

## Supporting information

### Asymmetric synthesis of spirooxindole-pyranoindoles via Friedel-Crafts alkylation/cyclization of the indole carbocyclic ring

Yuan Gao, Xiaonan Wang, Zhonglin Wei, Jungang Cao, Dapeng Liang, Yingjie Lin, and Haifeng Duan

Department of Organic Chemistry, College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China

E-mail: linyj@jlu.edu.cn; duanhf@jlu.edu.cn; Tel: 0431-85168398

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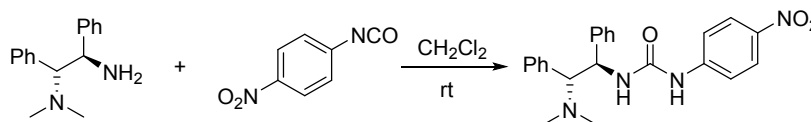
## 1. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without purification. All solvents were obtained from commercial sources and were purified according to standard procedures. TLC was carried out on silica gel plates (HSGF 254), which were visualized with UV light and/or staining with phosphomolybdic acids solution. Purification of reaction products was carried out by column chromatography using silica gel (200-300 mesh).  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, and  $^{19}\text{F}$  NMR spectra were recorded on a Varian Mercury-300BB (300 MHz), a Bruker NMR Spectrometer (400 MHz), or a Bruker NMR Spectrometer (500 MHz). All chemical shifts ( $\delta$ ) were given in ppm. Chemical shifts are relative to the resonance of the deuterated solvent as the internal standard ( $\text{CDCl}_3$ ,  $\delta 77.26$  ppm for proton NMR,  $\delta 77.16$  ppm for carbon NMR;  $\text{DMSO-}d_6$ ,  $\delta 2.50$  ppm for proton NMR,  $\delta 39.52$  ppm for carbon NMR). Data are presented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = double, t = triplet, q = quartet, m = multiplet), and coupling constant in hertz. Mass spectra were recorded on a Bruker Agilent 1290 MicroTOF-Q II instrument. Melting points were measured on a melting points apparatus and were uncorrected. The enantioselectivity value determination was carried out using chiral HPLC (Waters) instrumentation with a Chiracel AD-H column and IA-3 column. Optical rotations were measured on a Shanghai ShenGuang SGW-2 polarimeter at  $\lambda = 589$  nm. Optical rotations are reported as follows:  $[\alpha]_D^{25}$  (c = g/100mL, solvent).

## 2. Starting materials.

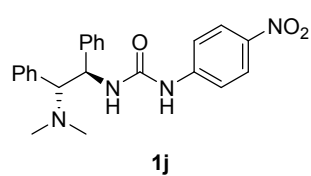
Isatylidene malononitriles were prepared according to literature procedures.<sup>1,2</sup>

## 3. Preparation and characterization of catalyst **1j**



1-isocyanato-4-nitrobenzene (164.1 mg, 1.0 mmol) was added to a solution of (1R, 2R)-N,N-dimethyl-1,2-diphenylethane-1,2-diamine (240.4mg, 1.0 mmol) in dichloromethane (4mL) at room temperature. The resulting mixture was stirred at room temperature for 12 h. Then the solvent was removed in vacuo via evaporation. The crude product was purified by chromatography ( $\text{CH}_2\text{Cl}_2/\text{MeOH} = 40:1$ ) to afford the desired organocatalyst (287.2mg, 71% yield) as a yellow solid.

1-((1R,2R)-2-(dimethylamino)-1,2-diphenylethyl)-3-(4-nitrophenyl)urea (**1j**)

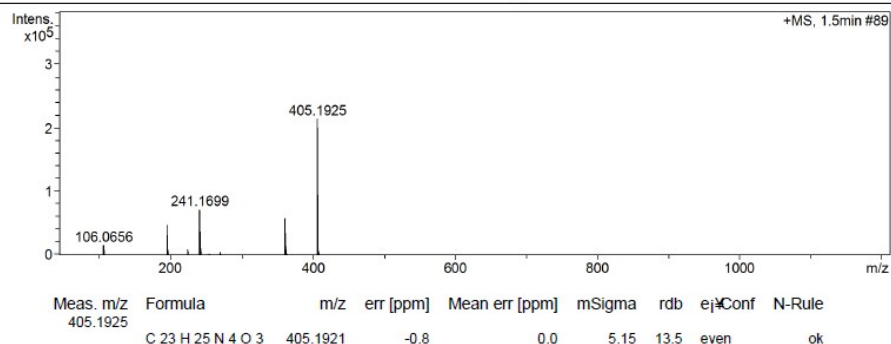


**m. p.** = 127-129°C,  $[\alpha]_D^{25} = +48.4$  (c = 0.1,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{Chloroform-}d$ )  $\delta$  8.09 (d,  $J = 8.8$  Hz, 2H), 7.66 (s, 1H), 7.42 (d,  $J = 8.7$  Hz, 2H), 7.33 – 6.83 (m, 11H), 5.05 (d,  $J = 10.7$  Hz, 1H), 3.67 (d,  $J = 10.8$  Hz, 1H), 2.17 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.9, 145.7, 142.0, 140.5, 131.8, 129.8, 128.4, 128.0, 127.9, 127.5, 127.4, 125.1, 117.7, 74.0, 55.5, 40.7. **HRMS** (ESI) calculated for  $\text{C}_{23}\text{H}_{24}\text{N}_4\text{O}_3$  [M + H]<sup>+</sup>: 405.1921, found 405.1925.

## Mass Spectrum SmartFormula Report

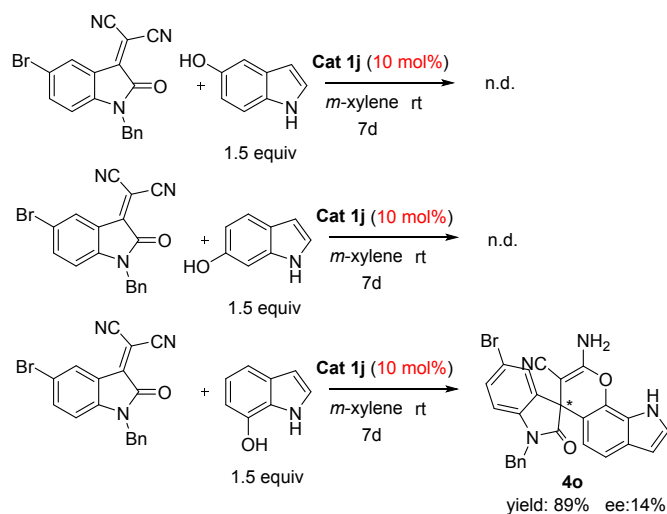
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Method	lc-ms-hr-low.m	Instrument / Ser#	micrOTOF-Q II 10351
Sample Name	L08-188-8		
Comment			

<b>Acquisition Parameter</b>					
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Scan End	1200 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

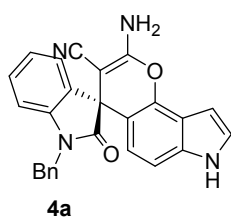


### 4. General procedure for the Friedel-Crafts alkylation/cyclization of 4-hydroxyindole to isatylidene malononitriles and characterization of products 4a-4n.

4-hydroxyindole **3a** (0.15 mmol) was added to a solution of isatylidene malononitriles **2** (0.1 mmol) and catalyst **1j** (0.010 mmol, 10 mol%) in *m*-xylene (1 mL). And the resulting mixture was stirred at room temperature until completion (TLC). Then the solvent was removed in vacuo via evaporation. The crude product was purified by chromatography (PE/EA = 1:1).



#### (R)-2'-amino-1-benzyl-2-oxo-7'H-spiro[indoline-3,4'-pyrano[2,3-e]indole]-3'-carbonitrile (**4a**)

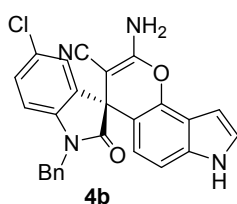


White solid, 41.0 mg, 98% yield, **m. p.** =256-258°C,  $[\alpha]_D^{25} = +16.4$  ( $c = 0.1$ , MeOH). The ee value was 76% (Chiralpak AD-H, hexane/*i*-PrOH =70:30, 220 nm, 1 mL/min,  $t_{\text{major}} = 27.86$ min,  $t_{\text{minor}} = 11.35$  min). <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  11.40 (s, 1H), 7.47 – 7.22 (m, 9H), 7.15 – 6.94 (m, 4H), 6.53 (s, 1H), 6.09 (d,  $J = 8.5$  Hz, 1H), 4.97 (q,  $J = 15.9$  Hz, 2H). <sup>13</sup>C NMR (101 MHz, DMSO)  $\delta$  178.5, 162.0, 142.8, 142.0, 137.2, 136.6,

135.2, 129.3, 129.1, 127.9, 127.6, 126.6, 125.2, 123.8, 119.4, 119.1, 117.1, 109.9, 109.4, 109.2,

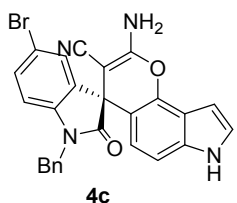
98.0, 54.8, 50.6, 43.5. **HRMS** (ESI) calculated for  $C_{26}H_{18}N_4O_2[M + H]^+$ : 419.1512, found 419.1503.

(R)-2'-amino-1-benzyl-5-chloro-2-oxo-7'H-spiro[indoline-3,4'-pyrano[2,3-e]indole]-3'-carbonitrile (**4b**)



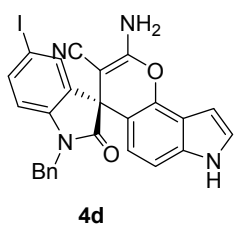
White solid, 44.4 mg, 98% yield, **m. p.** = 284-286°C,  $[\alpha]_D^{25} = +18.0$  ( $c = 0.1$ , MeOH). The ee value was 82% (Chiralpak AD-H, hexane/*i*-PrOH = 70:30, 220 nm, 1 mL/min,  $t_{major} = 22.72$ min,  $t_{minor} = 9.72$  min). **<sup>1</sup>H NMR** (400 MHz, DMSO- $d_6$ )  $\delta$  11.43 (s, 1H), 7.46 – 7.41 (m, 1H), 7.40 – 7.26 (m, 8H), 7.20 (d,  $J = 2.0$  Hz, 1H), 7.08 (d,  $J = 8.5$  Hz, 1H), 7.02 (d,  $J = 8.4$  Hz, 1H), 6.53 (s, 1H), 6.11 (d,  $J = 8.5$  Hz, 1H), 5.08 – 4.88 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, DMSO)  $\delta$  178.3, 162.0, 142.0, 141.7, 137.3, 137.2, 136.3, 129.3, 129.1, 128.0, 128.0, 127.6, 126.7, 125.4, 119.4, 119.0, 117.1, 111.5, 109.6, 108.4, 98.1, 54.1, 50.9, 43.6. **HRMS** (ESI) calculated for  $C_{26}H_{17}ClN_4O_2[M + H]^+$ : 453.1118, found 453.1113.

(R)-2'-amino-1-benzyl-5-bromo-2-oxo-7'H-spiro[indoline-3,4'-pyrano[2,3-e]indole]-3'-carbonitrile (**4c**)



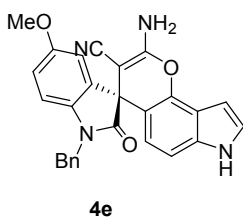
White solid, 48.7mg, 98% yield, **m. p.** = 277-279°C,  $[\alpha]_D^{25} = +15.2$  ( $c = 0.1$ , MeOH). The ee value was 84% (Chiralpak AD-H, hexane/*i*-PrOH = 70:30, 220 nm, 1 mL/min,  $t_{major} = 24.04$ min,  $t_{minor} = 10.19$  min). **<sup>1</sup>H NMR** (400 MHz, DMSO- $d_6$ )  $\delta$  11.43 (s, 1H), 7.52 – 7.25 (m, 10H), 7.08 (d,  $J = 8.4$  Hz, 1H), 6.97 (d,  $J = 8.3$  Hz, 1H), 6.53 (s, 1H), 6.12 (d,  $J = 8.4$  Hz, 1H), 5.10 – 4.85 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, DMSO)  $\delta$  178.1, 162.0, 142.1, 142.0, 137.6, 137.3, 136.2, 132.2, 129.1, 128.0, 128.0, 127.6, 126.7, 119.4, 119.0, 117.1, 115.7, 112.1, 109.6, 108.4, 98.1, 54.1, 50.9, 43.6. **HRMS**(ESI) calculated for  $C_{26}H_{17}BrN_4O_2[M + H]^+$ : 497.0604, found 497.0608.

(R)-2'-amino-1-benzyl-5-iodo-2-oxo-7'H-spiro[indoline-3,4'-pyrano[2,3-e]indole]-3'-carbonitrile (**4d**)



White solid, 49.5 mg, 91% yield, **m. p.** = 272-274°C,  $[\alpha]_D^{25} = +13.2$  ( $c = 0.1$ , MeOH). The ee value was 83% (Chiralpak AD-H, hexane/*i*-PrOH = 70:30, 220 nm, 1 mL/min,  $t_{major} = 27.19$ min,  $t_{minor} = 11.03$  min). **<sup>1</sup>H NMR** (400 MHz, DMSO- $d_6$ )  $\delta$  11.43 (s, 1H), 7.63 (dd,  $J = 8.2, 1.7$  Hz, 1H), 7.46 – 7.26 (m, 9H), 7.08 (d,  $J = 8.5$  Hz, 1H), 6.85 (d,  $J = 8.3$  Hz, 1H), 6.53 (s, 1H), 6.11 (d,  $J = 8.5$  Hz, 1H), 5.08 – 4.83 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, DMSO)  $\delta$  177.9, 162.0, 142.6, 141.9, 138.0, 137.8, 137.3, 136.2, 133.4, 129.1, 128.0, 127.6, 126.7, 119.4, 119.0, 117.1, 112.5, 109.6, 108.4, 98.1, 87.1, 54.2, 50.6, 43.6. **HRMS** (ESI) calculated for  $C_{26}H_{17}IN_4O_2[M + H]^+$ : 545.0468, found 545.0469.

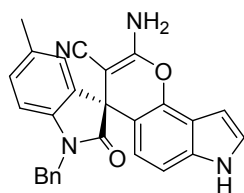
(R)-2'-amino-1-benzyl-5-methoxy-2-oxo-7'H-spiro[indoline-3,4'-pyrano[2,3-e]indole]-3'-carbonitrile (**4e**)



White solid, 42.1 mg, 94% yield, **m. p.** = 287-289°C,  $[\alpha]_D^{25} = +15.6$  ( $c = 0.1$ , MeOH). The ee value was 85% (Chiralpak AD-H, hexane/*i*-PrOH = 70:30, 220 nm, 1 mL/min,  $t_{major} = 42.64$ min,  $t_{minor} = 14.34$  min). **<sup>1</sup>H NMR** (400 MHz, DMSO- $d_6$ )  $\delta$  11.40 (s, 1H), 7.47 – 7.24 (m, 8H), 7.07 (d,  $J = 8.4$  Hz,

1H), 6.93 – 6.80 (m, 2H), 6.76 – 6.66 (m, 1H), 6.53 (s, 1H), 6.11 (d,  $J = 8.4$  Hz, 1H), 4.93 (q,  $J = 15.8$  Hz, 2H), 3.64 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  178.3, 162.0, 156.6, 142.0, 137.2, 136.7, 136.5, 136.1, 129.0, 127.9, 127.6, 126.6, 119.5, 119.2, 117.1, 114.0, 111.9, 110.5, 109.4, 109.2, 98.1, 55.9, 54.8, 51.1, 43.6. HRMS(ESI) calculated for  $\text{C}_{27}\text{H}_{20}\text{N}_4\text{O}_3[\text{M} + \text{H}]^+$ : 449.1621, found 449.1608.

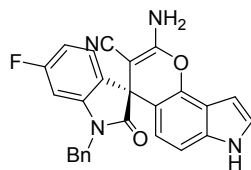
(R)-2'-amino-1-benzyl-5-methyl-2-oxo-7'H-spiro[indoline-3,4'-pyrano[2,3-e]indole]-3'-carbonitrile (**4f**)



**4f**

White solid, 38.9 mg, 90% yield, **m. p.** =240-242°C,  $[\alpha]_{\text{D}}^{25} = +14.4$  ( $c = 0.1$ , MeOH). The ee value was 68% (Chiralpak AD-H, hexane/*i*-PrOH =70:30, 220 nm, 1 mL/min,  $t_{\text{major}} = 24.66$ min,  $t_{\text{minor}} = 10.01$  min).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  11.39 (s, 1H), 7.44 – 7.40 (m, 1H), 7.32 (dd,  $J = 28.9$ , 13.4, 7.0 Hz, 7H), 7.05 (d,  $J = 8.3$  Hz, 2H), 6.93 (s, 1H), 6.86 (d,  $J = 8.0$  Hz, 1H), 6.52 (s, 1H), 6.10 (d,  $J = 8.5$  Hz, 1H), 5.03 – 4.85 (m, 2H), 2.20 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  178.5, 161.9, 141.9, 140.4, 137.2, 136.7, 135.4, 132.9, 129.5, 129.0, 127.9, 127.6, 126.6, 125.7, 119.5, 119.2, 117.1, 109.7, 109.4, 109.3, 98.0, 54.9, 50.7, 43.5, 21.0. HRMS(ESI) calculated for  $\text{C}_{27}\text{H}_{20}\text{N}_4\text{O}_2[\text{M} + \text{H}]^+$ : 433.1666, found 433.1659.

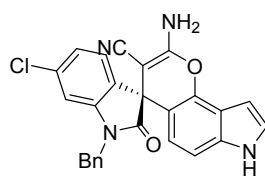
(R)-2'-amino-1-benzyl-6-fluoro-2-oxo-7'H-spiro[indoline-3,4'-pyrano[2,3-e]indole]-3'-carbonitrile (**4g**)



**4g**

White solid, 40.1 mg, 92% yield, **m. p.** = 258-260°C,  $[\alpha]_{\text{D}}^{25} = +14.0$  ( $c = 0.1$ , MeOH). The ee value was 73% (Chiralpak AD-H, hexane/*i*-PrOH =70:30, 220 nm, 1 mL/min,  $t_{\text{major}} = 20.12$ min,  $t_{\text{minor}} = 10.92$  min).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  11.40 (s, 1H), 7.36 (dd,  $J = 28.0$ , 16.4 Hz, 8H), 7.19 – 7.12 (m, 1H), 7.06 (d,  $J = 8.4$  Hz, 1H), 6.97 (d,  $J = 8.9$  Hz, 1H), 6.85 (t,  $J = 8.4$  Hz, 1H), 6.52 (s, 1H), 6.09 (d,  $J = 8.4$  Hz, 1H), 4.97 (q,  $J = 15.8$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  178.9, 162.0, 144.6 (d,  $J = 12.3$  Hz), 142.0, 137.2, 136.3, 130.9, 130.9, 129.1, 128.0, 127.7, 126.8 (d,  $J = 10.1$  Hz), 126.7, 119.0, 118.2 (d,  $J = 224.9$  Hz), 110.0, 109.8, 109.5, 108.9, 98.5 (d,  $J = 28.5$  Hz), 98.1, 54.5, 50.3, 43.6.  $^{19}\text{F}$  NMR (377 MHz, DMSO)  $\delta$  -111.61. HRMS (ESI) calculated for  $\text{C}_{26}\text{H}_{17}\text{FN}_4\text{O}_2[\text{M} + \text{H}]^+$ : 437.1411, found 437.1408.

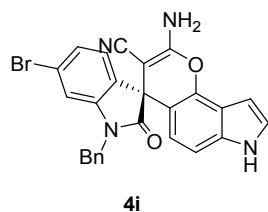
(R)-2'-amino-1-benzyl-6-chloro-2-oxo-7'H-spiro[indoline-3,4'-pyrano[2,3-e]indole]-3'-carbonitrile(**4h**)



**4h**

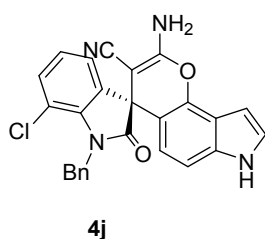
White solid, 44.3 mg, 98% yield, **m. p.** =267-269°C,  $[\alpha]_{\text{D}}^{25} = +18.4$  ( $c = 0.1$ , MeOH). The ee value was 77% (Chiralpak AD-H, hexane/*i*-PrOH =70:30, 220 nm, 1 mL/min,  $t_{\text{major}} = 19.81$ min,  $t_{\text{minor}} = 8.73$  min).  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  11.42, 7.44, 7.43, 7.42, 7.39, 7.39, 7.37, 7.35, 7.33, 7.32, 7.31, 7.31, 7.30, 7.28, 7.16, 7.14, 7.10, 7.10, 7.08, 7.08, 7.06, 6.52, 6.52, 6.51, 6.12, 6.10, 5.05, 5.01, 4.97, 4.93.  $^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  177.4, 160.9, 143.2, 140.8, 136.1, 135.1, 132.8, 132.5, 128.0, 126.9, 126.5, 125.6, 125.6, 122.4, 118.1, 117.8, 115.9, 109.1, 108.4, 107.4, 96.9, 53.1, 49.2, 42.4. HRMS (ESI) calculated for  $\text{C}_{26}\text{H}_{17}\text{ClN}_4\text{O}_2[\text{M} + \text{H}]^+$ : 453.1114, found 453.1113.

(R)-2'-amino-1-benzyl-6-bromo-2-oxo-7'H-spiro[indoline-3,4'-pyrano[2,3-e]indole]-3'-carbonitrile (**4i**)



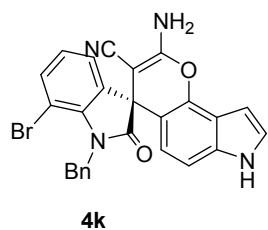
White solid, 44.6 mg, 90% yield, **m. p.** =272-274°C,  $[\alpha]_D^{25} = +11.2$  ( $c = 0.1$ , MeOH). The ee value was 78% (Chiralpak AD-H, hexane/*i*-PrOH =70:30, 220 nm, 1 mL/min,  $t_{\text{major}} = 20.72$ min,  $t_{\text{minor}} = 8.58$  min). **<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.42 (s, 1H), 7.49 – 7.19 (m, 10H), 7.15 – 7.03 (m, 2H), 6.53 (s, 1H), 6.12 (d,  $J = 8.4$  Hz, 1H), 5.00 (q,  $J = 15.9$  Hz, 2H). **<sup>13</sup>C NMR** (101 MHz, DMSO)  $\delta$  178.5, 162.1, 144.5, 142.0, 137.3, 136.3, 134.4, 129.1, 128.0, 127.6, 127.2, 126.7, 126.5, 122.1, 119.3, 119.0, 117.1, 113.0, 109.6, 108.5, 98.1, 54.2, 50.5, 43.5. **HRMS** (ESI) calculated for C<sub>26</sub>H<sub>17</sub>BrN<sub>4</sub>O<sub>2</sub>[M + H]<sup>+</sup>: 497.0621, found 497.0608.

(R)-2'-amino-1-benzyl-7-chloro-2-oxo-7'H-spiro[indoline-3,4'-pyrano[2,3-e]indole]-3'-carbonitrile (**4j**)



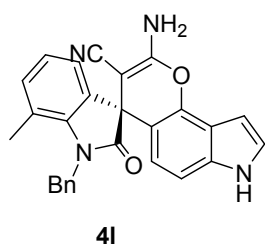
White solid, 40.6 mg, 90% yield, **m. p.** =266-268°C,  $[\alpha]_D^{25} = +13.2$  ( $c = 0.1$ , MeOH). The ee value was 75% (Chiralpak AD-H, hexane/*i*-PrOH =70:30, 220 nm, 1 mL/min,  $t_{\text{major}} = 24.50$ min,  $t_{\text{minor}} = 10.71$  min). **<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.43 (s, 1H), 7.46 – 7.23 (m, 9H), 7.17 – 7.06 (m, 3H), 6.56 – 6.48 (m, 1H), 6.23 (d,  $J = 8.5$  Hz, 1H), 5.30 (s, 2H). **<sup>13</sup>C NMR** (101 MHz, DMSO)  $\delta$  179.3, 162.0, 141.9, 138.8, 138.3, 137.9, 137.3, 131.6, 129.0, 127.5, 126.8, 126.5, 125.3, 124.7, 119.4, 119.1, 117.1, 114.8, 109.7, 108.7, 98.1, 54.5, 50.6, 45.1. **HRMS** (ESI) calculated for C<sub>26</sub>H<sub>17</sub>ClN<sub>4</sub>O<sub>2</sub>[M + H]<sup>+</sup>: 453.1119, found 453.1113.

(R)-2'-amino-1-benzyl-7-bromo-2-oxo-7'H-spiro[indoline-3,4'-pyrano[2,3-e]indole]-3'-carbonitrile (**4k**)



White solid, 48.5 mg, 98% yield, **m. p.** =275-277°C,  $[\alpha]_D^{25} = +33.2$  ( $c = 0.1$ , MeOH). The ee value was 78% (Chiralpak AD-H, hexane/*i*-PrOH =70:30, 220 nm, 1 mL/min,  $t_{\text{major}} = 25.35$ min,  $t_{\text{minor}} = 11.32$  min). **<sup>1</sup>H NMR** (400 MHz, )  $\delta$  11.47 (s, 1H), 7.56 – 7.28 (m, 9H), 7.23 (d,  $J = 7.3$  Hz, 1H), 7.16 (d,  $J = 8.5$  Hz, 1H), 7.08 (t,  $J = 7.7$  Hz, 1H), 6.58 (s, 1H), 6.28 (d,  $J = 8.5$  Hz, 1H), 5.48 – 5.31 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, DMSO)  $\delta$  179.4, 162.0, 141.9, 140.3, 138.7, 137.8, 137.3, 135.0, 128.9, 127.4, 126.8, 126.5, 125.7, 125.3, 119.4, 119.1, 117.1, 109.6, 108.7, 102.3, 98.1, 54.6, 50.5, 44.8. **HRMS** (ESI) calculated for C<sub>26</sub>H<sub>17</sub>BrN<sub>4</sub>O<sub>2</sub>[M + H]<sup>+</sup>: 497.0606, found 497.0608.

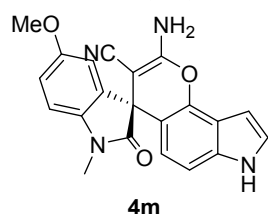
(R)-2'-amino-1-benzyl-7-methyl-2-oxo-7'H-spiro[indoline-3,4'-pyrano[2,3-e]indole]-3'-carbonitrile (**4l**)



White solid, 41.8 mg, 97% yield, **m. p.** =272-274°C,  $[\alpha]_D^{25} = +12.0$  ( $c = 0.1$ , MeOH). The ee value was 47% (Chiralpak AD-H, hexane/*i*-PrOH =70:30, 220 nm, 1 mL/min,  $t_{\text{major}} = 42.42$ min,  $t_{\text{minor}} = 10.81$  min). **<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.39 (s, 1H), 7.47 – 7.17 (m, 8H), 7.13 – 6.90 (m, 4H), 6.52 (s, 1H), 6.23 (d,  $J = 8.5$  Hz, 1H), 5.31 – 5.06 (m, 2H), 2.29 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, DMSO)  $\delta$  179.6, 162.0, 142.0,

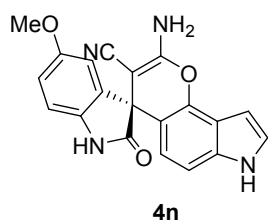
140.9, 138.3, 137.2, 136.0, 133.0, 129.2, 127.6, 126.6, 126.1, 123.9, 123.5, 120.1, 119.7, 119.3, 117.1, 109.6, 109.4, 98.1, 55.3, 50.1, 45.1, 18.6. **HRMS** (ESI) calculated for  $C_{27}H_{20}N_4O_2[M + H]^+$ : 433.1653, found 433.1659.

(R)-2'-amino-5-methoxy-1-methyl-2-oxo-7'H-spiro[indoline-3,4'-pyrano[2,3-e]indole]-3'-carbonitrile (**4m**)



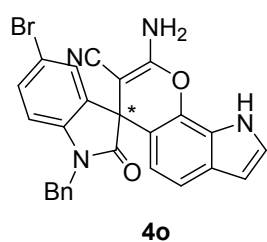
White solid, 33.8 mg, 91% yield, **m. p.** = 248-250°C,  $[\alpha]_D^{25} = +14.4$  ( $c = 0.1$ , MeOH). The ee value was 63% (Chiralpak AD-H, hexane/*i*-PrOH = 70:30, 220 nm, 1 mL/min,  $t_{major} = 14.92$  min,  $t_{minor} = 10.46$  min). **<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.37 (s, 1H), 7.41 (s, 1H), 7.23 (s, 2H), 7.06 (t,  $J = 7.5$  Hz, 2H), 6.93 (d,  $J = 8.1$  Hz, 1H), 6.68 (s, 1H), 6.51 (s, 1H), 6.11 (d,  $J = 8.4$  Hz, 1H), 3.67 (s, 3H), 3.18 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, DMSO)  $\delta$  178.0, 161.9, 156.6, 156.6, 151.0, 141.9, 137.2, 137.2, 136.5, 126.5, 119.3, 117.0, 114.0, 111.7, 109.8, 109.4, 109.2, 98.0, 56.0, 54.9, 51.0, 26.9. **HRMS** (ESI) calculated for  $C_{21}H_{16}N_4O_3[M + H]^+$ : 373.1295, found 373.1309.

(R)-2'-amino-5-methoxy-2-oxo-7'H-spiro[indoline-3,4'-pyrano[2,3-e]indole]-3'-carbonitrile (**4n**)



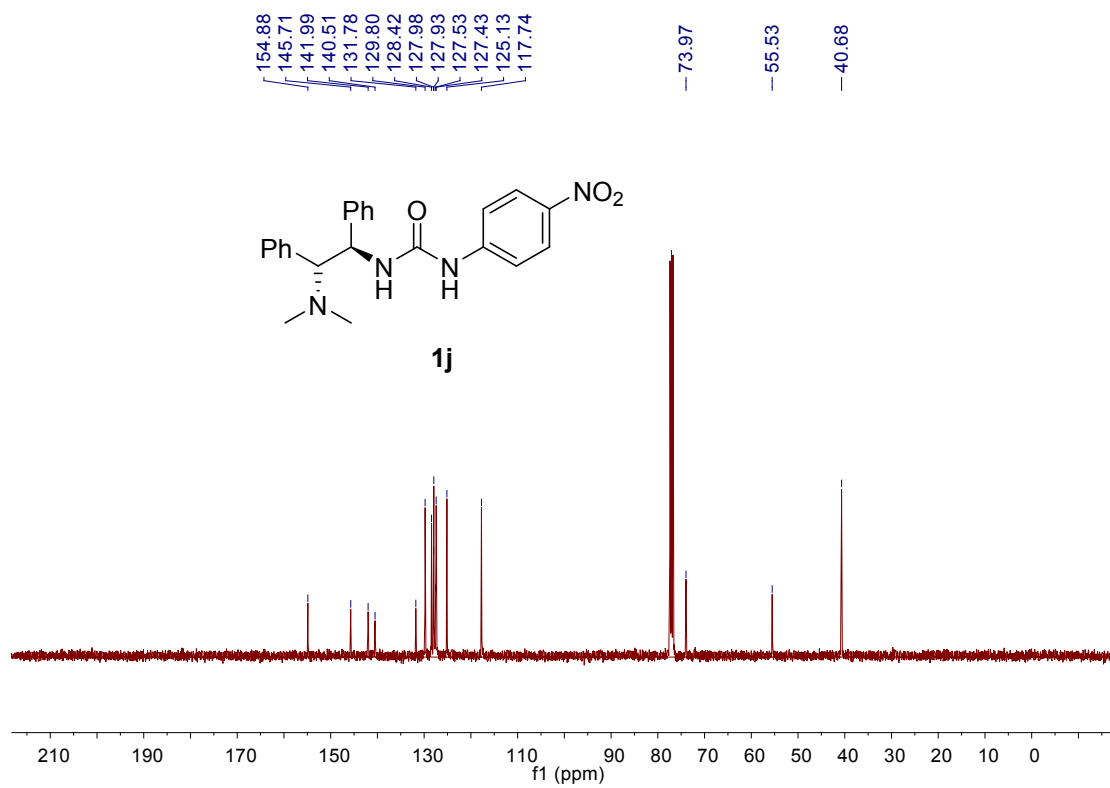
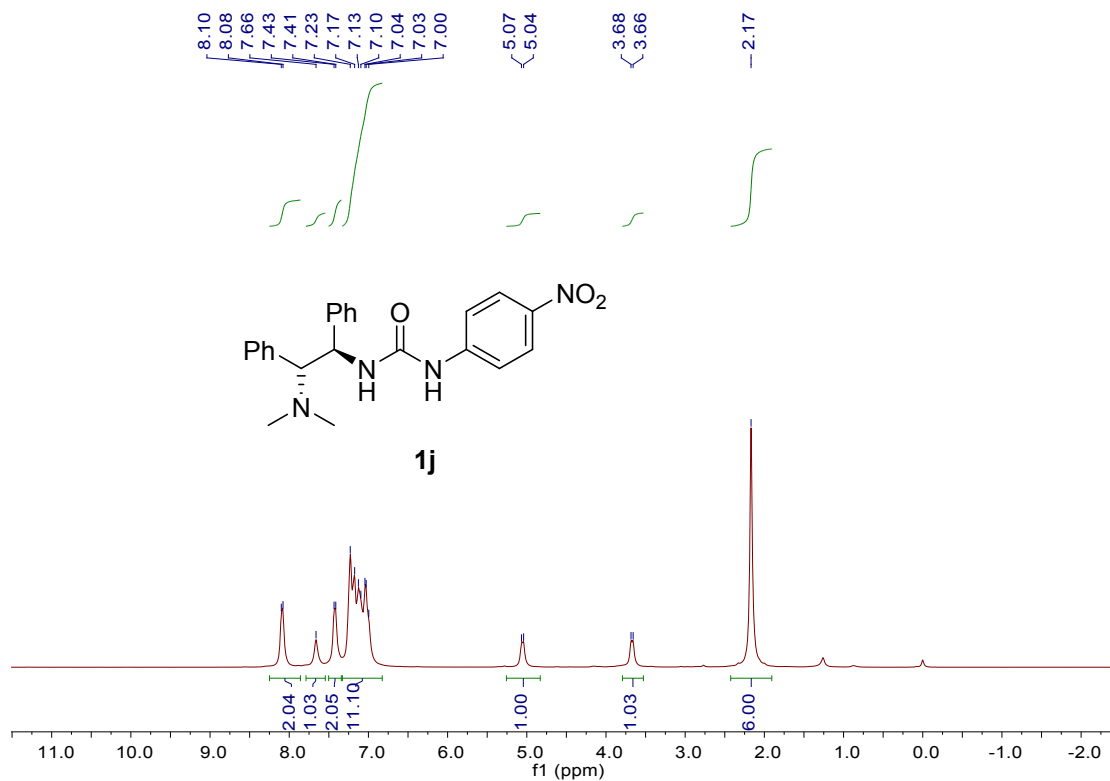
White solid, 27.9 mg, 78% yield, **m. p.** = 252-254°C,  $[\alpha]_D^{25} = +16.8$  ( $c = 0.1$ , MeOH). The ee value was 20% (Chiralpak AD-H, hexane/*i*-PrOH = 70:30, 220 nm, 1 mL/min,  $t_{major} = 16.78$  min,  $t_{minor} = 10.81$  min). **<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.36 (s, 1H), 10.31 (s, 1H), 7.43–7.37 (m, 1H), 7.18 (s, 2H), 7.07 (d,  $J = 8.5$  Hz, 1H), 6.89–6.80 (m, 2H), 6.61 (d,  $J = 2.1$  Hz, 1H), 6.49 (s, 1H), 6.17 (d,  $J = 8.5$  Hz, 1H), 3.64 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, DMSO)  $\delta$  179.9, 161.8, 156.0, 141.9, 137.3, 137.1, 135.6, 126.4, 119.5, 119.3, 117.0, 114.3, 111.6, 110.7, 109.4, 109.4, 98.0, 55.9, 55.1, 51.5. **HRMS** (ESI) calculated for  $C_{20}H_{14}N_4O_3[M + H]^+$ : 359.1139, found 359.1143.

2'-amino-1-benzyl-5-bromo-2-oxo-7'H-spiro[indoline-3,4'-pyrano[2,3-e]indole]-3'-carbonitrile (**4o**)

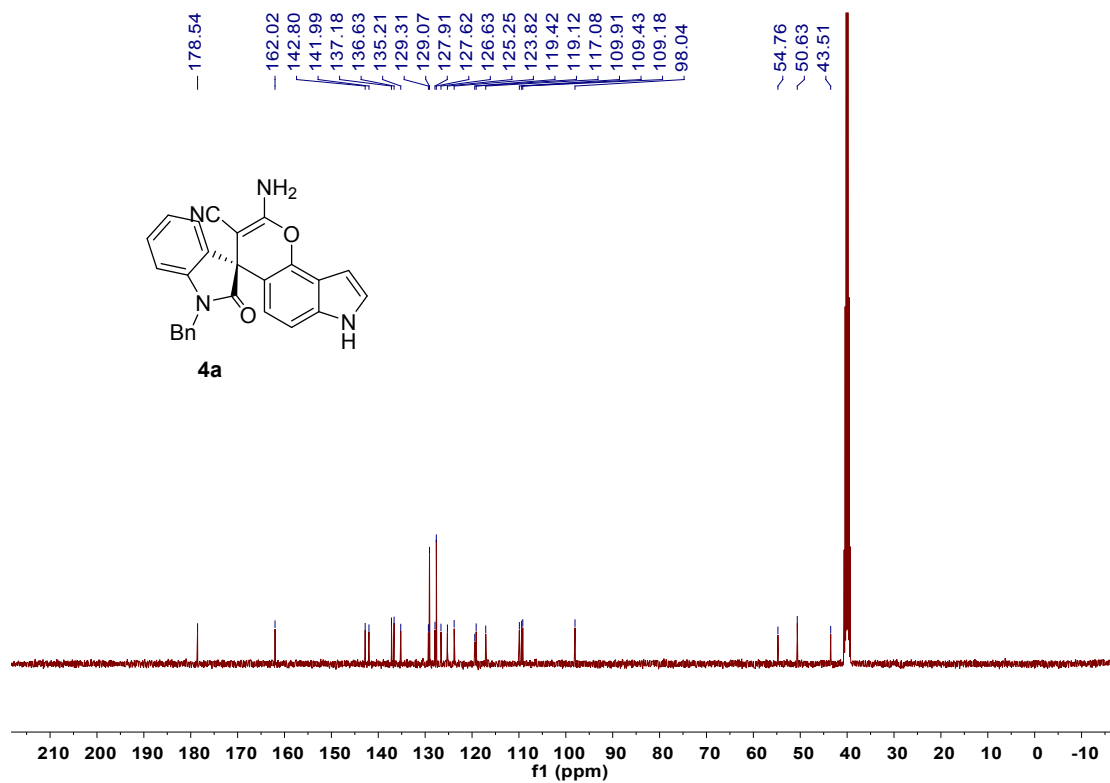
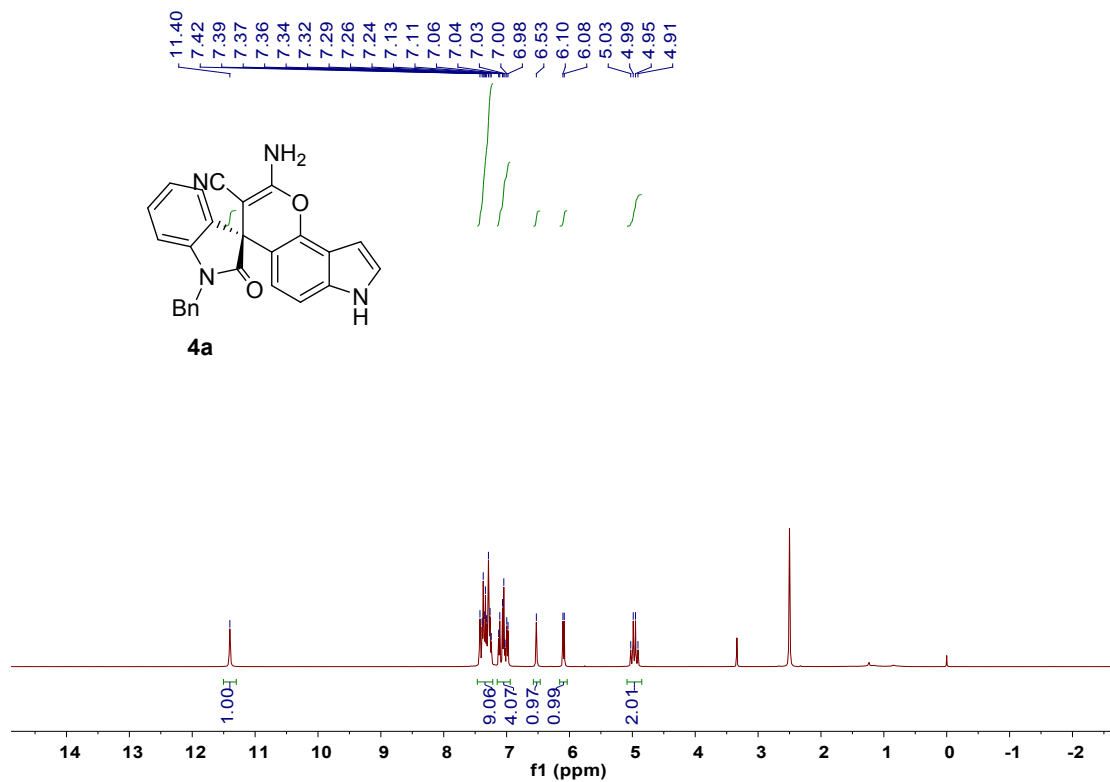


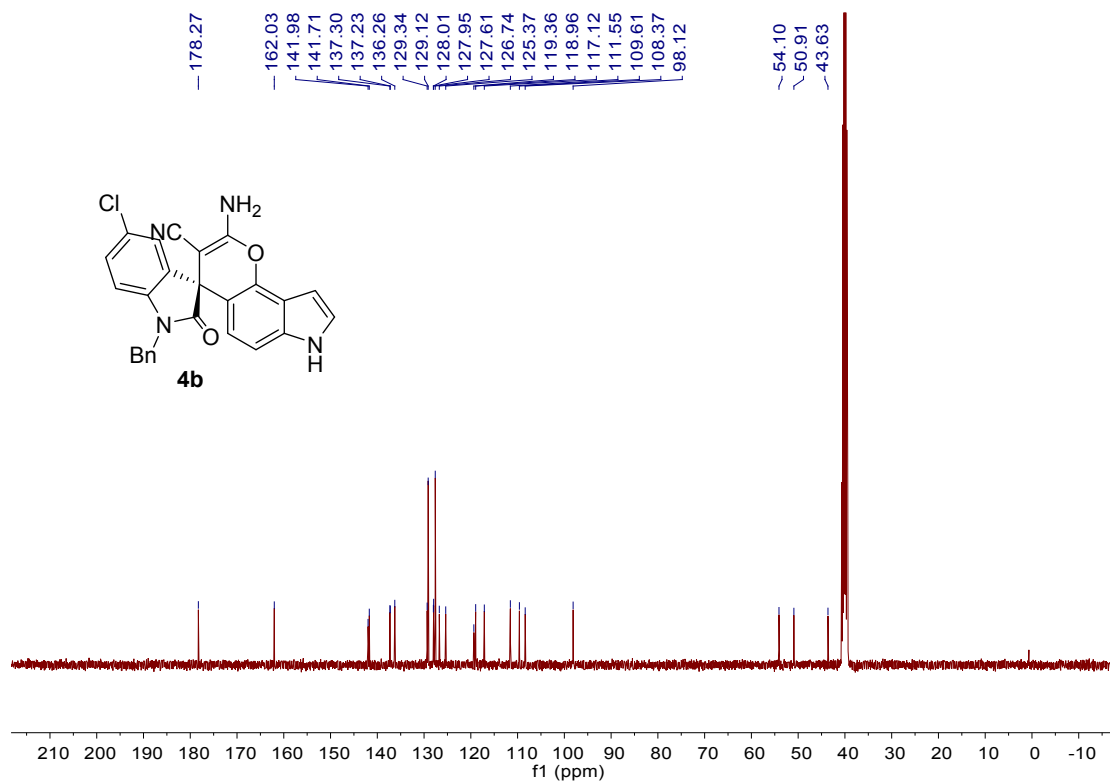
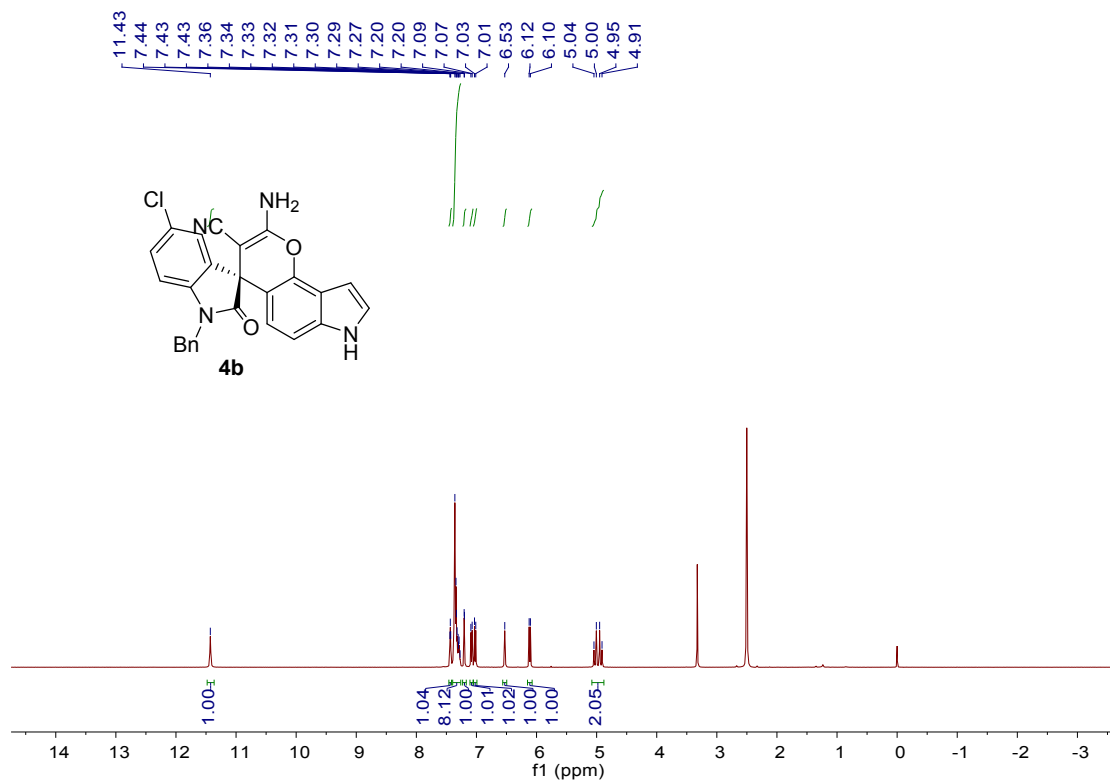
Brown solid, 44.4 mg, 89% yield, **m. p.** = 271-273°C,  $[\alpha]_D^{25} = +8.1$  ( $c = 0.1$ , MeOH). The ee value was 14% (Chiralpak AD-H, hexane/*i*-PrOH = 70:30, 220 nm, 1 mL/min,  $t_{major} = 47.93$  min,  $t_{minor} = 9.46$  min). **<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.38 (s, 1H), 7.48 (d,  $J = 8.3$  Hz, 1H), 7.42 (s, 1H), 7.32 (dq,  $J = 19.4, 7.5, 6.1$  Hz, 6H), 7.20 (d,  $J = 9.3$  Hz, 3H), 6.98 (d,  $J = 8.4$  Hz, 1H), 6.47 (s, 1H), 6.04 (d,  $J = 8.2$  Hz, 1H), 5.07–4.88 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, DMSO)  $\delta$  177.9, 161.6, 142.1, 137.3, 136.2, 136.1, 132.3, 130.3, 129.1, 128.1, 128.0, 127.6, 127.0, 124.1, 119.1, 117.5, 116.7, 115.7, 112.1, 110.7, 102.6, 54.8, 50.9, 43.6. **HRMS** (ESI) calculated for  $C_{26}H_{17}BrN_4O_2[M + H]^+$ : 497.0606, found 497.0615.

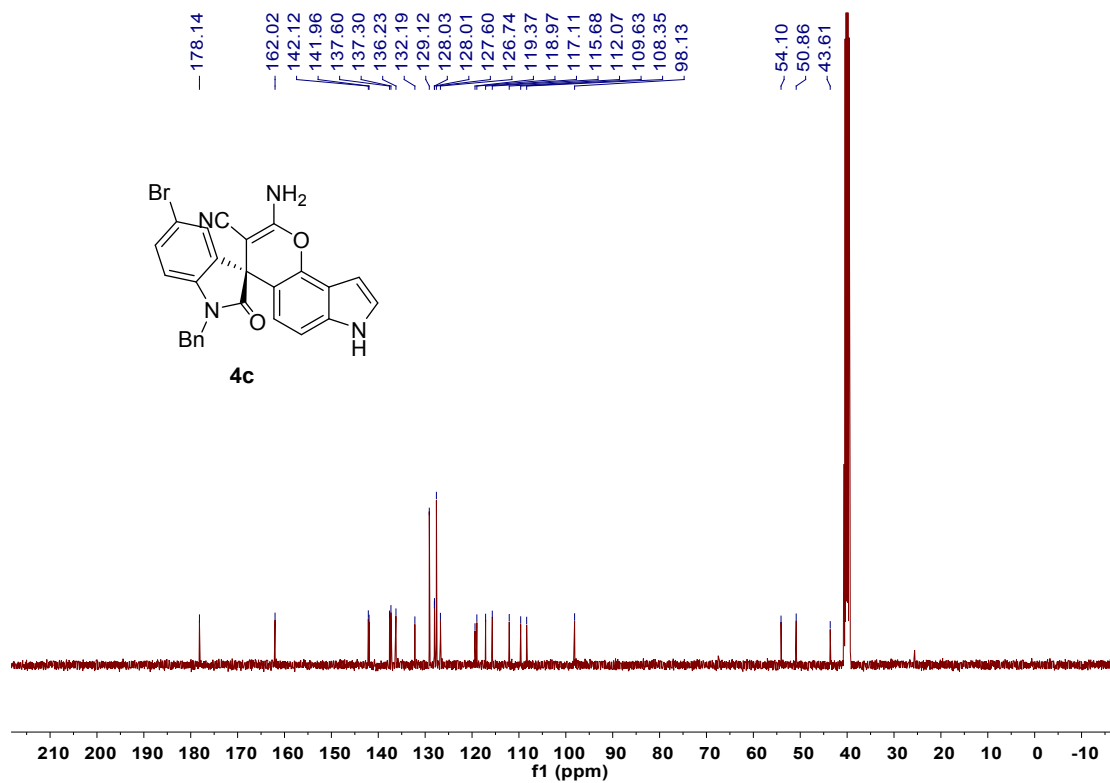
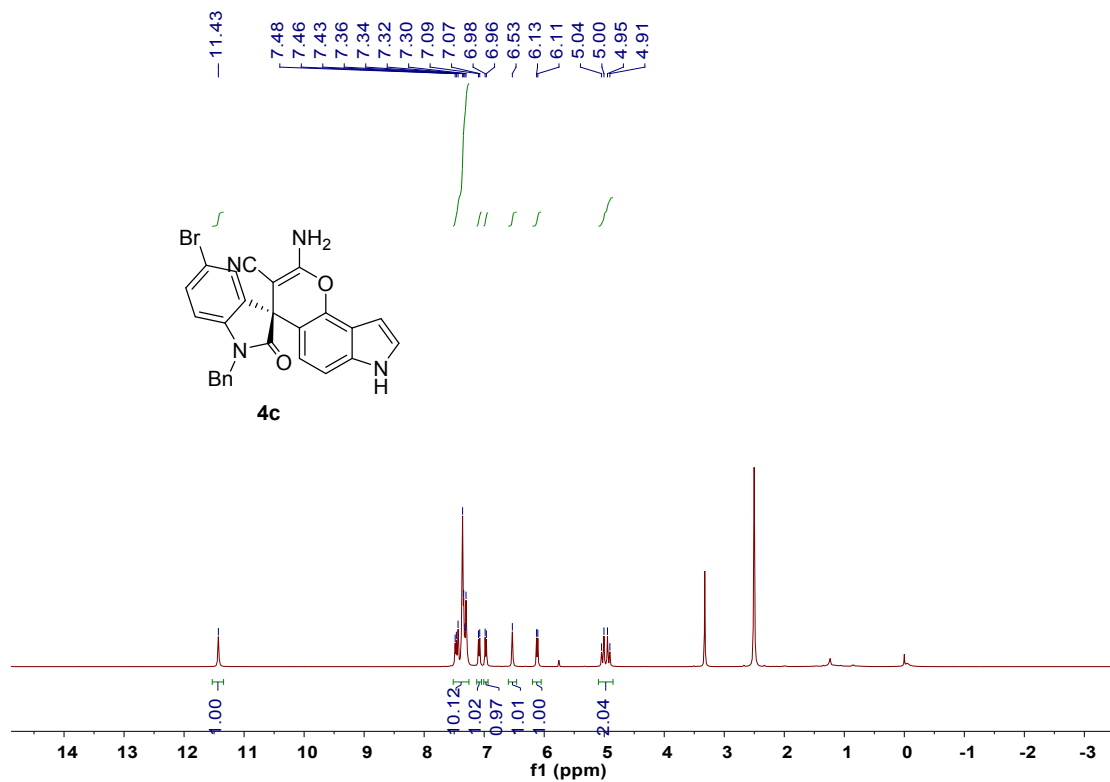
5. NMR spectra of catalyst 1j and addition products 4a-4o

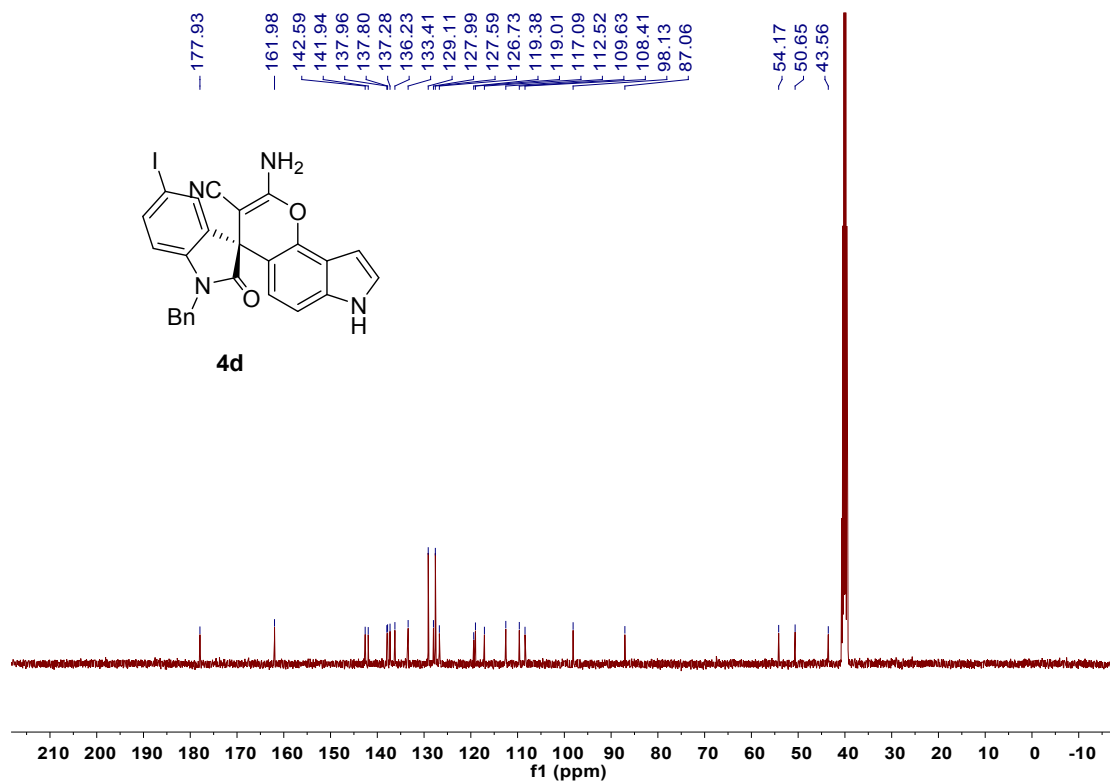
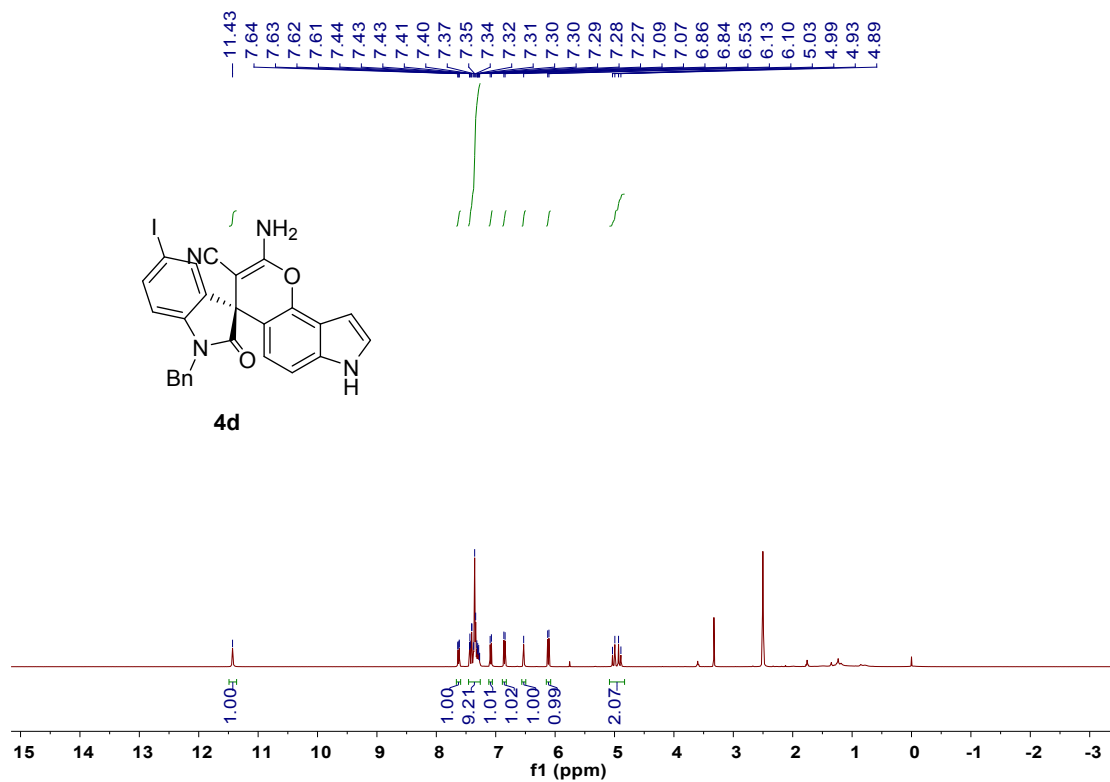


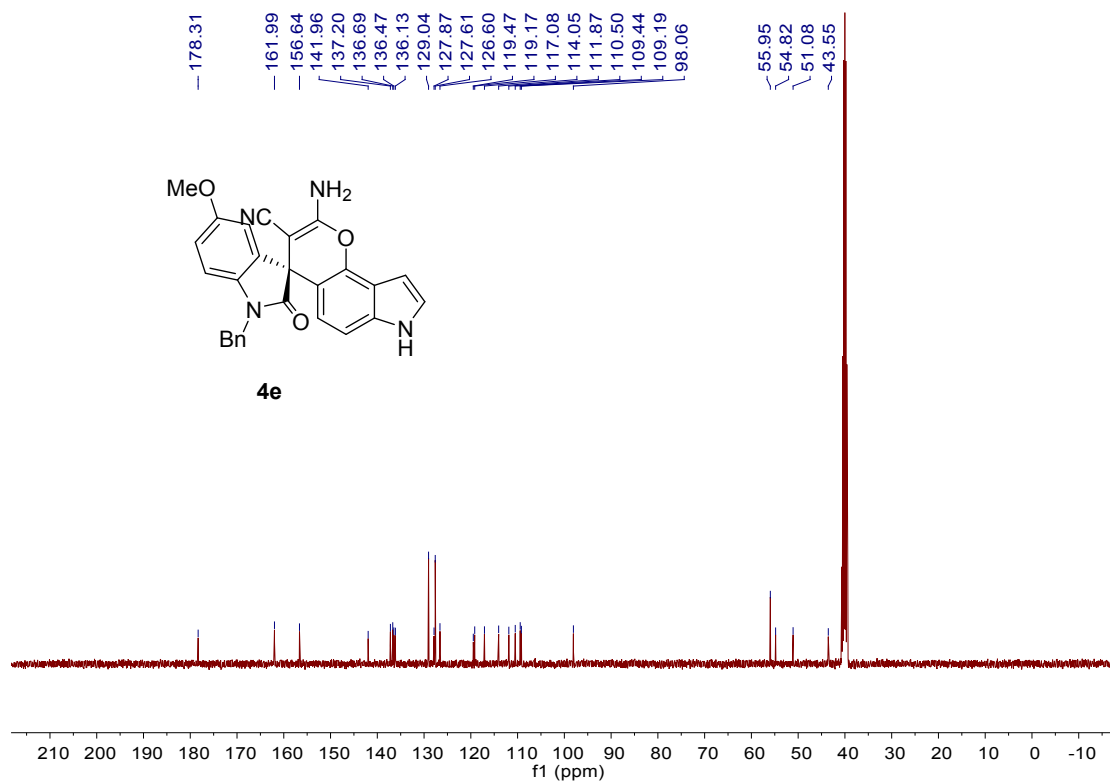
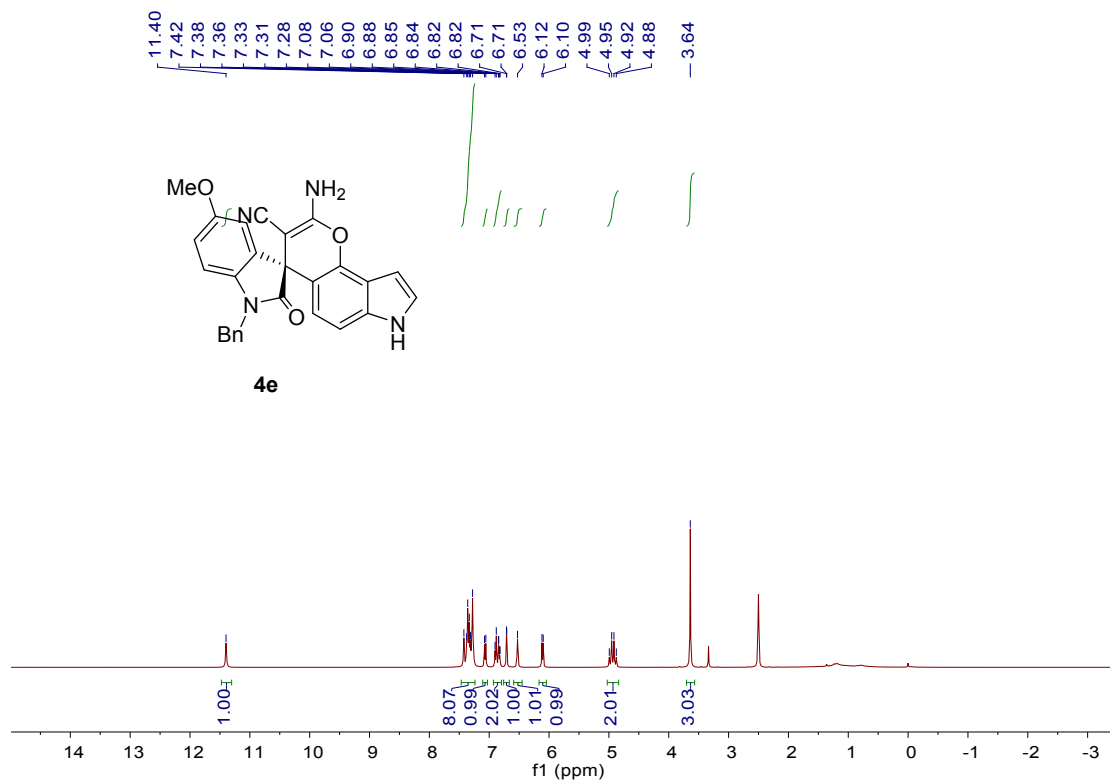


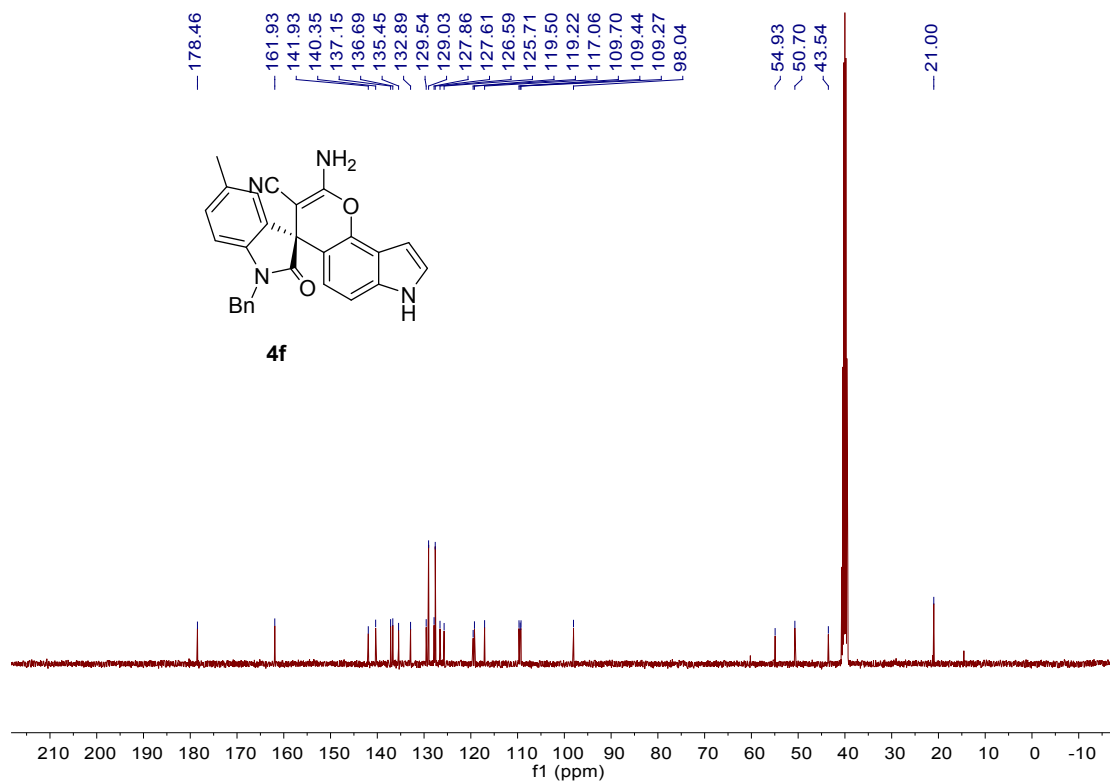
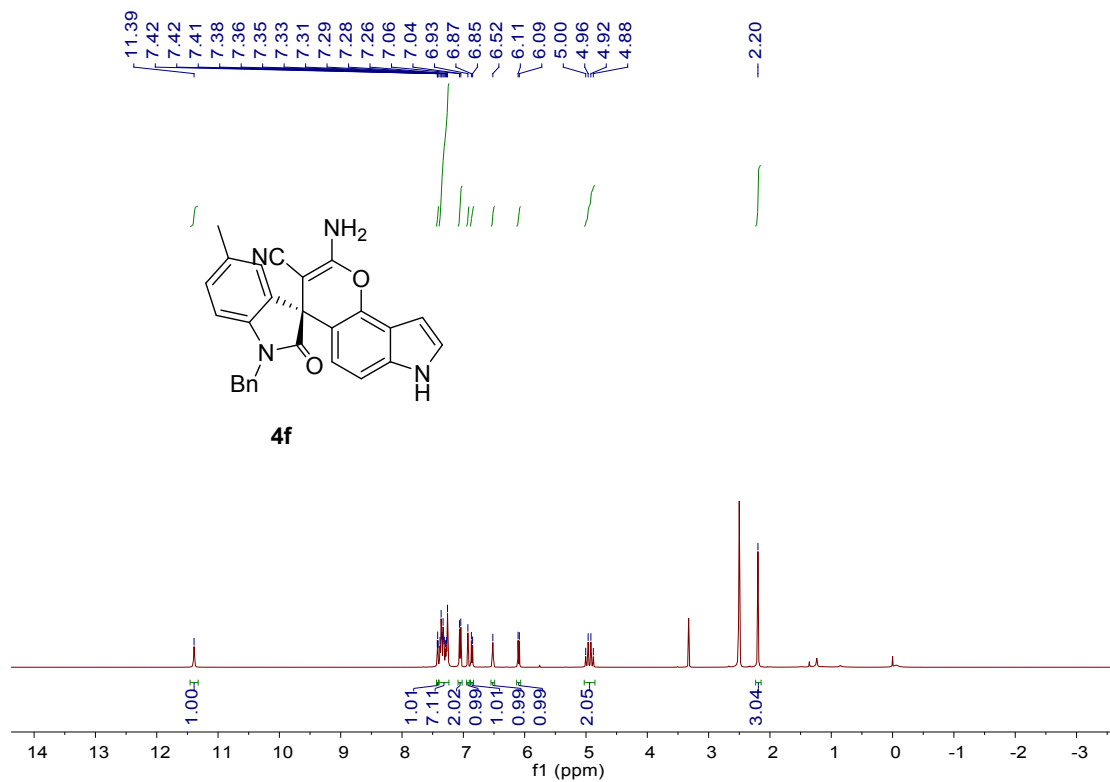


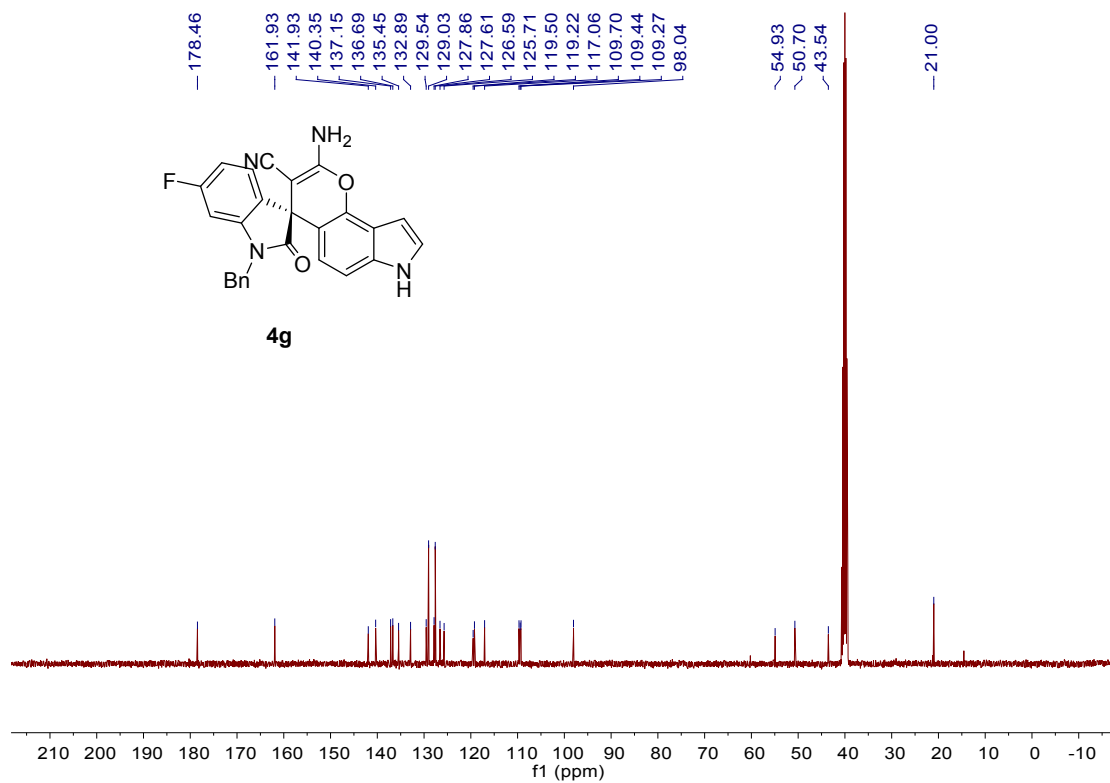
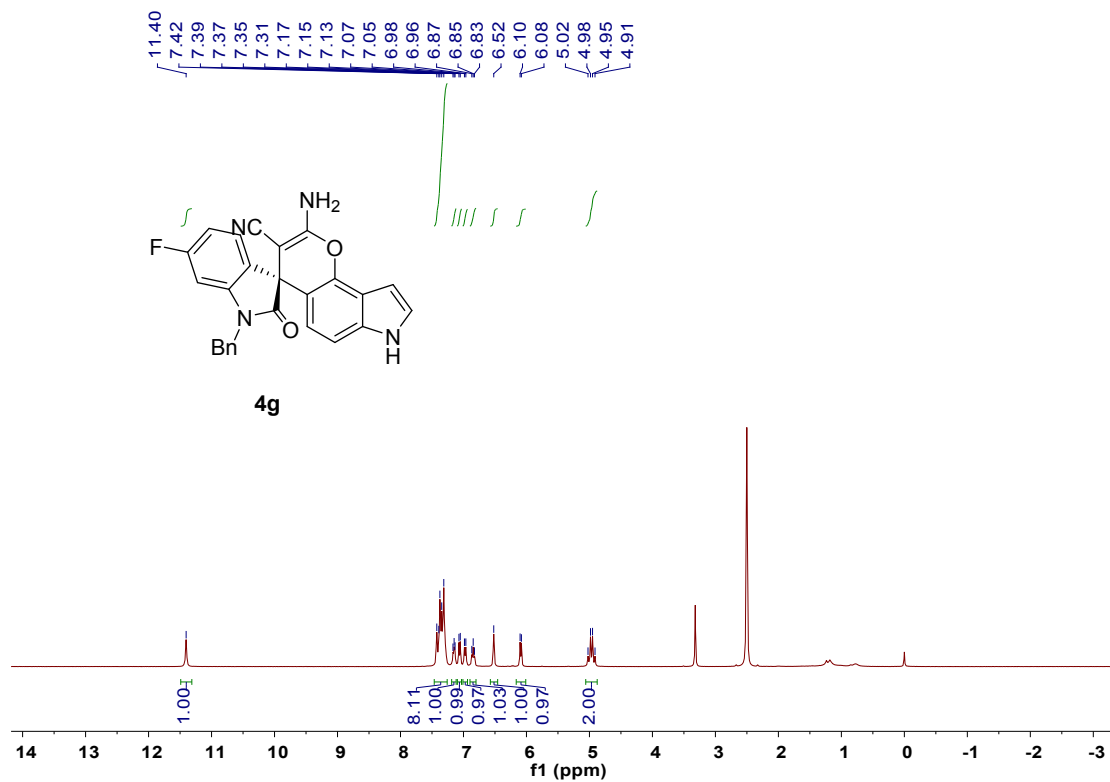


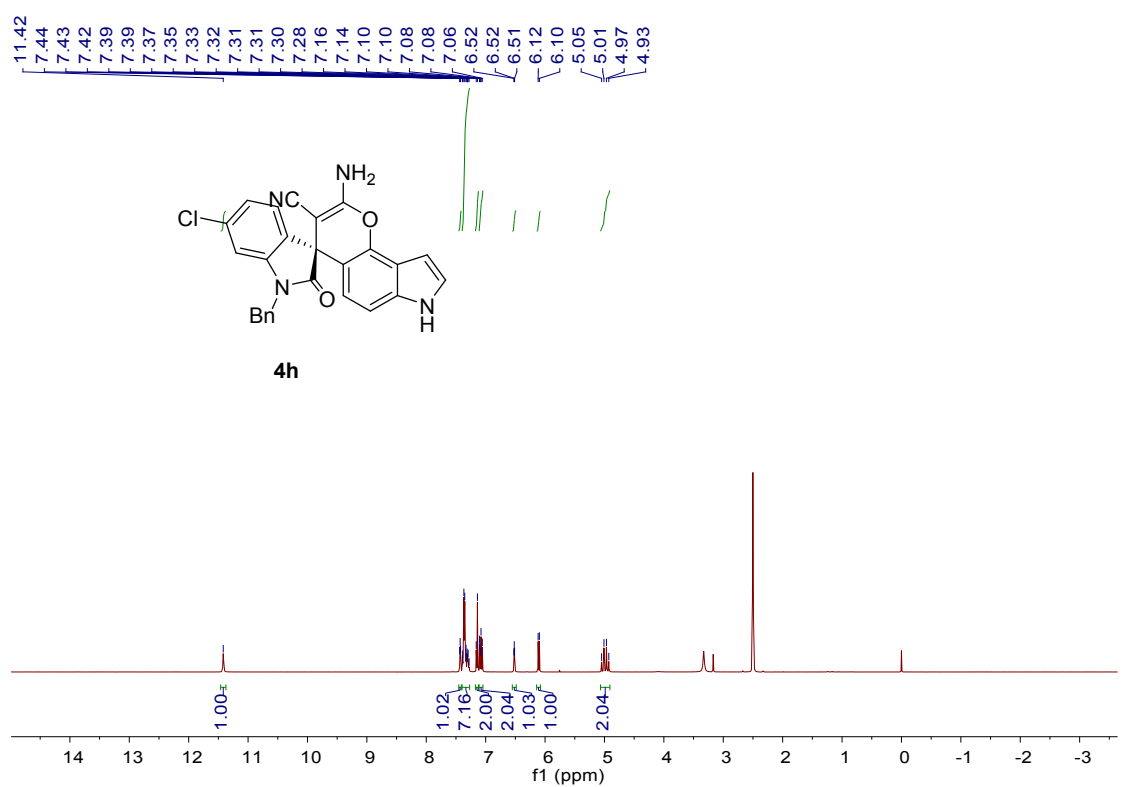
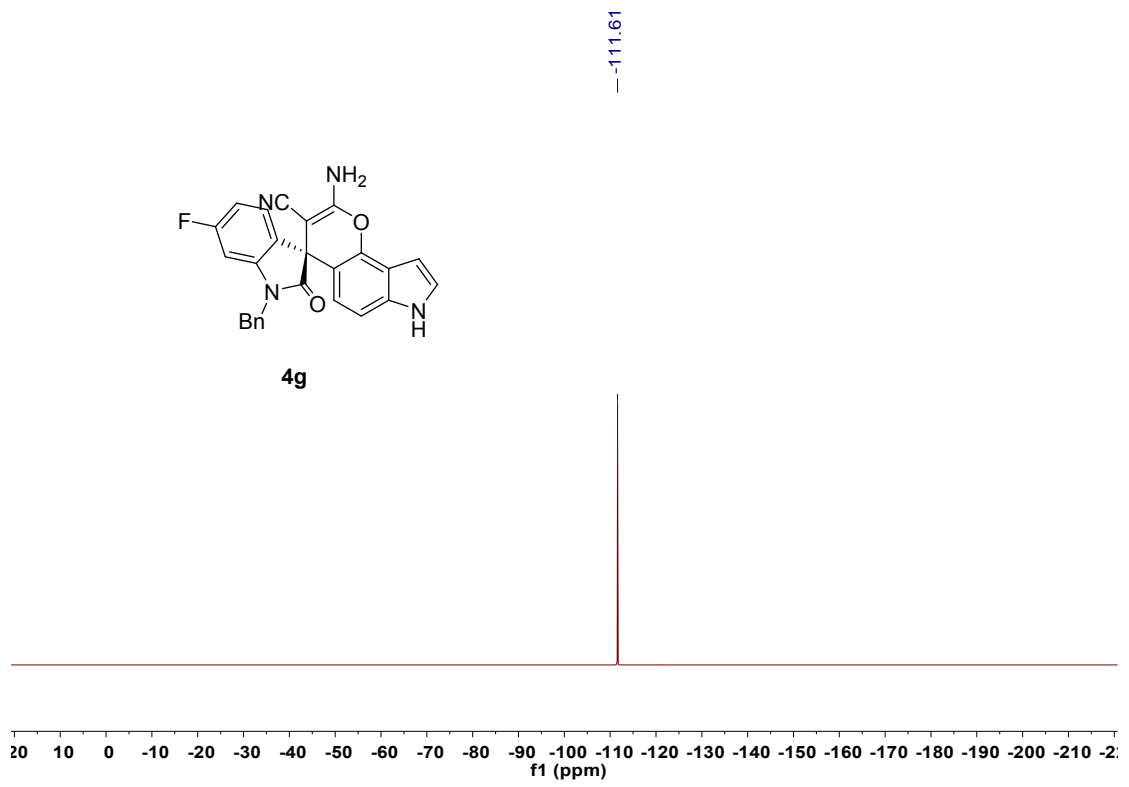




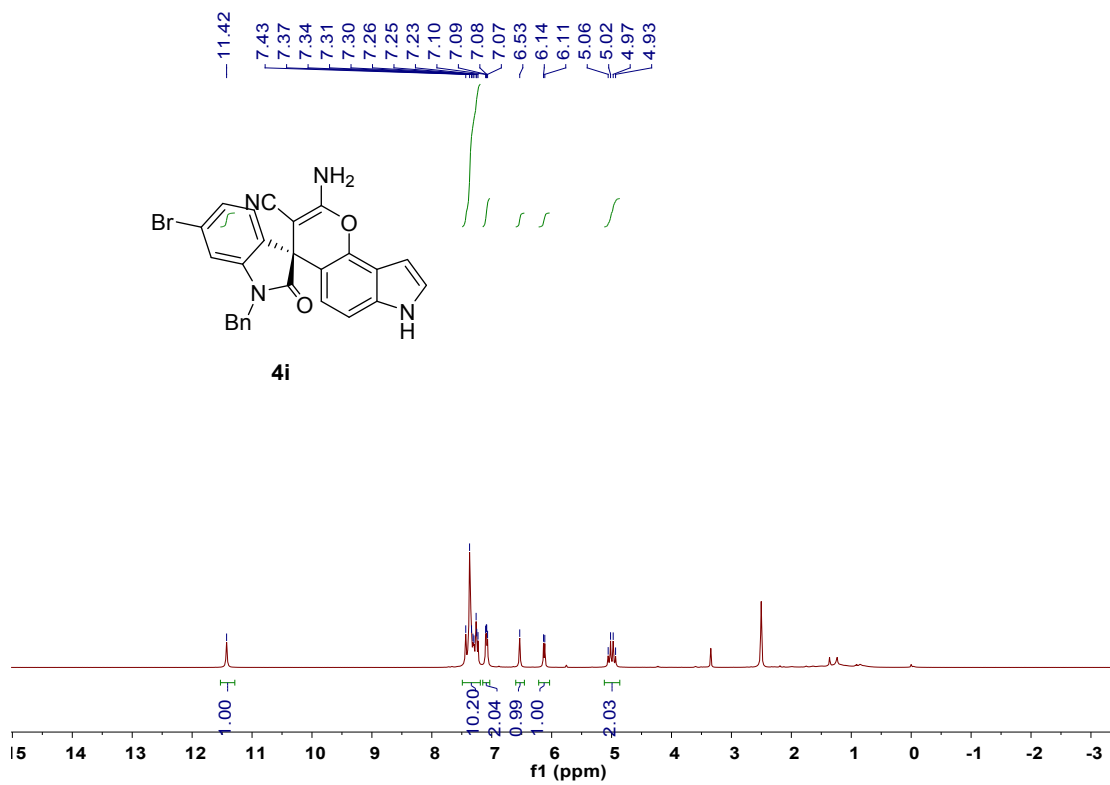
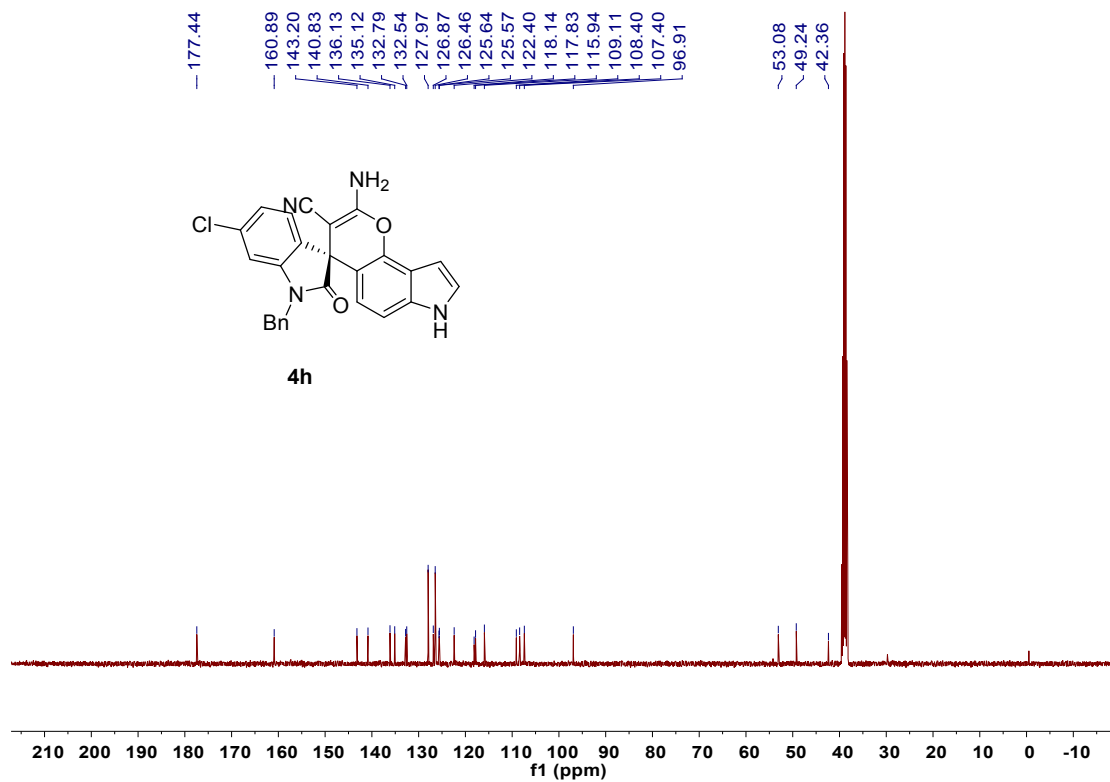


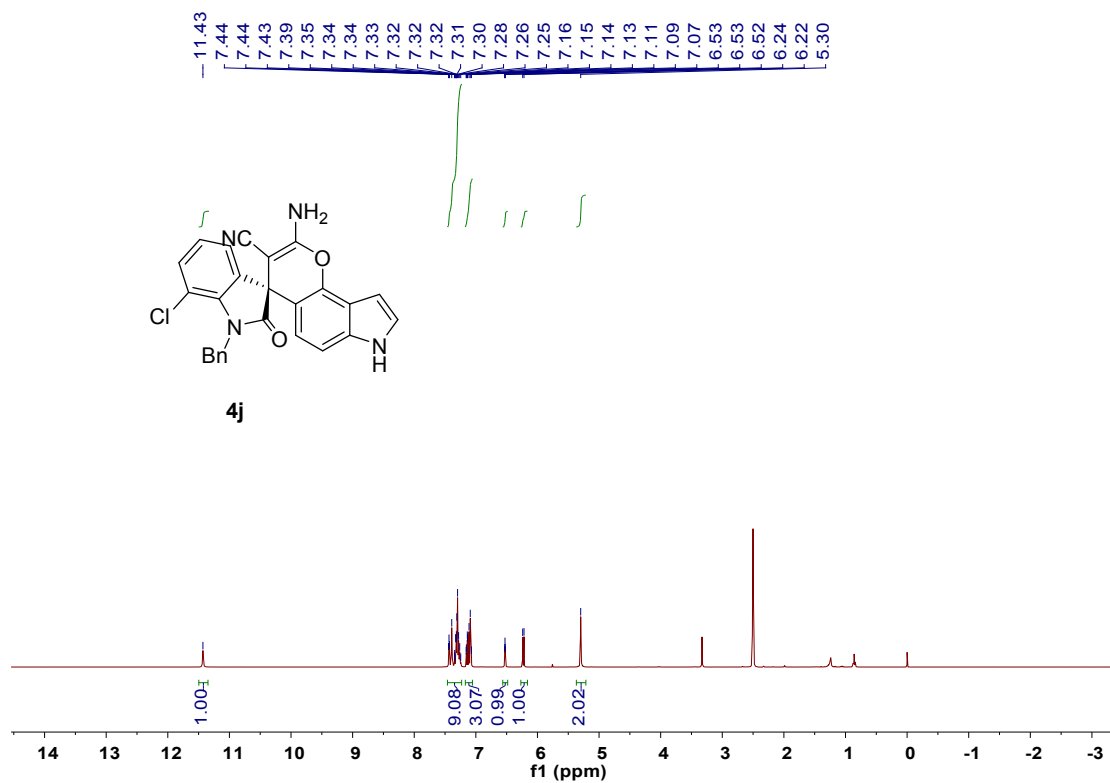
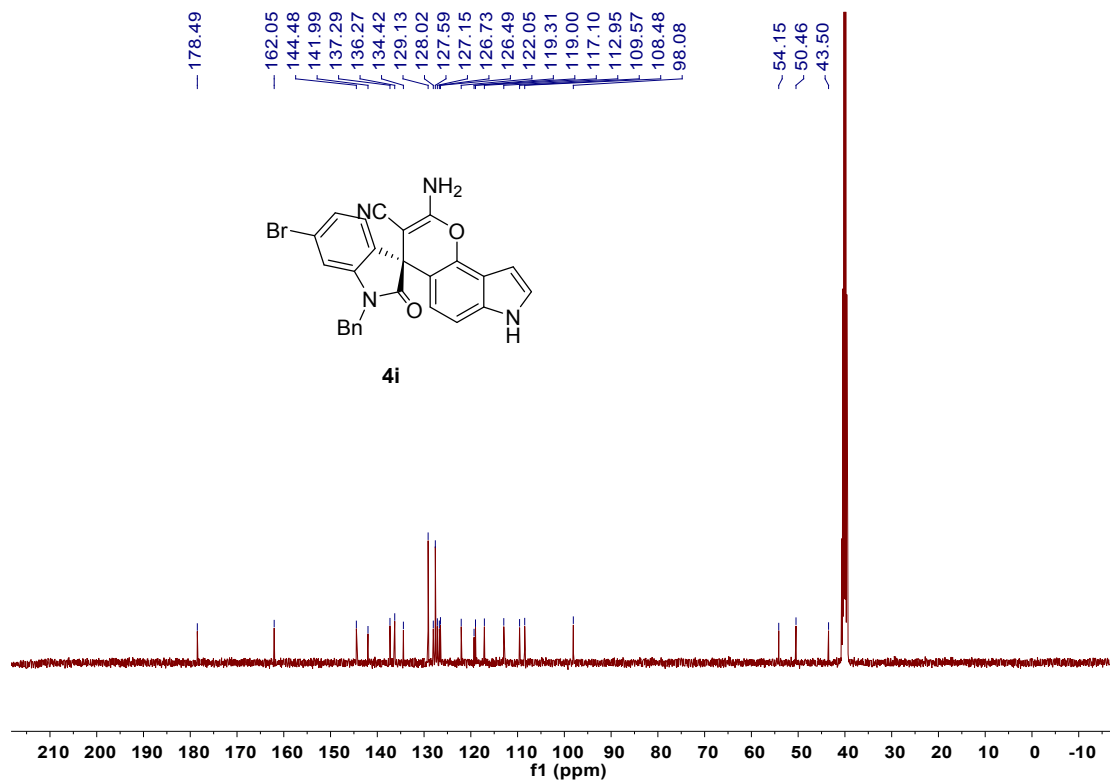


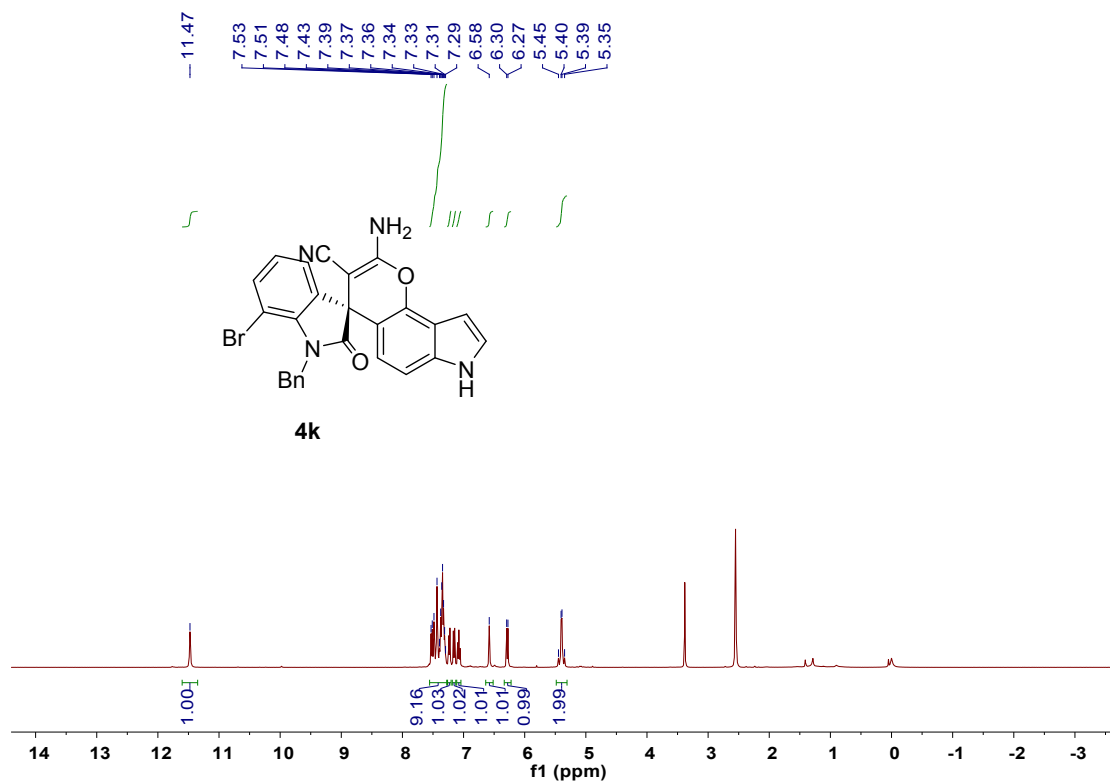
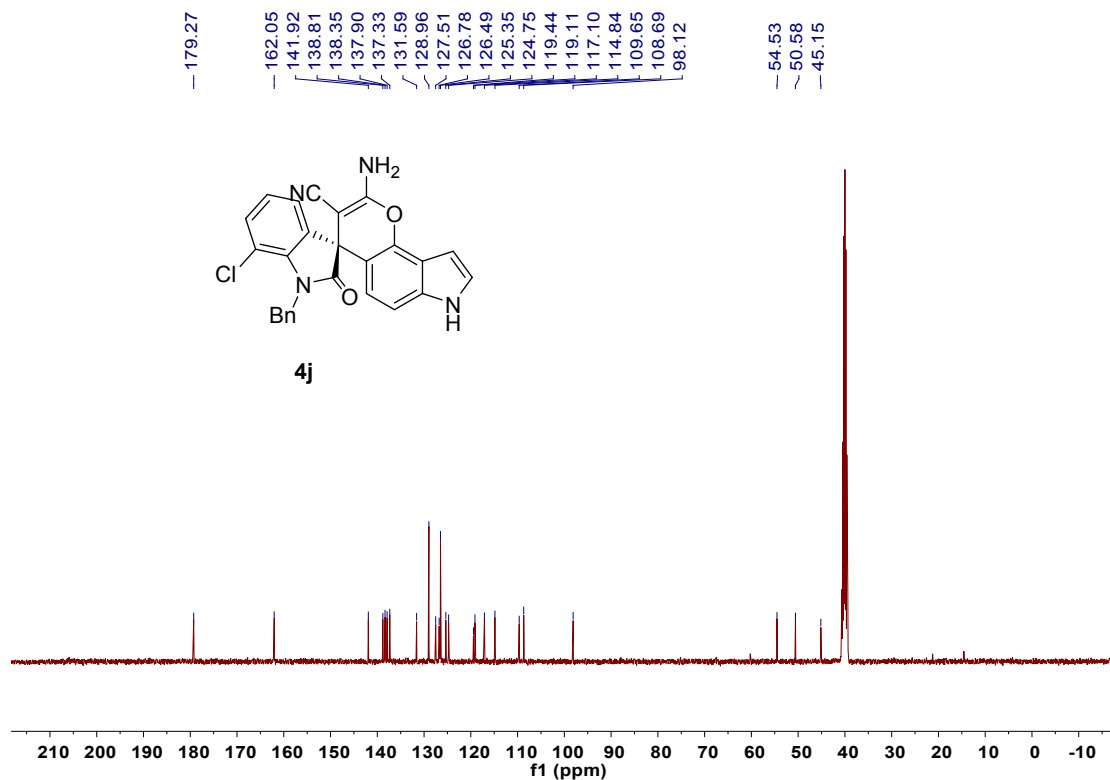


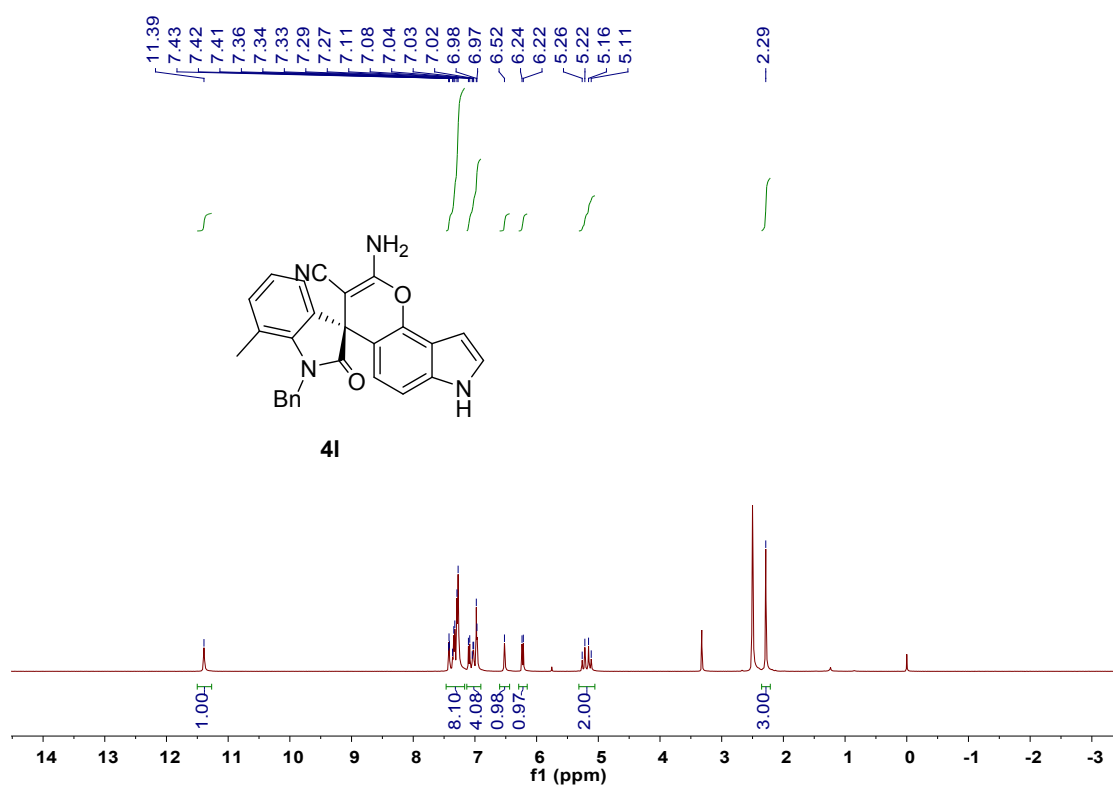
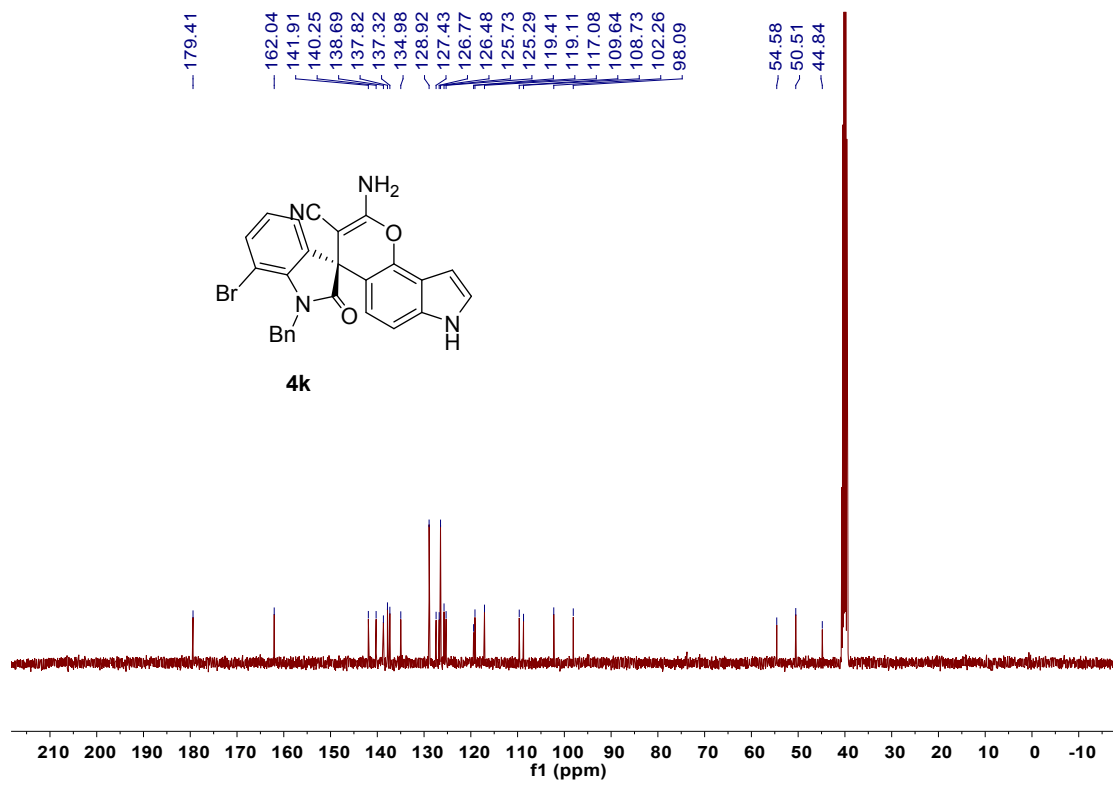


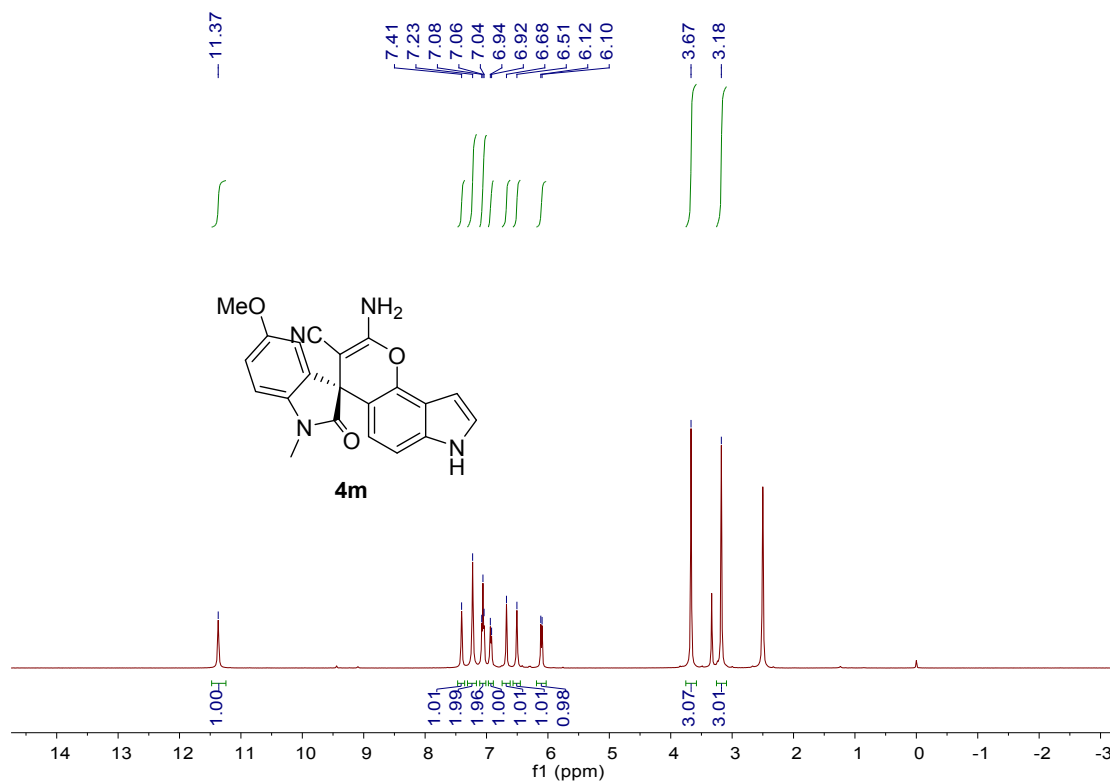
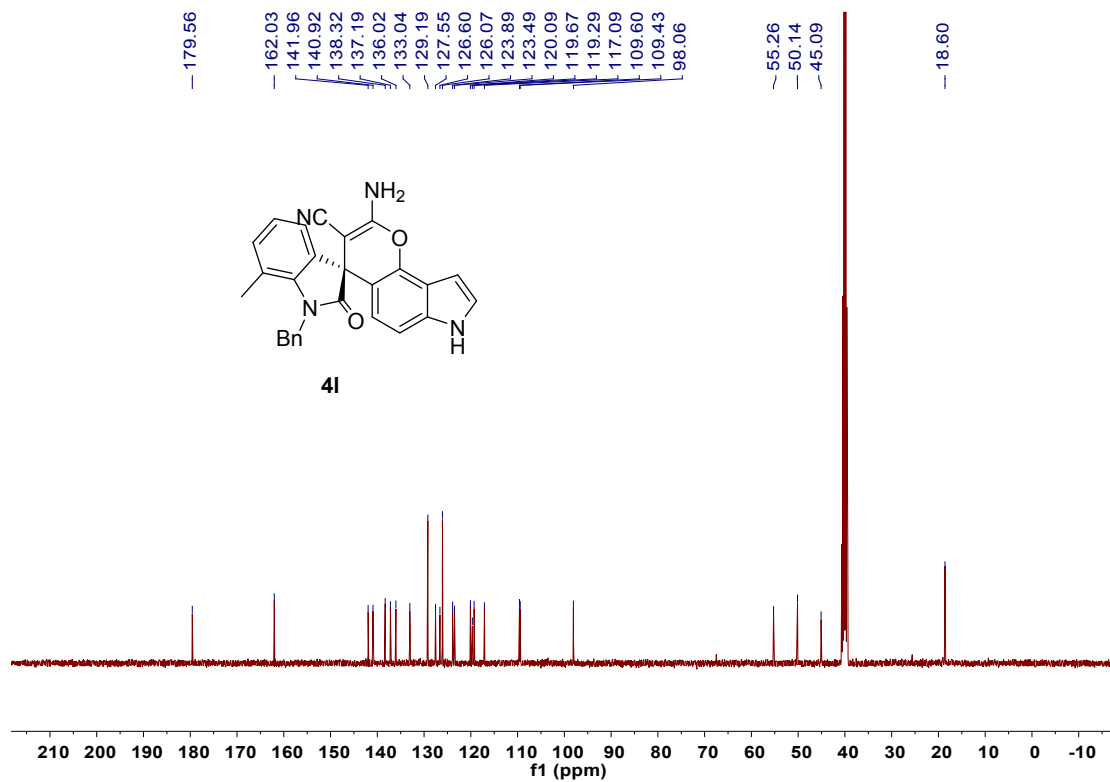


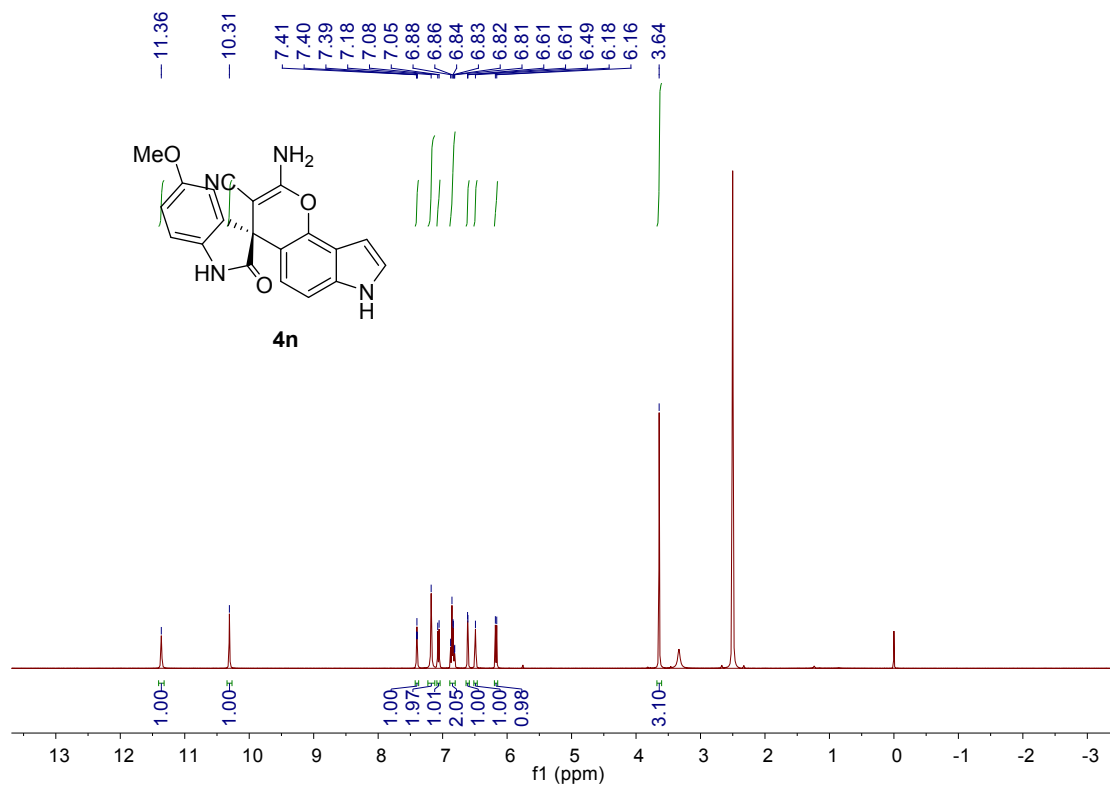
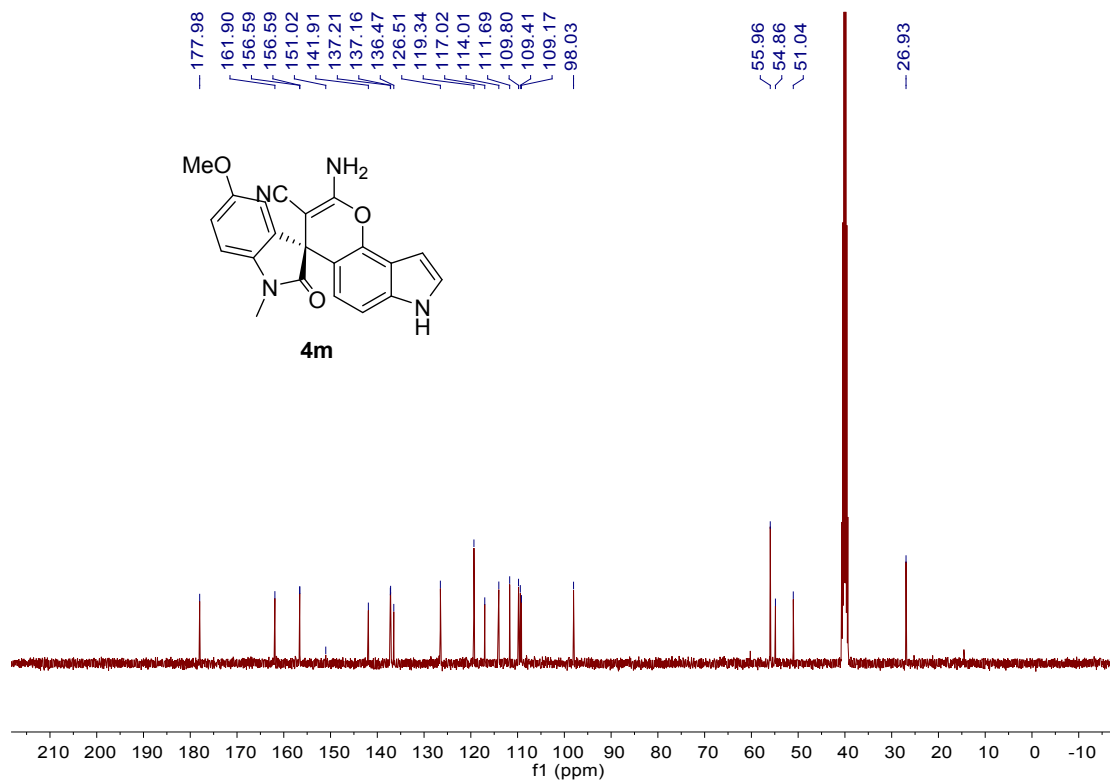


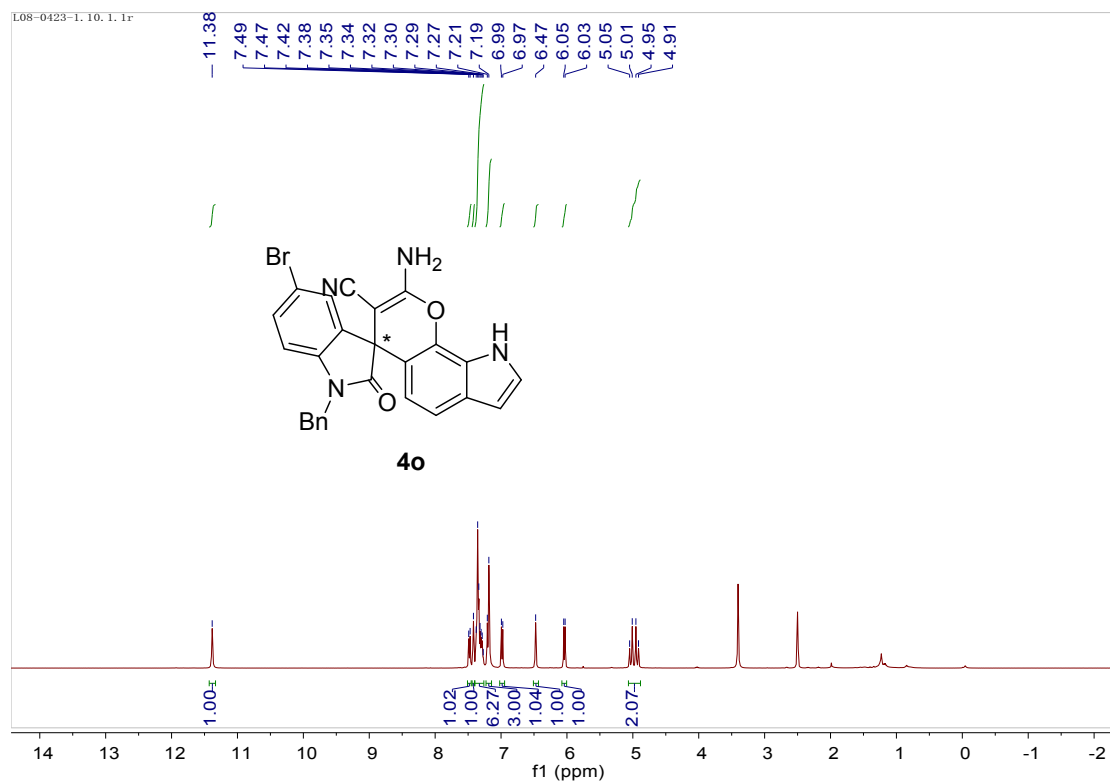
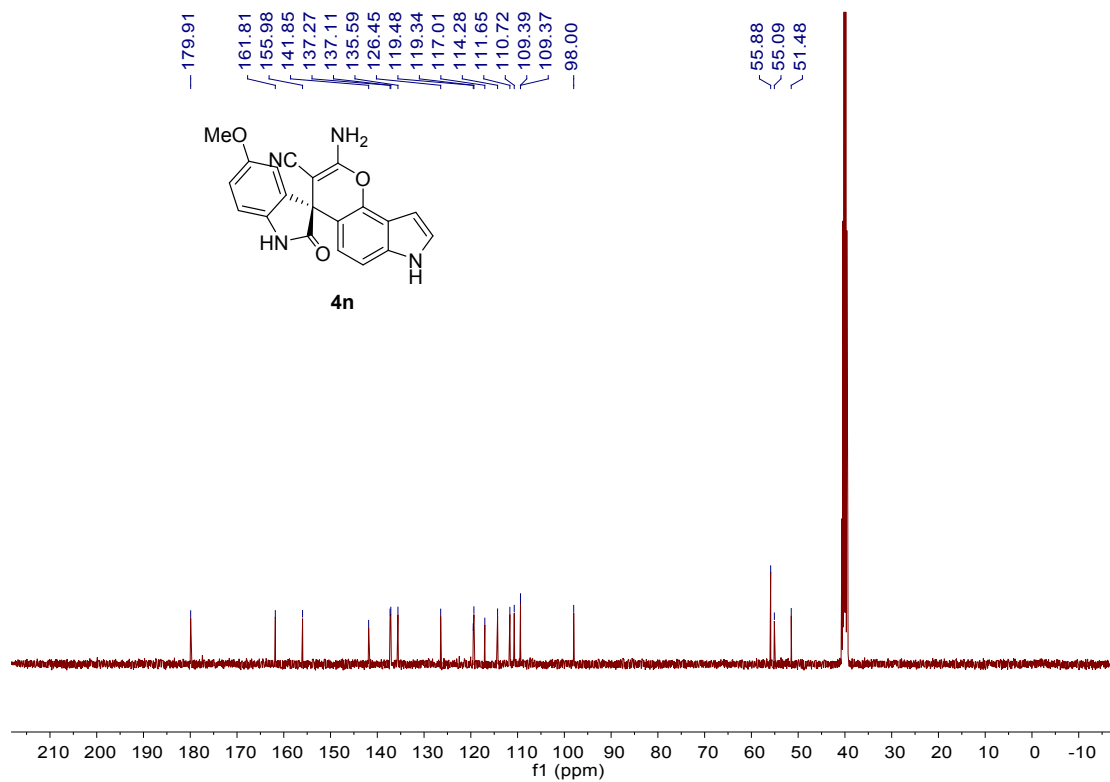


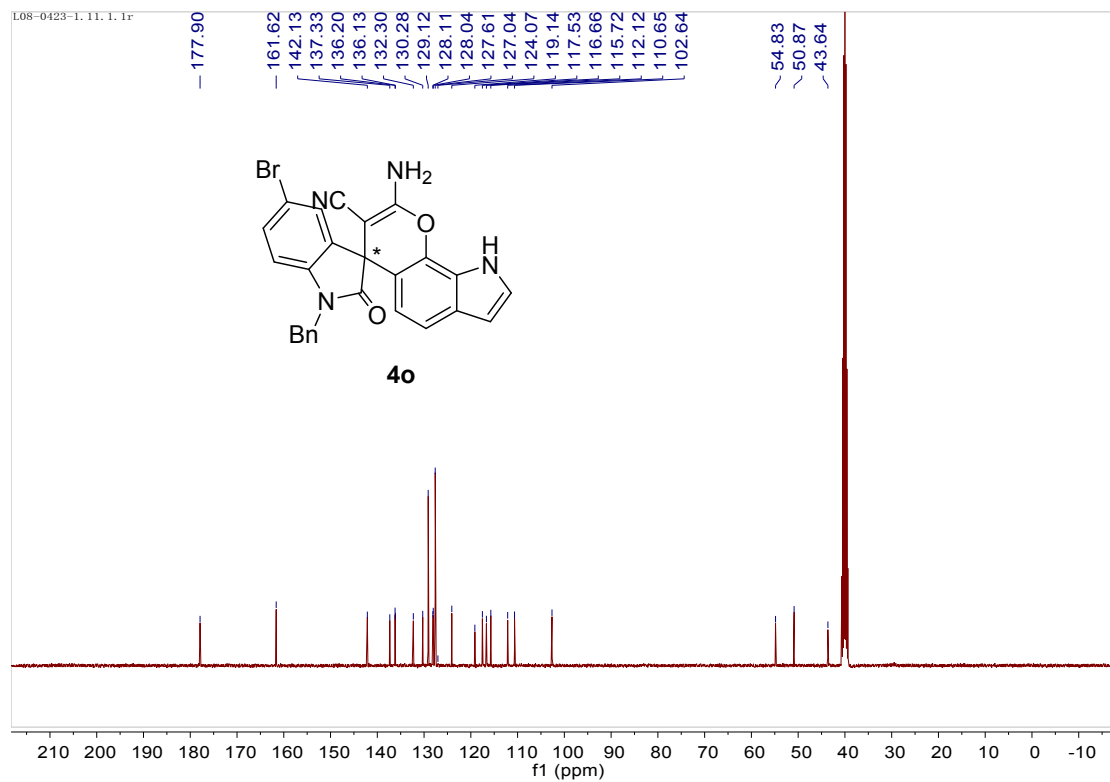






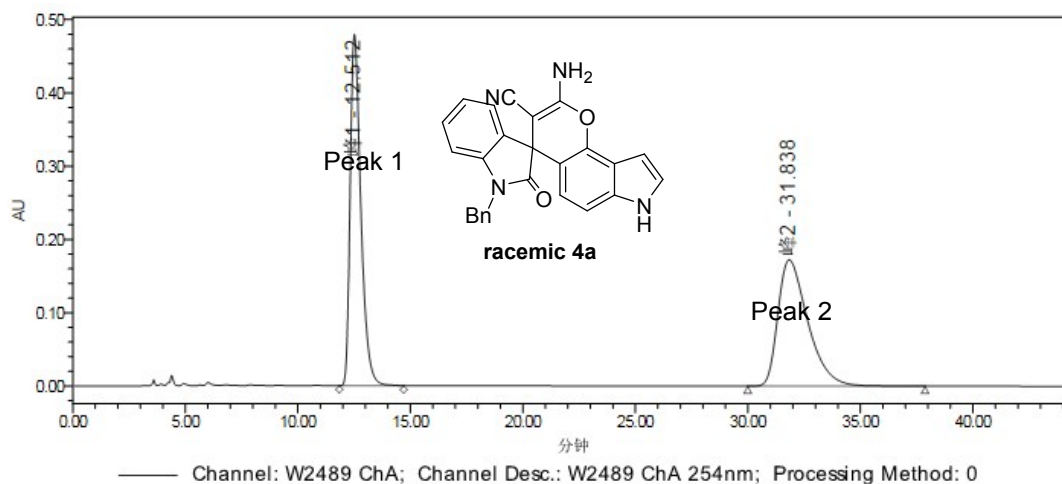




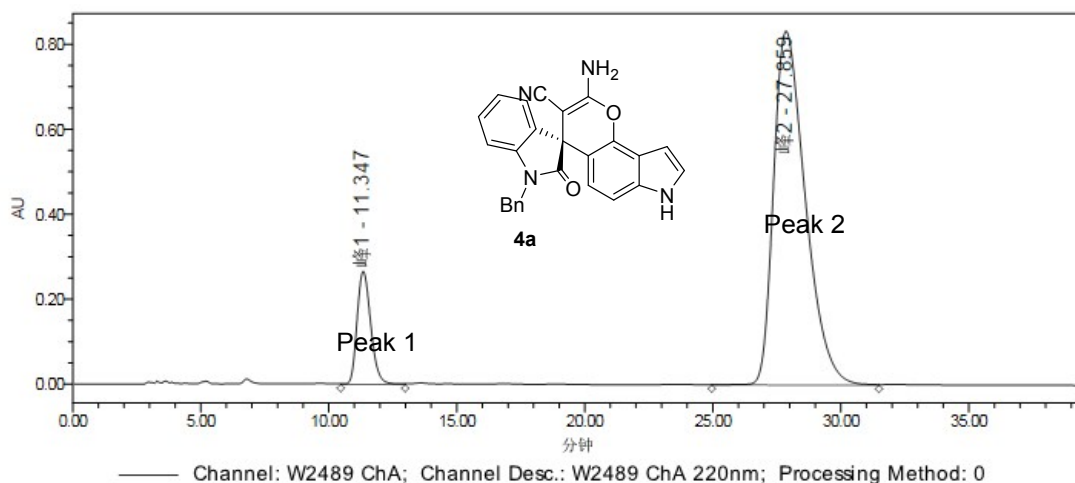




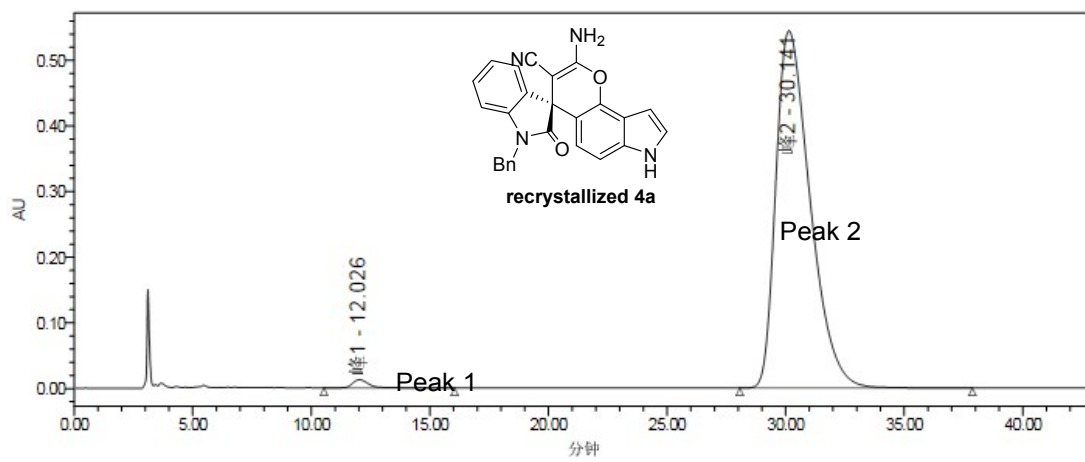
## 6. HPLC traces of compounds 4a-4o.



	Channel Description	Peak Name	RT (min)	Area (峰*sec) μAU*sec	% Area	Height (峰) μAU
1	W2489 ChA 254nm	峰1	12.512	15839375	49.93	479050
2	W2489 ChA 254nm	峰2	31.838	15882636	50.07	172434

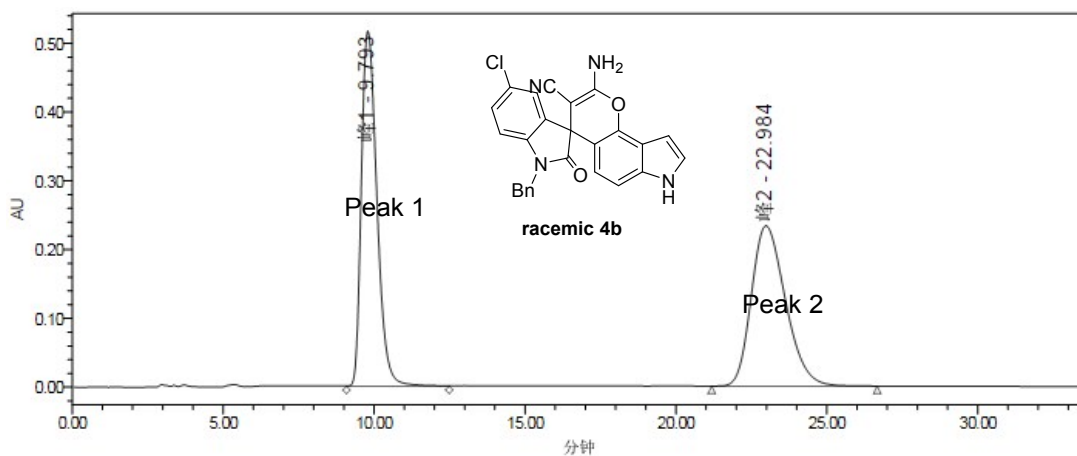


	Channel Description	Peak Name	RT (min)	Area (峰*sec) μAU*sec	% Area	Height (峰) μAU
1	W2489 ChA 220nm	峰1	11.347	9957721	12.19	265882
2	W2489 ChA 220nm	峰2	27.859	71745414	87.81	832427



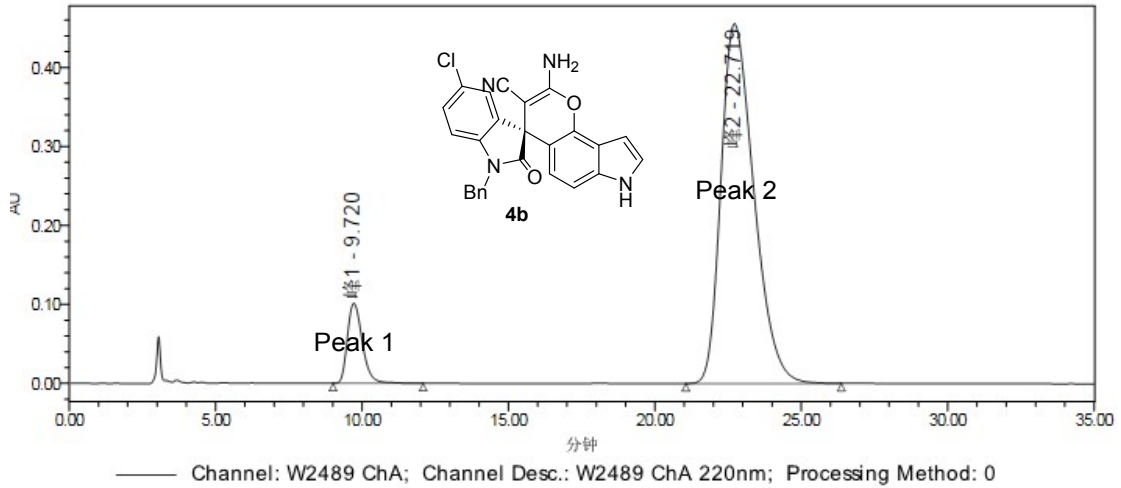
Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (峰*sec) μAU*sec	% Area	Height (峰) μAU
1	W2489 ChA 220nm	峰1 Peak 1	12.026	576823	1.05	12332
2	W2489 ChA 220nm	峰2 Peak 2	30.141	54608278	98.95	544292

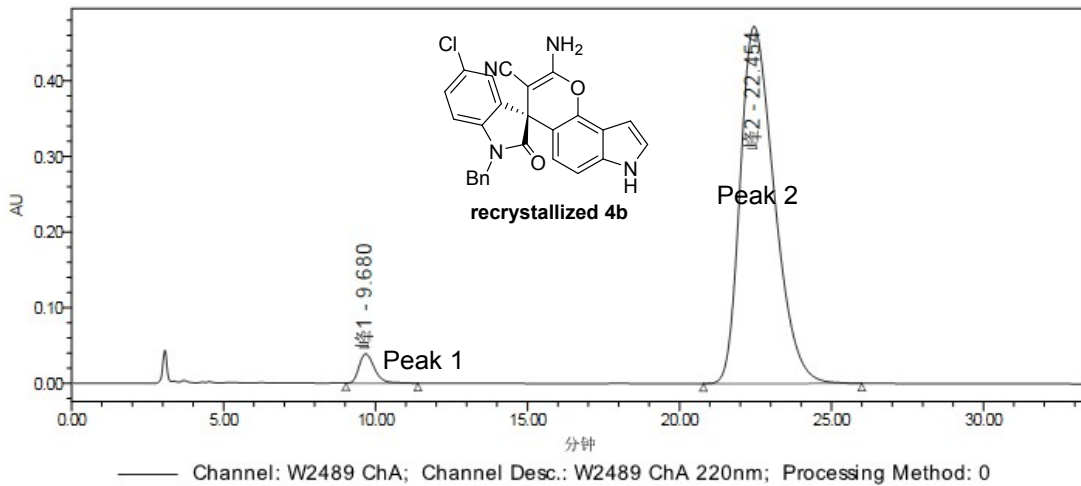


Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

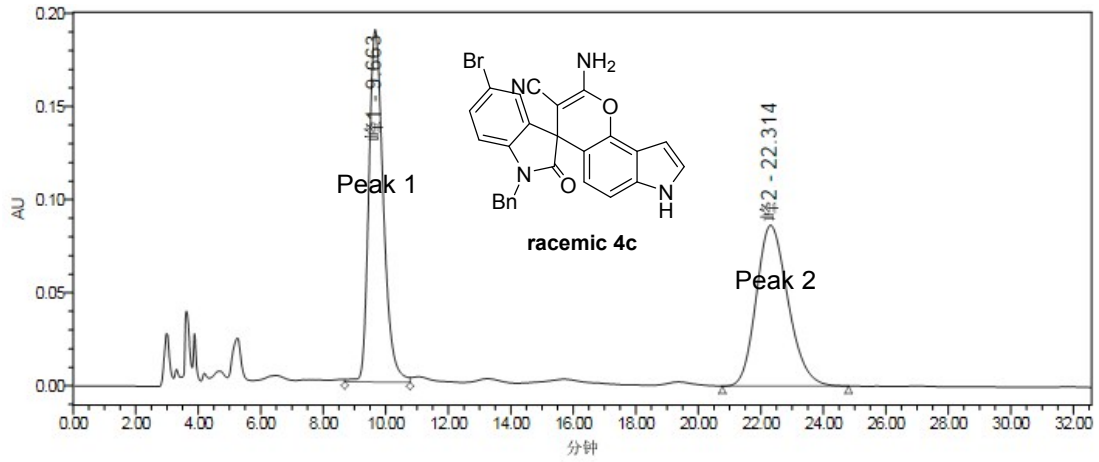
	Channel Description	Peak Name	RT (min)	Area (峰*sec) μAU*sec	% Area	Height (峰) μAU
1	W2489 ChA 220nm	峰1 Peak 1	9.793	18478837	50.18	516136
2	W2489 ChA 220nm	峰2 Peak 2	22.984	18344202	49.82	233166



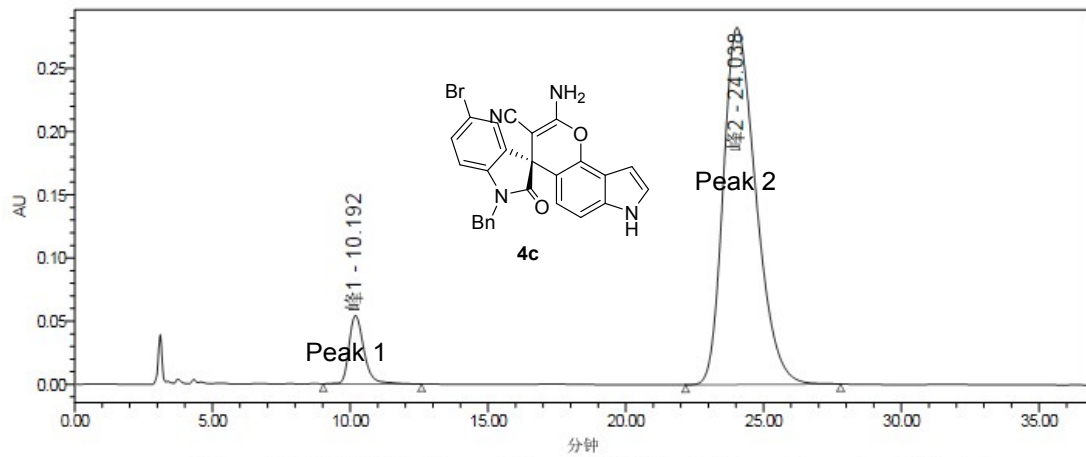
	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1	9.720	3583658	9.15	101132
2	W2489 ChA 220nm	峰2	22.719	35577433	90.85	455199



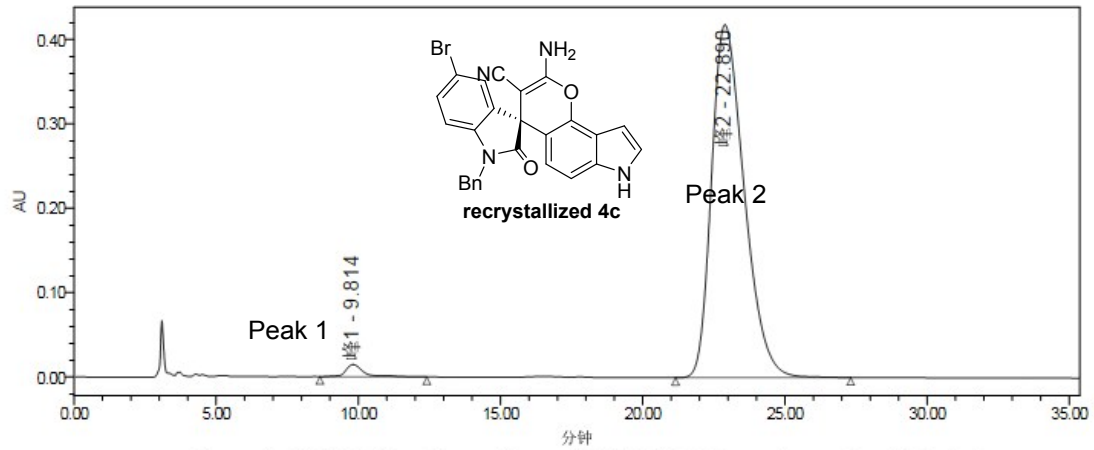
	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1	9.680	1359386	3.57	38585
2	W2489 ChA 220nm	峰2	22.454	36740237	96.43	472150



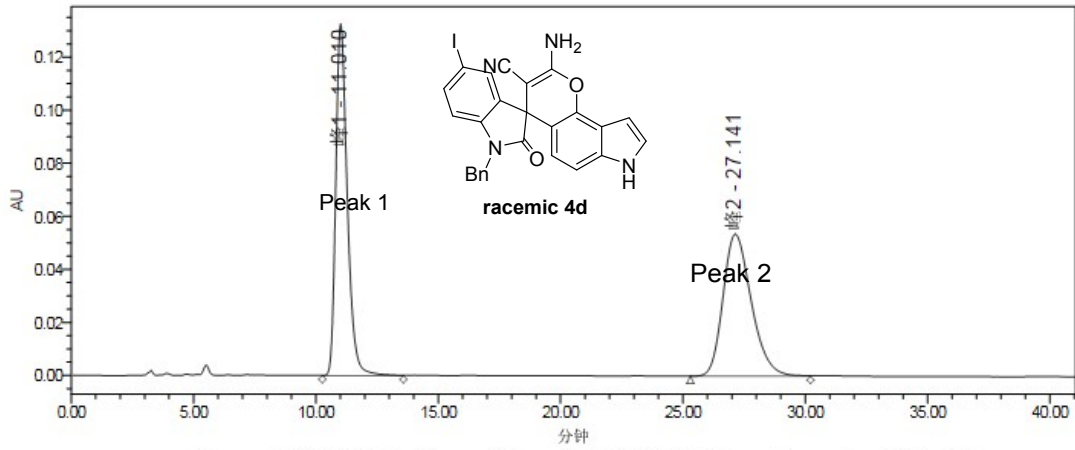
	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1 Peak 1	9.663	6126328	50.17	189015
2	W2489 ChA 220nm	峰2 Peak 2	22.314	6085694	49.83	86325



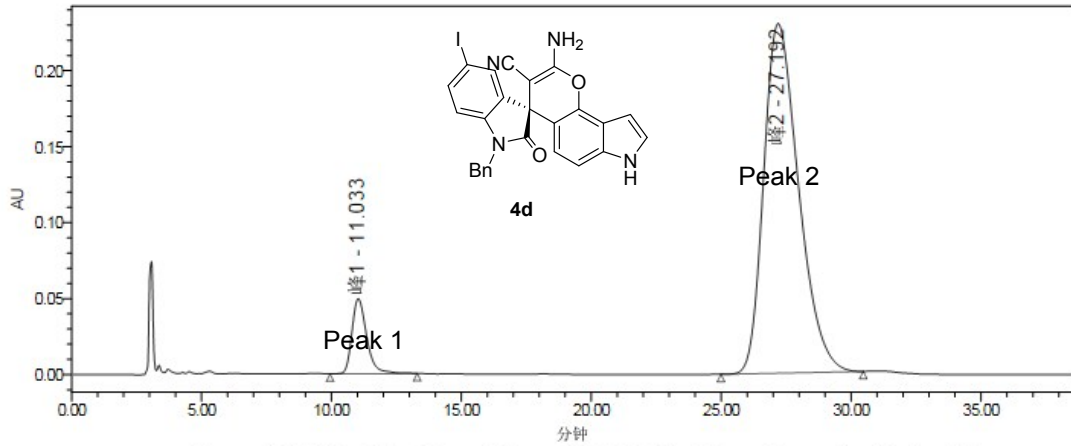
	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1 Peak 1	10.192	2051513	8.09	54071
2	W2489 ChA 220nm	峰2 Peak 2	24.038	23311115	91.91	282515



	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	Peak 1 峰1	9.814	652187	1.92	14548
2	W2489 ChA 220nm	Peak 2 峰2	22.890	33393600	98.08	418198

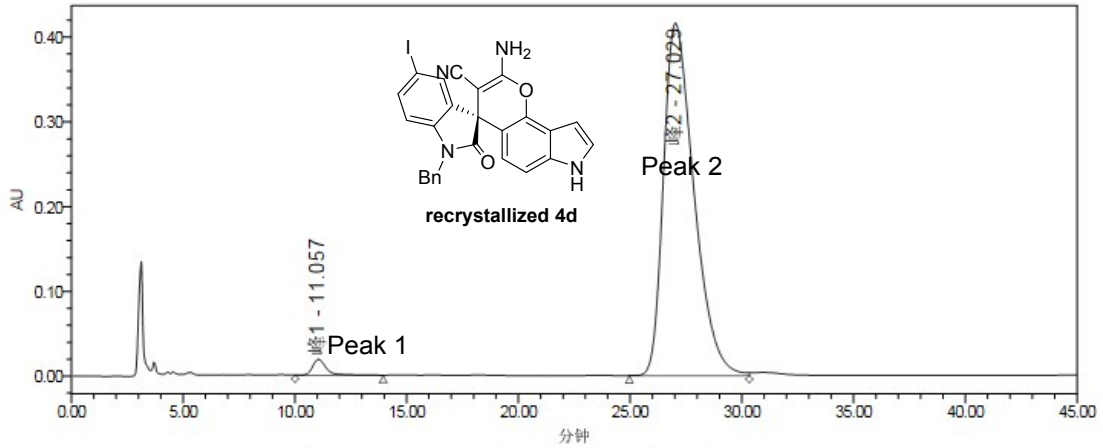


	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 254nm	Peak 1 峰1	11.010	4340804	50.19	152493
2	W2489 ChA 254nm	Peak 2 峰2	27.141	4307404	49.81	53543



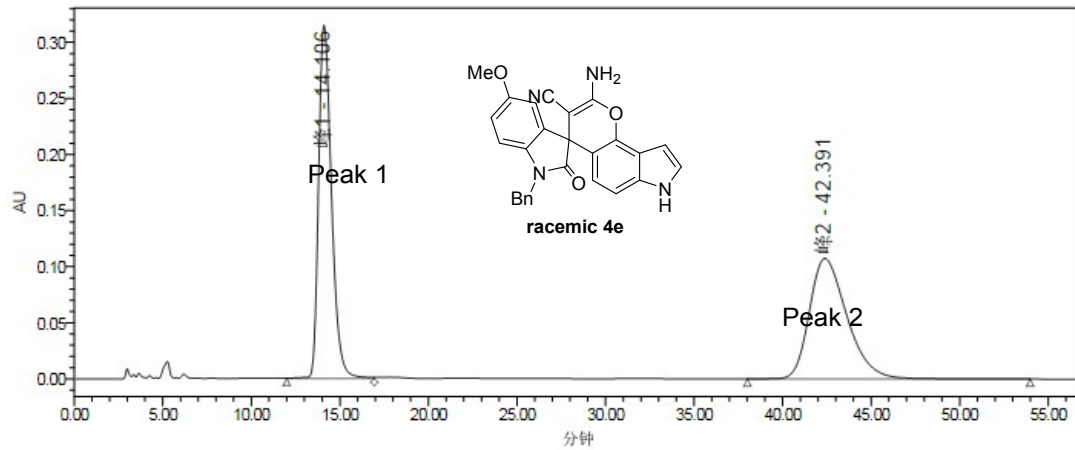
Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1	11.033	1951618	8.32	49388
2	W2489 ChA 220nm	峰2	27.192	21500044	91.68	230111

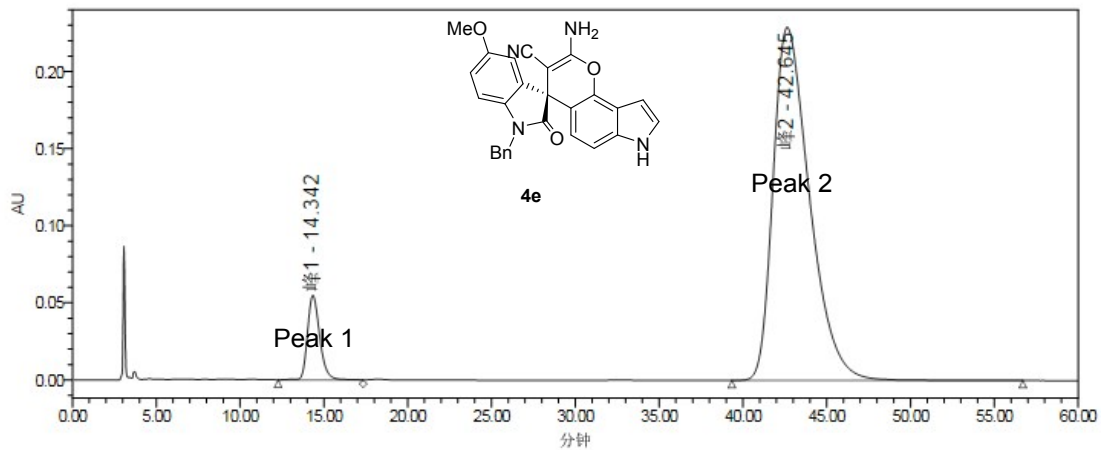


Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1	11.057	810928	2.02	18676
2	W2489 ChA 220nm	峰2	27.029	39274983	97.98	415462

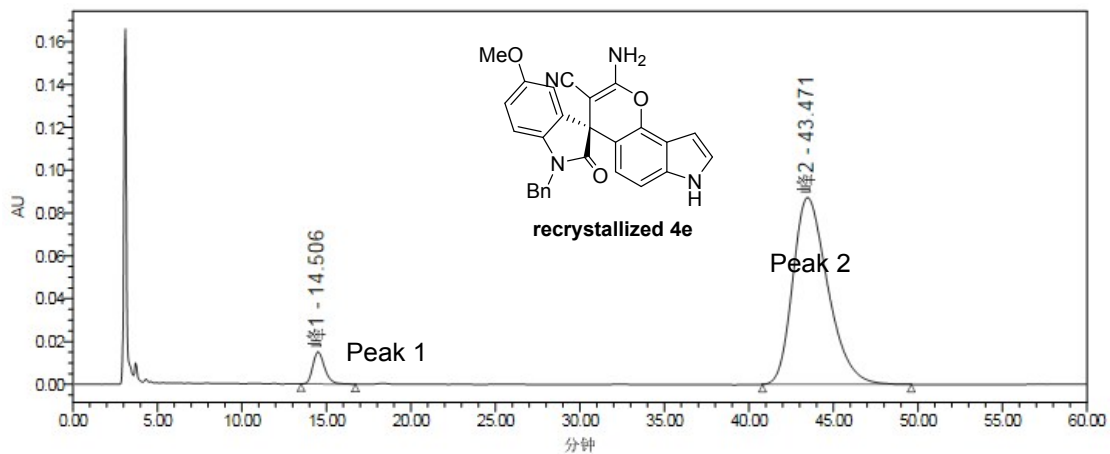


	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1	14.106	15917608	50.14	314378
2	W2489 ChA 220nm	峰2	42.391	15829349	49.86	107328



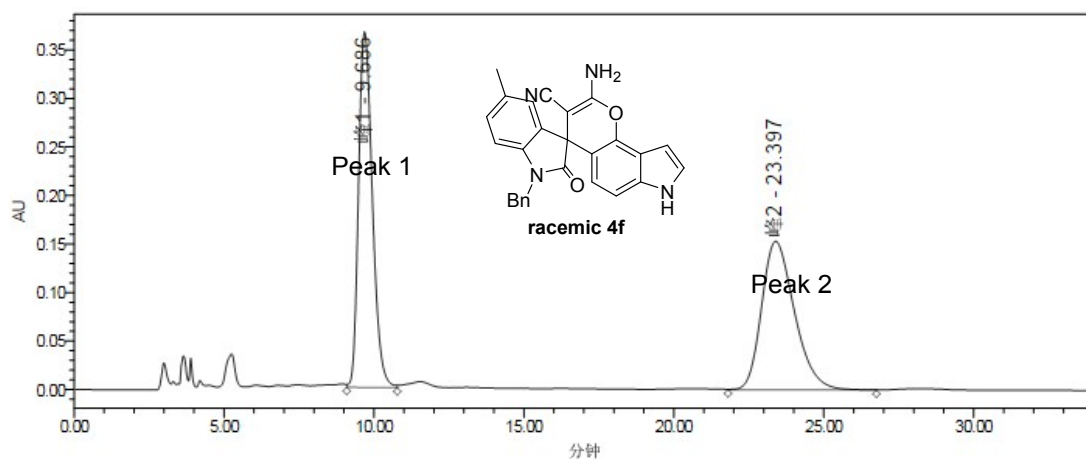
	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1	14.342	2795431	7.48	54664
2	W2489 ChA 220nm	峰2	42.645	34575557	92.52	228844





Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

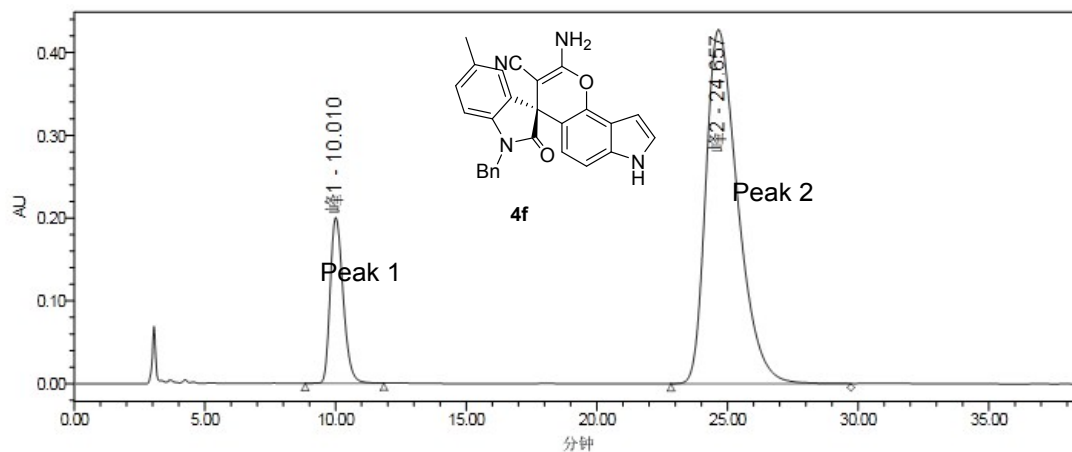
	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1 Peak 1	14.506	725361	5.46	14876
2	W2489 ChA 220nm	峰2 Peak 2	43.471	12565098	94.54	87215



Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

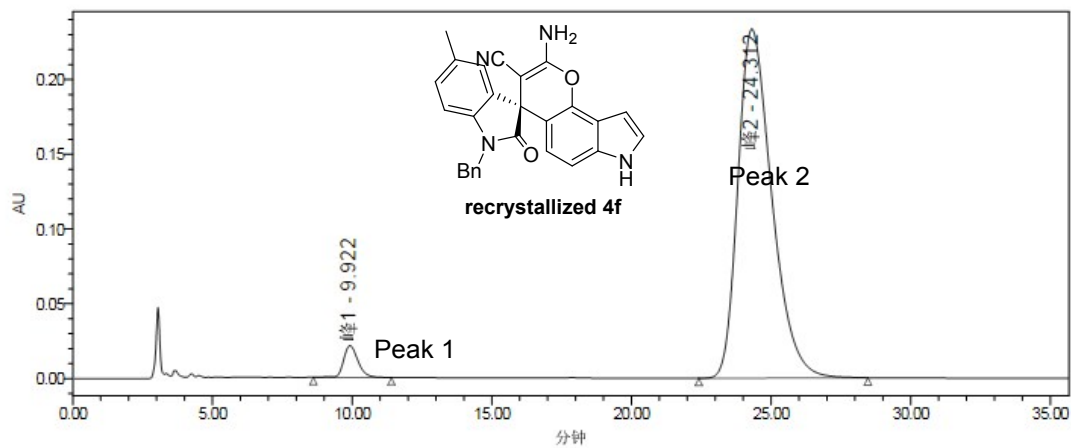
	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1 Peak 1	9.686	11696124	50.06	366145
2	W2489 ChA 220nm	峰2 Peak 2	23.397	11669585	49.94	153012





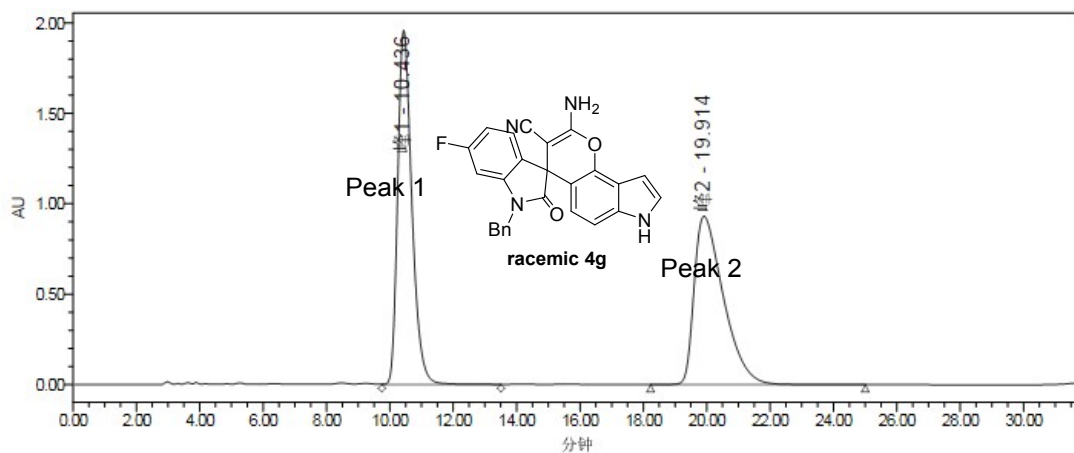
Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1	10.010	6889855	15.97	200132
2	W2489 ChA 220nm	峰2	24.657	36249111	84.03	427578



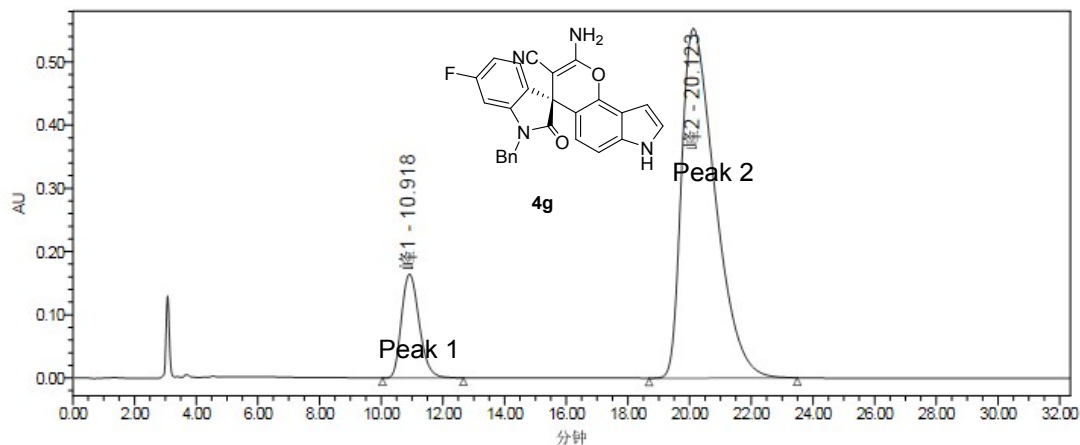
Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1	9.922	764028	3.74	21229
2	W2489 ChA 220nm	峰2	24.312	19678438	96.26	233522



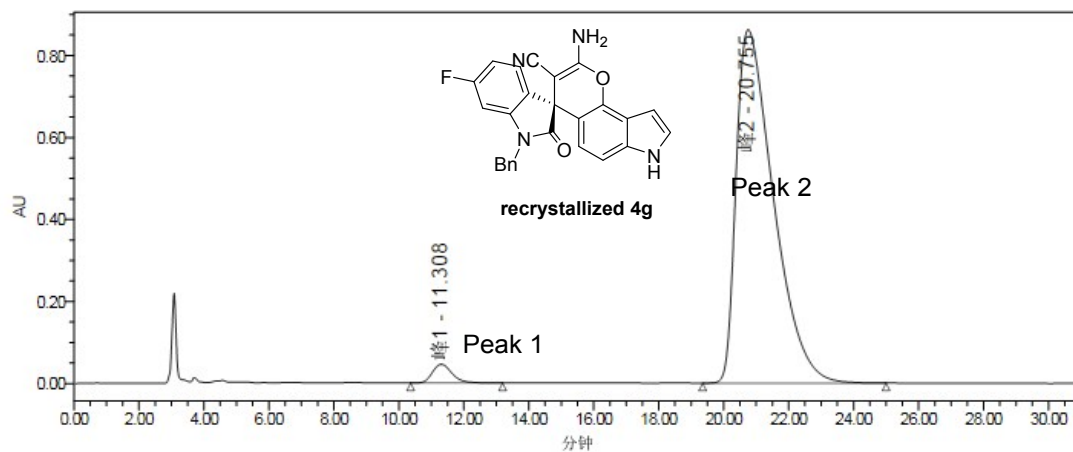
Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1 Peak 1	10.436	60692336	50.44	1955652
2	W2489 ChA 220nm	峰2 Peak 2	19.914	59633281	49.56	930828

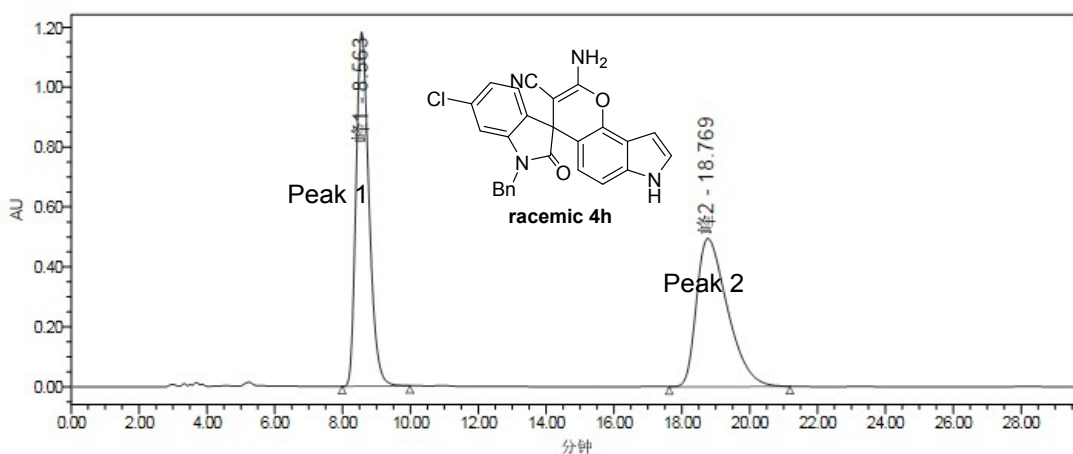


Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

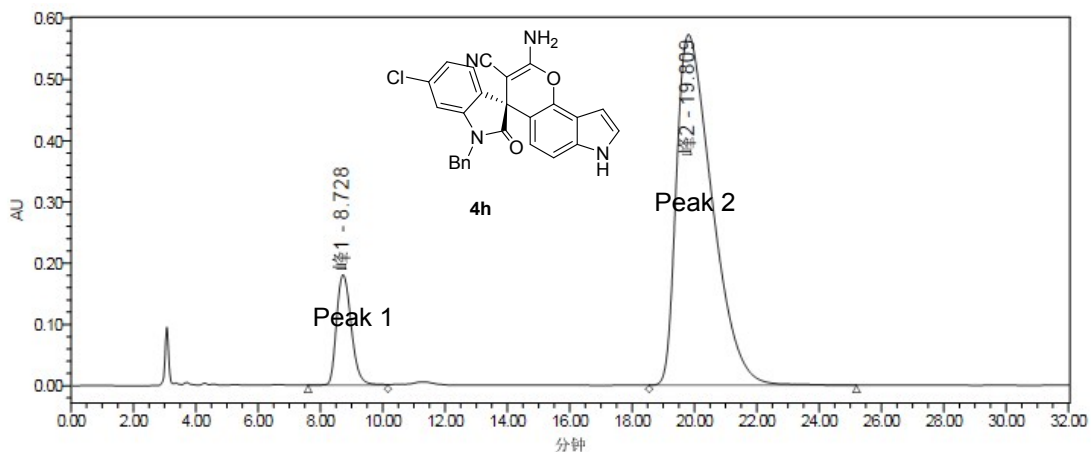
	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1 Peak 1	10.918	6574227	13.61	163994
2	W2489 ChA 220nm	峰2 Peak 2	20.123	41736494	86.39	552639



Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
W2489 ChA 220nm	峰1	11.308	1929778	2.73	45772
W2489 ChA 220nm	峰2	20.755	68709938	97.27	862048

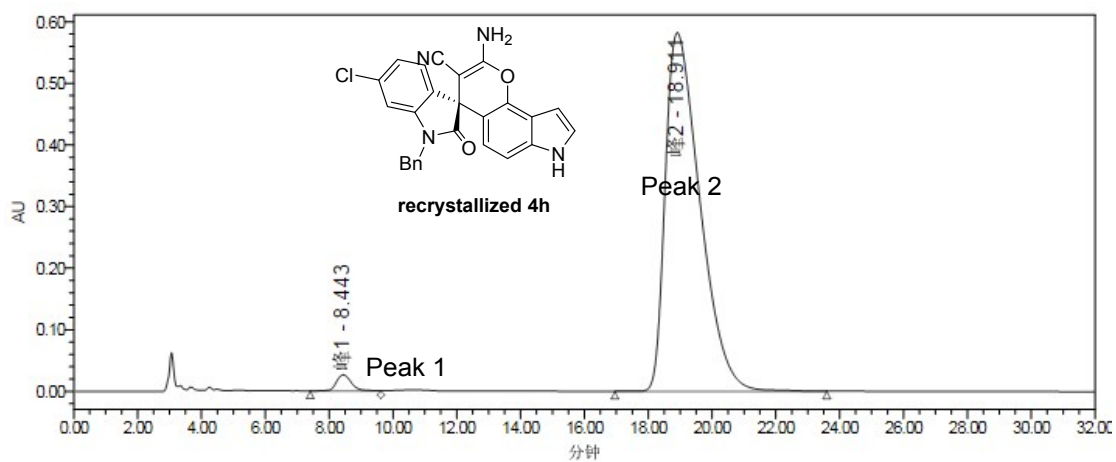


Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
W2489 ChA 220nm	峰1	8.563	31382041	50.05	1180366
W2489 ChA 220nm	峰2	18.769	31323318	49.95	494057



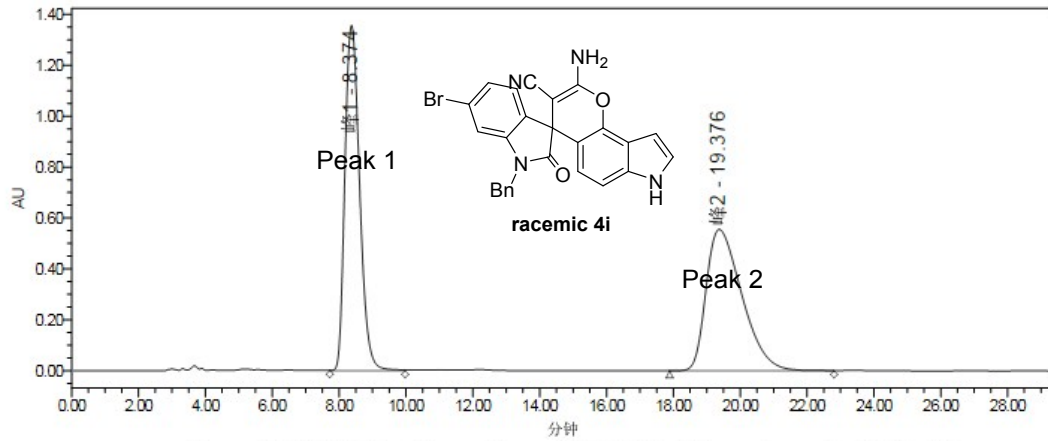
Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1	8.728	5933669	11.55	180057
2	W2489 ChA 220nm	峰2	19.809	45446878	88.45	572719

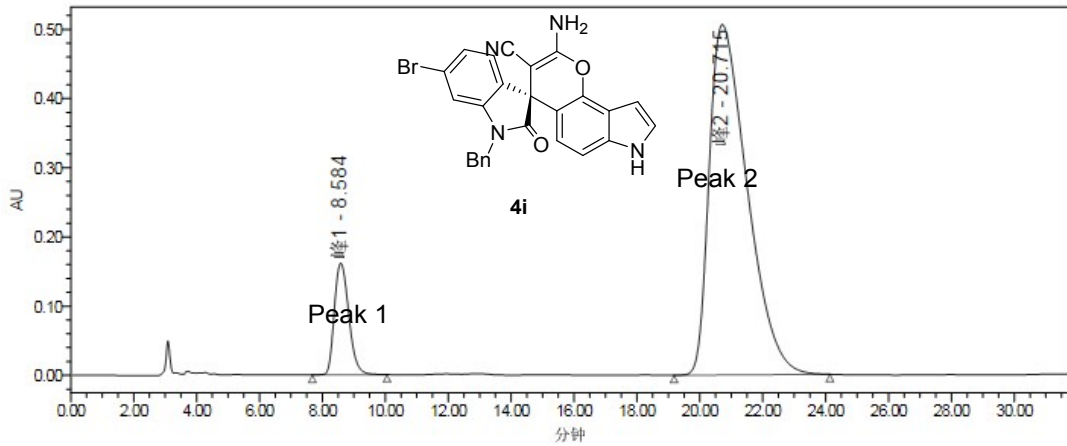


Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

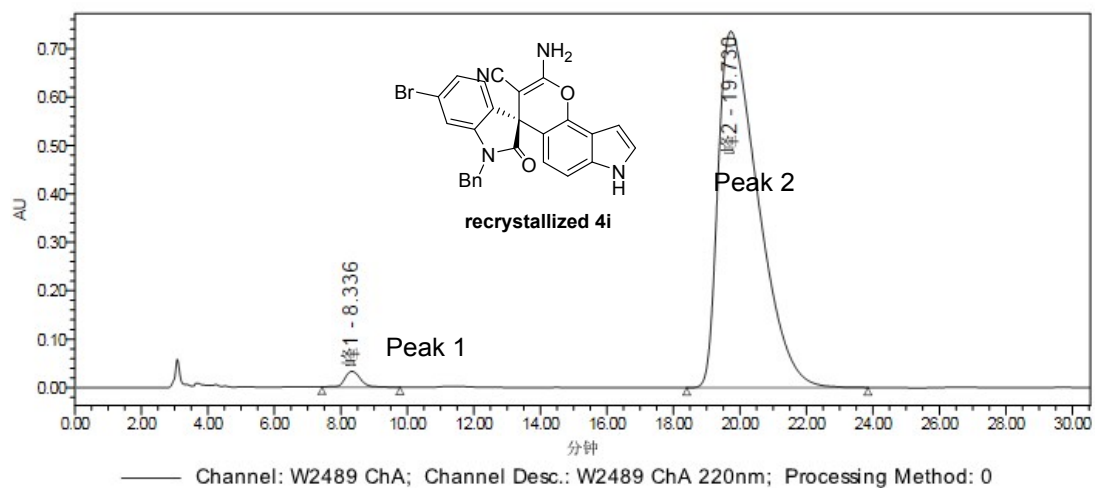
	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1	8.443	866818	1.94	26169
2	W2489 ChA 220nm	峰2	18.911	43777057	98.06	581711



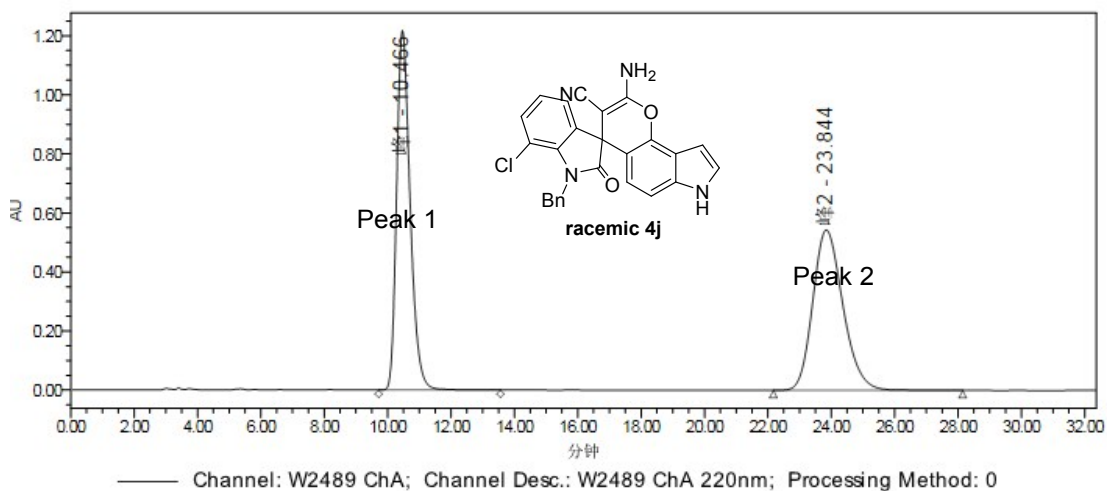
	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1	8.374	41310707	49.97	1355712
2	W2489 ChA 220nm	峰2	19.376	41365228	50.03	555616



	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1	8.584	5159676	10.83	161125
2	W2489 ChA 220nm	峰2	20.715	42485909	89.17	506283

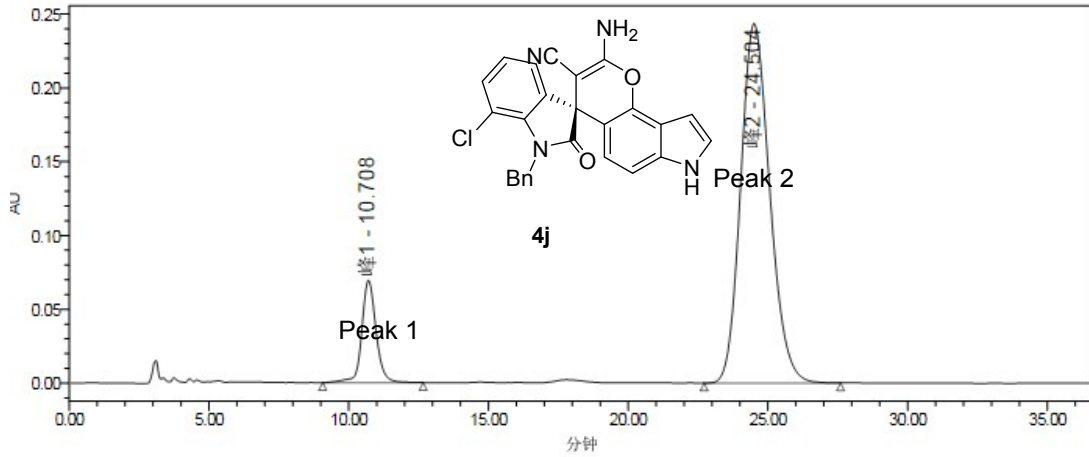


	Channel Description	Peak Name	RT (min)	Area (峰*sec) μAU*sec	% Area	Height (峰) μAU
1	W2489 ChA 220nm	峰1 Peak 1	8.336	1034444	1.66	32242
2	W2489 ChA 220nm	峰2 Peak 2	19.730	61103511	98.34	735715

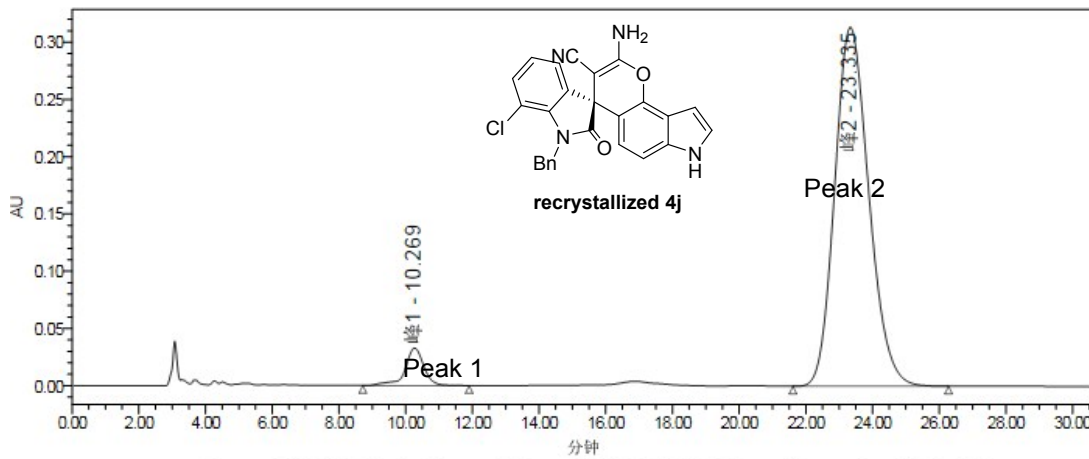


	Channel Description	Peak Name	RT (min)	Area (峰*sec) μAU*sec	% Area	Height (峰) μAU
1	W2489 ChA 220nm	峰1 Peak 1	10.466	35992383	50.07	1216508
2	W2489 ChA 220nm	峰2 Peak 2	23.844	35888964	49.93	543191

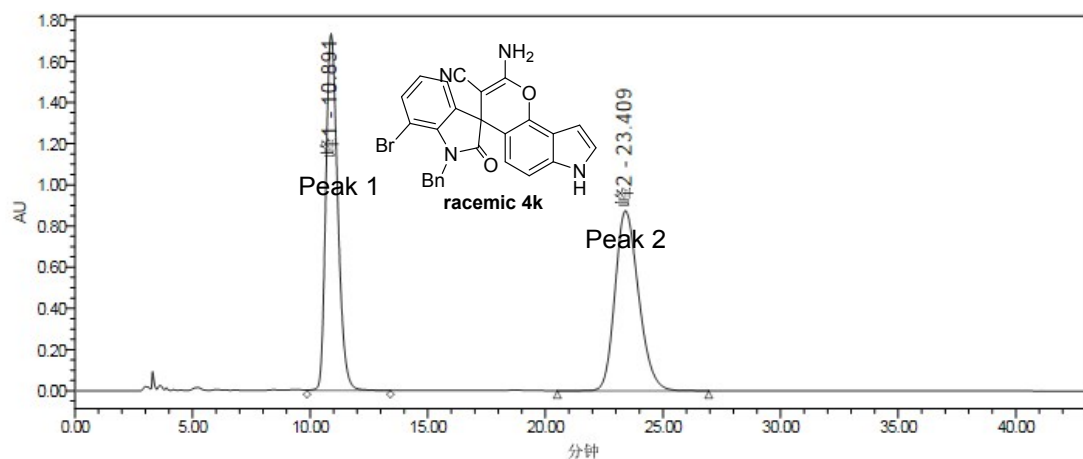




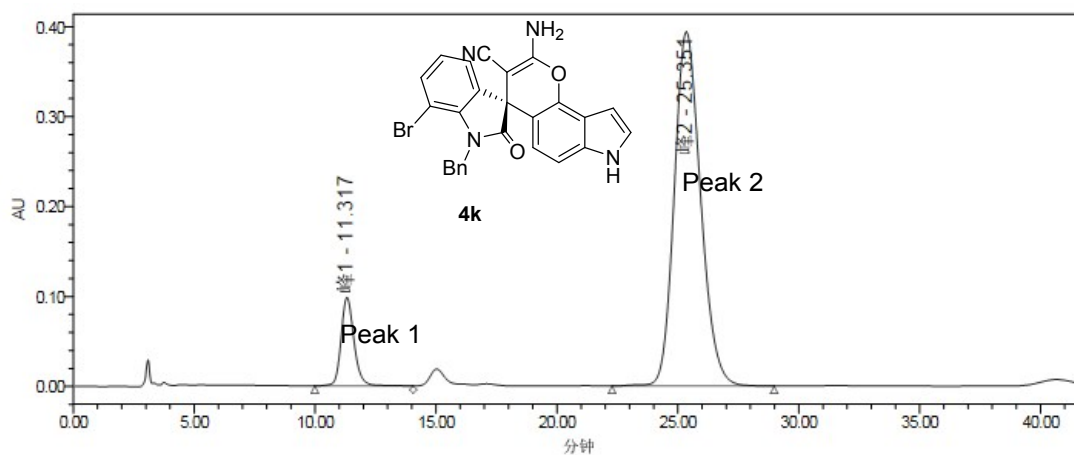
	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1	10.708	2463889	12.28	69238
2	W2489 ChA 220nm	峰2	24.504	17596030	87.72	243414



	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1	10.269	1292696	5.48	32766
2	W2489 ChA 220nm	峰2	23.335	22293677	94.52	313506

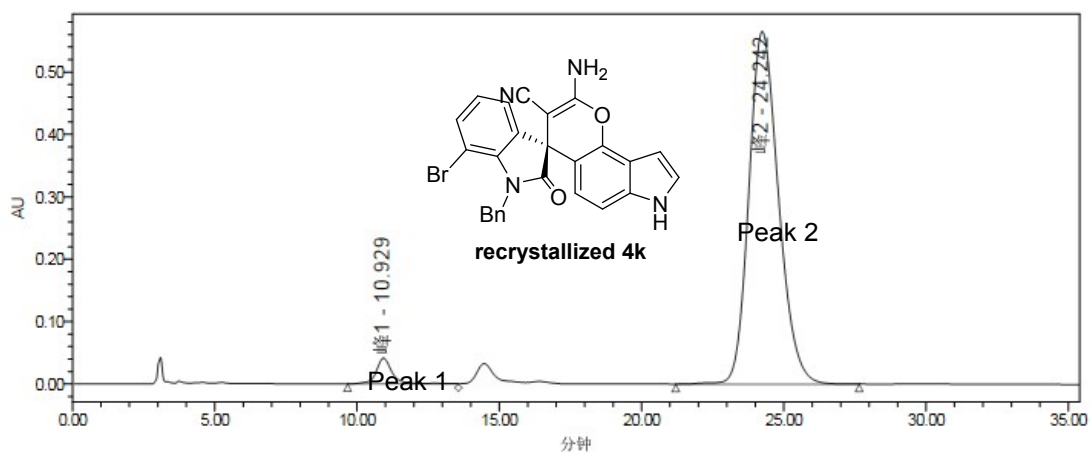


	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1 Peak 1	10.891	60698544	49.89	1731048
2	W2489 ChA 220nm	峰2 Peak 2	23.409	60965581	50.11	872936



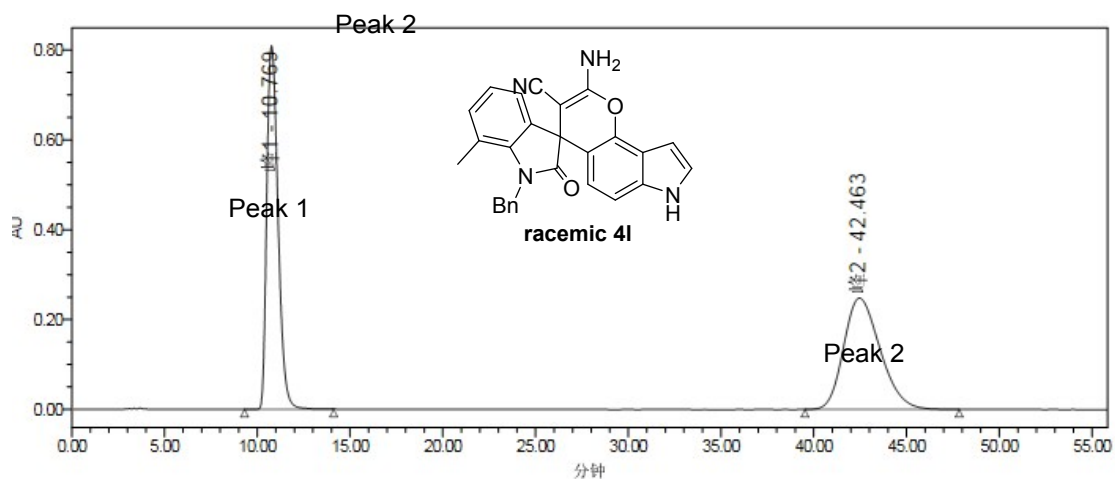
	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1 Peak 1	11.317	3675408	10.95	98327
2	W2489 ChA 220nm	峰2 Peak 2	25.351	29887780	89.05	393712





Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

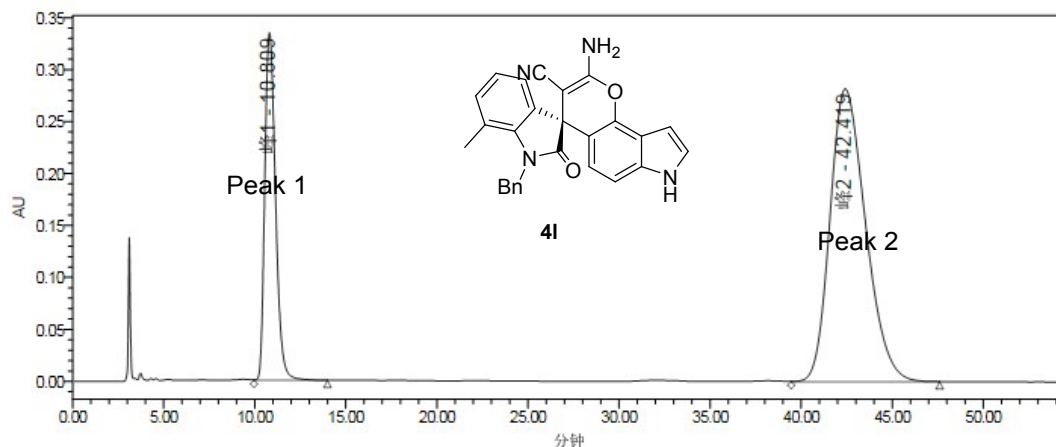
	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1	10.929	1619745	3.81	41212
2	W2489 ChA 220nm	峰2	24.242	40938379	96.19	565095



Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1	10.769	34065610	50.09	808705
2	W2489 ChA 220nm	峰2	42.463	33945983	49.91	248045

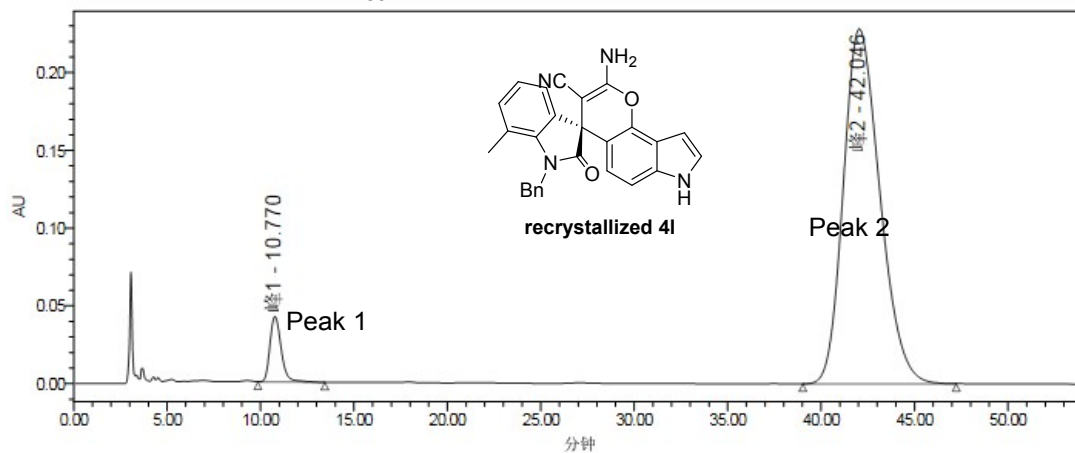
Peak 2



Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1	10.809	13638112	26.30	334116
2	W2489 ChA 220nm	峰2	42.419	38211458	73.70	281553

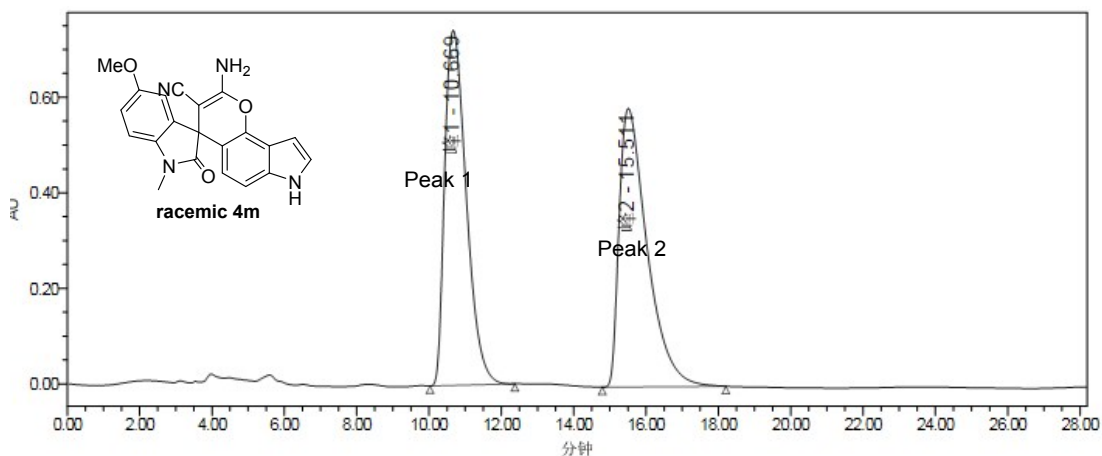
Peak 2



Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

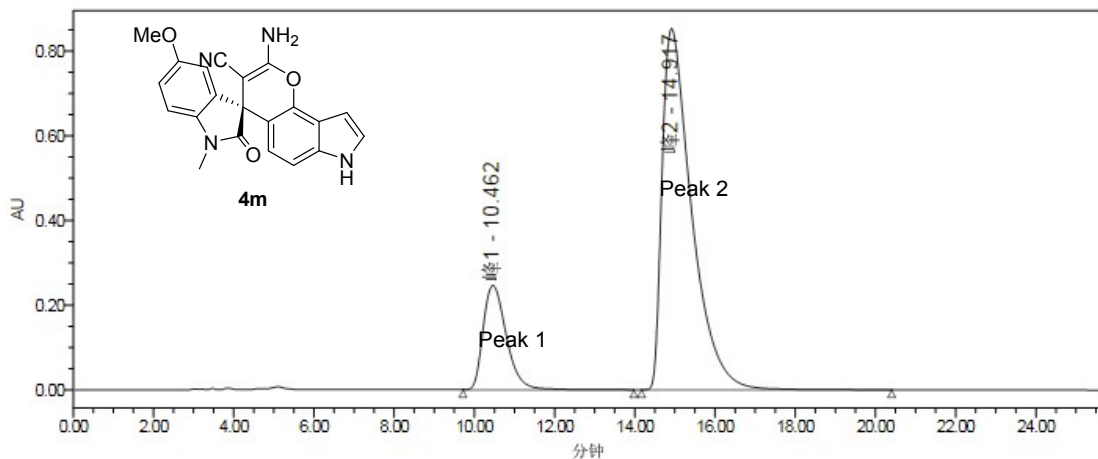
	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1	10.770	1762260	5.38	42018
2	W2489 ChA 220nm	峰2	42.046	30983756	94.62	228163

Peak 2



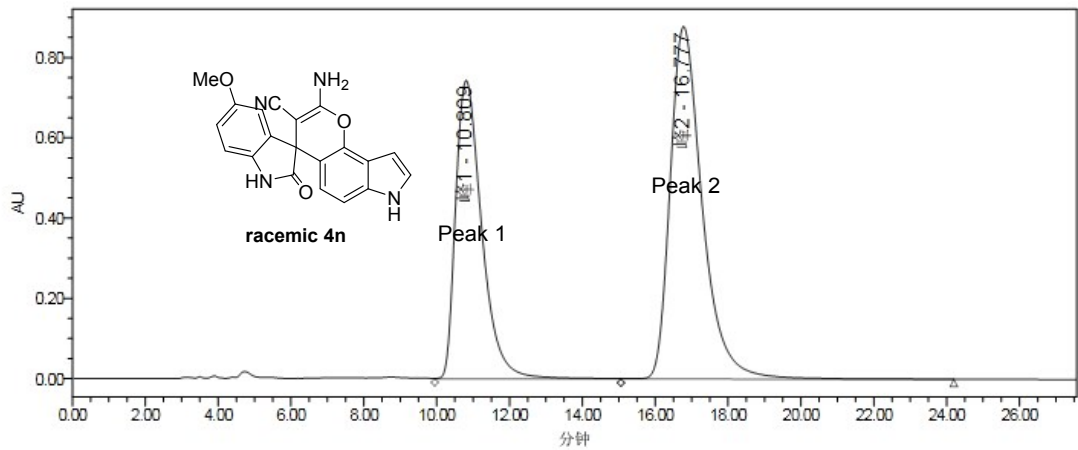
Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1 Peak 1	10.669	30752686	49.57	743040
2	W2489 ChA 220nm	峰2 Peak 2	15.511	31283288	50.43	583113



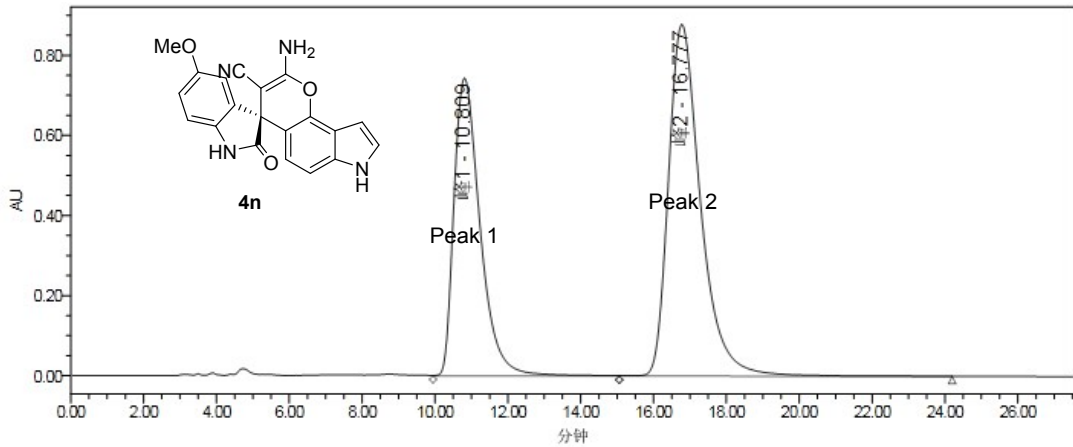
Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 220nm	峰1 Peak 1	10.462	9938274	18.55	246215
2	W2489 ChA 220nm	峰2 Peak 2	14.917	43628303	81.45	853108



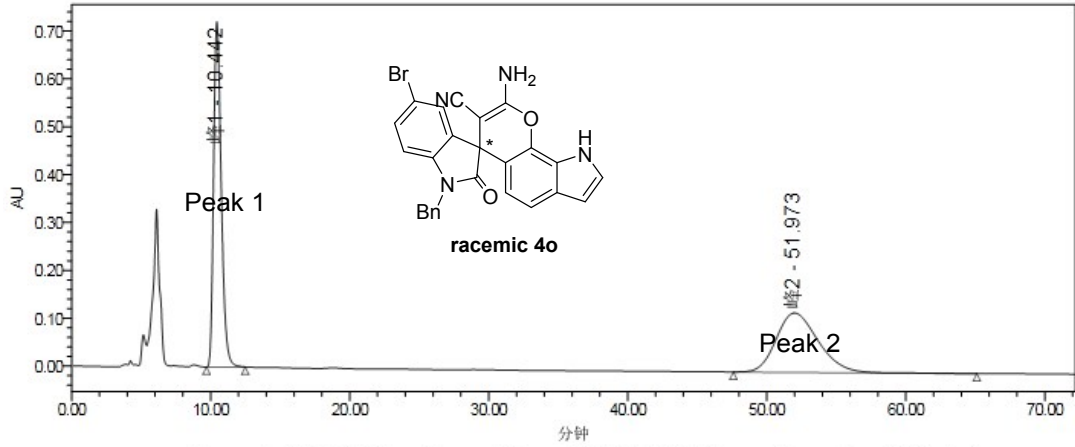
Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (μAU*sec)	% Area	Height (μAU)
1	W2489 ChA 220nm	峰1 Peak 1	10.809	37034587	40.75	743097
2	W2489 ChA 220nm	峰2 Peak 2	16.777	53841100	59.25	877796

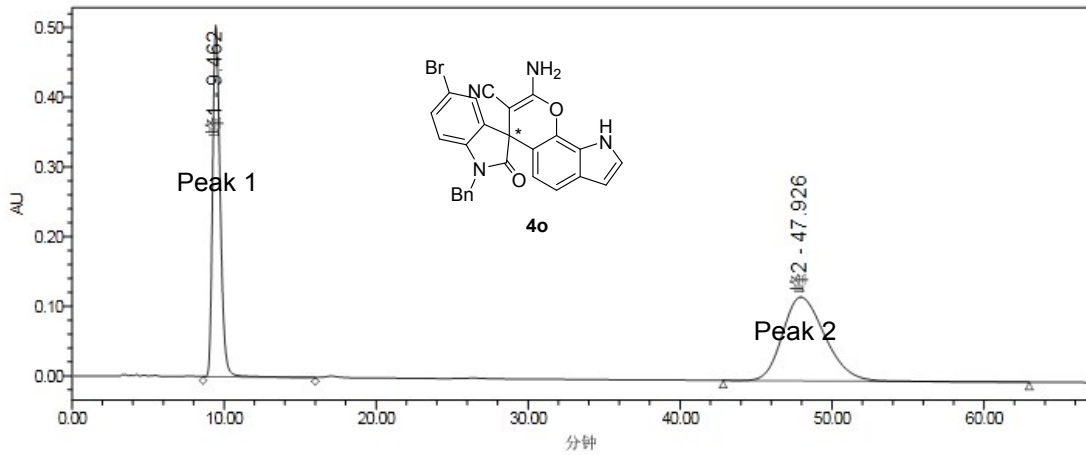


Channel: W2489 ChA; Channel Desc.: W2489 ChA 220nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (μAU*sec)	% Area	Height (μAU)
1	W2489 ChA 220nm	峰1 Peak 1	10.809	37034587	40.75	743097
2	W2489 ChA 220nm	峰2 Peak 2	16.777	53841100	59.25	877796



	Channel Description	Peak Name	RT (min)	Area (min*sec) μAU*sec	% Area	Height μAU
1	W2489 ChA 220nm	峰1	10.442	27567183	51.46	720471
2	W2489 ChA 220nm	峰2	51.973	26003631	48.54	124131



	Channel Description	Peak Name	RT (min)	Area (min*sec) μAU*sec	% Area	Height μAU
1	W2489 ChA 220nm	峰1	9.462	17497019	42.87	504288
2	W2489 ChA 220nm	峰2	47.926	23321110	57.13	120210

## 7. X-ray Crystallographic Data of compound 4e

**Table 1 Crystal data and structure refinement for 1.**

Identification code	1974647
Empirical formula	C <sub>27</sub> H <sub>20</sub> N <sub>4</sub> O <sub>3</sub>
Formula weight	448.48
Temperature/K	297.0
Crystal system	monoclinic
Space group	P2 <sub>1</sub>
a/Å	11.5749(3)
b/Å	8.9564(2)
c/Å	12.5886(4)
α /°	90.00
β /°	116.2140(10)
γ /°	90.00
Volume/Å <sup>3</sup>	1170.83(5)
Z	23
ρ <sub>calc</sub> /cm <sup>3</sup>	1.272
μ /mm <sup>-1</sup>	0.085
F(000)	468.0
Crystal size/mm <sup>3</sup>	? × ? × ?
Radiation	MoK α ( λ = 0.71073)
2θ range for data collection/°	5.8 to 56.84
Index ranges	-15 ≤ h ≤ 15, -11 ≤ k ≤ 11, -16 ≤ l ≤ 16
Reflections collected	29710
Independent reflections	5819 [R <sub>int</sub> = 0.0512, R <sub>sigma</sub> = 0.0386]
Data/restraints/parameters	5819/1/310
Goodness-of-fit on F <sup>2</sup>	1.022
Final R indexes [I>=2 σ (I)]	R <sub>1</sub> = 0.0430, wR <sub>2</sub> = 0.0942
Final R indexes [all data]	R <sub>1</sub> = 0.0766, wR <sub>2</sub> = 0.1147
Largest diff. peak/hole / e Å <sup>-3</sup>	0.17/-0.15
Flack parameter	0.2(11)

## 8. References

1. J. Li, N. Wang, C. Li and X. Jia, *Chem. - Eur. J.*, 2012, **18**, 9645-9650.
2. T.-Z. Li, J. Xie, Y. Jiang, F. Sha and X.-Y. Wu, *Adv. Synth. Catal.*, 2015, **357**, 3507-3511.