

## SUPPLEMENTARY MATERIALS

# Nano-FGT: A green and sustainable catalyst for the synthesis of spirooxindoles in aqueous medium

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## Experimental

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on Spectrum BX FT-IR, Perkin Elmer ( $\nu_{\max}$  in  $\text{cm}^{-1}$ ) on KBr disks.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR (400 MHz and 100 MHz respectively) spectra were recorded on Bruker Avance II-400 spectrometer in  $\text{CDCl}_3$  and  $\text{DMSO-d}_6$  (chemical shifts in  $\delta$  with TMS as internal standard). Mass spectra were recorded on Waters ZQ-4000. Transmission Electron Microscope (TEM) was recorded on JEOL JSM 100CX. Scanning electron microscope (SEM) was recorded on JSM-6360 (JEOL). Thermogravimetric analysis (TGA) was recorded on a Perkin Elmer Precisely STA 6000 simultaneous thermal analyzer. CHN were recorded on CHN-OS analyzer (Perkin Elmer 2400, Series II).

## X-ray crystallography

The X-ray diffraction data were collected at 293 K with Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using Agilent Xcalibur (Eos, Gemini) diffractometer equipped with a graphite monochromator. The software used for data collection CrysAlis PRO (Agilent, 2011), data reduction CrysAlis PRO and cell refinement CrysAlis PRO. The structure were solved by direct methods and refined by full-matrix least-squares calculation using SHELXS-97<sup>1</sup> and SHELXL-97.<sup>2</sup>

## Procedure for the synthesis of $\text{Fe}_3\text{O}_4$ NPs.

A mixture of 3.4 g of ferric nitrate and 3 g of ferrous sulphate was taken in a clean 250 mL round bottom flask. To it 100 mL of deionized water was added and stirred for a period of 15 min, and solution became homogeneous. After that ammonium hydroxide (25 %) was then added drop-wise till the pH of the resulting solution was attained 10. During addition of ammonium hydroxide, the formation of black precipitate was observed. The solution was

then heated at 50-60 °C for 1 h. After the time mentioned, the magnetic black precipitate was separated, washed with water until the pH became neutral and dried in oven for 5 h.

#### **Procedure for the synthesis of nano-FGT.**

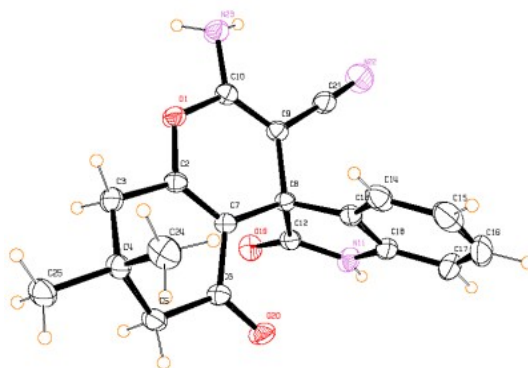
The Fe<sub>3</sub>O<sub>4</sub> NPs (0.5 g) were dispersed in 15 mL of deionized water and 5 mL of MeOH. The resulting colloidal solution was then sonicated for a period of 15 mins. Glutathione (0.4 g) was dissolved in 5 mL of water and added to this colloidal solution. The resulting solution was sonicated for 2h. The magnetic glutathione-functionalized nano-material was then isolated by external magnet, washed with water (3 x 5 mL), MeOH (3 X 5 mL) and dried under vacuum at 50-60 °C.

#### **Procedure for the synthesis of spirooxindole derivatives (4aaa-4cac).**

In a clean round bottom flask, 1,2-diketone (**1a-c**, 1 mmol), malonates (**2a-c**, 1 mmol), enolizable C-H activated compounds (**3a-f**, 1mmol) and nano-FGT (8 mg) in aqueous medium (3 mL) was heated at 80 °C for 15 min. After completion of reaction, the catalyst was separated via simple external magnet, washed with MeOH (3 X 5 mL) and reused. The reaction mixture was allowed to cool. The precipitate formed was then separated by simple filtration and washed with hot water (3 X 10 mL) to afford the pure product (**4aaa-4cac**).

#### **References**

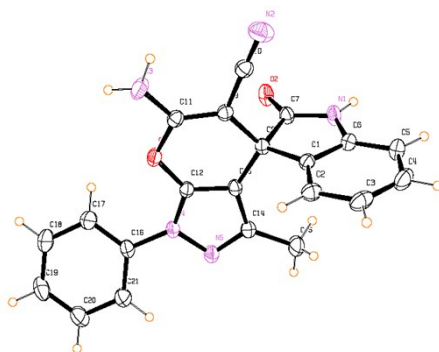
- [1] Sheldrick, G. M. Phase Annealing in SHELX-90: Direct Methods for Larger Structures. *Acta. Crystallog. Sec A.* **1990**, *46*, 467-473.
- [2] Sheldrick, G. M. A short history of SHELX. *Acta. Crystallog. Sec A.* **2008**, *64*, 112-122.



**Table S.I.1.** X-ray crystallography data for compound **4aaa** (CCDC No. 1031108).

|   |                      |
|---|----------------------|
| Empirical formula                               | $C_{19}H_{17}N_3O_3$ |
| Formula weight                                  | 335.37               |
| Crystal system                                  | Monoclinic           |
| Space group                                     | $P2_1/n$             |
| $a(\text{\AA})$                                 | 8.6467(4)            |
| $b(\text{\AA})$                                 | 11.5046(5)           |
| $c(\text{\AA})$                                 | 17.1290(7)           |
| $\alpha(^{\circ})$                              | 90.00                |
| $\beta(^{\circ})$                               | 92.114(4)            |
| $\gamma(^{\circ})$                              | 90.00                |
| Volume ( $\text{\AA}^3$ )                       | 1702.79(12)          |
| $\rho$ (calculated) ( $\text{mg mm}^{-3}$ )     | 1.3081               |
| T(K)  | 291.7(3)             |
| Absorption coefficient ( $\mu/\text{mm}^{-1}$ ) | 0.091                |
| Total reflection collected                      | 7748                 |
| Independent reflection                          | 3886                 |
| $\theta$ range ( $^{\circ}$ )                   | 6.42 to 57.2         |

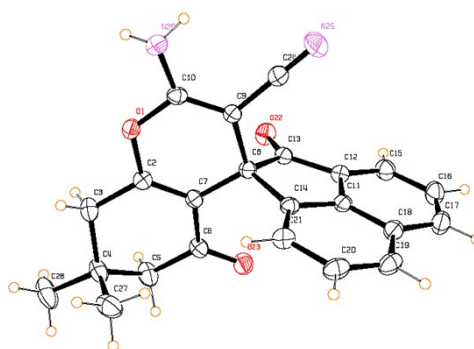
|   |                           |
|---|---------------------------|
| Final R Indexes [ $1 \geq 2\sigma(I)$ ] | R1 = 0.0579, wR2 = N/A    |
| Final R indexes [all data]              | R1 = 0.1037, wR2 = 0.1367 |
| Goodness-of-fit on $F^2$                | 1.044                     |



**Table S.I.2.** X-ray crystallography data for compound **4aab** (CCDC No. 1031133).

|   |                      |
|---|----------------------|
| Empirical formula                           | $C_{21}H_{15}N_5O_2$ |
| Formula weight                              | 369.39               |
| Crystal system                              | Monoclinic           |
| Space group                                 | $P2_1/n$             |
| $a(\text{\AA})$                             | 10.0071(13)          |
| $b(\text{\AA})$                             | 22.038(3)            |
| $c(\text{\AA})$                             | 8.2460(11)           |
| $\alpha(^{\circ})$                          | 90.00                |
| $\beta(^{\circ})$                           | 98.552(12)           |
| $\gamma(^{\circ})$                          | 90.00                |
| Volume ( $\text{\AA}^3$ )                   | 1798.3(4)            |
| $\rho$ (calculated) ( $\text{mg mm}^{-3}$ ) | 1.3642               |
| T(K)  | 291.76(10)           |

|   |                           |
|---|---------------------------|
| Absorption coefficient ( $\mu/\text{mm}^{-1}$ ) | 0.092                     |
| Total reflection collected                      | 7788                      |
| Independent reflection                          | 4087                      |
| $\theta$ range ( $^\circ$ )                     | 7.04 to 57.56             |
| Final R Indexes [ $1 \geq 2\sigma(I)$ ]         | R1 = 0.0563, wR2 = 0.1574 |
| Final R indexes [all data]                      | R1 = 0.0726, wR2 = 0.1719 |
| Goodness-of-fit on $F^2$                        | 1.213                     |



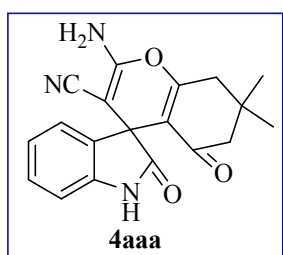
**Table S.I.3.** X-ray crystallography data for compound **4caa** (CCDC No. 1032132).

|                       |  |
|-----------------------|--|
| Empirical formula     | $\text{C}_{23}\text{H}_{16}\text{N}_2\text{O}_3$ |
| Formula weight        | 370.41   |
| Crystal system        | Monoclinic                                       |
| Space group           | $P2_1/n$   |
| $a$ ( $\text{\AA}$ )  | 8.7800(4)  |
| $b$ ( $\text{\AA}$ )  | 11.9326(6)                                       |
| $c$ ( $\text{\AA}$ )  | 17.9072(11)                                      |
| $\alpha$ ( $^\circ$ ) | 90.00  |
| $\beta$ ( $^\circ$ )  | 94.842(5)  |

|   |                           |
|---|---------------------------|
| $\gamma(^{\circ})$                              | 90.00                     |
| Volume ( $\text{\AA}^3$ )                       | 1869.39(18)               |
| $\rho$ (calculated) ( $\text{mg mm}^{-3}$ )     | 1.3160                    |
| T(K)  | 291.7(3)                  |
| Absorption coefficient ( $\mu/\text{mm}^{-1}$ ) | 0.088                     |
| Total reflection collected                      | 8306                      |
| Independent reflection                          | 4262                      |
| $\theta$ range ( $^{\circ}$ )                   | 6.36 to 57.58             |
| Final R Indexes [ $1 \geq 2\sigma(I)$ ]         | R1 = 0.0524, wR2 = N/A    |
| Final R indexes [all data]                      | R1 = 0.0903, wR2 = 0.1356 |
| Goodness-of-fit on $F^2$                        | 1.028                     |

## SPECTRAL DATA

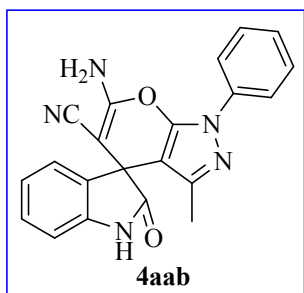
### 1. Compound 4aaa



White solid. IR (KBr): 3381, 3314, 2960, 2926, 2192, 1682, 1656, 1055  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta$  = 10.39 (s, 1H), 7.22 (s, 2H), 7.14 (t,  $J = 7.4$  Hz, 1H), 6.97 (d,  $J = 7.2$  Hz, 1H), 6.89 (t,  $J = 7.4$  Hz, 1H), 6.78 (d,  $J = 7.6$  Hz, 1H), 2.55 (d,  $J = 5.2$  Hz, 2H), 2.18-2.05 (m, 2H), 1.01 (s, 3H), 0.98 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):

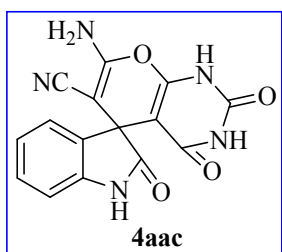
$\delta = 195.3, 178.4, 164.6, 159.2, 142.5, 134.8, 128.6, 123.4, 122.1, 117.8, 111.2, 109.6, 57.8, 50.4, 47.2, 32.4, 28.0, 27.4$ . ESI- MS:  $m/z$  336  $[M + H]^+$ . Anal. Calcd for  $C_{19}H_{17}N_3O_3$ : C, 68.05; H, 5.11; N, 12.53. Found: C, 67.88; H, 5.25; N, 12.59.

## 2. Compound 4aab



White solid. IR (KBr): 3461, 3296, 3177, 3071, 2952, 2922, 2196, 1654, 1070  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3 + DMSO-d_6$ , 400 MHz):  $\delta = 10.55$  (s, 1H), 7.78 (d,  $J = 8$  Hz, 2H), 7.48 (t,  $J = 7.6$  Hz, 2H), 7.32-7.23 (m, 2H), 7.12-7.01 (m, 4H), 6.96 (d,  $J = 8$  Hz, 1H), 1.63 (s, 3H).  $^{13}C$  NMR ( $CDCl_3 + DMSO-d_6$ , 400 MHz):  $\delta = 177.5, 160.9, 144.7, 143.9, 141.4, 137.2, 131.9, 128.9, 128.8, 126.0, 124.5, 122.3, 119.9, 117.8, 109.7, 96.0, 56.3, 47.7, 11.6$ . ESI- MS:  $m/z$  370  $[M + H]^+$ . Anal. Calcd for  $C_{21}H_{15}N_5O_2$ : C, 68.28; H, 4.09; N, 18.96. Found: C, 68.48; H, 3.99; N, 18.85.

## 3. Compound 4aac

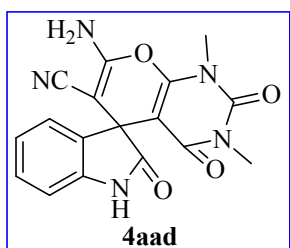


White solid. IR (KBr): 3354, 3306, 3271, 3250, 3146, 3086, 2919, 2850, 2204, 1718, 1693, 1675, 1113  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3 + DMSO-d_6$ , 400 MHz):  $\delta = 12.22$  (brs, 1H), 11.06 (s,



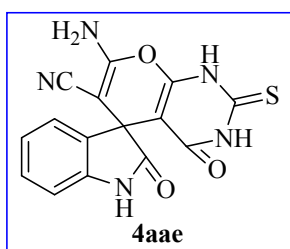
1H), 10.44 (s, 1H), 7.27 (s, 2H), 7.13 (t,  $J = 7.8$  Hz, 1H), 7.06 (d,  $J = 7.2$  Hz, 1H), 6.89 (t,  $J = 7.8$  Hz, 1H), 6.77 (d,  $J = 7.2$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 178.1$ , 161.8, 158.7, 153.7, 149.7, 142.5, 133.8, 128.7, 123.9, 122.1, 117.3, 109.7, 87.2, 58.2, 47.0. ESI- MS:  $m/z$  324  $[\text{M} + \text{H}]^+$ . Anal. Calcd for  $\text{C}_{15}\text{H}_9\text{N}_5\text{O}_4$ : C, 55.73; H, 2.81; N, 21.66. Found: C, 55.94; H, 2.63; N, 21.73.

#### 4. Compound 4aad



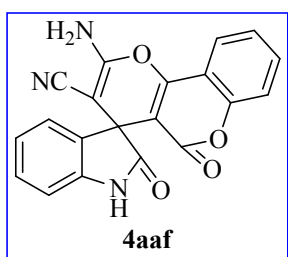
White solid. IR (KBr): 3431, 3077, 2926, 2853, 2230, 1724, 1697, 1682, 1101  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 10.51$  (s, 1H), 7.40 (s, 2H), 7.18 (t,  $J = 7.8$  Hz, 1H), 7.07 (d,  $J = 7.2$  Hz, 1H), 6.95 (t,  $J = 7.8$  Hz, 1H), 6.86 (d,  $J = 8$  Hz, 1H), 3.45 (s, 3H), 3.09 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 177.7$ , 159.2, 157.9, 151.7, 149.4, 141.9, 133.1, 128.2, 123.3, 121.6, 116.5, 109.3, 87.1, 57.7, 47.3, 29.0, 27.4. ESI- MS:  $m/z$  352  $[\text{M} + \text{H}]^+$ . Anal. Calcd for  $\text{C}_{17}\text{H}_{13}\text{N}_5\text{O}_4$ : C, 58.12; H, 3.73; N, 19.93. Found: C, 58.17; H, 3.54; N, 20.16.

#### 5. Compound 4aae



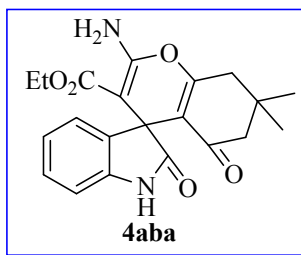
White solid. IR (KBr): 3354, 3306, 3145, 2912, 2833, 2204, 1718, 1686, 1113  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 13.59$  (brs, 1H), 12.37 (s, 1H), 10.47 (s, 1H), 7.19 (t,  $J = 8$  Hz, 1H), 7.09-7.05 (m, 3H), 6.97 (t,  $J = 8$  Hz, 1H), 6.85 (d,  $J = 7.4$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 177.1, 173.9, 158.9, 158.0, 152.5, 142.0, 132.7, 128.3, 123.5, 121.6, 116.6, 109.2, 91.4, 57.4, 46.5$ . ESI- MS:  $m/z$  340  $[\text{M} + \text{H}]^+$ . Anal. Calcd for  $\text{C}_{15}\text{H}_9\text{N}_5\text{O}_3\text{S}$ : C, 53.09; H, 2.67; N, 20.64. Found: C, 52.93; H, 2.65; N, 20.72.

## 6. Compound 4aaf



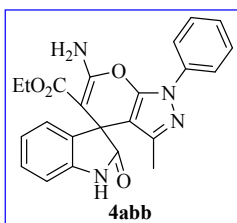
White solid. IR (KBr): 3360, 3297, 3254, 3060, 2924, 2853, 2207, 1711, 1677, 1083  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 10.69$  (s, 1H), 7.98 (d,  $J = 7.6$  Hz, 1H), 7.75 (t,  $J = 8$  Hz, 1H), 7.61 (s, 2H), 7.51 (t,  $J = 7.4$  Hz, 1H), 7.44 (d,  $J = 8.8$  Hz, 1H), 7.23 (t,  $J = 7.8$  Hz, 1H), 7.15 (d,  $J = 7.2$  Hz, 1H), 6.96 (t,  $J = 7.4$  Hz, 1H), 6.89 (d,  $J = 8.8$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 177.1, 158.4, 158.1, 155.0, 152.0, 142.1, 133.3, 132.9, 128.7, 124.6, 123.7, 122.7, 121.9, 116.8, 116.4, 112.4, 109.4, 101.3, 56.9, 47.5$ . ESI- MS:  $m/z$  358  $[\text{M} + \text{H}]^+$ . Anal. Calcd for  $\text{C}_{20}\text{H}_{11}\text{N}_3\text{O}_4$ : C, 67.23; H, 3.10; N, 11.76. Found: C, 67.19; H, 3.01; N, 11.61.

## 7. Compound 4aba



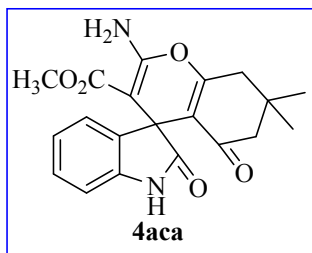
White solid. IR (KBr): 3372, 3241, 3181, 2926, 2849, 1714, 1688, 1670, 1053  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 10.01$  (s, 1H), 7.59 (brs, 2H), 7.06 (t,  $J = 7.6$  Hz, 1H), 6.85 (d,  $J = 7.2$  Hz, 1H), 6.80 (t,  $J = 7.6$  Hz, 1H), 6.74 (d,  $J = 8$  Hz, 1H), 3.80-3.75 (m, 2H), 2.56-2.42 (dd,  $J = 18, 34.8$  Hz, 2H), 2.18-2.02 (dd,  $J = 15.4, 48$  Hz, 2H), 1.08 (s, 3H), 1.00 (s, 3H), 0.87 (t,  $J = 7$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 194.3, 179.9, 167.5, 162.1, 159.0, 143.8, 135.8, 126.9, 122.0, 120.4, 113.1, 108.1, 76.2, 58.7, 50.6, 46.5, 31.4, 27.9, 26.7, 12.9$ . ESI- MS:  $m/z$  383  $[\text{M} + \text{H}]^+$ . Anal. Calcd for  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_5$ : C, 65.96; H, 5.80; N, 7.33. Found: C, 66.20; H, 5.68; N, 7.20.

## 8. Compound 4abb



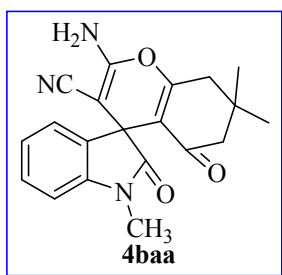
White solid. IR (KBr): 3370, 3210, 3038, 2905, 2849, 1701, 1642, 1035  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 10.28$  (s, 1H), 7.99 (s, 2H), 7.68 (d,  $J = 8.8$  Hz, 2H), 7.36 (t,  $J = 7.8$  Hz, 2H), 7.18 (t,  $J = 7.2$  Hz, 1H), 7.03 (t,  $J = 7.4$  Hz, 1H), 6.82-6.72 (m, 3H), 3.69-3.63 (m, 2H), 1.52 (s, 3H), 0.68 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 179.5, 167.9, 161.3, 144.2, 143.8, 141.8, 137.3, 135.6, 128.8, 127.3, 125.8, 122.8, 121.57, 121.52, 119.8, 108.7, 97.9, 74.6, 58.8, 12.9, 11.6$ . ESI- MS:  $m/z$  417  $[\text{M} + \text{H}]^+$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{20}\text{N}_4\text{O}_4$ : C, 66.34; H, 4.84; N, 13.45. Found: C, 66.18; H, 4.77; N, 13.39.

## 9. Compound 4aca



White solid. IR (KBr): 3355, 3242, 1715, 1686, 1054  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 10.15$  (bs, 1H), 7.81 (bs, 2H), 7.04-6.75 (m, 3H), 6.71 (d,  $J = 8.4$  Hz, 1H), 3.27 (s, 3H), 2.63-2.45 (m, 2H), 2.19 (d,  $J = 16.0$  Hz, 1H), 2.04 (d,  $J = 16.0$  Hz, 1H), 1.05 (s, 3H), 0.97 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 100 MHz):  $\delta = 193.9, 179.4, 167.1, 161.7, 158.4, 143.0, 135.1, 126.5, 121.5, 119.9, 112.5, 107.5, 75.8, 50.0, 49.4, 46.0, 30.9, 27.3, 26.1$ . ESI- MS:  $m/z$  369  $[\text{M} + \text{H}]^+$ . Anal. Calcd for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_5$ : C, 65.21; H, 5.47; N, 7.60. Found: C, 65.29; H, 5.64; N, 7.35.

## 10. Compound 4baa

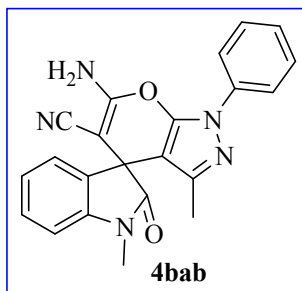


White solid. IR (KBr): 3435, 3172, 2960, 2931, 2187, 1684, 1667, 1054  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 7.28$ -7.24 (m, 1H), 7.02-6.98 (m, 2H), 6.90-6.88 (m, 3H), 3.22 (s, 3H), 2.55 (d,  $J = 1.2$  Hz, 2H), 2.19-2.08 (dd,  $J = 16.4, 27.2$  Hz, 2H), 1.10 (s, 3H), 1.06 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 194.5, 176.4, 163.8, 158.8, 143.3, 133.3, 128.2, 122.5, 122.2, 117.0, 110.8, 107.8, 57.1, 50.0, 46.4, 31.8, 27.7, 27.1, 26.1$ .

ESI- MS:  $m/z$  350  $[M + H]^+$ . Anal. Calcd for  $C_{20}H_{19}N_3O_3$ : C, 68.75; H, 5.48; N, 12.03.

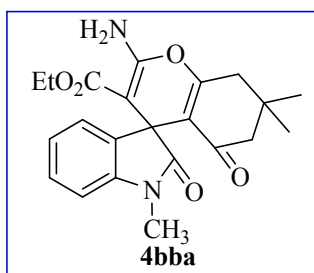
Found: C, 68.46; H, 5.57; N, 12.14.

### 11. Compound 4bab



White solid. IR (KBr): 3359, 3314, 3068, 2956, 2853, 2197, 1657, 1129  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3 + DMSO-d_6$ , 400 MHz):  $\delta$  = 7.79 (d,  $J$  = 8 Hz, 2H), 7.49 (t,  $J$  = 7.8 Hz, 2H), 7.39 (t,  $J$  = 7.6 Hz, 1H), 7.32-7.26 (m, 3H), 7.19 (d,  $J$  = 7.6 Hz, 1H), 7.14 (t,  $J$  = 7.8 Hz, 1H), 7.04 (d,  $J$  = 8.4 Hz, 1H), 3.30 (s, 3H), 1.53 (s, 3H).  $^{13}C$  NMR ( $CDCl_3 + DMSO-d_6$ , 400 MHz):  $\delta$  = 175.7, 161.1, 144.7, 143.8, 142.7, 137.1, 131.1, 129.0, 128.8, 126.0, 124.2, 123.0, 120.0, 117.6, 108.1, 95.8, 56.1, 47.3, 26.2, 11.6. ESI- MS:  $m/z$  384  $[M + H]^+$ . Anal. Calcd for  $C_{22}H_{17}N_5O_2$ : C, 68.92; H, 4.47; N, 18.27. Found: C, 69.06; H, 4.53; N, 18.24.

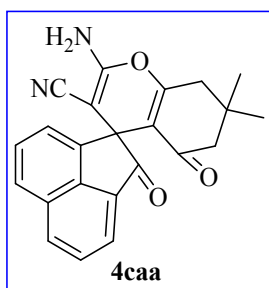
### 12. Compound 4bba



White solid. IR (KBr): 3360, 3275, 2960, 2931, 1696, 1686, 1675, 1054  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3 + DMSO-d_6$ , 400 MHz):  $\delta$  = 7.56 (brs, 2H), 7.20 (t,  $J$  = 7.2 Hz, 1H), 6.93-6.87 (m, 2H), 6.77 (d,  $J$  = 7.2 Hz, 1H), 3.78-3.72 (q,  $J$  = 7.2 Hz, 2H), 3.22 (s, 3H), 2.57-2.44 (dd,  $J$  =

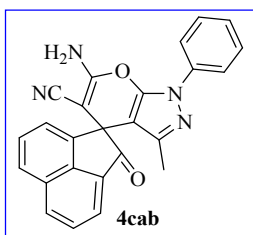
17.2, 31.2 Hz, 2H), 2.18-2.02 (dd,  $J = 16, 46$  Hz, 2H), 1.09 (s, 3H), 1.00 (s, 3H), 0.83 (t,  $J = 7$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 195.0, 178.9, 168.0, 162.6, 159.5, 145.1, 135.0, 127.7, 122.3, 121.7, 113.6, 106.8, 76.5, 59.2, 51.1, 46.6, 31.8, 28.6, 27.2, 26.3, 13.7$ . ESI- MS:  $m/z$  397  $[\text{M} + \text{H}]^+$ . Anal. Calcd for  $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_5$ : C, 66.65; H, 6.10; N, 7.07. Found: C, 66.53; H, 5.92; N, 6.79.

### 13. Compound 4caa



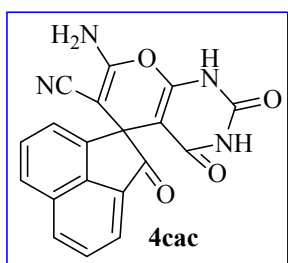
Light yellow solid. IR (KBr): 3370, 3295, 3061, 2954, 2874, 2194, 1718, 1666, 1053  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 8.20$  (d,  $J = 8.4$  Hz, 1H), 7.92-7.87 (m, 2H), 7.82 (t,  $J = 8$  Hz, 1H), 7.65 (t,  $J = 8$  Hz, 1H), 7.35 (d,  $J = 7.6$  Hz, 1H), 7.07 (brs, 2H), 2.61 (s, 2H), 2.14-2.04 (m, 2H), 1.10 (s, 3H), 1.07 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 203.2, 194.8, 164.0, 158.6, 142.9, 140.5, 132.3, 131.0, 129.6, 128.4, 128.0, 124.2, 121.1, 119.4, 117.3, 112.1, 58.2, 50.8, 49.8, 31.8, 27.6, 27.3$ . ESI- MS:  $m/z$  371  $[\text{M} + \text{H}]^+$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_3$ : C, 74.58; H, 4.90; N, 7.56. Found: C, 74.68; H, 4.95; N, 7.62.

### 14. Compound 4cab

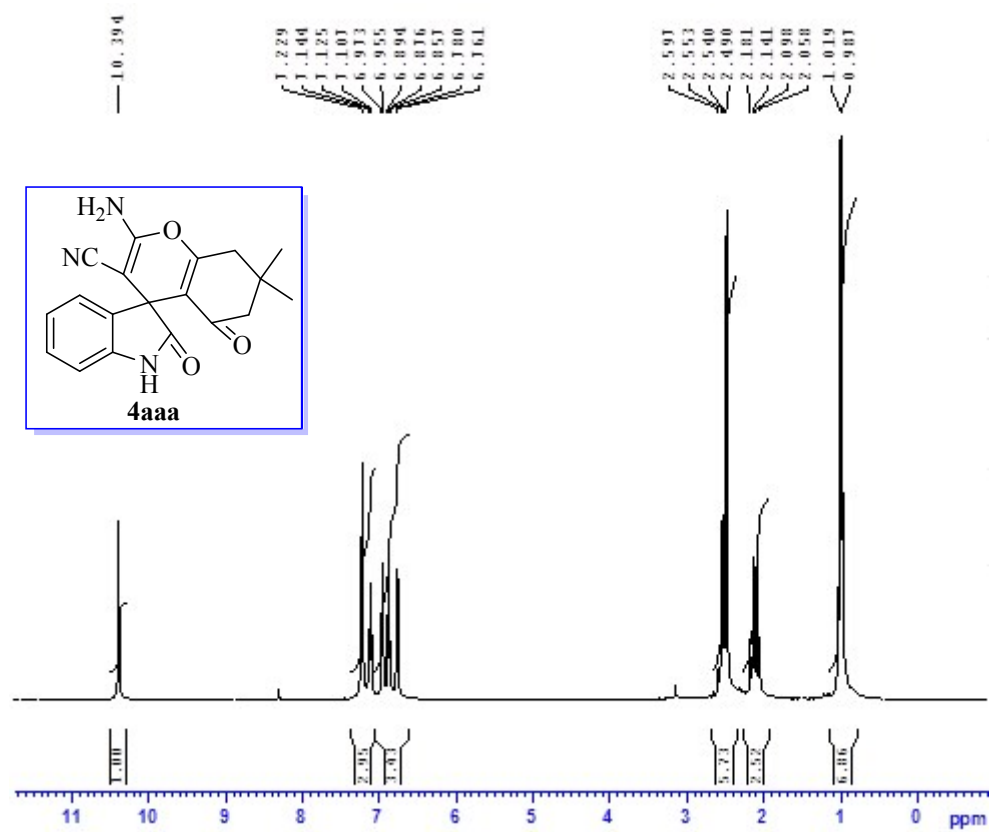


Yellow solid. IR (KBr): 3454, 3310, 3068, 2931, 2853, 2198, 1707, 1073  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 8.38$  (d,  $J = 7.2$  Hz, 1H), 8.08 (t,  $J = 8$  Hz, 2H), 7.93 (t,  $J = 7.4$  Hz, 1H), 7.84-7.78 (m, 3H), 7.56-7.48 (m, 5H), 7.35 (t,  $J = 6.8$  Hz, 1H), 1.10 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 203.1, 161.0, 144.7, 143.8, 141.1, 140.3, 137.2, 132.3, 130.5, 129.9, 129.0, 128.9, 128.5, 128.1, 126.1, 124.9, 122.3, 121.3, 121.2, 120.0, 117.9, 97.0, 57.0, 51.9, 11.9$ . ESI- MS:  $m/z$  405  $[\text{M} + \text{H}]^+$ . Anal. Calcd for  $\text{C}_{25}\text{H}_{16}\text{N}_4\text{O}_2$ : C, 74.25; H, 3.99; N, 13.85. Found: C, 74.12; H, 3.83; N, 14.11.

### 15. Compound 4cac

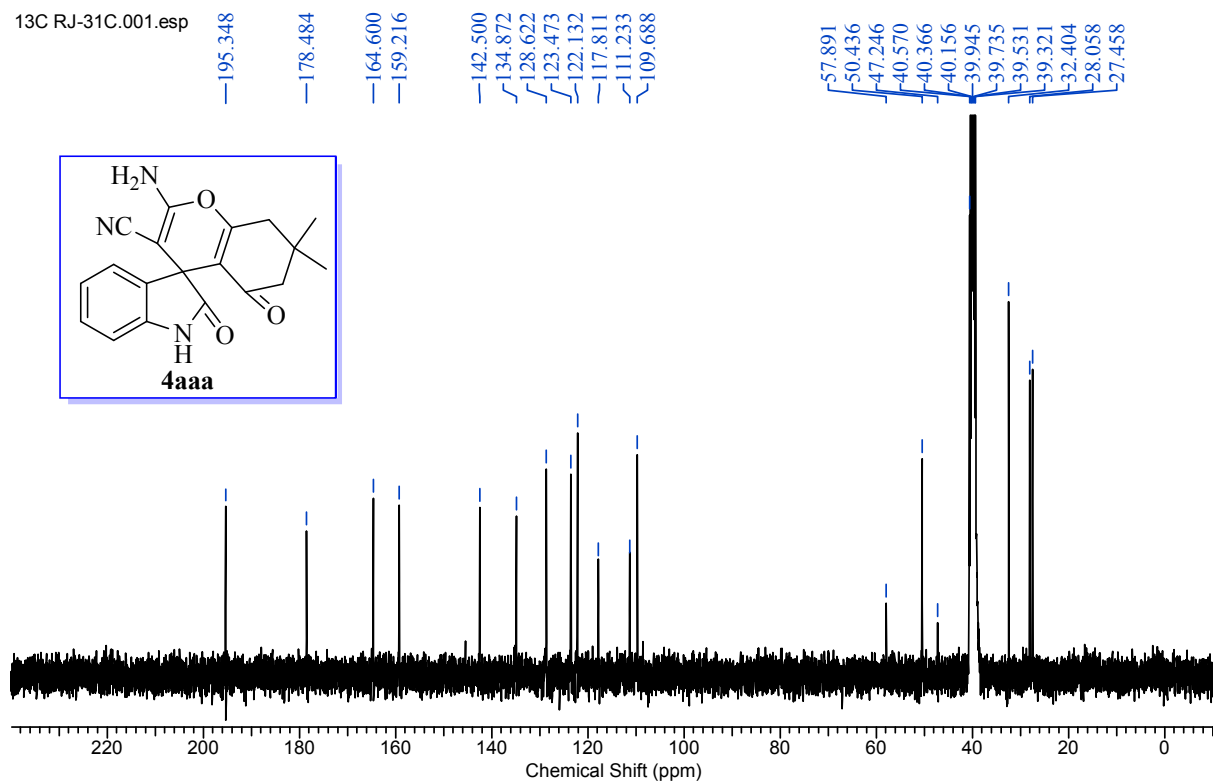


Light yellow solid. IR (KBr): 3377, 3317, 3258, 3210, 2924, 2857, 2203, 1716, 1695, 1681, 1106  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 13.74$  (brs, 1H), 12.28 (s, 1H), 8.35-8.03 (m, 2H), 7.81 (s, 2H), 7.69-7.29 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3 + \text{DMSO-d}_6$ , 400 MHz):  $\delta = 203.4, 161.6, 158.2, 153.3, 149.2, 142.2, 140.9, 131.7, 131.3, 129.7, 128.5, 128.0, 124.4, 121.2, 120.0, 116.9, 87.8, 58.3, 50.5$ . ESI- MS:  $m/z$  359  $[\text{M} + \text{H}]^+$ . Anal. Calcd for  $\text{C}_{19}\text{H}_{10}\text{N}_4\text{O}_4$ : C, 63.69; H, 2.81; N, 15.64. Found: C, 63.83; H, 2.60; N, 15.45.

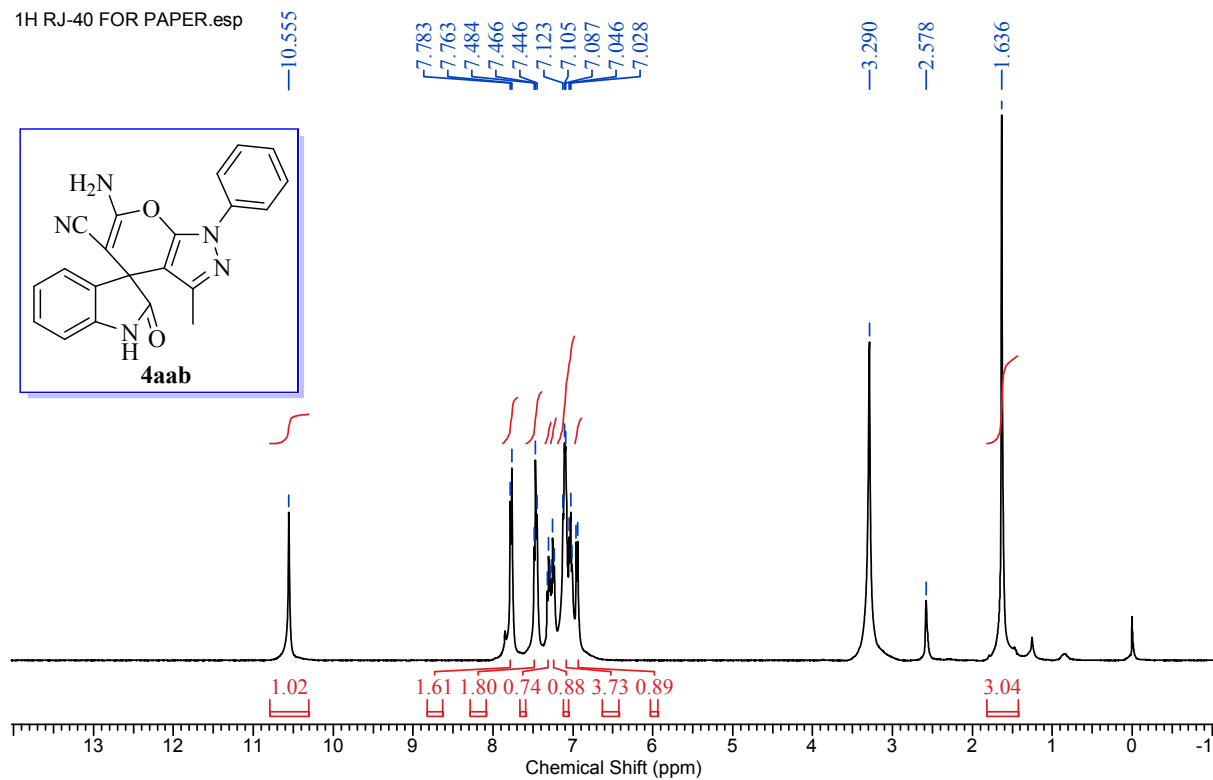
$^1\text{H}$  and  $^{13}\text{C}$ NMR of Compound **4aaa**



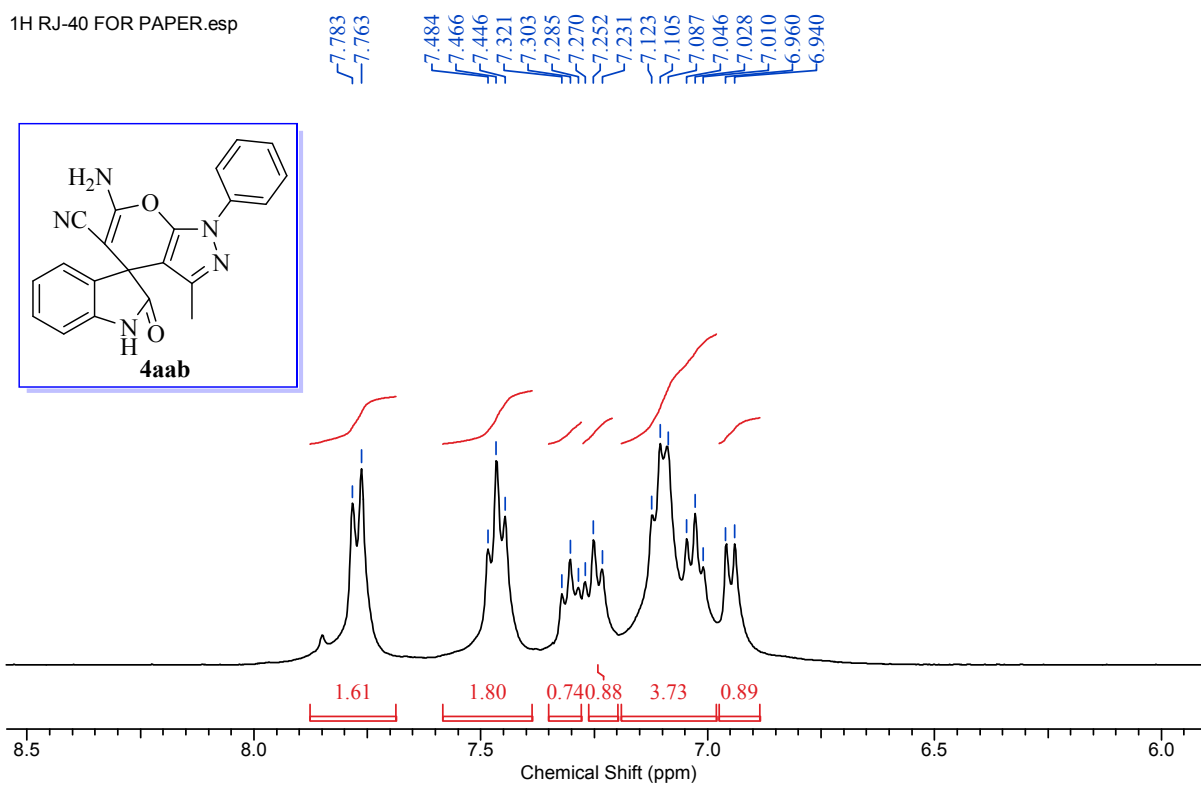
13C RJ-31C.001.esp

<sup>1</sup>H and <sup>13</sup>CNMR of Compound **4aab**

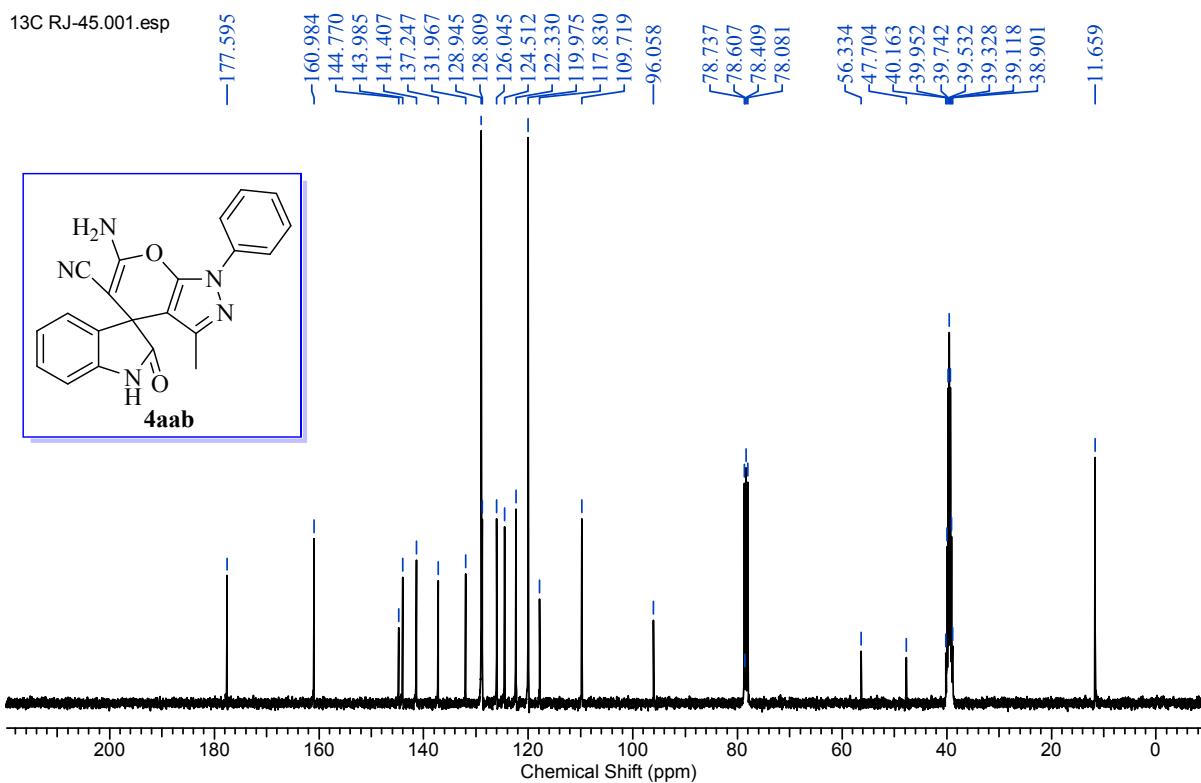
1H RJ-40 FOR PAPER.esp



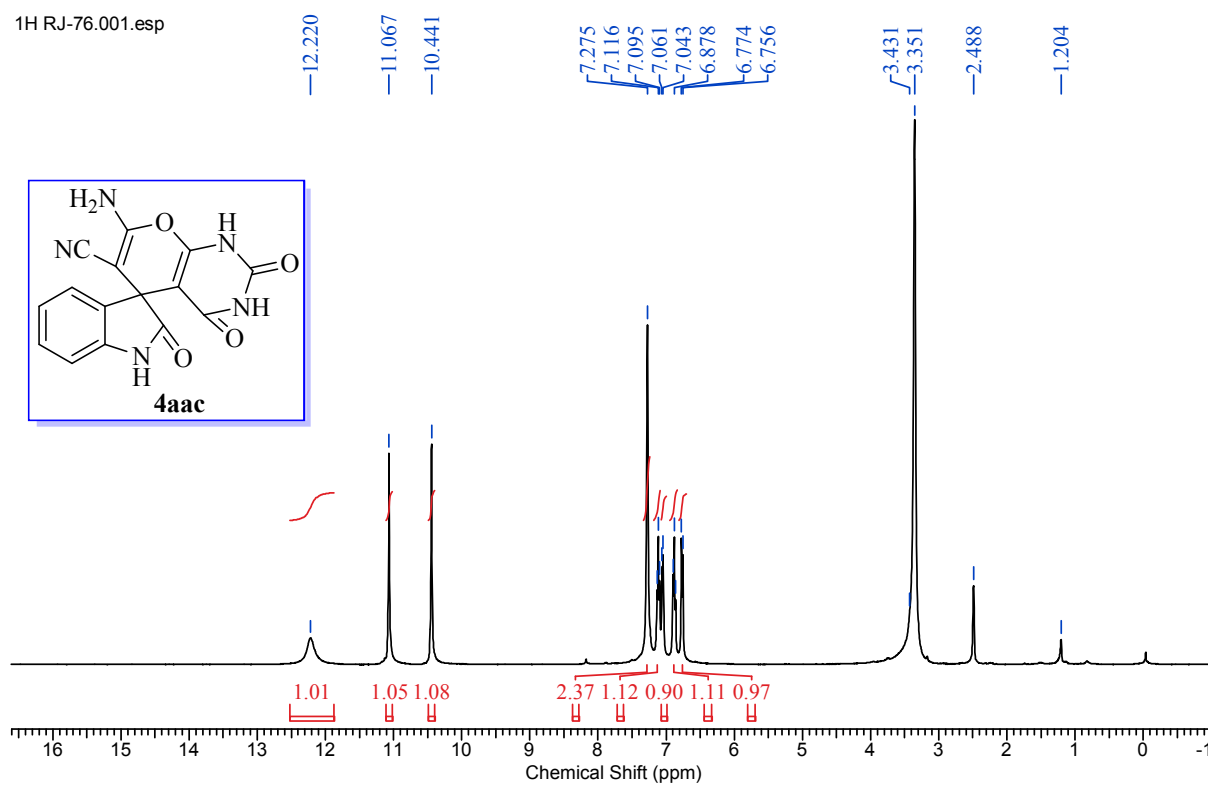
1H RJ-40 FOR PAPER.esp



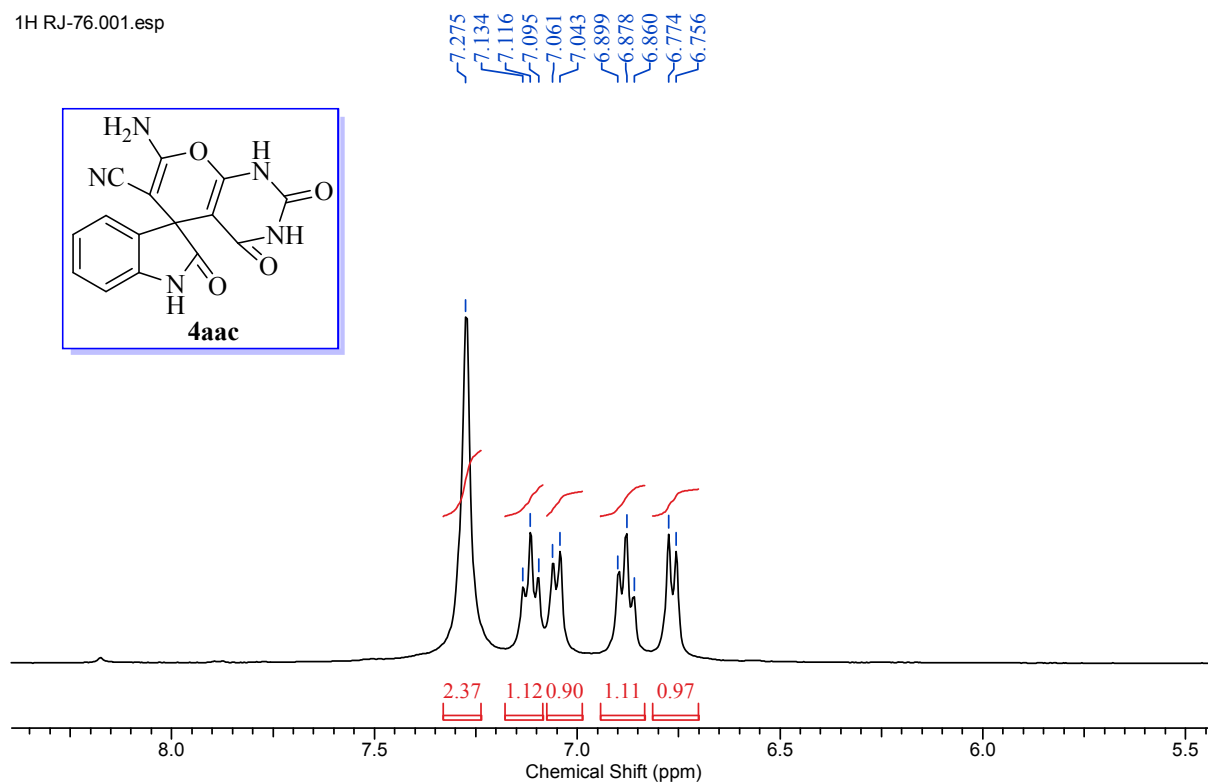
13C RJ-45.001.esp

<sup>1</sup>H and <sup>13</sup>C NMR of Compound **4aac**

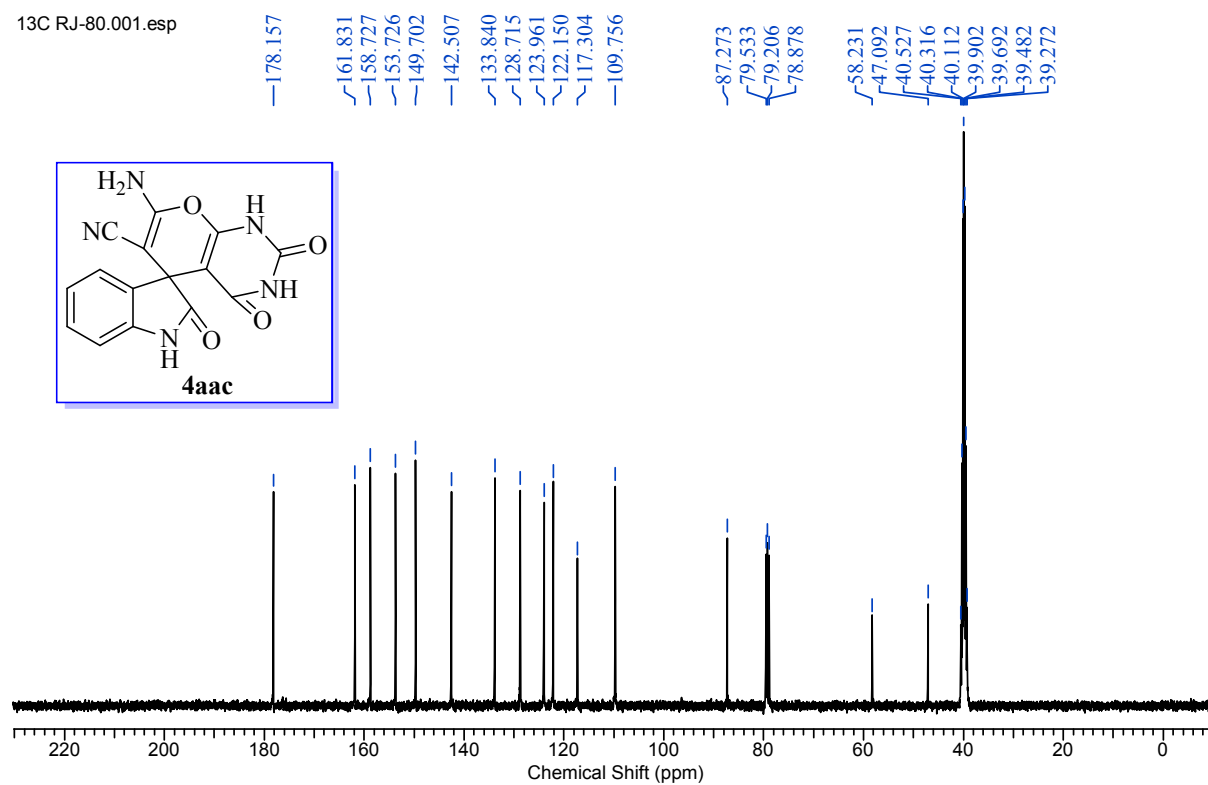
1H RJ-76.001.esp



1H RJ-76.001.esp

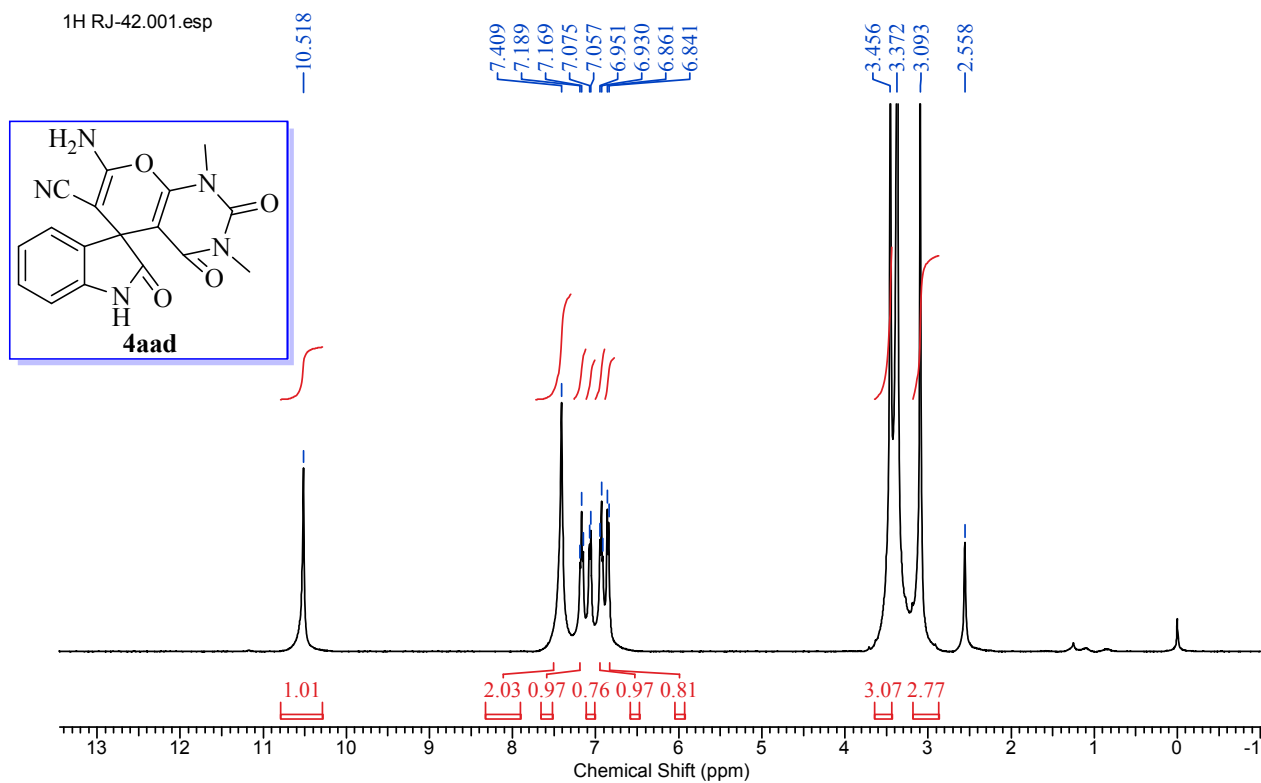


13C RJ-80.001.esp

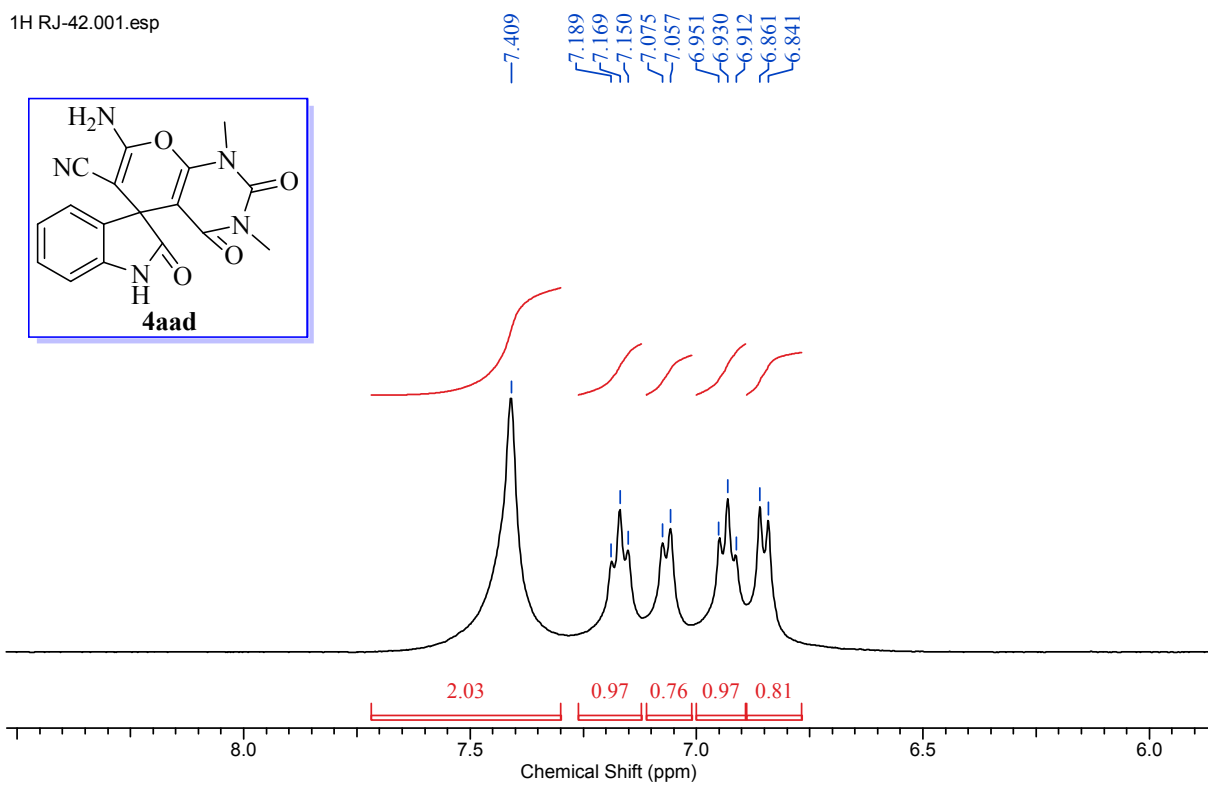


### $^1\text{H}$ and $^{13}\text{C}$ NMR of Compound **4aad**

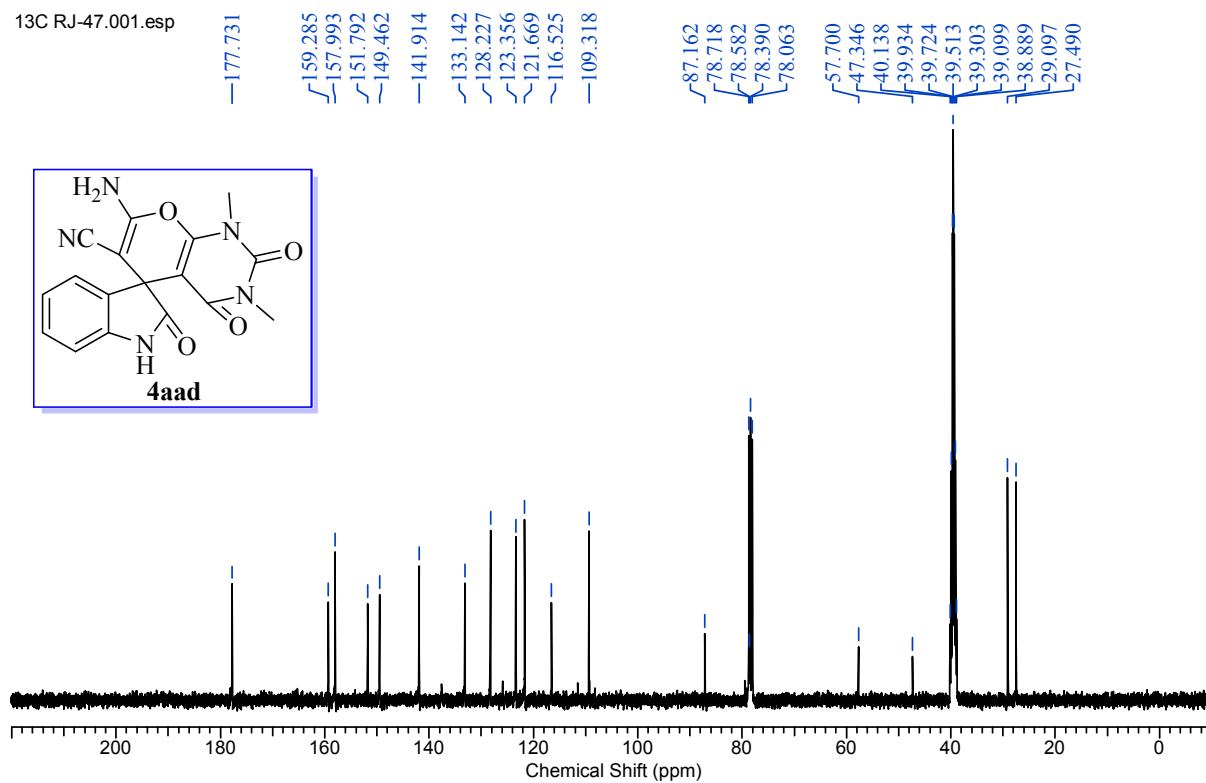
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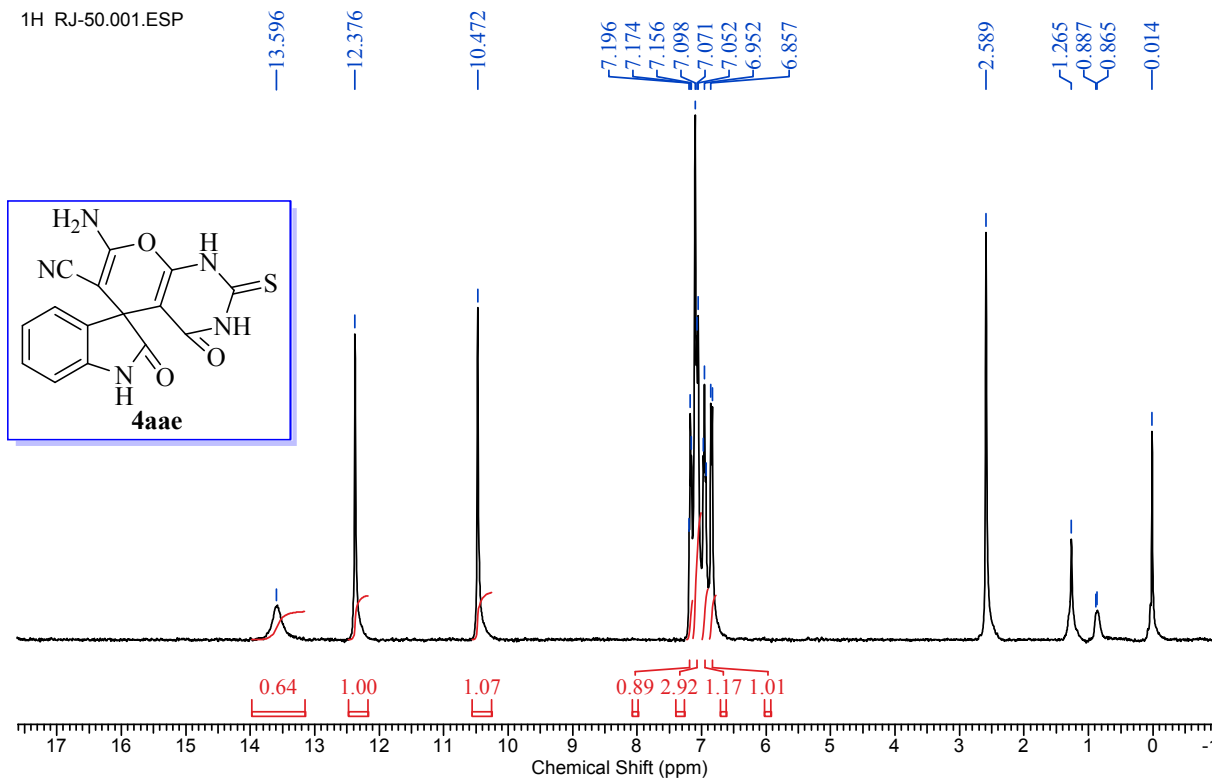
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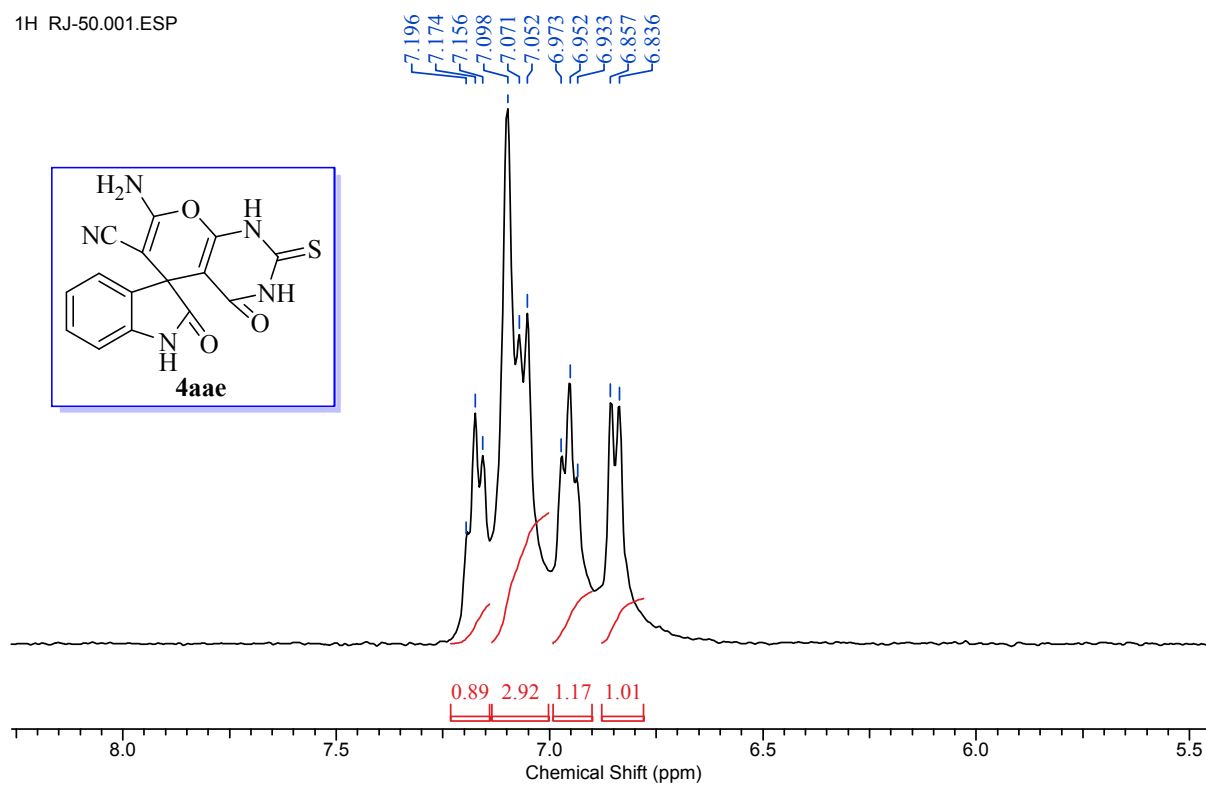
13C RJ-47.001.esp

<sup>1</sup>H and <sup>13</sup>CNMR of Compound **4aae**

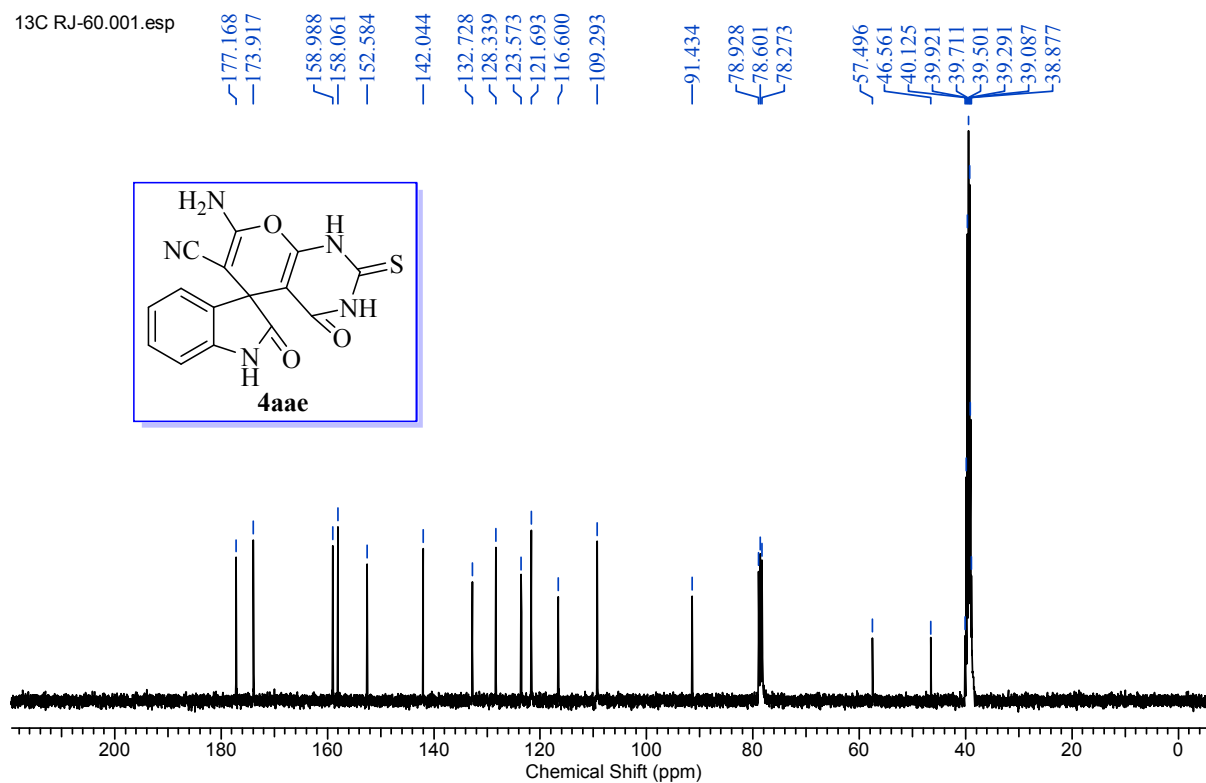
1H RJ-50.001.ESP

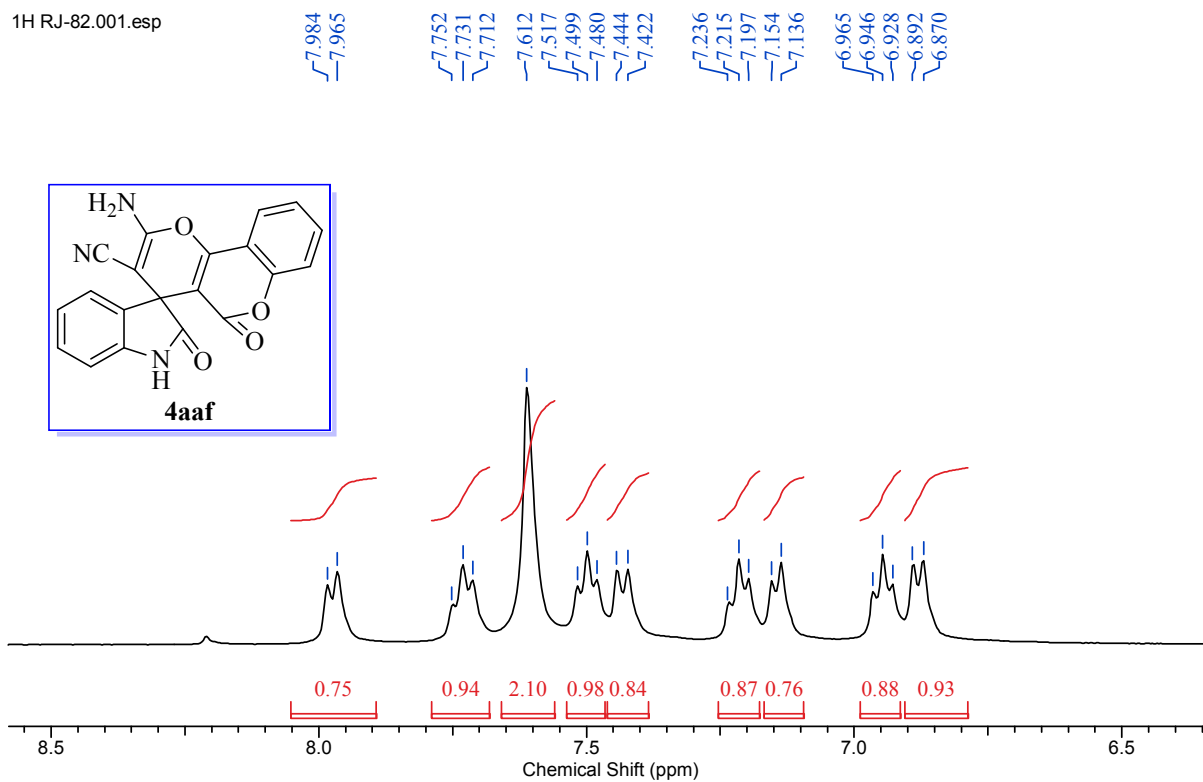
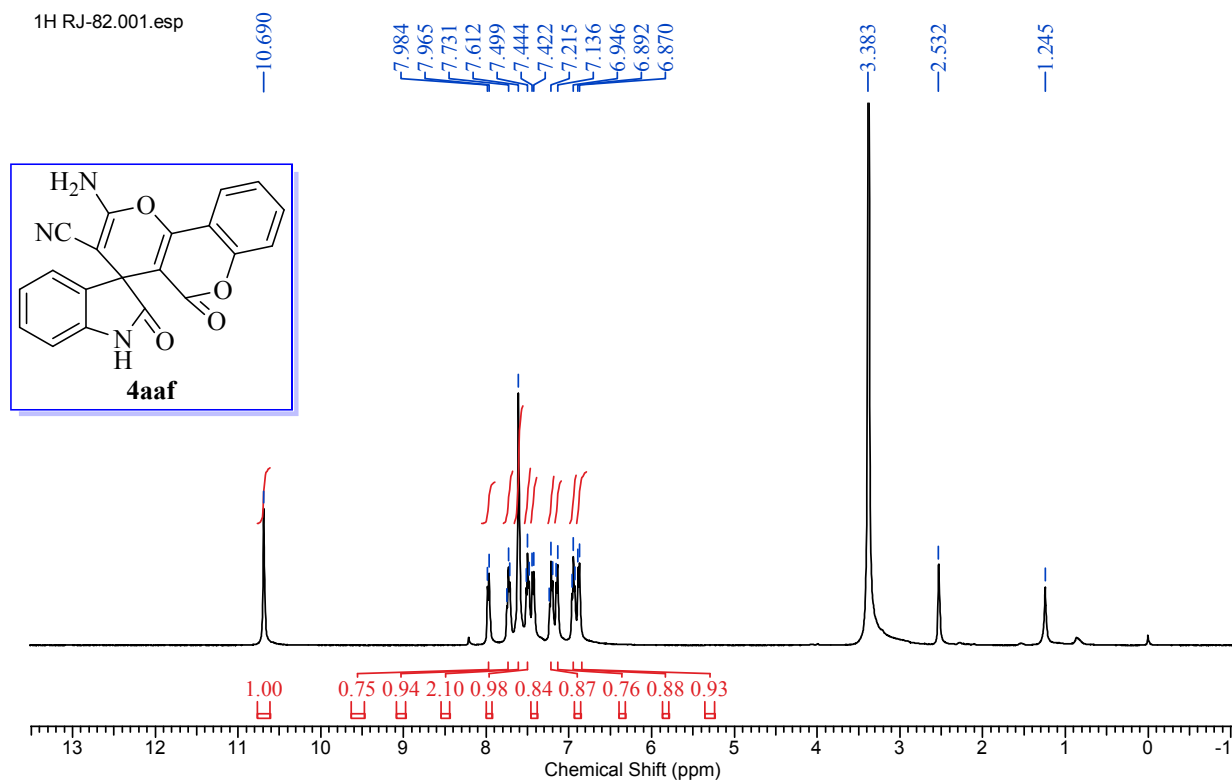


1H RJ-50.001.ESP



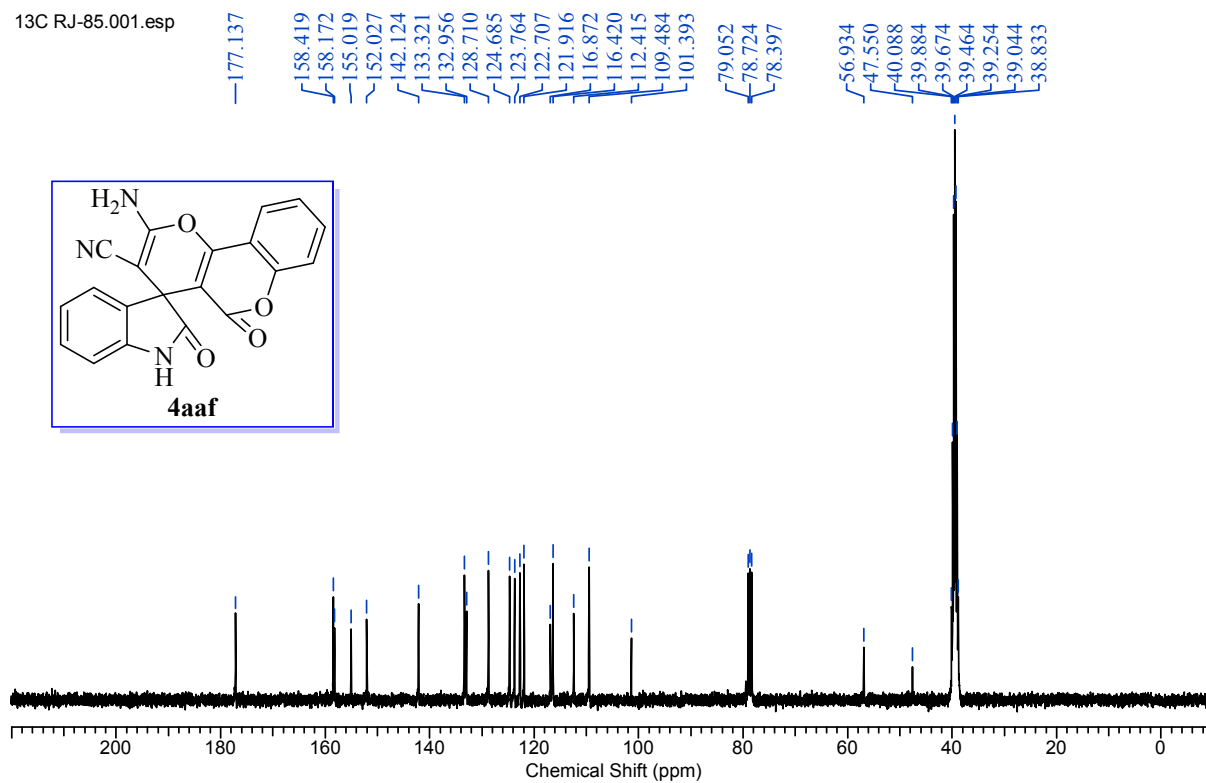
13C RJ-60.001.esp



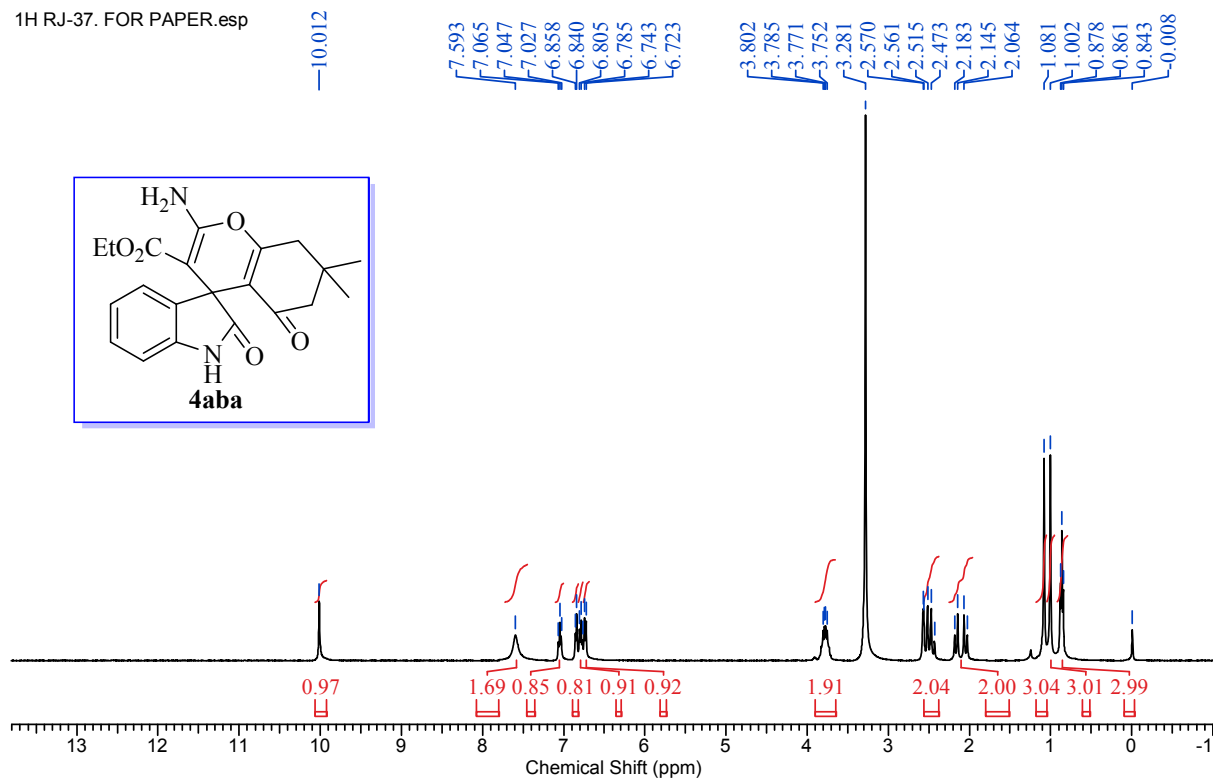
$^1\text{H}$  and  $^{13}\text{C}$ NMR of Compound **4aaf**



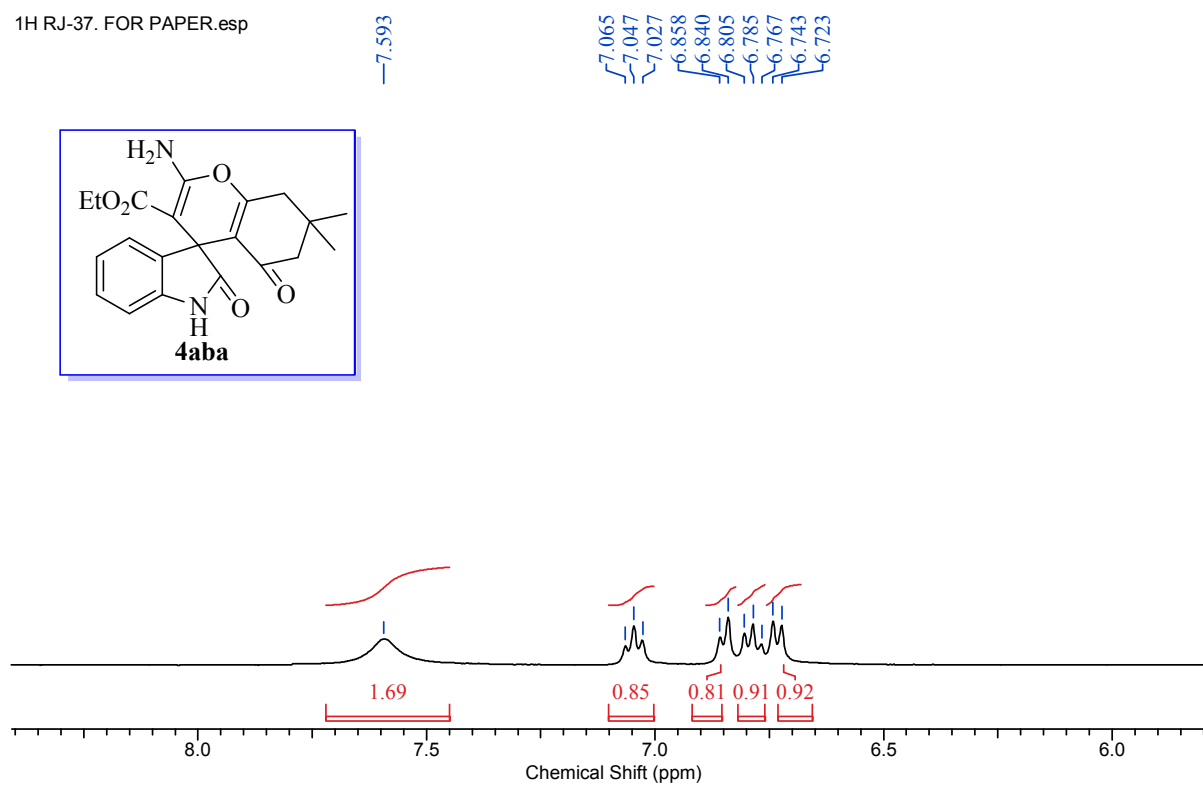
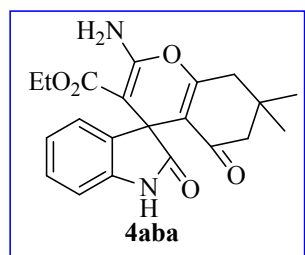
13C RJ-85.001.esp

**<sup>1</sup>H and <sup>13</sup>CNMR of Compound 4aba**

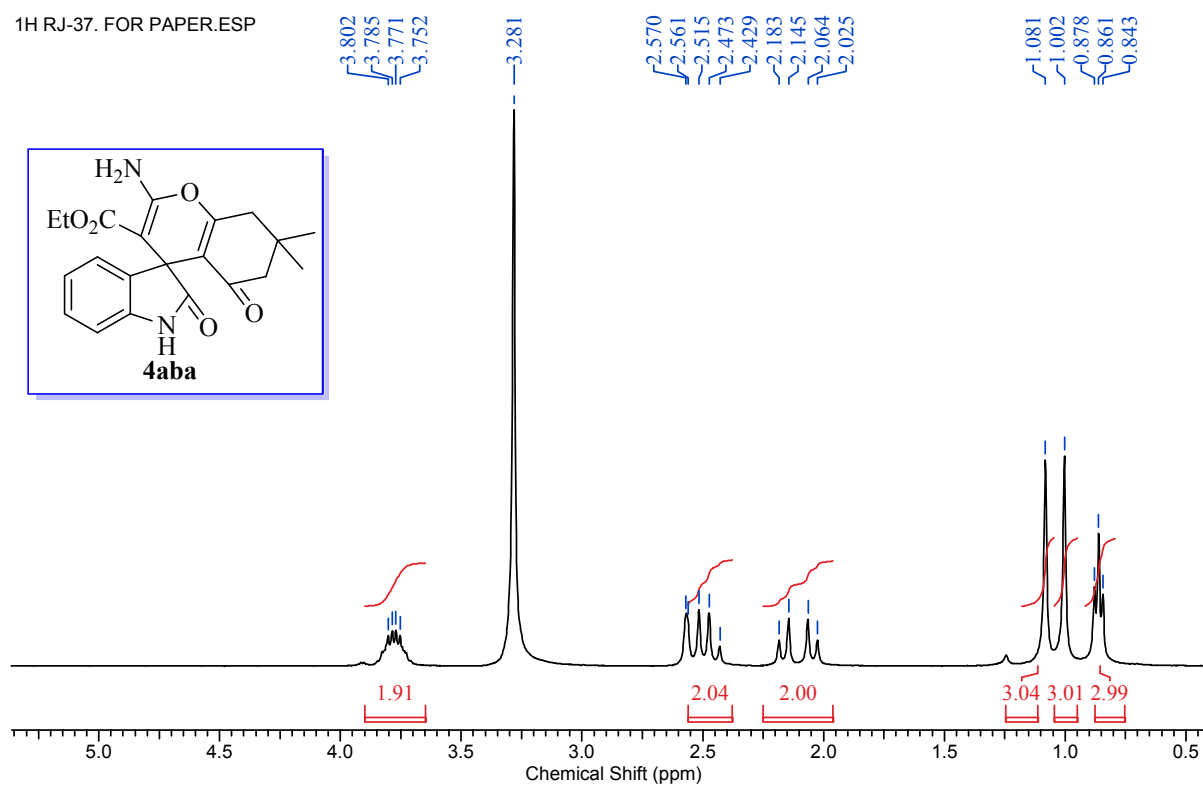
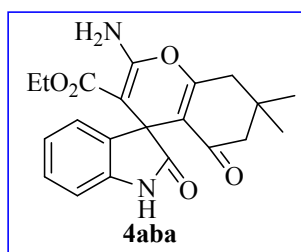
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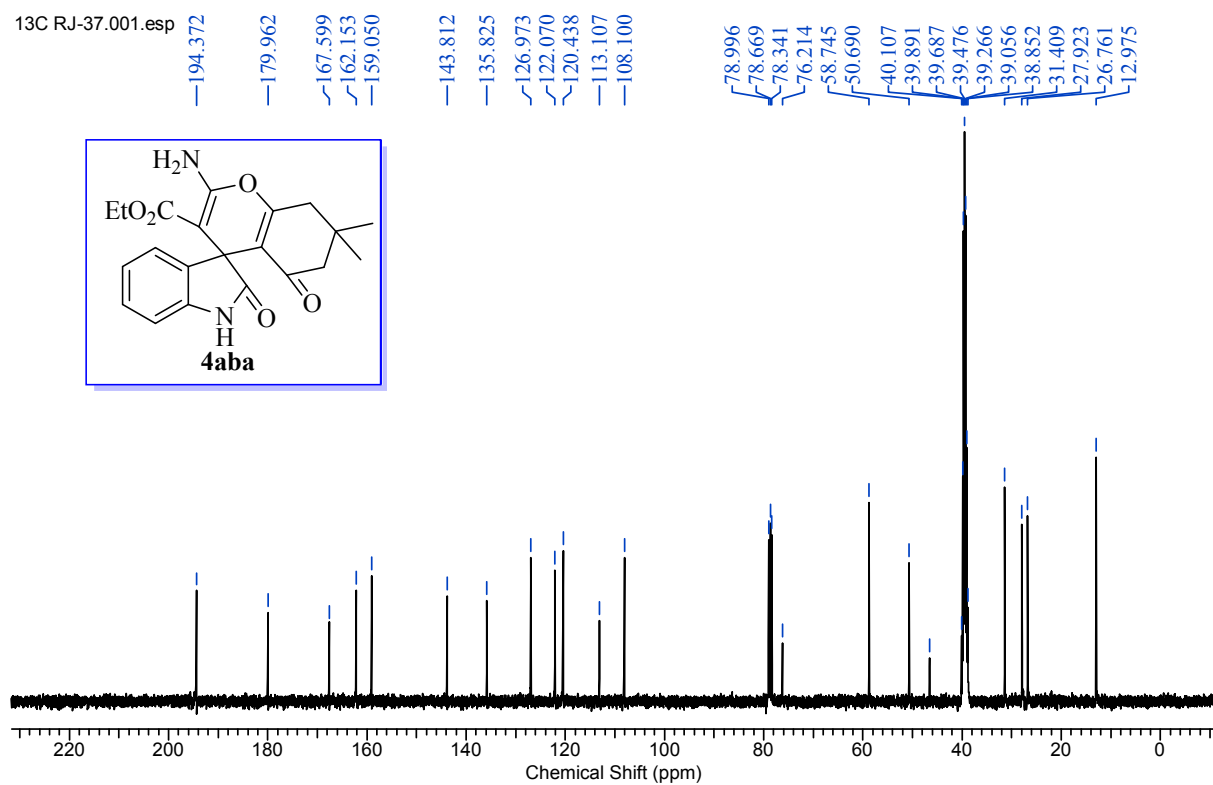
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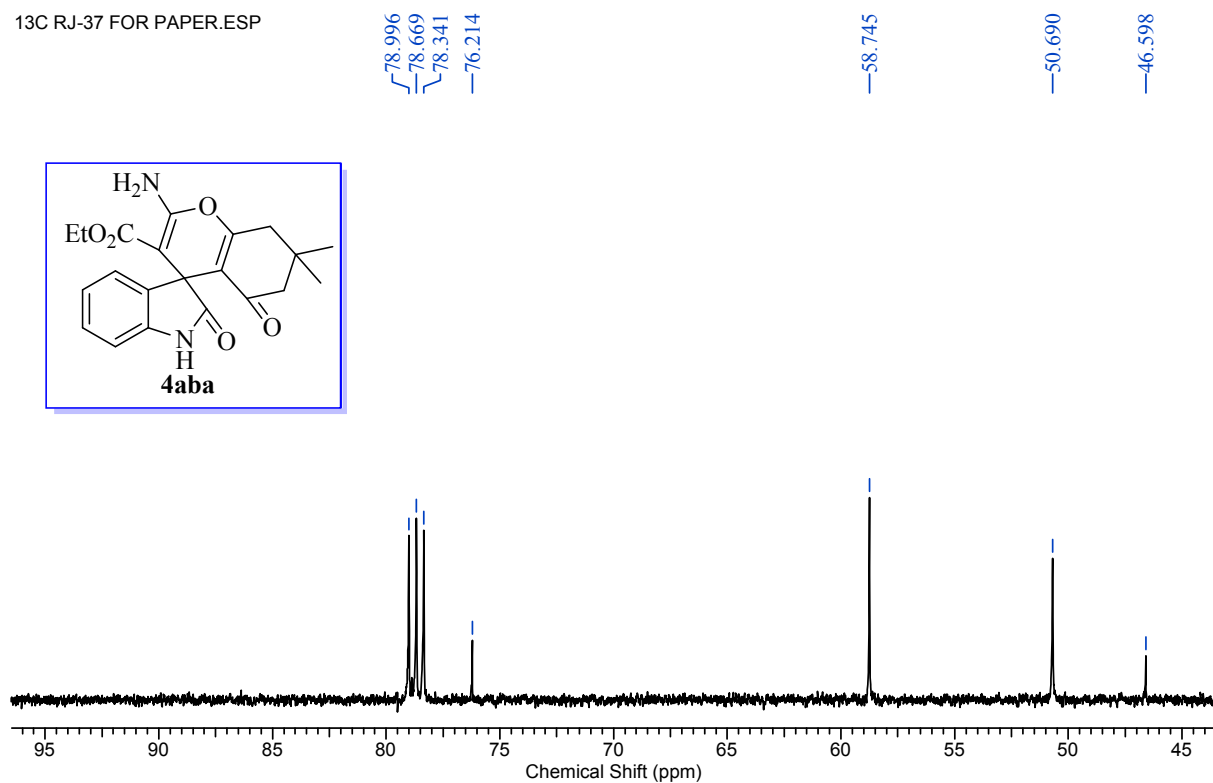
1H RJ-37. FOR PAPER.ESP

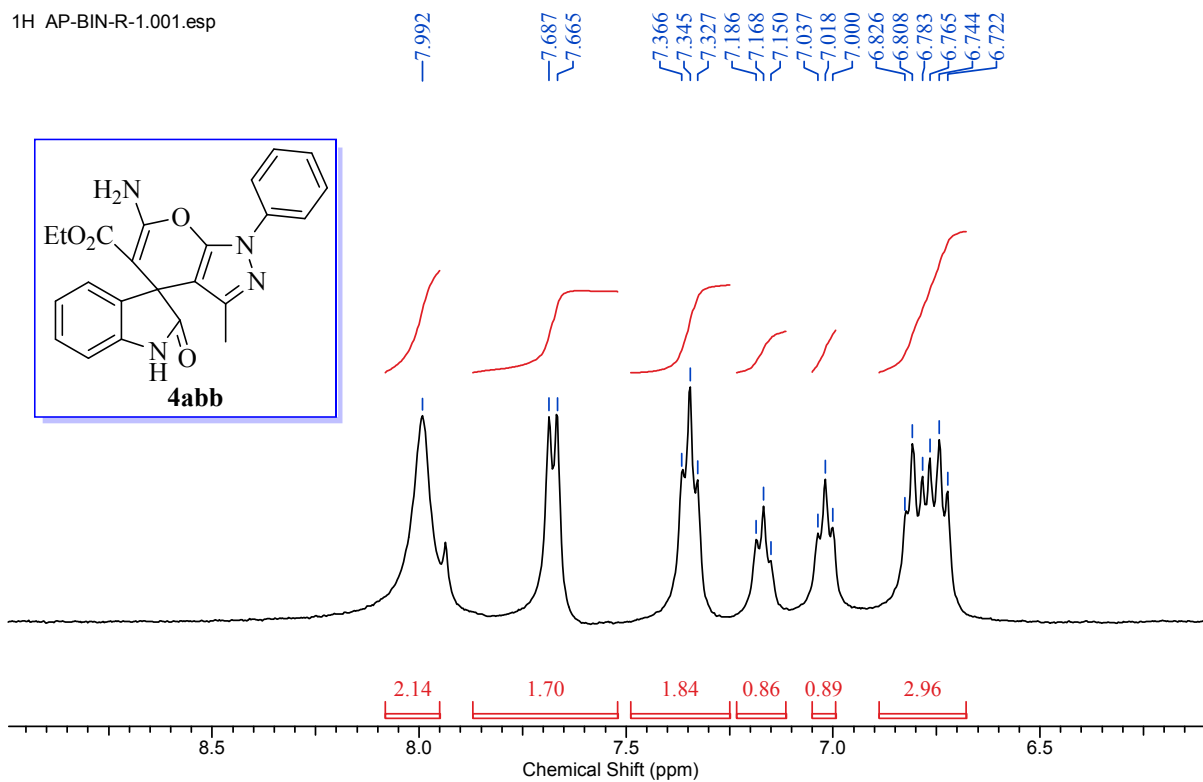
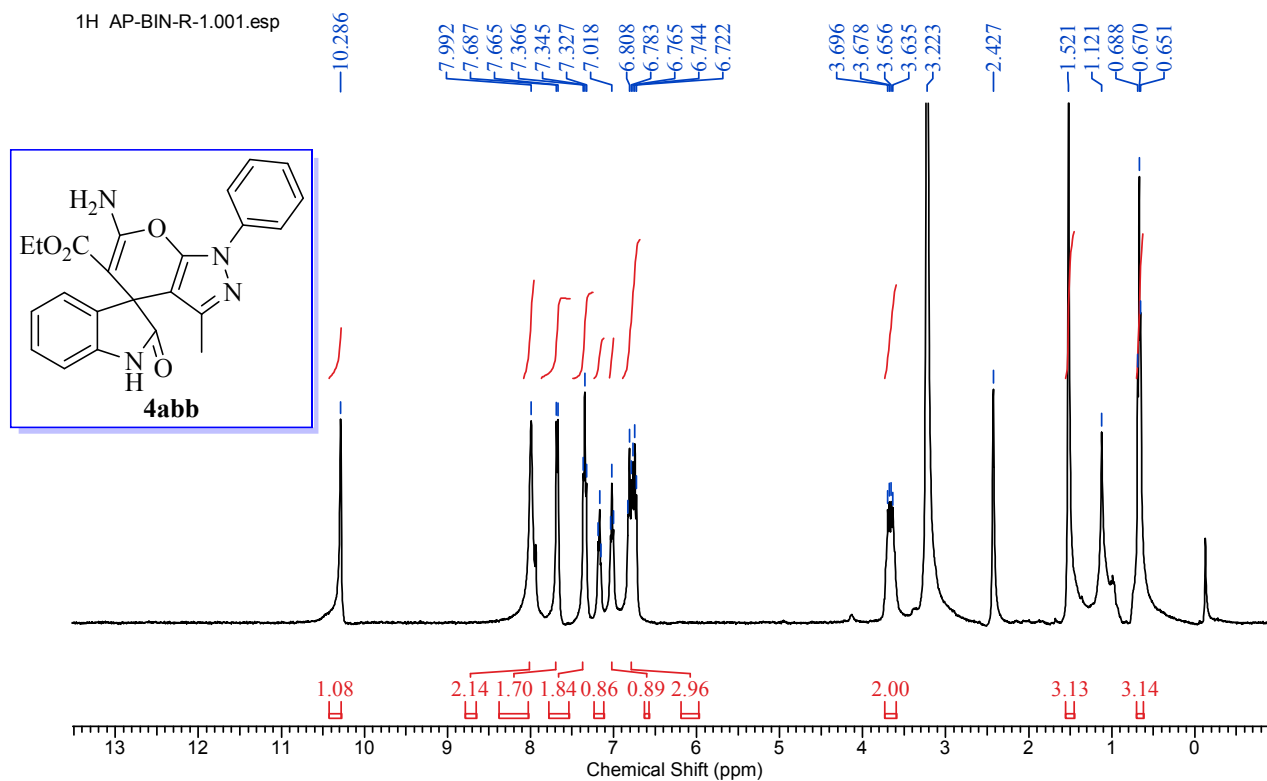


13C RJ-37.001.esp

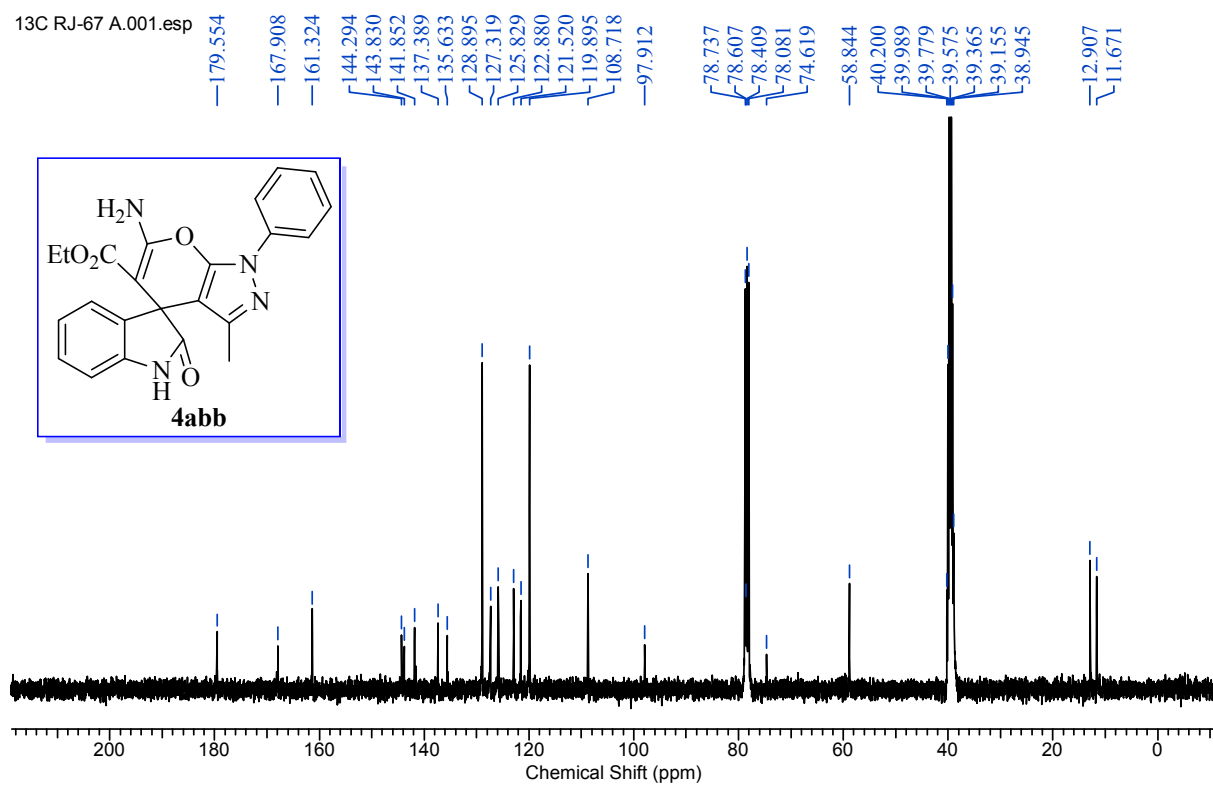


13C RJ-37 FOR PAPER.ESP

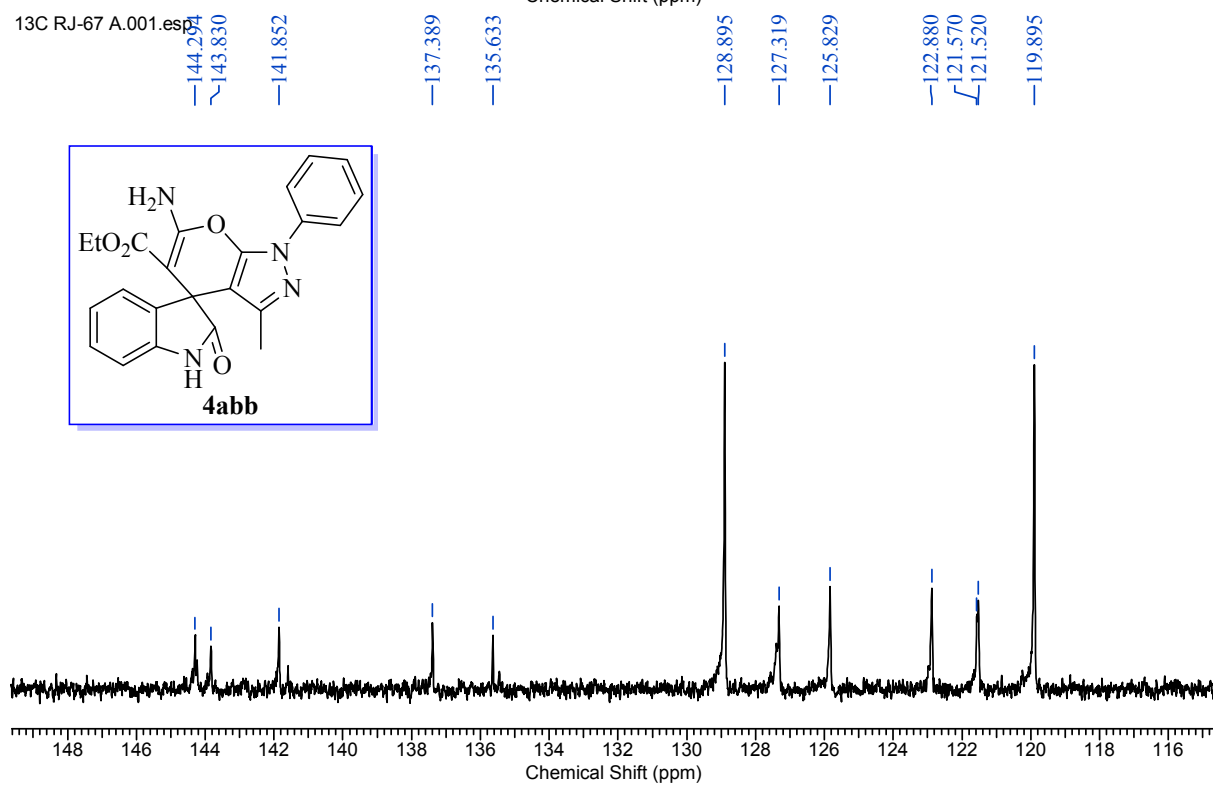


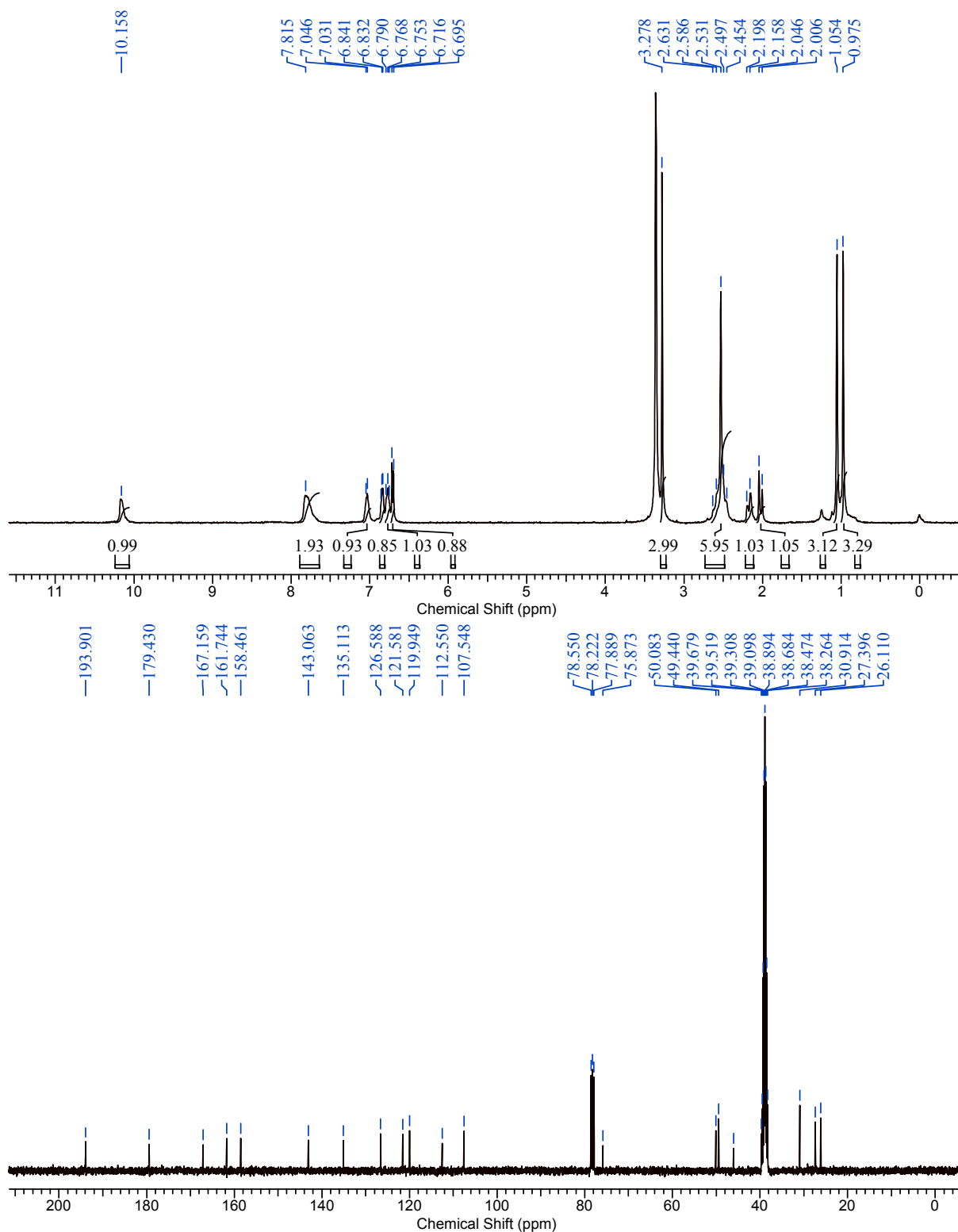
$^1\text{H}$  and  $^{13}\text{C}$ NMR of Compound **4abb**

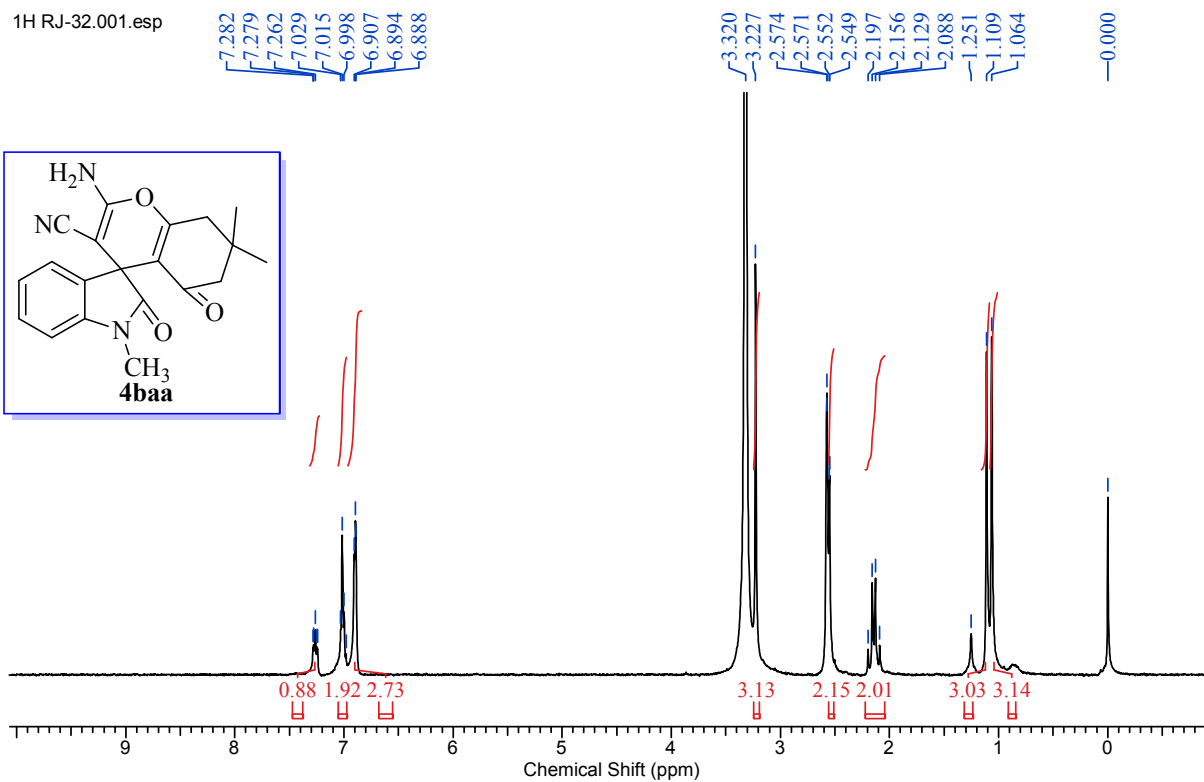
13C RJ-67 A.001.esp



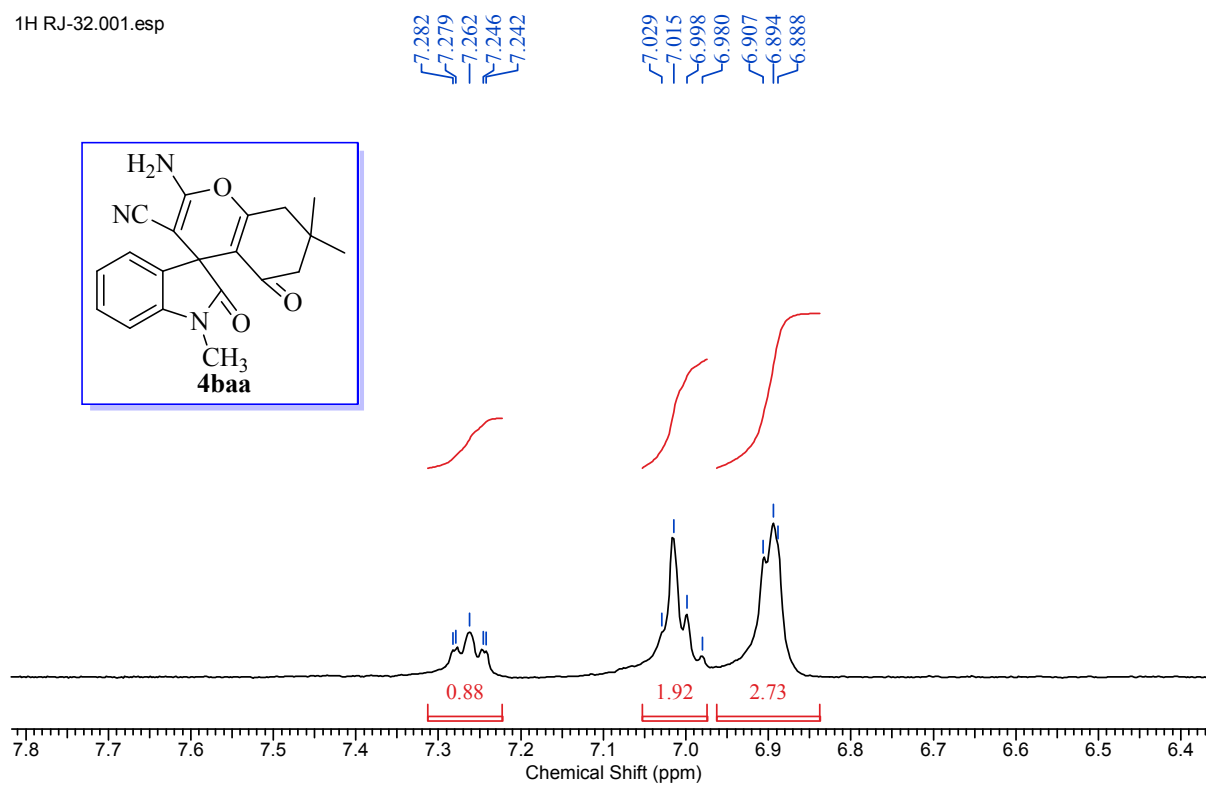
13C RJ-67 A.001.esa



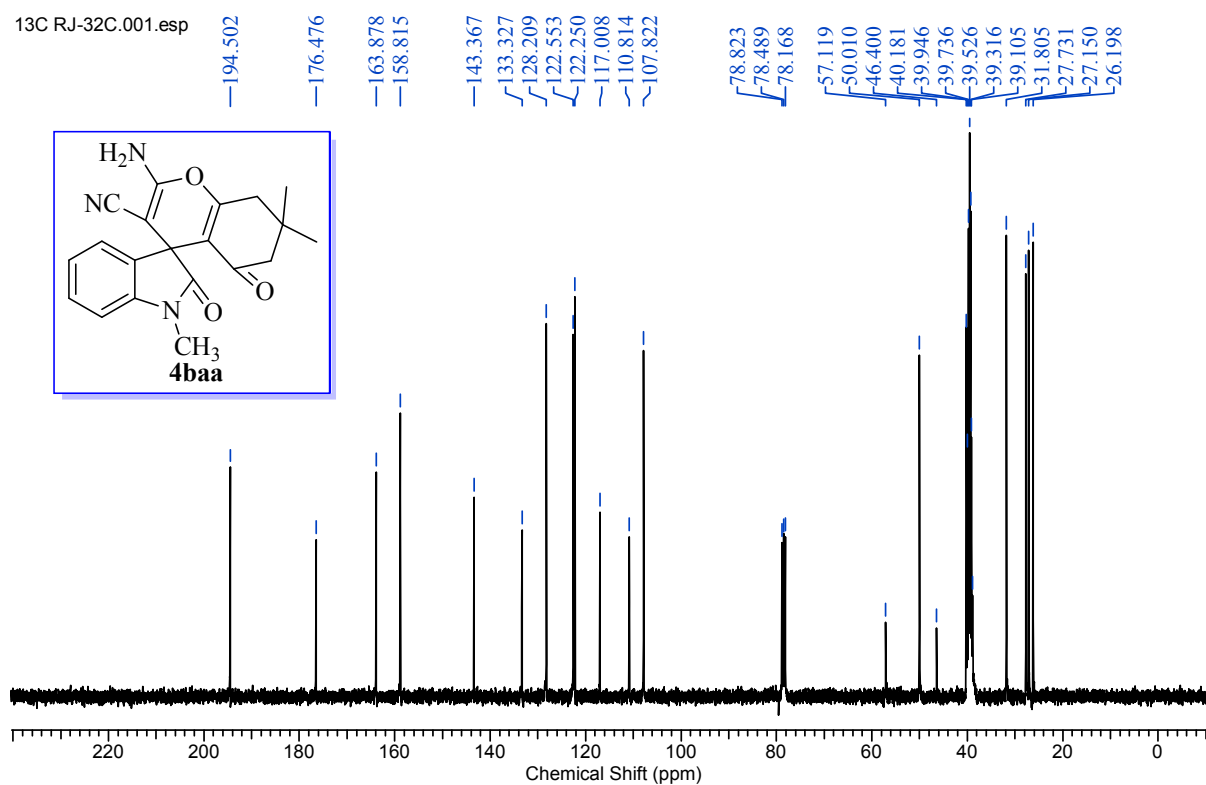
$^1\text{H}$  and  $^{13}\text{C}$  NMR of Compound **4aca**

$^1\text{H}$  and  $^{13}\text{C}$ NMR of Compound **4baa**

1H RJ-32.001.esp

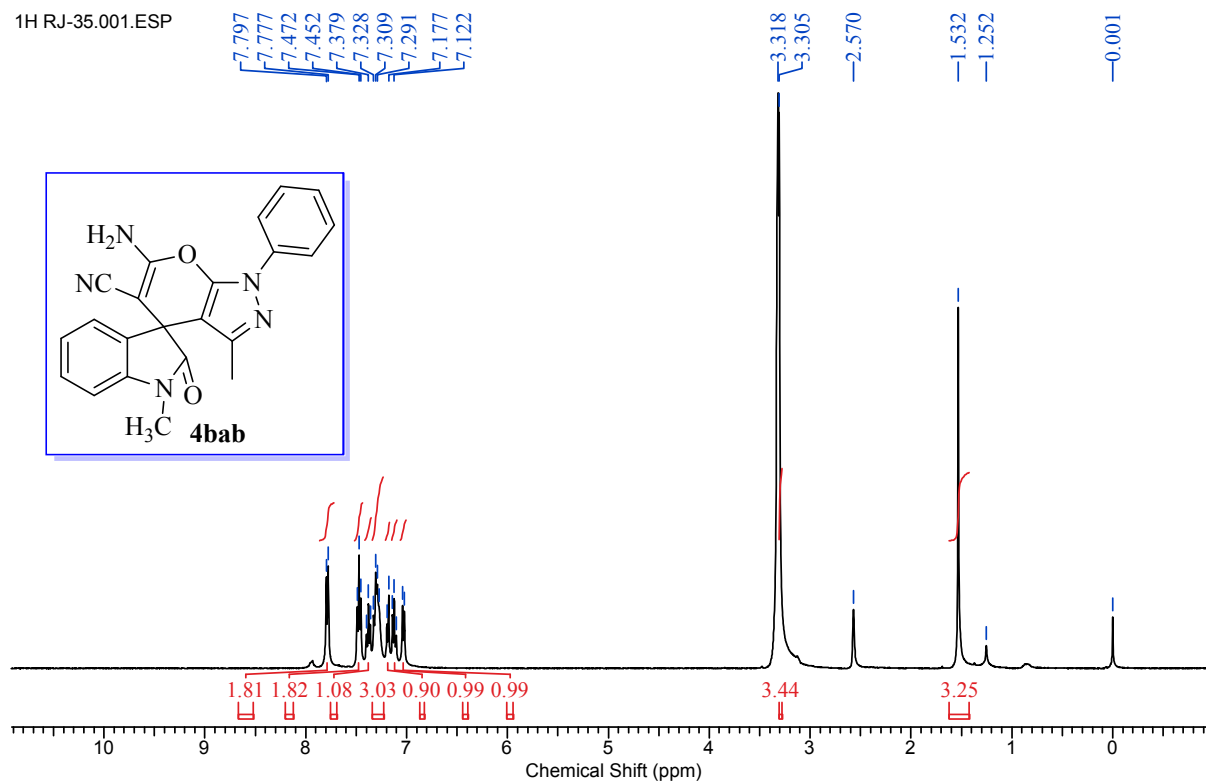


13C RJ-32C.001.esp

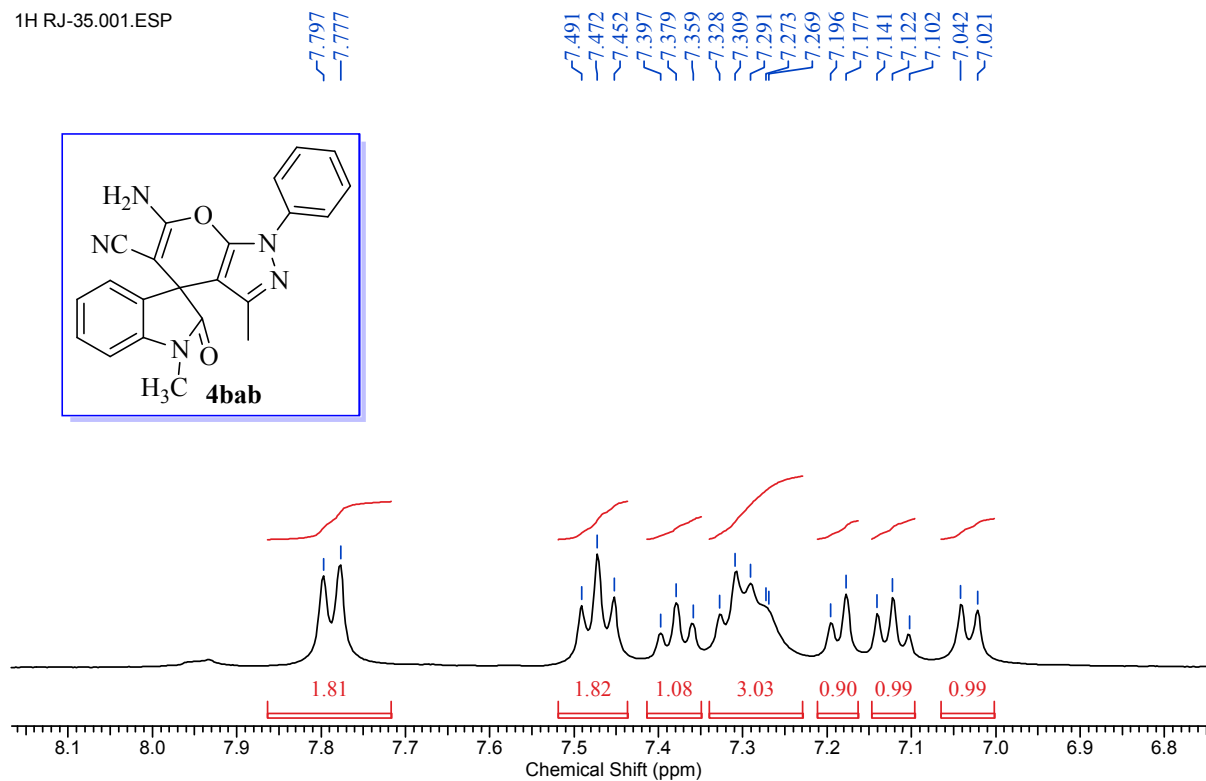
<sup>1</sup>H and <sup>13</sup>C NMR of Compound 4baa

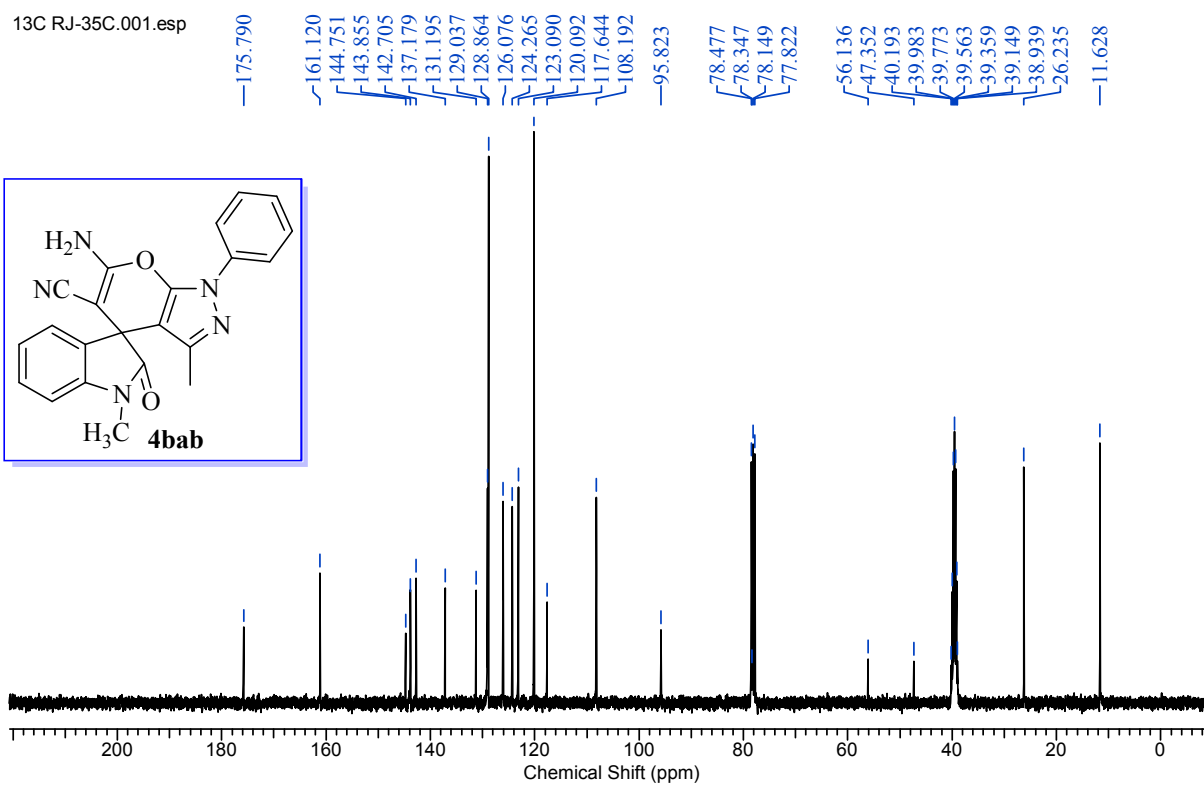


1H RJ-35.001.ESP



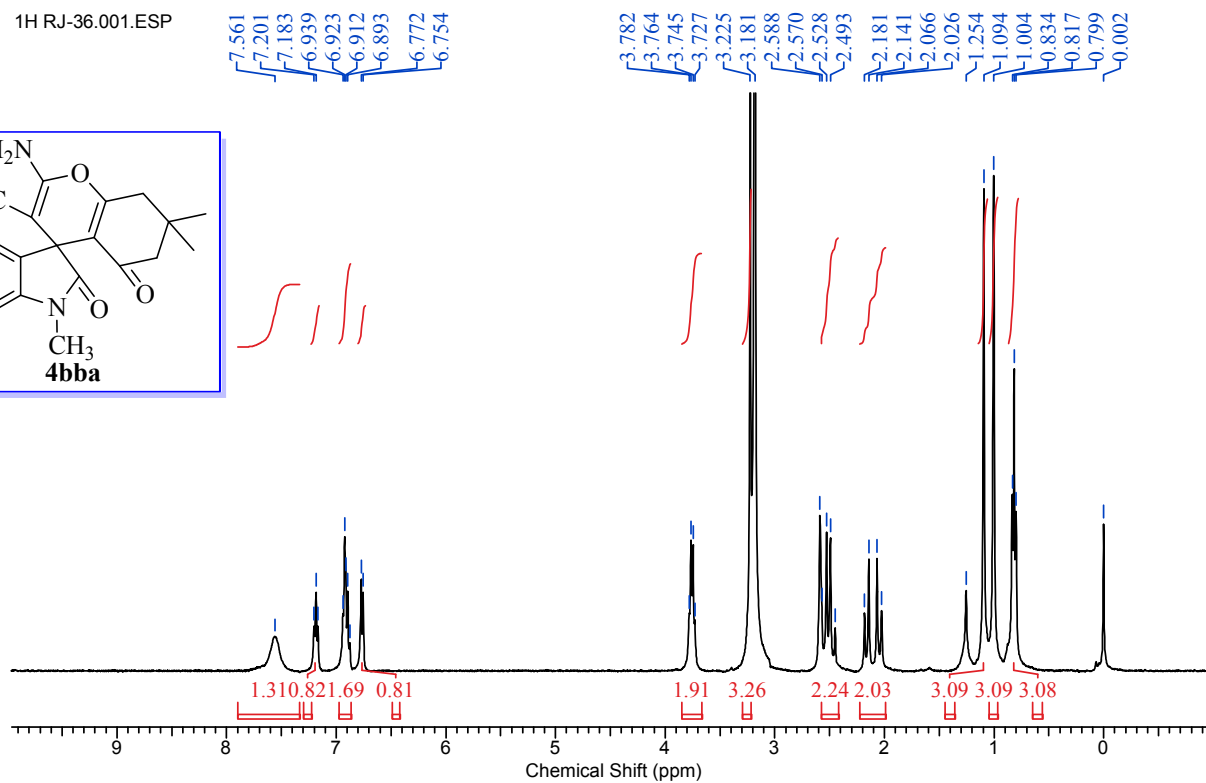
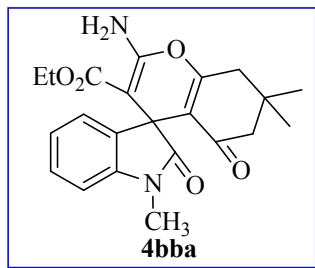
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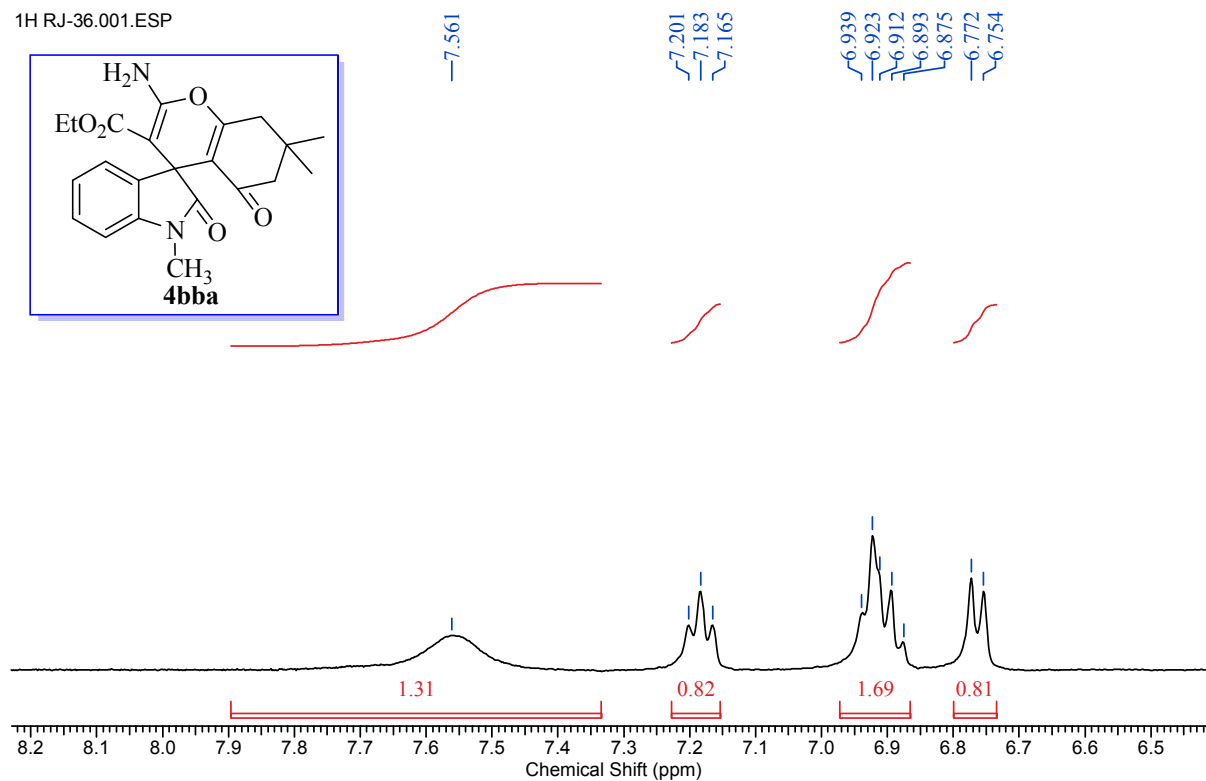
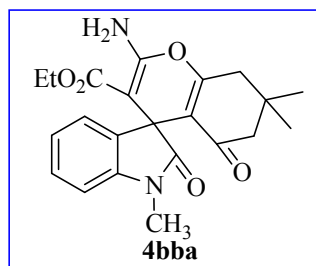


$^1\text{H}$  and  $^{13}\text{C}$ NMR of Compound **4bba**

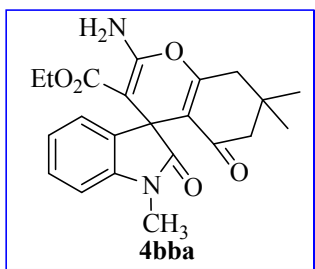
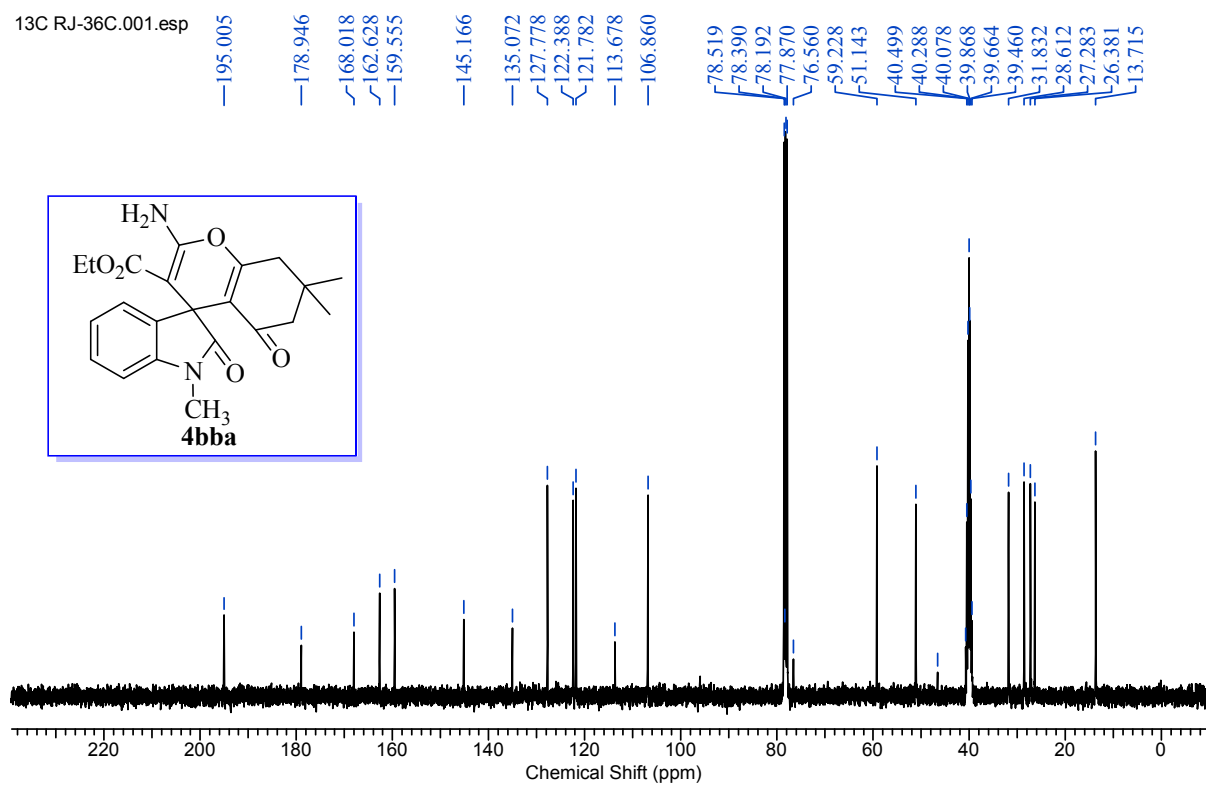
1H RJ-36.001.ESP



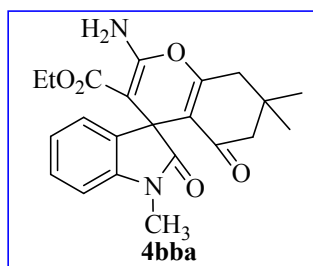
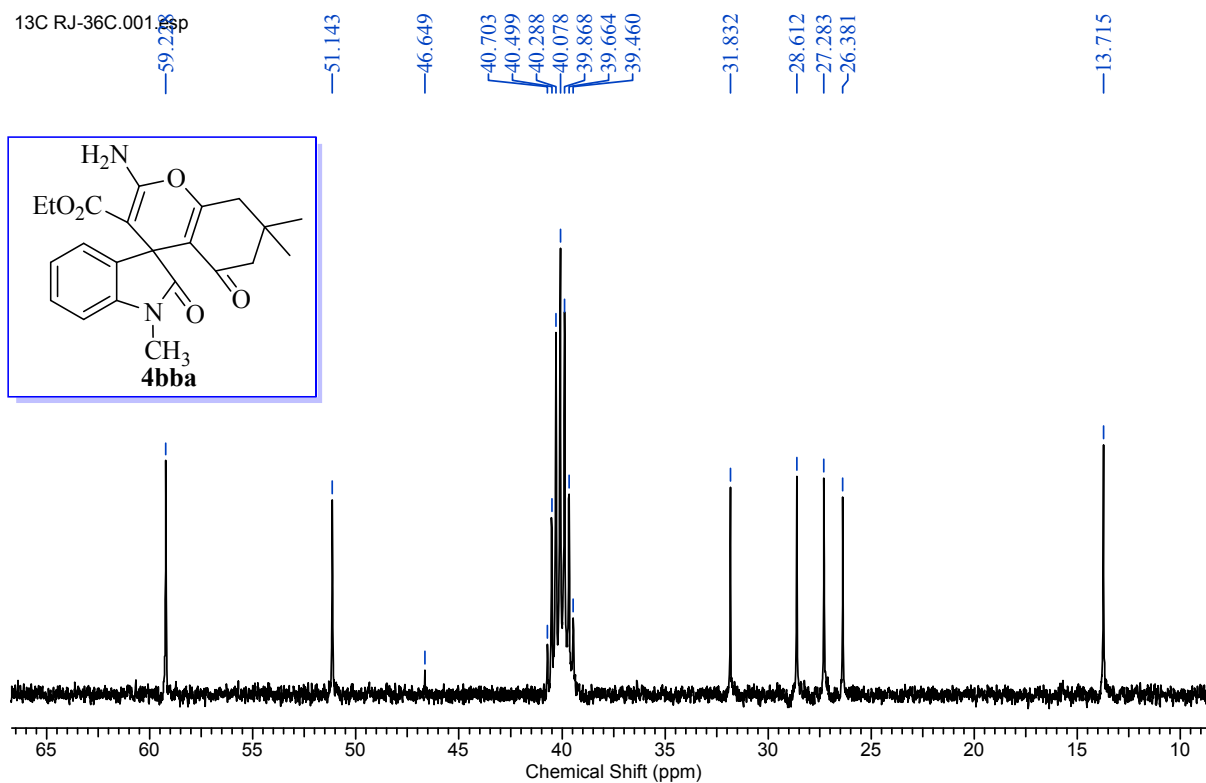
1H RJ-36.001.ESP



13C RJ-36C.001.esp

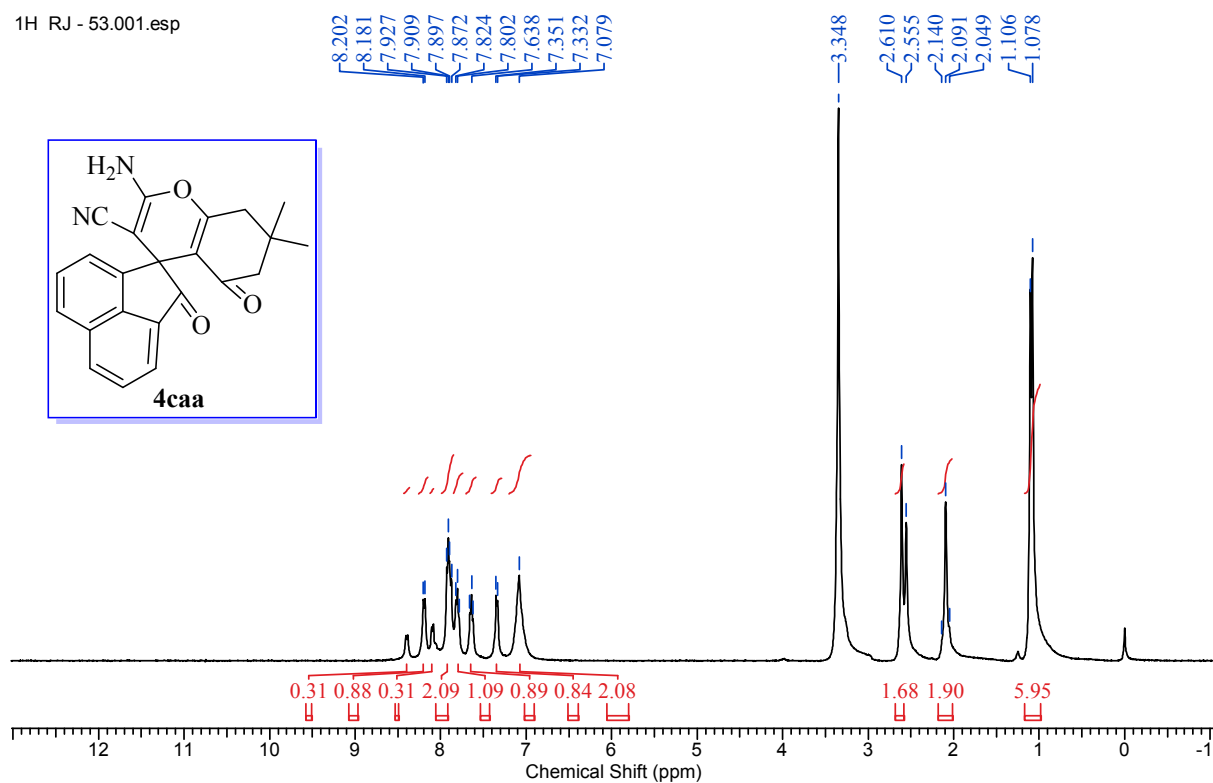


13C RJ-36C.001.esp

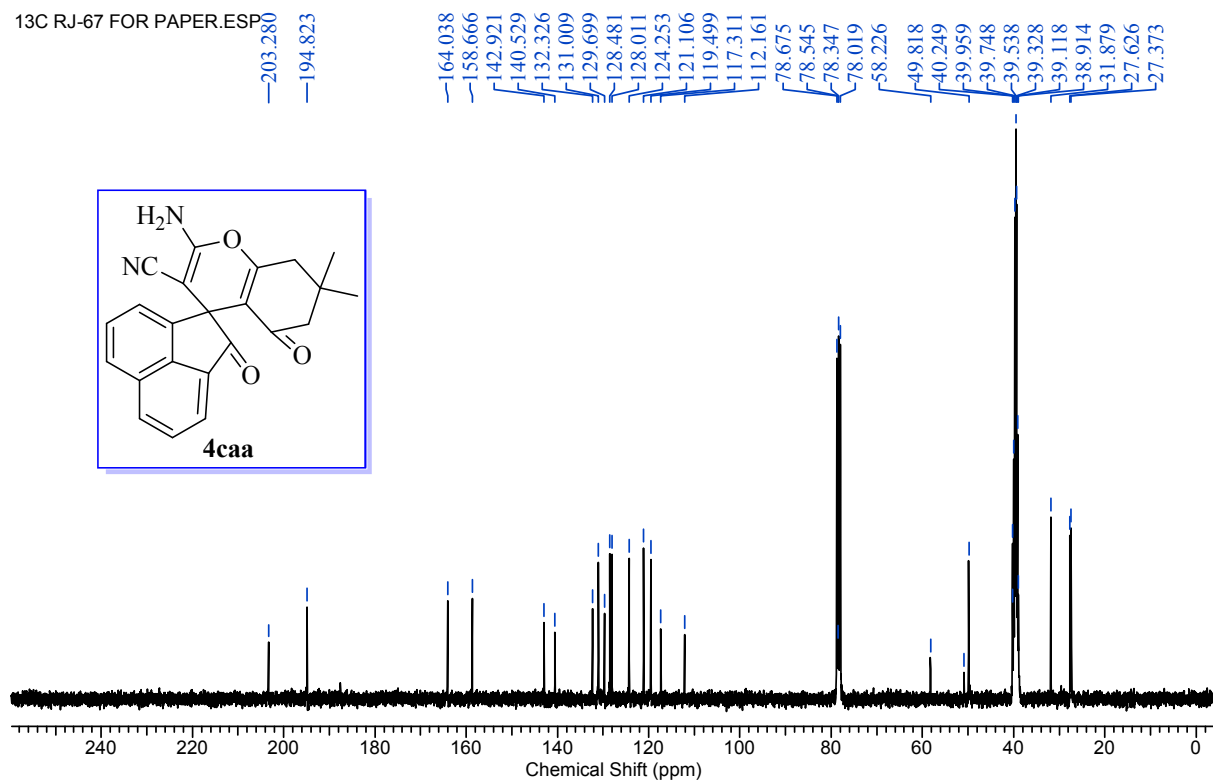


$^1\text{H}$  and  $^{13}\text{C}$ NMR of Compound **4caa**

1H RJ - 53.001.esp

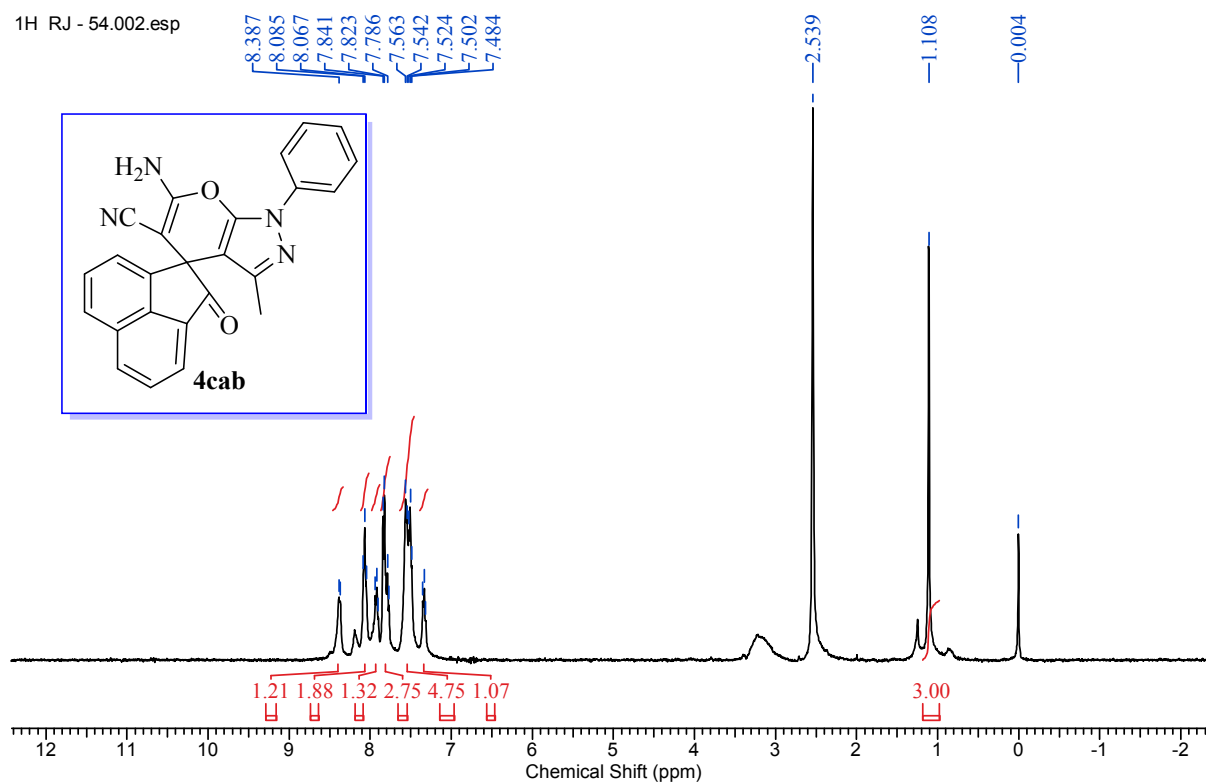


13C RJ-67 FOR PAPER.ESP

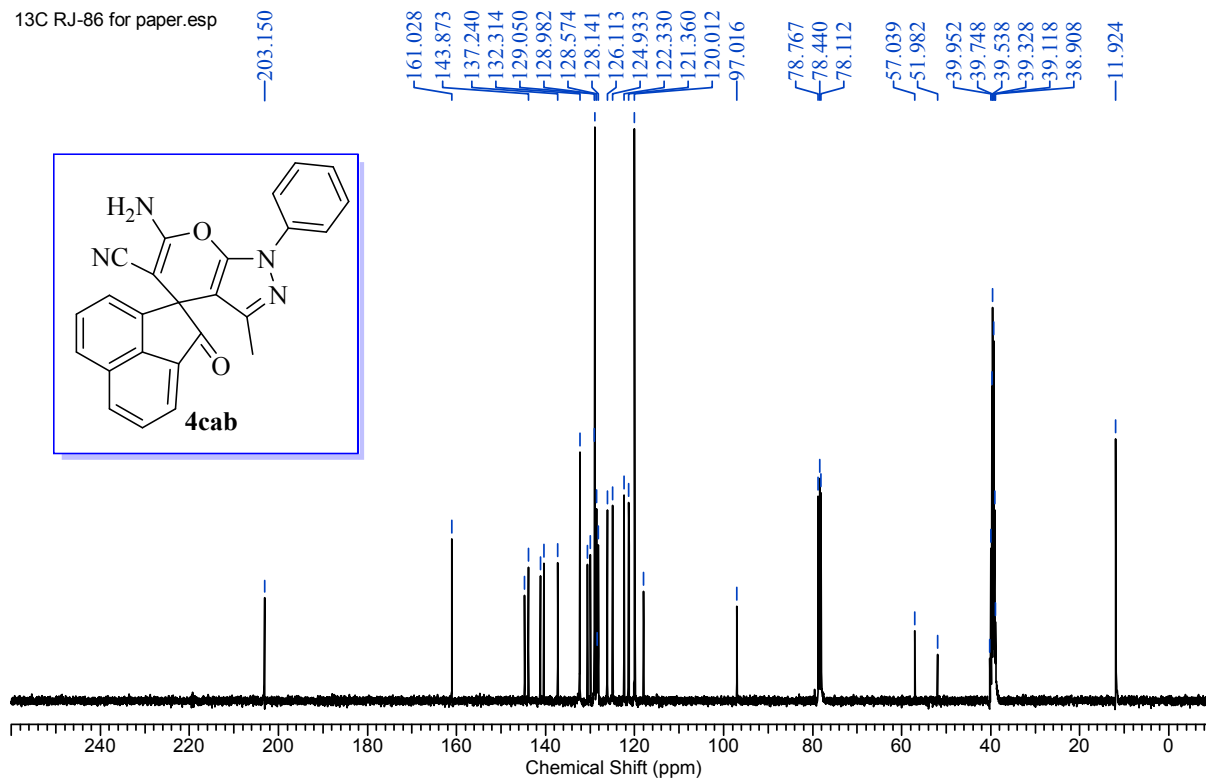


$^1\text{H}$  and  $^{13}\text{C}$ NMR of Compound **4cab**

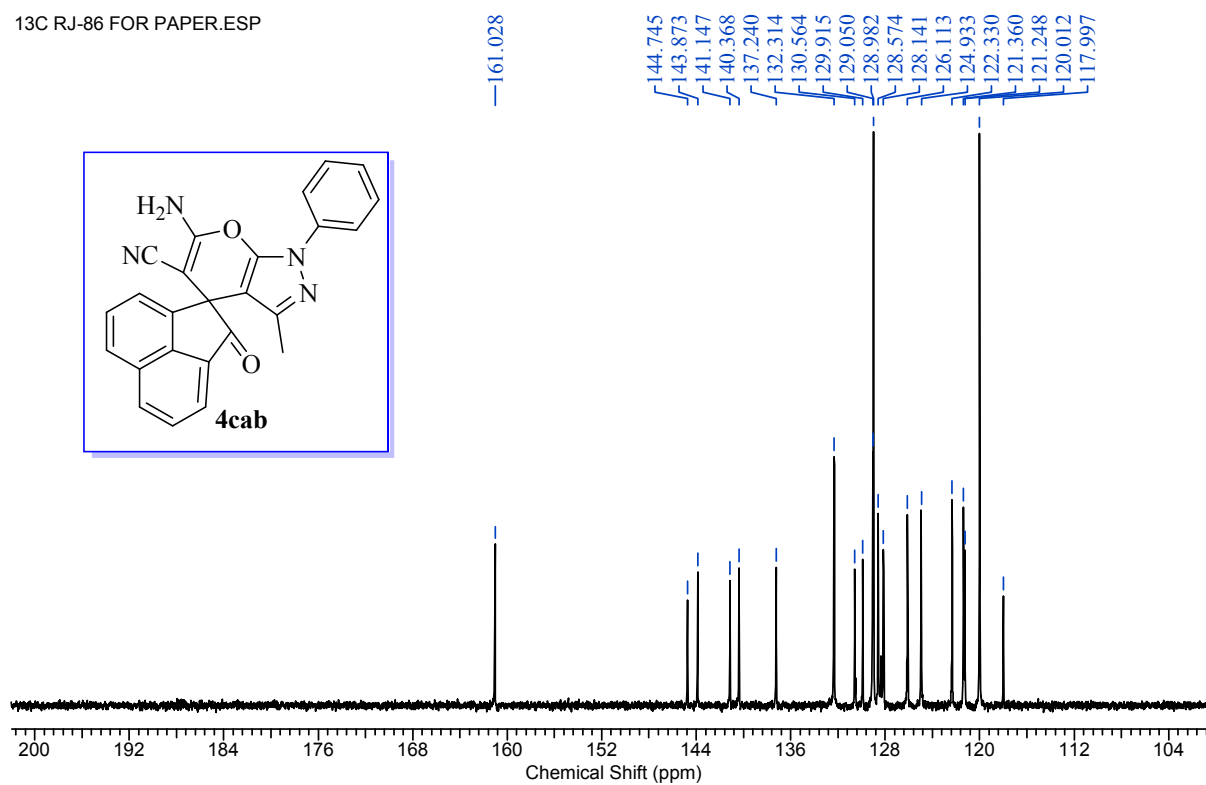
1H RJ - 54.002.esp



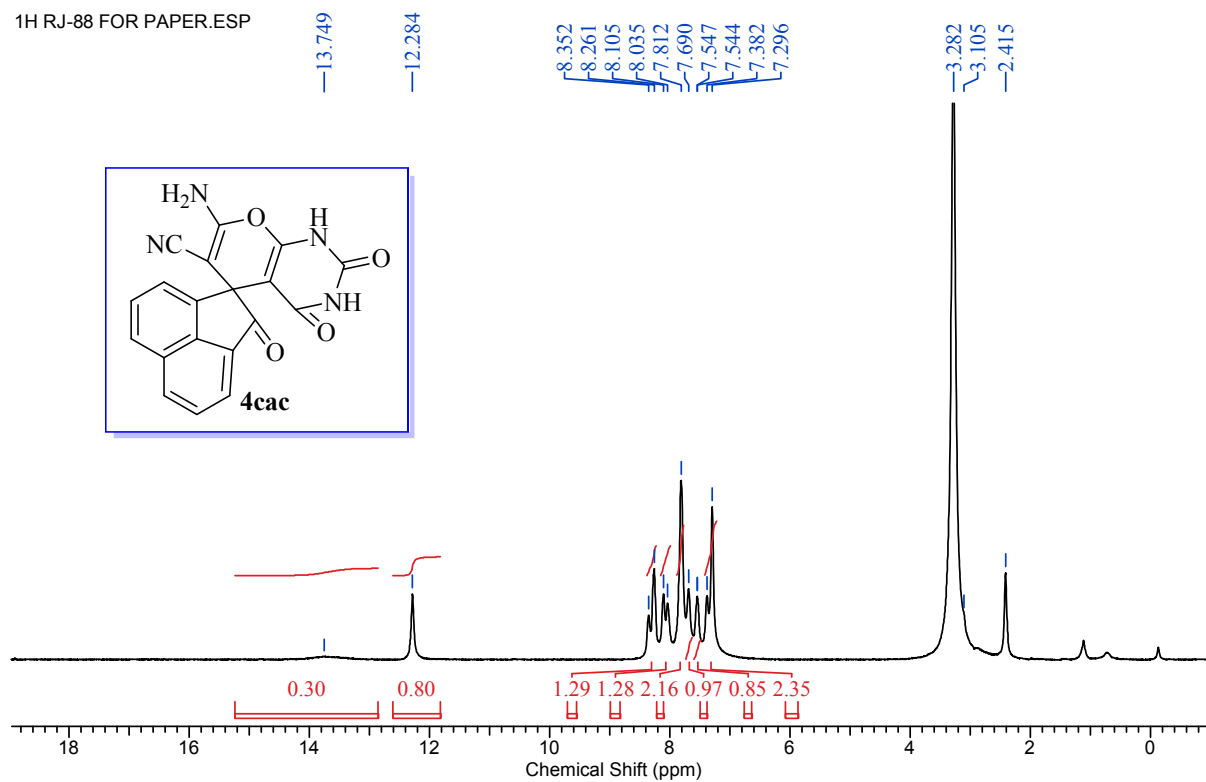
13C RJ-86 for paper.esp



13C RJ-86 FOR PAPER.ESP

<sup>1</sup>H and <sup>13</sup>CNMR of Compound **4cac**

1H RJ-88 FOR PAPER.ESP



13C RJ-87C.001.esp

