

## Supplementary Material

### Synthesis of novel imidazopyridine-oxadiazole molecular hybrids by a regioselective sulfenylation of imidazo[1,2-*a*]pyridines with 1,3,4-oxadiazole-2-thiols using I<sub>2</sub>-FeCl<sub>3</sub> catalytic system and O<sub>2</sub>/air as co-oxidant

Kartik Dutta,<sup>a,b</sup> Nisha Kushwah,<sup>c</sup> Amey P. Wadawale,<sup>c</sup> and Sunil K. Ghosh<sup>\*a,b</sup>

<sup>a</sup>Bio-Organic Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085

<sup>b</sup>Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094

<sup>c</sup>Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India

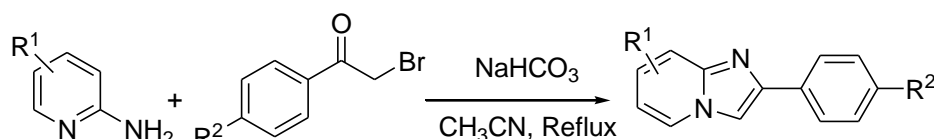
Email: [qhsunil@barc.gov.in](mailto:qhsunil@barc.gov.in)

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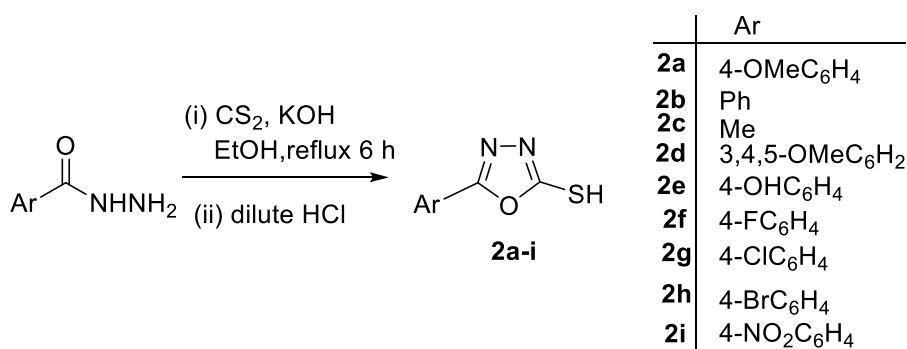
### 1. General procedure for synthesis imidazo[1,2-a]pyridine derivatives 1a-h

Following the reported procedure,<sup>1</sup> sodium bicarbonate (1.6 g, 20 mmol) was added to a stirred solution of 2-bromoacetophenone derivatives (10 mmol) and 2-aminopyridine derivatives (10 mmol) in 50 mL of acetonitrile and the mixture was refluxed for 2 h. After completion of reaction as monitored by TLC, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic phase was then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography using petroleum ether and ethyl acetate as the eluent to afford pure **1a-h**. Spectroscopic data for **1a,f**<sup>2</sup>; **1b-e**<sup>3</sup> and **1g,h**<sup>4</sup> were similar as reported.



### 2. General procedure for synthesis 2a-i

Following the reported procedure,<sup>5</sup> a vigorously stirred solution of appropriately substituted carboxy benzohydrazide (10 mmol) in 30 mL absolute ethanol was basified with potassium hydroxide (10 mmol) until a solid precipitate came out. Carbon disulphide (15 mmol) was added to the mixture and refluxed for 6 h. After completion of the reaction as verified by TLC, ethanol was removed under vacuum. Then sticky mass was diluted with cold water and acidified with 0.5 M HCl to maintain pH = 3-4. The precipitated crude product was filtered, washed with water and air dried. Recrystallization from ethanol gave pure **2a-i** in 68-75% yield. Spectroscopic data for **2a,c**<sup>5</sup> and **2e-h**<sup>5</sup> were similar as reported.



### Scheme S1 synthesis of 1,3,4-oxadiazole-2-thiols 2a-i

### 3. Characterization data for 2b, 2d and 2i

**5-phenyl-1,3,4-oxadiazole-2-thiol (2b)** White solid (1.3 g, 75% yield); mp 202.2 – 221.9 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 7.86 (d, *J* = 6.9 Hz, 2 H), 7.62–7.55 (m, 3 H); <sup>13</sup>C NMR (75

MHz, DMSO- $d_6$ )  $\delta$  (ppm) 177.8, 160.9, 132.7, 129.9, 126.5, 122.9; Elemental Anal. Calcd. for  $C_8H_6N_2OS$  C, 53.92; H, 3.39; N, 15.72; S, 17.99%. Found C, 54.25; H, 3.52; N, 15.69; S, 18.24%.

**5-(3,4,5-trimethoxyphenyl)-1,3,4-oxadiazole-2-thiol (2d)** White solid (1.9 g, 71% yield); mp 185.6- 186.9 °C;  $^1H$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 7.09 (s, 2 H), 3.85 (s, 6 H), 3.73 (s, 3.09); NMR (75 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 177.7, 160.8, 153.9, 141.2, 117.9, 103.8, 60.7, 56.6; Elemental Anal. Calcd. for  $C_{11}H_{12}N_2O_4S$  C, 49.25; H, 4.51; N, 10.44; S, 11.95%. Found C, 49.25; H, 4.37; N, 10.31; S, 12.26%.

**5-(4-nitrophenyl)-1,3,4-oxadiazole-2-thiol (2i)** Yellow solid (1.5 g, 68% yield); mp 190.1-191.9 °C;  $^1H$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 8.37 (d  $J$  = 8.7 Hz 2 H), 8.10 (d  $J$  = 8.7 Hz 2 H); NMR (75 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 178.1, 159.3, 149.6, 128.5, 127.9, 125.0; Elemental Anal. Calcd. for  $C_8H_5N_3O_3S$  C, 43.05; H, 2.26; N, 18.83; S, 14.36%. Found C, 43.18; H, 2.54; N, 18.70; S, 14.67%.

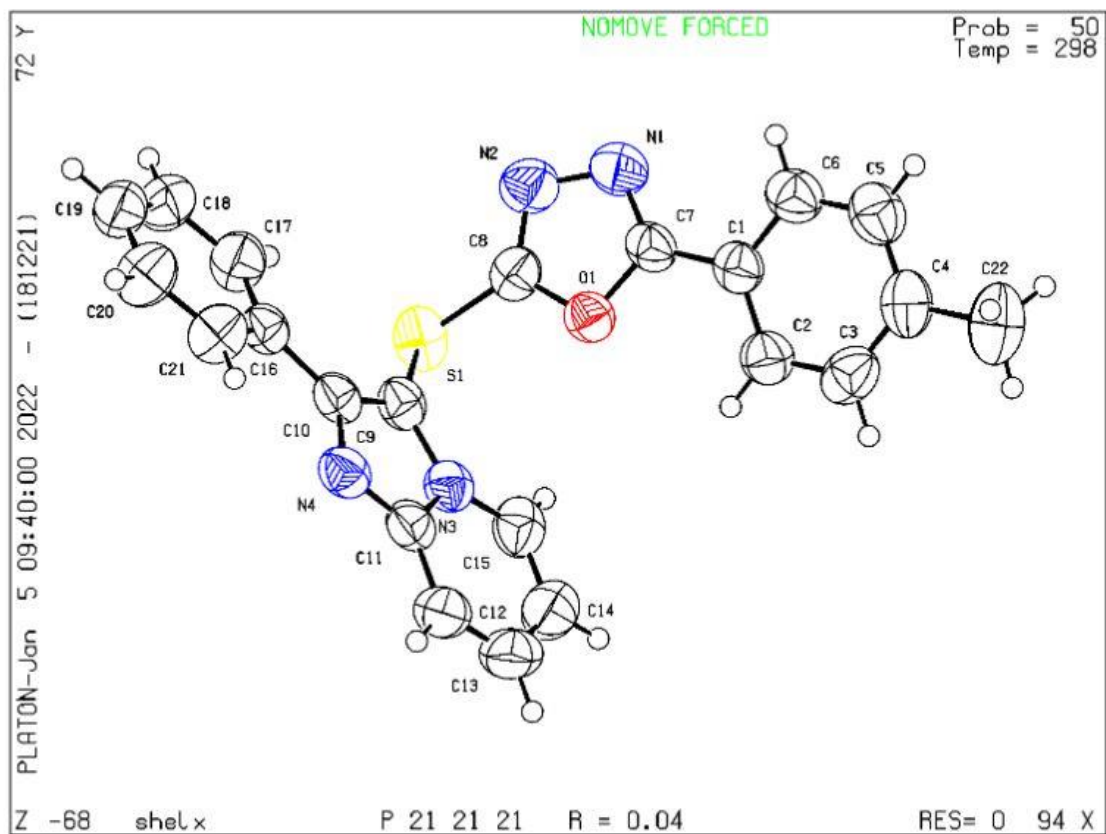
### 3. X-ray crystallographic Characterization of compound 3c

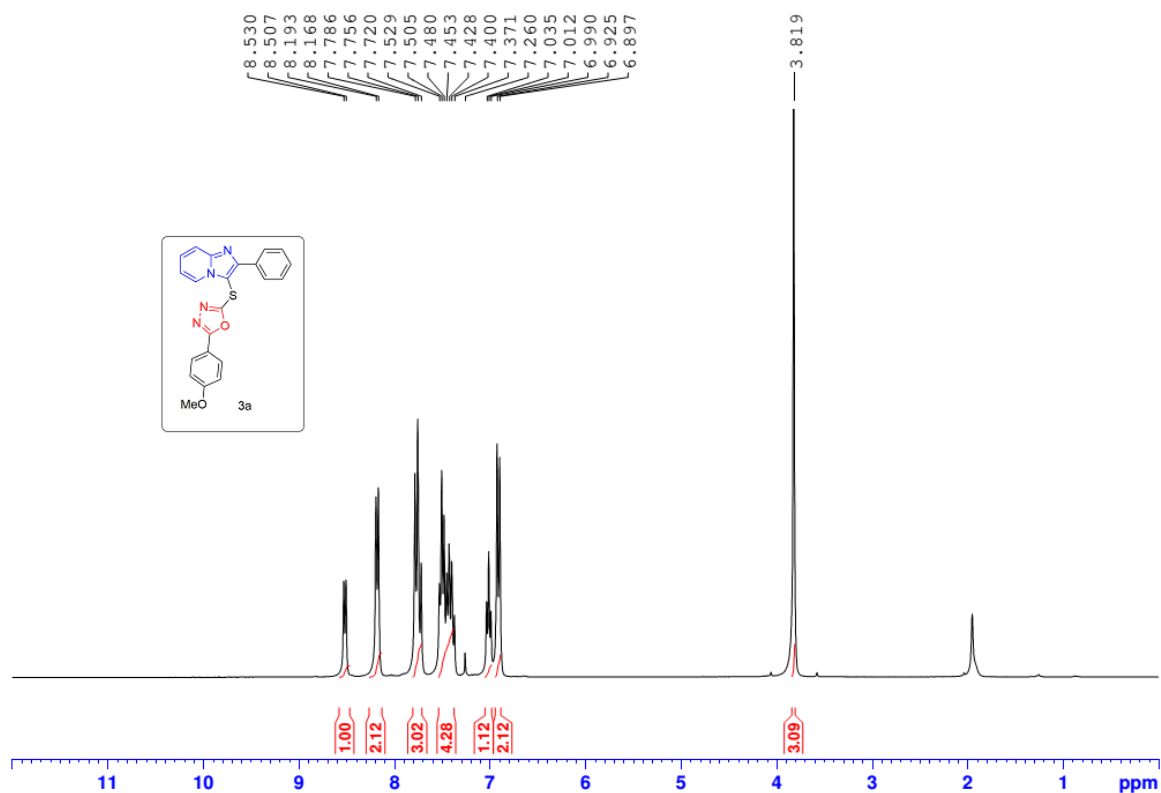
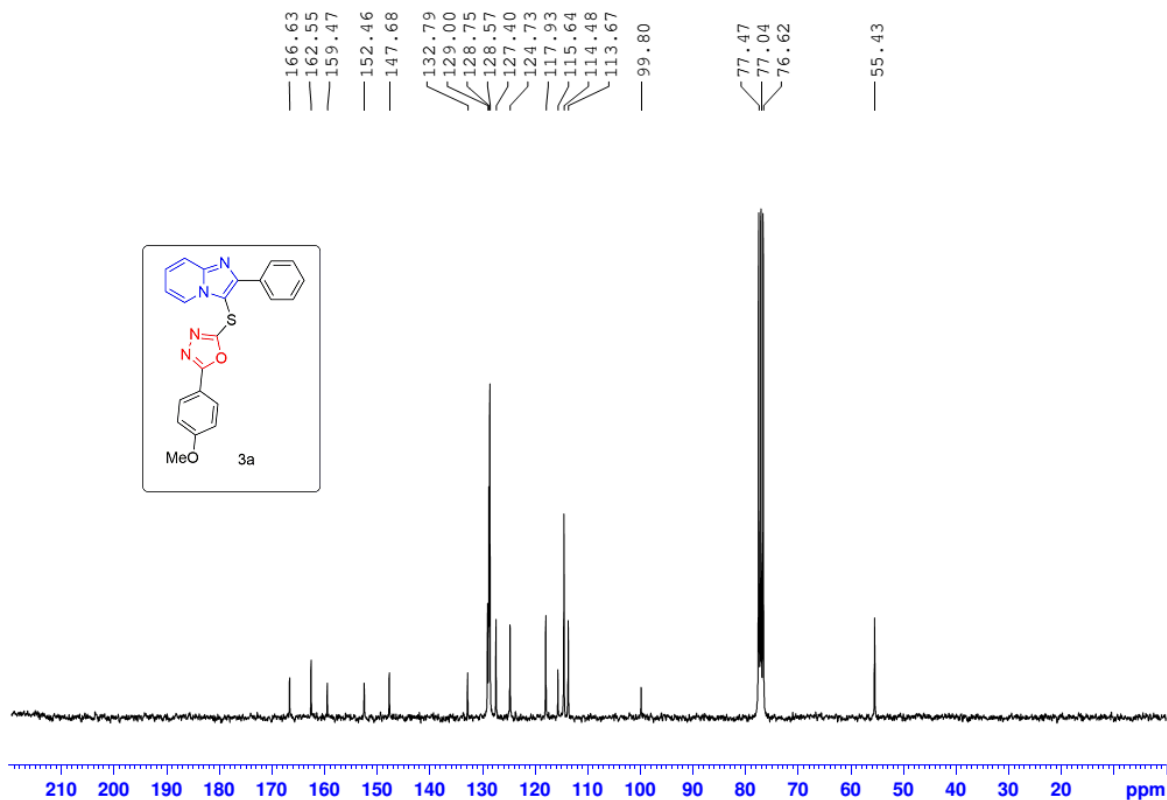
**Table S1.** Crystal data and structure refinement for **3c**

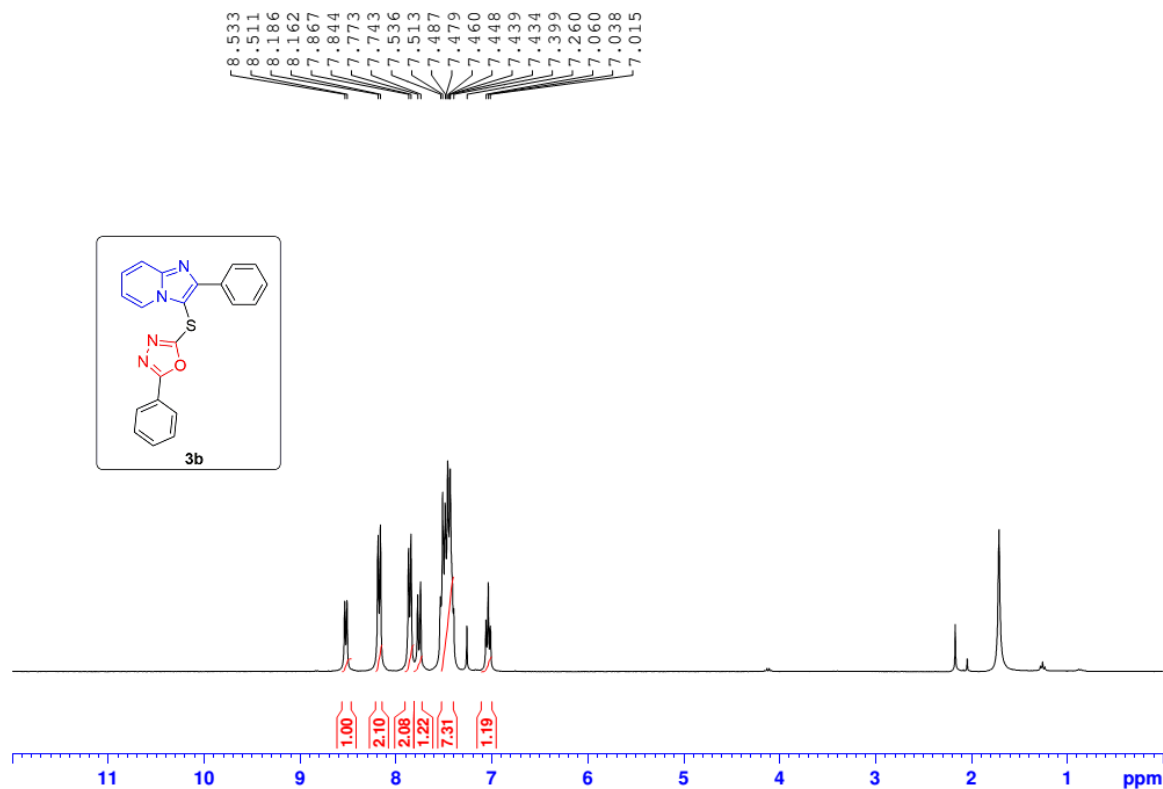
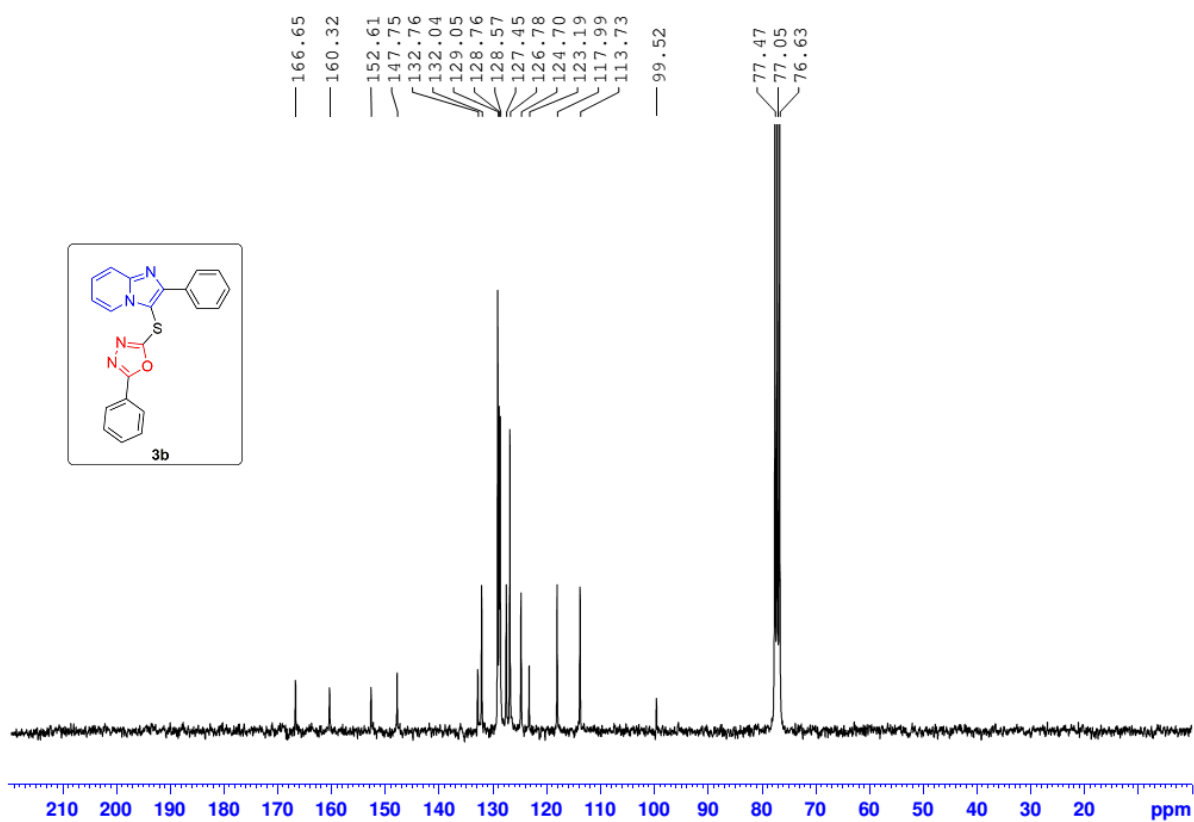
CCDC number	2184609
Empirical formula	$C_{22}H_{16}N_4OS$
Formula weight	384.45
Temperature [K]	298(2)
Crystal system	orthorhombic
Space group (number)	$P2_12_12_1$ (19)
$a$ [Å]	8.3230(3)
$b$ [Å]	10.8098(3)
$c$ [Å]	20.8096(6)
$\alpha$ [Å]	90
$\beta$ [Å]	90
$\gamma$ [Å]	90
Volume [Å <sup>3</sup> ]	1872.24(10)
$Z$	4
$\rho_{calc}$ [g/cm <sup>3</sup> ]	1.364

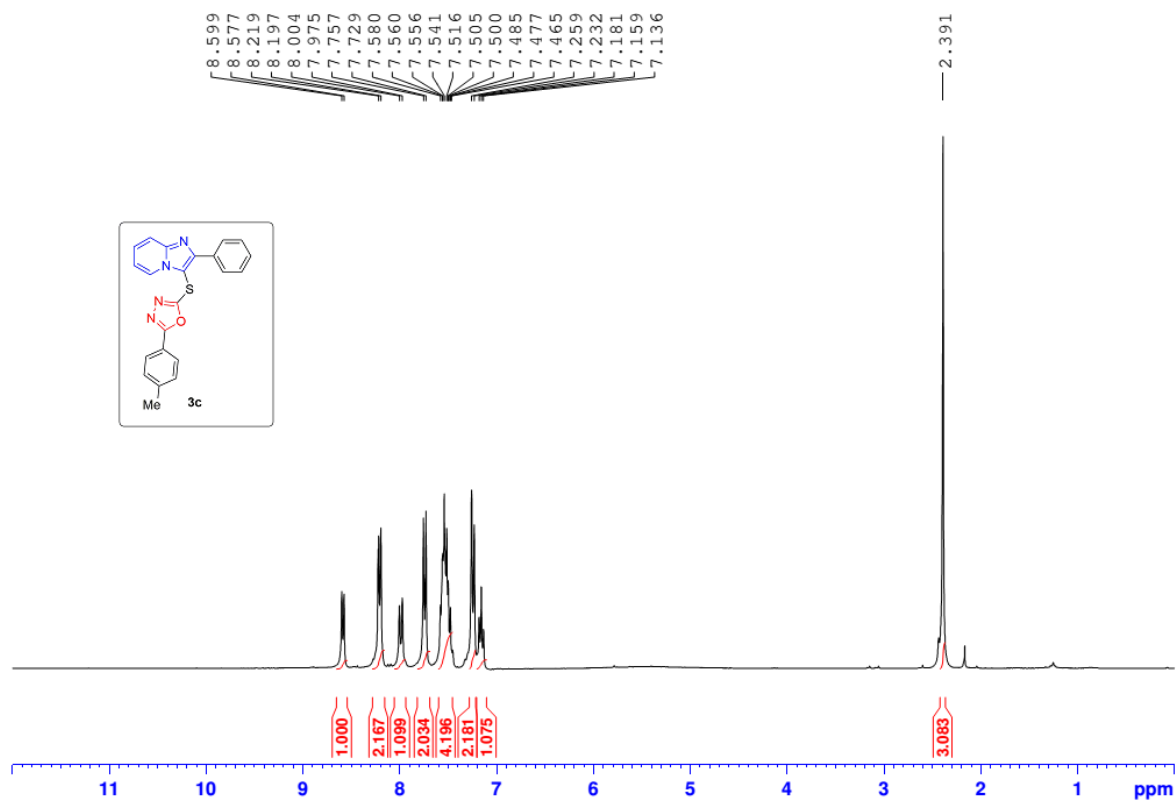
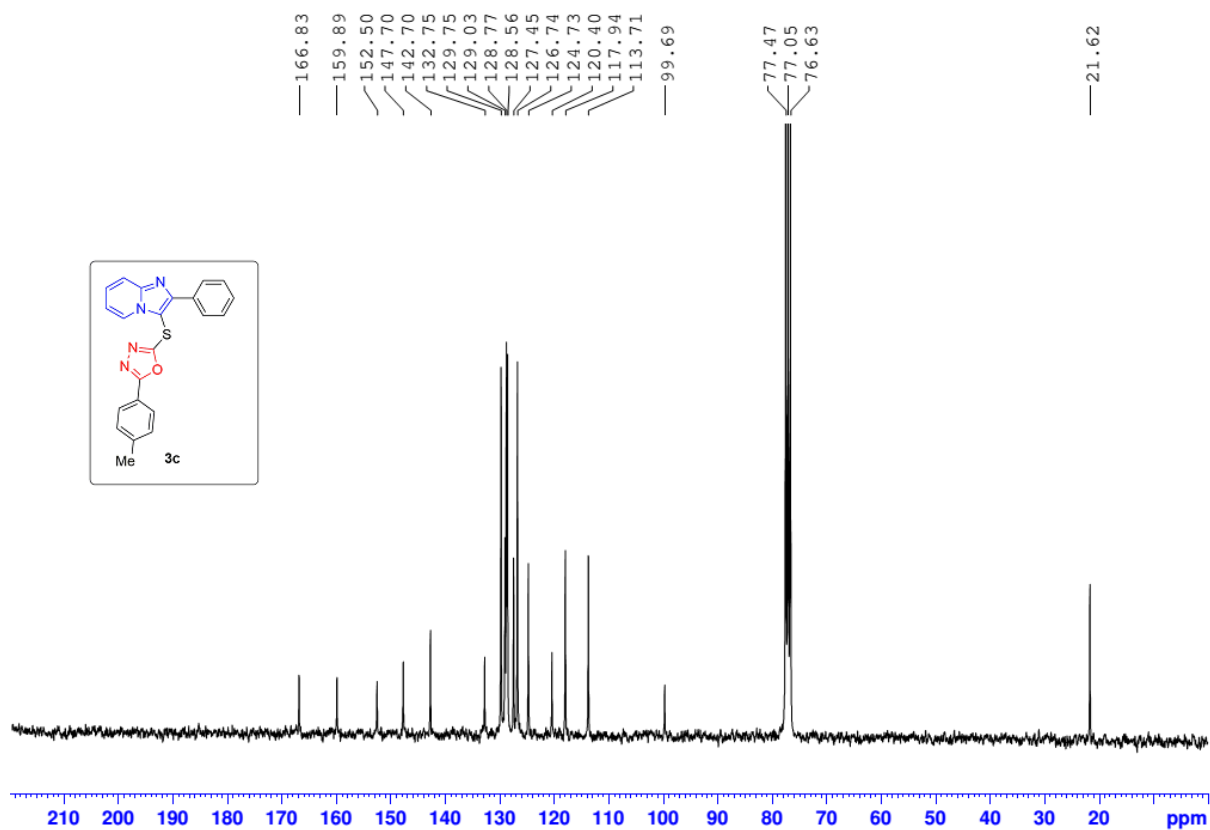
$\mu$ [mm <sup>-1</sup> ]	1.699
$F(000)$	800
Crystal size [mm <sup>3</sup> ]	0.150×0.050×0.050
Crystal colour	colorless
Crystal shape	needle
Radiation	Cu $K_{\alpha}$ ( $\lambda=1.54184$ Å)
2 $\theta$ range [°]	9.22 to 153.70 (0.79 Å)
Index ranges	-9 ≤ $h$ ≤ 10 -13 ≤ $k$ ≤ 13 -24 ≤ $l$ ≤ 26
Reflections collected	29635
Independent reflections	3791 $R_{\text{int}} = 0.1362$ $R_{\text{sigma}} = 0.0653$
Completeness to $\theta = 67.684^{\circ}$	99.9 %
Data / Restraints / Parameters	3791/0/256
Goodness-of-fit on $F^2$	1.008
Final $R$ indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0432$ $wR_2 = 0.1008$
Final $R$ indexes [all data]	$R_1 = 0.0629$ $wR_2 = 0.1150$
Largest peak/hole [eÅ <sup>3</sup> ]	0.15/-0.23
Flack X parameter	-0.02(3)
Extinction coefficient	0.0021(5)

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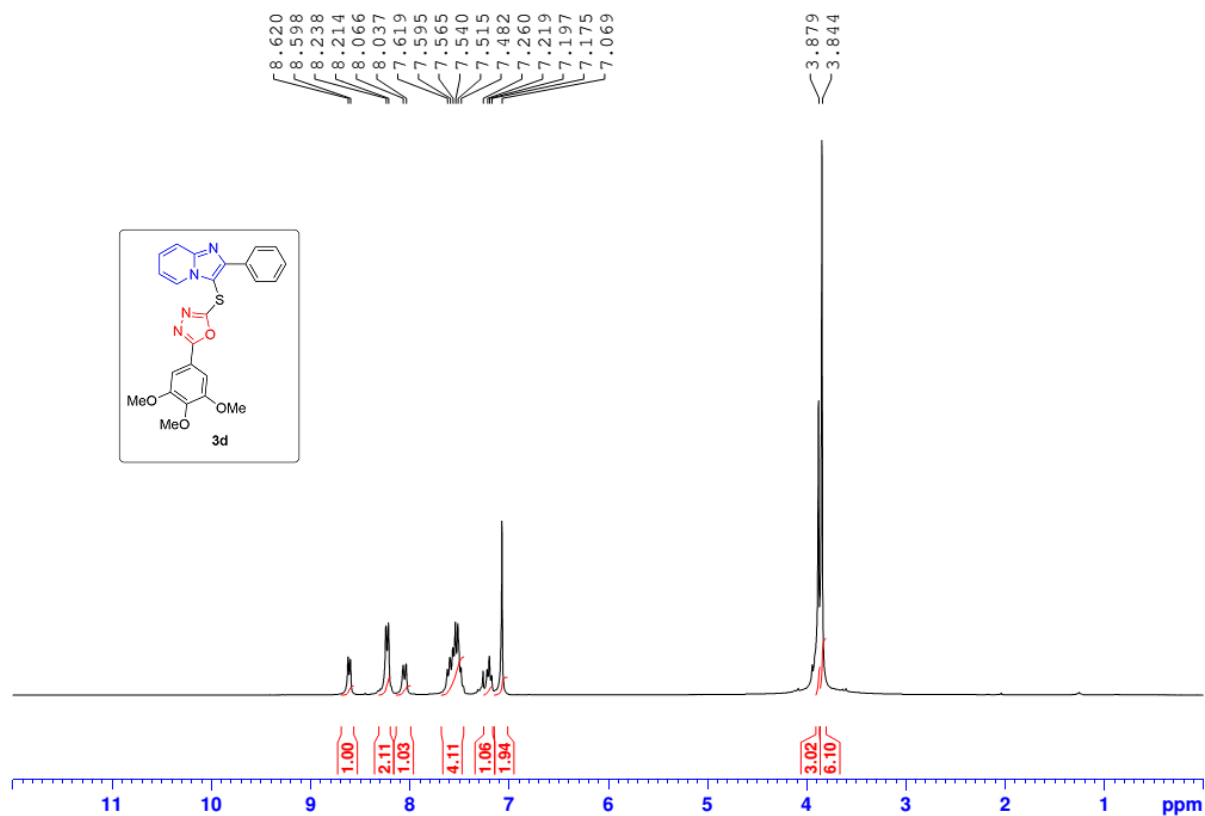
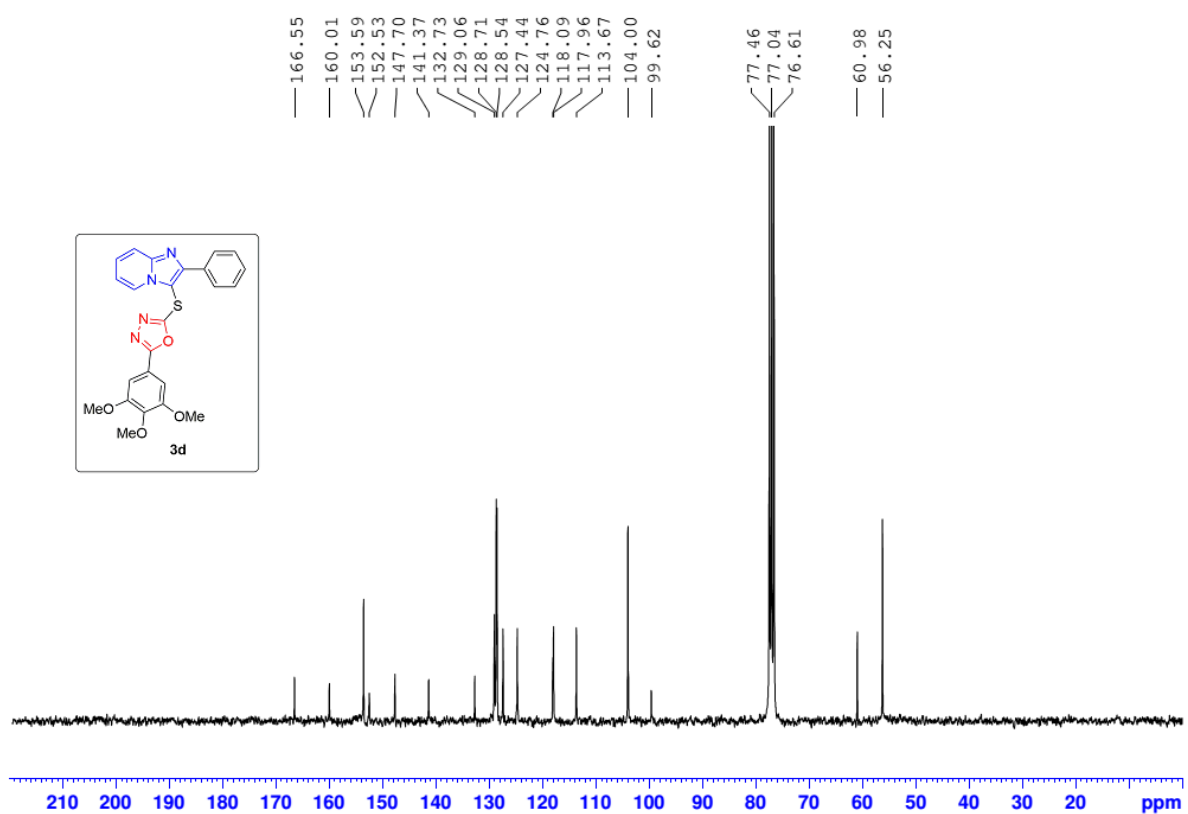


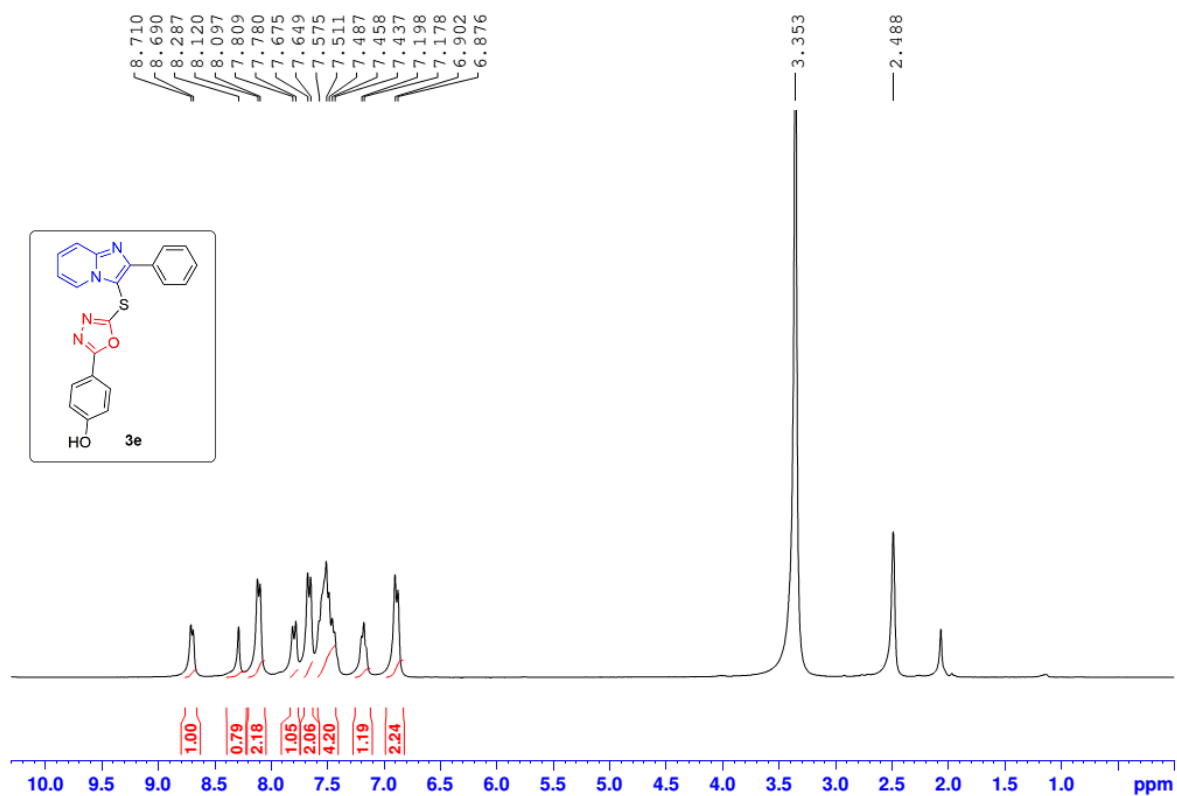
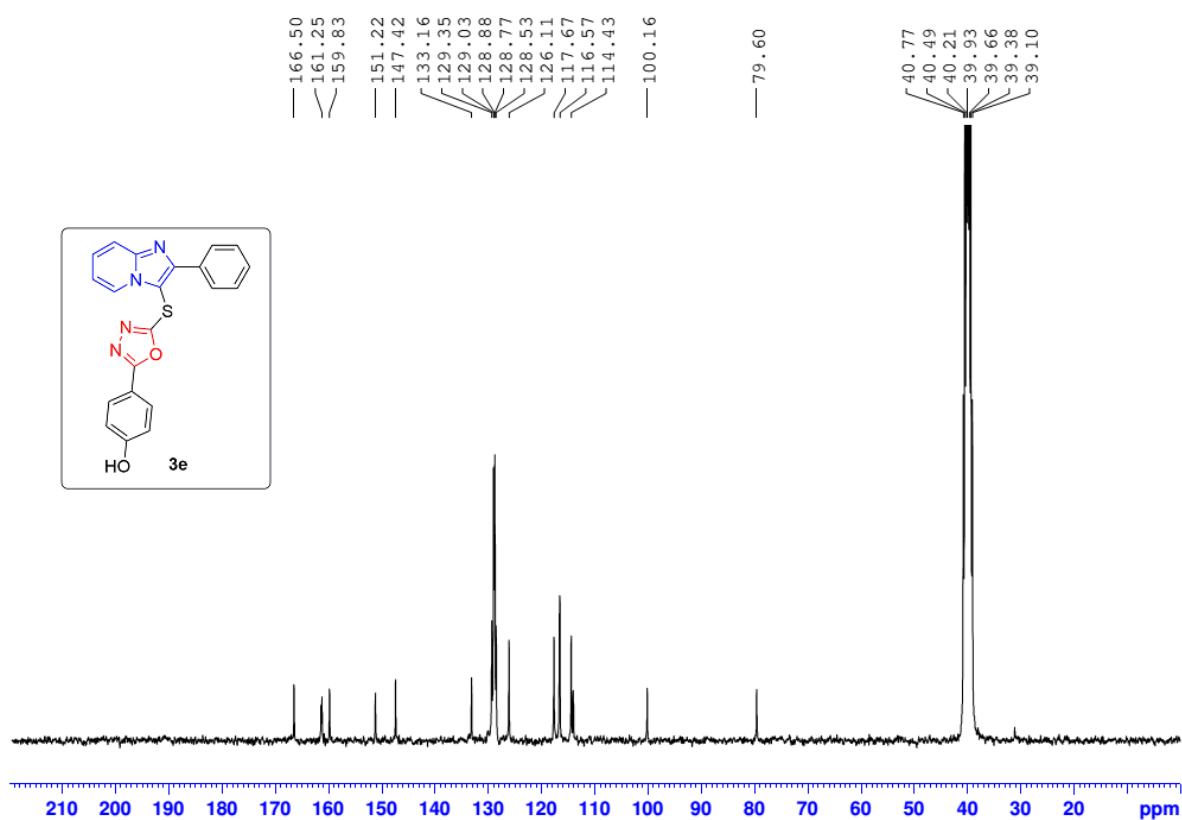
4.  $^1\text{H}$  &  $^{13}\text{C}$  NMR SpectraFigure S1.  $^1\text{H}$  NMR spectrum of **3a**Figure S2.  $^{13}\text{C}$  NMR spectrum of **3a**

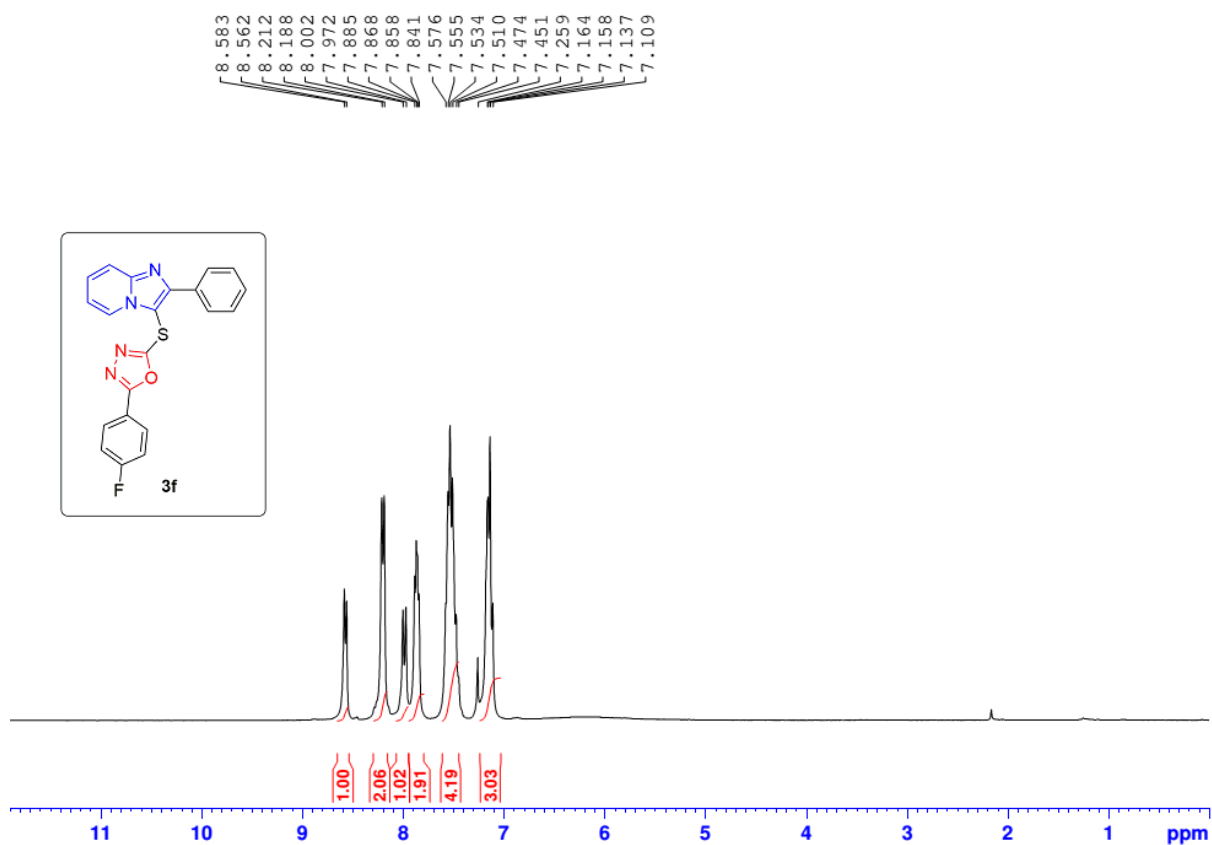
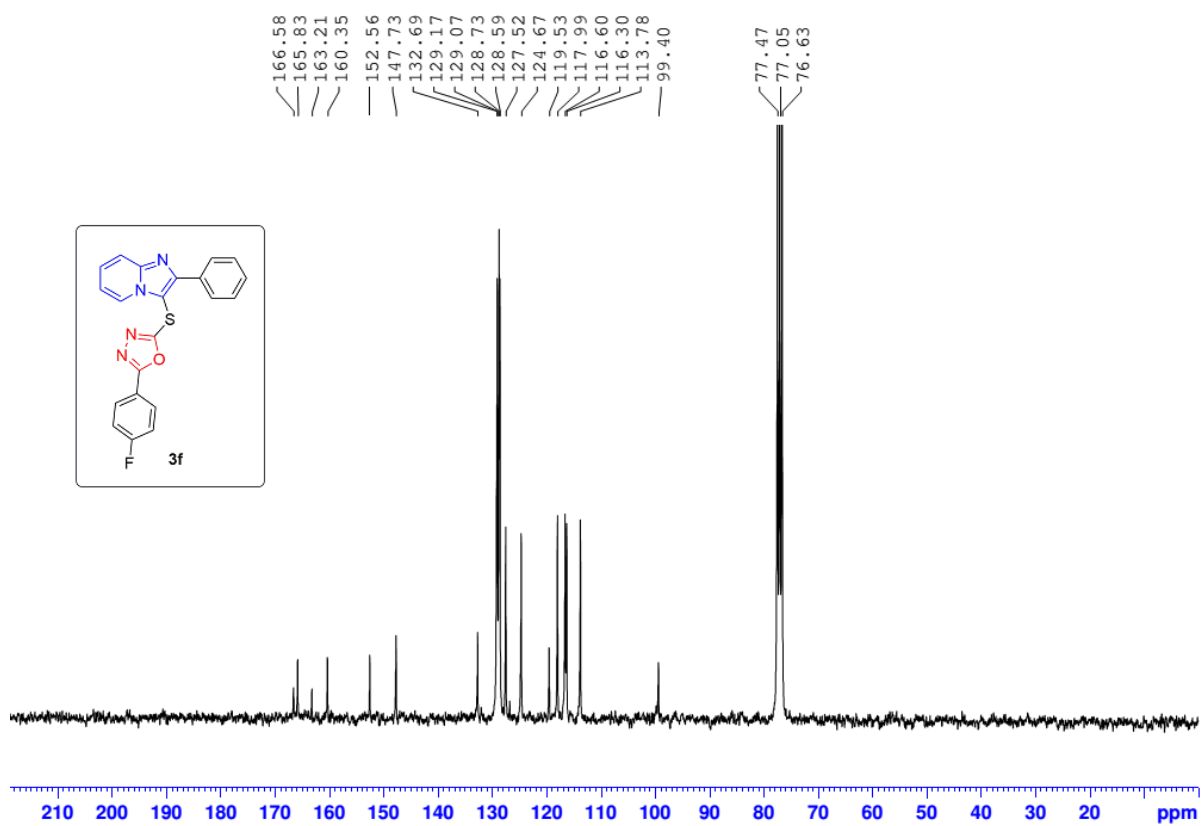
Figure S3. <sup>1</sup>H NMR spectrum of **3b**Figure S4. <sup>13</sup>C NMR spectrum of **3b**

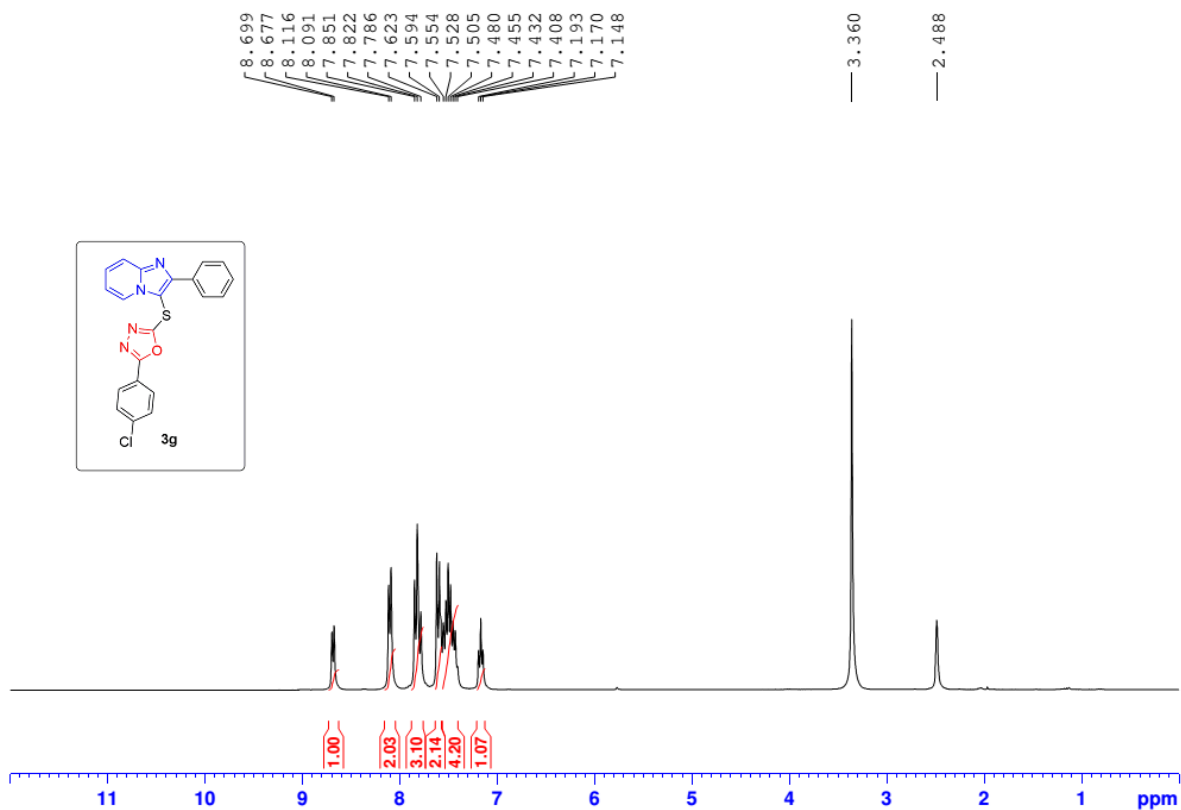
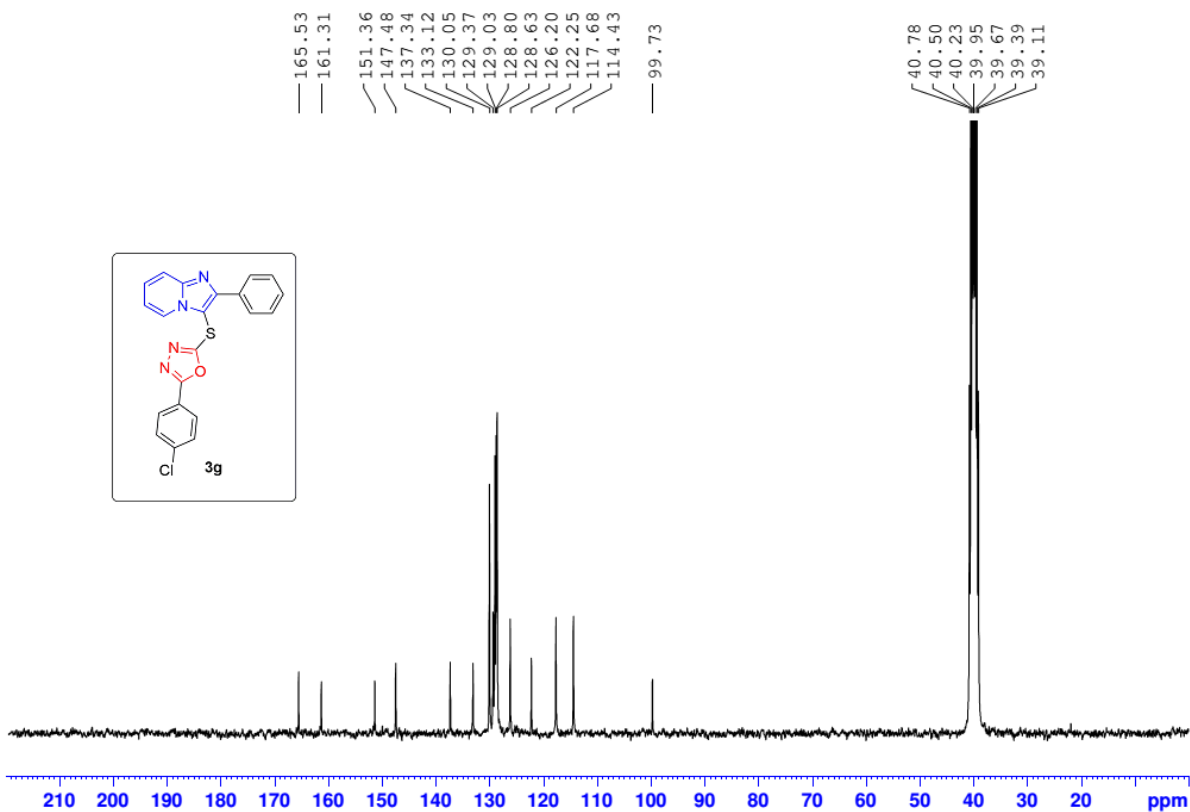
Figure S5.  $^1\text{H}$  NMR spectrum of **3c**Figure S6.  $^{13}\text{C}$  NMR spectrum of **3c**

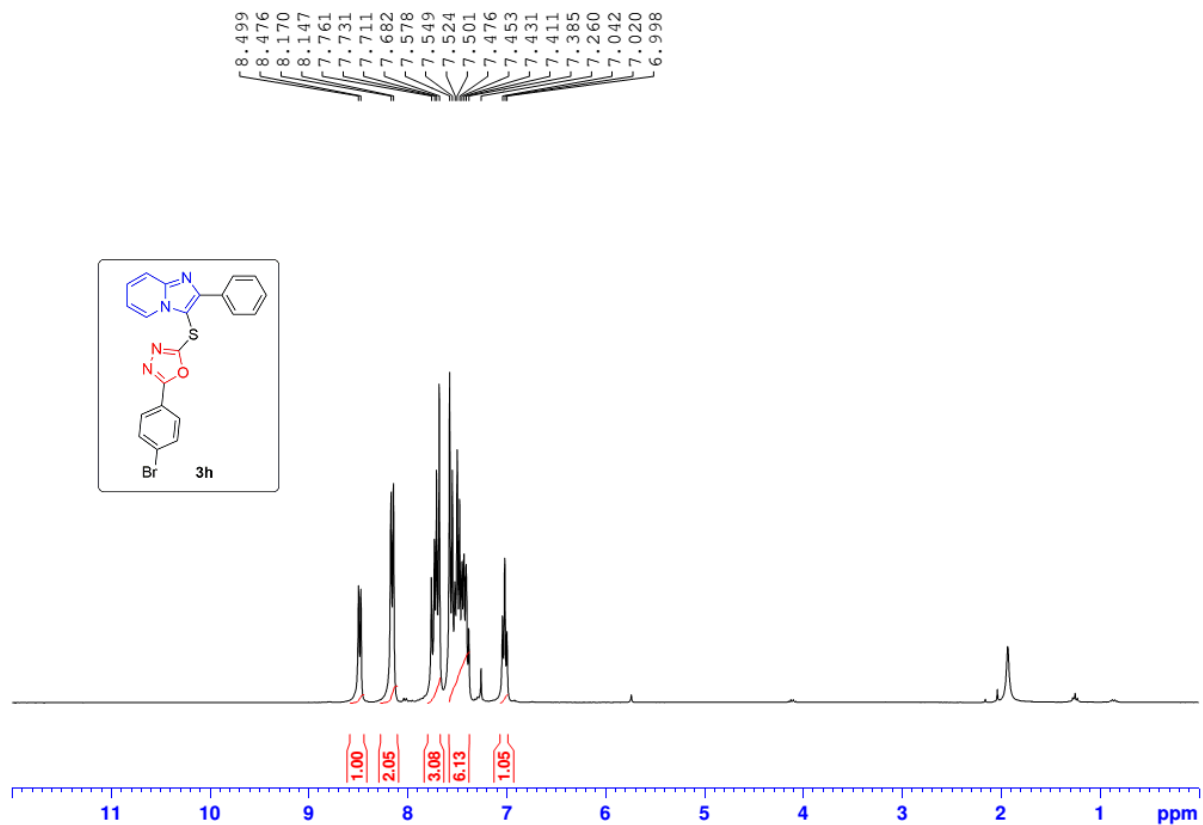
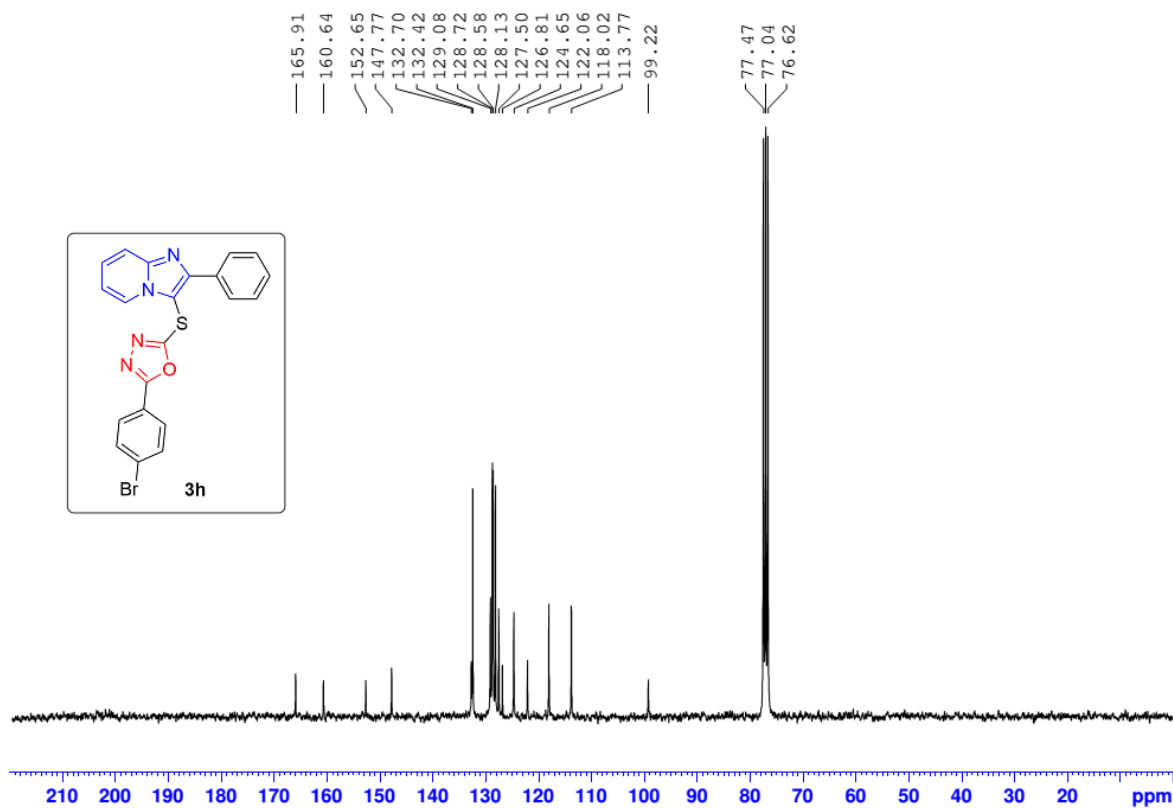


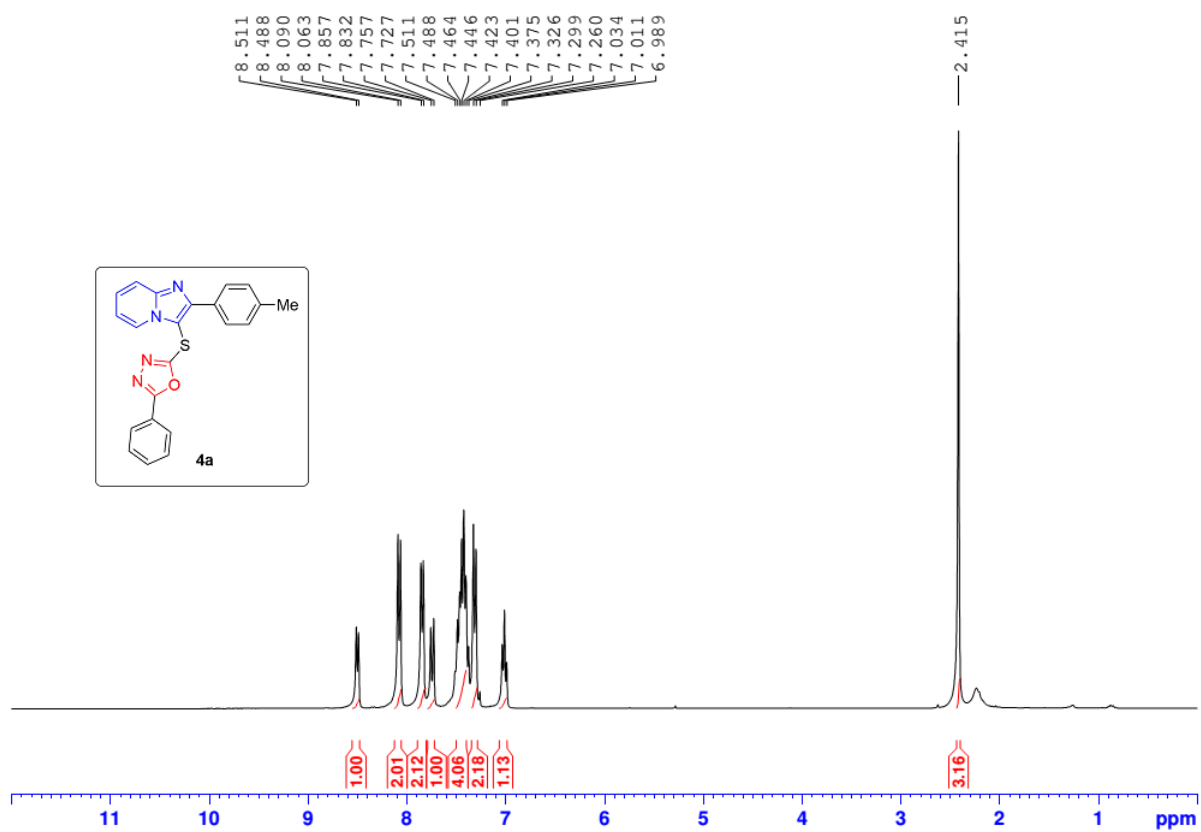
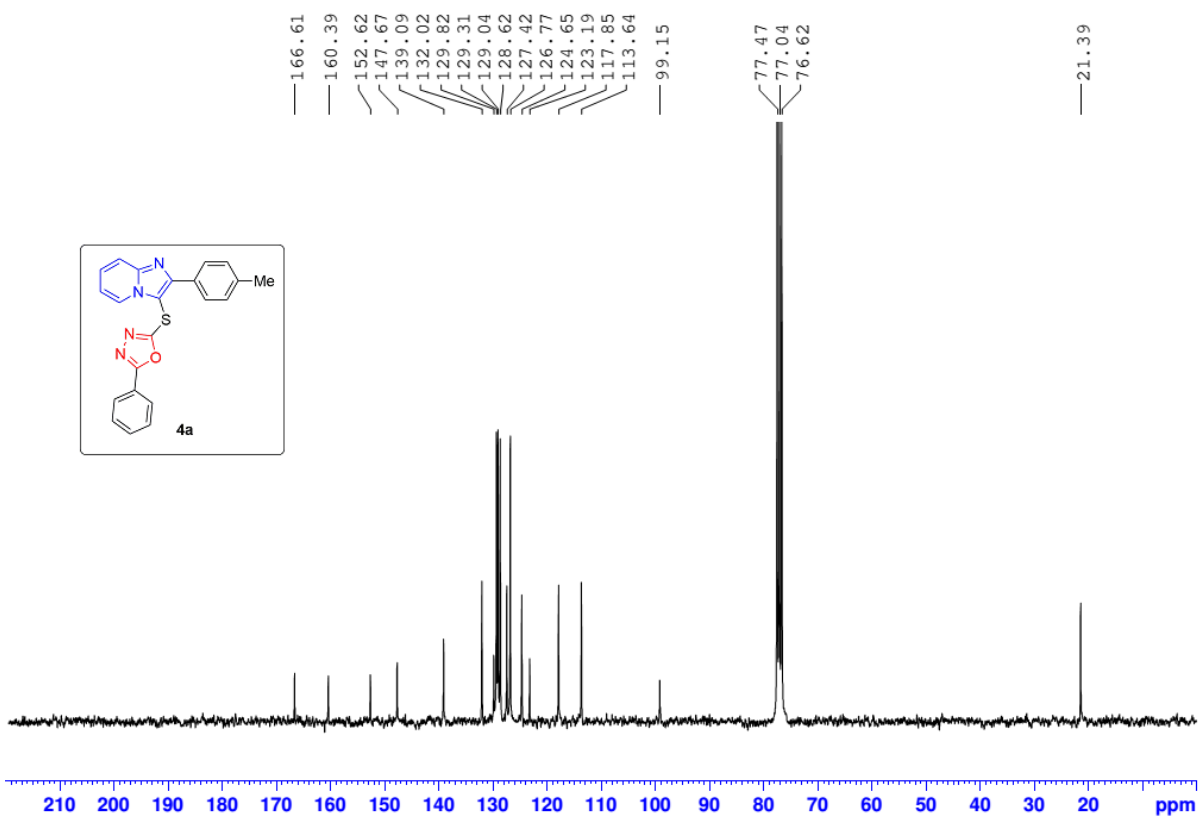
Figure S7. <sup>1</sup>H NMR spectrum of 3dFigure S8. <sup>13</sup>C NMR spectrum of 3d

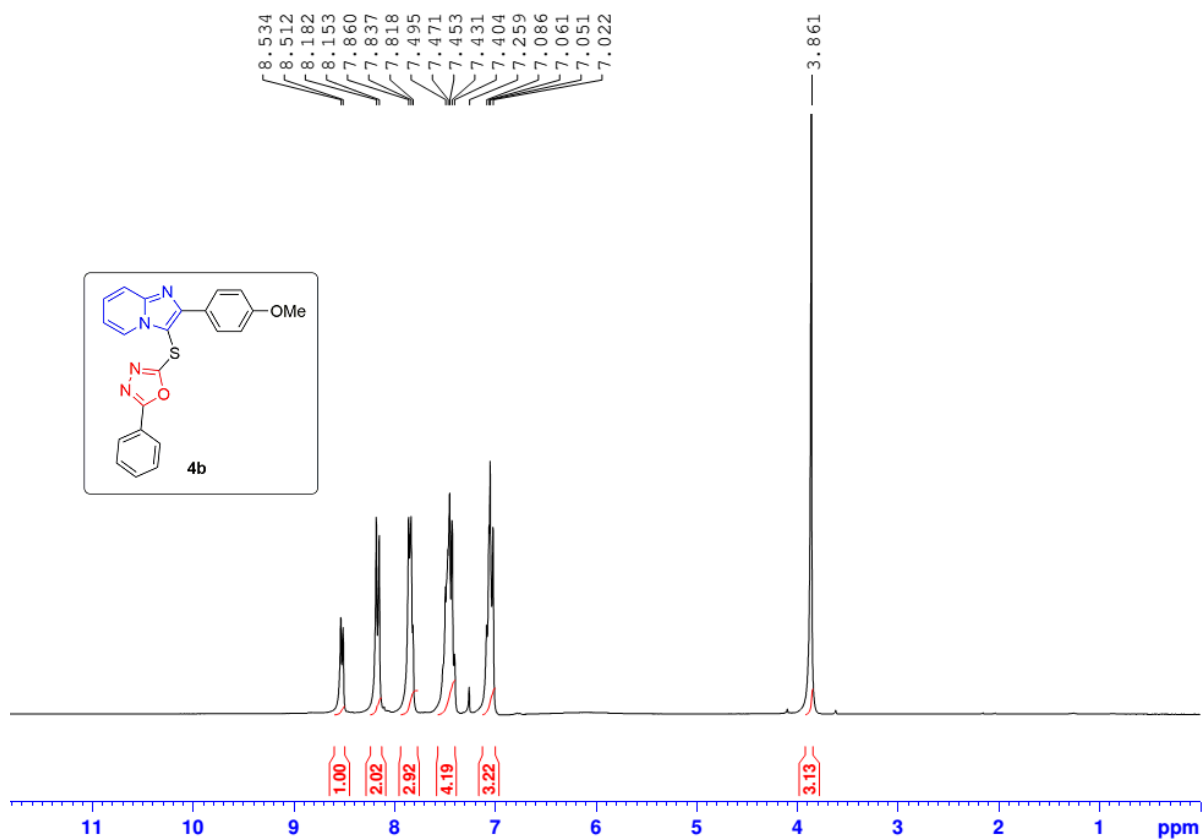
Figure S9.  $^1\text{H}$  NMR spectrum of **3e**Figure S10.  $^{13}\text{C}$  NMR spectrum of **3e**

Figure S11. <sup>1</sup>H NMR spectrum of **3f**Figure S12. <sup>13</sup>C NMR spectrum of **3f**

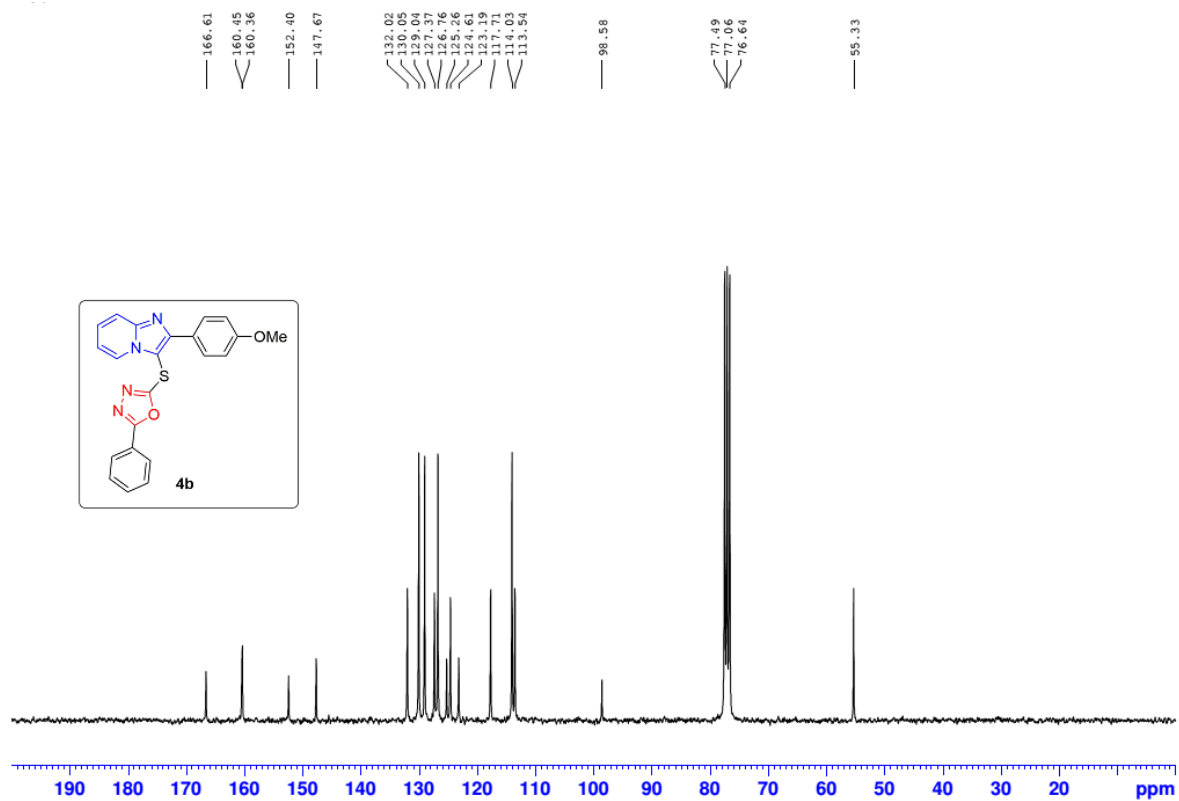
Figure S13.  $^1\text{H}$  NMR spectrum of **3g**Figure S14.  $^{13}\text{C}$  NMR spectrum of **3g**

Figure S15. <sup>1</sup>H NMR spectrum of **3h**Figure S16. <sup>13</sup>C NMR spectrum of **3h**

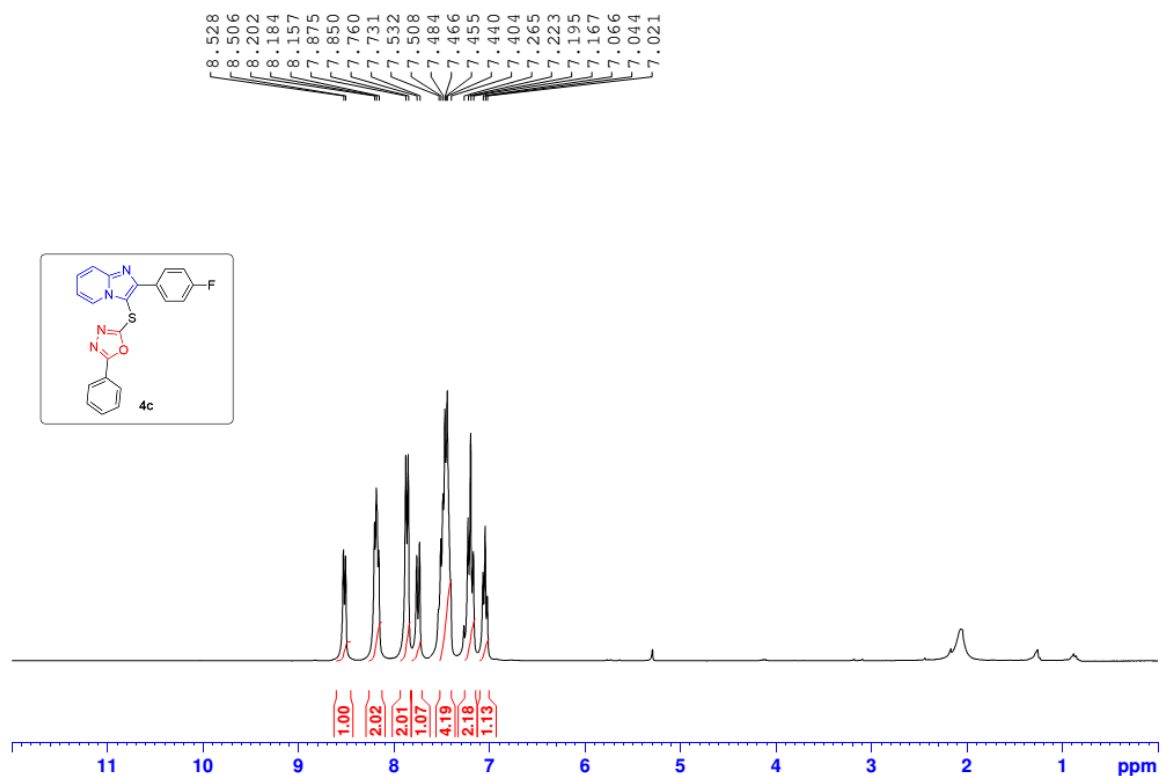
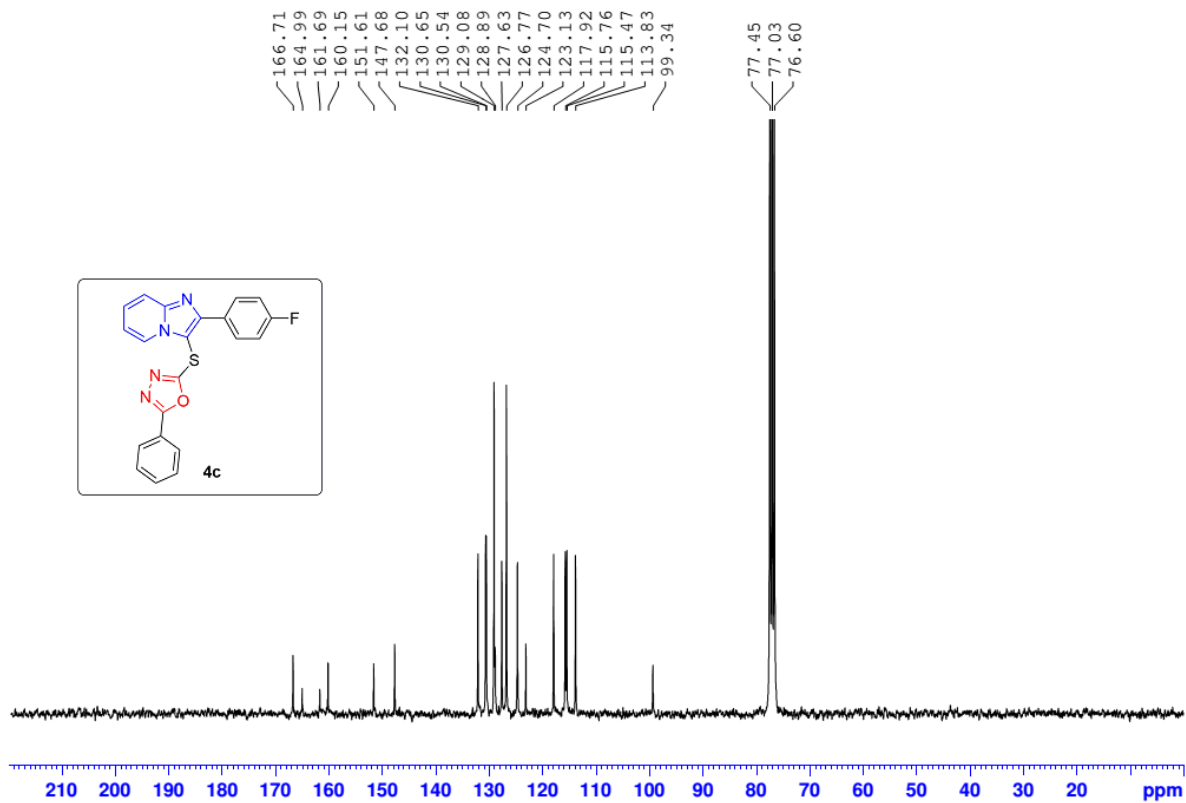
Figure S17. <sup>1</sup>H NMR spectrum of **4a**Figure S18. <sup>13</sup>C NMR spectrum of **4a**



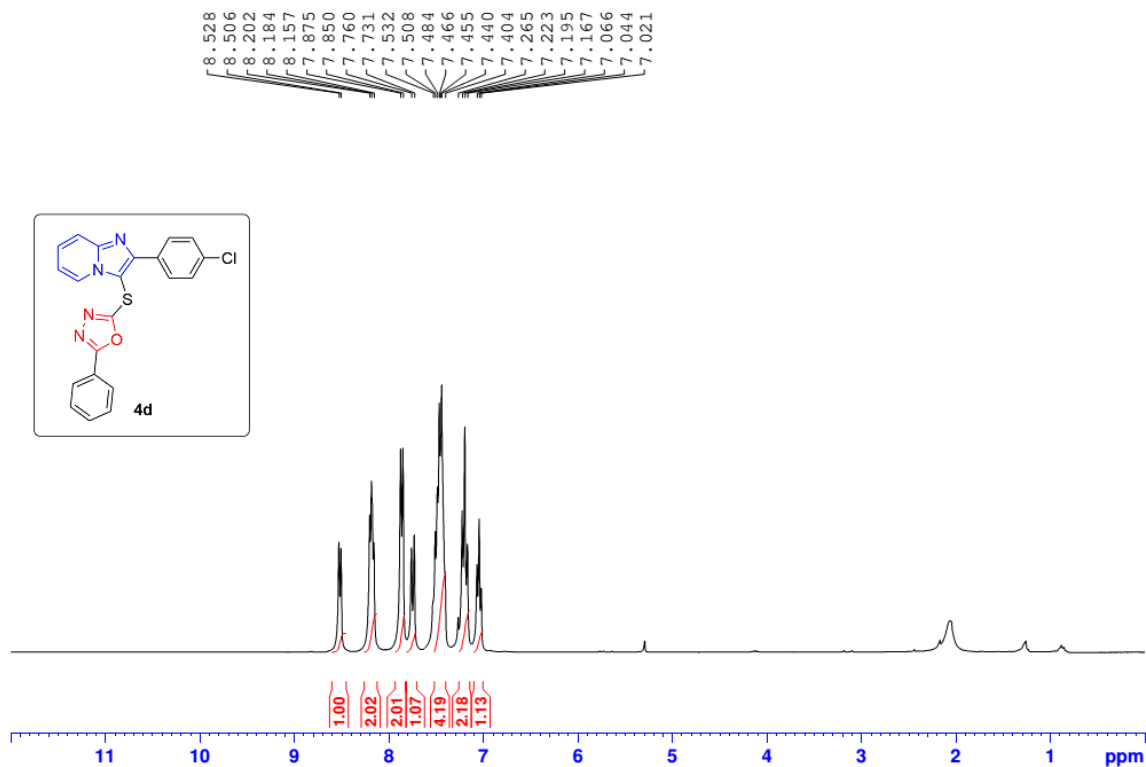
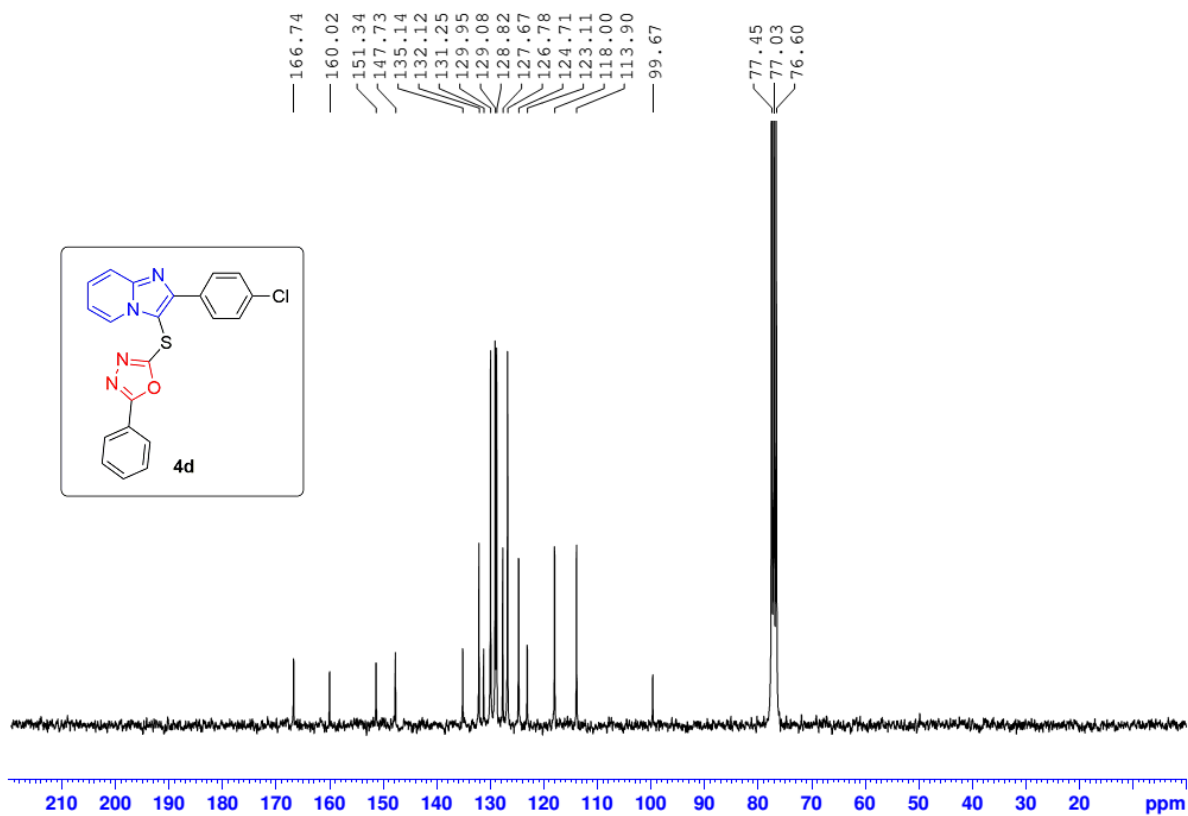
**Figure S19.**  $^1\text{H}$  NMR spectrum of **4b**

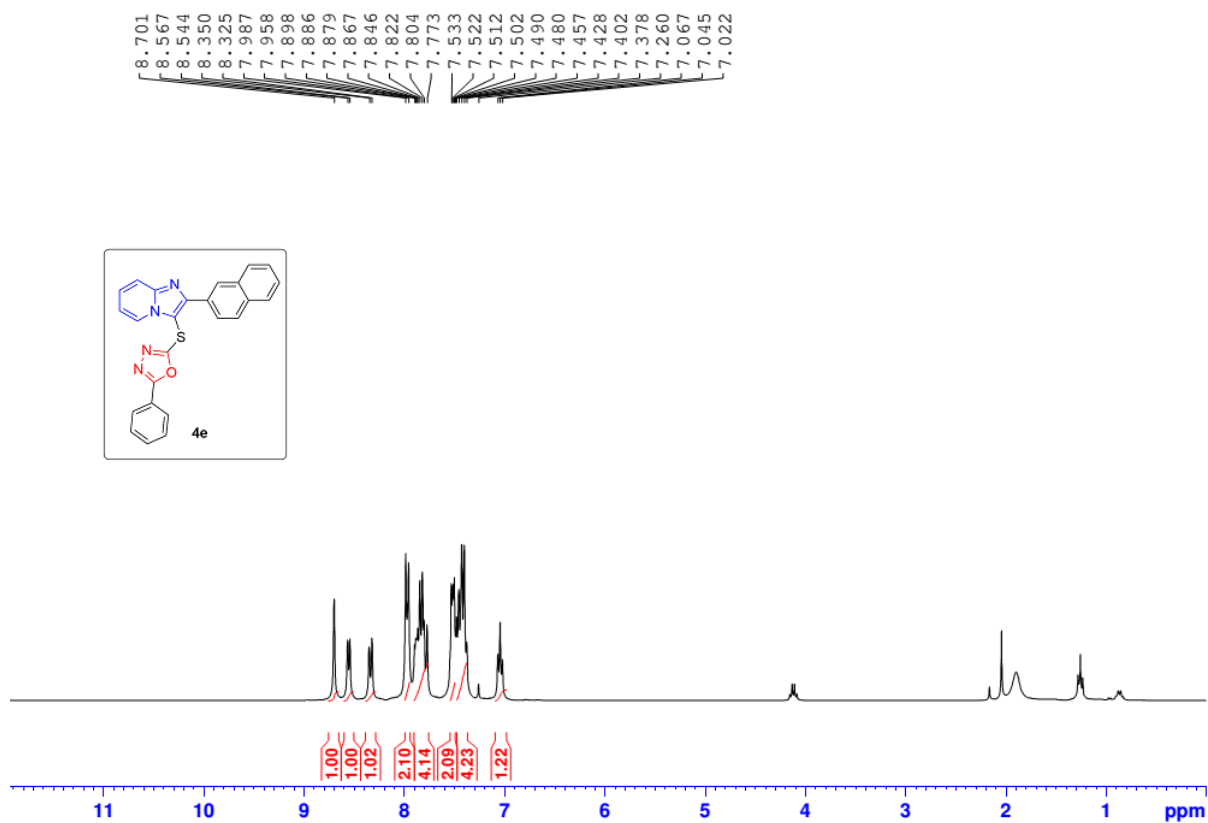
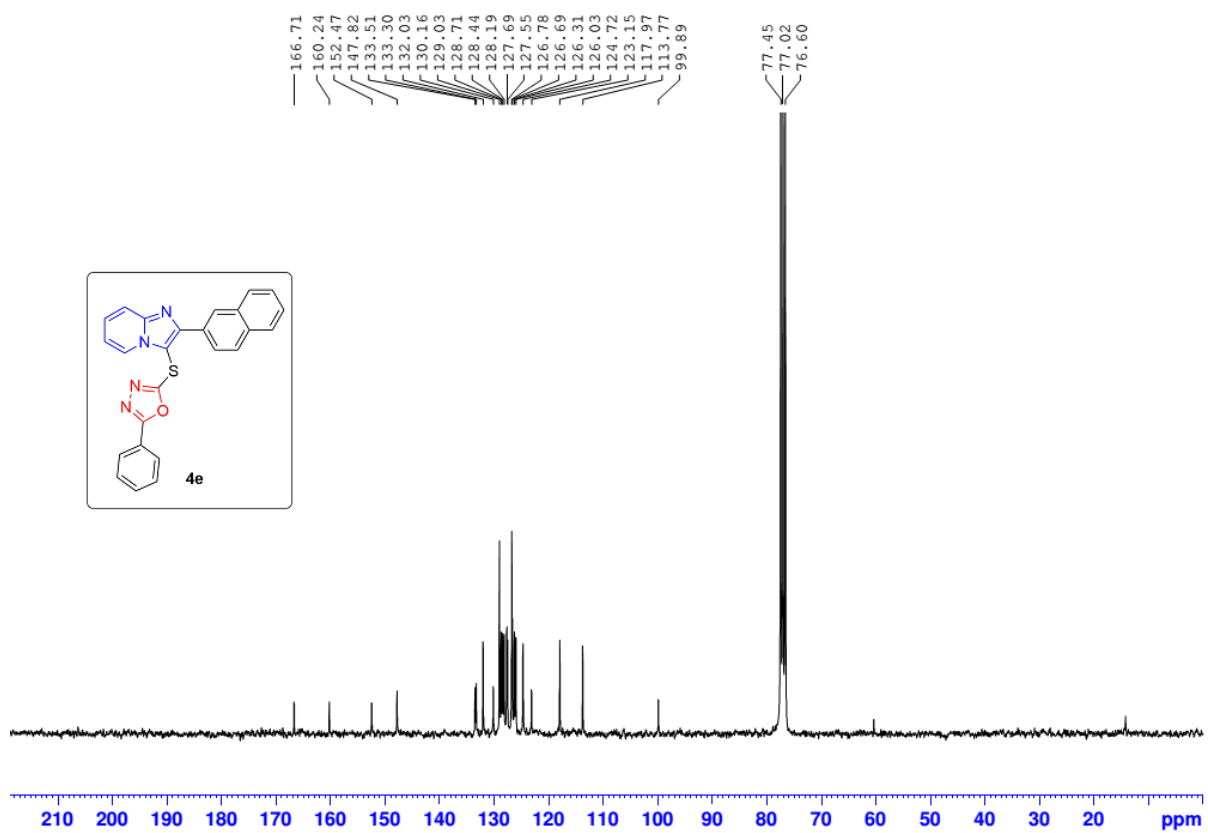


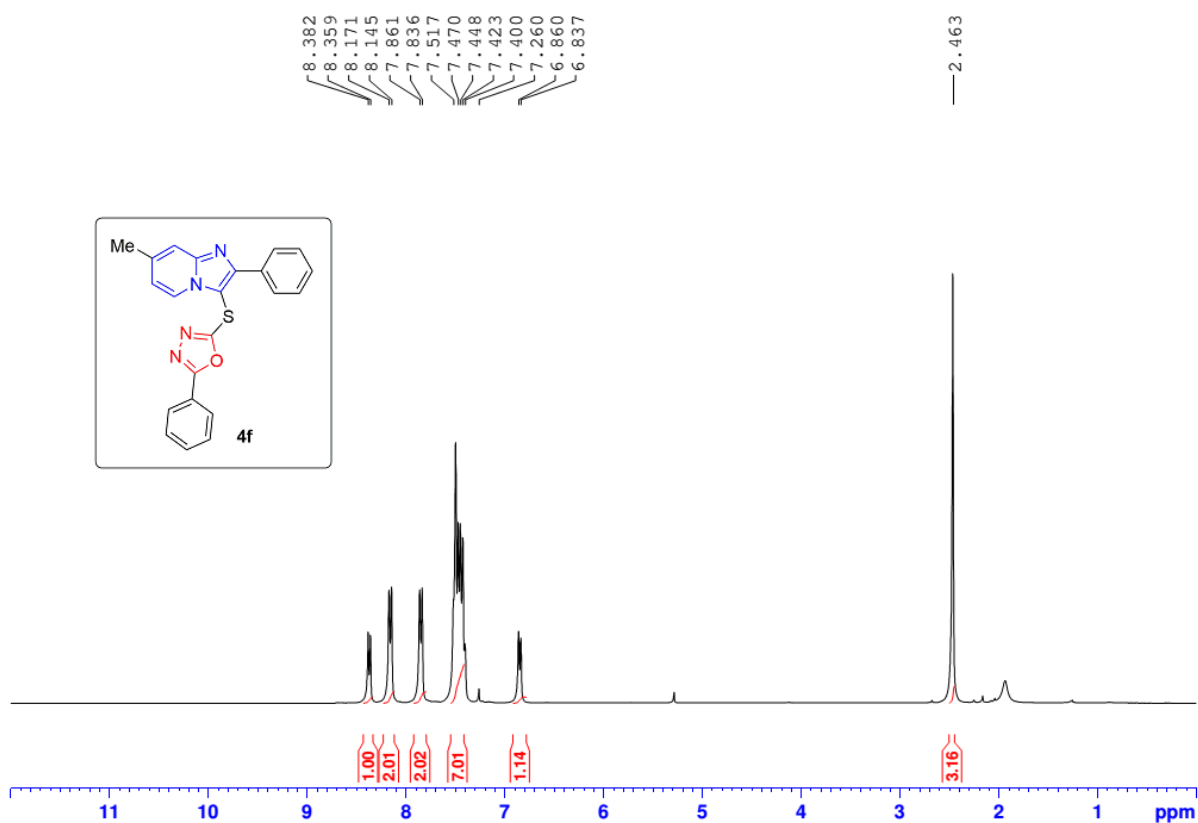
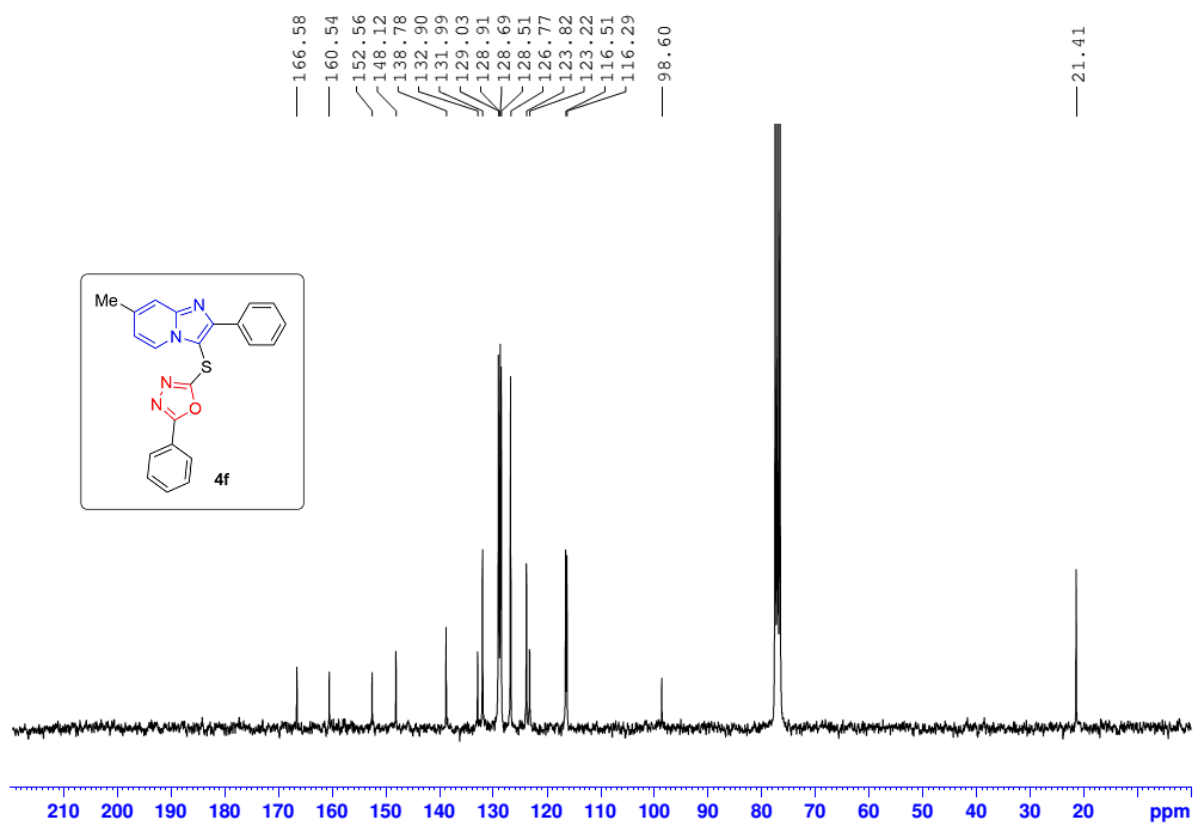
**Figure S20.**  $^{13}\text{C}$  NMR spectrum of **4b**

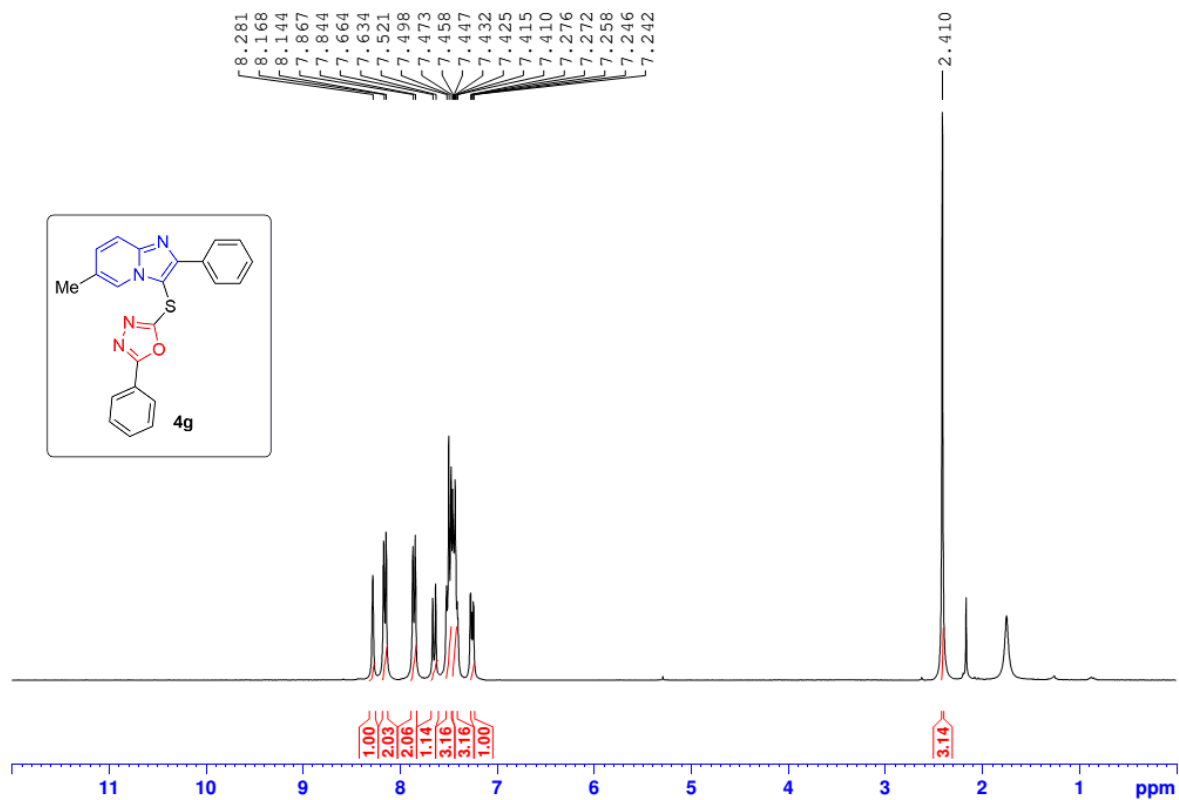
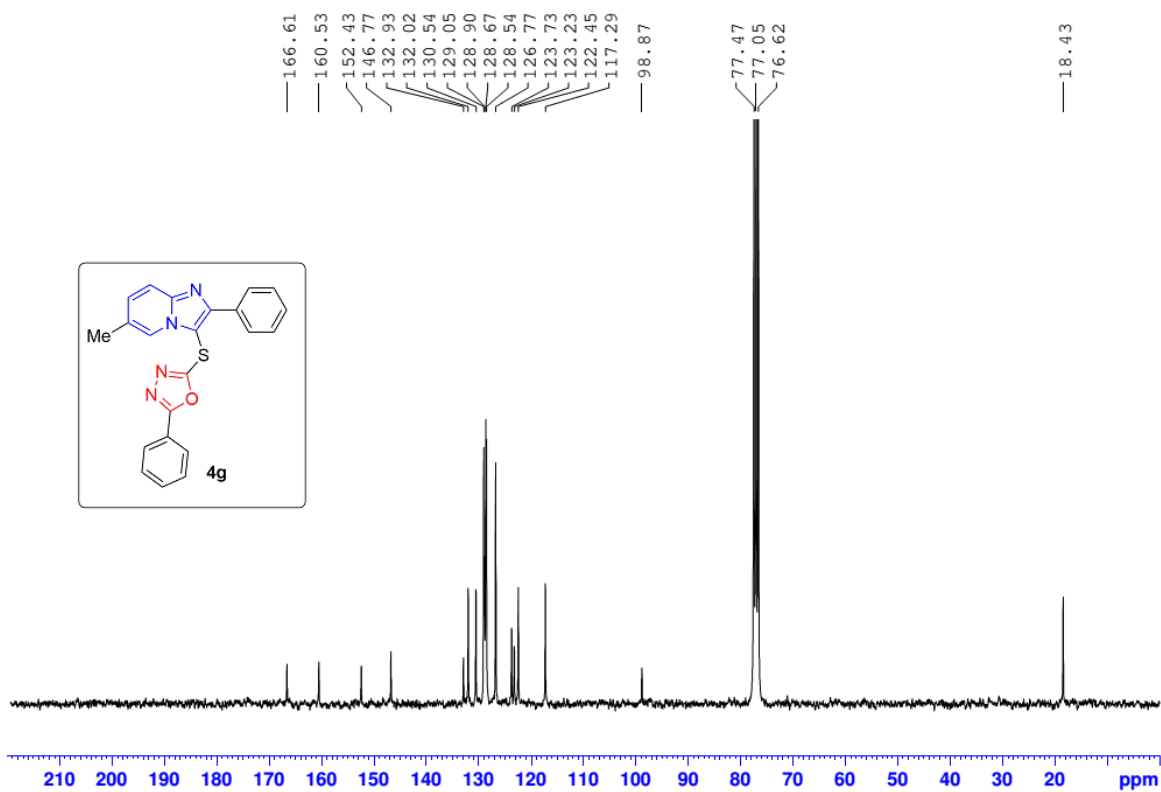
Figure S21.  $^1\text{H}$  NMR spectrum of **4c**Figure S22.  $^{13}\text{C}$  NMR spectrum of **4c**

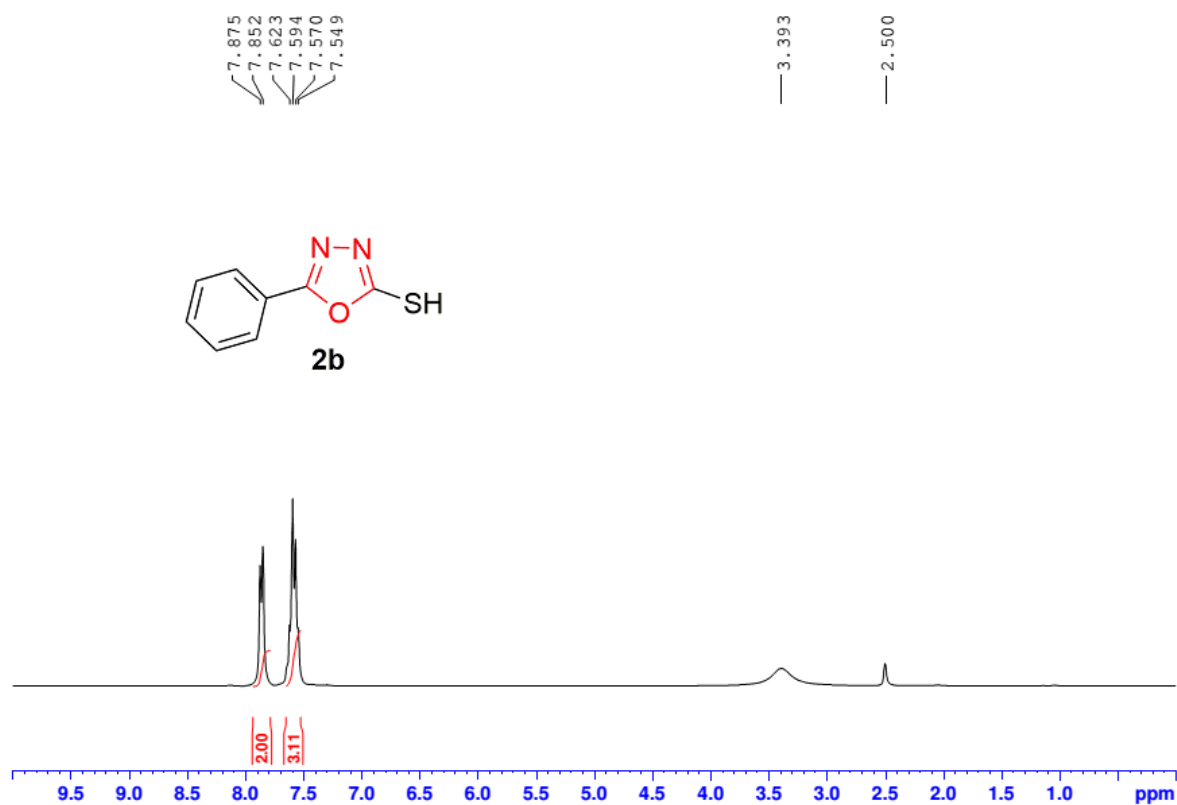
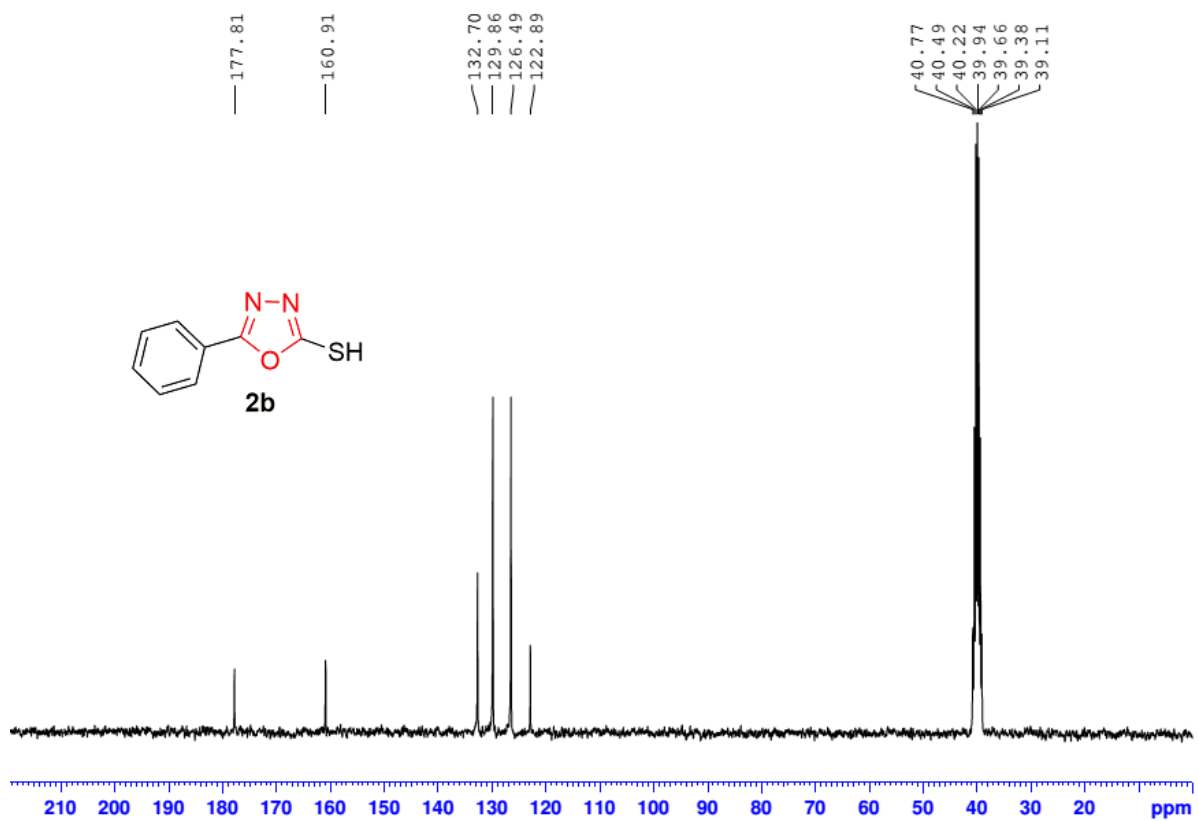


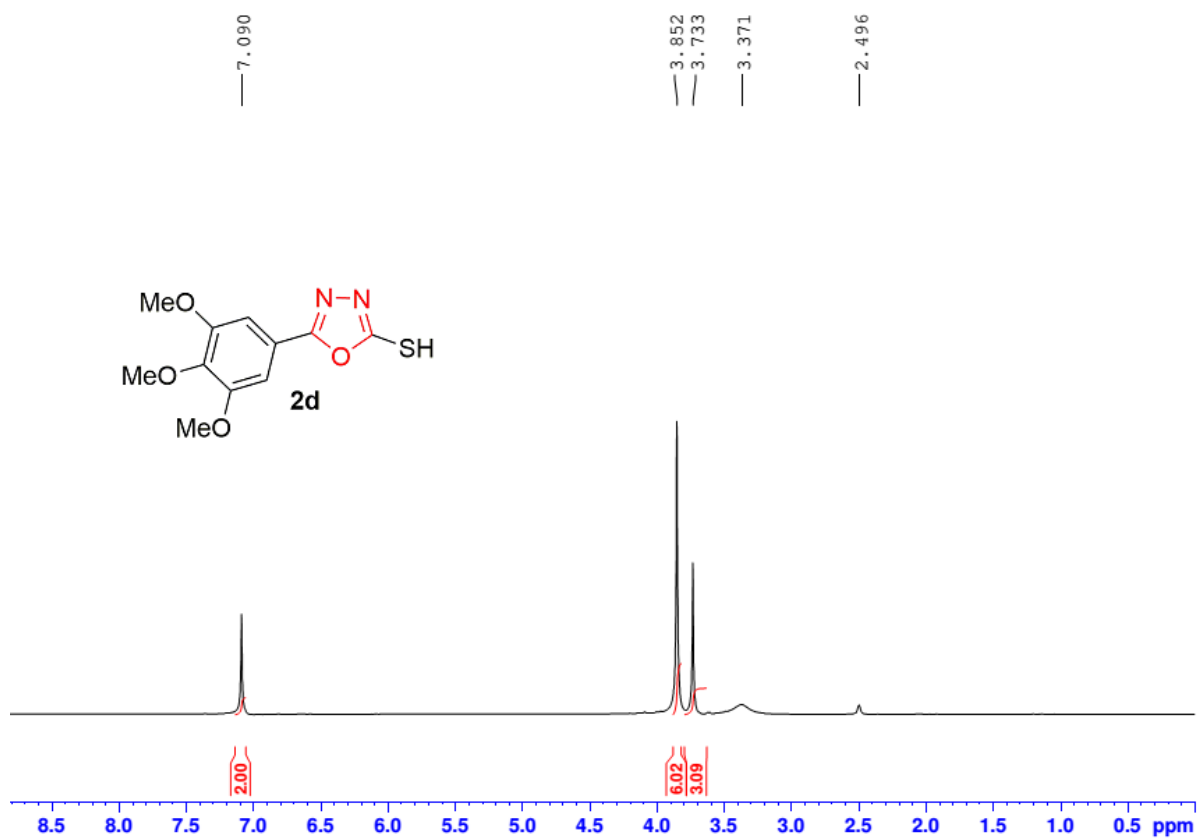
Figure S23. <sup>1</sup>H NMR spectrum of **4d**Figure S24. <sup>13</sup>C NMR spectrum of **4d**

Figure S25. <sup>1</sup>H NMR spectrum of **4e**Figure S26. <sup>13</sup>C NMR spectrum of **4e**

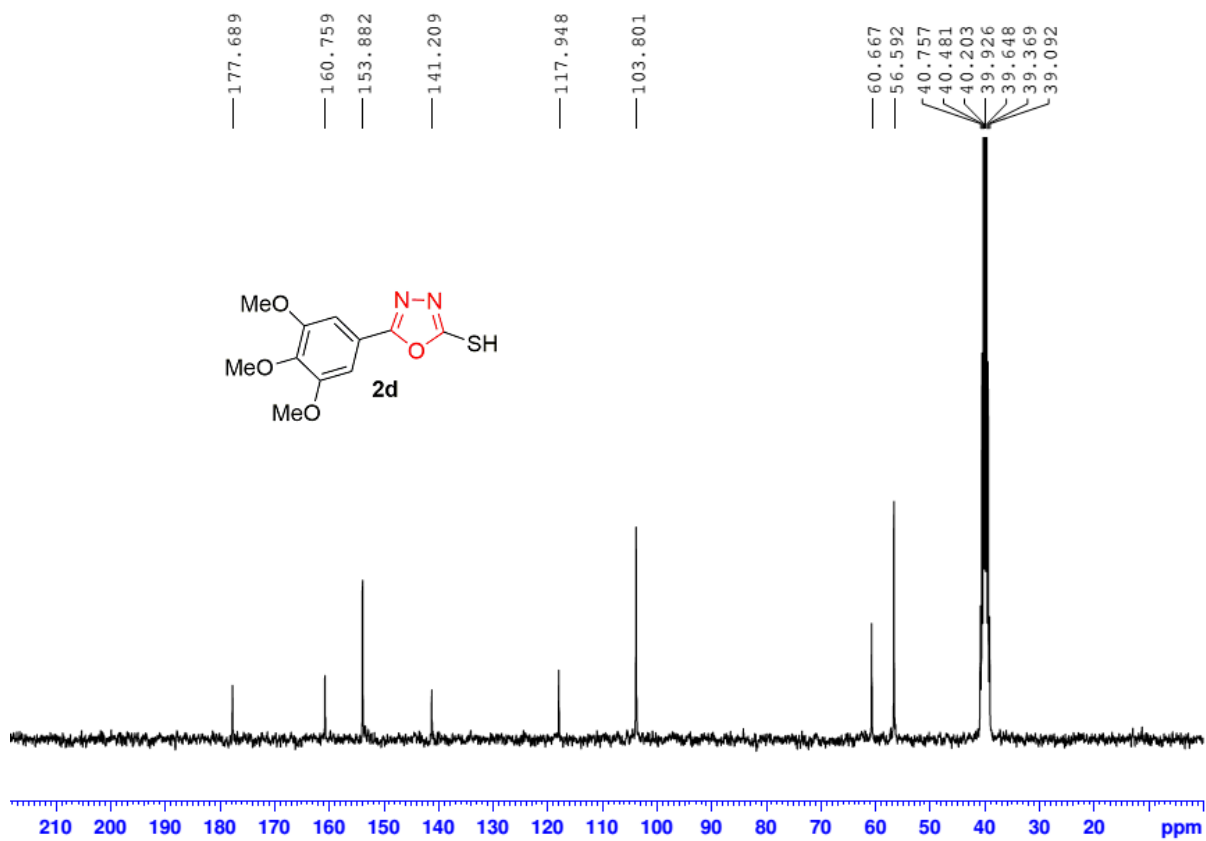
Figure S27.  $^1\text{H}$  NMR spectrum of **4f**Figure S28.  $^{13}\text{C}$  NMR spectrum of **4f**

Figure S29. <sup>1</sup>H NMR spectrum of **4g**Figure S30. <sup>13</sup>C NMR spectrum of **4g**

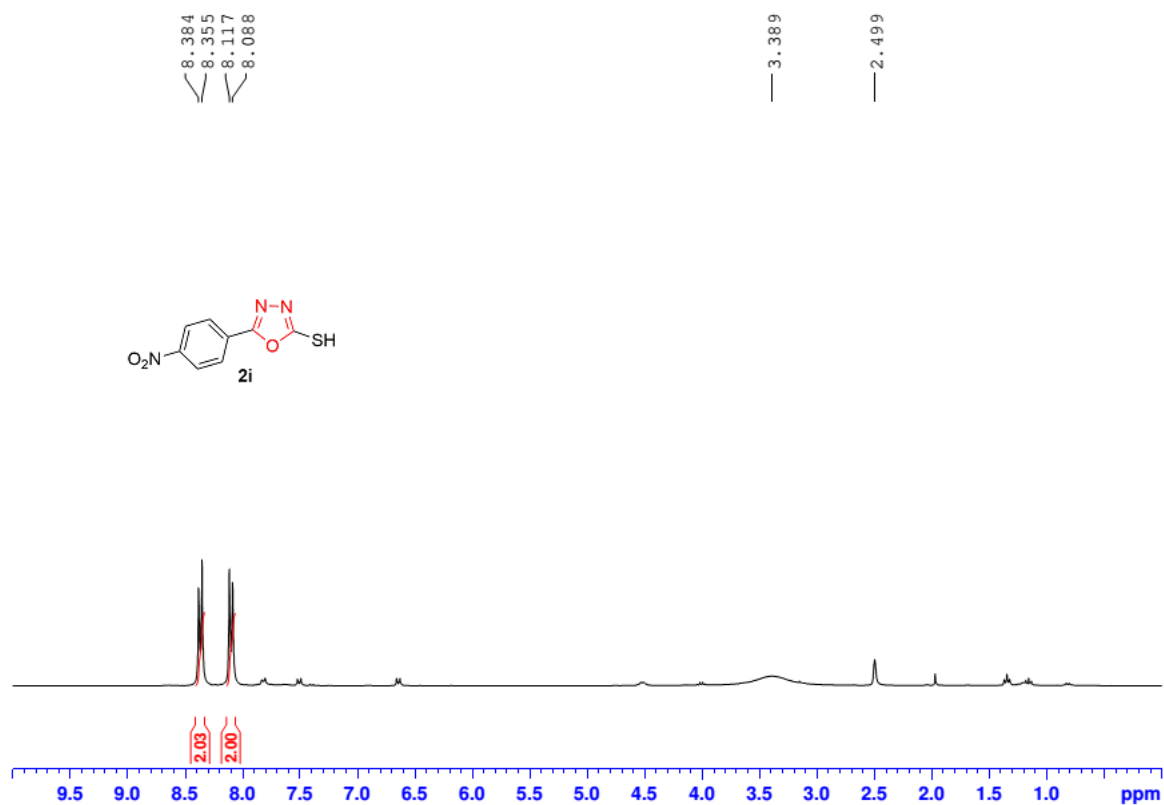
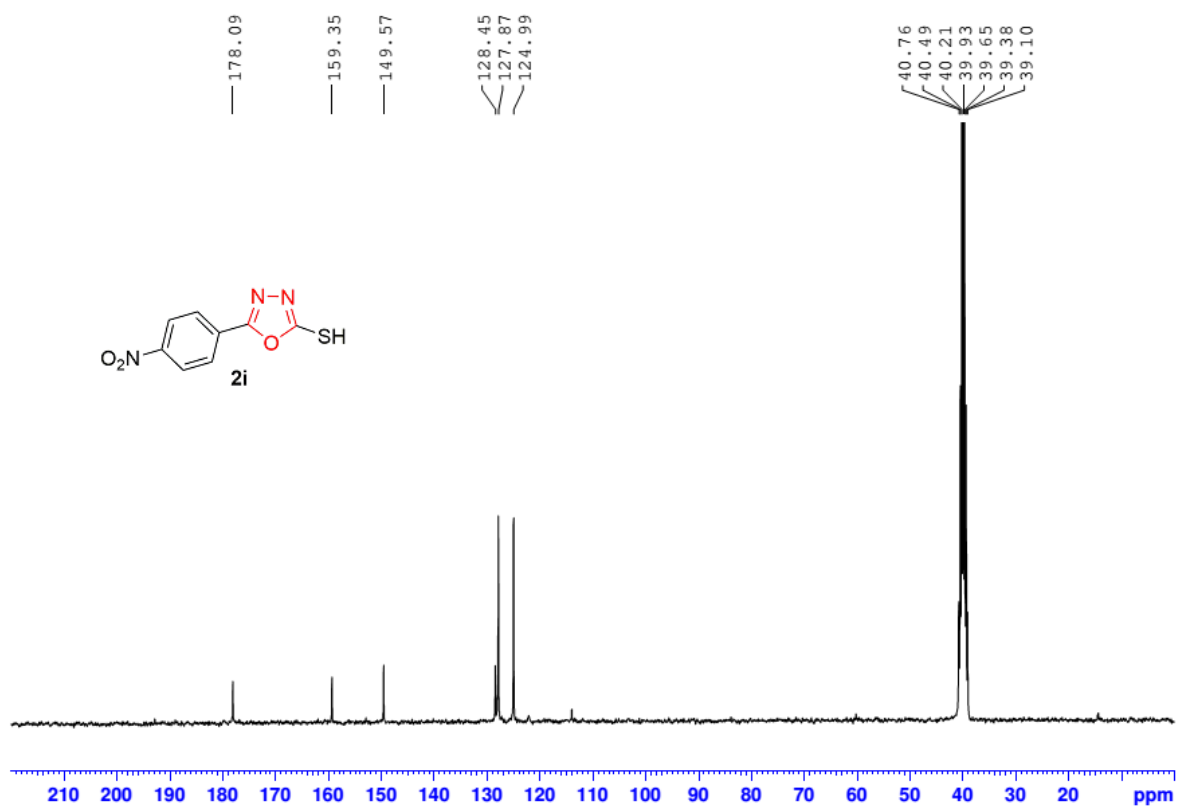
Figure S31. <sup>1</sup>H NMR spectrum of **2b**Figure S32. <sup>13</sup>C NMR spectrum of **2b**



**Figure S33.**  $^1\text{H}$  NMR spectrum of **2d**



**Figure S34.**  $^{13}\text{C}$  NMR spectrum of **2d**

Figure S35. <sup>1</sup>H NMR spectrum of **2i**Figure S36. <sup>13</sup>C NMR spectrum of **2i**

## 5. References

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