Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


*Supporting Information*

*For*

# Copper-Catalyzed, *N*-Auxiliary Group-Controlled Switchable, Transannulation/Nitration Initiated by Nitro Radicals: Selective Synthesis of Pyridoquinazolones and 3-Nitroindoles

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## 1. General Information

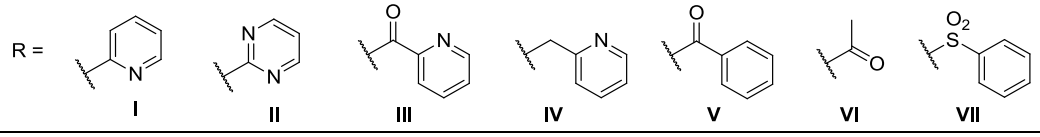
Unless otherwise noted, all reagents were obtained from commercial sources and used without further purification. NMR spectra were recorded on a Varian Inova–400 MHz, Inova–300 MHz, Bruker DRX–400 or Bruker DRX–500 instruments using $CDCl_3$ or DMSO-$d_6$ as solvent and tetramethylsilane (TMS) as internal standard. All chemical shifts ($\delta$) were reported in ppm and coupling constants ($J$) in Hz. High resolution mass spectra were recorded on a TOF machine (ESI). Column chromatography was performed with 300-400 mesh silica gel using flash column techniques.

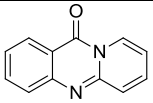
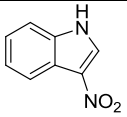
## 2. Reaction Development/Screening of Auxiliary Groups on Indole

**General procedure for screening of auxiliary groups using $Cu(NO_3)_3.3H_2O$/Pivalic acid system (GP1)**

*N*-protected indole (0.5 mmol), $Cu(NO_3)_2.3H_2O$ (181 mg, 1.5 equiv) and pivalic acid (10.2 mg, 20 mol%) were weighed into a tube, followed by the addition of 3 mL of $CH_3CN$. The tube was capped and the mixture stirred at 70 $^oC$. After the reaction was complete (approximately 3 hours), the mixture was cooled and diluted with 10 mL of saturated $NH_4Cl$ solution (containing 1% aqueous ammonia). This mixture was extracted with EtOAc (15 mL × 3). The combined organic extract was washed with 10 mL of $H_2O$ and dried over anhydrous $Na_2SO_4$. The dried extract was concentrated under vacuum and purification by column chromatography on silica gel to afford the pure product **2a** or **5a**.

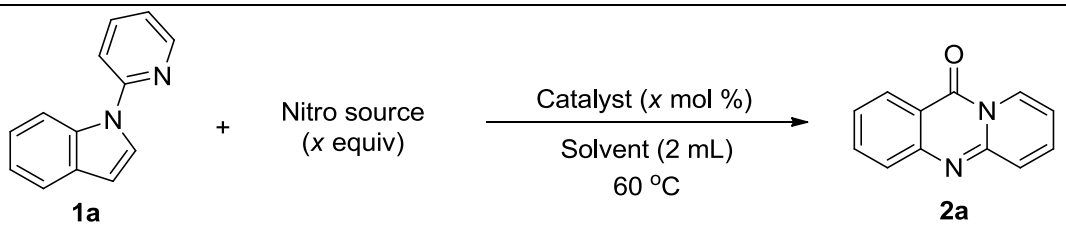
**Table S1**: Screening of Auxiliary Groups




| Entry | Auxiliary Group | Result |
|---|---|---|
| 1 | **I** |  **2a**, 73% |
| 2 | **II** | No reaction |
| 3 | **III** |  **5a**, 67% |
| 4 | **IV** | Messy, unidentified mixture of products |
| 5 | **V** | No reaction |
| 6 | **VI** | No reaction |
| 7 | **VII** | No reaction |

## 3. Optimization of Reaction Conditions

**Table S2: Optimization of reaction conditions for formation of pyridoquinazolone 2a**[a]



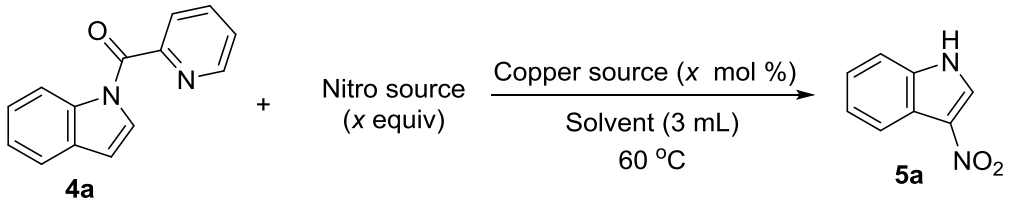

**1a** **2a**

| Entry | Nitro source (*x* equiv) | Catalyst (*x* mol%) | Time (h) | Solvent (mL) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | $Cu(NO_3)_2.3H_2O$ (1.5) | Pivalic acid (20) | 3 | $CH_3CN$ | 73 |
| 2 | TBN (3) | $Cu(NO_3)_2.3H_2O$ (20) | 12 | $CH_3CN$ | 61 (10)[c] |
| 3 | TBN (3) | $Cu(OAc)_2.H_2O$ (20) | 12 | $CH_3CN$ | 63 (14)[c] |
| 4 | $Fe(NO_3)_3.9H_2O$ (2) | $Cu(OAc)_2.H_2O$ (20) | 12 | $CH_3CN$ | 58 |
| 5 | $AgNO_3$ (2) | $Cu(OAc)_2.H_2O$ (20) | 12 | $CH_3CN$ | N.D.[d] |
| 6 | $NaNO_2$ (4) | $Cu(OAc)_2.H_2O$ (20) | 12 | $CH_3CN$ | N.R.[e] |
| 7 | $NaNO_2$ (4) | $Cu(OAc)_2.H_2O$ (20) | 12 | DMF | 14[f] (63)[c] |
| 8 | $NaNO_2$ (4) | – | 12 | DMF | 12[f] (51)[c] |
| 9 | TBN (3) | $Cu(OAc)_2.H_2O$ (20) | 12 | DCE | 69 (9)[c] |
| 10 | TBN (3) | $Cu(OAc)_2.H_2O$ (20) | 12 | DMF | 73 |
| **11** | **TBN (3)** | **$Cu(OAc)_2.H_2O$ (20)** | **12** | **DMSO** | **85** |
| 12 | TBN (3) | $Cu(OAc)_2.H_2O$ (20) | 12 | Dioxane | 67 (25)[c] |
| 13 | TBN (3) | $Cu(OAc)_2.H_2O$ (20) | 12 | $H_2O$ | 56 |
| 14 | TBN (3) | $Cu(OAc)_2$ (20) | 12 | DMSO | 71 |
| 15 | TBN (3) | $CuCl_2$ (20) | 12 | DMSO | 77 |
| 16 | TBN (3) | CuCl (20) | 12 | DMSO | 76 |
| 17 | TBN (3) | CuBr (20) | 12 | DMSO | 84 |
| 18 | TBN (3) | CuI (20) | 12 | DMSO | 81 |
| 19 | TBN (3) | $Cu(OAc)_2.H_2O$ (20) | 12 | Dioxane–$H_2O$ (10:1) | 89 |
| 20 | TBN (3) | $Cu(OAc)_2.H_2O$ (20) | 12 | Dioxane–$H_2O$ (3:1) | 72 |
| 21 | TBN (3) | $Cu(OAc)_2.H_2O$ (20) | 12 | Dioxane–$H_2O$ (2:1) | 68 |
| 22 | TBN (3) | $Cu(OAc)_2.H_2O$ (20) | 12 | Dioxane–$H_2O$ (1:1) | 61 |
| 23 | TBN (3) | $Cu(OAc)_2$ (20) | 12 | Dioxane–$H_2O$ (10:1) | 88 |
| 24 | TBN (3) | $CuBr_2$ (20) | 12 | Dioxane–$H_2O$ (10:1) | 24 |
| 25 | TBN (3) | $CuCl_2$ (20) | 12 | Dioxane–$H_2O$ (10:1) | 78 |
| 26 | TBN (3) | $Cu(OAc)_2.H_2O$ (10) | 12 | Dioxane–$H_2O$ (10:1) | 78 |
| 27 | TBN (3) | $Cu(OAc)_2.H_2O$ (30) | 12 | Dioxane–$H_2O$ (10:1) | 84 |
| 28 | TBN (3) | – | 12 | Dioxane–$H_2O$ (10:1) | 64 |
| 29 | TBN (2) | $Cu(OAc)_2.H_2O$ (20) | 12 | Dioxane–$H_2O$ (10:1) | 91 |
| 30 | TBN (1.5) | $Cu(OAc)_2.H_2O$ (20) | 12 | Dioxane–$H_2O$ (10:1) | 85 |
| 31 | TBN (1) | $Cu(OAc)_2.H_2O$ (20) | 12 | Dioxane–$H_2O$ (10:1) | 62 |
| 32 | – | $Cu(OAc)_2.H_2O$ (20) | 12 | Dioxane–$H_2O$ (10:1) | N.R.[e] |
| 33 | TBN (3) | $Cu(OAc)_2.H_2O$ (20) | 12 | Dioxane–$H_2O$ (10:1) | 53[g] |
| 34 | TBN (3) | $Cu(OAc)_2.H_2O$ (20) | 12 | Dioxane–$H_2O$ (10:1) | 88[h] |
| 35 | TBN (3) | $Cu(OAc)_2.H_2O$ (20) | 12 | Dioxane–$H_2O$ (10:1) | 85[i] |
| 36 | TBN (3) | $Cu(OAc)_2.H_2O$ (20) | 12 | Dioxane–$H_2O$ (10:1) | N.D.[d, j] |

[a] Conditions: **1a** (0.5 mmol) in 3 mL of solvent at 60 °C. [b]Isolated yields. [c]Amount of recovered starting material in parenthesis. [d] N.D. = not detected. [e] N. R. = no reaction. [f] $K_2S_2O_8$ (2 equiv) was added. [g] Under $O_2$ atmosphere. [h] Under $N_2$ atmosphere. [i] 70 °C. [j] 25 °C. TBN = *tert*-butyl nitrite.

Although the use of catalytic amounts of CuI or CuBr salts appeared to give good yields, side reactions such as the formation of 3-iodo and 3-bromoindole derivatives were observed with electron-deficient substrates.

**Table S3: Optimization of reaction conditions for formation of 3-nitroindole 5a**[a]




| Entry | Nitro source (*x* equiv) | Catalyst (*x* mol%) | Time (h) | Solvent (mL) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | $Cu(NO_3)_2.3H_2O$ (1.5) | Pivalic acid (20) | 3 | $CH_3CN$ | 67 |
| 2 | TBN (3) | $Cu(OAc)_2.H_2O$ (20) | 24 | Dioxane–$H_2O$ (10:1) | 19 (37)[c] |
| 3 | TBN (3) | $Cu(OAc)_2.H_2O$ (20) | 24 | Dioxane | 22 (45)[c] |
| 4 | TBN (3) | $Cu(OAc)_2.H_2O$ (30) | 24 | Dioxane | 47 (24)[c] |
| 5 | TBN (3) | $Cu(OAc)_2.H_2O$ (50) | 24 | Dioxane | 86 |
| 6 | TBN (3) | $Cu(OAc)_2.H_2O$ (50) | 18 | Dioxane | 87 |
| 7 | TBN (3) | CuCl (50) | 18 | Dioxane | 41 |
| 8 | TBN (3) | CuCN (50) | 18 | Dioxane | 36 |
| 9 | TBN (3) | CuO (50) | 18 | Dioxane | N.R.[d] |
| 10 | TBN (3) | $CuCl_2$ (50) | 18 | Dioxane | Trace |
| 11 | TBN (3) | $CuBr_2$ (50) | 18 | Dioxane | Trace |
| 12 | TBN (3) | CuI (50) | 18 | Dioxane | 71 |
| 13 | TBN (3) | $[Cu(CH_3CN)_4]PF_6$ (50) | 18 | Dioxane | 12 (17)[c] |
| 14 | TBN (3) | $Cu(acac)_2$ (50) | 18 | Dioxane | 15 (21)[c] |
| 15 | TBN (3) | $CuSO_4$ $5H_2O$ (50) | 18 | Dioxane | 9 (36)[c] |
| 16 | TBN (3) | $Cu(OTf)_2$ (50) | 18 | Dioxane | 6 (26)[c] |
| 17 | TBN (3) | $Cu(OAc)_2$ (50) | 18 | Dioxane | 78 |
| 18 | TBN (3) | $Cu(OAc)_2.H_2O$ (50) | 18 | DCE | 74 |
| 19 | TBN (3) | $Cu(OAc)_2.H_2O$ (50) | 18 | PhCN | 68 |
| 20 | TBN (3) | $Cu(OAc)_2.H_2O$ (50) | 18 | DMF | 43 |
| 21 | TBN (3) | $Cu(OAc)_2.H_2O$ (50) | 18 | DMSO | 32 |
| 22 | TBN (3) | $Cu(OAc)_2.H_2O$ (50) | 18 | Ethanol | N.D.[e] |
| 23 | TBN (3) | – | 18 | Dioxane | N.R.[d] |
| 24 | TBN (2) | $Cu(OAc)_2.H_2O$ (50) | 18 | Dioxane | 89 |
| 25 | TBN (1.5) | $Cu(OAc)_2.H_2O$ (50) | 18 | Dioxane | 90 |
| 26 | TBN (1) | $Cu(OAc)_2.H_2O$ (50) | 18 | Dioxane | 75 |
| 27 | $NaNO_3$ (3) | $Cu(OAc)_2.H_2O$ (50) | 18 | Dioxane | N.R.[e] |

[a]Conditions: **4a** (0.5 mmol) in 3 mL of solvent at 60 °C. [b]Isolated yields. [c]Amount of recovered starting material in parenthesis. [d]N.R. = no reaction. [e]N.D. = not detected. TBN = *tert*-butyl nitrite

## 4. General Procedure for the Formation of 2 and 3

### With TBN/$Cu(OAc)_2.H_2O$ system (GP2)

*N*-(pyridin-2-yl)indole **1** (0.5 mmol) and $Cu(OAc)_2.H_2O$ (20 mg, 20 mol%) were weighed into a tube, followed by the addition of 3 mL of a mixture of dioxane-$H_2O$ (10:1 to 3:1) or DMSO. Then, TBN (0.2 mL, 3 equiv) was added, the tube was capped and the mixture was stirred at 60 °C for 12-24 hours. After the reaction was complete (as indicated by TLC), the mixture was cooled and diluted with 10 mL of saturated $NH_4Cl$ solution (containing 1% aqueous ammonia). This mixture was extracted with EtOAc (15 mL × 3). The combined organic extract was washed with 10 mL of saturated NaCl solution and dried over anhydrous $Na_2SO_4$. The dried extract was concentrated under vacuum and purified by column chromatography on silica gel to afford the pure products **2** and **3**.

**With TBN (GP3)**

*N*-(pyridin-2-yl)indole **1** (0.5 mmol) was placed into a tube, followed by the addition of 3 mL of a mixture of dioxane-$H_2O$ (10:1) or DMSO. Then, TBN (0.2 mL, 3 equiv) was added, the tube was capped and the mixture stirred at 60 $^oC$ for 12-24 hours. After the reaction was complete (as indicated by TLC), the solvent was evaporated under vacuum. The crude mixture was purified directly by column chromatography on silica gel to afford the pure products **3j-m**.

## 5. General Procedure for the Formation of 5 (GP4)

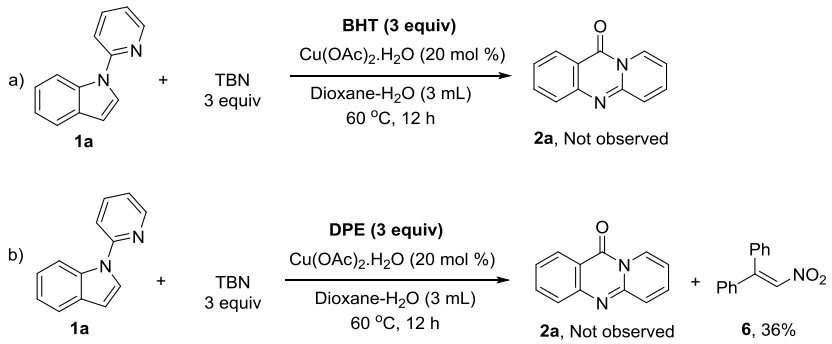
*N*-(2-pyridoyl) indole **4** (0.5 mmol) and $Cu(OAc)_2.H_2O$ (50 mg, 50 mol%) were weighed into a tube followed by the addition of 3 mL of dioxane. Then, TBN (0.2 mL, 3 equiv) was added, the tube was capped and the mixture was stirred at 60 $^oC$. After the reaction was complete (indicated by TLC), the reaction mixture was cooled and diluted with 10 mL of 3 M aqueous $NH_3$ solution. After separation of the two layers, the aqueous layer was extracted with EtOAc (15 mL × 3). The combined organic extract were dried over anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo. Purification of crude product by column chromatography on silica gel afforded the pure 3-nitro products **5**.

## 6. Mechanistic Studies

### Control experiments for formation of 2a

#### (a) Evidence of a Radical Process: Involvement of $NO_2$ Radicals

The addition of BHT or DPE to the reaction totally inhibited the formation of product **2a** (Scheme S1a,b). In addition, 36% yield of 2-nitro-1,1-diphenylethene (**6**) was isolated as a greenish yellow solid in the presence of DPE which confirmed the involvement of nitro radicals. **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 7.44 (m, 5H), 7.38 (m, 2H), 7.32 – 7.26 (m, 2H), 7.26 – 7.20 (m, 2H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 150.5, 137.1, 135.6, 134.4, 130.9, 129.3, 128.93, 128.91, 128.8, 128.5. These data are in agreement with those reported previously in the literature.[1]



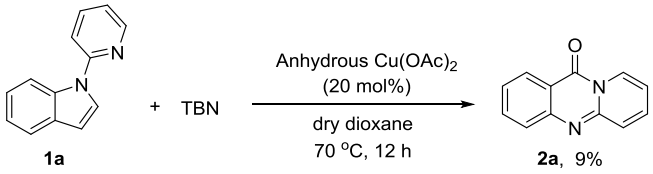

**Scheme S1.** Radical trapping experiments involving **2a**.

Procedure for radical trapping experiment: *N*-(pyridin-2-yl)indole **1a** (49 mg, 0.25 mmol), $Cu(OAc)_2.H_2O$ (10 mg, 20 mol%) and radical scavenger (butylated hydroxytoluene, BHT or 1,1-diphenylethene, DPE) (0.75 mmol)

were weighed into a tube, followed by the addition of 3 mL of a mixture of dioxane-$H_2O$ (10:1). Then, TBN (0.09 mL, 3 equiv) was added, the tube was capped and the mixture was stirred at 60 $^oC$ for 12 hours.

**(b) Investigation of the role of $H_2O$**

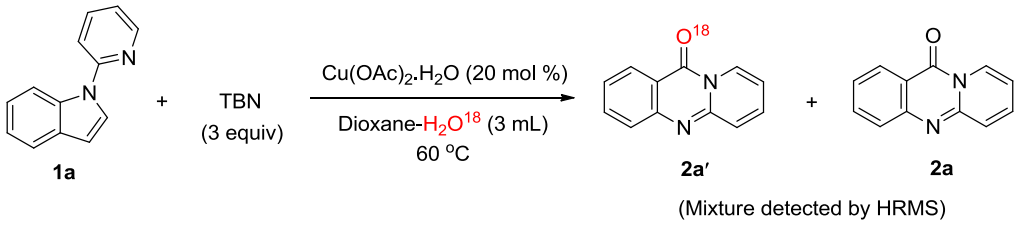
The transannulation reaction barely took place under anhydrous conditions, with a substantial recovery of starting material (Scheme S2). The fact that **2a** was formed at all was probably due to adventitious $H_2O$ present in the reaction medium**.** This result underlines the importance of $H_2O$ in driving this reaction forward.




**Scheme S2**. Importance of $H_2O$

**(c) Isotope Labeling Experiment: Sources of O-atom in 2a**

Since water was required to promote the transformation of **1a** in dioxane, a mixture of dry dioxane and labeled water ($H_2O^{18}$) (used *in lieu* of $H_2O^{16}$) was employed as solvent to determine the source of the oxygen atom in **2a**. Mass analysis revealed the formation of a mixture of products **2a** and **2a′** which proves that $H_2O$ contributed to the oxygen atom content present in product **2a** (**Scheme S3**, **Figure S1**).




**Scheme S3**. Isotope labeling experiment involving pyridoquinazolone **2a**.

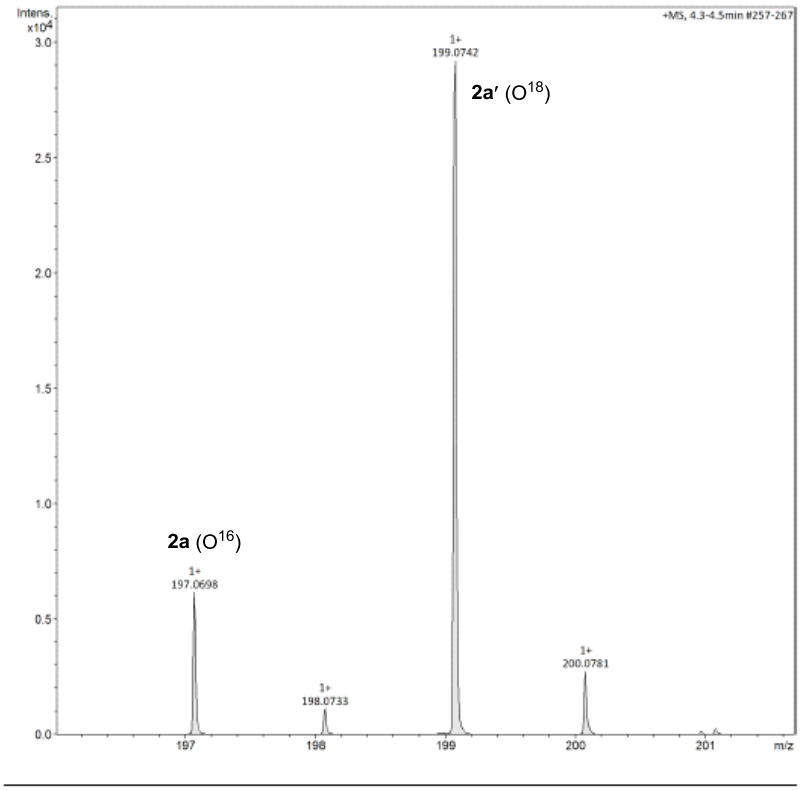


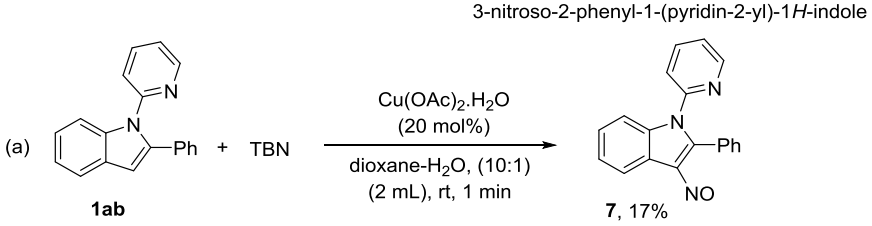

**Figure S1.** High resolution mass spectrum of pyridoquinazolone **2a** and **2a′**

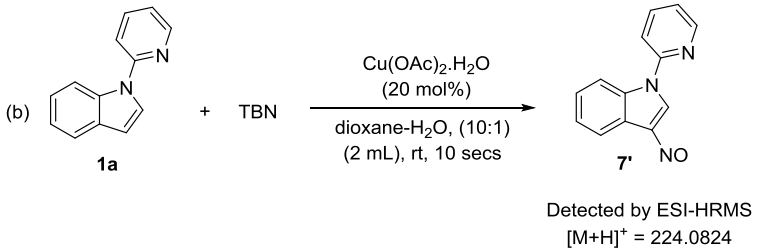
**(d) Isolation of Probable Intermediates in the Formation of 2a**

Moreover, a series of experiments were carried out to identify and possibly isolate intermediates *en route* to the formation of pyridoquinazolones **2a**. *N*-2-pyridylindoles **1a** or **1ab** (which contains the stabilizing 2-phenyl substituent group) were employed for this purpose.

(i) Isolation/Detection of 3-nitrosoindole intermediates

Upon the addition of TBN to a mixture of **1ab** and $Cu(OAc)_2.H_2O$ in dioxane-$H_2O$ at room temperature, immediate reaction took place (indicated by a color change of the mixture to green). The formed intermediate **7** was isolated as a relatively unstable light-green solid (Scheme S4a). Although not isolable, the 3-nitroso-1-(pyridin-2-yl)-1*H*-indole **7′** corresponding to indole **1a** (indicated by a color change of the mixture light yellow to reddish brown) was detected in the ESI-HRMS spectrum of its crude mixture, *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{10}N_3O$ 224.0824, found 224.0824 (Scheme S4b).






**Scheme S4**. Isolation/Detection of intermediate **7** and **7′**

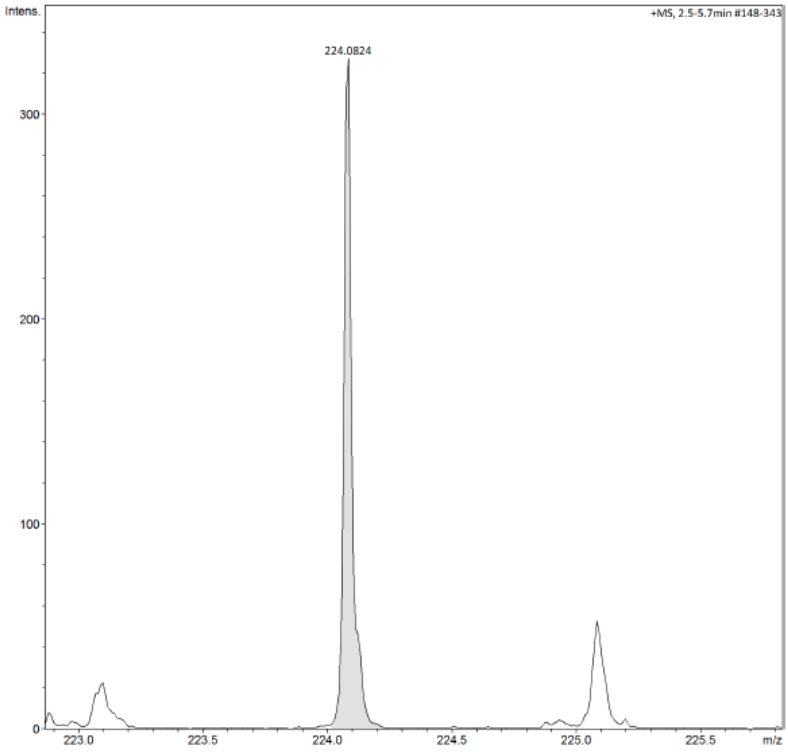
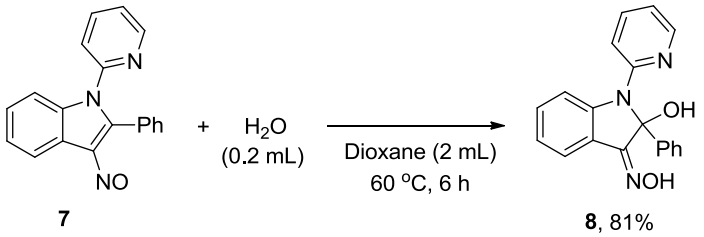



**Figure S2.** High resolution mass spectrum of intermediate **7′** (from **1a**)

*Procedure for isolation of intermediate **7**:* 2-phenyl-1-(pyridin-2-yl)-1*H*-indole **1ab** (49 mg, 0.25 mmol) and $Cu(OAc)_2.H_2O$ (10 mg, 20 mol%) were weighed into a tube, followed by the addition of 2 mL of a mixture of dioxane-$H_2O$ (10:1). Then, TBN (0.03 mL, 1 equiv) was added and the mixture was allowed to stir for a minute at room temperature (green coloration of reaction mixture is observed which becomes intensified). Afterwards, the solvent was evaporated and the crude mixture was purified by column chromatography to give 3-nitroso-2-phenyl-1-(pyridin-2-yl)-1*H*-indole **7** as a light green solid (12.7 mg, 17% yield). **$^1$H NMR** (DMSO-$d_6$, 400 MHz): $\delta$ 8.72 (s, 1H), 8.25 – 7.93 (m, 2H), 7.81 – 7.56 (m, 4H), 7.45 (m, 6H). **$^{13}$C NMR** (DMSO-$d_6$, 100 MHz): $\delta$ 136.1, 133.9, 132.30, 132.27, 132.1, 131.8, 131.7, 130.7, 128.7, 128.6, 128.5, 128.1, 126.7, 124.1, 124.0. **HRMS** (ESI-TOF) *m/z*: $[M+1]^+$ calcd for $C_{19}H_{14}N_3O$ 300.1137, found 300.1146.

(ii) Evidence for the intermediacy of hydroxyimino compound (**8**)

The intercepted 3-nitrosoindole **7** underwent nucleophilic attack by $H_2O$ to form the hydroxyimino intermediate **8** as shown in Scheme S5 below.

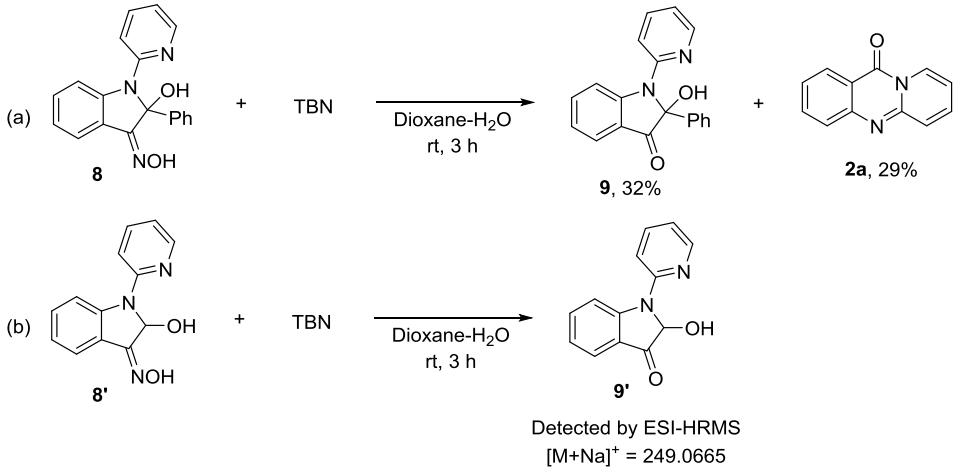



**Scheme S5.** Isolation of intermediate **8**

*Procedure for isolation of intermediate **8**:* 3-nitrosoindole **7** (75 mg, 0.25 mmol) was weighed into a tube followed by the addition of 2 mL of a mixture of dioxane-$H_2O$ (10:1), and the mixture was allowed to stir for 6 hours at 60 $^oC$. The reaction was stopped after 6 hours; the solvent was evaporated and the crude mixture was purified by column chromatography to give to afford **8** as a yellow solid (64.2 mg, 81%). **$^1$H NMR** (DMSO-$d_6$, 400 MHz): $\delta$ 11.62 (s, 1H), 8.59 (d, $J$ = 8.4 Hz, 1H), 8.39 – 8.25 (m, 1H), 8.23 – 8.09 (m, 1H), 7.66 (s, 1H), 7.48 – 7.43 (m, 1H), 7.42 – 7.33 (m, 3H), 7.29 – 7.23 (m, 2H), 7.22 – 7.16 (m, 1H), 7.06 – 6.93 (m, 2H), 6.88 – 6.77 (m, 1H). **$^{13}$C NMR** (DMSO-$d_6$, 100 MHz): $\delta$ 157.2, 153.6, 147.5, 147.5, 142.5, 137.0, 132.2, 128.7, 128.6, 128.0, 125.8, 121.0, 118.5, 116.9, 114.9, 113.9, 92.5. **HRMS** (ESI-TOF) *m/z*: $[M]^+$ calcd for $C_{19}H_{15}N_3O_2$ 317.1164, found 317.1155.

**(iii) Evidence for the intermediacy of hydroxyketone compound (9)**

In the presence of TBN, the hydroxyimino intermediate **8** was easily oxidized to the corresponding hydroxyketone intermediate **9**, where the active oxidizing species is probably $NO^+$ produced from the reaction of $H_2O$ and TBN (Scheme S6a). Moreover, the intermediate **9′** (derived from substrate **1a**) was detected in the ESI-HRMS spectrum of the crude reaction mixture (i.e $[M+Na]^+$ = 249.0665) (Scheme S4b).




**Scheme S6.** Isolation/Detection of intermediate **9** and **9′**

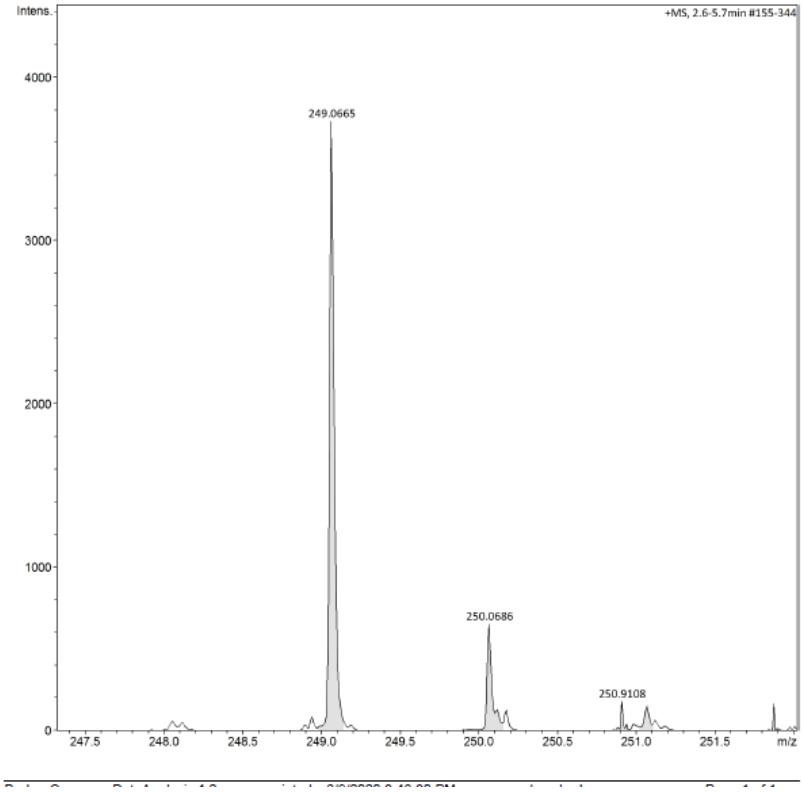
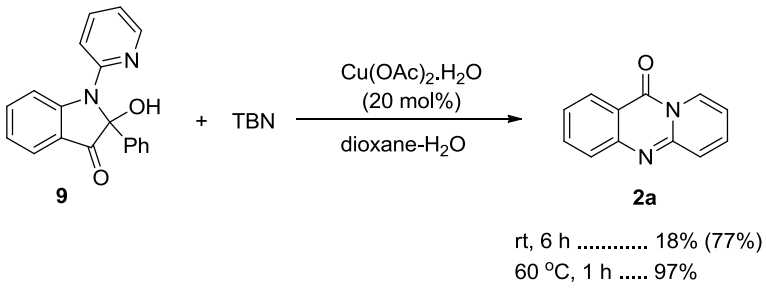



**Figure S3.** High resolution mass spectrum of intermediate **9′** (from **1a**)

*Procedure for isolation of intermediate **9**:* Hydroxyimino intermediate **8** (79.3 mg, 0.25 mmol) and $Cu(OAc)_2.H_2O$ (10 mg, 20 mol%) were weighed into a tube, followed by the addition of 2 mL of a mixture of dioxane-$H_2O$ (10:1). Then, TBN (0.03 mL, 1 equiv) was added and the mixture was allowed to stir for 3 hours at room temperature. Afterwards, the solvent was evaporated and the crude mixture was purified by column chromatography to afford hydroxyketone **9** as a yellow solid (24.2 mg, 32% yield) alongside pyridoquinazolone **2a** (14 mg, 29% yield). Compound **9**: **$^1$H NMR** (DMSO-$d_6$, 400 MHz): $\delta$ 8.82 (d, $J$ = 8.5 Hz, 1H), 8.43 – 8.33 (m, 1H), 7.88 – 7.72 (m, 2H), 7.68 – 7.60 (m, 1H), 7.55 – 7.45 (m, 1H), 7.40 – 7.24 (m, 5H), 7.12 (t, $J$ = 7.4 Hz, 1H), 6.99 – 6.84 (m, 2H). **$^{13}$C NMR** (DMSO-$d_6$, 100 MHz): $\delta$ 197.7, 155.2, 153.0, 147.7, 138.4, 137.5, 137.2, 129.3, 128.9, 126.1, 125.2, 122.0, 119.3, 117.5, 116.8, 113.5, 91.2. **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{14}N_2NaO_2$ 325.0953, found 325.0960.

**(iv) Oxidation of hydroxyketone intermediate (9) to pyridoquinazolone 2a**

The intermediacy of **9** was further validated by its facile transformation into pyridoquinazolone **2a** in 97% yield under standard conditions (Scheme S7). This process most probably occurred *via* the cleavage of the indole ring, however, attempts to isolate any ring-opening intermediate at room temperature were unsuccessful. The inability to observe any intermediate at this stage is suggestive of the occurrence of a highly reactive/short-lived intermediate species.



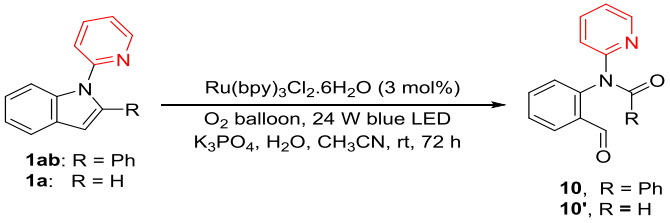

**Scheme S7.** Detection/isolation of intermediate during the transformation of compound **9** to **2a**

*Procedure for transformation of compound **9** to **2a**:* Hydroxyketone intermediate, **9** (75.5 mg, 0.25 mmol) and $Cu(OAc)_2.H_2O$ (10 mg, 20 mol%) were weighed into a tube, followed by the addition of 2 mL of a mixture of dioxane-$H_2O$ (10:1). Then, TBN (0.03 mL, 1 equiv) was added and the mixture was allowed to stir for either 6 hours at room temperature or 1 hour at 60 $^oC$ (standard conditions). After the indicated periods elapsed, the solvent was evaporated and the crude mixture purified by column chromatography. The reaction at room temperature afforded pyridoquinazolone **2a** (8.8 mg, 18% yield) and recovered hydroxyketone **9** (58 mg, 77% yield). Meanwhile, the reaction at 60 $^oC$ (i.e. standard conditions) furnished pyridoquinazolone **2a** (47.5 mg, 97% yield).

**(v) Synthesis of indole ring-cleavage compounds and their investigation as possible intermediates**

In a bid to validate the occurrence of an indole C2–C3 bond cleavage process, possible intermediates arising from intermediates **8** (or **8′**) and **9** (or **9′**) were synthesized, and then subjected to the standard conditions (Scheme S8, 9).

Synthesis of *N*-(2-formylphenyl)-*N*-(pyridin-2-yl)benzamide **10** and *N*-(2-formylphenyl)-*N*-(pyridin-2-yl)formamide **10′**:




**Scheme S8.** Synthesis of compounds **10** and **10′**

Compounds **10** and **10′** were synthesized according to a previously described method.[1]

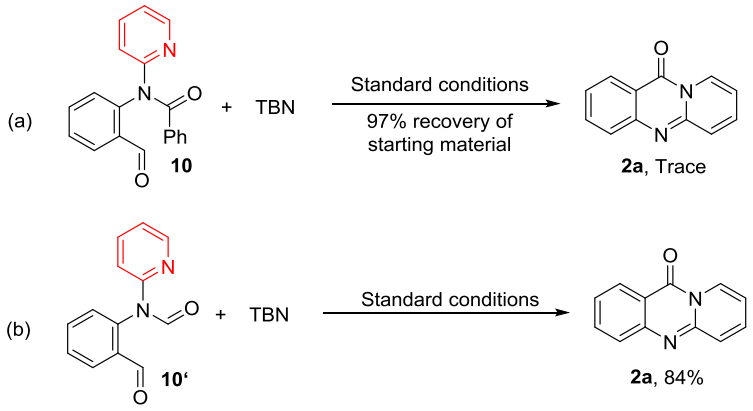
*N*-(2-formylphenyl)-*N*-(pyridin-2-yl)benzamide **10** was obtained as a brown oil (106 mg, 35% yield). **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 10.27 (s, 1H), 8.33 – 8.19 (m, 1H), 7.93 (dd, $J$ = 7.7, 1.7 Hz, 1H), 7.66 – 7.56 (m, 2H), 7.50 – 7.42 (m, 3H), 7.36 – 7.30 (m, 1H), 7.29 – 7.20 (m, 4H), 7.12 – 7.00 (m, 1H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 189.9, 171.3, 155.9, 148.9, 143.6, 137.9, 135.3, 134.9, 132.8, 130.9, 130.7, 130.2, 128.9, 128.2, 128.2, 121.5, 121.4.

*N*-(2-formylphenyl)-*N*-(pyridin-2-yl)formamide **10′** was obtained as a brown oil (11 mg, 5% yield) together with 84% recovery of the starting material. **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 9.99 (s, 1H), 9.77 (s, 1H), 8.42 – 8.35 (m, 1H), 8.12 – 8.00 (m, 1H), 7.79 – 7.73 (m, 1H), 7.67 – 7.56 (m, 2H), 7.37 – 7.29 (m, 1H), 7.17 – 7.08 (m, 1H), 6.59 –

6.40 (m, 1H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 189.1, 162.5, 148.7, 138.7, 135.6, 135.1, 134.2, 130.7, 130.3, 129.5, 127.3, 125.3, 120.8.

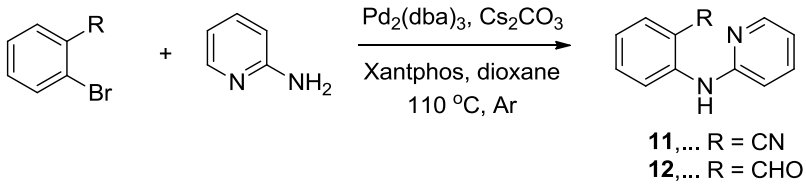
*Investigation as possible reaction intermediates:*

Compounds **10** and **10′** bearing the *N*-benzoyl and *N*-formyl fragments, respectively were subjected to the standard conditions. Under these conditions, **10** barely reacted and was recovered almost quantitatively (Scheme S9a); on the other hand, **10′** reacted to afford the product **2a** in 84% yield (Scheme S9b). Although **10′** underwent complete conversion to **2a** under standard conditions, the poor conversion of **10** might point to the occurrence of a more reactive intermediate.




**Scheme S9.** Investigation of compounds **10** and **10′** as possible reaction intermediates.

Synthesis of 2-(pyridin-2-ylamino)benzonitrile **11** and 2-(pyridin-2-ylamino)benzaldehyde **12**:



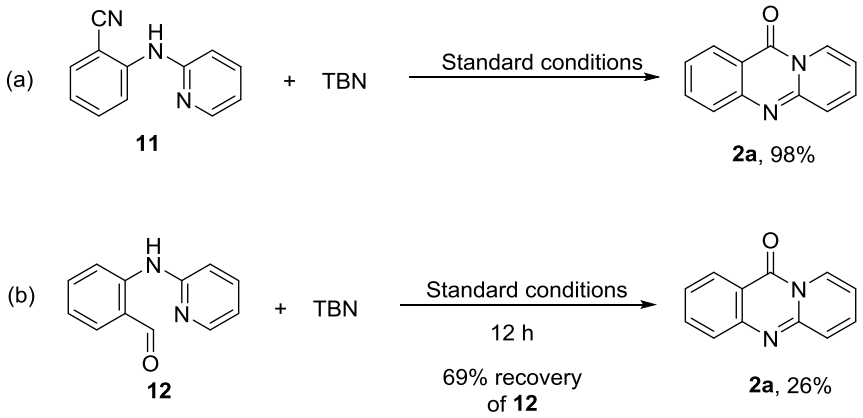

**Scheme S10.** Synthesis of compounds **11** and **12**

Compounds **11** and **12** were synthesized according to a literature procedure.[2]

2-(pyridin-2-ylamino)benzonitrile **11** was obtained as a yellow solid after 12 hours of reflux (162 mg, 83% yield). **$^{1}$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 9.07 – 9.02 (m, 1H), 8.35 – 8.22 (m, 1H), 7.91 – 7.83 (m, 1H), 7.70 – 7.58 (m, 2H), 7.45 – 7.30 (m, 2H), 7.30 – 7.18 (m, 1H), 6.71 – 6.55 (m, 1H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 155.8, 147.9, 144.8, 134.2, 133.0, 127.9, 127.2, 125.7, 124.6, 124.0, 115.4, 111.1.

2-(pyridin-2-ylamino)benzaldehyde **12** was obtained as a yellow solid after 2 hours of reflux (152 mg, 77% yield). **$^{1}$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 10.88 (s, 1H), 9.87 (s, 1H), 9.05 – 8.68 (m, 1H), 8.50 – 8.16 (m, 1H), 7.79 – 7.45 (m, 2H), 7.09 – 6.95 (m, 1H), 6.93 – 6.72 (m, 1H).

*Investigation as possible reaction intermediates*:

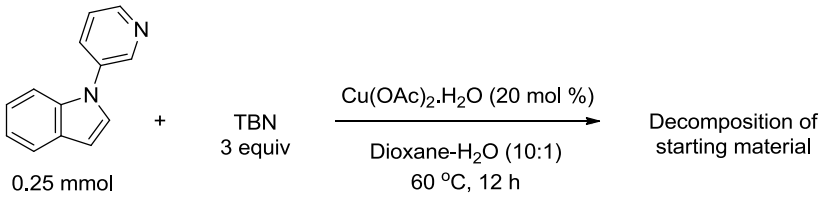



**Scheme S11.** Investigation of compounds **11** and **12** as possible reaction intermediates

Compounds **11** and **12** bearing the cyano and formyl groups, respectively were subjected to the standard conditions. While **11** underwent facile transformation to produce **2a** in excellent yield, the reaction of **12** was surprisingly sluggish, affording only 26% yield of **2a** after 12 hours.

**(e) Importance of the 2-pyridyl Auxiliary**

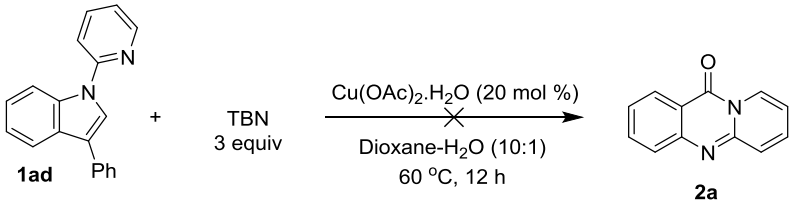
The importance of the 2-pyridyl group was demonstrated by the loss of efficiency observed with the 3-pyridyl auxiliary group (Scheme S12).




**Scheme S12**. Investigation of 3-pyridyl auxiliary group.

**(f) Evidence that C3-position is the Primary Site of Radical Attack**

Due to the blockage of the C-3 position of indole, no transannulation occurred with 3-phenylindole (**1ad**) which ultimately proves the importance of a free C3 position for this reaction (Scheme S13).

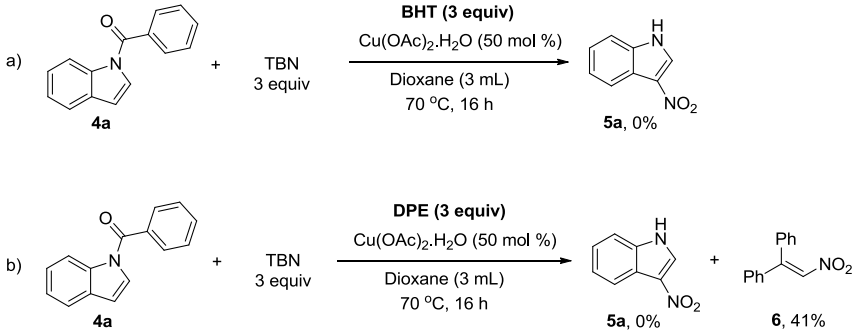



**Scheme S13**. Investigation of the reaction of 3-phenylindole

## Control experiments for the formation of 5a

### (a) Evidence of a Radical Process: Involvement of $NO_2$ Radicals

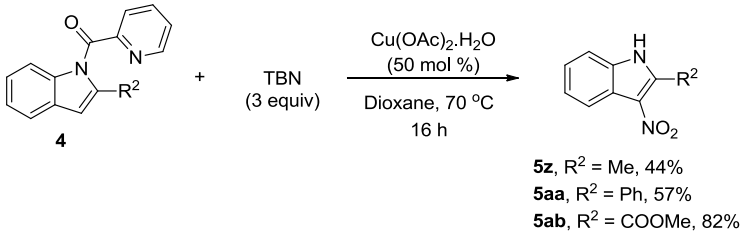
The addition of 1,1-diphenylethene (DPE) or butylated hydroxytoluene (BHT) to the reaction involving **4a** totally inhibited the formation of product **5a** (Scheme S14a,b). Meanwhile, 2-nitro-1,1-diphenylethene (**6**, 41%) was isolated from the reaction involving DPE which indicated the participation of nitro radicals.




**Scheme S14**. Radical trapping experiments involving **5a**

### (b) Experiment to rule out direct $Cu^{II}$ coordination at *C*2 position

According to **GP4**, the successful nitration of 2-substituted indoles **4z**, **4aa**, **4ab** to give the corresponding 3-nitroindoles rules out any possible copper coordination at *C*2 position of the indole moiety.

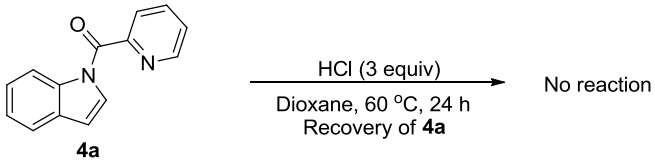



**Scheme S15**. C3-nitration of 2-substituted indoles.

### (c) Factors Responsible for the Dissociation of 2-Pyridoyl Auxiliary Group: Role of $Cu(OAc)_2.H_2O$

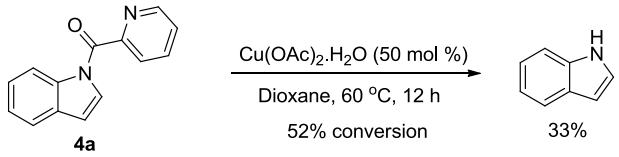
In order to determine the factors responsible for the dissociation of 2-pyridoyl auxiliary, some reactions involving substrate **4a** were carried out as described below.

Firstly, it was speculated that the relative acidity of the reaction mixture might promote the hydrolysis of 2-pyridoyl. So, a mixture of compound **4a** (56 mg, 0.25 mmol) and 37% (w/w) HCl (0.061 mL, 3 equiv) was stirred in dioxane (2 mL) at 60 °C. After 24 hours, indole **4a** remained unconsumed which rules out any possible acid-promoted hydrolysis of the 2-pyridoyl auxiliary (Scheme S16).




**Scheme S16**. Attempted hydrolysis of 2-pyridoyl group under acidic conditions.

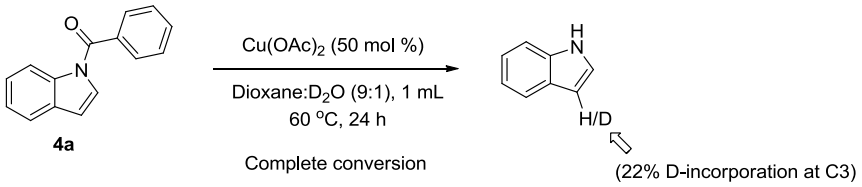
Secondly, a mixture of **4a** (56 mg, 0.25 mmol) and $Cu(OAc)_2.H_2O$ (25 mg, 50 mol%) in dioxane (2 mL) was stirred at 60 °C. After 12 hours, a sizeable portion (52%) of **4a** had been degraded to the parent indole (39 mg, 33% yield). This indicates that $Cu(OAc)_2.H_2O$ is responsible for the dissociation of the 2-pyridoyl auxiliary group *via* its coordination with 2-pyridoyl group, which weakens the amide bond.[5]




**Scheme S17**. Reaction of indole **4a** with $Cu(OAc)_2.H_2O$.

**(d) Deuterium Incorporation Experiment:**

The deuterium incorporation at C3 position confirms the strong reactivity at that position (Scheme S18).




**Scheme S18**. Deuterium incorporation experiment involving indole **4a**.

*N*-(2-pyridoyl) indole **4a** (28 mg, 0.125 mmol) and anhydrous $Cu(OAc)_2$ (11.3 mg, 50 mol%) were weighed into a tube followed by the addition of 1 mL of a mixture of dry dioxane-$D_2O$ (9:1). The tube was capped and the mixture was stirred at 60 °C for 24 hours. $^1$H NMR integration revealed 22% deuterium incorporation at C3 position of indole.

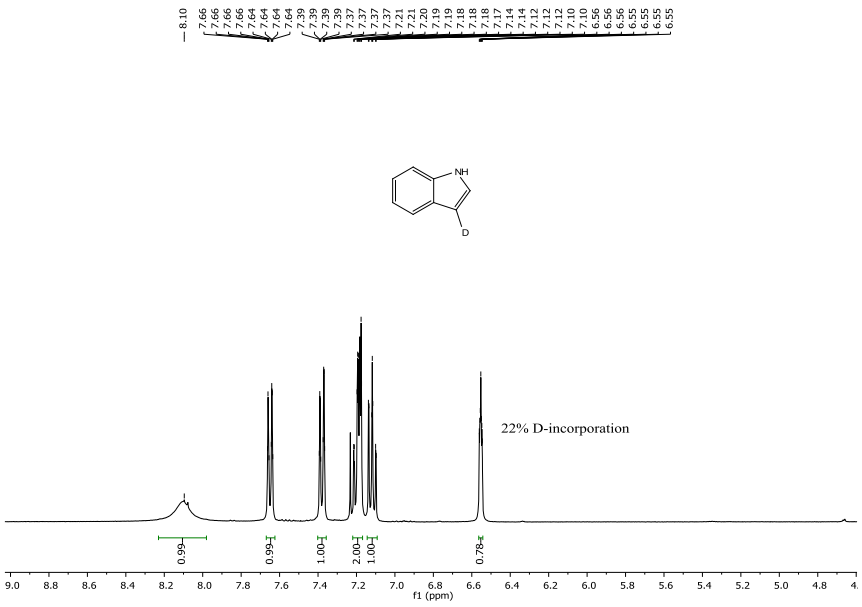
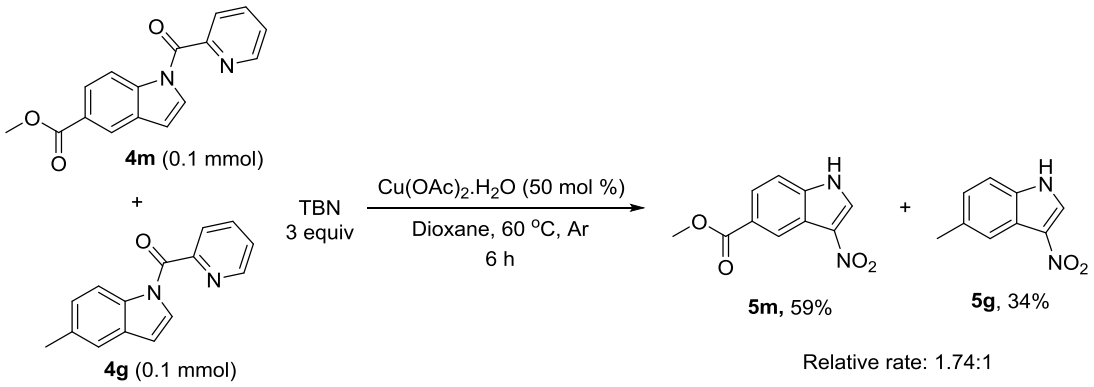



**Figure S4**. $^{1}$H NMR of Deuterium experiment involving **4a**.

**(e) Competition Experiment**

Competition experiment involving equimolar amounts of substrates **4g** and **4m** indicate that electron-deficient indoles tend to react faster than their electron-rich counterparts, which clearly rules out an electrophilic aromatic substitution ($S_EAr$) pathway (Scheme S19).[6]




**Scheme S19**. Competition experiment involving indoles **4g** and **4m**.

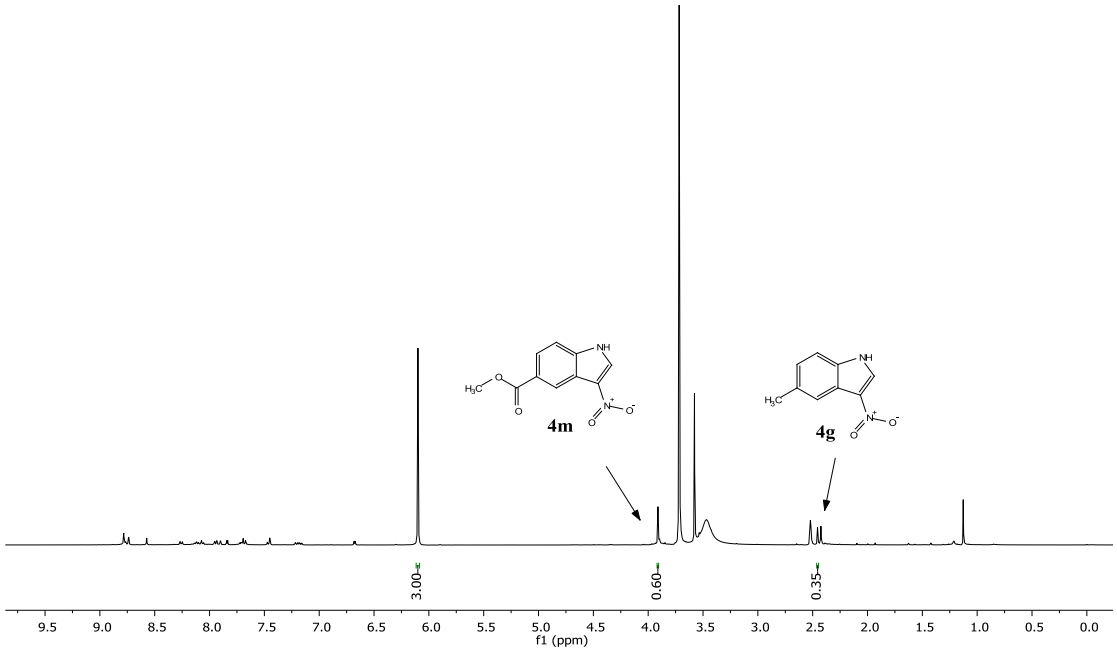
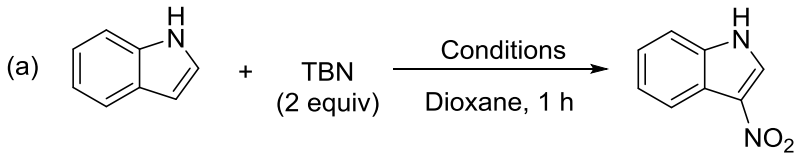



**Figure S5**. $^{1}$H NMR spectra showing product distribution between **5g** and **5m**.

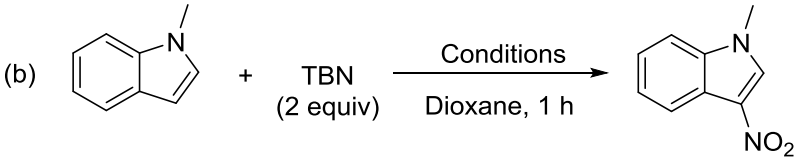
*Experimental procedure:* 5-Methyl-substituted indole **4g** (23.6 mg, 0.1 mmol) and 5-methoxycarbonyl-subsituted indole **4m** (28 mg, 0.1 mmol) and $Cu(OAc)_2.H_2O$ (12.5 mg, 50 mol%) were weighed into a tube followed by the addition of 2 mL of dioxane. Then, TBN (0.036 mL, 3 equiv) was added, the tube was capped and the mixture was stirred at 60 $^{o}$C. After 6 hours, the reaction mixture was cooled and diluted with 10 mL of 3 M aqueous $NH_3$ solution. After separation of the two layers, the aqueous layer was extracted with EtOAc (15 mL × 3). The combined organic extract were dried over anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo. The $^{1}$H NMR analysis of the product distribution was determined by integration using 1,3,5-trimethoxybenzene as an internal standard.

**(f) Importance of the Co-ordinating 2-pyridoyl Auxiliary**

The promoting as well as stabilizing effect of the 2-pyridoyl auxiliary was confirmed by the lack of efficiency demonstrated by some substrates. For instance, indole or 1-methylindole did not furnish the desired products even though TLC indicated both substrates were completely consumed in the reaction.

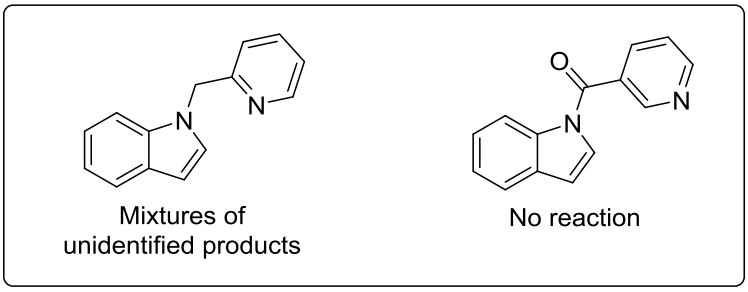



With $Cu(OAc)_2.H_2O$ at 60 °C ..... 0%
Without $Cu(OAc)_2.H_2O$ at 60 °C ..... 0%
With $Cu(OAc)_2.H_2O$ at 25 °C ..... 0%
Without $Cu(OAc)_2.H_2O$ at 25 °C ..... 0%




With $Cu(OAc)_2.H_2O$ at 60 °C ..... 0%
Without $Cu(OAc)_2.H_2O$ at 60 °C ..... 0%
With $Cu(OAc)_2.H_2O$ at 25 °C ..... 0%
Without $Cu(OAc)_2.H_2O$ at 25 °C ..... 0%

Moreover, similar results were obtained with 1-(pyridin-2-ylmethyl)-1*H*-indole. However, (1*H*-indol-1-yl)(pyridin-3-yl)methanone failed to react under the standard conditions. These results proves the importance of the coordinating oxygen and nitrogen atoms of the 2-pyridoyl auxiliary.

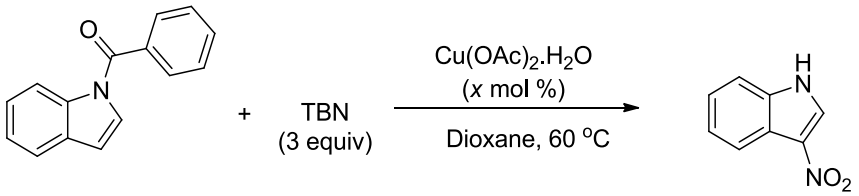



**Scheme S20**. Importance of the 2-pyridoyl auxiliary

**(g) Effect of Copper Salt Concentration on the Formation of 5a with Time**

The reaction was monitored under standard conditions using different concentrations of $Cu(OAc)_2.H_2O$ (see table below). Firstly, $Cu(OAc)_2.H_2O$ (25 mol%) was not enough to drive the reaction to completion, even after 72 hours (entries 1 & 2). Meanwhile, higher loadings of $Cu(OAc)_2.H_2O$ (i.e. 75 & 100 mol%) appeared to increase the rate of reaction (**4a** was completely consumed in 12 h and 7 h, respectively), albeit with a drop in the yields of **5a** (compare entries 3 vs 4 & 5). The higher loading of the copper salt presumably increases the rate of dissociation of 2-pyridoyl relative to nitration; the resulting parent indole undergoes oxidative decomposition, thus limiting reaction efficiency.

**Table S4: Effect of $Cu(OAc)_2.H_2O$ Concentration on the Formation of 5a**[a]




| S/N | Amount of $Cu(OAc)_2.H_2O$ | Time | Yield (%) |
|---|---|---|---|
| 1 | 25 mol% | 24 h | 33% (52)[b] |
| 2 | 25 mol% | 72 h | 36% (49)[b] |
| 3 | 50 mol% | 18 h | 87% (0)[b] |
| 4 | 75 mol% | 12 h | 82% (0)[b] |
| 5 | 100 mol% | 7 h | 62% (0)[b] |

[a]Conditions: **4a** (0.5 mmol) in 3 mL of dioxane at 60 °C. [b]Amount of recovered **4a** in parenthesis.

**(h) Evidence for the Dependence of the Nitration Reaction on the Rate of Amide Bond Dissociation**

The success of this reaction lies in the prior dissociation of the 2-pyridoyl auxiliary as illustrated by the reaction profile of **4a** shown below. This was demonstrated by monitoring substrate conversion/product formation with time over a 6-hour period (Figure S6). The induction period observed in the product formation appeared to correlate with the rate of dissociation of the 2-pyridoyl auxiliary in the substrate.

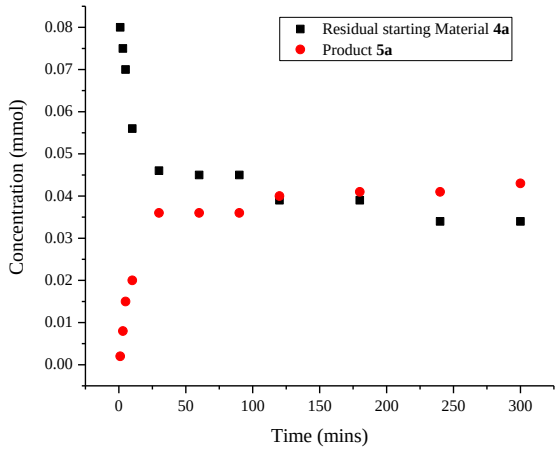
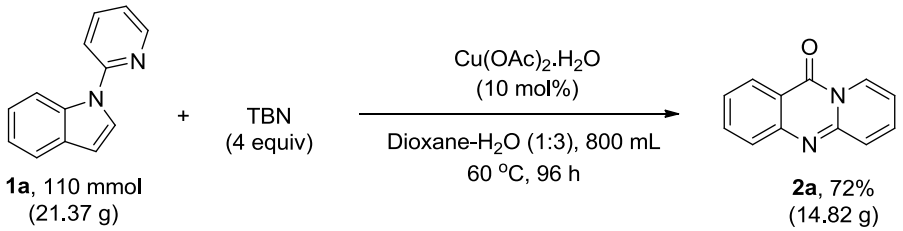



**Figure S6.** Reaction profile of **4a** showing rate of consumption *versus* rate of formation of **5a.**

*Experimental procedure:* Several independent reactions of **4a** (0.1 mmol each) were carried out under the optimized nitration conditions, and quenched at the indicated time points. The reaction mixture was cooled and diluted with 10 mL of 3 M aqueous $NH_3$ solution. After separation of the two layers, the aqueous layer was extracted with EtOAc (15 mL × 3). The combined organic extract were dried over anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo. The concentrations of product and starting material were determined by $^1H$ NMR using 1,3,5-trimethoxybenzene (0.1 mmol) as internal standard.

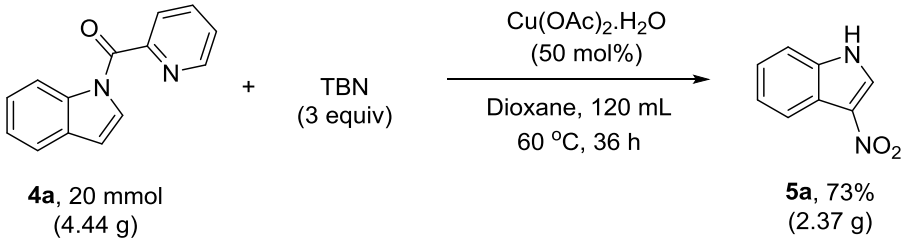
## 7. Gram–Scale Synthesis of 2a and 5a

(a) Procedure for the preparation of **2a** on a 110 mmol scale




*Experimental procedure: N*-(pyridin-2-yl)indole **1a** (21.37 g, 110 mmol) and $Cu(OAc)_2.H_2O$ (2.19 g, 10 mol%) were weighed into 1000 mL flask, followed by the addition of 700 mL of a mixture of dioxane-$H_2O$ (1:3). The flask was covered and the mixture stirred at 60 $^oC$ for 96 hours. Meanwhile, TBN (52 mL, 4 equiv) was added in portions over the duration of reaction, the tube was capped. After the reaction was complete (as indicated by TLC), the mixture was cooled and the solvent evaporated under vacuum, followed by dilution of the residue with 500 mL of saturated $NH_4Cl$ solution (containing 1% aqueous ammonia). The aqueous mixture was extracted with EtOAc (200 mL × 5), and the combined organic extract was washed with saturated NaCl solution (100 mL × 3), and dried over anhydrous $Na_2SO_4$. The dried extract was concentrated under vacuum and purified by column chromatography on silica gel to afford the pure product **2a** (14.82 g, 72%).

(b) Procedure for the preparation of **5a** on a 20 mmol scale




*Experimental procedure: N*-(2-pyridoyl) indole **4a** (4.44 g, 20 mmol) and $Cu(OAc)_2.H_2O$ (2.00 g, 50 mol%) were weighed into a flask followed by the addition of 120 mL of dioxane. After TBN (7.10 mL, 3 equiv) was added, the flask was covered and the mixture was stirred at 60 $^oC$ for 36 hours under argon atmosphere. After the reaction was complete (indicated by TLC), the reaction mixture was cooled and diluted with 100 mL of 3 M aqueous $NH_3$ solution. After separation of the two layers, the aqueous layer was extracted with EtOAc (100 mL × 3). The combined organic extract were dried over anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo. Purification of crude product by column chromatography on silica gel afforded the pure product **5a** (2.37 g, 73%).

## 8. Unsuccessful Substrates

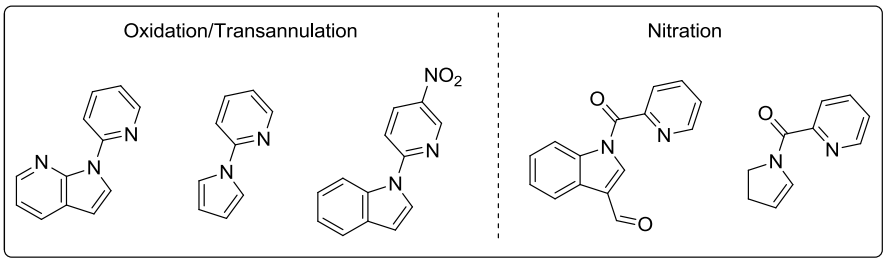
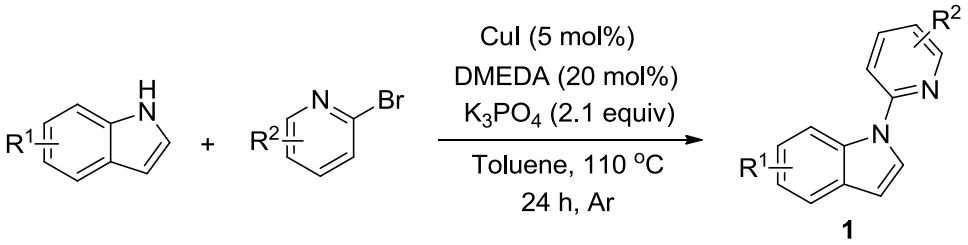


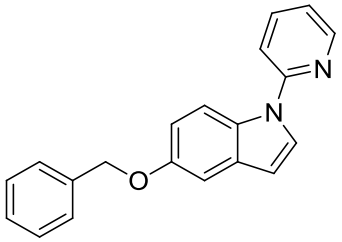

**Figure S7**. Unsuccessful substrates under both protocols.

## 9. Preparation and Characterization of Unknown Starting Materials

**Preparation of substrates 1a-q and 1aa-1am**[7]

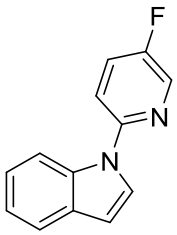



To a screw-cap test tube,was added CuI (9.5 mg, 5 mol %), indole (1 mmol), and $K_3PO_4$ (445 mg, 2.1 mmol), and the reaction vessel was fitted with a rubber septum. The vessel was evacuated and back-filled with argon twice. Then the heteroaryl halide (1.0 mmol), *N*,*N*′-dimethyl-ethylenediamine (0.022 mL, 20 mol %), and toluene (3 mL) were then successively added under a stream of argon. The reaction tube was sealed and the mixture was stirred in at 110 °C. After 24 h, the reaction mixture was cooled, diluted with ethyl acetate (3 mL), and filtered through a plug of silica gel, eluting with additional ethyl acetate (20 mL). The filtrate was concentrated and the resulting residue was purified by column chromatography to provide the pure compounds **1**.



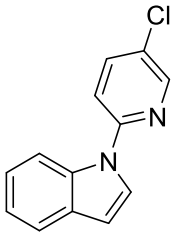
**5-(Benzyloxy)-1-(pyridin-2-yl)-1*H*-indole (1g)**

**1g** was obtained as a solid; Mp: 103−105 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.58 – 8.53 (m, 1H), 8.24 – 8.17 (m, 1H), 7.82 – 7.76 (m, 1H), 7.70 (d, *J* = 3.4 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.47 – 7.38 (m, 3H), 7.37 – 7.31 (m, 1H), 7.23 – 7.20 (m, 1H), 7.16 – 7.11 (m, 1H), 7.07 – 7.02 (m, 1H), 6.65 (d, *J* = 3.4 Hz, 1H), 5.15 (s, 2H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 154.2, 152.5, 148.9, 138.4, 137.6, 131.1, 130.4, 128.6, 127.8, 127.6, 126.3, 119.8, 114.2, 113.9, 113.5, 105.4, 104.5, 70.7; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{20}H_{17}N_2O$ 301.1341, found 301.1338.



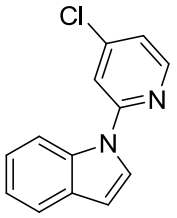
**1-(5-Fluoropyridin-2-yl)-1*H*-indole (1ae)**

**1ae** was obtained as a solid; Mp: 79−81 ℃; **$^{1}$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.41 – 8.39 (m, 1H), 8.10 – 8.07 (m, 1H), 7.67 – 7.64 (m, 1H), 7.61 (d, $J$ = 3.5 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.44 – 7.41 (m, 1H), 7.31 – 7.26 (m, 1H), 7.22 – 7.18 (m, 1H), 6.71 – 6.69 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 158.2, 155.7, 148.7 (d, $J_{C\text{-}F}$ = 2.4 Hz), 136.7, 136.4, 135.0, 130.3, 126.1, 125.6 (d, $J_{C\text{-}F}$ = 20.2 Hz), 123.2, 121.3 (d, $J_{C\text{-}F}$ = 16.8 Hz), 115.5 (d, $J_{C\text{-}F}$ = 4.5 Hz), 112.5, 105.6; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{10}FN_2$ 213.0828, found 213.0841.



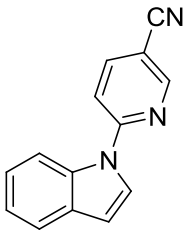
**1-(5-Chloropyridin-2-yl)-1*H*-indole (1af)**

**1af** was obtained as a solid; Mp: 57−59 ℃; **$^{1}$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.53 – 8.50 (m, 1H), 8.19 – 8.16 (m, 1H), 7.79 – 7.76 (m, 1H), 7.68 – 7.65 (m, 2H), 7.46 – 7.43 (m, 1H), 7.34 – 7.29 (m, 1H), 7.25 – 7.21 (m, 1H), 6.74 – 6.72 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 150.7, 147.5, 138.1, 135.0, 130.4, 127.5, 125.7, 123.4, 121.5, 121.2, 114.9, 113.0, 106.1; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{10}ClN_2$ 229.0533, found 229.0543.



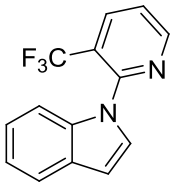
**1-(4-Chloropyridin-2-yl)-1*H*-indole (1ag)**

**1ag** was obtained as yellow oil; **$^{1}$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.44 (d, $J$ = 5.4 Hz, 1H), 8.25 – 8.22 (m, 1H), 7.68 – 7.63 (m, 2H), 7.49 (d, $J$ = 1.7 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.24 – 7.20 (m, 1H), 7.17 – 7.13 (m, 1H), 6.74 – 6.71 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 150 MHz): $\delta$ 153.5, 149.7, 145.7, 135.1, 130.6, 125.6, 123.5, 121.7, 121.2, 120.2, 114.3, 113.3, 106.4; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{10}ClN_2$ 229.0533, found 229.0542.



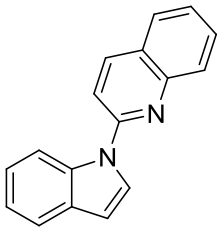

**1-(5-Cyanopyridin-2-yl)-1*H*-indole (1ai)**

**1ai** was obtained as a solid; Mp: 122−124 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.82 – 8.77 (m, 1H), 8.41 – 8.36 (m, 1H), 8.01 – 7.97 (m, 1H), 7.71 (d, $J$ = 3.7 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.55 – 7.50 (m, 1H), 7.38 – 7.33 (m, 1H), 7.29 – 7.25 (m, 1H), 6.80 – 6.77 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 154.5, 152.4, 141.2, 135.1, 131.0, 125.0, 124.2, 122.7, 121.4, 116.9, 114.5, 112.7, 108.3, 104.5; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{10}N_3$ 220.0875, found 220.0864.



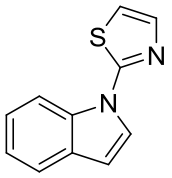

**1-(3-Trifluoromethylpyridin-2-yl)-1*H*-indole (1ak)**

**1ak** was obtained as colorless oil. **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.83 – 8.78 (m, 1H), 8.26 – 8.20 (m, 1H), 7.71 – 7.65 (m, 1H), 7.52 – 7.47 (m, 1H), 7.43 – 7.39 (m, 1H), 7.37 – 7.33 (m, 1H), 7.26 – 7.18 (m, 2H), 6.75 – 6.70 (m, 1H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 151.9, 149.3, 137.0 (q, $J$ = 4.7 Hz), 136.9, 128.7, 127.7 (q, $J$ = 2.6 Hz), 122.5, 122.3 (q, $J$ = 273.3 Hz), 121.9, 121.5 (q, $J$ = 32.8 Hz), 120.7, 120.5, 111.0, 104.5. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{10}F_3N_2$ 263.0796, found 263.0791.




**2-(1*H*-indol-1-yl)quinoline (1al)**

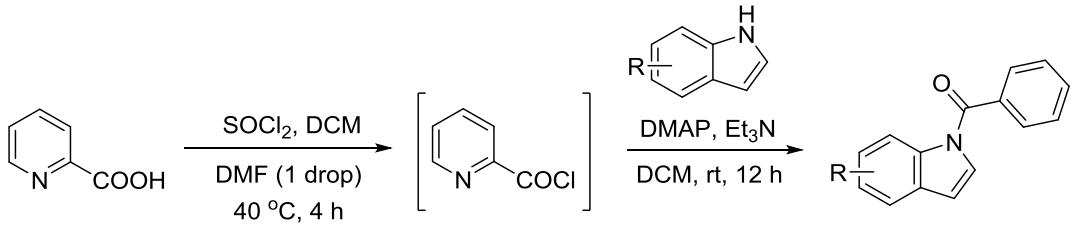
**1al** was obtained as a white solid; Mp: 111−113 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.62 – 8.57 (m, 1H), 8.24 – 8.19 (m, 1H), 8.12 – 8.07 (m, 1H), 7.83 – 7.78 (m, 2H), 7.75 – 7.66 (m, 2H), 7.62 (d, $J$ = 8.8 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.38 – 7.33 (m, 1H), 7.27 – 7.22 (m, 1H), 6.78 – 6.71 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 150 MHz): $\delta$ 151.2, 147.3, 138.7, 135.4, 130.6, 130.3, 128.4, 127.5, 125.9, 125.8, 125.6, 123.4, 121.6, 121.0, 114.2, 113.9, 106.1; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{13}N_2$ 245.1079, found 245.1088.



**2-(1*H*-indol-1-yl)thiazole (1am)**

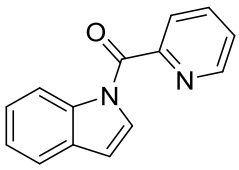
**1am** was obtained as pale yellow oil; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.33 – 8.28 (m, 1H), 7.70 – 7.60 (m, 3H), 7.40 – 7.34 (m, 1H), 7.27 – 7.24 (m, 1H), 7.06 (d, $J$ = 3.6 Hz, 1H), 6.74 – 6.70 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 160.7, 140.0, 135.0, 130.1, 126.5, 124.1, 122.2, 121.3, 113.2, 112.9, 107.1; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{11}H_9N_2S$ 201.0486, found 201.0479.

**Preparation of *N*-(2-pyridoyl) indoles 4**[8]



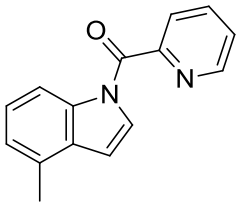

**4**

To a solution of the picolinic acid (4.2 mmol) in dichloromethane (8 mL) at room temperature was added thionyl chloride (0.8 mL) and one drop of dry DMF. The reaction was allowed to stir at 40 ℃ for 4 hours. The solvent was then removed under reduced pressure to afford the corresponding crude acid chloride. Then dichloromethane (10 mL) was added and the solution was cooled to 0 ℃ followed by dropwise addition of triethylamine (1.4 mL), 4-dimethylaminopyridine (0.1 mmol) and indole derivative (4.0 mmol, 1 equiv). The reaction mixture was stirred for 12 hours at room temperature. After completion of reaction as indicated by TLC, the mixture was extracted by dichloromethane and the organic layer was dried over $Na_2SO_4$ and the solvent was evaporated. Purification by flash column chromatography on silica gel afforded the substrates **4**.



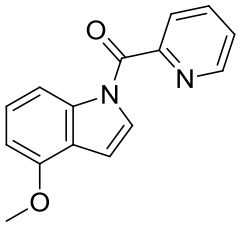
**(1*H*-indol-1-yl)(pyridin-2-yl)methanone (4a)**

**4a** was obtained as a white solid; Mp: 82−84 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.76 – 8.70 (m, 1H), 8.55 (d, $J$ = 8.2 Hz, 1H), 8.10 – 8.04 (m, 1H), 7.98 (d, $J$ = 3.8 Hz, 1H), 7.91 (td, $J$ = 7.7, 1.5 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.52 – 7.46 (m, 1H), 7.43 – 7.37 (m, 1H), 7.35 – 7.30 (m, 1H), 6.64 (d, $J$ = 3.8 Hz, 1H); **$^{13}$C NMR** ($CDCl_3$, 150 MHz): $\delta$ 165.7, 152.3, 148.5, 137.4, 136.4, 130.7, 128.5, 126.1, 125.7, 124.9, 124.2, 120.8, 116.9, 109.1; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{11}N_2O$ 223.0871, found 223.0868.



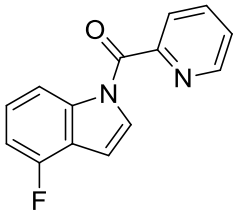
**(4-Methyl-1*H*-indol-1-yl)(pyridin-2-yl)methanone (4b)**

**4b** was obtained as pale yellow oil; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.76 – 8.72 (m, 1H), 8.40 – 8.34 (m, 1H), 8.09 – 8.05 (m, 1H), 7.95 (d, $J$ = 3.9 Hz, 1H), 7.91 (td, $J$ = 7.8, 1.8 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.32 – 7.27 (m, 1H), 7.15 – 7.11 (m, 1H), 6.69 – 6.66 (m, 1H), 2.55 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 150 MHz): $\delta$ 165.8, 152.4, 148.5, 137.3, 136.1, 130.2, 130.1, 127.8, 126.1, 125.7, 125.0, 124.6, 114.4, 107.5, 18.5; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{13}N_2O$ 237.1028, found 237.1047.



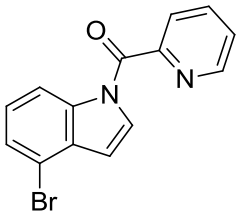
**(4-Methoxy-1*H*-indol-1-yl)(pyridin-2-yl)methanone (4c)**

**4c** was obtained as a white solid; Mp: 137−139 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.75 – 8.72 (m, 1H), 8.14 (d, $J$ = 8.3 Hz, 1H), 8.08 – 8.05 (m, 1H), 7.94 – 7.89 (m, 1H), 7.88 (d, $J$ = 3.8 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.32 (t, $J$ = 8.2 Hz, 1H), 6.79 – 6.76 (m, 2H), 3.96 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 166.0, 152.9, 152.5, 148.7, 137.8, 137.5, 127.0, 126.2, 126.0, 125.8, 120.9, 110.1, 106.2, 104.9, 55.6; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{15}H_{12}N_2NaO_2$ 275.0796, found 275.0804.



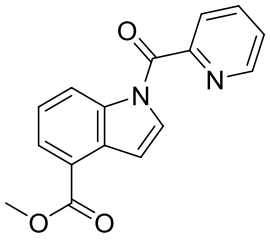
**(4-Fluoro-1*H*-indol-1-yl)(pyridin-2-yl)methanone (4d)**

**4d** was obtained as a white solid; Mp: 154−156 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.76 – 8.72 (m, 1H), 8.32 (d, $J$ = 8.3 Hz, 1H), 8.14 – 8.09 (m, 1H), 8.03 (d, $J$ = 3.9 Hz, 1H), 7.98 – 7.92 (m, 1H), 7.55 – 7.50 (m, 1H), 7.36 – 7.28 (m, 1H), 7.04 – 6.97 (m, 1H), 6.76 – 6.73 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 165.2, 155.1 (d, $J_{C\text{-}F}$ = 247.6 Hz), 151.4, 148.1, 138.0 (d, $J_{C\text{-}F}$ = 9.3 Hz), 137.0, 128.1, 125.9, 125.5, 125.3 (d, $J_{C\text{-}F}$ = 7.2 Hz), 118.9 (d, $J_{C\text{-}F}$ = 22.0 Hz), 112.5 (d, $J_{C\text{-}F}$ = 3.8 Hz), 109.1 (d, $J_{C\text{-}F}$ = 18.6 Hz), 103.9; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_9FN_2NaO$ 263.0597, found 263.0599.



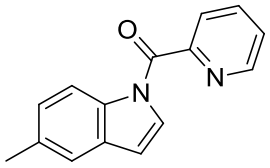
**(4-Bromo-1*H*-indol-1-yl)(pyridin-2-yl)methanone (4e)**

**4e** was obtained as a white solid; Mp: 73−75 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.80 – 8.76 (m, 1H), 8.53 (d, $J$ = 8.3 Hz, 1H), 8.16 – 8.12 (m, 2H), 8.01 – 7.95 (m, 1H), 7.59 – 7.54 (m, 1H), 7.53 – 7.49 (m, 1H), 7.31 – 7.27 (m, 1H), 6.74 (dd, $J$ = 3.9, 0.6 Hz, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 165.7, 151.8, 148.6, 137.5, 136.8, 131.3, 129.2, 127.1, 126.4, 126.0, 125.9, 115.9, 114.5, 108.7; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_9BrN_2NaO$ 322.9796, found 322.9776.



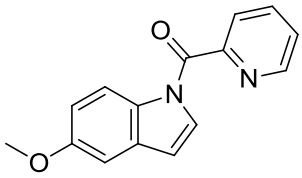
**Methyl 1-picolinoyl-1*H*-indole-4-carboxylate (4f)**

**4f** was obtained as a white solid; Mp: 118−120 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.79 – 8.73 (m, 2H), 8.14 – 8.08 (m, 2H), 8.06 – 8.03 (m, 1H), 7.97 – 7.91 (m, 1H), 7.55 – 7.50 (m, 1H), 7.43 (t, $J$ = 8.0 Hz, 1H), 7.36 – 7.34 (m, 1H), 3.98 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 166.8, 165.3, 151.4, 148.1, 137.0, 136.6, 130.4, 129.9, 126.2, 125.9, 125.5, 123.9, 121.4, 120.9, 109.0, 51.5; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{16}H_{12}N_2NaO_3$ 303.0746, found 303.0737.



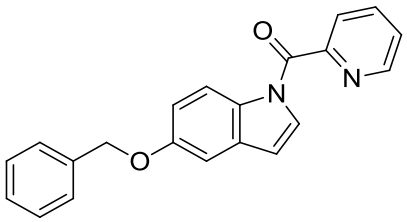
**(5-Methyl-1*H*-indol-1-yl)(pyridin-2-yl)methanone (4g)**

**4g** was obtained as a white solid; Mp: 78−80 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.76 – 8.72 (m, 1H), 8.41 (d, $J$ = 8.4 Hz, 1H), 8.09 – 8.06 (m, 1H), 7.96 – 7.90 (m, 2H), 7.52 – 7.48 (m, 1H), 7.39 – 7.36 (m, 1H), 7.22 – 7.19 (m, 1H), 6.58 – 6.56 (m, 1H), 2.47 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 165.5, 152.5, 148.5, 137.4, 134.6, 133.8, 130.9, 128.5, 126.2, 126.0, 125.7, 120.8, 116.5, 109.0, 21.5; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{15}H_{12}N_2NaO$ 259.0847, found 259.0852.



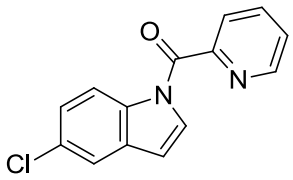
**(5-Methoxy-1*H*-indol-1-yl)(pyridin-2-yl)methanone (4h)**

**4h** was obtained as a white solid; Mp: 118−120 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.75 – 8.71 (m, 1H), 8.44 (d, $J$ = 9.0 Hz, 1H), 8.10 – 8.06 (m, 1H), 7.98 (d, $J$ = 3.8 Hz, 1H), 7.95 – 7.91 (m, 1H), 7.54 – 7.48 (m, 1H), 7.06 (d, $J$ = 2.5 Hz, 1H), 7.01 – 6.96 (m, 1H), 6.58 – 6.56 (m, 1H), 3.88 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 164.8, 156.4, 151.9, 148.0, 136.9, 131.3, 130.5, 128.7, 125.6, 125.3, 117.2, 112.6, 108.6, 103.3, 55.2; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{15}H_{12}N_2NaO_2$ 275.0796, found 275.0802.



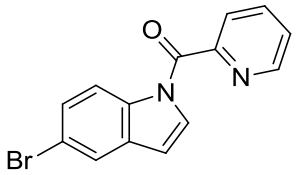
**(5-(Benzyloxy)-1*H*-indol-1-yl)(pyridin-2-yl)methanone(4i)**

**4i** was obtained as a white solid; Mp: 131−133 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.75 – 8.71 (m, 1H), 8.46 (d, $J$ = 9.0 Hz, 1H), 8.10 – 8.06 (m, 1H), 7.99 (d, $J$ = 3.8 Hz, 1H), 7.92 (td, $J$ = 7.8, 1.7 Hz, 1H), 7.52 – 7.47 (m, 3H), 7.43 – 7.38 (m, 2H), 7.36 – 7.31 (m, 1H), 7.15 – 7.13 (m, 1H), 7.10 – 7.06 (m, 1H), 6.56 (d, $J$ = 3.8 Hz, 1H), 5.15 (s, 2H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 165.3, 156.0, 152.4, 148.5, 1374, 137.2, 131.8, 131.2, 129.2, 128.6, 127.9, 127.5, 126.1, 125.7, 117.7, 113.9, 109.1, 105.1, 70.5; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{21}H_{16}N_2NaO_2$ 351.1109, found 351.1119.



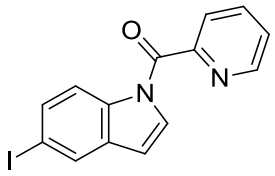
**(5-Chloro-1*H*-indol-1-yl)(pyridin-2-yl)methanone (4j)**

**4j** was obtained as a white solid; Mp: 143−144 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.75 – 8.70 (m, 1H), 8.47 (d, $J$ = 8.8 Hz, 1H), 8.12 – 8.06 (m, 2H), 7.96 – 7.91 (m, 1H), 7.56 – 7.49 (m, 2H), 7.35 – 7.30 (m, 1H), 6.58 – 6.55 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 164.9, 151.4, 148.1, 137.0, 134.3, 131.5, 129.4, 129.1, 125.9, 125.5, 124.5, 119.9, 117.4, 107.8; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_9ClN_2NaO$ 279.0301, found 279.0275.



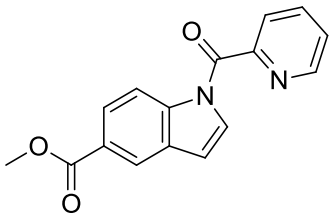
**(5-Bromo-1*H*-indol-1-yl)(pyridin-2-yl)methanone (4k)**

**4k** was obtained as a white solid; Mp: 134−136 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.78 (d, $J$ = 4.8 Hz, 1H), 8.53 (d, $J$ = 8.3 Hz, 1H), 8.18 – 8.11 (m, 2H), 8.01 – 7.95 (m, 1H), 7.59 – 7.54 (m, 1H), 7.51 (d, $J$ = 7.8 Hz, 1H), 7.32 – 7.27 (m, 1H), 6.74 (d, $J$ = 3.9 Hz, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 164.9, 151.3, 148.0, 137.0, 134.7, 132.0, 129.3, 127.2, 125.9, 125.5, 123.0, 117.8, 116.9, 107.6; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{10}BrN_2O$ 300.9977, found 300.9969.



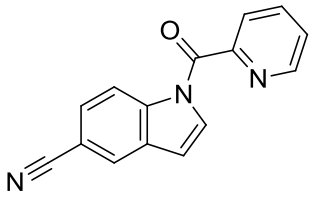
**(5-Iodo-1*H*-indol-1-yl)(pyridin-2-yl)methanone (4l)**

**4l** was obtained as a white solid; Mp: 141−143 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.75 – 8.72 (m, 1H), 8.30 (d, $J$ = 8.7 Hz, 1H), 8.12 – 8.09 (m, 1H), 8.03 (d, $J$ = 3.9 Hz, 1H), 7.97 – 7.92 (m, 2H), 7.67 – 7.64 (m, 1H), 7.54 – 7.51 (m, 1H), 6.57 – 6.54 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 165.5, 151.9, 148.5, 137.5, 135.7, 133.4, 132.9, 129.6, 129.4, 126.4, 126.0, 118.7, 107.9, 88.4; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_9IN_2NaO$ 370.9657, found 370.9653.



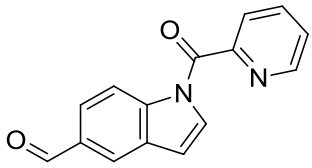
**Methyl 1-picolinoyl-1*H*-indole-5-carboxylate (4m)**

**4m** was obtained as a white solid; Mp: 155−157 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.77 – 8.71 (m, 1H), 8.55 (d, $J$ = 8.7 Hz, 1H), 8.31 (d, $J$ = 1.7 Hz, 1H), 8.14 – 8.06 (m, 3H), 7.98 – 7.91 (m, 1H), 7.56 – 7.50 (m, 1H), 6.69 (d, $J$ = 3.9 Hz, 1H), 3.95 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 166.9, 165.2, 151.3, 148.1, 138.6, 137.0, 130.0, 129.4, 126.0, 125.8, 125.6, 125.5, 122.4, 116.0, 108.7, 51.6; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{16}H_{12}N_2NaO_3$ 303.0746, found 303.0743.



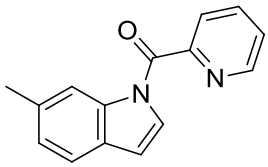
**(5-Cyano-1*H*-indol-1-yl)(pyridin-2-yl)methanone (4n)**

**4n** was obtained as a white solid; Mp: 144−146 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.79 – 8.72 (m, 1H), 8.63 (d, $J$ = 8.6 Hz, 1H), 8.25 (d, $J$ = 3.8 Hz, 1H), 8.19 – 8.13 (m, 1H), 7.98 (td, $J$ = 7.8, 1.7 Hz, 1H), 7.95 – 7.90 (m, 1H), 7.67 – 7.61 (m, 1H), 7.60 – 7.54 (m, 1H), 6.69 (d, $J$ = 3.8 Hz, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 165.6, 151.3, 148.7, 138.4, 137.7, 130.9, 130.7, 128.1, 126.8, 126.3, 125.4, 119.6, 117.6, 108.2, 107.4; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{15}H_9N_3NaO$ 270.0643, found 270.0653.



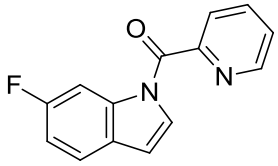
**1-Picolinoyl-1*H*-indole-5-carbaldehyde (4o)**

**4o** was obtained as a white solid; Mp: 147−149 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 10.15 (s, 1H), 8.83 – 8.80 (m, 1H), 8.71 (d, $J$ = 8.6 Hz, 1H), 8.23 – 8.18 (m, 3H), 8.05 – 8.00 (m, 1H), 7.99 – 7.96 (m, 1H), 7.64 – 7.59 (m, 1H), 6.80 (d, $J$ = 3.9 Hz, 1H); **$^{13}$C NMR** ($CDCl_3$, 150 MHz): $\delta$ 192.3, 165.8, 151.7, 148.8, 140.2, 137.7, 133.0, 131.1, 130.6, 126.8, 126.4, 126.3, 123.6, 117.4, 109.3; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{11}N_2O_2$ 251.0821, found 251.0821.



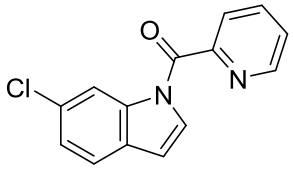
**(6-Methyl-1*H*-indol-1-yl)(pyridin-2-yl)methanone (4p)**

**4p** was obtained as an off-white solid; Mp: 64-66 °C; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.81 – 8.77 (m, 1H), 8.45 (s, 1H), 8.14 – 8.10 (m, 1H), 7.98 (td, $J$ = 7.8, 1.7 Hz, 1H), 7.93 (d, $J$ = 3.8 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.52 (d, $J$ = 7.9 Hz, 1H), 7.20 (d, $J$ = 7.8 Hz, 1H), 6.64 (d, $J$ = 3.8 Hz, 1H), 2.58 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 165.7, 152.4, 148.5, 137.3, 136.8, 135.0, 128.4, 127.8, 126.0, 125.6, 125.5, 120.3, 117.2, 109.0, 22.0; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{15}H_{12}N_2NaO$ 259.0847, found 259.0858.



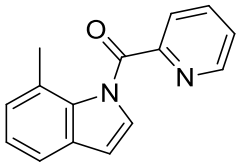
**(6-Fluoro-1*H*-indol-1-yl)(pyridin-2-yl)methanone (4q)**

**4q** was obtained as a white solid; Mp: 98−100 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.77 – 8.73 (m, 1H), 8.33 – 8.26 (m, 1H), 8.13 – 8.09 (m, 1H), 8.03 (d, $J$ = 3.9 Hz, 1H), 7.98 – 7.92 (m, 1H), 7.55 – 7.48 (m, 2H), 7.11 – 7.04 (m, 1H), 6.63 – 6.58 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 165.6, 161.2 (d, $J_{C\text{-}F}$ = 240.4 Hz), 152.0, 148.5, 137.5, 136.6 (d, $J_{C\text{-}F}$ = 12.9 Hz), 128.9 (d, $J_{C\text{-}F}$ = 4.0 Hz), 126.9 (d, $J_{C\text{-}F}$ = 1.6 Hz), 126.3, 125.9, 121.2 (d, $J_{C\text{-}F}$ = 9.8 Hz, 1H), 112.2 (d, $J_{C\text{-}F}$ = 24.1 Hz), 108.7, 104.5 (d, $J_{C\text{-}F}$ = 28.7 Hz); **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_9FN_2NaO$ 263.0597, found 263.0604.



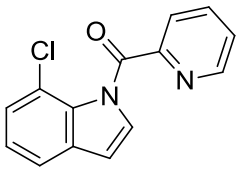

**(6-Chloro-1*H*-indol-1-yl)(pyridin-2-yl)methanone (4r)**

**4r** was obtained as a white solid; Mp: 137−139 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.76 – 8.72 (m, 1H), 8.62 – 8.57 (m, 1H), 8.12 – 8.04 (m, 2H), 7.97 – 7.91 (m, 1H), 7.54 – 7.47 (m, 2H), 7.31 – 7.27 (m, 1H), 6.60 (d, $J$ = 3.7 Hz, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 165.0, 151.4, 148.1, 137.0, 136.3, 130.3, 128.7, 128.6, 125.9, 125.5, 124.2, 120.9, 116.7, 108.2; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_9ClN_2NaO$ 279.0301, found 279.0291.



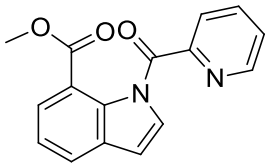

**(7-Methyl-1*H*-indol-1-yl)(pyridin-2-yl)methanone (4s)**

**4s** was obtained as a white solid; Mp: 97−99 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.79 – 8.76 (m, 1H), 8.18 – 8.14 (m, 1H), 7.97 – 7.92 (m, 1H), 7.56 – 7.52 (m, 1H), 7.49 (d, $J$ = 3.8 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.26 – 7.22 (m, 1H), 7.18 (d, $J$ = 7.3 Hz, 1H), 6.61 (d, $J$ = 3.7 Hz, 1H), 2.52 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 165.1, 151.6, 149.1, 137.4, 135.8, 132.1, 129.4, 127.7, 126.7, 126.5, 126.2, 124.3, 118.5, 108.7, 21.9; **HRMS** (ESI-TOF) *m/z*: calcd for $C_{15}H_{12}N_2NaO$ $[M+Na]^+$ 259.0847, found 259.0853.



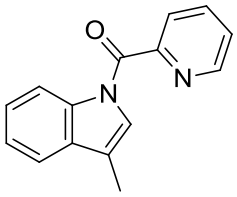

**(7-Chloro-1*H*-indol-1-yl)(pyridin-2-yl)methanone (4t)**

**4t** was obtained as pale yellow oil; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.74 – 8.69 (m, 1H), 8.24 – 8.18 (m, 1H), 7.96 – 7.89 (m, 1H), 7.65 (d, $J$ = 3.7 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.35 – 7.30 (m, 1H), 7.25 – 7.20 (m, 1H), 6.65 (d, $J$ = 3.7 Hz, 1H); **$^{13}$C NMR** ($CDCl_3$, 150 MHz): $\delta$ 164.8, 150.8, 149.1, 137.4, 134.1, 133.5, 130.2, 127.1, 126.27, 126.25, 124.5, 121.1, 119.6, 107.9; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_9ClN_2NaO$ 279.0301, found 279.0323.



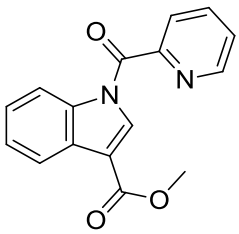
**Methyl 1-picolinoyl-1*H*-indole-7-carboxylate (4u)**

**4u** was obtained as a white solid; Mp: 74−76 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.78 – 8.69 (m, 1H), 8.17 – 8.08 (m, 1H), 7.96 – 7.85 (m, 1H), 7.83 – 7.75 (m, 1H), 7.77 – 7.63 (m, 2H), 7.56 – 7.46 (m, 1H), 7.38 – 7.28 (m, 1H), 6.70 – 6.63 (m, 1H), 3.77 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 167.7, 165.3, 150.4, 148.6, 136.9, 132.3, 131.8, 129.5, 126.4, 125.7, 124.8, 123.8, 123.0, 121.2, 107.8, 51.5; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{13}N_2O_3$ 281.0926, found 281.0921.



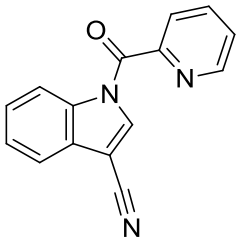
**(3-Methyl-1*H*-indol-1-yl)(pyridin-2-yl)methanone (4v)**

**4v** was obtained as a white solid; Mp: 119−121 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.73 (d, $J$ = 4.7 Hz, 1H), 8.53 (d, $J$ = 8.0 Hz, 1H), 8.05 – 8.01 (m, 1H), 7.92 – 7.86 (m, 1H), 7.70 (d, $J$ = 1.1 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.49 – 7.45 (m, 1H), 7.42 – 7.37 (m, 1H), 7.37 – 7.32 (m, 1H), 2.27 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 165.4, 152.7, 148.5, 137.3, 136.7, 131.8, 126.0, 125.5, 125.0, 124.9, 124.0, 118.8, 118.4, 116.9, 9.8; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{15}H_{12}N_2NaO$ 259.0847, found 259.0857.



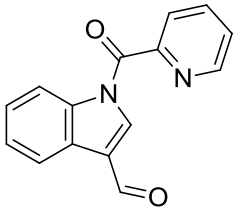
**Methyl 1-picolinoyl-1*H*-indole-3-carboxylate (4w)**

**4w** was obtained as a white solid; Mp: 129−131 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.57 – 8.52 (m, 1H), 8.26 – 8.18 (m, 2H), 7.94 – 7.88 (m, 1H), 7.71 – 7.66 (m, 1H), 7.49 – 7.40 (m, 2H), 7.36 – 7.29 (m, 2H), 3.45 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 167.0, 161.4, 151.8, 147.9, 138.3, 136.9, 131.3, 127.1, 127.0, 125.9, 124.7, 123.5, 121.9, 115.1, 114.4, 51.4; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{13}N_2O_3$ 281.0926, found 281.0917.



**(3-Cyano-1*H*-indol-1-yl)(pyridin-2-yl)methanone (4x)**

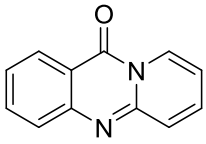
**4x** was obtained as a white solid; Mp: 124−126 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.95 (s, 1H), 8.81 – 8.77 (m, 1H), 8.58 – 8.54 (m, 1H), 8.26 – 8.22 (m, 1H), 8.00 (td, $J$ = 7.8, 1.7 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.63 – 7.59 (m, 1H), 7.54 – 7.49 (m, 1H), 7.49 – 7.44 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 164.6, 150.5, 148.7, 137.8, 136.9, 135.7, 127.8, 127.2, 126.8, 126.7, 125.5, 119.6, 117.3, 114.2, 93.9; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{10}N_3O$ 248.0824, found 248.0820.



**1-Picolinoyl-1*H*-indole-3-carbaldehyde (4y)**

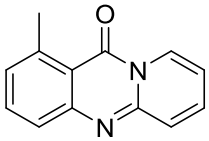
**4y** was obtained as a white solid; Mp: 114−116 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 10.12 (s, 1H), 8.95 (s, 1H), 8.80 – 8.76 (m, 1H), 8.54 – 8.50 (m, 1H), 8.34 – 8.29 (m, 1H), 8.25 – 8.21 (m, 1H), 8.02 – 7.97 (m, 1H), 7.62 – 7.57 (m, 1H), 7.50 – 7.41 (m, 2H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 185.7, 164.7, 150.4, 148.2, 139.5, 137.3, 136.9, 126.6, 126.2, 126.1, 125.6, 125.2, 122.2, 121.5, 116.3; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{11}N_2O_2$ 251.0821, found 251.0823.

## 10. Characterization Data for Synthesized Products 2 and 3



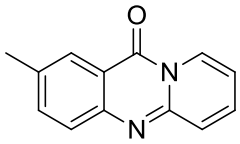
**11*H*-pyrido[2,1-b]quinazolin-11-one (2a)**[9]

According to **GP2**, the reaction of 1-(pyridin-2-yl)indole (**1a**) (97 mg, 0.5 mmol) in dioxane-$H_2O$ (10:1) for 12 hours afforded **2a** as a yellow solid (87 mg, 89% yield); Mp: 209−211 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.89 (d, $J$ = 7.3 Hz, 1H), 8.46 (d, $J$ = 8.0 Hz, 1H), 7.90 – 7.76 (m, 2H), 7.56 – 7.46 (m, 3H), 6.91 – 6.84 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 159.0, 148.5, 147.7, 135.1, 134.1, 127.3, 126.9, 126.7, 126.3, 125.2, 116.3, 112.5; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{12}H_9N_2O$ 197.0715, found 197.0706.



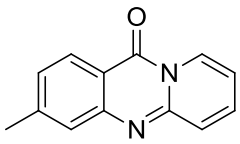
**1-Methyl-11*H*-pyrido[2,1-b]quinazolin-11-one (2b)**[10]

According to **GP2**, the reaction of 7-methyl-1-(pyridin-2-yl)indole (**1b**) (105 mg, 0.5 mmol) in dioxane-$H_2O$ (10:1) for 12 hours afforded **2b** as a yellow solid (84 mg, 80% yield). **Melting point**: 143−145 ℃. **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.85 (d, $J$ = 7.5 Hz, 1H), 7.72 – 7.59 (m, 2H), 7.54 – 7.43 (m, 2H), 7.23 (d, $J$ = 7.0 Hz, 1H), 6.86 – 6.80 (m, 1H), 2.98 (s, 3H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 158.4, 149.5, 147.1, 141.1, 133.64, 133.59, 127.0, 126.0, 125.5, 124.5, 114.5, 111.7, 23.2. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{11}N_2O$ 211.0871, found 211.0879.



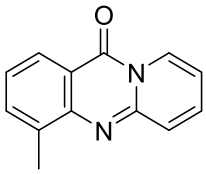
**2-Methyl-11*H*-pyrido[2,1-b]quinazolin-11-one (2c)**[11]

According to **GP2**, the reaction of 5-methyl-1-(pyridin-2-yl)indole (**1c**) (105 mg, 0.5 mmol) in dioxane-$H_2O$ (10:1) for 12 hours afforded **2c** as a yellow solid (86 mg, 82% yield); Mp: 138−140 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.92 – 8.83 (m, 1H), 8.38 – 8.30 (m, 1H), 7.62 – 7.46 (m, 3H), 7.35 – 7.38 (m, 1H), 6.85 (s, 1H), 2.55 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 158.9, 147.2, 146.7, 136.9, 135.4, 133.6, 126.8, 126.7, 126.4, 126.3, 116.1, 112.4, 21.4; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{11}N_2O$ 211.0871, found 211.0878.



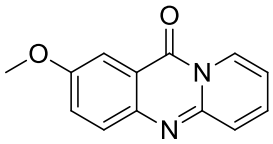
**3-Methyl-11*H*-pyrido[2,1-b]quinazolin-11-one (2d)**[11]

According to **GP2**, the reaction of 6-methyl-1-(pyridin-2-yl)indole (**1d**) (105 mg, 0.5 mmol) in dioxane-$H_2O$ (10:1) for 12 hours afforded **2d** as a yellow solid (91 mg, 86% yield); Mp: 146−147 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.87 (d, $J$ = 7.4 Hz, 1H), 8.34 (d, $J$ = 8.3 Hz, 1H), 7.58 (s, 1H), 7.52 – 7.46 (m, 2H), 7.34 – 7.29 (m, 1H), 6.87 – 6.76 (m, 1H), 2.50 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 157.7, 147.6, 146.8, 145.2, 133.0, 126.2, 126.0, 125.7, 125.1, 112.9, 111.3, 21.1; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{11}N_2O$ 211.0871, found 211.0875.



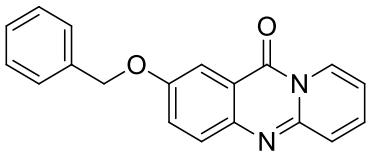
**4-Methyl-11*H*-pyrido[2,1-b]quinazolin-11-one (2e)**[11]

According to **GP2**, the reaction of 7-methyl-1-(pyridin-2-yl)indole (**1e**) (105 mg, 0.5 mmol) in dioxane-$H_2O$ (10:1) for 12 hours afforded **2e** as a yellow solid (75 mg, 71% yield); Mp: 179−181 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.86 (d, $J$ = 6.9 Hz, 1H), 8.31 (d, $J$ = 7.8 Hz, 1H), 7.69 (d, $J$ = 6.3 Hz, 1H), 7.60 – 7.42 (m, 2H), 7.42 – 7.32 (m, 1H), 6.90 – 6.79 (m, 1H), 2.70 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 158.9, 147.0, 146.2, 134.9, 134.6, 132.9, 126.4, 126.1, 124.4, 124.3, 115.7, 111.9, 17.2; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{11}N_2O$ 211.0871, found 211.0863.



**2-Methoxy-11*H*-pyrido[2,1-b]quinazolin-11-one (2f)**[12]

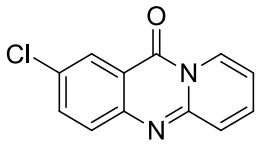
According to **GP2**, the reaction of 5-methoxy-1-(pyridin-2-yl)indole (**1f**) (113 mg, 0.5 mmol) in dioxane-$H_2O$ (10:1) for 12 hours afforded **2f** as a yellow solid (70 mg, 62% yield); Mp: 175−177 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.88 (d, $J$ = 7.4 Hz, 1H), 7.78 – 7.71 (m, 2H), 7.53 – 7.42 (m, 3H), 6.90 – 6.81 (m, 1H), 3.96 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 158.7, 157.4, 146.1, 143.7, 132.9, 128.7, 126.9, 126.42, 126.40, 116.9, 112.6, 105.1, 55.9; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{11}N_2O_2$ 227.0821, found 227.0820.



**2-Benzyloxy-11*H*-pyrido[2,1-b]quinazolin-11-one (2g)**[13]

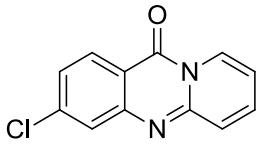
According to **GP2**, the reaction of 5-(benzyloxy)-1-(pyridin-2-yl)indole (**1g**) (150 mg, 0.5 mmol) in dioxane-$H_2O$ (10:1) for 12 hours afforded **2g** as a yellow solid (118 mg, 78% yield); Mp: 164−166 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.89 – 8.84 (m, 1H), 7.86 (d, $J$ = 2.9 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.58 – 7.54 (m, 1H), 7.52 – 7.48 (m, 3H), 7.48 – 7.44 (m, 1H), 7.44 – 7.39 (m, 2H), 7.38 – 7.34 (m, 1H), 6.91 – 6.80 (m, 1H), 5.21 (s, 2H); **$^{13}$C NMR**

($CDCl_3$, 100 MHz): $\delta$ 158.2, 155.9, 145.6, 143.3, 135.8, 132.4, 128.3, 128.1, 127.7, 127.2, 126.7, 125.92, 125.90, 116.3, 112.1, 105.9, 70.1; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{19}H_{15}N_2O_2$ 303.1134, found 303.1132.



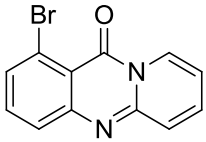
**2-Chloro-11*H*-pyrido[2,1-b]quinazolin-11-one (2h)**[13]

According to **GP2**, the reaction of 5-chloro-1-(pyridin-2-yl)indole (**1h**) (114 mg, 0.5 mmol) in dioxane-$H_2O$ (3:1) for 12 hours afforded **2h** as a yellow solid (95 mg, 83% yield); Mp: 176−178 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.93 – 8.82 (m, 1H), 8.41 (s, 1H), 7.81 – 7.70 (m, 2H), 7.60 – 7.47 (m, 2H), 6.97 – 6.85 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 157.6, 147.3, 146.6, 135.2, 134.0, 130.3, 128.2, 126.3, 125.9, 125.8, 116.5, 112.5; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{12}H_8ClN_2O$ 231.0325, found 231.0323.



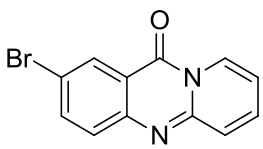
**3-Chloro-11*H*-pyrido[2,1-b]quinazolin-11-one (2i)**[9]

According to **GP2**, the reaction of 6-chloro-1-(pyridin-2-yl)indole (**1i**) (114 mg, 0.5 mmol) in dioxane-$H_2O$ (3:1) for 12 hours afforded **2i** as a yellow solid (94 mg, 82% yield); Mp: 199−201 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.85 (d, $J$ = 6.8 Hz, 1H), 8.35 (d, $J$ = 8.5 Hz, 1H), 7.74 (s, 1H), 7.61 – 7.45 (m, 2H), 7.43 – 7.35 (m, 1H), 6.95 – 6.85 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 157.4, 148.3, 147.5, 140.3, 133.8, 127.8, 125.7, 125.2, 125.1, 124.9, 113.5, 111.9; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{12}H_8ClN_2O$ 231.0325, found 231.0318.



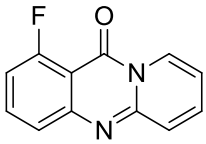
**1-Bromo-11*H*-pyrido[2,1-b]quinazolin-11-one (2j)**

According to **GP2**, the reaction of 4-bromo-1-(pyridin-2-yl)indole (**1j**) (136 mg, 0.5 mmol) in dioxane-$H_2O$ (3:1) for 12 hours afforded **2j** as a yellow solid (110 mg, 80% yield); Mp: 146−148 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.89 (d, $J$ = 7.3 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.62 – 7.53 (m, 2H), 7.47 (d, $J$ = 9.1 Hz, 1H), 6.94 – 6.87 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 156.5, 150.2, 147.4, 134.6, 134.0, 131.1, 126.5, 126.4, 125.5, 121.3, 113.8, 112.5; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{12}H_7BrN_2NaO$ 296.9639, found 296.9637.



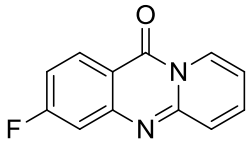
**2-Bromo-11*H*-pyrido[2,1-b]quinazolin-11-one (2k)**[10]

According to **GP2**, the reaction of 5-bromo-1-(pyridin-2-yl)indole (**1k**) (136 mg, 0.5 mmol) in dioxane-$H_2O$ (3:1) for 12 hours afforded **2k** as a yellow solid (115 mg, 84% yield); Mp: 166−168 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.90 – 8.86 (m, 1H), 8.58 (d, $J$ = 2.2 Hz, 1H), 7.92 – 7.88 (m, 1H), 7.69 – 7.65 (m, 1H), 7.60 – 7.50 (m, 2H), 6.94 – 6.89 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 157.9, 147.8, 147.3, 138.2, 134.5, 129.5, 128.7, 126.7, 126.4, 118.3, 117.4, 113.0; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{12}H_8BrN_2O$ 274.9820, found 274.9820.



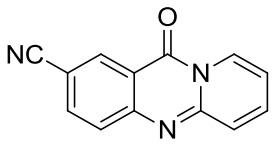
**1-Fluoro-11*H*-pyrido[2,1-b]quinazolin-11-one (2l)**[10]

According to **GP2**, the reaction of 4-fluoro-1-(pyridin-2-yl)indole (**1l**) (106 mg, 0.5 mmol) in dioxane-$H_2O$ (3:1) for 12 hours afforded **2l** as a yellow solid (81 mg, 76% yield); Mp: 167−169 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.90 (d, $J$ = 7.3 Hz, 1H), 7.79 – 7.72 (m, 1H), 7.60 – 7.54 (m, 2H), 7.52 – 7.46 (m, 1H), 7.14 – 7.06 (m, 1H), 6.94 – 6.87 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 163.0, 160.3, 155.9 (d, $J_{C\text{-}F}$ = 4.6 Hz), 150.4, 148.4, 135.2, 135.1, 126.4 (d, $J_{C\text{-}F}$ = 46.7 Hz), 122.8 (d, $J_{C\text{-}F}$ = 4.4 Hz), 112.8, 110.8 (d, $J_{C\text{-}F}$ = 20.6 Hz), 106.5 (d, $J_{C\text{-}F}$ = 6.5 Hz); **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{12}H_8FN_2O$ 215.0621, found 215.0634.



**3-Fluoro-11*H*-pyrido[2,1-b]quinazolin-11-one (2m)**[9]

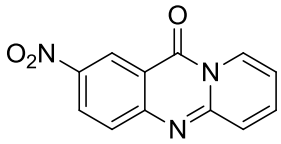
According to **GP2**, the reaction of 6-fluoro-1-(pyridin-2-yl)indole (**1m**) (106 mg, 0.5 mmol) in dioxane-$H_2O$ (3:1) for 12 hours afforded **2m** as a yellow solid (89 mg, 83% yield); Mp: 220−222 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.89 (d, $J$ = 7.3 Hz, 1H), 8.50 – 8.44 (m, 1H), 7.61 – 7.53 (m, 1H), 7.52 – 7.48 (m, 1H), 7.43 – 7.38 (m, 1H), 7.24 – 7.18 (m, 1H), 6.94 – 6.88 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 167.1 (d, $J_{C\text{-}F}$ = 255.4 Hz), 158.3, 150.7 (d, $J_{C\text{-}F}$ = 14.0 Hz), 148.6, 134.9, 130.3 (d, $J_{C\text{-}F}$ = 11.2 Hz), 126.8, 126.1, 114.8 (d, $J_{C\text{-}F}$ = 24.5 Hz), 113.1, 112.8, 111.3 (d, $J_{C\text{-}F}$ = 21.5 Hz); **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for$C_{12}H_8FN_2O$ 215.0621, found 211.0630.



**2-Cyano-11*H*-pyrido[2,1-b]quinazolin-11-one (2n)**

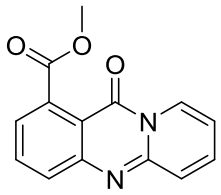
According to **GP2**, the reaction of 5-cyano-1-(pyridin-2-yl)indole (**1n**) (110 mg, 0.5 mmol) in DMSO with the addition of 6 equiv of TBN in 4 portions over 30 hours, afforded **2n** as a yellow solid (78 mg, 71% yield); Mp: 269−271 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.95 – 8.90 (m, 1H), 8.78 (d, $J$ = 1.7 Hz, 1H), 7.98 – 7.94 (m, 1H),

7.84 – 7.80 (m, 1H), 7.73 – 7.65 (m, 1H), 7.61 – 7.57 (m, 1H), 7.05 – 6.99 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 157.4, 150.3, 149.0, 135.8, 135.6, 133.1, 127.8, 126.6, 126.1, 117.9, 115.6, 113.4, 107.5; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{13}H_8N_3O$ 222.0667, found 222.0676.



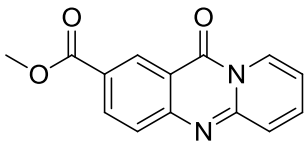
**2-Nitro-11*H*-pyrido[2,1-b]quinazolin-11-one (2o)**[11]

According to **GP2**, the reaction of 5-nitro-1-(pyridin-2-yl)indole (**1o**) (120 mg, 0.5 mmol) in DMSO with the addition of 6 equiv of TBN in 4 portions over 30 hours, afforded **2o** as a yellow solid (95 mg, 79% yield); Mp: 261−262 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 9.35 (d, $J$ = 2.5 Hz, 1H), 8.95 (d, $J$ = 7.4 Hz, 1H), 8.61 – 8.56 (m, 1H), 7.85 (d, $J$ = 9.3 Hz, 1H), 7.77 – 7.69 (m, 1H), 7.64 – 7.59 (m, 1H), 7.06 (t, $J$ = 6.8 Hz, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 158.3, 152.2, 149.8, 143.9, 136.8, 128.8, 128.4, 127.2, 126.6, 124.8, 115.3, 114.1; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{12}H_8N_3O_3$ 242.0566, found 242.0577.



**Methyl 11-oxo-11*H*-pyrido[2,1-b]quinazoline-1-carboxylate (2p)**

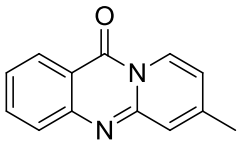
According to **GP2**, the reaction of methyl 1-(pyridin-2-yl)-1*H*-indole-4-carboxylate (**1p**) (126 mg, 0.5 mmol) in DMSO with the addition of 6 equiv of TBN in 4 portions over 30 hours, afforded **2p** as a yellow solid (51 mg, 40% yield); Mp: 169−171 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.87 – 8.83 (m, 1H), 7.92 – 7.77 (m, 2H), 7.63 – 7.49 (m, 2H), 7.45 – 7.42 (m, 1H), 6.94 – 6.88 (m, 1H), 4.06 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 150 MHz): $\delta$ 170.0, 157.4, 148.9, 148.0, 134.9, 134.3, 134.2, 128.6, 126.6, 126.2, 123.8, 113.0, 112.6, 53.0; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{11}N_2O_3$ 255.0770, found 255.0774.



**Methyl 11-oxo-11*H*-pyrido[2,1-b]quinazoline-2-carboxylate (2q)**

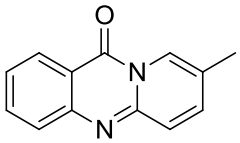
According to **GP2**, the reaction of methyl 1-(pyridin-2-yl)-1*H*-indole-5-carboxylate (**1q**) (126 mg, 0.5 mmol) in dioxane-$H_2O$ (3:1) with the addition of 6 equiv of TBN in 4 portions over 30 hours, afforded **2q** as a yellow solid (104 mg, 82% yield); Mp: 230−232 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 9.15 (s, 1H), 8.92 (d, $J$ = 6.7 Hz, 1H), 8.43 (d, $J$ = 7.9 Hz, 1H), 7.79 (d, $J$ = 8.2 Hz, 1H), 7.67 – 7.52 (m, 2H), 7.00 – 6.91 (m, 1H), 3.99 (s, 3H); **$^{13}$C NMR**

($CDCl_3$, 100 MHz): $\delta$ 165.7, 158.3, 150.9, 148.6, 135.1, 134.5, 130.0, 126.7, 126.6, 126.01, 125.98, 115.1, 112.8, 51.9; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{11}N_2O_3$ 255.0770, found 255.0780.



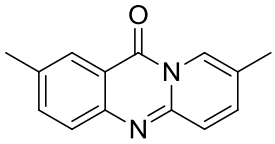
**7-Methyl-11*H*-pyrido[2,1-b]quinazolin-11-one (3a)**[9]

According to **GP2**, the reaction of 1-(4-methylpyridin-2-yl)-1*H*-indole (**1aa**) (105 mg, 0.5 mmol) in dioxane-$H_2O$ (10:1) for 12 hours afforded **3a** as a yellow solid (63 mg, 60% yield); Mp: 135−137 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.79 (d, *J* = 7.3 Hz, 1H), 8.43 (d, *J* = 7.9 Hz, 1H), 7.86 – 7.73 (m, 2H), 7.44 (t, *J* = 7.1 Hz, 1H), 7.30 (s, 1H), 6.72 (d, *J* = 7.1 Hz, 1H), 2.42 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 159.0, 148.8, 147.9, 146.0, 135.1, 127.3, 126.6, 126.0, 124.8, 123.6, 116.0, 115.7, 21.5; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{11}N_2O$ 211.0871, found 211.0868.



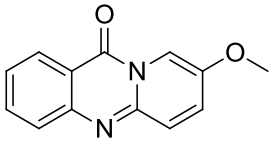
**8-Methyl-11*H*-pyrido[2,1-b]quinazolin-11-one (3b)**[9]

According to **GP2**, the reaction of 1-(5-methylpyridin-2-yl)-1*H*-indole (**1ab**) (105 mg, 0.5 mmol) in dioxane-$H_2O$ (10:1) for 12 hours afforded **3b** as a yellow solid (76 mg, 72% yield); Mp: 129−131 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.68 (s, 1H), 8.49 – 8.42 (m, 1H), 7.86 – 7.75 (m, 2H), 7.50 – 7.43 (m, 2H), 7.41 – 7.37 (m, 1H), 2.37 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 158.8, 148.4, 146.9, 137.5, 134.8, 127.3, 126.8, 125.7, 125.0, 123.5, 122.4, 116.2, 18.3; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{11}N_2O$ 211.0871, found 211.0869.



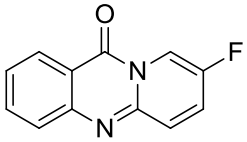
**2,8-Dimethyl-11*H*-pyrido[2,1-b]quinazolin-11-one (3c)**[13]

According to **GP2**, the reaction of 5-methyl-1-(5-methylpyridin-2-yl)-1*H*-indole (**1ac**) (111 mg, 0.5 mmol) in dioxane-$H_2O$ (10:1) for 12 hours afforded **3c** as a yellow solid (68 mg, 61% yield); Mp: 196−198 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.71 – 8.66 (m, 1H), 8.26 – 8.23 (m, 1H), 7.72 – 7.64 (m, 2H), 7.47 – 7.43 (m, 1H), 7.38 – 7.33 (m, 1H), 2.53 (s, 3H), 2.36 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 158.2, 146.1, 145.9, 136.5, 136.2, 134.7, 126.1, 125.7, 125.3, 123.0, 121.7, 115.5, 20.9, 17.8; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{13}N_2O$ 225.1028, found 225.1027.



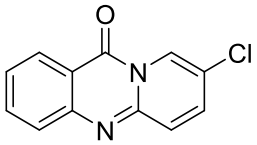
**8-Methoxy-11*H*-pyrido[2,1-b]quinazolin-11-one (3d)**

According to **GP2**, the reaction of 1-(5-methoxypyridin-2-yl)-1*H*-indole (**1ad**) (114 mg, 0.5 mmol) in DMSO for 12 hours afforded **3d** as a pale yellow solid (46 mg, 41% yield); Mp: 167−169 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.47 (d, $J$ = 7.7 Hz, 1H), 8.39 – 8.35 (m, 1H), 7.88 – 7.76 (m, 2H), 7.54 – 7.46 (m, 2H), 7.40 – 7.34 (m, 1H), 3.94 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 158.7, 148.7, 148.0, 145.6, 134.6, 131.1, 127.1, 126.8, 125.3, 115.7, 105.3, 56.3; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{11}N_2O_2$ 227.0821, found 227.0832.



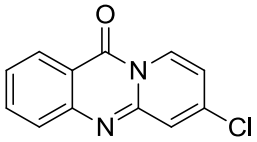
**8-Fluoro-11*H*-pyrido[2,1-b]quinazolin-11-one (3e)**[11]

According to **GP2**, the reaction of 1-(5-fluoropyridin-2-yl)-1*H*-indole (**1ae**) (106 mg, 0.5 mmol) in DMSO for 12 hours afforded **3e** as a yellow solid (48 mg, 45% yield); Mp: 173−175 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.82 – 8.78 (m, 1H), 8.48 – 8.44 (m, 1H), 7.91 – 7.85 (m, 1H), 7.84 – 7.79 (m, 1H), 7.60 – 7.45 (m, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 158.3 (d, $J_{C\text{-}F}$ = 2.1 Hz), 152.3 (d, $J_{C\text{-}F}$ = 243.1 Hz), 148.0, 145.6, 135.0, 128.2 (d, $J_{C\text{-}F}$ = 7.5 Hz), 127.6 (d, $J_{C\text{-}F}$ = 27.3 Hz), 127.02, 126.98, 125.8, 115.5, 112.0 (d, $J_{C\text{-}F}$ = 41.8 Hz); **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{12}H_8FN_2O$ 215.0621, found 215.0631.



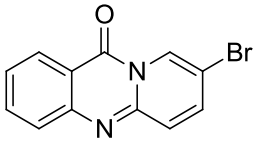
**8-Chloro-11*H*-pyrido[2,1-b]quinazolin-11-one (3f)**[13]

According to **GP2**, the reaction of 1-(5-chloropyridin-2-yl)-1*H*-indole (**1af**) (136 mg, 0.5 mmol) in dioxane-$H_2O$ (10:1) for 12 hours afforded **3f** as a yellow solid (74 mg, 64% yield); Mp: 166−168 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.94 – 8.86 (m, 1H), 8.49 – 8.41 (m, 1H), 7.91 – 7.76 (m, 2H), 7.57 – 7.40 (m, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 158.0, 148.1, 145.9, 135.5, 135.3, 127.5, 127.4, 127.2, 125.9, 124.2, 121.1, 116.2; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{12}H_8ClN_2O$ 231.0325, found 231.0335.



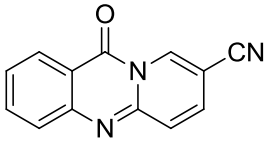
**7-Chloro-11*H*-pyrido[2,1-b]quinazolin-11-one (3g)**

According to **GP2**, the reaction of 1-(4-chloropyridin-2-yl)-1*H*-indole (**1ag**) (114 mg, 0.5 mmol) in DMSO for 12 hours afforded **3g** as a yellow solid (65 mg, 56% yield); Mp: 165−167 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.81 (d, $J$ = 7.8 Hz, 1H), 8.46 – 8.41 (m, 1H), 7.89 – 7.83 (m, 1H), 7.79 – 7.74 (m, 1H), 7.54 – 7.46 (m, 2H), 6.83 – 6.79 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 158.7, 148.7, 147.1, 141.3, 135.5, 127.7, 127.4, 127.1, 125.7, 124.2, 116.3, 114.4; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{12}H_8ClN_2O$ 231.0325, found 231.0317.



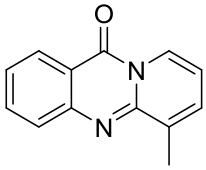

**8-Bromo-11*H*-pyrido[2,1-b]quinazolin-11-one (3h)**[13]

According to **GP2**, the reaction of 1-(5-bromopyridin-2-yl)-1*H*-indole (**1ai**) (136 mg, 0.5 mmol) in dioxane-$H_2O$ (10:1) for 12 hours afforded **3i** as a yellow solid (69 mg, 50% yield); Mp: 165−167 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 9.00 (d, $J$ = 1.9 Hz, 1H), 8.47 – 8.41 (m, 1H), 7.90 – 7.84 (m, 1H), 7.81 – 7.76 (d, $J$ = 8.2 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.41 -7.36 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 156.8, 147.0, 144.8, 136.5, 134.3, 126.4, 126.3, 126.1, 125.5, 124.9, 115.2, 106.6; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{12}H_8BrN_2O$ 274.9820, found 274.9822.



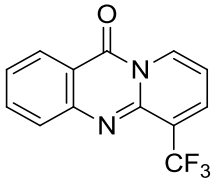

**8-Cyano-11*H*-pyrido[2,1-b]quinazolin-11-one (3i)**[13]

According to **GP2**, the reaction of 1-(5-cyanopyridin-2-yl)-1*H*-indole (**1ai**) (110 mg, 0.5 mmol) in DMSO for 12 hours afforded **3i** as a pale yellow solid (73 mg, 66% yield); Mp: 237−239 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 9.27 – 9.25 (m, 1H), 8.49 – 8.44 (m, 1H), 7.96 – 7.91 (m, 1H), 7.84 – 7.81 (m, 1H), 7.62 – 7.55 (m, 1H), 7.52 – 7.48 (m, 1H), 7.46 – 7.42 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 157.8, 147.9, 145.5, 136.2, 134.5, 131.6, 127.8, 127.7, 127.6, 126.8, 116.6, 115.6, 98.8; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{13}H_8N_3O$ 222.0667, found 222.0668.



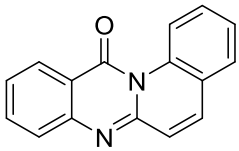

**6-Methyl-11*H*-pyrido[2,1-b]quinazolin-11-one (3j)**[11]

According to **GP3**, the reaction of 1-(3-methylpyridin-2-yl)-1*H*-indole (**1aj**) (105 mg, 0.5 mmol) in dioxane-$H_2O$ (10:1) for 12 hours afforded **3j** as a yellow solid (77 mg, 73% yield); Mp: 127−129 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 8.79 (d, $J$ = 7.3 Hz, 1H), 8.46 – 8.40 (m, 1H), 7.85 – 7.80 (m, 2H), 7.49 – 7.43 (m, 1H), 7.38 – 7.33 (m, 1H), 6.76 (t, $J$ = 7.0 Hz, 1H), 2.59 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 159.0, 147.8, 147.1, 134.2, 134.0, 131.7, 127.0, 126.7, 124.6, 124.3, 115.6, 111.6, 18.1; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{13}H_{10}N_2ONa$ 233.0691, found 233.0685.



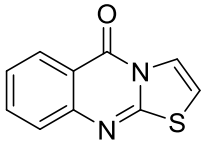
**6-Trifluoromethyl-11*H*-pyrido[2,1-b]quinazolin-11-one (3k)**

According to **GP3**, the reaction of 1-(3-(trifluoromethyl)pyridin-2-yl)-1*H*-indole (**1ak**) (131 mg, 0.5 mmol) in dioxane-$H_2O$ (10:1) for 12 hours afforded **3k** as a yellow solid (70 mg, 53% yield); Mp: 189−191 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 9.02 – 8.97 (m, 1H), 8.46 – 8.41 (m, 1H), 7.93 – 7.86 (m, 3H), 7.57 – 7.51 (m, 1H), 6.86 (t, $J$ = 7.1 Hz, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 158.1, 147.0, 142.4, 135.0, 133.4 (q, $J_{C\text{-}F}$ = 5.5 Hz), 130.0, 127.6, 126.7, 125.8, 125.0 (q, $J_{C\text{-}F}$ = 31.6 Hz), 121.8 (q, $J_{C\text{-}F}$ = 271.7 Hz), 116.2, 109.3; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{13}H_8F_3N_2O$ 265.0589, found 265.0586.



**12*H*-quinolino[2,1-b]quinazolin-12-one (3l)**[10]

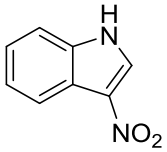
According to **GP3**, the reaction of 2-(1*H*-indol-1-yl)quinolone (**1al**) (122 mg, 0.5 mmol) in dioxane-$H_2O$ (10:1) for 12 hours afforded **3l** as a yellow solid (76 mg, 62% yield); Mp: 156−158 ℃; **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 9.58 (d, $J$ = 9.0 Hz, 1H), 8.45 (d, $J$ = 7.8 Hz, 1H), 7.89 – 7.70 (m, 2H), 7.66 – 7.55 (m, 3H), 7.54 – 7.42 (m, 2H), 7.31 – 7.18 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 163.1, 148.0, 146.5, 135.6, 135.2, 134.6, 129.5, 128.1, 127.5, 126.5, 126.4, 126.2, 125.1, 124.4, 121.9, 120.0; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{11}N_2O$ 247.0871, found 247.0869.



**5*H*-thiazolo[2,3-b]quinazolin-5-one (3m)**[10]

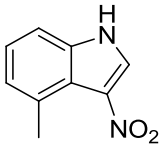
According to **GP3**, the reaction of 2-(1*H*-indol-1-yl)thiazole (**1am**) (100 mg, 0.5 mmol) in dioxane-$H_2O$ (10:1) for 12 hours afforded **3m** as a yellow solid (87 mg, 87% yield); Mp: 148−150 ℃; **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.41 – 8.37 (m, 1H), 7.94 (d, $J$ = 5.1 Hz, 1H), 7.83 – 7.77 (m, 1H), 7.71 – 7.66 (m, 1H), 7.50 – 7.44 (m, 1H), 6.84 (d, $J$ = 5.1 Hz, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): $\delta$ 158.7, 158.0, 148.4, 134.9, 127.1, 126.2, 125.4, 121.2, 116.5, 109.5; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{10}H_6N_2NaOS$ 225.0099, found 225.0091.

## 11. Characterization Data for Synthesized Product 5



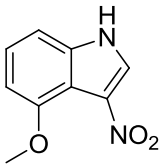
**3-Nitro-1*H*-indole (5a)**[14]

According to **GP4**, the reaction of 1-(2-pyridoyl)indole (**4a**) (111 mg, 0.5 mmol) afforded **5a** as a yellow solid (71 mg, 87% yield); Mp: 207−209 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.66 (brs, 1H), 8.66 (s, 1H), 8.13 – 8.07 (m, 1H), 7.62 – 7.55 (m, 1H), 7.40 – 7.33 (m, 2H); **$^{13}$C NMR** (100 MHz, DMSO-$d_6$): $\delta$ 135.0, 130.5, 128.4, 124.2, 123.7, 119.8, 119.4, 113.4; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_8H_6N_2NaO_2$ 185.0327, found 185.0310.



**4-Methyl-3-nitro-1*H*-indole (5b)**

According to **GP4** under argon atmosphere, the reaction of 4-methyl-1-(2-pyridoyl)indole (**4b**) (118 mg, 0.5 mmol) afforded **5b** as a yellow solid (55 mg, 62% yield); Mp: 186−187 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.56 (brs, 1H), 8.61 (s, 1H), 7.40 –7.38 (d, $J$ = 8.1 Hz, 1H), 7.24 –7.20 (t, $J$ = 7.7 Hz, 1H), 7.10 –7.09 (d, $J$ = 7.2 Hz, 1H), 2.75 (s, 3H); **$^{13}$C NMR** (100 MHz, DMSO-$d_6$): $\delta$ 135.9, 131.4, 130.3, 130.0, 125.6, 124.1, 118.1, 111.0, 22.3; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_9H_9N_2O_2$ 177.0664, found 177.0651.

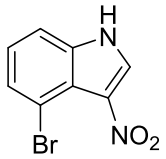


**4-Methoxy-3-nitro-1*H*-indole (5c)**

According to **GP4** under argon atmosphere, the reaction of 4-methoxy-1-(2-pyridoyl)indole (**4c**) (126 mg, 0.5 mmol) afforded **5c** as a yellow solid (56 mg, 58% yield); Mp: 171−173 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 13.06 (brs, 1H), 8.78 (s, 1H), 8.03 (d, $J$ = 1.9 Hz, 1H), 7.53 (d, $J$ = 1.8 Hz, 1H), 4.00 (s, 3H); **$^{13}$C NMR** (100 MHz, DMSO-$d_6$): $\delta$ 152.9, 145.1, 135.4, 134.3, 113.7, 103.3, 98.8, 56.7; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_9H_8N_2NaO_3$ 215.0433, found 215.0437.

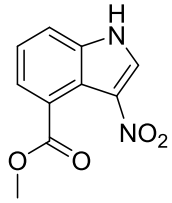
**4-Fluoro-3-nitro-1*H*-indole (5d)**

According to **GP4**, the reaction of 4-fluoro-1-(2-pyridoyl)indole (**4d**) (120 mg, 0.5 mmol) afforded **5d** as a yellow solid (79 mg, 88% yield); Mp: 243−245 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.86 (brs, 1H), 8.69 (s, 1H), 7.42 – 7.38 (m, 1H), 7.36 – 7.29 (m, 1H), 7.14 – 7.08 (m, 1H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$): $\delta$ 154.5 (d, $J_{C\text{-}F}$ = 251.4 Hz), 138.4 (d, $J_{C\text{-}F}$ = 8.6 Hz), 131.9, 128.5, 125.4 (d, $J_{C\text{-}F}$ = 7.8 Hz), 110.1 (d, $J_{C\text{-}F}$ = 4.0 Hz), 109.7 (d, $J_{C\text{-}F}$ = 21.1 Hz), 108.3 (d, $J_{C\text{-}F}$ = 17.8 Hz); **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_8H_5FN_2NaO_2$ 203.0233, found 203.0245.



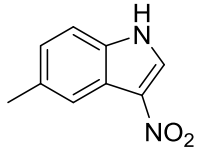

**4-Bromo-3-nitro-1*H*-indole (5e)**

According to **GP4**, the reaction of 4-bromo-1-(2-pyridoyl)indole (**4e**) (151 mg, 0.5 mmol) afforded **5e** as a yellow solid (91 mg, 75% yield); Mp: 201−202 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.85 (brs, 1H), 8.70 (s, 1H), 7.63 – 7.55 (m, 2H), 7.28 – 7.22 (m, 1H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$): $\delta$ 142.1, 137.2, 134.3, 133.8, 130.2, 123.2, 118.1, 116.7; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_8H_5BrN_2NaO_2$ 262.9432, found 262.9432.



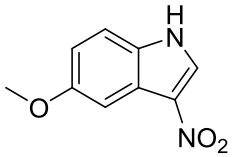

**Methyl 3-nitro-1*H*-indole-4-carboxylate (5f)**

According to **GP4**, the reaction of methyl 1-(2-pyridoyl)indole-4-carboxylate (**4f**) (140 mg, 0.5 mmol) afforded **5f** as a yellow solid (98 mg, 89% yield); Mp: 193−194 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.89 (brs, 1H), 8.72 (s, 1H), 7.76 – 7.73 (m, 1H), 7.50 – 7.47 (m, 1H), 7.45 – 7.39 (m, 1H), 3.82 (s, 3H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$): $\delta$ 173.6, 140.7, 136.9, 134.2, 130.3, 128.9, 128.4, 121.2, 120.7, 57.0; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{10}H_8N_2NaO_4$ 243.0382, found 243.0378.



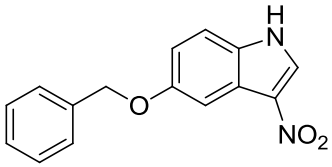

**5-Methyl-3-nitro-1*H*-indole (5g)**

According to **GP4** under argon atmosphere, the reaction of 5-methyl-1-(2-pyridoyl)indole (**4g**) (118 mg, 0.5 mmol) afforded **5g** as a yellow solid (69 mg, 78% yield); Mp: 206−207 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.59 (brs, 1H), 8.63 (s, 1H), 7.94 (s, 1H), 7.53 – 7.47 (m, 1H), 7.23 – 7.19 (m, 1H), 2.50 (s, 3H); **$^{13}$C NMR** (100 MHz, DMSO-$d_6$): $\delta$ 138.6, 138.2, 135.5, 133.2, 130.8, 125.3, 124.2, 118.2, 26.5; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_9H_8N_2NaO_2$ 199.0483, found 199.0470.



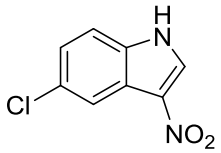
**5-Methoxy-3-nitro-1*H*-indole (5h)**

According to **GP4** under argon atmosphere, the reaction of 5-methoxy-1-(2-pyridoyl)indole (**4h**) (126 mg, 0.5 mmol) afforded **5h** as a yellow solid (76 mg, 79% yield); Mp: 162−163 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.56 (brs, 1H), 8.57 (d, $J$ = 3.4 Hz, 1H), 7.57 – 7.54 (m, 1H), 7.50 – 7.46 (m, 1H), 6.99 – 6.95 (m, 1H), 3.84 (s, 3H); **$^{13}$C NMR** (100 MHz, DMSO-$d_6$): $\delta$ 156.8, 130.3, 129.8, 128.2, 120.7, 114.4, 114.0, 101.0, 55.4; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_9H_8N_2NaO_3$ 215.0433, found 215.0435.



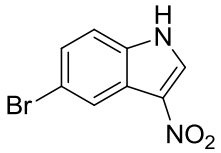
**5-(Benzyloxy)-3-nitro-1*H*-indole (5i)**

According to **GP4** under argon atmosphere, the reaction of 5-(benzyloxy)-1-(2-pyridoyl)indole (**4i**) (164 mg, 0.5 mmol) afforded **5i** as a yellow solid (92 mg, 69% yield); Mp: 239−241 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.58 (brs, 1H), 8.58 (d, $J$ = 3.4 Hz, 1H), 7.68 (d, $J$ = 2.3, 1H), 7.53 – 7.48 (m, 3H), 7.44 – 7.39 (m, 2H), 7.37 – 7.31 (m, 1H), 7.08 – 7.04 (m, 1H), 5.19 (s, 2H); **$^{13}$C NMR** (100 MHz, DMSO-$d_6$): $\delta$ 155.8, 137.1, 130.4, 130.0, 128.4, 128.3, 127.8, 127.6, 120.7, 114.6, 114.4, 102.6, 69.7; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{13}N_2O_3$ 269.0929, found 269.0945.



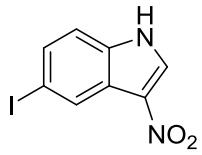
**5-Chloro-3-nitro-1*H*-indole (5j)**[14]

According to **GP4**, the reaction of 5-chloro-1-(2-pyridoyl)indole (**4j**) (128 mg, 0.5 mmol) afforded **5j** as a yellow solid (83 mg, 85% yield); Mp: 256−258 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.79 (brs, 1H), 8.67 (s, 1H), 8.00 (s, 1H), 7.61 – 7.52 (m, 1H), 7.37 – 7.28 (m, 1H); **$^{13}$C NMR** (100 MHz, DMSO-$d_6$): $\delta$ 133.6, 131.8, 128.4, 127.9, 124.3, 120.9, 118.5, 115.2; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_8H_5ClN_2NaO_2$ 218.9937, found 218.9931.



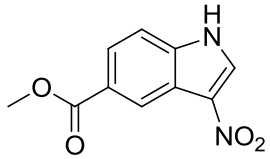
**5-Bromo-3-nitro-1*H*-indole (5k)**[14]

According to **GP4**, the reaction of 5-bromo-1-(2-pyridoyl)indole (**4k**) (151 mg, 0.5 mmol) afforded **5k** as a yellow solid (104 mg, 86% yield); Mp: 240−241 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.84 (brs, 1H), 8.71 (s, 1H), 8.22 – 8.19 (m, 1H), 7.57 – 7.53 (m, 1H), 7.51 – 7.47 (m, 1H); **$^{13}$C NMR** (100 MHz, DMSO-$d_6$): $\delta$ 133.8, 131.5, 127.7, 126.9, 121.5, 121.4, 116.5, 115.5; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_8H_6BrN_2O_2$ 240.9613, found 240.9609.



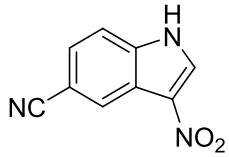
**5-Iodo-3-nitro-1*H*-indole (5l)**

According to **GP4**, the reaction of 5-iodo-1-(2-pyridoyl)indole (**4l**) (178 mg, 0.5 mmol) afforded **5l** as a yellow solid (105 mg, 73% yield); Mp: 230−231 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.86 (brs, 1H), 8.84 – 8.62 (m, 1H), 8.56 – 8.15 (m, 1H), 7.72 – 7.57 (m, 1H), 7.56 – 7.41 (m, 1H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$): $\delta$ 134.6, 132.8, 131.6, 128.0, 127.8, 122.4, 116.1, 89.0; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_8H_5IN_2NaO_2$ 310.9293, found 310.9310.



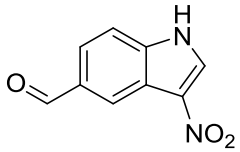
**Methyl 3-nitro-1*H*-indole-5-carboxylate (5m)**[14]

According to **GP4**, the reaction of methyl 1-(2-pyridoyl)indole-5-carboxylate (**4m**) (140 mg, 0.5 mmol) afforded **5m** as a yellow solid (89 mg, 81% yield); Mp: 291−293 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.95 (brs, 1H), 8.84 – 8.69 (m, 2H), 7.98 – 7.89 (m, 1H), 7.72 – 7.63 (m, 1H), 3.91 (s, 3H); **$^{13}$C NMR** (100 MHz, DMSO-$d_6$): $\delta$ 166.9, 137.9, 132.7, 129.5, 125.32, 125.28, 121.9, 119.9, 114.0, 52.6; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{10}H_9N_2O_4$ 221.0562, found 221.0569.



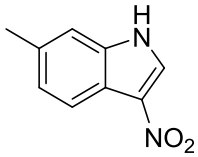
**5-Cyano-3-nitro-1*H*-indole (5n)**

According to **GP4**, the reaction of 5-cyano-1-(2-pyridoyl)indole (**4n**) (124 mg, 0.5 mmol) afforded **5n** as a yellow solid (76 mg, 81% yield); Mp: 284−285 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 13.10 (brs, 1H), 8.86 (s, 1H), 8.46 (s, 1H), 7.78 – 7.71 (m, 2H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$): $\delta$ 137.2, 133.2, 129.0, 127.4, 124.9, 120.0, 119.9, 115.4, 106.5; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_9H_5N_3NaO_2$ 210.0279, found 210.0281.



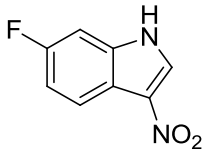
**3-Nitro-1*H*-indole-5-carbaldehyde (5o)**

According to **GP4**, the reaction of 1-picolinoyl-1*H*-indole-3-carbaldehyde (**4o**) (125 mg, 0.5 mmol) afforded **5o** as a yellow solid (67.4 mg, 71% yield); Mp: 263−265 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 13.03 (brs, 1H), 10.13 (s, 1H), 8.83 (s, 1H), 8.69 – 8.66 (m, 1H), 7.87 (m, 1H), 7.74 (d, $J$ = 8.5 Hz, 1H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$): $\delta$ 192.9, 138.2, 132.5, 132.3, 129.3, 123.84, 123.78, 119.8, 114.3; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_9H_6N_2O_3Na$ 213.0276, found 213.0285.



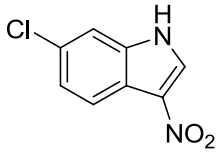
**6-Methyl-3-nitro-1*H*-indole (5p)**

According to **GP4** under argon atmosphere, the reaction of 6-methyl-1-(2-pyridoyl)indole (**4p**) (118 mg, 0.5 mmol) afforded **5p** as a yellow solid (67 mg, 76% yield); Mp: 201−203 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.53 (brs, 1H), 8.58 (d, $J$ = 3.5 Hz, 1H), 7.96 (d, $J$ = 8.2, 1H), 7.36 (s, 1H), 7.20 (d, $J$ = 8.1, 1H), 2.44 (s, 3H); **$^{13}$C NMR** (100 MHz, DMSO-$d_6$): $\delta$ 135.5, 133.7, 130.0, 128.4, 125.3, 119.1, 117.7, 113.0, 21.1; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_9H_8N_2NaO_2$ 199.0483, found 199.0472.



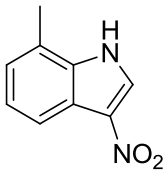
**6-Fluoro-3-nitro-1*H*-indole (5q)**

According to **GP4**, the reaction of 6-fluoro-1-(2-pyridoyl)indole (**4q**) (120 mg, 0.5 mmol) afforded **5q** as a yellow solid (77 mg, 85% yield); Mp: 249−251 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.70 (brs, 1H), 8.67 (s, 1H), 8.11 – 8.06 (m, 1H), 7.41 – 7.38 (m, 1H), 7.28 – 7.21 (m, 1H); **$^{13}$C NMR** (100 MHz, DMSO-$d_6$): $\delta$ 159.7 (d, $J_{C\text{-}F}$ = 239.2 Hz), 135.1 (d, $J_{C\text{-}F}$ = 12.7 Hz), 131.1 (d, $J_{C\text{-}F}$ = 2.2 Hz), 128.4, 120.8 (d, $J_{C\text{-}F}$ = 10.1 Hz), 116.6, 112.1 (d, $J_{C\text{-}F}$ = 24.4 Hz), 99.7 (d, $J_{C\text{-}F}$ = 26.2 Hz); **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_8H_6FN_2O_2$ 181.0413, found 181.0415.



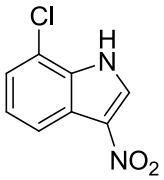
**6-Chloro-3-nitro-1*H*-indole (5r)**[14]

According to **GP4**, the reaction of 6-chloro-1-(2-pyridoyl)indole (**4r**) (128 mg, 0.5 mmol) afforded **5r** as a yellow solid (80 mg, 82% yield); Mp: 259−261 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.75 (brs, 1H), 8.69 (s, 1H), 8.07 (d, $J$ = 8.5 Hz, 1H), 7.63 (s, 1H), 7.42 – 7.37 (m, 1H); **$^{13}$C NMR** (100 MHz, DMSO-$d_6$): $\delta$ 140.2, 136.1, 133.4, 133.1, 128.7, 125.5, 123.3, 117.8; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_8H_6ClN_2O_2$ 197.0118, found 197.0111.



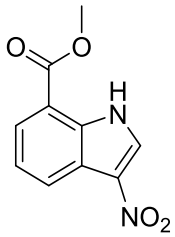
**7-Methyl-3-nitro-1*H*-indole (5s)**[14]

According to **GP4** under argon atmosphere, the reaction of 7-methyl-1-(2-pyridoyl)indole (**4s**) (118 mg, 0.5 mmol) afforded **5s** as a yellow solid (66 mg, 75% yield); Mp: 193−194 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.70 (brs, 1H), 8.66 ($J$ = 3.5 Hz, 1H), 7.93 (d, $J$ = 8.0 Hz, 1H), 7.27 (t, $J$ = 7.6 Hz, 1H), 7.15 (d, $J$ = 7.2 Hz, 1H), 2.53 (s, 3H); **$^{13}$C NMR** (100 MHz, DMSO-$d_6$): $\delta$ 134.5, 130.1, 128.8, 124.7, 123.8, 122.9, 119.7, 116.9, 16.3; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_9H_9N_2O_2$ 177.0664, found 177.0651.



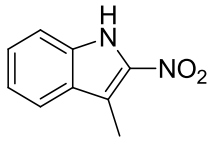
**7-Chloro-3-nitro-1*H*-indole (5t)**

According to **GP4**, the reaction of 7-chloro-1-(2-pyridoyl)indole (**4t**) (128 mg, 0.5 mmol) afforded **5t** as a yellow solid (78 mg, 80% yield); Mp: 187−189 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 13.13 (brs, 1H), 8.71 (s, 1H), 8.10 – 8.03 (m, 1H), 7.49 – 7.42 (m, 1H), 7.40 – 7.34 (m, 1H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$): $\delta$ 132.3, 131.6, 129.5, 125.1, 124.2, 122.1, 118.8, 118.1; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_8H_6ClN_2O_2$ 197.0118, found 197.0111.



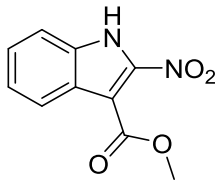
**Methyl 3-nitro-1*H*-indole-7-carboxylate (5u)**

According to **GP4**, the reaction of methyl 1-(2-pyridoyl)indole-7-carboxylate (**4u**) (140 mg, 0.5 mmol) afforded **5u** as a yellow solid (89 mg, 81% yield); Mp: 183−184 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.42 (brs, 1H), 8.54 (s, 1H), 8.42 – 8.36 (m, 1H), 7.99 – 7.92 (m, 1H), 7.53 – 7.46 (m, 1H), 3.98 (s, 3H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$): $\delta$ 165.9, 133.3, 131.7, 129.2, 126.9, 125.4, 123.9, 121.6, 115.1, 52.8; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{10}H_8N_2NaO_4$ 243.0382, found 243.0378.



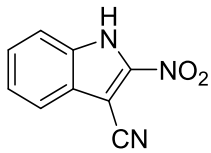
**3-Methyl-2-nitro-1*H*-indole (5v)**[15]

According to **GP4**, the reaction of 3-methyl-1-(2-pyridoyl)indole (**4v**) (118 mg, 0.5 mmol) afforded **5v** as a yellow solid (16 mg, 18% yield); Mp: 140−142 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 11.17 (brs, 1H), 7.48 (d, $J$ = 7.5 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.10 – 7.06 (m, 1H), 6.99 (d, $J$ = 7.8 Hz, 1H), 1.92 (s, 3H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$): $\delta$ 170.7, 143.1, 132.0, 127.2, 124.3, 123.2, 111.3, 90.2, 19.8; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_9H_9N_2O_2$ 177.0664, found 177.0657.



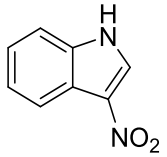
**Methyl 2-nitro-1*H*-indole-3-carboxylate (5w)**

According to **GP4**, the reaction of methyl 1-(2-pyridoyl)indole-3-carboxylate (**4w**) (140 mg, 0.5 mmol) afforded **5w** as a yellow solid (63 mg, 57% yield); Mp: 234−235 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.59 (brs, 1H), 8.48 (d, $J$ = 3.1 Hz, 1H), 8.42 – 8.41 (m, 1H), 8.17 – 8.15 (m, 1H), 8.10 – 8.07 (m, 1H), 3.87 (s, 3H); **$^{13}$C NMR** (100 MHz, DMSO-$d_6$): $\delta$ 164.0, 142.8, 137.9, 135.0, 130.4, 120.6, 116.3, 109.0, 107.2, 51.0; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{10}H_8N_2NaO_4$ 243.0382, found 243.0378.



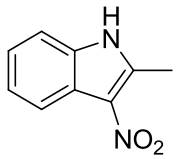
**3-Cyano-2-nitro-1*H*-indole (5x)**

According to **GP4**, the reaction of 3-cyano-1-(2-pyridoyl)indole (**4x**) (124 mg, 0.5 mmol) afforded **5x** as a yellow solid (51 mg, 54% yield); Mp: 178−179 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.84 (brs, 1H), 8.64 – 8.62 (m, 1H), 8.47 – 8.45 (m, 1H), 8.11 – 8.08 (m, 1H), 7.87 – 7.85 (m, 1H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$): $\delta$ 144.1, 140.4, 134.3, 131.9, 119.5, 117.1, 115.6, 110.1, 85.9; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_9H_5N_3NaO_2$ 210.0279, found 210.0281.



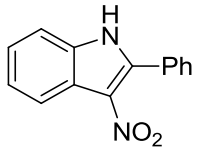
**3-Nitro-1*H*-indole (5a)**[14]

According to **GP4**, the reaction of 1-picolinoyl-1*H*-indole-3-carbaldehyde (**4y**) (125 mg, 0.5 mmol) afforded **5a** as a yellow solid (19 mg, 23% yield); Mp: 207−209 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.67 (brs, 1H), 8.66 (s, 1H), 8.12 – 8.09 (m, 1H), 7.60 – 7.57 (m, 1H), 7.39 – 7.34 (m, 2H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$): $\delta$ 140.2, 135.6, 133.6, 129.3, 128.9, 125.0, 124.6, 118.6; **HRMS (ESI-TOF)** *m/z*: $[M+Na]^+$ calcd for $C_8H_6N_2NaO_2$ 185.0327, found 185.0312.



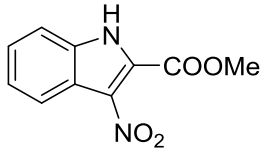
**2-Methyl-3-nitro-1*H*-indole (5z)**[16]

According to **GP4**, the reaction of (2-methyl-1*H*-indol-1-yl)(pyridin-2-yl)methanone (**4z**) (118 mg, 0.5 mmol) afforded **5z** as a yellow solid (39 mg, 44% yield); Mp: 245−246 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.60 (brs, 1H), 8.08 – 8.04 (m, 1H), 7.49 – 7.46 (m, 1H), 7.34 – 7.27 (m, 2H), 2.78 (s, 3H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$): $\delta$ 143.8, 133.3, 125.7, 124.2, 123.7, 121.6, 119.8, 112.7, 15.0; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_9H_9N_2O_2$ 177.0664, found 177.0651.



**3-Nitro-2-phenyl -1*H*-indole (5aa)**[16,17]

According to **GP4**, the reaction of 2-phenyl-1-(2-pyridoyl)indole (**4aa**) (150 mg, 0.5 mmol) afforded **5aa** as a yellow solid (68 mg, 57% yield); Mp: 226−228 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 12.84 (brs, 1H), 8.20 – 8.15 (m, 1H), 7.80 – 7.74 (m, 2H), 7.61 – 7.52 (m, 4H), 7.42 – 7.35 (m, 2H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$): $\delta$ 146.9, 138.8, 135.2, 135.1, 134.9, 133.4, 129.6, 129.0, 126.7, 125.3, 125.2, 118.0; **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{11}N_2O_2$ 239.0821, found 239.0818.



**Methyl 3-nitro-1*H*-indole-2-carboxylate (5ab)**[17]

According to **GP4**, the reaction of methyl 1-(2-pyridoyl)indole-2-carboxylate (**4ab**) (140 mg, 0.5 mmol) afforded **5ab** as a yellow solid (90 mg, 82% yield); Mp: 262−263 ℃; **$^1$H NMR** (400 MHz, DMSO-$d_6$): $\delta$ 13.42 (brs, 1H), 8.08 – 8.04 (m, 1H), 7.65 – 7.60 (m, 1H), 7.49 – 7.41 (m, 2H), 4.00 (s, 3H); **$^{13}$C NMR** (150 MHz, DMSO-$d_6$): $\delta$ 160.5, 133.7, 128.5, 127.6, 126.5, 125.1, 120.4, 120.3, 114.2, 53.8; **HRMS** (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{10}H_8N_2NaO_4$ 243.0382, found 243.0382.

## 12. References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## 13. Copies of $^{1}$H NMR and $^{13}$C NMR Spectra of all Synthesized and Isolated Compounds

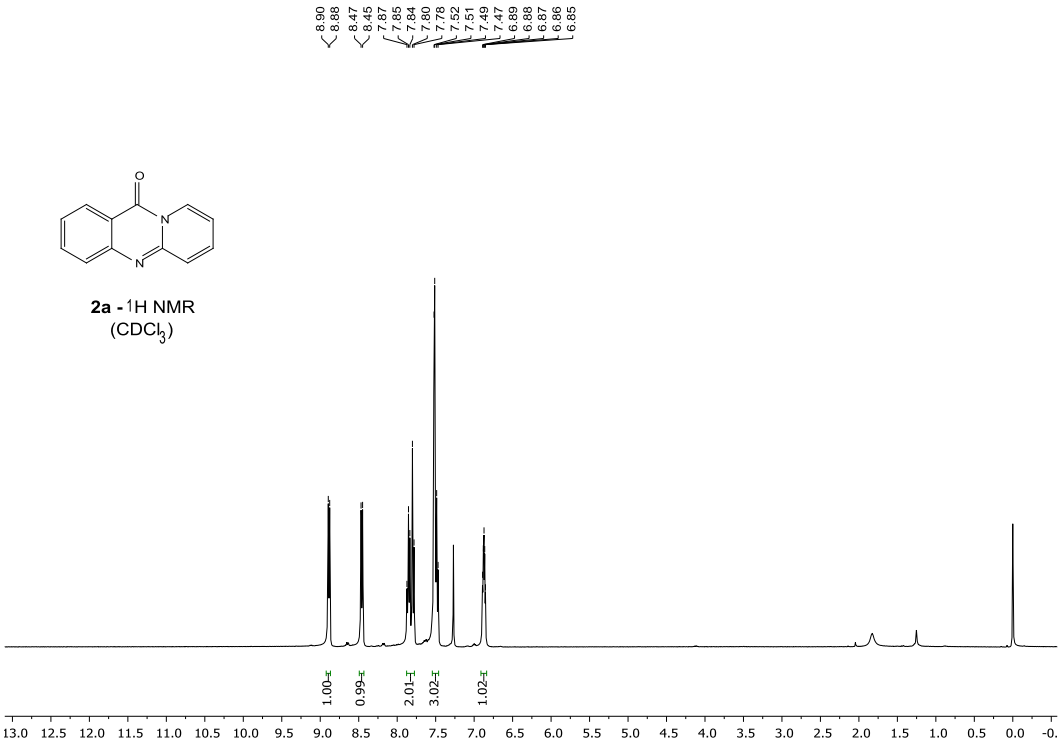



**Figure S7.** $^{1}$H NMR spectrum of **2a**

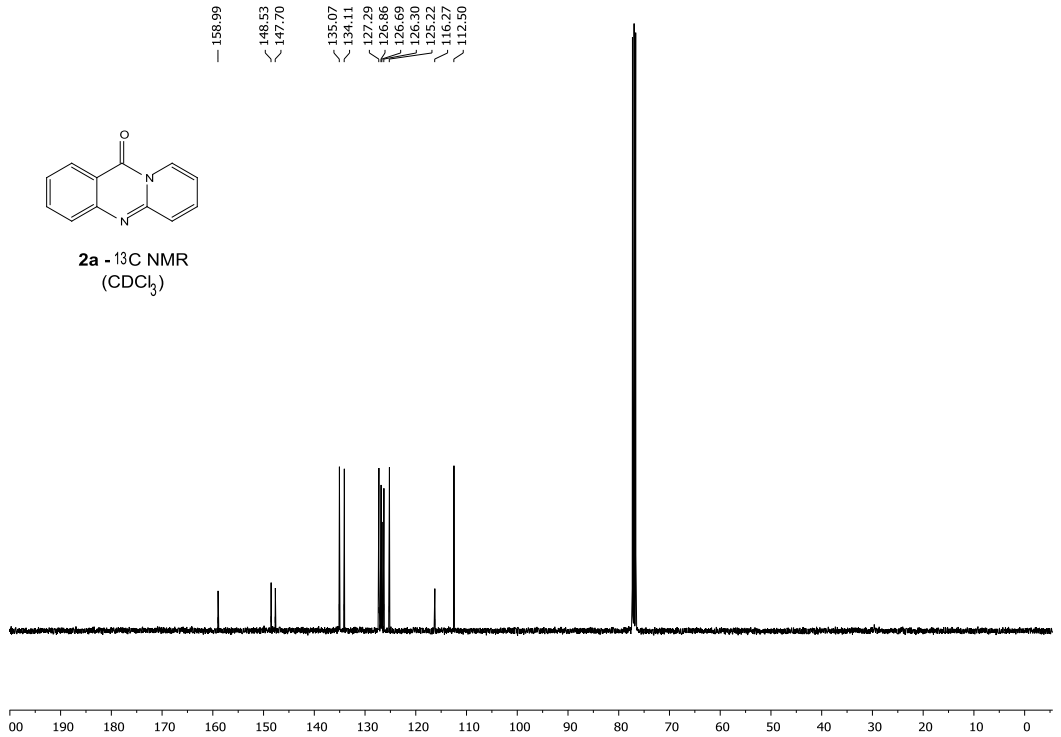



**Figure S8**. $^{13}$C NMR spectrum of **2a**

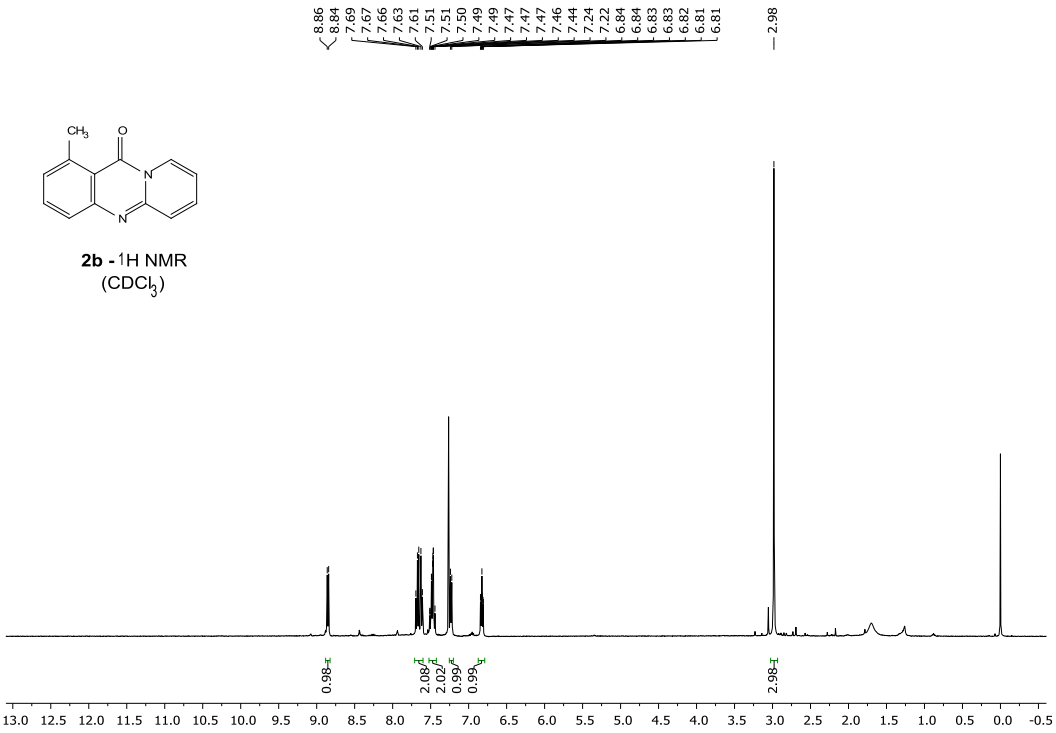



**Figure S9.** $^{1}$H NMR spectrum of **2b**

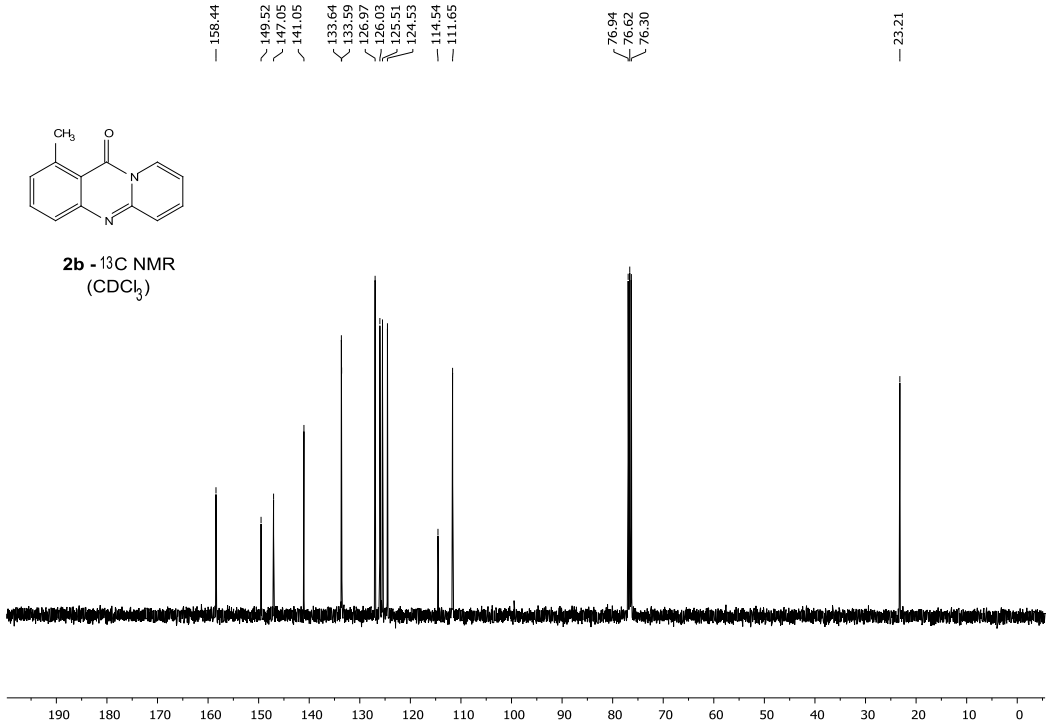



**Figure S10.** $^{13}$C NMR spectrum of **2b**

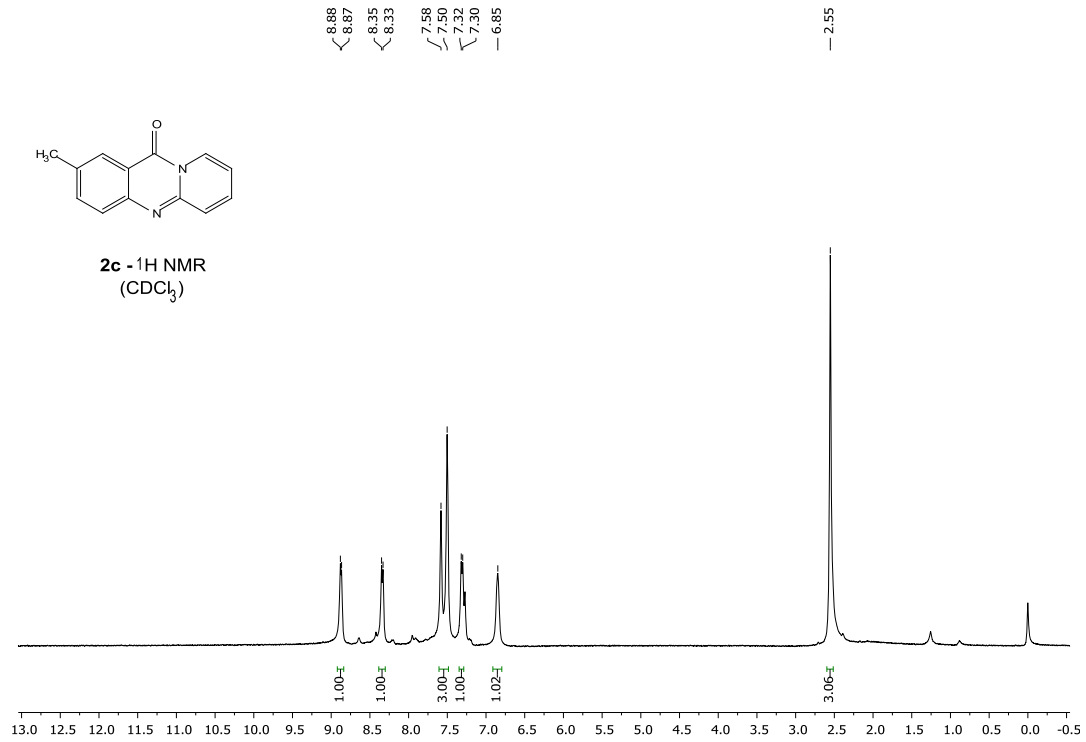



**Figure S11.** $^{1}$H NMR spectrum of **2c**

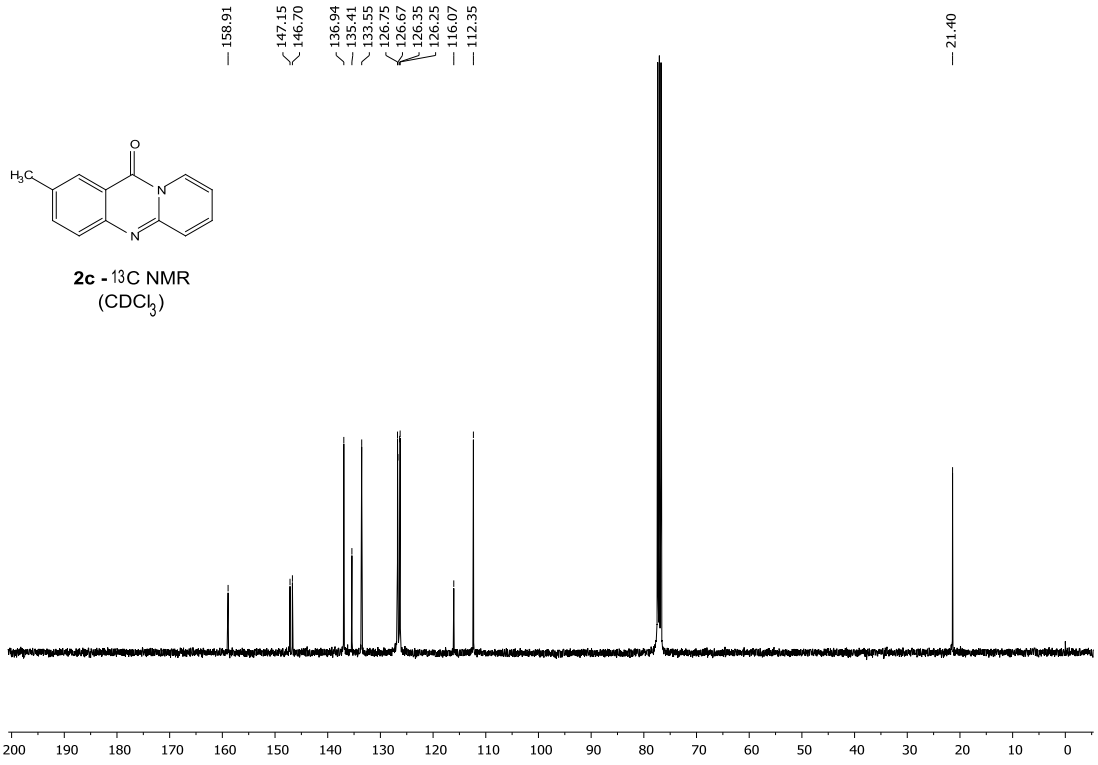



**Figure S12.** $^{13}$C NMR spectrum of **2c**

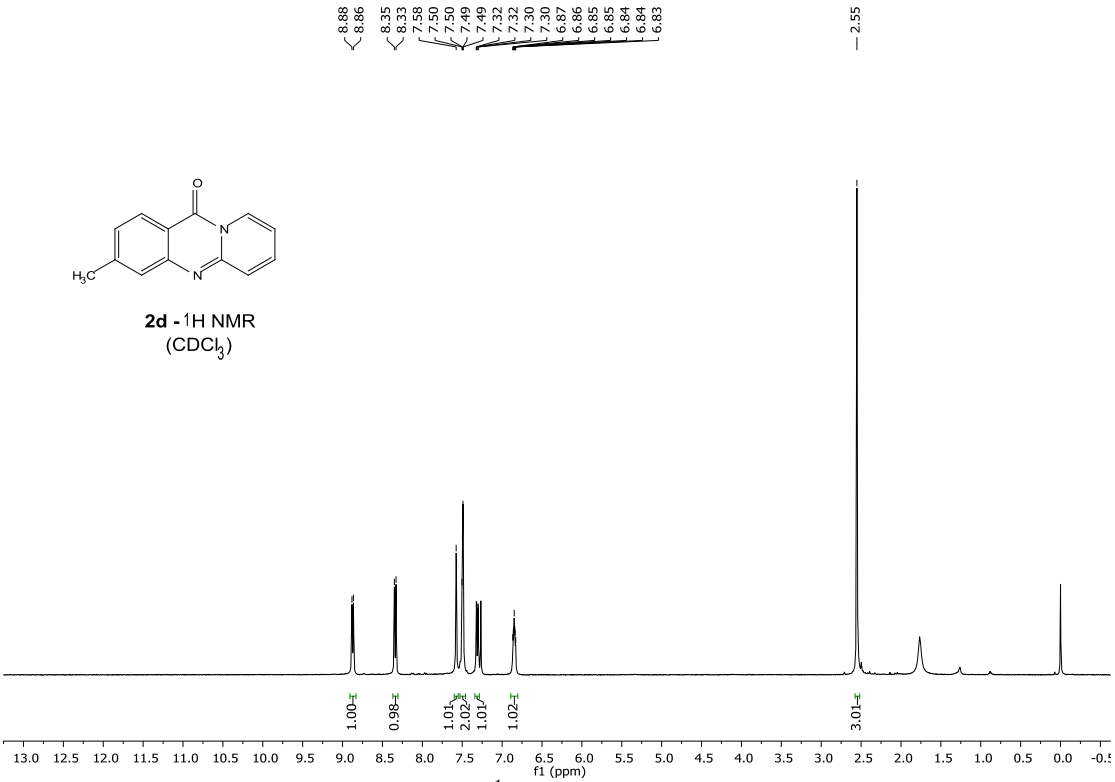



**Figure S13.** $^{1}$H NMR spectrum of **2d**

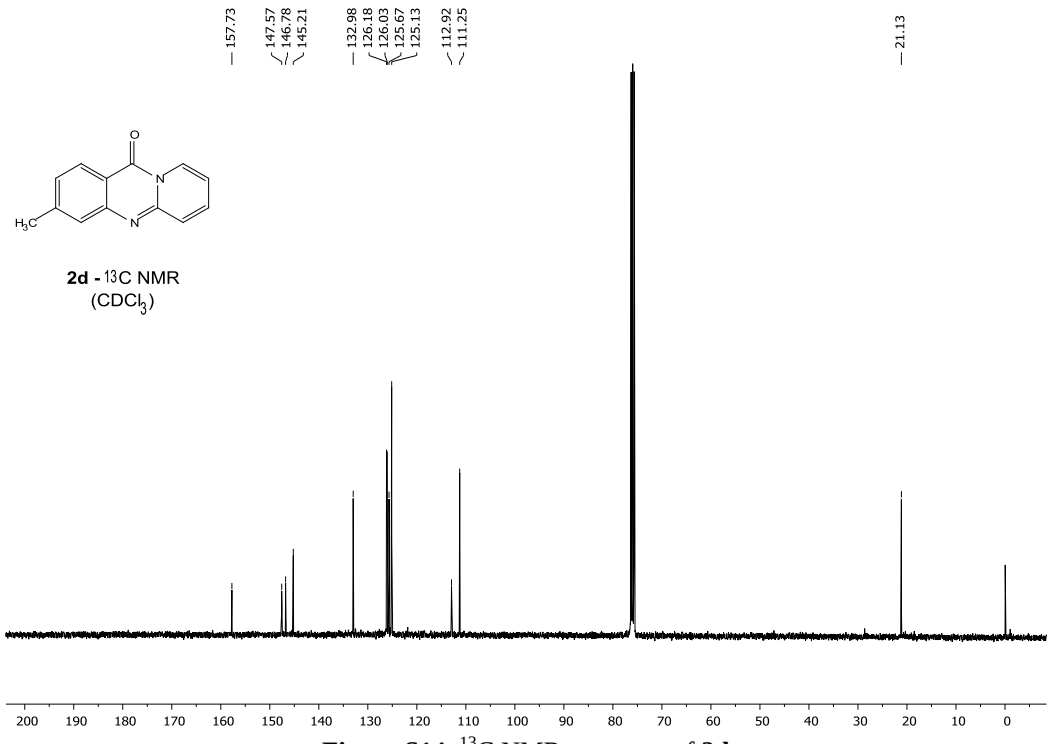



**Figure S14.** $^{13}$C NMR spectrum of **2d**

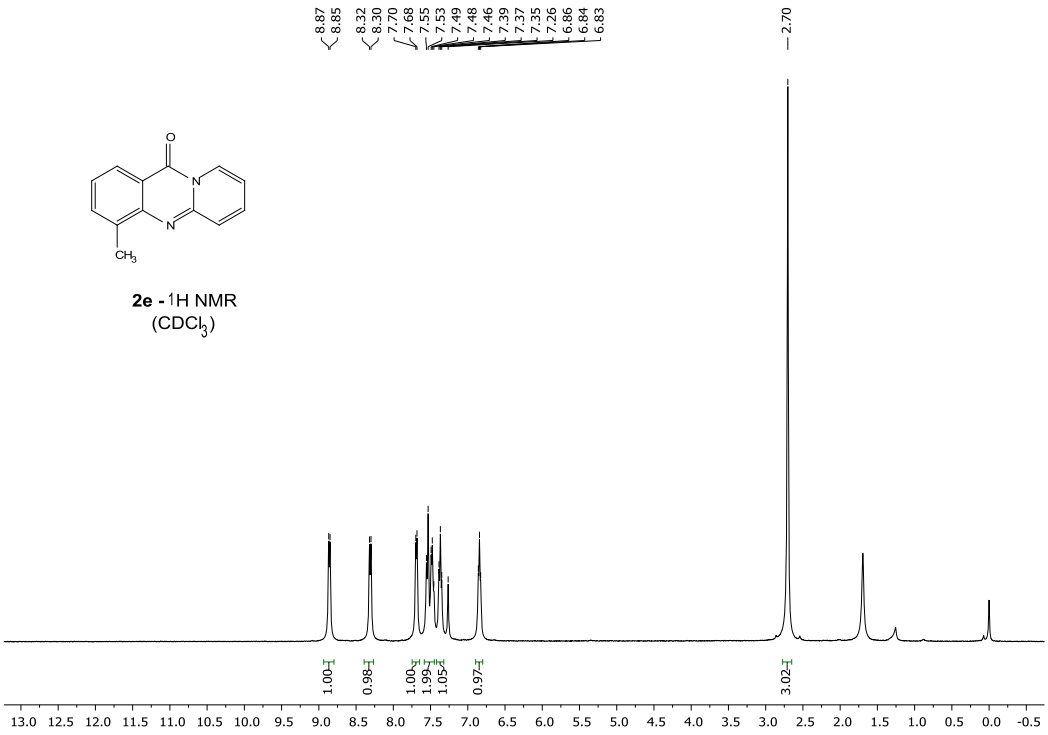



**Figure S15.** $^{1}$H NMR spectrum of **2e**

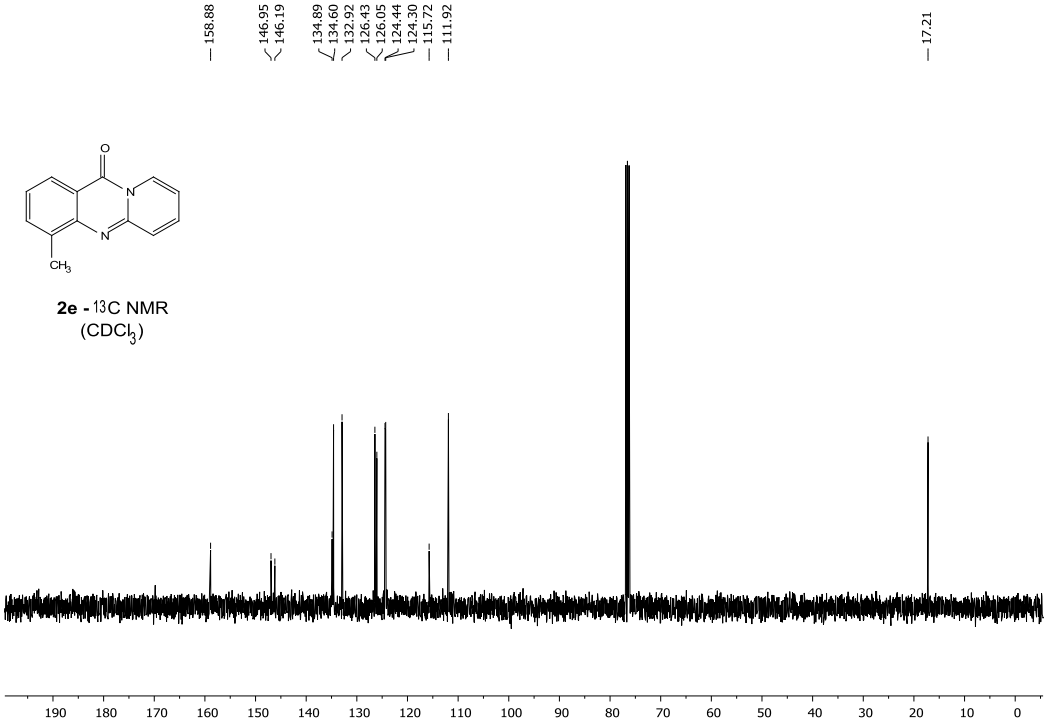



**Figure S16.** $^{13}$C NMR spectrum of **2e**

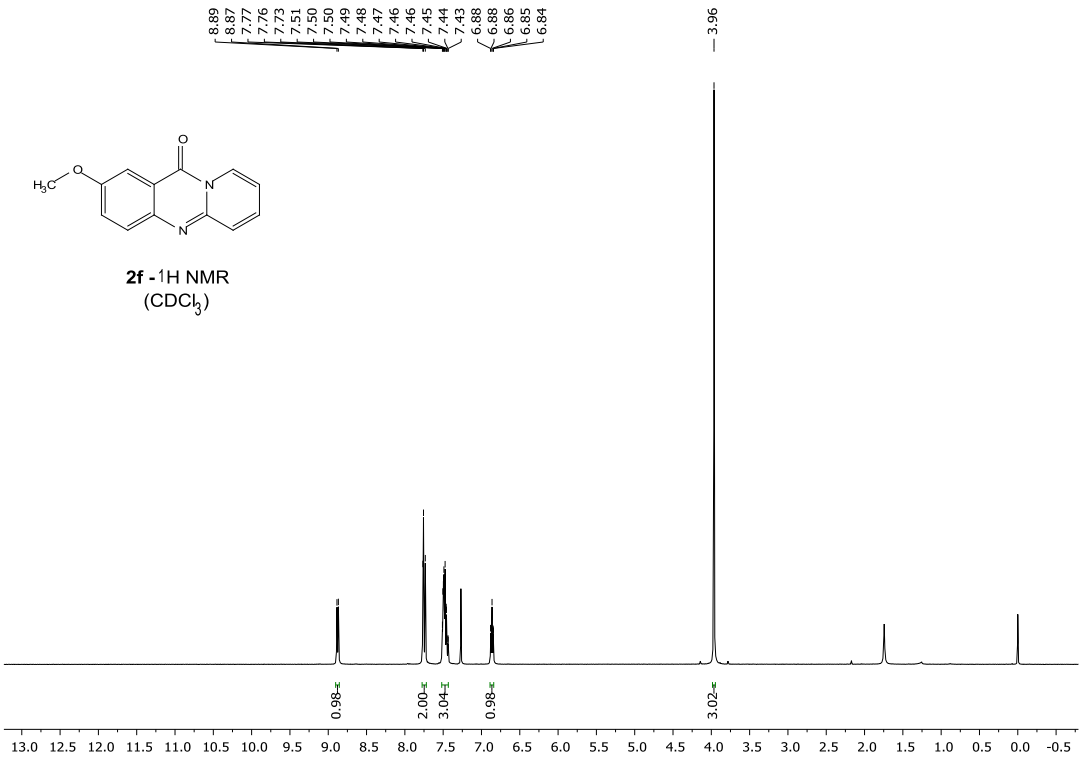



**Figure S17.** $^{1}$H NMR spectrum of **2f**

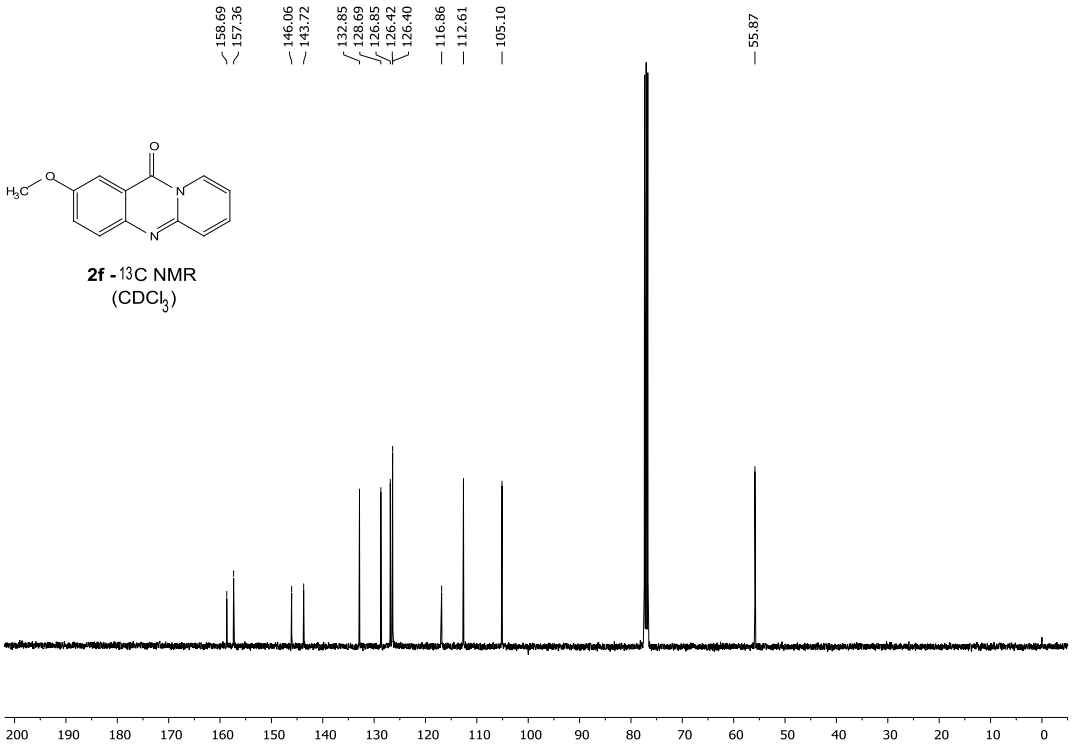



**Figure S18.** $^{13}$C NMR spectrum of **2f**

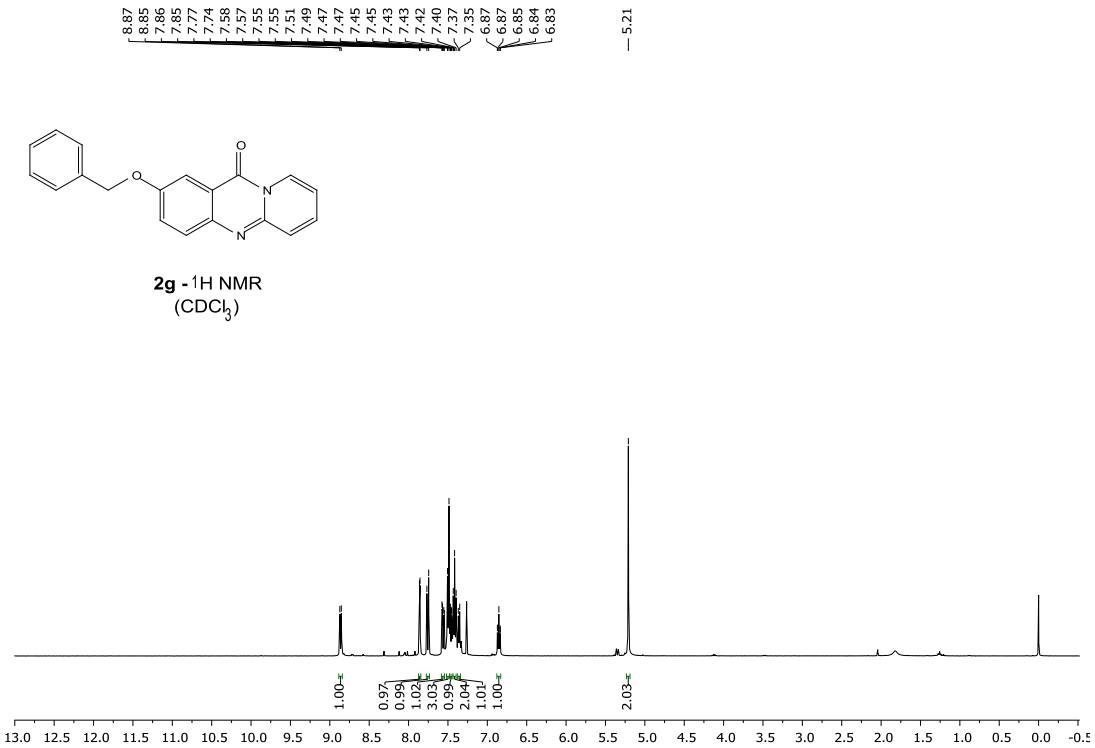



**Figure S19.** $^{1}$H NMR spectrum of **2g**

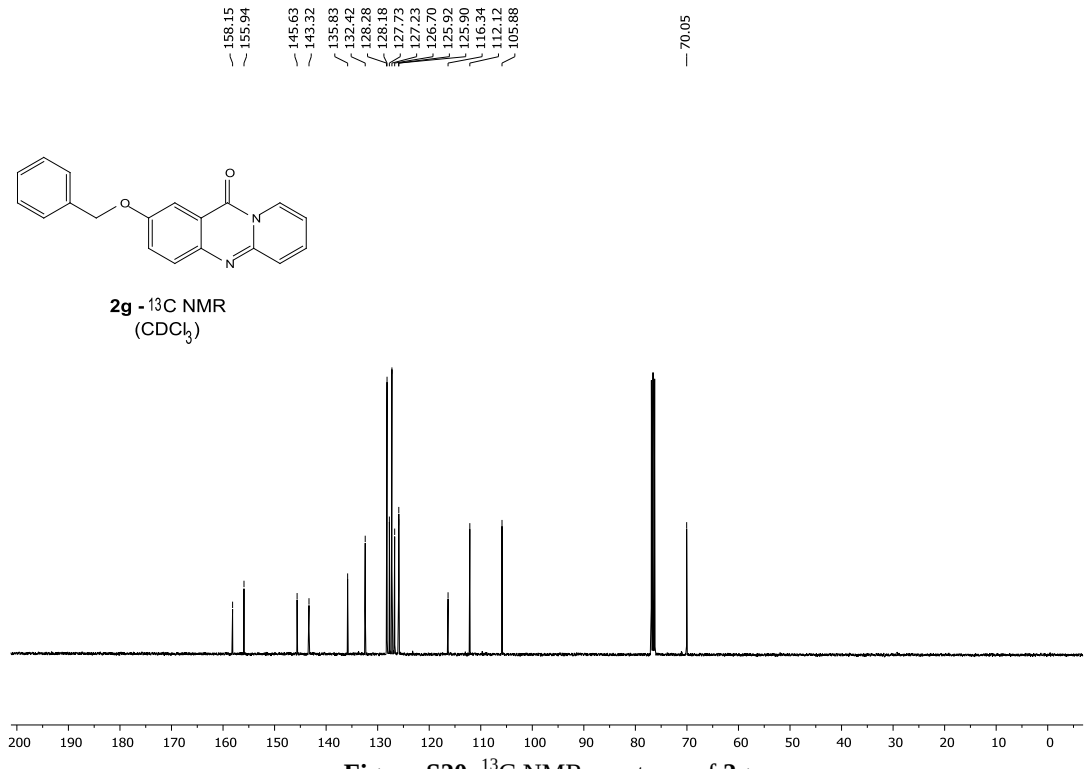



**Figure S20.** $^{13}$C NMR spectrum of **2g**

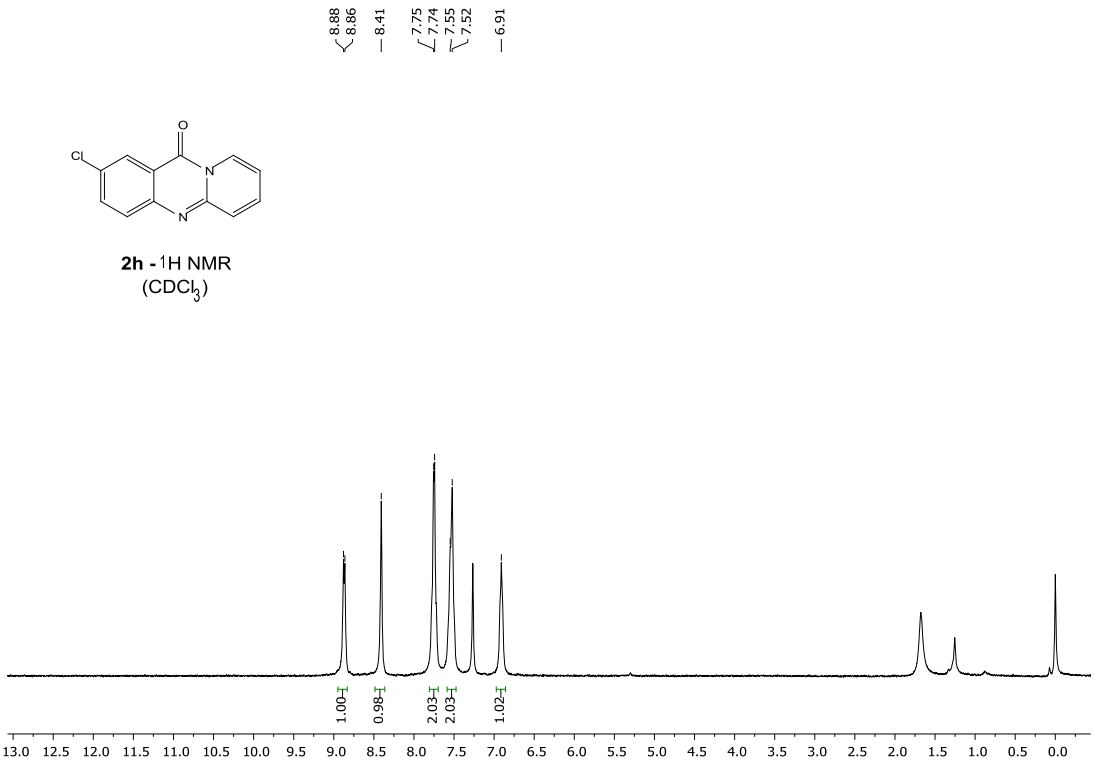



**Figure S21.** $^{1}$H NMR spectrum of **2h**

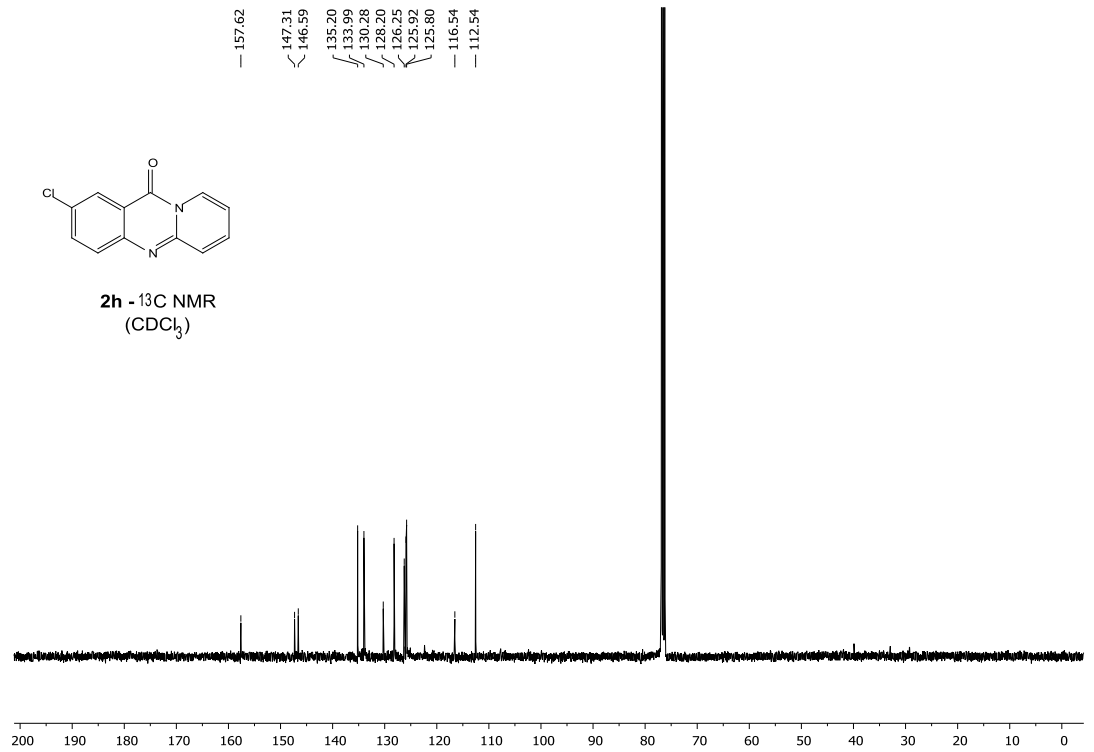



**Figure S22.** $^{13}$C NMR spectrum of **2h**

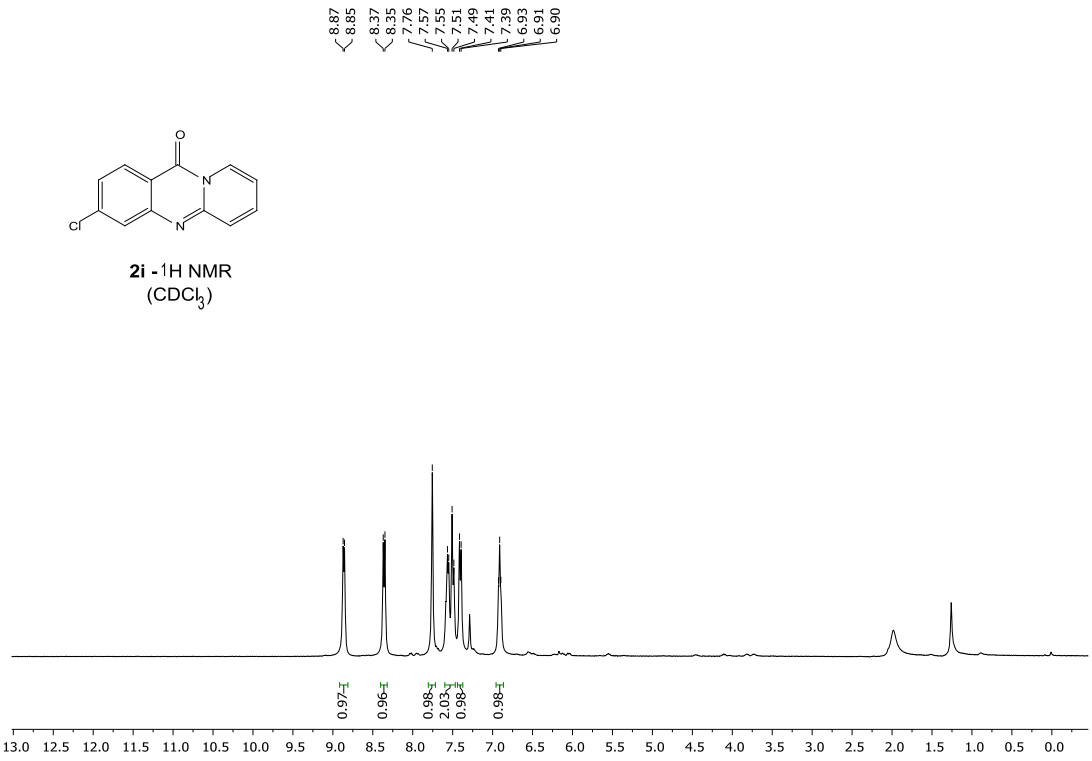



**Figure S23.** $^{1}$H NMR spectrum of **2i**

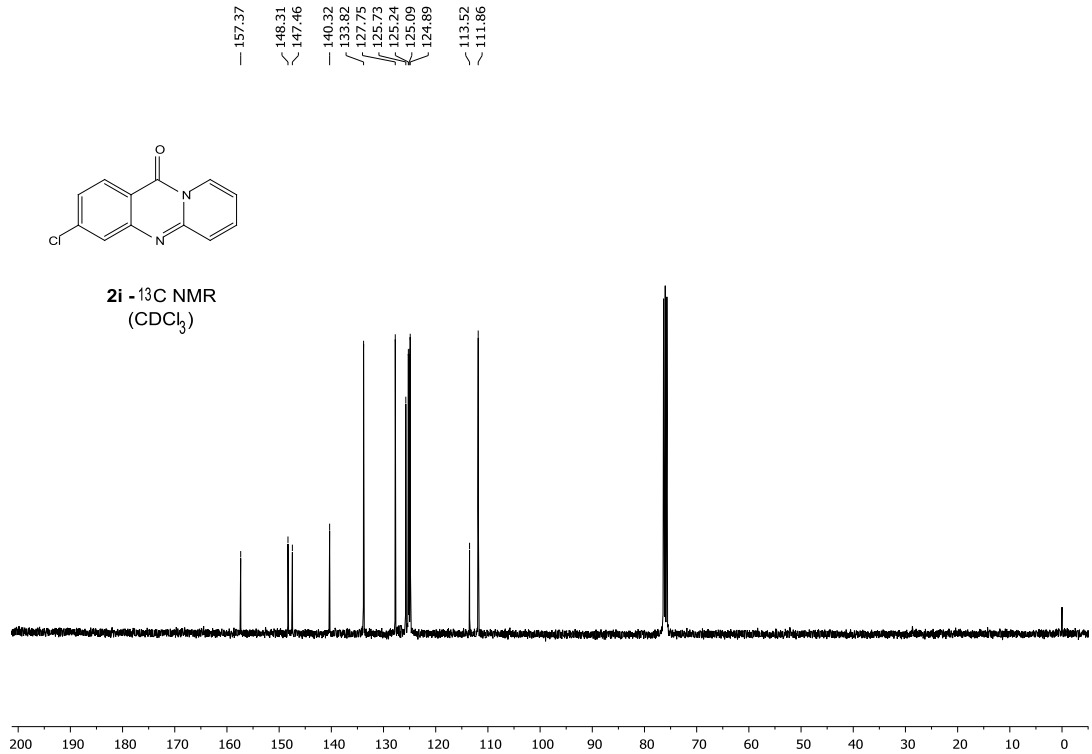



**Figure S24.** $^{13}$C NMR spectrum of **2i**

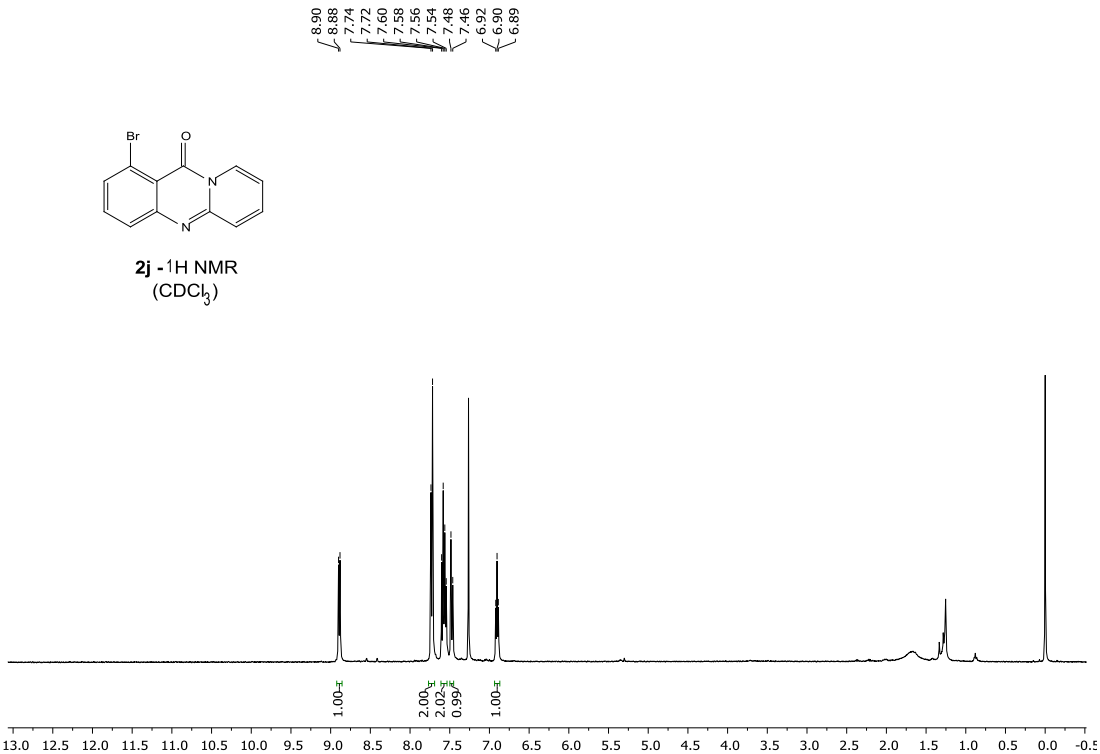



**Figure S25.** $^{1}$H NMR spectrum of **2j**

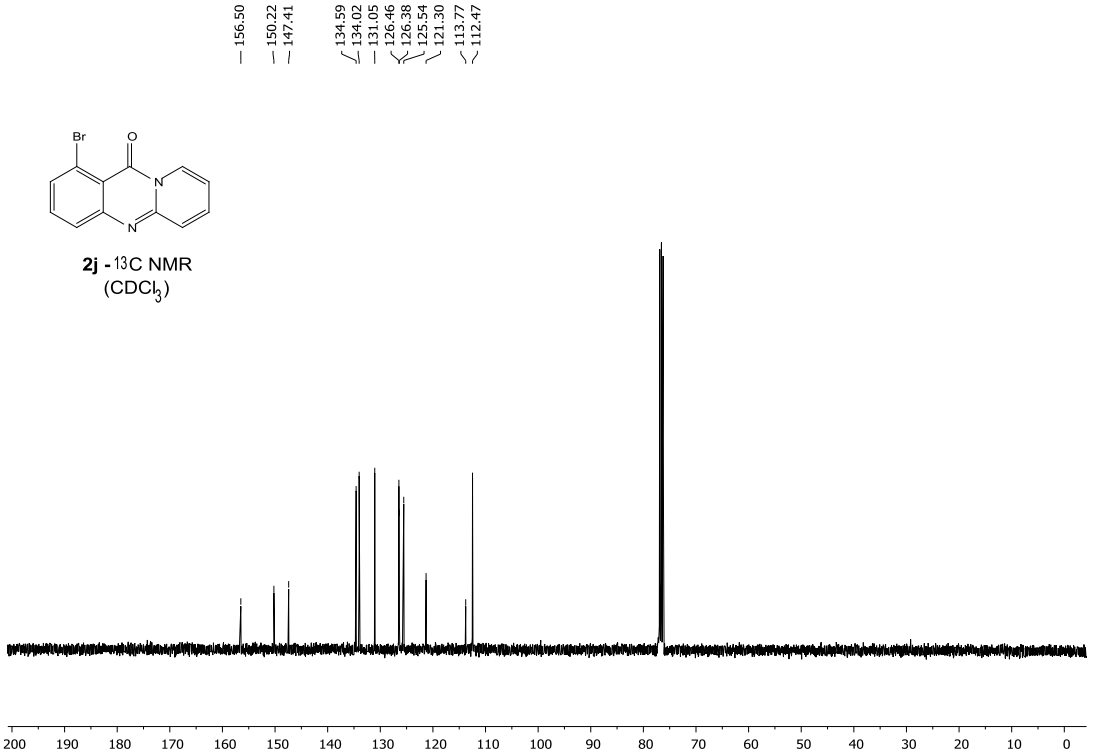



**Figure S26.** $^{13}$C NMR spectrum of **2j**

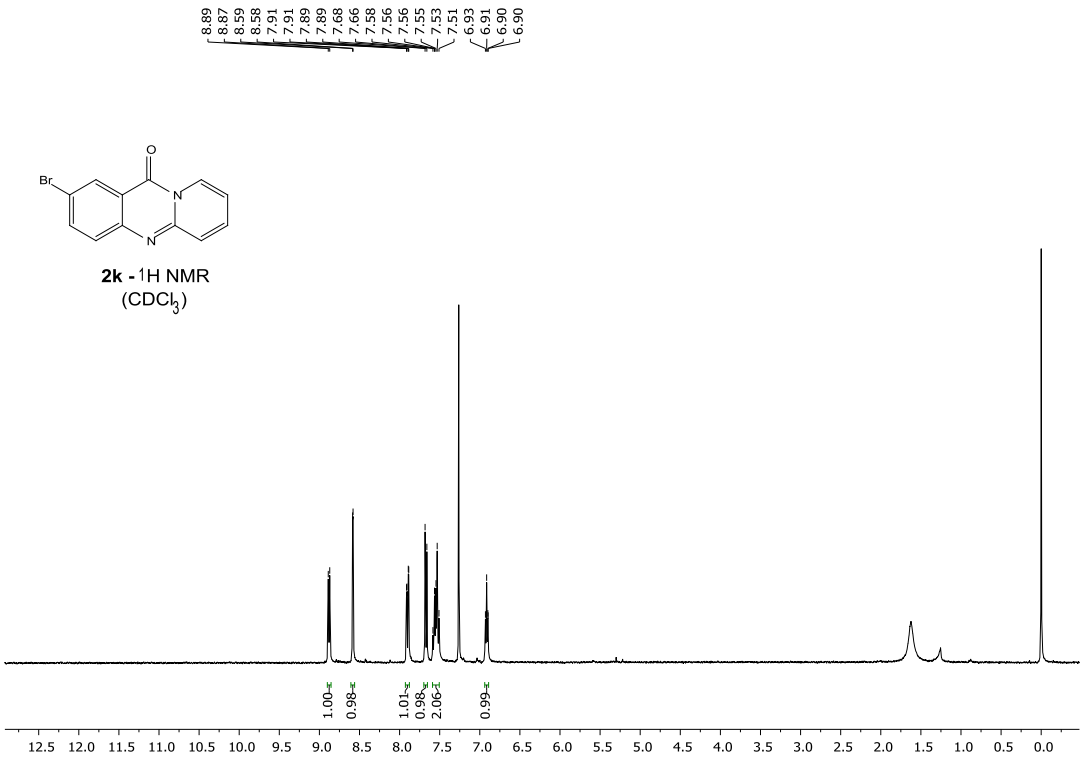



**Figure S27.** $^{1}$H NMR spectrum of **2k**

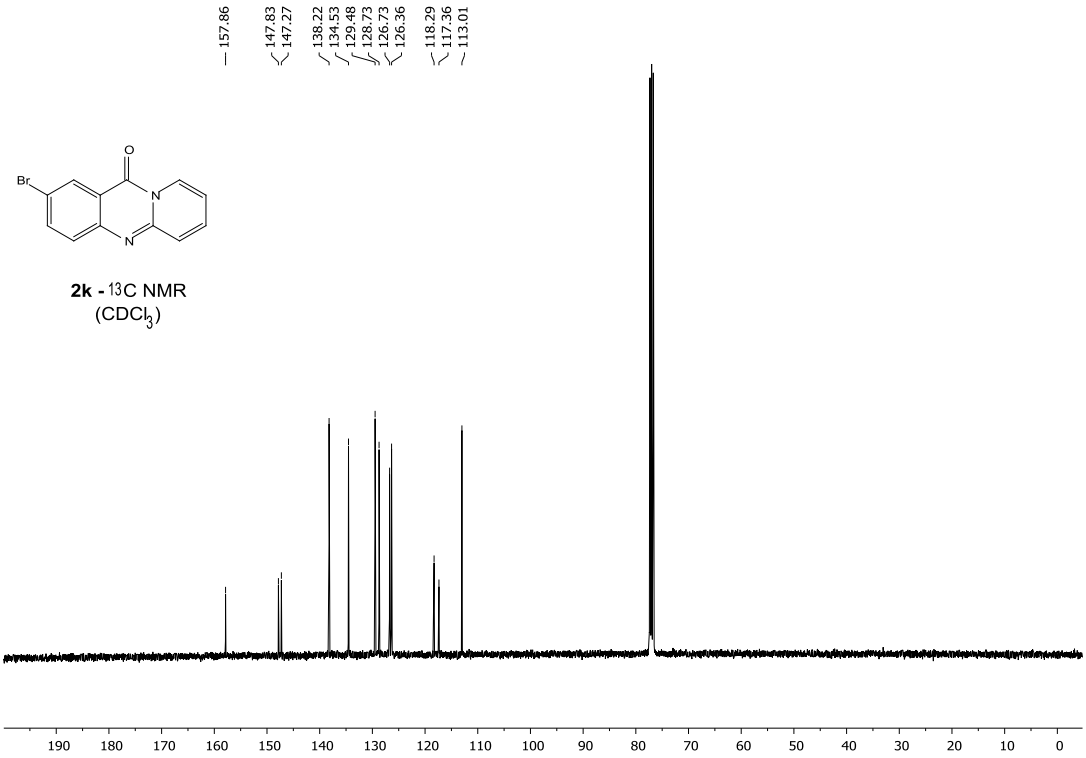



**Figure S28.** $^{13}$C NMR spectrum of **2k**

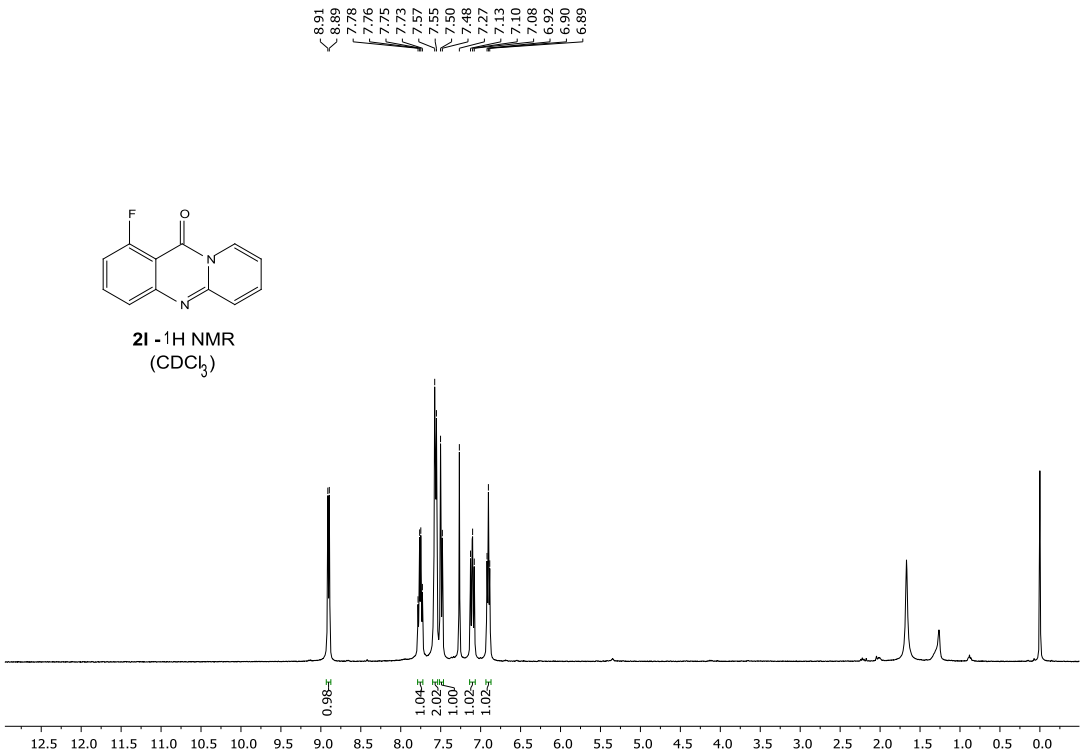



**Figure S29.** $^{1}$H NMR spectrum of **2l**

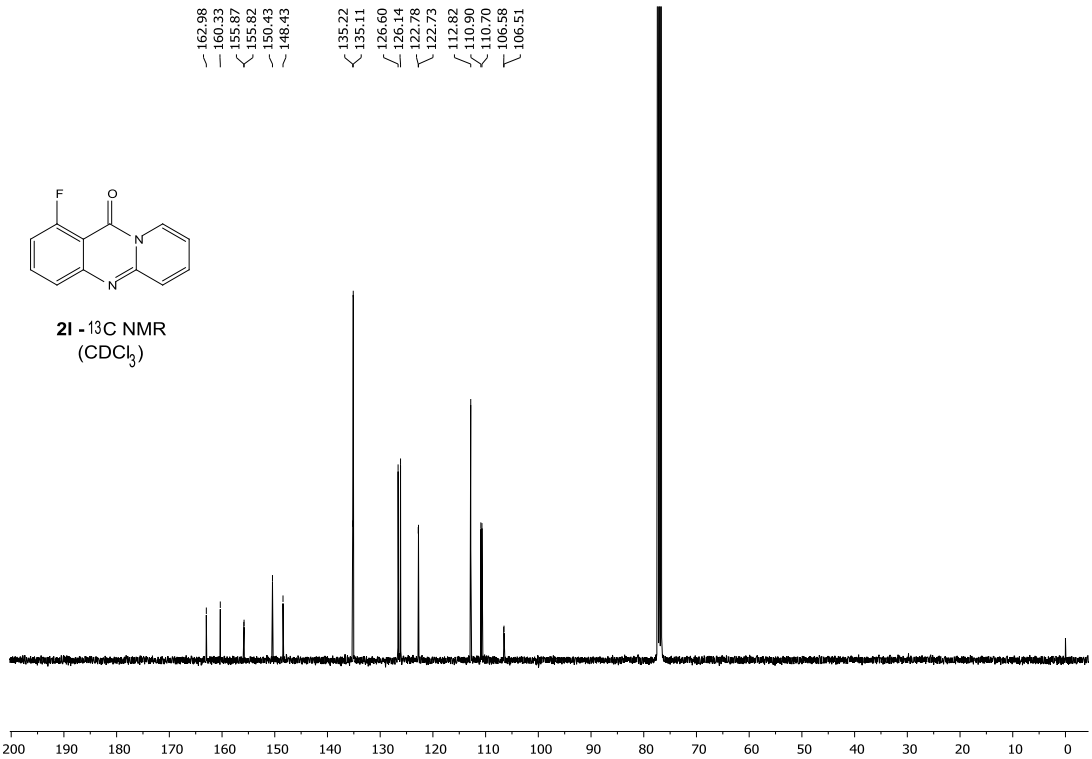



**Figure S30.** $^{13}$C NMR spectrum of **2l**

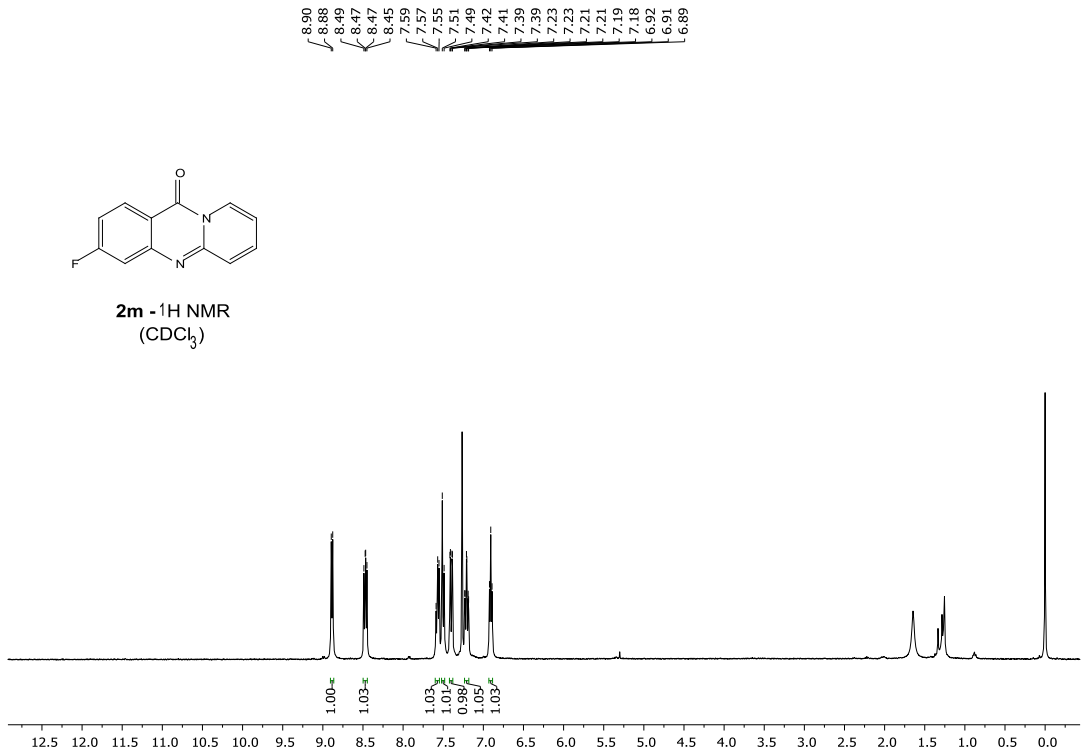



**Figure S31.** $^{1}$H NMR spectrum of **2m**

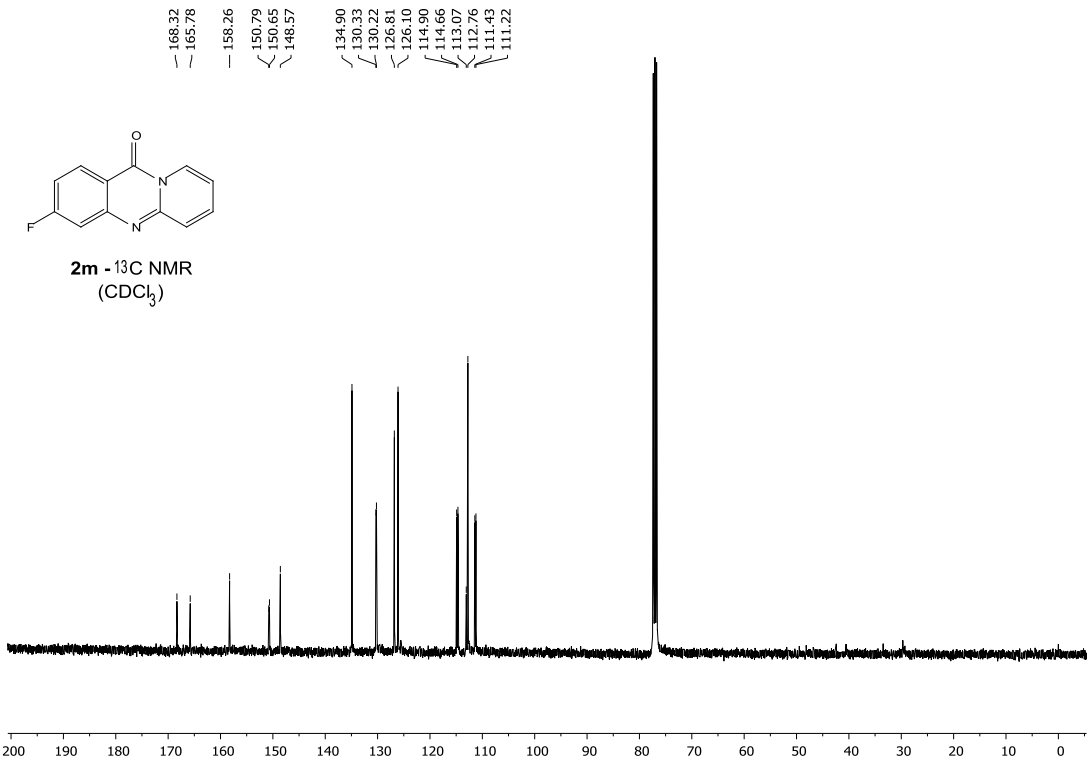



**Figure S32.** $^{13}$C NMR spectrum of **2m**

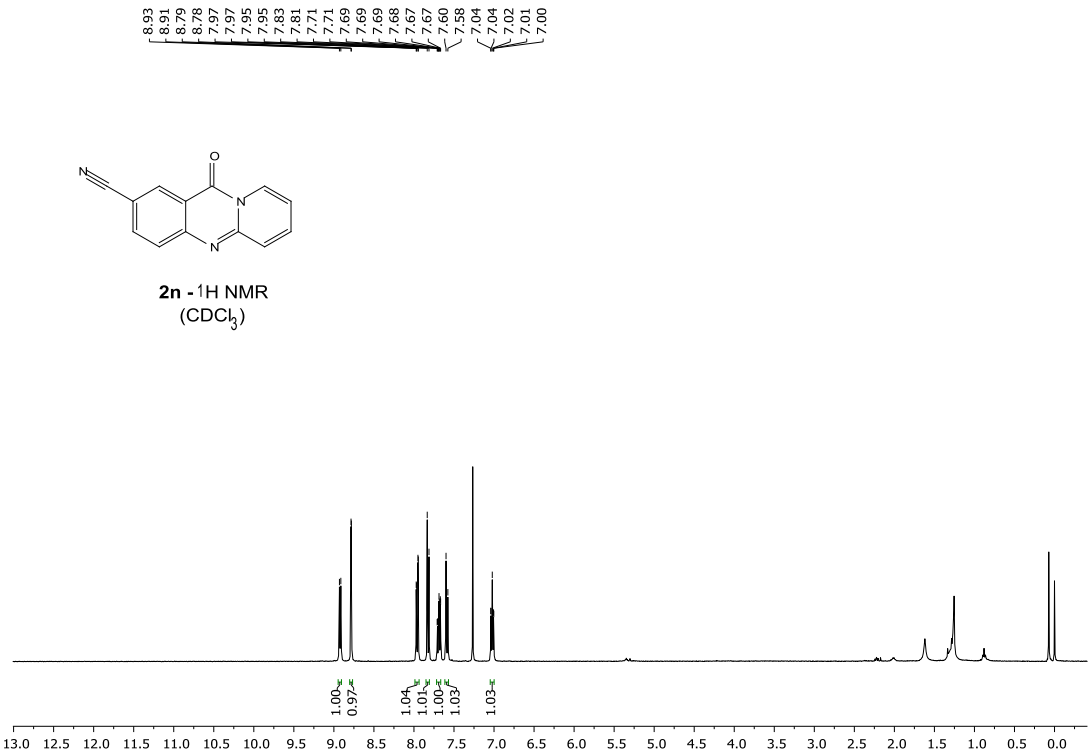



**Figure S33.** $^{1}$H NMR spectrum of **2n**

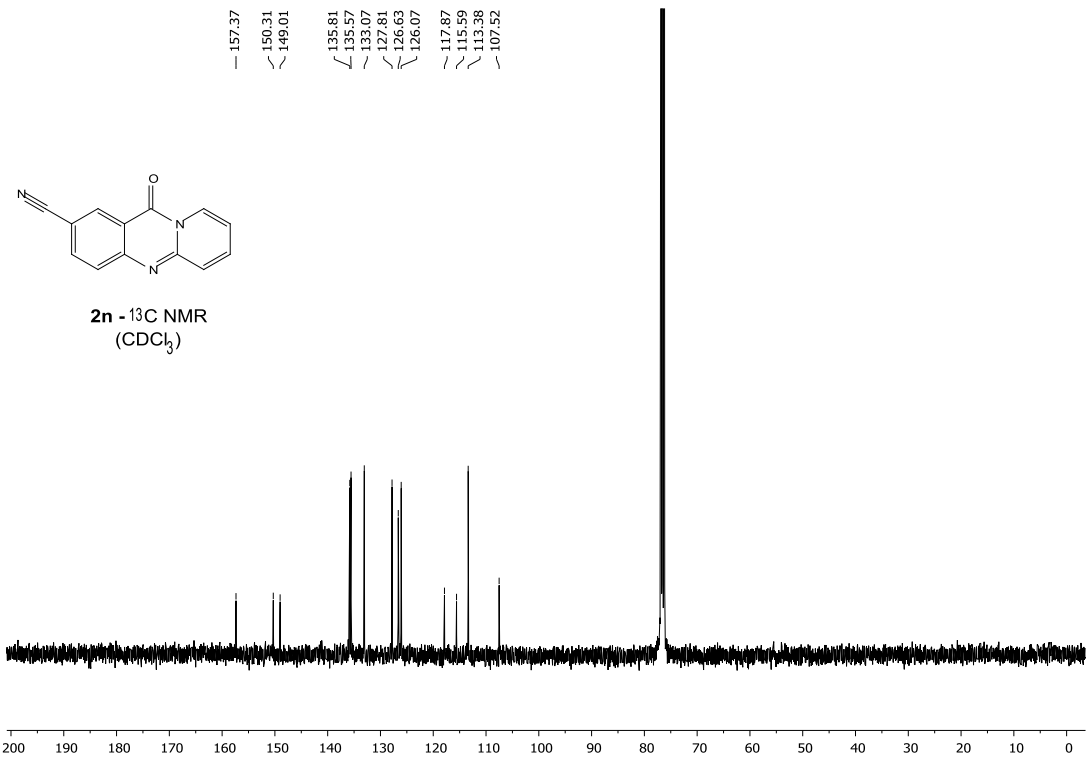



**Figure S34.** $^{13}$C NMR spectrum of **2n**

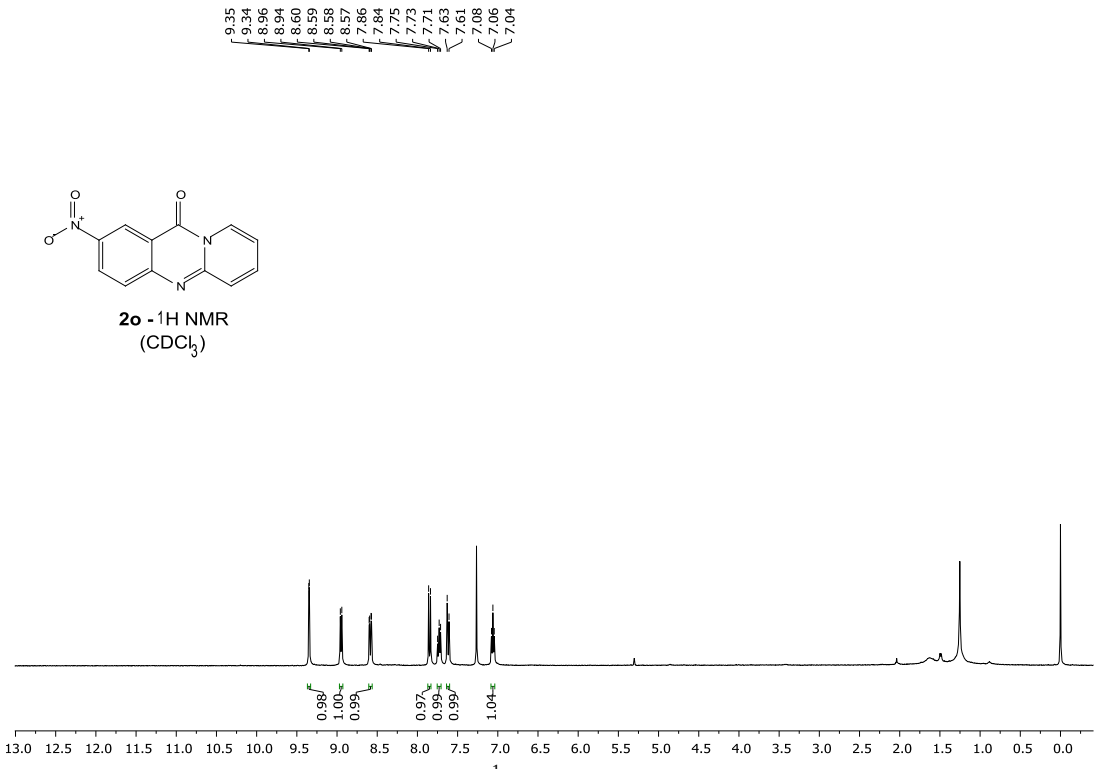



**Figure S35.** $^{1}$H NMR spectrum of **2o**

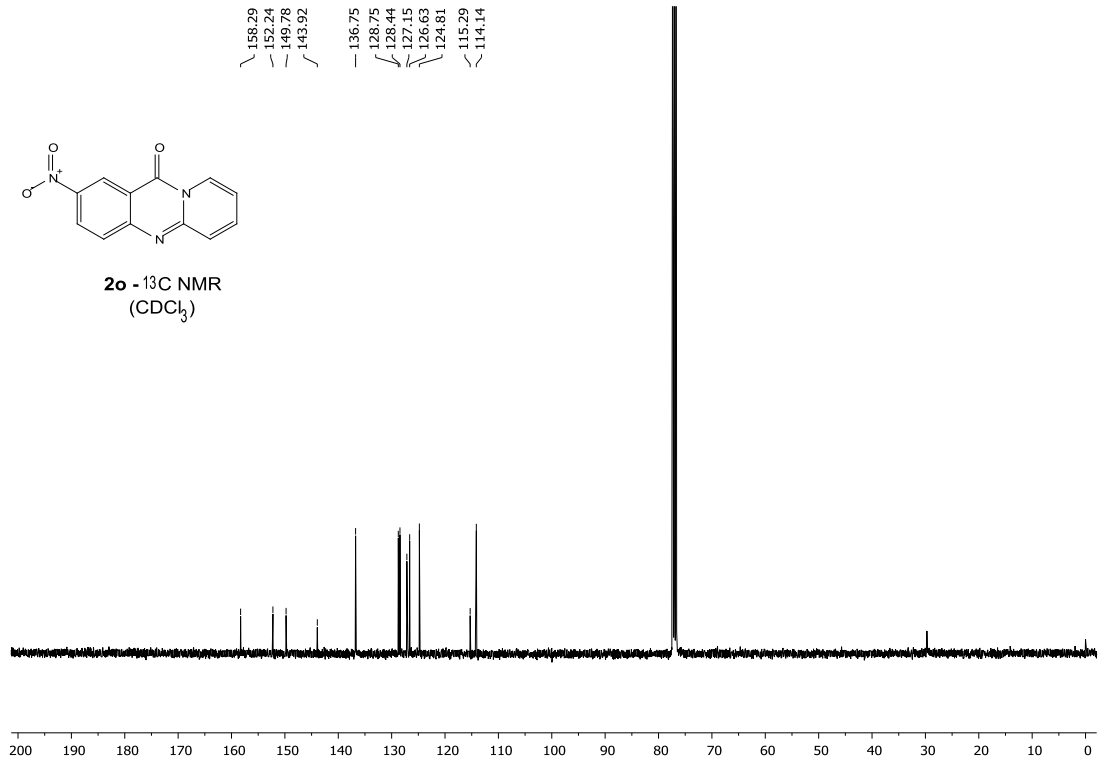



**Figure S36.** $^{13}$C NMR spectrum of **2o**

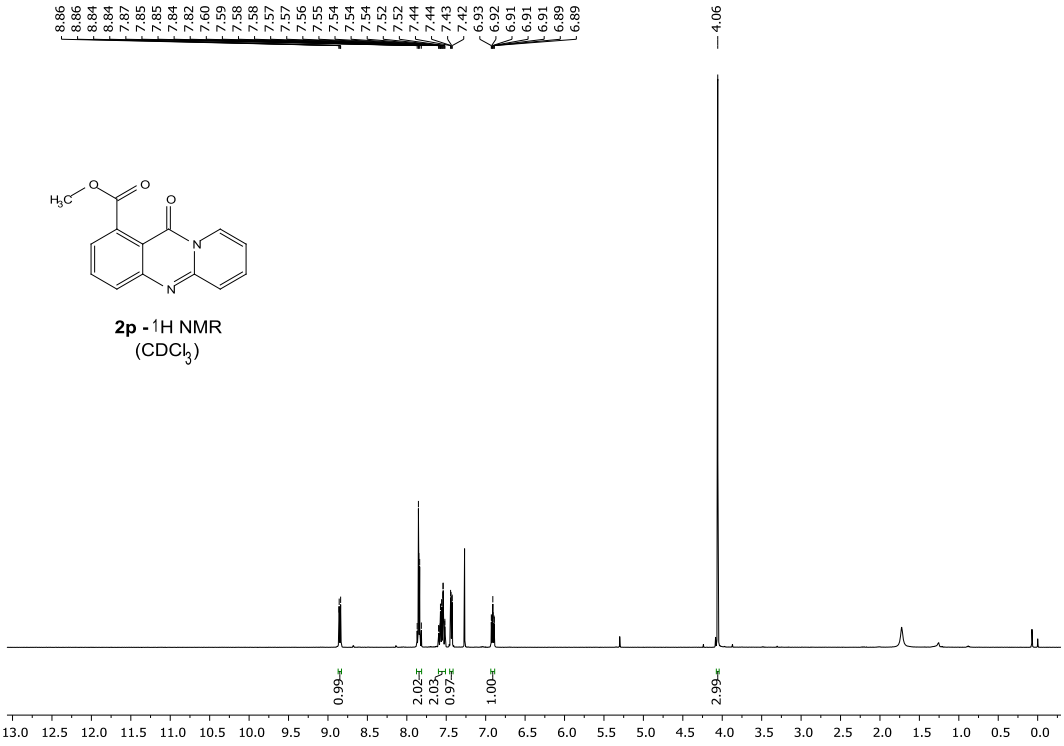



**Figure S37.** $^{1}$H NMR spectrum of **2p**

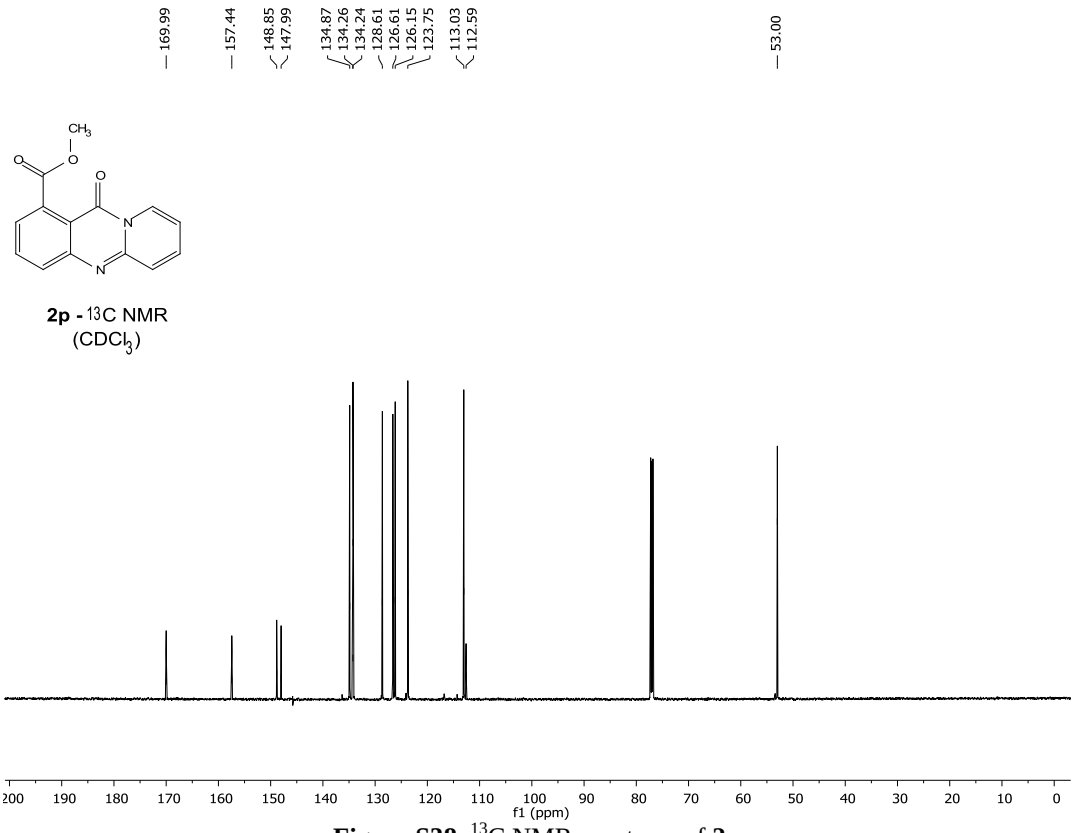



**Figure S38.** $^{13}$C NMR spectrum of **2p**

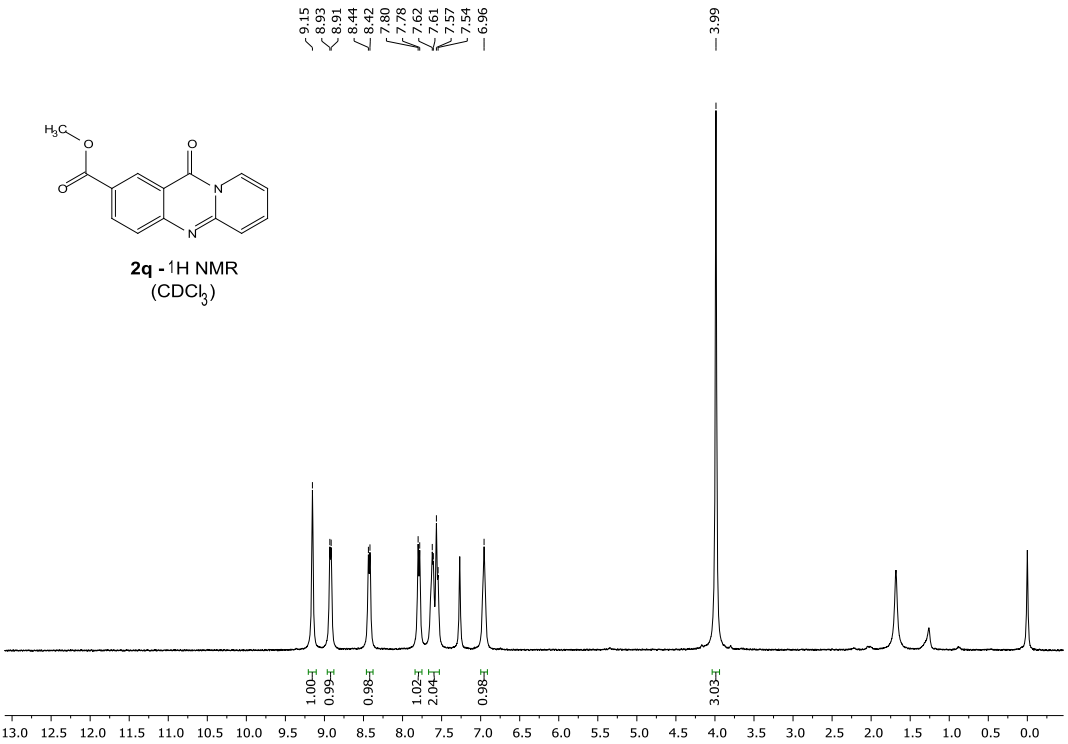



**Figure S39.** $^{1}$H NMR spectrum of **2q**

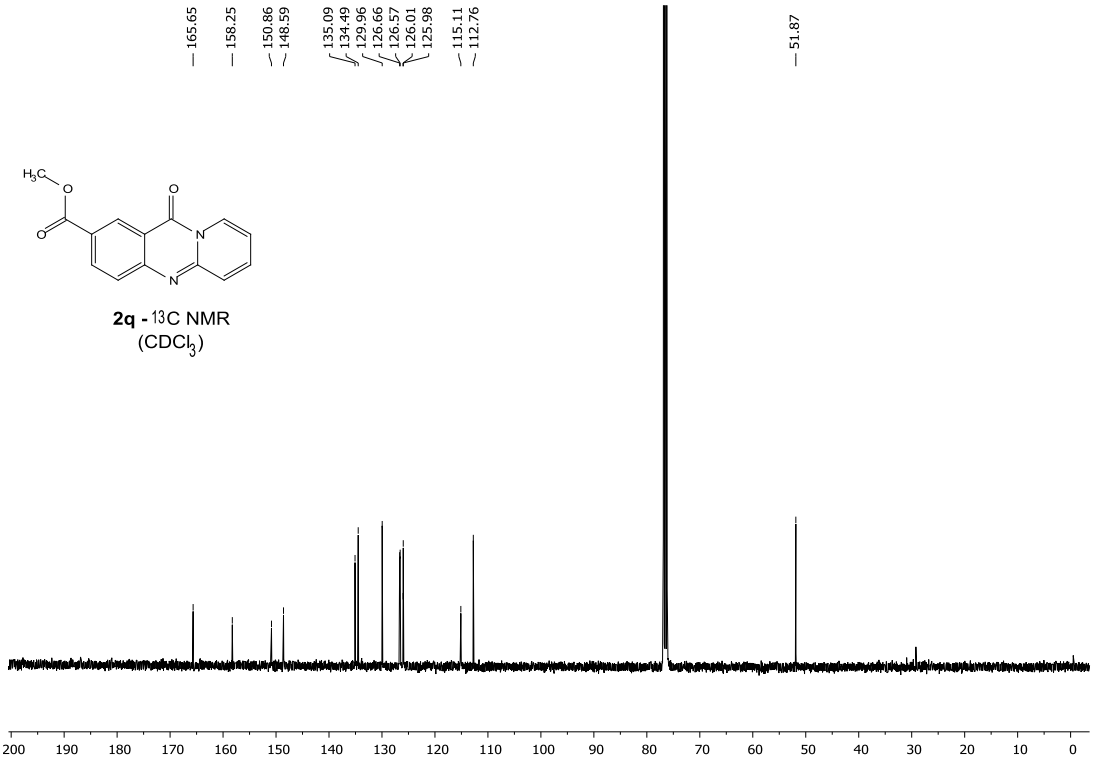



**Figure S40.** $^{13}$C NMR spectrum of **2q**

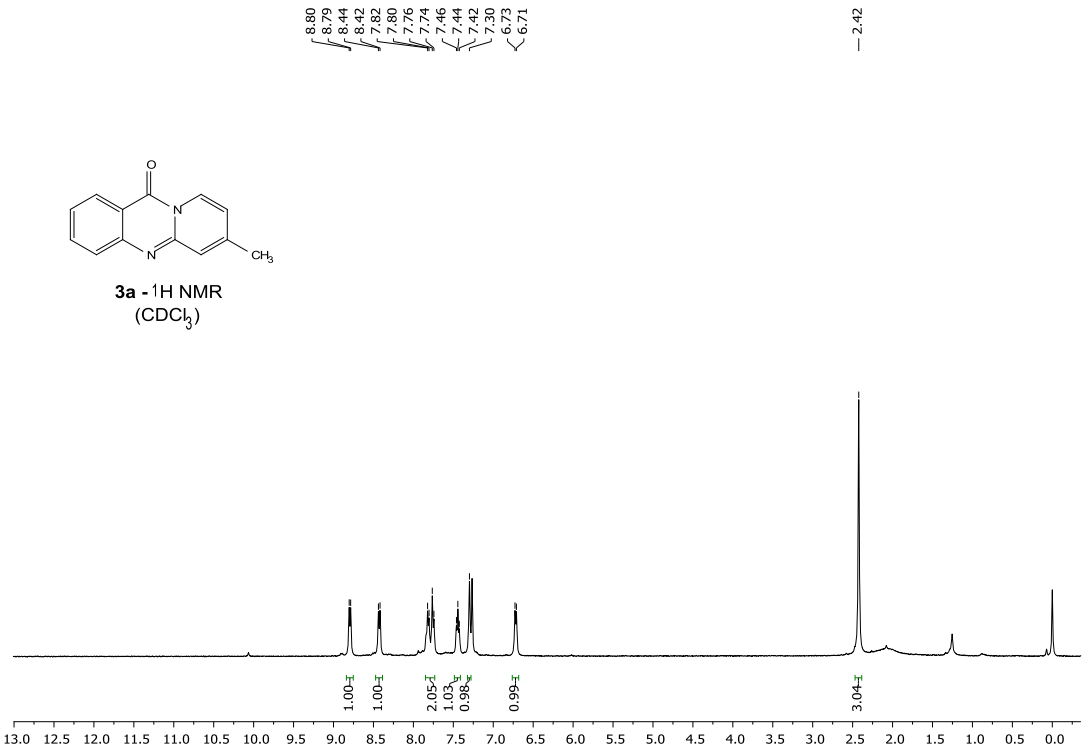



**Figure S41.** $^{1}$H NMR spectrum of **3a**

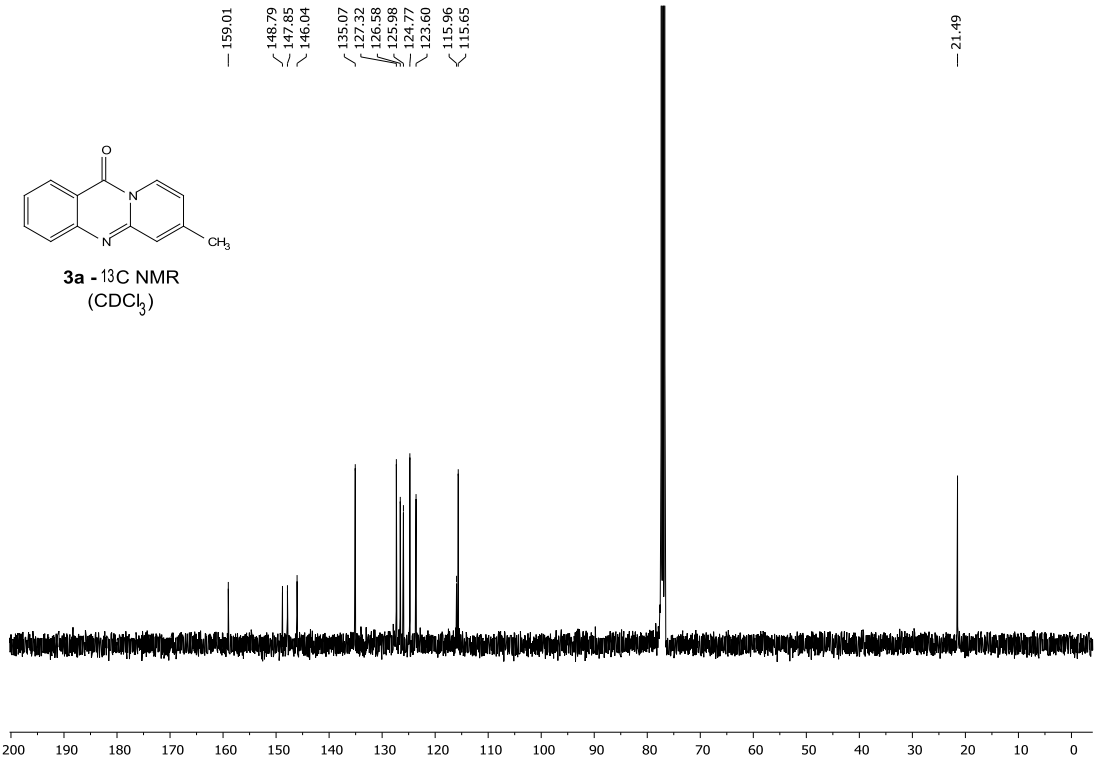



**Figure S42.** $^{13}$C NMR spectrum of **3a**

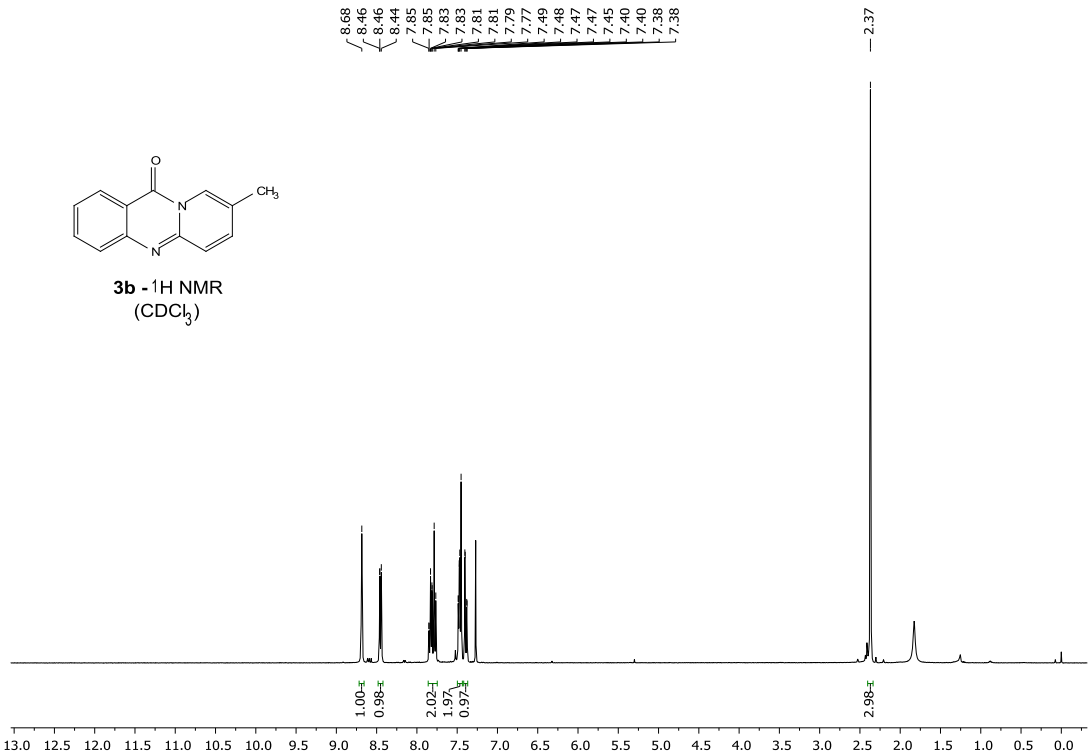



**Figure S43.** $^{1}$H NMR spectrum of **3b**

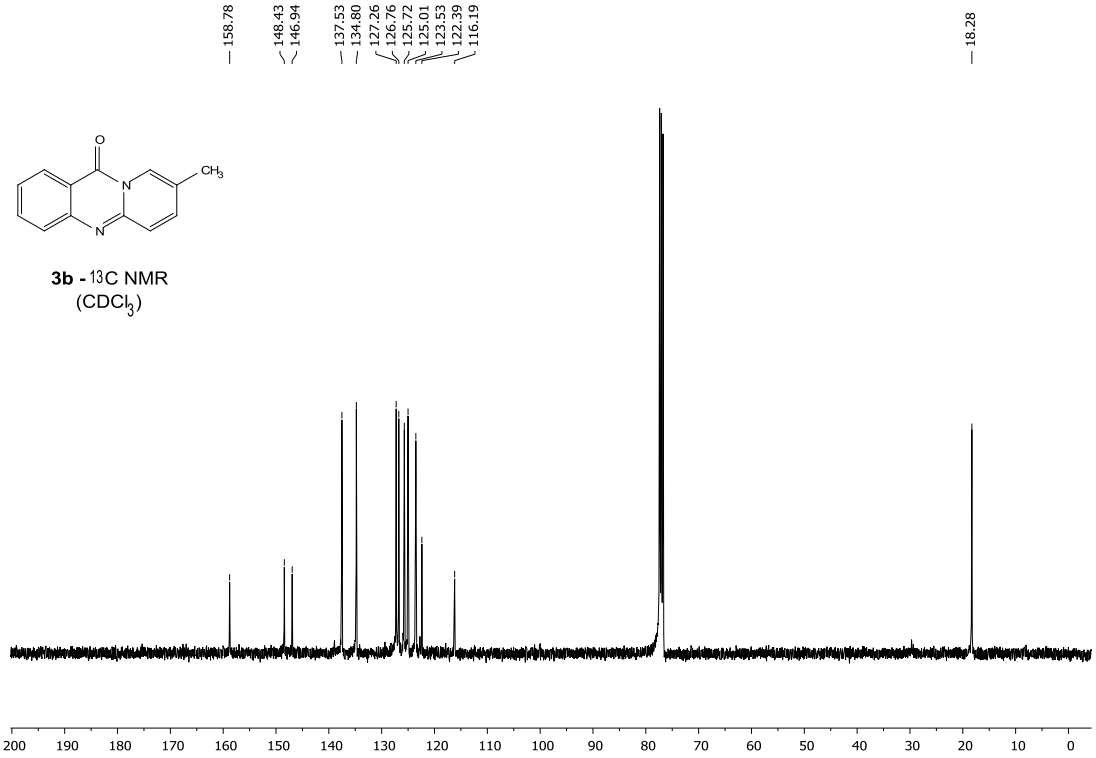



**Figure S44.** $^{1}$H NMR spectrum of **3b**

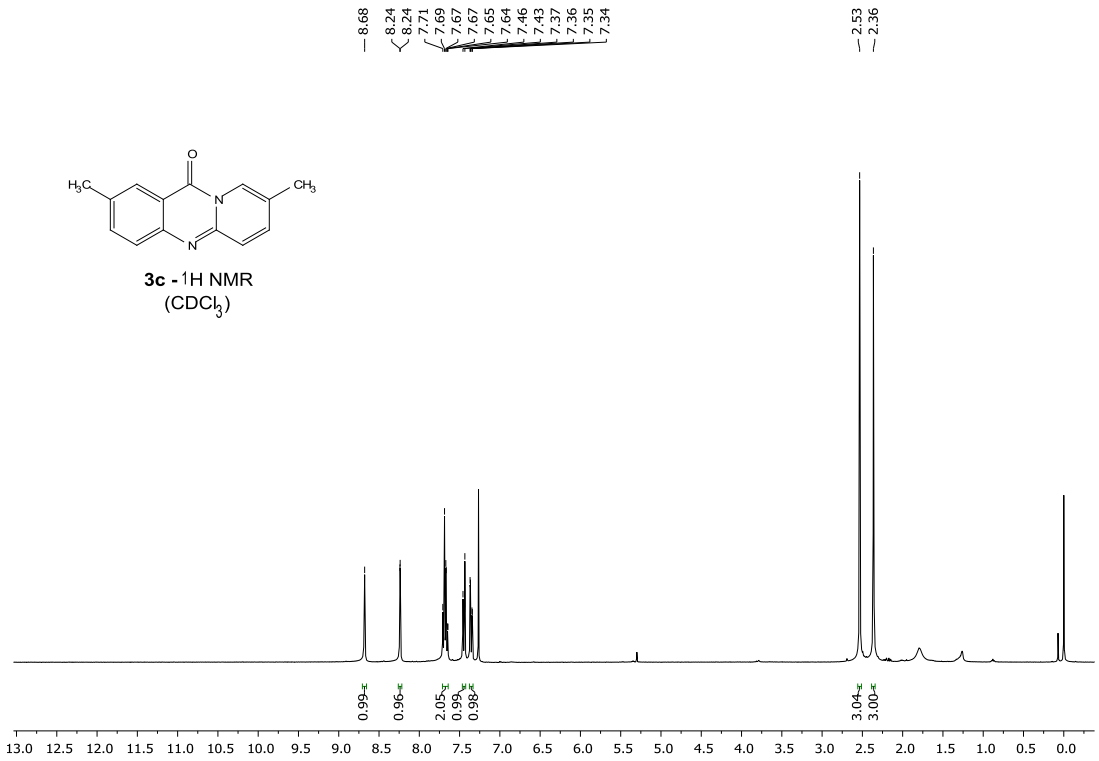



**Figure S45.** $^{1}$H NMR spectrum of **3c**

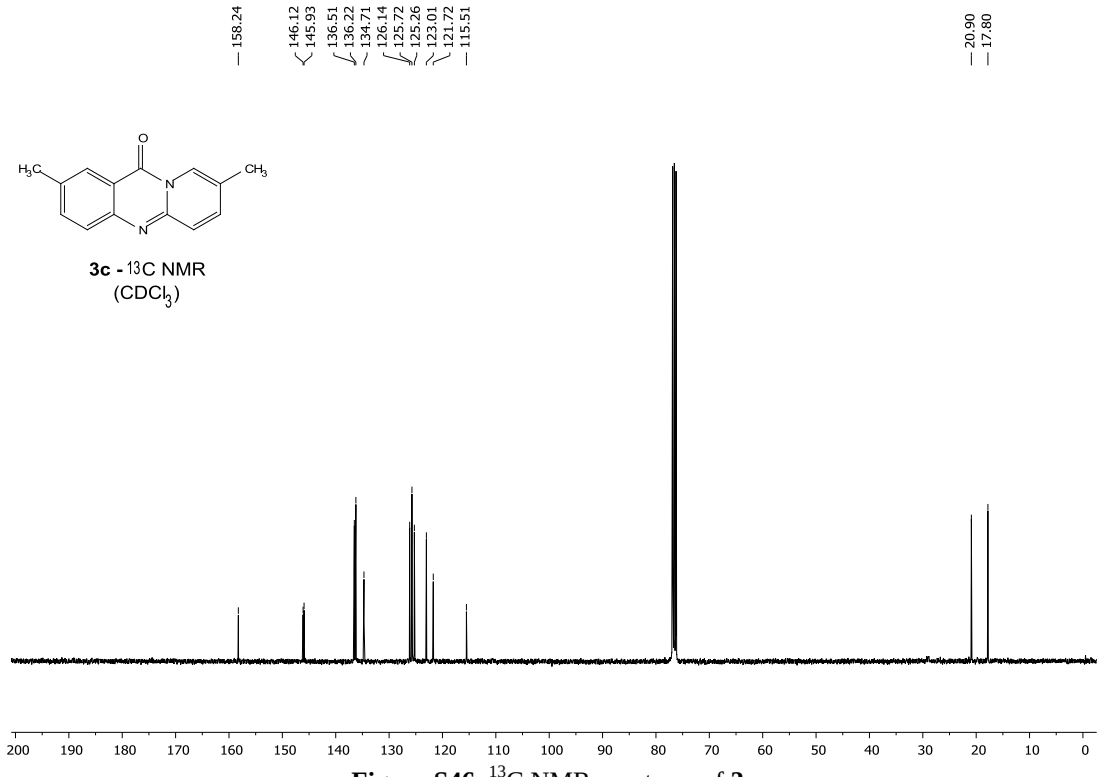



**Figure S46.** $^{13}$C NMR spectrum of **3c**

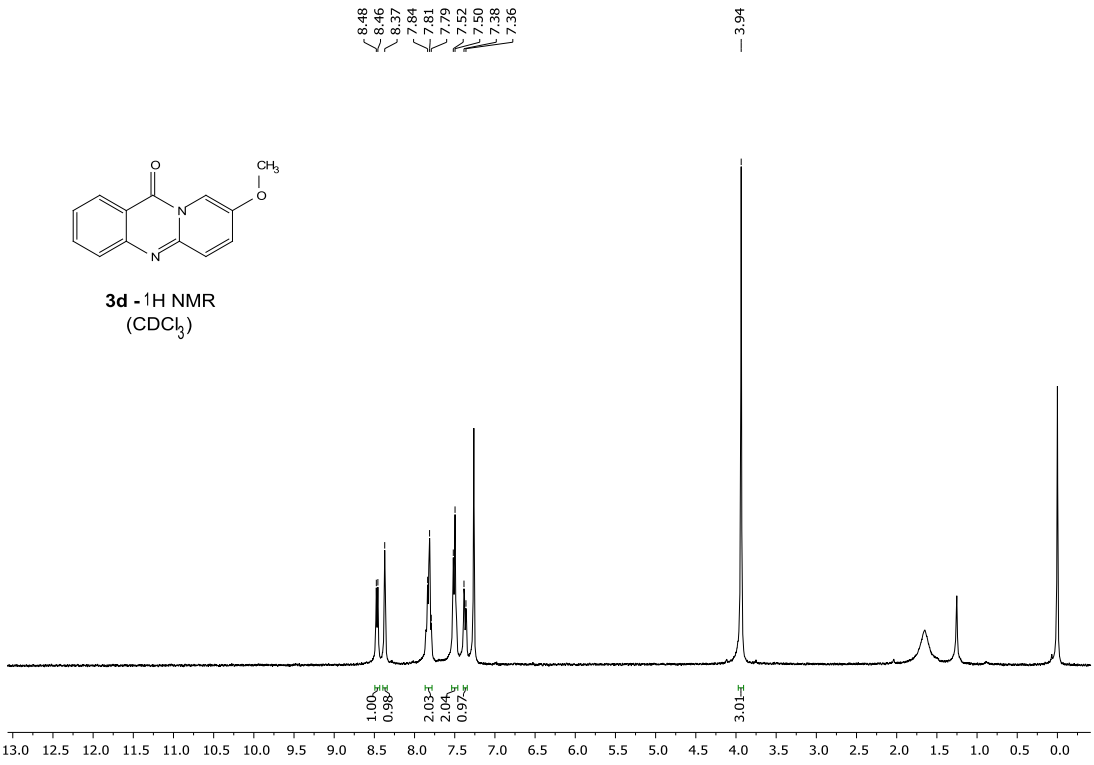



**Figure S47.** $^{1}$H NMR spectrum of **3d**

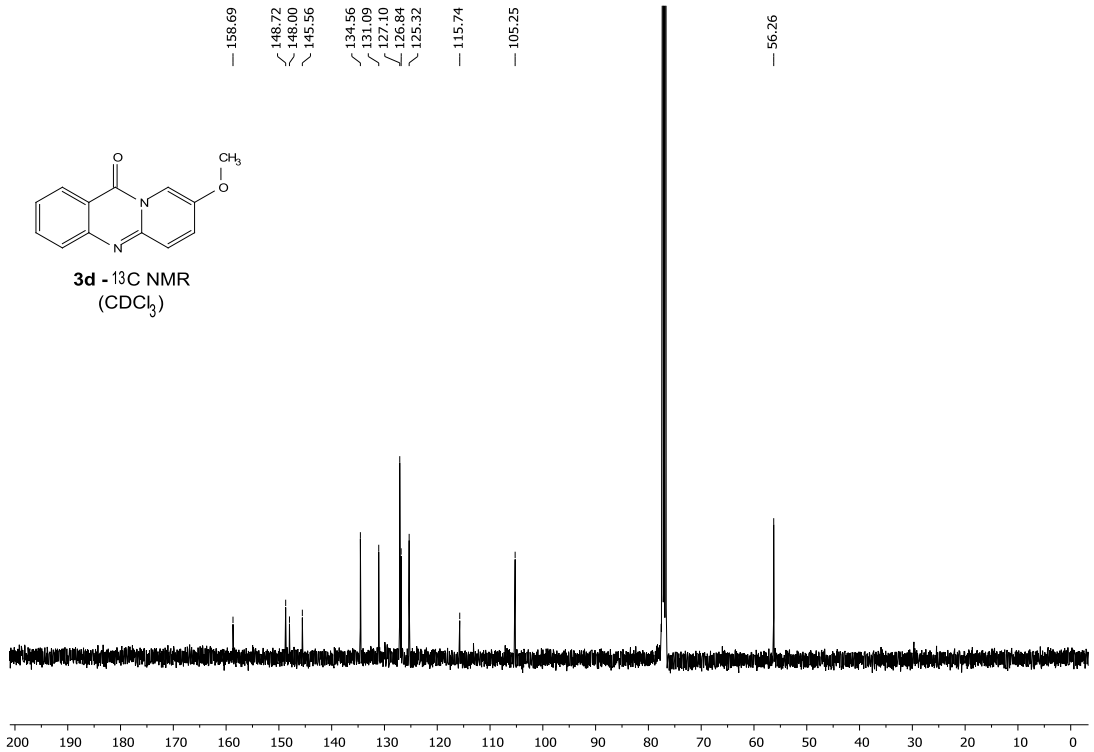



**Figure S48.** $^{13}$C NMR spectrum of **3d**

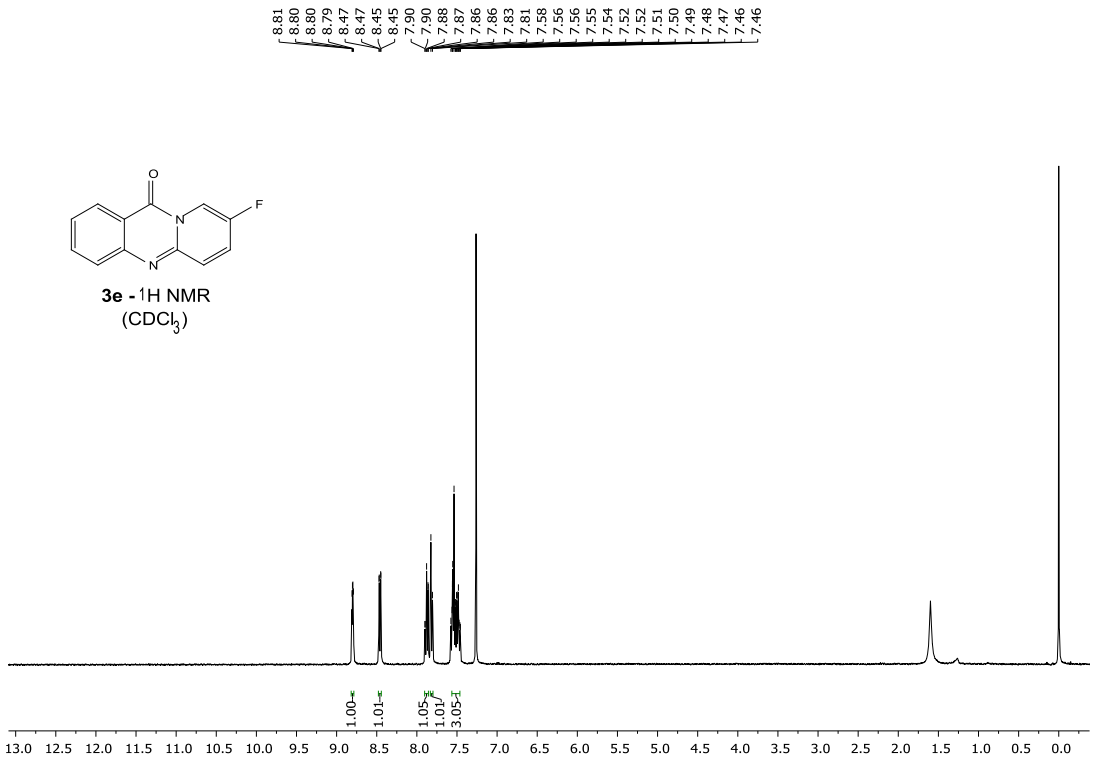



**Figure S49.** $^{1}$H NMR spectrum of **3e**

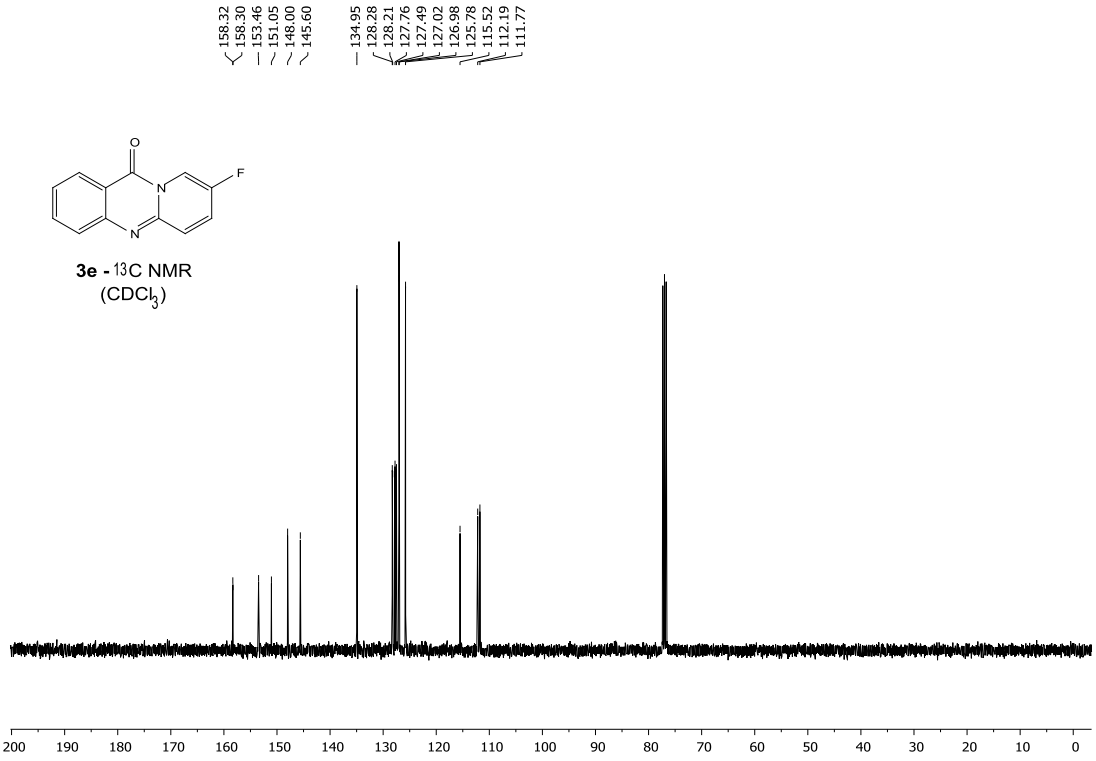



**Figure S50.** $^{13}$C NMR spectrum of **3e**

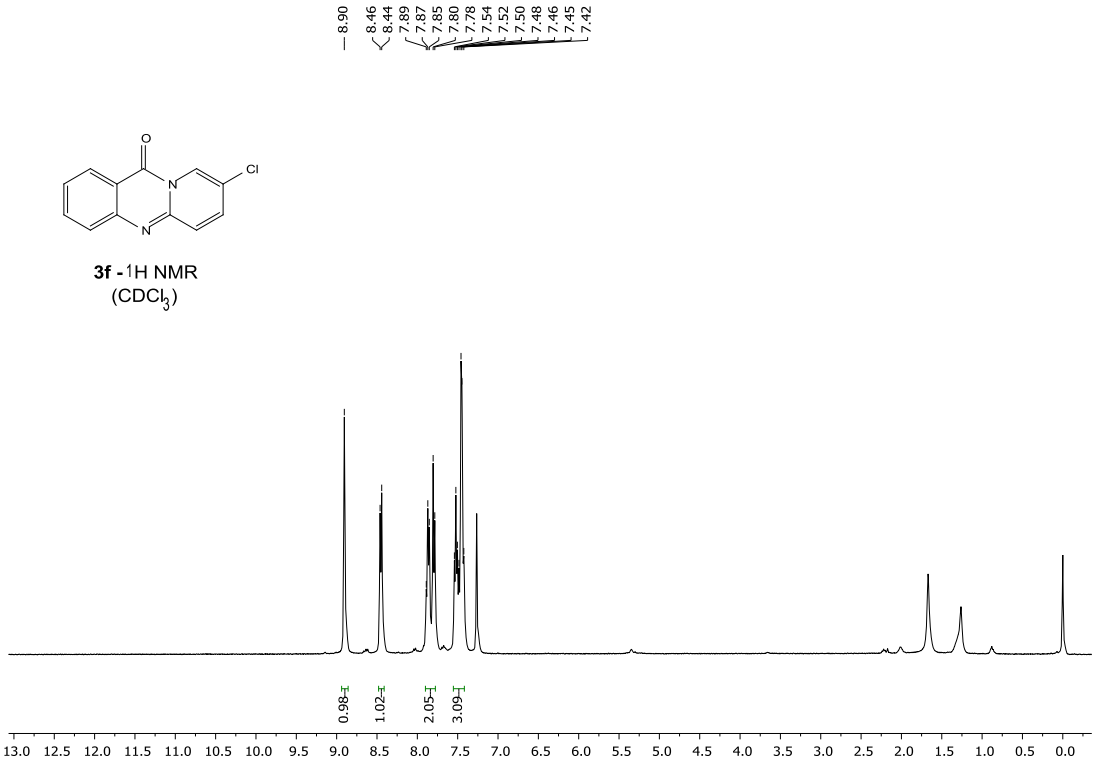



**Figure S51.** $^{1}$H NMR spectrum of **3f**

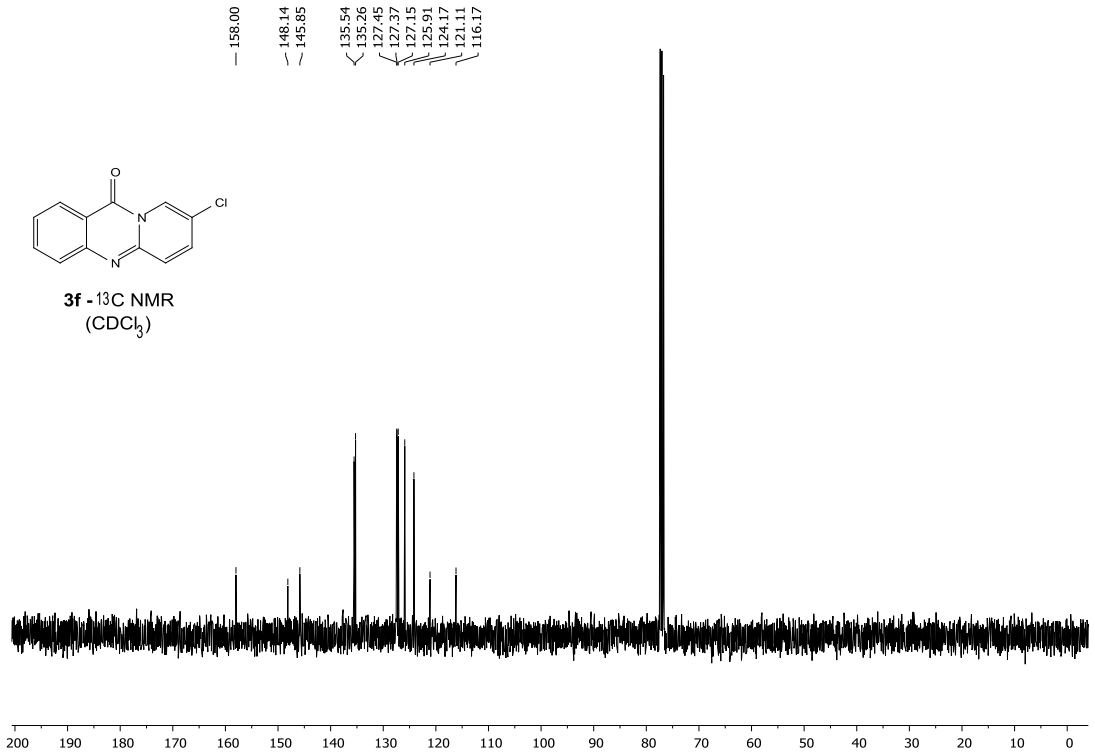



**Figure S52.** $^{13}$C NMR spectrum of **3f**

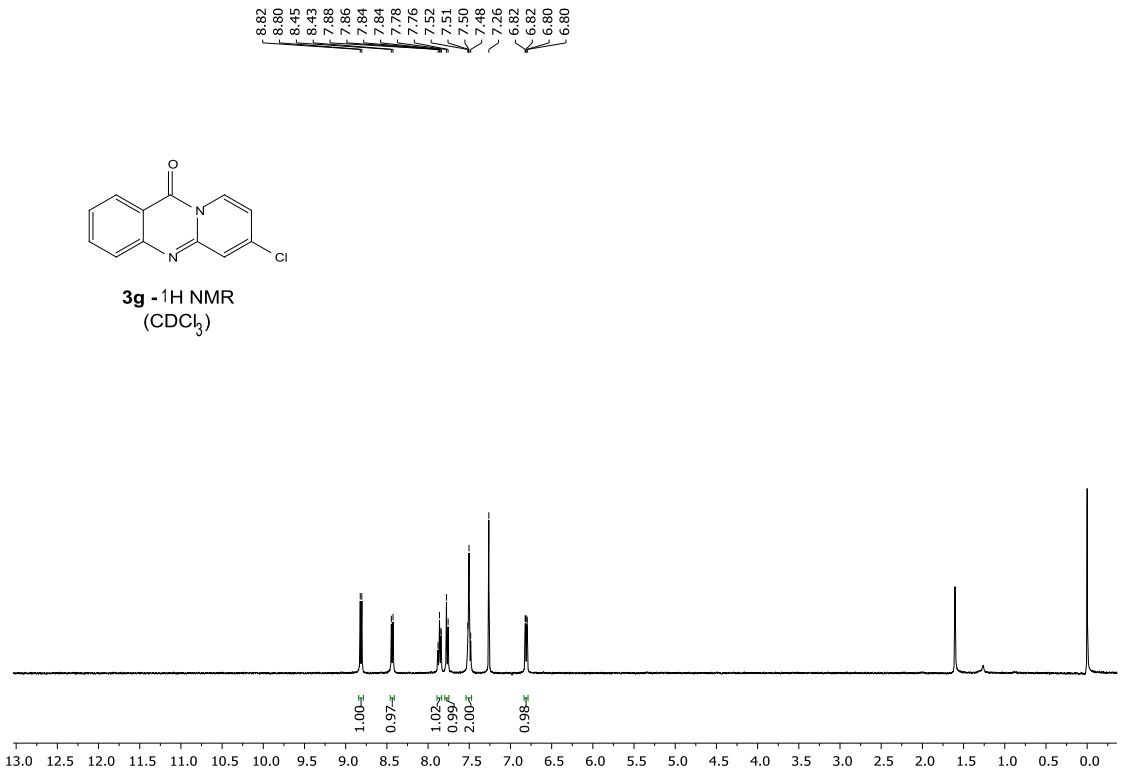



**Figure S53.** $^{1}$H NMR spectrum of **3g**

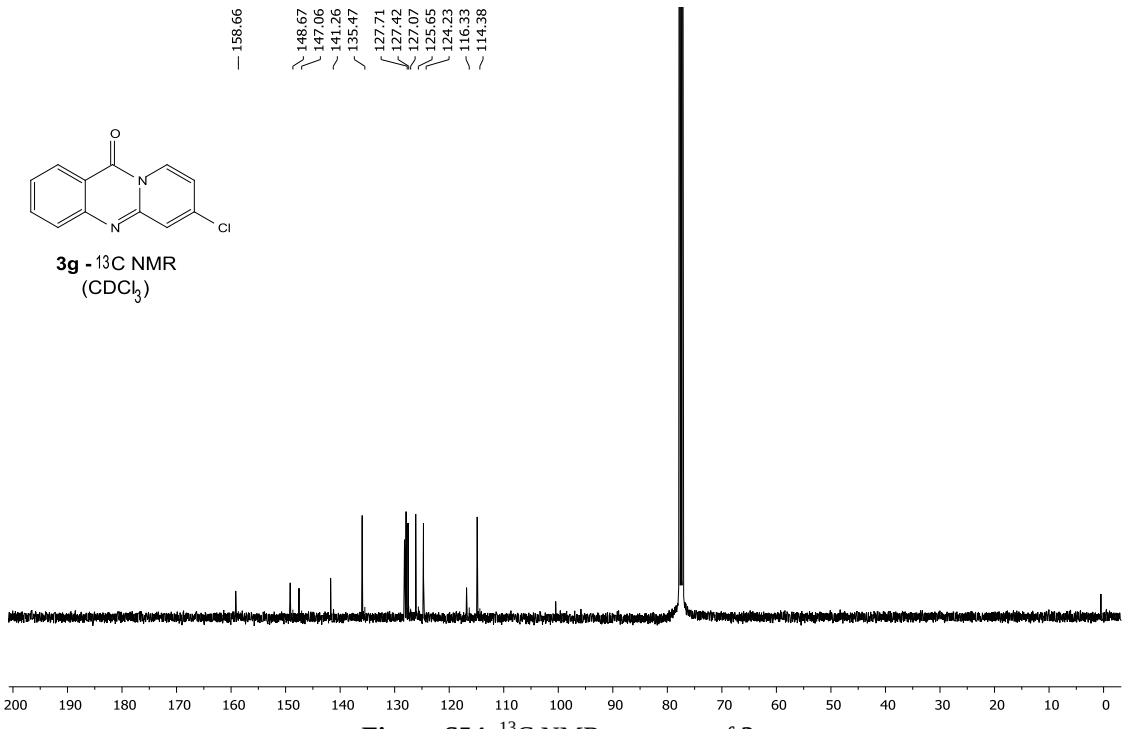



**Figure S54.** $^{13}$C NMR spectrum of **3g**

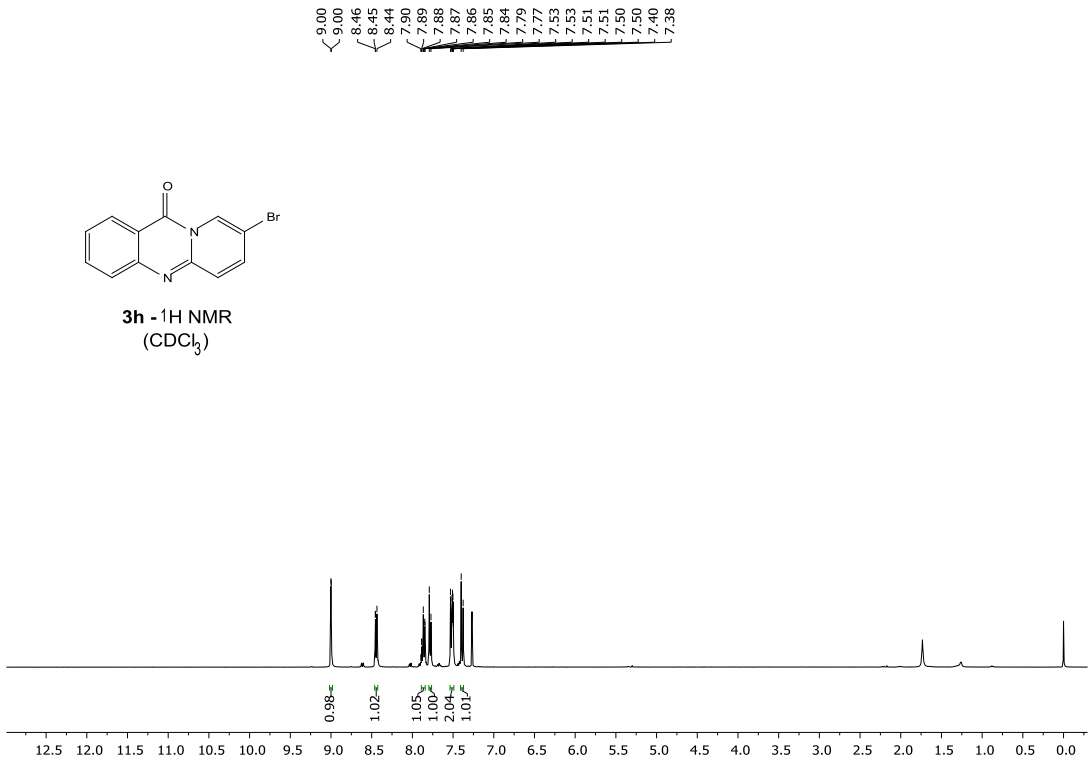



**Figure S55.** $^{1}$H NMR spectrum of **3h**

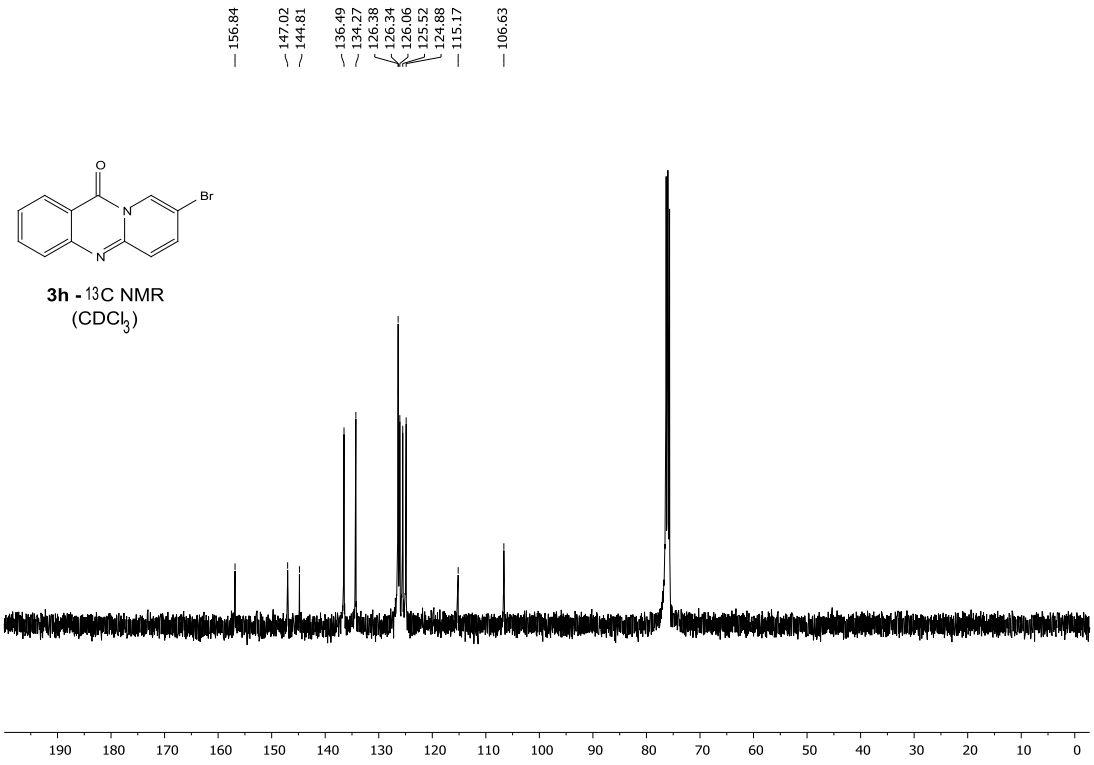



**Figure S56.** $^{13}$C NMR spectrum of **3h**

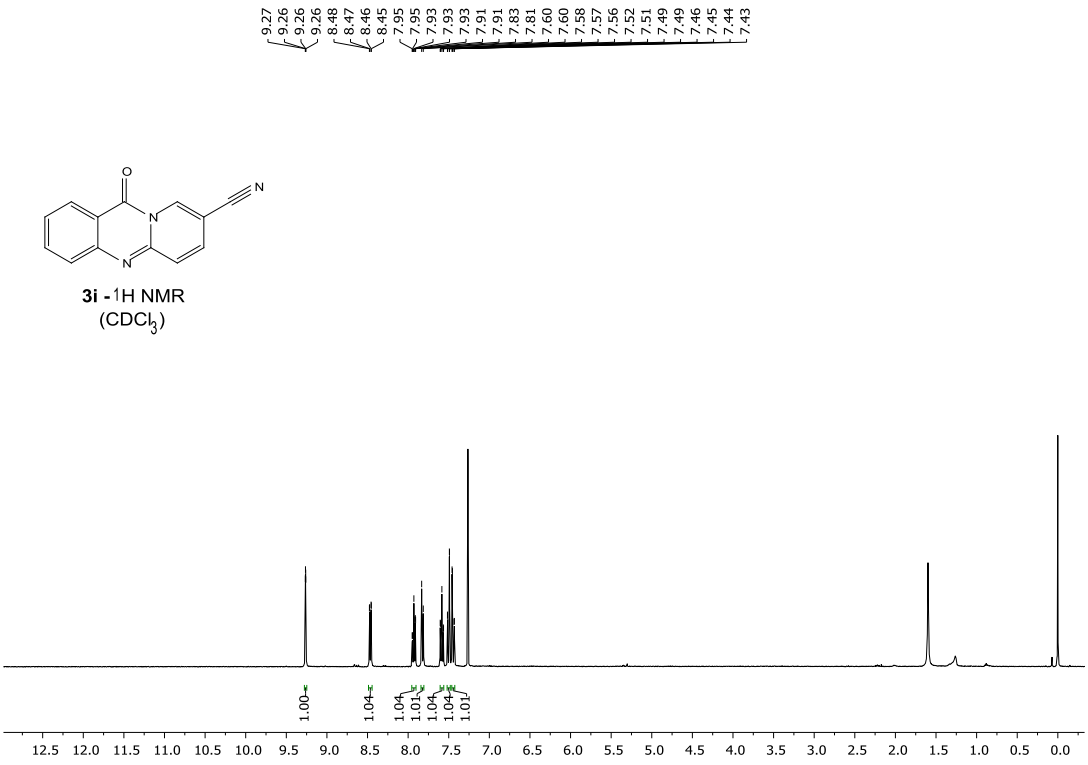



**Figure S57.** $^{1}$H NMR spectrum of **3i**

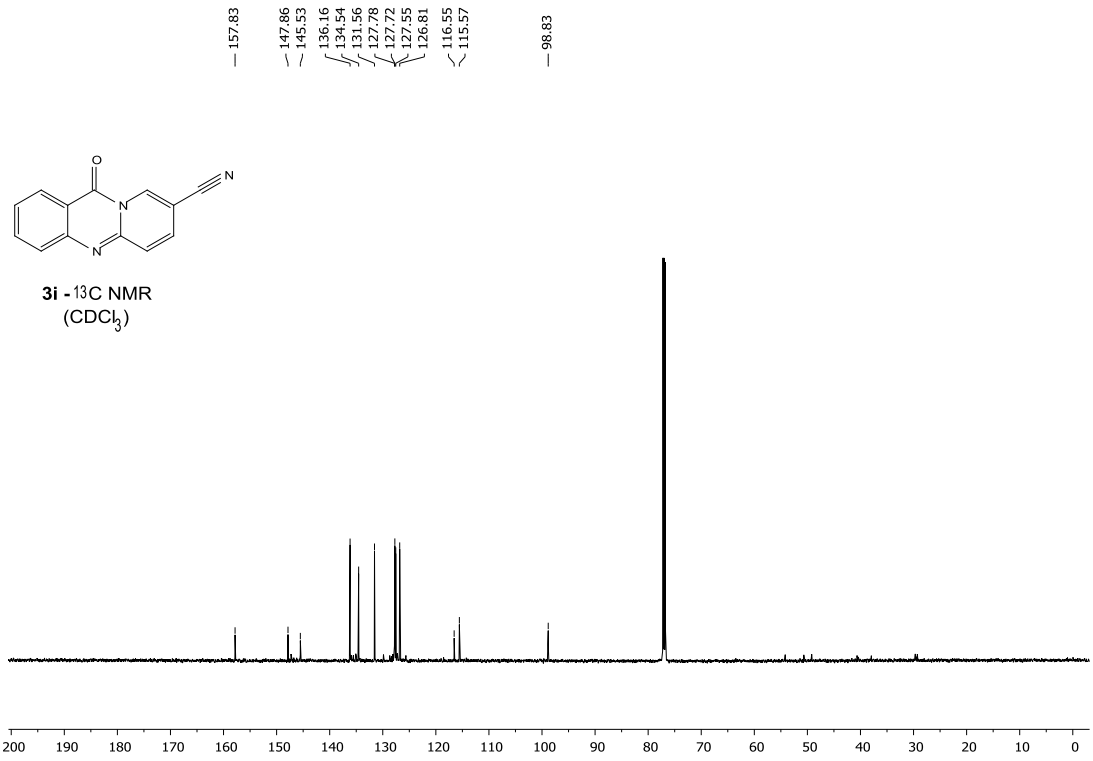



**Figure S58.** $^{13}$C NMR spectrum of **3i**

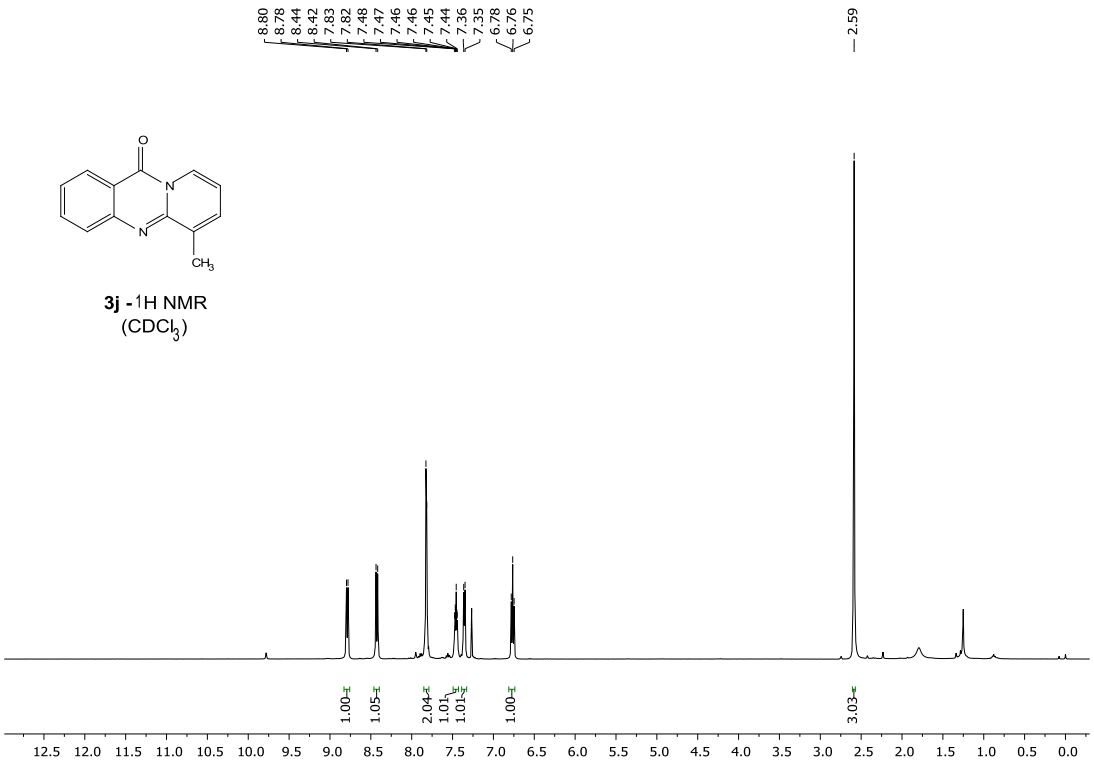



**Figure S59.** $^{1}$H NMR spectrum of **3j**

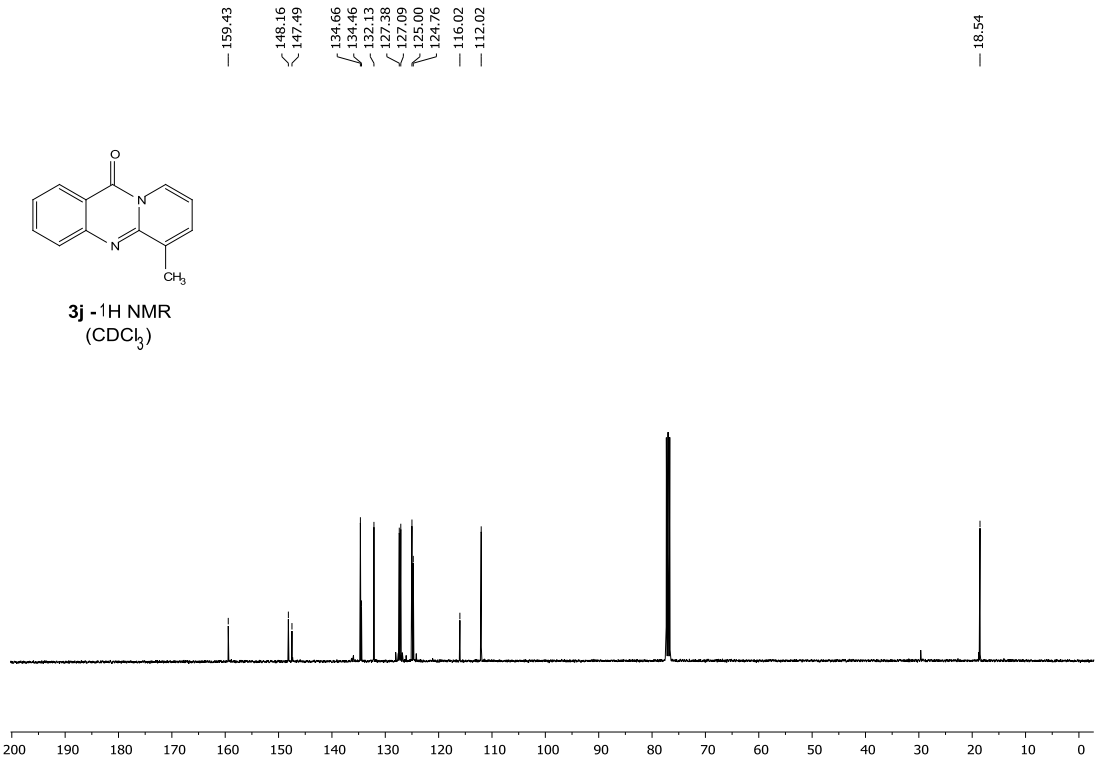



**Figure S60.** $^{13}$C NMR spectrum of **3j**

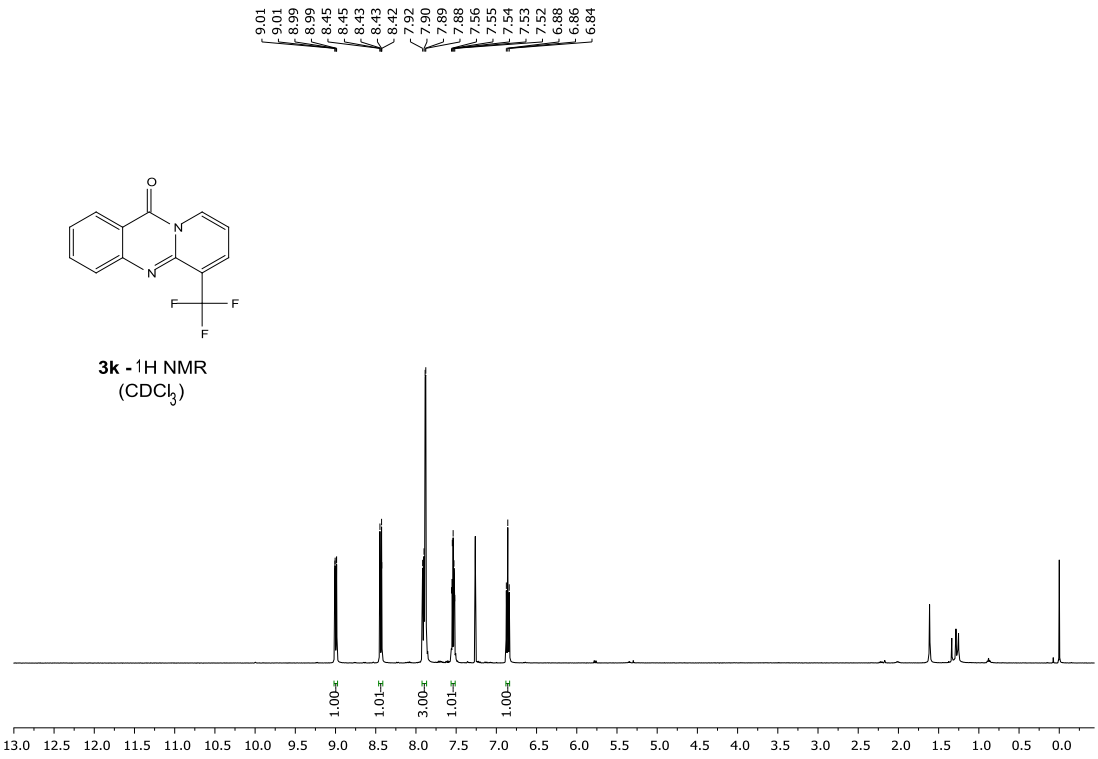



**Figure S61.** $^{1}$H NMR spectrum of **3k**

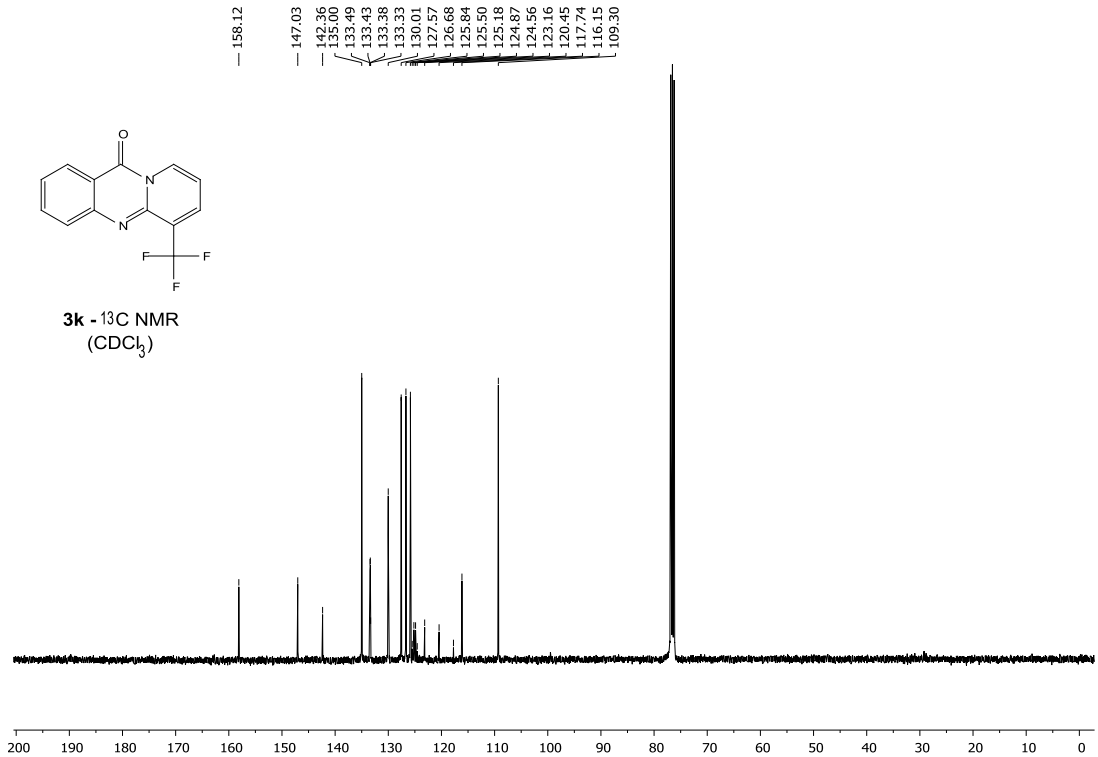



**Figure S62.** $^{13}$C NMR spectrum of **3k**

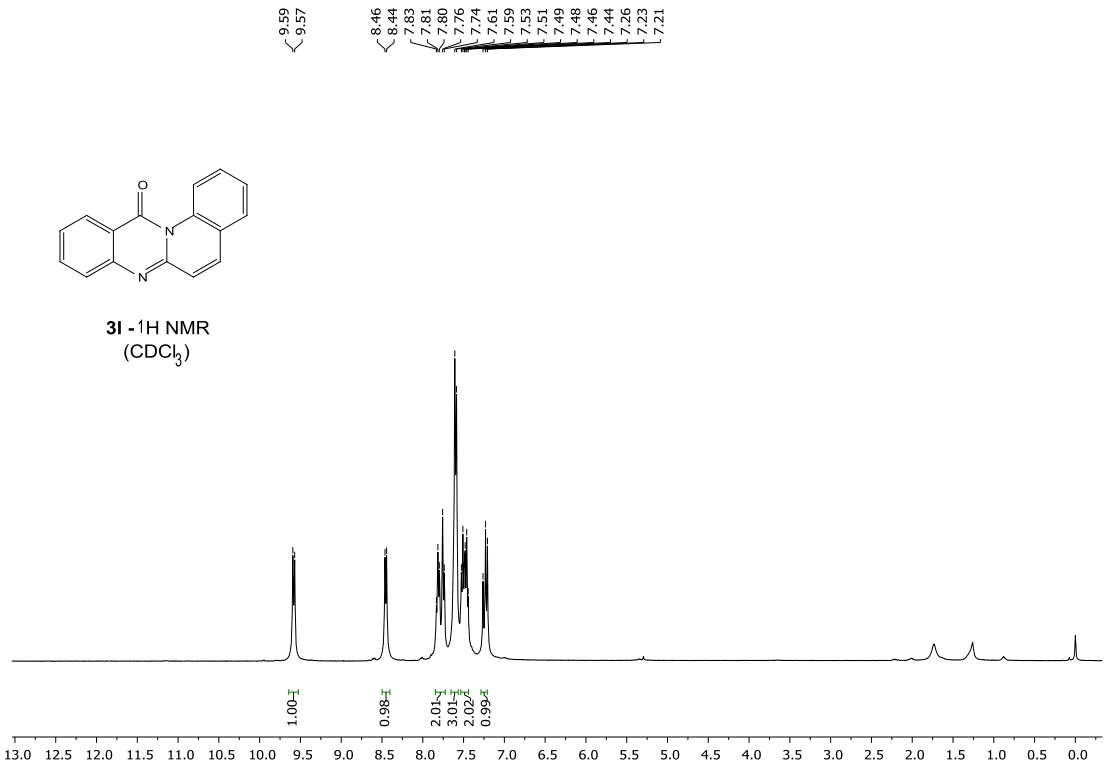



**Figure S63.** $^{1}$H NMR spectrum of **3l**

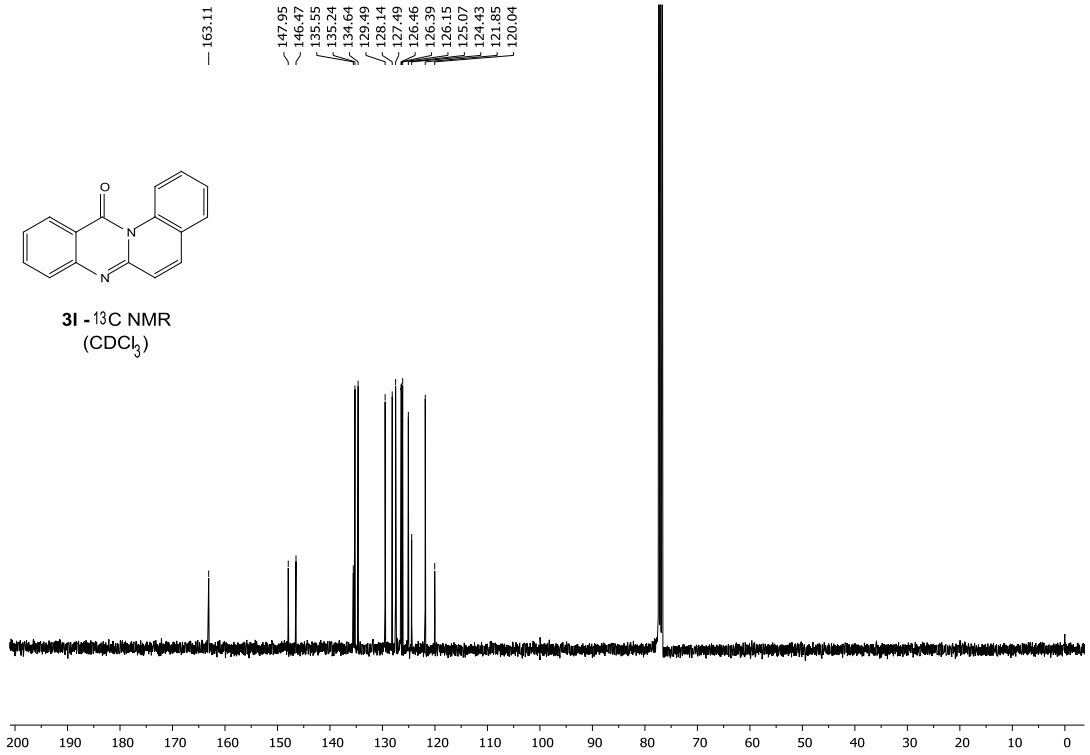



**Figure S64.** $^{13}$C NMR spectrum of **3l**

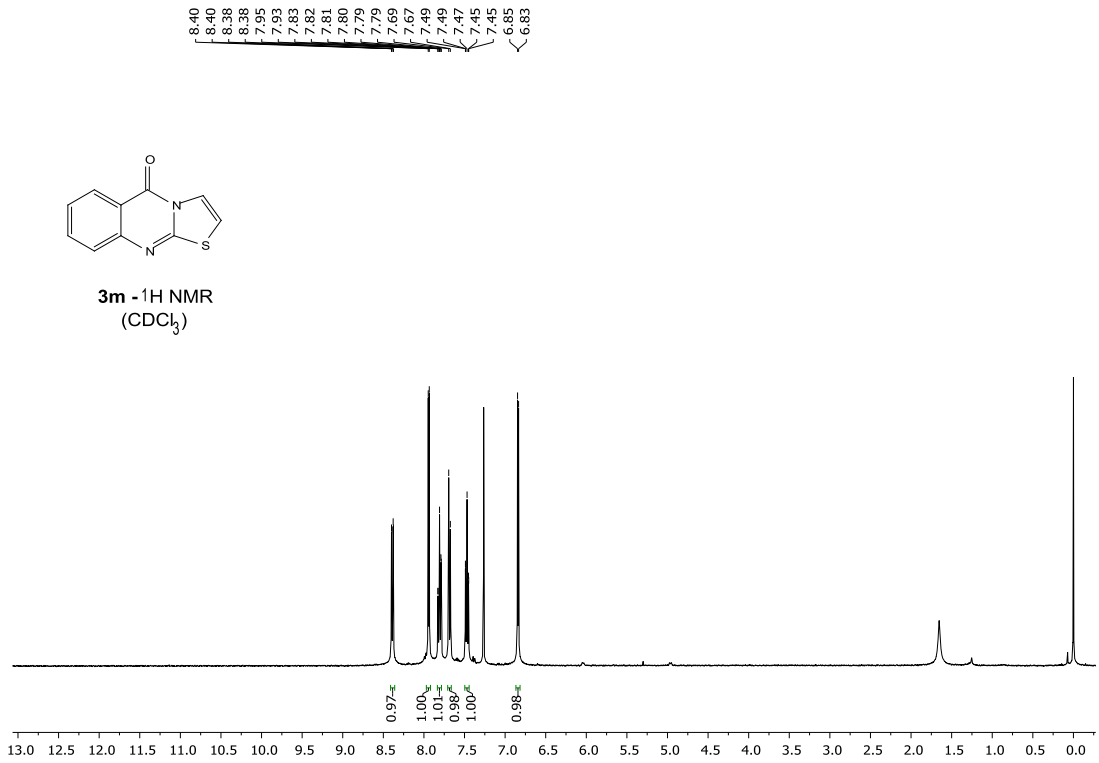



**Figure S65.** $^{1}$H NMR spectrum of **3m**

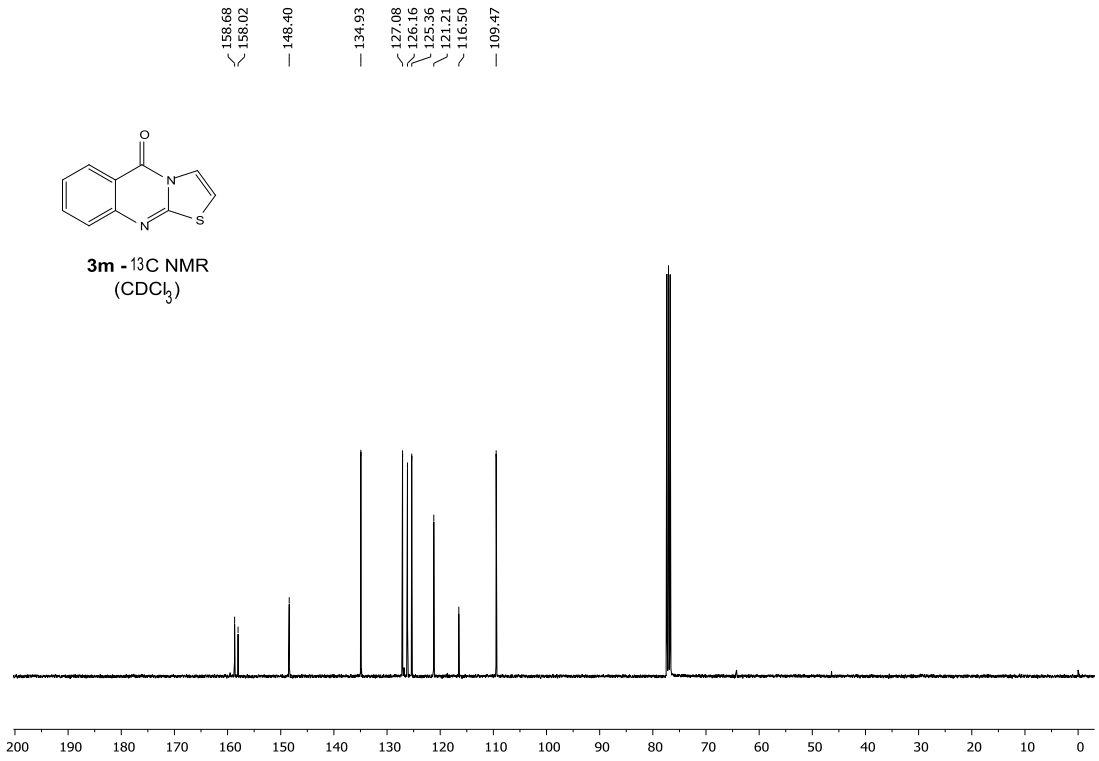



**Figure S66.** $^{13}$C NMR spectrum of **3m**

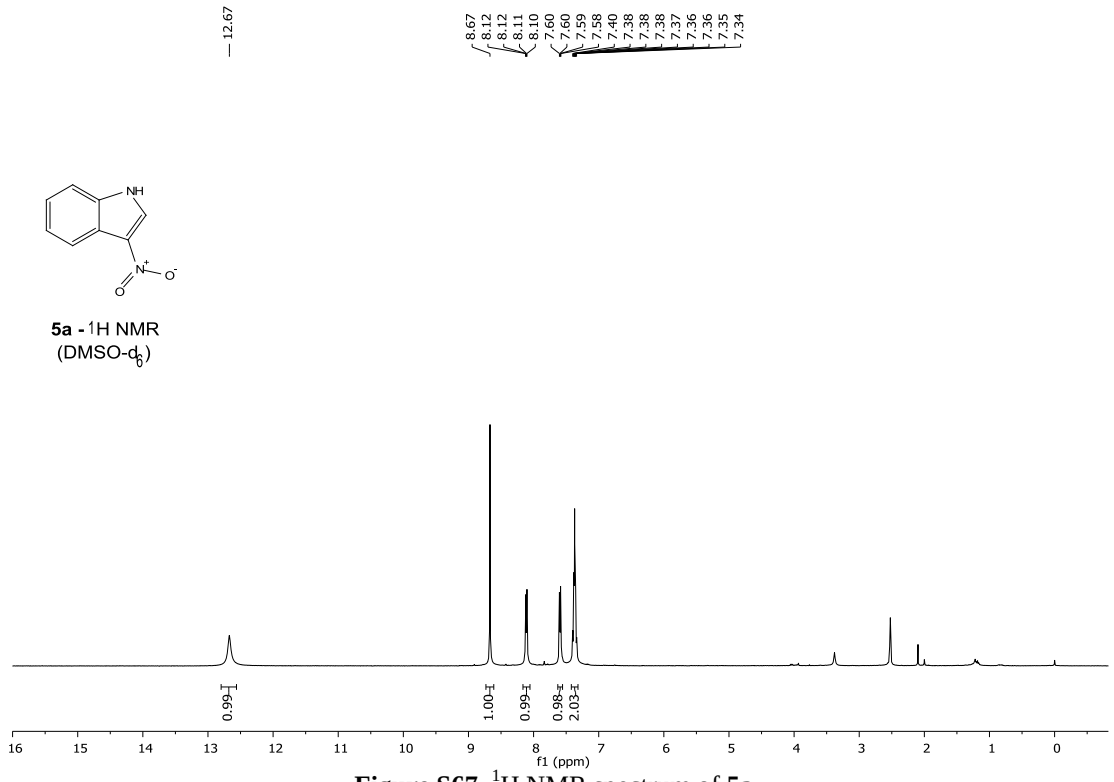



**Figure S67.** $^{1}$H NMR spectrum of **5a**

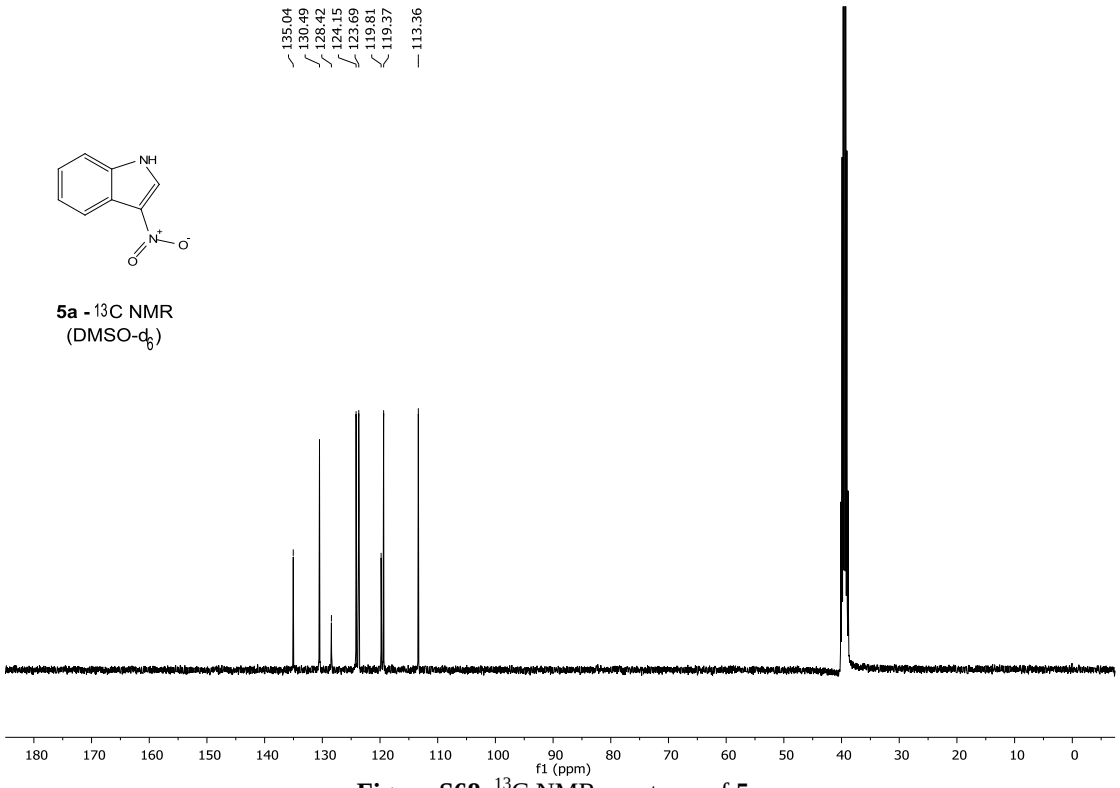



**Figure S68.** $^{13}$C NMR spectrum of **5a**

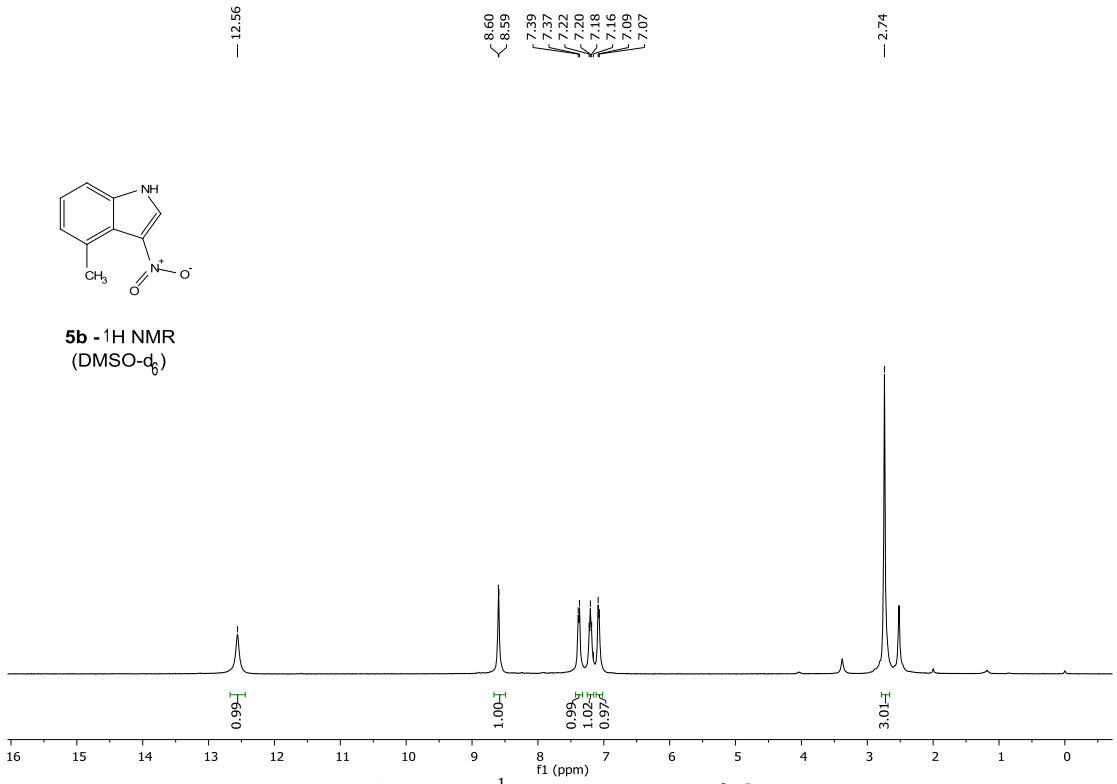



**Figure S69.** $^{1}$H NMR spectrum of **5b**

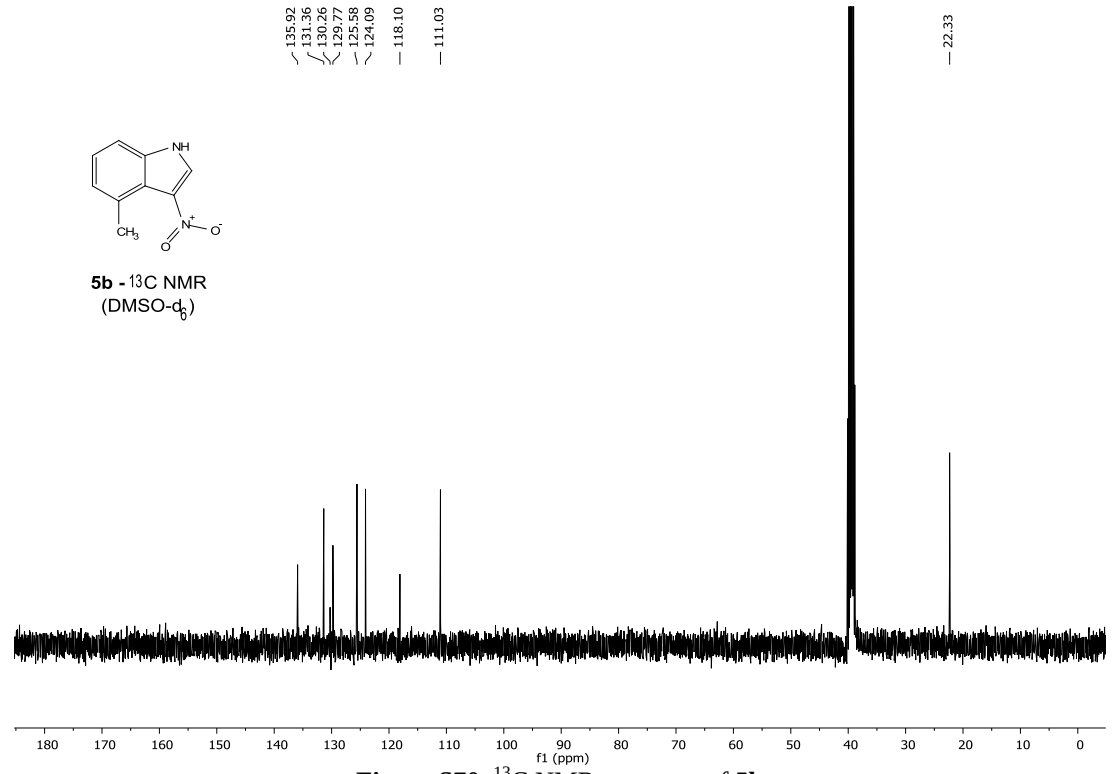



**Figure S70.** $^{13}$C NMR spectrum of **5b**

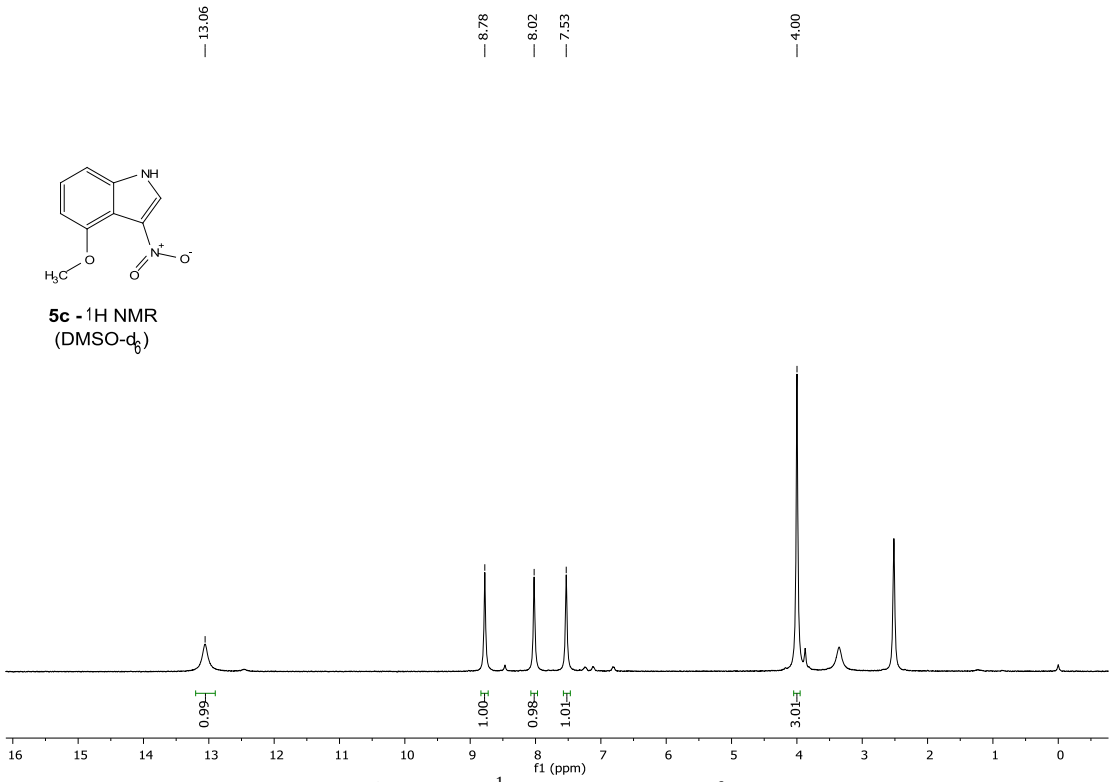



**Figure S71.** $^{1}$H NMR spectrum of **5c**

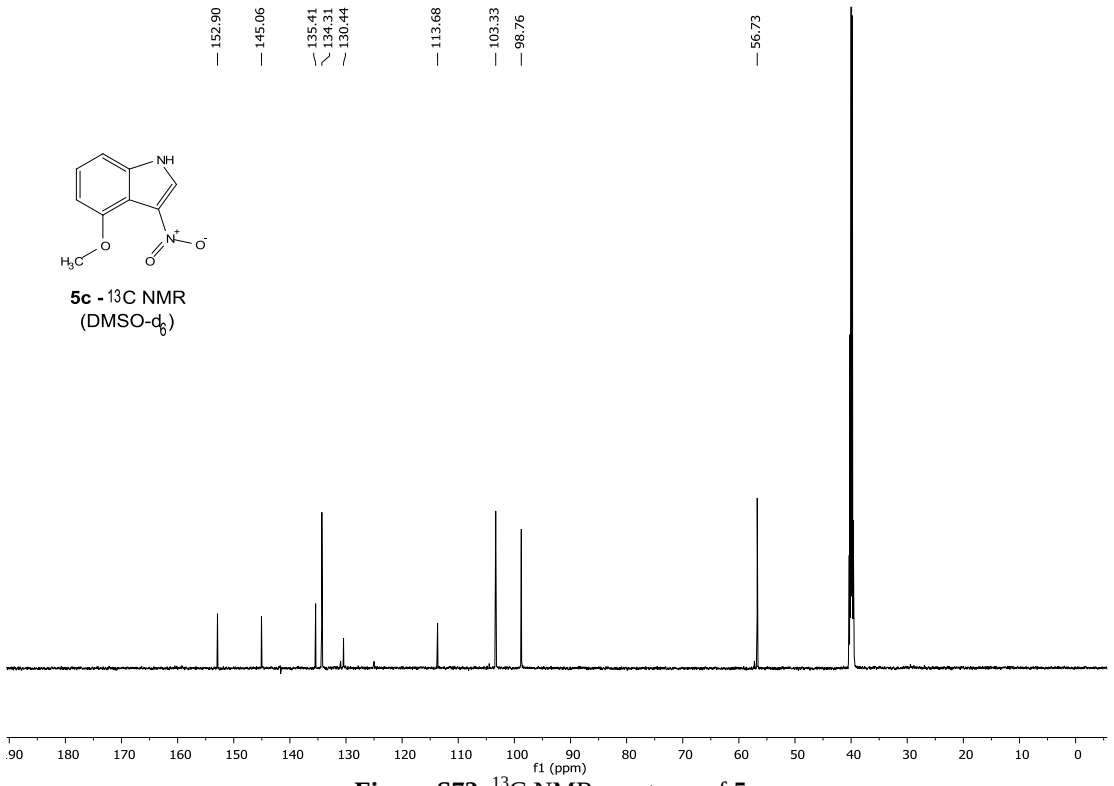



**Figure S72.** $^{13}$C NMR spectrum of **5c**

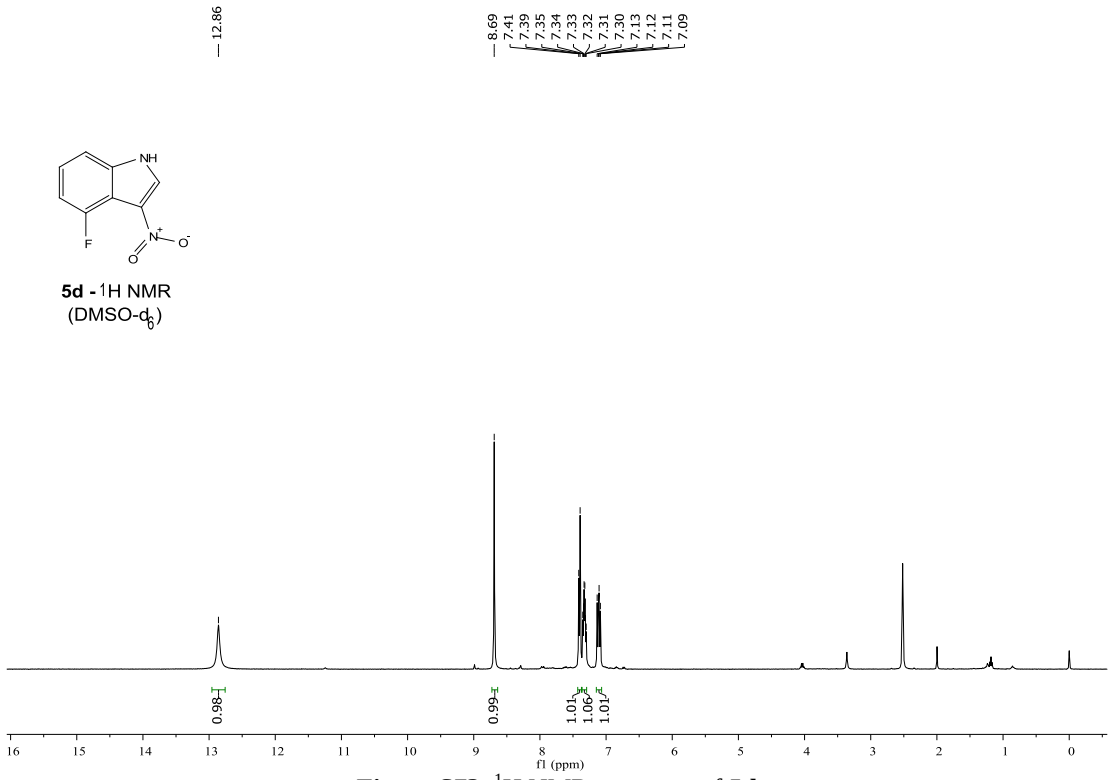



**Figure S73.** $^{1}$H NMR spectrum of **5d**

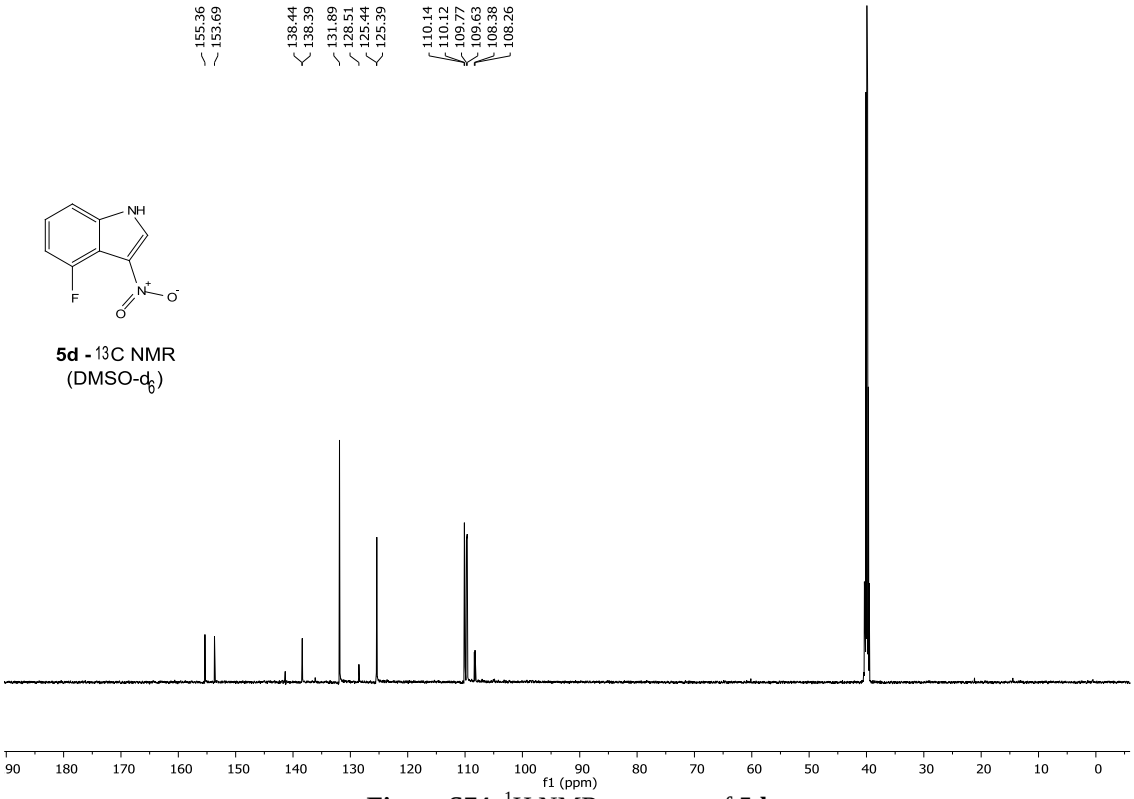



**Figure S74.** $^{1}$H NMR spectrum of **5d**

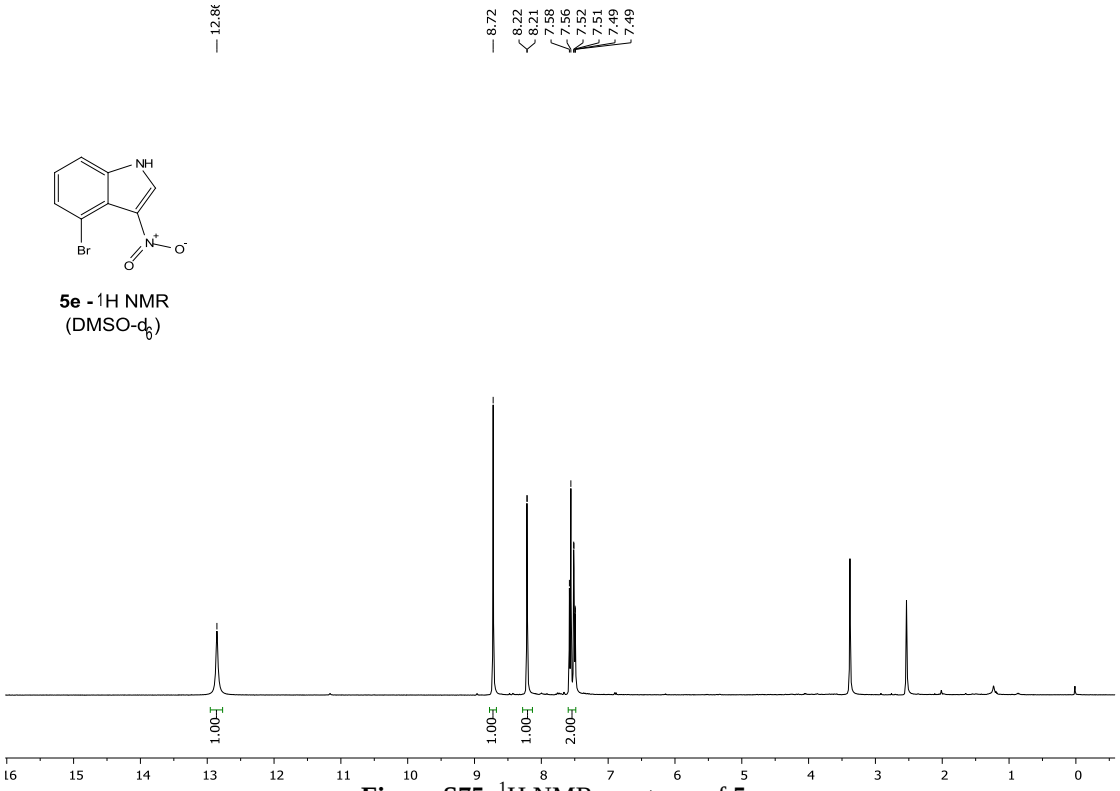



**Figure S75.** $^{1}$H NMR spectrum of **5e**

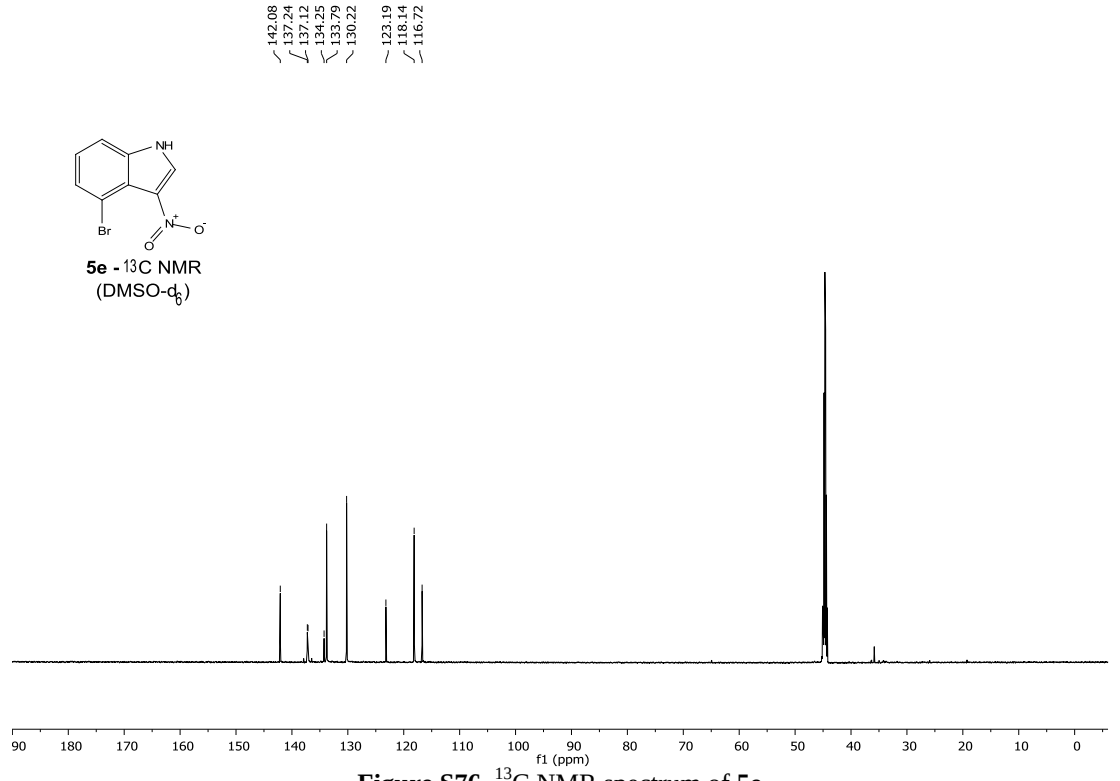



**Figure S76.** $^{13}$C NMR spectrum of **5e**

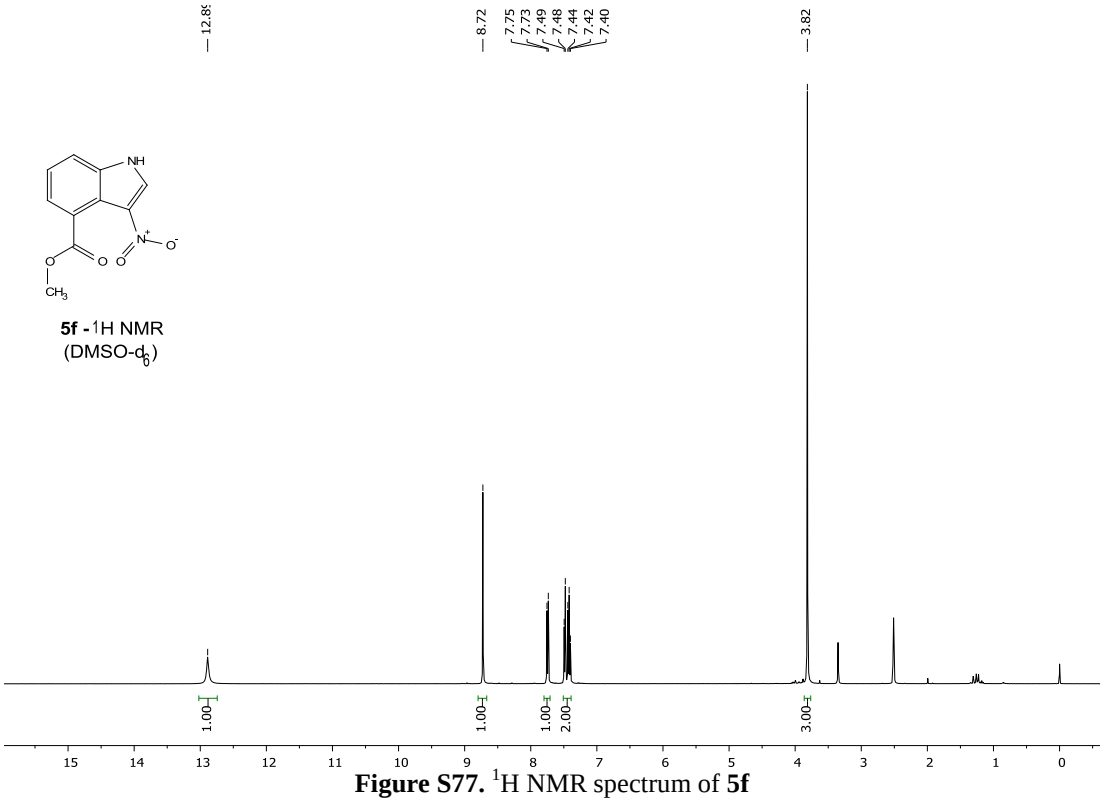



**Figure S77.** $^{1}$H NMR spectrum of **5f**

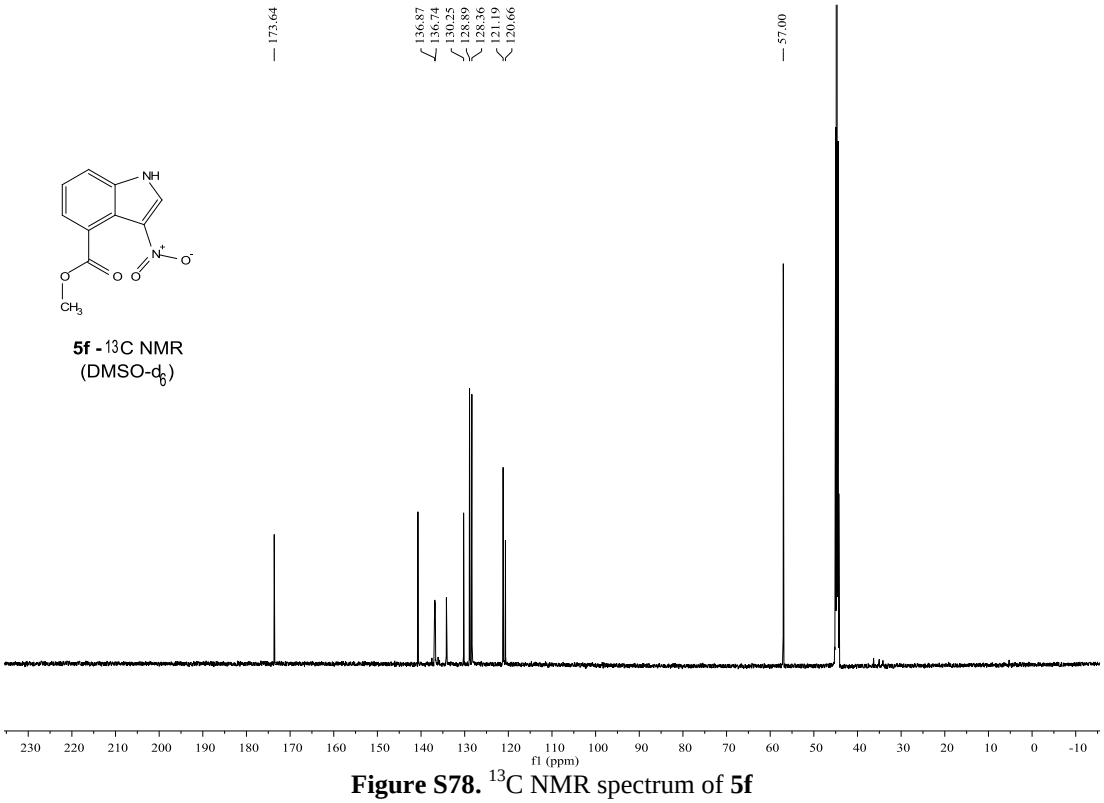



**Figure S78.** $^{13}$C NMR spectrum of **5f**

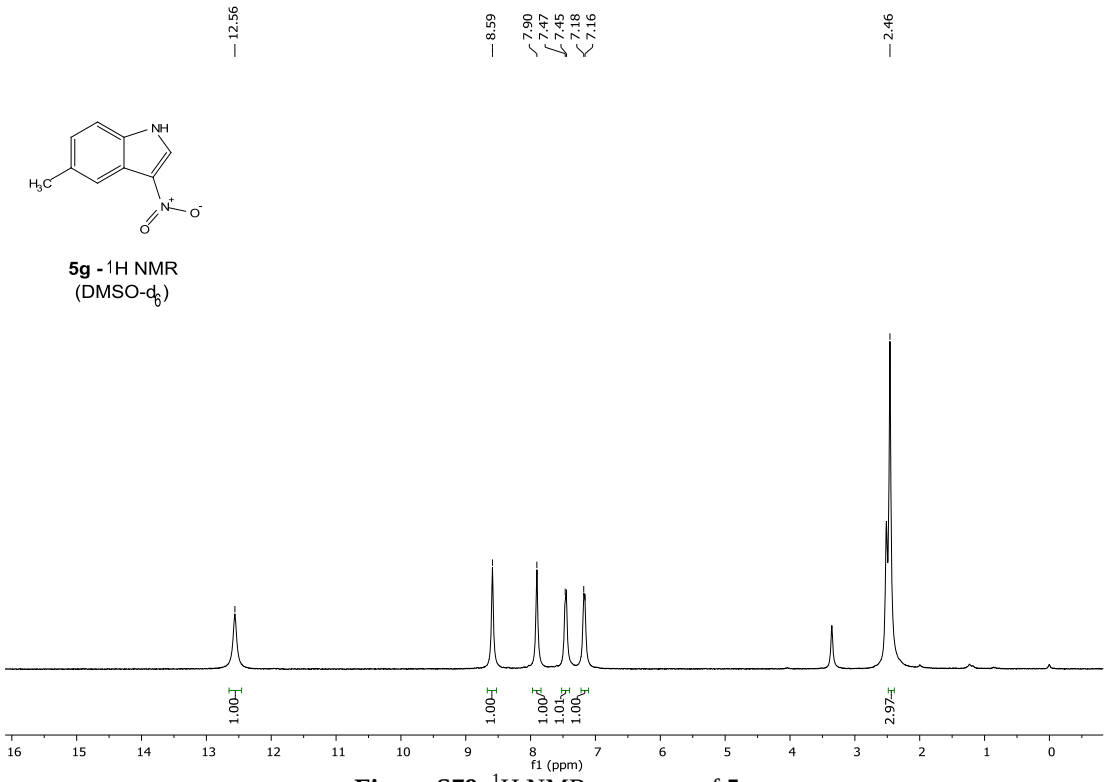



**Figure S79.** $^{1}$H NMR spectrum of **5g**

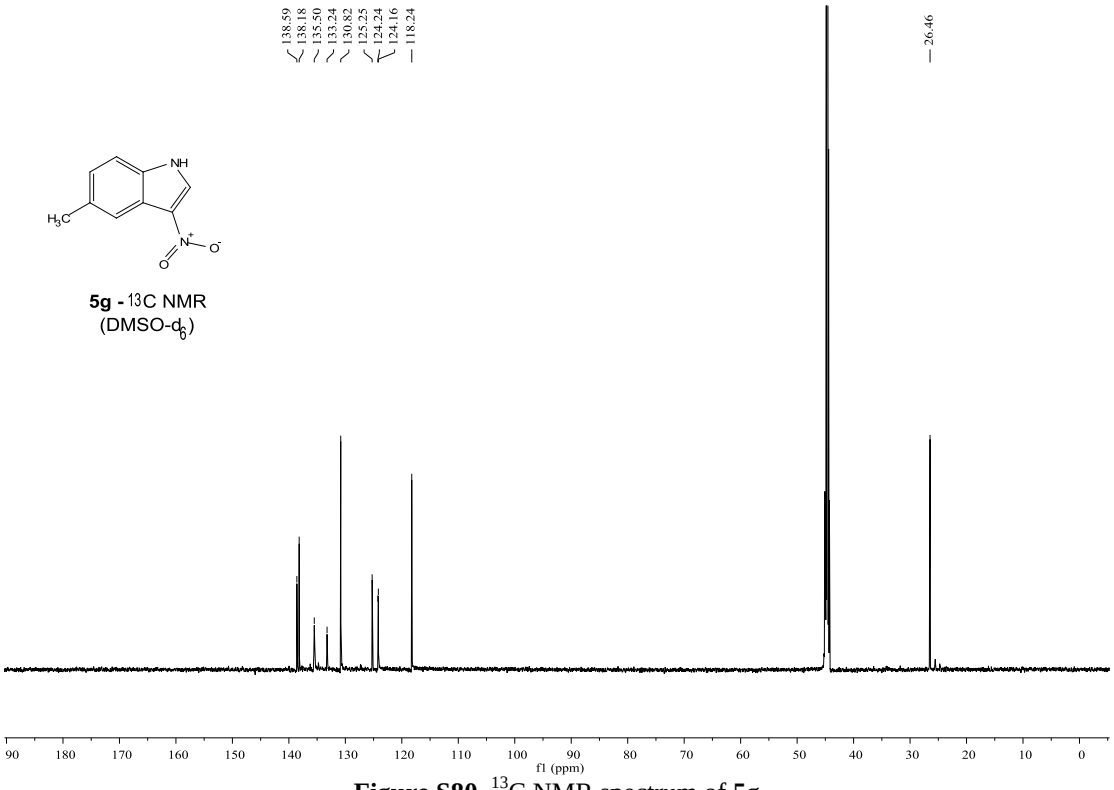



**Figure S80.** $^{13}$C NMR spectrum of **5g**

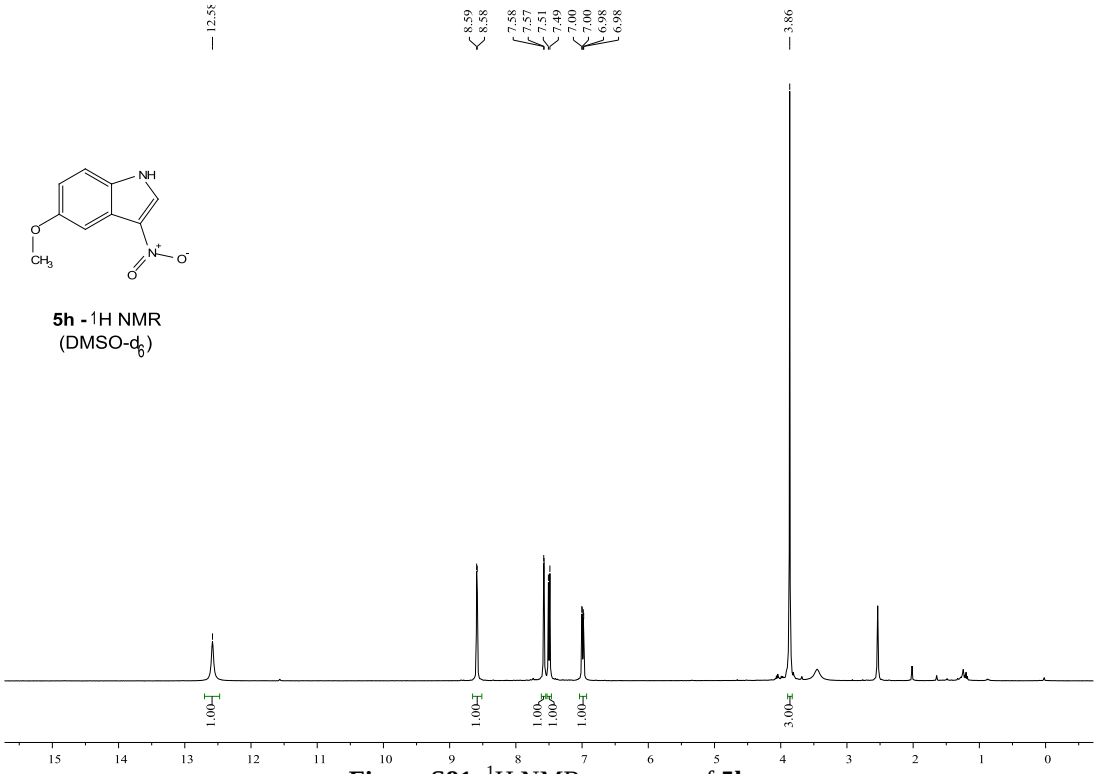



**Figure S81**. $^{1}$H NMR spectrum of **5h**

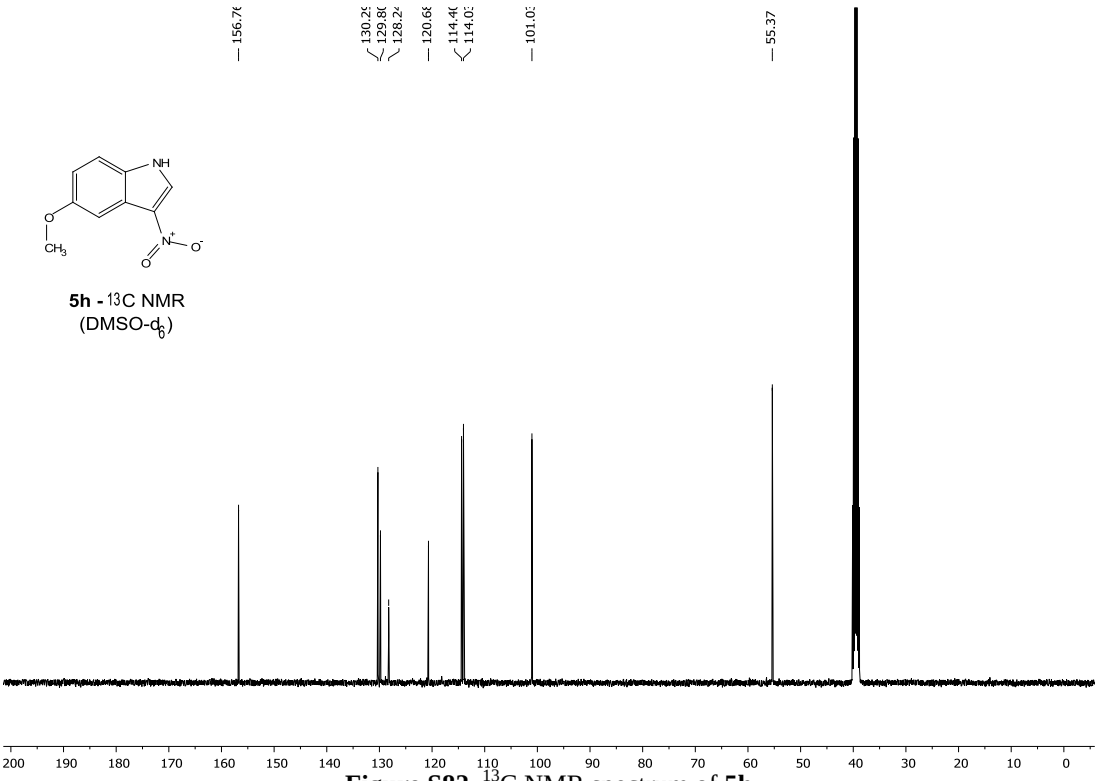



**Figure S82**. $^{13}$C NMR spectrum of **5h**

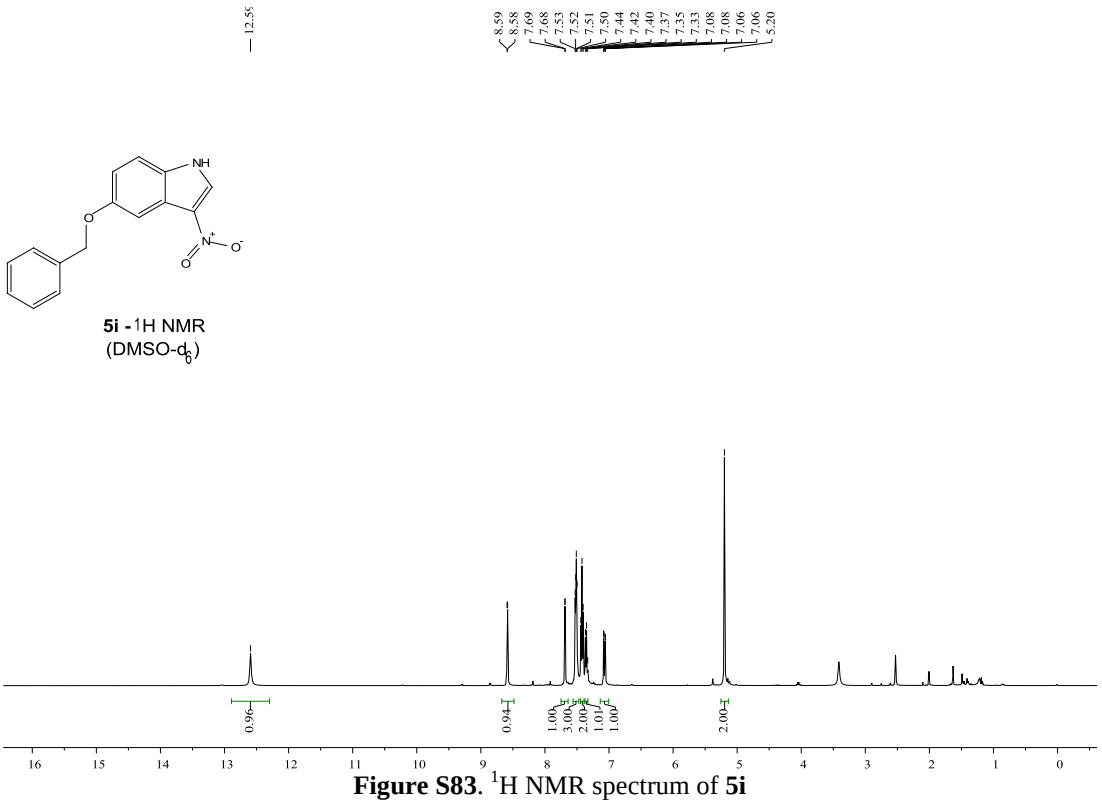



**Figure S83**. $^{1}$H NMR spectrum of **5i**

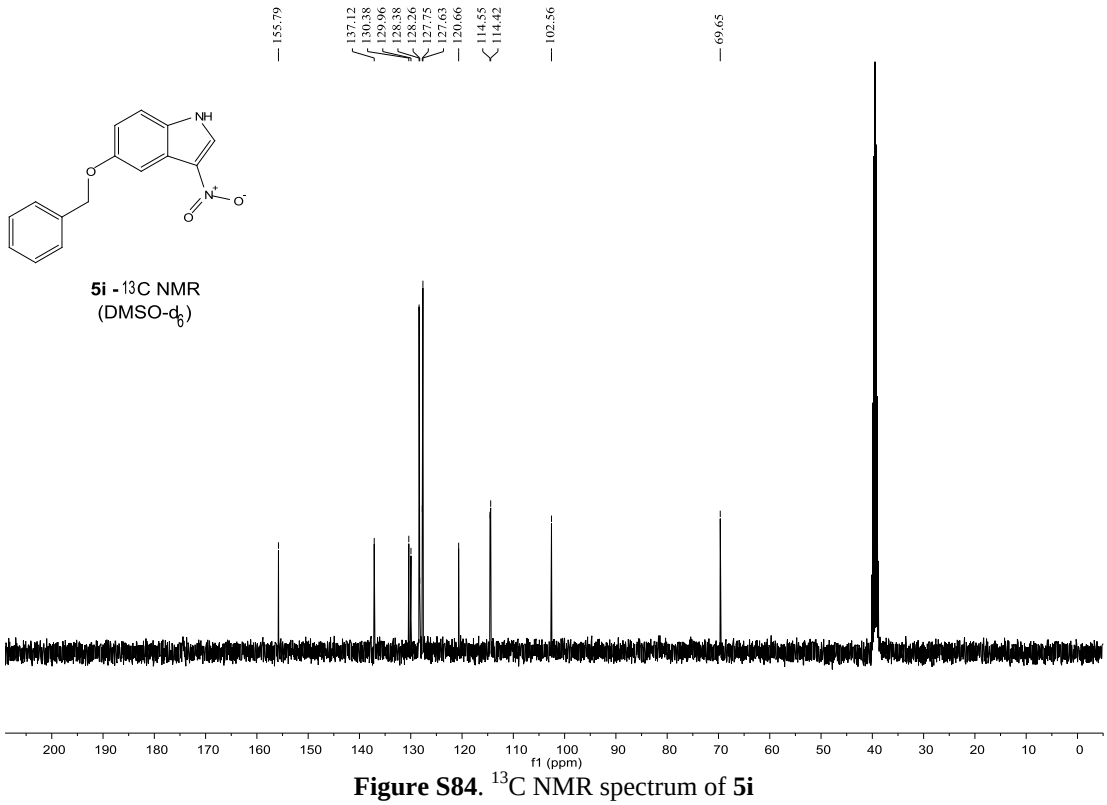



**Figure S84**. $^{13}$C NMR spectrum of **5i**

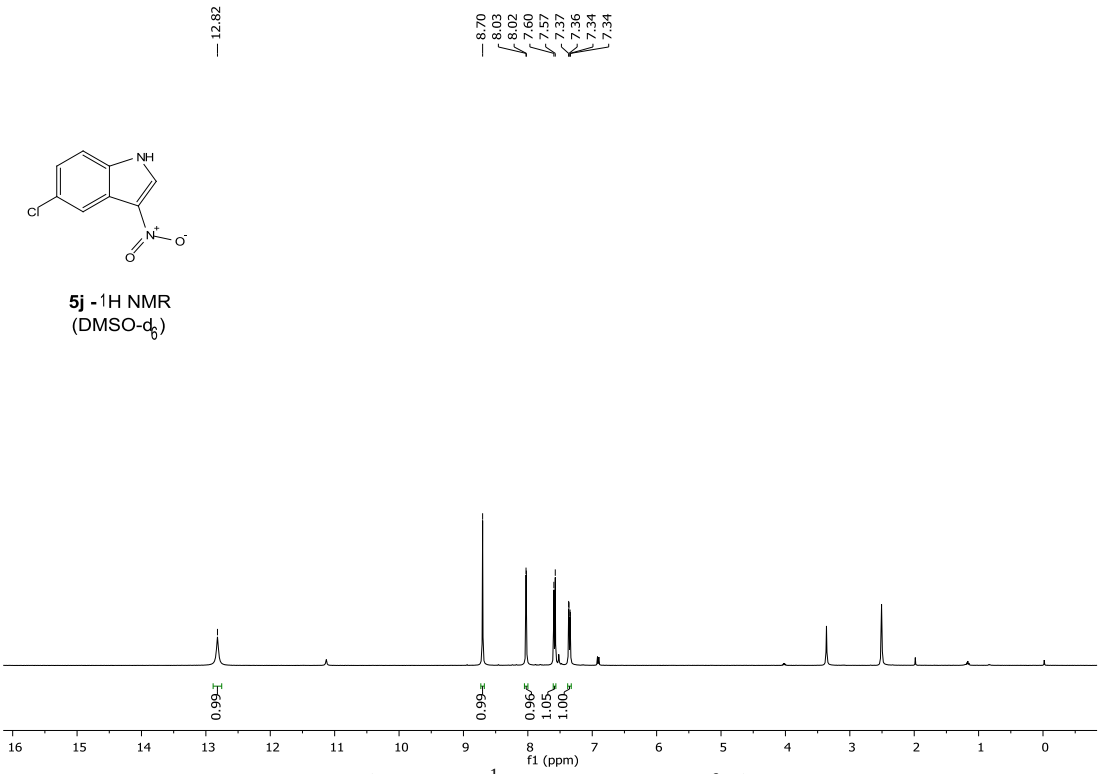



**Figure S85**. $^{1}$H NMR spectrum of **5j**

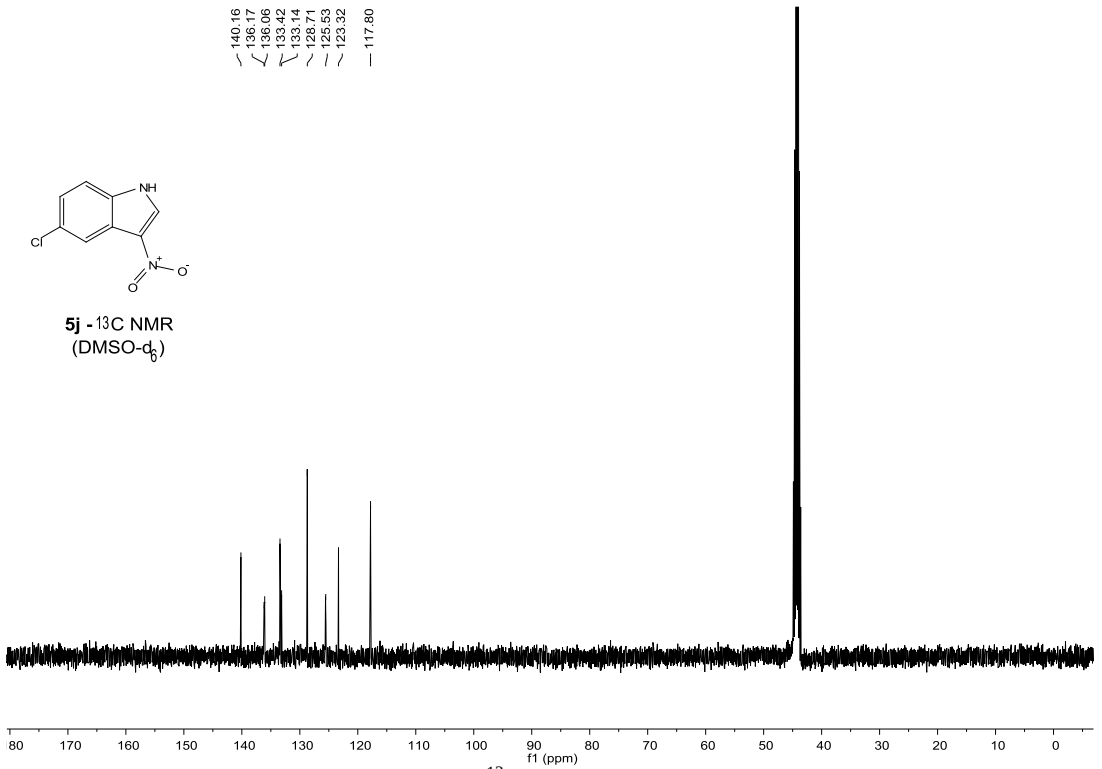



**Figure S86**. $^{13}$C NMR spectrum of **5j**

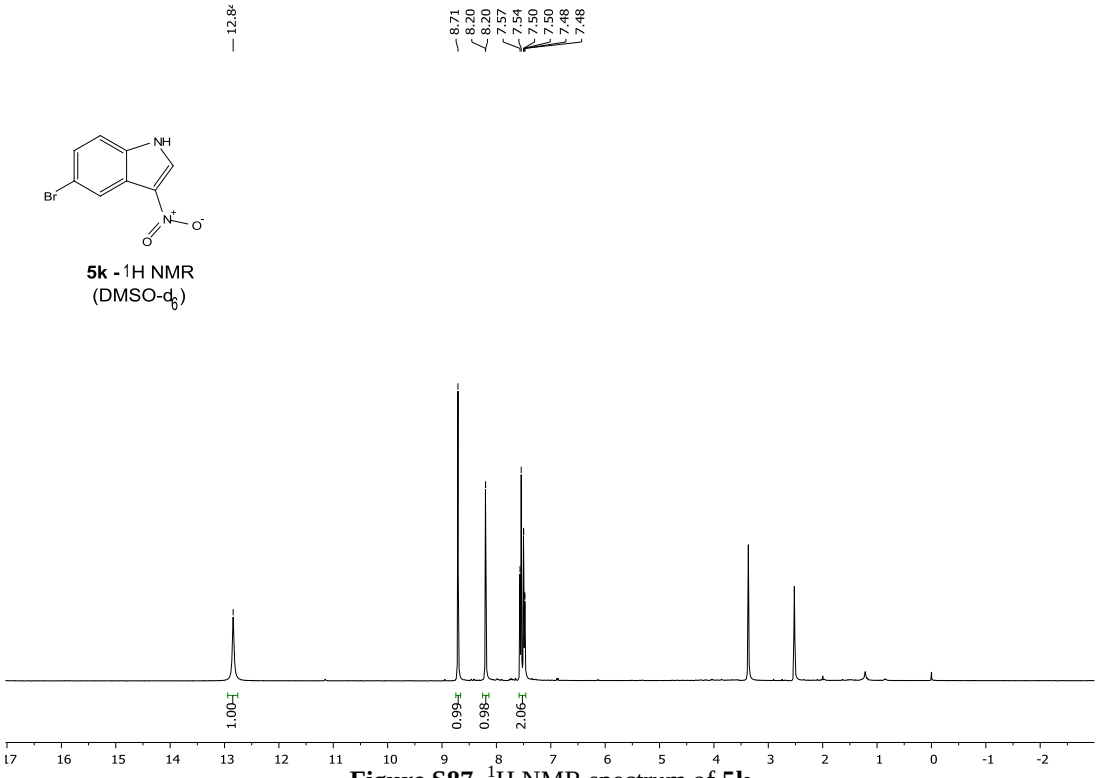



**Figure S87**. $^{1}$H NMR spectrum of **5k**

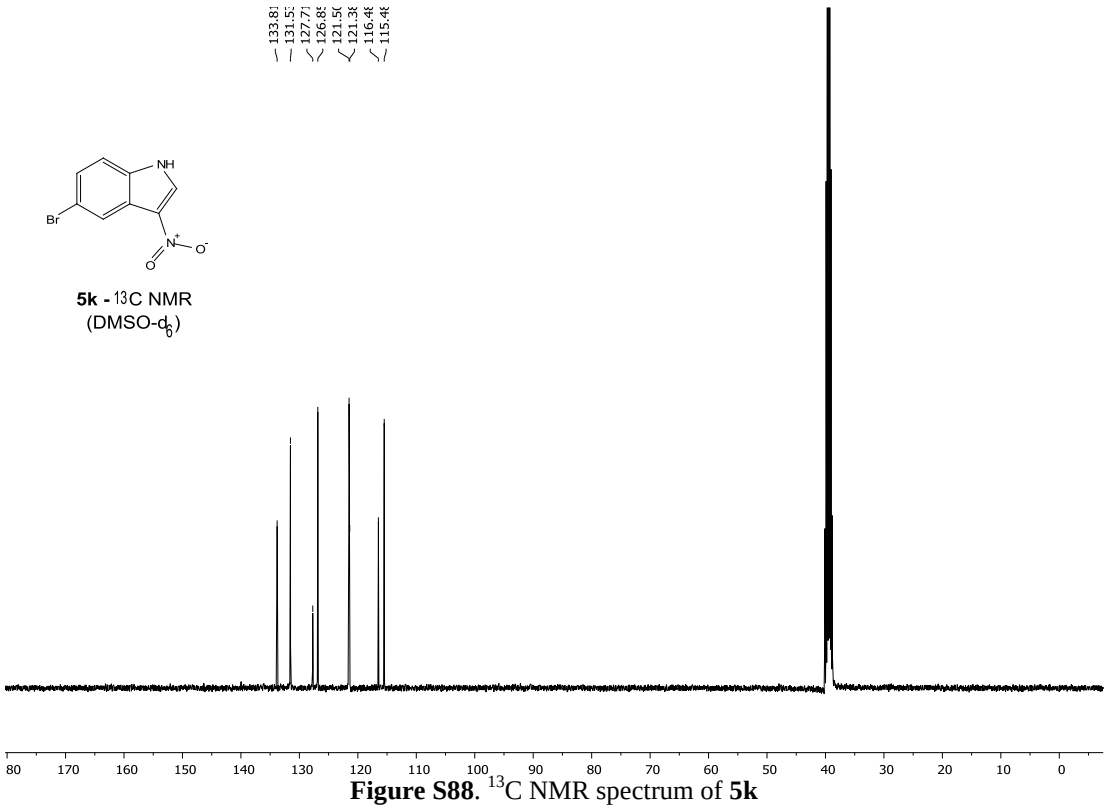



**Figure S88**. $^{13}$C NMR spectrum of **5k**

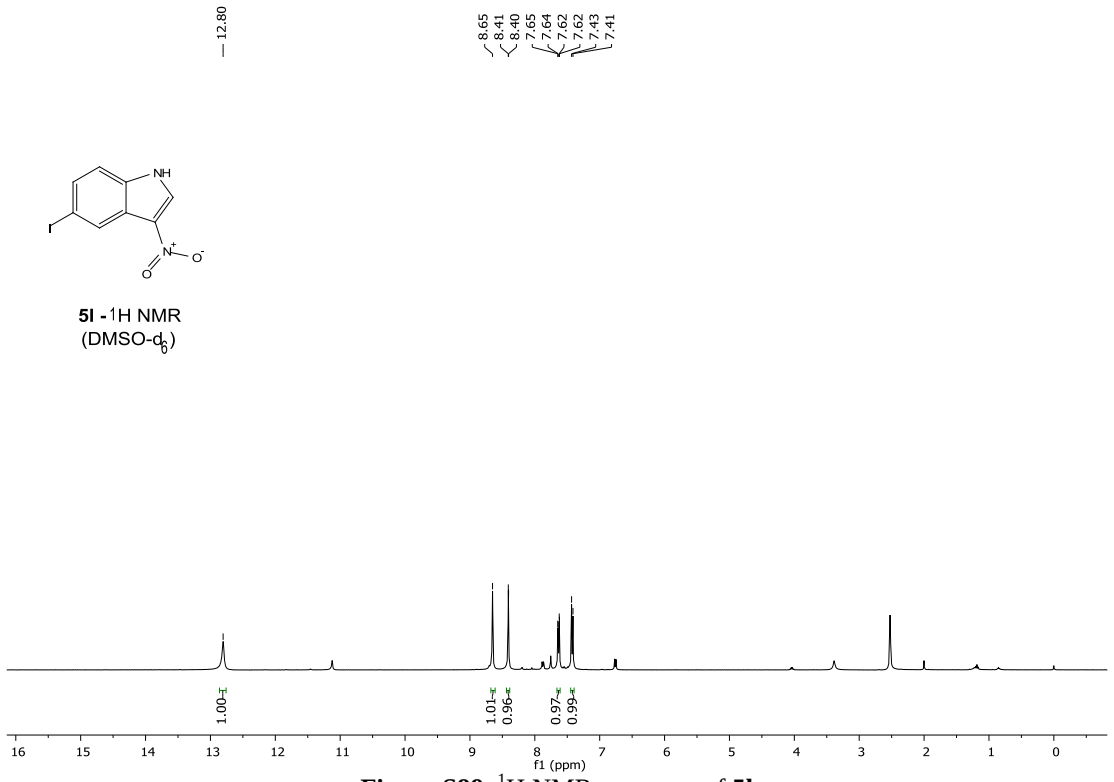



**Figure S89**. $^{1}$H NMR spectrum of **5l**

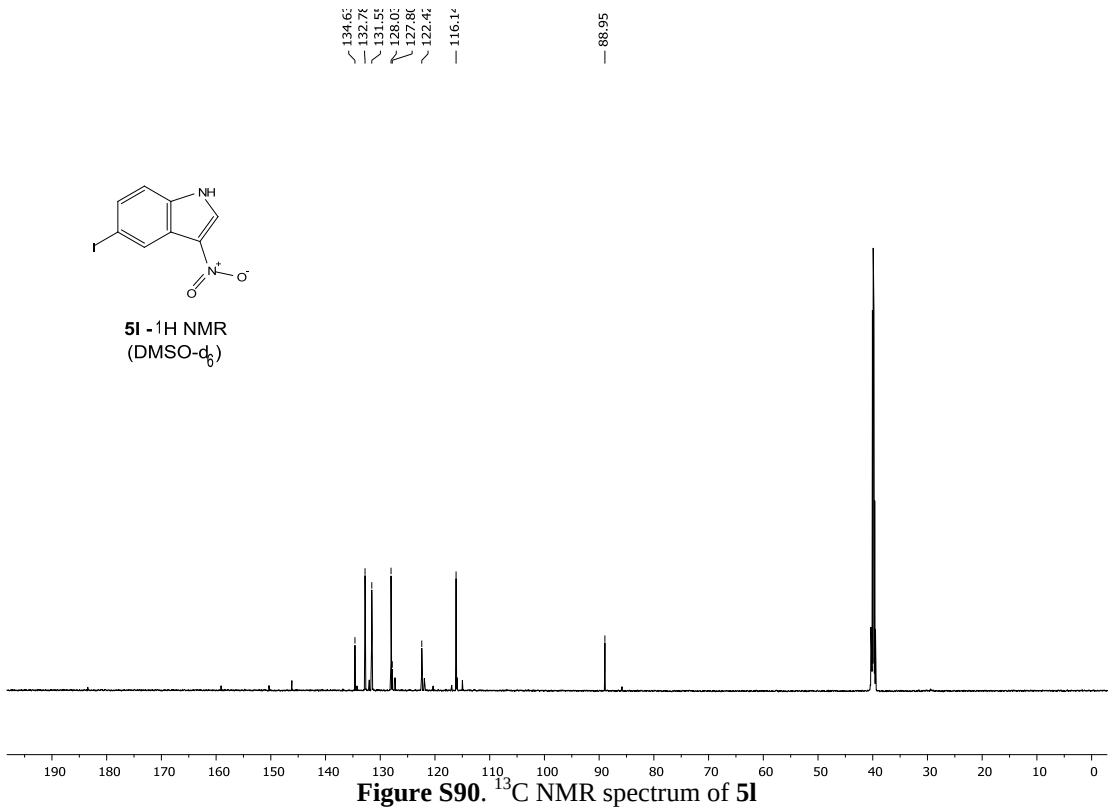



**Figure S90**. $^{13}$C NMR spectrum of **5l**

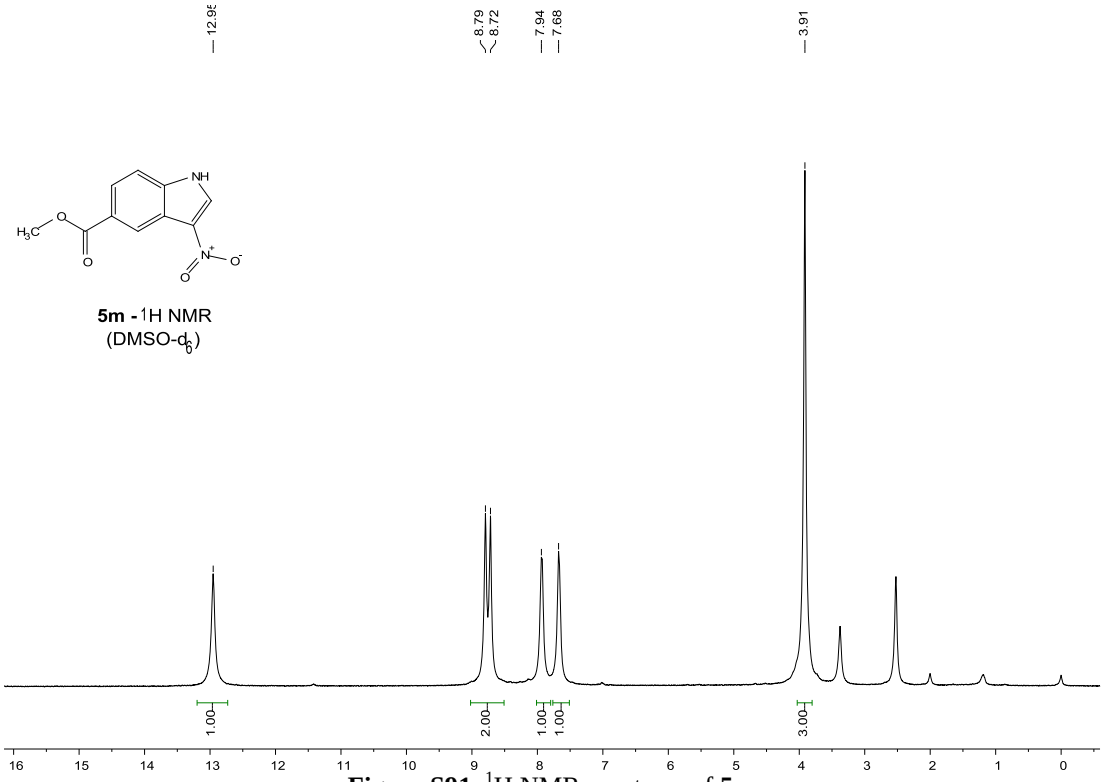



**Figure S91**. $^{1}$H NMR spectrum of **5m**

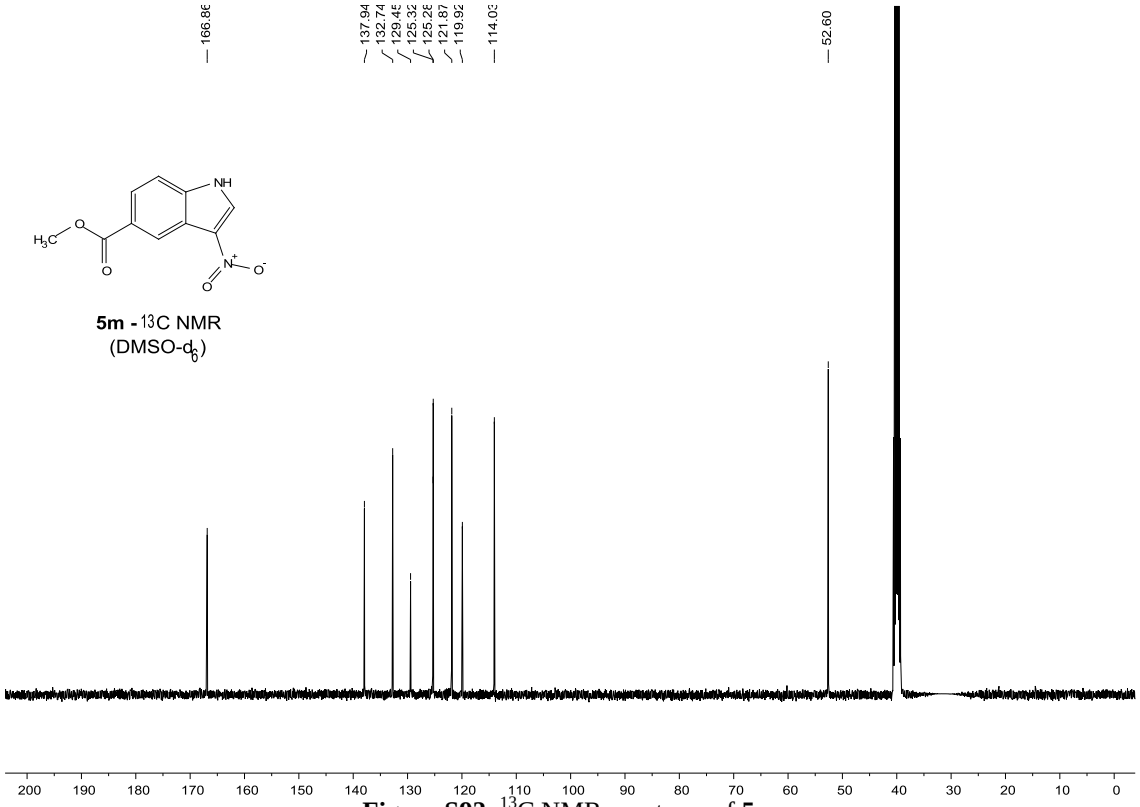



**Figure S92**. $^{13}$C NMR spectrum of **5m**

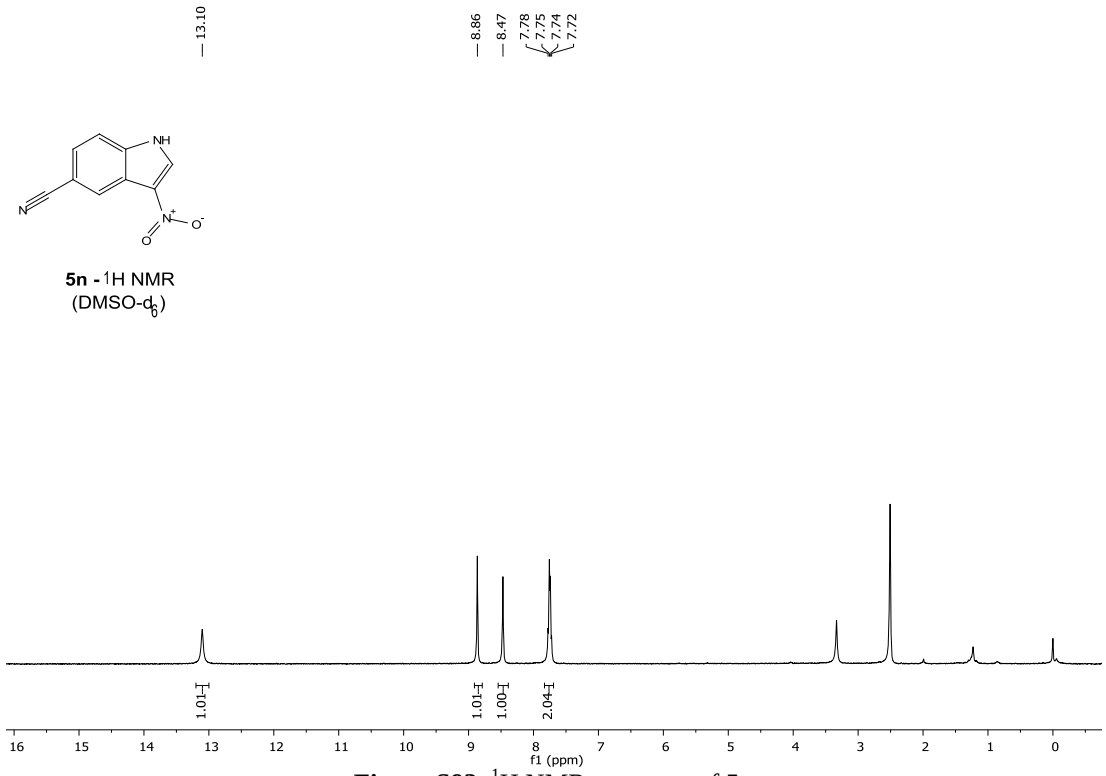



**Figure S93**. $^{1}$H NMR spectrum of **5n**

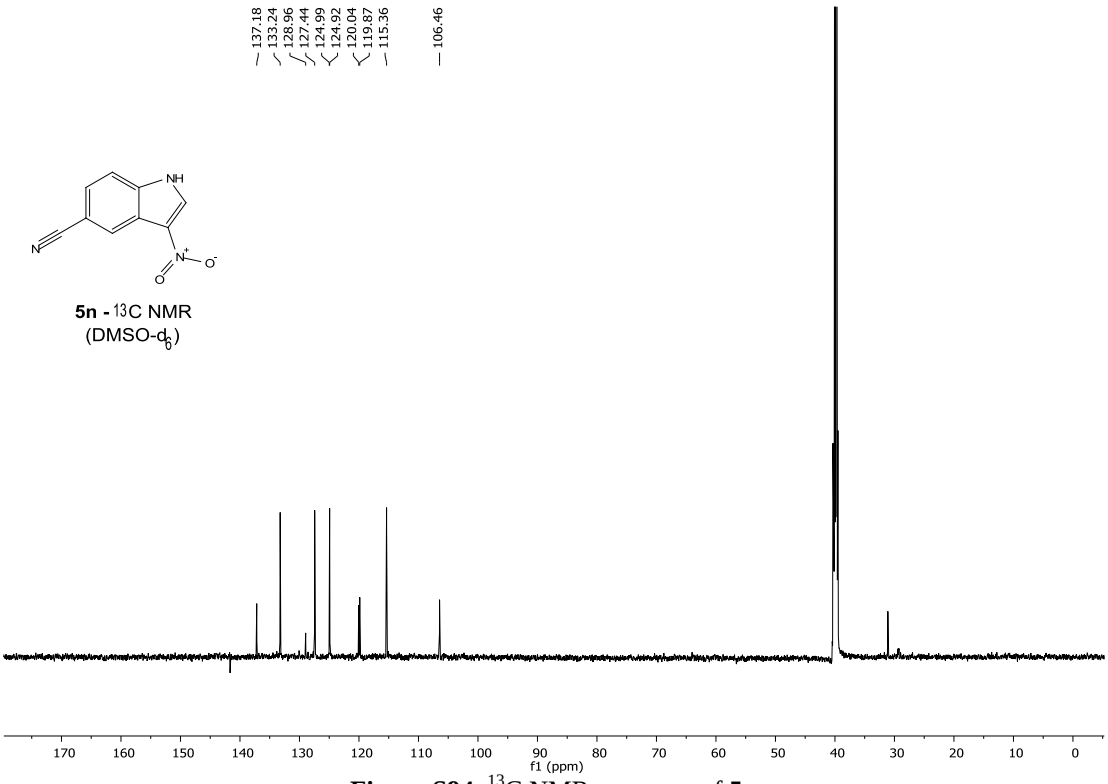



**Figure S94**. $^{13}$C NMR spectrum of **5n**

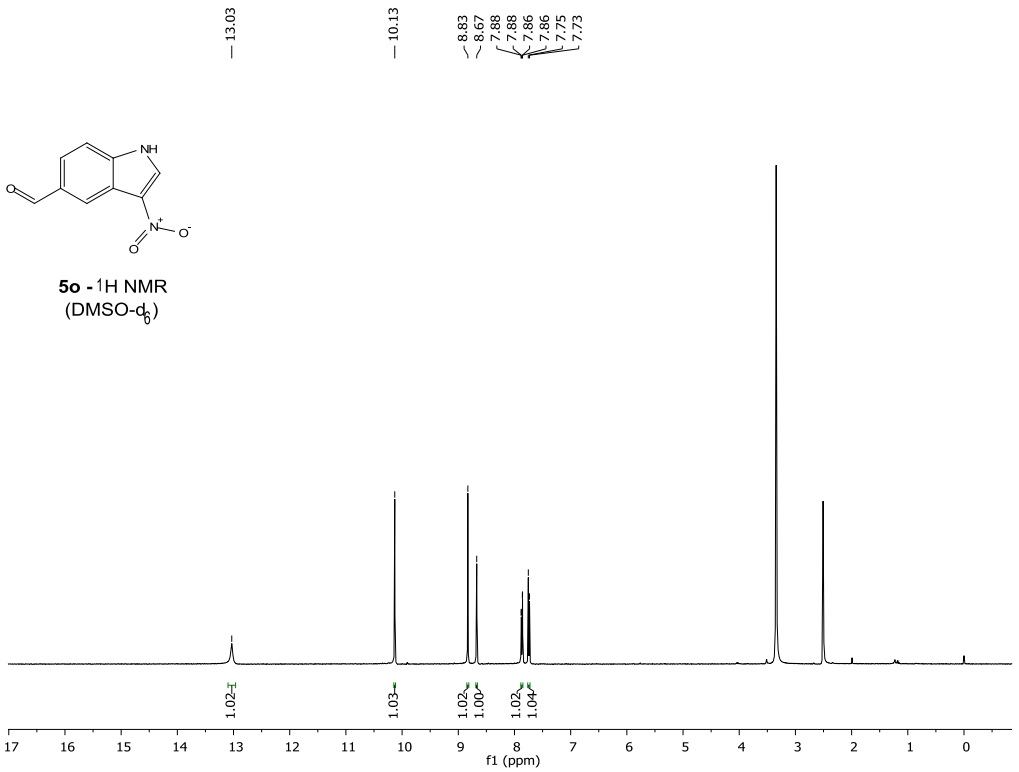



**Figure S95**. $^{1}$H NMR spectrum of **5o**

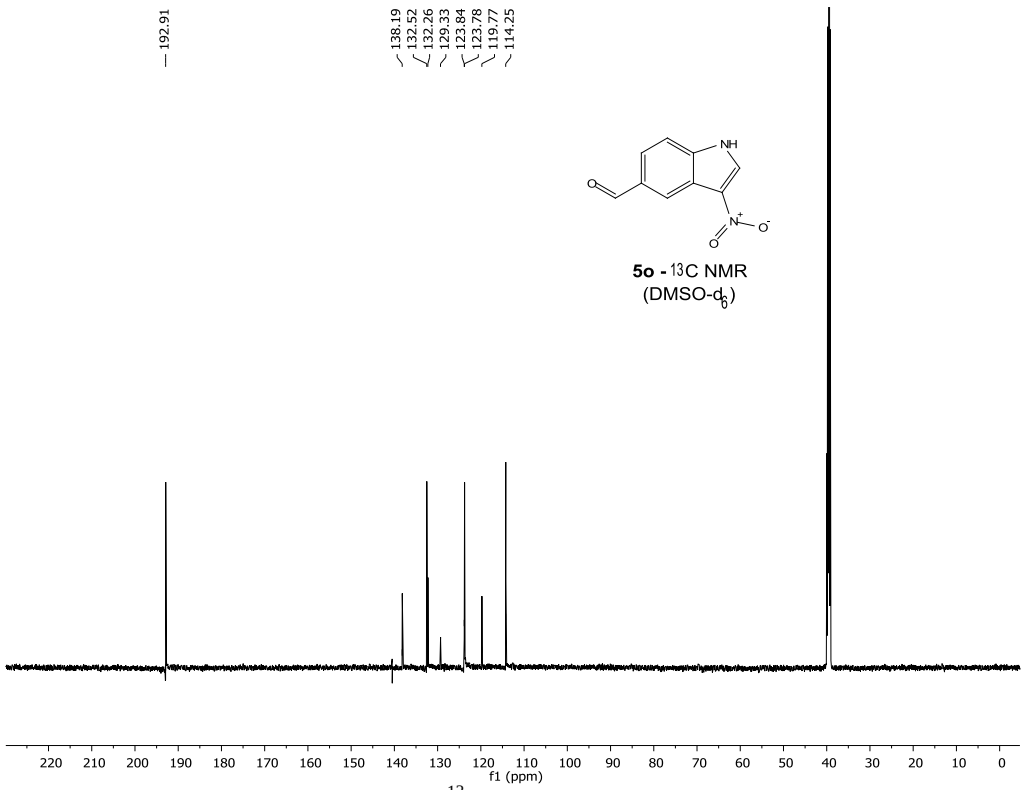



**Figure S96**. $^{13}$C NMR spectrum of **5o**

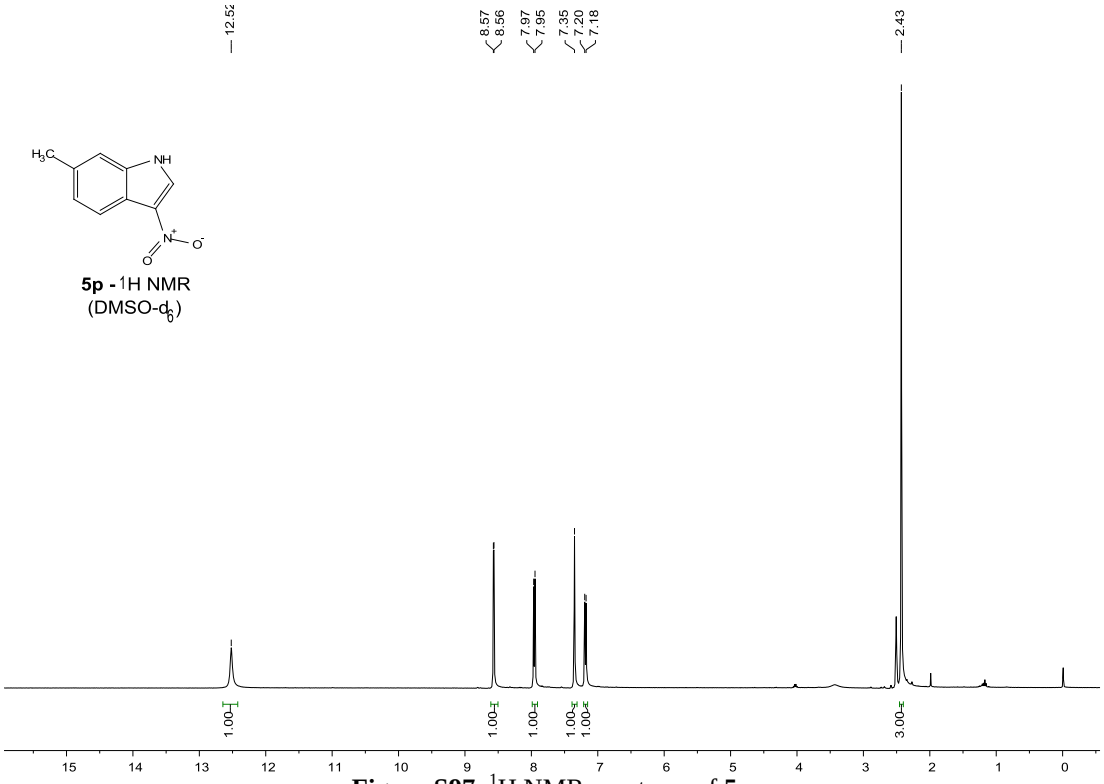



**Figure S97**. $^{1}$H NMR spectrum of **5p**

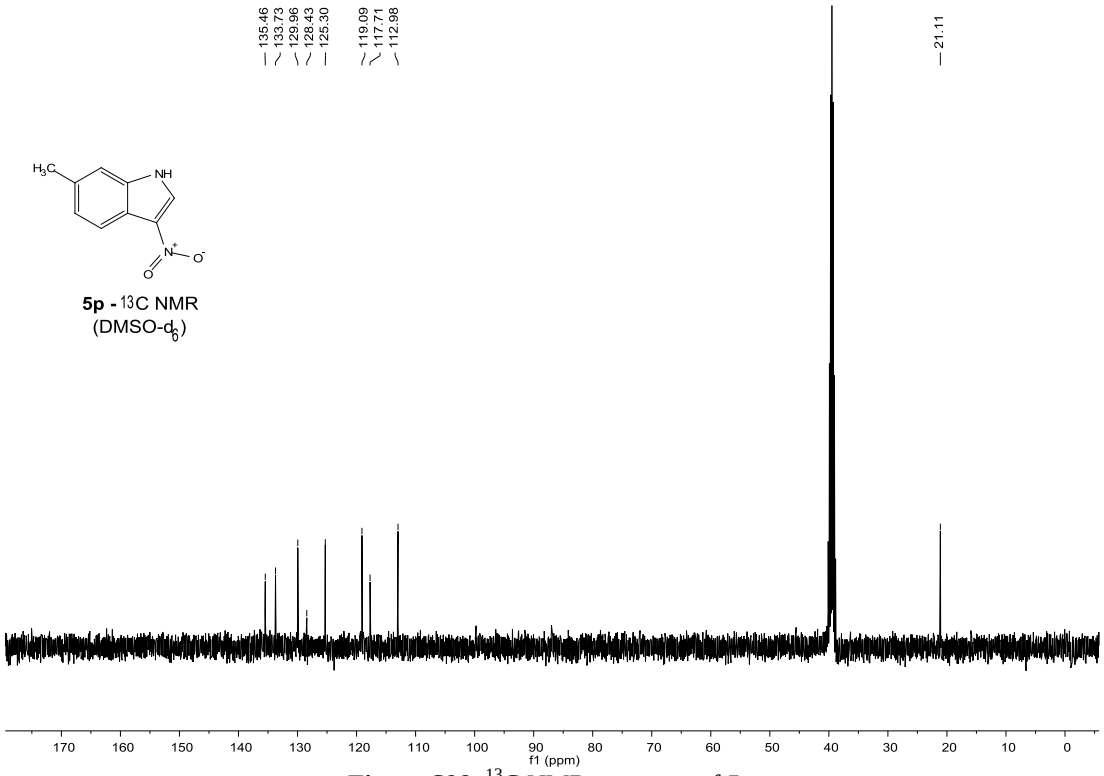



**Figure S98**. $^{13}$C NMR spectrum of **5p**

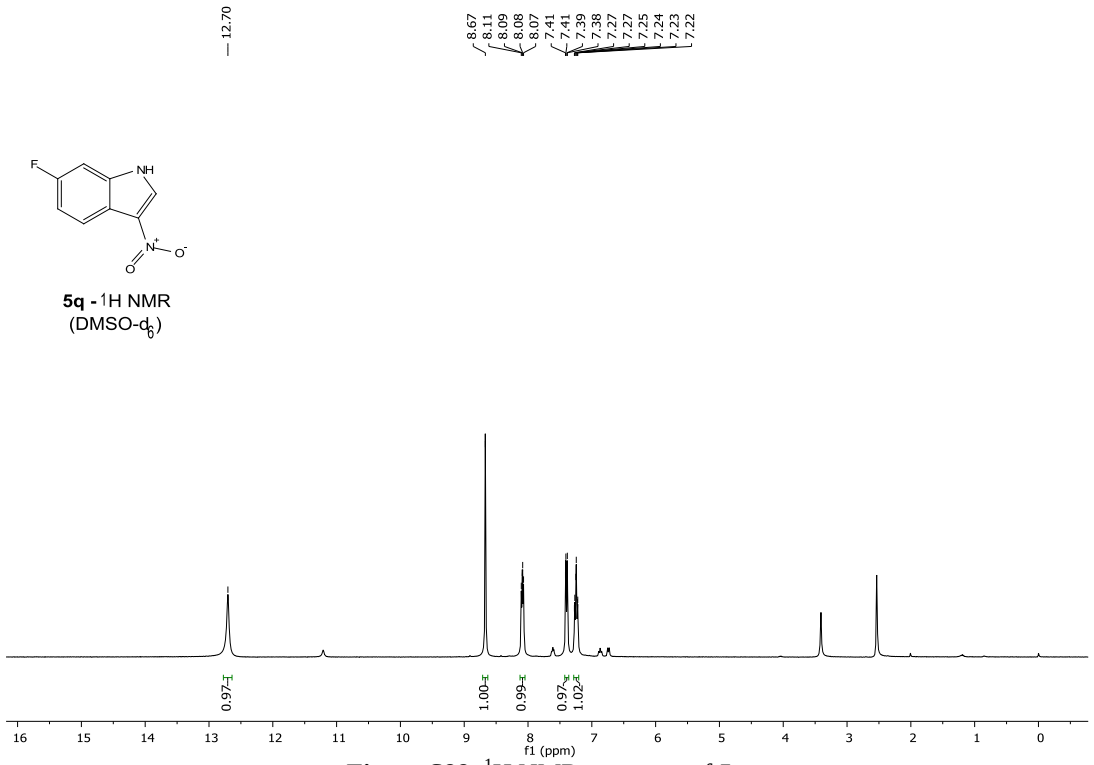



**Figure S99**. $^{1}$H NMR spectrum of **5q**

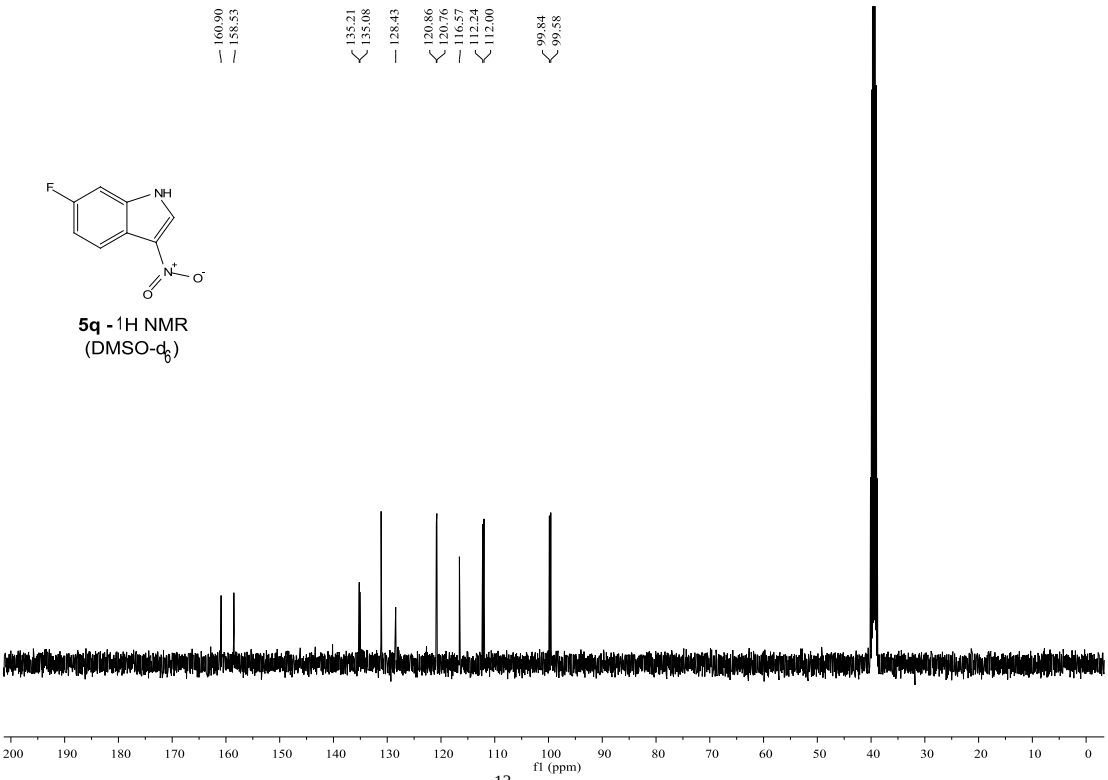



**Figure S100**. $^{13}$C NMR spectrum of **5q**

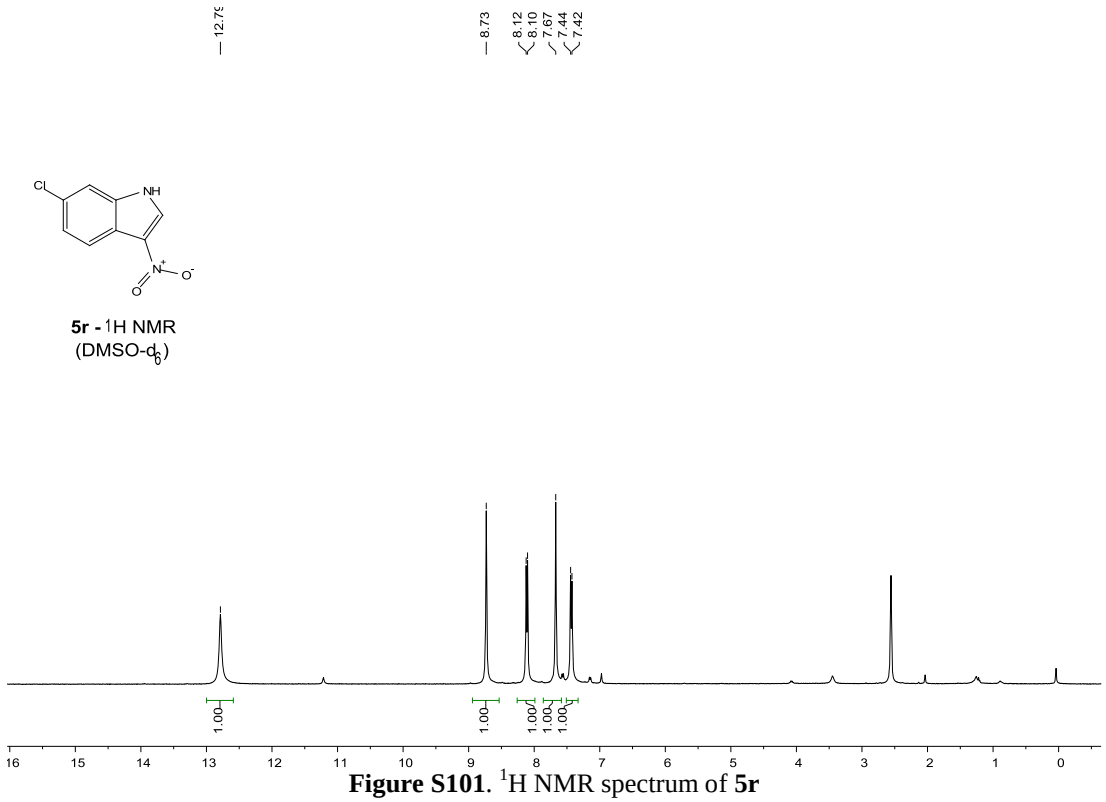



**Figure S101**. $^{1}$H NMR spectrum of **5r**

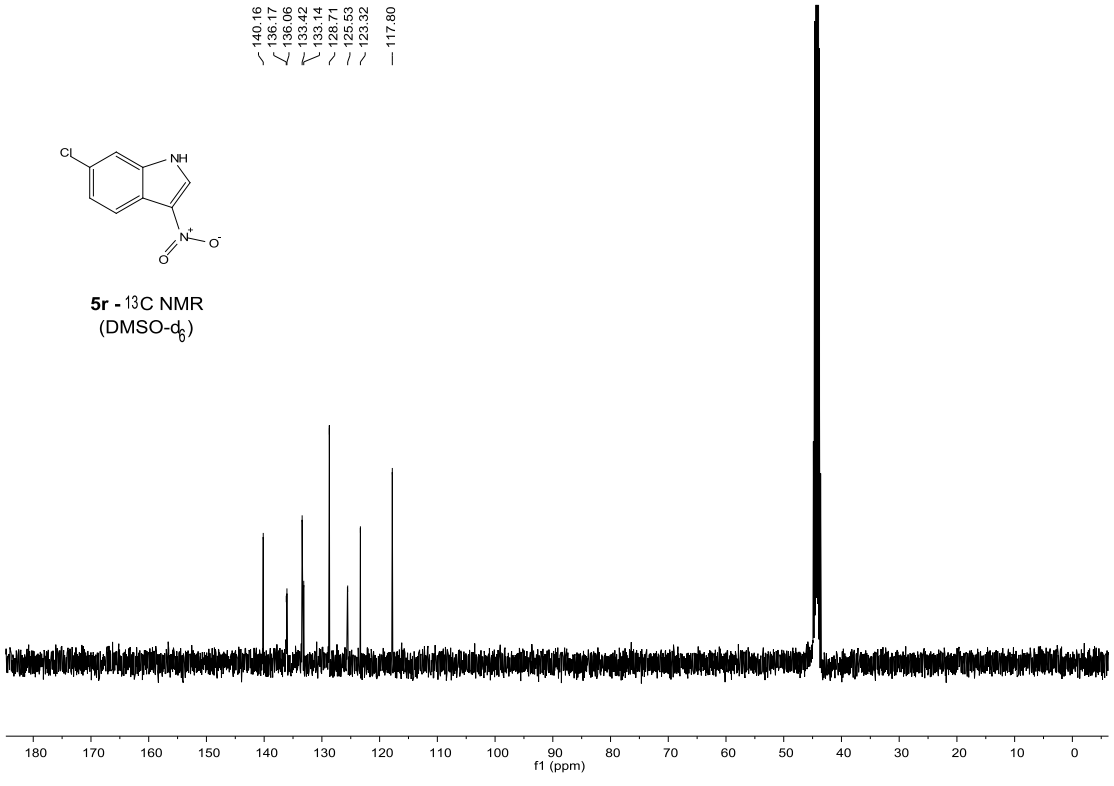



**Figure S102**. $^{13}$C NMR spectrum of **5r**

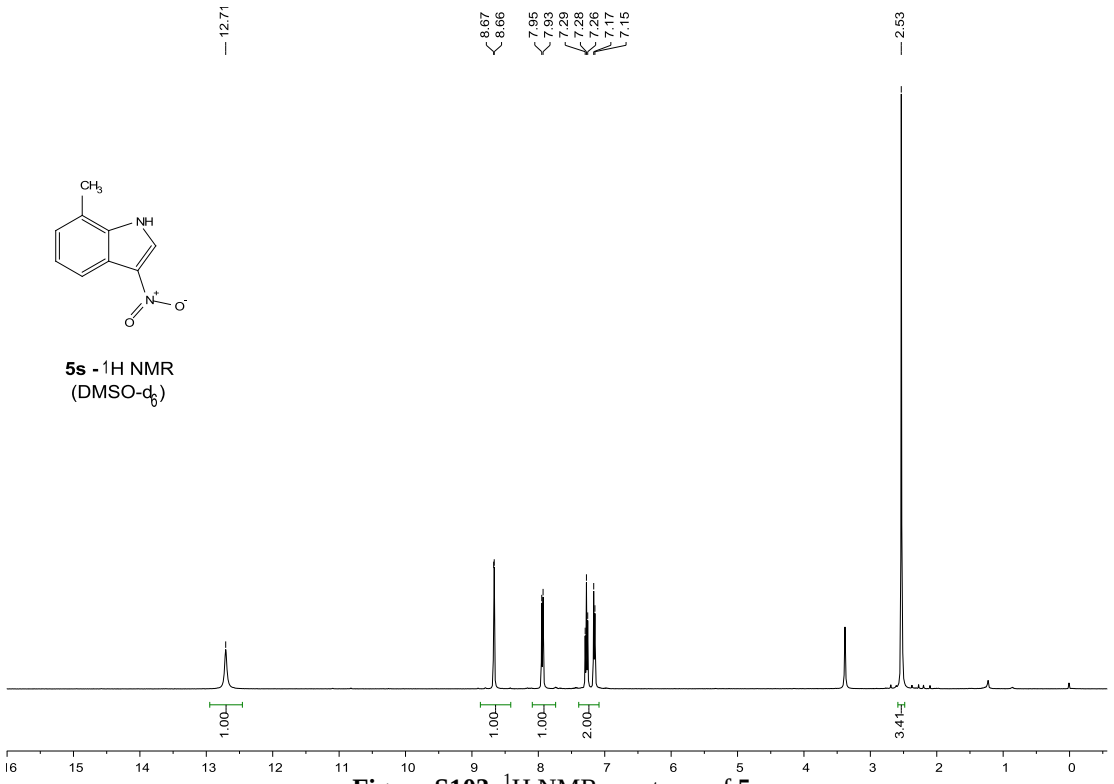



**Figure S103**. $^{1}$H NMR spectrum of **5s**

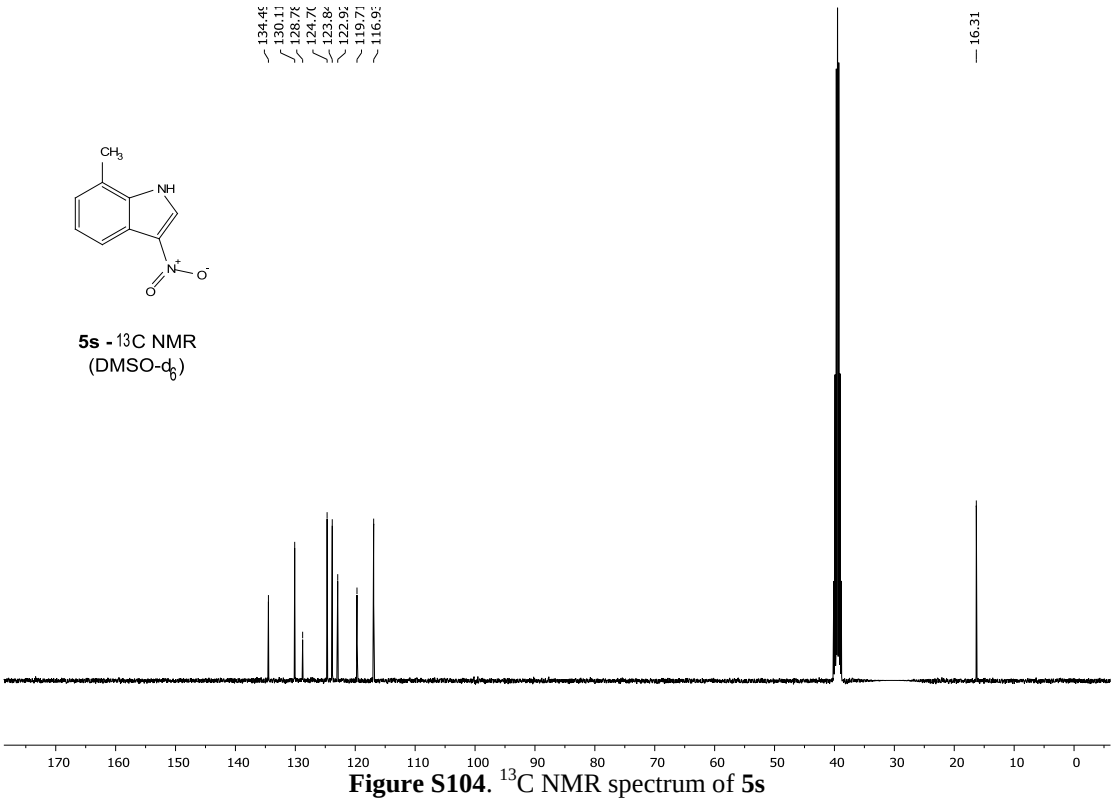



**Figure S104**. $^{13}$C NMR spectrum of **5s**

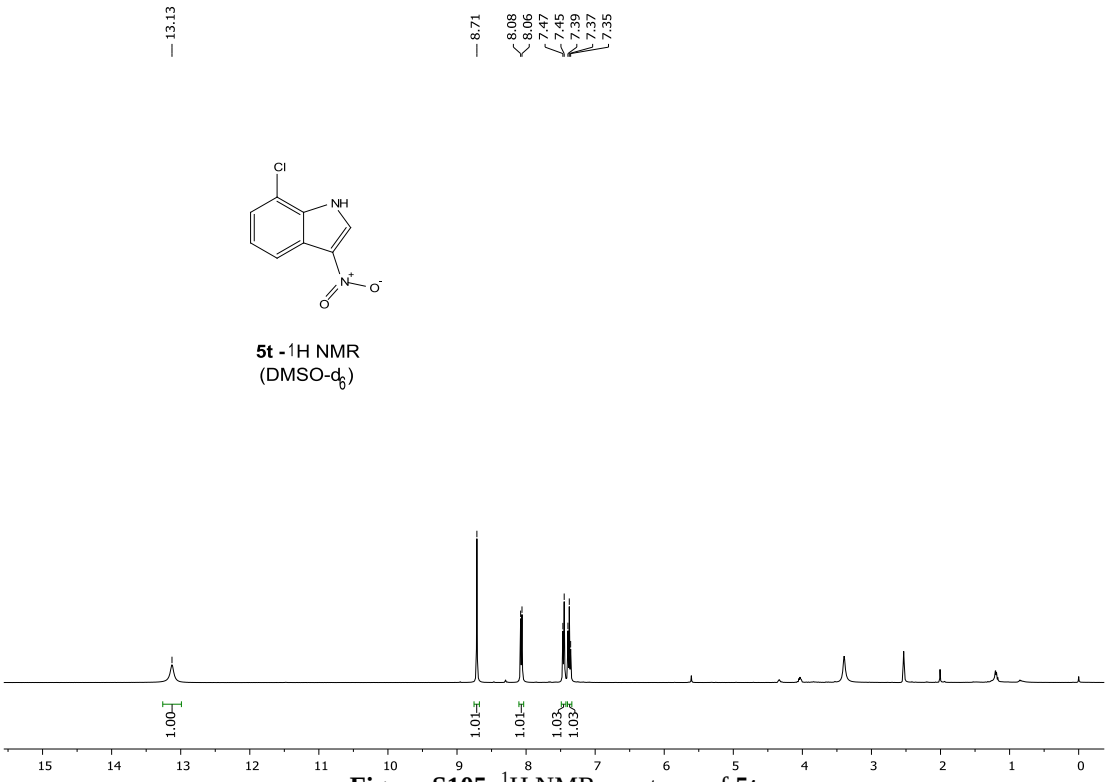



**Figure S105**. $^{1}$H NMR spectrum of **5t**

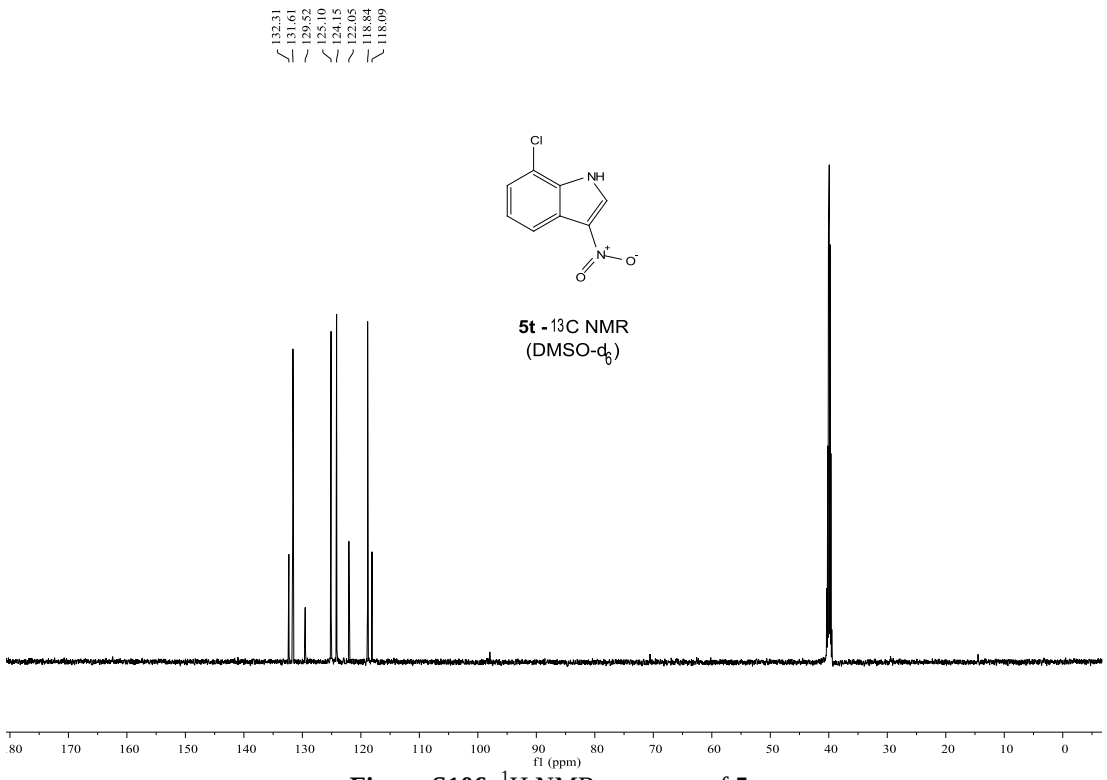



**Figure S106**. $^{1}$H NMR spectrum of **5t**

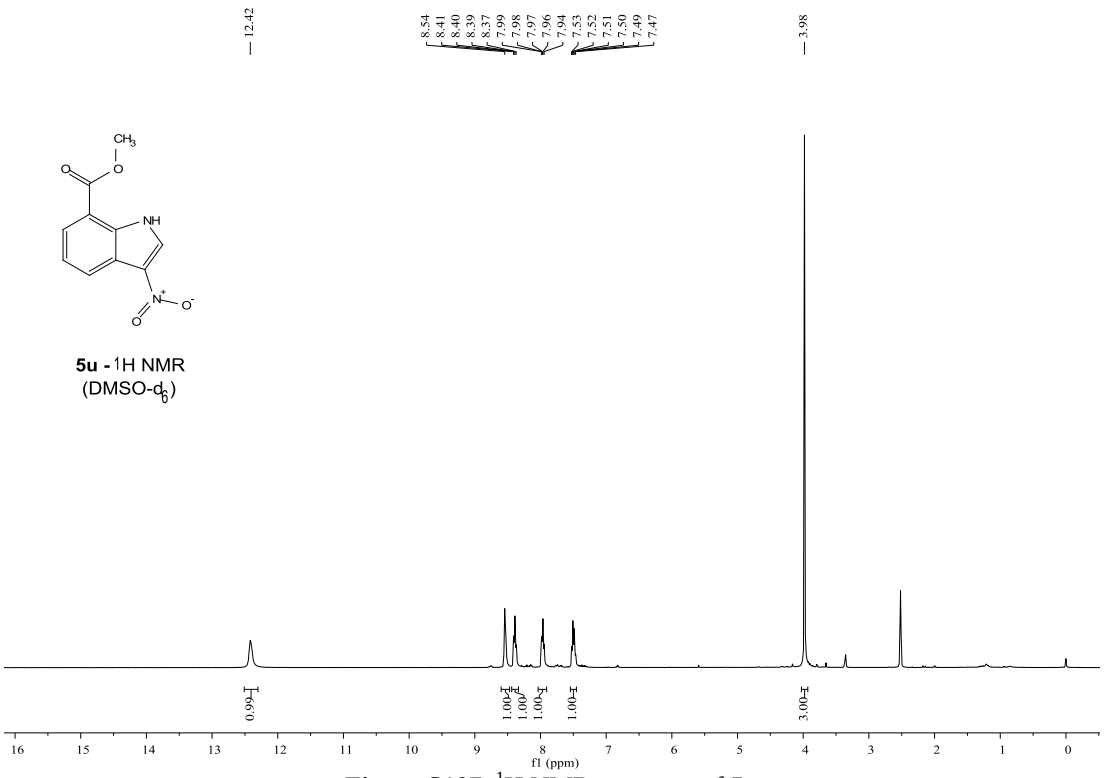



**Figure S107**. $^{1}$H NMR spectrum of **5u**

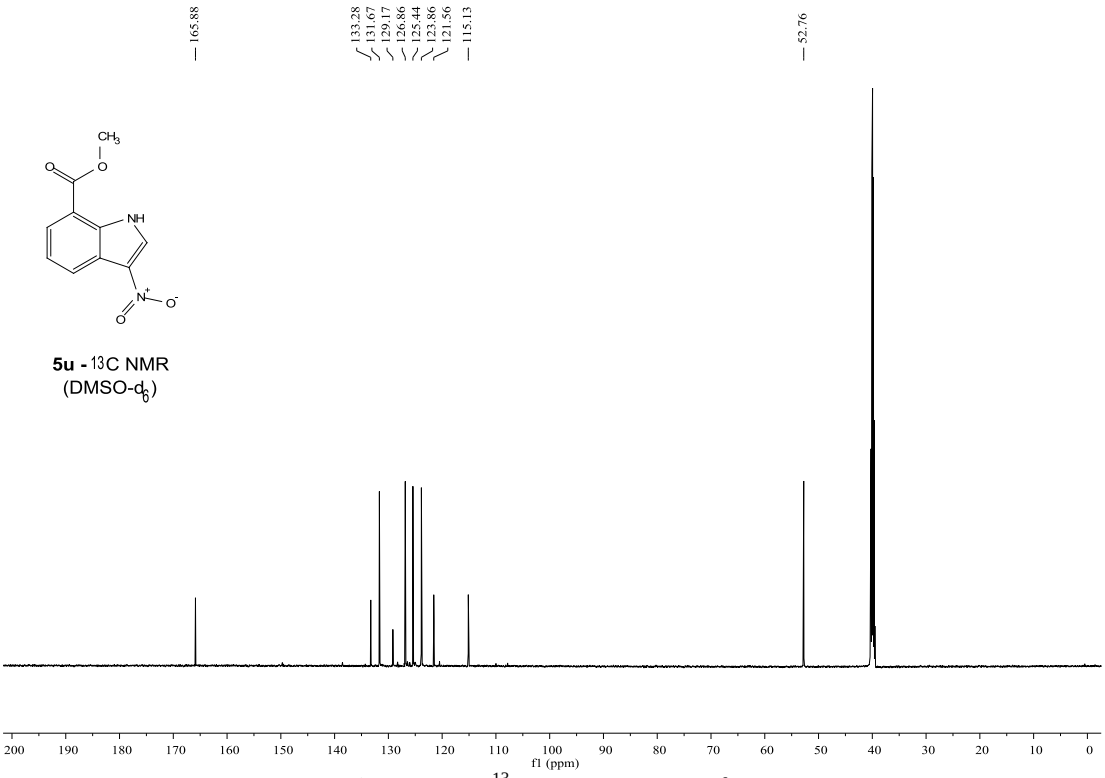



**Figure S108**. $^{13}$C NMR spectrum of **5u**

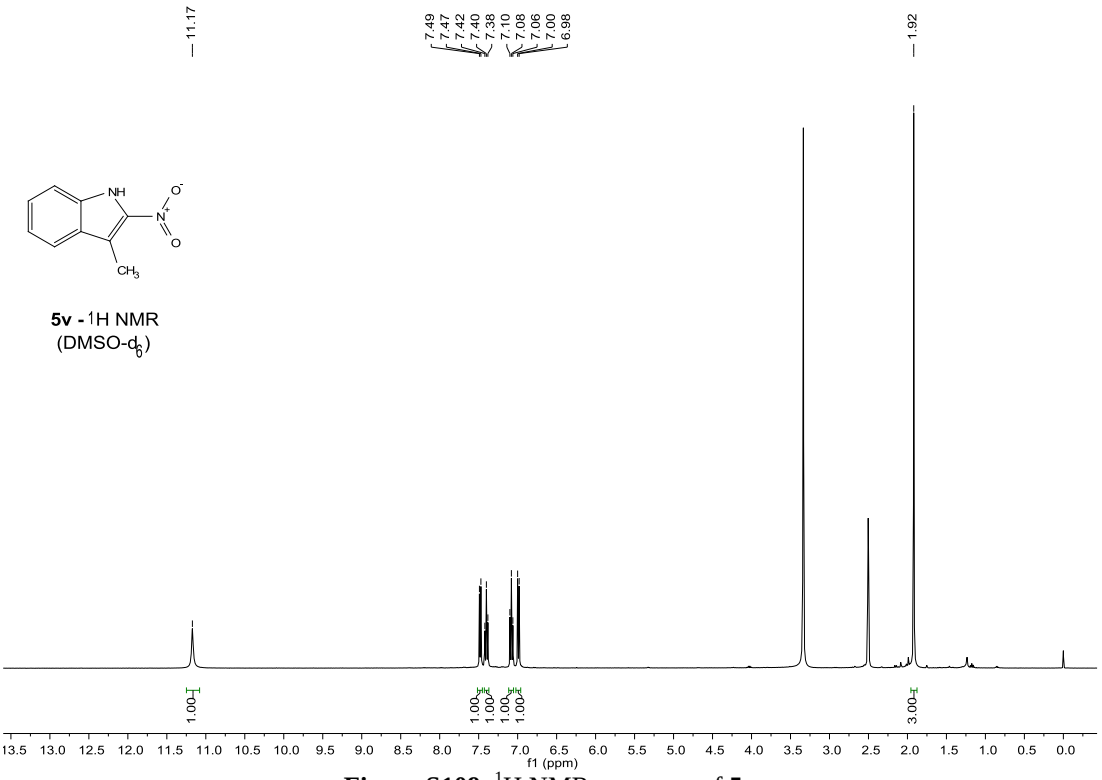



**Figure S109**. $^{1}$H NMR spectrum of **5v**

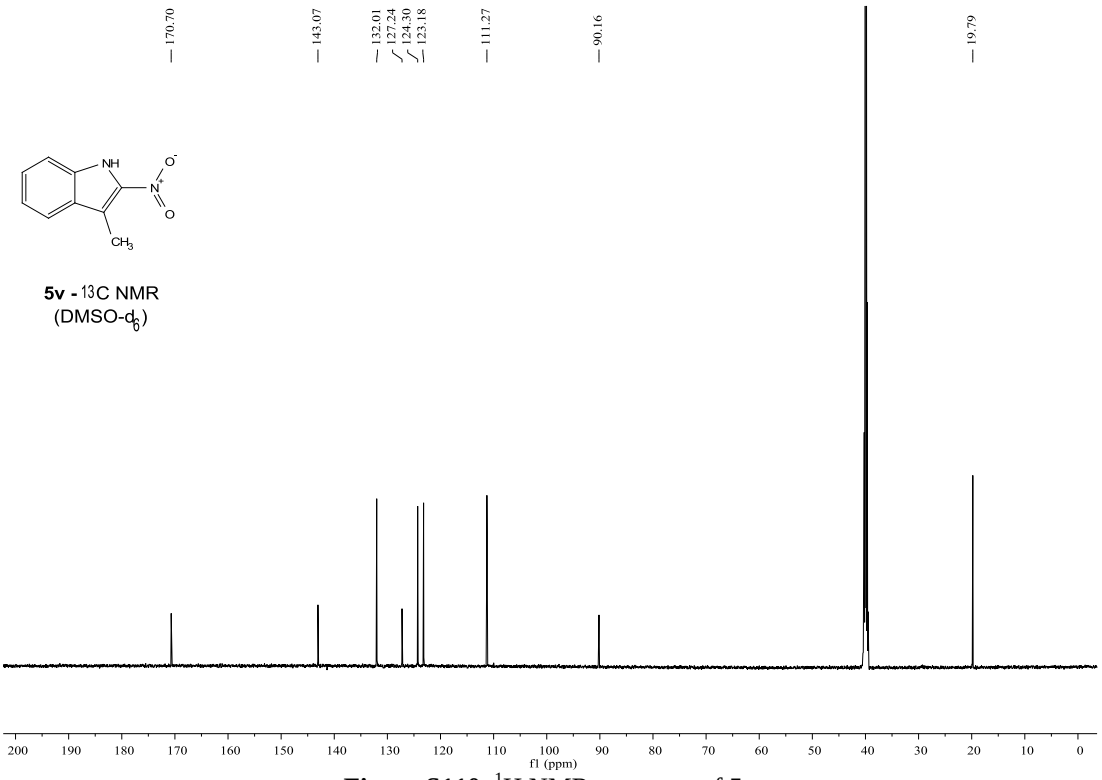



**Figure S110**. $^{1}$H NMR spectrum of **5v**

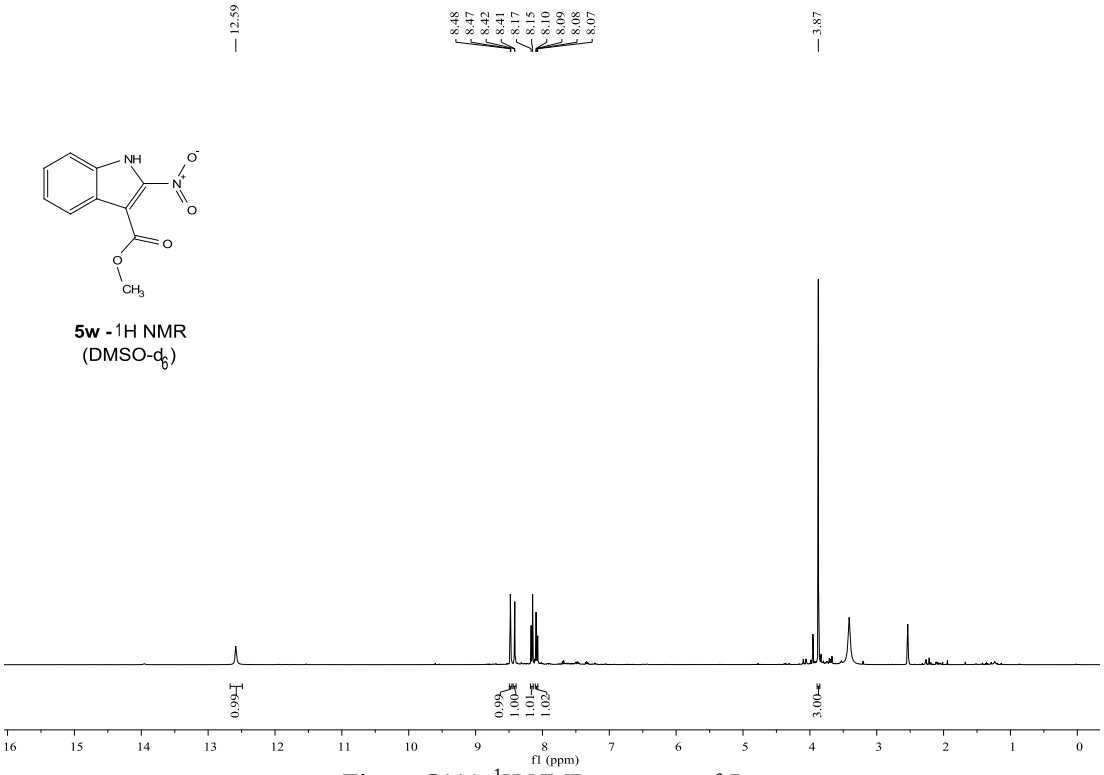



**Figure S111**. $^{1}$H NMR spectrum of **5w**

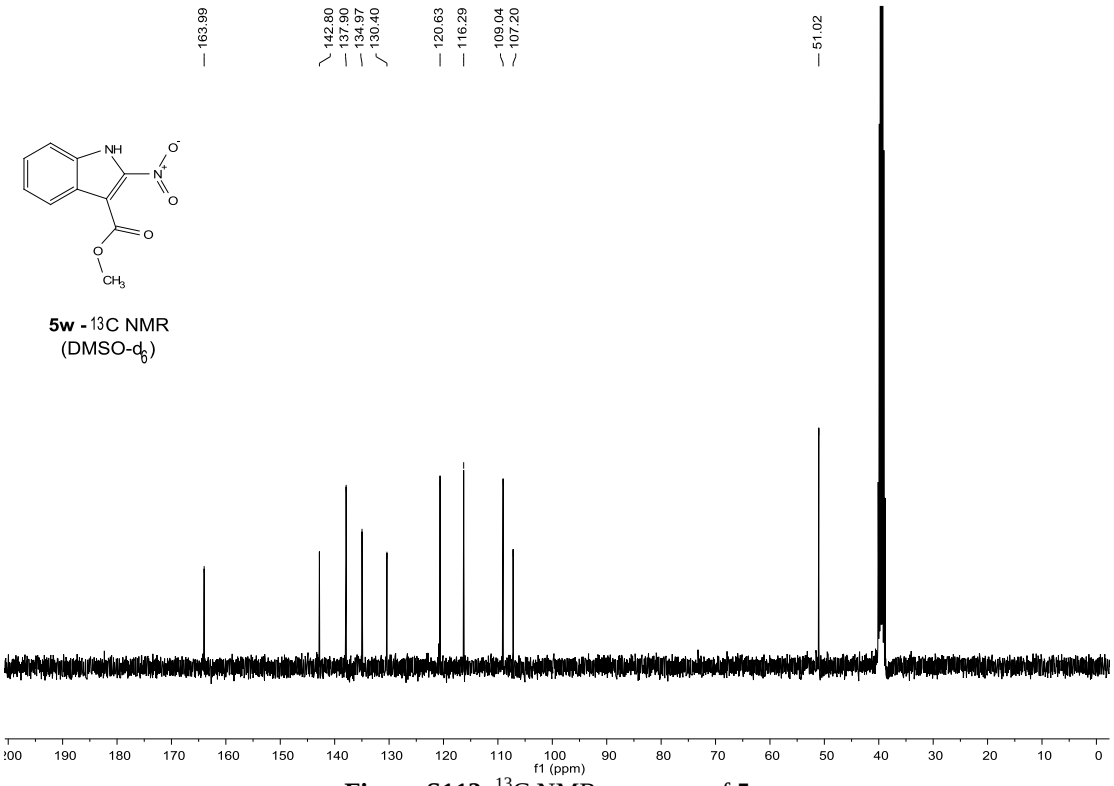



**Figure S112**. $^{13}$C NMR spectrum of **5w**

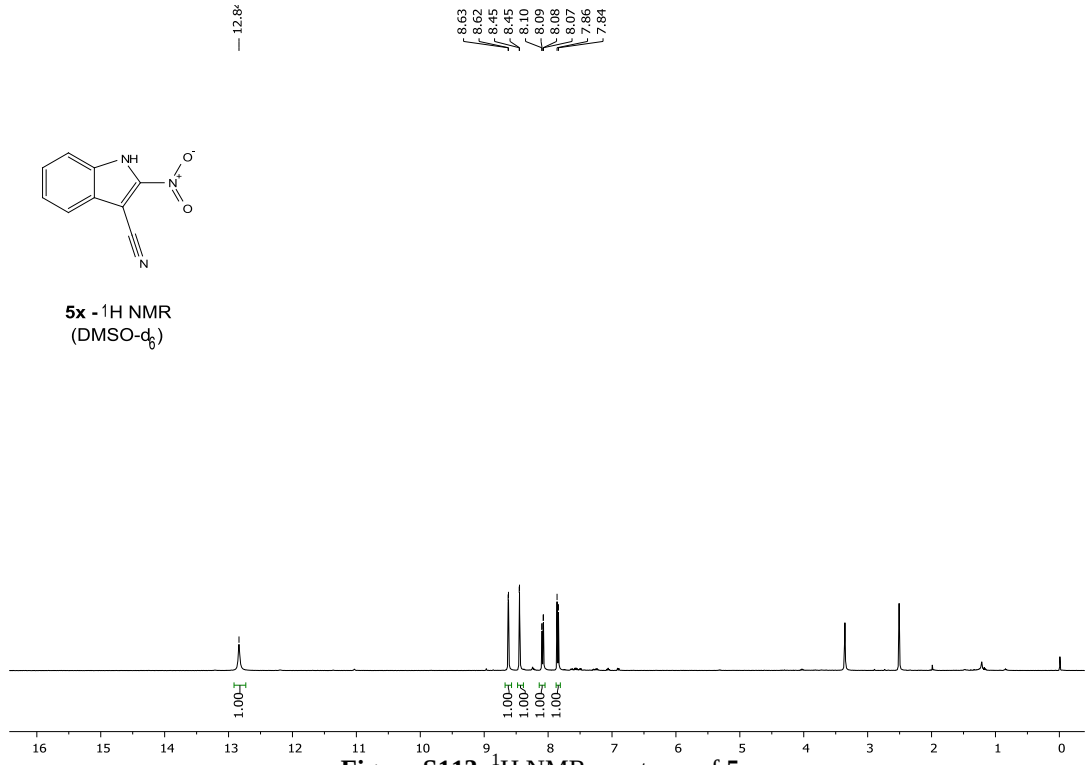



**Figure S113**. $^{1}$H NMR spectrum of **5x**

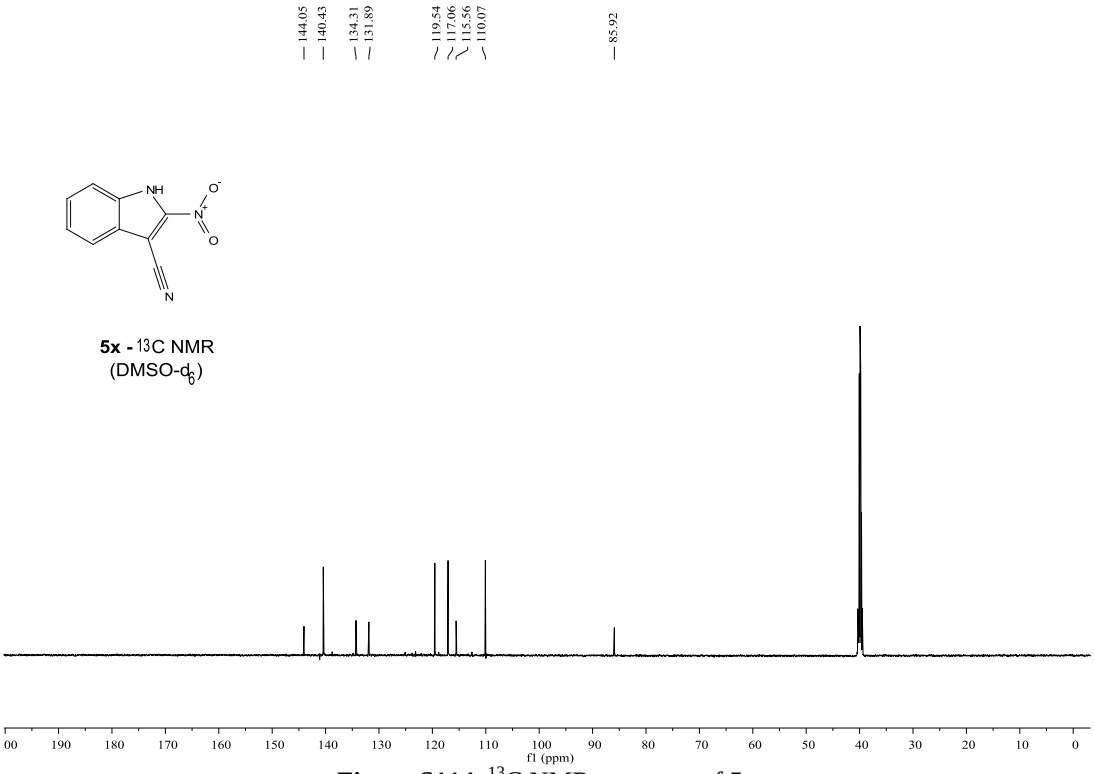



**Figure S114**. $^{13}$C NMR spectrum of **5x**

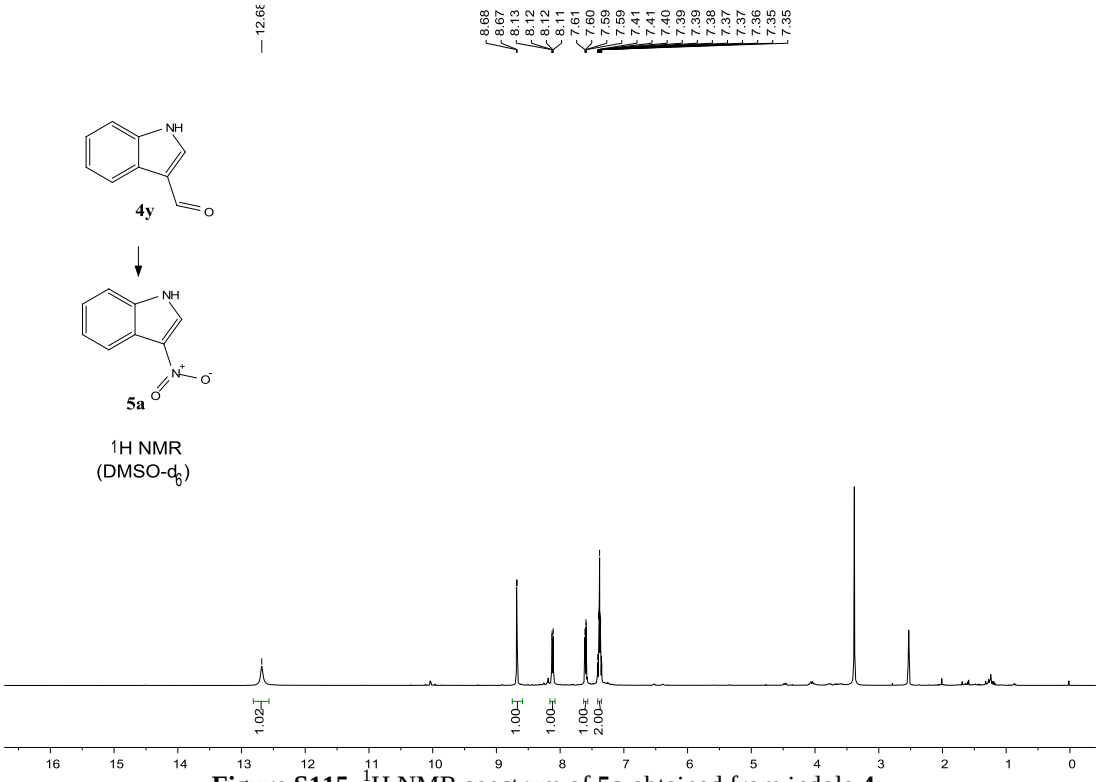



**Figure S115**. $^{1}$H NMR spectrum of **5a** obtained from indole **4y**

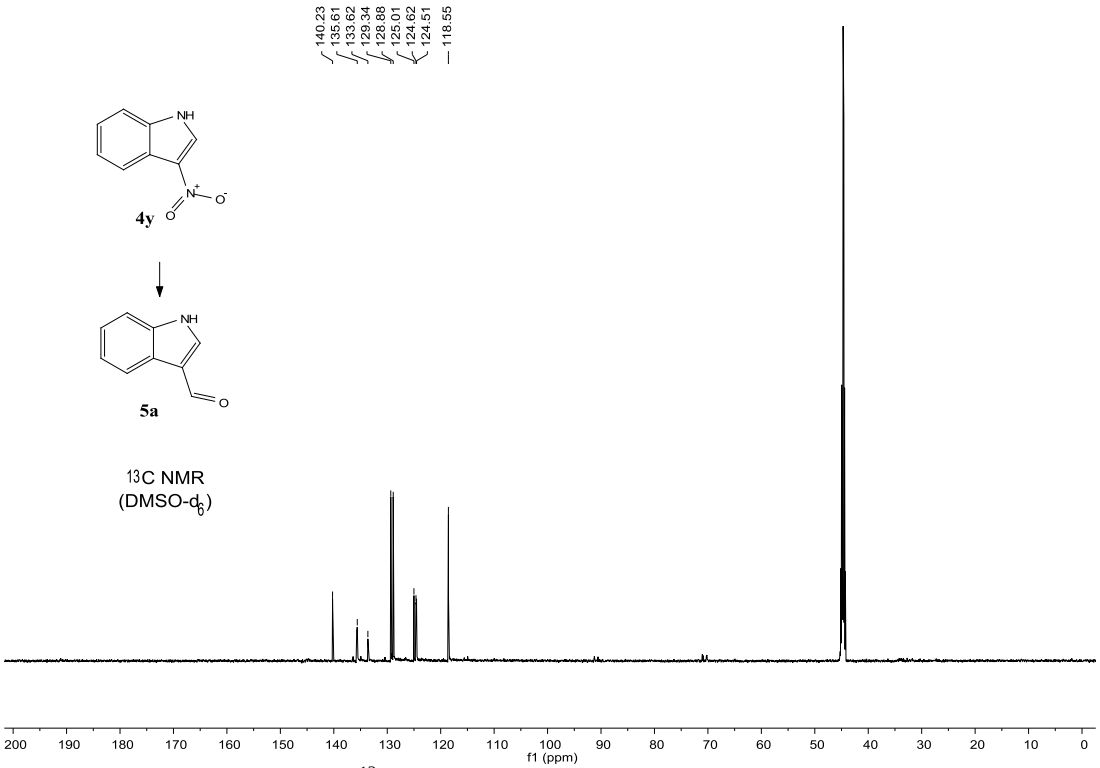



**Figure S116**. $^{13}$C NMR spectrum of **5a** obtained from indole **4y**

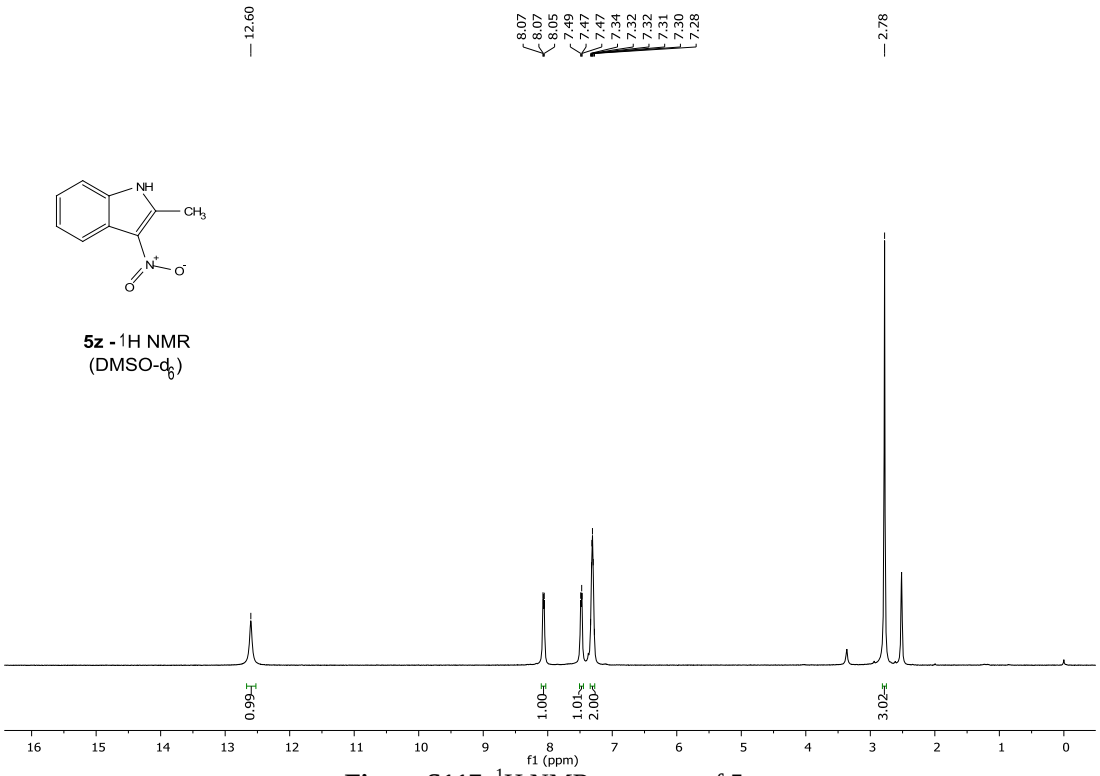



**Figure S117**. $^{1}$H NMR spectrum of **5z**

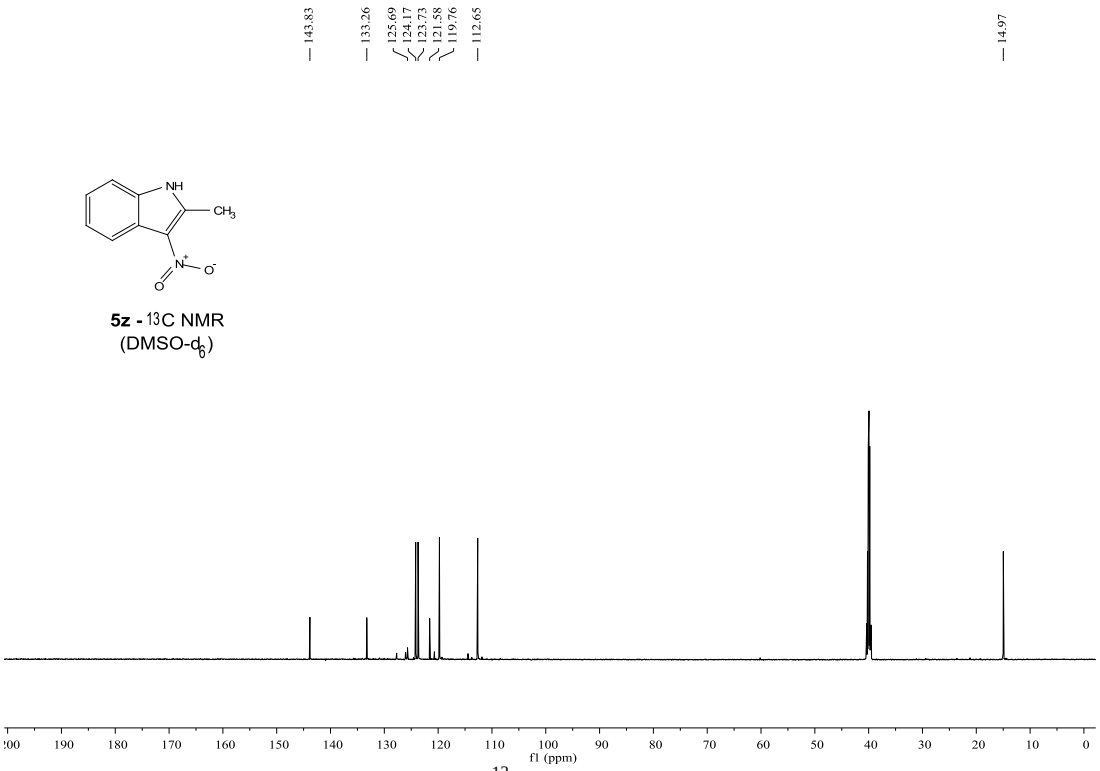



**Figure S118**. $^{13}$C NMR spectrum of **5z**

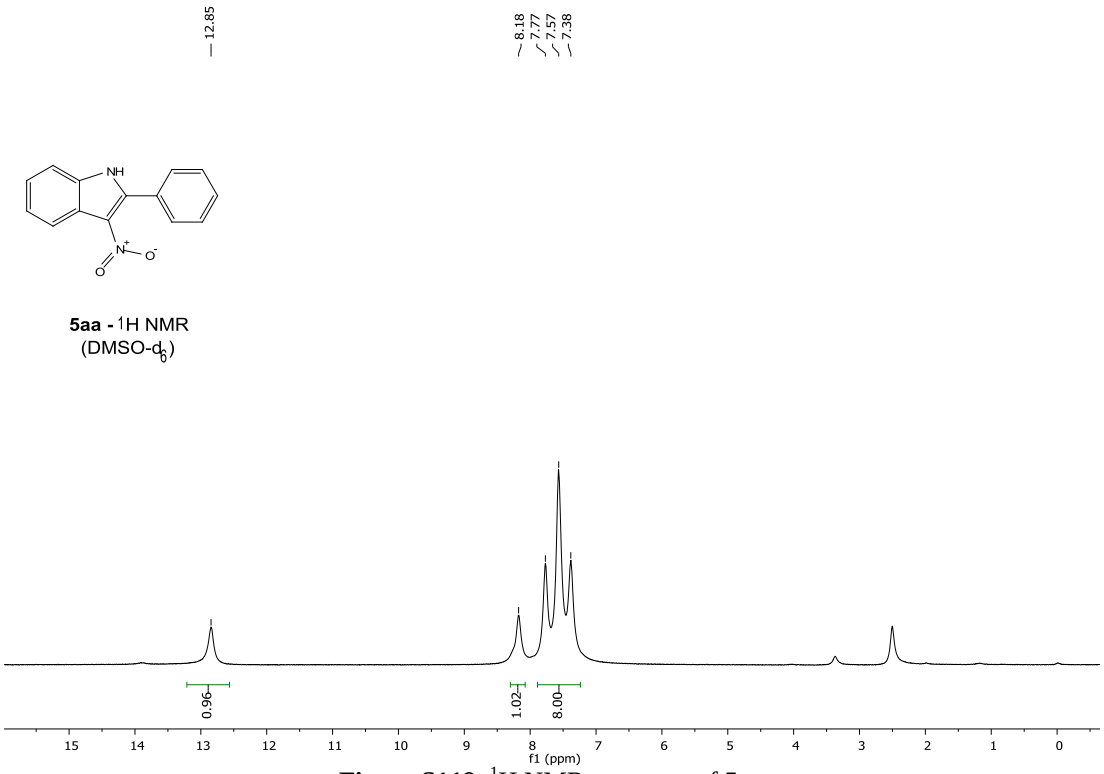



**Figure S119**. $^{1}$H NMR spectrum of **5aa**

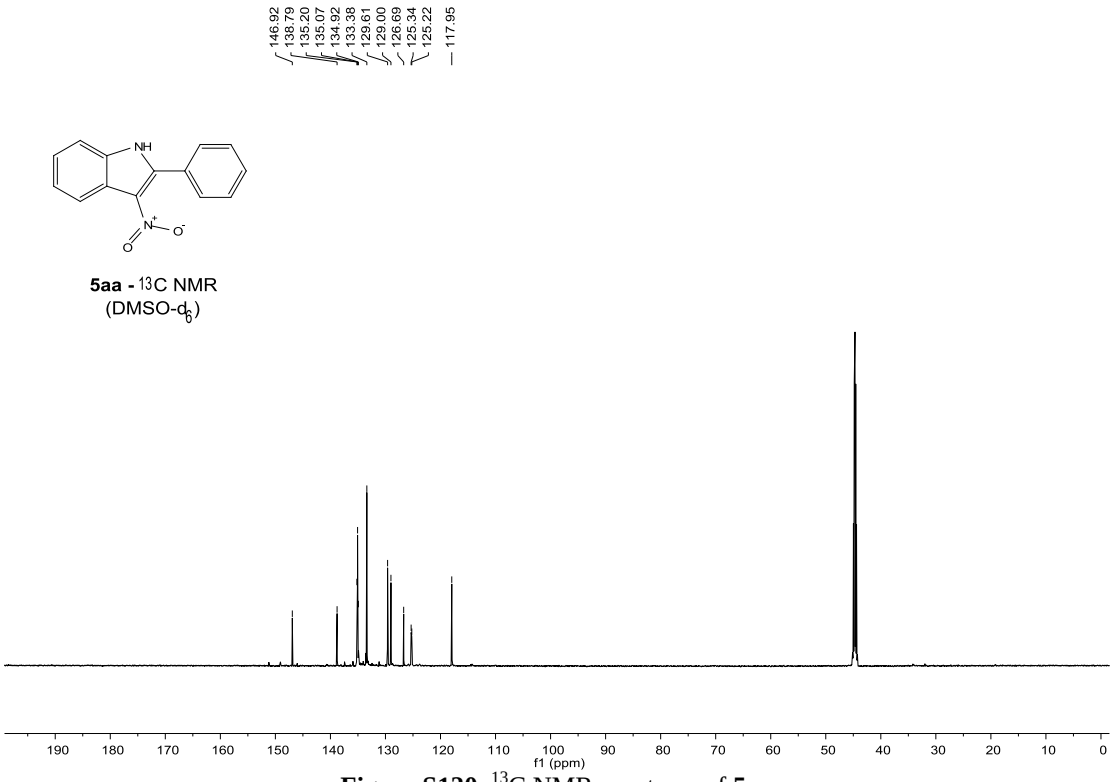



**Figure S120**. $^{13}$C NMR spectrum of **5aa**

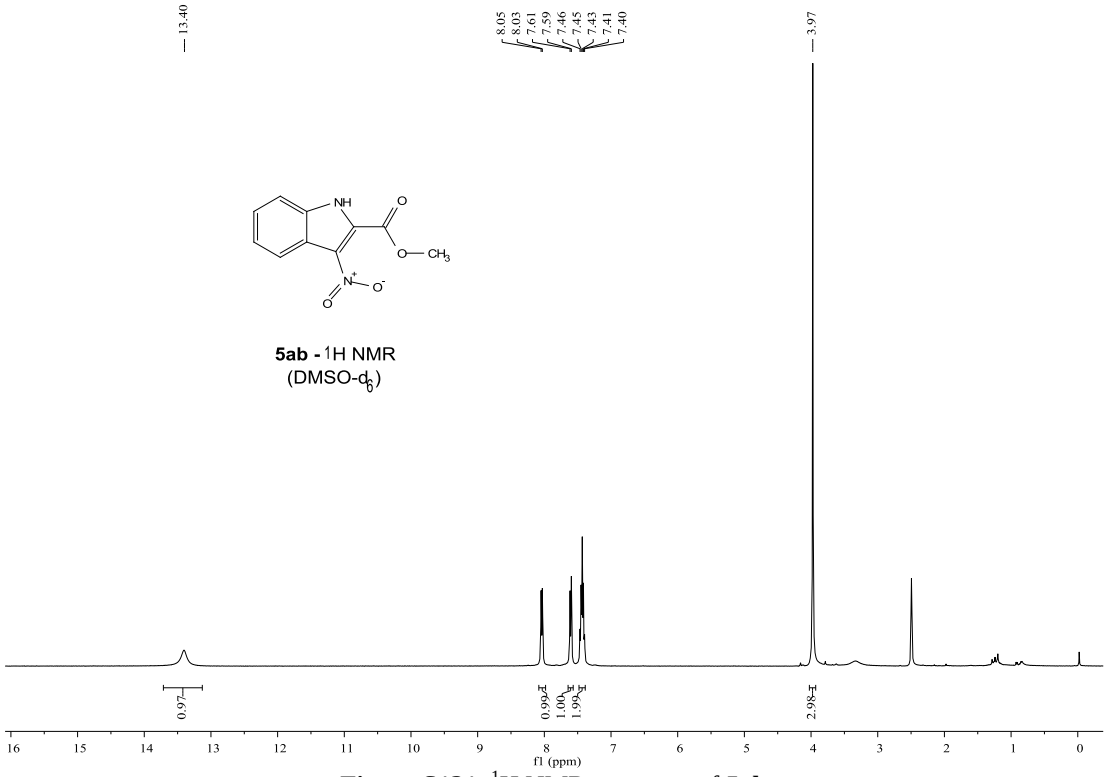



**Figure S121**. $^{1}$H NMR spectrum of **5ab**

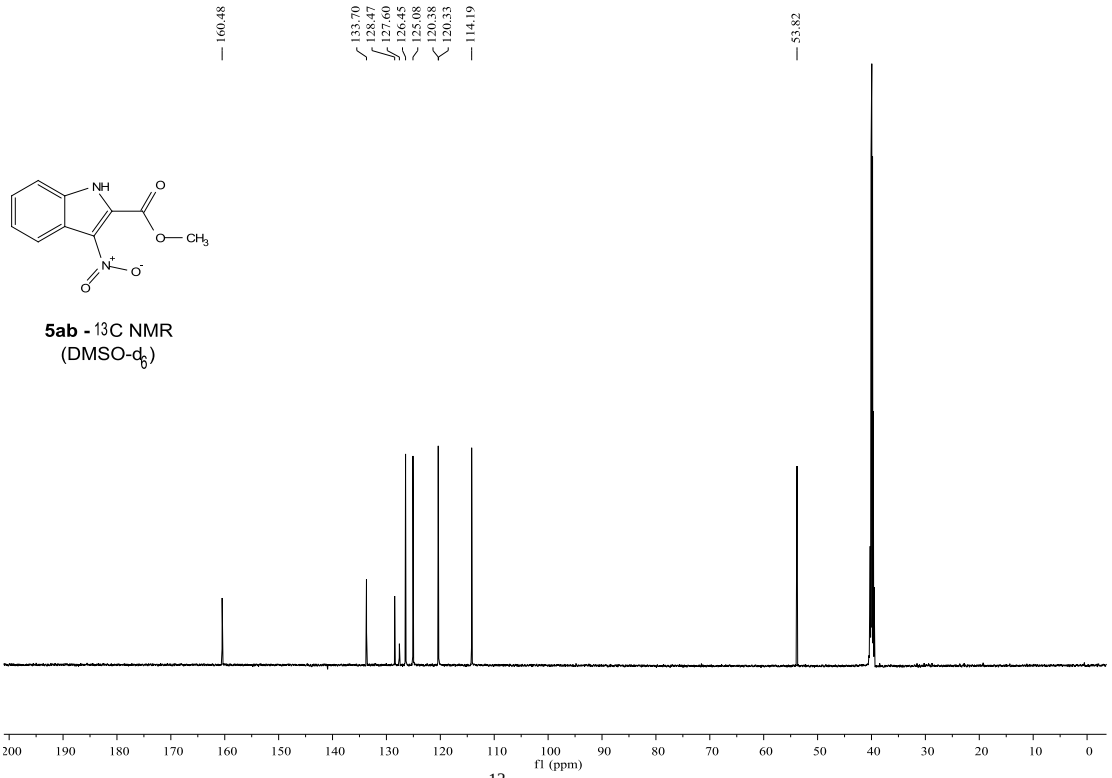



**Figure S122**. $^{13}$C NMR spectrum of **5ab**

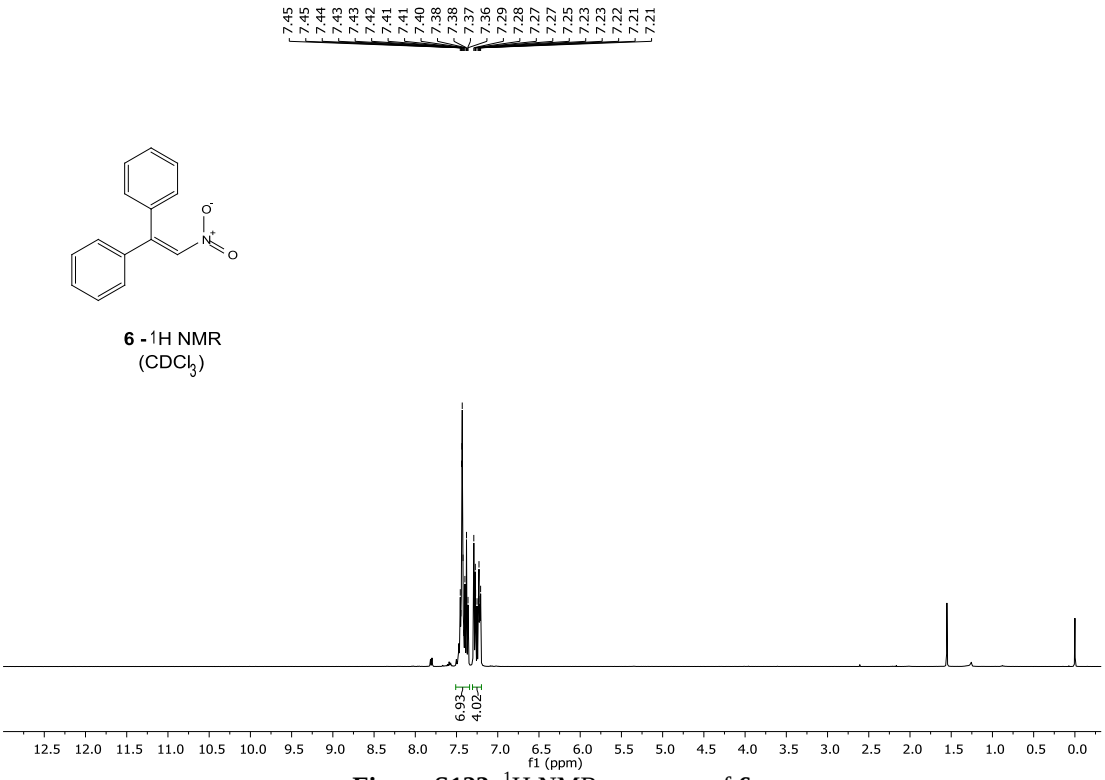



**Figure S123**. $^{1}$H NMR spectrum of **6**

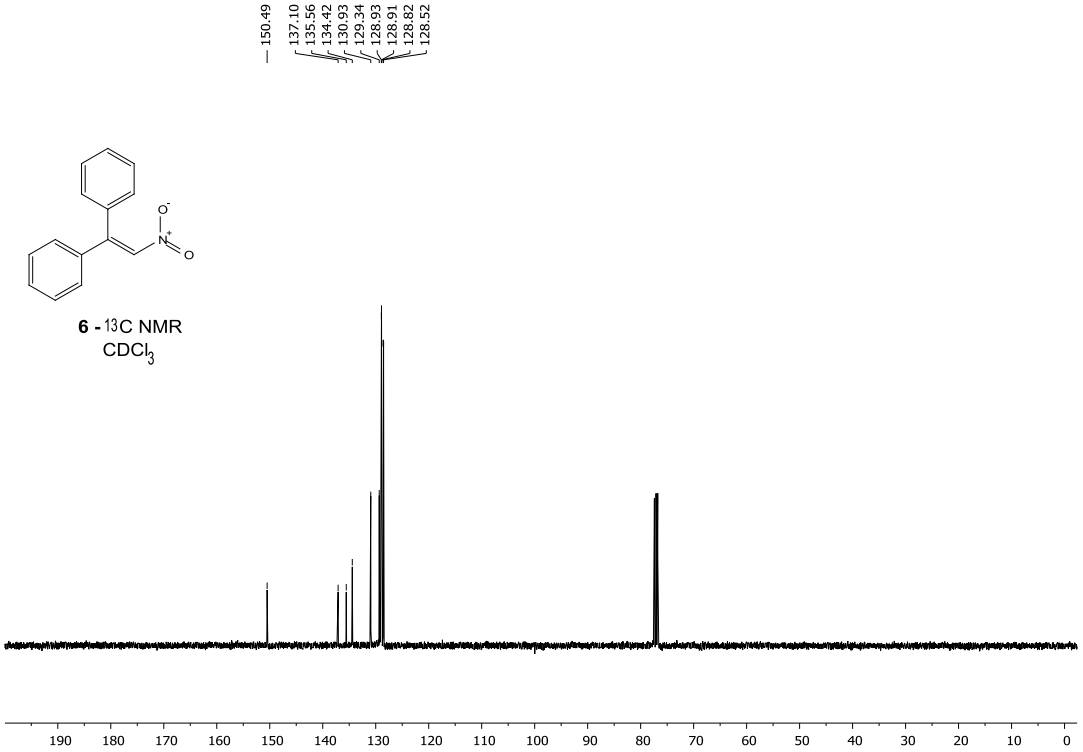
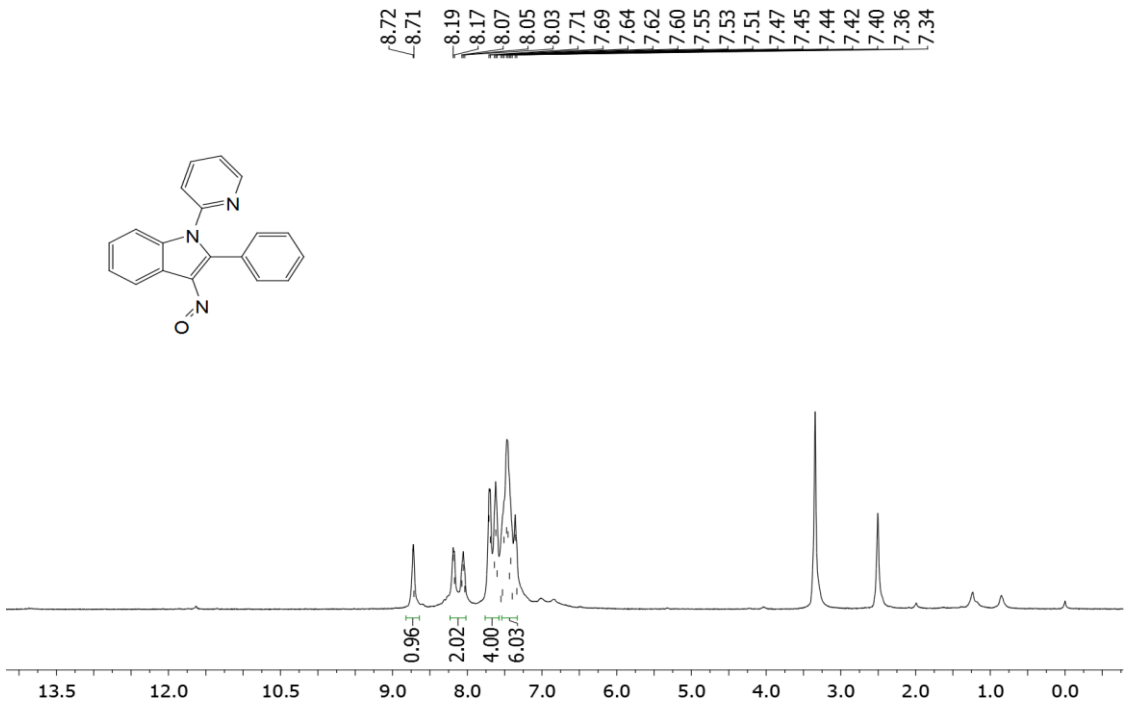
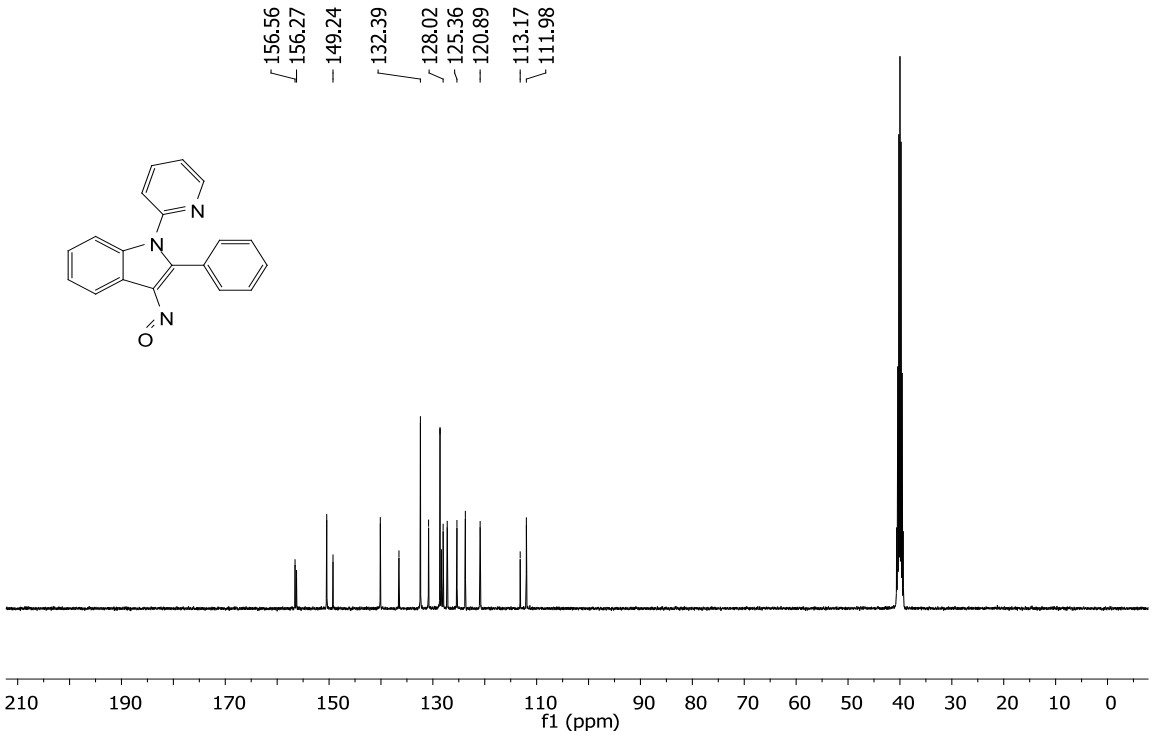



**Figure S124**. $^{13}$C NMR spectrum of **6**

Compound **7**

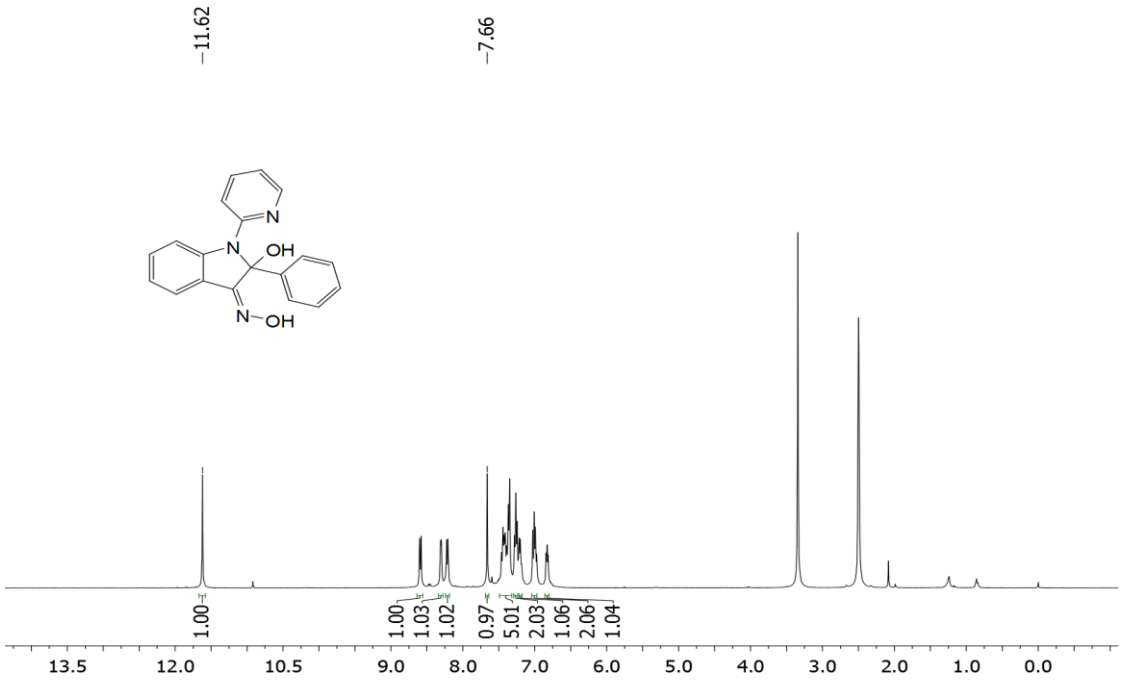



**$^{1}$H NMR spectrum of 7**



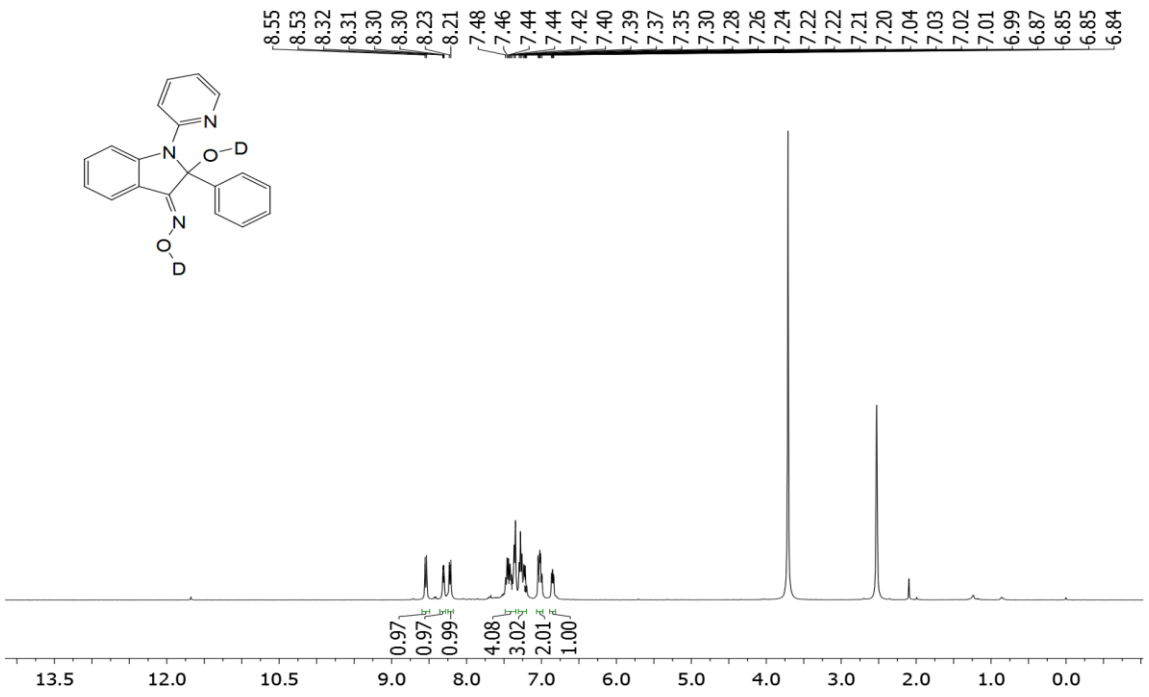

**$^{13}$C NMR spectrum of 7**

Compound **8**

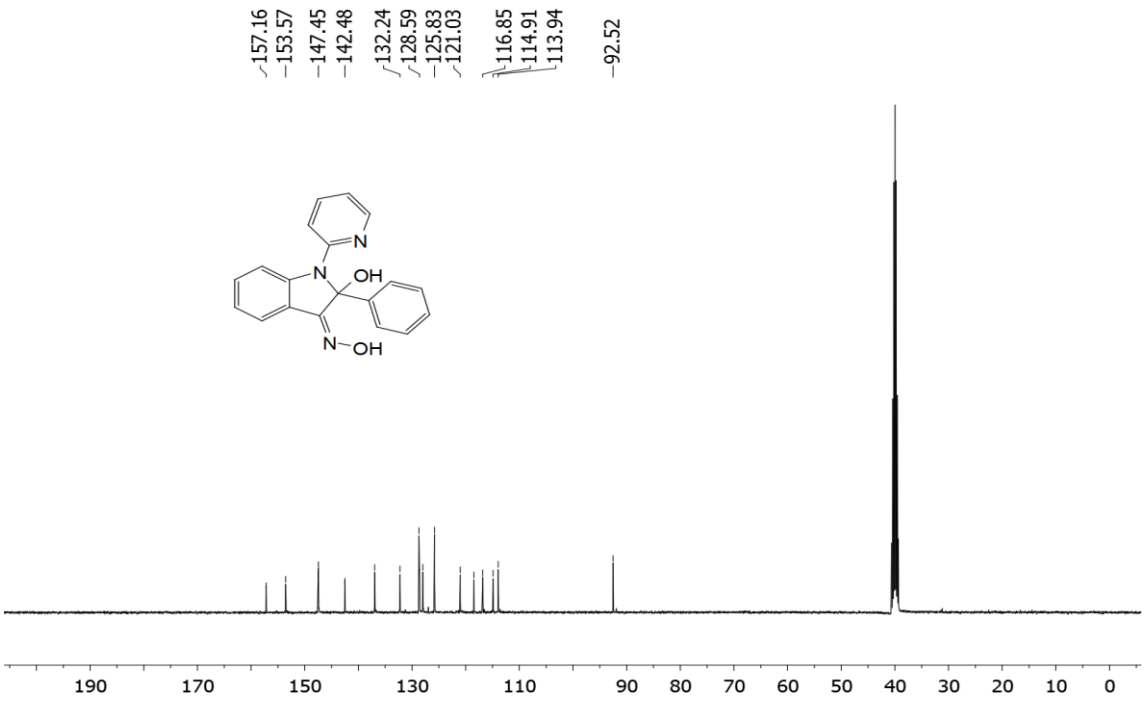



**$^{1}$H NMR spectrum of 8**

Compound **8-*d*$_2$**

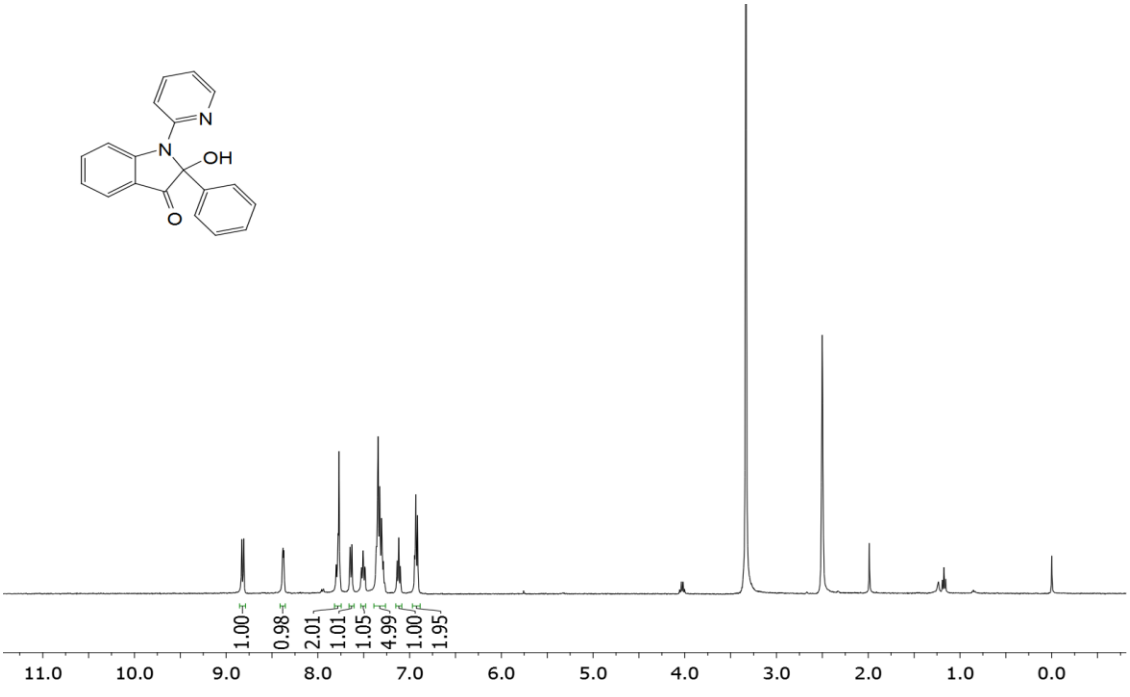



**D$_2$O-exchange of $^{1}$H NMR spectrum of 8**

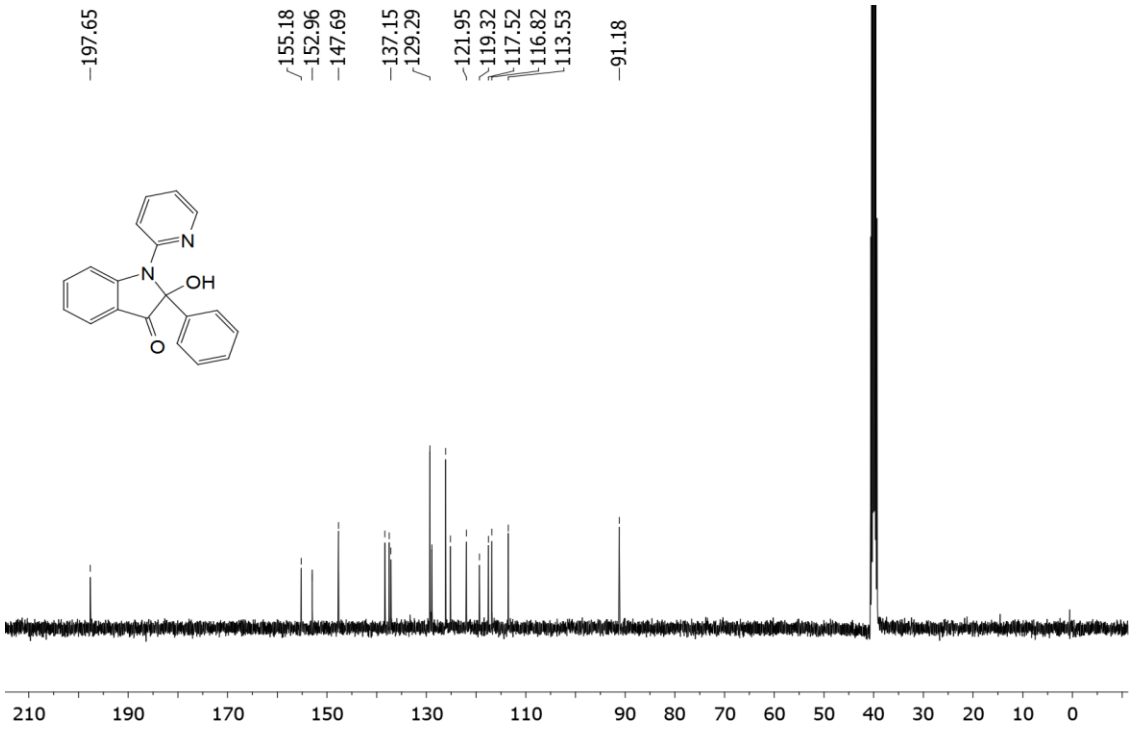



**$^{13}$C NMR spectrum of 8**

Compound **9**




**$^{1}$H NMR spectrum of 9**




**$^{13}$C NMR spectrum of 9**