

# Development of chiral modular bifunctional $C_2$ -symmetric bipyridine/phenanthroline-bipyrroloimidazolone ligands and application in noncovalent interaction-assisted enantioselective catalysis

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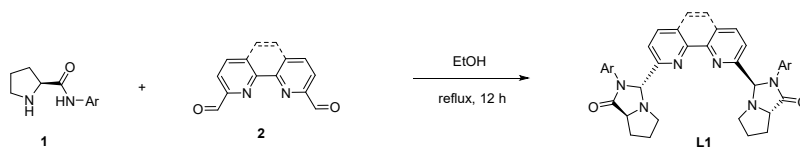
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## 1. General information

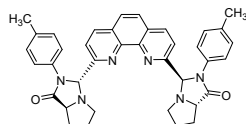
Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography.  $^1\text{H}$  and  $^{13}\text{C}$ NMR spectra were obtained using a Bruker DPX-400 spectrometer.  $^1\text{H}$  NMR chemical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

## 2. General procedure for preparation of chiral Bpy/Phen-BPI ligands L1



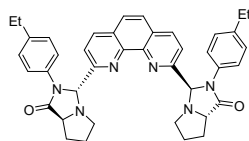
In a sealed tube equipped with a magnetic stirring bar, optically pure prolinamide **1** (2.4 mmol, 2.4 equiv) and bipyridine/phenanthroline-dicarbaldehyde **2** (1.0 mmol) were added. Then, ethanol (10.0 mL) was added and the reaction was heated with stirring at reflux for 12 h. After completion of the reaction, as indicated by TLC, the aftertreatment residue was purified by flash column chromatography to give the Bpy/Phen-BPI ligands **L1**.

## 3. Characterization data of ligands L

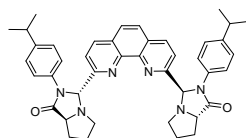


**L1a**: Yellow solid, yield 75%, >20:1 dr;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 1.84-1.89 (m, 4H), 2.13 (s, 6H), 2.17-2.22 (m, 4H), 3.06-3.12 (m, 2H), 3.47-3.53 (m, 2H), 4.20-4.24 (m, 2H), 6.13 (s, 2H), 6.96 (d,  $J = 8.4$  Hz, 4H), 7.45-7.49 (m, 6H), 7.62 (s, 2H), 8.09 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 19.7, 23.8, 27.0, 55.4, 63.9, 83.8, 118.5, 120.3, 125.4, 127.4, 128.4, 133.7, 133.8, 136.4, 144.6, 157.7, 173.8; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{38}\text{H}_{36}\text{N}_6\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ :

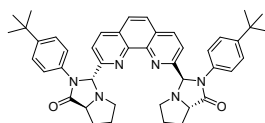
631.2792; Found: 631.2783.



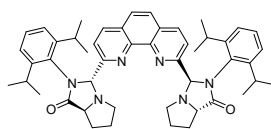
**L1b:** Yellow solid, yield 73%, >20:1 dr;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 1.02-1.05 (m, 6H), 1.83-1.89 (m, 4H), 2.16-2.22 (m, 4H), 2.40-2.46 (m, 4H), 3.04-3.10 (m, 2H), 3.47-3.52 (m, 2H), 4.19-4.23 (m, 2H), 6.14 (s, 2H), 6.99 (d,  $J = 8.8$  Hz, 4H), 7.47-7.50 (m, 6H), 7.60 (s, 2H), 8.08 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 15.4, 24.9, 28.1, 28.2, 56.5, 65.0, 85.0, 119.6, 121.5, 126.5, 128.4, 128.5, 135.0, 137.6, 141.3, 145.7, 158.9, 175.0; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{40}\text{H}_{40}\text{N}_6\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 659.3105; Found: 659.3099.



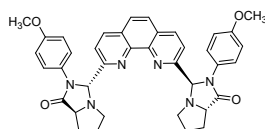
**L1c:** Yellow solid, yield 73%, >20:1 dr;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 1.12-1.14 (m, 12H), 1.90-1.96 (m, 4H), 2.24-2.30 (m, 4H), 2.74-2.81 (m, 2H), 3.12-3.18 (m, 2H), 3.55-3.60 (m, 2H), 4.28-4.32 (m, 2H), 6.22 (s, 2H), 7.11 (d,  $J = 8.4$  Hz, 4H), 7.55-7.60 (m, 6H), 7.65 (s, 2H), 8.14 (d,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 23.9, 24.9, 28.1, 33.5, 56.5, 65.0, 85.0, 119.6, 121.4, 126.5, 127.0, 128.5, 135.1, 137.6, 145.7, 145.8, 158.9, 175.0; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{42}\text{H}_{44}\text{N}_6\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 687.3418; Found: 687.3423.



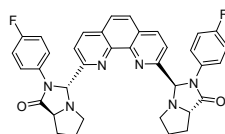
**L1d:** Yellow solid, yield 72%, >20:1 dr;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 1.13 (s, 18H), 1.84-1.90 (m, 4H), 2.17-2.23 (m, 4H), 3.06-3.12 (m, 2H), 3.51-3.57 (m, 2H), 4.18-4.21 (m, 2H), 6.17 (s, 2H), 7.18-7.21 (m, 4H), 7.47-7.52 (m, 6H), 7.61 (s, 2H), 8.09 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 23.9, 27.1, 30.2, 33.3, 55.5, 63.9, 83.8, 118.5, 119.8, 124.9, 125.5, 127.5, 133.8, 136.6, 144.7, 147.0, 157.9, 174.0; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{44}\text{H}_{48}\text{N}_6\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 715.3731; Found: 715.3722.



**L1e:** Yellow solid, yield 67%, >20:1 dr;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.83 (s, 3H), 0.85 (s, 3H), 1.16-1.19 (m, 12H), 1.48 (s, 3H), 1.49 (s, 3H), 1.89-1.94 (m, 4H), 2.18-2.26 (m, 4H), 2.28-2.36 (m, 2H), 3.08-3.14 (m, 4H), 3.39-3.44 (m, 2H), 4.49-4.53 (m, 2H), 5.58 (s, 2H), 6.74-6.76 (m, 2H), 7.16-7.19 (m, 4H), 7.38 (d,  $J = 8.4$  Hz, 2H), 7.63 (s, 2H), 8.03 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 22.4, 23.3, 24.9, 25.3, 25.6, 28.4, 28.9, 29.0, 57.3, 65.2, 88.0, 122.2, 123.8, 124.2, 126.5, 128.5, 129.3, 129.8, 136.5, 145.5, 146.4, 148.1, 158.6, 175.1; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{48}\text{H}_{56}\text{N}_6\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 771.4357; Found: 771.4348.

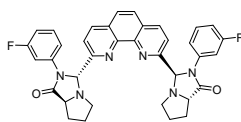


**L1f:** Yellow solid, yield 75%, >20:1 dr;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 1.84-1.88 (m, 4H), 2.17-2.22 (m, 4H), 3.06-3.12 (m, 2H), 3.46-3.51 (m, 2H), 3.59 (s, 6H), 4.22-4.25 (m, 2H), 6.08 (s, 2H), 6.68 (d,  $J = 9.2$  Hz, 4H), 7.42-7.49 (m, 6H), 7.64 (s, 2H), 8.11 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 22.9, 26.2, 53.3, 54.5, 63.0, 83.4, 112.2, 117.8, 121.6, 124.5, 126.5, 128.2, 135.6, 143.6, 155.1, 156.9, 172.7; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{38}\text{H}_{36}\text{N}_6\text{NaO}_4$   $[\text{M}+\text{Na}]^+$ : 663.2690; Found: 663.2681.

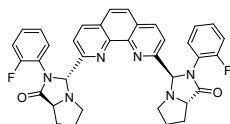


**L1g:** Yellow solid, yield 75%, >20:1 dr;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 1.85-1.91 (m, 4H), 2.17-2.24 (m, 4H), 3.03-3.09 (m, 2H), 3.45-3.50 (m, 2H), 4.25-4.29 (m, 2H), 6.07 (s, 2H), 6.82-6.86 (m, 4H), 7.48-7.54 (m, 6H), 7.65 (s, 2H), 8.13 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 23.9, 27.1, 55.5, 63.9, 84.2, 114.7 (d,  $J_{CF} = 22.3$  Hz), 118.8, 122.6 (d,  $J_{CF} = 7.3$  Hz), 125.6, 127.6, 132.3 (d,  $J_{CF} = 3.2$  Hz), 136.6, 144.6, 157.5, 159.8 (d,  $J_{CF} = 244.2$  Hz), 174.0; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{36}\text{H}_{30}\text{F}_2\text{N}_6\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 639.2291; Found: 639.2287.

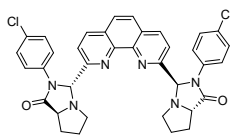




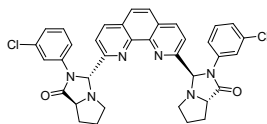
**L1h:** Yellow solid, yield 70%, >20:1 dr;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 1.82-1.89 (m, 4H), 2.17-2.22 (m, 4H), 3.02-3.08 (m, 2H), 3.49-3.54 (m, 2H), 4.19-4.22 (m, 2H), 6.14 (s, 2H), 6.65-6.70 (m, 2H), 7.05-7.11 (m, 2H), 7.19-7.21 (m, 2H), 7.47 (d,  $J = 8.0$  Hz, 2H), 7.64 (s, 2H), 7.69-7.73 (m, 2H), 8.13 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 22.9, 26.0, 54.5, 62.9, 82.6, 106.7 (d,  $J_{CF} = 26.3$  Hz), 109.8 (d,  $J_{CF} = 22.2$  Hz), 114.2 (d,  $J_{CF} = 3.4$  Hz), 117.6, 124.6, 126.6, 128.1 (d,  $J_{CF} = 10.2$  Hz), 135.7, 137.1, 137.2, 143.7, 156.3, 161.8 (d,  $J_{CF} = 244.1$  Hz), 173.4; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{36}\text{H}_{30}\text{F}_2\text{N}_6\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 639.2291; Found: 639.2297.



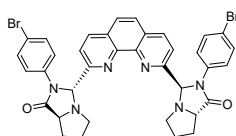
**L1i:** Yellow solid, yield 70%, >20:1 dr;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 1.83-1.96 (m, 4H), 2.16-2.30 (m, 4H), 3.14-3.20 (m, 2H), 3.41-3.46 (m, 2H), 4.39-4.42 (m, 2H), 5.96 (s, 2H), 6.82-6.86 (m, 2H), 6.96-7.07 (m, 4H), 7.30-7.34 (m, 2H), 7.56-7.61 (m, 4H), 8.09 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 25.0, 28.1, 56.5, 64.3, 85.6, 116.4 (d,  $J_{CF} = 20.3$  Hz), 120.5, 124.0 (d,  $J_{CF} = 11.2$  Hz), 124.5, 126.5, 128.5, 128.8 (d,  $J_{CF} = 8.2$  Hz), 129.8, 137.2, 145.7, 158.5, 158.7 (d,  $J_{CF} = 249.0$  Hz), 175.5; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{36}\text{H}_{30}\text{F}_2\text{N}_6\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 639.2291; Found: 639.2285.



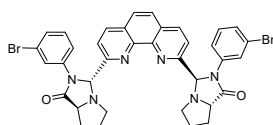
**L1j:** Yellow solid, yield 71%, >20:1 dr;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 1.83-1.91 (m, 4H), 2.18-2.23 (m, 4H), 3.02-3.08 (m, 2H), 3.47-3.52 (m, 2H), 4.22-4.25 (m, 2H), 6.11 (s, 2H), 7.10-7.14 (m, 4H), 7.48 (d,  $J = 8.4$  Hz, 2H), 7.54-7.58 (m, 4H), 7.66 (s, 2H), 8.13 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 23.0, 26.3, 54.7, 63.1, 82.9, 117.8, 120.5, 124.8, 126.7, 127.2, 128.4, 134.2, 135.9, 143.8, 156.5, 173.3; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{N}_6\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 671.1700; Found: 671.1708.



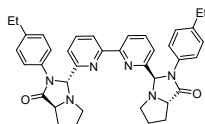
**L1k:** Yellow solid, yield 74%, >20:1 dr;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 1.84-1.90 (m, 4H), 2.18-2.23 (m, 4H), 3.02-3.08 (m, 2H), 3.49-3.54 (m, 2H), 4.21-4.25 (m, 2H), 6.12 (s, 2H), 6.93-6.96 (m, 2H), 7.03-7.07 (m, 2H), 7.30-7.33 (m, 2H), 7.48 (d,  $J = 8.4$  Hz, 2H), 7.65 (s, 2H), 7.90-7.91 (m, 2H), 8.12 (d,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 23.9, 27.0, 55.5, 63.9, 83.6, 117.9, 118.6, 120.3, 124.1, 125.6, 127.5, 128.9, 133.6, 136.6, 137.7, 144.7, 157.2, 174.4; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{N}_6\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 671.1700; Found: 671.1709.



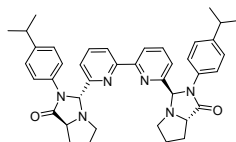
**L1l:** Yellow solid, yield 73%, >20:1 dr;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 1.86-1.92 (m, 4H), 2.18-2.24 (m, 4H), 3.03-3.09 (m, 2H), 3.48-3.53 (m, 2H), 4.22-4.26 (m, 2H), 6.11 (s, 2H), 7.25-7.29 (m, 4H), 7.48-7.54 (m, 6H), 7.66 (s, 2H), 8.14 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 24.9, 28.2, 56.6, 65.0, 84.7, 118.1, 119.7, 122.7, 126.7, 128.6, 132.0, 136.6, 137.7, 145.7, 158.3, 175.2; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{36}\text{H}_{30}\text{Br}_2\text{N}_6\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 759.0689; Found: 759.0694.



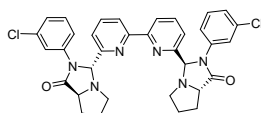
**L1m:** Yellow solid, yield 70%, >20:1 dr;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 1.85-1.91 (m, 4H), 2.18-2.23 (m, 4H), 3.02-3.08 (m, 2H), 3.48-3.53 (m, 2H), 4.23-4.26 (m, 2H), 6.11 (s, 2H), 6.97-7.01 (m, 2H), 7.09-7.12 (m, 2H), 7.34-7.37 (m, 2H), 7.48 (d,  $J = 8.4$  Hz, 2H), 7.65 (s, 2H), 8.05-8.06 (m, 2H), 8.13 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 23.2, 26.4, 54.8, 63.2, 82.9, 117.7, 118.0, 121.0, 122.4, 124.9, 126.3, 126.9, 128.5, 136.0, 137.2, 144.1, 156.5, 173.7; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{36}\text{H}_{30}\text{Br}_2\text{N}_6\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 759.0689; Found: 759.0695.



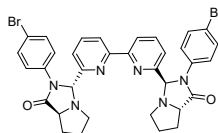
**L1n**: Light yellow solid, yield 71%, >20:1 dr; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 1.05-1.09 (m, 6H), 1.81-1.87 (m, 4H), 2.13-2.19 (m, 4H), 2.44-2.49 (m, 4H), 2.87-2.93 (m, 2H), 3.39-3.44 (m, 2H), 4.18-4.21 (m, 2H), 5.66 (s, 2H), 7.00 (d, *J* = 8.8 Hz, 4H), 7.19-7.27 (m, 6H), 7.67-7.71 (m, 2H), 8.20-8.22 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ: 15.5, 24.9, 27.7, 28.3, 56.4, 64.8, 84.6, 120.9, 121.0, 121.8, 128.4, 128.9, 135.1, 138.3, 141.4, 155.7, 157.2, 175.3; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>38</sub>H<sub>40</sub>N<sub>6</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 635.3105; Found: 635.3112.



**L1o**: Light yellow solid, yield 70%, >20:1 dr; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 1.07 (s, 6H), 1.08 (s, 6H), 1.80-1.86 (m, 4H), 2.12-2.18 (m, 4H), 2.69-2.76 (m, 2H), 2.86-2.92 (m, 2H), 3.38-3.43 (m, 2H), 4.17-4.21 (m, 2H), 5.66 (s, 2H), 7.02 (d, *J* = 8.4 Hz, 4H), 7.20-7.28 (m, 6H), 7.67-7.71 (m, 2H), 8.20 (d, *J* = 7.6 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ: 23.9, 24.9, 27.7, 33.6, 56.4, 64.8, 84.6, 120.9, 121.0, 121.8, 127.0, 135.2, 138.3, 146.0, 155.7, 157.3, 175.3; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>40</sub>H<sub>44</sub>N<sub>6</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 663.3418; Found: 663.3405.

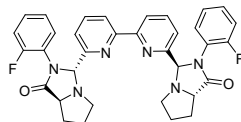


**L1p**: Light yellow solid, yield 67%, >20:1 dr; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 1.81-1.86 (m, 4H), 2.13-2.19 (m, 4H), 2.84-2.90 (m, 2H), 3.39-3.44 (m, 2H), 4.14-4.17 (m, 2H), 5.71 (s, 2H), 6.95-6.98 (m, 2H), 7.05-7.09 (m, 2H), 7.19-7.27 (m, 4H), 7.61-7.62 (m, 2H), 7.71-7.75 (m, 2H), 8.16 (d, *J* = 7.6 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ: 23.9, 26.7, 55.3, 63.8, 83.0, 117.9, 119.9, 120.1, 120.3, 124.0, 128.9, 133.6, 137.5, 137.9, 154.5, 155.6, 174.6; HRMS (ESI-TOF) *m/z*: Calcd. for C<sub>34</sub>H<sub>30</sub>Cl<sub>2</sub>N<sub>6</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 647.1700; Found: 647.1691.

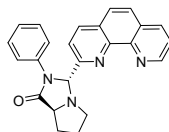


**L1q**: Light yellow solid, yield 68%, >20:1 dr; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 1.81-1.85 (m, 4H), 2.12-2.18 (m, 4H), 2.85-2.91 (m, 2H), 3.39-3.44 (m, 2H), 4.13-4.16 (m, 2H), 5.68 (s, 2H), 7.19-

7.32 (m, 10H), 7.69-7.73 (m, 2H), 8.12 (d,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 23.0, 25.8, 54.4, 62.9, 82.2, 116.2, 119.0, 119.2, 120.9, 130.1, 134.9, 136.6, 153.6, 154.8, 173.6; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{34}\text{H}_{30}\text{Br}_2\text{N}_6\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 735.0689; Found: 735.0685.

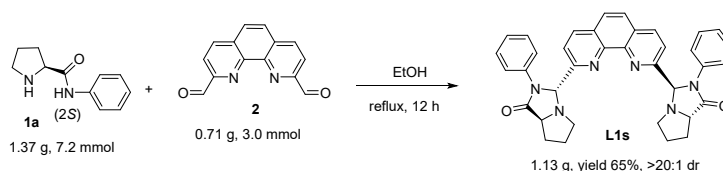


**L1r**: Light yellow solid, yield 63%, >20:1 dr;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 1.75-1.81 (m, 2H), 1.87-1.92 (m, 2H), 2.01-2.08 (m, 2H), 2.14-2.20 (m, 2H), 3.02-3.08 (m, 2H), 3.34-3.39 (m, 2H), 4.27-4.30 (m, 2H), 5.79 (s, 2H), 6.91-6.95 (m, 2H), 7.03-7.08 (m, 4H), 7.13-7.18 (m, 2H), 7.34-7.36 (m, 2H), 7.73-7.77 (m, 2H), 8.07-8.09 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 24.4, 27.4, 55.9, 64.3, 84.7, 116.0 (d,  $J_{\text{CF}} = 20.3$  Hz), 120.4, 122.0, 123.7 (d,  $J_{\text{CF}} = 12.0$  Hz), 124.3, 128.9, 129.2 (d,  $J_{\text{CF}} = 8.1$  Hz), 138.2, 155.3, 156.9, 157.8 (d,  $J_{\text{CF}} = 257.0$  Hz), 176.1; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{34}\text{H}_{30}\text{F}_2\text{N}_6\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 615.2292; Found: 615.2299.



**L5a**: Light yellow solid, yield 65%, >20:1 dr;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 400 MHz)  $\delta$ : 1.72-1.85 (m, 2H), 2.07-2.14 (m, 2H), 3.10-3.16 (m, 1H), 3.27-3.33 (m, 1H), 4.19-4.23 (m, 1H), 6.24 (s, 1H), 6.88-6.92 (m, 1H), 7.09-7.13 (m, 2H), 7.50-7.59 (m, 6H), 8.11-8.16 (m, 2H), 8.94-8.95 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 100 MHz)  $\delta$ : 24.3, 28.2, 56.2, 65.0, 85.4, 119.8, 122.2, 123.3, 125.6, 126.0, 126.7, 128.3, 128.6, 129.1, 136.6, 136.7, 137.8, 144.5, 145.0, 149.6, 158.8, 174.8; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{24}\text{H}_{20}\text{N}_4\text{NaO}$   $[\text{M}+\text{Na}]^+$ : 403.1529; Found: 403.1534.

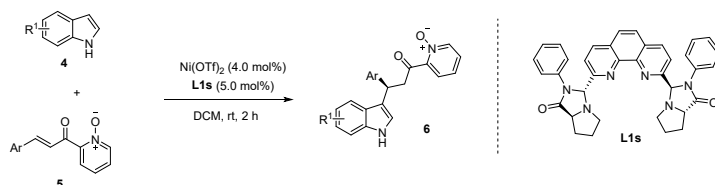
#### 4. The gram scale synthesis of the Phen-BPI ligand L1s



In a sealed tube equipped with a magnetic stirring bar, phenanthroline-dicarbaldehyde **2** (0.71 g, 3.0 mmol) and optically pure prolinamide **1a** (1.37 g, 7.2 mmol) were added. Then, anhydrous ethanol (30.0 mL) was added and the reaction was heated with stirring at reflux for 12 h. After

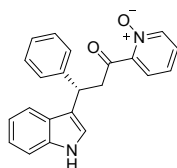
completion of the reaction, as indicated by TLC, the aftertreatment residue was purified by flash column chromatography to give the Phen-BPI ligand **L1s** (1.13 g, yield 65%, >20:1 dr).

## 5. Catalytic asymmetric synthesis of compounds **6**

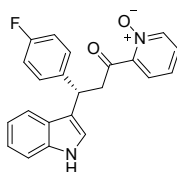


In a sealed tube equipped with a magnetic stirring bar, to the mixture of Ni(OTf)<sub>2</sub> (4.0 mol %), **L1s** (5.0 mol %) in 1.5 mL of DCM was added **4** (0.30 mmol), and **5** (0.20 mmol). The reaction mixture was stirred at room temperature for 2 h and was directly loaded onto a silica gel and purified by flash chromatography to give the desired product **6**, using hexane/EtOAc (8/1, v/v) as the eluent.

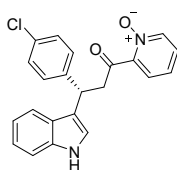
## 6. Characterization data of compounds **6**



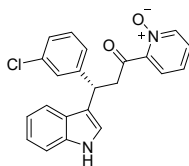
**6aa**: Product in accordance with literature characterization data<sup>8</sup>. 91%, 95% ee,  $[\alpha]_D^{20} = -16.4$  (*c* 0.50, CHCl<sub>3</sub>). The ee was determined by HPLC analysis using a Chiralpak IC column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{major} = 15.65$  min;  $\tau_{minor} = 19.01$  min). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 3.85-3.91 (m, 1H), 3.97-4.03 (m, 1H), 4.83-4.87 (m, 1H), 6.87-6.91 (m, 1H), 6.95-7.06 (m, 5H), 7.10-7.14 (m, 3H), 7.17-7.23 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 6.8 Hz, 1H), 8.20 (br s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 37.5, 48.0, 110.1, 117.6, 118.3, 118.4, 120.6, 121.0, 124.7, 125.3, 125.4, 125.6, 126.5, 126.9, 127.3, 135.5, 139.0, 142.8, 146.0, 196.1.



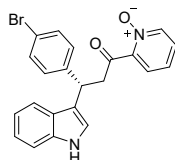
**6ab**: Product in accordance with literature characterization data<sup>8</sup>. 92%, 93% ee,  $[\alpha]_{\text{D}}^{20} = -8.2$  (*c* 0.50, CHCl<sub>3</sub>). The ee was determined by HPLC analysis using a Chiralpak IC column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 12.66$  min;  $\tau_{\text{minor}} = 14.84$  min). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$ : 3.79-3.85 (m, 1H), 3.99-4.05 (m, 1H), 4.81-4.85 (m, 1H), 6.87-6.91 (m, 1H), 7.02-7.06 (m, 3H), 7.22-7.24 (m, 1H), 7.30-7.38 (m, 6H), 7.49-7.53 (m, 1H), 8.32 (d,  $J = 6.4$  Hz, 1H), 10.91 (br s, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz)  $\delta$ : 37.4, 48.6, 111.9, 115.3 (d,  $J_{\text{CF}} = 21.2$  Hz), 117.7, 118.9 (d,  $J_{\text{CF}} = 23.3$  Hz), 121.6, 122.6, 126.3, 126.5 (d,  $J_{\text{CF}} = 8.2$  Hz), 126.7, 128.9, 129.8 (d,  $J_{\text{CF}} = 8.1$  Hz), 136.9, 140.6, 141.2, 141.3, 146.8, 161.2 (d,  $J_{\text{CF}} = 240.3$  Hz), 197.6.



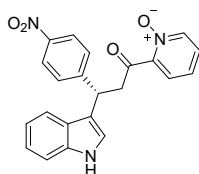
**6ac**: Product in accordance with literature characterization data<sup>8</sup>. 93%, 99% ee,  $[\alpha]_{\text{D}}^{20} = -18.2$  (*c* 0.50, CHCl<sub>3</sub>). The ee was determined by HPLC analysis using a Chiralpak IA column (70/30 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 14.69$  min;  $\tau_{\text{minor}} = 13.44$  min). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$ : 3.79-3.85 (m, 1H), 3.98-4.04 (m, 1H), 4.80-4.83 (m, 1H), 6.87-6.90 (m, 1H), 7.01-7.05 (m, 1H), 7.26-7.36 (m, 9H), 7.46-7.52 (m, 1H), 8.32 (d,  $J = 6.0$  Hz, 1H), 10.91 (br s, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz)  $\delta$ : 37.5, 48.3, 111.9, 117.3, 118.9, 119.0, 121.6, 122.7, 126.3, 126.4, 126.6, 128.6, 128.9, 130.0, 131.0, 136.9, 140.6, 144.1, 146.7, 197.5.



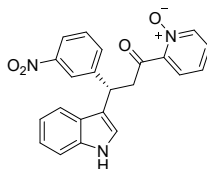
**6ad**: Product in accordance with literature characterization data<sup>8</sup>. 91%, 90% ee,  $[\alpha]_{\text{D}}^{20} = -1.3$  (*c* 0.50, CHCl<sub>3</sub>). The ee was determined by HPLC analysis using a Chiralpak IC column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 11.24$  min;  $\tau_{\text{minor}} = 15.82$  min). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 3.84-3.91 (m, 1H), 3.97-4.06 (m, 1H), 4.84-4.88 (m, 1H), 6.90-6.94 (m, 1H), 7.02-7.09 (m, 5H), 7.14-7.23 (m, 5H), 7.32 (d,  $J = 8.0$  Hz, 1H), 8.07 (d,  $J = 6.4$  Hz, 1H), 8.10 (br s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 37.0, 47.9, 110.1, 117.0, 118.2, 118.5, 120.6, 121.2, 124.8, 125.2, 125.5, 125.6, 125.7, 126.7, 127.0, 128.6, 133.1, 135.5, 139.2, 145.1, 145.8, 195.4.



**6ae:** Product in accordance with literature characterization data<sup>8</sup>. 90%, 94% ee,  $[\alpha]_{\text{D}}^{20} = -17.1$  (*c* 0.50,  $\text{CHCl}_3$ ). The ee was determined by HPLC analysis using a Chiralpak IC column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 12.64$  min;  $\tau_{\text{minor}} = 15.32$  min). <sup>1</sup>H NMR ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 3.78-3.85 (m, 1H), 3.97-4.04 (m, 1H), 4.77-4.81 (m, 1H), 6.86-6.90 (m, 1H), 7.01-7.05 (m, 1H), 7.28-7.42 (m, 9H), 7.50-7.57 (m, 1H), 8.32 (d,  $J = 6.4$  Hz, 1H), 10.90 (br s, 1H); <sup>13</sup>C NMR ( $\text{DMSO-}d_6$ , 100 MHz)  $\delta$ : 37.5, 48.2, 111.9, 117.3, 118.9, 119.0, 119.4, 121.6, 122.7, 126.3, 126.4, 126.6, 128.9, 130.4, 131.5, 136.9, 140.6, 144.6, 146.7, 197.4.

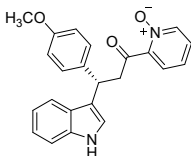


**6af:** Product in accordance with literature characterization data<sup>8</sup>. 88%, 93% ee,  $[\alpha]_{\text{D}}^{20} = -20.3$  (*c* 0.50,  $\text{CHCl}_3$ ). The ee was determined by HPLC analysis using a Chiralpak IC column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 22.05$  min;  $\tau_{\text{minor}} = 29.97$  min). <sup>1</sup>H NMR ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 3.91-3.98 (m, 1H), 4.05-4.11 (m, 1H), 4.97-5.00 (m, 1H), 6.88-6.91 (m, 1H), 7.02-7.06 (m, 1H), 7.32-7.40 (m, 5H), 7.52-7.55 (m, 1H), 7.64 (d,  $J = 8.4$  Hz, 2H), 8.09 (d,  $J = 8.4$  Hz, 2H), 8.32 (d,  $J = 6.4$  Hz, 1H), 10.99 (br s, 1H); <sup>13</sup>C NMR ( $\text{DMSO-}d_6$ , 100 MHz)  $\delta$ : 37.8, 47.9, 112.0, 116.6, 118.9, 119.0, 121.7, 123.0, 123.9, 126.4, 126.5, 126.6, 129.0, 129.4, 136.9, 140.6, 146.3, 146.6, 153.3, 197.0.

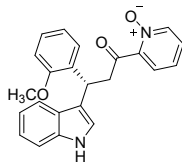


**6ag:** Product in accordance with literature characterization data<sup>8</sup>. 89%, 93% ee,  $[\alpha]_{\text{D}}^{20} = +3.0$  (*c* 0.50,  $\text{CHCl}_3$ ). The ee was determined by HPLC analysis using a Chiralpak IC column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 18.06$  min;  $\tau_{\text{minor}} = 26.36$  min). <sup>1</sup>H NMR ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 3.90-3.97 (m, 1H), 3.99-4.05 (m, 1H), 4.97-5.01 (m, 1H), 6.85-

6.89 (m, 1H), 7.00-7.03 (m, 1H), 7.28-7.34 (m, 3H), 7.37-7.39 (m, 2H), 7.48-7.52 (m, 2H), 7.84 (d,  $J = 7.6$  Hz, 1H), 7.97-7.99 (m, 1H), 8.16 (s, 1H), 8.29 (d,  $J = 6.4$  Hz, 1H), 10.96 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 37.6, 48.0, 112.0, 116.8, 118.9, 119.0, 121.6, 121.7, 122.7, 123.0, 126.3, 126.4, 126.5, 129.0, 130.1, 135.1, 136.9, 140.6, 146.6, 147.5, 148.2, 197.2.

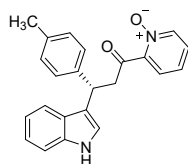


**6ah:** Product in accordance with literature characterization data<sup>8</sup>. 87%, 90% ee,  $[\alpha]_{\text{D}}^{20} = -12.2$  ( $c$  0.50,  $\text{CHCl}_3$ ). The ee was determined by HPLC analysis using a Chiralpak IA column (70/30 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 16.42$  min;  $\tau_{\text{minor}} = 14.71$  min).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 3.66 (s, 3H), 3.74-3.80 (m, 1H), 3.97-4.03 (m, 1H), 4.73-4.77 (m, 1H), 6.77 (d,  $J = 8.4$  Hz, 2H), 6.86-6.90 (m, 1H), 7.01-7.04 (m, 1H), 7.16-7.37 (m, 7H), 7.46-7.50 (m, 1H), 8.31 (d,  $J = 6.4$  Hz, 1H), 10.86 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 37.5, 48.8, 55.4, 111.8, 114.0, 118.1, 118.7, 119.2, 121.5, 122.4, 126.2, 126.3, 126.8, 128.8, 129.0, 136.9, 137.0, 140.5, 146.9, 157.9, 197.9.

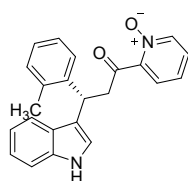


**6ai:** Product in accordance with literature characterization data<sup>8</sup>. 85%, 90% ee,  $[\alpha]_{\text{D}}^{20} = -20.3$  ( $c$  0.50,  $\text{CHCl}_3$ ). The ee was determined by HPLC analysis using a Chiralpak IE column (70/30 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 14.64$  min;  $\tau_{\text{minor}} = 15.77$  min).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 3.54-3.60 (m, 1H), 3.71 (s, 3H), 3.99-4.07 (m, 1H), 5.19-5.23 (m, 1H), 6.73-6.77 (m, 1H), 6.84-6.89 (m, 2H), 6.97-7.01 (m, 1H), 7.07-7.11 (m, 3H), 7.18 (s, 1H), 7.26-7.29 (m, 2H), 7.33 (d,  $J = 8.0$  Hz, 1H), 7.46-7.50 (m, 1H), 8.29 (d,  $J = 6.4$  Hz, 1H), 10.79 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 30.4, 47.8, 55.9, 111.2, 111.8, 117.5, 118.7, 119.1, 120.7, 121.5, 122.9, 126.2, 126.3, 127.0, 127.7, 128.7, 128.8, 132.5, 136.8, 140.5, 146.9, 156.6, 198.0.

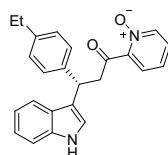




**6aj**: Product in accordance with literature characterization data<sup>8</sup>. 90%, 93% ee,  $[\alpha]_{\text{D}}^{20} = -4.1$  ( $c$  0.50,  $\text{CHCl}_3$ ). The ee was determined by HPLC analysis using a Chiralpak IA column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 12.39$  min;  $\tau_{\text{minor}} = 10.97$  min).  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 2.21 (s, 3H), 3.73-3.80 (m, 1H), 3.97-4.03 (m, 1H), 4.72-4.76 (m, 1H), 6.85-6.89 (m, 1H), 7.00-7.03 (m, 3H), 7.16-7.20 (m, 3H), 7.25-7.36 (m, 4H), 7.49-7.53 (m, 1H), 8.31 (d,  $J = 6.4$  Hz, 1H), 10.85 (br s, 1H);  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 100 MHz)  $\delta$ : 21.0, 37.8, 48.6, 111.8, 117.9, 118.7, 119.1, 121.5, 122.5, 126.2, 126.3, 126.7, 127.9, 128.8, 129.2, 135.4, 136.9, 140.5, 142.0, 146.8, 197.8.

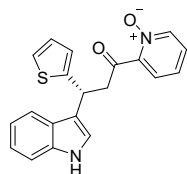


**6ak**: 87%, 90% ee. The ee was determined by HPLC analysis using a Chiralpak IC column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 12.05$  min;  $\tau_{\text{minor}} = 15.18$  min).  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 2.37 (s, 3H), 3.70-3.76 (m, 1H), 3.96-4.02 (m, 1H), 5.01-5.04 (m, 1H), 6.88-6.91 (m, 1H), 7.02-7.05 (m, 3H), 7.11-7.16 (m, 3H), 7.21-7.23 (m, 1H), 7.26-7.34 (m, 3H), 7.47-7.51 (m, 1H), 8.33 (d,  $J = 6.4$  Hz, 1H), 10.87 (br s, 1H);  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 100 MHz)  $\delta$ : 19.6, 33.8, 48.3, 111.9, 117.3, 118.8, 118.9, 121.5, 123.3, 126.3, 126.4, 126.5, 126.8, 127.4, 128.9, 130.7, 135.5, 136.9, 140.5, 142.7, 146.8, 197.9; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{23}\text{H}_{20}\text{N}_2\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 379.1417; Found: 379.1414.

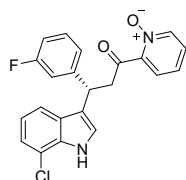


**6al**: 89%, 93% ee. The ee was determined by HPLC analysis using a Chiralpak IA column (70/30 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 11.86$  min;  $\tau_{\text{minor}} = 10.33$  min).  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 1.09-1.13 (m, 3H), 2.47-2.53 (m, 2H), 3.75-3.81 (m, 1H), 3.95-

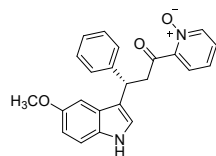
4.02 (m, 1H), 4.73-4.77 (m, 1H), 6.85-6.89 (m, 1H), 7.00-7.05 (m, 3H), 7.14-7.16 (m, 1H), 7.21 (d,  $J = 8.0$  Hz, 2H), 7.26-7.31 (m, 3H), 7.35 (d,  $J = 8.0$  Hz, 1H), 7.47-7.51 (m, 1H), 8.30 (d,  $J = 6.4$  Hz, 1H), 10.85 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 16.0, 28.2, 37.9, 48.6, 111.8, 117.9, 118.7, 119.1, 121.5, 122.4, 126.2, 126.3, 126.8, 128.0, 128.1, 128.8, 136.9, 140.5, 141.8, 142.3, 146.9, 197.9; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{24}\text{H}_{22}\text{N}_2\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 393.1573; Found: 393.1573.



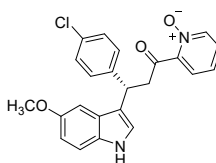
**6am**: Product in accordance with literature characterization data<sup>8</sup>. 90%, 93% ee,  $[\alpha]_{\text{D}}^{20} = -19.6$  ( $c$  0.50,  $\text{CHCl}_3$ ). The ee was determined by HPLC analysis using a Chiralpak IC column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 18.48$  min;  $\tau_{\text{minor}} = 23.41$  min).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 3.89-3.95 (m, 1H), 4.03-4.09 (m, 1H), 5.11-5.14 (m, 1H), 6.87-7.07 (m, 4H), 7.22-7.35 (m, 5H), 7.43-7.51 (m, 2H), 8.31 (d,  $J = 6.4$  Hz, 1H), 10.92 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 33.5, 49.5, 112.0, 117.6, 118.9, 119.1, 121.6, 122.7, 124.3, 124.4, 126.3, 126.5, 127.0, 129.0, 136.9, 140.6, 146.6, 149.5, 197.1.



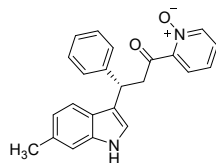
**6ba**: 87%, 94% ee. The ee was determined by HPLC analysis using a Chiralpak IC column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 11.98$  min;  $\tau_{\text{minor}} = 9.26$  min).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 3.83-3.89 (m, 1H), 4.03-4.10 (m, 1H), 4.84-4.88 (m, 1H), 6.90-6.98 (m, 2H), 7.12-7.45 (m, 8H), 7.52-7.56 (m, 1H), 8.33 (d,  $J = 6.4$  Hz, 1H), 11.31 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 37.6, 48.1, 113.4 (d,  $J_{\text{CF}} = 21.3$  Hz), 114.8 (d,  $J_{\text{CF}} = 21.4$  Hz), 116.3, 118.2, 118.7, 120.0, 121.1, 124.2 (d,  $J_{\text{CF}} = 9.1$  Hz), 126.3 (d,  $J_{\text{CF}} = 4.4$  Hz), 128.7, 129.0, 130.5 (d,  $J_{\text{CF}} = 8.3$  Hz), 133.6, 140.6, 146.7 (d,  $J_{\text{CF}} = 7.0$  Hz), 147.9, 162.6 (d,  $J_{\text{CF}} = 242.3$  Hz), 197.3; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{22}\text{H}_{16}\text{ClFN}_2\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 417.0777; Found: 417.0782.



**6ca:** Product in accordance with literature characterization data<sup>8</sup>. 92%, 90% ee,  $[\alpha]_{\text{D}}^{20} = -24.4$  ( $c$  0.50,  $\text{CHCl}_3$ ). The ee was determined by HPLC analysis using a Chiralpak IC column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 9.48$  min;  $\tau_{\text{minor}} = 8.43$  min).  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 3.68 (s, 3H), 3.78-3.84 (m, 1H), 4.02-4.08 (m, 1H), 4.75-4.79 (m, 1H), 6.69-6.72 (m, 1H), 6.86 (d,  $J = 2.0$  Hz, 1H), 7.12-7.18 (m, 2H), 7.22-7.31 (m, 5H), 7.35 (d,  $J = 7.6$  Hz, 2H), 7.47-7.51 (m, 1H), 8.32 (d,  $J = 6.8$  Hz, 1H), 10.73 (br s, 1H);  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 100 MHz)  $\delta$ : 38.3, 48.5, 55.8, 101.2, 111.4, 112.5, 117.5, 123.3, 126.2, 126.3, 126.5, 127.1, 128.1, 128.6, 128.8, 132.0, 140.5, 145.0, 146.9, 153.3, 197.9.

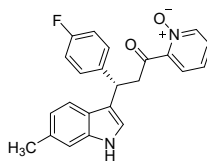


**6cb:** 93%, 92% ee. The ee was determined by HPLC analysis using a Chiralpak IA column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 11.31$  min;  $\tau_{\text{minor}} = 9.50$  min).  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 3.68 (s, 3H), 3.77-3.83 (m, 1H), 3.98-4.04 (m, 1H), 4.74-4.78 (m, 1H), 6.68-6.71 (m, 1H), 6.83 (s, 1H), 7.19-7.38 (m, 8H), 7.51-7.55 (m, 1H), 8.32 (d,  $J = 6.4$  Hz, 1H), 10.74 (br s, 1H);  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 100 MHz)  $\delta$ : 37.5, 48.2, 55.8, 101.1, 111.4, 112.5, 117.1, 123.3, 126.3, 126.4, 127.0, 128.5, 128.9, 130.0, 130.9, 132.0, 140.6, 144.0, 146.7, 153.4, 197.6; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{23}\text{H}_{19}\text{ClN}_2\text{NaO}_3$   $[\text{M}+\text{Na}]^+$ : 429.0976; Found: 429.0971.

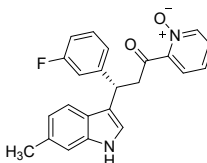


**6da:** 91%, 91% ee. The ee was determined by HPLC analysis using a Chiralpak IC column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{\text{major}} = 16.47$  min;  $\tau_{\text{minor}} = 18.91$  min).  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 2.31 (s, 3H), 3.83-3.89 (m, 1H), 3.94-4.00 (m, 1H), 4.80-4.84 (m, 1H), 6.74 (d,  $J = 8.0$  Hz, 1H), 6.91 (s, 1H), 6.99-7.07 (m, 5H), 7.12-7.20 (m, 5H), 8.05 (s, 1H), 8.07 (br s, 1H);  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 100 MHz)  $\delta$ : 21.8, 38.3, 48.6, 111.6, 117.6, 118.8, 120.5,

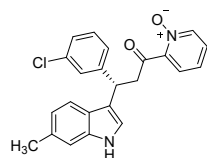
121.8, 124.7, 126.2, 126.3, 126.4, 128.1, 128.6, 128.8, 130.5, 137.3, 140.5, 145.1, 146.8, 197.8;  
HRMS (ESI-TOF)  $m/z$ : Calcd. for  $C_{23}H_{20}N_2NaO_2$   $[M+Na]^+$ : 379.1417; Found: 379.1418.



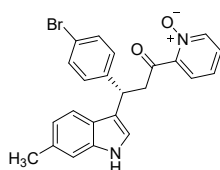
**6db**: 90%, 92% ee. The ee was determined by HPLC analysis using a Chiralpak IC column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda$  = 254 nm;  $\tau_{major}$  = 13.23 min;  $\tau_{minor}$  = 15.26 min).  $^1H$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 2.33 (s, 3H), 3.77-3.83 (m, 1H), 3.95-4.01 (m, 1H), 4.76-4.80 (m, 1H), 6.71 (d,  $J$  = 8.0 Hz, 1H), 7.01-7.05 (m, 2H), 7.10 (s, 1H), 7.18-7.23 (m, 3H), 7.30-7.35 (m, 3H), 7.49-7.53 (m, 1H), 8.31 (d,  $J$  = 6.4 Hz, 1H), 10.72 (br s, 1H);  $^{13}C$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 21.8, 37.5, 48.6, 111.7, 115.3 (d,  $J_{CF}$  = 21.3 Hz), 117.5, 118.8, 120.6, 121.8, 124.6, 126.3, 126.4, 128.9, 129.8 (d,  $J_{CF}$  = 8.1 Hz), 130.6, 137.4, 140.6, 141.2 (d,  $J_{CF}$  = 3.4 Hz), 146.8, 161.8 (d,  $J_{CF}$  = 240.3 Hz), 197.7; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $C_{23}H_{19}FN_2NaO_2$   $[M+Na]^+$ : 397.1323; Found: 397.1325.



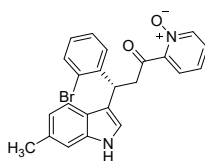
**6dc**: 92%, 90% ee. The ee was determined by HPLC analysis using a Chiralpak IC column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda$  = 254 nm;  $\tau_{major}$  = 11.24 min;  $\tau_{minor}$  = 15.17 min).  $^1H$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 2.33 (s, 3H), 3.80-3.86 (m, 1H), 3.95-4.01 (m, 1H), 4.77-4.81 (m, 1H), 6.73 (d,  $J$  = 8.0 Hz, 1H), 6.91-6.96 (m, 1H), 7.10-7.27 (m, 7H), 7.32-7.35 (m, 1H), 7.51-7.55 (m, 1H), 8.32 (d,  $J$  = 6.4 Hz, 1H), 10.73 (br s, 1H);  $^{13}C$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 21.8, 37.8, 48.2, 111.7, 113.2 (d,  $J_{CF}$  = 21.2 Hz), 114.7 (d,  $J_{CF}$  = 21.1 Hz), 117.0, 118.7, 120.6, 122.0, 124.2, 124.6, 126.3, 126.4, 128.9, 130.4 (d,  $J_{CF}$  = 8.4 Hz), 130.6, 137.3, 140.6, 146.8, 148.2 (d,  $J_{CF}$  = 7.3 Hz), 162.8 (d,  $J_{CF}$  = 242.0 Hz), 197.5; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $C_{23}H_{19}FN_2NaO_2$   $[M+Na]^+$ : 397.1323; Found: 397.1327.



**6dd**: 92%, 91% ee. The ee was determined by HPLC analysis using a Chiralpak IC column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{major} = 10.96$  min;  $\tau_{minor} = 14.59$  min).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 2.34 (s, 3H), 3.80-3.86 (m, 1H), 3.95-4.01 (m, 1H), 4.76-4.80 (m, 1H), 6.72 (d,  $J = 8.0$  Hz, 1H), 7.10 (s, 1H), 7.17-7.19 (m, 1H), 7.23-7.27 (m, 4H), 7.31-7.36 (m, 3H), 7.51-7.55 (m, 1H), 8.32 (d,  $J = 6.4$  Hz, 1H), 10.74 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 21.8, 37.8, 48.2, 111.7, 116.9, 118.7, 120.7, 122.0, 124.6, 126.3, 126.4, 126.5, 126.9, 127.9, 128.9, 130.5, 130.7, 133.3, 137.3, 140.6, 146.7, 147.8, 197.4; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{23}\text{H}_{19}\text{ClN}_2\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 413.1027; Found: 413.1026.

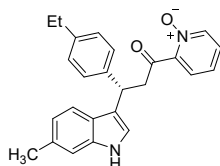


**6de**: 85%, 91% ee. The ee was determined by HPLC analysis using a Chiralpak IC column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{major} = 13.04$  min;  $\tau_{minor} = 15.64$  min).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 2.33 (s, 3H), 3.78-3.84 (m, 1H), 3.95-4.01 (m, 1H), 4.74-4.78 (m, 1H), 6.71 (d,  $J = 8.0$  Hz, 1H), 7.10 (s, 1H), 7.19-7.22 (m, 2H), 7.25-7.33 (m, 4H), 7.39-7.41 (m, 2H), 7.50-7.54 (m, 1H), 8.31 (d,  $J = 6.4$  Hz, 1H), 10.73 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 21.8, 37.6, 48.3, 111.7, 117.1, 118.7, 119.4, 120.6, 121.9, 124.6, 126.3, 126.4, 128.9, 130.4, 130.6, 131.4, 137.3, 140.6, 144.6, 146.7, 197.4; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{23}\text{H}_{19}\text{BrN}_2\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 457.0522; Found: 457.0524.

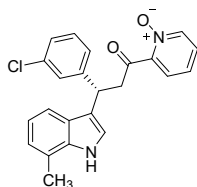


**6df**: 90%, 93% ee. The ee was determined by HPLC analysis using a Chiralpak IA column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{major} = 12.31$  min;  $\tau_{minor} = 9.76$  min).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 2.34 (s, 3H), 3.62-3.68 (m, 1H), 4.02-4.07 (m, 1H), 5.23-5.26 (m, 1H), 6.73 (d,  $J = 8.4$  Hz, 1H), 7.06-7.15 (m, 3H), 7.20-7.37 (m, 5H), 7.52-7.59 (m, 2H), 8.33 (d,  $J = 6.4$  Hz, 1H), 10.75 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 21.8, 37.2, 47.9, 111.8, 116.5, 118.7, 120.7, 122.6, 124.1, 124.7, 126.4, 126.5, 128.3, 128.6, 129.1, 129.9, 130.7, 133.0,

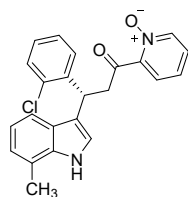
137.3, 140.7, 143.5, 146.6, 197.0; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $C_{23}H_{19}BrN_2NaO_2$   $[M+Na]^+$ : 457.0522; Found: 457.0525.



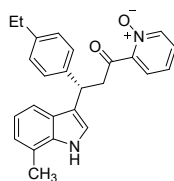
**6dg**: 88%, 91% ee. The ee was determined by HPLC analysis using a Chiralpak IA column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{major} = 10.01$  min;  $\tau_{minor} = 8.61$  min).  $^1H$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 1.06-1.10 (m, 3H), 2.30 (s, 3H), 2.44-2.50 (m, 2H), 3.71-3.77 (m, 1H), 3.90-3.96 (m, 1H), 4.66-4.70 (m, 1H), 6.66-6.68 (m, 1H), 7.00 (d,  $J = 8.0$  Hz, 2H), 7.06 (s, 1H), 7.10-7.12 (m, 2H), 7.16-7.20 (m, 3H), 7.23-7.27 (m, 1H), 7.44-7.48 (m, 1H), 8.27 (d,  $J = 6.0$  Hz, 1H), 10.66 (br s, 1H);  $^{13}C$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 16.1, 21.8, 28.2, 38.0, 48.6, 111.6, 117.8, 118.9, 120.5, 121.7, 124.7, 126.2, 126.3, 128.0, 128.1, 128.8, 130.5, 137.3, 140.5, 141.7, 142.3, 146.9, 197.9; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $C_{25}H_{24}N_2NaO_2$   $[M+Na]^+$ : 407.1730; Found: 407.1735.



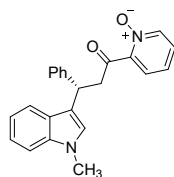
**6ea**: 91%, 93% ee. The ee was determined by HPLC analysis using a Chiralpak IC column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{major} = 11.73$  min;  $\tau_{minor} = 17.14$  min).  $^1H$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 2.42 (s, 3H), 3.83-3.89 (m, 1H), 4.00-4.06 (m, 1H), 4.80-4.84 (m, 1H), 6.79-6.84 (m, 2H), 7.16-7.28 (m, 4H), 7.32-7.37 (m, 4H), 7.50-7.54 (m, 1H), 8.33 (d,  $J = 6.4$  Hz, 1H), 10.89 (br s, 1H);  $^{13}C$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 17.2, 37.8, 48.2, 116.6, 117.5, 119.1, 121.0, 122.1, 122.5, 126.3, 126.4, 126.5, 126.6, 126.9, 128.0, 128.9, 130.5, 133.3, 136.3, 140.6, 146.7, 147.9, 197.4; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $C_{23}H_{19}ClN_2NaO_2$   $[M+Na]^+$ : 413.1027; Found: 413.1024.



**6eb**: 90%, 93% ee. The ee was determined by HPLC analysis using a Chiralpak IC column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{major} = 15.55$  min;  $\tau_{minor} = 18.83$  min).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 2.42 (s, 3H), 3.68-3.74 (m, 1H), 4.09-4.15 (m, 1H), 5.29-5.33 (m, 1H), 6.80-6.84 (m, 2H), 7.16-7.21 (m, 3H), 7.26-7.30 (m, 2H), 7.33-7.41 (m, 3H), 7.52-7.56 (m, 1H), 8.34 (d,  $J = 6.4$  Hz, 1H), 10.89 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 17.2, 34.3, 47.7, 116.4, 117.0, 119.2, 121.1, 122.1, 123.0, 126.3, 126.4, 126.5, 127.7, 128.3, 129.0, 129.7, 129.8, 132.9, 136.4, 140.7, 142.0, 146.6, 197.1; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{23}\text{H}_{19}\text{ClN}_2\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 413.1027; Found: 413.1023.



**6ec**: 88%, 91% ee. The ee was determined by HPLC analysis using a Chiralpak IA column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{major} = 8.53$  min;  $\tau_{minor} = 6.85$  min).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 1.09-1.13 (m, 3H), 2.41 (s, 3H), 2.47-2.53 (m, 2H), 3.75-3.81 (m, 1H), 3.95-4.01 (m, 1H), 4.71-4.75 (m, 1H), 6.76-6.82 (m, 2H), 7.03 (d,  $J = 8.0$  Hz, 2H), 7.14-7.31 (m, 6H), 7.47-7.51 (m, 1H), 8.31 (d,  $J = 6.4$  Hz, 1H), 10.81 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 16.1, 17.2, 28.2, 38.0, 48.6, 116.8, 118.4, 119.0, 120.9, 122.0, 122.1, 126.2, 126.3, 126.5, 128.0, 128.8, 136.4, 140.5, 141.7, 142.3, 146.9, 197.9; HRMS (ESI-TOF)  $m/z$ : Calcd. for  $\text{C}_{25}\text{H}_{24}\text{N}_2\text{NaO}_2$   $[\text{M}+\text{Na}]^+$ : 407.1730; Found: 407.1735.

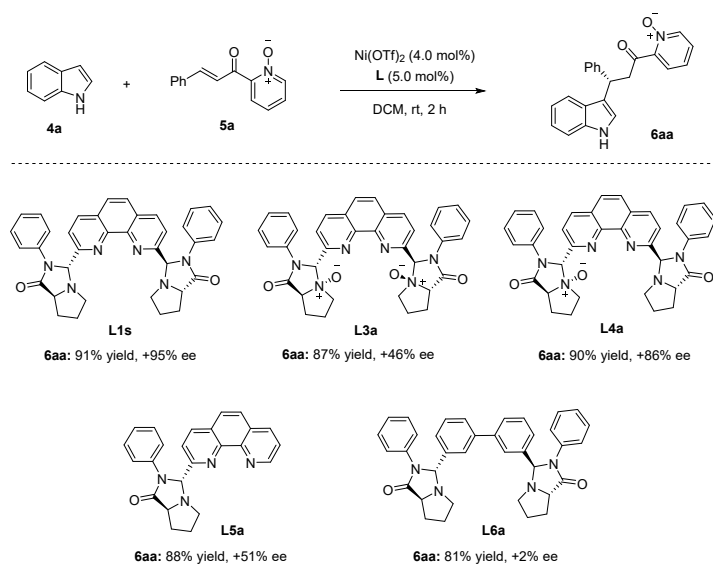


**6fa**: Product in accordance with literature characterization data<sup>8</sup>. 65% yield, 82% ee,  $[\alpha]_{\text{D}}^{20} = +2.0$  ( $c$  0.50,  $\text{CHCl}_3$ ). The ee was determined by HPLC analysis using a Chiralpak IA column

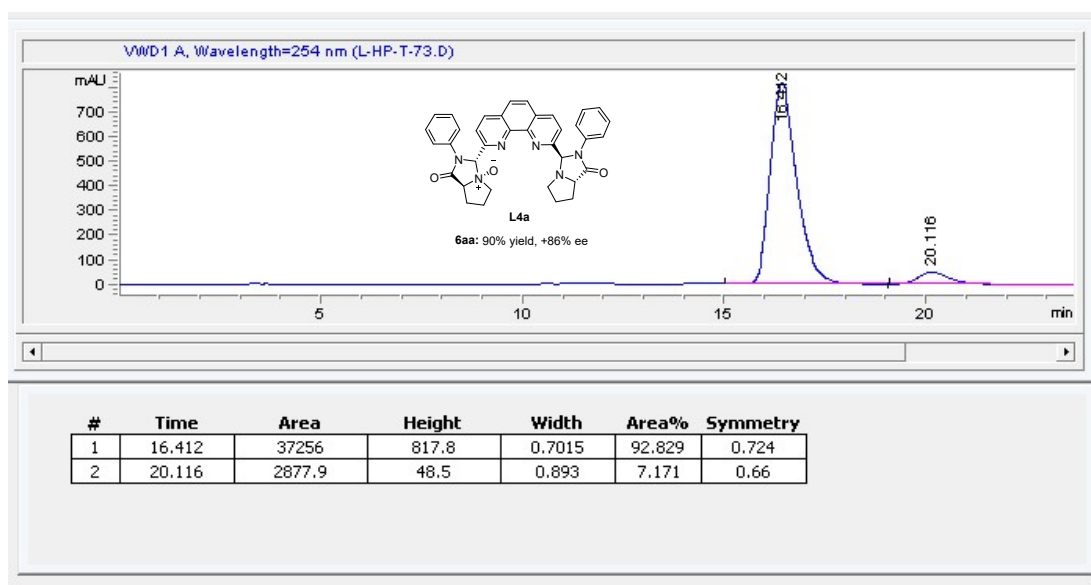
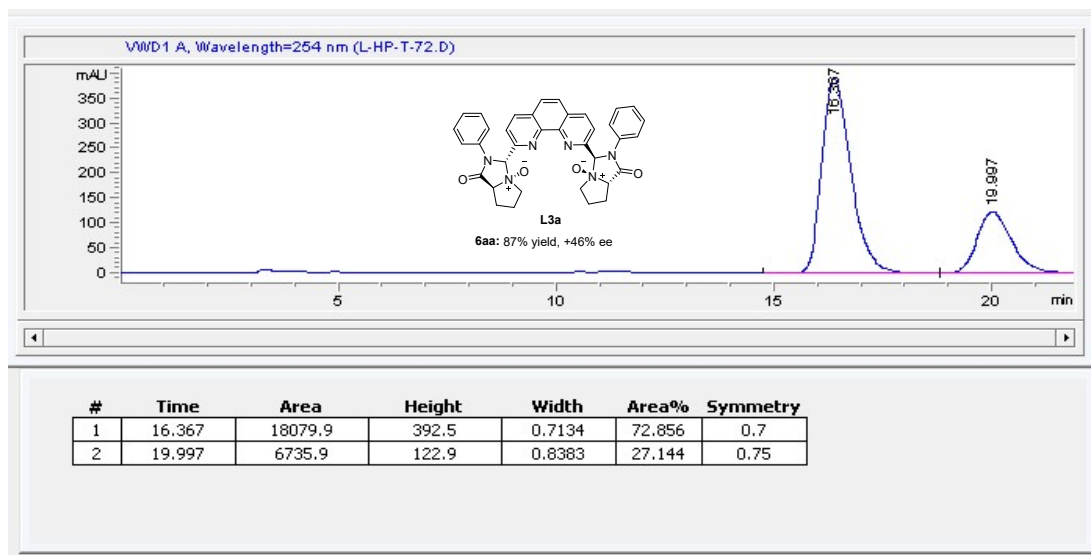
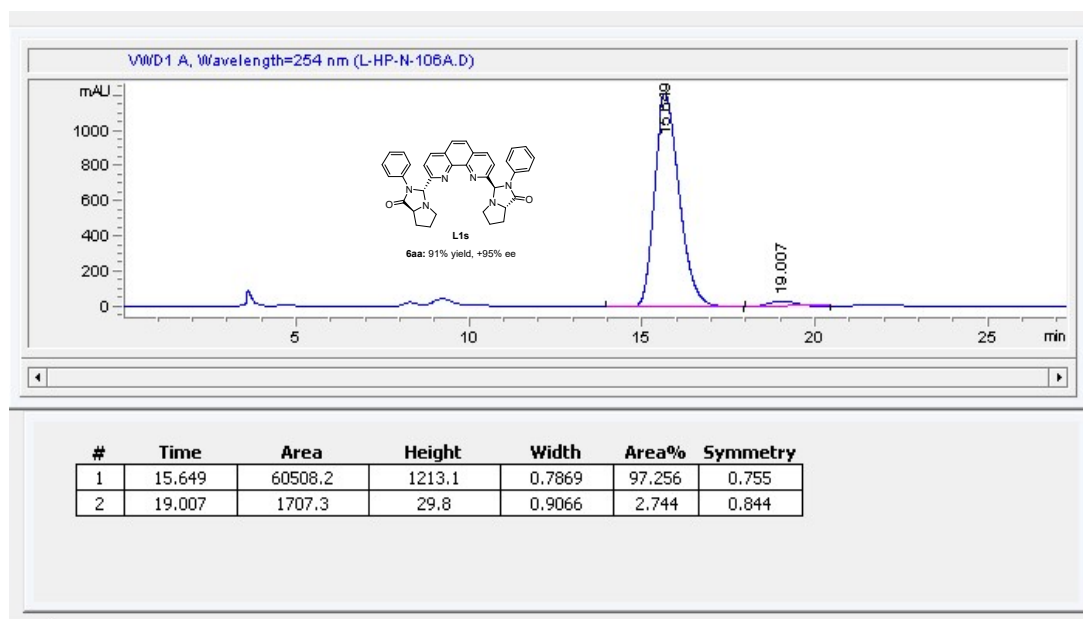
(70/30 hexane/*i*-PrOH; flow rate: 1.0 mL/min;  $\lambda = 254$  nm;  $\tau_{major} = 10.44$  min;  $\tau_{minor} = 9.83$  min).  
 $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 3.62 (s, 3H), 3.86-3.92 (m, 1H), 3.97-4.03 (m, 1H), 4.82-4.86 (m, 1H), 6.85 (s, 1H), 6.88-6.92 (m, 1H), 7.00-7.07 (m, 4H), 7.11-7.17 (m, 4H), 7.23-7.25 (m, 2H), 7.35 (d,  $J = 7.6$  Hz, 1H), 8.06 (d,  $J = 6.4$  Hz, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 31.6, 37.5, 48.1, 108.0, 116.3, 117.8, 118.5, 120.6, 124.5, 125.2, 125.3, 125.5, 126.0, 126.5, 126.8, 127.3, 136.2, 139.1, 143.0, 146.0, 196.1.

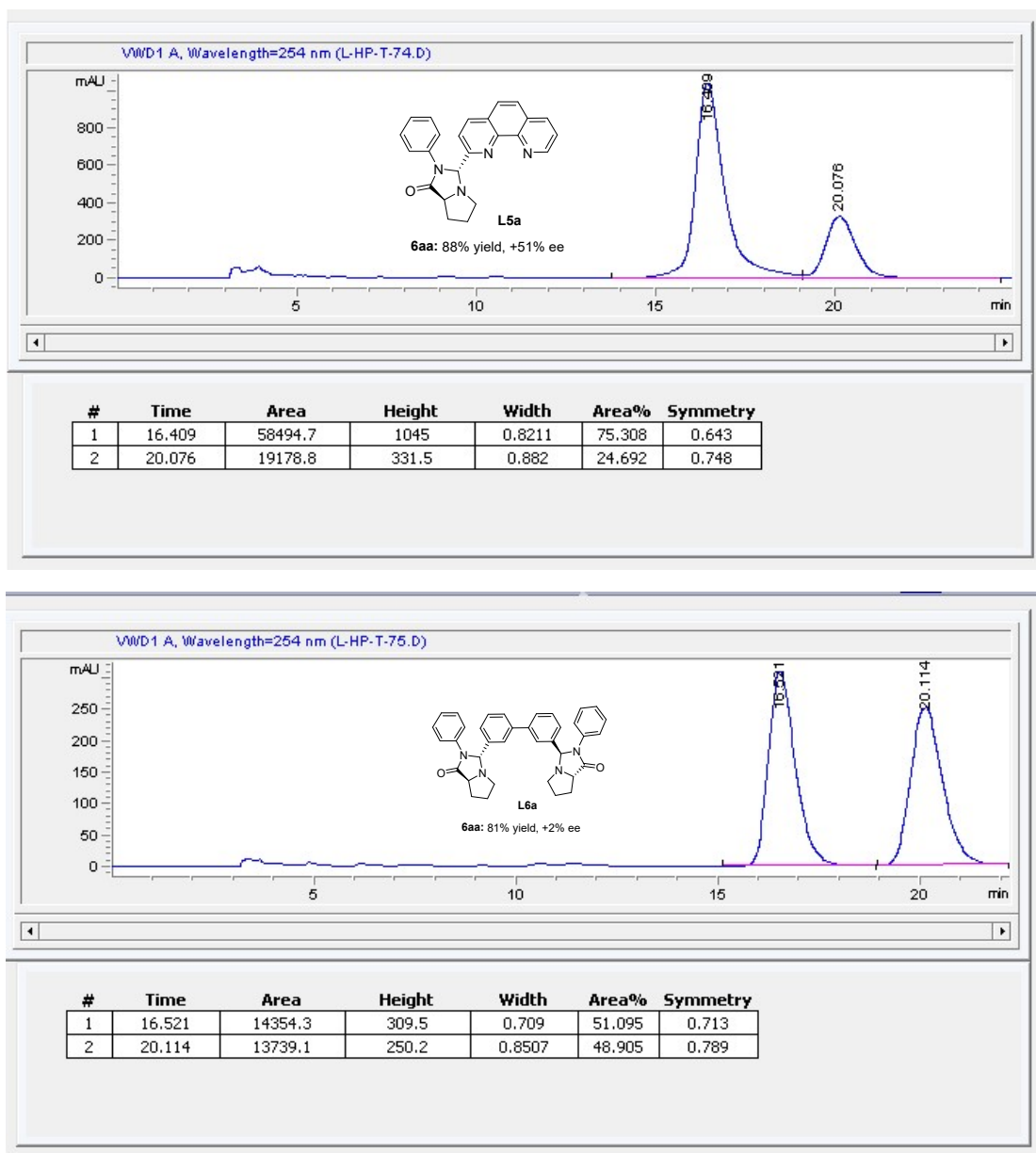
## 7. Control experiments and HPLC spectra for compound **6aa**

In a sealed tube equipped with a magnetic stirring bar, to the mixture of  $\text{Ni}(\text{OTf})_2$  (4.0 mol %), 5.0 mol % of **L** in 1.5 mL of DCM was added **4a** (0.30 mmol), and **5a** (0.20 mmol). The reaction mixture was stirred at room temperature for 2 h and was directly loaded onto a silica gel and purified by flash chromatography to give the desired product **6aa**, using hexane/EtOAc (10/1, v/v) as the eluent.





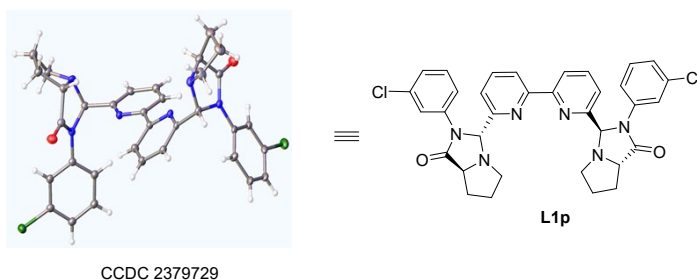




## 8. References

- (a) P. K. Singh and V. K. Singh, *Org. Lett.*, 2008, **10**, 4121-4124; (b) J. George and B. V. S. Reddy, *Org. Biomol. Chem.*, 2012, **10**, 4731-4738; (c) X. Liang, Y. Gui, K. Li, J. Li, Z. Zha, L. Shi and Z. Wang, *Chem. Commun.*, 2020, **56**, 11118-11121.

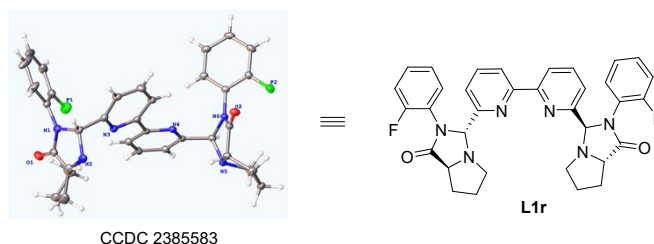
## 9. X-ray crystal data for compounds L1p, L1r and L1a-Ni(OTf)<sub>2</sub>·3H<sub>2</sub>O complex



**Table S1 Crystal data and structure refinement for L1p**

Identification code	<b>L1p</b>
Empirical formula	C <sub>34</sub> H <sub>30</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>2</sub>
Formula weight	625.54
Temperature/K	169.99(10)
Crystal system	monoclinic
Space group	P2 <sub>1</sub>
a/Å, b/Å, c/Å	13.2041(3), 8.8612(3), 14.7734(3)
α/°, β/°, γ/°	90, 92.657(2), 90
Volume/Å <sup>3</sup>	1726.69(8)
Z	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.203
μ/mm <sup>-1</sup>	1.993
F(000)	652.0
Radiation	Cu Kα (λ = 1.54184)
Crystal size/mm <sup>3</sup>	0.15 × 0.12 × 0.11
2θ range for data collection/°	5.988 to 147.192
Index ranges	-13 ≤ h ≤ 16, -10 ≤ k ≤ 10, -18 ≤ l ≤ 17
Reflections collected	25280
Independent reflections	6690 [R <sub>int</sub> = 0.0479, R <sub>sigma</sub> = 0.0370]
Data/restraints/parameters	6690/451/461
Goodness-of-fit on F <sup>2</sup>	1.057
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0696, wR <sub>2</sub> = 0.1974
Final R indexes [all data]	R <sub>1</sub> = 0.0716, wR <sub>2</sub> = 0.1991
Largest diff. peak/hole / e Å <sup>-3</sup>	0.76/-0.47
Flack parameter	0.033(12)

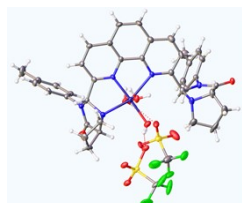
**Crystal Data** for C<sub>34</sub>H<sub>30</sub>Cl<sub>2</sub>N<sub>6</sub>O<sub>2</sub> (*M* = 625.54 g/mol): monoclinic, space group P2<sub>1</sub> (no. 4), *a* = 13.2041(3) Å, *b* = 8.8612(3) Å, *c* = 14.7734(3) Å, β = 92.657(2)°, *V* = 1726.69(8) Å<sup>3</sup>, *Z* = 2, *T* = 169.99(10) K, μ(Cu Kα) = 1.993 mm<sup>-1</sup>, *D*<sub>calc</sub> = 1.203 g/cm<sup>3</sup>, 25280 reflections measured (5.988° ≤ 2θ ≤ 147.192°), 6690 unique (*R*<sub>int</sub> = 0.0479, *R*<sub>sigma</sub> = 0.0370) which were used in all calculations. The final *R*<sub>1</sub> was 0.0696 (*I* > 2σ(*I*)) and *wR*<sub>2</sub> was 0.1991 (all data).



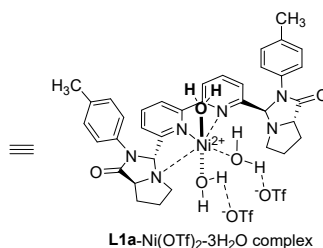
**Table S2 Crystal data and structure refinement for L1r**

Identification code	<b>L1r</b>
Empirical formula	C <sub>34</sub> H <sub>32</sub> F <sub>2</sub> N <sub>6</sub> O <sub>3</sub>
Formula weight	610.65
Temperature/K	149.98(10)
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å, b/Å, c/Å	8.7651(2), 13.5600(3), 24.7099(7)
α/°, β/°, γ/°	90, 90, 90
Volume/Å <sup>3</sup>	2936.88(14)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.381
μ/mm <sup>-1</sup>	0.820
F(000)	1280.0
Radiation	Cu Kα (λ = 1.54184)
Crystal size/mm <sup>3</sup>	0.14 × 0.12 × 0.1
2θ range for data collection/°	7.154 to 146.576
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 16, -29 ≤ l ≤ 30
Reflections collected	24274
Independent reflections	5730 [R <sub>int</sub> = 0.0405, R <sub>sigma</sub> = 0.0326]
Data/restraints/parameters	5730/3/412
Goodness-of-fit on F <sup>2</sup>	1.035
Final R indexes [I ≥ 2σ(I)]	R <sub>1</sub> = 0.0472, wR <sub>2</sub> = 0.1223
Final R indexes [all data]	R <sub>1</sub> = 0.0589, wR <sub>2</sub> = 0.1308
Largest diff. peak/hole / e Å <sup>-3</sup>	0.46/-0.24
Flack parameter	-0.09(9)/-0.05(7)

**Crystal Data** for C<sub>34</sub>H<sub>32</sub>F<sub>2</sub>N<sub>6</sub>O<sub>3</sub> (*M* = 610.65 g/mol): orthorhombic, space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (no. 19), *a* = 8.7651(2) Å, *b* = 13.5600(3) Å, *c* = 24.7099(7) Å, *V* = 2936.88(14) Å<sup>3</sup>, *Z* = 4, *T* = 149.98(10) K, μ(Cu Kα) = 0.820 mm<sup>-1</sup>, *D*<sub>calc</sub> = 1.381 g/cm<sup>3</sup>, 24274 reflections measured (7.154° ≤ 2θ ≤ 146.576°), 5730 unique (*R*<sub>int</sub> = 0.0405, *R*<sub>sigma</sub> = 0.0326) which were used in all calculations. The final *R*<sub>1</sub> was 0.0472 (*I* > 2σ(*I*)) and *wR*<sub>2</sub> was 0.1308 (all data).



CCDC: 2387992



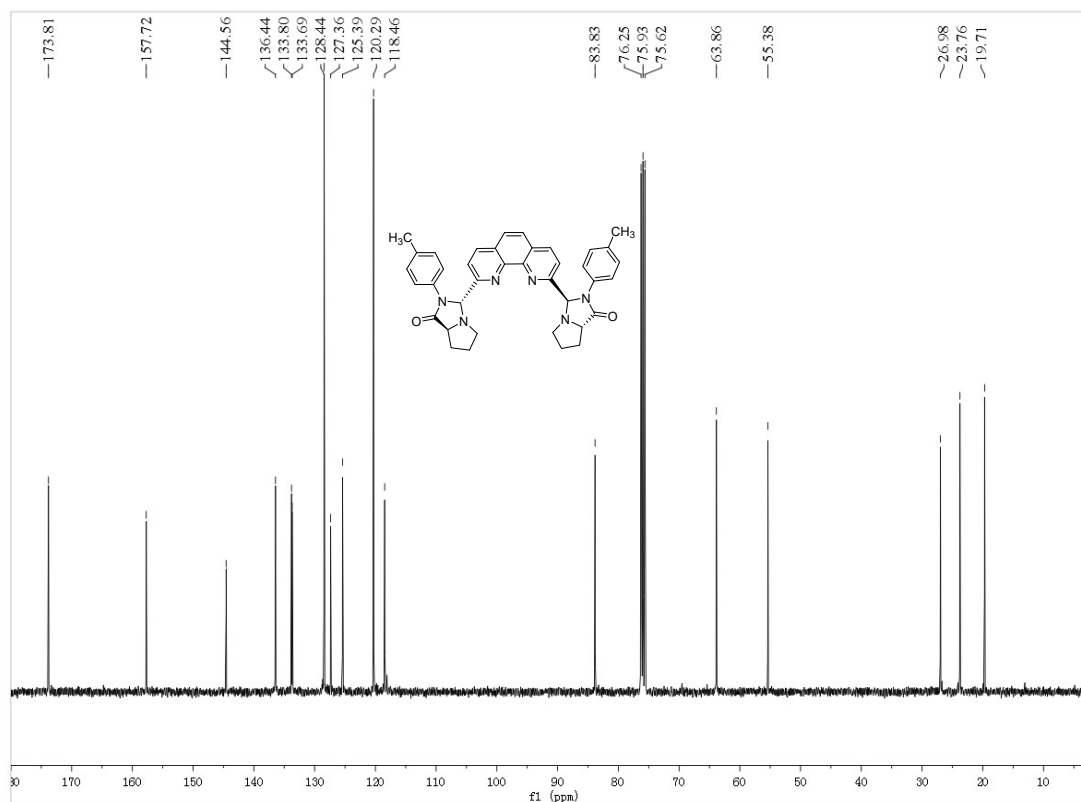
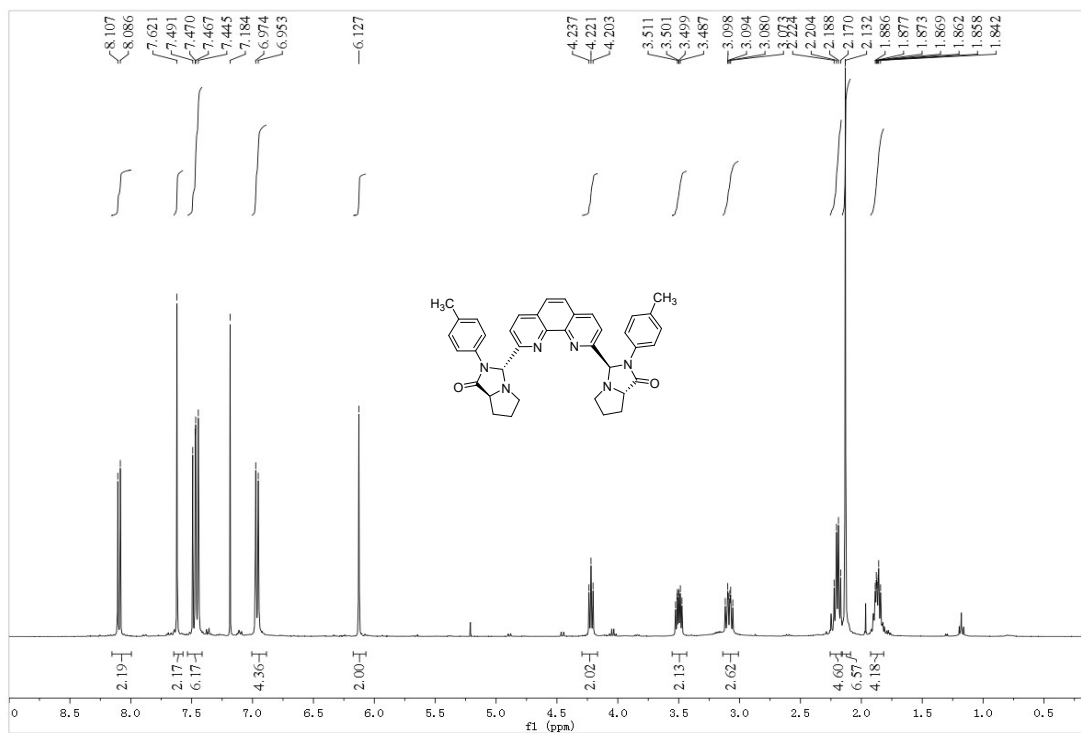
**Table S3 Crystal data and structure refinement for L1a-Ni(OTf)<sub>2</sub>-3H<sub>2</sub>O complex**

Identification code	<b>L1a-Ni(OTf)<sub>2</sub>-3H<sub>2</sub>O complex</b>
Empirical formula	C <sub>40</sub> H <sub>42</sub> F <sub>6</sub> N <sub>6</sub> NiO <sub>11</sub> S <sub>2</sub>
Formula weight	1019.62
Temperature/K	169.99(10)
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å, b/Å, c/Å	14.2901(4), 22.2090(8), 15.6839(4)
α/°, β/°, γ/°	90, 90, 90
Volume/Å <sup>3</sup>	4977.6(3)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.361
μ/mm <sup>-1</sup>	2.065
F(000)	2104.0
Radiation	Cu Kα (λ = 1.54184)
Crystal size/mm <sup>3</sup>	0.15 × 0.13 × 0.1
2θ range for data collection/°	6.9 to 147.906
Index ranges	-17 ≤ h ≤ 14, -22 ≤ k ≤ 27, -18 ≤ l ≤ 19
Reflections collected	27893
Independent reflections	9876 [R <sub>int</sub> = 0.0507, R <sub>sigma</sub> = 0.0504]
Data/restraints/parameters	9876/405/741
Goodness-of-fit on F <sup>2</sup>	1.016
Final R indexes [I >= 2σ(I)]	R <sub>1</sub> = 0.0616, wR <sub>2</sub> = 0.1675
Final R indexes [all data]	R <sub>1</sub> = 0.0666, wR <sub>2</sub> = 0.1730
Largest diff. peak/hole / e Å <sup>-3</sup>	0.53/-0.99
Flack parameter	0.011(16)/0.02(3)

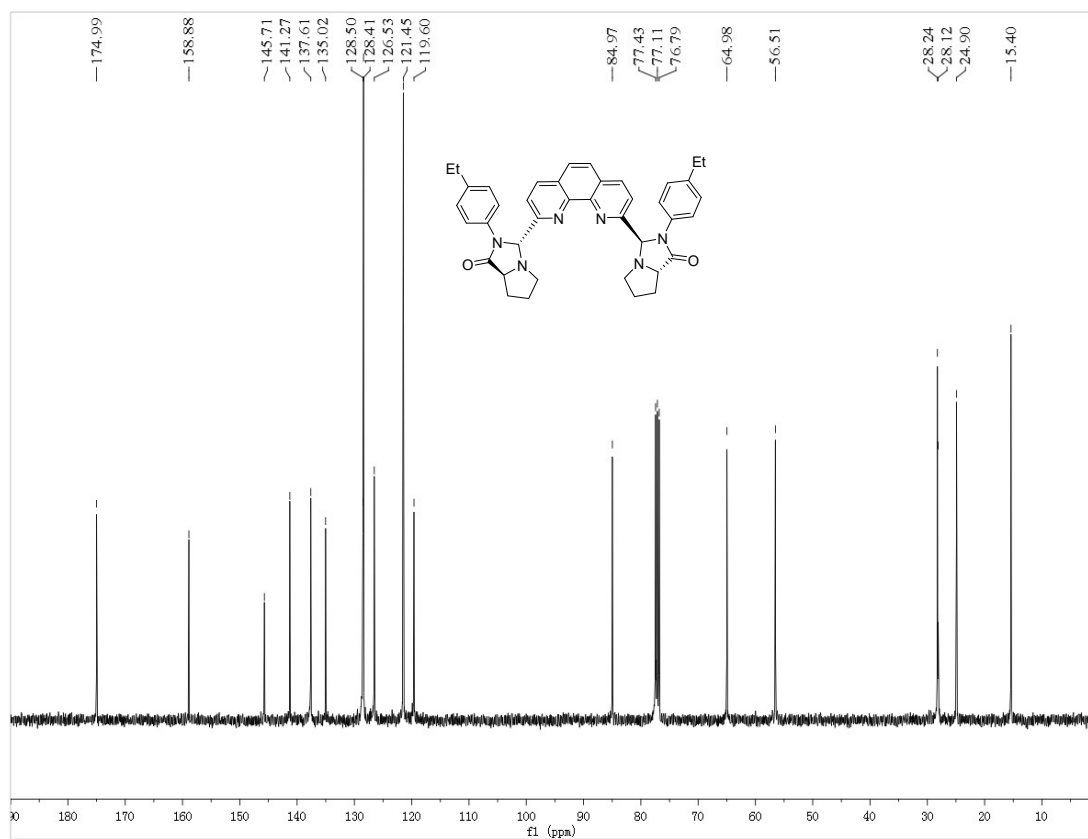
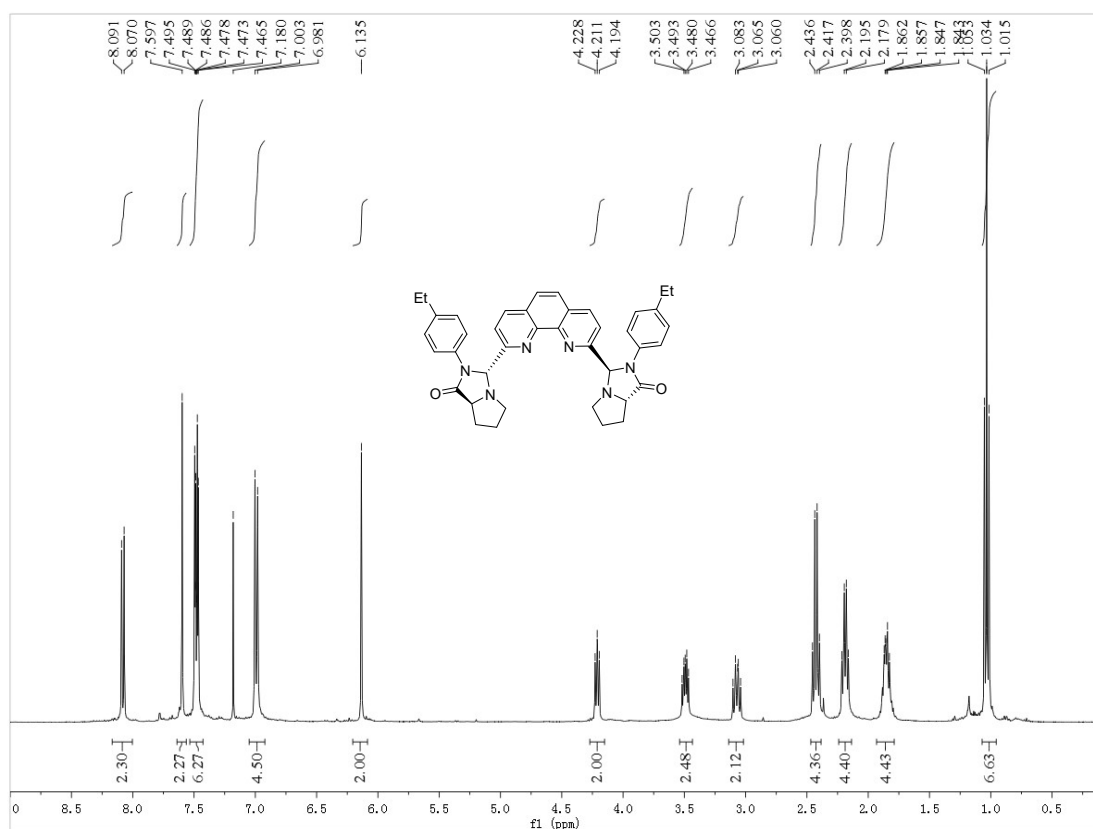
**Crystal Data** for C<sub>40</sub>H<sub>42</sub>F<sub>6</sub>N<sub>6</sub>NiO<sub>11</sub>S<sub>2</sub> (*M* = 1019.62 g/mol): orthorhombic, space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (no. 19), *a* = 14.2901(4) Å, *b* = 22.2090(8) Å, *c* = 15.6839(4) Å, *V* = 4977.6(3) Å<sup>3</sup>, *Z* = 4, *T* = 169.99(10) K, μ(Cu Kα) = 2.065 mm<sup>-1</sup>, *D*<sub>calc</sub> = 1.361 g/cm<sup>3</sup>, 27893 reflections measured (6.9° ≤ 2θ ≤ 147.906°), 9876 unique (*R*<sub>int</sub> = 0.0507, *R*<sub>sigma</sub> = 0.0504) which were used in all calculations. The final *R*<sub>1</sub> was 0.0616 (*I* > 2σ(*I*)) and *wR*<sub>2</sub> was 0.1730 (all data).

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

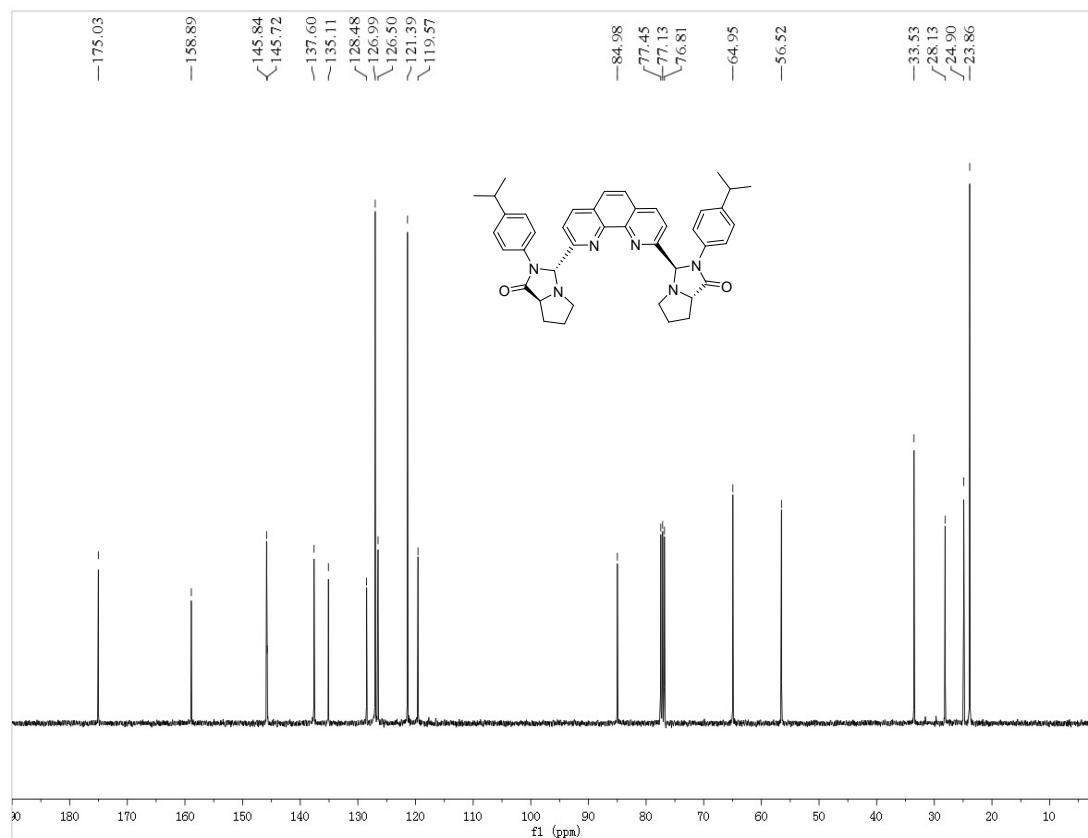
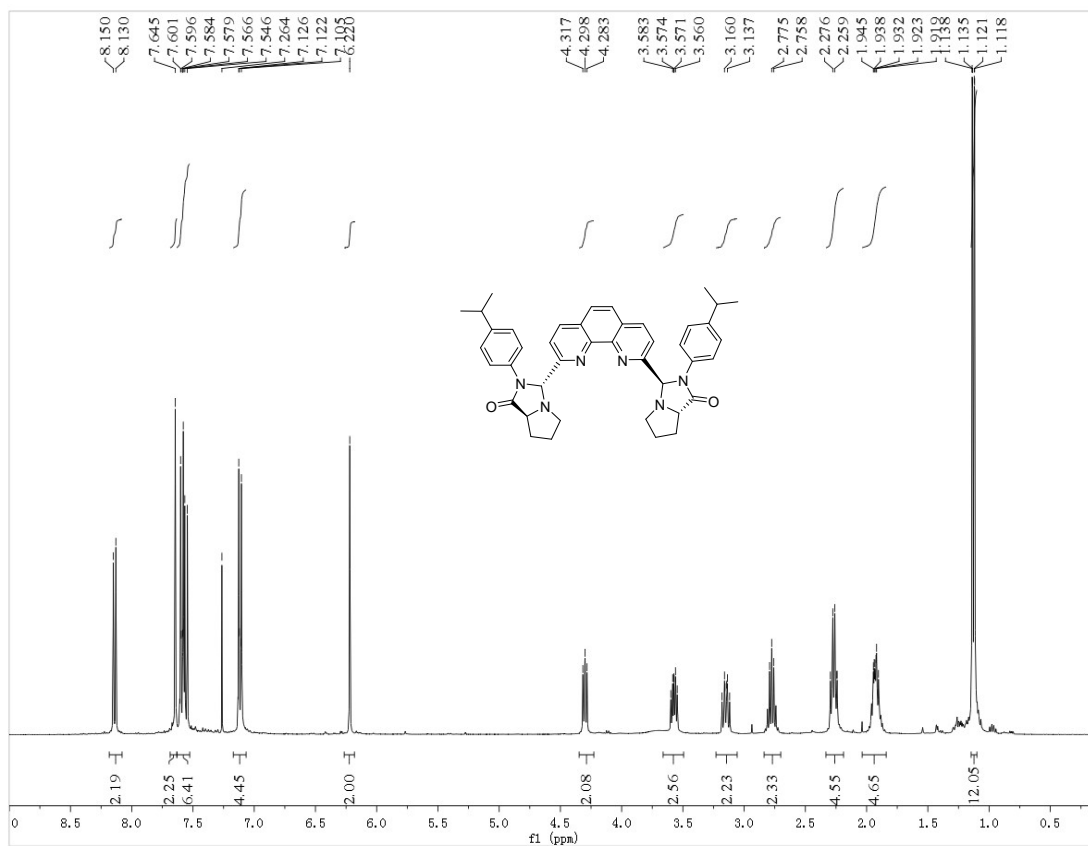
$^1\text{H}$  and  $^{13}\text{C}$  NMR of L1a



# <sup>1</sup>H and <sup>13</sup>C NMR of L1b

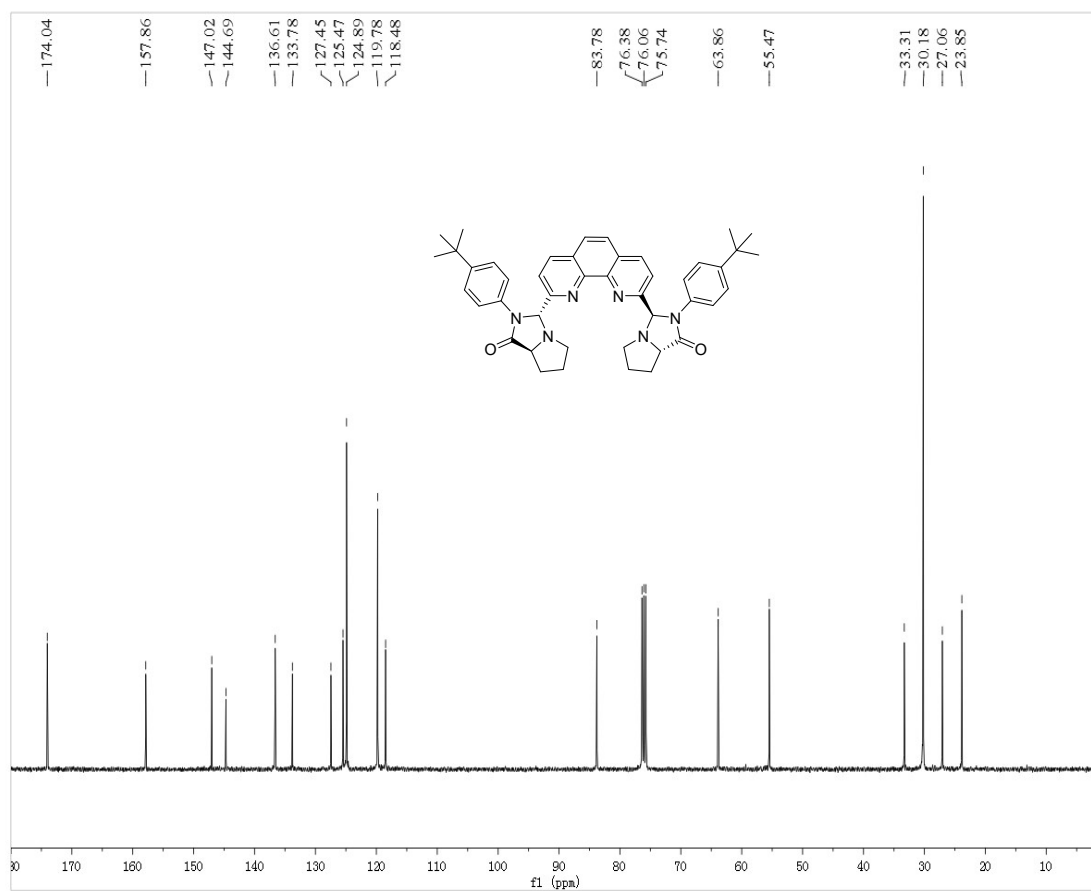
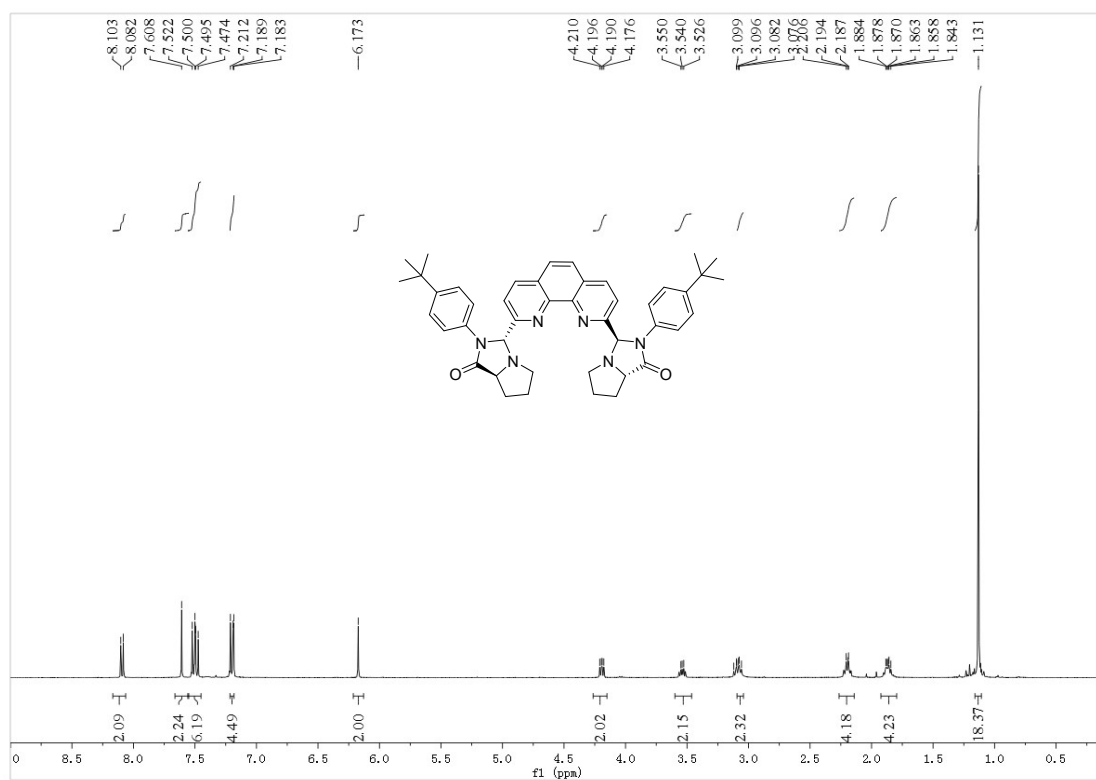


# <sup>1</sup>H and <sup>13</sup>C NMR of L1c

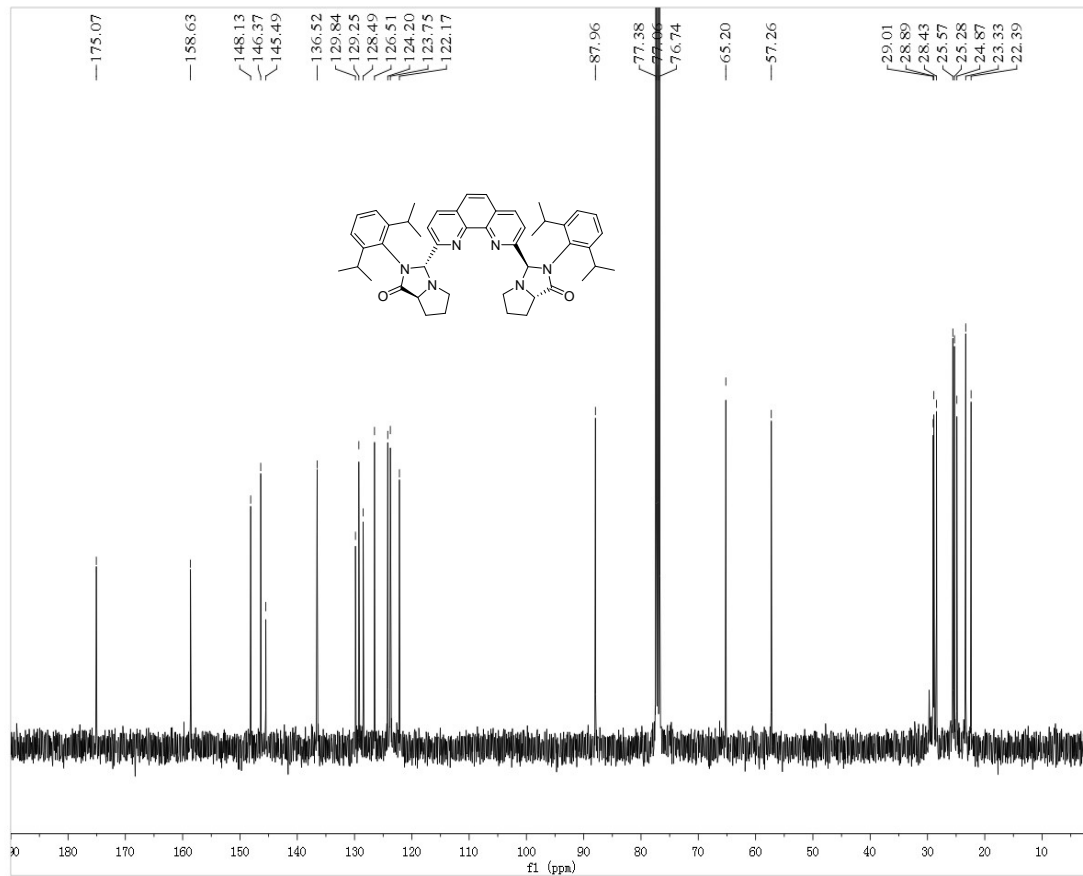
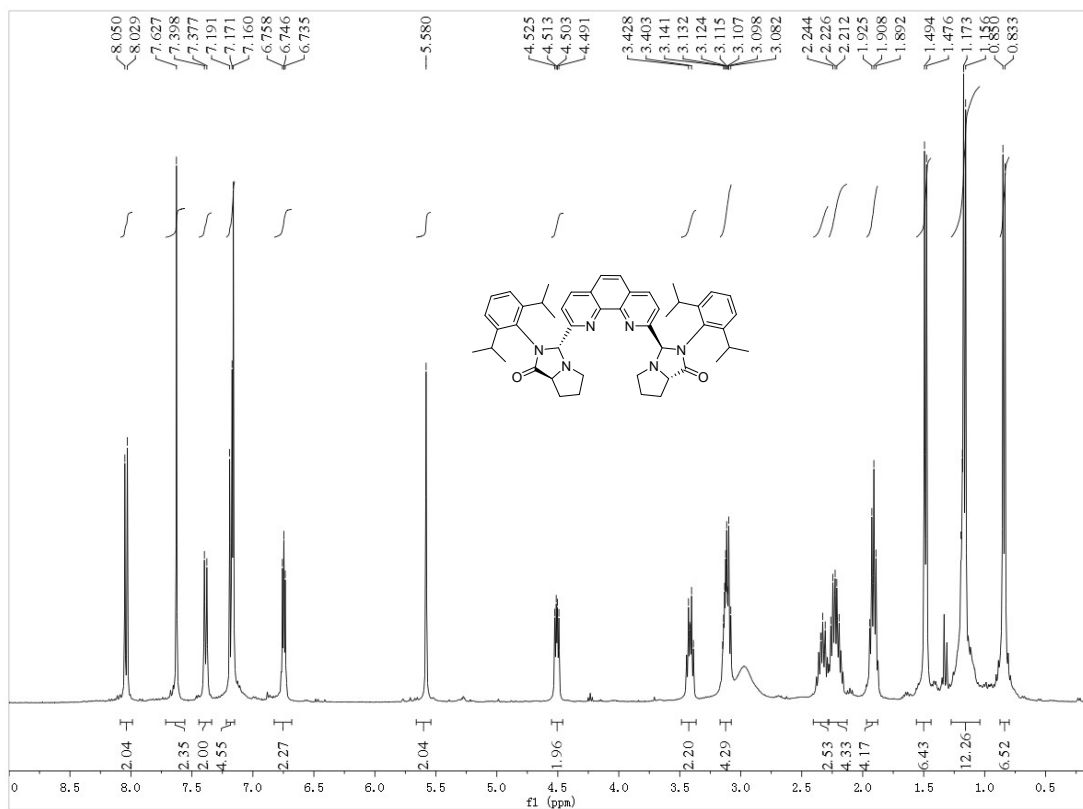




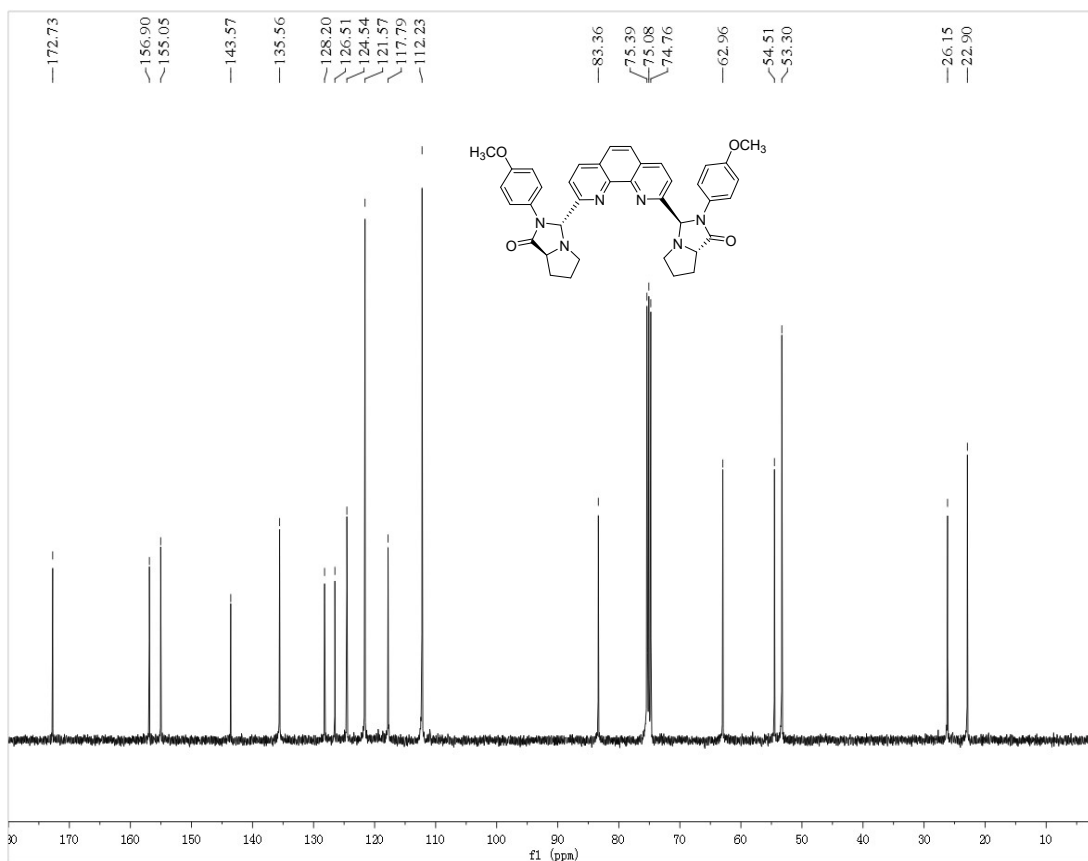
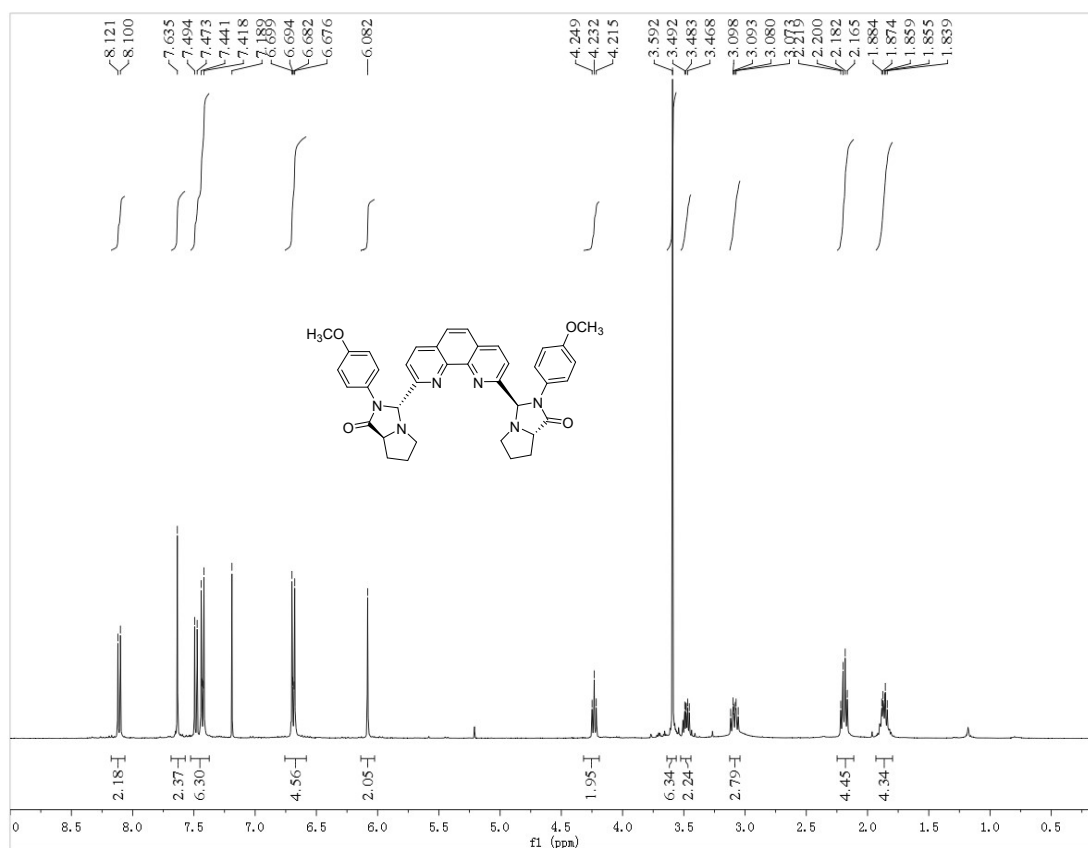
# <sup>1</sup>H and <sup>13</sup>C NMR of L1d



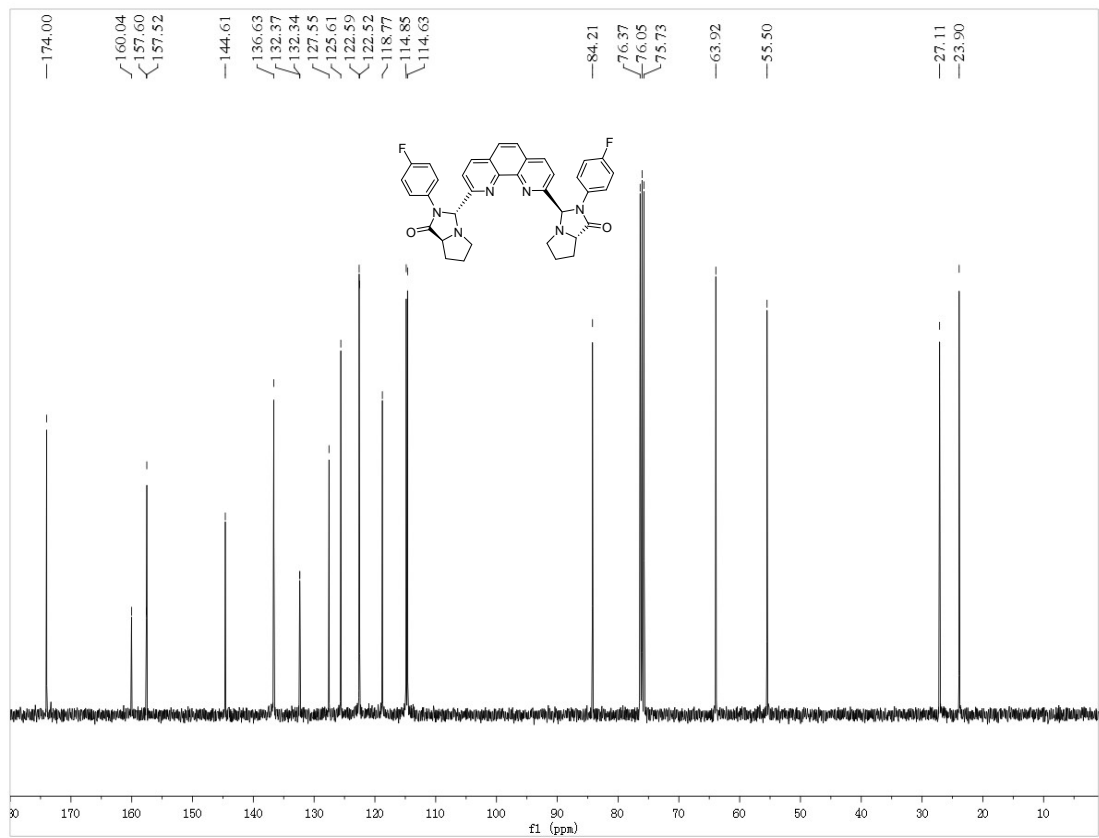
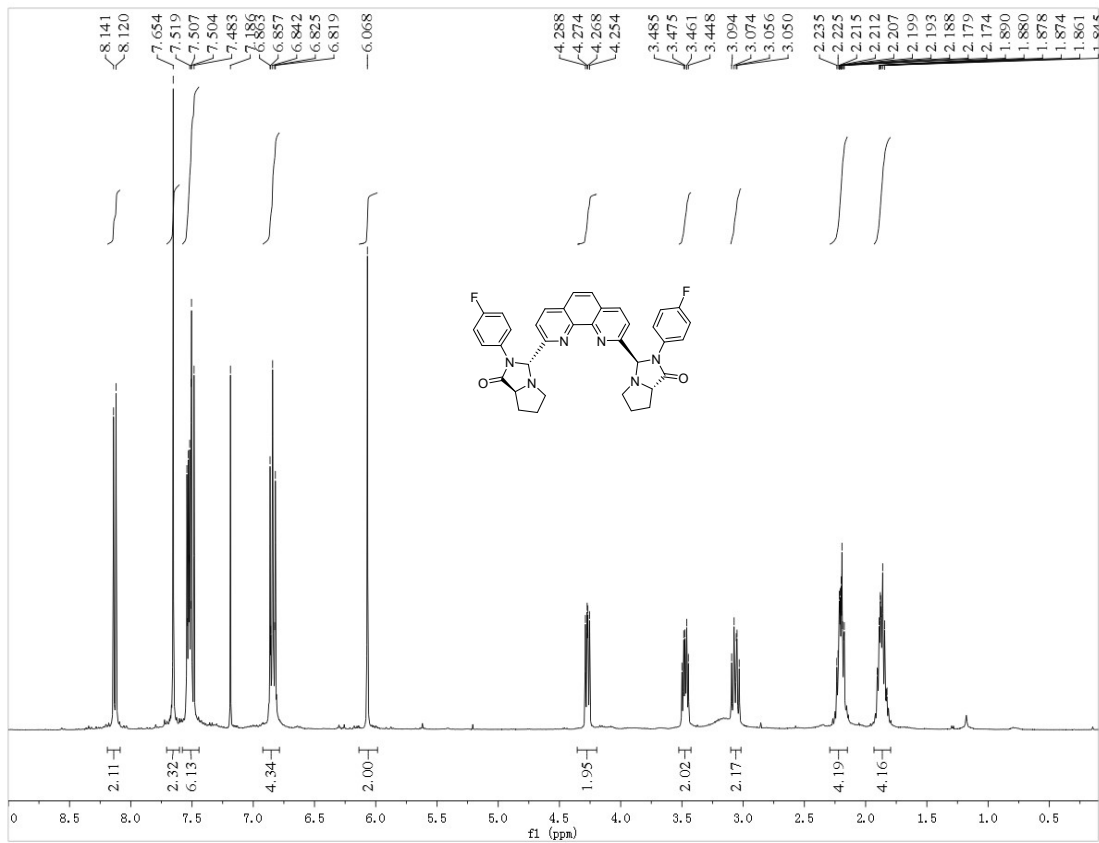
# <sup>1</sup>H and <sup>13</sup>C NMR of L1e



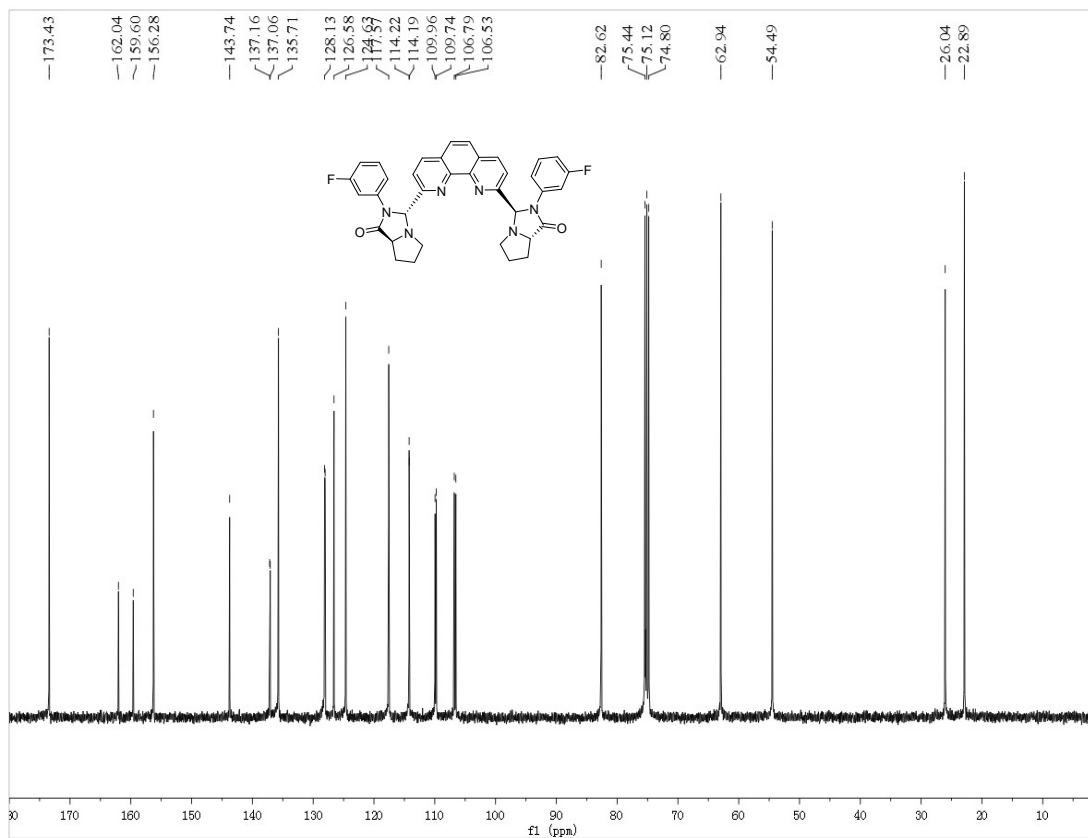
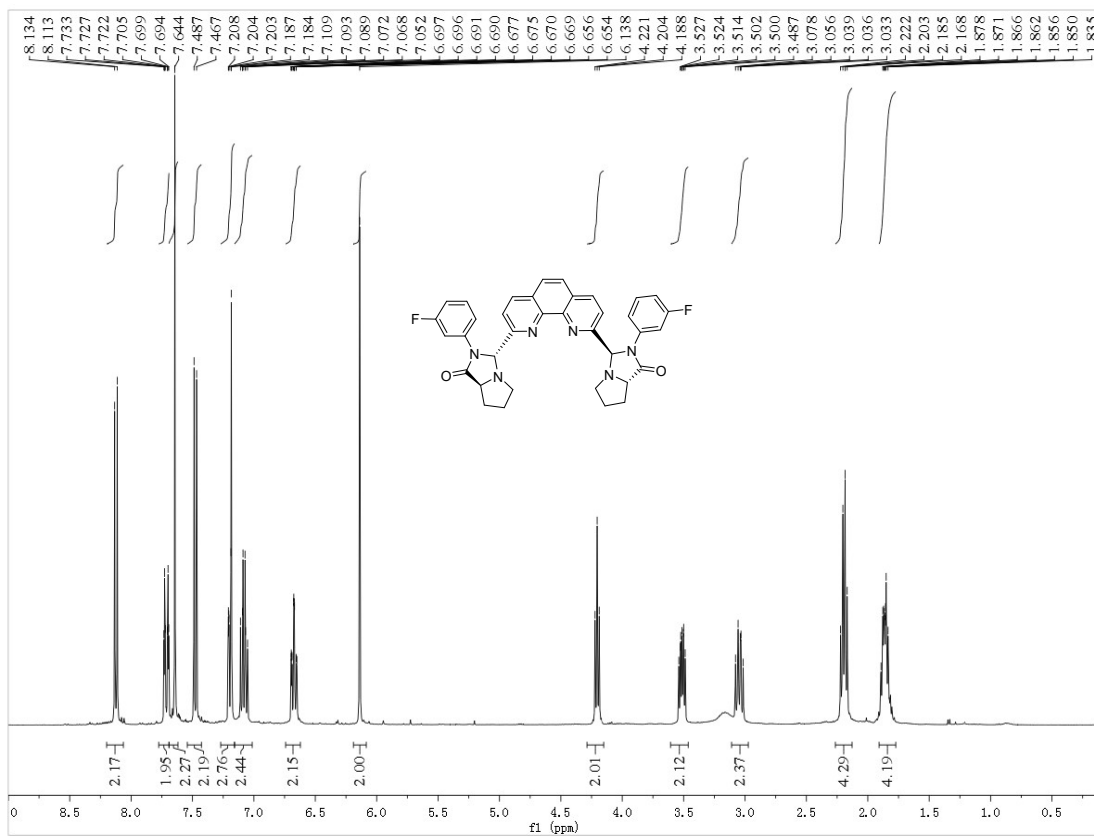
# <sup>1</sup>H and <sup>13</sup>C NMR of L1f



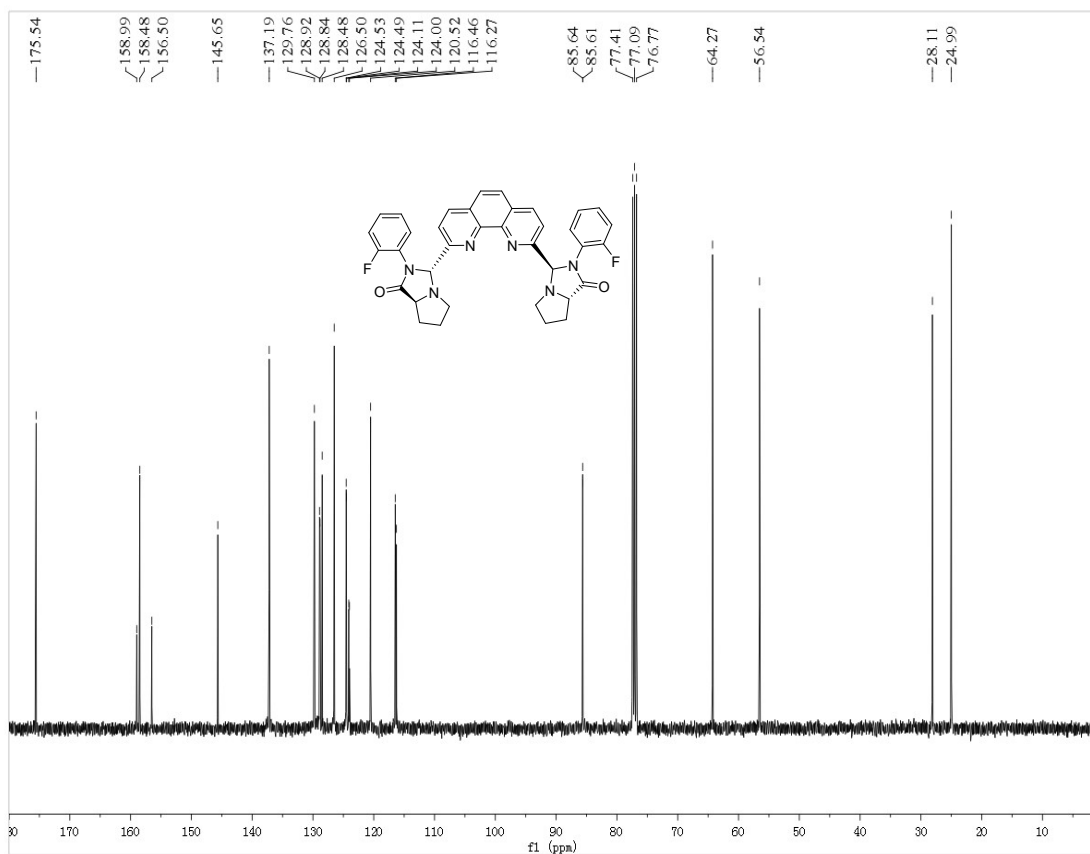
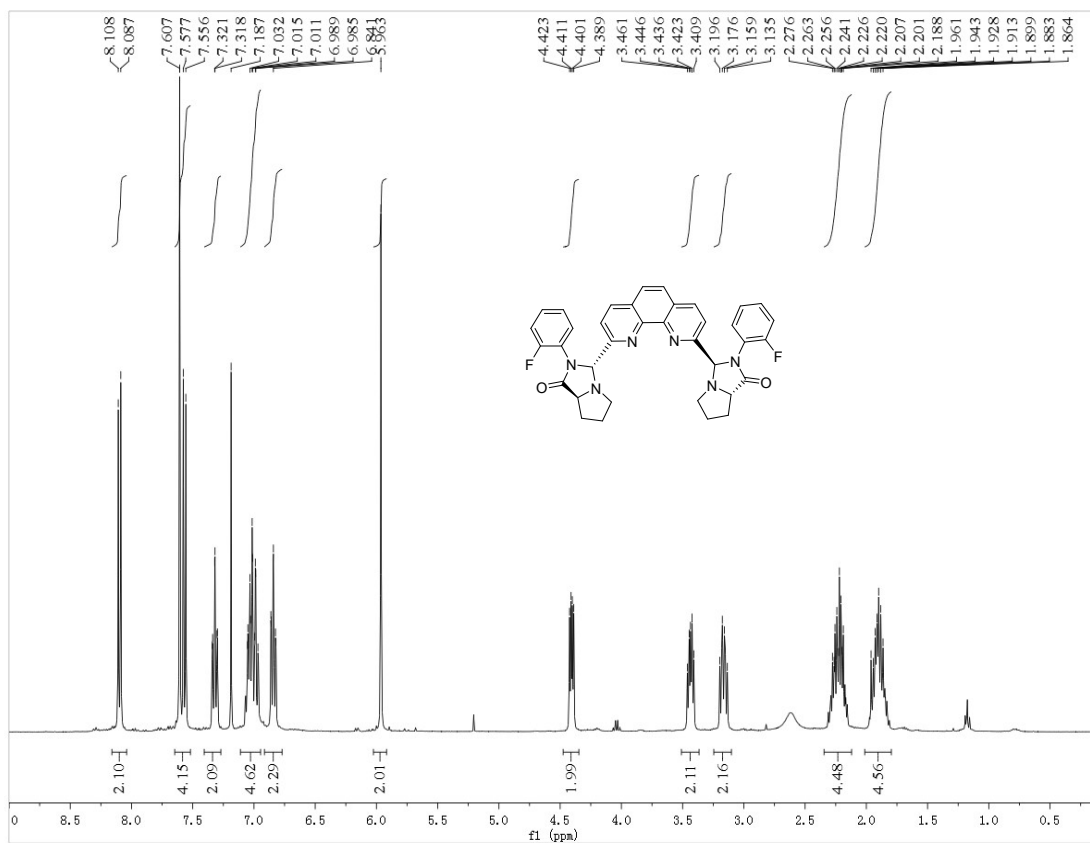
# <sup>1</sup>H and <sup>13</sup>C NMR of L1g



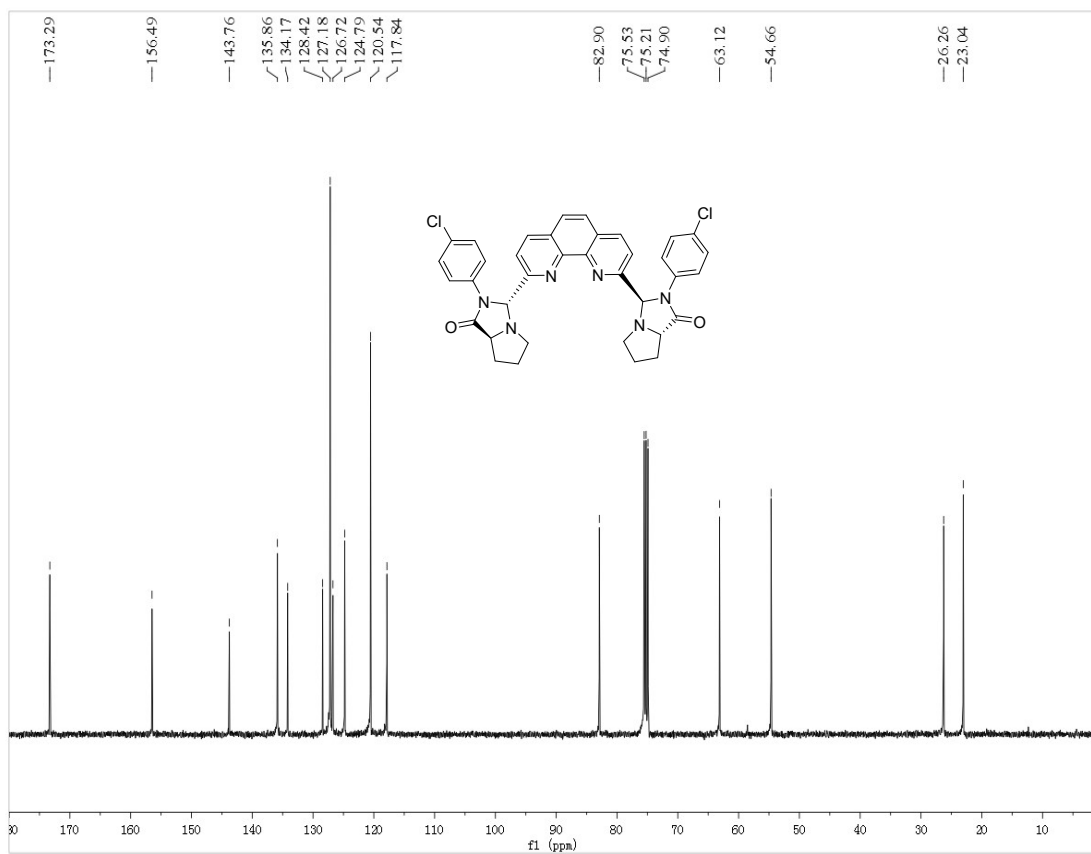
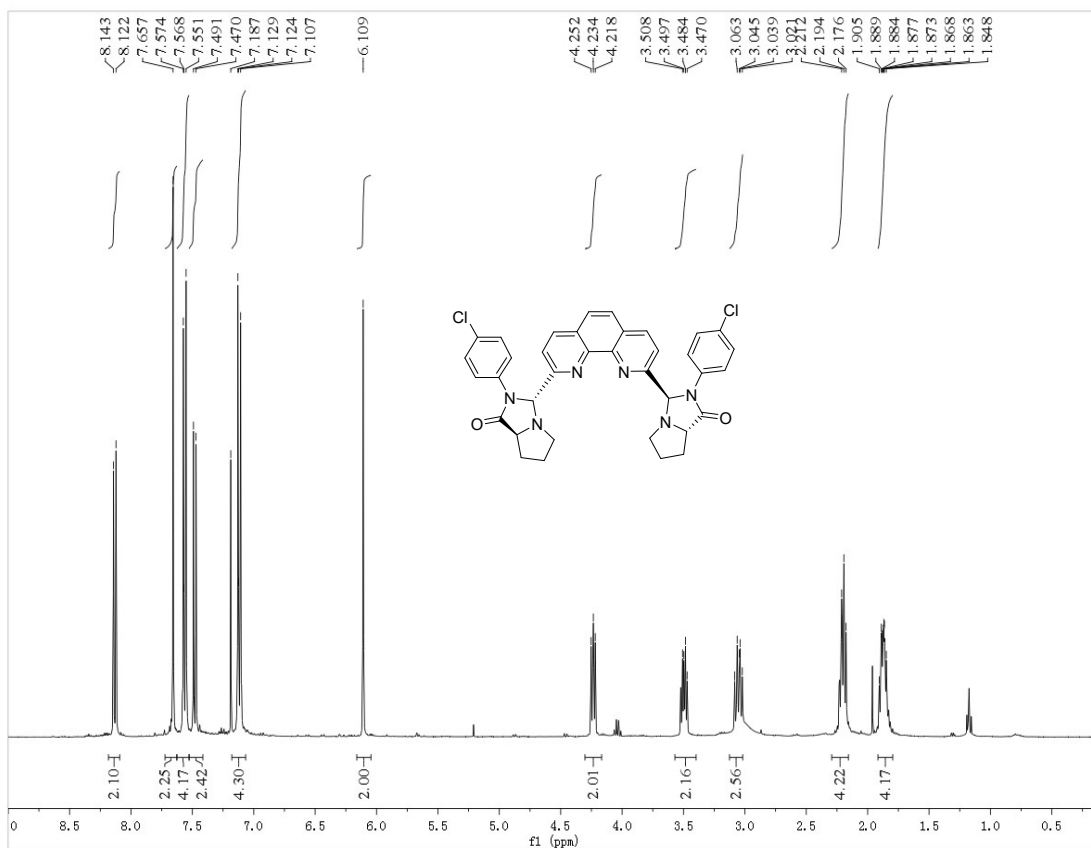
# <sup>1</sup>H and <sup>13</sup>C NMR of L1h



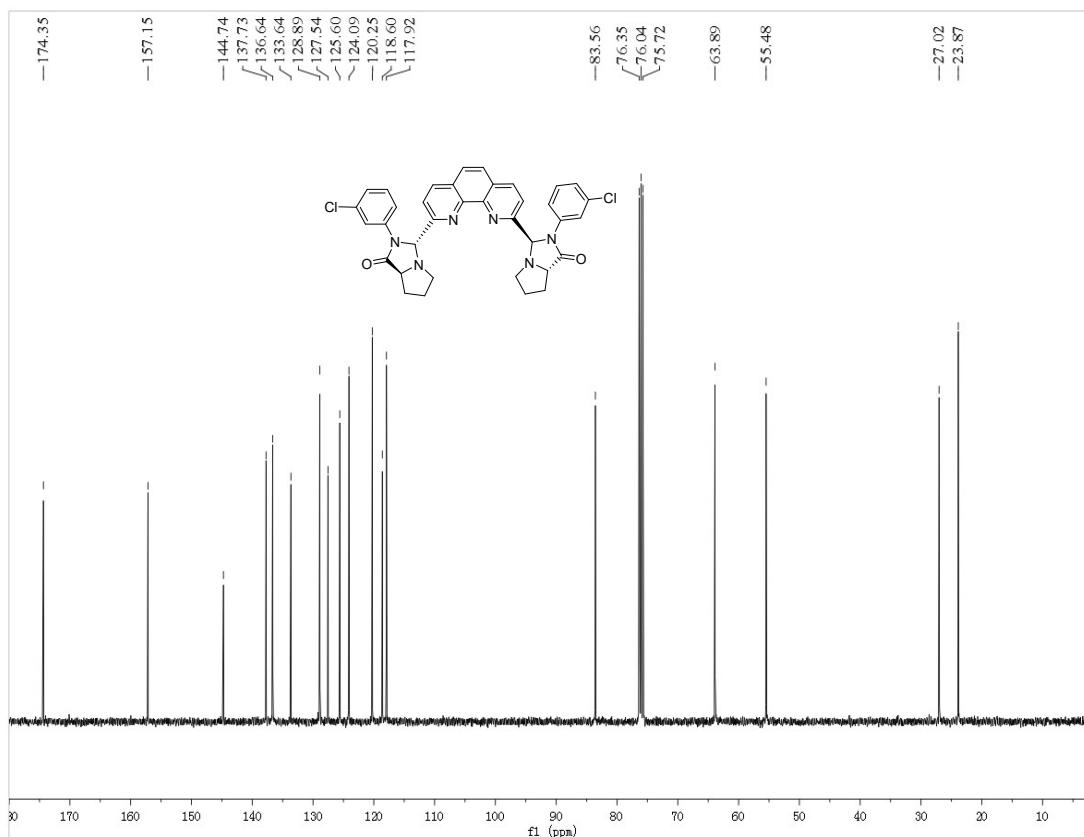
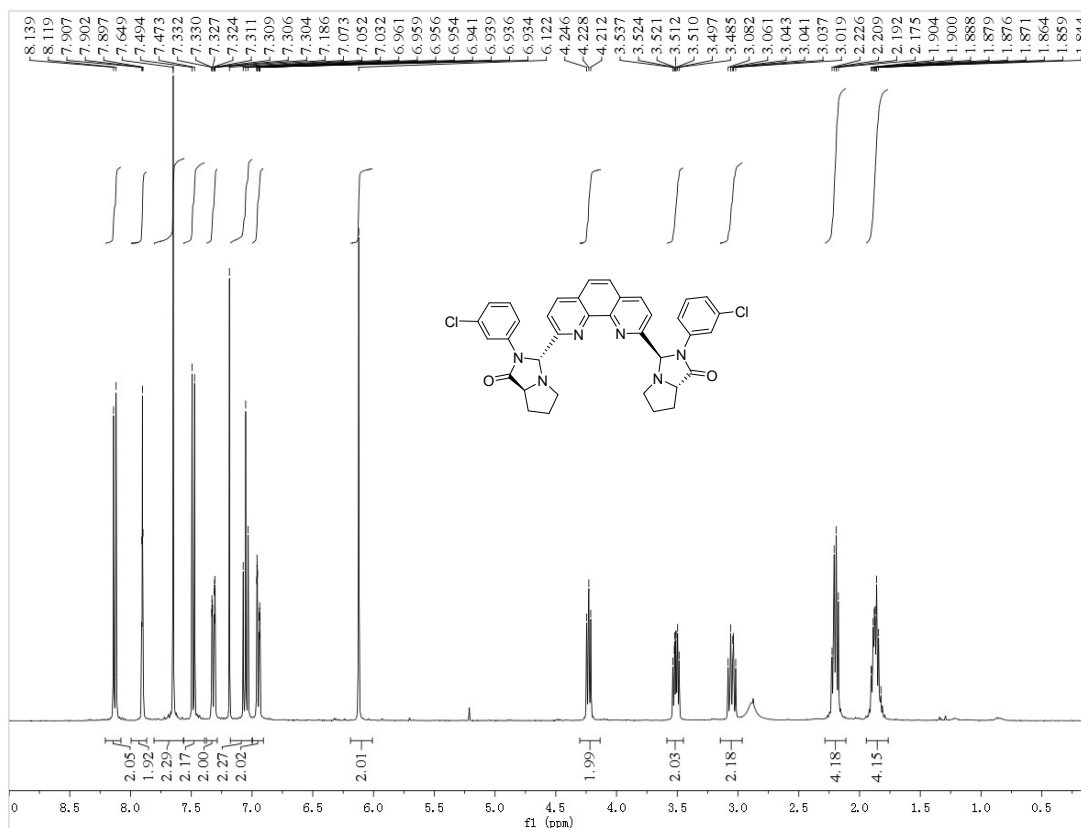
# $^1\text{H}$ and $^{13}\text{C}$ NMR of L1i



# <sup>1</sup>H and <sup>13</sup>C NMR of L1j

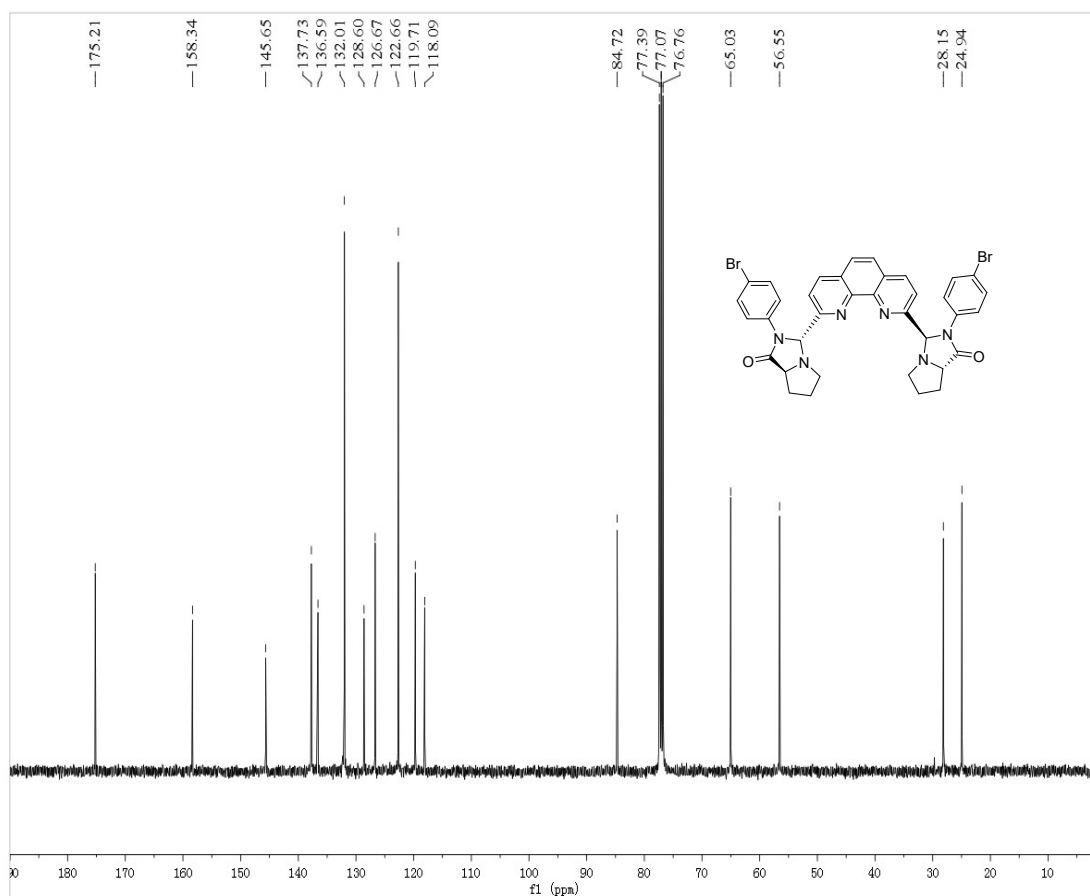
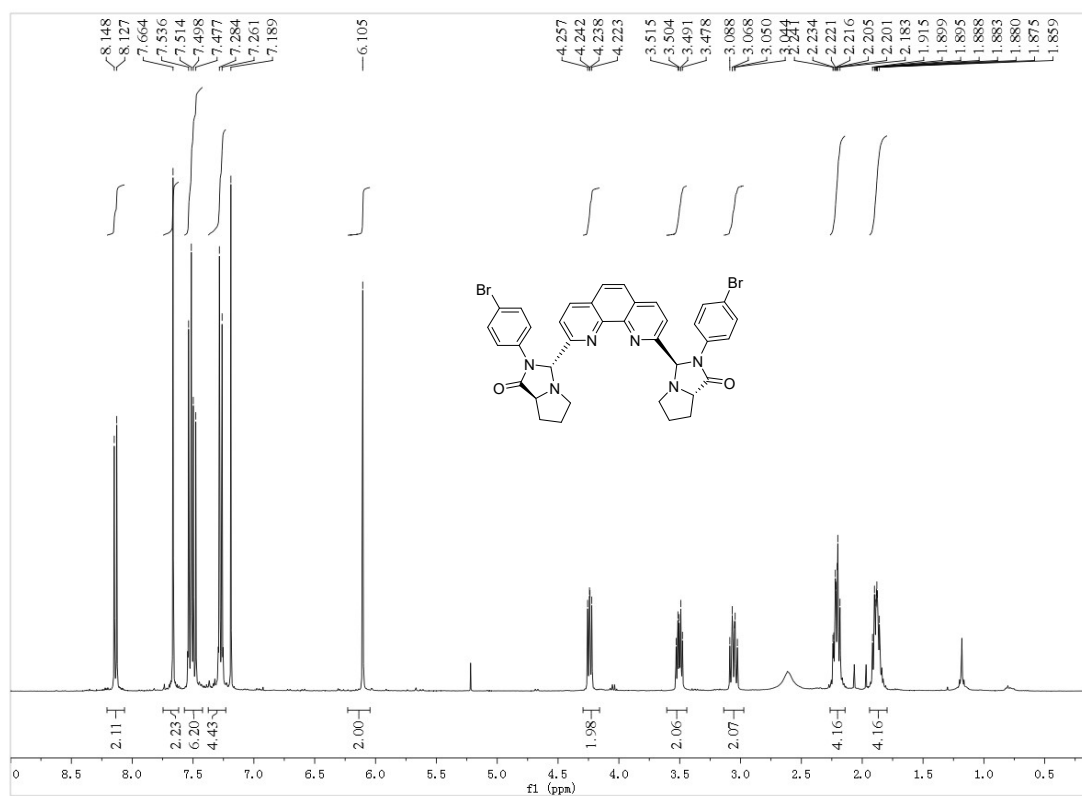


# <sup>1</sup>H and <sup>13</sup>C NMR of L1k

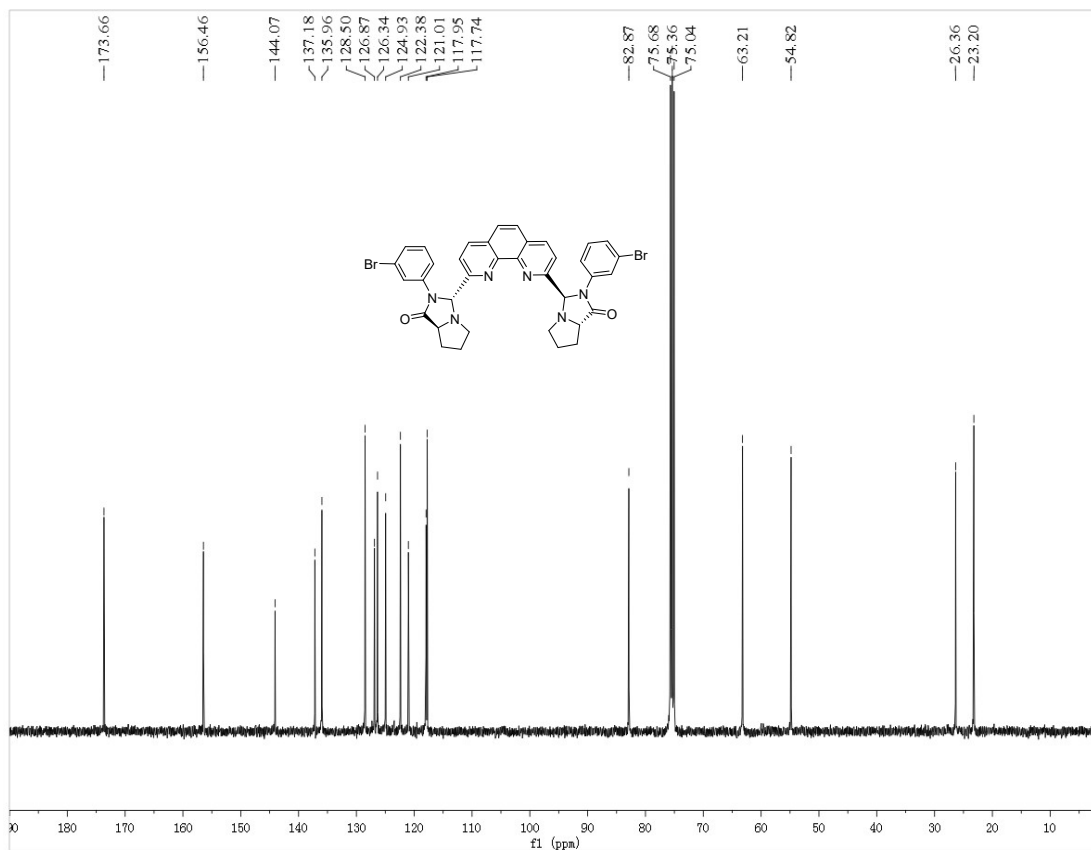
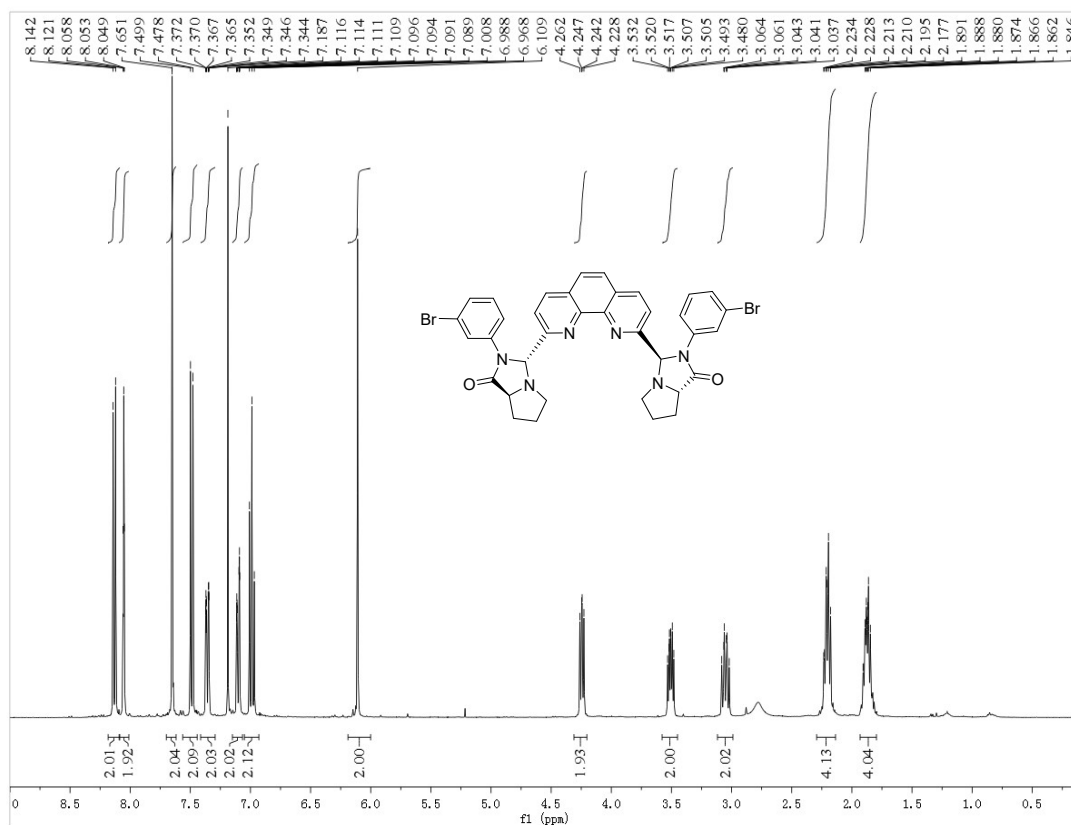




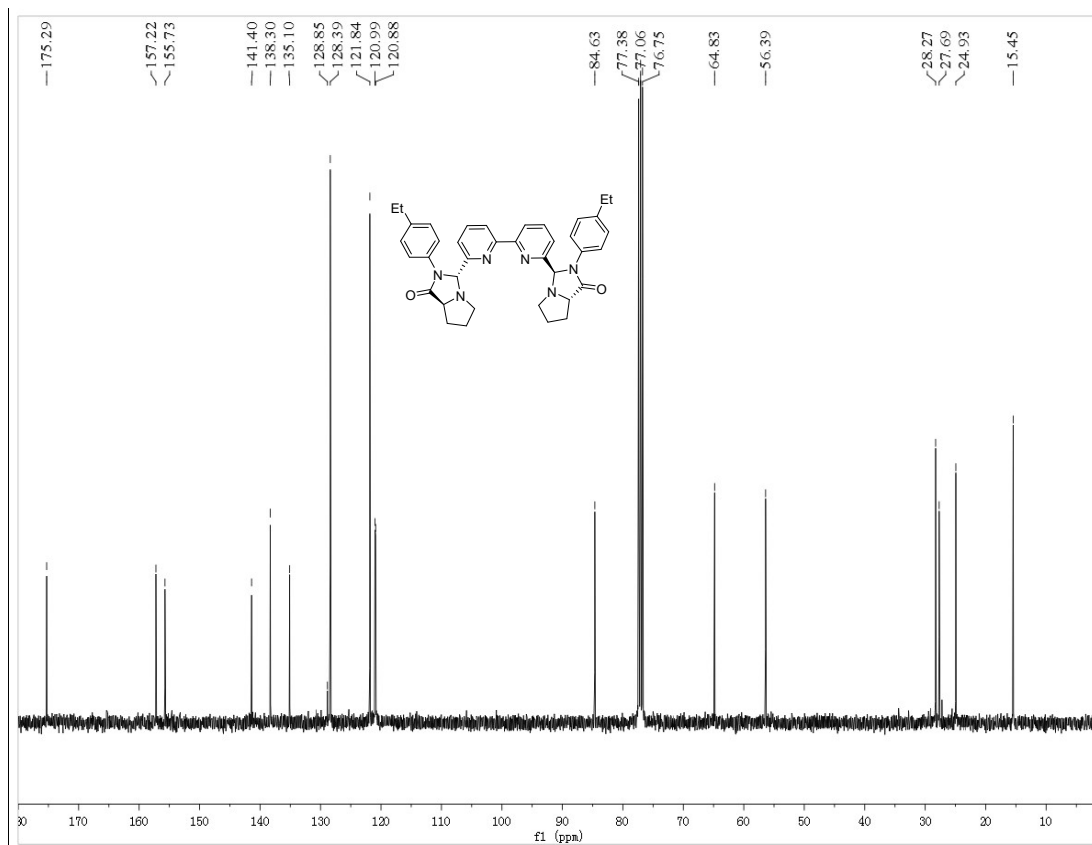
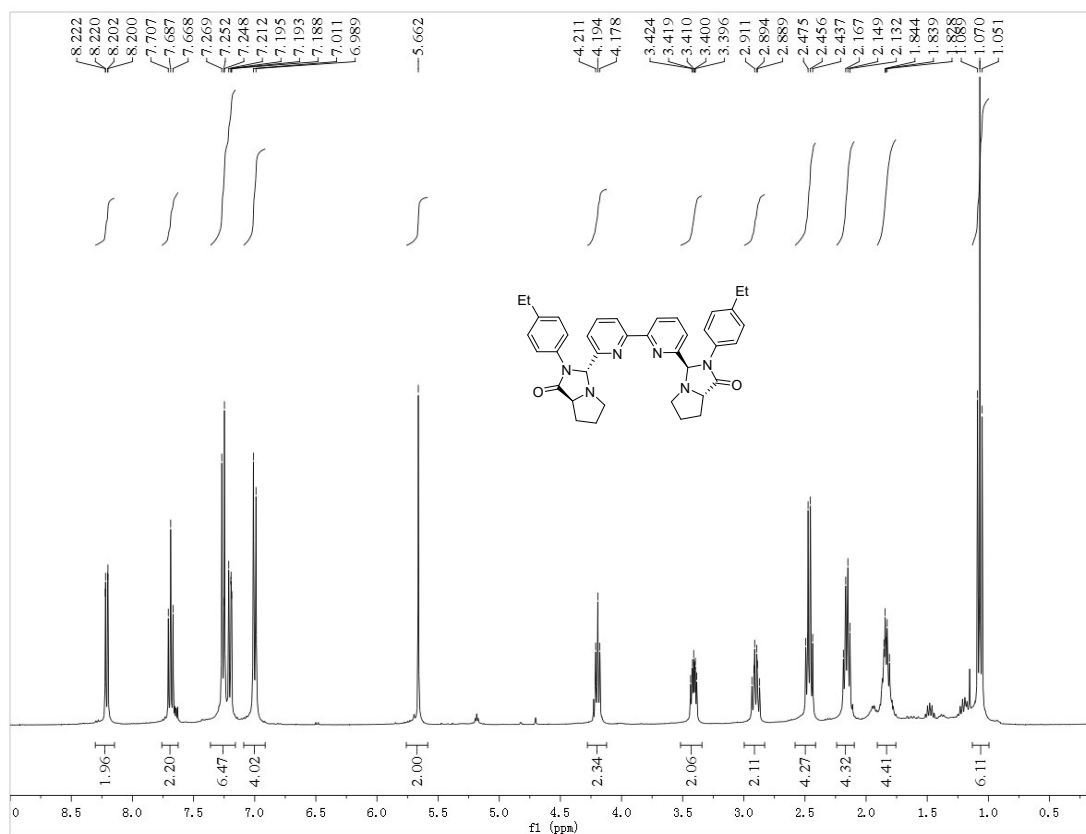
# $^1\text{H}$ and $^{13}\text{C}$ NMR of L11



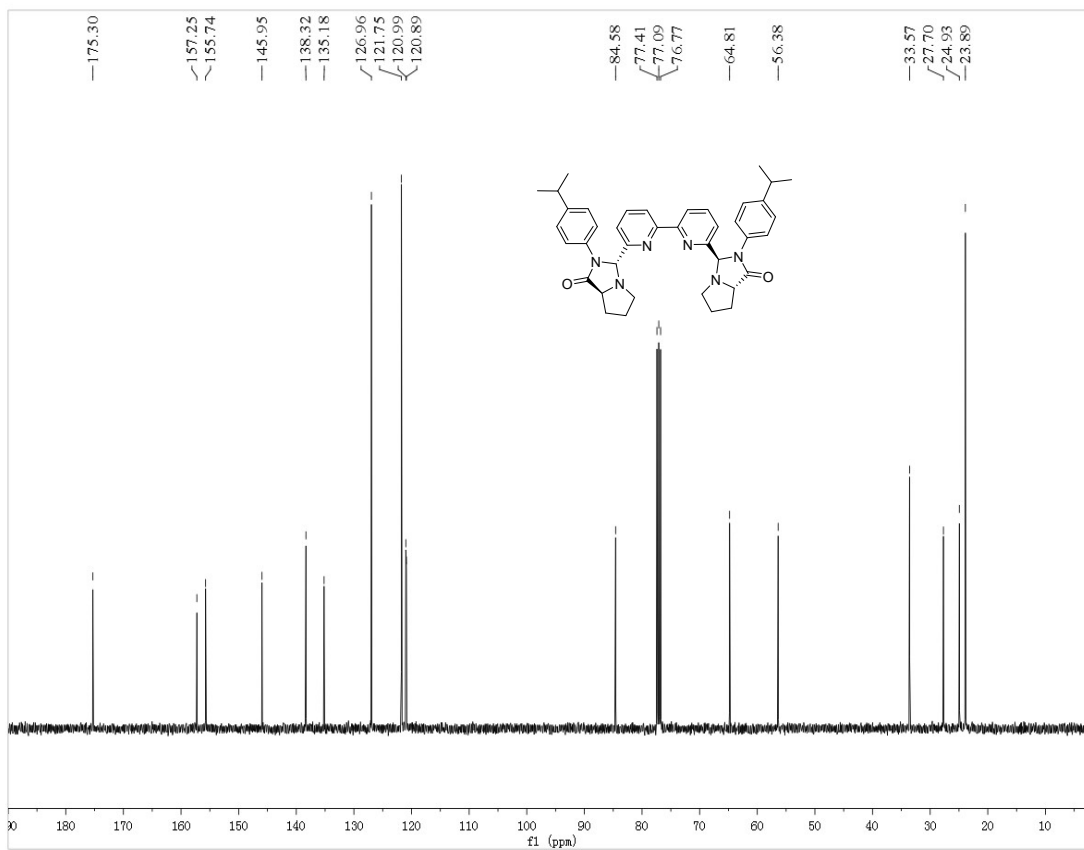
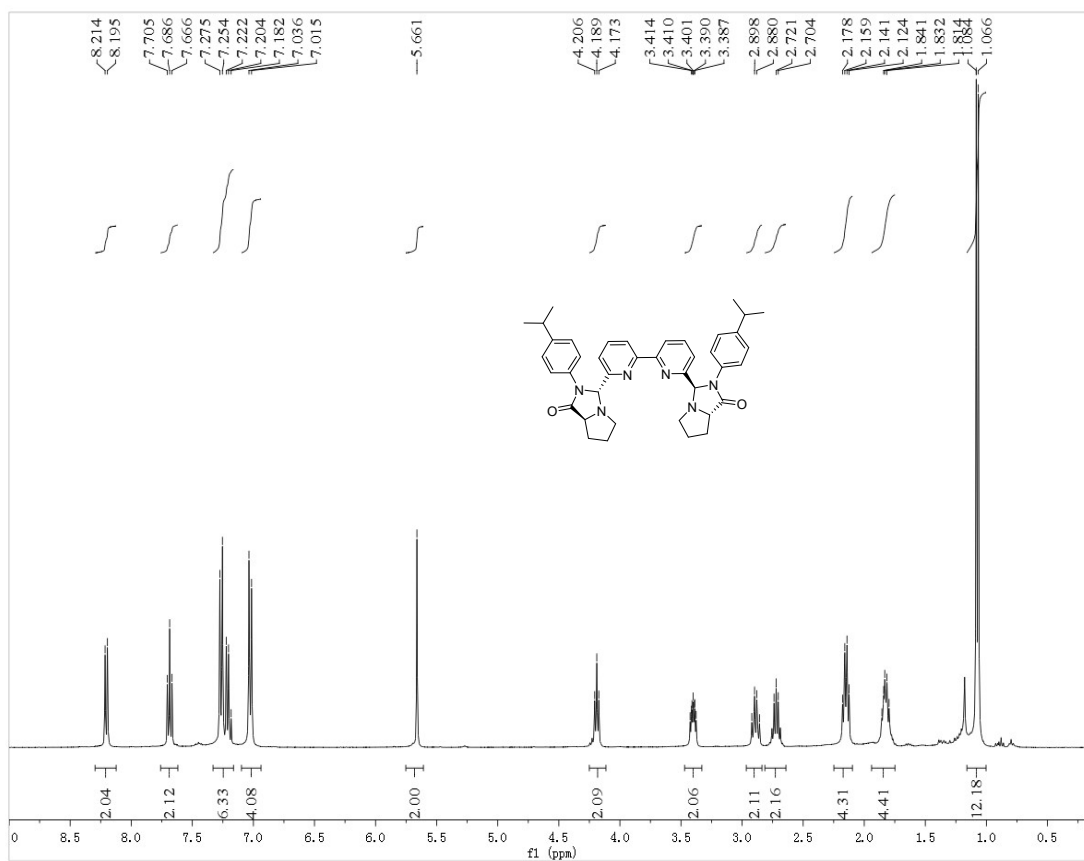
# <sup>1</sup>H and <sup>13</sup>C NMR of L1m



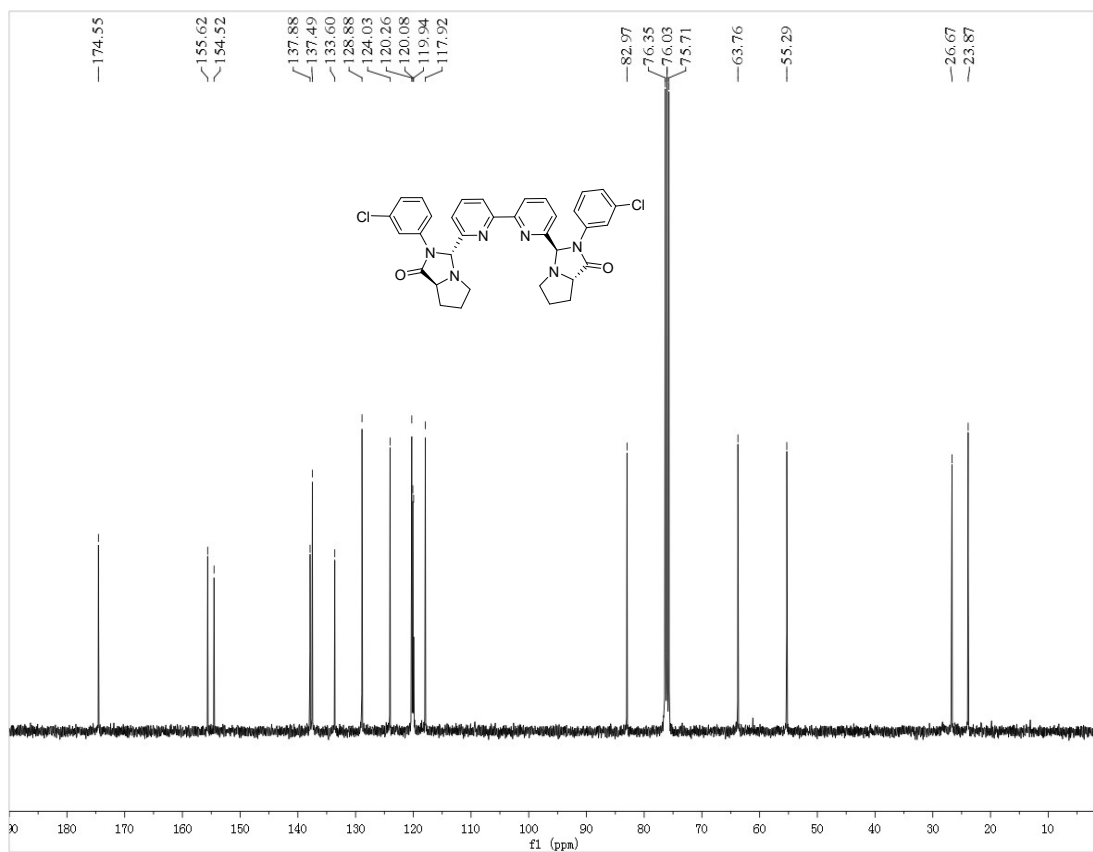
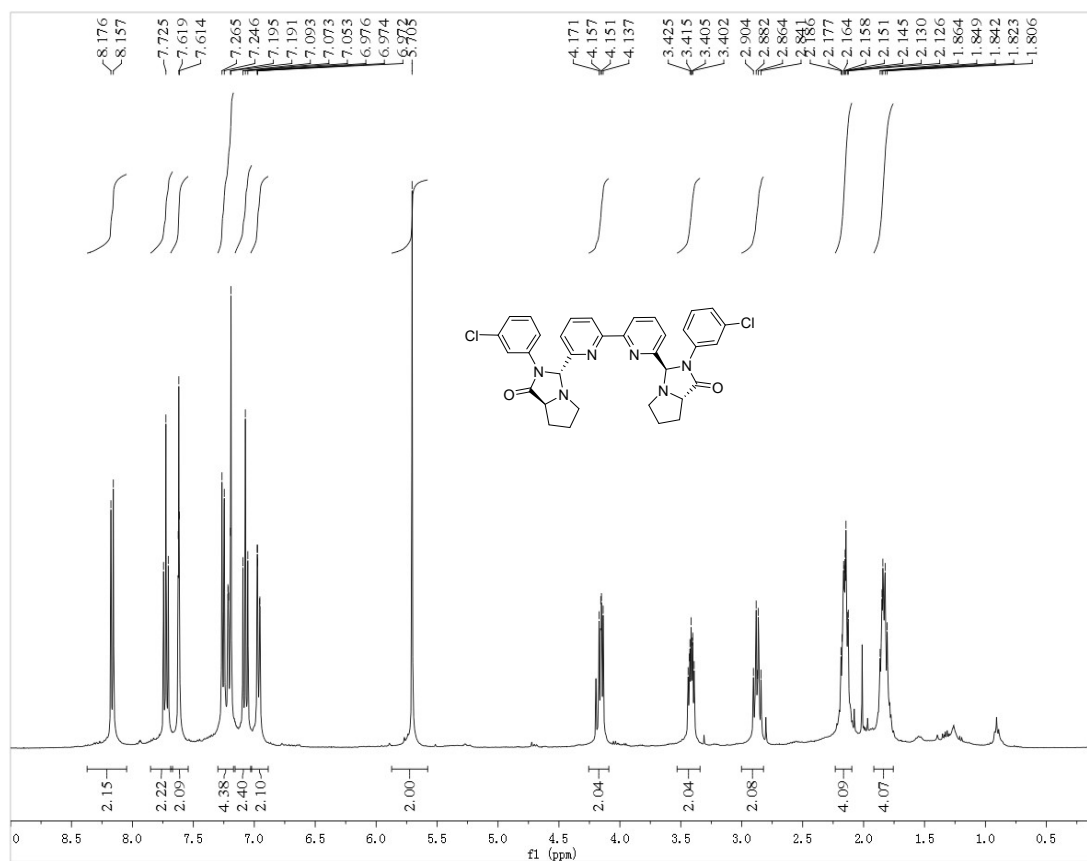
# <sup>1</sup>H and <sup>13</sup>C NMR of L1n



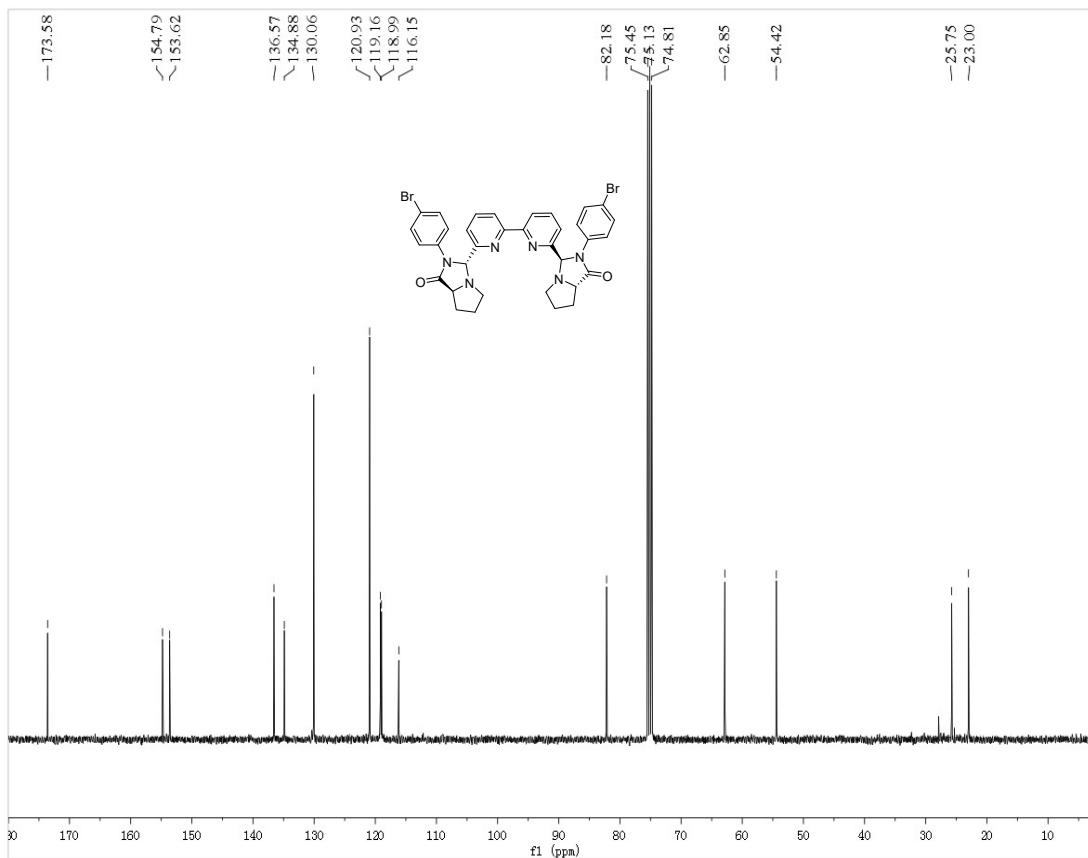
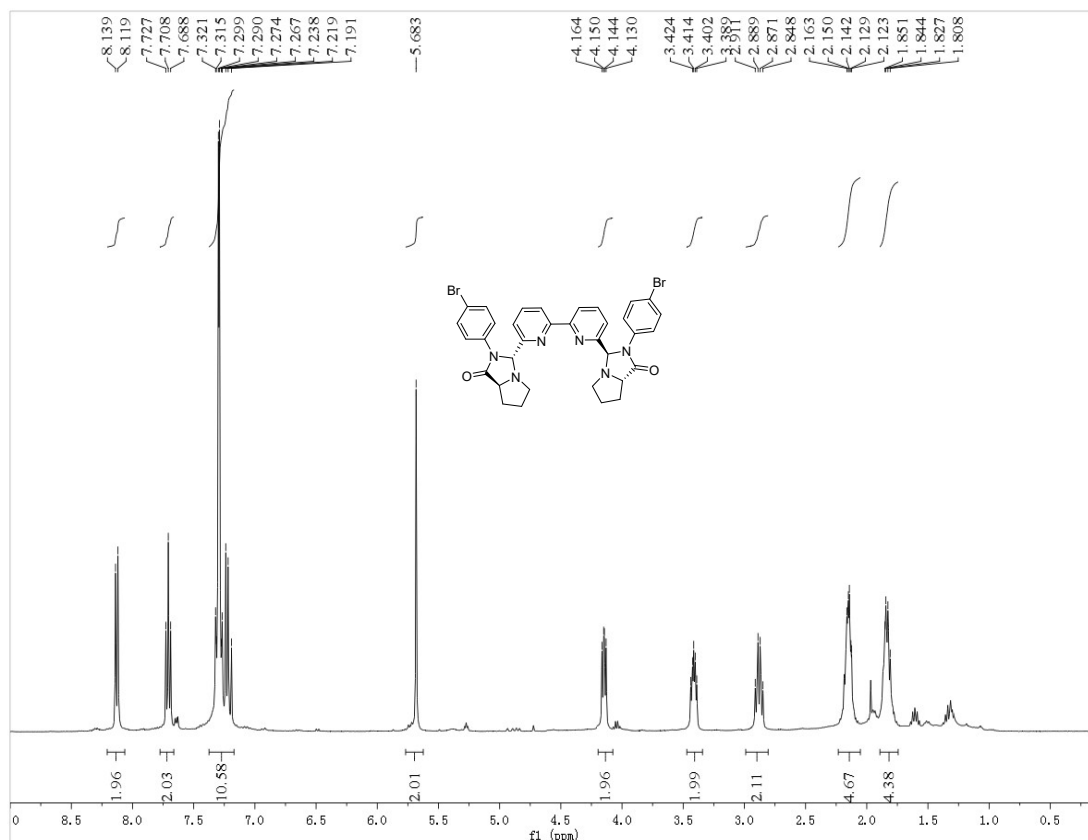
# <sup>1</sup>H and <sup>13</sup>C NMR of L10



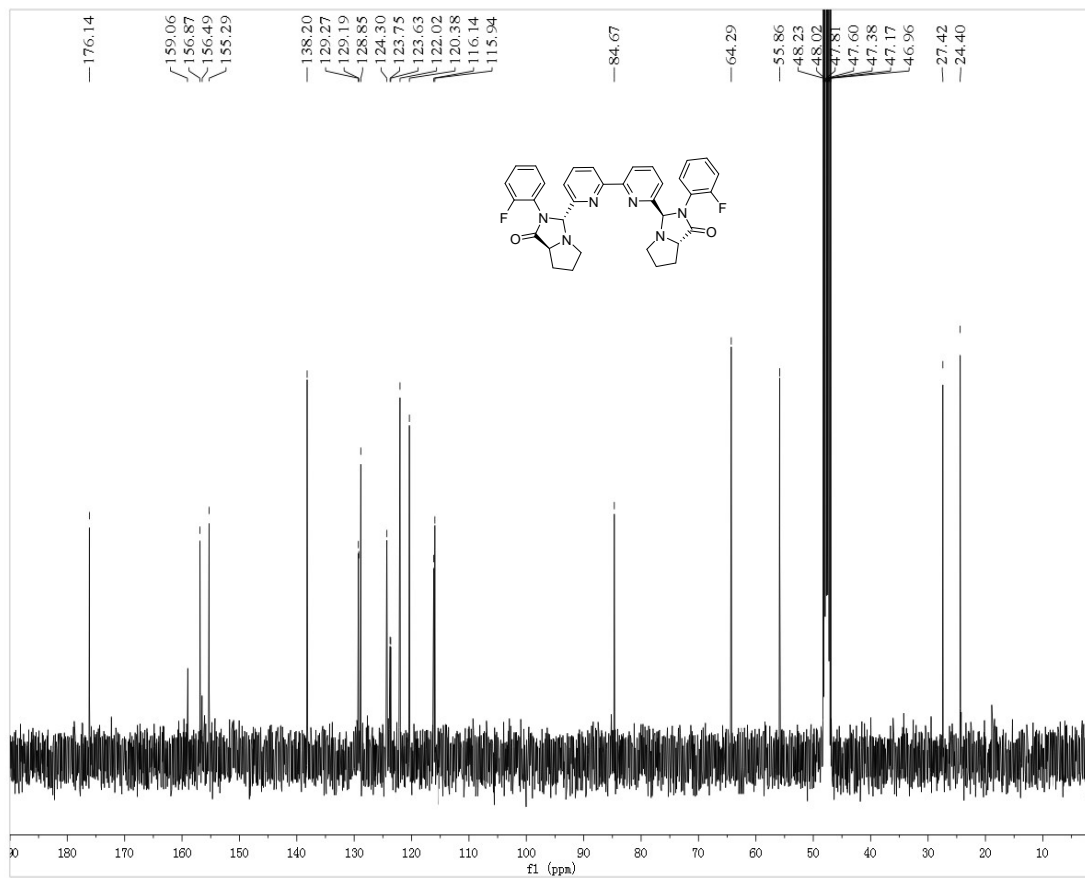
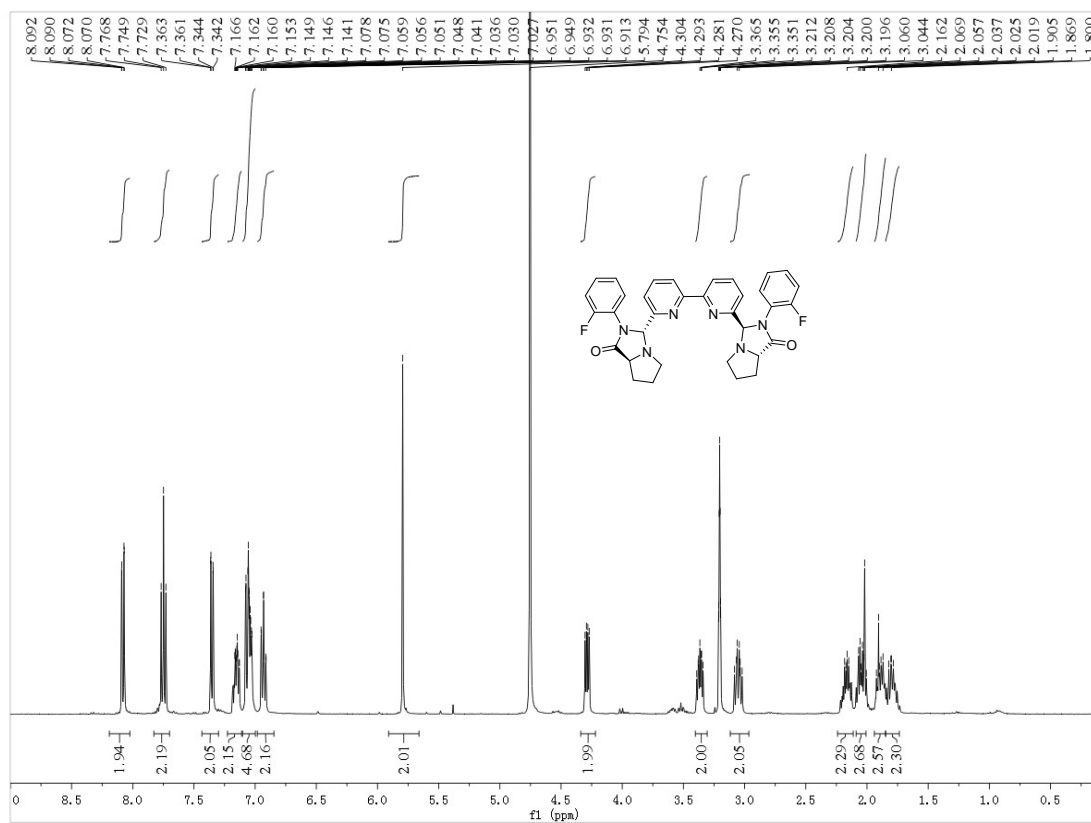
# <sup>1</sup>H and <sup>13</sup>C NMR of L1p



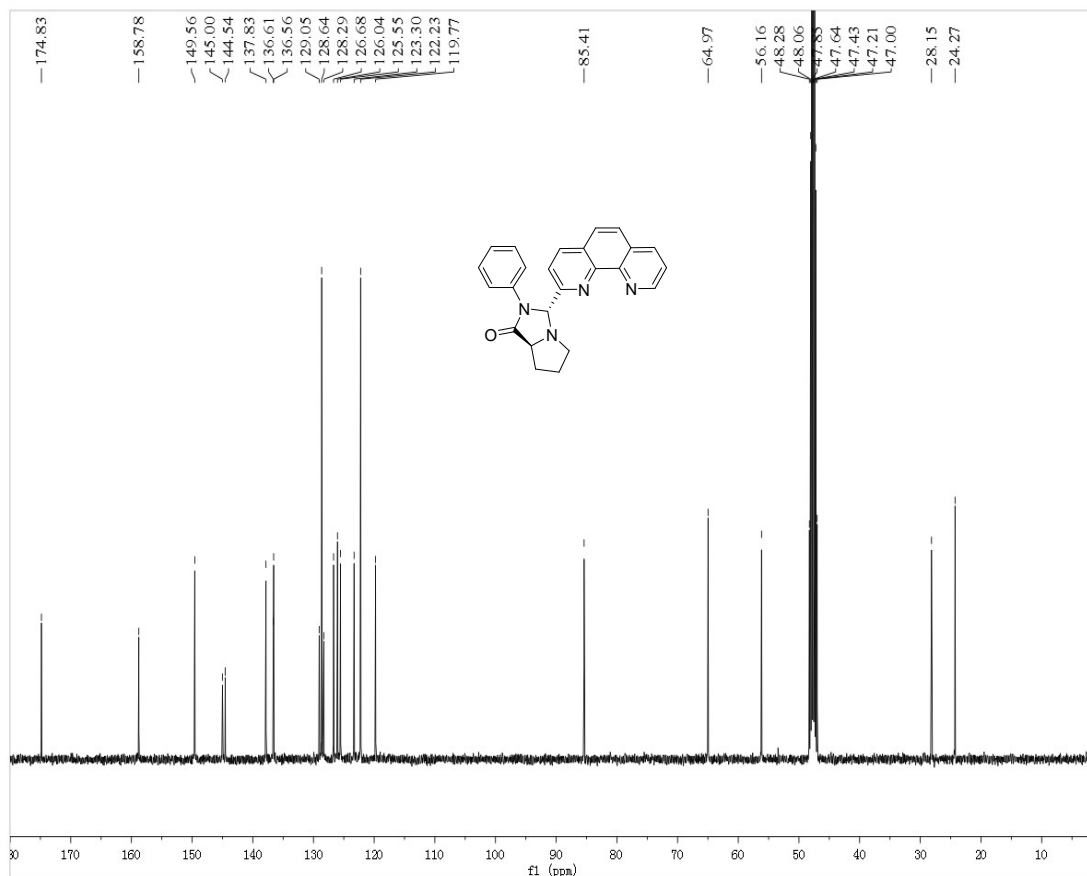
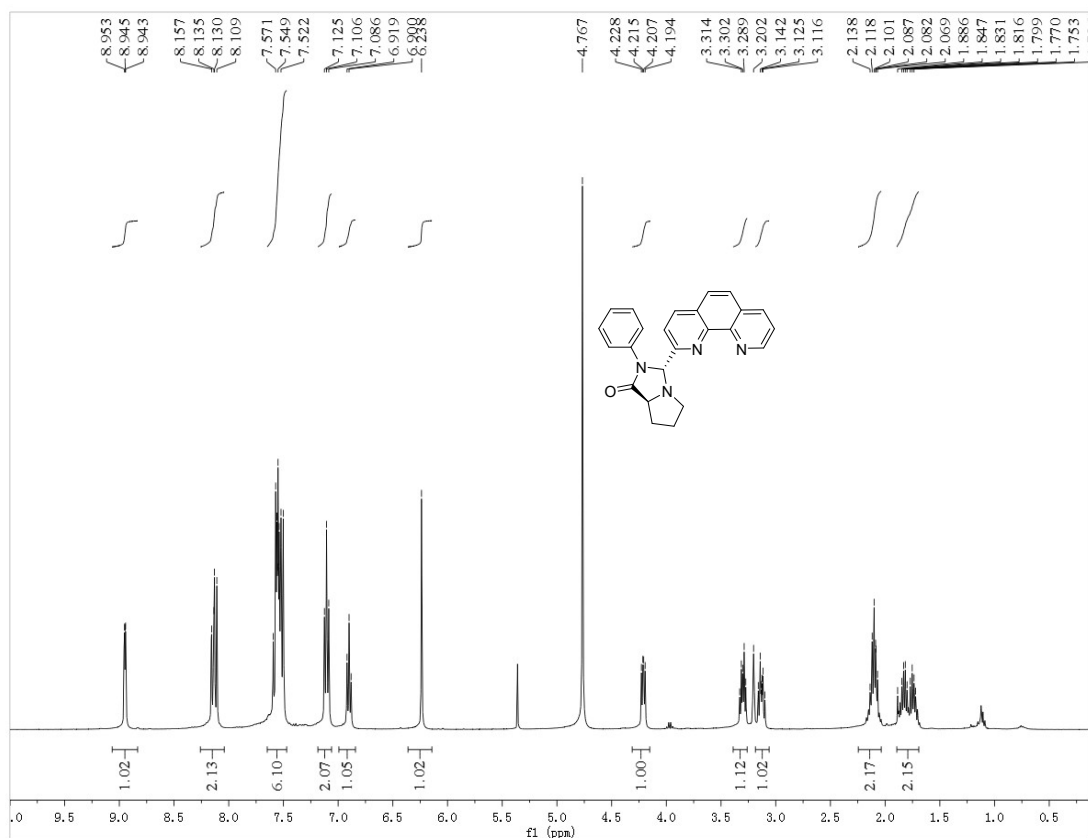
# <sup>1</sup>H and <sup>13</sup>C NMR of L1q



# <sup>1</sup>H and <sup>13</sup>C NMR of L1r

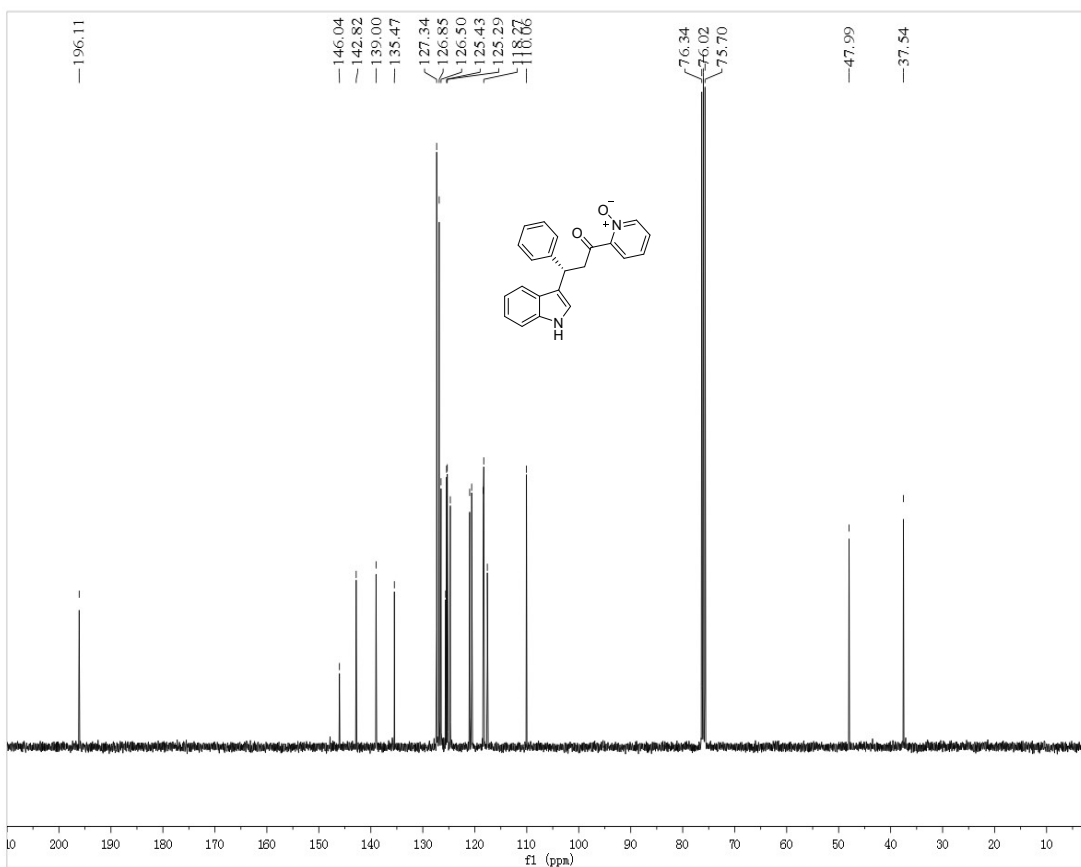
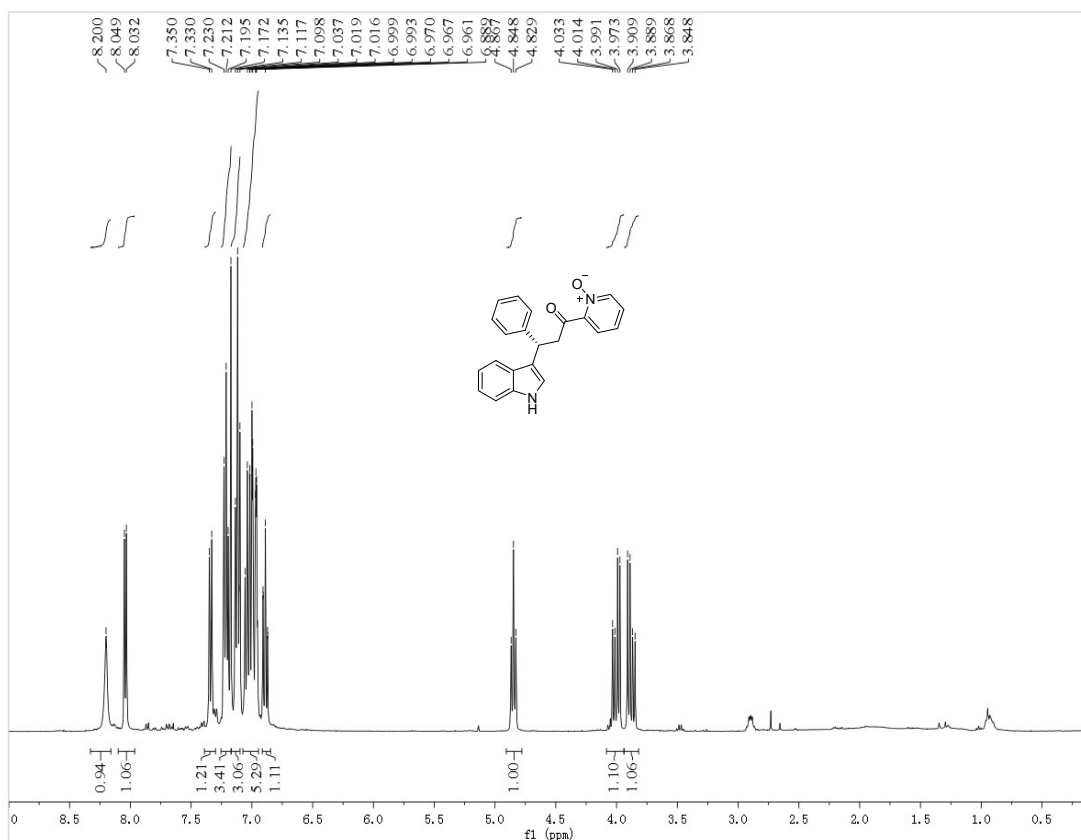


# <sup>1</sup>H and <sup>13</sup>C NMR of L5a

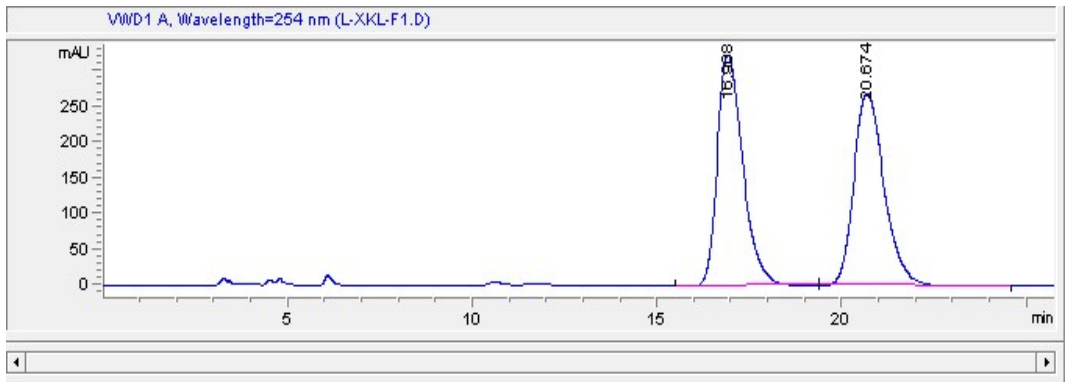




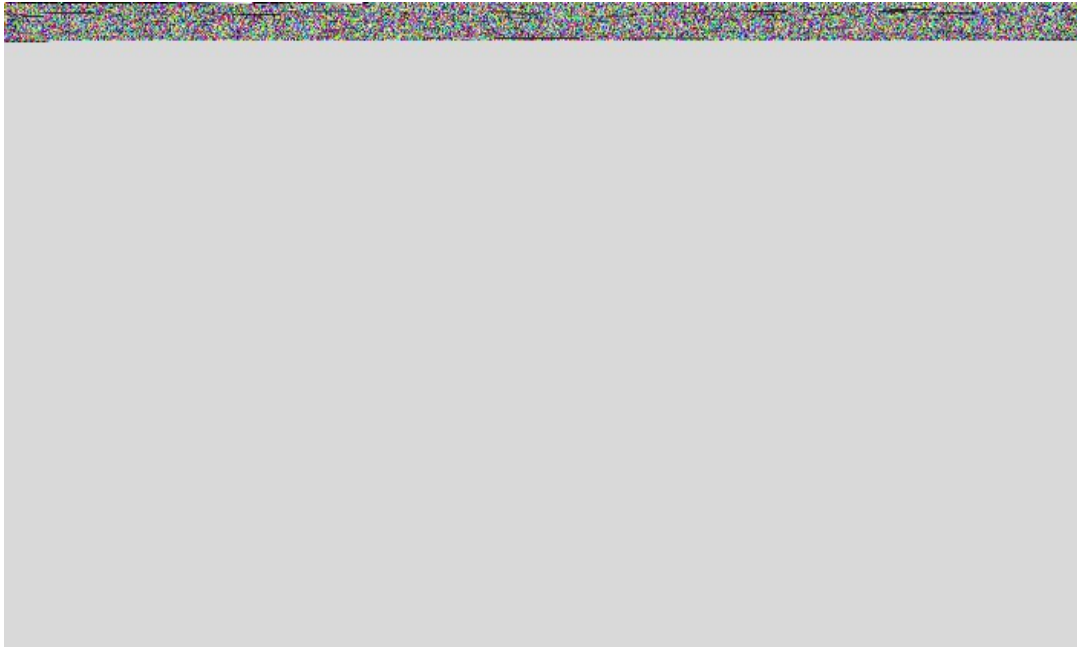
# <sup>1</sup>H and <sup>13</sup>C NMR of 6aa



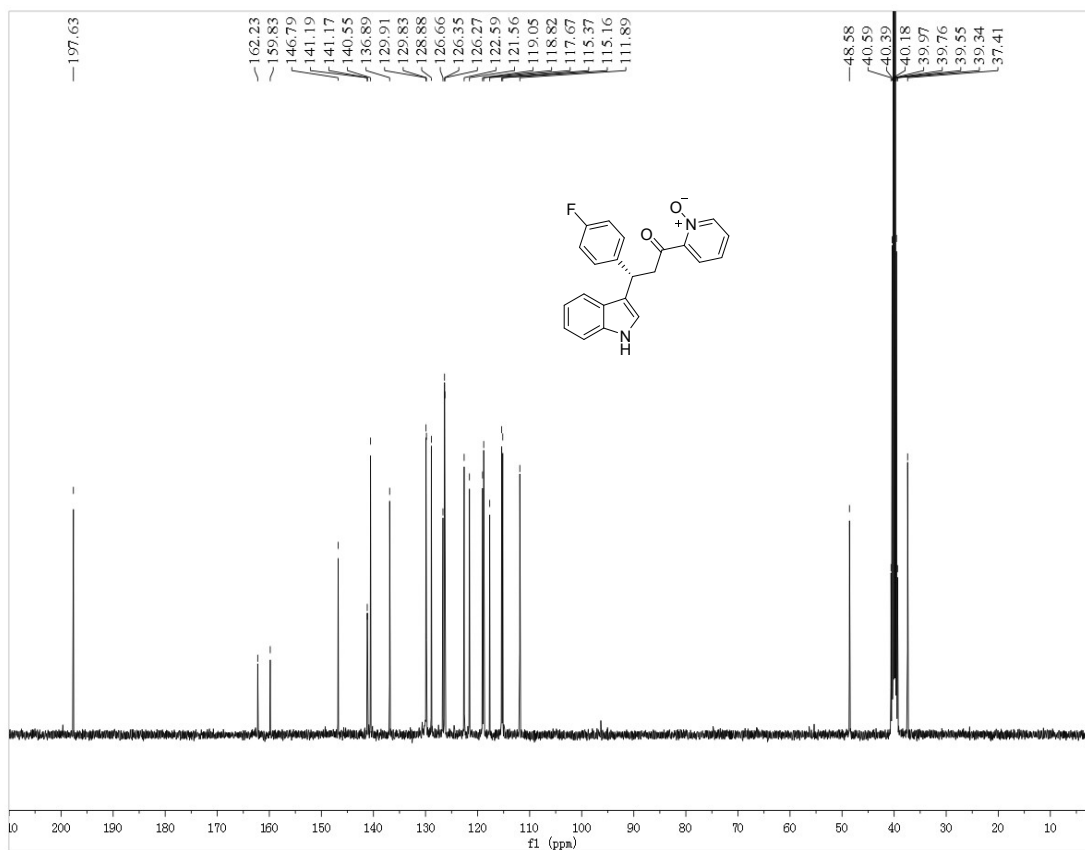
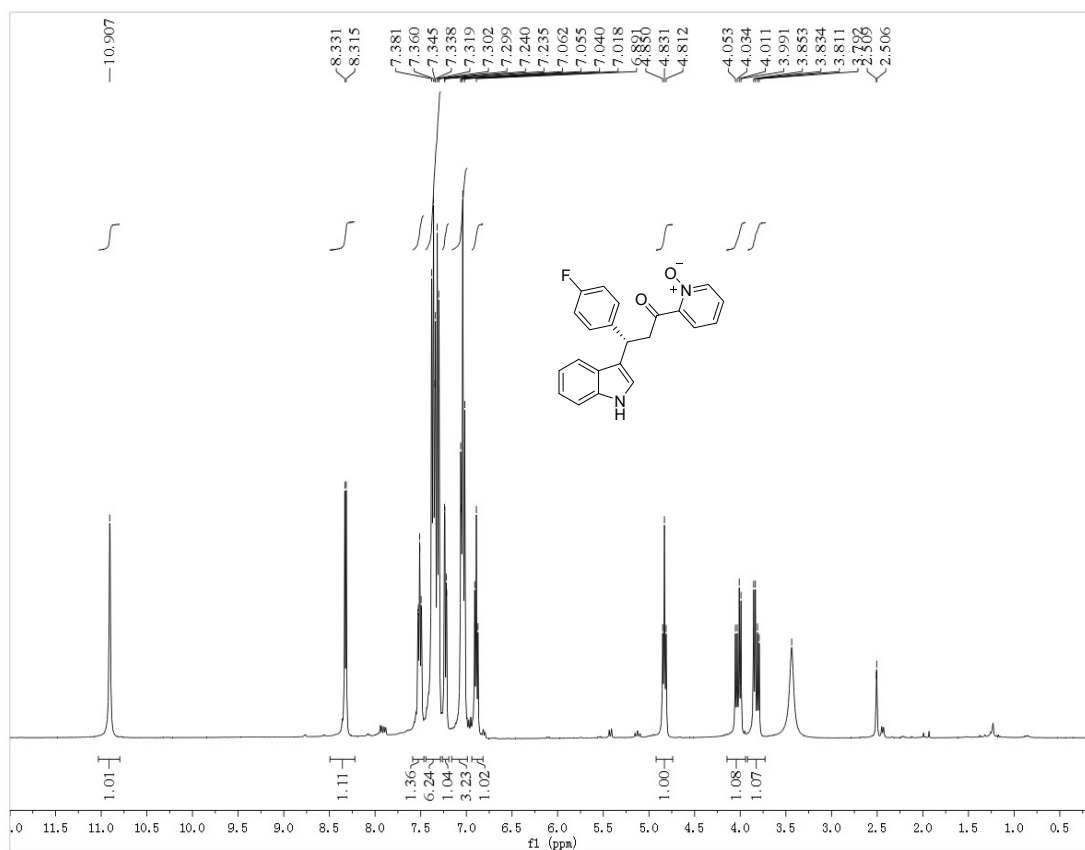
## HPLC of 6aa



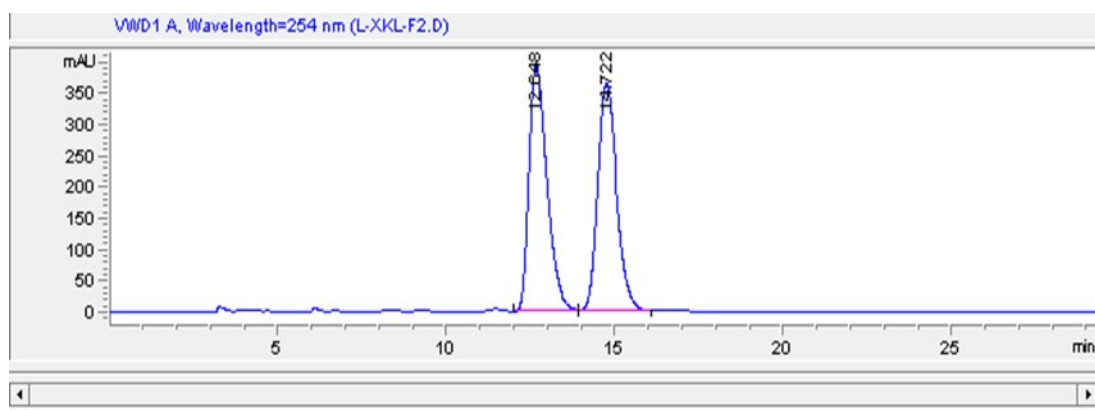
#	Time	Area	Height	Width	Area%	Symmetry
1	16.908	15469.6	322.8	0.7311	50.175	0.684
2	20.674	15361.4	269	0.8823	49.825	0.746



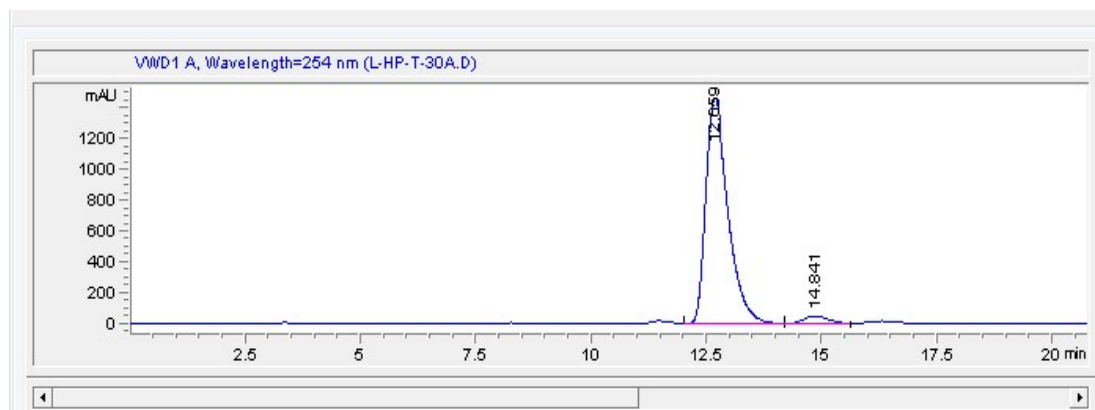
### <sup>1</sup>H and <sup>13</sup>C NMR of 6ab



## HPLC of 6ab

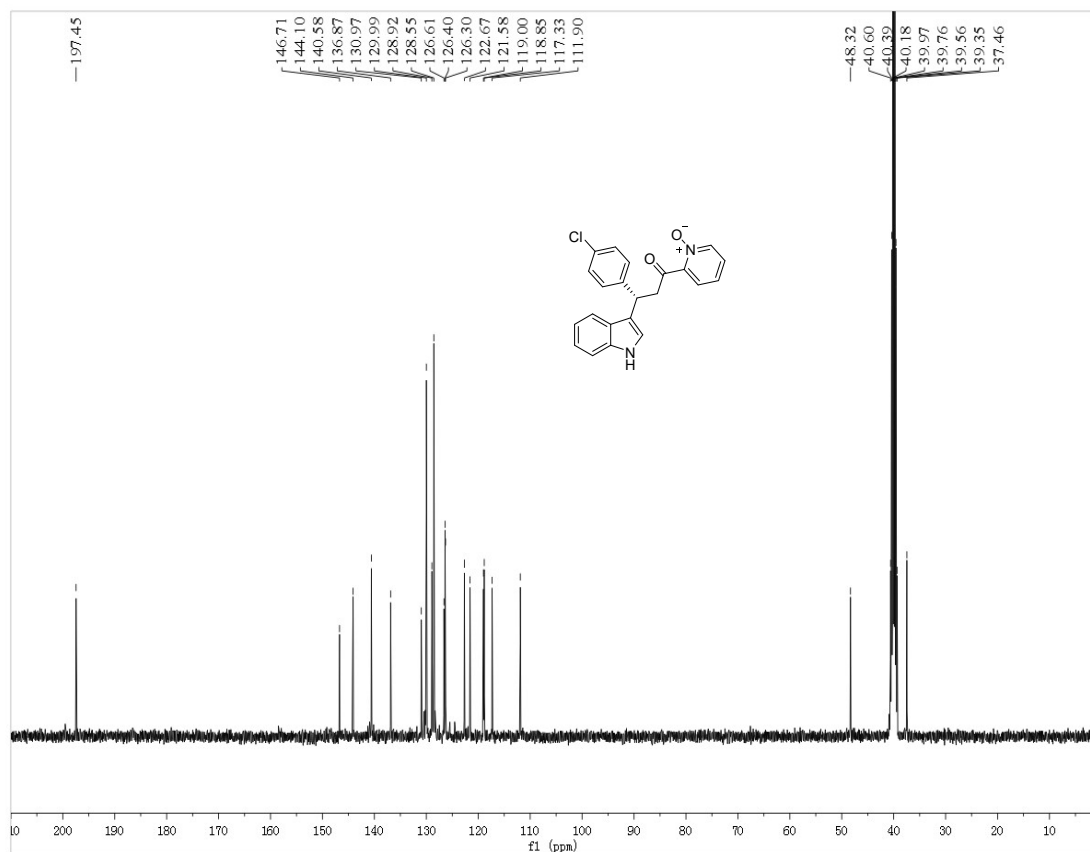
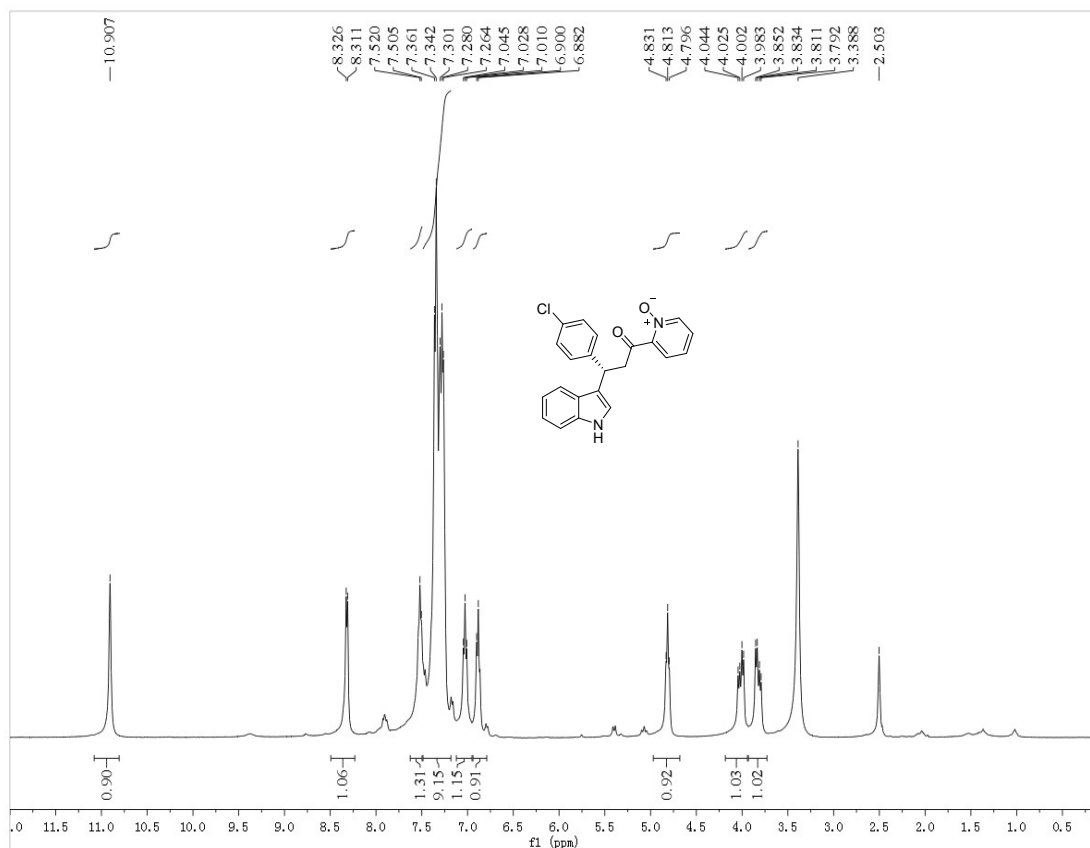


#	Time	Area	Height	Width	Area%	Symmetry
1	12.648	14400.3	396.7	0.5545	49.968	0.617
2	14.722	14418.9	365.4	0.6134	50.032	0.759

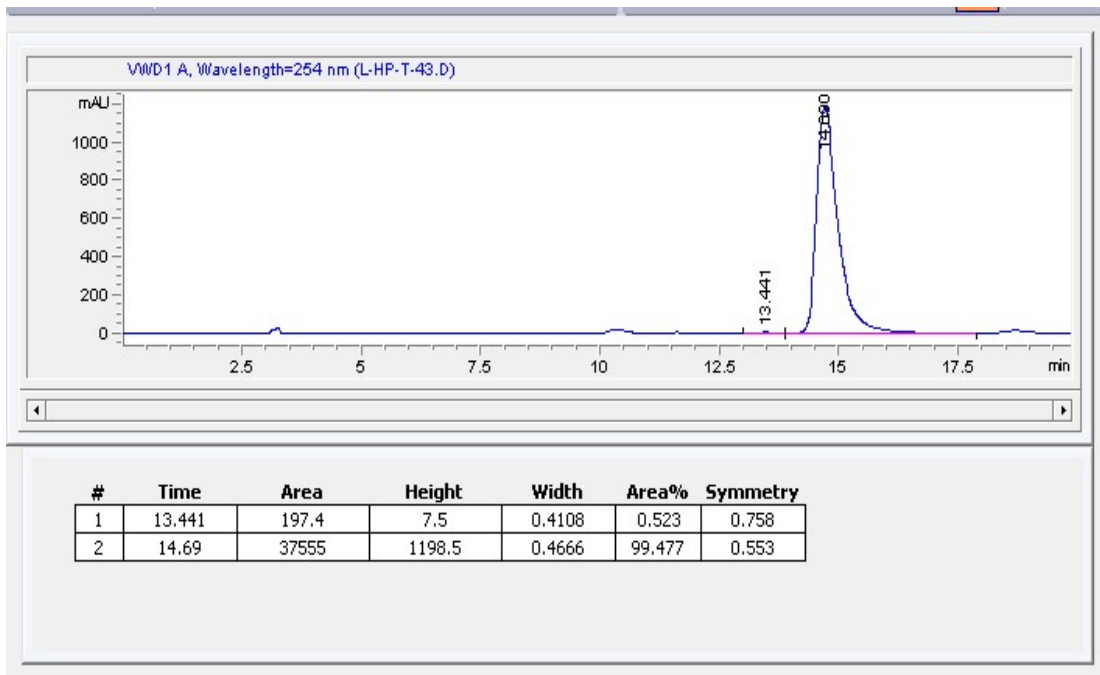
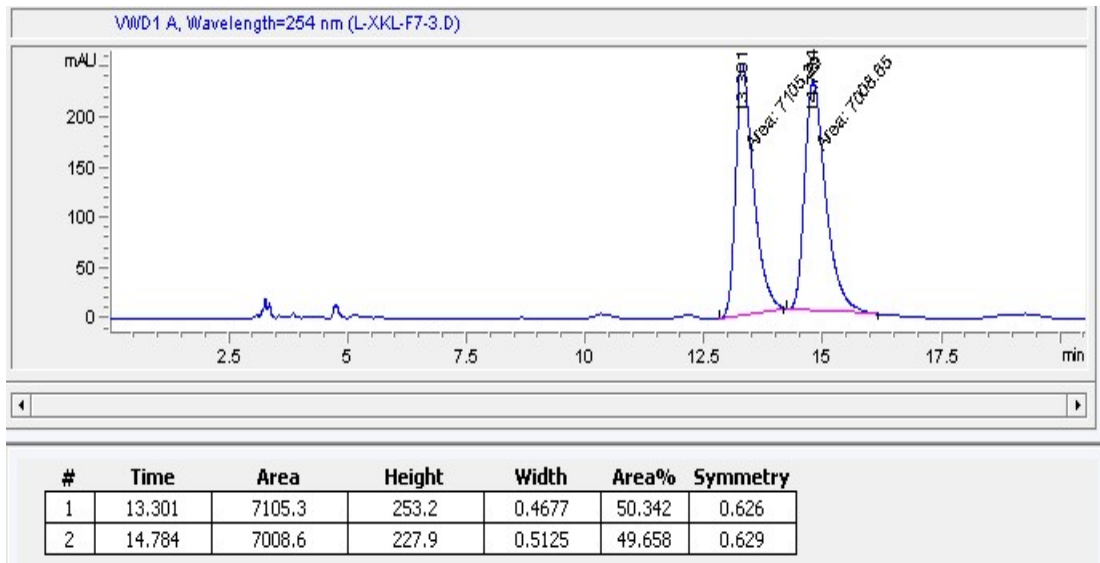


#	Time	Area	Height	Width	Area%	Symmetry
1	12.659	50583.1	1469.2	0.5257	96.257	0.603
2	14.841	1967.1	51.6	0.5889	3.743	0.866

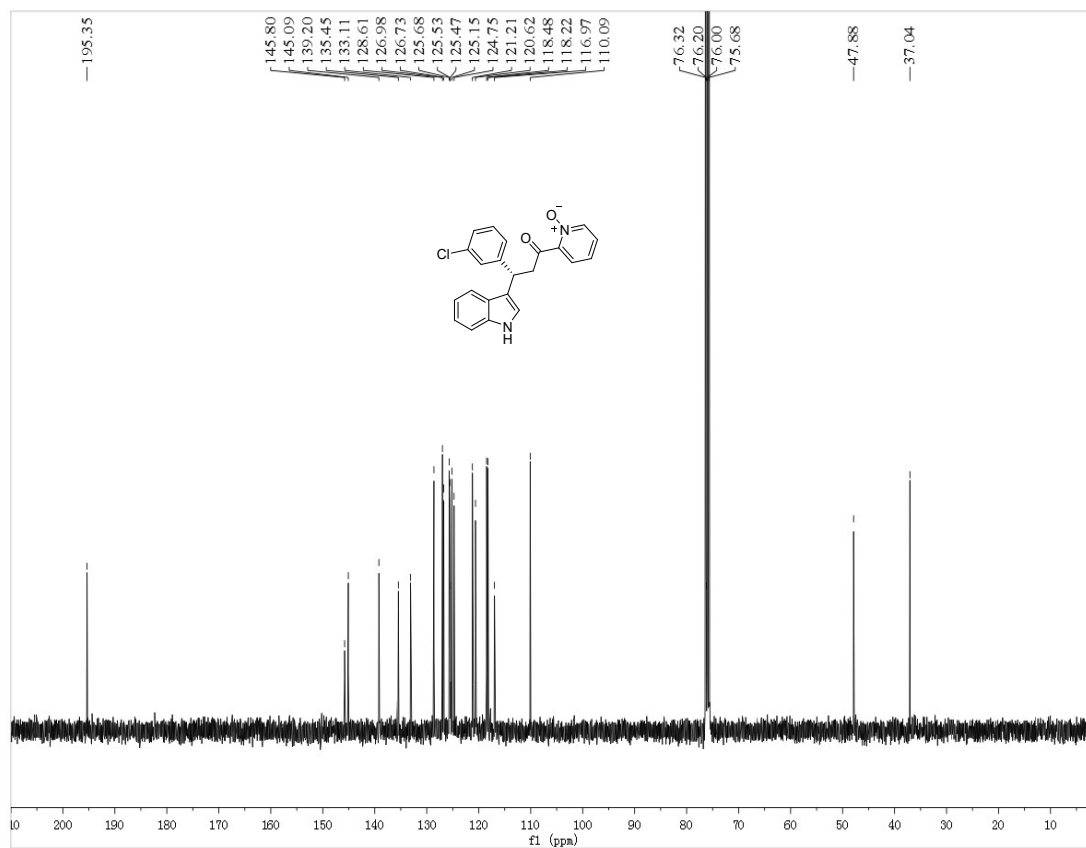
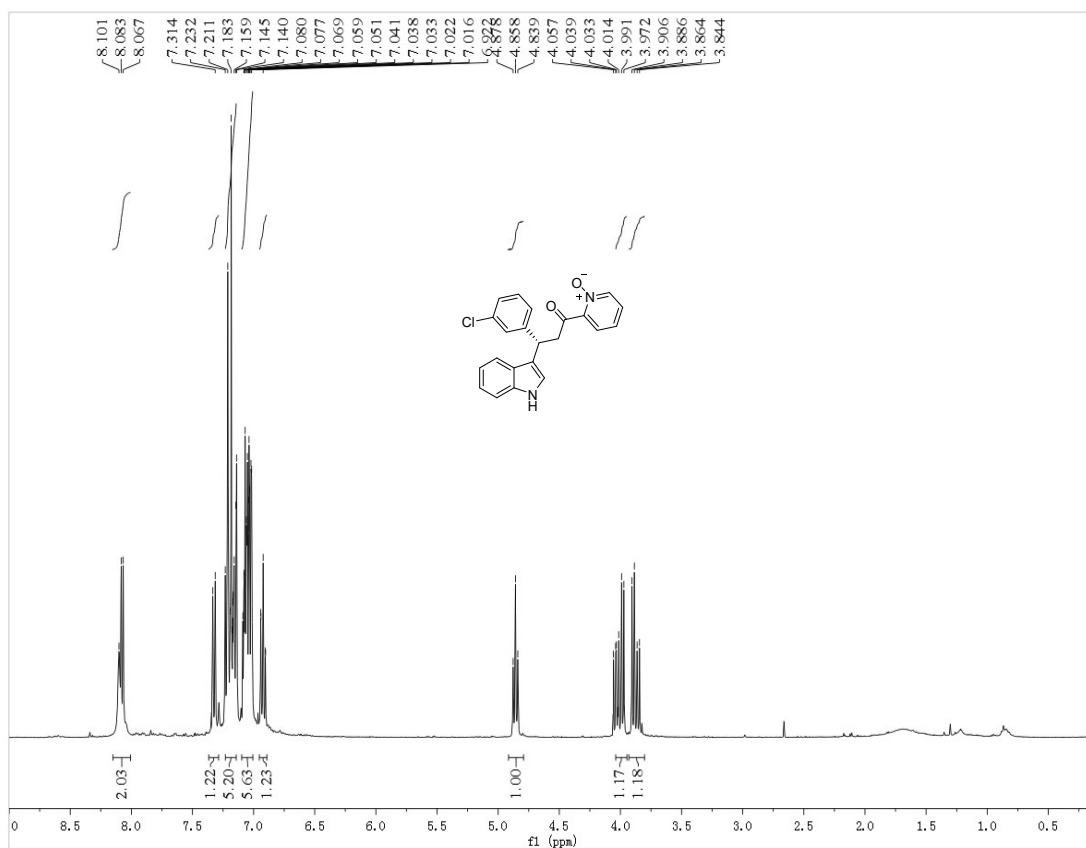
# <sup>1</sup>H and <sup>13</sup>C NMR of 6ac



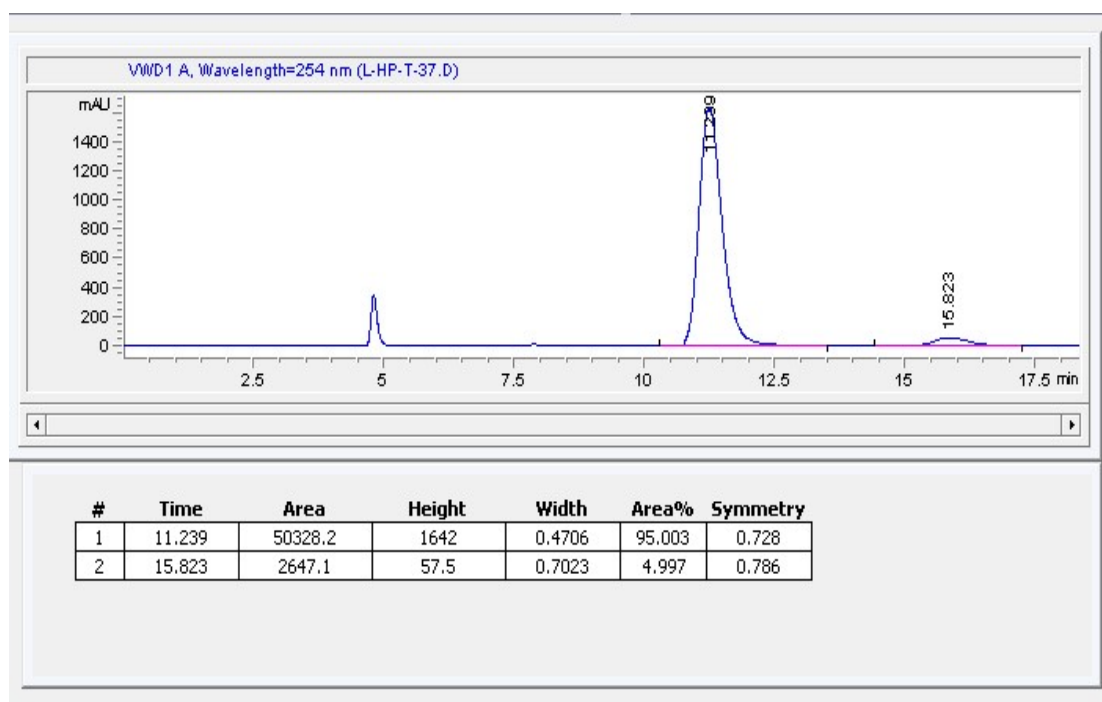
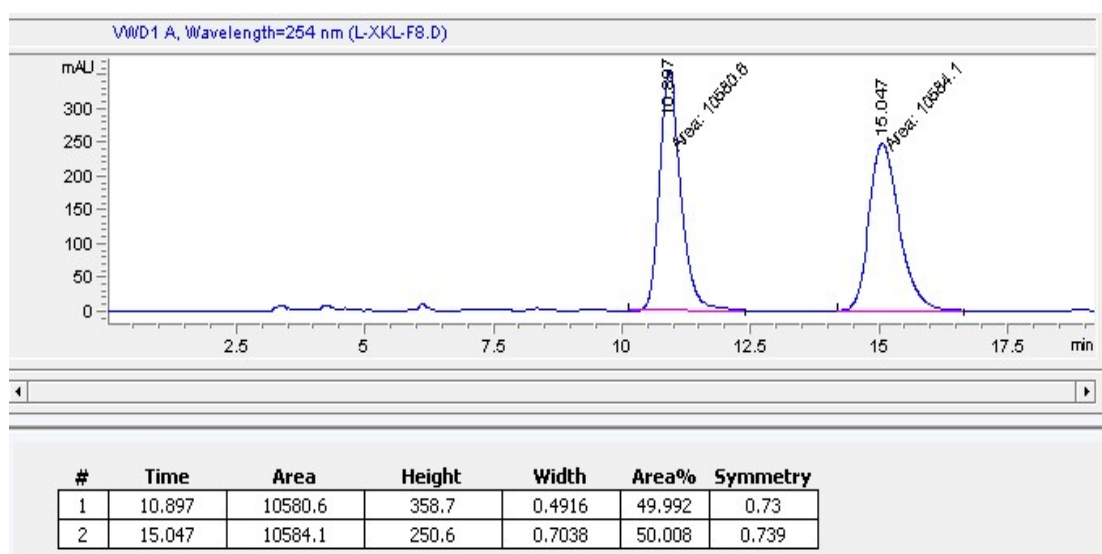
## HPLC of 6ac



# <sup>1</sup>H and <sup>13</sup>C NMR of 6ad

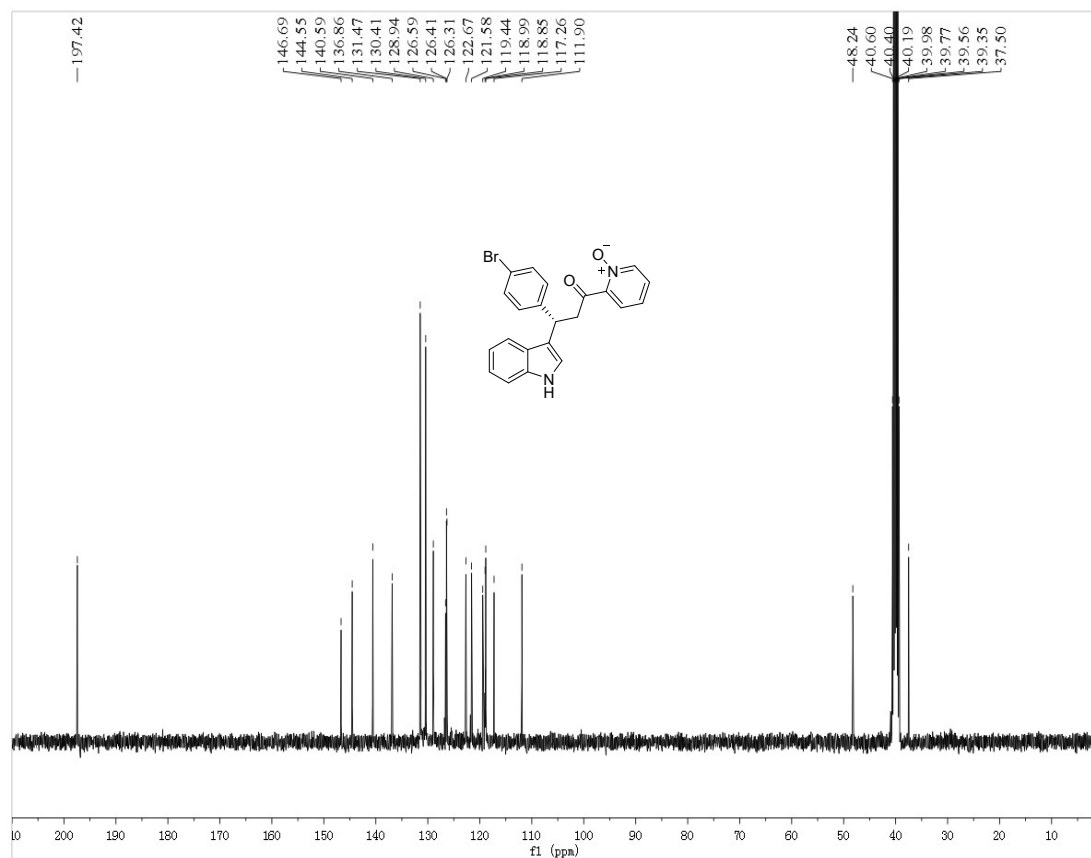
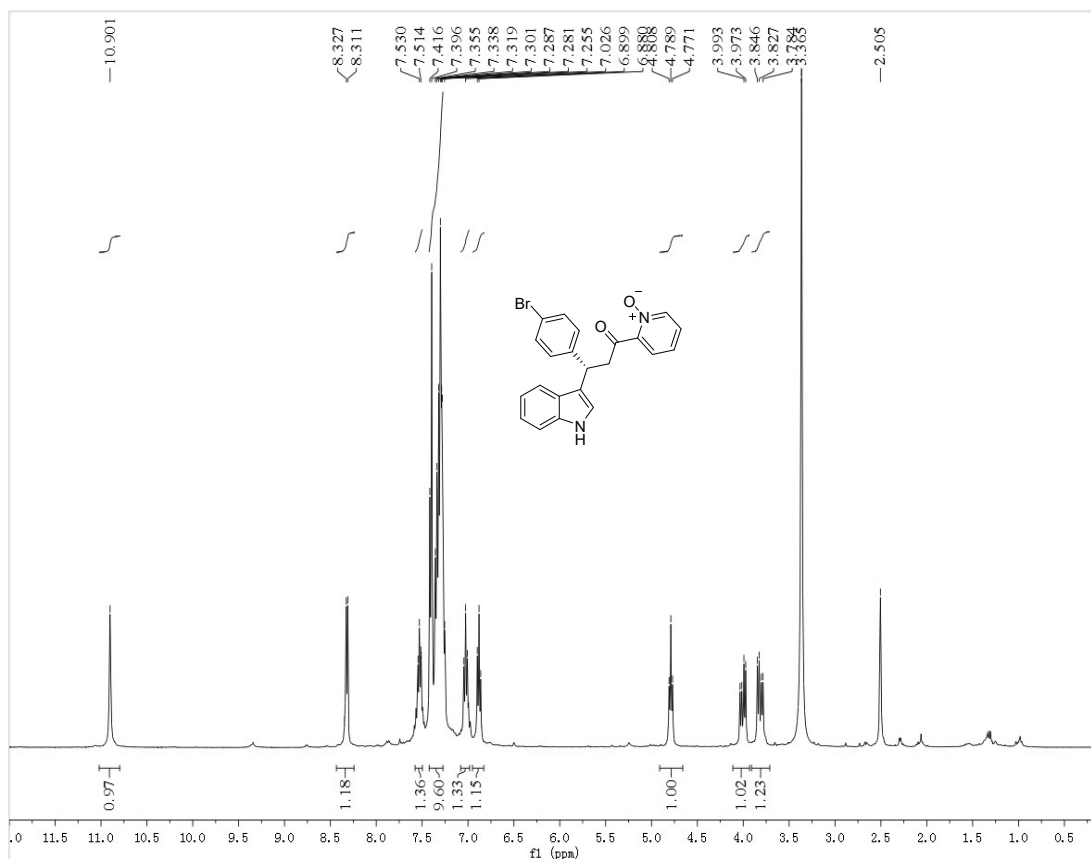


## HPLC of 6ad

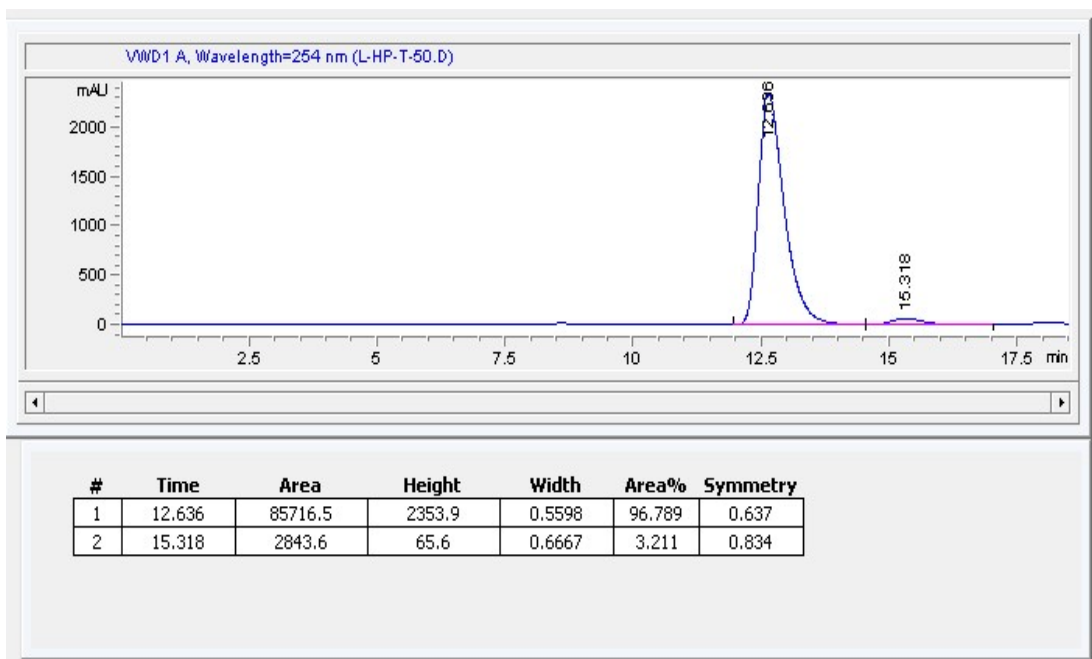
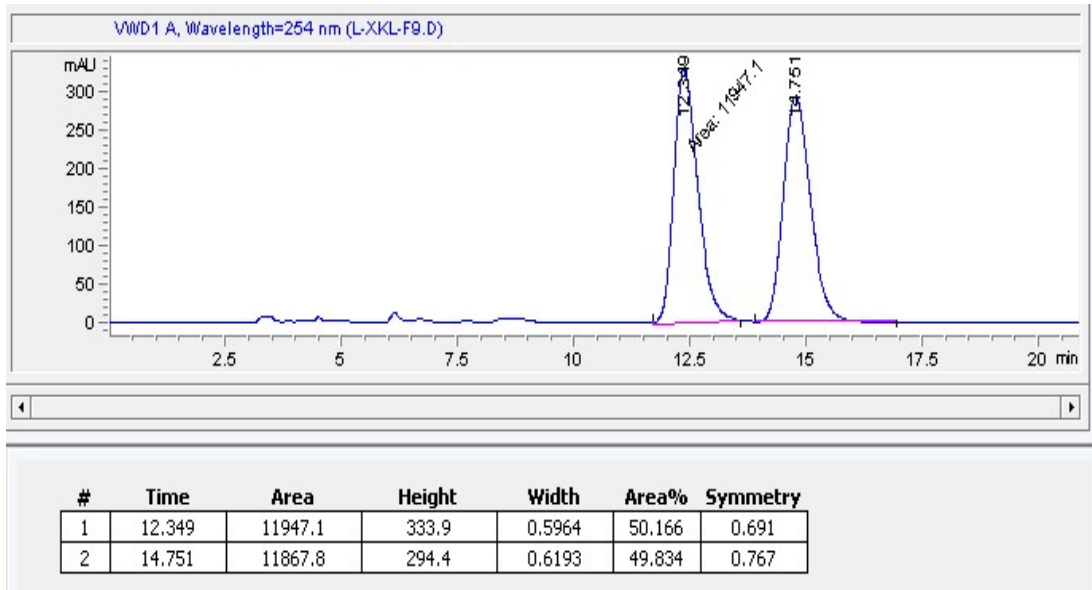




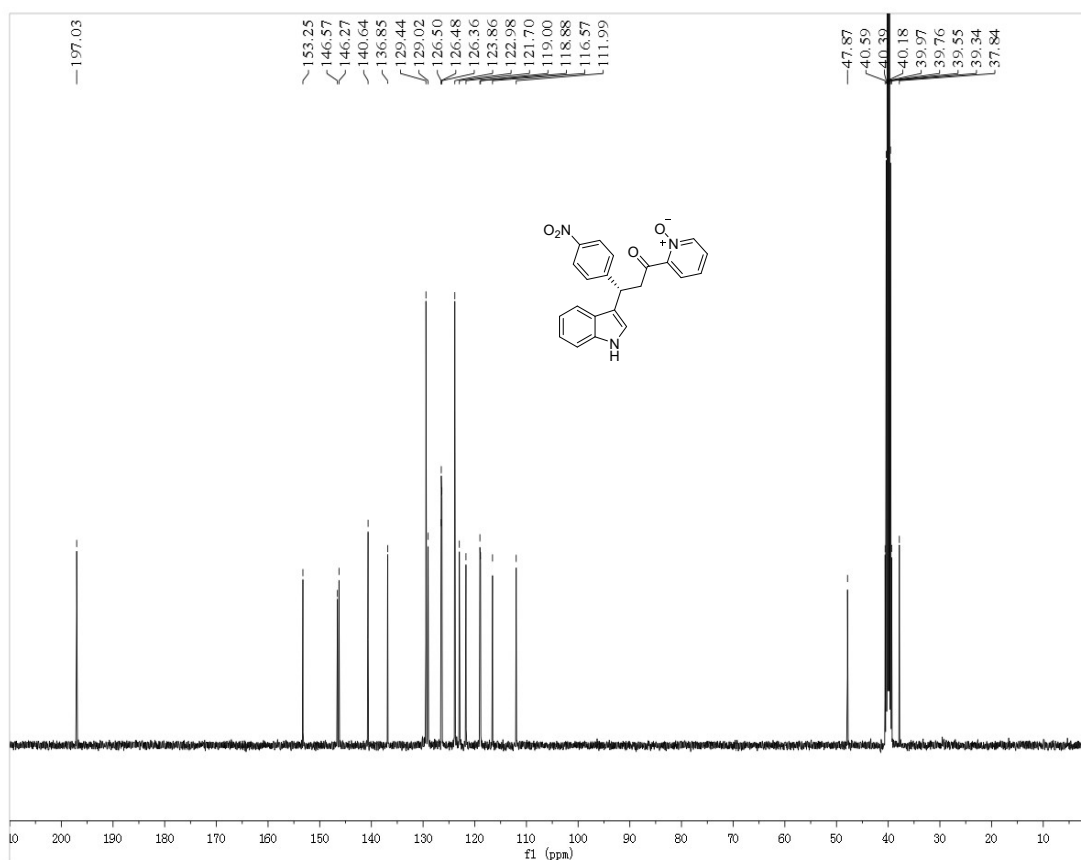
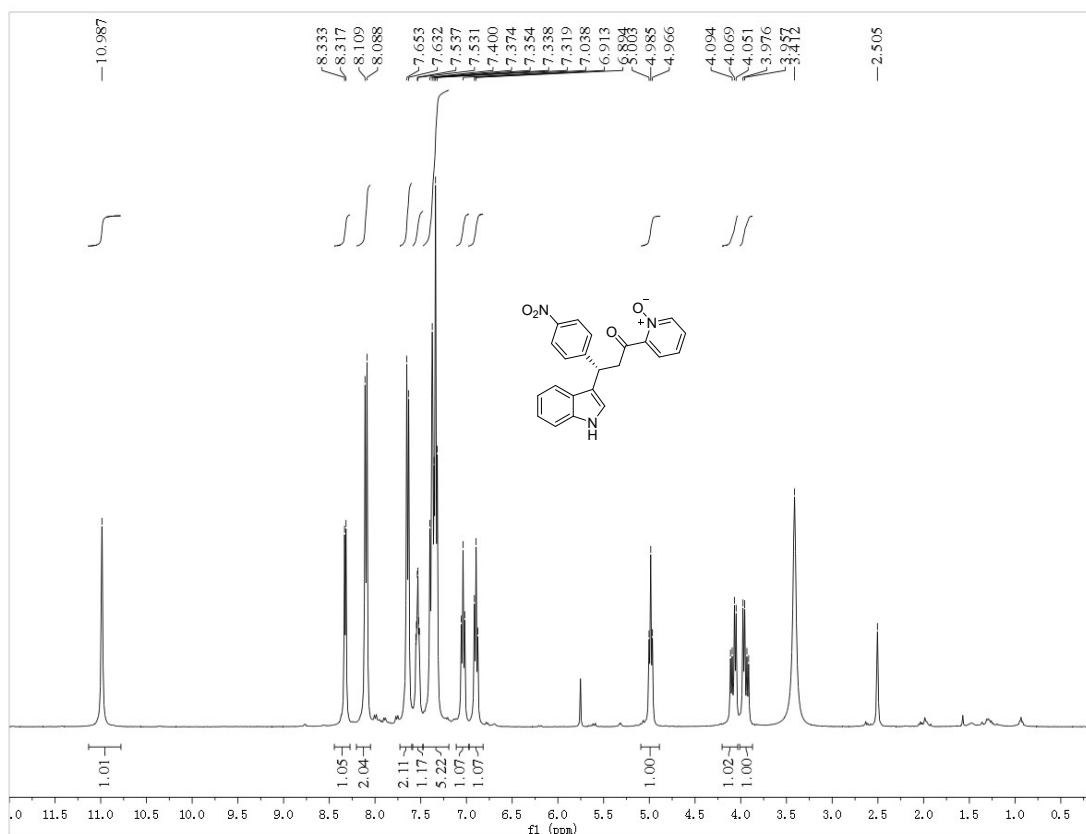
# <sup>1</sup>H and <sup>13</sup>C NMR of 6ae



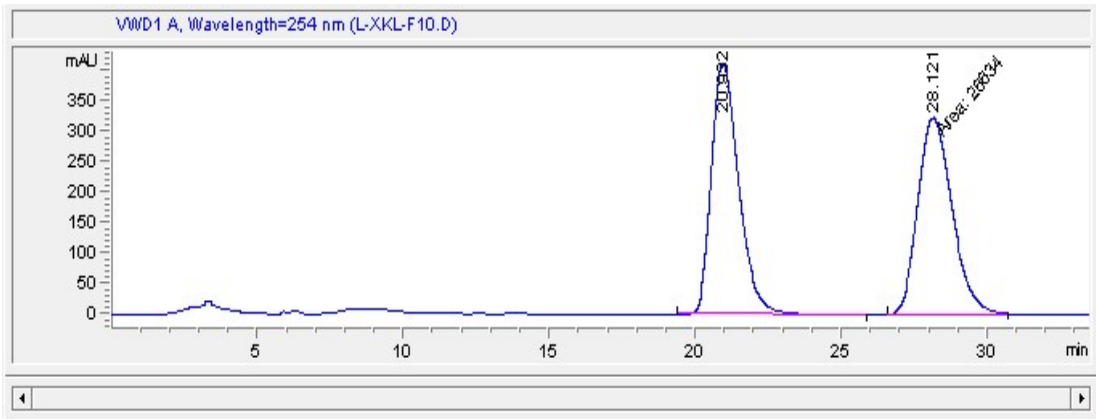
## HPLC of 6ae



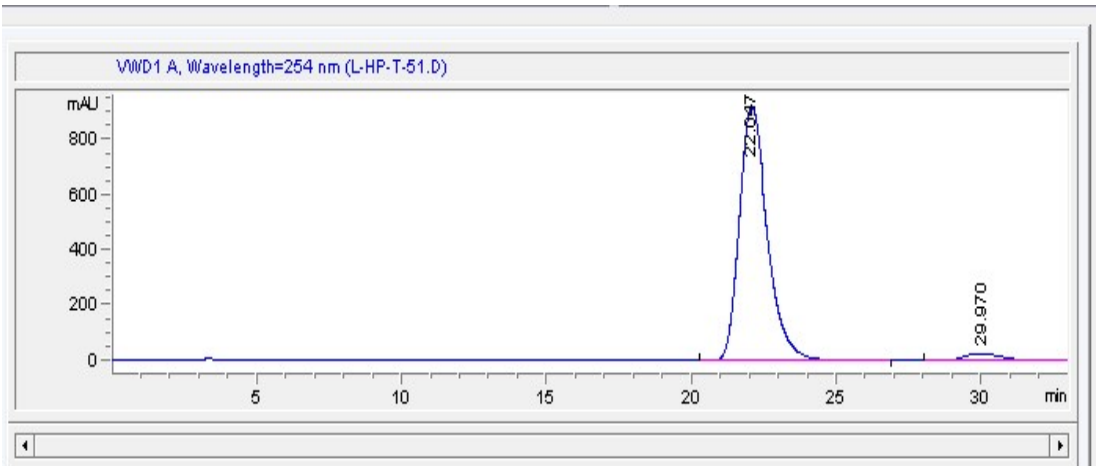
# <sup>1</sup>H and <sup>13</sup>C NMR of 6af



### HPLC of 6af

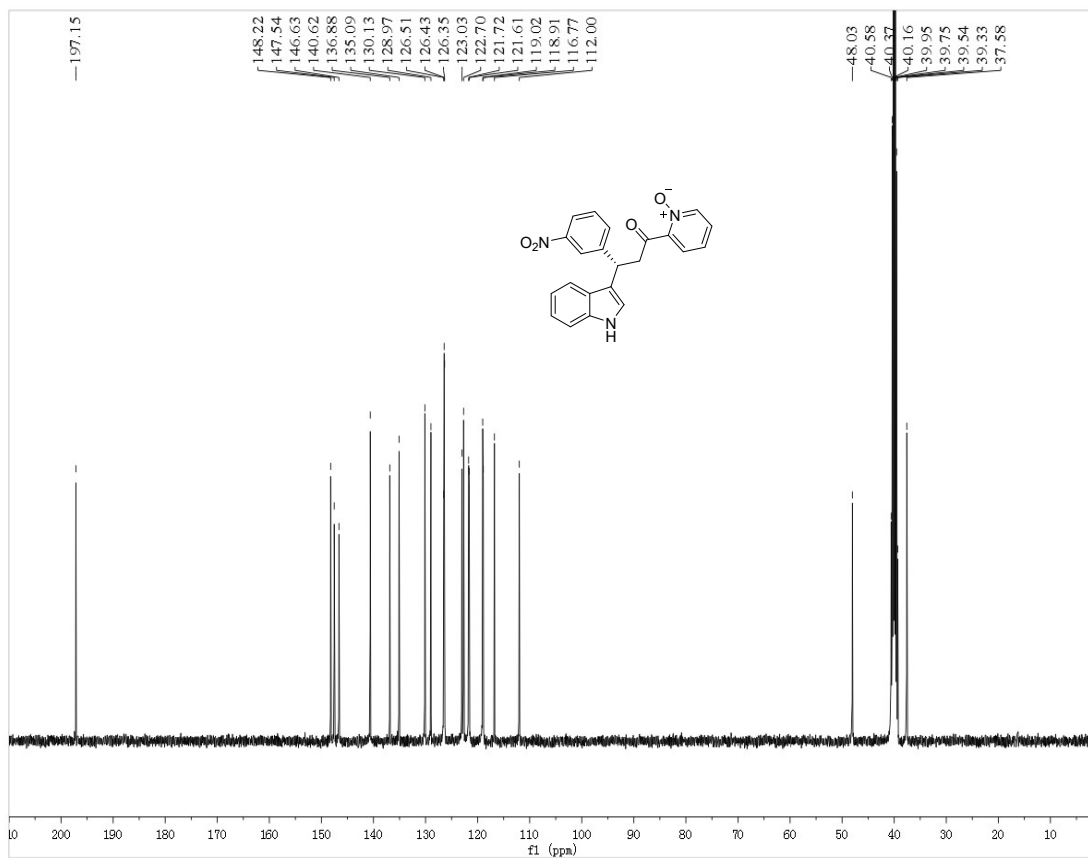
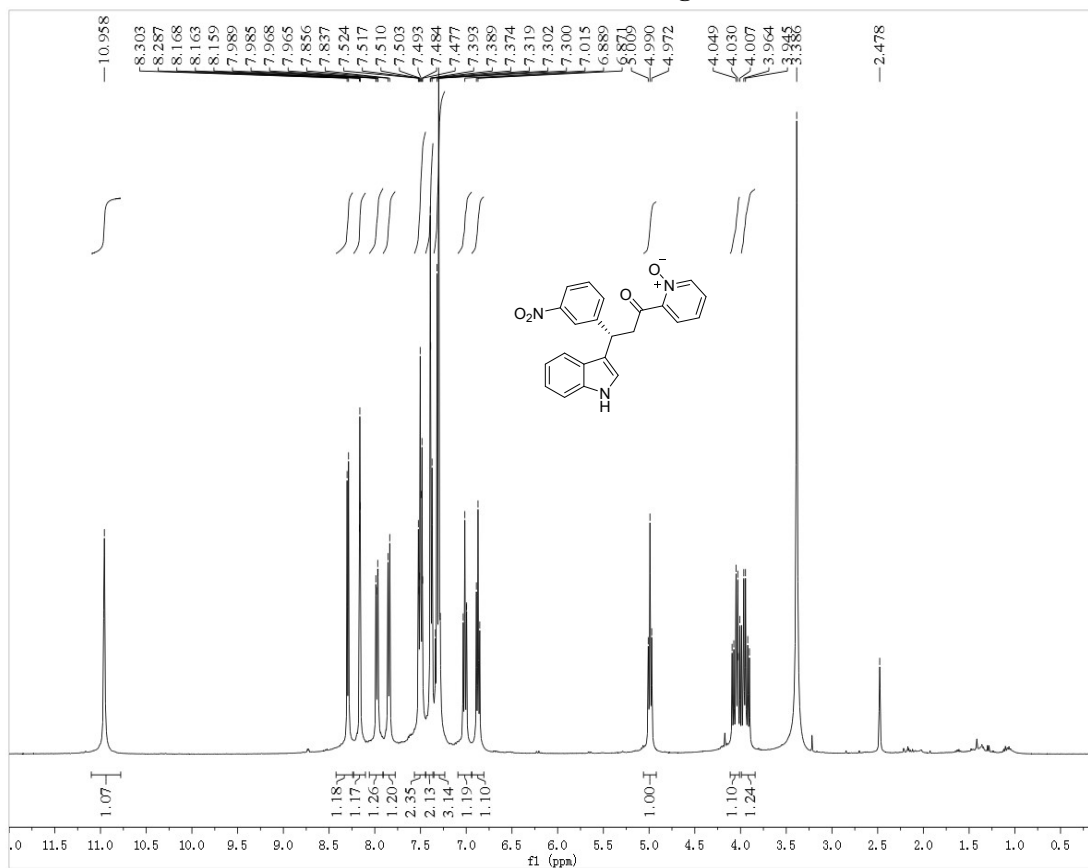


#	Time	Area	Height	Width	Area%	Symmetry
1	20.932	26457.1	412.8	0.9808	49.833	0.686
2	28.121	26634	324.6	1.3674	50.167	0.742

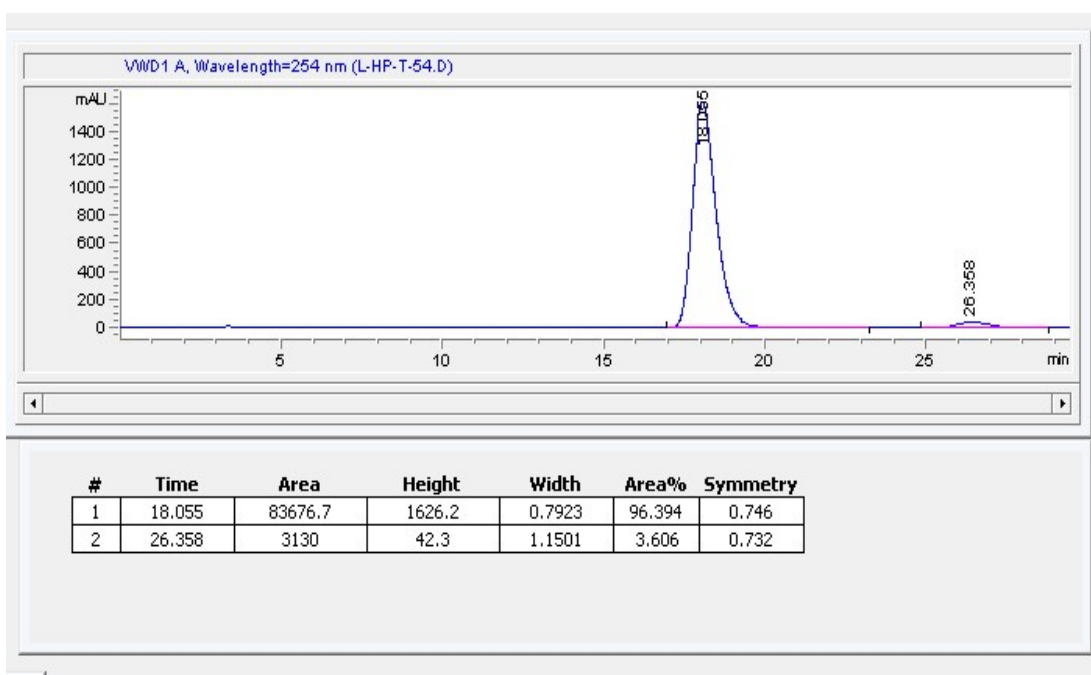
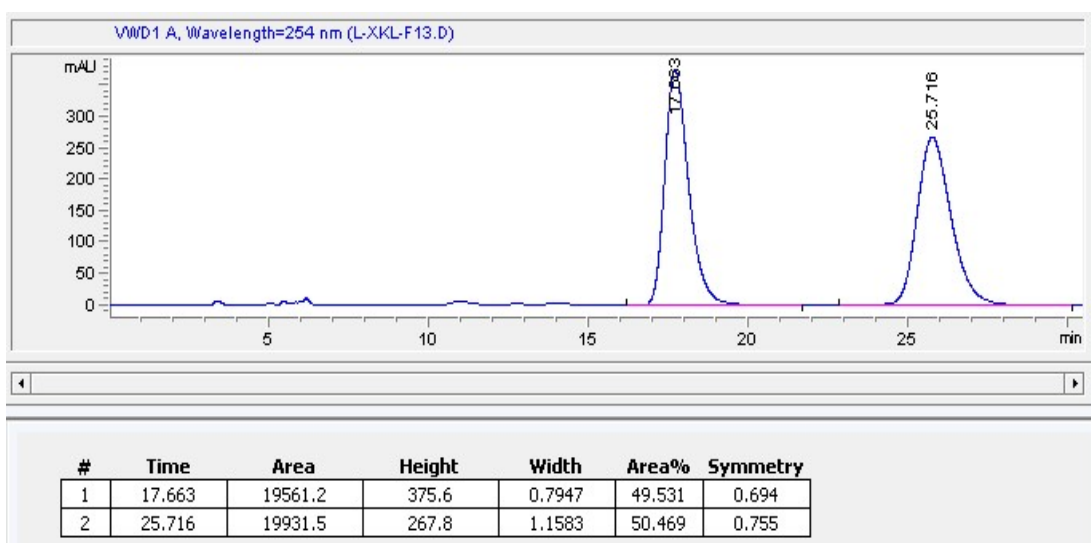


#	Time	Area	Height	Width	Area%	Symmetry
1	22.047	62850.2	921.9	1.0514	96.277	0.71
2	29.97	2430.7	27	1.3485	3.723	0.796

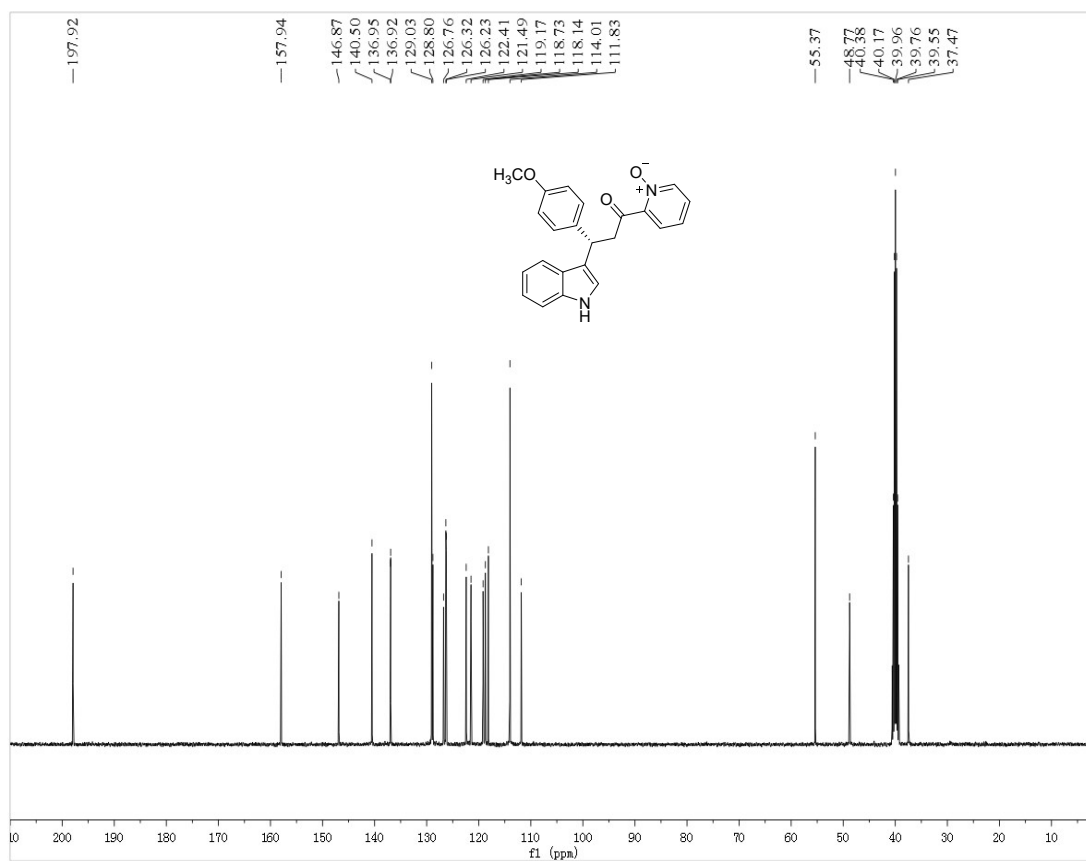
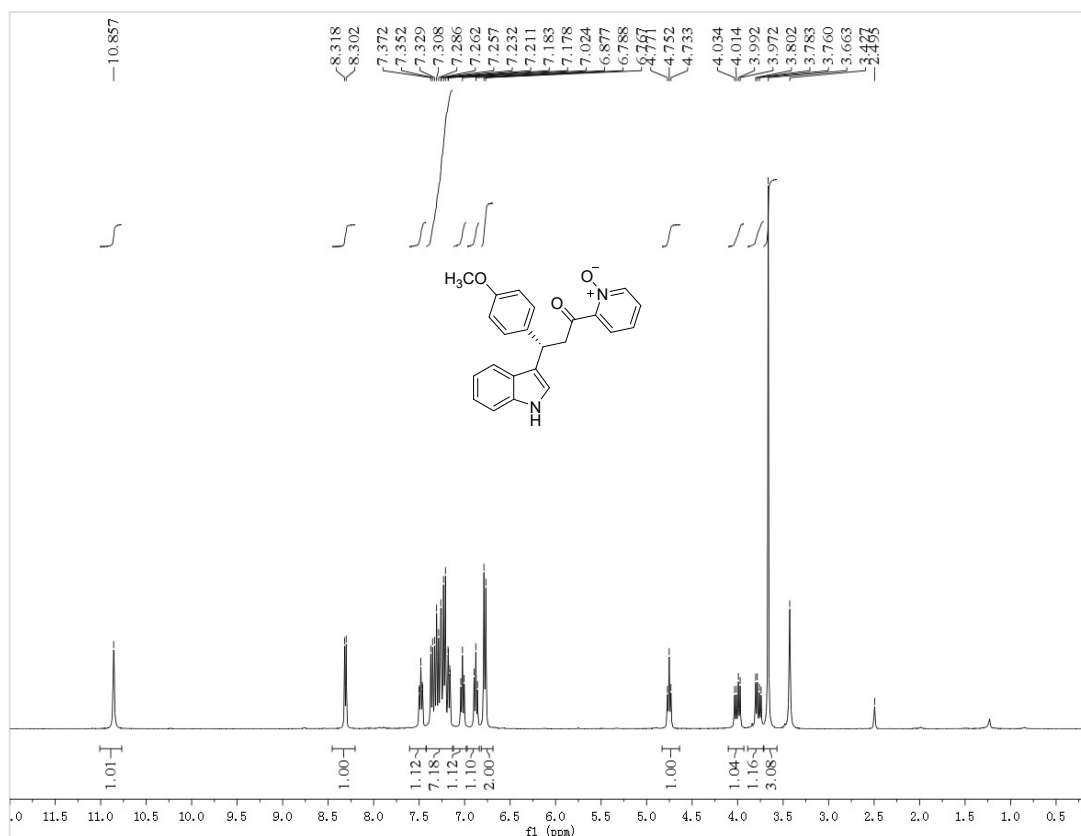
# <sup>1</sup>H and <sup>13</sup>C NMR of 6ag



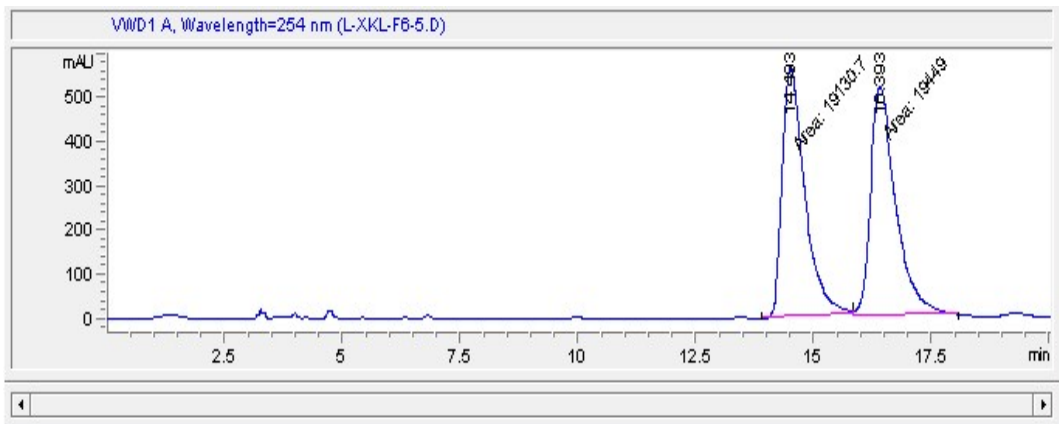
### HPLC of 6ag



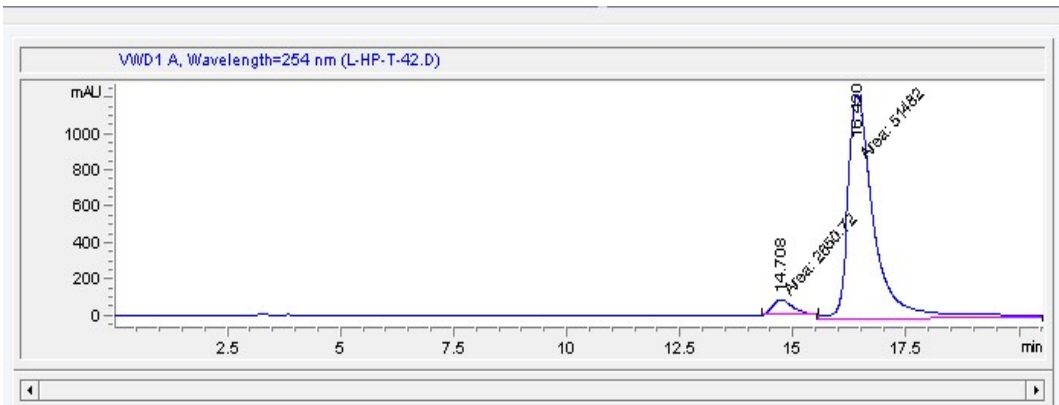
# <sup>1</sup>H and <sup>13</sup>C NMR of 6ah



### HPLC of 6ah



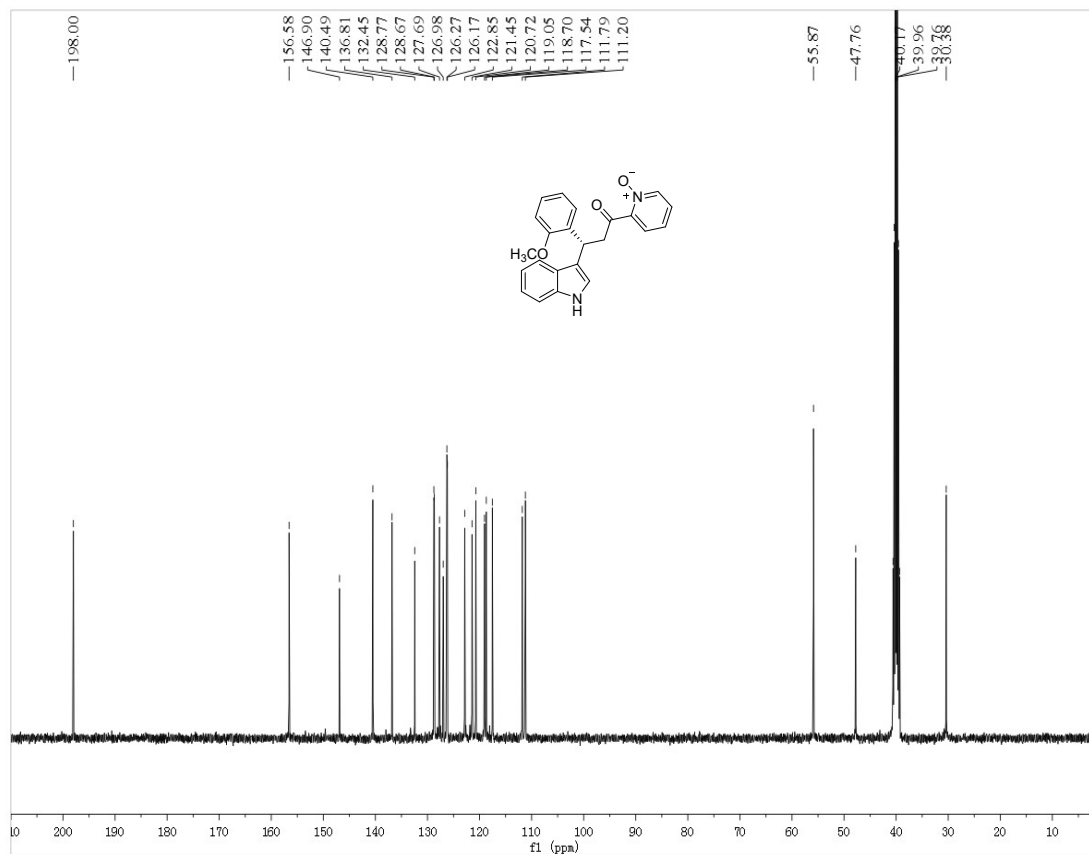
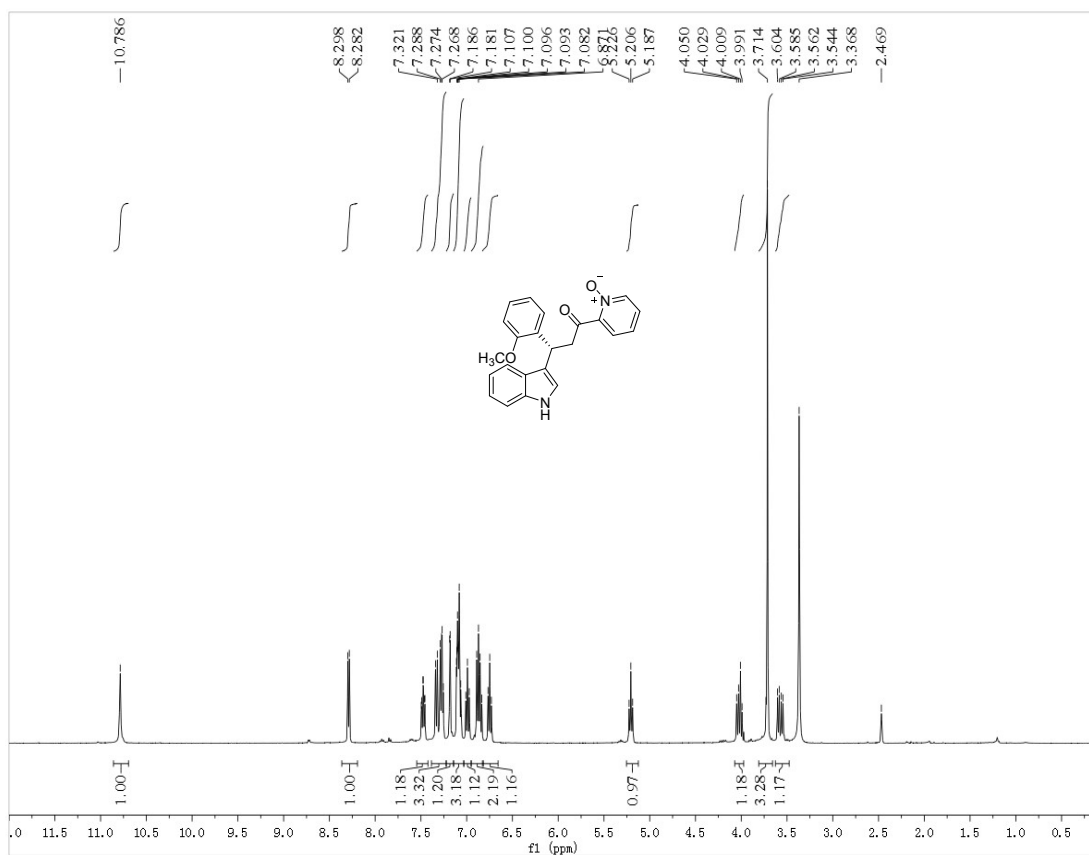
#	Time	Area	Height	Width	Area%	Symmetry
1	14.493	19130.7	572.9	0.5566	49.588	0.551
2	16.393	19449	518.3	0.6254	50.412	0.573



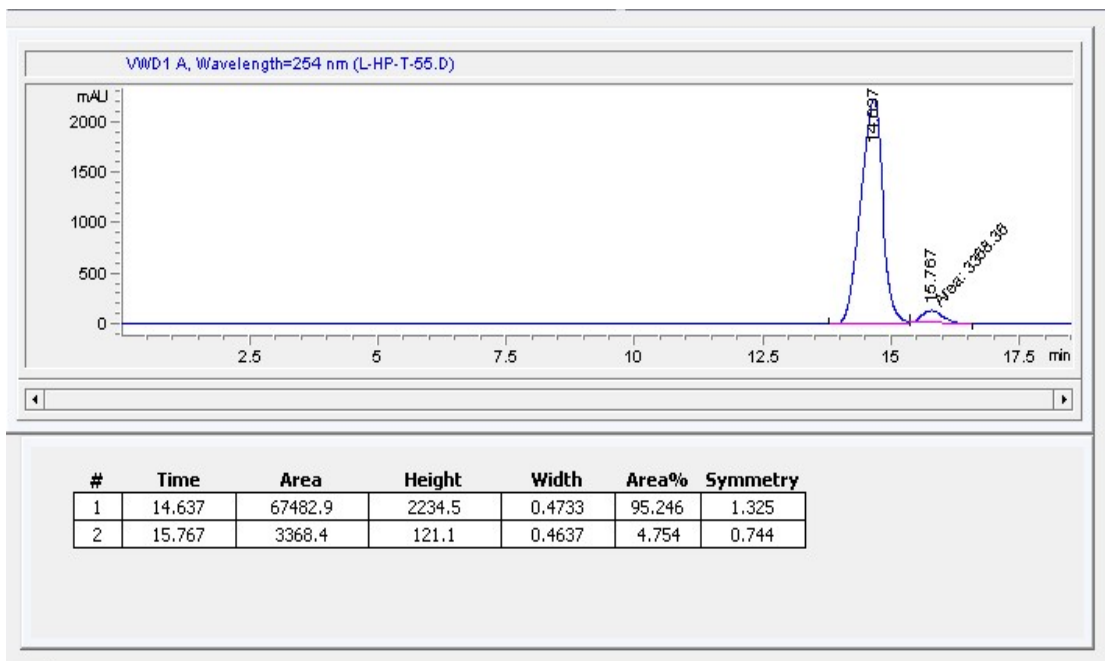
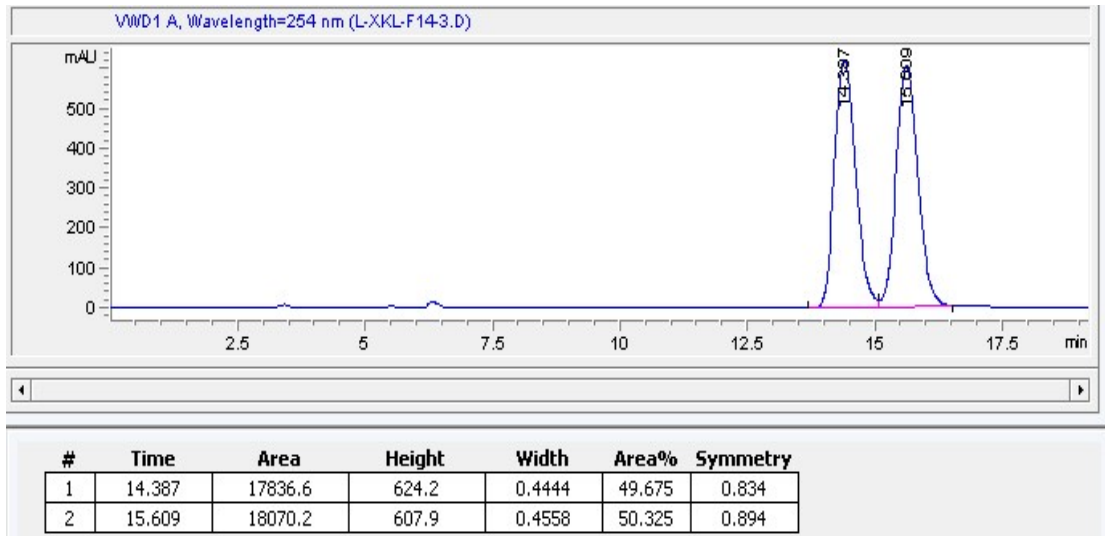
#	Time	Area	Height	Width	Area%	Symmetry
1	14.708	2650.7	84.1	0.5254	4.897	0.621
2	16.42	51482	1239.5	0.6922	95.103	0.554



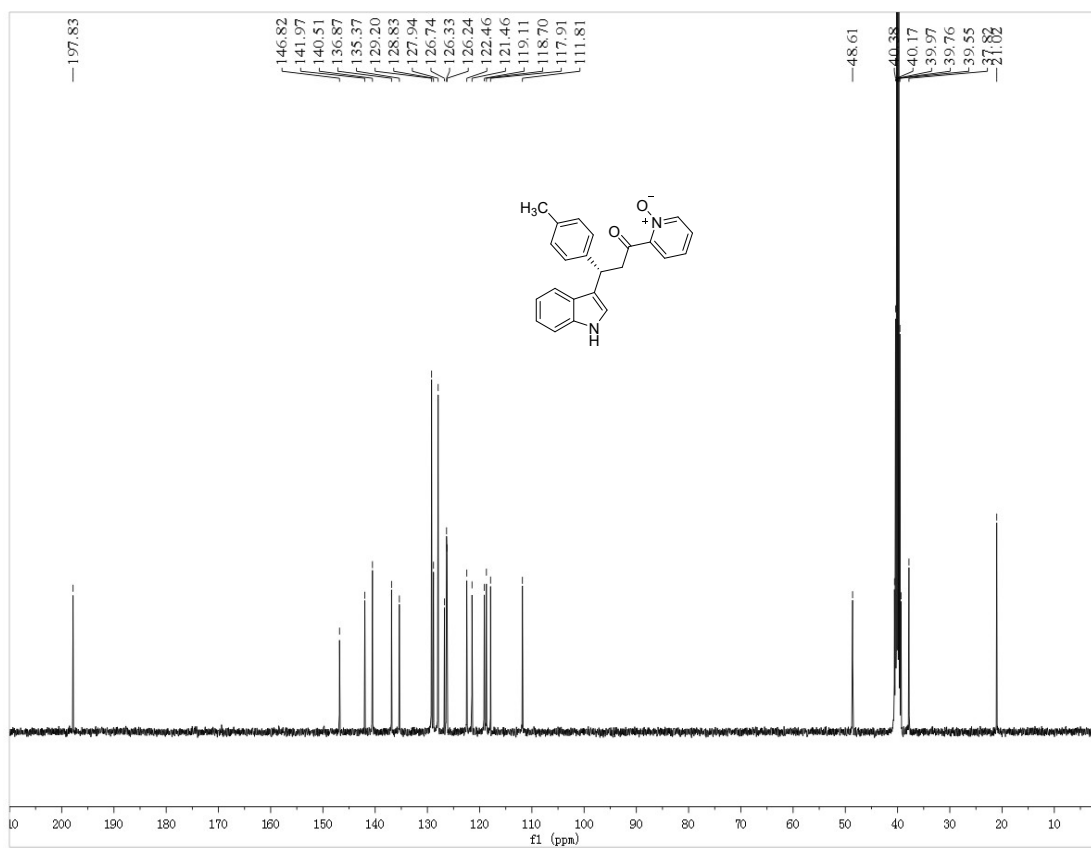
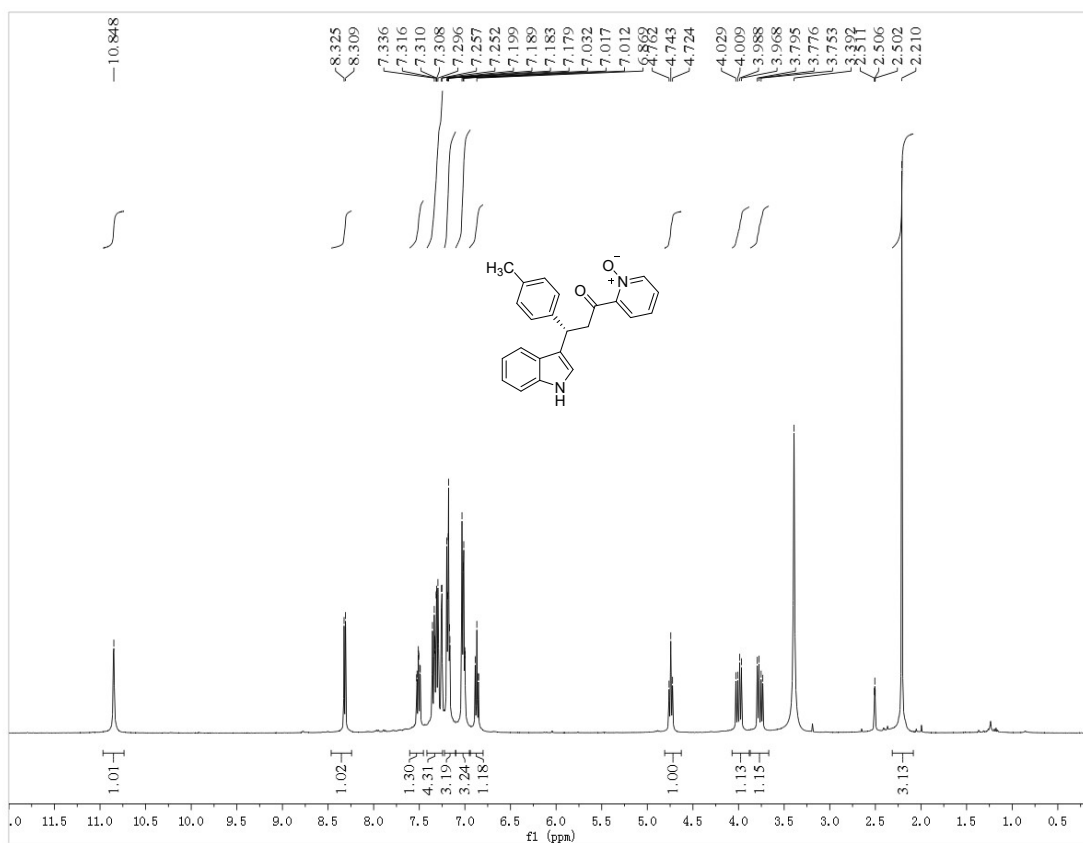
# <sup>1</sup>H and <sup>13</sup>C NMR of 6ai



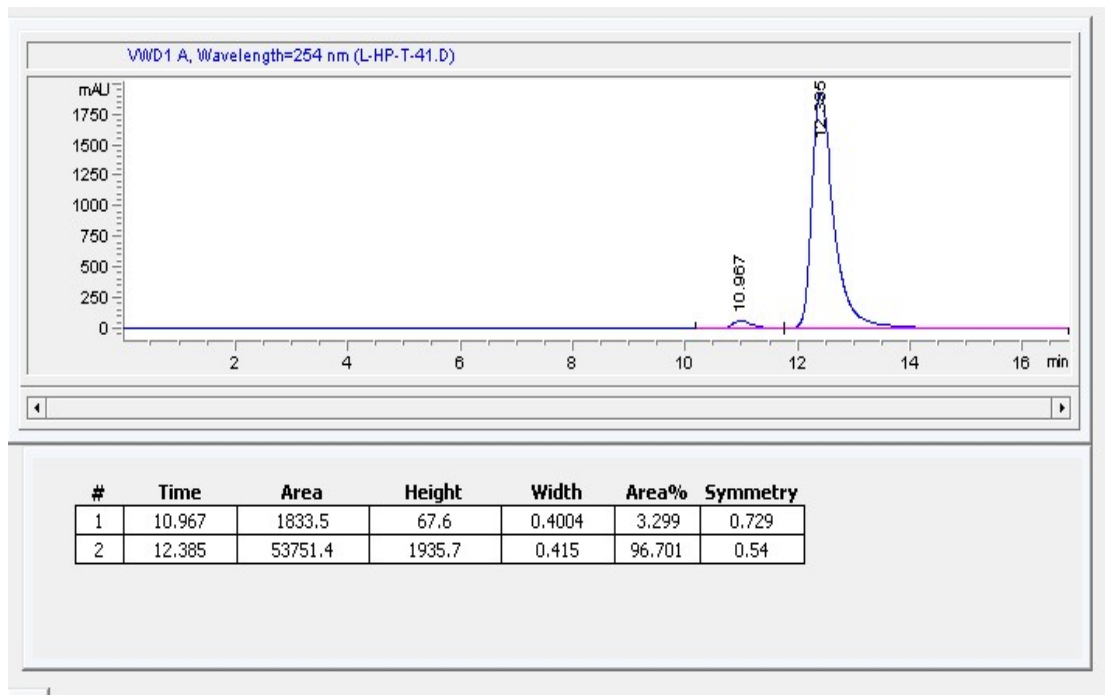
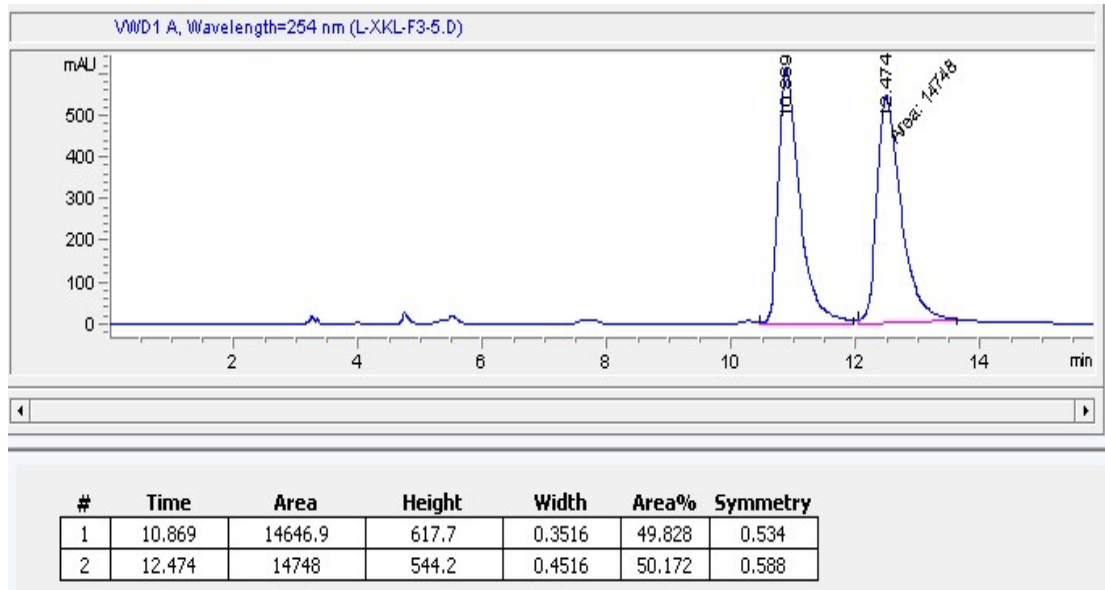
### HPLC of 6ai



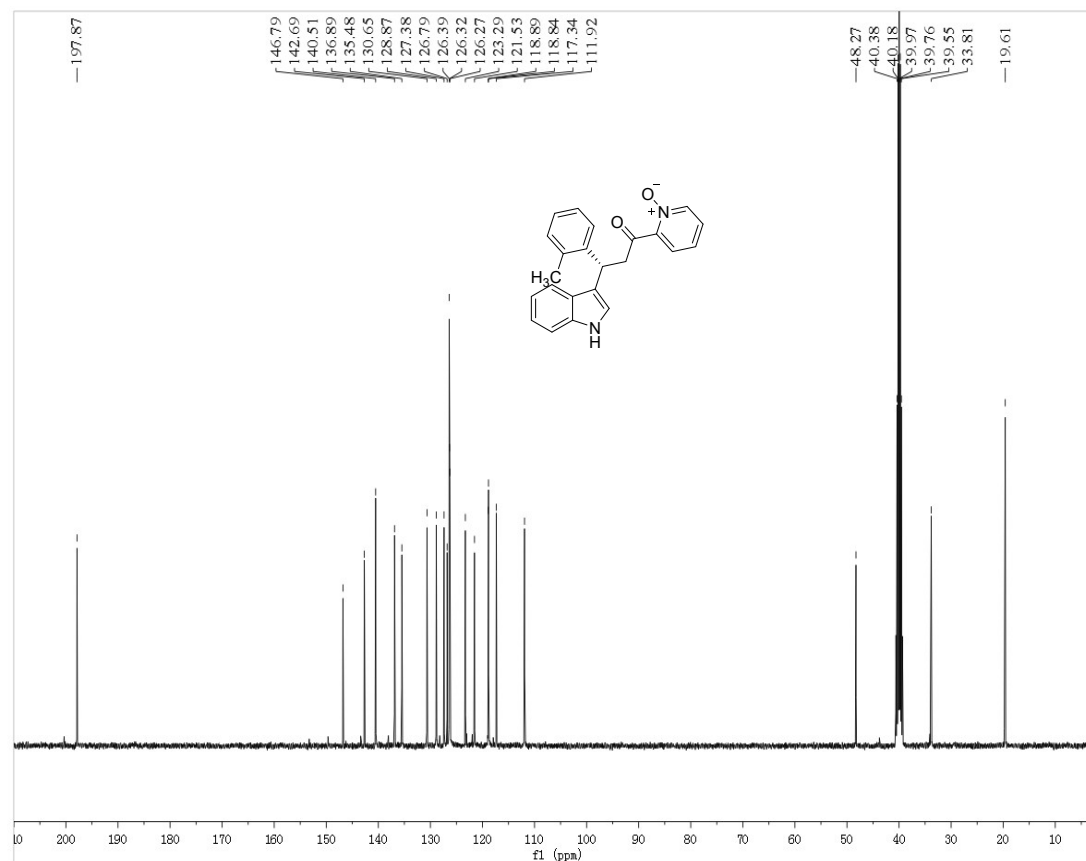
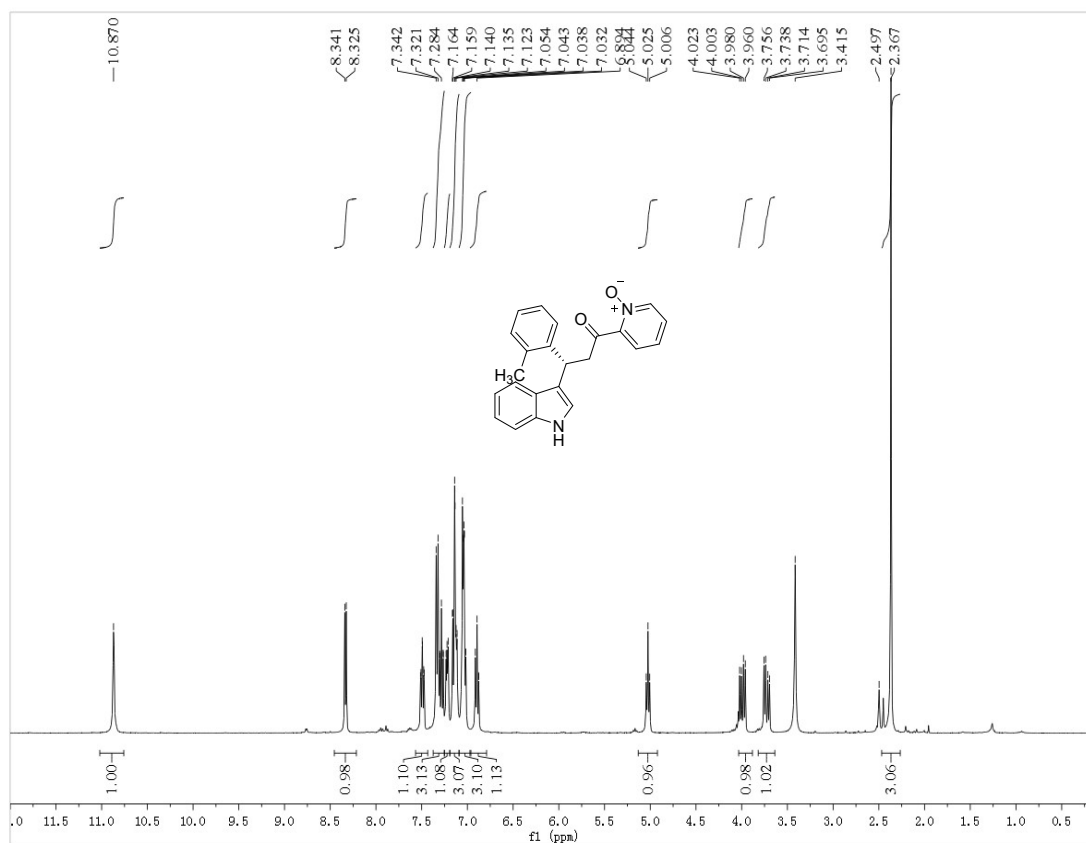
# <sup>1</sup>H and <sup>13</sup>C NMR of 6aj



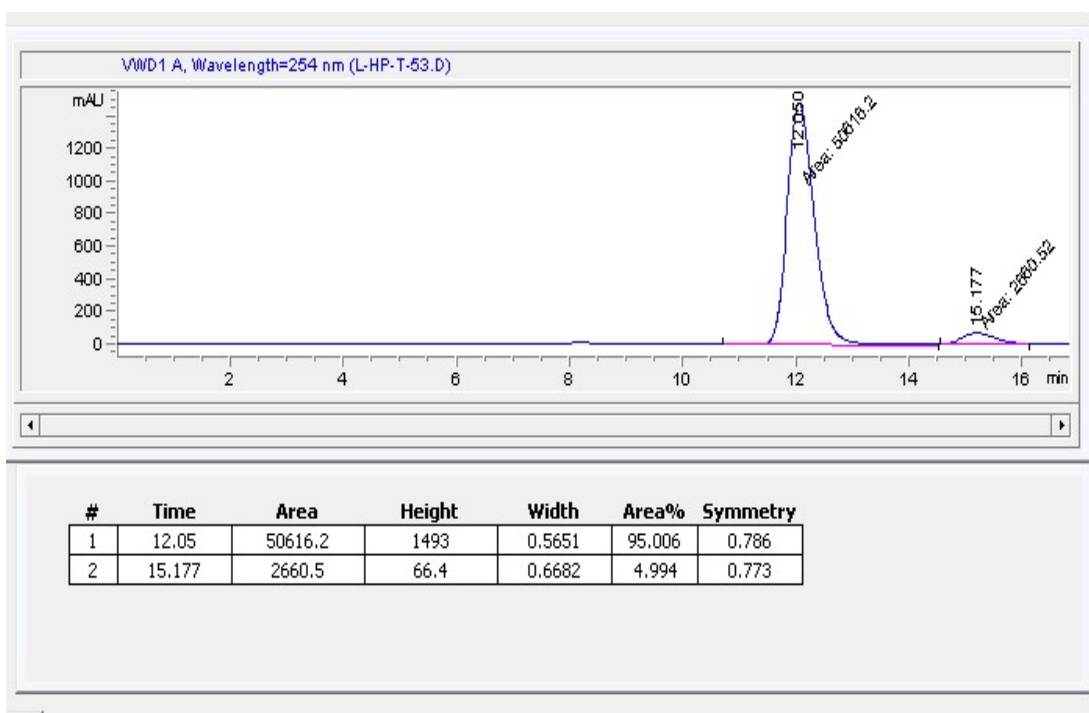
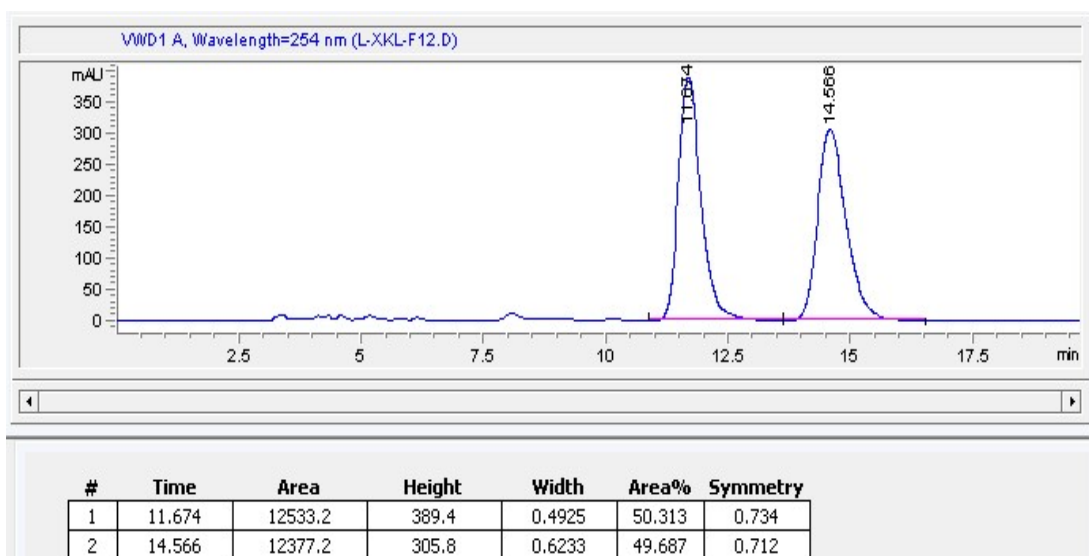
## HPLC of 6aj



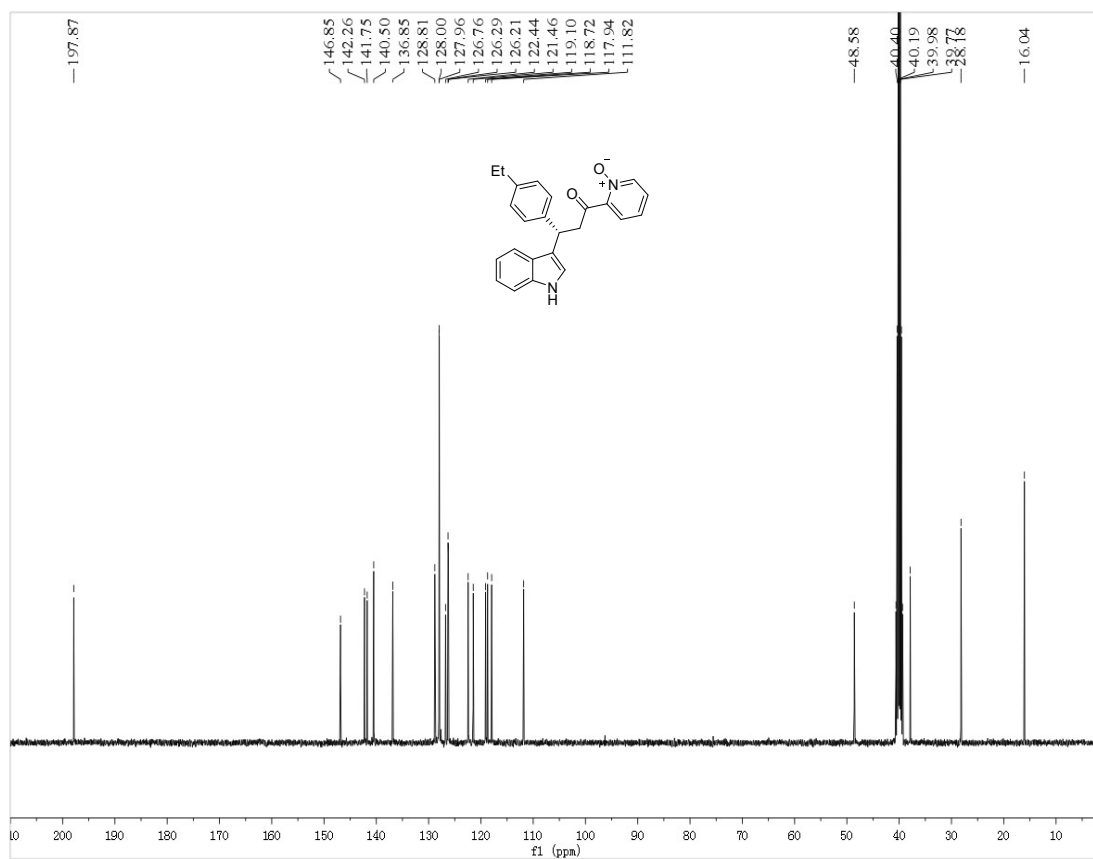
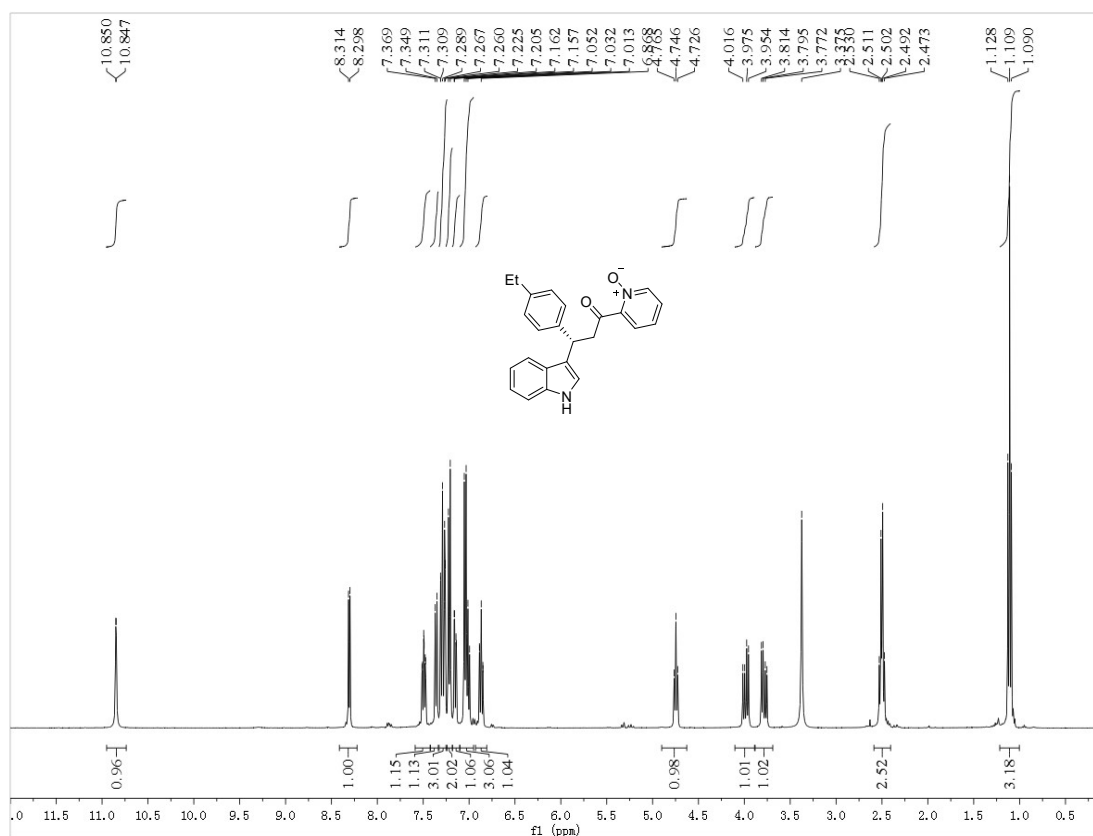
# $^1\text{H}$ and $^{13}\text{C}$ NMR of 6ak



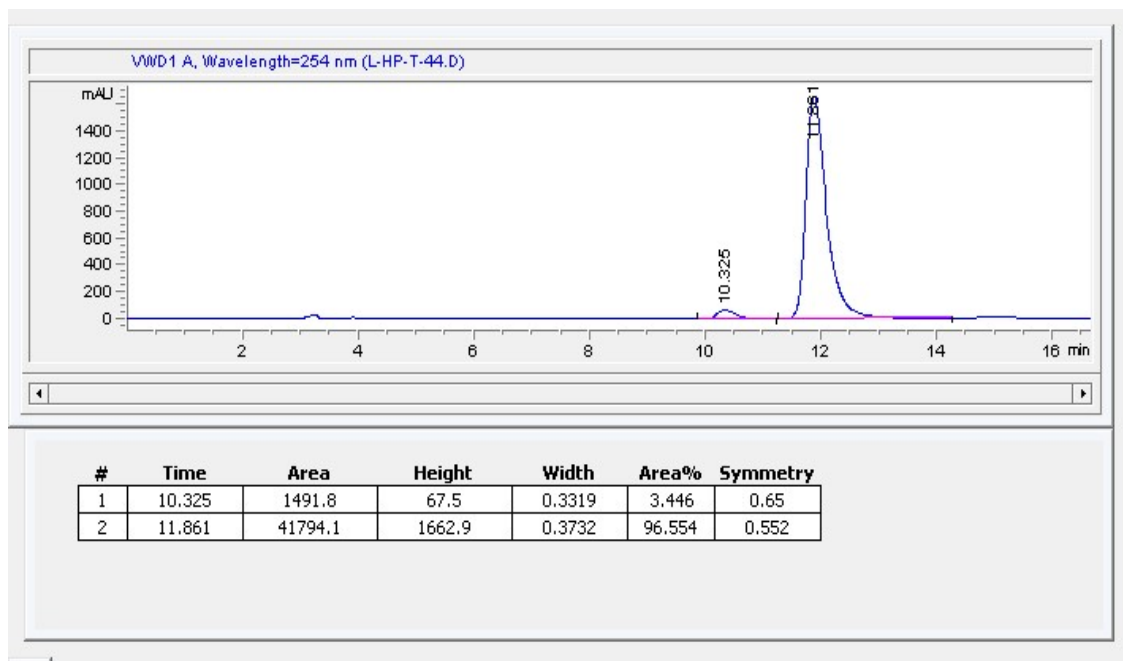
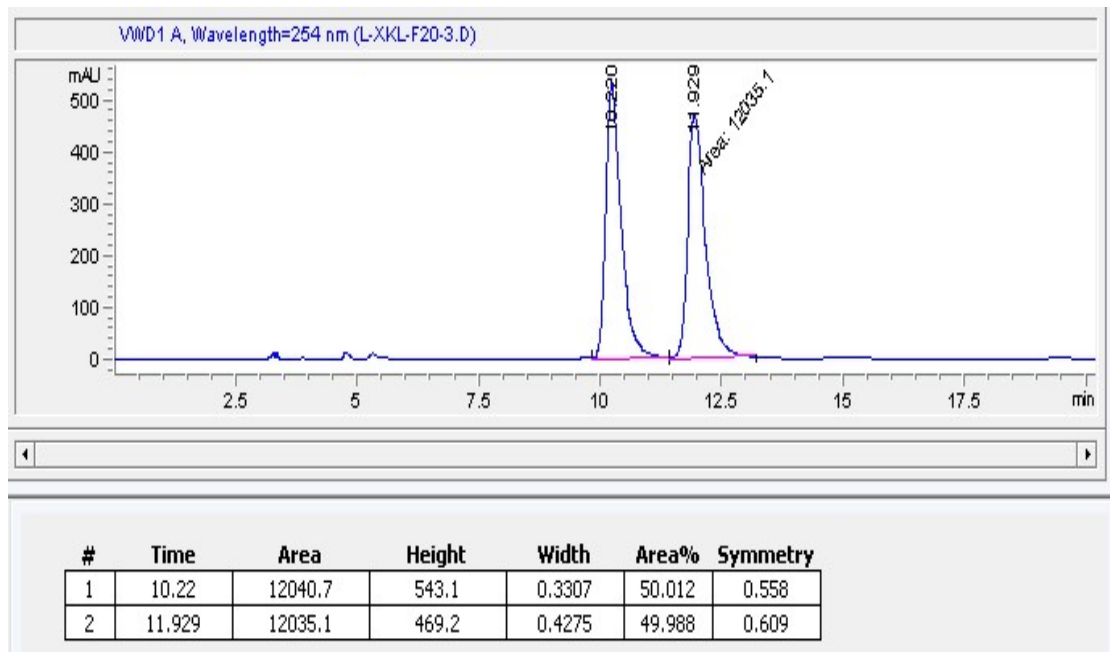
### HPLC of 6ak



# <sup>1</sup>H and <sup>13</sup>C NMR of 6al

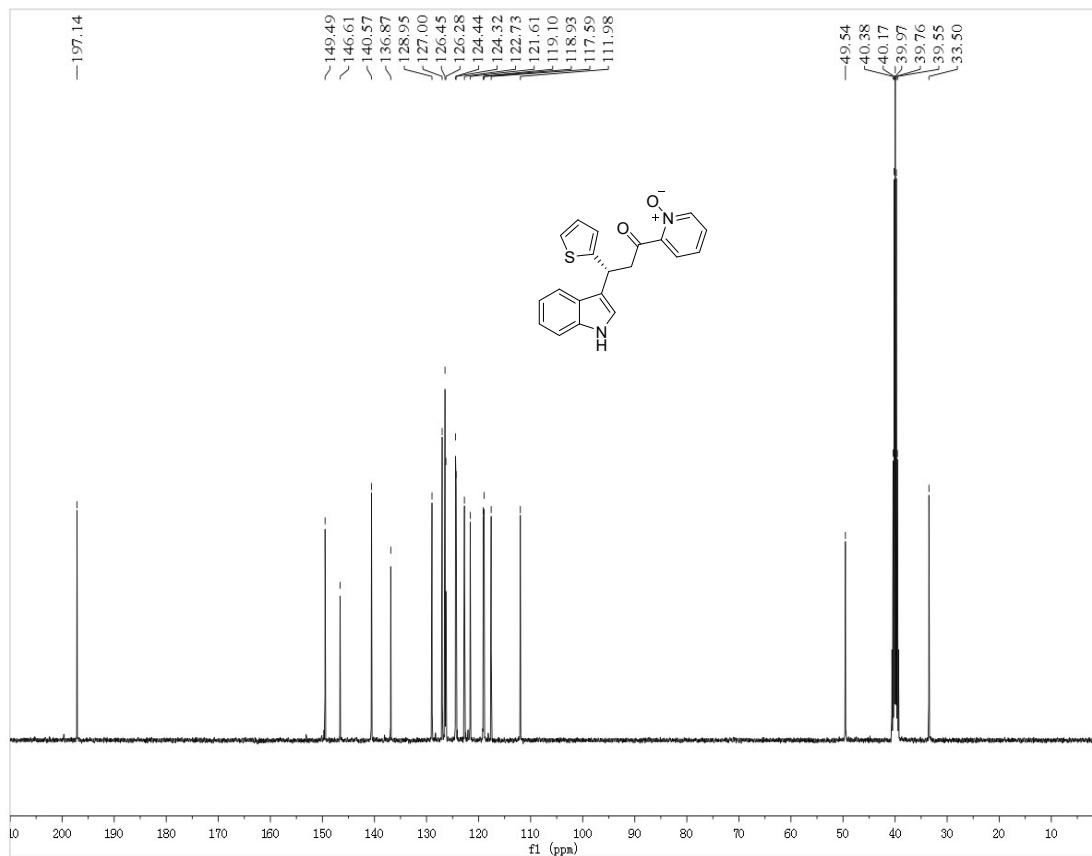
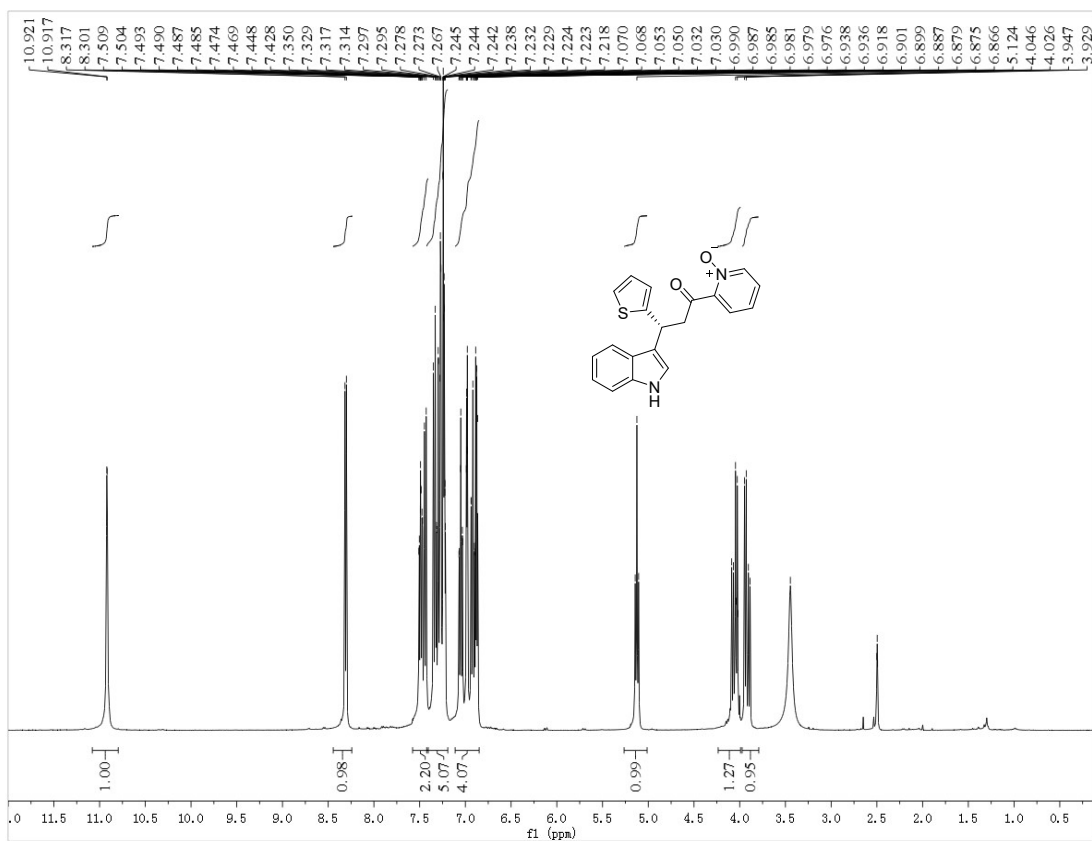


## HPLC of 6al

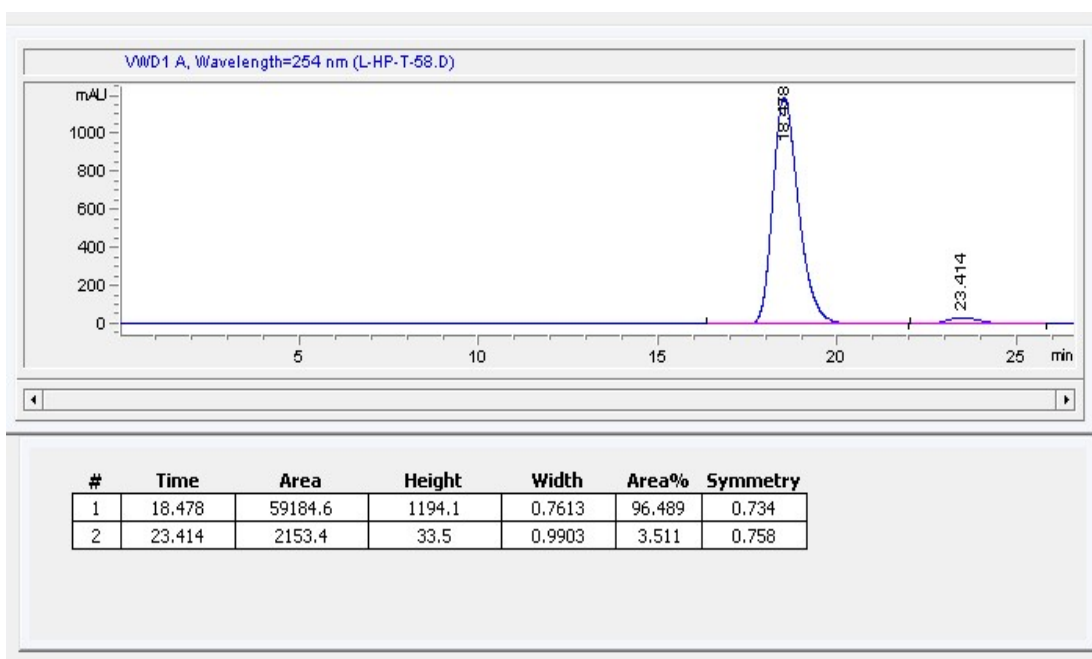
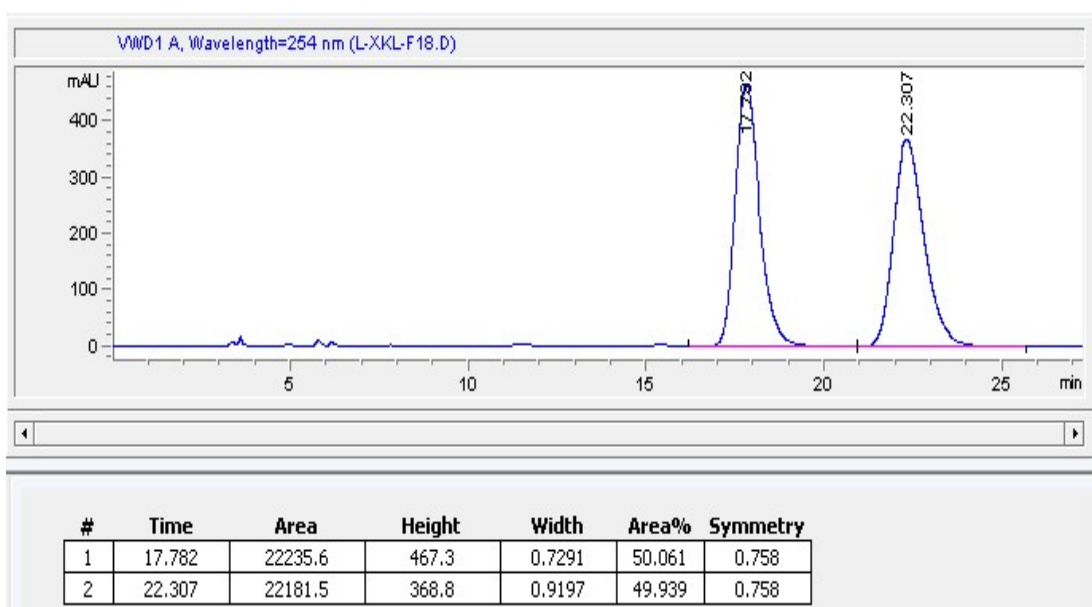




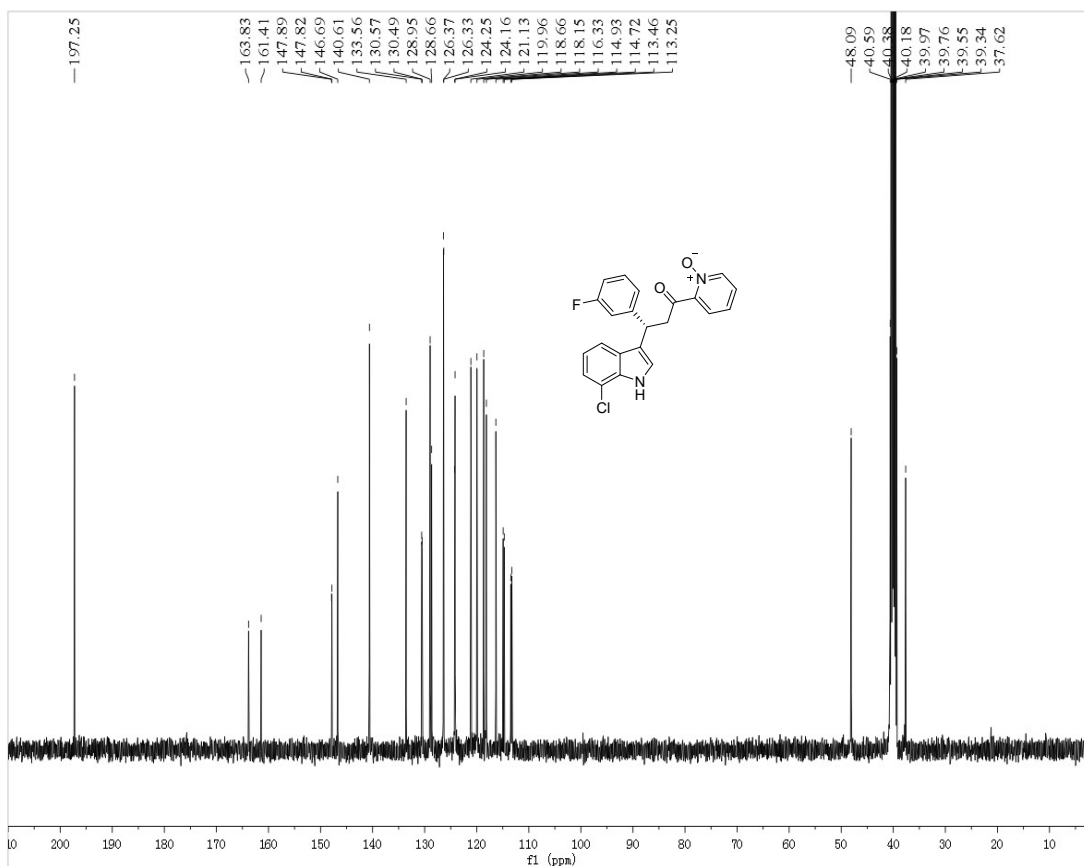
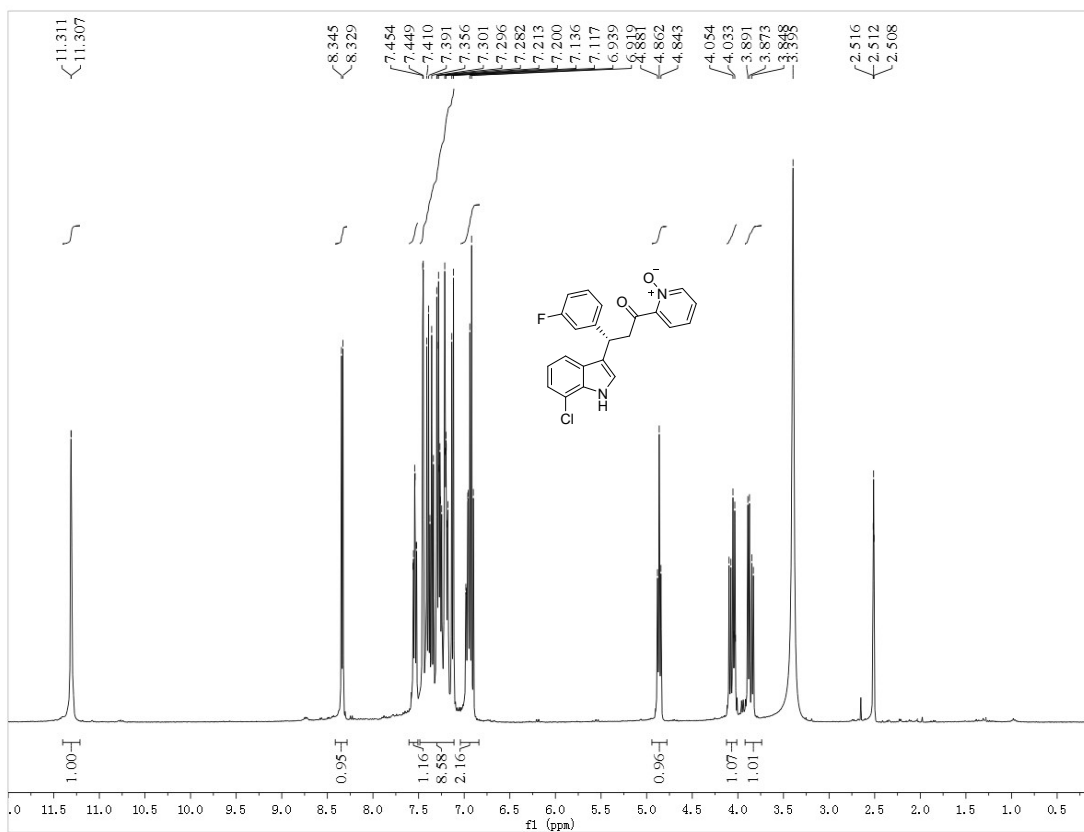
# <sup>1</sup>H and <sup>13</sup>C NMR of 6am



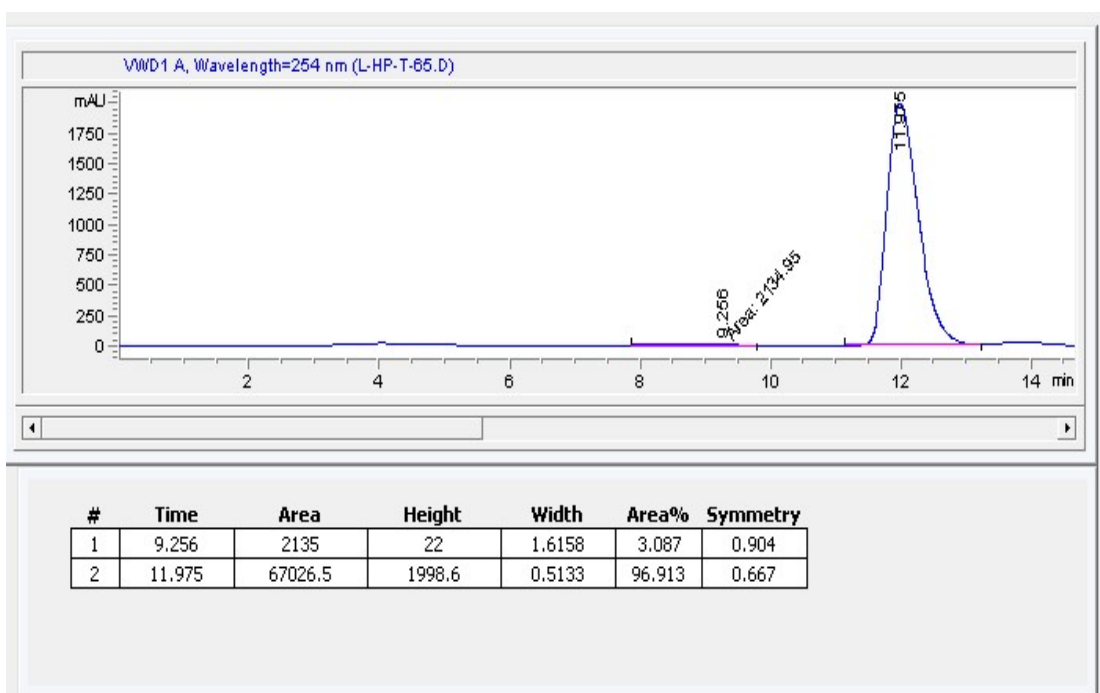
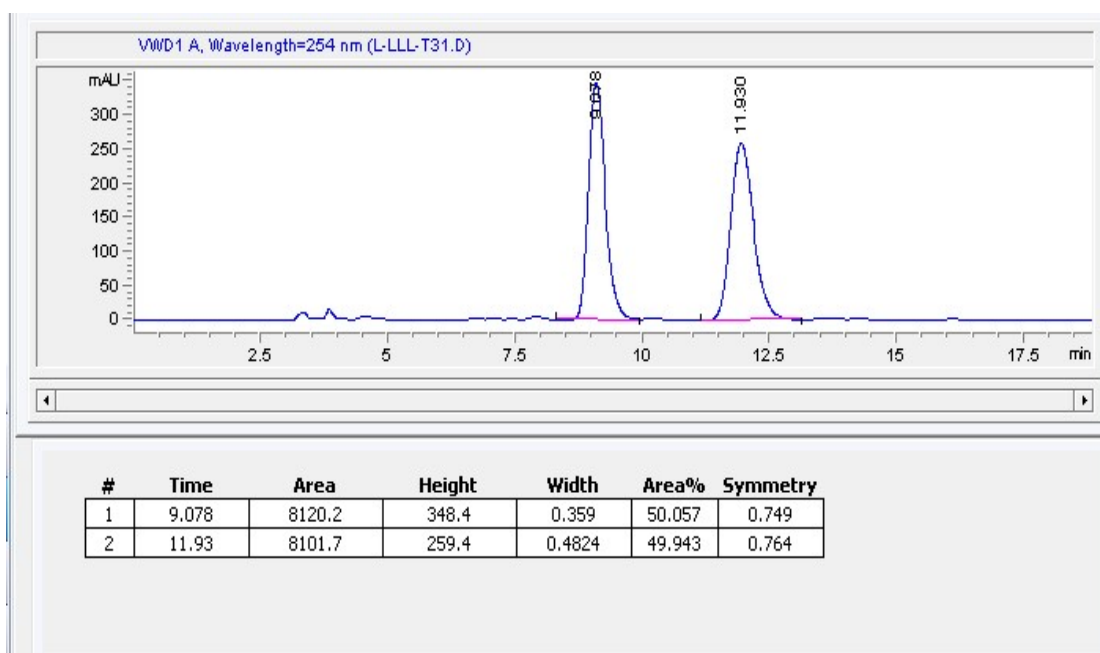
## HPLC of 6am



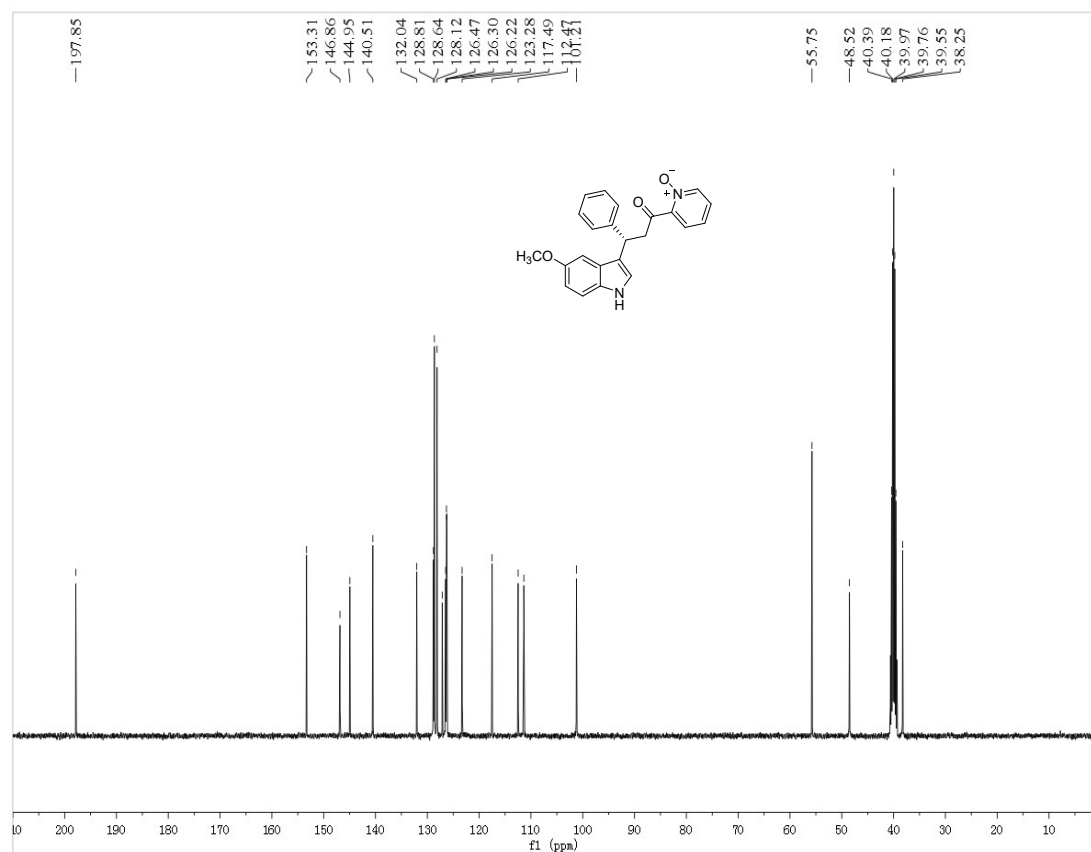
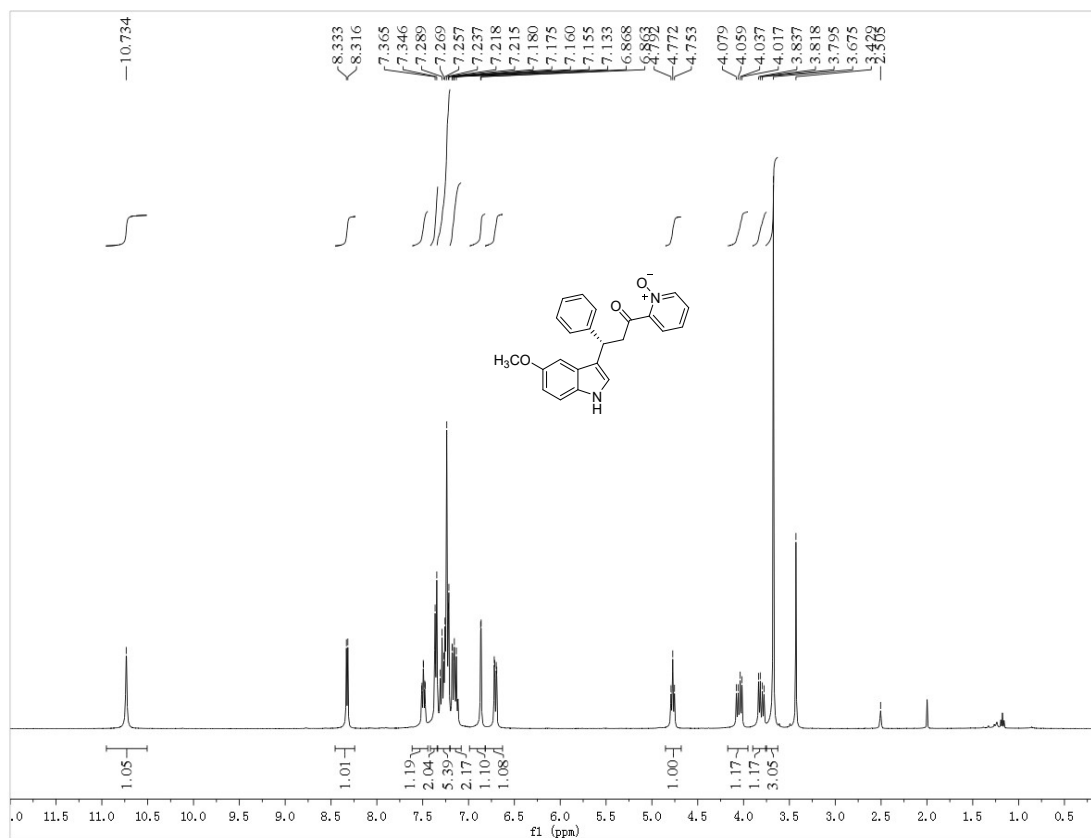
# <sup>1</sup>H and <sup>13</sup>C NMR of 6ba



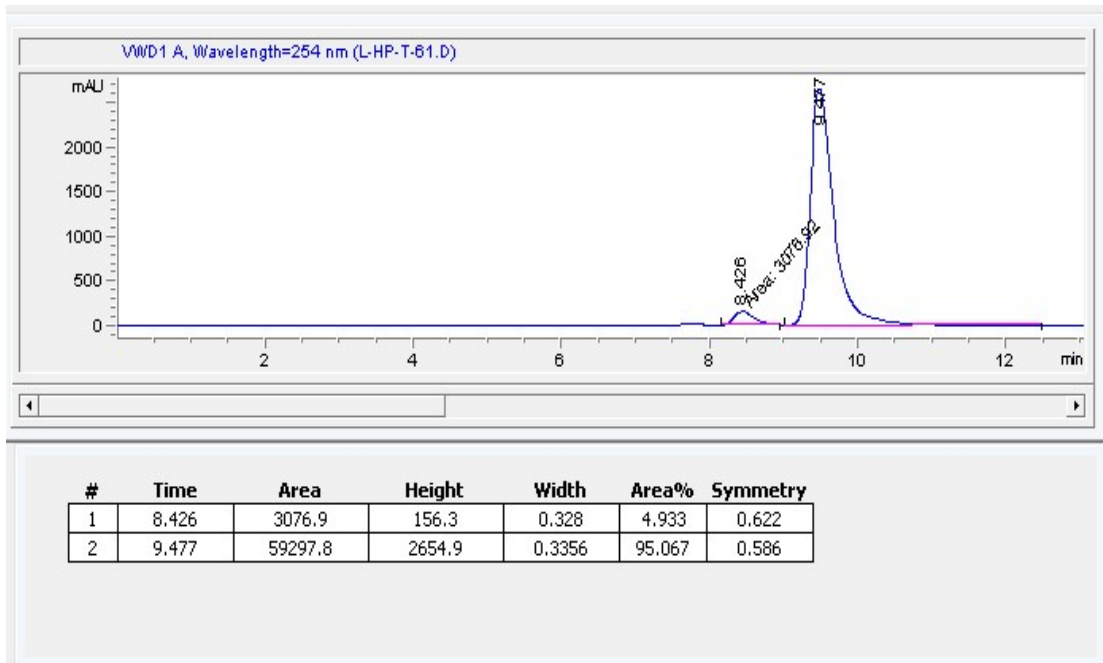
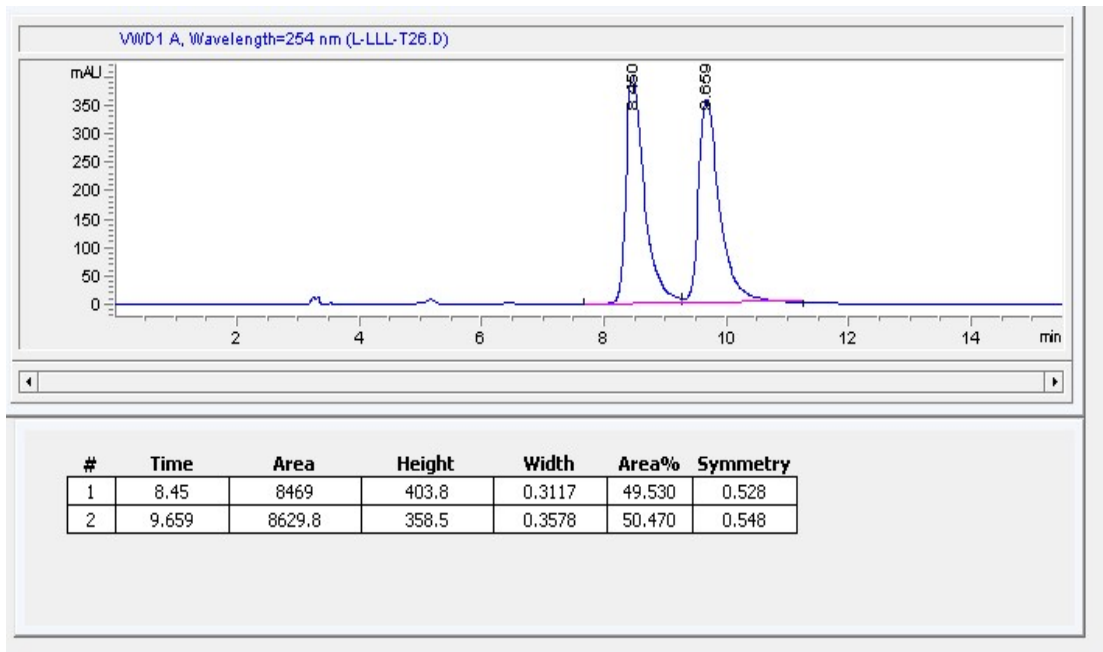
## HPLC of 6ba



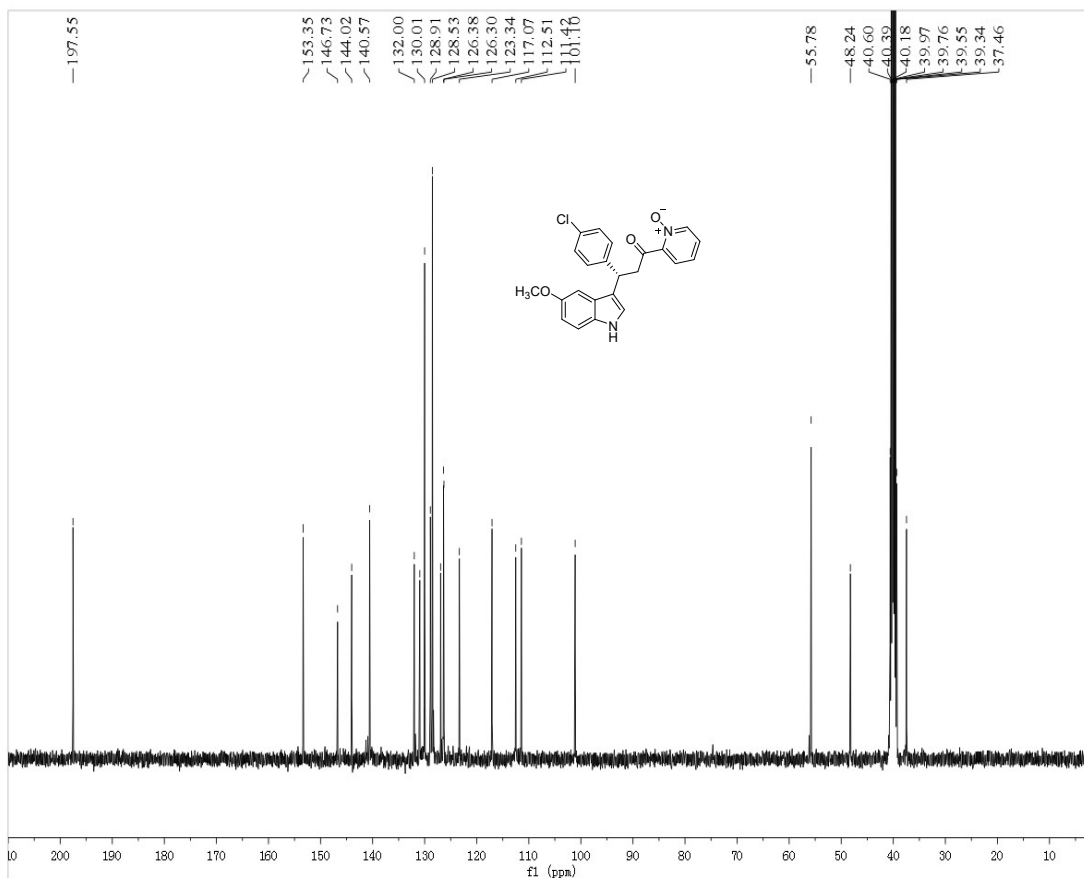
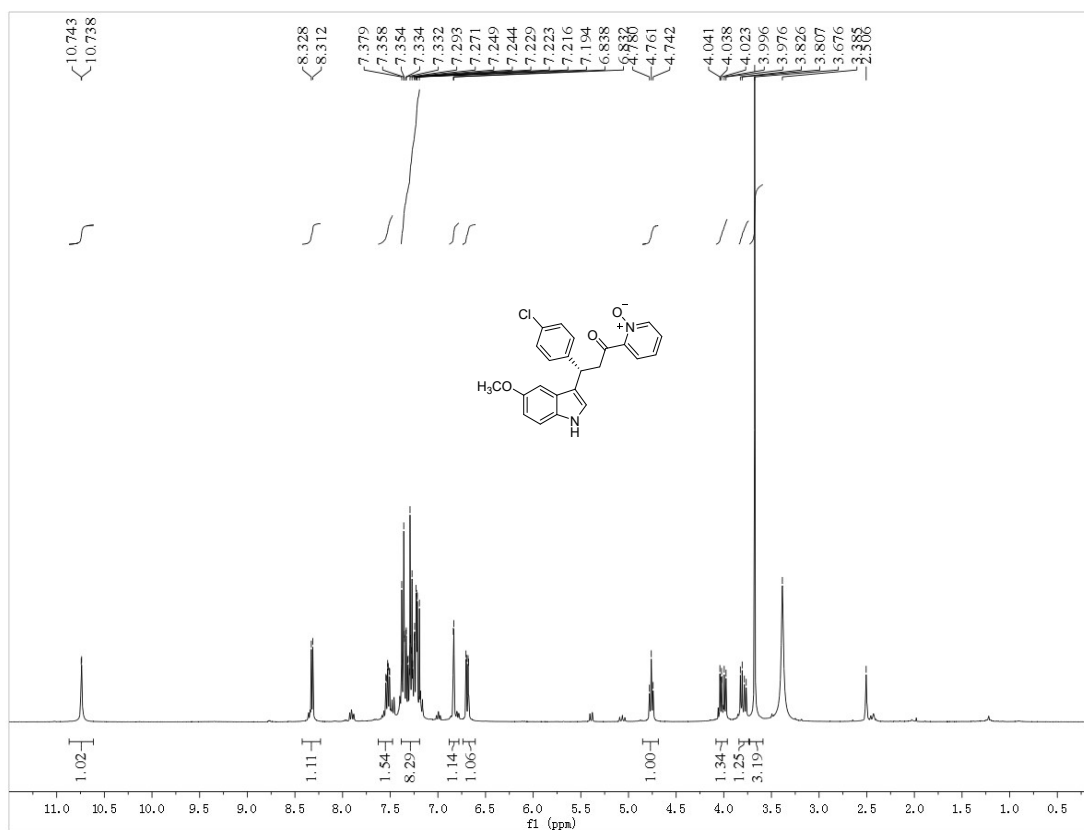
# <sup>1</sup>H and <sup>13</sup>C NMR of 6ca



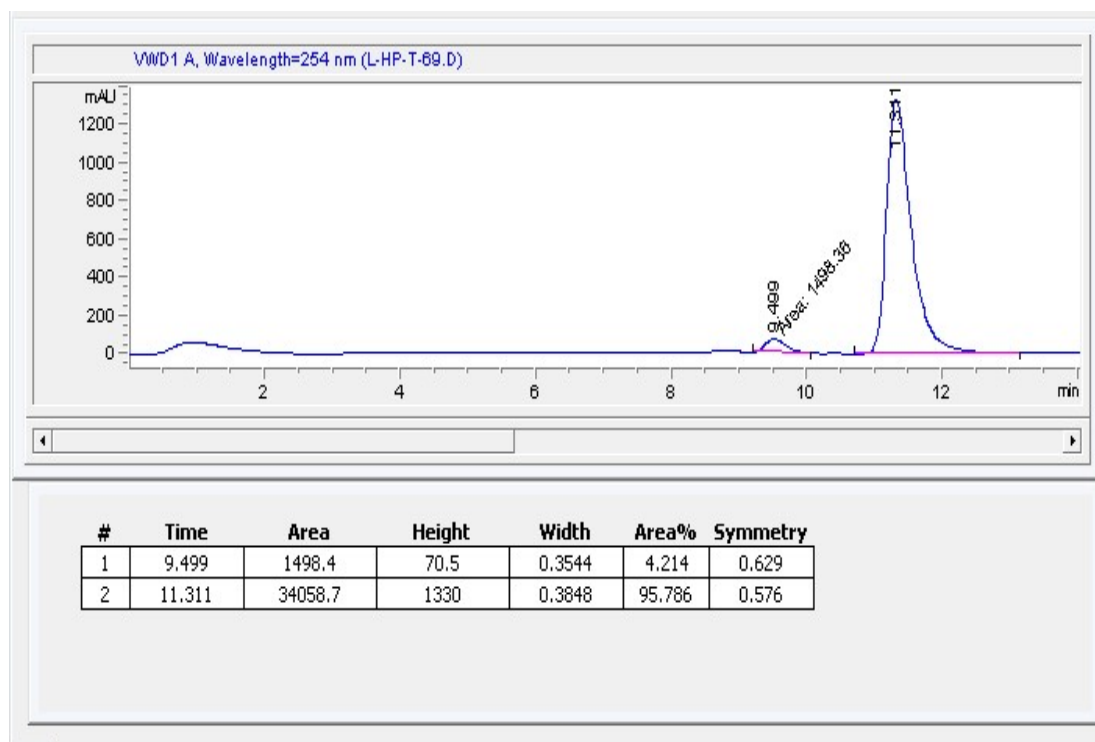
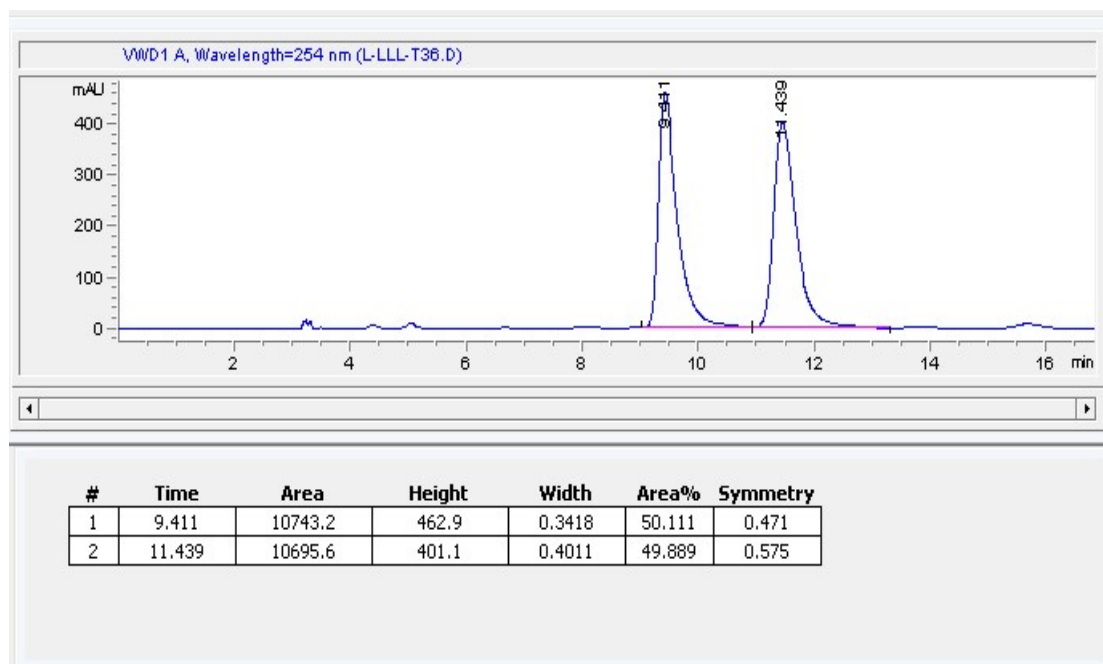
## HPLC of 6ca



# <sup>1</sup>H and <sup>13</sup>C NMR of 6cb

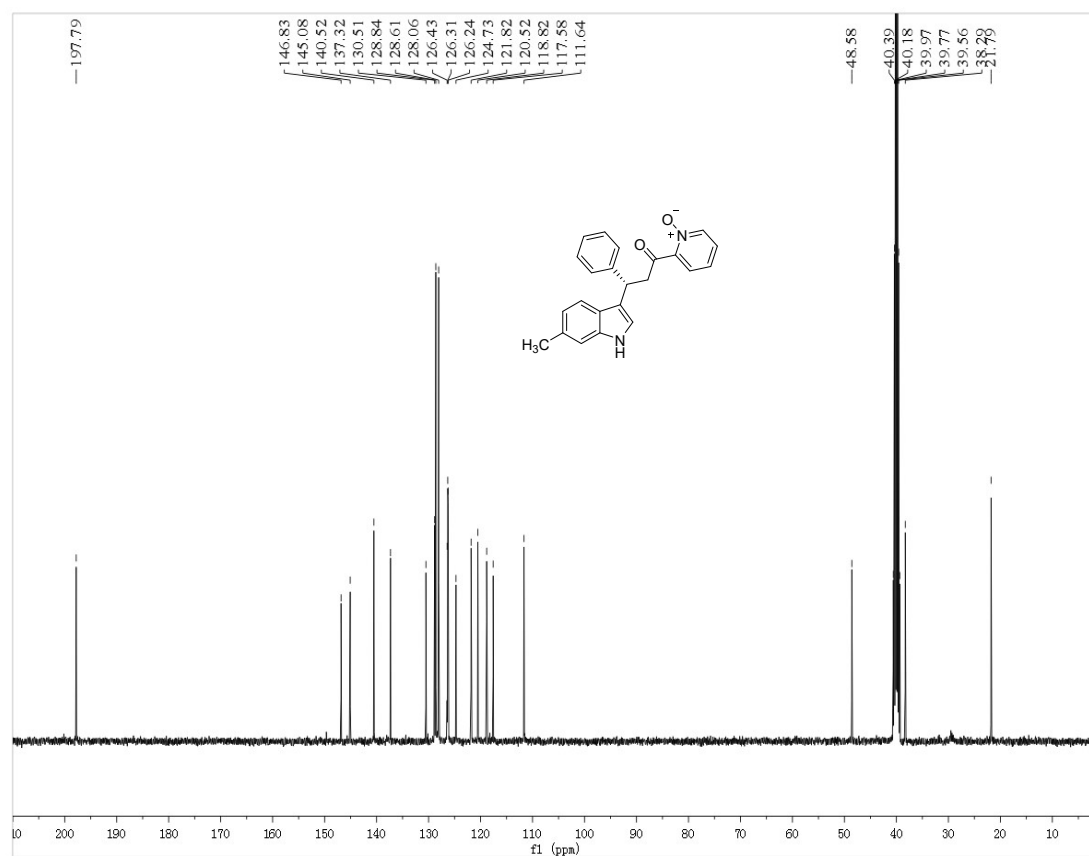
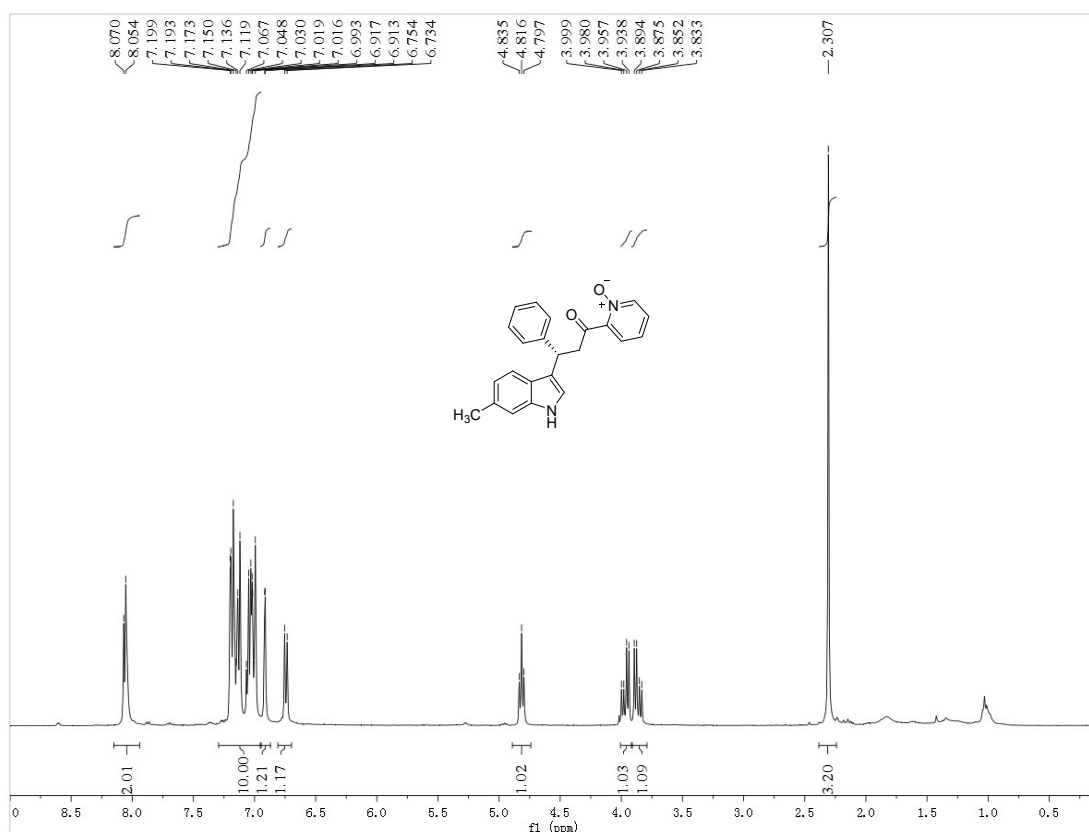


### HPLC of 6cb

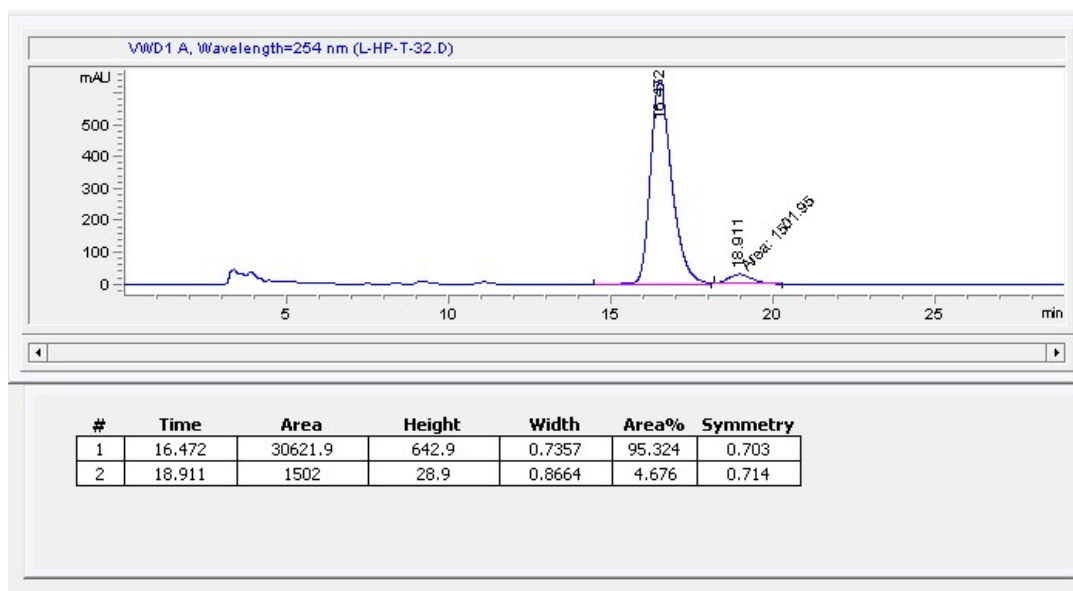
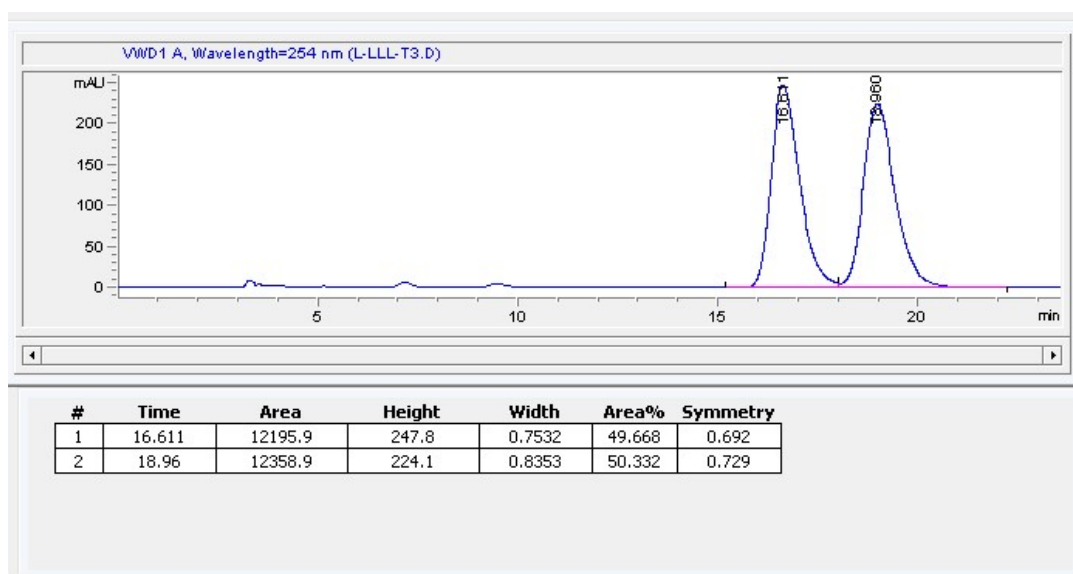




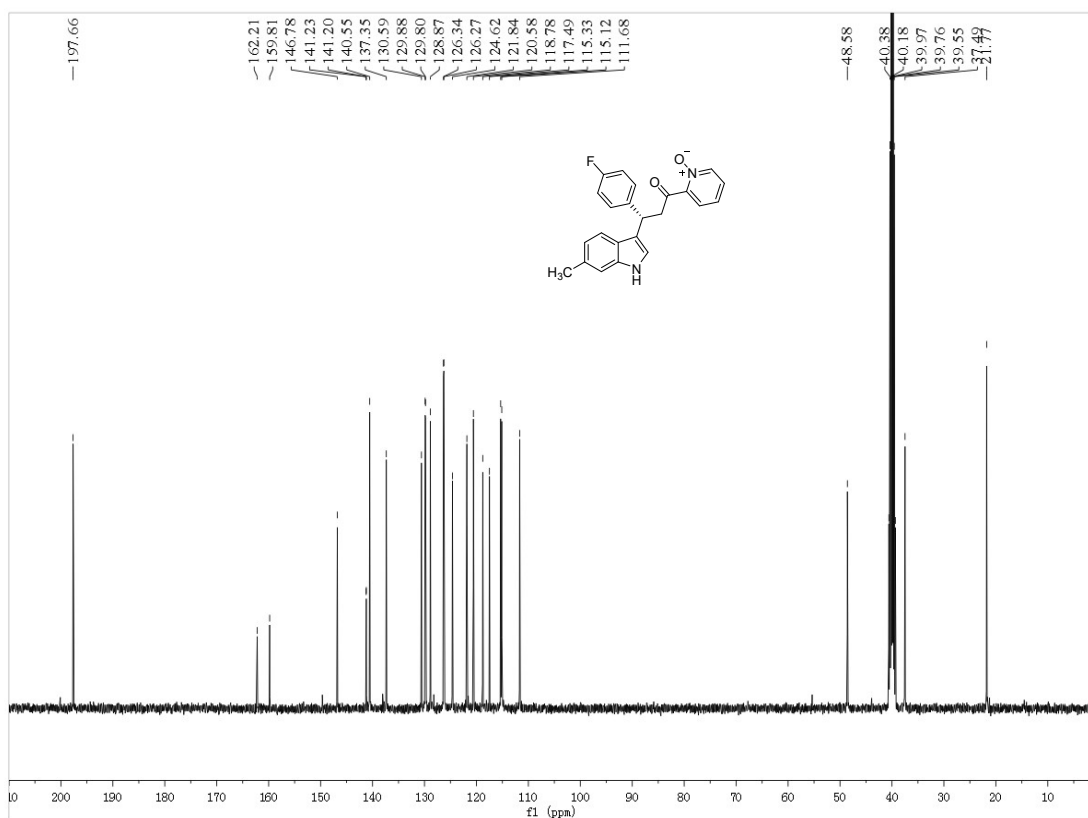
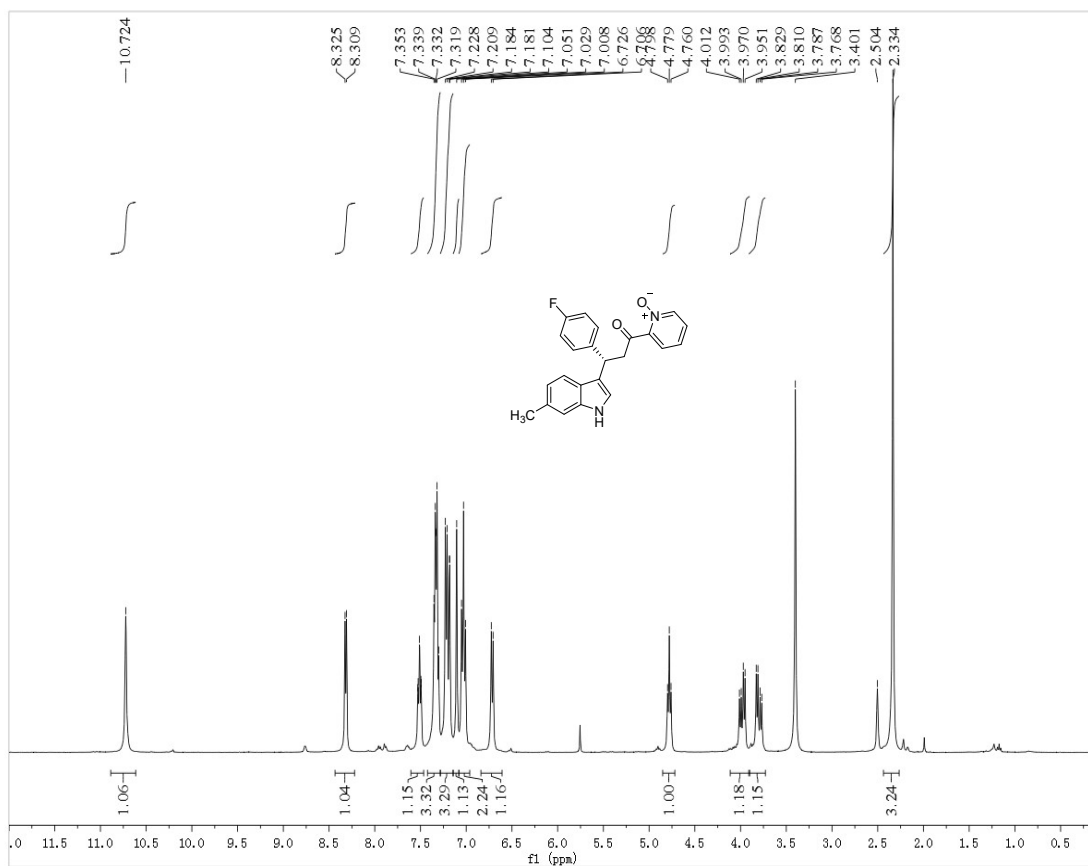
# <sup>1</sup>H and <sup>13</sup>C NMR of 6da



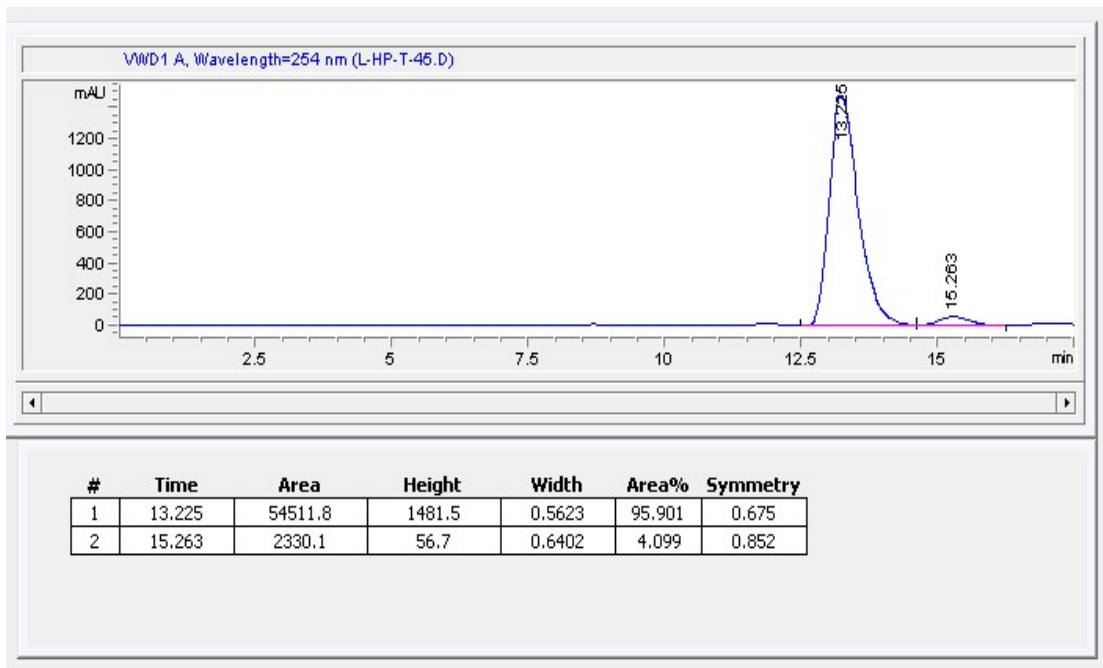
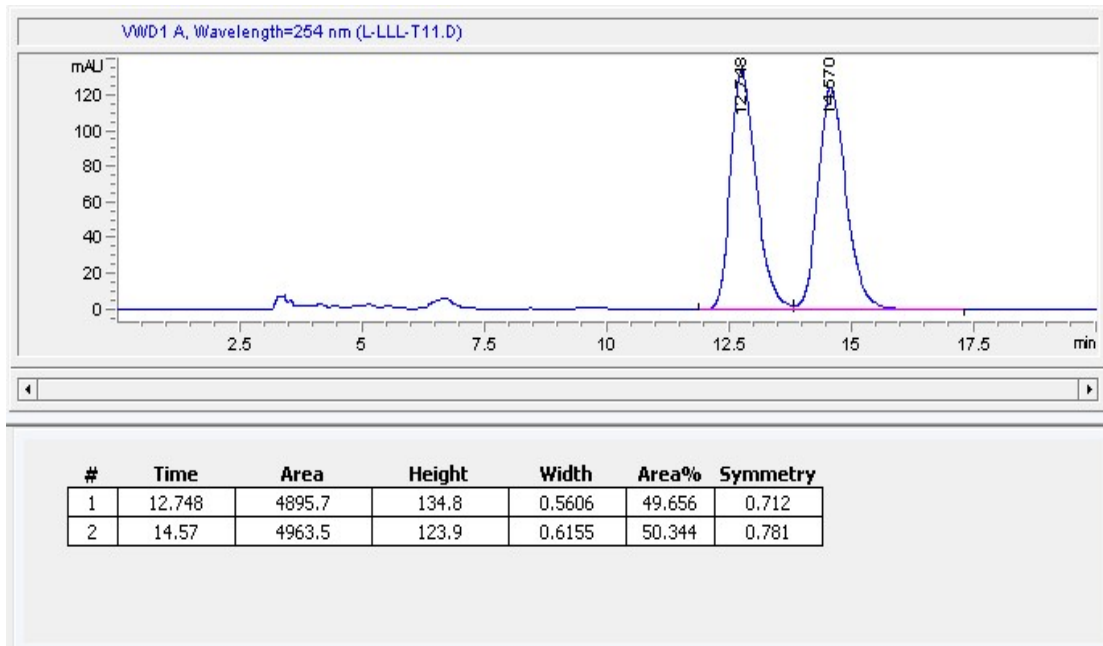
### HPLC of 6da



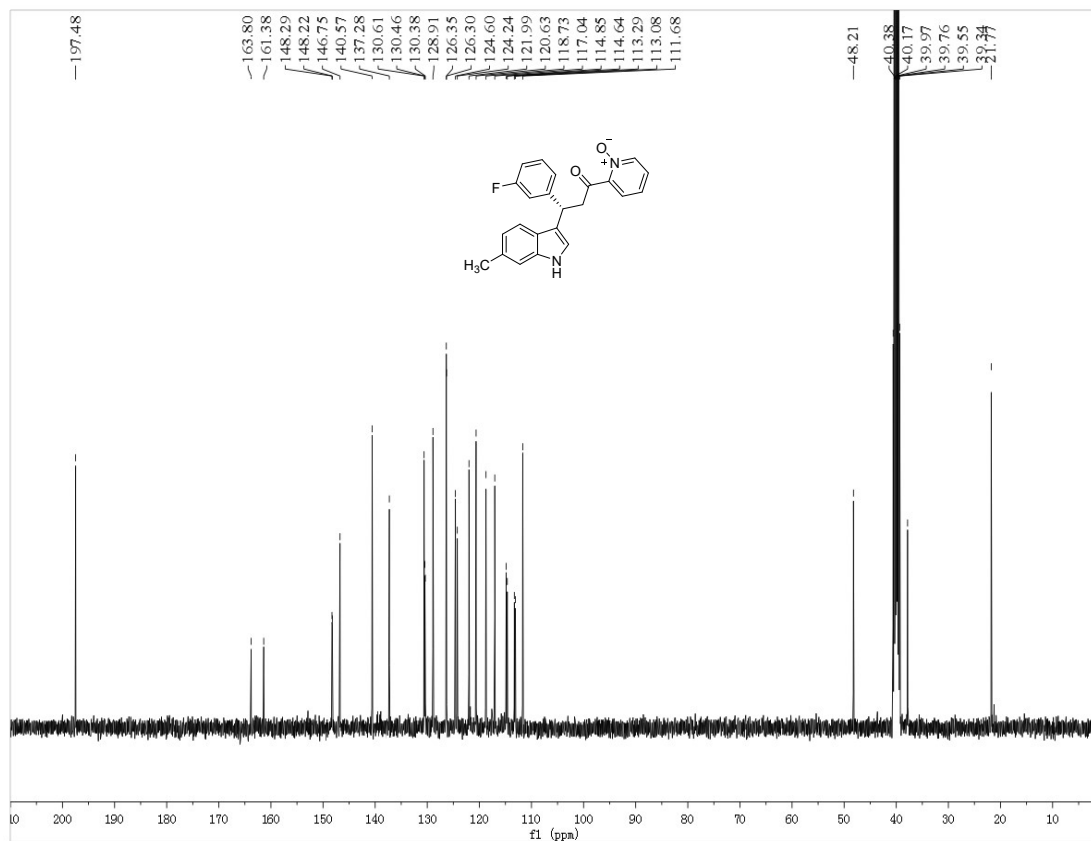
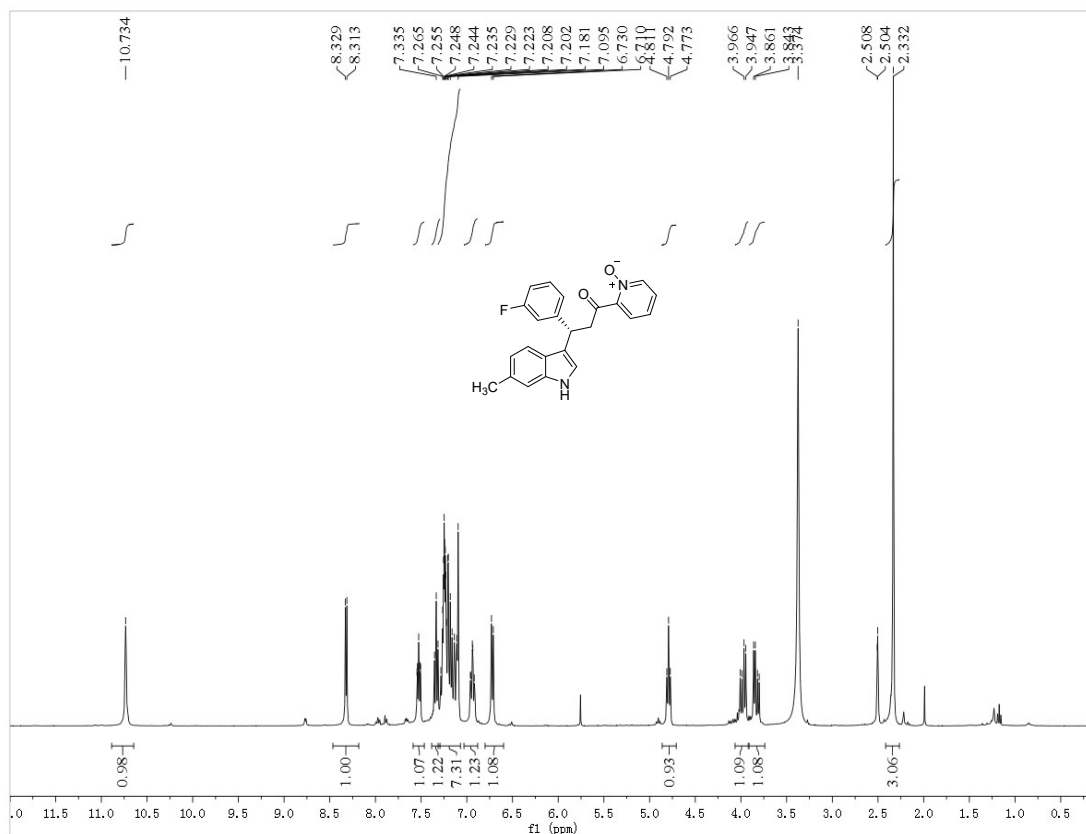
# <sup>1</sup>H and <sup>13</sup>C NMR of 6db



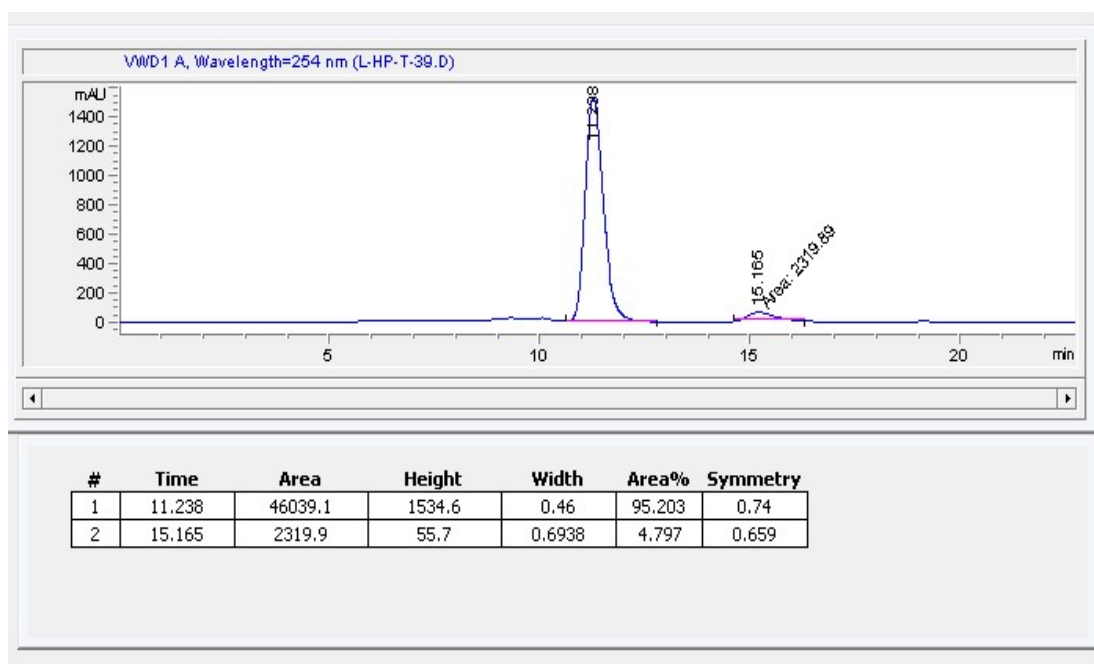
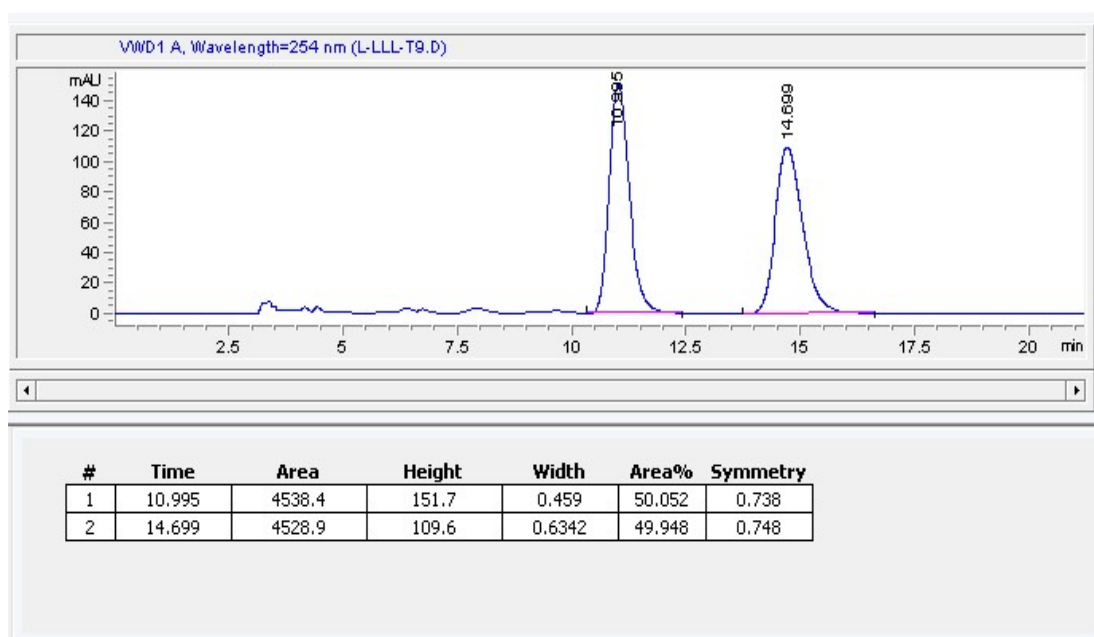
## HPLC of 6db



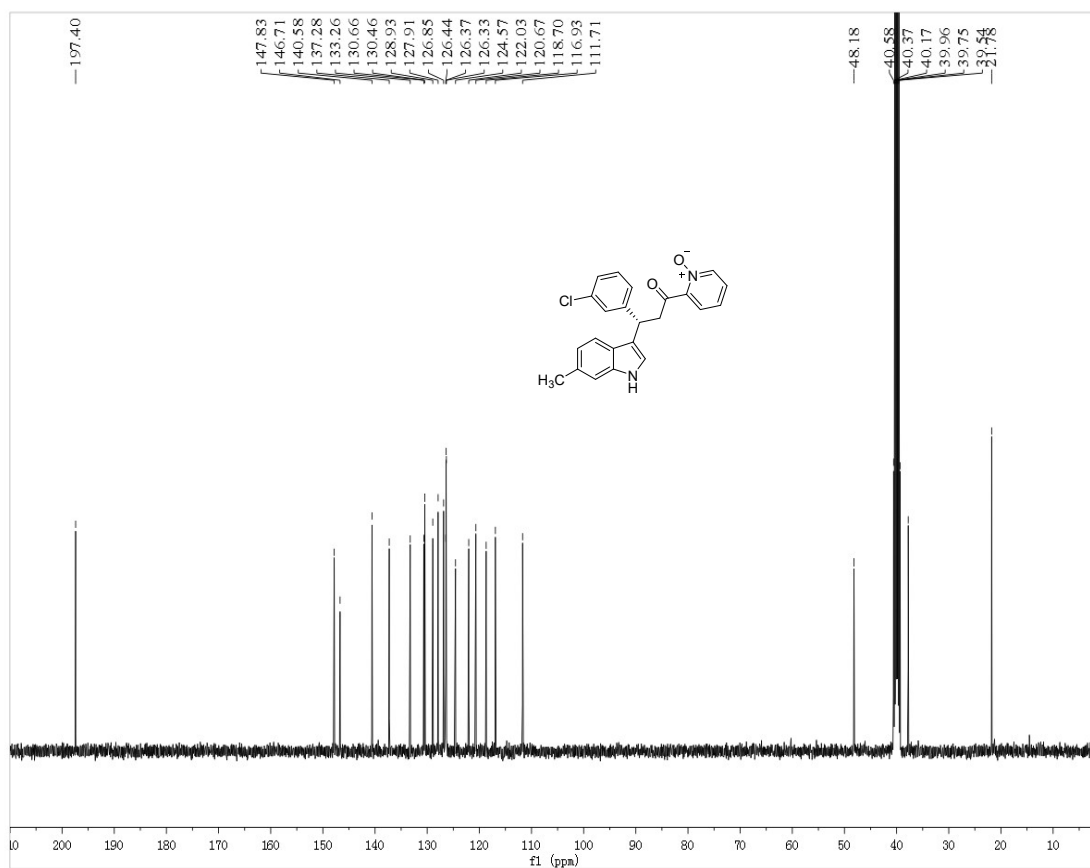
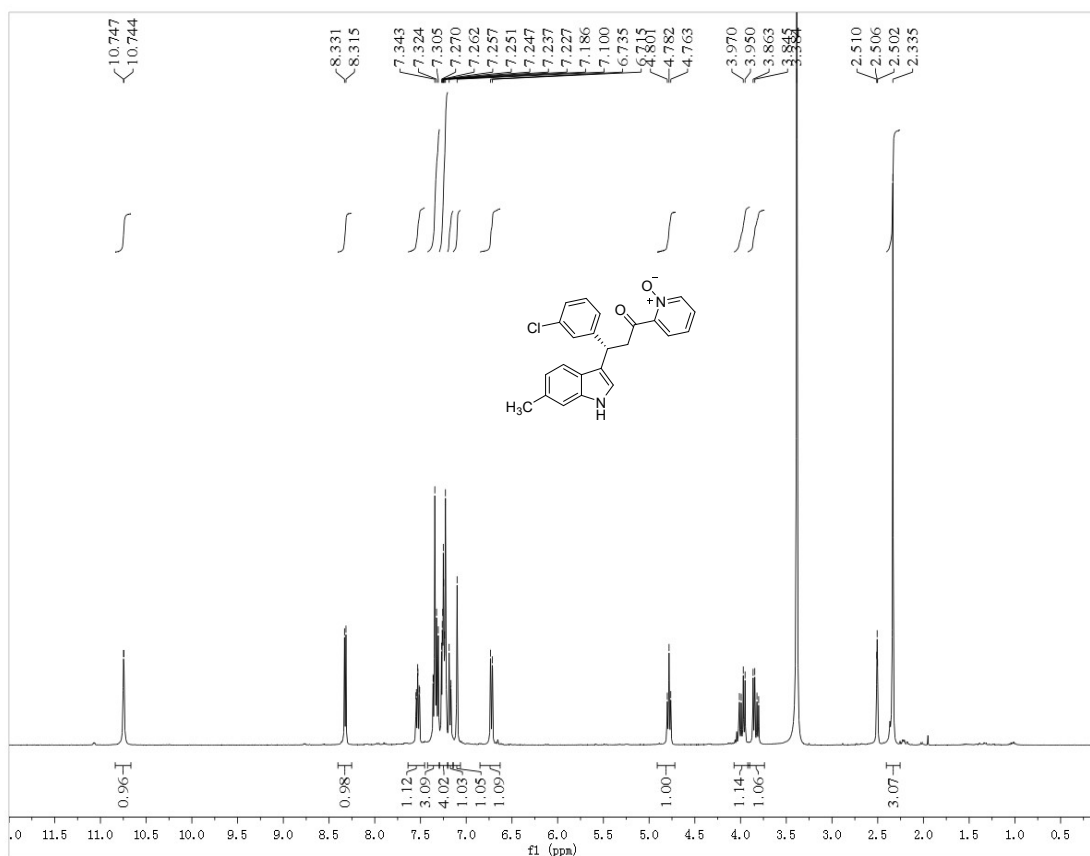
# <sup>1</sup>H and <sup>13</sup>C NMR of 6dc



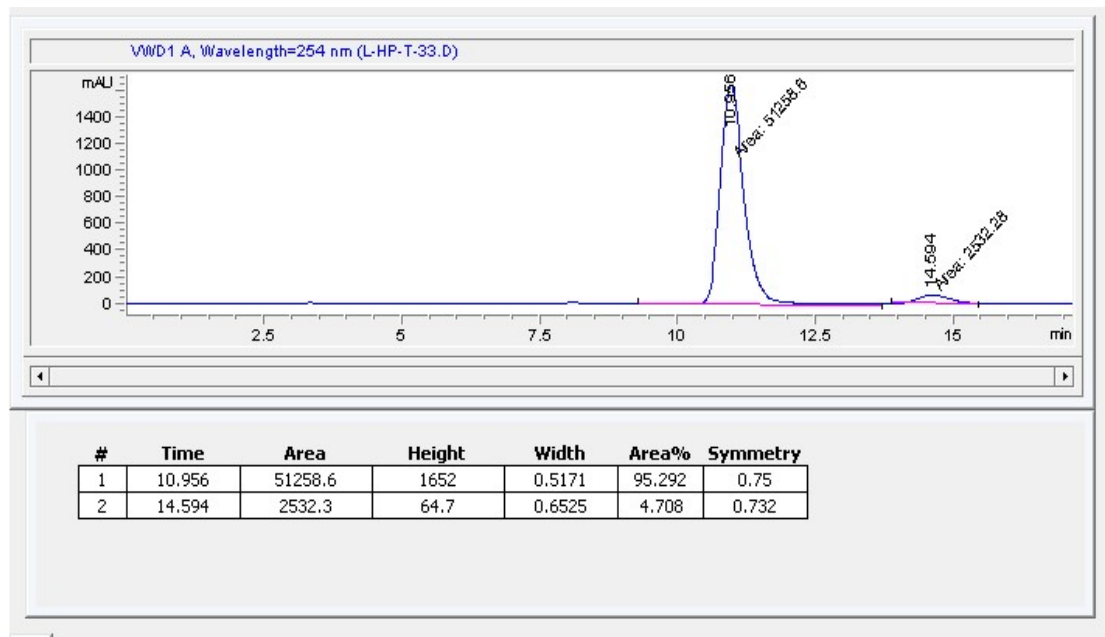
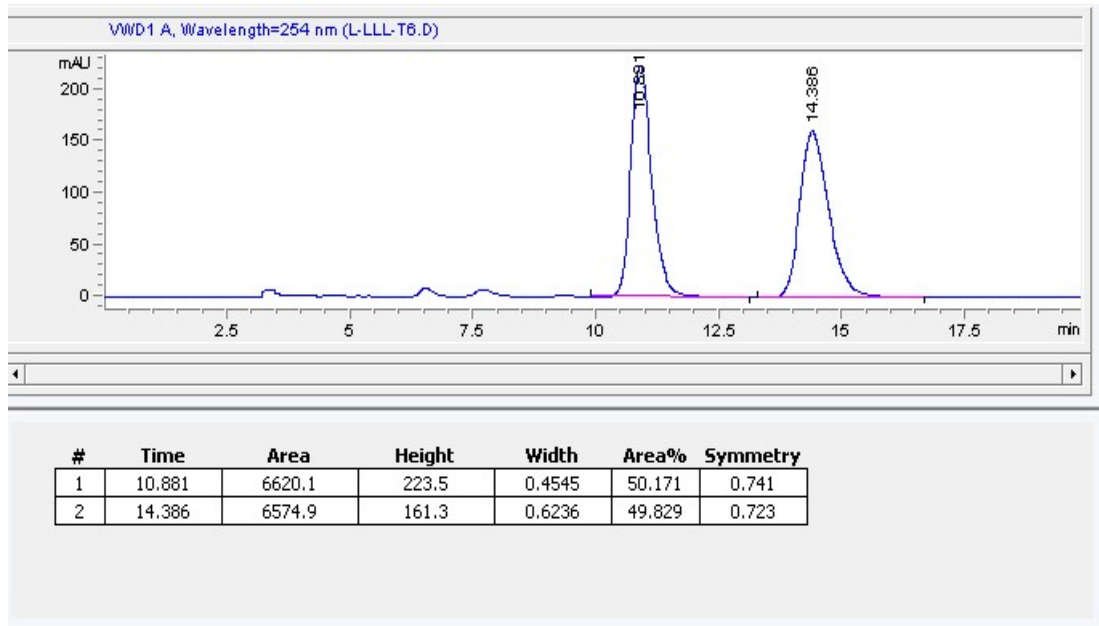
## HPLC of 6dc



**<sup>1</sup>H and <sup>13</sup>C NMR of 6dd**

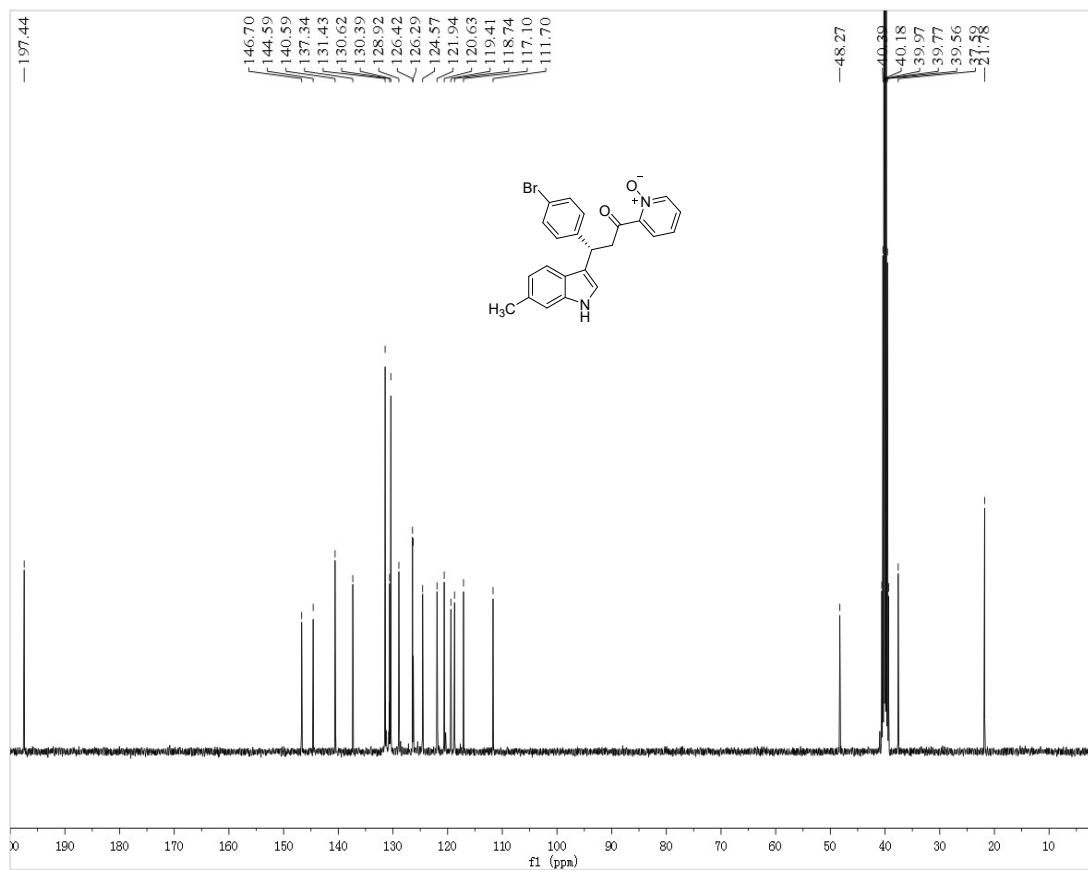
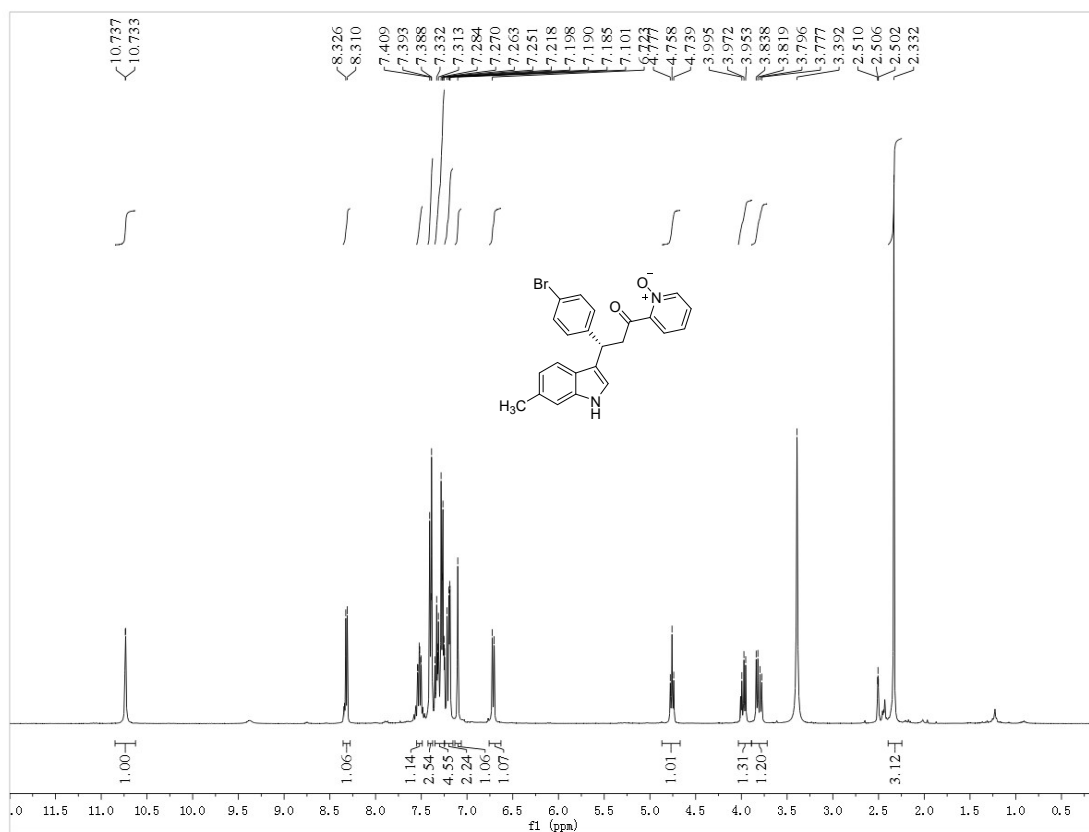


## HPLC of 6dd

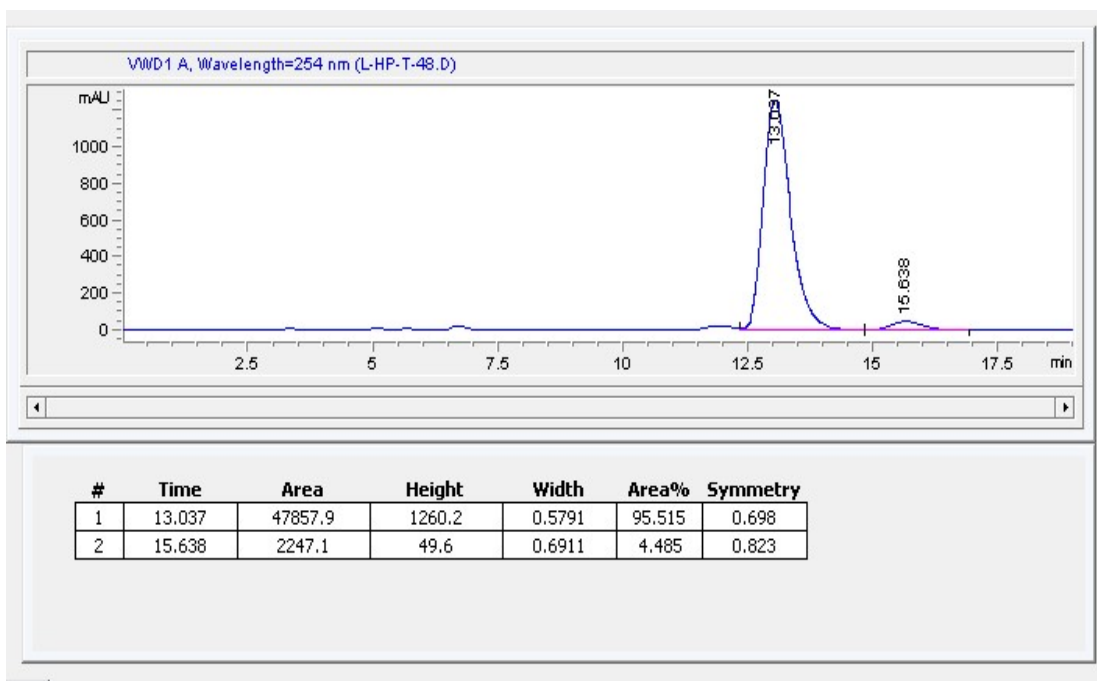
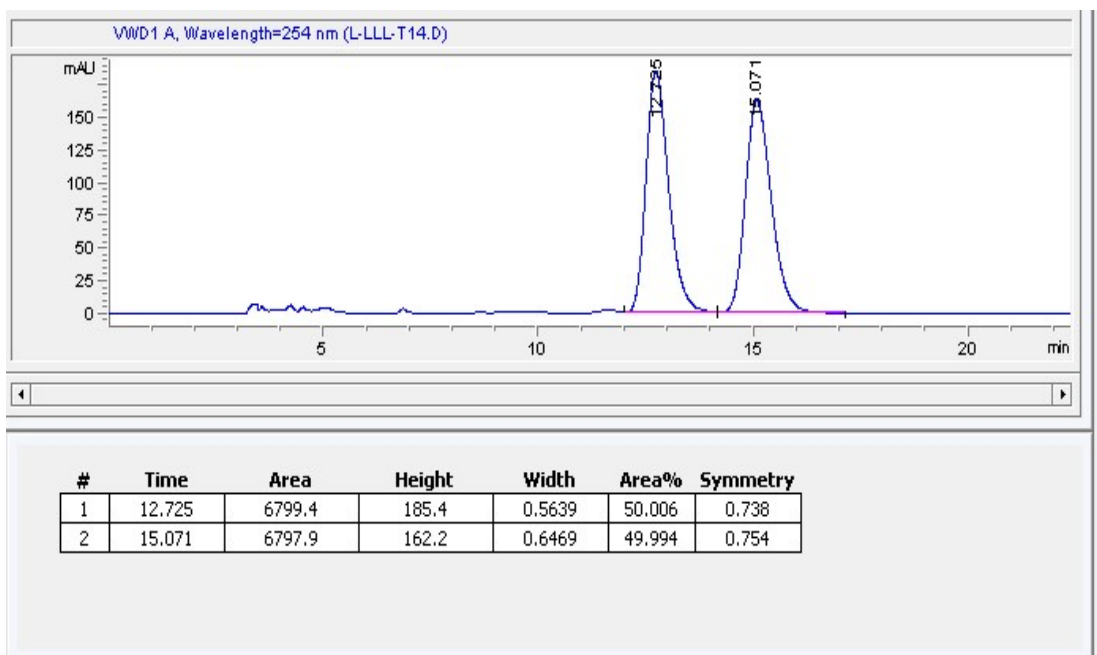




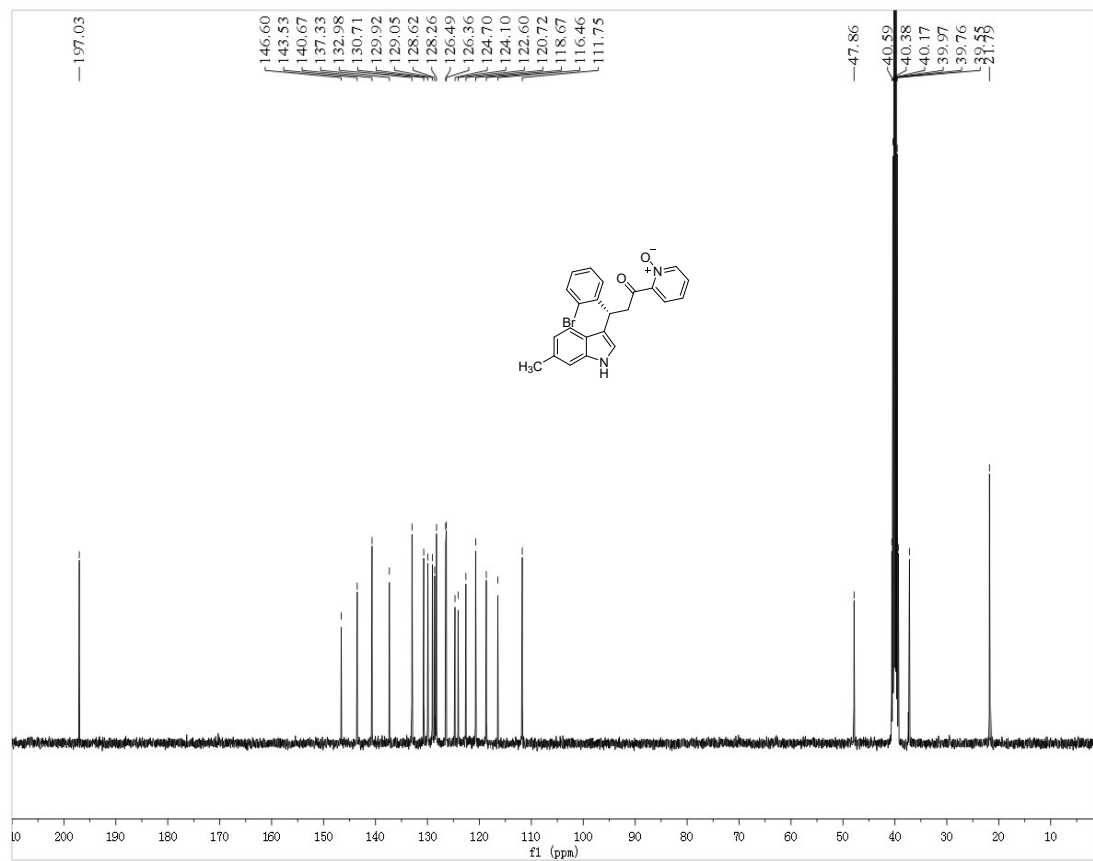
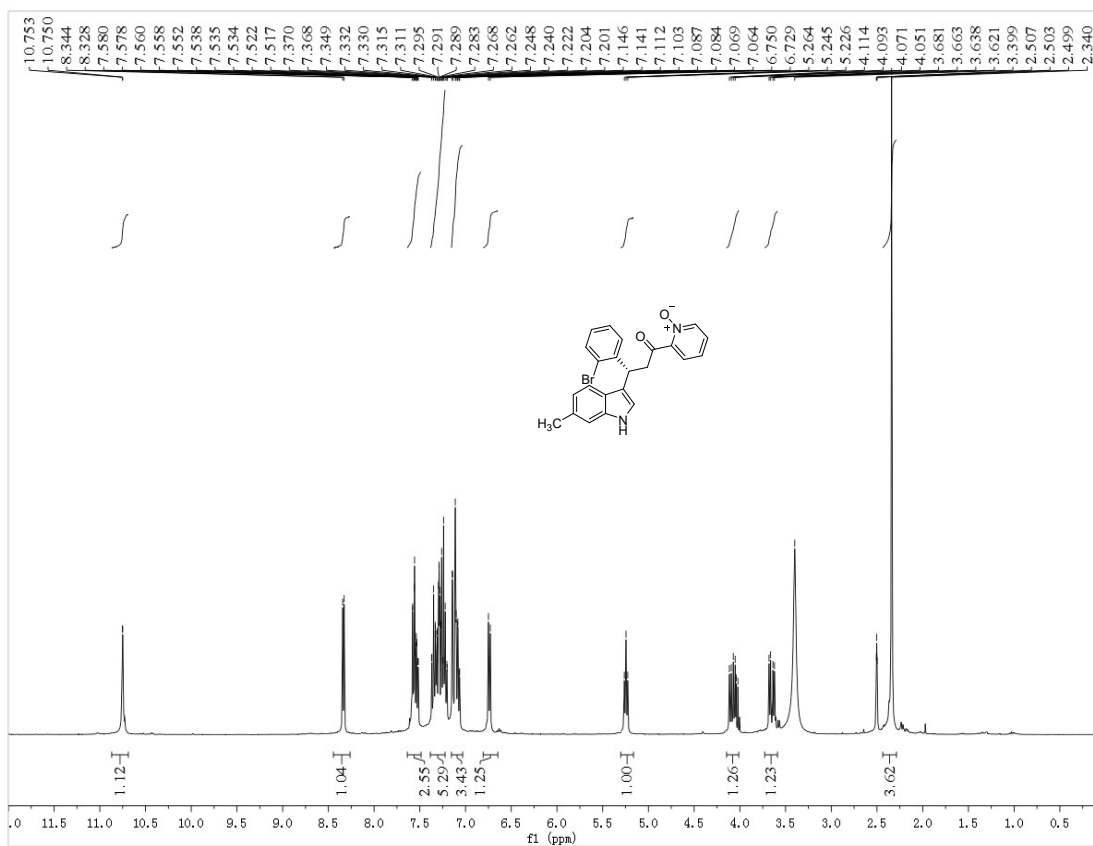
# <sup>1</sup>H and <sup>13</sup>C NMR of 6de



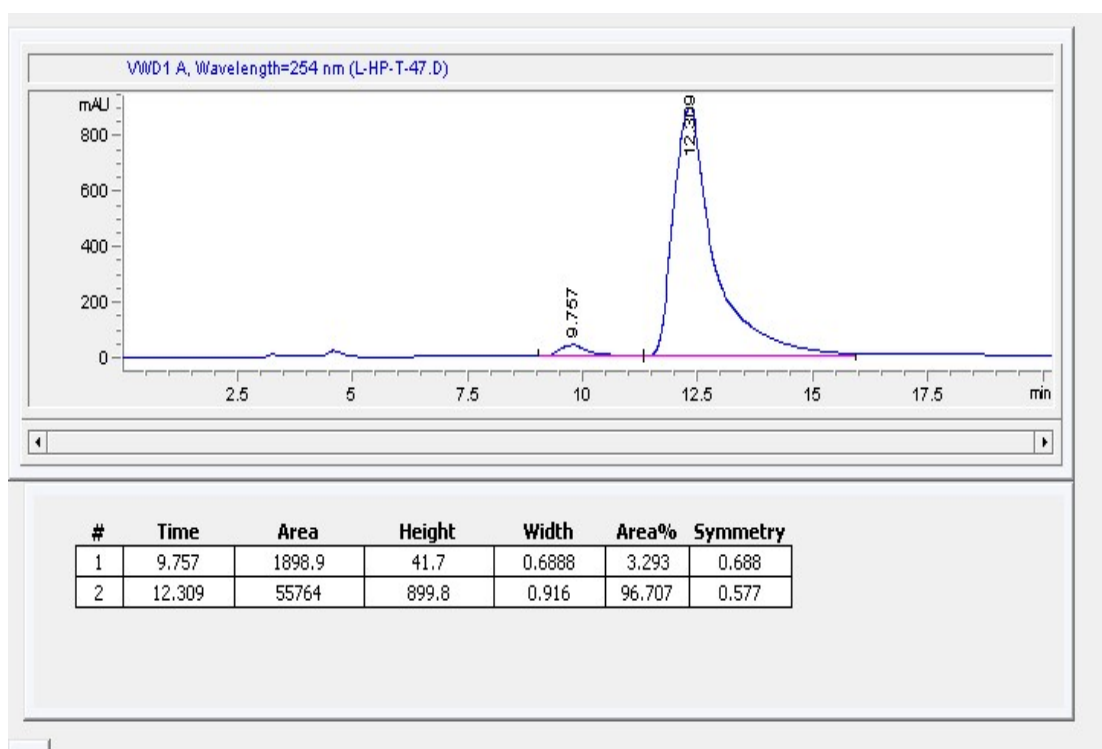
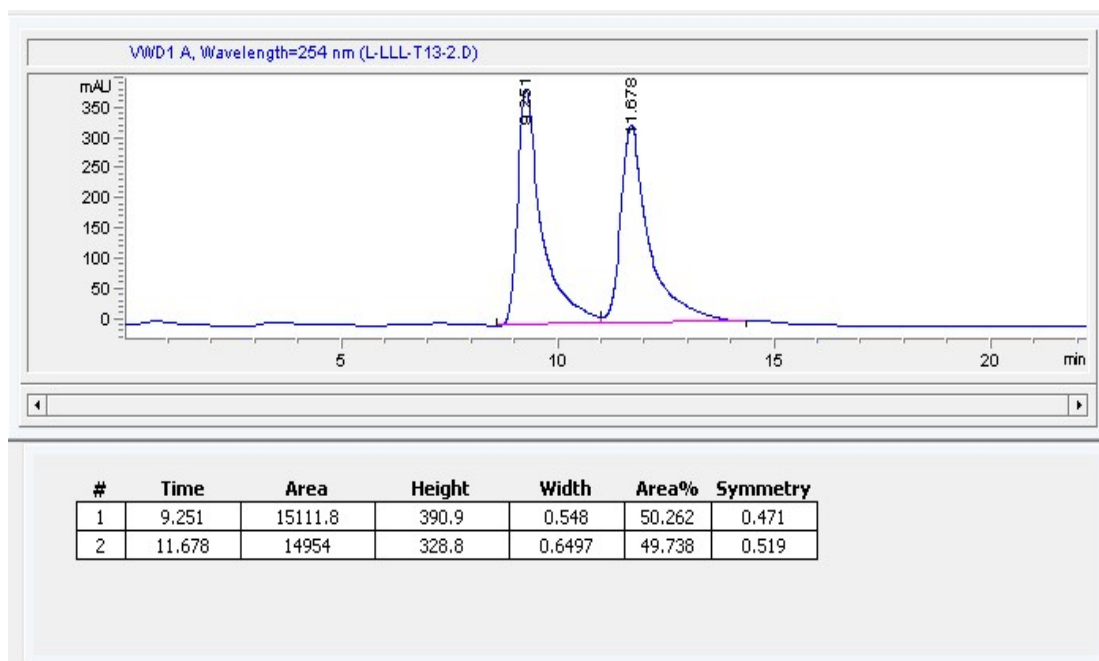
## HPLC of 6de



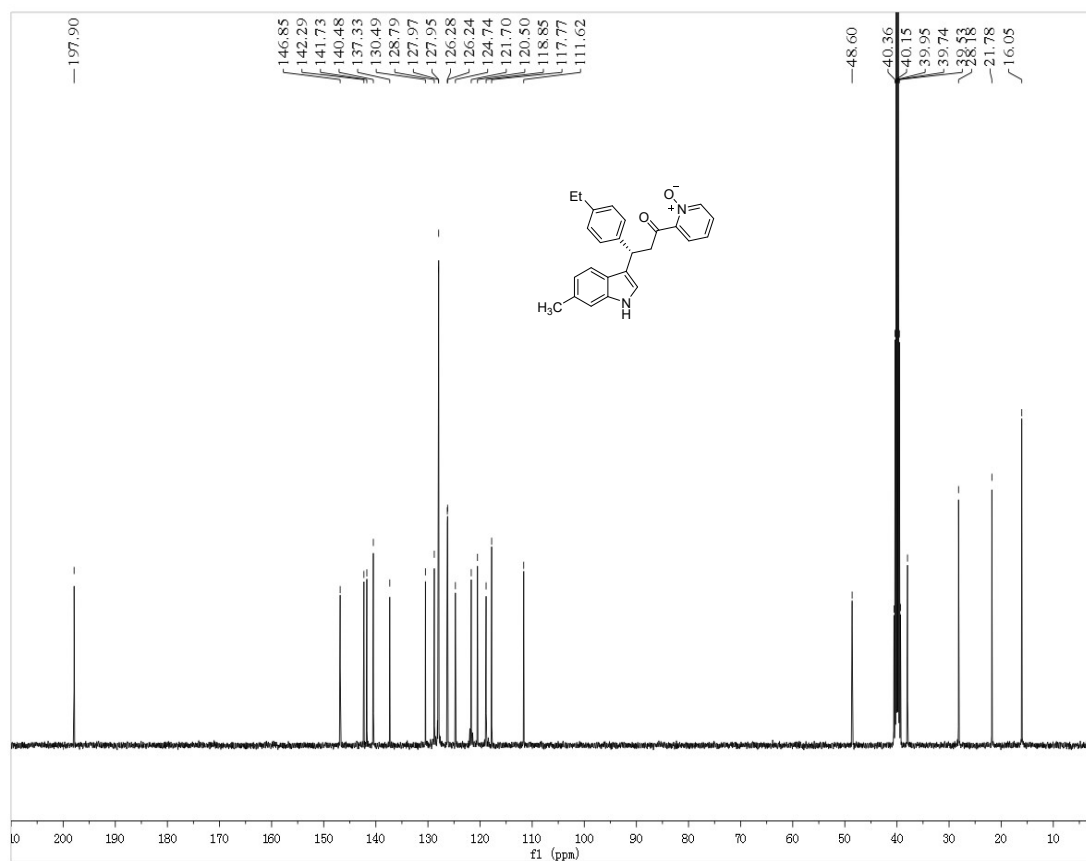
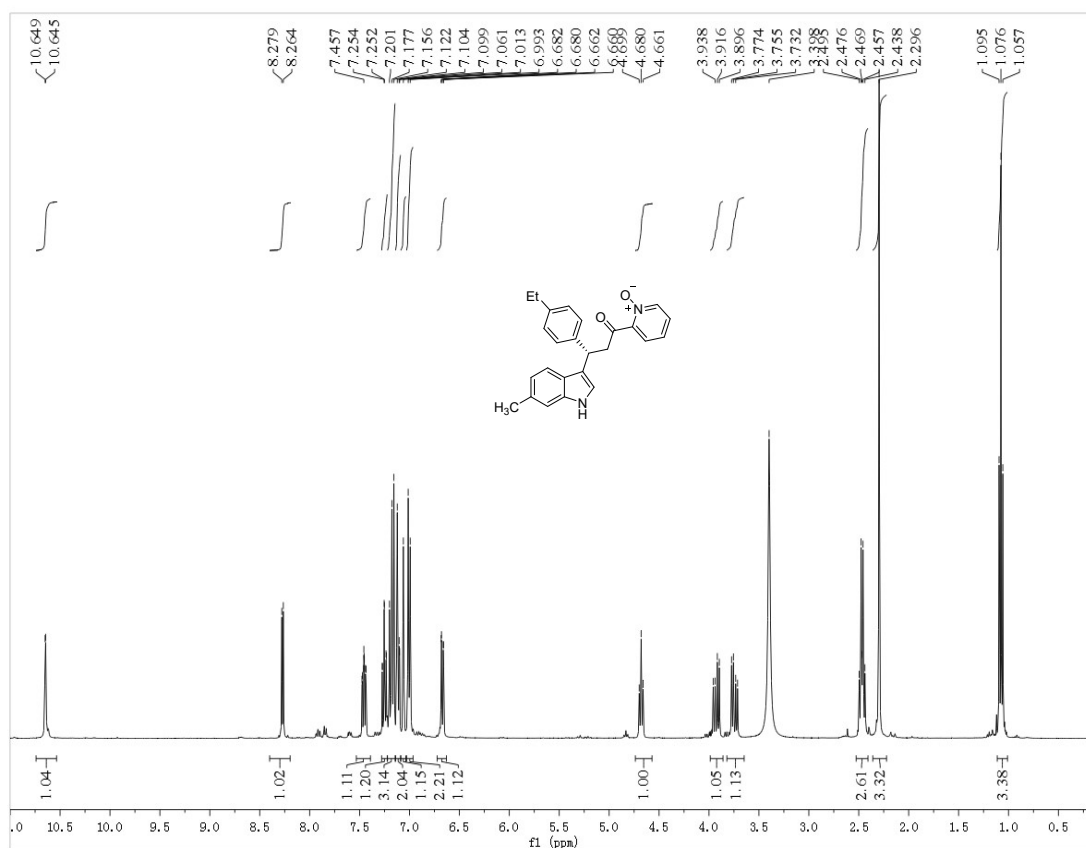
# <sup>1</sup>H and <sup>13</sup>C NMR of 6df



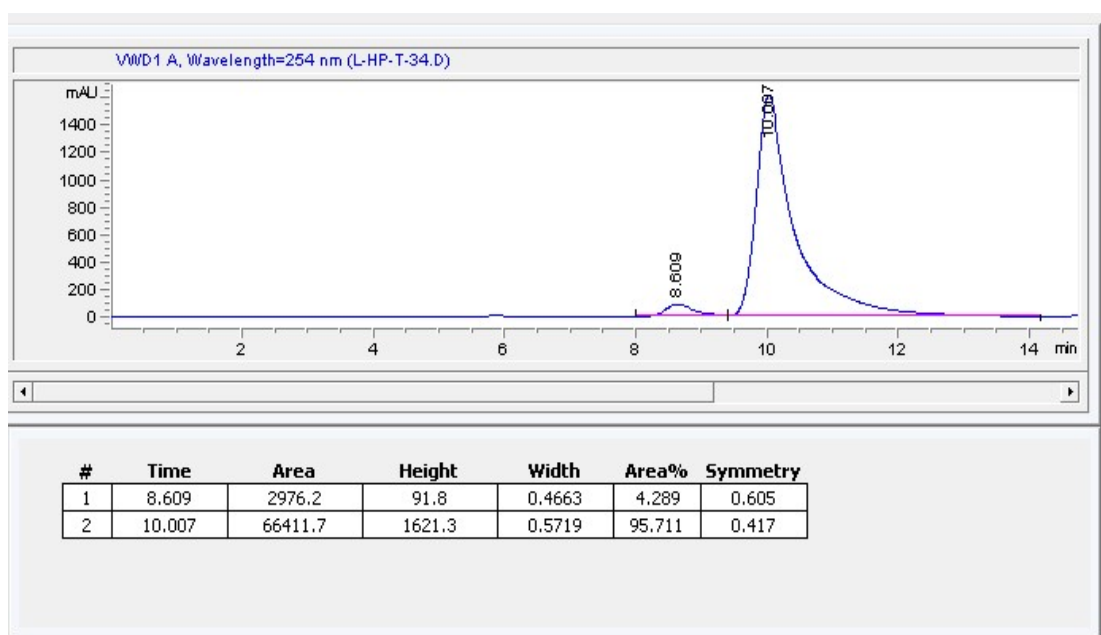
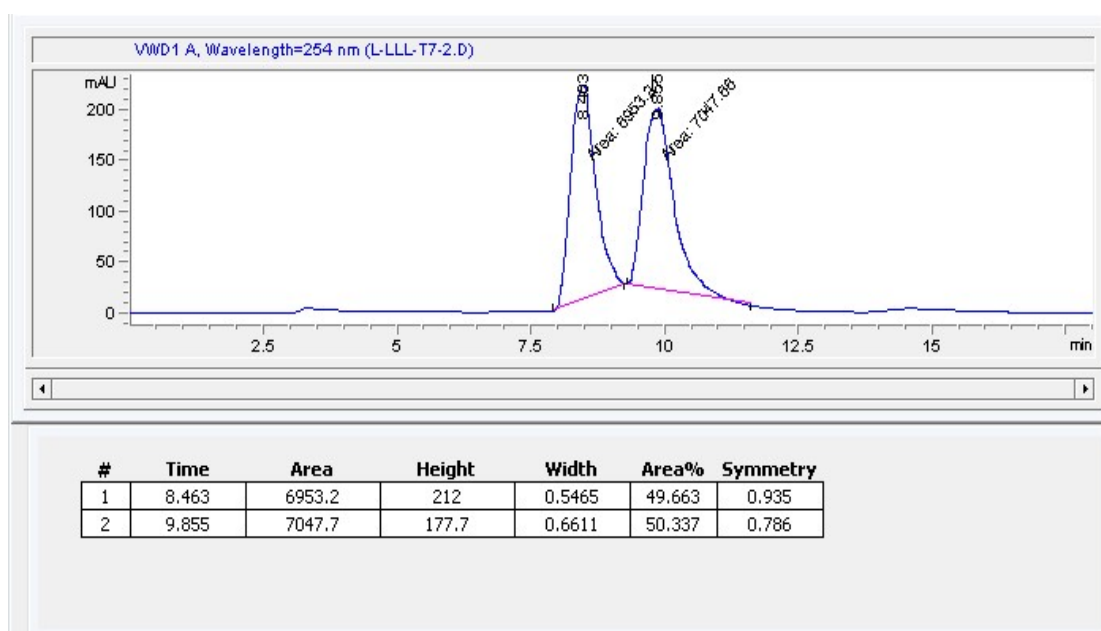
## HPLC of 6df



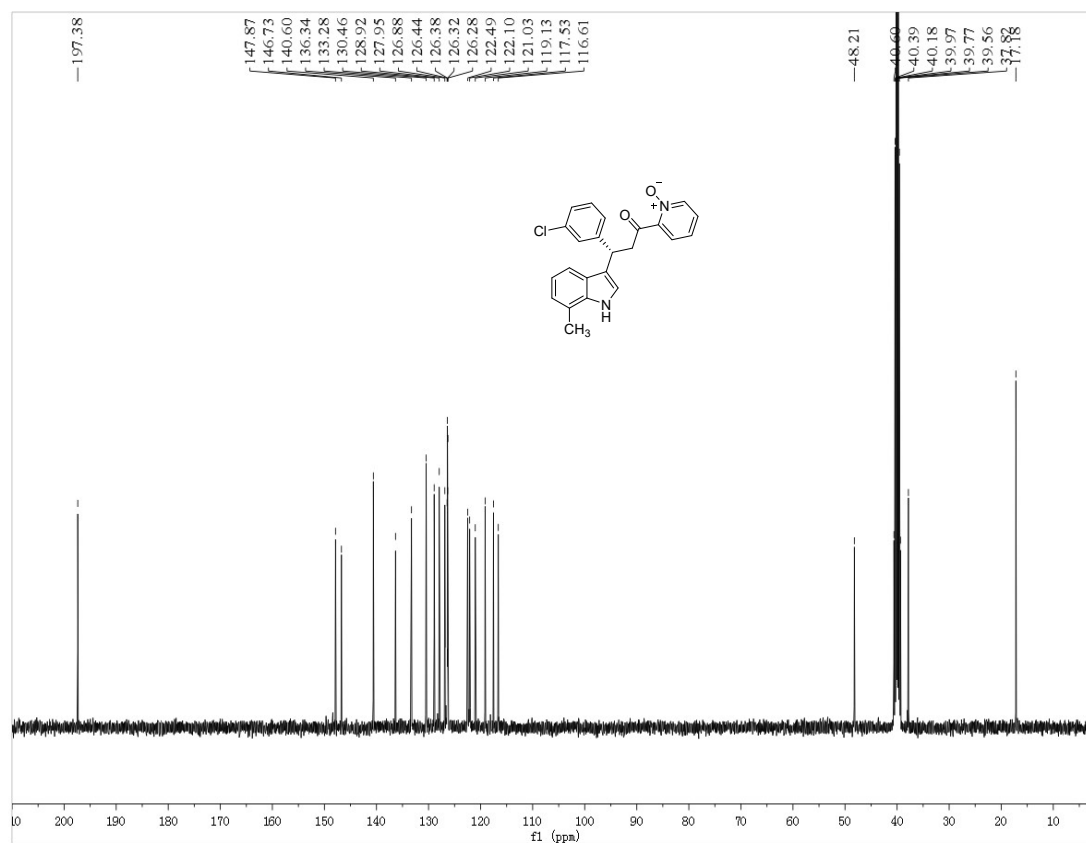
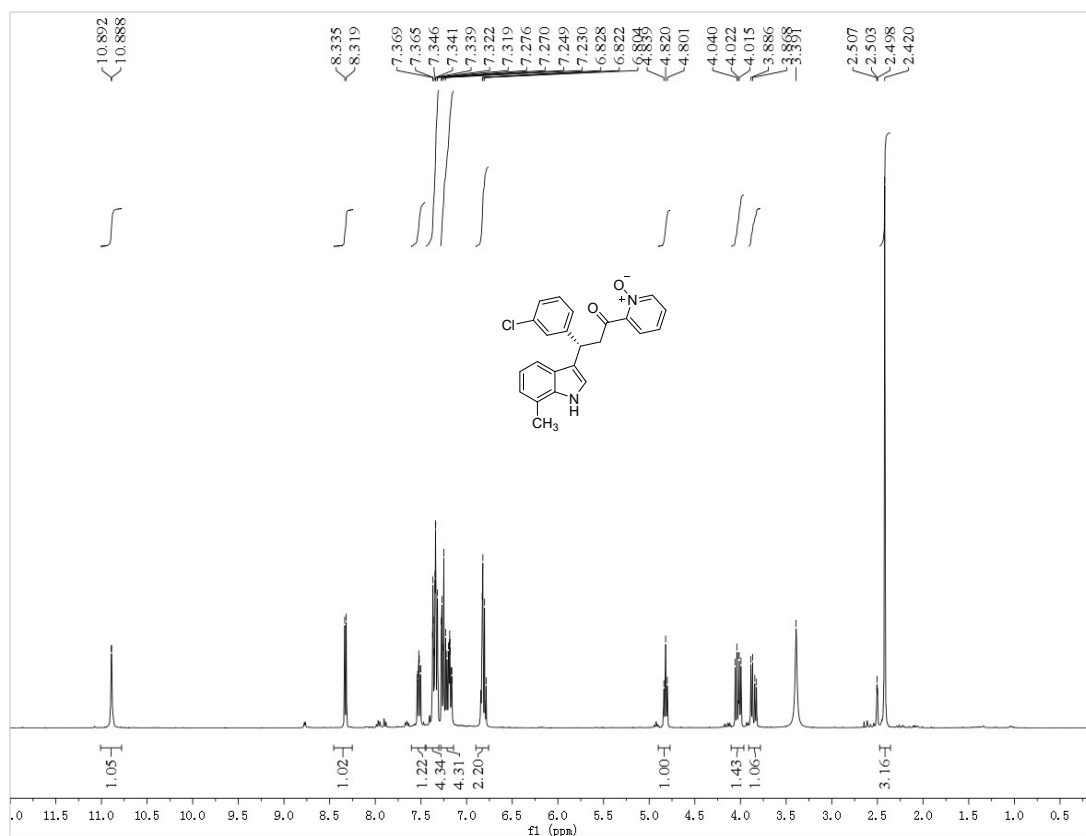
# <sup>1</sup>H and <sup>13</sup>C NMR of 6dg



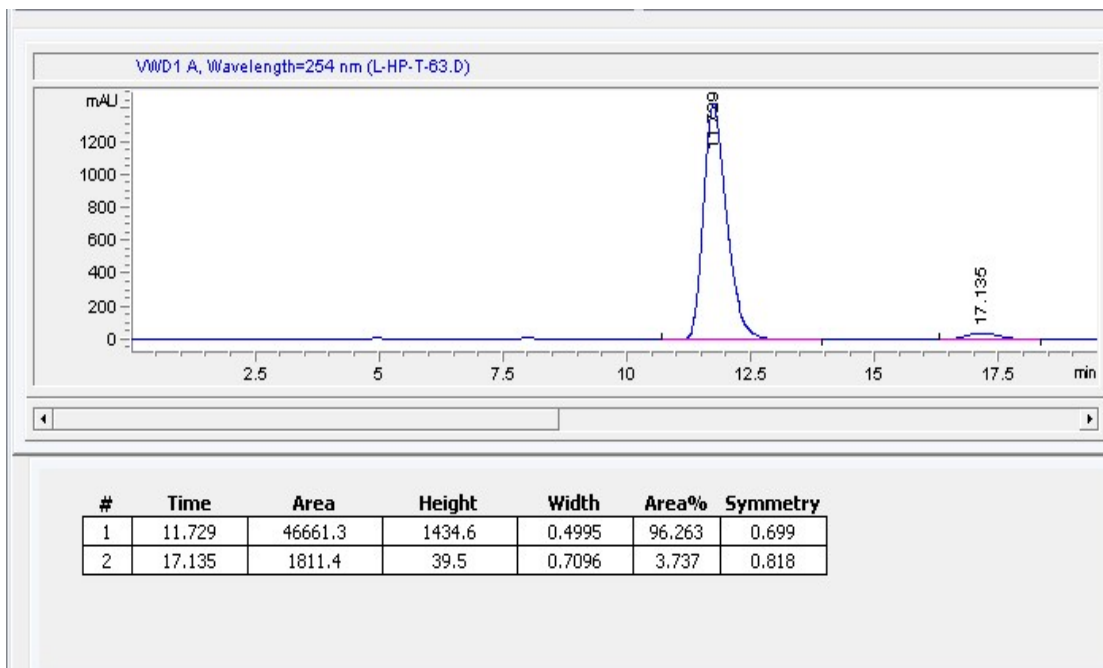
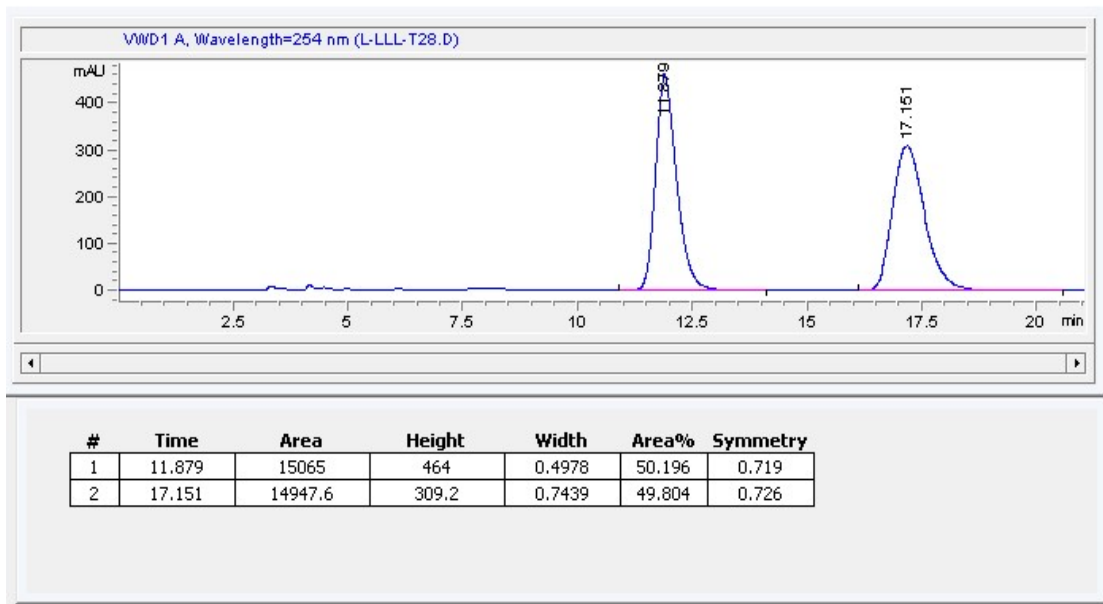
### HPLC of 6dg



# <sup>1</sup>H and <sup>13</sup>C NMR of 6ea

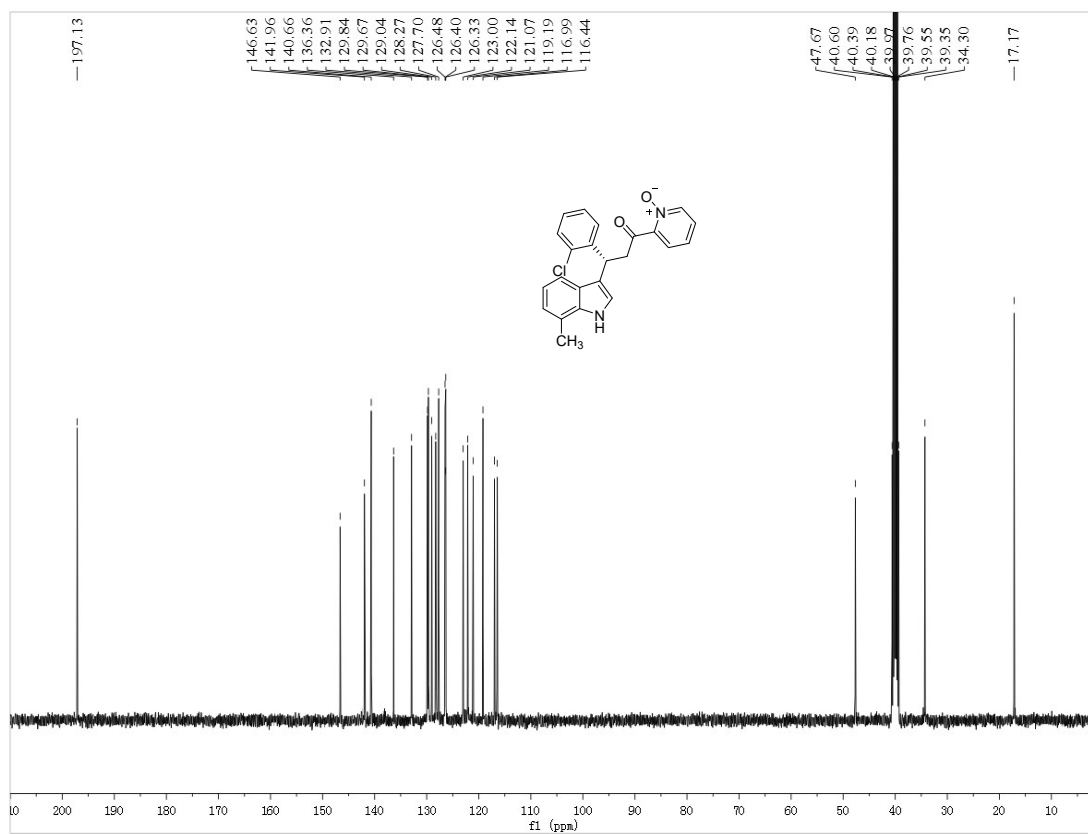
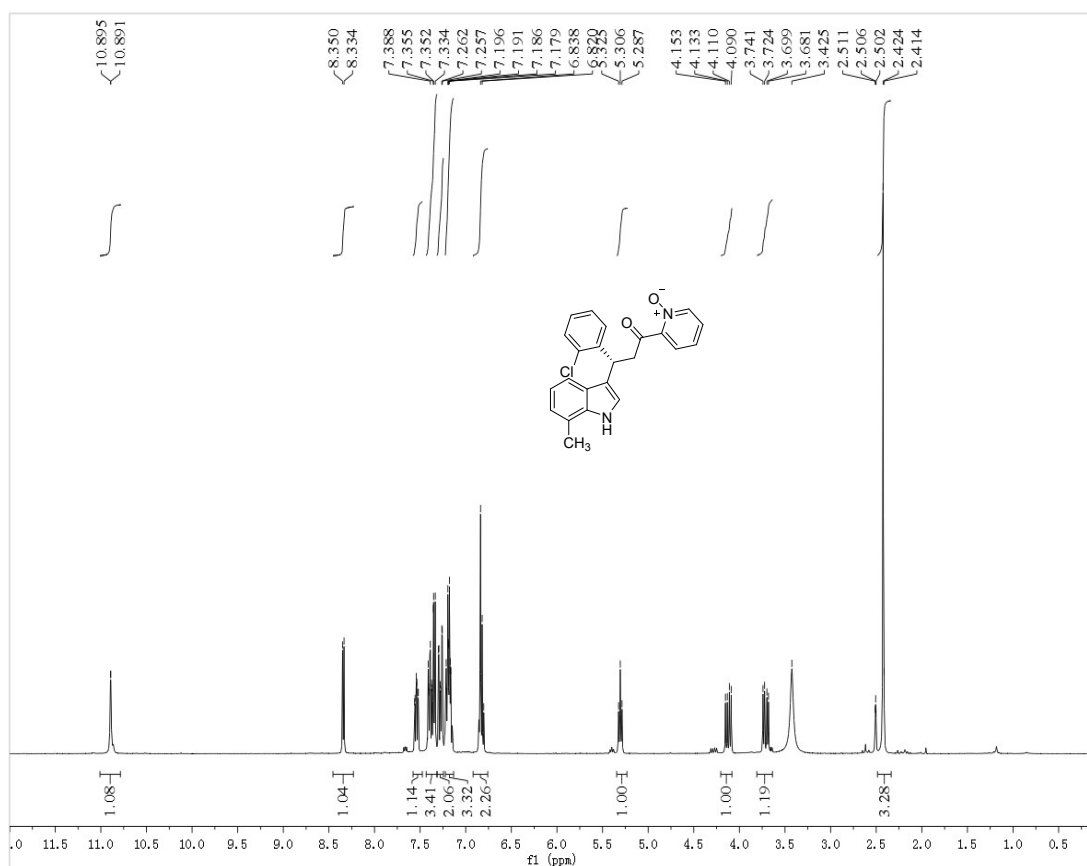


## HPLC of 6ea

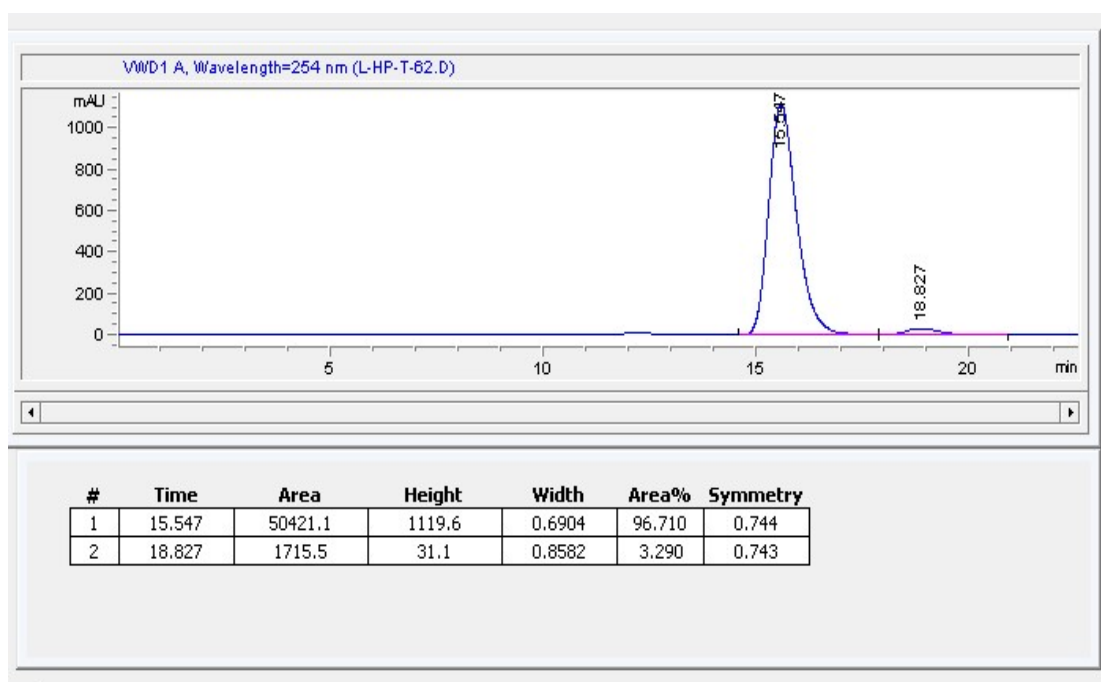
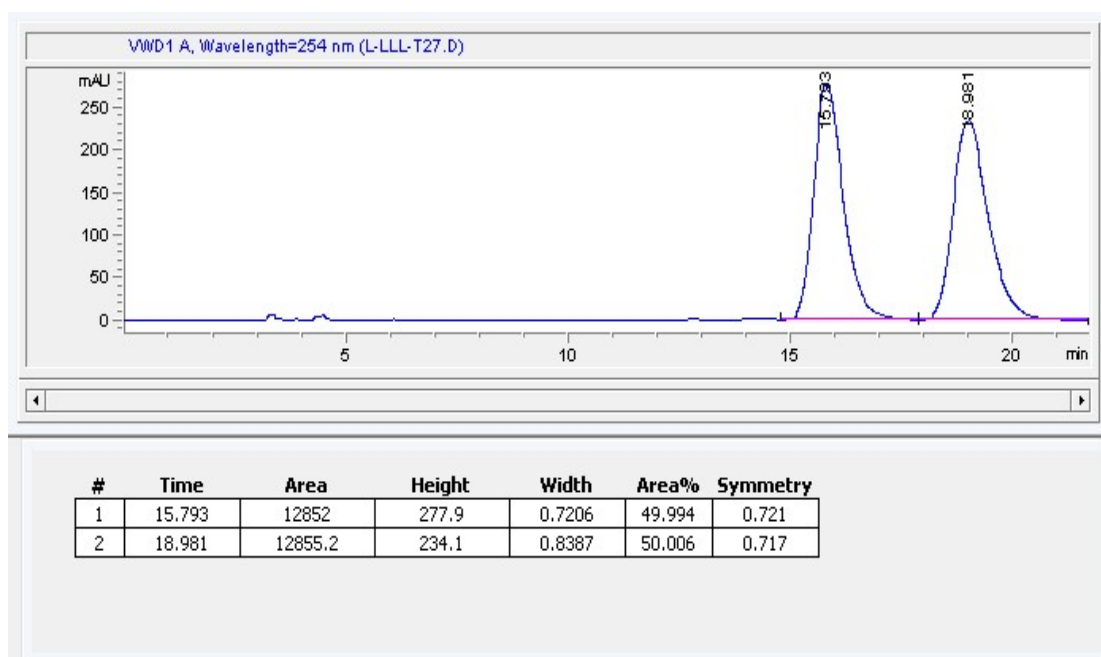




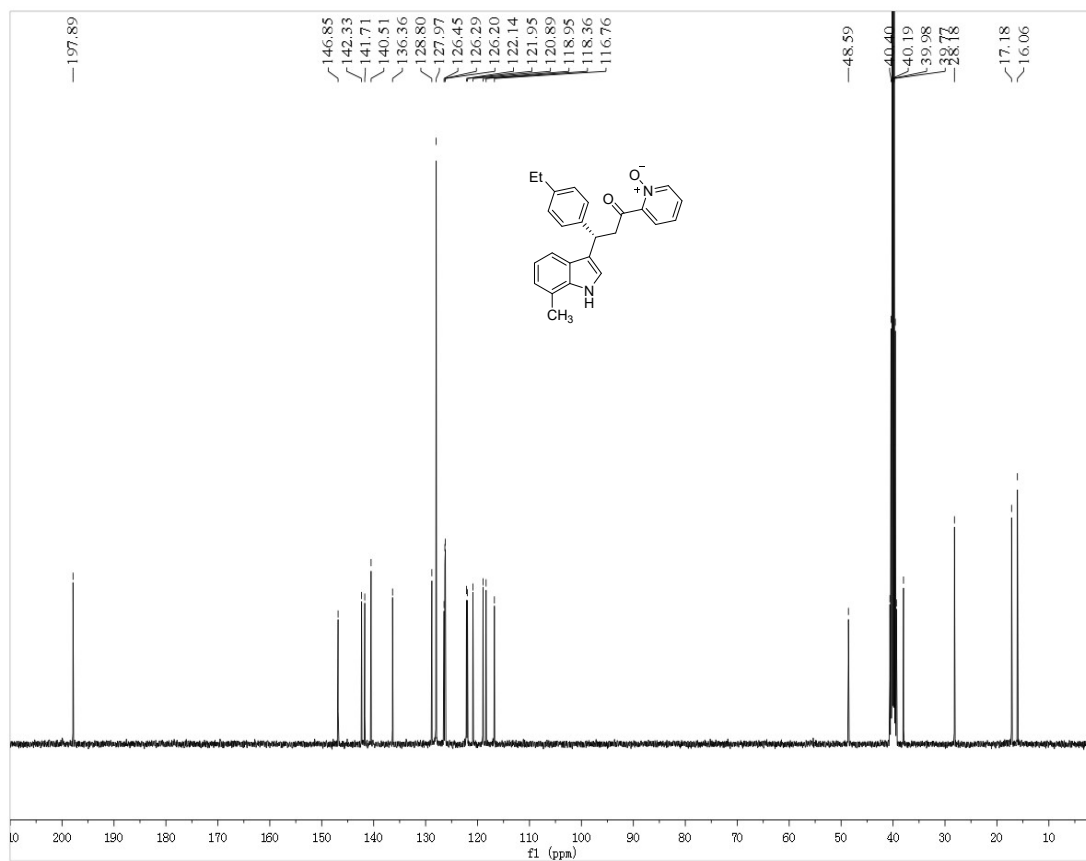
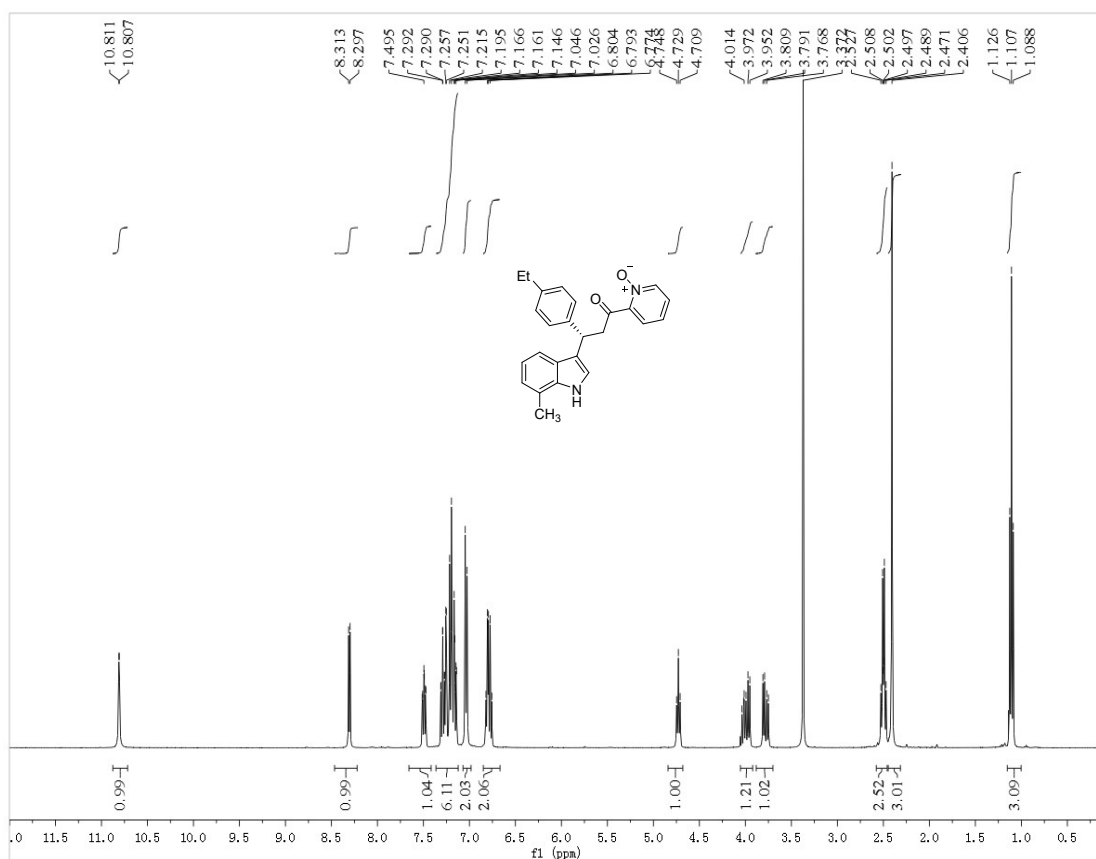
# <sup>1</sup>H and <sup>13</sup>C NMR of 6eb



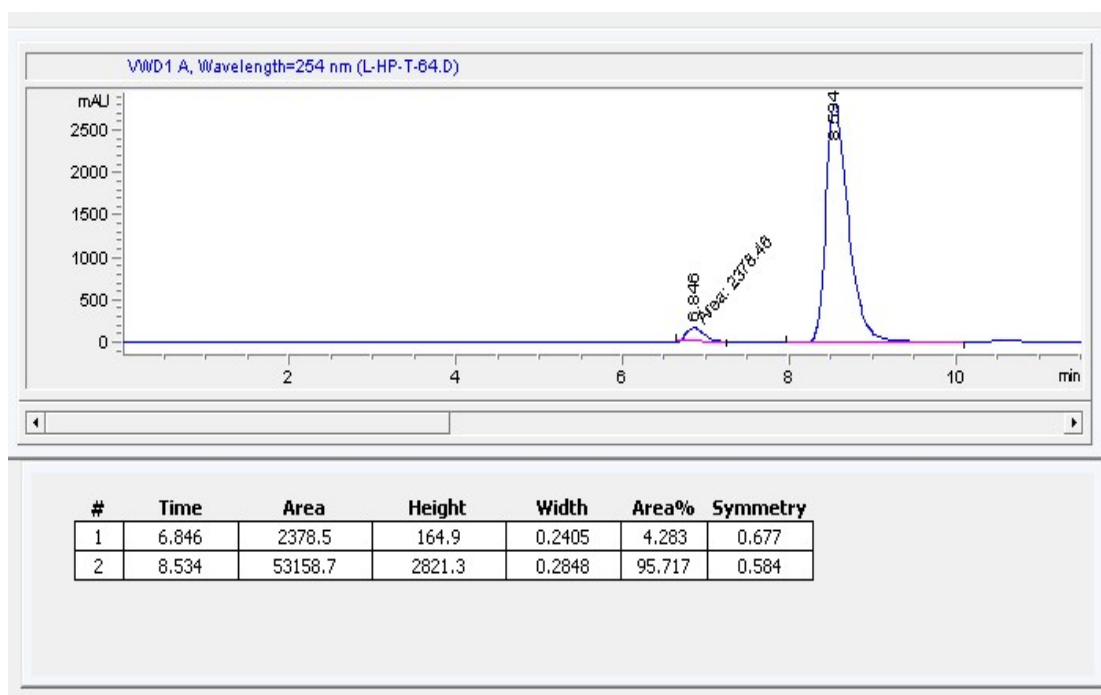
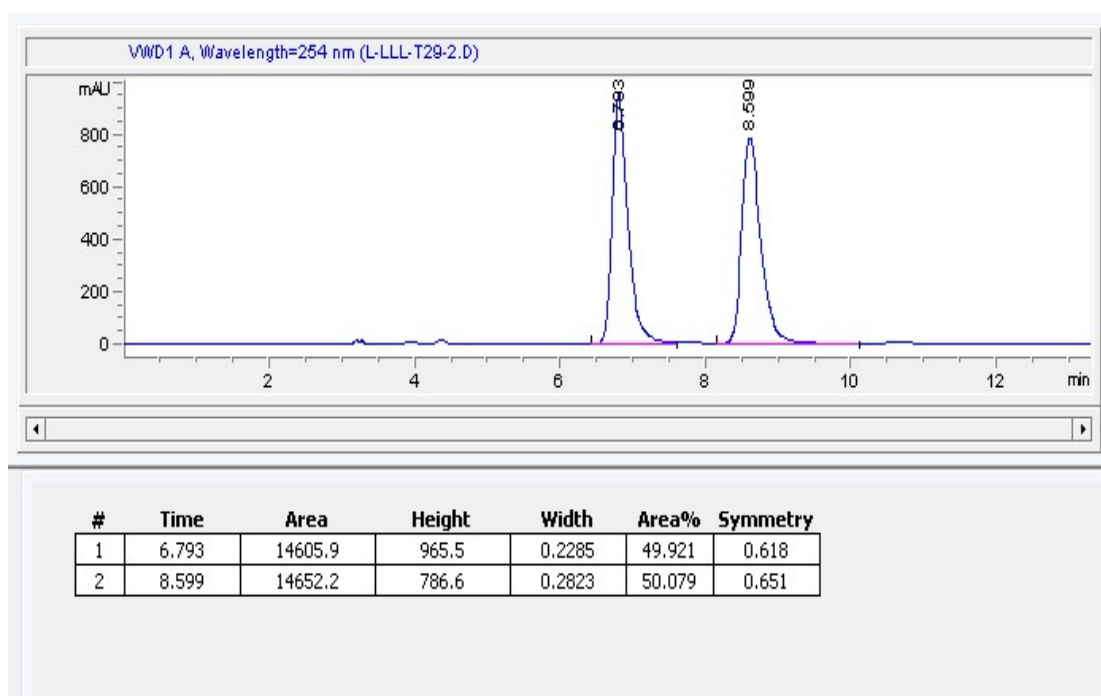
## HPLC of 6eb



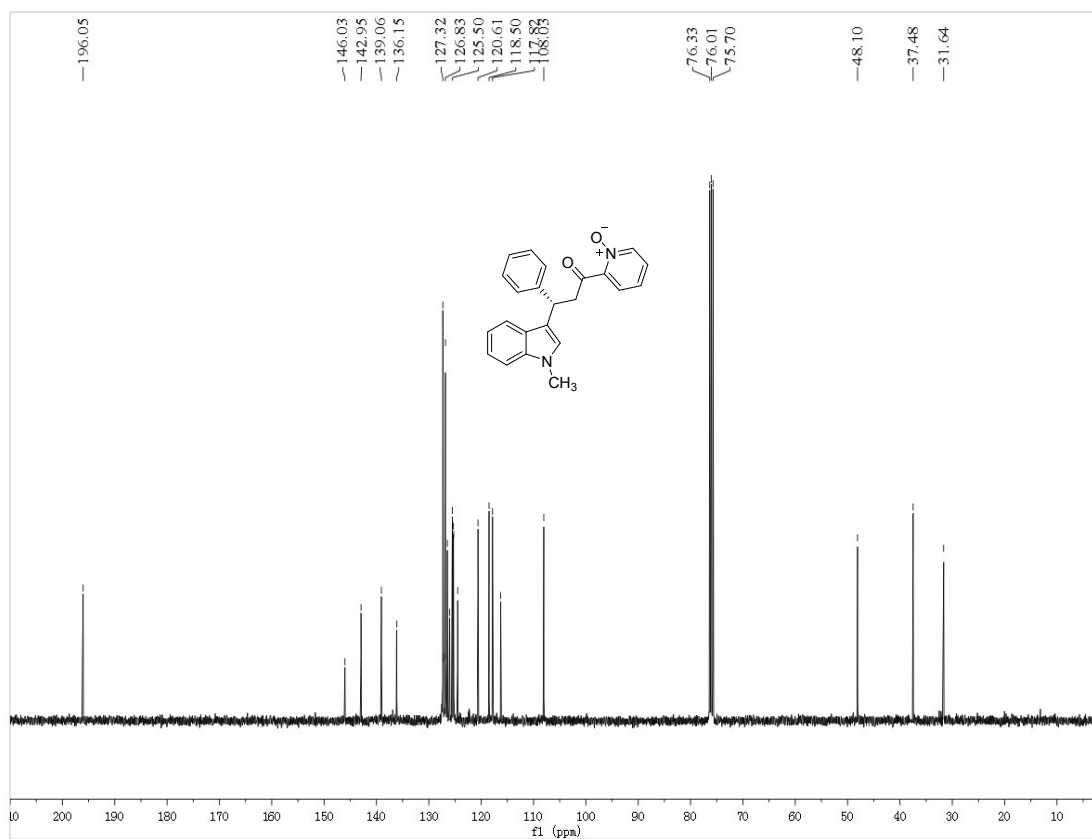
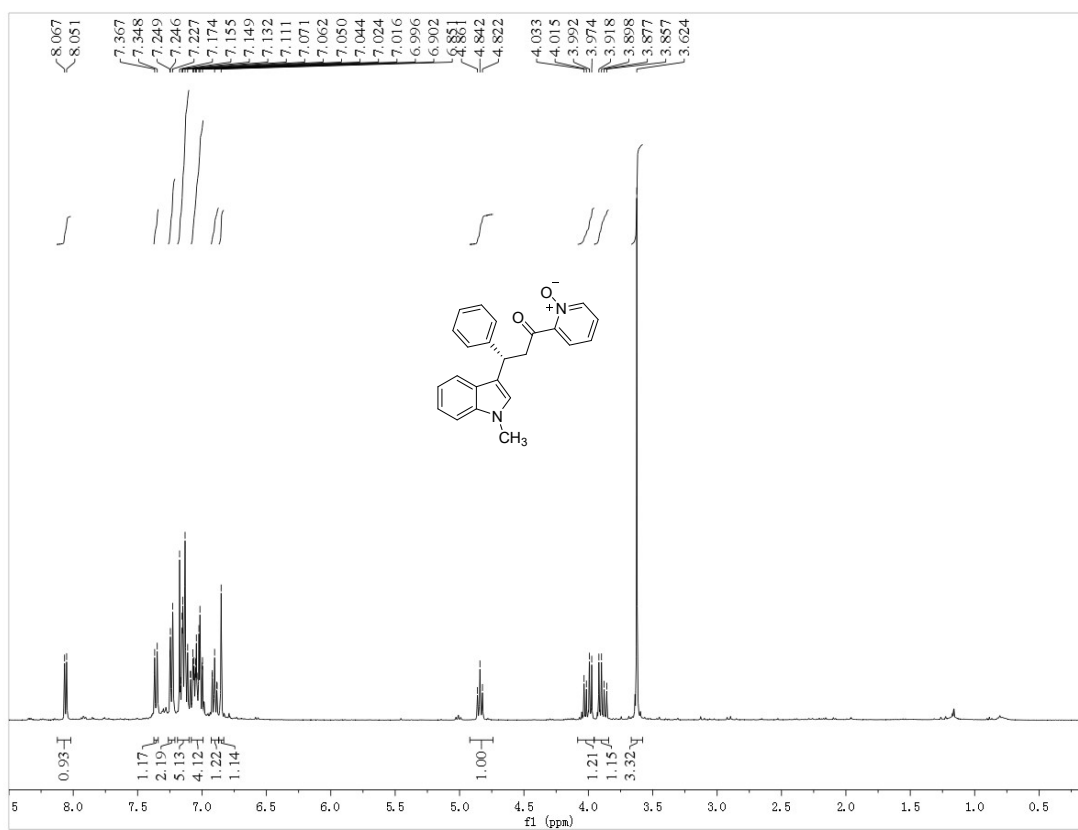
**<sup>1</sup>H and <sup>13</sup>C NMR of 6ec**



### HPLC of 6ec



### <sup>1</sup>H and <sup>13</sup>C NMR of 6fa



## HPLC of 6fa

