Supporting Information

Brønsted Acids of Anionic Chiral Co(III) Complexes as Catalysts for the Stereoselective Synthesis of *cis*-4-Aminofuranobenzopyrans

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1. Introduction

1.1. General data

NMR spectra were recorded on Bruker-400 MHz spectrometer. Melting points were measured on a digital melting point apparatus and the temperature was uncorrected. FT-ICRMS spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer. HPLC analysis was performed on Waters-Breeze (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump, UV detection monitored at 254nm). Chiralpak AD-H, OD-H, IC, OJ-H and AS-H columns were purchased from Daicel Chemical Industries, LTD. The absolute configuration of **3k** was assigned by the X-ray analysis.

1.2. Materials

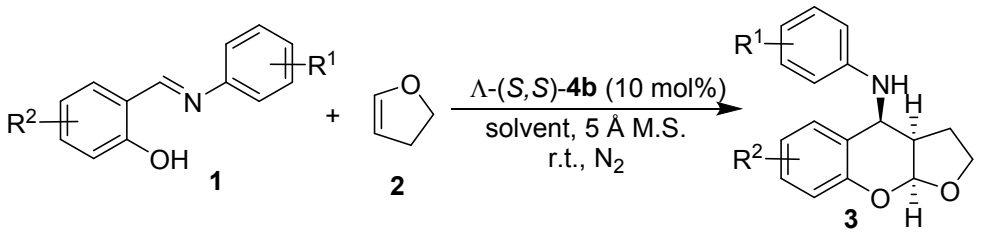
Analytic grade solvents for the column chromatography and commercially available reagents were used as received. CH_2Cl_2 and CCl_4 was dried over CaH_2 and distilled prior to use. Toluene, TBME and *n*-hexane were dried over Na and distilled prior to use. The salicylaldimines[1] and the catalysts (**Λ-4a** to **Λ-4h**)[2] were synthesized according to the literature. The products **3a**, **3b**, **3c** and **3g** have been reported in the literature[1].

2. Experimental Procedures and Characterization Data

2.1. General procedure for the preparation of racemic 4-aminofuranobenzopyrans 3

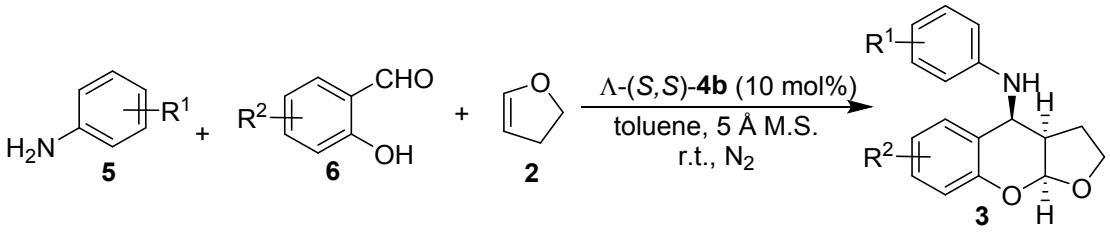
All authentic racemic samples were prepared according to the following procedure: A 15-mL oven-dried tube was charged with salicylaldimine **1** (0.20 mmol), $Sc(OTf)_3$ (10 mol%), 3 Å MS (20.0 mg) and MeCN (2.0 mL) at room temperature. 2,3-dihydrofuran **2** (0.40 mmol) was then added and the resulting solution was stirred vigorously with 12 h. The reaction was quenched with NEt_3 (140 μL, 1.0 mmol). The mixture was purified by flash column chromatography (silica gel, petrol ether/EtOAc = 10:1) to give the racemic 4-aminofuranobenzopyran derivatives **3**.

2.2. General procedure for the preparation of enantioenriched 4-aminofuranobenzopyrans 3



Under nitrogen atmosphere, a 10-mL oven-dried Schlenk tube was charged with salicylaldimine **1** (0.30 mmol for **1a**, 0.20 mmol for **1b-1n**), catalyst Λ-**4b** (15.0 mg, 0.02 mmol), activated 5 Å molecular sieves (10.0 mg) and solvent (1.0 mL, *n*-hexane for **1a**, toluene for **1b-1n**) at room temperature. The mixture was stirred for 30 min at room temperature. The 2,3-dihydrofuran **2** (0.20 mmol for **1a**, 0.60 mmol for **1b-1n**) was added and the resulting solution was stirred vigorously until the reaction was complete (monitored by TLC). The reaction was then quenched with NEt_3 (140 μL, 1.0 mmol). The mixture was purified by flash column chromatography (silica gel, petrol ether/EtOAc = 10:1) to give the enantioenriched 4-aminofuranobenzopyran derivatives **3**.

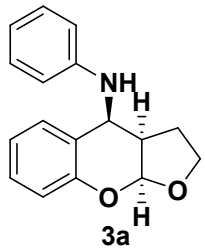
2.3. General procedure for the three-component asymmetric interrupted Povarov reaction



Under nitrogen atmosphere, a 10-mL oven-dried Schlenk tube was charged with anilines **5** (0.20 mmol), salicylaldehydes **6** (0.20 mmol), catalyst Λ-**4b** (15.0 mg, 0.02 mmol), activated 5 Å molecular sieves (10.0 mg) and toluene (1.0 mL) at room temperature. The mixture was stirred for 30 min at room temperature. The 2,3-dihydrofuran **2** (0.60 mmol) was added and the resulting solution was stirred vigorously until the reaction was complete (monitored by TLC). The reaction was then quenched with NEt_3 (140 μL, 1.0 mmol). The mixture was purified by flash column chromatography (silica gel, petrol ether/EtOAc = 10:1) to give the enantioenriched 4-aminofuranobenzopyran derivatives **3**.

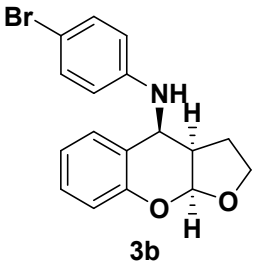
2.4. Characterization data of products 3

(3a*R*,4*S*,9a*S*)-*N*-phenyl-2,3,3a,9a-tetrahydro-4*H*-furo[2,3-*b*]chromen-4-amine 3a: yield: 95%;



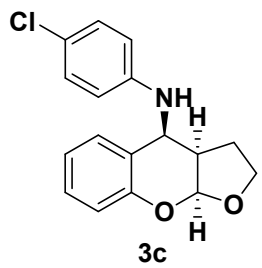
d.r. > 20:1; (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10/1); white foam; **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.36 (d, *J* = 7.3 Hz, 1H), 7.30-7.14 (m, 3H), 7.03-6.88 (m, 2H), 6.80-6.72 (m, 3H), 5.88 (d, *J* = 5.4 Hz, 1H), 4.97 (s, 1H), 3.96-3.89 (m, 1H), 3.88-3.76 (m, 2H), 3.22-2.98 (m, 1H), 2.01-1.80 (m, 1H), 1.69-1.55 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm): 153.05, 147.12, 129.68, 128.94, 126.28, 124.68, 121.95, 118.44, 117.32, 113.52, 102.44, 68.12, 48.87, 43.39, 24.05; **IR** (KBr): ν 3369, 3050, 2951, 1602, 1503, 1484, 1153, 982, 944, 751, 693 cm^{-1}; **HRMS** (ESI) calculated for $C_{17}H_{18}O_2N$ $[M+H]^+$: 268.13321, found 268.13266; **$[\alpha]_D^{20}$** = +89.74 (c 0.403, in CH_2Cl_2); **Enantiomeric ratio**: 96:4, determined by HPLC (Daicel Chirapak OD-H, hexane / isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): major diastereoisomer: t_{maj} = 43.570 min, t_{min} = 12.742 min.

(3a*R*,4*S*,9a*S*)-*N*-(4-bromophenyl)-2,3,3a,9a-tetrahydro-4*H*-furo[2,3-*b*]chromen-4-amine 3b: yield: 68%; d.r. = 12:1; (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10/1);



white foam; **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.34-7.27 (m, 3H), 7.22 (t, *J* = 7.7 Hz, 1H), 6.98-6.93 (m, 2H), 6.62 (d, *J* = 8.8 Hz, 2H), 5.90 (d, *J* = 5.6 Hz, 1H), 4.92 (s, 1H), 3.96-3.90 (m, 1H), 3.90-3.82 (m, 2H), 3.15-3.02 (m, 1H), 1.97-1.86 (m, 1H), 1.66-1.59 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm): 153.06, 146.21, 132.42, 129.14, 126.16, 124.34, 122.07, 117.51, 115.08, 110.02, 102.45, 68.14, 49.11, 43.45, 24.11; **IR** (KBr): ν 3373, 2919, 2850, 1594, 1487, 1454, 1299, 1094, 982, 815, 754, 733 cm^{-1}; **HRMS** (ESI) calculated for $C_{17}H_{17}O_2NBr$ $[M+H]^+$: 346.04372, found 346.04343; **$[\alpha]_D^{20}$** = +36.74 (c 0.460, in CH_2Cl_2); **Enantiomeric ratio**: 82:18, determined by HPLC (Daicel Chirapak IC, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): major diastereoisomer: t_{maj} = 13.364 min, t_{min} = 12.066 min.

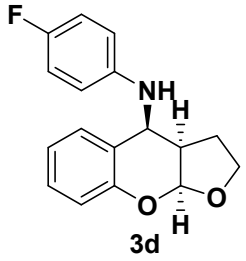
(3a*R*,4*S*,9a*S*)-*N*-(4-chlorophenyl)-3,3a,4,9a-tetrahydro-2*H*-furo[2,3-*b*]chromen-4-amine 3c:



yield: 85%; d.r. > 20:1; (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10/1); white foam; **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.30 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 2H), 7.01-6.90 (m, 2H), 6.66 (d, *J* = 8.7 Hz, 2H), 5.90 (d, *J* = 5.6 Hz, 1H), 4.92 (s, 1H), 3.97-3.90 (m, 1H), 3.90-3.80 (m, 2H), 3.18-3.02 (m, 1H), 1.98-1.84 (m, 1H), 1.65-1.59 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ

(ppm): 153.07, 145.77, 129.54, 129.11, 126.16, 124.42, 123.01, 122.06, 117.50, 114.62, 102.46, 68.13, 49.20, 43.46, 24.10; **IR** (KBr): ν 3375, 3050, 2919, 1598, 1497, 1454, 1277, 1091, 982, 817, 753 cm^{-1}; **HRMS** (ESI) calculated for $C_{17}H_{17}O_2NCl$ $[M+H]^+$: 302.09423, found 302.09389; $\mathbf{[\alpha]_D^{20}}$ = +49.40 (c 0.448, in CH_2Cl_2); **Enantiomeric ratio**: 81:19, determined by HPLC (Daicel Chirapak IC, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): major diastereoisomer: t_{maj} = 11.089 min, t_{min} = 12.623 min.

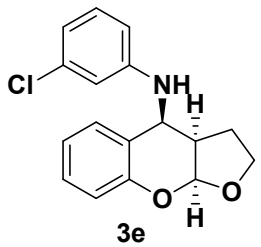
(3a*R*,4*S*,9a*S*)-*N*-(4-fluorophenyl)-3,3a,4,9a-tetrahydro-2*H*-furo[2,3-*b*]chromen-4-amine 3d:



3d

yield: 64%; d.r. > 20:1; (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10/1); white foam; **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.34 (d, *J* = 7.6 Hz, 1H), 7.25-7.18 (m, 1H), 7.00-6.89 (m, 4H), 6.71-6.64 (m, 2H), 5.89 (d, *J* = 5.6 Hz, 1H), 4.89 (d, *J* = 4.7 Hz, 1H), 3.94-3.89 (m, 1H), 3.86-3.83 (m, 1H), 3.73 (brs, 1H), 3.17-3.02 (m, 1H), 1.96-1.82 (m, 1H), 1.62-1.57 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm): 157.53, 155.18, 153.09, 143.43 (d, *J* = 1.9 Hz), 129.04, 126.19, 124.75, 122.04, 117.44, 116.29, 116.07, 114.54 (d, *J* = 7.4 Hz), 102.53, 68.14, 49.69, 43.48, 24.06; **IR** (KBr): ν 3365, 2925, 1609, 1586, 1511, 1484, 1454, 1218, 1105, 982, 822, 796, 761 cm^{-1}; **HRMS** (ESI) calculated for $C_{17}H_{17}O_2NF$ $[M+H]^+$: 286.12378, found 286.12347; $\mathbf{[\alpha]_D^{20}}$ = +64.68 (c 0.302, in CH_2Cl_2); **Enantiomeric ratio**: 81.5:18.5, determined by HPLC (Daicel Chirapak AS-H, hexane / isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): major diastereoisomer: t_{maj} = 7.012 min, t_{min} = 8.834 min.

(3a*R*,4*S*,9a*S*)-*N*-(3-chlorophenyl)-3,3a,4,9a-tetrahydro-2*H*-furo[2,3-*b*]chromen-4-amine 3e:

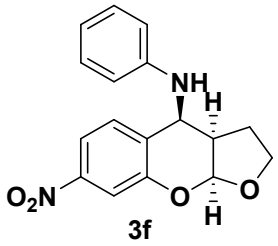


3e

yield: 74%; d.r. > 20:1; (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10/1); white foam; **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.30 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.03-6.88 (m, 2H), 6.80-6.69 (m, 2H), 6.60 (dd, *J* = 8.1, 1.9 Hz, 1H), 5.90 (d, *J* = 5.5 Hz, 1H), 4.97-4.93 (m, 1H), 3.94-3.84 (m, 3H), 3.17-3.03 (m, 1H), 1.97-1.87 (m, 1H), 1.65-1.52 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm): 153.01, 148.33, 135.44, 130.69, 129.17, 126.13, 124.08, 122.07, 118.33, 117.49, 113.18, 111.65, 102.33, 68.12, 48.90, 43.35, 24.08; **IR** (KBr): ν 3370, 2953, 1598, 1484, 1454, 1227, 1090, 986, 947, 850, 758, 736, 683 cm^{-1}; **HRMS** (ESI) calculated for $C_{17}H_{17}O_2NCl$ $[M+H]^+$: 302.09423, found 302.09387; $\mathbf{[\alpha]_D^{20}}$ = +51.03 (c 0.405, in CH_2Cl_2); **Enantiomeric ratio**: 80:20,

determined by HPLC (Daicel Chirapak OD-H, hexane / isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): major diastereoisomer: t_{maj} = 15.106 min, t_{min} = 11.825 min.

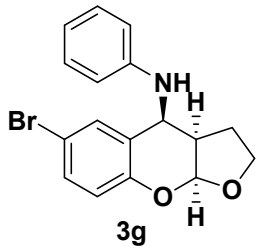
(3a*R*,4*S*,9a*S*)-7-nitro-*N*-phenyl-3,3a,4,9a-tetrahydro-2*H*-furo[2,3-*b*]chromen-4-amine 3f: yield:



3f

46%; d.r. = 7:1; (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10/1); yellow foam; **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ (ppm): 8.39-8.38 (m, 1H), 8.12 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.29-7.22 (m, 2H), 6.99 (d, *J* = 8.9 Hz, 1H), 6.88-6.83 (m, 1H), 6.79-6.75 (m, 2H), 5.97 (d, *J* = 5.1 Hz, 1H), 5.07 (s, 1H), 4.04 (td, *J* = 9.0, 3.5 Hz, 1H), 3.96-3.92 (m, 1H), 3.80 (brs, 1H), 3.21-3.13 (m, 1H), 2.08-1.94 (m, 1H), 1.68-1.58 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm): 158.57, 146.27, 142.46, 129.91, 125.34, 124.55, 123.13, 119.43, 117.72, 113.91, 103.14, 68.48, 48.82, 42.46, 23.49; **IR** (KBr): ν 3368, 3053, 2956, 2924, 1602, 1515, 1480, 1337, 1245, 1105, 1090, 981, 750cm^{-1}; **HRMS** (ESI) calculated for $C_{17}H_{17}O_4N_2$ $[M+H]^+$: 313.11828, found 313.11789; **$[\alpha]_D^{20}$** = +46.69 (c 0.287, in CH_2Cl_2); **Enantiomeric ratio**: 74.5:25.5, determined by HPLC (Daicel Chirapak AD-H, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): major diastereoisomer: t_{maj} = 23.194 min, t_{min} = 18.781 min.

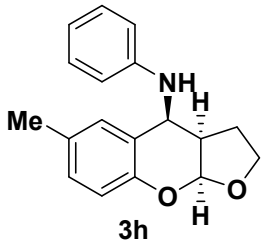
(3a*R*,4*S*,9a*S*)-6-bromo-*N*-phenyl-3,3a,4,9a-tetrahydro-2*H*-furo[2,3-*b*]chromen-4-amine 3g:



3g

yield: 57%; d.r. = 16:1; (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10/1); white foam; **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.51 (d, *J* = 1.2 Hz, 1H), 7.32 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.26-7.20 (m, 2H), 6.87-6.78 (m, 2H), 6.73 (d, *J* = 7.9 Hz, 2H), 5.88 (d, *J* = 5.5 Hz, 1H), 4.95 (s, 1H), 3.97-3.91 (m, 1H), 3.89-3.83 (m, 1H), 3.76 (brs, 1H), 3.15-3.07 (m, 1H), 1.99-1.86 (m, 1H), 1.67-1.59 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm): 152.24, 146.69, 131.93, 129.81, 129.16, 127.03, 119.22, 118.92, 114.39, 113.69, 102.61, 68.21, 49.04, 43.16, 23.99; **IR** (KBr): ν 3368, 3052, 2925, 1602, 1503, 1475, 1249, 1190, 1101, 1022, 982, 944, 950, 693 cm^{-1}; **HRMS** (ESI) calculated for $C_{17}H_{17}O_2NBr$ $[M+H]^+$: 346.04372, found 346.04312; **$[\alpha]_D^{20}$** = +43.99 (c 0.346, in CH_2Cl_2); **Enantiomeric ratio**: 87.5:12.5, determined by HPLC (Daicel Chirapak IC, hexane / isopropanol = 90/10, flow rate 0.7 mL/min, T = 30 °C, 254 nm): major diastereoisomer: t_{maj} = 10.644 min, t_{min} = 9.822 min.

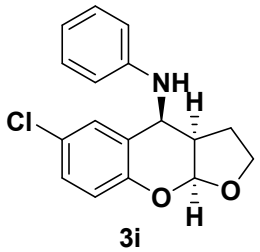
(3a*R*,4*S*,9a*S*)-6-methyl-*N*-phenyl-3,3a,4,9a-tetrahydro-2*H*-furo[2,3-*b*]chromen-4-amine 3h:



3h

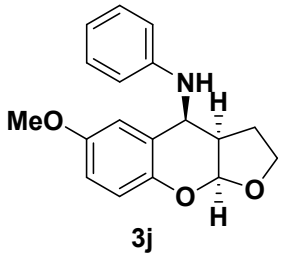
yield: 60%; d.r. > 20:1; (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10/1); white foam; **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.26-7.20 (m, 2H), 7.18 (s, 1H), 7.04-6.99 (m, 1H), 6.86-6.72 (m, 4H), 5.86 (d, *J* = 5.6 Hz, 1H), 4.96 (d, *J* = 4.6 Hz, 1H), 3.94-3.90 (m, 1H), 3.88-3.72 (m, 2H), 3.13-3.90 (m, 1H), 2.27 (s, 3H), 1.95-1.84 (m, 1H), 1.69-1.60 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm): 150.79, 147.16, 131.40, 129.72, 129.44, 126.55, 124.49, 118.46, 117.19, 113.59, 102.41, 68.10, 49.04, 43.41, 24.17, 20.98; **IR** (KBr): ν 3371, 3051, 2925, 1602, 1495, 1244, 1209, 1099, 1028, 982, 952, 905, 821, 750, 693 cm^{-1}; **HRMS** (ESI) calculated for $C_{18}H_{20}O_2N$ $[M+H]^+$: 282.14886, found 282.14857; **$[\alpha]_D^{20}$** = +21.51 (c 0.327, in CH_2Cl_2); **Enantiomeric ratio**: 84.5:15.5, determined by HPLC (Daicel Chirapak IC, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): major diastereoisomer: t_{maj} = 11.386 min, t_{min} = 12.661 min.

(3a*R*,4*S*,9a*S*)-6-chloro-*N*-phenyl-3,3a,4,9a-tetrahydro-2*H*-furo[2,3-*b*]chromen-4-amine 3i:



3i

yield: 69%; d.r. > 20:1; (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10/1); white foam; **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.36 (dd, *J* = 2.5, 1.1 Hz, 1H), 7.26-7.20 (m, 2H), 7.17 (ddd, *J* = 8.6, 2.6, 0.7 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 1H), 6.85-6.79 (m, 1H), 6.75-6.72 (m, 2H), 5.89 (d, *J* = 5.6 Hz, 1H), 4.94 (d, *J* = 4.9 Hz, 1H), 3.93 (td, *J* = 8.8, 3.9 Hz, 1H), 3.89-3.83 (m, 1H), 3.77 (brs, 1H), 3.15-3.08 (m, 1H), 1.99-1.88 (m, 1H), 1.65-1.58 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm): 151.69, 146.72, 129.80, 128.96, 127.07, 126.70, 126.28, 118.89, 118.77, 113.66, 102.67, 68.21, 49.09, 43.22, 24.03; **IR** (KBr): ν 3369, 3052, 2953, 2896, 1602, 1503, 1477, 1249, 1192, 1102, 1022, 982, 751, 693 cm^{-1}; **HRMS** (ESI) calculated for $C_{17}H_{17}O_2NCl$ $[M+H]^+$: 302.09423, found 302.09386; **$[\alpha]_D^{20}$** = +50.89 (c 0.317, in CH_2Cl_2); **Enantiomeric ratio**: 90:10, determined by HPLC (Daicel Chirapak IC, hexane / isopropanol = 90/10, flow rate 0.6 mL/min, T = 30 °C, 254 nm): major diastereoisomer: t_{maj} = 16.672 min, t_{min} = 15.571 min.

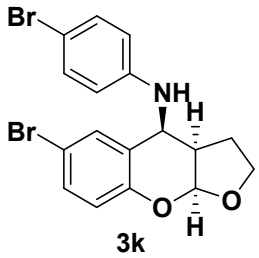


3j

(3a*R*,4*S*,9a*S*)-6-methoxy-*N*-phenyl-3,3a,4,9a-tetrahydro-2*H*-furo[2,3-*b*]chromen-4-amine 3j: yield: 44%; d.r. = 12:1; (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10/1); white foam; **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.25-7.18 (m, 2H), 6.94-6.93 (m, 1H), 6.89 (d, *J* = 8.7 Hz, 1H), 6.82 -6.70 (m, 4H), 5.87

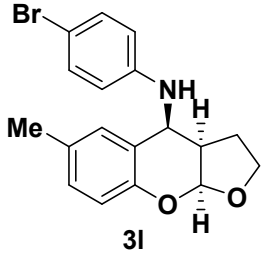
(d, J = 5.9 Hz, 1H), 4.92 (d, J = 4.0 Hz, 1H), 3.88 (td, J = 8.6, 4.1 Hz, 1H), 3.85-3.77 (m, 2H), 3.72 (s, 3H), 3.16-3.08 (m, 1H), 1.95-1.84 (m, 1H), 1.69-1.58 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm): 154.89, 147.03, 146.71, 129.69, 126.60, 118.58, 118.18, 113.73, 113.67, 111.79, 102.66, 68.08, 55.78, 49.37, 43.56, 24.32; **IR** (KBr): ν 3368, 3051, 2951, 1602, 1491, 1271, 1201, 1096, 1034, 984, 819, 751, 694 cm^{-1}; **HRMS** (ESI) calculated for $C_{18}H_{20}O_3N$ $[M+H]^+$: 298.14377, found 298.14330; **$[\alpha]_D^{20}$** = +38.80 (c 0.238, in CH_2Cl_2); **Enantiomeric ratio**: 76.5:23.5, determined by HPLC (Daicel Chirapak IC, hexane / isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): major diastereoisomer: t_{maj} = 8.173 min, t_{min} = 9.190 min.

(3a*R*,4*S*,9a*S*)-6-bromo-*N*-(4-bromophenyl)-3,3a,4,9a-tetrahydro-2*H*-furo[2,3-*b*]chromen-4-amine 3k: yield: 59%; d.r. = 10:1; (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10/1); white foam; **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.43 (s, 1H), 7.31 (d, J = 8.7 Hz, 3H), 6.82 (d, J = 8.6 Hz, 1H), 6.61 (d, J = 8.7 Hz, 2H), 5.88 (d, J = 5.6 Hz, 1H), 4.88 (s, 1H), 3.93 (td, J = 8.8, 4.0 Hz, 1H), 3.89-3.83 (m, 1H), 3.81 (brs, 1H), 3.11-3.05 (m, 1H), 1.97-1.85 (m, 1H), 1.69-1.59 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm): 152.22, 145.75, 132.53, 132.10, 129.02, 126.62, 119.37, 115.20, 114.45, 110.51, 102.57, 68.20, 49.17, 43.16, 24.00; **IR** (KBr): ν 3367, 2954, 2925, 1595, 1493, 1474, 1247, 1228, 1190, 1098, 1024, 982, 815, 737 cm^{-1}; **HRMS** (ESI) calculated for $C_{17}H_{16}O_2NBr_2$ $[M+H]^+$: 423.95423, found 423.95361; **$[\alpha]_D^{20}$** = +21.90 (c 0.239, in CH_2Cl_2); Enantiomeric ratio: 86:14, determined by HPLC (Daicel Chirapak IC, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): major diastereoisomer: t_{maj} = 12.310 min, t_{min} = 9.781 min.



3k

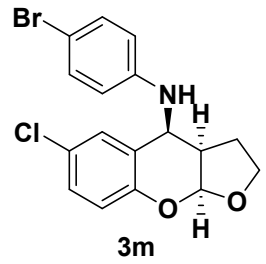
(3a*R*,4*S*,9a*S*)-*N*-(4-bromophenyl)-6-methyl-3,3a,4,9a-tetrahydro-2*H*-furo[2,3-*b*]chromen-4-amine 3l: yield: 64%; d.r. > 20:1; (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10/1); white foam; **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ (ppm): 7.31 (dd, J = 9.4, 2.6 Hz, 2H), 7.28 (d, J = 1.9 Hz, 1H), 7.17 (dd, J = 8.6, 2.5 Hz, 1H), 6.87 (d, J = 8.6 Hz, 1H), 6.61 (d, J = 8.8 Hz, 2H), 5.88 (d, J = 5.6 Hz, 1H), 4.88-4.85 (m, 1H), 3.97-3.74 (m, 3H), 3.13-3.02 (m, 1H), 2.26 (s, 3H), 1.98-1.86 (m, 1H), 1.60-1.56 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm): 150.78, 146.23, 132.42, 131.51, 129.59, 126.41, 124.14, 117.34, 115.11, 109.98, 102.40, 68.09, 49.21, 43.44, 24.19, 20.99; **IR** (KBr): ν 3367,



3l

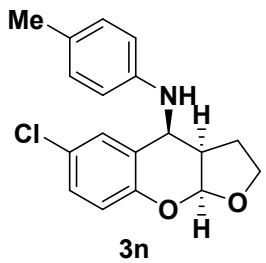
2951, 1594, 1494, 1310, 1278, 1243, 1095, 1074, 1028, 983, 816, 739 cm^{-1}; **HRMS** (ESI) calculated for $C_{18}H_{19}O_2NBr$ $[M+H]^+$: 360.05937, found 360.05923; $[\alpha]_D^{20}$ = +27.95 (c 0.464, in CH_2Cl_2); **Enantiomeric ratio**: 81.5:18.5, determined by HPLC (Daicel Chirapak IC, hexane / isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): major diastereoisomer: t_{maj} = 6.808 min, t_{min} = 6.433 min.

(3a*R*,4*S*,9a*S*)-*N*-(4-bromophenyl)-6-chloro-3,3a,4,9a-tetrahydro-2*H*-furo[2,3-*b*]chromen-4-amine 3m: yield: 58%; d.r. = 14:1; (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10/1); white foam; **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.36-7.27 (m, 3H), 7.17 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 1H), 6.64-6.57 (m, 2H), 5.88 (d, *J* = 5.6 Hz, 1H), 4.86 (dd, *J* = 7.9, 5.3 Hz, 1H), 3.97-3.89 (m, 1H), 3.89-3.83 (m, 1H), 3.84-3.75 (m, 1H), 3.14-3.03 (m, 1H), 1.96 -1.86 (m, 1H), 1.60-1.55 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm): 151.67, 145.77, 132.52, 129.11, 127.14, 126.27, 126.13, 118.92, 115.17, 110.47, 102.63, 68.19, 49.22, 43.21, 24.03; **IR** (KBr): ν 3359, 2953, 2868, 1603, 1466, 1417, 1101, 1026, 976, 934, 818, 502 cm^{-1}; **HRMS** (ESI) calculated for $C_{17}H_{16}O_2NBrCl$ $[M+H]^+$: 380.00475, found 380.00391; $[\alpha]_D^{20}$ = +31.13 (c 0.288, in CH_2Cl_2); **Enantiomeric ratio**: 87:13, determined by HPLC (Daicel Chirapak IC, hexane / isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): major diastereoisomer: t_{maj} = 12.553 min, t_{min} = 10.058 min.



3m

(3a*R*,4*S*,9a*S*)-6-chloro-*N*-(p-tolyl)-3,3a,4,9a-tetrahydro-2*H*-furo[2,3-*b*]chromen- 4-amine 3n: yield: 59%; d.r. = 17:1; (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10/1); white foam; **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.34-7.27 (m, 1H), 7.09 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 2H), 5.80 (d, *J* = 5.6 Hz, 1H), 4.82 (d, *J* = 4.6 Hz, 1H), 3.88-3.72 (m, 2H), 3.57 (s, 1H), 3.09-2.96 (m, 1H), 2.20 (s, 3H), 1.90-1.77 (m, 1H), 1.56-1.49 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm): 151.68, 144.35, 130.26, 128.88, 128.22, 127.03, 126.89, 126.30, 118.71, 113.90, 102.70, 68.19, 49.37, 43.14, 23.98, 20.56; **IR** (KBr): ν 3413, 2959, 2882, 1615, 1540, 1463, 1313, 1180, 1123, 972, 839, 802 cm^{-1}; **HRMS** (ESI) calculated for $C_{18}H_{19}O_2NCl$ $[M+H]^+$: 316.10988, found 316.10917; $[\alpha]_D^{20}$ = +49.09 (c 0.165, in CH_2Cl_2); **Enantiomeric ratio**: 86:14, determined by HPLC (Daicel Chirapak OJ-H, hexane / isopropanol = 80/20, flow rate 0.7 mL/min, T =



3n

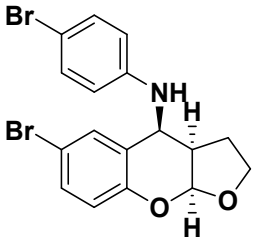
30 °C, 254 nm): major diastereoisomer: t_{maj} = 30.432 min, t_{min} = 36.569 min.

3. References

1. L. Bernardi, M. Comes-Franchini, M. Fochi, V. Leo, A. Mazzanti, A. Ricci, *Adv. Synth. Catal.* **2010**, *352*, 3399.

2. (a) J. Yu, H.-J. Jiang, Y. Zhou, S.-W. Luo, L.-Z. Gong, *Angew. Chem. Int. Ed.* **2015**, *54*, 11209. (b) H.-J. Jiang, K. Liu, J. Yu, L. Zhou, L.-Z. Gong, *Angew. Chem., Int. Ed.* **2017**, *56*, 11931.

4. X-ray single crystal data for 3k



3k

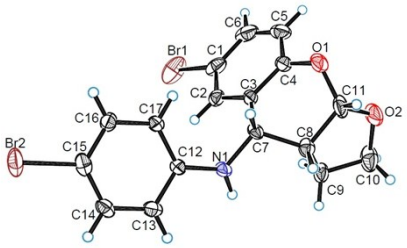


Table S1. Crystal data and structure refinement for **3k**

Empirical formula	$C_{17}H_{15}Br_2NO_2$
Formula weight	425.12
Temperature/K	290(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.19070(10)
b/Å	15.2739(3)
c/Å	17.2701(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1632.99(5)
Z	4
ρ_{calc}g/cm^3	1.729
μ/mm^{-1}	6.349
F(000)	840.0
Crystal size/mm^3	0.290 × 0.250 × 0.250
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.728 to 139.534
Index ranges	$-7 \le h \le 7$, $-7 \le k \le 18$, $-21 \le l \le 20$
Reflections collected	5808
Independent reflections	2978 [R_{int} = 0.0301, R_{sigma} = 0.0383]

Data/restraints/parameters	2978/0/199
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0466, wR_2 = 0.1233
Final R indexes [all data]	R_1 = 0.0472, wR_2 = 0.1244
Largest diff. peak/hole / e Å^{-3}	0.85/-1.02
Flack parameter	-0.006(12)

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **3k**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br2	11500.6(14)	5556.4(4)	4541.6(4)	59.0(3)
Br1	7854(2)	7979.3(6)	513.8(5)	83.1(4)
C12	9811(8)	8386(3)	3704(3)	26.4(9)
O1	3338(6)	10193(3)	2903(3)	55.3(12)
N1	9363(6)	9229(3)	3461(3)	34(1)
O2	4714(8)	11578(3)	2876(5)	75.6(19)
C14	12298(9)	7370(4)	4302(3)	36.5(11)
C9	8288(9)	11107(3)	2903(4)	40.6(12)
C2	7357(9)	8805(3)	1968(3)	35.0(11)
C15	10817(10)	6714(4)	4205(3)	37.6(12)
C4	4330(9)	9681(3)	2345(4)	41.6(13)
C1	6375(13)	8654(4)	1258(4)	49.6(15)
C11	4648(10)	10814(4)	3302(5)	48.8(16)
C6	4326(13)	8987(5)	1100(5)	61(2)
C3	6341(8)	9320(3)	2518(3)	28.8(9)
C16	8817(9)	6868(3)	3881(3)	34.3(11)
C17	8317(8)	7707(3)	3627(3)	32.9(10)
C7	7210(7)	9528(3)	3313(3)	28.4(9)
C10	6849(13)	11876(5)	2812(5)	61.6(19)
C8	6971(8)	10515(4)	3441(3)	34.2(10)

C5	3330(10)	9510(5)	1641(5)	60(2)
C13	11812(8)	8209(4)	4052(3)	34.8(11)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **3k**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br2	91.1(6)	35.4(3)	50.4(4)	-1.9(2)	-22.4(4)	26.0(3)
Br1	138.5(10)	64.0(5)	46.7(4)	-15.8(3)	10.1(5)	-17.8(6)
C12	24(2)	28(2)	27(2)	1.2(17)	0.1(17)	1.6(18)
O1	25.0(16)	40(2)	101(4)	7(2)	13(2)	2.6(17)
N1	20.8(18)	30(2)	52(3)	8.9(19)	-0.8(18)	-2.3(16)
O2	46(2)	32(2)	148(6)	28(3)	-8(3)	7(2)
C14	33(2)	46(3)	30(2)	-3(2)	-6(2)	10(2)
C9	39(3)	24(2)	58(3)	7(2)	12(3)	1(2)
C2	40(3)	27(2)	38(2)	3.1(19)	-1(2)	-3(2)
C15	51(3)	39(3)	23(2)	-2.9(19)	-3(2)	17(3)
C4	29(2)	28(2)	68(4)	11(2)	-6(3)	-2(2)
C1	65(4)	39(3)	45(3)	8(2)	-11(3)	-20(3)
C11	36(3)	33(3)	77(4)	2(3)	21(3)	12(2)
C6	71(4)	49(4)	64(4)	16(3)	-35(4)	-25(4)
C3	25.0(19)	23(2)	38(2)	6.5(19)	1.3(19)	-0.6(17)
C16	41(3)	27(2)	35(2)	-1.7(19)	-5(2)	1(2)
C17	28(2)	28(2)	42(2)	4.7(19)	-10(2)	1(2)
C7	19.1(18)	32(2)	34(2)	6.7(19)	5.9(17)	1.5(18)
C10	69(4)	38(3)	79(5)	17(3)	19(4)	11(3)
C8	35(2)	31(2)	38(2)	3(2)	9(2)	3(2)
C5	39(3)	47(3)	94(5)	28(4)	-28(4)	-11(3)
C13	27(2)	42(3)	36(2)	-4(2)	-4(2)	-1(2)

Table S4. Bond Lengths for **3k.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br2	C15	1.908(5)	C9	C8	1.532(7)
Br1	C1	1.885(8)	C2	C3	1.384(7)
C12	N1	1.382(6)	C2	C1	1.388(8)
C12	C17	1.396(7)	C15	C16	1.379(8)
C12	C13	1.403(7)	C4	C5	1.389(10)
O1	C4	1.385(8)	C4	C3	1.394(7)
O1	C11	1.427(9)	C1	C6	1.394(12)
N1	C7	1.433(6)	C11	C8	1.528(8)
O2	C11	1.380(8)	C6	C5	1.375(13)
O2	C10	1.403(10)	C3	C7	1.508(7)
C14	C15	1.368(9)	C16	C17	1.389(7)
C14	C13	1.386(8)	C7	C8	1.531(7)
C9	C10	1.483(8)			

Table S5. Bond Angles for **3k.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	C12	C17	122.0(4)	O2	C11	O1	108.7(7)
N1	C12	C13	119.1(5)	O2	C11	C8	108.0(5)
C17	C12	C13	118.9(5)	O1	C11	C8	114.3(5)
C4	O1	C11	117.4(4)	C5	C6	C1	119.2(7)
C12	N1	C7	122.6(4)	C2	C3	C4	118.9(5)
C11	O2	C10	110.2(5)	C2	C3	C7	125.6(4)
C15	C14	C13	119.6(5)	C4	C3	C7	115.5(5)
C10	C9	C8	102.2(5)	C15	C16	C17	119.0(5)
C3	C2	C1	120.1(6)	C16	C17	C12	120.5(5)
C14	C15	C16	121.7(5)	N1	C7	C3	115.3(4)
C14	C15	Br2	119.5(4)	N1	C7	C8	112.2(4)
C16	C15	Br2	118.7(5)	C3	C7	C8	107.8(4)
O1	C4	C5	121.2(5)	O2	C10	C9	107.5(5)

O1	C4	C3	118.0(5)	C11	C8	C7	111.2(5)
C5	C4	C3	120.8(6)	C11	C8	C9	103.3(5)
C2	C1	C6	120.7(7)	C7	C8	C9	116.2(4)
C2	C1	Br1	118.7(6)	C6	C5	C4	120.2(6)
C6	C1	Br1	120.5(6)	C14	C13	C12	120.2(5)

Table S6. Hydrogen Bonds for **3k.**

D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
N1	H1	O1	0.86	2.20	3.026(6)	160.2

Table S7. Torsion Angles for **3k.**

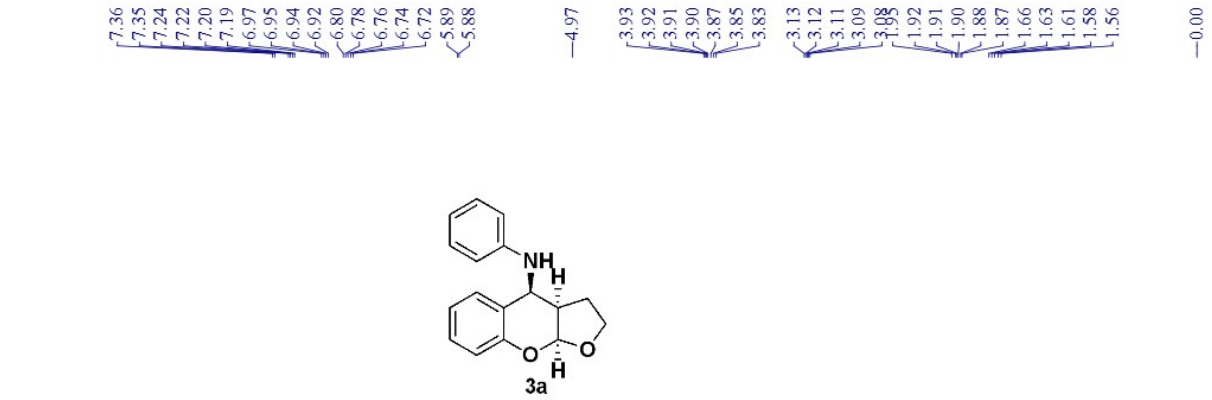
A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
C17	C12	N1	C7	17.3(8)	C12	N1	C7	C3	-84.0(6)
C13	C12	N1	C7	-161.5(5)	C12	N1	C7	C8	152.0(5)
C13	C14	C15	C16	-1.7(8)	C2	C3	C7	N1	6.5(7)
C13	C14	C15	Br2	179.5(4)	C4	C3	C7	N1	-174.2(4)
C11	O1	C4	C5	-137.9(6)	C2	C3	C7	C8	132.7(5)
C11	O1	C4	C3	43.9(7)	C4	C3	C7	C8	-47.9(5)
C3	C2	C1	C6	-2.6(8)	C11	O2	C10	C9	25.0(10)
C3	C2	C1	Br1	178.0(4)	C8	C9	C10	O2	-30.3(8)
C10	O2	C11	O1	-132.8(7)	O2	C11	C8	C7	-136.2(6)
C10	O2	C11	C8	-8.2(9)	O1	C11	C8	C7	-15.1(7)
C4	O1	C11	O2	86.2(6)	O2	C11	C8	C9	-10.9(7)
C4	O1	C11	C8	-34.5(8)	O1	C11	C8	C9	110.3(6)
C2	C1	C6	C5	3.6(9)	N1	C7	C8	C11	-178.3(5)
Br1	C1	C6	C5	-177.0(5)	C3	C7	C8	C11	53.7(5)
C1	C2	C3	C4	-0.1(7)	N1	C7	C8	C9	63.9(6)
C1	C2	C3	C7	179.3(5)	C3	C7	C8	C9	-64.1(6)
O1	C4	C3	C2	179.9(5)	C10	C9	C8	C11	24.2(7)
C5	C4	C3	C2	1.7(8)	C10	C9	C8	C7	146.3(6)

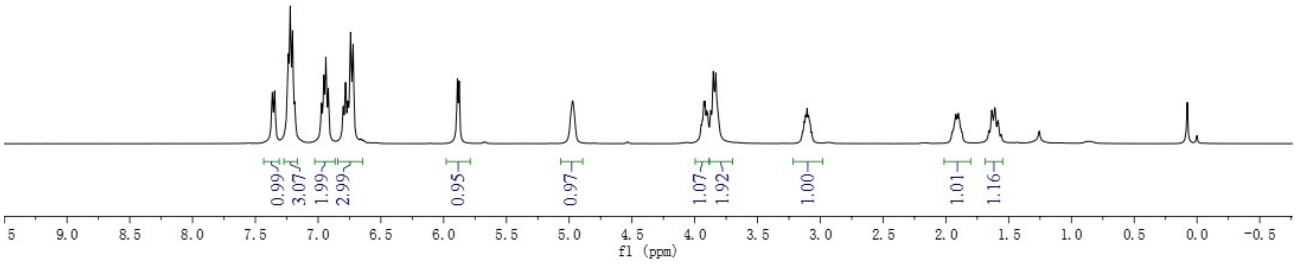
O1	C4	C3	C7	0.4(7)	C1	C6	C5	C4	-2.0(10)
C5	C4	C3	C7	-177.8(5)	O1	C4	C5	C6	-178.8(6)
C14	C15	C16	C17	1.8(8)	C3	C4	C5	C6	-0.6(9)
Br2	C15	C16	C17	-179.4(4)	C15	C14	C13	C12	0.3(8)
C15	C16	C17	C12	-0.4(8)	N1	C12	C13	C14	179.9(5)
N1	C12	C17	C16	-179.7(5)	C17	C12	C13	C14	1.0(7)
C13	C12	C17	C16	-0.9(8)					

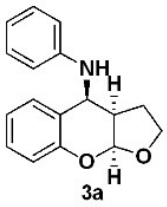
Table S8. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3k.**

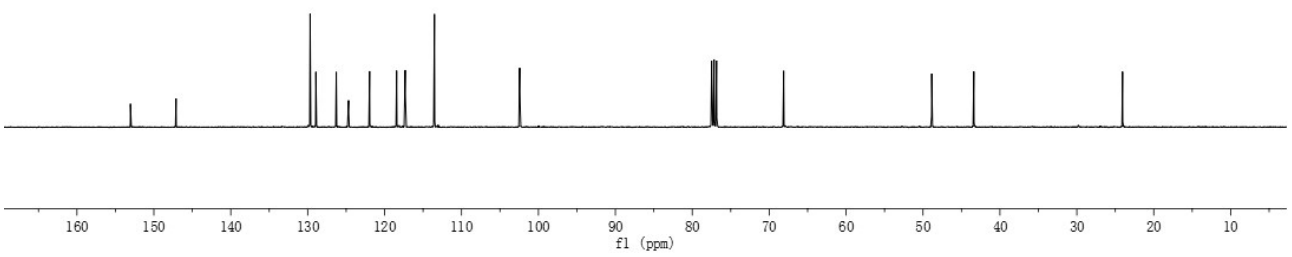
Atom	***x***	***y***	***z***	**U(eq)**
H1	10418	9587	3397	41
H14	13622	7253	4534	44
H9A	9654	11271	3137	49
H9B	8560	10825	2409	49
H2	8700	8560	2075	42
H11	3978	10941	3804	59
H6	3641	8857	635	73
H16	7818	6416	3833	41
H17	6977	7817	3405	39
H7	6263	9237	3688	34
H10A	7150	12306	3211	74
H10B	7076	12148	2311	74
H8	7363	10650	3978	41
H5	1982	9751	1535	72
H13	12816	8657	4115	42

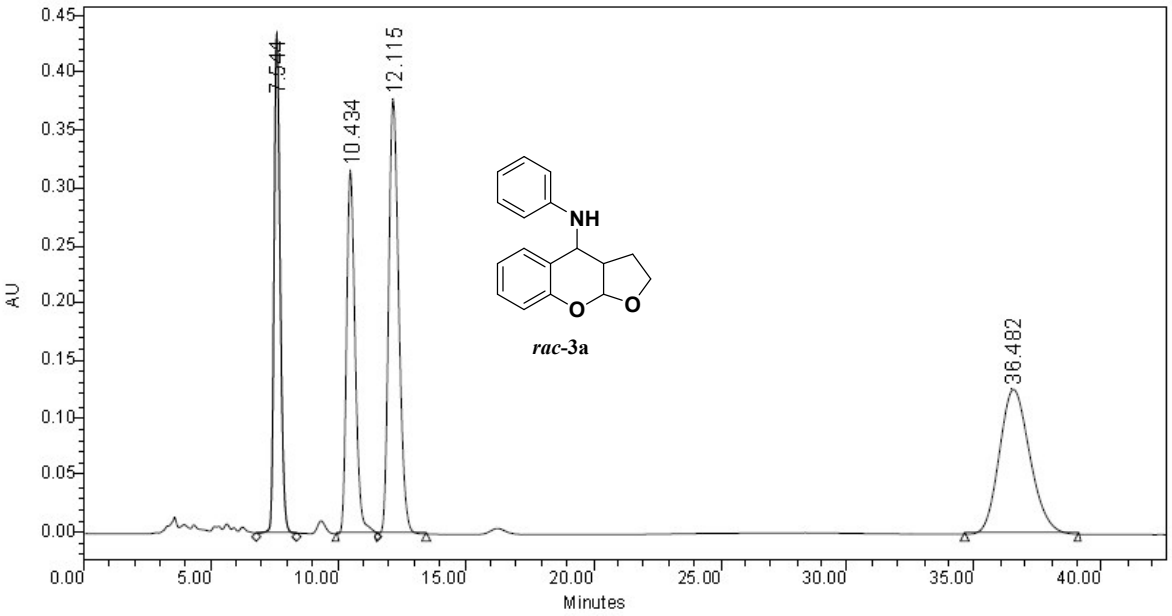
5. Selected NMR and HPLC





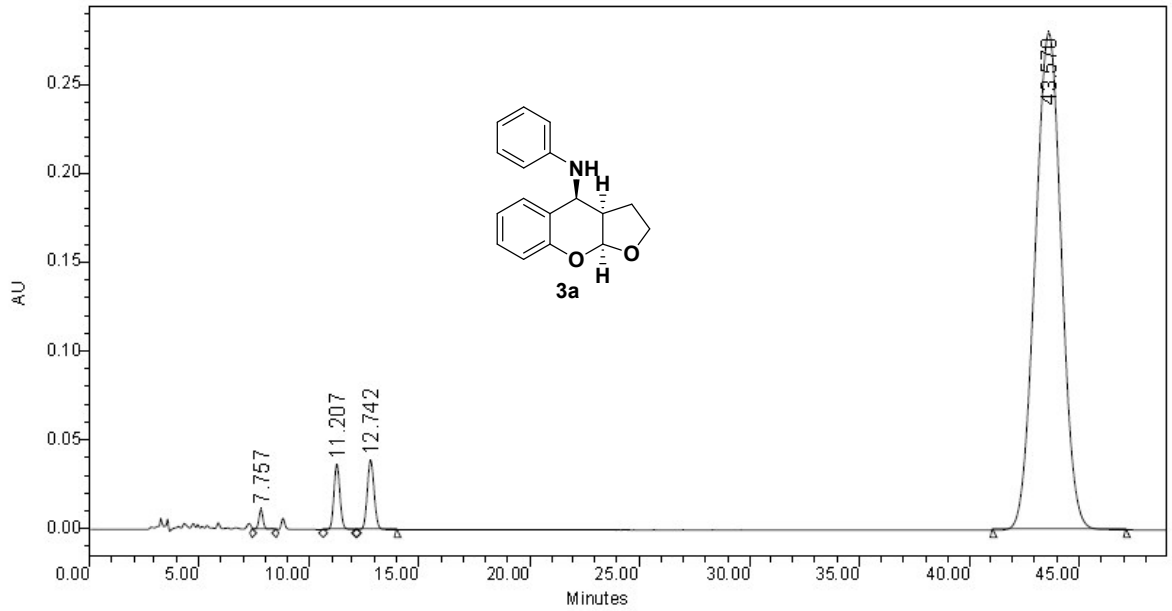






rac-**3a**

	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	7.544	7337386	20.50	436017	34.75
2	10.434	7461115	20.85	315106	25.11
3	12.115	10434147	29.16	377753	30.10
4	36.482	10552845	29.49	126009	10.04

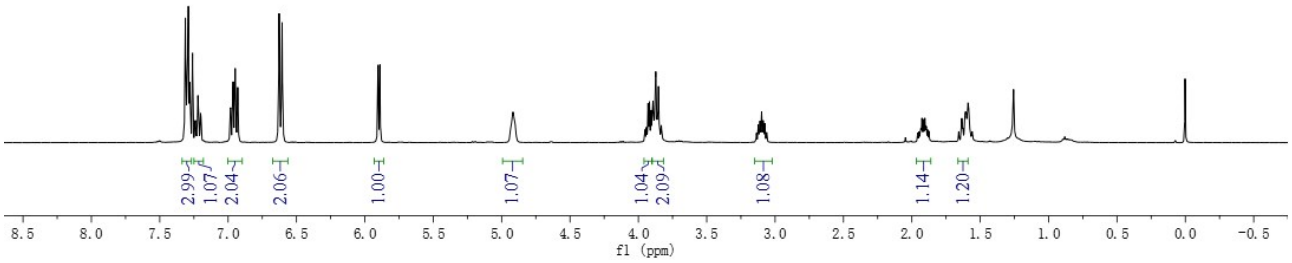


3a

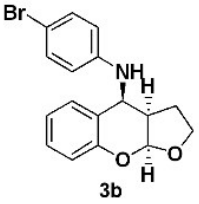
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	7.757	192380	0.77	11846	3.21
2	11.207	727599	2.90	37129	10.07
3	12.742	866536	3.45	39243	10.64
4	43.570	23304945	92.88	280439	76.07

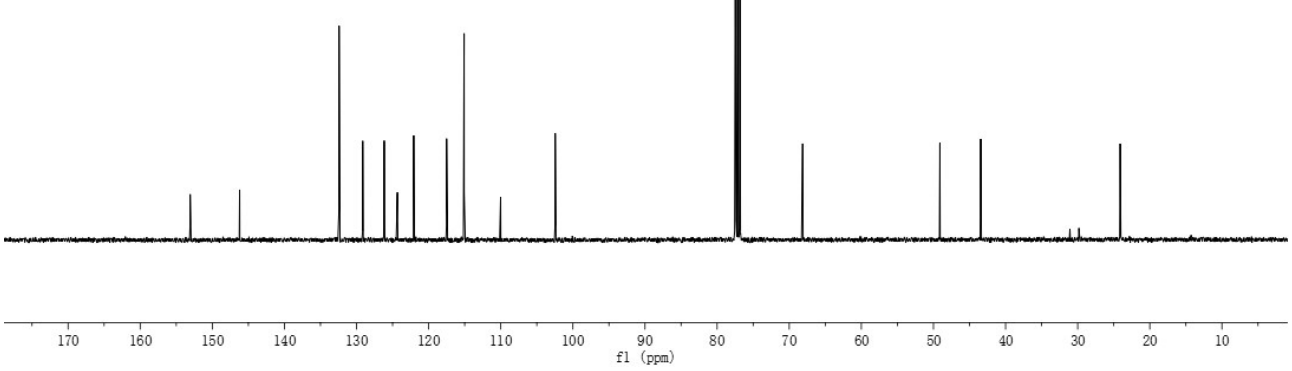

7.31
7.30
7.29
7.28
7.26
7.24
7.22
7.20
6.98
6.96
6.95
6.93
6.63
6.61
5.90
5.89
4.92
3.93
3.92
3.91
3.90
3.89
3.87
3.85
3.83
3.12
3.11
3.10
3.09
3.08
3.06
1.94
1.93
1.93
1.92
1.90
1.90
1.89
1.89
1.88
1.63
1.63
1.61
1.61
1.59
1.56
0.00

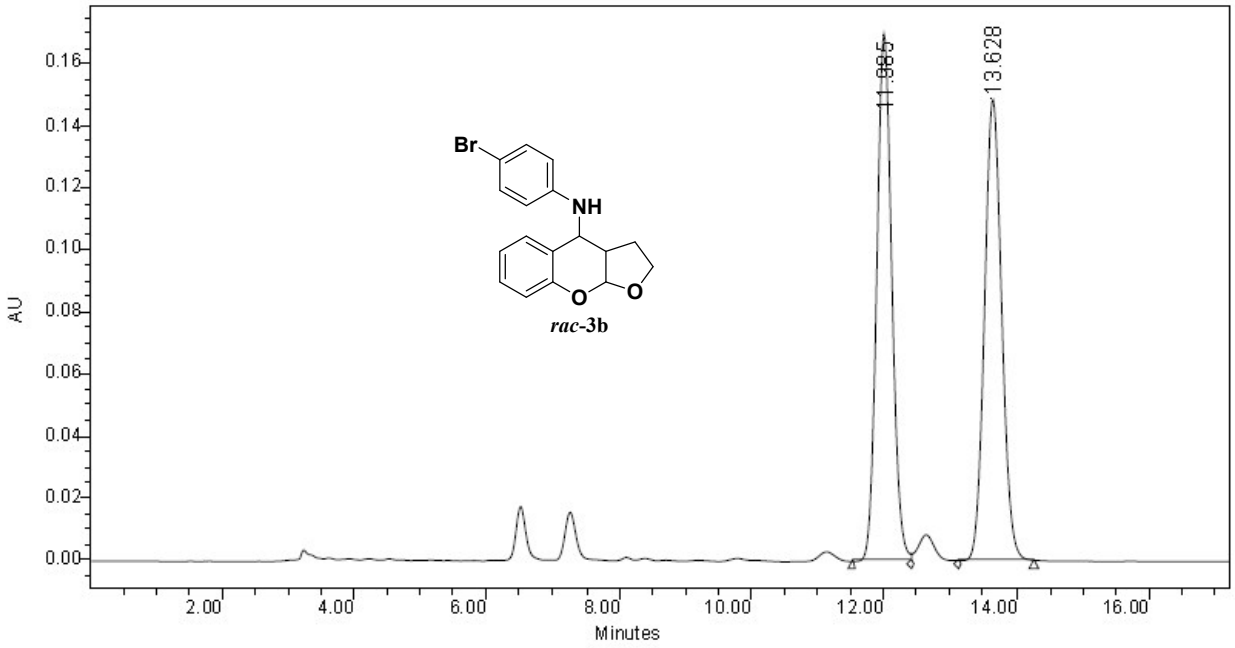

Br
NH
H
O
O
H
3b


2.99
1.07
2.04
2.06
1.00
1.07
1.04
2.09
1.08
1.14
1.20
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

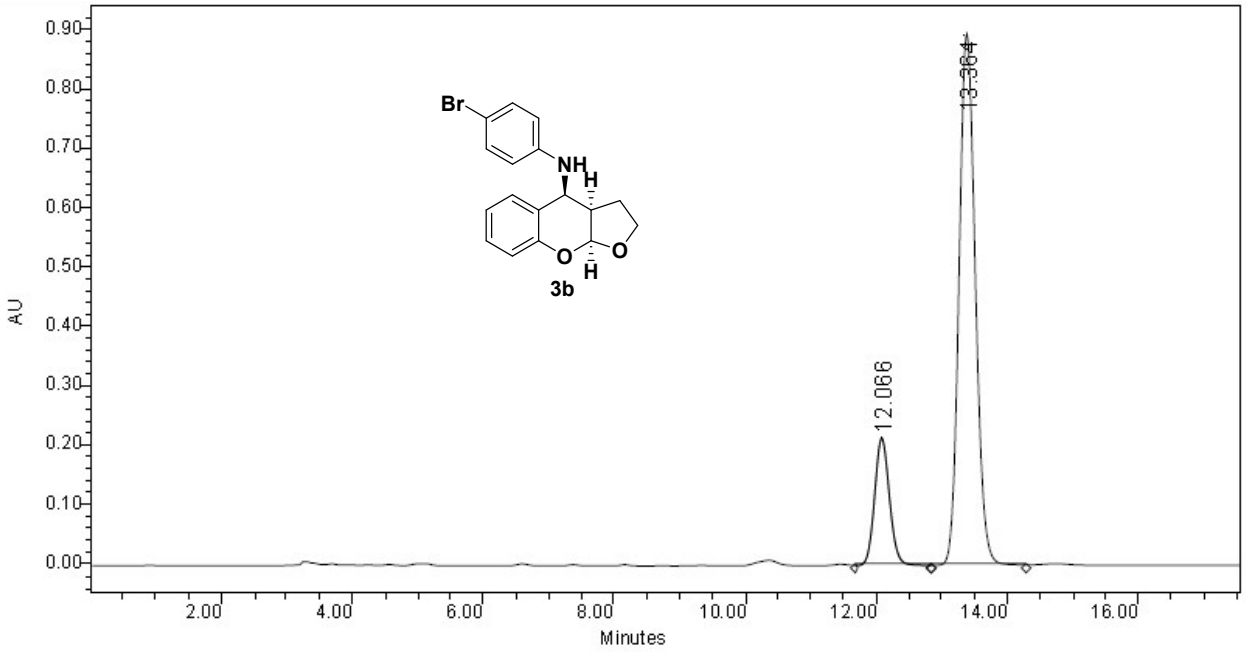

153.06
146.21
132.42
129.14
126.16
124.34
122.07
117.51
115.08
110.02
102.45
77.48
77.16
76.84
68.14
49.11
43.45
24.11


Br
NH
H
O
O
H
3b


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

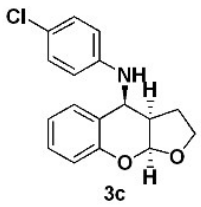


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.985	2692948	50.08	169898	53.33
2	13.628	2684237	49.92	148679	46.67

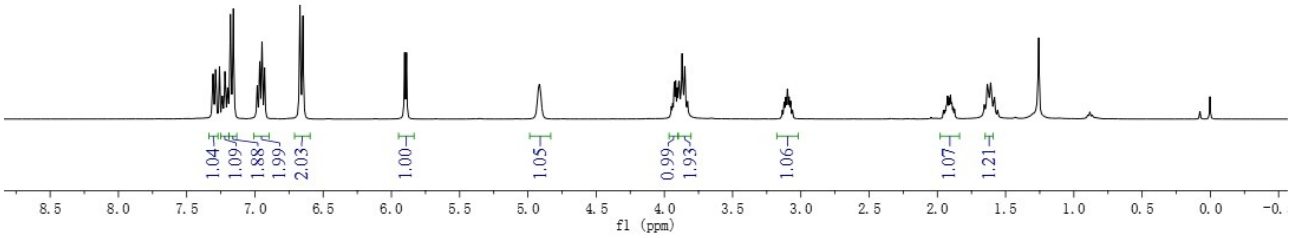


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	12.066	3371719	17.96	214087	19.32
2	13.364	15403389	82.04	894281	80.68

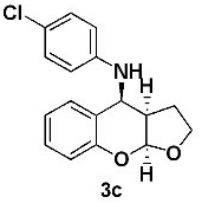

7.31
7.29
7.26
7.24
7.22
7.20
7.18
7.16
6.98
6.96
6.95
6.93
6.67
6.65
5.90
5.89
4.92
3.93
3.92
3.91
3.89
3.89
3.87
3.85
3.11
3.10
3.09
3.08
1.94
1.93
1.92
1.91
1.90
1.90
1.88
1.87
1.66
1.63
1.61
1.58
0.00


Cl
NH
H
O
O
H

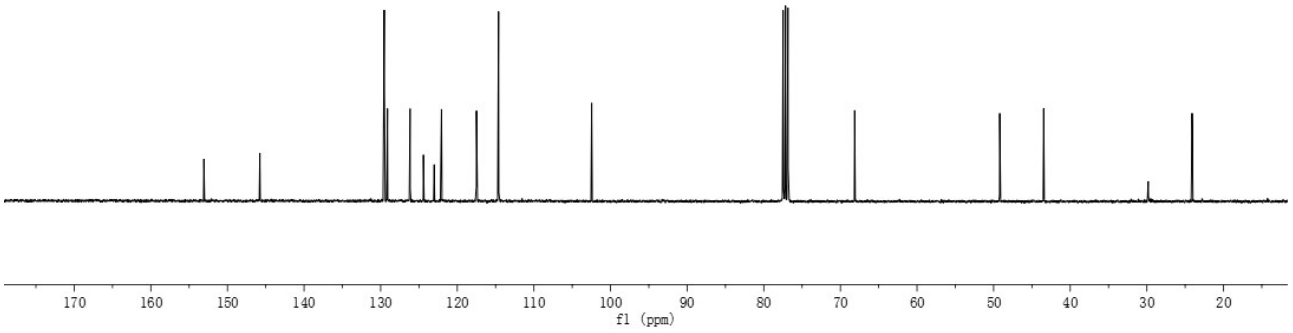
3c

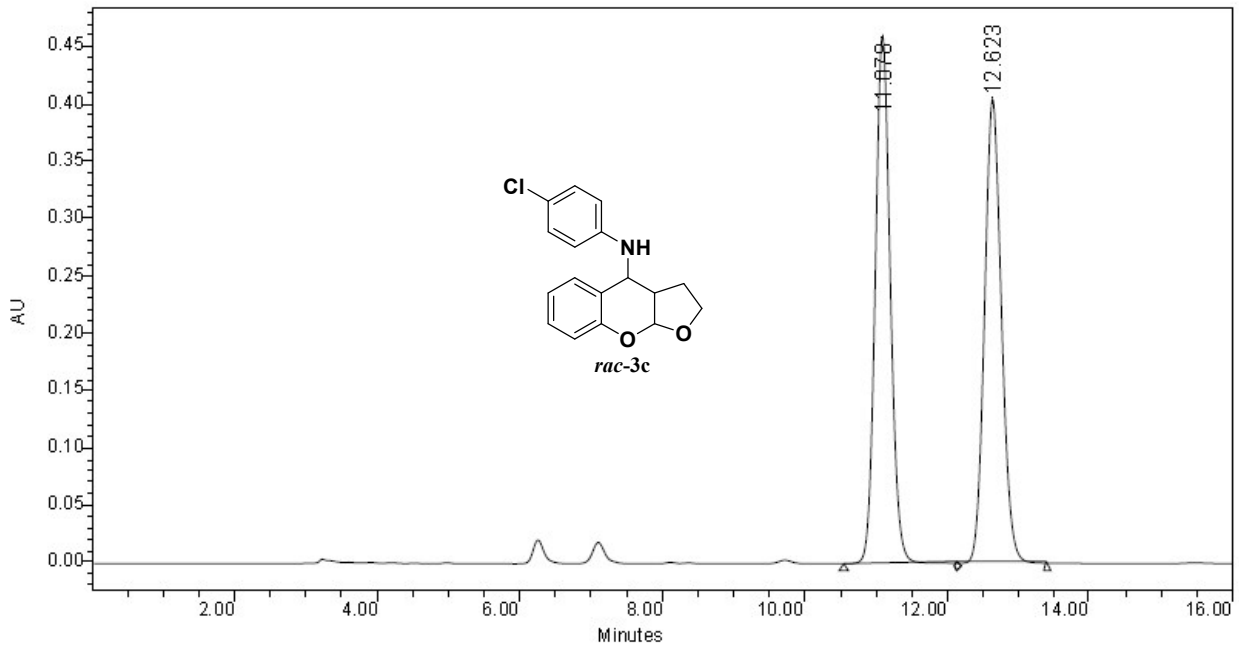

1.04
1.09
1.88
1.99
2.03
1.00
1.05
0.99
1.93
1.06
1.07
1.21
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


153.07
145.77
129.54
129.11
126.16
124.42
123.01
122.06
117.50
114.62
102.46
77.48
77.16
76.84
68.13
49.20
43.46
24.10


Cl
NH
H
O
O
H

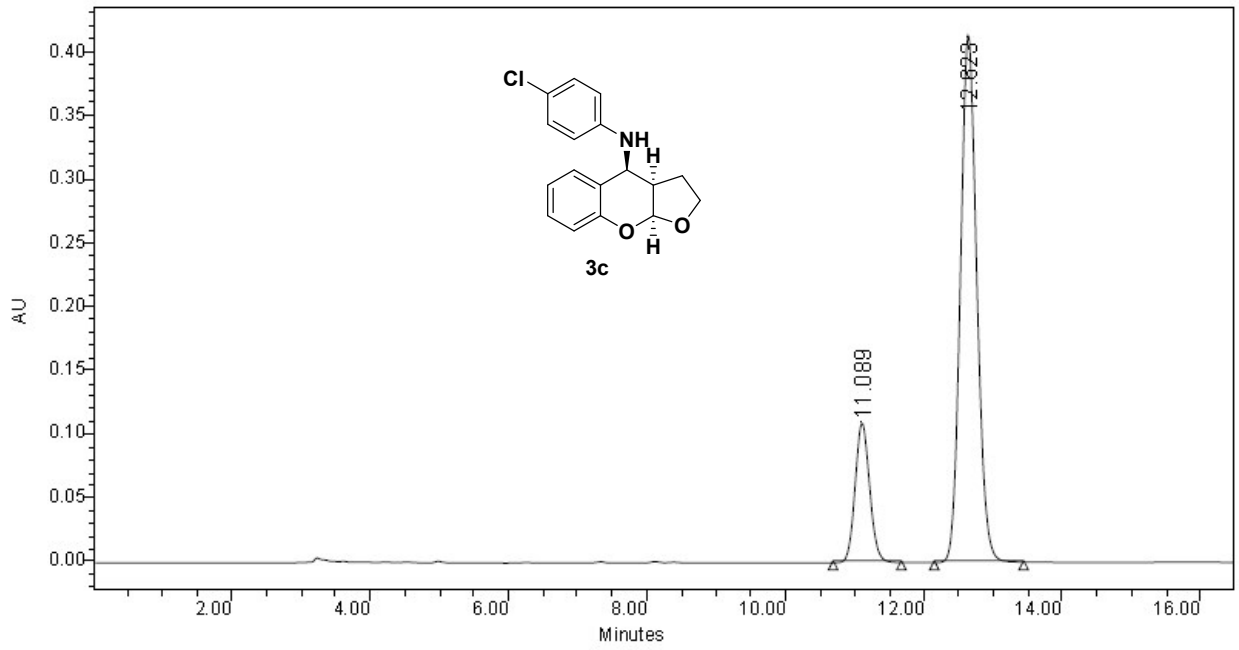
3c


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)



rac-3c

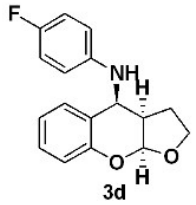
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.078	6784236	50.31	460982	53.20
2	12.623	6700544	49.69	405524	46.80



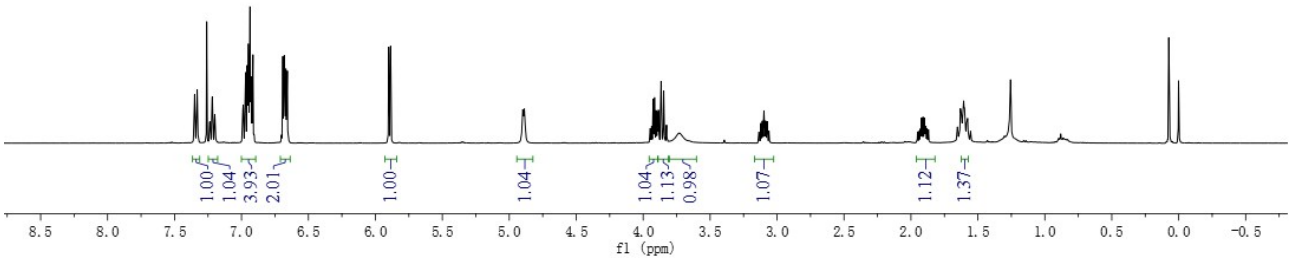
3c

	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.089	1599784	19.06	109368	20.90
2	12.623	6793154	80.94	413920	79.10

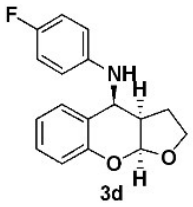

7.35
7.33
7.26
7.24
7.24
7.22
7.20
7.20
6.99
6.99
6.97
6.97
6.96
6.95
6.94
6.94
6.93
6.93
6.92
6.91
6.69
6.69
6.68
6.67
6.67
6.66
6.66
5.90
5.89
4.90
4.89
3.94
3.92
3.91
3.90
3.89
3.89
3.87
3.85
3.83
3.12
3.11
3.10
3.09
3.07
1.92
1.91
1.90
1.89
1.89
1.65
1.63
1.62
1.61
1.60
1.58
1.58
0.00


F
NH
H
O
O
H

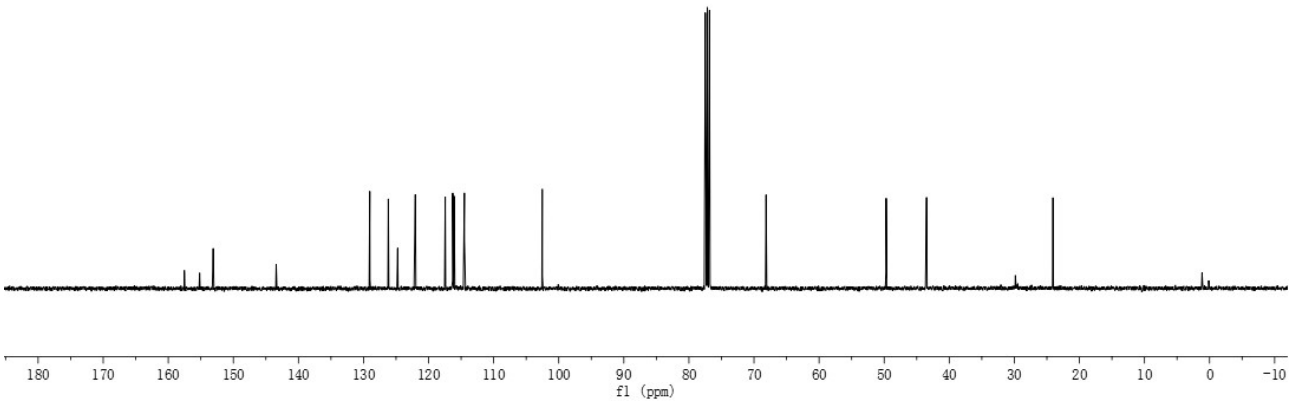
3d

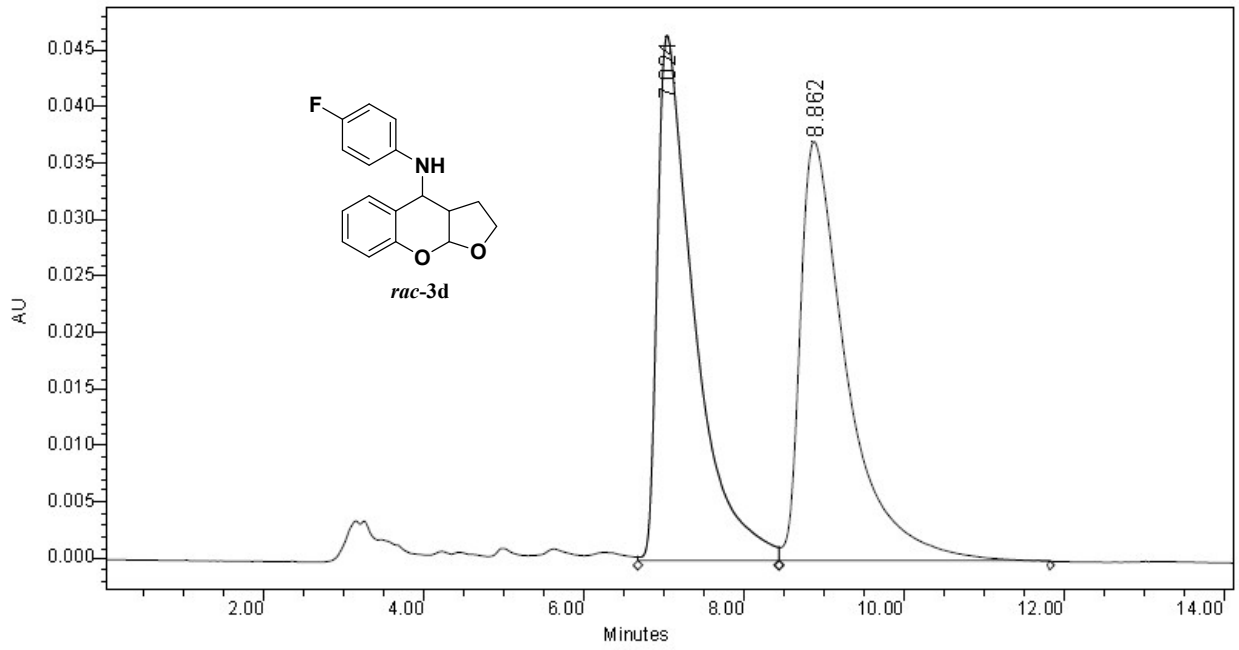

1.00
1.04
3.93
2.01
1.00
1.04
1.04
1.13
0.98
1.07
1.12
1.37
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


157.53
155.18
153.09
143.44
143.42
129.04
126.19
124.75
122.04
117.44
116.29
116.07
114.57
114.50
102.53
77.48
77.16
76.84
68.14
49.69
43.48
24.06

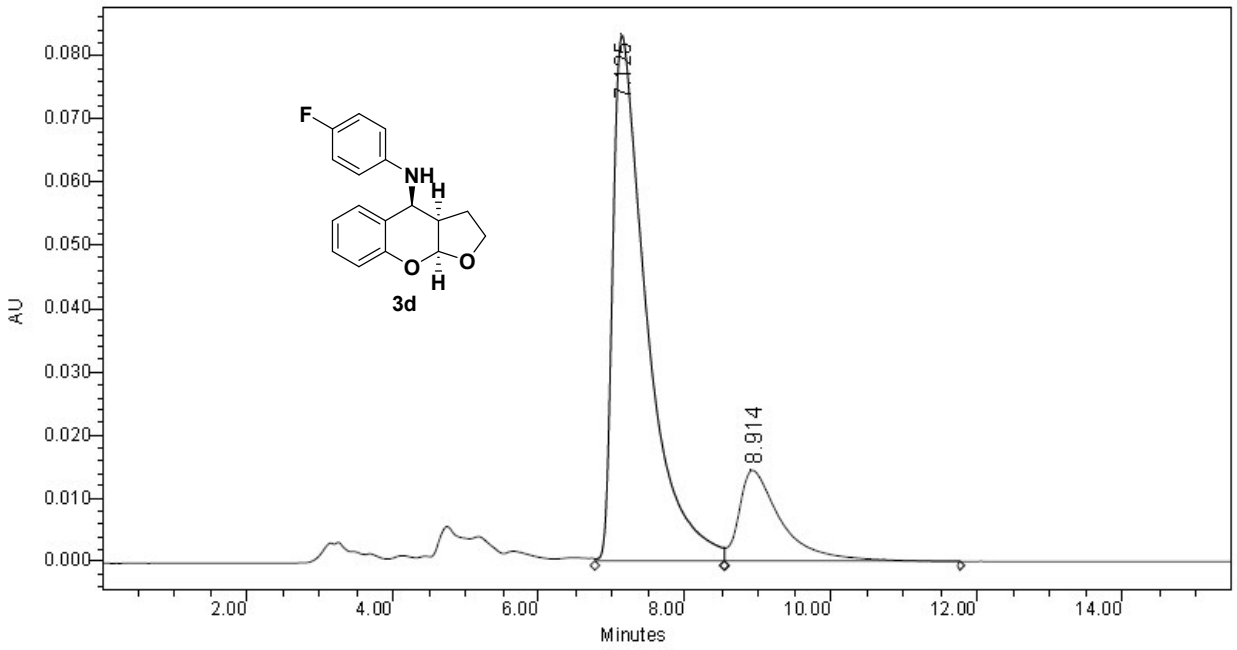

F
NH
H
O
O
H

3d


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	7.024	1503316	49.62	46727	55.63
2	8.862	1526352	50.38	37276	44.37



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	7.125	2702106	81.65	83464	85.15
2	8.914	607180	18.35	14561	14.85


7.31
7.29
7.26
7.25
7.23
7.21
7.15
7.13
7.11
6.99
6.97
6.95
6.93
6.75
6.73
6.73
6.72
6.61
6.61
6.59
6.59
5.91
5.89
4.97
4.95
4.95
4.93
3.97
3.96
3.95
3.94
3.92
3.91
3.90
3.88
3.86
3.84
3.13
3.12
3.10
3.09
3.08
3.07
1.96
1.95
1.95
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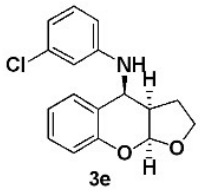
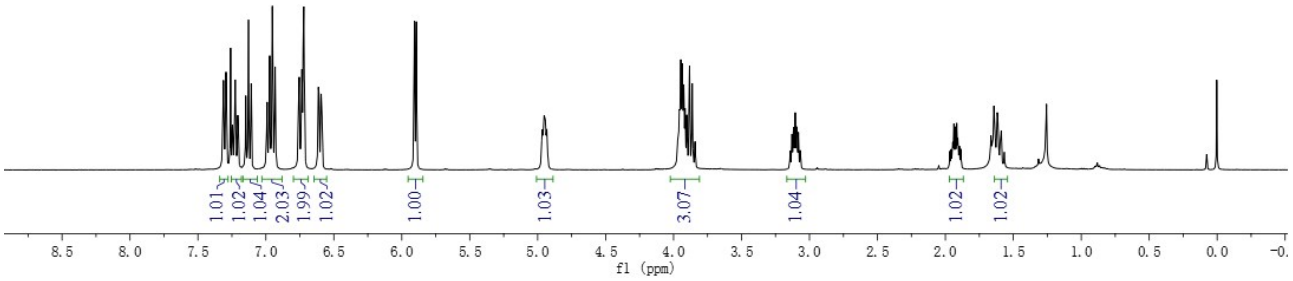
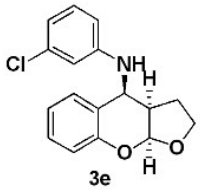
1.89
1.66
1.64
1.62
1.60
1.59


Cl
NH
H
O
O
H

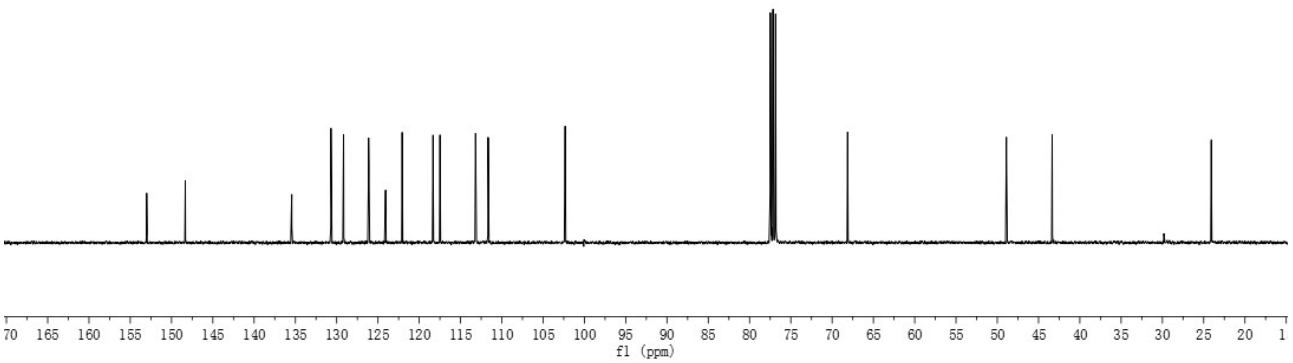
3e

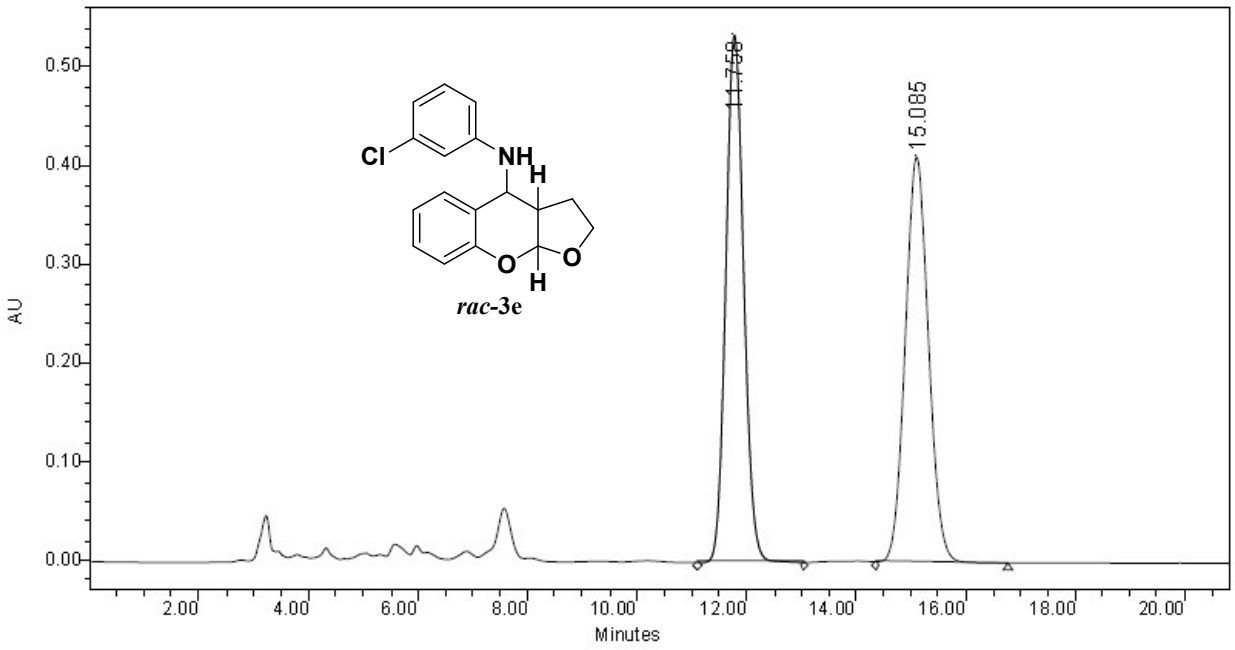

1.01
1.02
1.04
2.03
1.99
1.02
1.00
1.03
3.07
1.04
1.02
1.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


153.01
148.33
135.44
130.69
129.17
126.13
124.08
122.07
118.33
117.49
113.18
111.65
102.33
77.48
77.16
76.84
68.12
48.90
43.35
24.08


Cl
NH
H
O
O
H

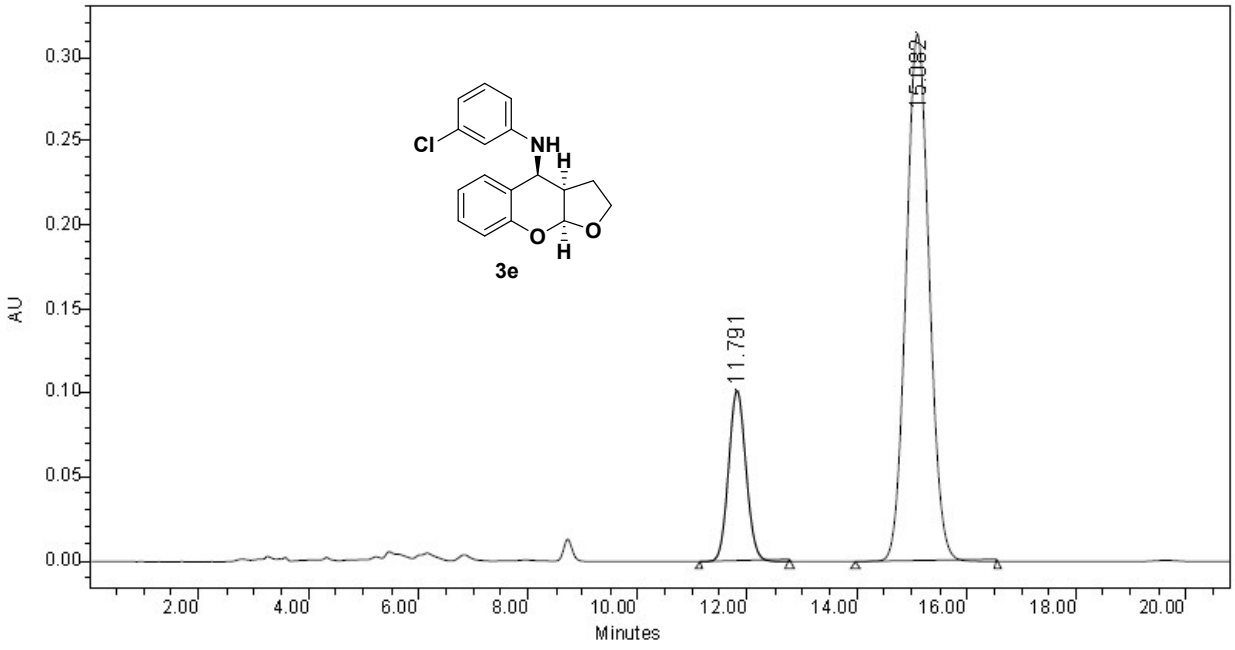
3e


70
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
1
f1 (ppm)



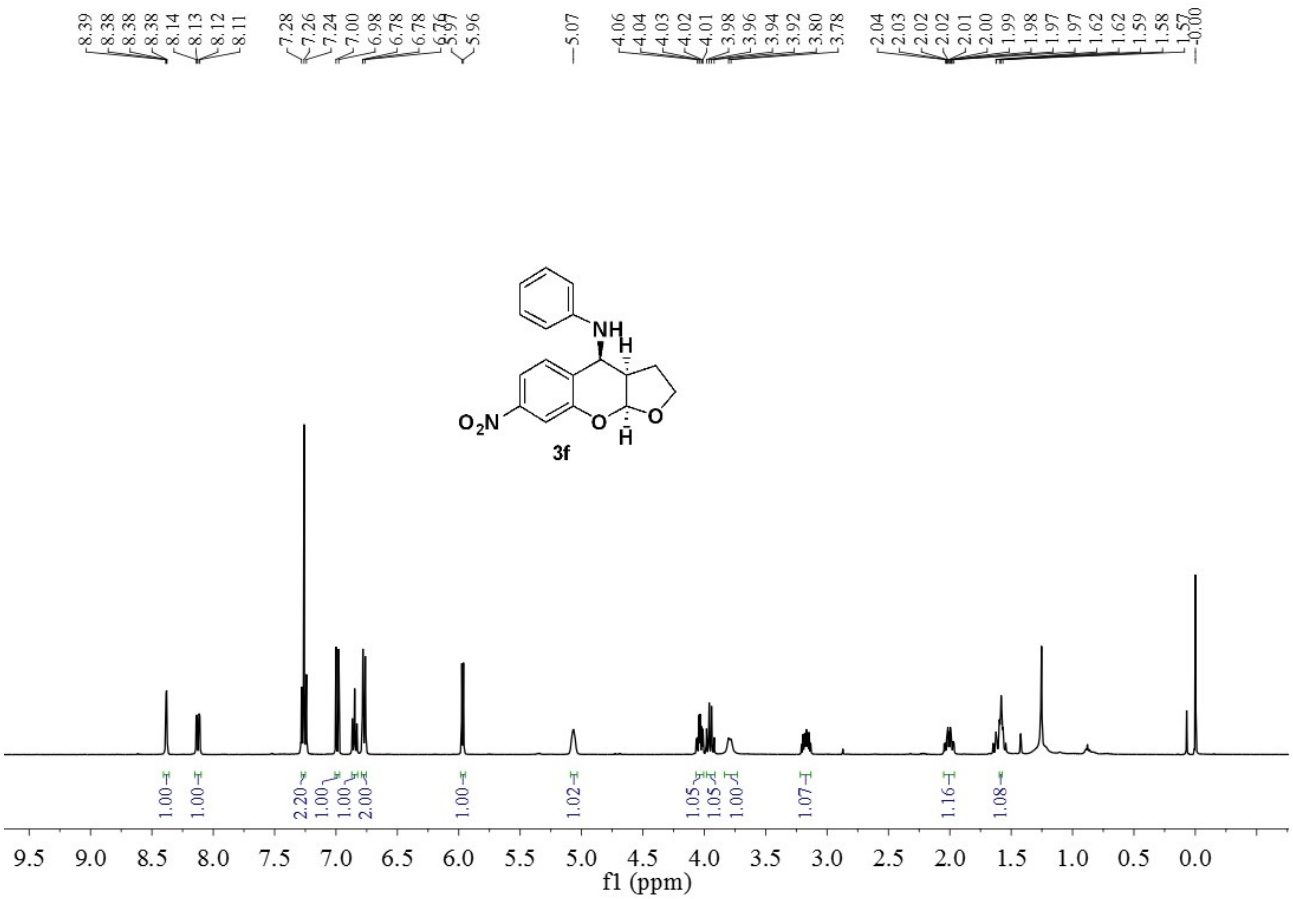
rac-3e

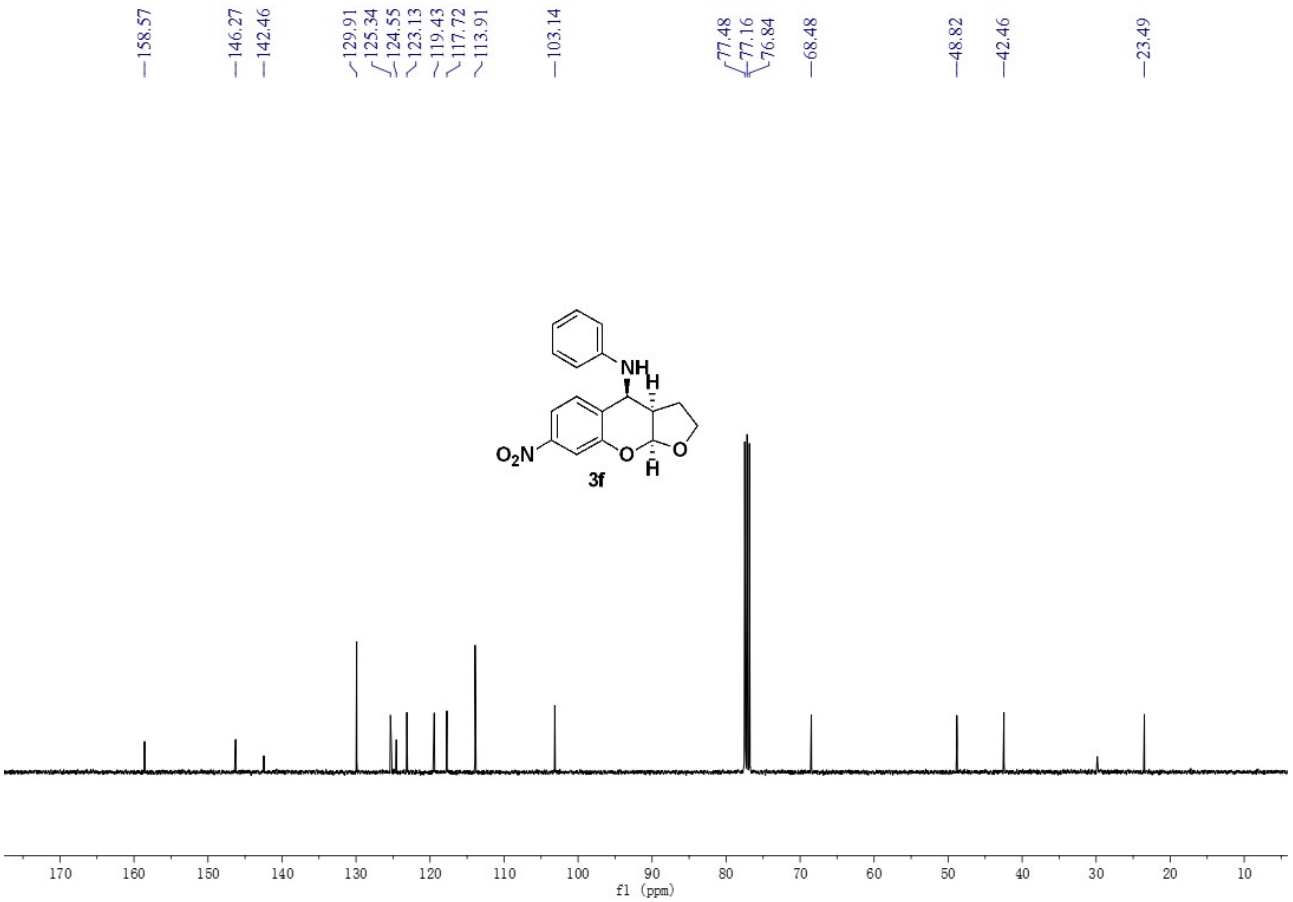
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.758	12165499	50.06	535138	56.54
2	15.085	12136952	49.94	411365	43.46

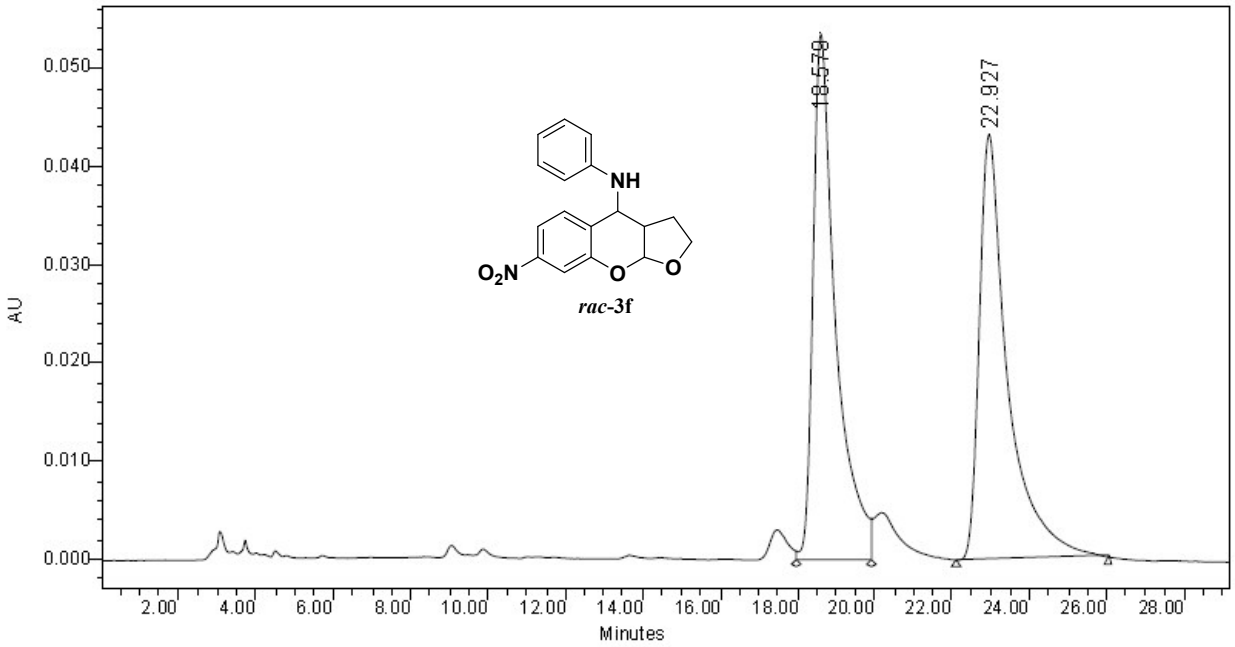


3e

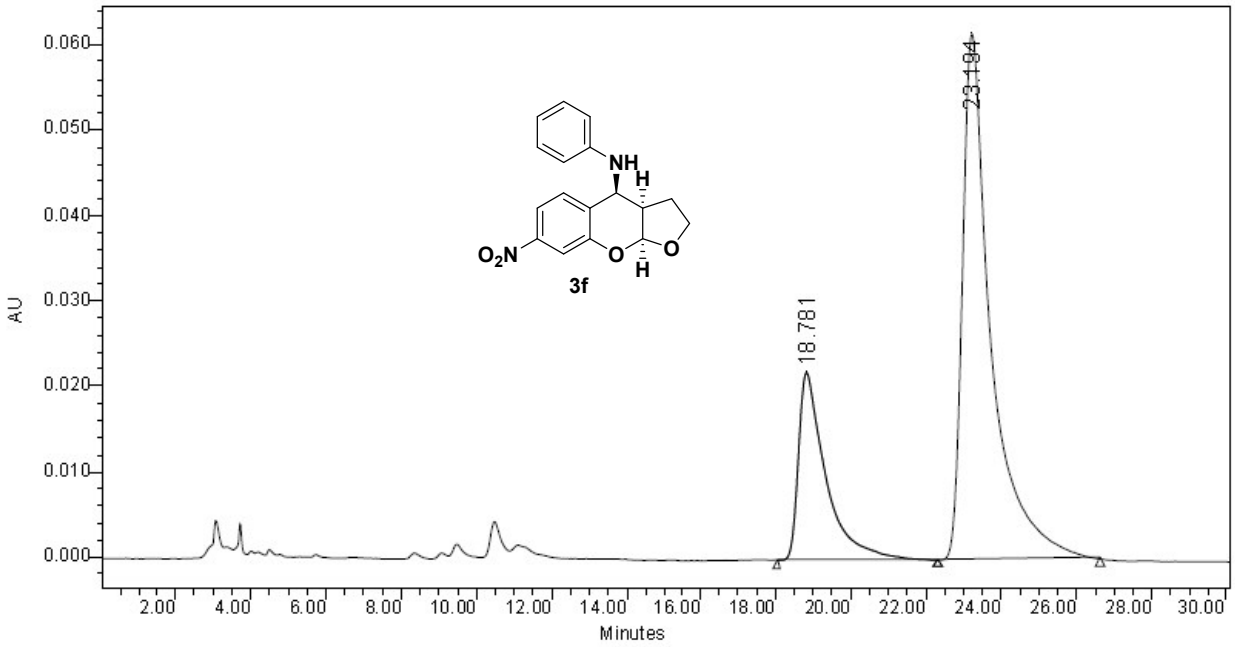
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.791	2257361	19.72	102018	24.50
2	15.082	9189369	80.28	314429	75.50


8.39
8.38
8.38
8.38
8.14
8.13
8.12
8.11
7.28
7.26
7.24
7.00
6.98
6.78
6.78
6.76
5.97
5.96
5.07
4.06
4.04
4.03
4.02
4.01
3.98
3.96
3.94
3.92
3.80
3.78
2.04
2.03
2.02
2.02
2.01
2.00
1.99
1.98
1.97
1.97
1.62
1.59
1.58
1.57
0.00
NH
H
O2N
O
O
H
3f
1.00
1.00
2.20
1.00
1.00
2.00
1.00
1.02
1.05
1.05
1.00
1.07
1.16
1.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


158.57
146.27
142.46
129.91
125.34
124.55
123.13
119.43
117.72
113.91
103.14
77.48
77.16
76.84
68.48
48.82
42.46
23.49
NH
H
O2N
O
O
H
3f
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



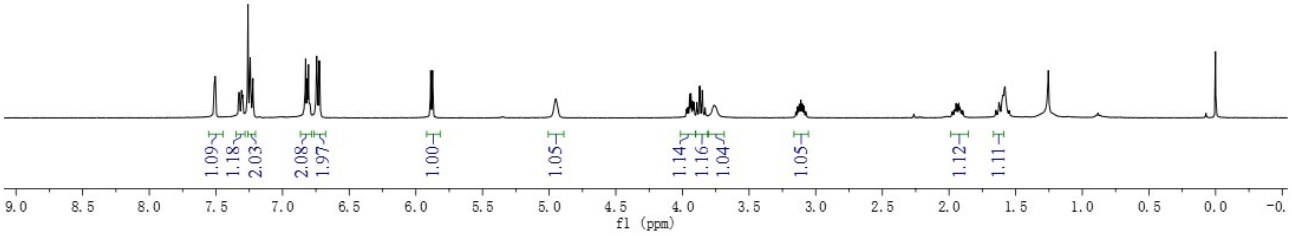
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	18.579	2190606	49.66	53507	55.31
2	22.927	2220949	50.34	43241	44.69



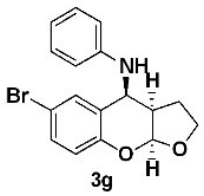
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	18.781	1119522	25.54	21949	26.30
2	23.194	3263654	74.46	61503	73.70

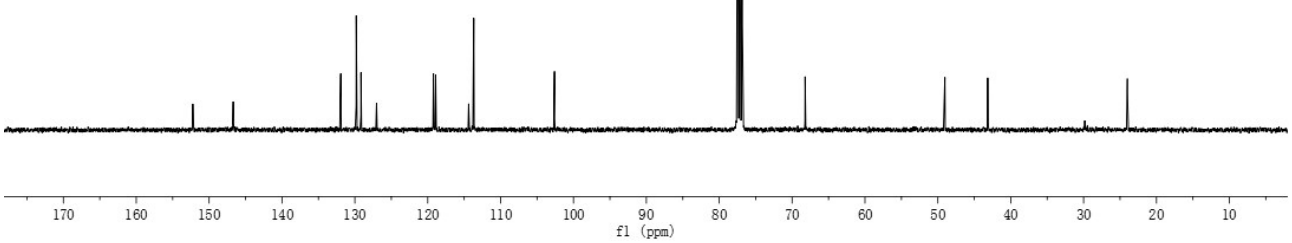

7.51
7.51
7.33
7.32
7.31
7.30
7.26
7.24
7.22
6.83
6.82
6.81
6.74
5.87
4.95
3.95
3.94
3.92
3.91
3.89
3.87
3.85
3.76
3.14
3.12
3.11
3.10
1.97
1.96
1.95
1.94
1.93
1.92
1.91
1.90
1.65
1.63
1.58
1.55
0.00

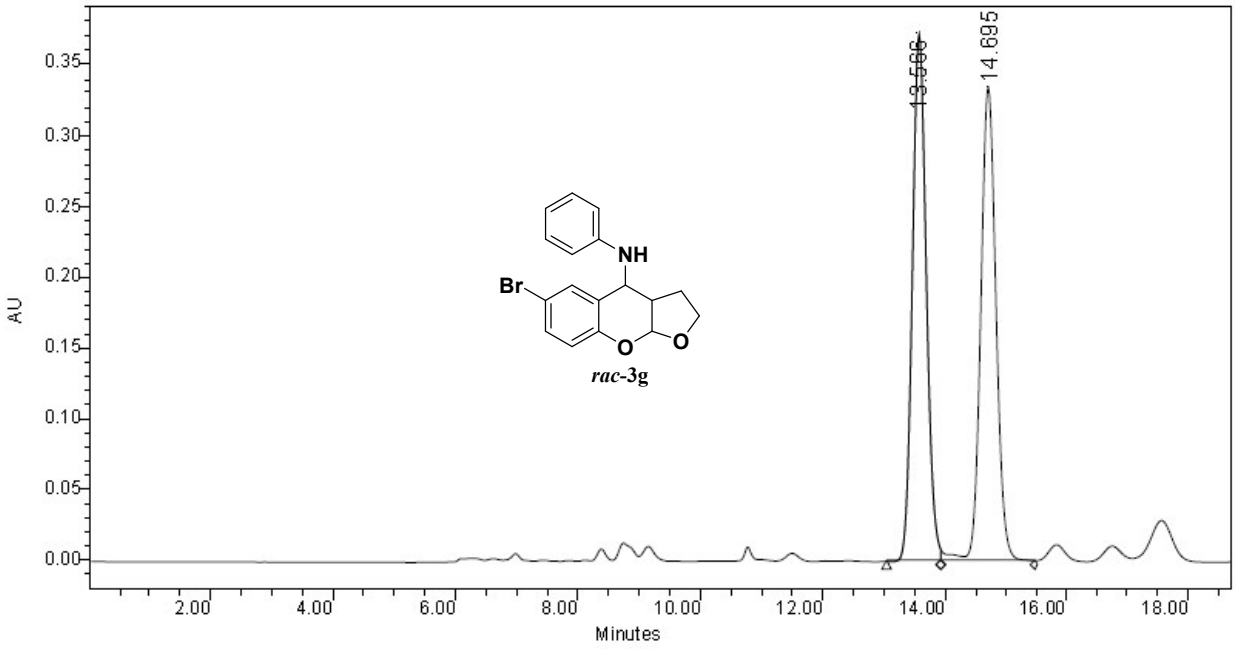

NH
H
Br
O
O
H
3g


1.09
1.18
2.03
2.08
1.97
1.00
1.05
1.14
1.16
1.04
1.05
1.12
1.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


152.24
146.69
131.93
129.81
129.16
127.03
119.22
118.92
114.39
113.69
102.61
77.48
77.16
76.84
68.21
49.04
43.16
23.99

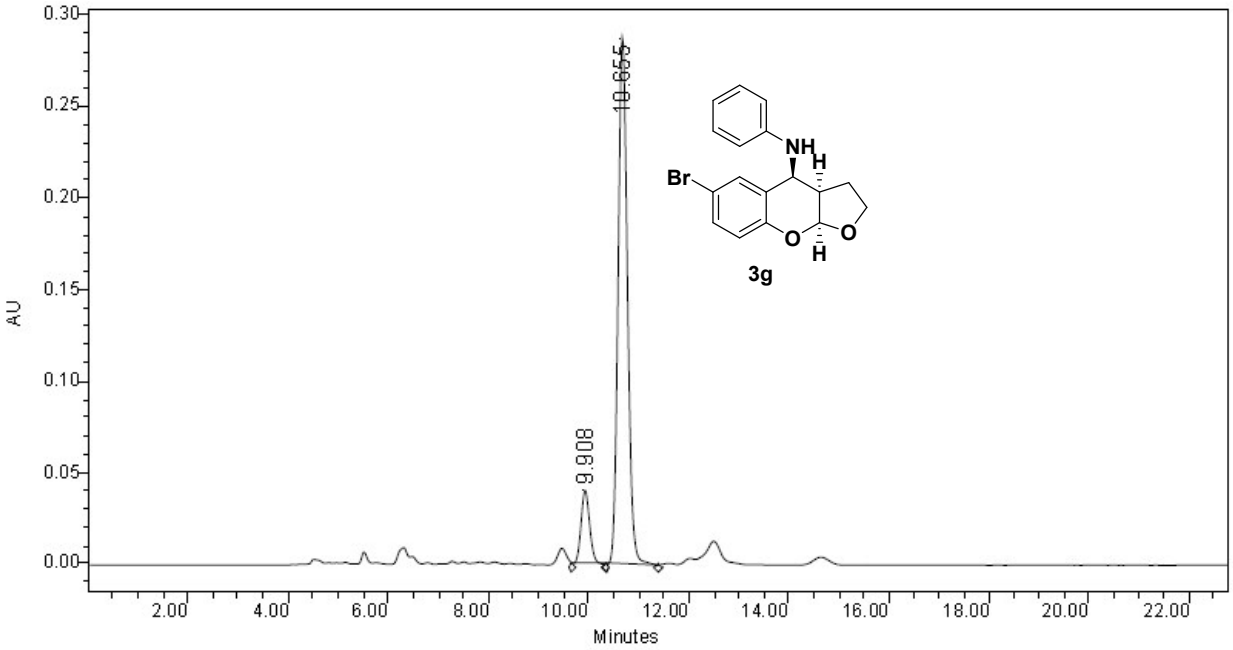

NH
H
Br
O
O
H
3g


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



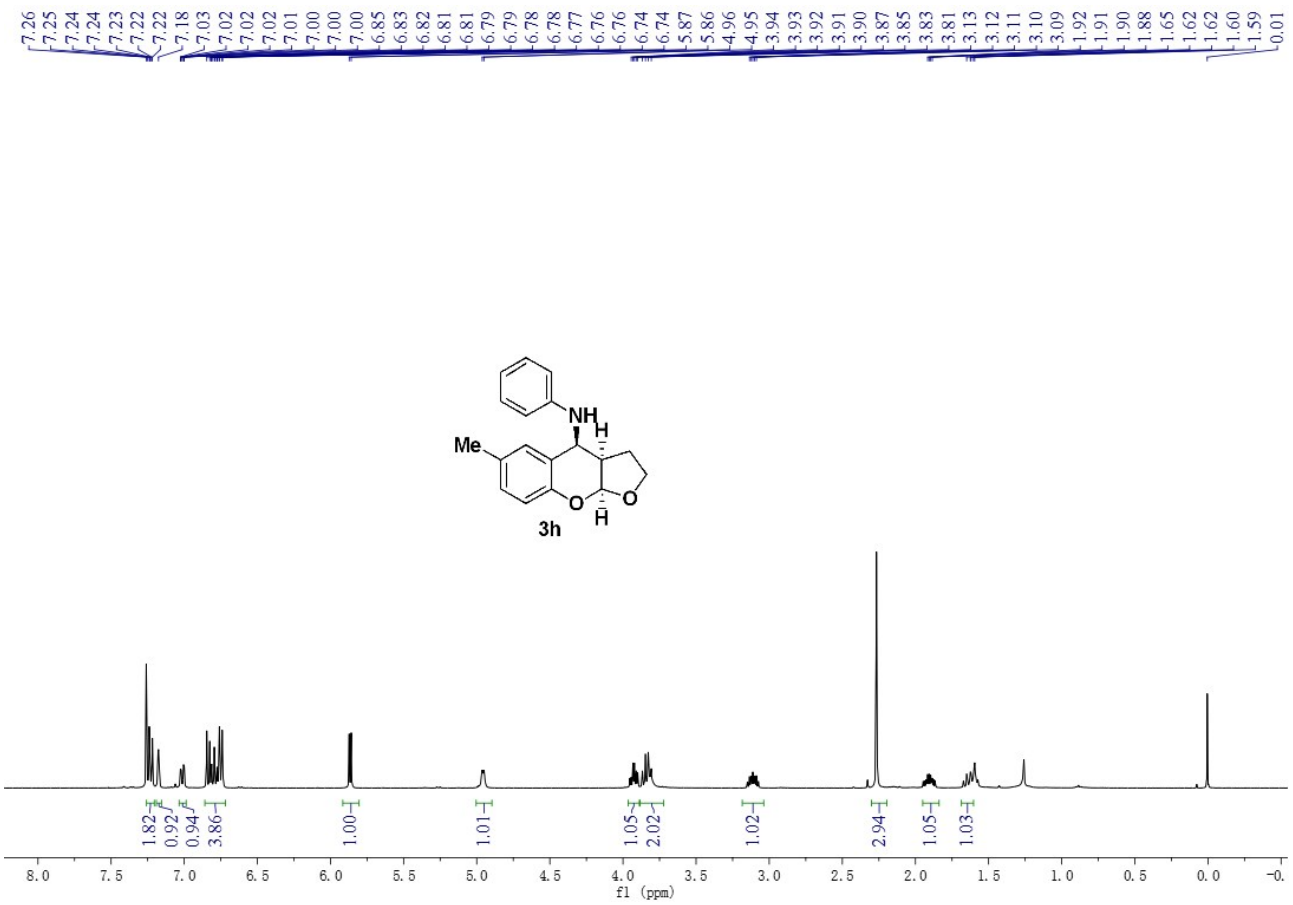
rac-3g

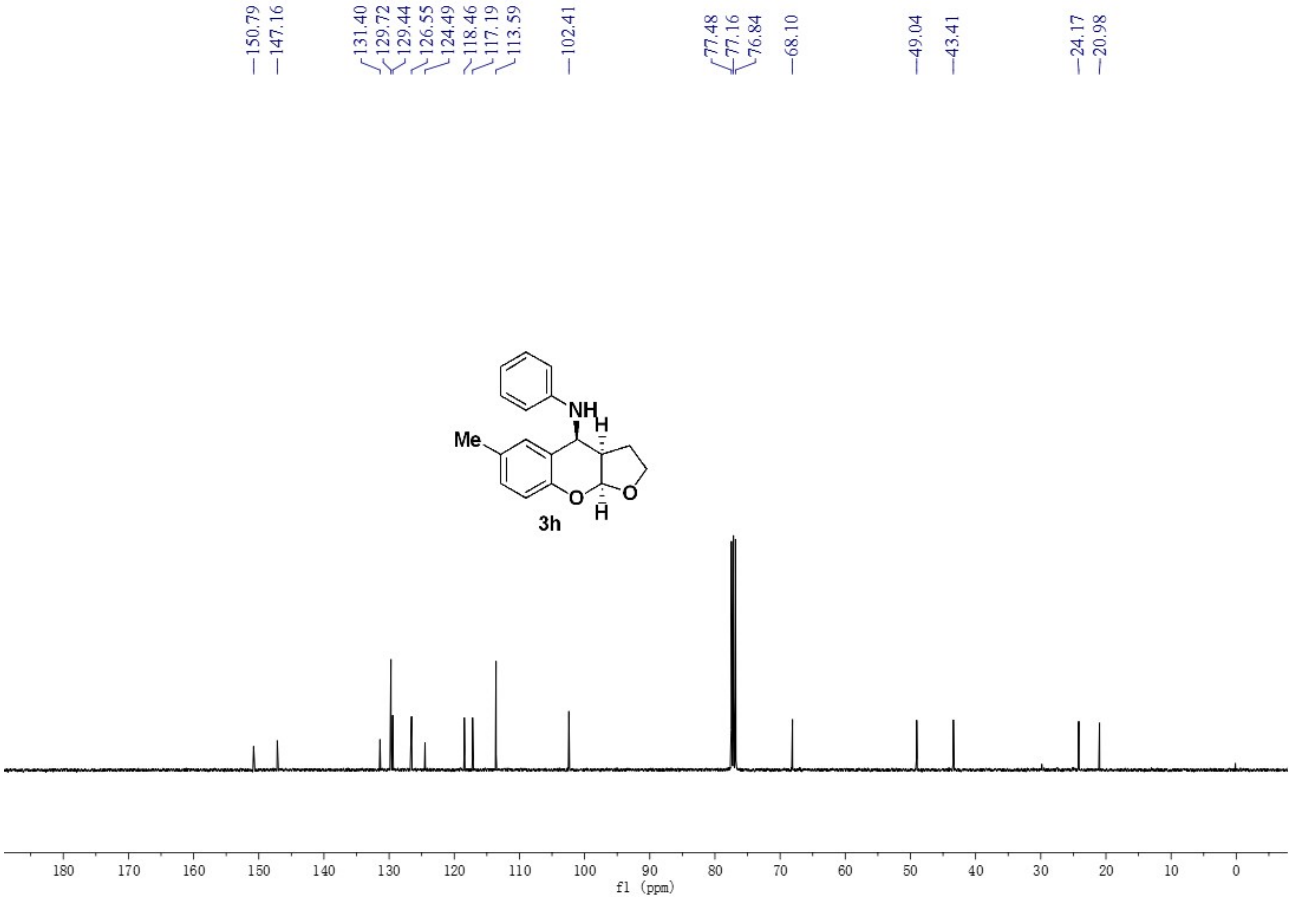
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	13.566	5896991	50.05	371863	52.63
2	14.695	5886040	49.95	334673	47.37

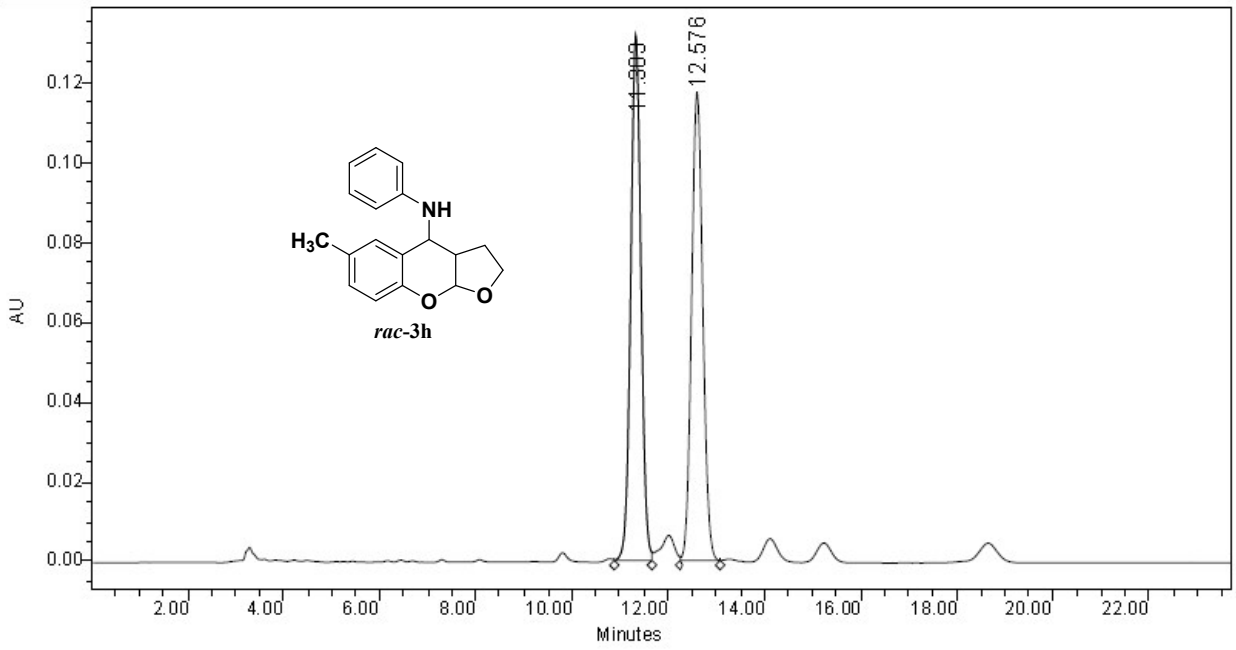


3g

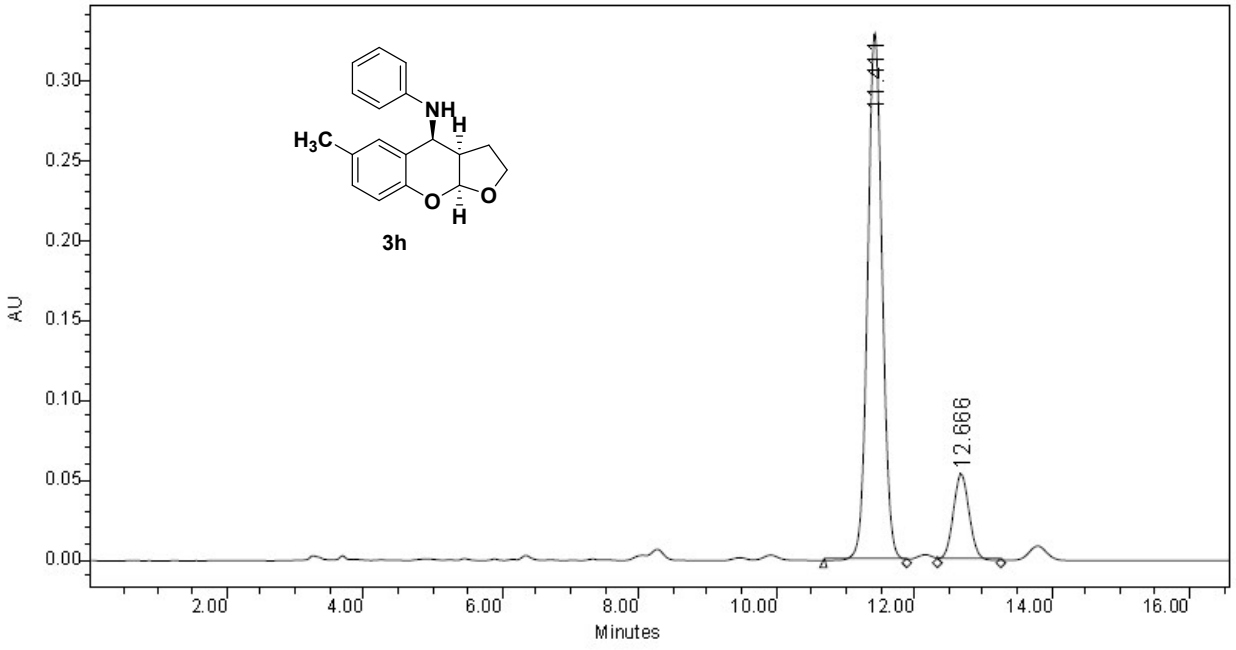
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.908	504789	11.81	40970	12.42
2	10.655	3767972	88.19	288893	87.58


7.26 7.25 7.24 7.24 7.23 7.22 7.22 7.18 7.03 7.02 7.02 7.02 7.01 7.00 7.00 7.00 6.85 6.83 6.82 6.81 6.81 6.79 6.79 6.78 6.78 6.77 6.76 6.76 6.74 6.74 5.87 5.86 4.96 4.95 3.94 3.93 3.92 3.91 3.90 3.87 3.85 3.83 3.81 3.13 3.12 3.11 3.10 3.09 1.92 1.91 1.90 1.88 1.65 1.62 1.62 1.60 1.59 0.01
NH
H
Me
O
O
H
3h
1.82 0.92 0.94 3.86 1.00 1.01 1.05 2.02 1.02 2.94 1.05 1.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


150.79 147.16 131.40 129.72 129.44 126.55 124.49 118.46 117.19 113.59 102.41 77.48 77.16 76.84 68.10 49.04 43.41 24.17 20.98
NH
H
Me
O
O
H
3h
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.303	1972065	50.61	131962	52.84
2	12.576	1924859	49.39	117754	47.16

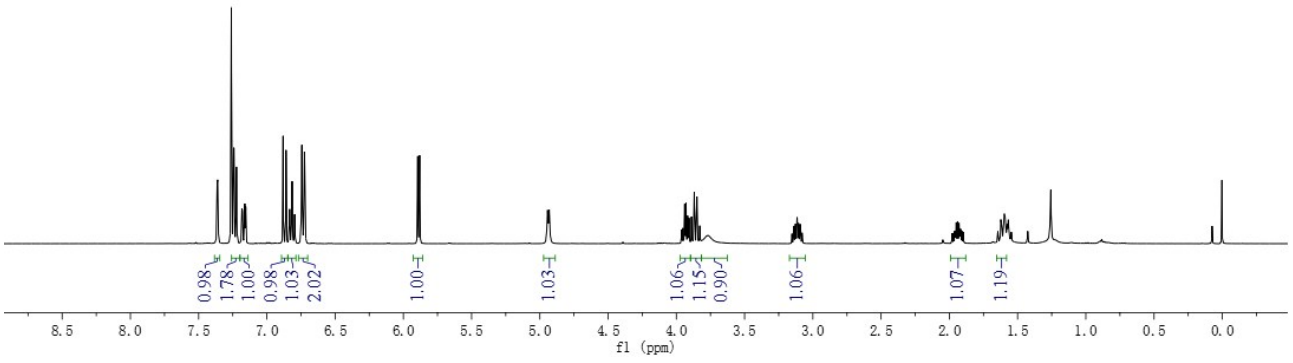


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.411	4881612	84.61	330276	85.94
2	12.666	887977	15.39	54052	14.06


7.37
7.36
7.36
7.36
7.26
7.24
7.24
7.23
7.22
7.18
7.18
7.18
7.18
7.16
7.16
7.16
7.16
6.88
6.86
6.83
6.83
6.81
6.80
6.80
6.79
6.75
6.74
6.72
6.72
5.89
5.88
4.94
4.93
3.95
3.94
3.93
3.92
3.91
3.89
3.87
3.85
3.83
3.14
3.13
3.12
3.10
3.09
1.95
1.94
1.93
1.92
1.92
1.62
1.61
1.60
1.59
1.58
1.57


NH
H
Cl
O
O
H

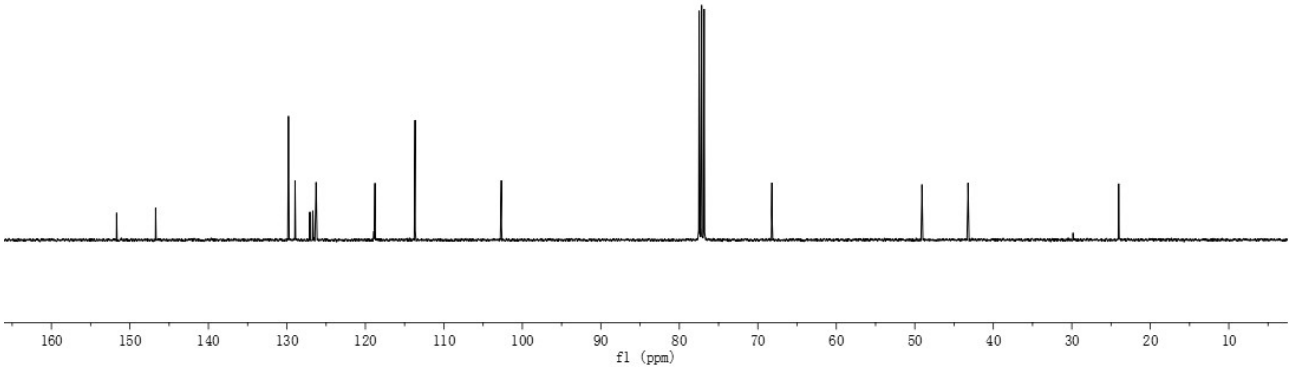
3i

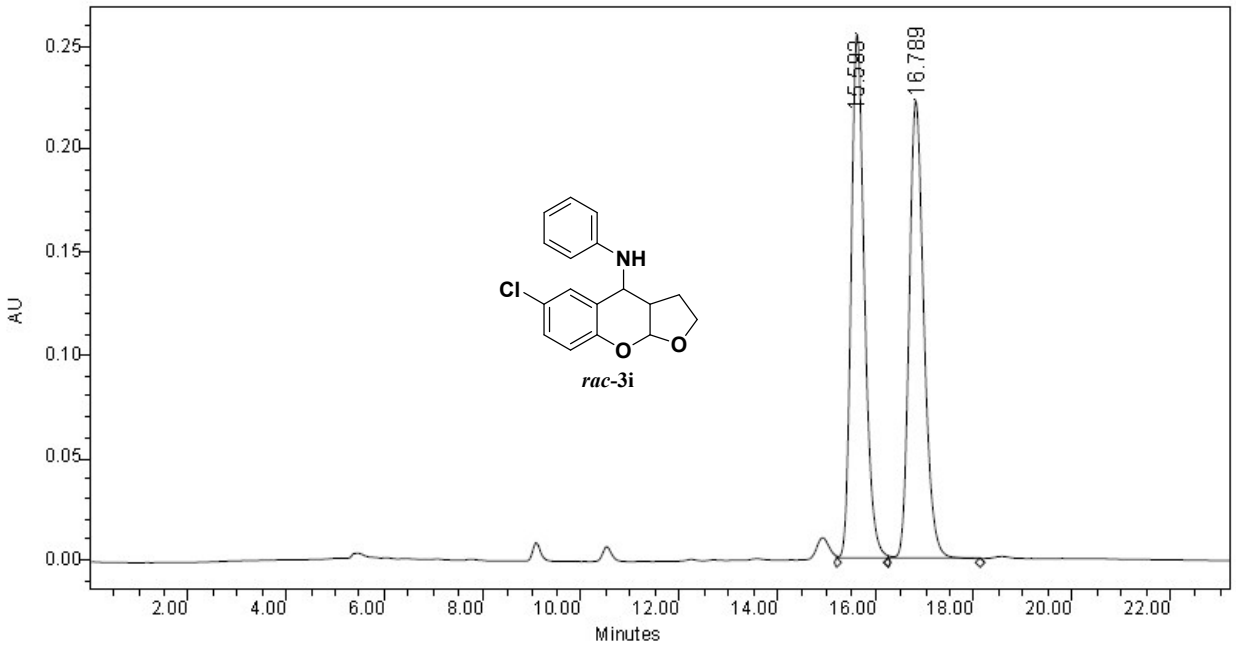

0.98
1.78
1.00
0.98
1.03
2.02
1.00
1.03
1.06
1.15
0.90
1.06
1.07
1.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


151.69
146.72
129.80
128.96
127.07
126.70
126.28
118.89
118.77
113.66
102.67
77.48
77.16
76.84
68.21
49.09
43.22
24.03


NH
H
Cl
O
O
H

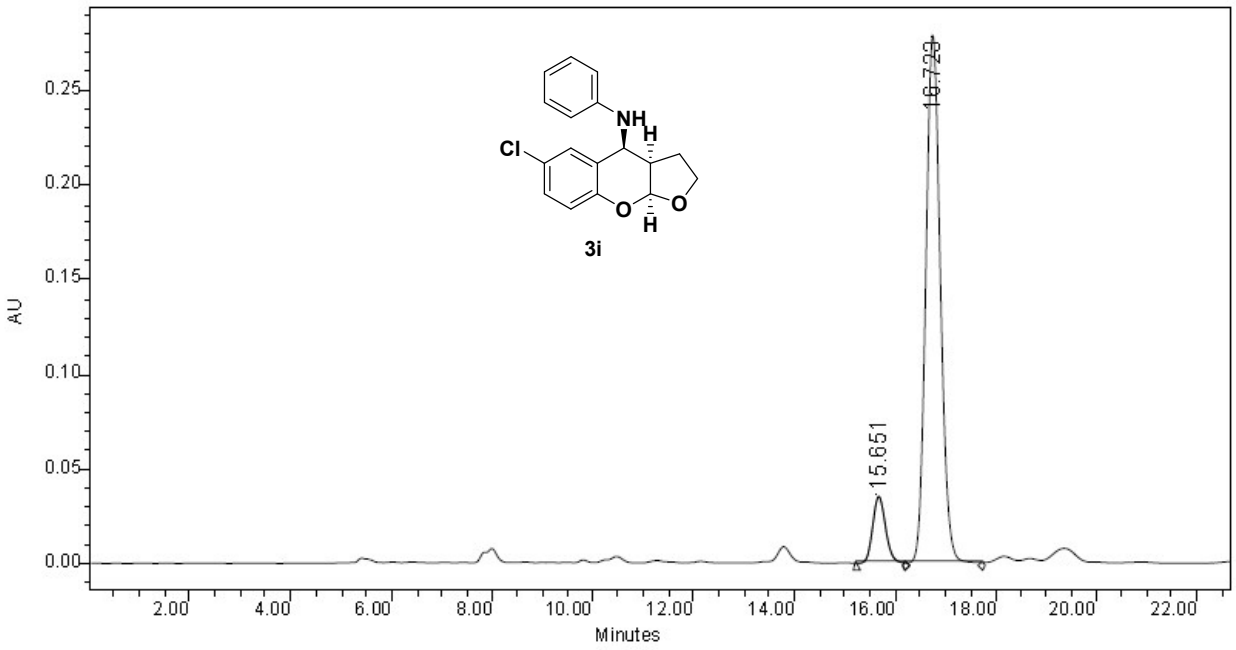
3i


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



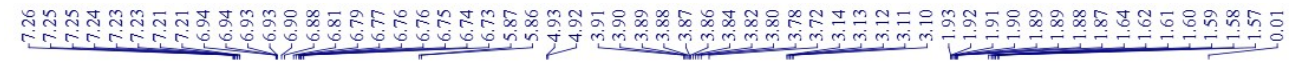
rac-3i

	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	15.593	4821228	50.79	255305	53.38
2	16.789	4671719	49.21	223013	46.62



3i

	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	15.651	624020	10.03	35285	11.19
2	16.723	5599548	89.97	280133	88.81


7.26
7.25
7.25
7.24
7.23
7.23
7.21
7.21
6.94
6.94
6.93
6.93
6.90
6.88
6.81
6.79
6.77
6.76
6.76
6.75
6.74
6.73
5.87
5.86
4.93
4.92
3.91
3.90
3.89
3.88
3.87
3.86
3.84
3.82
3.80
3.78
3.72
3.14
3.13
3.12
3.11
3.10
1.93
1.92
1.91
1.90
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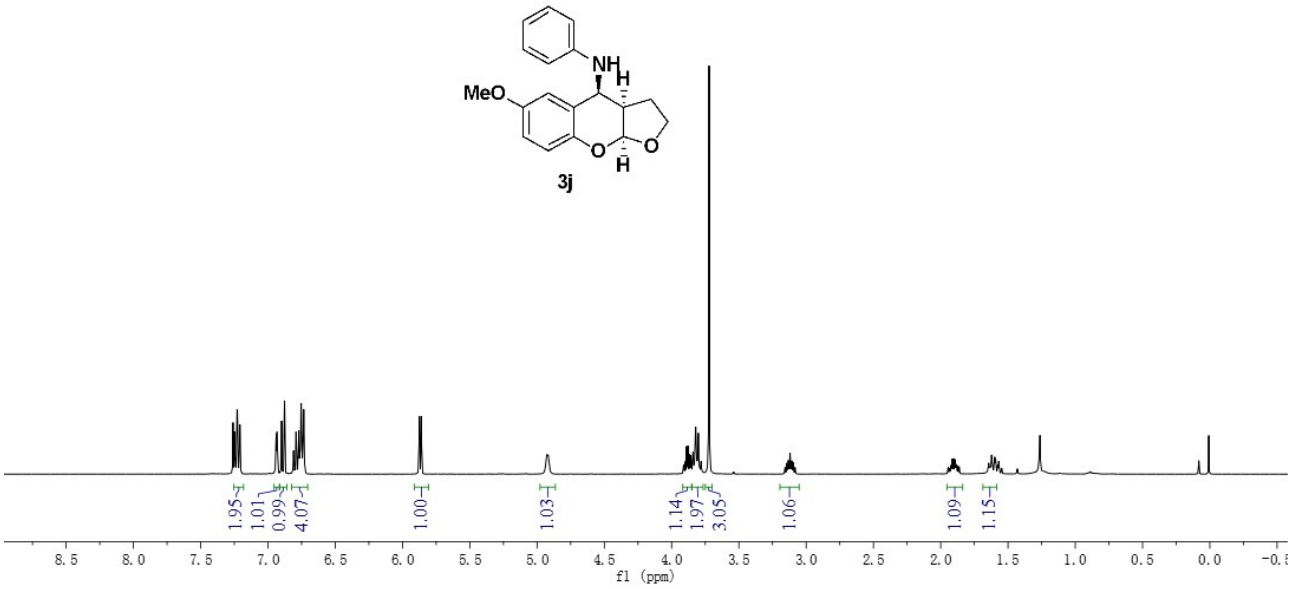
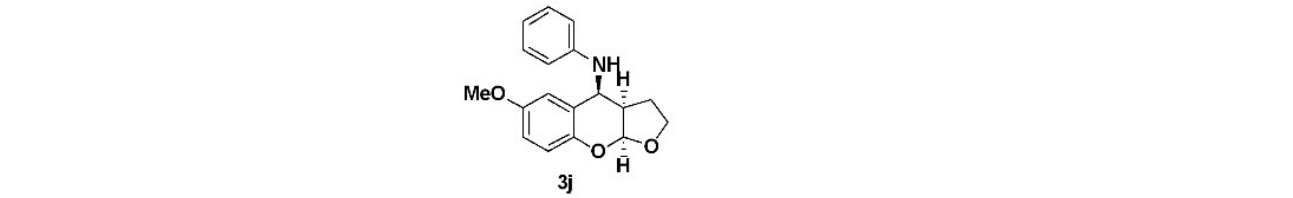
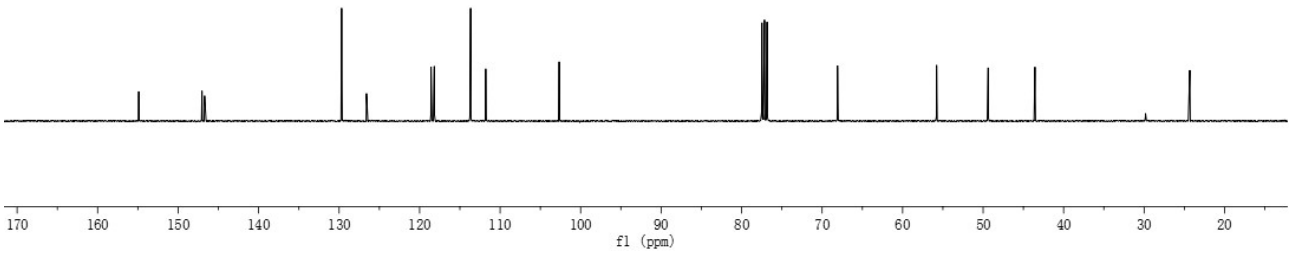
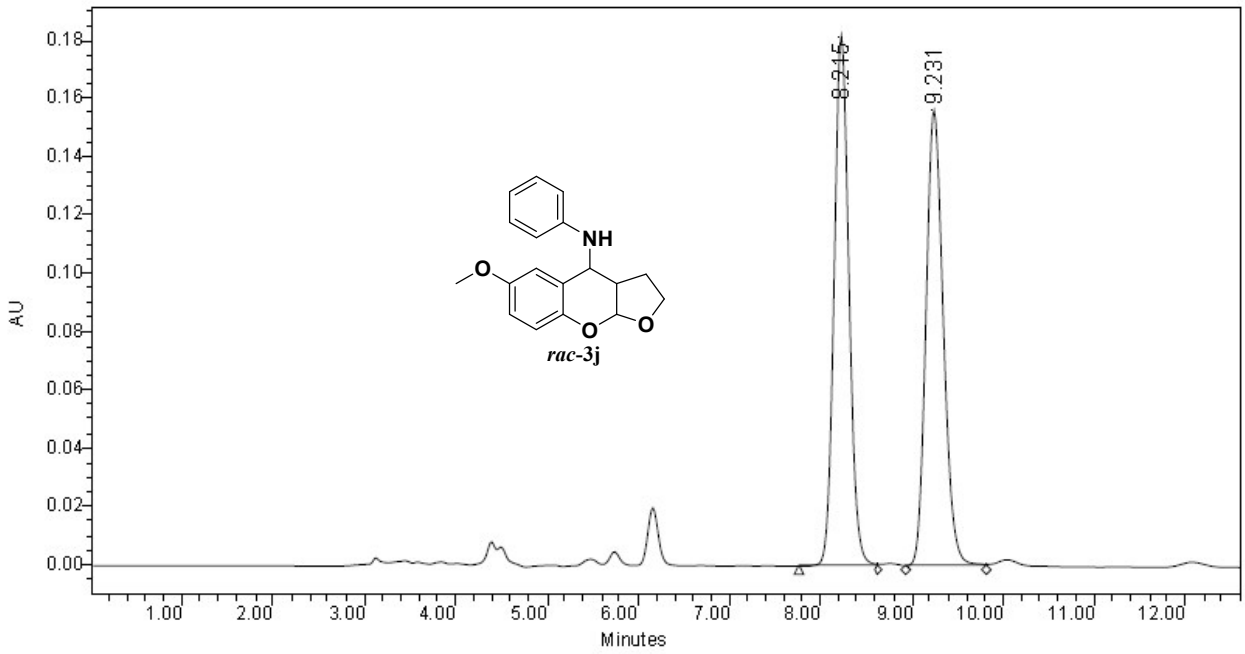
1.61
1.60
1.59
1.58
1.57
0.01


NH
H
MeO
O
O
H
3j
1.95
1.01
0.99
4.07
1.00
1.03
1.14
1.97
3.05
1.06
1.09
1.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


154.89
147.03
146.71
129.69
126.60
118.58
118.18
113.73
113.67
111.79
102.66
77.48
77.16
76.84
68.08
55.78
49.37
43.56
24.32

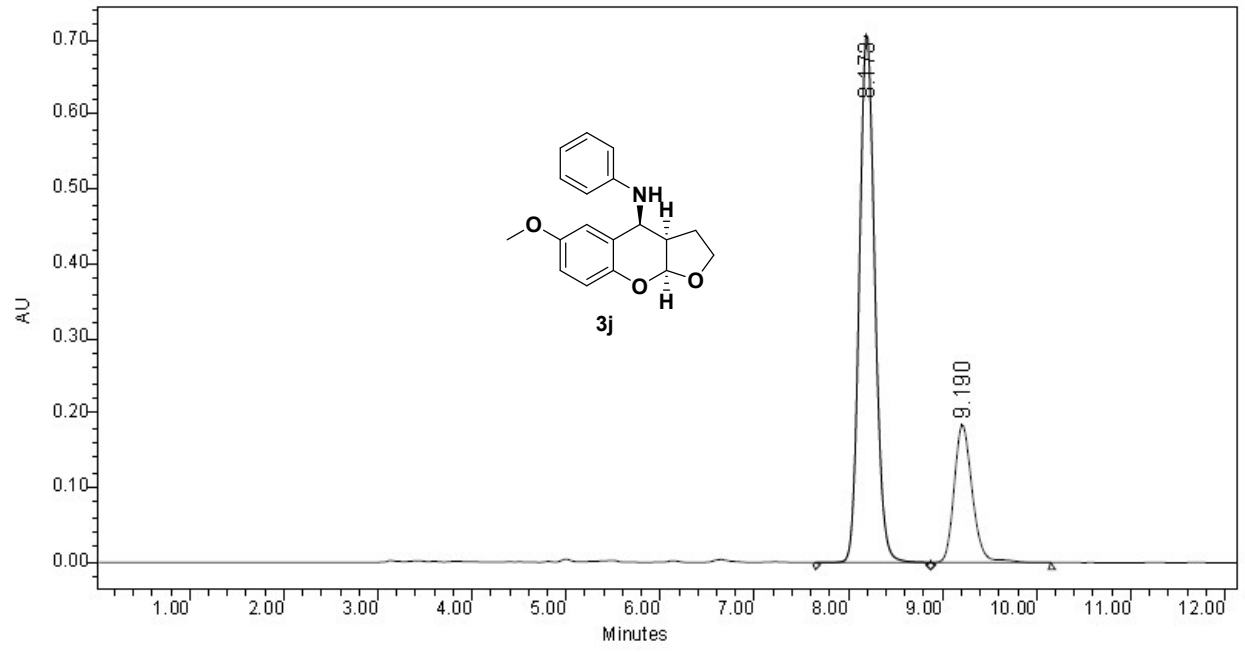

NH
H
MeO
O
O
H
3j


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)



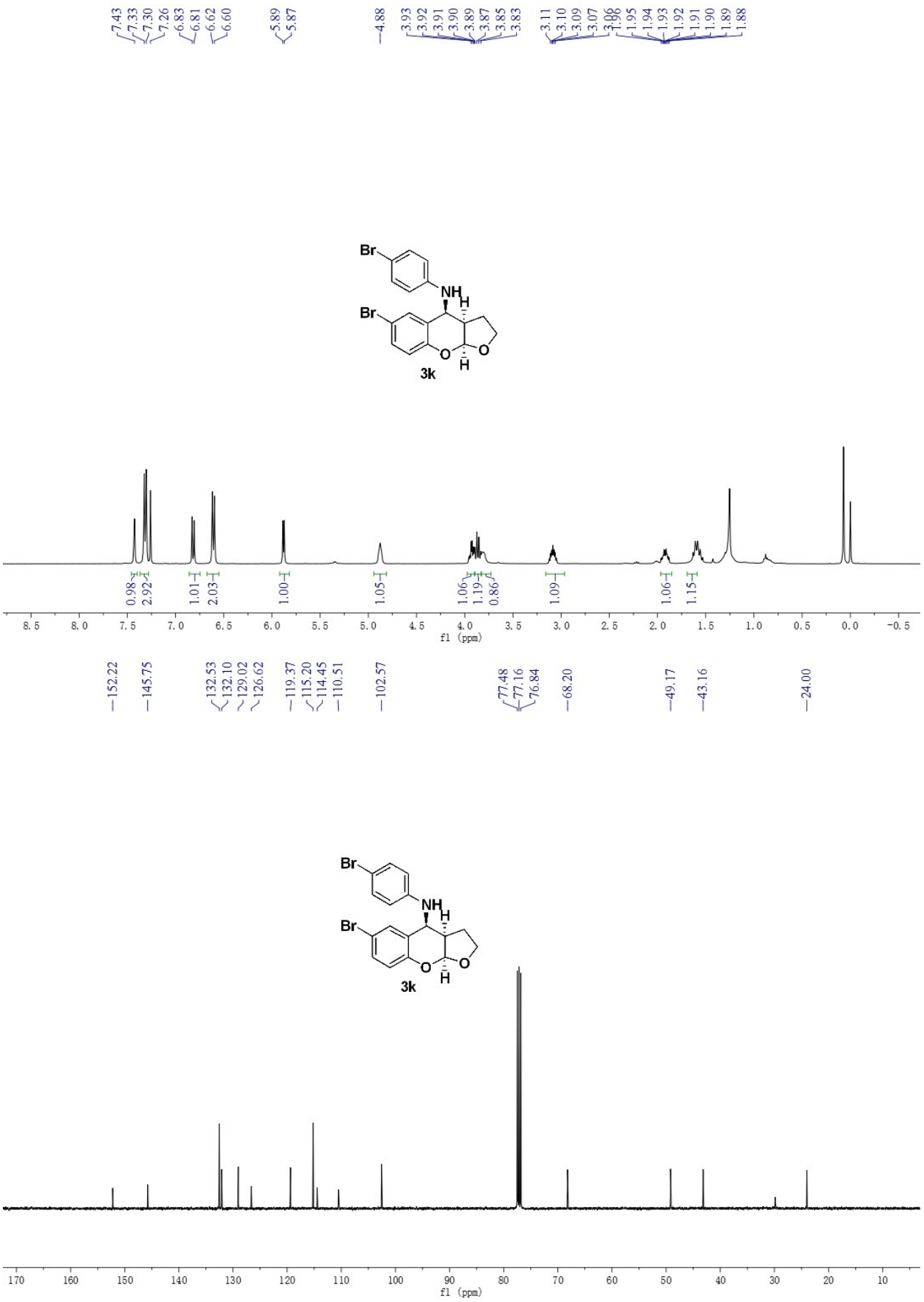
rac-3j

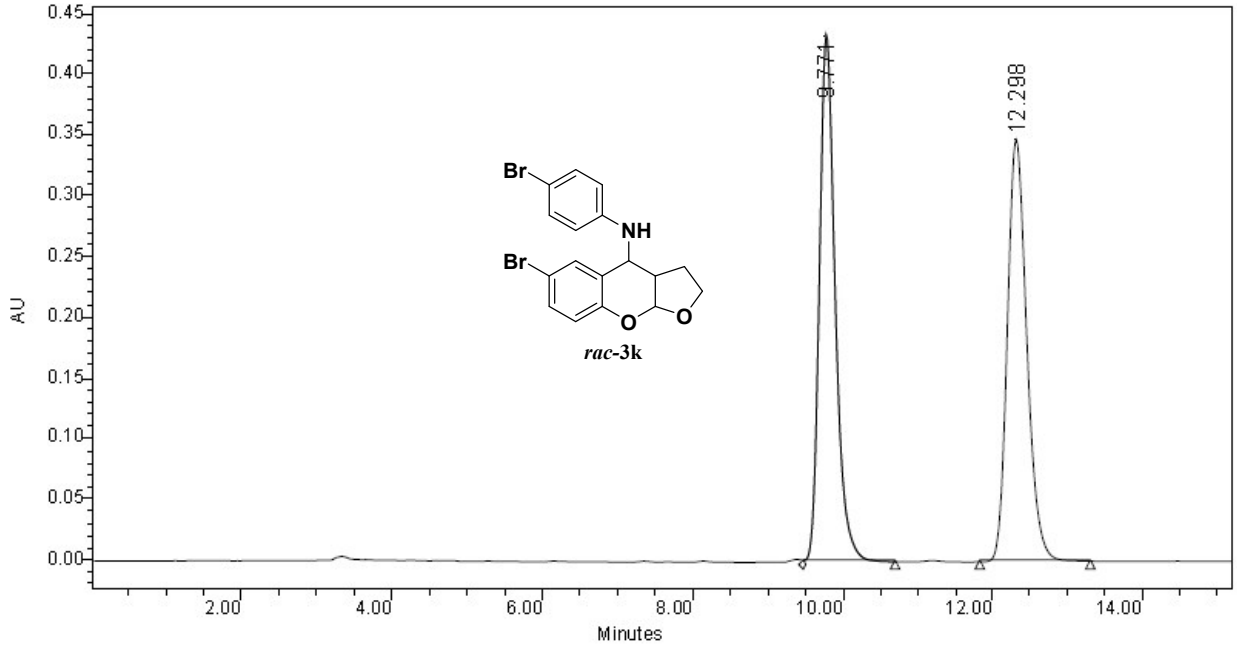
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.215	2065525	49.86	182137	53.76
2	9.231	2077315	50.14	156652	46.24



3j

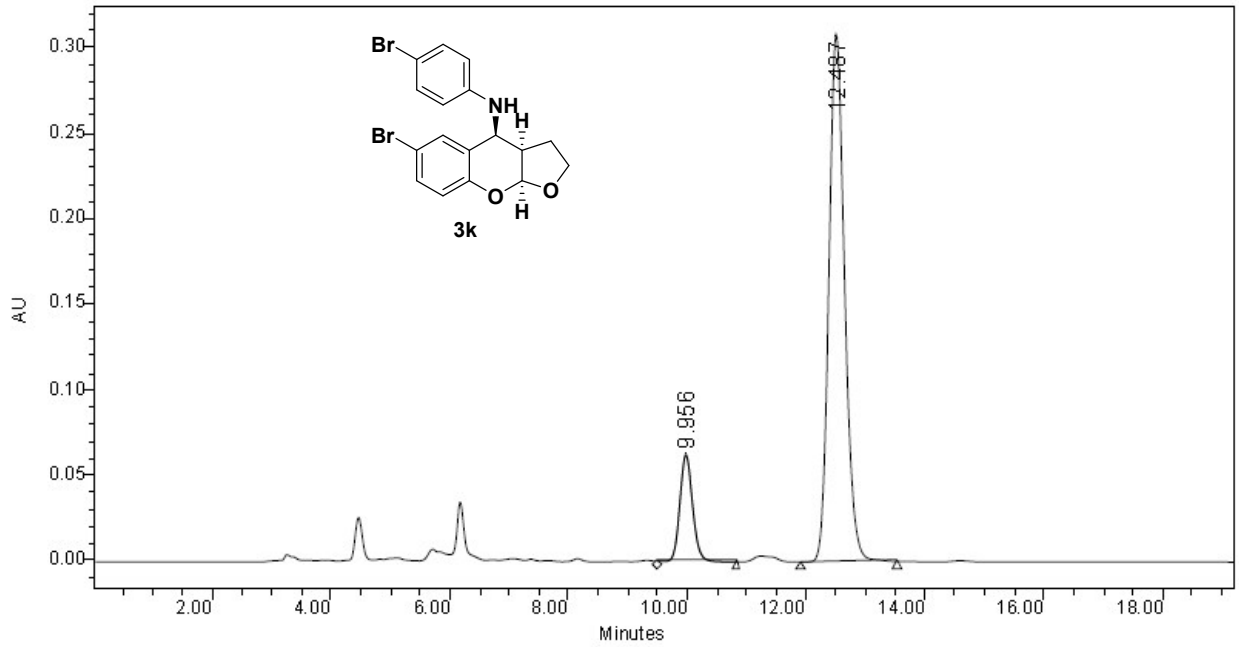
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.173	8115336	76.57	710266	79.35
2	9.190	2483135	23.43	184887	20.65


7.43
7.33
7.30
7.26
6.83
6.81
6.62
6.60
5.89
5.87
4.88
3.93
3.92
3.91
3.90
3.89
3.87
3.85
3.83
3.11
3.10
3.09
3.07
3.06
1.95
1.94
1.93
1.92
1.91
1.90
1.89
1.88
Br
NH
H
Br
O
O
H
3k
0.98
2.92
1.01
2.03
1.00
1.05
1.06
1.19
0.86
1.09
1.06
1.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
152.22
145.75
132.53
132.10
129.02
126.62
119.37
115.20
114.45
110.51
102.57
77.48
77.16
76.84
68.20
49.17
43.16
24.00
Br
NH
H
Br
O
O
H
3k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



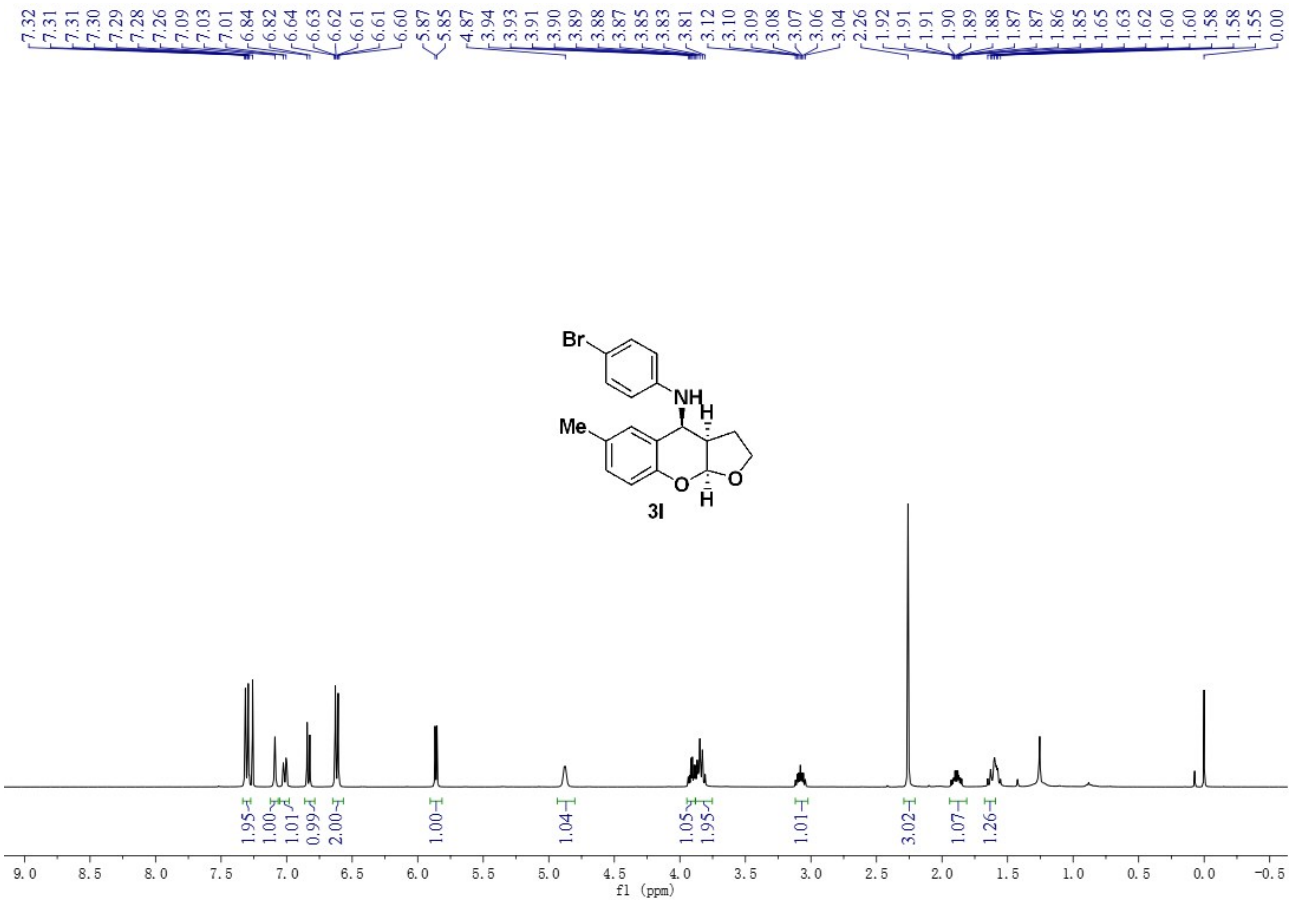
rac-3k

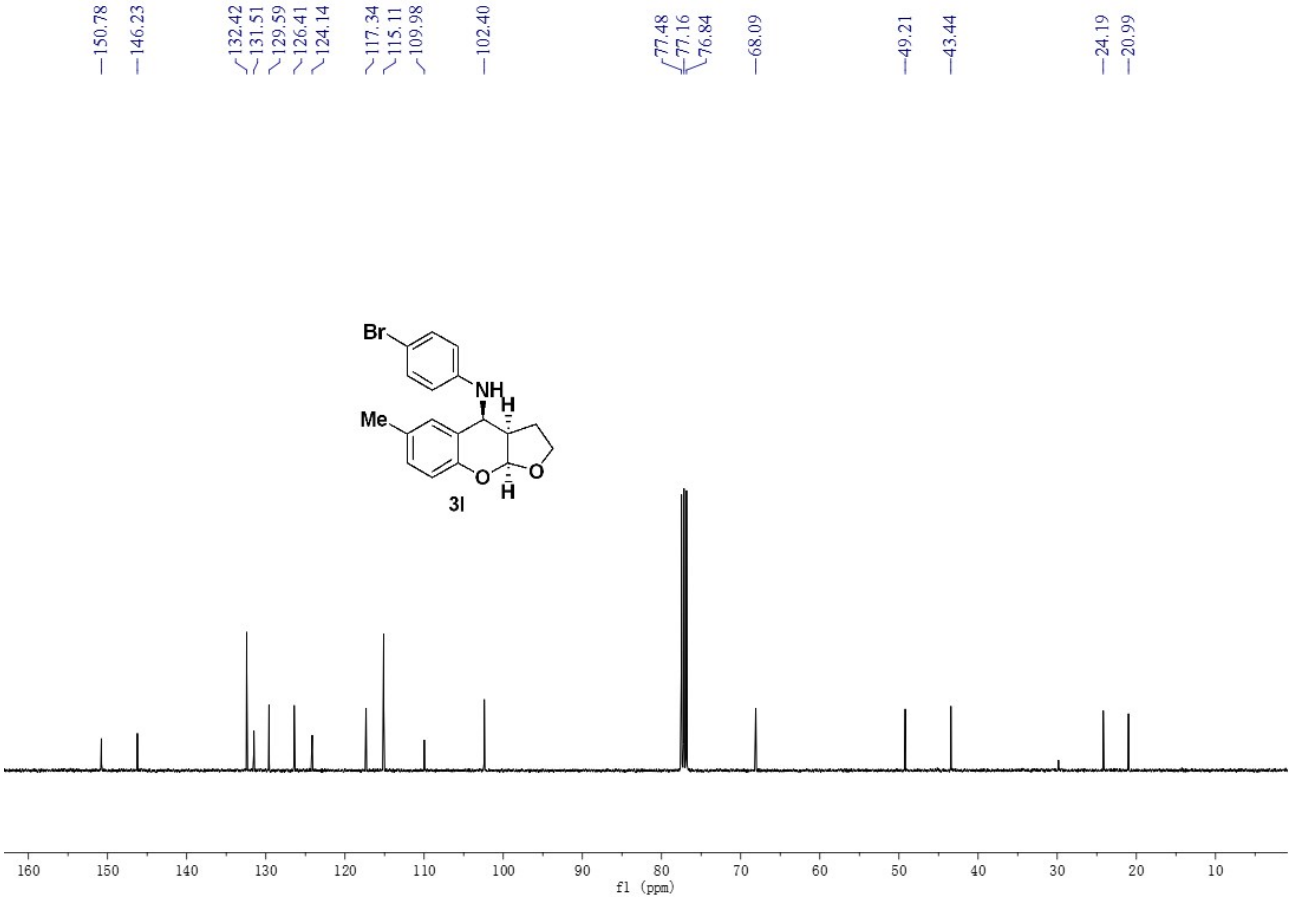
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.771	6341838	50.36	434497	55.57
2	12.298	6252275	49.64	347330	44.43

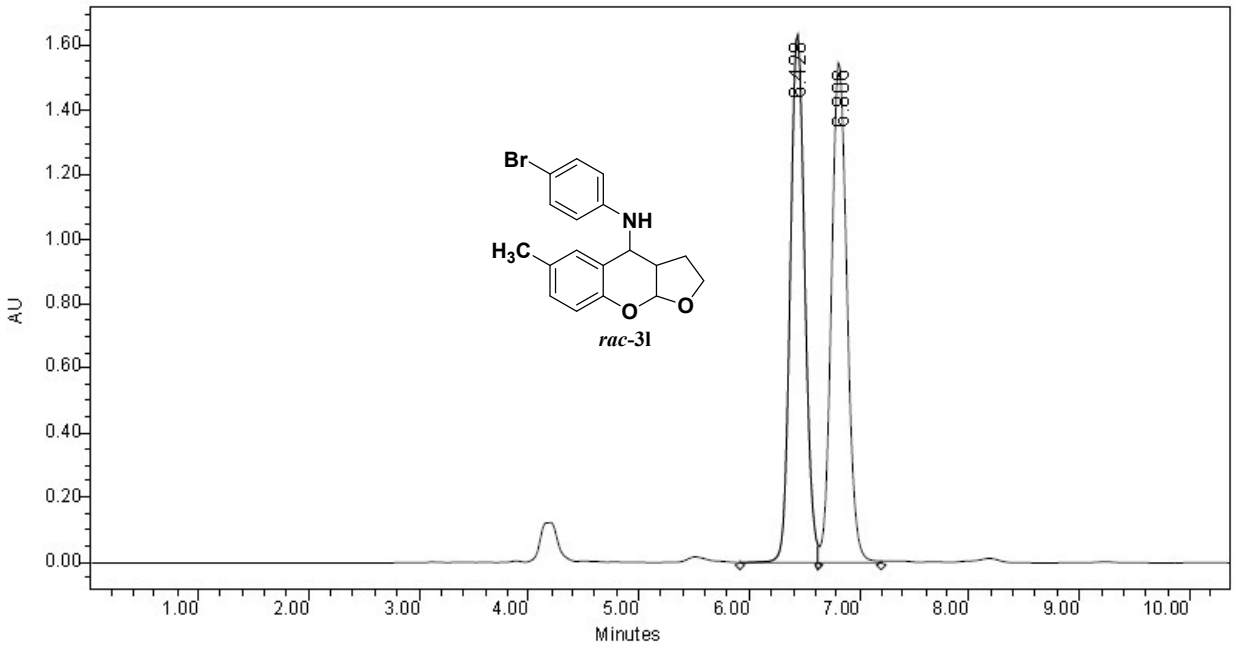


3k

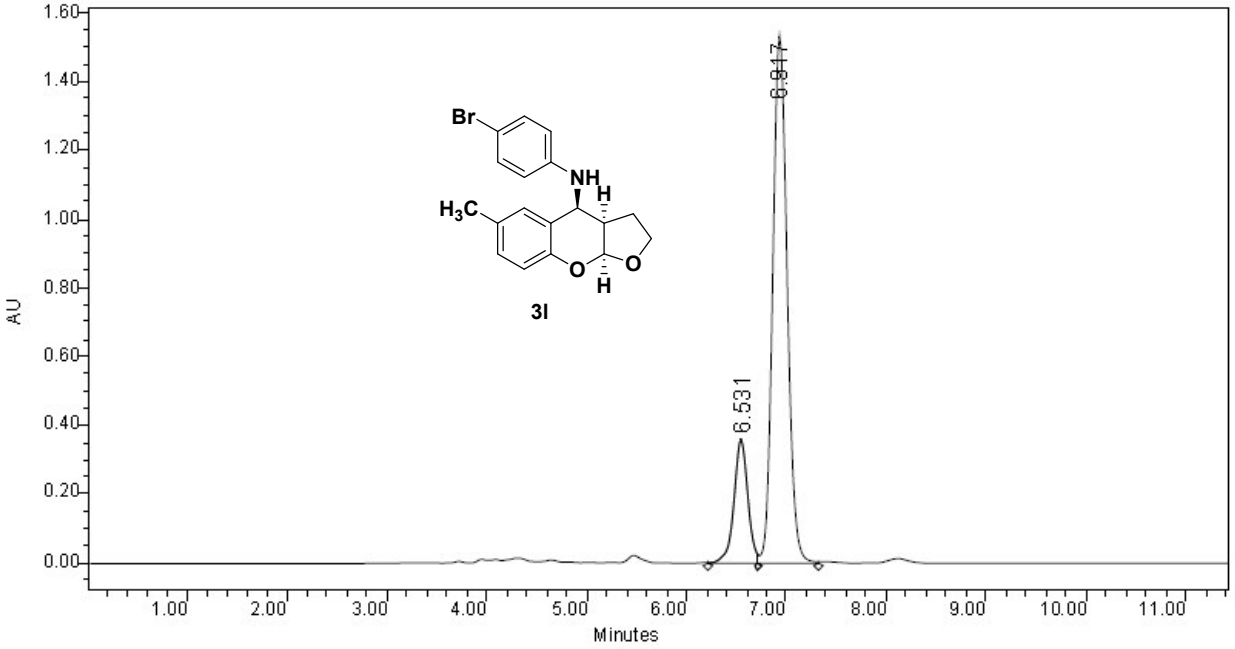
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.956	938831	14.22	62565	16.86
2	12.487	5665014	85.78	308592	83.14


7.32 7.31 7.31 7.30 7.29 7.28 7.26 7.09 7.03 7.01 6.84 6.82 6.64 6.63 6.62 6.61 6.61 6.60 5.87 5.85 4.87 3.94 3.93 3.91 3.90 3.89 3.88 3.87 3.85 3.83 3.81 3.12 3.10 3.09 3.08 3.07 3.06 3.04 2.26 1.92 1.91 1.91 1.90 1.89 1.88 1.87 1.87 1.86 1.85 1.65 1.63 1.62 1.60 1.60 1.58 1.58 1.55 0.00
Br
NH
H
Me
O
O
H
3l
1.95 1.00 1.01 0.99 2.00 1.00 1.04 1.05 1.95 1.01 3.02 1.07 1.26
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


150.78 146.23 132.42 131.51 129.59 126.41 124.14 117.34 115.11 109.98 102.40 77.48 77.16 76.84 68.09 49.21 43.44 24.19 20.99
Br
NH
H
Me
O
O
H
3l
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	6.428	15163651	49.88	1641535	51.34
2	6.806	15236758	50.12	1555926	48.66

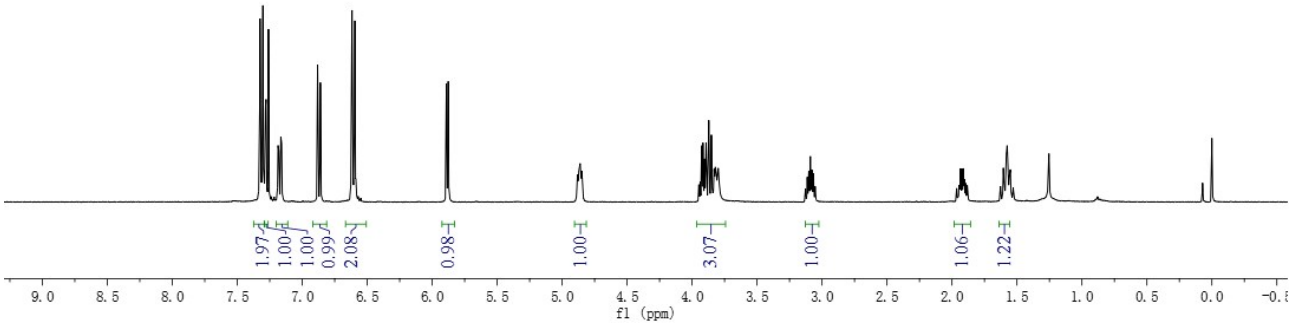


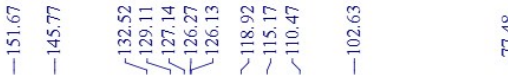
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	6.531	3515801	18.60	359972	19.00
2	6.917	15381761	81.40	1534302	81.00


7.32
7.32
7.30
7.29
7.28
7.28
7.26
7.19
7.18
7.16
7.16
6.88
6.86
6.62
6.60
5.89
5.88
4.88
4.87
4.86
4.85
3.93
3.92
3.90
3.89
3.87
3.85
3.11
3.10
3.09
3.08
3.07
1.94
1.94
1.93
1.92
1.91
1.90
1.90
1.89
1.60
1.60
1.58
1.58
1.56
1.55
1.25
0.00


Br
NH
H
Cl
O
O
H

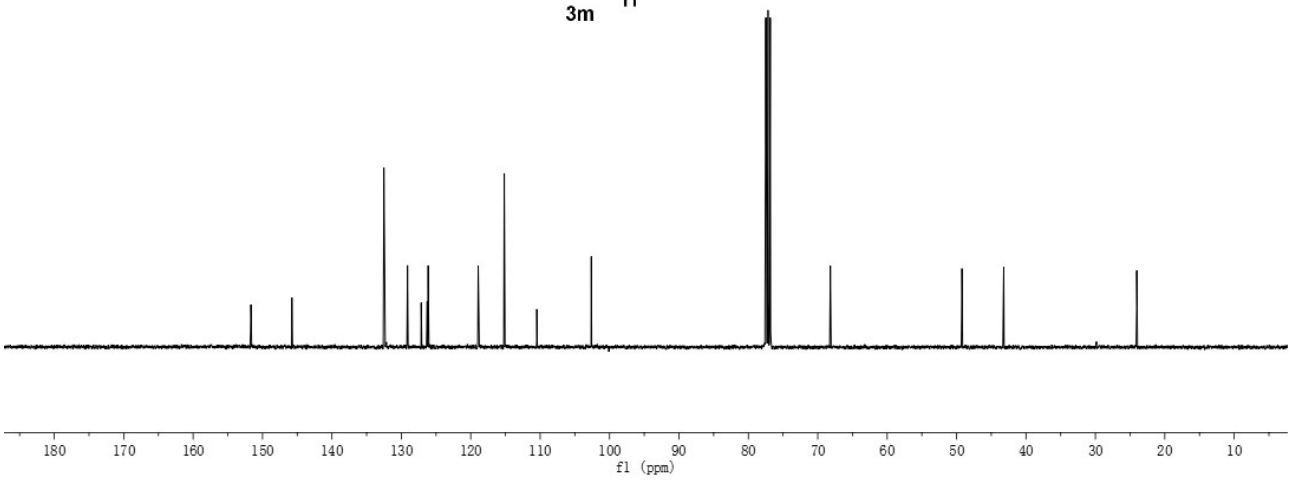
3m

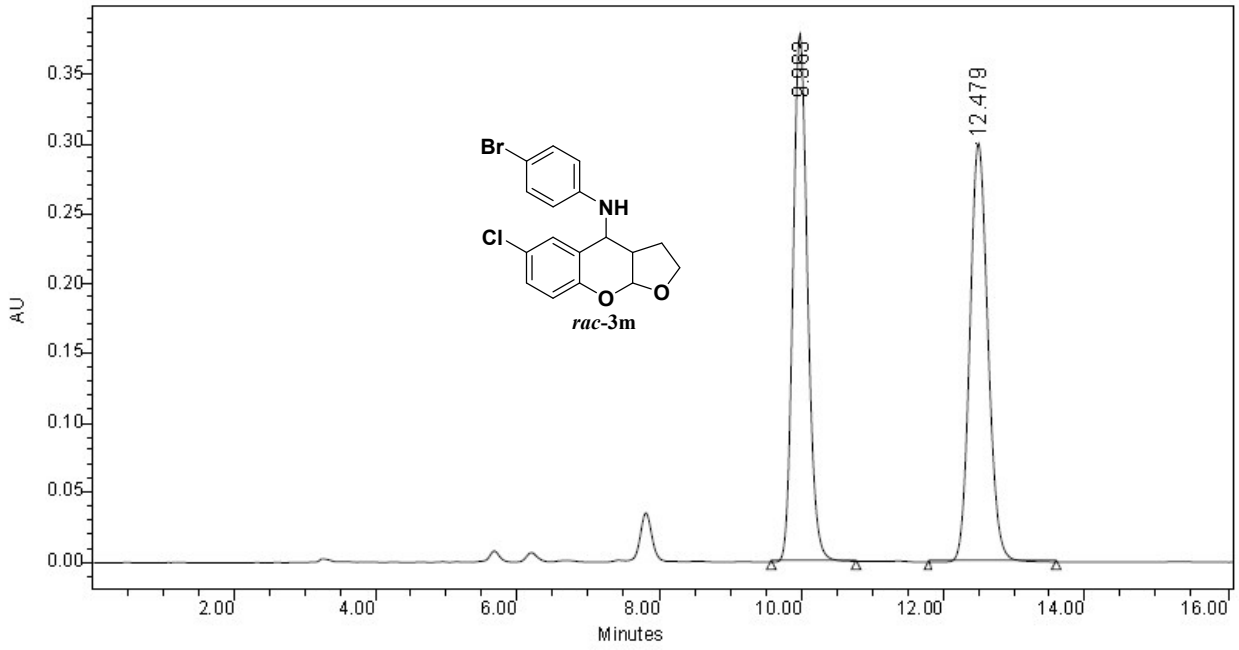

1.97
1.00
1.00
0.99
2.08
0.98
1.00
3.07
1.00
1.06
1.22
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


151.67
145.77
132.52
129.11
127.14
126.27
126.13
118.92
115.17
110.47
102.63
77.48
77.16
76.84
68.19
49.22
43.21
24.03

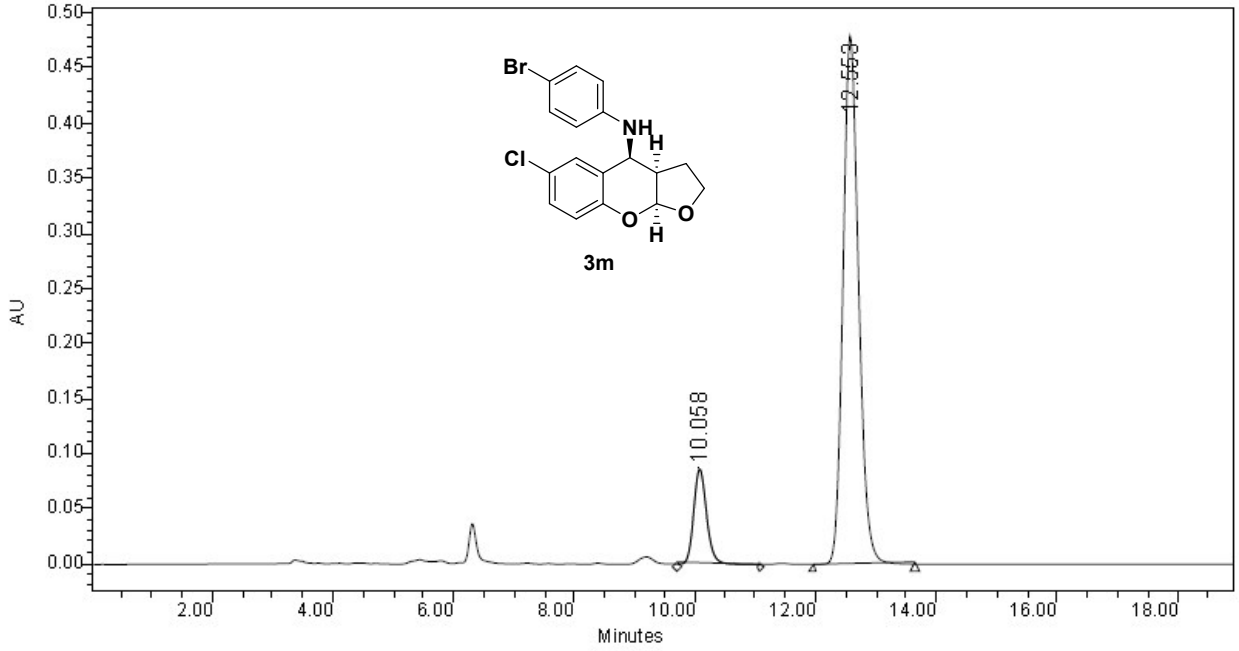

Br
NH
H
Cl
O
O
H

3m

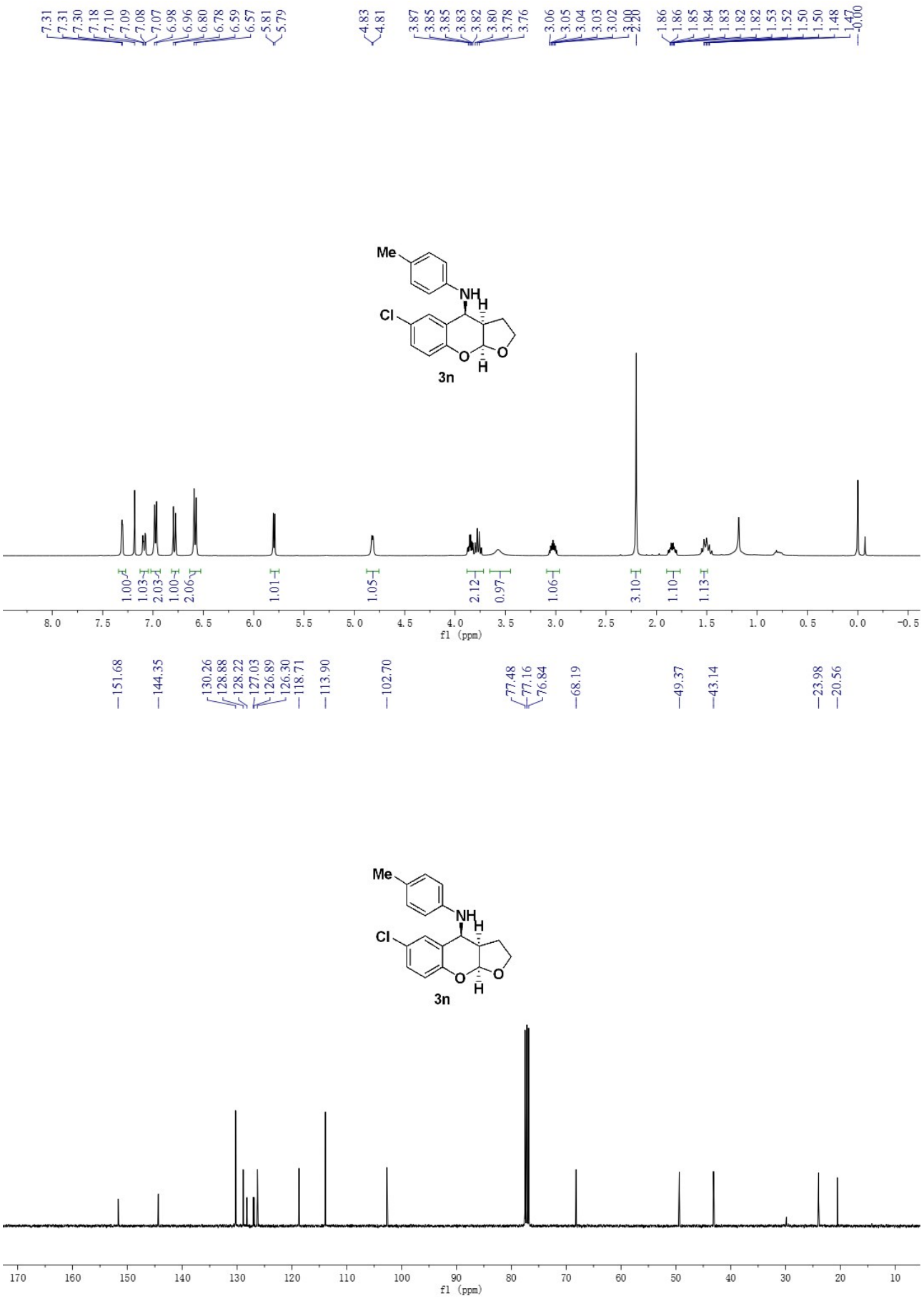

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

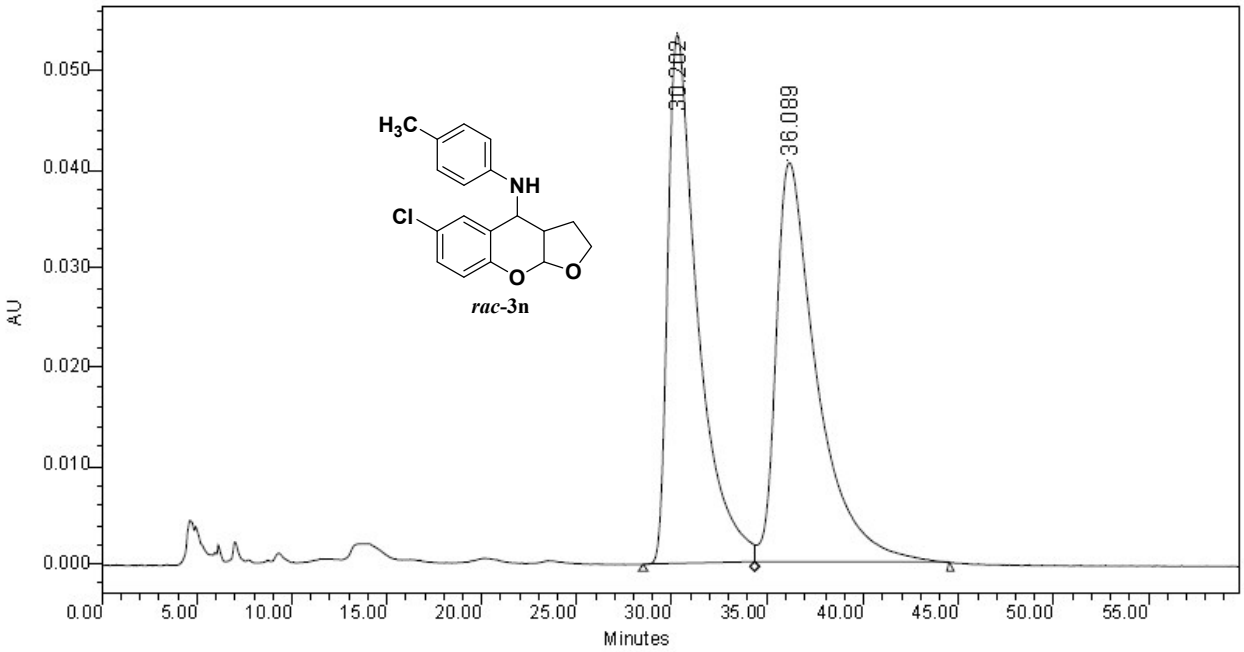


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.963	5425842	50.46	379558	55.76
2	12.479	5326122	49.54	301173	44.24

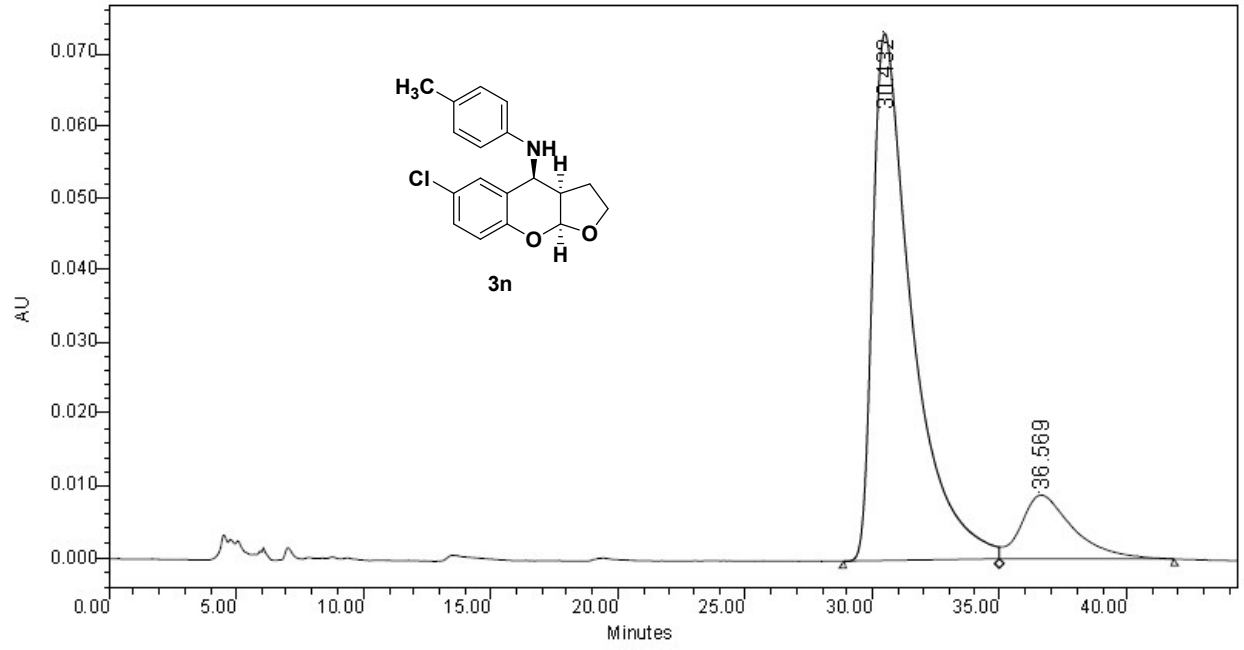


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.058	1296129	13.08	86651	15.29
2	12.553	8613027	86.92	480241	84.71


7.31
7.31
7.30
7.18
7.10
7.09
7.08
7.07
6.98
6.96
6.80
6.78
6.59
6.57
5.81
5.79
4.83
4.81
3.87
3.85
3.85
3.83
3.82
3.80
3.78
3.76
3.06
3.05
3.04
3.03
3.02
2.20
1.86
1.86
1.85
1.84
1.83
1.82
1.82
1.53
1.52
1.50
1.50
1.48
1.47
0.00
Me
NH
H
Cl
O
O
H
3n
1.00
1.03
2.03
1.00
2.06
1.01
1.05
2.12
0.97
1.06
3.10
1.10
1.13
f1 (ppm)
151.68
144.35
130.26
128.88
128.22
127.03
126.89
126.30
118.71
113.90
102.70
77.48
77.16
76.84
68.19
49.37
43.14
23.98
20.56
Me
NH
H
Cl
O
O
H
3n
f1 (ppm)



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	30.202	5902731	49.18	53601	56.91
2	36.089	6099971	50.82	40590	43.09



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	30.432	7873030	85.84	73285	89.04
2	36.569	1298259	14.16	9018	10.96