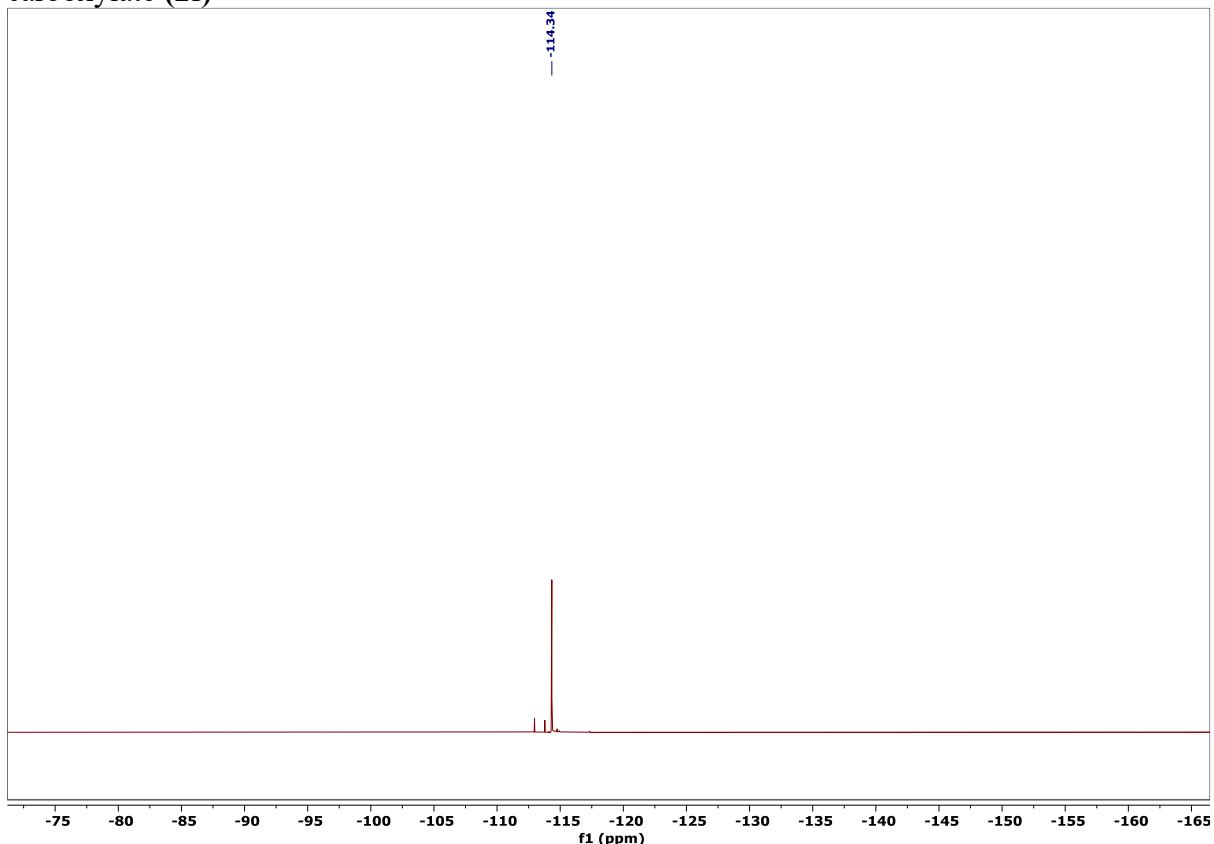
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 3-(4-fluorobenzyl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2f**)



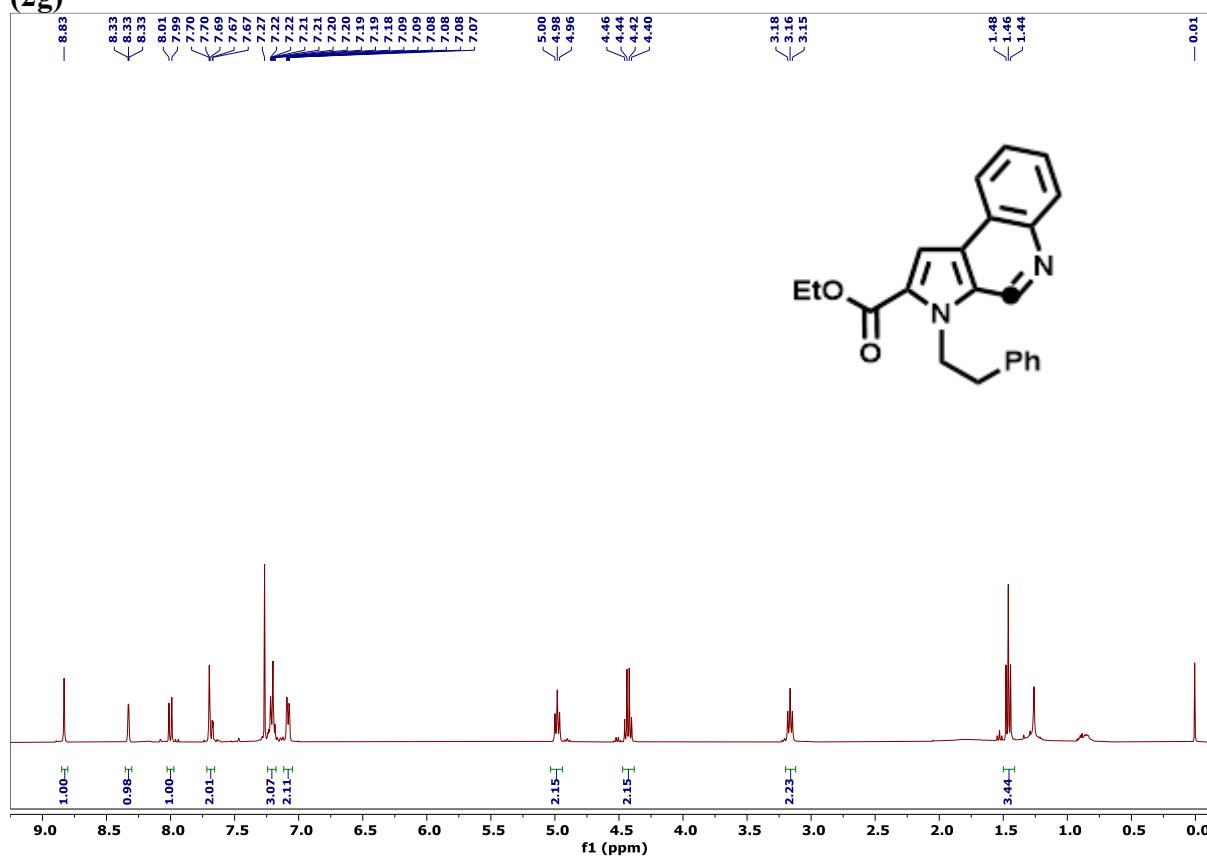
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of ethyl 3-(4-fluorobenzyl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2f**)



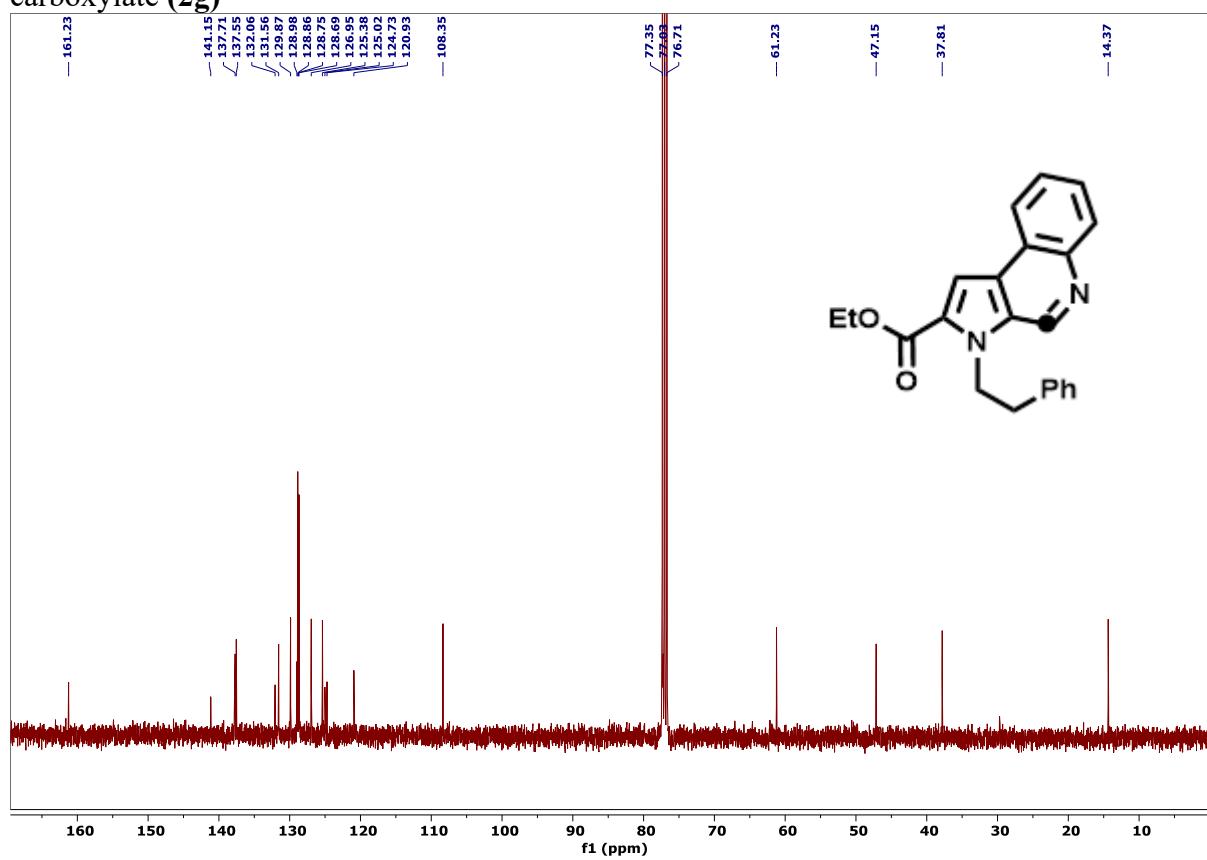
**<sup>19</sup>F NMR** ( $\text{CDCl}_3$ , 376 MHz) of ethyl 3-(4-fluorobenzyl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2f**)



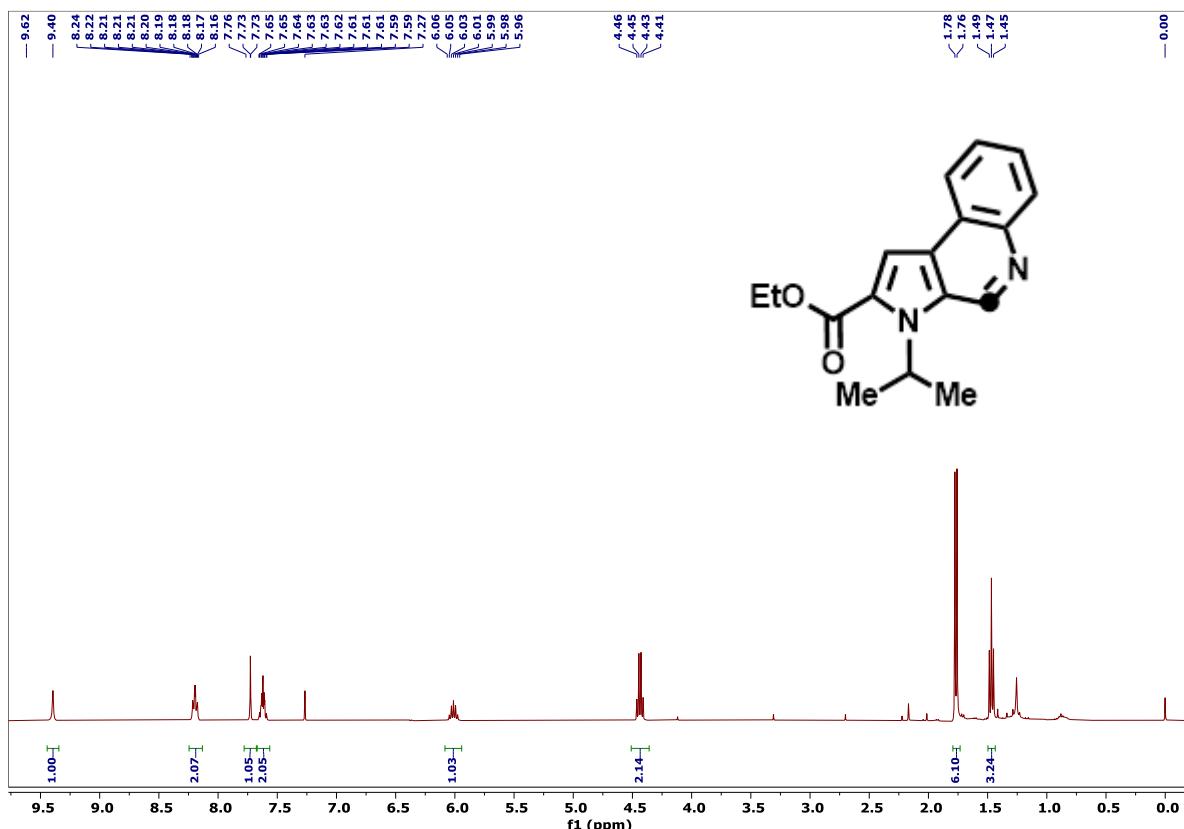
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 3-phenethyl-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2g**)



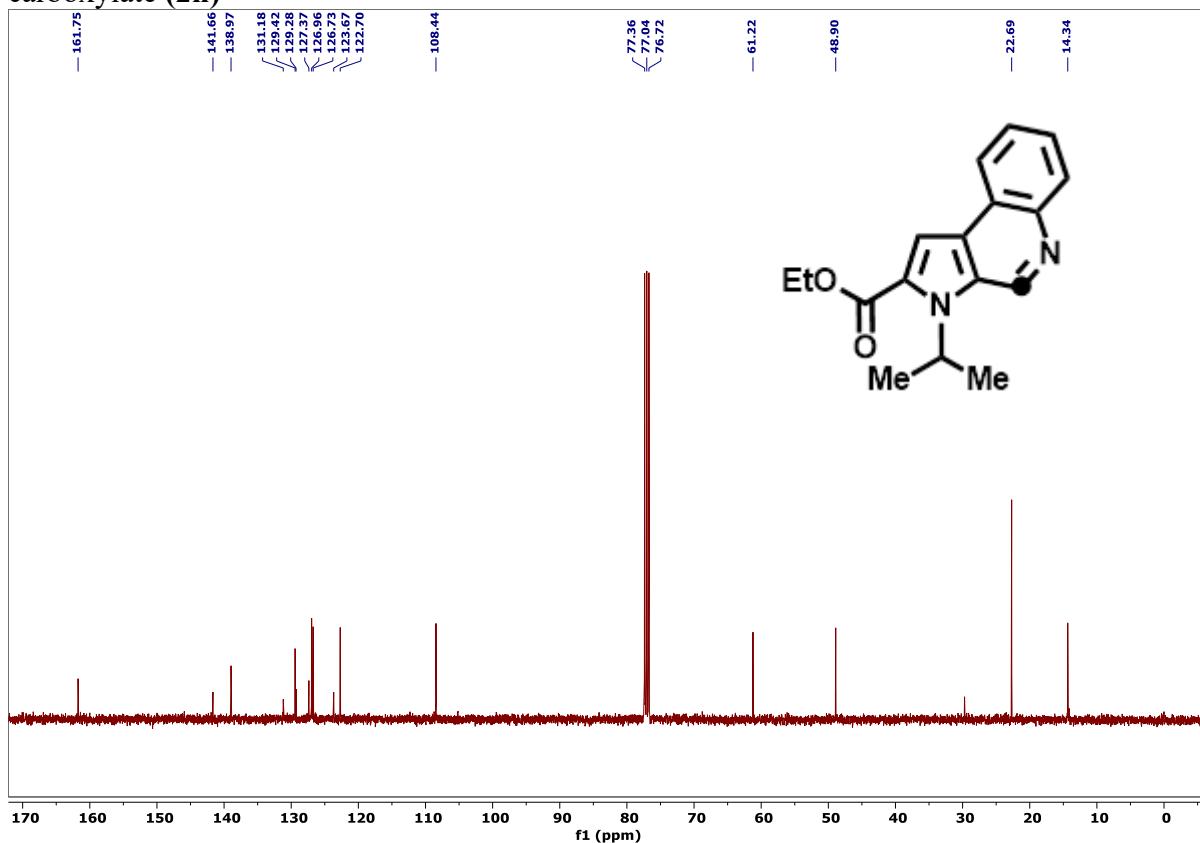
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of ethyl 3-phenethyl-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2g**)



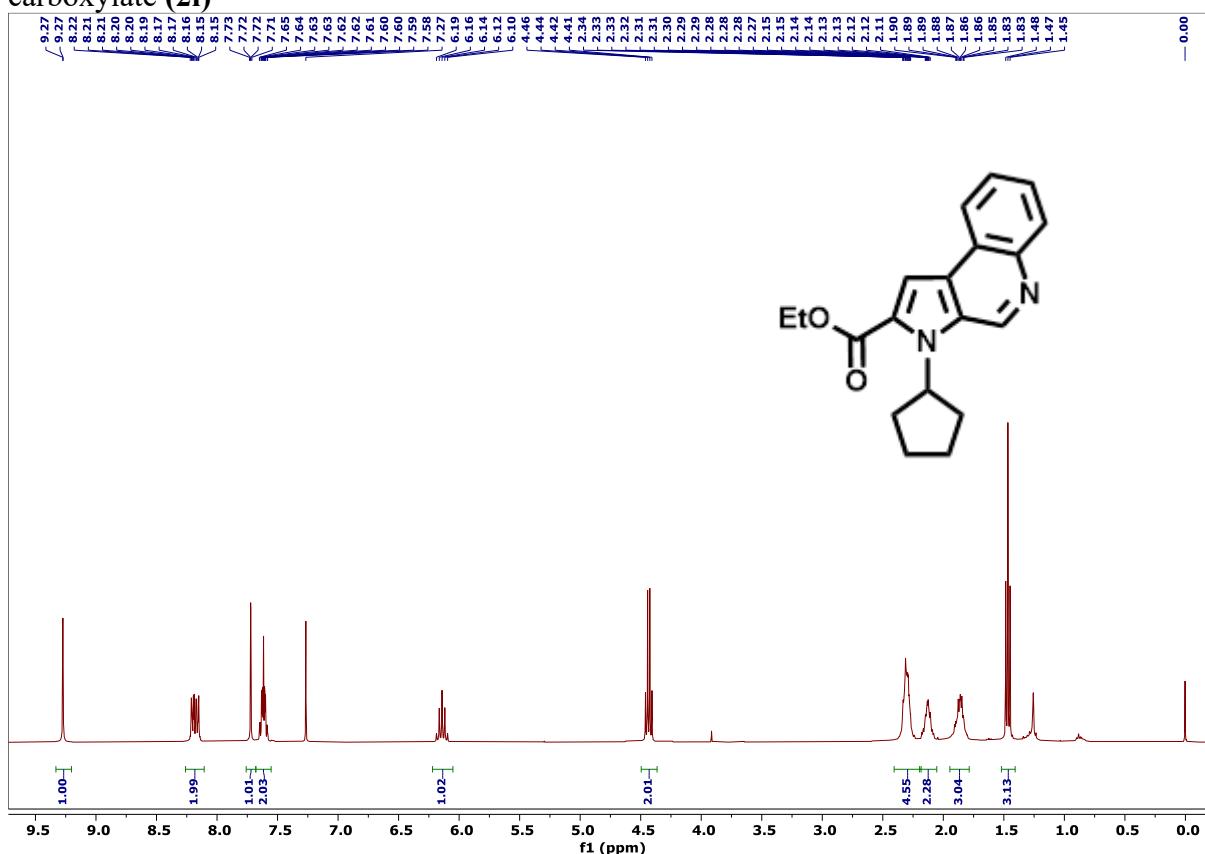
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 3-isopropyl-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2h**)



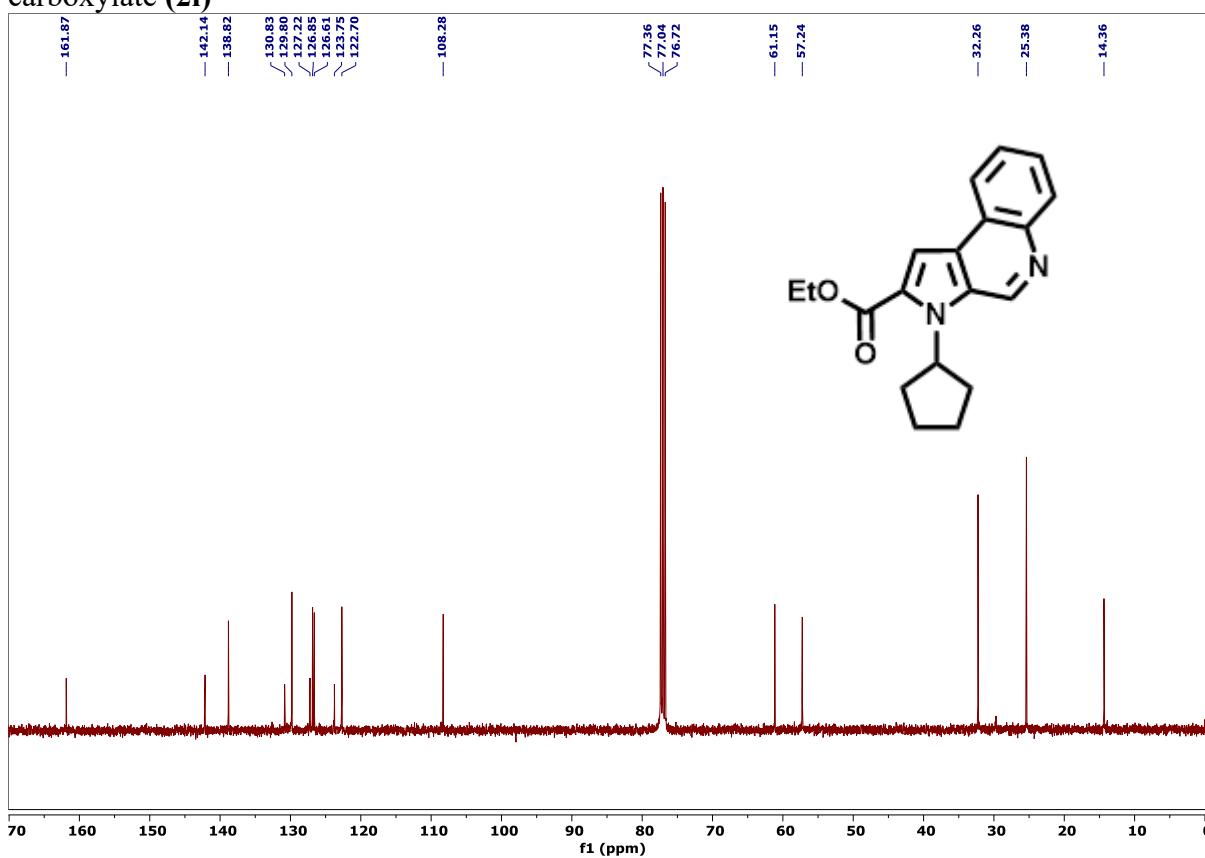
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of ethyl 3-isopropyl-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2h**)



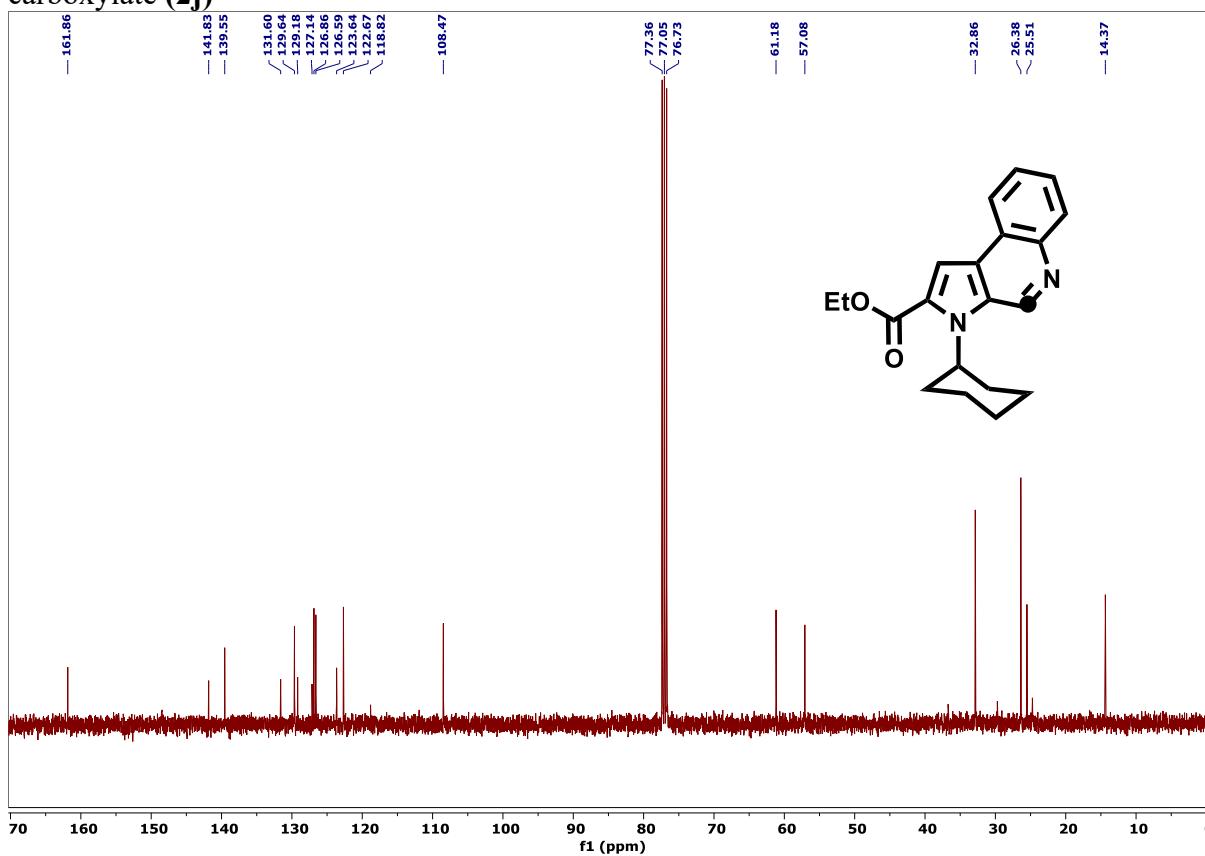
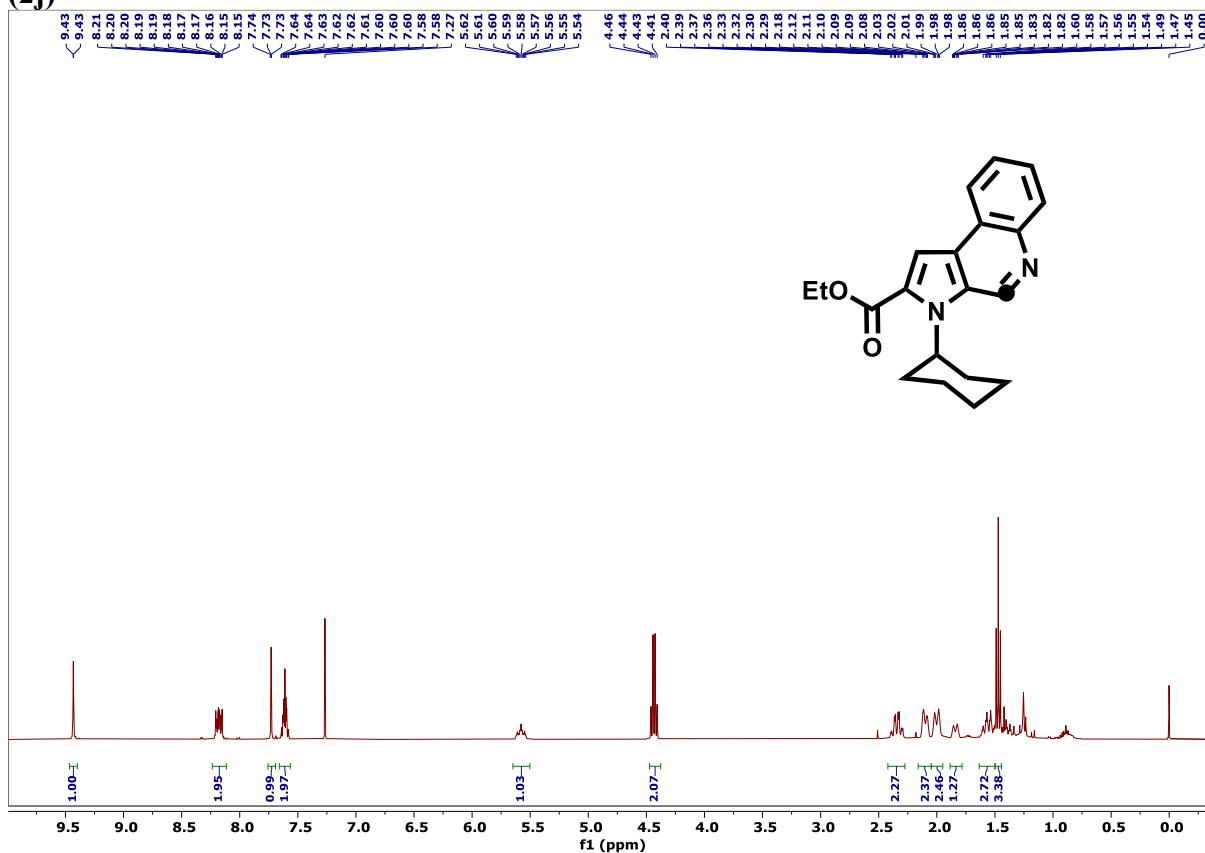
<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz) of ethyl 3-cyclopentyl-3H-pyrrolo[2,3-c]cquinoline-2-carboxylate (**2i**)



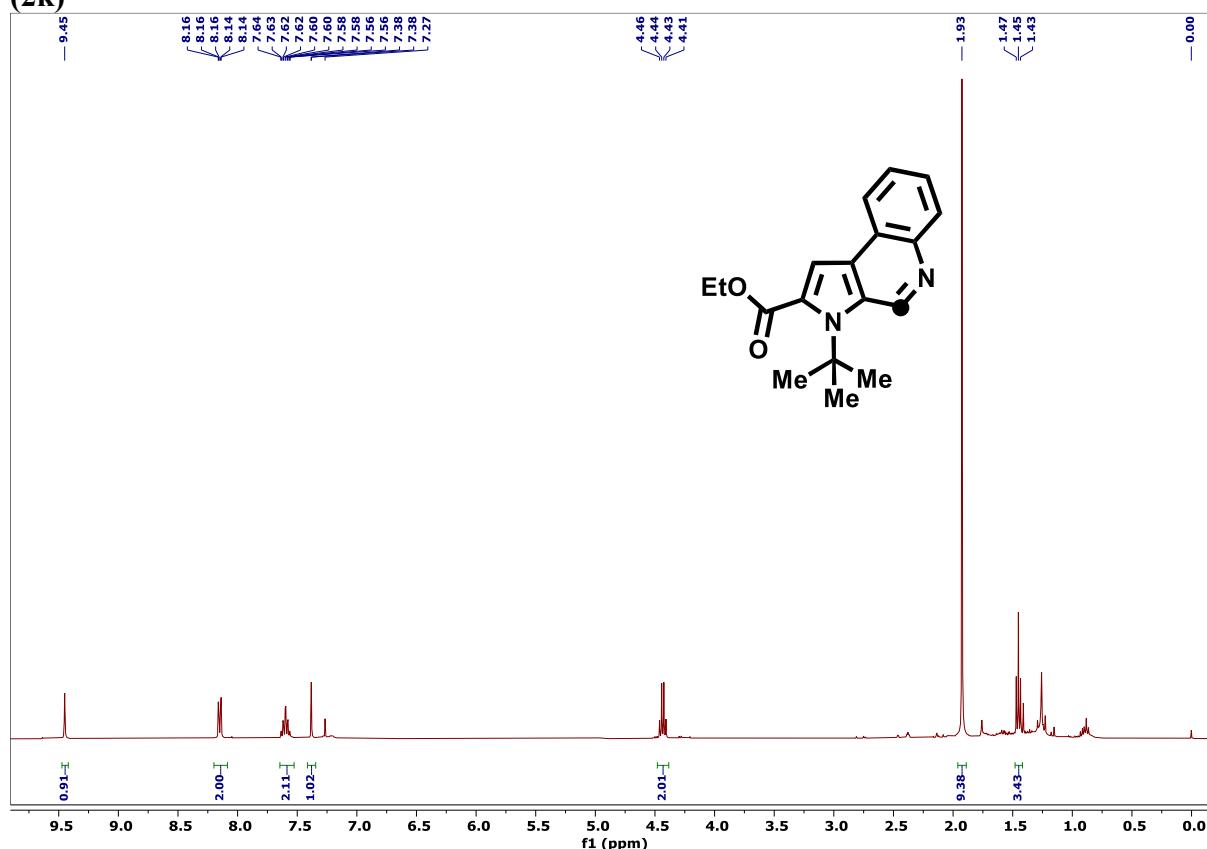
<sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , 100 MHz) of ethyl 3-cyclopentyl-3H-pyrrolo[2,3-c]cquinoline-2-carboxylate (**2i**)



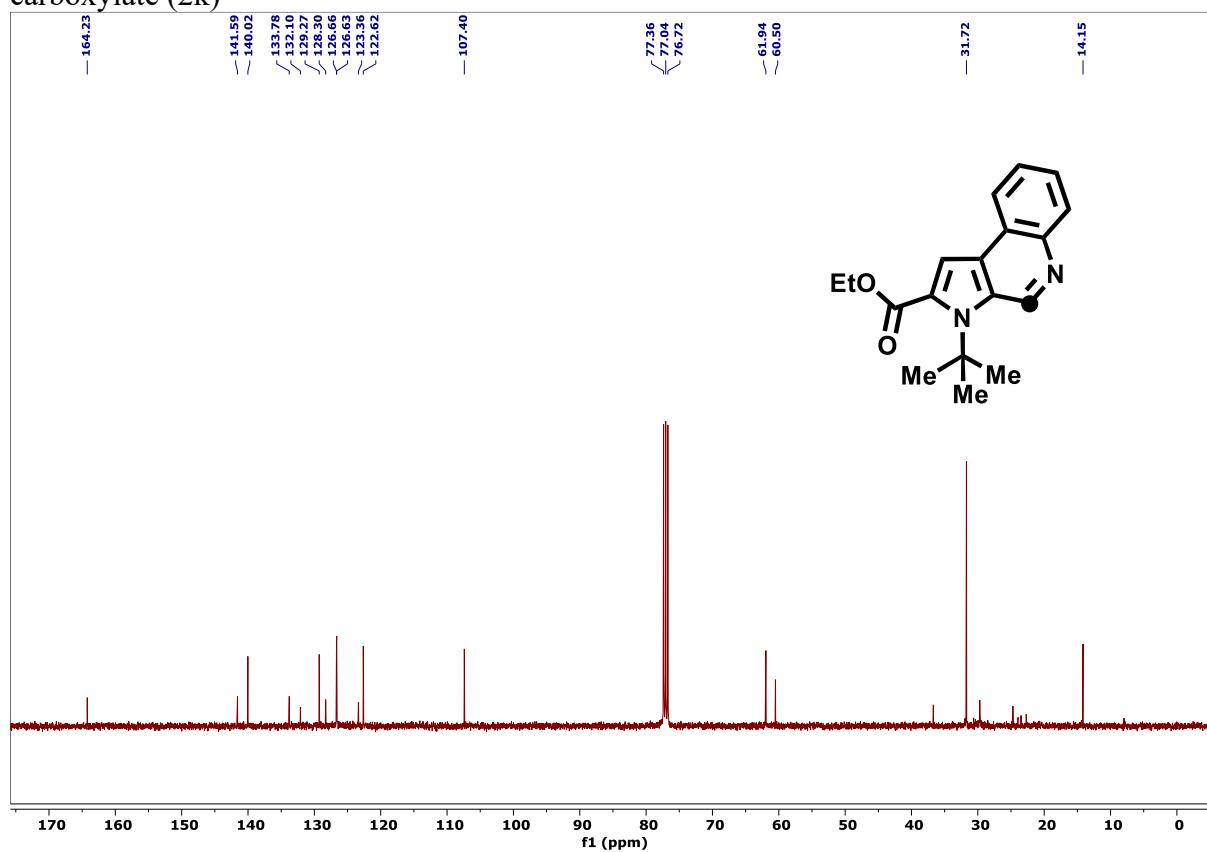
<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz) of ethyl 3-cyclohexyl-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (2j)



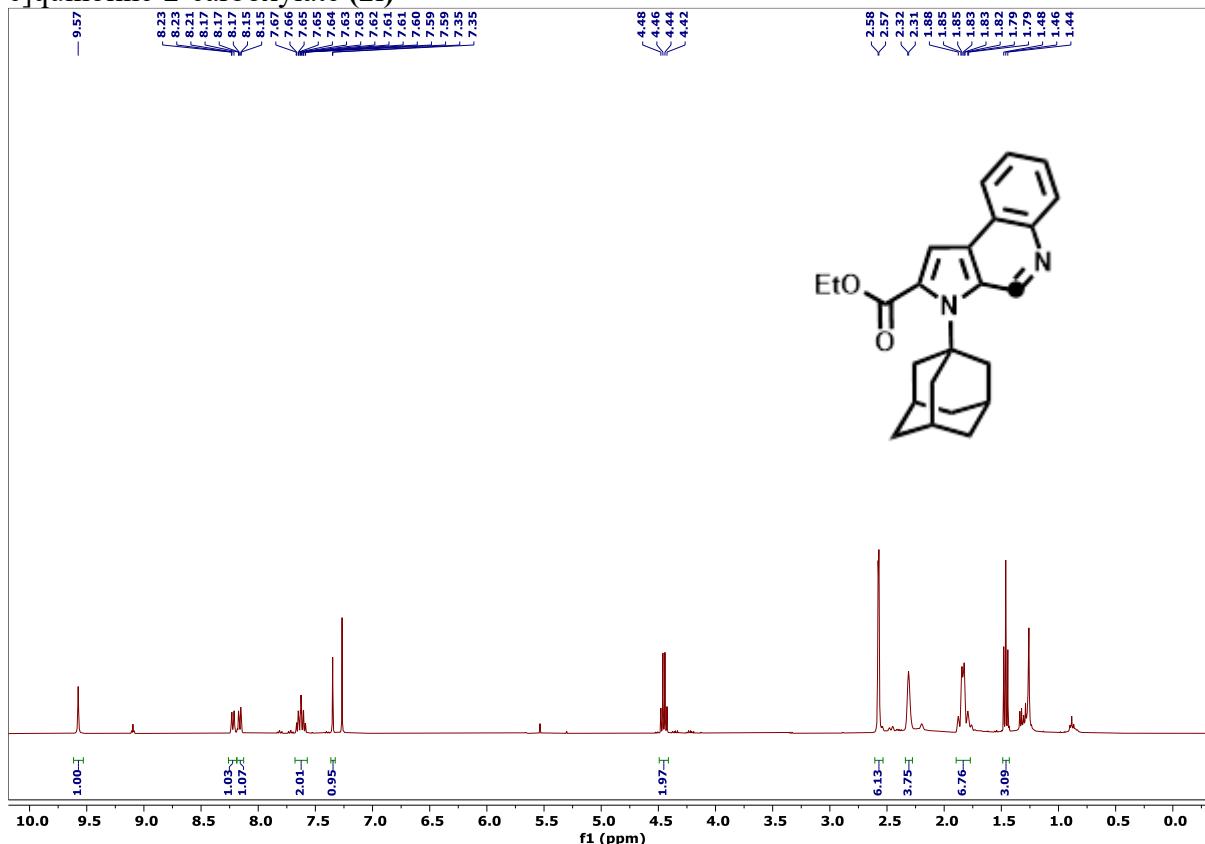
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 3-(tert-butyl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (2k)



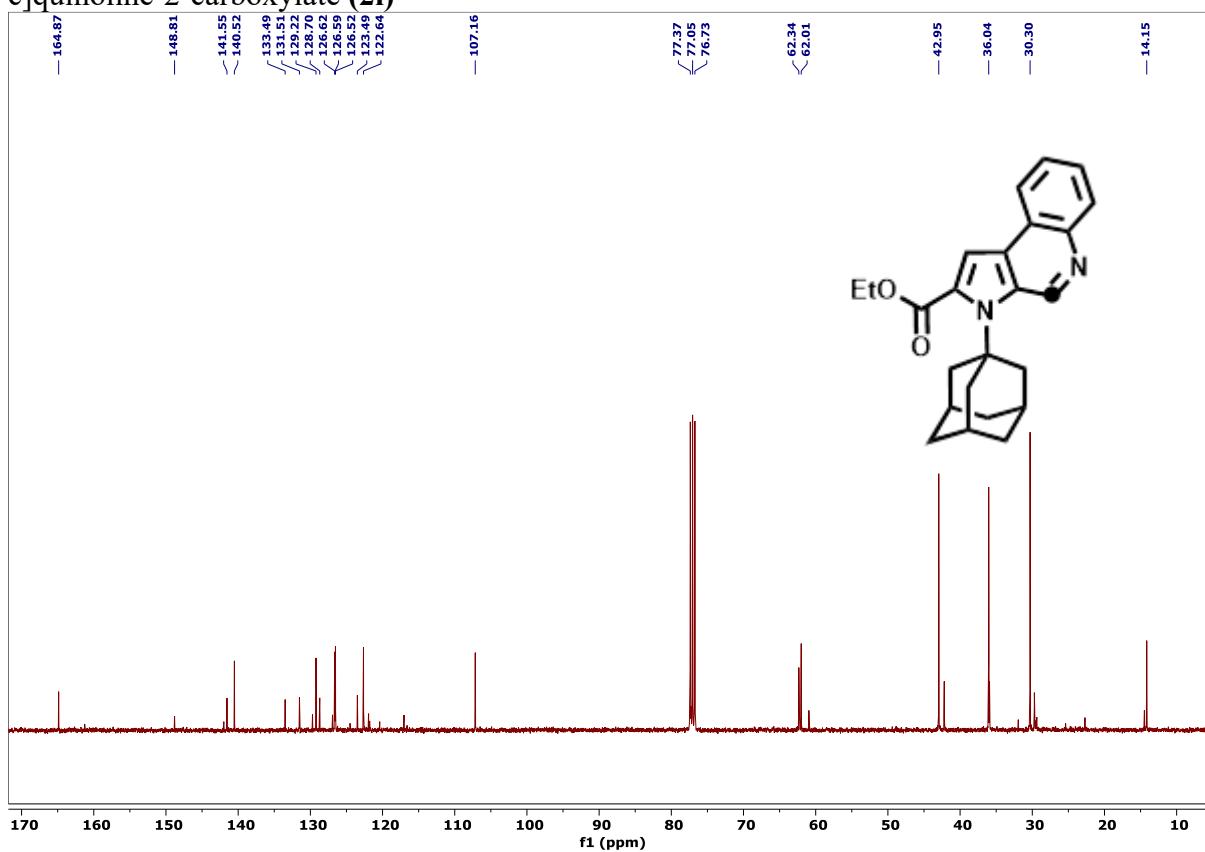
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of ethyl 3-(tert-butyl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (2k)



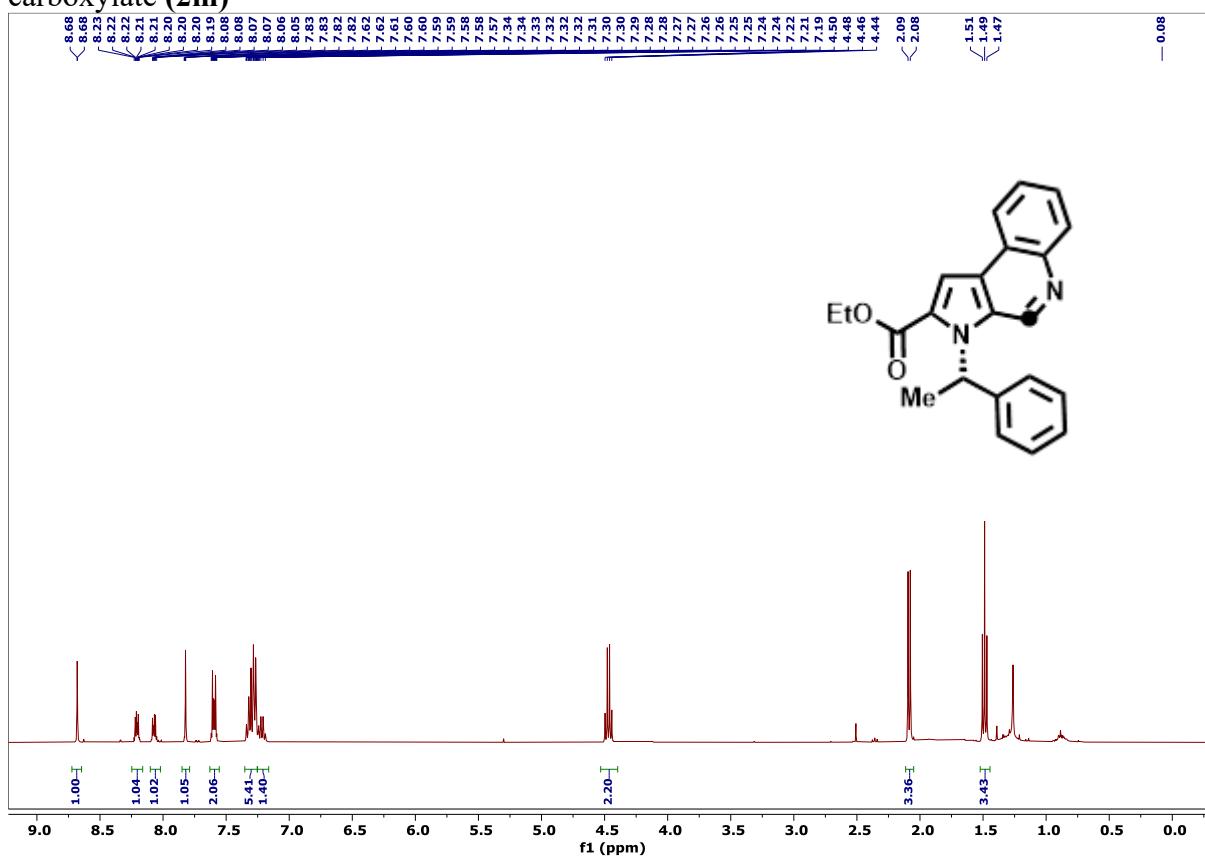
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 3-((3s,5s,7s)-adamantan-1-yl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2I**)



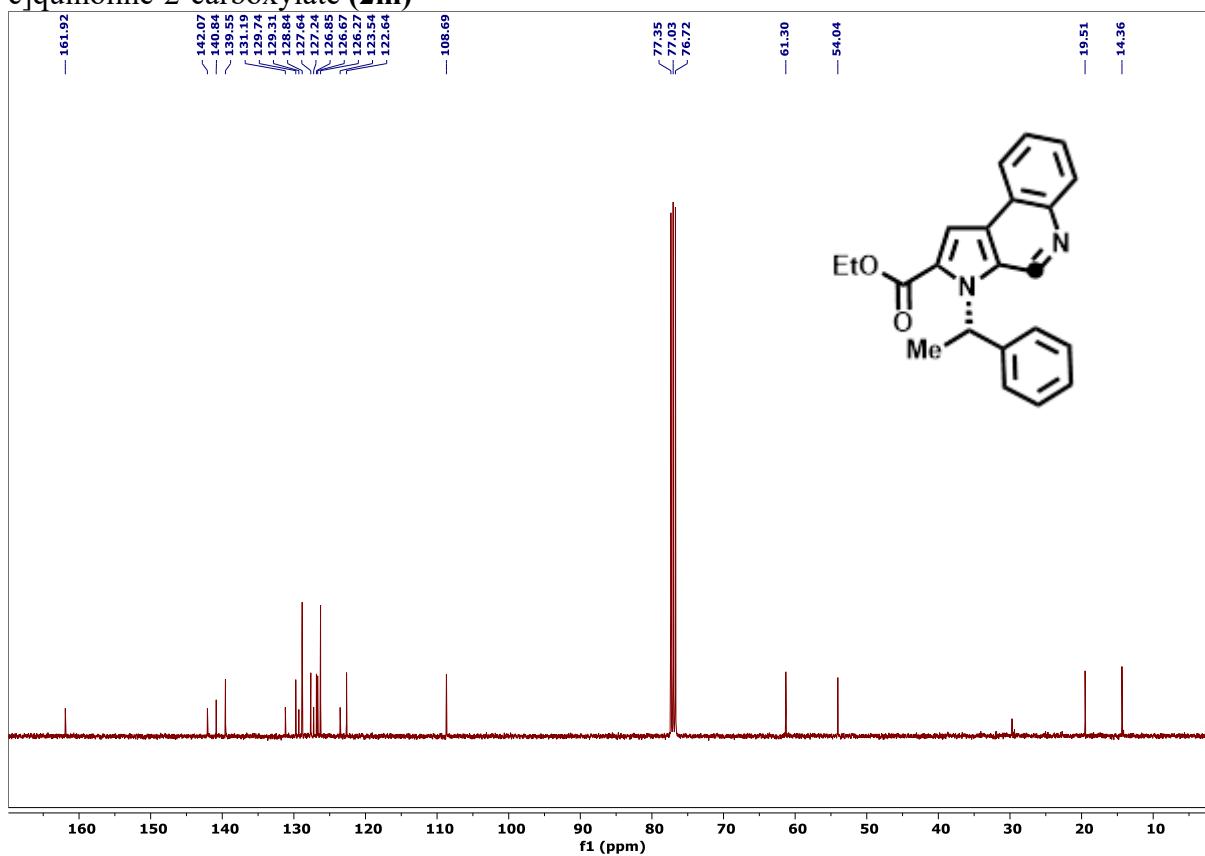
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of ethyl 3-((3s,5s,7s)-adamantan-1-yl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2l**)



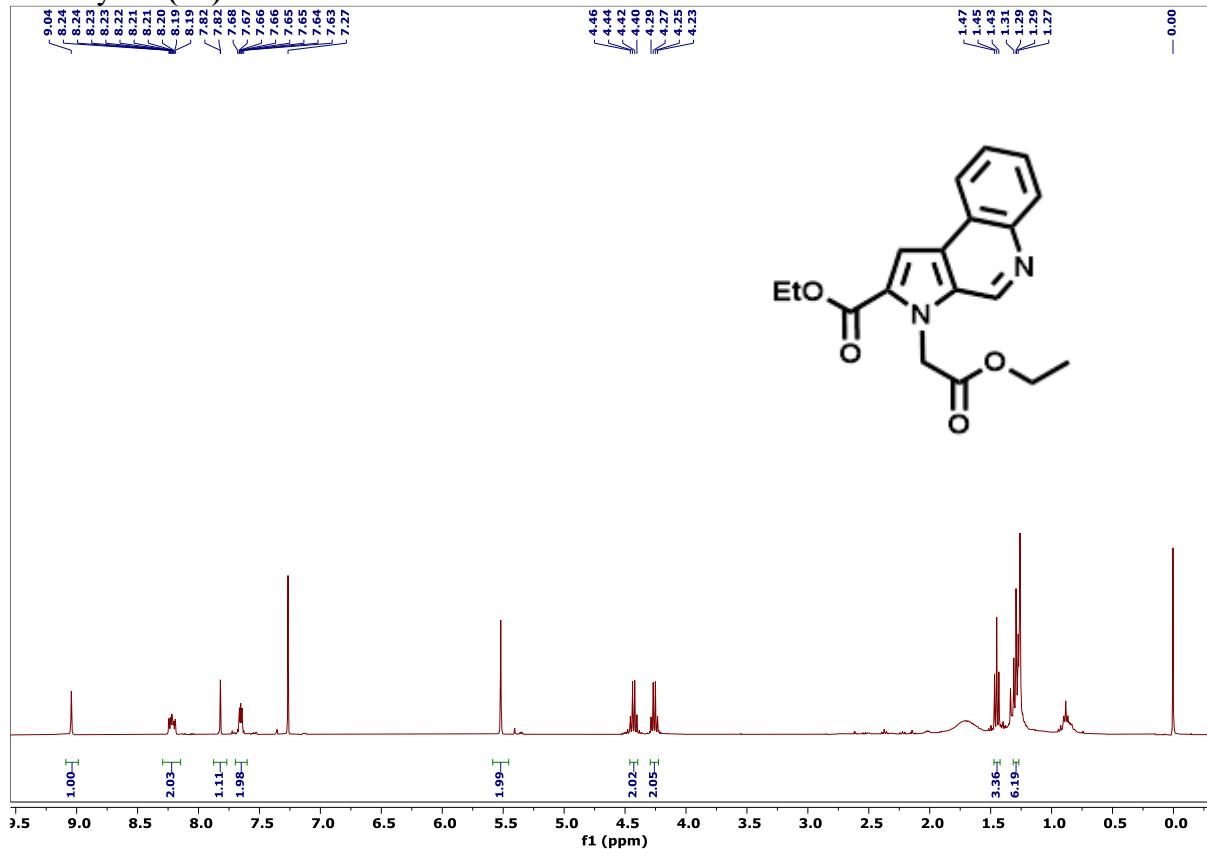
<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz) of ethyl (S)-3-(1-phenylethyl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2m**)



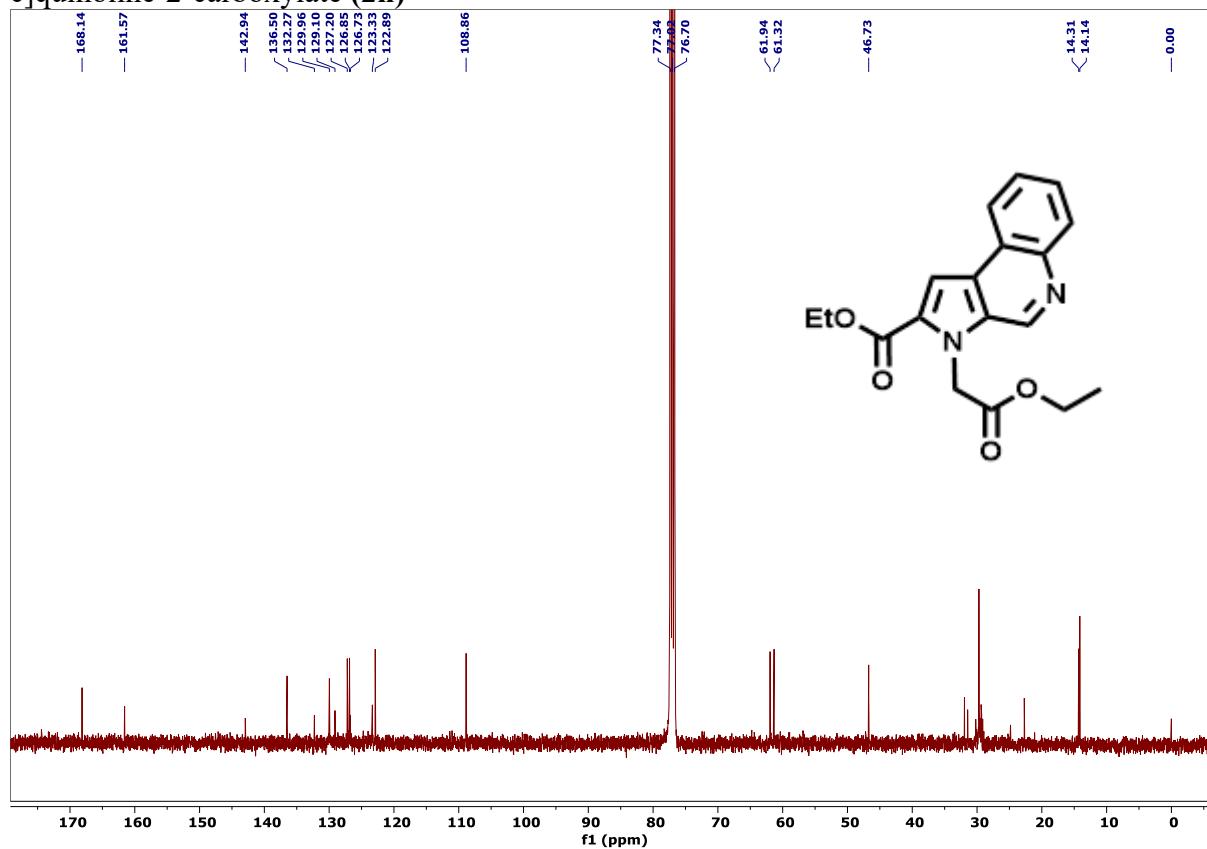
<sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , 100 MHz) of ethyl (S)-3-(1-phenylethyl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2m**)



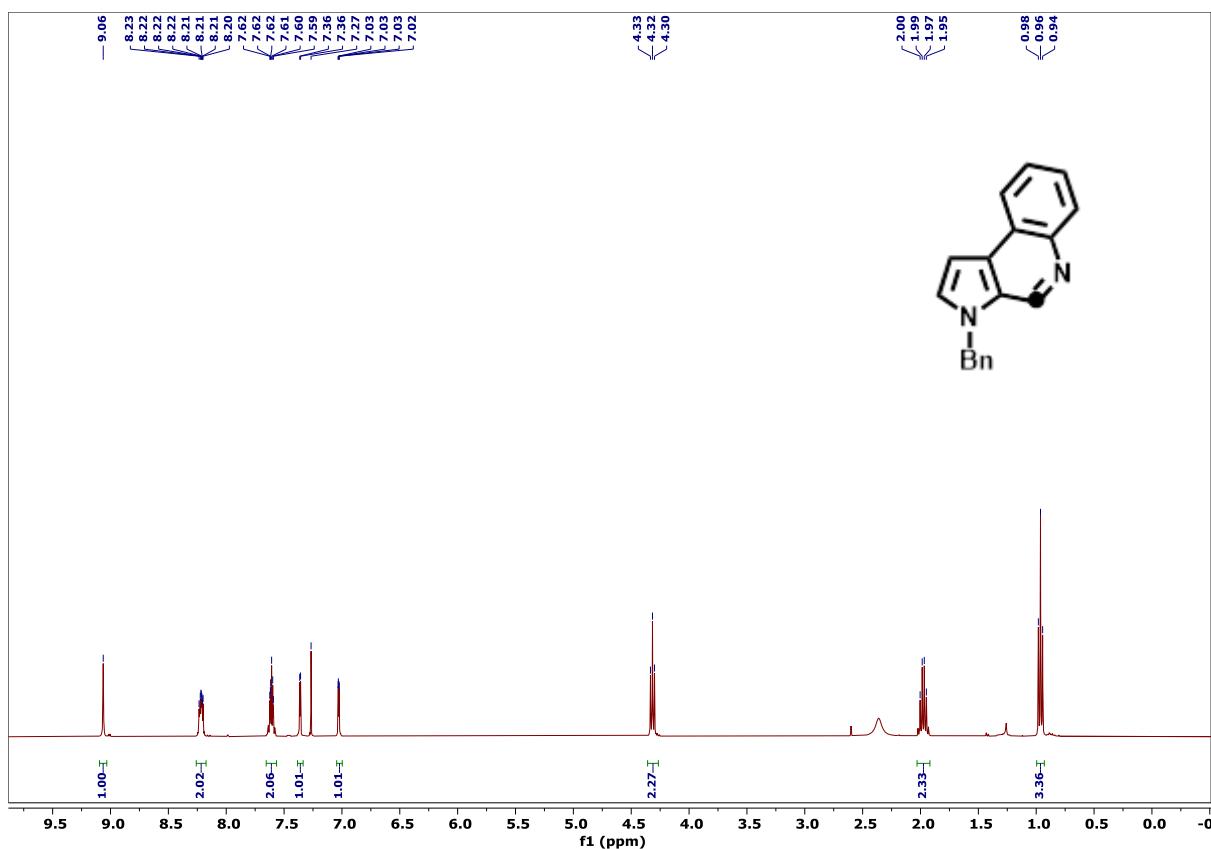
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of ethyl 3-(2-ethoxy-2-oxoethyl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2n**)



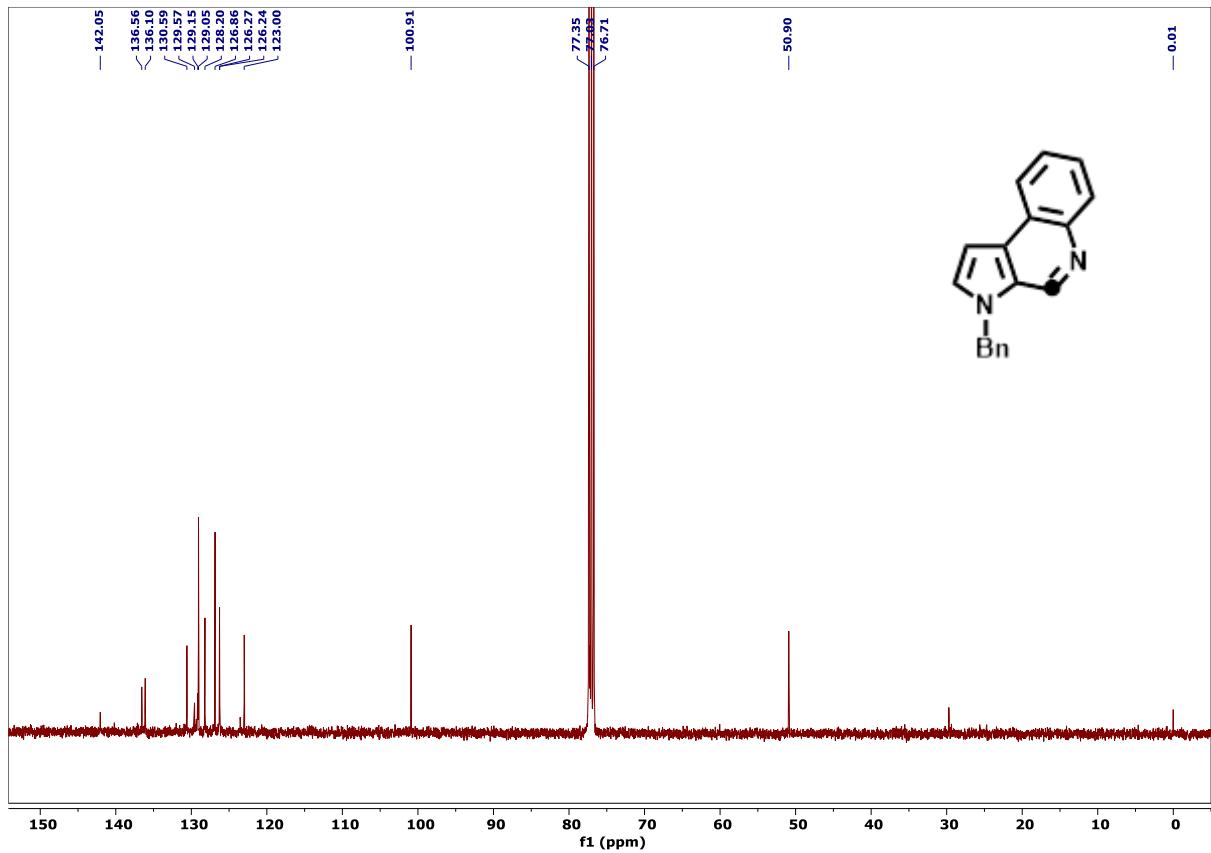
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of ethyl 3-(2-ethoxy-2-oxoethyl)-3H-pyrrolo[2,3-c]quinoline-2-carboxylate (**2n**)



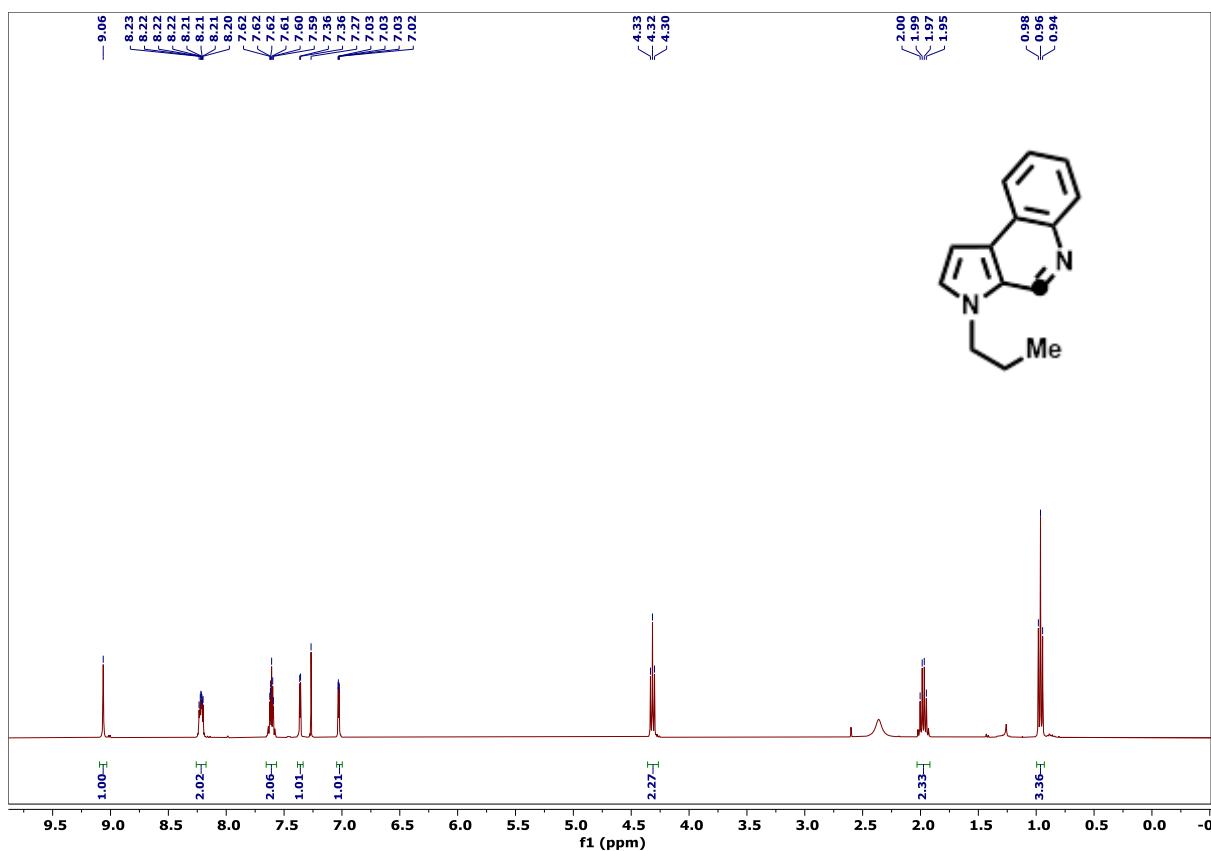
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 3-benzyl-3H-pyrrolo[2,3-c]quinoline (**4a**)



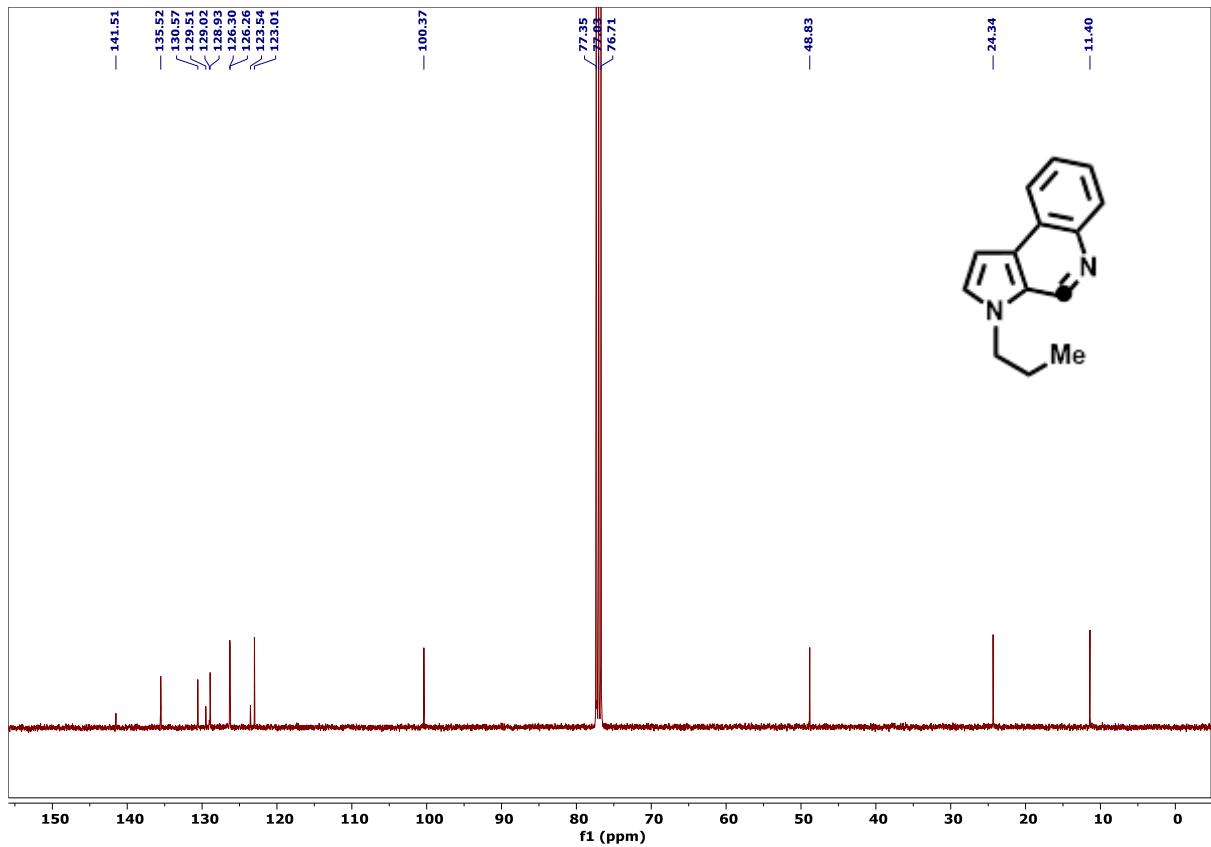
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 3-benzyl-3H-pyrrolo[2,3-c]quinoline (**4a**)



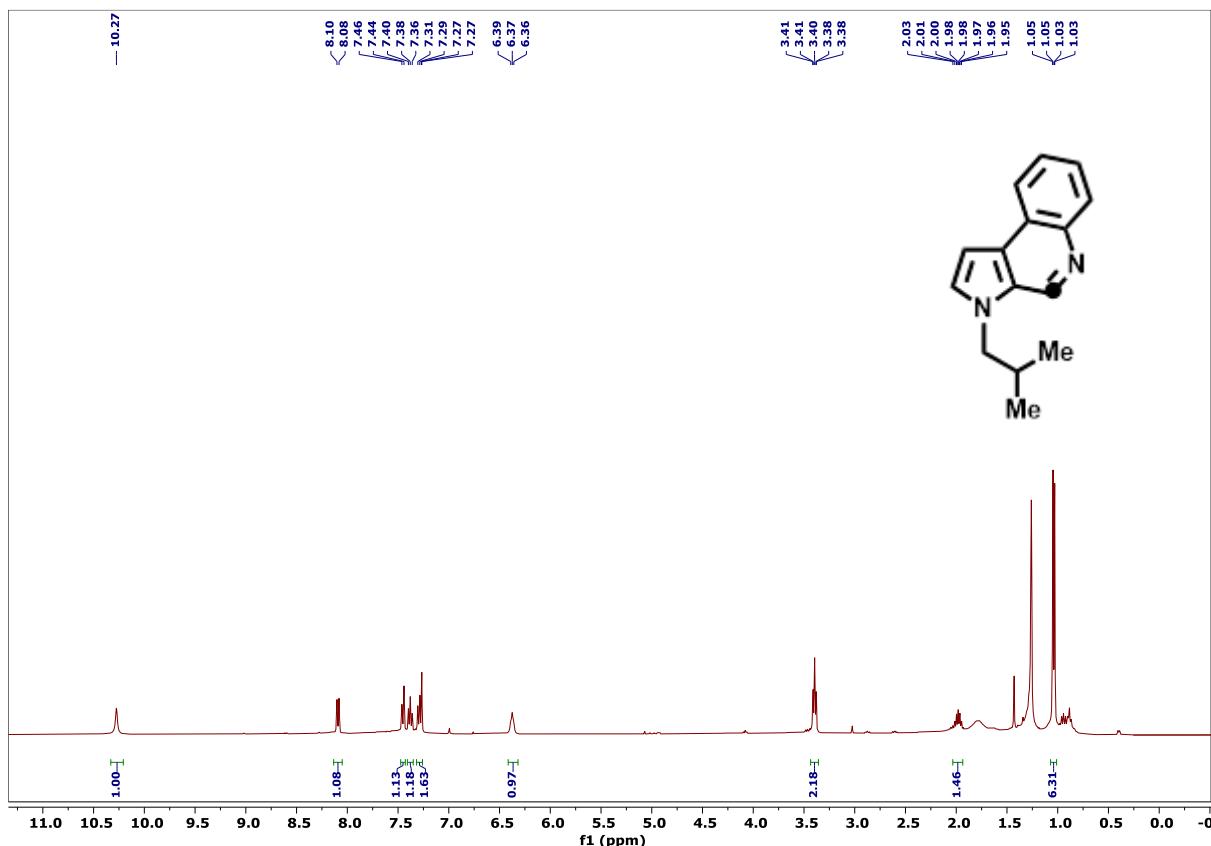
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 3-propyl-3H-pyrrolo[2,3-c]quinoline (**4b**)



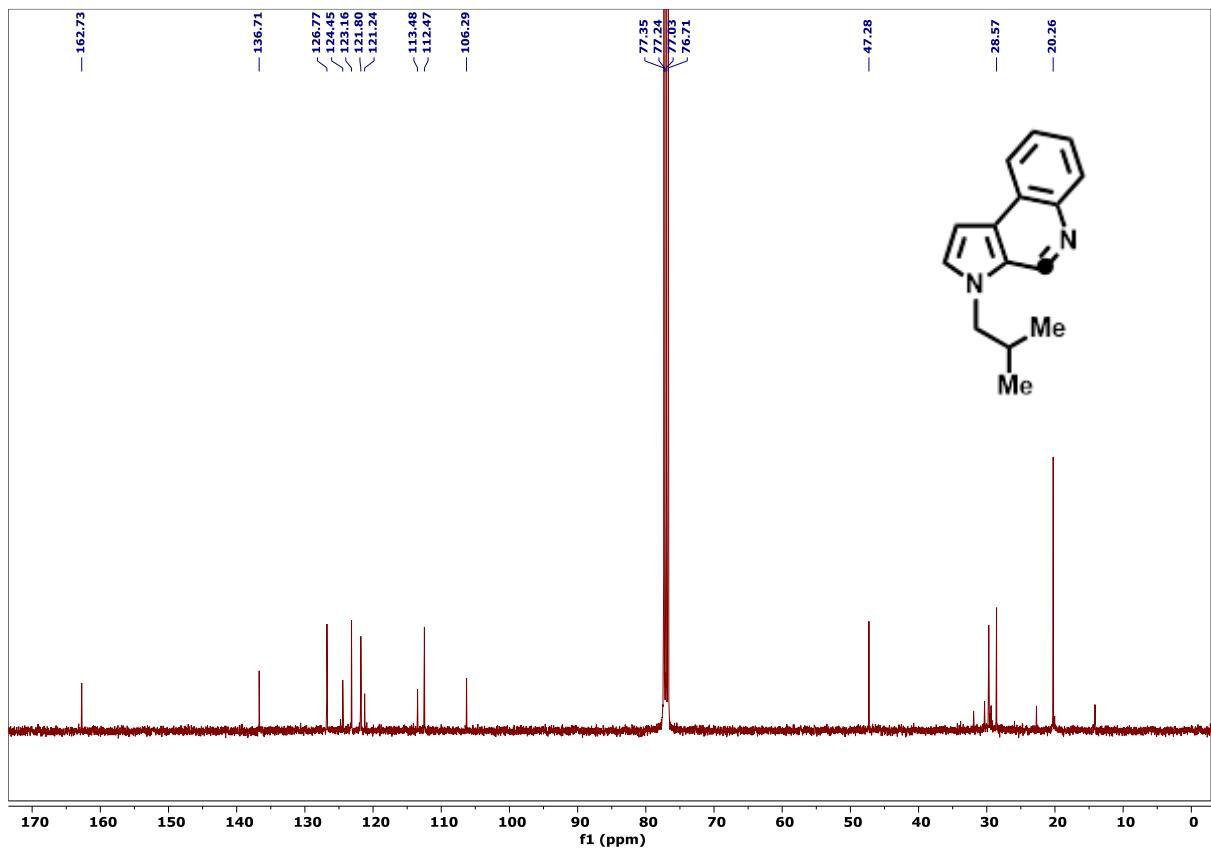
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 3-propyl-3H-pyrrolo[2,3-c]quinoline (**4b**)



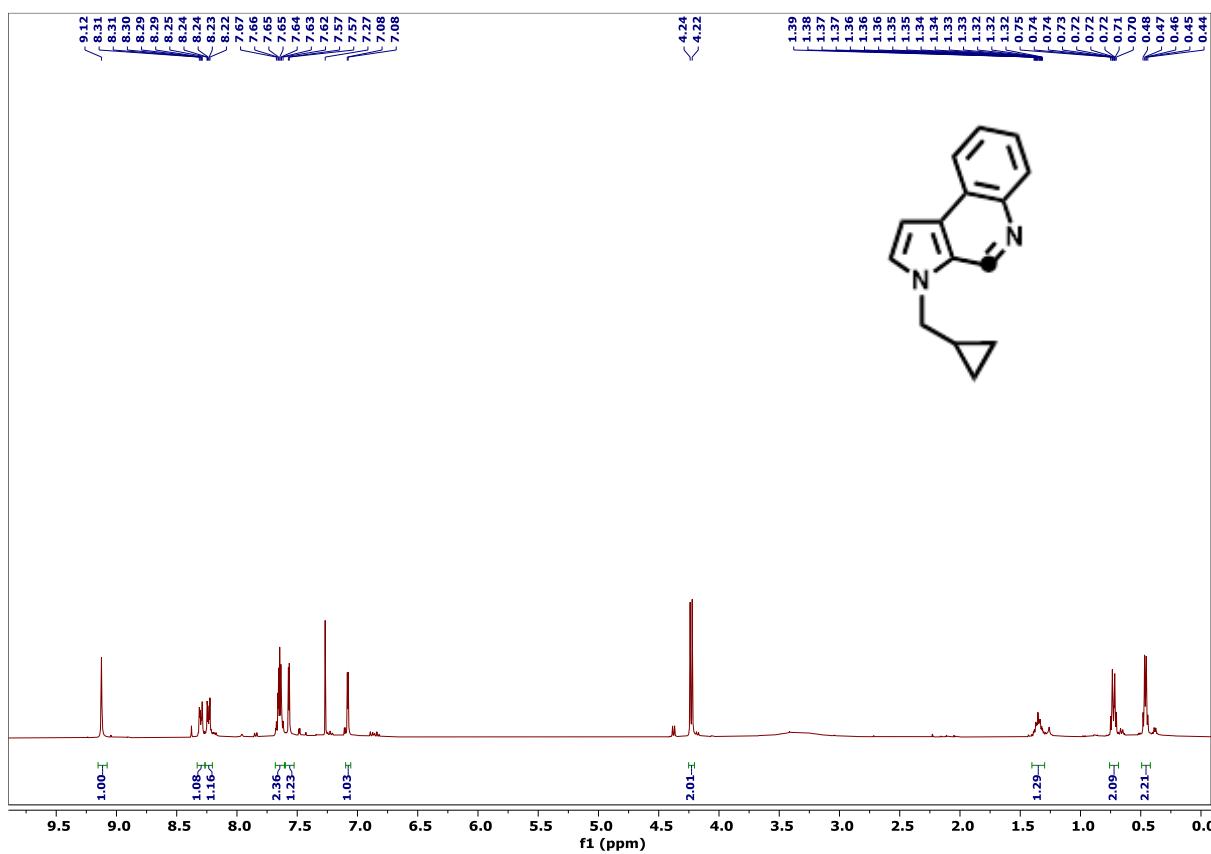
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of 3-isobutyl-3H-pyrrolo[2,3-c]quinoline (**4c**)**



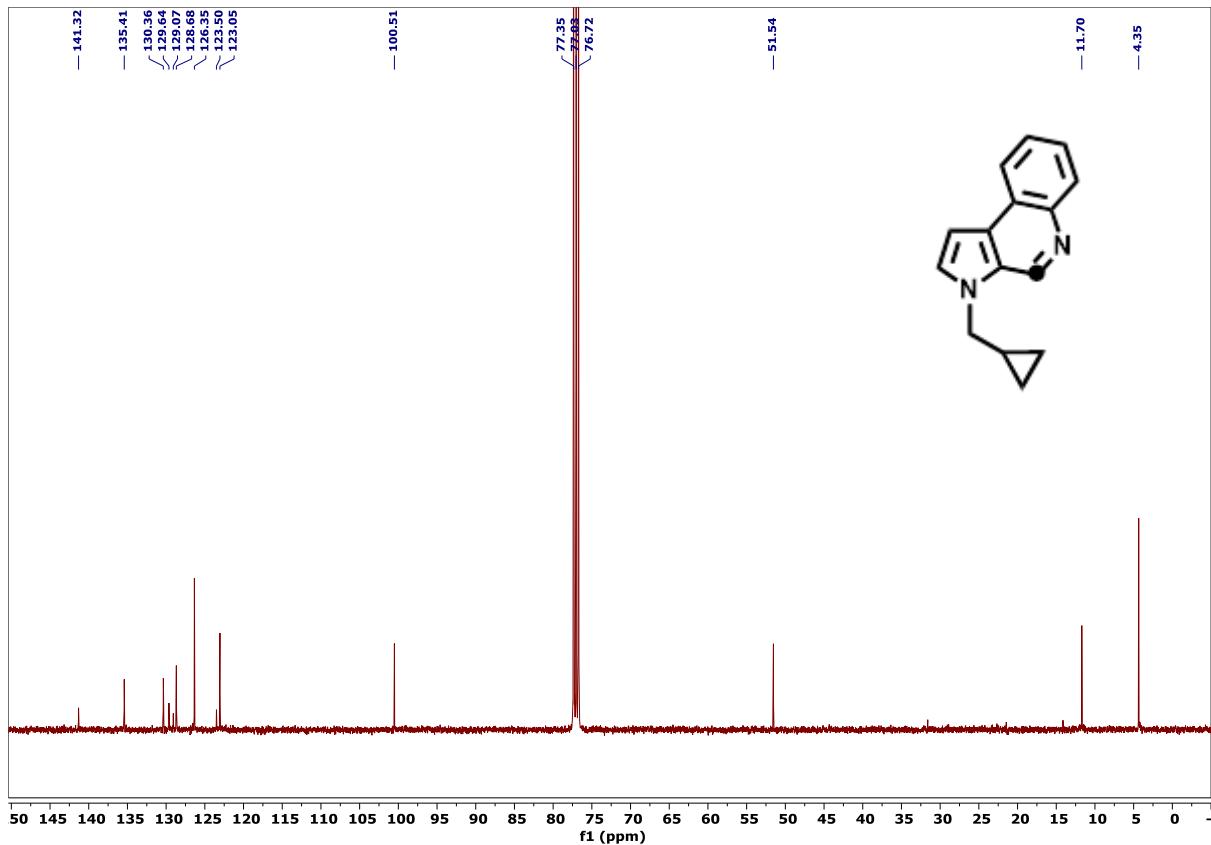
**<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of 3-isobutyl-3H-pyrrolo[2,3-c]quinoline (**4c**)**



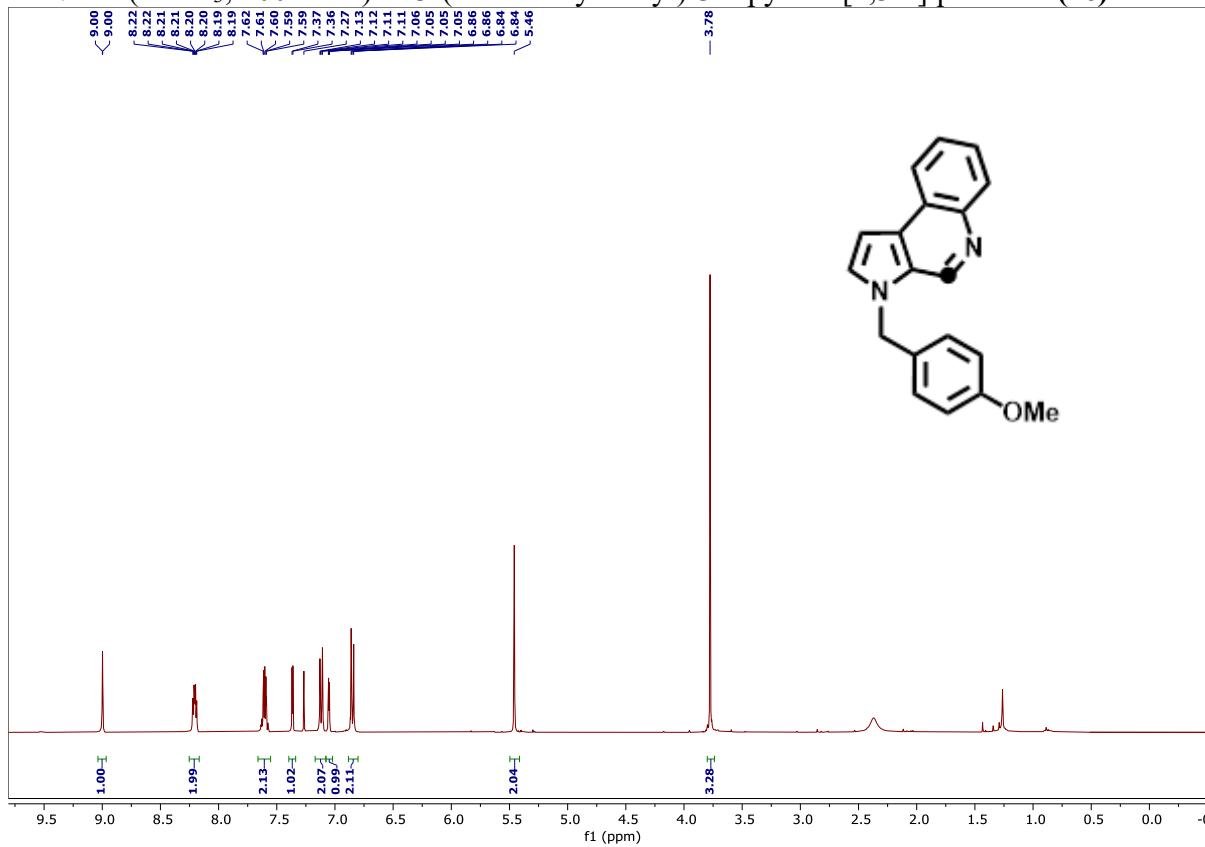
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 3-(cyclopropylmethyl)-3H-pyrrolo[2,3-c]quinoline (**4d**)



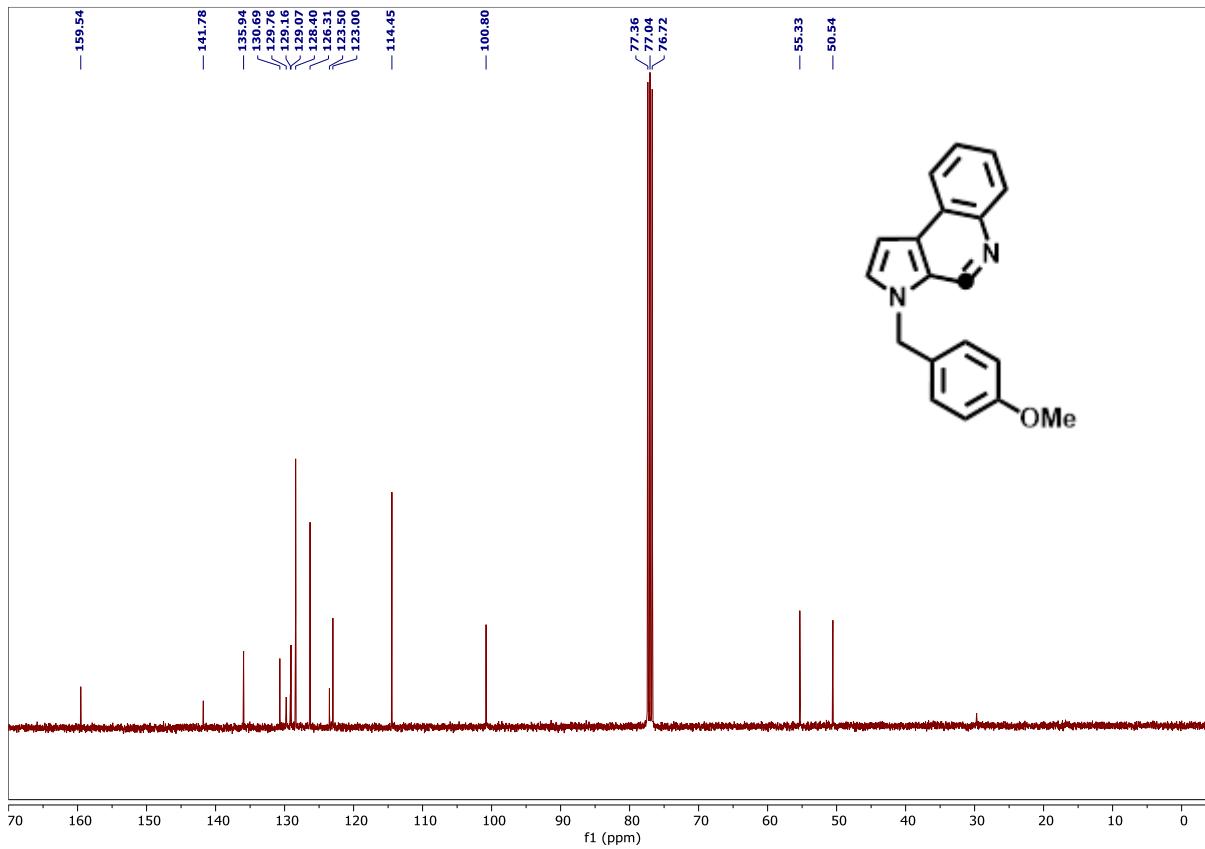
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 3-(cyclopropylmethyl)-3H-pyrrolo[2,3-c]quinoline (**4d**)



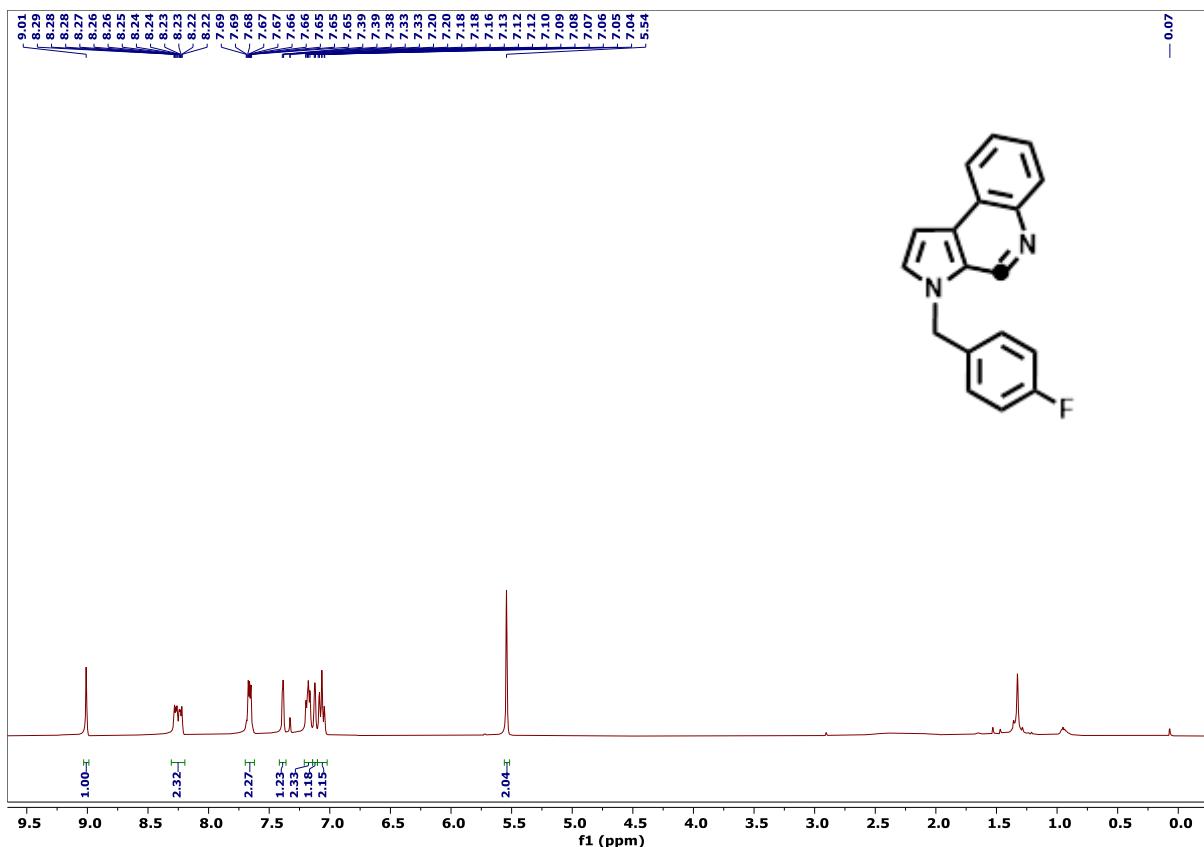
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of 3-(4-methoxybenzyl)-3H-pyrrolo[2,3-c]quinoline (**4e**)



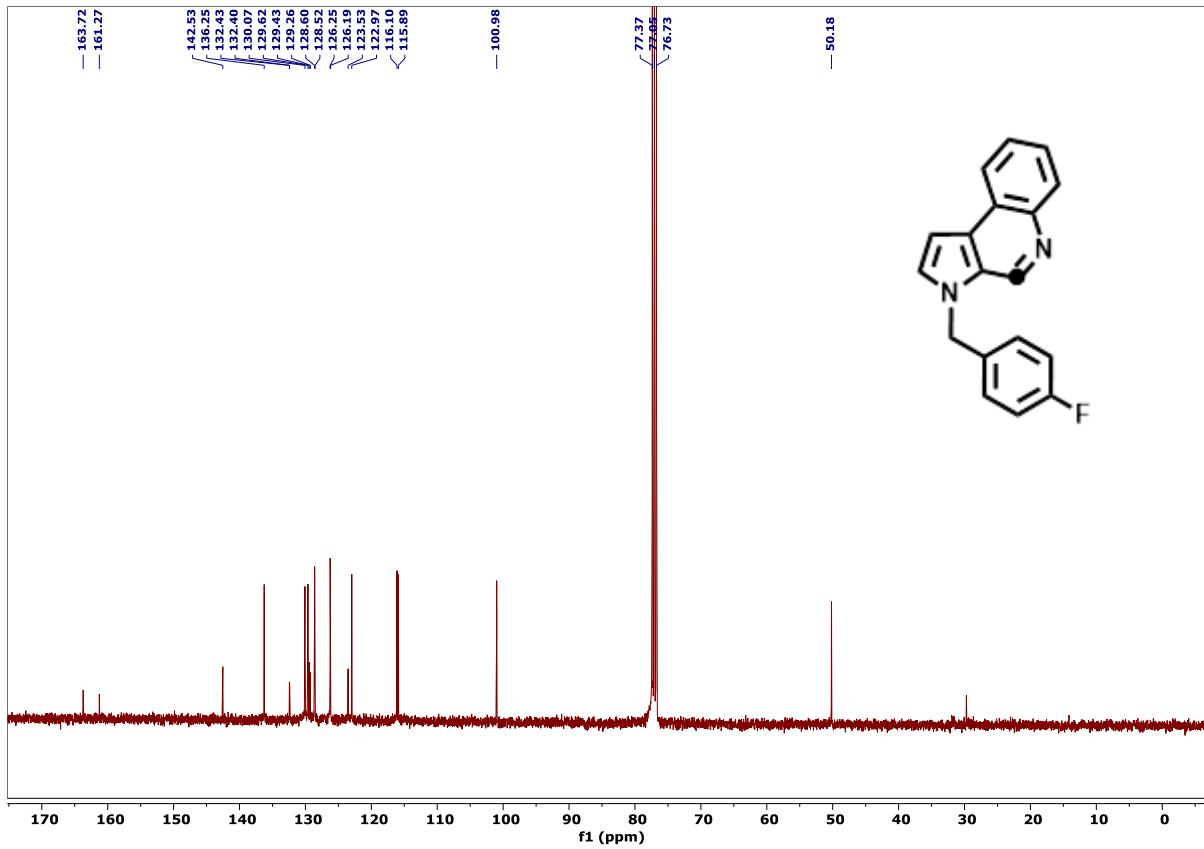
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of 3-(4-methoxybenzyl)-3H-pyrrolo[2,3-c]quinoline (**4e**)



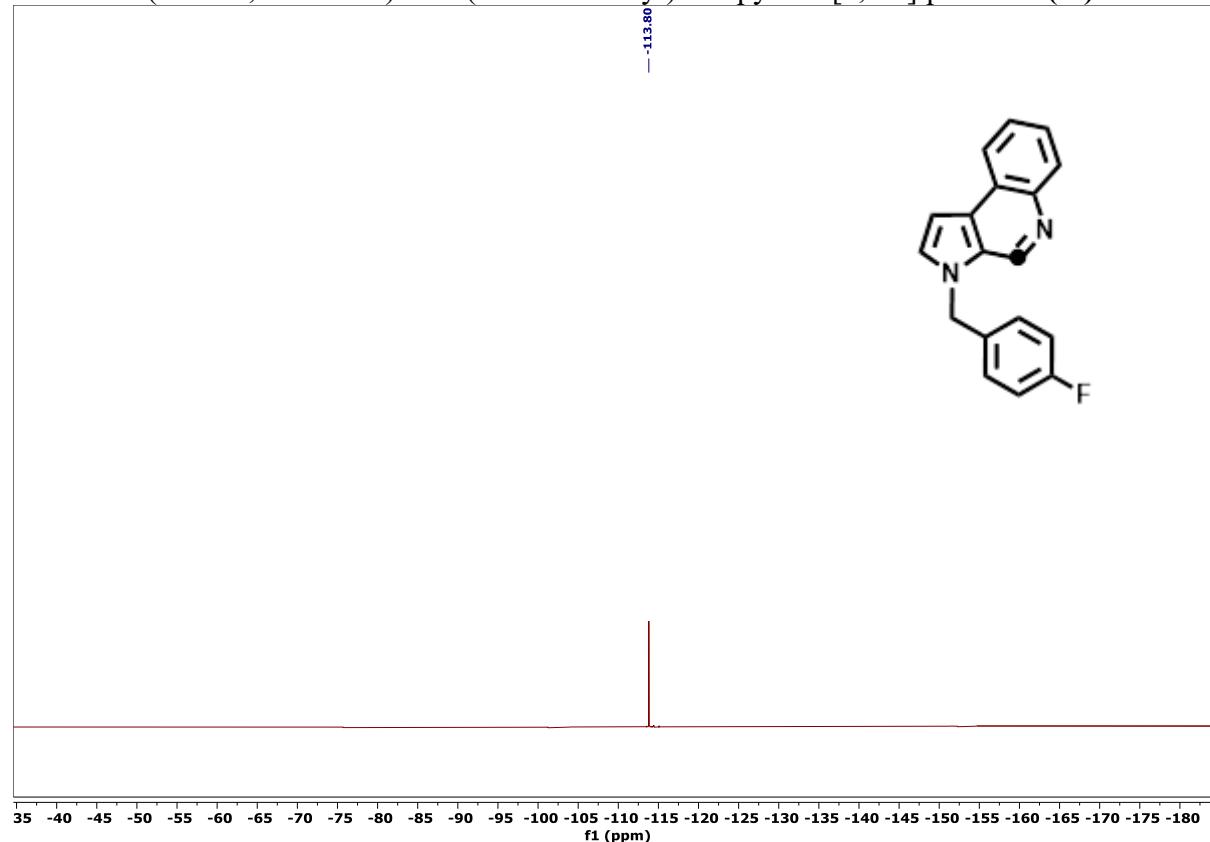
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of 3-(4-fluorobenzyl)-3H-pyrrolo[2,3-c]quinoline (**4f**)**



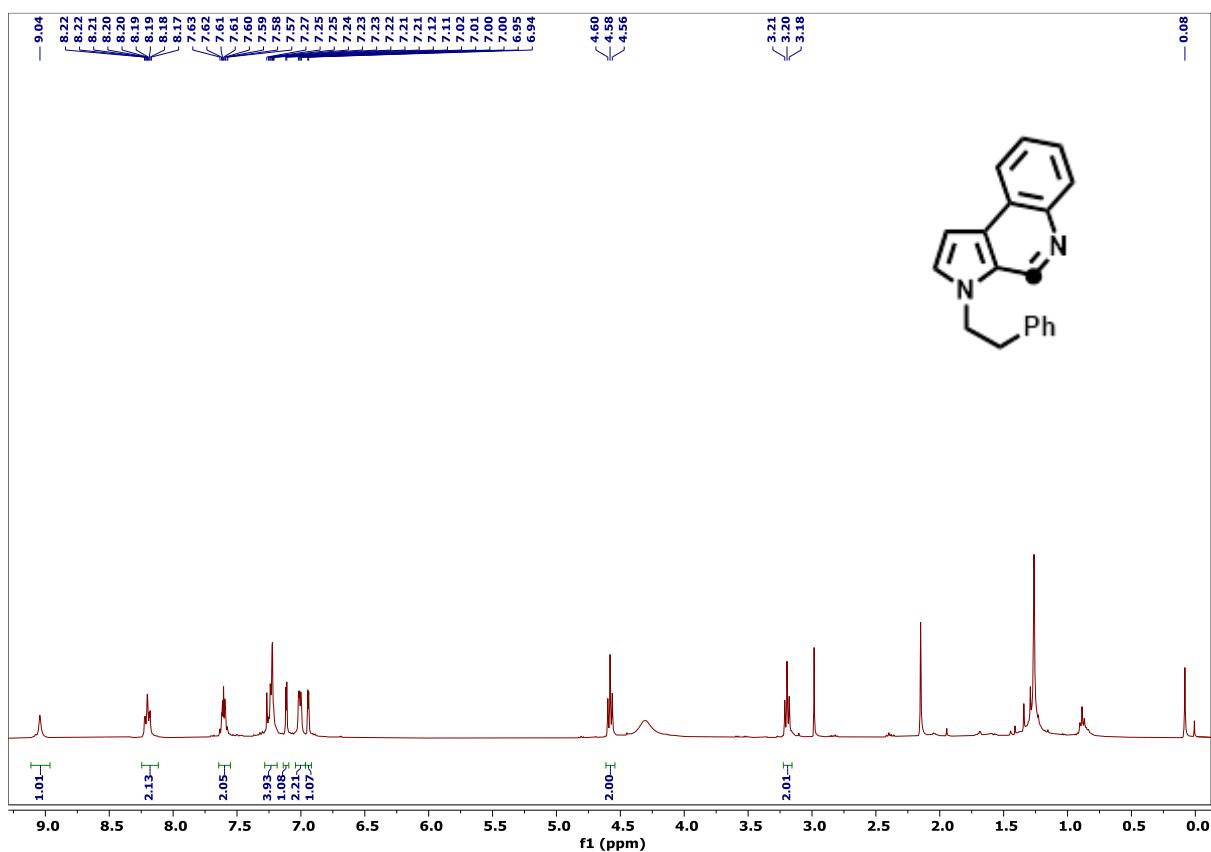
**<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of 3-(4-fluorobenzyl)-3H-pyrrolo[2,3-c]quinoline (**4f**)**



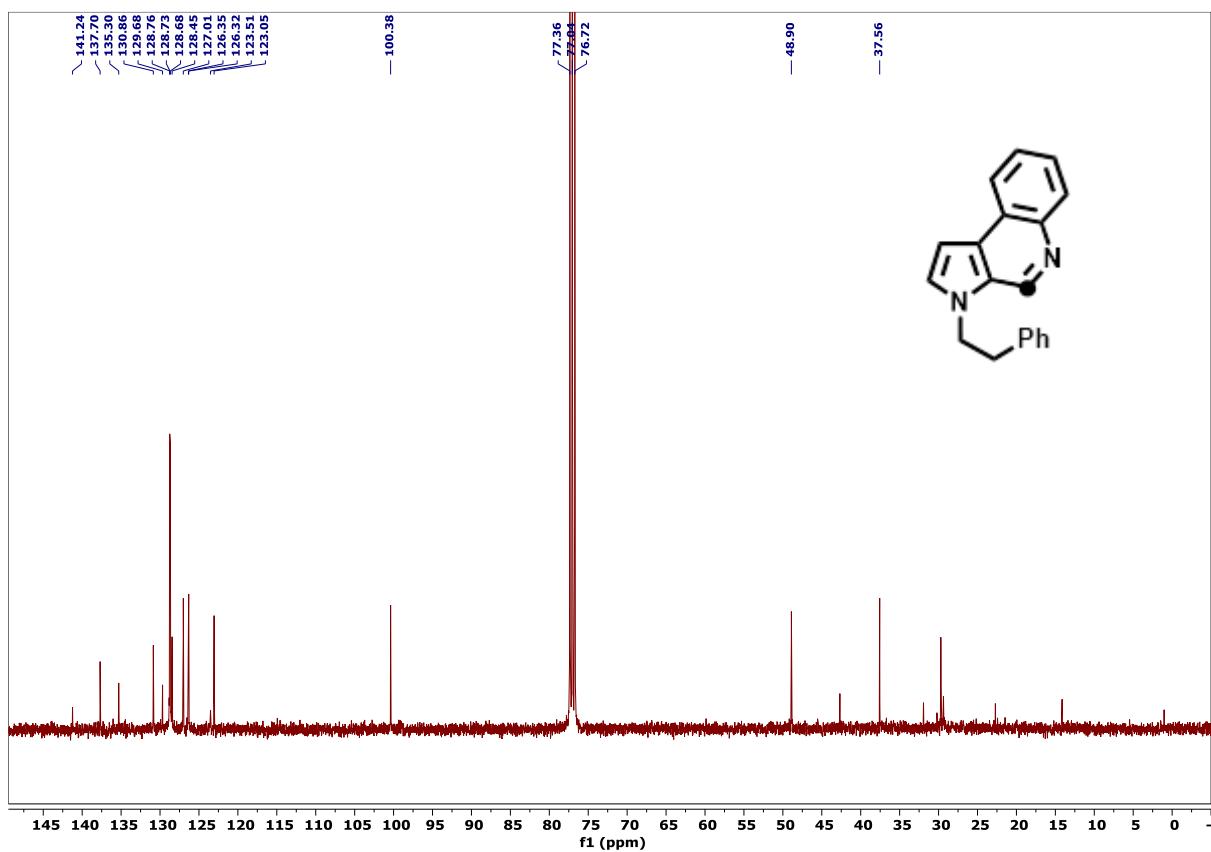
**<sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz) of 3-(4-fluorobenzyl)-3H-pyrrolo[2,3-c]quinoline (**4f**)**



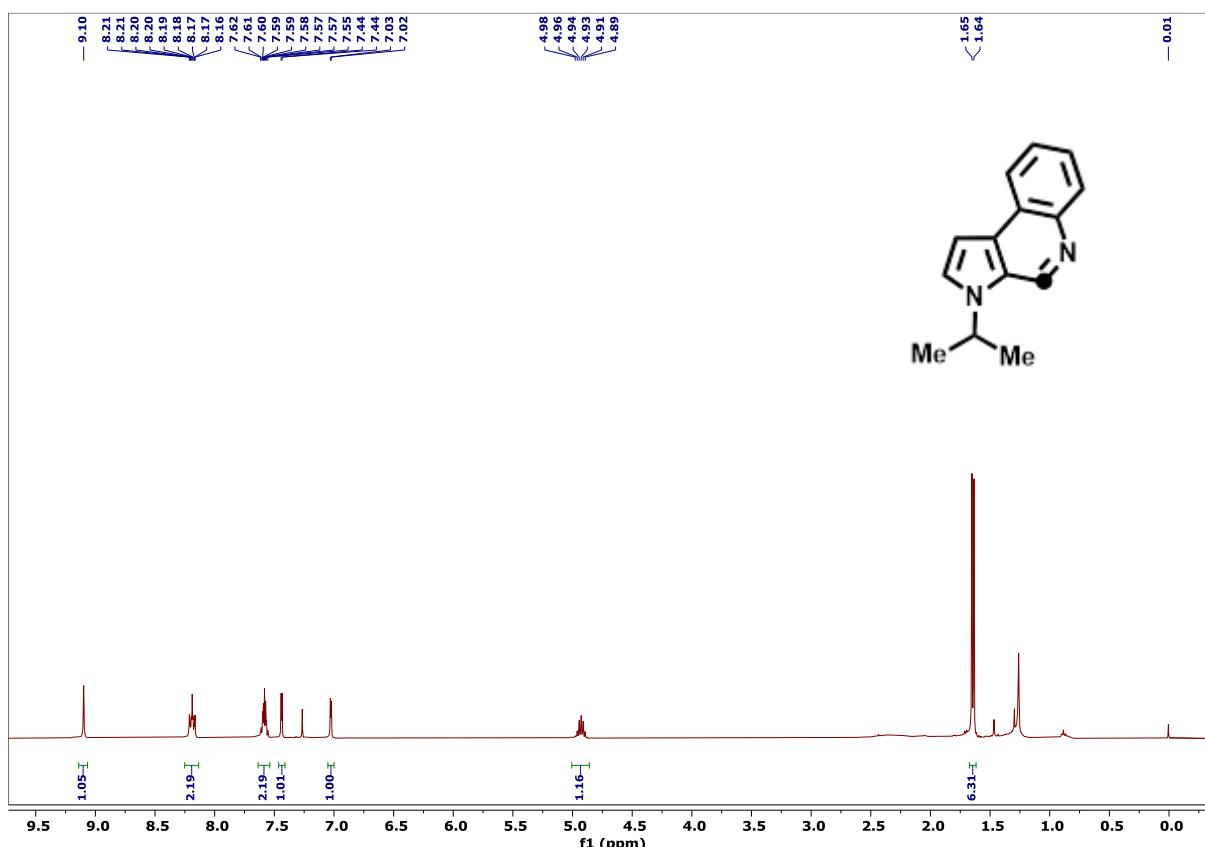
<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz) of 3-phenethyl-3H-pyrrolo[2,3-c]quinoline (**4g**)



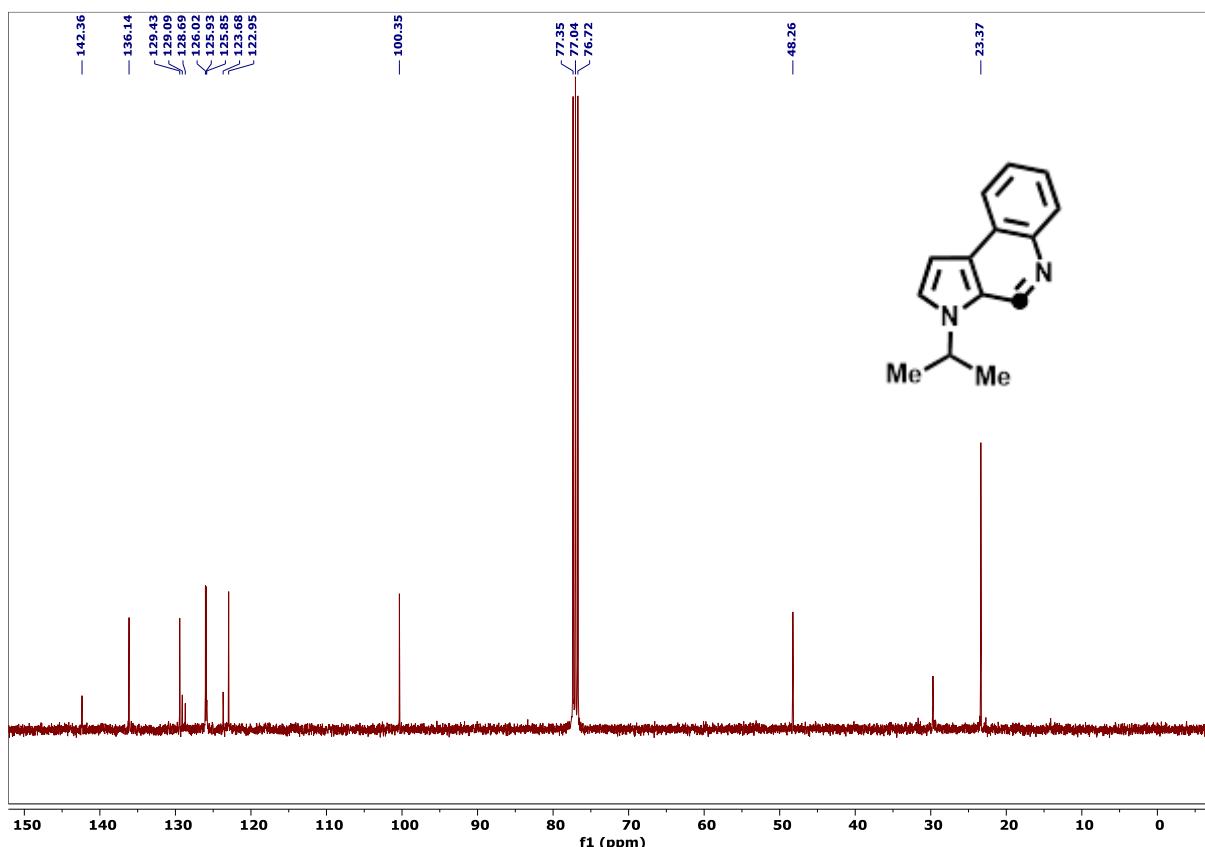
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of 3-phenethyl-3H-pyrrolo[2,3-c]quinoline (4g)



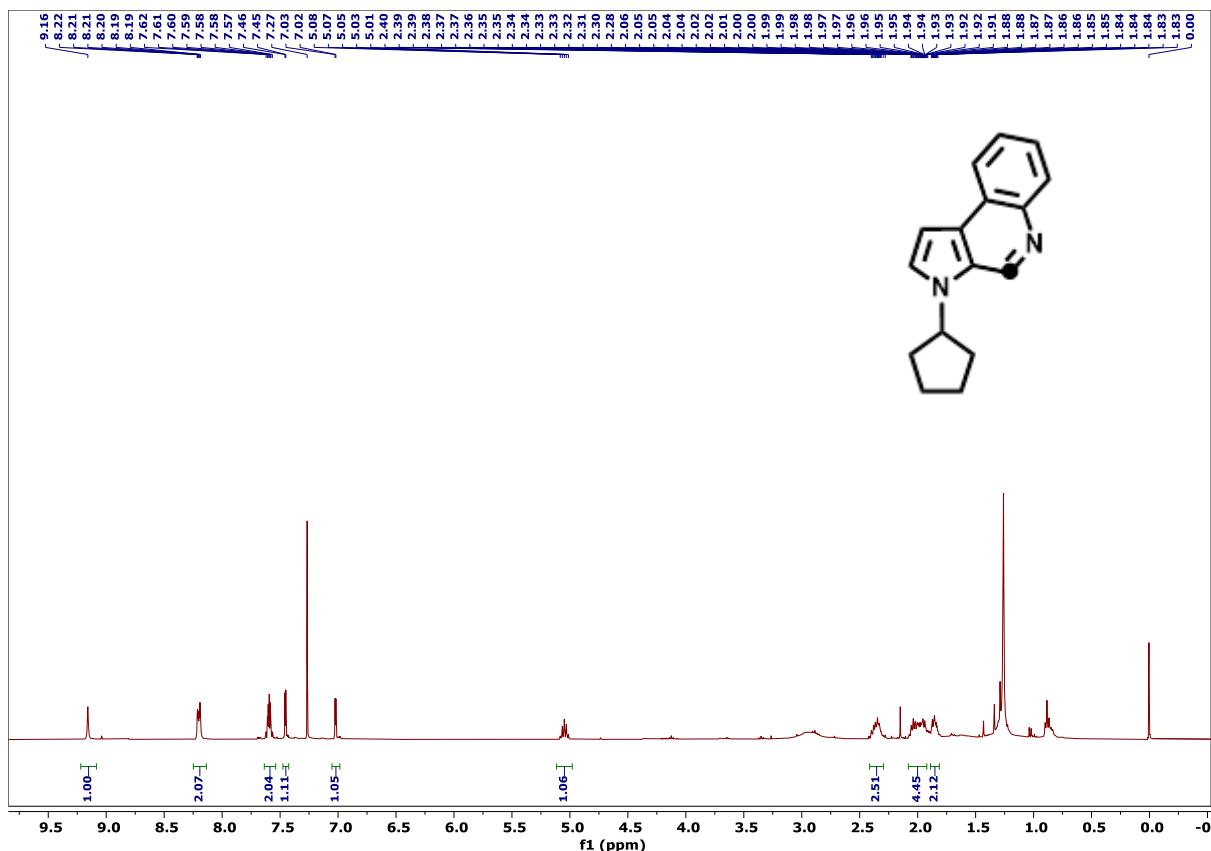
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 3-isopropyl-3H-pyrrolo[2,3-c]quinoline (**4h**)



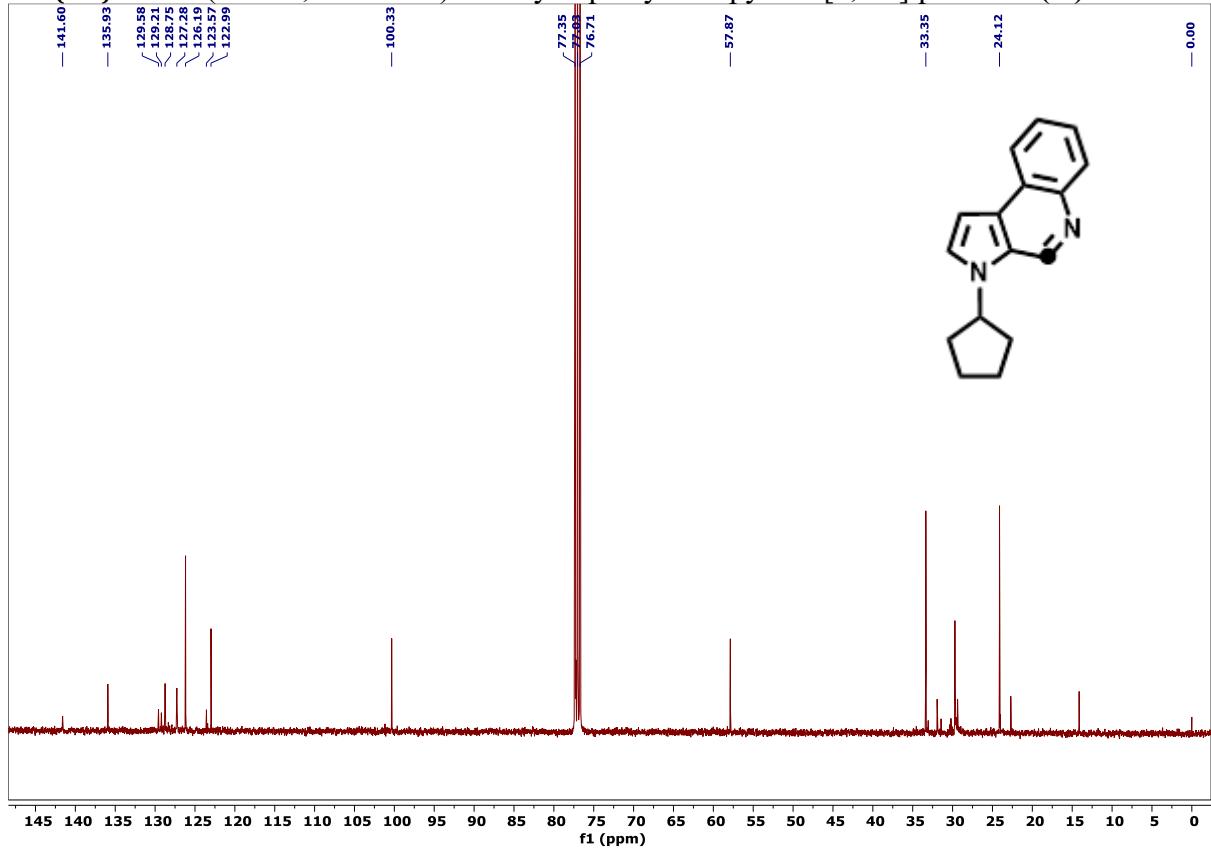
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 3-isopropyl-3H-pyrrolo[2,3-c]quinoline (**4h**)



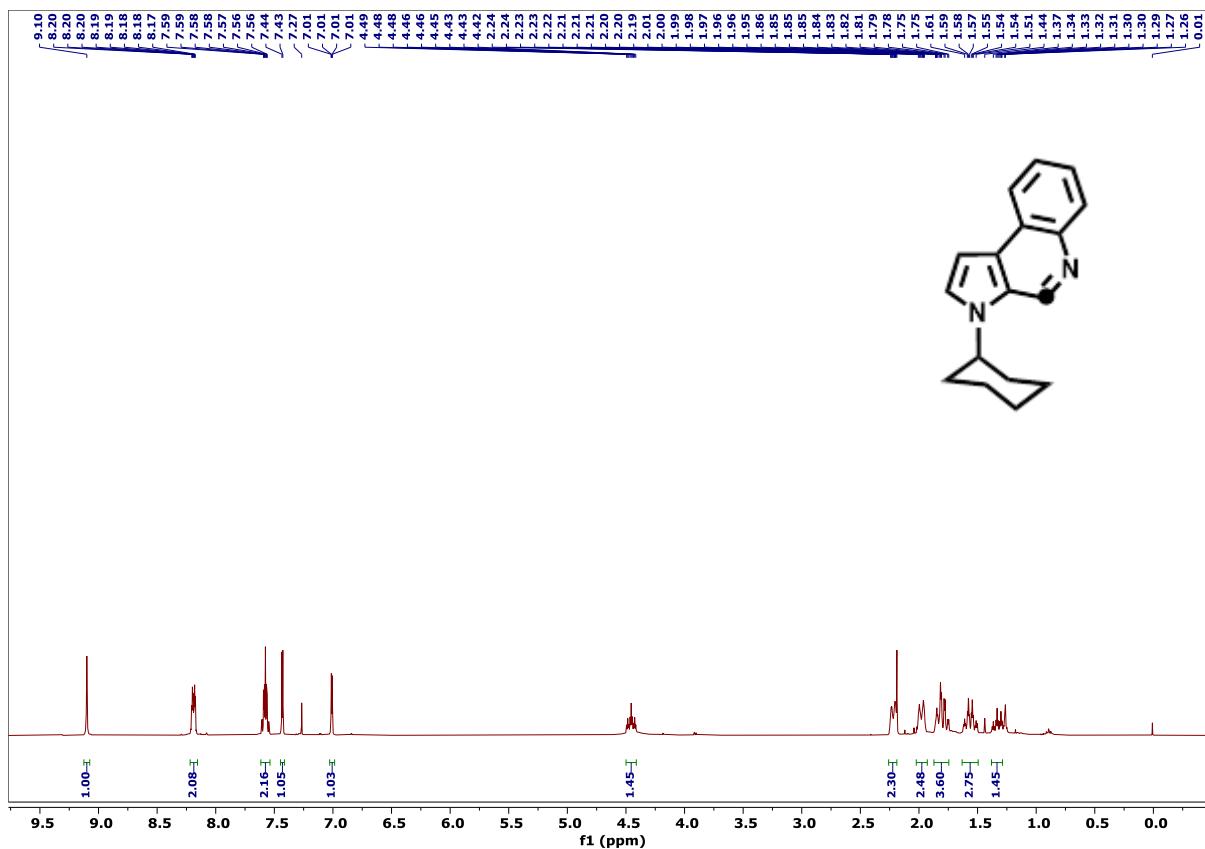
<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz) of 3-cyclopentyl-3H-pyrrolo[2,3-c]quinoline (**4i**)



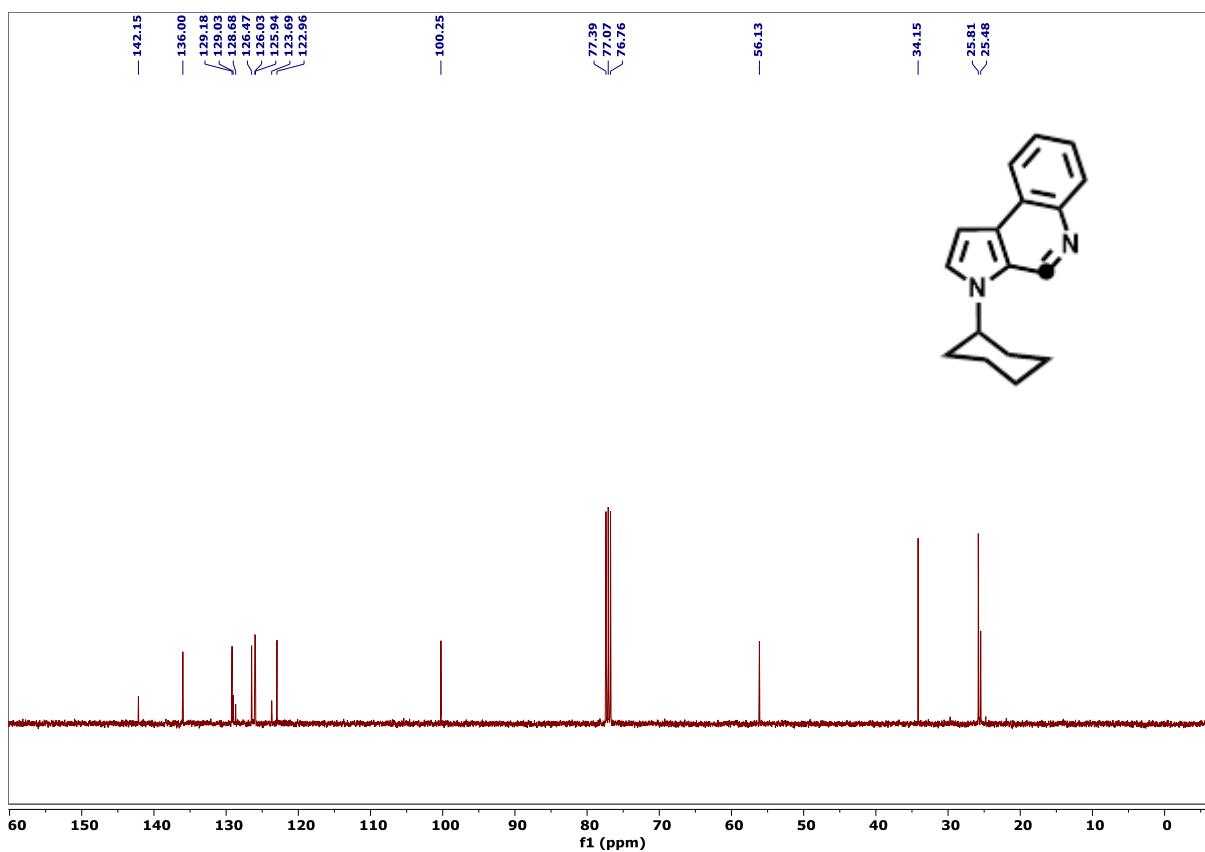
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of 3-cyclopentyl-3H-pyrrolo[2,3-c]quinoline (**4i**)



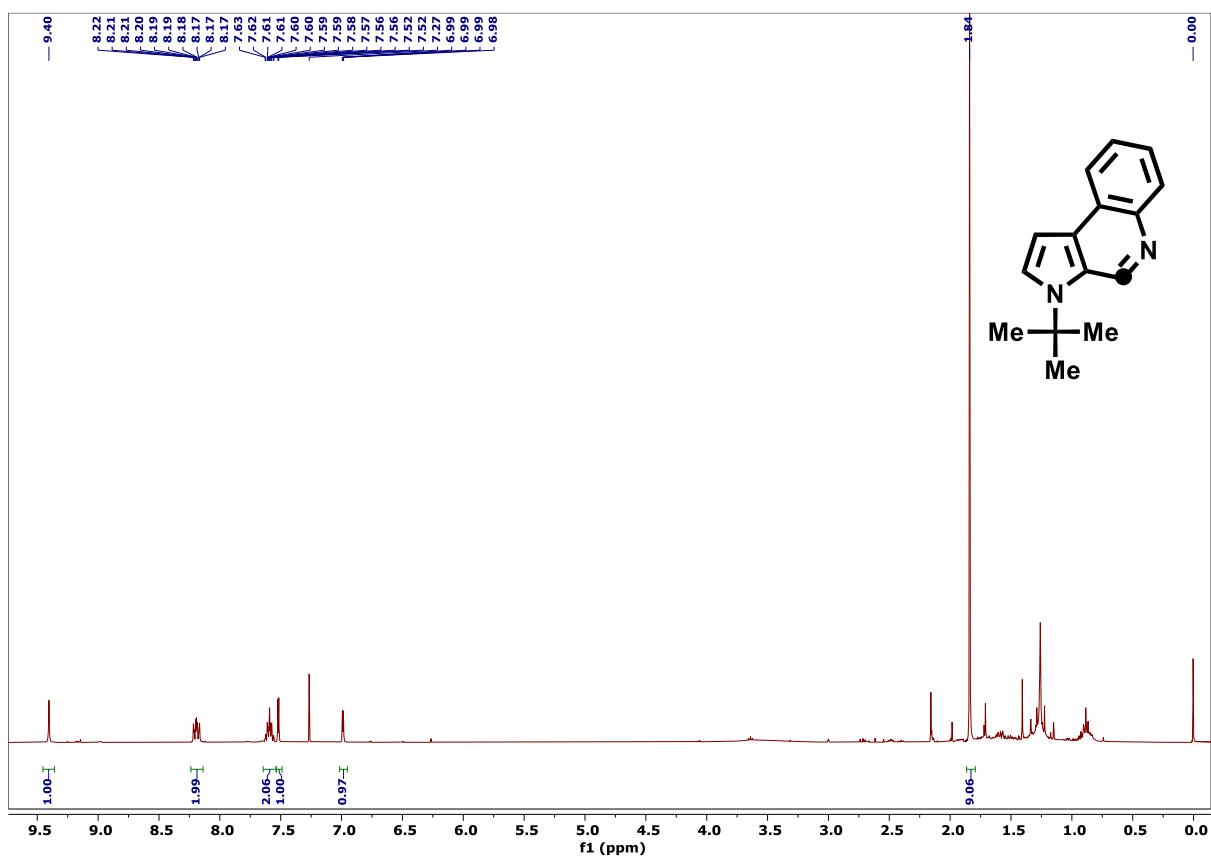
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of 3-cyclohexyl-3H-pyrrolo[2,3-c]quinoline (**4j**)



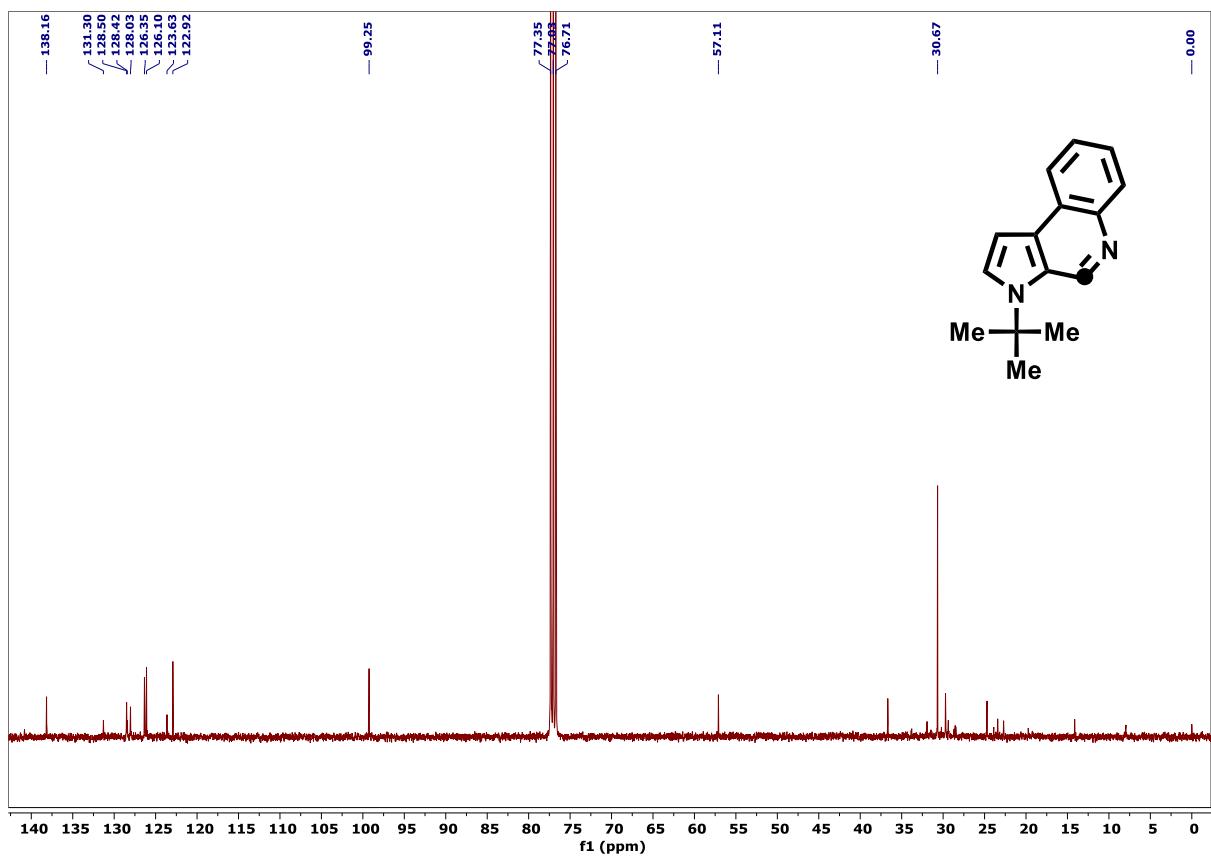
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of 3-cyclohexyl-3H-pyrrolo[2,3-c]quinoline (**4j**)



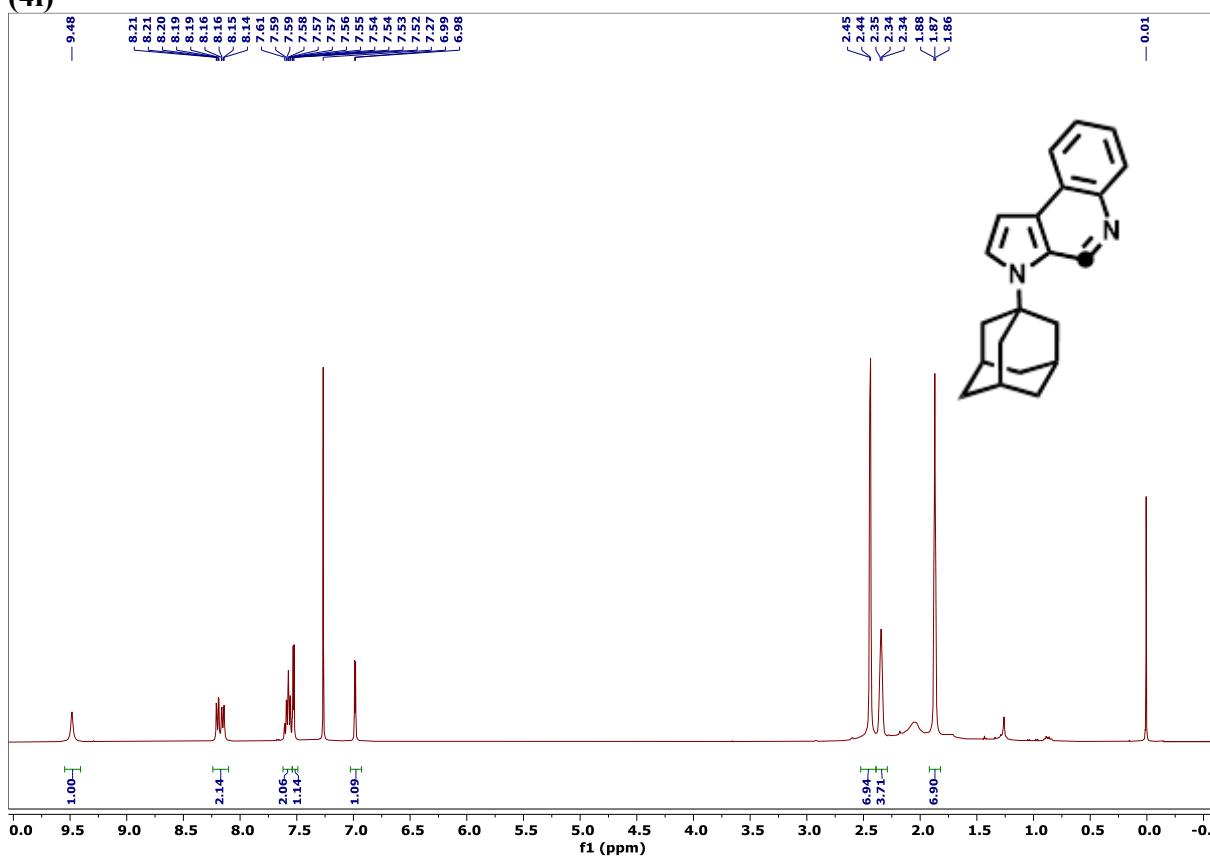
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 3-(tert-butyl)-3H-pyrrolo[2,3-c]quinoline (**4k**)



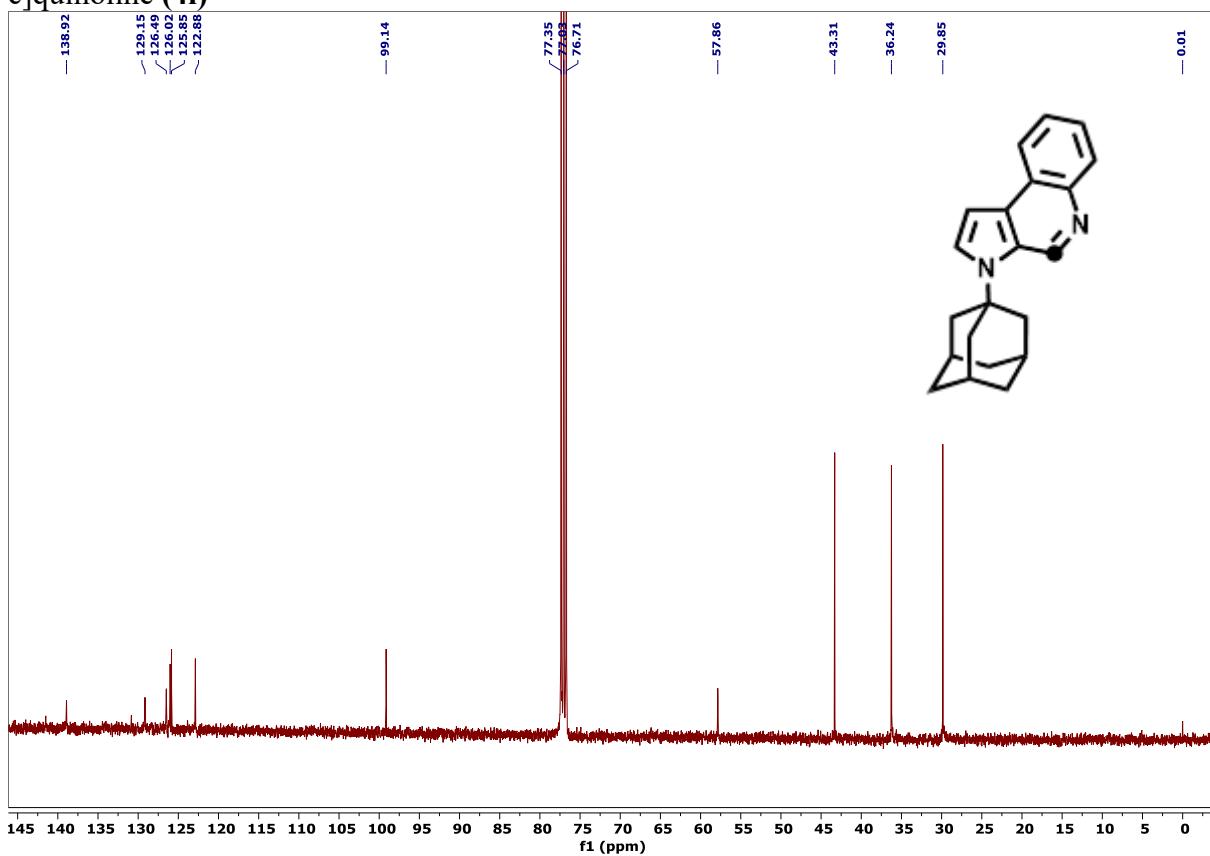
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 3-(tert-butyl)-3H-pyrrolo[2,3-c]quinoline (**4k**)



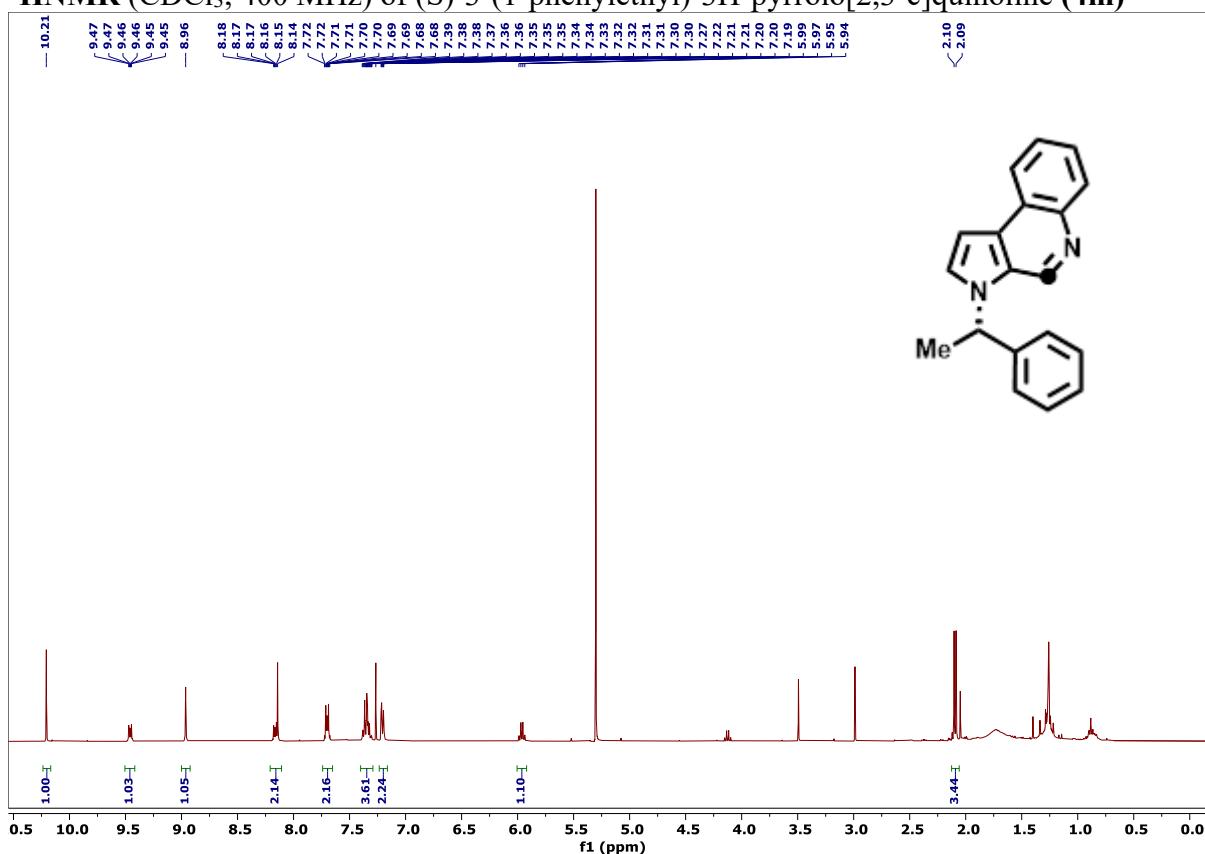
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 3-((3s,5s,7s)-adamantan-1-yl)-3H-pyrrolo[2,3-c]quinoline (**4l**)



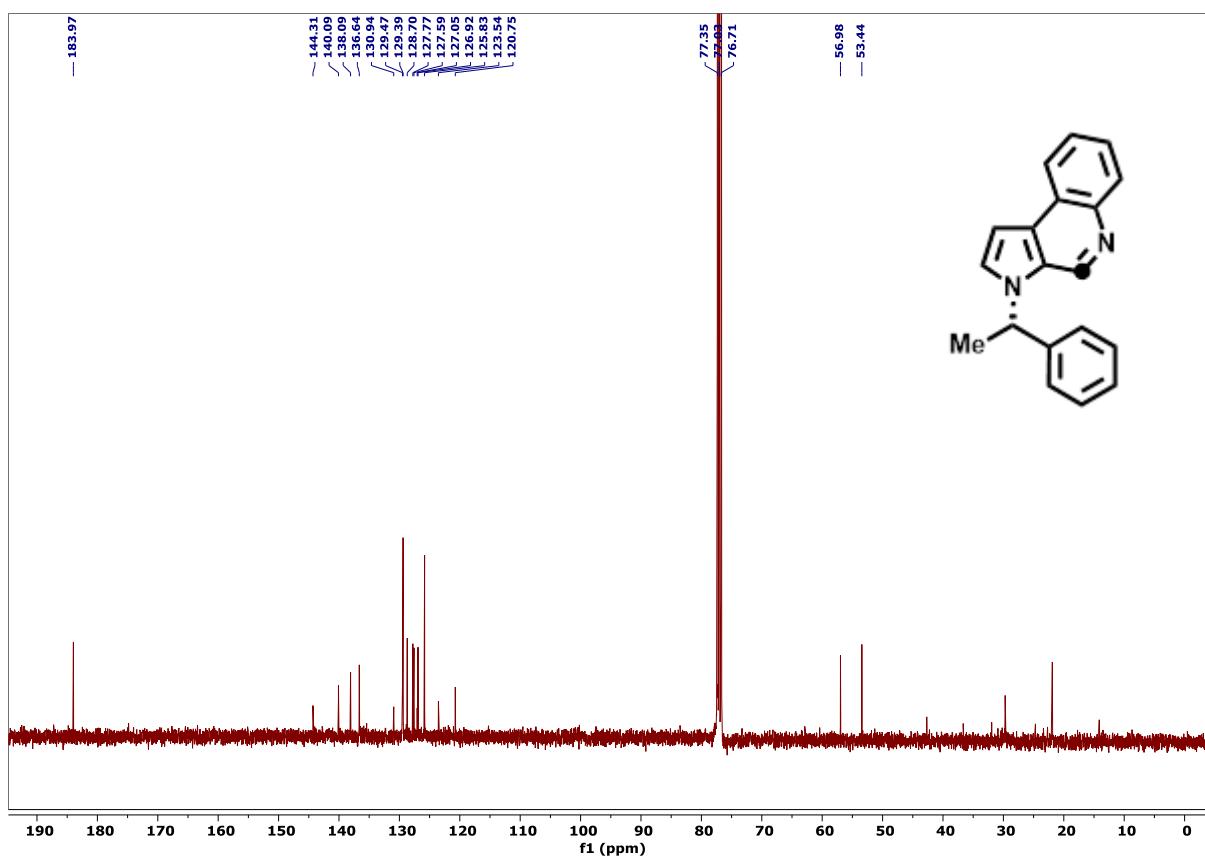
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 3-((3s,5s,7s)-adamantan-1-yl)-3H-pyrrolo[2,3-c]quinoline (**4l**)



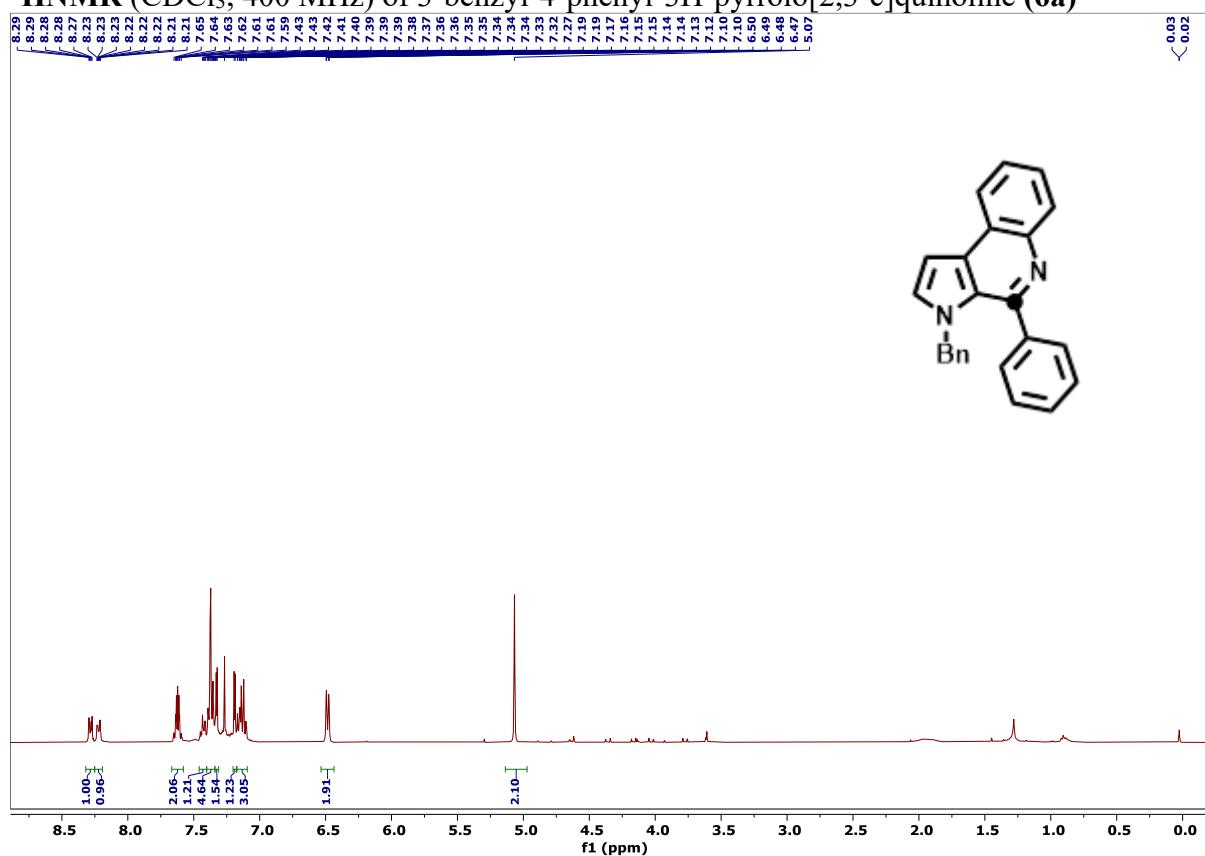
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of (S)-3-(1-phenylethyl)-3H-pyrrolo[2,3-c]quinoline (**4m**)**



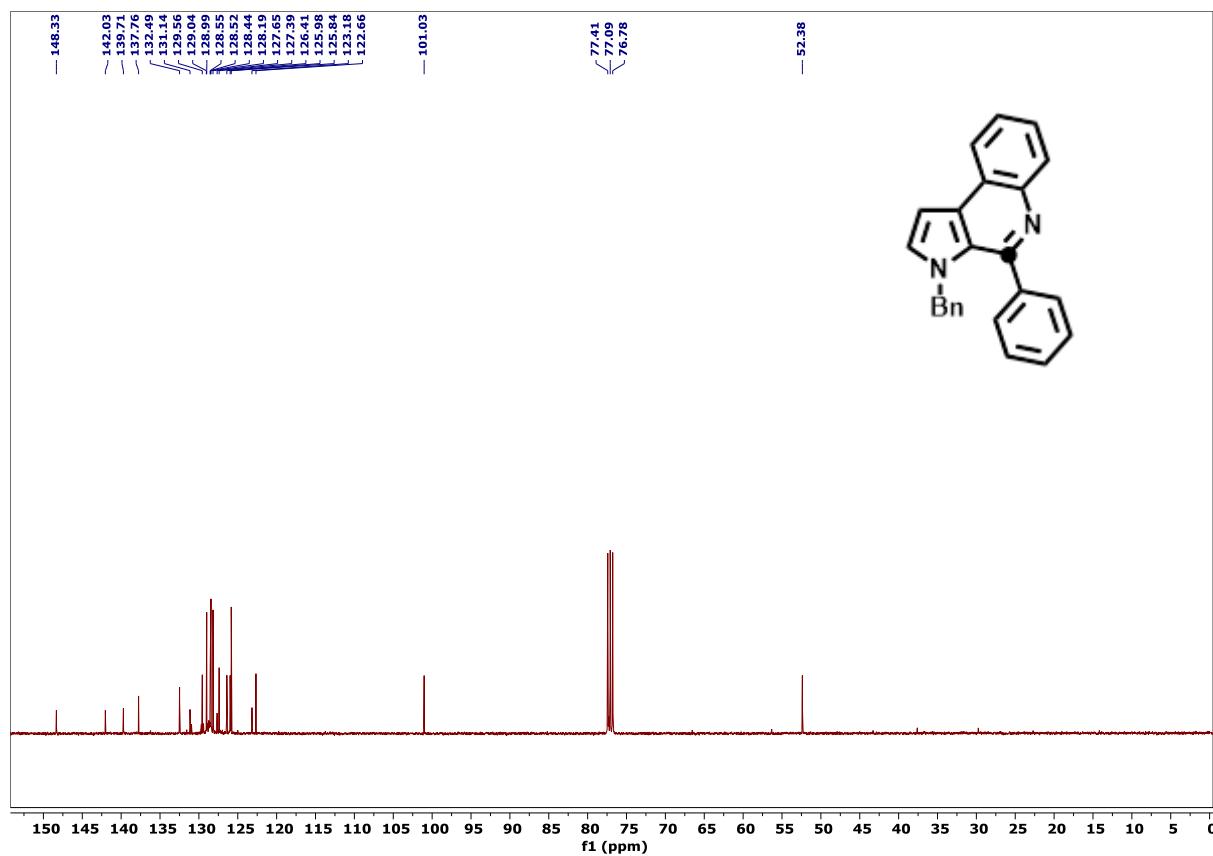
**<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of (S)-3-(1-phenylethyl)-3H-pyrrolo[2,3-c]quinoline (**4m**)**



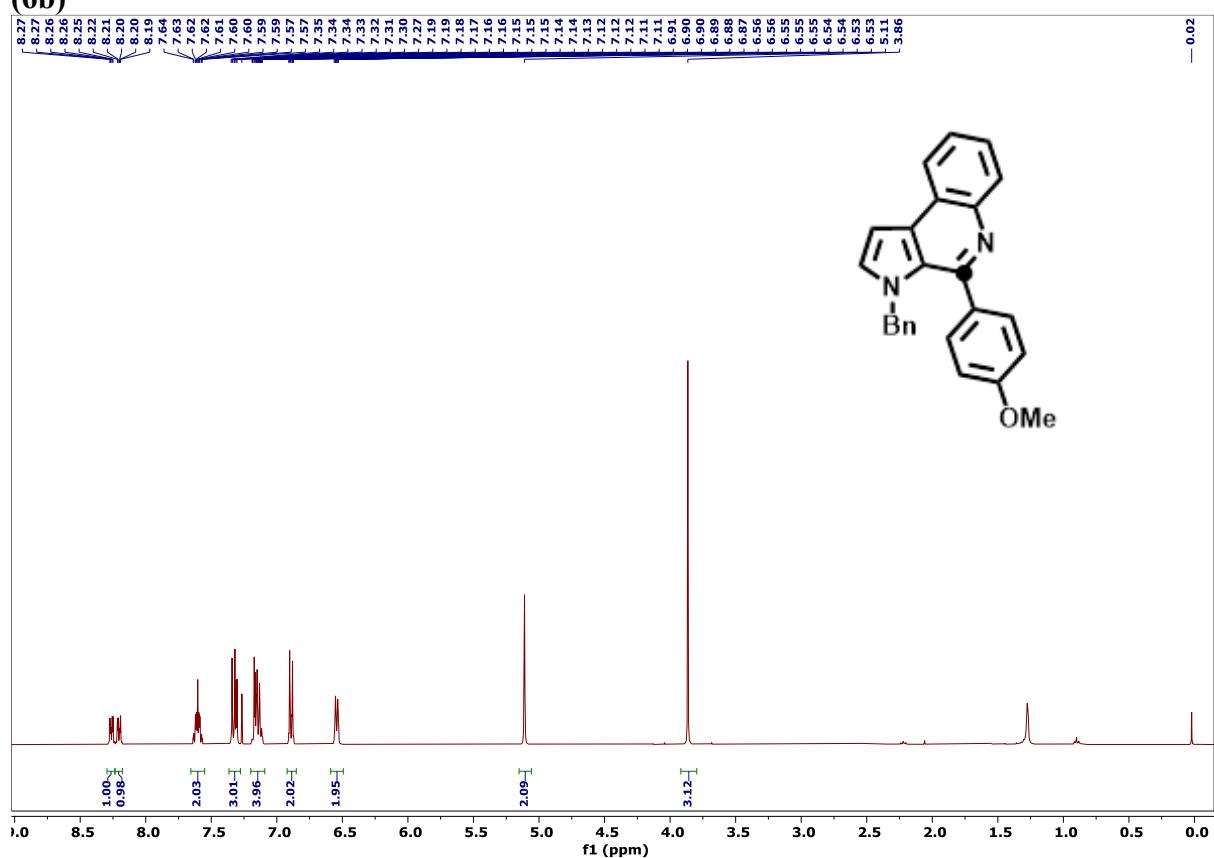
<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz) of 3-benzyl-4-phenyl-3H-pyrrolo[2,3-c]quinoline (**6a**)



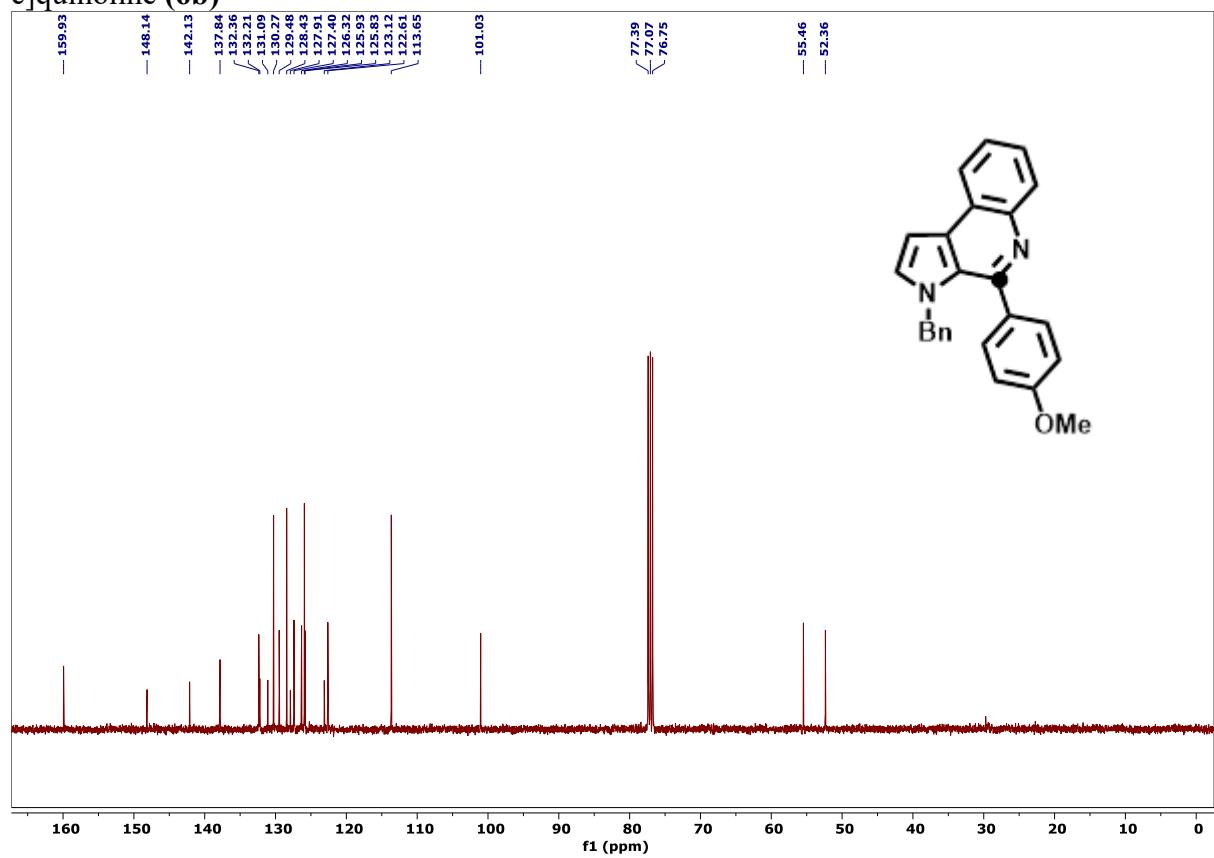
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of 3-benzyl-4-phenyl-3H-pyrrolo[2,3-c]quinoline (**6a**)



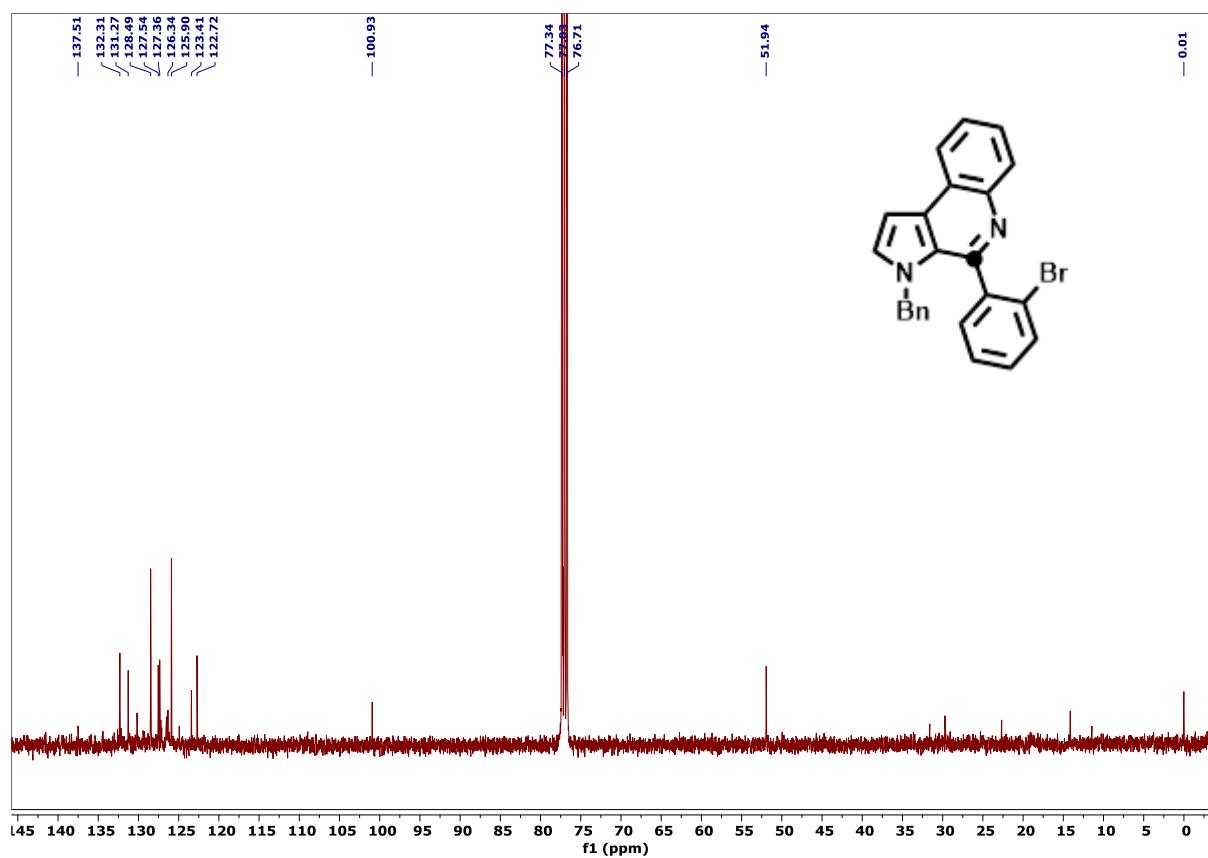
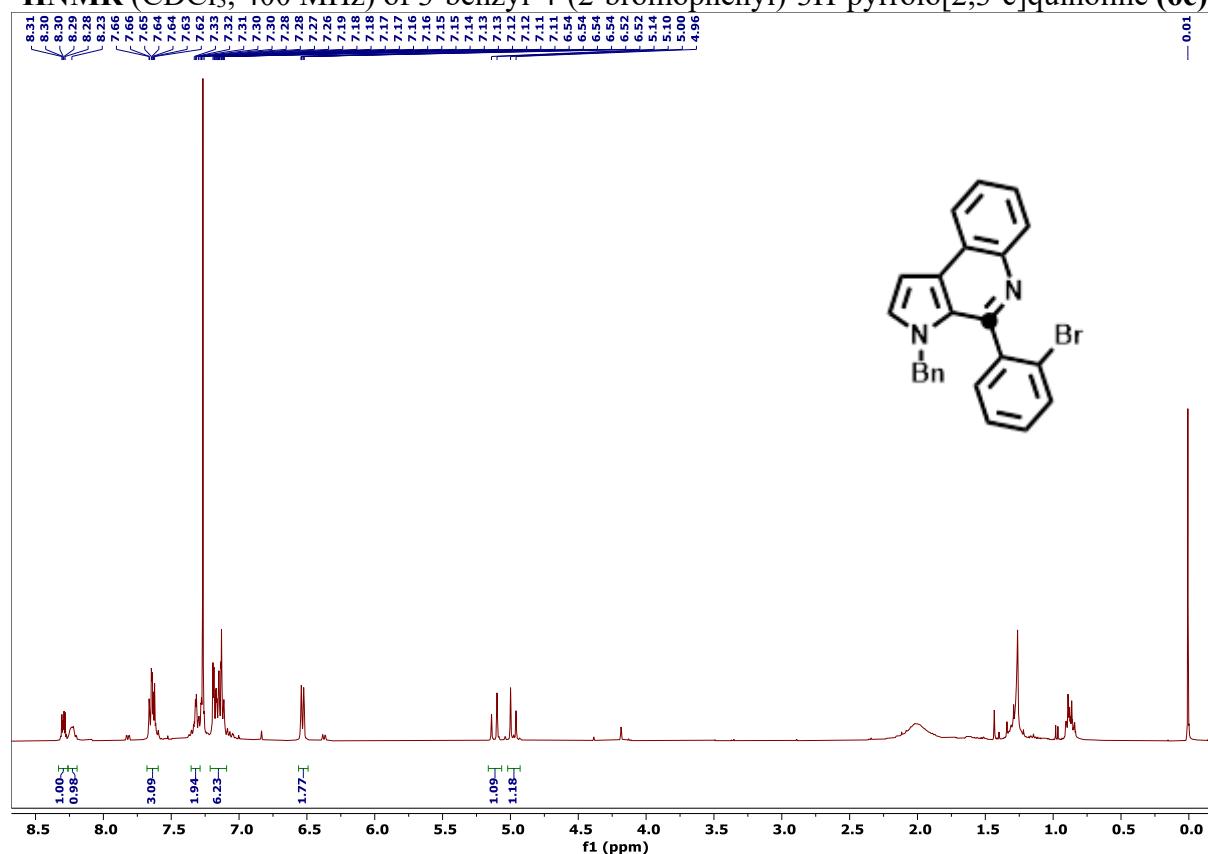
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 3-benzyl-4-(4-methoxyphenyl)-3H-pyrrolo[2,3-c]quinoline (**6b**)



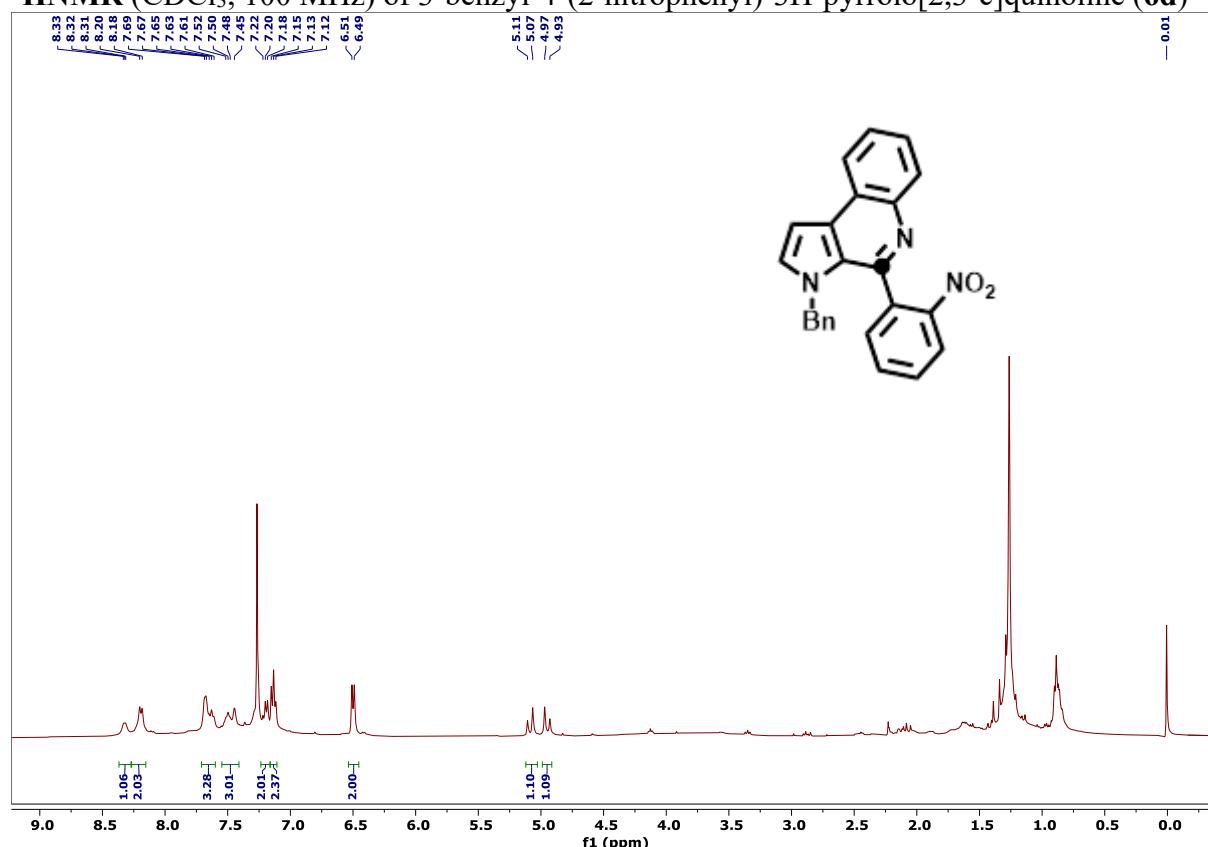
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 3-benzyl-4-(4-methoxyphenyl)-3H-pyrrolo[2,3-c]quinoline (**6b**)



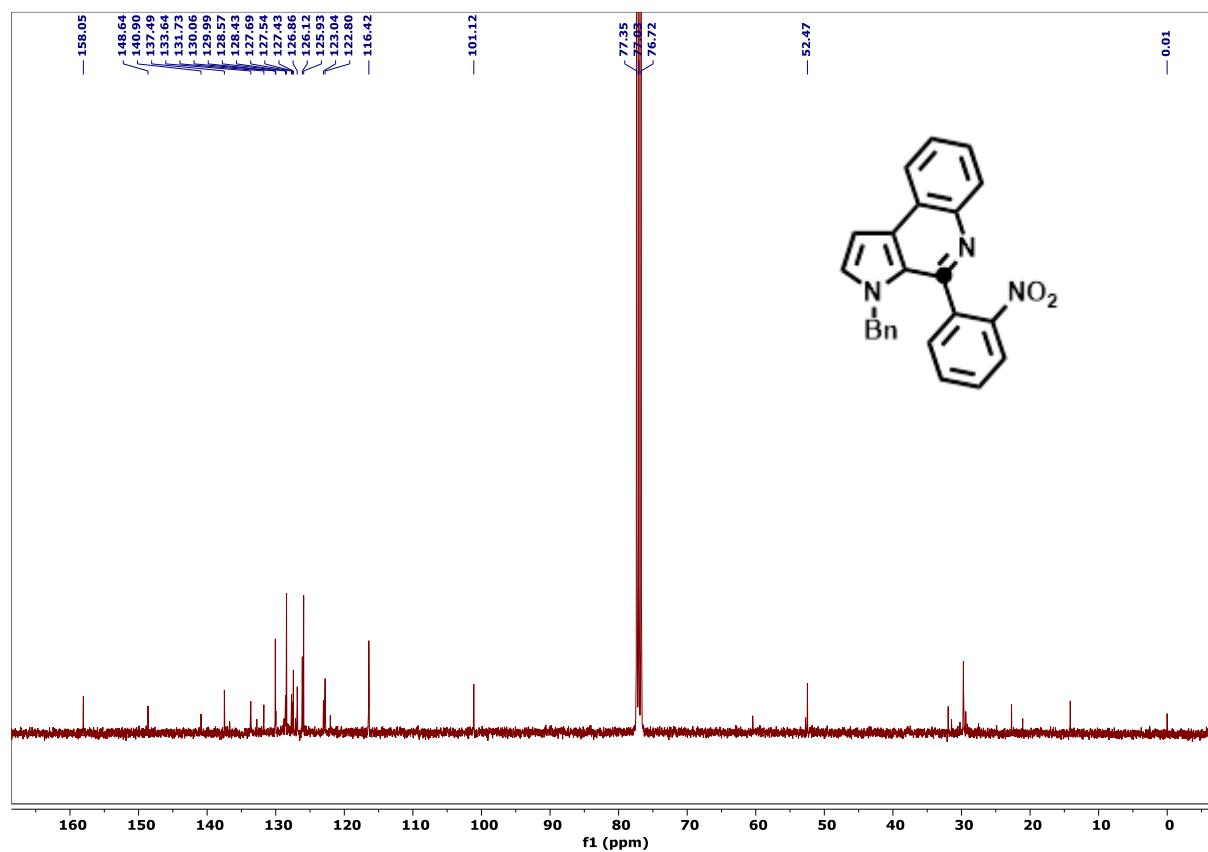
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of 3-benzyl-4-(2-bromophenyl)-3H-pyrrolo[2,3-c]quinoline (**6c**)**



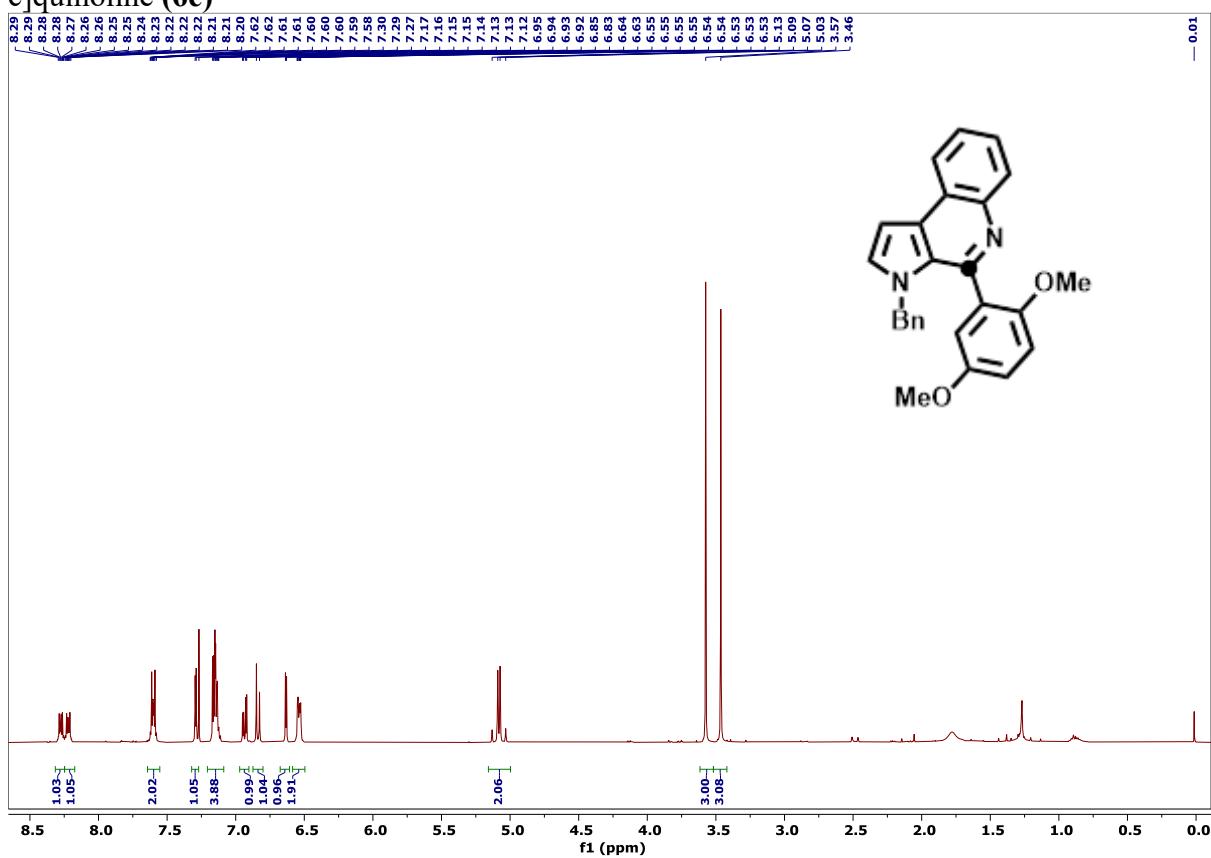
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 100 MHz) of 3-benzyl-4-(2-nitrophenyl)-3H-pyrrolo[2,3-c]quinoline (**6d**)**



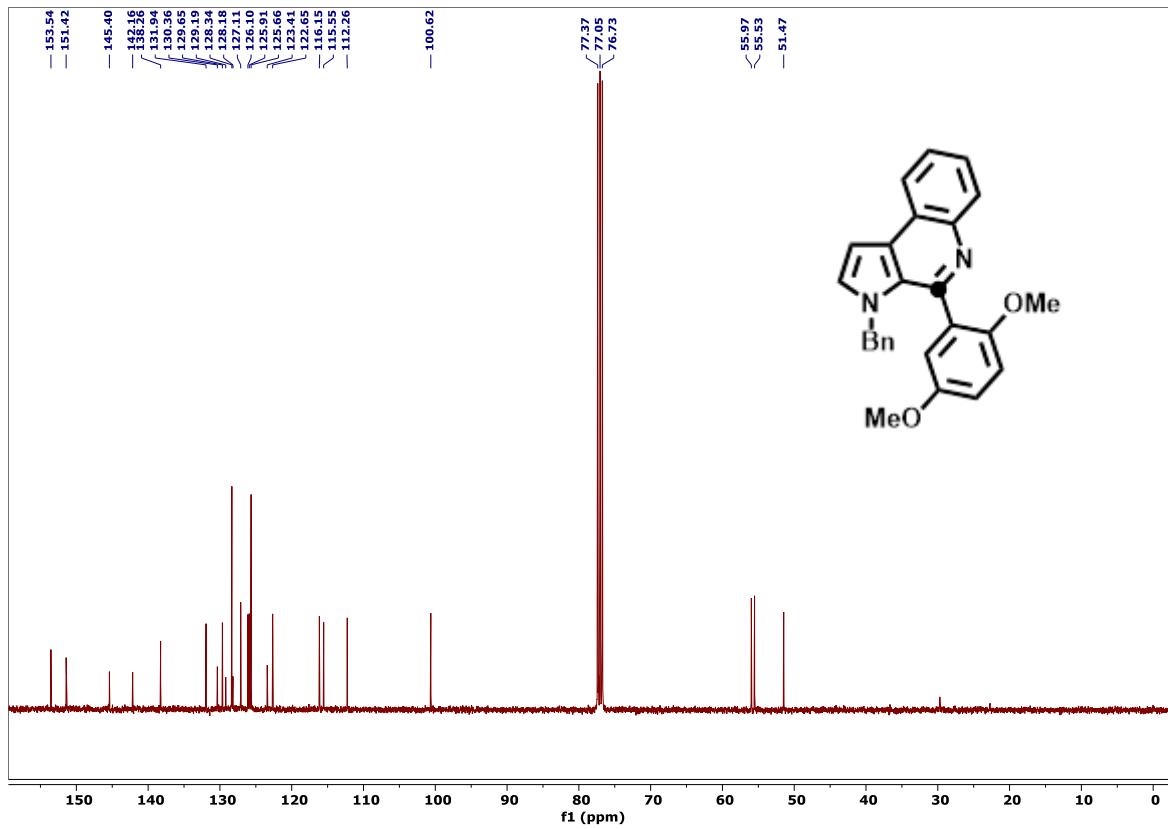
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 100 MHz) of 3-benzyl-4-(2-nitrophenyl)-3H-pyrrolo[2,3-c]quinoline (**6d**)**



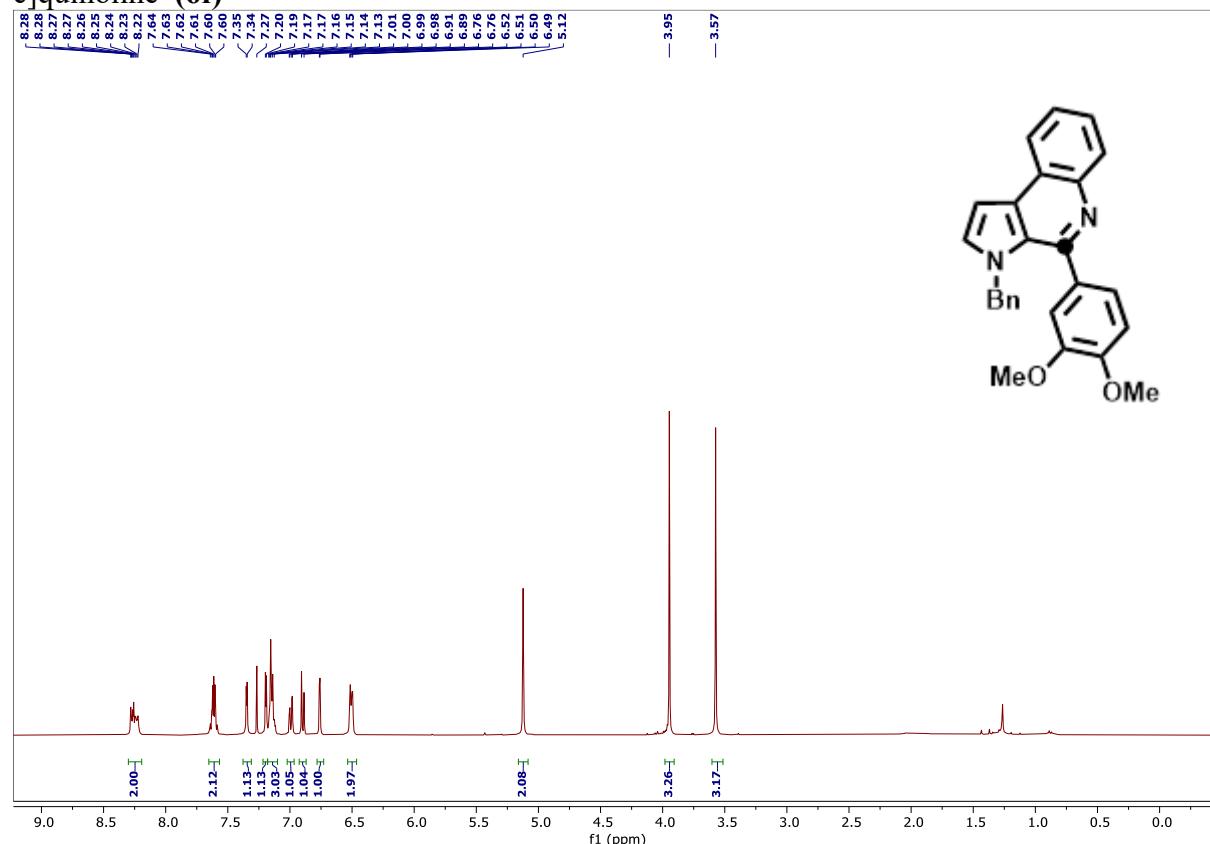
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 3-benzyl-4-(2,5-dimethoxyphenyl)-3H-pyrrolo[2,3-c]quinoline (6e)



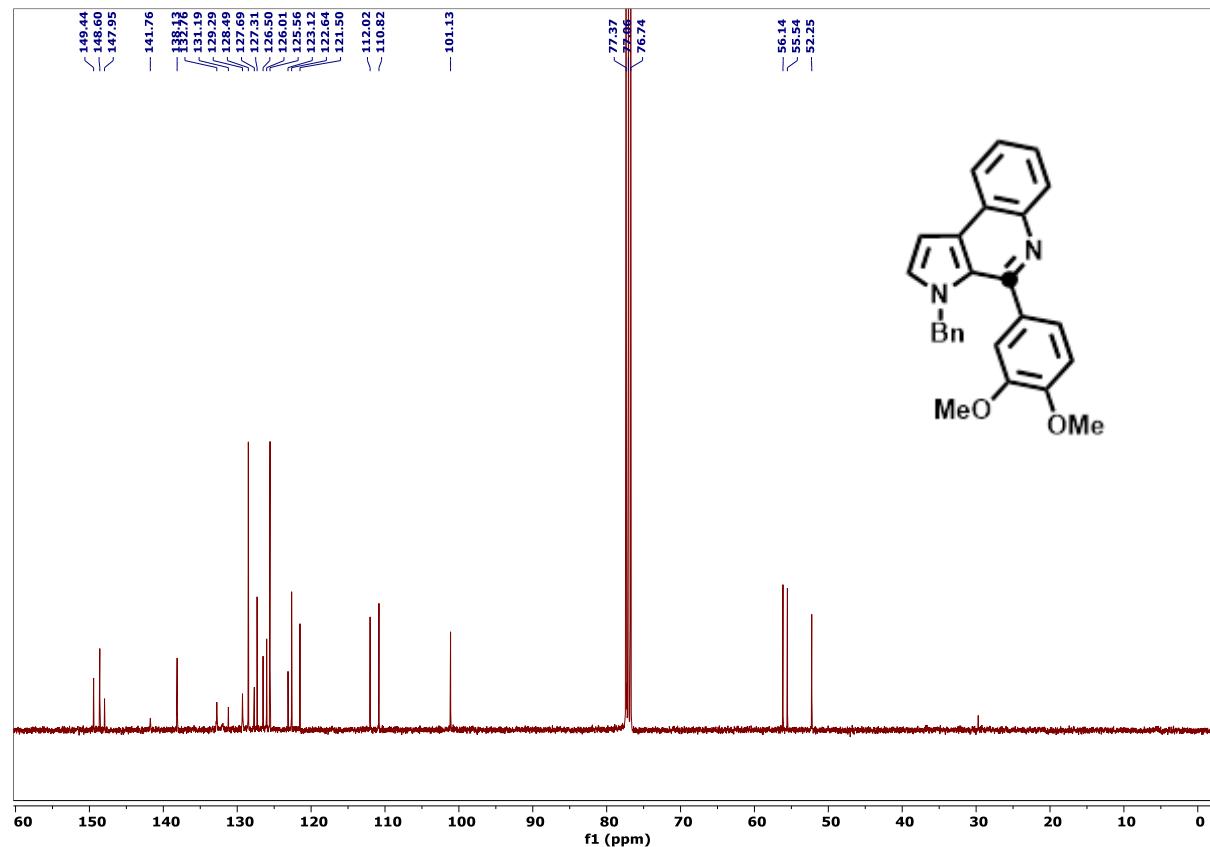
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of 3-benzyl-4-(2,5-dimethoxyphenyl)-3H-pyrrolo[2,3-c]quinoline (**6e**)



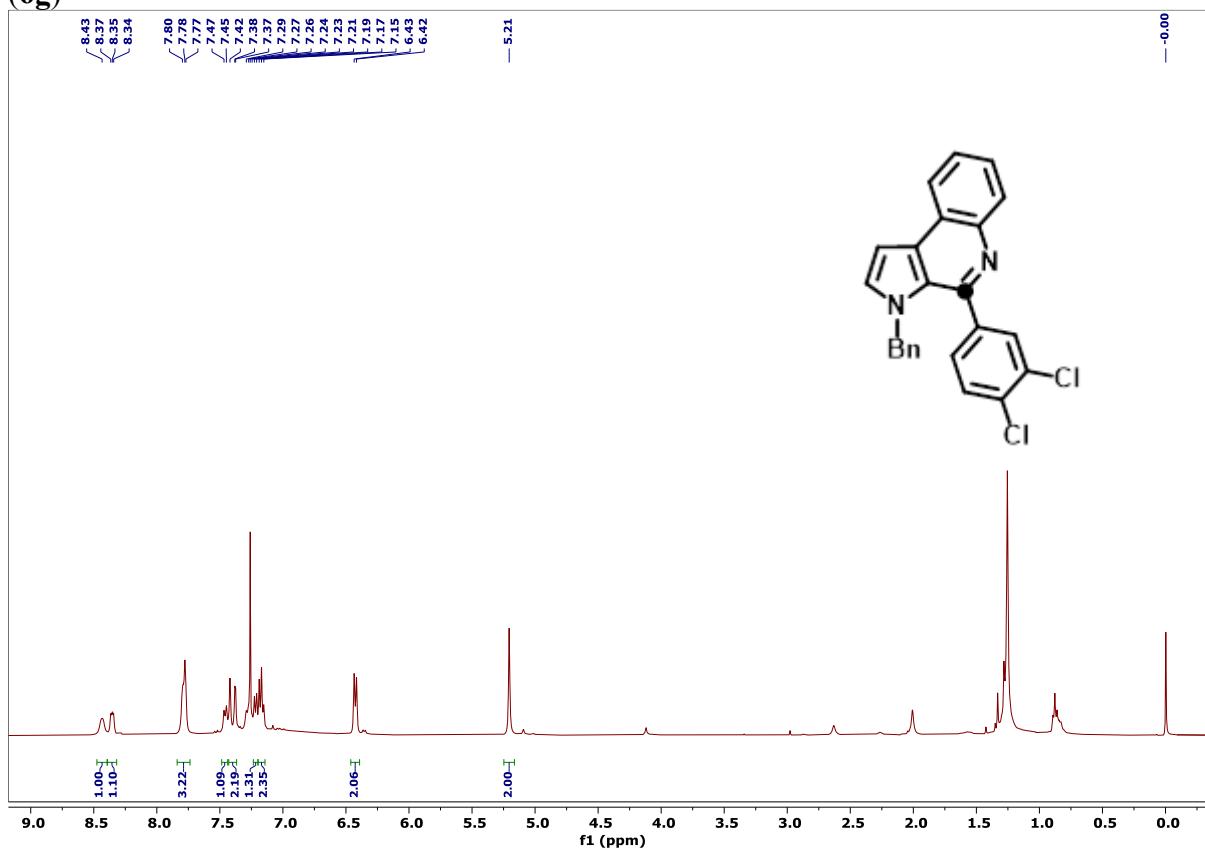
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 3-benzyl-4-(3,4-dimethoxyphenyl)-3H-pyrrolo[2,3-c]quinoline (**6f**)



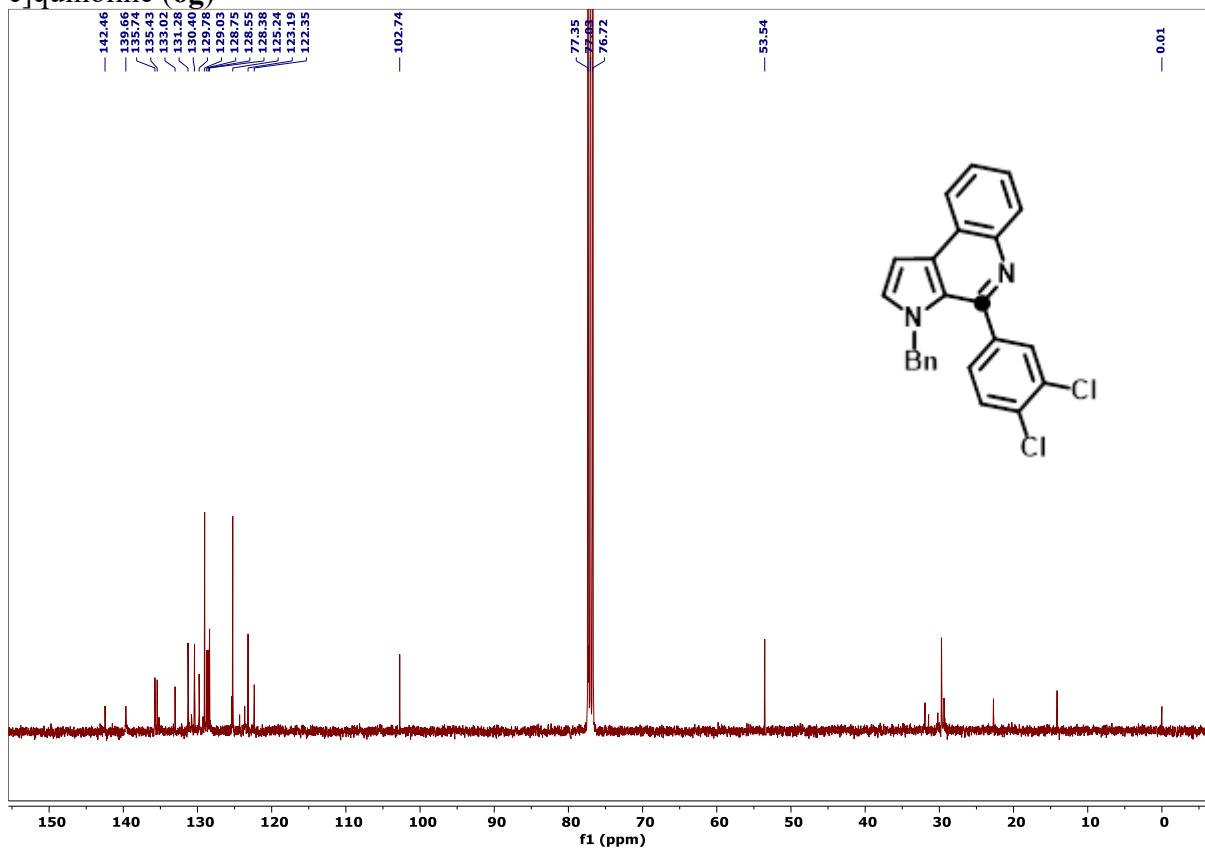
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 3-benzyl-4-(3,4-dimethoxyphenyl)-3H-pyrrolo[2,3-c]quinoline (**6f**)



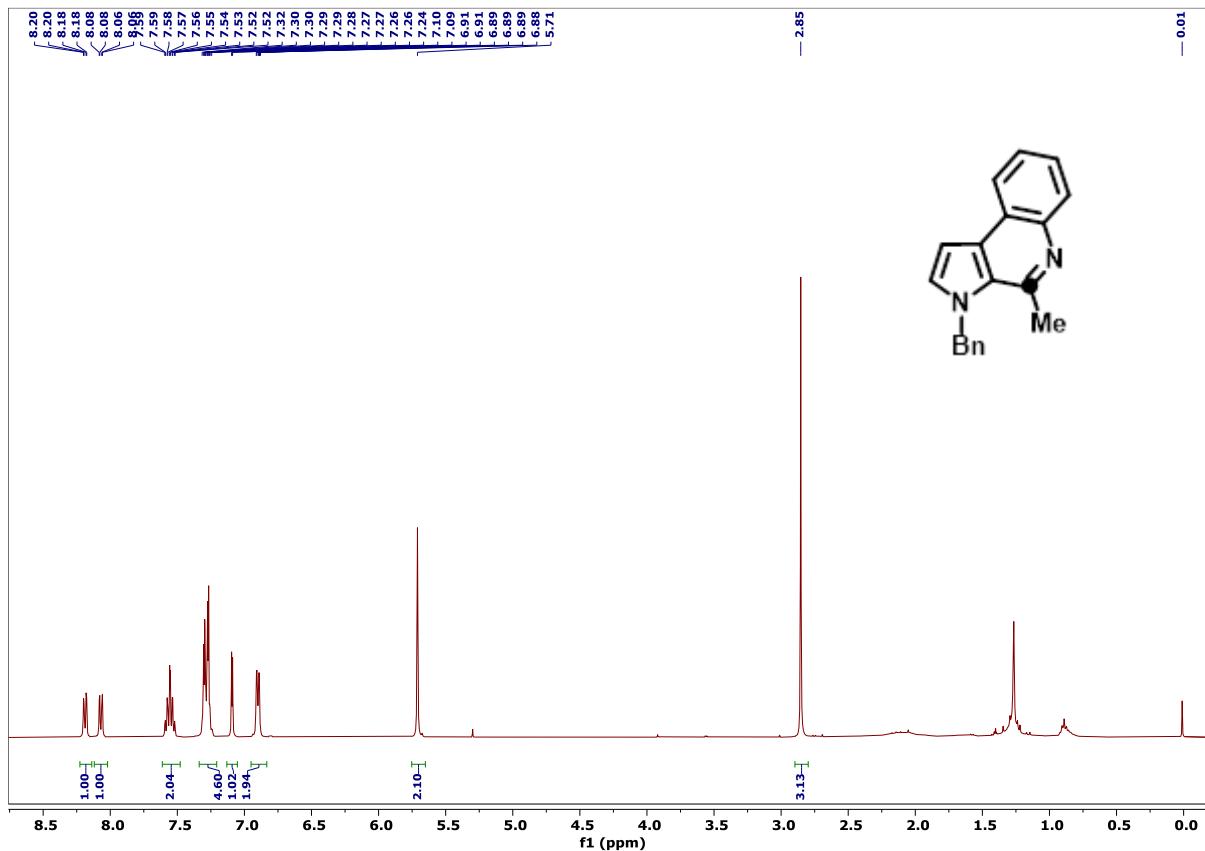
**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 3-benzyl-4-(3,4-dichlorophenyl)-3H-pyrrolo[2,3-c]quinoline (**6g**)



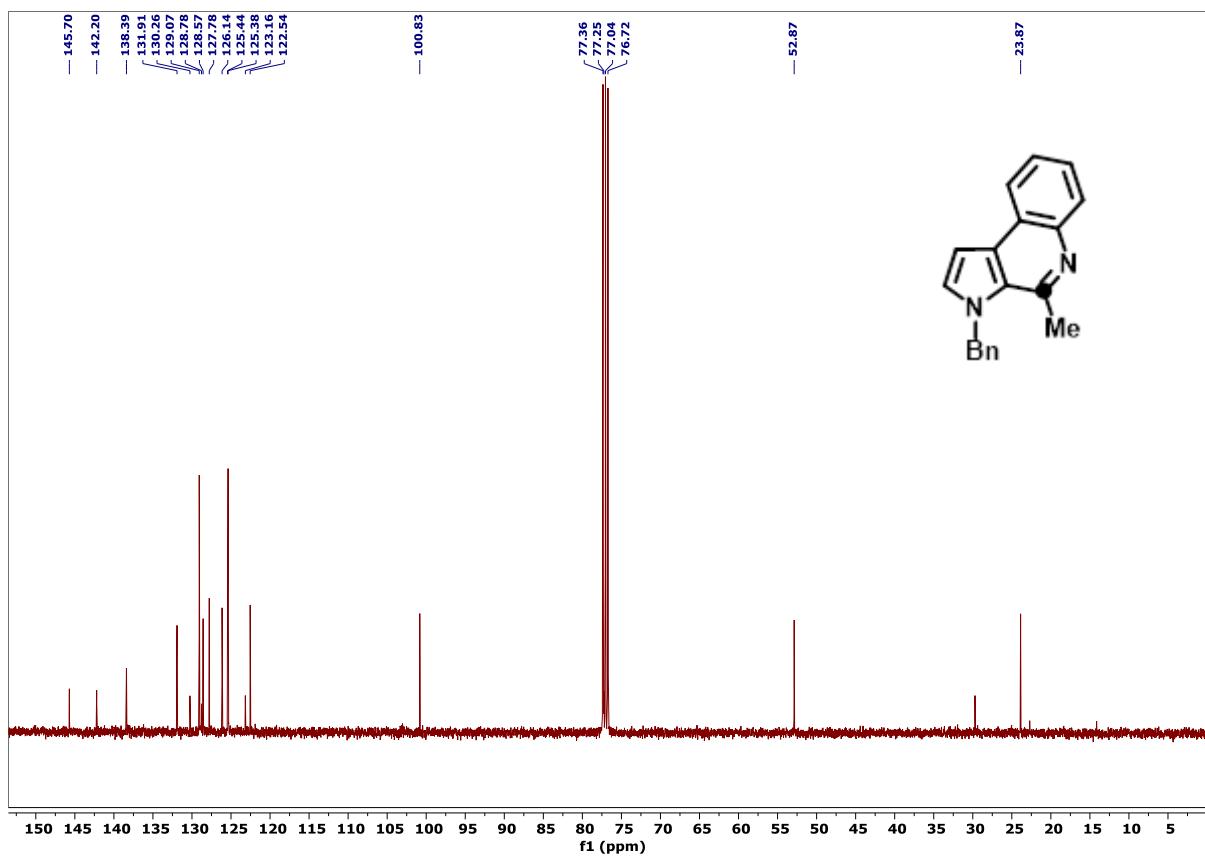
**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 3-benzyl-4-(3,4-dichlorophenyl)-3H-pyrrolo[2,3-c]quinoline (**6g**)



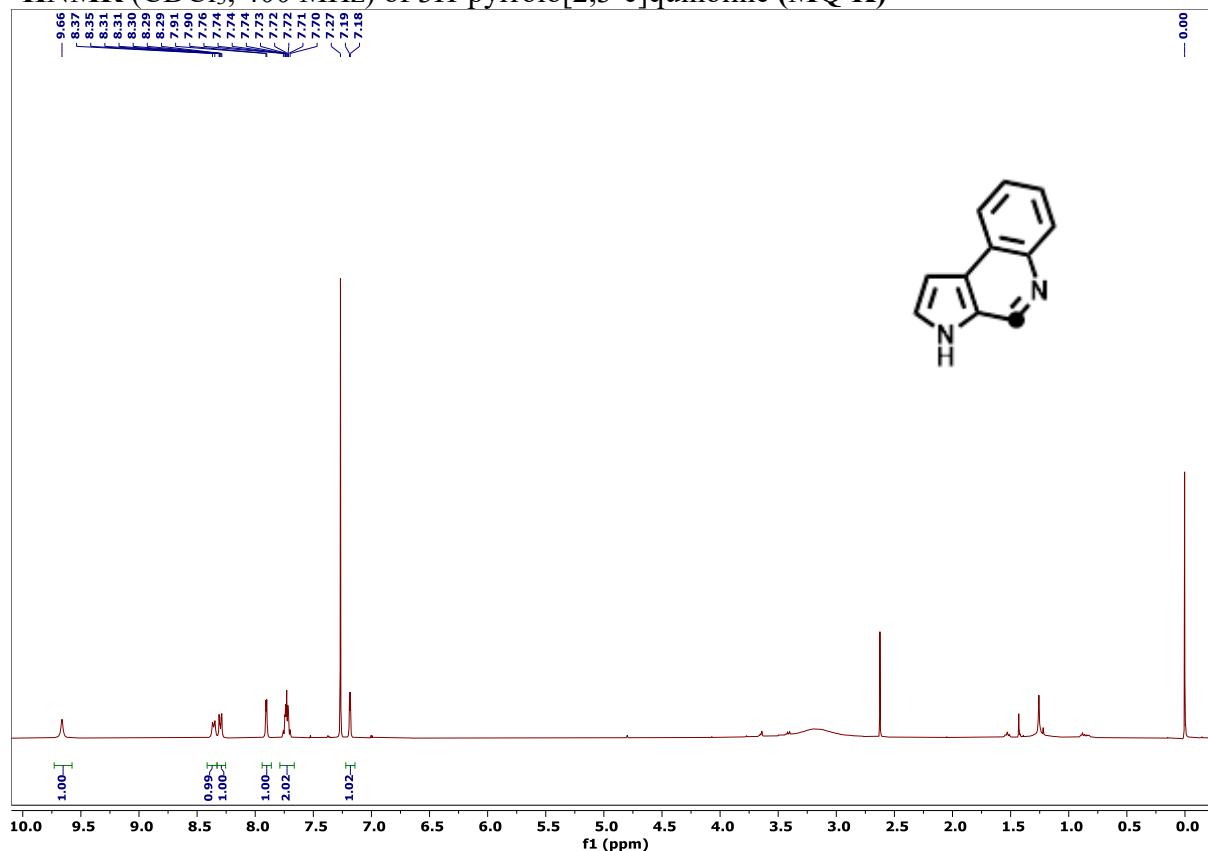
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of 3-benzyl-4-methyl-3H-pyrrolo[2,3-c]quinoline (**6h**)



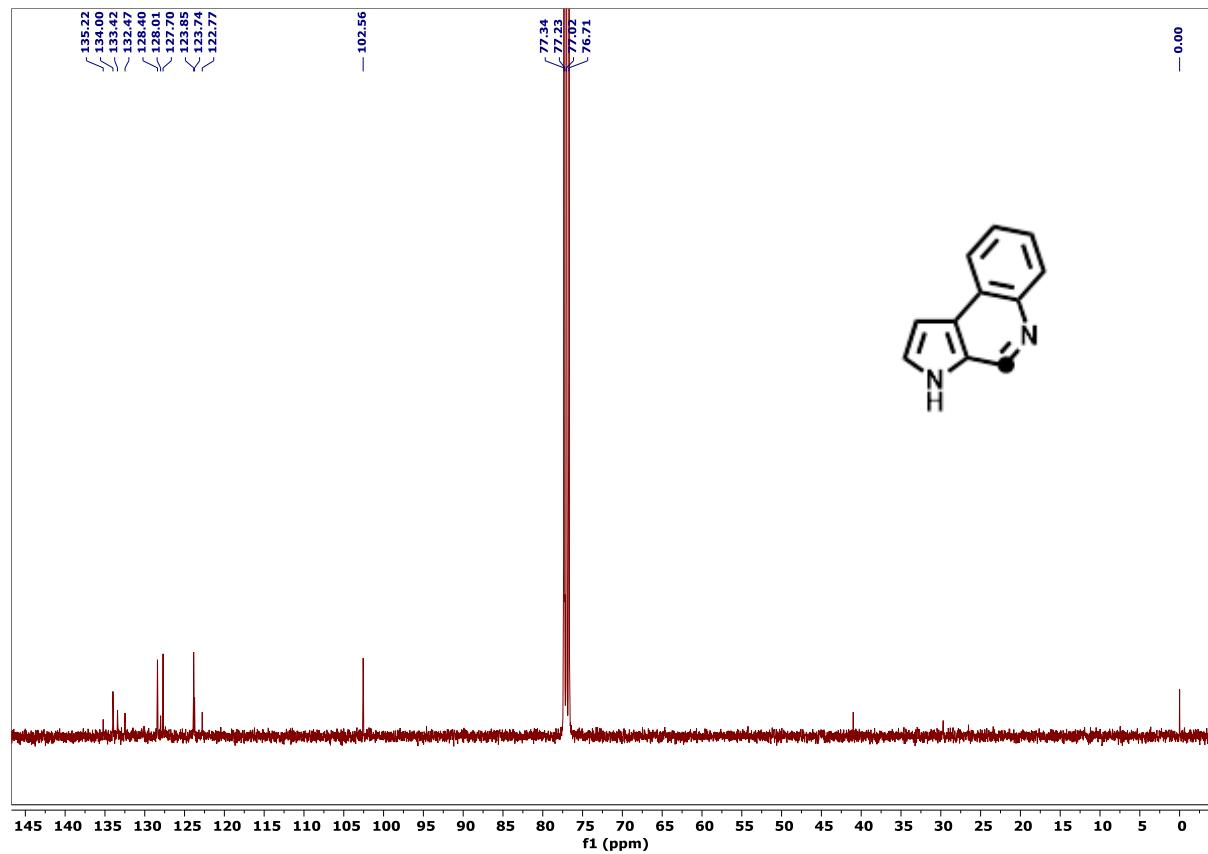
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of 3-benzyl-4-methyl-3H-pyrrolo[2,3-c]quinoline (**6h**)



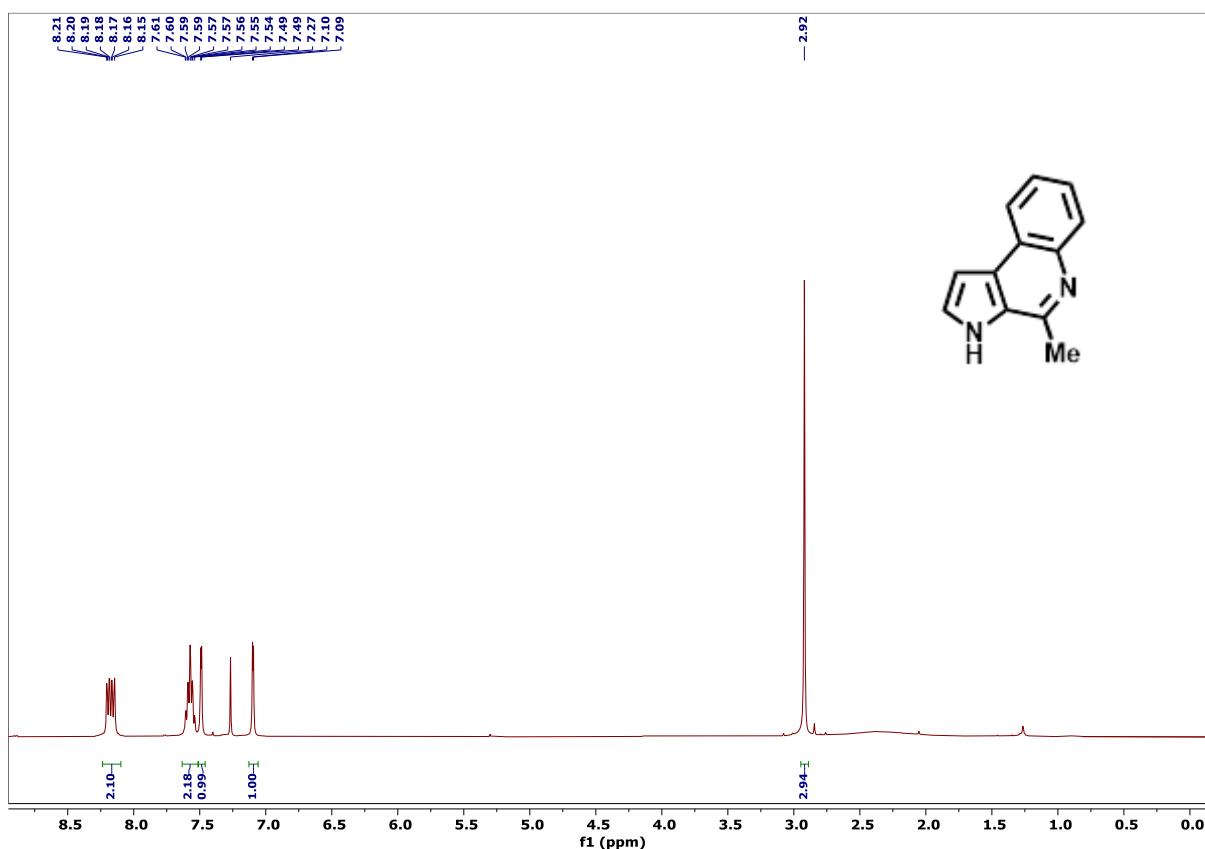
**$^1\text{H}$ NMR (CDCl<sub>3</sub>, 400 MHz) of 3H-pyrrolo[2,3-c]quinoline (**MQ K**)**



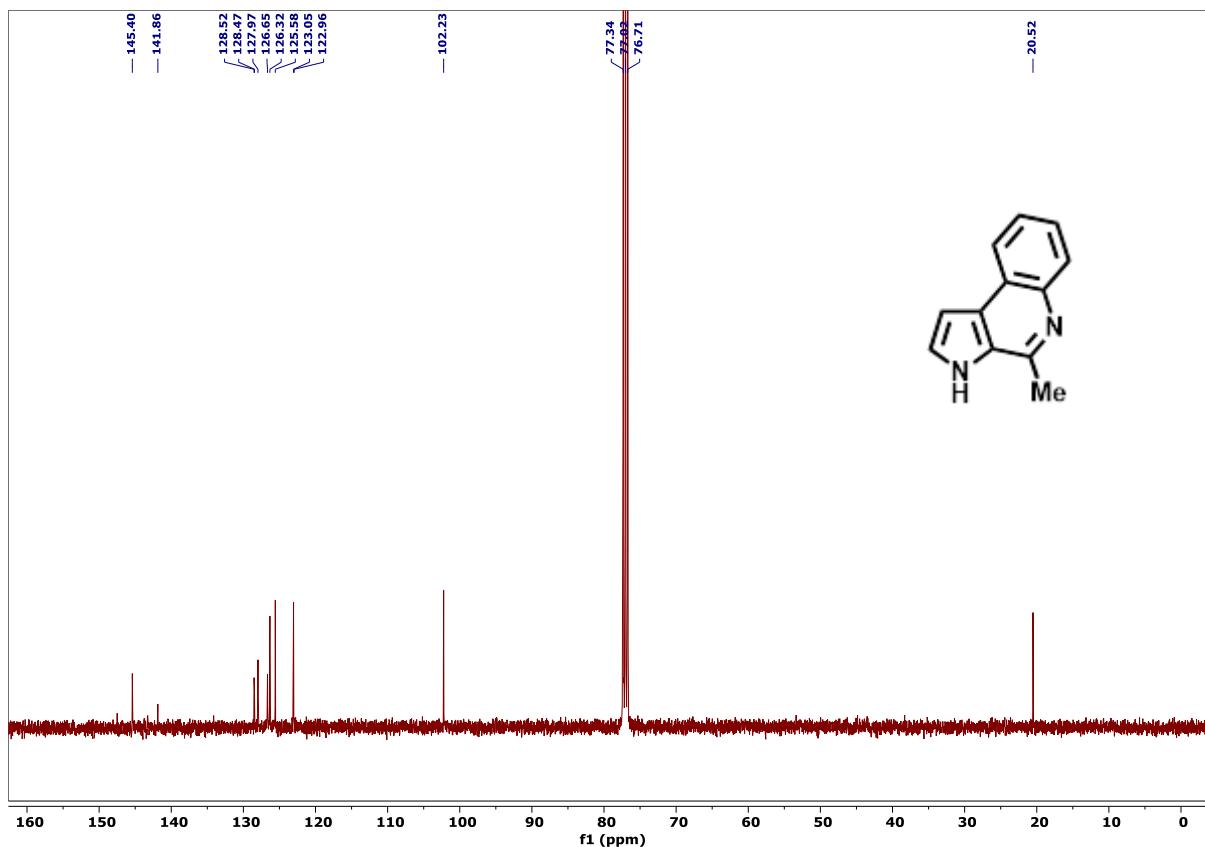
**$^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 100 MHz) of 3H-pyrrolo[2,3-c]quinoline (**MQ K**)**



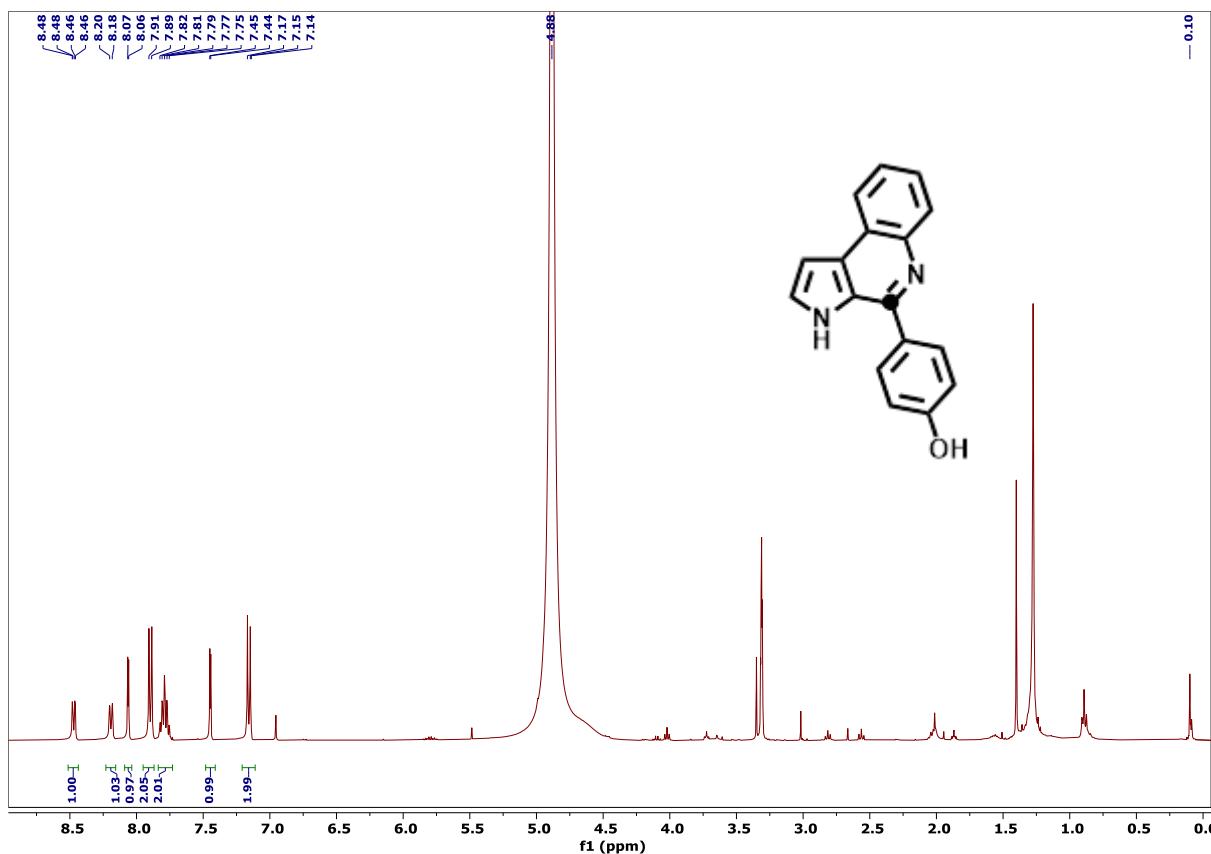
**$^1\text{H}$ NMR** ( $\text{CDCl}_3$ , 400 MHz) of 4-methyl-3H-pyrrolo[2,3-c]quinoline (**MQ A**)



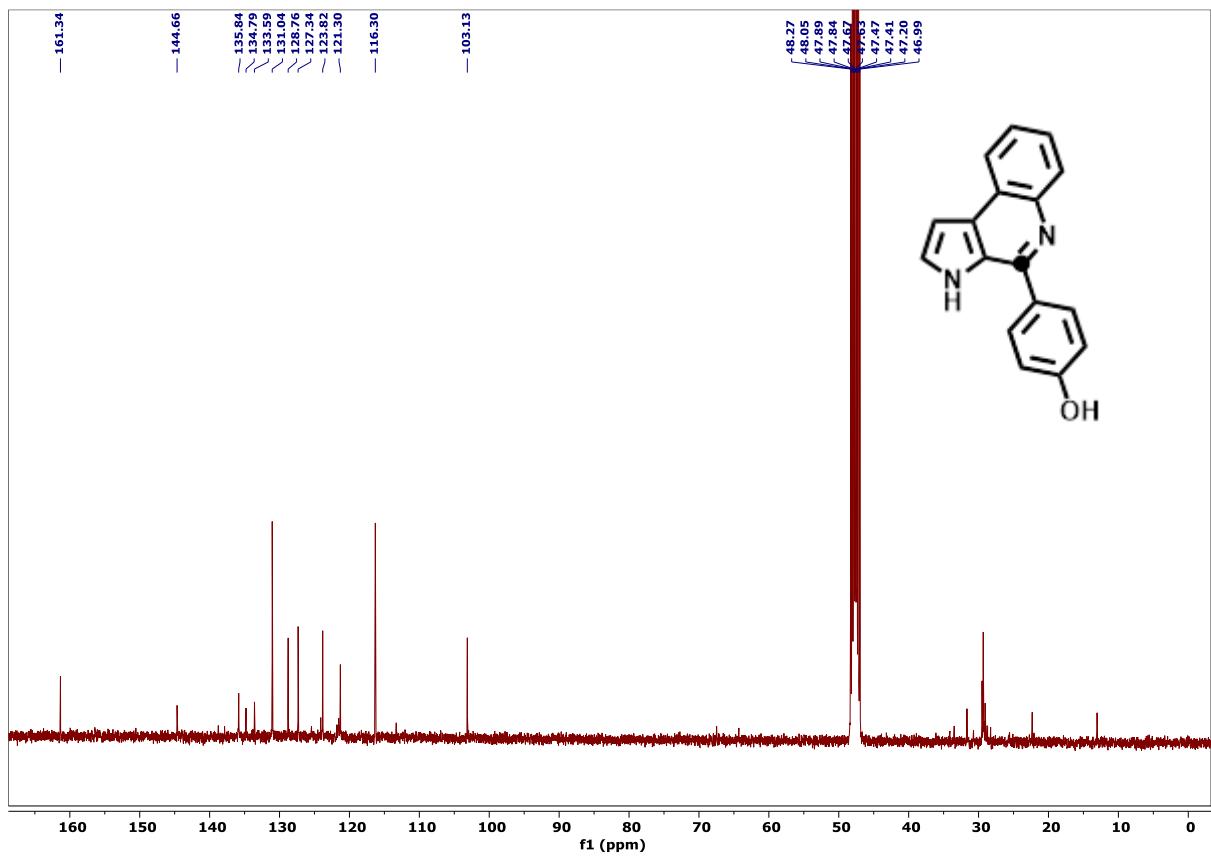
**$^{13}\text{C}\{^1\text{H}\}$  NMR** ( $\text{CDCl}_3$ , 100 MHz) of 4-methyl-3H-pyrrolo[2,3-c]quinoline (**MQ A**)



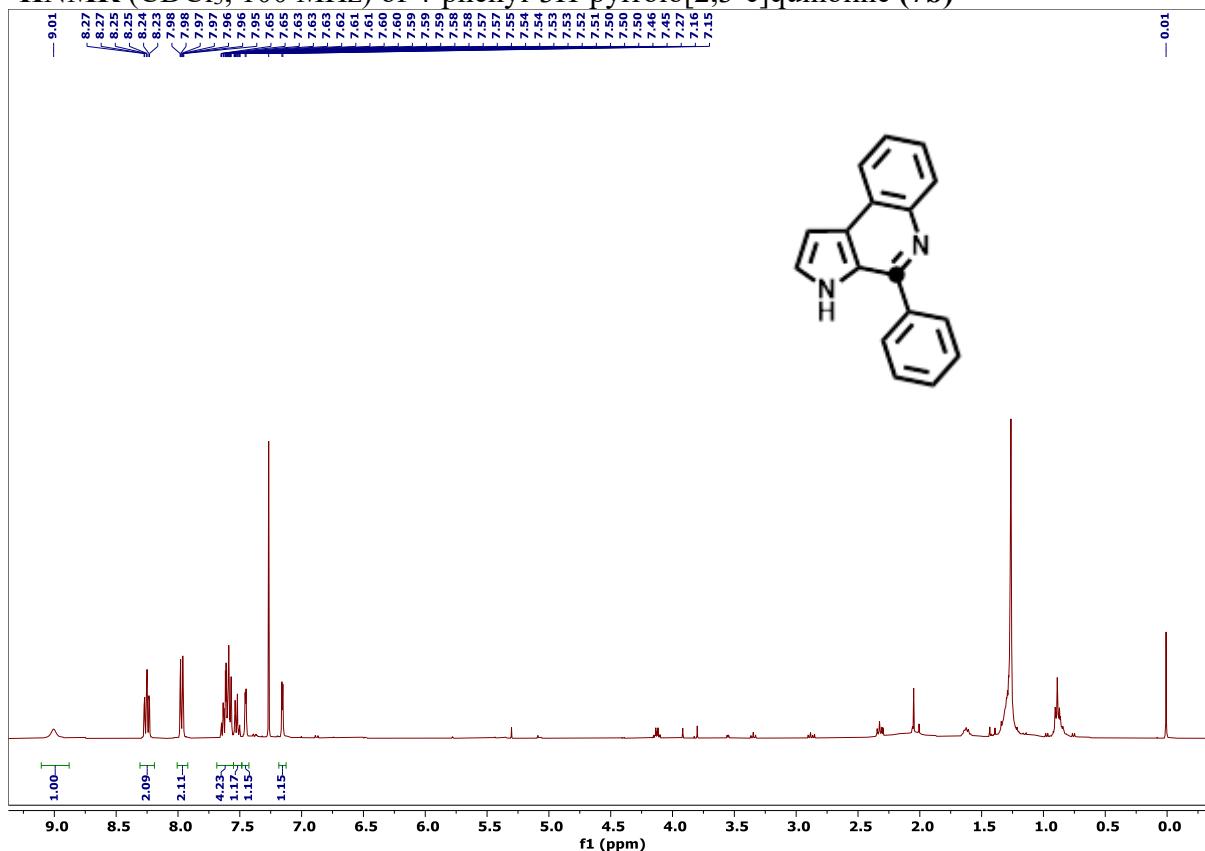
**$^1\text{H}$ NMR** ( $\text{MeOD}$ , 400 MHz) of 4-(3H-pyrrolo[2,3-c]quinolin-4-yl)phenol (**MQ H**)



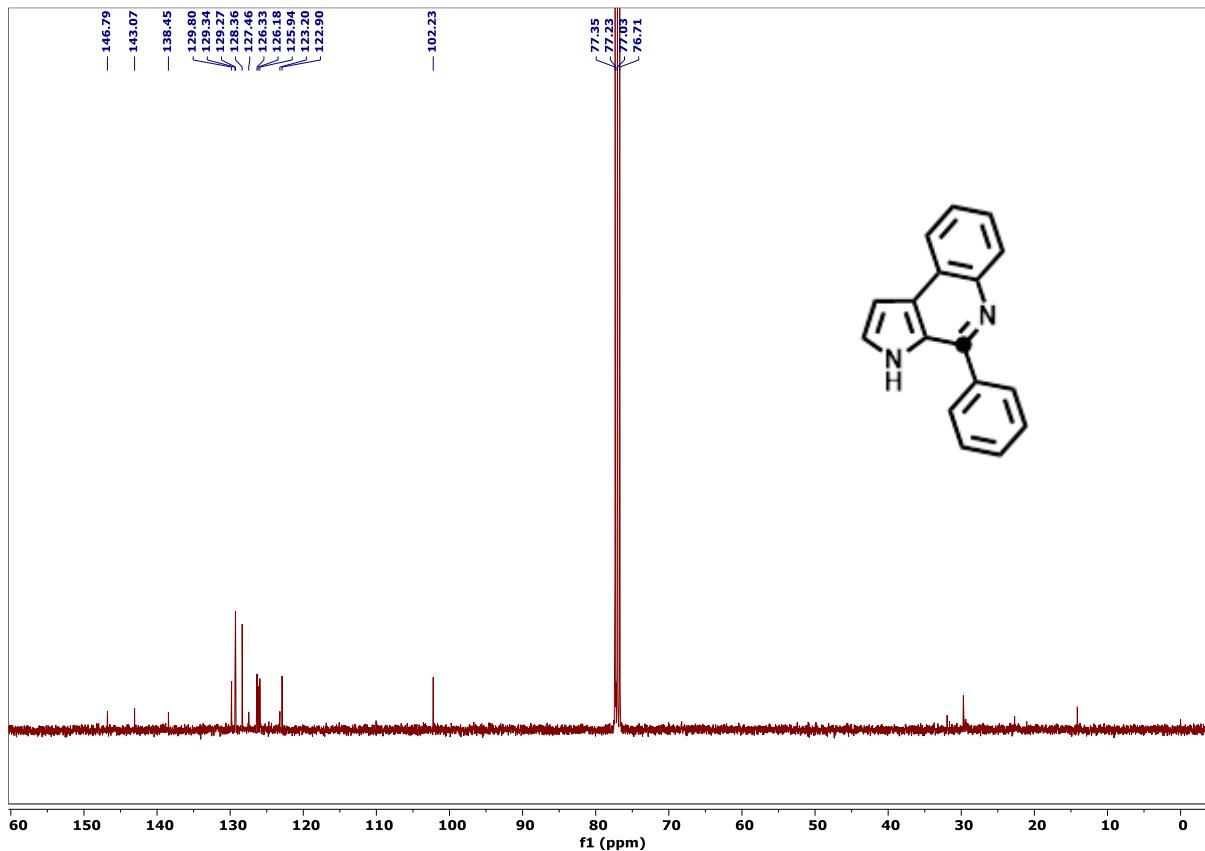
$^{13}\text{C}\{\text{H}\}$  NMR (MeOD, 100 MHz) of 4-(3H-pyrrolo[2,3-c]quinolin-4-yl)phenol (MQ H)



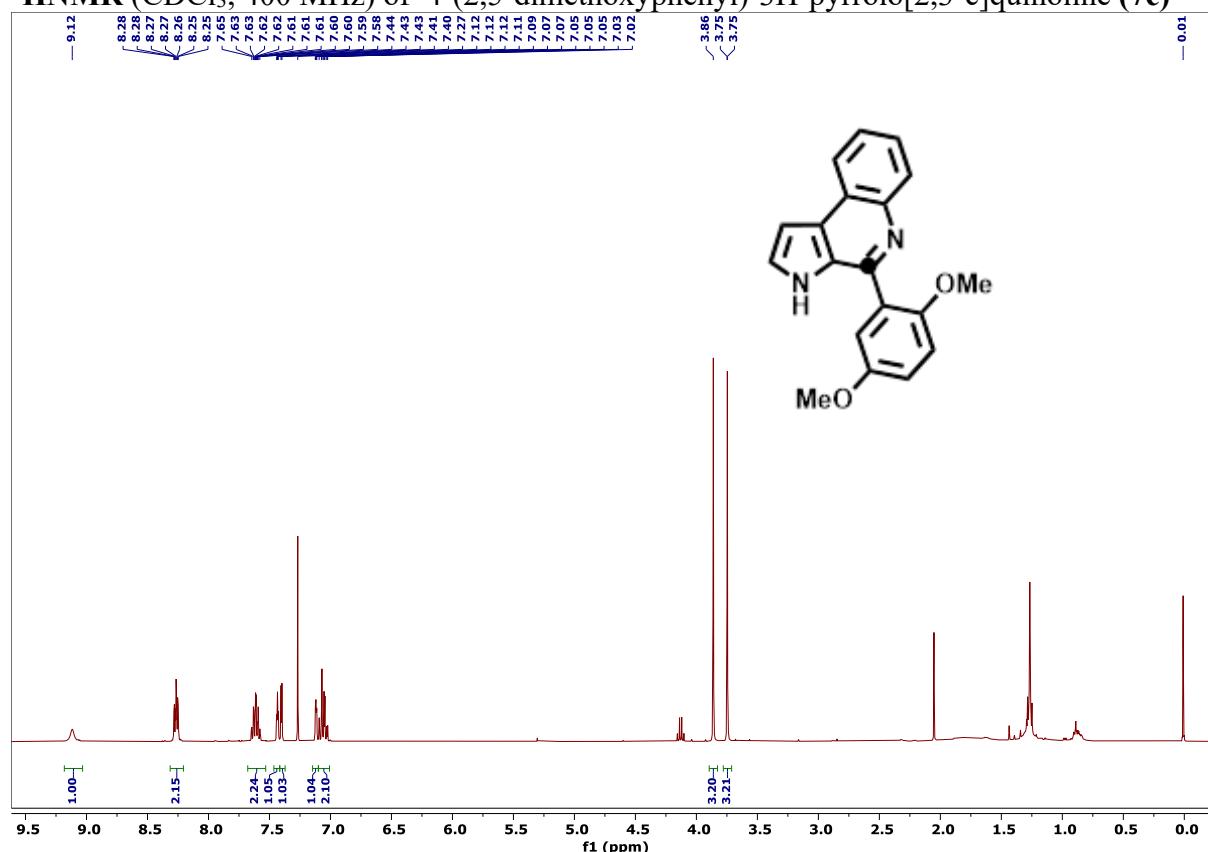
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 100 MHz) of 4-phenyl-3H-pyrrolo[2,3-c]quinoline (7b)**



**<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) of 4-phenyl-3H-pyrrolo[2,3-c]quinoline (7b)**



**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) of 4-(2,5-dimethoxyphenyl)-3H-pyrrolo[2,3-c]quinoline (**7c**)



**<sup>13</sup>C{<sup>1</sup>H} NMR** ( $\text{CDCl}_3$ , 100 MHz) of 4-(2,5-dimethoxyphenyl)-3H-pyrrolo[2,3-c]quinoline (**7c**)

