

Electronic Supplementary Information for

Ni(II)/SpiroBox catalyzed asymmetric Friedel-Crafts alkylation of indoles with nitroalkenes

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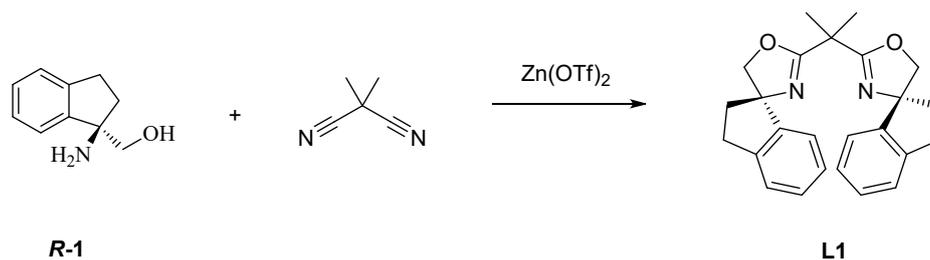
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1. Experimental Section

1.1. General

All the reagents were purchased from Aldrich, TCI, Energy chemical and other local suppliers, and used without purification. Toluene, methanol, dichloromethane, chloroform, acetonitrile and tetrahydrofuran were used without purification *unless* otherwise stated. All reactions were monitored by TLC. Chromatography refers to open column chromatography on silica gel (200-300 mesh). ¹H NMR spectra were recorded on 500 MHz, ¹³C NMR spectra were recorded on 126 MHz by using a Bruker Avance spectrometer. Chemical shifts were reported in parts per million (δ) relative to tetramethylsilane (TMS). Mass spectra were performed on an Ultima Global spectrometer with an ESI source. Optical rotations were measured on Rudolph Autopol IV-Tautomat polarimeter and reported as follows: $[\alpha]_D^{20}$ (c g/100 mL, solvent). Chiral HPLC analysis was performed using a Shimadzu LC-20AT UFLC. Substrates nitroalkenes were synthesized according to the already reported literatures^[1]. The (*R*)-indane-based chiral amino alcohol was synthesized according to reported literature^[2] and our pioneering studies^[3].

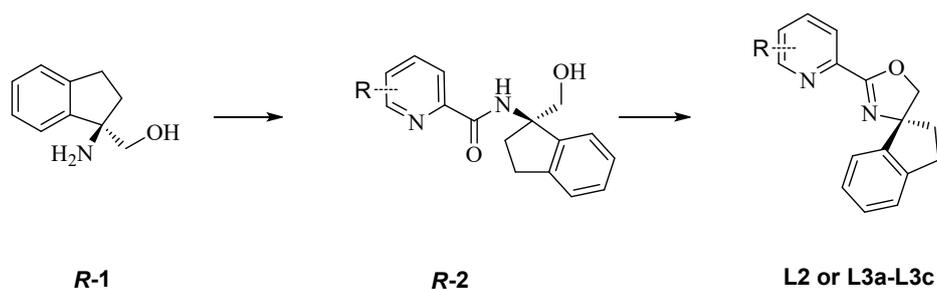
1.2. General procedure for synthesis of ligand **L1**



A 100-ml three-necked round-bottomed flask fitted with a reflux condenser was charged with 2, 2-dimethyl malononitrile (1.31 mmol), Zn(OTf)₂ (1.31 mmol) and chiral amino alcohol *R*-1 (2.62 mmol). The system was purged with argon and toluene (50 mL) was added. The solution was heated under reflux for 48 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by chromatography with petroleum ether/ethyl acetate 3:1 (v/v) to give **L1**.

Bis((*R*)-2,3-dihydro-5'*H*-spiro[indene-1,4'-oxazol]-2'-yl)propane (L1**)** White solid, m.p.: 66.1-67.5 °C, $[\alpha]_D^{20} = +18.4$ (c= 0.3, MeOH), 69% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.25-7.16 (m, 8H), 4.40 (d, *J* = 8.5 Hz, 2H), 4.34 (d, *J* = 8.5 Hz, 2H), 3.13-3.07 (m, 2H), 2.97-2.90 (m, 2H), 2.53-2.47 (m, 2H), 2.21-2.15 (m, 2H), 1.64 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 169.05, 146.30, 142.98, 128.11, 127.19, 124.60, 123.31, 80.28, 79.48, 39.58, 38.72, 30.21, 24.66. HRMS (ESI): calcd for C₂₅H₂₇N₂O₂ [M+H]⁺: 387.2073, found 387.2065, [M+Na]⁺ : 409.1892, found 409.1881.

1.3. General procedure for synthesis of ligands **L2** and **L3a-L3c**



To a solution of substituted 2-pyridine carboxylic acid or 2-Quinoline carboxylic acid (2.62 mmol) in anhydrous DCM (10 mL) was added *N*-hydroxybenzotriazole (HOBT) (2.88 mmol), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDCI·HCl) (2.88 mol), and triethylamine (4.32 mmol) at 0 °C sequentially. The reaction mixture was stirred at room temperature for 1 hour. Then chiral amino alcohol *R*-1 (2.62 mmol) was added and the reaction mixture was allowed warm to room temperature and stirred for 3 hours. The solvent was evaporated to obtain the intermediate *R*-2. The intermediate *R*-2 was used directly without further purification. To a solution of triphenylphosphine (3.14 mmol), and 2,3-dichloro-5,6-dicyano-1,4-benzoquinon (DDQ, 3.14 mmol) in DCM (10 mL) was added the intermediate *R*-2 slowly at 0 °C. The reaction mixture was warmed to room temperature and monitored by TLC. The reaction mixture was filtrated through celite, washed with 5% sodium hydroxide. The aqueous phase was extracted with DCM. The combined organic layers were dried over anhydrous sodium sulfate, filtrated, and concentrated under reduced pressure. The residue was purified by chromatography with petroleum ether/ethyl acetate 3:1 (v/v) to give **L2** or **L3a- L3c**.

(*R*)-2'-(Quinolin-2-yl)-2,3-dihydro-5'*H*-spiro[indene-1,4'-oxazole] (**L2**) White solid, m.p.: 132.5-133.2 °C, $[\alpha]_D^{20} = +89.7$ ($c = 0.3$, MeOH), 67% yield. $^1\text{H NMR}$

(500 MHz, CDCl₃) δ 8.31 (d, *J* = 8.5 Hz, 1H), 8.27-8.22 (m, 2H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.29-7.26 (m, 4H), 4.76 (d, *J* = 8.8 Hz, 1H), 4.67 (d, *J* = 8.8 Hz, 1H), 3.25-3.19 (m, 1H), 3.04-3.00 (m, 1H), 2.64-2.59 (m, 1H), 2.34-2.29 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 162.51, 147.63, 146.95, 145.74, 143.44, 136.72, 130.38, 130.08, 128.83, 128.38, 127.99, 127.57, 127.30, 124.80, 123.49, 121.14, 81.17, 79.27, 40.30, 30.30. HRMS (ESI): calcd for C₁₆H₁₄N₂O [M+Na]⁺ : 323.1160, found 323.1162.

(*R*)-2'-(Pyridin-2-yl)-2,3-dihydro-5'*H*-spiro[indene-1,4'-oxazole] (L3a) Yellow oil, $[\alpha]_D^{20} = +70.2$ (c = 0.4, MeOH), 49% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.74 (d, *J* = 4.9 Hz, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.43-7.40 (m, 1H), 7.27 (d, *J* = 11.5 Hz, 4H), 4.69 (d, *J* = 8.8 Hz, 1H), 4.59 (d, *J* = 8.8 Hz, 1H), 3.23-3.18 (m, 1H), 3.00-2.98 (m, 1H), 2.59-2.55 (m, 1H), 2.30-2.26 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 162.36, 149.96, 147.02, 145.93, 143.61, 136.83, 128.49, 127.39, 125.83, 124.92, 124.39, 123.60, 81.21, 79.12, 40.38, 30.44. HRMS (ESI): calcd for C₁₆H₁₄N₂O [M+Na]⁺ : 273.1004, found 273.1008.

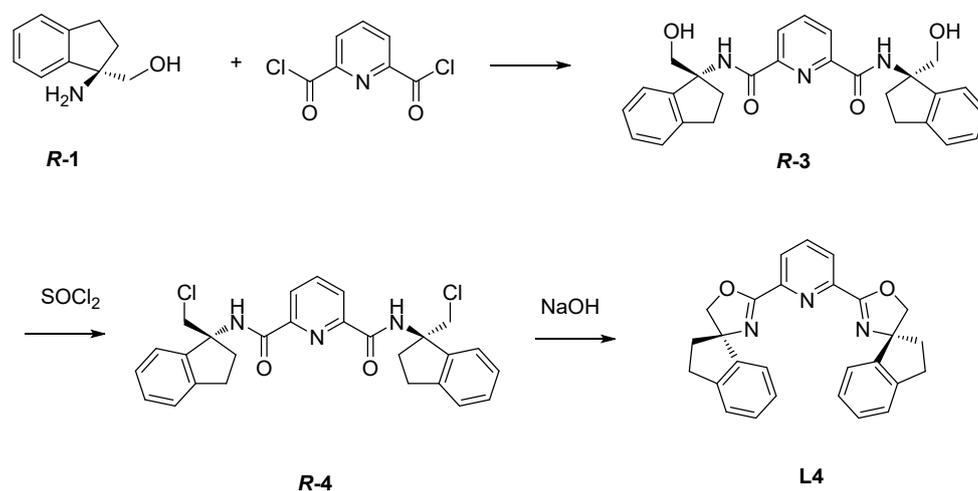
(*R*)-2'-(5-(Trifluoromethyl)pyridin-2-yl)-2,3-dihydro-5'*H*-spiro[indene-1,4'-oxazole] (L3b) White solid, m.p.: 104.5-105.3 °C, $[\alpha]_D^{20} = +87.5$ (c = 0.2, MeOH), 55% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.90 (s, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 7.95 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.23-7.12 (m, 4H), 4.64 (d, *J* = 8.8 Hz, 1H), 4.53 (d, *J* = 8.9 Hz, 1H), 3.17-3.11 (m, 1H), 2.92-2.89 (m, 1H), 2.53-2.47 (m, 1H), 2.23-2.18 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 161.09, 149.96, 146.62 (q, *J* = 4.1 Hz), 145.32, 143.46, 133.96 (q, *J* = 3.6 Hz), 128.49, 128.10 (q, *J* = 33.2 Hz), 127.27, 124.83, 123.94,

123.31, 123.14 (q, $J = 273.4$ Hz), 81.24, 79.09, 40.14, 30.25. HRMS (ESI): calcd for $C_{17}H_{13}F_3N_2O$ $[M+Na]^+$: 341.0878, found 341.0883.

(*R*)-2'-(5-Methoxypyridin-2-yl)-2,3-dihydro-5'*H*-spiro[indene-1,4'-oxazole]

(L3c) White solid, m.p.: 107.7-108.5 °C, $[\alpha]_D^{20} = +46.4$ ($c = 0.2$, MeOH), 56% yield. 1H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, $J = 2.9$ Hz, 1H), 8.08 (d, $J = 8.7$ Hz, 1H), 7.28-7.20 (m, 5H), 4.65 (d, $J = 8.7$ Hz, 1H), 4.56 (d, $J = 8.4$ Hz, 1H), 3.92 (s, 3H), 3.24-3.18 (m, 1H), 3.01-2.95 (m, 1H), 2.59-2.54 (m, 1H), 2.30-2.25 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.96, 157.23, 145.95, 143.37, 139.11, 137.81, 128.20, 127.16, 125.15, 124.69, 123.41, 120.08, 80.91, 78.87, 55.75, 40.20, 30.24. HRMS (ESI): calcd for $C_{17}H_{16}N_2O_2$ $[M+H]^+$: 281.1290, found 281.1288, $[M+Na]^+$: 303.1109, found 303.1106.

1.4. General procedure for synthesis of ligand **L4**



Pyridine-2,6-dicarboxylic acid (5 mmol) was treated with $SOCl_2$ (10 mL) at 80 °C over night. Excess $SOCl_2$ was then removed under reduced pressure to give the acid chloride as a white solid (100% yield). A solution of crude 2,6-pyridine carbonyl

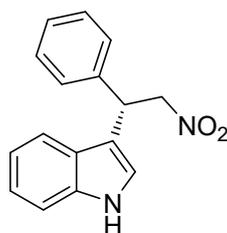
dichloride in DCM was slowly added to a solution of *R*-1 (10 mmol) and triethylamine (30 mmol) in DCM (20 mL) at 0 °C for 2h. The reaction mixture was warmed to room temperature, SOCl₂ (20 mmol) was added. The mixture was heated to reflux for 2 h and then poured into ice water. The organic layer was washed with brine and Na₂CO₃ aqueous and then dried over anhydrous Na₂SO₄. After evaporating the solvent, The solid was treated with alcohol (20 mL) and NaOH (40 mmol) at room temperature for 24h. The mixture was extracted with DCM and brine, the organic layer was dried over Na₂SO₄. After evaporating the solvent, the crude product was purified by chromatography with ether/ethyl acetate 2:1 (v/v) to give **L4** as white solid.

2,6-Bis((*R*)-2,3-dihydro-5'*H*-spiro[indene-1,4'-oxazol]-2'-yl)pyridine (L4)

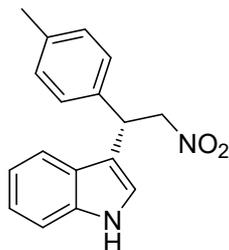
White solid, m.p.: 177.1-176.4 °C, $[\alpha]_D^{20} = +16.5$ (c = 0.3, MeOH), 47% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.28 (d, *J* = 7.8 Hz, 2H), 7.86 (t, *J* = 7.8 Hz, 1H), 7.25 (dd, *J* = 14.4, 2.5 Hz, 8H), 4.68 (d, *J* = 8.9 Hz, 2H), 4.61 (d, *J* = 8.8 Hz, 2H), 3.20-3.14 (m, 2H), 3.01-2.95 (m, 2H), 2.55-2.50 (m, 2H), 2.29-2.24 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 161.90, 146.81, 145.60, 143.40, 137.40, 128.39, 127.30, 126.27, 124.81, 123.46, 81.01, 79.19, 40.33, 30.23. HRMS (ESI): calcd for C₂₇H₂₃N₃O₂ [M+H]⁺ : 422.1869, found 422.1866, [M+Na]⁺ : 444.1688, found 444.1679.

2. General procedure for asymmetric Friedel-Crafts alkylation reaction

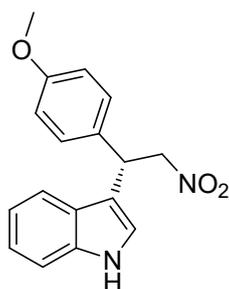
L1 (4.6 mg, 0.012 mmol) and Ni(ClO₄)₂·6H₂O (3.6 mg, 0.01 mmol) were dissolved in CHCl₃ (1.0 mL) in a Schlenk tube under an Ar atmosphere at room temperature for 1h. Then nitroalkene (0.15 mmol) was added and the mixture was stirred at 0 °C for 30 min before indole (0.1 mmol) was added. The mixture was stirred at 0 °C until the reaction was completed (monitored by TLC). The solvent was removed under vacuum, and the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate 3:1 (v/v) to give the product.



(S)-3-(2-nitro-1-phenylethyl)-1H-indole (1a) oil, $[\alpha]_D^{20} = +28.8$ (c= 0.2, DCM), 98% yield. Determined by chiral HPLC analysis (OD-H, isopropanol/hexane =35/65, 0.8 mL/min, UV 254 nm): 93% ee, retention times $t_r = 25.586$ min for (*S*)-isomer (major), $t_r = 29.235$ min for (*R*)-isomer (minor). ¹H NMR (500 MHz, CDCl₃), δ 8.05 (s, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.37-7.28 (m, 5H), 7.27-7.23 (m, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 2.5 Hz, 1H), 5.19 (t, *J* = 8.0 Hz, 1H), 5.06 (dd, *J* = 12.6, 7.6 Hz, 1H), 4.94 (dd, *J* = 12.6, 8.4 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 139.21, 136.50, 128.94, 127.79, 127.59, 126.12, 122.71, 121.64, 119.97, 118.94, 114.41, 111.43, 79.55, 41.57. HRMS (ESI): calcd for C₁₆H₁₄N₂O₂ [M+Na]⁺: 289.0953, found 289.0950.

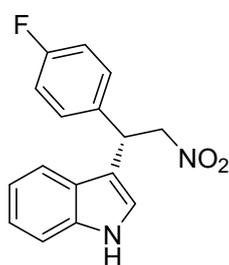


(S)-3-(2-nitro-1-(*p*-tolylethyl)-1*H*-indole (1b) oil, $[\alpha]_D^{20} = +14.7$ ($c = 0.2$, DCM), 98% yield. Determined by chiral HPLC analysis (OD-H, isopropanol/hexane =35/65, 0.8 mL/min, UV 254 nm): 89% ee, retention times $t_r = 24.840$ min for (*S*)-isomer (major), $t_r = 28.184$ min for (*R*)-isomer (minor). ^1H NMR (500 MHz, CDCl_3) δ 8.06 (s, 1H), 7.48 (d, $J = 8.0$ Hz, 1H), 7.35 (d, $J = 8.1$ Hz, 1H), 7.22 (q, $J = 8.1$ Hz, 3H), 7.15 (d, $J = 7.8$ Hz, 2H), 7.10 (t, $J = 7.5$ Hz, 1H), 7.01 (d, $J = 2.5$ Hz, 1H), 5.17 (t, $J = 8.0$ Hz, 1H), 5.06 (dd, $J = 12.4, 7.6$ Hz, 1H), 4.93 (dd, $J = 12.4, 8.4$ Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 137.23, 136.50, 136.15, 129.62, 127.64, 126.14, 122.68, 121.55, 119.94, 118.98, 114.66, 111.38, 79.65, 41.22, 21.07. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2$ $[\text{M}+\text{Na}]^+$: 303.1109, found 303.1101.

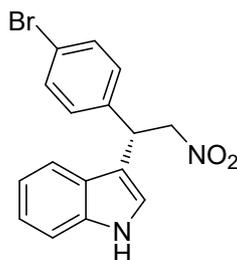


(S)-3-(1-(4-methoxyphenyl)-2-nitroethyl)-1*H*-indole (1c), solid, m.p.: 133.8-135.4 °C, $[\alpha]_D^{20} = +14.7$ ($c = 0.2$, MeOH), 96% yield. Determined by chiral HPLC analysis (OD-H, isopropanol/hexane =35/65, 0.8 mL/min, UV 254 nm): 89% ee, retention times $t_r = 16.682$ min for (*S*)-isomer (major), $t_r = 23.782$ min for (*R*)-isomer (minor).

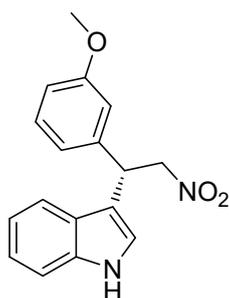
^1H NMR (500 MHz, DMSO-d_6) δ 10.93 (s, 1H), 7.38 (d, $J = 7.9$ Hz, 1H), 7.30 (d, $J = 2.5$ Hz, 1H), 7.25 (t, $J = 8.0$ Hz, 3H), 7.00-6.92 (m, 1H), 6.84 (t, $J = 7.5$ Hz, 1H), 6.75 (d, $J = 8.6$ Hz, 2H), 5.28-5.08 (m, 2H), 4.89 (t, $J = 8.2$ Hz, 1H), 3.60 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 158.23, 136.31, 132.68, 128.99, 126.09, 122.19, 121.44, 118.73, 118.56, 113.92, 113.89, 111.60, 79.50, 55.09, 40.12. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$: 319.1059, found 319.1055.



(S)-3-(1-(4-fluorophenyl)-2-nitroethyl)-1H-indole (1d), oil, $[\alpha]_D^{20} = +43.1$ ($c = 0.2$, DCM), 98% yield. Determined by chiral HPLC analysis (OD-H, isopropanol/hexane = 35/65, 0.8 mL/min, UV 254 nm): 88% ee, retention times $t_r = 14.935$ min for (*S*)-isomer (major), $t_r = 34.363$ min for (*R*)-isomer (minor). ^1H NMR (500 MHz, CDCl_3) δ 8.11 (s, 1H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.36 (d, $J = 8.2$ Hz, 1H), 7.31 (dd, $J = 8.6, 5.4$ Hz, 2H), 7.24 (t, $J = 7.7$ Hz, 1H), 7.12 (t, $J = 7.5$ Hz, 1H), 7.06-6.97 (m, 3H), 5.19 (t, $J = 8.0$ Hz, 1H), 5.06 (dd, $J = 12.5, 7.4$ Hz, 1H), 4.91 (dd, $J = 12.5, 8.6$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 161.10 (d, $J = 246.1$ Hz), 136.53, 135.0 (d, $J = 3.2$ Hz), 129.43 (d, $J = 8.1$ Hz), 125.97, 122.84, 121.53, 120.07, 118.88, 115.86 (d, $J = 21.5$ Hz), 114.16, 111.56, 99.99, 79.58, 40.90. HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{13}\text{FN}_2\text{O}_2$ $[\text{M}+\text{Na}]^+$: 307.0859, found 307.0852.

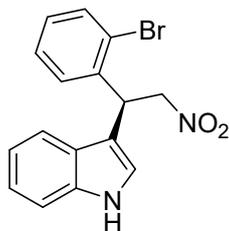


(S)-3-(1-(4-bromophenyl)-2-nitroethyl)-1H-indole (1e), oil, $[\alpha]_D^{20} = -20.6$ ($c = 0.3$, DCM), 97% yield. Determined by chiral HPLC analysis (OD-H, isopropanol/hexane = 35/65, 0.8 mL/min, UV 254 nm): 94% ee, retention times $t_r = 27.632$ min for (*S*)-isomer (major), $t_r = 41.936$ min for (*R*)-isomer (minor). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.12 (s, 1H), 7.45 (d, $J = 8.5$ Hz, 2H), 7.39 (dd, $J = 17.0, 8.1$ Hz, 2H), 7.22 (d, $J = 8.6$ Hz, 3H), 7.10 (t, $J = 7.5$ Hz, 1H), 7.02 (d, $J = 2.5$ Hz, 1H), 5.16 (t, $J = 8.0$ Hz, 1H), 5.06 (dd, $J = 12.6, 7.3$ Hz, 1H), 4.91 (dd, $J = 12.5, 8.5$ Hz, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 138.31, 136.51, 132.09, 129.55, 125.91, 122.91, 121.60, 121.55, 120.14, 118.82, 113.80, 111.57, 79.23, 41.04. HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{13}\text{BrN}_2\text{O}_2$ $[\text{M}+\text{Na}]^+$: 367.0058, found 367.0051.

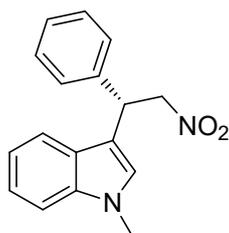


(S)-3-(1-(3-methoxyphenyl)-2-nitroethyl)-1H-indole (1f), oil, $[\alpha]_D^{20} = +19.3$ ($c = 0.2$, DCM), 97% yield. Determined by chiral HPLC analysis (OD-H, isopropanol/hexane = 35/65, 0.8 mL/min, UV 254 nm): 94% ee, retention times $t_r = 25.490$ min for (*S*)-isomer (major), $t_r = 38.356$ min for (*R*)-isomer (minor). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ

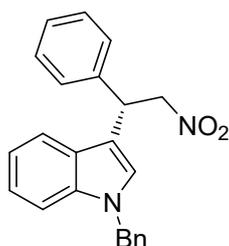
8.12 (s, 1H), 7.52 (d, $J = 8.0$ Hz, 1H), 7.37 (d, $J = 8.1$ Hz, 1H), 7.29 (t, $J = 7.9$ Hz, 1H), 7.24 (t, $J = 7.6$ Hz, 1H), 7.13 (t, $J = 7.5$ Hz, 1H), 7.02 (d, $J = 2.5$ Hz, 1H), 6.98 (d, $J = 7.7$ Hz, 1H), 6.93 (t, $J = 2.2$ Hz, 1H), 6.85 (dd, $J = 8.2, 2.6$ Hz, 1H), 5.21 (t, $J = 8.0$ Hz, 1H), 5.08 (dd, $J = 12.6, 7.7$ Hz, 1H), 4.97 (dd, $J = 12.5, 8.3$ Hz, 1H), 3.80 (d, $J = 2.5$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.95, 140.90, 136.48, 129.97, 126.13, 122.69, 121.65, 120.07, 119.97, 118.91, 114.22, 114.07, 112.53, 111.45, 79.49, 55.24, 41.54. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$: 319.1059, found 319.1055.



(*S*)-3-(1-(2-bromophenyl)-2-nitroethyl)-1*H*-indole (1g), oil, $[\alpha]_D^{20} = +58.8$ ($c = 0.3$, DCM), 97% yield. Determined by chiral HPLC analysis (OD-H, isopropanol/hexane = 35/65, 0.8 mL/min, UV 254 nm): 82% ee, retention times $t_r = 19.200$ min for (*R*)-isomer (minor), $t_r = 30.300$ min for (*S*)-isomer (major). ^1H NMR (500 MHz, CDCl_3) δ 8.10 (s, 1H), 7.65 (d, $J = 7.9$ Hz, 1H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.35 (d, $J = 8.2$ Hz, 1H), 7.22 (dd, $J = 11.8, 5.8$ Hz, 3H), 7.15-7.06 (m, 3H), 5.80-5.71 (m, 1H), 5.03-4.89 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 138.10, 136.49, 133.51, 129.20, 129.18, 127.98, 126.22, 124.52, 122.83, 122.01, 120.06, 119.04, 113.34, 111.47, 77.84, 40.64. HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{13}\text{BrN}_2\text{O}_2$ $[\text{M}+\text{Na}]^+$: 367.0058, found 367.0050.

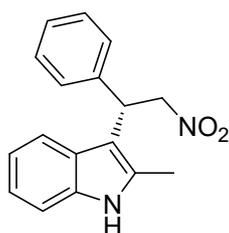


(S)-1-methyl-3-(2-nitro-1-phenylethyl)-1H-indole (1h), oil, $[\alpha]_D^{20} = +28.8$ ($c = 0.3$, DCM), 99% yield. Determined by chiral HPLC analysis (AS-H, isopropanol/hexane = 5/95, 0.8 mL/min, UV 254 nm): 94% ee, retention times $t_r = 14.722$ min for (*R*)-isomer (minor), $t_r = 21.223$ min for (*S*)-isomer (major). ^1H NMR (500 MHz, CDCl_3) δ 7.46 (d, $J = 8.0$ Hz, 1H), 7.37-7.27 (m, 5H), 7.23 (dd, $J = 16.2, 8.2$ Hz, 2H), 7.08 (t, $J = 7.4$ Hz, 1H), 6.85 (s, 1H), 5.18 (t, $J = 8.0$ Hz, 1H), 5.03 (dd, $J = 12.5, 7.6$ Hz, 1H), 4.91 (dd, $J = 12.6, 8.5$ Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 139.49, 137.34, 128.98, 127.82, 127.58, 126.62, 126.44, 122.28, 119.52, 119.05, 112.82, 109.62, 79.60, 41.58, 32.85. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2$ $[\text{M}+\text{Na}]^+$: 303.1109, found 303.1105.

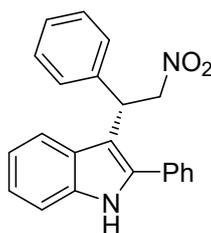


(S)-1-benzyl-3-(2-nitro-1-phenylethyl)-1H-indole (1i), oil, $[\alpha]_D^{20} = +19.5$ ($c = 0.3$, DCM), 96% yield. Determined by chiral HPLC analysis (AS-H, isopropanol/hexane = 5/95, 0.8 mL/min, UV 254 nm): 97% ee, retention times $t_r = 12.744$ min for (*R*)-isomer (minor), $t_r = 25.048$ min for (*S*)-isomer (major). ^1H NMR (500 MHz, CDCl_3) δ 7.51 (d, $J = 8.0$ Hz, 1H), 7.41-7.35 (m, 5H), 7.34-7.27 (m, 4H), 7.24-7.19 (m, 1H),

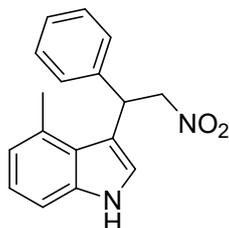
7.11 (t, $J = 5.9$ Hz, 3H), 7.02 (s, 1H), 5.30 (s, 2H), 5.25 (t, $J = 8.0$ Hz, 1H), 5.08 (dd, $J = 12.5, 7.6$ Hz, 1H), 4.97 (dd, $J = 12.5, 8.5$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 139.35, 137.28, 137.01, 128.99, 128.90, 127.83, 127.78, 127.61, 126.89, 126.71, 125.78, 122.51, 119.79, 119.22, 113.54, 110.11, 79.66, 50.13, 41.63. HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_2$ $[\text{M}+\text{Na}]^+$: 379.1422, found 379.1417.



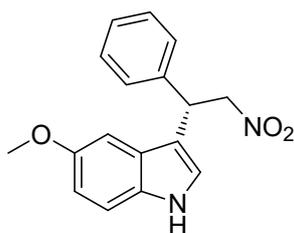
(S)-2-methyl-3-(2-nitro-1-phenylethyl)-1H-indole (1j), solid, m.p.: 151.9-153.3 °C, $[\alpha]_D^{20} = -3.3$ ($c = 0.2$, MeOH), 95% yield. Determined by chiral HPLC analysis (IC-3, isopropanol/hexane = 5/95, 0.8 mL/min, UV 254 nm): 10% ee, retention times $t_r = 12.328$ min for (*S*)-isomer (major), $t_r = 15.956$ min for (*R*)-isomer (minor). ^1H NMR (500 MHz, CDCl_3) δ 7.81 (s, 1H), 7.35 (d, $J = 5.6$ Hz, 1H), 7.32-7.23 (m, 4H), 7.21 (d, $J = 6.6$ Hz, 2H), 7.12-7.06 (m, 1H), 7.01 (t, $J = 6.2$ Hz, 1H), 5.22-5.15 (m, 2H), 5.12-5.06 (m, 1H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 139.54, 135.43, 132.94, 128.82, 127.35, 127.12, 126.86, 121.35, 119.76, 118.62, 110.77, 108.80, 78.66, 40.49, 11.98. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2$ $[\text{M}+\text{Na}]^+$: 303.1109, found 303.1108.



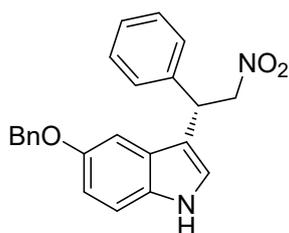
(S)-3-(2-nitro-1-phenylethyl)-2-phenyl-1H-indole (1k), oil, $[\alpha]_D^{20} = -5.6$ ($c = 0.3$, DCM), 89% yield. Determined by chiral HPLC analysis (OF, isopropanol/hexane = 10/90, 0.8 mL/min, UV 254 nm): 11% ee, retention times $t_r = 17.232$ min for (*R*)-isomer (minor), $t_r = 21.977$ min for (*S*)-isomer (major). ^1H NMR (500 MHz, CDCl_3) δ 8.16 (s, 1H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.50-7.41 (m, 5H), 7.39 (d, $J = 8.1$ Hz, 1H), 7.36 (d, $J = 7.5$ Hz, 2H), 7.31 (t, $J = 7.5$ Hz, 2H), 7.27-7.19 (m, 2H), 7.13 (t, $J = 7.6$ Hz, 1H), 5.34 (t, $J = 7.9$ Hz, 1H), 5.22-5.12 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 139.40, 136.49, 135.57, 131.69, 128.48, 128.41, 128.31, 128.16, 126.99, 126.71, 126.54, 122.01, 119.83, 119.48, 110.94, 109.09, 78.60, 40.31. HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2$ $[\text{M}+\text{Na}]^+$: 365.1266, found 365.1255.



4-Methyl-3-(2-nitro-1-phenylethyl)-1H-indole (1l), solid, m.p.: 109.1-110.6 °C, 83% yield. Determined by chiral HPLC analysis (OD-H, isopropanol/hexane = 35/65, 0.8 mL/min, UV 254 nm): 0 ee, retention times $t_r = 14.260$ min and $t_r = 15.912$ min. ^1H NMR (500 MHz, CDCl_3) δ 8.15 (s, 1H), 7.38-7.32 (m, 2H), 7.32-7.28 (m, 3H), 7.24 (d, $J = 8.1$ Hz, 1H), 7.16-7.07 (m, 2H), 6.85 (d, $J = 7.1$ Hz, 1H), 5.59 (t, $J = 8.1$ Hz, 1H), 5.01 (dd, $J = 12.7, 8.6$ Hz, 1H), 4.89 (dd, $J = 12.8, 7.6$ Hz, 1H), 2.60 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 140.19, 136.93, 130.71, 129.00, 128.08, 127.51, 125.05, 122.79, 121.82, 121.56, 114.68, 109.28, 80.44, 42.24, 20.59. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2$ $[\text{M}+\text{Na}]^+$: 303.1109, found 303.1100.

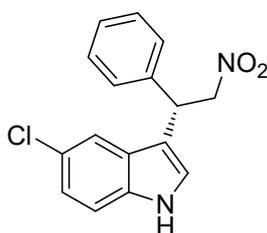


(S)-5-methoxy-3-(2-nitro-1-phenylethyl)-1H-indole (1m), oil, $[\alpha]_D^{20} = -15.7$ ($c = 0.2$, DCM), 92% yield. Determined by chiral HPLC analysis (OD-H, isopropanol/hexane = 35/65, 0.8 mL/min, UV 254 nm): 85% ee, retention times $t_r = 11.193$ min for (*R*)-isomer (minor), $t_r = 11.967$ min for (*S*)-isomer (major). ^1H NMR (500 MHz, CDCl_3) δ 7.98 (s, 1H), 7.34-7.24 (m, 4H), 7.23-7.20 (m, 1H), 7.17-7.12 (m, 1H), 6.90 (d, $J = 2.6$ Hz, 1H), 6.85-6.77 (m, 2H), 5.09 (t, $J = 8.0$ Hz, 1H), 4.98 (dd, $J = 12.5, 7.7$ Hz, 1H), 4.87 (dd, $J = 12.5, 8.4$ Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 154.16, 139.23, 131.64, 128.97, 127.81, 127.61, 126.59, 122.39, 113.96, 112.69, 112.23, 100.87, 79.54, 55.89, 41.56. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$: 319.1059, found 319.1043.

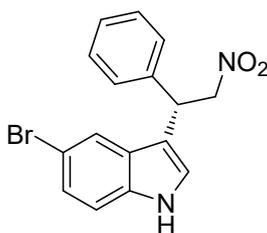


(S)-5-(benzyloxy)-3-(2-nitro-1-phenylethyl)-1H-indole (1n), oil, $[\alpha]_D^{20} = -36.9$ ($c = 0.3$, DCM), 94% yield. Determined by chiral HPLC analysis (AD-H, isopropanol/hexane = 35/65, 0.8 mL/min, UV 254 nm): 89% ee, retention times $t_r = 23.109$ min for (*R*)-isomer (minor), $t_r = 27.132$ min for (*S*)-isomer (major). ^1H NMR (500 MHz, CDCl_3) δ 7.93 (s, 1H), 7.41 (d, $J = 7.2$ Hz, 2H), 7.35 (t, $J = 6.5$ Hz, 2H),

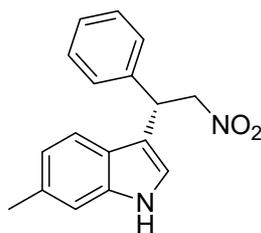
7.29 (dd, $J = 15.5, 4.2$ Hz, 5H), 7.24-7.21 (m, 1H), 7.14 (d, $J = 8.6$ Hz, 1H), 6.94-6.83 (m, 3H), 5.07 (t, $J = 8.1$ Hz, 1H), 4.98 (s, 2H), 4.97-4.91 (m, 1H), 4.89-4.81 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 153.30, 139.18, 137.46, 131.80, 128.99, 128.61, 127.95, 127.80, 127.73, 127.62, 126.54, 122.44, 114.01, 113.45, 112.23, 102.59, 79.47, 70.99, 41.58. HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$: 395.1372, found 395.1366.



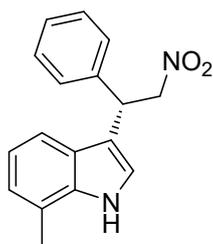
(S)-5-chloro-3-(2-nitro-1-phenylethyl)-1H-indole (10), oil, $[\alpha]_D^{20} = -25.7$ ($c = 0.2$, DCM), 92% yield. Determined by chiral HPLC analysis (AD-H, isopropanol/hexane = 10/90, 0.8 mL/min, UV 254 nm): 83% ee, retention times $t_r = 20.201$ min for (*R*)-isomer (minor), $t_r = 27.796$ min for (*S*)-isomer (major). ^1H NMR (500 MHz, CDCl_3) δ 8.13 (s, 1H), 7.38 (s, 1H), 7.34-7.24 (m, 5H), 7.21 (d, $J = 8.6$ Hz, 1H), 7.12 (d, $J = 8.6$ Hz, 1H), 7.03 (s, 1H), 5.11 (t, $J = 8.0$ Hz, 1H), 5.00 (dd, $J = 12.5, 8.1$ Hz, 1H), 4.90 (dd, $J = 12.5, 7.9$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 138.77, 134.83, 129.09, 127.80, 127.70, 127.21, 125.68, 123.09, 122.95, 118.38, 114.04, 112.53, 79.45, 41.36. HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{13}\text{ClN}_2\text{O}_2$ $[\text{M}+\text{Na}]^+$: 323.0563, found 323.0555.



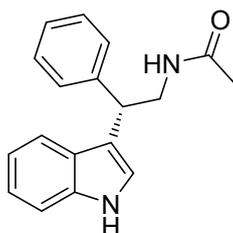
(S)-5-bromo-3-(2-nitro-1-phenylethyl)-1H-indole (1p), oil, $[\alpha]_D^{20} = -40.9$ ($c = 0.3$, DCM), 93% yield. Determined by chiral HPLC analysis (AD-H, isopropanol/hexane = 10/90, 0.8 mL/min, UV 254 nm): 90% ee, retention times $t_r = 20.539$ min for (*R*)-isomer (minor), $t_r = 26.912$ min for (*S*)-isomer (major). ^1H NMR (500 MHz, CDCl_3) δ 8.13 (s, 1H), 7.54 (s, 1H), 7.32-7.20 (m, 6H), 7.15 (d, $J = 8.6$ Hz, 1H), 6.99 (s, 1H), 5.10 (t, $J = 8.1$ Hz, 1H), 4.98 (dd, $J = 12.4, 8.1$ Hz, 1H), 4.89 (dd, $J = 12.5, 7.9$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 138.74, 135.10, 129.10, 127.87, 127.82, 127.70, 125.63, 122.84, 121.43, 113.91, 113.23, 112.99, 79.45, 41.32. HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{13}\text{BrN}_2\text{O}_2$ $[\text{M}+\text{Na}]^+$: 367.0058, found 367.0056.



(S)-6-methyl-3-(2-nitro-1-phenylethyl)-1H-indole (1q), solid, m.p.: 116.1-118.3 °C, $[\alpha]_D^{20} = -16.9$ ($c = 0.2$, MeOH), 90% yield. Determined by chiral HPLC analysis (OD-H, isopropanol/hexane = 35/65, 0.8 mL/min, UV 254 nm): 86% ee, retention times $t_r = 19.386$ min for (*R*)-isomer (minor), $t_r = 20.746$ min for (*S*)-isomer (major). ^1H NMR (500 MHz, CDCl_3) δ 7.98 (s, 1H), 7.36 (q, $J = 7.1, 6.7$ Hz, 5H), 7.31-7.26 (m, 2H), 7.19 (s, 1H), 6.99 (d, $J = 2.5$ Hz, 1H), 6.94 (d, $J = 8.1$ Hz, 1H), 5.20 (t, $J = 8.0$ Hz, 1H), 5.09 (dd, $J = 12.5, 7.6$ Hz, 1H), 4.97 (dd, $J = 12.4, 8.4$ Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 139.31, 136.98, 132.62, 128.92, 127.79, 127.54, 123.98, 121.75, 121.00, 118.60, 114.26, 111.35, 79.58, 41.64, 21.68. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2$ $[\text{M}+\text{Na}]^+$: 303.1109, found 303.1102.



(S)-7-methyl-3-(2-nitro-1-phenylethyl)-1H-indole (1r), oil, $[\alpha]_D^{20} = +11.8$ ($c = 0.2$, DCM), 86% yield. Determined by chiral HPLC analysis (AD-H, isopropanol/hexane =10/90, 1.0 mL/min, UV 254 nm): 87% ee, retention times $t_r = 7.972$ min for (*R*)-isomer (minor), $t_r = 8.446$ min for (*S*)-isomer (major). ^1H NMR (500 MHz, CDCl_3) δ 7.96 (s, 1H), 7.29 (q, $J = 7.1, 6.1$ Hz, 5H), 7.24-7.20 (m, 1H), 7.00-6.96 (m, 2H), 6.95 (d, $J = 2.6$ Hz, 1H), 5.15 (t, $J = 8.0$ Hz, 1H), 5.02 (dd, $J = 12.5, 7.7$ Hz, 1H), 4.90 (dd, $J = 12.5, 8.3$ Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 139.30, 136.11, 128.95, 127.81, 127.57, 125.69, 123.23, 121.39, 120.71, 120.22, 116.67, 114.85, 79.57, 41.71, 16.55. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2$ $[\text{M}+\text{Na}]^+$: 303.1109, found 303.1100.

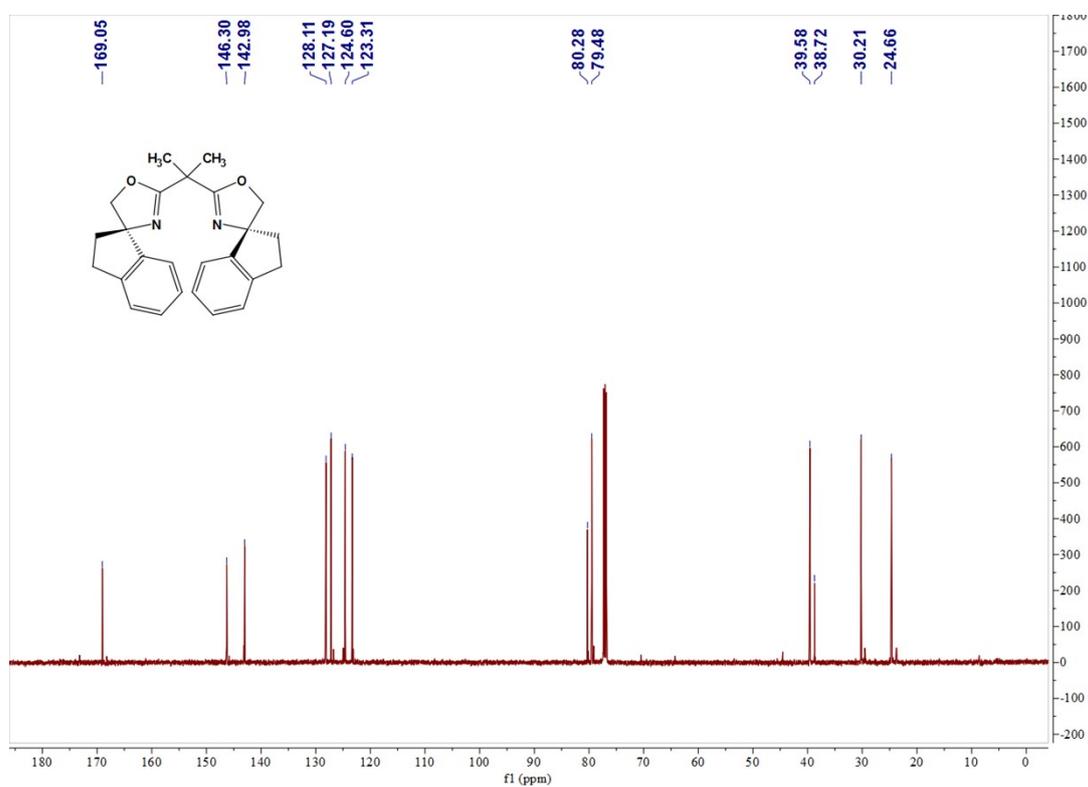
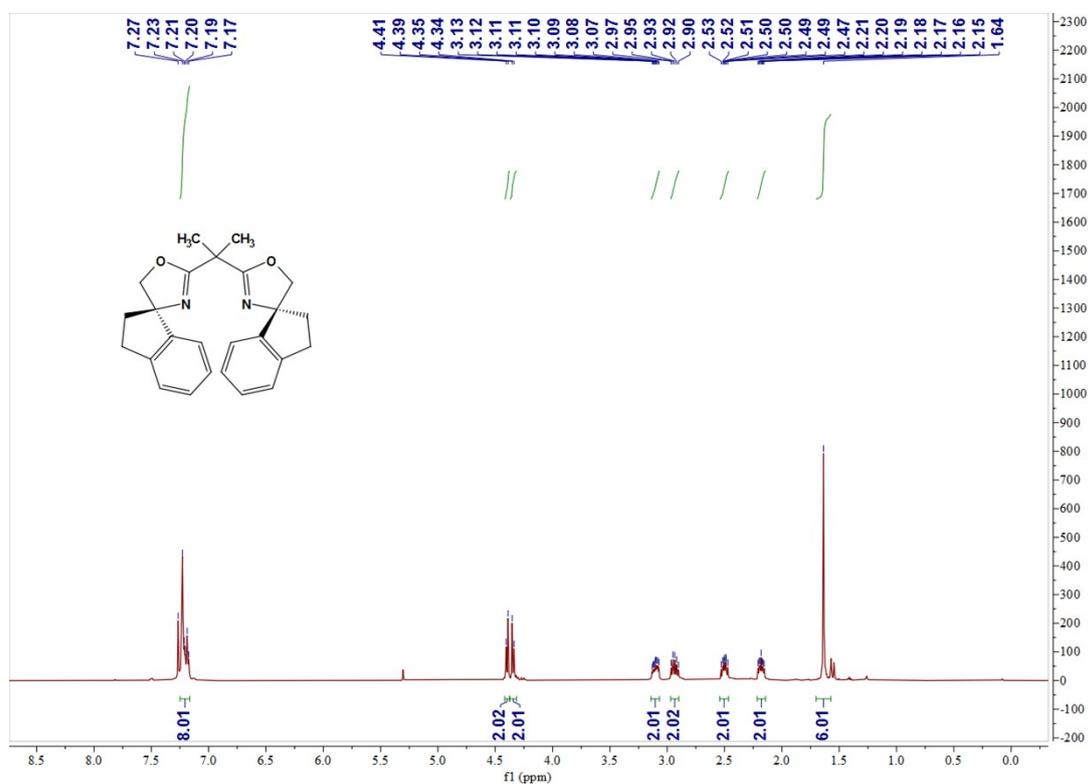


(S)-N-(2-(1H-indol-3-yl)-2-phenylethyl)acetamide (5), solid, m.p.: 155.2-156.0 °C, $[\alpha]_D^{20} = +34.7$ ($c = 0.5$, DCM), 75% yield. Determined by chiral HPLC analysis (AD-H, isopropanol/hexane =10/90, 1.0 mL/min, UV 254 nm): 83% ee, retention times $t_r = 21.722$ min for (*S*)-isomer (major), $t_r = 24.657$ min for (*R*)-isomer (minor). ^1H NMR (500 MHz, CDCl_3) δ 8.39 (s, 1H), 7.43 (d, $J = 7.9$ Hz, 1H), 7.34 (d, $J = 8.1$

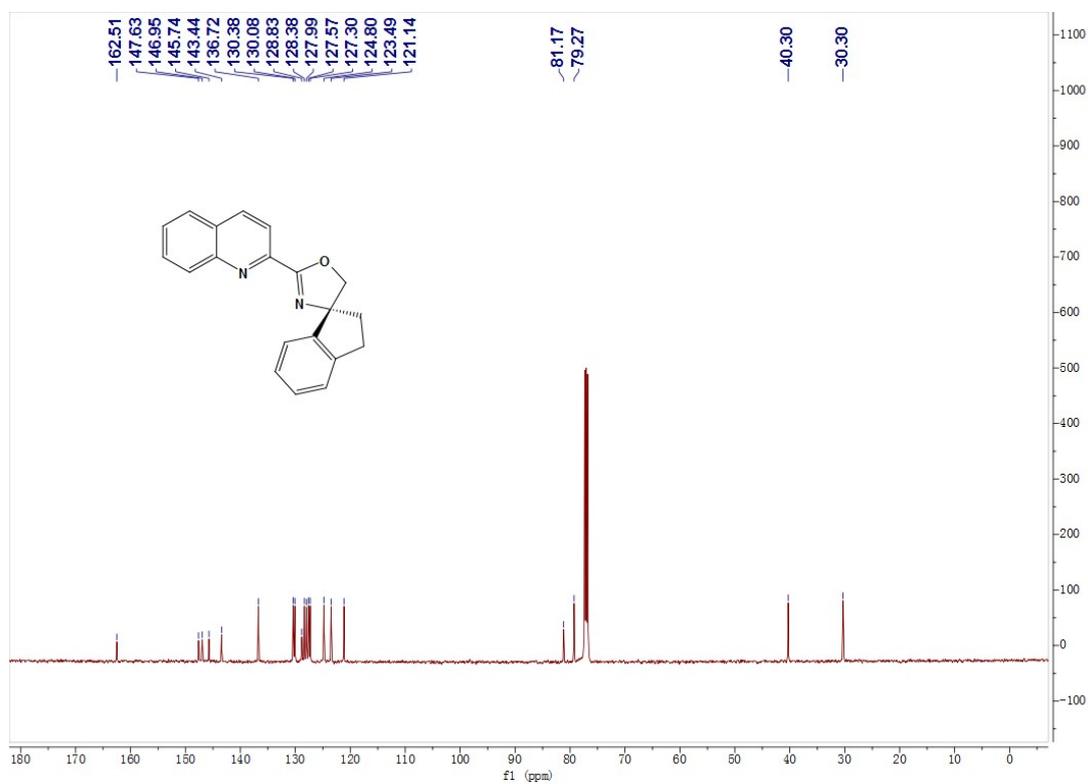
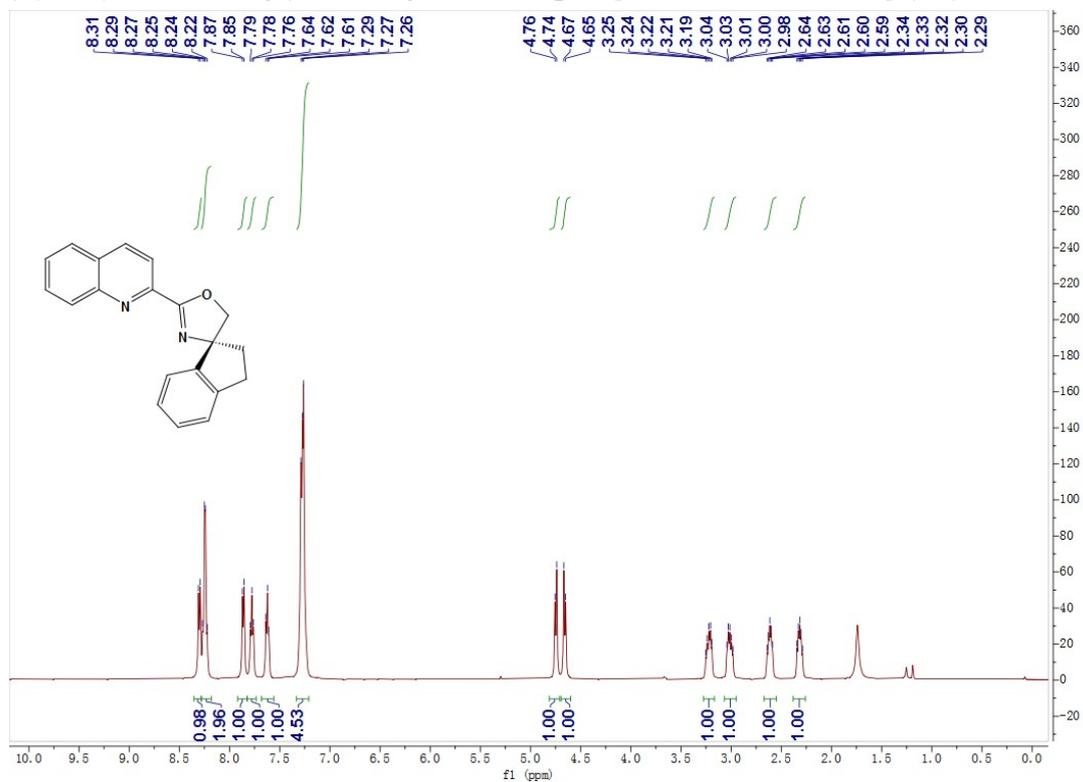
Hz, 1H), 7.28 (d, $J = 4.2$ Hz, 4H), 7.21 (q, $J = 4.2$ Hz, 1H), 7.15 (t, $J = 7.6$ Hz, 1H), 7.02 (dd, $J = 15.0, 7.5$ Hz, 2H), 5.56 (s, 1H), 4.41 (t, $J = 7.6$ Hz, 1H), 4.04 (ddd, $J = 13.6, 7.7, 6.0$ Hz, 1H), 3.79 (ddd, $J = 13.3, 7.6, 5.6$ Hz, 1H), 1.87 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 170.27, 142.17, 136.58, 128.67, 128.05, 126.85, 126.80, 122.25, 121.64, 119.52, 119.40, 116.56, 111.28, 44.24, 42.73, 23.39. HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}$ $[\text{M}+\text{Na}]^+$: 301.1317, found 301.1313.

3. NMR spectrum and HPLC trace of compounds

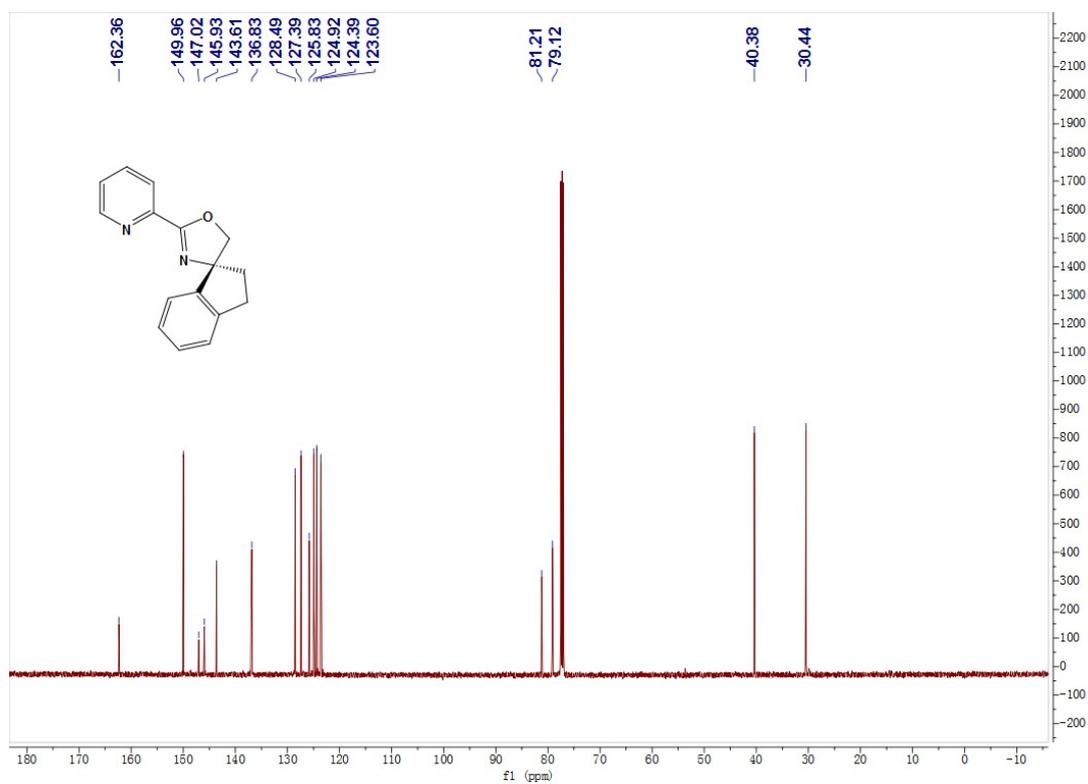
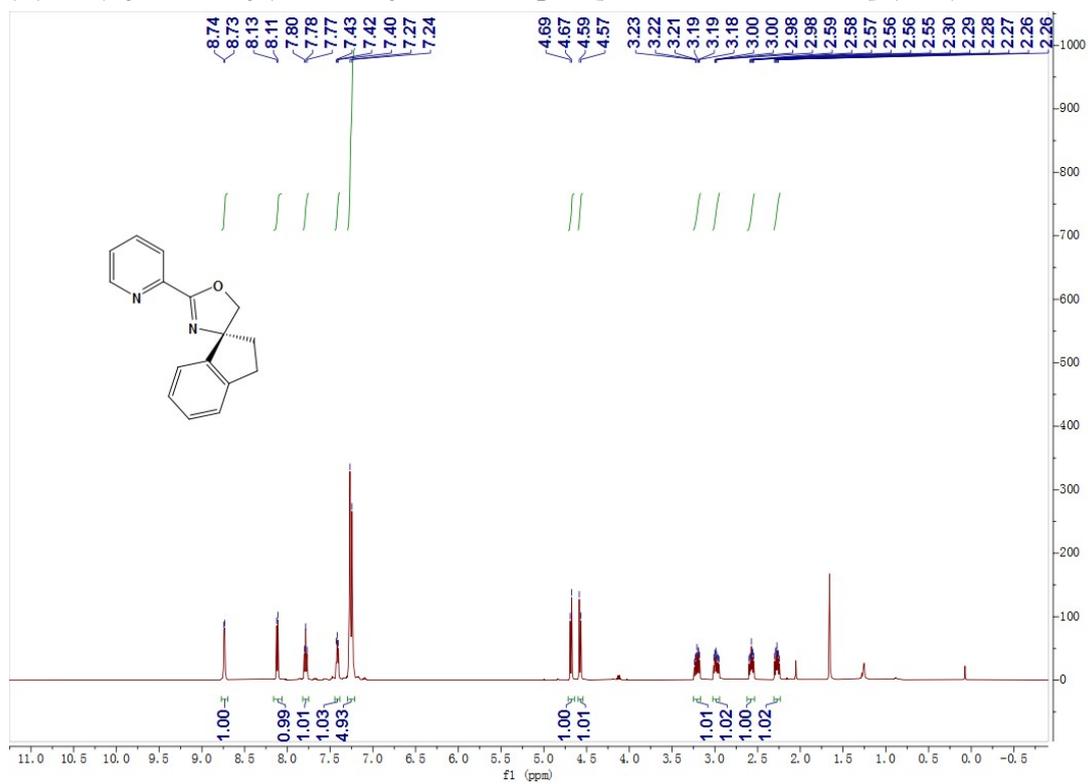
Bis((*R*)-2,3-dihydro-5'*H*-spiro[indene-1,4'-oxazol]-2'-yl)propane (L1)



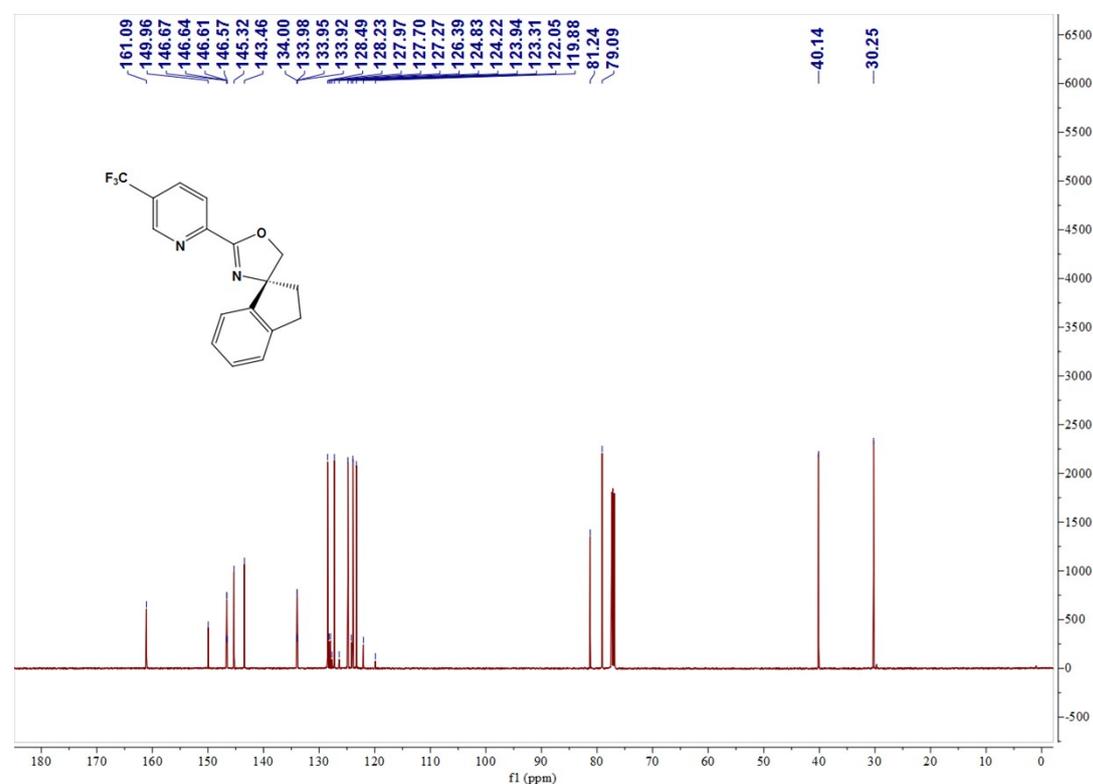
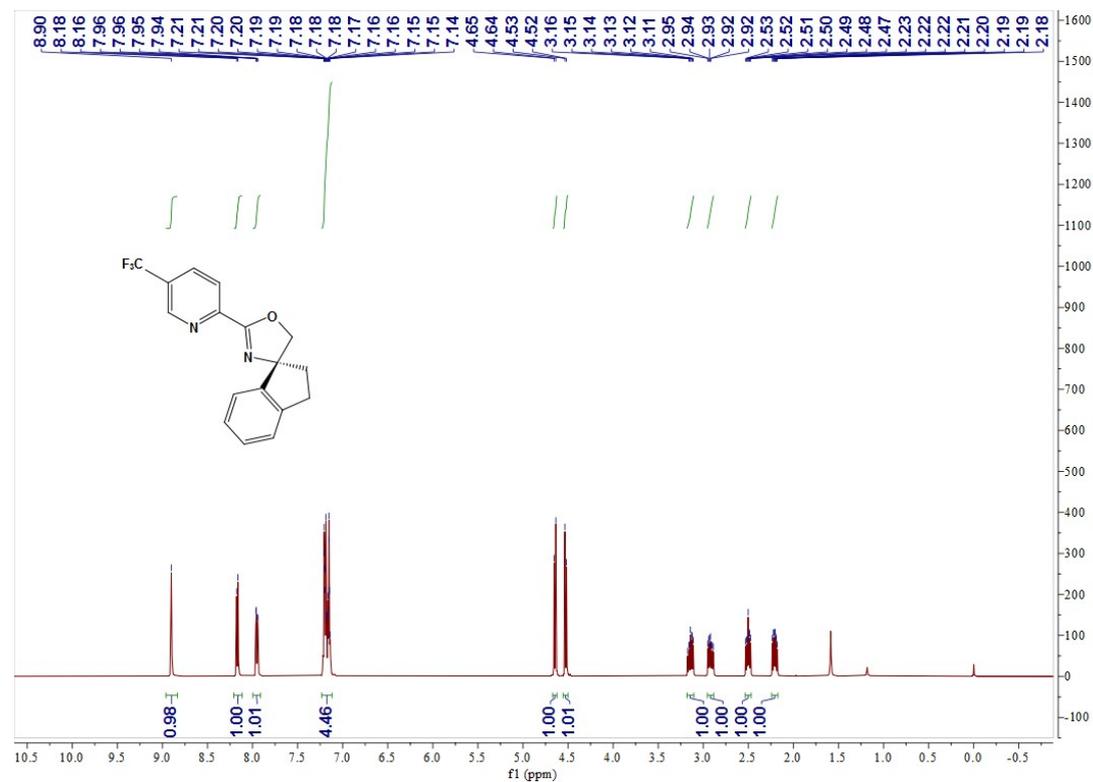
(R)-2'-(Quinolin-2-yl)-2,3-dihydro-5'H-spiro[indene-1,4'-oxazole] (L2)



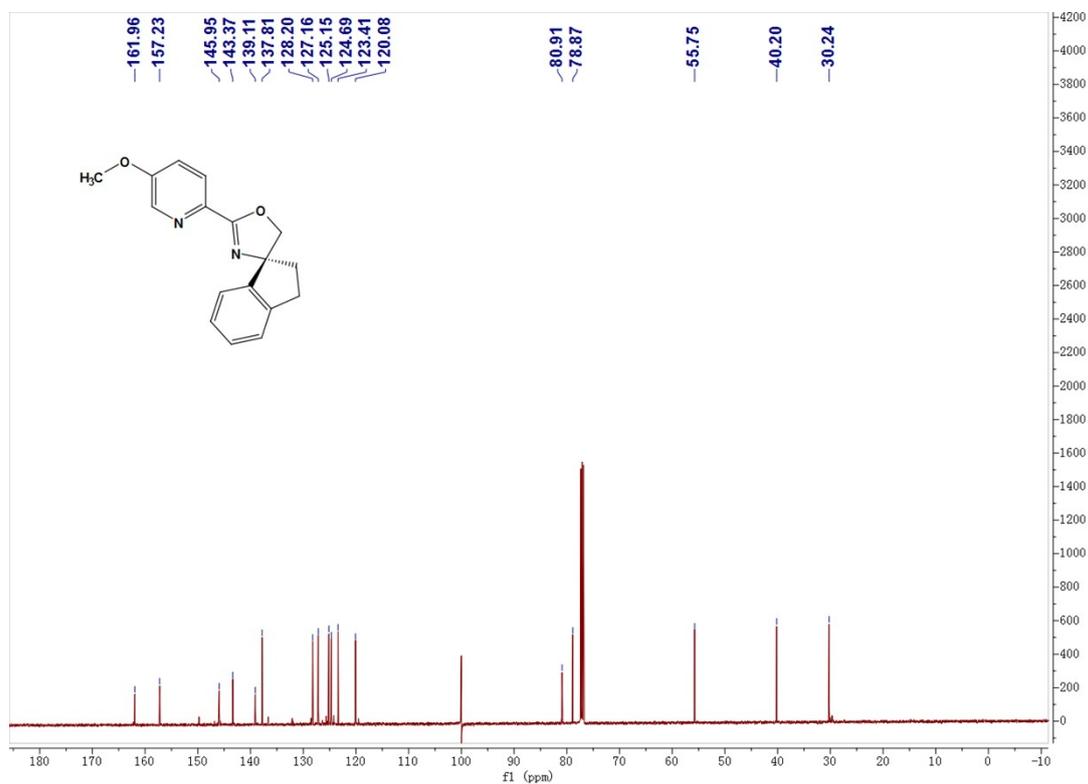
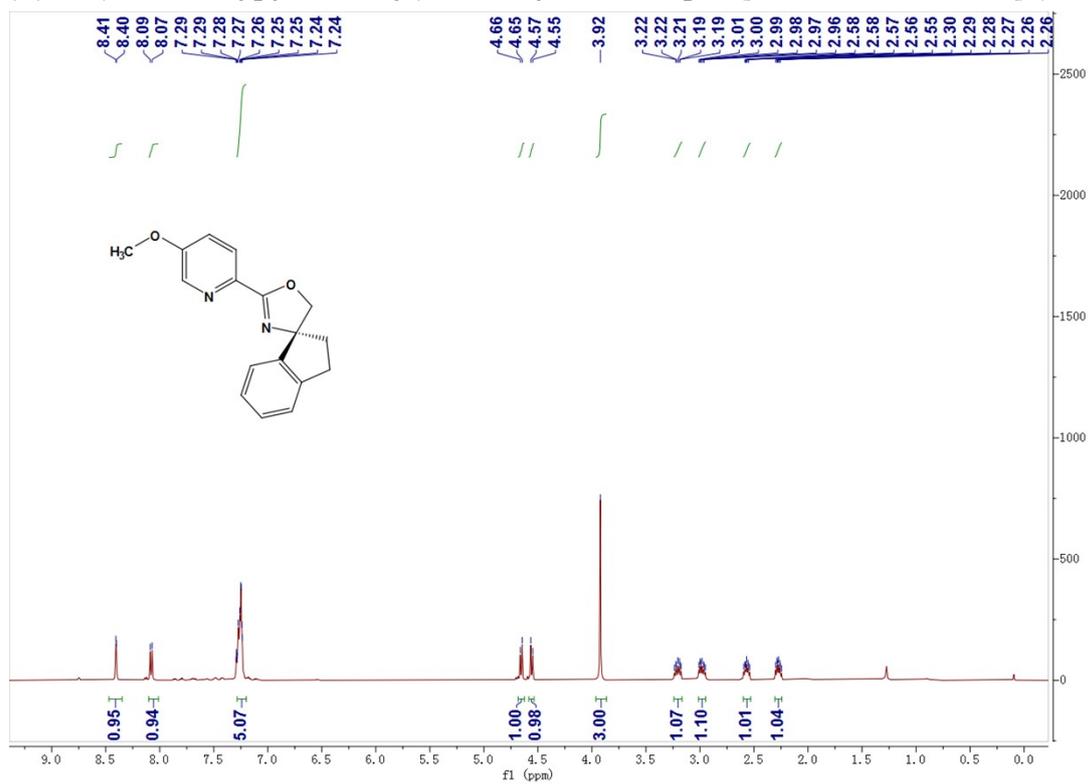
(R)-2'-(Pyridin-2-yl)-2,3-dihydro-5'H-spiro[indene-1,4'-oxazole] (L3a)



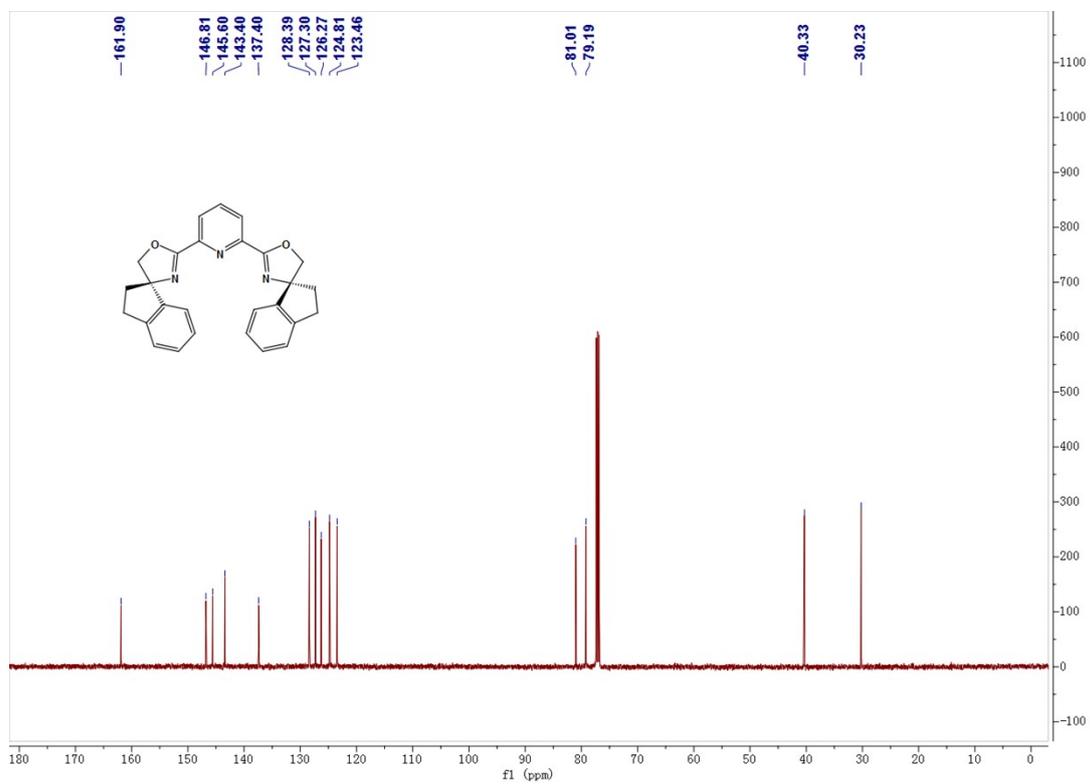
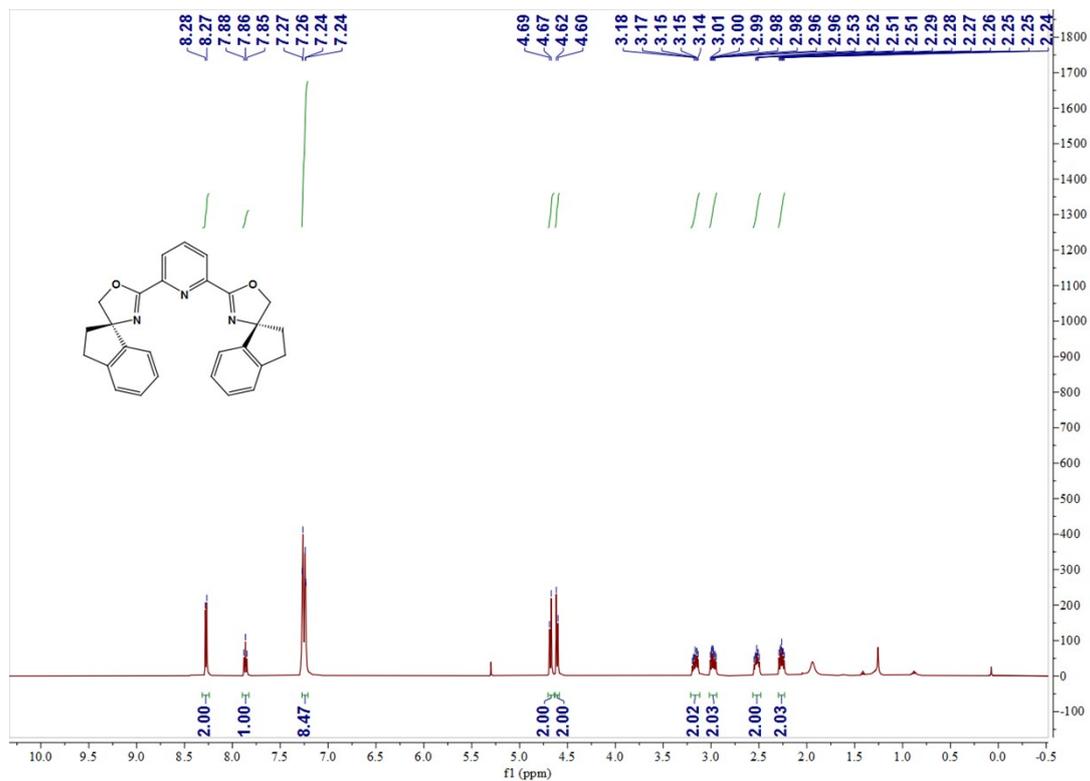
(R)-2'-(5-(Trifluoromethyl)pyridin-2-yl)-2,3-dihydro-5'H-spiro[indene-1,4'-oxazole] (L3b)



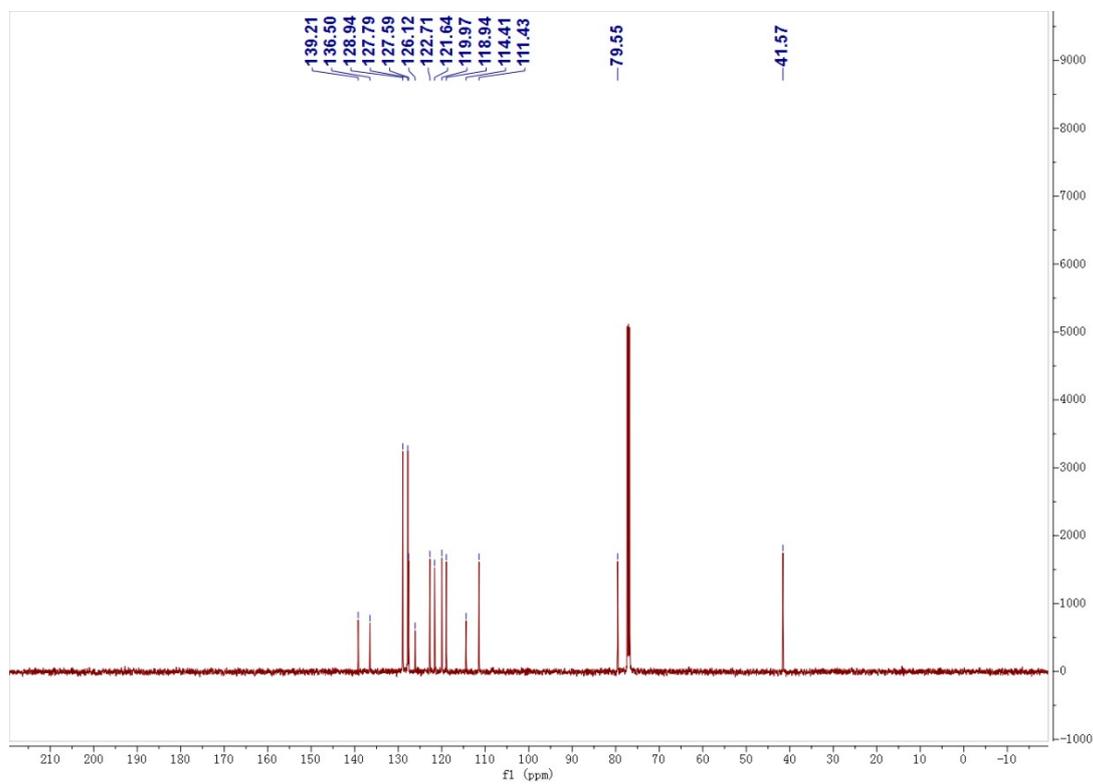
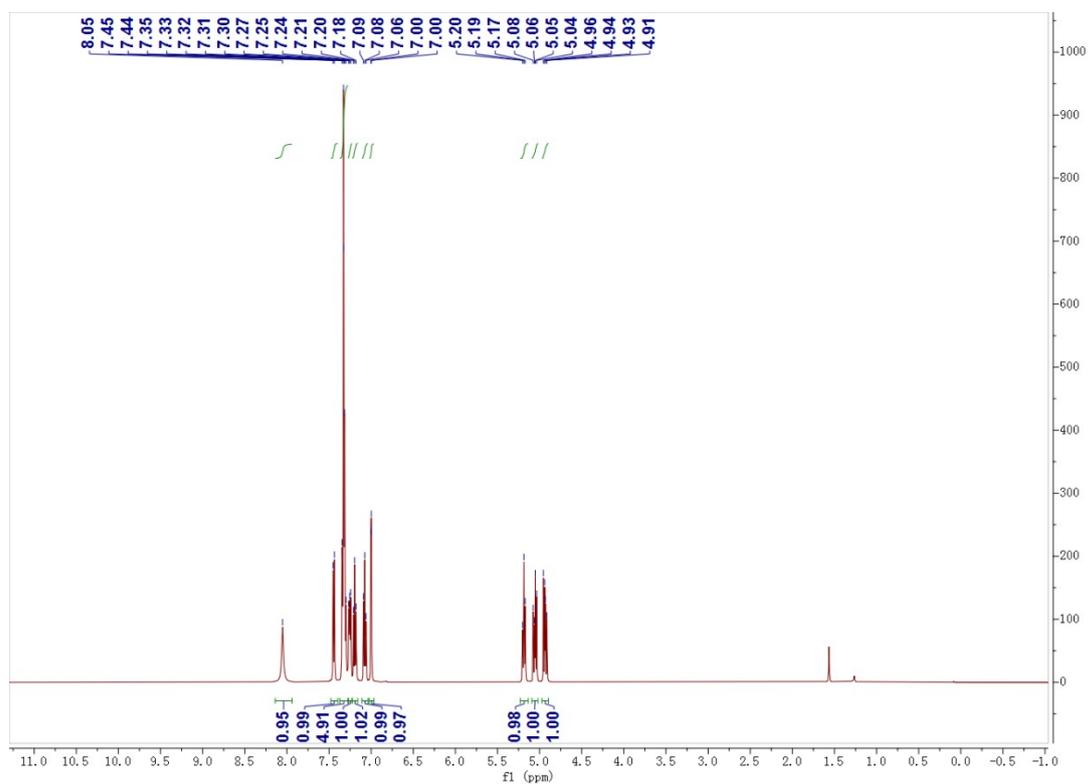
(R)-2'-(5-Methoxypyridin-2-yl)-2,3-dihydro-5'H-spiro[indene-1,4'-oxazole] (L3c)

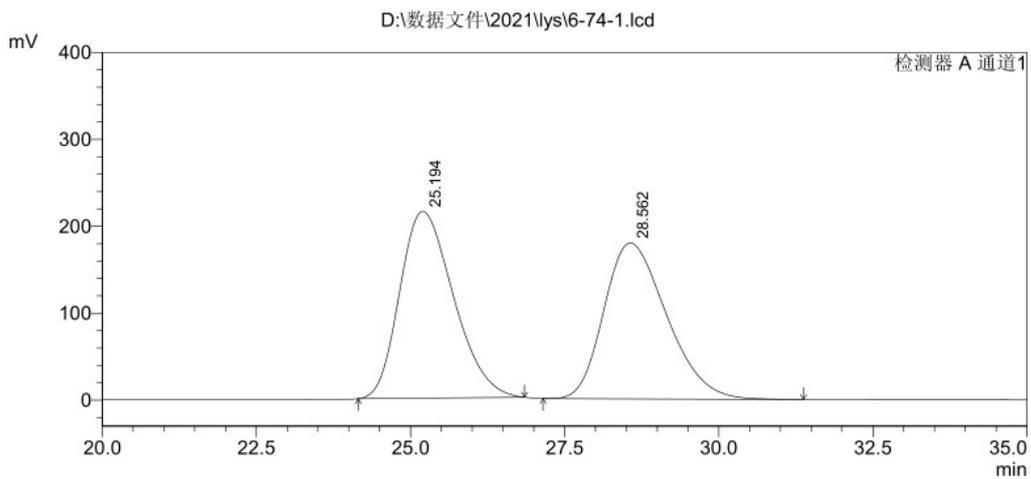


2,6-Bis((*R*)-2,3-dihydro-5'*H*-spiro[indene-1,4'-oxazol]-2'-yl)pyridine (L4)



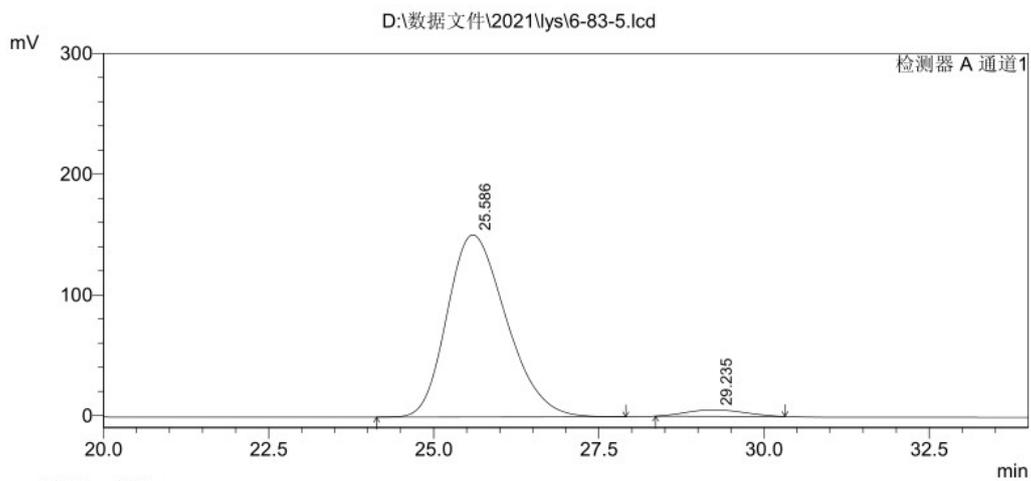
(S)-3-(2-nitro-1-phenylethyl)-1H-indole (1a)





峰表

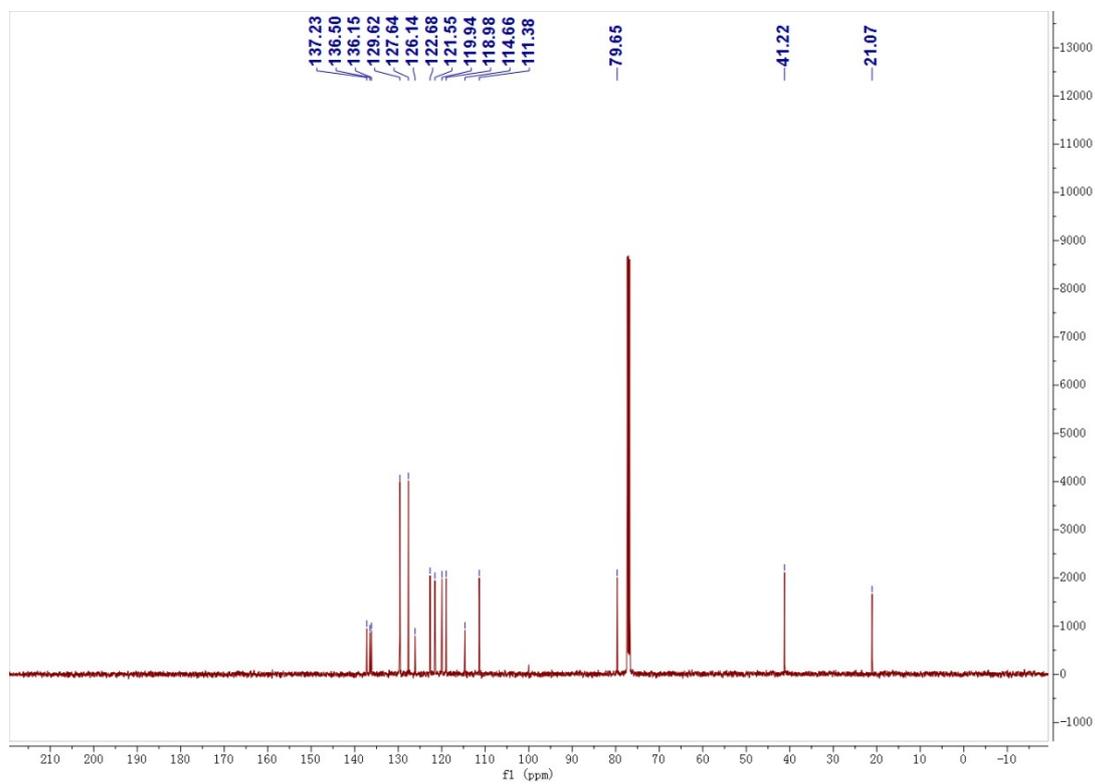
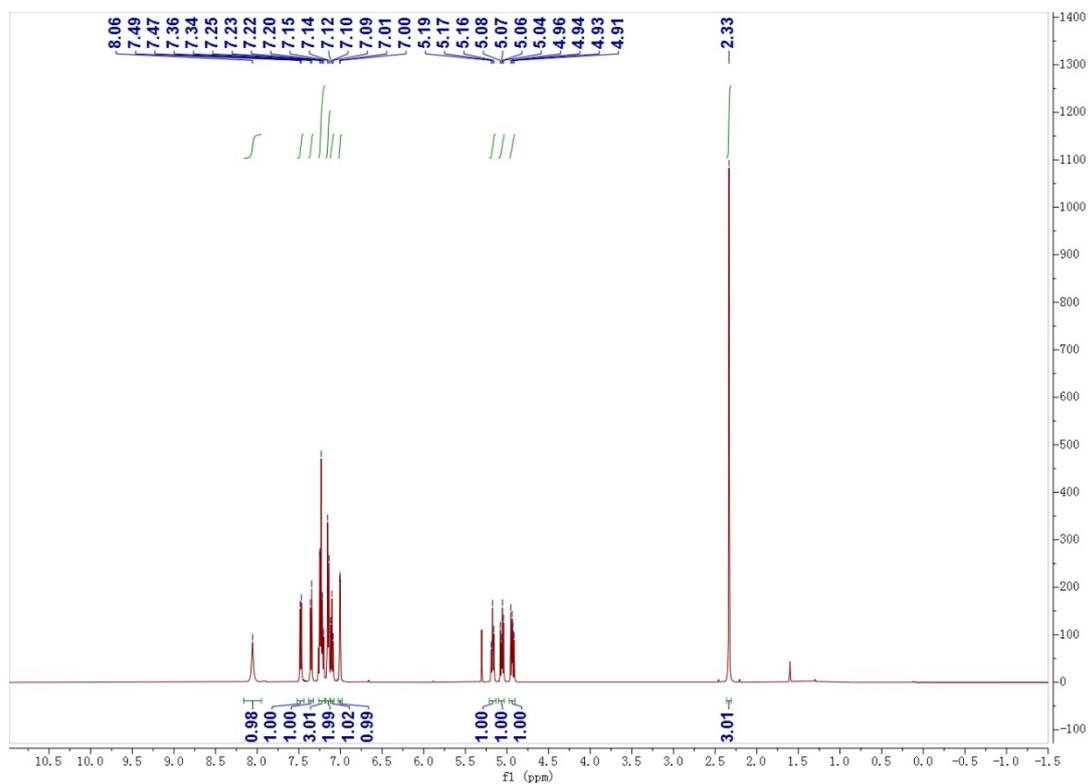
峰#	保留时间	面积	高度	面积 %	高度 %
1	25.194	13033179	214945	50.736	54.515
2	28.562	12655184	179342	49.264	45.485
总计		25688363	394286	100.000	100.000

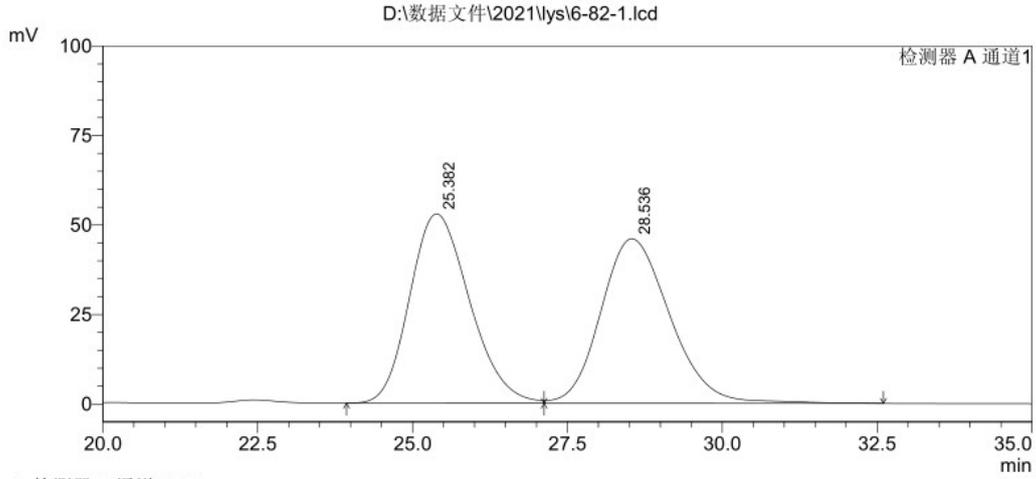


峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	25.586	9417405	150969	96.628	96.556
2	29.235	328601	5384	3.372	3.444
总计		9746006	156353	100.000	100.000

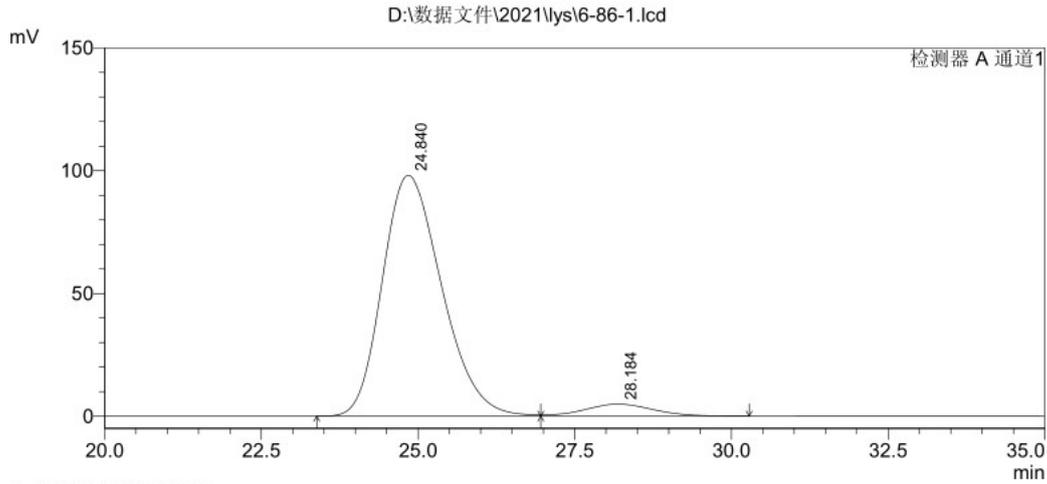
(S)-3-(2-nitro-1-(p-tolyl)ethyl)-1H-indole (1b)





峰表

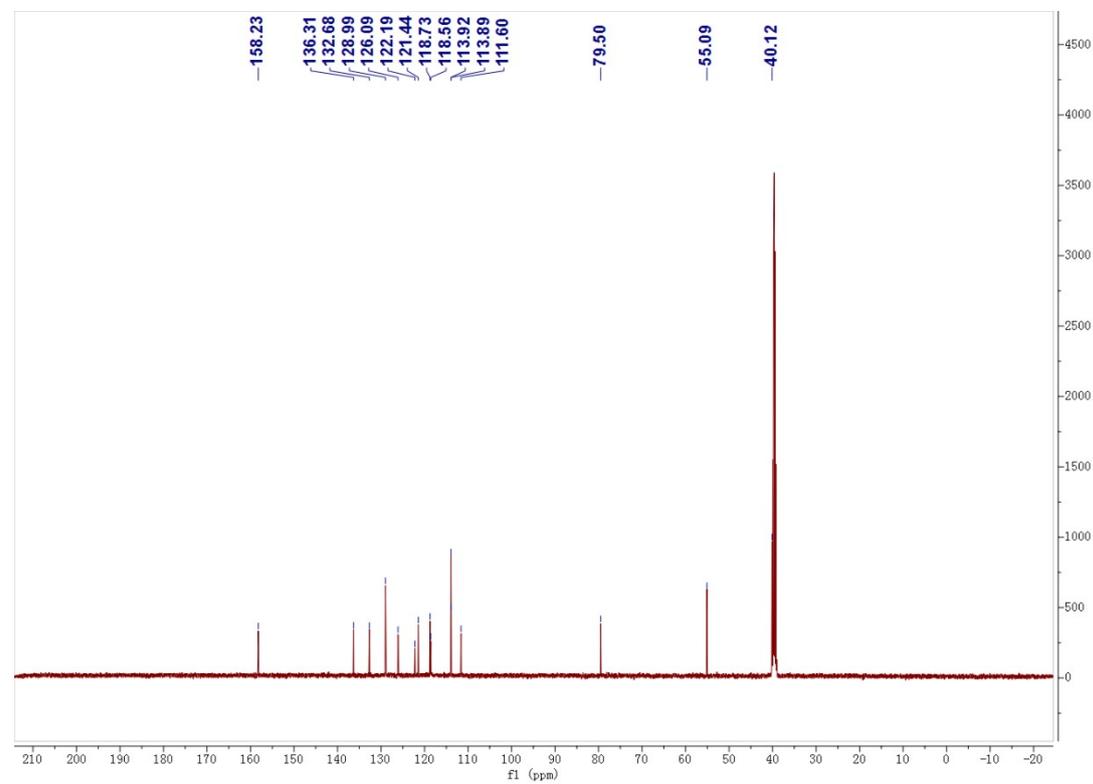
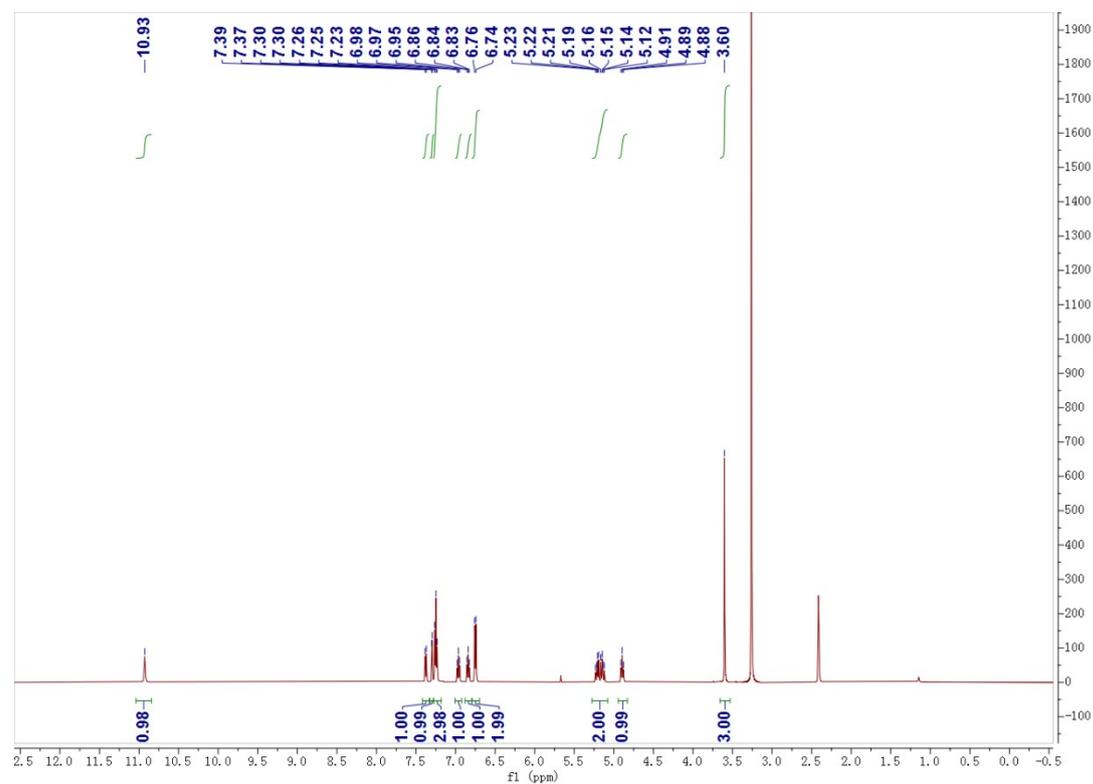
检测器 A Ch1 254nm					
峰#	保留时间	面积	高度	面积 %	高度 %
1	25.382	3561941	52885	49.876	53.489
2	28.536	3579625	45985	50.124	46.511
总计		7141566	98870	100.000	100.000

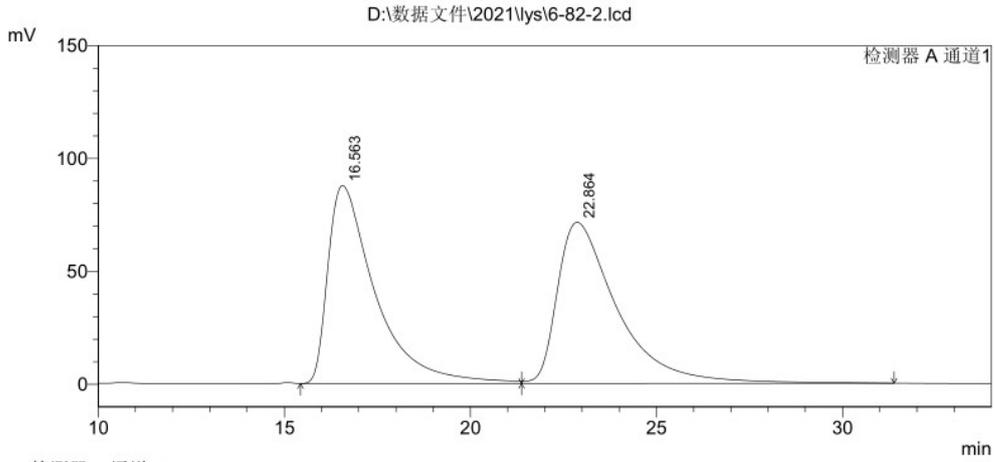


峰表

检测器 A Ch1 254nm					
峰#	保留时间	面积	高度	面积 %	高度 %
1	24.840	6464791	98113	94.593	95.268
2	28.184	369510	4873	5.407	4.732
总计		6834301	102986	100.000	100.000

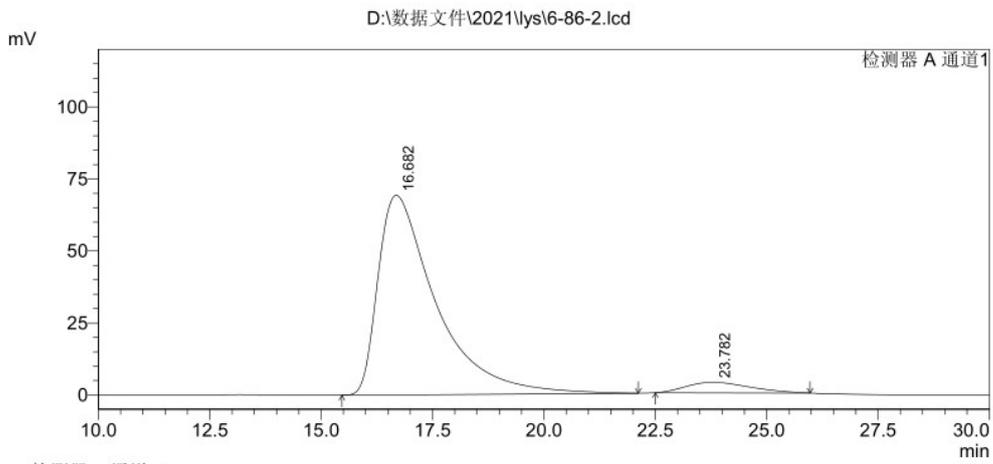
(S)-3-(1-(4-methoxyphenyl)-2-nitroethyl)-1H-indole (1c)





峰表

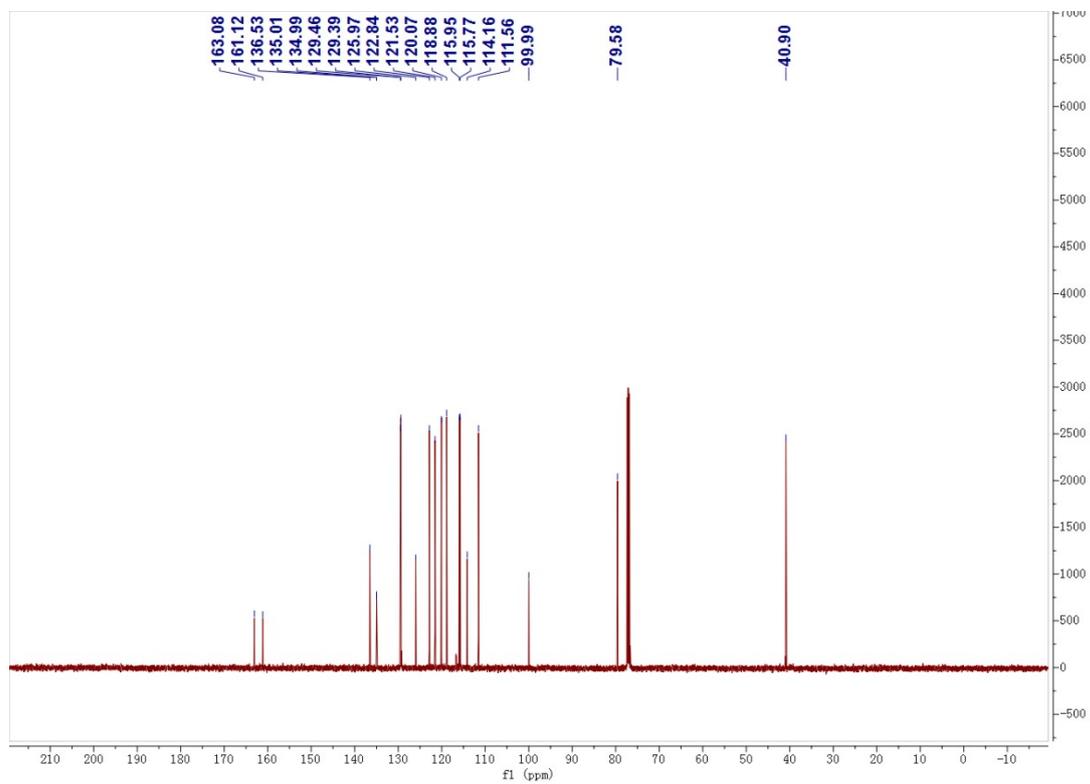
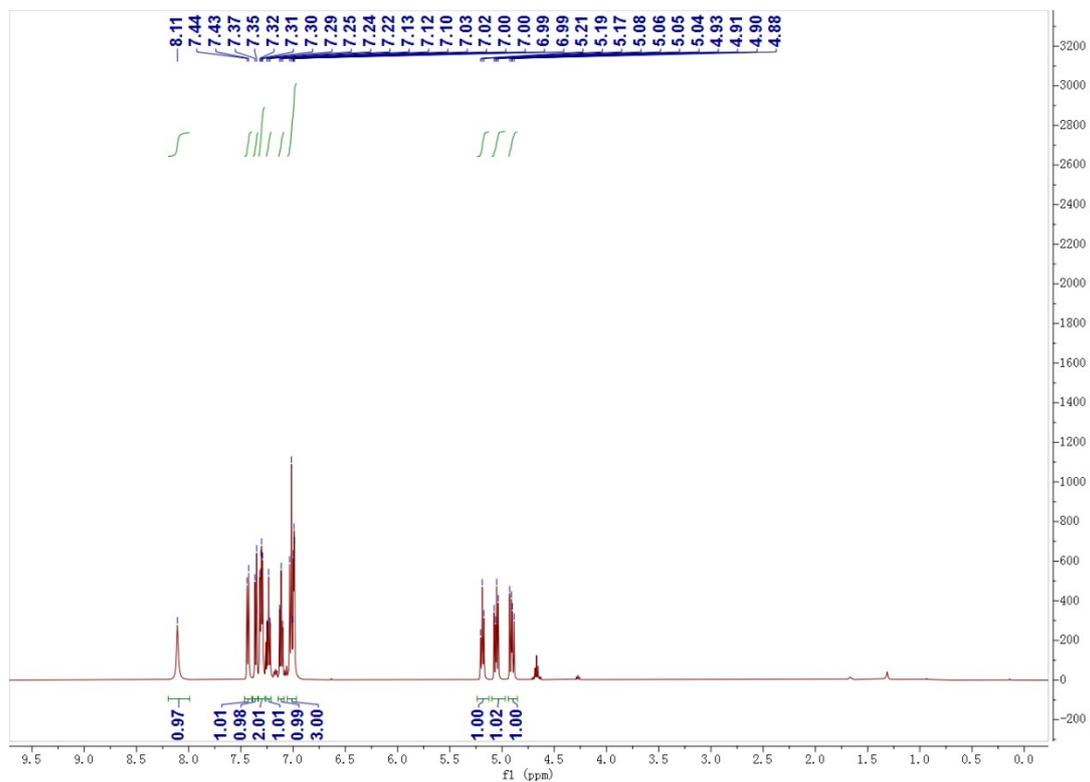
峰#	保留时间	面积	高度	面积 %	高度 %
1	16.563	7778648	87717	49.362	55.152
2	22.864	7979855	71328	50.638	44.848
总计		15758503	159044	100.000	100.000

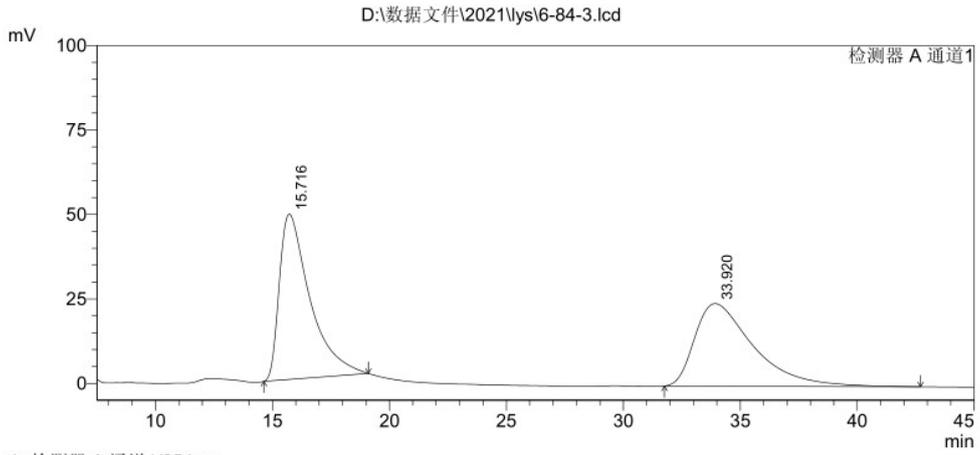


峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	16.682	6276485	69301	94.480	94.976
2	23.782	366738	3666	5.520	5.024
总计		6643223	72968	100.000	100.000

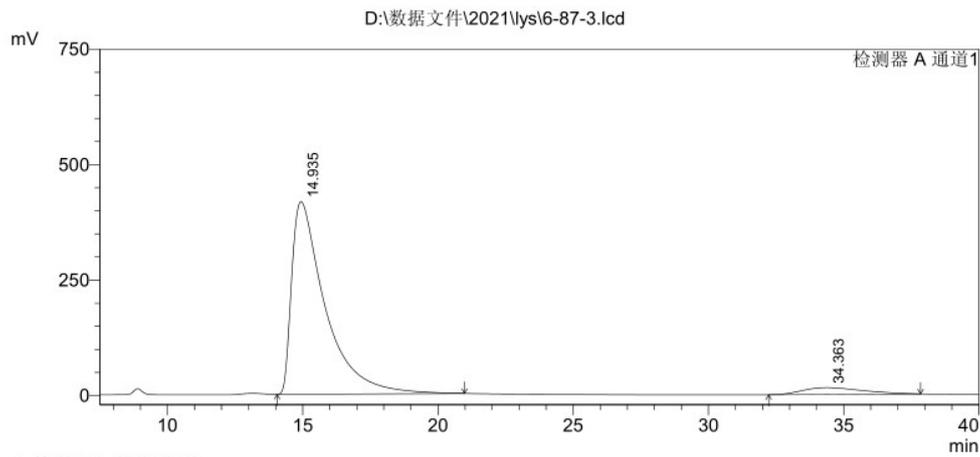
(S)-3-(1-(4-fluorophenyl)-2-nitroethyl)-1H-indole (1d)





峰表

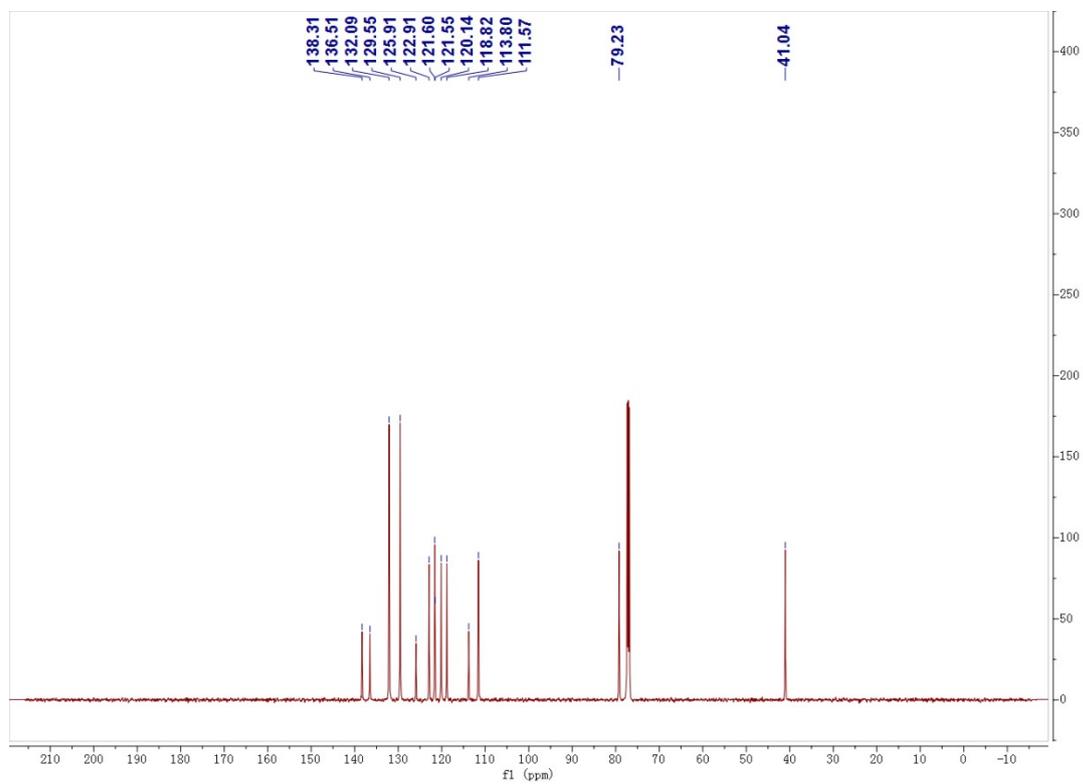
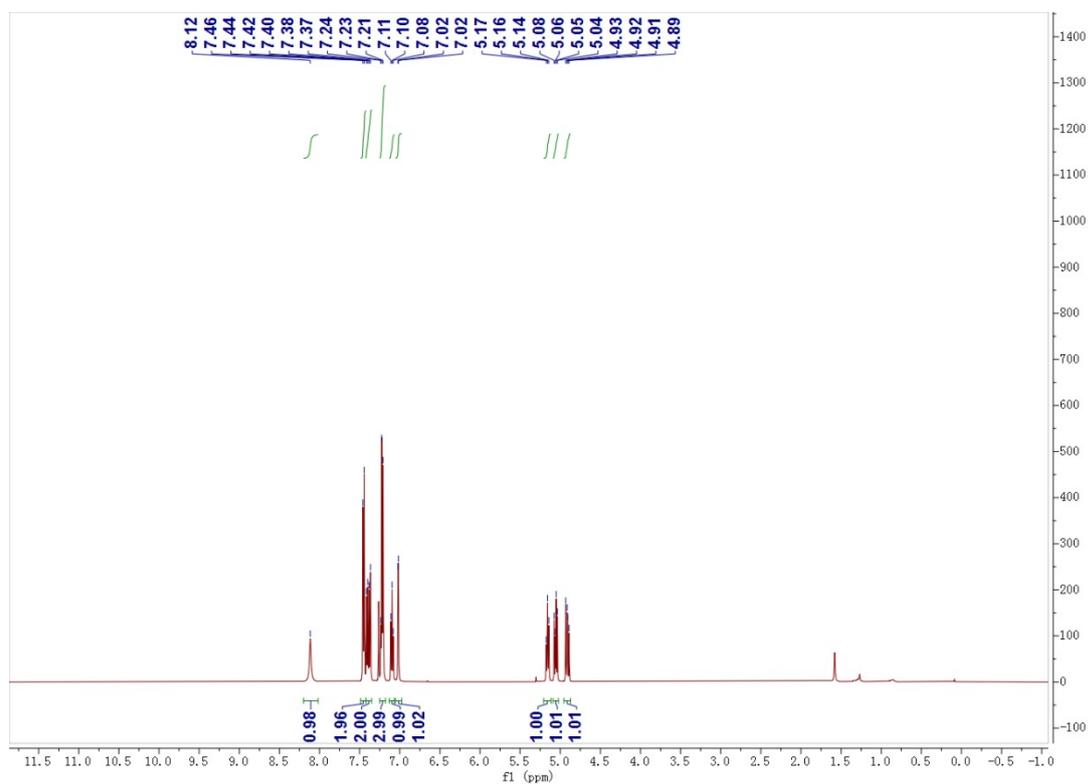
峰#	保留时间	面积	高度	面积 %	高度 %
1	15.716	4460573	48936	51.149	66.699
2	33.920	4260245	24433	48.851	33.301
总计		8720818	73368	100.000	100.000



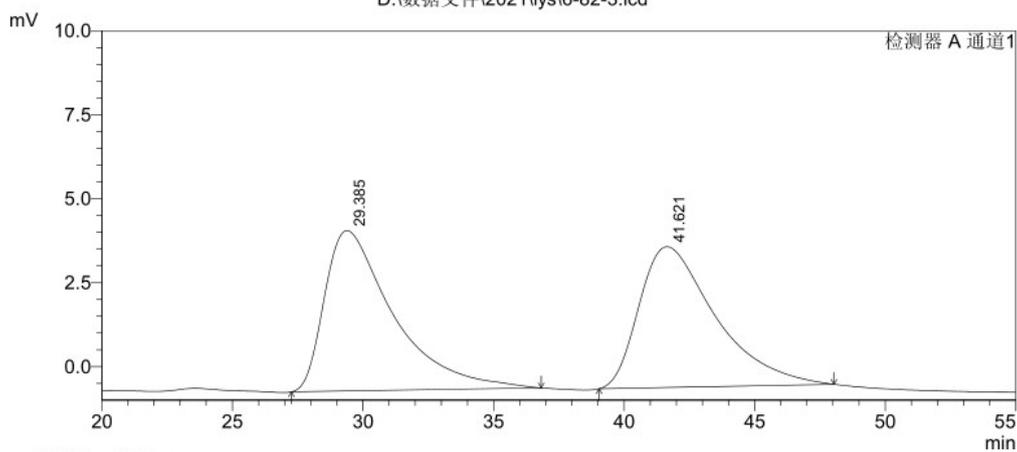
峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	14.935	35938918	417150	94.025	96.594
2	34.363	2283704	14708	5.975	3.406
总计		38222622	431858	100.000	100.000

(S)-3-(1-(4-bromophenyl)-2-nitroethyl)-1H-indole (1e)



D:\数据文件\2021\lys16-82-3.lcd



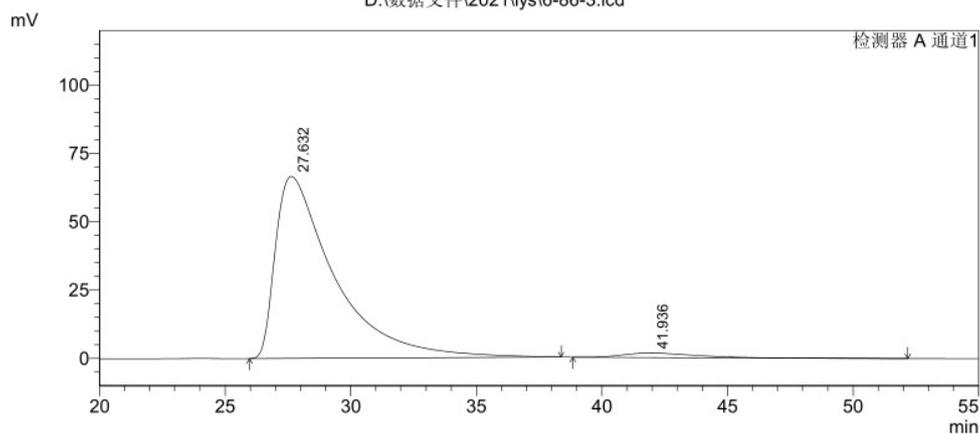
1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	29.385	874501	4778	50.679	53.273
2	41.621	851077	4191	49.321	46.727
总计		1725578	8969	100.000	100.000

D:\数据文件\2021\lys16-86-3.lcd



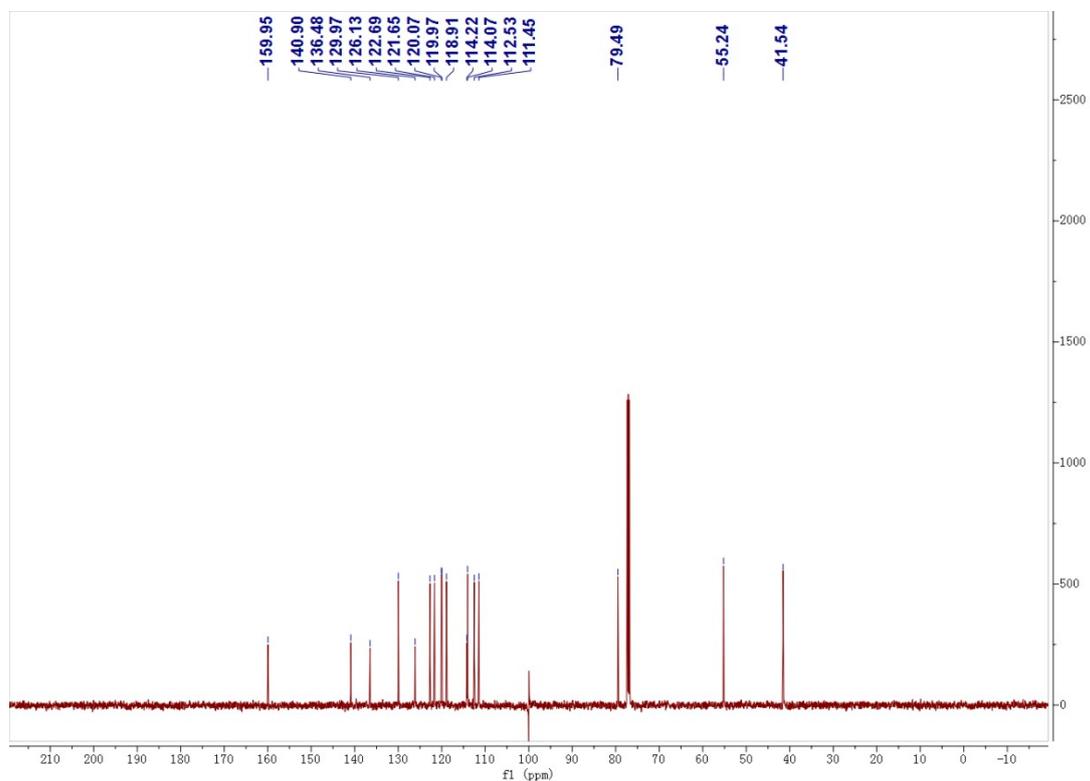
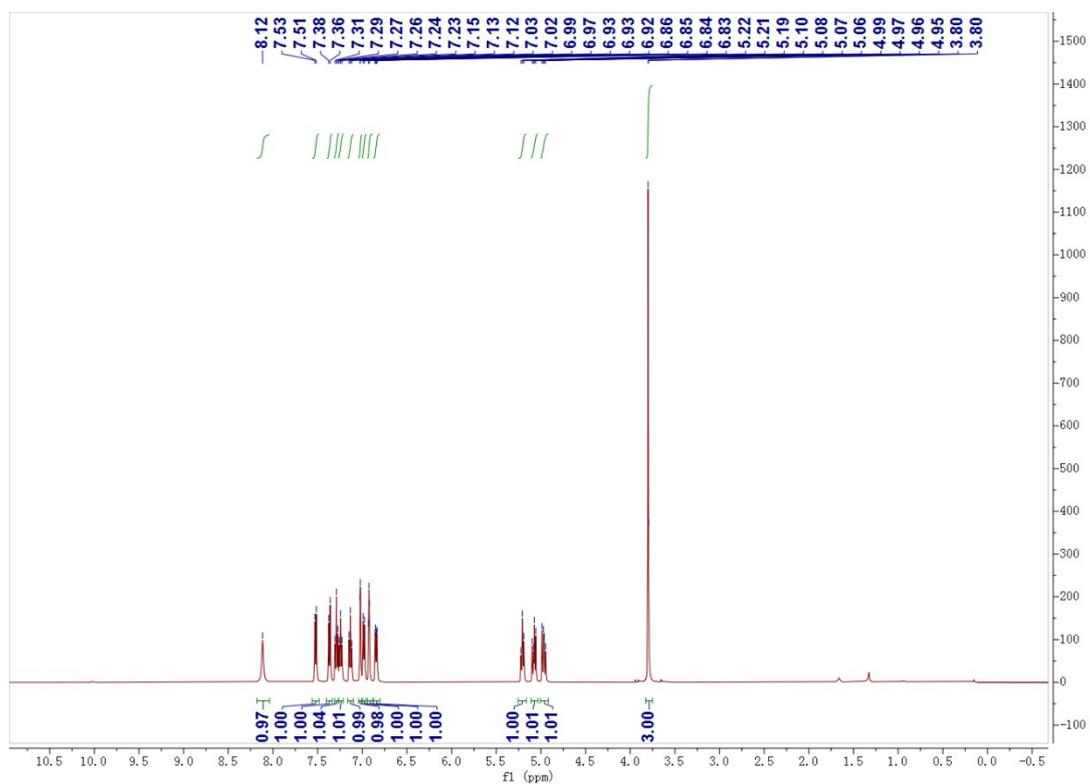
1 检测器 A 通道1/254nm

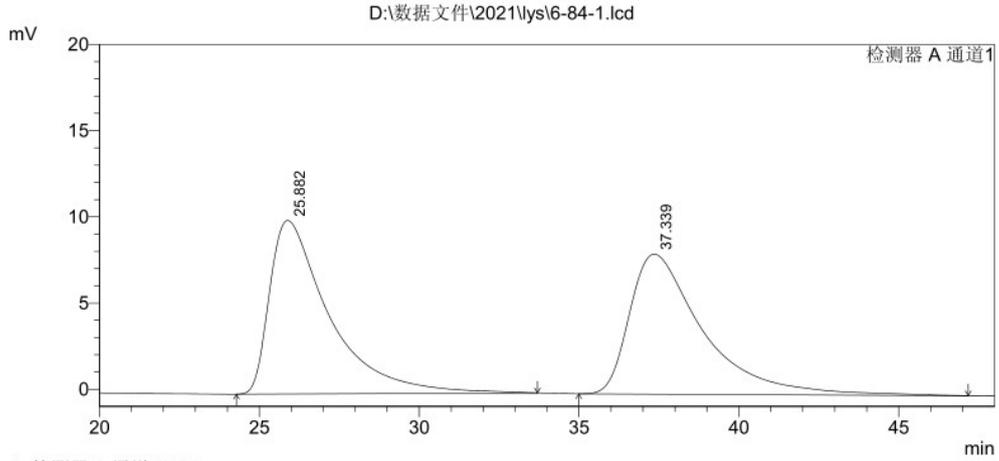
峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	27.632	10901964	66604	97.153	97.607
2	41.936	319448	1633	2.847	2.393
总计		11221413	68237	100.000	100.000

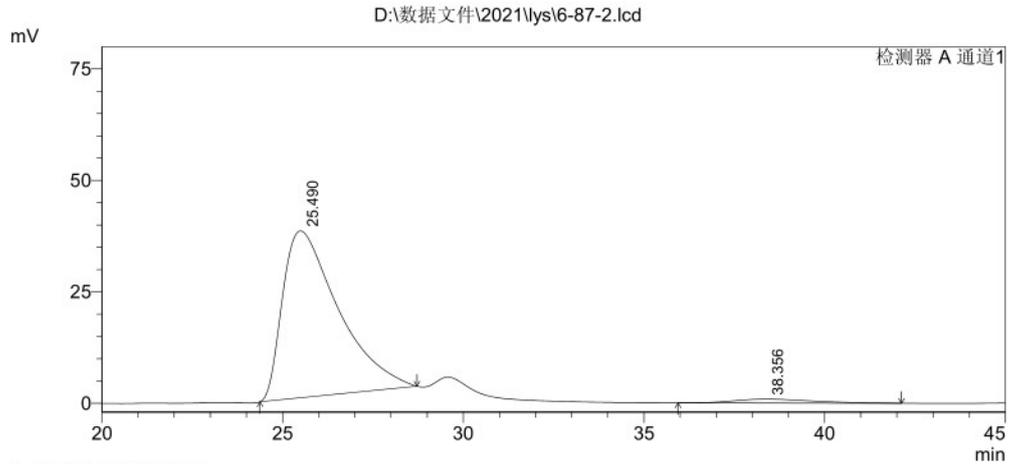
(S)-3-(1-(3-methoxyphenyl)-2-nitroethyl)-1H-indole (1f)





峰表

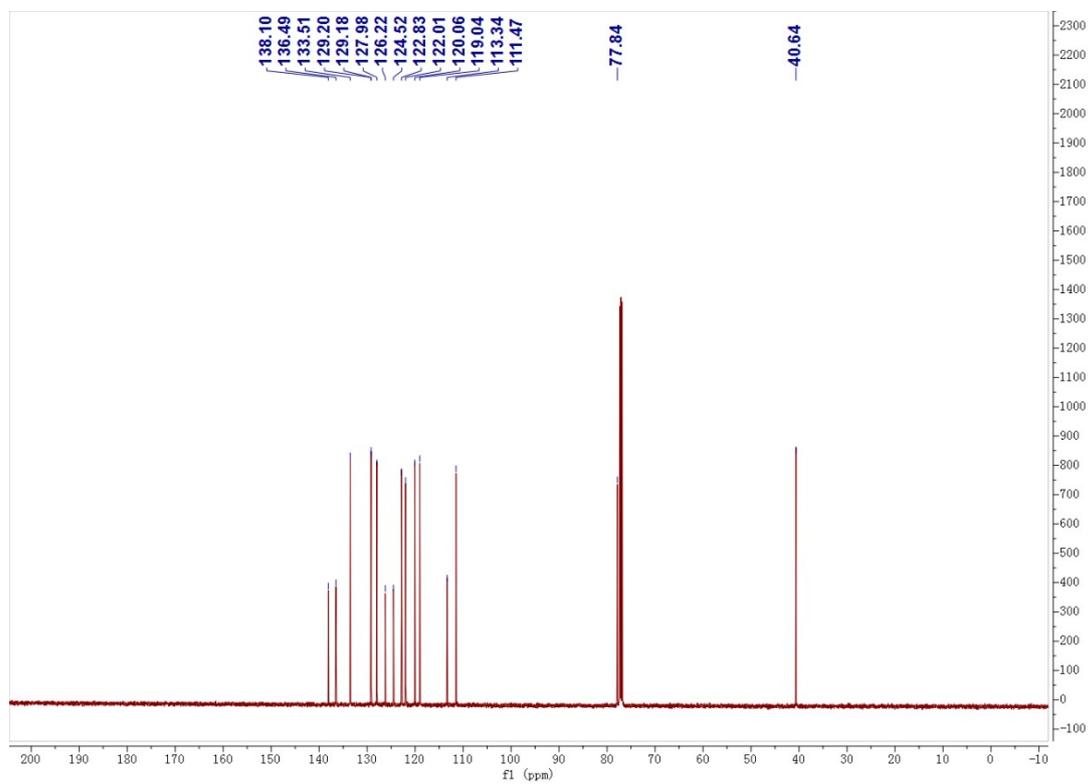
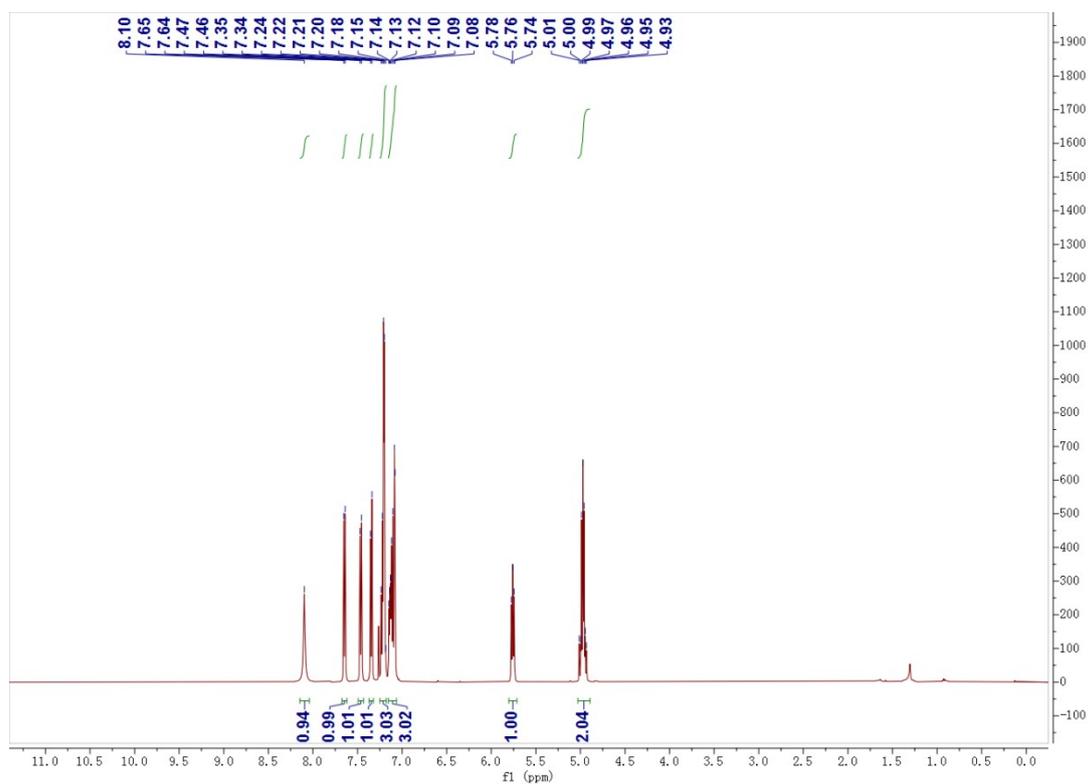
峰#	保留时间	面积	高度	面积 %	高度 %
1	25.882	1305418	10064	50.196	55.333
2	37.339	1295222	8124	49.804	44.667
总计		2600640	18189	100.000	100.000

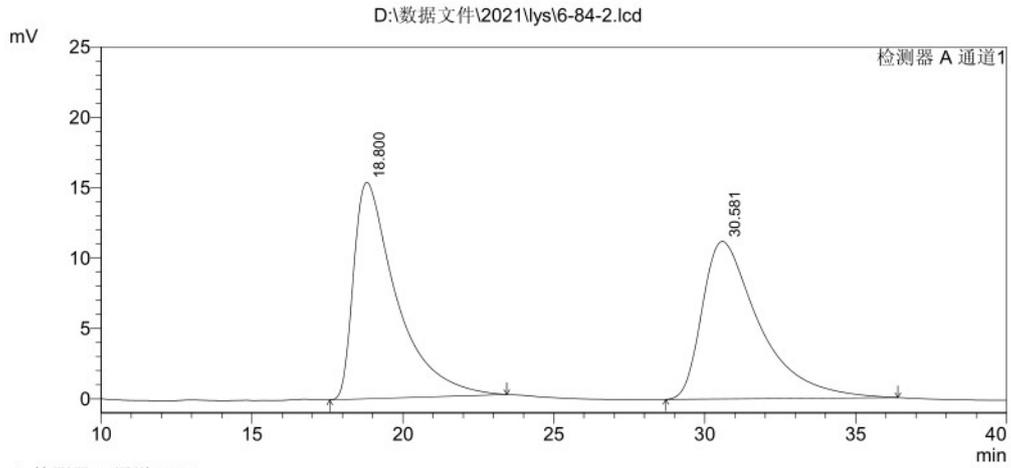


峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	25.490	4019271	37436	96.809	97.722
2	38.356	132472	873	3.191	2.278
总计		4151743	38308	100.000	100.000

(S)-3-(1-(2-bromophenyl)-2-nitroethyl)-1H-indole (1g)

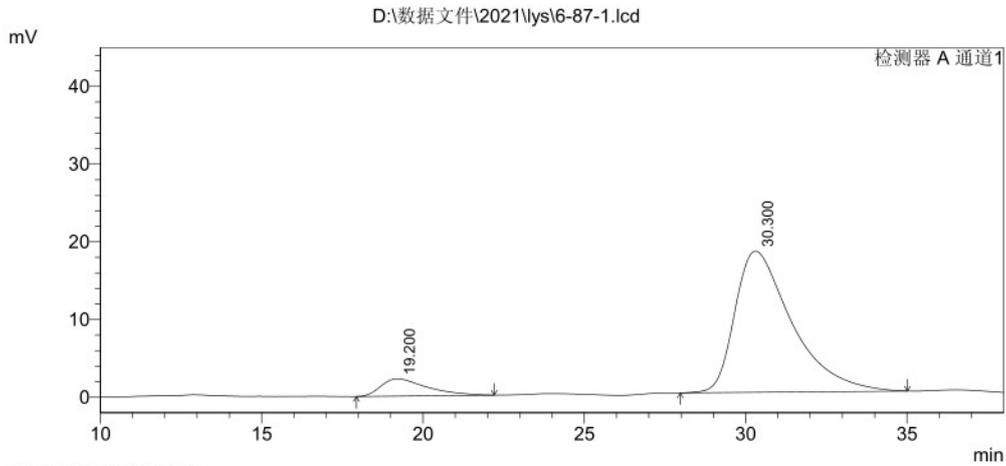




1 检测器 A 通道1/254nm

峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	18.800	1520390	15382	50.724	57.885
2	30.581	1476972	11191	49.276	42.115
总计		2997363	26573	100.000	100.000

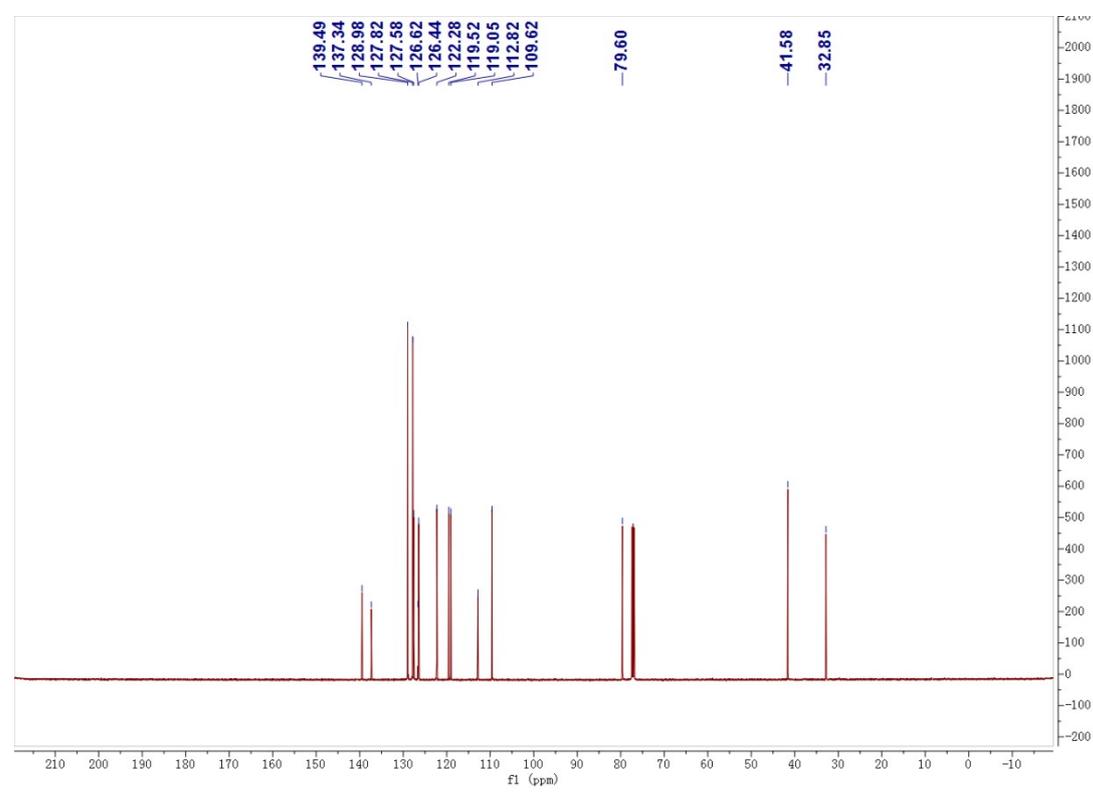
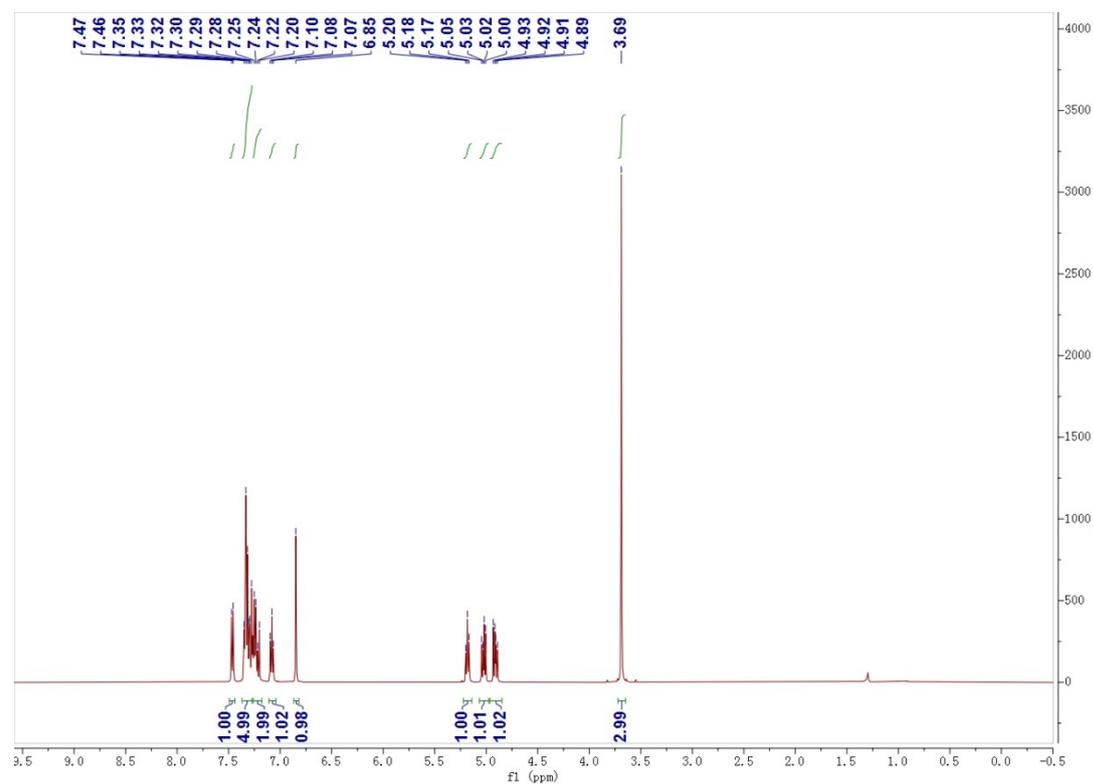


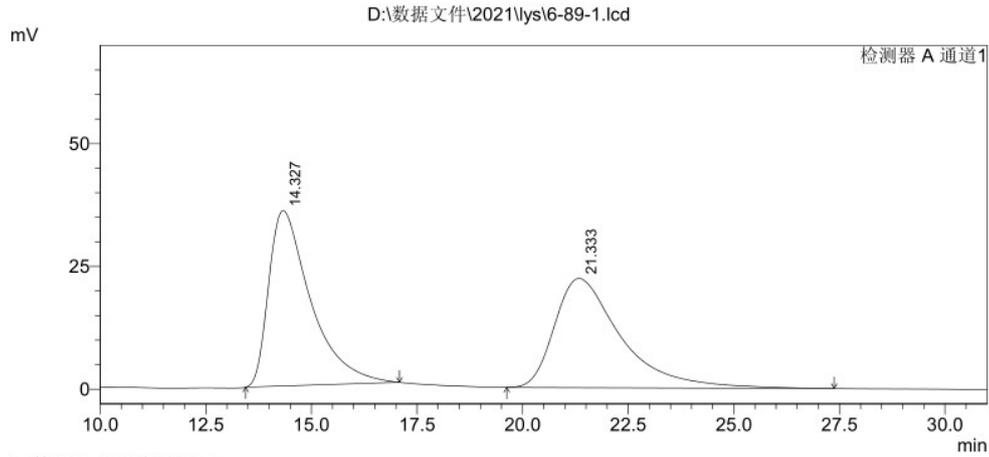
1 检测器 A 通道1/254nm

峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	19.200	220691	2231	8.983	10.933
2	30.300	2236144	18177	91.017	89.067
总计		2456834	20408	100.000	100.000

(S)-1-methyl-3-(2-nitro-1-phenylethyl)-1H-indole (1h)

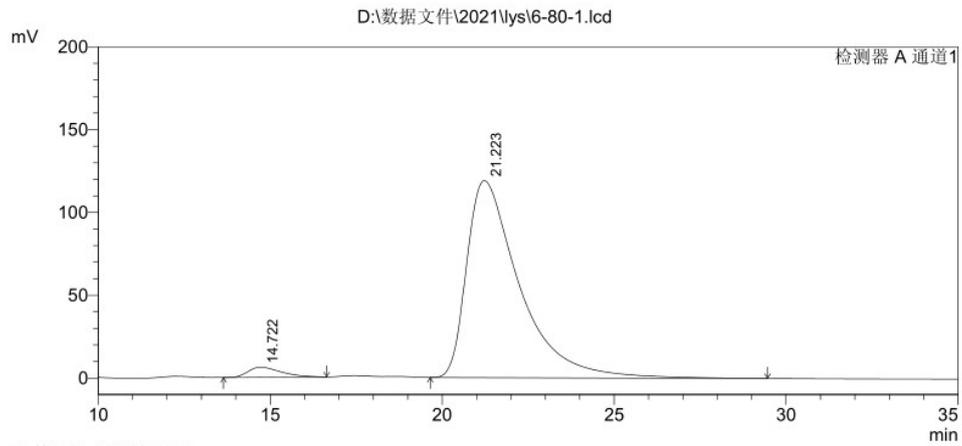




1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm					
峰#	保留时间	面积	高度	面积 %	高度 %
1	14.327	2476457	35710	50.506	61.640
2	21.333	2426805	22223	49.494	38.360
总计		4903262	57932	100.000	100.000

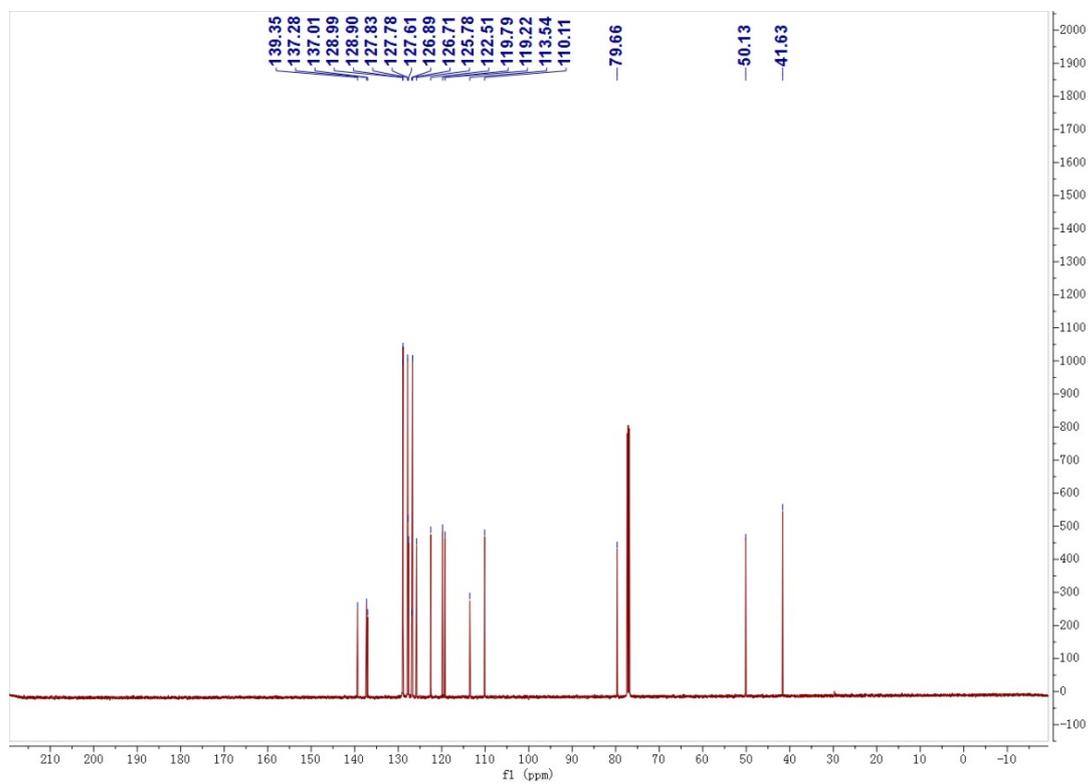
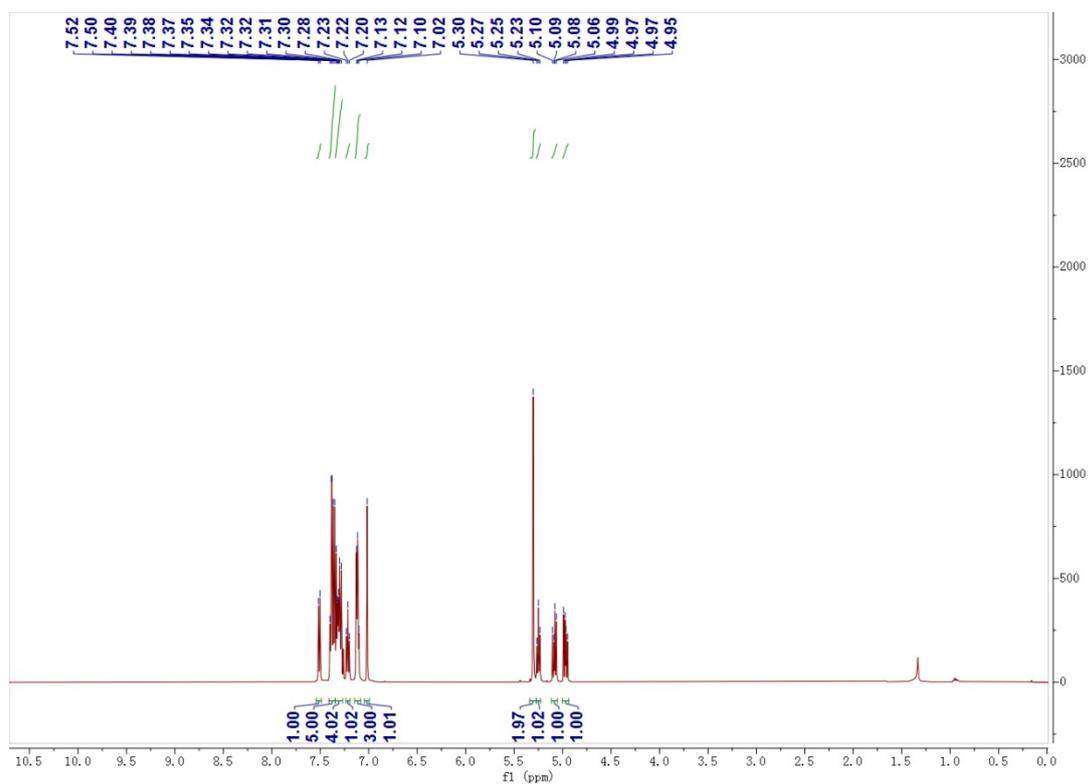


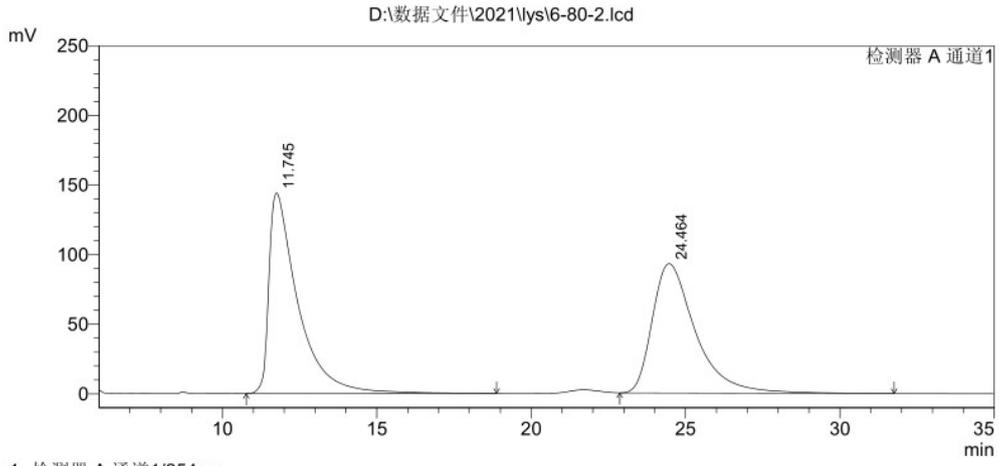
1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm					
峰#	保留时间	面积	高度	面积 %	高度 %
1	14.722	410734	6164	3.130	4.923
2	21.223	12710117	119045	96.870	95.077
总计		13120850	125210	100.000	100.000

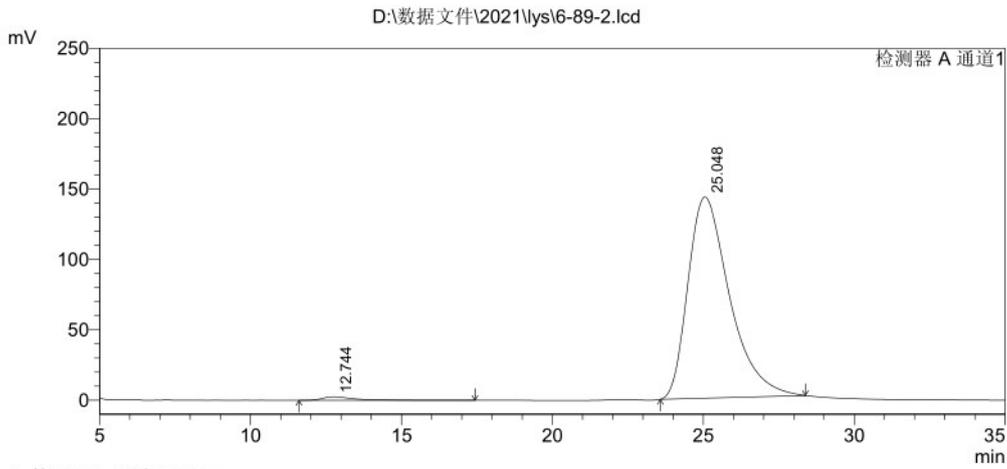
(S)-1-benzyl-3-(2-nitro-1-phenylethyl)-1H-indole (1i)





峰表

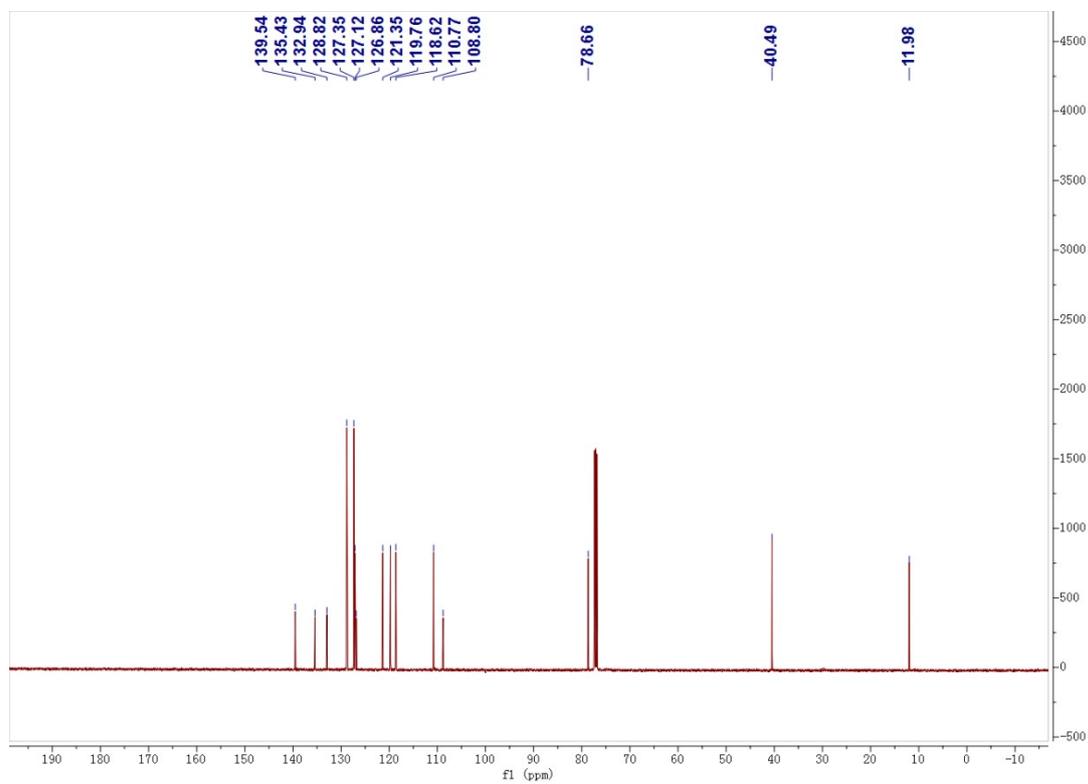
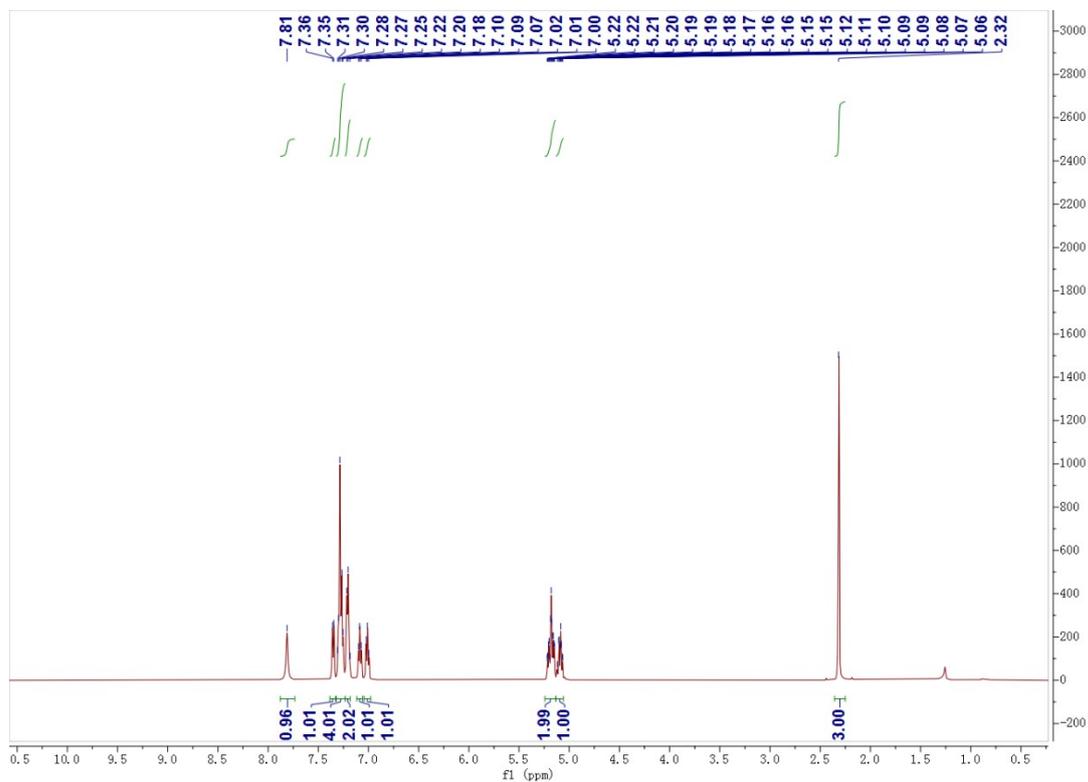
峰#	保留时间	面积	高度	面积 %	高度 %
1	11.745	9408025	144143	50.995	60.798
2	24.464	9041054	92943	49.005	39.202
总计		18449079	237086	100.000	100.000

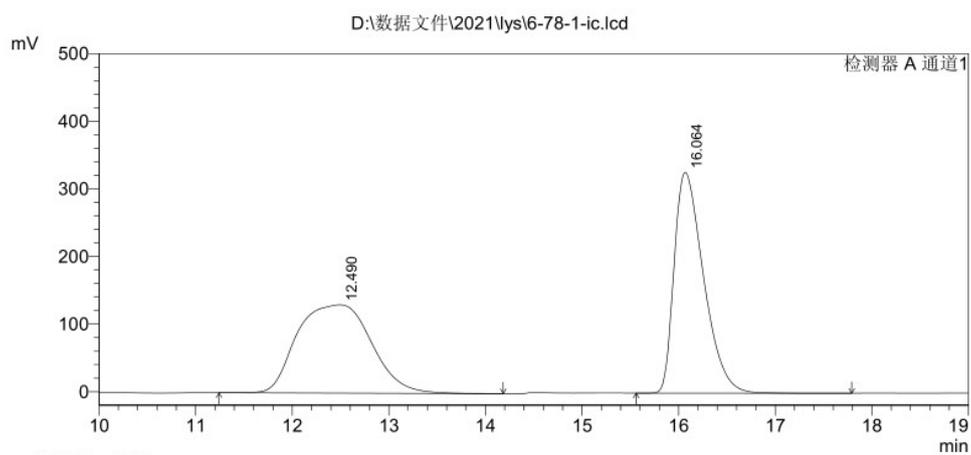


峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	12.744	189010	2563	1.360	1.762
2	25.048	13709949	142867	98.640	98.238
总计		13898960	145430	100.000	100.000

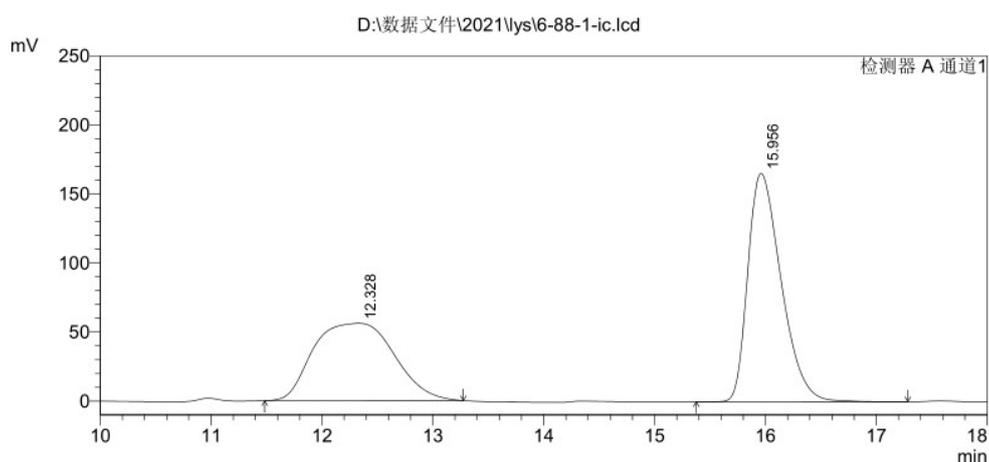
(S)-2-methyl-3-(2-nitro-1-phenylethyl)-1H-indole (1j)





峰表

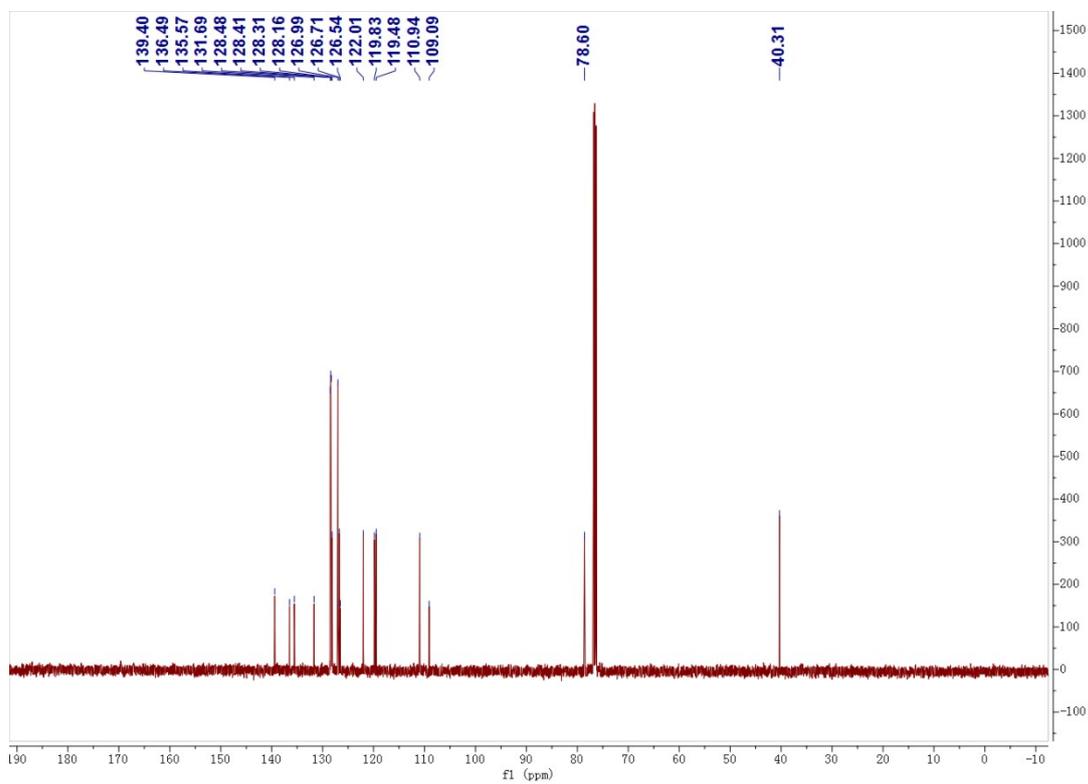
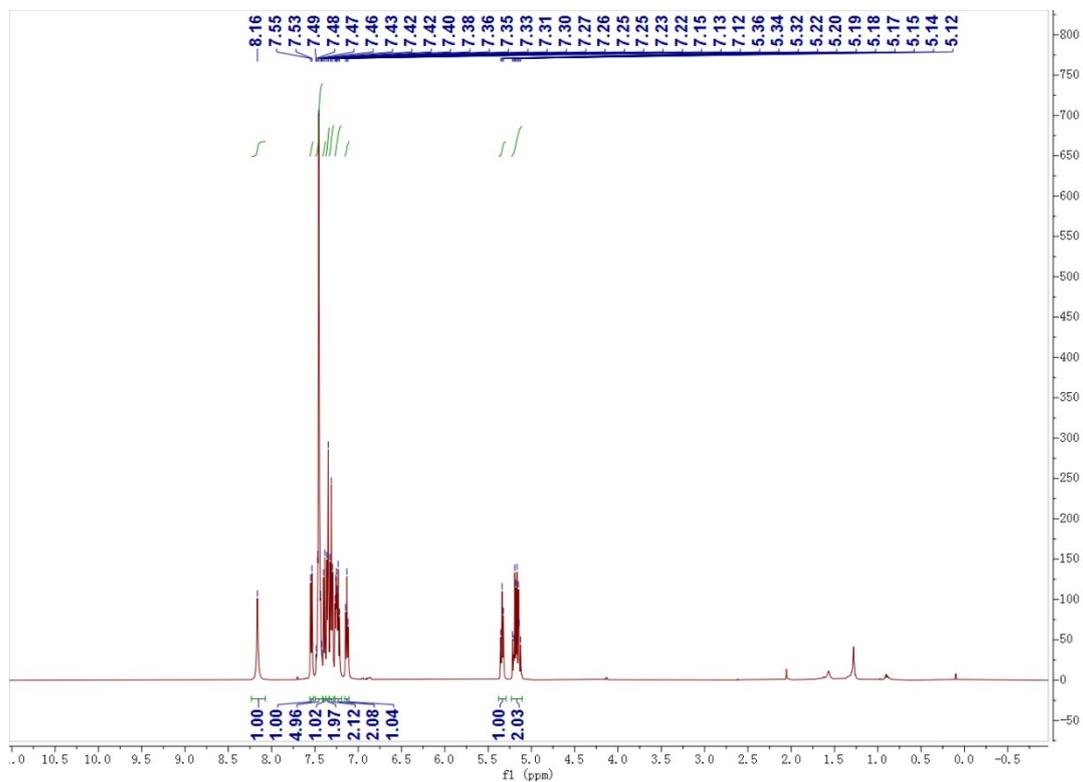
峰#	保留时间	面积	高度	面积 %	高度 %
1	12.490	6992232	130661	50.264	28.575
2	16.064	6918766	326588	49.736	71.425
总计		13910998	457249	100.000	100.000

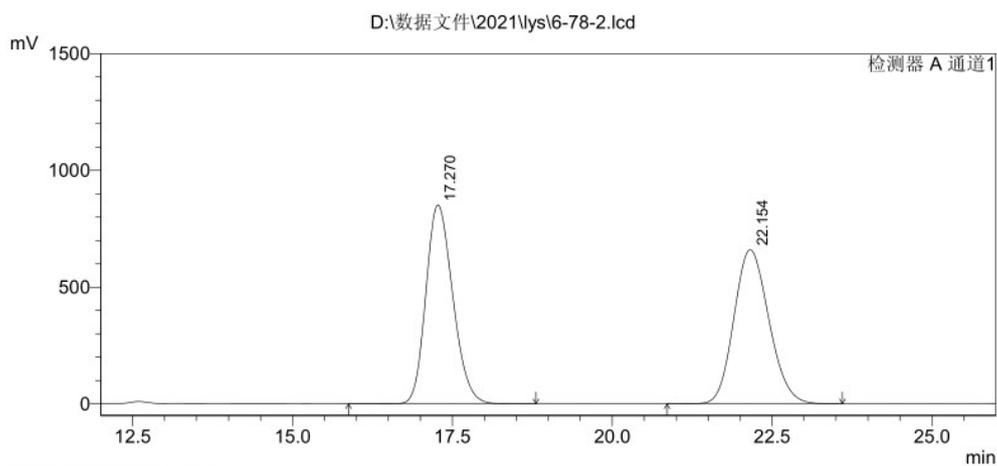


峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	12.328	2844541	56022	45.160	25.300
2	15.956	3454276	165410	54.840	74.700
总计		6298817	221432	100.000	100.000

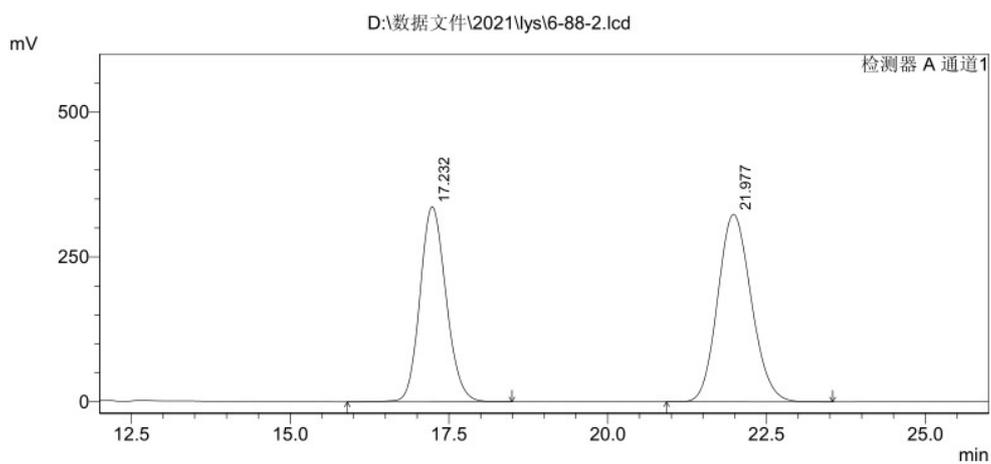
(S)-3-(2-nitro-1-phenylethyl)-2-phenyl-1H-indole (1k)





峰表

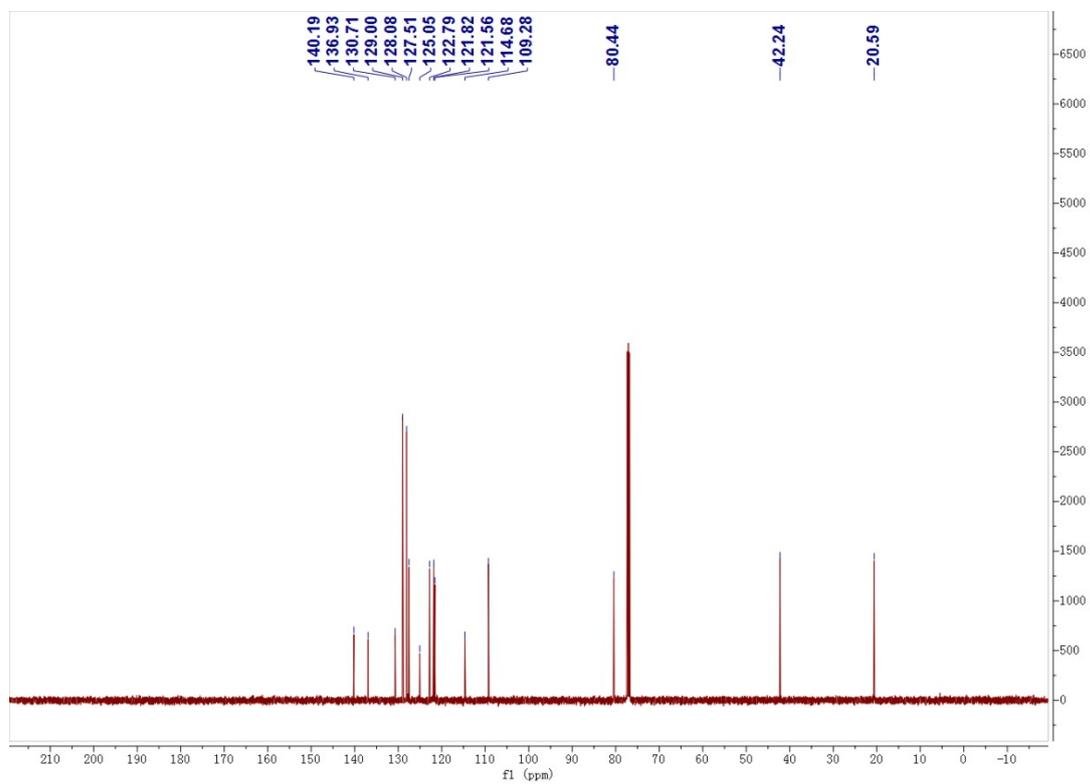
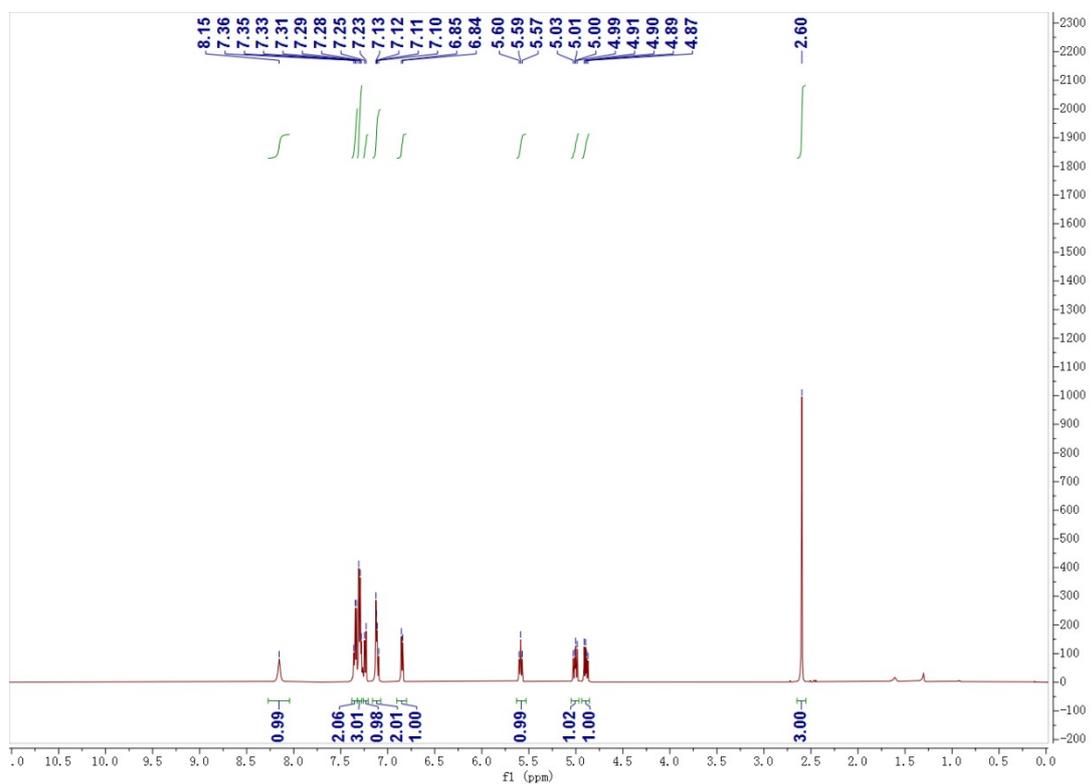
峰#	保留时间	面积	高度	面积 %	高度 %
1	17.270	25010373	852191	49.853	56.353
2	22.154	25157614	660043	50.147	43.647
总计		50167988	1512233	100.000	100.000

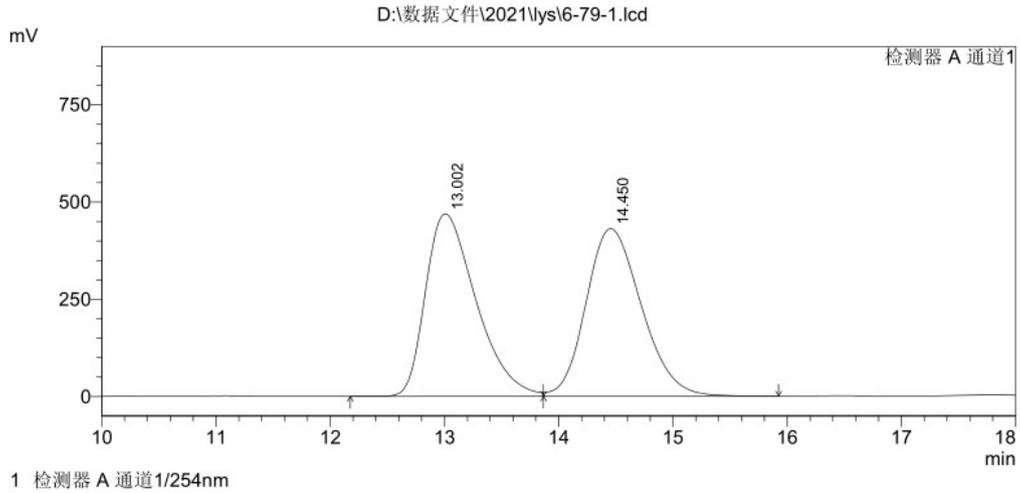


峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	17.232	9632997	336890	44.711	50.996
2	21.977	11911998	323728	55.289	49.004
总计		21544995	660618	100.000	100.000

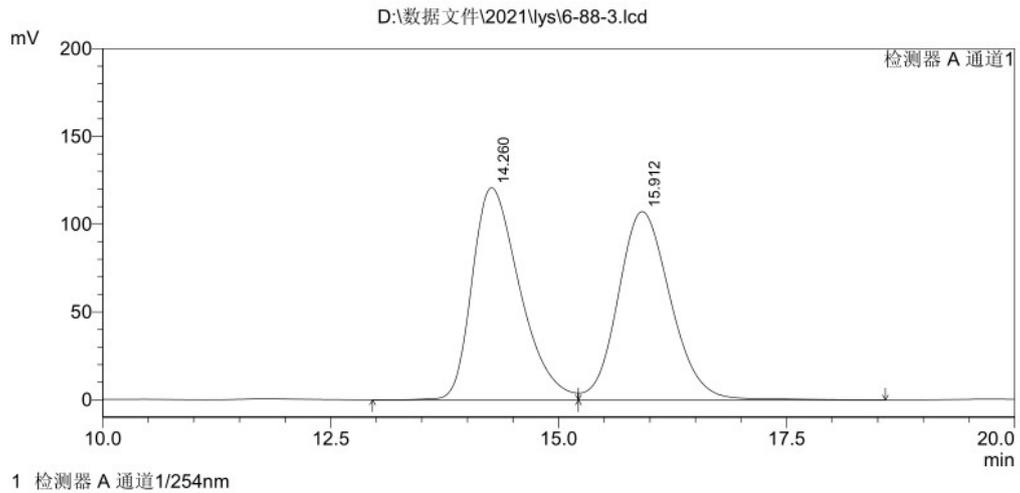
4-Methyl-3-(2-nitro-1-phenylethyl)-1H-indole (1I)





峰表

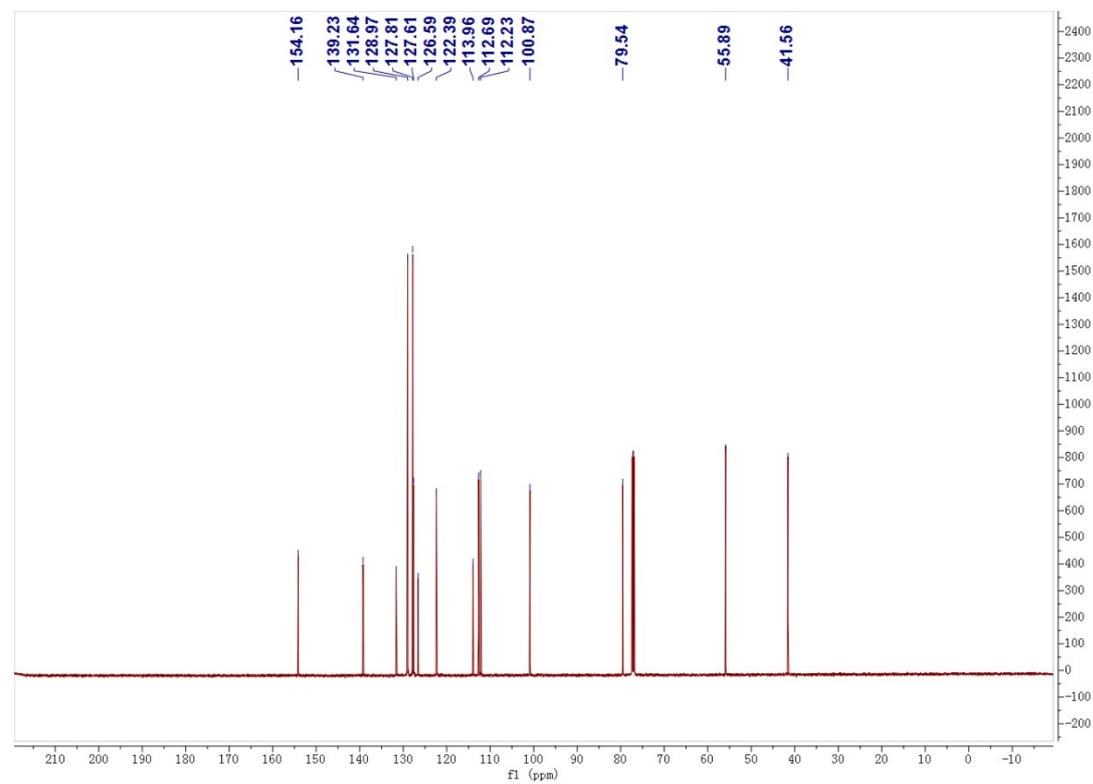
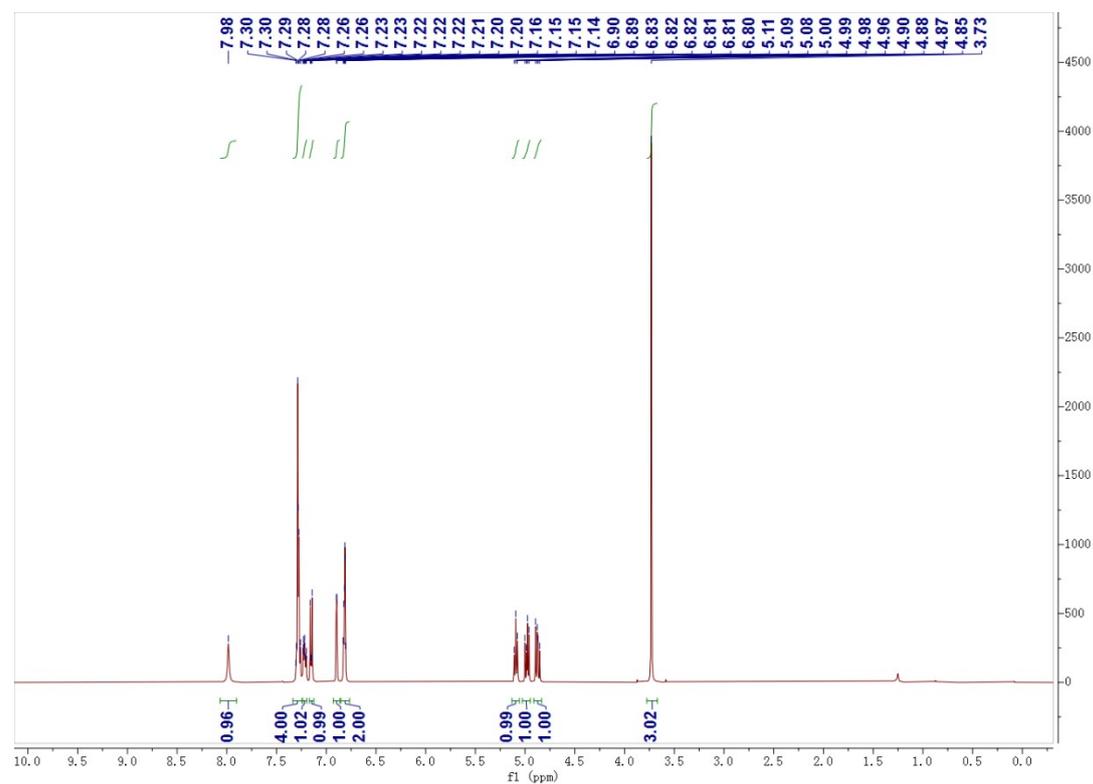
峰#	保留时间	面积	高度	面积 %	高度 %
1	13.002	14431376	469268	49.844	52.127
2	14.450	14521573	430971	50.156	47.873
总计		28952949	900238	100.000	100.000

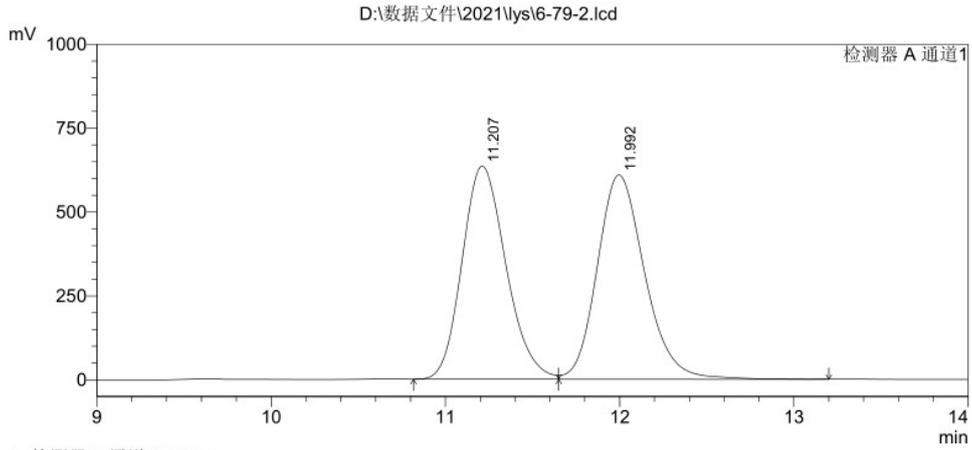


峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	14.260	4399747	120890	50.578	52.967
2	15.912	4299108	107345	49.422	47.033
总计		8698855	228235	100.000	100.000

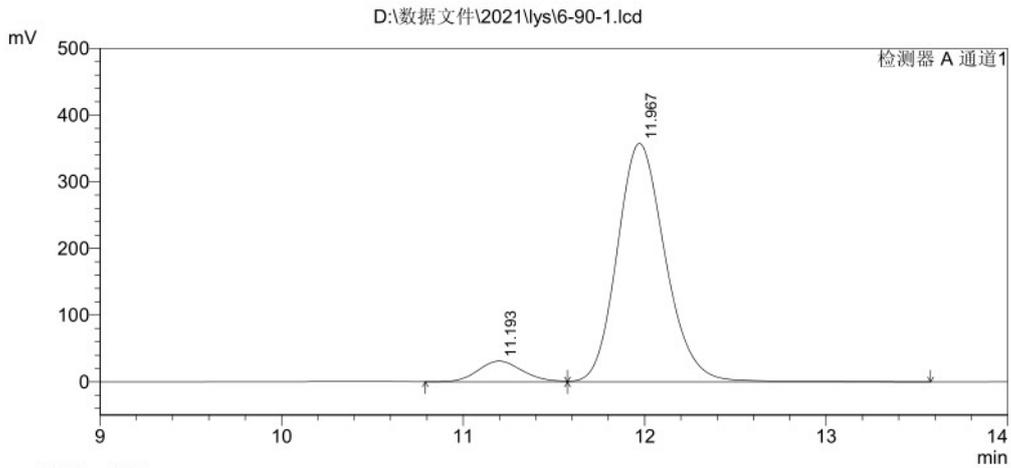
(S)-5-methoxy-3-(2-nitro-1-phenylethyl)-1H-indole (1m)





峰表

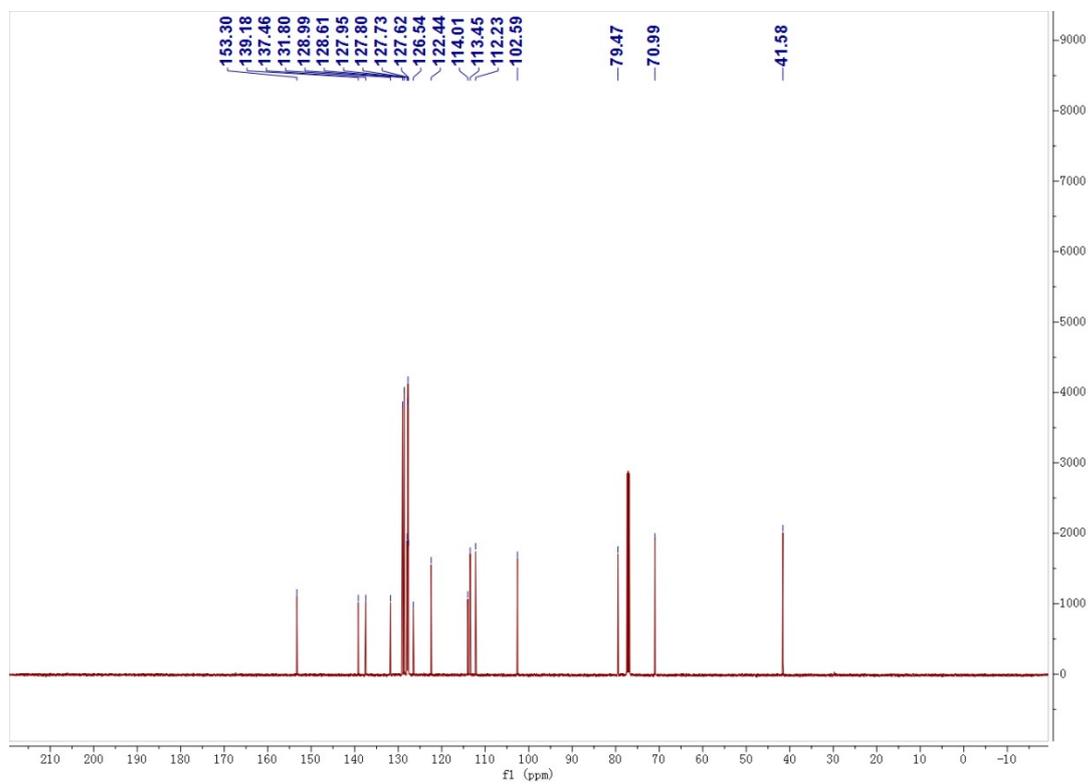
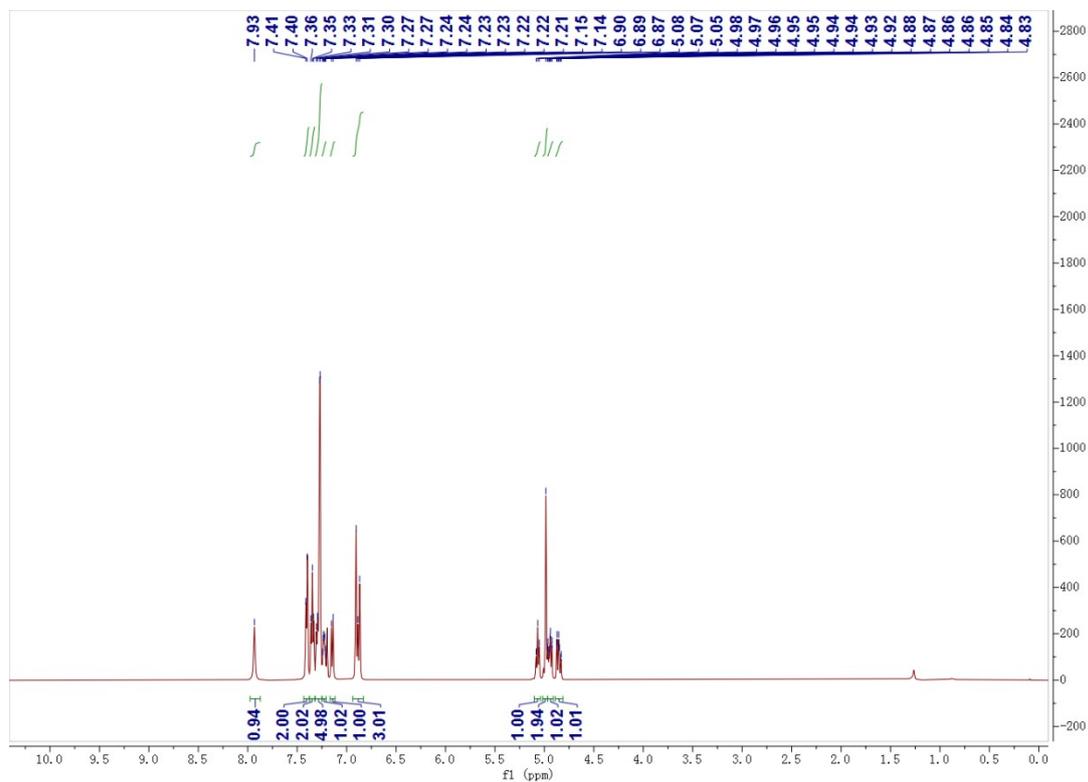
峰#	保留时间	面积	高度	面积 %	高度 %
1	11.207	11119696	635695	49.046	51.067
2	11.992	11552122	609139	50.954	48.933
总计		22671818	1244834	100.000	100.000

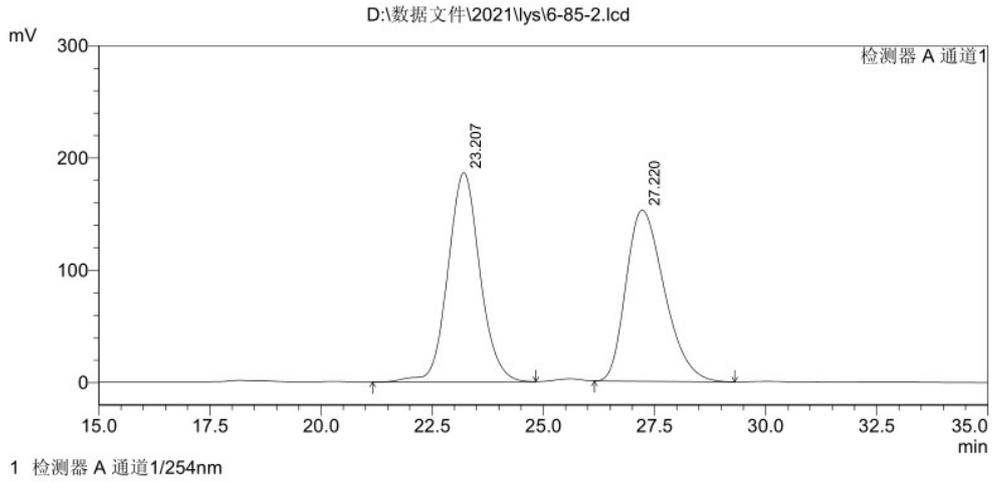


峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	11.193	533809	31148	7.491	8.011
2	11.967	6592527	357663	92.509	91.989
总计		7126336	388811	100.000	100.000

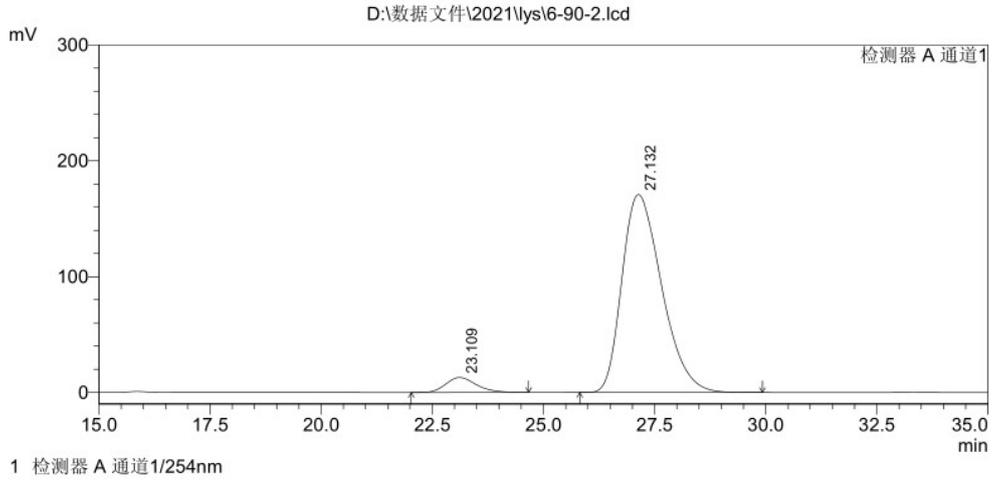
(S)-5-(benzyloxy)-3-(2-nitro-1-phenylethyl)-1H-indole (1n)





峰表

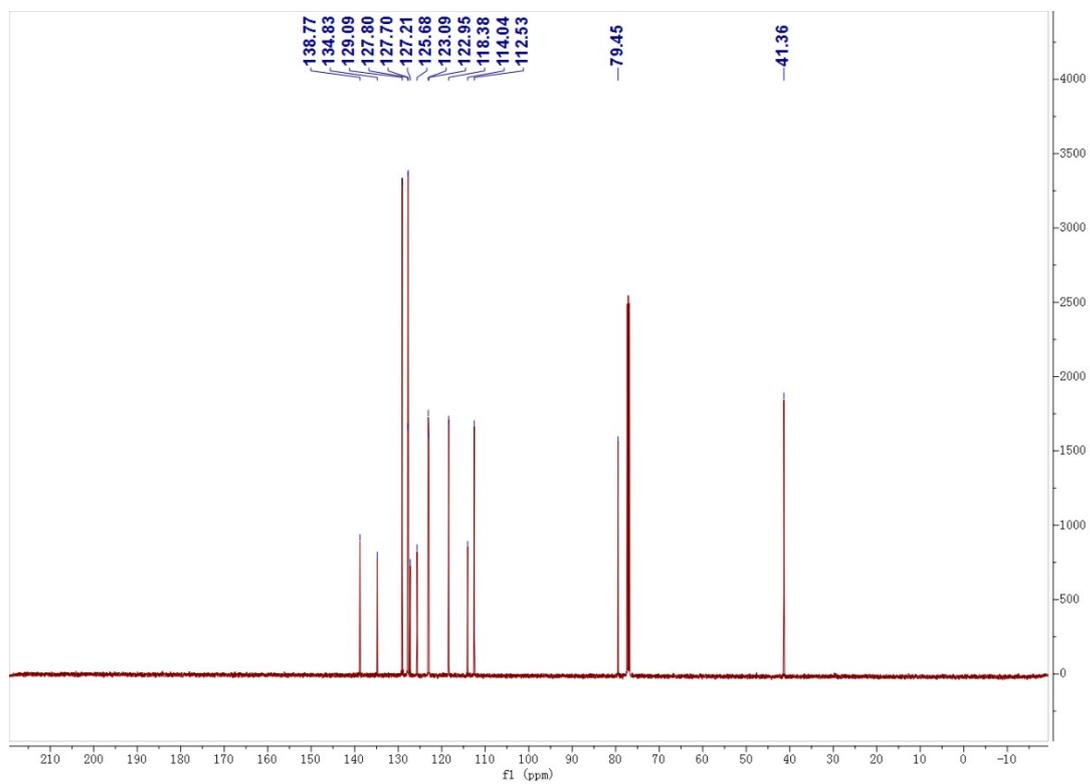
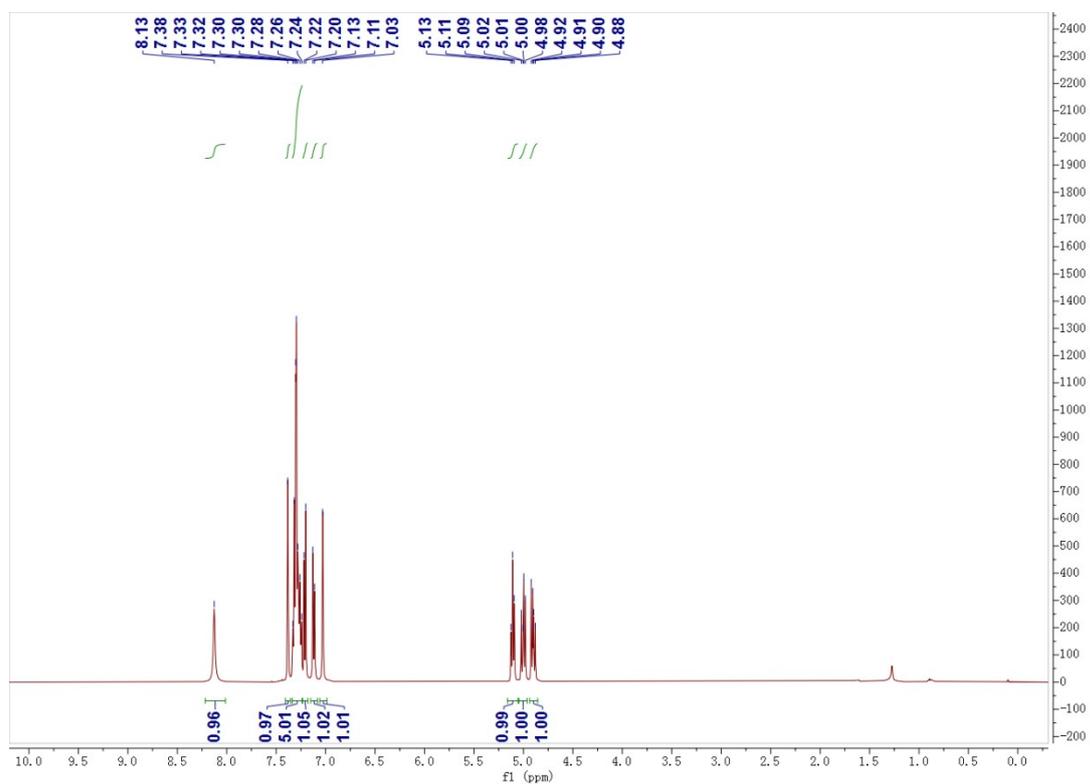
检测器 A Ch1 254nm					
峰#	保留时间	面积	高度	面积 %	高度 %
1	23.207	9353516	186305	50.496	54.995
2	27.220	9169823	152459	49.504	45.005
总计		18523339	338764	100.000	100.000

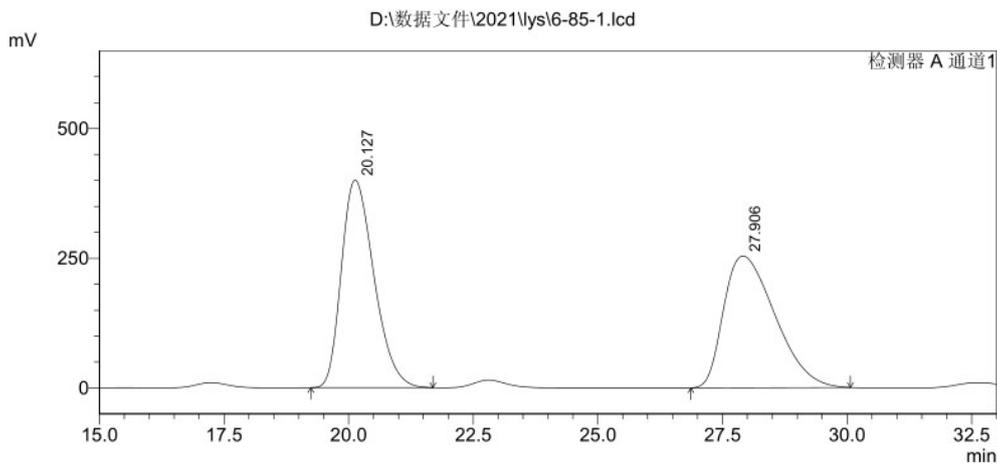


峰表

检测器 A Ch1 254nm					
峰#	保留时间	面积	高度	面积 %	高度 %
1	23.109	624793	12982	5.539	7.058
2	27.132	10655191	170950	94.461	92.942
总计		11279985	183932	100.000	100.000

(S)-5-chloro-3-(2-nitro-1-phenylethyl)-1H-indole (1o)

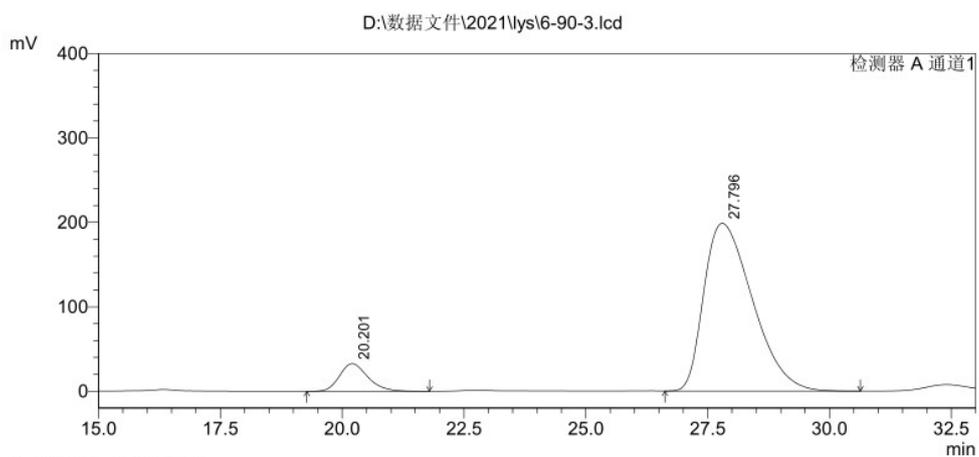




1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm					
峰#	保留时间	面积	高度	面积 %	高度 %
1	20.127	18243194	400429	50.038	61.179
2	27.906	18215654	254095	49.962	38.821
总计		36458848	654525	100.000	100.000

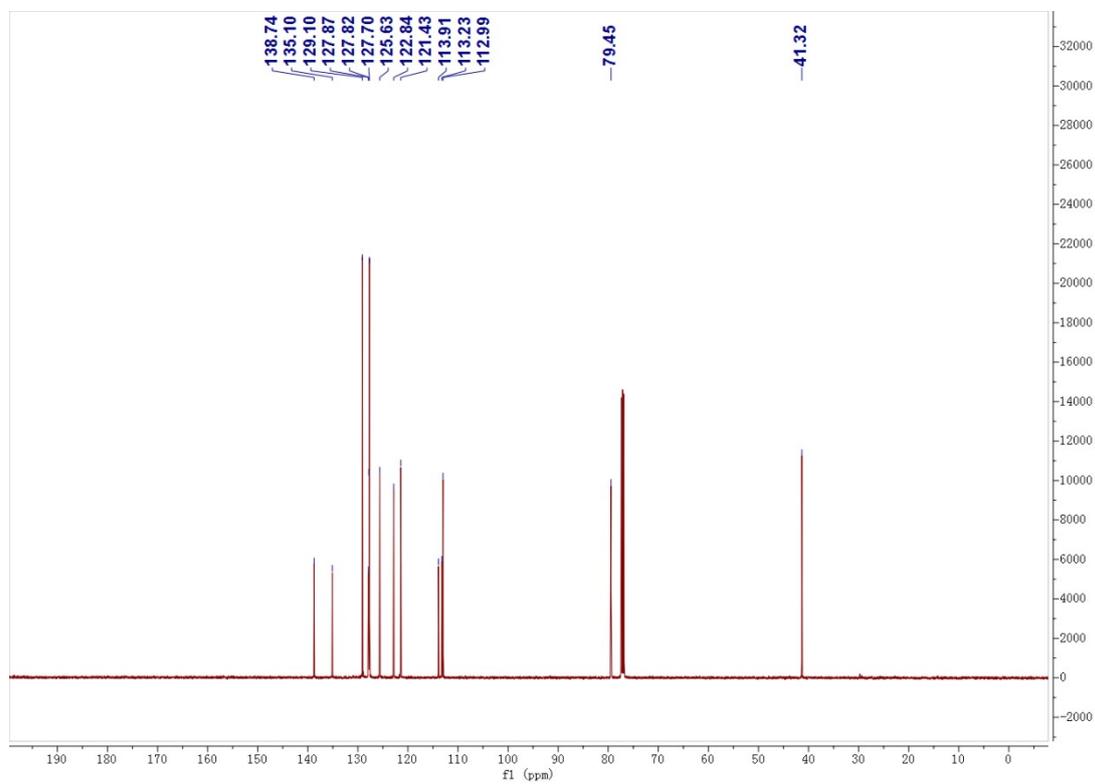
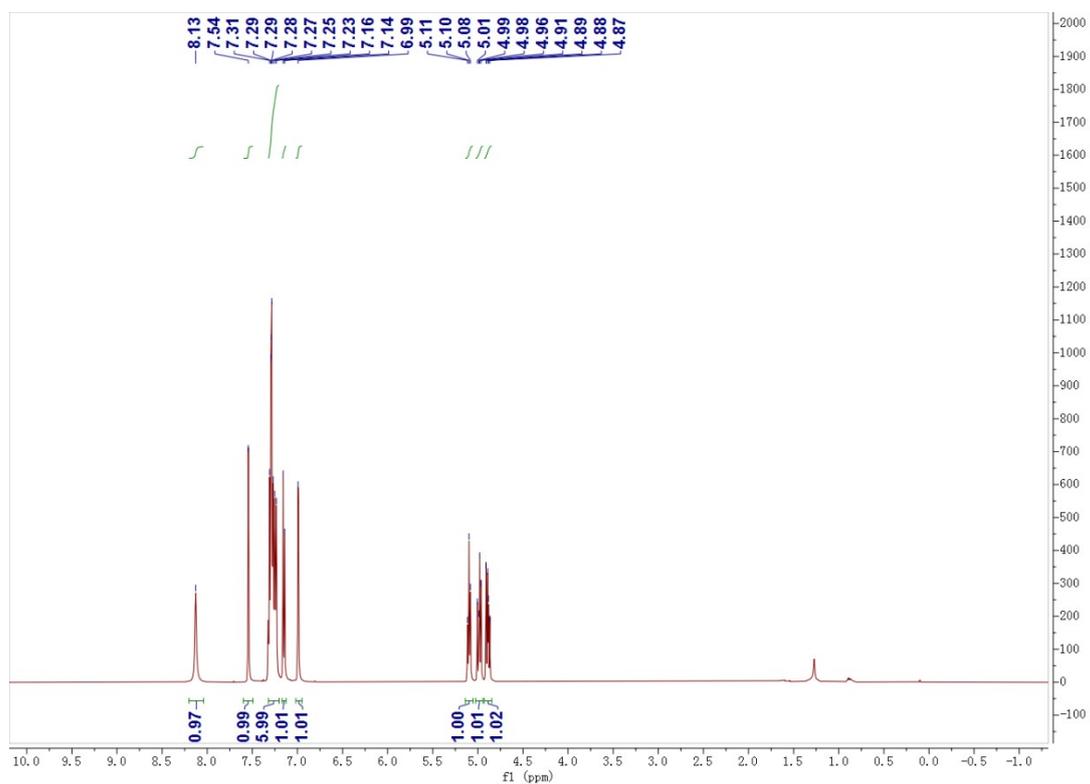


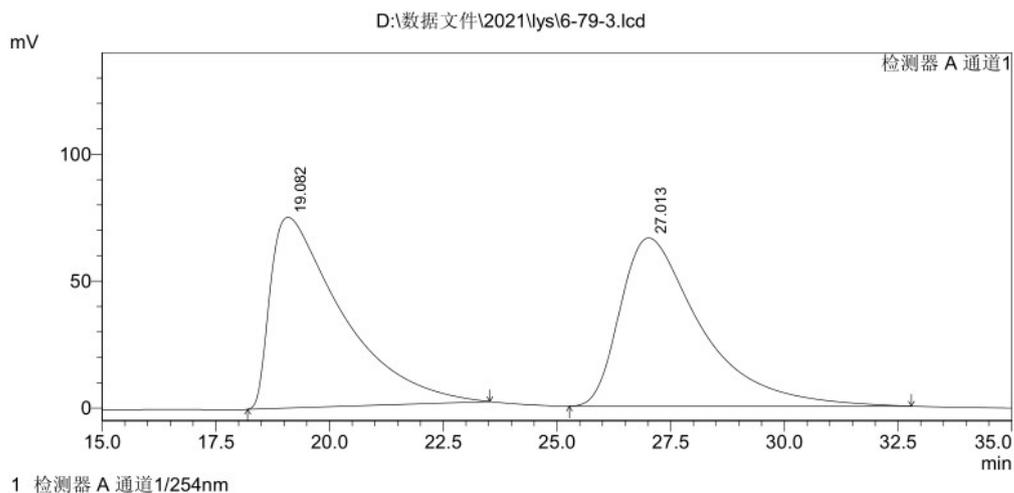
1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm					
峰#	保留时间	面积	高度	面积 %	高度 %
1	20.201	1323466	32799	8.752	14.169
2	27.796	13797922	198685	91.248	85.831
总计		15121387	231484	100.000	100.000

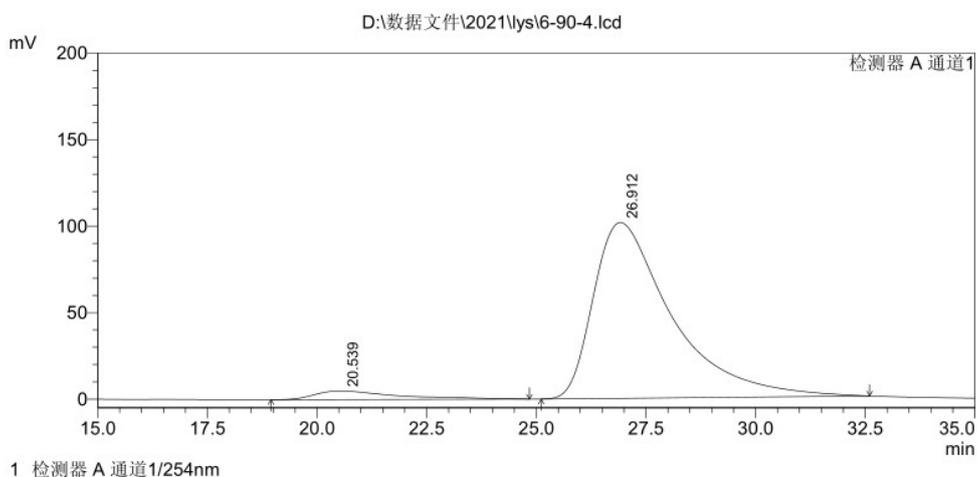
(S)-5-bromo-3-(2-nitro-1-phenylethyl)-1H-indole (1p)





峰表

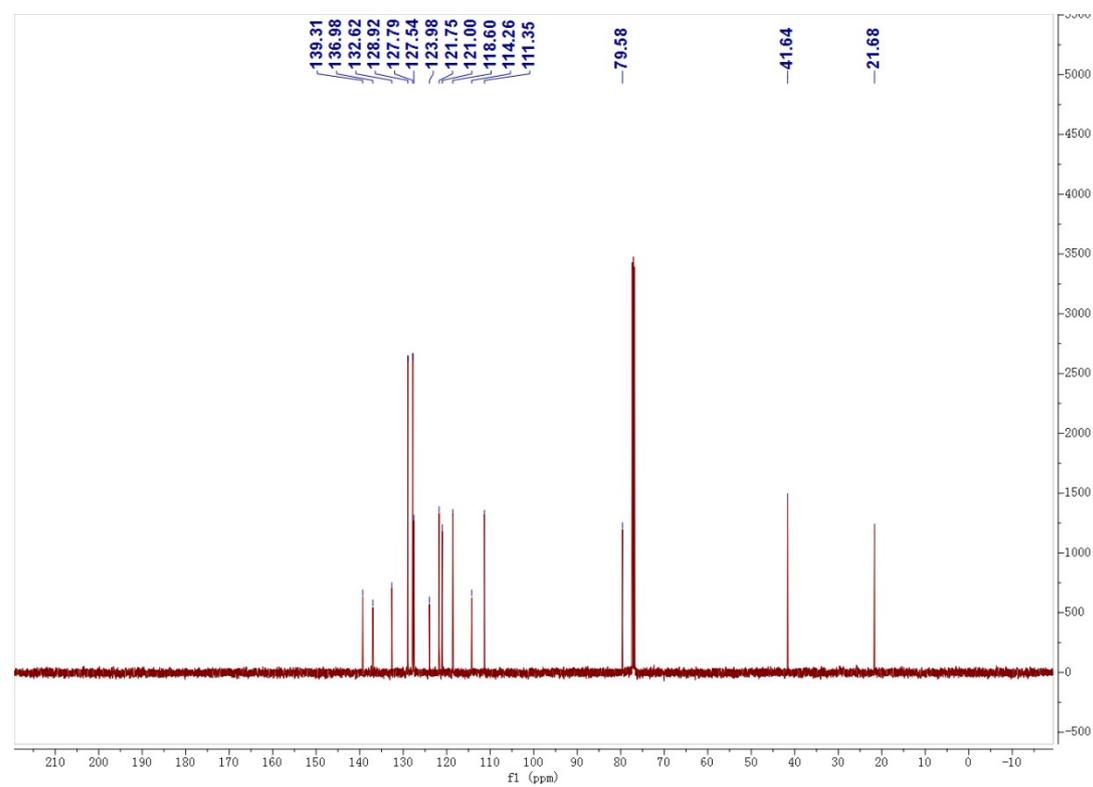
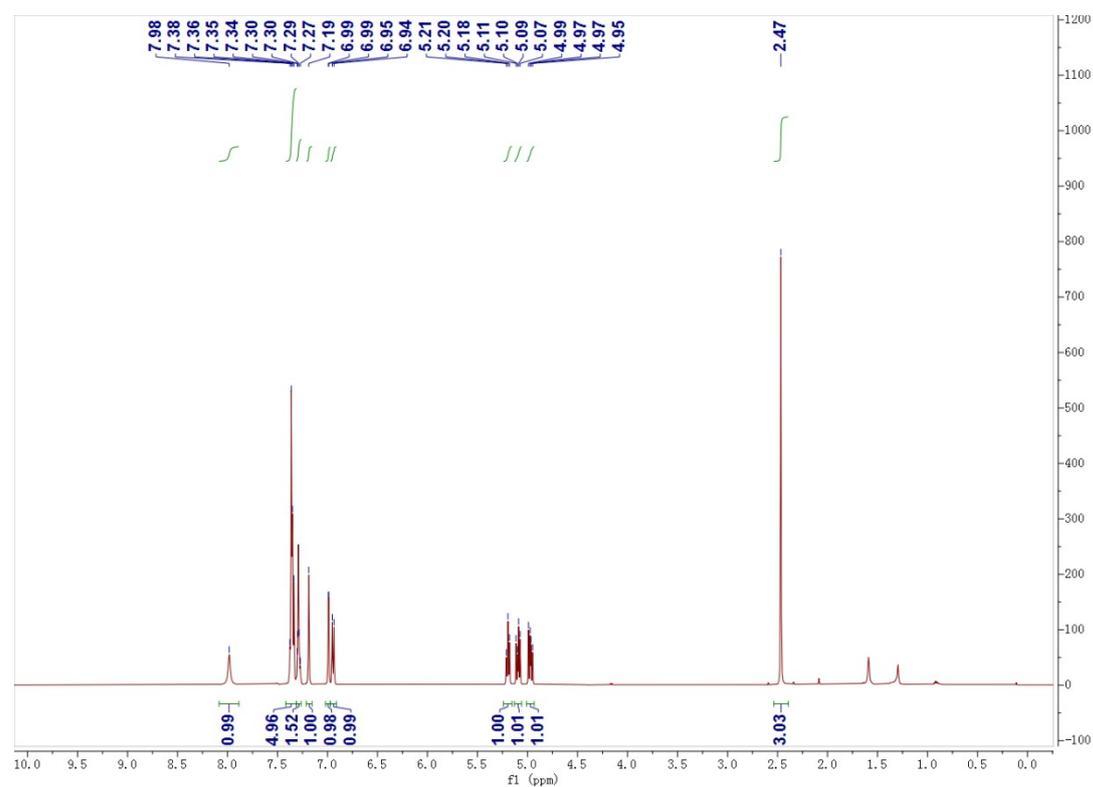
峰#	保留时间	面积	高度	面积 %	高度 %
1	19.082	8283786	75192	50.129	53.152
2	27.013	8241281	66273	49.871	46.848
总计		16525067	141465	100.000	100.000

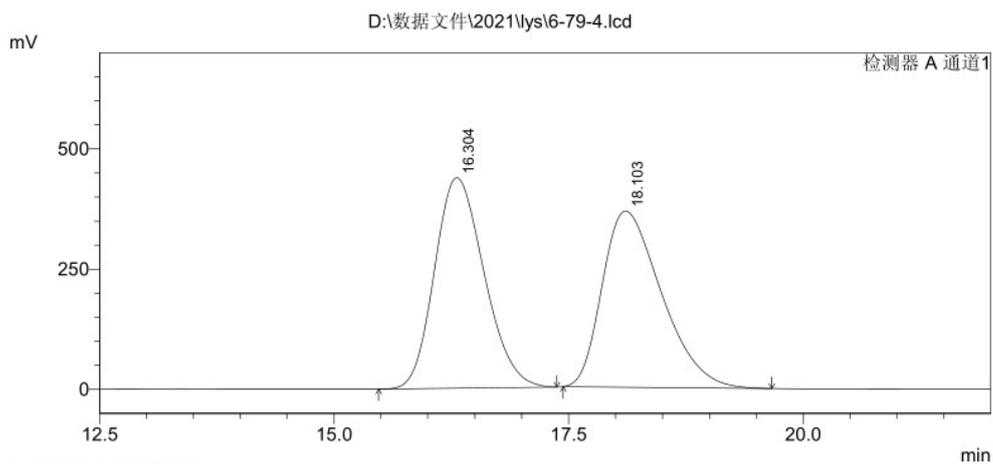


峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	20.539	639988	4958	4.812	4.653
2	26.912	12659038	101606	95.188	95.347
总计		13299026	106565	100.000	100.000

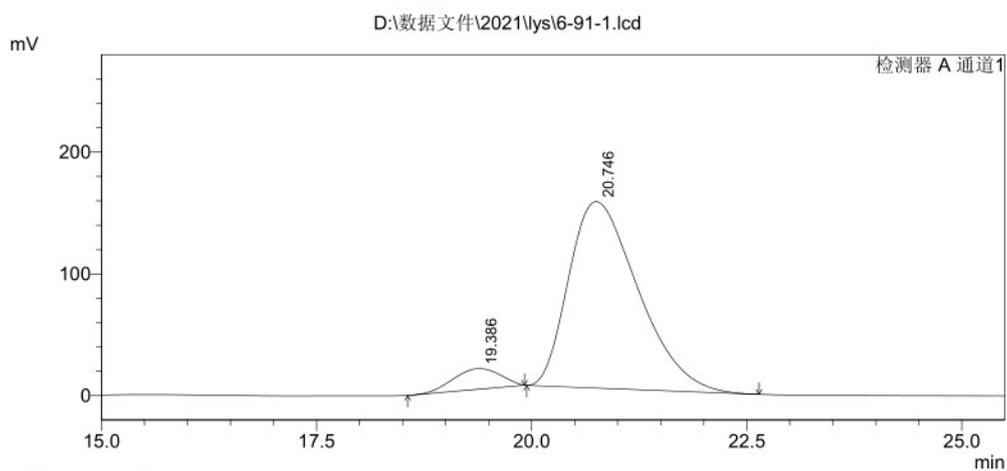
(S)-6-methyl-3-(2-nitro-1-phenylethyl)-1H-indole (1q)





峰表

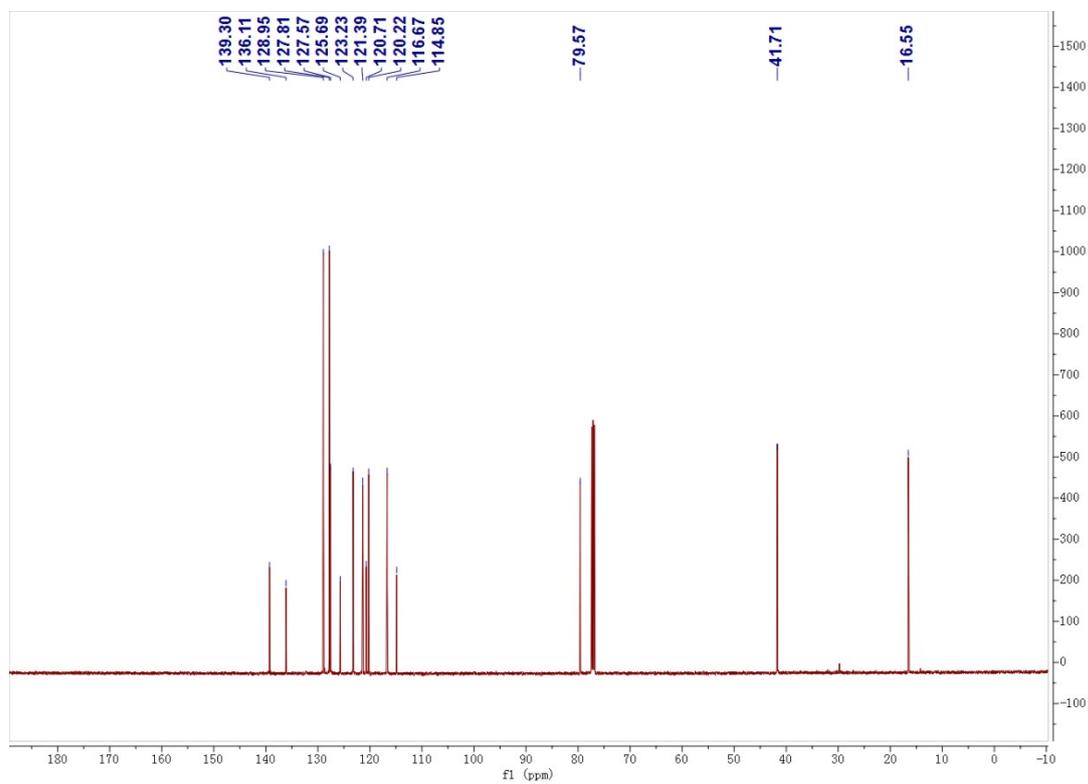
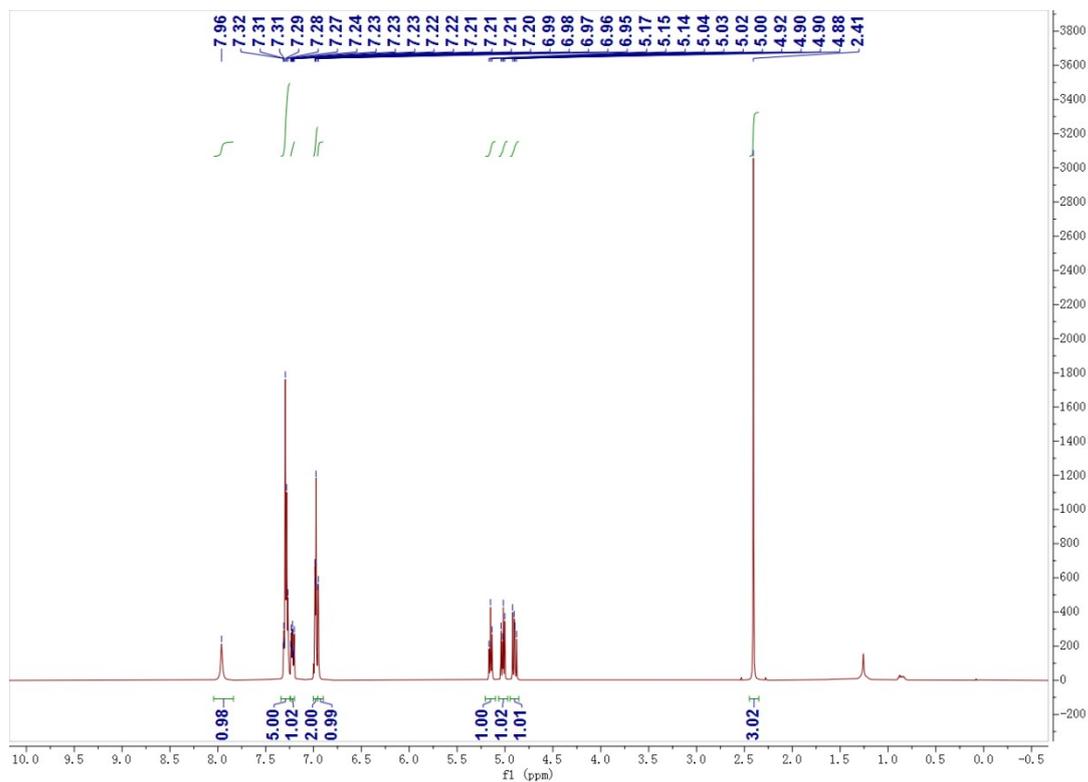
峰#	保留时间	面积	高度	面积 %	高度 %
1	16.304	16081943	437399	49.970	54.431
2	18.103	16101438	366192	50.030	45.569
总计		32183381	803591	100.000	100.000

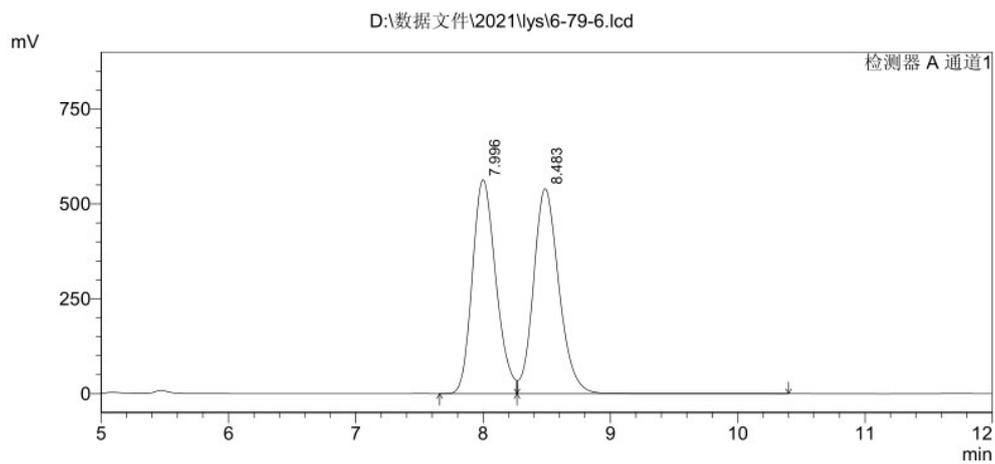


峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	19.386	647036	16915	7.003	9.949
2	20.746	8592993	153092	92.997	90.051
总计		9240029	170006	100.000	100.000

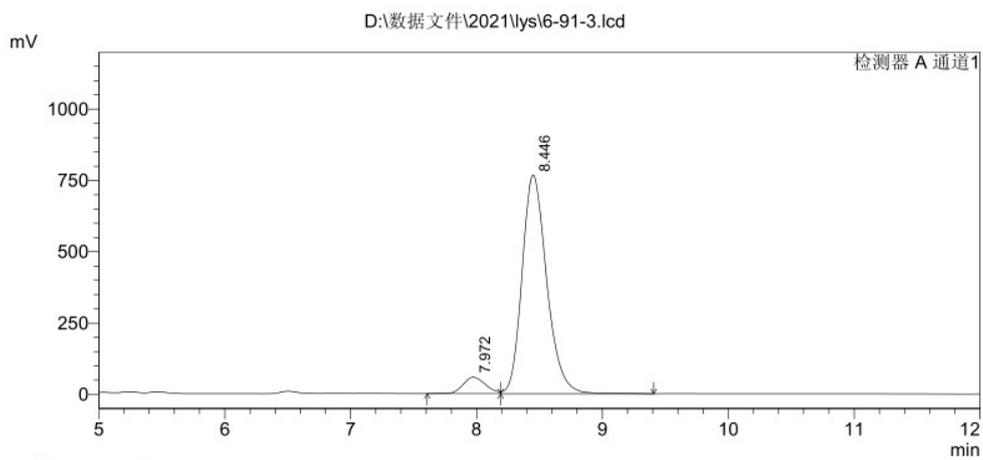
(S)-7-methyl-3-(2-nitro-1-phenylethyl)-1H-indole (1r)





峰表

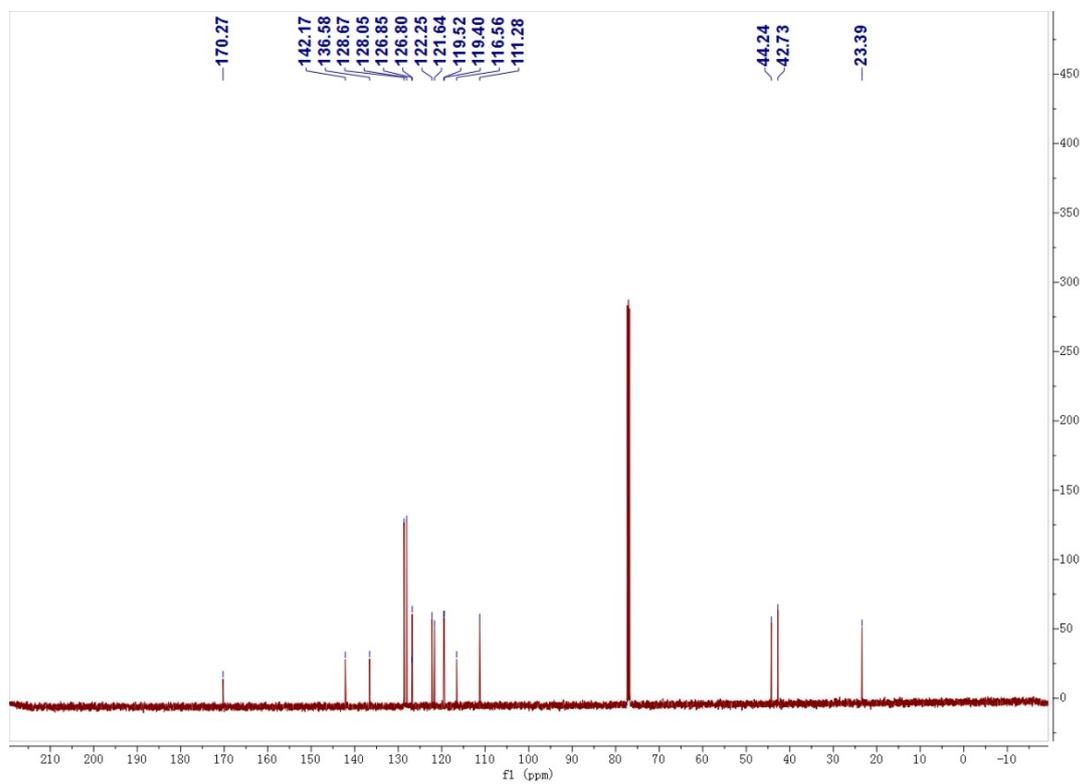
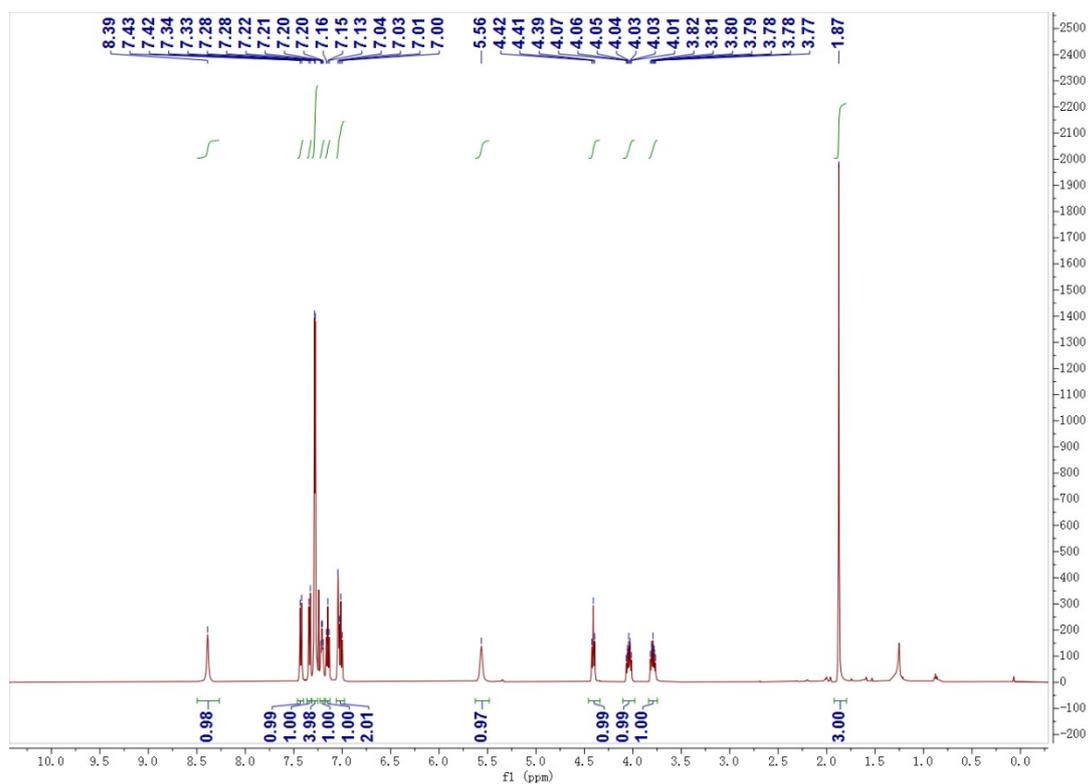
峰#	保留时间	面积	高度	面积 %	高度 %
1	7.996	7256478	564396	49.158	51.087
2	8.483	7505158	540388	50.842	48.913
总计		14761636	1104785	100.000	100.000

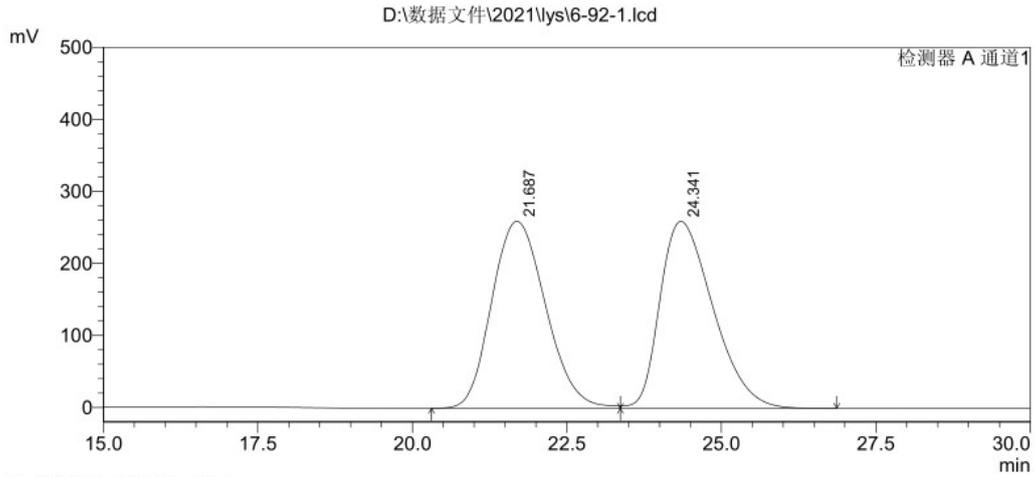


峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	7.972	723981	58198	6.482	7.051
2	8.446	10444974	767249	93.518	92.949
总计		11168956	825447	100.000	100.000

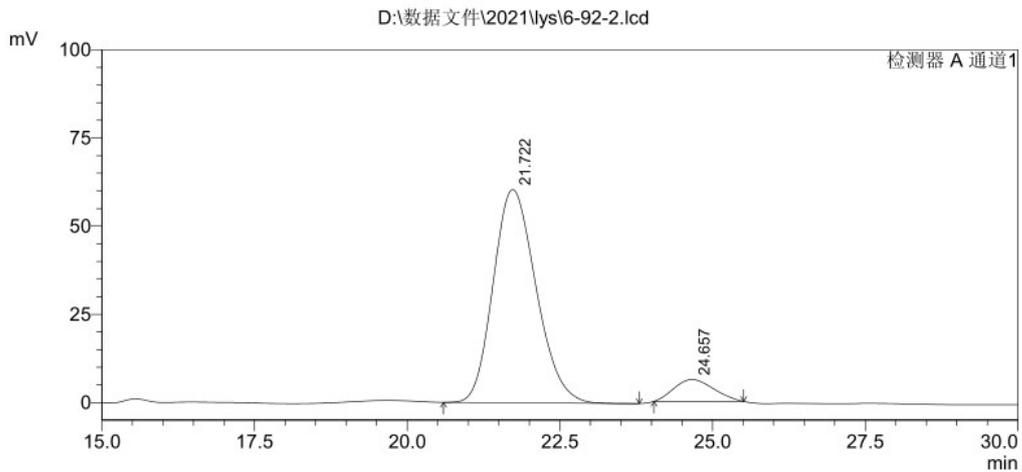
(S)-N-(2-(1H-indol-3-yl)-2-phenylethyl)acetamide (5)





峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	21.687	15743400	259662	50.383	50.011
2	24.341	15504309	259546	49.617	49.989
总计		31247709	519208	100.000	100.000



峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	21.722	2950252	60453	91.376	90.728
2	24.657	278450	6178	8.624	9.272
总计		3228702	66631	100.000	100.000

4. References

- [1] C J Peng, J P Pei, Y H Chen, Z Y Wu, M Liu, Y K Liu, *Organic Chemistry Frontiers*, **2021**, 8, 4217.
- [2] R. Warmuth, T. E. Munsch, R. A. Stalker, B. Li, A. Beatty, *Tetrahedron* **2001**, 57, 6383.
- [3] (a) Y. F. Gao, Z. X. Qiu, R. Sun, N. X. Gao, G. R. Cao, D. W. Teng, *Tetrahedron Lett.* **2018**, 59, 3938.
- (b) N. X. Gao, Y. S. Li, G. R. Cao, D. W. Teng, *New J. Chem.* **2021**, 45, 16477.