Naphthyridine-2NO, a new C_2-symmetric rigid tetradentate bimetallic ligand and its application in asymmetric Friedel-Crafts alkylation

Pan Hu[a,d], Ke-Lan Xu[a,d], Xi-Rui Wang[a,d], Zi-Yue Chen[a], Wen-Hui Zhang[b], Ying Zhou[b], Wen-Jing Zhang[c], and Xiong-Li Liu[a,*]

[a] National & Local Joint Engineering Research Center for the Exploitation of Homology Resources of Southwest Medicine and Food, Guizhou University, Guiyang 550025, Guizhou, China.

[b] College of Pharmaceutical Sciences, Guizhou University of Traditional Chinese Medicine, Guiyang, 550025, Guizhou, China.

[c] Green Catalysis Center, and College of Chemistry, Zhengzhou University, Zhengzhou 450001, Henan, China.

[d] These three authors contributed equally to this work.

*E-mail address: xlliu1@gzu.edu.cn

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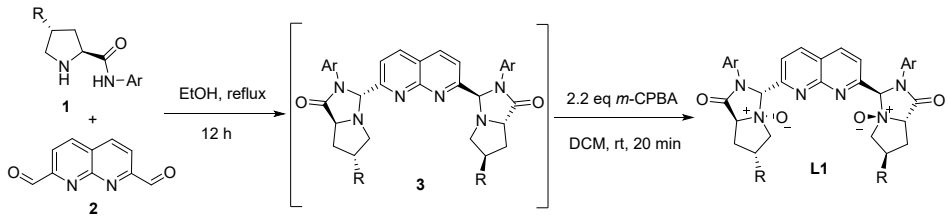
1. General information

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}H and ^{13}CNMR spectra were obtained using a Bruker DPX-400 spectrometer. ^{1}H NMR chemical shifts are reported in ppm (δ) 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}C NMR chemical shifts are reported in ppm (δ) from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Melting points were measured on an electrothermal digital melting point apparatus.

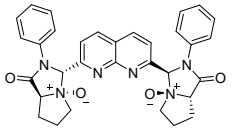
2. General procedure for preparation of chiral Nar-2NO ligands L1



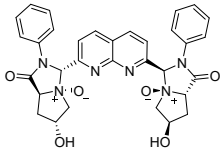
General procedure A-In a sealed tube equipped with a magnetic stirring bar, naphthyridine-dicarbaldehyde **2** (1.0 mmol) and optically pure prolinamide **1** (2.4 mmol, 2.4 equiv) were added. Then, ethanol (6.0 mL) was added and the reaction was heated with stirring at reflux for 12 h. After completion of the reaction, as indicated by TLC, the aftertreatment residue was purified by flash column chromatography to give the intermediate **3**.

In a sealed tube equipped with a magnetic stirring bar, to the intermediate **3** was added 3.0 mL of DCM and *m*-CPBA (2.2 eq). The reaction mixture was stirred at 0 ^{o}C for 20 min. After completion of the reaction, as indicated by TLC, the aftertreatment residue was purified by flash column chromatography to furnish the Nar-2NO ligand **L1**.

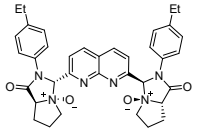
3. Characterization data of ligands L



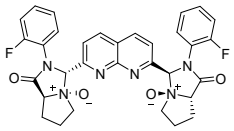
L1a: White solid, M.p. 247.1-247.9 °C, $[\alpha]_D^{20}$ = +55.7 (*c* 0.52, $CHCl_3$); overall yield 51%, >20:1 dr; ^1H NMR (CD_3OD, 400 MHz) *δ*: 2.20-2.27 (m, 2H), 2.44-2.58 (m, 6H), 3.92-3.96 (m, 2H), 4.13-4.20 (m, 2H), 4.80-4.82 (m, 2H), 7.02 (s, 2H), 7.14-7.18 (m, 2H), 7.26-7.30 (m, 4H), 7.47-7.50 (m, 4H), 7.95 (d, *J* = 8.4 Hz, 2H), 8.54 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (CD_3OD, 100 MHz) *δ*: 22.3, 24.1, 70.8, 76.8, 87.3, 122.4, 124.1, 125.6, 126.6, 129.0, 135.6, 138.5, 154.4, 156.0, 168.8; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{30}N_6NaO_4$ $[M+Na]^+$: 585.2221; Found: 585.2228.



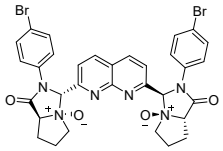
L1b: White solid, M.p. 248.2-249.0 °C, $[\alpha]_D^{20}$ = -33.3 (*c* 0.49, $CHCl_3$); overall yield 45%, >20:1 dr; ^1H NMR (CD_3OD, 400 MHz) *δ*: 2.57-2.63 (m, 2H), 2.83-2.90 (m, 2H), 3.95 (d, *J* = 12.4 Hz, 2H), 4.41-4.45 (m, 2H), 4.66 (s, 2H), 5.02-5.05 (m, 2H), 7.02 (s, 2H), 7.14-7.17 (m, 2H), 7.26-7.30 (m, 4H), 7.46-7.48 (m, 4H), 7.94 (d, *J* = 8.4 Hz, 2H), 8.52 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (CD_3OD, 100 MHz) *δ*: 35.1, 69.8, 76.5, 76.8, 87.9, 122.6, 124.2, 125.7, 126.7, 129.0, 135.4, 138.5, 154.3, 155.6, 168.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{30}N_6NaO_6$ $[M+Na]^+$: 617.2119; Found: 617.2118.



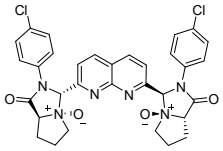
L1c: White solid, M.p. 231.3-232.2 °C, $[\alpha]_D^{20}$ = +164.7 (*c* 0.50, $CHCl_3$); overall yield 46%, 19:1 dr; ^1H NMR (CD_3OD, 400 MHz) *δ*: 1.08-1.12 (m, 6H), 2.22-2.27 (m, 2H), 2.45-2.59 (m, 10H), 3.93-3.97 (m, 2H), 4.13-4.20 (m, 2H), 4.80-4.83 (m, 2H), 6.99 (s, 2H), 7.11 (d, *J* = 8.8 Hz, 4H), 7.39 (d, *J* = 8.4 Hz, 4H), 7.94 (d, *J* = 8.4 Hz, 2H), 8.53 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (CD_3OD, 100 MHz) *δ*: 14.6, 22.3, 24.1, 27.9, 70.8, 76.9, 87.6, 122.7, 124.1, 125.6, 128.3, 133.1, 138.4, 143.2, 154.4, 156.0, 168.7; HRMS (ESI-TOF) m/z: Calcd. for $C_{36}H_{38}N_6NaO_4$ $[M+Na]^+$: 641.2834; Found: 641.2826.



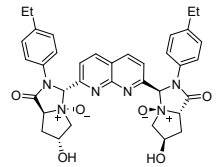
L1d: White solid, M.p. 246.7-247.1 °C, $[\alpha]_D^{20}$ = -309.7 (*c* 0.58, $CHCl_3$); overall yield 41%, >20:1 dr; ^1H NMR (CD_3OD, 400 MHz) δ: 2.30-2.34 (m, 2H), 2.46-2.64 (m, 6H), 4.01-4.05 (m, 2H), 4.25-4.34 (m, 2H), 4.82-4.84 (m, 2H), 6.85 (s, 2H), 7.06-7.10 (m, 2H), 7.22-7.27 (m, 2H), 7.32-7.40 (m, 4H), 7.90 (d, J = 8.4 Hz, 2H), 8.52 (d, J = 8.4 Hz, 2H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 22.4, 24.1, 71.1, 76.2, 87.7, 116.3 (d, J_{CF} = 19.4 Hz), 121.9 (d, J_{CF} = 12.1 Hz), 124.2, 124.8 (d, J_{CF} = 3.3 Hz), 125.8, 129.5, 130.5(d, J_{CF} = 8.2 Hz), 138.3, 154.2, 155.7, 157.8 (d, J_{CF} = 248.4 Hz), 169.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{28}F_2N_6NaO_4$ $[M+Na]^+$: 621.2032; Found: 621.2037.



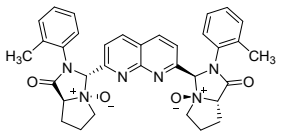
L1e: White solid, M.p. 247.3-248.3 °C, $[\alpha]_D^{20}$ = +21.0 (*c* 0.47, $CHCl_3$); overall yield 51%, 18:1 dr; ^1H NMR (CD_3OD, 400 MHz) δ: 2.22-2.27 (m, 2H), 2.46-2.58 (m, 6H), 3.93-3.97 (m, 2H), 4.14-4.21 (m, 2H), 4.75-4.78 (m, 2H), 7.05 (s, 2H), 7.41-7.47 (m, 8H), 7.97 (d, J = 8.0 Hz, 2H), 8.56 (d, J = 8.4 Hz, 2H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 26.2, 28.1, 74.8, 80.6, 90.9, 123.4, 127.9, 128.1, 129.7, 135.9, 138.7, 142.5, 158.3, 159.6, 172.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{28}Br_2N_6NaO_4$ $[M+Na]^+$: 741.0417; Found: 741.0405.



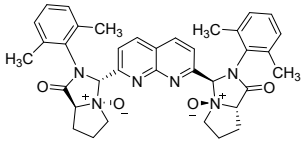
L1f: White solid, M.p. 260.4-260.9 °C, $[\alpha]_D^{20}$ = +10.3 (*c* 0.50, $CHCl_3$); overall yield 52%, 17:1 dr; ^1H NMR (CD_3OD, 400 MHz) δ: 2.23-2.28 (m, 2H), 2.45-2.59 (m, 6H), 3.93-3.97 (m, 2H), 4.14-4.21 (m, 2H), 4.75-4.78 (m, 2H), 7.05 (s, 2H), 7.27-7.30 (m, 4H), 7.49-7.53 (m, 4H), 7.97 (d, J = 8.4 Hz, 2H), 8.57 (d, J = 8.4 Hz, 2H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 22.3, 24.1, 70.8, 76.7, 87.0, 123.8, 124.2, 125.7, 128.9, 131.8, 134.3, 138.6, 154.4, 155.7, 168.7; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{28}Cl_2N_6NaO_4$ $[M+Na]^+$: 653.1434; Found: 653.1428.



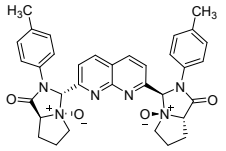
L1g: White solid, M.p. 241.6-242.3 °C, $[\alpha]_D^{20}$ = -150.9 (*c* 0.45, $CHCl_3$); overall yield 45%, 17:1 dr; ^1H NMR (CD_3OD, 400 MHz) δ: 1.07-1.10 (m, 6H), 2.47-2.53 (m, 4H), 2.57-2.63 (m, 2H), 2.83-2.89 (m, 2H), 3.96 (d, *J* = 12.4 Hz, 2H), 4.41-4.45 (m, 2H), 4.66 (s, 2H), 5.03-5.06 (m, 2H), 6.99 (s, 2H), 7.10 (d, *J* = 8.8 Hz, 4H), 7.37 (d, *J* = 8.4 Hz, 4H), 7.93 (d, *J* = 8.4 Hz, 2H), 8.50 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 14.6, 27.9, 35.1, 69.9, 76.4, 76.8, 88.1, 122.8, 124.2, 125.7, 128.3, 132.9, 138.5, 143.3, 154.3, 155.6, 168.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{36}H_{38}N_6NaO_6$ $[M+Na]^+$: 673.2745; Found: 673.2745.



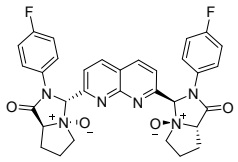
L1h: White solid, M.p. 223.2-224.0 °C, $[\alpha]_D^{20}$ = -110.9 (*c* 0.47, $CHCl_3$); overall yield 41%, 15:1 dr; ^1H NMR (CD_3OD, 400 MHz) δ: 2.30-2.36 (m, 4H), 2.51 (s, 6H), 2.56-2.62 (m, 4H), 3.99-4.04 (m, 2H), 4.28-4.35 (m, 2H), 4.82-4.86 (m, 2H), 6.92 (s, 2H), 7.08-7.12 (m, 2H), 7.17-7.26 (m, 6H), 7.84 (d, *J* = 8.4 Hz, 2H), 8.46 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 17.8, 22.5, 23.8, 70.9, 76.7, 88.7, 124.2, 125.8, 126.5, 126.8, 128.7, 131.4, 133.0, 136.6, 138.1, 153.9, 155.7, 168.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{34}H_{34}N_6NaO_4$ $[M+Na]^+$: 613.2517; Found: 613.2509.



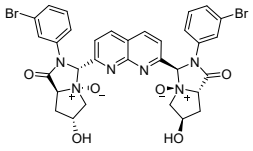
L1i: White solid, M.p. 236.0-237.1 °C, $[\alpha]_D^{20}$ = +273.7 (*c* 0.50, $CHCl_3$); overall yield 40%, >20:1 dr; ^1H NMR (CD_3OD, 400 MHz) δ: 2.33 (s, 6H), 2.36-2.42 (m, 2H), 2.48 (s, 6H), 2.52-2.59 (m, 4H), 2.63-2.70 (m, 2H), 3.91-3.96 (m, 2H), 4.30-4.37 (m, 2H), 4.96-5.00 (m, 2H), 6.80 (s, 2H), 6.94-6.97 (m, 2H), 7.04-7.10 (m, 4H), 7.88 (d, *J* = 8.4 Hz, 2H), 8.36 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 18.4, 18.7, 22.8, 24.0, 70.6, 77.2, 88.2, 123.9, 125.7, 128.8, 129.0, 129.5, 131.0, 135.4, 137.6, 138.0, 153.0, 155.0, 168.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{36}H_{38}N_6NaO_4$ $[M+Na]^+$: 641.2845; Found: 641.2836.



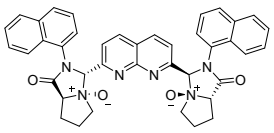
L1j: White solid, M.p. 239.0-239.9 °C, $[\alpha]_D^{20}$ = +71.5 (*c* 0.58, $CHCl_3$); overall yield 51%, 18:1 dr; ^{1}H NMR (CD_3OD, 400 MHz) *δ*: 2.21 (s, 6H), 2.24-2.28 (m, 2H), 2.45-2.58 (m, 6H), 3.92-3.96 (m, 2H), 4.13-4.20 (m, 2H), 4.79-4.82 (m, 2H), 6.97 (s, 2H), 7.08 (d, *J* = 8.4 Hz, 4H), 7.35 (d, *J* = 8.8 Hz, 4H), 7.93 (d, *J* = 8.4 Hz, 2H), 8.53 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (CD_3OD, 100 MHz) *δ*: 19.6, 22.3, 24.1, 70.8, 76.9, 87.6, 122.6, 124.0, 125.6, 129.4, 132.9, 136.8, 138.4, 154.4, 156.0, 168.7; HRMS (ESI-TOF) m/z: Calcd. for $C_{34}H_{34}N_6NaO_4$ $[M+Na]^+$: 613.2534; Found: 613.2529.



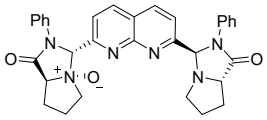
L1k: White solid, M.p. 245.7-246.6 °C, $[\alpha]_D^{20}$ = +31.4 (*c* 0.51, $CHCl_3$); overall yield 48%, 17:1 dr; ^{1}H NMR (CD_3OD, 400 MHz) *δ*: 2.26-2.29 (m, 2H), 2.46-2.60 (m, 6H), 3.95-3.99 (m, 2H), 4.18-4.25 (m, 2H), 4.78-4.81 (m, 2H), 7.01-7.07 (m, 6H), 7.50-7.53 (m, 4H), 7.95 (d, *J* = 8.4 Hz, 2H), 8.55 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (CD_3OD, 100 MHz) *δ*: 22.3, 24.1, 70.8, 76.7, 87.6, 115.6 (d, J_{CF} = 23.1 Hz), 124.2, 125.3 (d, J_{CF} = 8.3 Hz), 125.8, 131.5, 138.5, 154.4, 155.8, 160.8 (d, J_{CF} = 241.1 Hz), 168.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{28}F_2N_6NaO_4$ $[M+Na]^+$: 621.2032; Found: 621.2036.



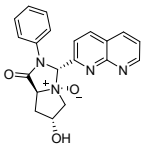
L1l: White solid, M.p. 232.9-233.2 °C; overall yield 44%, 12:1 dr; ^{1}H NMR (CD_3OD, 400 MHz) *δ*: 2.56-2.62 (m, 2H), 2.83-2.89 (m, 2H), 3.96 (d, *J* = 12.4 Hz, 2H), 4.41-4.45 (m, 2H), 4.65 (s, 2H), 4.95-4.98 (m, 2H), 7.09 (s, 2H), 7.14-7.18 (m, 2H), 7.28-7.30 (m, 2H), 7.36-7.39 (m, 2H), 7.87-7.88 (m, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 8.55 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (CD_3OD, 100 MHz) *δ*: 35.2, 69.9, 76.4, 76.6, 87.3, 120.7, 122.1, 124.3, 125.5, 125.9, 129.4, 130.4, 136.8, 138.6, 154.2, 155.1, 168.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{28}Br_2N_6NaO_6$ $[M+Na]^+$: 773.0308; Found: 773.0299.



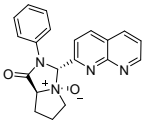
L1m: White solid; overall yield 41%, >20:1 dr; ^{1}H NMR (CD_3OD, 400 MHz) δ: 2.36-2.38 (m, 2H), 2.59-2.61 (m, 6H), 4.04-4.07 (m, 2H), 4.43-4.45 (m, 2H), 7.12 (s, 2H), 7.44-7.51 (m, 4H), 7.62-7.67 (m, 4H), 7.76-7.85 (m, 8H), 8.28 (d, J = 7.6 Hz, 2H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 22.5, 23.6, 70.6, 77.0, 89.3, 124.2, 125.1, 125.7, 126.3, 128.1, 129.2, 129.4, 134.7, 137.7, 153.7, 155.3, 169.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{40}H_{34}N_6NaO_4$ $[M+Na]^+$: 685.2534; Found: 685.2531.



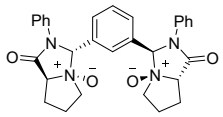
L2a: White solid; overall yield 31%, 12:1 dr; ^{1}H NMR (CD_3OD, 400 MHz) δ: 1.85-1.93 (m, 2H), 2.14-2.21 (m, 3H), 2.47-2.54 (m, 3H), 3.11-3.17 (m, 1H), 3.34-3.38 (m, 1H), 3.92-3.97 (m, 1H), 4.16-4.20 (m, 1H), 4.28-4.31 (m, 1H), 4.81-4.84 (m, 1H), 6.12 (s, 1H), 6.99 (s, 1H), 7.04-7.08 (m, 1H), 7.13-7.16 (m, 1H), 7.20-7.28 (m, 4H), 7.46-7.49 (m, 4H), 7.73 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 8.44 (d, J = 8.4 Hz, 2H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 22.3, 24.1, 24.4, 28.0, 56.1, 65.1, 70.8, 76.9, 85.0, 87.6, 120.9, 122.5, 122.7, 123.2, 125.7, 126.6, 128.7, 128.9, 135.5, 136.4, 138.3, 139.5, 154.2, 155.4, 163.3, 168.7, 175.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{32}H_{30}N_6NaO_3$ $[M+Na]^+$: 569.2270; Found: 569.2265.



L3a: White solid, M.p. 203.4-204.7 ^{o}C; overall yield 47%, 13:1 dr; ^{1}H NMR (CD_3OD, 400 MHz) δ: 2.62-2.69 (m, 1H), 2.87-2.93 (m, 1H), 3.99 (d, J = 8.4 Hz, 1H), 4.48-4.53 (m, 1H), 4.69-4.72 (m, 1H), 5.08-5.11 (m, 1H), 7.07 (s, 1H), 7.13-7.17 (m, 1H), 7.26-7.30 (m, 2H), 7.50-7.53 (m, 2H), 7.64-7.67 (m, 1H), 7.91 (d, J = 8.0 Hz, 1H), 8.44-8.49 (m, 2H), 9.06-9.08 (m, 1H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 35.1, 69.9, 76.4, 76.8, 88.0, 123.0, 123.3, 123.7, 125.1, 126.8, 128.9, 135.3, 138.3, 138.5, 154.0, 154.4, 154.7, 168.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{20}H_{18}N_4NaO_3$ $[M+Na]^+$: 385.1271; Found: 385.1267.

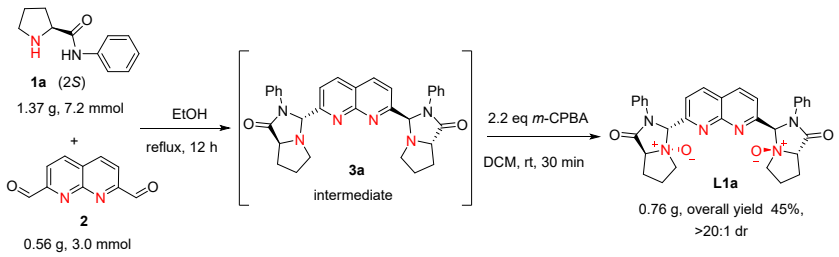


L4a: White solid, M.p. 215.5-216.9 °C; overall yield 51%, 12:1 dr; ^{1}H NMR (CD_3OD, 400 MHz) δ: 2.25-2.32 (m, 1H), 2.48-2.62 (m, 3H), 3.96-4.01 (m, 1H), 4.20-4.27 (m, 1H), 4.85-4.88 (m, 1H), 7.06 (s, 1H), 7.13-7.17 (m, 1H), 7.26-7.30 (m, 2H), 7.53-7.55 (m, 2H), 7.63-7.66 (m, 1H), 7.93 (d, J = 8.4 Hz, 1H), 8.44-8.47 (m, 1H), 8.49 (d, J = 8.0 Hz, 1H), 9.05-9.07 (m, 1H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 22.3, 24.1, 70.8, 76.9, 87.5, 122.9, 123.3, 123.7, 125.1, 126.7, 128.9, 135.5, 138.3, 138.5, 153.9, 154.5, 155.1, 168.7; HRMS (ESI-TOF) m/z: Calcd. for $C_{20}H_{18}N_4NaO_2$ $[M+Na]^+$: 369.1322; Found: 369.1316.



L7a: White solid; overall yield 47%, 18:1 dr; ^{1}H NMR (CD_3OD, 400 MHz) δ: 2.22-2.25 (m, 2H), 2.39-2.53 (m, 6H), 3.83-3.86 (m, 2H), 3.96-4.05 (m, 2H), 4.26-4.29 (m, 2H), 6.76 (s, 2H), 7.18-7.22 (m, 2H), 7.29-7.33 (m, 4H), 7.48-7.51 (m, 5H), 7.63-7.70 (m, 3H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 22.3, 24.0, 70.4, 76.1, 87.8, 122.6, 126.6, 128.8, 129.1, 131.0, 135.5, 167.8; HRMS (ESI-TOF) m/z: Calcd. for $C_{30}H_{30}N_4NaO_4$ $[M+Na]^+$: 533.2159; Found: 533.2152.

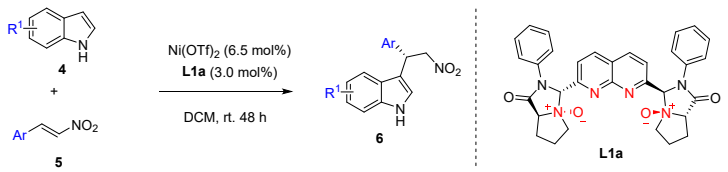
4. The gram scale synthesis of the Nar-2NO ligand L1a



In a sealed tube equipped with a magnetic stirring bar, naphthyridine-dicarbaldehyde **2** (0.56 g, 3.0 mmol) and optically pure prolinamide **1a** (1.37 g, 7.2 mmol) were added. Then, 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 intermediate **3a**.

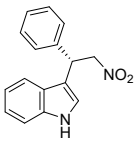
In a sealed tube equipped with a magnetic stirring bar, to the intermediate **3** was added 20.0 mL of DCM and *m*-CPBA (2.2 eq). The reaction mixture was stirred at rt for 30 min. After completion of the reaction, as indicated by TLC, the aftertreatment residue was purified by flash column chromatography to furnish the Nar-2NO ligand **L1a** (0.76 g, overall yield 45%, >20:1 dr).

5. Catalytic asymmetric synthesis of compounds 6

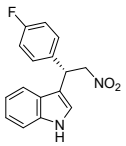


In a sealed tube equipped with a magnetic stirring bar, to the mixture of $Ni(OTf)_2$ (6.5 mol %), **L1a** (3.0 mol %) in 2.0 mL of CH_2Cl_2 was added **4** (0.30 mmol), and **5** (0.20 mmol). The reaction mixture was stirred at room temperature for 48 h and was directly loaded onto a silica gel and purified by flash chromatography to give the desired product **6**, using hexane/EtOAc (10/1, v/v) as the eluent.

6. Characterization data of compounds 6

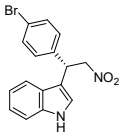


6a: Product in accordance with literature characterization data[7]. Light yellow oil, $[\alpha]_D^{20} = +20.3$ (*c* 0.8, $CHCl_3$), 90% yield, 93% ee; The ee was determined by HPLC analysis using a Chiralpak IC column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 8.38 min; τ_{minor} = 10.39 min); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.82-4.87 (m, 1H), 4.94-4.99 (m, 1H), 5.08-5.12 (m, 1H), 6.91 (d, J = 2.4 Hz, 1H), 6.97-7.01 (m, 1H), 7.09-7.26 (m, 7H), 7.36 (d, J = 8.0 Hz, 1H), 7.99 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 40.5, 78.5, 110.4, 113.3, 117.9, 118.9, 120.6, 121.6, 125.0, 126.5, 126.7, 127.9, 135.4, 138.2.

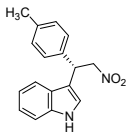


6b: Product in accordance with literature characterization data[7]. Light yellow oil, $[\alpha]_D^{20} = +30.7$ (*c* 1.01, $CHCl_3$), 91% yield, 90% ee; The ee was determined by HPLC analysis using a Chiralpak IC column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 13.83 min; τ_{minor} = 18.89 min); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.78-4.83 (m, 1H), 4.93-4.98 (m, 1H), 5.06-5.10 (m, 1H), 6.89-6.93 (m, 3H), 6.97-7.01 (m, 1H), 7.10-7.14 (m, 1H), 7.18-7.22 (m, 2H), 7.25 (d, J = 8.0

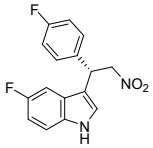
Hz, 1H), 7.30-7.32 (m, 1H), 8.06 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 39.8, 78.5, 110.4, 113.1, 114.8 (d, J_{CF} = 21.3 Hz), 117.8, 119.0, 120.4, 121.7, 124.9, 128.3 (d, J_{CF} = 8.4 Hz), 133.9 (d, J_{CF} = 3.3 Hz), 135.5, 161.7 (d, J_{CF} = 245.3 Hz).



6c: Product in accordance with literature characterization data[7]. Light yellow oil, $[\alpha]_D^{20}$ = -1.5 (*c* 0.91, $CHCl_3$), 92% yield, 92% ee; The ee was determined by HPLC analysis using a Chiralpak IC column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 15.10 min; τ_{minor} = 20.24 min); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.78-4.83 (m, 1H), 4.93-4.98 (m, 1H), 5.04-5.08 (m, 1H), 6.90-6.91 (m, 1H), 6.98-7.02 (m, 1H), 7.10-7.14 (m, 3H), 7.26-7.37 (m, 4H), 8.04 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 40.0, 78.2, 110.5, 112.8, 117.7, 119.1, 120.5, 120.6, 121.8, 124.8, 128.5, 131.0, 135.5, 137.2.

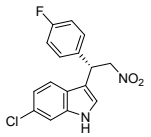


6d: Product in accordance with literature characterization data[7]. Light yellow oil, $[\alpha]_D^{20}$ = +16.0 (*c* 1.01, $CHCl_3$), 90% yield, 92% ee; The ee was determined by HPLC analysis using a Chiralpak IC column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 14.11 min; τ_{minor} = 18.90 min); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.22 (s, 3H), 4.80-4.85 (m, 1H), 4.93-4.98 (m, 1H), 5.04-5.08 (m, 1H), 6.90-6.91 (m, 1H), 6.97-7.04 (m, 3H), 7.08-7.14 (m, 3H), 7.23-7.26 (m, 1H), 7.35-7.37 (m, 1H), 7.99 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 20.0, 40.2, 78.6, 110.3, 113.5, 117.9, 118.9, 120.5, 121.6, 125.1, 126.6, 128.6, 135.1, 135.4, 136.2.

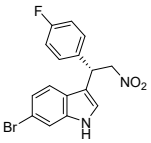


6e: Product in accordance with literature characterization data[7]. Light yellow oil, 83% yield, 92% ee; The ee was determined by HPLC analysis using a Chiralpak IB column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 6.54 min; τ_{minor} = 7.43 min); ^{1}H NMR ($CDCl_3$, 400

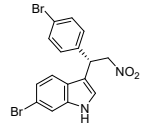
MHz) δ: 4.78-4.83 (m, 1H), 4.91-4.96 (m, 1H), 5.00-5.03 (m, 1H), 6.84-6.95 (m, 4H), 7.09 (d, J = 2.4 Hz, 1H), 7.17-7.21 (m, 3H), 8.10 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 39.7, 78.4, 102.8 (d, J_{CF} = 22.1 Hz), 110.2 (d, J_{CF} = 26.3 Hz), 111.1 (d, J_{CF} = 9.3 Hz), 113.5 (d, J_{CF} = 5.1 Hz), 114.9 (d, J_{CF} = 22.3 Hz), 122.0, 125.3 (d, J_{CF} = 10.0 Hz), 128.3 (d, J_{CF} = 8.4 Hz), 132.0, 133.6 (d, J_{CF} = 3.1 Hz), 157.1 (d, J_{CF} = 235.3 Hz), 161.2 (d, J_{CF} = 245.0 Hz).



6f: Light yellow oil, 89% yield, 91% ee; The ee was determined by HPLC analysis using a Chiralpak IB column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 7.17 min; τ_{minor} = 6.26 min); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.77-4.82 (m, 1H), 4.91-4.96 (m, 1H), 5.02-5.06 (m, 1H), 6.90-6.96 (m, 4H), 7.16-7.19 (m, 3H), 7.24-7.25 (m, 1H), 8.08 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 39.7, 78.4, 110.4, 113.3, 114.9 (d, J_{CF} = 22.3 Hz), 118.7, 119.8, 121.0, 123.5, 127.7, 128.3 (d, J_{CF} = 8.2 Hz), 133.6 (d, J_{CF} = 4.4 Hz), 135.8, 161.6 (d, J_{CF} = 245.1 Hz); HRMS (ESI-TOF) m/z: Calcd. for $C_{16}H_{12}ClFN_2NaO_2$ $[M+Na]^+$: 341.0464; Found: 341.0458.

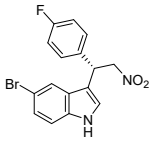


6g: Light yellow oil, 87% yield, 92% ee; The ee was determined by HPLC analysis using a Chiralpak IC column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 12.50 min; τ_{minor} = 14.88 min); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.77-4.82 (m, 1H), 4.91-4.96 (m, 1H), 5.03-5.07 (m, 1H), 6.90-6.95 (m, 3H), 7.06-7.20 (m, 4H), 7.42 (d, J = 1.2 Hz, 1H), 8.10 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 39.7, 78.4, 113.4, 114.9 (d, J_{CF} = 22.4 Hz), 115.4, 119.1, 120.9, 122.3, 123.8, 128.3 (d, J_{CF} = 8.4 Hz), 133.6 (d, J_{CF} = 3.2 Hz), 136.3, 161.7 (d, J_{CF} = 245.2 Hz); HRMS (ESI-TOF) m/z: Calcd. for $C_{16}H_{12}BrFN_2NaO_2$ $[M+Na]^+$: 384.9958; Found: 384.9963.

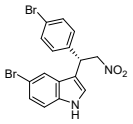


6h: Light yellow oil, 88% yield, 94% ee; The ee was determined by HPLC analysis using a

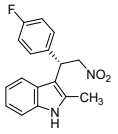
Chiralpak IC column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 13.52 min; τ_{minor} = 15.83 min); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.77-4.82 (m, 1H), 4.90-4.95 (m, 1H), 5.00-5.03 (m, 1H), 6.92-6.93 (m, 1H), 7.06-7.11 (m, 4H), 7.34-7.37 (m, 2H), 7.42 (d, J = 1.2 Hz, 1H), 8.16 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 38.5, 76.8, 111.7, 112.1, 114.1, 117.7, 119.4, 119.7, 121.1, 122.5, 127.1, 129.8, 134.9, 135.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{16}H_{12}Br_2N_2NaO_2$ $[M+Na]^+$: 444.9158; Found: 444.9163.



6i: Product in accordance with literature characterization data[7]. Light yellow oil, $[\alpha]_D^{20}$ = -20.0 (*c* 0.91, $CHCl_3$), 84% yield, 91% ee; The ee was determined by HPLC analysis using a Chiralpak IB column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 8.24 min; τ_{minor} = 6.33 min); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.76-4.81 (m, 1H), 4.89-4.94 (m, 1H), 5.00-5.04 (m, 1H), 6.90-6.96 (m, 3H), 7.12-7.20 (m, 4H), 7.42 (d, J = 1.2 Hz, 1H), 8.15 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 39.6, 78.4, 111.9, 112.2, 112.7, 114.9 (d, J_{CF} = 21.4 Hz), 120.3, 121.6, 124.7, 126.7, 128.2 (d, J_{CF} = 9.0 Hz), 133.4 (d, J_{CF} = 3.3 Hz), 134.1, 161.5 (d, J_{CF} = 245.0 Hz).

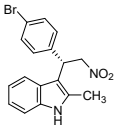


6j: Product in accordance with literature characterization data[7]. Light yellow oil, 83% yield, 93% ee; The ee was determined by HPLC analysis using a Chiralpak IB column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 9.65 min; τ_{minor} = 7.99 min); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 5.07-5.12 (m, 1H), 5.28-5.38 (m, 2H), 7.18-7.20 (m, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.44-7.52 (m, 5H), 7.74 (d, J = 1.6 Hz, 1H), 11.31 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 40.6, 79.1, 112.0, 113.4, 114.1, 120.6, 121.1, 124.5, 124.6, 128.2, 130.6, 131.9, 135.3, 140.5.

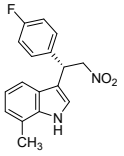


6k: Product in accordance with literature characterization data[7]. Light yellow oil, 90% yield, 91%

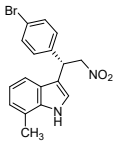
ee; The ee was determined by HPLC analysis using a Chiralpak IC column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 20.60 min; τ_{minor} = 13.93 min); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 2.29 (s, 3H), 4.97-5.01 (m, 1H), 5.06-5.14 (m, 2H), 6.87-6.97 (m, 3H), 7.02-7.06 (m, 1H), 7.17-7.21 (m, 3H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.83 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 10.9, 38.8, 77.6, 107.6, 109.8, 114.6 (d, J_{CF} = 22.3 Hz), 117.4, 118.8, 120.4, 125.6, 127.8 (d, J_{CF} = 8.4 Hz), 131.8, 134.2 (d, J_{CF} = 3.3 Hz), 134.4, 160.5 (d, J_{CF} = 244.3 Hz).



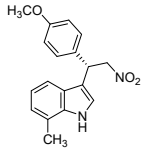
6l: Product in accordance with literature characterization data[7]. Light yellow oil, 91% yield, 90% ee; The ee was determined by HPLC analysis using a Chiralpak IC column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 19.29 min; τ_{minor} = 13.02 min); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 2.31 (s, 3H), 4.96-5.14 (m, 3H), 6.94-6.98 (m, 1H), 7.02-7.06 (m, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.18-7.25 (m, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.85 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 11.0, 38.9, 77.3, 107.3, 109.8, 117.4, 118.9, 120.0, 120.5, 125.6, 128.0, 130.8, 131.9, 134.4, 137.5.



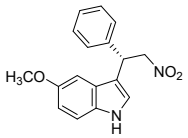
6m: Product in accordance with literature characterization data[7]. Light yellow oil, 86% yield, 90% ee; The ee was determined by HPLC analysis using a Chiralpak IC column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 11.11 min; τ_{minor} = 12.70 min); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 2.37 (s, 3H), 4.78-4.83 (m, 1H), 4.93-4.98 (m, 1H), 5.05-5.09 (m, 1H), 6.88-6.93 (m, 5H), 7.16-7.22 (m, 3H), 7.98 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 15.5, 39.9, 78.5, 113.7, 114.7 (d, J_{CF} = 22.1 Hz), 115.5, 119.2, 119.7, 120.1, 122.3, 124.5, 128.3 (d, J_{CF} = 8.4 Hz), 134.0 (d, J_{CF} = 3.1 Hz), 135.1, 160.7 (d, J_{CF} = 244.4 Hz).



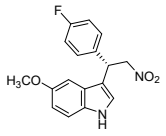
6n: Light yellow oil, 85% yield, 90% ee; The ee was determined by HPLC analysis using a Chiralpak IC column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 12.08 min; τ_{minor} = 13.53 min); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 2.37 (s, 3H), 4.78-4.83 (m, 1H), 4.93-4.98 (m, 1H), 5.03-5.07 (m, 1H), 6.91-6.93 (m, 3H), 7.10-7.13 (m, 2H), 7.15-7.17 (m, 1H), 7.33-7.36 (m, 2H), 7.99 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 15.5, 40.1, 78.2, 113.2, 115.4, 119.3, 119.7, 120.2, 120.4, 122.3, 124.4, 128.5, 131.0, 135.1, 137.3; HRMS (ESI-TOF) m/z: Calcd. for $C_{17}H_{15}BrN_2NaO_2$ $[M+Na]^+$: 381.0209; Found: 381.0204.



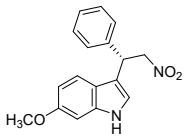
6o: Light yellow oil, 84% yield, 91% ee; The ee was determined by HPLC analysis using a Chiralpak IC column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 19.60 min; τ_{minor} = 22.08 min); ^{1}H NMR (DMSO-d_6, 400 MHz) *δ*: 2.42 (s, 3H), 3.68 (s, 3H), 4.95-5.00 (m, 1H), 5.20-5.33 (m, 2H), 6.82-6.85 (m, 4H), 7.28-7.39 (m, 4H), 10.98 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) *δ*: 17.2, 39.4, 55.4, 79.9, 114.3, 114.7, 116.5, 119.3, 121.1, 122.3, 126.2, 129.3, 133.1, 136.2, 158.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{18}H_{18}N_2NaO_3$ $[M+Na]^+$: 333.1210; Found: 333.1213.



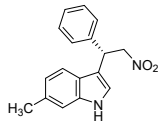
6p: Product in accordance with literature characterization data[7]. Light yellow oil, $[\alpha]_D^{20}$ = -20.7 (*c* 1.21, $CHCl_3$), 92% yield, 90% ee; The ee was determined by HPLC analysis using a Chiralpak IC column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 13.04 min; τ_{minor} = 14.86 min); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 3.67 (s, 3H), 4.80-4.85 (m, 1H), 4.91-4.96 (m, 1H), 5.02-5.06 (m, 1H), 6.74-6.77 (m, 2H), 6.86 (d, *J* = 2.4 Hz, 1H), 7.10-7.23 (m, 6H), 7.96 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 40.5, 54.8, 78.4, 99.8, 111.1, 111.6, 112.9, 121.3, 125.5, 126.5, 126.7, 127.9, 130.6, 138.2, 153.1.



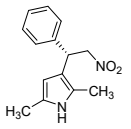
6q: Product in accordance with literature characterization data[7]. Light yellow oil, 91% yield, 90% ee; The ee was determined by HPLC analysis using a Chiralpak IB column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 25.57 min; τ_{minor} = 31.41 min); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.69 (s, 3H), 4.77-4.83 (m, 1H), 4.92-4.97 (m, 1H), 5.01-5.05 (m, 1H), 6.72 (d, J = 2.4 Hz, 1H), 6.76-6.79 (m, 1H), 6.89-6.94 (m, 3H), 7.14-7.23 (m, 3H), 8.01 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 39.8, 54.8, 78.5, 99.8, 111.2, 111.7, 112.8, 114.8 (d, J_{CF} = 22.4 Hz), 121.1, 125.4, 128.3 (d, J_{CF} = 8.3 Hz), 130.6, 133.9 (d, J_{CF} = 3.2 Hz) , 153.2, 161.6 (d, J_{CF} = 245.1 Hz).



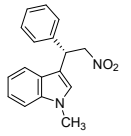
6r: Product in accordance with literature characterization data[7]. Light yellow oil, 92% yield, 99% ee; The ee was determined by HPLC analysis using a Chiralpak IB column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 7.84 min; τ_{minor} = 10.24 min); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.70 (s, 3H), 4.78-4.83 (m, 1H), 4.90-4.95 (m, 1H), 5.01-5.05 (m, 1H), 6.62-6.65 (m, 1H), 6.71 (d, J = 2.0 Hz, 1H), 6.77 (d, J = 1.6 Hz, 1H), 7.14-7.22 (m, 6H), 7.90 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 40.5, 54.5, 78.6, 93.7, 93.8, 108.9, 113.2, 113.3, 118.5, 119.3, 119.4, 119.5, 126.5, 126.7, 127.8, 136.3, 138.2, 138.3, 155.7.



6s: Product in accordance with literature characterization data[7]. Light yellow oil, 91% yield, 92% ee; The ee was determined by HPLC analysis using a Chiralpak IC column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 35.16 min; τ_{minor} = 39.26 min); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.33 (s, 3H), 4.78-4.83 (m, 1H), 4.90-4.95 (m, 1H), 5.02-5.06 (m, 1H), 6.78-6.82 (m, 2H), 7.01 (s, 1H), 7.13-7.23 (m, 6H), 7.88 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 20.6, 40.6, 78.5, 110.3, 123.0, 117.5, 120.0, 120.6, 122.9, 126.4, 126.7, 127.8, 131.4, 135.9, 138.3.



6t: Light yellow oil, 81% yield, 80% ee; The ee was determined by HPLC analysis using a Chiralpak IA column (85/15 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 7.50 min; τ_{minor} = 10.34 min); ^{1}H NMR (CD_3OD, 400 MHz) *δ*: 2.05 (s, 3H), 2.11 (s, 3H), 4.62-4.66 (m, 1H), 4.74-4.79 (m, 1H), 4.82-4.87 (m, 1H), 5.66 (s, 1H), 7.12-7.16 (m, 1H), 7.20-7.26 (m, 4H), 9.53 (br s, 1H); ^{13}C NMR (CD_3OD, 100 MHz) *δ*: 9.4, 11.5, 41.5, 79.9, 103.2, 116.1, 122.2, 125.2, 126.3, 127.4, 128.1, 141.5; HRMS (ESI-TOF) m/z: Calcd. for $C_{14}H_{16}N_2NaO_2$ $[M+Na]^+$: 267.1104; Found: 267.1107.

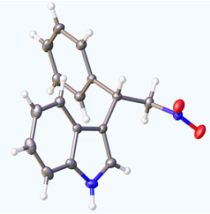


6u: Product in accordance with literature characterization data[7]. Light yellow oil, $[\alpha]_D^{20}$ = +17.1 (*c* 1.12, $CHCl_3$), 68% yield, 83% ee; The ee was determined by HPLC analysis using a Chiralpak IB column (85/15 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 28.57 min; τ_{minor} = 31.67 min); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 3.74 (s, 3H), 5.03-5.07 (m, 1H), 5.25-5.35 (m, 2H), 6.96-7.00 (m, 1H), 7.11-7.15 (m, 1H), 7.18-7.22 (m, 1H), 7.27-7.31 (m, 2H), 7..36-7.41 (m, 3H), 7.45 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 32.9, 41.0, 79.5, 110.3, 113.3, 119.1, 119.3, 122.0, 127.1, 127.4, 127.8, 128.3, 129.0, 137.0, 141.1.

7. References

(a) Z. Y. Yu, J. N. Zhao, F. Yang, X. F. Tang, Y. F. Wu, C. F. Ma, B. Song, L. Yun and Q. W. Meng, *RSC Advances*, 2020, **10**, 4825; *(b)* J. Ma and S. R. Kass, *J. Org. Chem.*, 2019, **84**, 11125; *(c)* S. F. Lu, D. M. Du, and J. Xu, *Org. Lett.*, 2006, **8**, 2115; *(d)* Y. X. Jia, S. F. Zhu, Y. Yang, and Q. L. Zhou, *J. Org. Chem.*, 2006, **71**, 75; *(e)* P. K. Singh, A. Bisai, V. K. Singh, *Tetrahedron Lett.*, 2007, **48**, 1127; *(f)* M. S. Islam, A. S. Alammari, A. Barakat, S. Alshahrani, M. Haukka and A. M. Al-Majid, *Molecules,* 2021, **26**, 7408.

8. X-ray crystal data for compounds 6a



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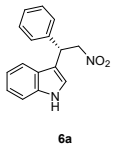


6a

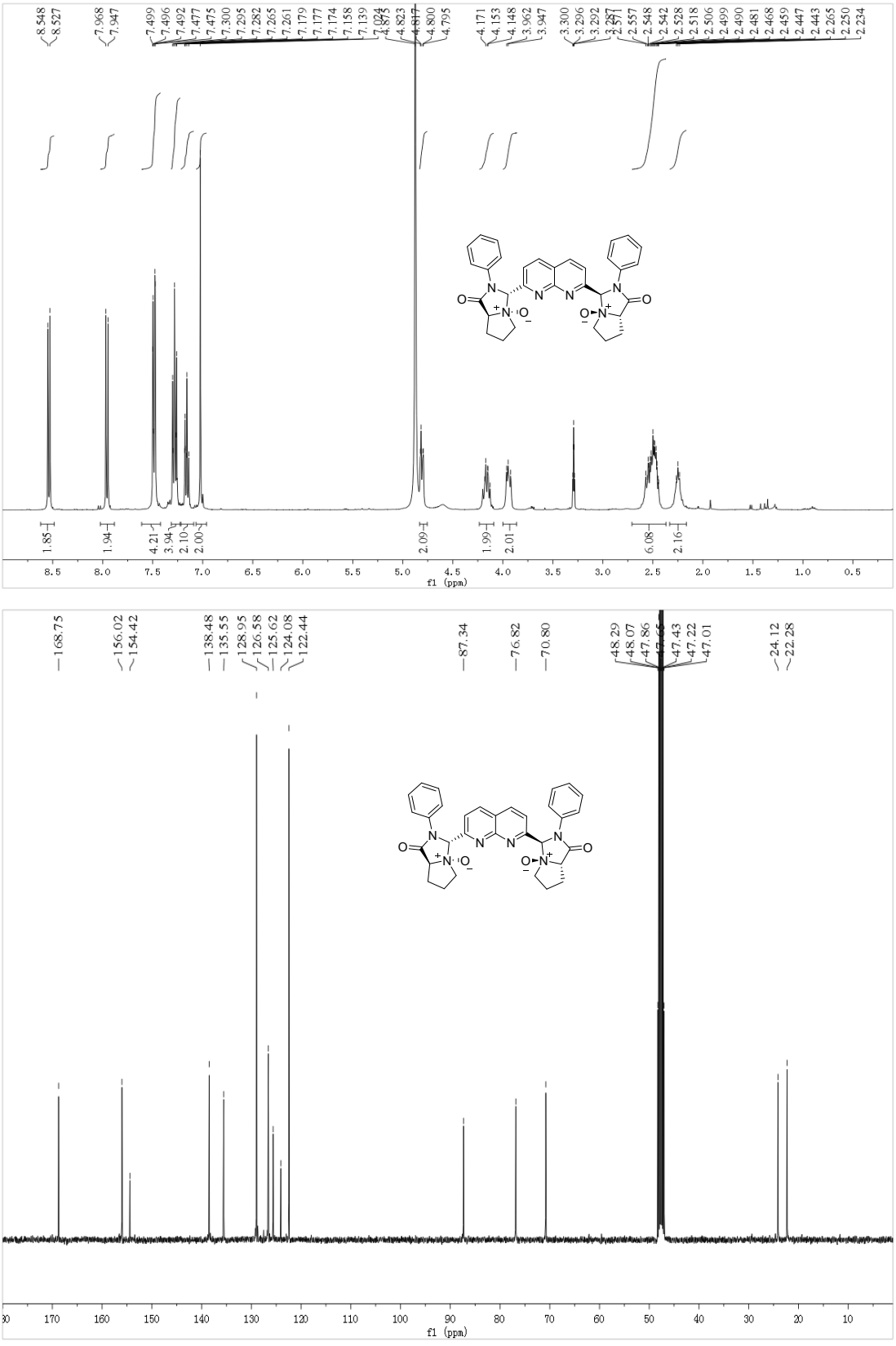
Table S1 Crystal data and structure refinement for 6a

Identification code	**6a**
Empirical formula	$C_{17}H_{15}Cl_3N_2O_2$
Formula weight	385.66
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å, b/Å, c/Å	12.7168(2), 5.91860(8), 13.1408(2)
α/°, β/°, γ/°,	90, 114.224(2), 90
Volume/Å^3	901.97(3)
Z	2
ρ_{calc}g/cm^3	1.420
μ/mm^{-1}	4.704
F(000)	396.0
Radiation	Cu Kα (λ = 1.54184)
Crystal size/mm^3	0.15 × 0.13 × 0.12
2Θ range for data collection/°	7.376 to 153.066
Index ranges	-15 ≤ h ≤ 15, -5 ≤ k ≤ 7, -16 ≤ l ≤ 15
Reflections collected	7626
Independent reflections	3022 [R_{int} = 0.0197, R_{sigma} = 0.0170]
Data/restraints/parameters	3022/1/218
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0685, wR_2 = 0.2019
Final R indexes [all data]	R_1 = 0.0695, wR_2 = 0.2034
Largest diff. peak/hole / e Å^{-3}	0.61/-0.47
Flack parameter	0.033(8)/0.045(4)

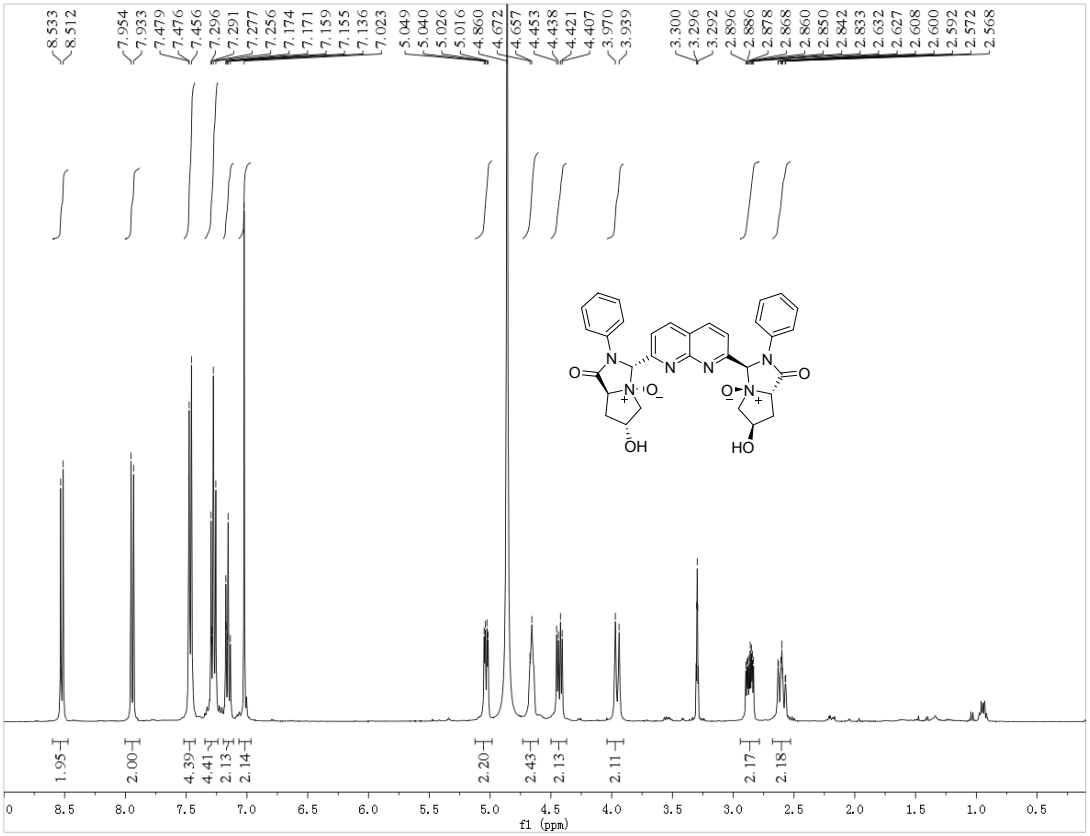
Crystal Data for $C_{17}H_{15}Cl_3N_2O_2$ (M =385.66 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 12.7168(2) Å, b = 5.91860(8) Å, c = 13.1408(2) Å, β = 114.224(2)°, V = 901.97(3) Å^3, Z = 2, T = 293.15 K, μ(Cu Kα) = 4.704 mm^{-1}, *Dcalc* = 1.420 g/cm^3, 7626 reflections measured (7.376° ≤ 2Θ ≤ 153.066°), 3022 unique (R_{int} = 0.0197, R_{sigma} = 0.0170) which were used in all calculations. The final R_1 was 0.0685 (I > 2σ(I)) and wR_2 was 0.2034 (all data).

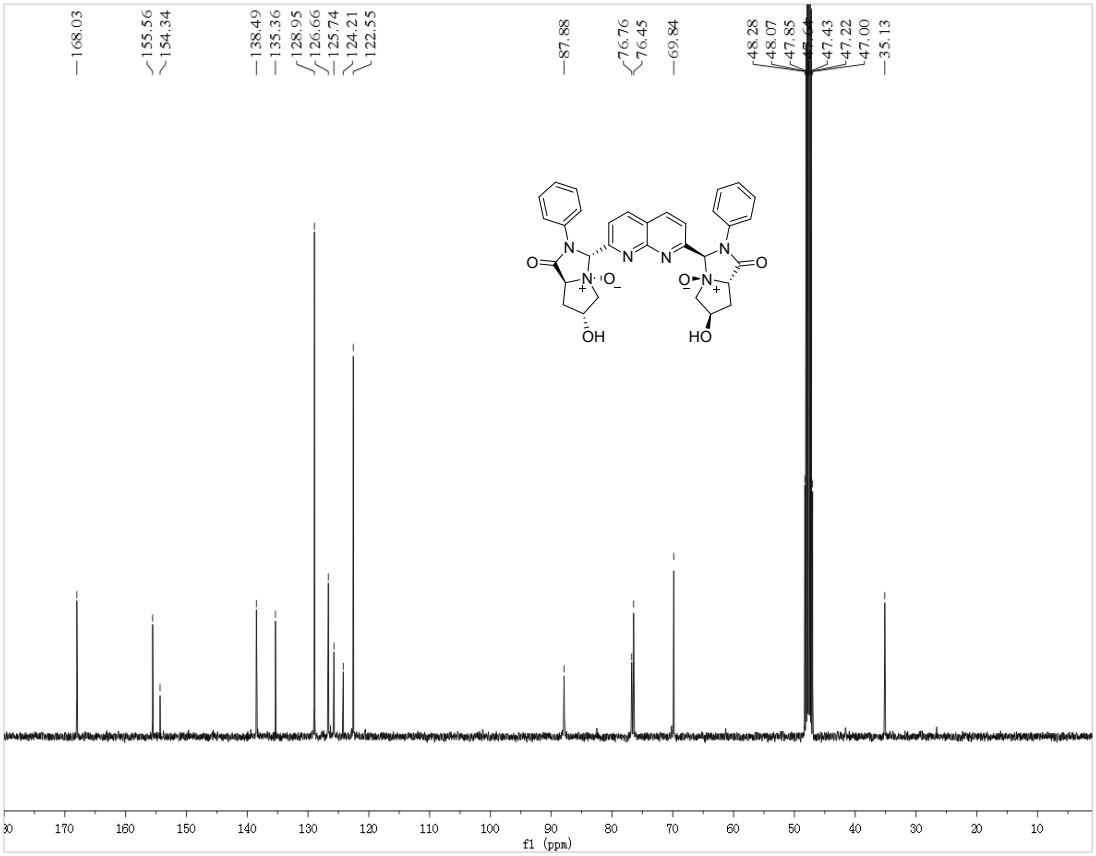
9. The copies of ^{1}H NMR, ^{13}C NMR and HPLC spectra for compounds L and 6

^{1}H and ^{13}C NMR of L1a

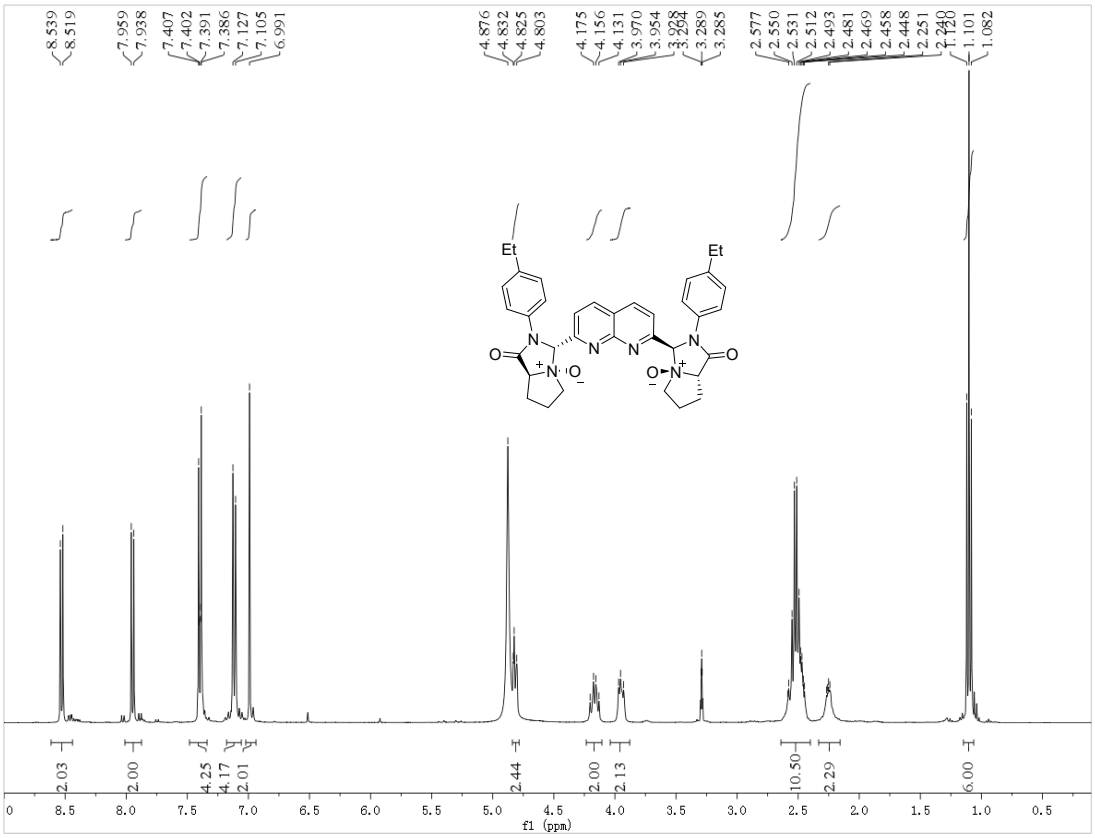


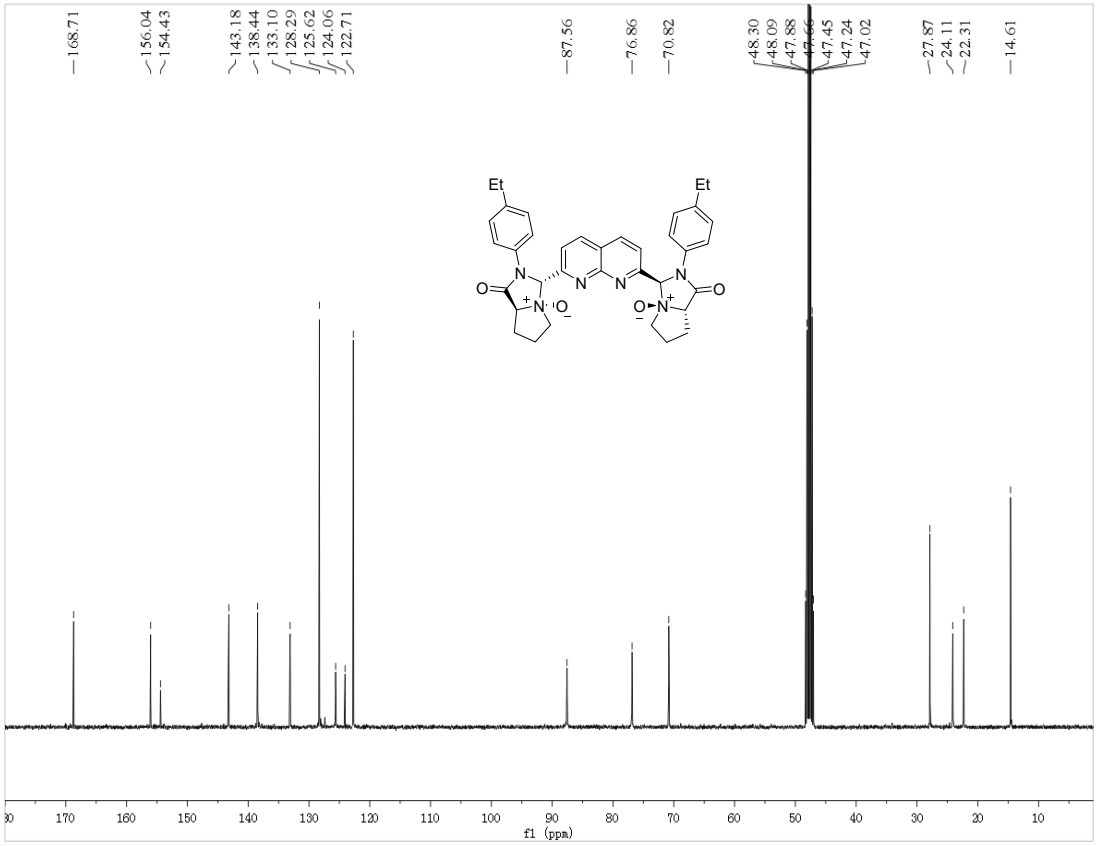
^{1}H and ^{13}C NMR of L1b



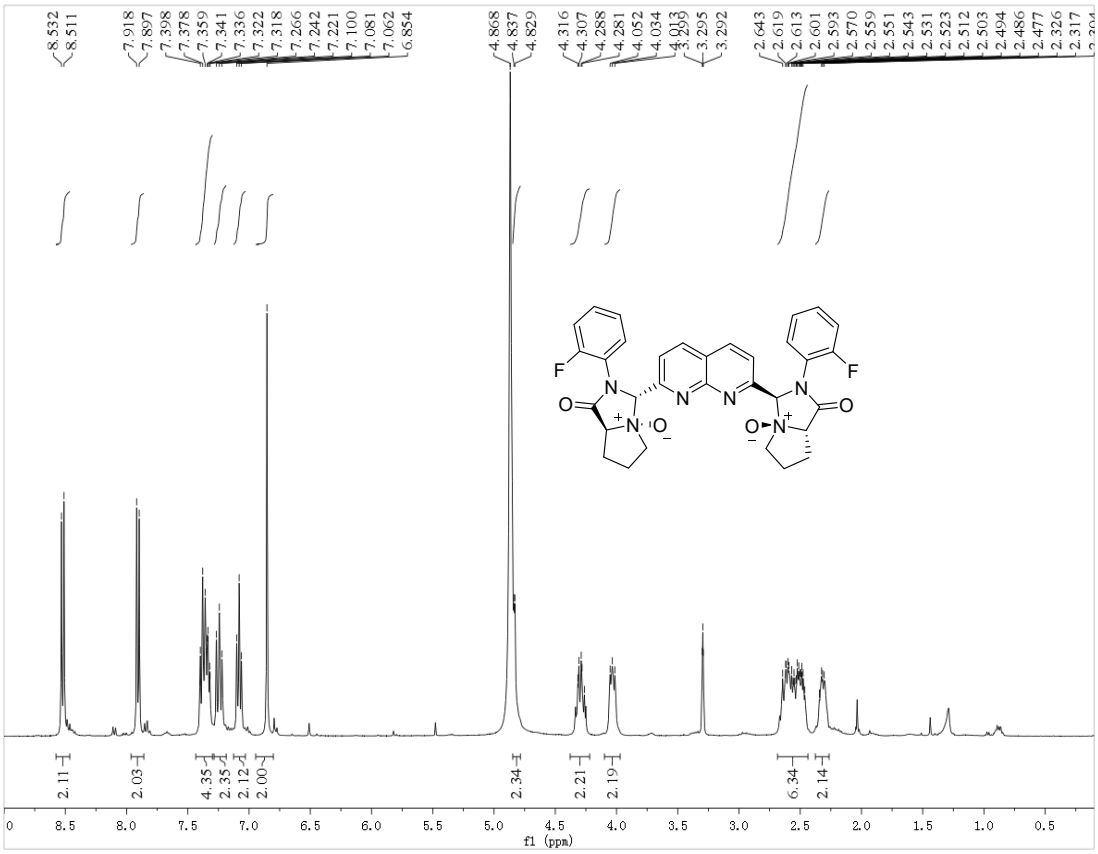


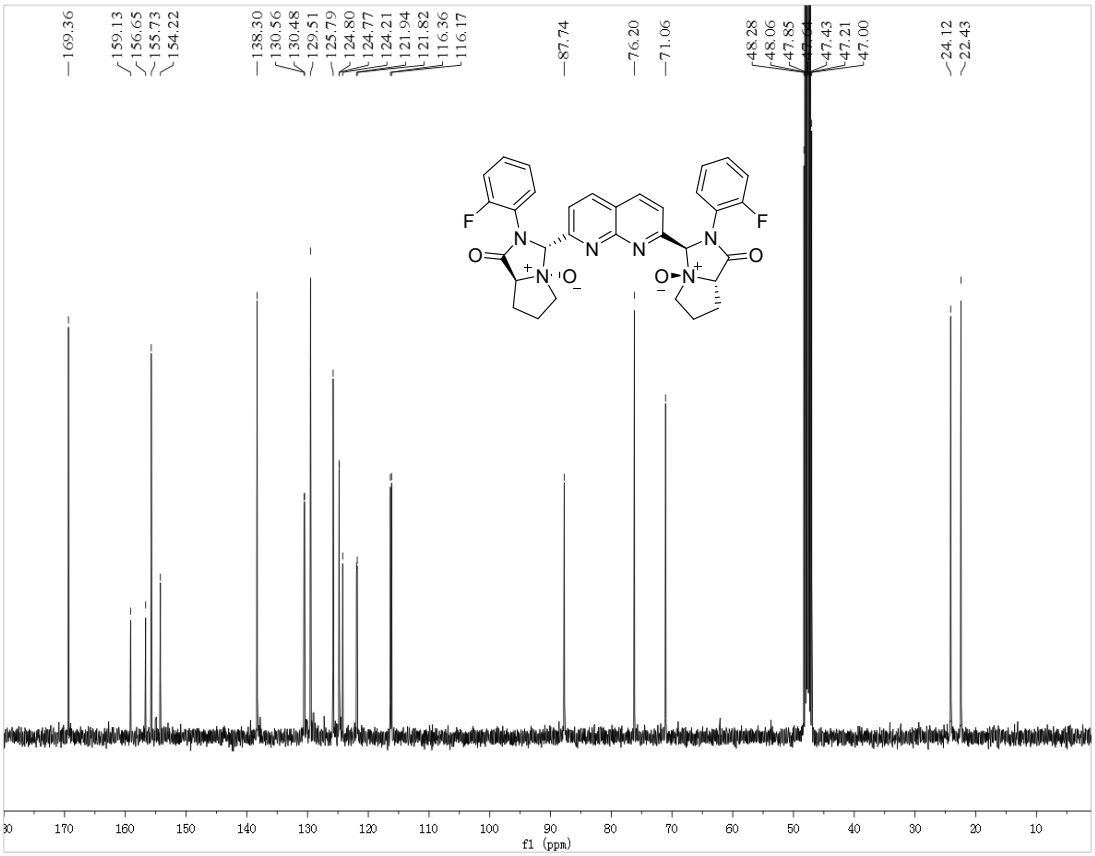
^{1}H and ^{13}C NMR of L1c



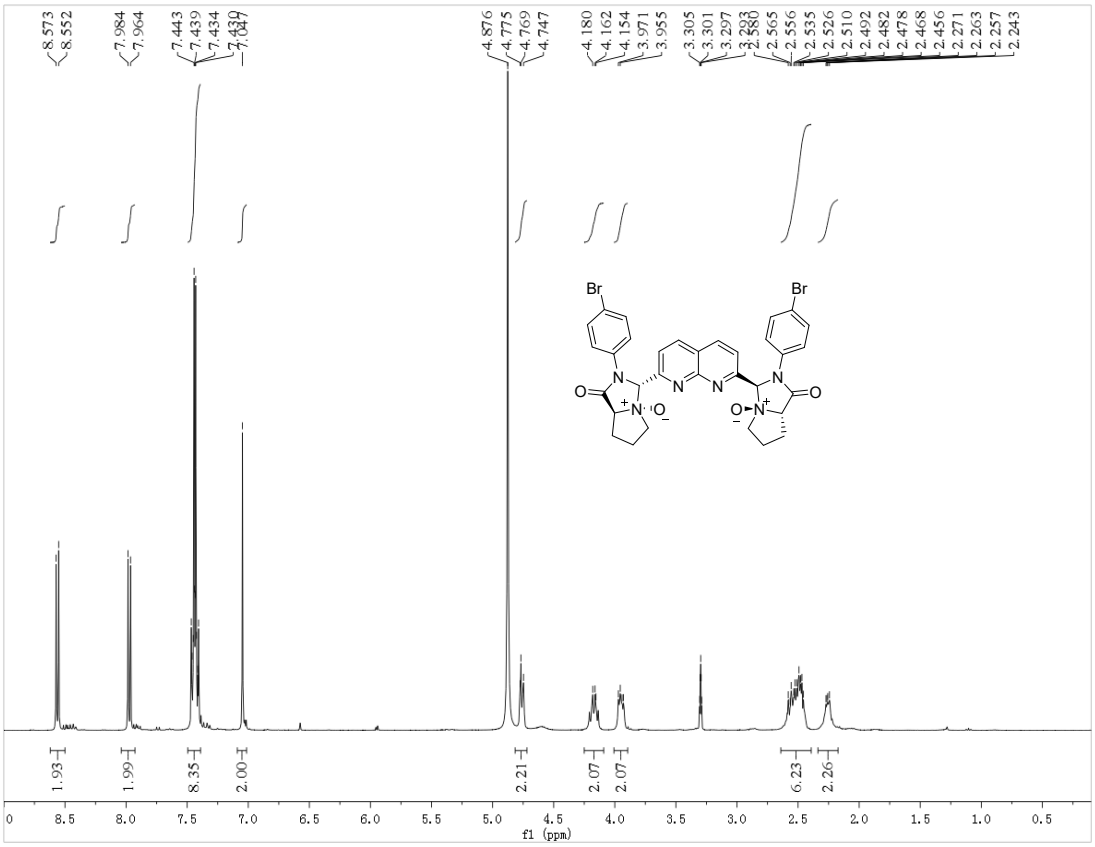


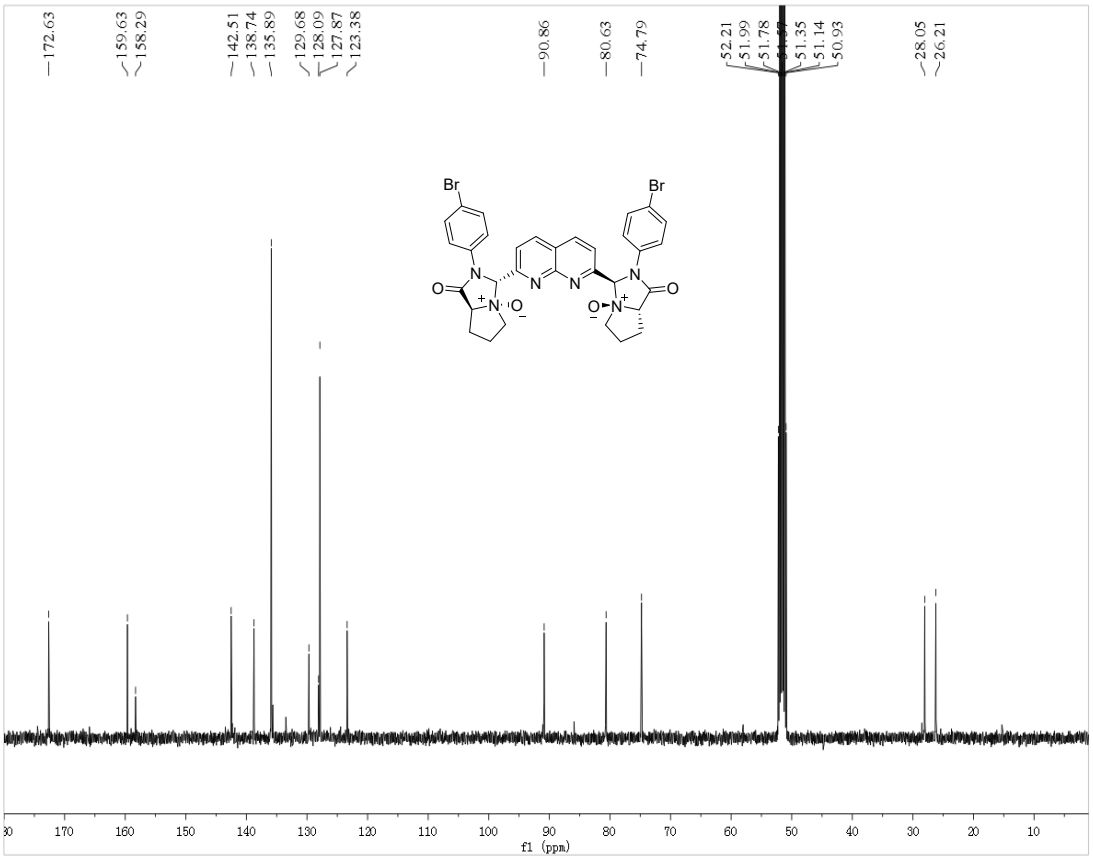
^{1}H and ^{13}C NMR of L1d



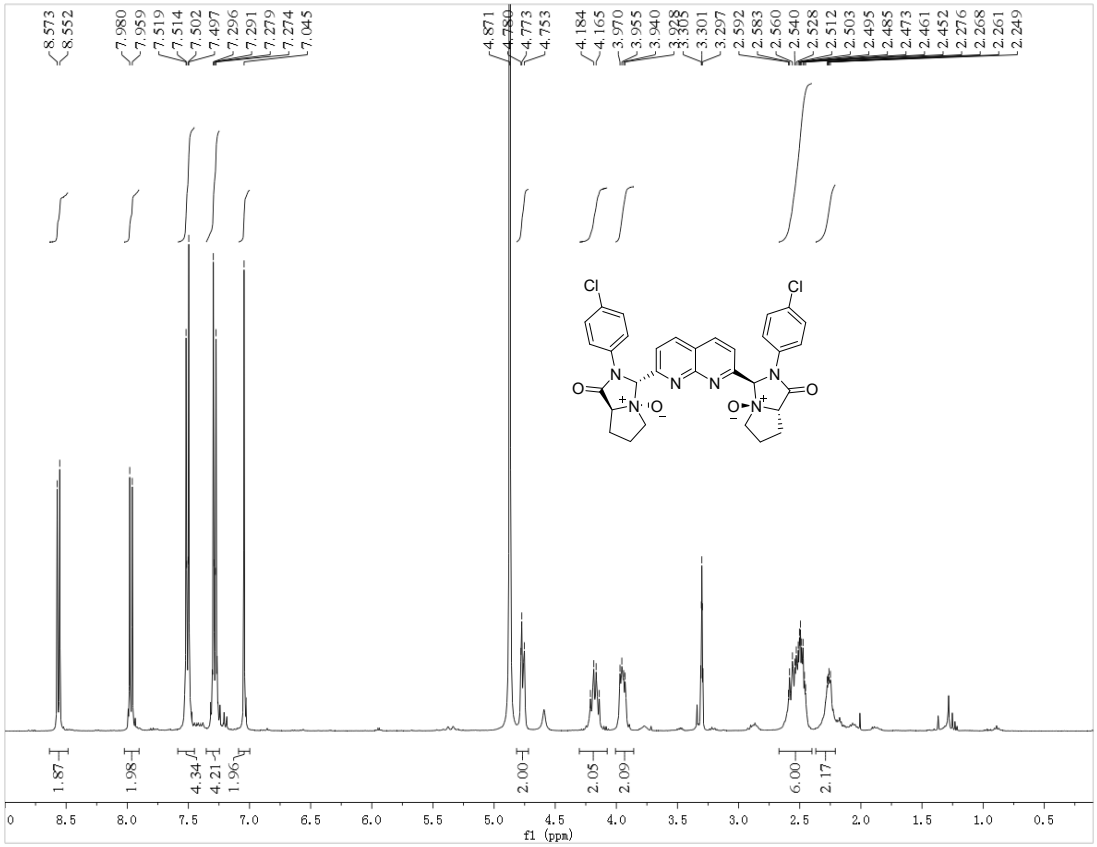


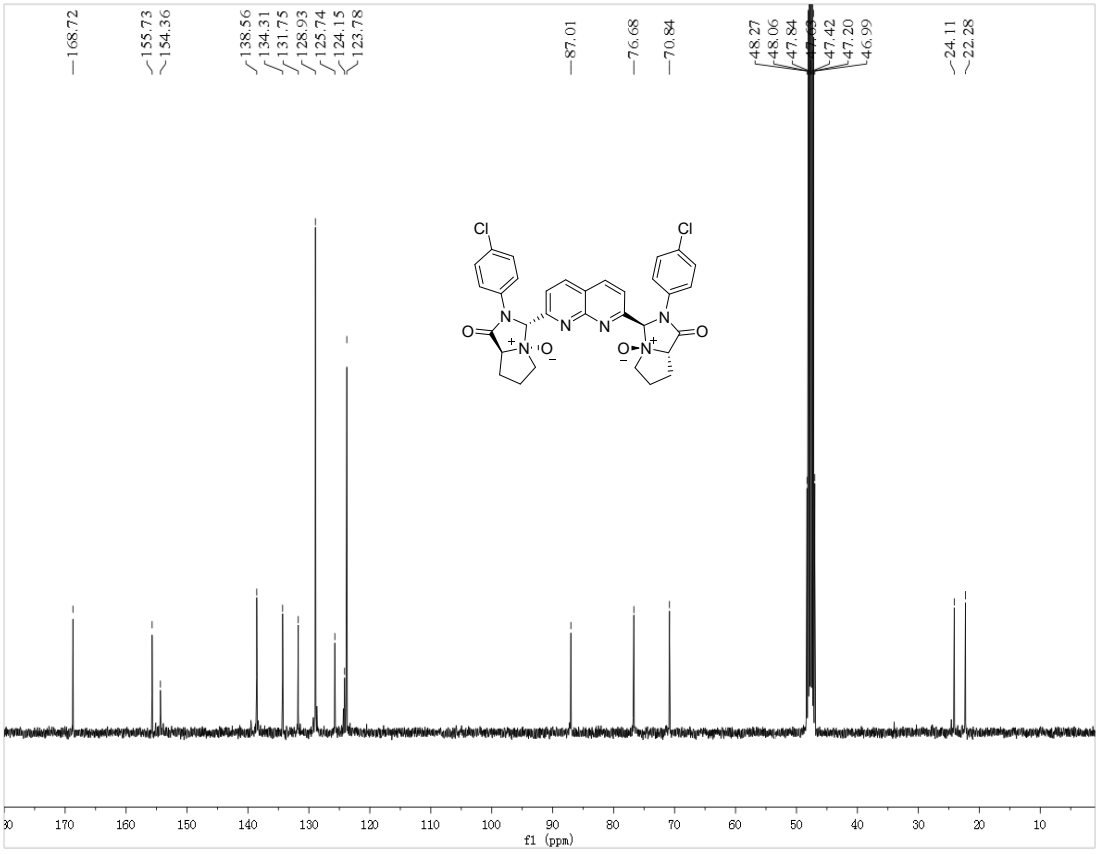
^{1}H and ^{13}C NMR of L1e



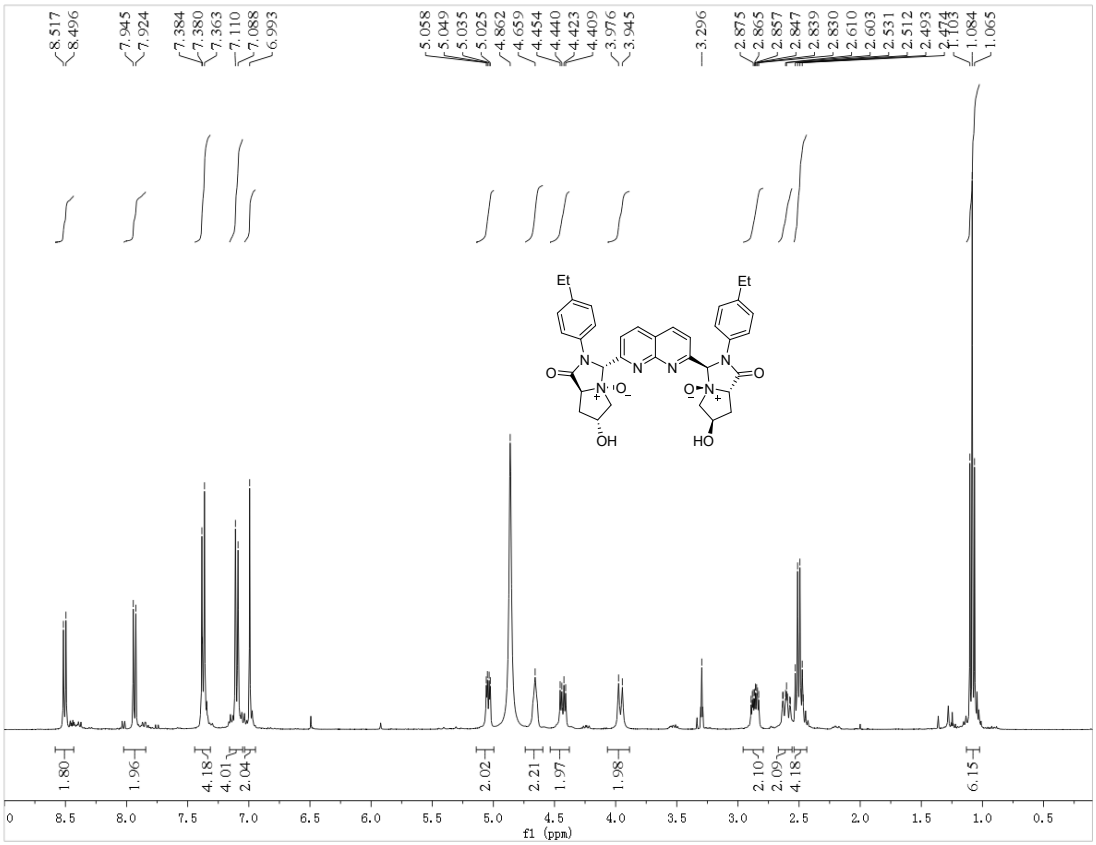


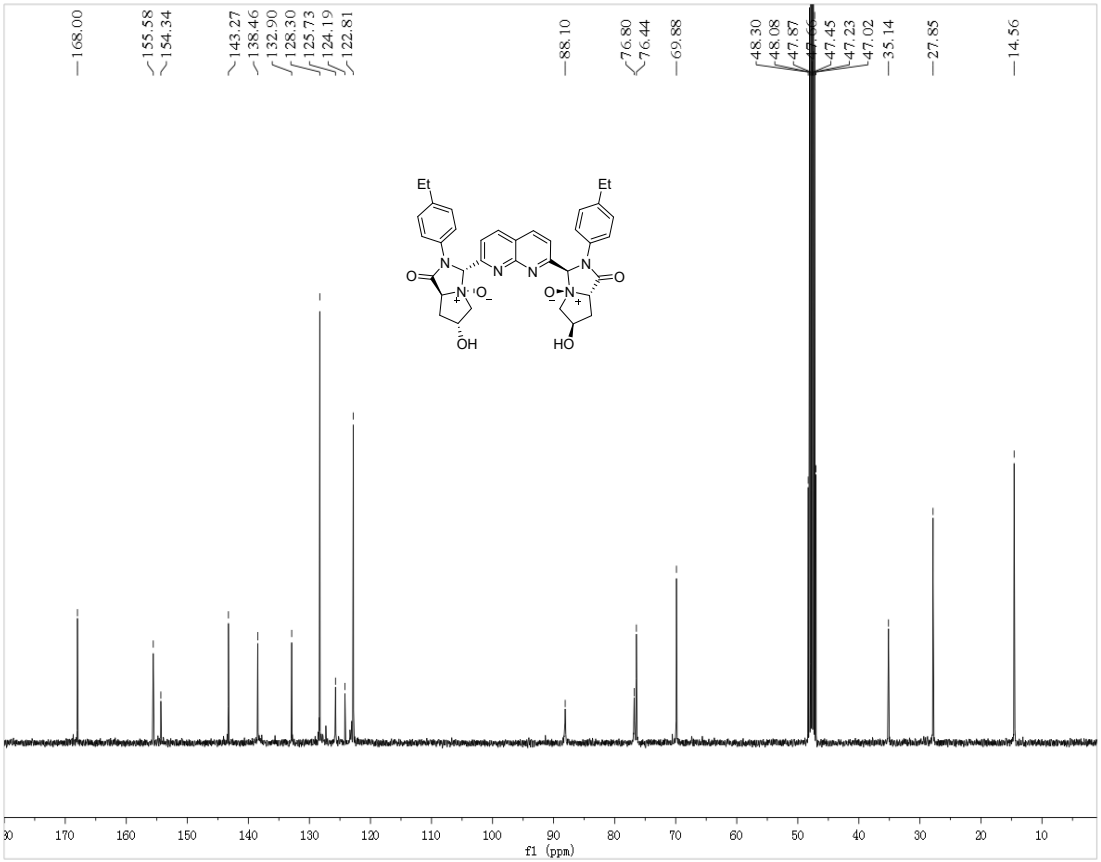
^{1}H and ^{13}C NMR of L1f



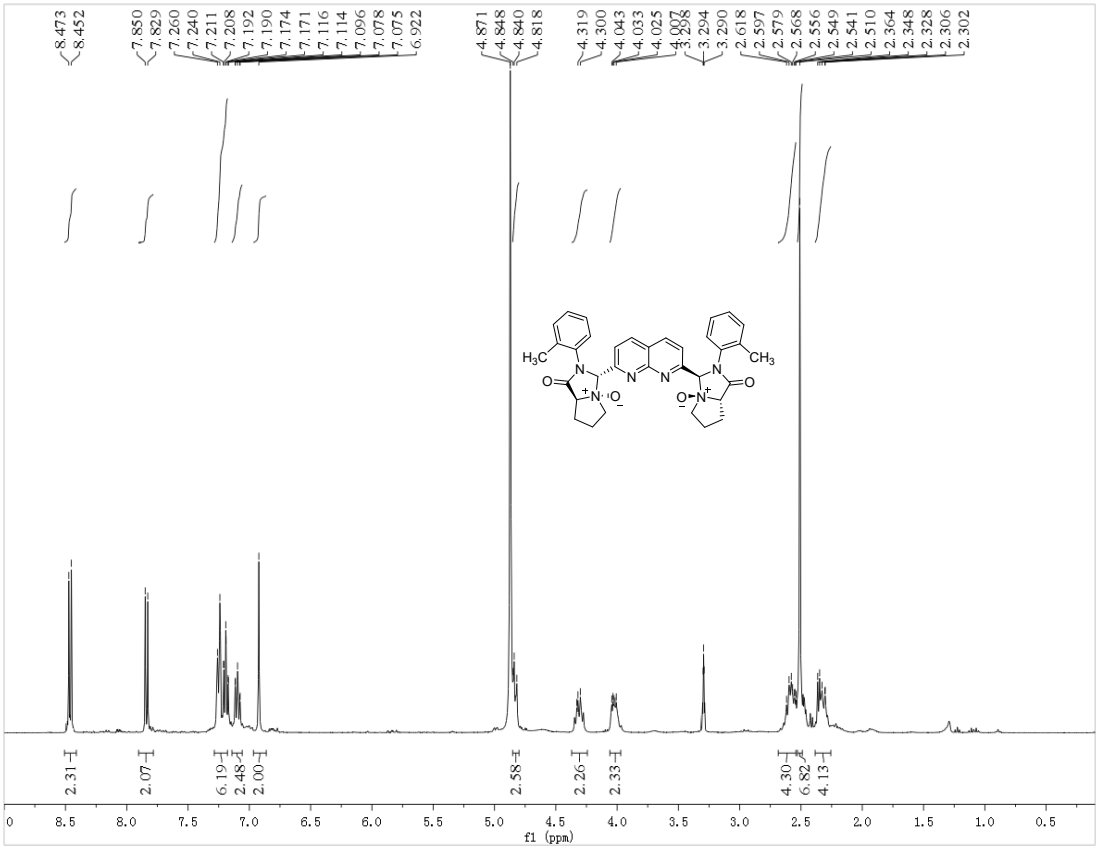


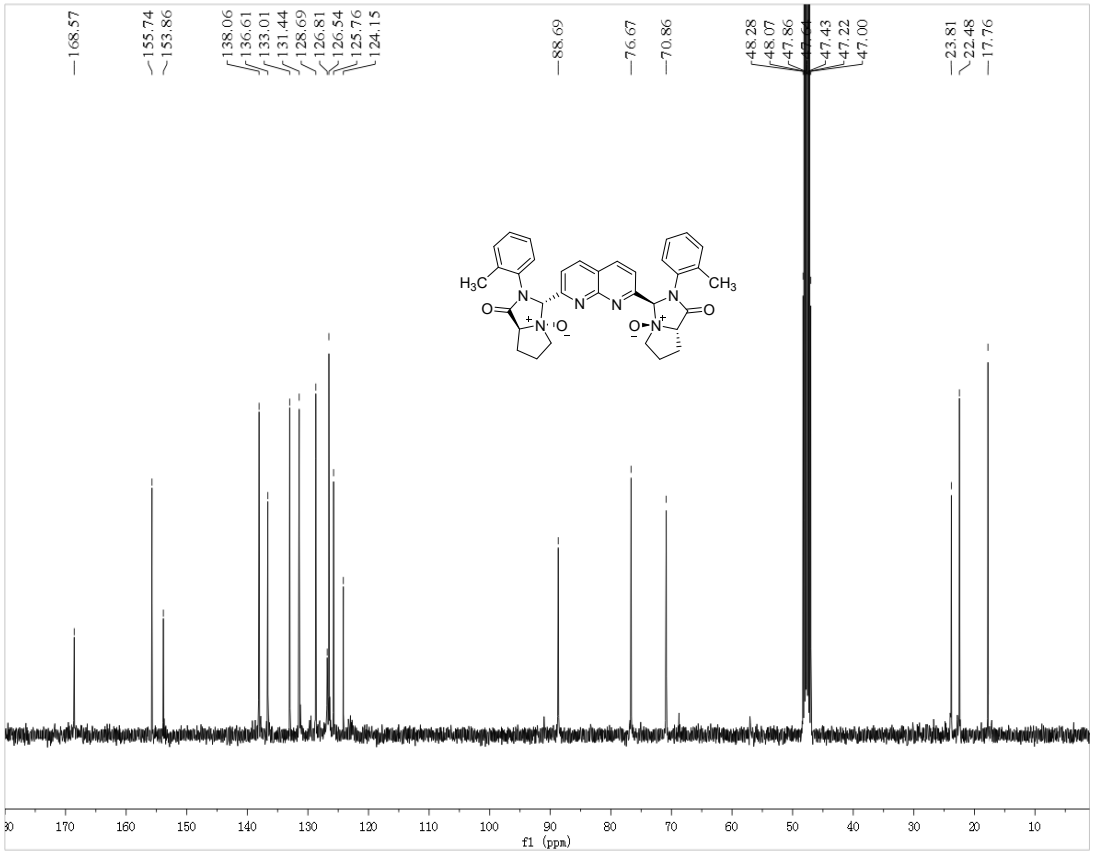
^{1}H and ^{13}C NMR of L1g



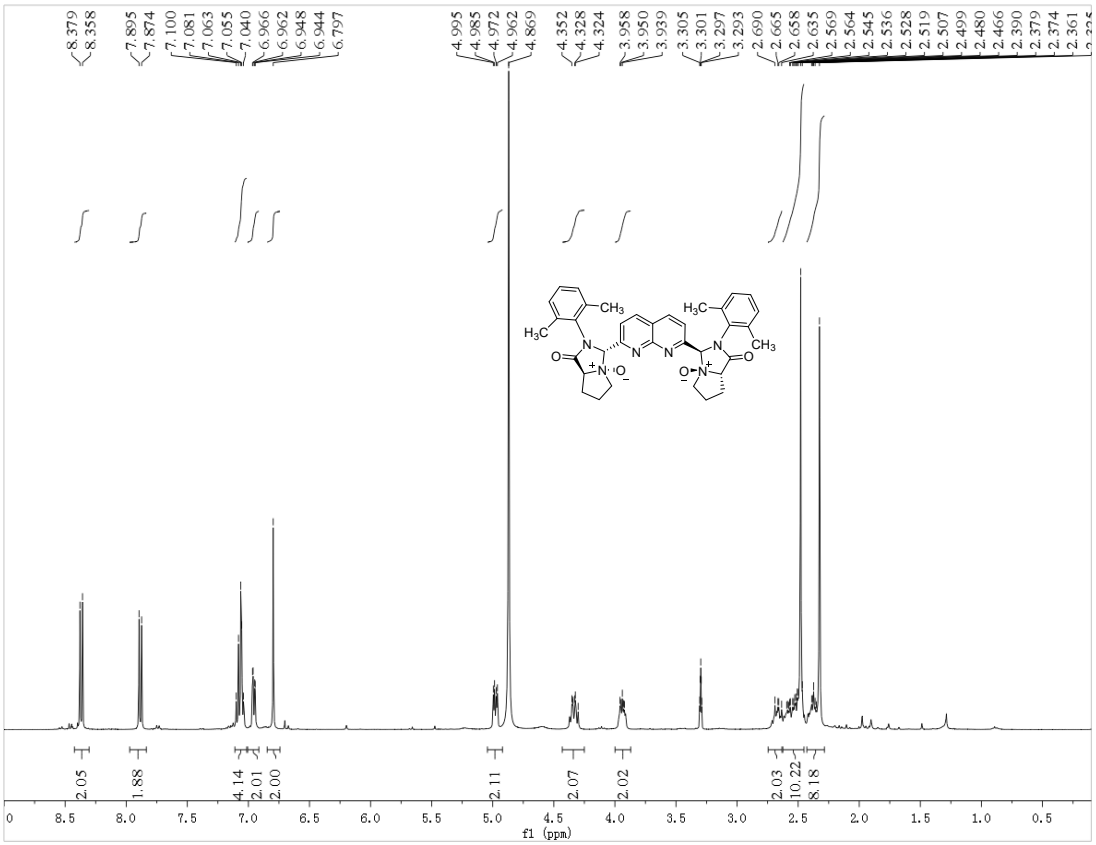


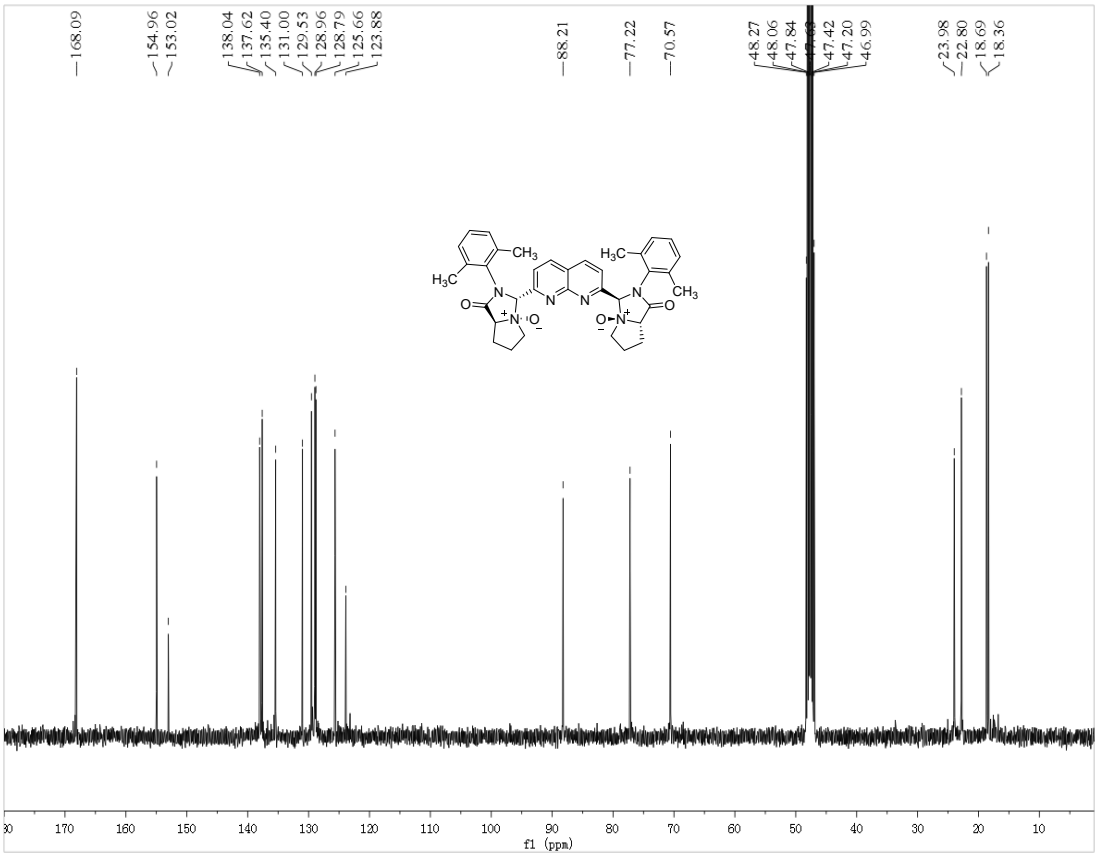
^{1}H and ^{13}C NMR of L1h



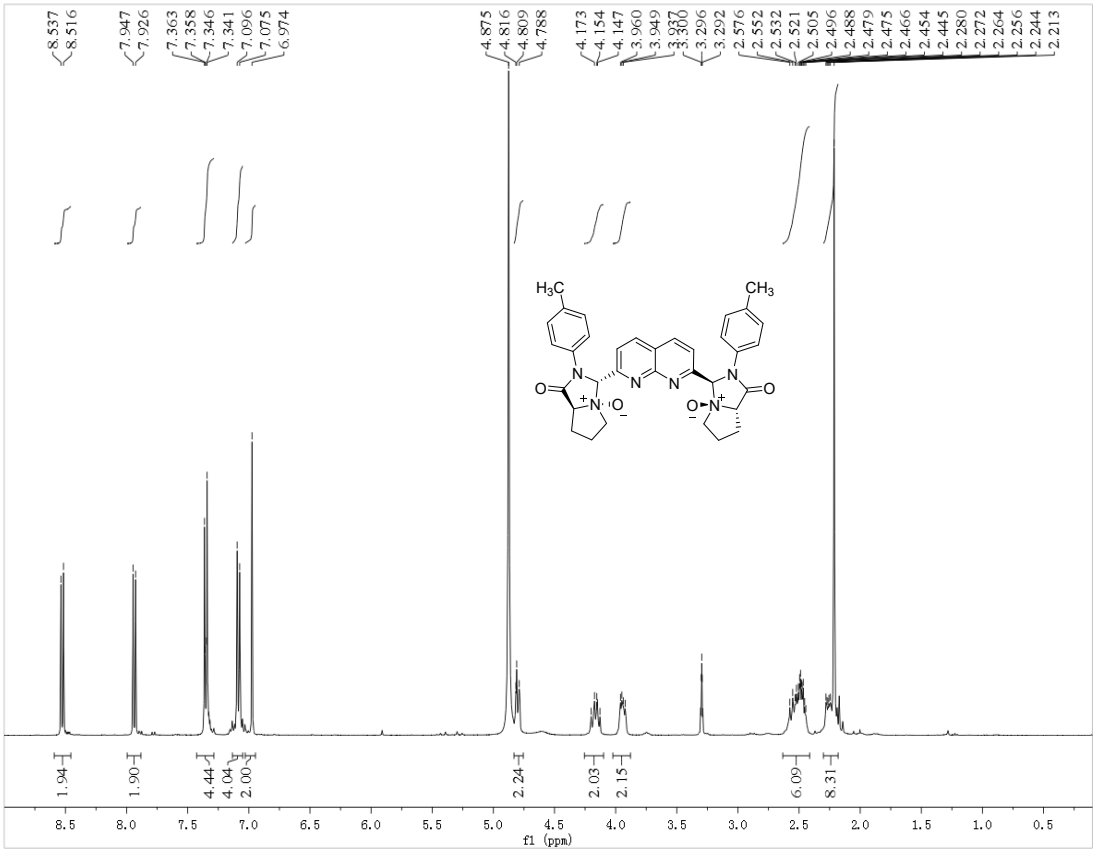


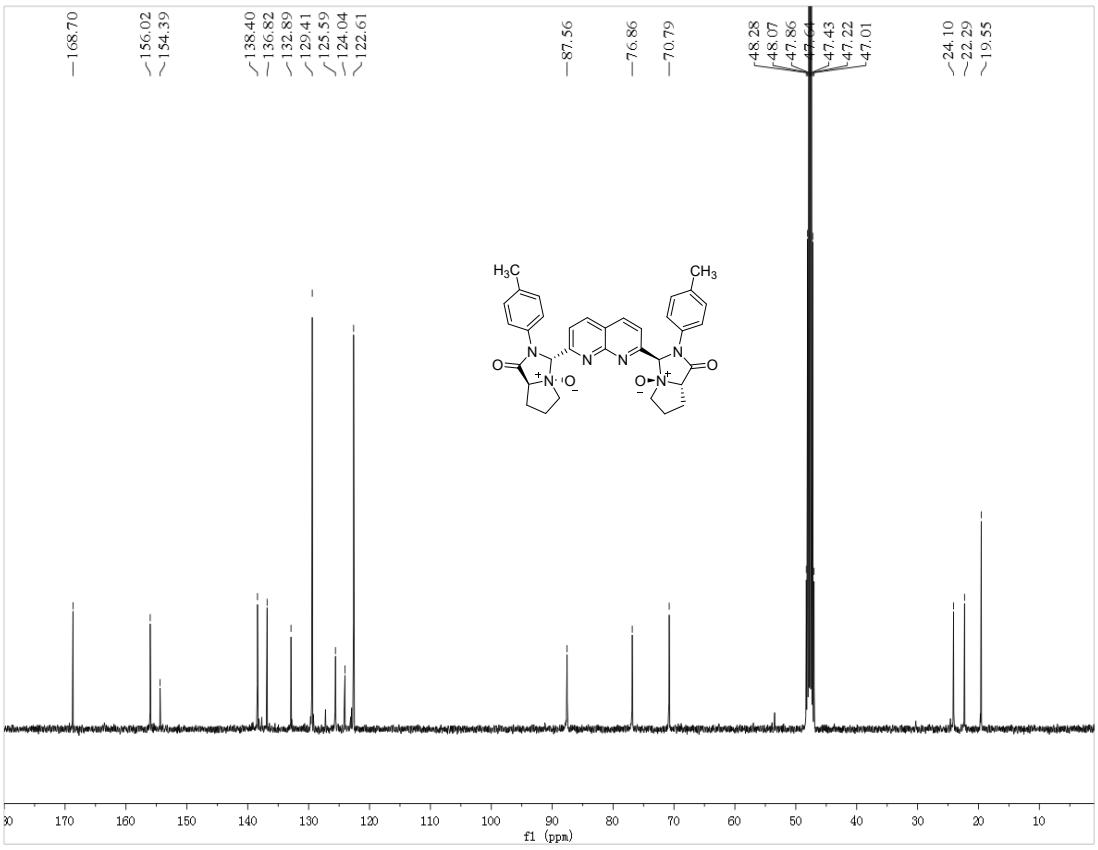
^{1}H and ^{13}C NMR of L1i



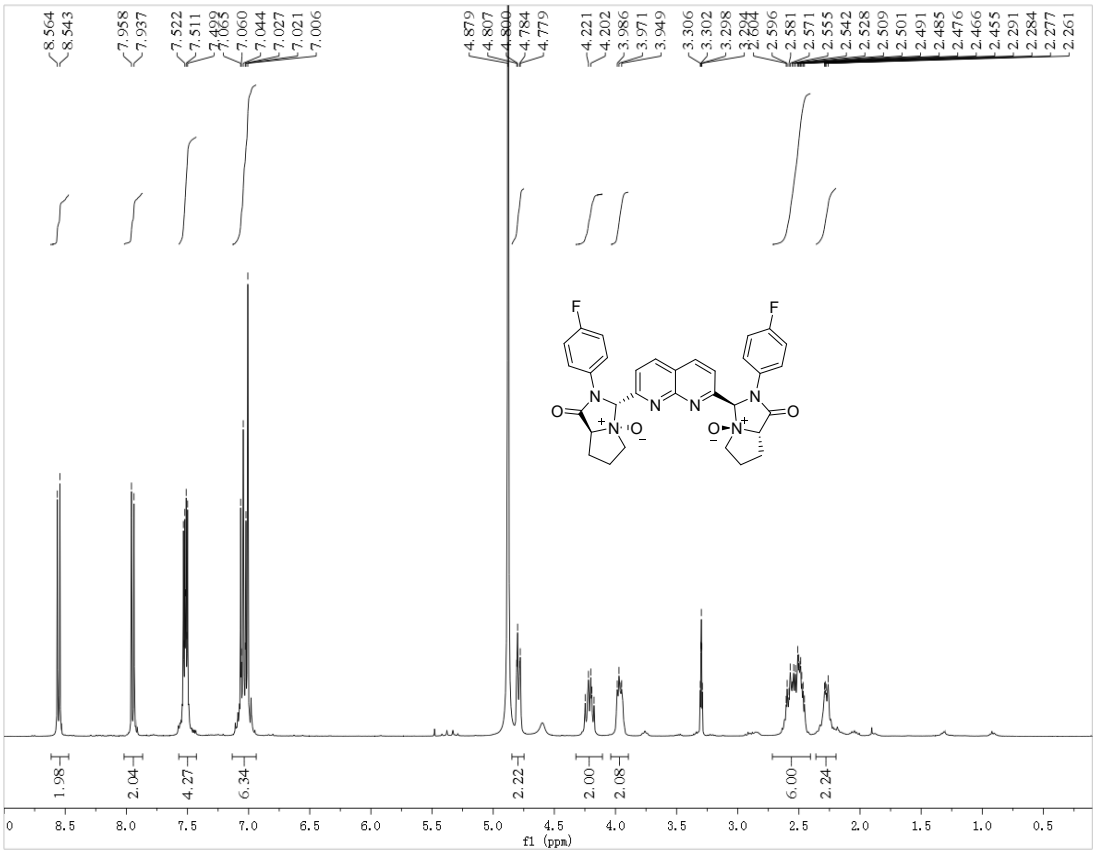


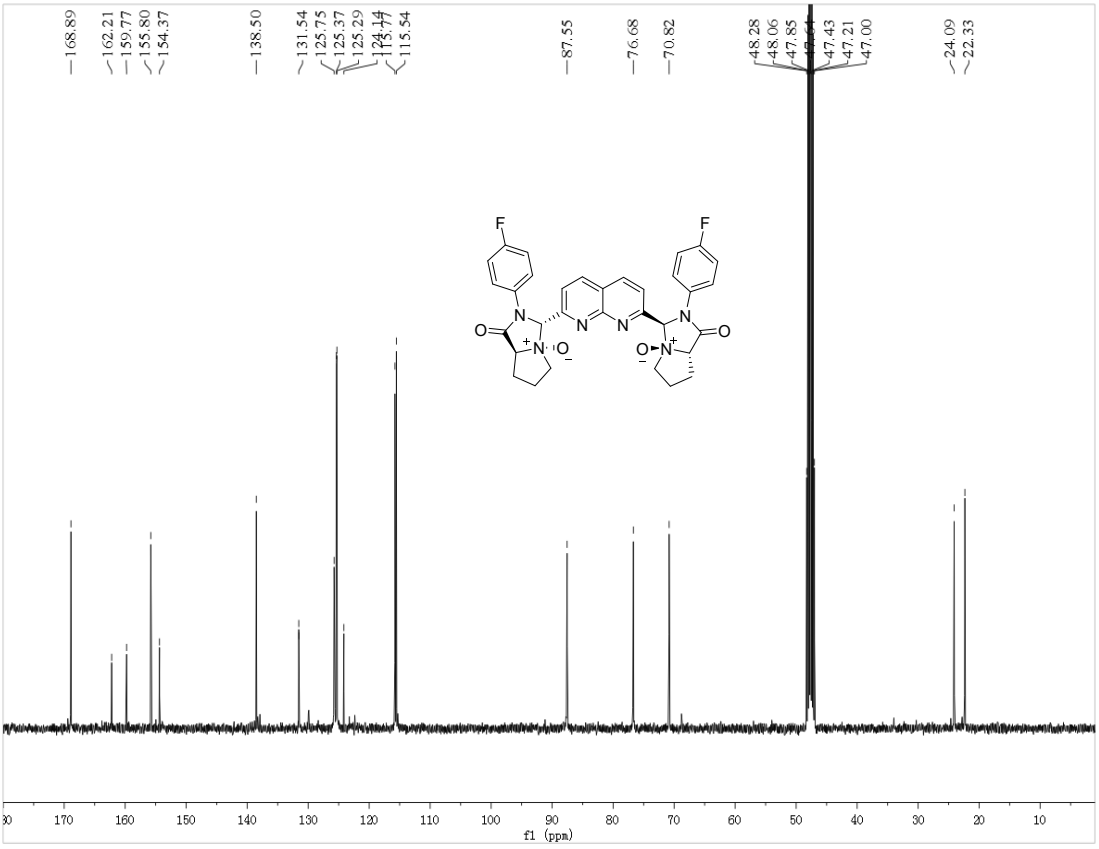
^{1}H and ^{13}C NMR of L1j



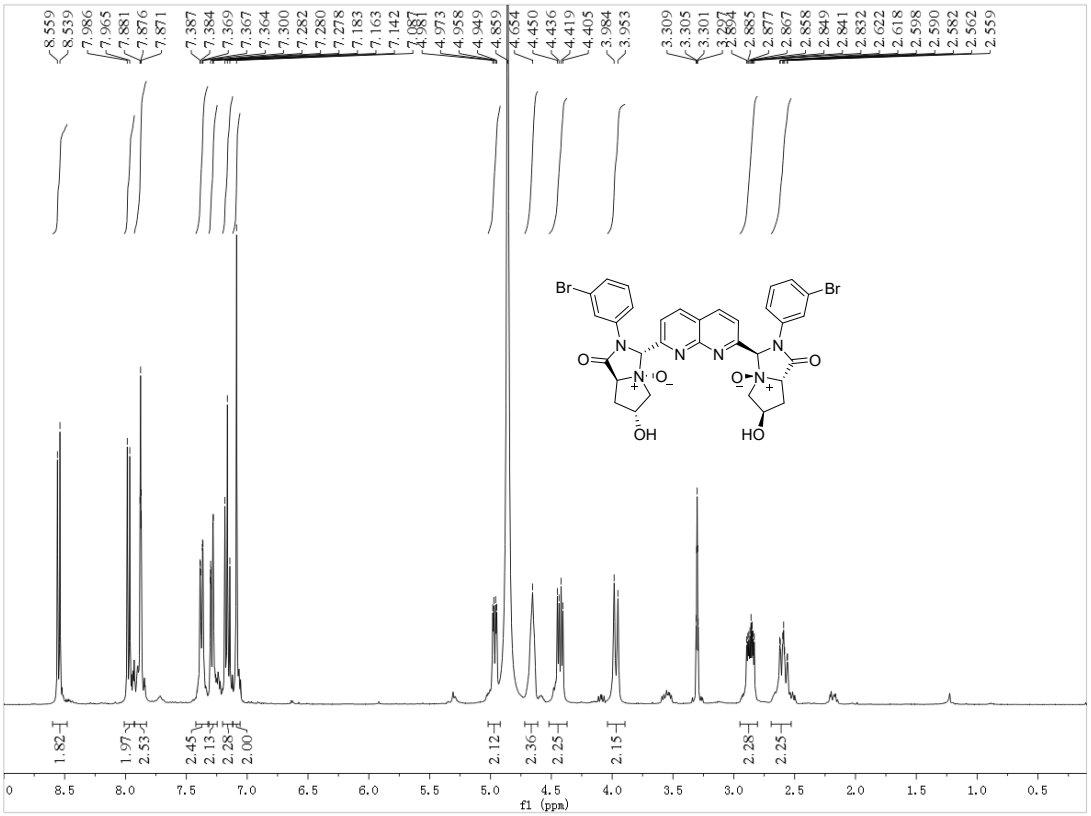


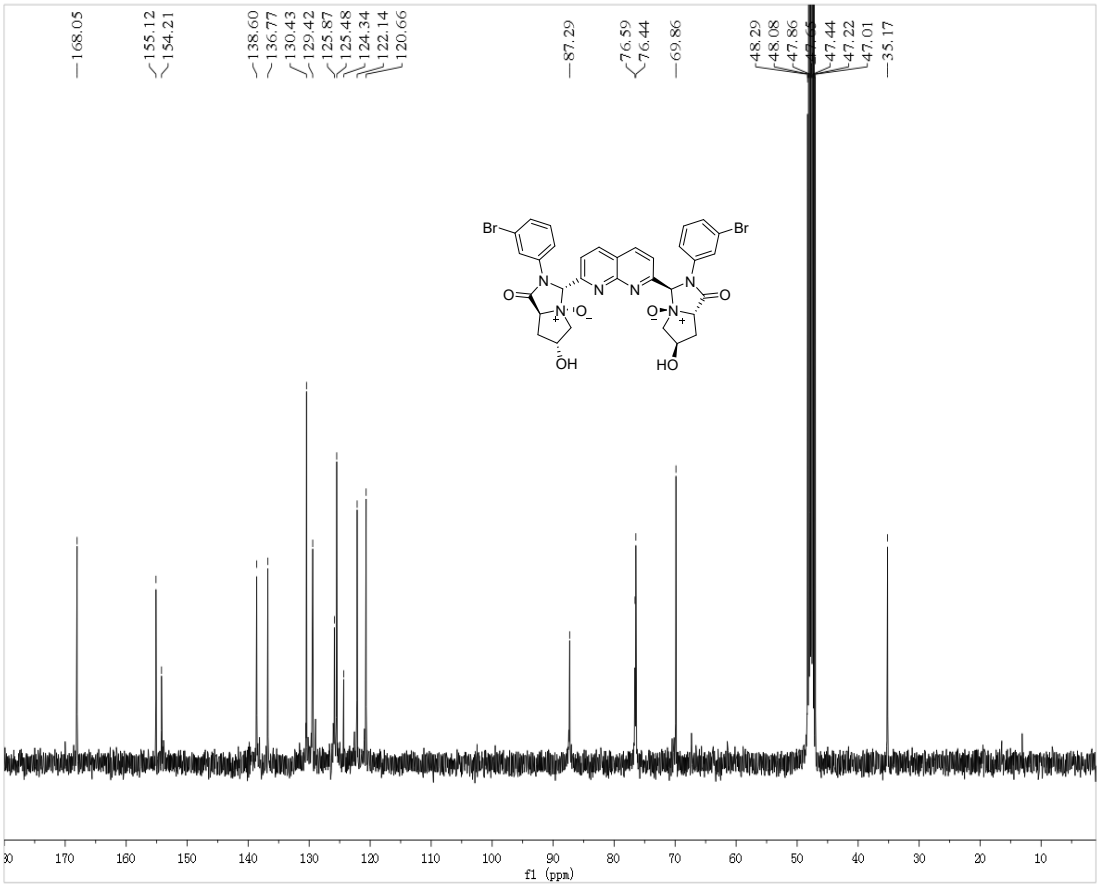
^{1}H and ^{13}C NMR of L1k



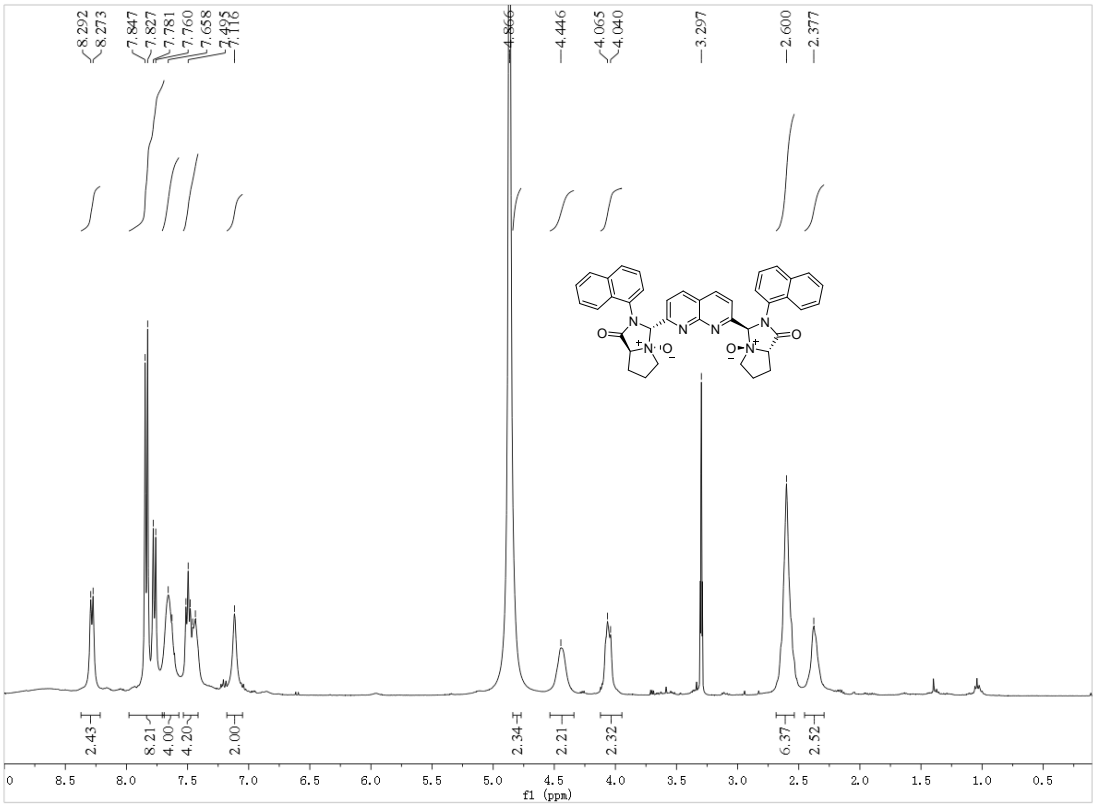


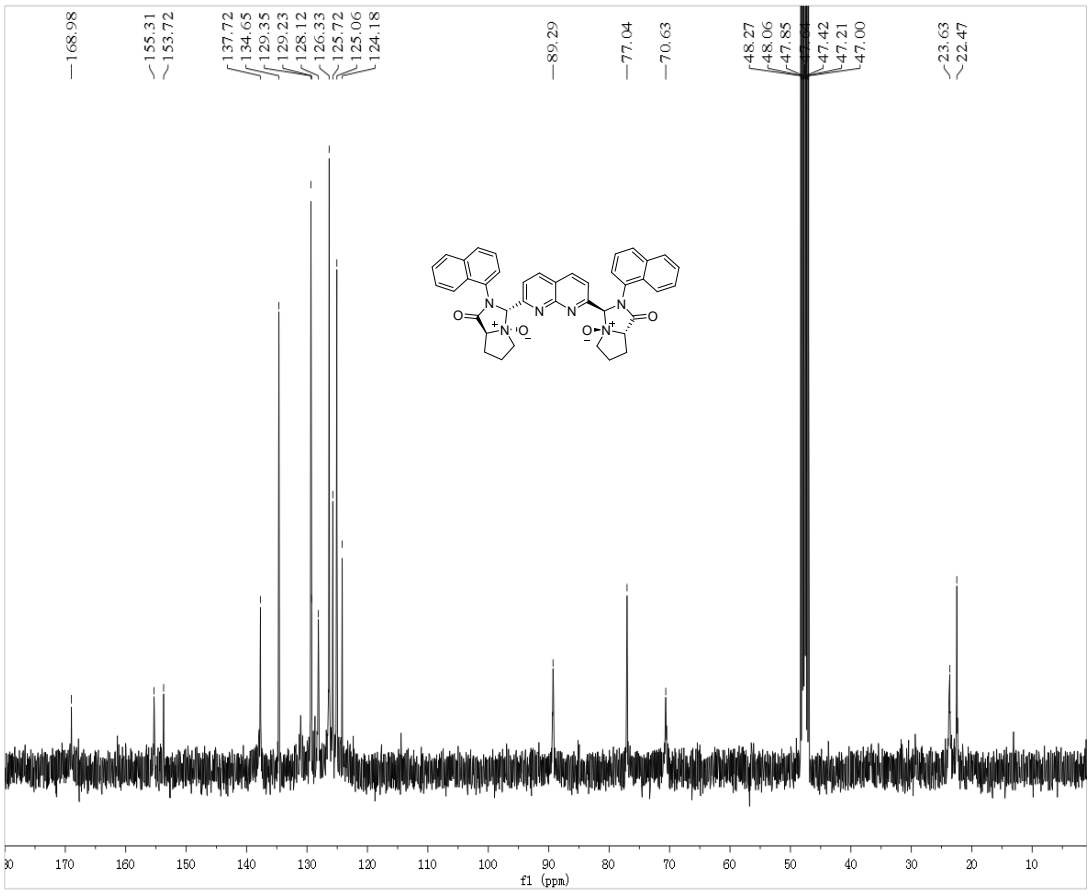
^{1}H and ^{13}C NMR of L1l



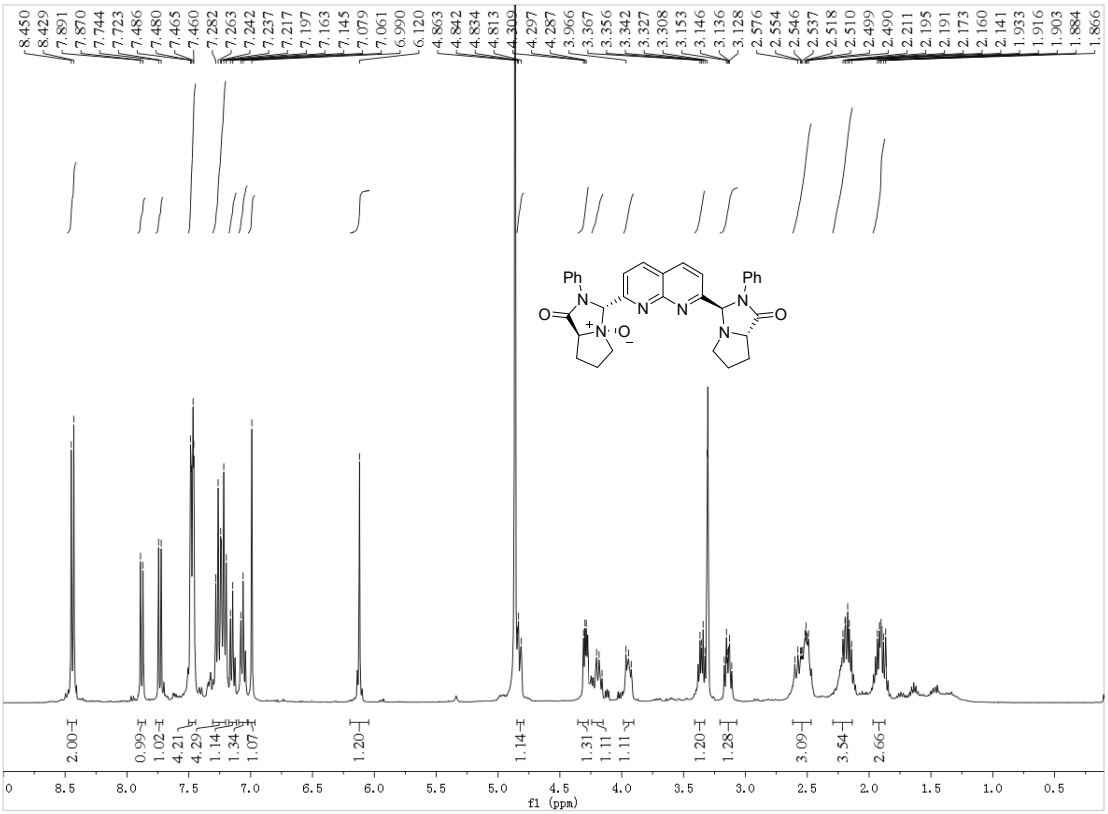


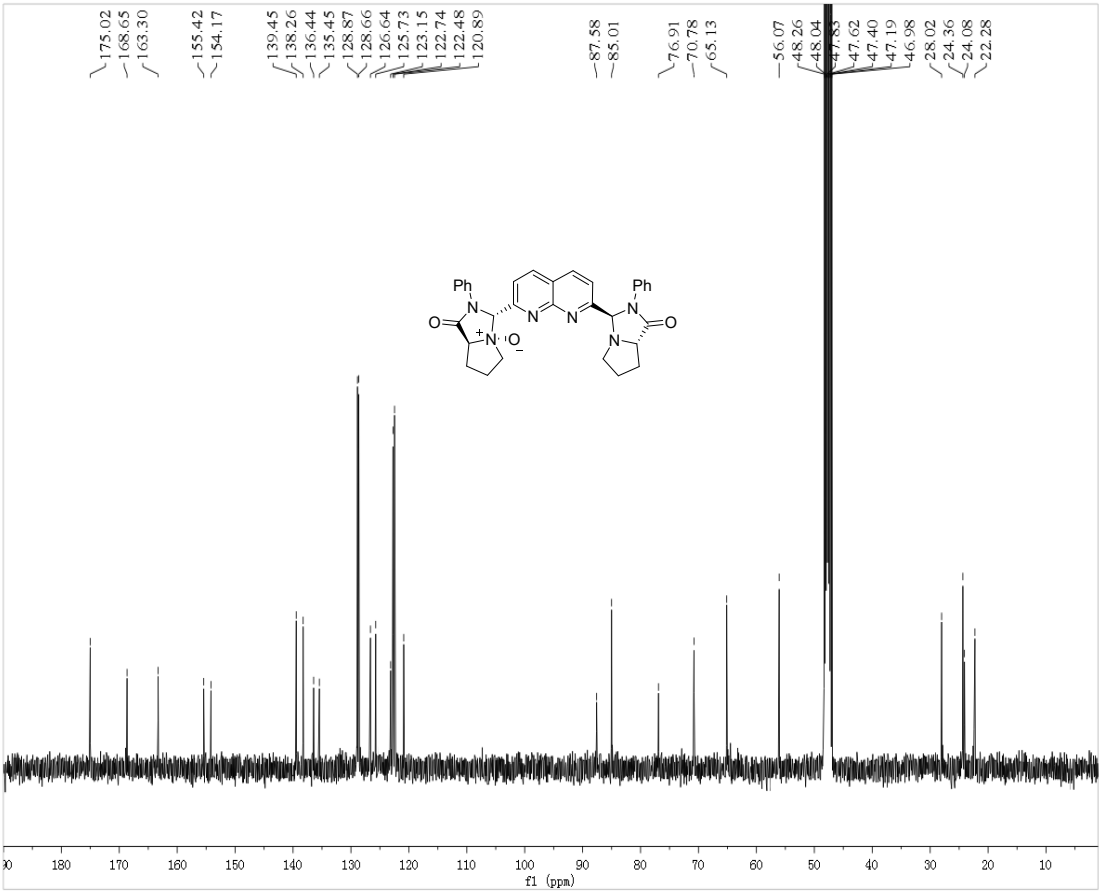
^{1}H and ^{13}C NMR of L1m



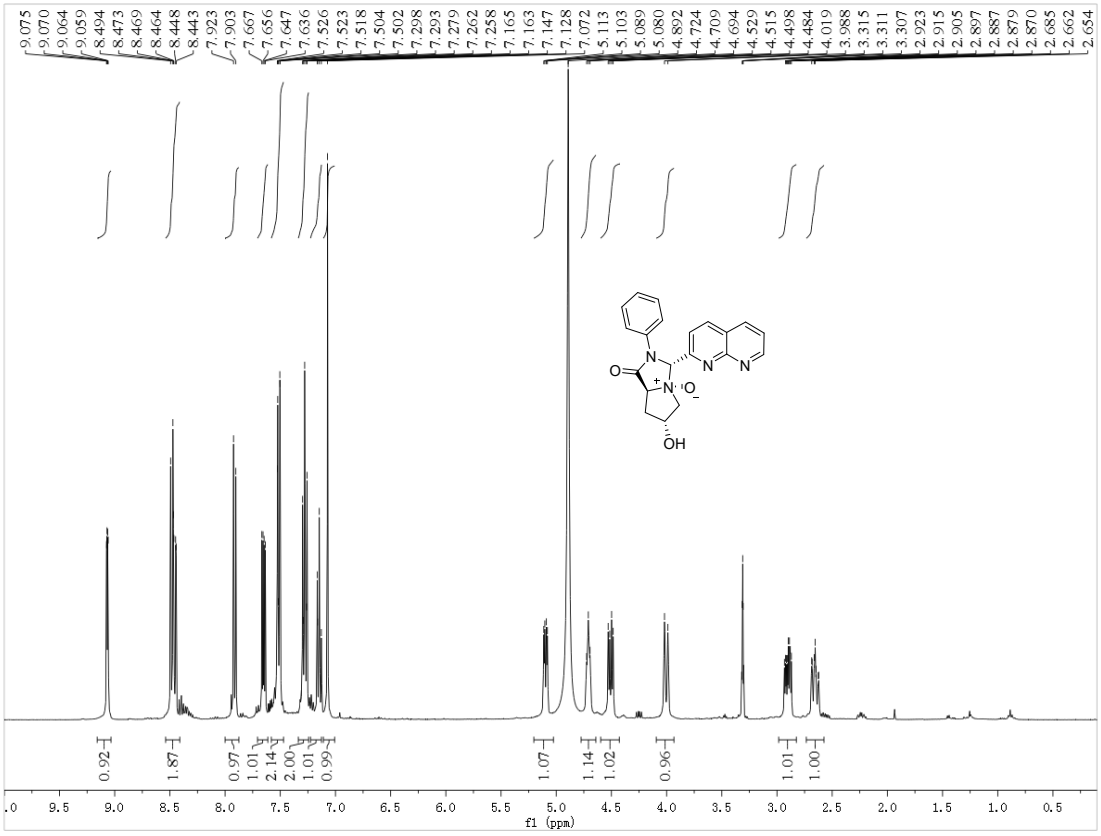


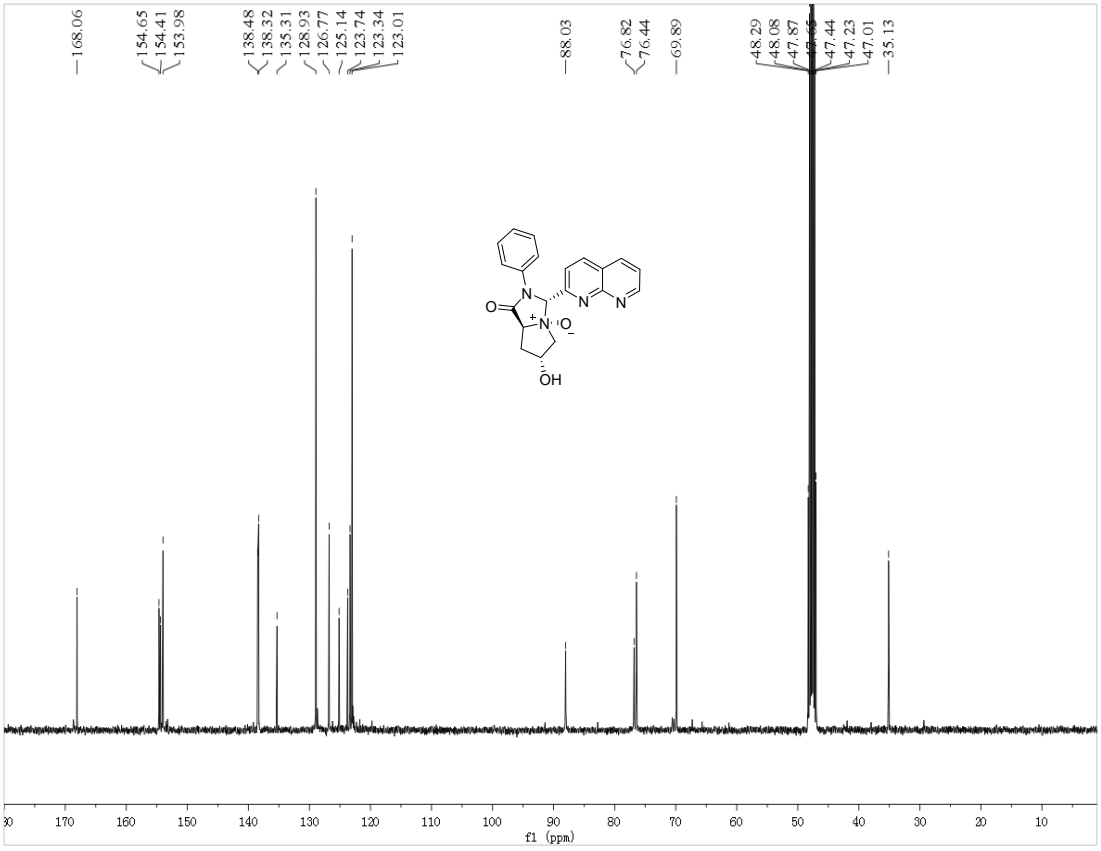
^{1}H and ^{13}C NMR of L2a



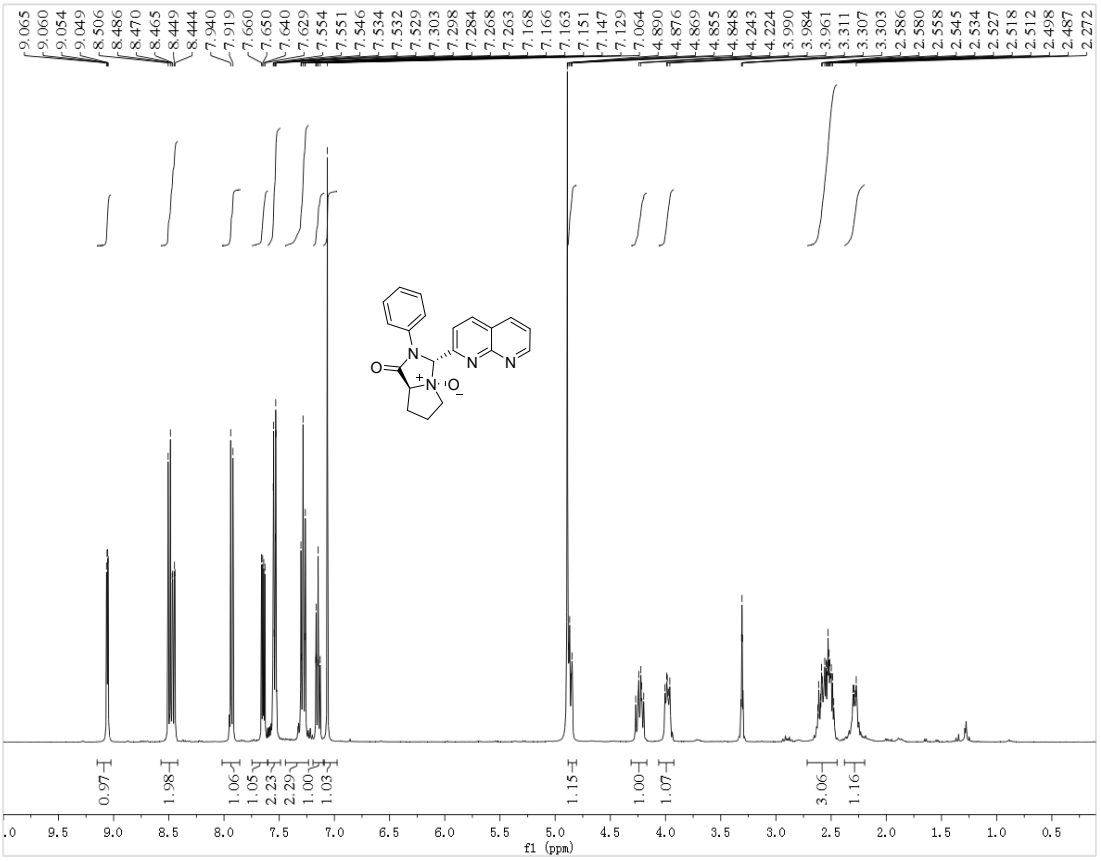


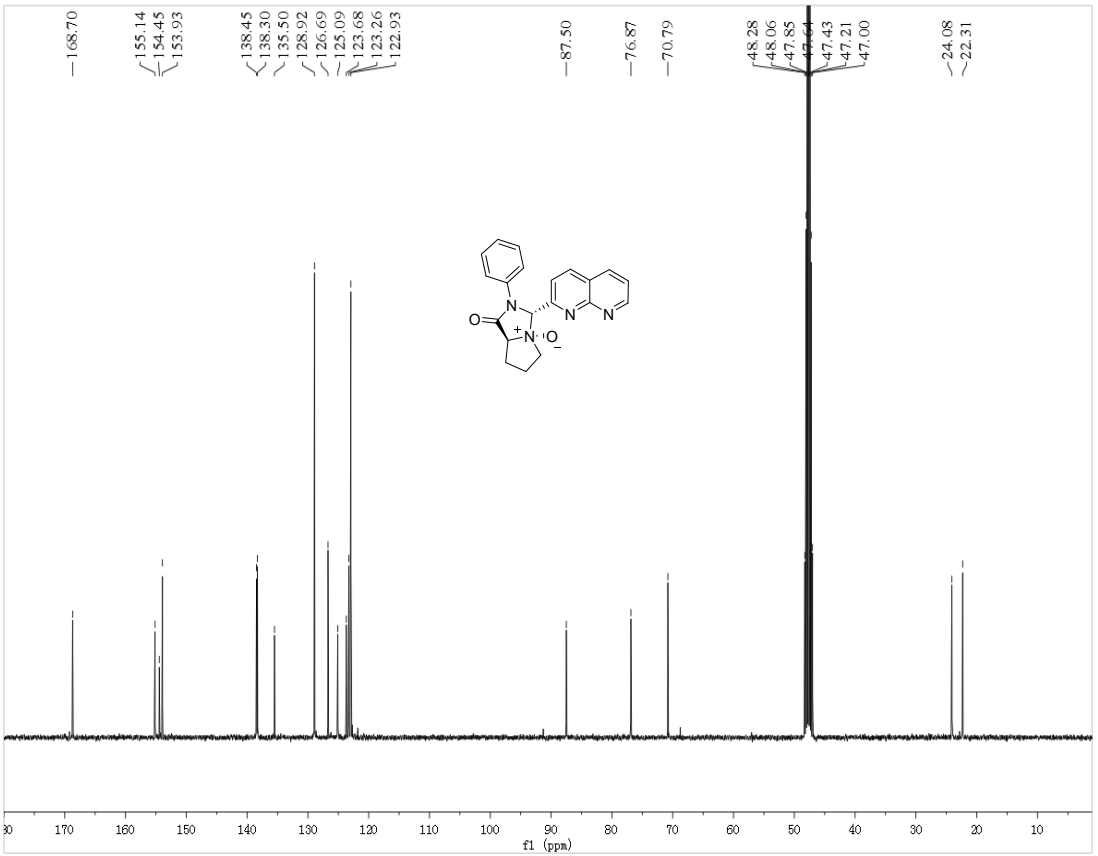
^{1}H and ^{13}C NMR of L3a



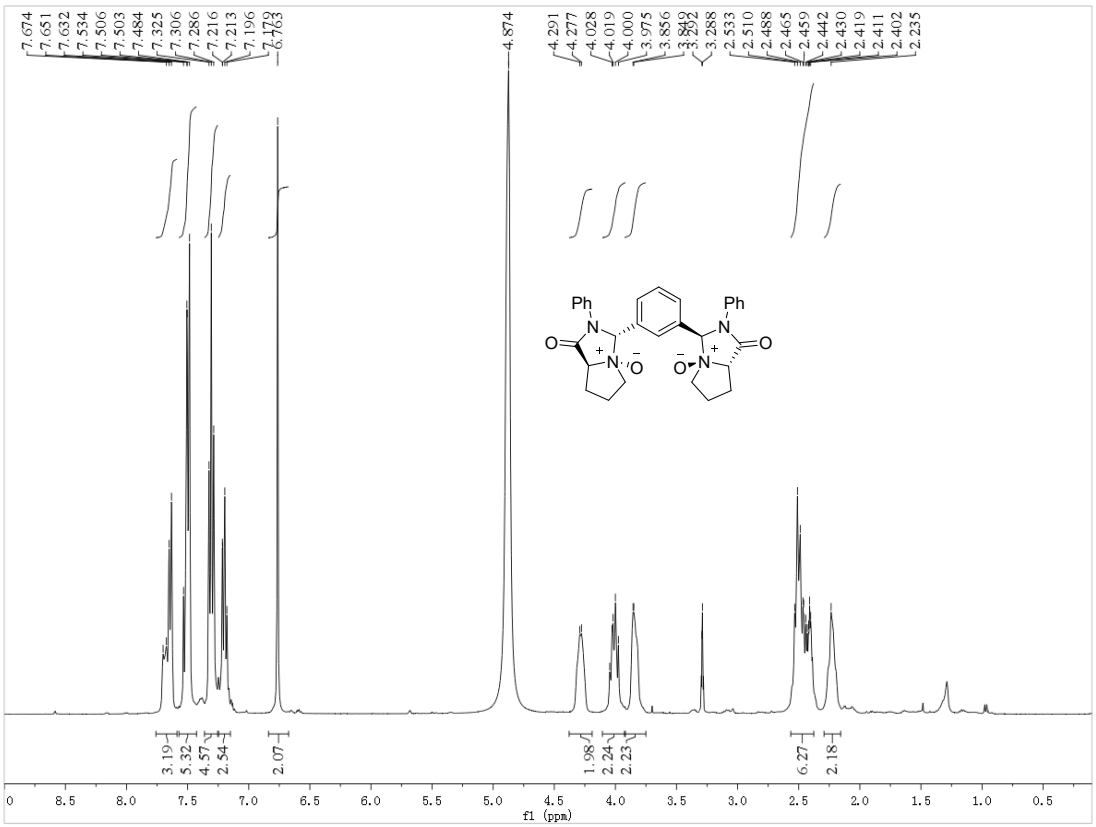


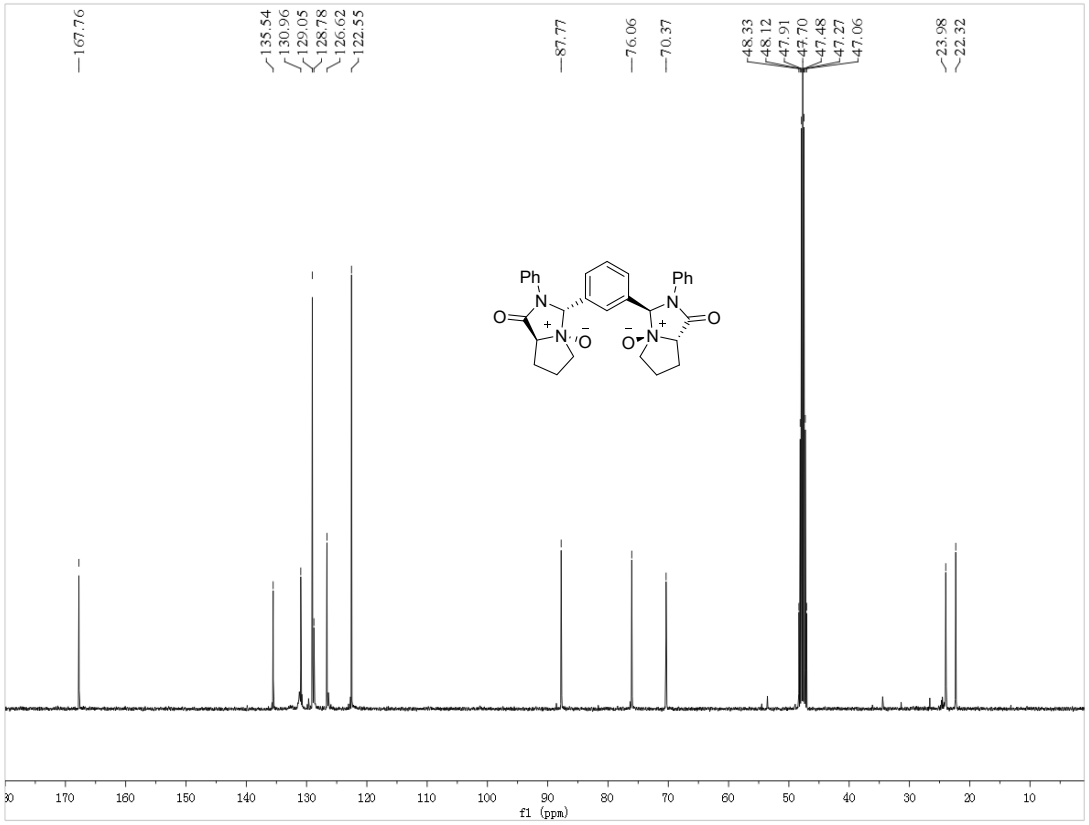
^{1}H and ^{13}C NMR of L4a



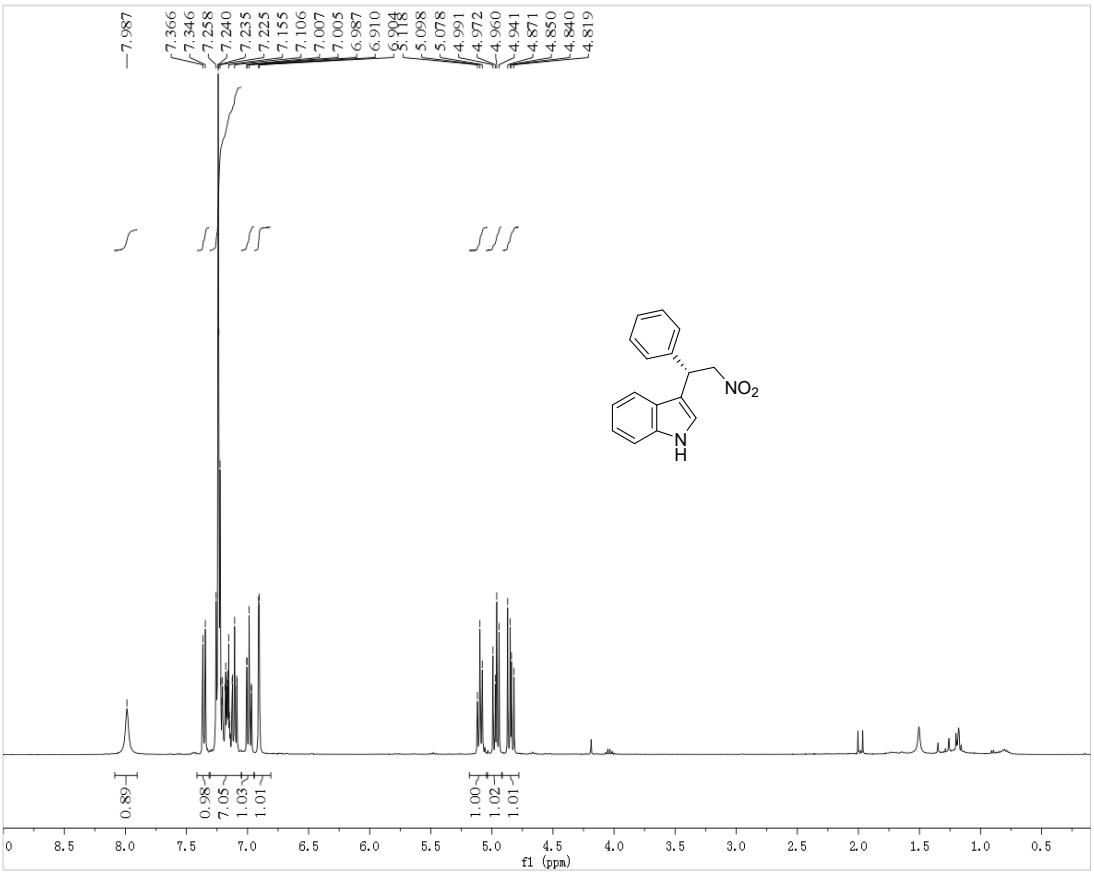


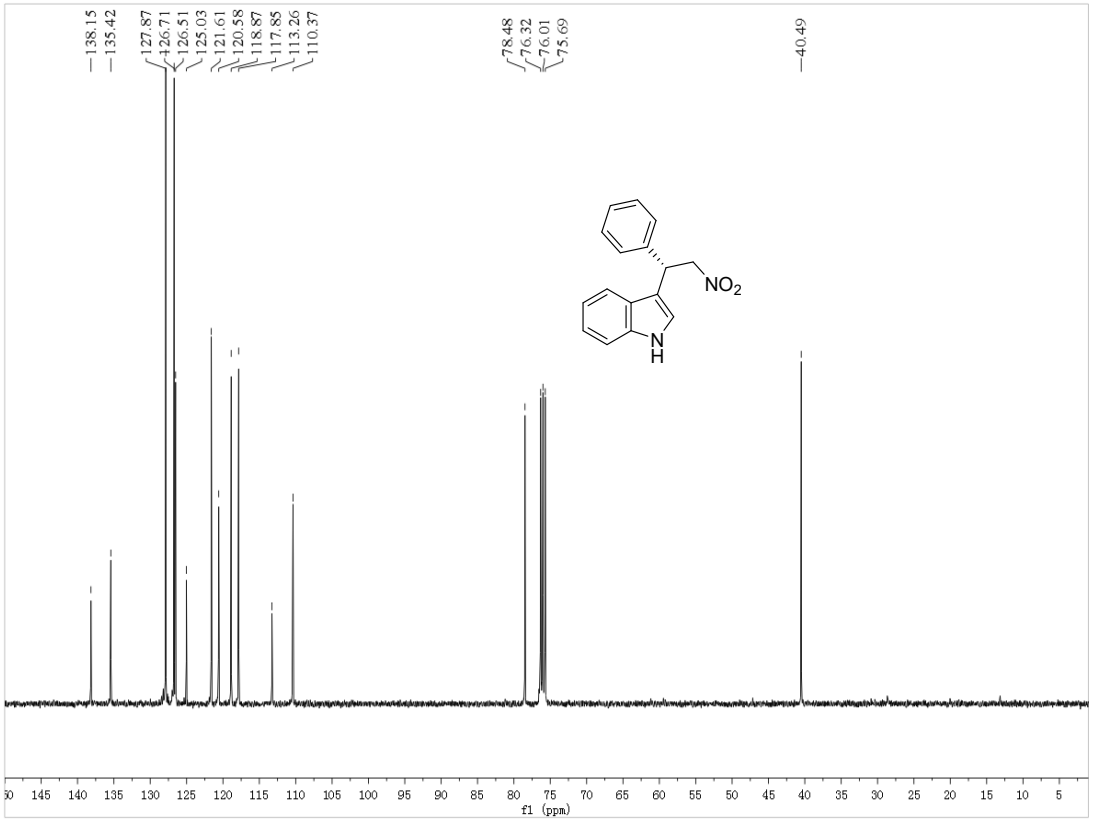
^{1}H and ^{13}C NMR of L7a



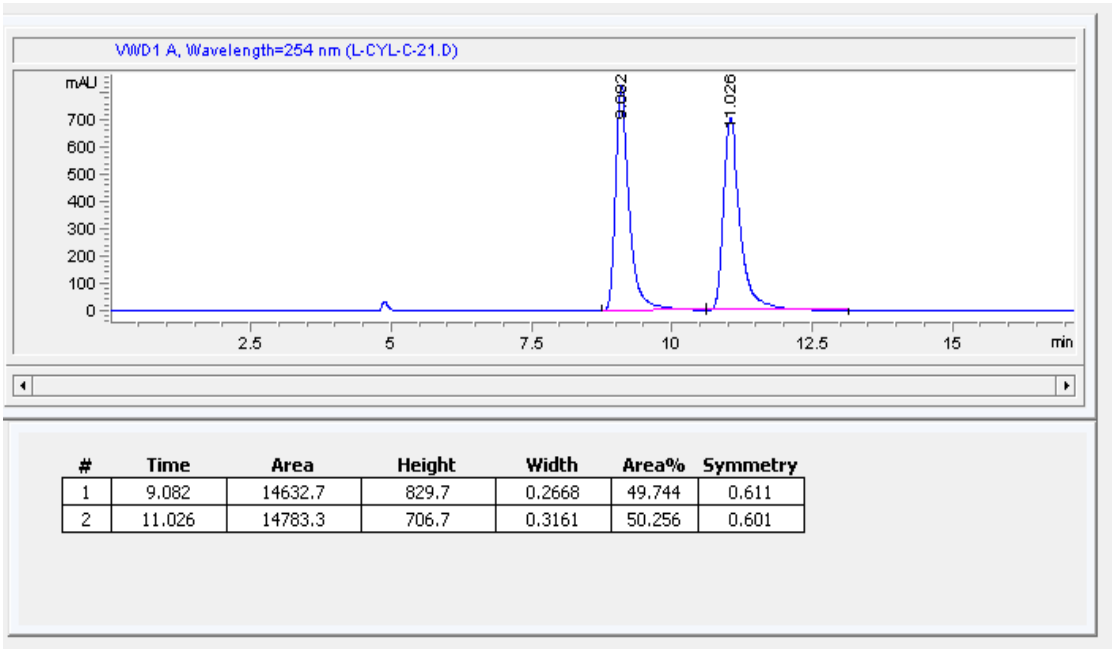


^{1}H and ^{13}C NMR of 6a

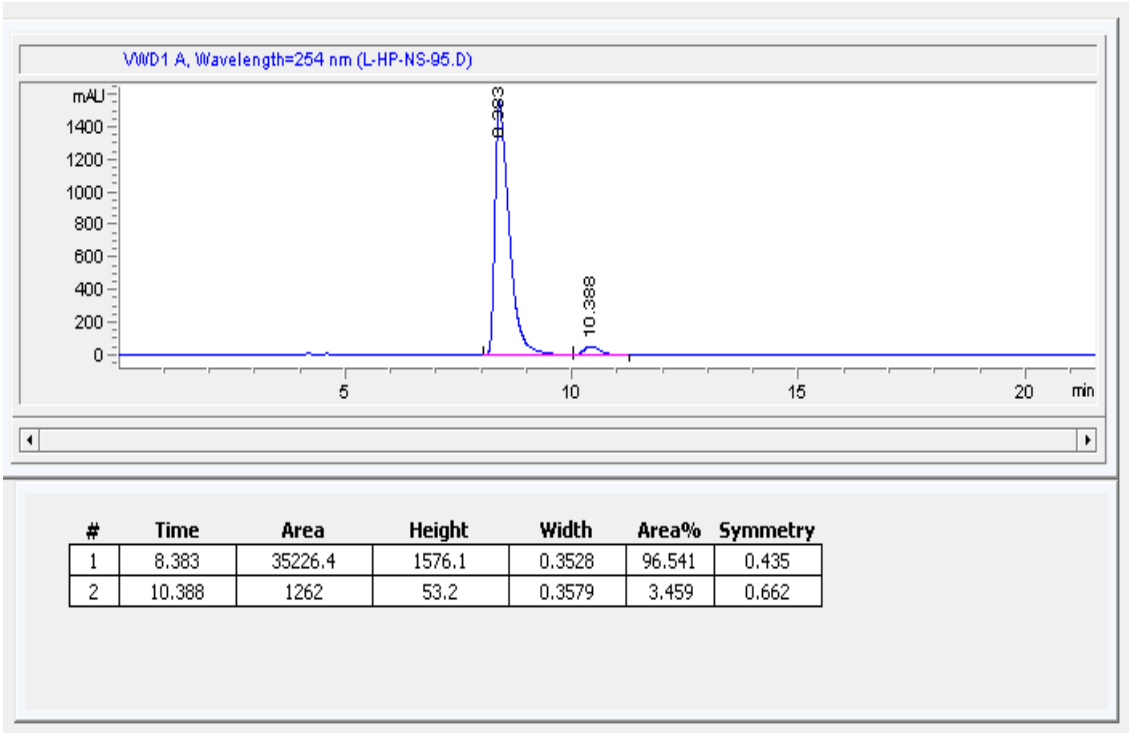

7.987
7.366
7.346
7.258
7.240
7.235
7.225
7.155
7.106
7.007
7.005
6.987
6.910
6.904
5.118
5.098
5.078
4.991
4.972
4.960
4.941
4.871
4.850
4.840
4.819
NO2
N
H
0.89
0.98
7.05
1.03
1.01
1.00
1.02
1.01
f1 (ppm)


138.15
135.42
127.87
126.71
126.51
125.03
121.61
120.58
118.87
117.85
113.26
110.37
78.48
76.32
76.01
75.69
40.49
NO2
N
H
f1 (ppm)

HPLC of 6a

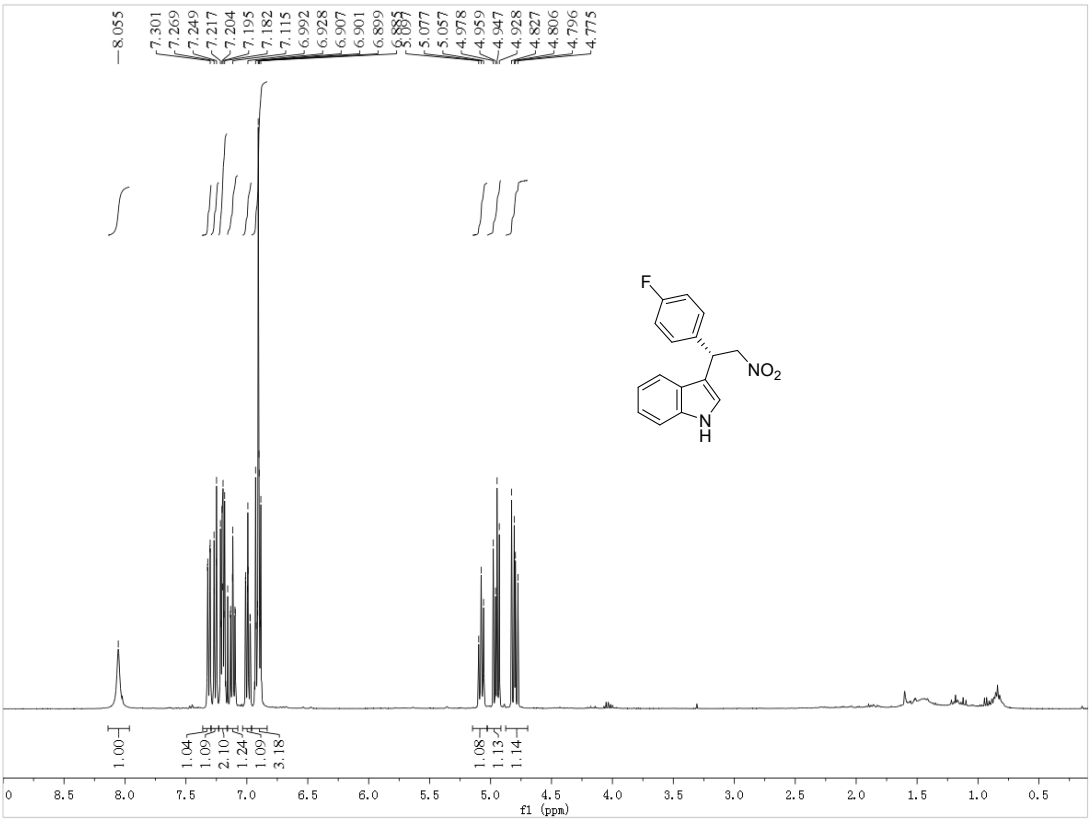


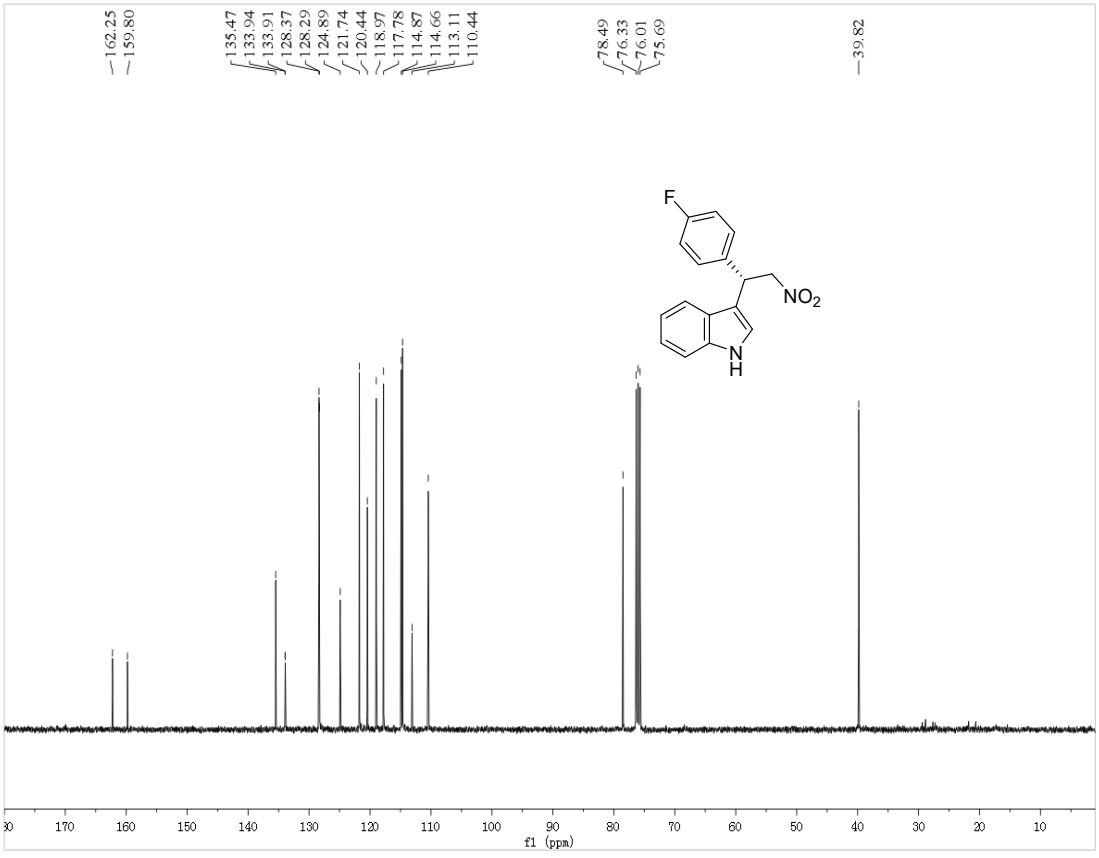
#	Time	Area	Height	Width	Area%	Symmetry
1	9.082	14632.7	829.7	0.2668	49.744	0.611
2	11.026	14783.3	706.7	0.3161	50.256	0.601



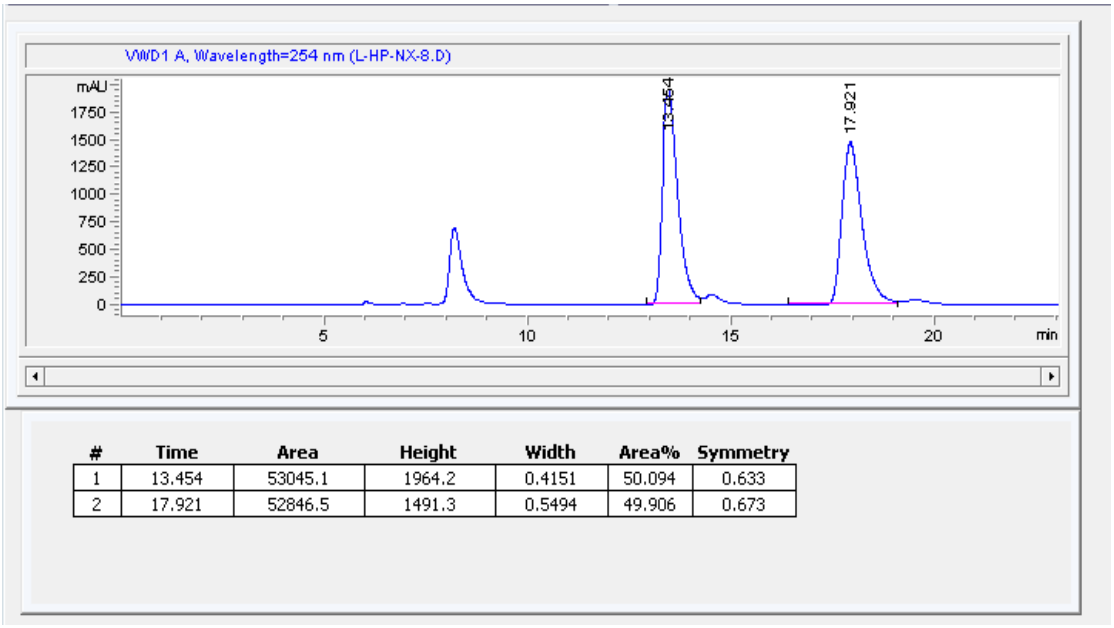
#	Time	Area	Height	Width	Area%	Symmetry
1	8.383	35226.4	1576.1	0.3528	96.541	0.435
2	10.388	1262	53.2	0.3579	3.459	0.662

^{1}H and ^{13}C NMR of 6b

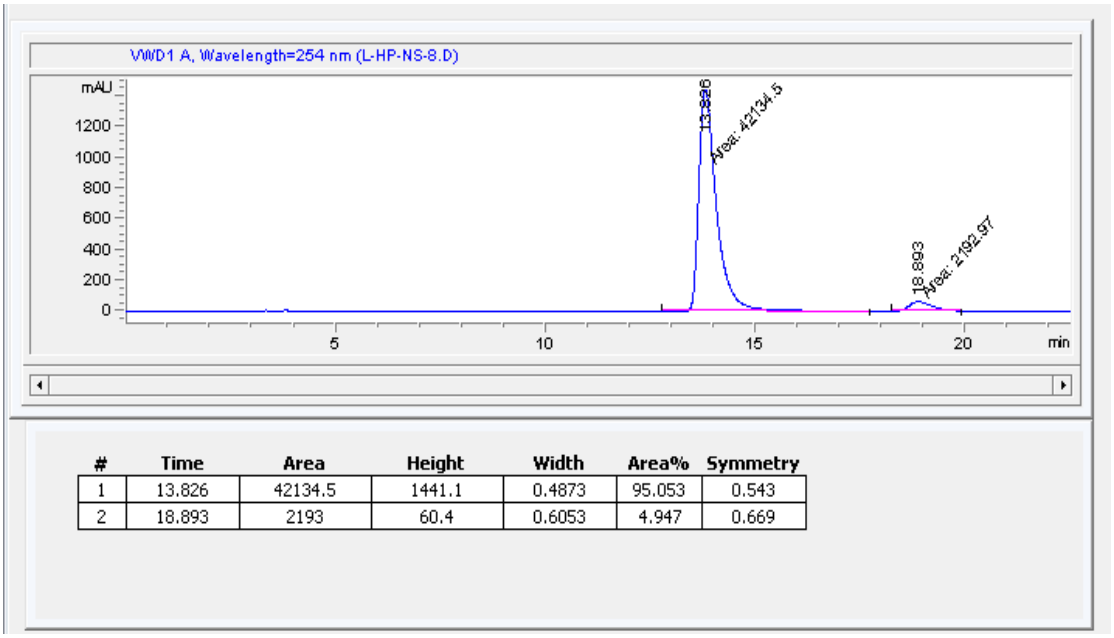

8.055
7.301
7.269
7.249
7.217
7.204
7.195
7.182
7.115
6.992
6.928
6.907
6.901
6.899
5.077
5.057
4.978
4.959
4.947
4.928
4.827
4.806
4.796
4.775
1.00
1.04
1.09
2.10
1.24
1.09
3.18
1.08
1.13
1.14
F
NO2
N
H
f1 (ppm)


162.25
159.80
135.47
133.94
133.91
128.37
128.29
124.89
121.74
120.44
118.97
117.78
114.87
114.66
113.11
110.44
78.49
76.33
76.01
75.69
39.82
F
NO2
N
H
f1 (ppm)

HPLC of 6b

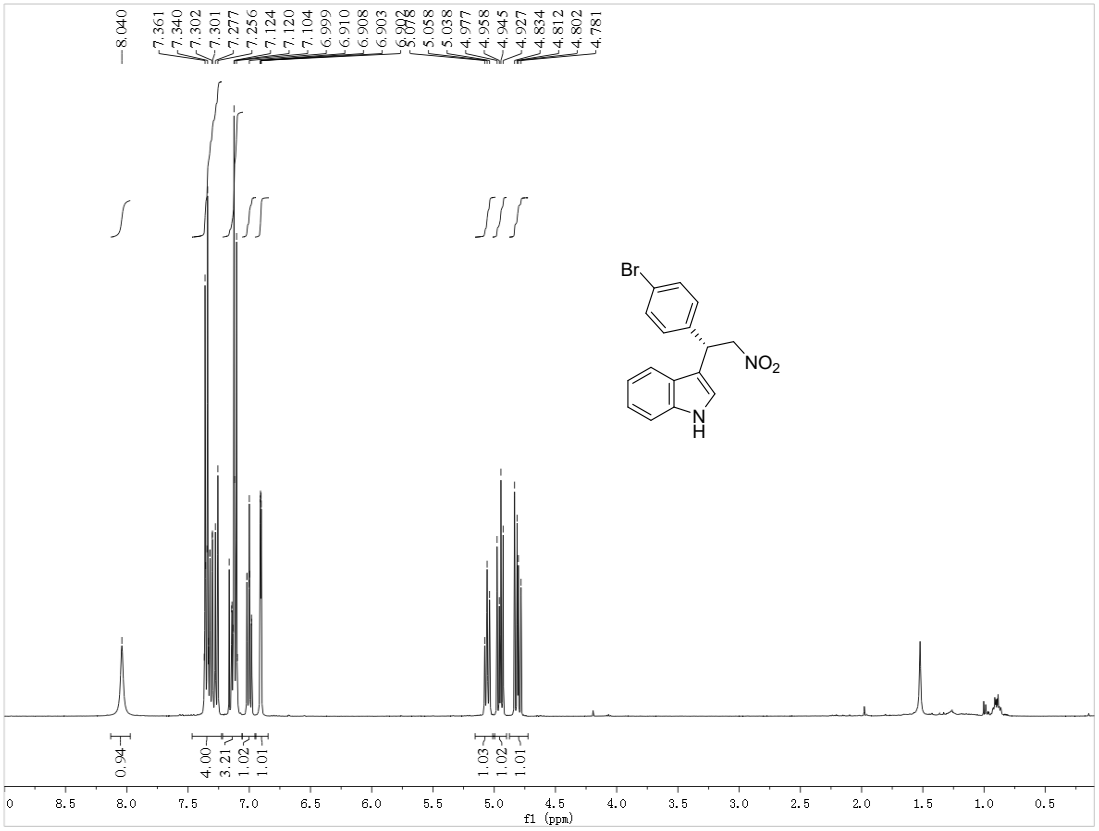


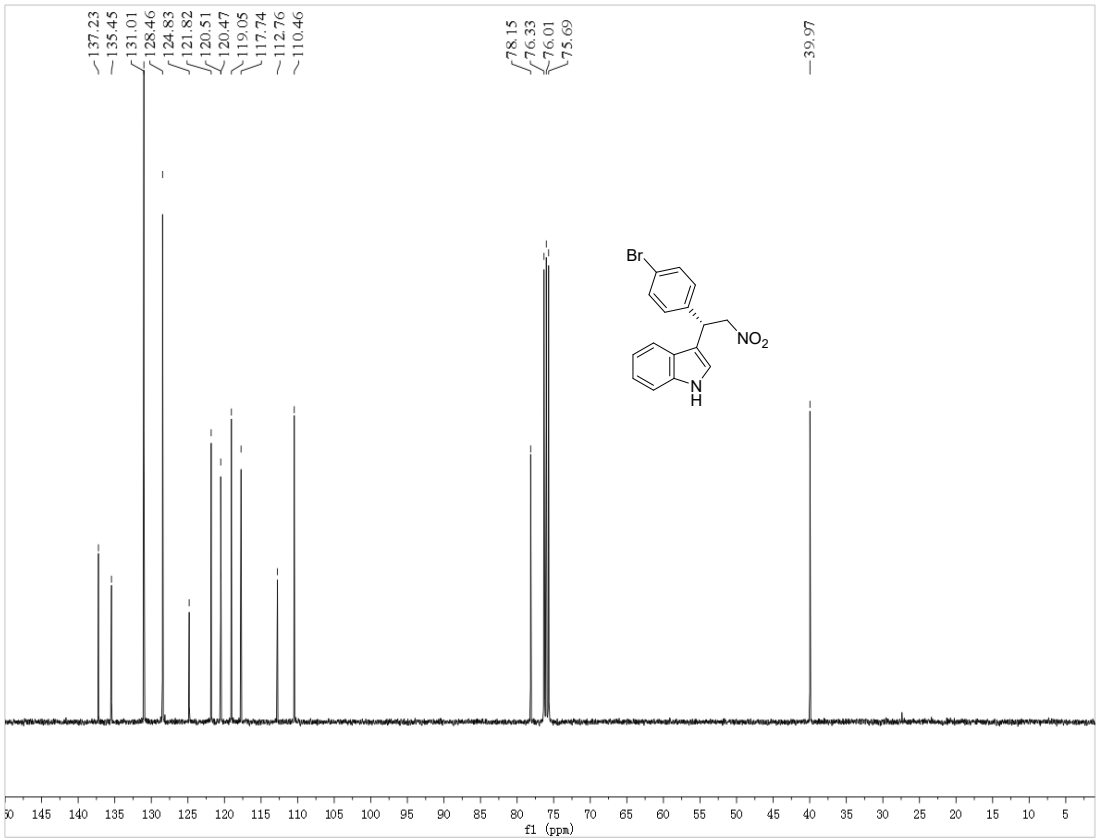
#	Time	Area	Height	Width	Area%	Symmetry
1	13.454	53045.1	1964.2	0.4151	50.094	0.633
2	17.921	52846.5	1491.3	0.5494	49.906	0.673



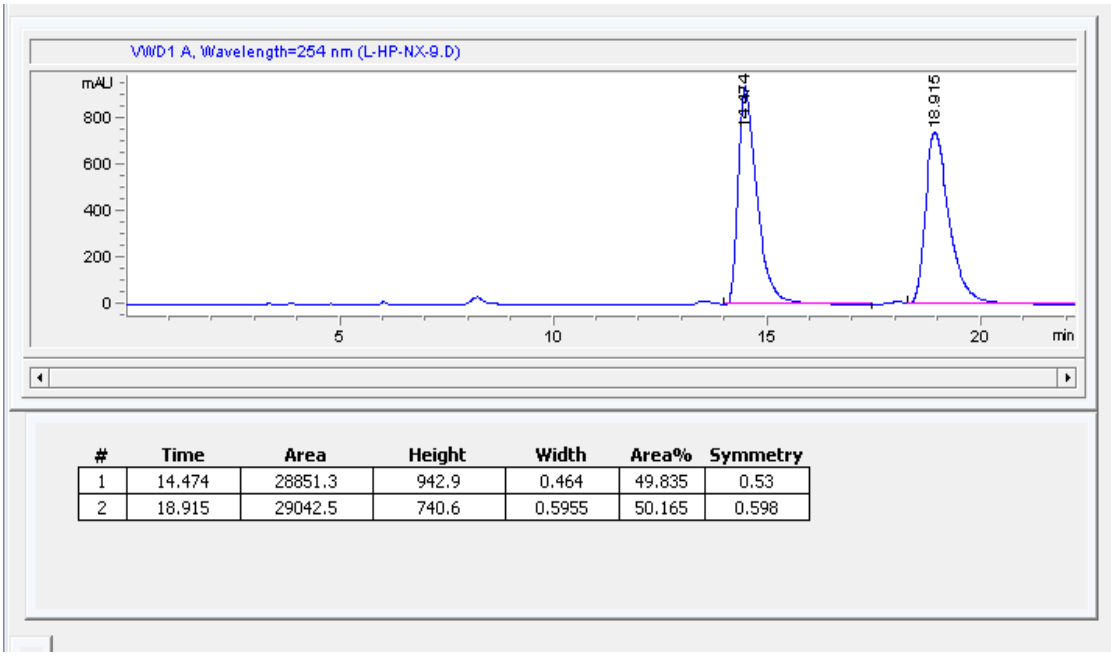
#	Time	Area	Height	Width	Area%	Symmetry
1	13.826	42134.5	1441.1	0.4873	95.053	0.543
2	18.893	2193	60.4	0.6053	4.947	0.669

^{1}H and ^{13}C NMR of 6c

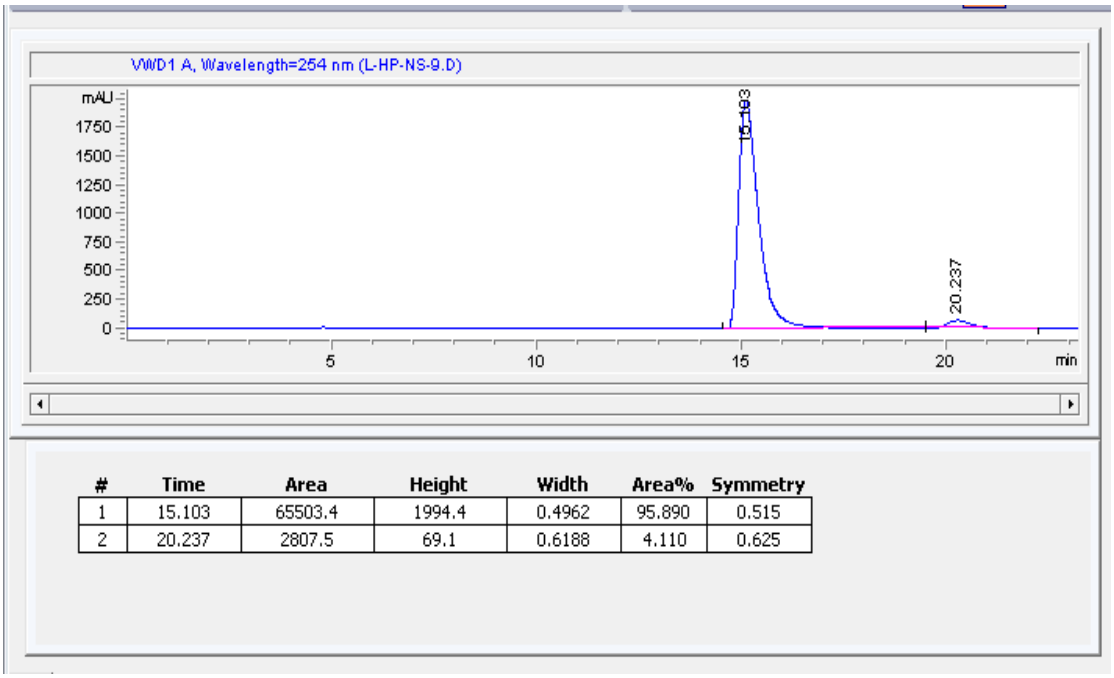

8.040
7.361
7.340
7.302
7.301
7.277
7.256
7.124
7.120
7.104
6.999
6.910
6.908
6.903
5.058
5.038
4.977
4.958
4.945
4.927
4.834
4.812
4.802
4.781
Br
NO2
N
H
0.94
4.00
3.21
1.02
1.01
1.03
1.02
1.01
f1 (ppm)


137.23
135.45
131.01
128.46
124.83
121.82
120.51
120.47
119.05
117.74
112.76
110.46
78.15
76.33
76.01
75.69
39.97
Br
NO2
N
H
f1 (ppm)

HPLC of 6c

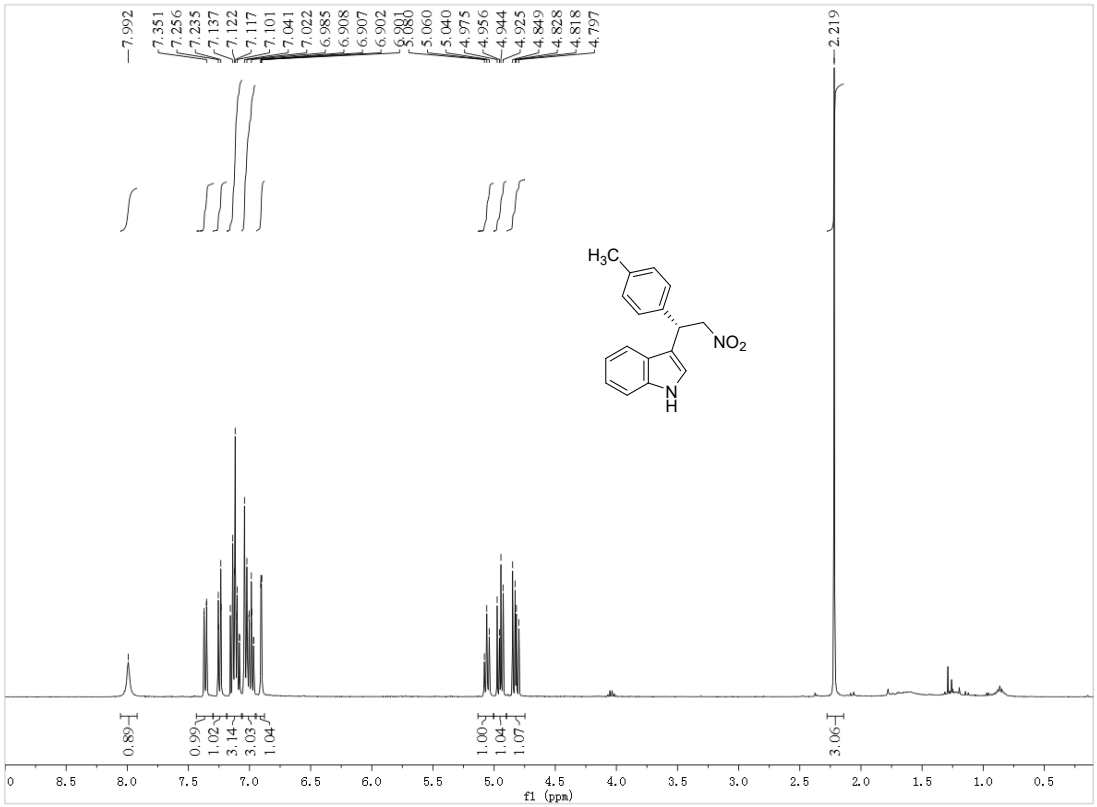


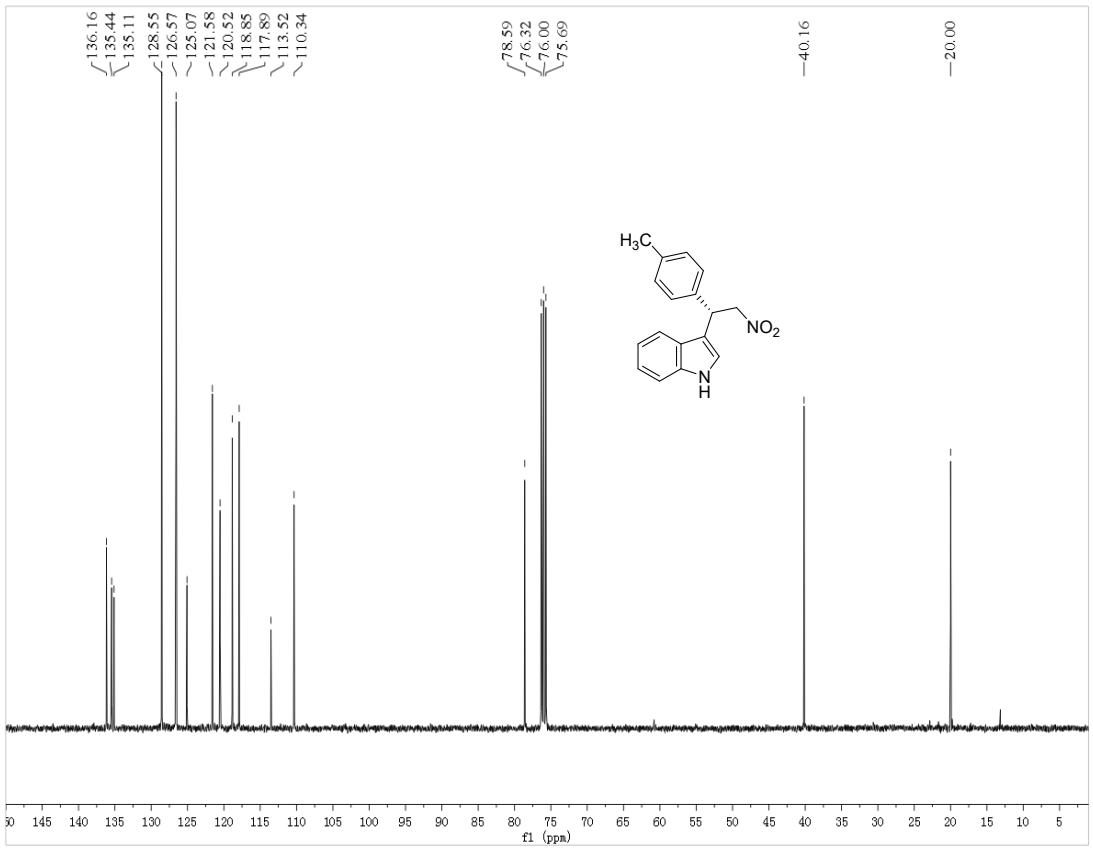
#	Time	Area	Height	Width	Area%	Symmetry
1	14.474	28851.3	942.9	0.464	49.835	0.53
2	18.915	29042.5	740.6	0.5955	50.165	0.598



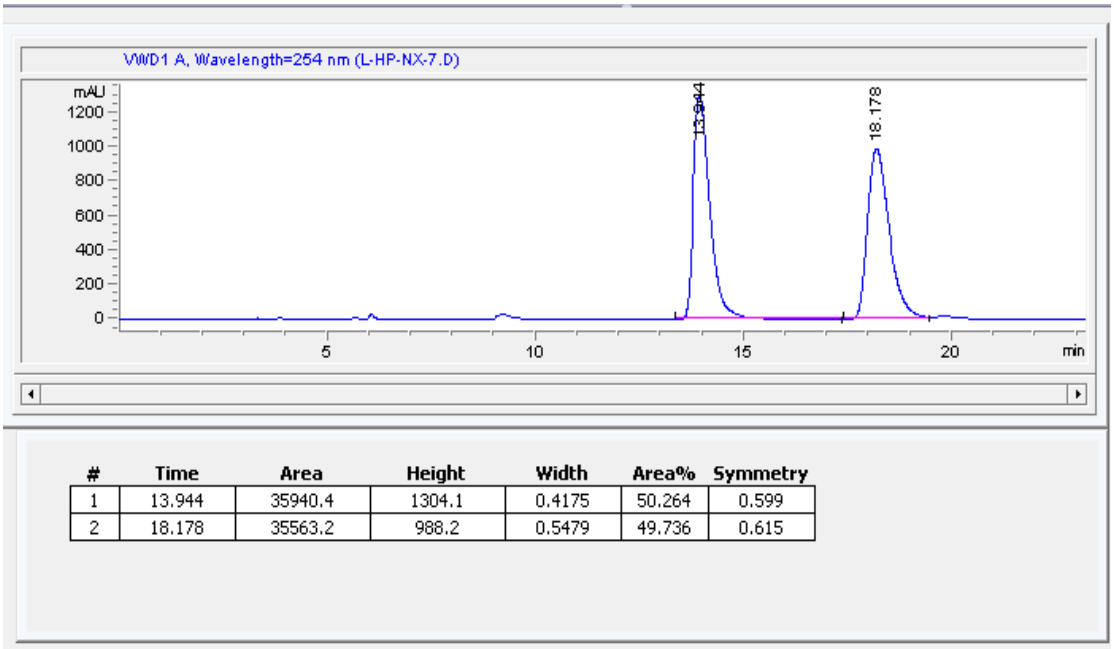
#	Time	Area	Height	Width	Area%	Symmetry
1	15.103	65503.4	1994.4	0.4962	95.890	0.515
2	20.237	2807.5	69.1	0.6188	4.110	0.625

^{1}H and ^{13}C NMR of 6d

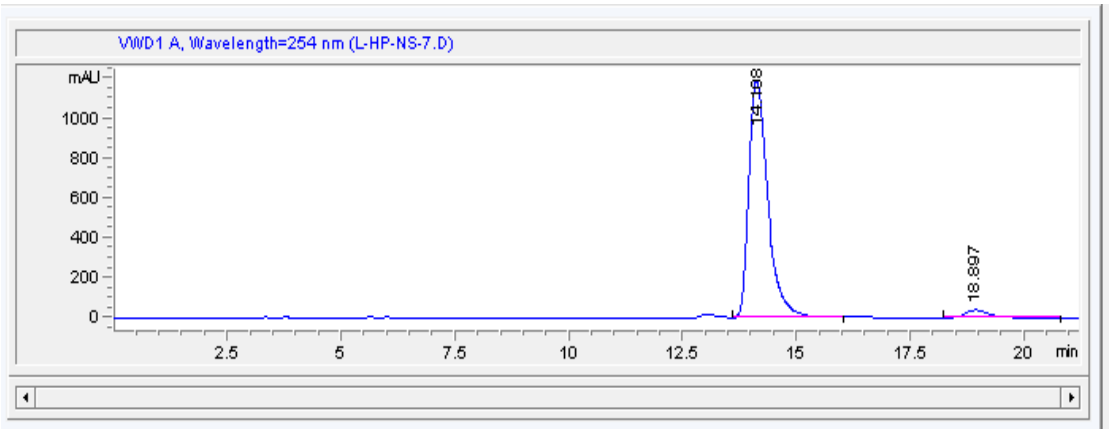

7.992
7.351
7.256
7.235
7.137
7.122
7.117
7.101
7.041
7.022
6.985
6.908
6.907
6.902
5.060
5.040
4.975
4.956
4.944
4.925
4.849
4.828
4.818
4.797
2.219
H3C
NO2
N
H
0.89
0.99
1.02
3.14
3.03
1.04
1.00
1.04
1.07
3.06
f1 (ppm)


136.16
135.44
135.11
128.55
126.57
125.07
121.58
120.52
118.85
117.89
113.52
110.34
78.59
76.32
76.00
75.69
40.16
20.00
H3C
NO2
N
H
f1 (ppm)

HPLC of 6d

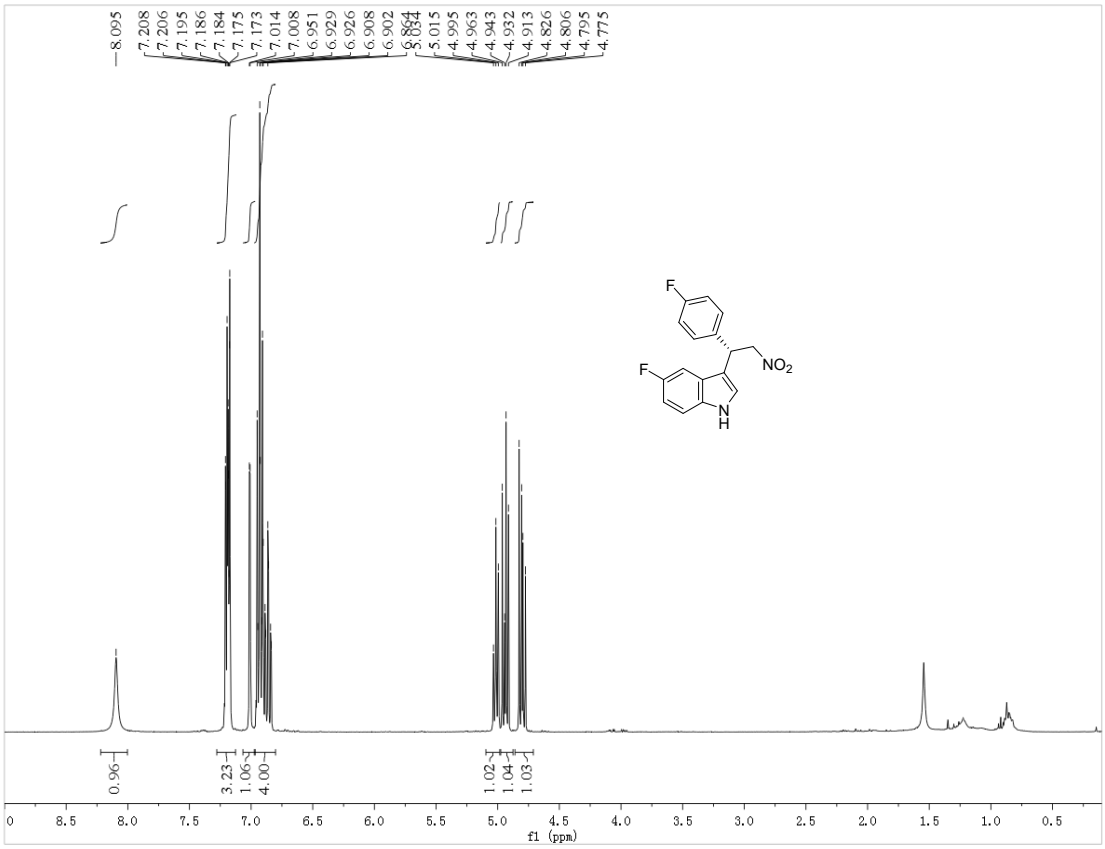


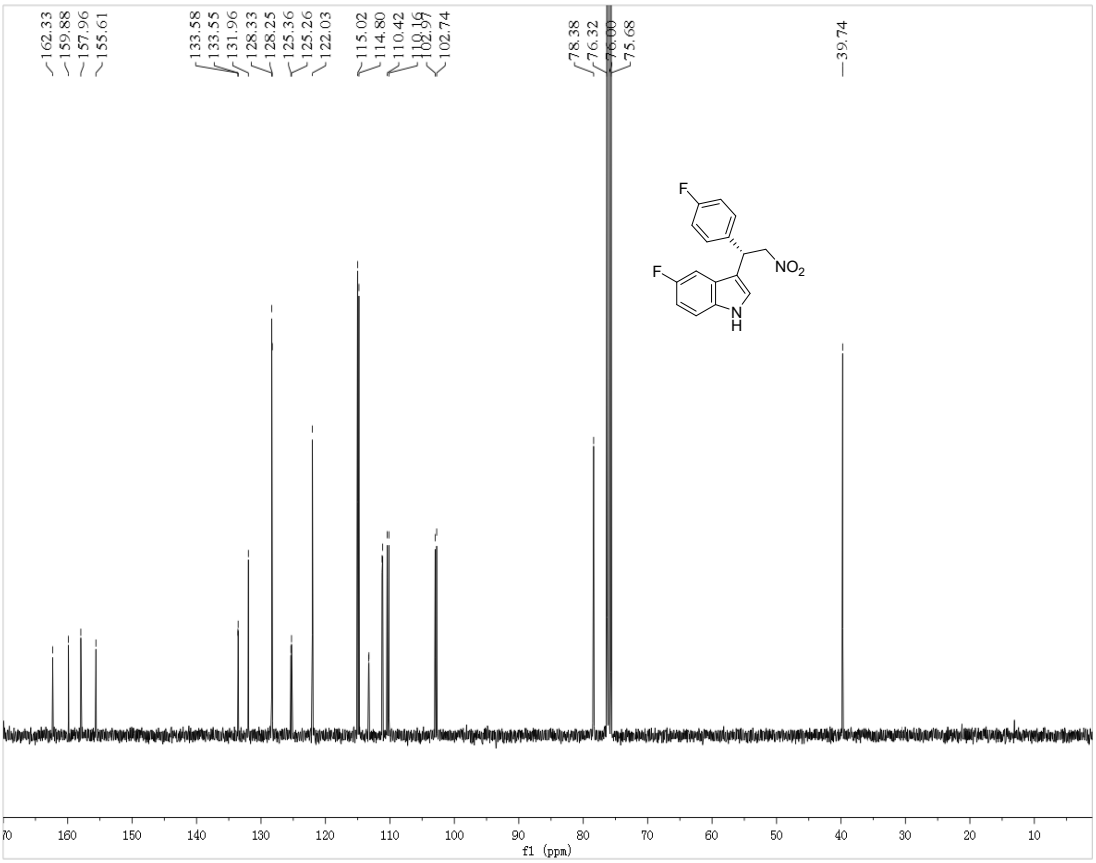
#	Time	Area	Height	Width	Area%	Symmetry
1	13.944	35940.4	1304.1	0.4175	50.264	0.599
2	18.178	35563.2	988.2	0.5479	49.736	0.615



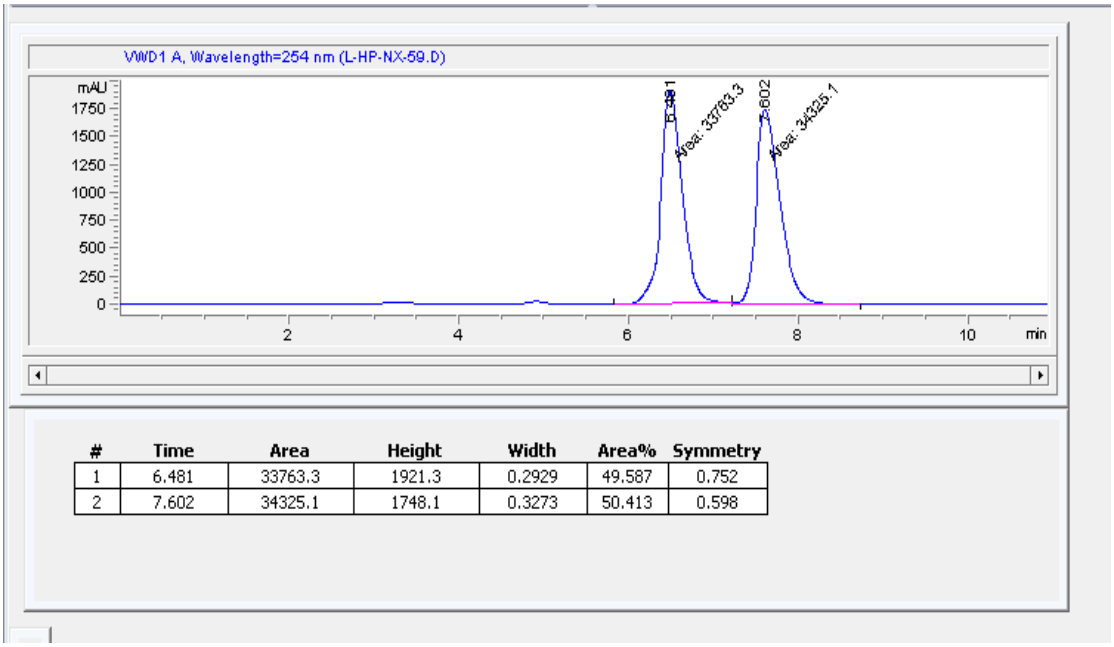
#	Time	Area	Height	Width	Area%	Symmetry
1	14.108	33957.8	1192.9	0.4331	95.993	0.603
2	18.897	1417.5	38.6	0.5566	4.007	0.645

^{1}H and ^{13}C NMR of 6e

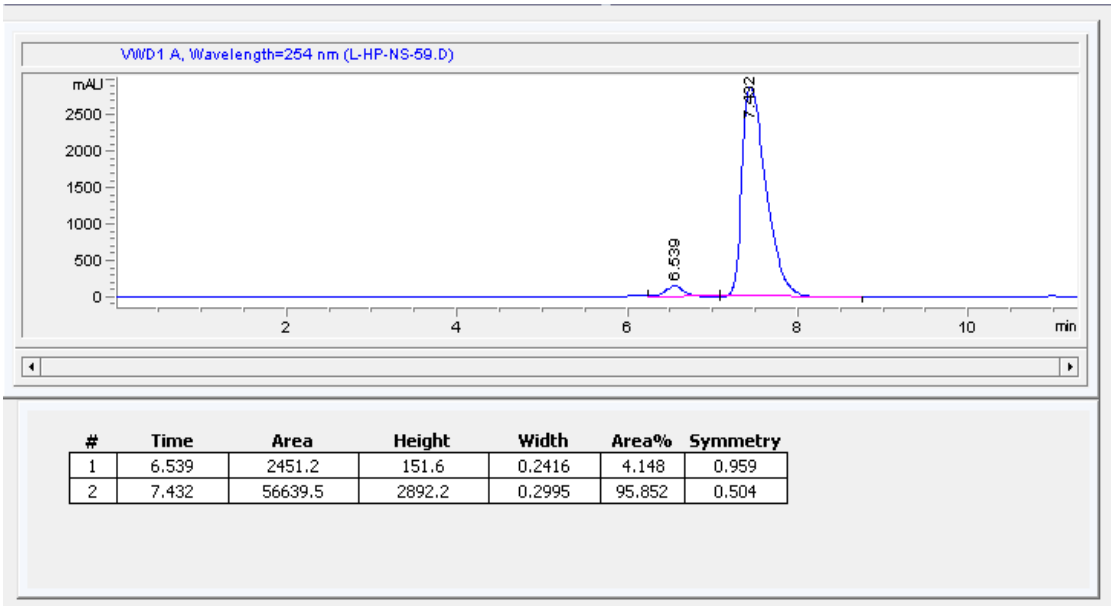

8.095
7.208
7.206
7.195
7.186
7.184
7.175
7.173
7.014
7.008
6.951
6.929
6.926
6.908
6.902
5.034
5.015
4.995
4.963
4.943
4.932
4.913
4.826
4.806
4.795
4.775
F
F
NO2
N
H
0.96
3.23
1.06
4.00
1.02
1.04
1.03
f1 (ppm)


162.33
159.88
157.96
155.61
133.58
133.55
131.96
128.33
128.25
125.36
125.26
122.03
115.02
114.80
110.42
102.97
102.74
78.38
76.32
75.68
39.74
F
F
NO2
N
H
f1 (ppm)

HPLC of 6e

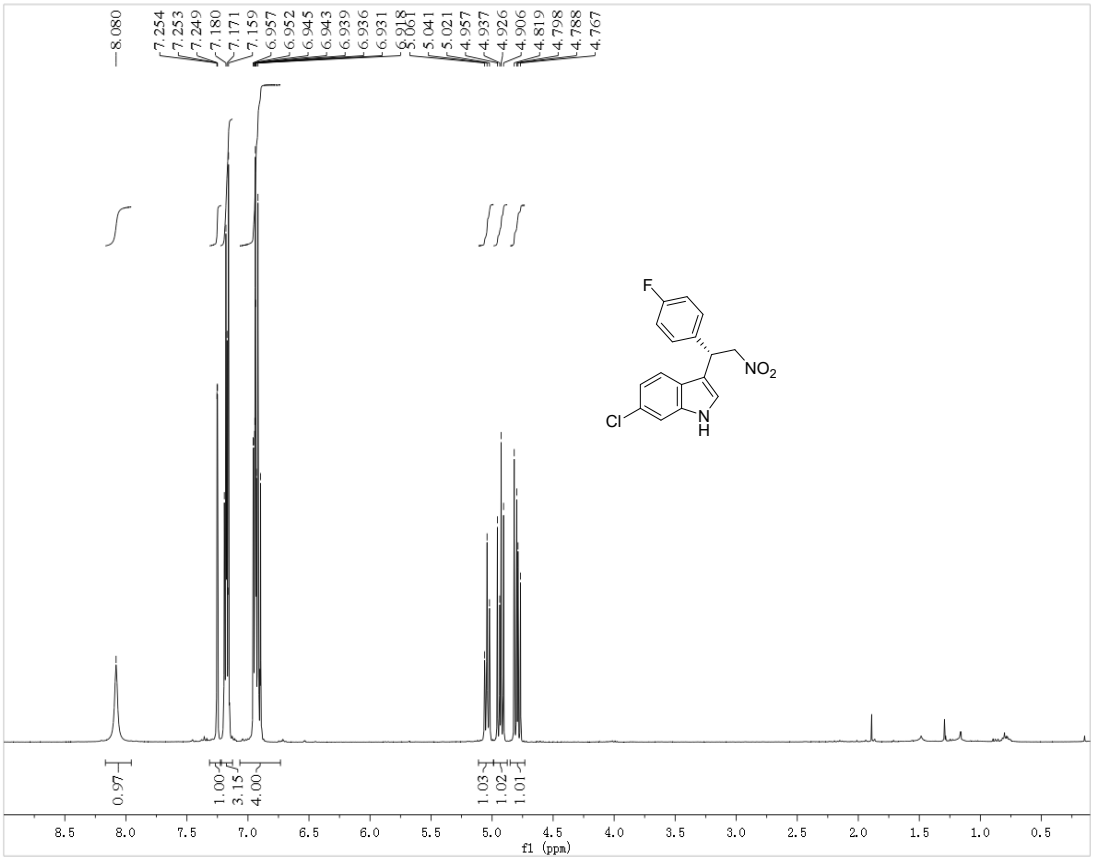


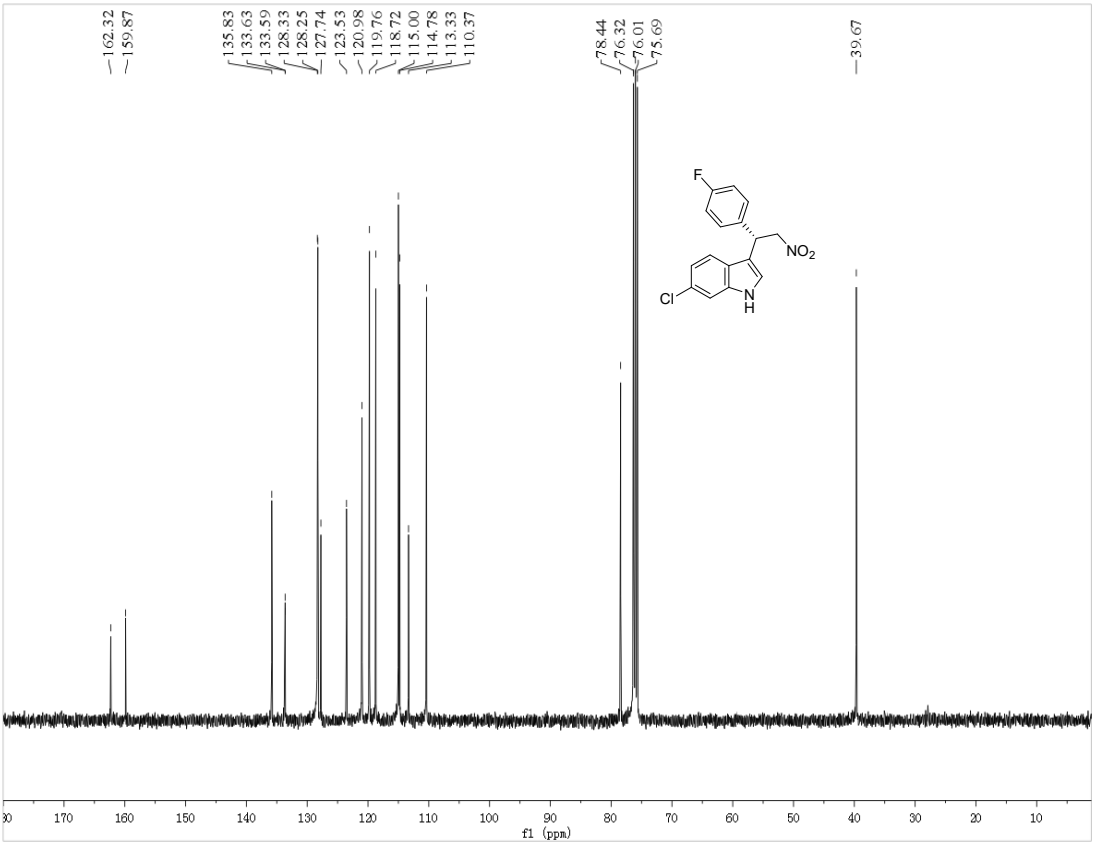
#	Time	Area	Height	Width	Area%	Symmetry
1	6.481	33763.3	1921.3	0.2929	49.587	0.752
2	7.602	34325.1	1748.1	0.3273	50.413	0.598



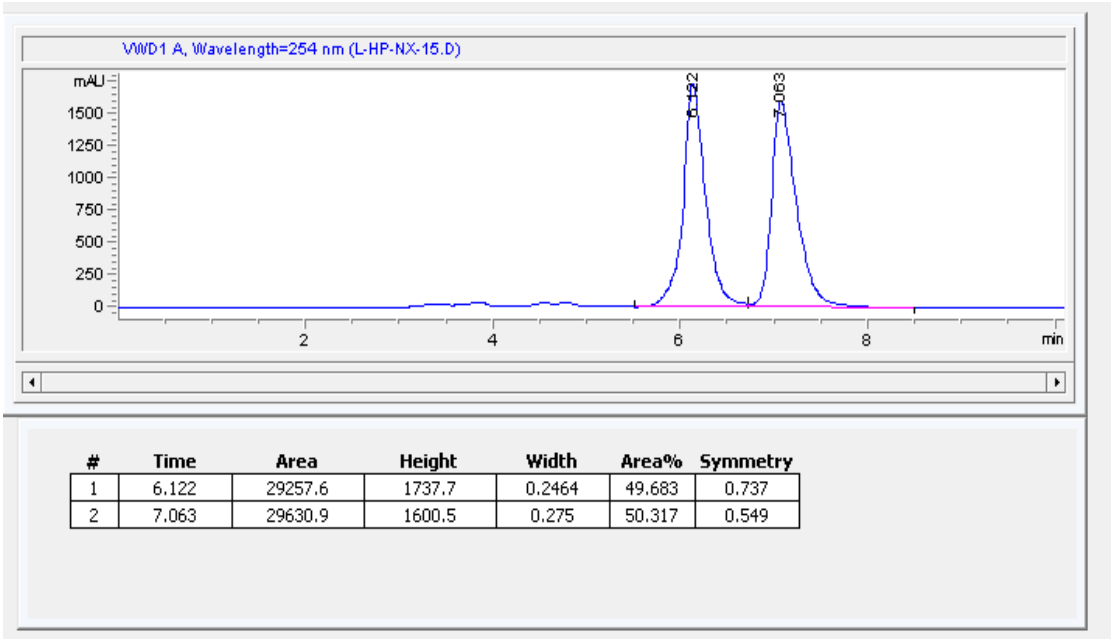
#	Time	Area	Height	Width	Area%	Symmetry
1	6.539	2451.2	151.6	0.2416	4.148	0.959
2	7.432	56639.5	2892.2	0.2995	95.852	0.504

^{1}H and ^{13}C NMR of 6f

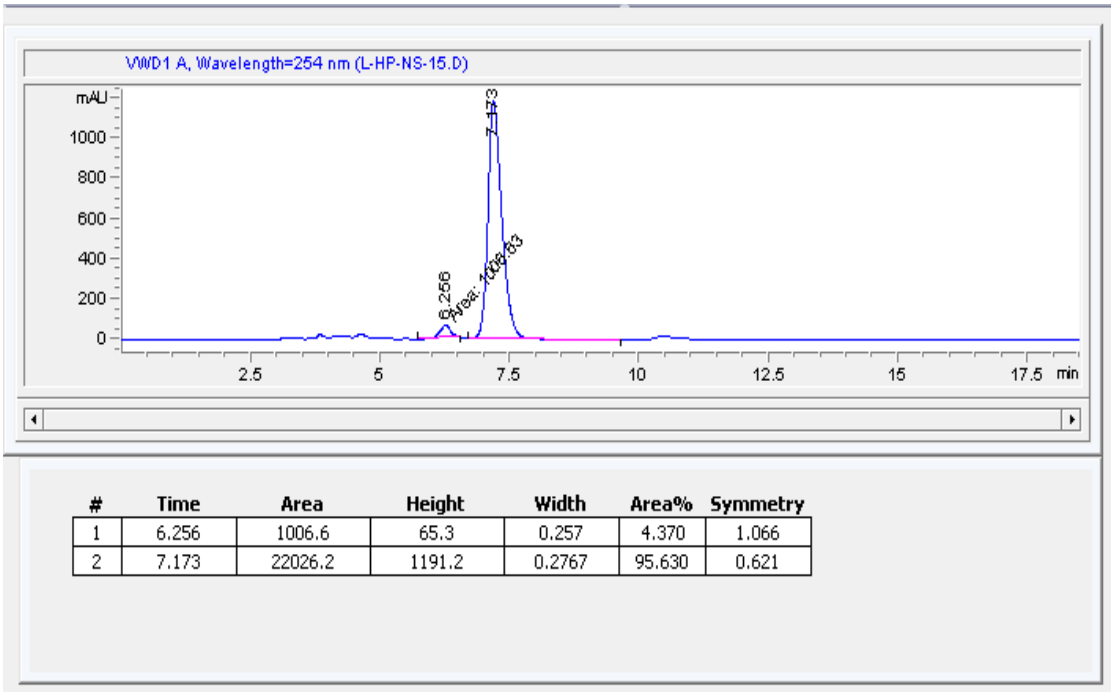




HPLC of 6f

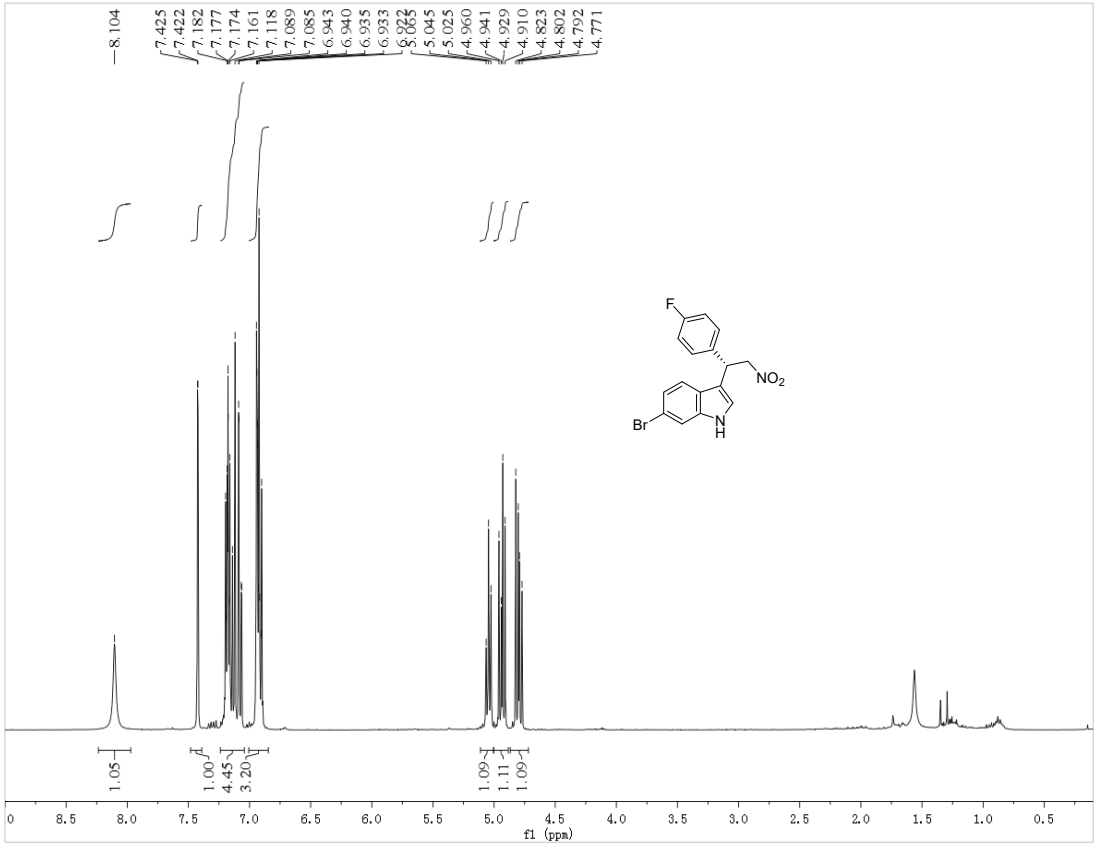


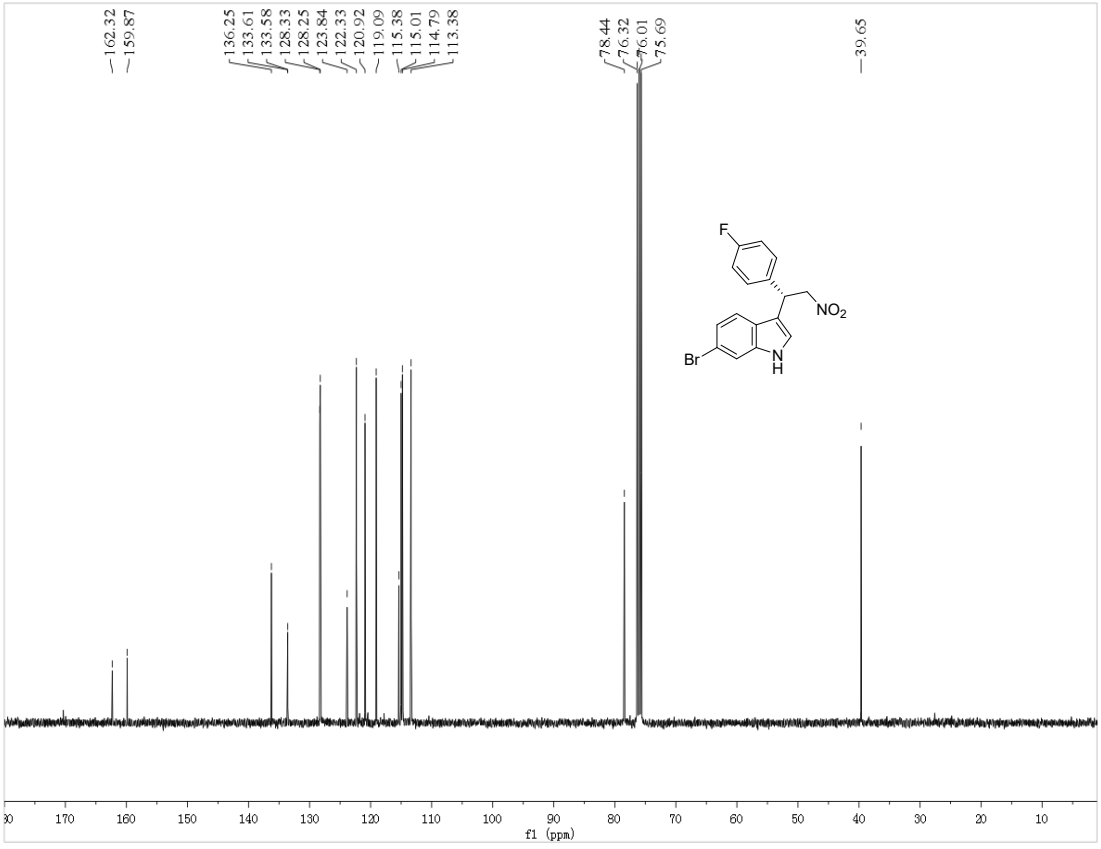
#	Time	Area	Height	Width	Area%	Symmetry
1	6.122	29257.6	1737.7	0.2464	49.683	0.737
2	7.063	29630.9	1600.5	0.275	50.317	0.549



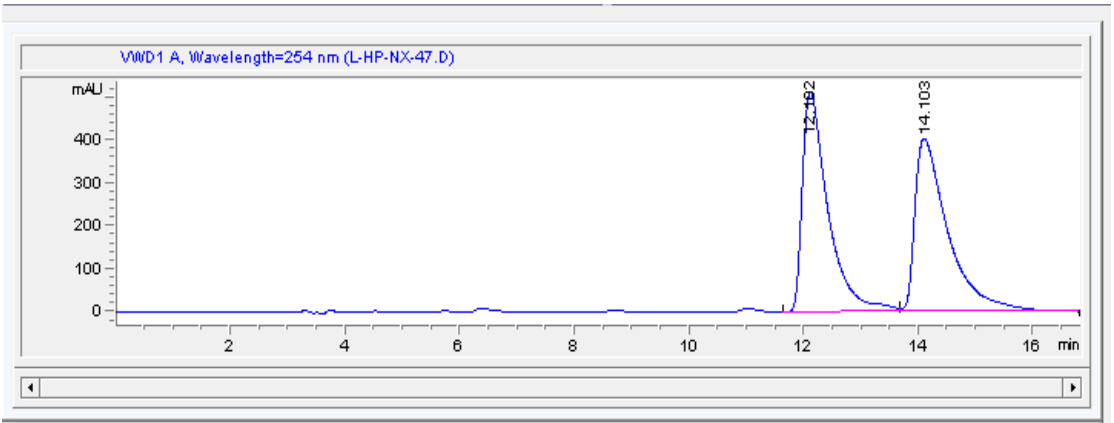
#	Time	Area	Height	Width	Area%	Symmetry
1	6.256	1006.6	65.3	0.257	4.370	1.066
2	7.173	22026.2	1191.2	0.2767	95.630	0.621

^{1}H and ^{13}C NMR of 6g

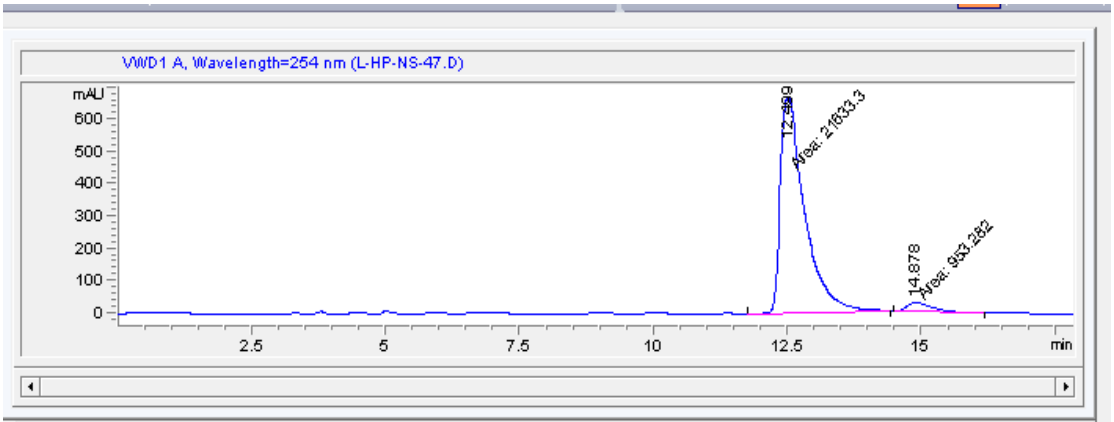




HPLC of 6g

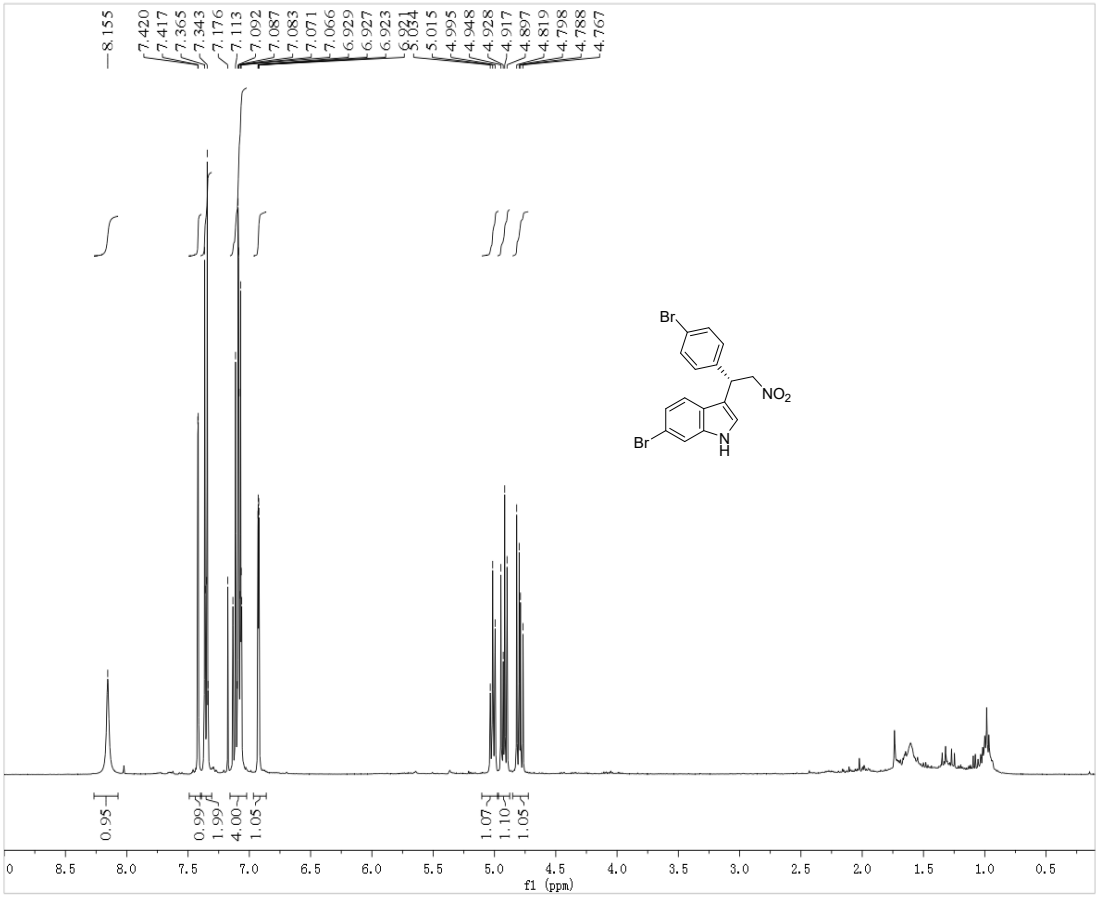


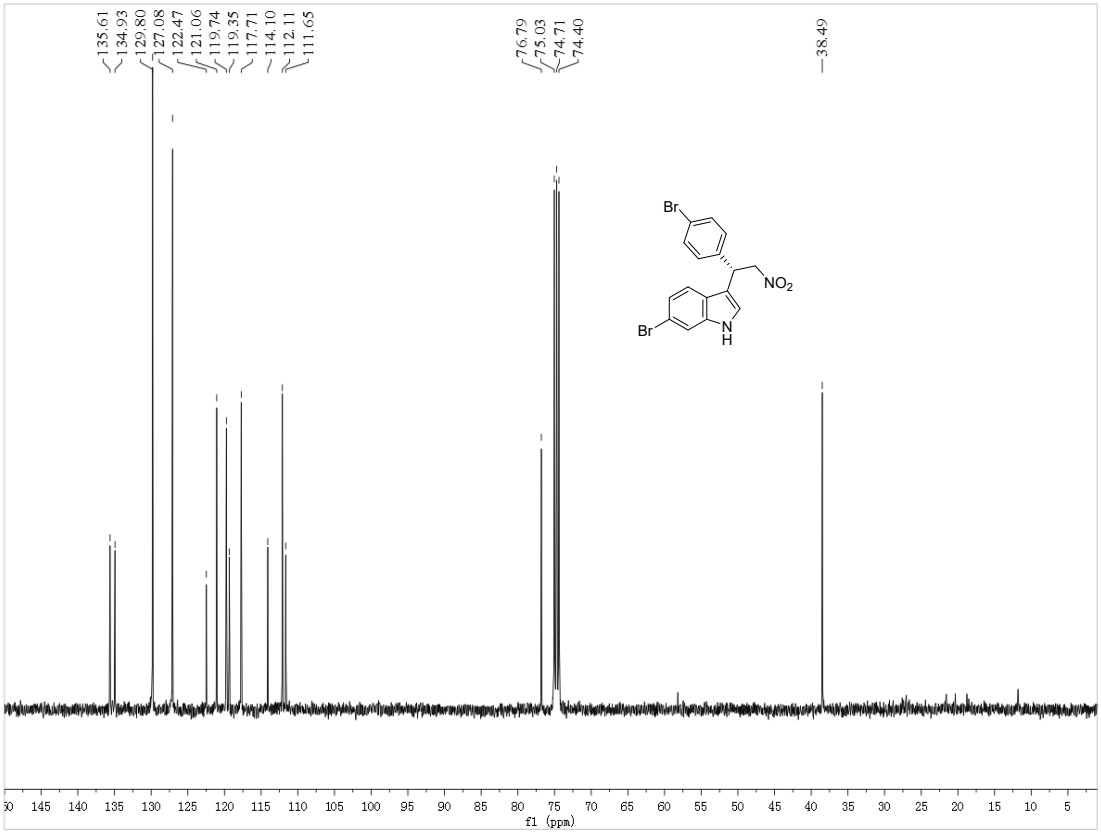
#	Time	Area	Height	Width	Area%	Symmetry
1	12.102	15931.2	514	0.4546	49.664	0.407
2	14.103	16146.9	404	0.5833	50.336	0.349



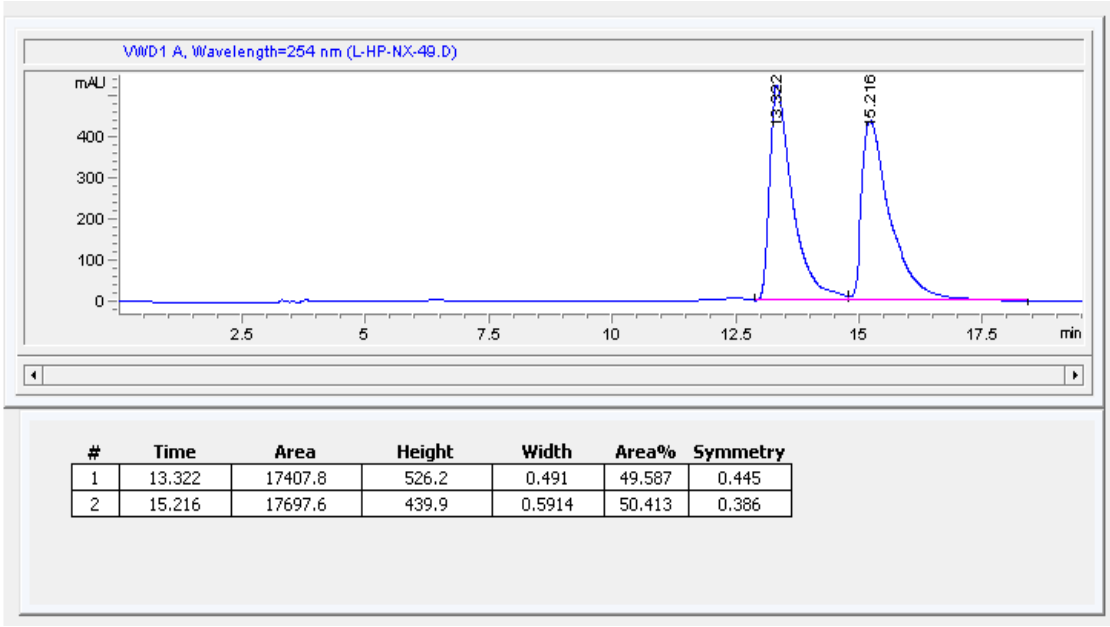
#	Time	Area	Height	Width	Area%	Symmetry
1	12.499	21633.3	675.3	0.5339	95.779	0.425
2	14.878	953.3	27.1	0.5871	4.221	0.465

^{1}H and ^{13}C NMR of 6h

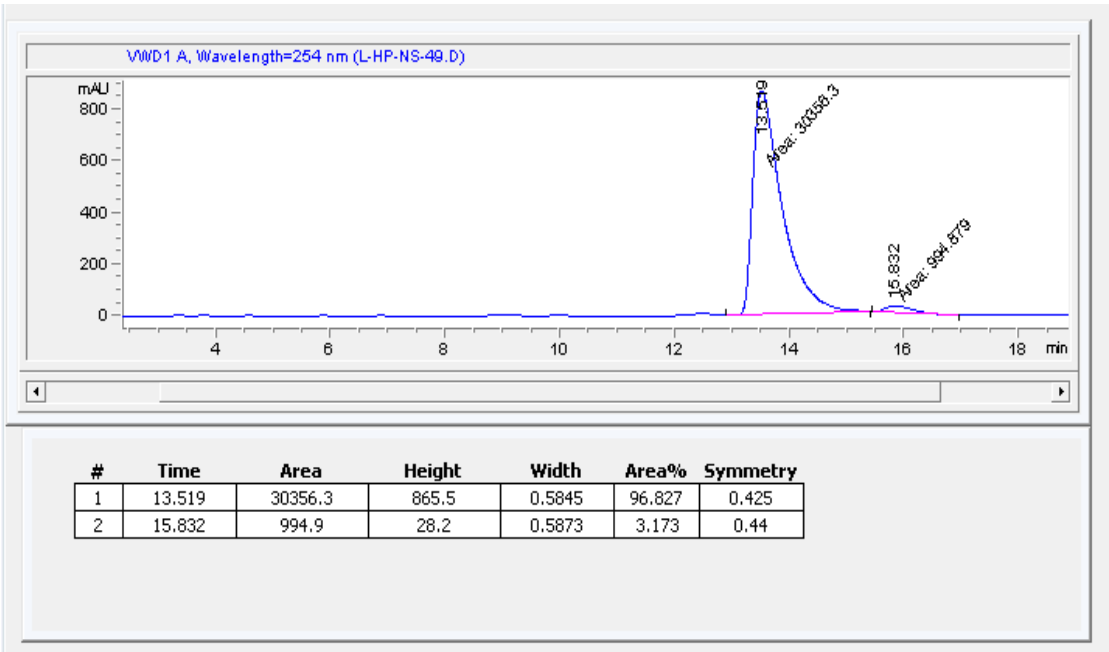




HPLC of 6h

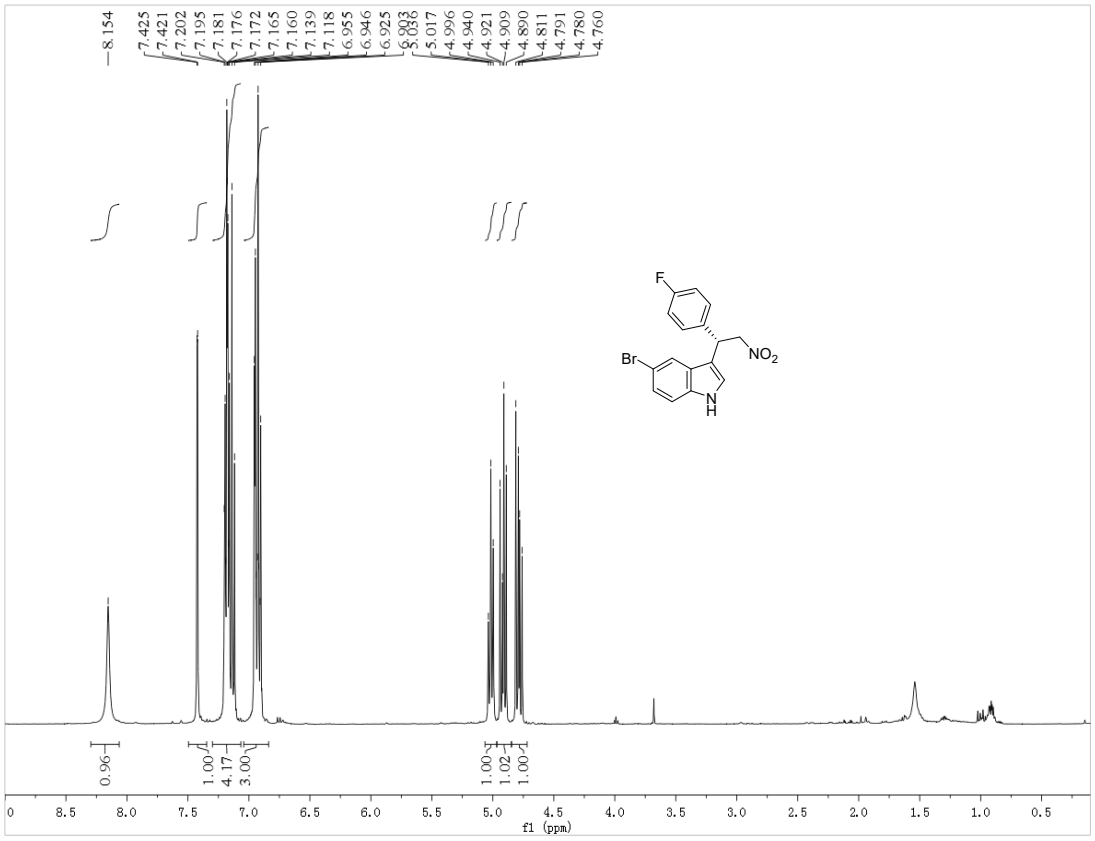


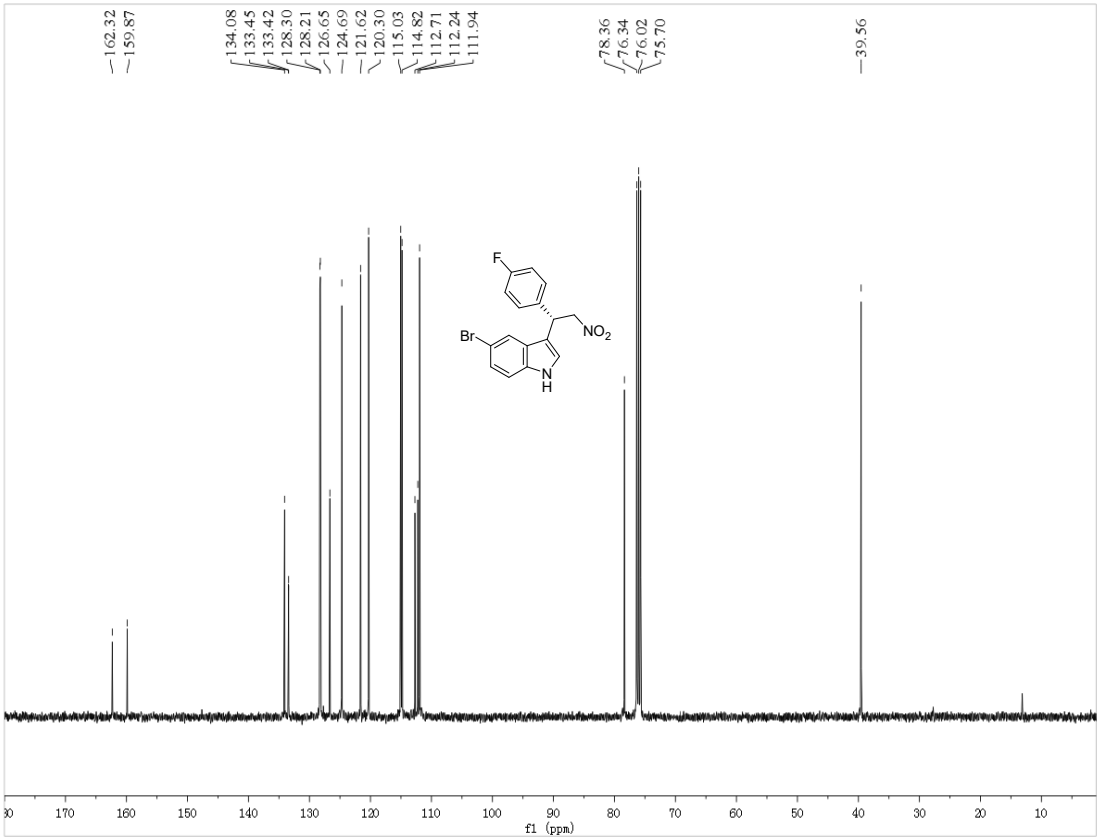
#	Time	Area	Height	Width	Area%	Symmetry
1	13.322	17407.8	526.2	0.491	49.587	0.445
2	15.216	17697.6	439.9	0.5914	50.413	0.386



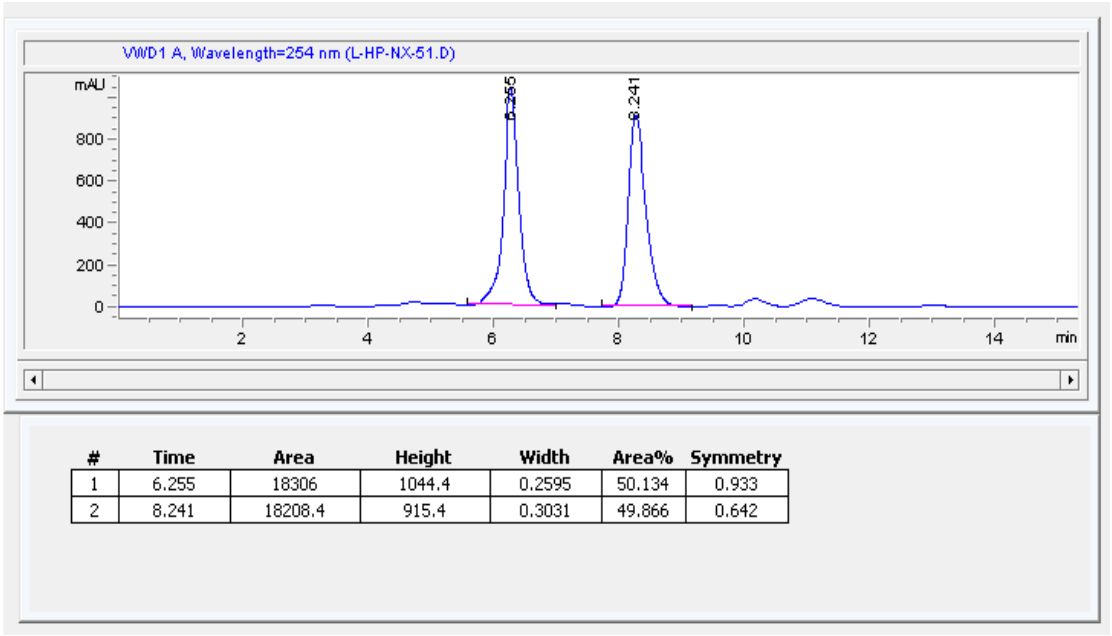
#	Time	Area	Height	Width	Area%	Symmetry
1	13.519	30356.3	865.5	0.5845	96.827	0.425
2	15.832	994.9	28.2	0.5873	3.173	0.44

^{1}H and ^{13}C NMR of 6i

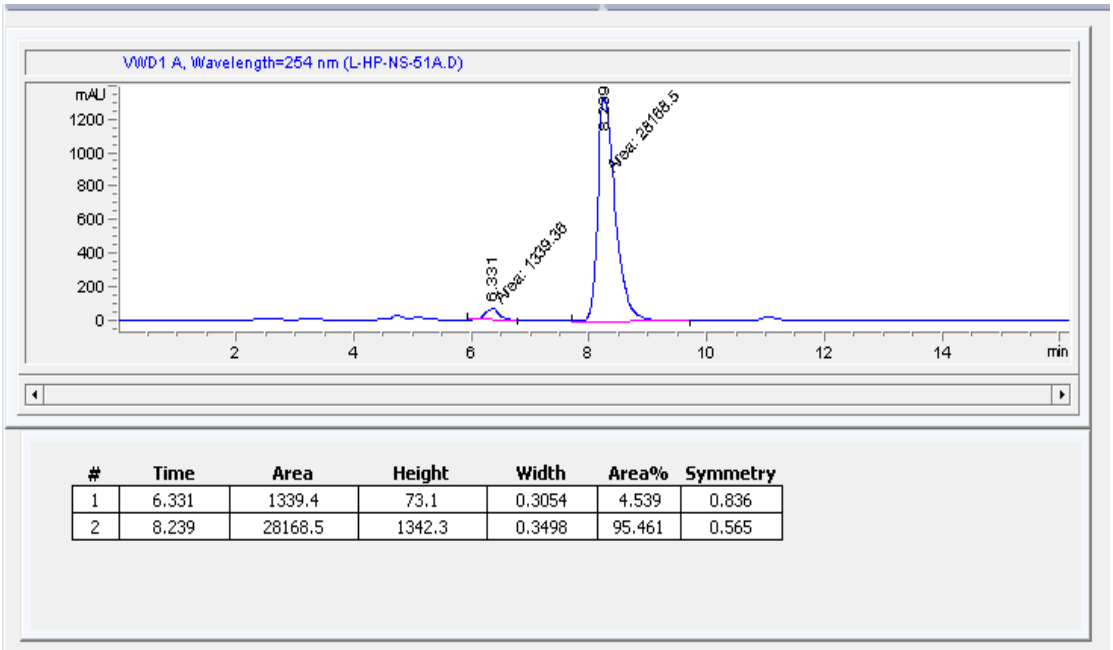




HPLC of 6i

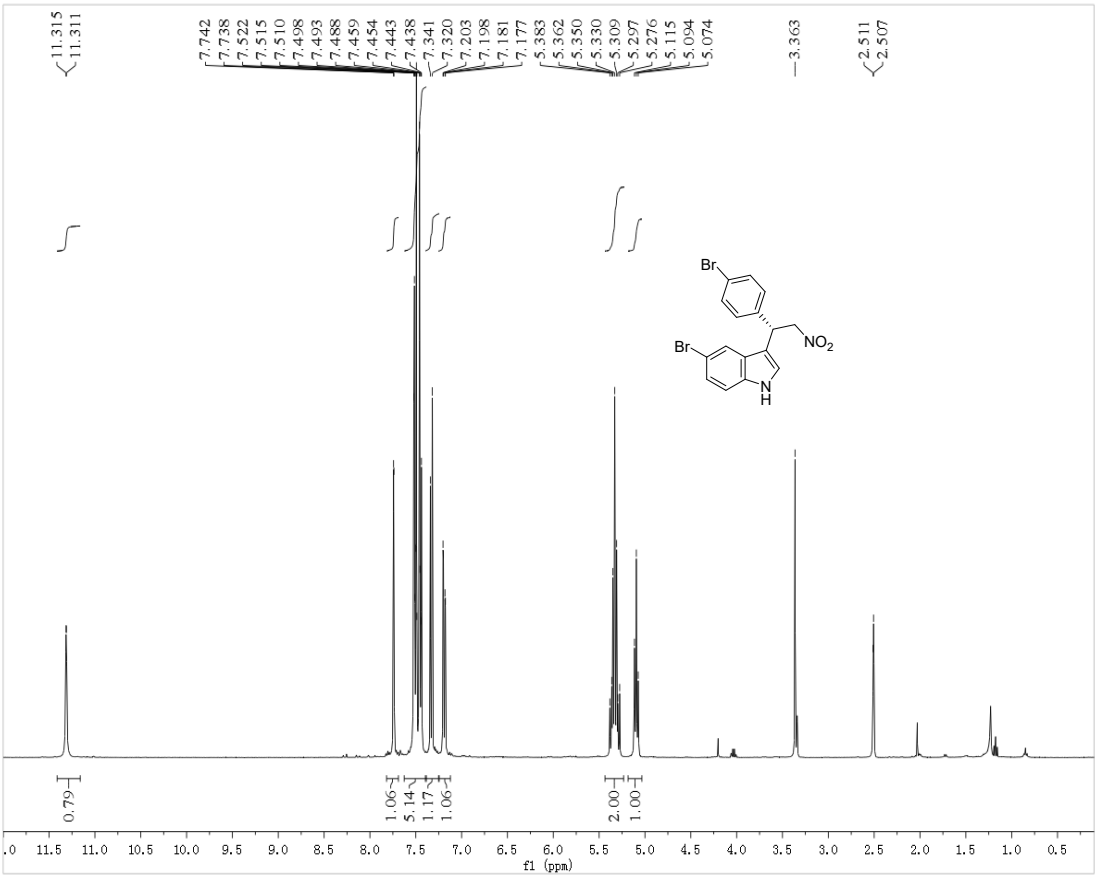


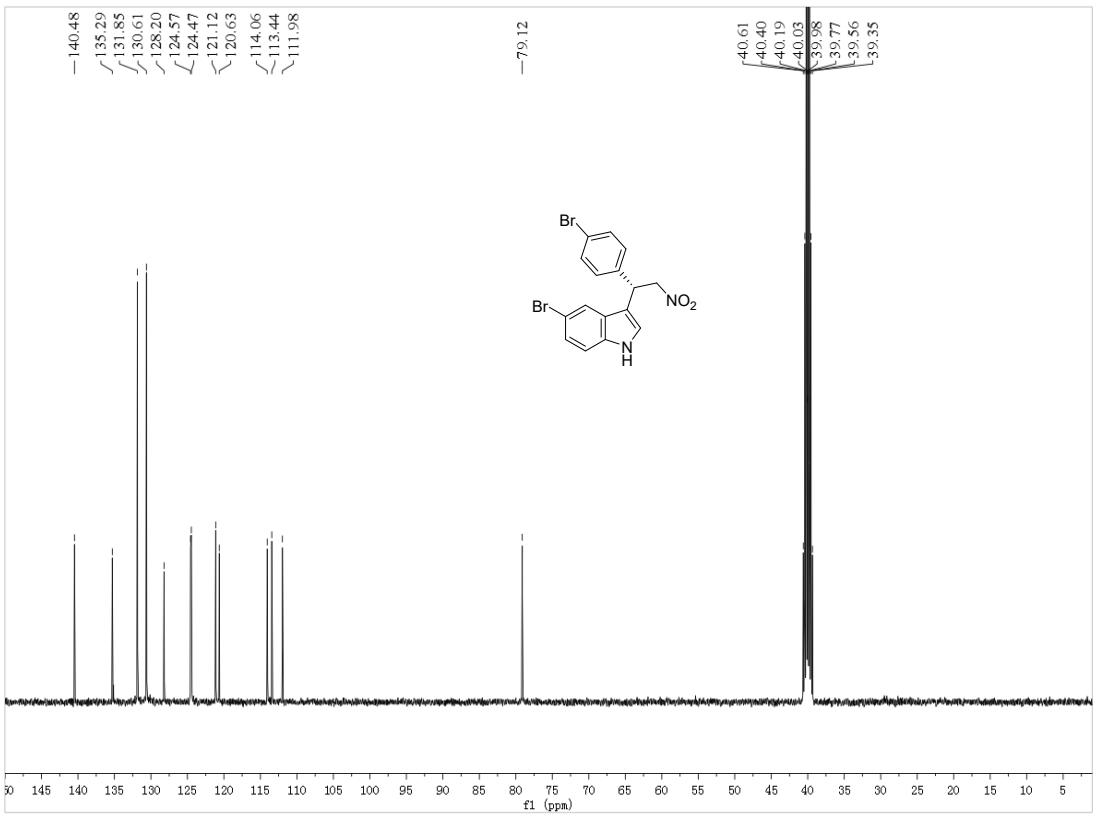
#	Time	Area	Height	Width	Area%	Symmetry
1	6.255	18306	1044.4	0.2595	50.134	0.933
2	8.241	18208.4	915.4	0.3031	49.866	0.642



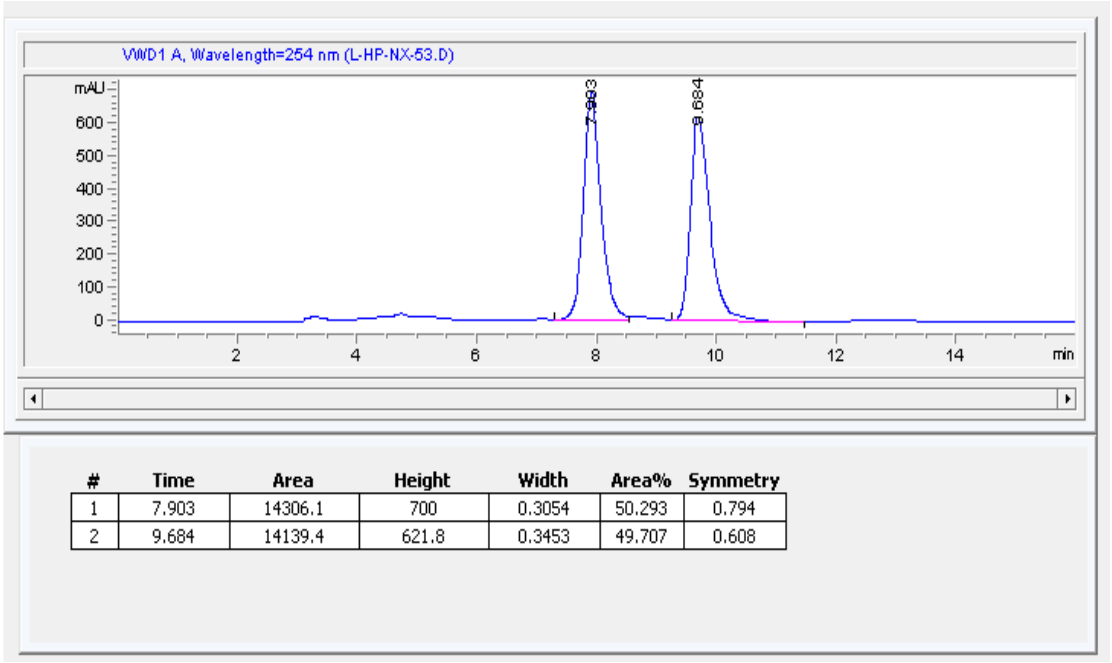
#	Time	Area	Height	Width	Area%	Symmetry
1	6.331	1339.4	73.1	0.3054	4.539	0.836
2	8.239	28168.5	1342.3	0.3498	95.461	0.565

^{1}H and ^{13}C NMR of 6j

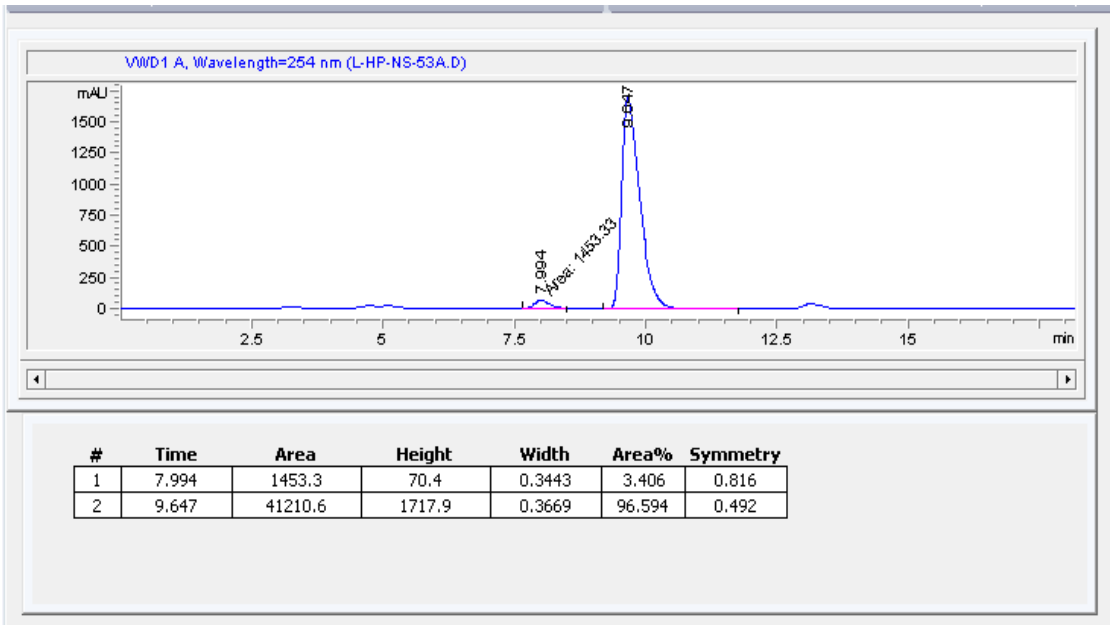




HPLC of 6j

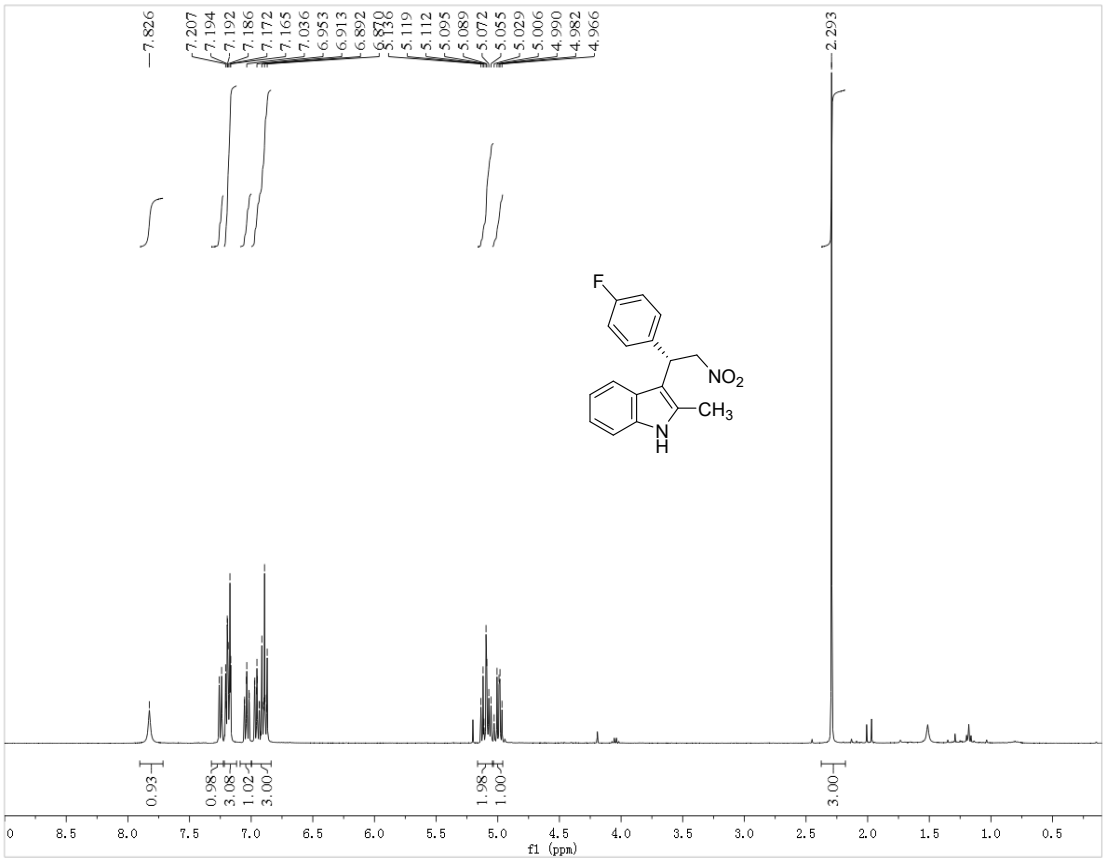


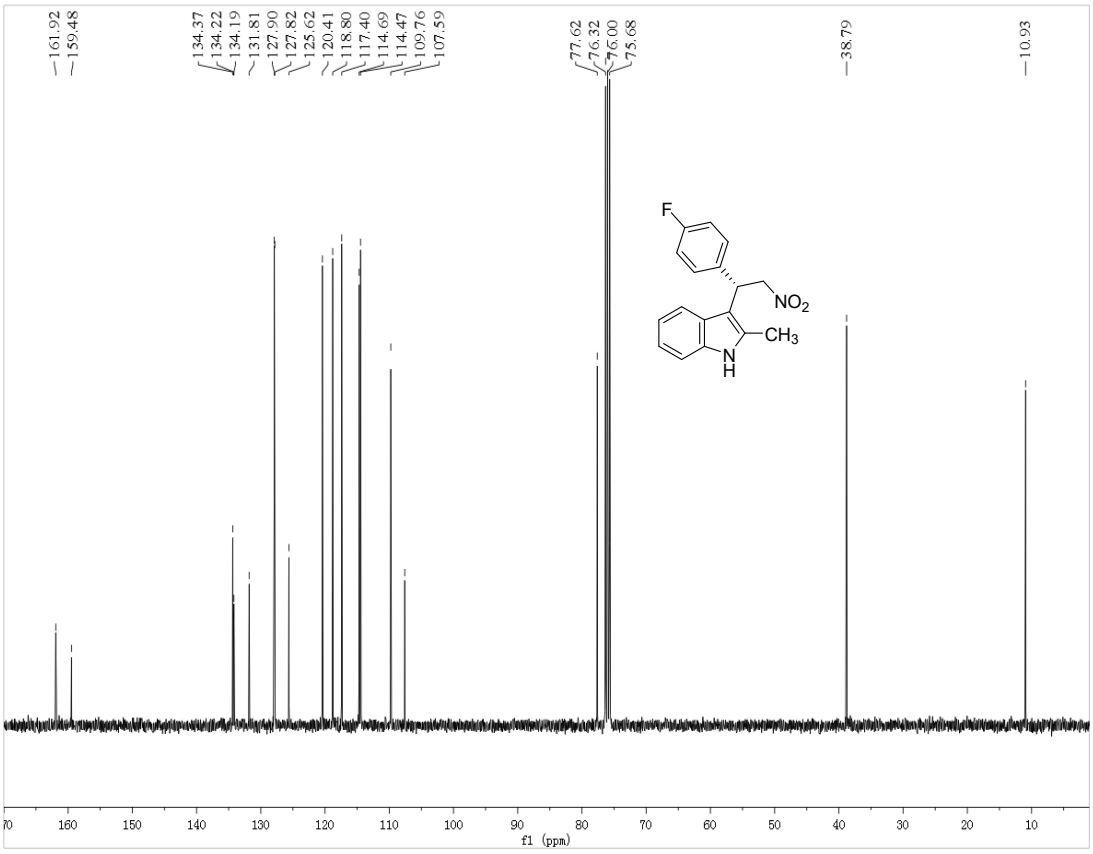
#	Time	Area	Height	Width	Area%	Symmetry
1	7.903	14306.1	700	0.3054	50.293	0.794
2	9.684	14139.4	621.8	0.3453	49.707	0.608



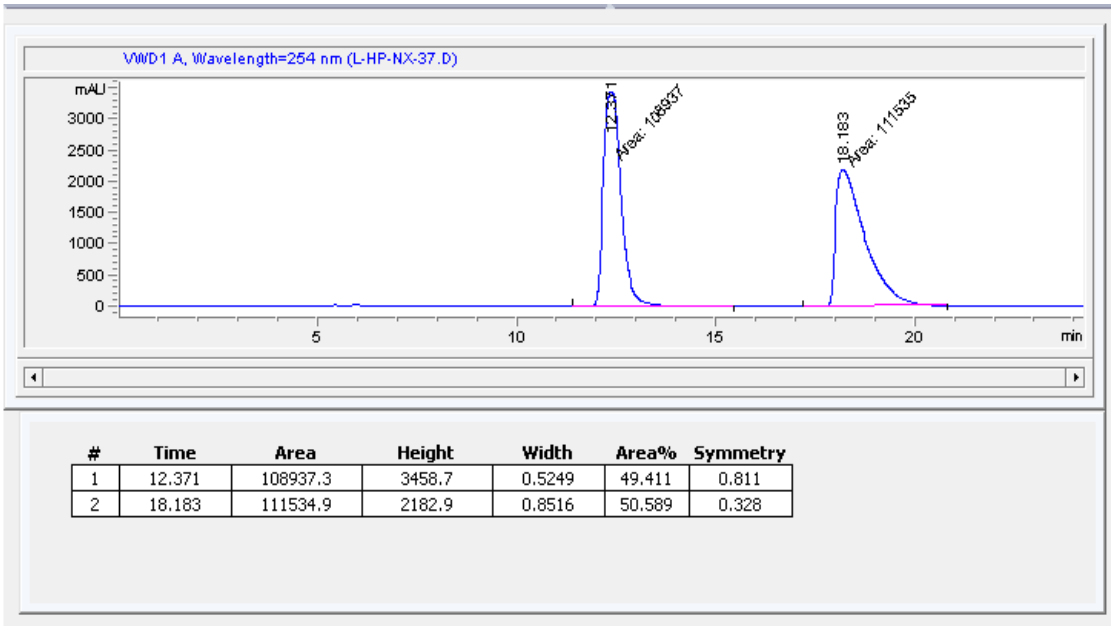
#	Time	Area	Height	Width	Area%	Symmetry
1	7.994	1453.3	70.4	0.3443	3.406	0.816
2	9.647	41210.6	1717.9	0.3669	96.594	0.492

^{1}H and ^{13}C NMR of 6k

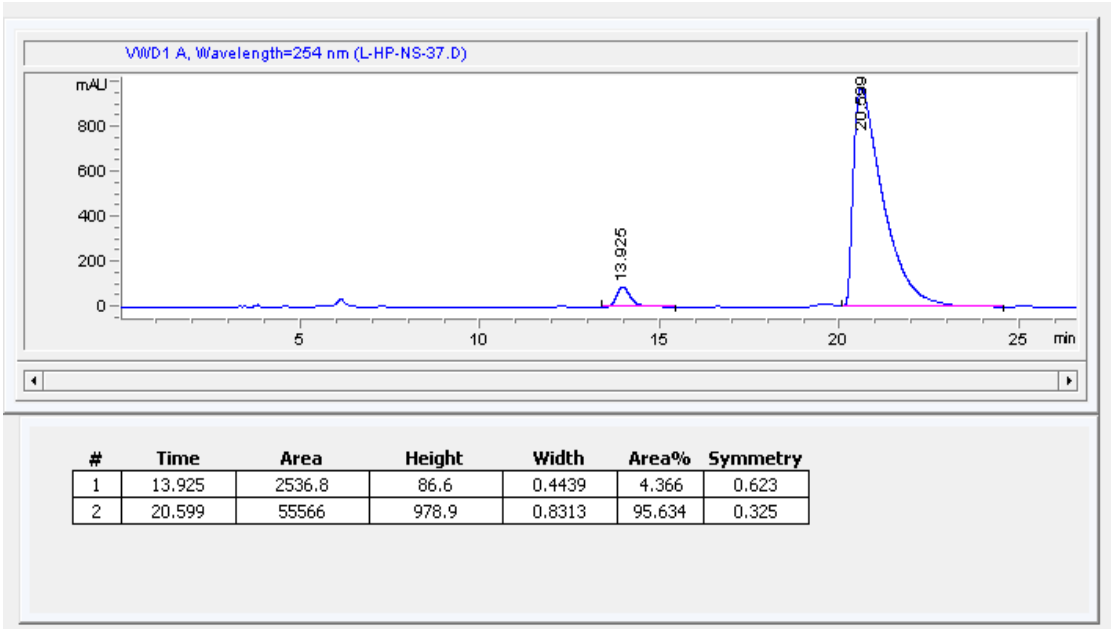




HPLC of 6k

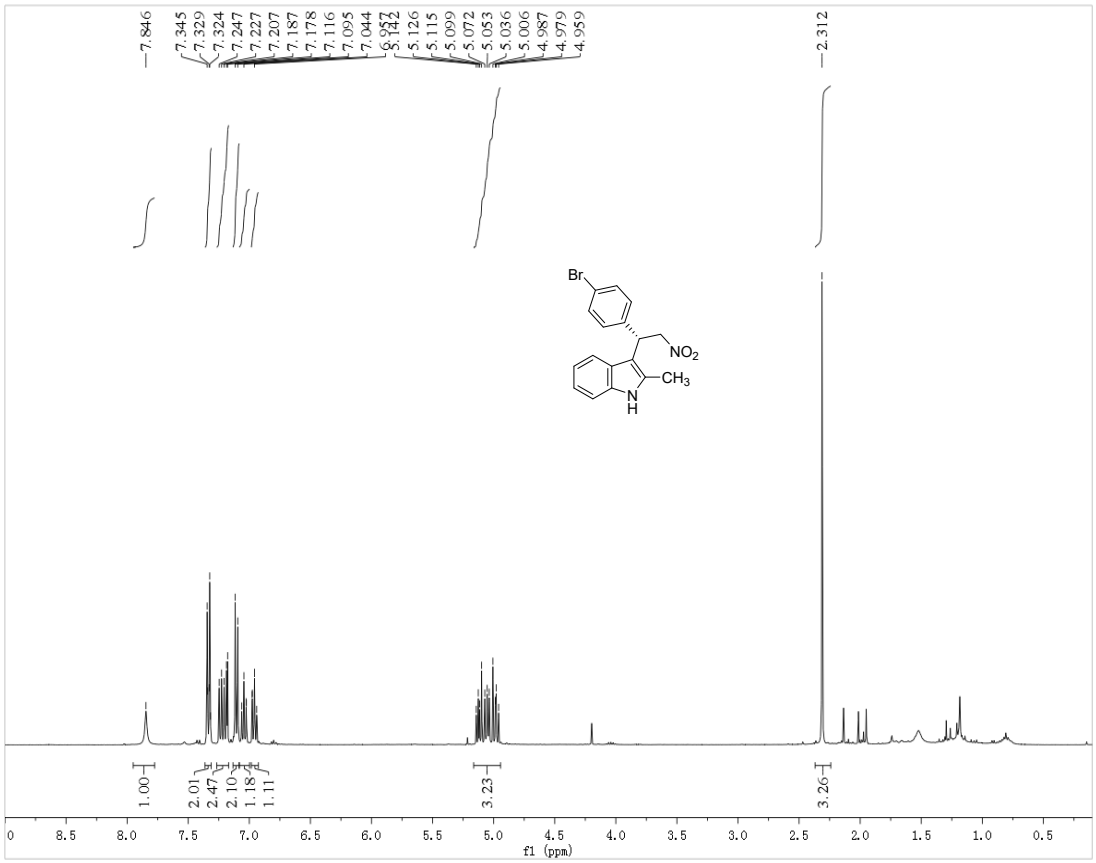


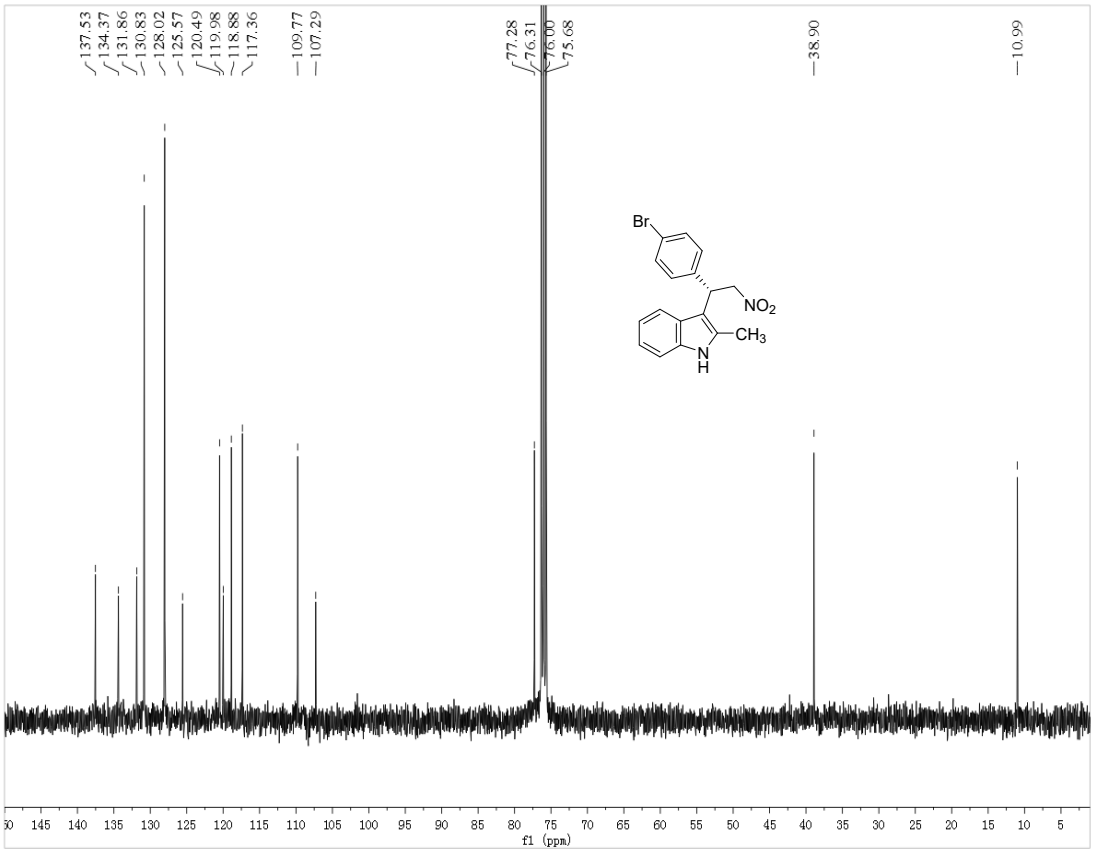
#	Time	Area	Height	Width	Area%	Symmetry
1	12.371	108937.3	3458.7	0.5249	49.411	0.811
2	18.183	111534.9	2182.9	0.8516	50.589	0.328



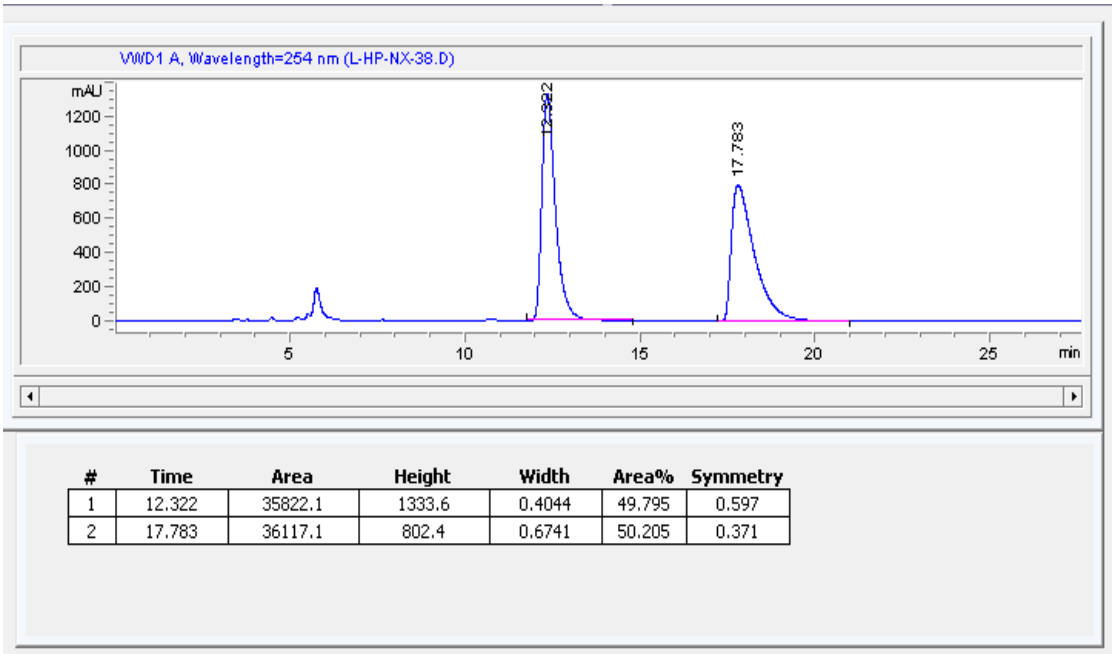
#	Time	Area	Height	Width	Area%	Symmetry
1	13.925	2536.8	86.6	0.4439	4.366	0.623
2	20.599	55566	978.9	0.8313	95.634	0.325

^{1}H and ^{13}C NMR of 6l

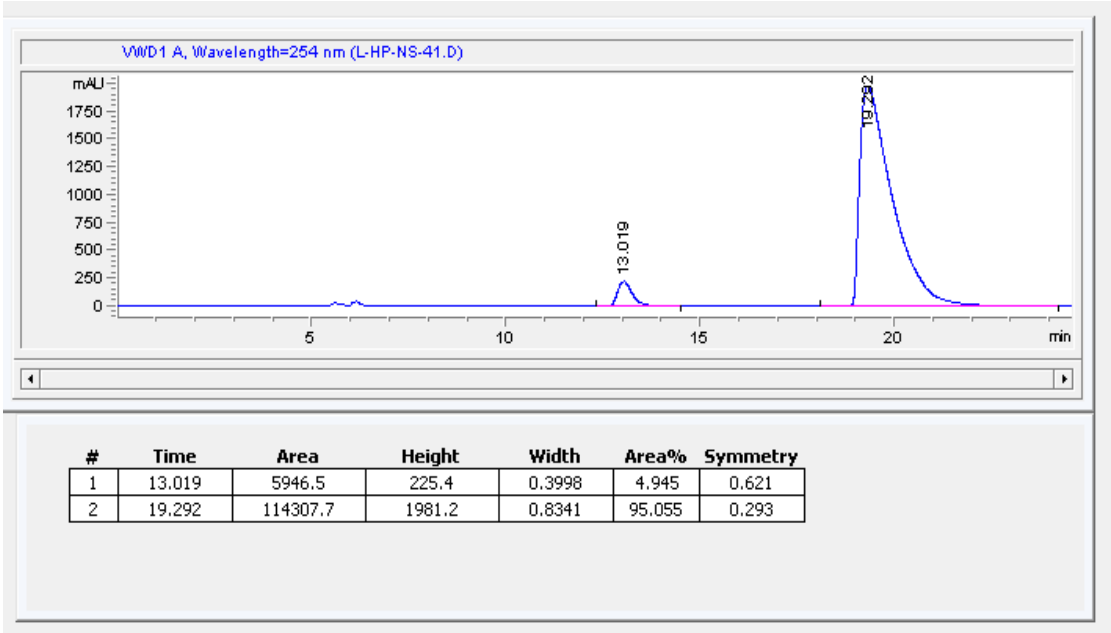




HPLC of 6l

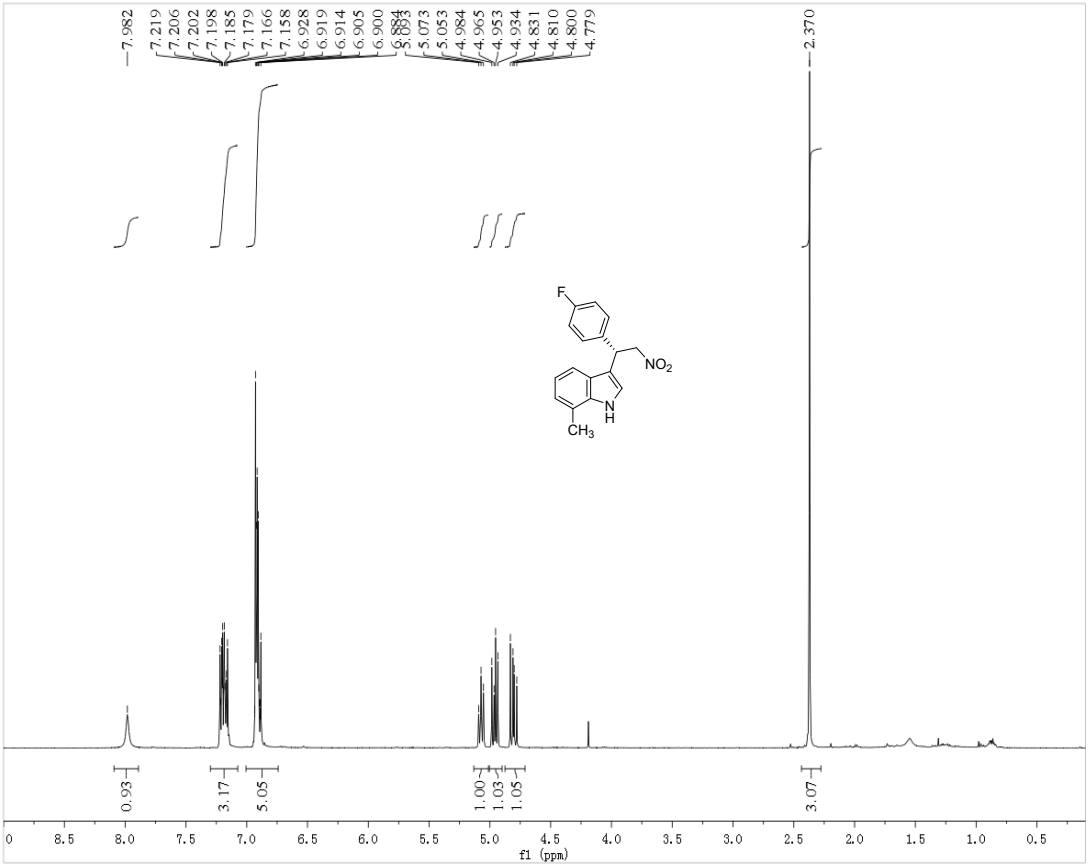


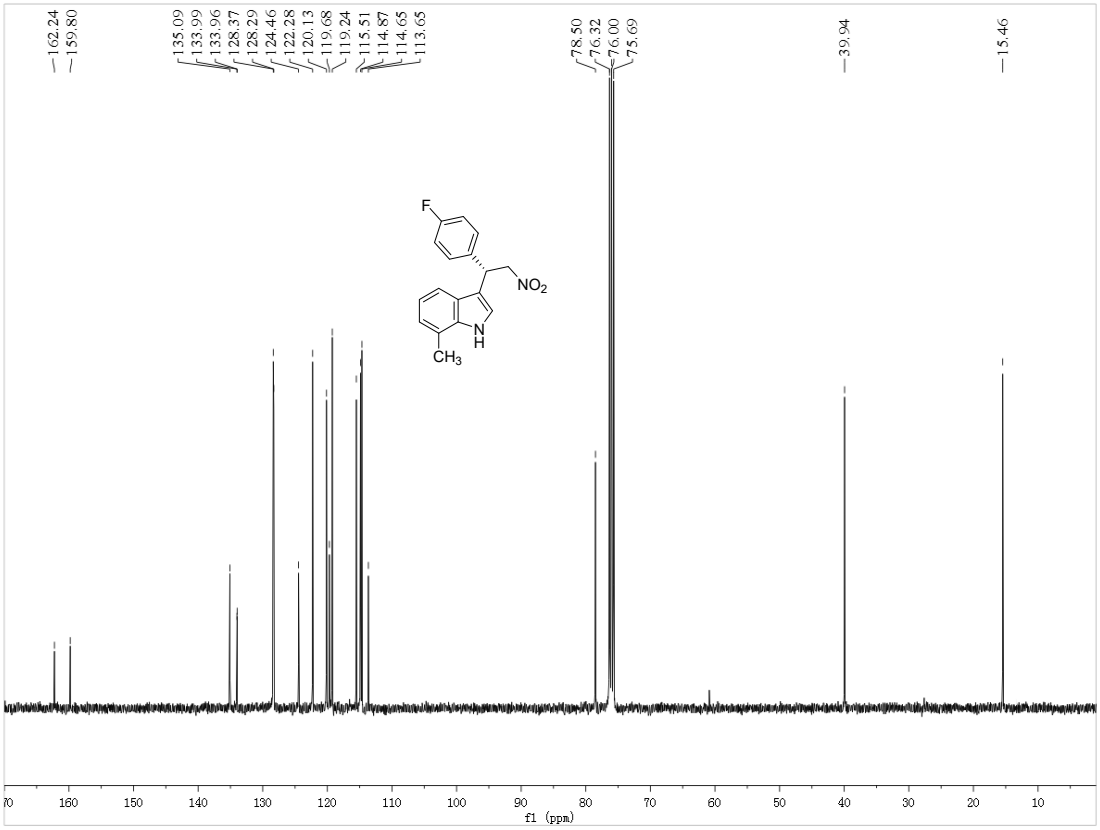
#	Time	Area	Height	Width	Area%	Symmetry
1	12.322	35822.1	1333.6	0.4044	49.795	0.597
2	17.783	36117.1	802.4	0.6741	50.205	0.371



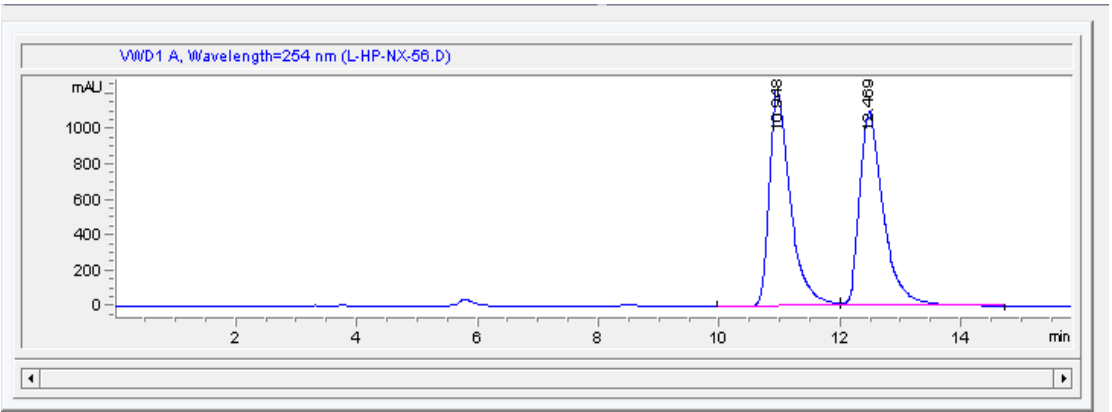
#	Time	Area	Height	Width	Area%	Symmetry
1	13.019	5946.5	225.4	0.3998	4.945	0.621
2	19.292	114307.7	1981.2	0.8341	95.055	0.293

^{1}H and ^{13}C NMR of 6m

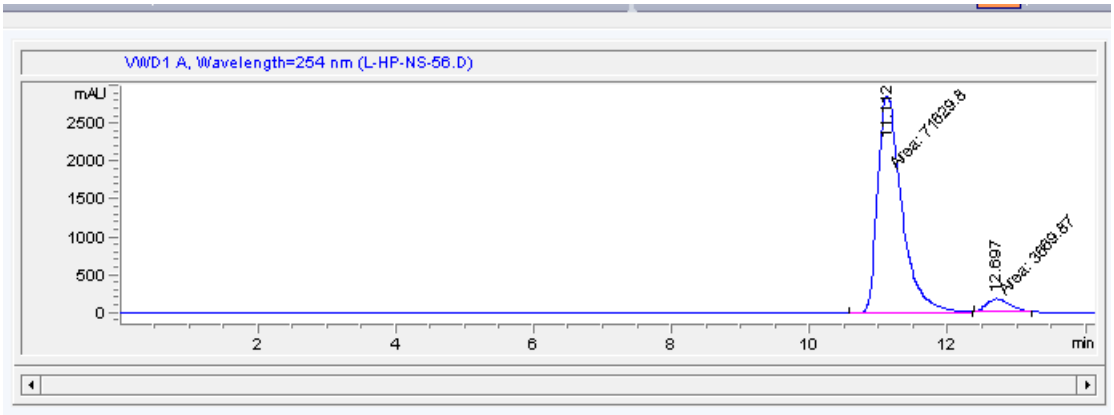




HPLC of 6m

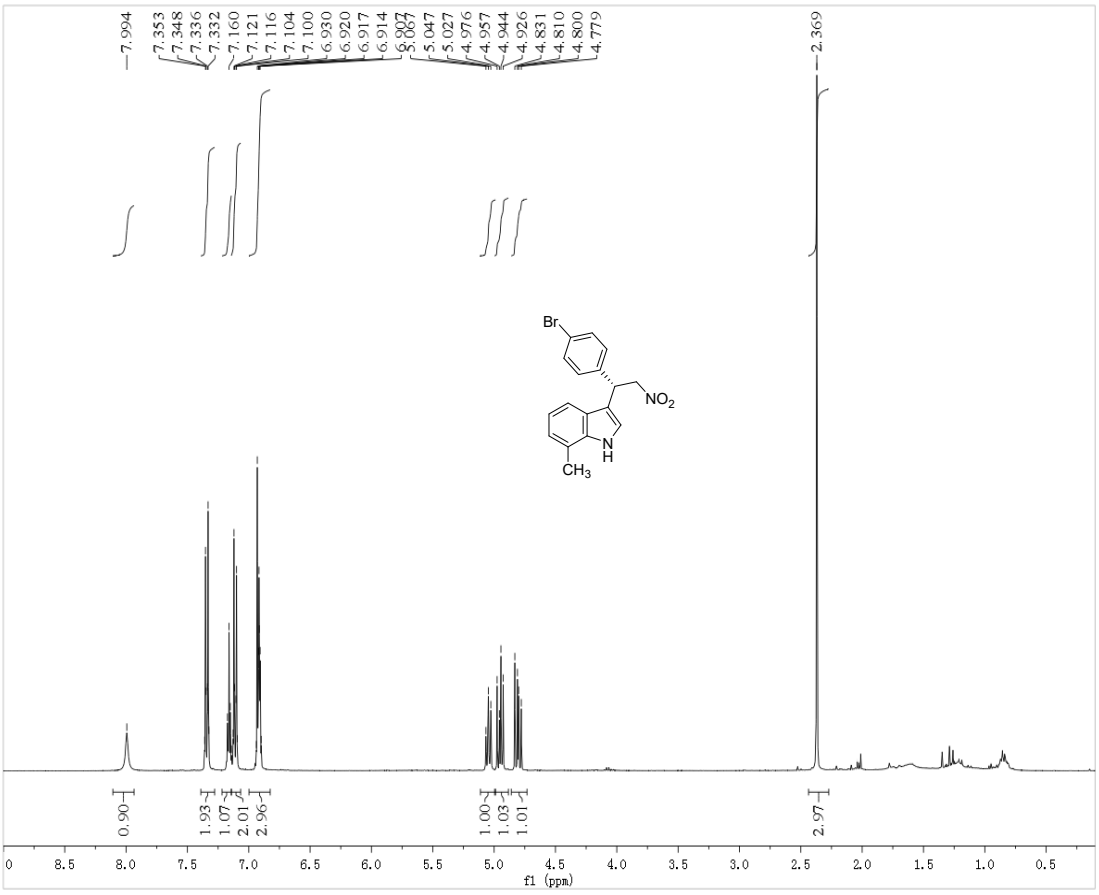


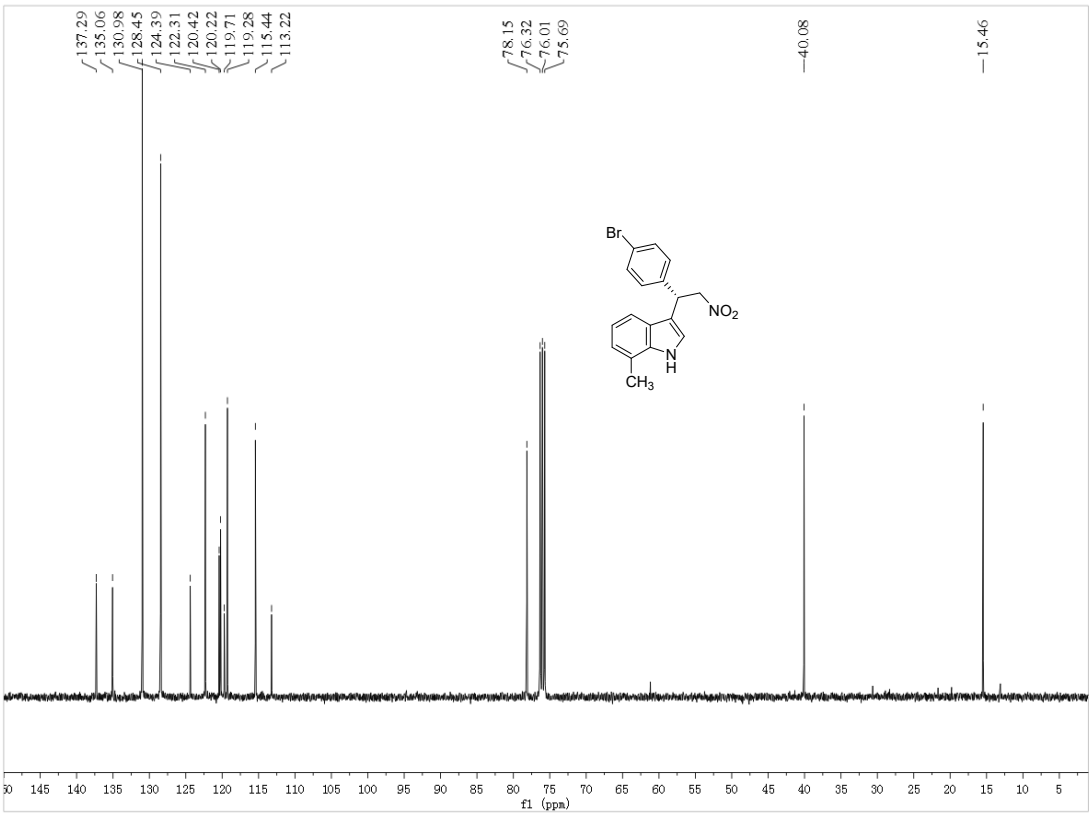
#	Time	Area	Height	Width	Area%	Symmetry
1	10.948	29825.8	1225.7	0.3649	49.582	0.572
2	12.469	30328.8	1097.6	0.4164	50.418	0.618



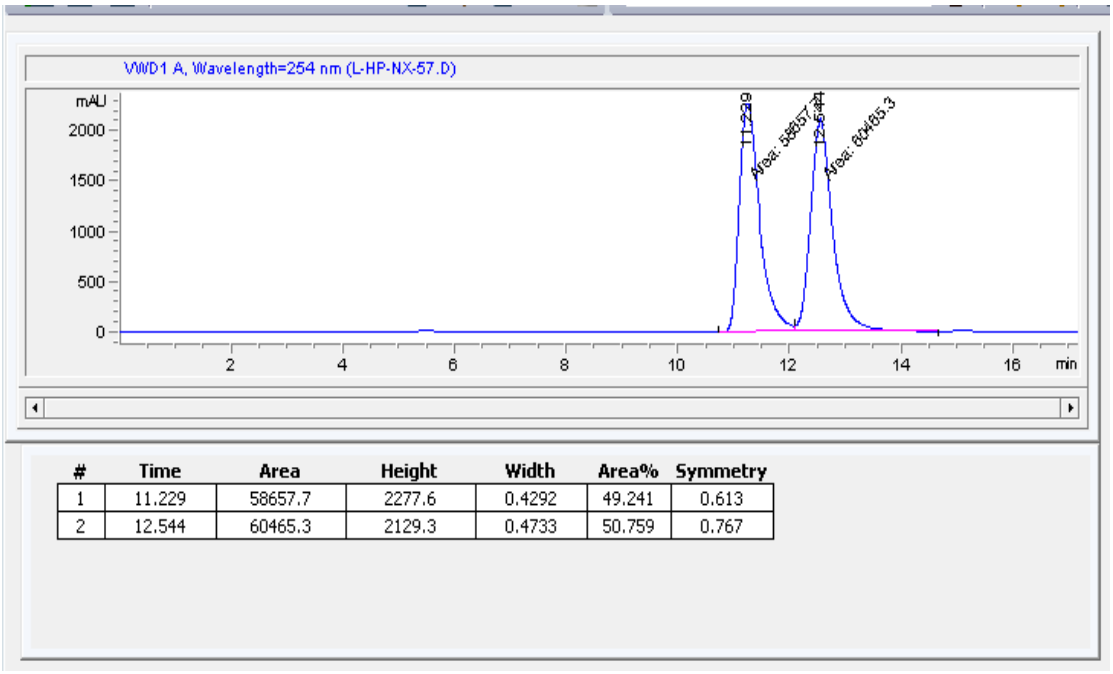
#	Time	Area	Height	Width	Area%	Symmetry
1	11.112	71629.8	2882	0.4142	95.126	0.606
2	12.697	3669.9	163.3	0.3745	4.874	0.754

^{1}H and ^{13}C NMR of 6n

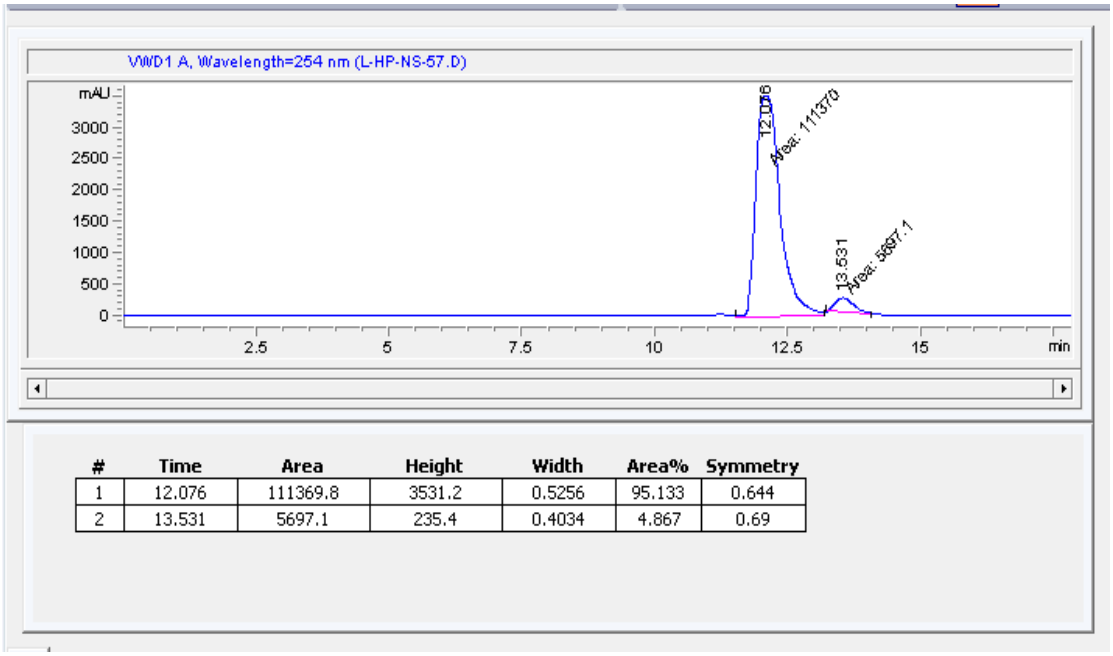




HPLC of 6n

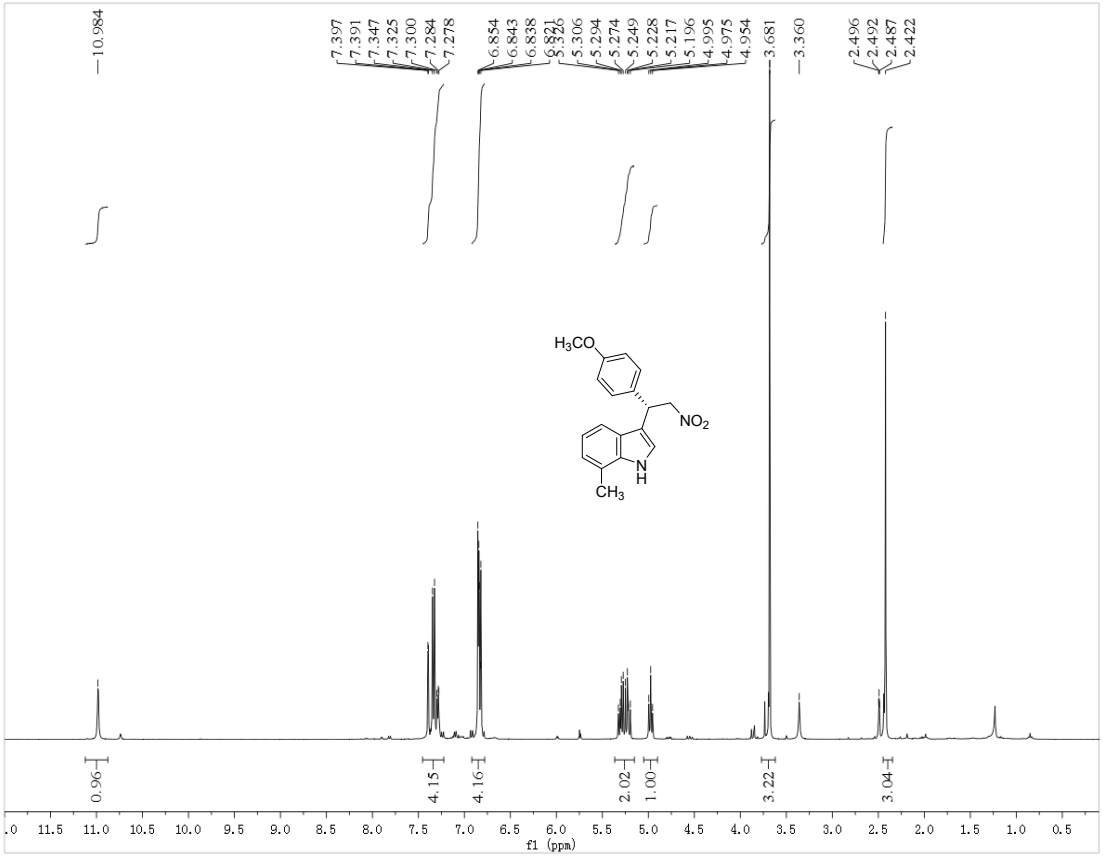


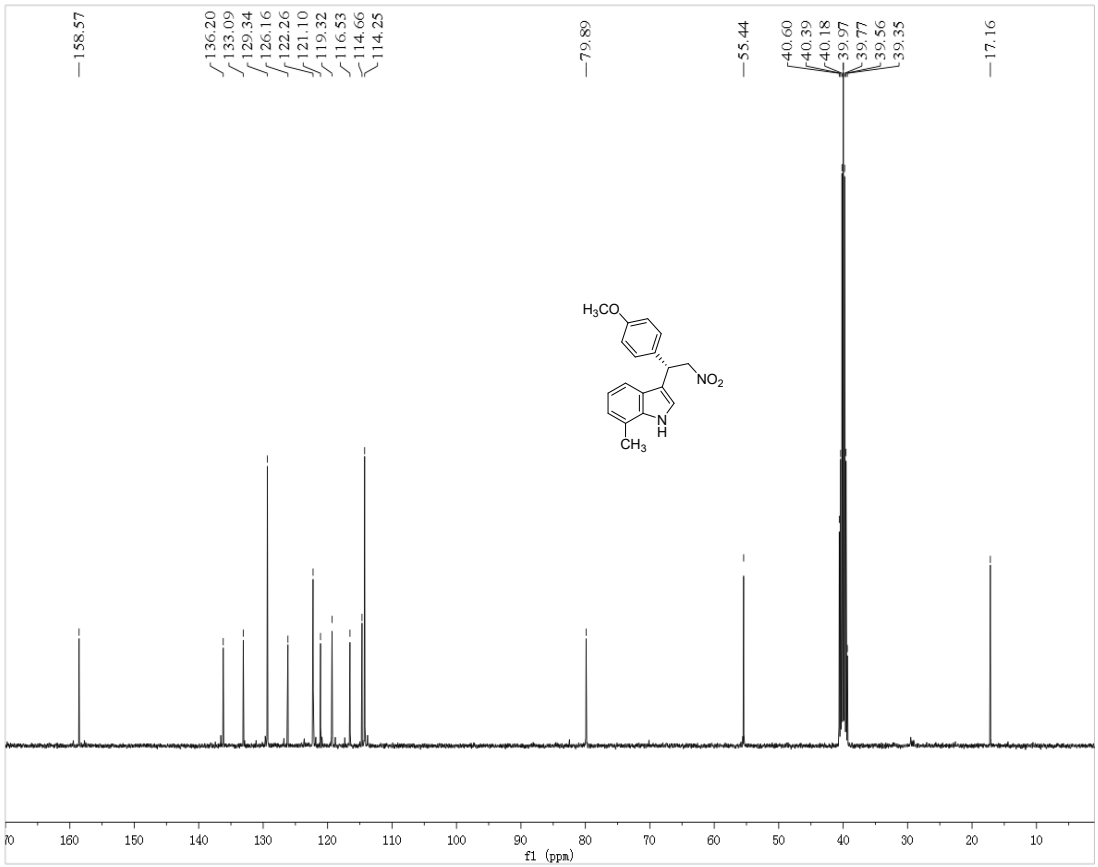
#	Time	Area	Height	Width	Area%	Symmetry
1	11.229	58657.7	2277.6	0.4292	49.241	0.613
2	12.544	60465.3	2129.3	0.4733	50.759	0.767



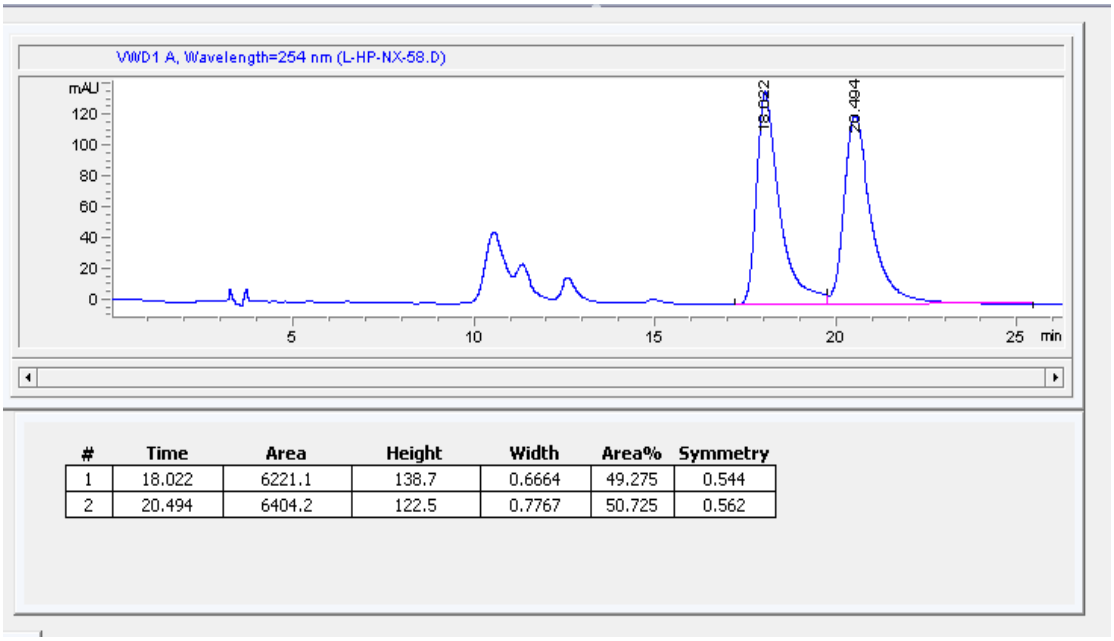
#	Time	Area	Height	Width	Area%	Symmetry
1	12.076	111369.8	3531.2	0.5256	95.133	0.644
2	13.531	5697.1	235.4	0.4034	4.867	0.69

^{1}H and ^{13}C NMR of 6o

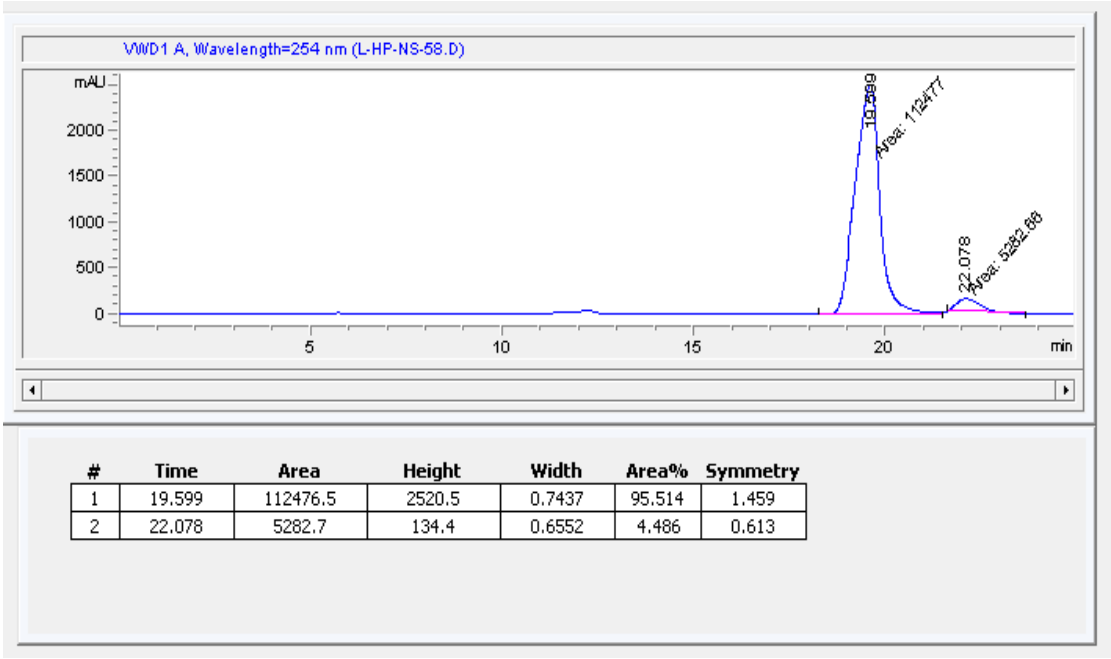




HPLC of 6o

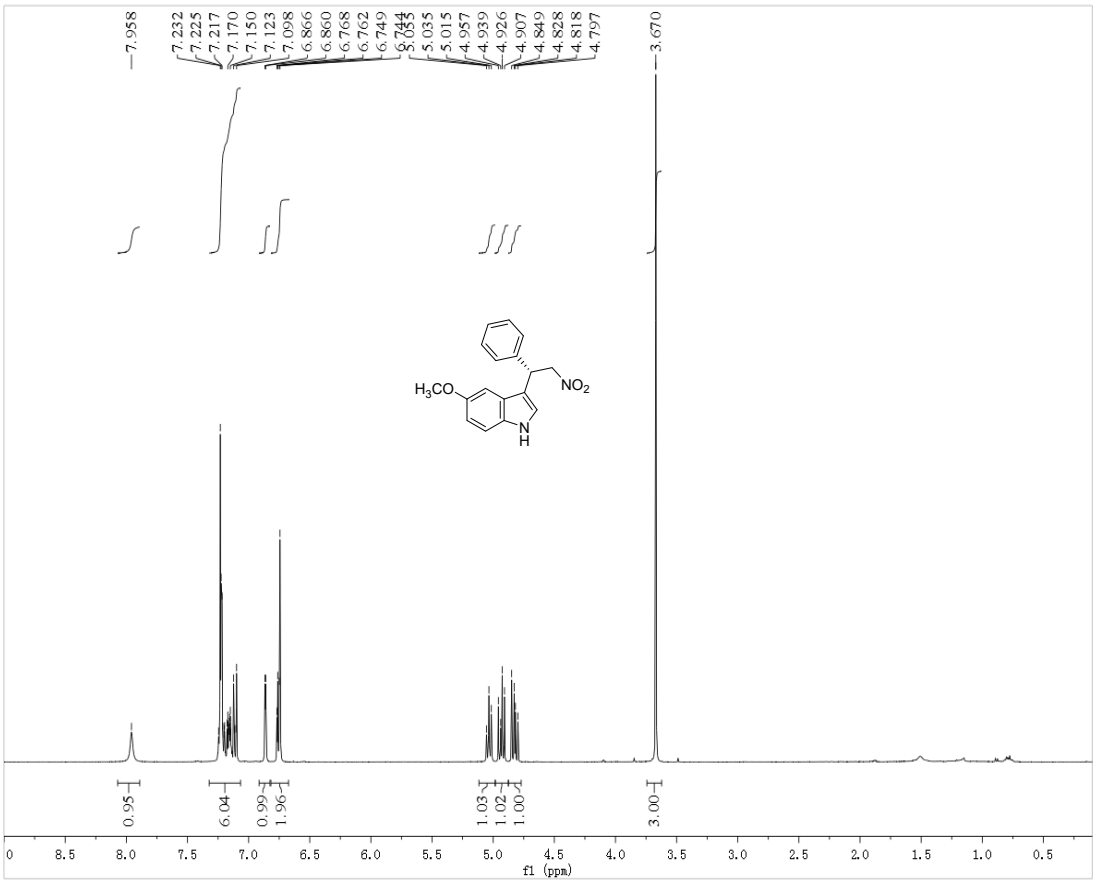


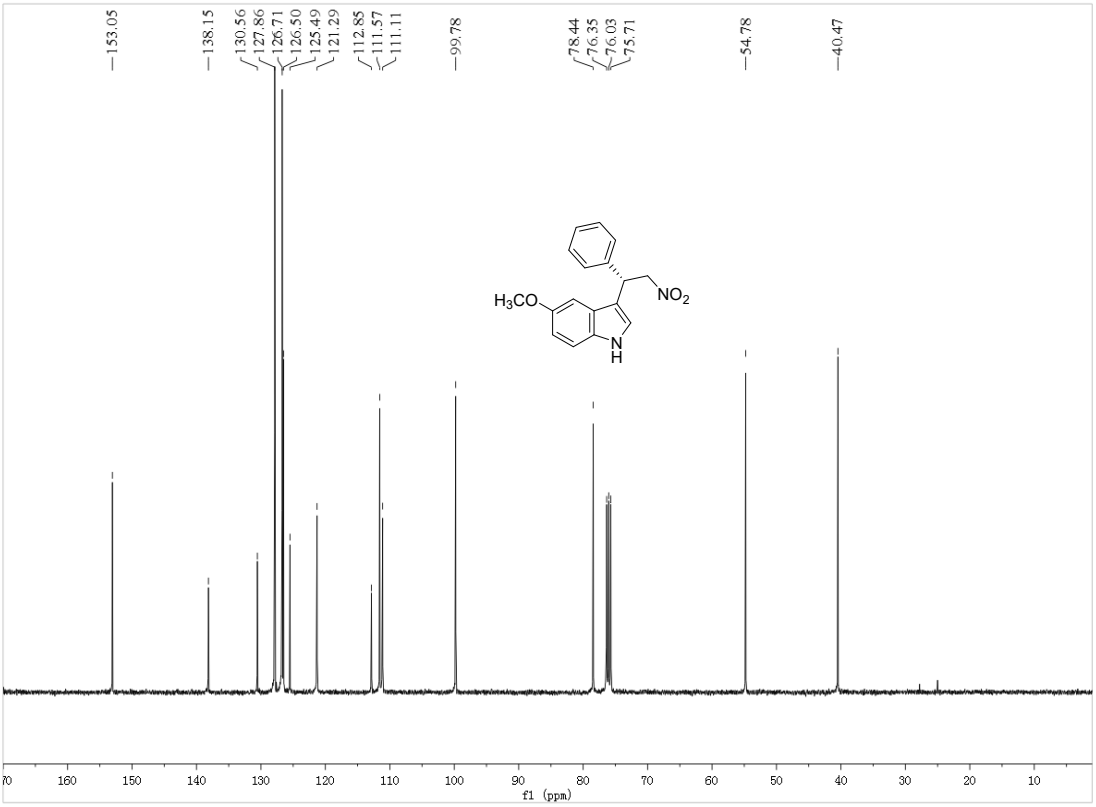
#	Time	Area	Height	Width	Area%	Symmetry
1	18.022	6221.1	138.7	0.6664	49.275	0.544
2	20.494	6404.2	122.5	0.7767	50.725	0.562



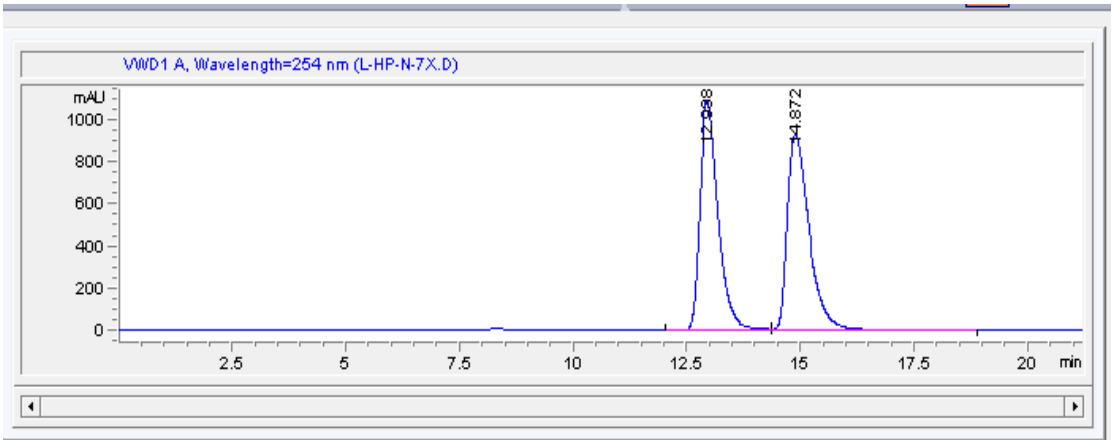
#	Time	Area	Height	Width	Area%	Symmetry
1	19.599	112476.5	2520.5	0.7437	95.514	1.459
2	22.078	5282.7	134.4	0.6552	4.486	0.613

^{1}H and ^{13}C NMR of 6p

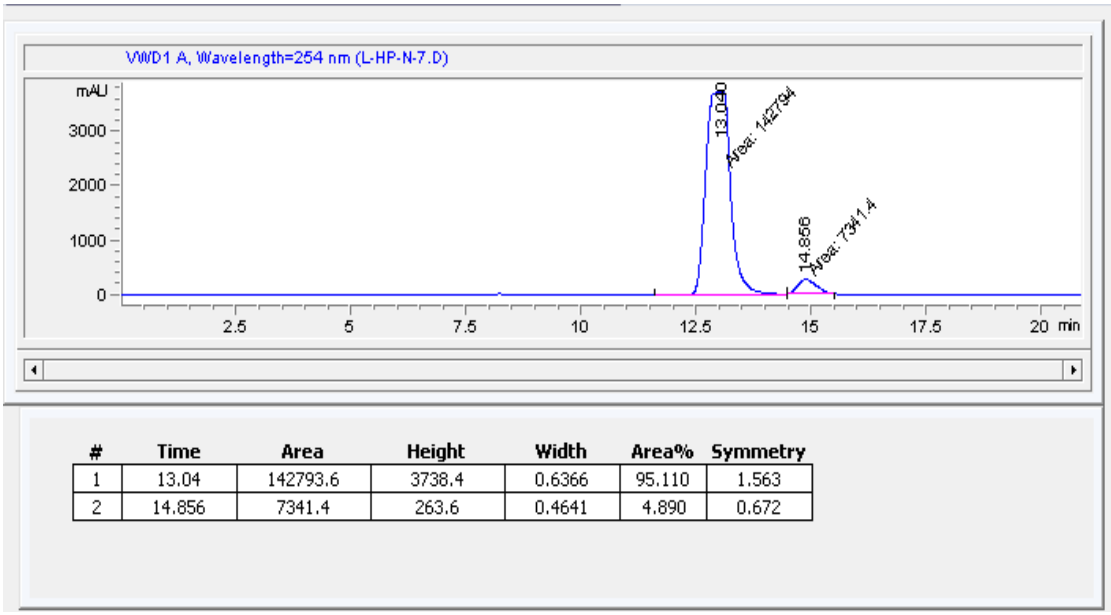




HPLC of 6p

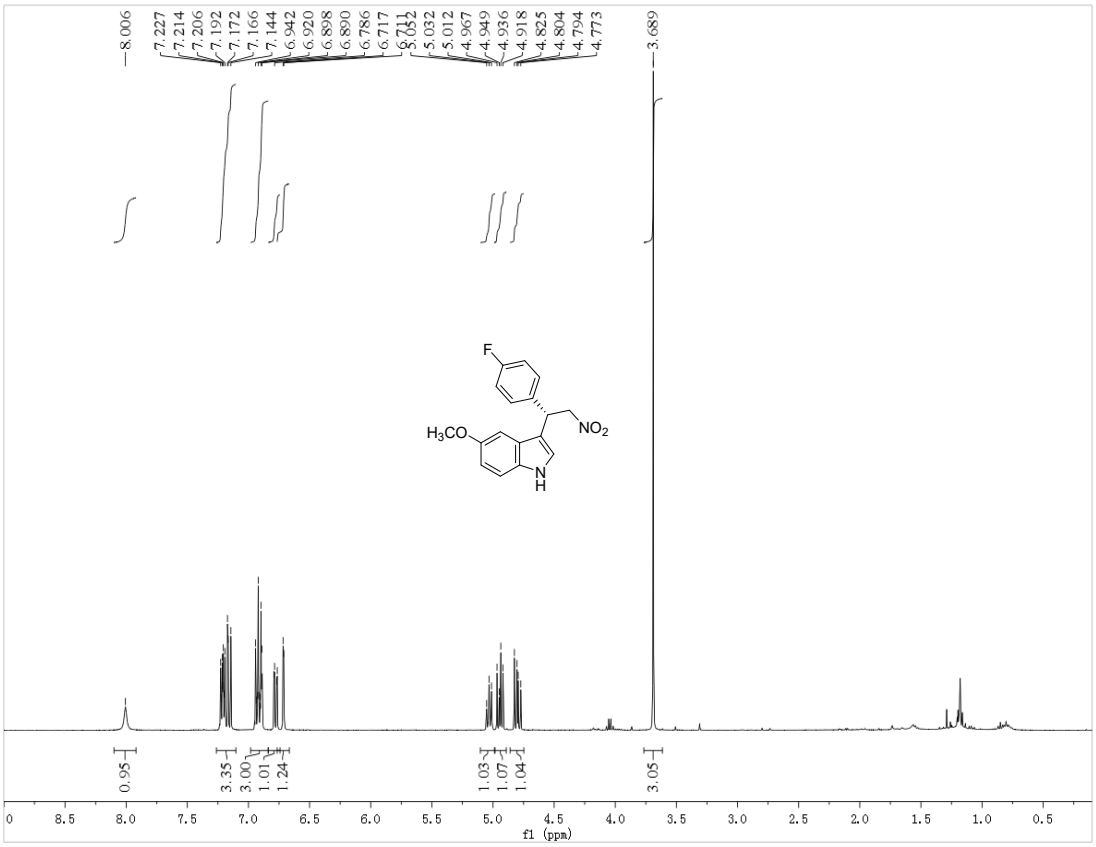


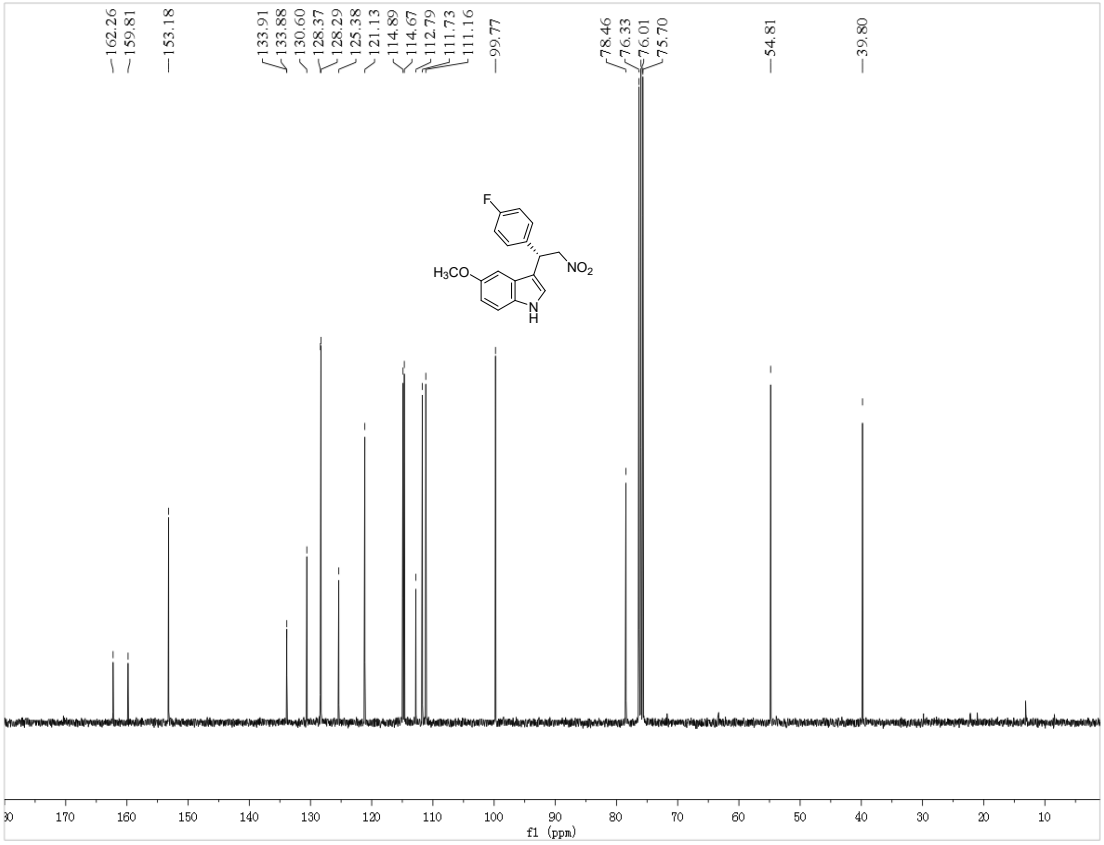
#	Time	Area	Height	Width	Area%	Symmetry
1	12.938	30713.5	1098.2	0.4273	49.902	0.648
2	14.872	30834.6	931.2	0.5033	50.098	0.515



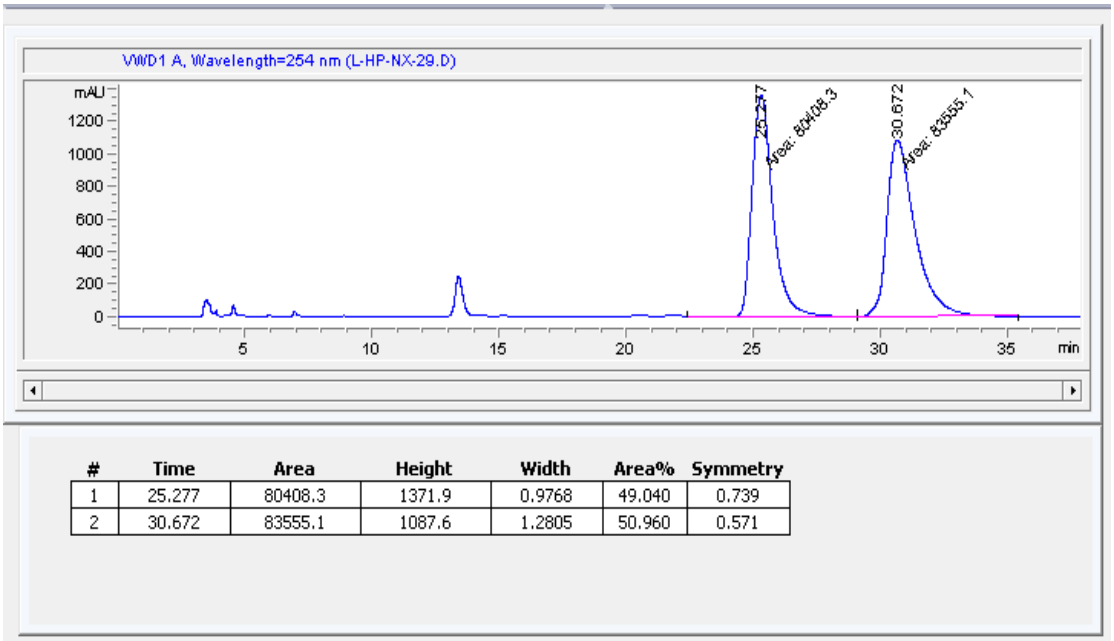
#	Time	Area	Height	Width	Area%	Symmetry
1	13.04	142793.6	3738.4	0.6366	95.110	1.563
2	14.856	7341.4	263.6	0.4641	4.890	0.672

^{1}H and ^{13}C NMR of 6q

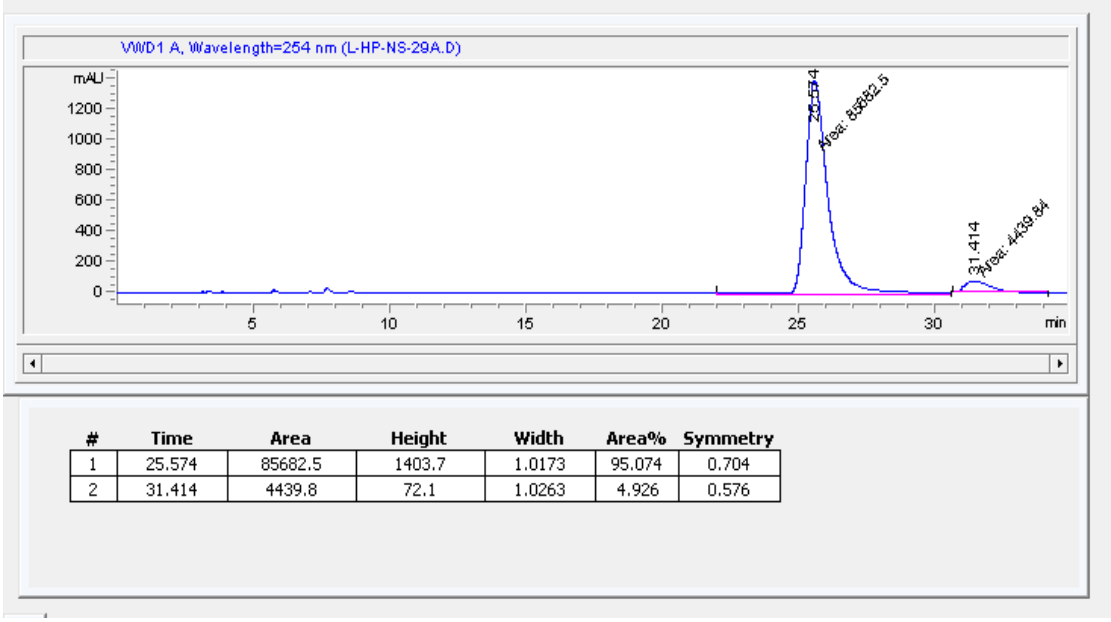




HPLC of 6q

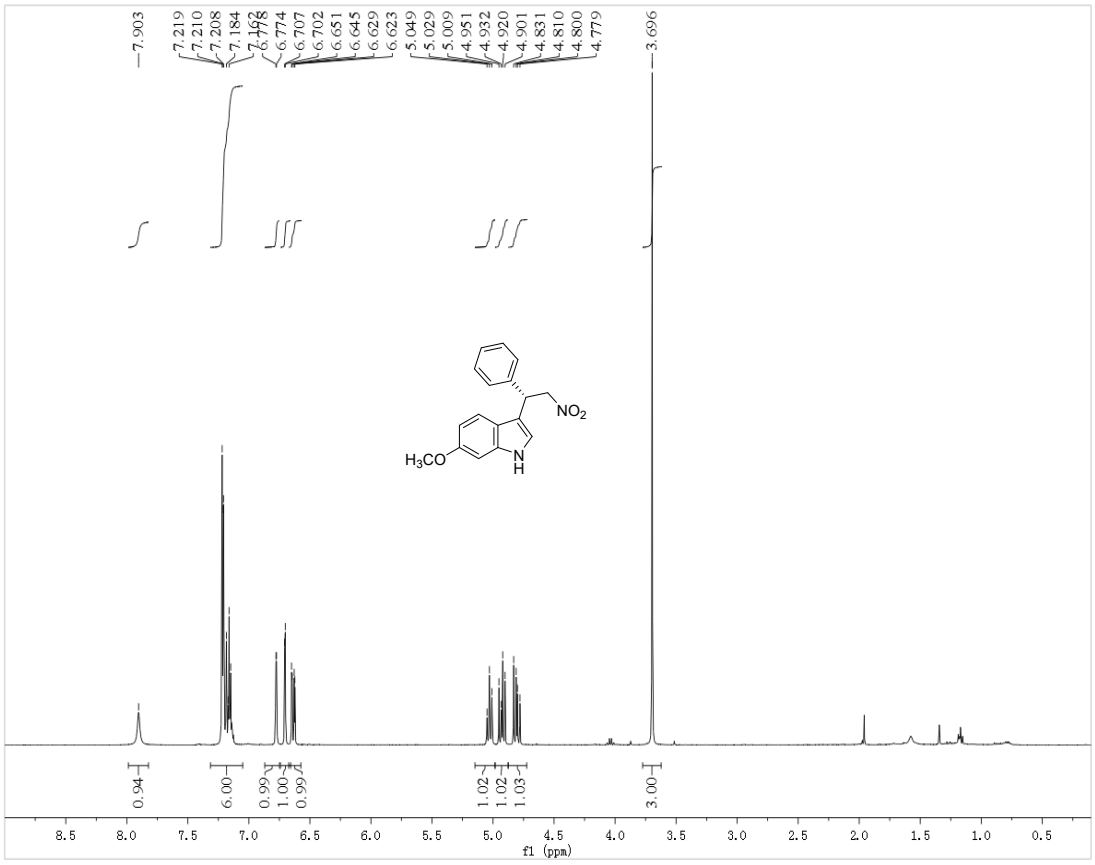


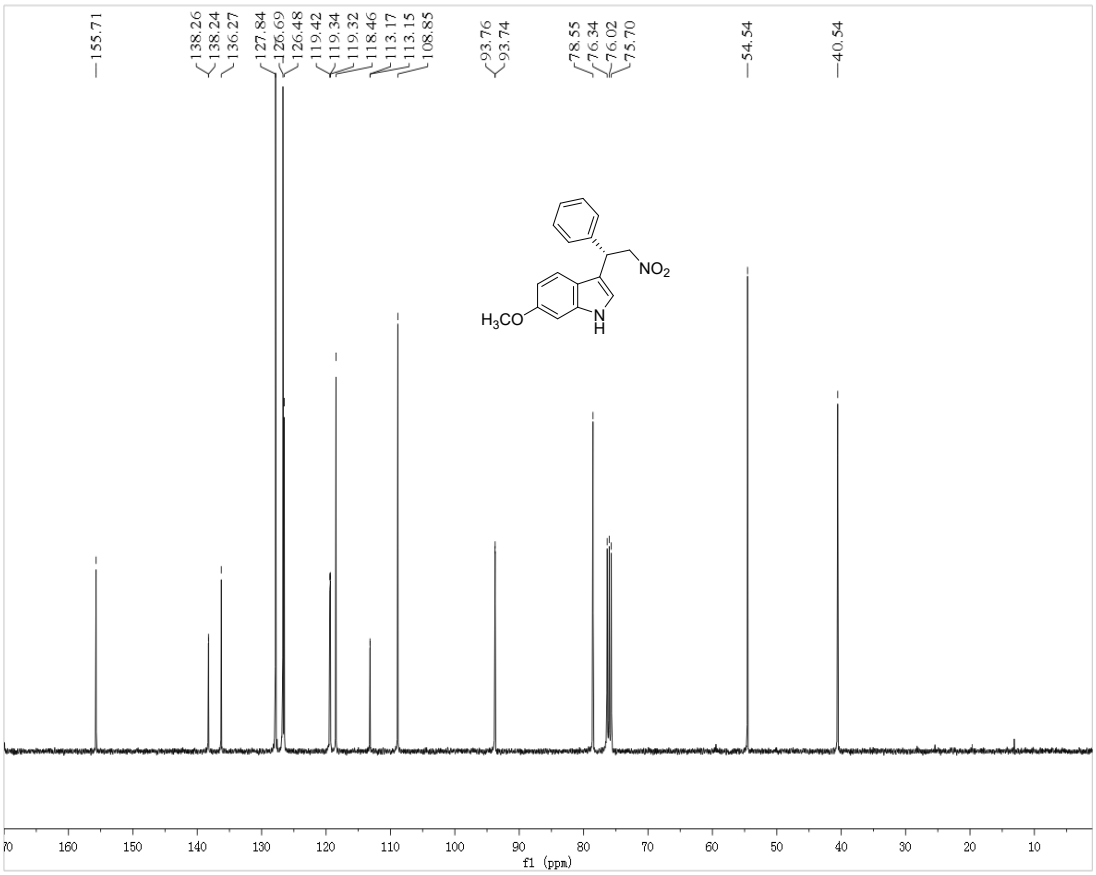
#	Time	Area	Height	Width	Area%	Symmetry
1	25.277	80408.3	1371.9	0.9768	49.040	0.739
2	30.672	83555.1	1087.6	1.2805	50.960	0.571



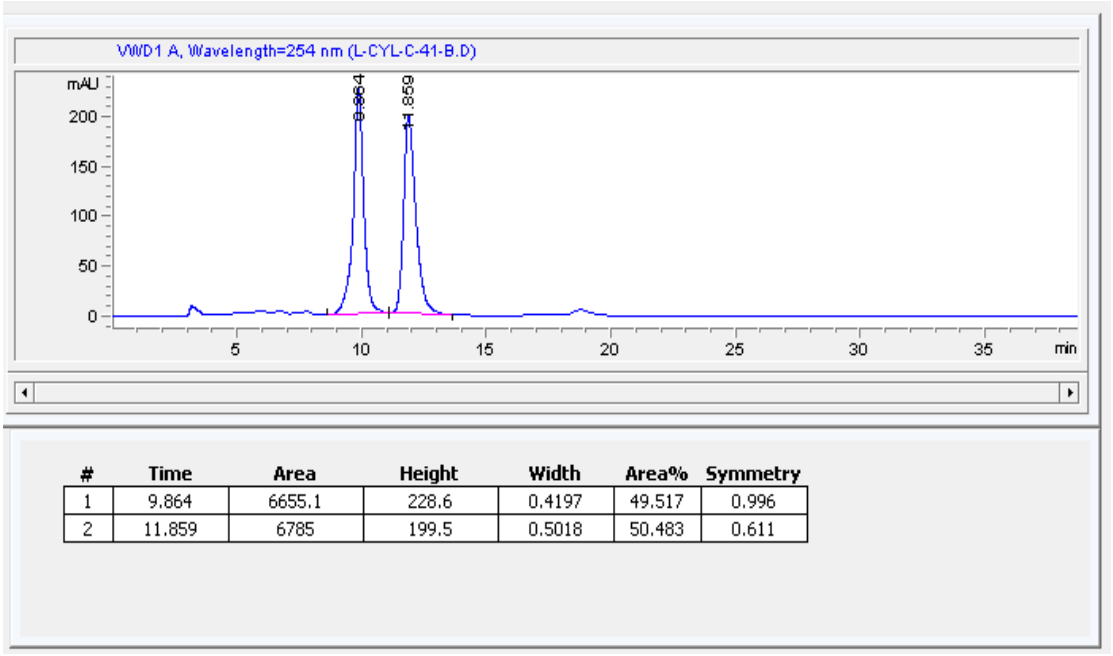
#	Time	Area	Height	Width	Area%	Symmetry
1	25.574	85682.5	1403.7	1.0173	95.074	0.704
2	31.414	4439.8	72.1	1.0263	4.926	0.576

^{1}H and ^{13}C NMR of 6r

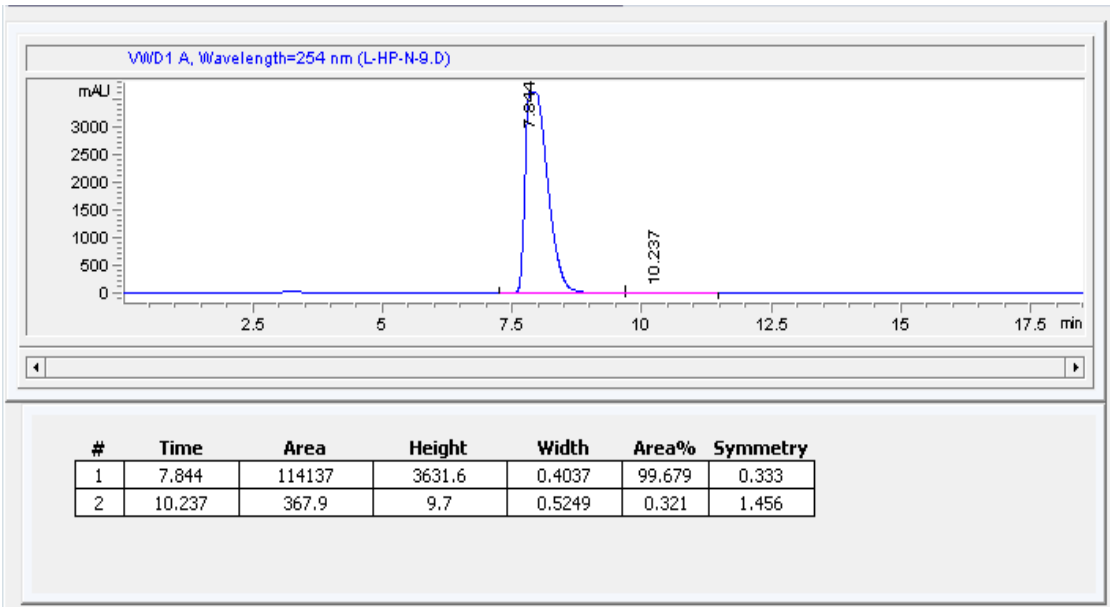




HPLC of 6r

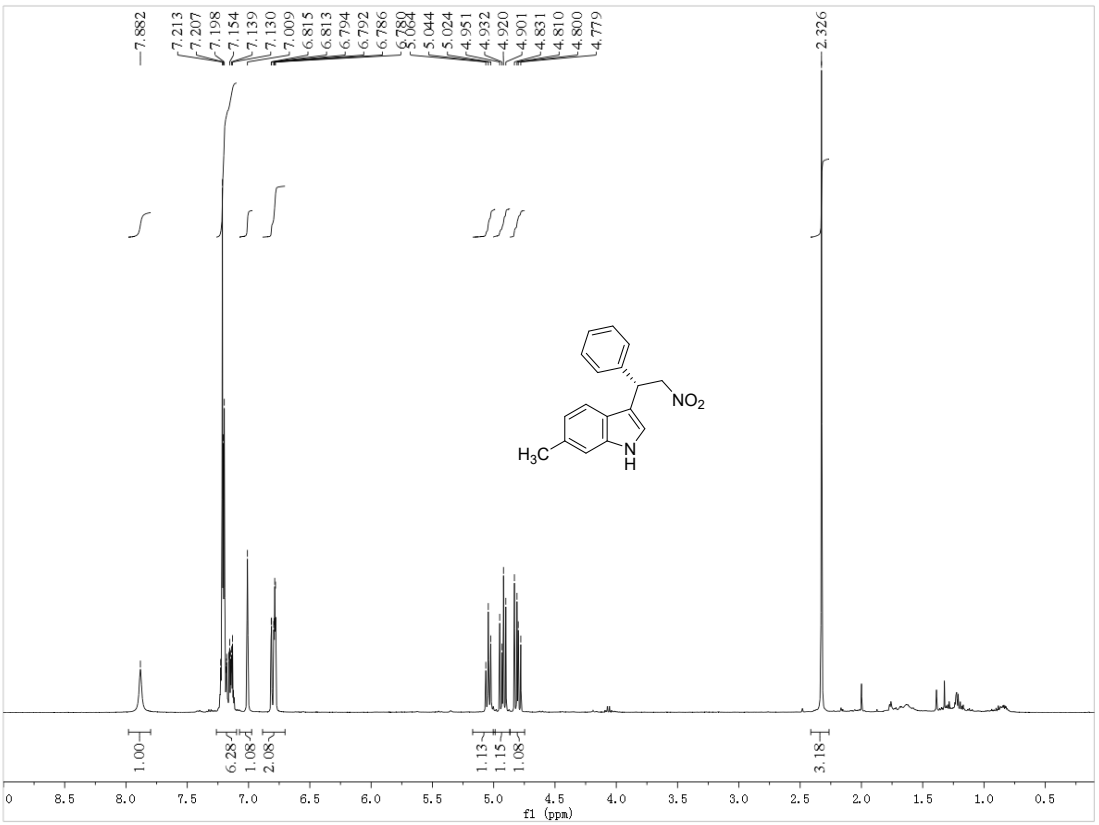


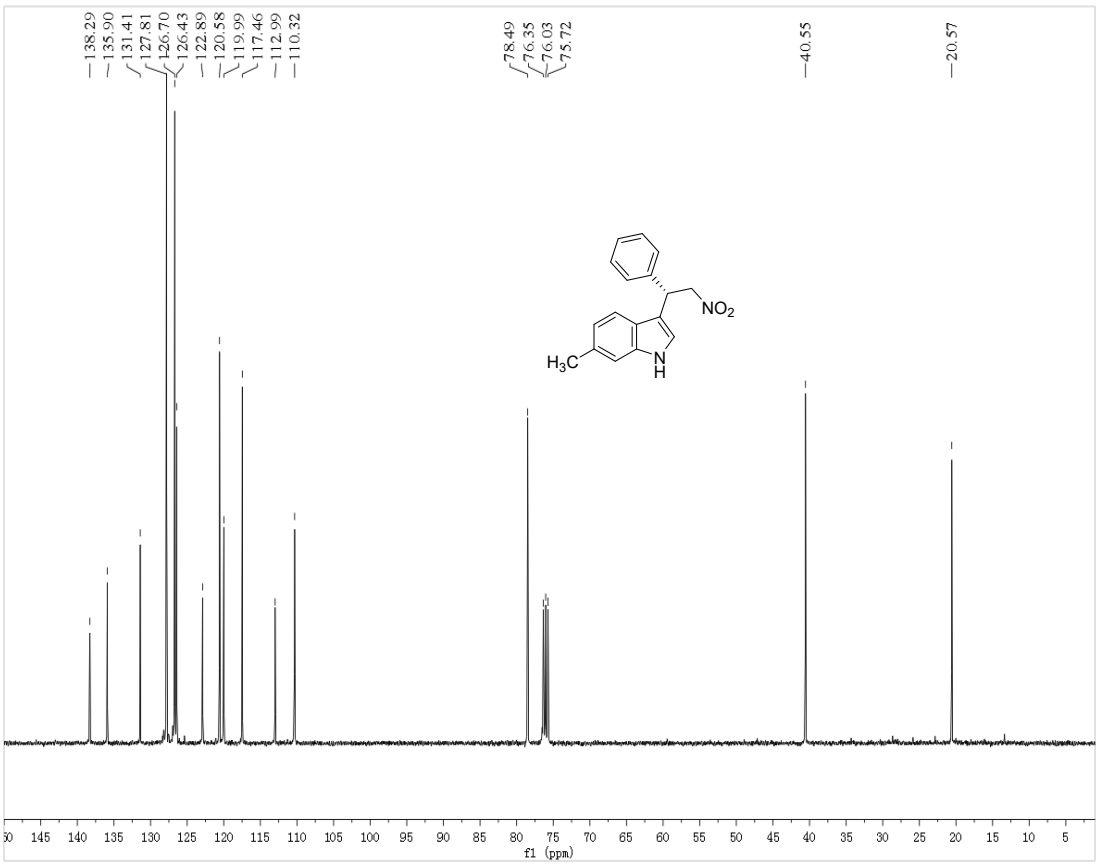
#	Time	Area	Height	Width	Area%	Symmetry
1	9.864	6655.1	228.6	0.4197	49.517	0.996
2	11.859	6785	199.5	0.5018	50.483	0.611



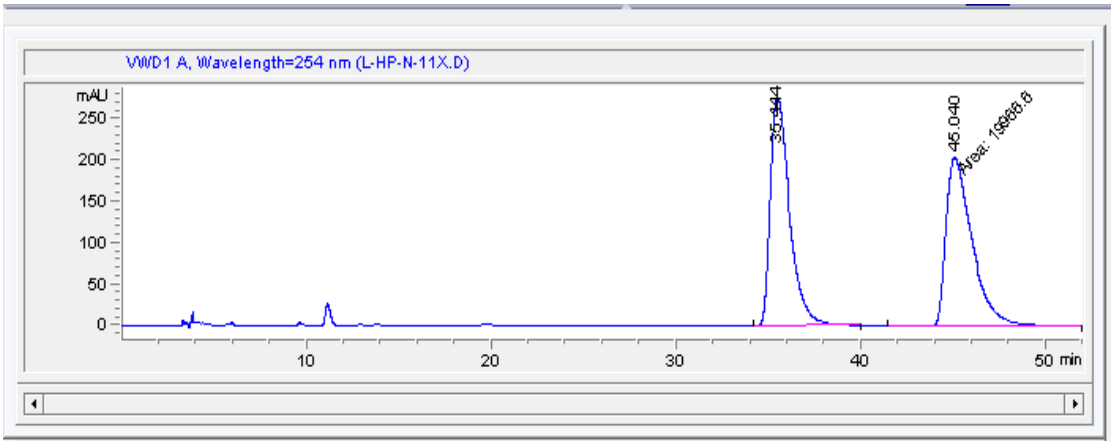
#	Time	Area	Height	Width	Area%	Symmetry
1	7.844	114137	3631.6	0.4037	99.679	0.333
2	10.237	367.9	9.7	0.5249	0.321	1.456

^{1}H and ^{13}C NMR of 6s

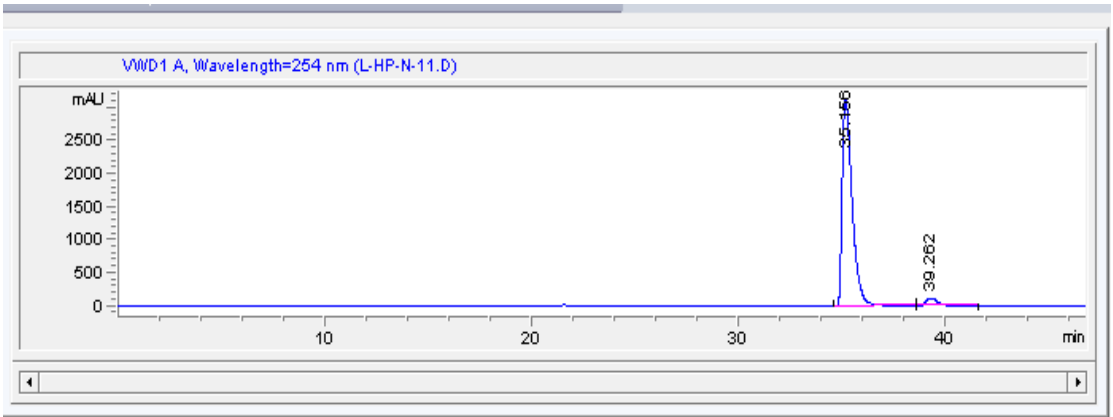




HPLC of 6s

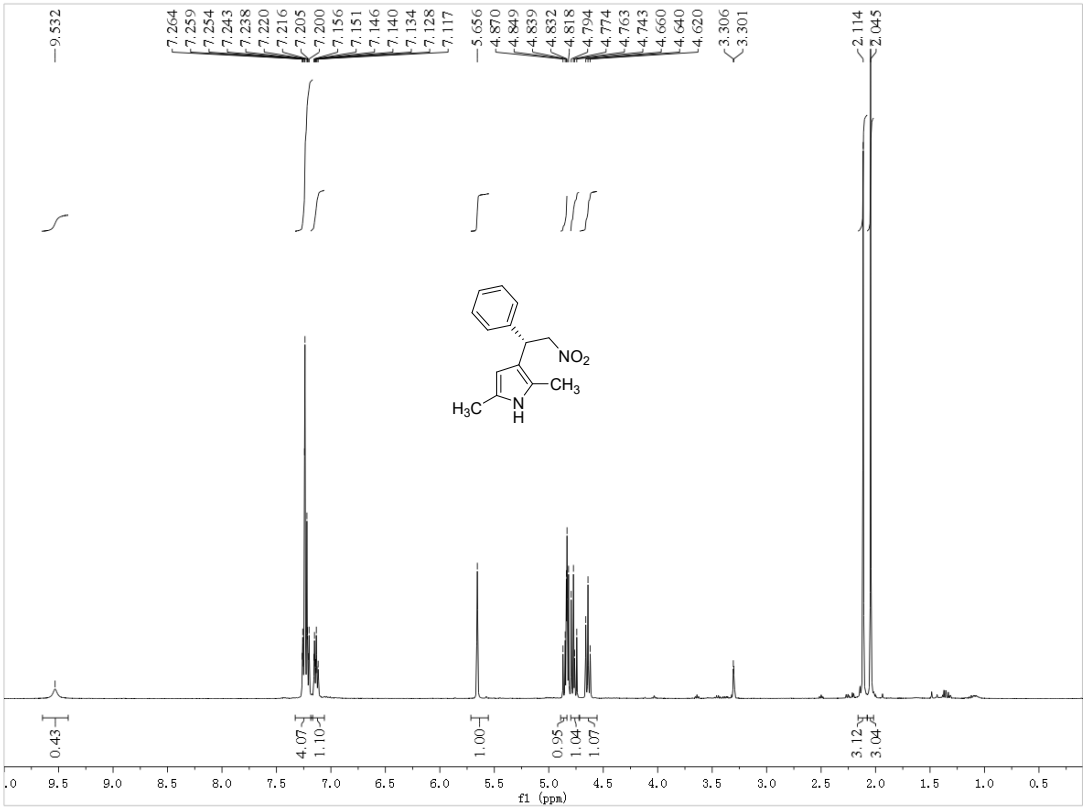


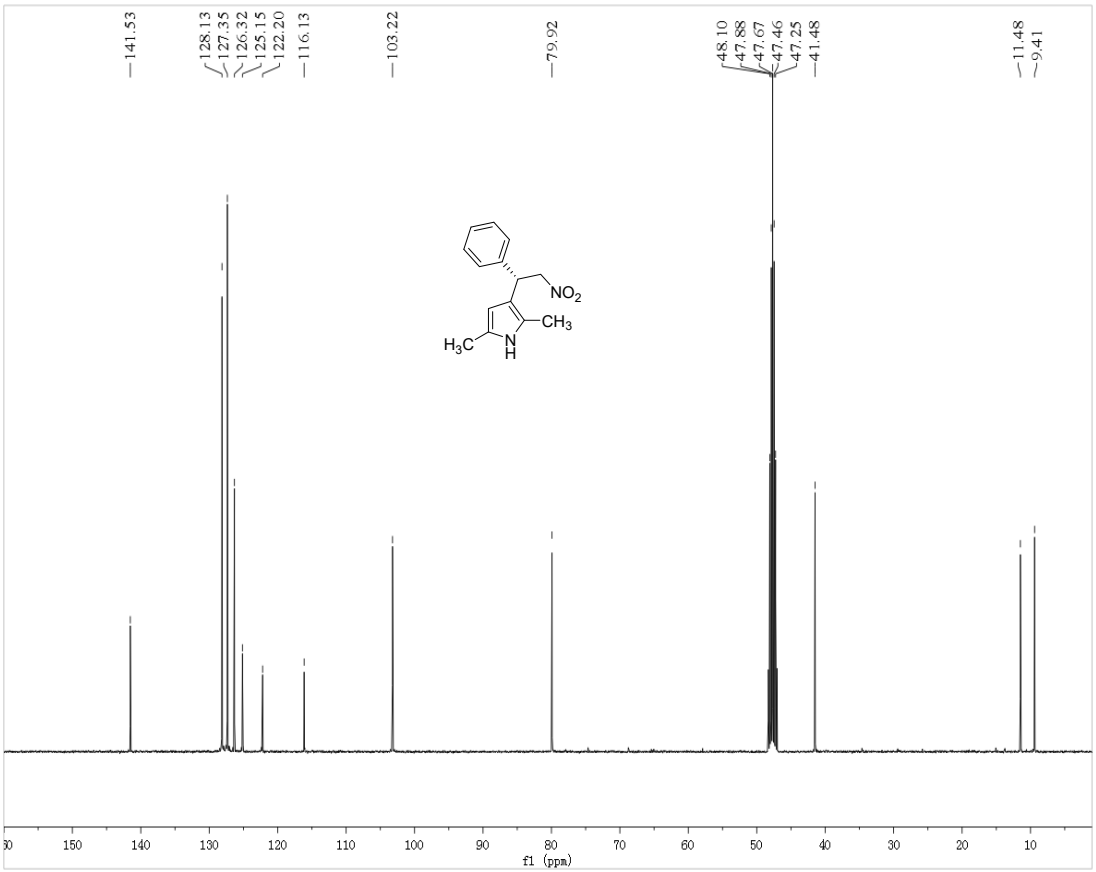
#	Time	Area	Height	Width	Area%	Symmetry
1	35.444	20544.4	276.3	1.1384	50.713	0.523
2	45.04	19966.6	203.8	1.6328	49.287	0.466



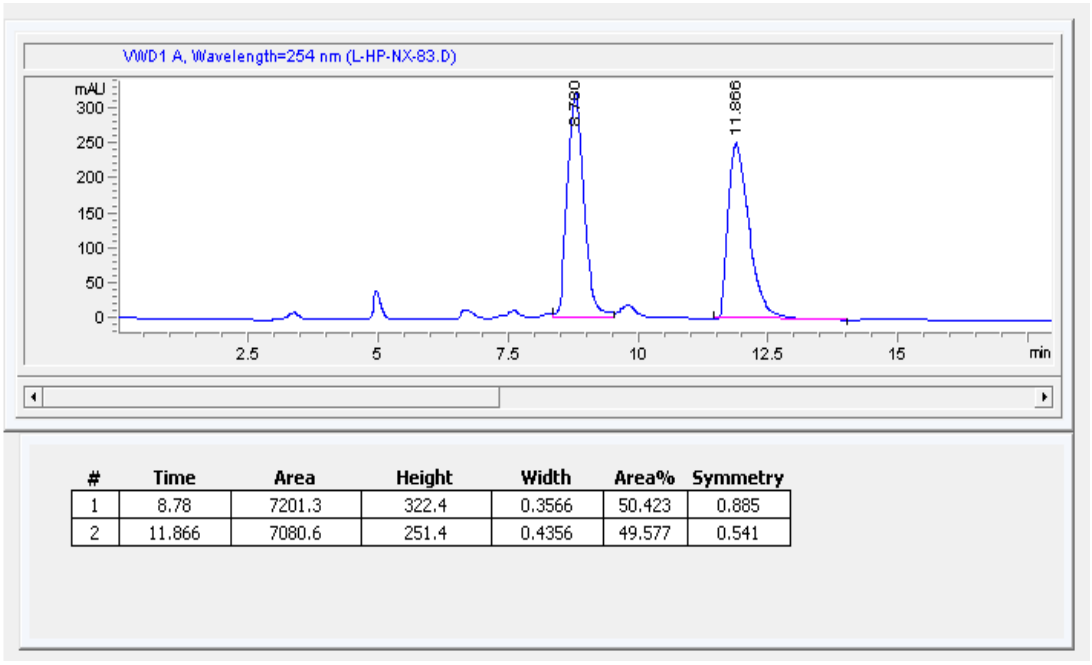
#	Time	Area	Height	Width	Area%	Symmetry
1	35.156	104815.7	3121.7	0.5097	95.982	0.472
2	39.262	4387.6	116.8	0.5773	4.018	0.606

^{1}H and ^{13}C NMR of 6t

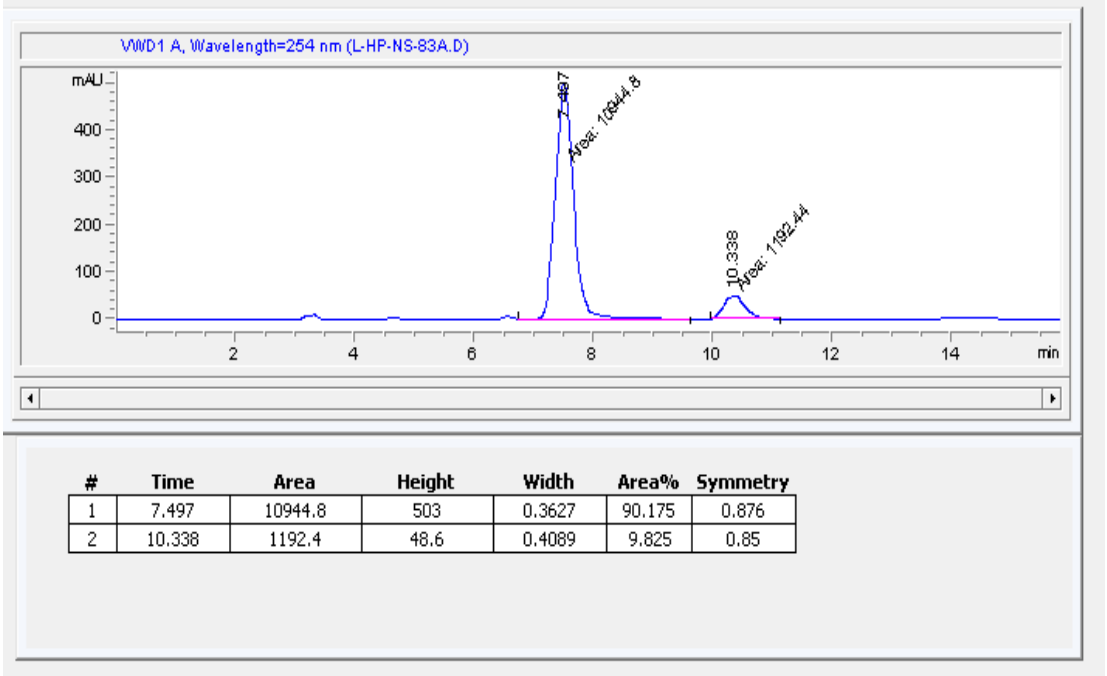




HPLC of 6t

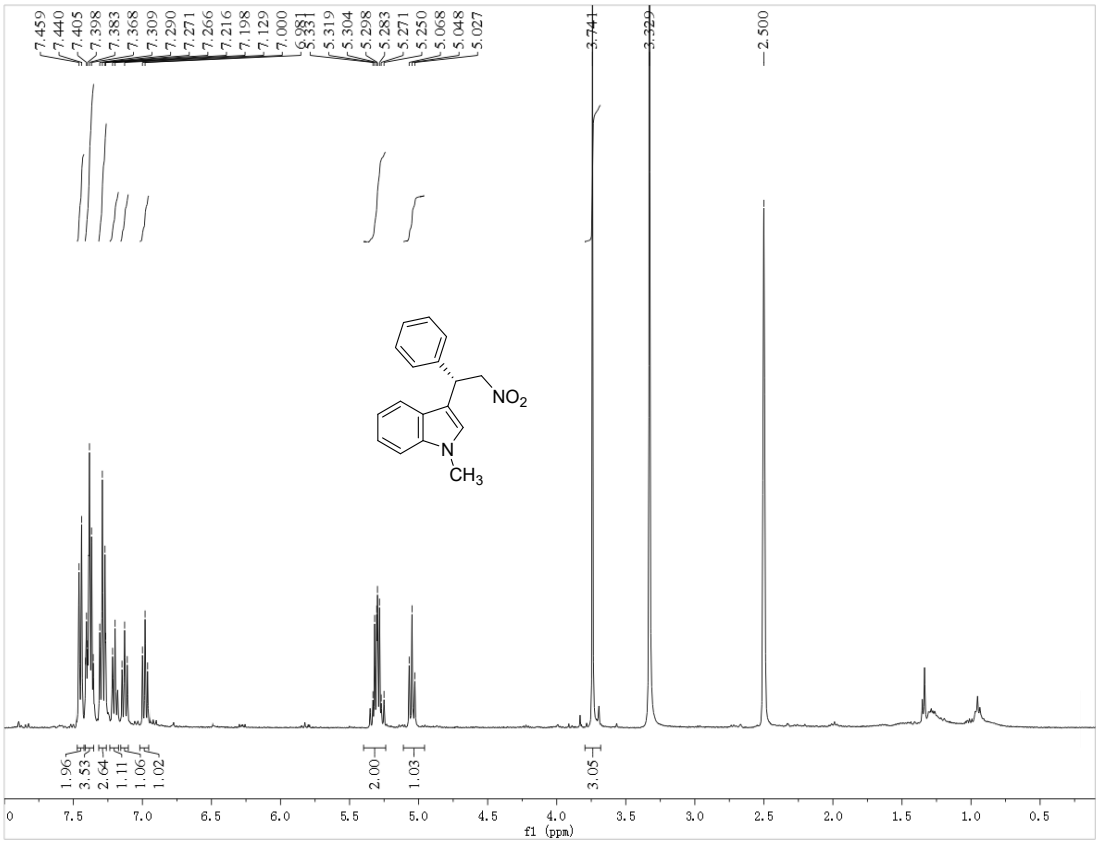


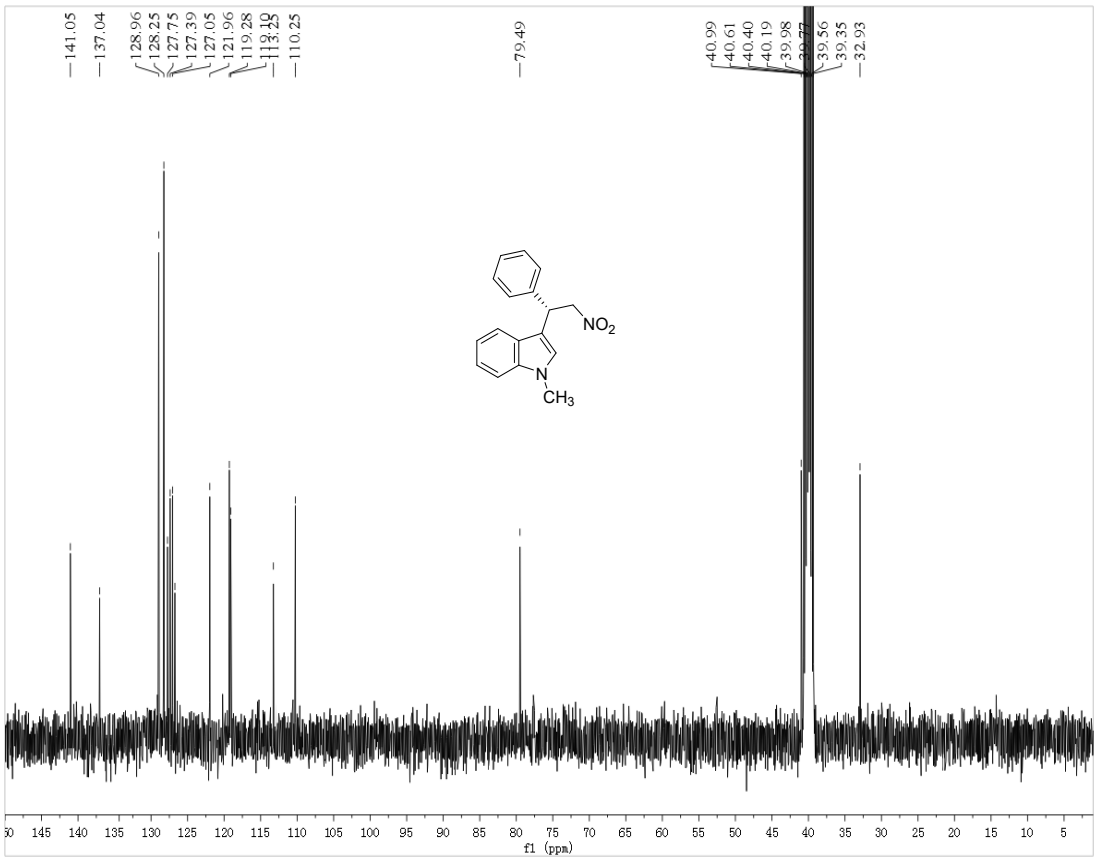
#	Time	Area	Height	Width	Area%	Symmetry
1	8.78	7201.3	322.4	0.3566	50.423	0.885
2	11.866	7080.6	251.4	0.4356	49.577	0.541



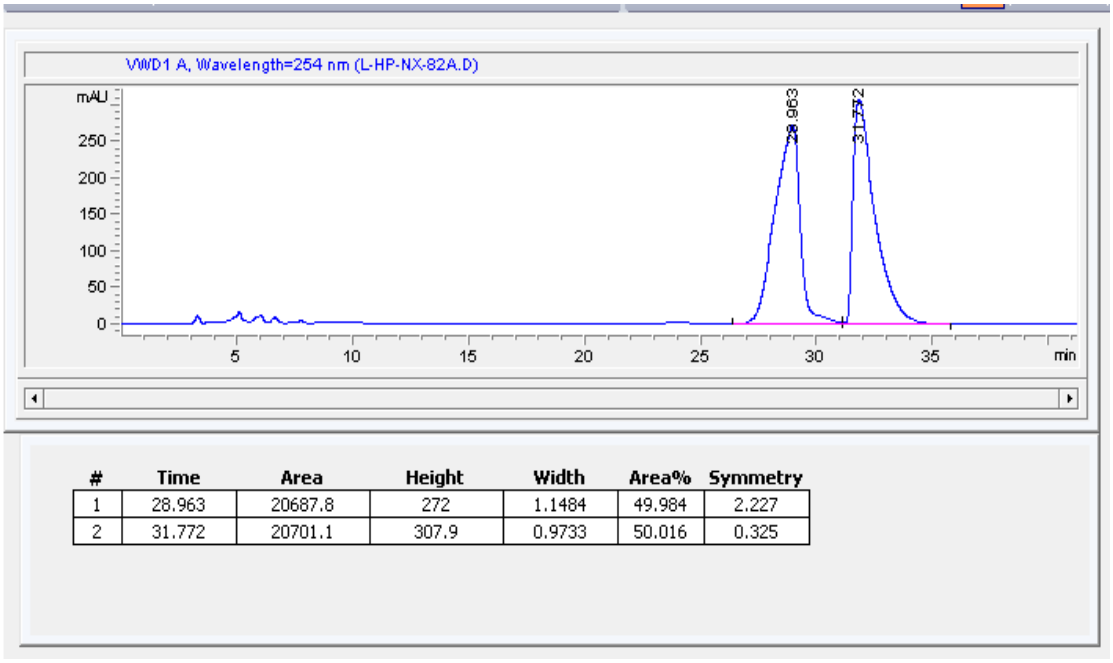
#	Time	Area	Height	Width	Area%	Symmetry
1	7.497	10944.8	503	0.3627	90.175	0.876
2	10.338	1192.4	48.6	0.4089	9.825	0.85

^{1}H and ^{13}C NMR of 6u

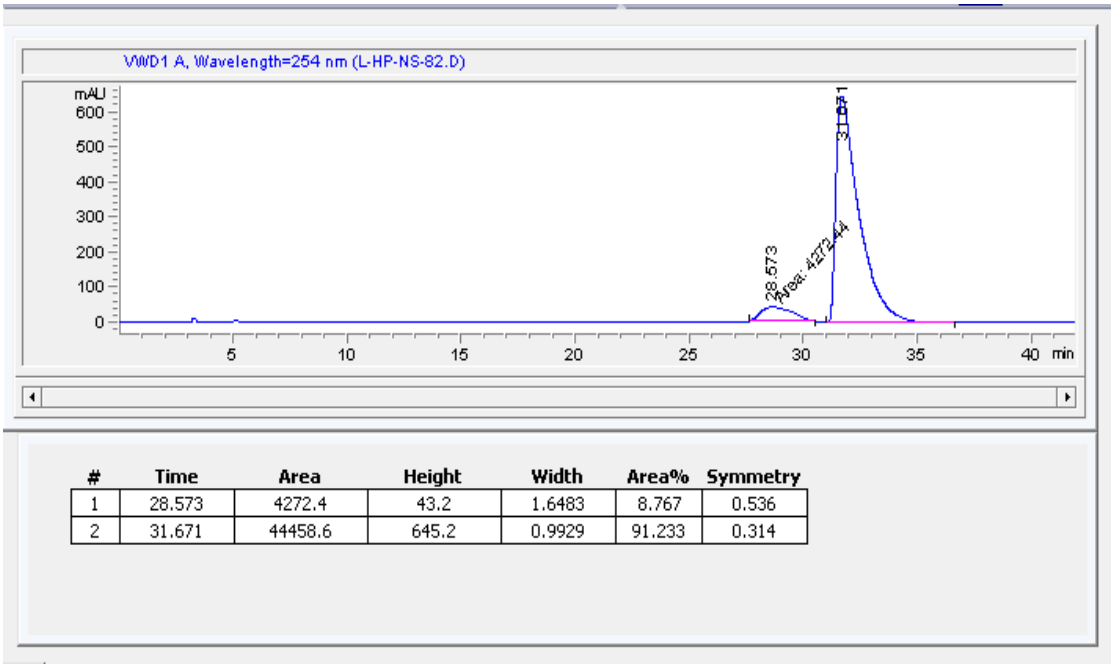




HPLC of 6u



#	Time	Area	Height	Width	Area%	Symmetry
1	28.963	20687.8	272	1.1484	49.984	2.227
2	31.772	20701.1	307.9	0.9733	50.016	0.325



#	Time	Area	Height	Width	Area%	Symmetry
1	28.573	4272.4	43.2	1.6483	8.767	0.536
2	31.671	44458.6	645.2	0.9929	91.233	0.314