

Regio- and stereoselective [3+2] cycloaddition reaction: access  
to isoxazole-dispirobisoxindoles featuring three contiguous stereocenters

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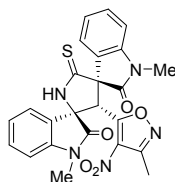
## 1: General experimental information

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 or DPX-500 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. Optical rotations were measured with a polarimeter with the solvent indicated. Melting points were measured on an electrothermal digital melting point apparatus.

## 2. Typical experimental procedures for catalytic asymmetric synthesis of isoxazole-dispirobisoxindoles **3**

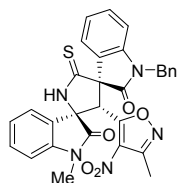
In an ordinary vial equipped with a magnetic stirring bar, the compound **2** (0.13 mmol, 1.3 equiv.), 5Å molecular sieve (180 mg) and catalyst quinine (3.24 mg, 10 mmol %, 0.01 mmol) were dissolved in 25.0 mL of freshly distilled DCM at  $-35\text{ }^\circ\text{C}$ , and then 3-isothiocyanato oxindole **1** (0.1 mmol) was added. After completion of the reaction, as indicated by TLC, the reaction mixture was directly purified by flash chromatography to yield the desired product **3**.

## 3. Characterization data and HPLC conditions of compounds **3**

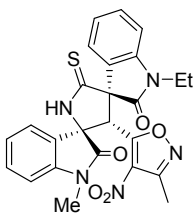


**3aa**: White solid, m.p. 215.2-217.0  $^\circ\text{C}$ ; Yield 93%; 90% ee, >20:1 dr,  $[\alpha]_{\text{D}}^{20} = 129.64$  (c 0.37,  $\text{CH}_2\text{Cl}_2$ ); The ee was determined by HPLC analysis using a Chiralpak IF column (80/20 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254\text{ nm}$ ;  $\tau_{\text{major}} = 32.94\text{ min}$ ;  $\tau_{\text{minor}} = 25.33\text{ min}$ );  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 2.07 (s, 3H), 3.10 (s, 3H), 3.11 (s, 3H), 5.88 (s, 1H), 6.97-7.02 (m, 2H),

7.08-7.12 (m, 1H), 7.15-7.18 (m, 1H), 7.29-7.33 (m, 1H), 7.36-7.40 (m, 1H), 7.64 (d,  $J = 7.6$  Hz, 1H), 7.75 (d,  $J = 7.2$  Hz, 1H), 11.32 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 11.3, 27.4, 27.5, 49.6, 70.5, 72.6, 109.5, 110.0, 123.0, 123.3, 125.1, 126.9, 127.8, 130.3, 131.6, 144.0, 145.1, 155.4, 166.0, 173.5, 173.8, 200.2; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{24}\text{H}_{19}\text{N}_5\text{NaO}_5\text{S}$   $[\text{M}+\text{Na}]^+$ : 512.0999; Found: 512.1004.

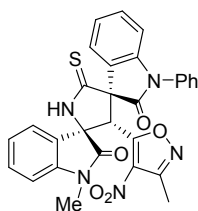


**3ab**: White solid, m.p. 174.5-176.1 °C; Yield 96%; 88% ee, >20:1 dr,  $[\alpha]_{\text{D}}^{20} = 137.00$  (c 0.46,  $\text{CH}_2\text{Cl}_2$ ); The ee was determined by HPLC analysis using a Chiralpak IF column (80/20 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 83.70$  min;  $\tau_{\text{minor}} = 51.02$  min);  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 2.09 (s, 3H), 3.12 (s, 3H), 4.75 (d,  $J = 16.0$  Hz, 1H), 5.00 (d,  $J = 16.0$  Hz, 1H), 6.00 (s, 1H), 6.77 (d,  $J = 8.0$  Hz, 1H), 7.03 (d,  $J = 8.0$  Hz, 1H), 7.07-7.10 (m, 1H), 7.17-7.26 (m, 5H), 7.33 (d,  $J = 6.8$  Hz, 2H), 7.37-7.41 (m, 1H), 7.70 (d,  $J = 7.6$  Hz, 1H), 7.81 (d,  $J = 7.6$  Hz, 1H), 11.42 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 11.4, 27.5, 43.9, 49.7, 70.6, 72.7, 110.0, 110.2, 124.9, 127.6, 127.8, 127.9, 129.0, 131.8, 136.2, 144.0, 144.1, 155.4, 165.8, 173.8, 200.0; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{30}\text{H}_{23}\text{N}_5\text{NaO}_5\text{S}$   $[\text{M}+\text{Na}]^+$ : 588.1312; Found: 588.1315.

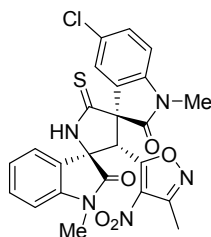


**3ac**: White solid, m.p. 139.9-142.0 °C; Yield 92%; 82% ee, >20:1 dr,  $[\alpha]_{\text{D}}^{20} = 140.61$  (c 0.27,  $\text{CH}_2\text{Cl}_2$ ); The ee was determined by HPLC analysis using a Chiralpak IF column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 49.71$  min;  $\tau_{\text{minor}} = 18.79$  min);  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 1.06-1.09 (m, 3H), 2.07 (s, 3H), 3.11 (s, 3H), 3.66-3.68 (m, 2H), 5.90 (s, 1H), 7.01-7.09 (m, 3H), 7.16-7.20 (m, 1H), 7.26-7.31 (m, 1H), 7.37-7.41 (m, 1H), 7.61 (d,  $J = 7.2$  Hz, 1H), 7.78 (d,  $J = 7.2$  Hz, 1H), 11.32 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 11.3, 12.6, 27.4, 49.4, 70.4, 72.5, 109.6, 109.9, 122.8, 123.3, 125.3, 127.1, 127.8, 130.4, 131.6, 144.1, 155.4, 166.0, 173.1, 173.8, 200.0; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{25}\text{H}_{21}\text{N}_5\text{NaO}_5\text{S}$   $[\text{M}+\text{Na}]^+$ :

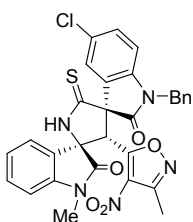
526.1156; Found: 526.1159.



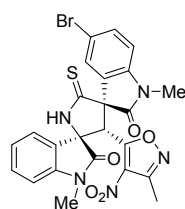
**3ad**: White solid, m.p. 242.7-243.6 °C; Yield 90%; 94% ee, >20:1 dr,  $[\alpha]_{\text{D}}^{20} = 219.68$  (c 0.21, CH<sub>2</sub>Cl<sub>2</sub>); The ee was determined by HPLC analysis using a Chiralpak IF column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 51.34$  min;  $\tau_{\text{minor}} = 22.04$  min); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$ : 2.11 (s, 3H), 3.12 (s, 3H), 5.95 (s, 3H), 6.67 (d,  $J = 7.2$  Hz, 1H), 7.04 (d,  $J = 7.6$  Hz, 1H), 7.10-7.14 (m, 1H), 7.19-7.26 (m, 2H), 7.36-7.47 (m, 4H), 7.55-7.59 (m, 2H), 7.66 (d,  $J = 7.6$  Hz, 1H), 7.81 (d,  $J = 7.2$  Hz, 1H), 11.43 (br s, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz)  $\delta$ : 11.3, 27.4, 49.6, 70.7, 72.7, 109.9, 125.4, 126.5, 127.1, 128.9, 130.3, 131.6, 134.4, 144.1, 144.9, 155.4, 166.4, 173.7, 200.0; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>29</sub>H<sub>21</sub>N<sub>5</sub>NaO<sub>5</sub>S [M+Na]<sup>+</sup>: 574.1156; Found: 574.1155.



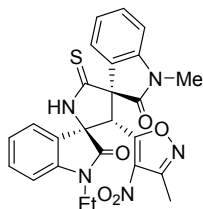
**3ae**: White solid, m.p. 158.9-160.7 °C; Yield 90%; 83% ee, >20:1 dr,  $[\alpha]_{\text{D}}^{20} = 216.00$  (c 0.33, CH<sub>2</sub>Cl<sub>2</sub>); The ee was determined by HPLC analysis using a Chiralpak IF column (93/7 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 23.77$  min;  $\tau_{\text{minor}} = 31.83$  min); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$ : 2.10 (s, 3H), 3.10 (s, 3H), 3.11 (s, 3H), 5.86 (s, 1H), 7.00-7.06 (m, 2H), 7.16-7.20 (m, 1H), 7.36-7.42 (m, 2H), 7.56 (s, 1H), 7.65 (d,  $J = 7.6$  Hz, 1H), 11.43 (br s, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz)  $\delta$ : 11.3, 27.4, 27.7, 49.4, 70.5, 72.7, 110.0, 111.1, 123.3, 124.9, 126.2, 126.5, 126.7, 129.6, 144.0, 144.3, 155.5, 165.9, 173.2, 173.7, 199.4; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>24</sub>H<sub>18</sub>ClN<sub>5</sub>NaO<sub>5</sub>S [M+Na]<sup>+</sup>: 546.0609; Found: 546.0607.



**3af**: White solid, m.p. 119.6-121.3 °C; Yield 90%; 80% ee, >20:1 dr,  $[\alpha]_{\text{D}}^{20} = 137.34$  (c 0.37, CH<sub>2</sub>Cl<sub>2</sub>); The ee was determined by HPLC analysis using a Chiralpak IF column (80/20 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 23.75$  min;  $\tau_{\text{minor}} = 29.04$  min); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$ : 2.11 (s, 3H), 4.73 (d,  $J = 16.4$  Hz, 1H), 5.04 (d,  $J = 16.0$  Hz, 1H), 5.98 (s, 1H), 6.82 (d,  $J = 8.8$  Hz, 1H), 7.03 (d,  $J = 7.6$  Hz, 1H), 7.17-7.28 (m, 4H), 7.30-7.41 (m, 4H), 7.62 (d,  $J = 2.0$  Hz, 1H), 7.69 (d,  $J = 7.6$  Hz, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz)  $\delta$ : 11.4, 27.4, 44.1, 49.6, 70.6, 72.8, 110.0, 111.8, 123.4, 124.7, 126.9, 127.6, 129.0, 129.7, 131.9, 135.8, 143.2, 144.1, 155.5, 165.7, 173.5, 173.6, 199.2; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>30</sub>H<sub>22</sub>ClN<sub>5</sub>NaO<sub>5</sub>S [M+Na]<sup>+</sup>: 622.0922; Found: 622.0927.

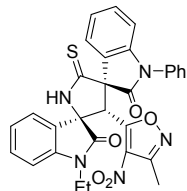


**3ag**: White solid, m.p. 252.2-254.0 °C; Yield 93%; 75% ee, >20:1 dr,  $[\alpha]_{\text{D}}^{20} = 237.05$  (c 0.24, CH<sub>2</sub>Cl<sub>2</sub>); The ee was determined by HPLC analysis using a Chiralpak IC column (85/15 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 18.57$  min;  $\tau_{\text{minor}} = 37.38$  min); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$ : 2.10 (s, 3H), 3.10 (s, 3H), 3.11 (s, 3H), 5.86 (s, 1H), 6.99-7.03 (m, 2H), 7.16-7.20 (m, 1H), 7.36-7.40 (m, 1H), 7.52-7.55 (m, 1H), 7.60 (d,  $J = 7.2$  Hz, 1H), 7.66 (s, 1H), 11.43 (br s, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz)  $\delta$ : 11.3, 27.4, 27.6, 49.4, 70.5, 72.7, 110.0, 111.7, 114.2, 123.3, 124.9, 126.4, 128.8, 129.9, 133.2, 144.1, 144.7, 155.5, 165.9, 173.1, 173.6, 199.4; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>24</sub>H<sub>18</sub>BrN<sub>5</sub>NaO<sub>5</sub>S [M+Na]<sup>+</sup>: 590.0104; Found: 590.0109.

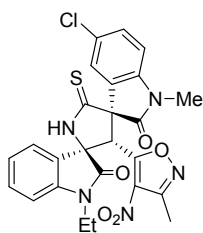


**3ba**: White solid, m.p. 213.6-215.2 °C; Yield 90%; 87% ee, >20:1 dr,  $[\alpha]_{\text{D}}^{20} = 98.63$  (c 0.39, CH<sub>2</sub>Cl<sub>2</sub>); The ee was determined by HPLC analysis using a Chiralpak IE column (85/15 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 33.76$  min;  $\tau_{\text{minor}} = 29.77$  min); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz)  $\delta$ : 1.09-1.12 (m, 3H), 2.11 (s, 3H), 3.14 (s, 3H), 3.64-3.74 (m, 2H), 5.96 (s,

1H), 7.02 (d,  $J = 8.0$  Hz, 1H), 7.07 (d,  $J = 8.0$  Hz, 1H), 7.13-7.19 (m, 2H), 7.34-7.41 (m, 2H), 7.71 (d,  $J = 8.0$  Hz, 1H), 7.77 (d,  $J = 7.5$  Hz, 1H), 11.39 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 125 MHz)  $\delta$ : 10.8, 12.0, 27.0, 34.9, 54.9, 70.0, 72.1, 109.0, 109.4, 122.5, 122.7, 124.6, 126.0, 127.4, 129.8, 131.2, 142.5, 144.6, 154.9, 165.4, 173.0, 199.8; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{25}\text{H}_{21}\text{N}_5\text{NaO}_5\text{S}$   $[\text{M}+\text{Na}]^+$ : 526.1156; Found: 526.1158.

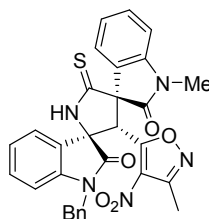


**3bd**: White solid, m.p. 223.3-225.4 °C; Yield 91%; 94% ee, >20:1 dr,  $[\alpha]_{\text{D}}^{20} = 142.01$  (c 0.20,  $\text{CH}_2\text{Cl}_2$ ); The ee was determined by HPLC analysis using a Chiralpak IF column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 23.40$  min;  $\tau_{\text{minor}} = 14.71$  min);  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz)  $\delta$ : 1.15-1.18 (m, 3H), 2.19 (s, 3H), 3.73-3.78 (m, 2H), 6.07 (s, 1H), 6.76 (d,  $J = 8.0$  Hz, 1H), 7.14 (d,  $J = 8.0$  Hz, 1H), 7.20-7.27 (m, 2H), 7.31-7.34 (m, 1H), 7.44-7.48 (m, 3H), 7.51-7.54 (m, 1H), 7.62-7.66 (m, 2H), 7.77 (d,  $J = 8.0$  Hz, 1H), 7.87 (d,  $J = 7.5$  Hz, 1H), 11.54 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 125 MHz)  $\delta$ : 10.9, 12.1, 35.0, 49.0, 70.2, 72.2, 109.4, 109.5, 122.7, 125.0, 126.6, 127.0, 128.5, 129.7, 134.0, 142.5, 144.5, 155.0, 165.8, 172.7, 172.9, 199.5; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{30}\text{H}_{23}\text{N}_5\text{NaO}_5\text{S}$   $[\text{M}+\text{Na}]^+$ : 588.1312; Found: 588.1315.

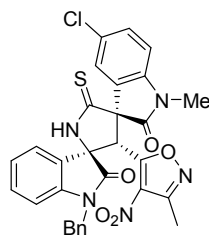


**3be**: White solid, m.p. 164.8-166.2 °C; Yield 94%; 79% ee, >20:1 dr,  $[\alpha]_{\text{D}}^{20} = 206.38$  (c 0.26,  $\text{CH}_2\text{Cl}_2$ ); The ee was determined by HPLC analysis using a Chiralpak IF column (55/45 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 33.77$  min;  $\tau_{\text{minor}} = 60.19$  min);  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz)  $\delta$ : 1.08-1.12 (m, 3H), 2.14 (s, 3H), 3.15 (s, 3H), 3.64-3.74 (m, 2H), 5.94 (s, 1H), 7.06-7.10 (m, 2H), 7.15-7.20 (m, 1H), 7.37-7.41 (m, 1H), 7.44-7.46 (m, 1H), 7.63-7.66 (m, 2H), 11.48 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 125 MHz)  $\delta$ : 11.3, 12.4, 27.6, 35.4, 49.3, 70.5, 72.7, 110.0, 111.1, 124.9, 126.3, 126.6, 129.6, 130.3, 131.7, 142.9, 144.3, 155.4, 165.8, 173.1, 173.3, 199.5, 218.0; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{25}\text{H}_{20}\text{ClN}_5\text{NaO}_5\text{S}$   $[\text{M}+\text{Na}]^+$ : 560.0766; Found:

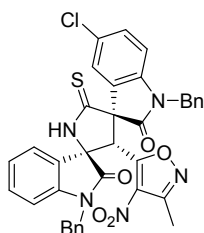
560.0769.



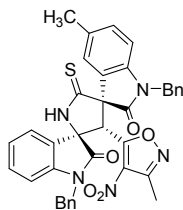
**3ca**: White solid, m.p. 126.5-128.2 °C; Yield 93%; 77% ee, 15:1 dr,  $[\alpha]_D^{20} = 145.20$  (c 0.27, CH<sub>2</sub>Cl<sub>2</sub>); The ee was determined by HPLC analysis using a Chiralpak IC column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 17.68$  min;  $\tau_{\text{minor}} = 34.33$  min); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 2.10 (s, 3H), 3.17 (s, 3H), 4.79 (d,  $J = 15.6$  Hz, 1H), 4.89 (d,  $J = 15.6$  Hz, 1H), 6.17 (s, 1H), 6.68 (d,  $J = 8.0$  Hz, 1H), 6.76 (d,  $J = 7.6$  Hz, 1H), 7.02-7.11 (m, 2H), 7.15-7.20 (m, 6H), 7.24-7.28 (m, 1H), 7.52-7.54 (m, 1H), 7.64-7.66 (m, 1H), 8.73 (br s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 10.3, 26.3, 43.8, 49.0, 68.9, 70.9, 107.9, 109.2, 121.9, 122.3, 126.5, 126.9, 127.9, 129.3, 134.0, 141.6, 143.8, 154.0, 164.4, 172.3, 172.8, 200.1; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>30</sub>H<sub>23</sub>N<sub>5</sub>NaO<sub>5</sub>S [M+Na]<sup>+</sup>: 588.1312; Found: 588.1312.



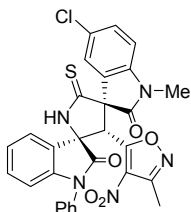
**3ce**: White solid, m.p. 186.7-188.1 °C; Yield 92%; 91% ee, 12:1 dr,  $[\alpha]_D^{20} = 220.92$  (c 0.29, CH<sub>2</sub>Cl<sub>2</sub>); The ee was determined by HPLC analysis using a Chiralpak IC column (75/25 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 18.71$  min;  $\tau_{\text{minor}} = 46.66$  min); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 2.13 (s, 3H), 3.13 (s, 3H), 4.78 (d,  $J = 15.6$  Hz, 1H), 4.87 (d,  $J = 15.6$  Hz, 1H), 6.15 (s, 1H), 6.67-6.71 (m, 1H), 7.05-7.09 (m, 1H), 7.14-7.25 (m, 7H), 7.50-7.52 (m, 1H), 7.57 (d,  $J = 7.6$  Hz, 1H), 8.83 (br s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 10.3, 26.5, 43.9, 48.7, 68.8, 71.0, 108.8, 109.3, 125.4, 126.5, 126.9, 127.1, 127.9, 129.3, 141.7, 142.4, 154.1, 164.1, 171.9, 172.7, 199.2; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>30</sub>H<sub>22</sub>ClN<sub>5</sub>NaO<sub>5</sub>S [M+Na]<sup>+</sup>: 622.0922; Found: 622.0925.



**3cf**: White solid, m.p. 200.1-201.7 °C; Yield 94%; 76% ee, >20:1 dr,  $[\alpha]_D^{20} = 293.56$  (c 0.15, CH<sub>2</sub>Cl<sub>2</sub>); The ee was determined by HPLC analysis using a Chiralpak IC column (65/35 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 38.46$  min;  $\tau_{\text{minor}} = 25.56$  min); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$ : 2.13 (s, 3H), 4.73-4.83 (m, 2H), 4.94-5.08 (m, 2H), 6.10 (s, 1H), 6.83-6.88 (m, 2H), 7.18-7.36 (m, 13H), 7.66 (s, 1H), 7.75 (d,  $J = 7.2$  Hz, 1H), 11.79 (br s, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz)  $\delta$ : 11.4, 44.0, 49.9, 70.7, 73.0, 110.7, 111.8, 124.9, 127.0, 127.6, 127.7, 129.0, 129.1, 135.8, 135.9, 142.9, 143.3, 155.6, 165.4, 173.5, 174.0, 199.5; HRMS (ESI-TOF)  $m/z$ : Calcd. for C<sub>36</sub>H<sub>26</sub>ClN<sub>5</sub>NaO<sub>5</sub>S [M+Na]<sup>+</sup>: 698.1235; Found: 698.1242.



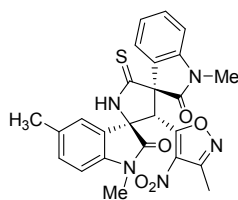
**3ch**: White solid, m.p. 126.5-127.8 °C; Yield 96%; 70% ee, >20:1 dr,  $[\alpha]_D^{20} = 54.69$  (c 0.55, CH<sub>2</sub>Cl<sub>2</sub>); The ee was determined by HPLC analysis using a Chiralpak IC column (65/35 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 77.23$  min;  $\tau_{\text{minor}} = 41.94$  min); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$ : 2.10 (s, 3H), 2.29 (s, 3H), 4.72-4.84 (m, 2H), 4.93-5.01 (m, 2H), 6.12 (s, 1H), 6.67 (d,  $J = 8.0$  Hz, 1H), 6.87 (d,  $J = 8.0$  Hz, 1H), 7.01 (d,  $J = 7.6$  Hz, 1H), 7.18-7.33 (m, 12H), 7.49 (s, 1H), 7.85 (d,  $J = 6.4$  Hz, 1H), 11.69 (br s, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz)  $\delta$ : 11.4, 21.3, 43.9, 50.1, 70.8, 72.8, 110.1, 110.7, 127.5, 127.6, 127.7, 129.0, 129.1, 136.0, 136.2, 141.8, 142.9, 155.4, 165.5, 173.8, 174.2, 200.4; HRMS (ESI-TOF)  $m/z$ : Calcd. for C<sub>37</sub>H<sub>29</sub>N<sub>5</sub>NaO<sub>5</sub>S [M+Na]<sup>+</sup>: 678.1782; Found: 678.1780.



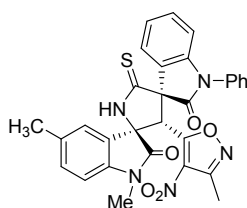
**3de**: White solid, m.p. 140.8-142.1 °C; Yield 94%; 77% ee, >20:1 dr,  $[\alpha]_D^{20} = 296.52$  (c 0.12,



CH<sub>2</sub>Cl<sub>2</sub>); The ee was determined by HPLC analysis using a Chiralpak IC column (82/18 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 36.02$  min;  $\tau_{\text{minor}} = 14.39$  min); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$ : 2.14 (s, 3H), 3.13 (s, 3H), 5.97 (s, 1H), 6.68 (d,  $J = 8.0$  Hz, 1H), 7.07-7.09 (m, 1H), 7.20-7.23 (m, 1H), 7.29-7.33 (m, 1H), 7.36 (d,  $J = 6.8$  Hz, 2H), 7.43-7.50 (m, 2H), 7.58-7.61 (m, 2H), 7.67 (s, 1H), 7.72 (d,  $J = 7.6$  Hz, 1H), 11.53 (br s, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz)  $\delta$ : 11.3, 27.7, 49.6, 70.6, 72.9, 110.3, 111.2, 124.5, 126.7, 127.0, 129.9, 130.4, 134.1, 143.9, 144.3, 155.6, 166.2, 173.2, 173.3, 199.5; HRMS (ESI-TOF)  $m/z$ : Calcd. for C<sub>29</sub>H<sub>20</sub>ClN<sub>5</sub>NaO<sub>5</sub>S [M+Na]<sup>+</sup>: 608.0766; Found: 608.0769.

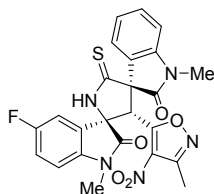


**3ea**: White solid, m.p. 249.8-251.6 °C; Yield 95%; 96% ee, >20:1 dr,  $[\alpha]_{\text{D}}^{20} = 93.77$  (c 0.41, CH<sub>2</sub>Cl<sub>2</sub>); The ee was determined by HPLC analysis using a Chiralpak IF column (98/2 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 24.56$  min;  $\tau_{\text{minor}} = 16.83$  min); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz)  $\delta$ : 2.11 (s, 3H), 3.11 (s, 3H), 3.14 (s, 3H), 5.91 (s, 1H), 6.93 (d,  $J = 8.0$  Hz, 1H), 7.01 (d,  $J = 7.5$  Hz, 1H), 7.13-7.17 (m, 1H), 7.21-7.23 (m, 1H), 7.32-7.36 (m, 1H), 7.53 (s, 1H), 7.65 (d,  $J = 7.5$  Hz, 1H), 11.34 (br s, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz)  $\delta$ : 10.8, 20.7, 26.9, 27.0, 49.1, 70.0, 72.2, 82.3, 109.0, 109.2, 122.5, 124.8, 126.7, 127.3, 129.8, 131.8, 141.2, 144.6, 154.9, 165.5, 173.1, 173.2, 187.3, 199.7, 217.3; HRMS (ESI-TOF)  $m/z$ : Calcd. for C<sub>25</sub>H<sub>21</sub>N<sub>5</sub>NaO<sub>5</sub>S [M+Na]<sup>+</sup>: 526.1156; Found: 526.1162.

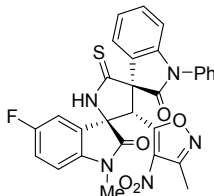


**3ed**: White solid, m.p. 125.5-127.2 °C; Yield 94%; 92% ee, >20:1 dr,  $[\alpha]_{\text{D}}^{20} = 170.00$  (c 0.19, CH<sub>2</sub>Cl<sub>2</sub>); The ee was determined by HPLC analysis using a Chiralpak IF column (98/2 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 42.45$  min;  $\tau_{\text{minor}} = 15.71$  min); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz)  $\delta$ : 2.19 (s, 3H), 2.46 (s, 3H), 3.16 (s, 3H), 6.02 (s, 1H), 6.75 (d,  $J = 7.5$  Hz, 1H), 7.00 (d,  $J = 8.0$  Hz, 1H), 7.21-7.24 (m, 1H), 7.28-7.33 (m, 2H), 7.44 (d,  $J = 7.5$  Hz, 2H), 7.52-7.55 (m, 1H), 7.63-7.66 (m, 3H), 7.71 (d,  $J = 7.5$  Hz, 1H), 11.47 (br s, 1H); <sup>13</sup>C NMR

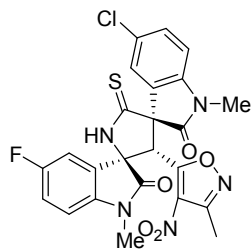
(DMSO-*d*<sub>6</sub>, 125 MHz)  $\delta$ : 11.3, 21.2, 27.4, 49.6, 70.6, 72.7, 109.7, 109.8, 125.5, 127.0, 127.3, 130.2, 130.3, 131.8, 132.3, 134.4, 141.7, 144.9, 155.4, 166.3, 173.1, 173.6, 199.7, 218.0; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>30</sub>H<sub>23</sub>N<sub>5</sub>NaO<sub>5</sub>S [M+Na]<sup>+</sup>: 588.1312; Found: 588.1317.



**3fa**: White solid, m.p. 125.2-127.0 °C; Yield 92%; 83% ee, >20:1 dr,  $[\alpha]_D^{20} = 151.30$  (c 0.19, CH<sub>2</sub>Cl<sub>2</sub>); The ee was determined by HPLC analysis using a Chiralpak IE column (80/20 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 19.21$  min;  $\tau_{\text{minor}} = 13.82$  min); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz)  $\delta$ : 2.12 (s, 3H), 3.13 (s, 3H), 3.14 (s, 3H), 5.91 (s, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 7.07-7.09 (m, 1H), 7.12-7.15 (m, 1H), 7.29-7.35 (m, 2H), 7.61-7.65 (m, 2H), 11.37 (br s, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz)  $\delta$ : 10.8, 27.0, 27.1, 49.2, 70.0, 72.2, 109.0, 110.5, 114.3 (d, *J*<sub>CF</sub> = 25.0 Hz), 117.6 (d, *J*<sub>CF</sub> = 22.5 Hz), 122.6, 125.8, 126.2, 126.3, 127.1, 129.9, 131.3, 140.0, 144.6, 155.0, 158.3 (d, *J*<sub>CF</sub> = 237.5 Hz), 165.4, 172.9, 173.3, 199.9; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>24</sub>H<sub>18</sub>FN<sub>5</sub>NaO<sub>5</sub>S [M+Na]<sup>+</sup>: 530.0905; Found: 530.0909.

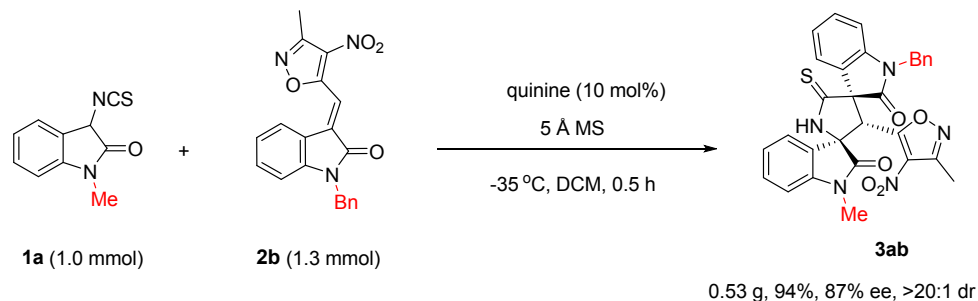


**3fd**: White solid, m.p. 187.8-188.6 °C; Yield 93%; 94% ee, >20:1 dr,  $[\alpha]_D^{20} = 187.10$  (c 0.13, CH<sub>2</sub>Cl<sub>2</sub>); The ee was determined by HPLC analysis using a Chiralpak IC column (85/15 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 29.02$  min;  $\tau_{\text{minor}} = 20.26$  min); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz)  $\delta$ : 2.21 (s, 3H), 3.19 (s, 3H), 6.01 (s, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 7.13-7.16 (m, 1H), 7.19-7.22 (m, 1H), 7.29-7.32 (m, 1H), 7.36-7.40 (m, 1H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.51-7.54 (m, 1H), 7.63-7.66 (m, 2H), 7.69-7.74 (m, 2H), 11.50 (br s, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz)  $\delta$ : 11.2, 27.6, 49.6, 70.6, 72.7, 109.7, 110.9, 114.9 (d, *J*<sub>CF</sub> = 25.0 Hz), 118.1 (d, *J*<sub>CF</sub> = 23.8 Hz), 123.6, 126.5, 126.9, 127.0, 127.2, 128.9, 130.2, 130.4, 131.8, 134.4, 140.5, 144.8, 155.5, 158.8 (d, *J*<sub>CF</sub> = 238.8 Hz), 166.2, 173.0, 173.6, 200.0; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>29</sub>H<sub>20</sub>FN<sub>5</sub>NaO<sub>5</sub>S [M+Na]<sup>+</sup>: 592.1061; Found: 592.1068.



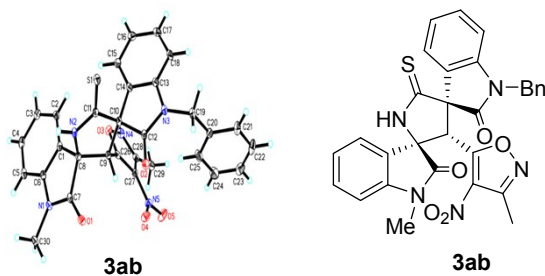
**3fe**: White solid, m.p. 167.7-168.2 °C; Yield 91%; 83% ee, 12:1 dr,  $[\alpha]_D^{20} = 66.02$  (c 0.27, CH<sub>2</sub>Cl<sub>2</sub>); The ee was determined by HPLC analysis using a Chiralpak IF column (60/40 hexane/i-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 29.62$  min;  $\tau_{\text{minor}} = 25.50$  min); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz)  $\delta$ : 2.15 (s, 3H), 3.13 (s, 3H), 3.14 (s, 3H), 5.88 (s, 1H), 7.05-7.08 (m, 2H), 7.28-7.32 (m, 1H), 7.42-7.44 (m, 1H), 7.60-7.62 (m, 1H), 7.64 (d,  $J = 2.0$  Hz, 1H), 11.44 (br s, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz)  $\delta$ : 10.8, 27.1, 27.2, 49.1, 70.0, 72.3, 110.5, 114.2 (d,  $J_{CF} = 26.3$  Hz), 117.6 (d,  $J_{CF} = 22.5$  Hz), 125.9, 126.2, 128.9, 129.8, 139.9, 143.8, 155.1, 158.2 (d,  $J_{CF} = 237.5$  Hz), 165.2, 172.6, 173.1, 199.0; HRMS (ESI-TOF)  $m/z$ : Calcd. for C<sub>24</sub>H<sub>17</sub>ClFN<sub>5</sub>NaO<sub>5</sub>S [M+Na]<sup>+</sup>: 564.0515; Found: 564.0519.

#### 4. One-mmol-scale synthesis of the product **3ab**



In an ordinary vial equipped with a magnetic stirring bar, the compound **2b** (1.3 mmol, 1.3 equiv.), 5Å molecular sieve (1.0 g) and catalyst quinine (32.4 mg, 10 mmol %, 0.1 mmol) were dissolved in 160.0 mL of freshly distilled DCM at -35 °C, and then 3-isothiocyanato oxindole **1a** (1.0 mmol) was added. After completion of the reaction, as indicated by TLC, the reaction mixture was directly purified by flash chromatography to yield the desired product **3ab** (0.53 g, 94%, 87% ee, >20:1 dr).

## 5. X-Ray crystal data for compounds 3ab and 3ad

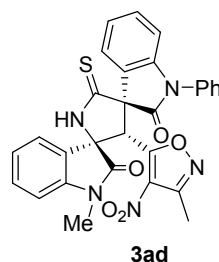
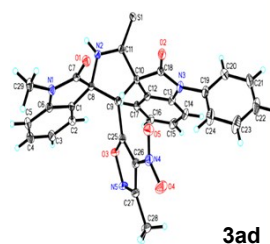


**Table S1 Crystal data and structure refinement for 3ab**

Identification code	<b>3ab</b>
Empirical formula	C <sub>34</sub> H <sub>35.51</sub> N <sub>5</sub> O <sub>7</sub> S
Formula weight	658.24
Temperature/K	100.01(10)
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å, b/Å, c/Å	10.69410(10), 16.3625(2), 18.2683(2)
α/°, β/°, γ/°	90, 90, 90.
Volume/Å <sup>3</sup>	3196.63(6)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.368
μ/mm <sup>-1</sup>	1.382
F(000)	1386.0
Crystal size/mm <sup>3</sup>	0.14 × 0.13 × 0.12
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	7.252 to 147.252
Index ranges	-10 ≤ h ≤ 13, -20 ≤ k ≤ 18, -22 ≤ l ≤ 18
Reflections collected	27624
Independent reflections	6388 [R <sub>int</sub> = 0.0445, R <sub>sigma</sub> = 0.0285]
Data/restraints/parameters	6388/0/440
Goodness-of-fit on F <sup>2</sup>	1.042
Final R indexes [I >= 2σ(I)]	R <sub>1</sub> = 0.0383, wR <sub>2</sub> = 0.1012
Final R indexes [all data]	R <sub>1</sub> = 0.0390, wR <sub>2</sub> = 0.1020
Largest diff. peak/hole / e Å <sup>-3</sup>	0.55/-0.37
Flack/Hooft parameter	0.001(8)/-0.003(6)

### Crystal structure determination of 3ab

**Crystal Data** for C<sub>34</sub>H<sub>35.5075</sub>N<sub>5</sub>O<sub>7</sub>S (*M* = 658.24 g/mol): orthorhombic, space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (no. 19), *a* = 10.69410(10) Å, *b* = 16.3625(2) Å, *c* = 18.2683(2) Å, *V* = 3196.63(6) Å<sup>3</sup>, *Z* = 4, *T* = 100.01(10) K, μ(CuKα) = 1.382 mm<sup>-1</sup>, *D*<sub>calc</sub> = 1.368 g/cm<sup>3</sup>, 27624 reflections measured (7.252° ≤ 2θ ≤ 147.252°), 6388 unique (*R*<sub>int</sub> = 0.0445, *R*<sub>sigma</sub> = 0.0285) which were used in all calculations. The final *R*<sub>1</sub> was 0.0383 (*I* > 2σ(*I*)) and *wR*<sub>2</sub> was 0.1020 (all data).



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

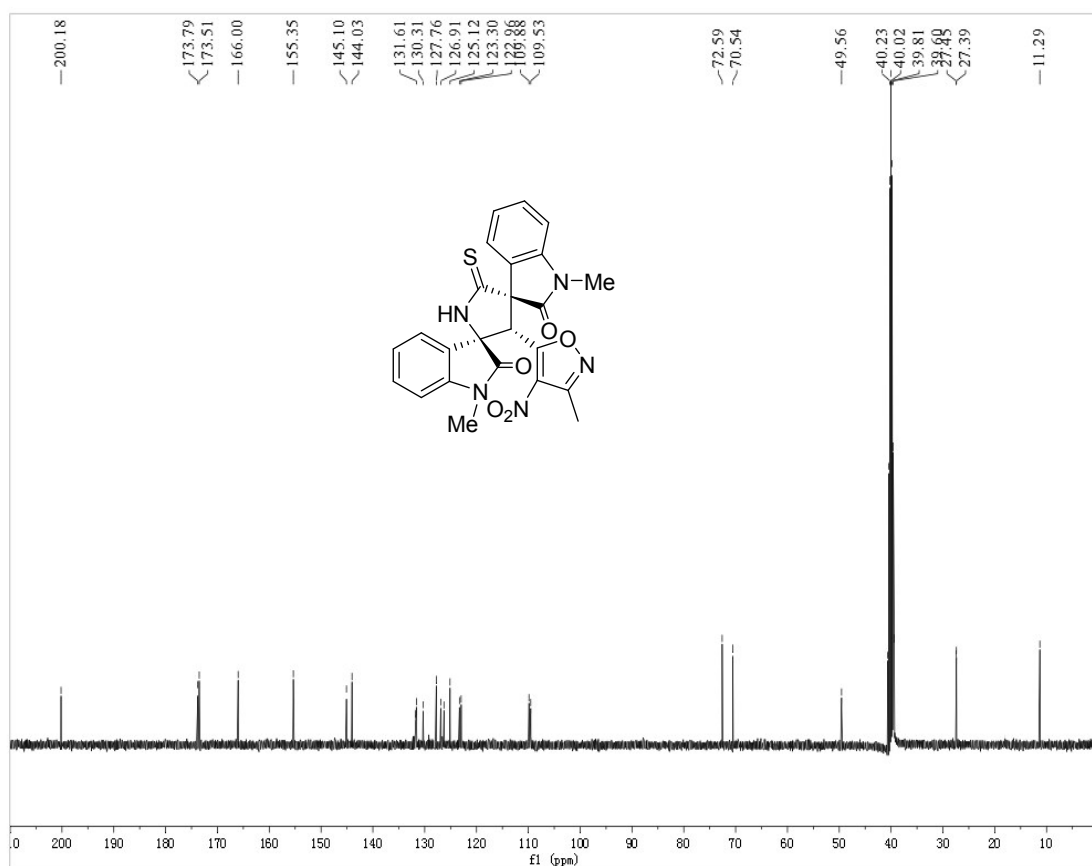
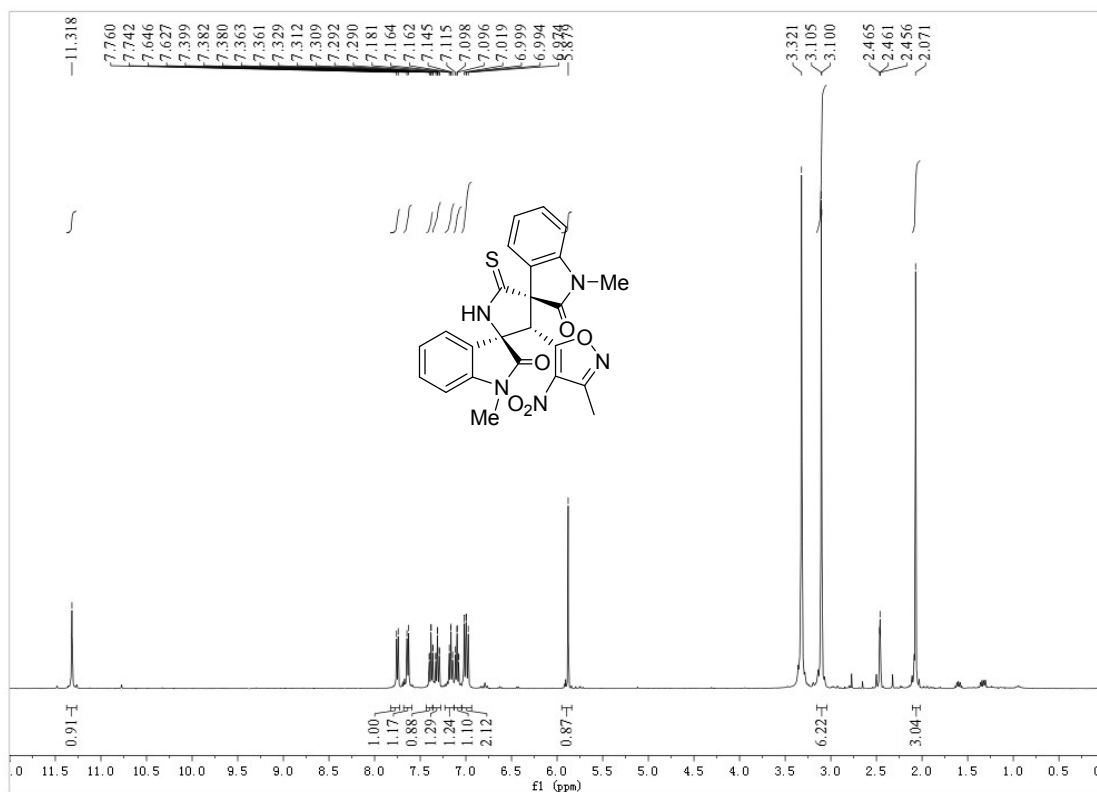
Identification code	<b>3ad</b>
Empirical formula	$C_{33}H_{33}N_5O_7S$
Formula weight	643.70
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
$a/\text{\AA}$ , $b/\text{\AA}$ , $c/\text{\AA}$	11.1703(2), 15.8824(3), 18.1124(3)
$\alpha/^\circ$ , $\beta/^\circ$ , $\gamma/^\circ$	90, 90, 90.
Volume/ $\text{\AA}^3$	3213.34(10)
Z	4
$\rho_{\text{calc}}/\text{g/cm}^3$	1.331
$\mu/\text{mm}^{-1}$	1.363
F(000)	1352.0
Crystal size/ $\text{mm}^3$	$0.14 \times 0.13 \times 0.12$
Radiation	$\text{CuK}\alpha$ ( $\lambda = 1.54184$ )
$2\theta$ range for data collection/ $^\circ$	7.402 to 147.612
Index ranges	$-13 \leq h \leq 13$ , $-19 \leq k \leq 17$ , $-15 \leq l \leq 22$
Reflections collected	18187
Independent reflections	6341 [ $R_{\text{int}} = 0.0323$ , $R_{\text{sigma}} = 0.0302$ ]
Data/restraints/parameters	6341/0/421
Goodness-of-fit on $F^2$	1.048
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0376$ , $wR_2 = 0.0971$
Final R indexes [all data]	$R_1 = 0.0386$ , $wR_2 = 0.0980$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.26/-0.25
Flack/Hooft parameter	0.006(8)/0.003(7)

### Crystal structure determination of 3ad

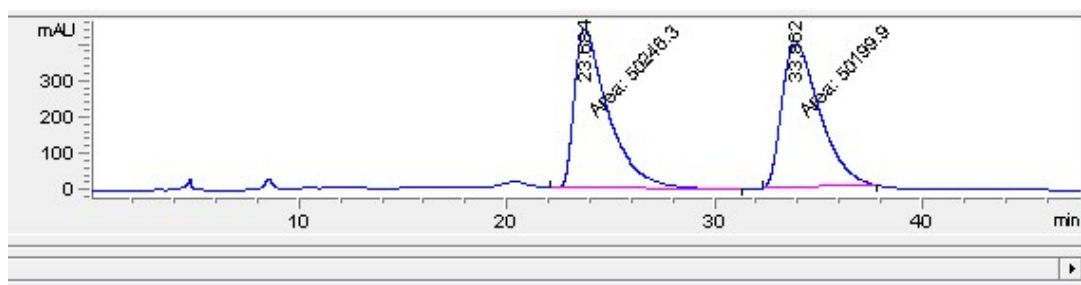
**Crystal Data** for  $C_{33}H_{33}N_5O_7S$  ( $M = 643.70$  g/mol): orthorhombic, space group  $P2_12_12_1$  (no. 19),  $a = 11.1703(2)$   $\text{\AA}$ ,  $b = 15.8824(3)$   $\text{\AA}$ ,  $c = 18.1124(3)$   $\text{\AA}$ ,  $V = 3213.34(10)$   $\text{\AA}^3$ ,  $Z = 4$ ,  $T = 100.00(10)$  K,  $\mu(\text{CuK}\alpha) = 1.363$   $\text{mm}^{-1}$ ,  $D_{\text{calc}} = 1.331$   $\text{g/cm}^3$ , 18187 reflections measured ( $7.402^\circ \leq 2\theta \leq 147.612^\circ$ ), 6341 unique ( $R_{\text{int}} = 0.0323$ ,  $R_{\text{sigma}} = 0.0302$ ) which were used in all calculations. The final  $R_1$  was 0.0376 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0980 (all data).

## 6. The copies of $^1\text{H}$ NMR, $^{13}\text{C}$ NMR and HPLC spectra for compounds 3

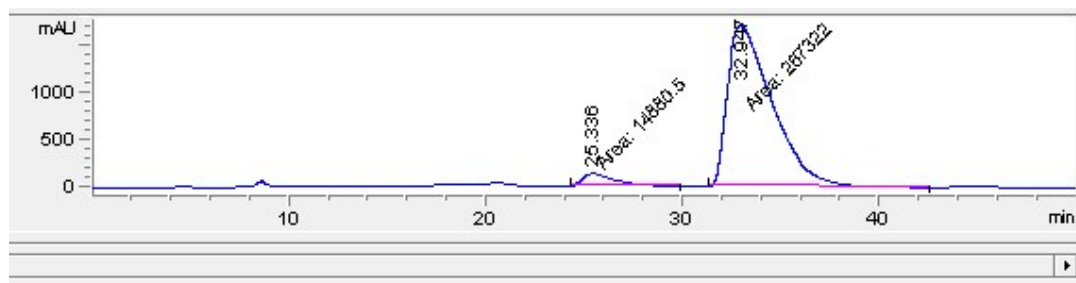
### $^1\text{H}$ and $^{13}\text{C}$ NMR of 3aa



### HPLC of 3aa

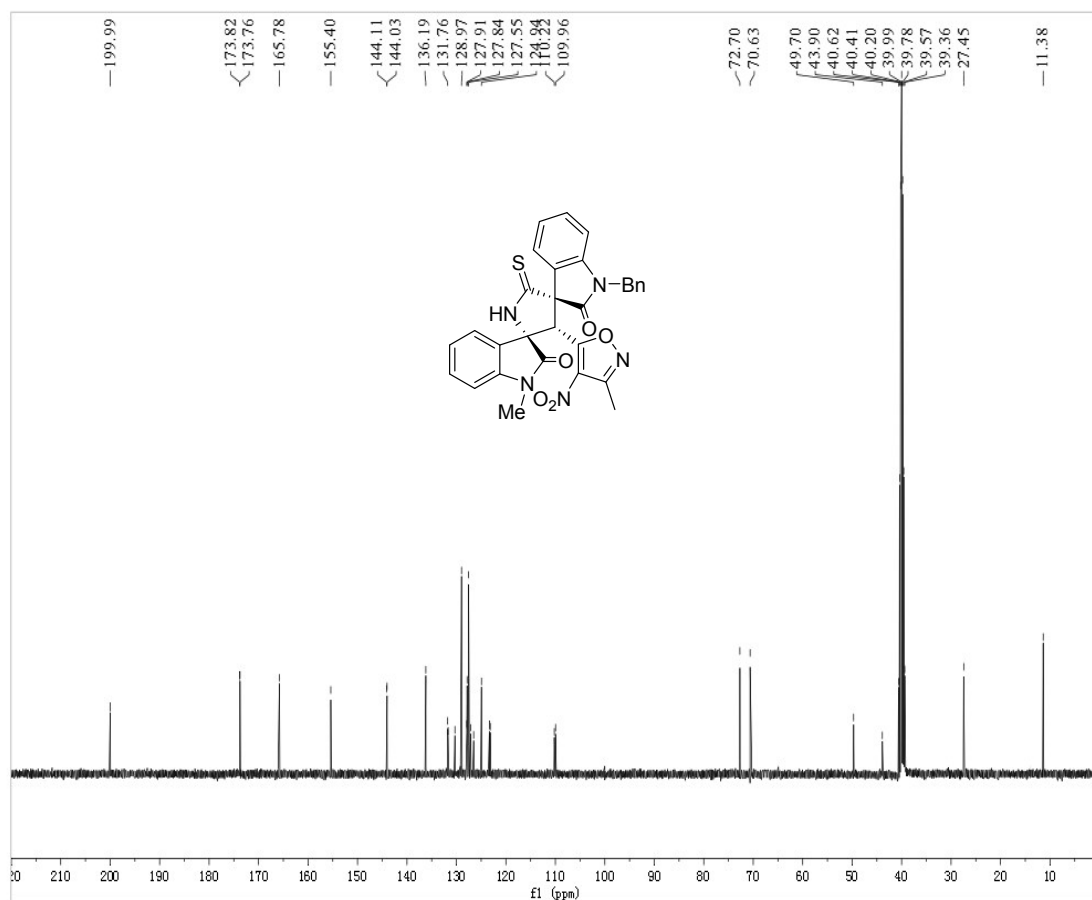
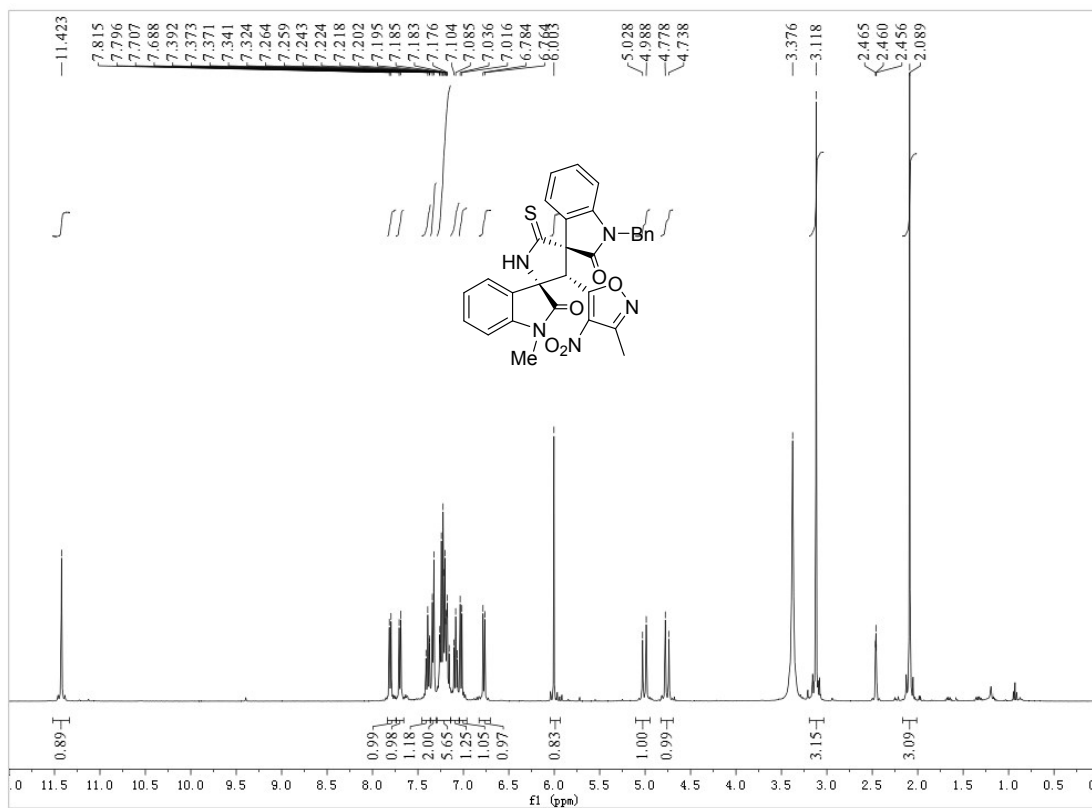


#	Time	Area	Height	Width	Area%	Symmetry
1	23.684	50246.3	441.2	1.8979	50.023	0.409
2	33.862	50199.9	398.4	2.1002	49.977	0.543



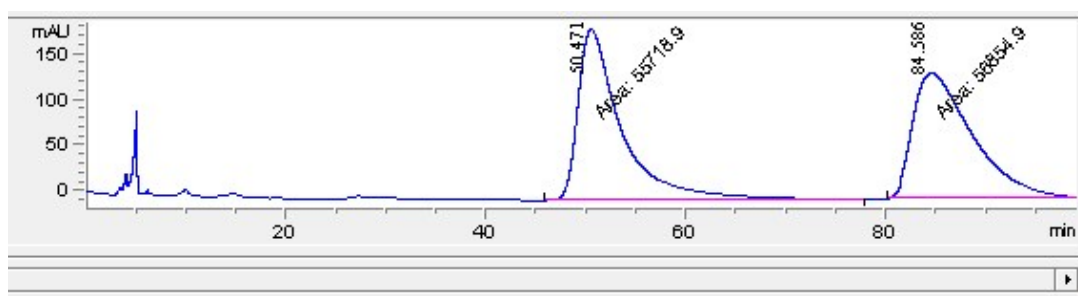
#	Time	Area	Height	Width	Area%	Symmetry
1	25.336	14880.5	129.7	1.9119	5.273	0.399
2	32.947	267322.2	1685.2	2.6439	94.727	0.444

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

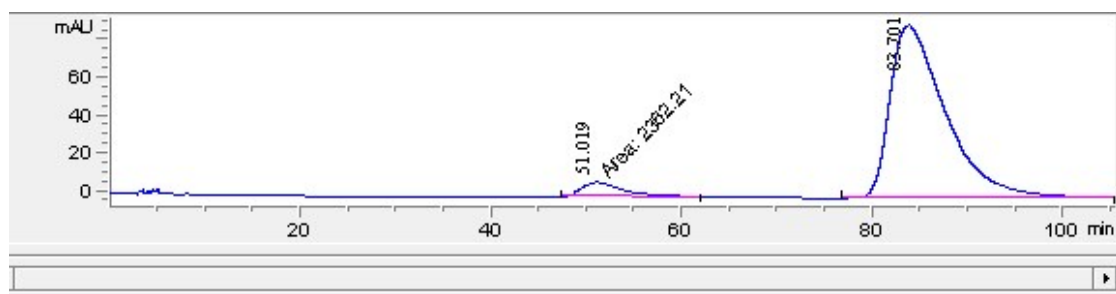




### HPLC of 3ab

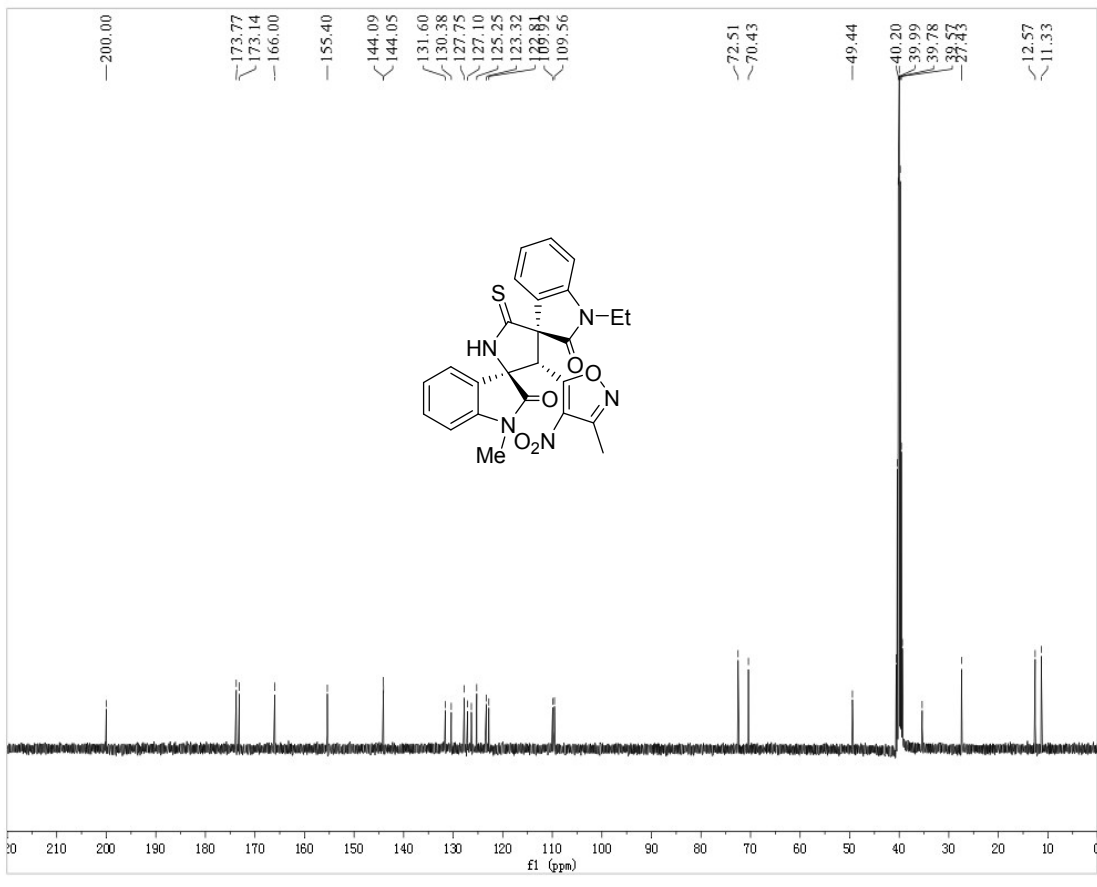
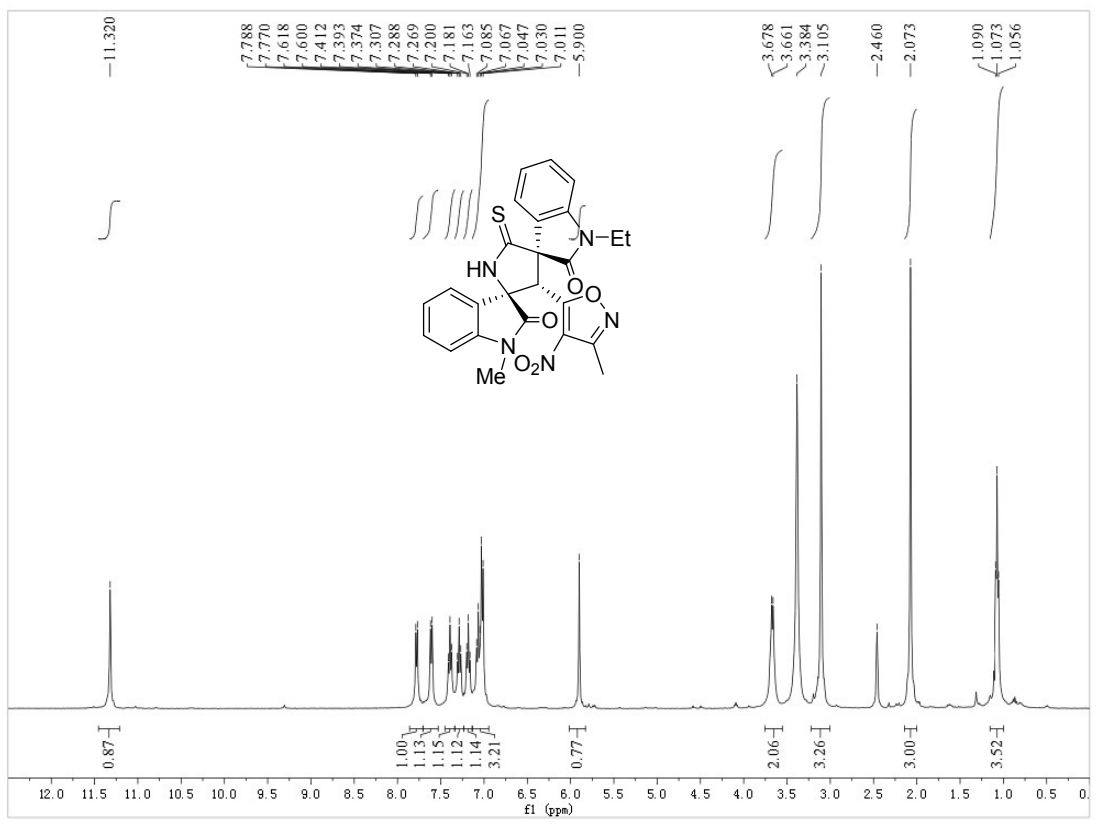


#	Time	Area	Height	Width	Area%	Symmetry
1	50.471	55718.9	185.6	5.0047	49.495	0.419
2	84.586	56854.9	137.5	6.8939	50.505	0.447

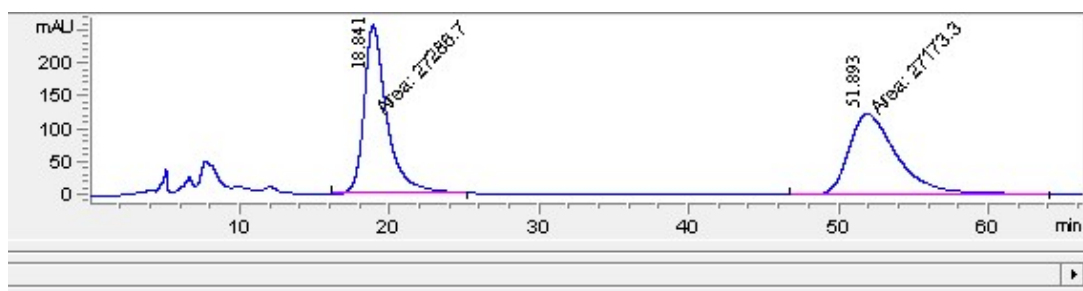


#	Time	Area	Height	Width	Area%	Symmetry
1	51.019	2362.2	7.7	5.1241	6.036	0.51
2	83.701	36774.4	91.1	5.9312	93.964	0.453

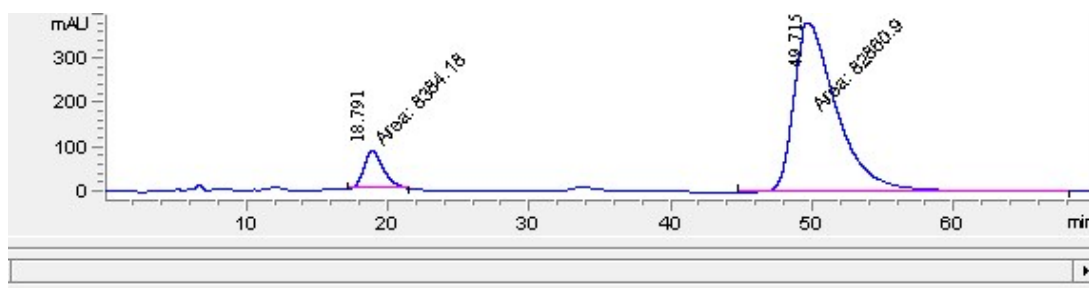
**<sup>1</sup>H and <sup>13</sup>C NMR of 3ac**



### HPLC of 3ac

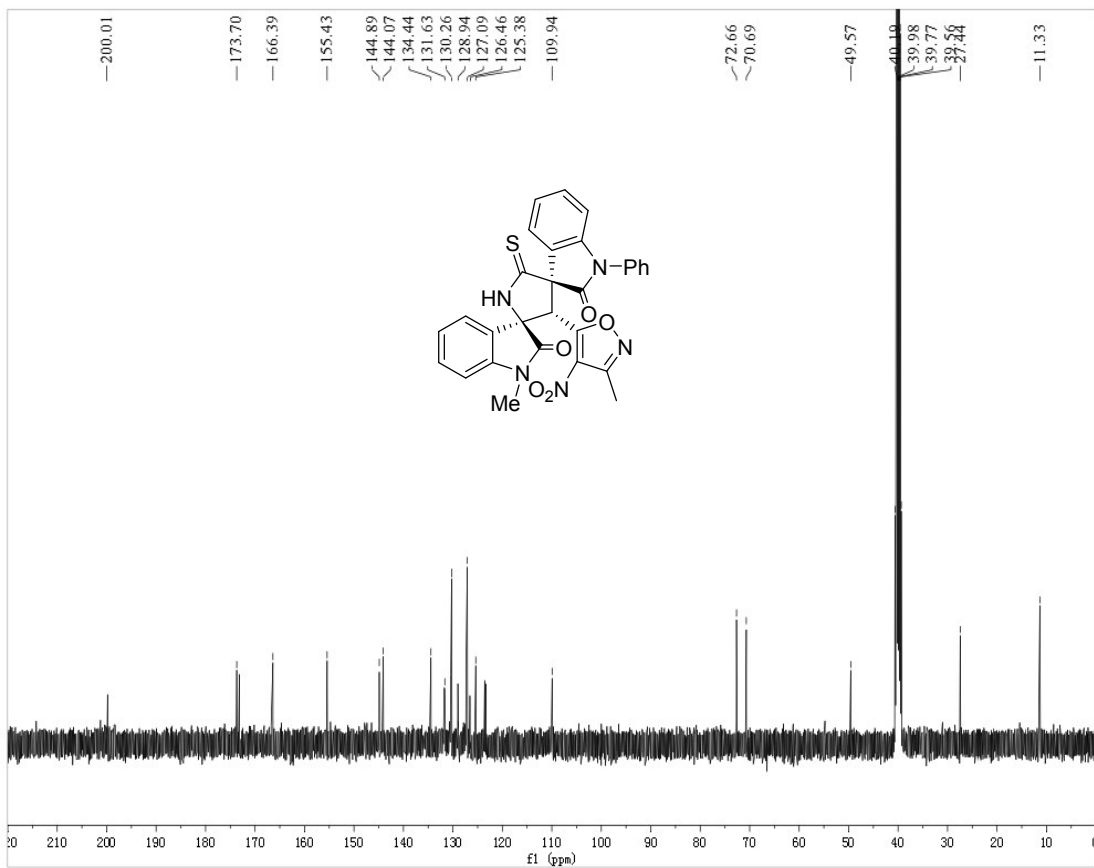
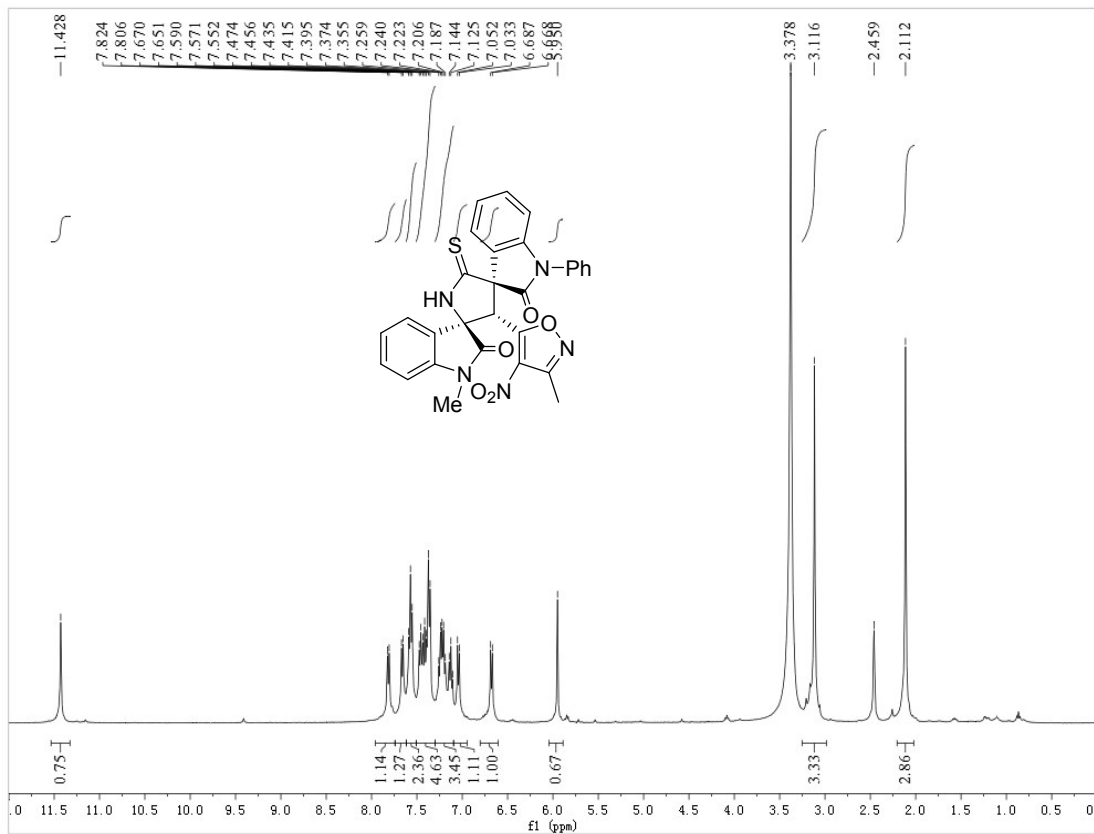


#	Time	Area	Height	Width	Area%	Symmetry
1	18.841	27286.7	256.9	1.7703	50.104	0.618
2	51.893	27173.3	122	3.7135	49.896	0.588

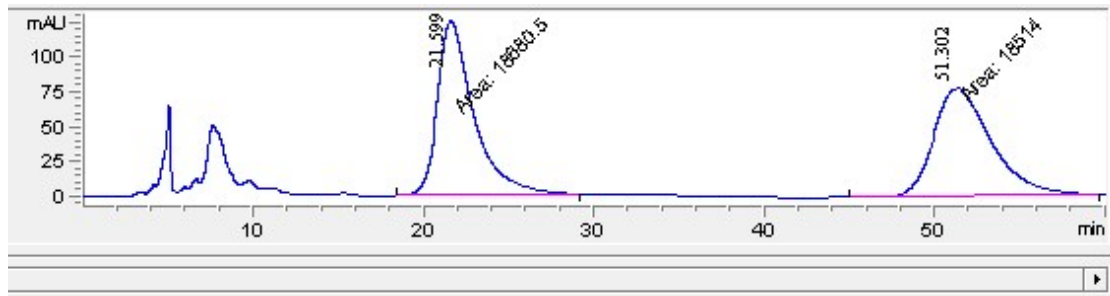


#	Time	Area	Height	Width	Area%	Symmetry
1	18.791	8384.2	86.8	1.6093	9.189	0.728
2	49.715	82860.9	382.2	3.6129	90.811	0.524

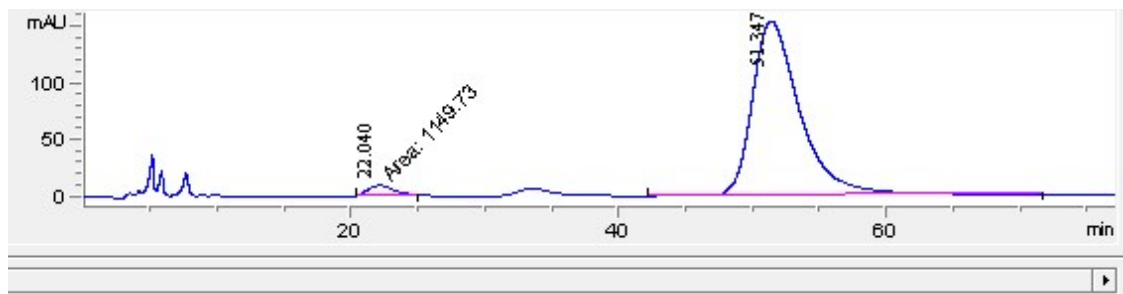
# $^1\text{H}$ and $^{13}\text{C}$ NMR of 3ad



### HPLC of 3ad

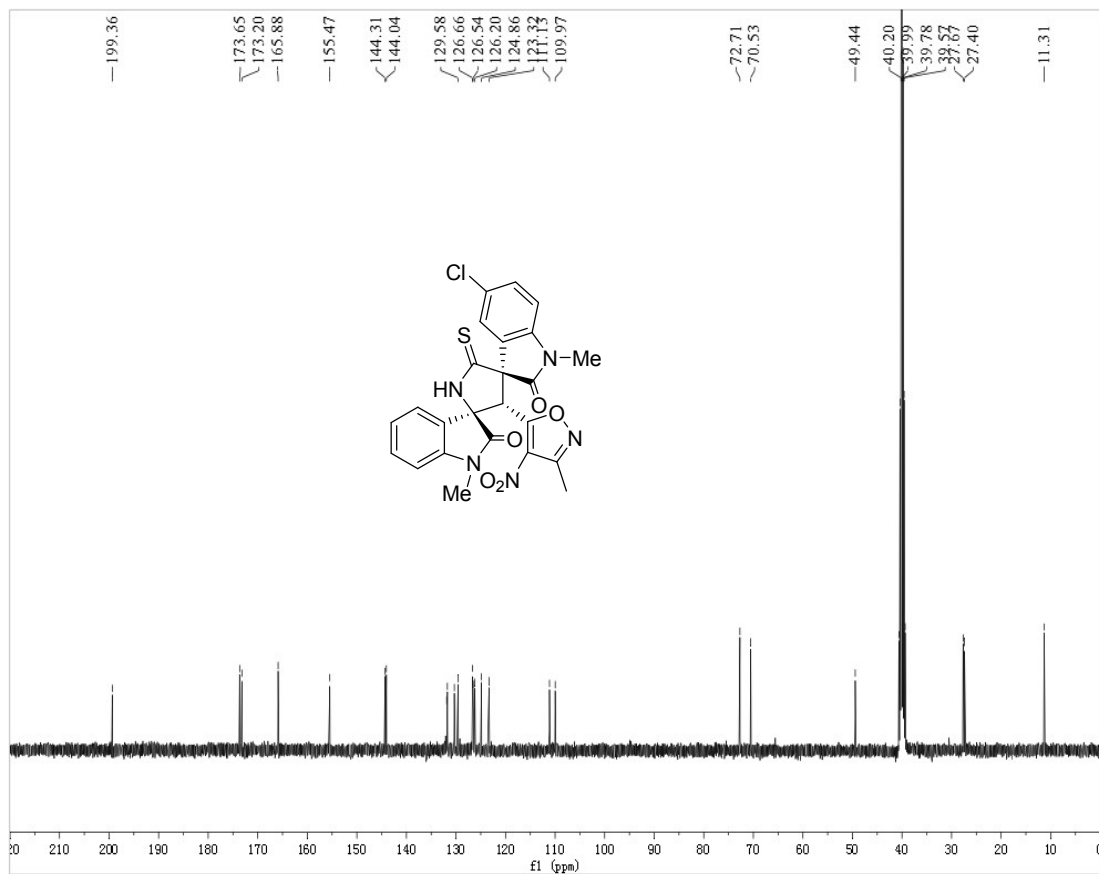
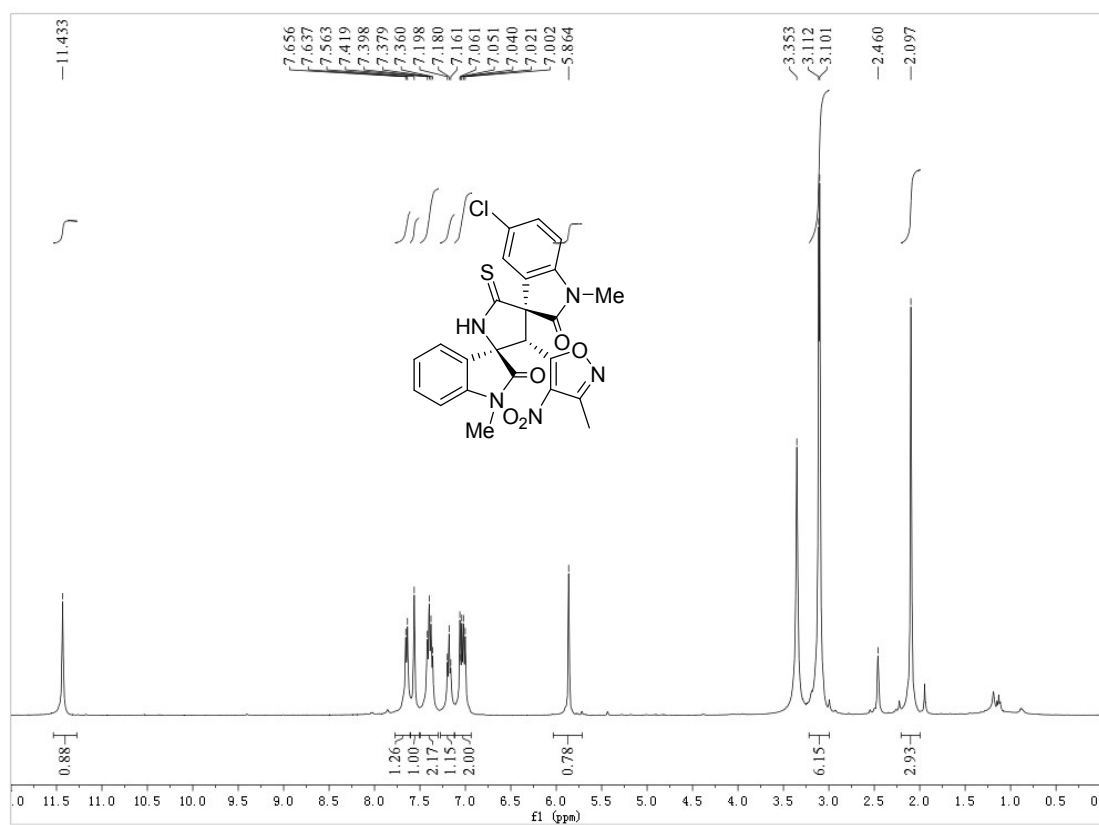


#	Time	Area	Height	Width	Area%	Symmetry
1	21.599	18680.5	125	2.4903	50.224	0.58
2	51.302	18514	77.9	3.963	49.776	0.67

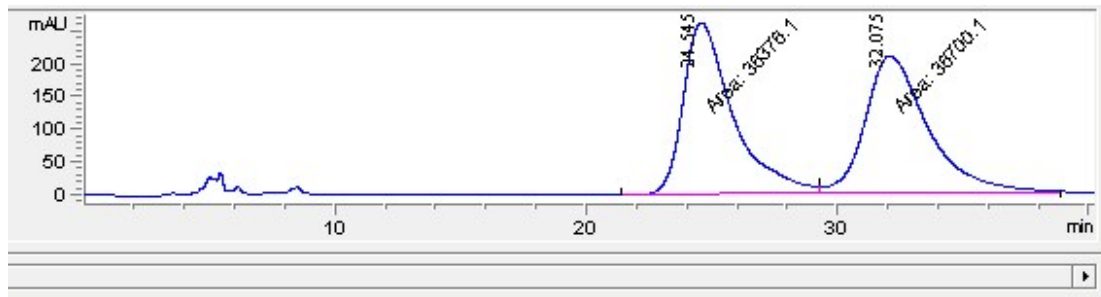


#	Time	Area	Height	Width	Area%	Symmetry
1	22.04	1149.7	8.7	2.1952	2.938	0.669
2	51.347	37984.5	154	3.7008	97.062	0.596

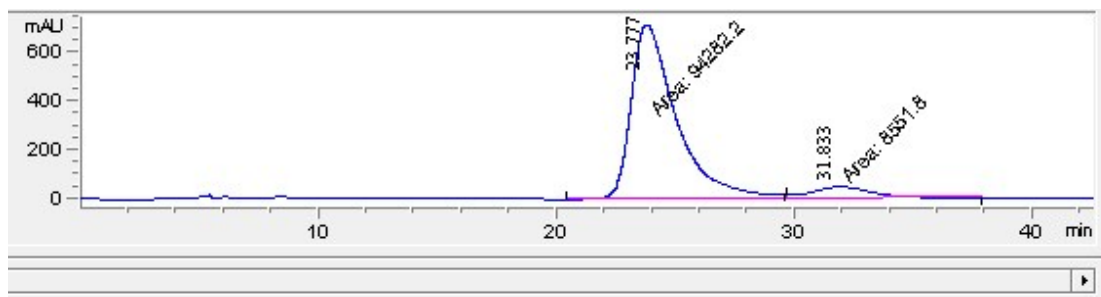
# <sup>1</sup>H and <sup>13</sup>C NMR of 3ae



### HPLC of 3ae

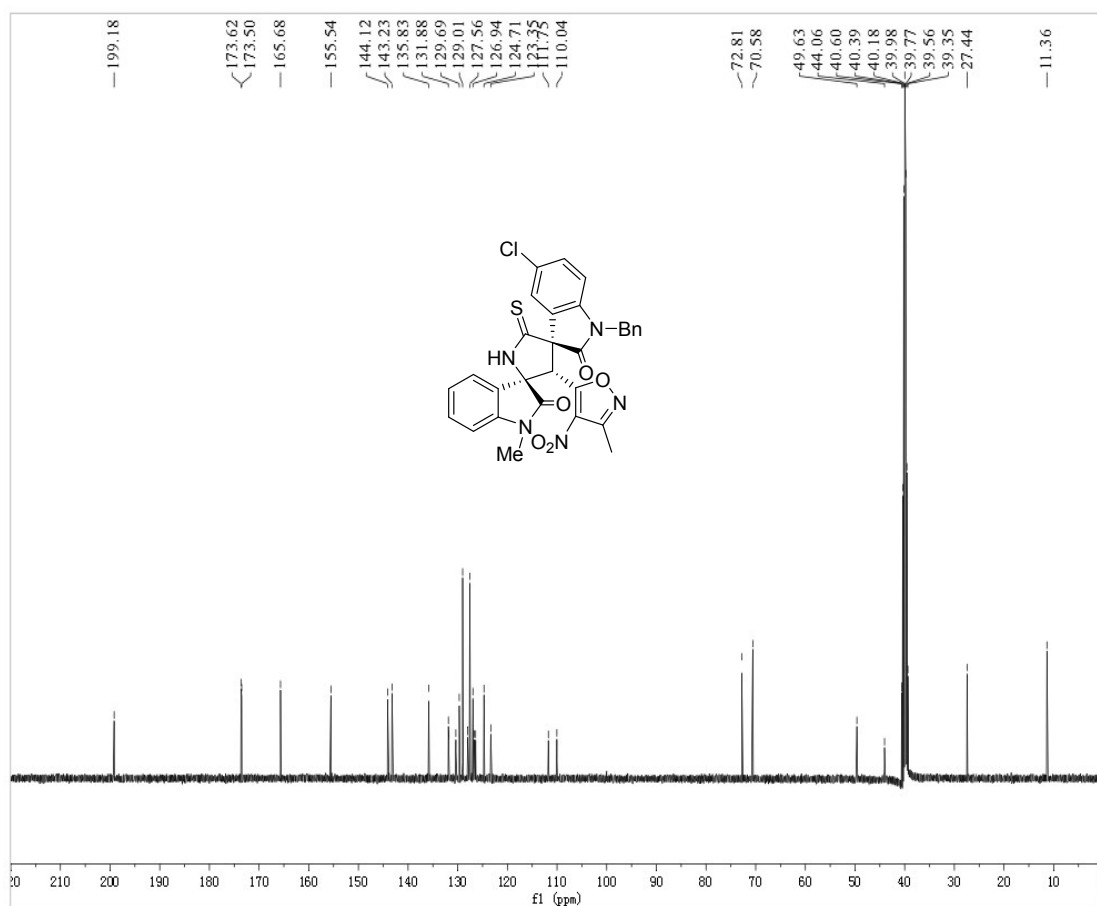
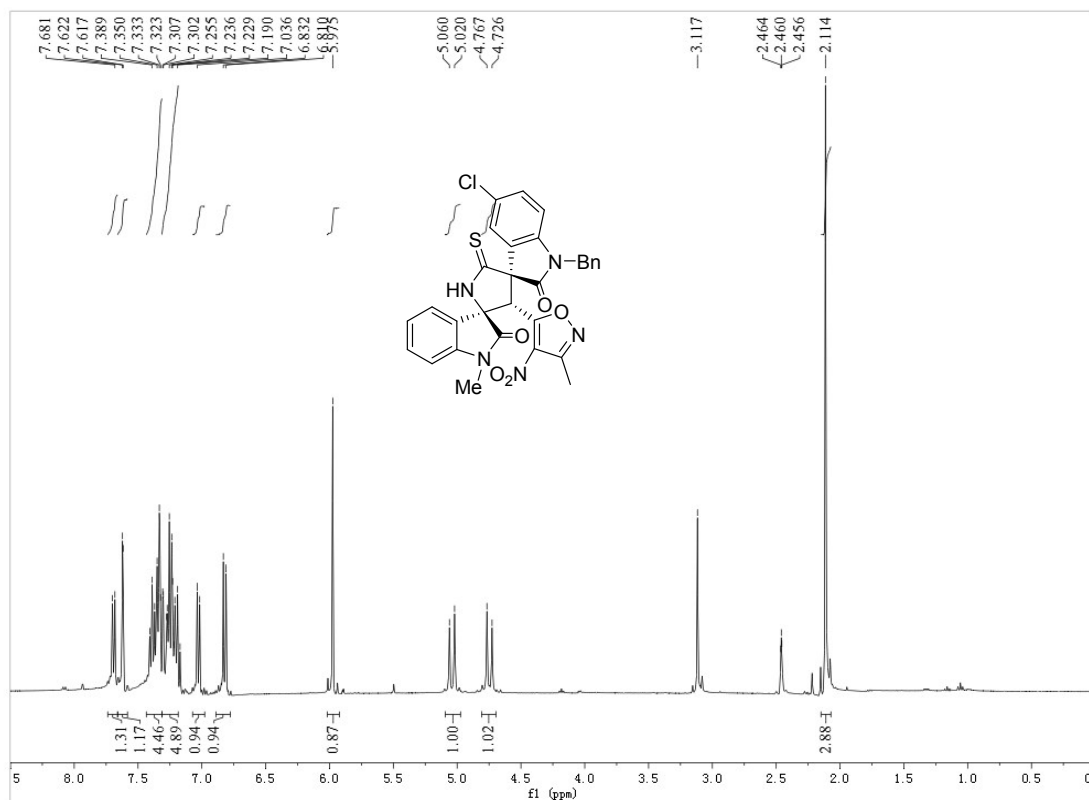


#	Time	Area	Height	Width	Area%	Symmetry
1	24.545	36376.1	263.6	2.2997	49.778	0.546
2	32.075	36700.1	210.5	2.9059	50.222	0.644



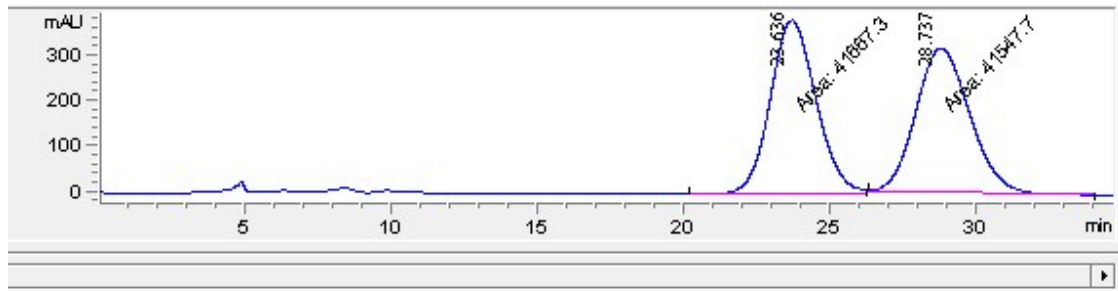
#	Time	Area	Height	Width	Area%	Symmetry
1	23.777	94282.2	716.8	2.1923	91.684	0.495
2	31.833	8551.8	47.1	3.0231	8.316	0.802

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

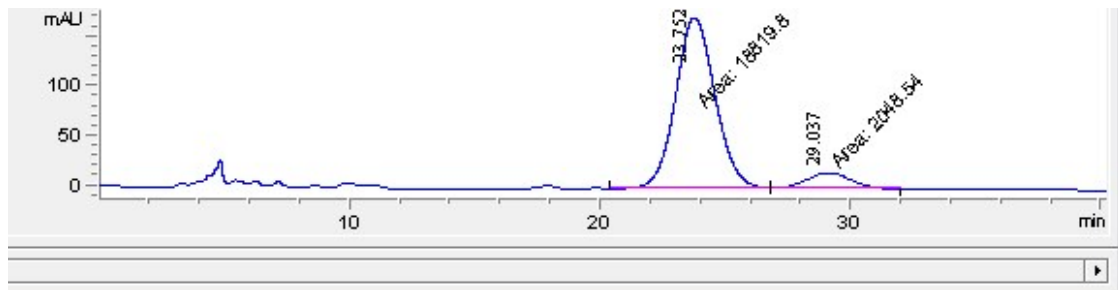




### HPLC of 3af

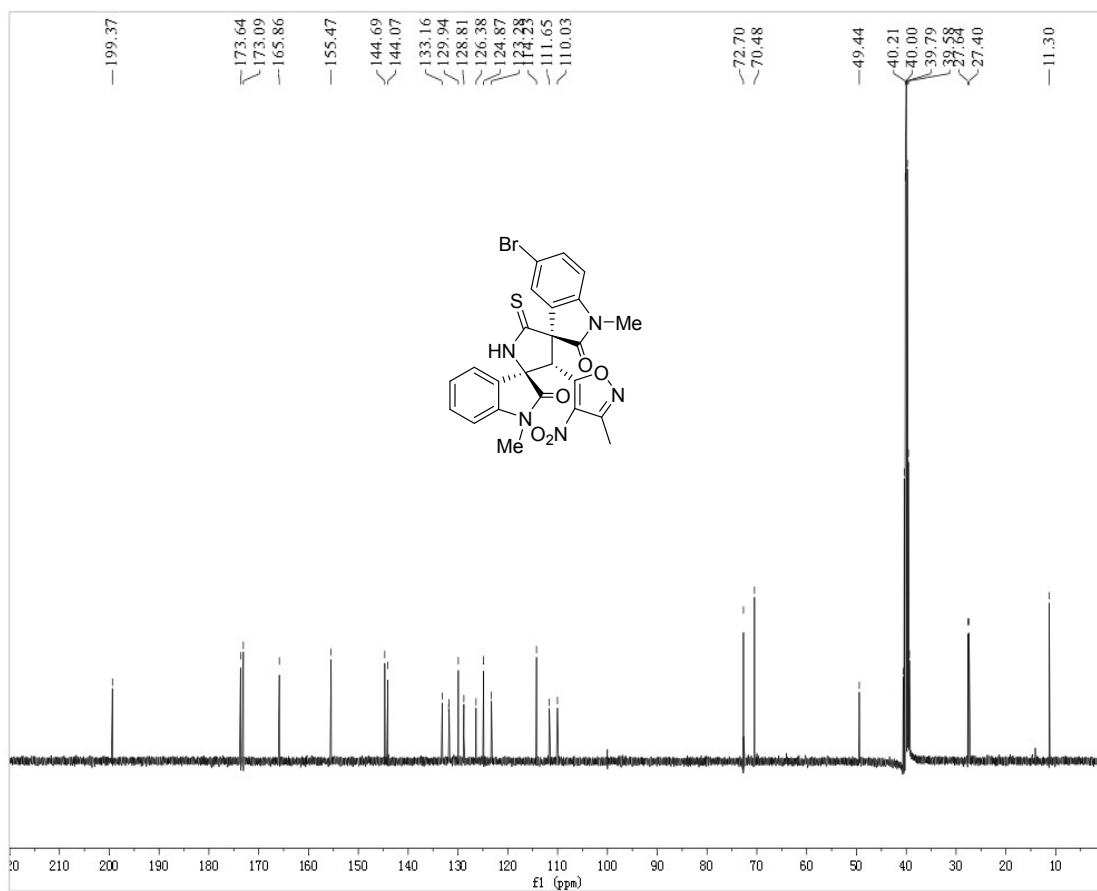
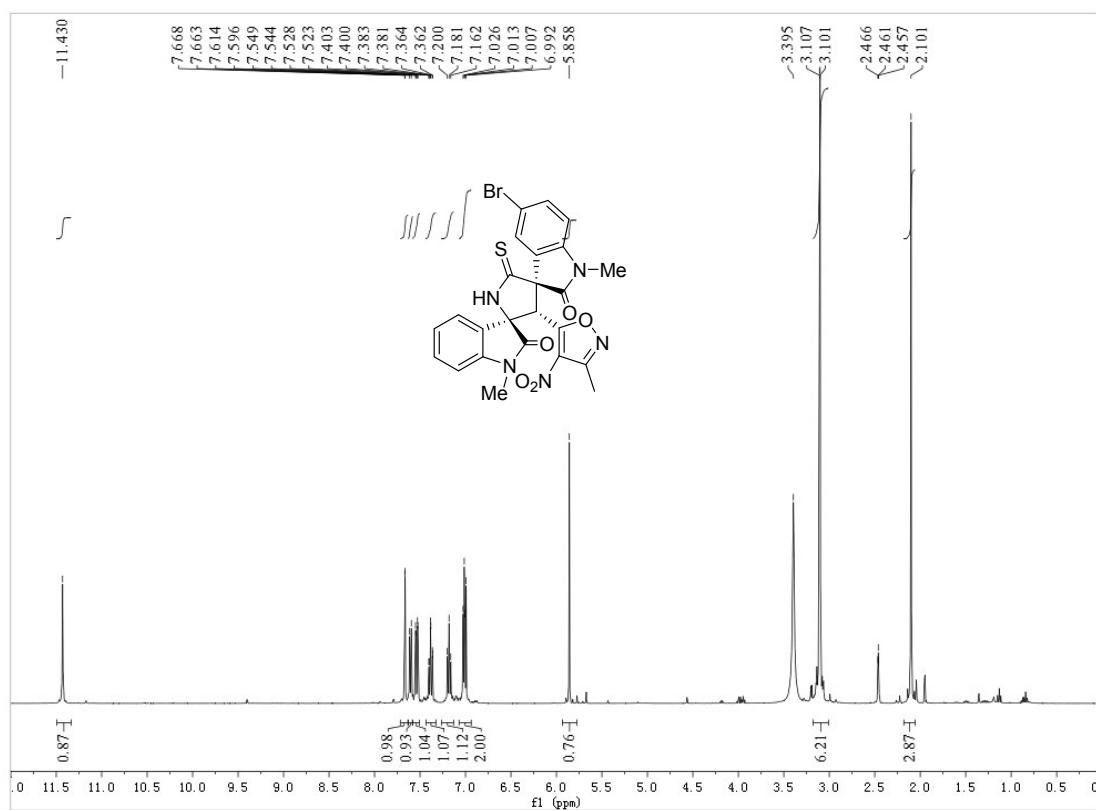


#	Time	Area	Height	Width	Area%	Symmetry
1	23.636	41667.3	381.6	1.8197	50.072	0.865
2	28.737	41547.7	319.6	2.1667	49.928	0.849

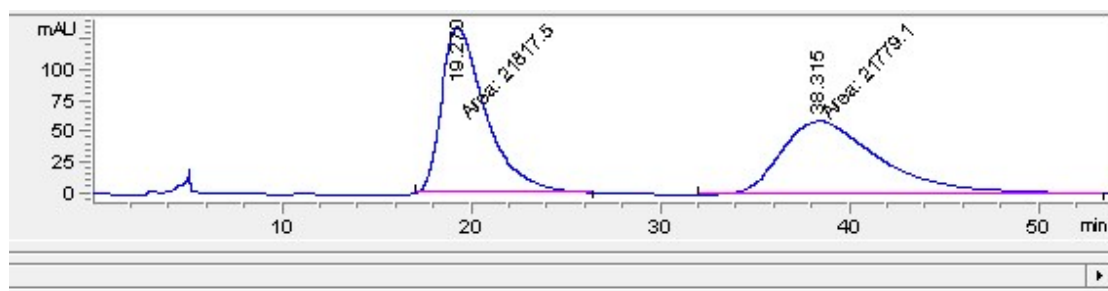


#	Time	Area	Height	Width	Area%	Symmetry
1	23.752	18819.8	172.2	1.821	90.184	0.89
2	29.037	2048.5	16.1	2.1165	9.816	0.974

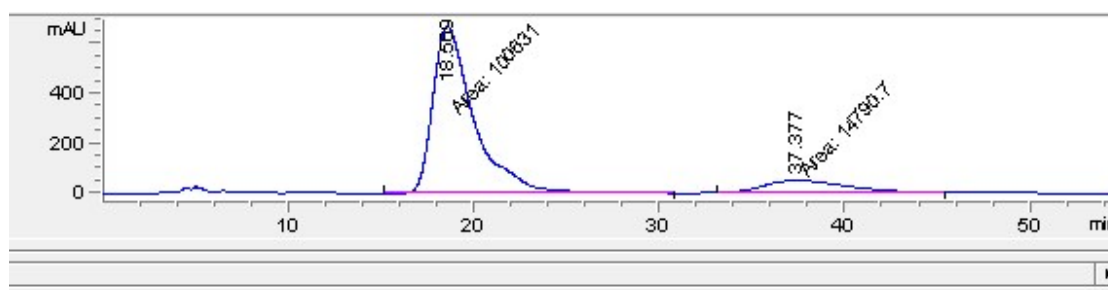
# $^1\text{H}$ and $^{13}\text{C}$ NMR of 3ag



### HPLC of 3ag

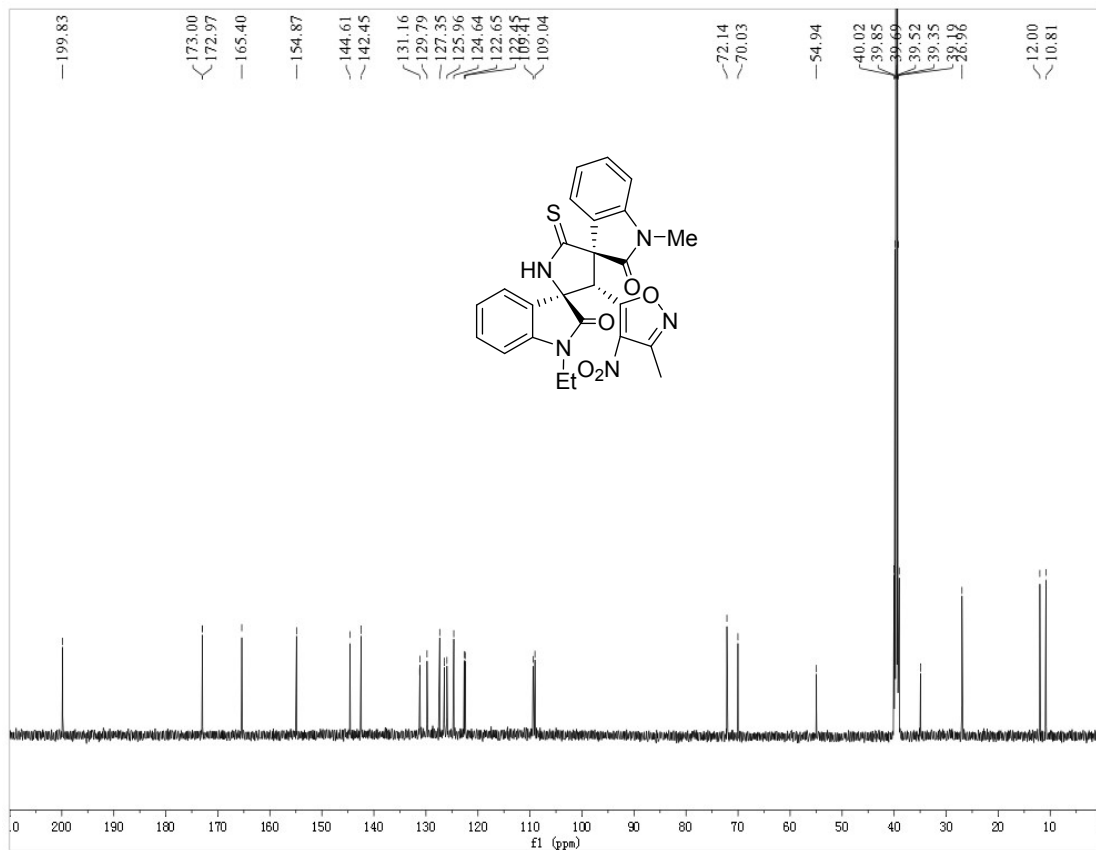
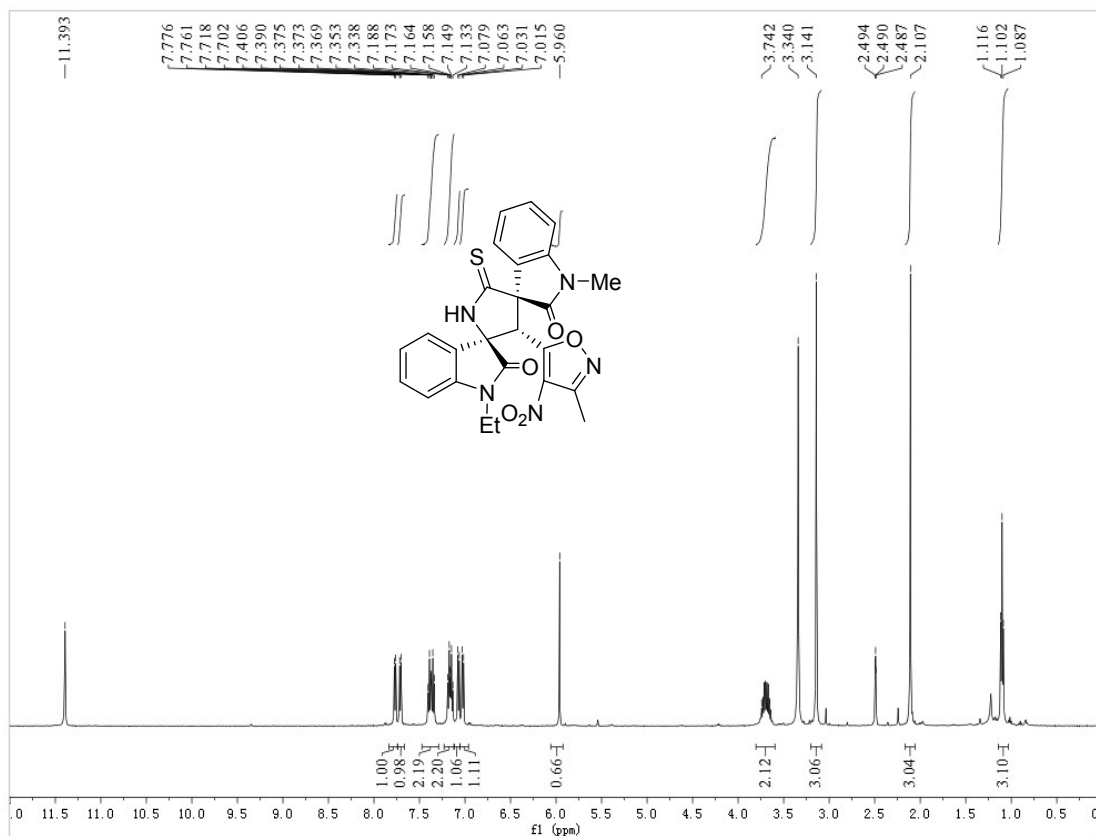


#	Time	Area	Height	Width	Area%	Symmetry
1	19.27	21817.5	134.7	2.6986	50.044	0.583
2	38.315	21779.1	59.5	6.0997	49.956	0.583

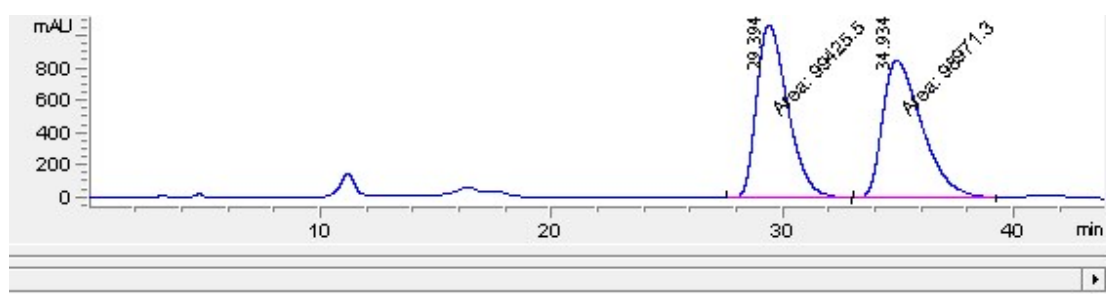


#	Time	Area	Height	Width	Area%	Symmetry
1	18.569	100630.9	665.5	2.5201	87.186	0.538
2	37.377	14790.7	48.1	5.1224	12.814	0.68

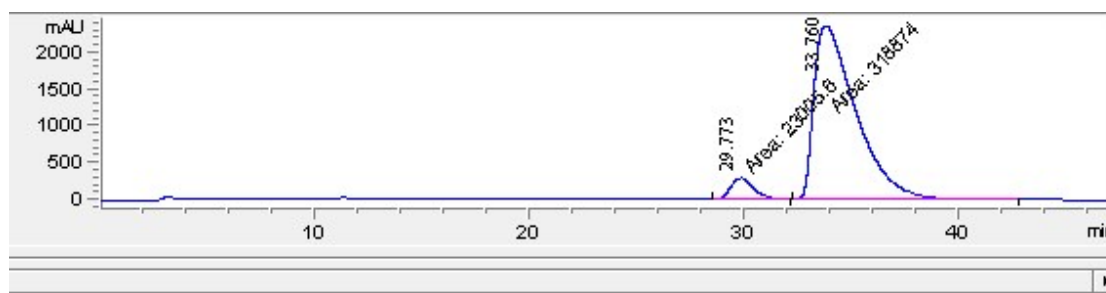
# <sup>1</sup>H and <sup>13</sup>C NMR of 3ba



### HPLC of 3ba

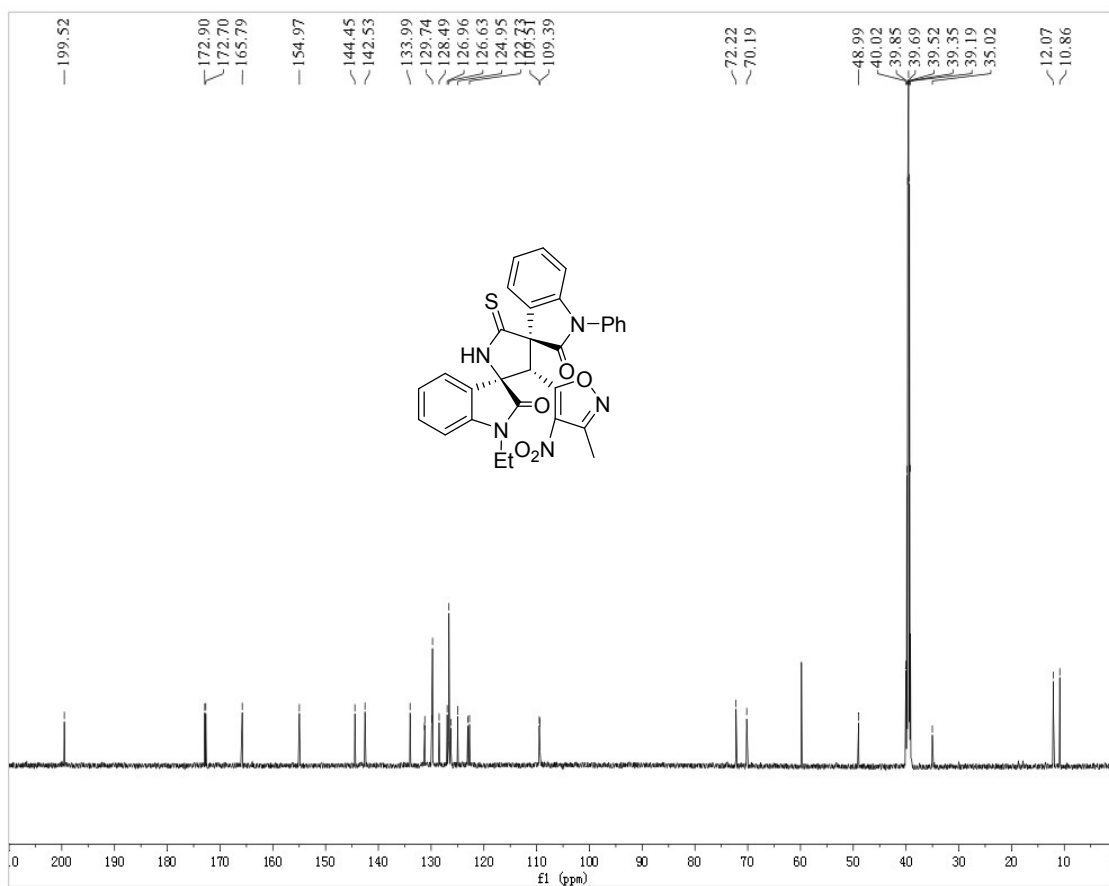
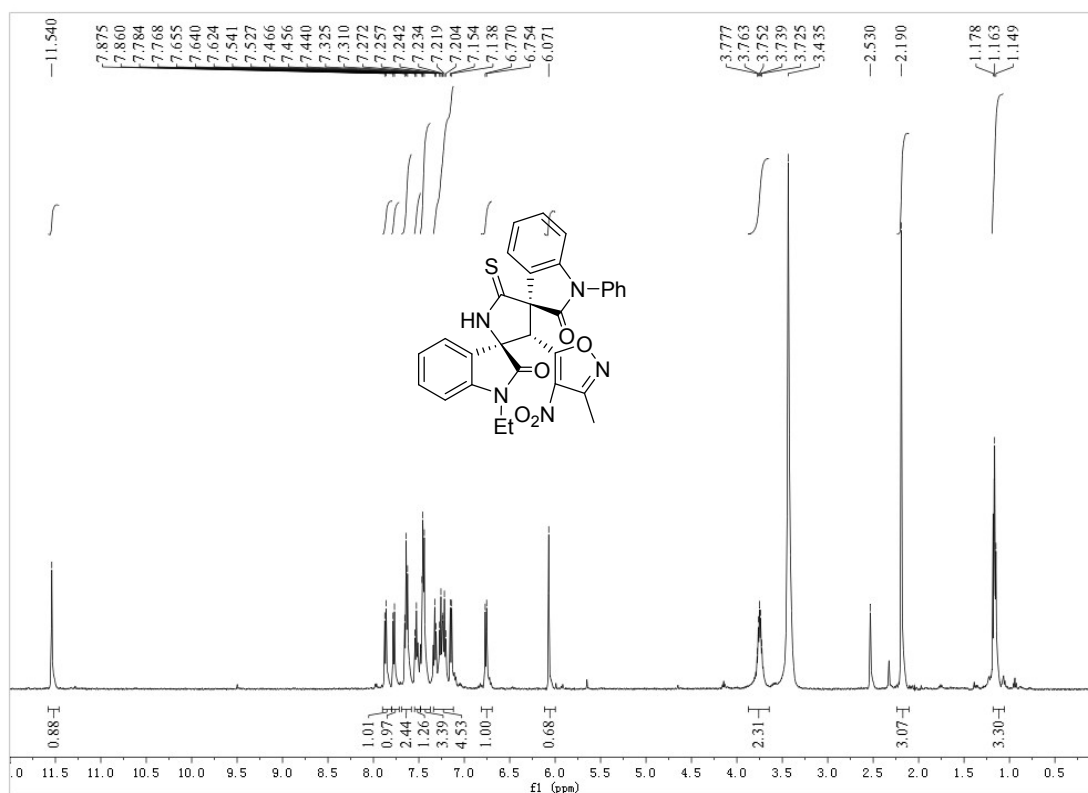


#	Time	Area	Height	Width	Area%	Symmetry
1	29.394	99425.5	1075.4	1.5409	50.114	0.641
2	34.934	98971.3	849.1	1.9427	49.886	0.555

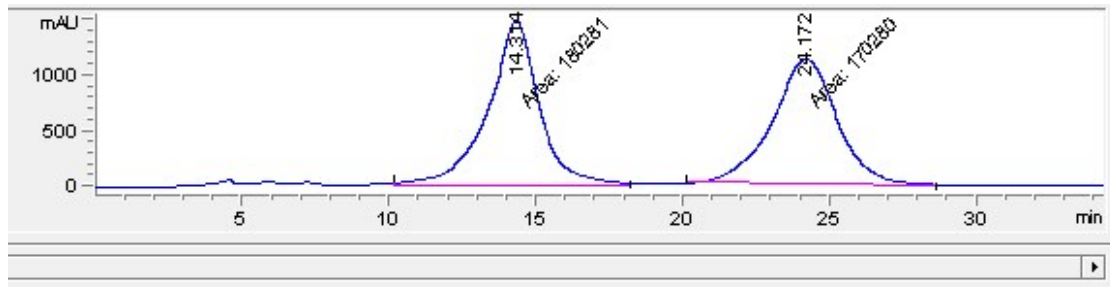


#	Time	Area	Height	Width	Area%	Symmetry
1	29.773	23005.6	293.4	1.3068	6.729	0.718
2	33.76	318873.7	2365.7	2.2465	93.271	0.382

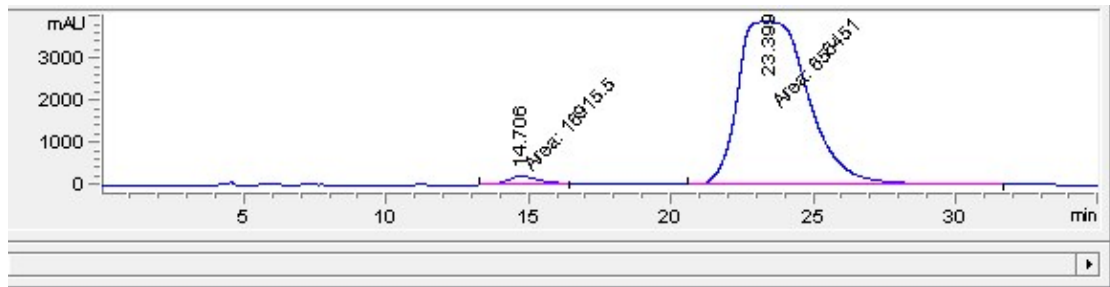
# $^1\text{H}$ and $^{13}\text{C}$ NMR of 3bd



### HPLC of 3bd

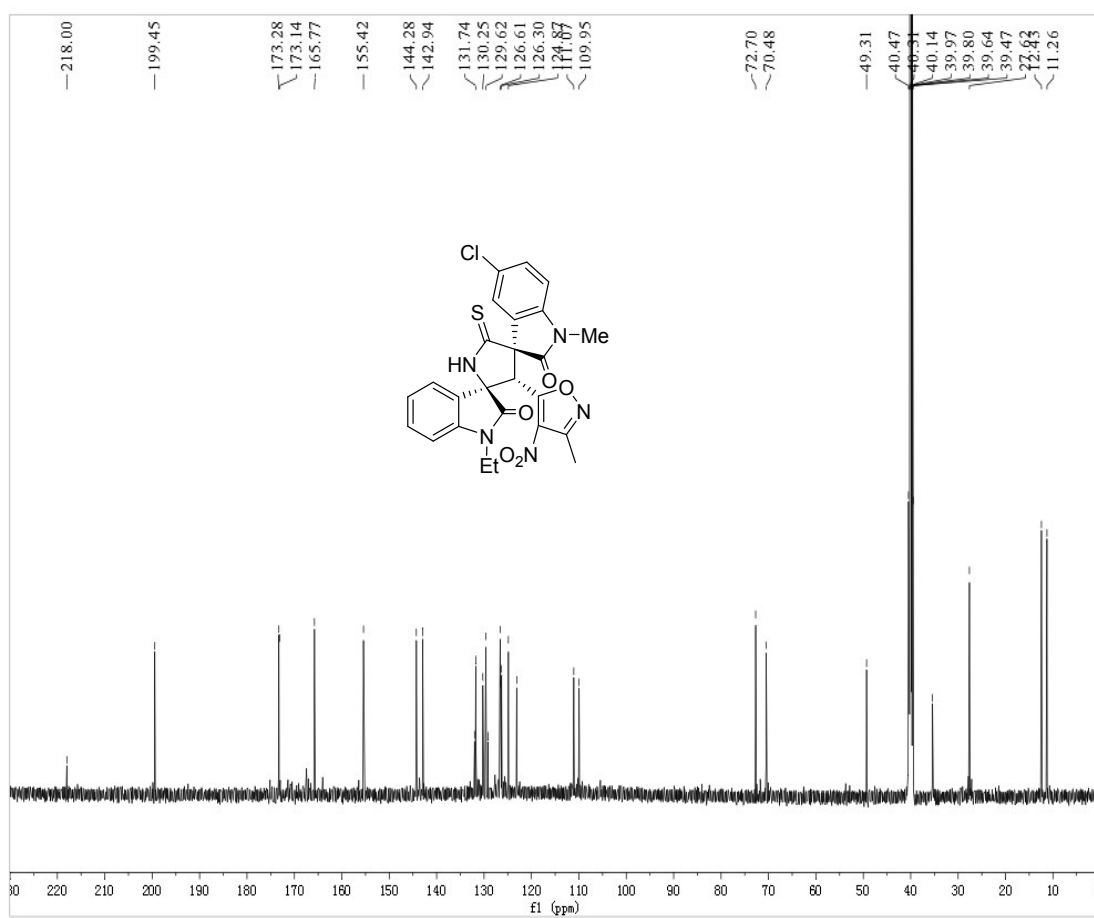
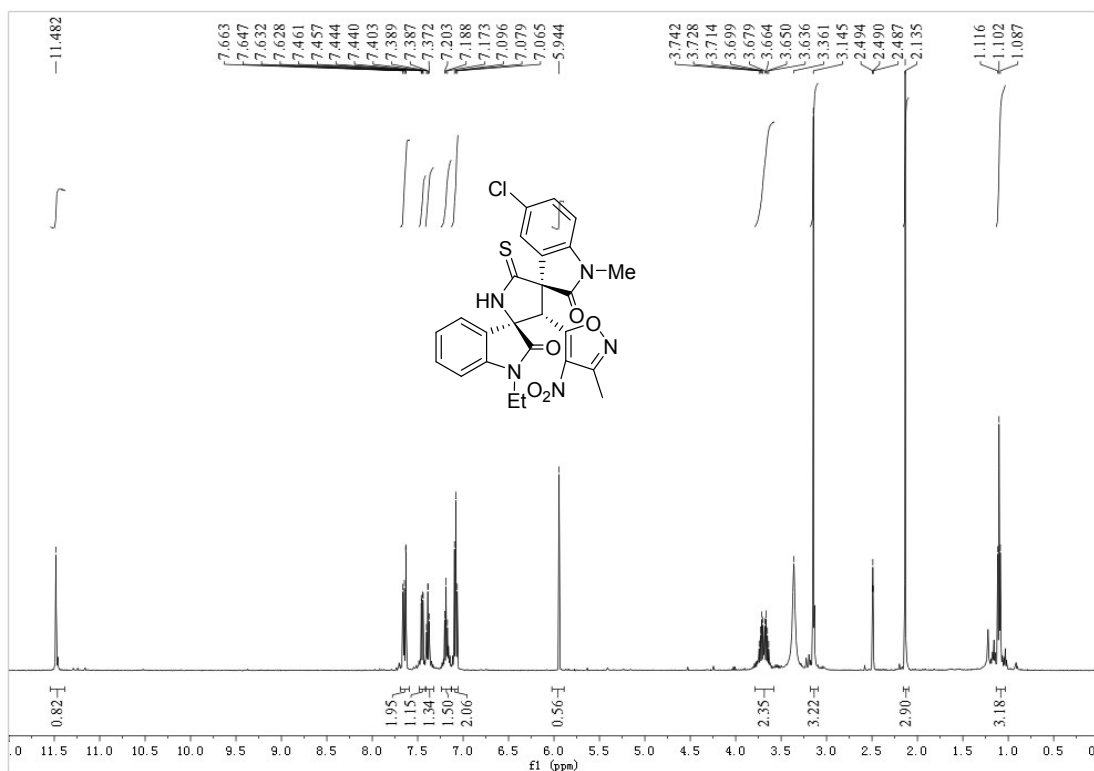


#	Time	Area	Height	Width	Area%	Symmetry
1	14.314	180281.5	1477.2	2.034	51.427	1.213
2	24.172	170279.8	1113.5	2.5488	48.573	1.049



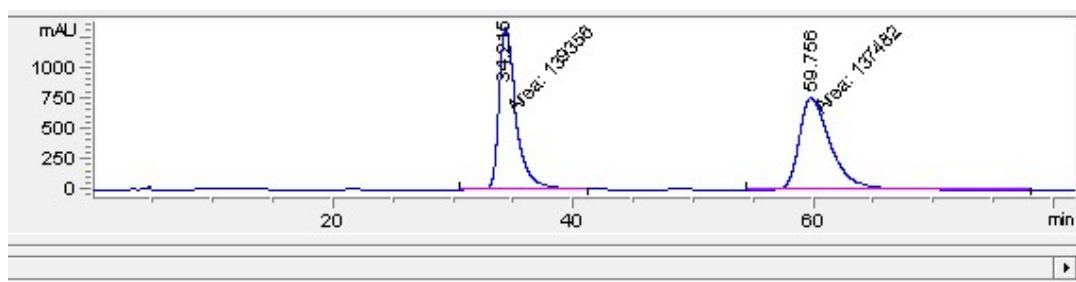
#	Time	Area	Height	Width	Area%	Symmetry
1	14.706	16915.5	204.9	1.3756	2.512	0.685
2	23.399	656450.8	3864.3	2.8313	97.488	0.573

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

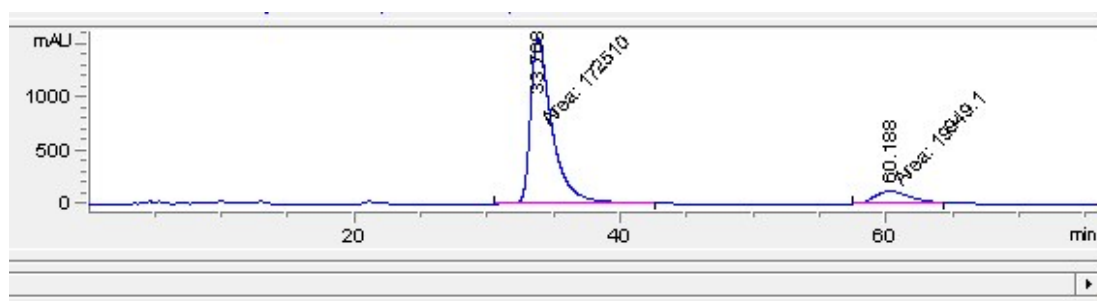




### HPLC of 3be

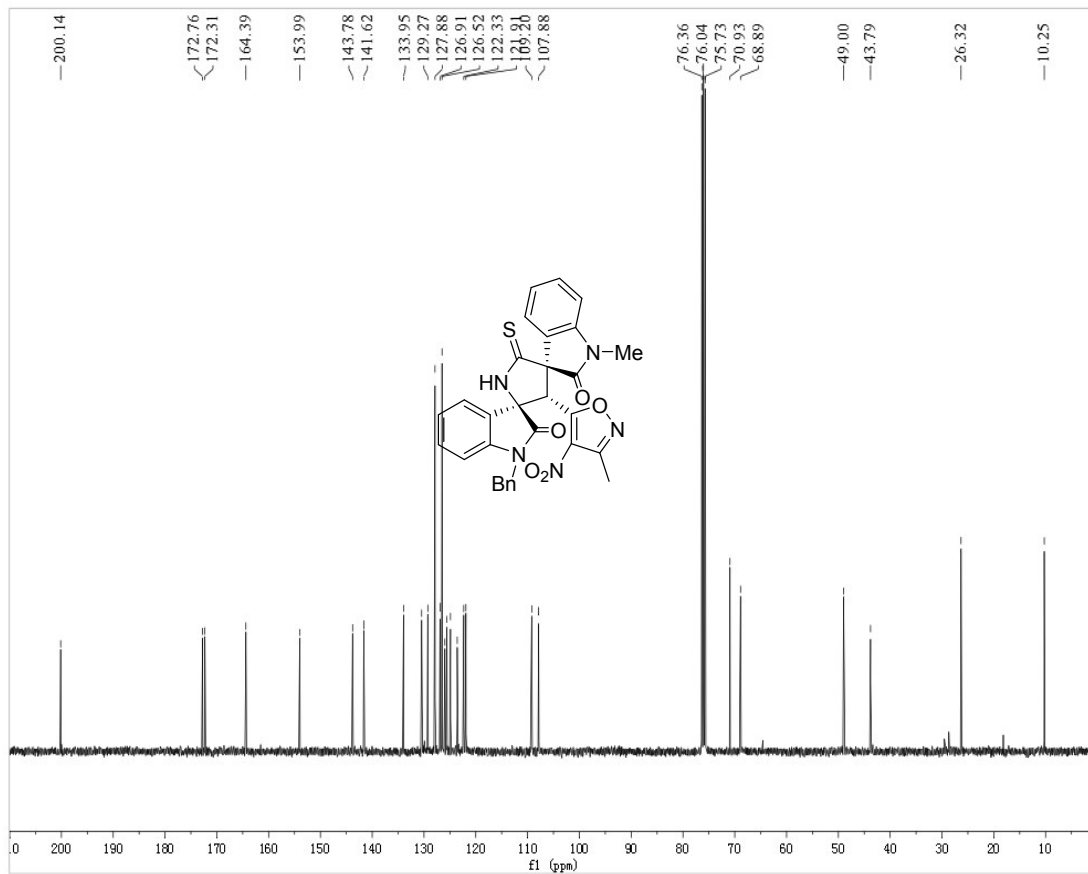
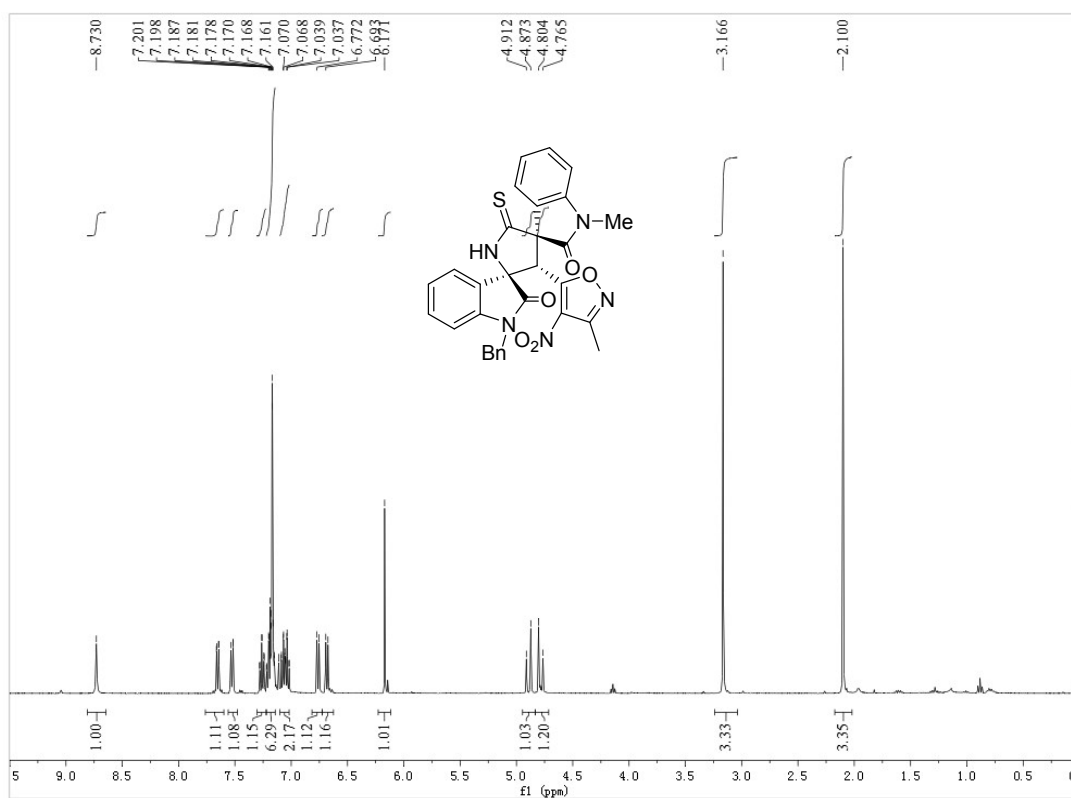


#	Time	Area	Height	Width	Area%	Symmetry
1	34.215	139356.5	1323.8	1.7545	50.338	0.559
2	59.756	137482.3	754.5	3.037	49.662	0.581

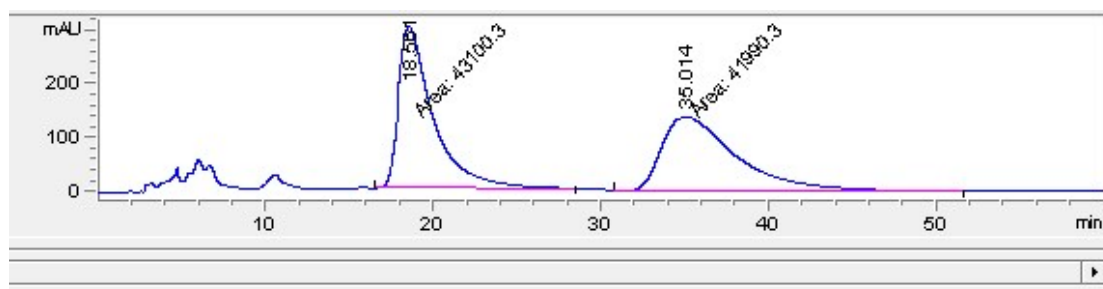


#	Time	Area	Height	Width	Area%	Symmetry
1	33.768	172510.2	1548.5	1.8567	89.635	0.501
2	60.188	19949.1	115.8	2.8721	10.365	0.726

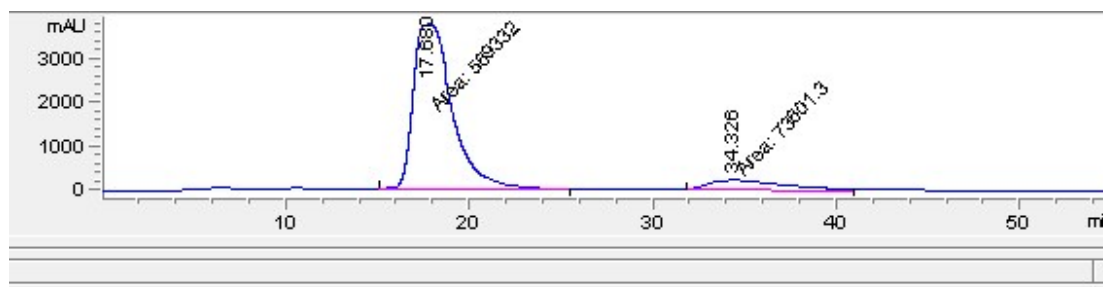
# <sup>1</sup>H and <sup>13</sup>C NMR of 3ca



### HPLC of 3ca

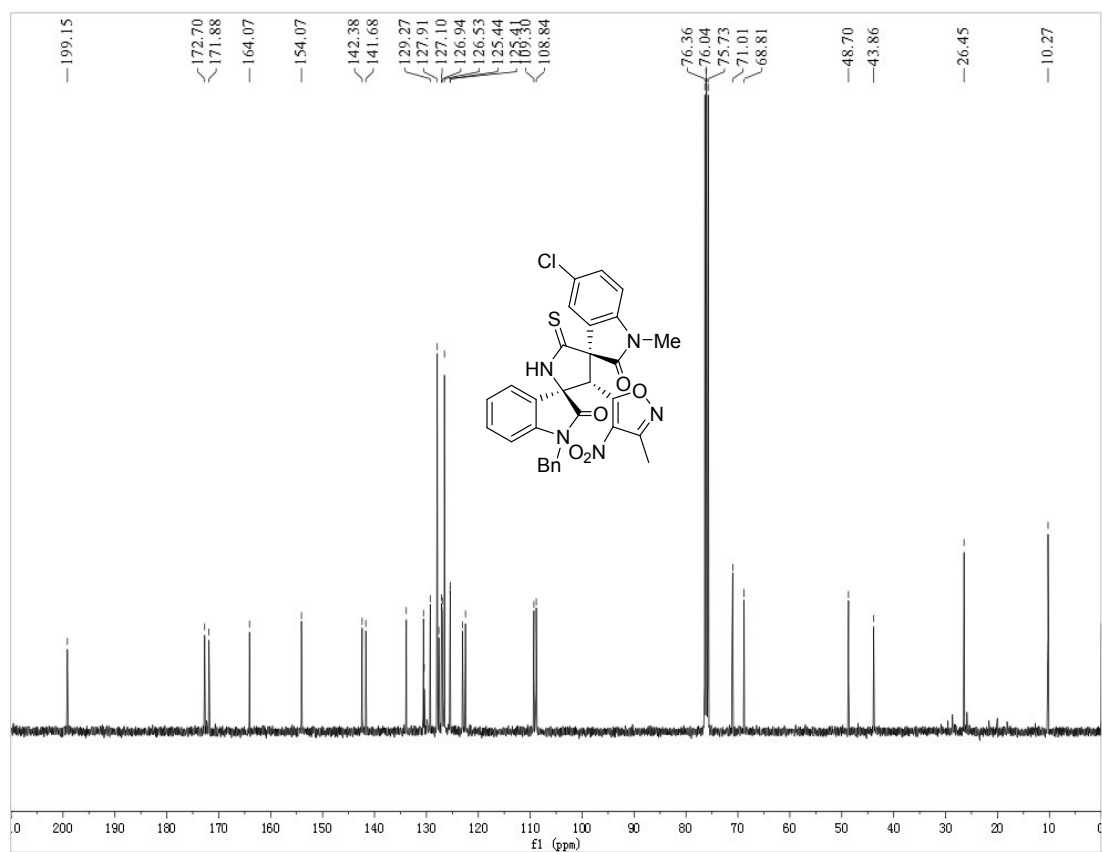
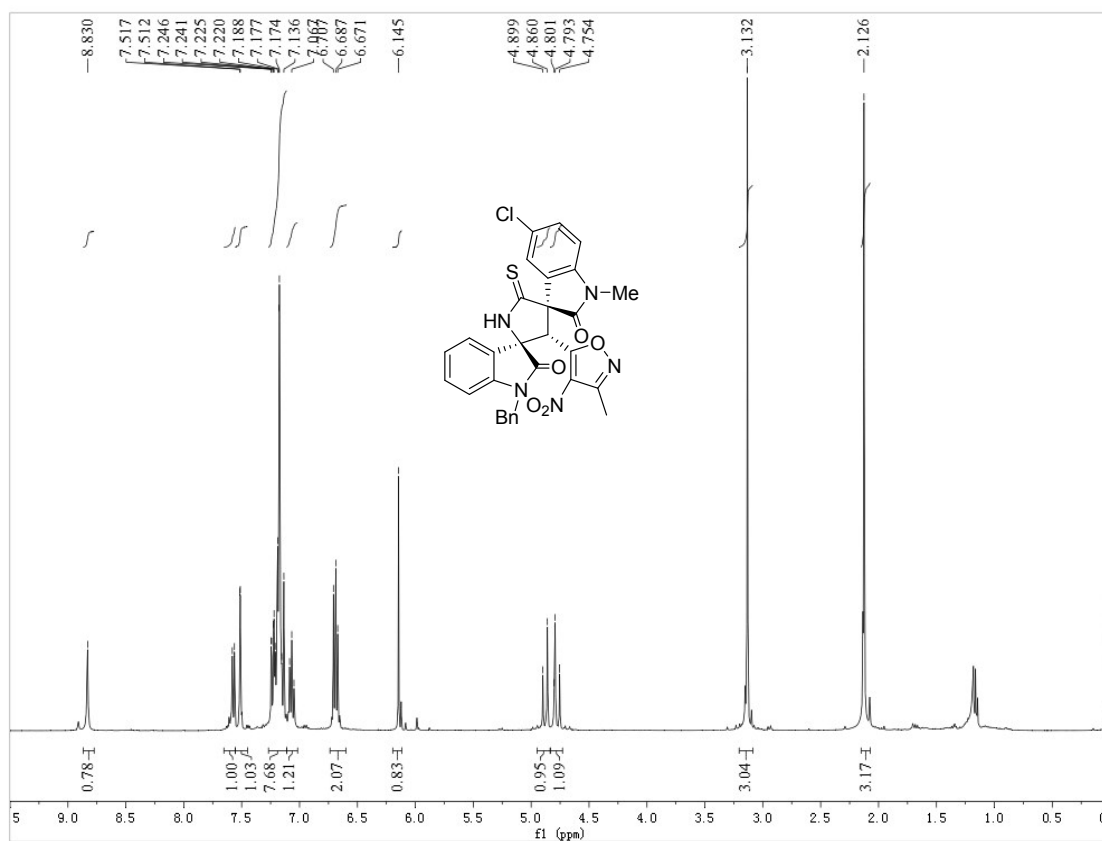


#	Time	Area	Height	Width	Area%	Symmetry
1	18.561	43100.3	298.2	2.4085	50.652	0.455
2	35.014	41990.3	138.2	5.0631	49.348	0.457

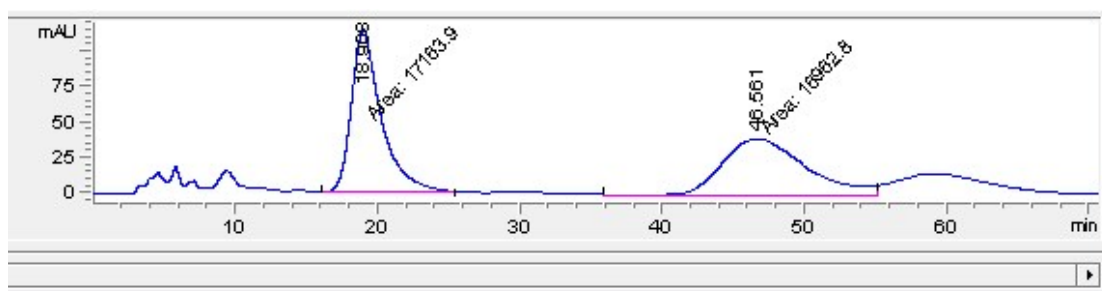


#	Time	Area	Height	Width	Area%	Symmetry
1	17.68	569331.6	3791.7	2.5026	88.552	0.561
2	34.326	73601.3	233.7	5.2495	11.448	0.417

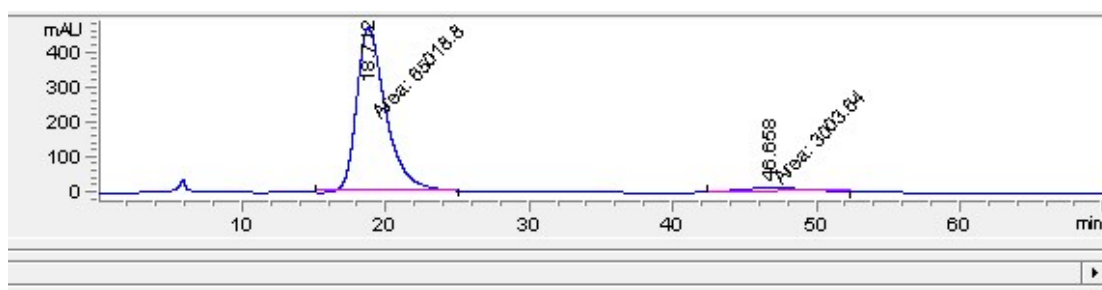
### $^1\text{H}$ and $^{13}\text{C}$ NMR of 3c



### HPLC of 3ce

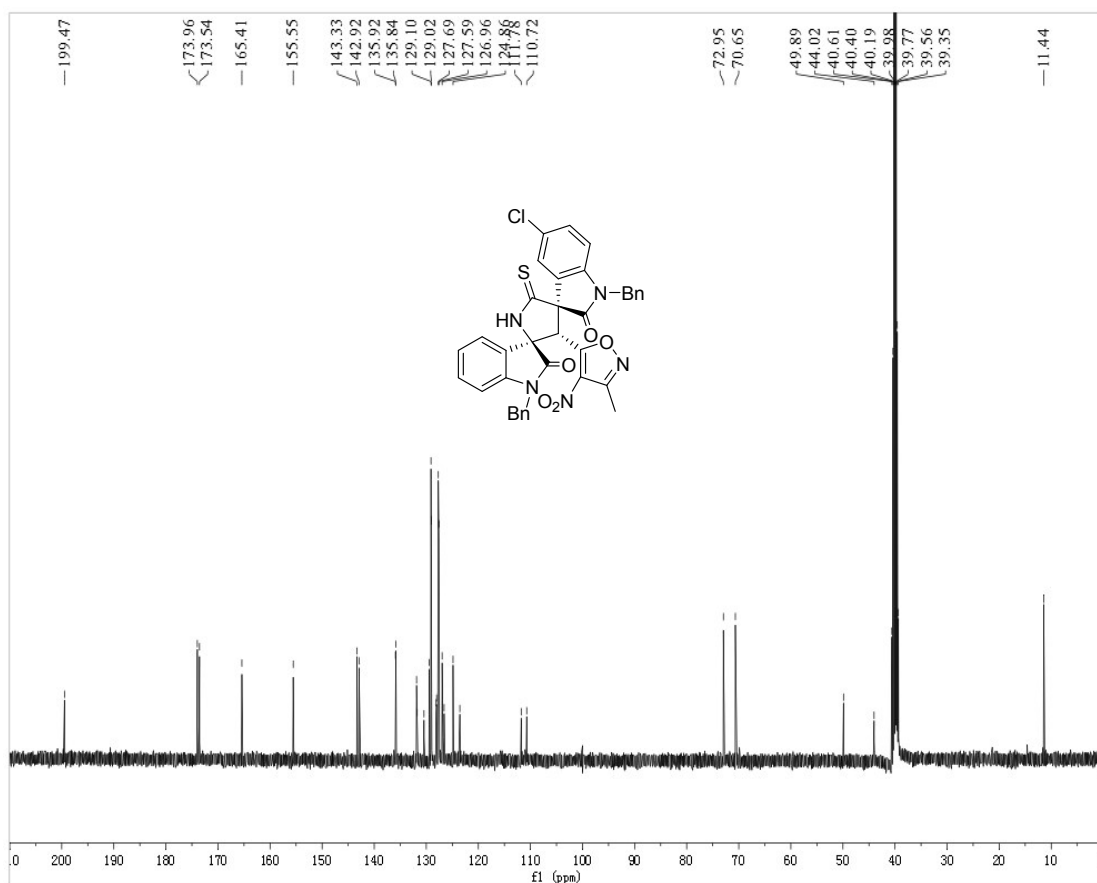
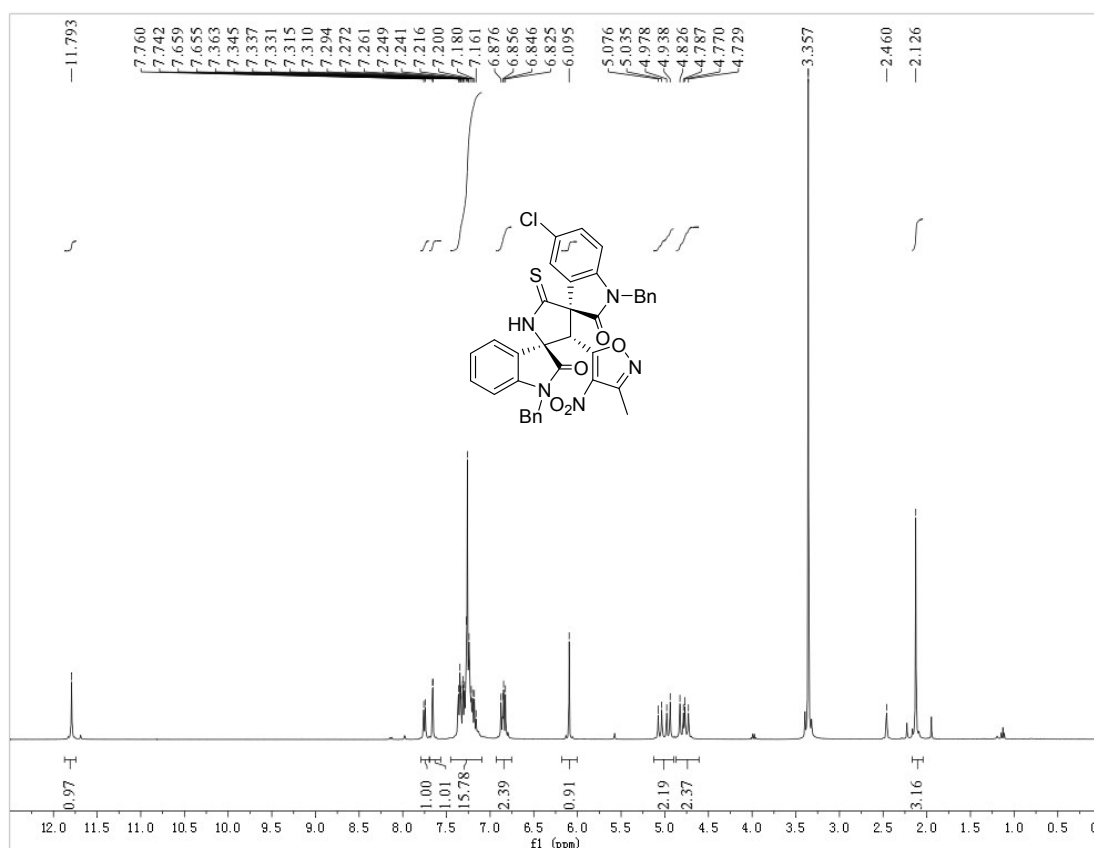


#	Time	Area	Height	Width	Area%	Symmetry
1	18.908	17163.9	114.4	2.5012	50.295	0.616
2	46.561	16962.8	40.5	6.9774	49.705	0.699

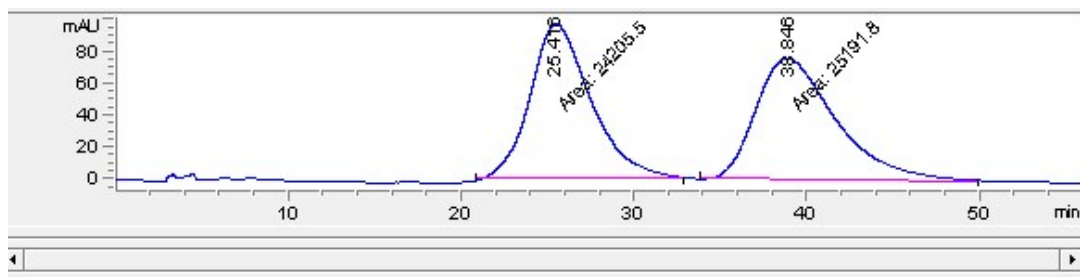


#	Time	Area	Height	Width	Area%	Symmetry
1	18.712	65018.8	464.5	2.3328	95.584	0.636
2	46.658	3003.6	9.8	3.6116	4.416	0.781

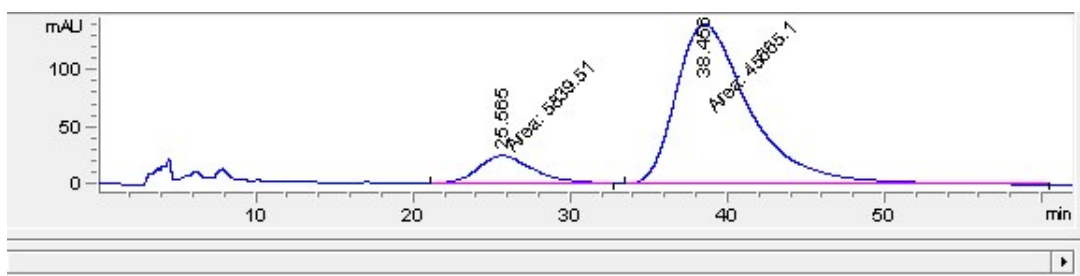
# <sup>1</sup>H and <sup>13</sup>C NMR of 3cf



### HPLC of 3cf

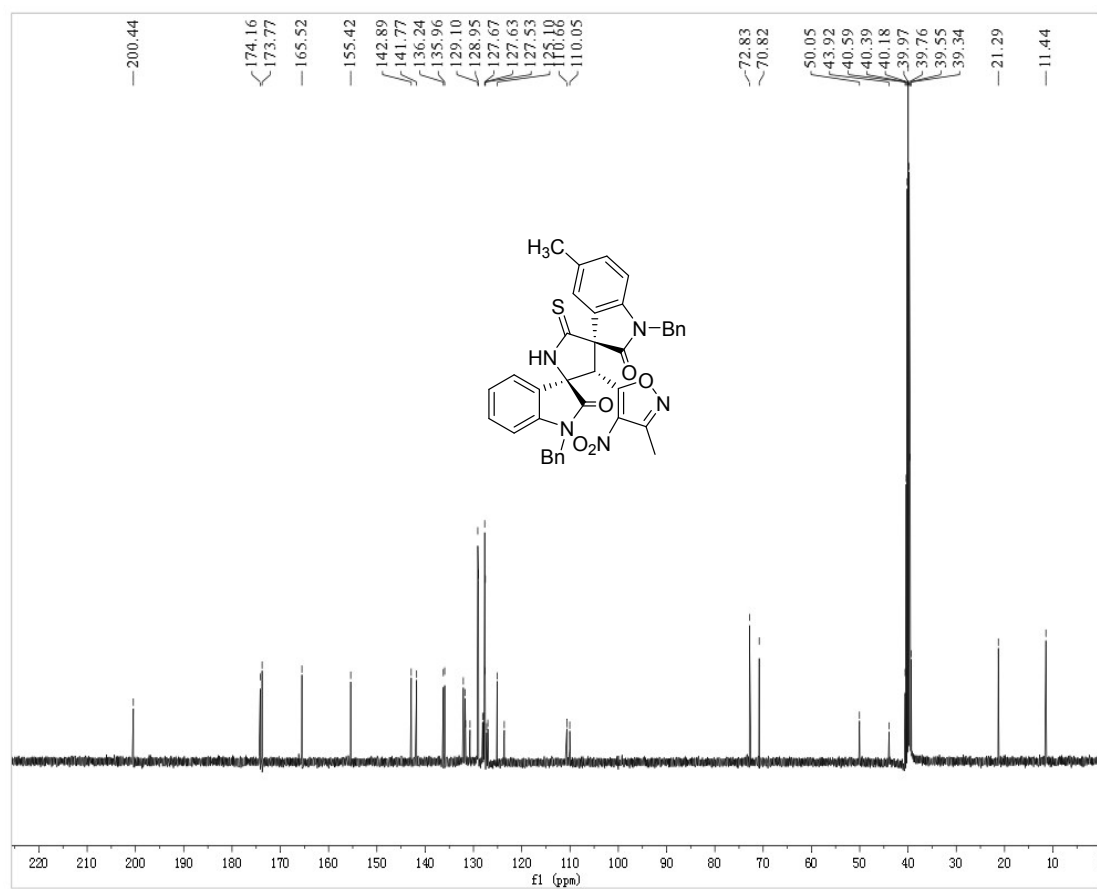
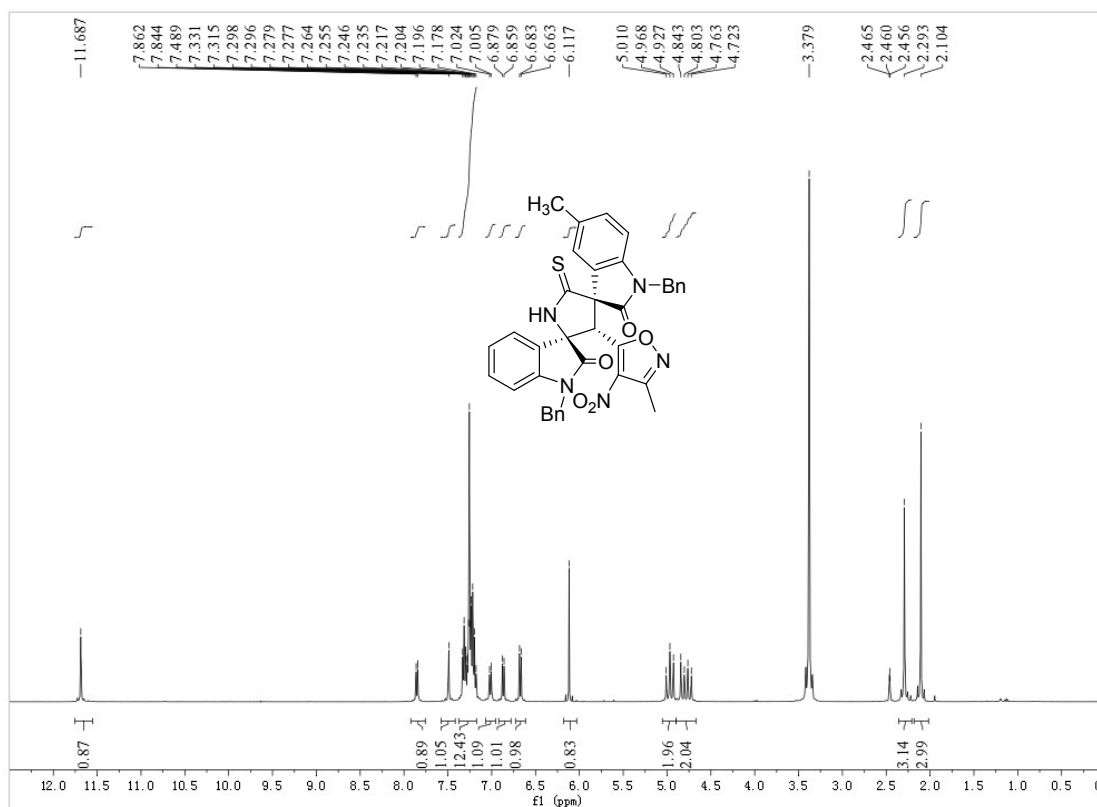


#	Time	Area	Height	Width	Area%	Symmetry
1	25.416	24205.5	97.3	4.1441	49.002	0.72
2	38.846	25191.8	76.4	5.4955	50.998	0.615



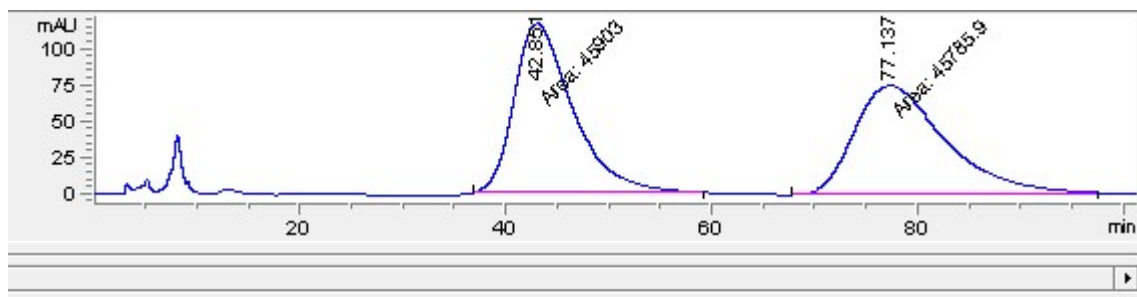
#	Time	Area	Height	Width	Area%	Symmetry
1	25.565	5839.5	24.3	4.0005	11.338	0.738
2	38.456	45665.1	140.5	5.4172	88.662	0.585

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

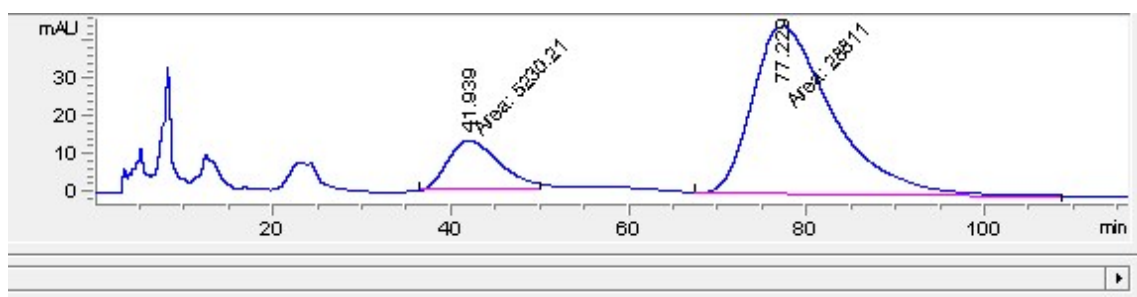




### HPLC of 3ch

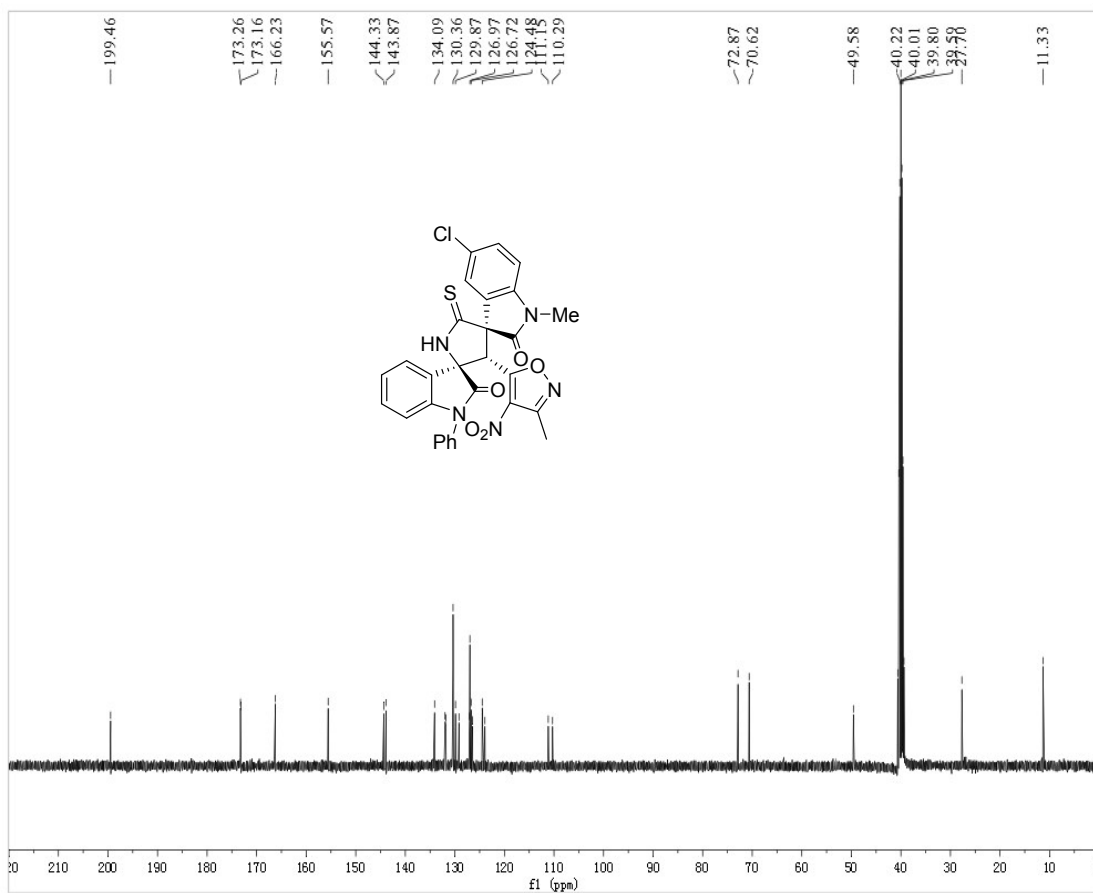
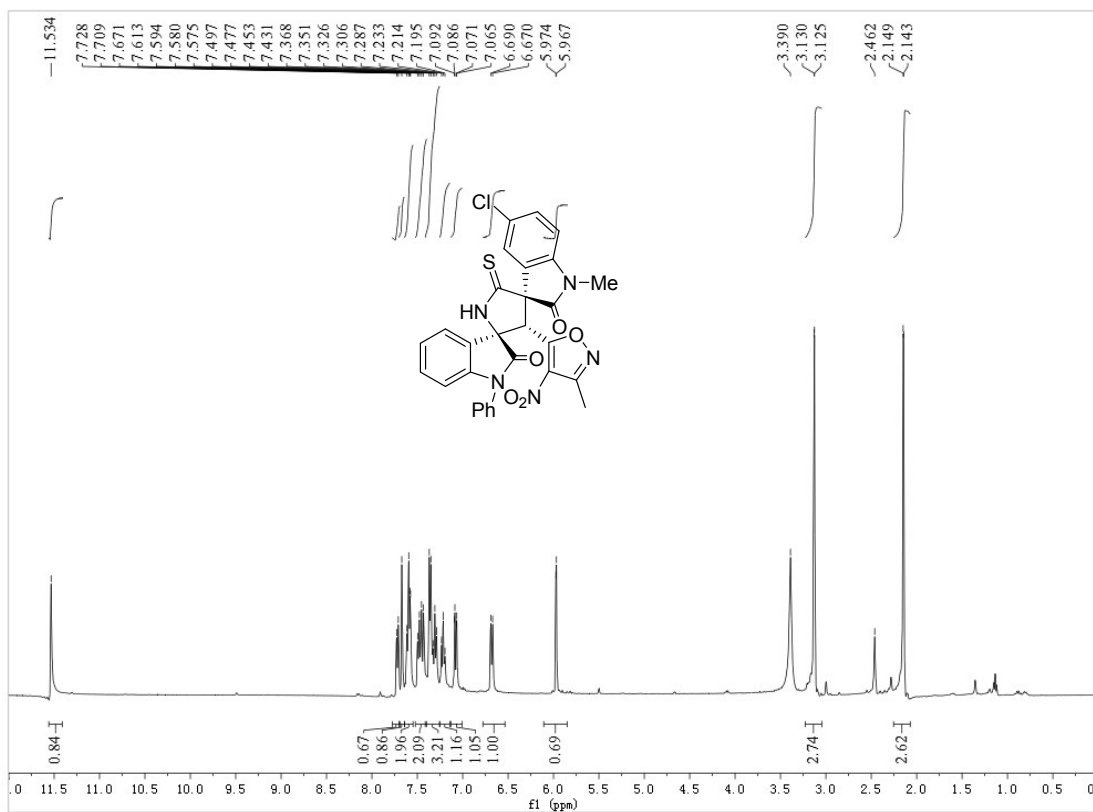


#	Time	Area	Height	Width	Area%	Symmetry
1	42.851	45903	116.1	6.5876	50.064	0.603
2	77.137	45785.9	74.3	10.2637	49.936	0.599

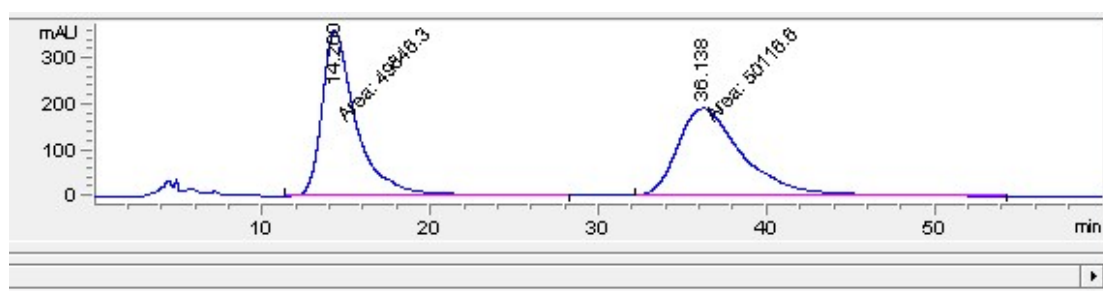


#	Time	Area	Height	Width	Area%	Symmetry
1	41.939	5230.2	12.9	6.7555	15.364	0.676
2	77.229	28811	44.6	10.7686	84.636	0.575

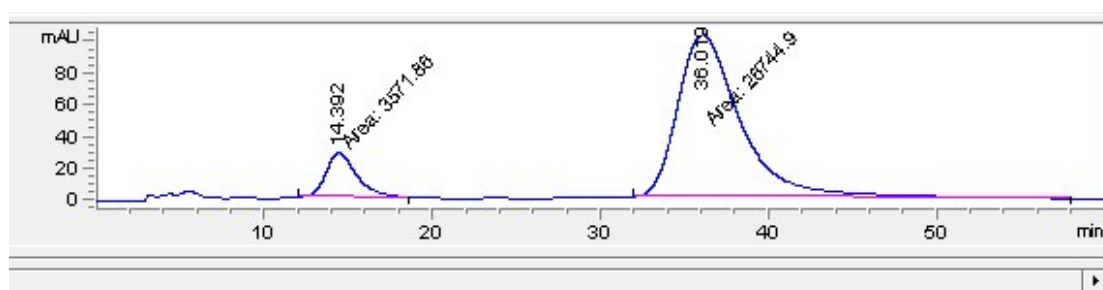
# <sup>1</sup>H and <sup>13</sup>C NMR of 3de



### HPLC of 3de

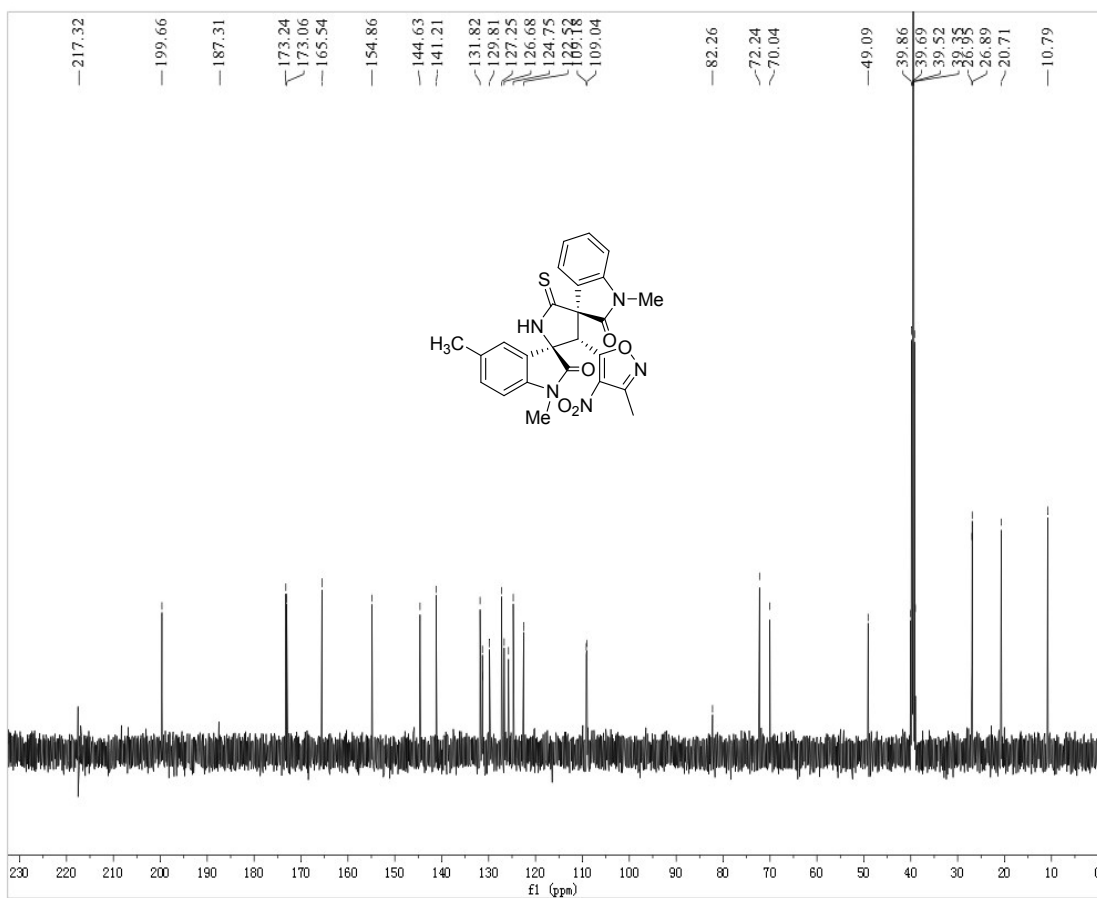
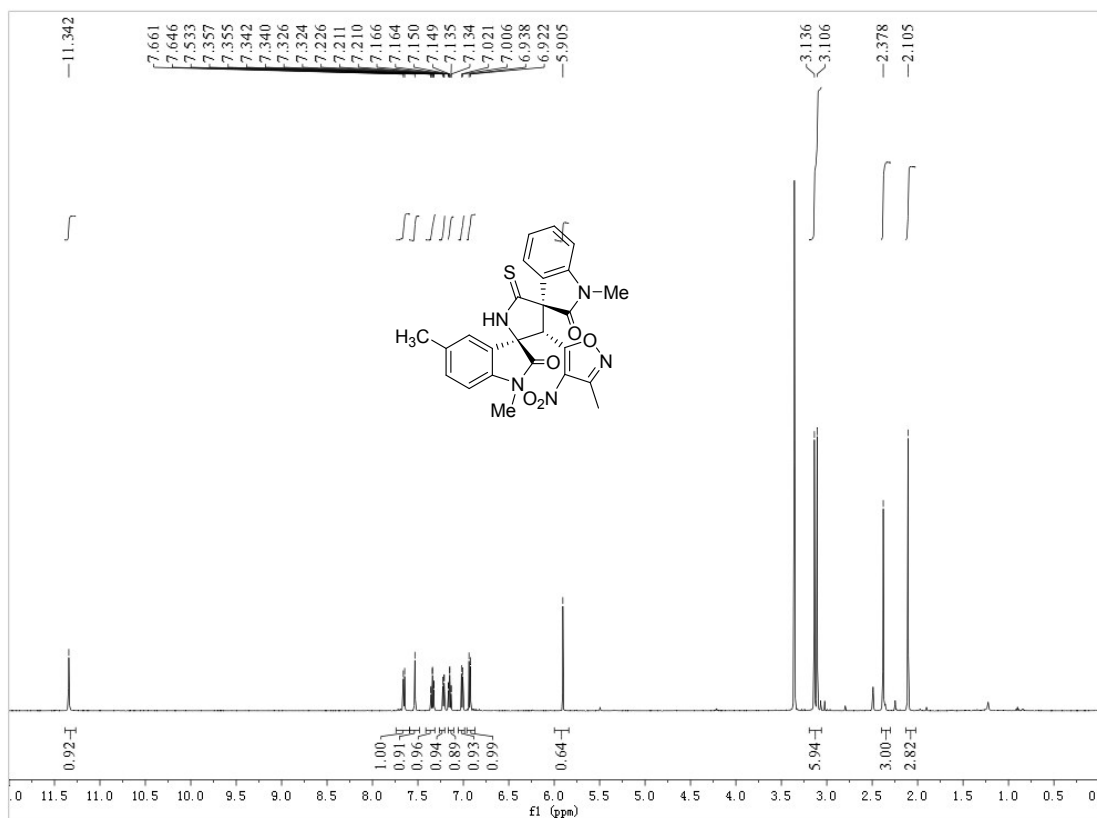


#	Time	Area	Height	Width	Area%	Symmetry
1	14.26	49846.3	359.8	2.3092	49.865	0.567
2	36.138	50116.6	189.4	4.4101	50.135	0.59

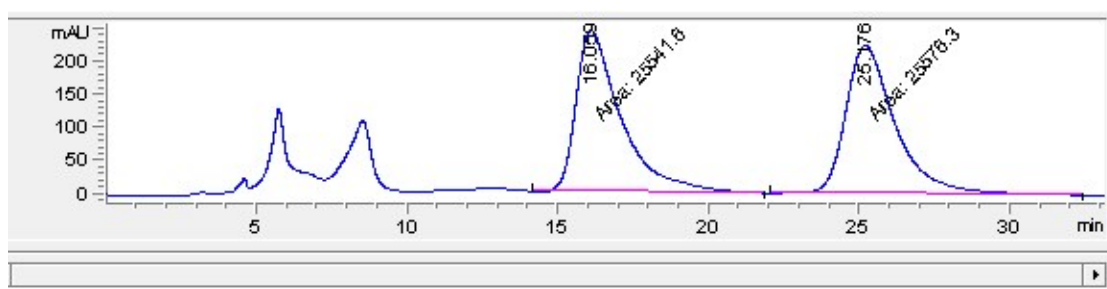


#	Time	Area	Height	Width	Area%	Symmetry
1	14.392	3571.9	27.8	2.1389	11.782	0.674
2	36.019	26744.9	102.2	4.3613	88.218	0.603

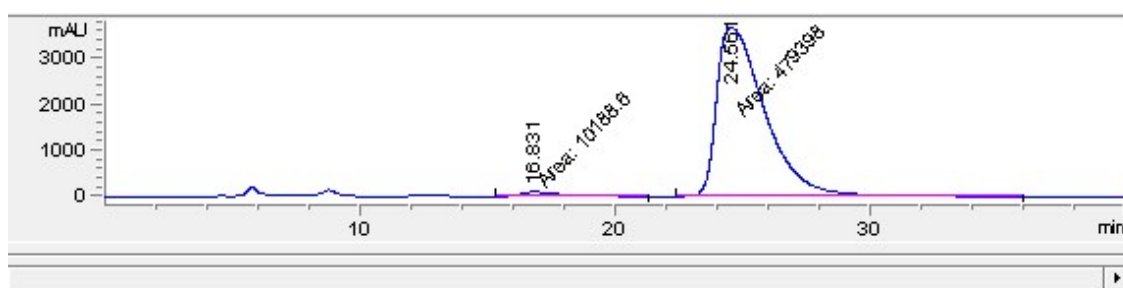
# <sup>1</sup>H and <sup>13</sup>C NMR of 3ea



### HPLC of 3ea

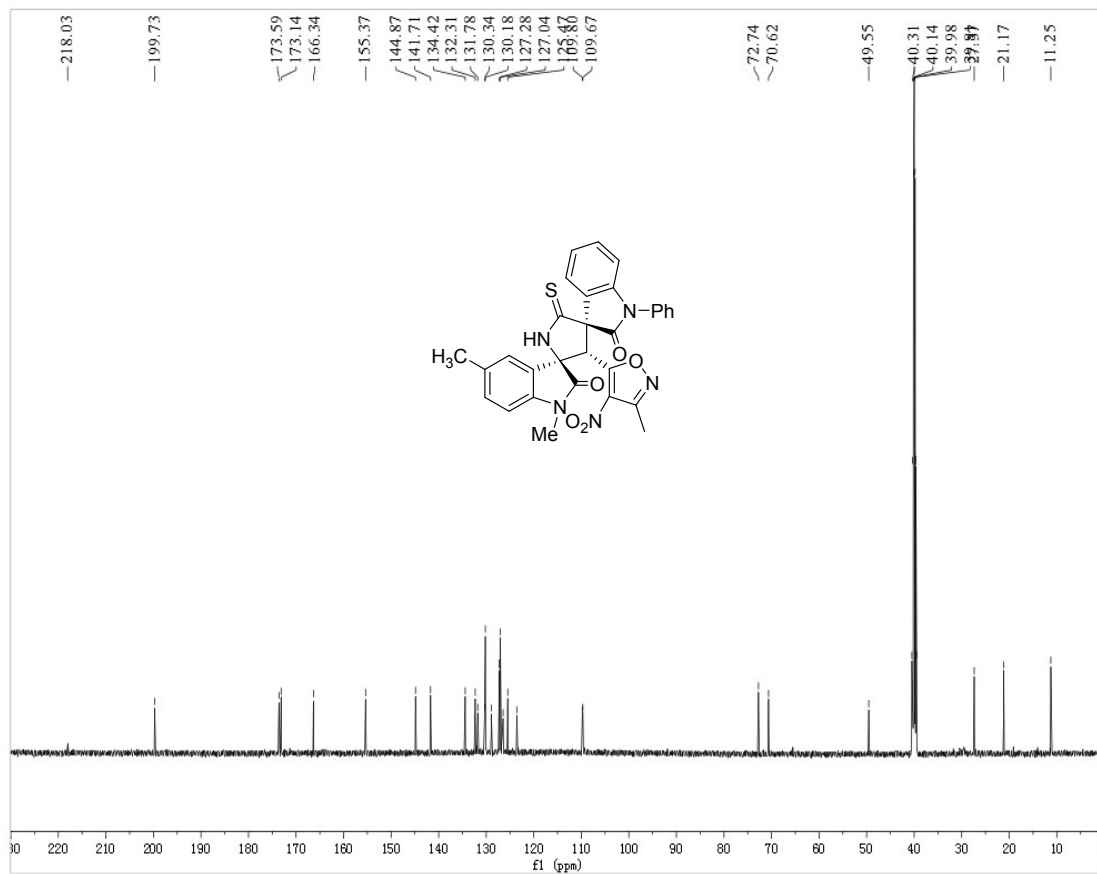
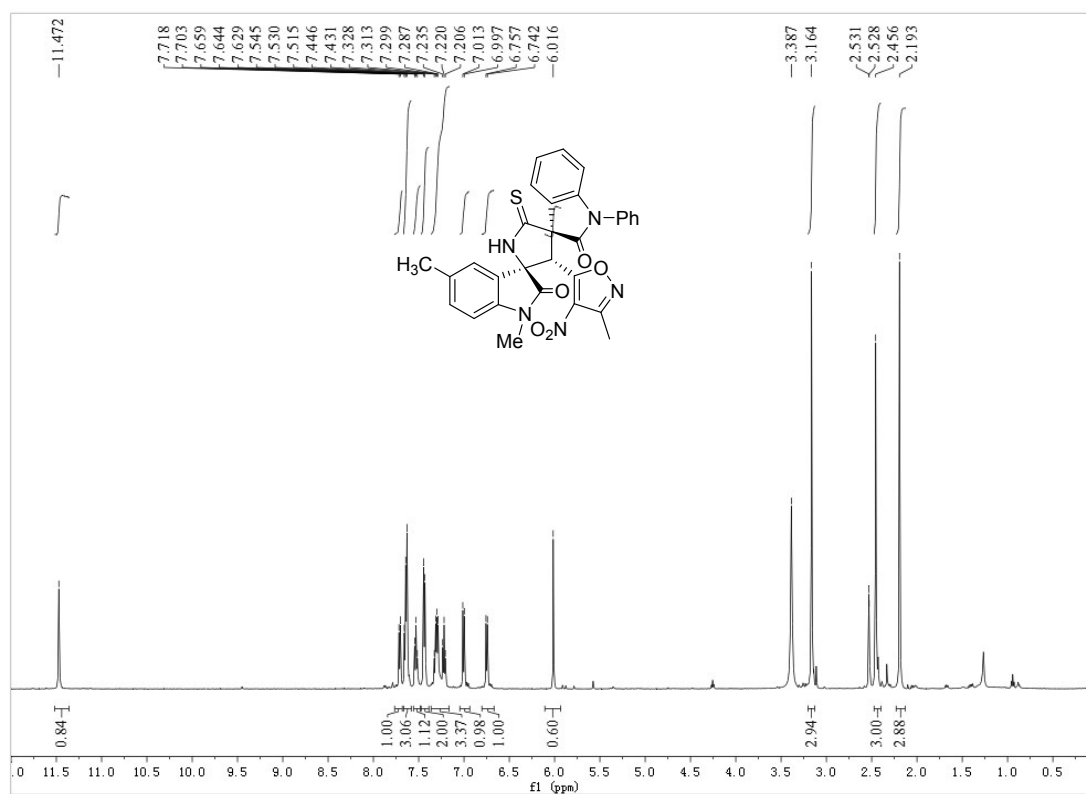


#	Time	Area	Height	Width	Area%	Symmetry
1	16.059	25541.6	244	1.7448	49.966	0.477
2	25.176	25576.3	223.1	1.9107	50.034	0.615

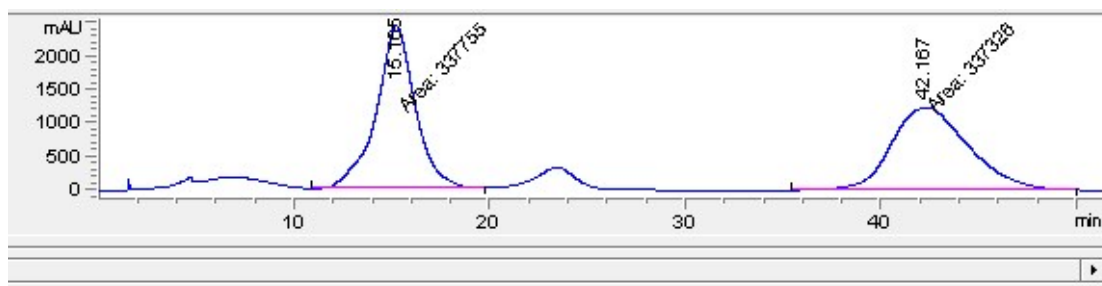


#	Time	Area	Height	Width	Area%	Symmetry
1	16.831	10188.6	96.6	1.7571	2.081	0.489
2	24.561	479398.2	3659.5	2.1834	97.919	0.433

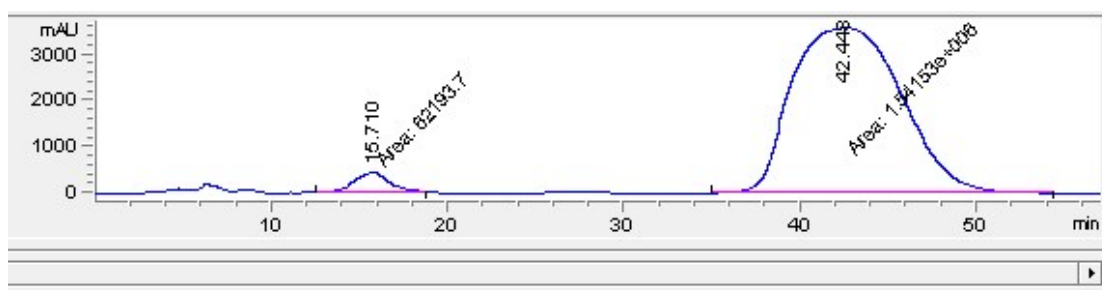
# $^1\text{H}$ and $^{13}\text{C}$ NMR of 3ed



### HPLC of 3ed

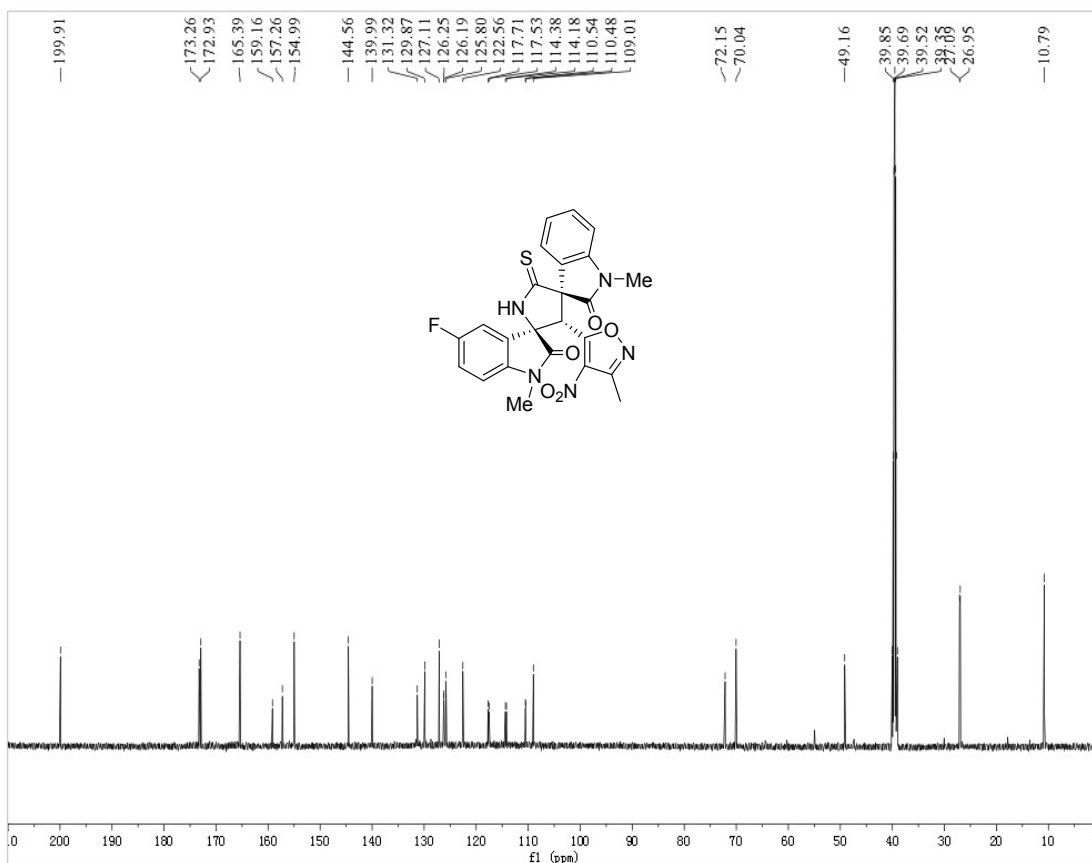
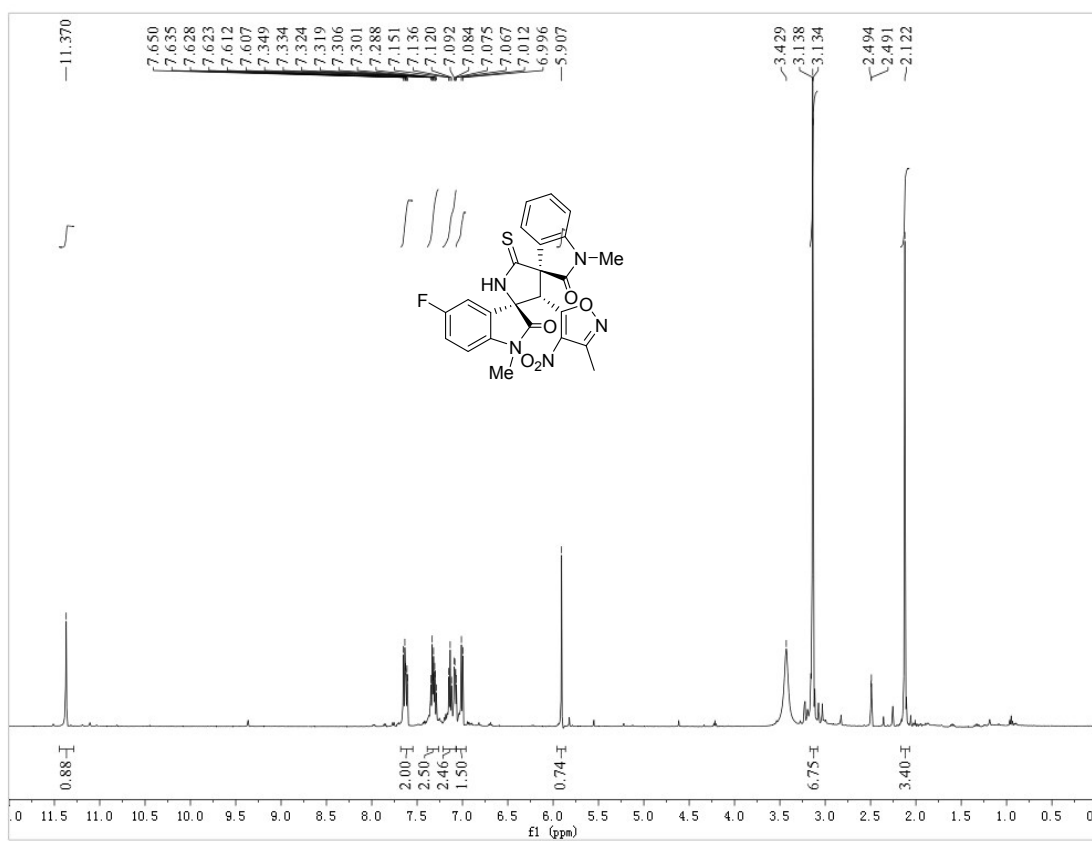


#	Time	Area	Height	Width	Area%	Symmetry
1	15.165	337755.3	2441.1	2.306	50.032	1.015
2	42.167	337326.4	1230.8	4.5677	49.968	0.734



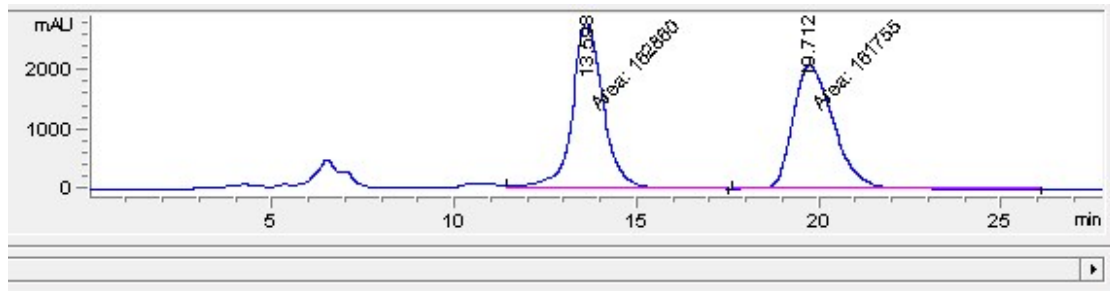
#	Time	Area	Height	Width	Area%	Symmetry
1	15.71	62193.7	438.3	2.3652	3.878	1.053
2	42.448	1541525.9	3575	7.1866	96.122	0.871

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

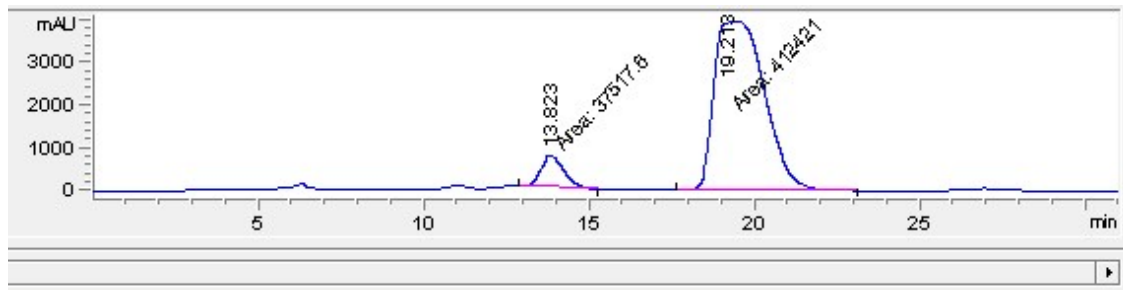




### HPLC of 3fa

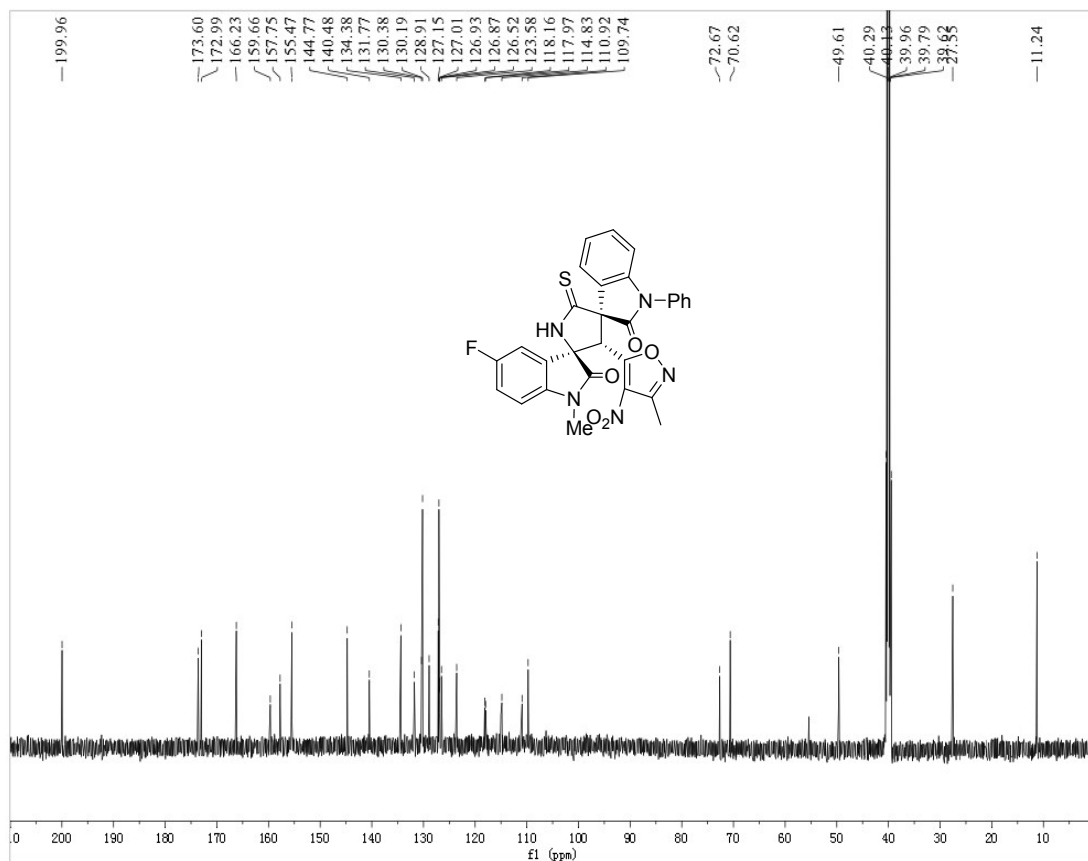
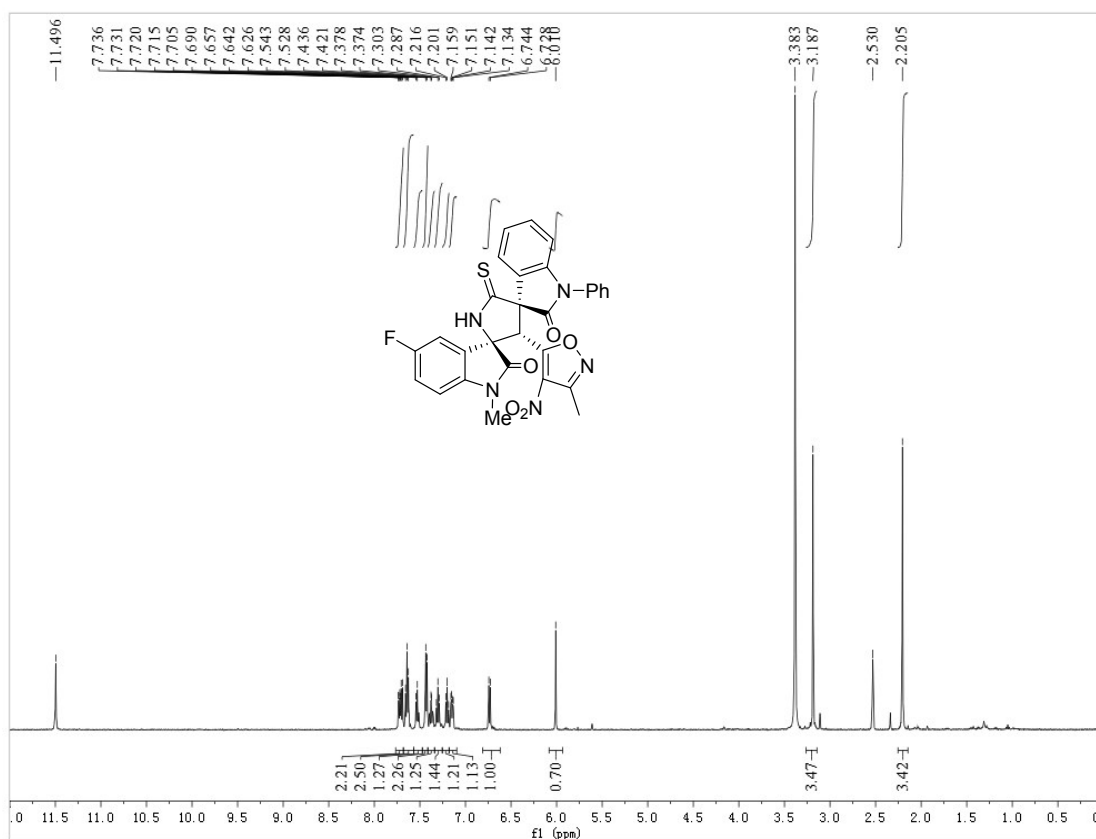


#	Time	Area	Height	Width	Area%	Symmetry
1	13.598	162860.4	2788.8	0.9733	50.170	0.874
2	19.712	161754.5	2099.5	1.2841	49.830	0.66

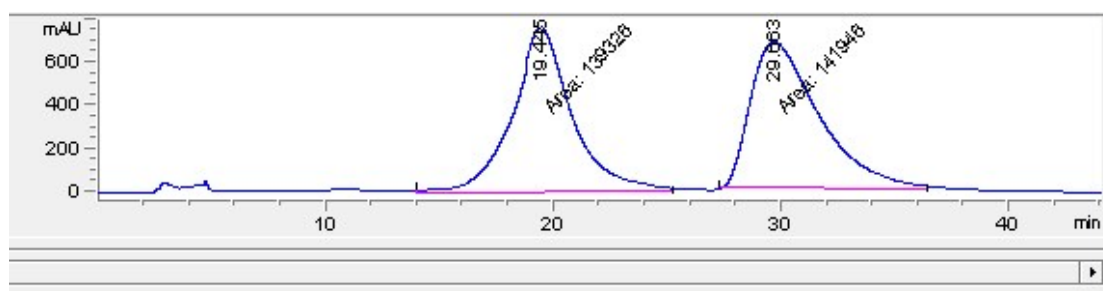


#	Time	Area	Height	Width	Area%	Symmetry
1	13.823	37517.6	747.8	0.8361	8.338	0.774
2	19.213	412421.3	3931.2	1.7485	91.662	0.429

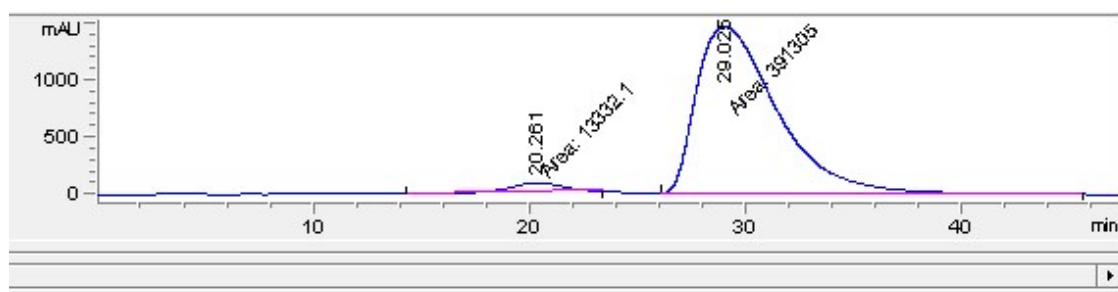
# <sup>1</sup>H and <sup>13</sup>C NMR of 3fd



### HPLC of 3fd

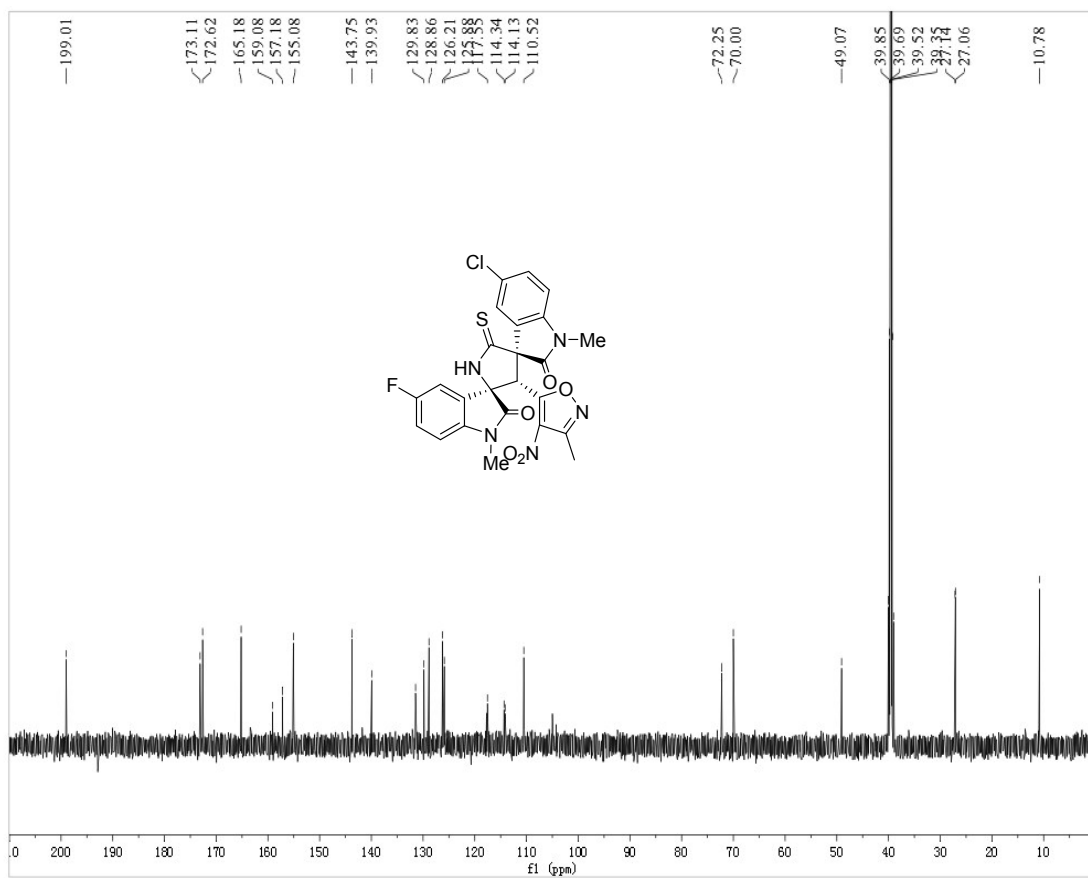
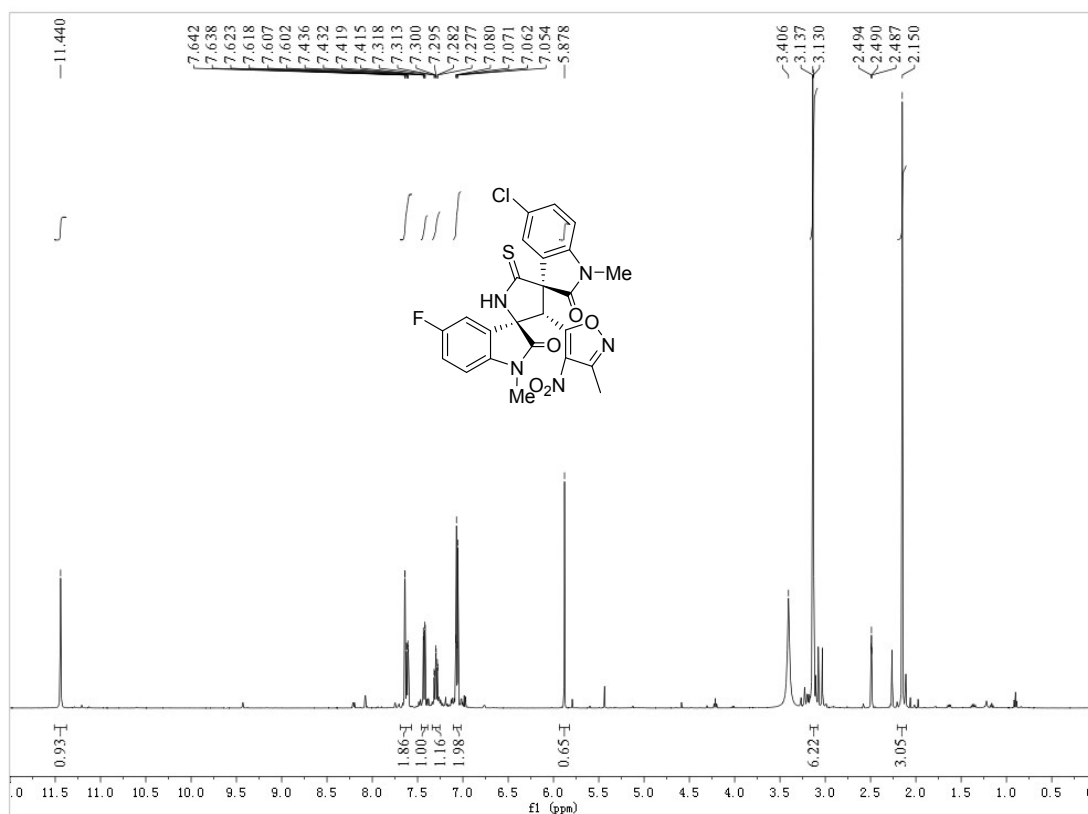


#	Time	Area	Height	Width	Area%	Symmetry
1	19.445	139325.9	763	3.0435	49.534	0.92
2	29.663	141946.5	675.9	3.5004	50.466	0.51

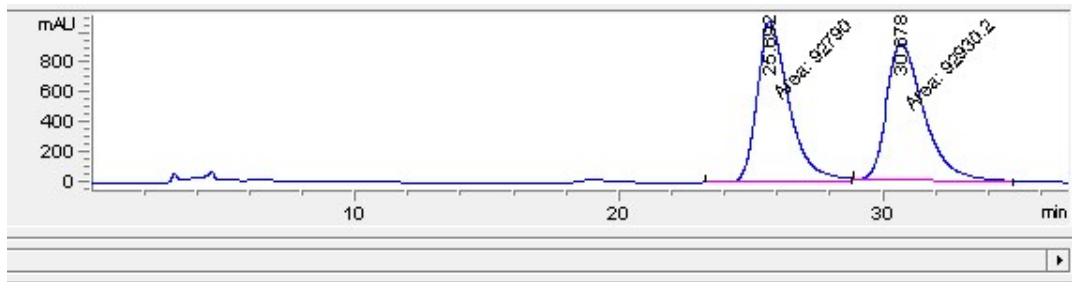


#	Time	Area	Height	Width	Area%	Symmetry
1	20.261	13332.1	83.3	2.668	3.295	0.994
2	29.025	391304.6	1474.9	4.4219	96.705	0.507

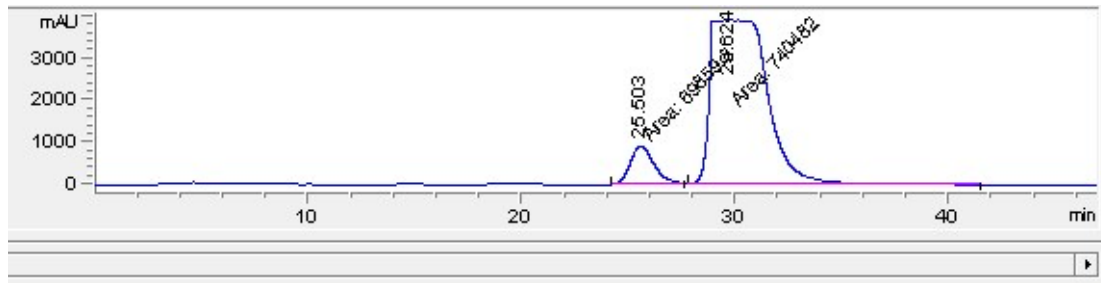
# <sup>1</sup>H and <sup>13</sup>C NMR of 3fe



### HPLC of 3fe



#	Time	Area	Height	Width	Area%	Symmetry
1	25.692	92790	1068	1.4481	49.962	0.669
2	30.678	92930.2	924.2	1.676	50.038	0.652



#	Time	Area	Height	Width	Area%	Symmetry
1	25.503	69859.8	897.6	1.2971	8.621	0.731
2	29.624	740482.1	3902.7	3.1623	91.379	0.441