

## Solvent-Free Mechanochemical Synthesis of Azo Dyes

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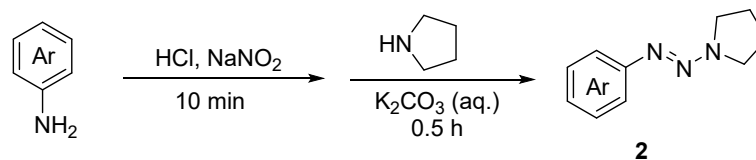
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## I. General Information

Unless otherwise noted, all reagents and solvents were purchased from commercial sources (Adamas-beta, Alfa Aesar) and used without further purification. Reactions were monitored using Thin Layer Chromatography (TLC) carried out on Merck silica gel plates (60F<sub>254</sub>) using UV light as the visualizing agent. Column chromatography was performed using silica gel 60 (300-400 mesh). HRMS data were recorded on Thermo Fisher Scientific Q-Exactive. All <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra were recorded on 600 MHz NMR spectrometers (Bruker AVANCE NEO 600) or 400 MHz NMR spectrometers (Varian Inova-400). Chemical shifts were given in parts per million (ppm,  $\delta$ ), referenced to the solvent peak of CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub>, defined at  $\delta = 7.26$  or 2.50 (<sup>1</sup>H NMR), defined at  $\delta = 77.0$  or 39.70 (<sup>13</sup>C NMR). Coupling constants were quoted in Hz (*J*). <sup>1</sup>H NMR Spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet

(t), quartet (q). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m). Melting point (M.P.) was recorded on BÜCHI (M-560). Planetary Ball Mill (QM-3SP04-1). UV-visible spectra were recorded on UV-2601 spectrophotometer (Beijing Beifen Ruili Analytical Instrument (Group) Co., Ltd).

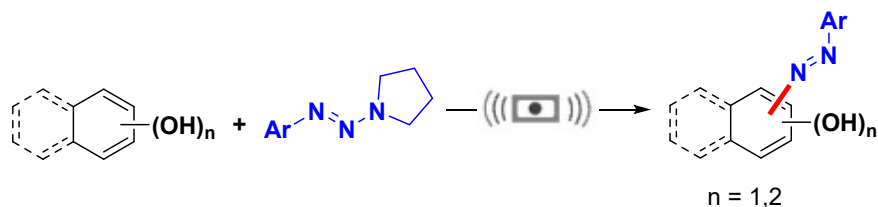
## II. Synthesis of Aryltriazenes<sup>[1]</sup>



A solution of arylamine (20 mmol) in concentrated HCl (4 mL) was cooled in an ice bath while a solution of NaNO<sub>2</sub> (20 mmol) in water (10 mL) was added dropwise. The resulting solution of the diazonium salt was stirred in an ice bath for 10 min and then added all at once to a chilled solution of amine (22 mmol) and 1.2 M K<sub>2</sub>CO<sub>3</sub> aqueous (20 mL) to the above solution, and the resulting mixture was stirred for 0.5 h. The resulting precipitate was recrystallized in EtOH or separated by column chromatography to obtain the desired purified aryltriazenes products.

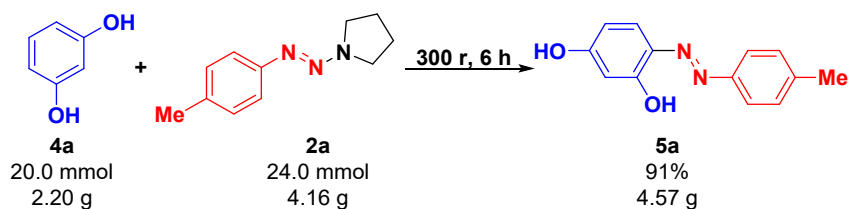
### III. Experimental Procedures

#### Reaction procedure for the synthesis of azo dyes



To a 50 mL stainless steel milling jar was added a stainless-steel ball (5 mm, 20 balls), phenolic compounds (1.0 mmol) and substituted aryltriazenes (1.2 mmol). The jar was then closed and securely fitted to the mill, which was milled at 300 rpm for 3 hours. For naphthol azo dyes, once the reaction completed, the jar was opened and EtOAc (~2 mL) and water (~1 mL) were added to the jar which was then closed shaken and the mixture transferred to a separating funnel, and repeated the process twice. The aqueous mixture was extracted with ethyl acetate (3×5 mL). The combined organic phase was dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 50:1 to 20:1, v/v) to afford the desired product. For resorcinol azo dyes, once the reaction was completed, the jar was opened and petroleum ether (5 mL) was added to the jar to wash and filtered dry the product. The process was repeated twice and the product was then washed and dried with water (3×5 mL) to obtain the corresponding product.

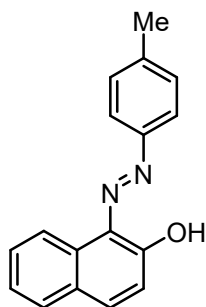
#### Gram-scale reaction



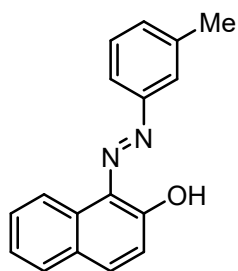
To a 50 mL stainless steel milling jar was added a stainless-steel ball (5 mm, 20 balls), resorcinol **4a** (20.0 mmol) and *p*-methylphenyltriazene **2a** (24.0 mmol). The jar was then closed and securely fitted to the mill, which was set at 300 rpm milled for 6 hours. When the reaction completed, the jar was opened and petroleum ether (15 mL) was added to the jar to wash, filter and finally dried the product. The process was

repeated twice and the product was then washed with water (3×15 mL) and dried to obtain the (*E*)-4-(p-tolyldiazenyl)benzene-1,3-diol (**5a**).

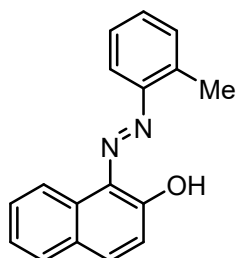
## IV. Analytical Data of Products



**(E)-1-(*p*-tolyl diazenyl)naphthalen-2-ol (3a)**<sup>[2]</sup>: Known compound. 240.7 mg, 92%, red solid, mp: 134.6-135.7 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 16.17 (s, 1H), 8.61 (dt, *J* = 8.3, 0.5 Hz, 1H), 7.72 (d, *J* = 9.4 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.63 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.56 (td, *J* = 7.0, 1.2 Hz, 1H), 7.39 (td, *J* = 8.0, 1.2 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 9.4 Hz, 1H), 2.42 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.44, 143.47, 138.83, 138.28, 133.48, 130.13, 129.71, 128.53, 128.44, 127.97, 125.27, 123.95, 121.58, 119.09, 21.25.

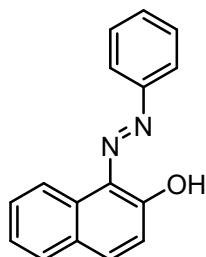


**(E)-1-(*m*-tolyl diazenyl)naphthalen-2-ol (3b)**<sup>[2]</sup>: Known compound. 210.1 mg, 80%, red solid, mp: 134.5-135.8 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.57 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 9.4 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.58-7.51 (m, 3H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 7.3 Hz, 1H), 6.87 (d, *J* = 9.4 Hz, 1H), 2.46 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 172.00, 144.67, 139.96, 139.64, 133.68, 129.98, 129.41, 128.82, 128.59, 128.35, 128.01, 125.64, 124.90, 121.69, 119.02, 115.89, 21.52.

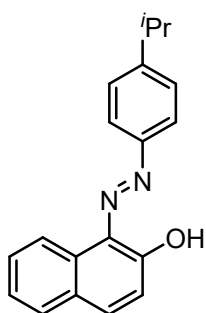


**(E)-1-(*o*-tolyl diazenyl)naphthalen-2-ol (3c)**<sup>[2]</sup>: Known compound. 98.4 mg, 38%, red solid, mp: 183.4-184.5 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.59 (d, *J* = 8.2 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 9.5 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 7.4 Hz, 1H),

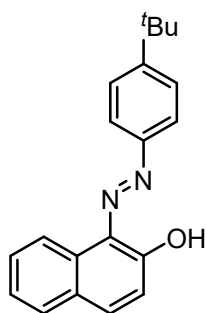
7.37 (t,  $J = 7.8$  Hz, 1H), 7.29 (d,  $J = 7.4$  Hz, 1H), 7.21 (t,  $J = 7.3$  Hz, 1H), 6.88 (d,  $J = 9.5$  Hz, 1H), 2.56 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.54, 142.26, 140.28, 133.52, 131.03, 130.60, 128.83, 128.56, 128.49, 127.89, 127.31, 126.89, 125.70, 125.18, 121.60, 115.64, 17.48.



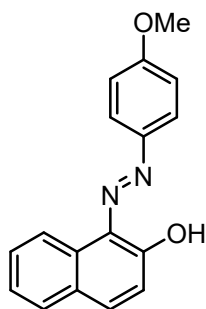
**(E)-1-(Phenyldiazenyl)naphthalen-2-ol (3d)**<sup>[2]</sup>: Known compound. 223.5 mg, 90%, red solid, mp: 172.3-173.1 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  16.24 (s, 1H), 8.55 (dt,  $J = 8.3, 1.0$  Hz, 1H), 7.73 (dt,  $J = 8.7, 1.5$  Hz, 2H), 7.70 (d,  $J = 9.4$  Hz, 1H), 7.59 (dd,  $J = 7.6, 1.3$  Hz, 1H), 7.55 (td,  $J = 7.2, 1.3$  Hz, 1H), 7.48 (tt,  $J = 7.4, 1.8$  Hz, 2H), 7.39 (ddd,  $J = 8.2, 7.3, 1.2$  Hz, 1H), 7.30 (tt,  $J = 7.4, 1.1$  Hz, 1H), 6.86 (d,  $J = 9.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.88, 144.58, 139.94, 133.45, 129.90, 129.45, 128.71, 128.48, 127.91, 127.25, 125.57, 124.71, 121.60, 118.43.



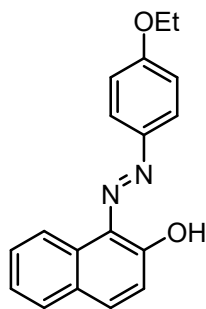
**(E)-1-((4-Isopropylphenyl)diazenyl)naphthalen-2-ol (3e)**<sup>[2]</sup>: Known compound. 189.3 mg, 65%, red solid, mp: 74.1-75.5 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  16.19 (s, 1H), 8.61 (d,  $J = 8.1$  Hz, 1H), 7.71 (dd,  $J = 9.1, 6.5$  Hz, 3H), 7.62 (d,  $J = 7.8$  Hz, 1H), 7.56 (td,  $J = 8.5, 1.4$  Hz, 1H), 7.39 (td,  $J = 7.0, 1.0$  Hz, 1H), 7.35 (d,  $J = 8.4$  Hz, 2H), 6.93 (d,  $J = 9.4$  Hz, 1H), 2.98 (sept,  $J = 7.0$  Hz, 1H), 1.31 (d,  $J = 6.9$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.69, 149.26, 143.68, 138.91, 133.53, 129.79, 128.57, 128.47, 127.99, 127.56, 125.30, 124.06, 121.60, 119.19, 33.93, 23.90.



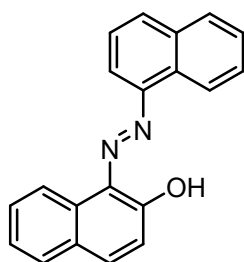
**(E)-1-((4-*tert*-butyl)phenyl)diazenyl)naphthalen-2-ol (3f)**<sup>[2]</sup>: Known compound. 188.0 mg, 62%, red semisolid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 16.22 (s, 1H), 8.60 (d, *J* = 7.8 Hz, 1H), 7.73-7.68 (m, 3H), 7.62 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.56 (td, *J* = 7.2, 1.4 Hz, 1H), 7.51 (dt, *J* = 8.7, 2.5 Hz, 2H), 7.39 (ddd, *J* = 8.0, 7.1, 1.2 Hz, 1H), 6.92 (d, *J* = 9.4 Hz, 1H), 1.38 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.02, 151.36, 143.14, 138.96, 133.50, 129.79, 128.55, 128.44, 127.94, 126.41, 125.60, 125.28, 124.10, 121.56, 119.85, 118.77, 34.77, 31.25.



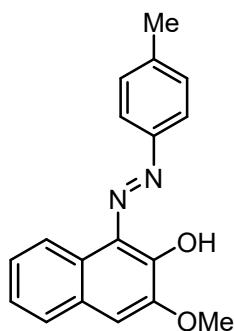
**(E)-1-((4-Methoxyphenyl)diazenyl)naphthalen-2-ol (3g)**<sup>[2]</sup>: Known compound. 273.2 mg, 98%, red solid, mp: 139.2-140.3 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 15.71 (s, 1H), 8.71 (d, *J* = 8.4 Hz, 1H), 7.83 (dt, *J* = 9.1, 3.2 Hz, 2H), 7.76 (d, *J* = 9.2 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.58 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H), 7.41 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 7.04 (t, *J* = 8.8 Hz, 3H), 3.89 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.33, 160.66, 141.83, 136.71, 133.30, 129.52, 128.33, 128.15, 124.80, 122.19, 122.06, 121.59, 114.78, 55.64.



**(E)-1-((4-Ethoxyphenyl)diazenyl)naphthalen-2-ol (3h)**: New compound. 265.7 mg, 91%, red solid, mp: 134.9-135.2 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 15.71 (s, 1H), 8.72 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 9.2 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 9.3 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 2H), 4.12 (q, *J* = 6.9 Hz, 2H), 1.47 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.11, 160.11, 141.71, 136.58, 133.29, 129.48, 128.30, 128.10, 124.75, 122.13, 122.09, 121.59, 115.25, 63.89, 14.76. HRMS (ESI) *m/z* calculated for C<sub>18</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 293.1284; Found: 293.1280. UV - visible absorption (DMSO, *c* = 4 × 10<sup>-5</sup> mol · L<sup>-1</sup>): λ<sub>max</sub> = 422 (19509) nm (L·mol<sup>-1</sup>·cm<sup>-1</sup>).

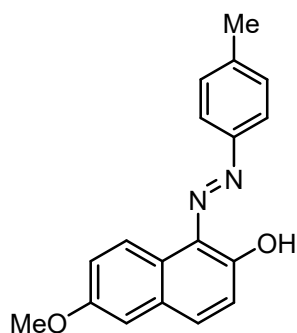


**(E)-1-(Naphthalen-1-ylidiazenyl)naphthalen-2-ol (3i)**<sup>[3]</sup>: Known compound. 234.9 mg, 79%, brown solid, mp: 199.5-200.3 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.65 (d, *J* = 8.2 Hz, 1H), 8.34 (d, *J* = 8.5 Hz, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 9.4 Hz, 1H), 7.67 (t, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.0 Hz, 3H), 7.41 (t, *J* = 7.5 Hz, 1H), 6.93 (dd, *J* = 9.4, 1.4 Hz, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.97, 140.48, 139.67, 134.17, 133.52, 131.28, 129.00, 128.71, 128.65, 128.11, 127.49, 127.24, 126.57, 126.16, 125.92, 125.20, 125.00, 121.82, 120.73, 112.91. HRMS (ESI) *m/z* calculated for C<sub>20</sub>H<sub>15</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 299.1179; Found: 299.1174. UV - visible absorption (DMSO, *c* = 4 × 10<sup>-5</sup> mol • L<sup>-1</sup>): λ<sub>max</sub> = 502 (13439) nm (L•mol<sup>-1</sup>•cm<sup>-1</sup>).

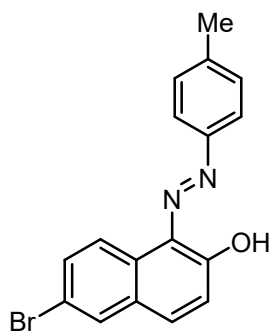


**(E)-3-Methoxy-1-(*p*-tolyldiazenyl)naphthalen-2-ol (3j)**: New compound. 248.2 mg, 85%, red solid, mp: 190.9-192.3 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.38 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.56 (dd, *J* = 6.5, 1.9 Hz, 2H), 7.45 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.39 (td, *J* = 7.2, 1.4 Hz, 1H), 7.33 (td, *J* = 7.4, 1.3 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 6.89 (s, 1H), 3.94 (s, 3H), 2.39 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 169.42, 151.36, 140.89, 137.14, 130.24, 129.76, 129.28, 127.55, 127.13, 126.36, 126.04, 121.23, 117.75, 113.38, 55.79, 21.17. HRMS (ESI) *m/z* calculated for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup>: 315.1104; Found: 315.1099. UV - visible absorption (DMSO, *c* = 4 × 10<sup>-5</sup> mol • L<sup>-1</sup>): λ<sub>max</sub> = 483 (14924) nm (L•mol<sup>-1</sup>•cm<sup>-1</sup>).

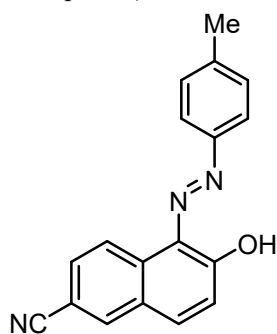




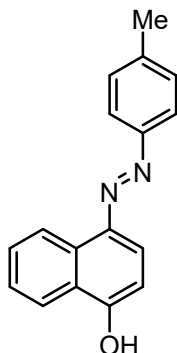
**(E)-6-Methoxy-1-(p-tolyldiazenyl)naphthalen-2-ol (3k):** New compound. 254.2 mg, 87%, red solid, mp: 190.9-192.3 °C.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  15.66 (s, 1H), 8.53 (d,  $J = 9.0$  Hz, 1H), 7.68-7.62 (m, 3H), 7.27 (d,  $J = 7.8$  Hz, 2H), 7.19 (dd,  $J = 8.9, 2.6$  Hz, 1H), 7.02 (d,  $J = 2.6$  Hz, 1H), 6.93 (d,  $J = 9.3$  Hz, 1H), 3.91 (s, 3H), 2.41 (s, 3H).  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  166.58, 157.53, 143.96, 138.30, 137.98, 130.16, 130.02, 129.45, 129.06, 127.75, 124.26, 123.38, 120.19, 119.22, 118.73, 108.89, 55.30, 21.31. **HRMS** (ESI)  $m/z$  calculated for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2\text{Na}$   $[\text{M}+\text{Na}]^+$ : 315.1104; Found: 315.1099. UV - visible absorption (DMSO,  $c = 2 \times 10^{-5}$  mol  $\cdot$  L $^{-1}$ ):  $\lambda_{\text{max}} = 494$  (18148) nm ( $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ).



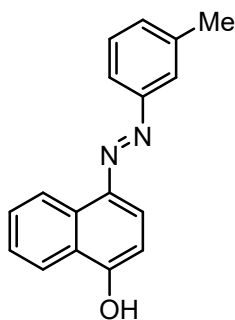
**(E)-6-Bromo-1-(p-tolyldiazenyl)naphthalen-2-ol (3l):** New compound. 238.4 mg, 87%, red solid, mp: 196.5-197.7 °C.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  16.01 (s, 1H), 8.49 (d,  $J = 8.8$  Hz, 1H), 7.79 (t,  $J = 2.0$  Hz, 1H), 7.68 (dd,  $J = 6.4, 1.9$  Hz, 2H), 7.63 (td,  $J = 8.8, 2.0$  Hz, 2H), 7.30 (d,  $J = 8.1$  Hz, 1H), 6.99 (d,  $J = 9.4$  Hz, 1H), 2.43 (s, 3H).  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  166.22, 143.96, 139.17, 136.95, 132.09, 131.40, 130.43, 130.23, 129.45, 129.28, 124.78, 123.47, 119.63, 118.82, 21.35. **HRMS** (ESI)  $m/z$  calculated for  $\text{C}_{17}\text{H}_{13}\text{BrN}_2\text{O}$   $[\text{M}+\text{H}]^+$ : 341.0284; Found: 341.0278. UV - visible absorption (DMSO,  $c = 8 \times 10^{-5}$  mol  $\cdot$  L $^{-1}$ ):  $\lambda_{\text{max}} = 468$  (18555) nm ( $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ).



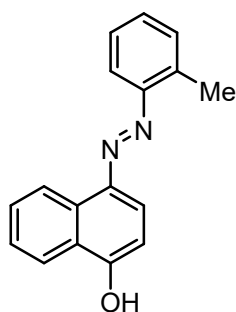
**(E)-6-Hydroxy-5-(p-tolyldiazenyl)-2-naphthonitrile (3m):** New compound. 230.0 mg, 80%, red solid, mp: 208.9-210.0 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.69 (d, *J* = 8.6 Hz, 1H), 7.99 (s, 1H), 7.74 (d, *J* = 9.3 Hz, 1H), 7.72-7.68 (m, 3H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 9.3 Hz, 1H), 2.44 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 166.22, 143.99, 140.16, 136.84, 135.83, 133.47, 130.73, 129.59, 128.90, 127.18, 125.23, 122.57, 120.08, 119.13, 108.23, 21.41. **HRMS** (ESI) *m/z* calculated for C<sub>18</sub>H<sub>14</sub>N<sub>3</sub>O [M+H]<sup>+</sup>: 310.0951; Found: 310.0948. UV - visible absorption (DMSO, *c* = 4 × 10<sup>-5</sup> mol · L<sup>-1</sup>): λ max = 413 (16460) nm (L·mol<sup>-1</sup>·cm<sup>-1</sup>).



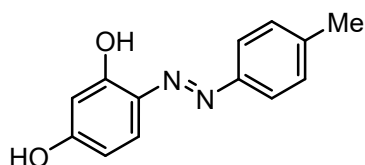
**(E)-4-(p-tolyldiazenyl)naphthalen-1-ol (3n)**<sup>[4]</sup>: Known compound. 184.2 mg, 70%, red solid, mp: 200.6-201.6 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 11.10 (s, 1H), 8.88 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.86 (t, *J* = 8.4 Hz, 3H), 7.70 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 7.3 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 1H), 2.41 (s, 3H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 157.57, 151.04, 140.68, 139.71, 132.76, 130.10, 127.83, 125.58, 124.55, 122.78, 122.57, 113.79, 108.54, 21.18.



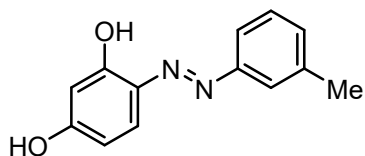
**(E)-4-(m-tolyldiazenyl)naphthalen-1-ol (3o):** New compound. 219.5 mg, 84%, red solid, mp: 155.9-156.9 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.59 (s, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 9.8 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.43-7.29 (m, 3H), 7.01 (s, 1H), 6.77 (d, *J* = 9.8 Hz, 1H), 2.44 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.74, 152.79, 138.87, 131.07, 129.21, 128.71, 127.83, 126.36, 125.55, 122.66, 119.97, 113.80, 108.40, 21.06. **HRMS** (ESI) *m/z* calculated for C<sub>17</sub>H<sub>15</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 263.1179; Found: 263.1175. UV - visible absorption (DMSO, *c* = 4 × 10<sup>-6</sup> mol · L<sup>-1</sup>): λ max = 386 (18660) nm (L·mol<sup>-1</sup>·cm<sup>-1</sup>).



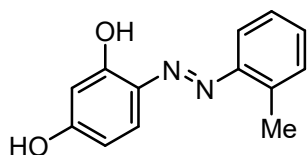
**(E)-4-(*o*-tolyl diazenyl)naphthalen-1-ol (3p):** New compound. 107.7 mg, 41%, red solid, mp: 195.1-195.9 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.47 (d,  $J = 8.0$  Hz, 1H), 7.98 (d,  $J = 8.2$  Hz, 1H), 7.63 (t,  $J = 7.6$  Hz, 1H), 7.58 (d,  $J = 7.4$  Hz, 1H), 7.47 (t,  $J = 7.4$  Hz, 1H), 7.34 (t,  $J = 7.7$  Hz, 1H), 7.27 (d,  $J = 6.3$  Hz, 1H), 7.25 (d,  $J = 7.1$  Hz, 1H), 7.17 (t,  $J = 7.4$  Hz, 1H), 7.02 (d,  $J = 9.3$  Hz, 1H), 2.56 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.00, 132.36, 131.02, 128.36, 127.65, 127.44, 126.85, 126.46, 126.26, 121.07, 115.36, 17.50. **HRMS** (ESI)  $m/z$  calculated for  $\text{C}_{17}\text{H}_{15}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$ : 263.1179; Found: 263.1175. UV - visible absorption (DMSO,  $c = 4 \times 10^{-5}$  mol  $\cdot$  L $^{-1}$ ):  $\lambda_{\text{max}} = 413$  (16775) nm (L $\cdot$ mol $^{-1}\cdot$ cm $^{-1}$ ).



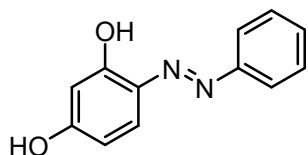
**(E)-4-(*p*-tolyl diazenyl)benzene-1,3-diol (5a)**<sup>[5]</sup>: Known compound. 203.1 mg, 89%, red solid, mp: 190.1-191.2 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  12.51 (s, 1H), 10.49 (s, 1H), 7.74 (d,  $J = 8.4$  Hz, 2H), 7.67 (d,  $J = 8.8$  Hz, 1H), 7.33 (d,  $J = 8.6$  Hz, 2H), 6.51 (dd,  $J = 8.8, 2.5$  Hz, 1H), 6.36 (d,  $J = 2.5$  Hz, 1H), 2.37 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.57, 154.88, 140.27, 135.03, 129.96, 122.85, 109.64, 104.93, 20.98.



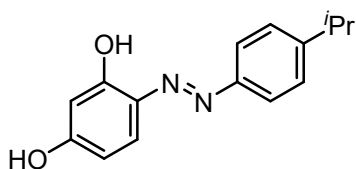
**(E)-4-(*m*-tolyl diazenyl)benzene-1,3-diol (5b):** New compound. 148.5 mg, 65%, red solid, mp: 131.5-133.0 °C.  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  12.55 (s, 1H), 10.56 (s, 1H), 7.68 (d,  $J = 8.8$  Hz, 1H), 7.67 (s, 1H), 7.64 (d,  $J = 9.0$  Hz, 2H), 7.42 (t,  $J = 7.7$  Hz, 1H), 7.28 (d,  $J = 7.5$  Hz, 1H), 6.51 (dd,  $J = 8.8, 2.5$  Hz, 1H), 6.36 (d,  $J = 2.5$  Hz, 1H), 2.39 (s, 3H).  $^{13}\text{C NMR}$  (150 MHz,  $\text{DMSO-}d_6$ )  $\delta$  163.11, 156.51, 150.76, 139.11, 132.39, 130.99, 130.54, 129.41, 121.94, 119.33, 109.27, 103.16, 21.10. **HRMS** (ESI)  $m/z$  calculated for  $\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$ : 229.0972; Found: 229.0968. UV - visible absorption (DMSO,  $c = 6 \times 10^{-5}$  mol  $\cdot$  L $^{-1}$ ):  $\lambda_{\text{max}} = 387$  (17903) nm (L $\cdot$ mol $^{-1}\cdot$ cm $^{-1}$ ).



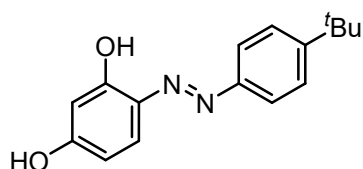
**(E)-4-(*o*-tolyl diazenyl)benzene-1,3-diol (5c):** New compound. 80.0 mg, 35%, red solid, mp: 188.5-189.5 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 14.26 (s, 1H), 7.83-7.78 (m, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.33-7.29 (m, 3H), 6.56 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.49 (d, *J* = 2.5 Hz, 1H), 2.58 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 163.06, 156.55, 148.20, 134.77, 132.66, 131.67, 131.31, 130.00, 126.90, 115.23, 109.34, 102.92, 17.42. **HRMS** (ESI) *m/z* calculated for C<sub>13</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 229.0972; Found: 229.0968. UV - visible absorption (DMSO, *c* = 4 × 10<sup>-5</sup> mol · L<sup>-1</sup>): λ max = 413 (16716) nm (L·mol<sup>-1</sup>·cm<sup>-1</sup>).



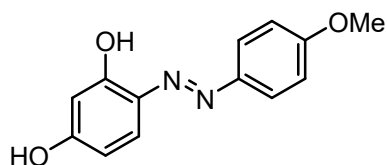
**(E)-4-(Phenyldiazenyl)benzene-1,3-diol (5d)**<sup>[6]</sup>: Known compound. 175.5 mg, 82%, red solid, mp: 149.6-151.4 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 13.93 (s, 1H), 7.80 (dd, *J* = 7.2, 1.4 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.49 (td, *J* = 7.2, 1.8 Hz, 2H), 7.43 (dt, *J* = 7.4, 1.3 Hz, 1H), 6.55 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.43 (d, *J* = 2.6 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 163.23, 156.57, 150.78, 132.44, 130.53, 130.27, 129.58, 121.83, 109.33, 103.20. **HRMS** (ESI) *m/z* calculated for C<sub>12</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 215.0815; Found: 215.0812.



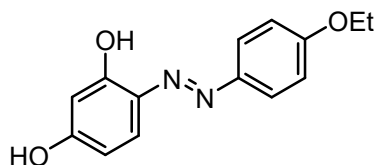
**(E)-4-((4-isopropylphenyl)diazenyl)benzene-1,3-diol (5e):** New compound. 163.2 mg, 64%, red solid, mp: 139.6-141.4 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 14.06 (s, 1H), 7.72 (dd, *J* = 8.8, 2.6 Hz, 3H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.54 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.43 (d, *J* = 2.6 Hz, 1H), 2.97 (sept, *J* = 6.9 Hz, 1H), 1.29 (d, *J* = 6.9 Hz, 6H). **<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 162.85, 156.23, 151.09, 149.03, 132.30, 130.67, 127.47, 121.86, 109.15, 103.16, 33.51, 23.86. **HRMS** (ESI) *m/z* calculated for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 257.1284; Found: 257.1280. UV - visible absorption (DMSO, *c* = 4 × 10<sup>-5</sup> mol · L<sup>-1</sup>): λ max = 387 (16986) nm (L·mol<sup>-1</sup>·cm<sup>-1</sup>).



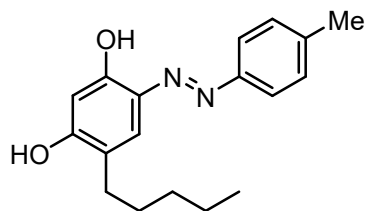
**(E)-4-((4-*tert*-butylphenyl)diazenyl)benzene-1,3-diol (5f)**<sup>[7]</sup>: Known compound. 161.5 mg, 60%, red solid, mp: 150.8-152.3 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 14.25 (s, 1H), 7.71 (dd, *J* = 8.6, 2.8 Hz, 3H), 7.50 (d, *J* = 8.6 Hz, 2H), 6.54 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.43 (d, *J* = 2.6 Hz, 1H), 1.36 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.18, 158.39, 153.59, 146.76, 135.20, 133.03, 126.29, 120.92, 109.26, 103.89, 34.94, 31.23.



**(E)-4-((4-methoxyphenyl)diazenyl)benzene-1,3-diol (5g)**<sup>[5]</sup>: Known compound. 234.5 mg, 96%, red solid, mp: 144.4-146.1 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 13.71 (s, 1H), 7.78 (dt, *J* = 9.0, 3.2 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.00 (dt, *J* = 9.1, 3.2 Hz, 2H), 6.53 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.43 (d, *J* = 2.6 Hz, 1H), 3.88 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.51, 159.45, 155.67, 144.30, 134.62, 132.94, 123.39, 114.51, 108.27, 103.70, 55.61.



**(E)-4-((4-ethoxyphenyl)diazenyl)benzene-1,3-diol (5h)**: New compound. 252.7 mg, 98%, red solid, mp: 170.0-171.8 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 13.71 (s, 2H), 7.77 (dt, *J* = 9.0, 3.2 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 1H), 6.98 (dt, *J* = 9.0, 3.2 Hz, 2H), 6.53 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.42 (d, *J* = 2.6 Hz, 1H), 4.11 (q, *J* = 7.0 Hz, 2H), 1.46 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.96, 159.37, 155.66, 144.15, 134.57, 132.95, 123.39, 114.98, 108.23, 103.70, 63.87, 14.74. **HRMS** (ESI) *m/z* calculated for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 259.1077; Found: 259.1076. UV - visible absorption (DMSO, *c* = 8 × 10<sup>-6</sup> mol · L<sup>-1</sup>): λ<sub>max</sub> = 391 (19763) nm (L · mol<sup>-1</sup> · cm<sup>-1</sup>).



**(E)-4-pentyl-6-(*p*-tolyldiazenyl)benzene-1,3-diol (5i)**: New compound. 154.8 mg, 52%, red solid, mp: 136.8-138.0 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 15.38 (s, 1H), 7.60 (dd, *J* = 6.7, 1.9 Hz, 2H),

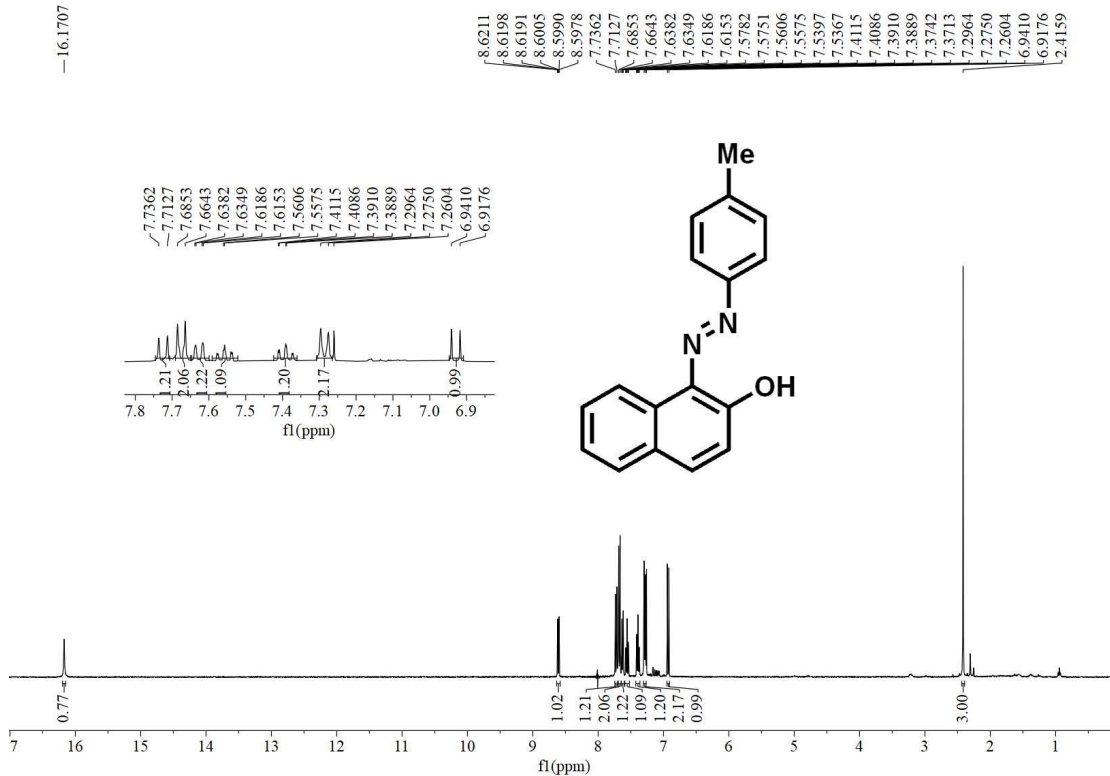
7.26 (d,  $J = 8.2$  Hz, 2H), 6.32 (d,  $J = 2.6$  Hz, 1H), 6.26 (d,  $J = 2.6$  Hz, 1H), 2.91 (dd,  $J = 9.7, 6.1$  Hz, 2H), 2.40 (s, 3H), 1.67-1.61 (m, 2H), 1.37-1.31 (m, 4H), 0.89 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  163.06, 162.41, 148.89, 145.99, 139.41, 130.84, 130.02, 120.41, 110.52, 102.17, 31.92, 31.86, 31.24, 22.53, 21.36, 14.08. HRMS (ESI)  $m/z$  calculated for  $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2\text{Na}$   $[\text{M}+\text{Na}]^+$ : 279.1104; Found: 279.1099. UV - visible absorption (DMSO,  $c = 5 \times 10^{-6}$  mol  $\cdot$  L $^{-1}$ ):  $\lambda_{\text{max}} = 393$  (16109) nm (L $\cdot$ mol $^{-1}\cdot$ cm $^{-1}$ ).

## V. References

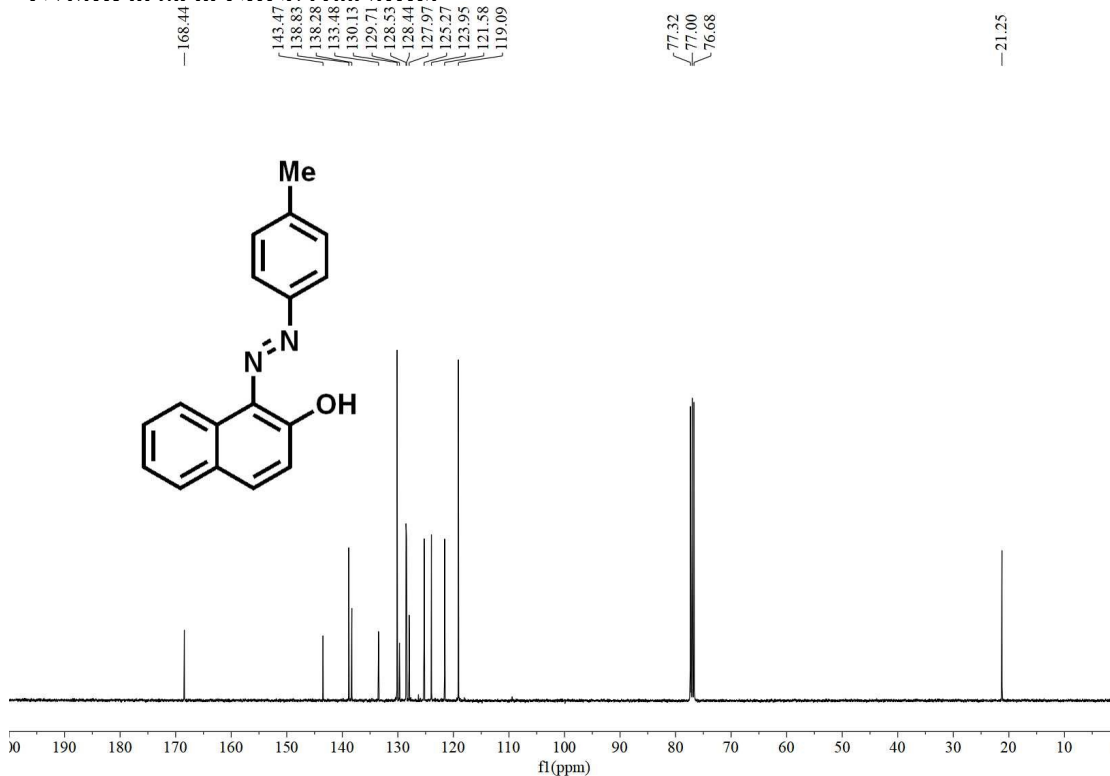
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## VI. Copies of $^1\text{H}$ NMR, $^{13}\text{C}$ NMR and UV-Vis Absorption Spectrum

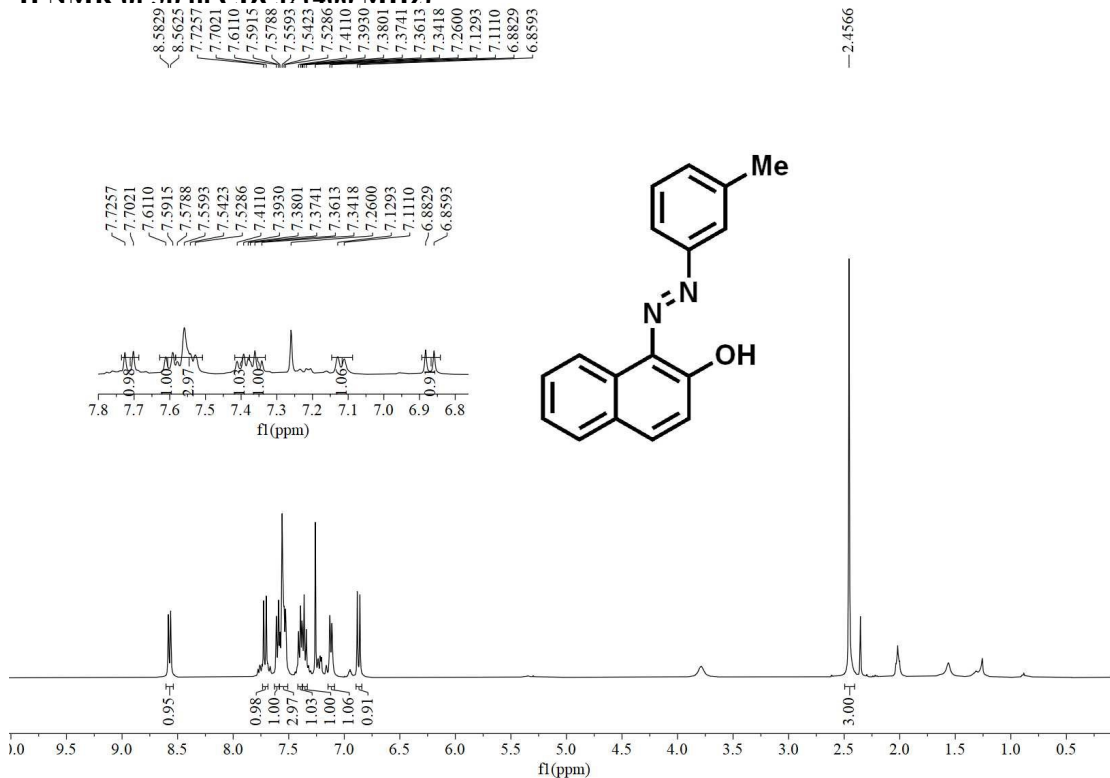
$^1\text{H}$  NMR of **3a** in  $\text{CDCl}_3$  (400 MHz)



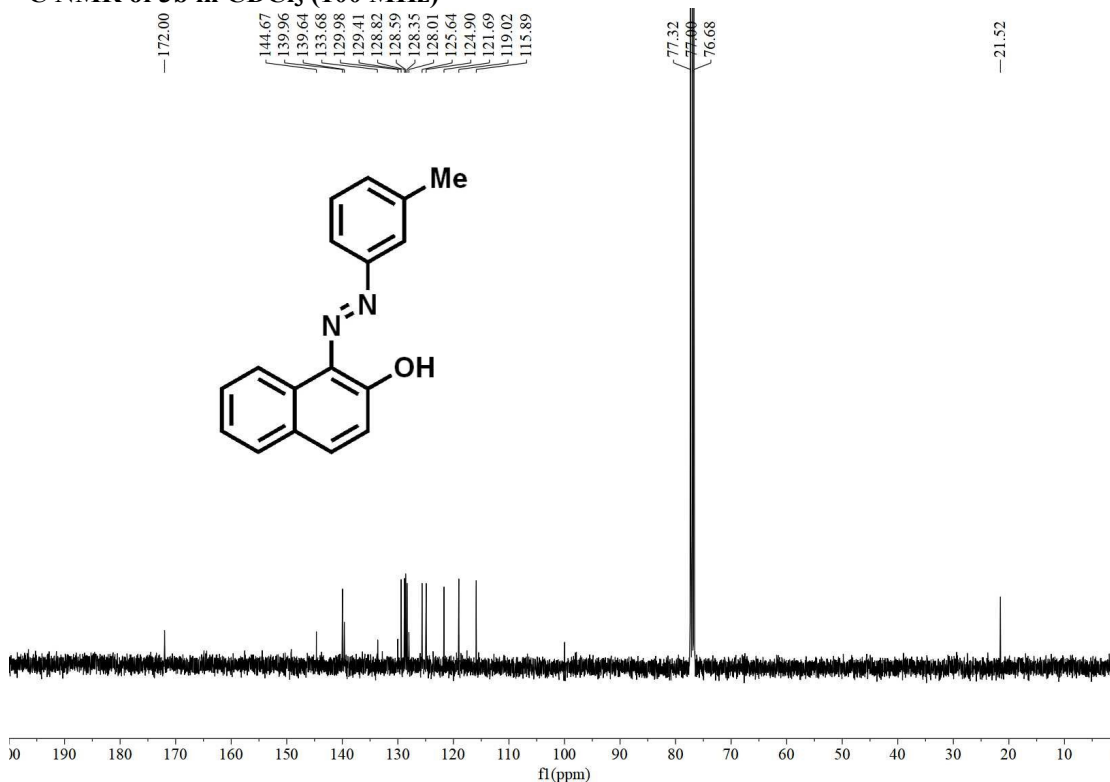
$^{13}\text{C}$  NMR of **3a** in  $\text{CDCl}_3$  (100 MHz)



**<sup>1</sup>H NMR of 3b in CDCl<sub>3</sub> (400 MHz)**

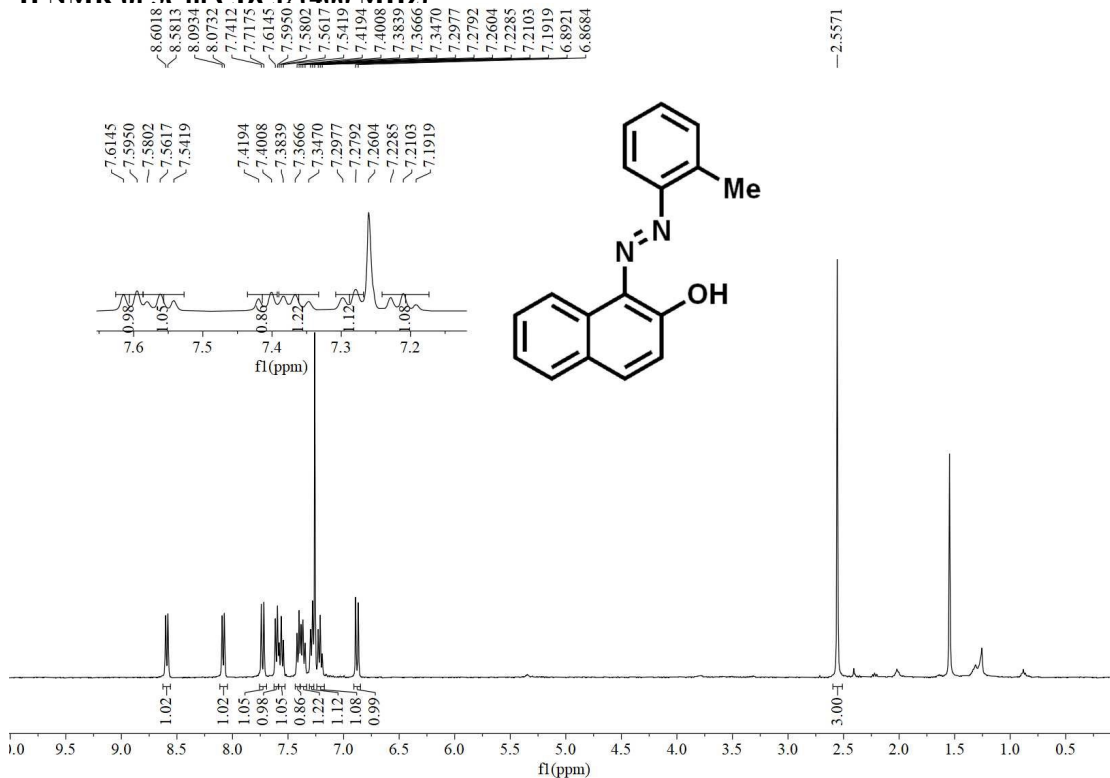


**<sup>13</sup>C NMR of 3b in CDCl<sub>3</sub> (100 MHz)**

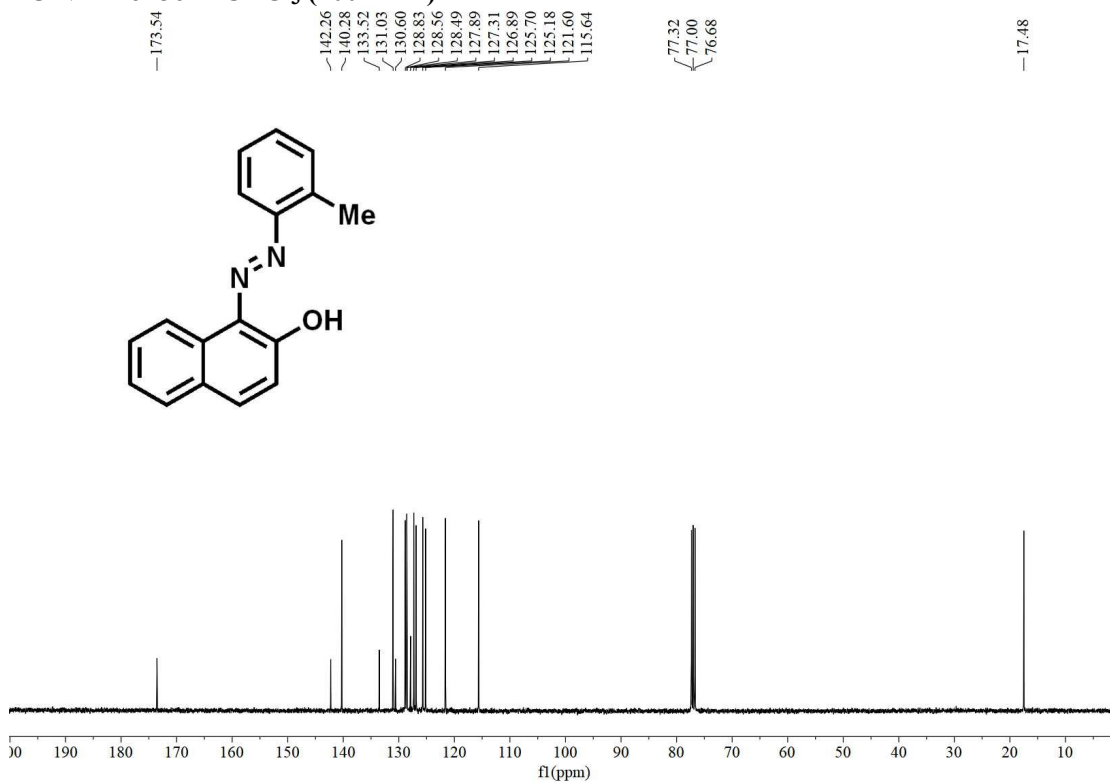




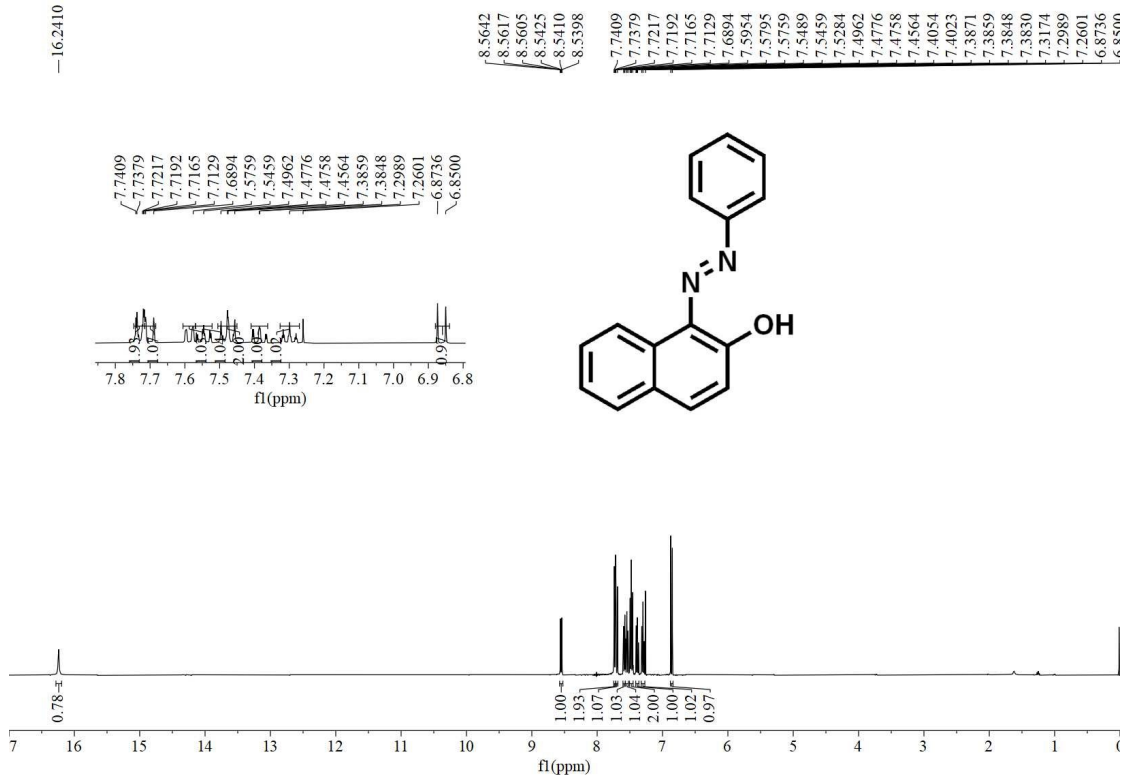
**<sup>1</sup>H NMR of 3c in CDCl<sub>3</sub> (400 MHz)**



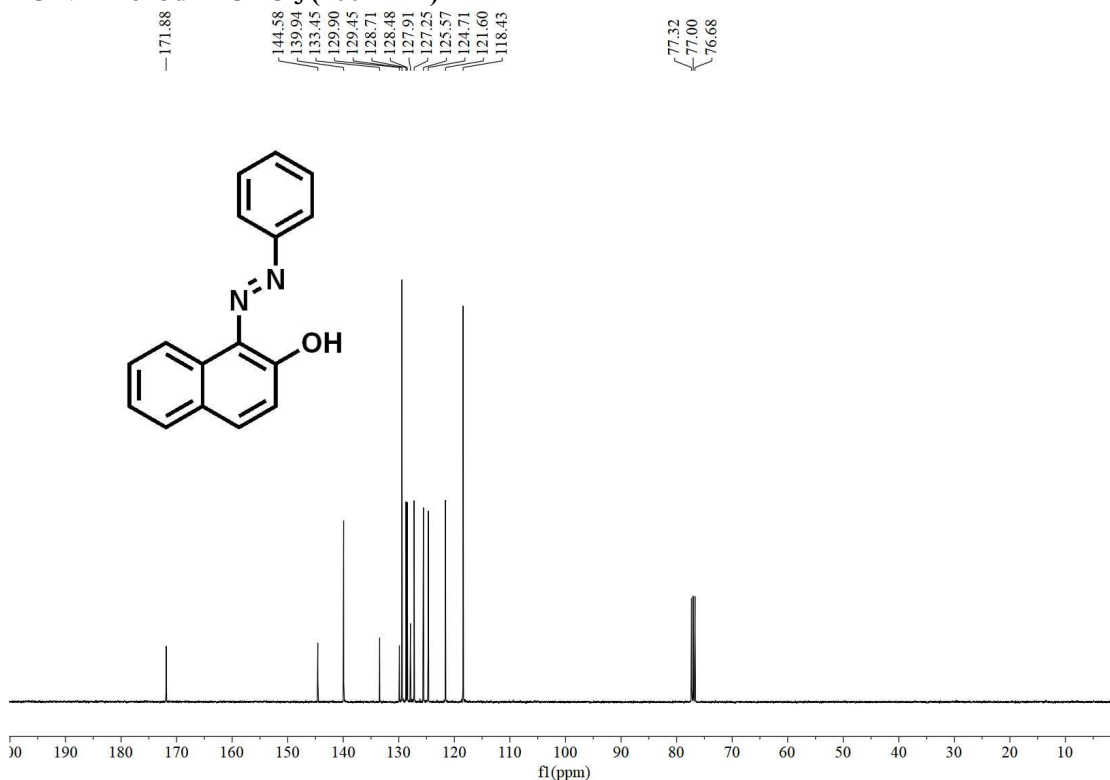
**<sup>13</sup>C NMR of 3c in CDCl<sub>3</sub> (100 MHz)**



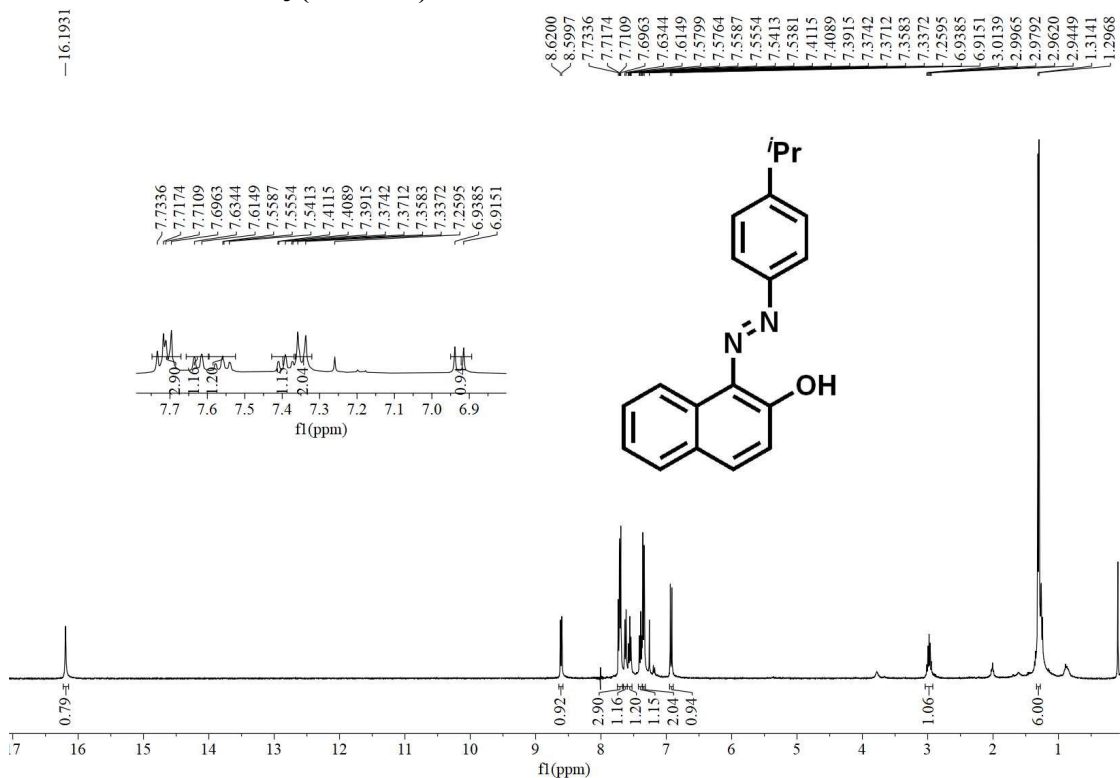
**<sup>1</sup>H NMR of 3d in CDCl<sub>3</sub> (400 MHz)**



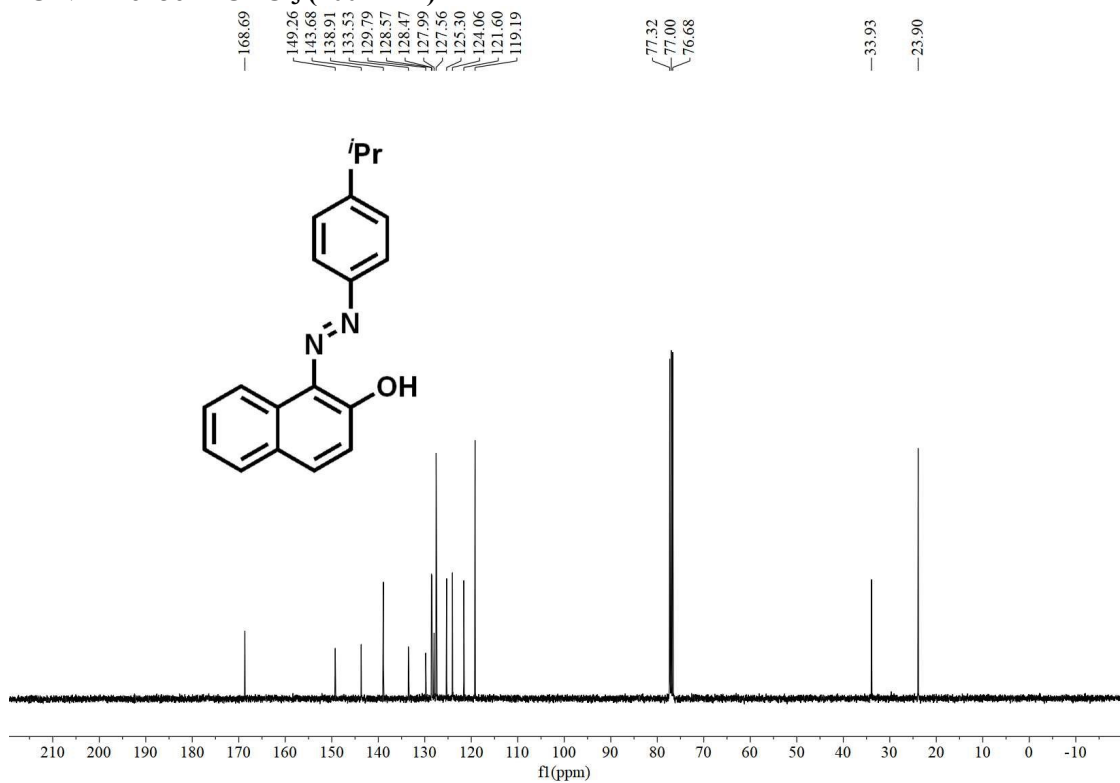
**<sup>13</sup>C NMR of 3d in CDCl<sub>3</sub> (100 MHz)**



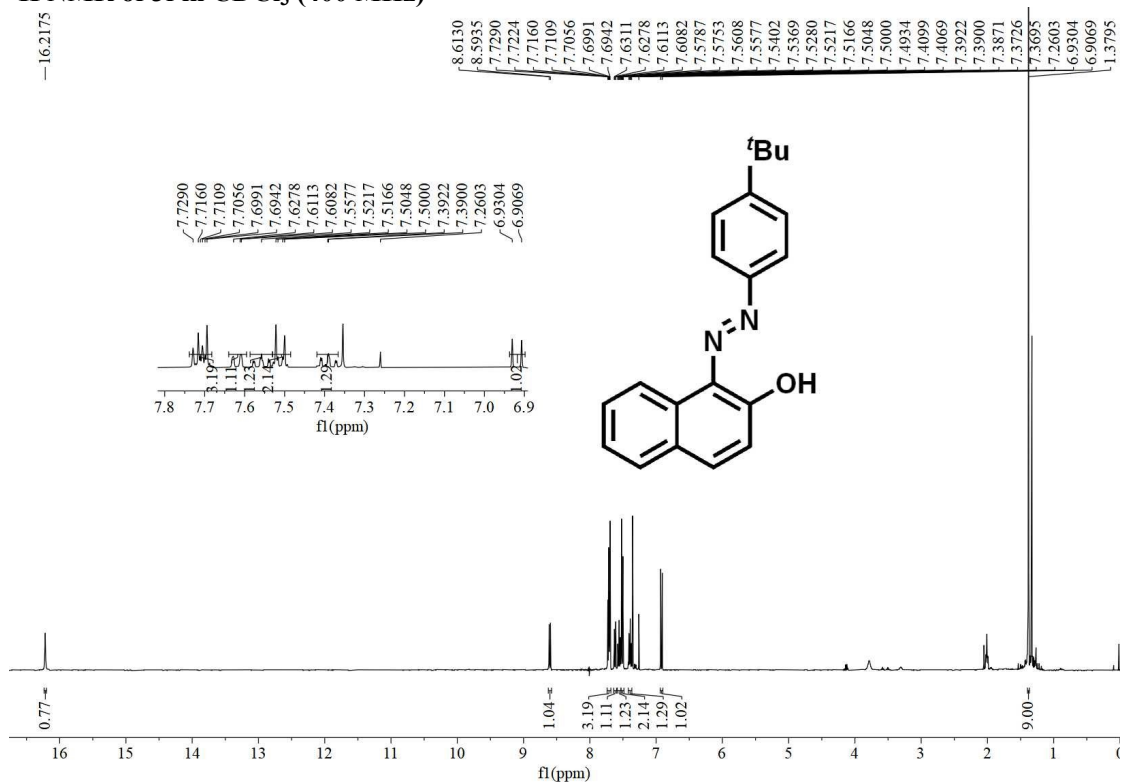
**<sup>1</sup>H NMR of 3e in CDCl<sub>3</sub> (400 MHz)**



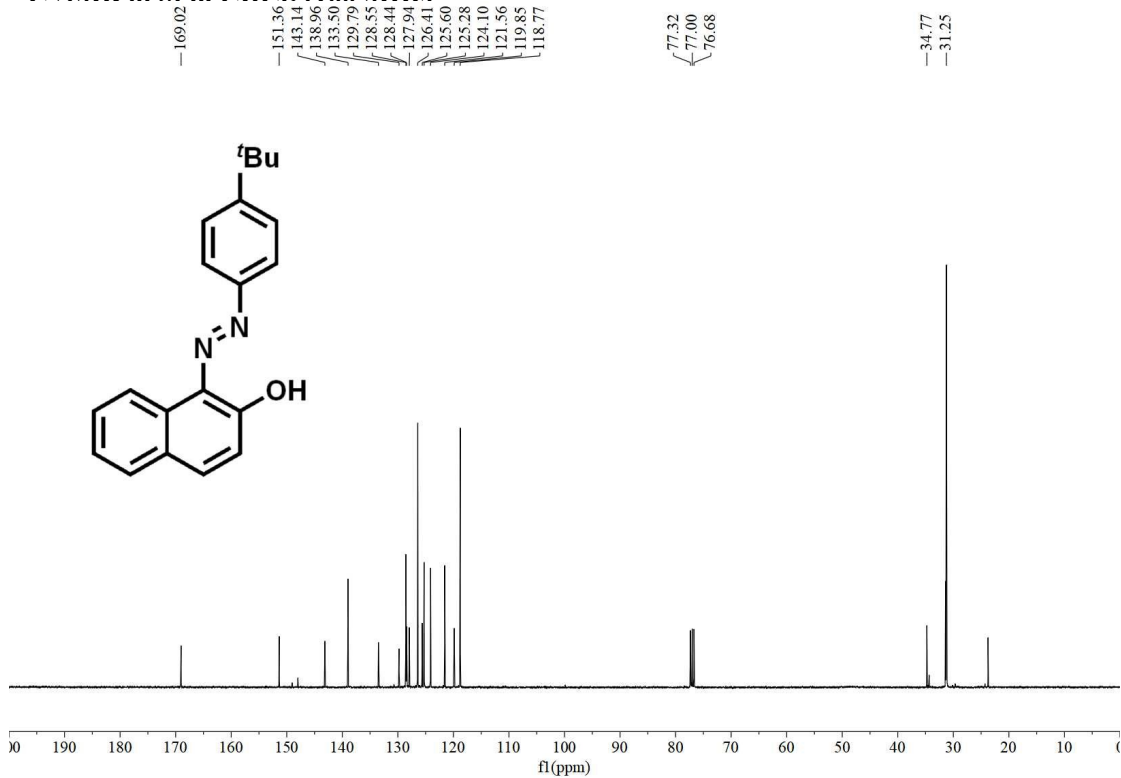
**<sup>13</sup>C NMR of 3e in CDCl<sub>3</sub> (100 MHz)**



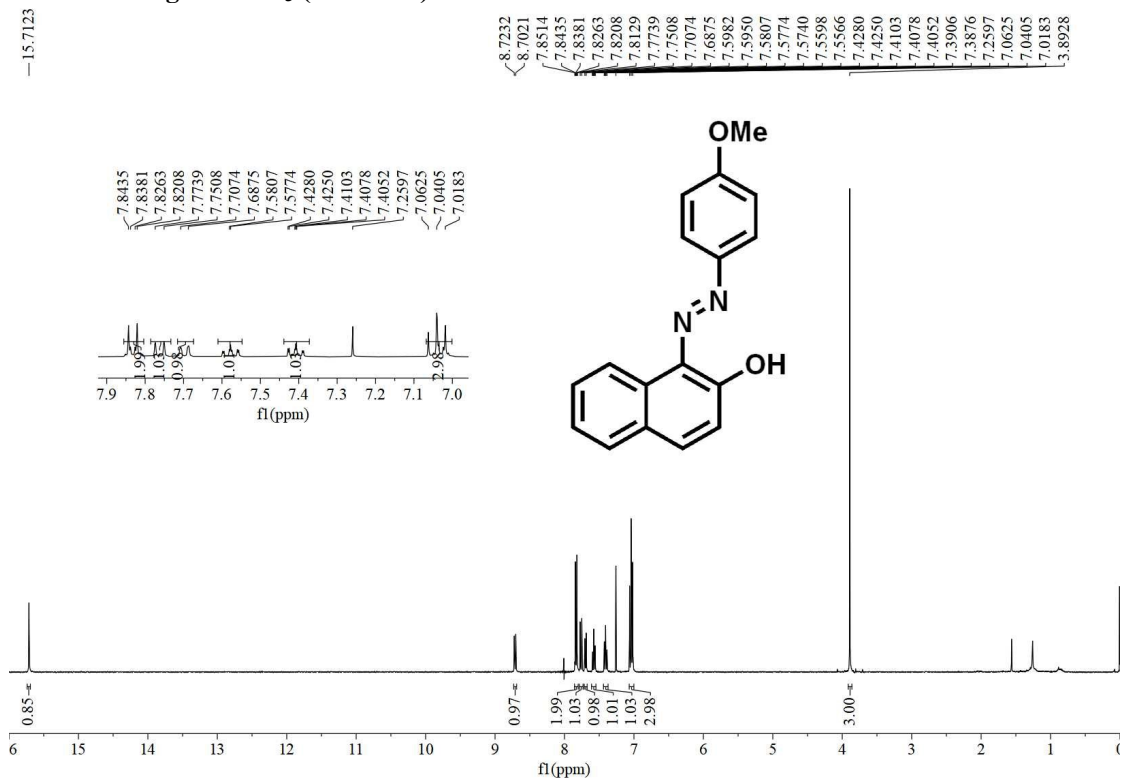
**<sup>1</sup>H NMR of 3f in CDCl<sub>3</sub> (400 MHz)**



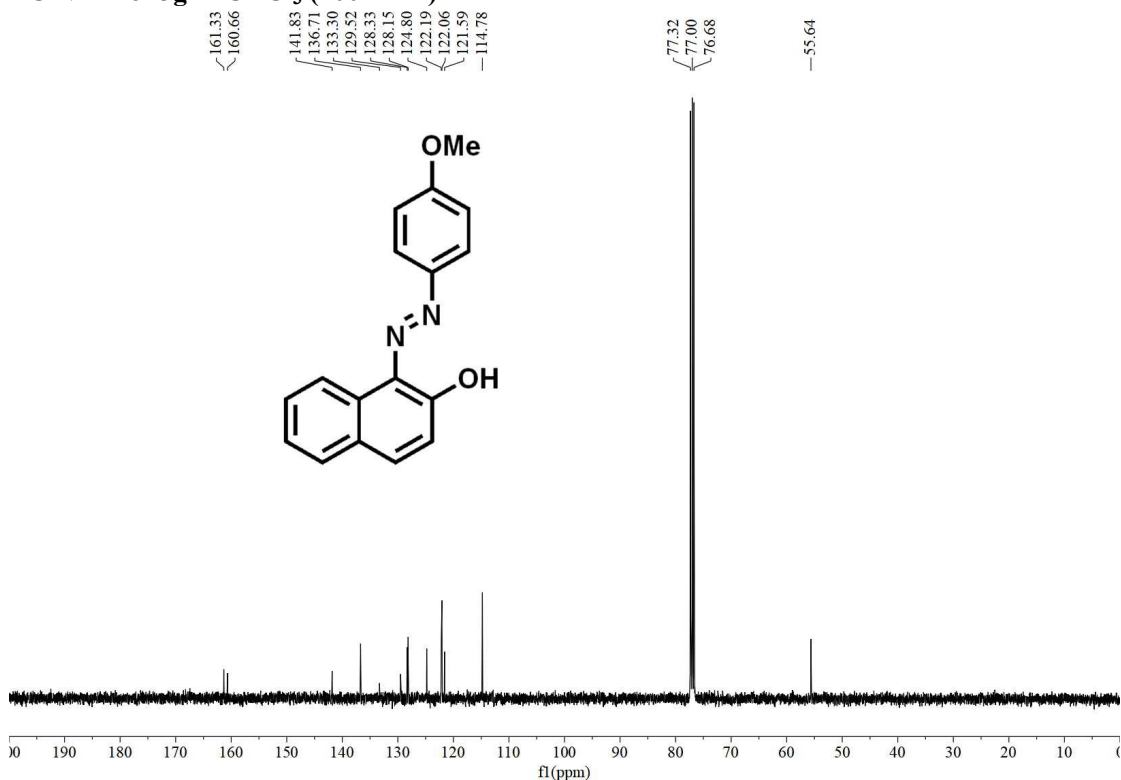
**<sup>13</sup>C NMR of 3f in CDCl<sub>3</sub> (100 MHz)**



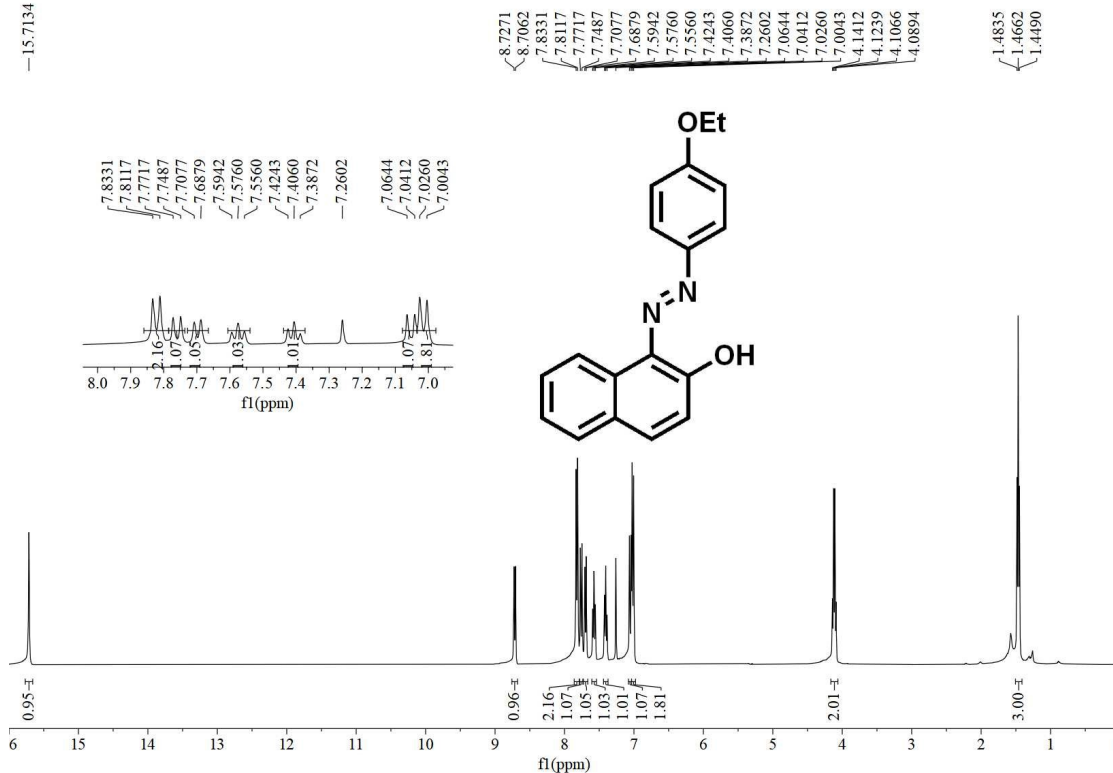
### $^1\text{H}$ NMR of 3g in $\text{CDCl}_3$ (400 MHz)



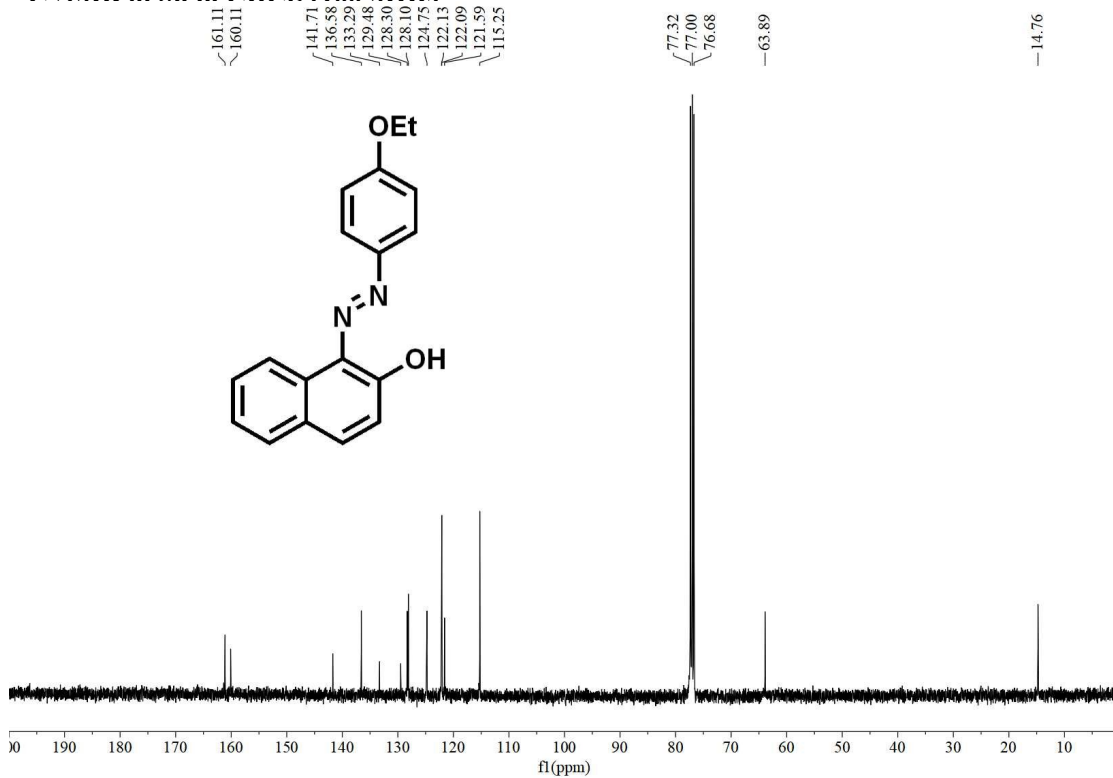
### $^{13}\text{C}$ NMR of 3g in $\text{CDCl}_3$ (100 MHz)



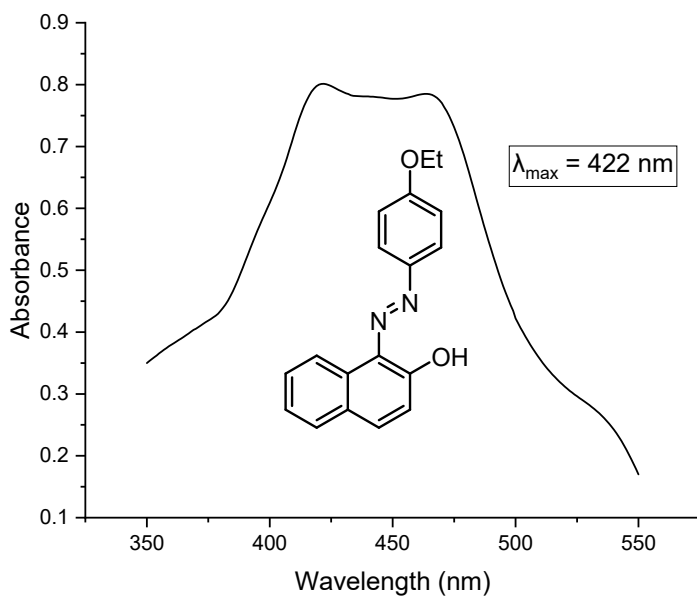
**<sup>1</sup>H NMR of 3h in CDCl<sub>3</sub> (400 MHz)**



**<sup>13</sup>C NMR of 3h in CDCl<sub>3</sub> (100 MHz)**

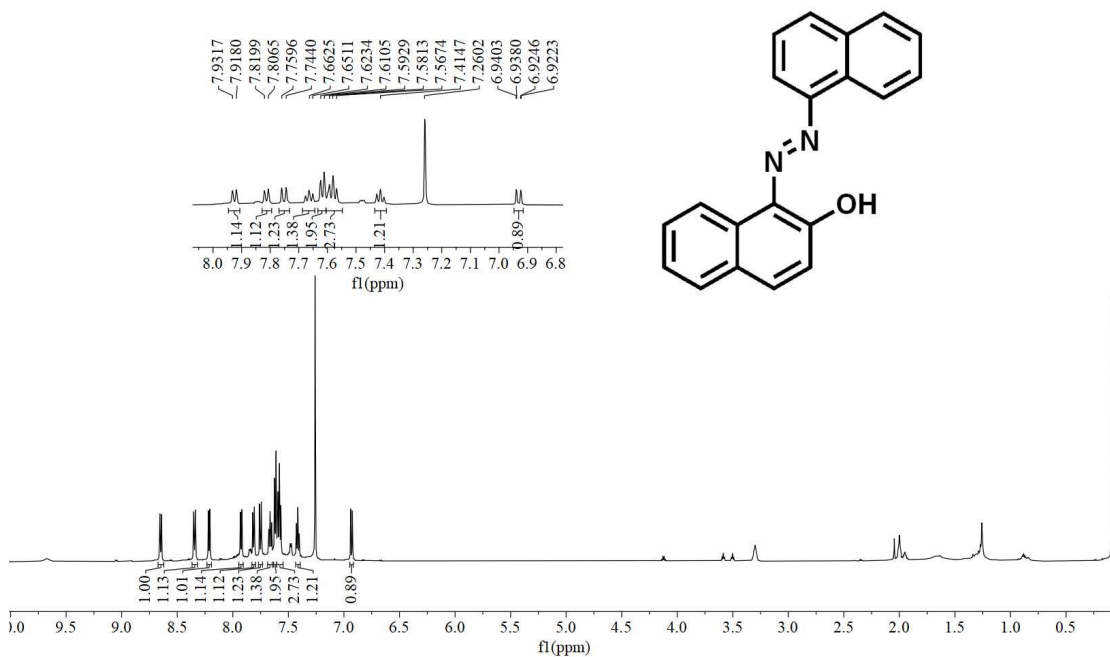


### UV-Vis Absorption Spectrum of 3h

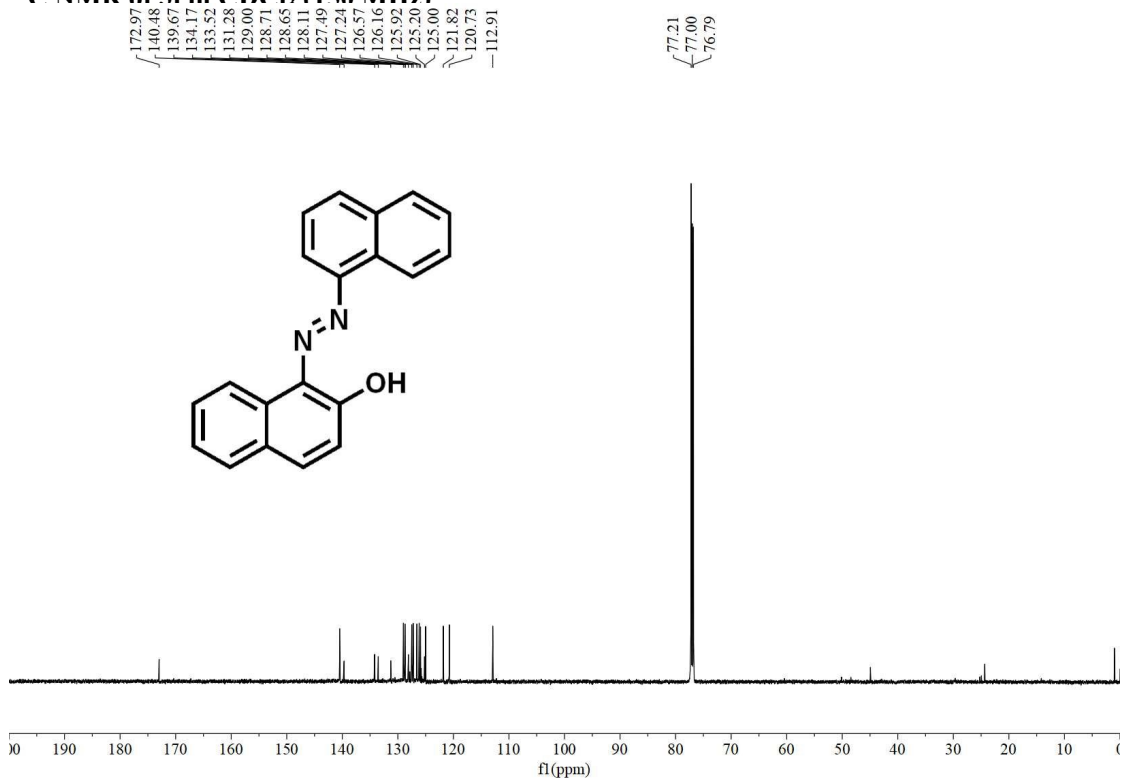


### <sup>1</sup>H NMR of 3i in CDCl<sub>3</sub> (600 MHz)

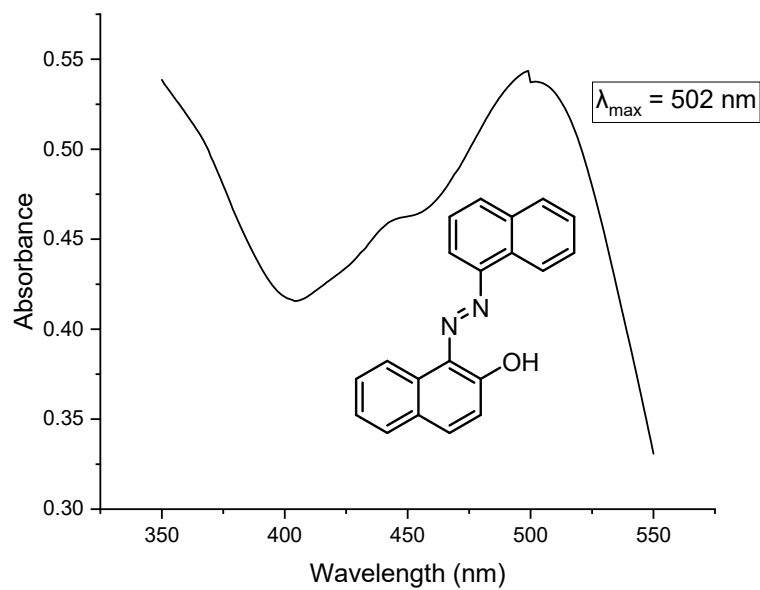
8.6569  
8.6433  
8.3518  
8.3377  
8.2196  
8.2070  
7.9317  
7.9180  
7.8199  
7.8065  
7.7596  
7.7440  
7.6766  
7.6625  
7.6511  
7.6234  
7.6105  
7.5929  
7.5813  
7.5674  
7.4272  
7.4147  
7.4025  
7.2602  
6.9403  
6.9380  
6.9246  
6.9223



**<sup>13</sup>C NMR of 3i in CDCl<sub>3</sub> (150 MHz)**

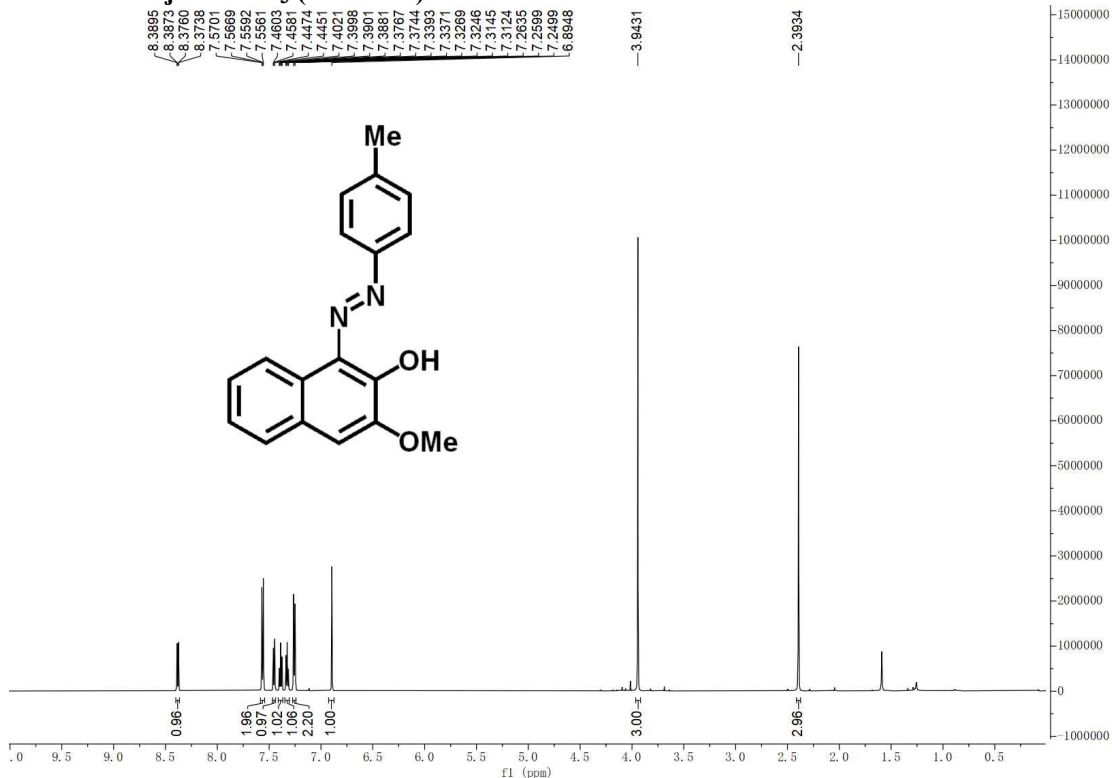


**UV-Vis Absorption Spectrum of 3i**

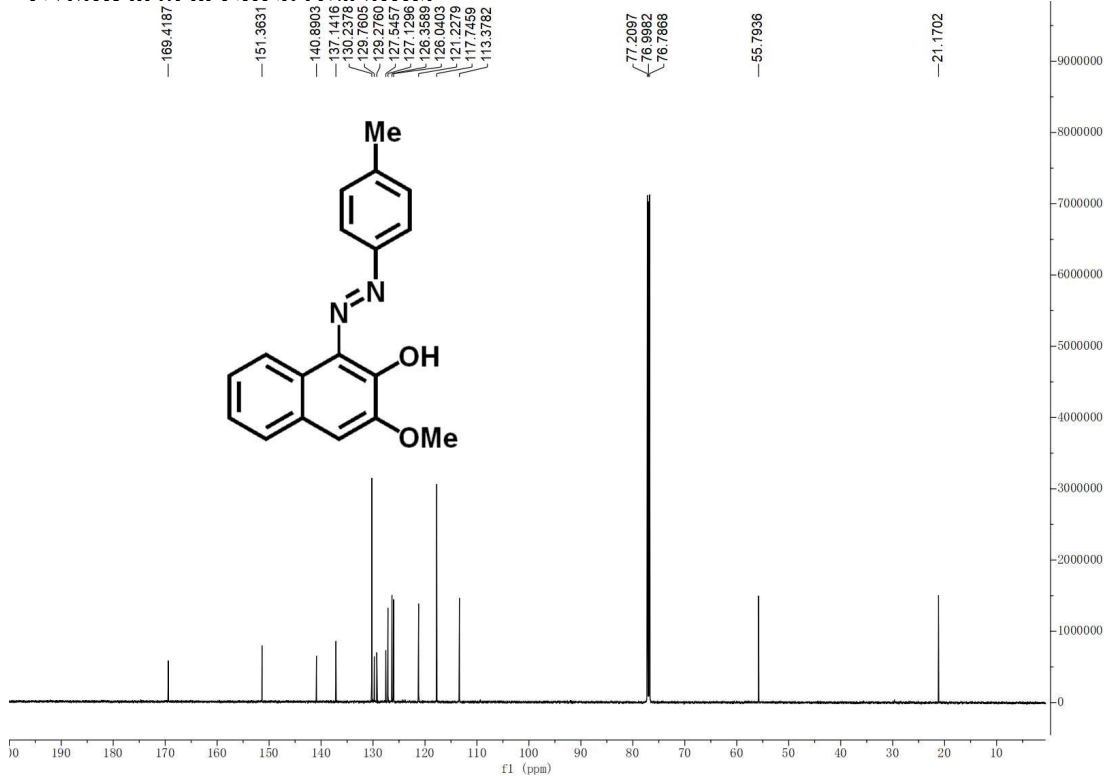




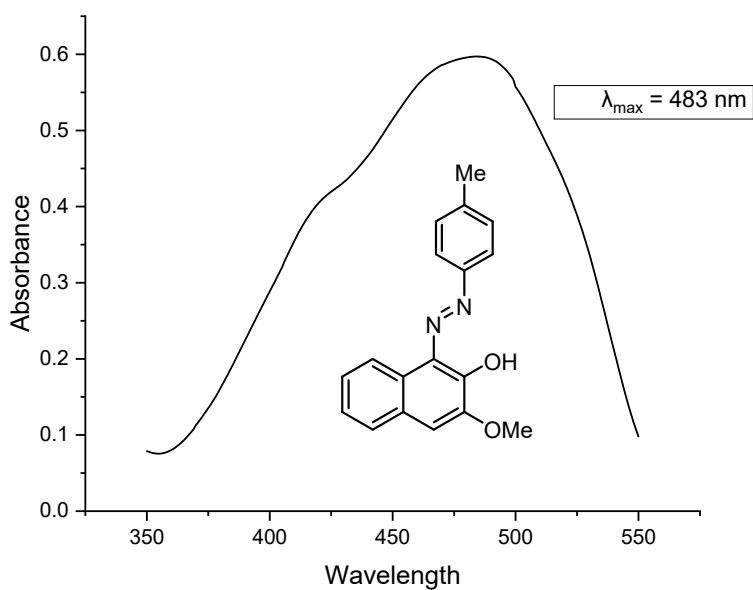
**<sup>1</sup>H NMR of 3j in CDCl<sub>3</sub> (600 MHz)**



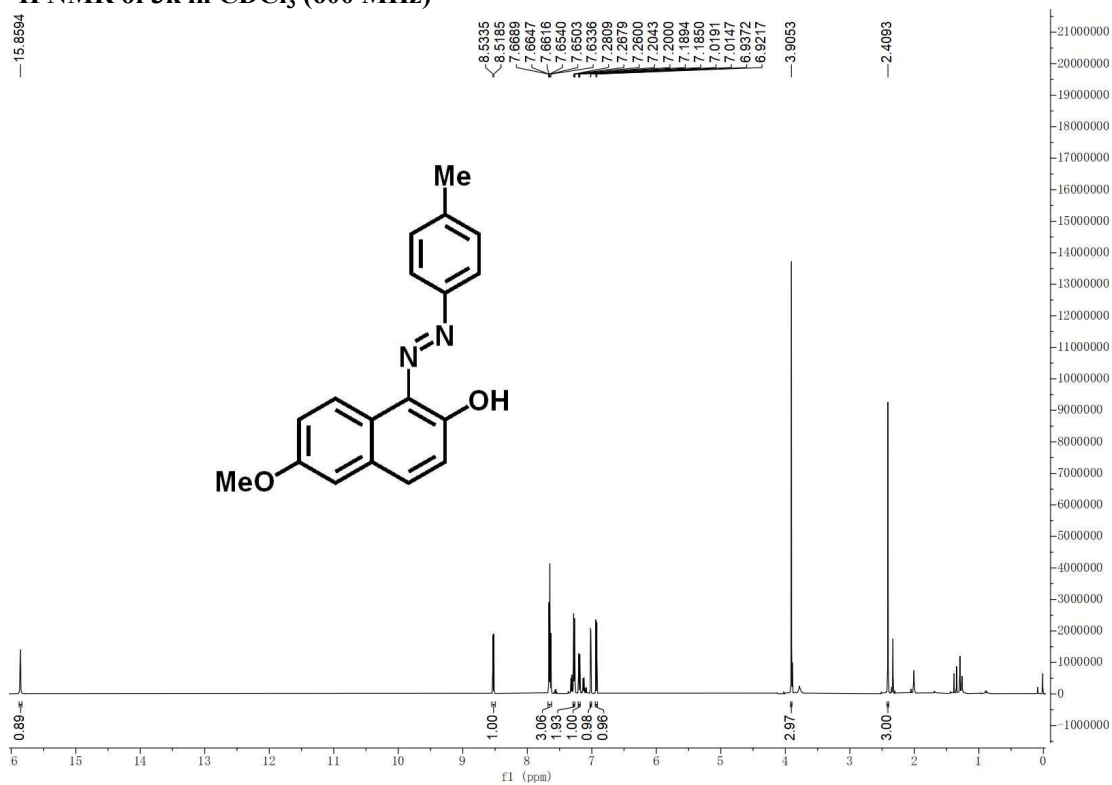
**<sup>13</sup>C NMR of 3i in CDCl<sub>3</sub> (150 MHz)**



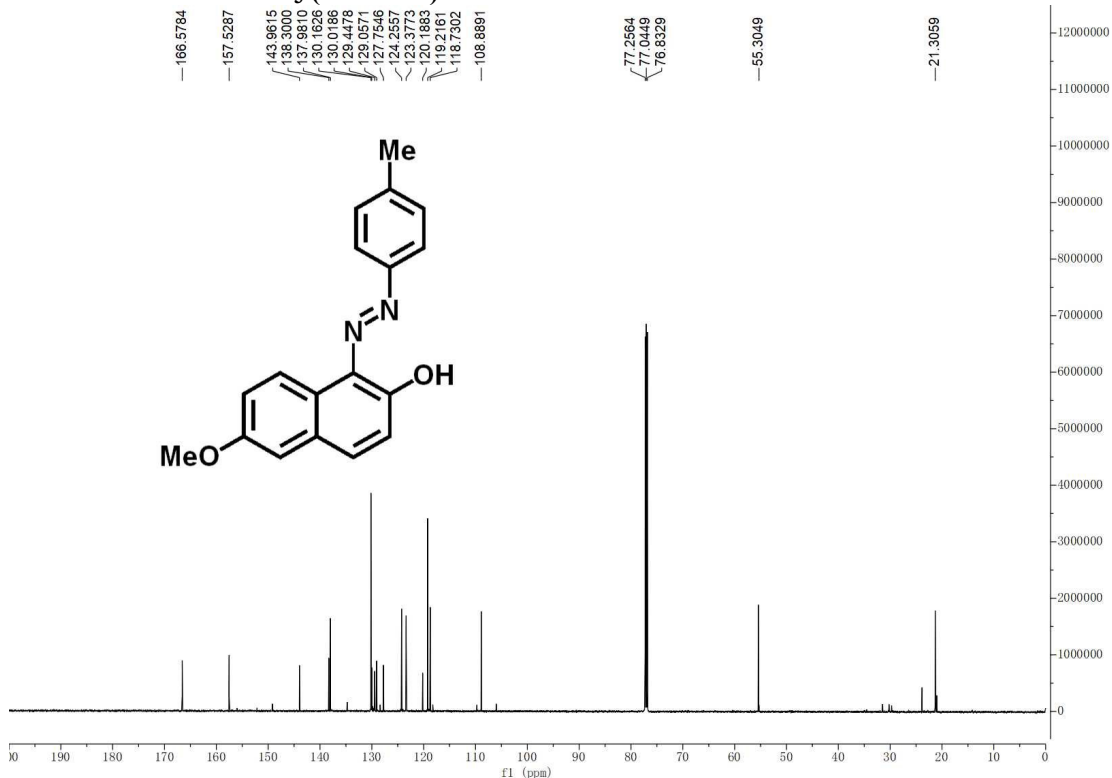
### UV-Vis Absorption Spectrum of 3j



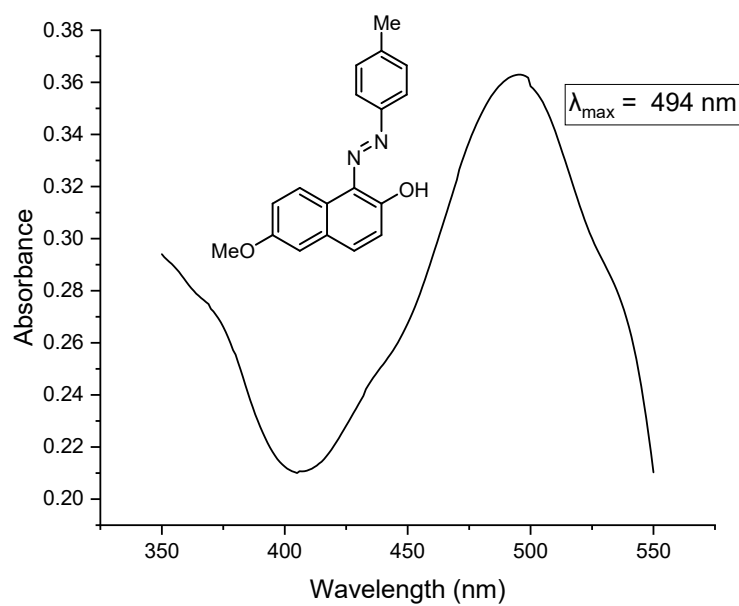
### $^1\text{H}$ NMR of 3k in $\text{CDCl}_3$ (600 MHz)



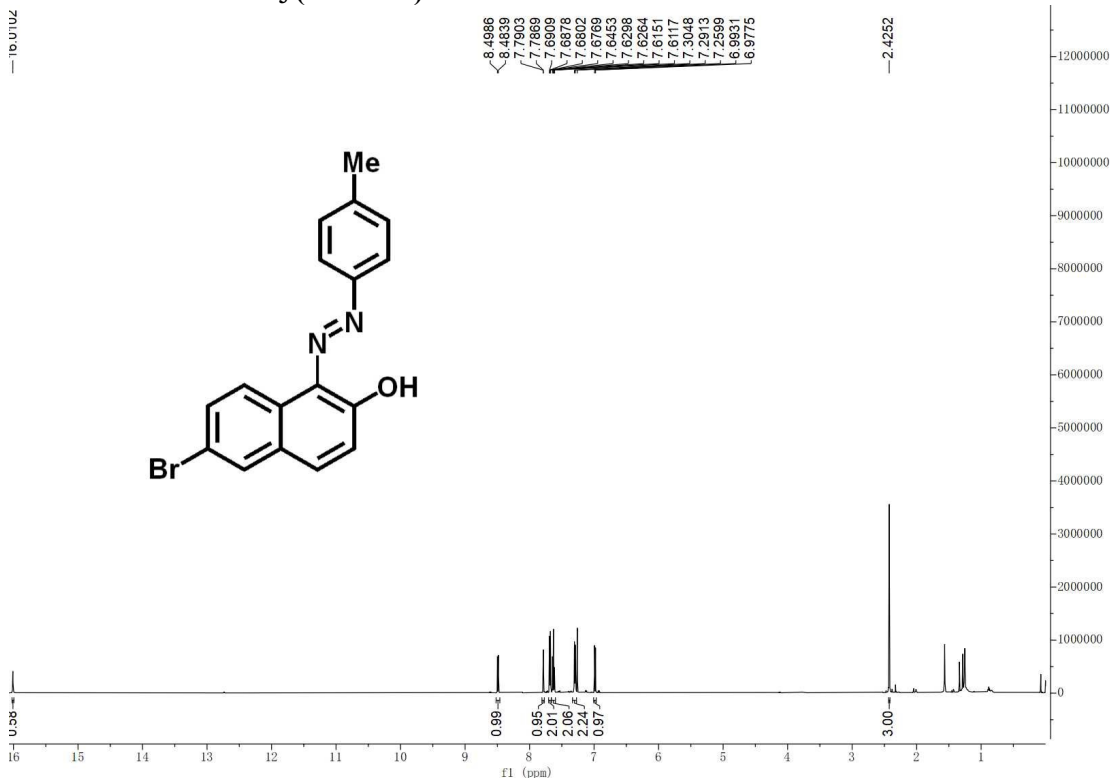
### $^{13}\text{C}$ NMR of 3k in $\text{CDCl}_3$ (150 MHz)



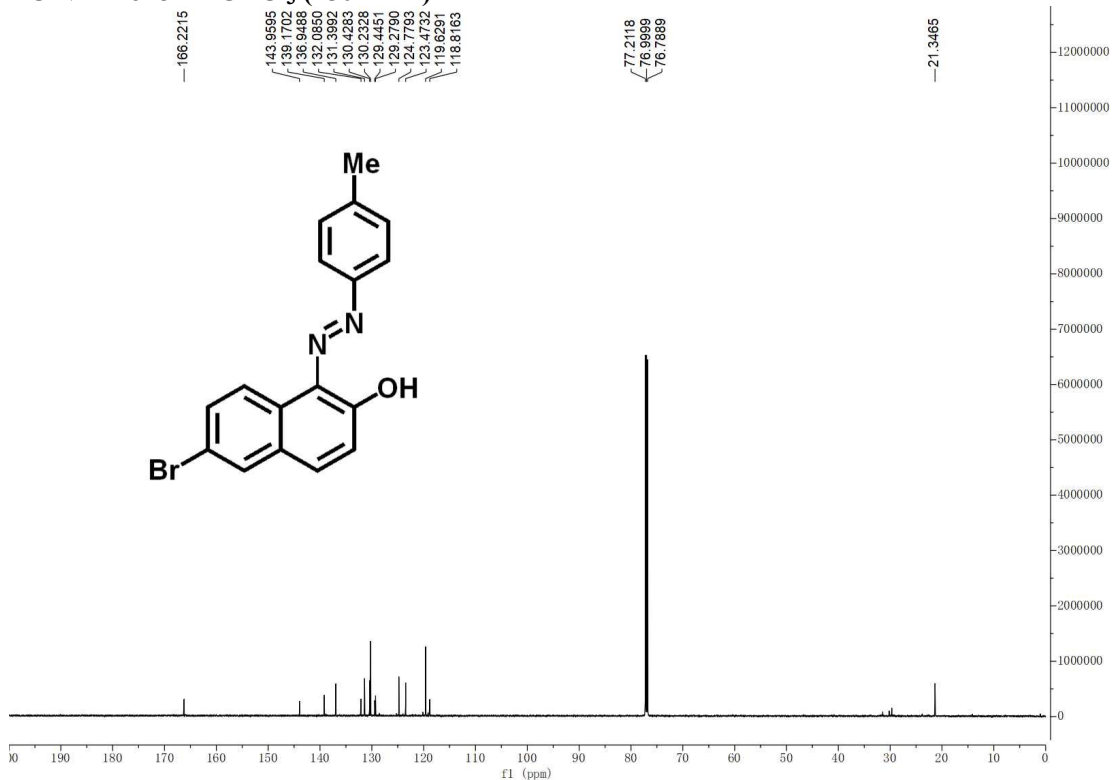
### UV-Vis Absorption Spectrum of 3k



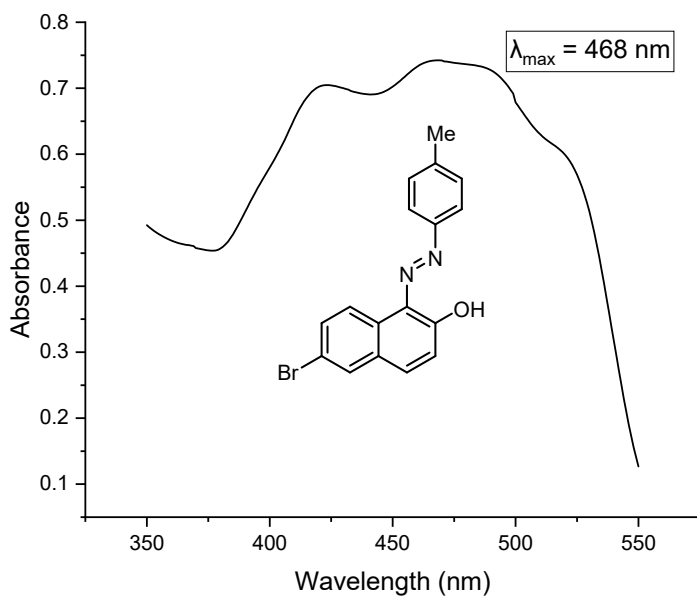
### $^1\text{H}$ NMR of 3l in $\text{CDCl}_3$ (600 MHz)



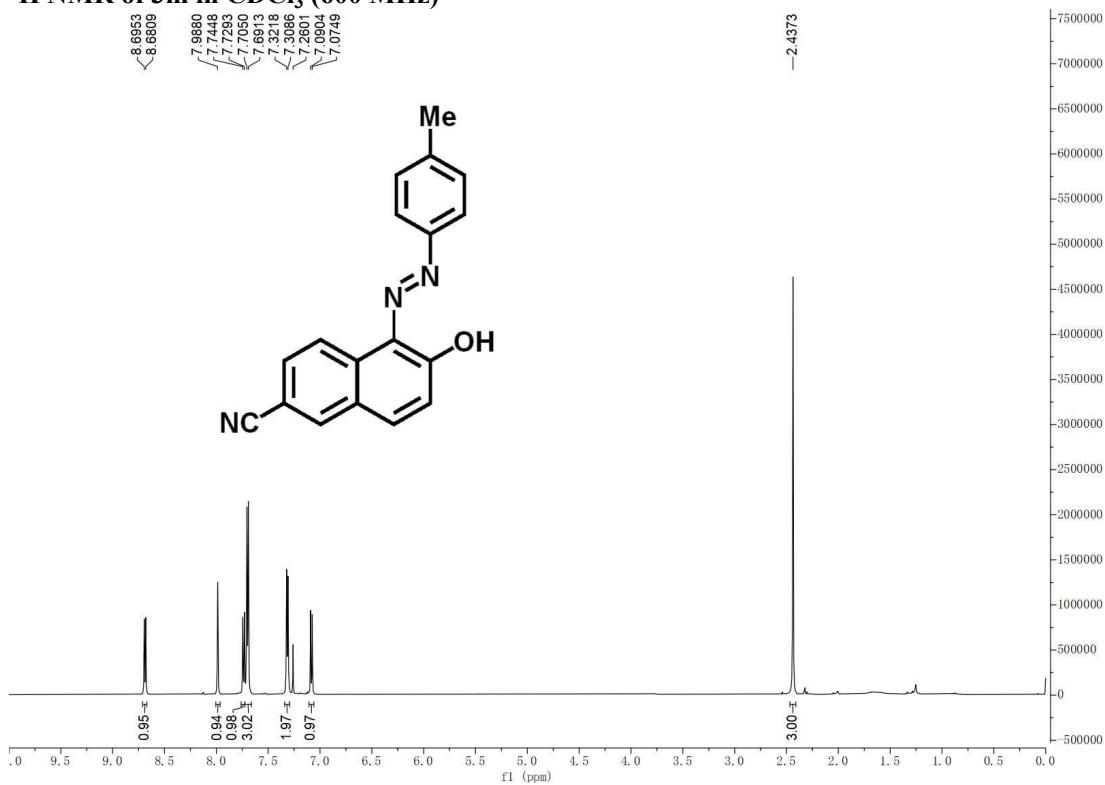
### $^{13}\text{C}$ NMR of 3l in $\text{CDCl}_3$ (150 MHz)



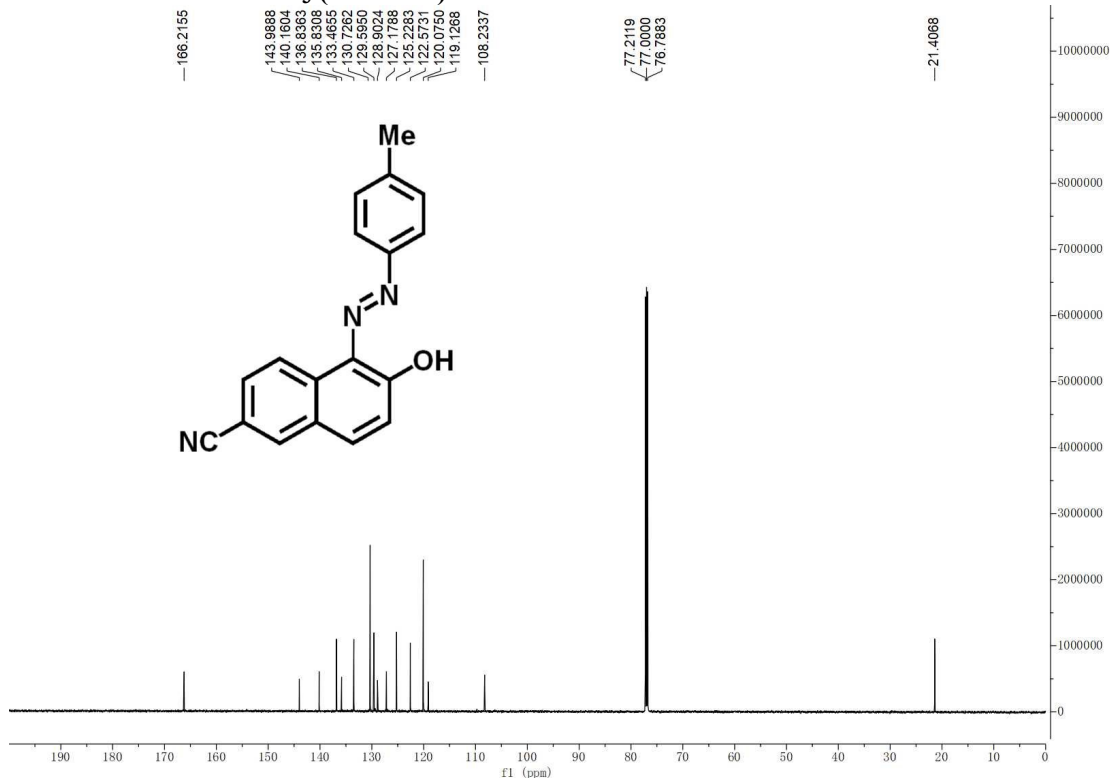
### UV-Vis Absorption Spectrum of 3l



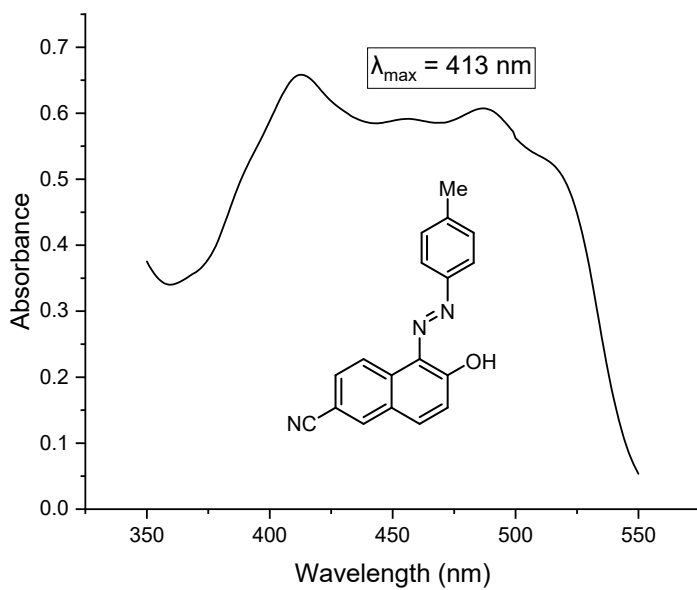
### $^1\text{H}$ NMR of 3m in $\text{CDCl}_3$ (600 MHz)



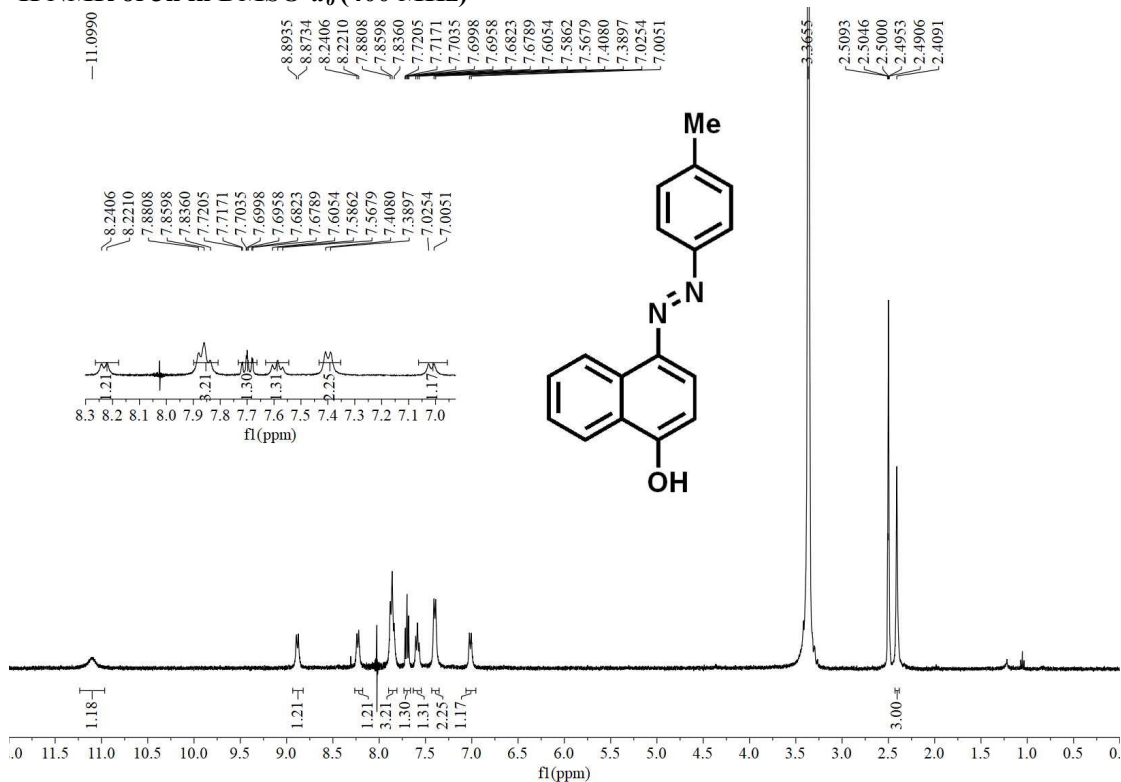
### <sup>13</sup>C NMR of 3m in CDCl<sub>3</sub> (150 MHz)



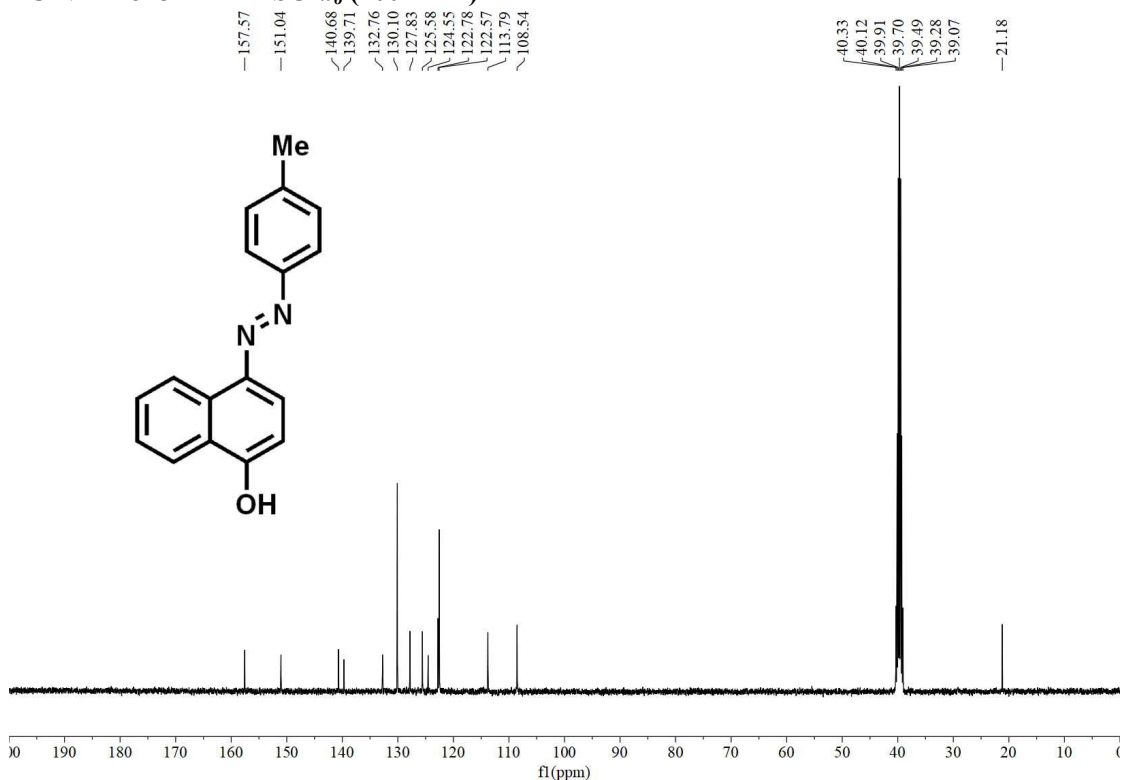
### UV-Vis Absorption Spectrum of 3m



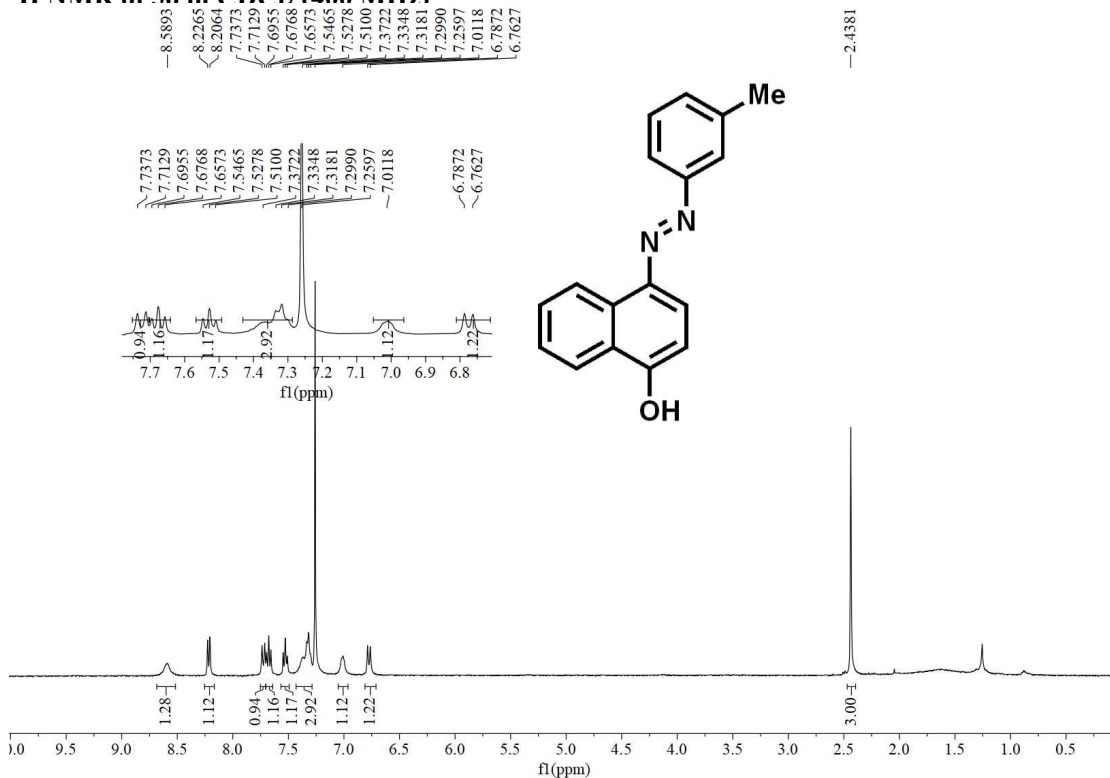
**<sup>1</sup>H NMR of 3n in DMSO-*d*<sub>6</sub> (400 MHz)**



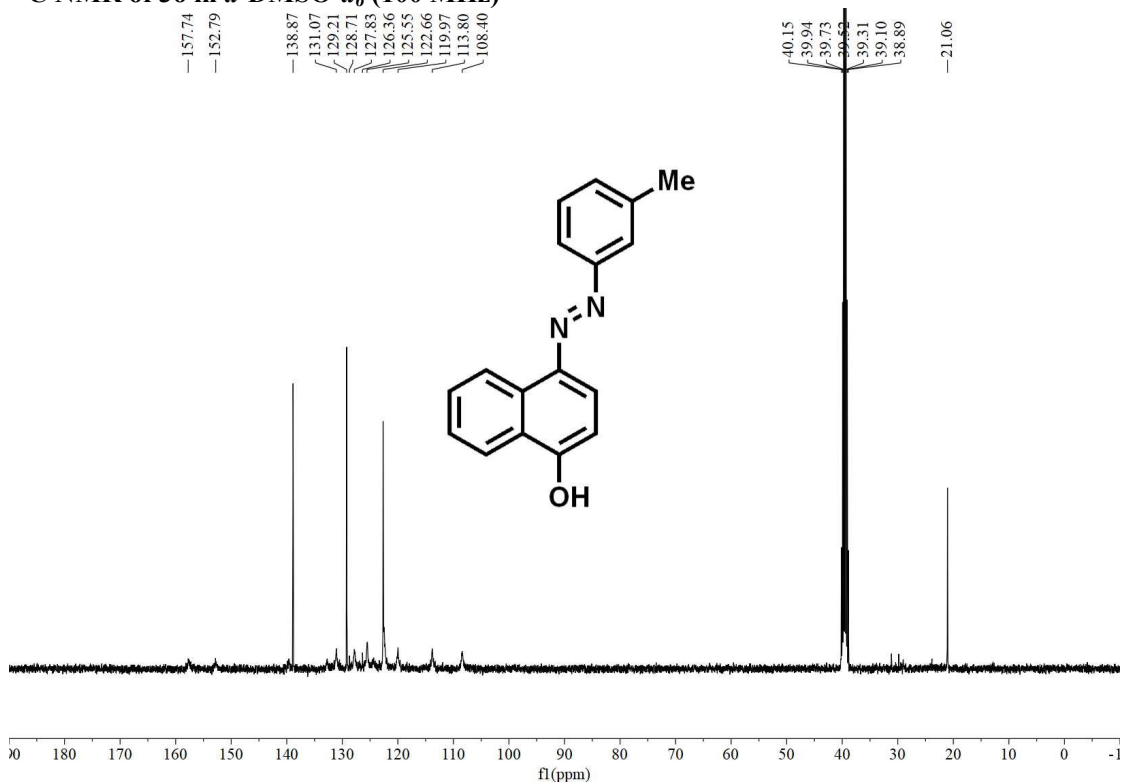
**<sup>13</sup>C NMR of 3n in DMSO-*d*<sub>6</sub> (100 MHz)**



**<sup>1</sup>H NMR of 3o in CDCl<sub>3</sub> (400 MHz)**

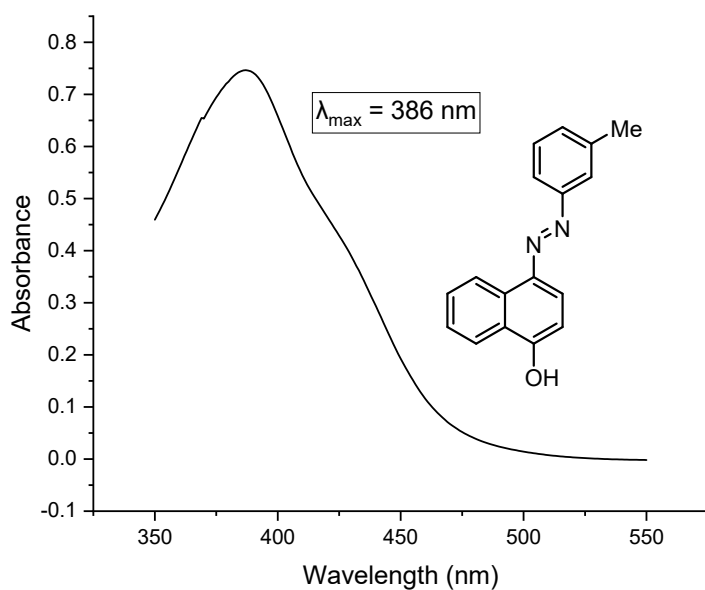


**<sup>13</sup>C NMR of 3o in d-DMSO-d<sub>6</sub> (100 MHz)**

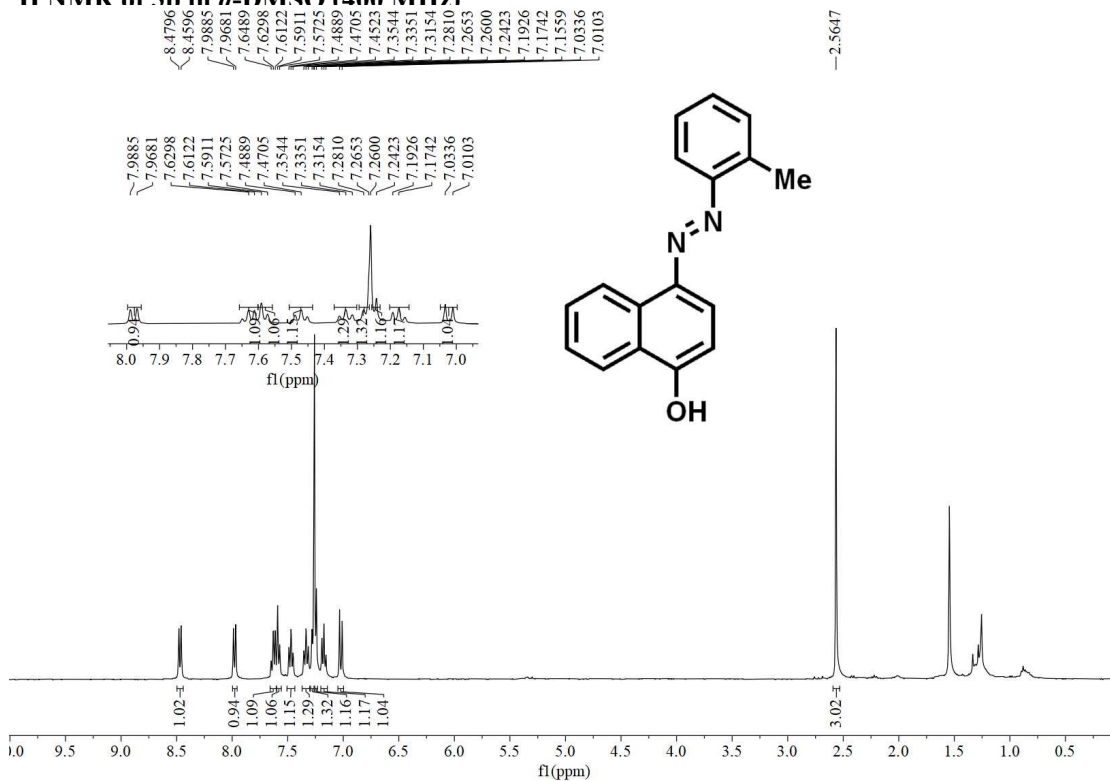




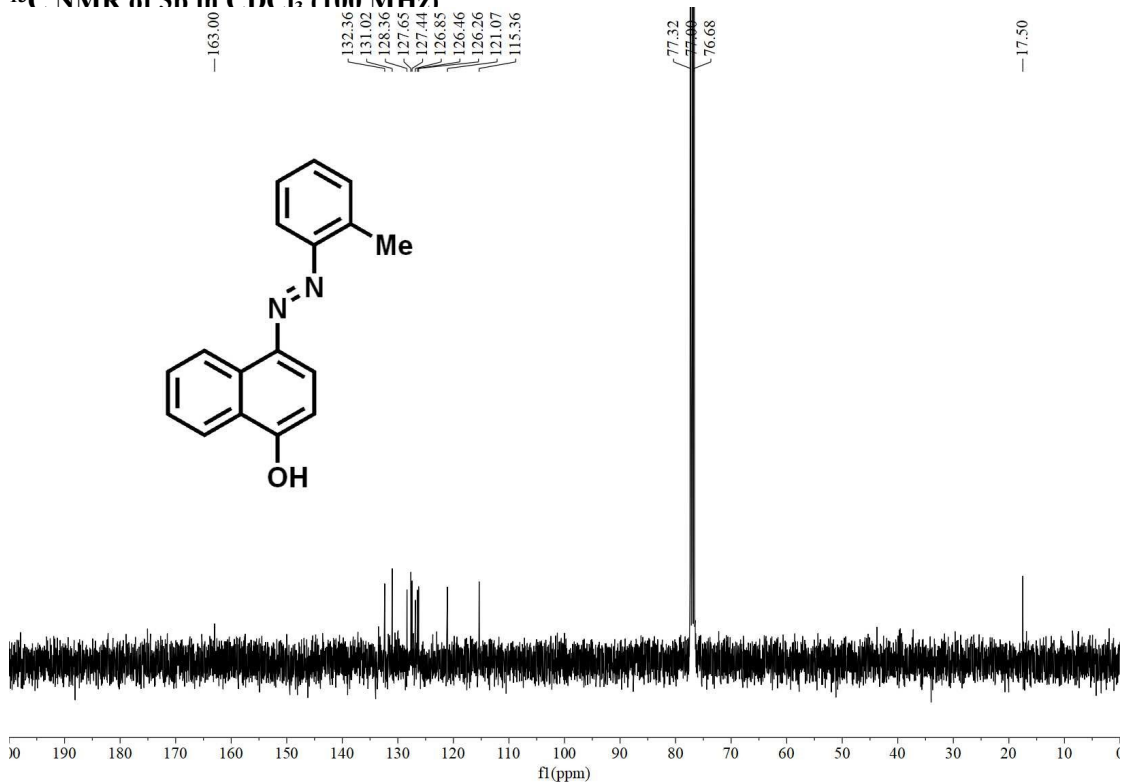
### UV-Vis Absorption Spectrum of 3o



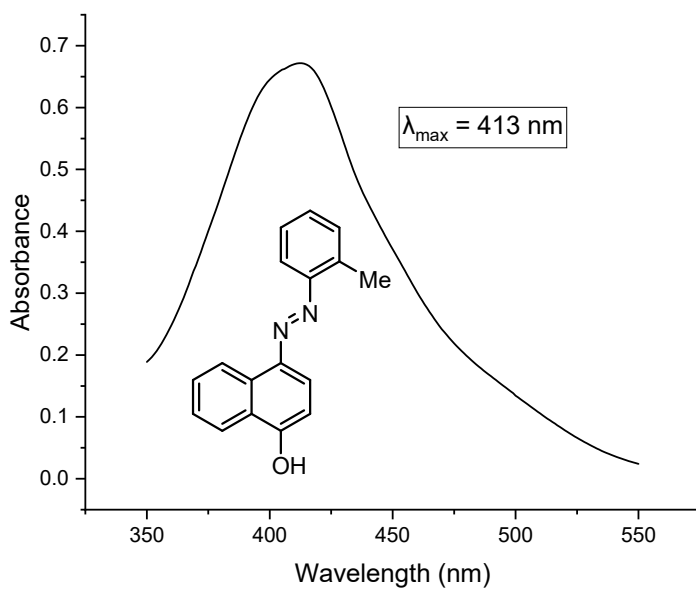
### <sup>1</sup>H NMR of 3o in *d*-DMSO (400 MHz)



**<sup>13</sup>C NMR of 3n in CDCl<sub>3</sub> (100 MHz)**

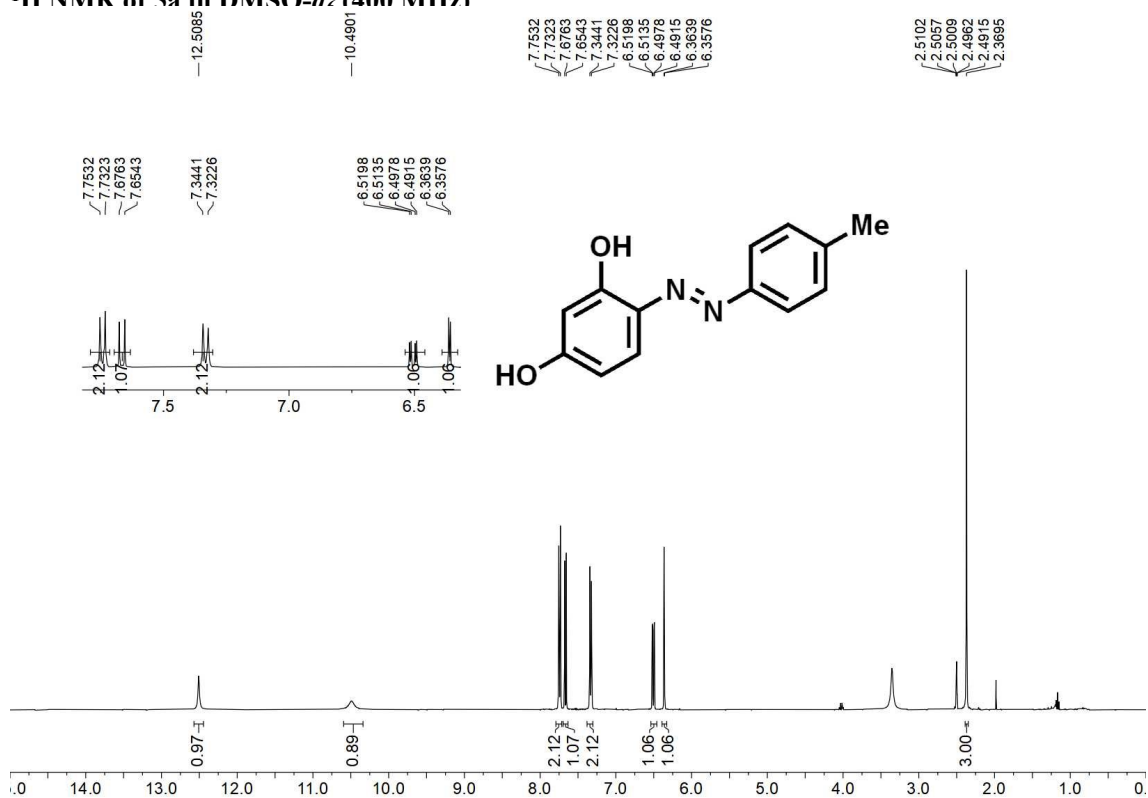


**UV-Vis Absorption Spectrum of 3p**

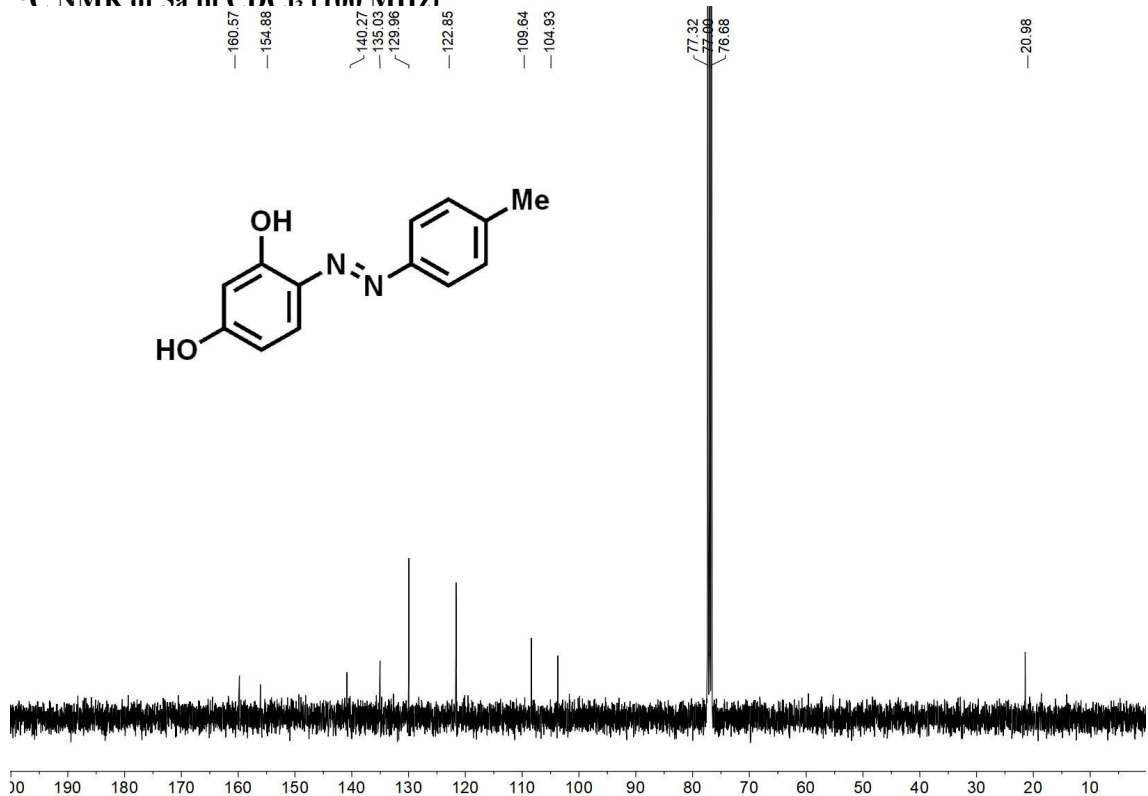


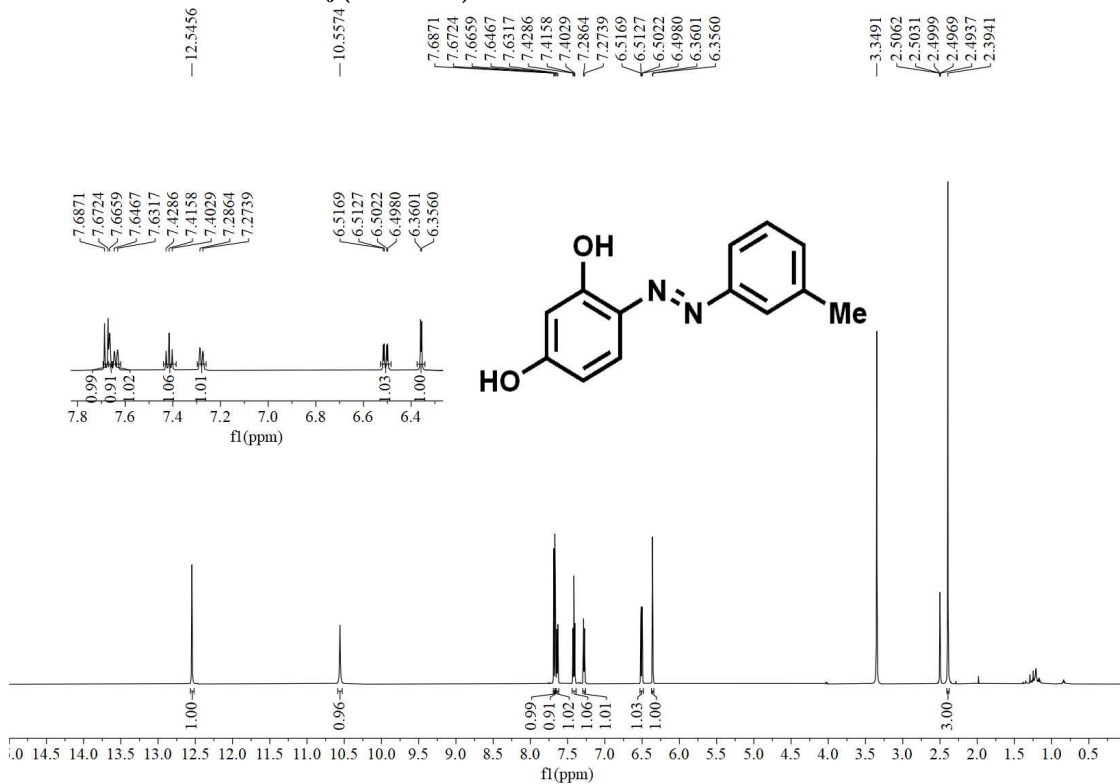
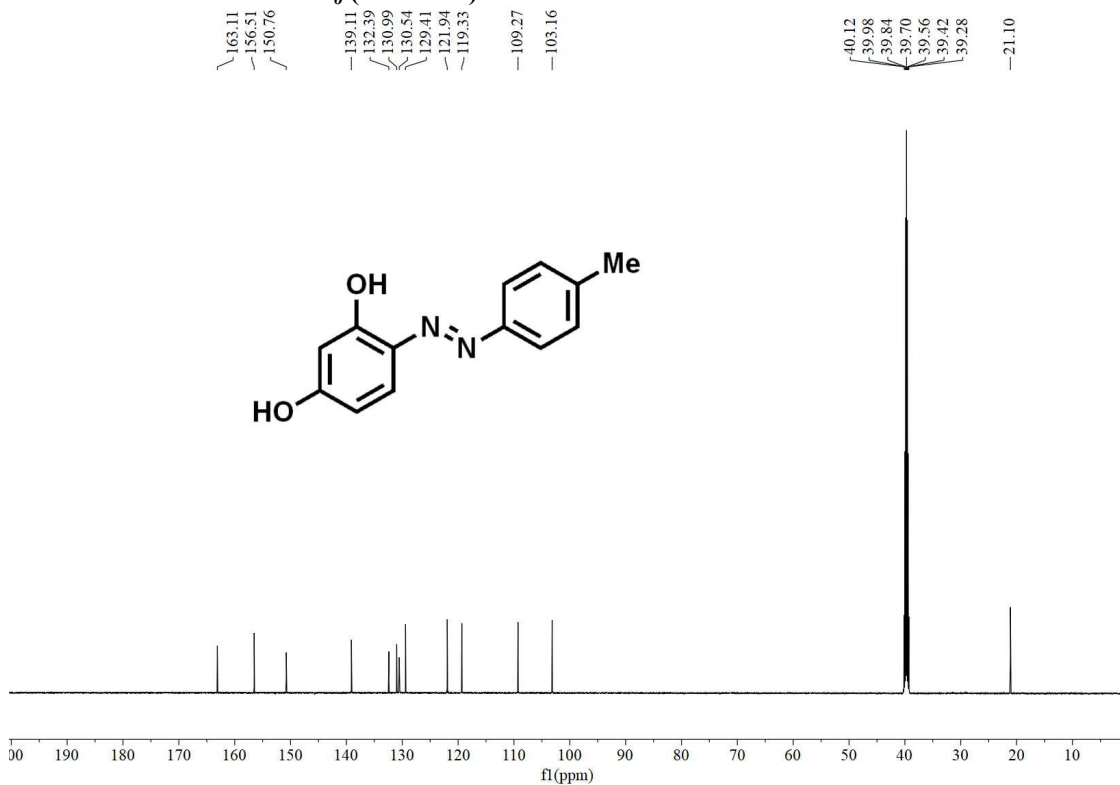
附录

<sup>1</sup>H NMR of 5a in DMSO-d<sub>6</sub> (400 MHz)

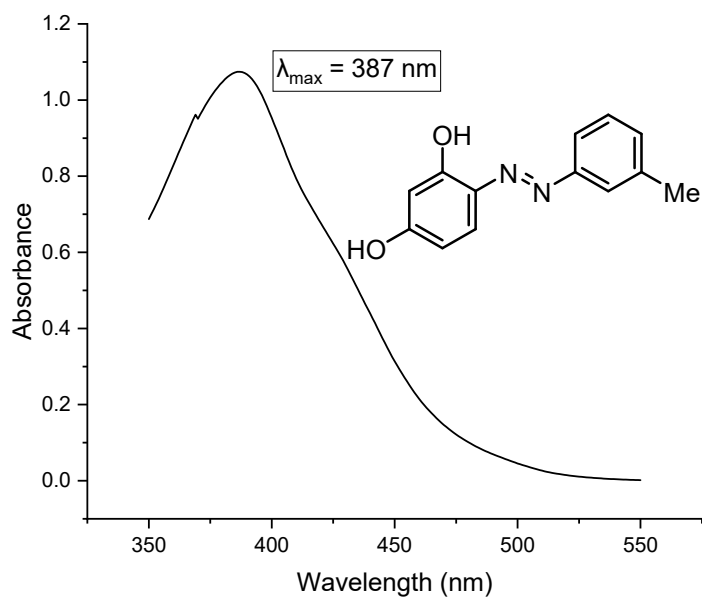
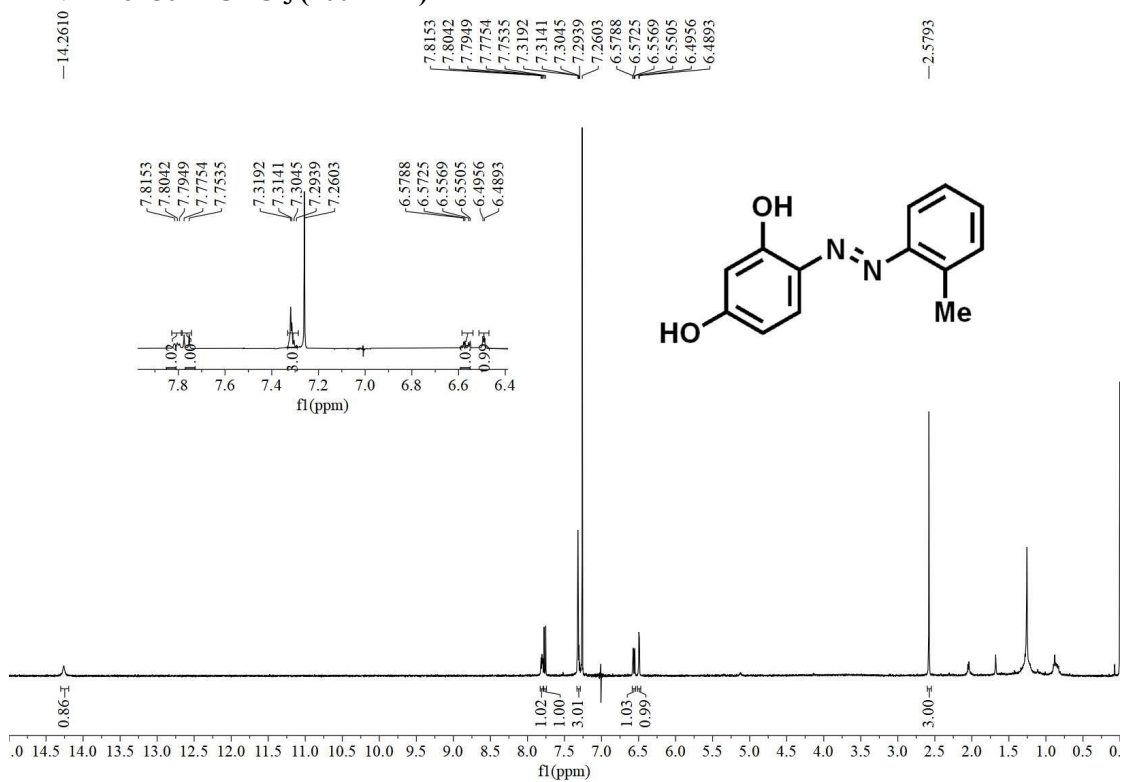


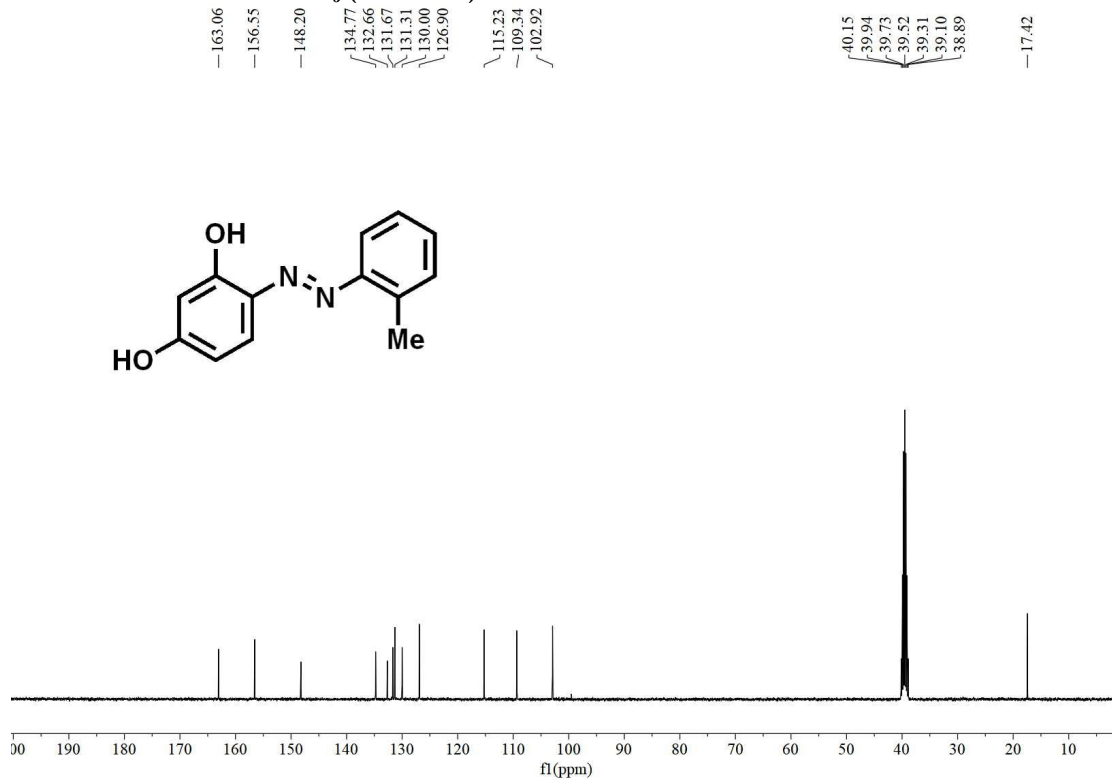
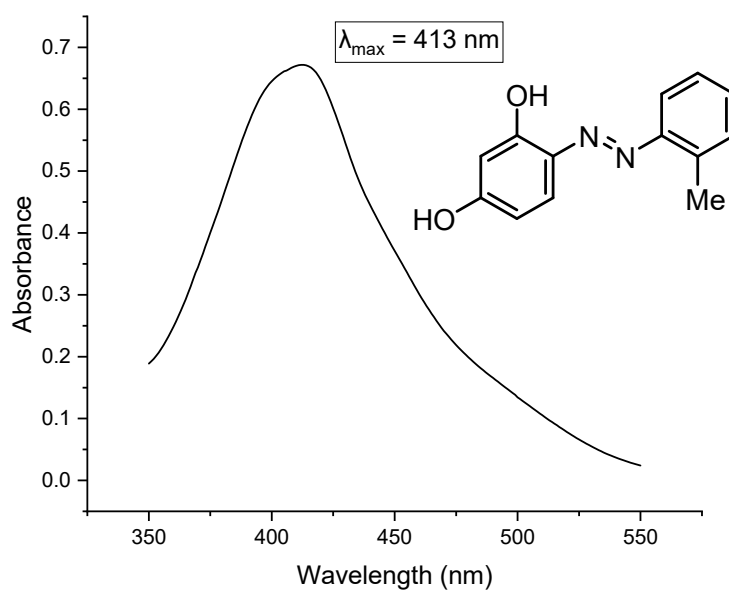
<sup>13</sup>C NMR of 5a in CDCl<sub>3</sub> (100 MHz)

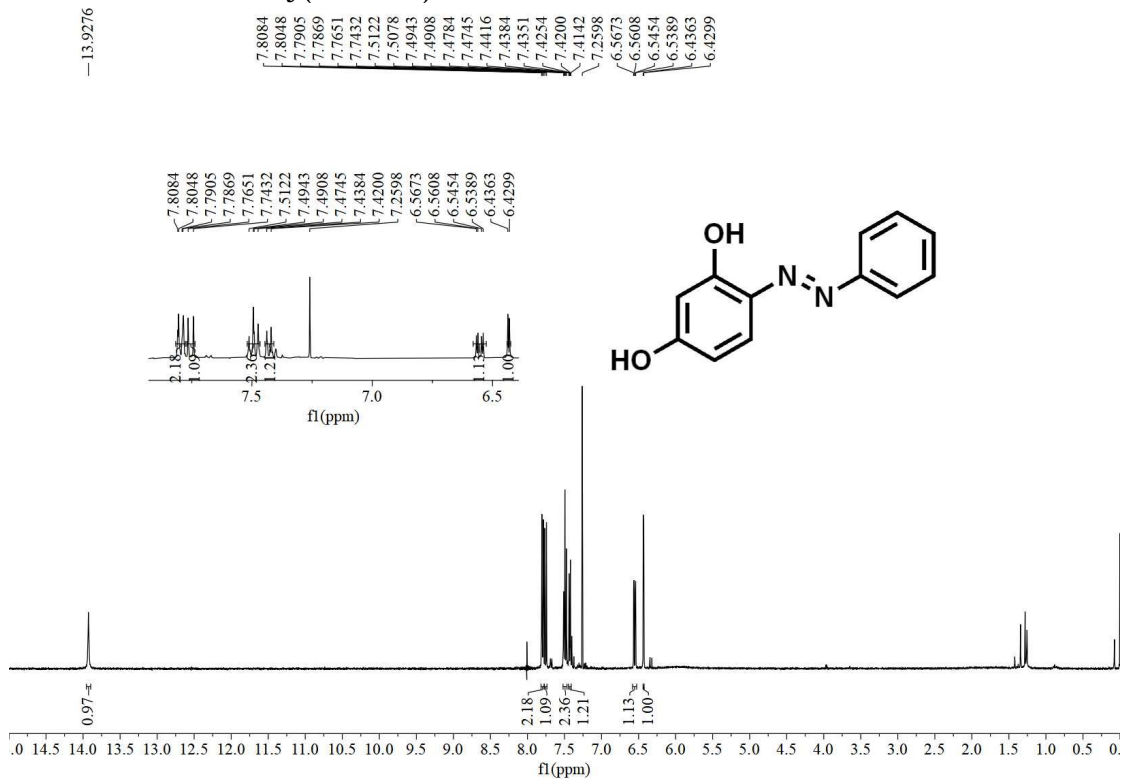
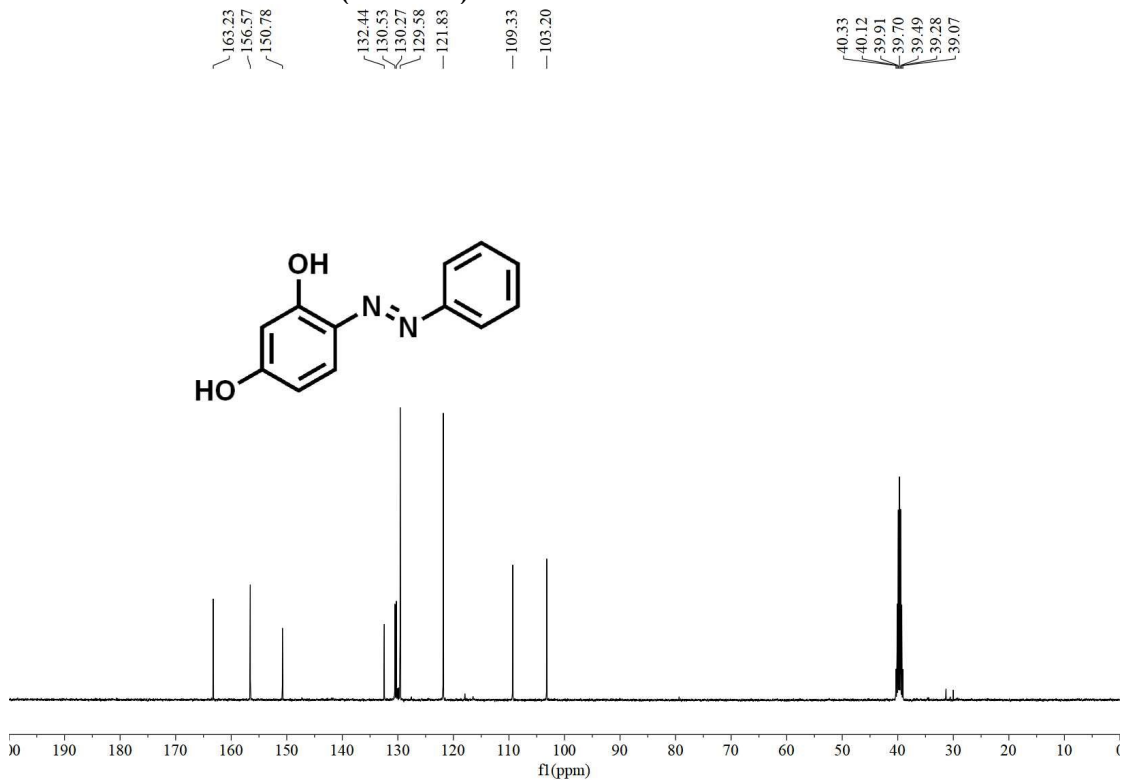


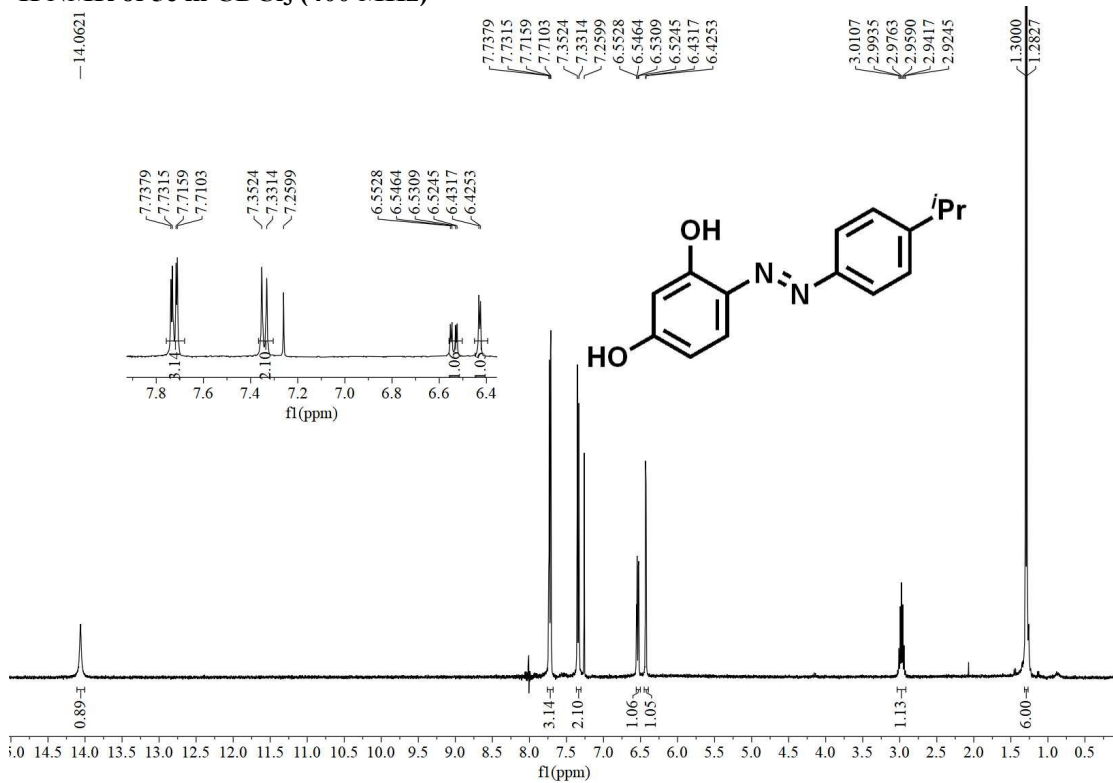
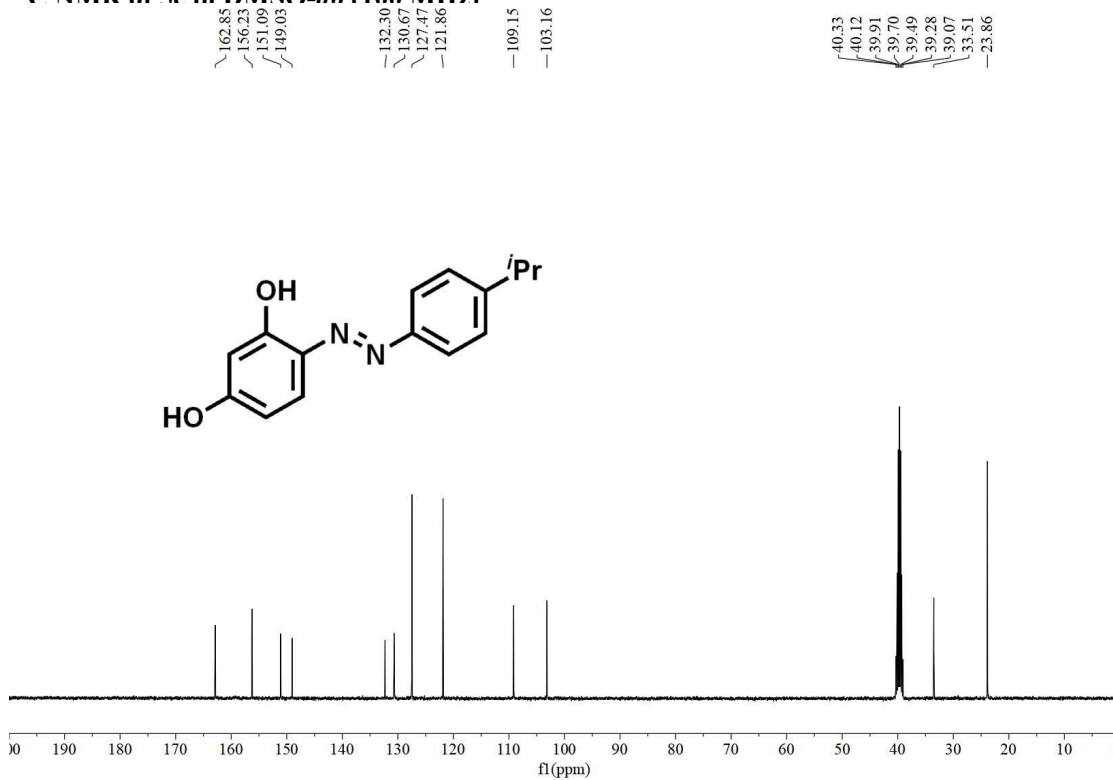
**<sup>1</sup>H NMR of 5b in DMSO-*d*<sub>6</sub> (600 MHz)****<sup>13</sup>C NMR of 5b in DMSO-*d*<sub>6</sub> (150 MHz)**

## UV-Vis Absorption Spectrum of 5b

 $^1\text{H}$  NMR of 5c in  $\text{CDCl}_3$  (400 MHz)

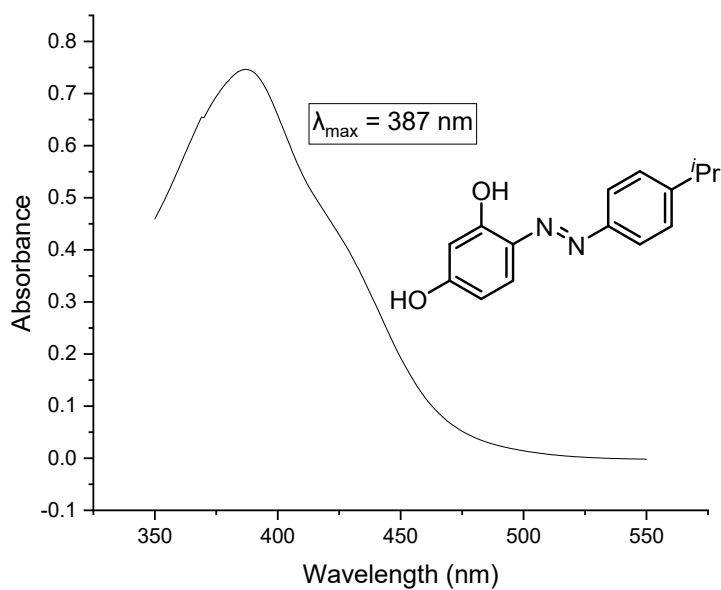
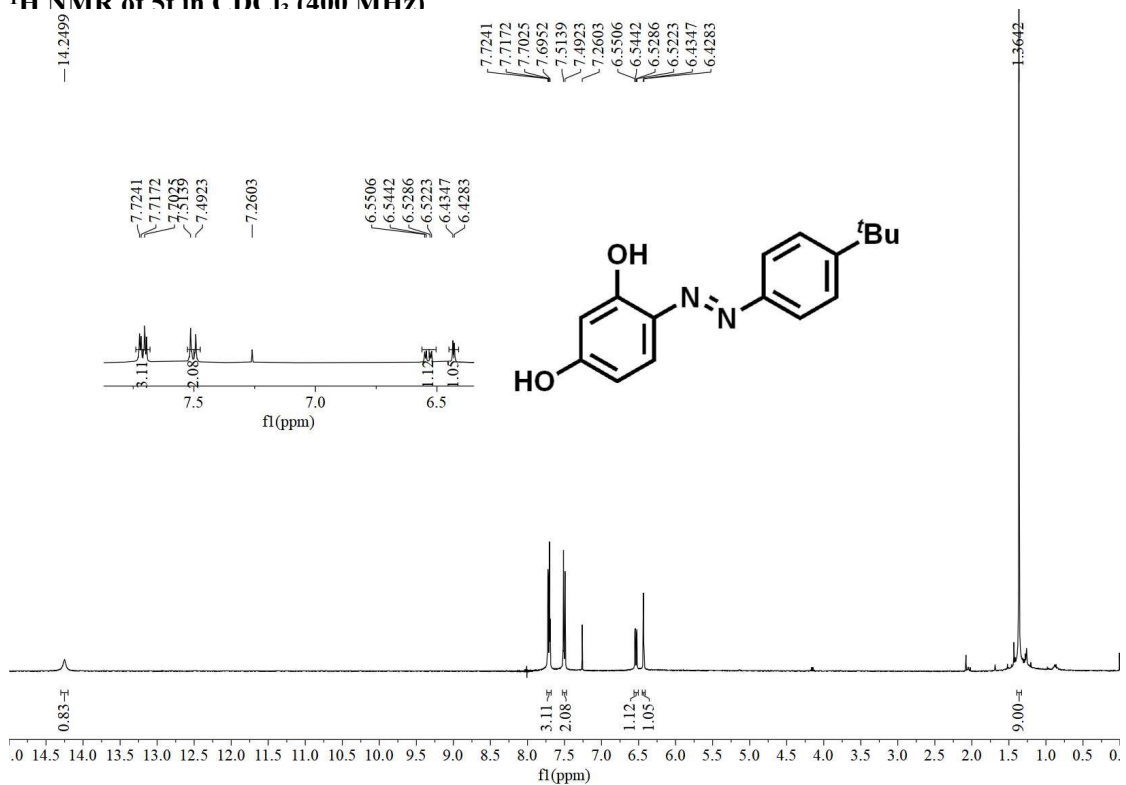
**$^{13}\text{C}$  NMR of 5c in  $\text{DMSO-}d_6$  (100 MHz)****UV-Vis Absorption Spectrum of 5c**

**<sup>1</sup>H NMR of 5d in CDCl<sub>3</sub> (400 MHz)****<sup>13</sup>C NMR of 5d in d-DMSO (100 MHz)**

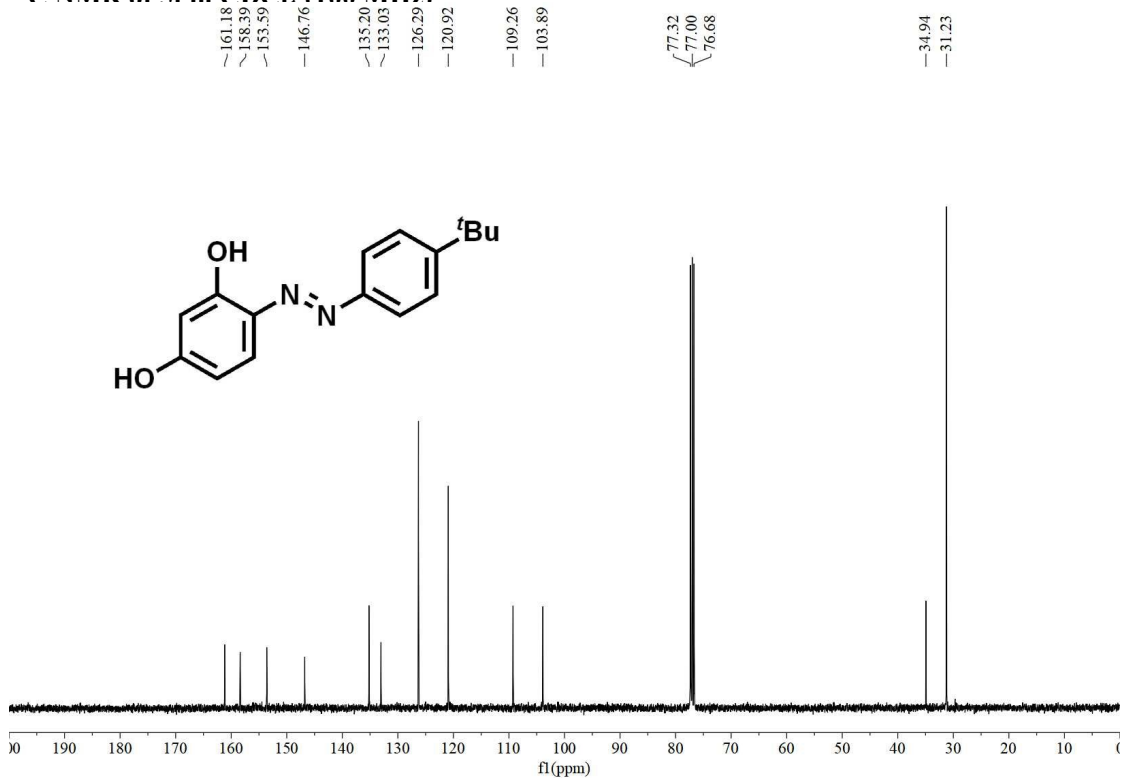
**<sup>1</sup>H NMR of 5e in CDCl<sub>3</sub> (400 MHz)****<sup>13</sup>C NMR of 5e in DMSO-*d*<sub>6</sub> (100 MHz)**



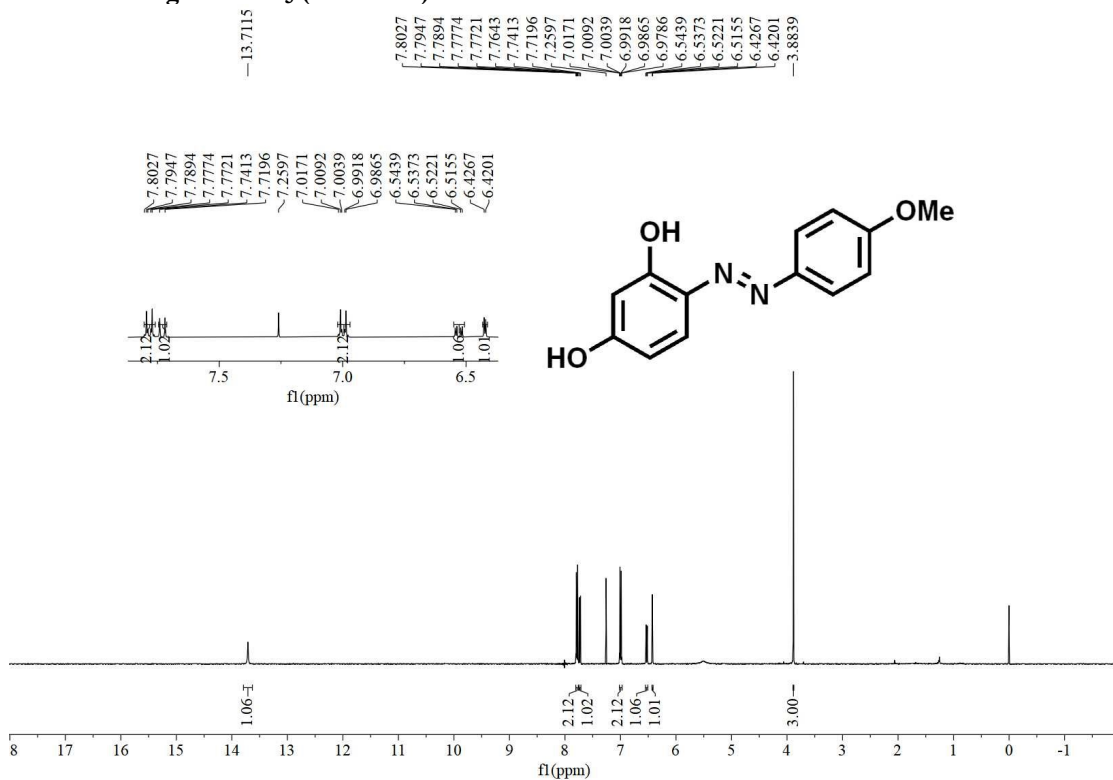
## UV-Vis Absorption Spectrum of 5e

 $^1\text{H}$  NMR of 5f in  $\text{CDCl}_3$  (400 MHz)

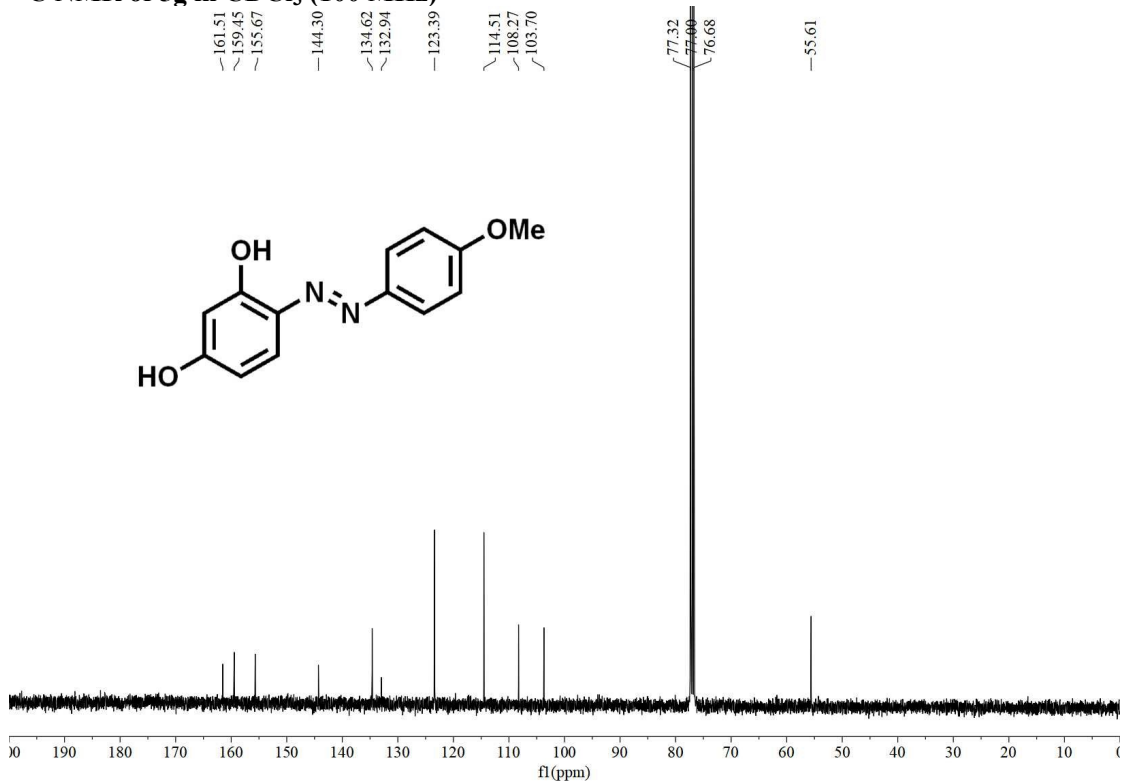
<sup>13</sup>C NMR of 5f in CDCl<sub>3</sub> (100 MHz)



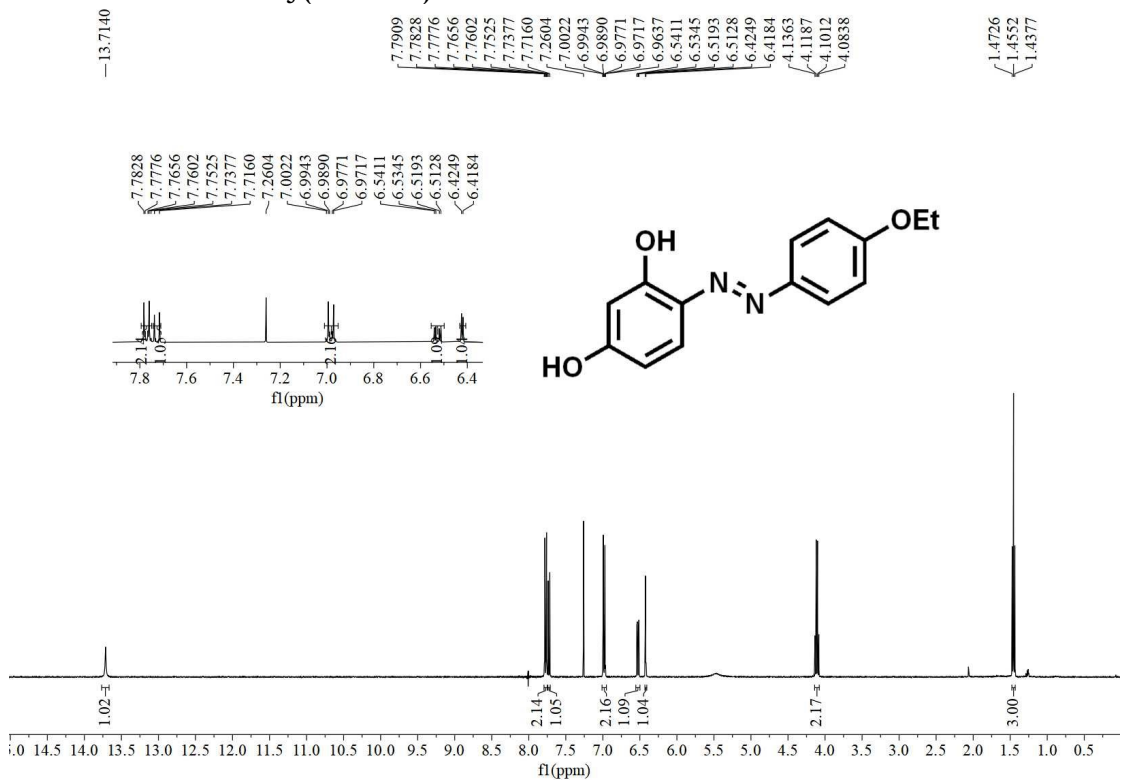
<sup>1</sup>H NMR of 5g in CDCl<sub>3</sub> (400 MHz)

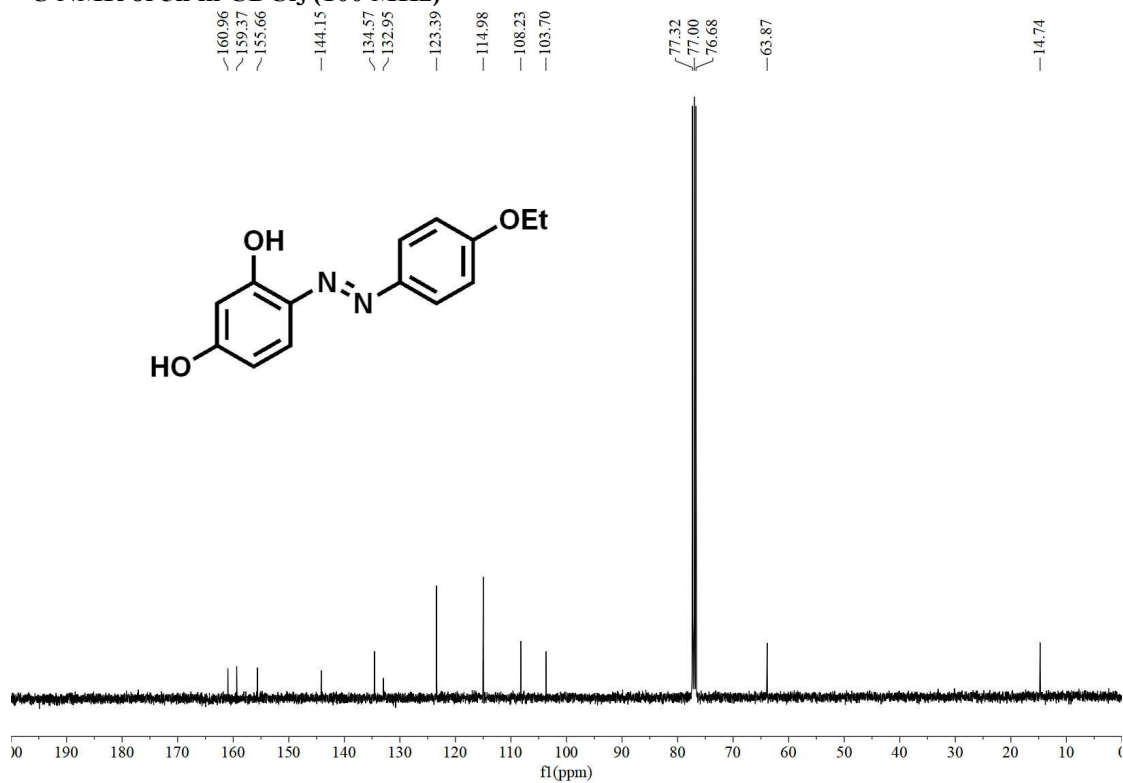
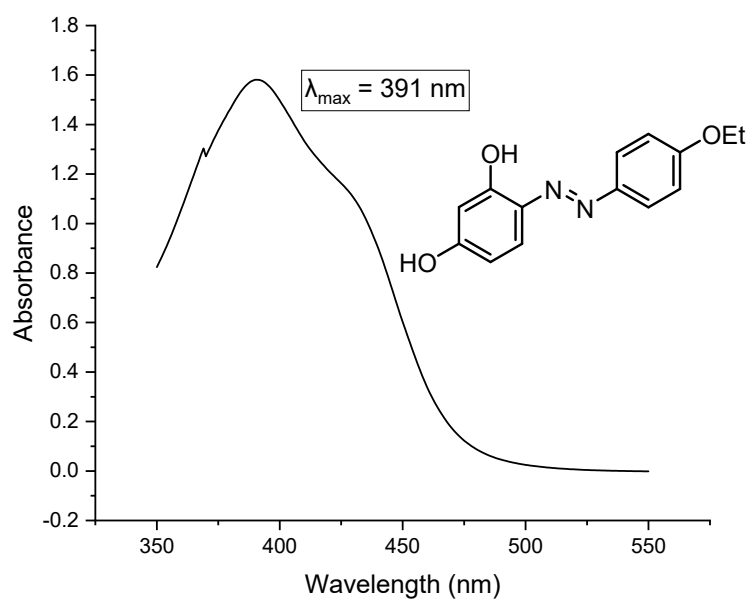


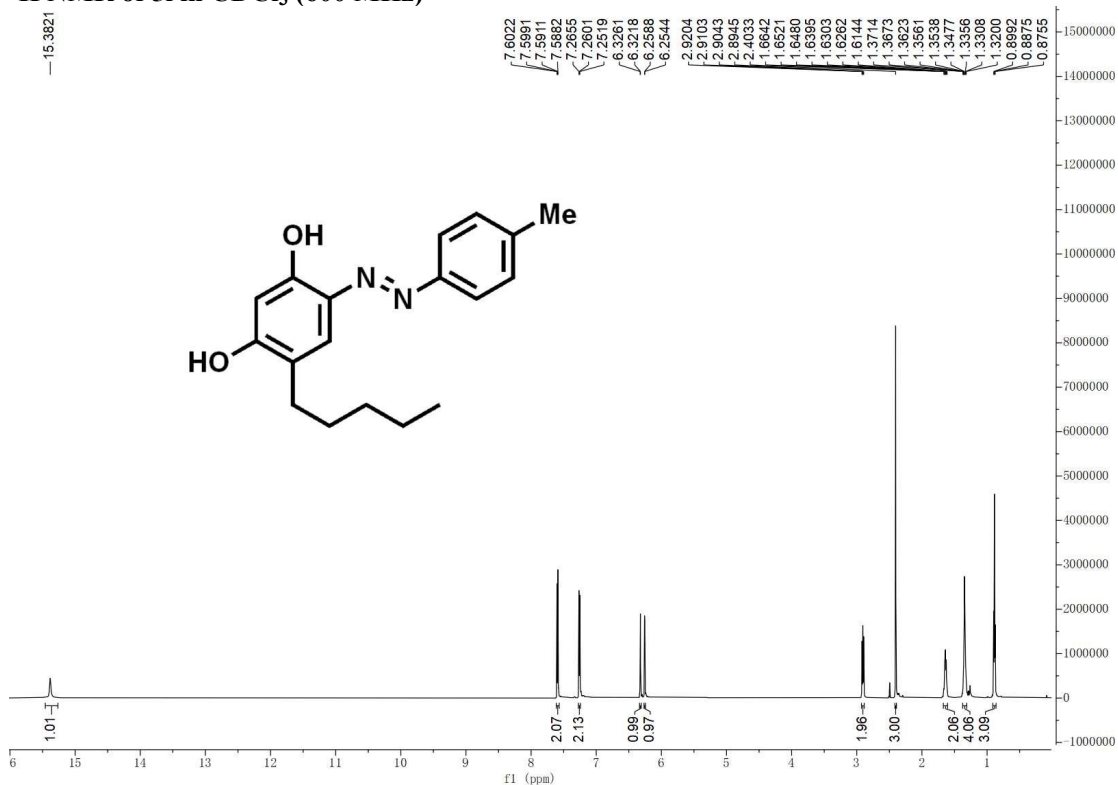
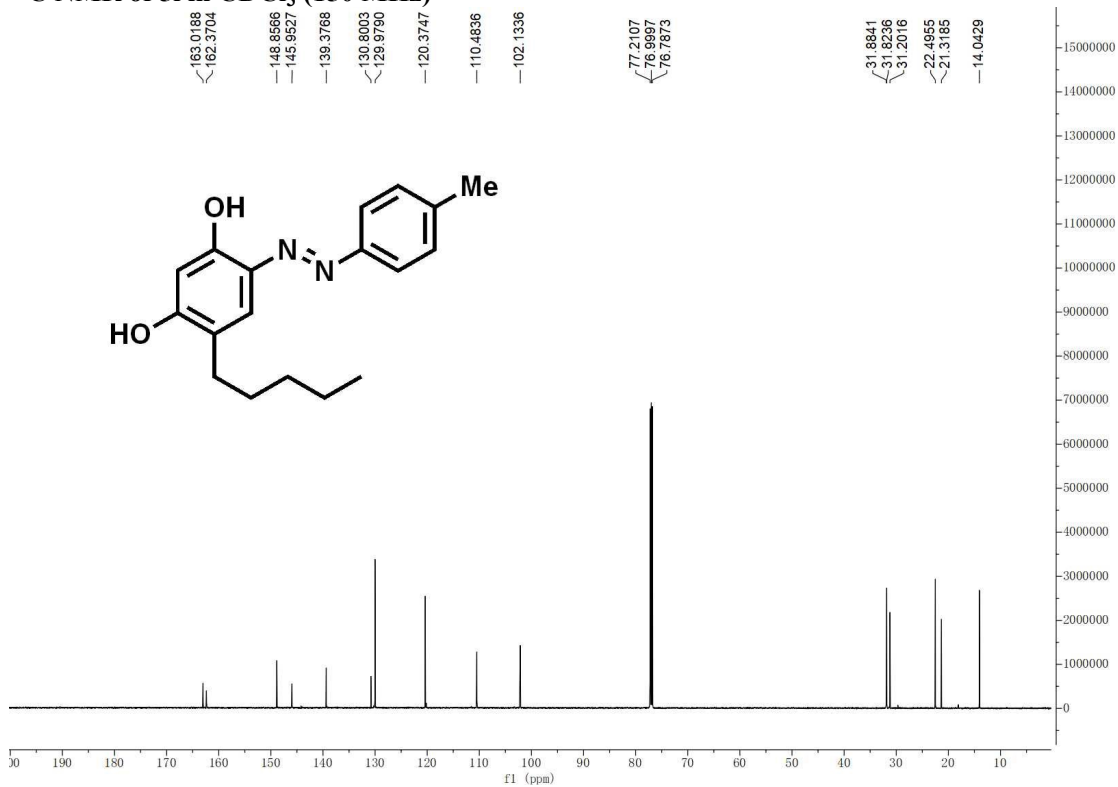
**<sup>13</sup>C NMR of 5g in CDCl<sub>3</sub> (100 MHz)**



**<sup>1</sup>H NMR of 5h in CDCl<sub>3</sub> (400 MHz)**



**$^{13}\text{C}$  NMR of 5h in  $\text{CDCl}_3$  (100 MHz)****UV-Vis Absorption Spectrum of 5h**

$^1\text{H}$  NMR of 5i in  $\text{CDCl}_3$  (600 MHz) $^{13}\text{C}$  NMR of 5i in  $\text{CDCl}_3$  (150 MHz)

## UV-Vis Absorption Spectrum of 5i

