Supporting Information

Catalytic Asymmetric Formal Aza-Diels-Alder Reactions of α,β-Unsaturated Ketones and 3*H*-Indoles

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A: General Information and Starting Materials

General Information. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker AV-400 spectrometer (400 MHz and 100 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$: δ 7.26) Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.16). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). High resolution mass spectrometry (EI) was carried out using a Waters Micromass GCT spectrometer. Optical rotations were measured on an Autopol III automatic polarimeter (Rudolph Research analytical). Enantiomeric excess was determined by chiral HPLC using Agilent 1200 Series, Chiralpak AD-H (0.46cm x 25 cm), Chiralpak AS-H (0.46cm x 25 cm).

Starting Materials. All solvents and inorganic reagents were from commercial sources and used without purification unless otherwise noted. Imines **2** were synthesized following the literature procedure.[1–3]

Reference

(1) Rodriguez, J. G.; Benito, Y.; Temprano, F. *J. Heterocycl. Chem.* **1985**, *22*, 1207–1210.
(2) Liu, K. G.; Robichaud, A. J. *Tetrahedron Lett*. **2007**, *48*, 461–463.
(3) Shao, Y.-D.; Tian, S.-K. *Chem. Commun*. **2012**, *48*, 4899–4901.

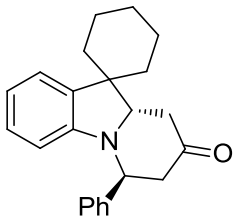
B: Experimental Details

General procedure for the Formal Aza-Diels-Alder Reaction

Unless otherwise noted, Imine **2a** (0.6 mmol, 3.0 equiv.) was added to a mixture of catalyst **1i** (0.04 mmol, 0.2 equiv.), benzoic acid (0.04 mmol, 0.2 equiv.) and α, β-unsaturated ketones **3a** (0.2 mmol, 1 equiv.) in xylene (0.4 mL) at 30°C. The reaction mixture was maintained at this temperature for 3 days and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired FADA product. The enantiomeric ratio was determined by HPLC analysis on chiral column.

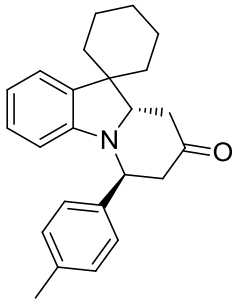
C: Characterization Data of Formal ADA Products

(6'S,9a'S)-6'-phenyl-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4a)



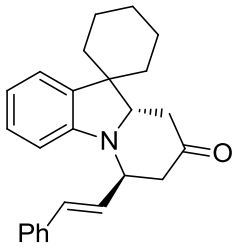
Yellow solid; mp: 80-83°C; ^{1}H NMR (400MHz, $CDCl_3$): δ 0.90-2.43 (10H, m), δ 2.81 (1H, dd, *J* = 5.6, 15.2 Hz), δ 3.06 (1H, dd, *J* = 6.8, 15.2 Hz), δ 4.06 (1H, dd, *J* = 5.2, 9.6 Hz), δ 5.03 (1H, t, *J* = 6 Hz), δ 6.52 (1H, d, *J* = 7.6 Hz), δ 6.81-6.85 (1H, m), δ 7.12-7.17 (2H, m), δ 7.32 (1H, t, *J* = 7.2 Hz), δ 7.39-7.44 (2H, m), δ 7.50 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100MHz, $CDCl_3$): δ 22.9, 23.7, 23.7, 25.7, 29.7, 37.0, 40.5, 43.9, 47.4, 56.5, 64.4, 107.1, 118.8, 123.0, 126.5, 127.4, 128.0, 128.8, 137.0, 141.2, 148.6, 209.3; $[\alpha]_D^{30}$ -50.1 (*c* 0.5, CH_2Cl_2); HRMS(EI) calcd for $C_{23}H_{25}NO$ $[M]^+$ 331.1936, found: 331.1935; HPLC (DAICEL Chiralpak AD-H, hexane/*i*-PrOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 6.981 min (major) and 13.353 min (minor).

(6'S,9a'S)-6'-(p-tolyl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4b)



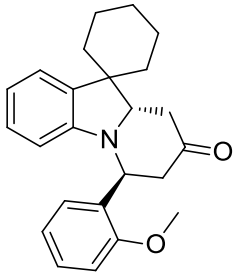
Yellow solid; mp: 117-120°C; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.17-1.98 (10H, m), δ 2.27-2.30 (2H, m), δ 2.34 (3H, s), δ 2.37 (1H, t, *J* = 2 Hz), δ 2.74 (1H, dd, *J* = 5.6, 14.8 Hz), δ 3.00 (1H, dd, *J* = 6.4, 14.8 Hz), δ 3.99 (1H, dd, *J* = 6.0, 8.8 Hz), δ 4.98 (1H, t, *J* = 6.0 Hz), δ 6.49 (1H, d, *J* = 8.0 Hz), δ 6.78 (1H, t, *J* = 7.2 Hz), δ 7.08-7.18 (4H, m), δ 7.34 (2H, d, *J* = 8.0 Hz); ^{13}C NMR (100MHz, $CDCl_3$): δ 21.1, 22.9, 23.7, 25.7, 29.70, 36.9, 40.5, 43.8, 47.4, 56.1, 64.4, 107.1, 118.7, 123.0, 126.5, 127.9, 129.5, 137.1, 137.1, 138.0, 148.6, 209.4; $[\alpha]_D^{30}$ -131.34 (*c* 0.75, CH_2Cl_2); HRMS(EI) calcd for $C_{24}H_{27}NO$ $[M]^+$ 345.2093, found: 345.2091; HPLC (DAICEL Chiralpak AS-H, hexane/EtOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 10 min (major) and 15.858 min (minor).

(6'S,9a'S)-6'-((E)-styryl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4c)



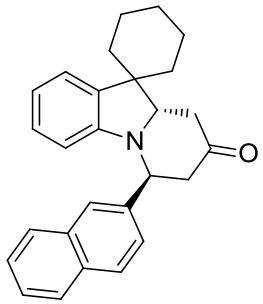
Yellow solid; mp: 160-163°C; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.24-1.98 (10H, m), δ 2.30-2.35 (2H, m), δ 2.69-2.78 (2H, m), δ 4.05 (1H, t, *J* = 7.4 Hz), δ 4.83-4.86 (1H, m), δ 6.26 (1H, dd, *J* = 4.4, 16.0 Hz), δ 6.65-6.70 (2H, m), δ 6.81-6.85 (1H, m), δ 7.16-7.20 (2H, m), δ 7.25-7.29 (1H, m), δ 7.34 (2H, t, *J* = 7.4 Hz), δ 7.39-7.42 (2H, m); ^{13}C NMR (100MHz, $CDCl_3$): δ 23.0, 23.4, 25.8, 29.8, 36.2, 41.1, 43.2, 47.5, 54.3, 65.1, 107.1, 118.9, 123.4, 126.5, 127.9, 127.9, 128.5, 128.6, 132.2, 136.4, 137.4, 147.9, 209.1; $[\alpha]_D^{30}$ -103.4 (*c* 0.75, CH_2Cl_2); HRMS(EI) calcd for $C_{25}H_{27}NO$ $[M]^+$ 357.2093, found: 357.2086; HPLC (DAICEL Chiralpak AD-H, hexane/*i*-PrOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 7.704 min (major) and 10.022 min (minor).

(6'S,9a'S)-6'-(2-methoxyphenyl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4d)



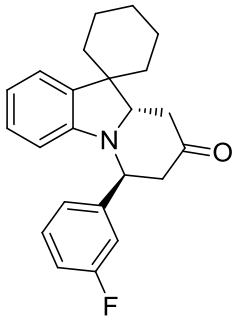
Yellow solid; mp: 117-120°C; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.23-2.02 (10H, m), 2.33-2.45 (2H, m), δ 2.77 (1H, dd, *J* = 10.8, 16.4 Hz), δ 2.94 (1H, dd, *J* = 4.8, 16.0 Hz), δ 3.88 (3H, s), δ 4.31 (1H, dd, *J* = 2.8, 12.0 Hz), δ 4.98 (1H, dd, *J* = 4.8, 10.8 Hz), δ 6.22 (1H, d, *J* = 8.0 Hz), δ 6.74 (1H, t, *J* = 7.2 Hz), δ 6.92-7.03 (3H, m), δ 7.09 (1H, d, *J* = 7.2 Hz), δ 7.26-7.30 (1H, m), δ 7.52 (1H, dd, *J* = 1.6, 7.6 Hz); ^{13}C NMR (100MHz, $CDCl_3$): δ 22.9, 23.9, 25.7, 30.1, 37.6, 40.1, 43.7, 46.8, 52.4, 55.2, 64.0, 107.7, 110.4, 118.3, 120.8, 122.4, 126.6, 127.8, 128.4, 130.2, 136.6, 149.2, 156.3, 210.6; $[\alpha]_D^{30}$ -244.1 (*c* 1.00, CH_2Cl_2); HRMS(EI) calcd for $C_{24}H_{27}NO_2$ $[M]^+$ 361.2042, found: 361.2041; HPLC (DAICEL Chiralpak AD-H, hexane/*i*-PrOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 6.596 min (major) and 8.435 min (minor).

(6'S,9a'S)-6'-(naphthalen-2-yl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4e)



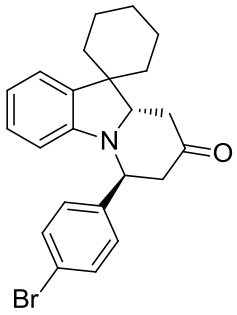
Yellow solid; mp: 152-154ºC; ^{1}H NMR (400MHz, $CDCl_3$): δ 0.92-2.10 (10H, m), δ 2.36 (2H, d, *J* = 7.6 Hz), δ 2.88 (1H, dd, *J* = 5.6, 14.8 Hz), δ 3.18 (1H, dd, *J* = 6.0, 14.8 Hz), δ 4.03 (1H, t, *J* = 7.4 Hz), δ 5.20 (1H, t, *J* = 6.0 Hz), δ 6.59 (1H, d, *J* = 7.6 Hz), δ 6.84-6.88 (1H, m), δ 7.17 (2H, dd, *J* = 6.8, 13.2 Hz), δ 7.51-7.54 (2H, m), δ 7.63 (1H, d, *J* = 8.4 Hz), δ 7.86-7.92 (4H, m); ^{13}C NMR (100MHz, $CDCl_3$): δ 22.9, 23.7, 25.8, 29.7, 36.9, 40.6, 43.5, 47.6, 56.4, 64.5, 107.2, 119.0, 123.1, 124.9, 125.4, 126.1, 126.3, 127.6, 128.0, 128.2, 128.8, 132.8, 133.4, 137.2, 138.6, 148.5, 209.2; $[\alpha]_D^{30}$ -191.32 (*c* 1.00, CH_2Cl_2); HRMS(EI) calcd for $C_{27}H_{27}NO$ $[M]^+$ 381.2093, found: 381.2094; HPLC (DAICEL Chiralpak AD-H, hexane/*i*-PrOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 8.593 min (major) and 15.463 min (minor).

(6'S,9a'S)-6'-(3-fluorophenyl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4f)



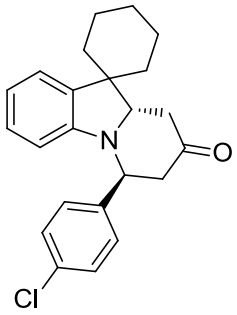
Yellow solid; mp: 79-82ºC; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.19-1.98 (10H, m), δ 2.24-2.38 (2H, m), δ 2.76 (1H, dd, *J* = 5.6, 15.2 Hz), δ 2.96 (1H, dd, *J* = 7.2, 15.2 Hz), δ 4.03 (1H, dd, *J* = 3.6, 10.4 Hz), δ 4.93 (1H, t, *J* = 6.2 Hz), δ 6.43 (1H, d, *J* = 7.6 Hz), δ 6.80 (1H, t, *J* = 7.2 Hz), δ 6.97 (1H, t, *J* = 8.0 Hz), δ 7.07-7.36 (6H, m); ^{13}C NMR (100MHz, $CDCl_3$): δ 22.9, 23.7, 25.7, 29.7, 37.0, 40.3, 43.9, 47.4, 56.3, 56.3, 64.5, 107.3, 113.5, 113.7, 114.4, 114.6, 119.2, 122.0, 122.1, 123.1, 128.0, 130.3, 130.4, 137.0, 144.1, 148.4, 208.8; $[\alpha]_D^{30}$ -57.5 (*c* 0.5, CH_2Cl_2); HRMS(EI) calcd for $C_{23}H_{24}FNO$ $[M]^+$ 349.1842, found: 349.1843; HPLC (DAICEL Chiralpak AS-H, hexane/EtOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 10.402 min (major) and 19.882 min (minor).

(6'S,9a'S)-6'-(4-bromophenyl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4g)



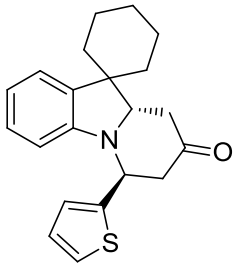
Yellow solid; mp: 132-135ºC; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.19-1.99 (10H, m), δ 2.28-2.37 (2H, m), δ 2.78 (1H, dd, *J* = 5.6, 14.8 Hz), δ 2.99 (1H, dd, *J* = 6.8, 15.2 Hz), δ 4.02 (1H, dd, *J* = 4.8, 10.0 Hz), δ 4.97 (1H, t, *J* = 6.2 Hz), δ 6.49 (1H, d, *J* = 8.0 Hz), δ 6.84 (1H, t, *J* = 7.4 Hz), δ 7.12-7.17 (2H, m), δ 7.38 (2H, d, *J* = 8.4 Hz), δ 7.52 (2H, d, *J* = 8.4 Hz); ^{13}C NMR (100MHz, $CDCl_3$): δ 23.0, 23.8, 25.8, 29.8, 37.0, 40.5, 43.7, 47.5, 56.2, 64.6, 107.2, 119.2, 121.5, 123.2, 128.0, 128.4, 132.0, 137.1, 140.3, 148.4, 208.8; $[\alpha]_D^{30}$ -160 (*c* 1.00, CH_2Cl_2); HRMS(EI) calcd for $C_{23}H_{24}BrNO$ $[M]^+$ 409.1041, found: 409.1040; HPLC (DAICEL Chiralpak AD-H, hexane/*i*-PrOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 7.816 min (major) and 11.558 min (minor).

(6'S,9a'S)-6'-(4-chlorophenyl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido [1,2-a]indol]-8'(7'H)-one (4h)



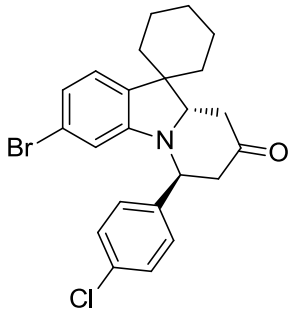
Yellow solid; mp: 121-123ºC; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.18-1.99 (10H, m), 2.31-2.33 (2H, m), δ 2.78 (1H, dd, *J* = 6.0, 15.2 Hz), δ 2.99 (1H, dd, *J* = 6.8, 14.8 Hz), δ 4.01 (1H, dd, *J* = 4.8, 10.0 Hz), δ 4.98 (1H, t, *J* = 6.2 Hz), δ 6.49 (1H, d, *J* = 7.6 Hz), δ 6.81-6.85 (1H, m), δ 7.10-7.16 (2H, m), δ 7.35-7.37 (2H, m), δ 7.42 (2H, d, *J* = 8.4 Hz); ^{13}C NMR (100MHz, $CDCl_3$): δ 22.9, 23.7, 23.7, 25.7, 29.6, 36.9, 40.4, 43.6, 43.6, 47.4, 56.0, 64.4, 107.1, 119.1, 123.0, 127.9, 128.0, 128.9, 133.2, 137.0, 139.6, 148.3, 208.8; $[\alpha]_D^{30}$ -142.3 (*c* 1.00, CH_2Cl_2); HRMS(EI) calcd for $C_{23}H_{24}ClNO$ $[M]^+$ 365.1546, found:365.1545; HPLC (DAICEL Chiralpak AD-H, hexane/*i*-PrOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 6.977 min (major) and 9.616 min (minor).

(6'S,9a'S)-6'-(thiophen-2-yl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1 ,2-a]indol]-8'(7'H)-one (4i)



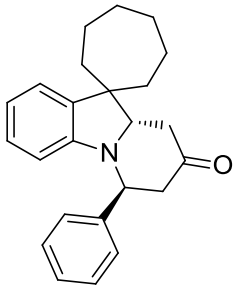
Yellow solid; mp: 114-117°C; ^{1}H NMR (400MHz, $CDCl_3$): δ 0.82-2.36 (10H, m), δ 2.84 (1H, dd, *J* = 6.4, 14.0 Hz), δ 3.00-3.04 (1H, m), δ 4.02 (1H, dd, *J* = 5.2, 10.0 Hz), δ 5.48 (1H, d, *J* = 5.2 Hz), δ 6.72 (1H, d, *J* = 8.0 Hz), δ 6.87 (1H, t, *J* = 7.4 Hz), δ 6.97-7.04 (2H, m), δ 7.18 (2H, dd, *J* = 7.6, 15.2 Hz), δ 7.27-7.29 (1H, m); ^{13}C NMR (100MHz, $CDCl_3$): δ 22.9, 23.5, 25.8, 29.4, 36.0, 40.9, 42.8, 47.9, 53.3, 65.0, 107.1, 119.5, 123.5, 125.4, 126.1, 127.0, 127.9, 137.5, 145.3, 147.2, 208.2; $[\alpha]_D^{30}$ -2.2 (*c* 0.75, CH_2Cl_2); HRMS(EI) calcd for $C_{21}H_{23}NOS$ $[M]^+$ 337.1500, found: 337.1501; HPLC (DAICEL Chiralpak AD-H, hexane/EtOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 8.435 min (major).

(6'S,9a'S)-3'-bromo-6'-(4-chlorophenyl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1, 10'-pyrido[1,2-a]indol]-8'(7'H)-one (4j)



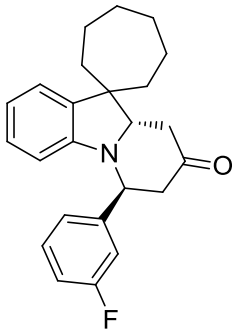
Yellow solid; mp: 50-53°C; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.19-1.94 (10H, m), δ 2.25-2.37 (2H, m), δ 2.78 (1H, dd, *J* = 6.0, 15.2 Hz), δ 2.98 (1H, dd, *J* = 6.8, 15.2 Hz), δ 3.99 (1H, dd, *J* = 3.6, 11.2 Hz), δ 4.94 (1H, t, *J* = 6.0 Hz), δ 6.59 (1H, d, *J* = 1.6 Hz), δ 6.92-6.99 (2H, m), δ 7.35-7.40 (4H, m); ^{13}C NMR (100MHz, $CDCl_3$): δ 22.7, 23.6, 25.5, 29.5, 36.8, 40.4, 43.6, 47.1, 55.8, 64.7, 110.2, 121.4, 121.7, 124.3, 127.8, 129.0, 133.4, 136.2, 138.9, 149.7, 208.0; $[\alpha]_D^{30}$ -187.96 (*c* 1.00, CH_2Cl_2); HRMS(EI) calcd for $C_{23}H_{23}BrClNO$ $[M]^+$ 443.0652, found: 443.0649; HPLC (DAICEL Chiralpak AD-H, hexane/EtOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 10.878 min (major) and 14.425 min (minor).

(6'S,9a'S)-6'-phenyl-9',9a'-dihydro-6'H-spiro[cycloheptane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4k)



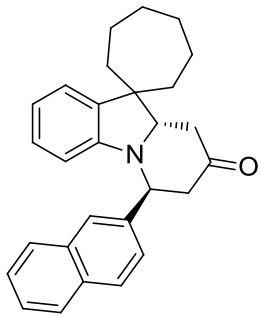
Yellow oil; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.46-2.09 (12H, m), 2.31-2.39 (2H, m), δ 2.82 (1H, dd, *J* = 5.6, 15.2 Hz), δ 3.03 (1H, dd, *J* = 6.4, 14.8 Hz), δ 3.89 (1H, dd, *J* = 5.6, 9.6 Hz), δ 5.03 (1H, t, *J* = 6.2 Hz), δ 6.51 (1H, d, *J* = 7.6 Hz), δ 6.81 (1H, t, *J* = 7.4 Hz), δ 7.10-7.15 (1H, m), δ 7.21-7.33 (2H, m), δ 7.38-7.42 (2H, m), δ 7.48 (2H, d, *J* = 7.6 Hz); ^{13}C NMR (100MHz, $CDCl_3$): δ 23.3, 24.2, 30.2, 30.6, 32.8, 40.5, 41.3, 44.0, 50.3, 56.4, 67.9, 107.2, 118.8, 122.8, 126.6, 127.5, 127.8, 128.8, 138.5, 141.1, 148.3, 209.2; $[\alpha]_D^{30}$ -182.28 (*c* 1.00, CH_2Cl_2); HRMS(EI) calcd for $C_{24}H_{27}NO$ $[M]^+$ 345.2093, found: 345.2094; HPLC (DAICEL Chiralpak AD-H, hexane/EtOH = 7/3, flow 0.6 ml/min, detection at 220nm) retention time = 8.332 min (major) and 13.198 min (minor).

(6'S,9a'S)-6'-(3-fluorophenyl)-9',9a'-dihydro-6'H-spiro[cycloheptane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4l)



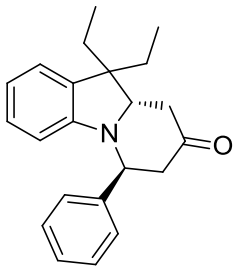
Yellow oil; ^{1}H NMR (400MHz, $CDCl_3$): δ 0.83-2.05 (12H, m), δ 2.27-2.34 (2H, m), δ 2.78 (1H, dd, *J* = 5.6, 15.2 Hz), δ 2.95 (1H, dd, *J* = 7.2, 15.2 Hz), δ 3.87 (1H, dd, *J* = 4.4, 10.4 Hz), δ 4.94 (1H, t, *J* = 6.4 Hz), δ 6.44 (1H, d, *J* = 8.0 Hz), δ 6.80 (1H, t, *J* = 7.2 Hz), δ 6.96-7.00 (1H, m), δ 7.09 (1H, t, *J* = 7.6 Hz), δ 7.17-7.22 (3H, m), δ 7.33 (1H, dd, *J* = 7.6, 13.6 Hz); ^{13}C NMR (100MHz, $CDCl_3$): δ 23.3, 24.2, 30.1, 30.5, 32.9, 40.6, 41.2, 44.1, 50.4, 56.3, 68.0, 107.3, 113.6, 113.8, 114.4, 114.6, 119.2, 122.1, 122.2, 122.9, 127.8, 130.3, 130.4, 138.5, 144.1, 144.1, 148.1, 162.1, 164.5, 208.7; $[\alpha]_D^{30}$ -43.16 (*c* 0.75, CH_2Cl_2); HRMS(EI) calcd for $C_{24}H_{26}FNO$ $[M]^+$ 363.1998, found: 363.2000; HPLC (DAICEL Chiralpak AD-H, hexane/EtOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 8.204 min (major) and 13.354 min (minor).

(6'S,9a'S)-6'-(naphthalen-2-yl)-9',9a'-dihydro-6'H-spiro[cycloheptane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4m)



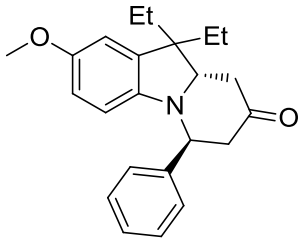
Yellow oil; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.43-2.11 (12H, m), δ 2.37 (2H, d, *J* = 7.6 Hz), δ 2.89 (1H, dd, *J* = 5.6, 14.8 Hz), δ 3.15 (1H, dd, *J* = 6.4, 15.2 Hz), δ 3.87 (1H, t, *J* = 7.2 Hz), δ 5.21 (1H, t, *J* = 6.0 Hz), δ 6.59 (1H, d, *J* = 7.6 Hz), δ 6.83 (1H, t, *J* = 7.2 Hz), δ 7.14 (1H, t, *J* = 7.6 Hz), δ 7.24 (1H, d, *J* = 7.2 Hz), δ 7.51-7.53 (2H, m), δ 7.61 (1H, d, *J* = 8.4 Hz), δ 7.85-7.89 (4H, m); ^{13}C NMR (100MHz, $CDCl_3$): δ 23.3, 24.2, 30.1, 30.5, 32.7, 40.5, 41.4, 43.6, 50.5, 56.4, 67.9, 107.2, 119.0, 123.0, 125.0, 125.5, 126.1, 126.3, 127.6, 127.8, 128.2, 128.7, 132.8, 133.4, 138.6, 148.2, 209.1; $[\alpha]_D^{30}$ -147.2 (*c* 1.00, CH_2Cl_2); HRMS(EI) calcd for $C_{28}H_{29}NO$ $[M]^+$ 395.2249, found: 395.2248; HPLC (DAICEL Chiralpak AD-H, hexane/EtOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 9.991 min (major) and 16.724 min (minor).

(6S,9aS)-10,10-diethyl-6-phenyl-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4n)



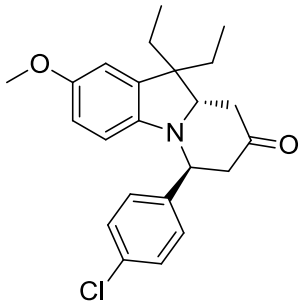
Yellow oil; ^{1}H NMR (400MHz, $CDCl_3$): δ 0.84 (3H, t, *J* = 7.6 Hz), δ 0.94 (3H, t, *J* = 7.6 Hz), δ 1.47-1.56 (1H, m), δ 1.64-1.72 (1H, m), δ 1.79-1.88 (1H, m), δ 1.96-2.05 (1H, m), δ 2.35-2.46 (1H, m), δ 2.83 (1H, dd, *J* = 6.0, 14.4 Hz), δ 3.02 (1H, dd, *J* = 6.0, 14.8 Hz), δ 3.81 (1H, d, *J* = 10.8 Hz), δ 5.04-5.06 (1H, m), δ 6.54 (1H, d, *J* = 8.0 Hz), δ 6.79-6.82 (1H, m), δ 7.08 (1H, d, *J* = 6.8 Hz), δ 7.13-7.16 (1H, m), δ 7.29-7.33 (1H, m), δ 7.38-7.48 (4H, m); ^{13}C NMR (100MHz, $CDCl_3$): δ 8.2, 9.2, 22.4, 28.3, 41.1, 44.0, 50.3, 56.3, 67.7, 107.2, 118.2, 124.4, 126.8, 127.4, 127.9, 128.8, 134.7, 141.0, 148.9, 209.3; $[\alpha]_D^{30}$ -133.92 (*c* 0.75, CH_2Cl_2); HRMS(EI) calcd for $C_{22}H_{25}NO$ $[M]^+$ 319.1936, found: 319.1937; HPLC (DAICEL Chiralpak AS-H, hexane/*i*-PrOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 8.054 min (major) and 13.692 min (minor).

(6S,9aS)-10,10-diethyl-2-methoxy-6-phenyl-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4o)



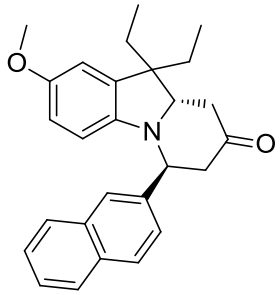
Yellow oil; ^{1}H NMR (400MHz, $CDCl_3$): δ 0.85 (3H, t, *J* = 7.6 Hz), δ 0.93 (3H, t, *J* = 7.6 Hz), δ 1.50 (1H, dd, *J* = 7.2, 14.4 Hz), δ 1.68 (1H, dd, *J* = 7.2, 14.4 Hz), δ 1.72-1.98 (2H, m), δ 2.32-2.44 (2H, m), 2.80 (1H, dd, *J* = 5.6, 15.2 Hz), δ 2.98 (1H, dd, *J* = 6.8, 15.2 Hz), δ 3.78 (3H, s), δ 3.78-3.82 (1H, m), δ 4.94 (1H, t, *J* = 6.0 Hz), δ 6.41 (1H, d, *J* = 8.4 Hz), δ 6.66-6.71 (2H, m), δ 7.28-7.32 (1H, m), δ 7.36-7.40 (2H, m), δ 7.46 (2H, d, *J* = 7.6 Hz); ^{13}C NMR (100MHz, $CDCl_3$): δ 8.3, 9.1, 22.5, 28.3, 40.9, 44.1, 50.5, 56.0, 57.0, 67.9, 107.4, 111.6, 112.5, 126.8, 127.4, 128.8, 136.5, 141.3, 143.3, 153.1, 209.4; $[\alpha]_D^{30}$ -124.26 (*c* 0.75, CH_2Cl_2); HRMS(EI) calcd for $C_{23}H_{27}NO_2$ $[M]^+$ 349.2042, found: 349.2043; HPLC (DAICEL Chiralpak AS-H, hexane/EtOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 9.189 min (major) and 23.883 min (minor).

(6S,9aS)-6-(4-chlorophenyl)-10,10-diethyl-2-methoxy-6,7,9a,10-tetrahydropyrido [1,2-a]indol-8(9H)-one (4p)



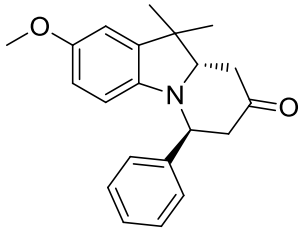
Yellow oil; ^{1}H NMR (400MHz, $CDCl_3$): δ 0.84 (3H, t, *J* = 7.6 Hz), δ 0.91 (3H, d, *J* = 7.6 Hz), δ 1.48 (1H, dd, *J* = 7.2, 14.4 Hz), δ 1.67 (1H, dd, *J* = 7.2, 14.4 Hz), δ 1.83 (1H, dd, *J* = 7.6, 13.6 Hz), δ 1.95 (1H, dd, *J* = 7.6, 14.4 Hz), δ 2.31-2.43 (2H, m), δ 2.78 (1H, dd, *J* = 5.6, 15.2 Hz), δ 2.93 (1H, dd, *J* = 6.4, 14.8 Hz), δ 3.71-3.77 (1H, m), δ 3.78 (3H, s), δ 4.90 (1H, t, *J* = 6.2 Hz), δ 6.39 (1H, d, *J* = 8.4 Hz), δ 6.66-6.71 (2H, m), δ 7.33-7.40 (4H, m); ^{13}C NMR (100MHz, $CDCl_3$): δ 8.3, 9.0, 22.4, 28.2, 35.5, 40.8, 43.8, 50.5, 55.9, 55.9, 56.5, 56.5, 68.0, 107.4, 111.6, 112.5, 128.2, 128.9, 133.2, 136.5, 139.7, 142.9, 153.2, 209.0; $[\alpha]_D^{30}$ -144.56 (*c* 1.00, CH_2Cl_2); HRMS(EI) calcd for $C_{23}H_{26}ClNO_2$ $[M]^+$ 383.1652, found: 383.1649; HPLC (DAICEL Chiralpak AS-H, hexane/EtOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 8.334 min (major) and 21.294 min (minor).

(6S,9aS)-10,10-diethyl-2-methoxy-6-(naphthalen-2-yl)-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4q)



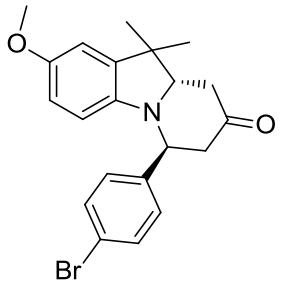
Yellow solid; mp: 45-48ºC; ^{1}H NMR (400MHz, $CDCl_3$): δ 0.86 (3H, t, *J* = 7.6 Hz), δ 0.91 (3H, t, *J* = 7.6 Hz), δ 1.50 (1H, dd, *J* = 7.2, 14.4 Hz), δ 1.66 (1H, dd, *J* = 7.2, 14.4 Hz), δ 1.86-1.99 (2H, m), δ 2.32-2.46 (2H, m), δ 2.88 (1H, dd, *J* = 5.6, 15.2 Hz), δ 3.11 (1H, dd, *J* = 6.0, 15.2 Hz), δ 3.71-3.78 (1H, m), δ 3.79 (3H, s), δ 5.11 (1H, t, *J* = 6.0 Hz), δ 6.49 (1H, d, *J* = 8.4 Hz), δ 6.67-6.73 (2H, m), δ 7.50-7.52 (2H, m), δ 7.59 (1H, dd, *J* = 1.6, 8.8 Hz), δ 7.84-7.88 (4H, m); ^{13}C NMR (100MHz, $CDCl_3$): δ 8.3, 9.1, 22.3, 28.2, 40.9, 43.6, 50.6, 56.0, 57.0, 68.1, 107.3, 111.6, 112.6, 125.2, 125.5, 126.1, 126.3, 127.6, 128.2, 128.6, 132.7, 133.3, 136.6, 138.8, 143.2, 153.1, 209.3; $[\alpha]_D^{30}$ -60.52 (*c* 0.5, CH_2Cl_2); HRMS(EI) calcd for $C_{27}H_{29}NO_2$ $[M]^+$ 399.2198, found: 399.2195; HPLC (DAICEL Chiralpak AS-H, hexane/EtOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 9.921 min (major) and 32.284 min (minor).

(6S,9aS)-2-methoxy-10,10-dimethyl-6-phenyl-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4r)



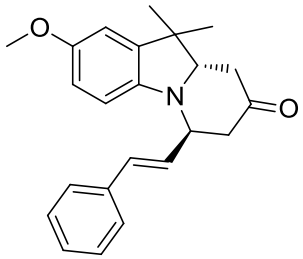
Yellow oil; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.27 (3H, s), δ 1.36 (3H, s), δ 2.31-2.42 (2H, m), δ 2.82 (1H, dd, *J* = 5.6, 15.2 Hz), δ 2.96 (1H, dd, *J* = 6.8, 15.2 Hz), δ 3.71-3.79 (1H, m), δ 3.78 (3H, s), δ 4.94 (1H, t, *J* = 6.0 Hz), δ 6.40 (1H, d, *J* = 8.4 Hz), δ 6.65 (1H, dd, *J* = 2.4, 8.4 Hz), δ 6.74 (1H, d, *J* = 2.8 Hz), δ 7.28-7.31 (1H, m), δ 7.36-7.39 (2H, m), δ 7.45 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100MHz, $CDCl_3$): δ 21.1, 29.1, 41.3, 43.4, 44.6, 56.0, 57.0, 68.9, 107.6, 110.2, 111.8, 126.8, 127.5, 128.8, 138.9, 141.2, 142.6, 153.6, 209.1; $[\alpha]_D^{30}$ -121.02 (*c* 0.75, CH_2Cl_2); HRMS(EI) calcd for $C_{21}H_{23}NO_2$ $[M]^+$ 321.1729, found: 321.1728; HPLC (DAICEL Chiralpak AS-H, hexane/EtOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 13.150 min (major) and 25.260 min (minor).

(6S,9aS)-6-(4-bromophenyl)-2-methoxy-10,10-dimethyl-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4s)



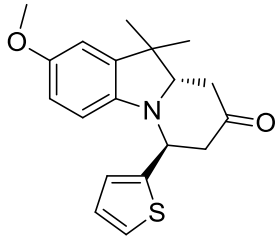
Yellow solid; mp: 99-102ºC; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.26 (3H, s), δ 1.34 (3H, s), δ 2.30-2.39 (2H, m), δ 2.78 (1H, dd, *J* = 5.6, 15.2 Hz), δ 2.89 (1H, dd, *J* = 6.8, 15.2 Hz), δ 3.71 (1H, dd, *J* = 4.8, 10.4 Hz), δ 3.76 (3H, s), δ 4.87 (1H, t, *J* = 6.2 Hz), δ 6.36 (1H, d, *J* = 8.4 Hz), δ 6.64 (1H, dd, *J* = 2.4, 8.4 Hz), δ 6.73 (1H, d, *J* = 2.4 Hz), δ 7.32 (2H, d, *J* = 8.4 Hz), δ7.48 (2H, d, *J* = 8.4 Hz); ^{13}C NMR (100MHz, $CDCl_3$): δ 21.1, 29.1, 41.2, 43.4, 44.3, 55.9, 56.7, 68.9, 107.7, 110.2, 111.8, 121.4, 128.6, 131.9, 138.9, 140.2, 142.3, 153.8, 208.7; $[\alpha]_D^{30}$ -184.52 (*c* 1.00, CH_2Cl_2); HRMS(EI) calcd for $C_{21}H_{22}BrNO_2$ $[M]^+$ 399.0834, found: 399.0835; HPLC (DAICEL Chiralpak AS-H, hexane/EtOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 11.684min (major) and 19.758 min (minor).

(6S,9aS)-2-methoxy-10,10-dimethyl-6-((E)-styryl)-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4t)



Yellow solid; mp: 47-50ºC; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.16 (3H, s), δ 1.31 (3H, s), δ 2.34-2.39 (1H, m), δ 2.46-2.52 (1H, m), 2.70-2.75 (1H, m), δ 2.91 (1H, dd, *J* = 6.4, 14.4 Hz), δ 3.59 (1H, dd, *J* = 3.2, 12.0 Hz), δ 3.78 (3H, s), δ 4.78 (1H, t, *J* = 6.0 Hz), δ 6.21 (1H, dd, *J* = 5.6, 16.4 Hz), δ 6.53-6.63 (2H, m), δ 6.69-6.73 (2H, m), δ 7.23-7.34 (5H, m); ^{13}C NMR (100MHz, $CDCl_3$): δ 22.0, 26.0, 41.7, 42.8, 44.0, 54.1, 55.8, 68.4, 76.6, 76.7, 76.9, 77.0, 77.3, 77.3, 107.9, 109.9, 109.9, 111.6, 126.4, 126.4, 127.8, 128.4, 133.2, 136.1, 140.2, 141.4, 153.5, 208.8; $[\alpha]_D^{30}$ -8.88 (*c* 0.15, CH_2Cl_2); HRMS(EI) calcd for $C_{23}H_{25}NO_2$ $[M]^+$ 347.1885, found: 347.1882; HPLC (DAICEL Chiralpak AS, hexane/EtOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 10.401 min (major) and 16.502 min (minor).

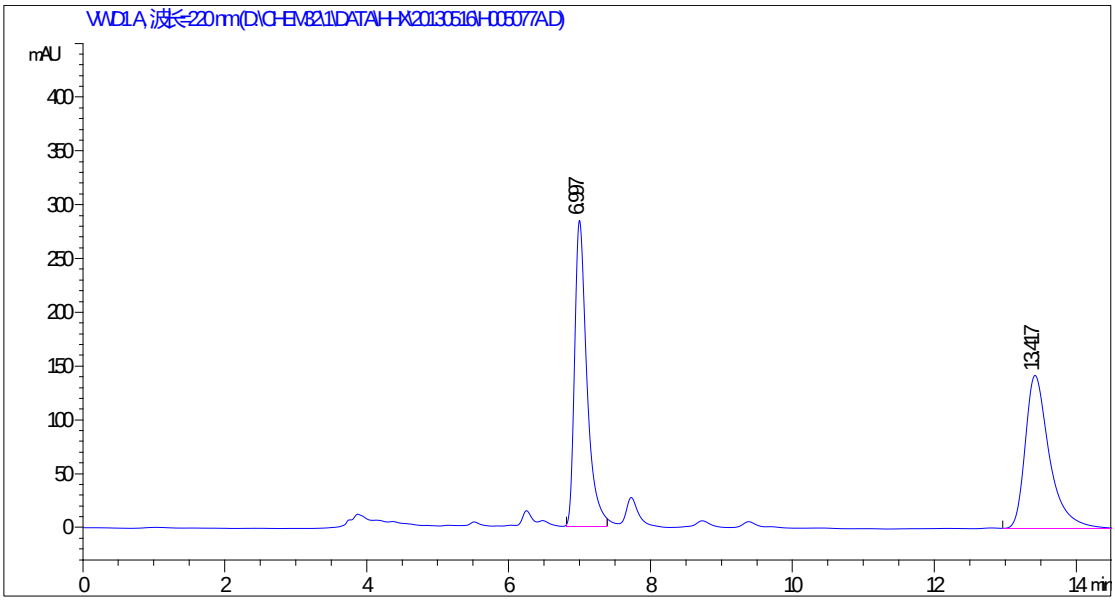
(6S,9aS)-2-methoxy-10,10-dimethyl-6-(thiophen-2-yl)-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4u)



Yellow oil; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.19 (3H, s), δ 1.29 (3H, s), δ 2.27-2.43 (2H, m), δ 2.91-3.01 (2H, m), δ 3.54 (1H, dd, *J* = 3.6, 11.2 Hz), δ 3.79 (3H, s), δ 5.41 (1H, dd, *J* = 3.6, 5.6 Hz), δ 6.63 (1H, dd, *J* = 2.4, 6.8 Hz), δ 6.72 (1H, dd, *J* = 2.4, 6.8 Hz), δ 6.92-6.94 (2H, m), δ 7.20-7.22 (1H, m); ^{13}C NMR (100MHz, $CDCl_3$): δ 21.5, 27.1, 41.7, 43.3, 44.1, 52.9, 55.9, 68.5, 107.9, 110.2, 111.6, 125.6, 125.8, 126.7, 139.7, 141.1, 143.6, 153.9, 208.2; $[\alpha]_D^{30}$ -68.38 (*c* 1.00, CH_2Cl_2); HRMS(EI) calcd for $C_{19}H_{21}NO_2S$ $[M]^+$ 327.1293, found: 327.1292; HPLC (DAICEL Chiralpak AS-H, hexane/EtOH = 9/1, flow 0.8 ml/min, detection at 220nm) retention time = 14.95 min (major) and 30.199 min (minor).

D: HPLC Charts of Formal ADA Products

(6'S,9a'S)-6'-phenyl-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4a)



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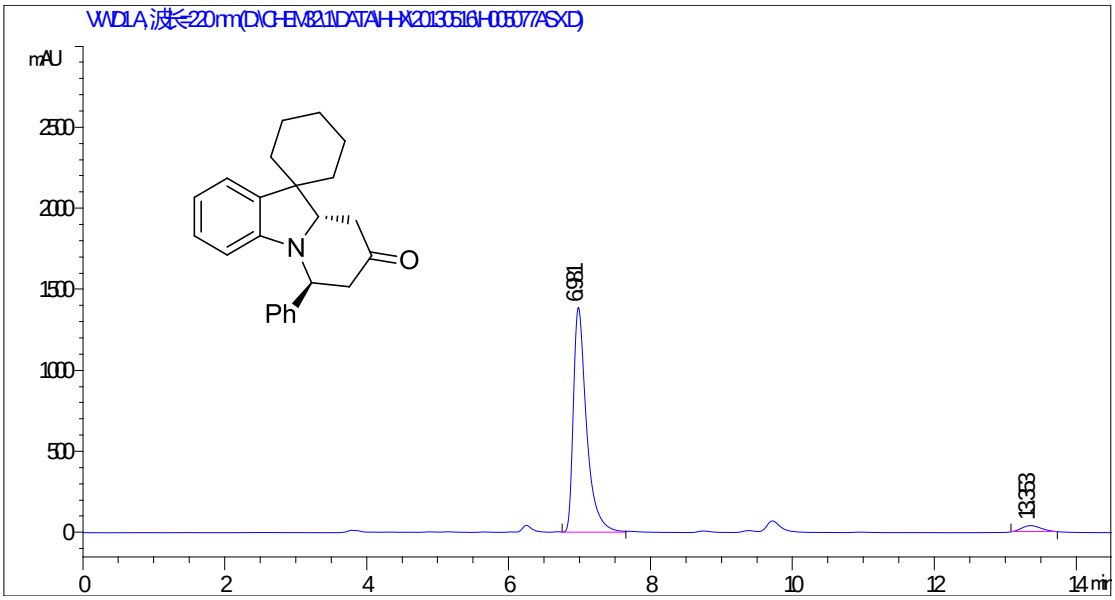
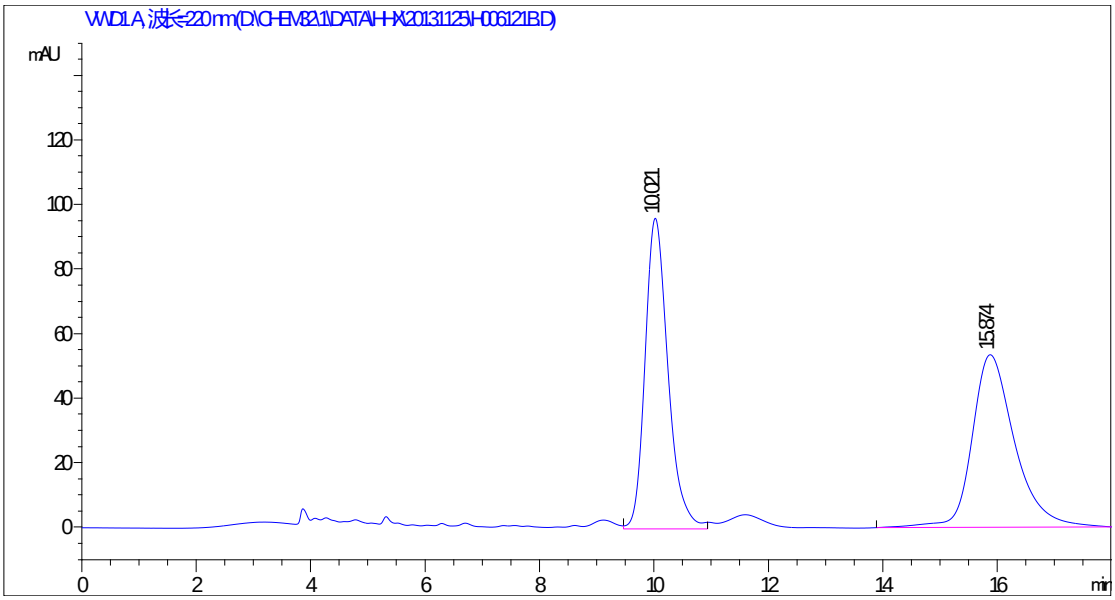
2	13.417	3378.6	142.4	0.3554	0.632	49.628

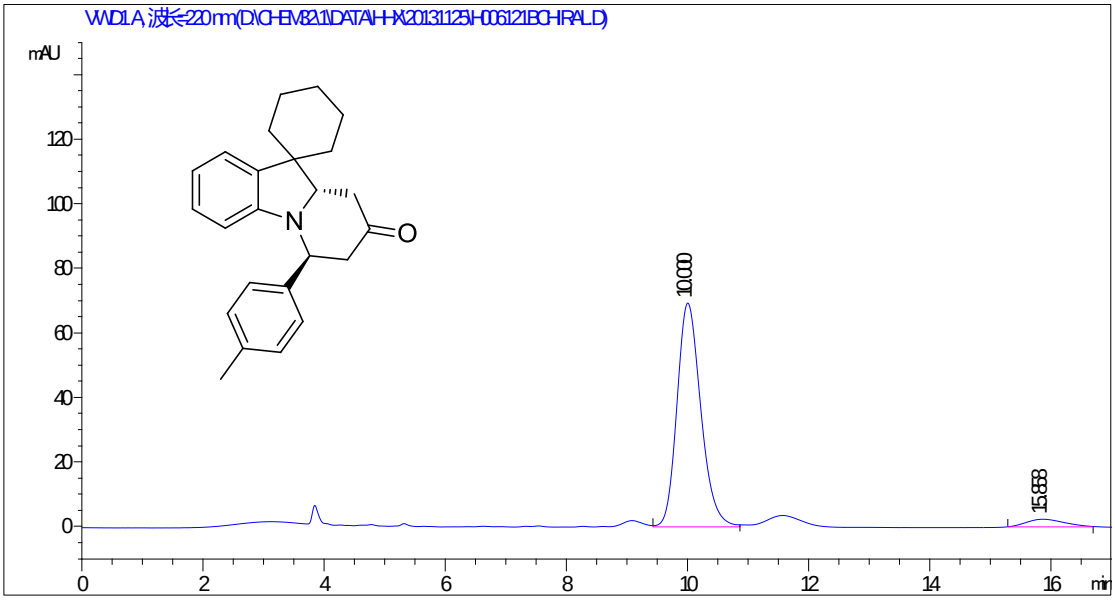


#	Time	Area	Height	Width	Symmetry	Area %
1	6.981	18025.3	1390.5	0.1935	0.56	95.927
2	13.353	765.4	39	0.3269	0.789	4.073

(6'S,9a'S)-6'-(p-tolyl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4b)

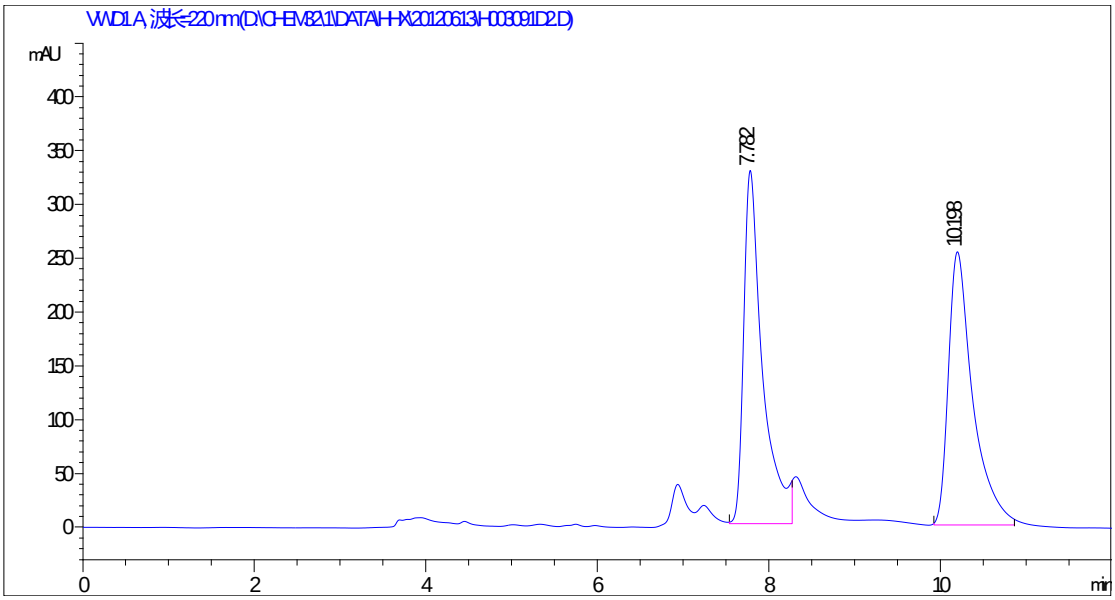


#	Time	Area	Height	Width	Symmetry	Area %
1	10.021	2694.2	96.3	0.4661	0.769	49.133
2	15.874	2789.3	53.6	0.785	0.716	50.867

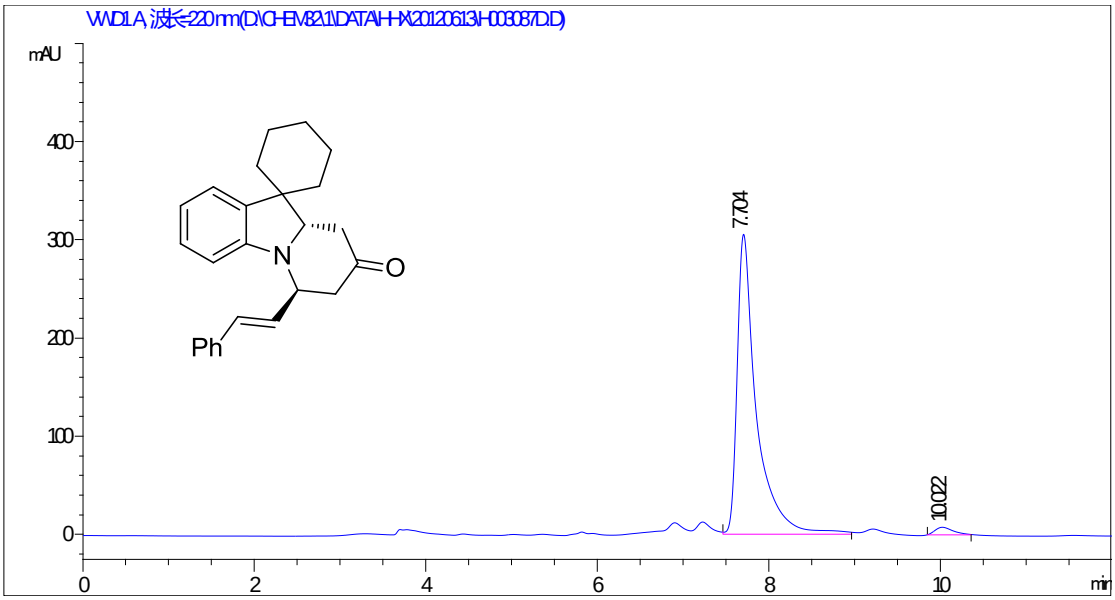


#	Time	Area	Height	Width	Symmetry	Area %
1	10	1905.1	69.5	0.4219	0.781	94.776
2	15.858	105	2.4	0.7332	0.728	5.224

(6'S,9a'S)-6'-((E)-styryl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4c)

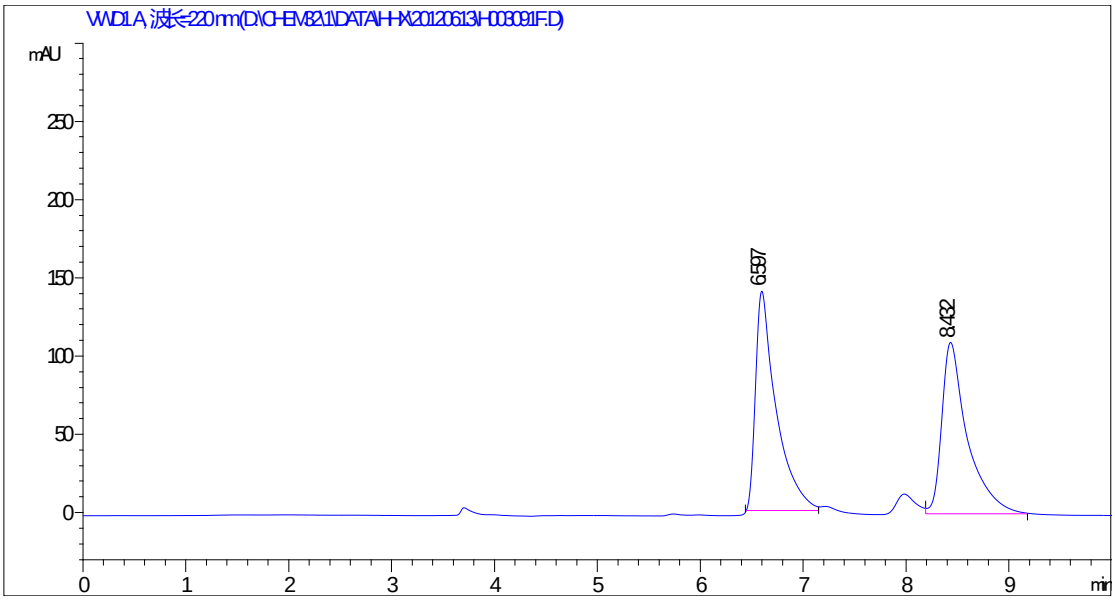


#	Time	Area	Height	Width	Symmetry	Area %
1	7.782	5028.6	328.6	0.255	0.509	50.114
2	10.198	5005.7	254	0.3285	0.564	49.886

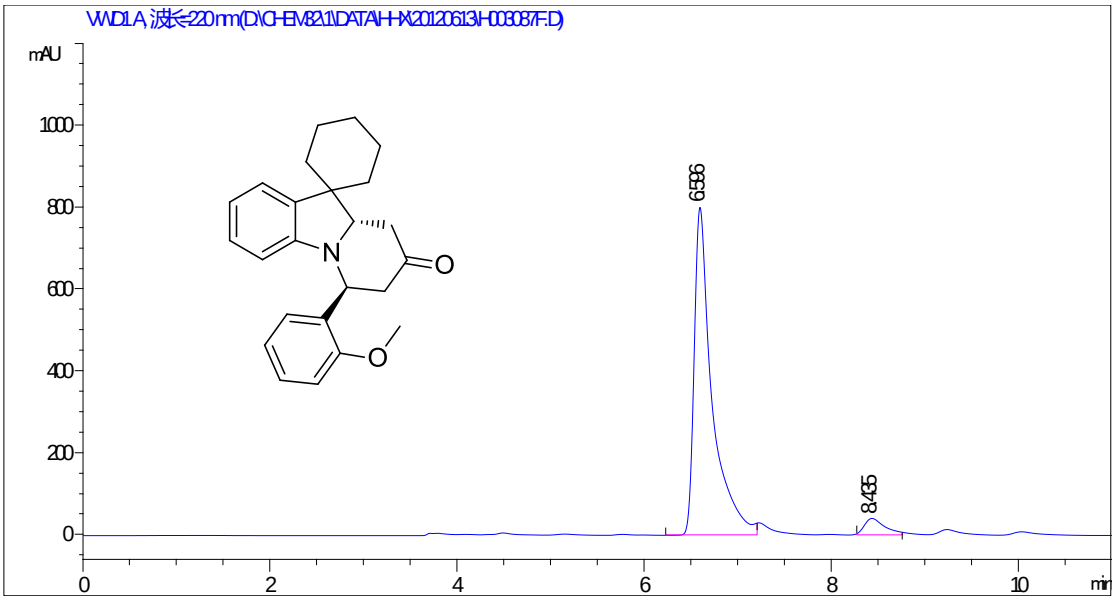


#	Time	Area	Height	Width	Symmetry	Area %
1	7.704	4944.6	307.2	0.2285	0.432	97.195
2	10.022	142.7	8.4	0.2842	0.563	2.805

(6'S,9a'S)-6'-(2-methoxyphenyl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4d)

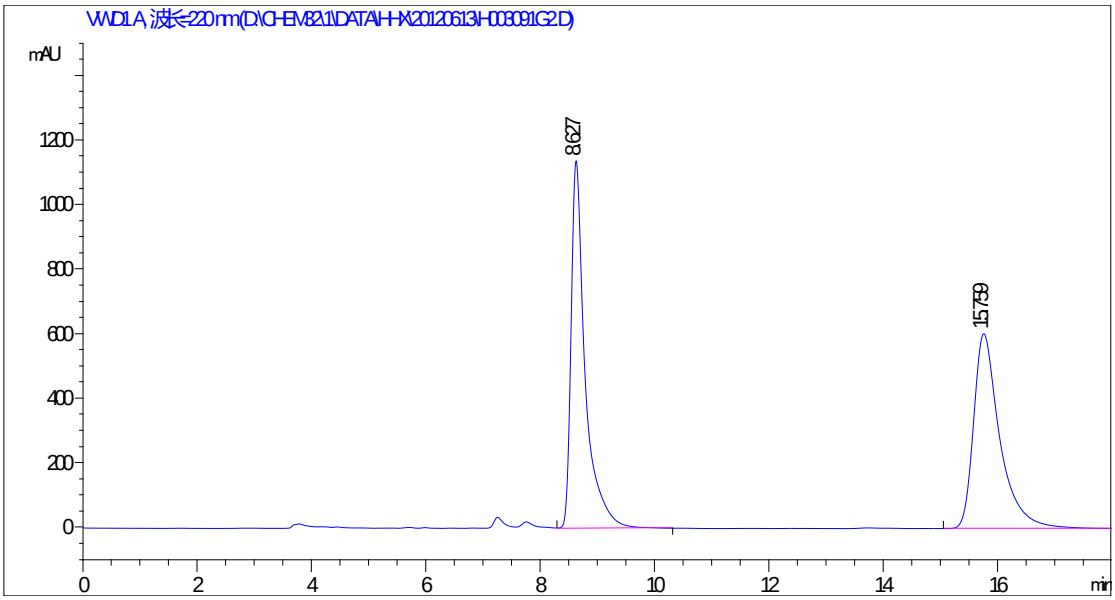


#	Time	Area	Height	Width	Symmetry	Area %
1	6.597	1963.7	140.4	0.233	0.42	50.735
2	8.432	1906.8	109.8	0.2894	0.51	49.265

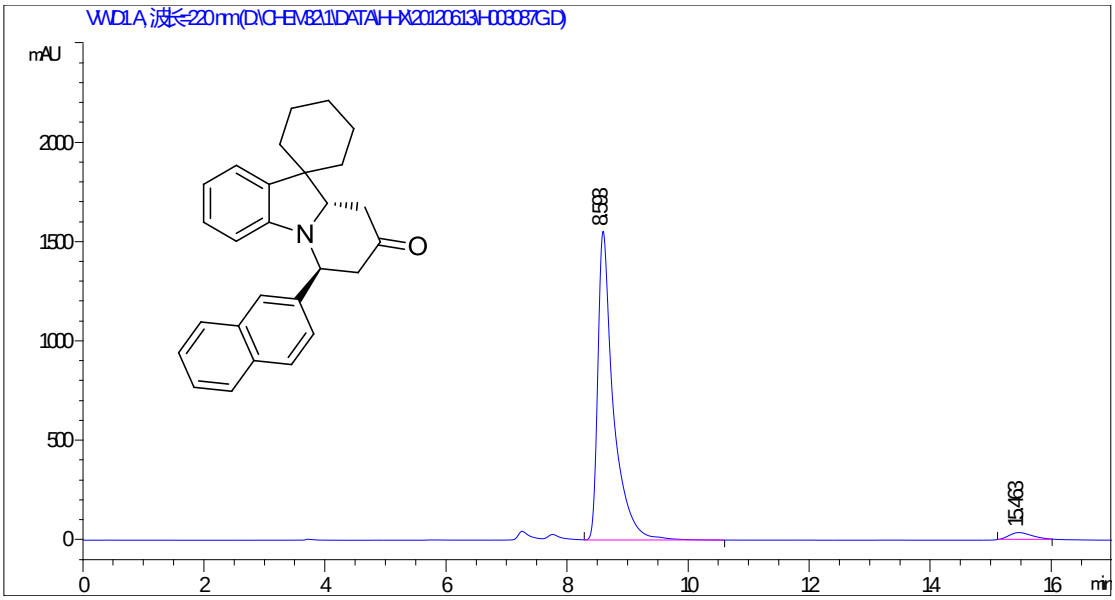


#	Time	Area	Height	Width	Symmetry	Area %
1	6.596	10706.5	801.8	0.2225	0.459	94.542
2	8.435	618.1	40.4	0.2552	0.563	5.458

(6'S,9a'S)-6'-(naphthalen-2-yl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4e)

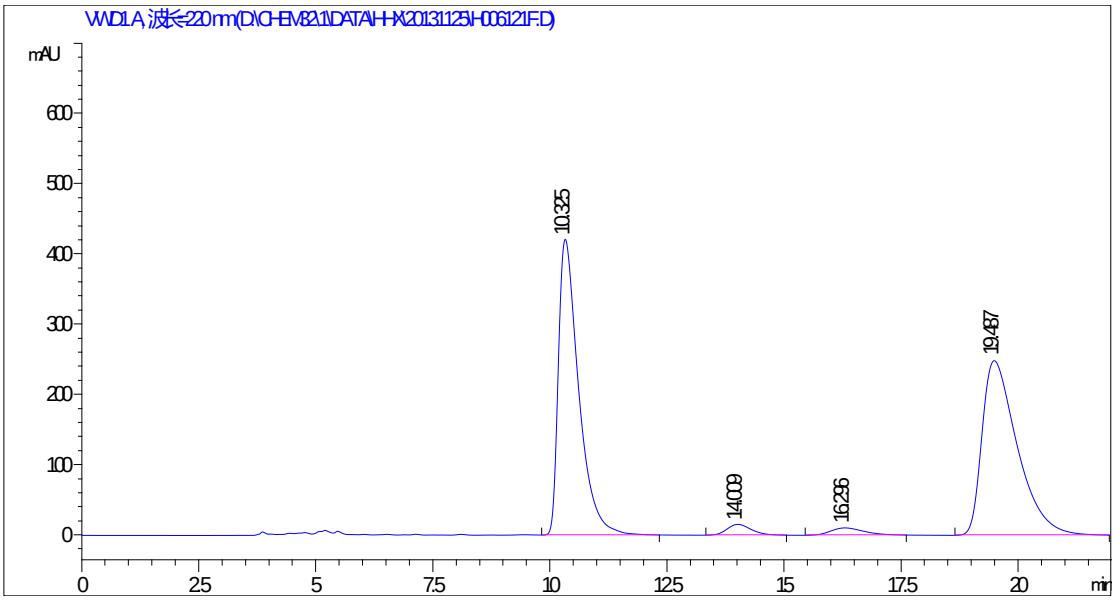


#	Time	Area	Height	Width	Symmetry	Area %
1	8.627	19470.5	1138.6	0.2476	0.499	50.220
2	15.759	19300.2	603.7	0.4734	0.578	49.780

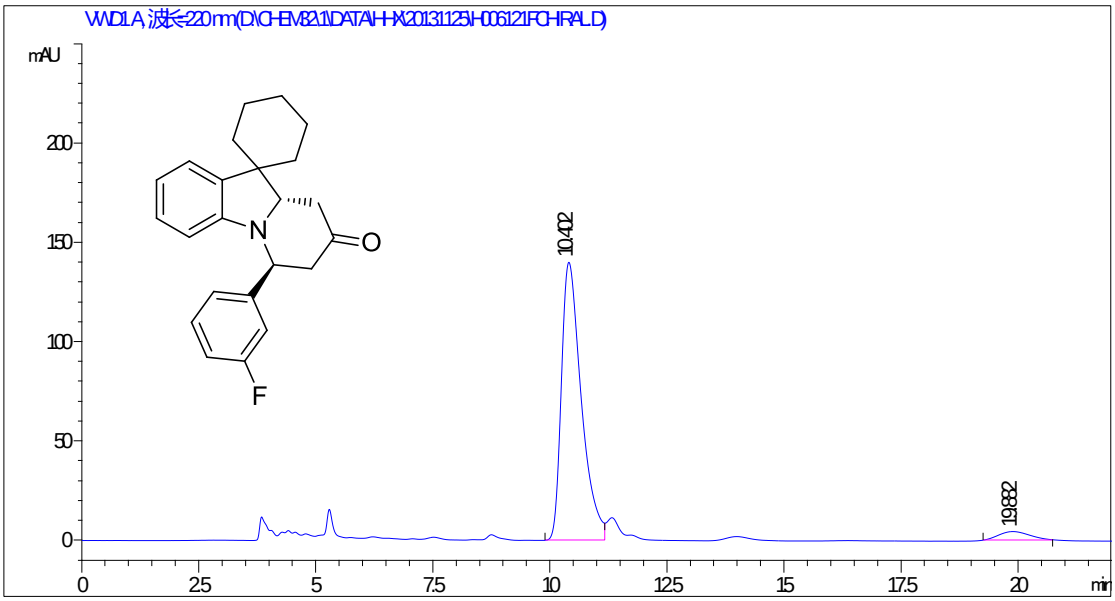


#	Time	Area	Height	Width	Symmetry	Area %
1	8.593	27717.6	1555.6	0.2574	0.465	96.413
2	15.463	1031.3	36.7	0.4687	0.682	3.587

(6'S,9a'S)-6'-(3-fluorophenyl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4f)

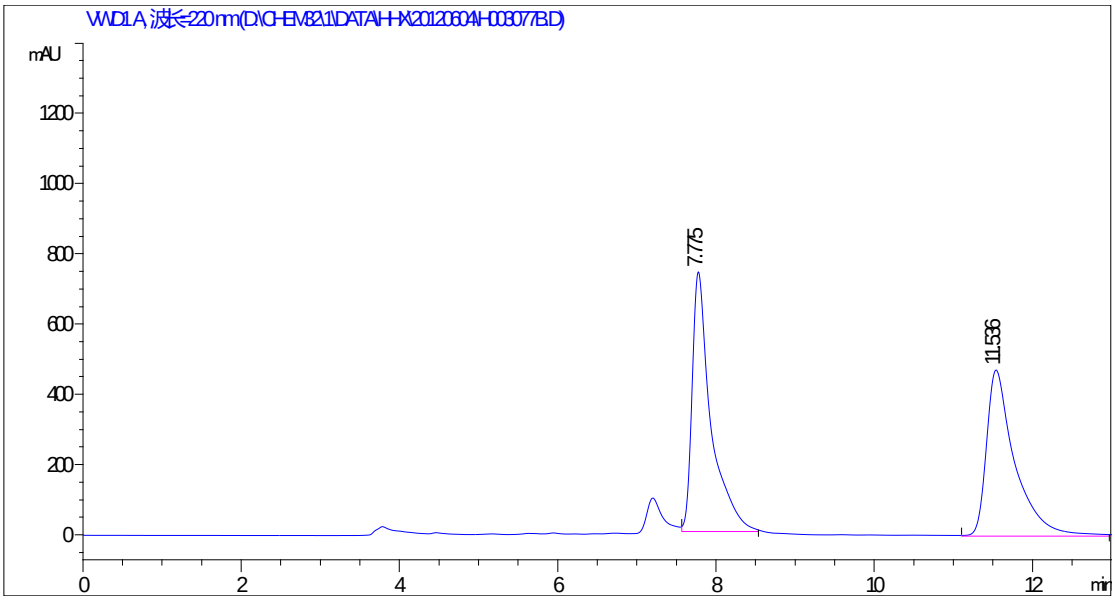


#	Time	Area	Height	Width	Symmetry	Area %
1	10.325	12679.8	420.9	0.4519	0.469	47.349
2	14.009	555.4	15.4	0.5555	0.764	2.074
3	16.296	512.3	10.4	0.7379	0.71	1.913
4	19.487	13032	248.5	0.7952	0.493	48.664

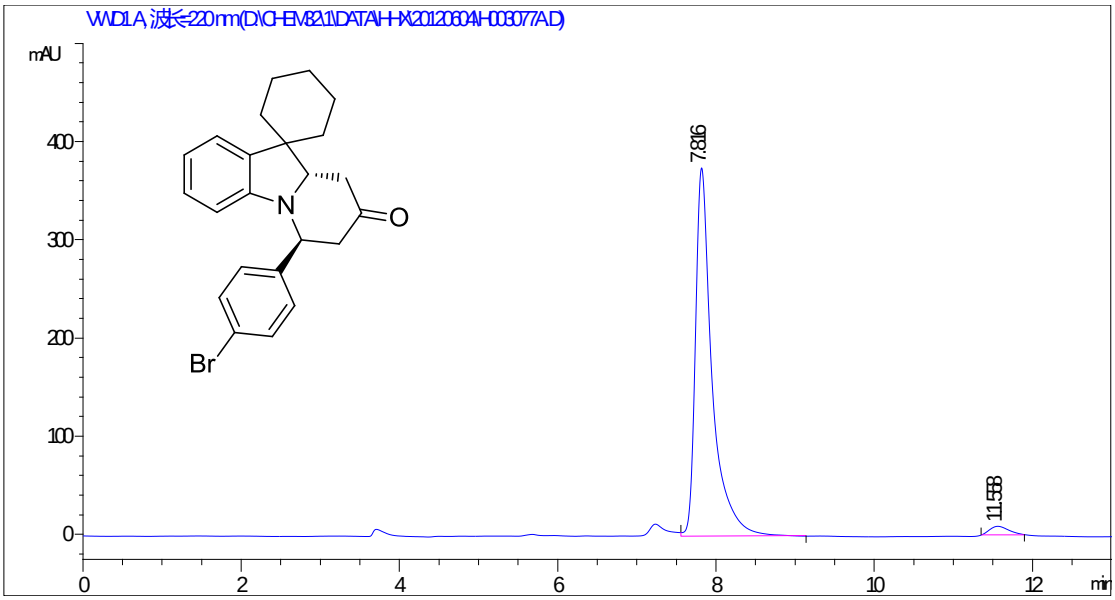


#	Time	Area	Height	Width	Symmetry	Area %
1	10.402	4133.7	140	0.445	0.562	95.157
2	19.882	210.4	4.4	0.7897	0.789	4.843

(6'S,9a'S)-6'-(4-bromophenyl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido [1,2-a]indol]-8'(7'H)-one (4g)

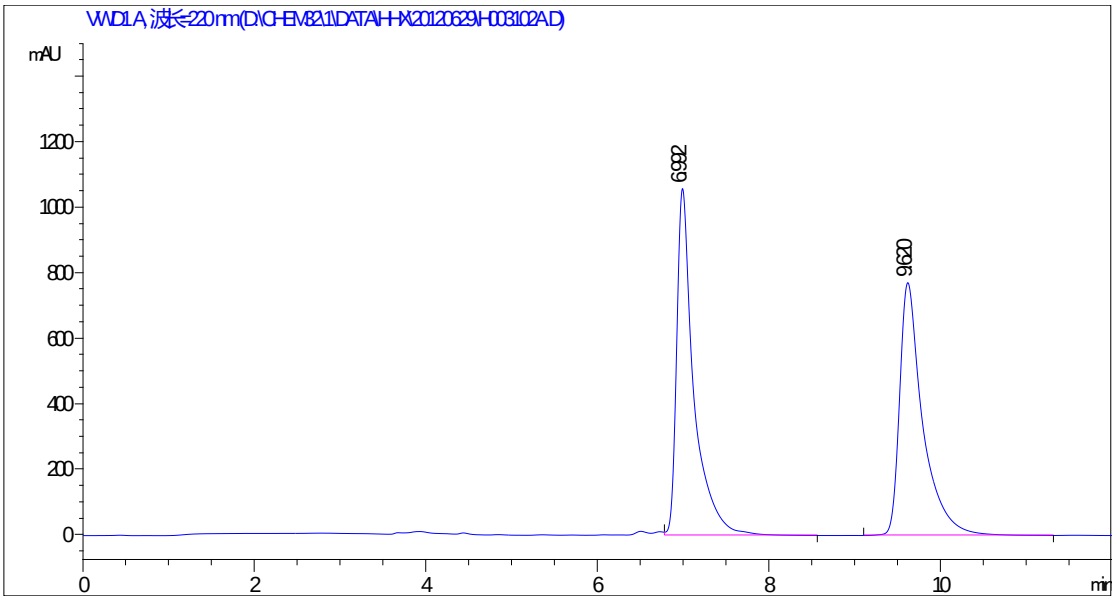


#	Time	Area	Height	Width	Symmetry	Area %
1	7.775	12281.1	740.8	0.2763	0.479	50.848
2	11.536	11871.5	473.6	0.4178	0.489	49.152

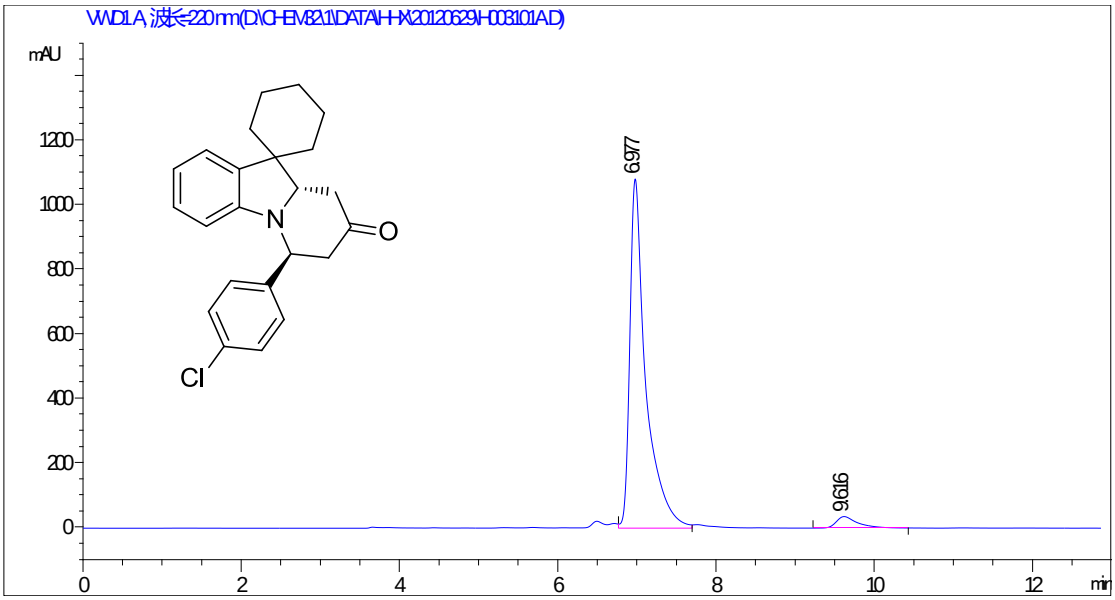


#	Time	Area	Height	Width	Symmetry	Area %
1	7.816	5486.9	374.9	0.213	0.528	97.162
2	11.558	160.2	9.2	0.2902	0.728	2.838

(6'S,9a'S)-6'-(4-chlorophenyl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido [1,2-a]indol]-8'(7'H)-one (4h)

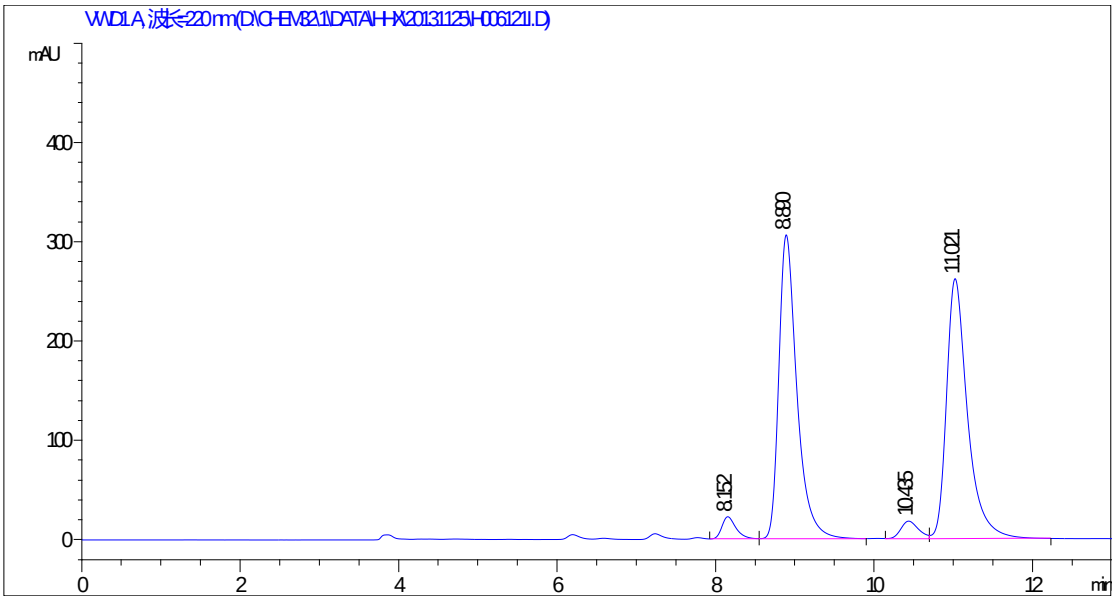


#	Time	Area	Height	Width	Symmetry	Area %
1	6.992	14751.2	1059.7	0.1988	0.463	50.433
2	9.62	14498	772.3	0.27	0.501	49.567

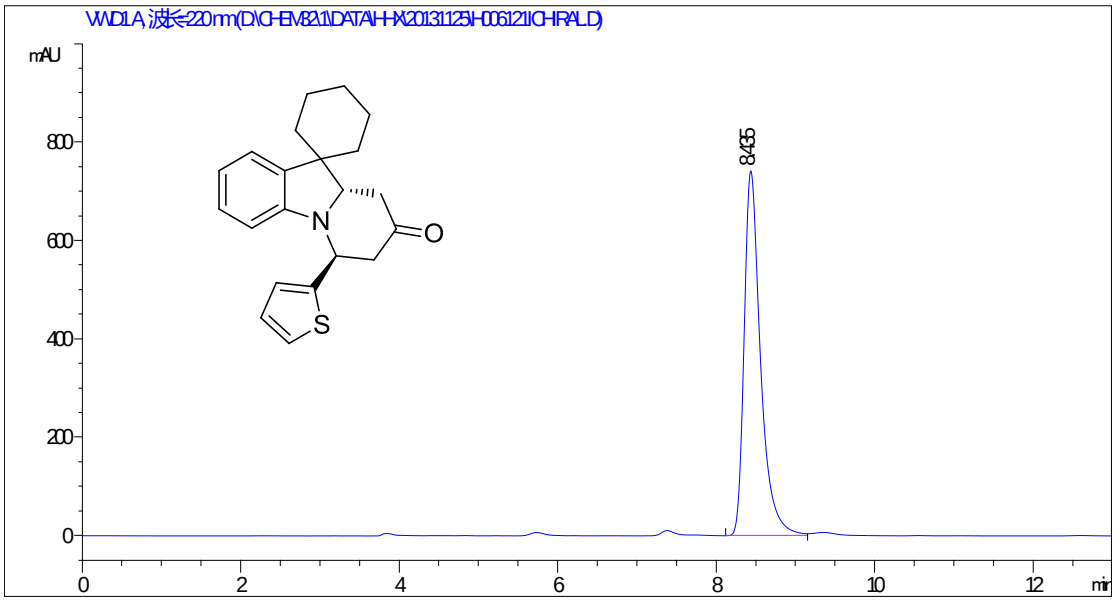


#	Time	Area	Height	Width	Symmetry	Area %
1	6.977	15110.5	1082.3	0.1993	0.457	95.689
2	9.616	680.7	35.7	0.2761	0.527	4.311

(6'S,9a'S)-6'-(thiophen-2-yl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4i)

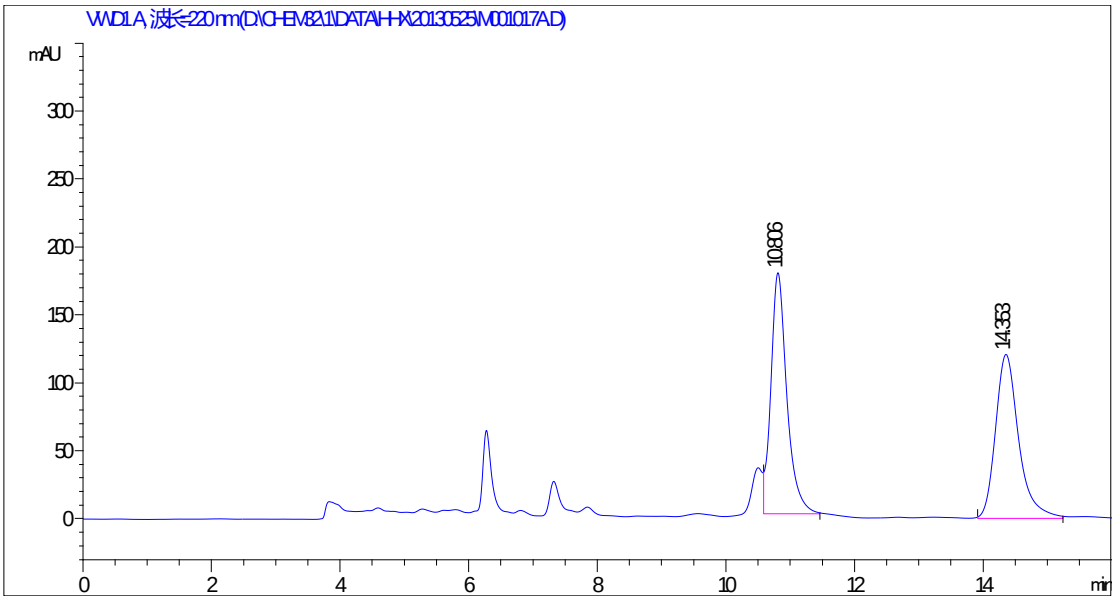


#	Time	Area	Height	Width	Symmetry	Area %
1	8.152	289.1	22.7	0.1905	0.671	2.811
2	8.89	4874.7	306.5	0.2394	0.634	47.391
3	10.435	281.7	17.9	0.2388	0.77	2.739
4	11.021	4840.7	262	0.2767	0.637	47.060

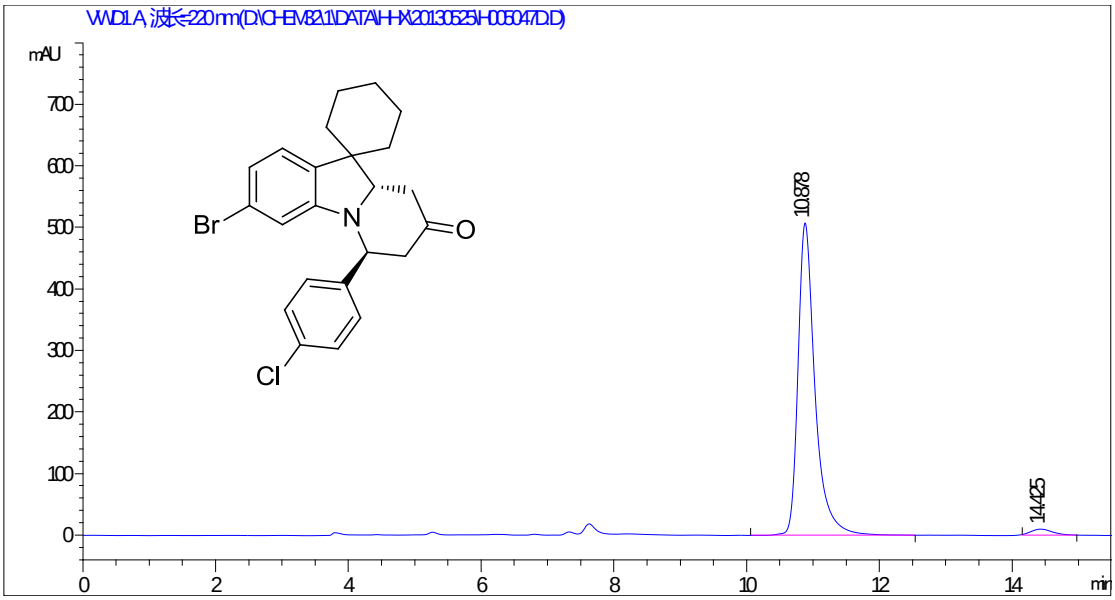


#	Time	Area	Height	Width	Symmetry	Area %
1	8.435	10688.4	742.1	0.2146	0.626	100.000

(6'S,9a'S)-3'-bromo-6'-(4-chlorophenyl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1, 10'-pyrido[1,2-a]indol]-8'(7'H)-one (4j)

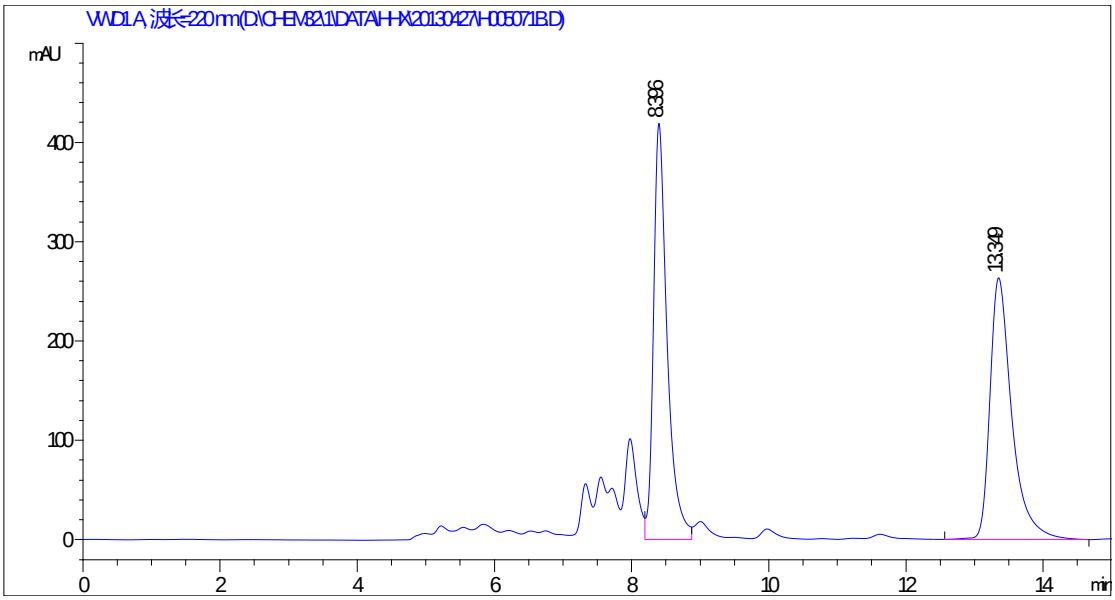


#	Time	Area	Height	Width	Symmetry	Area %
1	10.806	3079.9	177.9	0.2886	0.746	50.276
2	14.353	3046	121.1	0.4193	0.781	49.724

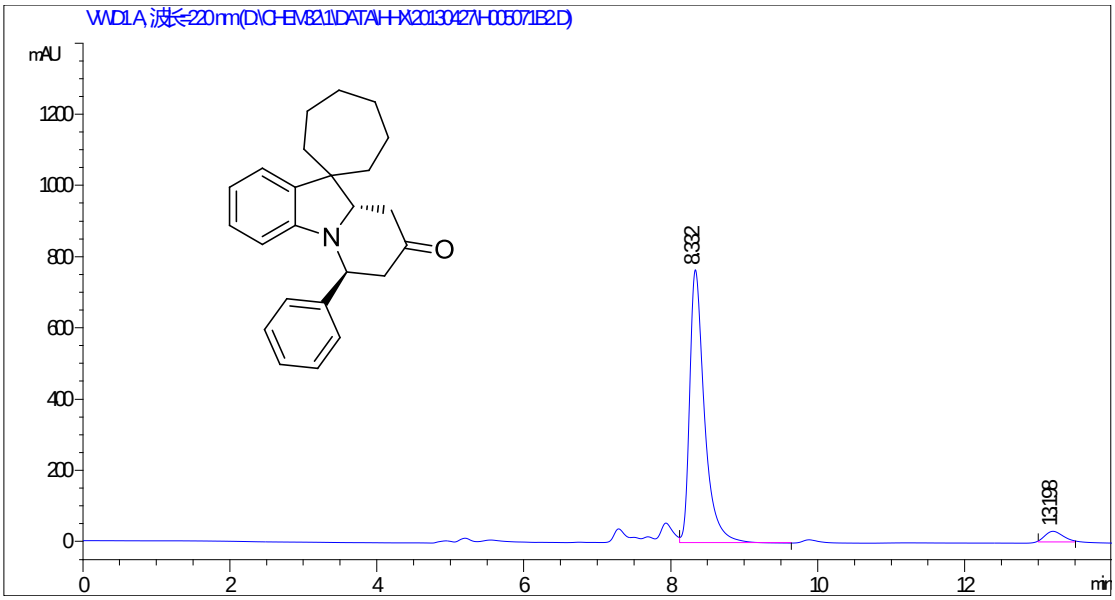


#	Time	Area	Height	Width	Symmetry	Area %
1	10.878	9043	507.7	0.2675	0.656	97.335
2	14.425	247.6	10.4	0.3975	0.76	2.665

(6'S,9a'S)-6'-phenyl-9',9a'-dihydro-6'H-spiro[cycloheptane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4k)

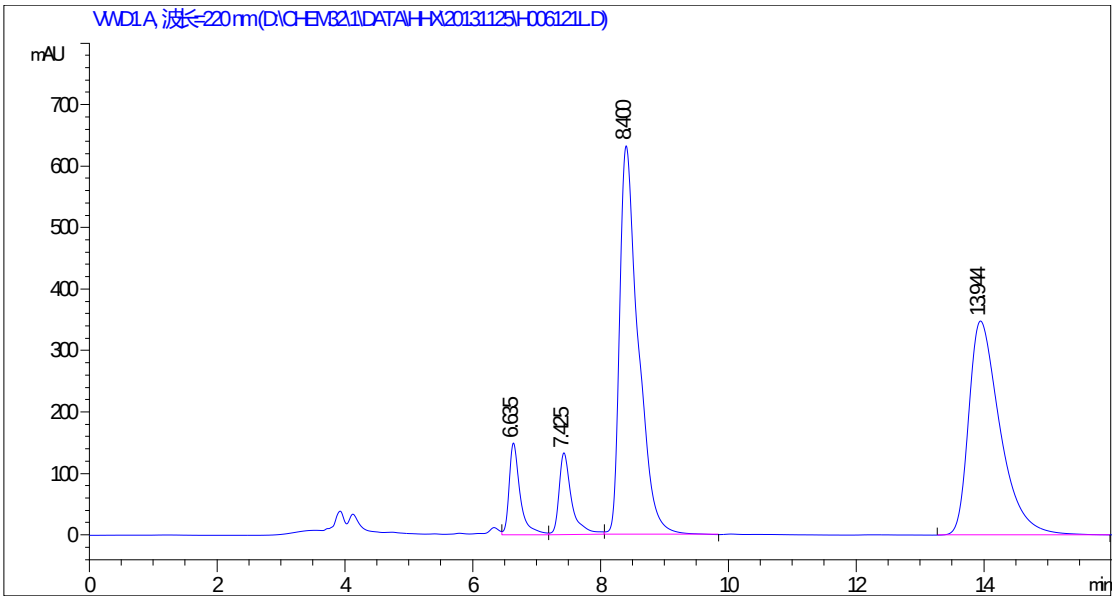


#	Time	Area	Height	Width	Symmetry	Area %
1	8.396	5809.6	419.6	0.2052	0.609	49.639
2	13.349	5894	264.1	0.3361	0.613	50.361

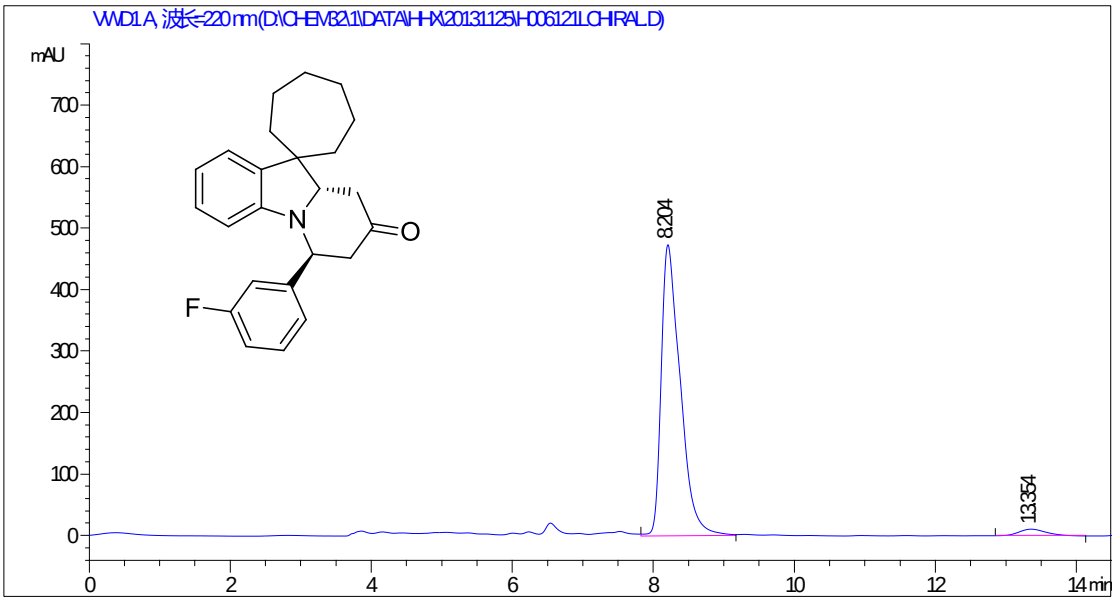


#	Time	Area	Height	Width	Symmetry	Area %
1	8.332	10777.3	767.5	0.209	0.571	95.214
2	13.198	541.7	31	0.2912	0.747	4.786

(6'S,9a'S)-6'-(3-fluorophenyl)-9',9a'-dihydro-6'H-spiro[cycloheptane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4l)

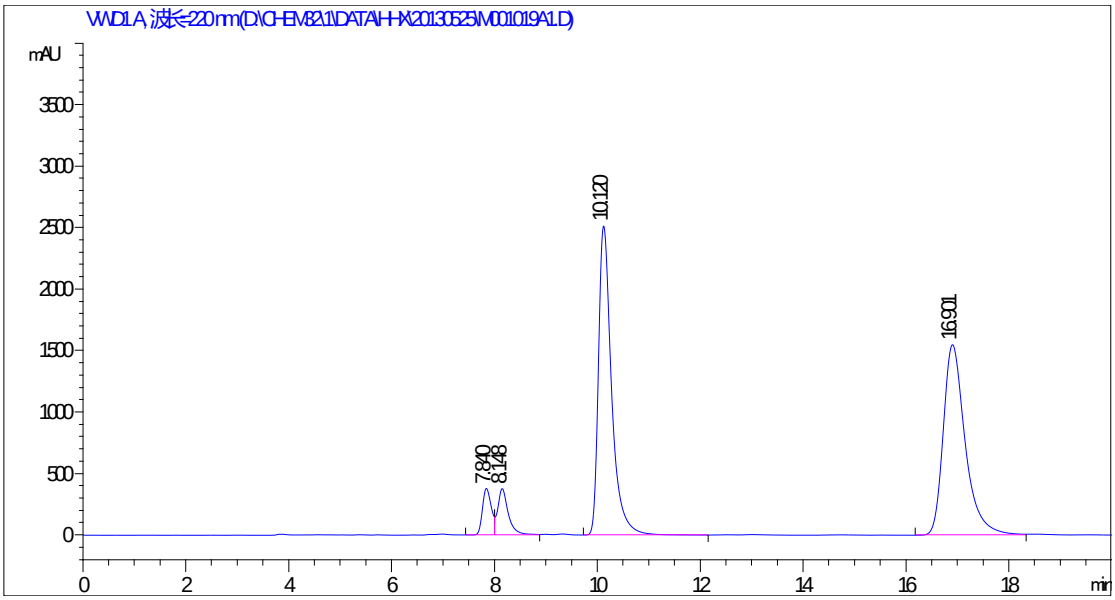


#	Time	Area	Height	Width	Symmetry	Area %
1	6.635	1788.9	149.5	0.176	0.584	6.324
2	7.425	1840.6	133.4	0.2032	0.567	6.507
3	8.4	12811.2	632.7	0.2959	0.502	45.288
4	13.944	11847.3	348.1	0.5164	0.559	41.881

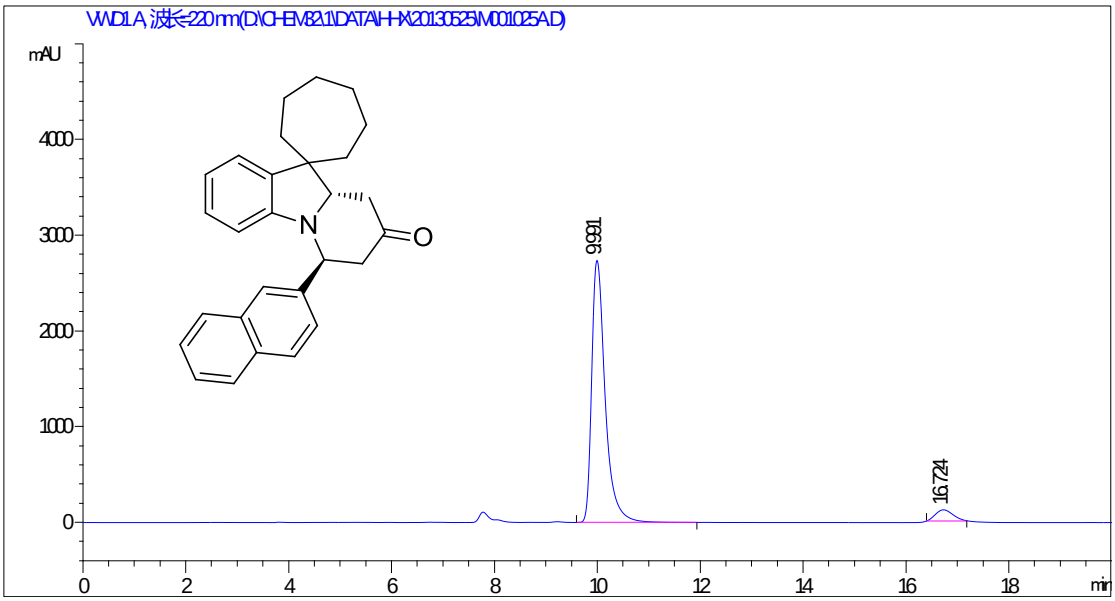


#	Time	Area	Height	Width	Symmetry	Area %
1	8.204	8926.8	473.9	0.2693	0.51	96.782
2	13.354	296.8	10.8	0.4186	0.757	3.218

(6'S,9a'S)-6'-(naphthalen-2-yl)-9',9a'-dihydro-6'H-spiro[cycloheptane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4m)

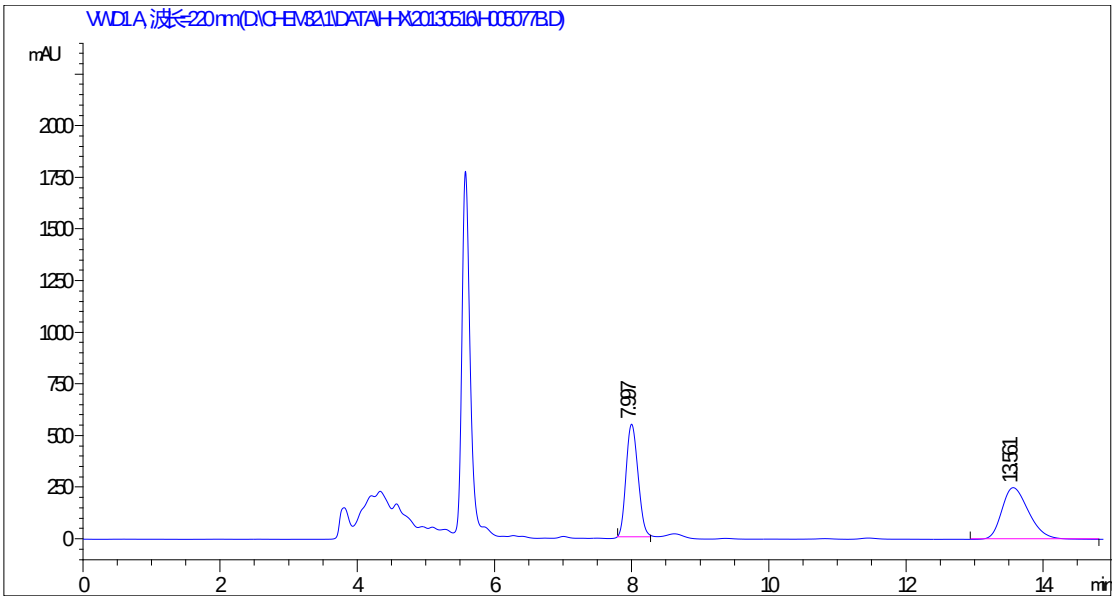


#	Time	Area	Height	Width	Symmetry	Area %
1	7.84	4635.2	380.6	0.1858	0.784	4.597
2	8.148	5505.9	379.1	0.2102	0.635	5.460
3	10.12	44674.9	2515	0.2669	0.594	44.303
4	16.901	46023.6	1549.7	0.4455	0.67	45.640

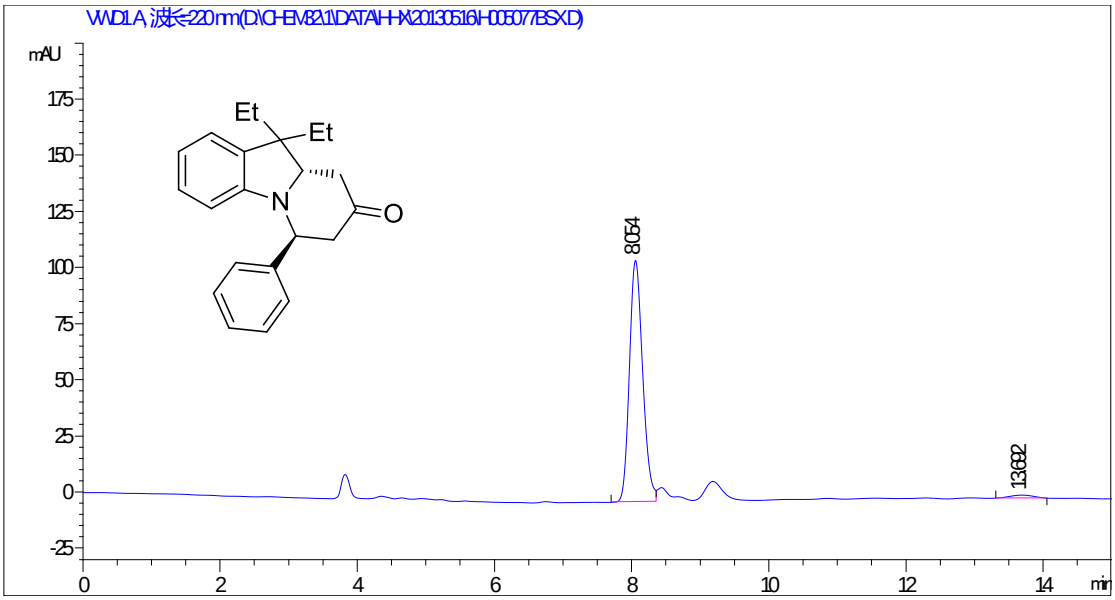


#	Time	Area	Height	Width	Symmetry	Area %
1	9.991	49849.2	2737.2	0.2765	0.593	94.800
2	16.724	2734.2	117.1	0.3891	0.816	5.200

(6S,9aS)-10,10-diethyl-6-phenyl-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4n)

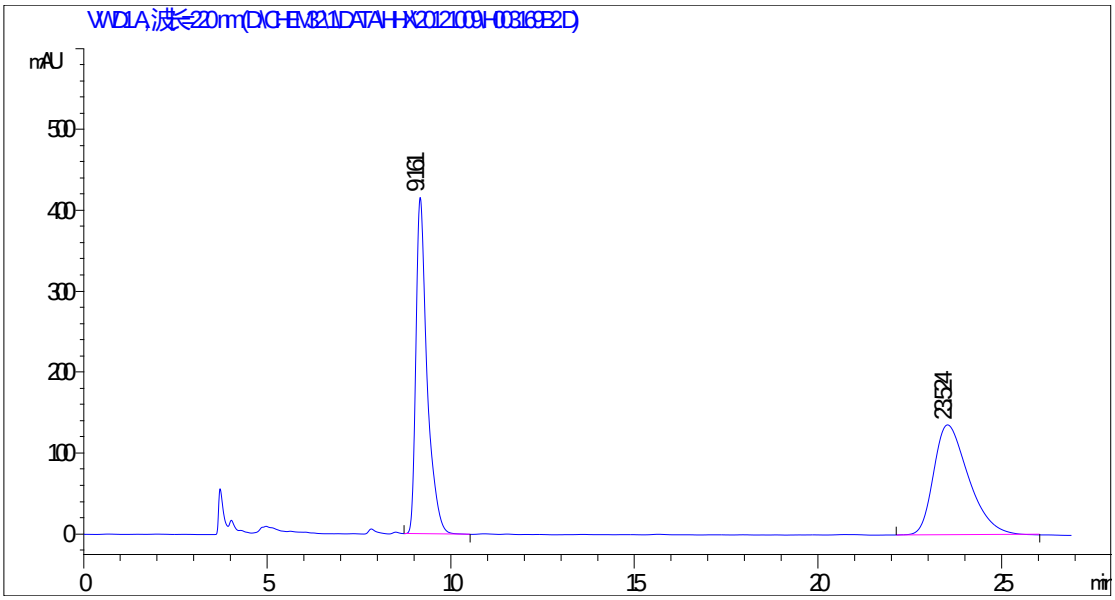


#	Time	Area	Height	Width	Symmetry	Area %
1	7.997	6616.9	546.2	0.2019	0.829	49.339
2	13.561	6794.2	250.1	0.4174	0.697	50.661

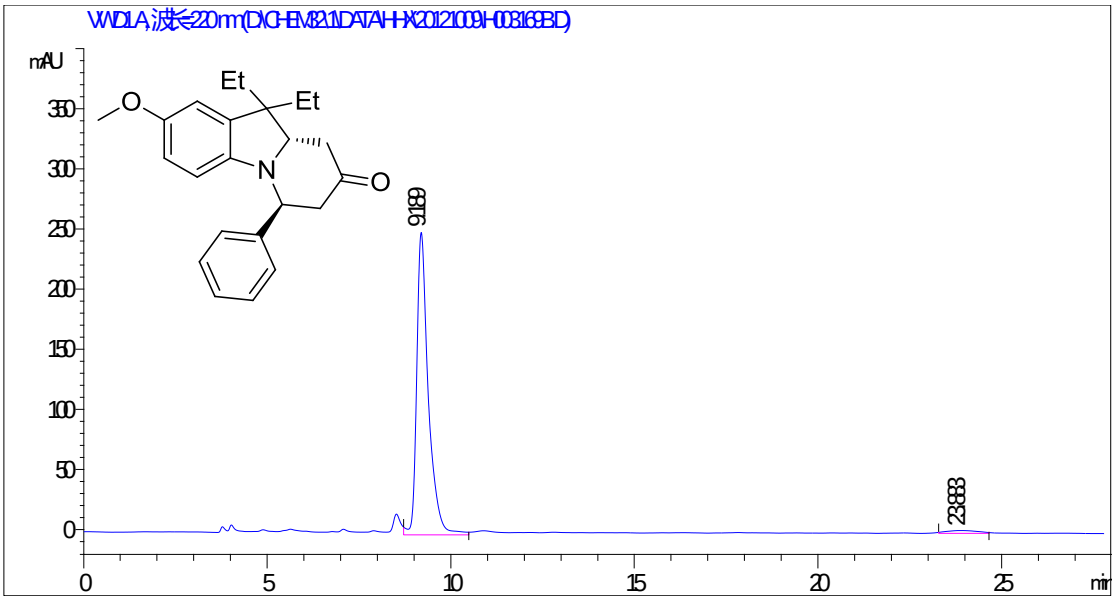


#	Time	Area	Height	Width	Symmetry	Area %
1	8.054	1447.2	107.6	0.2064	0.796	97.847
2	13.692	31.8	1.3	0.3964	1.066	2.153

(6S,9aS)-10,10-diethyl-2-methoxy-6-phenyl-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4o)

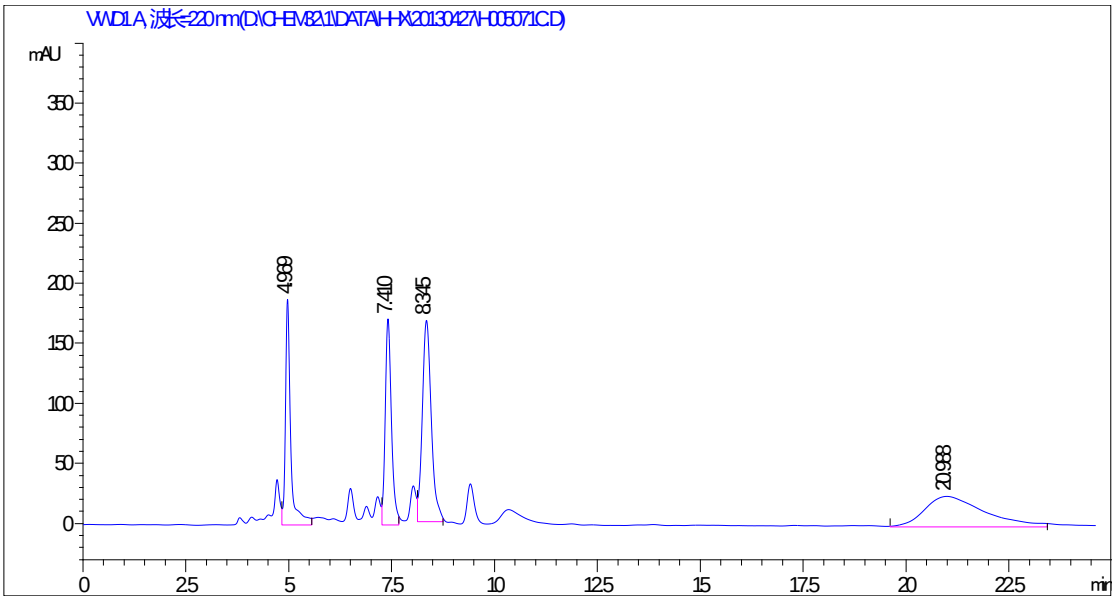


#	Time	Area	Height	Width	Symmetry	Area %
1	9.161	8808.2	416.1	0.3139	0.57	49.446
2	23.524	9005.5	136	0.9806	0.628	50.554

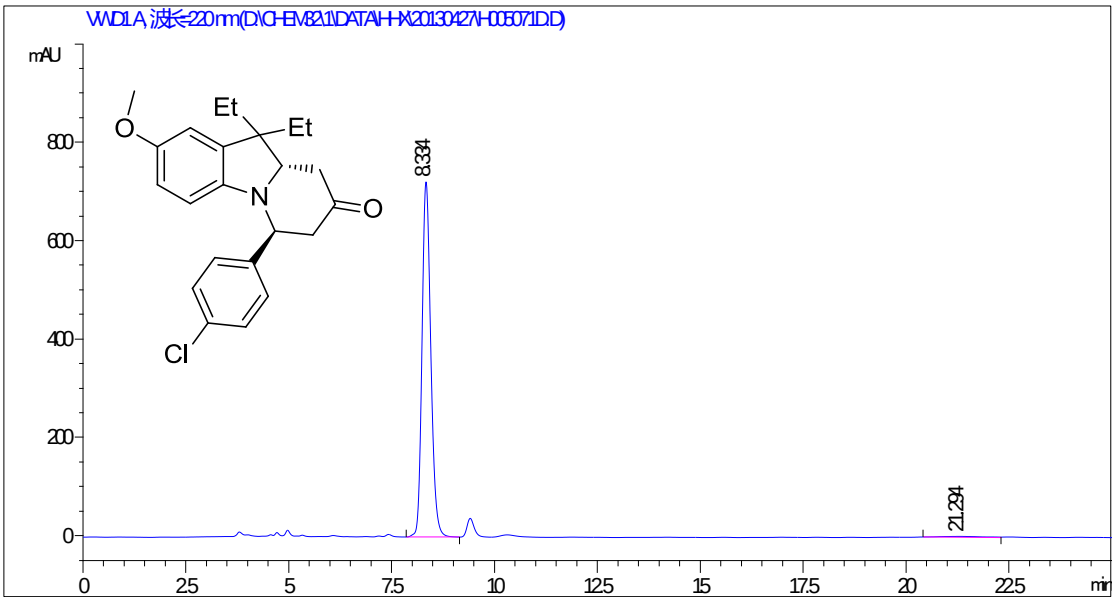


#	Time	Area	Height	Width	Symmetry	Area %
1	9.189	5582.4	251.6	0.3698	0.604	97.508
2	23.883	142.6	2.3	1.0144	0.808	2.492

(6S,9aS)-6-(4-chlorophenyl)-10,10-diethyl-2-methoxy-6,7,9a,10-tetrahydropyrido [1,2-a]indol-8(9H)-one (4p)

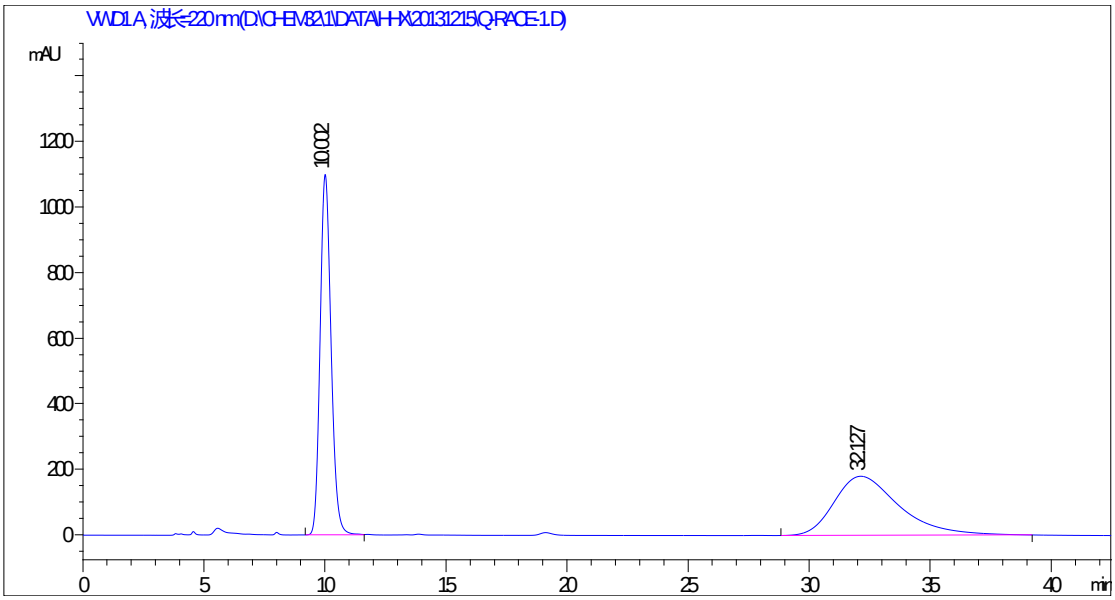


#	Time	Area	Height	Width	Symmetry	Area %
1	4.969	1671.8	188.1	0.1299	0.573	19.356
2	7.41	1807.6	172	0.1752	0.763	20.929
3	8.345	2534.9	167.8	0.2518	0.817	29.349
4	20.988	2622.6	25.6	1.7106	0.575	30.365

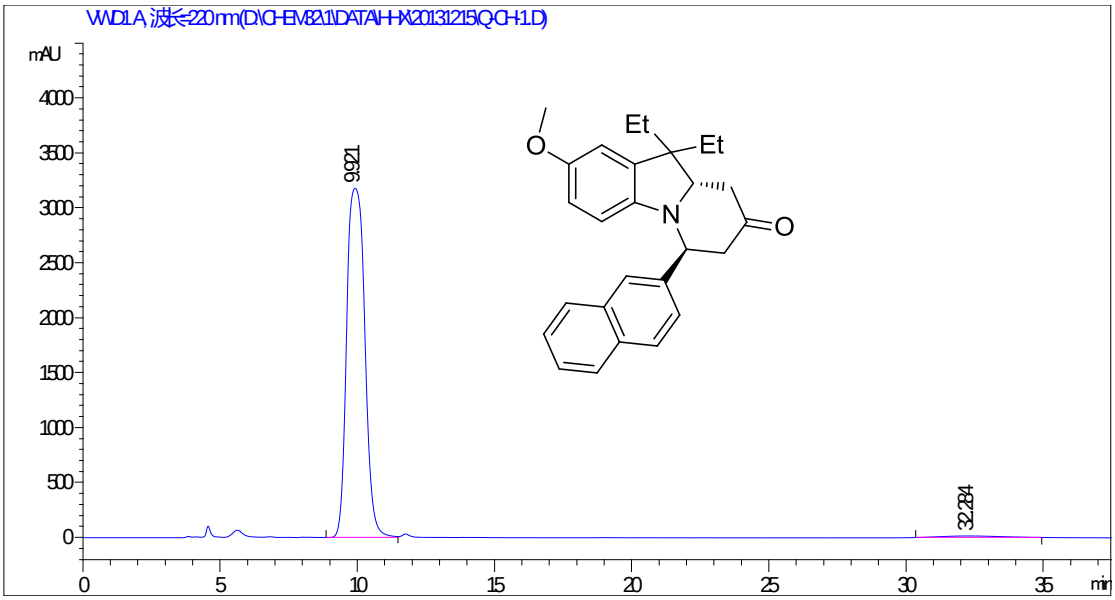


#	Time	Area	Height	Width	Symmetry	Area %
1	8.334	10772.9	722.5	0.2278	0.803	98.171
2	21.294	200.7	2.4	1.3773	0.982	1.829

(6S,9aS)-10,10-diethyl-2-methoxy-6-(naphthalen-2-yl)-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4q)

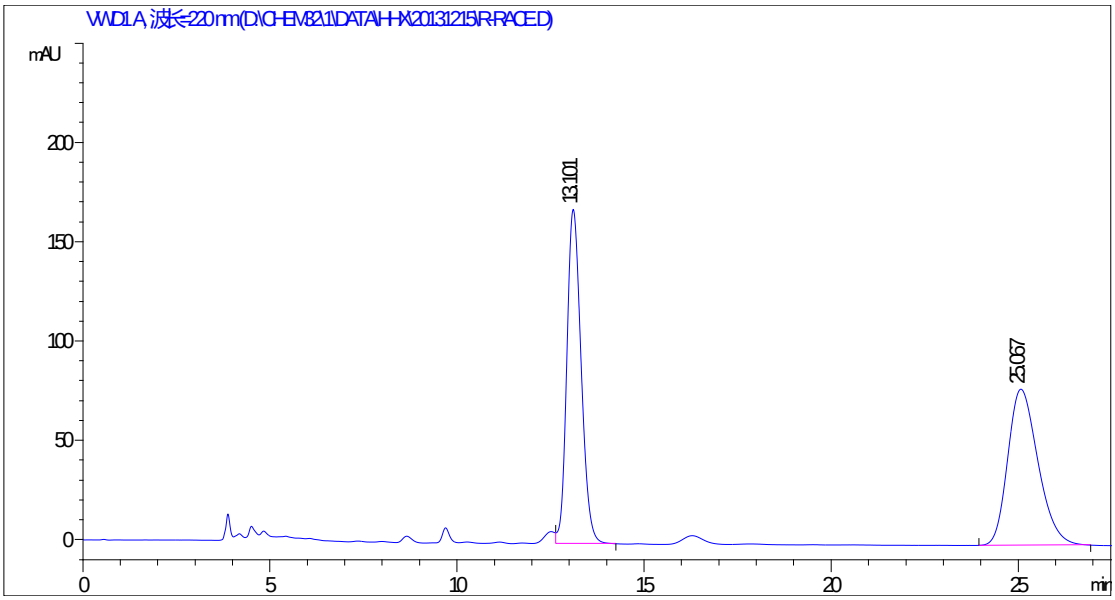


#	Time	Area	Height	Width	Symmetry	Area %
1	10.002	34612.1	1099.4	0.4881	0.814	50.685
2	32.127	33676.7	180.3	2.7985	0.654	49.315

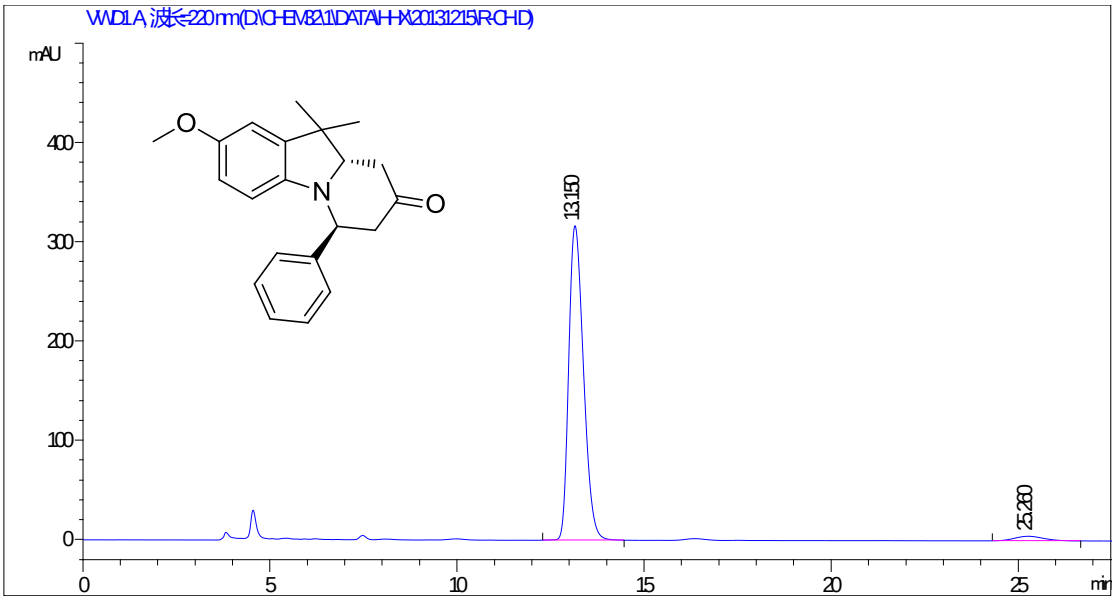


#	Time	Area	Height	Width	Symmetry	Area %
1	9.921	146160.6	3181.7	0.7325	0.844	98.057
2	32.284	2896.6	16.8	2.8726	0.786	1.943

(6S,9aS)-2-methoxy-10,10-dimethyl-6-phenyl-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4r)

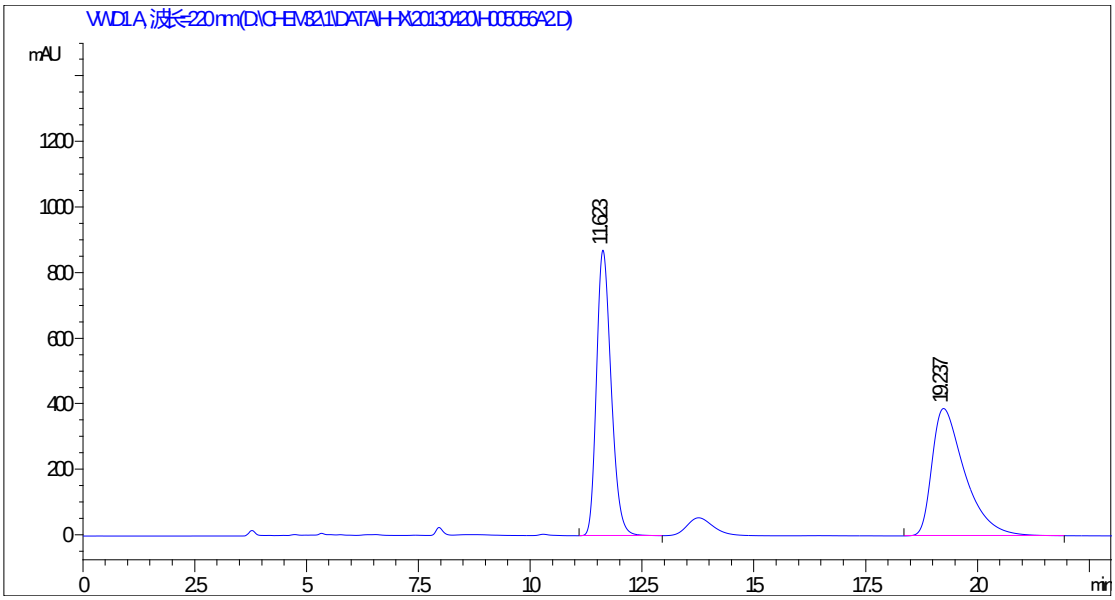


#	Time	Area	Height	Width	Symmetry	Area %
1	13.101	4473.5	168.4	0.4133	0.771	50.277
2	25.067	4424.1	78.6	0.869	0.727	49.723

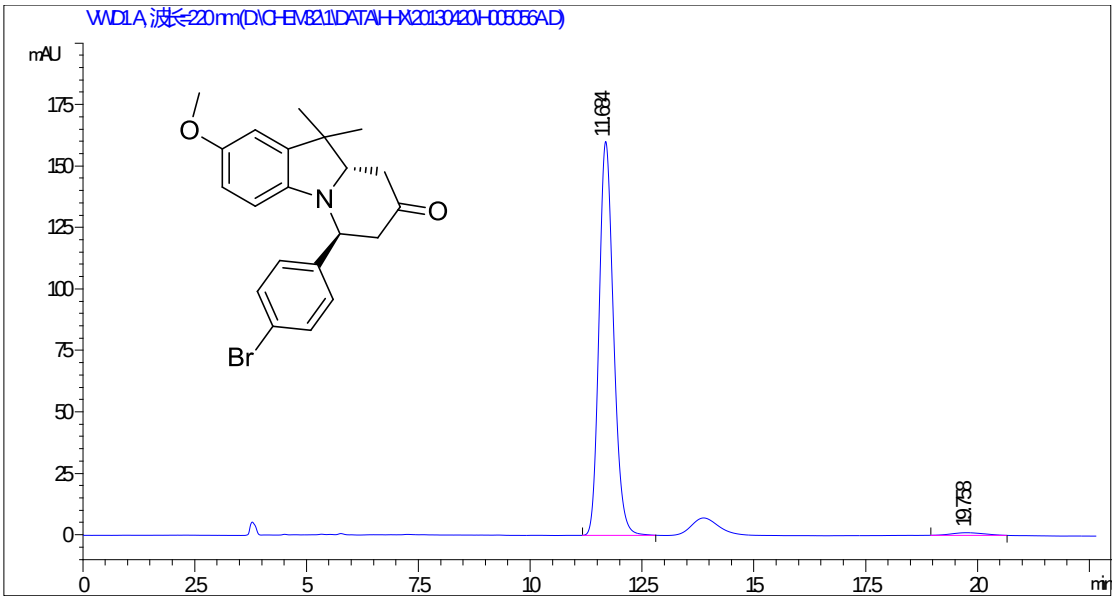


#	Time	Area	Height	Width	Symmetry	Area %
1	13.15	8669.1	316.7	0.4286	0.699	97.196
2	25.26	250.1	4.6	0.7905	0.844	2.804

(6S,9aS)-6-(4-bromophenyl)-2-methoxy-10,10-dimethyl-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4s)

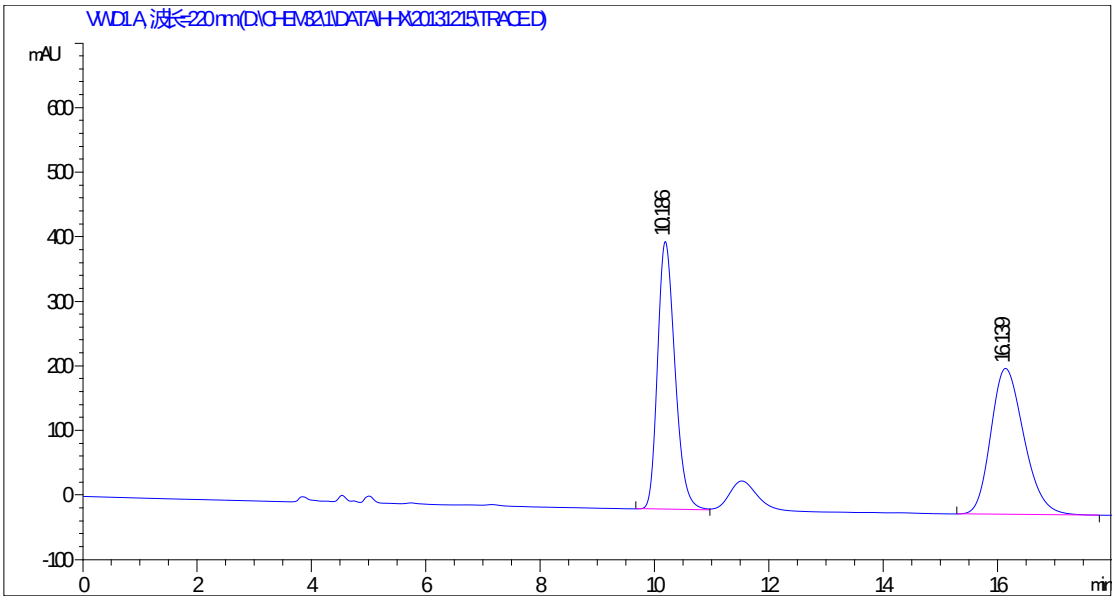


#	Time	Area	Height	Width	Symmetry	Area %
1	11.623	19832.1	871	0.3515	0.741	50.047
2	19.237	19794.6	388.4	0.7621	0.506	49.953

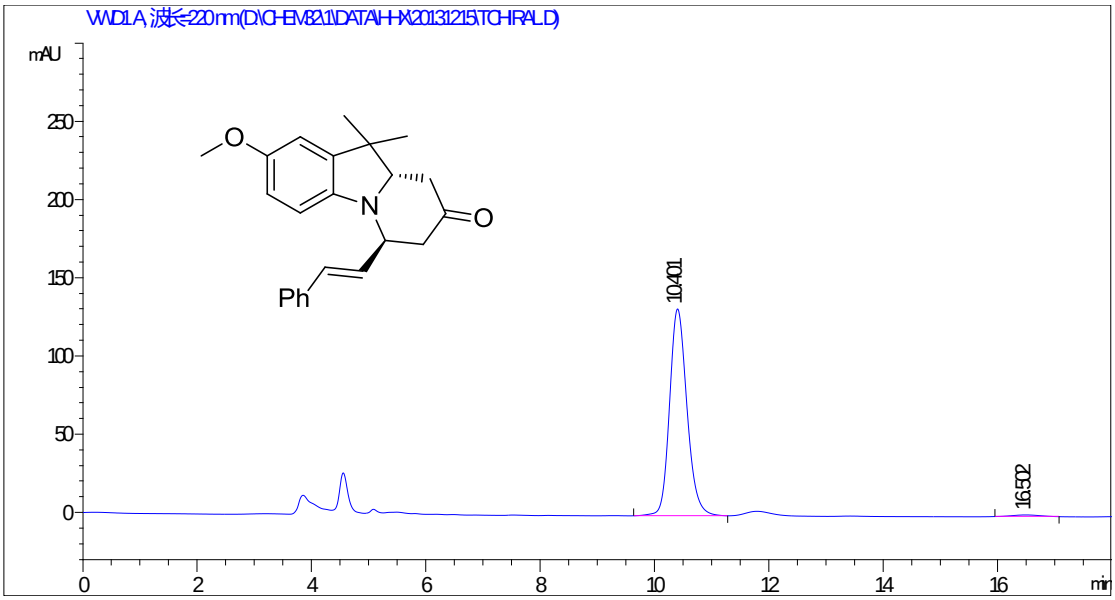


#	Time	Area	Height	Width	Symmetry	Area %
1	11.684	3601.6	160.2	0.3467	0.802	98.308
2	19.758	62	1.1	0.8986	0.877	1.692

(6S,9aS)-2-methoxy-10,10-dimethyl-6-((E)-styryl)-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4t)

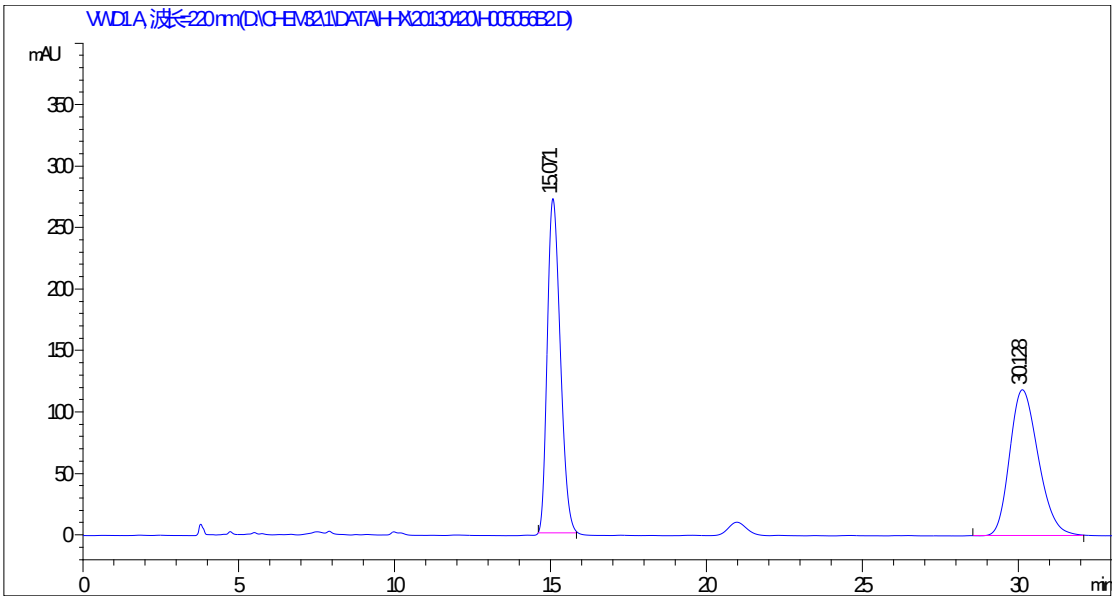


#	Time	Area	Height	Width	Symmetry	Area %
1	10.186	8789.2	414.9	0.3287	0.744	49.148
2	16.139	9094.1	226.1	0.6222	0.758	50.852

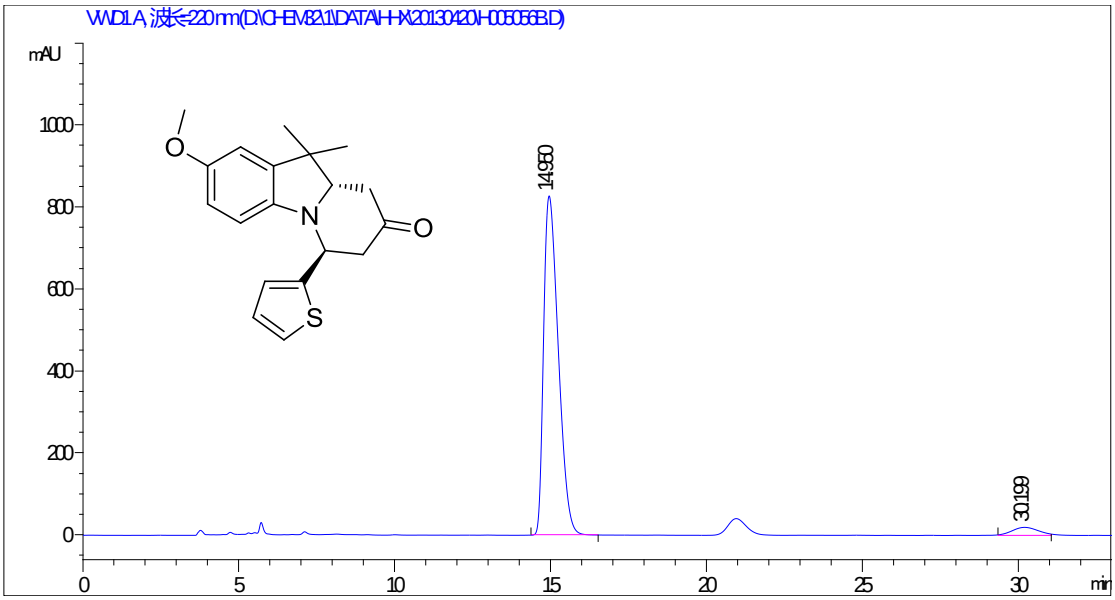


#	Time	Area	Height	Width	Symmetry	Area %
1	10.401	2808.3	132.3	0.3263	0.811	98.787
2	16.502	34.5	1	0.5542	1.054	1.213

(6S,9aS)-2-methoxy-10,10-dimethyl-6-(thiophen-2-yl)-6,7,9a,10-tetrahydropyrido [1,2-a]indol-8(9H)-one (4u)



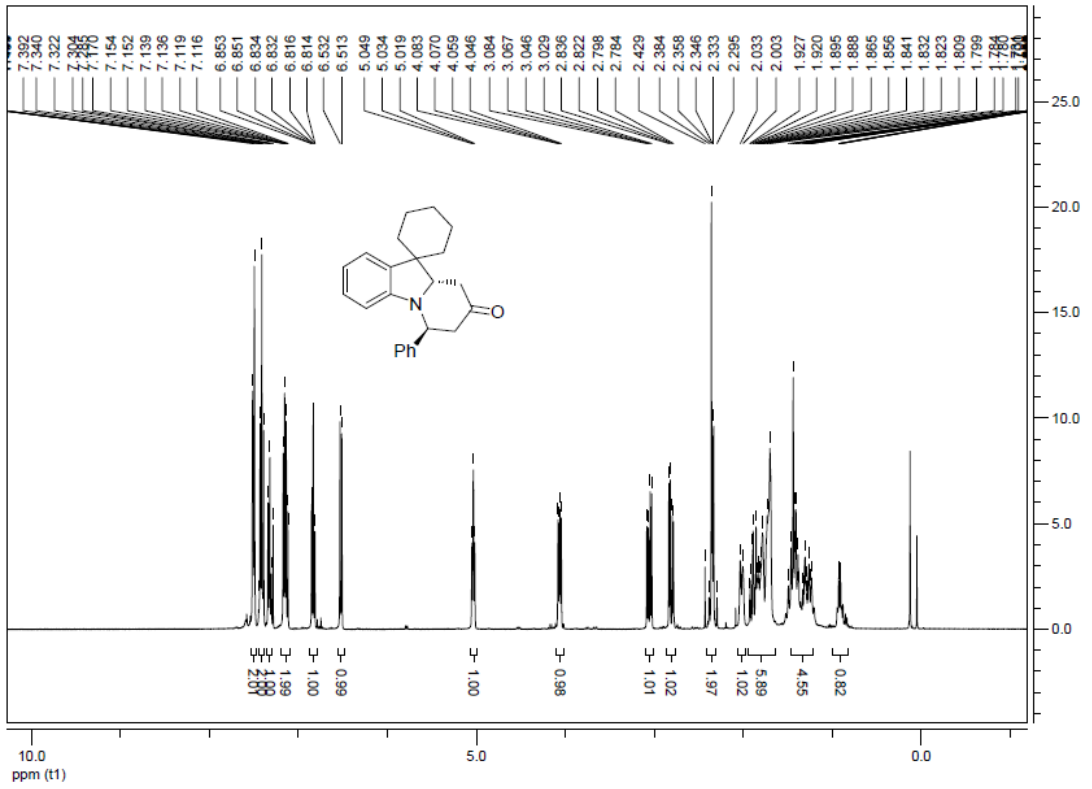
#	Time	Area	Height	Width	Symmetry	Area %
1	15.071	7911.6	272.4	0.4841	0.739	51.156
2	30.128	7554.2	118.6	1.0618	0.767	48.844

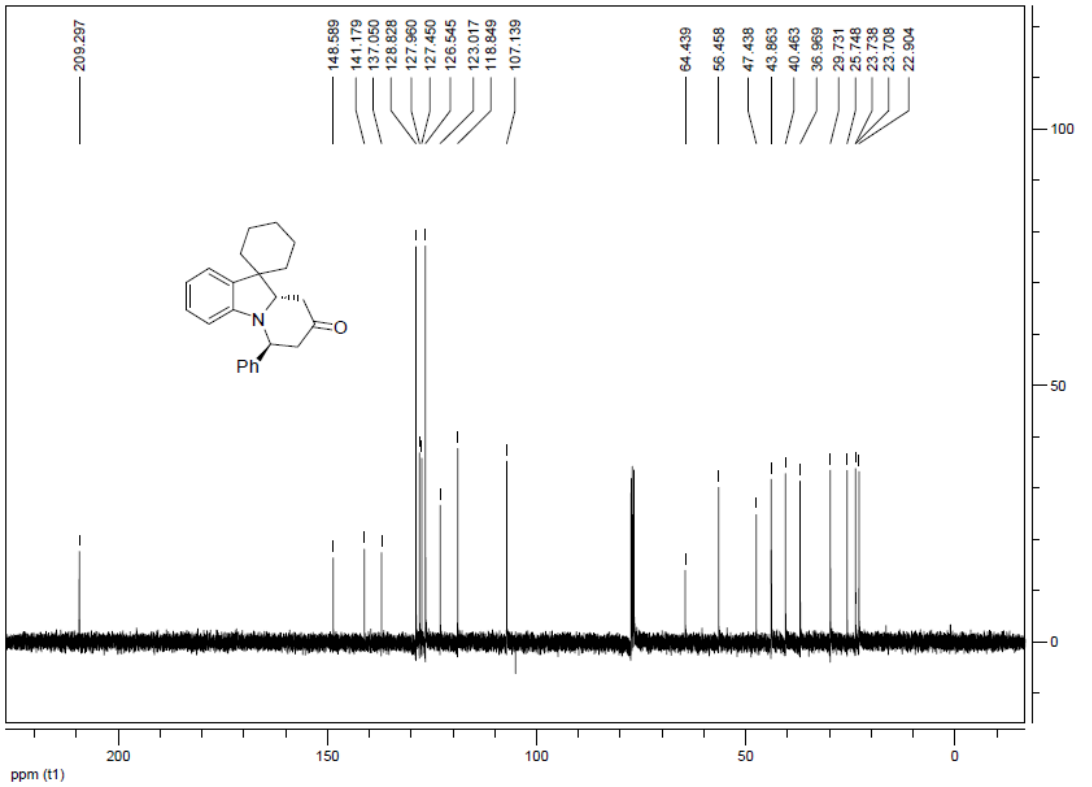


#	Time	Area	Height	Width	Symmetry	Area %
1	14.95	27083.5	827.7	0.5084	0.568	95.917
2	30.199	1152.8	19.6	0.9787	0.888	4.083

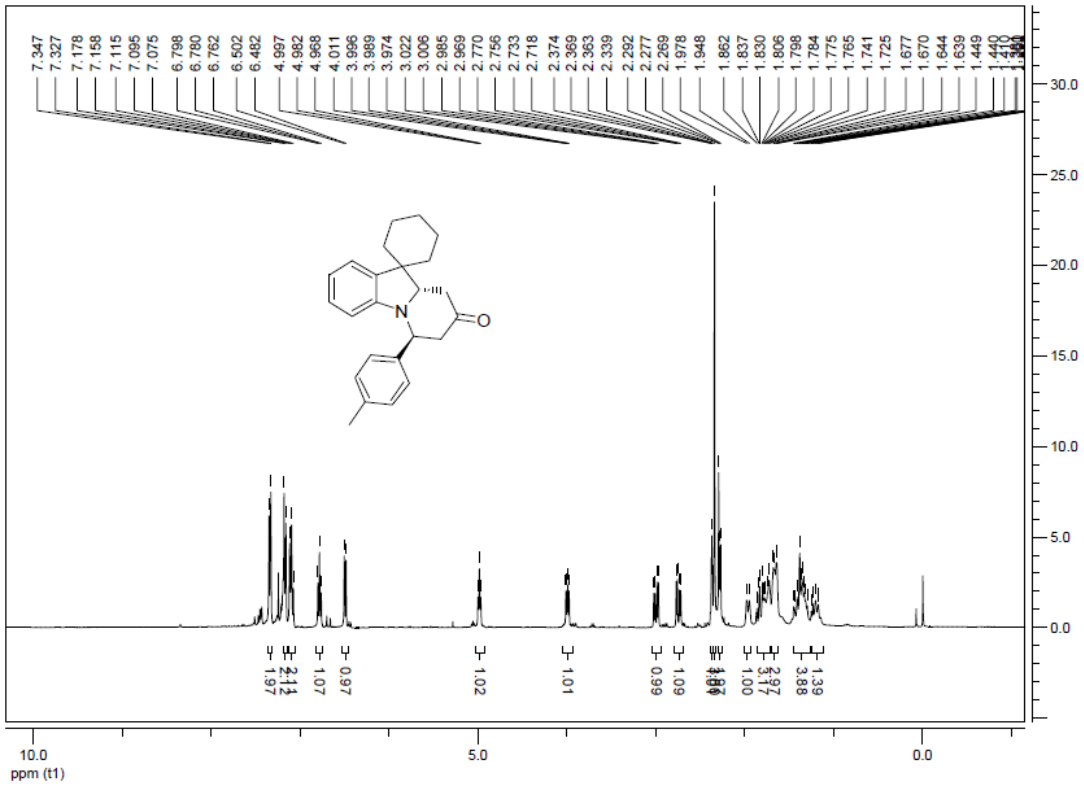
E: NMR Spectra of Formal ADA Products

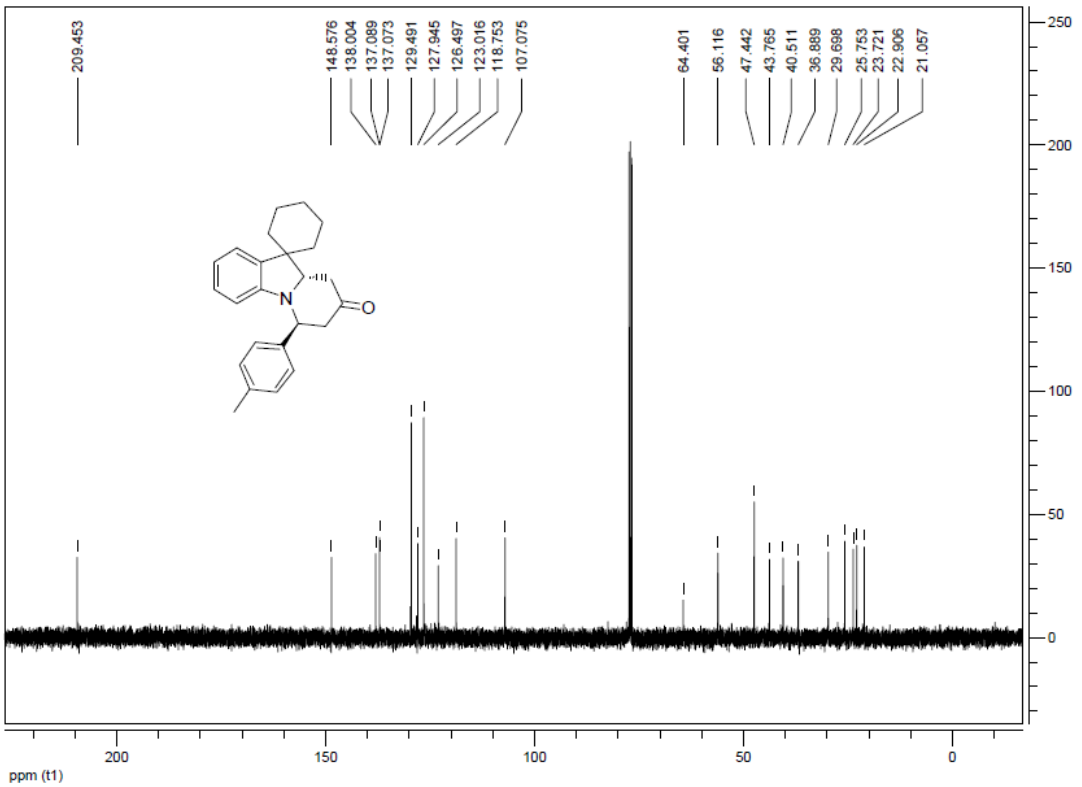
(6'S,9a'S)-6'-phenyl-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4a)



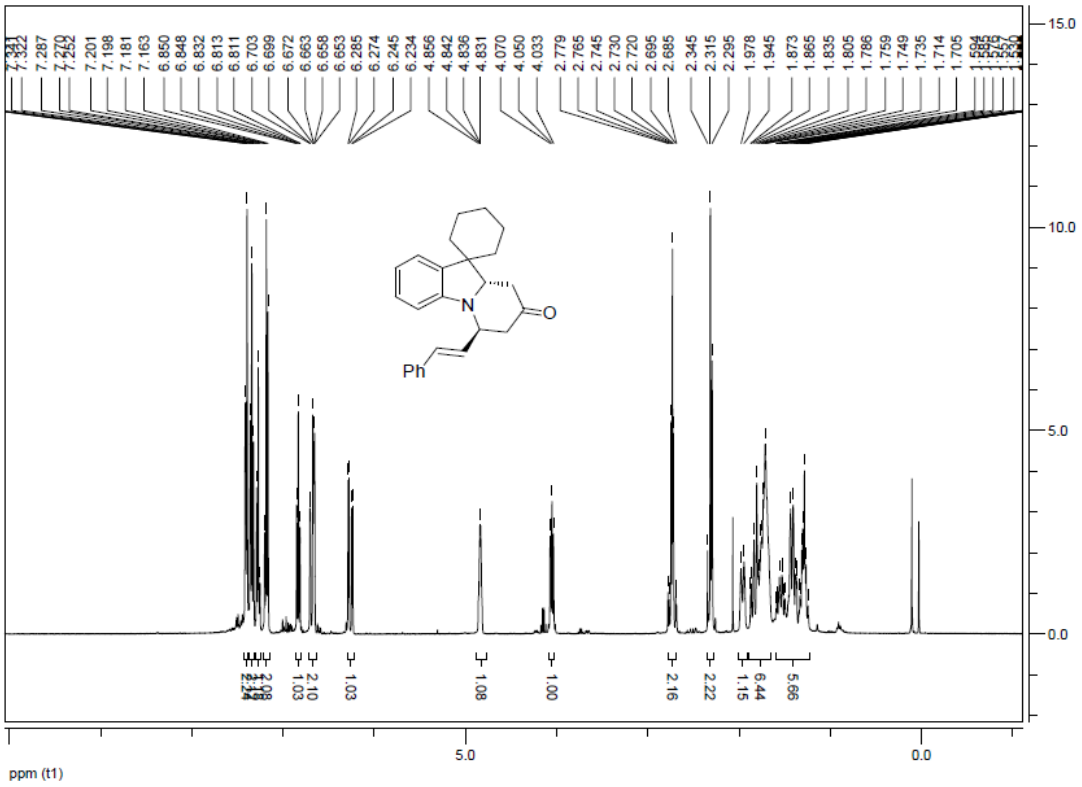


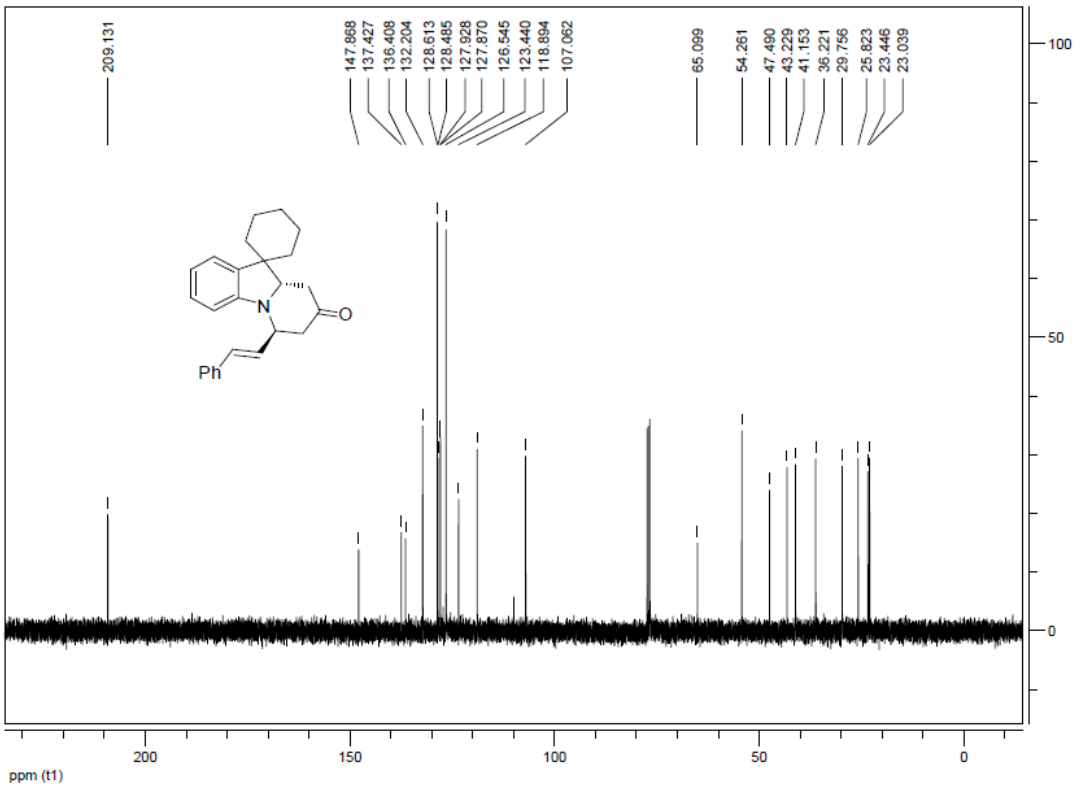
(6'S,9a'S)-6'-(p-tolyl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4b)



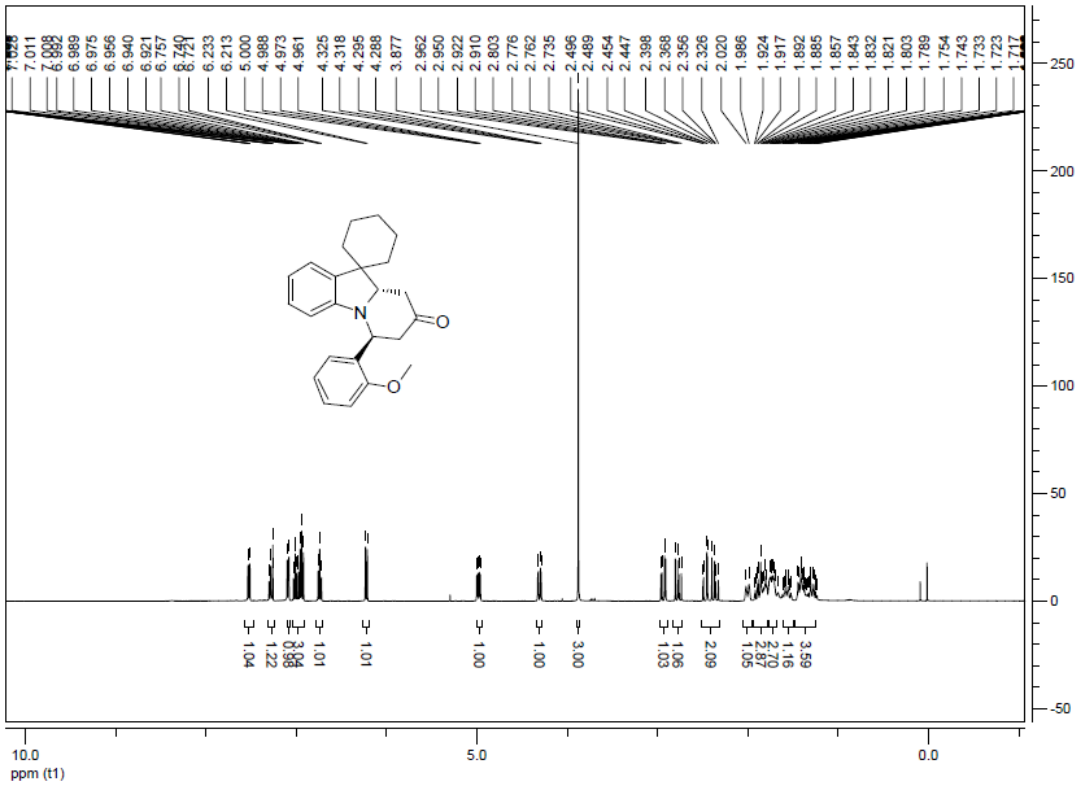


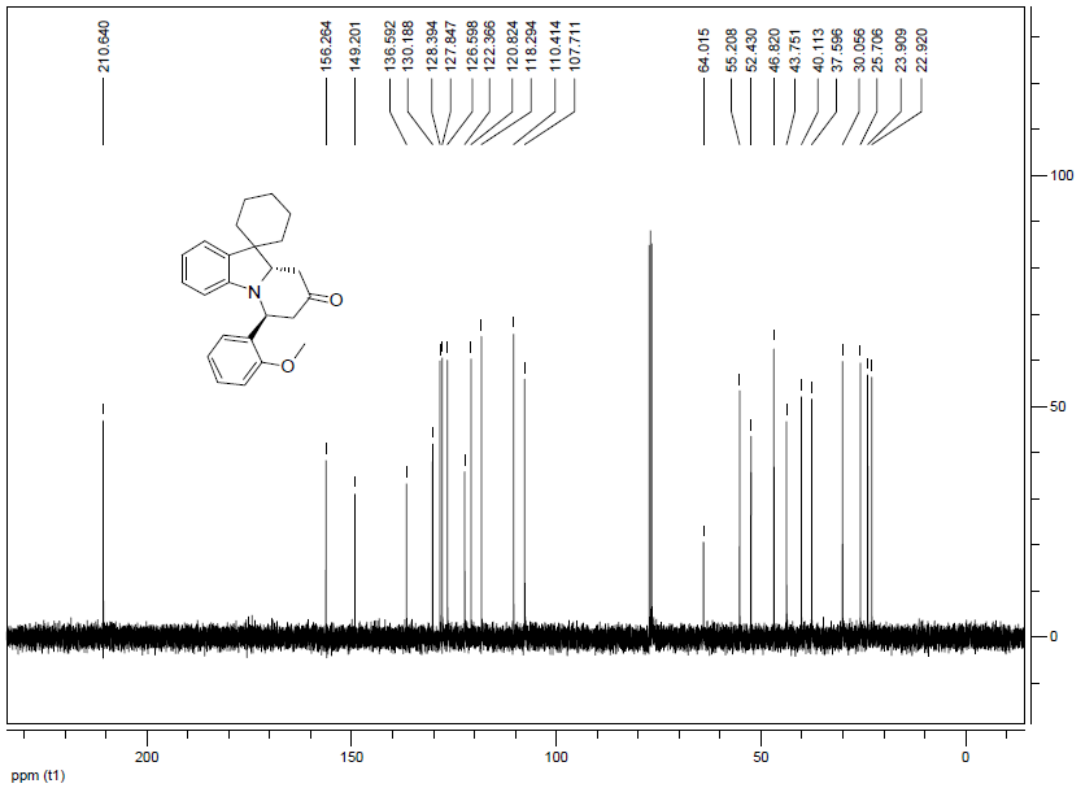
(6'S,9a'S)-6'-((E)-styryl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4c)



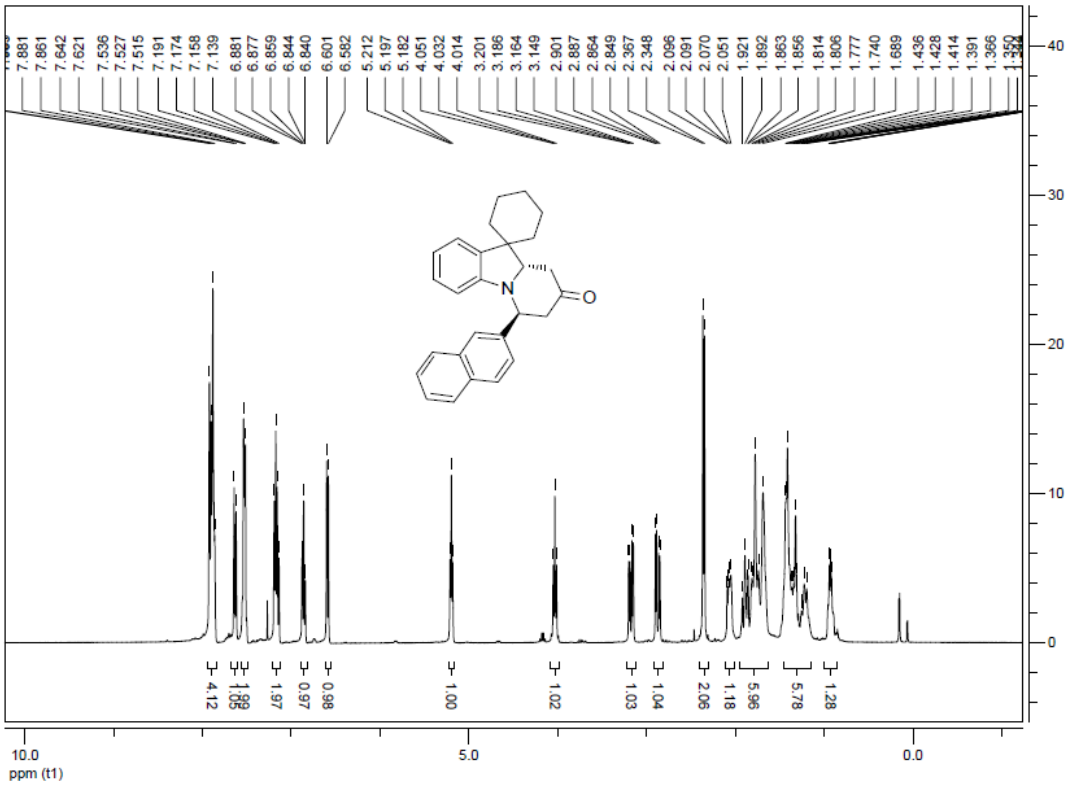


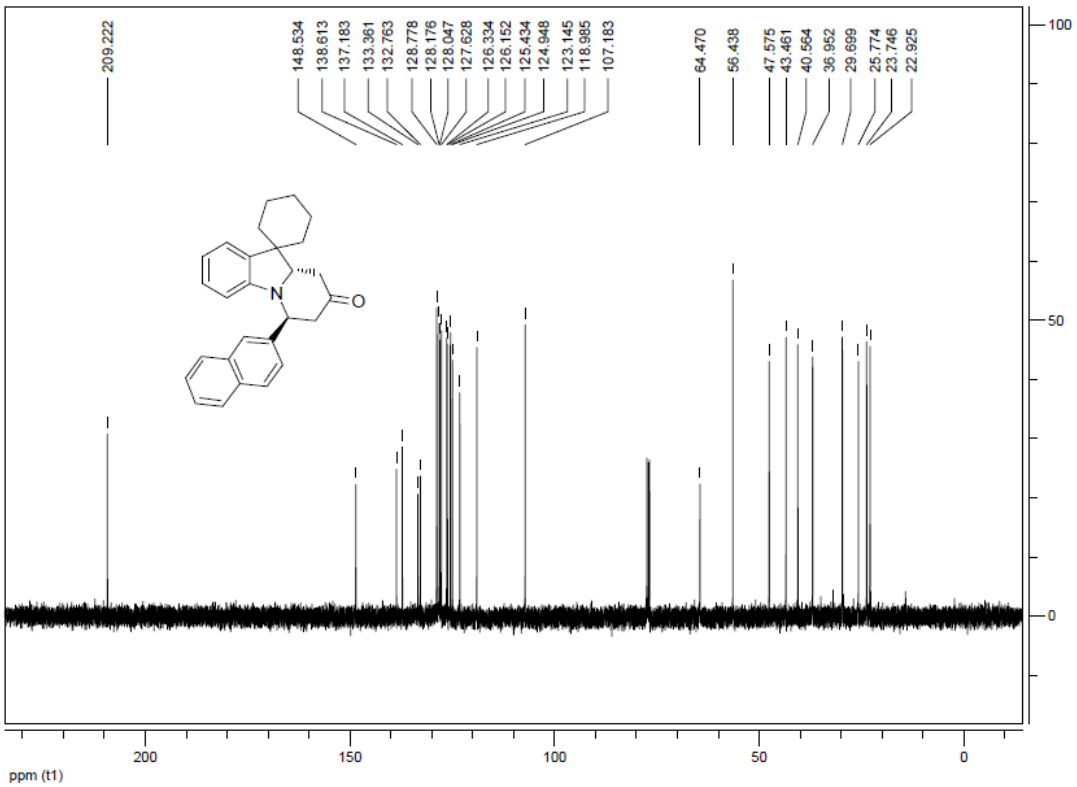
(6'S,9a'S)-6'-(2-methoxyphenyl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4d)



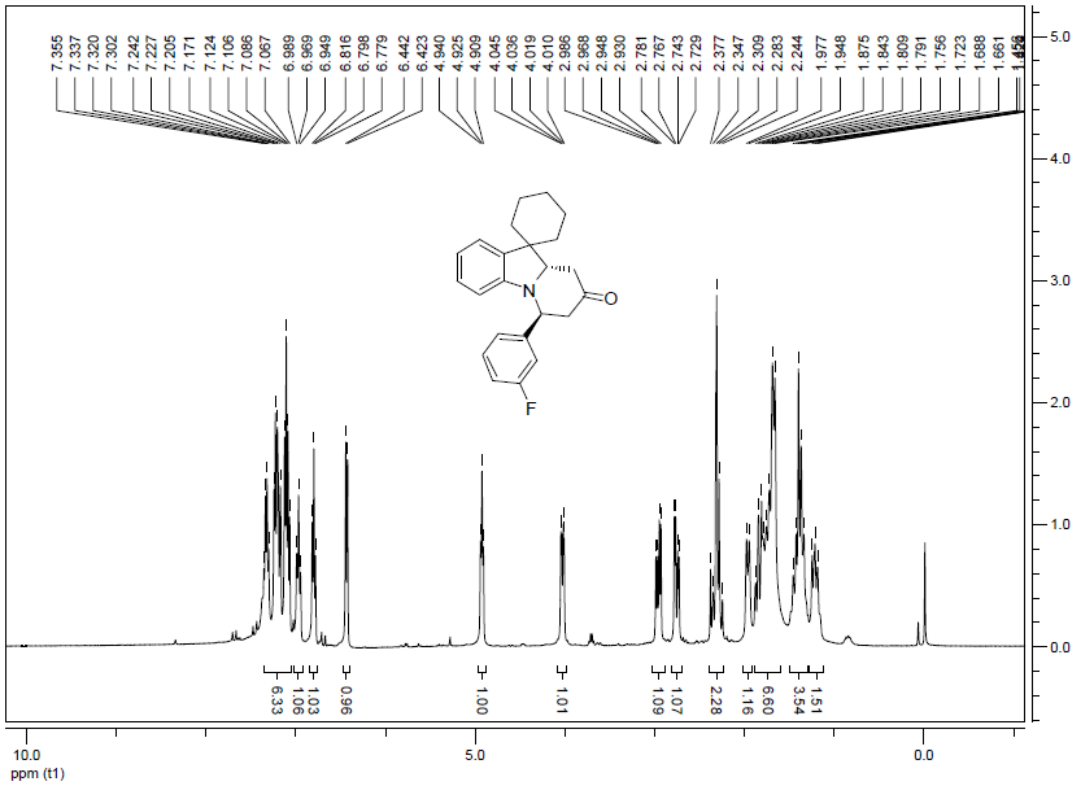


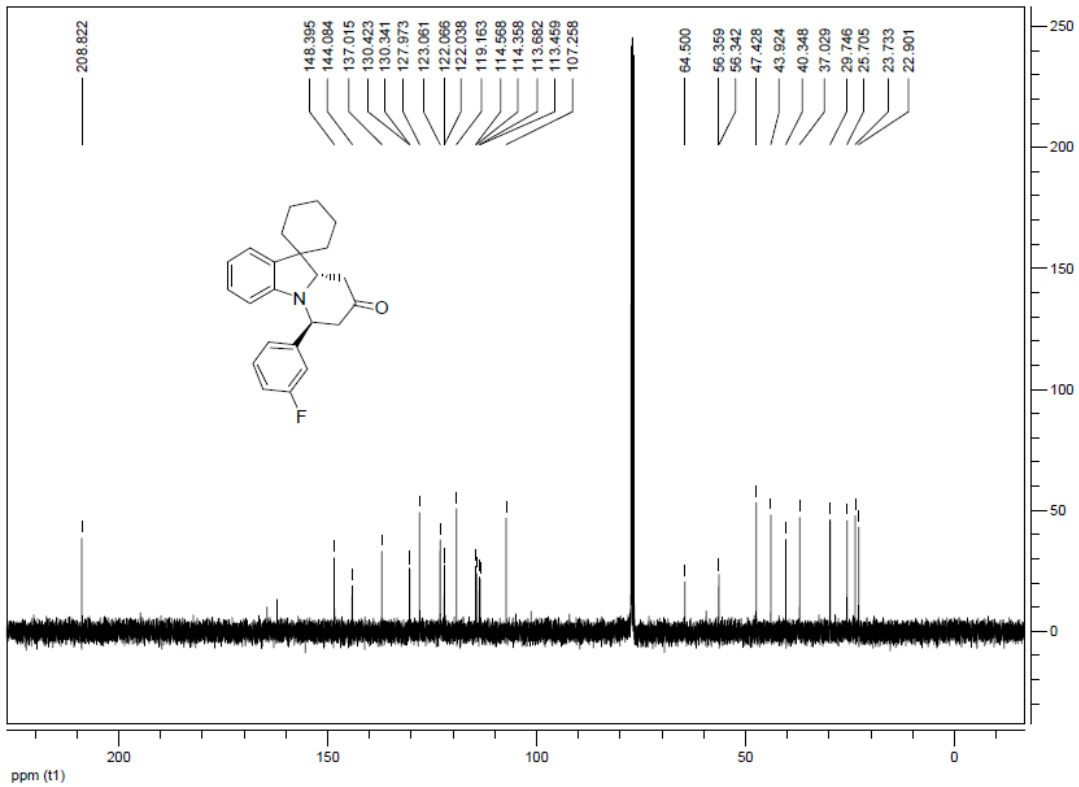
(6'S,9a'S)-6'-(naphthalen-2-yl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4e)



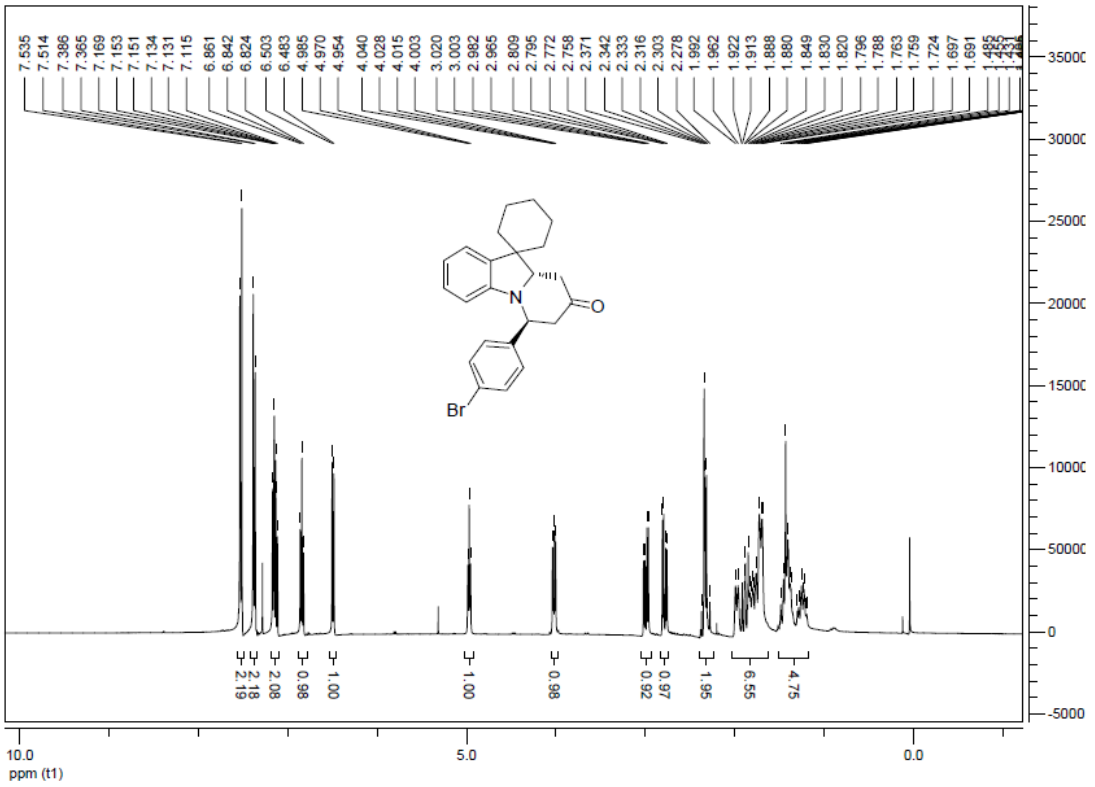


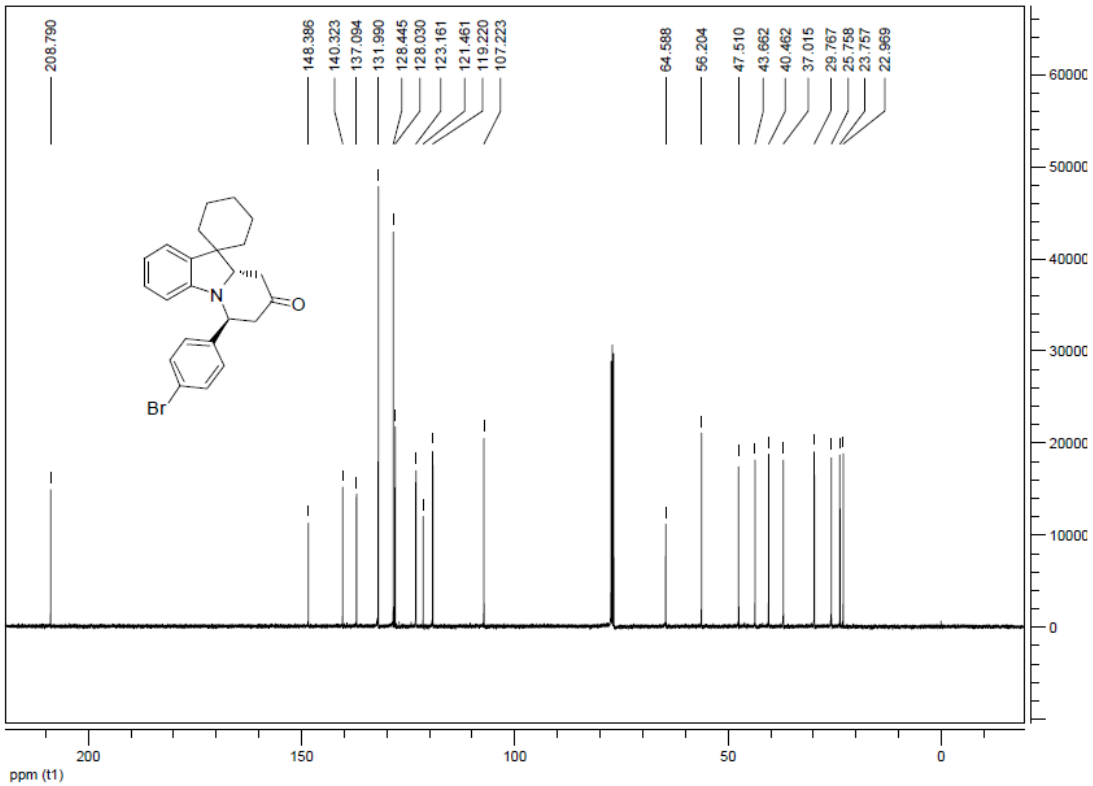
(6'S,9a'S)-6'-(3-fluorophenyl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4f)



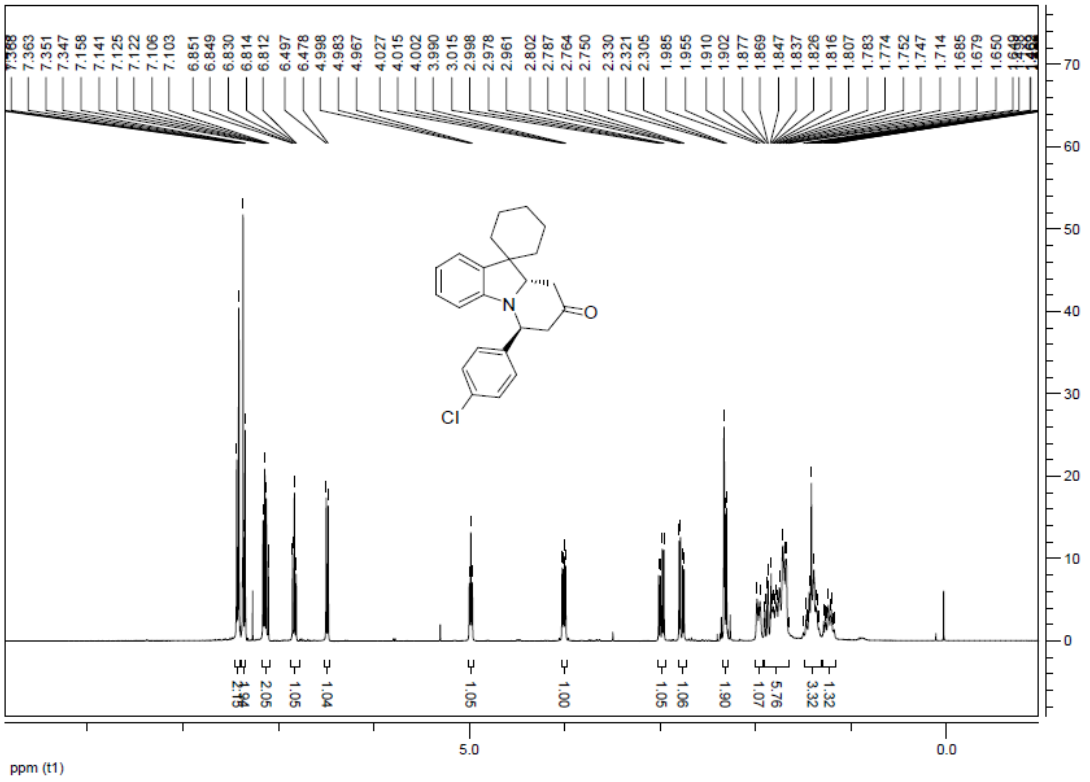


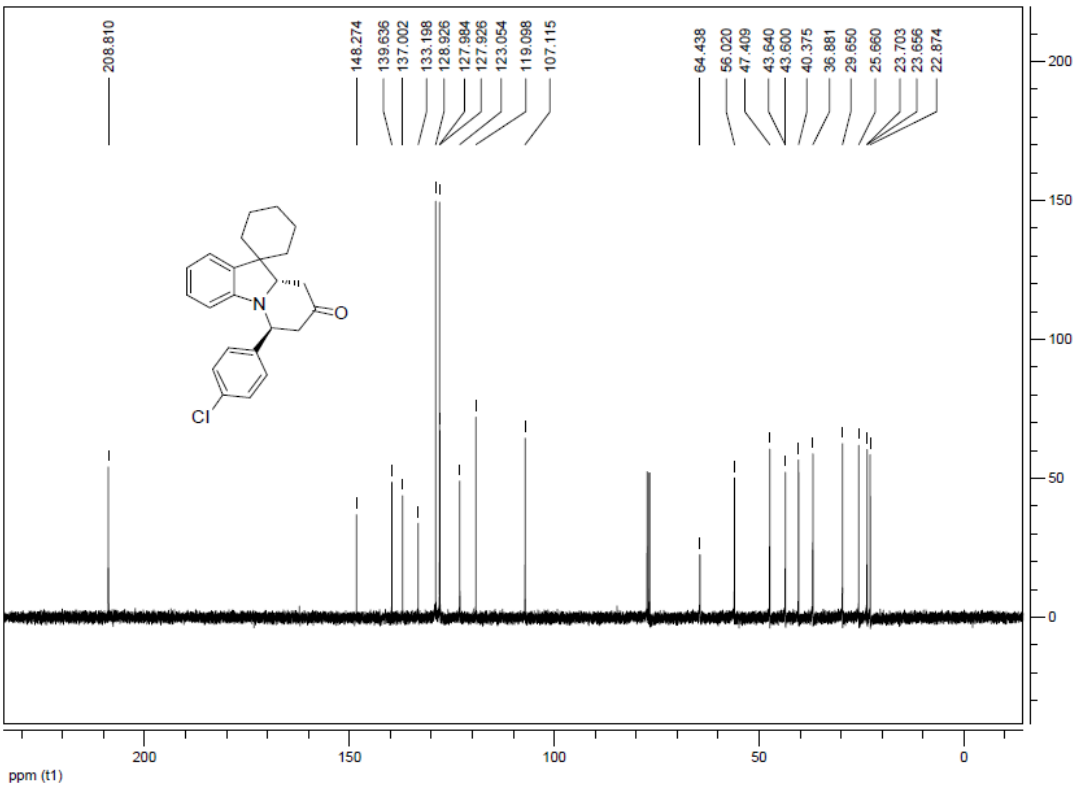
(6'S,9a'S)-6'-(4-bromophenyl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4g)



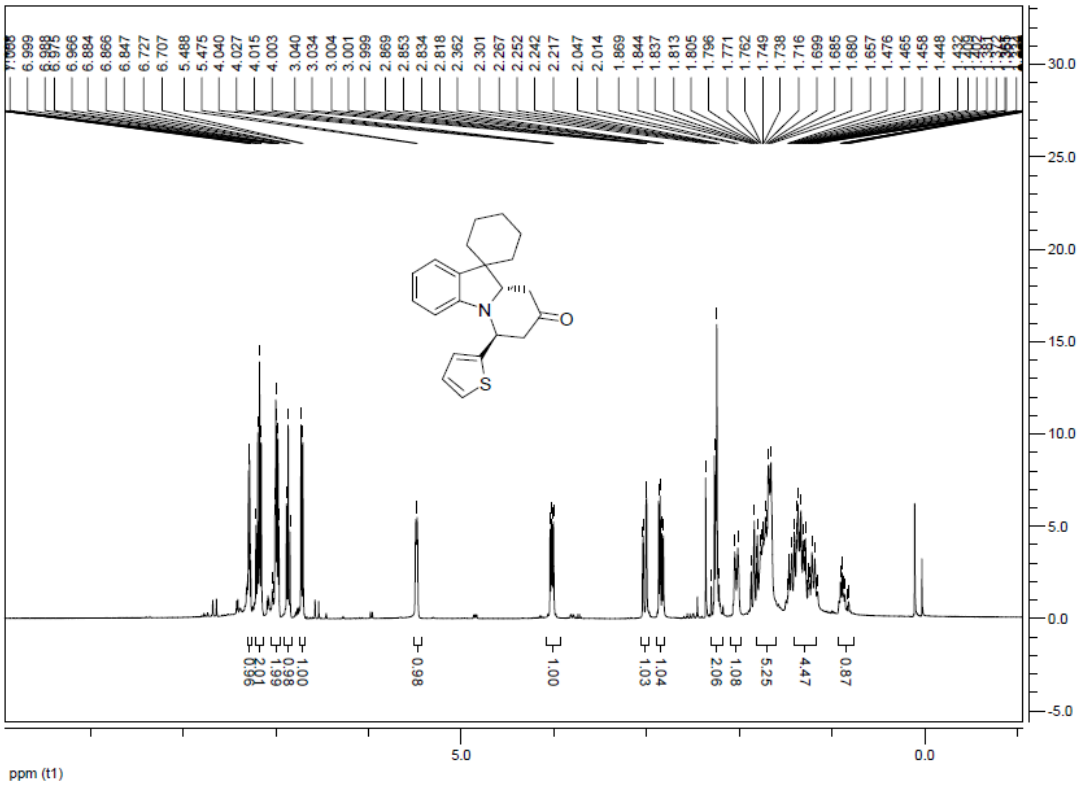


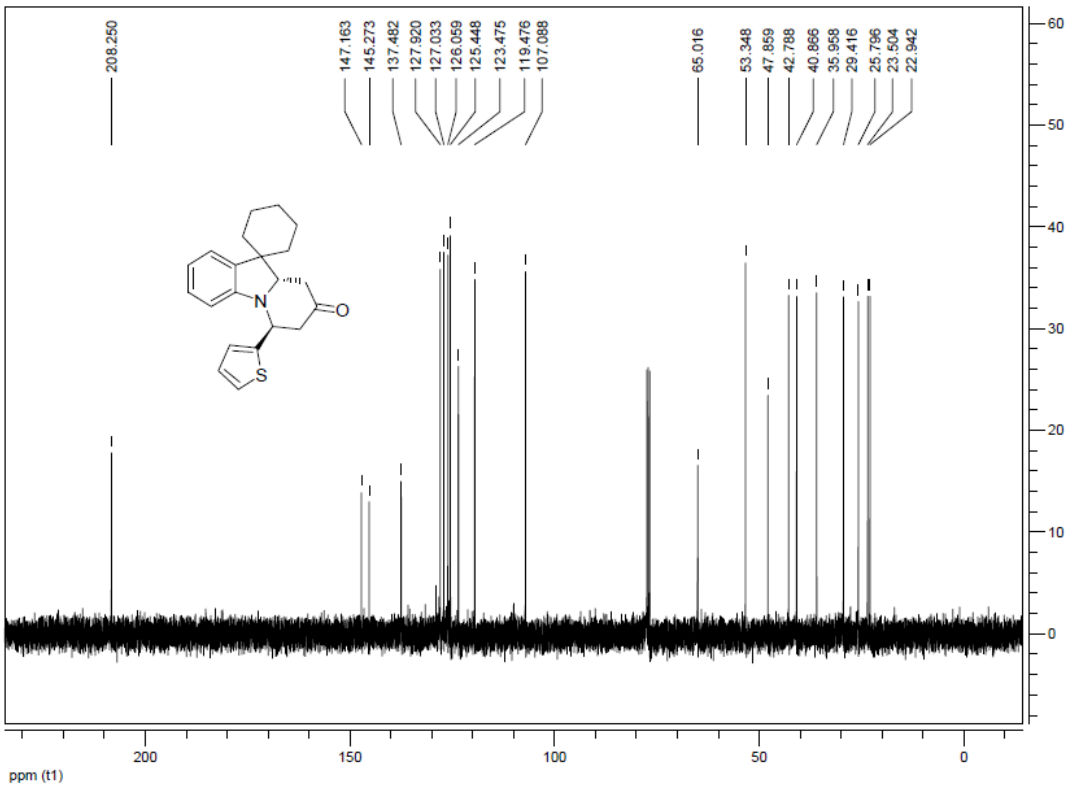
(6'S,9a'S)-6'-(4-chlorophenyl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido [1,2-a]indol]-8'(7'H)-one (4h)



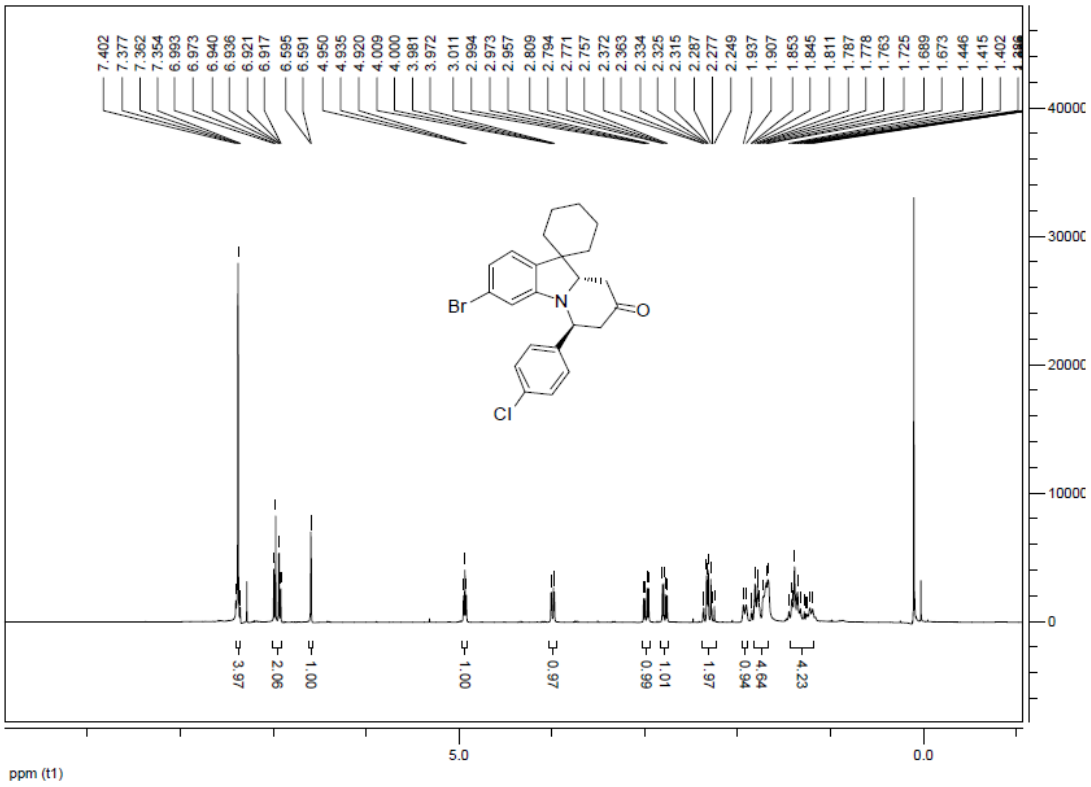


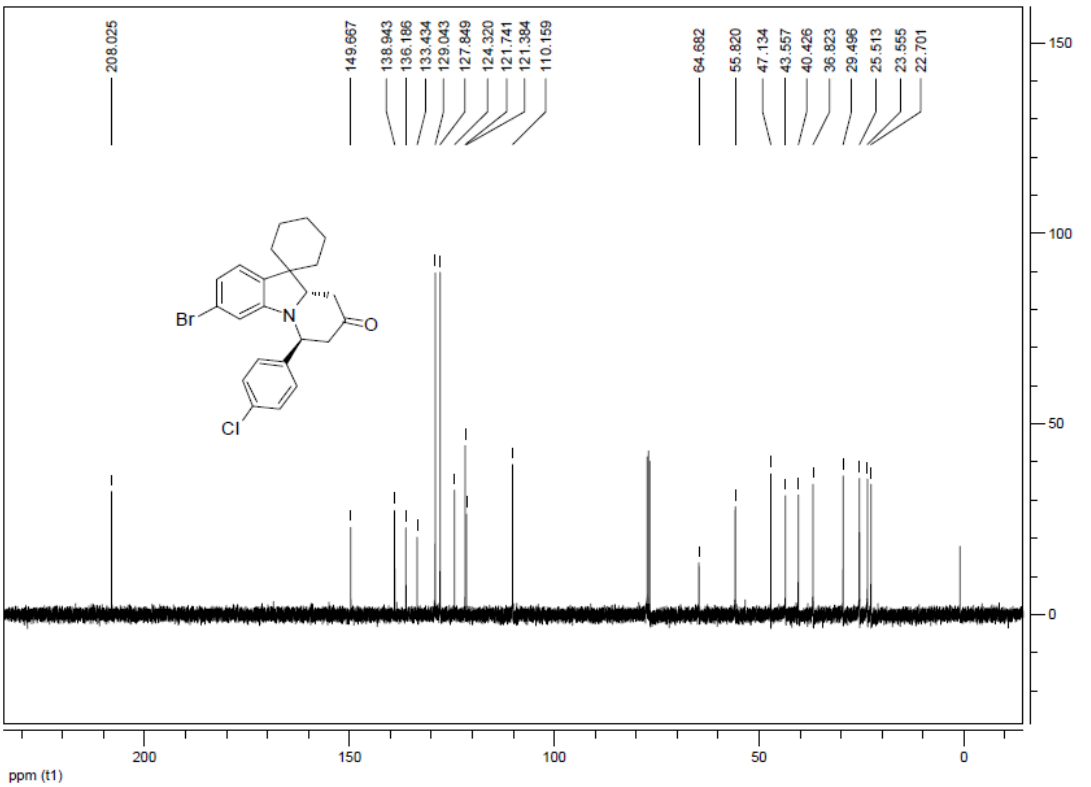
(6'S,9a'S)-6'-(thiophen-2-yl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4i)



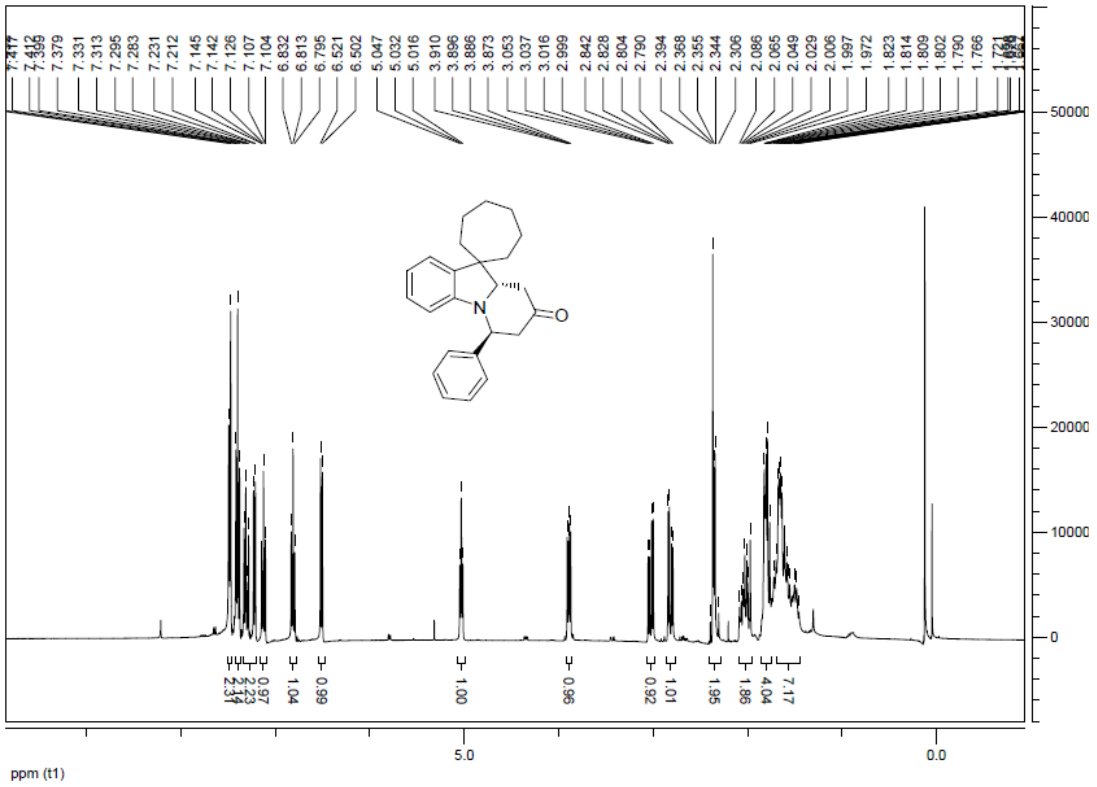


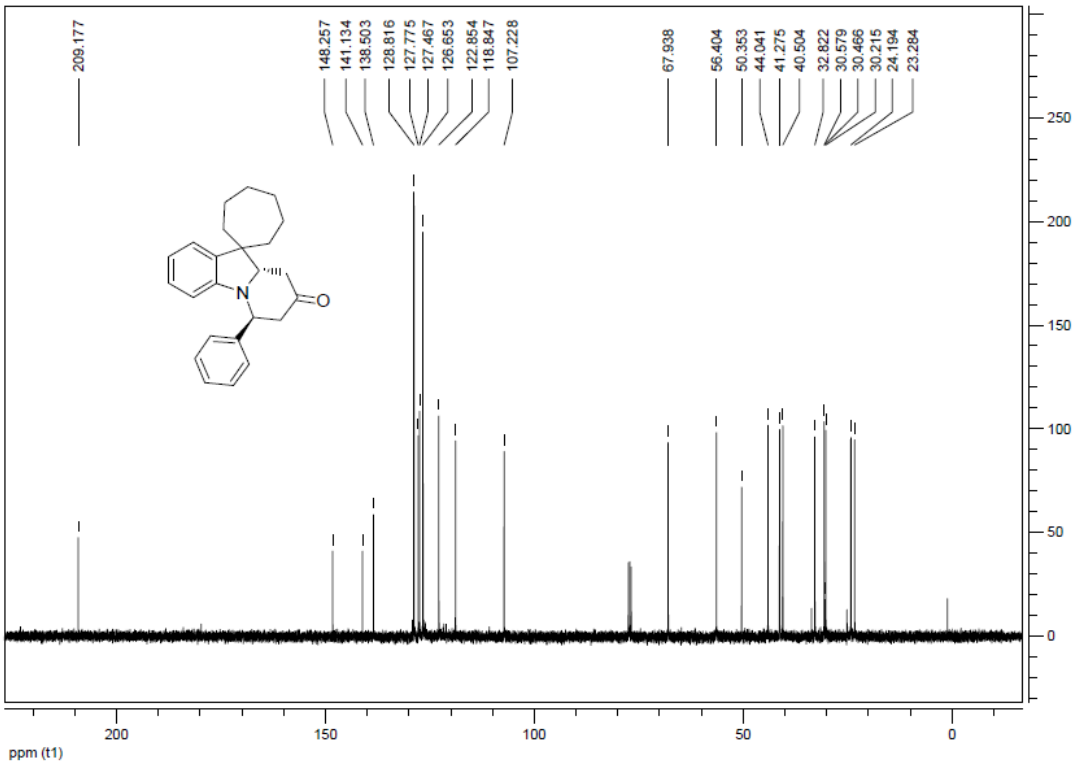
(6'S,9a'S)-3'-bromo-6'-(4-chlorophenyl)-9',9a'-dihydro-6'H-spiro[cyclohexane-1, 10'-pyrido[1,2-a]indol]-8'(7'H)-one (4j)



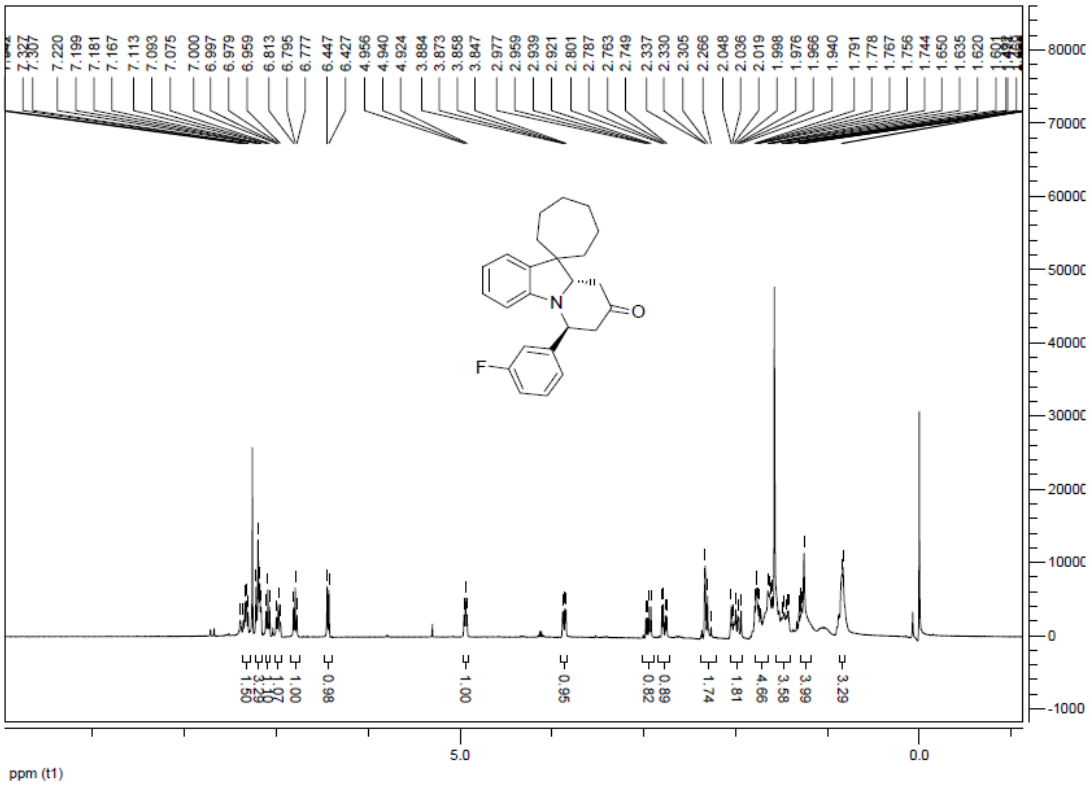


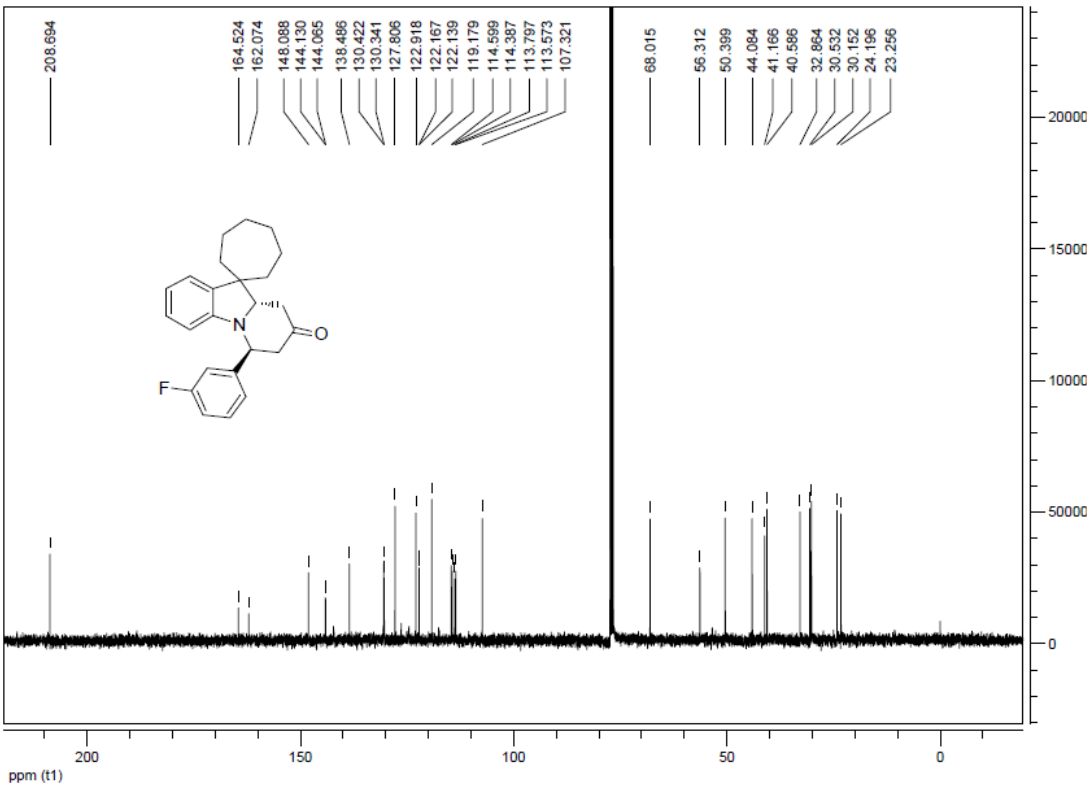
(6'S,9a'S)-6'-phenyl-9',9a'-dihydro-6'H-spiro[cycloheptane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4k)



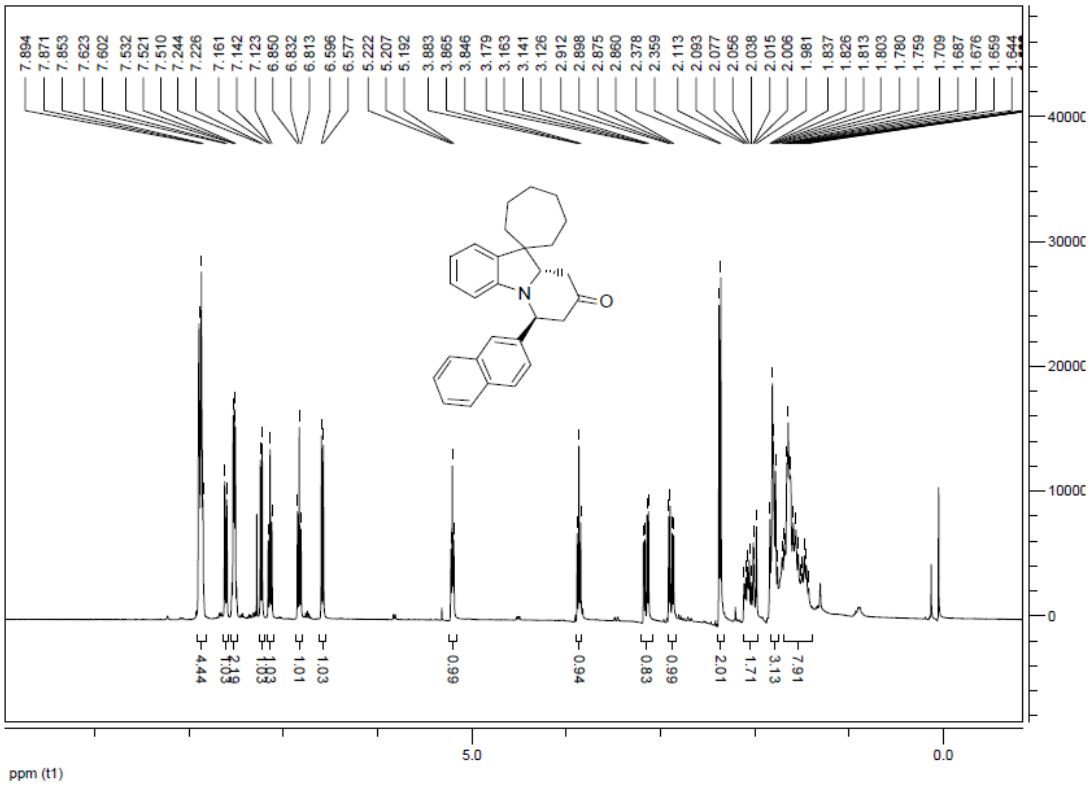


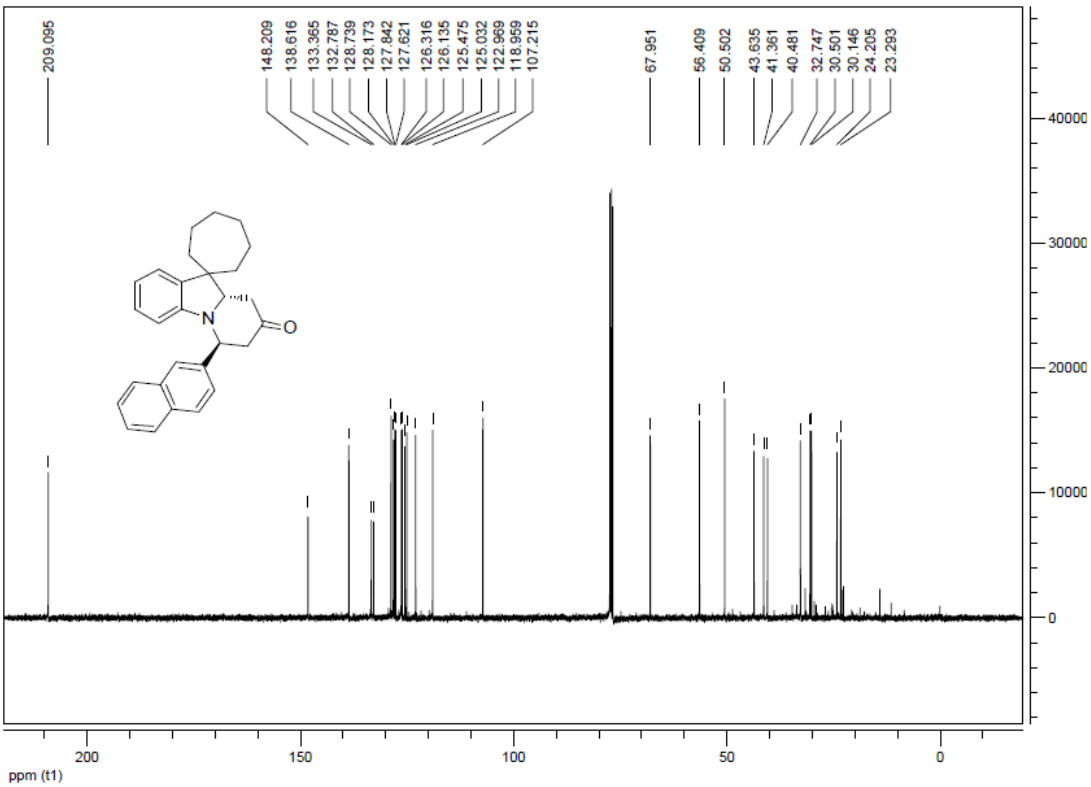
(6'S,9a'S)-6'-(3-fluorophenyl)-9',9a'-dihydro-6'H-spiro[cycloheptane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4l)



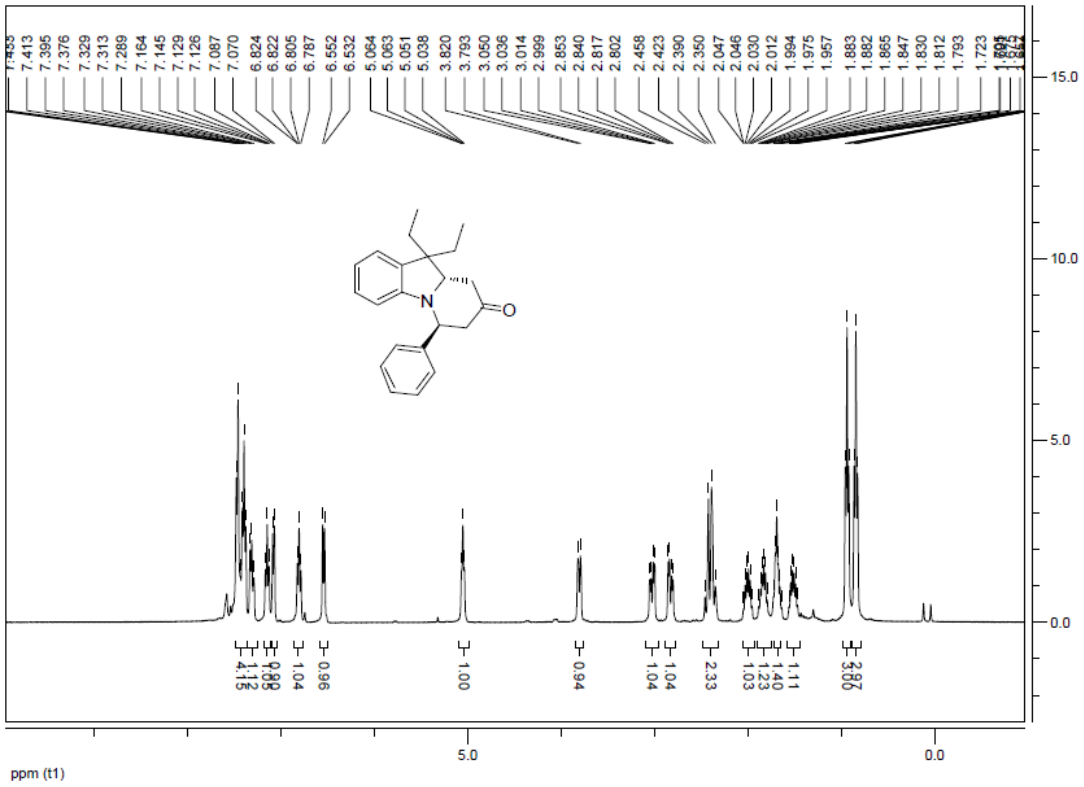


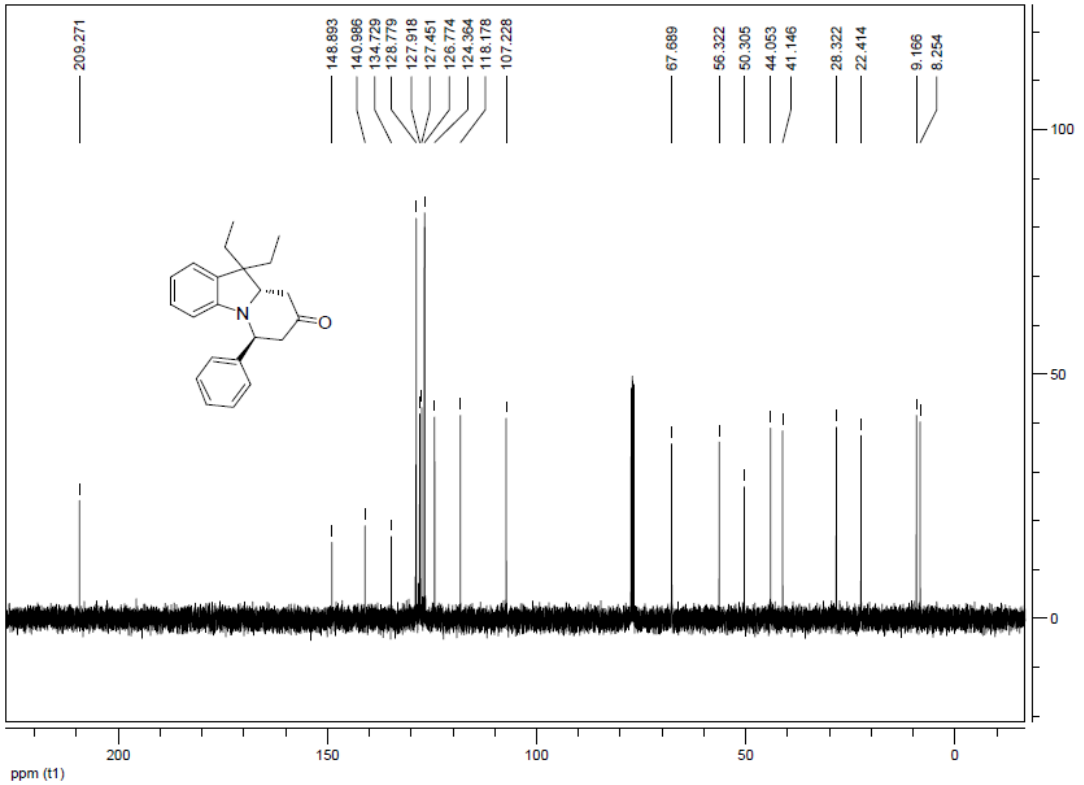
(6'S,9a'S)-6'-(naphthalen-2-yl)-9',9a'-dihydro-6'H-spiro[cycloheptane-1,10'-pyrido[1,2-a]indol]-8'(7'H)-one (4m)



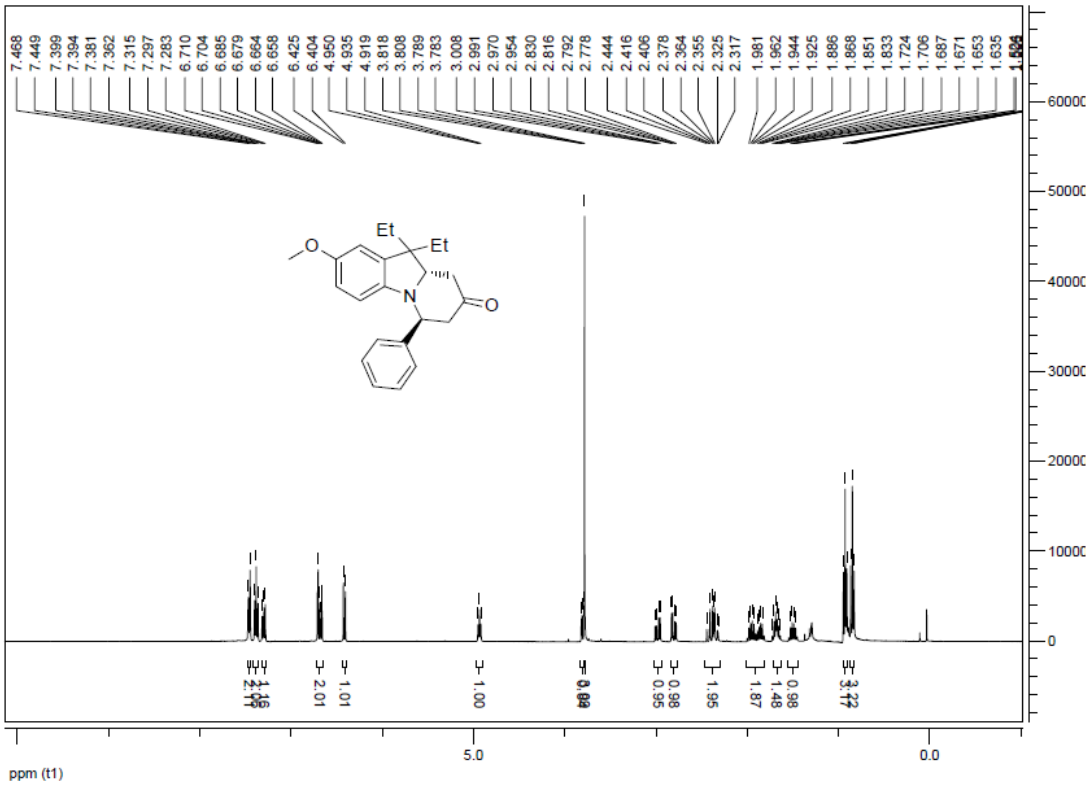


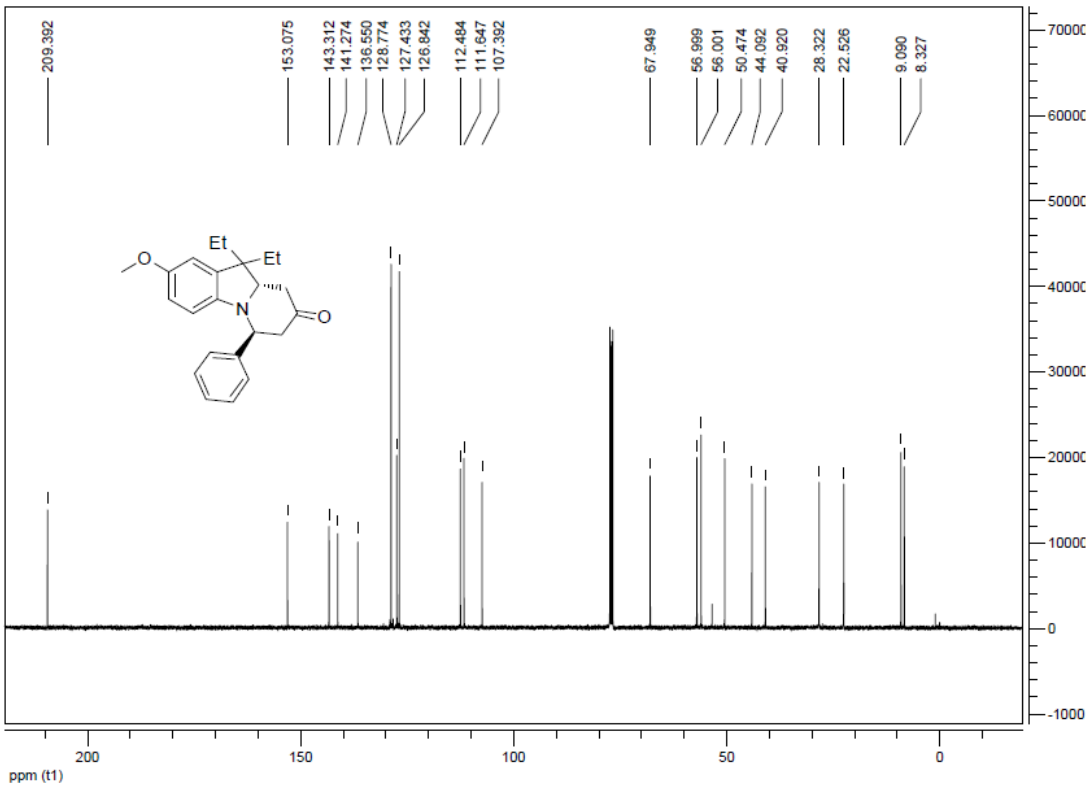
(6S,9aS)-10,10-diethyl-6-phenyl-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4n)



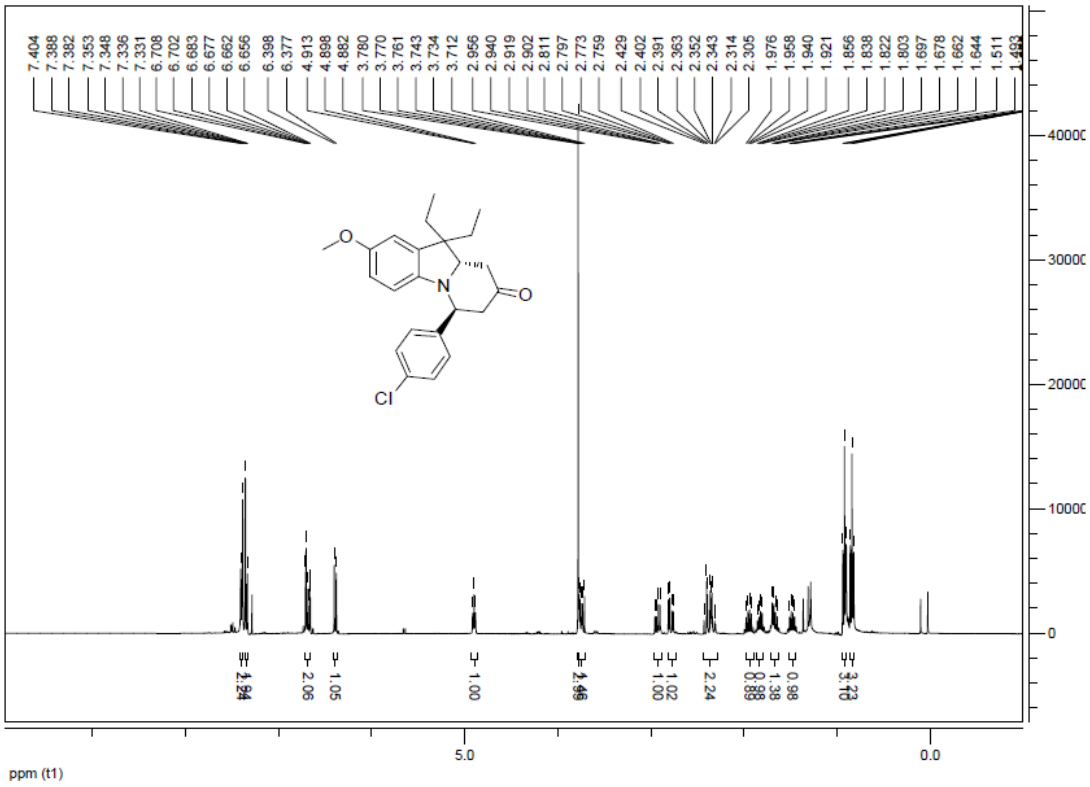


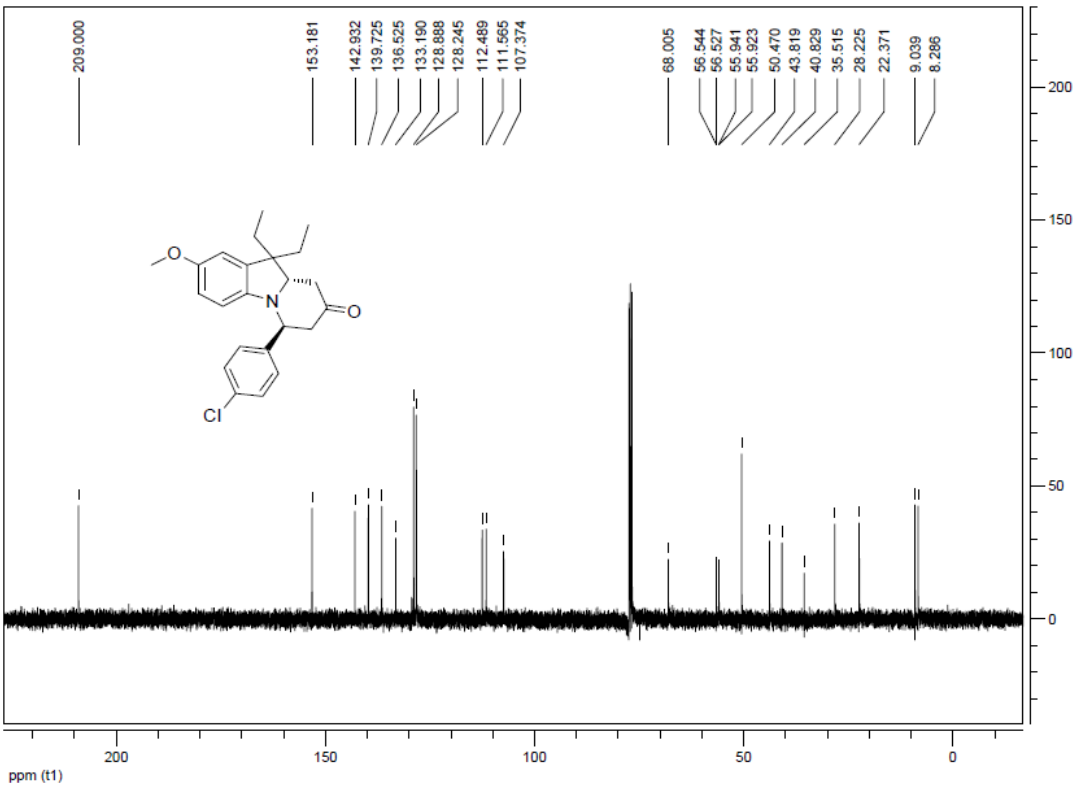
(6S,9aS)-10,10-diethyl-2-methoxy-6-phenyl-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4o)



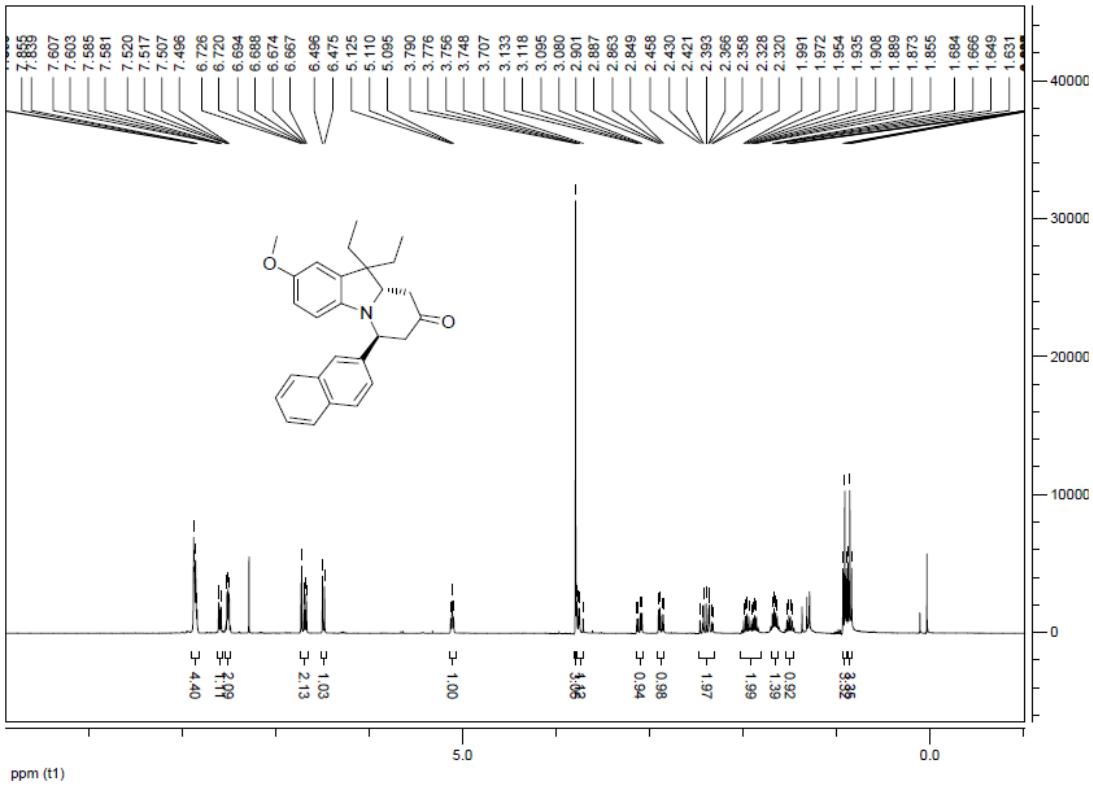


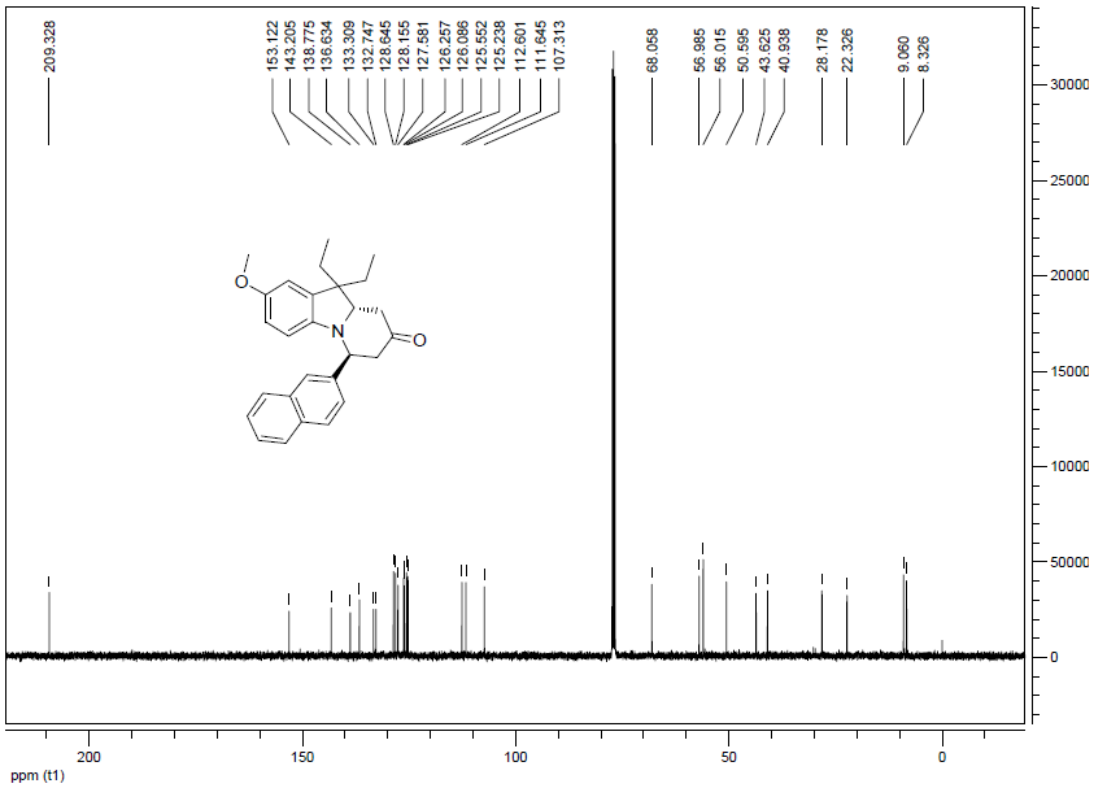
(6S,9aS)-6-(4-chlorophenyl)-10,10-diethyl-2-methoxy-6,7,9a,10-tetrahydropyrido [1,2-a]indol-8(9H)-one (4p)



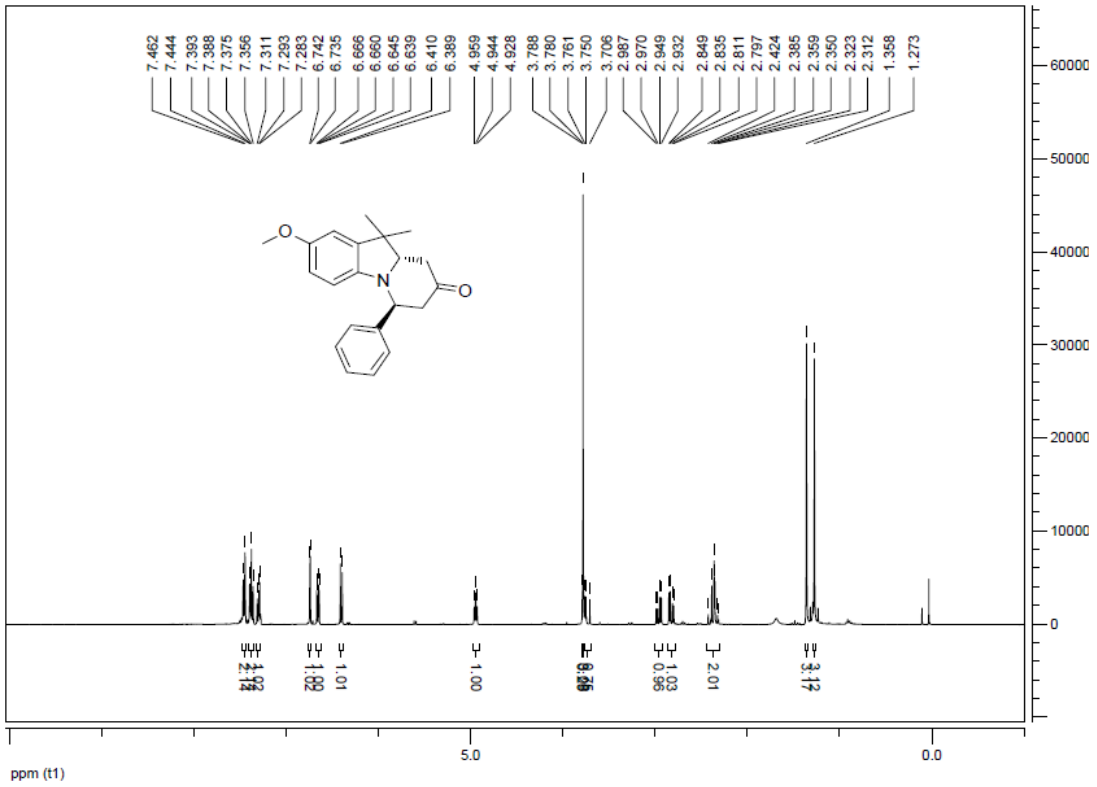


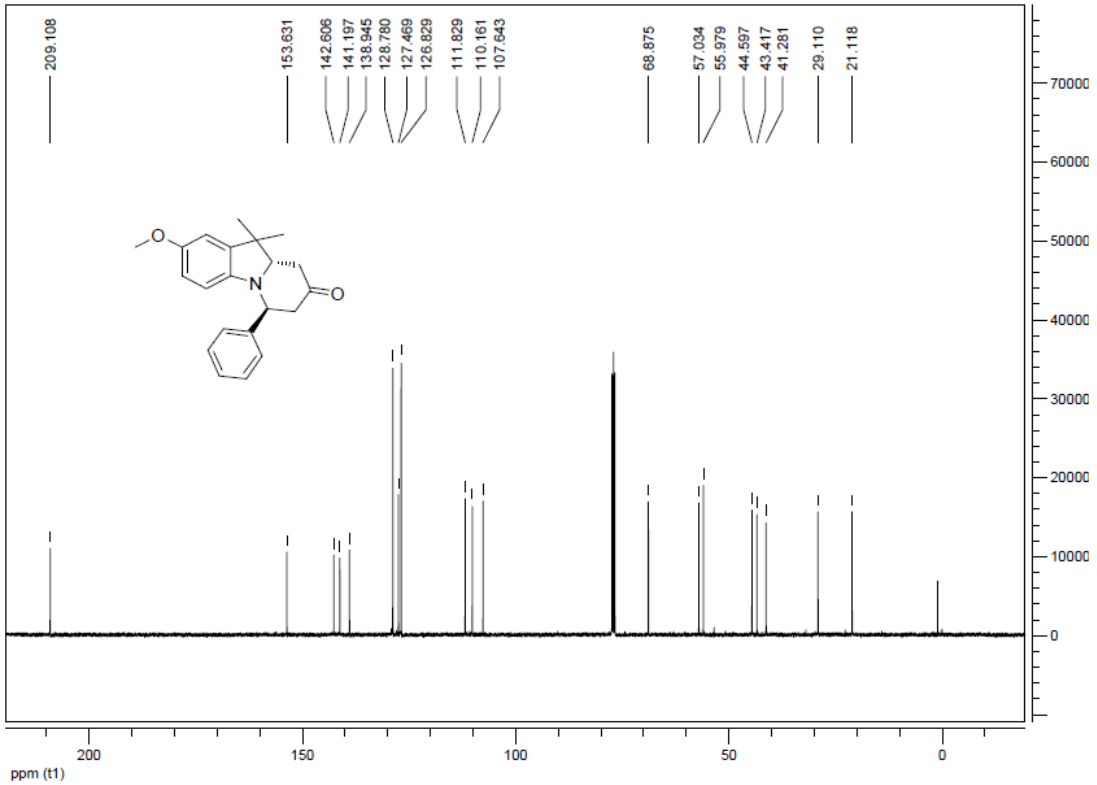
(6S,9aS)-10,10-diethyl-2-methoxy-6-(naphthalen-2-yl)-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4q)



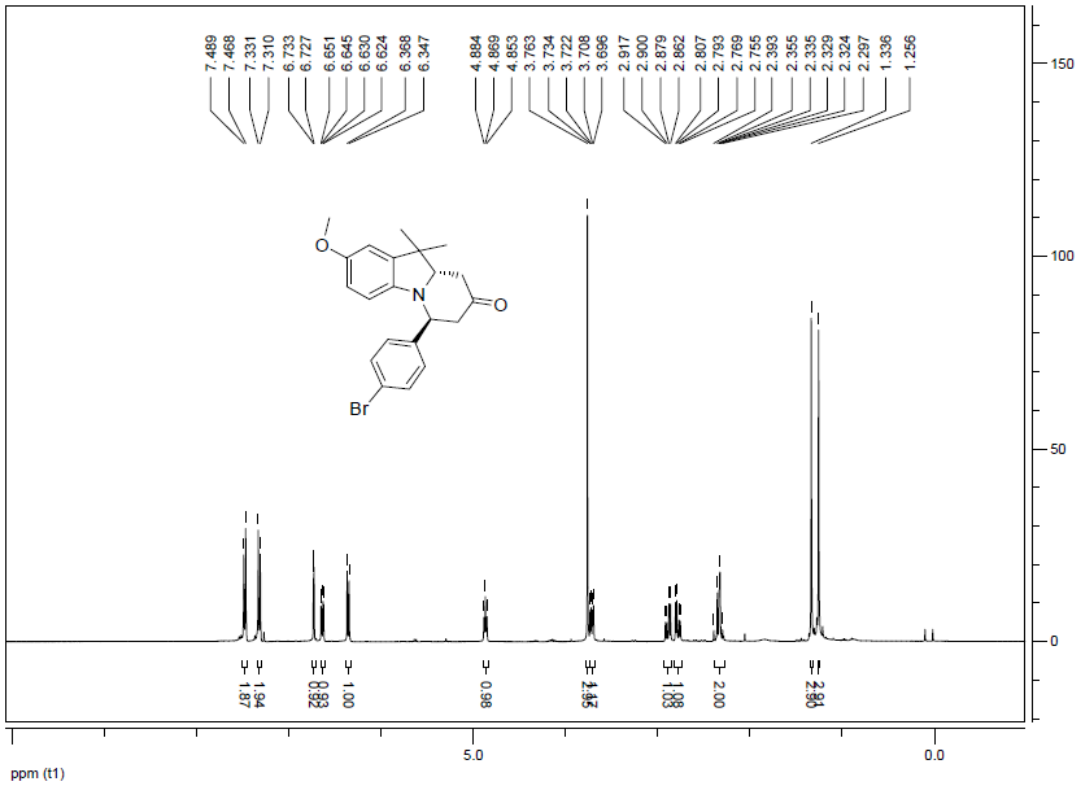


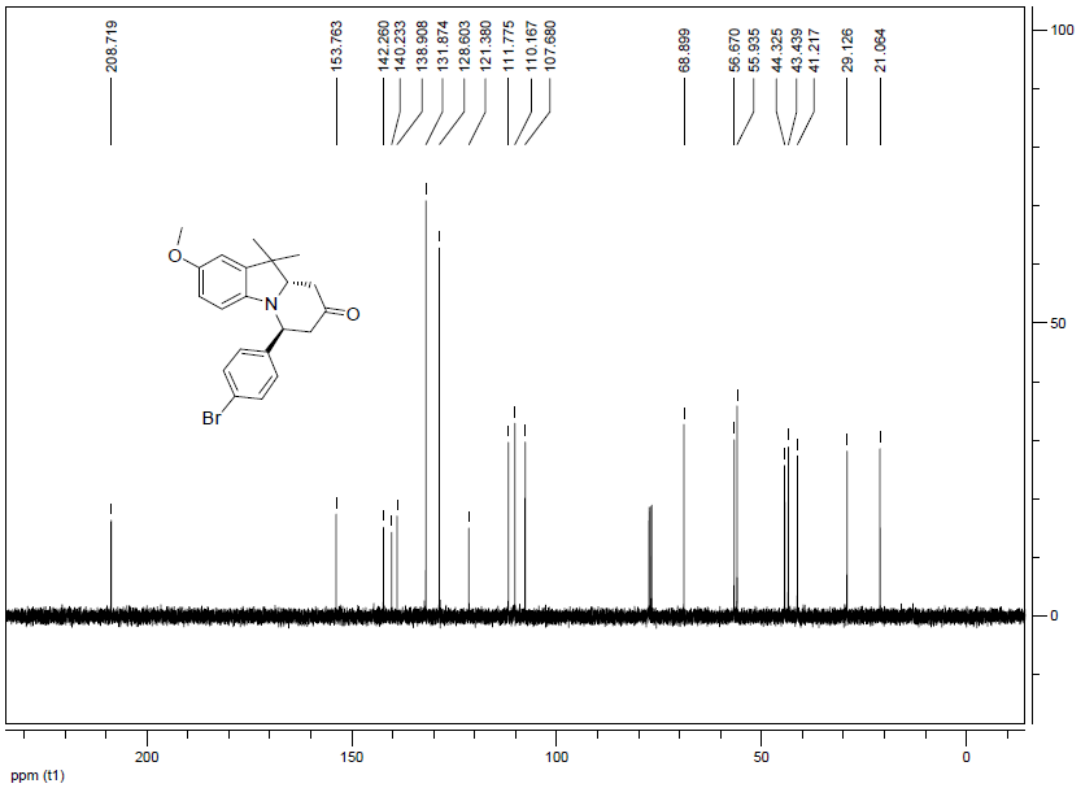
(6S,9aS)-2-methoxy-10,10-dimethyl-6-phenyl-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4r)



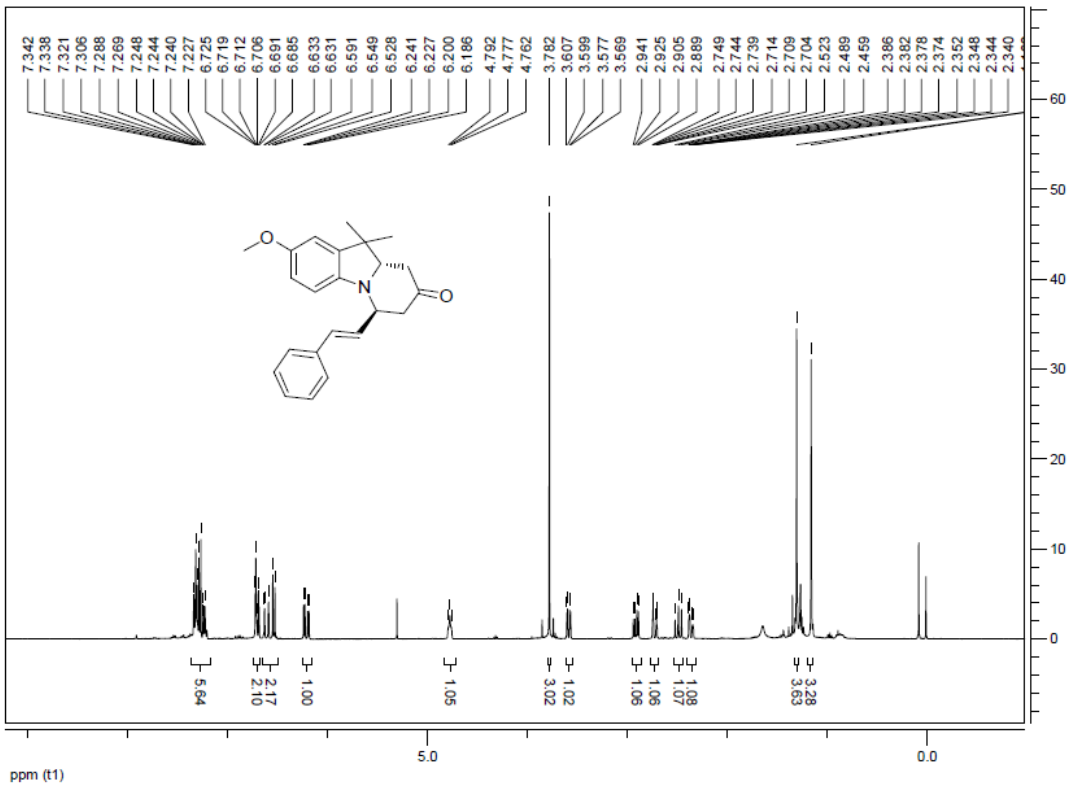


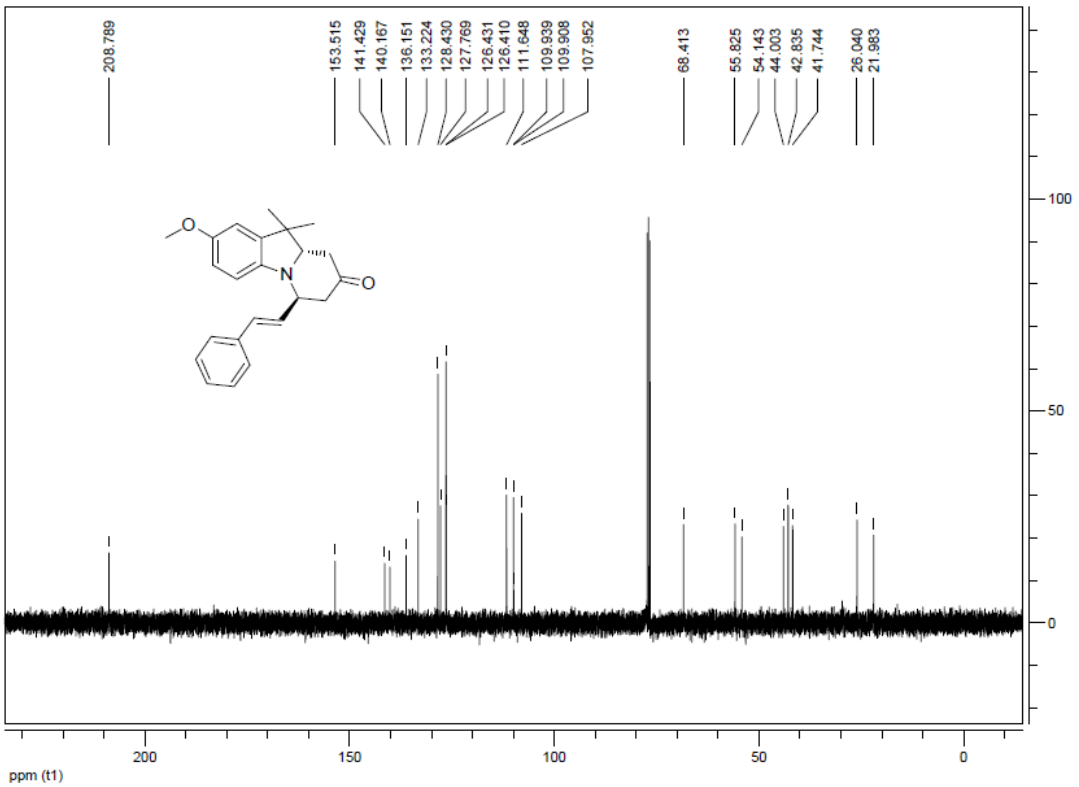
(6S,9aS)-6-(4-bromophenyl)-2-methoxy-10,10-dimethyl-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4s)



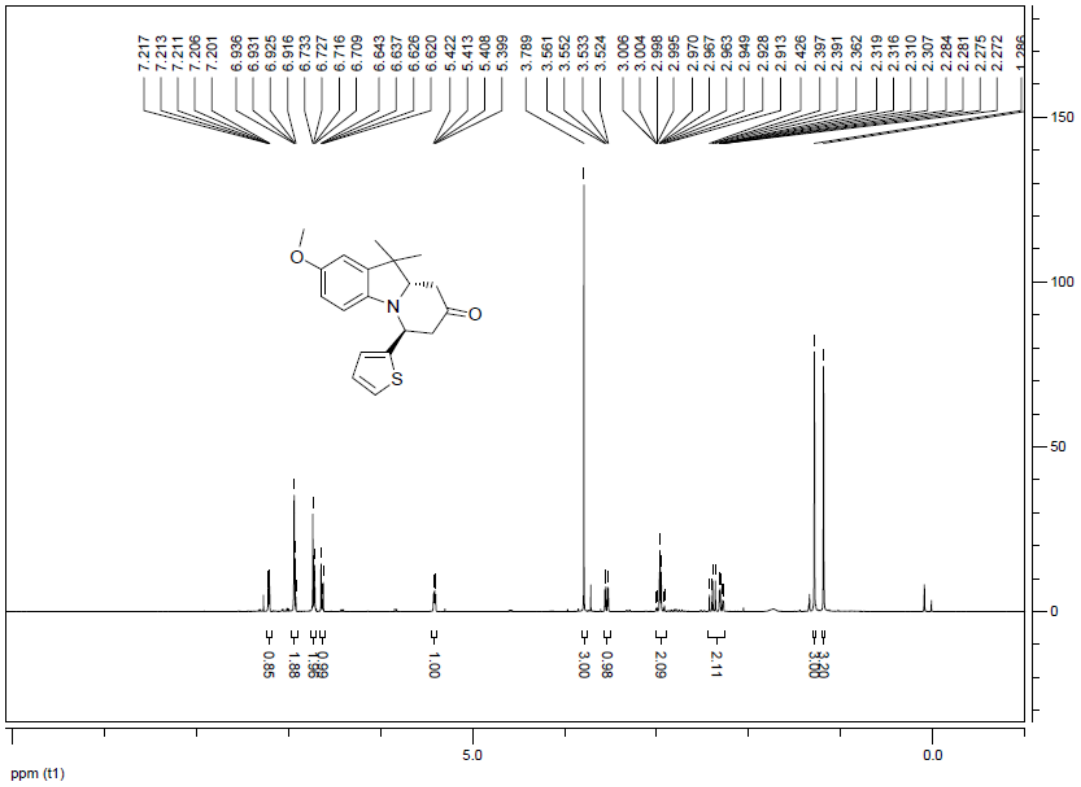


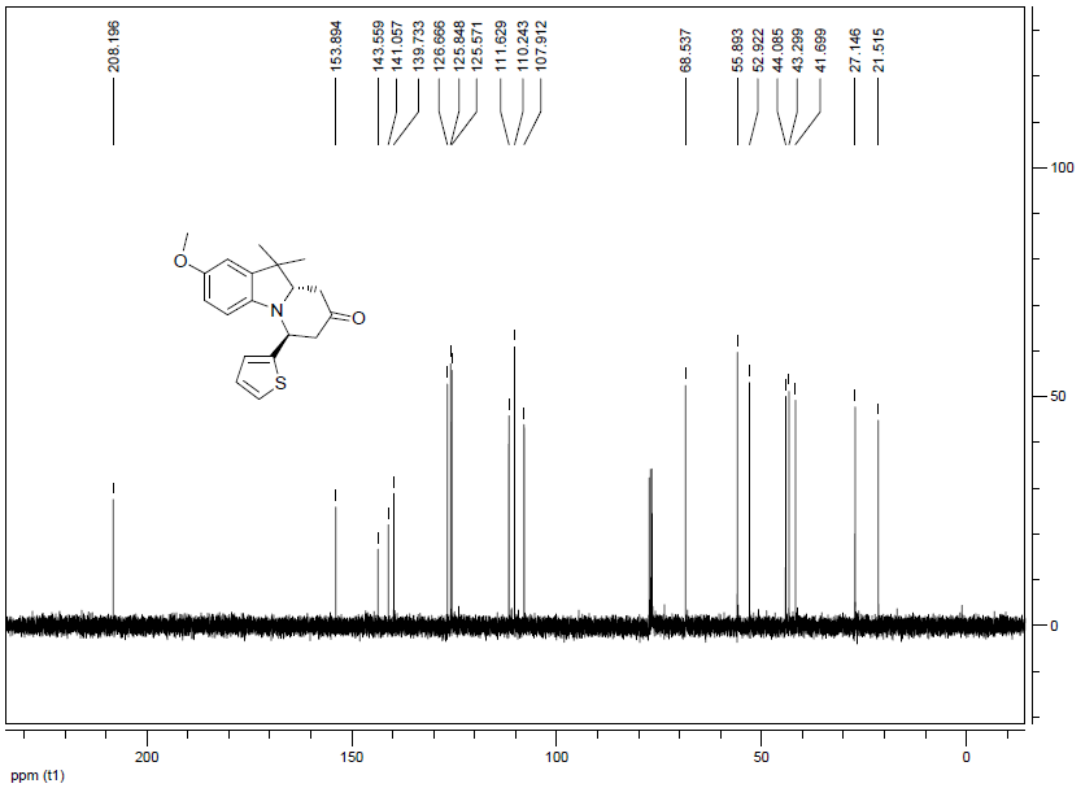
(6S,9aS)-2-methoxy-10,10-dimethyl-6-((E)-styryl)-6,7,9a,10-tetrahydropyrido[1,2-a]indol-8(9H)-one (4t)



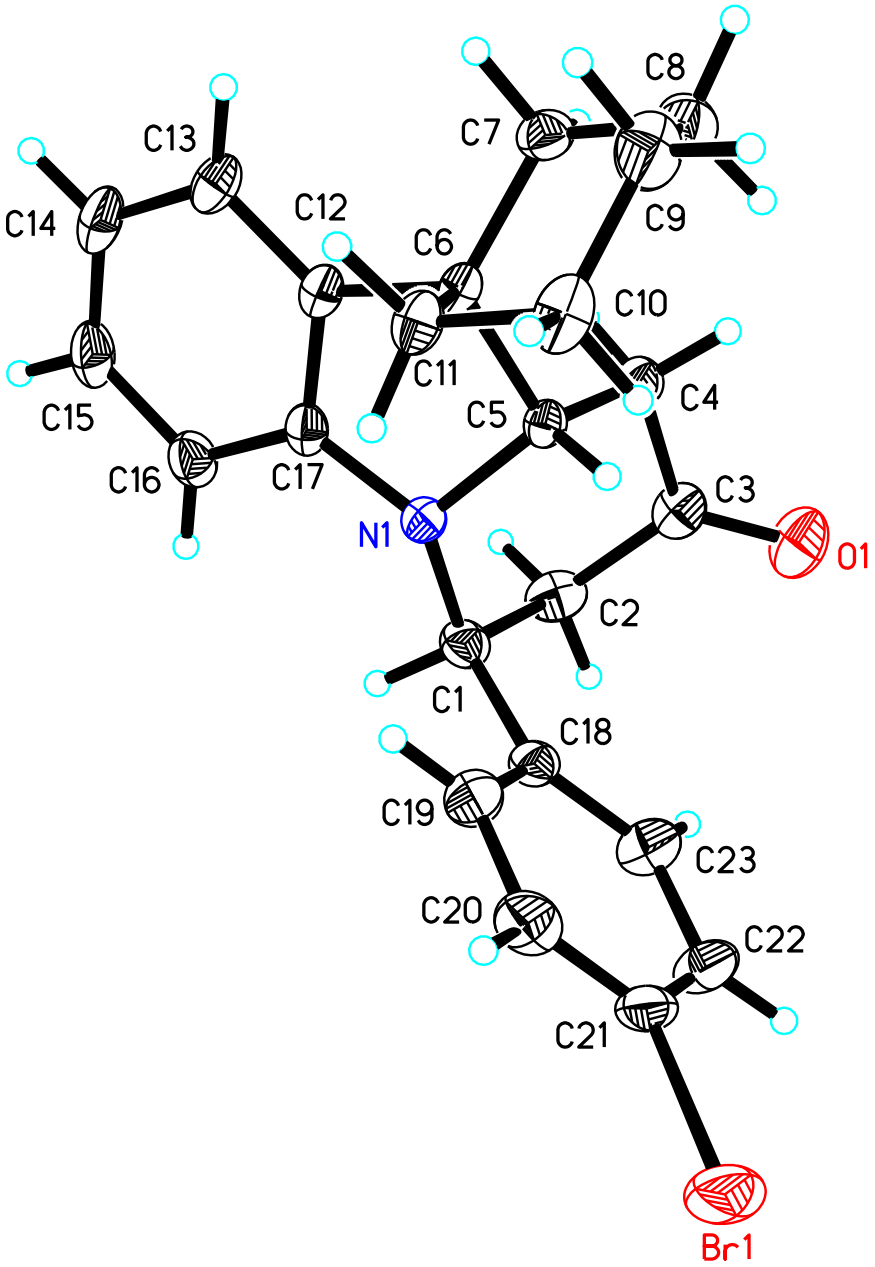


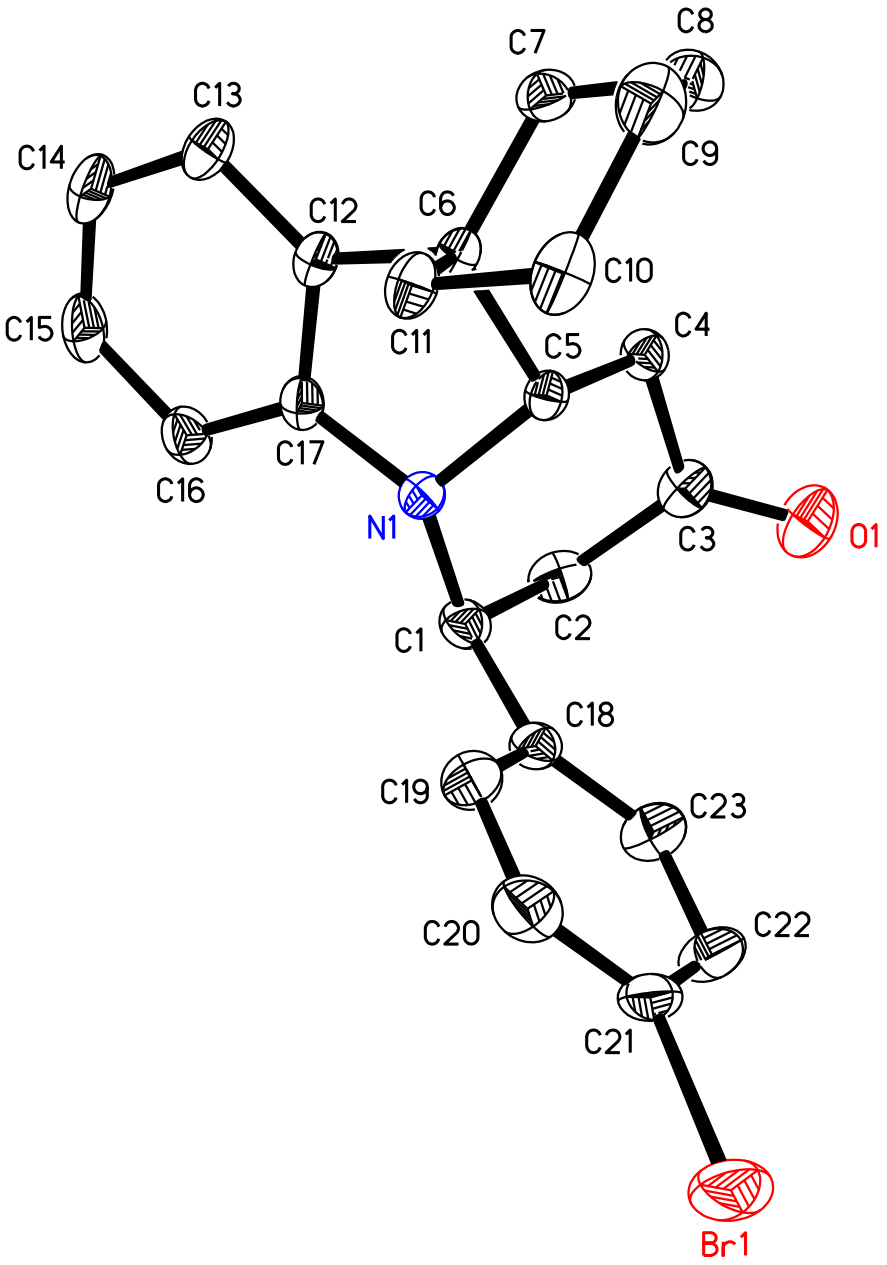
(6S,9aS)-2-methoxy-10,10-dimethyl-6-(thiophen-2-yl)-6,7,9a,10-tetrahydropyrido [1,2-a]indol-8(9H)-one (4u)





F: Determination of Absolute Configuration of 4g




C8
C7
C13
C9
C14
C12
C6
C10
C15
C11
C5
C4
C17
C16
N1
C3
O1
C2
C1
C18
C19
C23
C20
C22
C21
Br1

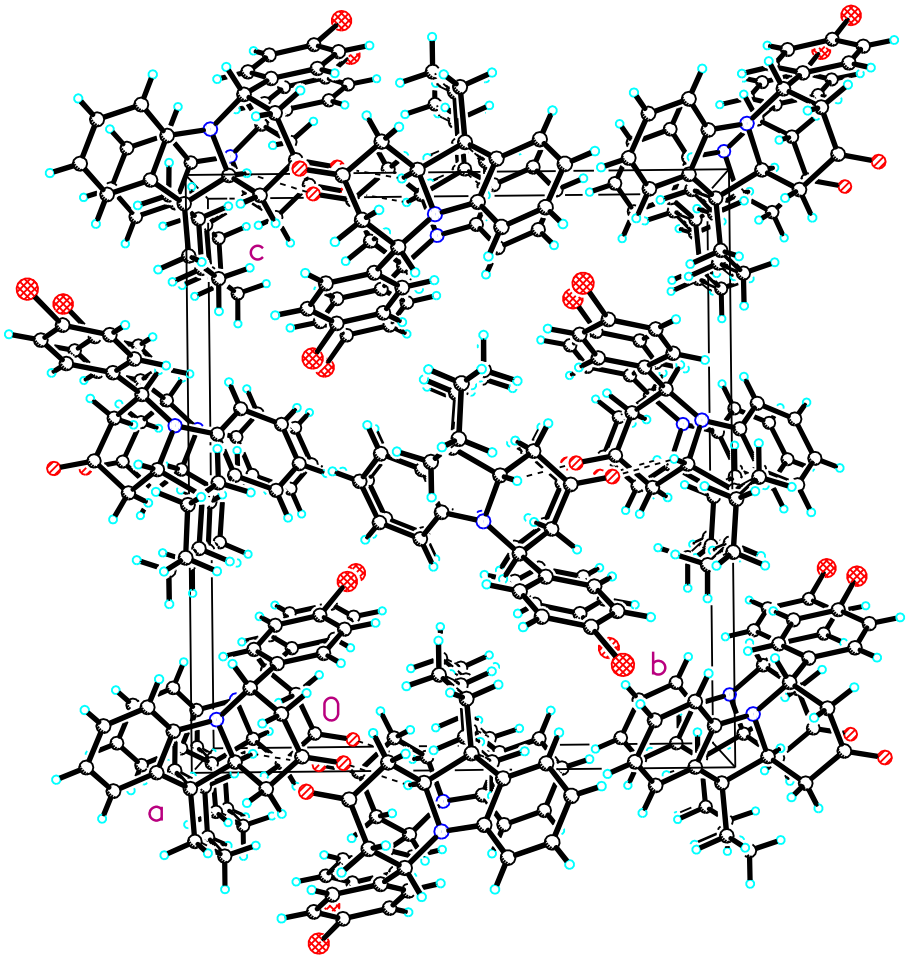

c
b
0
a

Table S1 Crystal data and structure refinement for **4g**.

Identification code	cd212313
Empirical formula	$C_{23}H_{24}BrNO$
Formula weight	410.34
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 7.2425(8) Å α = 90 °. b = 15.4541(17) Å β = 90 °. c = 17.0100(18) Å γ = 90 °.
Volume	1903.9(4) $Å^3$
Z	4
Calculated density	1.432 Mg/m^3
Absorption coefficient	2.171 mm^{-1}
F(000)	848
Crystal size	0.313 x 0.212 x 0.145 mm^3
θ range for data collection	2.39 to 25.99 °.
Limiting indices	-8≤h≤8, -19≤k≤18, -16≤l≤20
Reflections collected / unique	11521 / 3726 [R_{int} = 0.0725]
Completeness to θ = 25.99 °	100.0 %
Absorption correction（μ）	Empirical
Max. and min. transmission	1.00000 and 0.32387
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3726 / 0 / 236
Goodness-of-fit on F^2	0.973
Final R indices [I>2σ(I)]	R_1 = 0.0378, wR_2 = 0.0836
R indices (all data)	R_1 = 0.0515, wR_2 = 0.0885
Absolute structure parameter	0.003(9)
Extinction coefficient	0.0238(12)
Largest diff. peak and hole	0.209 and -0.330 e^-. $Å^{-3}$