

**Chromone-indanedione reactant: a bifunctional 3C synthon for  
diastereoselective construction of skeleton-diversified  
b Spiro-[chromanocyclopentane-oxindole-indanedione]**

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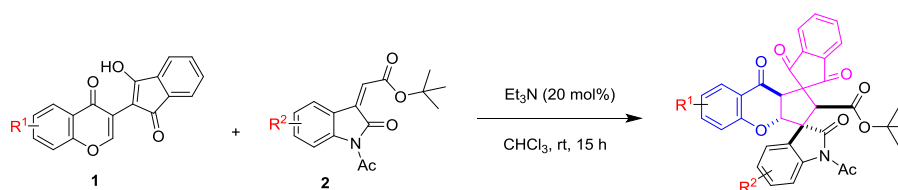
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## 1. General experimental information

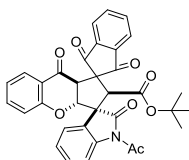
Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel.  $^1\text{H}$  and  $^{13}\text{C}$ NMR spectra were obtained using a Bruker DPX-400 spectrometer.  $^1\text{H}$  NMR chemical shifts are reported in ppm ( $\delta$ ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration.  $^{13}\text{C}$  NMR chemical shifts are reported in ppm ( $\delta$ ) from tetramethylsilane (TMS) with the solvent resonance as the internal standard.

## 2. Typical experimental procedures for synthesis of compounds 3



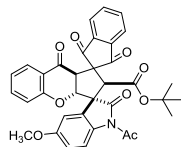
Compound **1** (0.30 mmol) and compound **2** (0.20 mmol) were dissolved in  $\text{CHCl}_3$  (1.5 mL).  $\text{Et}_3\text{N}$  (20 mol%, 0.04 mmol) was added to this solution at room temperature, and the mixture was stirred for 15 h. After the removal of solvent, purification by flash column chromatography (hexane/ethyl acetate = 8:1~5:1) delivered the product **3** as a light yellow solid.

## 3. Characterization data of compounds 3

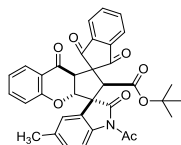


**3a**: Light yellow solid, m.p. 195.7-197.2  $^\circ\text{C}$ , yield 76%, 20:1 *dr*;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.73 (s, 9H), 2.75 (s, 3H), 4.11 (d,  $J = 14.4$  Hz, 1H), 4.41 (s, 1H), 5.68 (d,  $J = 14.0$  Hz, 1H), 6.83 (d,  $J = 8.4$  Hz, 1H), 6.88-6.92 (m, 1H), 7.21-7.25 (m, 1H), 7.33-7.37 (m, 2H), 7.56-7.59 (m, 1H), 7.82-7.89 (m, 3H), 8.02-8.06 (m, 2H), 8.25 (d,  $J = 8.4$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 25.7, 26.1, 54.7, 54.9, 55.0, 58.6, 82.1, 86.0, 115.2, 117.2, 119.9, 121.3, 121.9, 122.9, 123.8, 125.0, 126.2, 127.8, 128.4, 129.9, 134.5, 135.1, 135.4, 139.8, 140.0, 142.8, 159.9, 164.9, 169.7, 176.3,

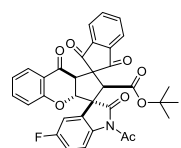
188.5, 197.3, 199.9; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $C_{34}H_{27}NNaO_8 [M+Na]^+$ : 600.1629; Found: 600.1633; The chiral column and the method for HPLC analysis: using a Chiralpak ID column (93/7 hexane/i-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau = 22.60$  min;  $\tau = 47.67$  min).



**3b**: Light yellow solid, m.p. 244.9-246.4 °C, yield 71%, >20:1 *dr*;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$ : 0.77 (s, 9H), 2.73 (s, 3H), 3.77 (s, 3H), 4.09 (d,  $J = 14.4$  Hz, 1H), 5.65 (d,  $J = 14.4$  Hz, 1H), 6.83-6.92 (m, 3H), 7.34-7.38 (m, 1H), 7.49 (d,  $J = 2.8$  Hz, 1H), 7.56-7.58 (m, 1H), 7.81-7.89 (m, 2H), 8.02-8.06 (m, 2H), 8.17 (d,  $J = 9.2$  Hz, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$ : 25.2, 25.7, 54.3, 54.6, 54.6, 54.7, 58.1, 81.7, 85.7, 108.7, 113.5, 115.9, 116.8, 119.6, 120.9, 121.6, 122.5, 125.8, 128.7, 132.8, 134.1, 134.7, 135.0, 139.6, 142.5, 156.6, 159.5, 164.5, 169.0, 175.9, 188.1, 197.0, 199.4; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $C_{35}H_{29}NNaO_9 [M+Na]^+$ : 630.1735; Found: 630.1737.

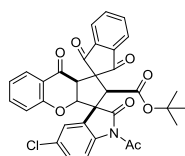


**3c**: Light yellow solid, m.p. 276.9-278.4 °C, yield 69%, >20:1 *dr*;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$ : 0.75 (s, 9H), 2.32 (s, 3H), 2.74 (s, 3H), 4.11 (d,  $J = 14.0$  Hz, 1H), 5.66 (d,  $J = 14.0$  Hz, 1H), 6.83 (d,  $J = 8.4$  Hz, 1H), 6.88-6.92 (m, 1H), 7.14 (d,  $J = 8.4$  Hz, 1H), 7.33-7.37 (m, 1H), 7.56-7.58 (m, 1H), 7.60 (s, 1H), 7.82-7.90 (m, 2H), 8.02-8.07 (m, 2H), 8.12 (d,  $J = 8.4$  Hz, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$ : 20.3, 25.7, 26.1, 54.7, 54.8, 55.0, 58.5, 82.1, 86.0, 115.0, 117.2, 120.0, 121.2, 121.9, 122.8, 124.2, 126.2, 127.7, 128.8, 134.4, 134.8, 135.1, 135.3, 137.5, 139.9, 142.9, 160.0, 165.0, 169.6, 176.5, 188.6, 197.5, 199.8; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $C_{35}H_{29}NNaO_8 [M+Na]^+$ : 614.1785; Found: 614.1783.

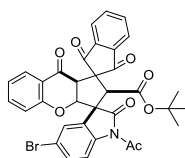


**3d**: Light yellow solid, m.p. 259.0-260.5 °C, yield 75%, >20:1 *dr*;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$ : 0.78 (s, 9H), 2.74 (s, 3H), 4.09 (d,  $J = 14.0$  Hz, 1H), 4.41 (s, 1H), 5.62 (d,  $J = 14.4$  Hz, 1H),

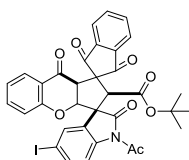
6.84 (d,  $J = 8.4$  Hz, 1H), 6.89-6.93 (m, 1H), 7.02-7.07 (m, 1H), 7.35-7.38 (m, 1H), 7.57 (d,  $J = 6.8$  Hz, 1H), 7.63-7.66 (m, 1H), 7.83-7.90 (m, 2H), 8.02-8.06 (m, 2H), 8.24-8.27 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 25.6, 26.1, 54.8, 54.9, 55.1, 58.2, 82.5, 85.9, 111.5 (d,  $J_{\text{C,F}} = 25.2$  Hz), 114.8 (d,  $J_{\text{C,F}} = 23.3$  Hz), 116.7 (d,  $J_{\text{C,F}} = 8.1$  Hz), 117.1, 119.9, 121.4, 122.0, 122.9, 126.2, 129.8, 134.6, 135.1, 135.4, 135.8, 140.0, 142.7, 159.7 (d,  $J_{\text{C,F}} = 244.1$  Hz), 159.8, 164.6, 169.5, 175.8, 188.2, 197.1, 199.9; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{34}\text{H}_{26}\text{FNNaO}_8$   $[\text{M}+\text{Na}]^+$ : 618.1535; Found: 618.1539.



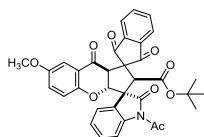
**3e**: Light yellow solid, m.p. 285.5-287.0 °C, yield 76%, >20:1 *dr*;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.79 (s, 9H), 2.74 (s, 3H), 4.08 (d,  $J = 14.4$  Hz, 1H), 4.40 (s, 1H), 5.63 (d,  $J = 14.0$  Hz, 1H), 6.84 (d,  $J = 8.4$  Hz, 1H), 6.89-6.93 (m, 1H), 7.32-7.39 (m, 2H), 7.56-7.59 (m, 1H), 7.83-7.91 (m, 3H), 8.03-8.08 (m, 2H), 8.21 (d,  $J = 8.8$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 25.2, 25.7, 54.2, 54.3, 54.6, 57.6, 82.1, 85.3, 116.0, 116.6, 119.4, 120.9, 121.5, 122.4, 123.6, 125.8, 127.9, 129.2, 130.0, 134.1, 134.7, 135.0, 137.7, 139.5, 142.3, 159.3, 164.1, 169.0, 175.2, 187.7, 196.6, 199.3; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{34}\text{H}_{26}\text{ClNNaO}_8$   $[\text{M}+\text{Na}]^+$ : 634.1239; Found: 634.1241.



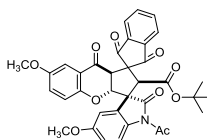
**3f**: Light yellow solid, m.p. 269.4-270.9 °C, yield 74%, >20:1 *dr*;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.80 (s, 9H), 2.74 (s, 3H), 4.08 (d,  $J = 14.0$  Hz, 1H), 4.40 (s, 1H), 5.63 (d,  $J = 14.0$  Hz, 1H), 6.84 (d,  $J = 8.0$  Hz, 1H), 6.90-6.93 (m, 1H), 7.35-7.39 (m, 1H), 7.47-7.50 (m, 1H), 7.56-7.59 (m, 1H), 7.83-7.91 (m, 2H), 7.97 (d,  $J = 2.0$  Hz, 1H), 8.03-8.08 (m, 2H), 8.16 (d,  $J = 8.8$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 25.7, 26.2, 54.6, 54.7, 55.1, 58.1, 82.6, 85.8, 116.9, 117.1, 118.1, 119.9, 121.4, 122.1, 122.9, 126.2, 126.8, 130.0, 131.3, 134.6, 135.1, 135.4, 138.7, 140.0, 142.8, 159.7, 164.6, 169.5, 175.5, 188.2, 197.1, 199.8; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{34}\text{H}_{26}\text{BrNNaO}_8$   $[\text{M}+\text{Na}]^+$ : 678.0734; Found: 678.0731.



**3g:** Light yellow solid, m.p. 269.0-270.5 °C, yield 64%, >20:1 *dr*; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 0.80 (s, 9H), 2.73 (s, 3H), 4.08 (d, *J* = 14.0 Hz, 1H), 5.62 (d, *J* = 14.0 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.90-6.93 (m, 1H), 7.35-7.39 (m, 1H), 7.56-7.58 (m, 1H), 7.68-7.70 (m, 1H), 7.83-7.91 (m, 2H), 8.03 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 6.8 Hz, 1H), 8.12 (d, *J* = 1.6 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 25.7, 26.2, 54.4, 54.7, 55.1, 58.1, 82.7, 85.8, 88.6, 117.1, 117.2, 119.9, 121.4, 122.1, 122.9, 126.2, 130.2, 132.5, 134.5, 135.1, 135.4, 137.4, 139.4, 140.0, 142.8, 159.7, 164.6, 169.5, 175.4, 188.2, 197.2, 199.7; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>34</sub>H<sub>26</sub>INNaO<sub>8</sub> [M+Na]<sup>+</sup>: 726.0595; Found: 726.0598.

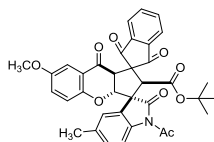


**3h:** Light yellow solid, m.p. 216.9-218.4 °C, yield 66%, >20:1 *dr*; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 0.82 (s, 9H), 2.21 (s, 3H), 2.38 (s, 3H), 2.80 (s, 3H), 4.15 (d, *J* = 14.0 Hz, 1H), 4.46 (s, 1H), 5.70 (d, *J* = 14.4 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 7.20-7.24 (m, 2H), 7.42 (d, *J* = 1.6 Hz, 1H), 7.66 (s, 1H), 7.90-7.95 (m, 2H), 8.09-8.13 (m, 2H), 8.18 (d, *J* = 8.4 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 19.3, 20.3, 25.7, 26.1, 54.8, 54.9, 55.1, 58.4, 82.0, 86.1, 115.0, 116.9, 119.6, 121.9, 122.8, 124.2, 125.8, 127.7, 128.7, 130.7, 134.4, 134.8, 135.0, 136.3, 137.5, 139.9, 142.9, 158.1, 165.0, 169.6, 176.5, 188.8, 197.5, 199.8; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>35</sub>H<sub>29</sub>NNaO<sub>9</sub> [M+Na]<sup>+</sup>: 630.1735; Found: 630.1736.

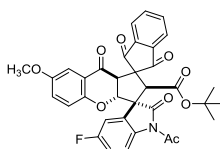


**3i:** Light yellow solid, m.p. 213.3-214.8 °C, yield 64%, >20:1 *dr*; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 0.77 (s, 9H), 2.73 (s, 3H), 3.60 (s, 3H), 3.77 (s, 3H), 4.07 (d, *J* = 14.4 Hz, 1H), 4.41 (s, 3H), 5.61 (d, *J* = 14.4 Hz, 1H), 6.77 (d, *J* = 9.2 Hz, 1H), 6.84-6.87 (m, 1H), 6.94-6.97 (m, 1H), 6.99 (d, *J* = 3.2 Hz, 1H), 7.49 (d, *J* = 2.8 Hz, 1H), 7.81-7.89 (m, 2H), 8.02-8.05 (m, 2H), 8.16 (d, *J* = 8.8 Hz,

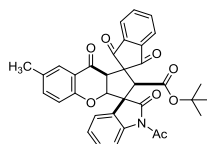
1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 25.6, 26.1, 54.6, 54.7, 55.0, 55.1, 58.5, 82.1, 86.3, 106.6, 109.0, 113.8, 116.3, 118.4, 119.9, 121.9, 122.8, 124.3, 129.1, 133.2, 134.4, 135.0, 140.0, 142.8, 153.5, 154.6, 156.9, 164.9, 169.4, 176.3, 188.6, 197.4, 199.8; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{36}\text{H}_{31}\text{NNaO}_{10}$   $[\text{M}+\text{Na}]^+$ : 660.1840; Found: 660.1844.



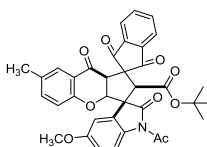
**3j**: Light yellow solid, m.p. 211.3-212.8  $^{\circ}\text{C}$ , yield 65%, >20:1 *dr*;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.75 (s, 9H), 2.31 (s, 3H), 2.73 (s, 3H), 3.59 (s, 3H), 4.09 (d,  $J = 14.0$  Hz, 1H), 4.39 (s, 1H), 5.62 (d,  $J = 14.4$  Hz, 1H), 6.75 (d,  $J = 8.8$  Hz, 1H), 6.93-6.96 (m, 1H), 6.99 (d,  $J = 2.8$  Hz, 1H), 7.12-7.15 (m, 1H), 7.59 (s, 1H), 7.81-7.89 (m, 2H), 8.02-8.07 (m, 2H), 8.11 (d,  $J = 8.4$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 20.3, 25.7, 26.1, 54.6, 54.8, 54.9, 55.1, 58.4, 82.0, 86.2, 106.5, 115.0, 118.4, 119.9, 121.9, 122.8, 124.2, 124.3, 128.7, 134.4, 134.8, 135.0, 153.5, 154.7, 165.0, 169.6, 188.7, 197.5; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{36}\text{H}_{31}\text{NNaO}_9$   $[\text{M}+\text{Na}]^+$ : 644.1891; Found: 644.1889.



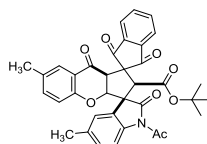
**3k**: Light yellow solid, m.p. 246.4-247.9  $^{\circ}\text{C}$ , yield 63%, >20:1 *dr*;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.79 (s, 9H), 2.74 (s, 3H), 3.60 (s, 3H), 4.06 (d,  $J = 14.0$  Hz, 1H), 4.41 (s, 1H), 5.57 (d,  $J = 14.0$  Hz, 1H), 6.76 (d,  $J = 8.8$  Hz, 1H), 6.94-6.97 (m, 1H), 6.99 (d,  $J = 8.1$  Hz, 1H), 7.02-7.07 (m, 1H), 7.63-7.66 (m, 1H), 7.83-7.91 (m, 2H), 8.03-8.06 (m, 2H), 8.23-8.27 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 25.6, 26.1, 54.6, 54.8, 54.9, 55.1, 58.2, 82.5, 86.1, 106.6, 111.5 (d,  $J_{\text{C,F}} = 26.2$  Hz), 114.8 (d,  $J_{\text{C,F}} = 22.4$  Hz), 116.6, 116.7, 118.3, 119.8, 121.9, 122.8, 124.4, 129.8 (d,  $J_{\text{C,F}} = 9.1$  Hz), 134.6, 135.1, 135.8, 140.0, 142.7, 153.6, 154.5, 159.7 (d,  $J_{\text{C,F}} = 244.3$  Hz), 164.7, 169.5, 175.9, 188.4, 197.1, 199.9; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{35}\text{H}_{28}\text{FNNaO}_9$   $[\text{M}+\text{Na}]^+$ : 648.1640; Found: 648.1643.



**3l:** Light yellow solid, m.p. 198.3-199.5 °C, yield 66%, >20:1 *dr*; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 0.76 (s, 9H), 2.16 (s, 3H), 2.77 (s, 3H), 4.11 (d, *J* = 14.4 Hz, 1H), 4.42 (s, 1H), 5.65 (d, *J* = 14.0 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 7.17-7.20 (m, 1H), 7.23-7.27 (m, 1H), 7.35-7.39 (m, 2H), 7.84-7.92 (m, 3H), 8.04-8.08 (m, 2H), 8.27 (d, *J* = 8.0 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 19.3, 25.7, 26.1, 54.7, 55.0, 55.1, 58.6, 82.1, 86.1, 115.2, 116.9, 119.6, 121.9, 122.8, 123.8, 125.0, 125.8, 127.9, 128.4, 130.8, 134.4, 135.1, 136.4, 139.8, 140.0, 142.9, 158.1, 164.9, 169.7, 176.3, 188.7, 197.4, 200.0; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>35</sub>H<sub>29</sub>NNaO<sub>8</sub> [M+Na]<sup>+</sup>: 614.1785; Found: 614.1789.

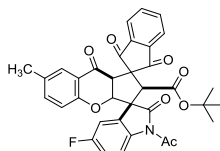


**3m:** Light yellow solid, m.p. 179.1-180.6 °C, yield 66%, >20:1 *dr*; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 0.84 (s, 9H), 2.21 (s, 3H), 2.80 (s, 3H), 3.84 (s, 3H), 4.13 (d, *J* = 14.0 Hz, 1H), 4.48 (s, 1H), 5.68 (d, *J* = 14.0 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.91-6.94 (m, 1H), 7.22-7.25 (m, 1H), 7.42 (d, *J* = 1.6 Hz, 1H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.88-7.96 (m, 2H), 8.09-8.12 (m, 2H), 8.24 (d, *J* = 9.2 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 20.3, 26.6, 27.1, 55.7, 56.0, 56.1, 56.2, 59.5, 83.1, 87.2, 110.1, 114.8, 117.3, 118.0, 120.6, 123.0, 123.8, 126.8, 130.2, 131.8, 134.2, 135.4, 136.1, 137.4, 141.0, 143.9, 158.0, 159.1, 166.0, 170.4, 177.3, 189.7, 198.5, 200.8; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>36</sub>H<sub>31</sub>NNaO<sub>9</sub> [M+Na]<sup>+</sup>: 644.1891; Found: 644.1895.

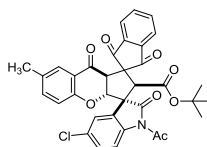


**3n:** Light yellow solid, m.p. 158.0-159.5 °C, yield 67%, >20:1 *dr*; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 0.82 (s, 9H), 2.21 (s, 3H), 2.38 (s, 3H), 2.80 (s, 3H), 4.15 (d, *J* = 14.0 Hz, 1H), 4.46 (s, 1H), 5.70 (d, *J* = 14.4 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 7.20-7.24 (m, 2H), 7.41 (d, *J* = 1.6 Hz, 1H), 7.66 (s, 1H), 7.88-7.96 (m, 2H), 8.09-8.13 (m, 2H), 8.19 (d, *J* = 8.4 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>,

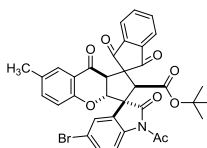
100 MHz)  $\delta$ : 19.3, 20.3, 25.7, 26.1, 54.8, 54.9, 55.1, 58.4, 82.0, 86.1, 115.0, 116.9, 119.6, 121.9, 122.8, 124.2, 125.8, 127.7, 128.7, 130.7, 134.4, 134.8, 135.0, 136.3, 137.5, 139.9, 142.9, 158.1, 165.0, 169.6, 176.5, 188.8, 197.5, 199.8; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $C_{36}H_{31}NNaO_8$   $[M+Na]^+$ : 628.1942; Found: 628.1947.



**3o**: Light yellow solid, m.p. 189.1-180.6 °C, yield 71%, >20:1 *dr*;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$ : 0.78 (s, 9H), 2.14 (s, 3H), 2.73 (s, 3H), 4.06 (d,  $J = 14.0$  Hz, 1H), 4.40 (s, 1H), 5.58 (d,  $J = 14.0$  Hz, 1H), 6.73 (d,  $J = 8.8$  Hz, 1H), 7.01-7.07 (m, 1H), 7.15-7.18 (m, 1H), 7.35 (d,  $J = 1.6$  Hz, 1H), 7.63-7.65 (m, 1H), 7.83-7.90 (m, 2H), 8.02-8.05 (m, 2H), 8.23-8.26 (m, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$ : 19.3, 25.6, 26.1, 55.0, 55.1, 58.2, 82.4, 86.0, 111.5 (d,  $J_{C,F} = 26.2$  Hz), 114.8 (d,  $J_{C,F} = 22.5$  Hz), 116.6 (d,  $J_{C,F} = 8.3$  Hz), 116.9, 119.5, 121.9, 122.8, 125.8, 129.9, 131.0, 134.6, 135.1, 136.4, 140.1, 142.8, 157.9, 159.7 (d,  $J_{C,F} = 245.2$  Hz), 164.7, 169.5, 175.9, 188.4, 197.2, 199.9; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $C_{35}H_{28}FNNaO_8$   $[M+Na]^+$ : 632.1691; Found: 632.1695.



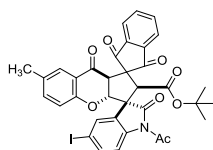
**3p**: Light yellow solid, m.p. 213.6-215.1 °C, yield 69%, >20:1 *dr*;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$ : 0.79 (s, 9H), 2.14 (s, 3H), 2.74 (s, 3H), 4.05 (d,  $J = 14.0$  Hz, 1H), 4.40 (s, 1H), 5.59 (d,  $J = 14.4$  Hz, 1H), 6.72 (d,  $J = 8.8$  Hz, 1H), 7.15-7.18 (m, 1H), 7.31-7.35 (m, 2H), 7.83-7.90 (m, 3H), 8.02-8.07 (m, 2H), 8.21 (d,  $J = 8.8$  Hz, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$ : 19.3, 25.7, 26.1, 54.7, 54.9, 55.1, 58.1, 82.6, 85.9, 116.5, 116.8, 119.5, 122.0, 122.8, 124.0, 125.8, 128.3, 129.8, 130.5, 131.0, 134.5, 135.1, 136.4, 138.2, 140.0, 142.8, 157.9, 164.7, 169.5, 175.7, 188.4, 197.2, 199.8; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $C_{35}H_{28}ClNNaO_8$   $[M+Na]^+$ : 648.1396; Found: 648.1397.



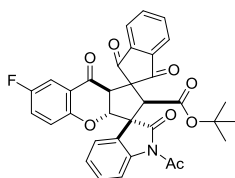
**3q**: Light yellow solid, m.p. 231.7-233.2 °C, yield 67%, >20:1 *dr*;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)



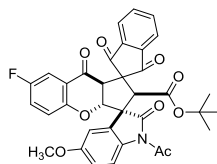
$\delta$ : 0.80 (s, 9H), 2.14 (s, 3H), 2.73 (s, 3H), 4.05 (d,  $J = 14.0$  Hz, 1H), 4.39 (s, 1H), 5.58 (d,  $J = 14.0$  Hz, 1H), 6.72 (d,  $J = 8.4$  Hz, 1H), 7.15-7.18 (m, 1H), 7.34 (d,  $J = 2.4$  Hz, 1H), 7.47-7.49 (m, 1H), 7.82-7.90 (m, 2H), 7.97 (d,  $J = 2.0$  Hz, 1H), 8.02-8.07 (m, 2H), 8.15 (d,  $J = 8.8$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 19.3, 25.7, 26.2, 54.6, 54.8, 55.1, 58.1, 82.6, 85.9, 116.8, 118.0, 119.5, 122.0, 122.8, 125.8, 126.8, 130.1, 131.0, 131.2, 134.5, 135.1, 136.4, 138.7, 140.0, 142.8, 157.9, 164.7, 169.5, 175.6, 188.4, 197.2, 199.8; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{35}\text{H}_{28}\text{BrNNaO}_8$   $[\text{M}+\text{Na}]^+$ : 692.0891; Found: 692.0896.



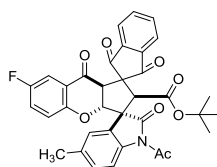
**3r**: Light yellow solid, m.p. 152.5-154.0 °C, yield 61%, >20:1 *dr*;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.80 (s, 9H), 2.14 (s, 3H), 2.73 (s, 3H), 4.05 (d,  $J = 14.0$  Hz, 1H), 4.39 (s, 1H), 5.57 (d,  $J = 14.4$  Hz, 1H), 6.72 (d,  $J = 8.4$  Hz, 1H), 7.15-7.18 (m, 1H), 7.34 (s, 1H), 7.67-7.69 (m, 1H), 7.85-7.89 (m, 2H), 8.02-8.08 (m, 3H), 8.12 (d,  $J = 1.6$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 20.3, 26.7, 27.2, 55.4, 55.9, 56.2, 59.1, 83.6, 86.9, 89.7, 117.9, 118.2, 120.6, 123.1, 123.9, 126.9, 131.4, 132.0, 133.5, 135.5, 136.1, 137.5, 138.3, 140.4, 141.1, 143.8, 158.9, 165.7, 170.6, 176.5, 189.4, 198.3, 200.7; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{35}\text{H}_{28}\text{INNaO}_8$   $[\text{M}+\text{Na}]^+$ : 740.0752; Found: 740.0752.



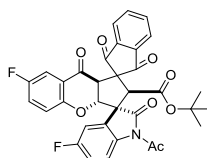
**3s**: Light yellow solid, m.p. 246.1-247.6 °C, yield 64%, >20:1 *dr*;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.80 (s, 9H), 2.82 (s, 3H), 4.16 (d,  $J = 14.0$  Hz, 1H), 4.47 (s, 1H), 5.74 (d,  $J = 14.0$  Hz, 1H), 6.88-6.92 (m, 1H), 7.13-7.18 (m, 1H), 7.26-7.32 (m, 2H), 7.41-7.45 (m, 1H), 7.89-7.96 (m, 3H), 8.09-8.13 (m, 2H), 8.32 (d,  $J = 8.0$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 25.0, 25.3, 53.8, 54.2, 58.0, 81.5, 85.5, 110.5 (d,  $J_{\text{C,F}} = 24.2$  Hz), 114.5, 118.1, 118.2, 119.8 (d,  $J_{\text{C,F}} = 6.3$  Hz), 121.2, 122.0 (d,  $J_{\text{C,F}} = 21.4$  Hz), 122.2, 123.0, 124.3, 126.9, 127.7, 133.8, 134.4, 139.1, 139.2, 142.0, 155.4, 155.7 (d,  $J_{\text{C,F}} = 242.3$  Hz), 164.0, 168.9, 175.4, 186.9, 196.4, 199.1; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{34}\text{H}_{26}\text{FNNaO}_8$   $[\text{M}+\text{Na}]^+$ : 618.1535; Found: 618.1536.



**3t:** Light yellow solid, m.p. 232.2-233.7 °C, yield 74%, >20:1 *dr*;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.84 (s, 9H), 2.80 (s, 3H), 3.85 (s, 3H), 4.14 (d,  $J = 14.4$  Hz, 1H), 4.47 (s, 1H), 5.71 (d,  $J = 14.4$  Hz, 1H), 6.89-6.95 (m, 2H), 7.13-7.18 (m, 1H), 7.26-7.31 (m, 1H), 7.54 (s, 1H), 7.90-7.98 (m, 2H), 8.09-8.13 (m, 2H), 8.24 (d,  $J = 8.8$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 24.6, 25.1, 53.7, 53.9, 54.0, 57.5, 81.2, 85.3, 108.1, 110.3 (d,  $J_{\text{C,F}} = 23.2$  Hz), 112.9, 115.4, 117.8 (d,  $J_{\text{C,F}} = 7.2$  Hz), 119.6, 121.0, 121.8 (d,  $J_{\text{C,F}} = 24.3$  Hz), 121.9, 127.9, 132.2, 133.6, 134.2, 138.9, 141.8, 155.1, 155.5 (d,  $J_{\text{C,F}} = 242.2$  Hz), 156.0, 163.8, 168.3, 175.1, 186.6, 196.2, 198.7; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{35}\text{H}_{28}\text{FNNaO}_9$   $[\text{M}+\text{Na}]^+$ : 648.1640; Found: 648.1640.

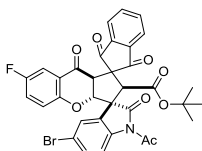


**3u:** Light yellow solid, m.p. 268.2-269.7 °C, yield 64%, >20:1 *dr*;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.82 (s, 9H), 2.39 (s, 3H), 2.80 (s, 3H), 4.16 (d,  $J = 14.0$  Hz, 1H), 4.45 (s, 1H), 5.73 (d,  $J = 14.4$  Hz, 1H), 6.88-6.91 (m, 1H), 7.12-7.17 (m, 1H), 7.21-7.23 (m, 1H), 7.23-7.30 (m, 1H), 7.65 (s, 1H), 7.90-7.98 (m, 2H), 8.09-8.14 (m, 2H), 8.19 (d,  $J = 8.4$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 20.3, 25.7, 26.0, 54.5, 54.6, 54.9, 58.5, 82.2, 86.2, 111.3 (d,  $J_{\text{C,F}} = 24.4$  Hz), 115.1, 118.8, 118.9, 120.6 (d,  $J_{\text{C,F}} = 7.5$  Hz), 122.0, 122.7 (d,  $J_{\text{C,F}} = 24.2$  Hz), 122.9, 124.1, 127.5, 128.8, 134.5, 134.9, 135.2, 137.5, 139.9, 142.8, 156.2, 156.7 (d,  $J_{\text{C,F}} = 243.3$  Hz), 164.9, 169.5, 176.4, 187.7, 197.3, 199.7; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{35}\text{H}_{28}\text{FNNaO}_8$   $[\text{M}+\text{Na}]^+$ : 632.1691; Found: 632.1694.

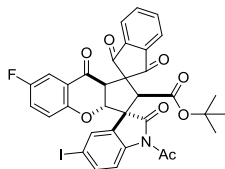


**3v:** Light yellow solid, m.p. 187.3-188.8 °C, yield 75%, >20:1 *dr*;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.85 (s, 9H), 2.81 (s, 3H), 4.14 (d,  $J = 14.0$  Hz, 1H), 4.47 (s, 1H), 5.68 (d,  $J = 14.0$  Hz, 1H), 6.89-6.92 (m, 1H), 7.10-7.19 (m, 2H), 7.28-7.31 (m, 1H), 7.68-7.71 (m, 1H), 7.92-7.99 (m, 2H), 8.10-8.13 (m, 2H), 8.31-8.34 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 25.6, 26.1, 54.6, 54.9, 58.3,

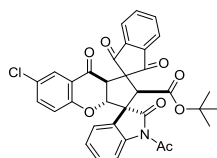
82.6, 86.1, 111.3 (d,  $J_{C,F} = 23.2$  Hz), 111.5 (d,  $J_{C,F} = 25.1$  Hz), 114.9 (d,  $J_{C,F} = 22.4$  Hz), 116.7 (d,  $J_{C,F} = 7.7$  Hz), 118.8 (d,  $J_{C,F} = 8.2$  Hz), 122.0, 122.9 (d,  $J_{C,F} = 24.1$  Hz), 123.0, 134.7, 135.2, 140.0, 142.7, 156.0, 156.4 (d,  $J_{C,F} = 243.1$  Hz), 159.5 (d,  $J_{C,F} = 244.1$  Hz), 164.5, 169.4, 175.7, 187.4, 196.9, 199.8; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $C_{34}H_{25}F_2NNaO_8$   $[M+Na]^+$ : 636.1440; Found: 636.1443.



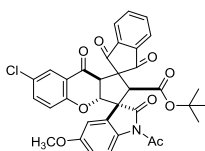
**3w**: Light yellow solid, m.p. 271.5-273.0 °C, yield 65%, >20:1 *dr*;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$ : 0.87 (s, 9H), 2.81 (s, 3H), 4.13 (d,  $J = 14.0$  Hz, 1H), 4.46 (s, 1H), 5.68 (d,  $J = 14.0$  Hz, 1H), 6.89-6.92 (m, 1H), 7.14-7.19 (m, 1H), 7.28-7.31 (m, 1H), 7.55-7.58 (m, 1H), 7.91-7.99 (m, 2H), 8.02 (d,  $J = 2.0$  Hz, 1H), 8.10-8.15 (m, 2H), 8.23 (d,  $J = 8.4$  Hz, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$ : 26.7, 27.2, 55.5, 56.0, 59.2, 83.8, 87.1, 112.3 (d,  $J_{C,F} = 23.4$  Hz), 117.9, 119.1, 119.8 (d,  $J_{C,F} = 8.1$  Hz), 123.1, 123.9, 124.0 (d,  $J_{C,F} = 24.3$  Hz), 127.9, 130.9, 132.4, 135.7, 136.2, 139.7, 141.0, 143.7, 157.0, 157.6 (d,  $J_{C,F} = 240.1$  Hz), 165.5, 170.5, 176.5, 188.4, 198.0, 200.7; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $C_{34}H_{25}BrFNNaO_8$   $[M+Na]^+$ : 696.0640; Found: 696.0645.



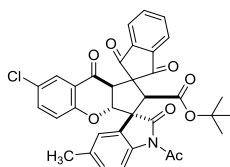
**3x**: Light yellow solid, m.p. 284.3-285.8 °C, yield 66%, >20:1 *dr*;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$ : 0.87 (s, 9H), 2.80 (s, 3H), 4.13 (d,  $J = 13.6$  Hz, 1H), 4.45 (s, 1H), 5.68 (d,  $J = 14.4$  Hz, 1H), 6.88-6.92 (m, 1H), 7.14-7.19 (m, 1H), 7.28-7.30 (m, 1H), 7.75-7.78 (m, 1H), 7.91-7.99 (m, 2H), 8.09-8.18 (m, 4H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$ : 25.7, 26.2, 54.2, 54.4, 54.9, 58.1, 82.8, 86.0, 88.7, 111.3 (d,  $J_{C,F} = 24.3$  Hz), 117.2, 118.8 (d,  $J_{C,F} = 7.5$  Hz), 122.1, 122.9, 123.0 (d,  $J_{C,F} = 25.2$  Hz), 130.1, 132.5, 134.7, 135.2, 137.4, 139.4, 140.0, 142.7, 156.0, 157.0 (d,  $J_{C,F} = 243.0$  Hz), 164.5, 169.5, 175.3, 187.3, 197.0, 199.6; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $C_{34}H_{25}FINNaO_8$   $[M+Na]^+$ : 744.0501; Found: 744.0504.



**3y:** Light yellow solid, m.p. 234.2-235.7 °C, yield 65%, >20:1 *dr*;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.80 (s, 9H), 2.82 (s, 3H), 4.15 (d,  $J = 14.0$  Hz, 1H), 4.46 (s, 1H), 5.73 (d,  $J = 14.4$  Hz, 1H), 6.88 (d,  $J = 8.8$  Hz, 1H), 7.29-7.33 (m, 1H), 7.36-7.38 (m, 1H), 7.41-7.45 (m, 1H), 7.59 (d,  $J = 2.8$  Hz, 1H), 7.89-7.98 (m, 3H), 8.09-8.13 (m, 2H), 8.32 (d,  $J = 8.0$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 25.7, 26.1, 54.5, 54.6, 54.9, 58.7, 82.3, 86.1, 115.3, 118.8, 120.9, 121.9, 122.9, 123.8, 125.1, 125.5, 126.9, 127.5, 128.5, 134.6, 135.1, 135.2, 139.8, 139.9, 142.8, 158.4, 164.7, 169.6, 176.1, 187.3, 197.1, 199.8; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{34}\text{H}_{26}\text{ClNNaO}_8$   $[\text{M}+\text{Na}]^+$ : 634.1239; Found: 634.1241.

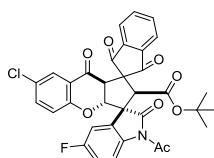


**3z:** Light yellow solid, m.p. 212.2-213.7 °C, yield 78%, >20:1 *dr*;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.84 (s, 9H), 2.79 (s, 3H), 3.84 (s, 3H), 4.13 (d,  $J = 14.0$  Hz, 1H), 4.46 (s, 1H), 5.71 (d,  $J = 14.0$  Hz, 1H), 6.88 (d,  $J = 8.8$  Hz, 1H), 6.92-6.95 (m, 1H), 7.36-7.39 (m, 1H), 7.53-7.59 (m, 2H), 7.89-7.96 (m, 2H), 8.09-8.13 (m, 2H), 8.23 (d,  $J = 8.8$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 24.8, 25.3, 53.8, 53.9, 54.0, 54.1, 57.8, 81.5, 85.4, 108.3, 113.1, 115.6, 118.1, 120.1, 121.2, 122.1, 124.8, 126.1, 128.0, 132.4, 133.8, 134.3, 134.4, 139.1, 142.0, 156.2, 157.6, 164.0, 168.5, 175.3, 186.5, 196.3, 198.9; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{35}\text{H}_{28}\text{ClNNaO}_9$   $[\text{M}+\text{Na}]^+$ : 664.1345; Found: 664.1346.

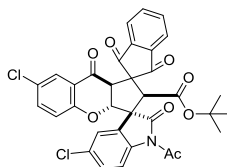


**3za:** Light yellow solid, m.p. 245.5-247.0 °C, yield 73%, >20:1 *dr*;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.82 (s, 9H), 2.39 (s, 3H), 2.80 (s, 3H), 4.16 (d,  $J = 14.0$  Hz, 1H), 4.45 (s, 1H), 5.72 (d,  $J = 14.0$  Hz, 1H), 6.87 (d,  $J = 8.8$  Hz, 1H), 7.21-7.23 (m, 1H), 7.35-7.38 (m, 1H), 7.59-7.65 (m, 2H),

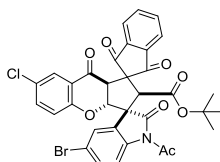
7.89-7.98 (m, 2H), 8.09-8.14 (m, 2H), 8.19 (d,  $J = 8.4$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 19.9, 25.3, 25.7, 54.1, 54.2, 54.5, 58.2, 81.8, 85.7, 114.7, 118.5, 120.5, 121.6, 122.5, 123.7, 125.2, 126.5, 127.1, 128.5, 134.2, 134.5, 134.7, 134.8, 137.0, 139.5, 142.5, 158.1, 164.5, 169.1, 176.0, 187.0, 196.9, 199.3; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{35}\text{H}_{28}\text{ClNNaO}_8$   $[\text{M}+\text{Na}]^+$ : 648.1396; Found: 648.1392.



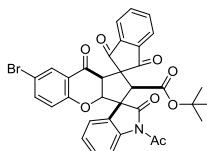
**3zb**: Light yellow solid, m.p. 241.0-242.5 °C, yield 74%, >20:1 *dr*;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.85 (s, 9H), 2.80 (s, 3H), 4.13 (d,  $J = 14.0$  Hz, 1H), 4.47 (s, 1H), 5.68 (d,  $J = 14.0$  Hz, 1H), 6.88 (d,  $J = 8.8$  Hz, 1H), 7.10-7.15 (m, 1H), 7.37-7.40 (m, 1H), 7.59 (d,  $J = 2.8$  Hz, 1H), 7.68-7.71 (m, 1H), 7.91-7.99 (m, 2H), 8.10-8.13 (m, 2H), 8.31-8.34 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 25.1, 25.6, 53.9, 54.1, 54.4, 57.7, 82.1, 85.4, 110.8 (d,  $J_{\text{C,F}} = 26.1$  Hz), 114.4 (d,  $J_{\text{C,F}} = 23.3$  Hz), 116.1 (d,  $J_{\text{C,F}} = 8.2$  Hz), 118.2, 120.3, 121.5, 122.4, 125.0, 126.5, 134.2, 134.7, 135.2, 139.5, 142.1, 157.7, 159.2 (d,  $J_{\text{C,F}} = 244.2$  Hz), 163.9, 168.8, 169.6, 175.2, 186.5, 196.3, 199.2; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{34}\text{H}_{25}\text{ClFNNaO}_8$   $[\text{M}+\text{Na}]^+$ : 652.1145; Found: 652.1145.



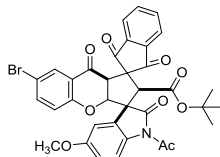
**3zc**: Light yellow solid, m.p. 231.5-233.0 °C, yield 67%, >20:1 *dr*;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.86 (s, 9H), 2.80 (s, 3H), 4.14 (d,  $J = 14.0$  Hz, 1H), 4.46 (s, 1H), 5.68 (d,  $J = 14.0$  Hz, 1H), 6.88 (d,  $J = 8.8$  Hz, 1H), 7.37-7.41 (m, 2H), 7.59 (d,  $J = 2.8$  Hz, 1H), 7.88 (d,  $J = 2.4$  Hz, 1H), 7.91-7.99 (m, 2H), 8.10-8.14 (m, 2H), 8.28 (d,  $J = 8.8$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 25.2, 25.7, 53.9, 54.0, 54.5, 57.7, 82.3, 85.5, 116.1, 118.3, 120.4, 121.6, 122.5, 123.6, 125.2, 126.7, 128.1, 129.0, 130.2, 134.3, 134.8, 137.8, 139.6, 142.3, 157.8, 164.1, 169.0, 175.1, 186.6, 196.4, 199.2; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{34}\text{H}_{25}\text{Cl}_2\text{NNaO}_8$   $[\text{M}+\text{Na}]^+$ : 668.0849; Found: 668.0852.



**3zd:** Light yellow solid, m.p. 211.4-212.9 °C, yield 65%, >20:1 *dr*; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 0.87 (s, 9H), 2.80 (s, 3H), 4.16 (d, *J* = 14.0 Hz, 1H), 4.45 (s, 1H), 5.68 (d, *J* = 14.0 Hz, 1H), 6.88 (d, *J* = 9.2 Hz, 1H), 7.37-7.40 (m, 1H), 7.55-7.59 (m, 2H), 7.91-7.99 (m, 2H), 8.02 (s, 1H), 8.10-8.15 (m, 2H), 8.22 (d, *J* = 8.8 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 25.7, 26.1, 54.4, 54.5, 54.9, 58.1, 82.8, 85.9, 116.9, 118.1, 118.8, 120.8, 122.1, 122.9, 125.6, 126.8, 127.1, 129.8, 131.4, 134.7, 135.2, 138.7, 140.0, 142.7, 158.2, 164.5, 169.4, 175.4, 187.0, 196.9, 199.6; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>34</sub>H<sub>25</sub>BrClNaO<sub>8</sub> [M+Na]<sup>+</sup>: 712.0344; Found: 712.0342.

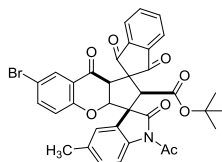


**3ze:** Light yellow solid, m.p. 233.3-234.8 °C, yield 65%, >20:1 *dr*; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 0.80 (s, 9H), 2.82 (s, 3H), 4.15 (d, *J* = 14.0 Hz, 1H), 4.46 (s, 1H), 5.73 (d, *J* = 14.0 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 7.29-7.33 (m, 1H), 7.41-7.45 (m, 1H), 7.49-7.52 (m, 1H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.89-7.98 (m, 3H), 8.09-8.12 (m, 2H), 8.32 (d, *J* = 8.0 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 25.7, 26.1, 54.4, 54.5, 54.9, 58.7, 82.3, 86.1, 114.0, 115.3, 119.2, 121.3, 121.9, 122.9, 123.8, 125.1, 127.5, 128.5, 128.7, 134.6, 135.2, 137.9, 139.8, 139.9, 142.8, 158.9, 164.7, 169.6, 176.1, 187.2, 197.1, 199.8; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>34</sub>H<sub>26</sub>BrNNaO<sub>8</sub> [M+Na]<sup>+</sup>: 678.0734; Found: 678.0732.

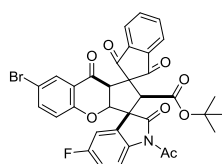


**3zf:** Light yellow solid, m.p. 239.9-241.4 °C, yield 68%, >20:1 *dr*; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 0.84 (s, 9H), 2.79 (s, 3H), 3.84 (s, 3H), 4.12 (d, *J* = 14.4 Hz, 1H), 4.46 (s, 1H), 5.70 (d, *J* = 14.4 Hz, 1H), 6.82 (d, *J* = 9.2 Hz, 1H), 6.92-6.95 (m, 1H), 7.49-7.54 (m, 2H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.89-7.97 (m, 2H), 8.09-8.12 (m, 1H), 8.23 (d, *J* = 8.8 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 25.6, 26.1, 54.5, 54.7, 54.8, 54.9, 58.5, 82.2, 86.1, 109.0, 113.9, 114.0, 116.4, 119.2, 121.3, 122.0,

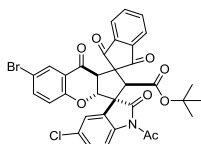
122.9, 128.7, 128.8, 133.2, 134.6, 135.2, 137.9, 139.9, 142.8, 157.0, 158.9, 164.8, 169.3, 176.1, 187.2, 197.1, 199.6; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $C_{35}H_{28}BrNNaO_9$   $[M+Na]^+$ : 708.0840; Found: 708.0842.



**3zg**: Light yellow solid, m.p. 263.0-264.5 °C, yield 67%, >20:1 *dr*;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$ : 0.81 (s, 9H), 2.39 (s, 3H), 2.80 (s, 3H), 4.15 (d,  $J = 14.0$  Hz, 1H), 4.45 (s, 1H), 5.73 (d,  $J = 14.0$  Hz, 1H), 6.81 (d,  $J = 8.8$  Hz, 1H), 7.21-7.23 (m, 1H), 7.48-7.51 (m, 1H), 7.65 (s, 1H), 7.74 (d,  $J = 2.8$  Hz, 1H), 7.90-7.98 (m, 2H), 8.09-8.14 (m, 2H), 8.19 (d,  $J = 8.4$  Hz, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$ : 20.3, 25.7, 26.0, 54.3, 54.6, 54.9, 58.5, 82.2, 86.1, 114.0, 115.1, 119.2, 121.3, 122.0, 122.9, 124.1, 127.4, 128.6, 128.9, 134.5, 134.9, 135.2, 137.5, 137.9, 139.9, 142.8, 158.9, 164.8, 169.5, 176.3, 187.3, 197.2, 199.6; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $C_{35}H_{28}BrNNaO_8$   $[M+Na]^+$ : 692.0891; Found: 692.0895.

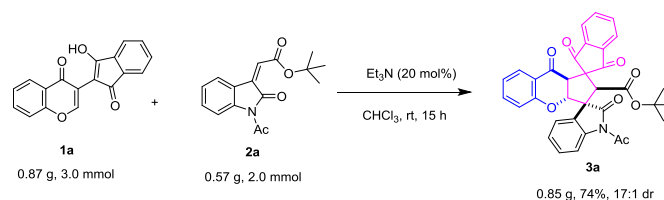


**3zh**: Light yellow solid, m.p. 176.9-178.4 °C, yield 66%, >20:1 *dr*;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$ : 0.85 (s, 9H), 2.80 (s, 3H), 4.13 (d,  $J = 14.0$  Hz, 1H), 4.46 (s, 1H), 5.67 (d,  $J = 14.4$  Hz, 1H), 6.83 (d,  $J = 9.2$  Hz, 1H), 7.10-7.15 (m, 1H), 7.50-7.53 (m, 1H), 7.68-7.71 (m, 1H), 7.74 (d,  $J = 2.4$  Hz, 1H), 7.92-7.99 (m, 2H), 8.10-8.13 (m, 2H), 8.30-8.34 (m, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$ : 25.6, 26.1, 54.4, 54.6, 54.9, 58.3, 82.6, 85.9, 111.5 (d,  $J_{C,F} = 25.3$  Hz), 114.2, 115.0 (d,  $J_{C,F} = 23.4$  Hz), 116.7 (d,  $J_{C,F} = 8.3$  Hz), 119.1, 121.3, 122.0, 122.9, 128.7, 129.5 (d,  $J_{C,F} = 8.4$  Hz), 134.7, 135.2, 135.8, 138.0, 140.0, 142.7, 158.7, 159.7 (d,  $J_{C,F} = 245.2$  Hz), 164.5, 169.4, 175.7, 187.0, 196.8, 199.7; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $C_{34}H_{25}BrFNNaO_8$   $[M+Na]^+$ : 696.0640; Found: 696.0645.



**3zi**: Light yellow solid, m.p. 213.3-214.8 °C, yield 65%, >20:1 *dr*; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 0.86 (s, 9H), 2.80 (s, 3H), 4.13 (d, *J* = 14.0 Hz, 1H), 4.45 (s, 1H), 5.69 (d, *J* = 14.0 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 7.39-7.42 (m, 1H), 7.50-7.53 (m, 1H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.89 (d, *J* = 2.4 Hz, 1H), 7.91-7.99 (m, 2H), 8.10-8.14 (m, 2H), 8.28 (d, *J* = 8.8 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 25.7, 26.1, 54.3, 54.5, 54.9, 58.1, 82.7, 85.9, 114.2, 116.5, 119.1, 121.3, 122.1, 122.9, 124.0, 128.5, 128.7, 129.4, 130.6, 134.7, 135.2, 138.0, 138.2, 140.0, 142.7, 158.7, 164.5, 169.4, 175.5, 186.9, 196.8, 199.6; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>34</sub>H<sub>25</sub>BrCINNaO<sub>8</sub> [M+Na]<sup>+</sup>: 712.0344; Found: 712.0343.

#### 4. Gram scale synthesis of the product 3a



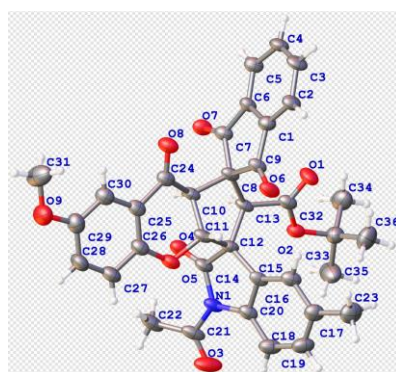
Compound **1a** (0.87 g, 3.0 mmol) and compound **2a** (0.57 g, 2.0 mmol) were dissolved in CHCl<sub>3</sub> (12 mL). Et<sub>3</sub>N (20 mol%, 0.04 mmol) was added to this solution at room temperature, and the mixture was stirred for 15 h. After the removal of solvent, purification by flash column chromatography (hexane/ethyl acetate = 8:1~5:1) was carried out to give product **3a** as a light yellow solid (0.85 g, 74%, 17:1 dr).

#### 5. General experimental procedures for in vitro cytotoxicity assay

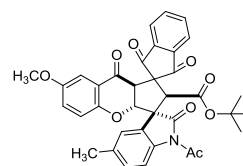
The human cancer cell line, K562 was purchased from Chinese Academy of Sciences. All the cells were cultured in RPMI-1640 medium (GIBICO, USA), supplemented with 10% fetal bovine serum (Hyclone, USA) and Penicillin-Streptomycin (respectively 100 U/mL) in 5% CO<sub>2</sub> at 37 °C. The cytotoxicity assay was performed according to the MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide) method in 96-well microplates. Briefly, 5000 cells were seeded into each well of 96-well cell culture plates and allowed to grow for 24 h before drug addition. The K562 tumor cell line was exposed to test compounds **3** at the concentrations of 3, 7, 15, 30, and 60 μmol·L<sup>-1</sup> in triplicates for 48 h, comparable to cisplatin (Aladdin, China). Then the MTT reagent was added to reaction with the cancer cells for 4 hours. At least, measure the OD value at 490 wavelengths. IC<sub>50</sub> of all the compounds were calculated by IBM SPSS Statistics (version 19).



## 6. X-Ray Crystal Data for Compounds 3j and 3p



3j

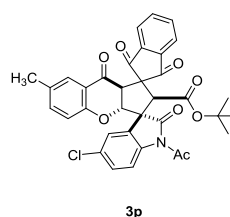
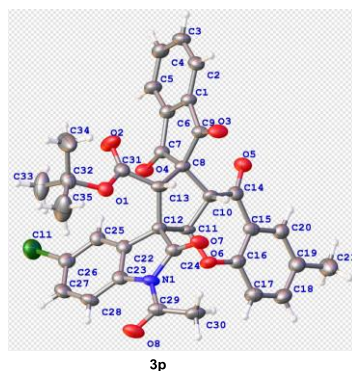


3j

**Table S1 Crystal data and structure refinement for 3j**

Identification code	<b>3j</b>
Empirical formula	C <sub>36</sub> H <sub>31</sub> NO <sub>9</sub>
Formula weight	621.62
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å, b/Å, c/Å	18.9979(8), 13.7617(4), 25.5949(16)
α/°, β/°, γ/°	90, 104.624(6), 90.
Volume/Å <sup>3</sup>	6474.8(6)
Z	8
ρ <sub>calc</sub> /cm <sup>3</sup>	1.275
μ/mm <sup>-1</sup>	0.762
F(000)	2608.0
Radiation	Cu Kα (λ = 1.54184)
Crystal size/mm <sup>3</sup>	0.13 × 0.12 × 0.11
2θ range for data collection/°	7.138 to 133.19
Index ranges	-22 ≤ h ≤ 19, -15 ≤ k ≤ 16, -26 ≤ l ≤ 30
Reflections collected	24364
Independent reflections	11434 [R <sub>int</sub> = 0.0608, R <sub>sigma</sub> = 0.0708]
Data/restraints/parameters	11434/0/841
Goodness-of-fit on F <sup>2</sup>	1.039
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0926, wR <sub>2</sub> = 0.2345
Final R indexes [all data]	R <sub>1</sub> = 0.1194, wR <sub>2</sub> = 0.2529
Largest diff. peak/hole / e Å <sup>-3</sup>	0.38/-0.38

**Crystal Data** for C<sub>36</sub>H<sub>31</sub>NO<sub>9</sub> (*M* = 621.62 g/mol): monoclinic, space group P2<sub>1</sub>/c (no. 14), *a* = 18.9979(8) Å, *b* = 13.7617(4) Å, *c* = 25.5949(16) Å, β = 104.624(6)°, *V* = 6474.8(6) Å<sup>3</sup>, *Z* = 8, *T* = 149.99(10) K, μ(Cu Kα) = 0.762 mm<sup>-1</sup>, *D*<sub>calc</sub> = 1.275 g/cm<sup>3</sup>, 24364 reflections measured (7.138° ≤ 2θ ≤ 133.19°), 11434 unique (*R*<sub>int</sub> = 0.0608, *R*<sub>sigma</sub> = 0.0708) which were used in all calculations. The final *R*<sub>1</sub> was 0.0926 (*I* > 2σ(*I*)) and *wR*<sub>2</sub> was 0.2529 (all data).



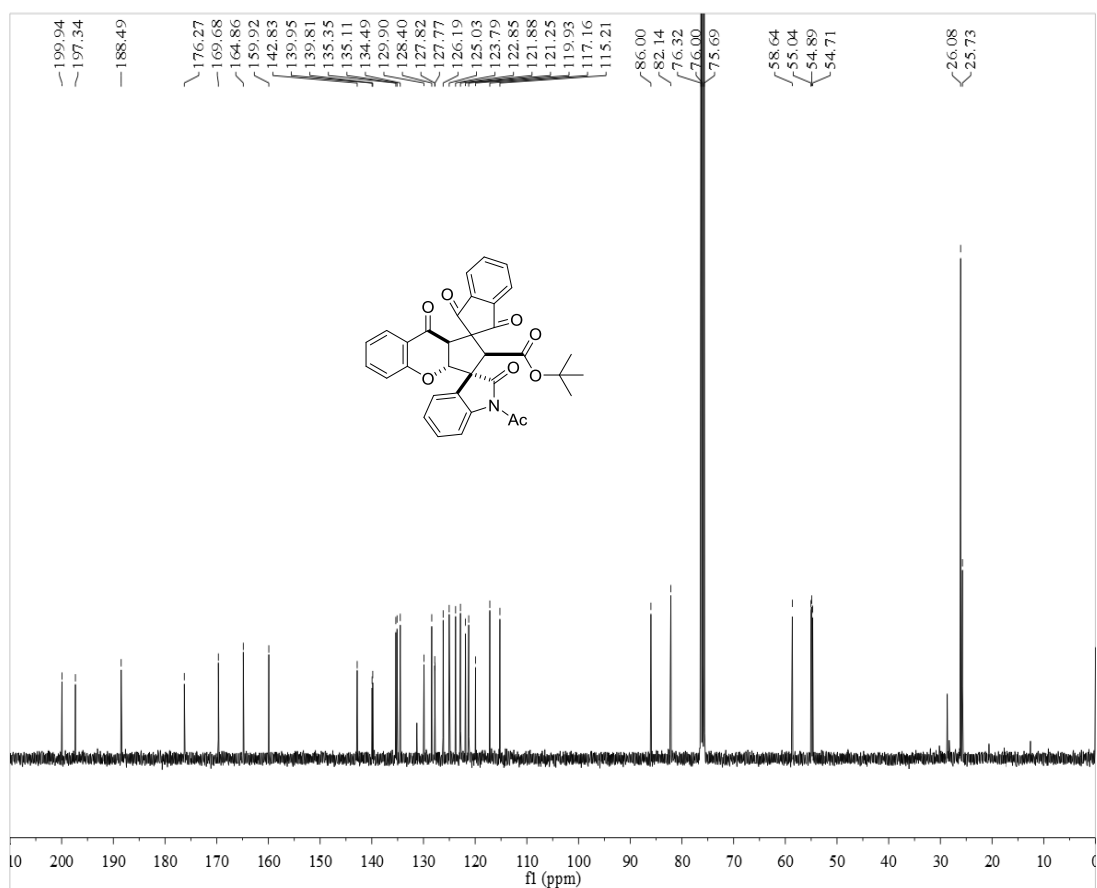
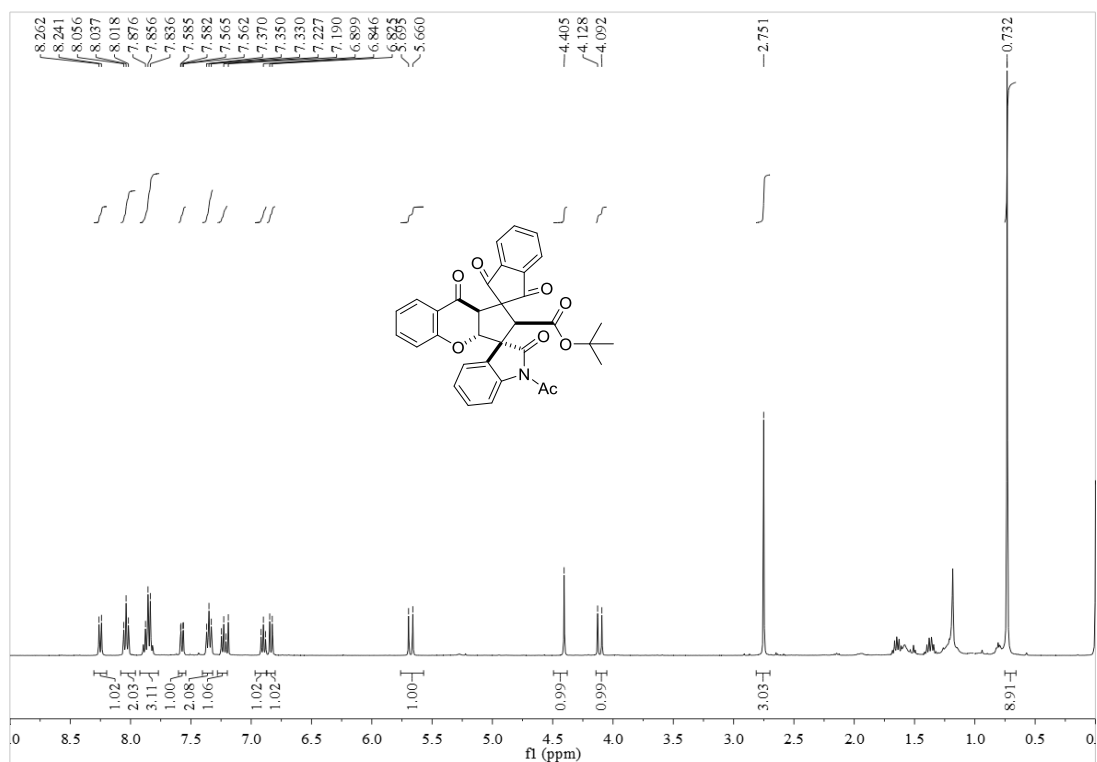
**Table S2 Crystal data and structure refinement for 3p**

Identification code	<b>3p</b>
Empirical formula	$C_{35}H_{28}ClNO_8$
Formula weight	626.03
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	I2/a
$a/\text{\AA}$ , $b/\text{\AA}$ , $c/\text{\AA}$	24.279(3), 13.6963(9), 19.1934(11)
$\alpha/^\circ$ , $\beta/^\circ$ , $\gamma/^\circ$ ,	90, 97.378(8), 90.
Volume/ $\text{\AA}^3$	6329.6(10)
Z	8
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.314
$\mu/\text{mm}^{-1}$	1.518
F(000)	2608.0
Radiation	Cu K $\alpha$ ( $\lambda = 1.54184$ )
Crystal size/ $\text{mm}^3$	0.13 $\times$ 0.12 $\times$ 0.09
2 $\theta$ range for data collection/ $^\circ$	7.342 to 133.15
Index ranges	-27 $\leq h \leq 28$ , -16 $\leq k \leq 14$ , -16 $\leq l \leq 22$
Reflections collected	11953
Independent reflections	5586 [ $R_{\text{int}} = 0.0364$ , $R_{\text{sigma}} = 0.0482$ ]
Data/restraints/parameters	5586/0/411
Goodness-of-fit on $F^2$	1.081
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0926$ , $wR_2 = 0.2966$
Final R indexes [all data]	$R_1 = 0.1089$ , $wR_2 = 0.3112$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.55/-0.46

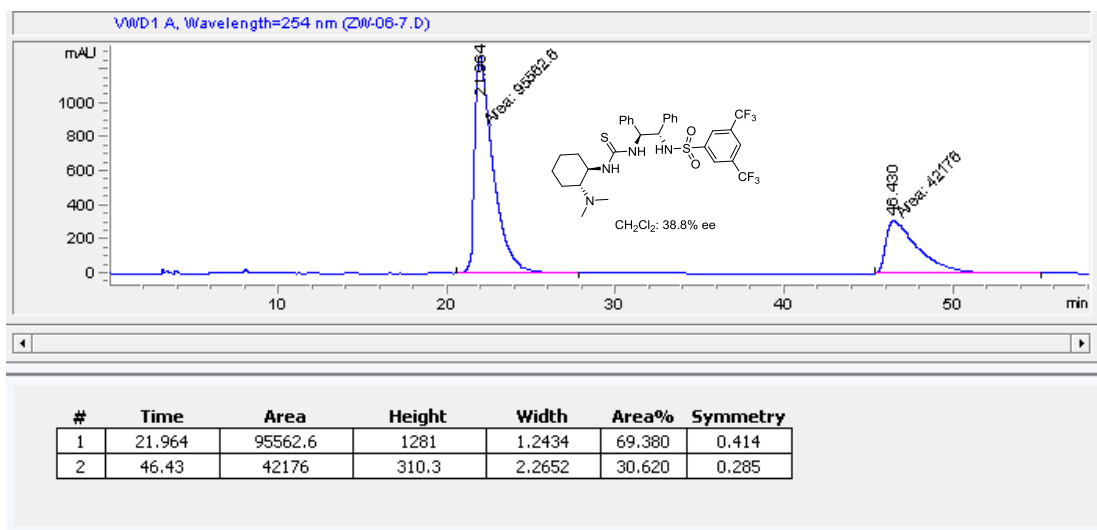
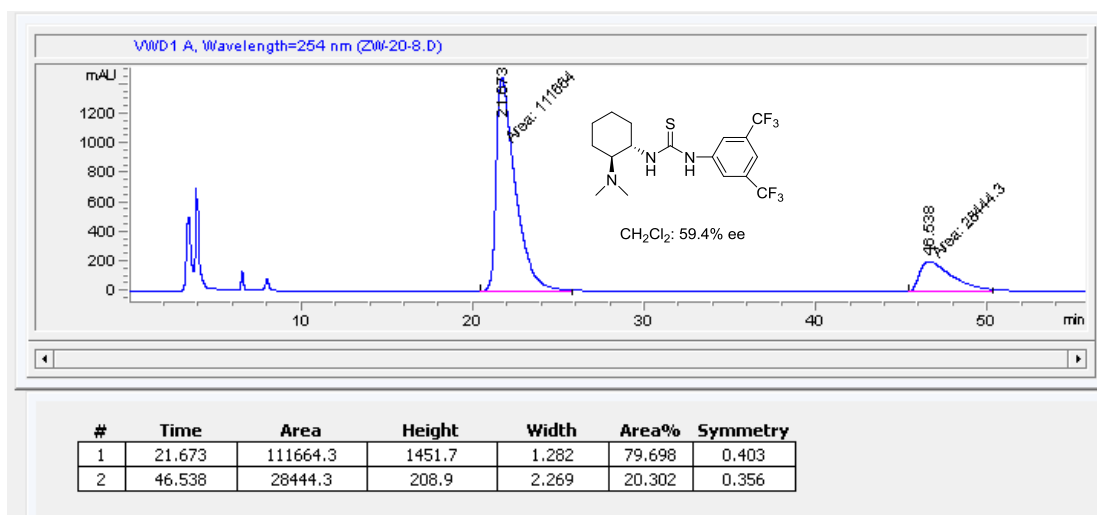
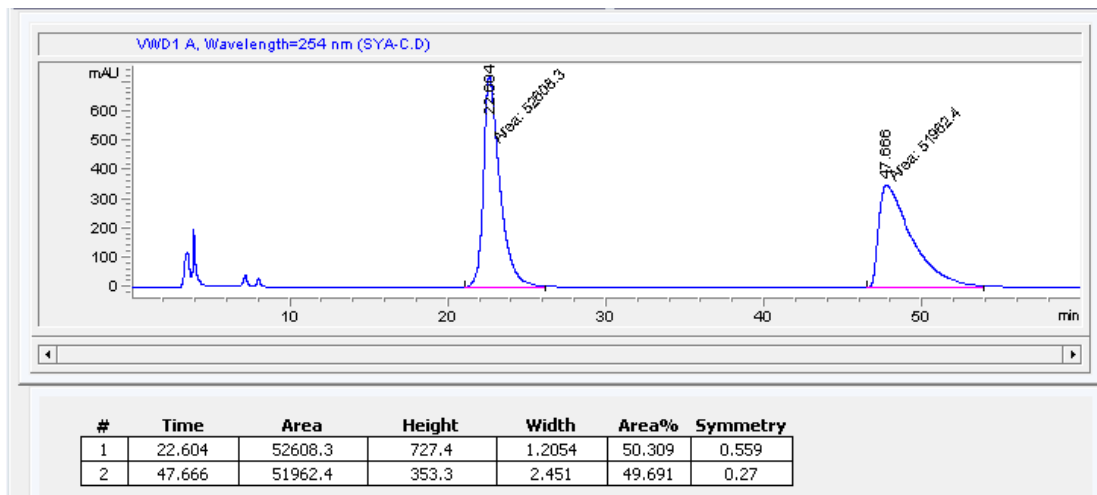
**Crystal Data** for  $C_{35}H_{28}ClNO_8$  ( $M = 626.03$  g/mol): monoclinic, space group I2/a (no. 15),  $a = 24.279(3)$   $\text{\AA}$ ,  $b = 13.6963(9)$   $\text{\AA}$ ,  $c = 19.1934(11)$   $\text{\AA}$ ,  $\beta = 97.378(8)^\circ$ ,  $V = 6329.6(10)$   $\text{\AA}^3$ ,  $Z = 8$ ,  $T = 149.99(10)$  K,  $\mu(\text{Cu K}\alpha) = 1.518$   $\text{mm}^{-1}$ ,  $D_{\text{calc}} = 1.314$   $\text{g cm}^{-3}$ , 11953 reflections measured ( $7.342^\circ \leq 2\theta \leq 133.15^\circ$ ), 5586 unique ( $R_{\text{int}} = 0.0364$ ,  $R_{\text{sigma}} = 0.0482$ ) which were used in all calculations. The final  $R_1$  was 0.0926 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.3112 (all data).

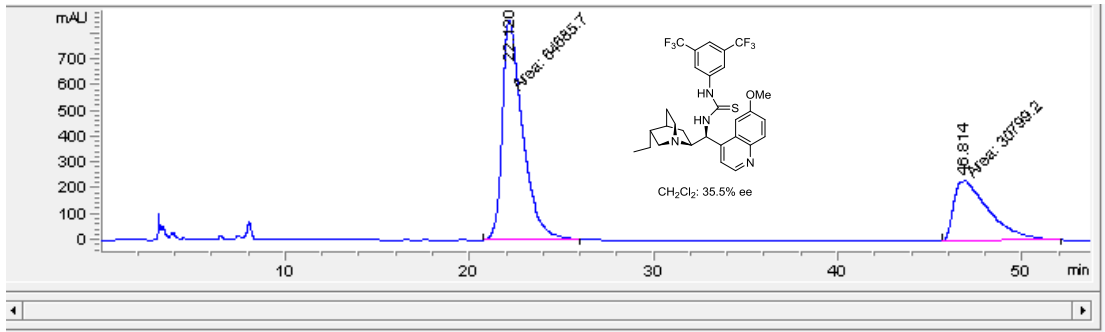
## 7. The Copies of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra for compounds 3

### $^1\text{H}$ and $^{13}\text{C}$ NMR of 3a

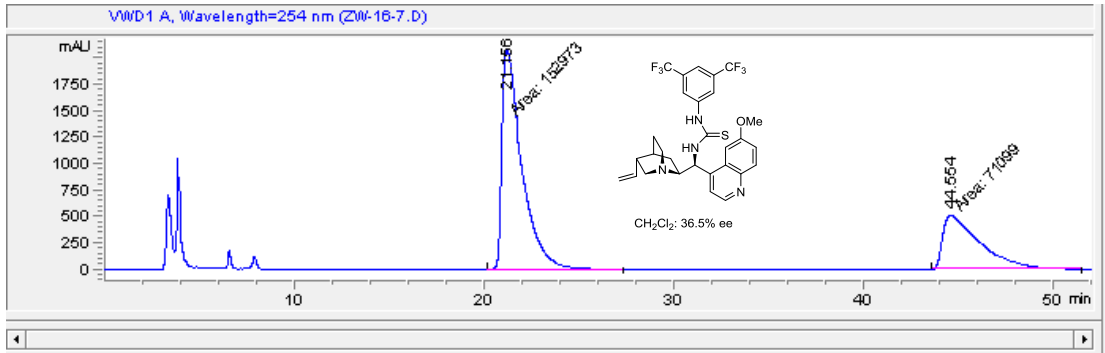


### HPLC of 3a

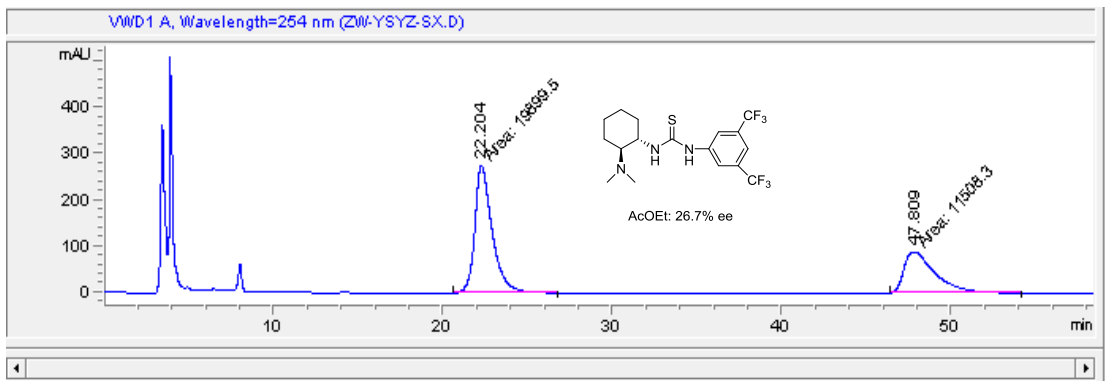




#	Time	Area	Height	Width	Area%	Symmetry
1	22.12	64685.7	852.8	1.2642	67.744	0.492
2	46.814	30799.2	232.3	2.21	32.256	0.385



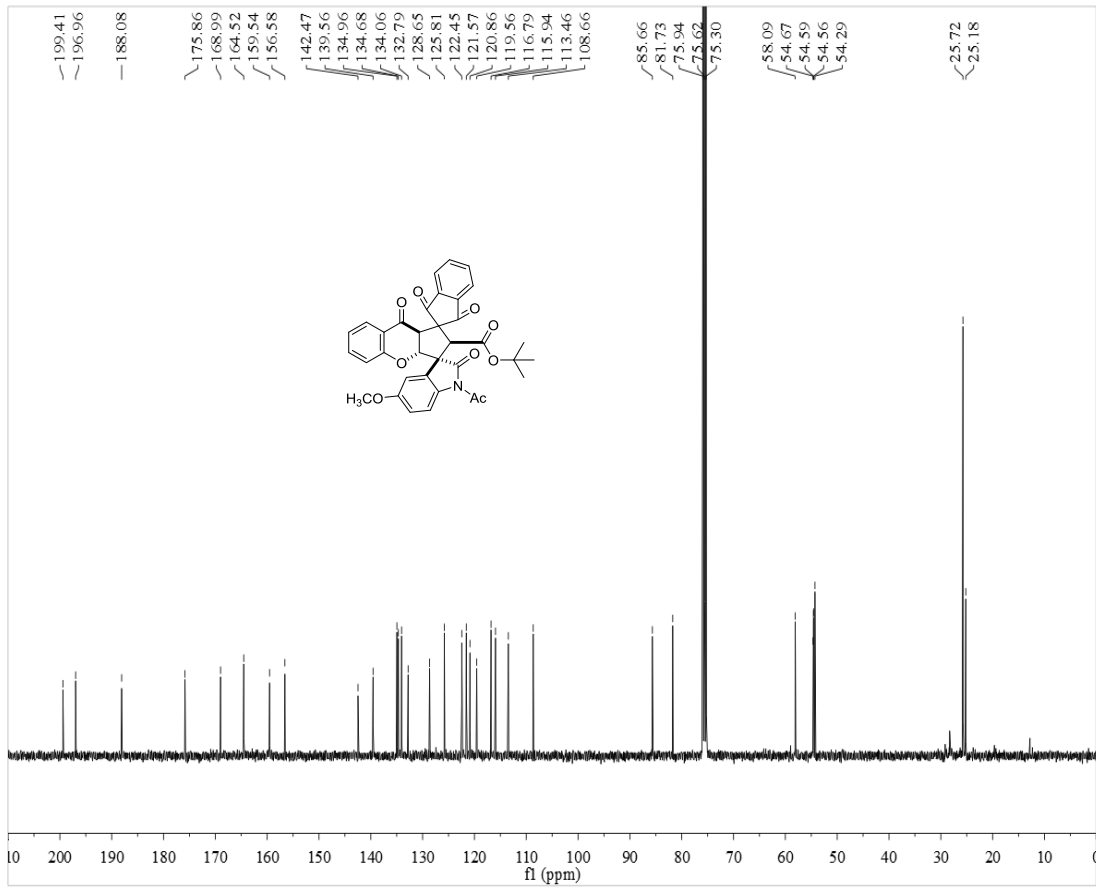
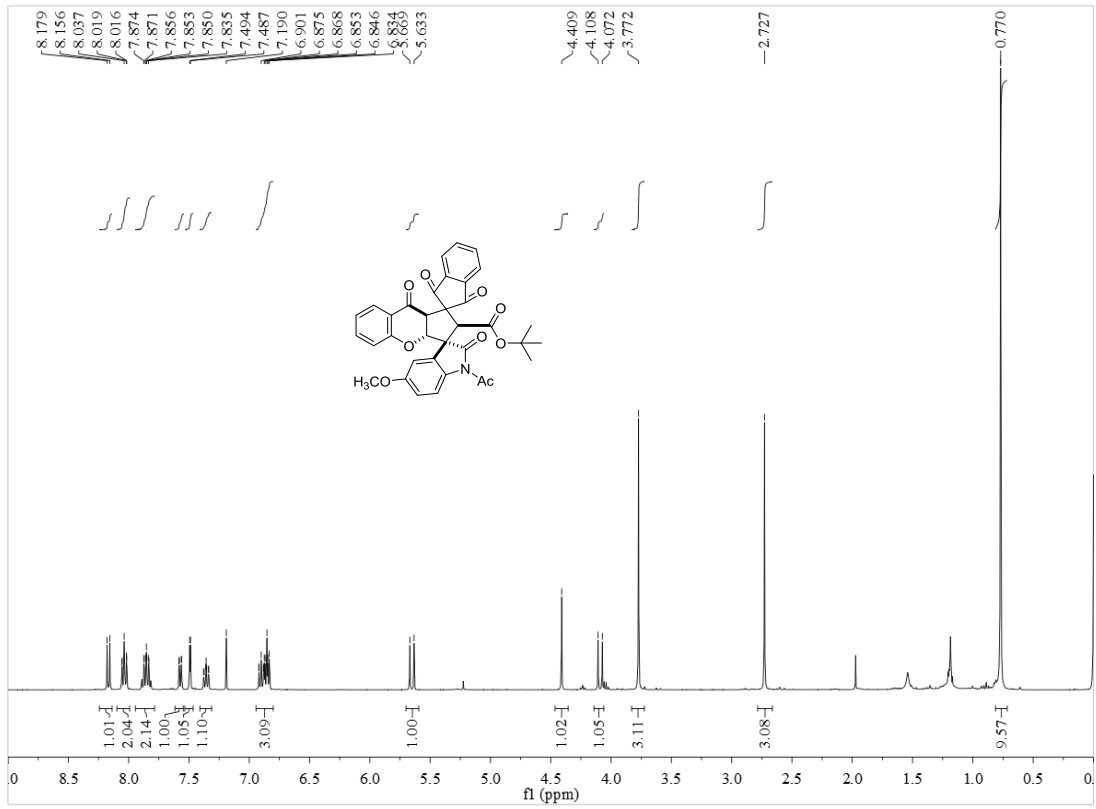
#	Time	Area	Height	Width	Area%	Symmetry
1	21.156	152972.6	2088.1	1.221	68.270	0.303
2	44.554	71099	509.8	2.3242	31.730	0.286



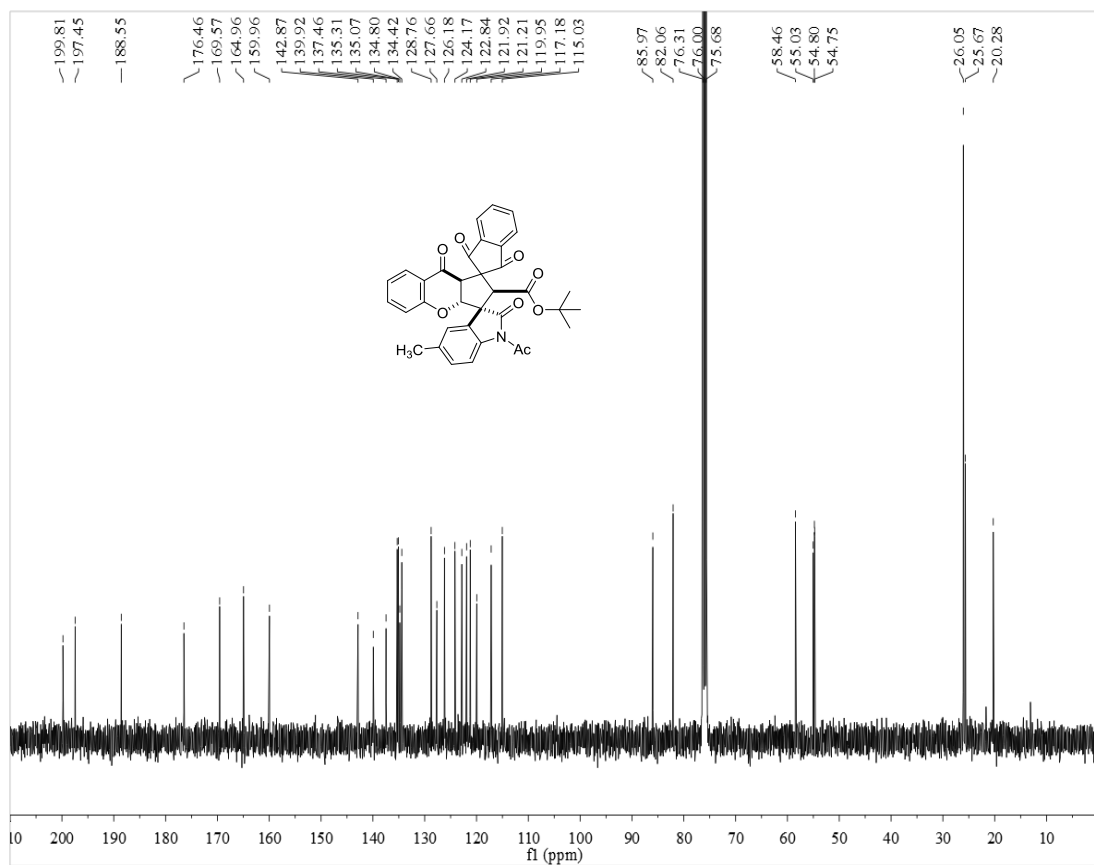
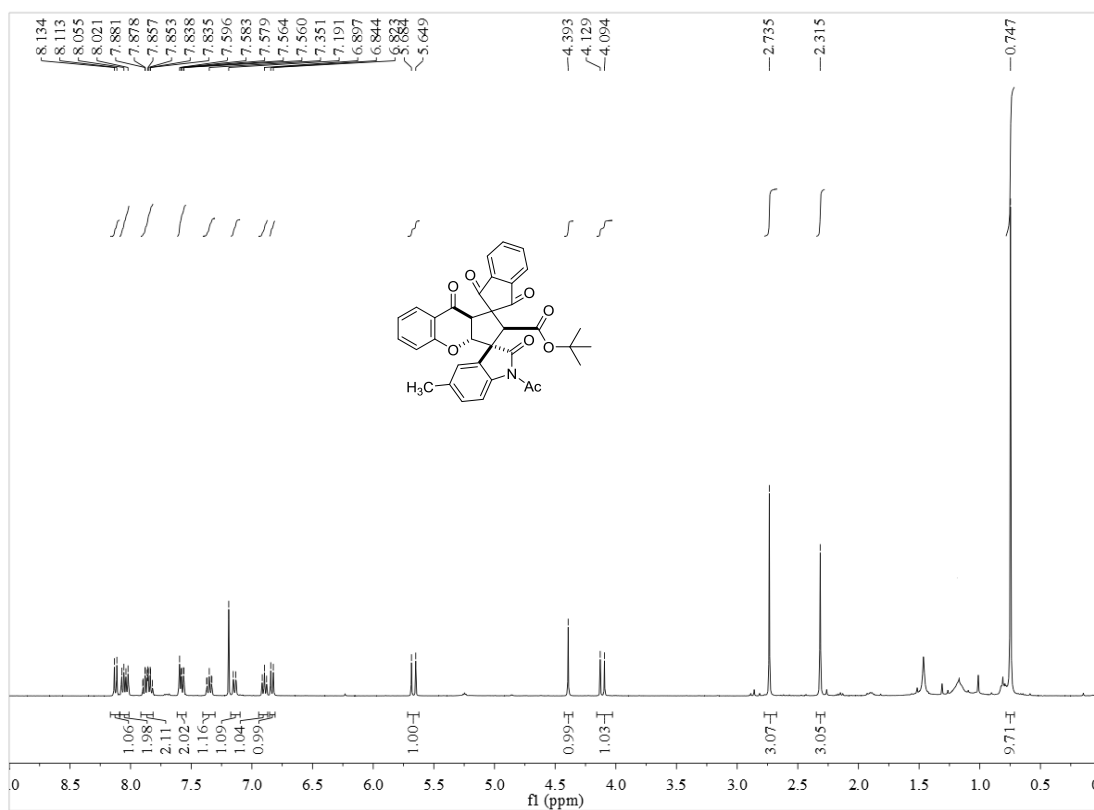
#	Time	Area	Height	Width	Area%	Symmetry
1	22.204	19899.5	276.4	1.2	63.358	0.593
2	47.809	11508.3	89.1	2.153	36.642	0.446



# <sup>1</sup>H and <sup>13</sup>C NMR of 3b

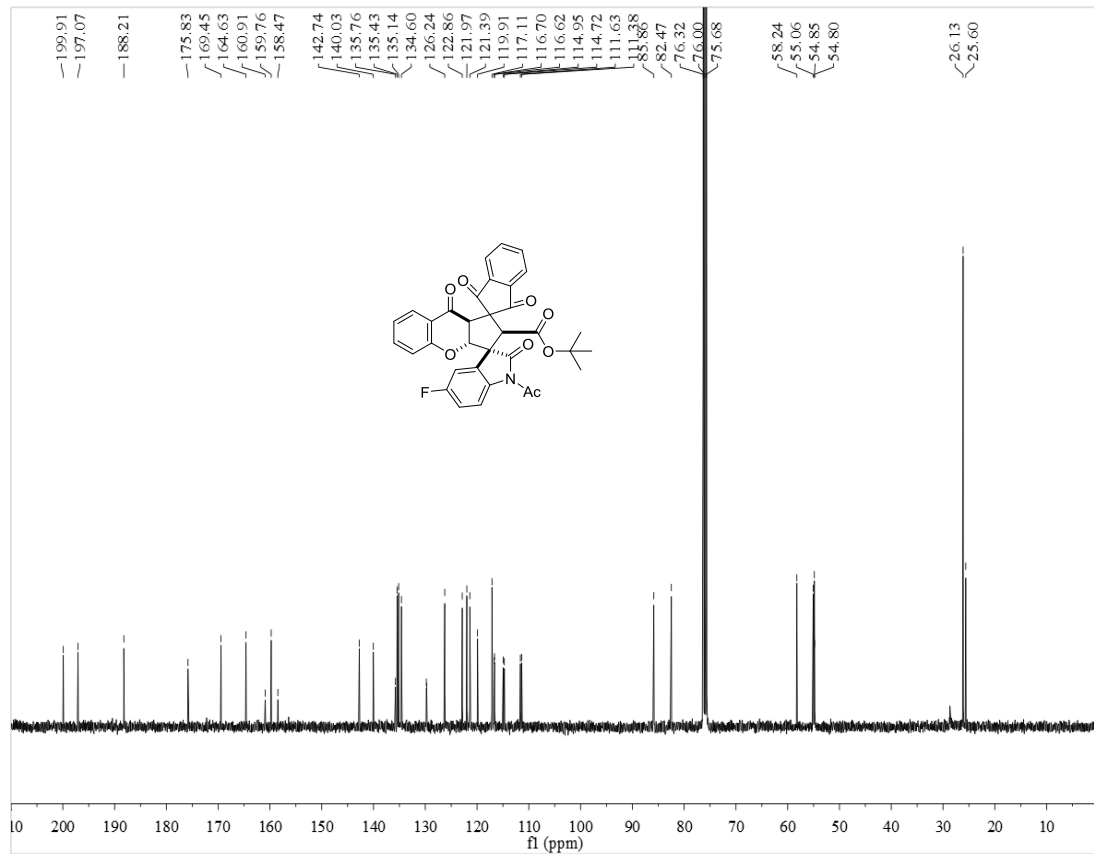
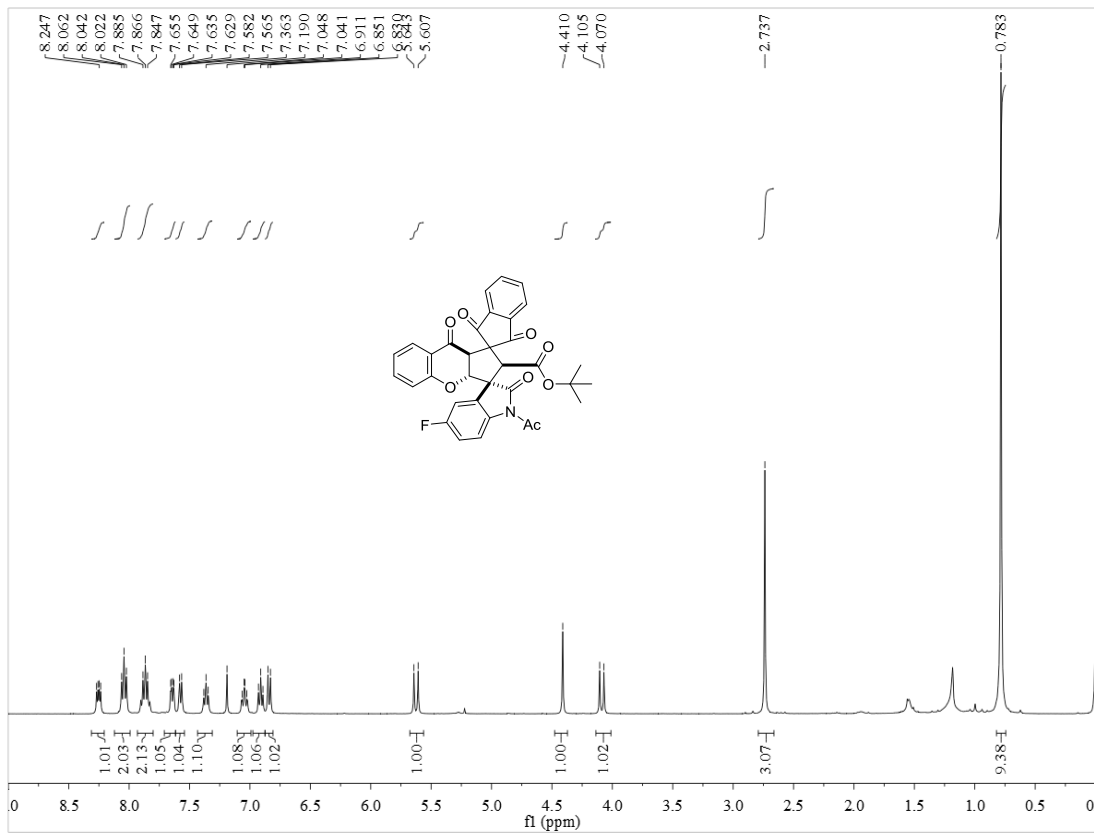


# <sup>1</sup>H and <sup>13</sup>C NMR of 3c

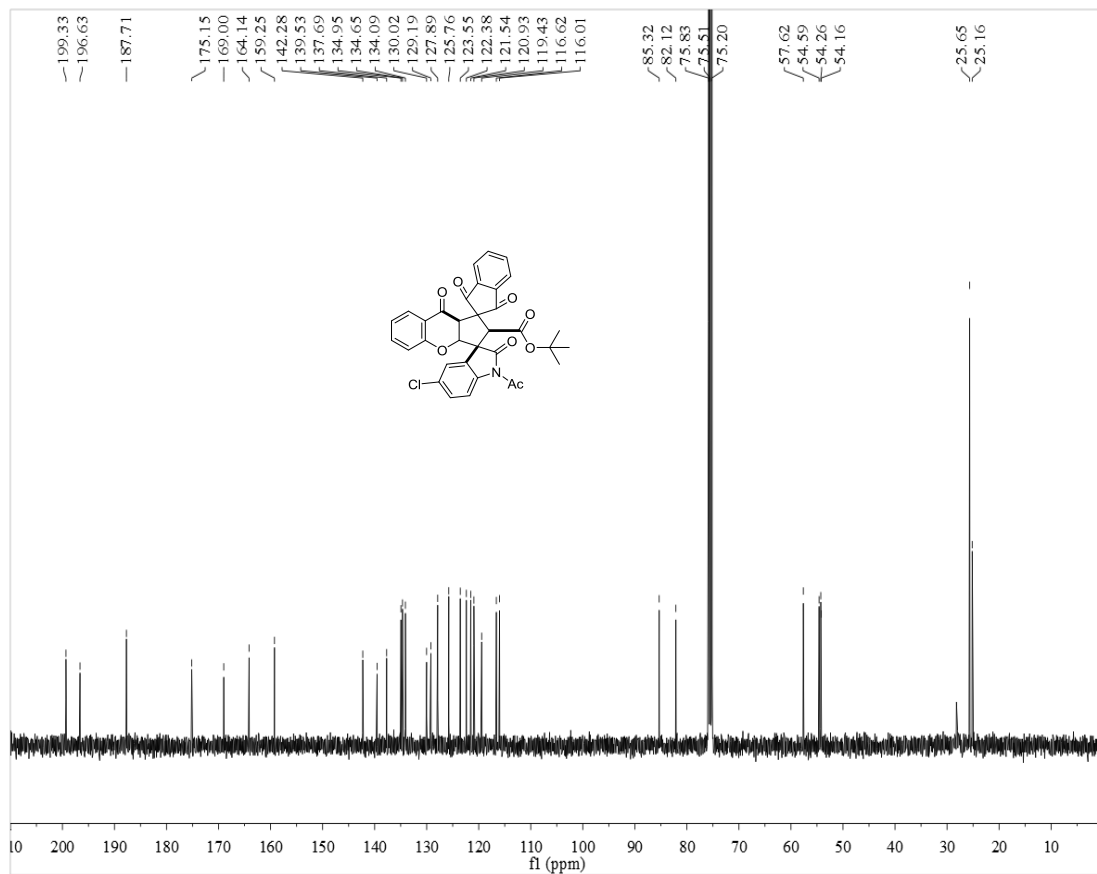
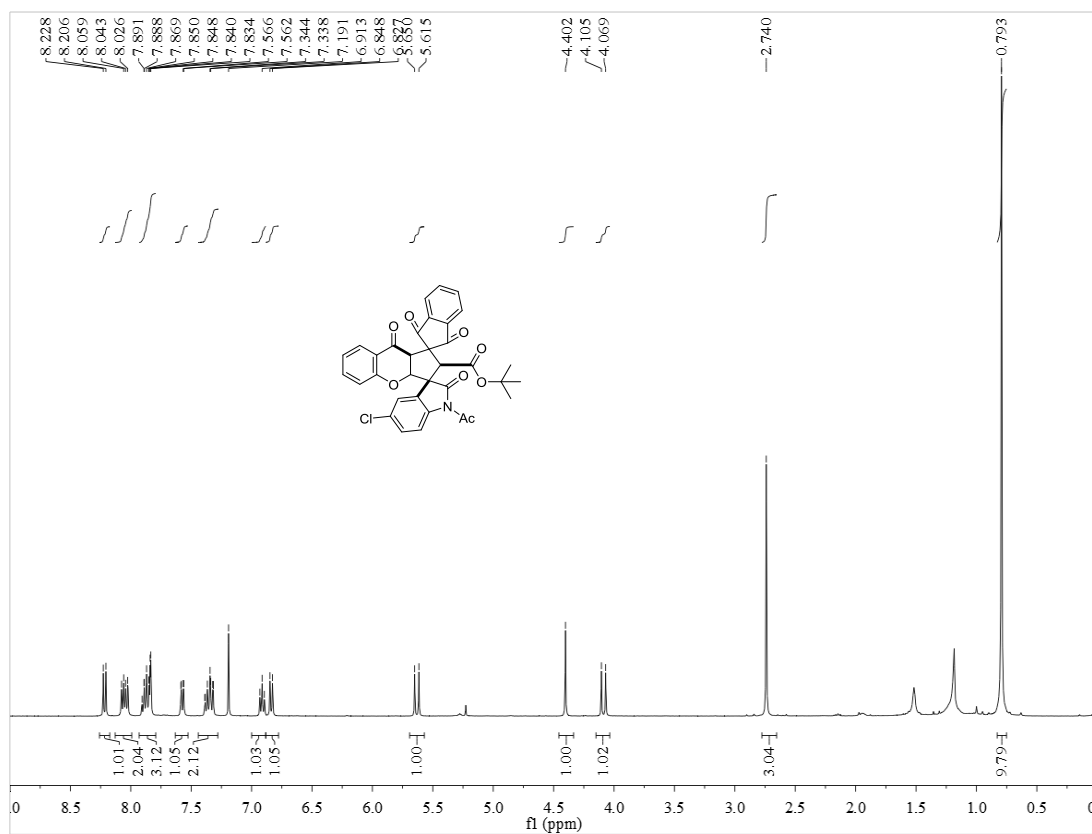




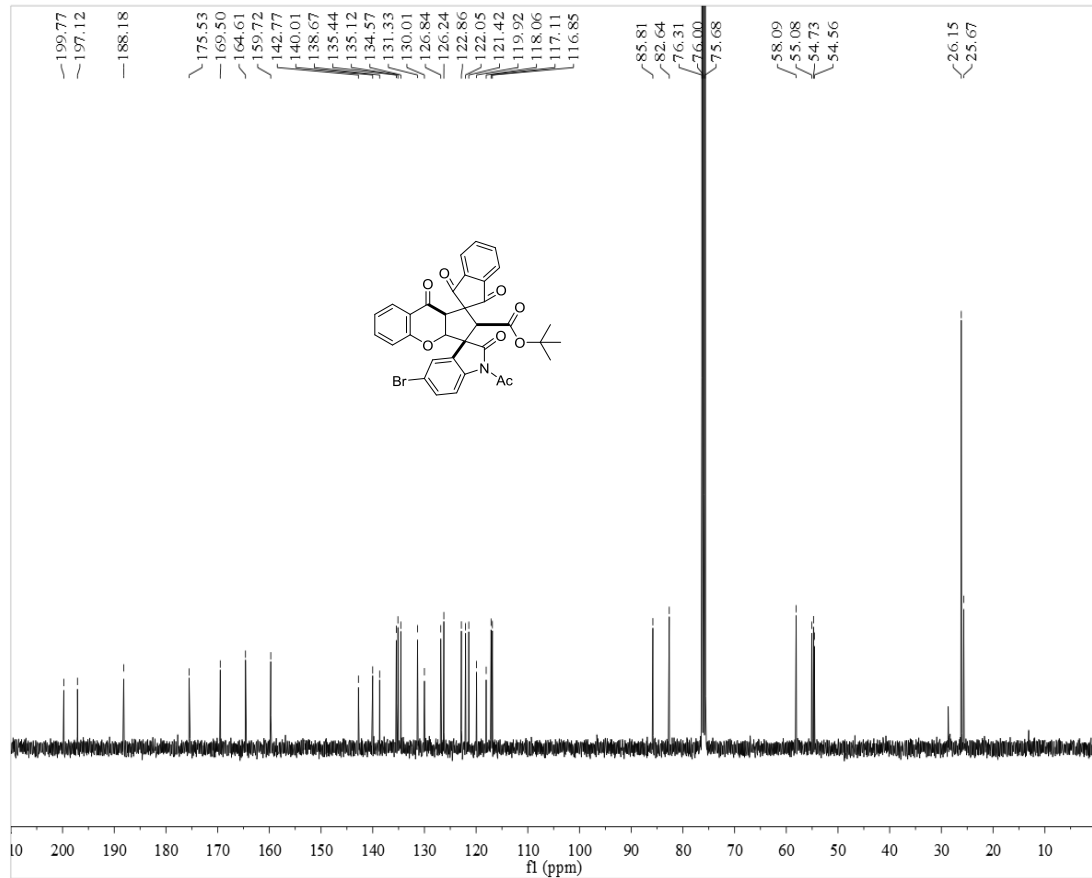
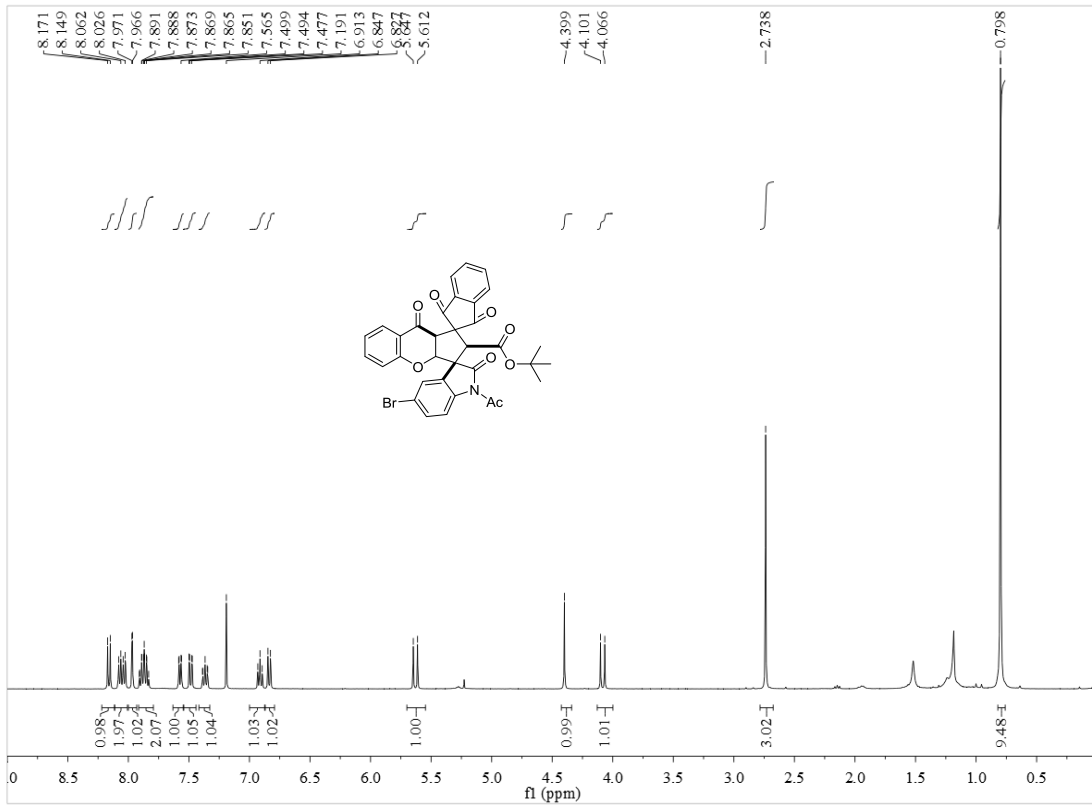
# $^1\text{H}$ and $^{13}\text{C}$ NMR of 3d



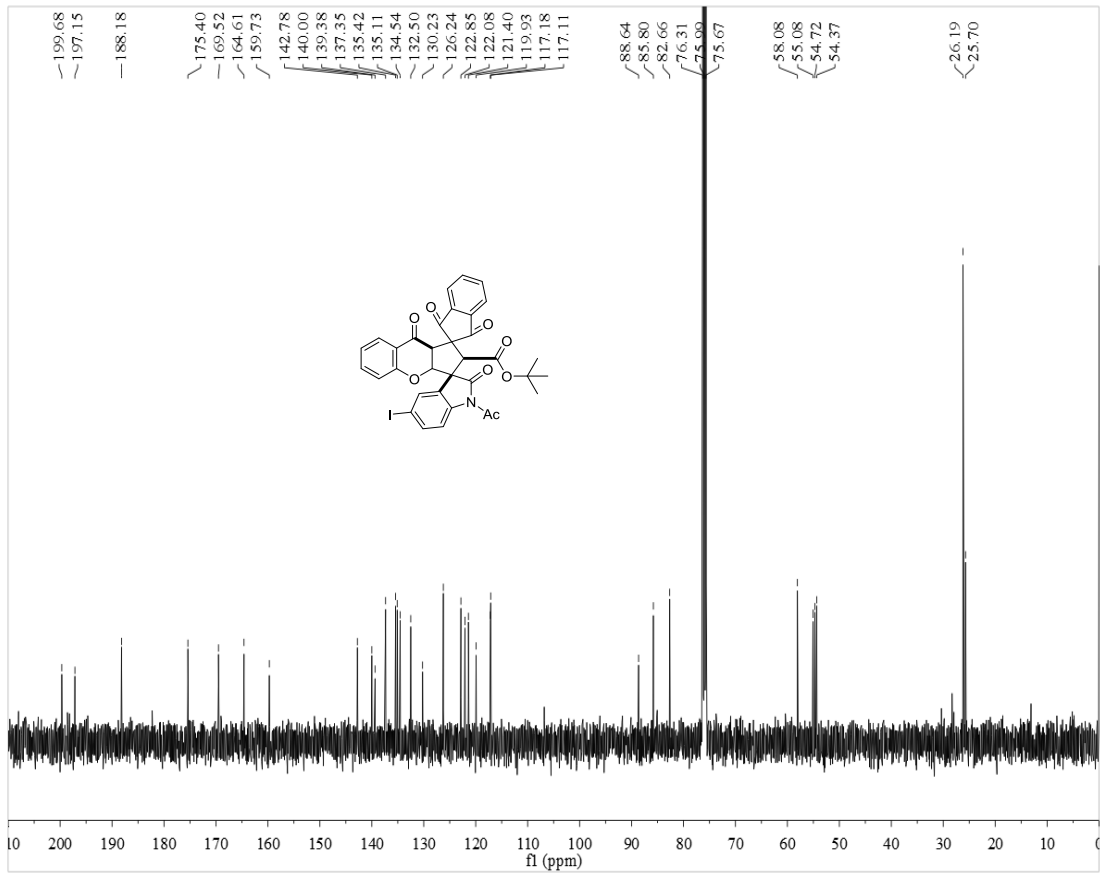
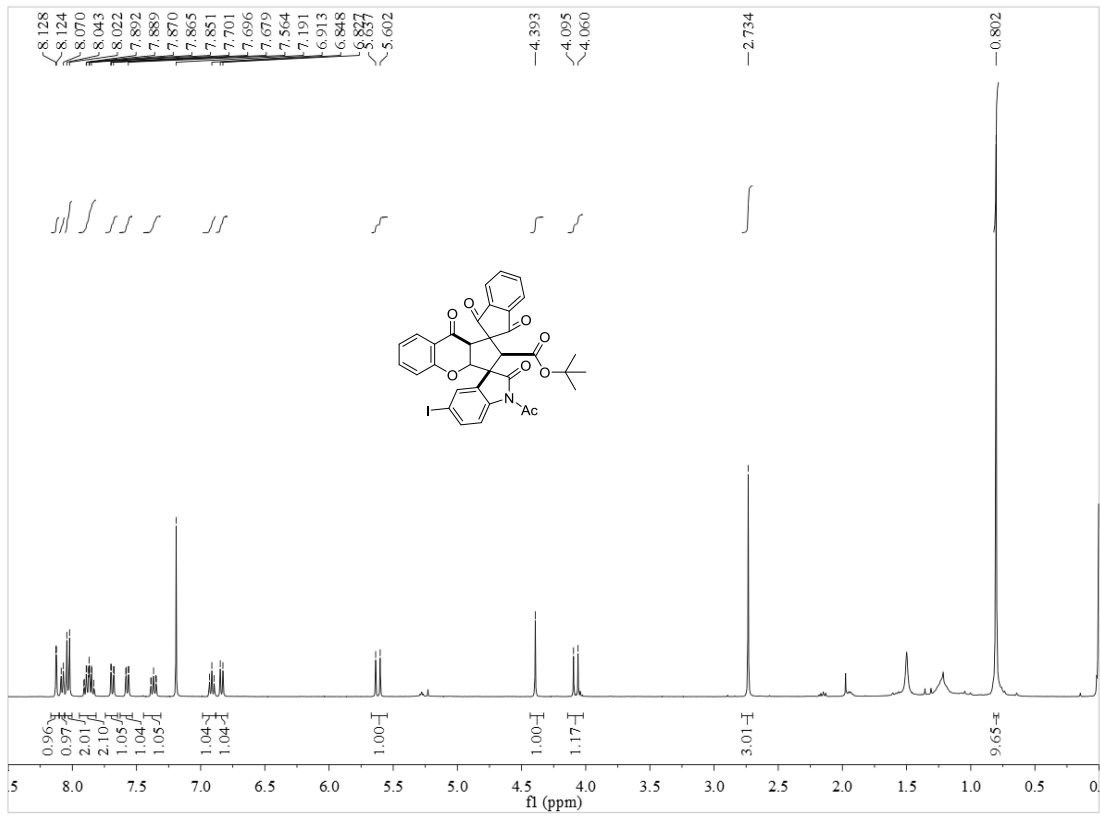
# $^1\text{H}$ and $^{13}\text{C}$ NMR of 3e



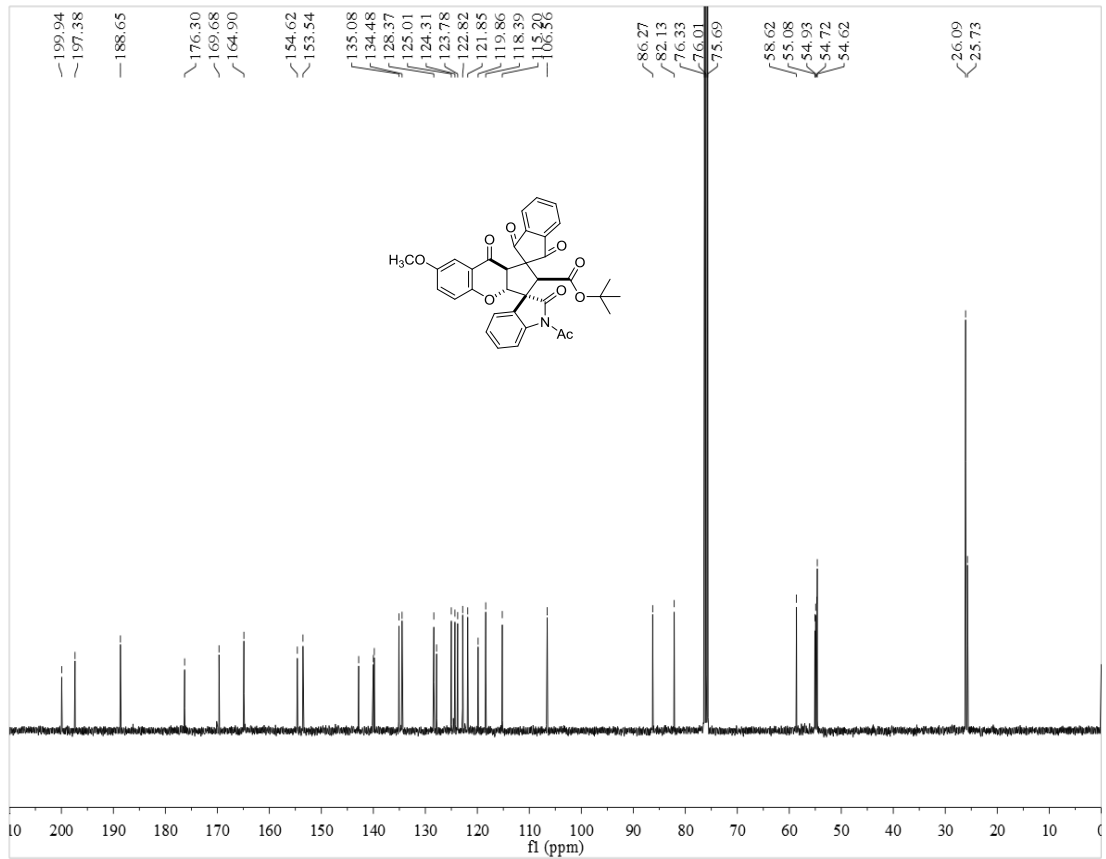
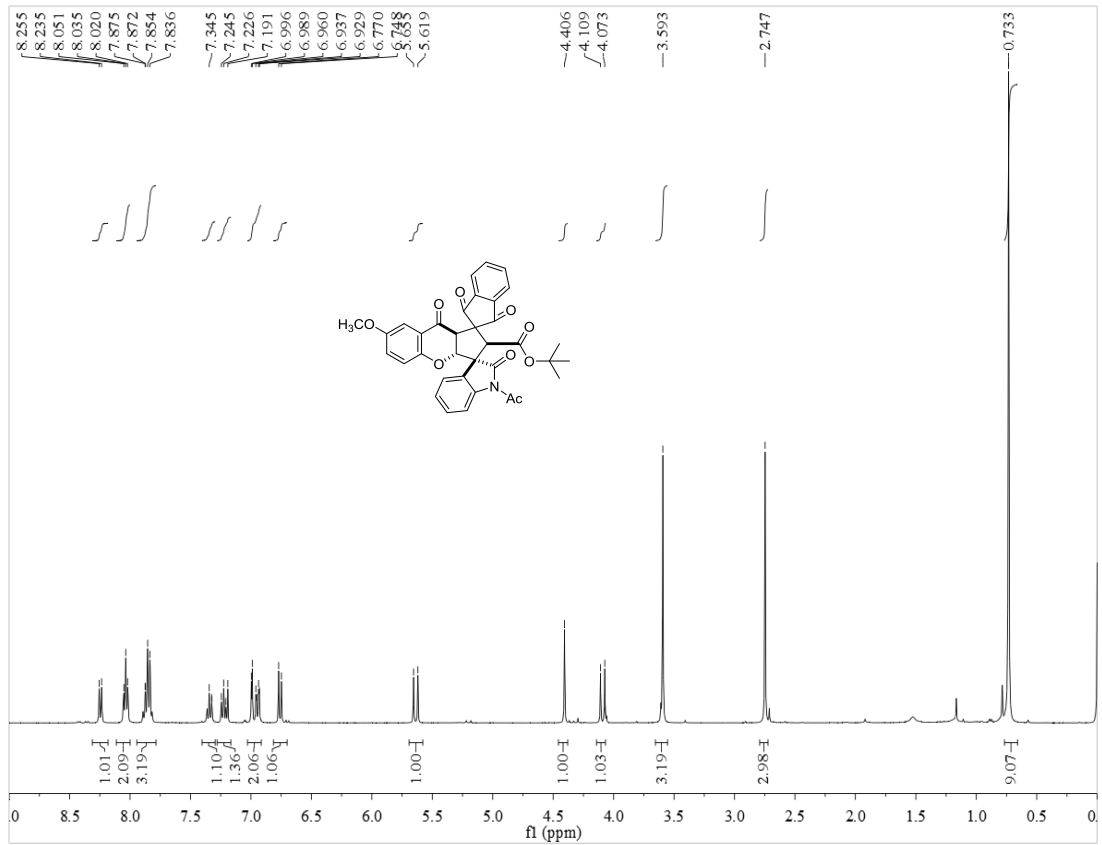
# $^1\text{H}$ and $^{13}\text{C}$ NMR of 3f



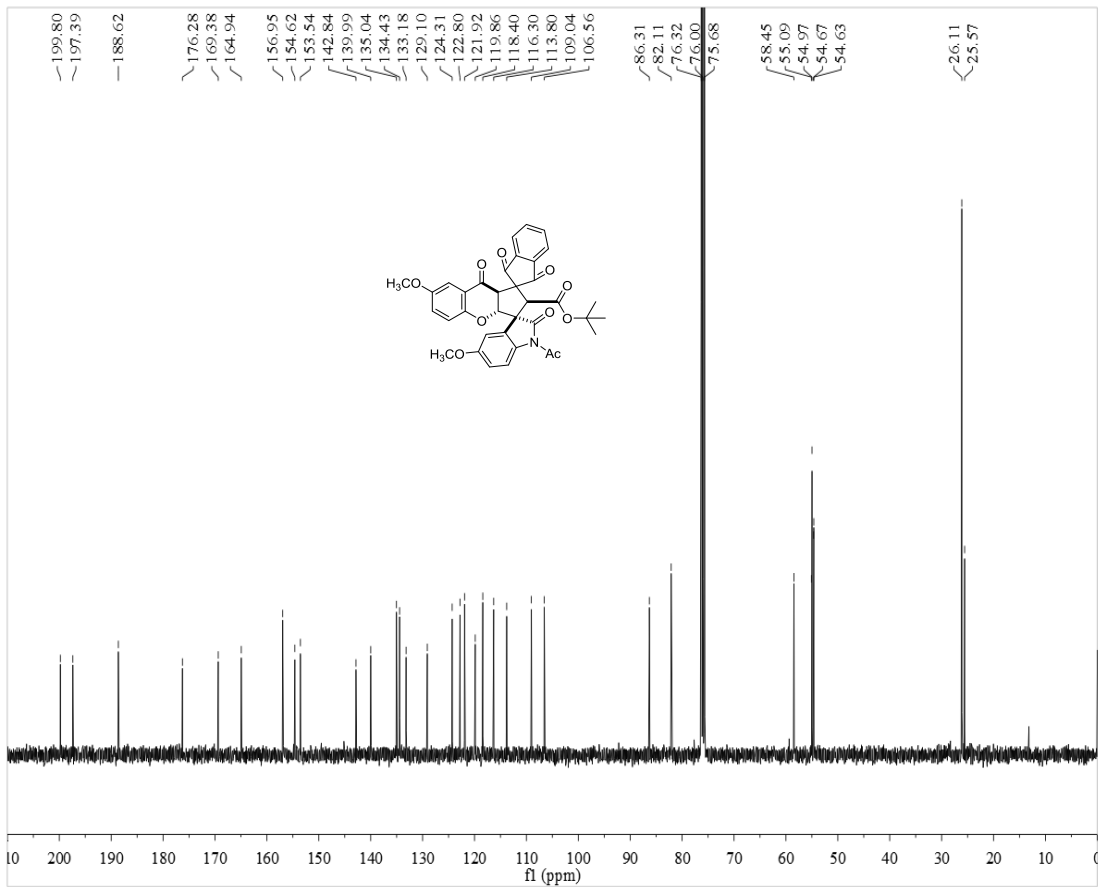
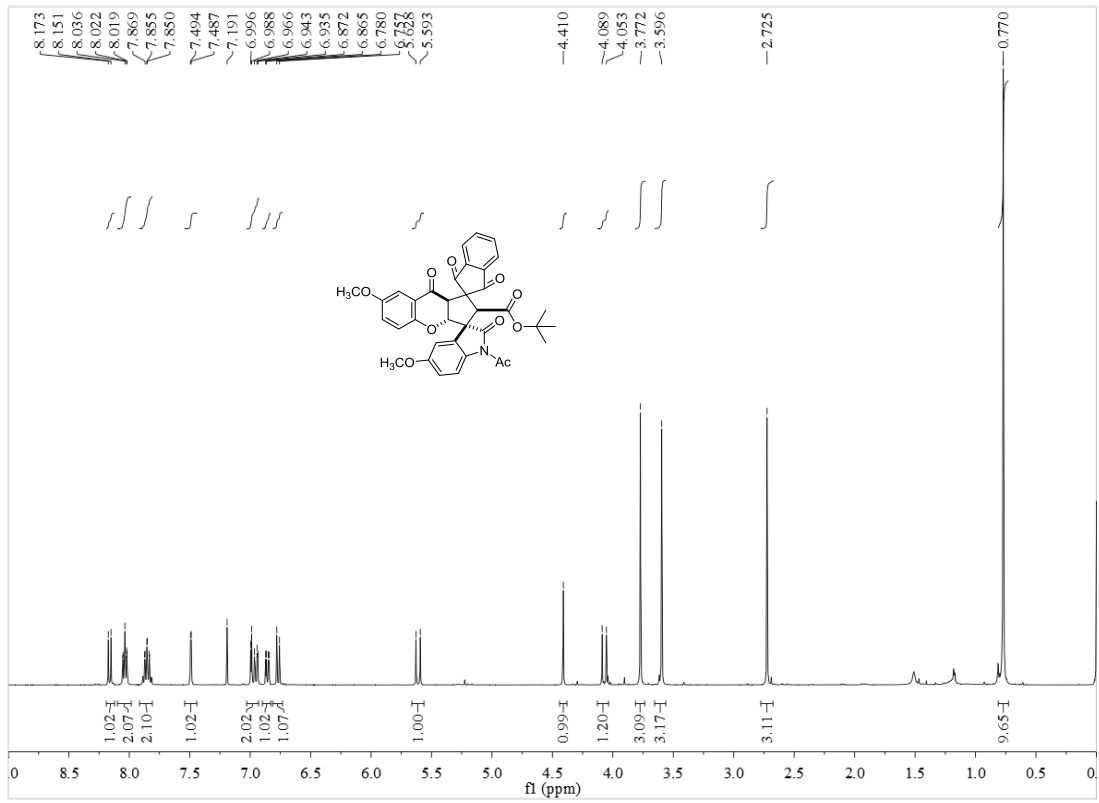
# <sup>1</sup>H and <sup>13</sup>C NMR of 3g



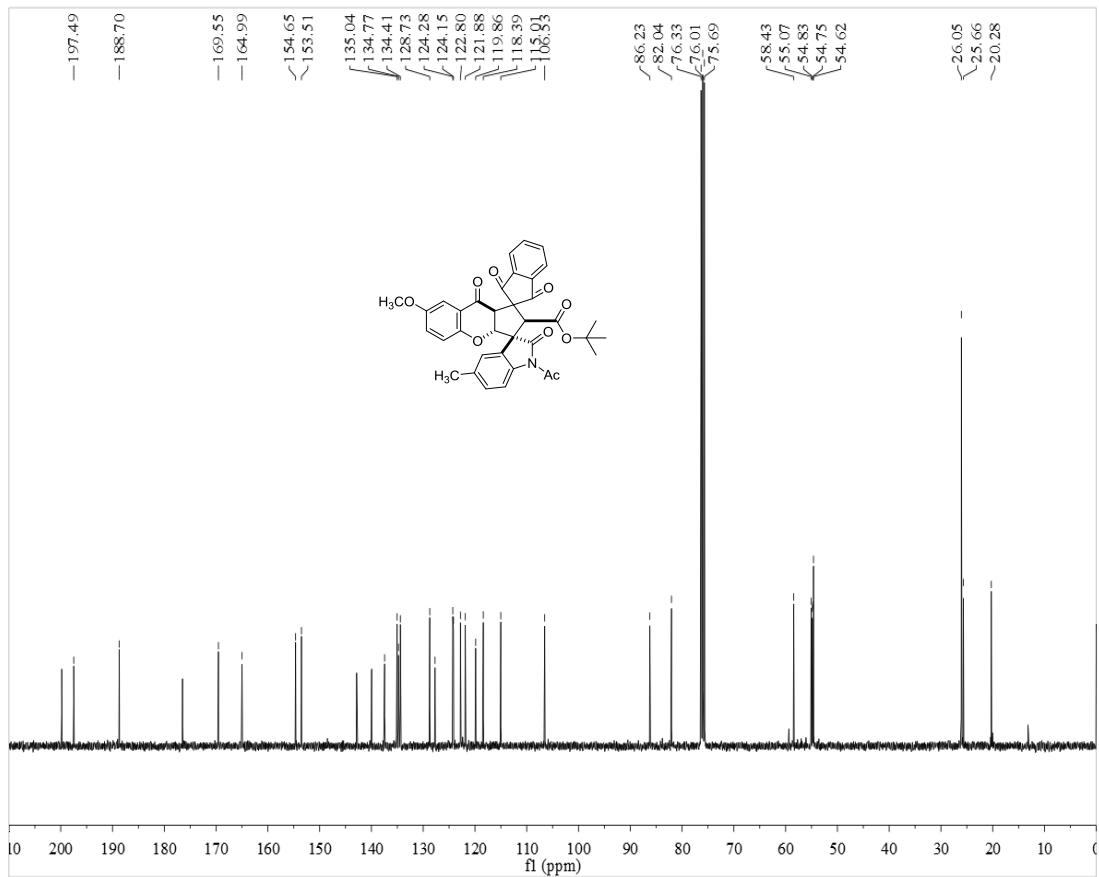
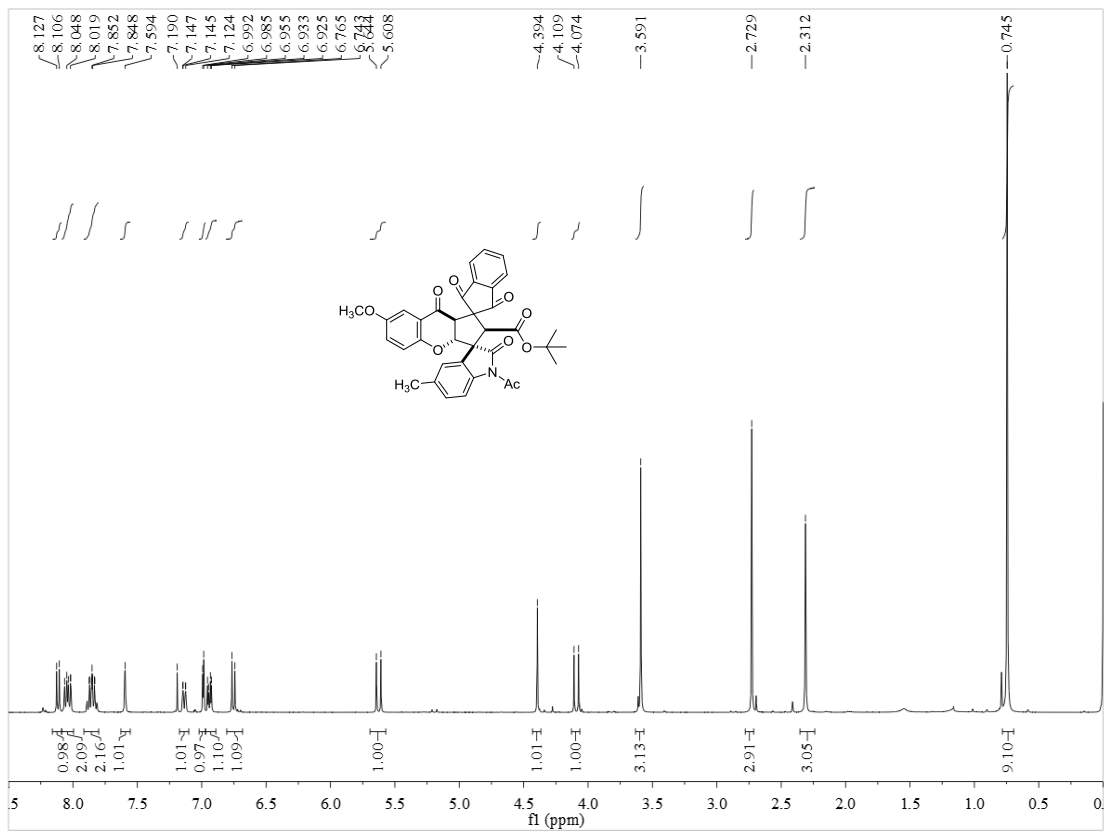
# <sup>1</sup>H and <sup>13</sup>C NMR of 3h



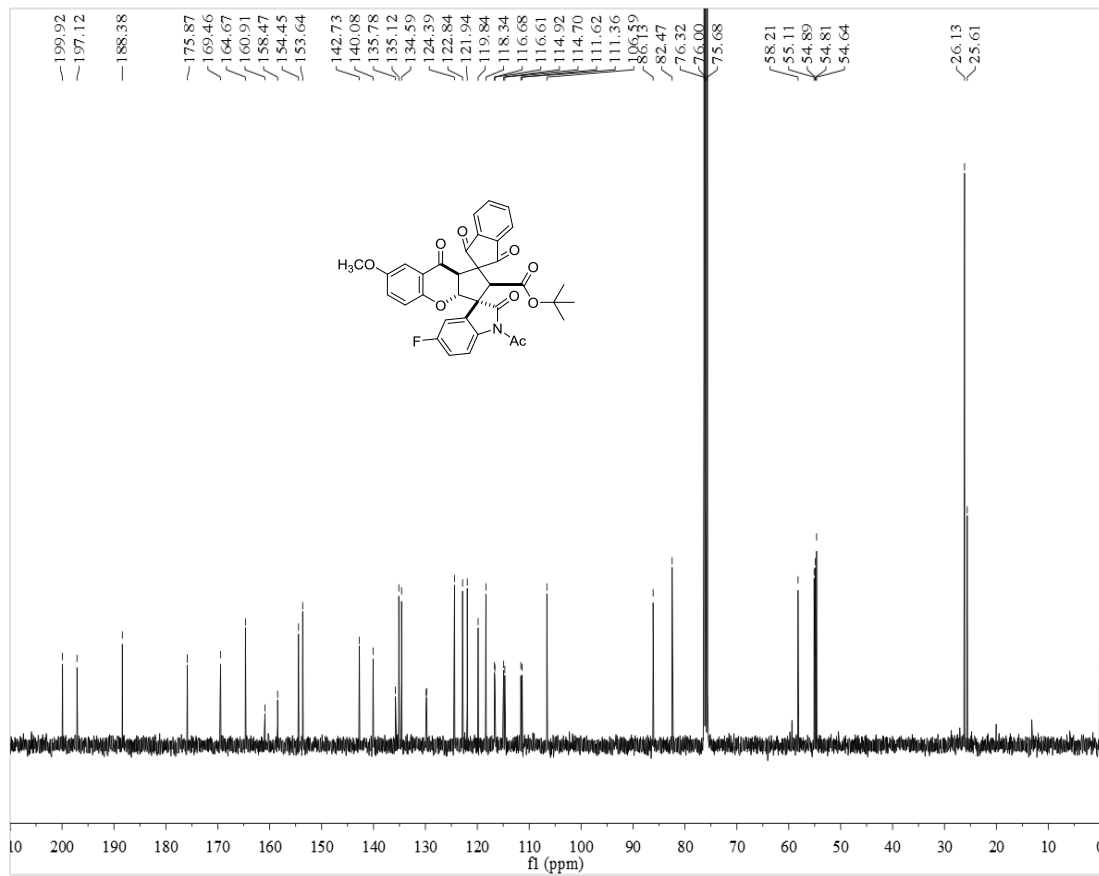
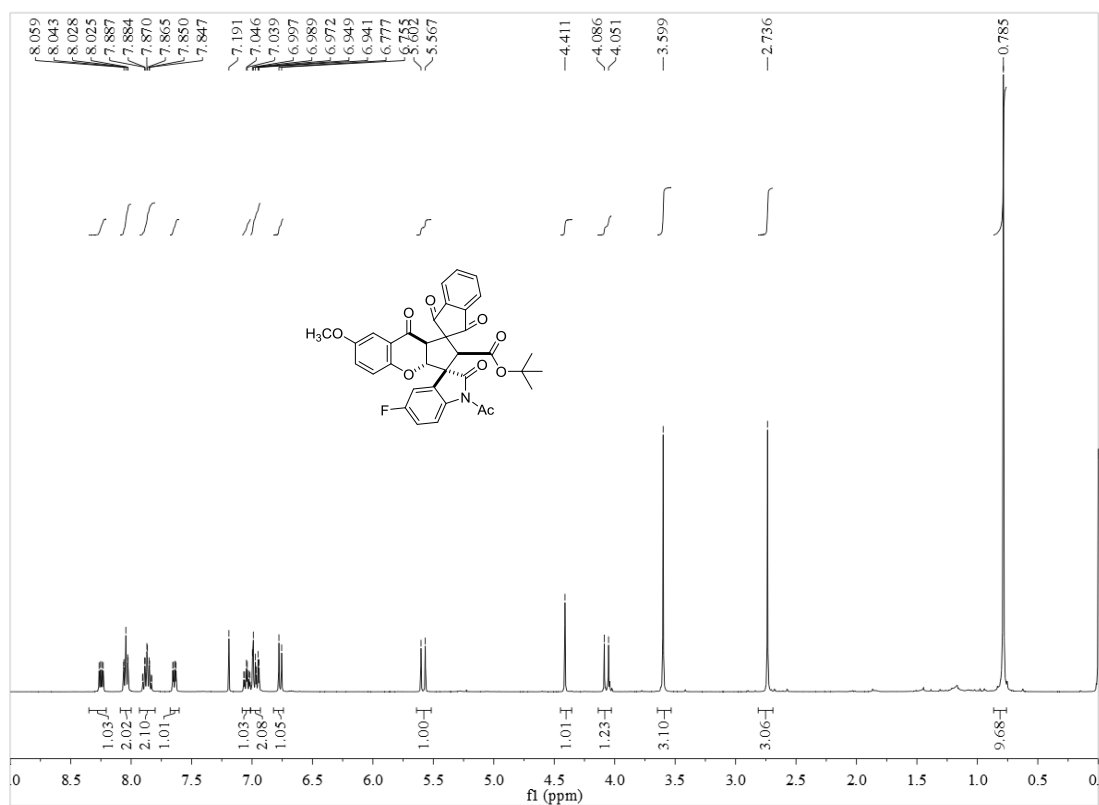
# <sup>1</sup>H and <sup>13</sup>C NMR of 3i



<sup>1</sup>H and <sup>13</sup>C NMR of 3j

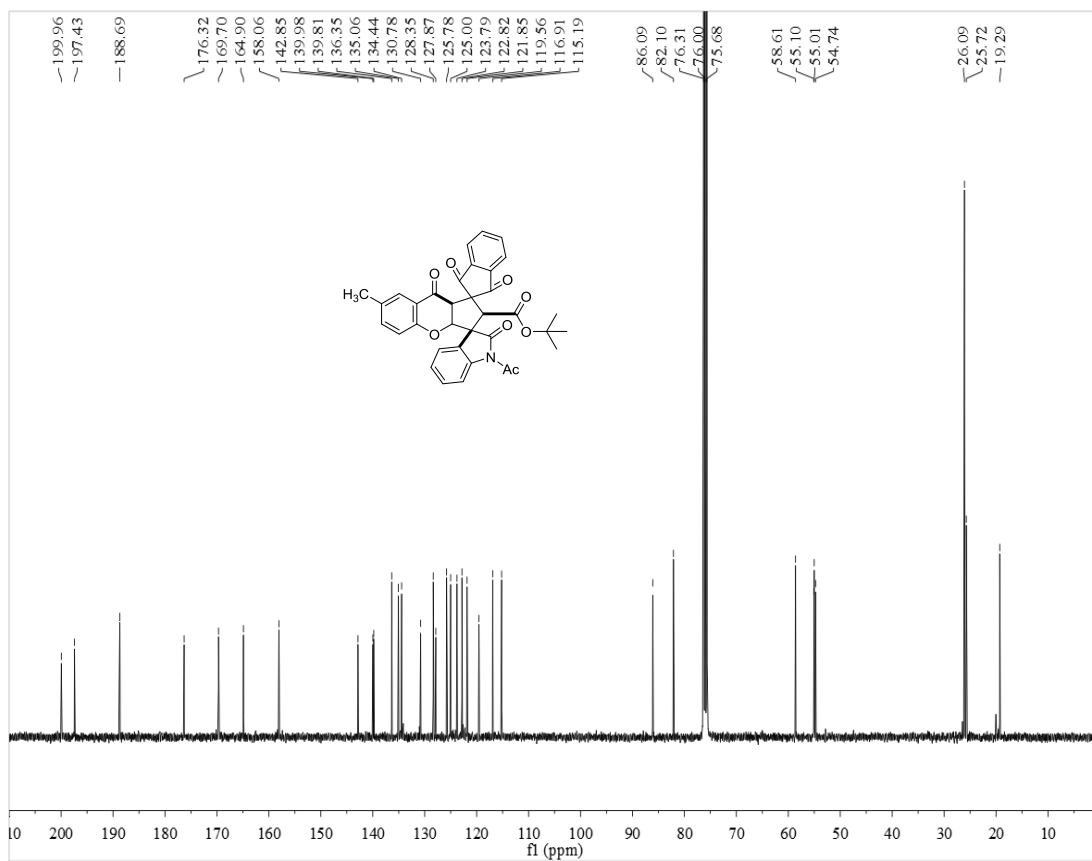
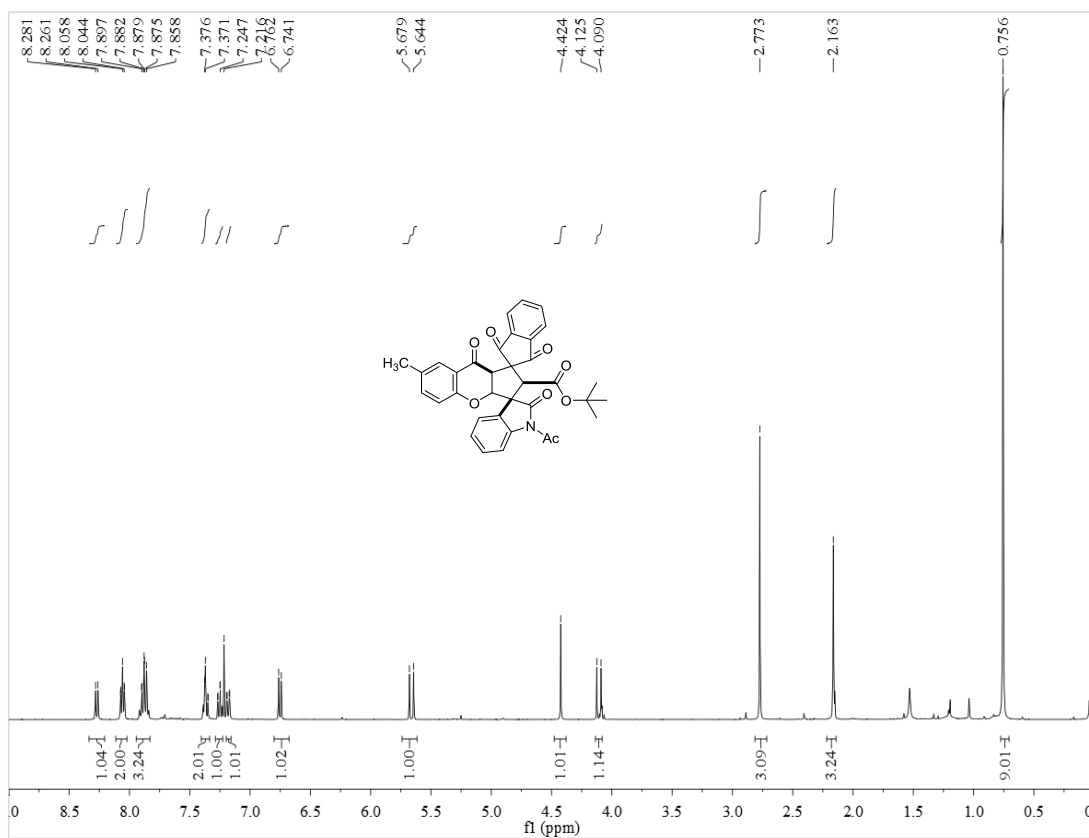


# <sup>1</sup>H and <sup>13</sup>C NMR of 3k

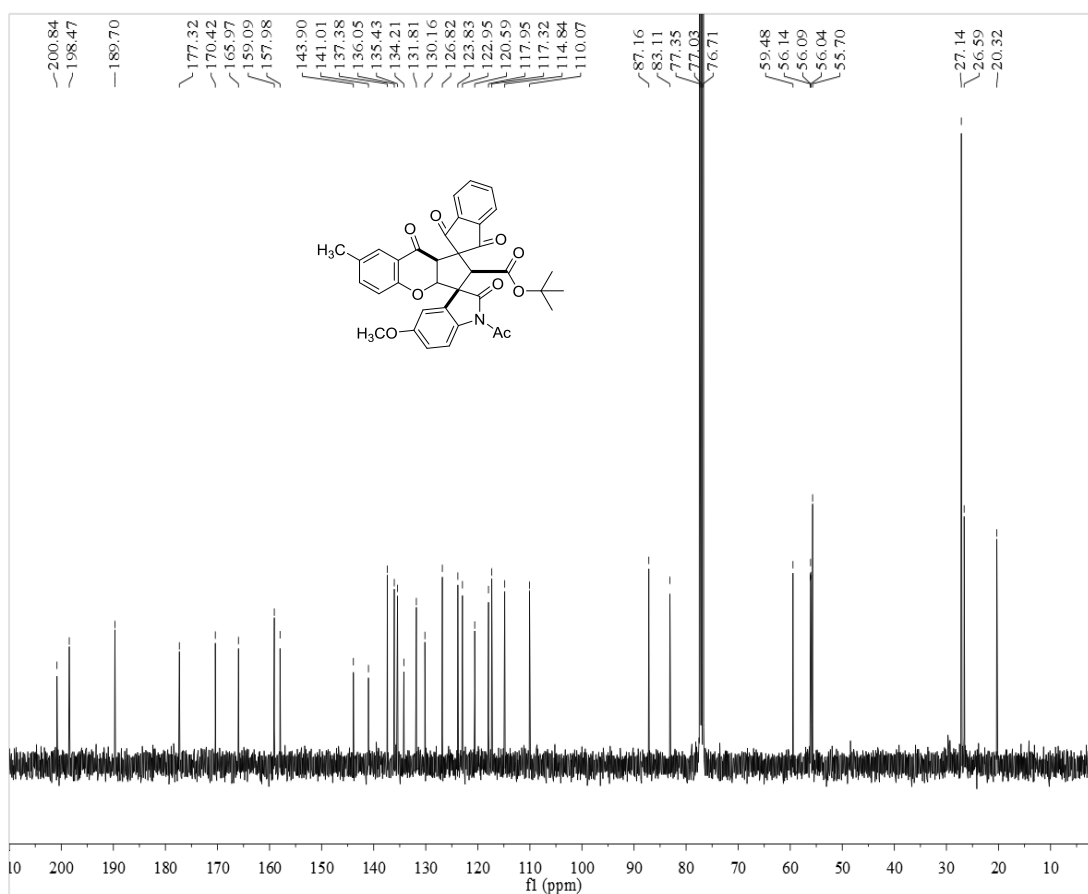
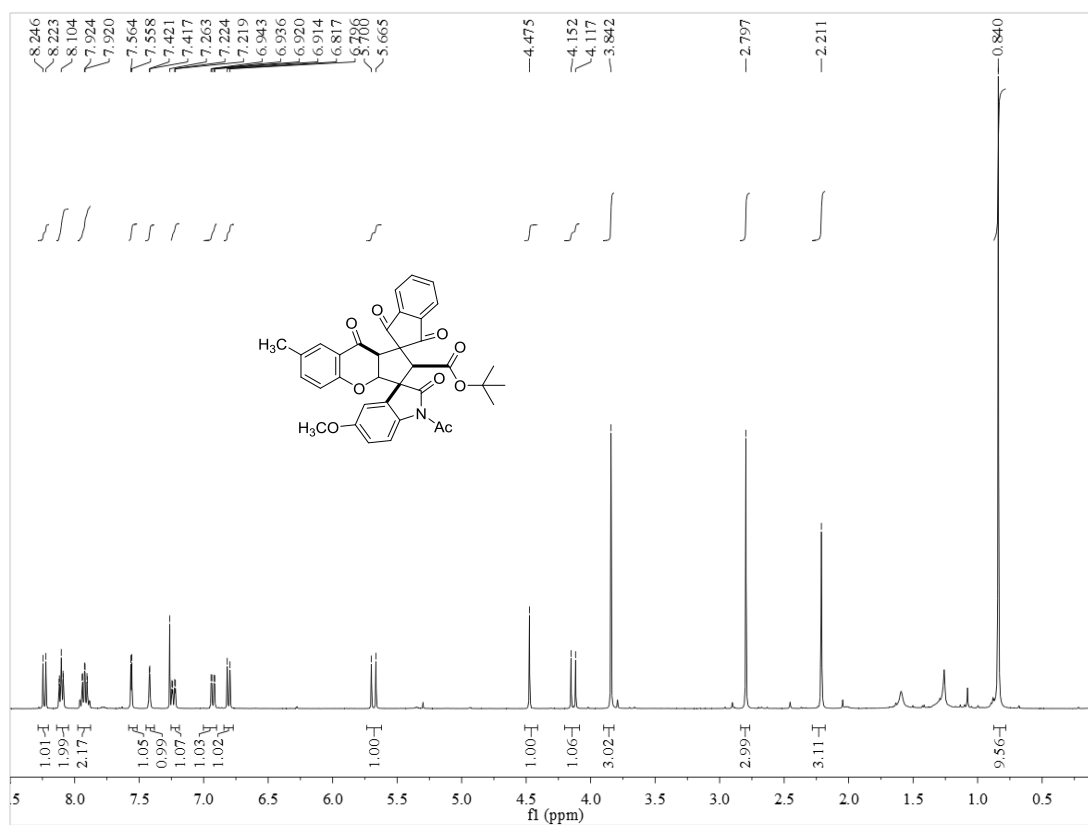




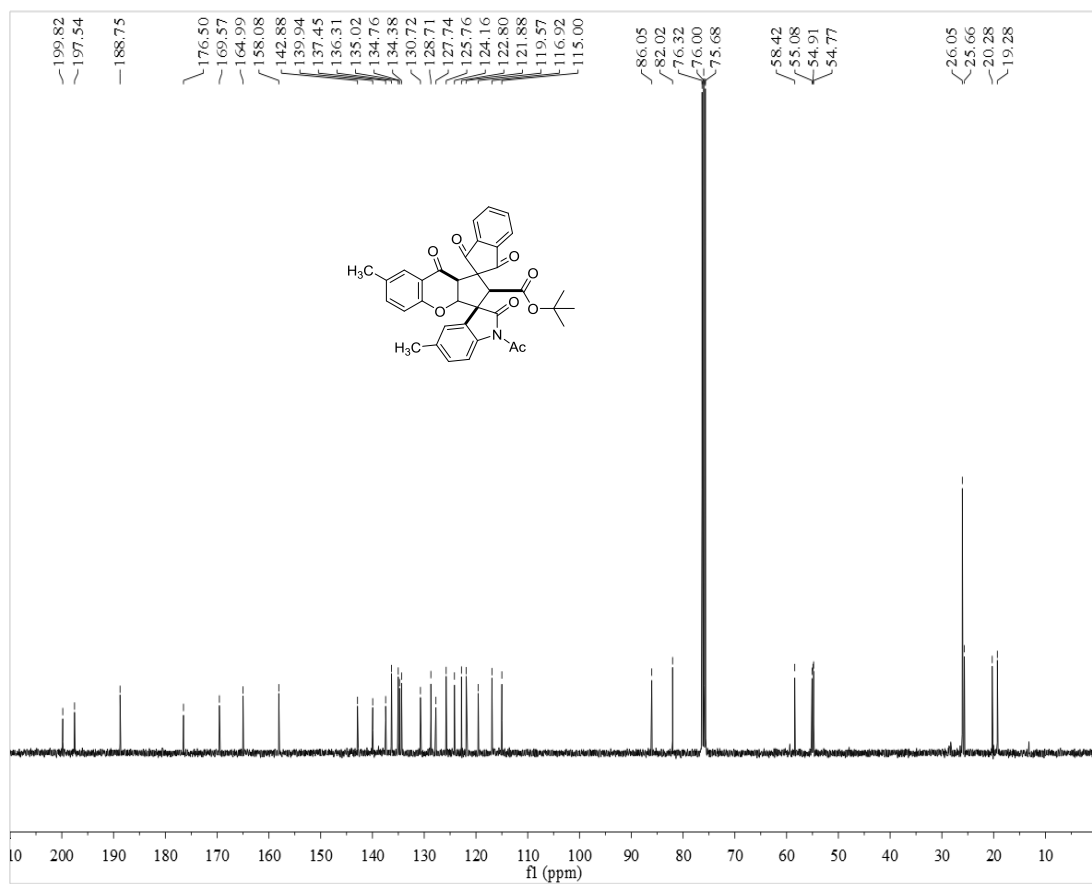
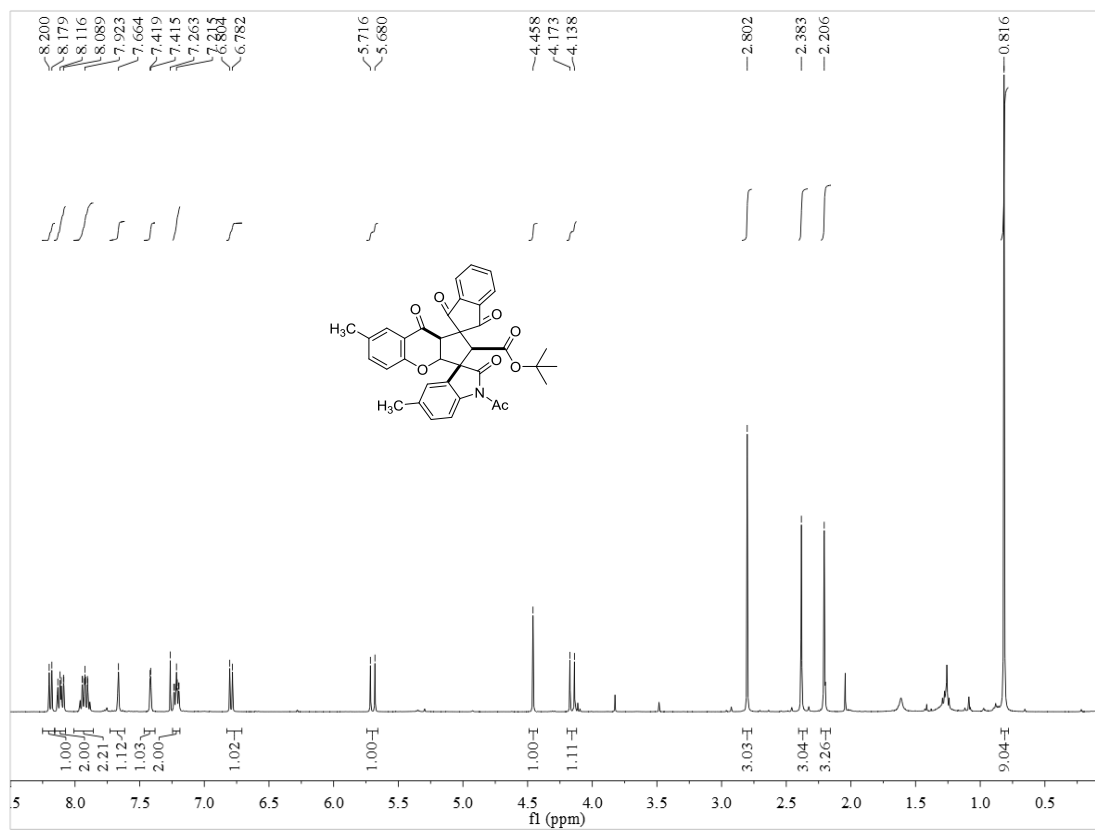
# $^1\text{H}$ and $^{13}\text{C}$ NMR of 3l



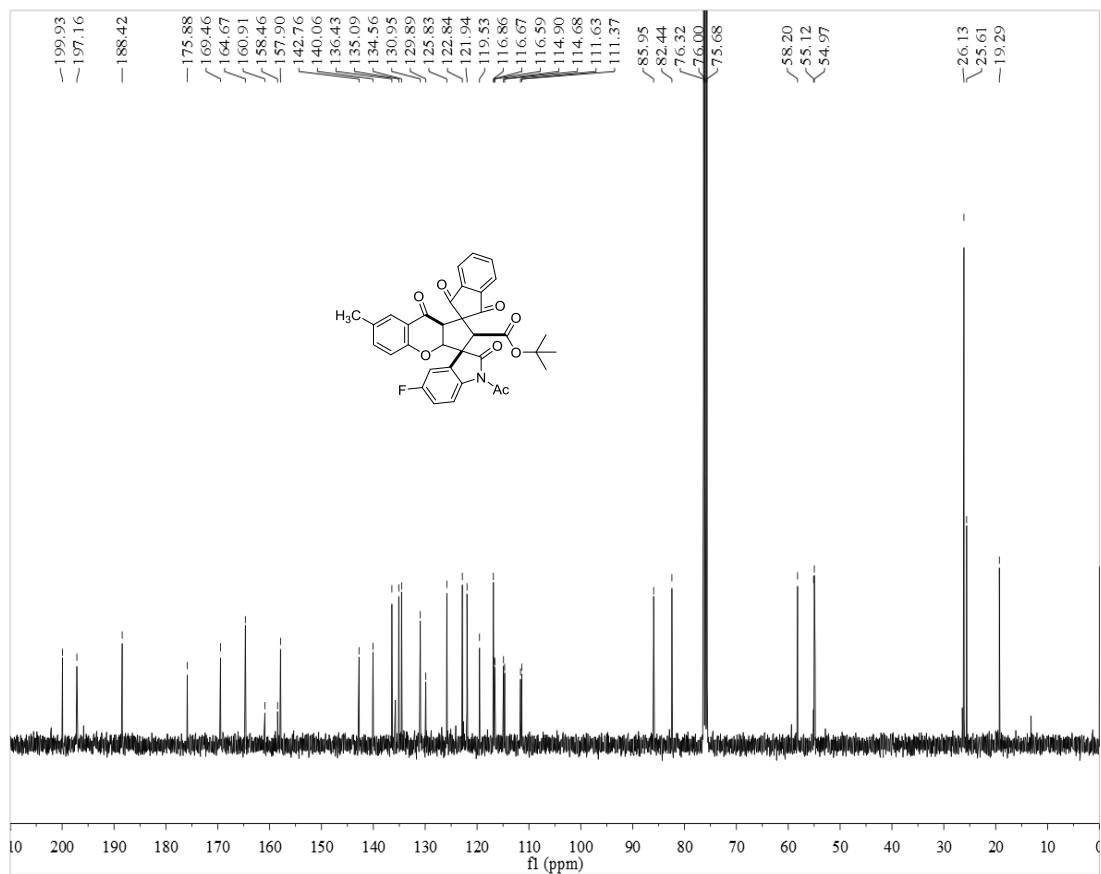
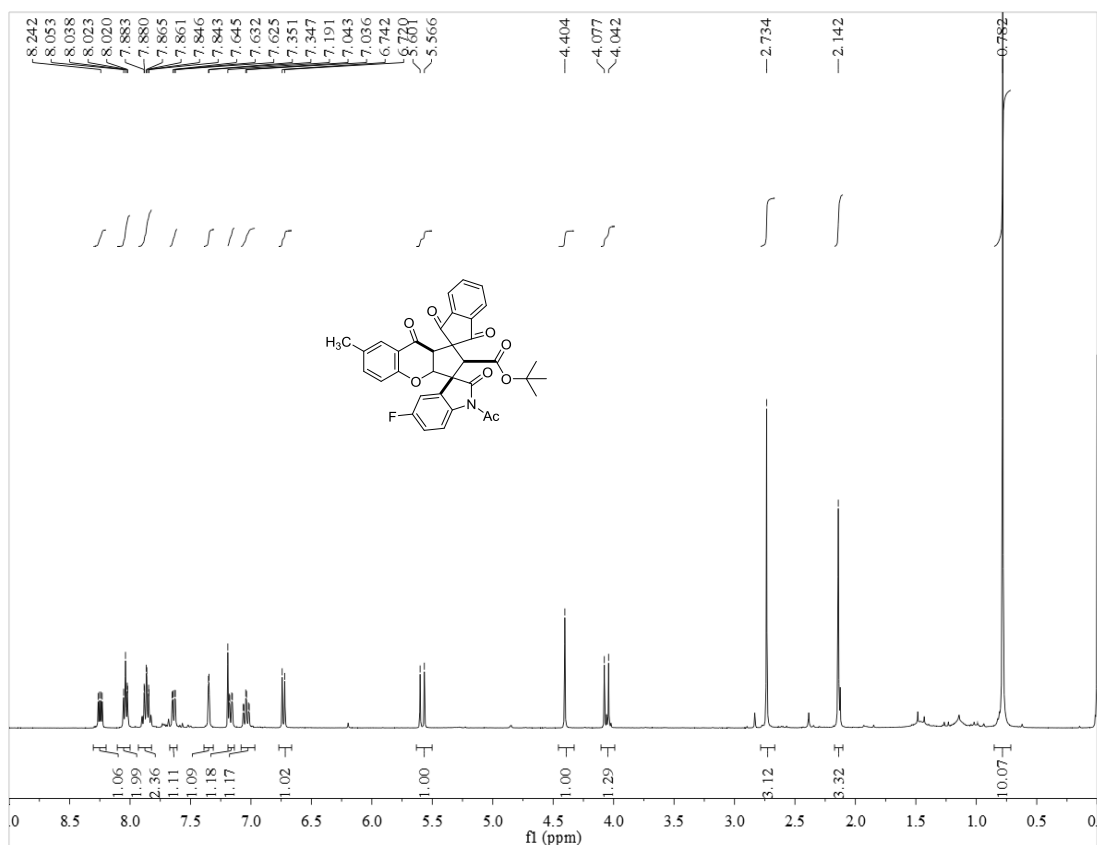
# <sup>1</sup>H and <sup>13</sup>C NMR of 3m



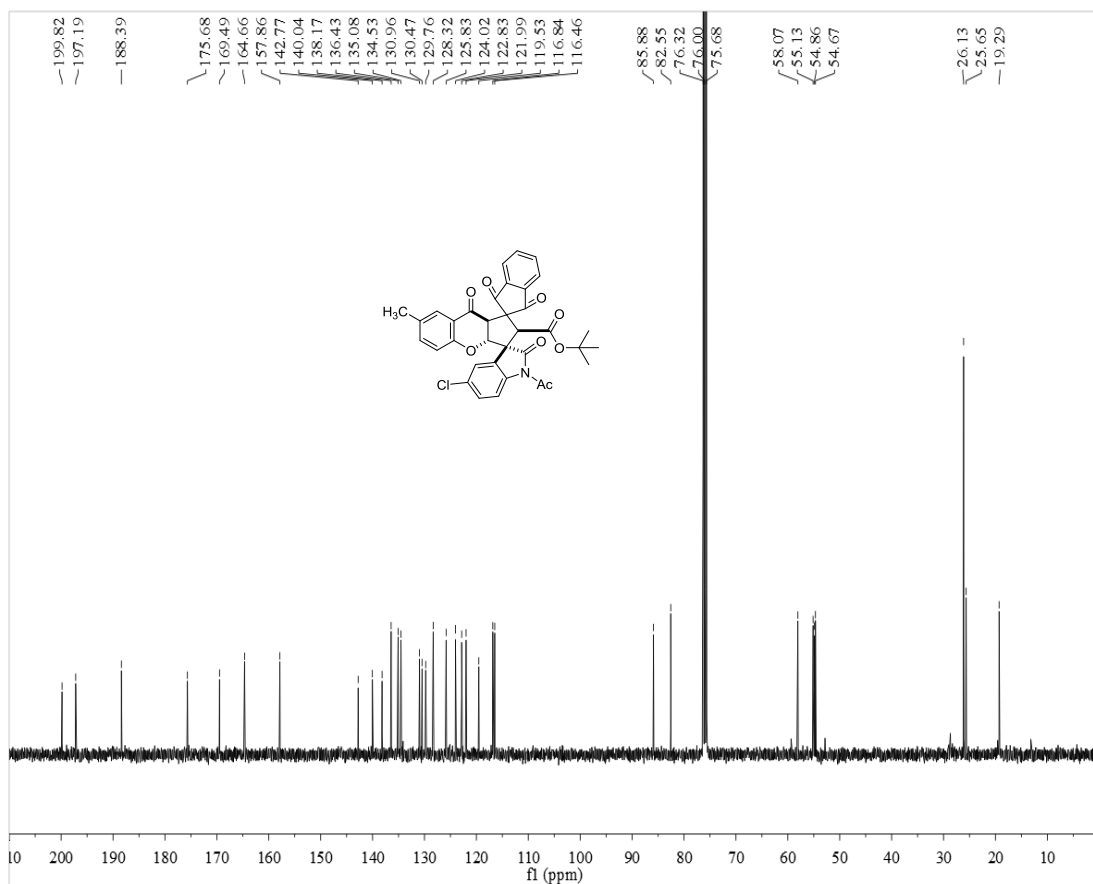
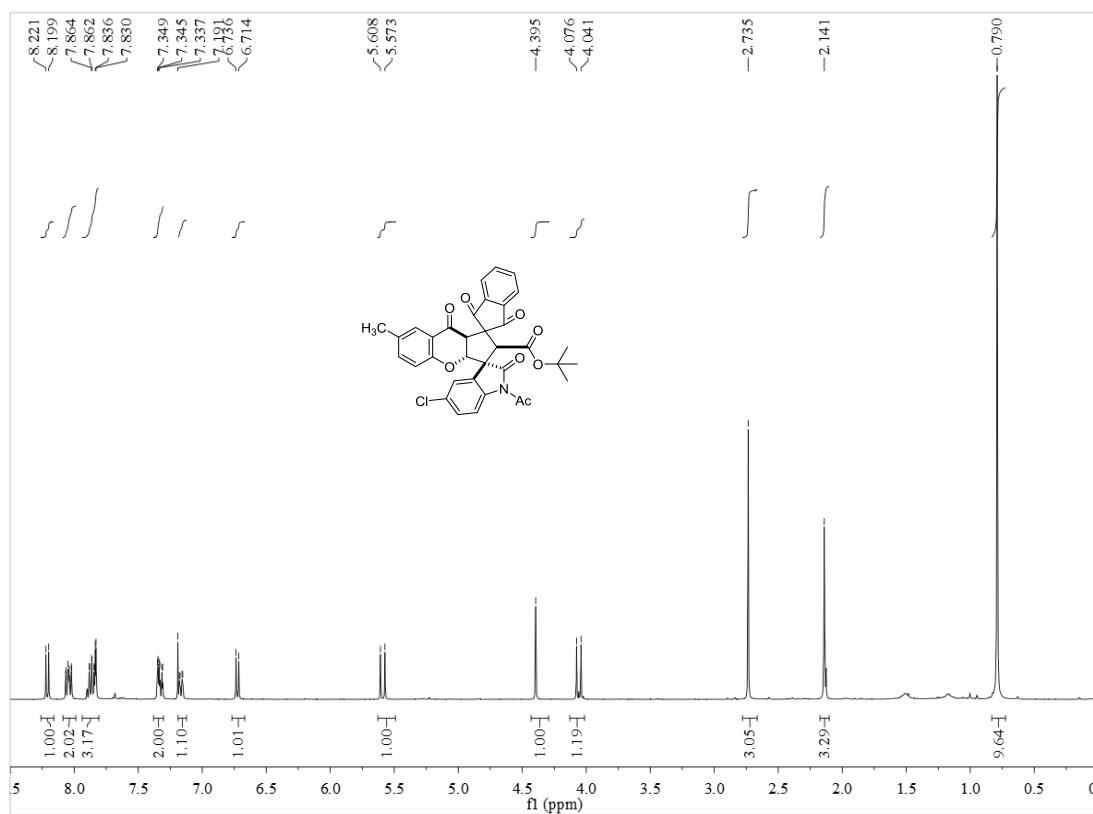
**<sup>1</sup>H and <sup>13</sup>C NMR of 3n**



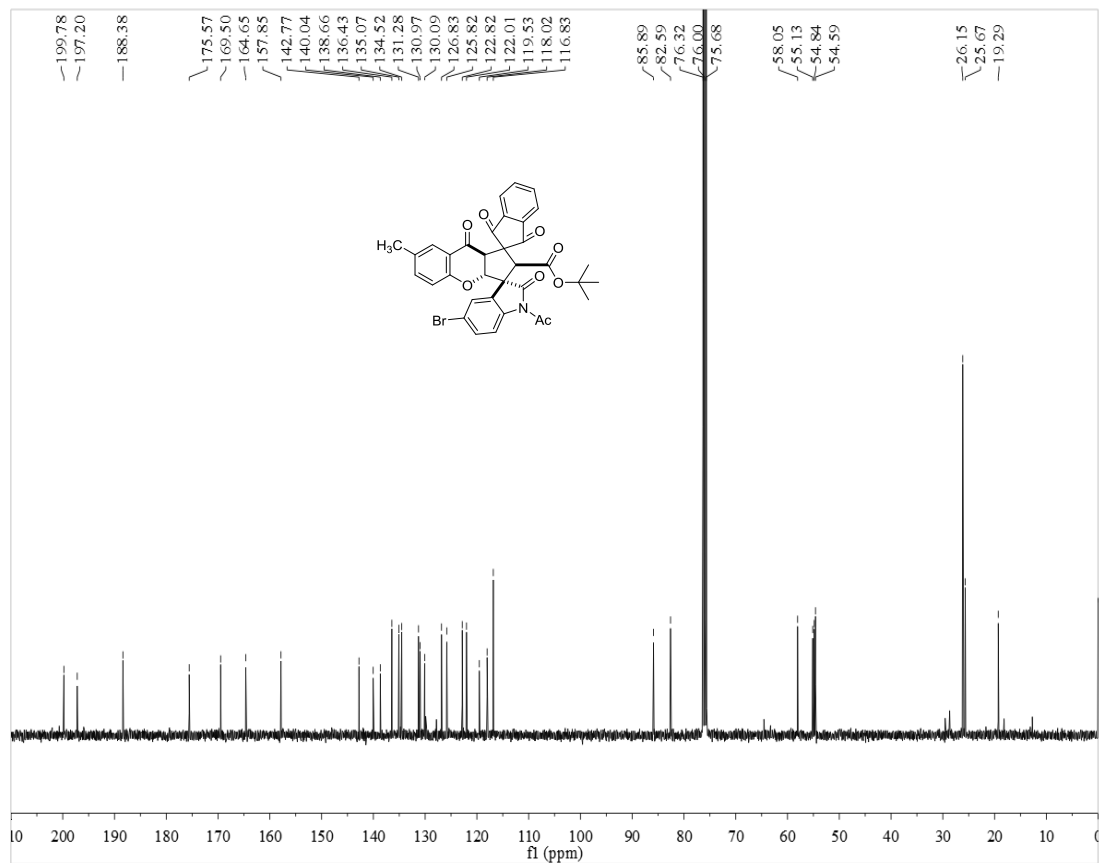
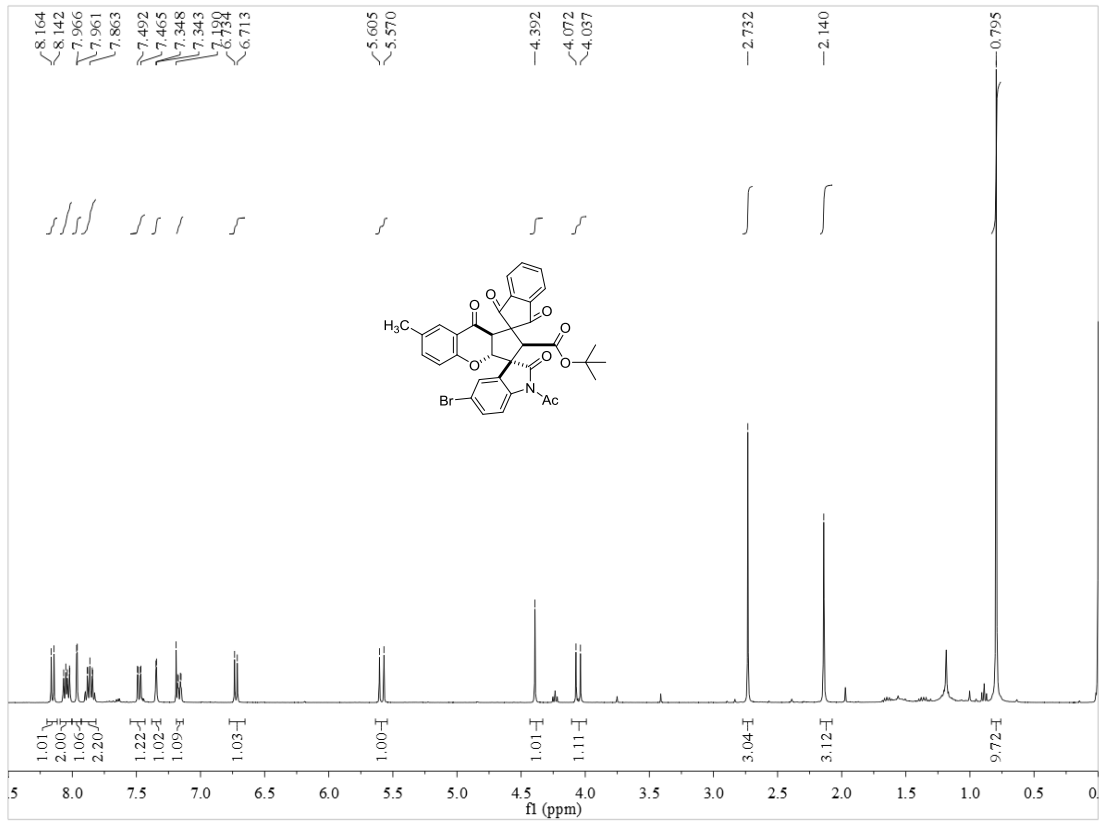
# $^1\text{H}$ and $^{13}\text{C}$ NMR of 3o



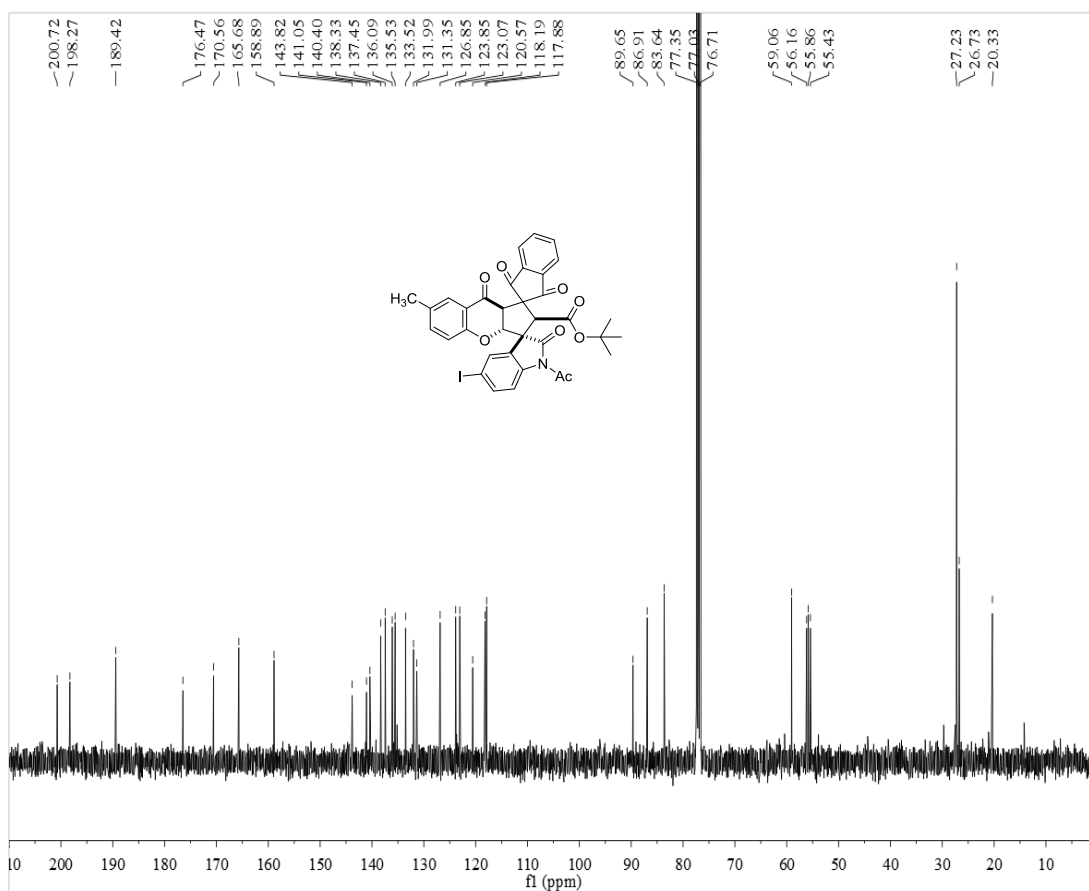
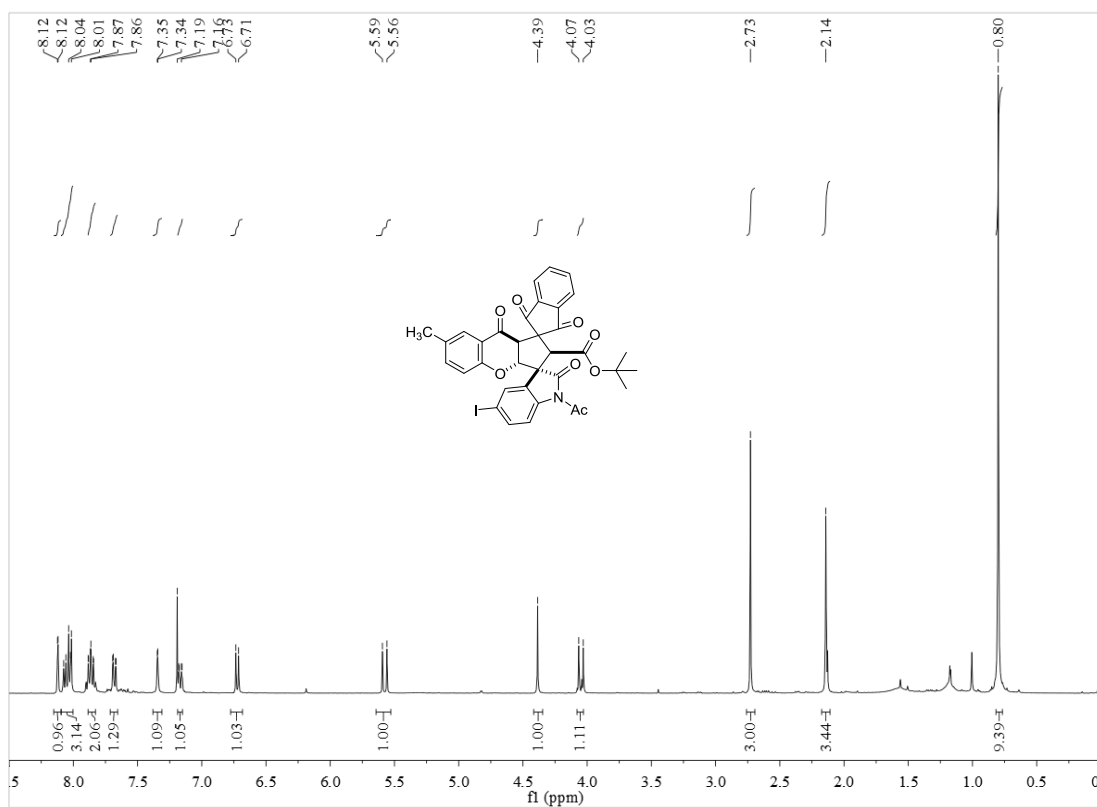
# <sup>1</sup>H and <sup>13</sup>C NMR of 3p



# <sup>1</sup>H and <sup>13</sup>C NMR of 3q



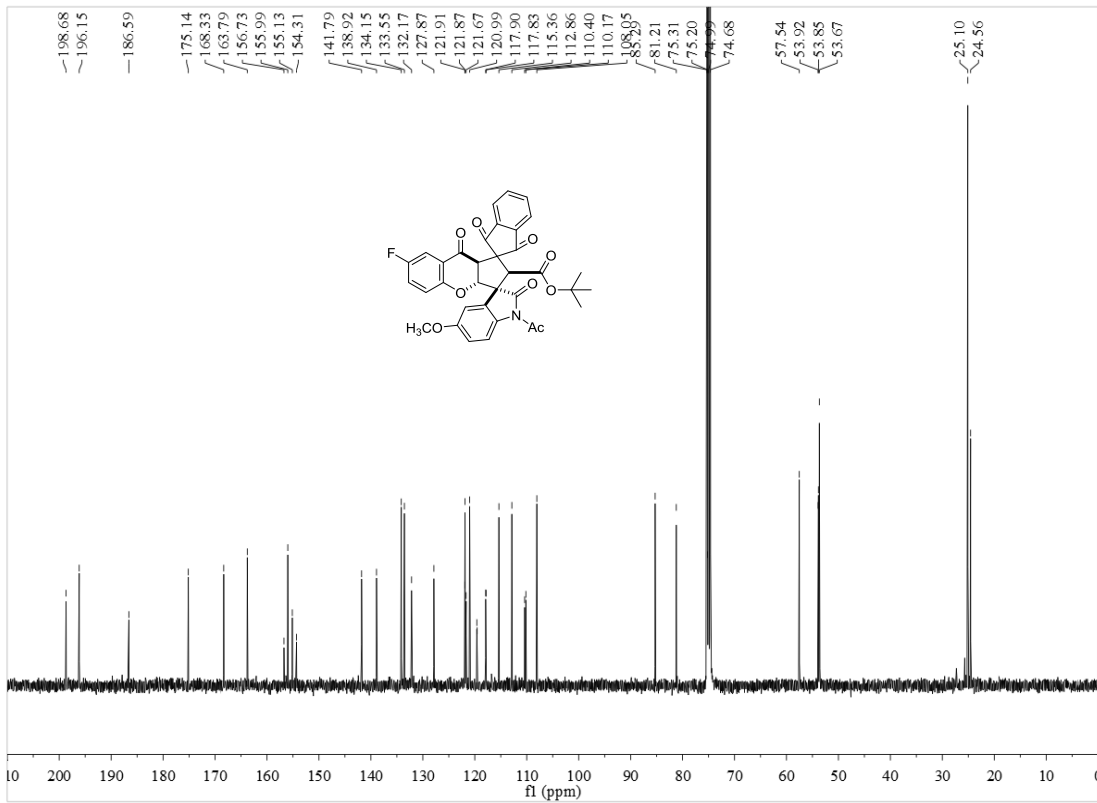
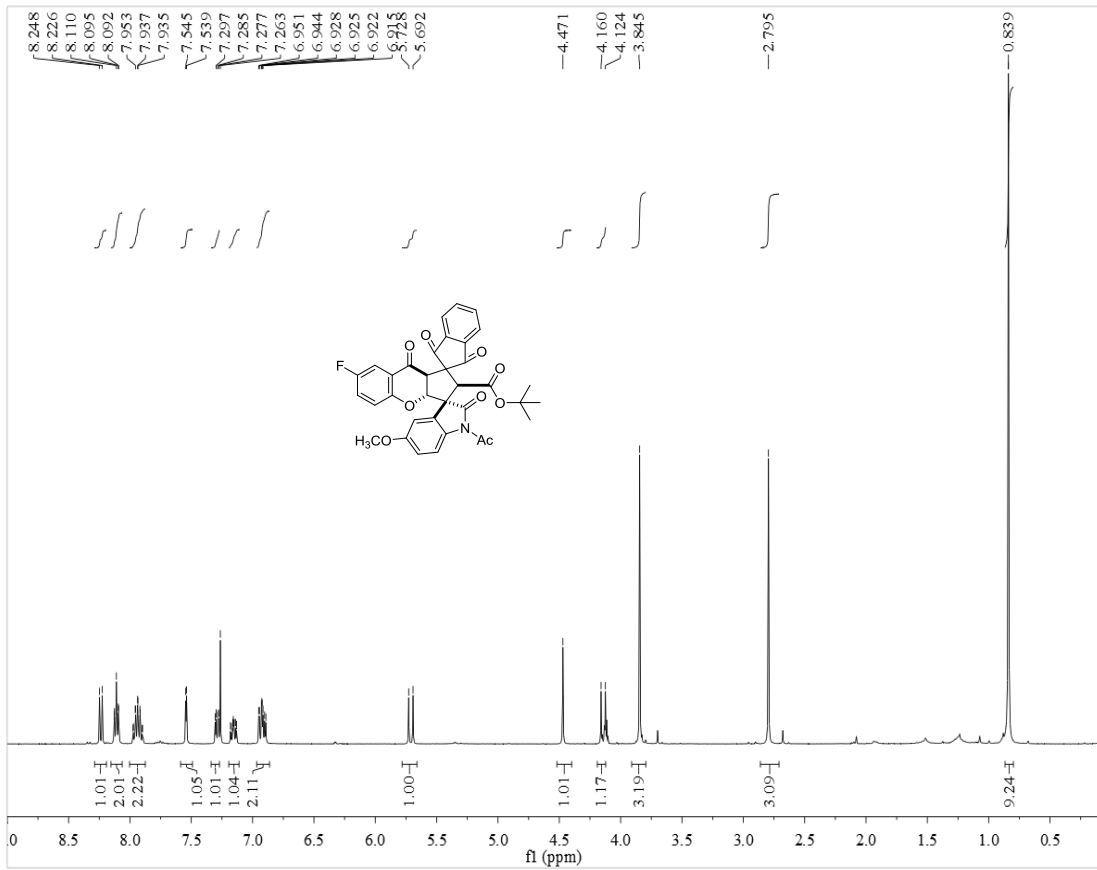
# $^1\text{H}$ and $^{13}\text{C}$ NMR of 3r



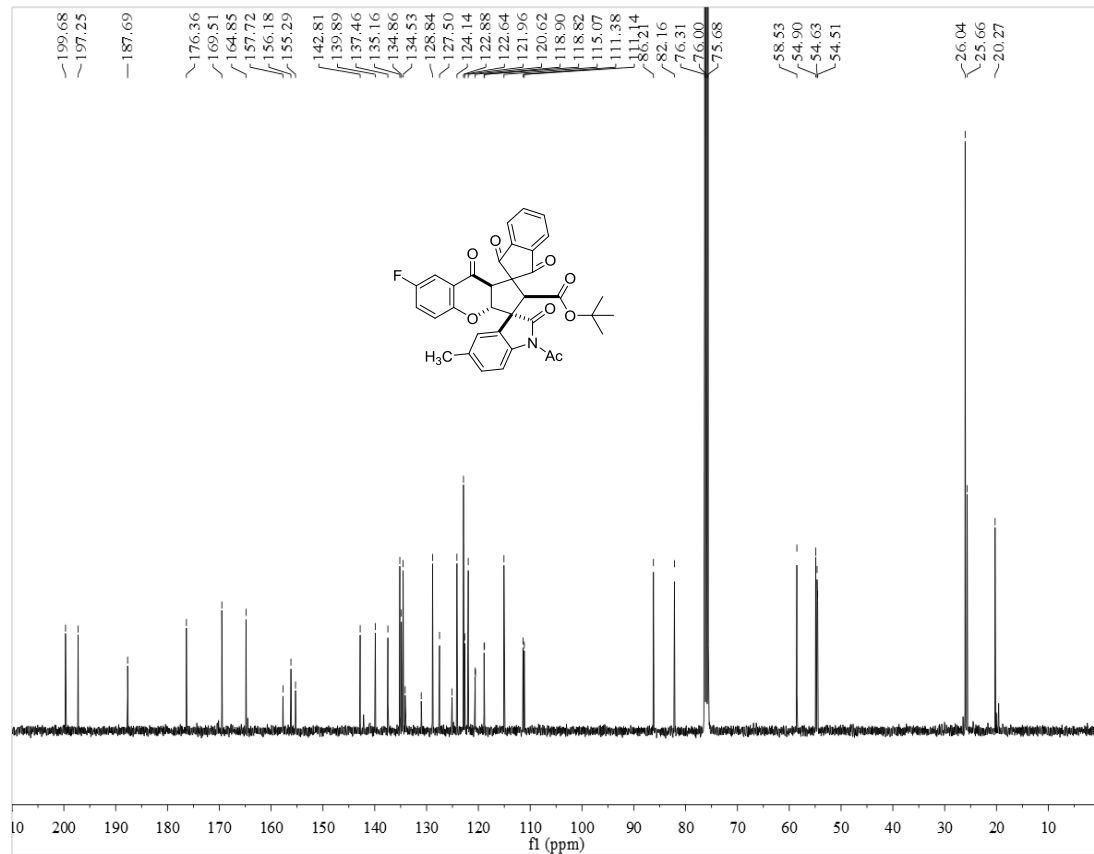
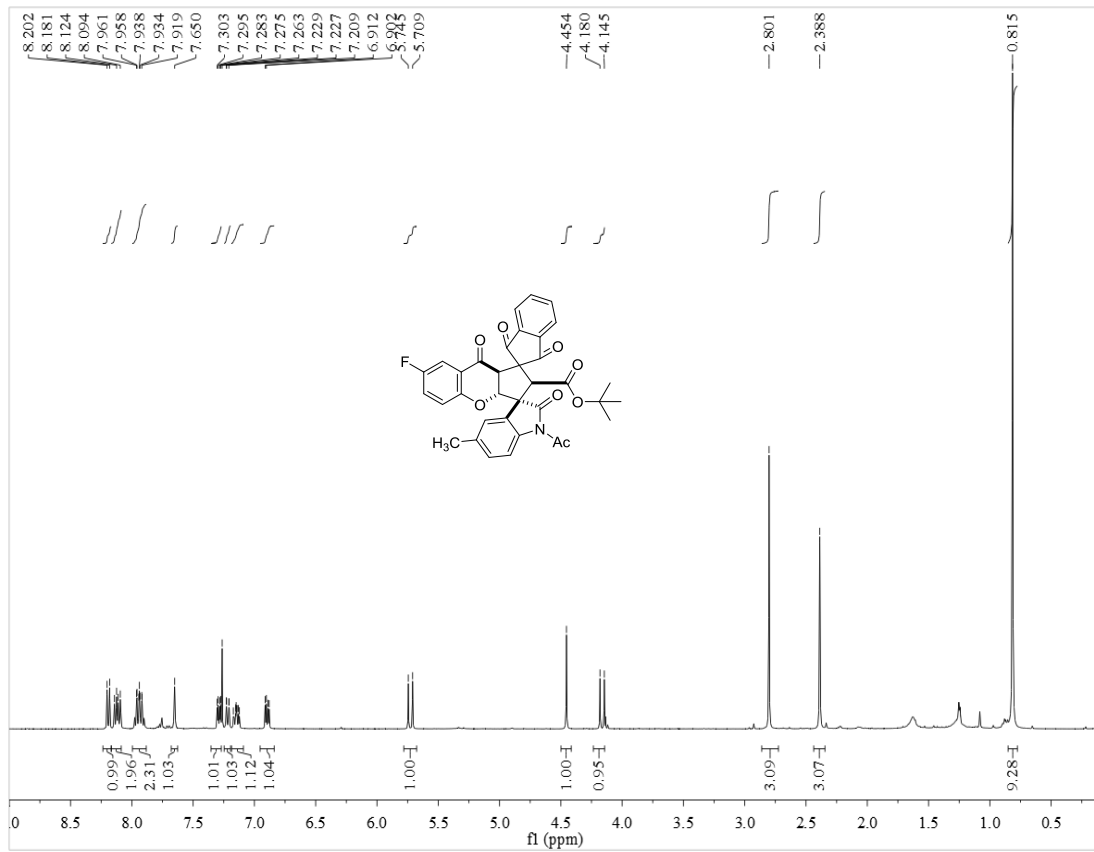




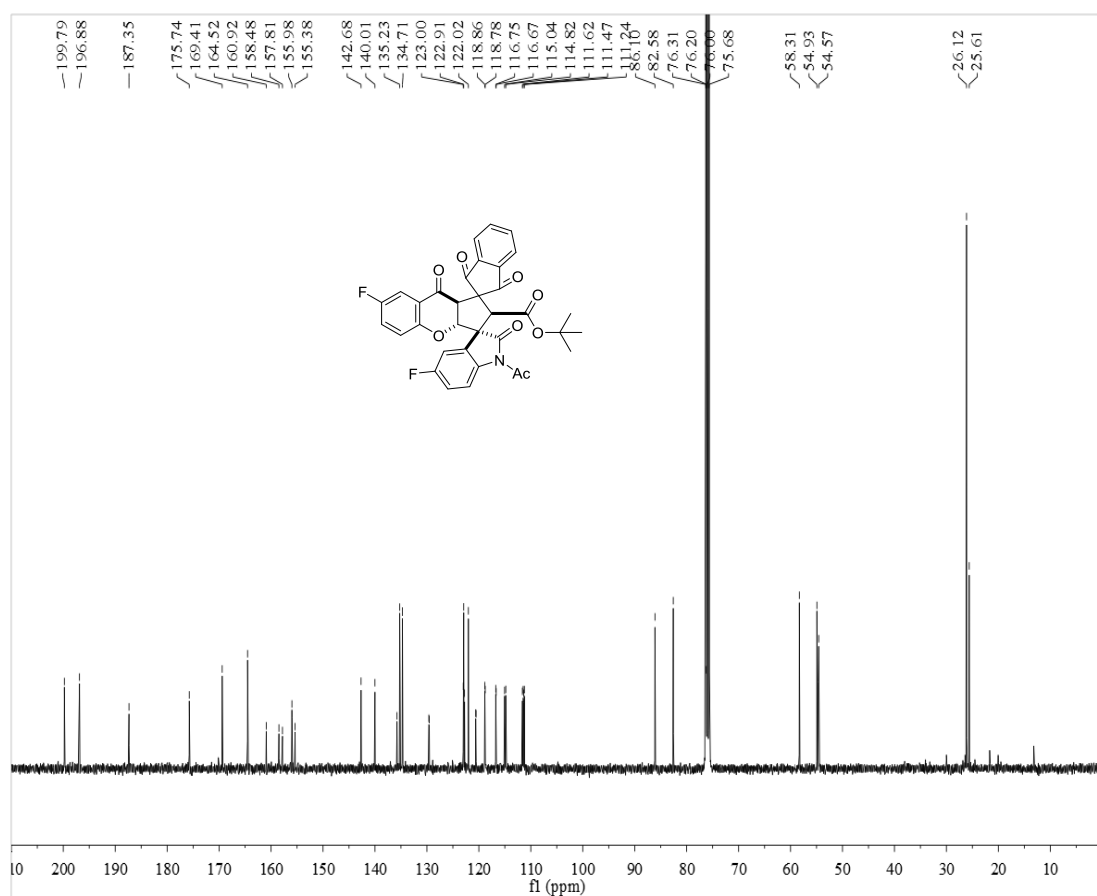
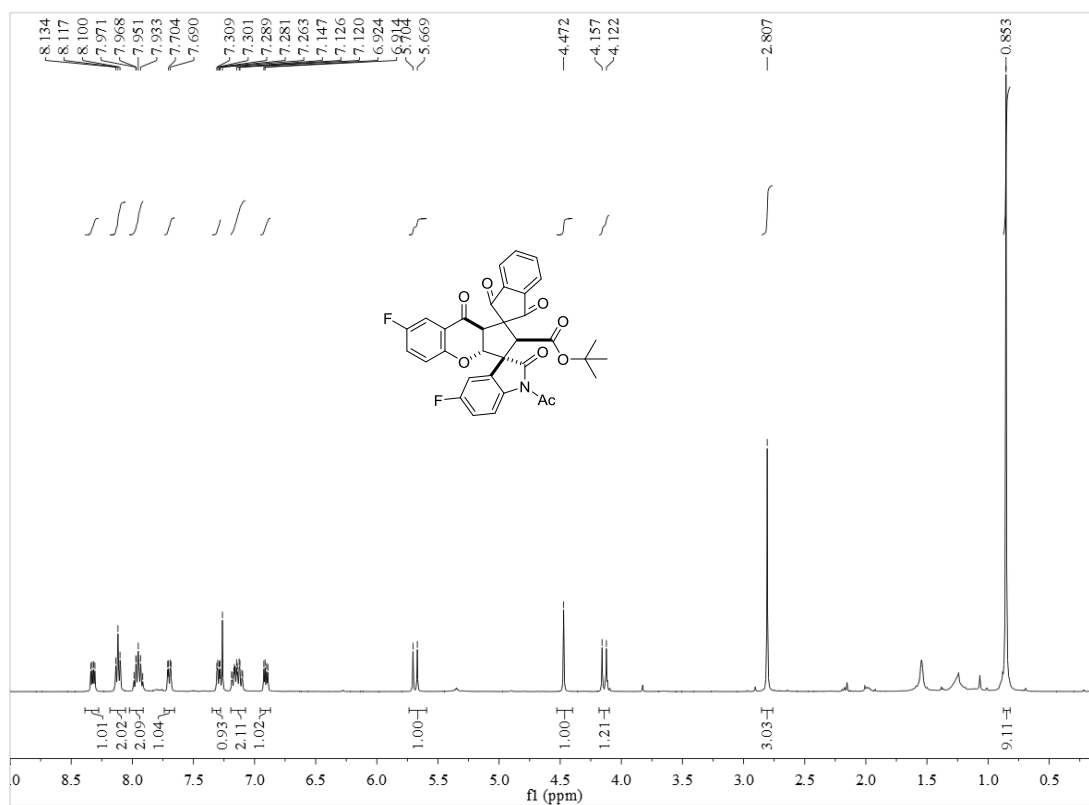
**<sup>1</sup>H and <sup>13</sup>C NMR of 3t**



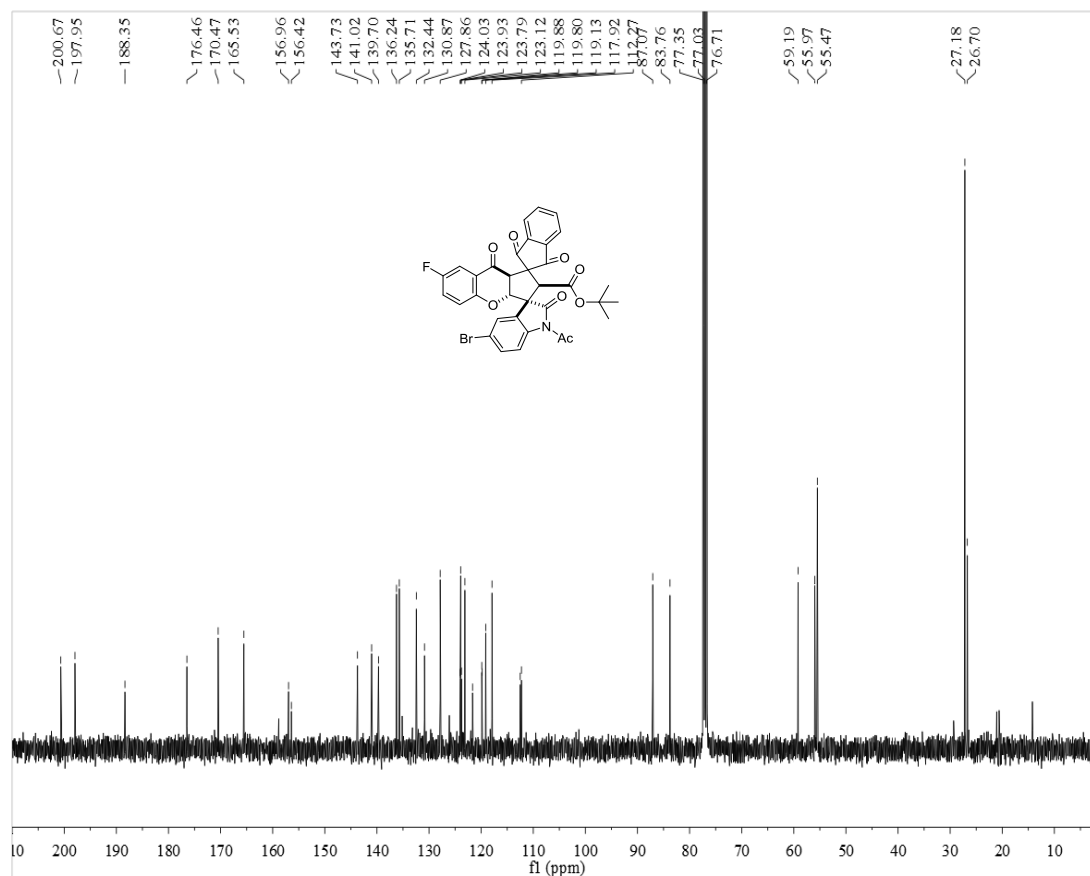
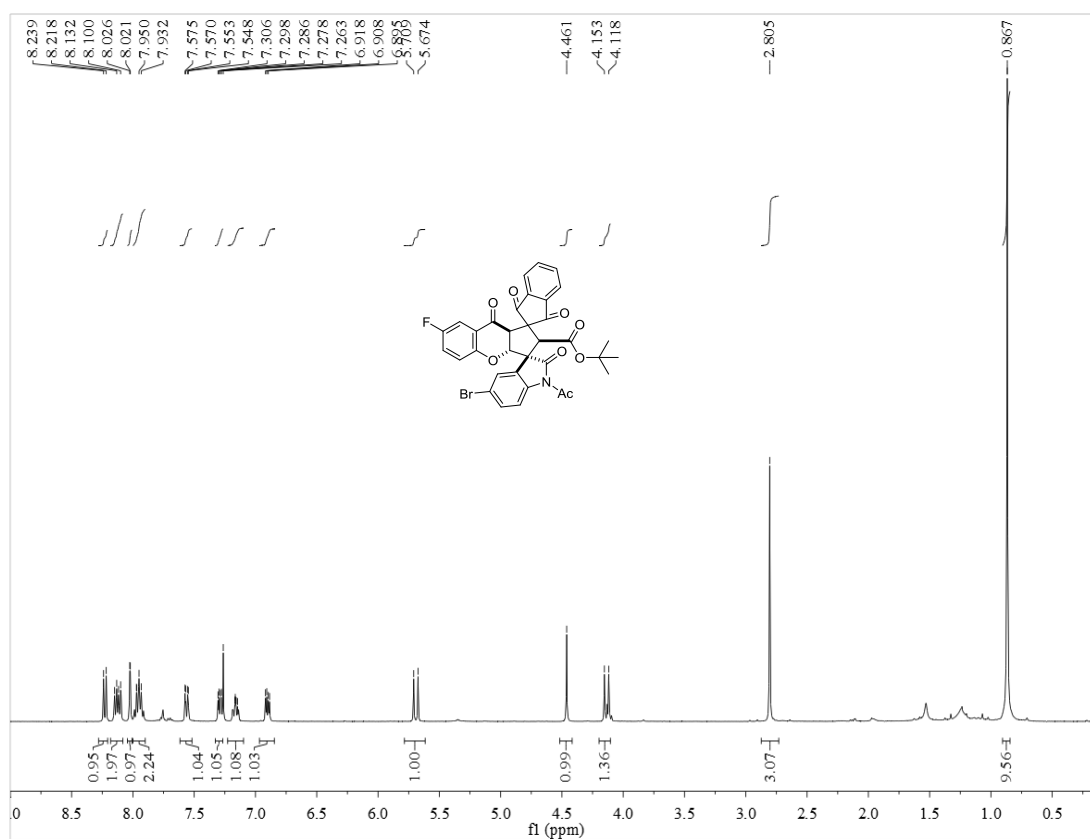
# $^1\text{H}$ and $^{13}\text{C}$ NMR of 3u



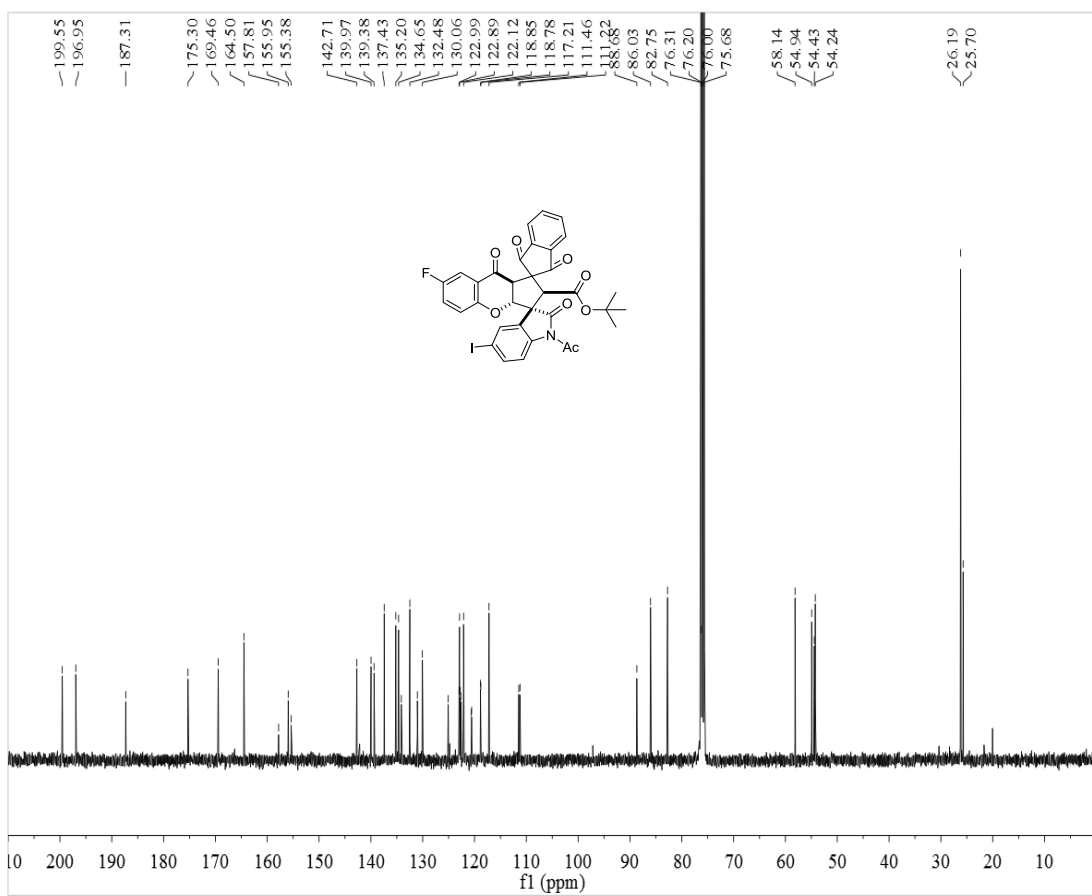
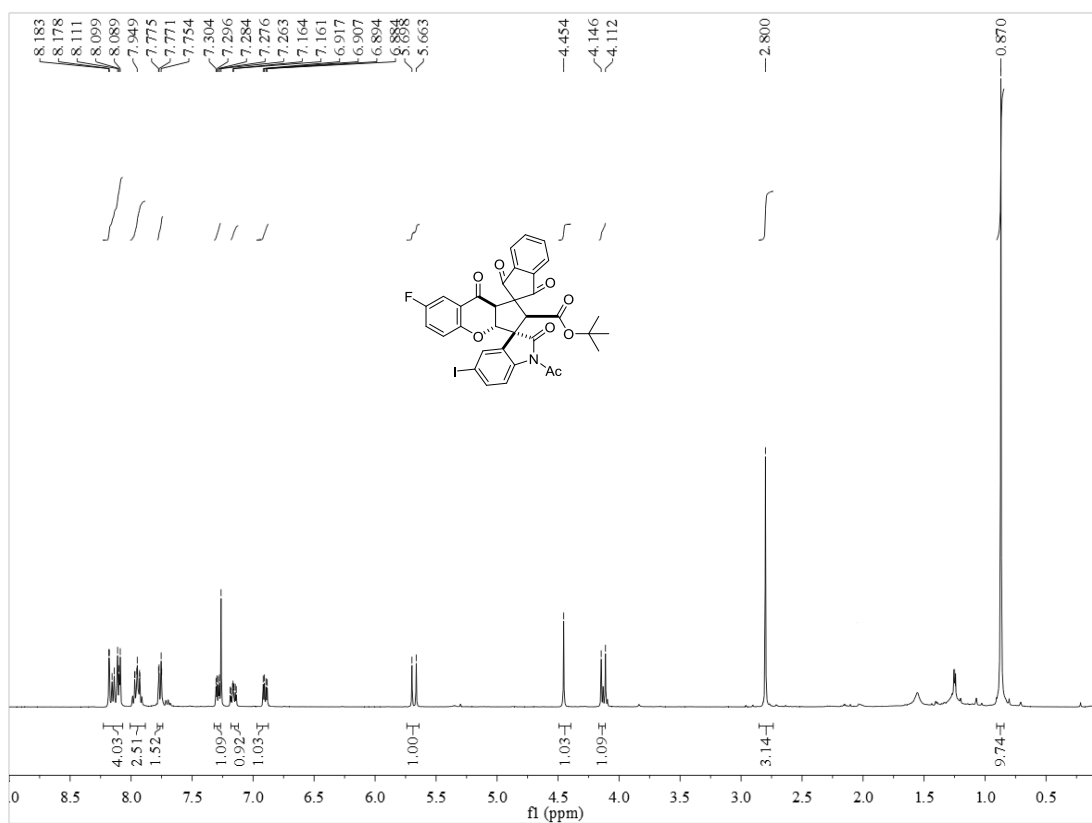
# $^1\text{H}$ and $^{13}\text{C}$ NMR of 3v



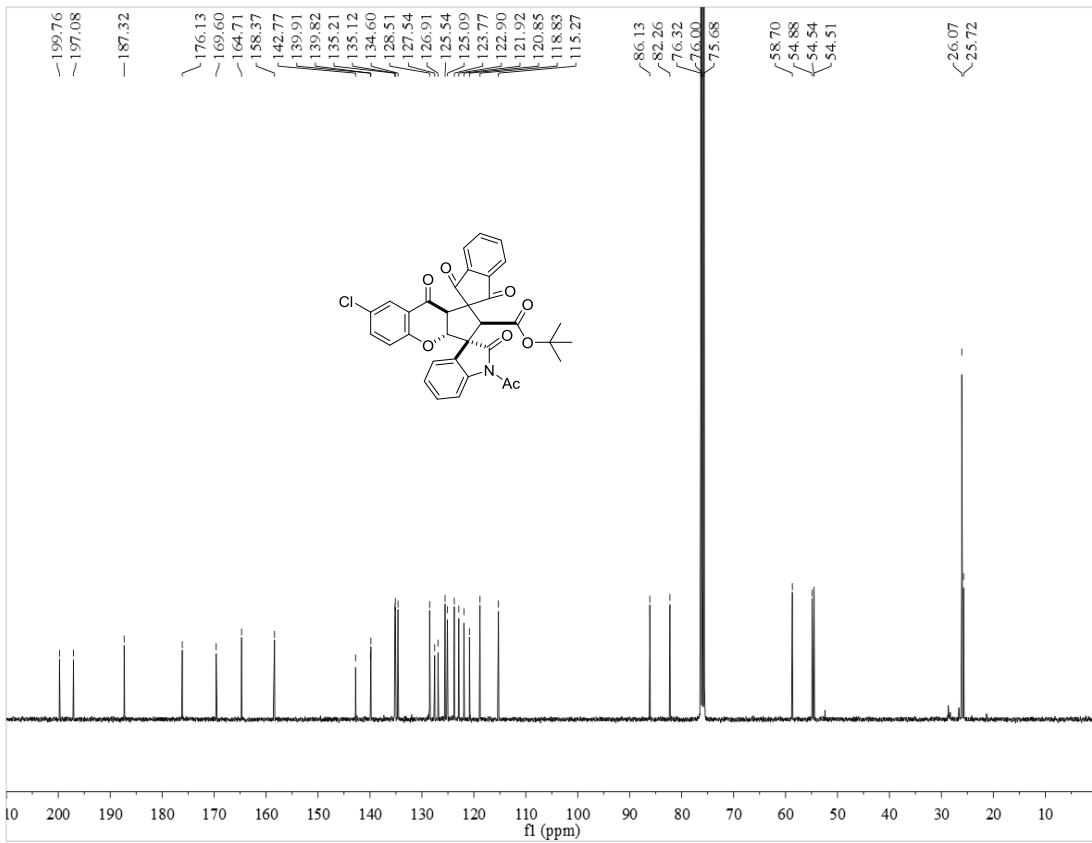
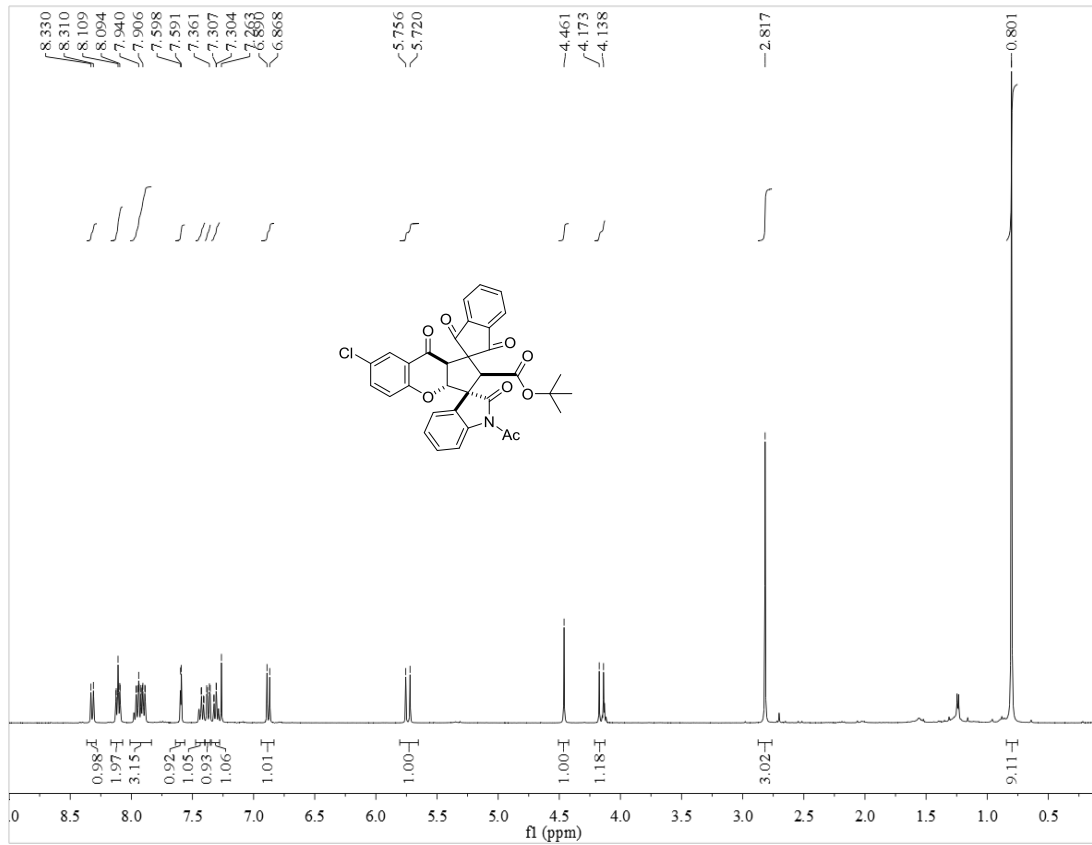
# $^1\text{H}$ and $^{13}\text{C}$ NMR of 3w



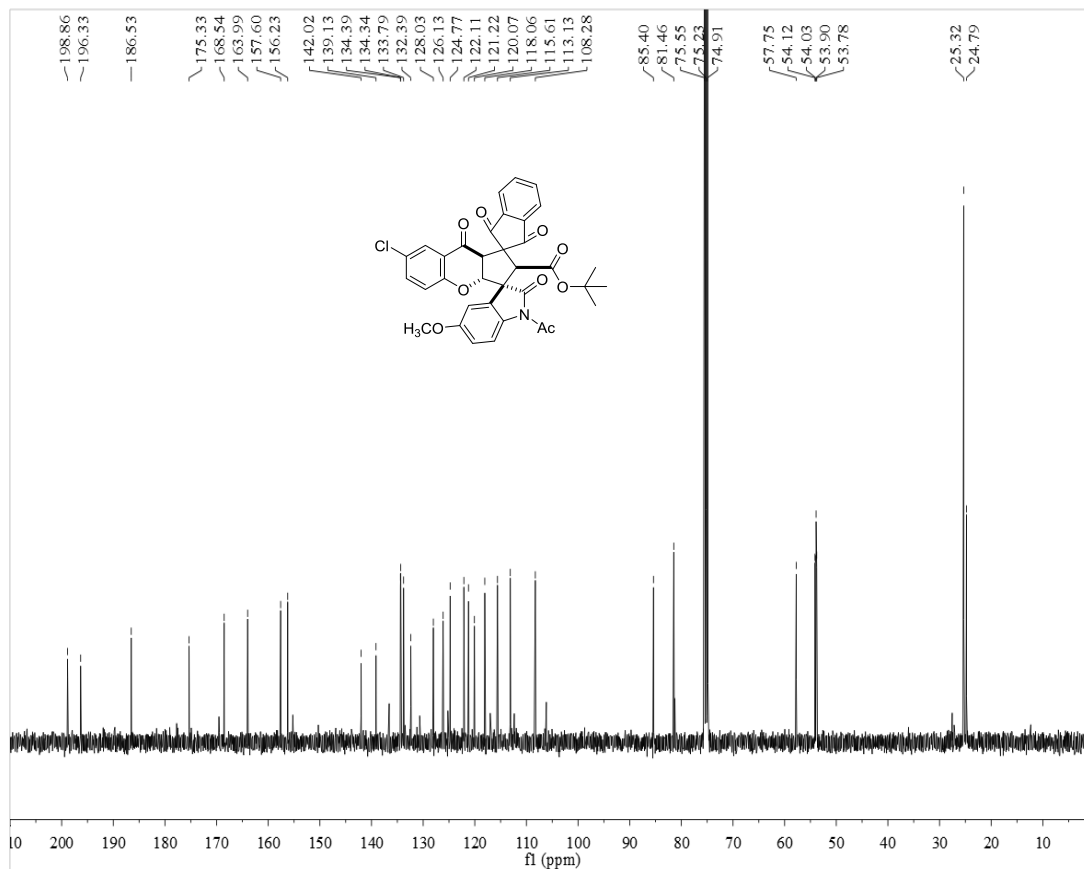
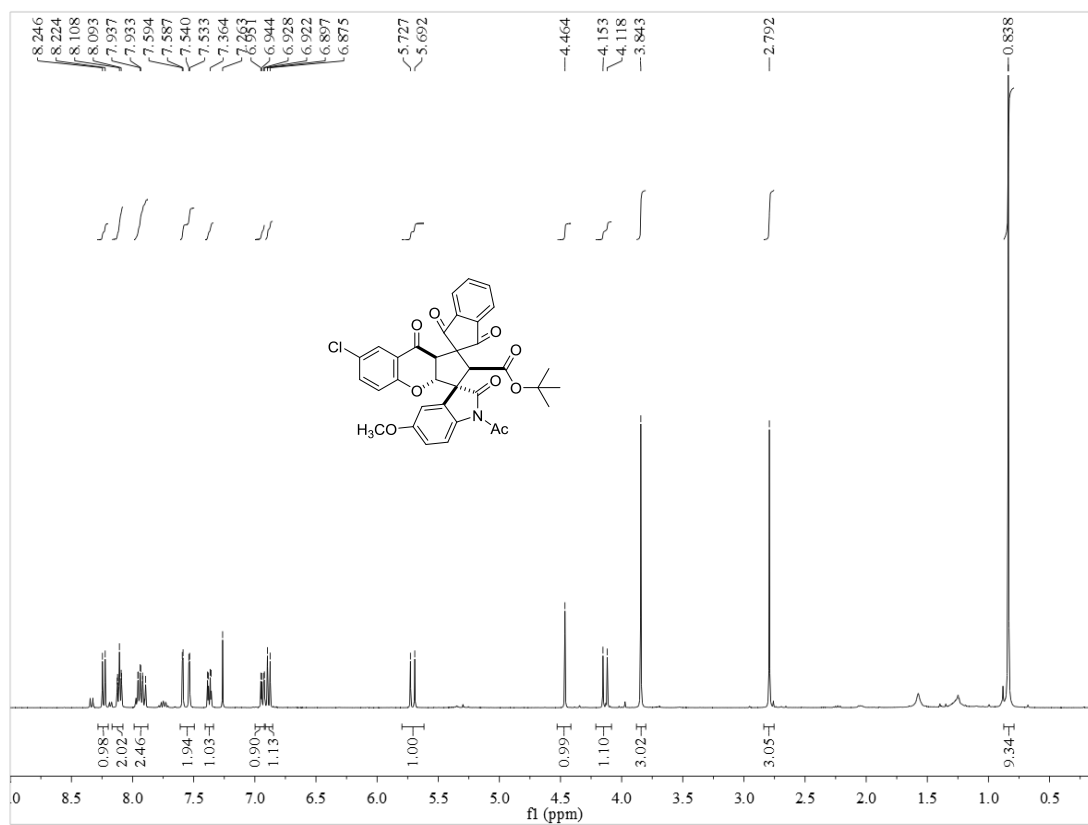
# <sup>1</sup>H and <sup>13</sup>C NMR of 3x



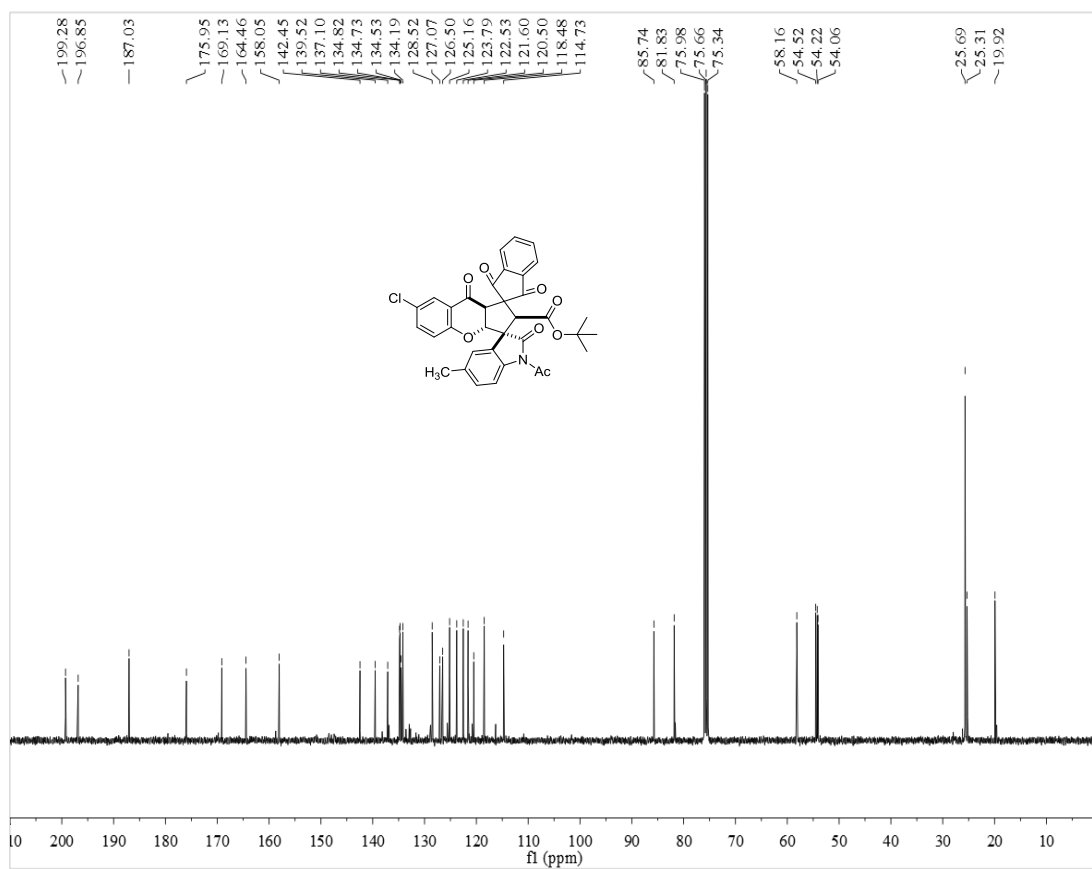
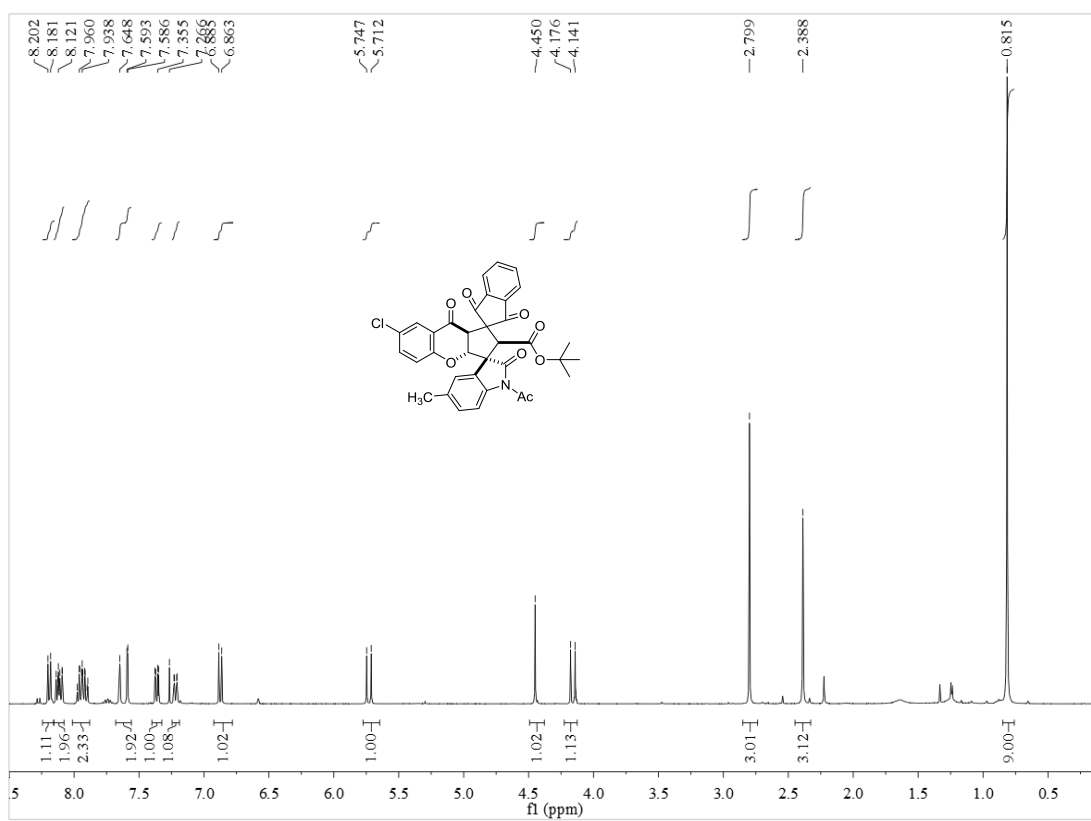
# <sup>1</sup>H and <sup>13</sup>C NMR of 3y



# $^1\text{H}$ and $^{13}\text{C}$ NMR of 3z

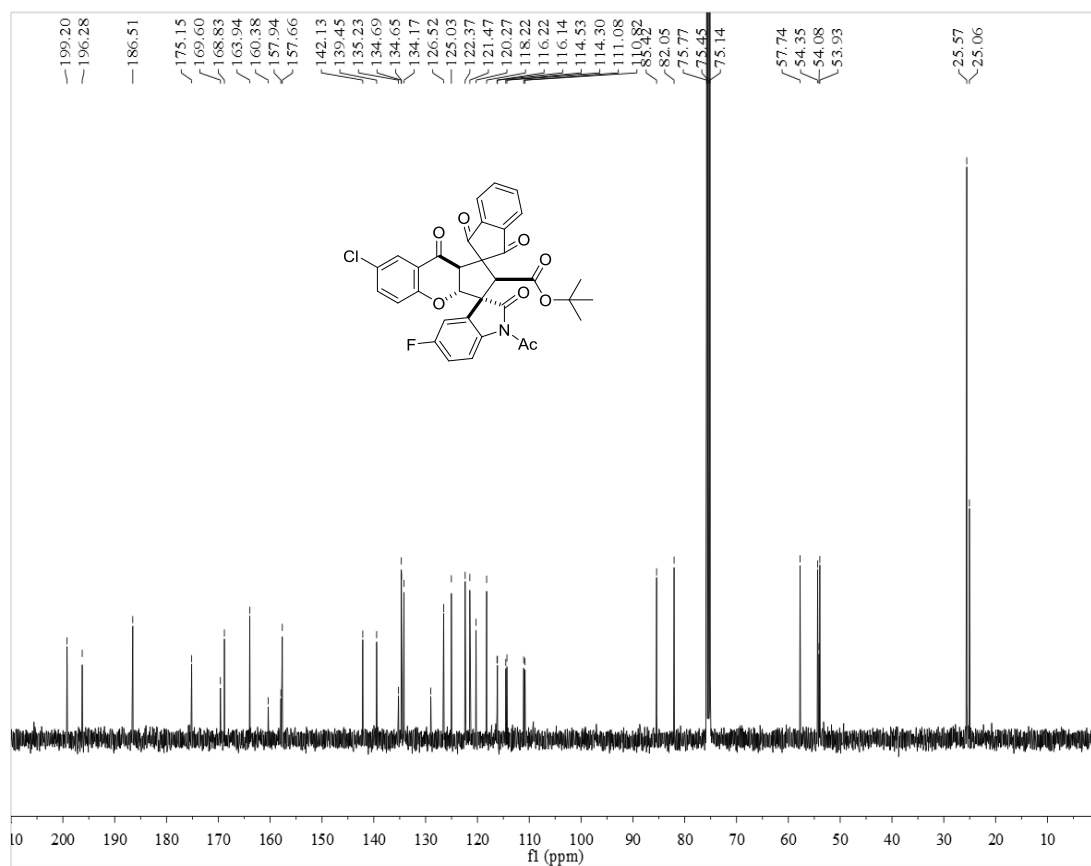
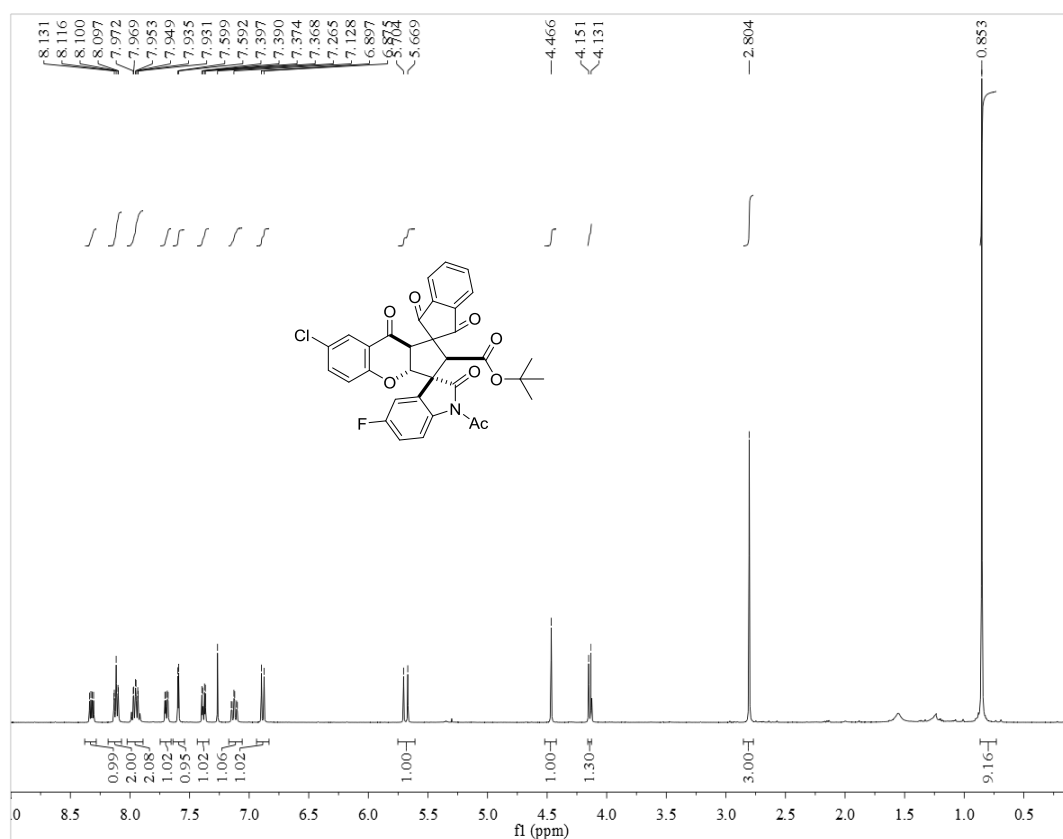


# <sup>1</sup>H and <sup>13</sup>C NMR of 3za

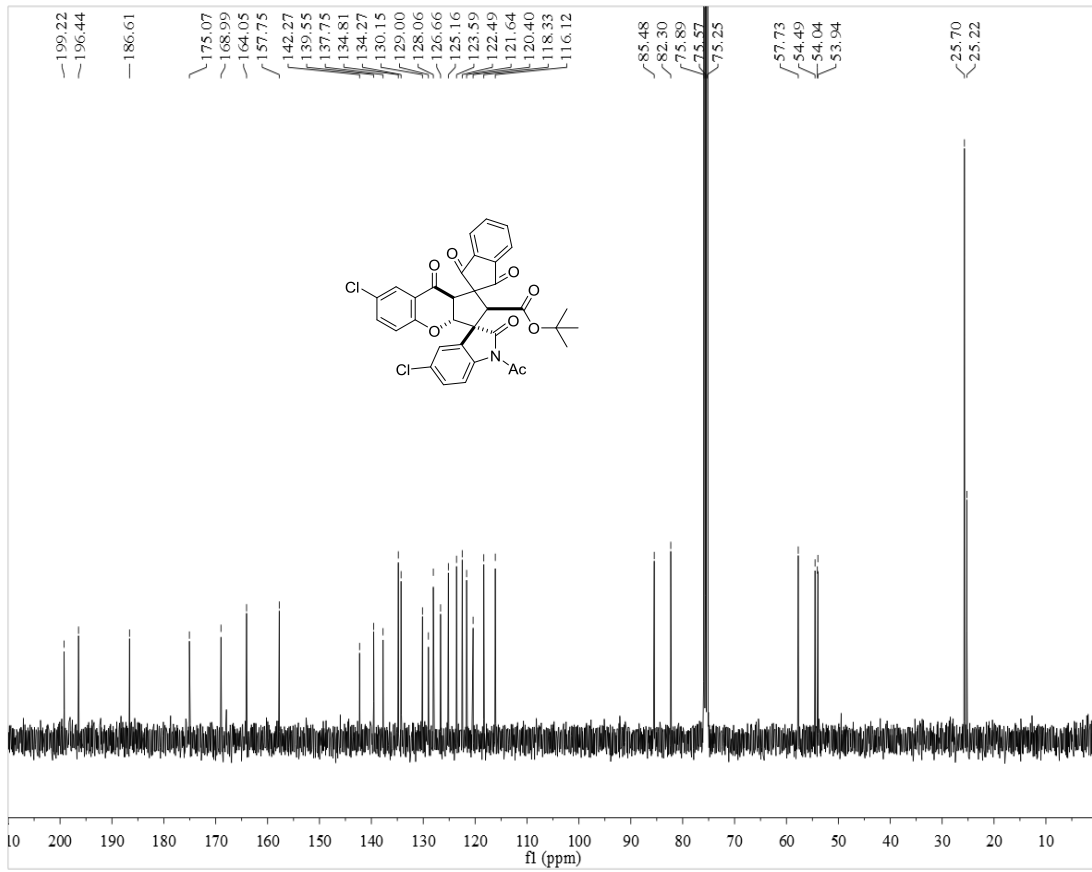
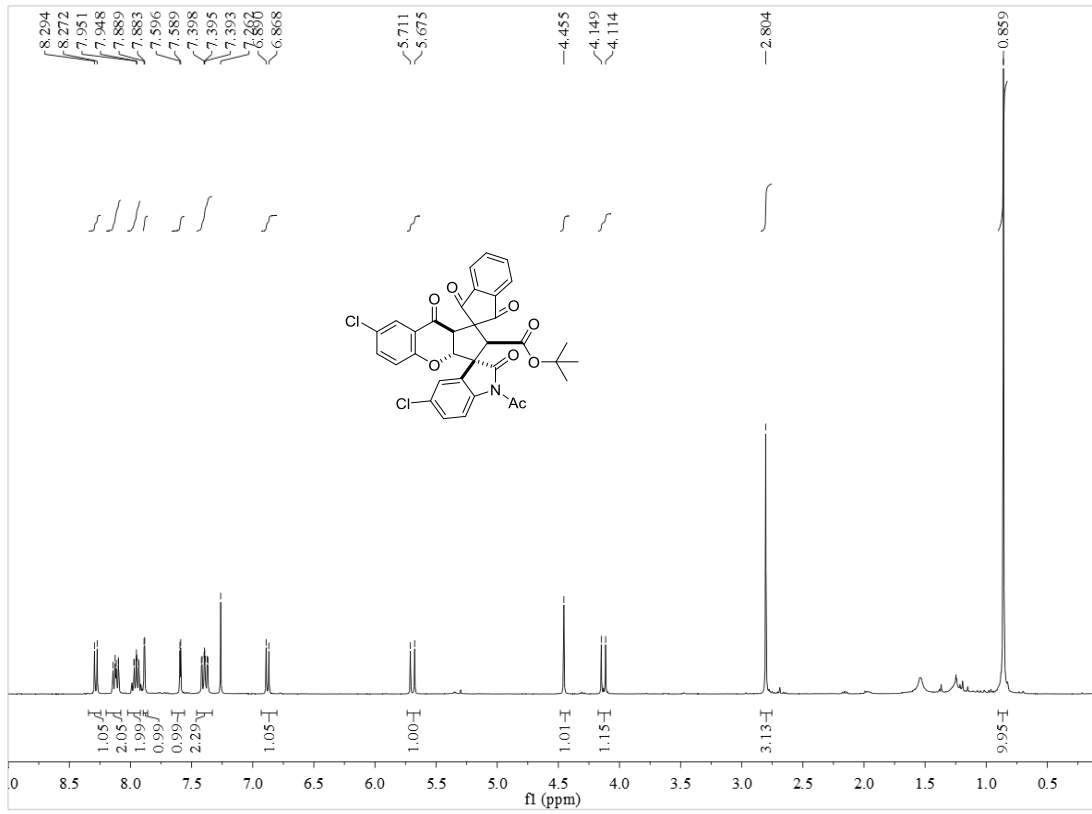




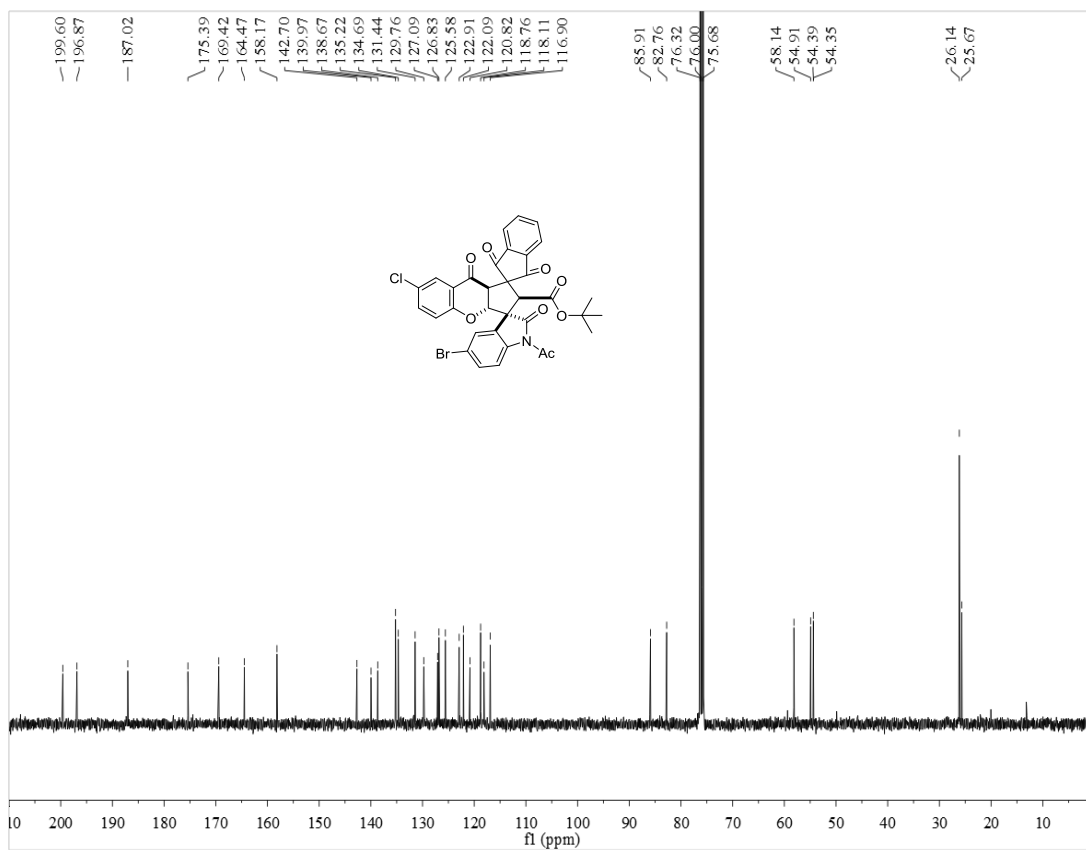
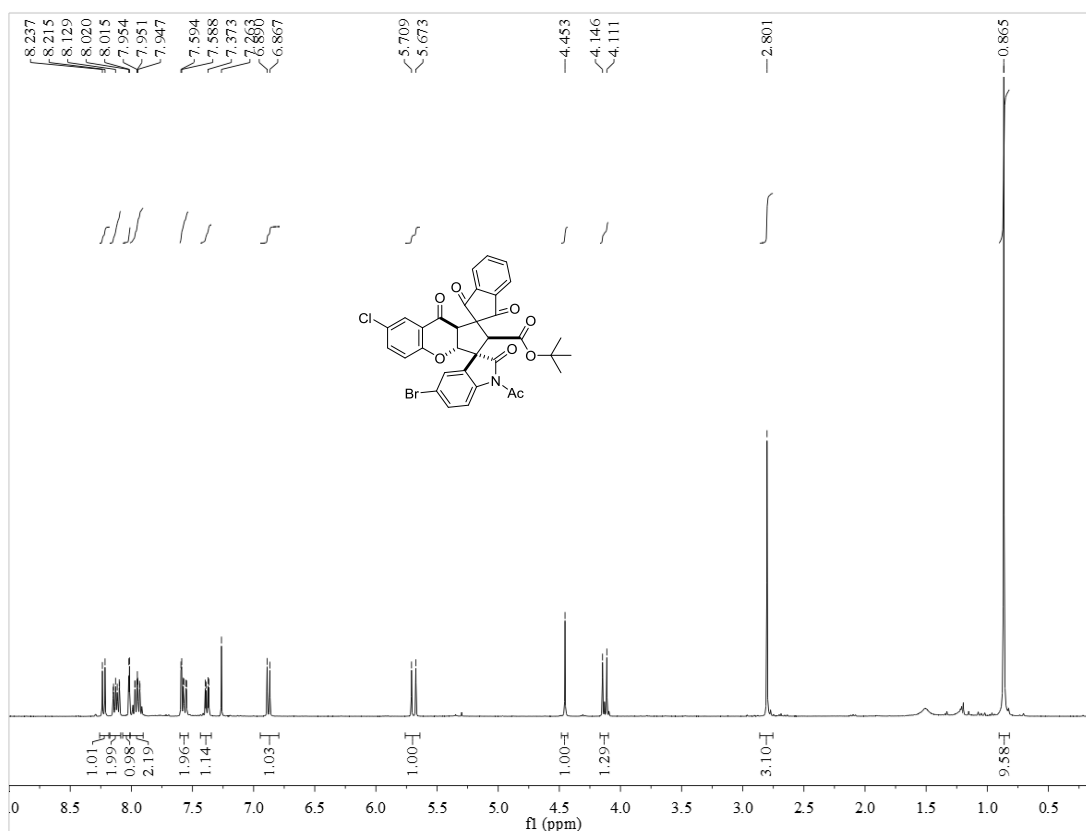
# <sup>1</sup>H and <sup>13</sup>C NMR of 3zb



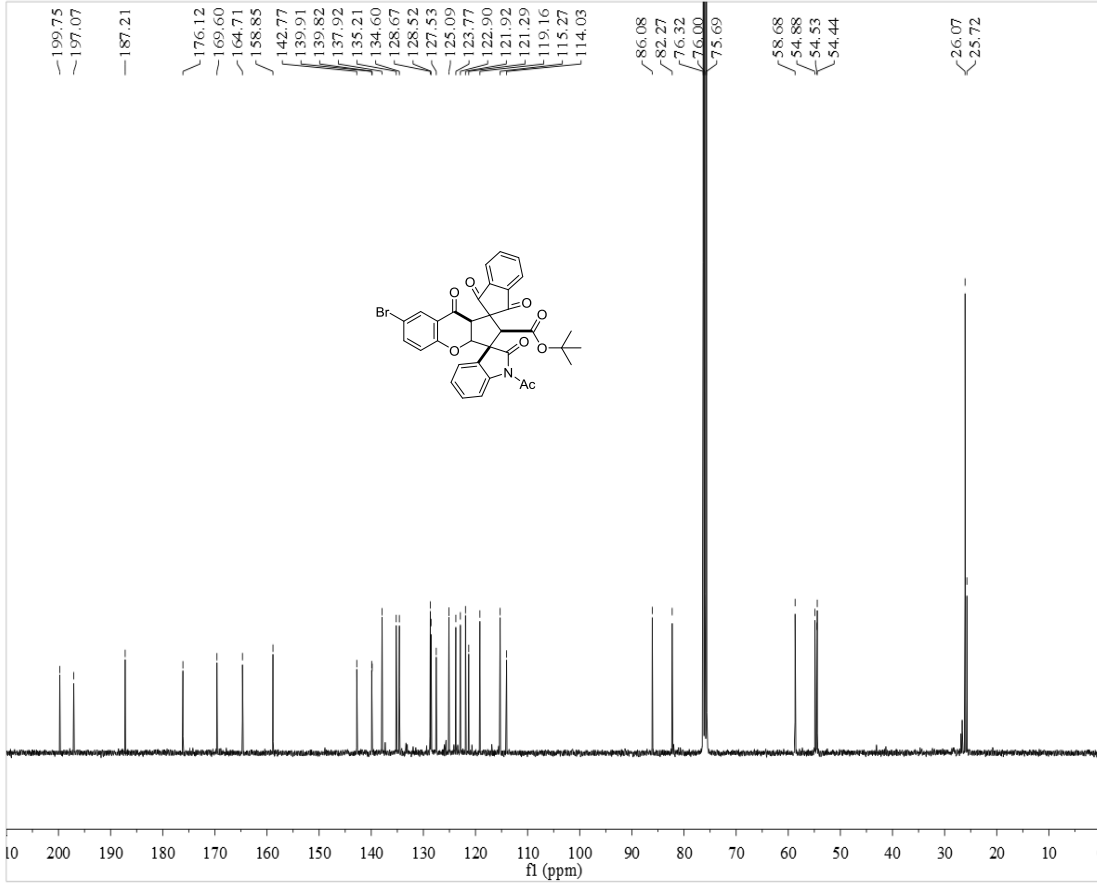
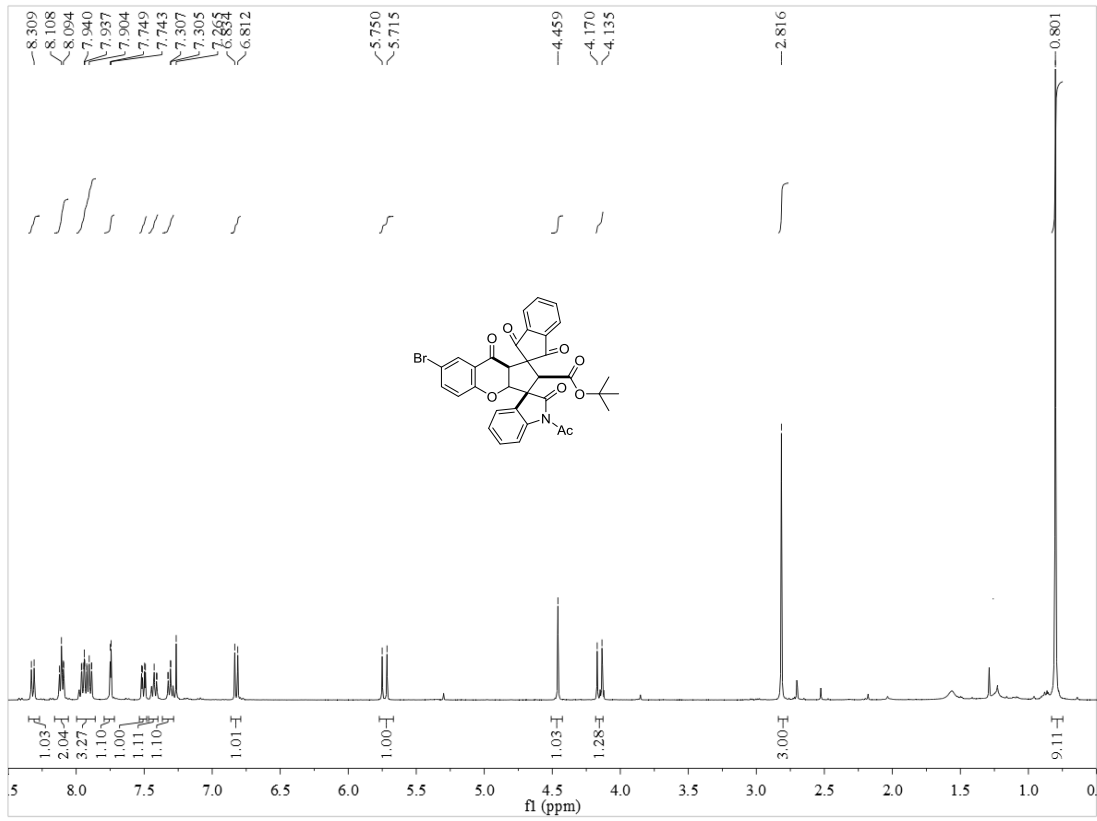
# <sup>1</sup>H and <sup>13</sup>C NMR of 3zc



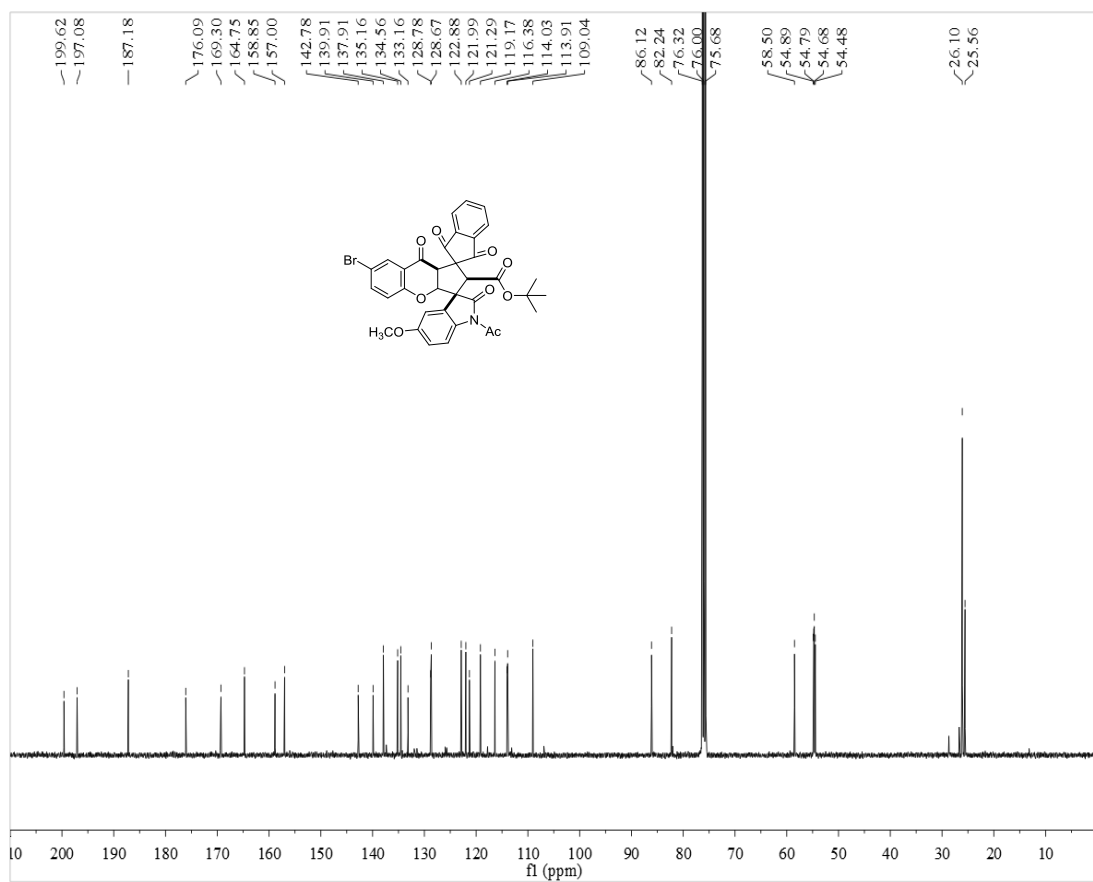
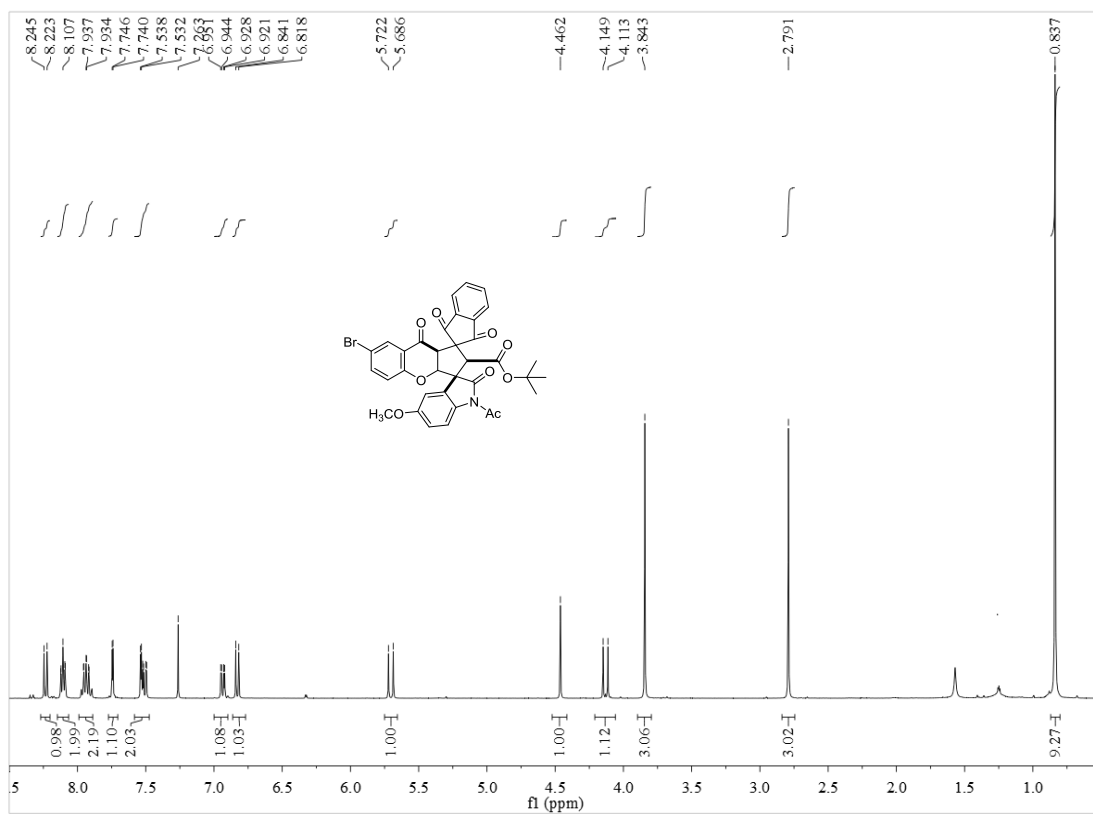
# <sup>1</sup>H and <sup>13</sup>C NMR of 3zd



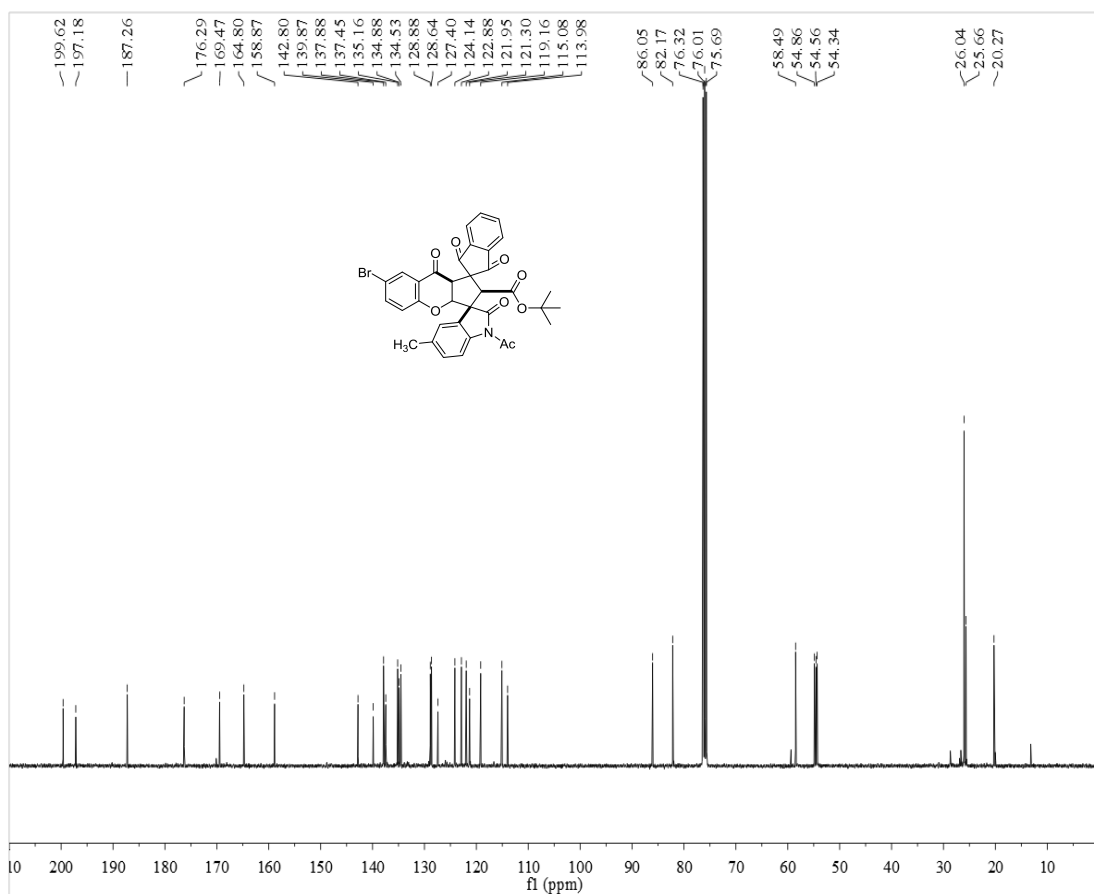
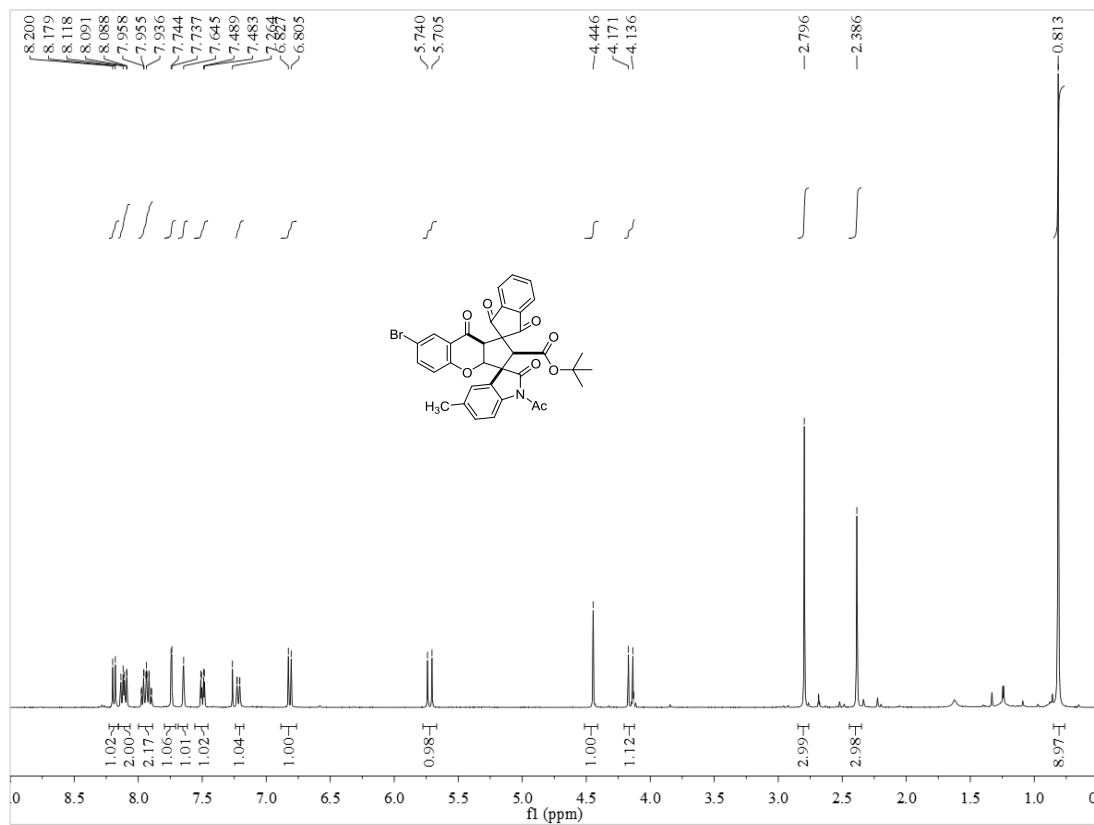
# <sup>1</sup>H and <sup>13</sup>C NMR of 3ze



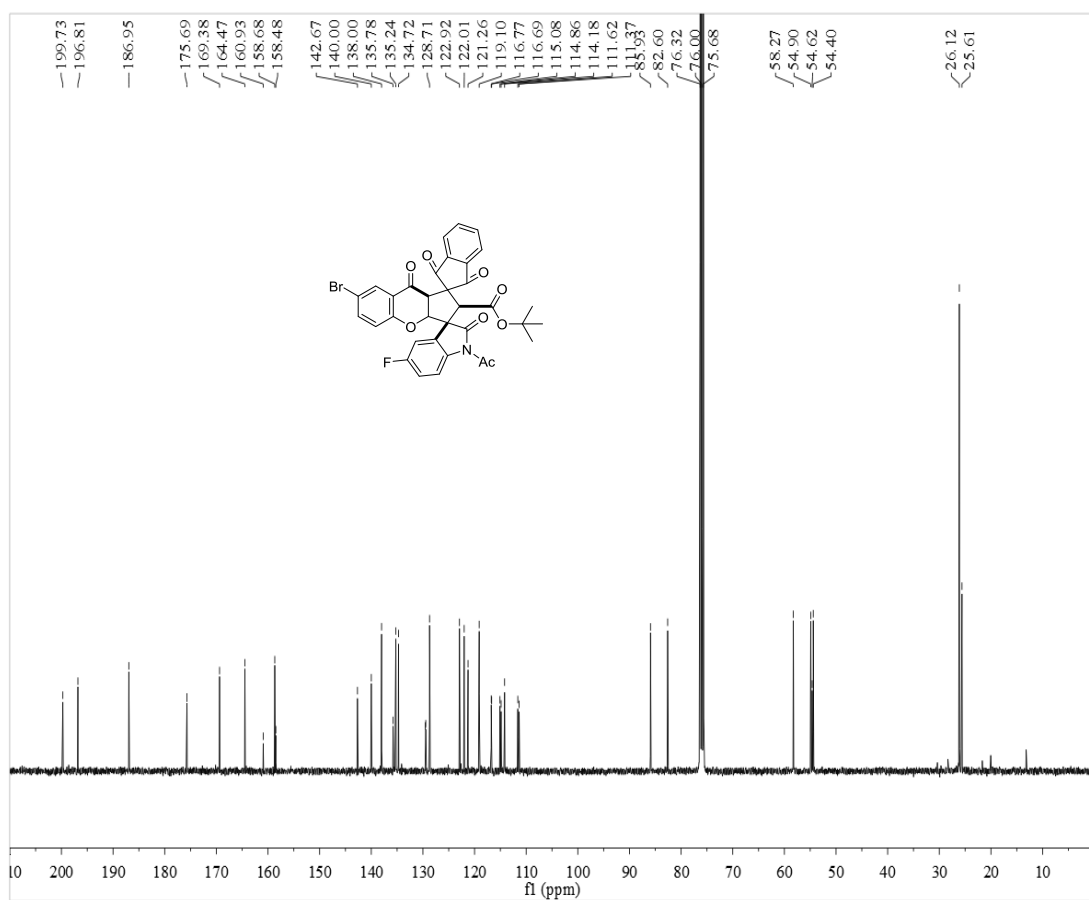
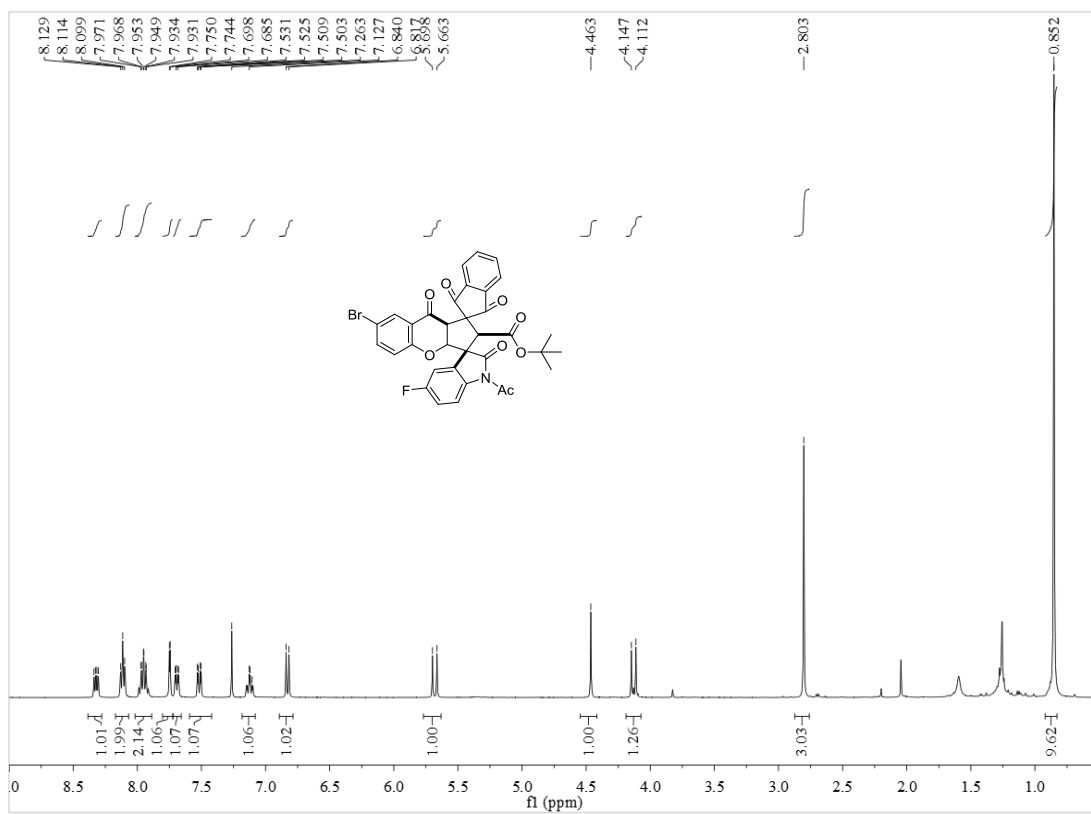
# <sup>1</sup>H and <sup>13</sup>C NMR of 3zf



# <sup>1</sup>H and <sup>13</sup>C NMR of 3zg



# $^1\text{H}$ and $^{13}\text{C}$ NMR of 3zh



# <sup>1</sup>H and <sup>13</sup>C NMR of 3zi

