Catalytic Asymmetric [4+2] Cycloaddition of 1-((2-Aryl)vinyl)naphthalen-2-ols with in situ Generated *ortho*-Quinone Methides for the Synthesis of Polysubstituted Chromanes

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Supporting Information

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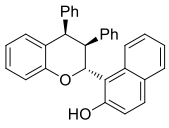
1. General Information

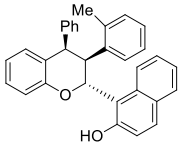
Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ and DMSO-d_6. ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.20 ppm, DMSO-d_6 at 39.51 ppm). The enantiomeric excesses were determined by chiral HPLC analysis. HPLC analysis was performed on Shimadzu SCL-10A*VP* HPLC systems consisting of the followings: pump, LC-10AD; detector, SPD-10A measured at 254 nm. HRMS was recorded on Bruker Q TOF. Optical rotations were measured with a Perkin-Elmer-341 polarimeter. Melting points were recorded on a Büchi Melting Point B-545.

2. General procedure for the synthesis of chromanes 3

In an ordinary vial equipped with a magnetic stirring bar, the *ortho*-hydroxy benzylic alcohols **2** (0.15 mmol, 1.5 equiv) were added to a solution of 1-vinylnaphthalen-2-ols **1** (0.10 mmol, 1.0 equiv), CPA **D** (5 mol %) and 3 Å MS (20 mg) in toluene (0.5 mL) at 0 ^{o}C. And then, the mixture was stirred at the same temperature for specified time. After completion of the reaction, as indicated by TLC, the chromanes **3** were isolated by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15/1~10/1).

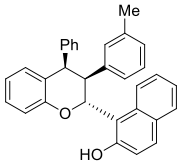


1-((2*R*,3*S*,4*R*)-3,4-diphenylchroman-2-yl)naphthalen-2-ol (3a): White solid; 42.5 mg, 99% yield; >95:5 dr, 97% ee; $[\alpha]_D^{20}$ = -212.9 (*c* 0.75, CH_2Cl_2); mp 190.8-192.6 ℃; The ee was determined by HPLC (Chiralpak IC, *i*-PrOH/hexane = 3/97, flow rate 0.8 mL/min, λ = 254 nm, t_{minor} = 6.8 min, t_{major} = 10.2 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.01 (s, 1H), 8.24 (d, *J* = 8.7 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.27-7.10 (m, 5H), 7.01 (q, *J* = 7.9, 6.6 Hz, 3H), 6.95-6.79 (m, 4H), 6.77-6.56 (m, 5H), 4.77 (dd, *J* = 10.7, 3.4 Hz, 1H), 4.45 (d, *J* = 4.9 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 155.0, 153.6, 141.7, 139.1, 133.0, 130.7, 130.4, 130.1, 128.7, 128.6, 128.5, 128.2, 127.4, 127.0, 126.4, 126.2, 125.3, 123.8, 122.3, 120.4, 117.9, 116.4, 115.4, 69.4, 49.2, 46.6; HRMS (ESI-TOF) calcd. for $C_{31}H_{24}NaO_2$ $[M + Na]^+$ 451.1669; found: 451.1670.

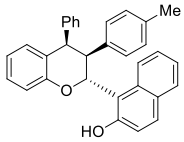


1-((2*R*,3*S*,4*R*)-4-phenyl-3-(o-tolyl)chroman-2-yl)naphthalen-2-ol (3b): White solid; 43.8 mg, 99% yield; >95:5 dr, 99% ee; $[\alpha]_D^{20}$ = -139.2 (*c* 1.02, CH_2Cl_2); mp 114.6-116.7 ℃; The ee was determined by HPLC (Chiralpak AS-H, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, t_{minor} = 9.7 min, t_{major} = 6.9 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.93 (s, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 8.9 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.22 (q, *J* = 6.8 Hz, 2H), 7.17-7.08 (m, 3H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.94-6.84 (m, 2H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.70-6.54 (m, 3H), 6.40 (t, *J* = 7.5 Hz, 1H), 6.09 (s, 1H), 5.15-4.80 (m, 1H), 4.48 (d, *J* = 5.0 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 155.0, 153.7, 141.9, 136.9, 135.3, 133.0, 130.8, 130.4, 130.0, 129.5, 128.7, 128.5, 128.2, 128.1, 127.2, 126.2, 126.1, 125.6, 125.3, 123.9, 123.4, 122.3, 120.3, 117.9, 116.4, 115.2, 69.7, 46.3, 41.9, 19.1; HRMS (ESI-TOF)

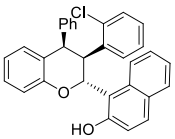
calcd. for $C_{32}H_{26}NaO_2$ $[M + Na]^+$ 465.1825; found: 465.1810.



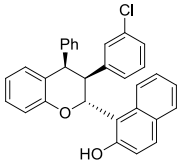
1-((2*R*,3*S*,4*R*)-4-phenyl-3-(m-tolyl)chroman-2-yl)naphthalen-2-ol (3c): White solid; 43.6 mg, 99% yield; >95:5 dr, 98% ee; $[\alpha]_D^{20}$ = -128.7 (*c* 1.10, CH_2Cl_2); mp 109.9-111.8 ℃; The ee was determined by HPLC (Chiralpak AS-H, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, t_{minor} = 9.4 min, t_{major} = 7.8 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.91 (s, 1H), 8.18 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.57 (d, *J* = 8.9 Hz, 1H), 7.36 (t, *J* = 7.1 Hz, 1H), 7.26-7.12 (m, 5H), 7.03 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.96 (t, *J* = 8.7 Hz, 2H), 6.89 (t, *J* = 7.3 Hz, 1H), 6.75-6.68 (m, 2H), 6.67-6.56 (m, 3H), 6.52 (s, 1H), 6.46 (d, *J* = 3.9 Hz, 1H), 4.68 (dd, *J* = 11.8, 5.0 Hz, 1H), 4.40 (d, *J* = 4.9 Hz, 1H), 1.95 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 154.9, 153.6, 141.6, 138.8, 135.6, 133.0, 130.5, 130.3, 129.9, 129.5, 128.6, 128.5, 128.1, 127.2, 126.7, 126.2, 126.0, 125.5, 125.3, 123.6, 122.2, 120.2, 117.8, 116.3, 115.4, 69.4, 49.2, 46.4, 20.9; HRMS (ESI-TOF) calcd. for $C_{32}H_{26}NaO_2$ $[M + Na]^+$ 465.1825; found: 465.1809.



1-((2*R*,3*S*,4*R*)-4-phenyl-3-(p-tolyl)chroman-2-yl)naphthalen-2-ol (3d): White solid; 43.8 mg, 99% yield; >95:5 dr, 98% ee; $[\alpha]_D^{20}$ = -151.9 (*c* 1.18, CH_2Cl_2); mp 137.2-139.0 ℃; The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, t_{minor} = 9.6 min, t_{major} = 6.1 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.90 (s, 1H), 8.19 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.28-7.09 (m, 5H), 7.07-6.83 (m, 4H), 6.74-6.49 (m, 7H), 4.70 (dd, *J* = 11.9, 5.1 Hz, 1H), 4.40 (d, *J* = 5.0 Hz, 1H), 2.04 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 154.9, 153.5, 141.7, 135.9, 134.8, 133.0, 130.5, 130.4, 129.9, 128.6, 128.5, 128.4, 128.1, 127.6, 127.3, 126.3, 126.0, 125.4, 123.7, 122.2, 120.2, 117.9, 116.3, 115.5, 69.4, 49.2, 46.1, 20.5; HRMS (ESI-TOF) calcd. for $C_{32}H_{26}NaO_2$ $[M + Na]^+$ 465.1825; found: 465.1820.

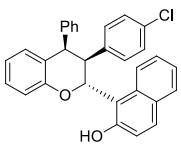


1-((2*R*,3*S*,4*R*)-3-(2-chlorophenyl)-4-phenylchroman-2-yl)naphthalen-2-ol (3e): White solid; 45.8 mg, 99% yield; 72:28 dr, 97% ee (major diastereoisomer); $[\alpha]_D^{20}$ = -263.2 (*c* 1.20, CH_2Cl_2); mp 131.5-133.4 ℃; The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereoisomer, t_{minor} = 13.6 min, t_{major} = 6.5 min); ^{1}H NMR (300 MHz, DMSO-d_6) (major diastereoisomer) δ 10.10 (s, 1H), 8.20 (d, *J* = 8.6 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.29-7.19 (m, 3H), 7.18-7.11 (m, 3H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.04-6.96 (m, 2H), 6.91 (t, *J* = 7.1 Hz, 2H), 6.72-6.54 (m, 4H), 6.30 (br s, 1H), 5.44-5.05 (m, 1H), 4.55 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 154.8, 153.7, 141.4, 136.0, 133.0, 132.9, 130.7, 130.3, 130.0, 129.7, 129.1, 128.7, 128.6, 128.5, 128.3, 127.9, 127.7, 127.4, 126.5, 126.2, 125.2, 124.5, 123.3, 122.4, 120.5, 117.9, 116.5, 114.5, 69.0, 46.0, 42.9; HRMS (ESI-TOF) calcd. for $C_{31}H_{23}ClNaO_2$ $[M + Na]^+$ 485.1279; found: 485.1273.

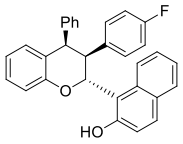


1-((2*R*,3*S*,4*R*)-3-(3-chlorophenyl)-4-phenylchroman-2-yl)naphthalen-2-ol (3f): White solid; 45.3 mg, 98% yield; >95:5 dr, 97% ee; $[\alpha]_D^{20}$ = -166.6 (*c* 0.76, CH_2Cl_2); mp 129.2-130.9 ℃; The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, t_{minor} = 8.8 min, t_{major} = 6.3 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.04 (s, 1H), 8.20 (d, *J* = 8.7 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.9 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.28-7.16 (m, 5H), 7.08-6.81 (m, 6H), 6.76-6.63 (m, 4H), 6.58 (d, *J* = 11.7 Hz, 1H), 4.77 (dd, *J* = 11.9, 5.2 Hz, 1H), 4.46 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 154.8, 153.5, 141.5, 141.4, 132.8,

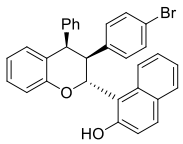
131.6, 130.6, 130.3, 130.2, 128.7, 128.6, 128.5, 128.2, 127.4, 127.3, 126.5, 126.2, 126.1, 124.9, 123.7, 122.3, 120.4, 117.7, 116.4, 114.8, 69.0, 48.8, 46.3; HRMS (ESI-TOF) calcd. for $C_{31}H_{23}ClNaO_2$ $[M + Na]^+$ 485.1279; found: 485.1261.



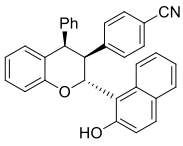
1-((2*R*,3*S*,4*R*)-3-(4-chlorophenyl)-4-phenylchroman-2-yl)naphthalen-2-ol (3g): White solid; 45.4 mg, 98% yield; >95:5 dr, 99% ee; $[\alpha]_D^{20}$ = -155.5 (*c* 1.21, CH_2Cl_2); mp 114.0-115.8 ℃; The ee was determined by HPLC (Chiralpak AS-H, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, t_{minor} = 10.5 min, t_{major} = 8.0 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.99 (s, 1H), 8.20 (d, *J* = 8.7 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.27-7.15 (m, 5H), 7.03 (d, *J* = 7.5 Hz, 1H), 7.01-6.93 (m, 2H), 6.93-6.84 (m, 3H), 6.76-6.63 (m, 4H), 6.59 (d, *J* = 11.7 Hz, 1H), 4.76 (dd, *J* = 11.7, 5.1 Hz, 1H), 4.45 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 154.8, 153.5, 141.5, 138.0, 132.8, 130.7, 130.6, 130.4, 130.2, 128.7, 128.5, 128.2, 127.5, 126.8, 126.5, 126.2, 125.0, 123.7, 122.3, 120.4, 117.8, 116.4, 115.0, 69.1, 48.8, 45.9; HRMS (ESI-TOF) calcd. for $C_{31}H_{23}ClNaO_2$ $[M + Na]^+$ 485.1279; found: 485.1262.



1-((2*R*,3*S*,4*R*)-3-(4-fluorophenyl)-4-phenylchroman-2-yl)naphthalen-2-ol (3h): White solid; 41.2 mg, 99% yield; >95:5 dr, 98% ee; $[\alpha]_D^{20}$ = -169.6 (*c* 1.31, CH_2Cl_2); mp 113.2-115.0 ℃; The ee was determined by HPLC (Chiralpak AS-H, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, t_{minor} = 10.6 min, t_{major} = 7.8 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.97 (s, 1H), 8.21 (d, *J* = 8.7 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.29-7.12 (m, 5H), 7.09-6.85 (m, 4H), 6.75-6.53 (m, 7H), 4.77 (dd, *J* = 11.7, 5.1 Hz, 1H), 4.43 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 160.6 (d, *J* = 240.7 Hz, 1C), 154.8, 153.5, 141.6, 135.2 (d, *J* = 3.1 Hz, 1C), 132.9, 130.6, 130.4, 130.2, 130.1, 128.6, 128.5, 128.1, 127.4, 126.4, 126.1, 125.1, 123.7, 122.3, 120.4, 117.8, 116.4, 115.2, 113.6 (d, *J* = 20.6 Hz, 1C), 69.3, 49.0, 45.8; HRMS (ESI-TOF) calcd. for $C_{31}H_{23}FNaO_2$ $[M + Na]^+$ 469.1574; found: 469.1575.

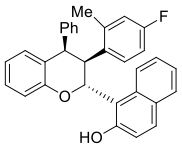


1-((2*R*,3*S*,4*R*)-3-(4-bromophenyl)-4-phenylchroman-2-yl)naphthalen-2-ol (3i): White solid; 49.2 mg, 99% yield; >95:5 dr, 99% ee; $[\alpha]_D^{20}$ = -88.9 (*c* 0.74, CH_2Cl_2); mp 112.8-114.7 ℃; The ee was determined by HPLC (Chiralpak AS-H, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, t_{minor} = 11.1 min, t_{major} = 8.4 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.97 (s, 1H), 8.19 (d, *J* = 8.7 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.29-7.14 (m, 5H), 7.08-6.94 (m, 5H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.76-6.66 (m, 2H), 6.66-6.51 (m, 3H), 4.74 (dd, *J* = 12.0, 5.0 Hz, 1H), 4.45 (d, *J* = 5.0 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 154.8, 153.5, 141.5, 138.5, 132.8, 130.7, 130.6, 130.4, 130.2, 129.7, 128.7, 128.5, 128.2, 127.5, 126.5, 126.2, 125.0, 123.7, 122.3, 120.4, 119.4, 117.8, 116.4, 115.0, 69.0, 48.7, 46.0; HRMS (ESI-TOF) calcd. for $C_{31}H_{23}BrNaO_2$ $[M + Na]^+$ 529.0774; found: 529.0773.

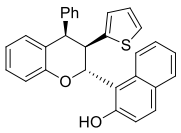


4-((2*R*,3*S*,4*R*)-2-(2-hydroxynaphthalen-1-yl)-4-phenylchroman-3-yl)benzonitrile (3j): White solid; 44.8 mg, 99% yield; >95:5 dr, 93% ee; $[\alpha]_D^{20}$ = -226.9 (*c* 1.49, CH_2Cl_2); mp 158.2-160.4 ℃; The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 15/85, flow rate 1.0 mL/min, λ = 254 nm, t_{minor} = 7.8 min, t_{major} = 6.2 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.05 (s, 1H), 8.20 (d, *J* = 8.7 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.44-7.35 (m, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.27-7.14 (m, 5H), 7.08-6.79 (m, 6H), 6.75-6.52 (m, 3H), 4.88 (dd, *J* = 10.6, 4.9 Hz, 1H), 4.50 (d,

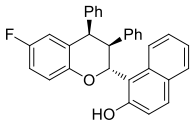
J = 5.1 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 154.8, 153.5, 145.1, 141.2, 132.8, 130.7, 130.7, 130.3, 130.3, 129.6, 128.7, 128.5, 128.2, 127.6, 126.6, 126.3, 124.8, 123.6, 122.4, 120.5, 118.7, 117.8, 116.4, 114.6, 108.9, 68.8, 48.6, 46.7; HRMS (ESI-TOF) calcd. for $C_{32}H_{23}NNaO_2$ $[M + Na]^+$ 476.1621; found: 476.1624.



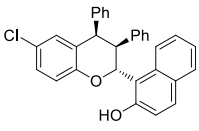
1-((2*R*,3*S*,4*R*)-3-(4-fluoro-2-methylphenyl)-4-phenylchroman-2-yl)naphthalen-2-ol (3k): White solid; 45.5 mg, 99% yield; >95:5 dr, 95% ee; $[\alpha]_D^{20}$ = -141.3 (*c* 1.31, CH_2Cl_2); mp 117.6-119.3 ℃; The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 20/80, flow rate 0.6 mL/min, λ = 254 nm, t_{minor} = 8.5 min, t_{major} = 7.6 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.08 (s, 1H), 8.25 (d, J = 8.8 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.9 Hz, 1H), 7.40 (t, J = 7.7 Hz, 1H), 7.30-7.13 (m, 5H), 7.11-6.96 (m, 3H), 6.96-6.83 (m, 2H), 6.79-6.63 (m, 2H), 6.63-6.49 (m, 2H), 5.87 (s, 1H), 4.92 (d, J = 13.1 Hz, 1H), 4.51 (d, J = 5.1 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 159.2 (d, J = 237.6 Hz, 1C), 154.9, 153.5, 141.7, 139.2 (d, J = 7.6 Hz, 1C), 132.9, 131.3, 130.9, 130.6, 130.5, 130.3, 130.2, 128.8, 128.5, 128.2, 127.4, 126.5, 126.2, 124.9, 123.5, 122.4, 120.5, 117.8, 116.5, 115.2, 114.9, 114.8, 112.2 (d, J = 20.6 Hz, 1C), 69.3, 46.0, 42.3, 18.3; HRMS (ESI-TOF) calcd. for $C_{32}H_{25}FNaO_2$ $[M + Na]^+$ 483.1731; found: 483.1730.



1-((2*R*,3*R*,4*R*)-4-phenyl-3-(thiophen-2-yl)chroman-2-yl)naphthalen-2-ol (3l): White solid; 42.5 mg, 98% yield; >95:5 dr, 99% ee; $[\alpha]_D^{20}$ = -106.7 (*c* 1.06, CH_2Cl_2); mp 115.8-118.0 ℃; The ee was determined by HPLC (Chiralpak AS-H, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, t_{minor} = 29.2 min, t_{major} = 9.2 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.93 (s, 1H), 8.10 (d, J = 8.7 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.29-7.14 (m, 5H), 7.10-6.98 (m, 3H), 6.98-6.86 (m, 2H), 6.86-6.72 (m, 2H), 6.62-6.44 (m, 2H), 6.17 (d, J = 3.5 Hz, 1H), 5.04 (dd, J = 11.7, 5.2 Hz, 1H), 4.49 (d, J = 5.1 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 154.6, 153.8, 141.8, 140.4, 133.0, 130.5, 130.1, 130.0, 128.7, 128.4, 128.2, 127.5, 126.5, 126.2, 126.0, 124.8, 124.7, 123.5, 123.2, 122.2, 120.4, 118.0, 116.3, 115.2, 69.7, 49.3, 41.4; HRMS (ESI-TOF) calcd. for $C_{29}H_{22}NaO_2S$ $[M + Na]^+$ 457.1233; found: 457.1228.

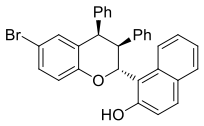


1-((2*R*,3*S*,4*R*)-6-fluoro-3,4-diphenylchroman-2-yl)naphthalen-2-ol (3m): White solid; 43.5 mg, 98% yield; >95:5 dr, 94% ee; $[\alpha]_D^{20}$ = -145.9 (*c* 1.18, CH_2Cl_2); mp 127.6-129.3 ℃; The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 5/95, flow rate 0.6 mL/min, λ = 254 nm, t_{minor} = 14.1 min, t_{major} = 14.9 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.96 (s, 1H), 8.20 (d, J = 8.7 Hz, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.57 (d, J = 8.9 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.26-7.12 (m, 4H), 7.12-7.03 (m, 1H), 7.03-6.93 (m, 2H), 6.92-6.78 (m, 4H), 6.74-6.53 (m, 5H), 4.75 (dd, J = 11.8, 5.1 Hz, 1H), 4.45 (d, J = 5.0 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 156.1 (d, J = 234.6 Hz, 1C), 153.6, 151.2, 141.1, 138.7, 132.9, 130.3, 130.1, 128.6, 128.5, 128.4, 127.4, 126.9, 126.6, 126.5, 126.2, 126.1, 123.6, 122.2, 117.9, 117.6 (d, J = 8.1 Hz, 1C), 116.0 (d, J = 22.1 Hz, 1C), 115.2, 115.1 (d, J = 23.0 Hz, 1C), 69.5, 49.1, 46.2; HRMS (ESI-TOF) calcd. for $C_{31}H_{23}FNaO_2$ $[M + Na]^+$ 469.1574; found: 469.1564.

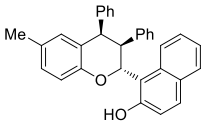


1-((2*R*,3*S*,4*R*)-6-chloro-3,4-diphenylchroman-2-yl)naphthalen-2-ol (3n): White solid; 45.8 mg, 99% yield; >95:5 dr, 92% ee; $[\alpha]_D^{20}$ = -114.9 (*c* 1.26, CH_2Cl_2); mp 126.2-127.8 ℃; The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{minor} = 9.2 min, t_{major} = 6.6 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.99 (s, 1H), 8.16 (d, J = 8.7 Hz, 1H), 7.67 (d,

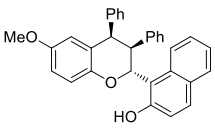
J = 8.1 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.30-7.07 (m, 6H), 6.99 (t, *J* = 7.7 Hz, 2H), 6.92-6.78 (m, 3H), 6.74-6.59 (m, 5H), 4.74 (dd, *J* = 12.3, 4.7 Hz, 1H), 4.46 (d, *J* = 4.9 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 153.8, 153.7, 141.0, 138.6, 132.9, 130.3, 130.2, 129.8, 128.7, 128.6, 128.5, 128.0, 127.5, 127.3, 127.0, 126.6, 126.2, 123.8, 123.5, 122.3, 118.3, 117.9, 114.9, 69.8, 48.8, 46.0; HRMS (ESI-TOF) calcd. for $C_{31}H_{23}ClNaO_2$ $[M + Na]^+$ 485.1279; found: 485.1292.



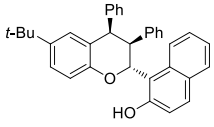
1-((2*R*,3*S*,4*R*)-6-bromo-3,4-diphenylchroman-2-yl)naphthalen-2-ol (3o): White solid; 50.2 mg, 99% yield; 95:5 dr, 96% ee; $[\alpha]_D^{20}$ = -112.3 (*c* 1.30, CH_2Cl_2); mp 135.2-137.1 ℃; The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm, t_{minor} = 12.1 min, t_{major} = 10.7 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.99 (s, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.45-7.31 (m, 2H), 7.27-7.11 (m, 5H), 6.97 (t, *J* = 8.6 Hz, 2H), 6.92-6.77 (m, 3H), 6.74-6.56 (m, 5H), 4.74 (dd, *J* = 12.1, 4.9 Hz, 1H), 4.47 (d, *J* = 5.0 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 154.2, 153.6, 141.0, 138.6, 132.9, 132.6, 130.8, 130.3, 130.2, 128.7, 128.5, 128.5, 127.9, 127.5, 127.0, 126.5, 126.2, 123.5, 122.3, 118.7, 117.9, 114.9, 111.5, 69.7, 48.7, 46.0; HRMS (ESI-TOF) calcd. for $C_{31}H_{23}BrNaO_2$ $[M + Na]^+$ 529.0774; found: 529.0782.



1-((2*R*,3*S*,4*R*)-6-methyl-3,4-diphenylchroman-2-yl)naphthalen-2-ol (3p): White solid; 43.8 mg, 99% yield; >95:5 dr, >99% ee; $[\alpha]_D^{20}$ = -92.8 (*c* 0.75, CH_2Cl_2); mp 112.0-113.8 ℃; The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, t_{minor} = 15.7 min, t_{major} = 6.4 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.92 (s, 1H), 8.19 (d, *J* = 8.7 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 8.9 Hz, 1H), 7.36 (t, *J* = 7.1 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.18-7.12 (m, 3H), 7.03 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 1H), 6.90-6.84 (m, 2H), 6.84-6.78 (m, 3H), 6.71-6.56 (m, 5H), 4.70 (dd, *J* = 11.8, 5.1 Hz, 1H), 4.37 (d, *J* = 5.0 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 153.4, 152.7, 141.7, 139.0, 132.9, 130.6, 130.3, 129.9, 128.8, 128.6, 128.5, 127.3, 126.9, 126.3, 126.0, 125.9, 124.9, 123.7, 122.2, 117.8, 116.1, 115.5, 69.2, 49.2, 46.6, 20.0; HRMS (ESI-TOF) calcd. for $C_{32}H_{26}NaO_2$ $[M + Na]^+$ 465.1825; found: 465.1826.

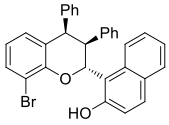


1-((2*R*,3*S*,4*R*)-6-methoxy-3,4-diphenylchroman-2-yl)naphthalen-2-ol (3q): White solid; 41.7 mg, 91% yield; >95:5 dr, 97% ee; $[\alpha]_D^{20}$ = -139.6 (*c* 1.38, CH_2Cl_2); mp 197.5-199.3 ℃; The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, t_{minor} = 15.6 min, t_{major} = 8.4 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.91 (s, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 8.9 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.27-7.09 (m, 4H), 6.97 (d, *J* = 8.9 Hz, 1H), 6.94-6.78 (m, 5H), 6.75-6.53 (m, 6H), 4.72 (dd, *J* = 11.7, 5.0 Hz, 1H), 4.41 (d, *J* = 5.1 Hz, 1H), 3.62 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 153.5, 153.0, 148.9, 141.5, 139.0, 133.0, 130.3, 129.9, 128.6, 128.5, 127.3, 126.9, 126.4, 126.1, 126.0, 125.6, 123.8, 122.2, 117.9, 117.0, 115.6, 114.7, 114.4, 69.2, 55.3, 49.5, 46.6; HRMS (ESI-TOF) calcd. for $C_{32}H_{26}NaO_3$ $[M + Na]^+$ 481.1774; found: 481.1778.

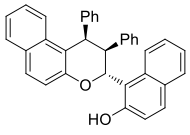


1-((2*R*,3*S*,4*R*)-6-(tert-butyl)-3,4-diphenylchroman-2-yl)naphthalen-2-ol (3r): White solid; 43.5 mg, 90% yield; >95:5 dr, 98% ee; $[\alpha]_D^{20}$ = -118.5 (*c* 0.93, CH_2Cl_2); mp 190.5-192.1 ℃; The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 5/95, flow rate 0.6 mL/min, λ = 254 nm, t_{minor}

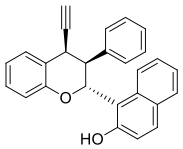
= 10.8 min, t_{major} = 11.6 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.88 (s, 1H), 8.17 (d, J = 8.7 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.9 Hz, 1H), 7.35 (t, J = 7.2 Hz, 1H), 7.26 (dd, J = 8.6, 2.2 Hz, 1H), 7.23-7.10 (m, 4H), 7.01 (d, J = 2.1 Hz, 1H), 6.94 (d, J = 8.9 Hz, 1H), 6.91-6.77 (m, 4H), 6.74-6.48 (m, 5H), 4.71 (dd, J = 11.2, 4.8 Hz, 1H), 4.40 (d, J = 4.9 Hz, 1H), 1.21 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 153.4, 152.6, 142.3, 141.6, 139.1, 132.9, 130.3, 129.9, 128.6, 128.5, 127.3, 126.9, 126.6, 126.3, 126.0, 125.3, 124.3, 123.7, 122.2, 117.8, 115.8, 115.5, 69.1, 49.5, 46.6, 33.8, 31.4; HRMS (ESI-TOF) calcd. for $C_{35}H_{32}NaO_2$ [M + Na]$^+$ 507.2295; found: 507.2273.



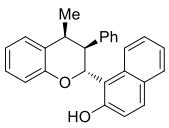
1-((2*R*,3*S*,4*R*)-8-bromo-3,4-diphenylchroman-2-yl)naphthalen-2-ol (3s): White solid; 50.0 mg, 99% yield; >95:5 dr, 96% ee; $[\alpha]_D^{20}$ = -143.6 (*c* 1.28, CH_2Cl_2); mp 113.2-115.0 ℃; The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{minor} = 7.4 min, t_{major} = 4.2 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.94 (s, 1H), 8.20 (d, J = 8.7 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.9 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.27-7.19 (m, 2H), 7.19-7.12 (m, 3H), 7.07-7.00 (m, 1H), 7.00-6.93 (m, 2H), 6.92-6.80 (m, 4H), 6.73-6.57 (m, 5H), 4.75 (dd, J = 11.7, 5.0 Hz, 1H), 4.43 (d, J = 5.0 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 154.9, 153.6, 141.6, 139.0, 132.9, 130.6, 130.3, 130.0, 128.7, 128.6, 128.5, 128.1, 128.0, 127.3, 126.9, 126.3, 126.1, 125.3, 123.7, 122.2, 121.0, 120.3, 117.9, 116.4, 115.3, 69.3, 49.2, 46.5; HRMS (ESI-TOF) calcd. for $C_{31}H_{23}BrNaO_2$ [M + Na]$^+$ 529.0774; found: 529.0771.



1-((1*R*,2*S*,3*R*)-1,2-diphenyl-2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl)naphthalen-2-ol (3t): White solid; 41.5 mg, 87% yield; 75:25 dr, 82% ee (major diastereoisomer); $[\alpha]_D^{20}$ = +2.5 (*c* 1.70, CH_2Cl_2); mp 181.5-183.5 ℃; The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereoisomer, t_{minor} = 8.9 min, t_{major} = 16.2 min); ^{1}H NMR (300 MHz, DMSO-d_6) (major diastereoisomer) δ 9.81 (s, 1H), 8.49 (br s, 1H), 7.83 (t, J = 7.3 Hz, 2H), 7.69 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.5 Hz, 1H), 7.48 (d, J = 8.3 Hz, 2H), 7.32-7.16 (m, 4H), 7.16-7.01 (m, 4H), 6.97 (s, 4H), 6.85 (s, 1H), 6.75 (s, 2H), 6.27 (d, J = 10.9 Hz, 1H), 5.05 (d, J = 9.7 Hz, 1H), 4.07 (br s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 155.2, 153.1, 145.6, 139.5, 132.7, 132.4, 129.8, 129.6, 128.5, 128.4, 128.3, 128.1, 127.5, 127.4, 126.4, 126.0, 125.8, 125.6, 124.5, 124.3, 123.0, 122.2, 119.0, 118.1, 117.6, 114.9, 75.5, 55.6, 49.0; HRMS (ESI-TOF) calcd. for $C_{35}H_{26}NaO_2$ [M + Na]$^+$ 501.1825; found: 501.1802.

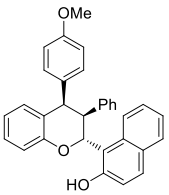


1-((2*R*,3*S*,4*R*)-4-ethynyl-3-phenylchroman-2-yl)naphthalen-2-ol (3u): White solid; 24.8 mg, 66% yield; >95:5 dr, 96% ee; $[\alpha]_D^{20}$ = +3.6 (*c* 0.62, CH_2Cl_2); mp 111.7-113.5 ℃; The ee was determined by HPLC (Chiralpak AS-H, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, t_{minor} = 20.4 min, t_{major} = 10.5 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.13 (s, 1H), 8.16 (d, J = 8.7 Hz, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.62 (d, J = 8.9 Hz, 1H), 7.43-7.29 (m, 4H), 7.22 (t, J = 7.5 Hz, 2H), 7.10-7.00 (m, 4H), 6.96 (t, J = 7.4 Hz, 1H), 6.85 (d, J = 8.2 Hz, 1H), 6.73 (d, J = 11.2 Hz, 1H), 4.47 (dd, J = 11.0, 4.6 Hz, 1H), 4.13 (s, 1H), 3.31 (d, J = 2.4 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 153.9, 153.8, 139.0, 132.9, 130.2, 129.8, 128.6, 128.4, 127.3, 126.6, 126.2, 123.5, 123.2, 122.3, 120.3, 118.0, 116.7, 114.9, 84.1, 77.3, 71.2, 44.5, 36.5; HRMS (ESI-TOF) calcd. for $C_{27}H_{20}NaO_2$ [M + Na]$^+$ 399.1356; found: 399.1366.

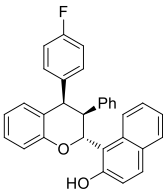


1-((2*R*,3*S*,4*S*)-4-methyl-3-phenylchroman-2-yl)naphthalen-2-ol (3v): White solid; 23.1 mg, 63% yield; >95:5 dr, 91% ee; $[\alpha]_D^{20}$ = +11.5 (*c* 1.15, CH_2Cl_2); mp 145.8-147.5 ℃; The ee was determined by HPLC (Chiralpak IA, EtOH/hexane =

10/90, flow rate 1.0 mL/min, λ = 254 nm, t_{minor} = 11.2 min, t_{major} = 6.9 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.17 (s, 1H), 8.25 (d, *J* = 8.7 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.30-7.18 (m, 4H), 7.17-6.97 (m, 5H), 6.92 (t, *J* = 7.3 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.53 (d, *J* = 11.3 Hz, 1H), 4.53 (dd, *J* = 11.4, 4.9 Hz, 1H), 3.15 (t, *J* = 6.1 Hz, 1H), 1.13 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 154.1, 153.6, 140.0, 132.9, 130.0, 129.7, 128.6, 128.5, 128.4, 127.5, 127.4, 126.1, 126.0, 124.0, 122.3, 120.0, 118.0, 116.3, 115.7, 69.1, 45.7, 36.9, 19.0; HRMS (ESI-TOF) calcd. for $C_{26}H_{22}NaO_2$ $[M + Na]^+$ 389.1512; found: 389.1514.



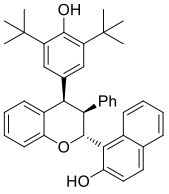
1-((2*R*,3*S*,4*R*)-4-(4-methoxyphenyl)-3-phenylchroman-2-yl)naphthalen-2-ol (3w): White solid; 45.3 mg, 99% yield; 88:12 dr, 96% ee (major diastereoisomer); $[\alpha]_D^{20}$ = -107.8 (*c* 0.81, CH_2Cl_2); mp 116.3-118.2 ℃; The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 10/90, flow rate 0.6 mL/min, λ = 254 nm, major diastereoisomer, t_{minor} = 20.9 min, t_{major} = 12.4 min); ^{1}H NMR (300 MHz, DMSO-d_6) (major diastereoisomer) δ 9.95 (s, 1H), 8.23 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 6.5 Hz, 2H), 7.08-6.94 (m, 3H), 6.93-6.79 (m, 4H), 6.73 (d, *J* = 6.9 Hz, 4H), 6.65 (d, *J* = 11.7 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 2H), 4.72 (dd, *J* = 12.0, 4.9 Hz, 1H), 4.38 (d, *J* = 4.8 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 157.7, 154.8, 153.5, 139.2, 133.6, 133.0, 131.3, 130.6, 130.0, 128.6, 128.5, 128.0, 126.9, 126.1, 125.7, 123.7, 122.2, 120.2, 117.9, 116.3, 115.5, 112.8, 69.4, 54.9, 48.4, 46.7; HRMS (ESI-TOF) calcd. for $C_{32}H_{26}NaO_3$ $[M + Na]^+$ 481.1774; found: 481.1771.



1-((2*R*,3*S*,4*R*)-4-(4-fluorophenyl)-3-phenylchroman-2-yl)naphthalen-2-ol (3x): White solid; 44.2 mg, 99% yield; >95:5 dr, 98% ee; $[\alpha]_D^{20}$ = -128.8 (*c* 1.35, CH_2Cl_2); mp 159.3-161.8 ℃; The ee was determined by HPLC (Chiralpak AS-H, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, t_{minor} = 12.4 min, t_{major} = 8.3 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.00 (s, 1H), 8.22 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.22 (q, *J* = 7.8, 7.3 Hz, 2H), 7.09-6.82 (m, 9H), 6.72 (d, *J* = 7.3 Hz, 2H), 6.69-6.51 (m, 3H), 4.75 (dd, *J* = 11.9, 5.0 Hz, 1H), 4.47 (d, *J* = 5.0 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 160.9 (d, *J* = 241.0 Hz, 1C), 154.8, 153.6, 138.9, 137.9 (d, *J* = 3.0 Hz, 1C), 133.0, 131.9 (d, *J* = 7.9 Hz, 1C), 130.6, 130.0, 128.6, 128.5, 128.2, 127.0, 126.2, 126.1, 125.0, 123.7, 122.3, 120.4, 117.9, 116.5, 115.2, 114.1 (d, *J* = 21.0 Hz, 1C), 69.2, 48.3, 46.5; HRMS (ESI-TOF) calcd. for $C_{31}H_{23}FNaO_2$ $[M + Na]^+$ 469.1574; found: 469.1567.

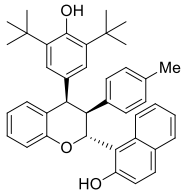
3. Procedure for the synthesis of chromane 5

In an ordinary vial equipped with a magnetic stirring bar, the *ortho*-hydroxyphenylsubstituted *para*-quinone methides **4** (0.15 mmol, 1.5 equiv) were added to a solution of 1-styrylnaphthalen-2-ols **1** (0.10 mmol, 1.0 equiv), CPA **D** (5 mol %) and 3 Å MS (20 mg) in toluene (0.5 mL) at 0 ^{o}C. And then, the mixture was stirred at the same temperature for specified time. After completion of the reaction, as indicated by TLC, the chromanes **5** were isolated by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20/1~15/1).

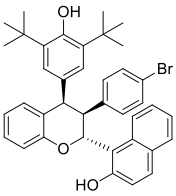


1-((2*R*,3*S*,4*R*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-phenylchroman-2-yl) naphthalen-2-ol (5a): Yellow solid; 45.3 mg, 82% yield; >95:5 dr, 80% ee; $[\alpha]_D^{20}$ = -84.5 (*c* 1.14, CH_2Cl_2); mp 107.1-109.3 ℃; The ee was determined by

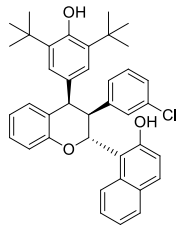
HPLC (Chiralpak IA, *i*-PrOH/hexane = 5/95, flow rate 0.8 mL/min, λ = 254 nm, t_{minor} = 9.6 min, t_{major} = 11.4 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.89 (s, 1H), 8.18 (d, *J* = 8.6 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.9 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 8.9 Hz, 1H), 6.95-6.77 (m, 5H), 6.73 (s, 1H), 6.69-6.50 (m, 3H), 6.38 (s, 2H), 4.66 (d, *J* = 11.4 Hz, 1H), 4.28 (d, *J* = 4.7 Hz, 1H), 1.22 (s, 18H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 155.1, 153.9, 152.1, 139.7, 137.5, 133.2, 132.0, 130.6, 129.9, 128.6, 128.4, 127.8, 126.8, 126.6, 126.0, 125.6, 123.6, 122.2, 120.0, 118.0, 116.0, 115.4, 69.1, 49.4, 46.9, 34.2, 30.2; HRMS (ESI-TOF) calcd. for $C_{39}H_{40}NaO_3$ $[M + Na]^+$ 579.2870; found: 579.2879.



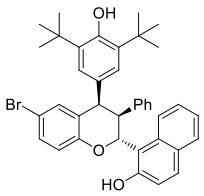
1-((2*R*,3*S*,4*R*)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-(p-tolyl)chroman-2-yl)naphthalen-2-ol (5b): Yellow solid; 45.0 mg, 79% yield; >95:5 dr, 82% ee; $[\alpha]_D^{20}$ = -117.7 (*c* 0.66, CH_2Cl_2); mp 120.6-122.4 ℃; The ee was determined by HPLC (Chiralpak IA, *i*-PrOH/hexane = 5/95, flow rate 0.8 mL/min, λ = 254 nm, t_{minor} = 9.3 min, t_{major} = 11.3 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.89 (s, 1H), 8.18 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.9 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.25-7.13 (m, 2H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.9 Hz, 1H), 6.95-6.82 (m, 2H), 6.70 (s, 1H), 6.67-6.54 (m, 3H), 6.54-6.41 (m, 2H), 6.35 (s, 2H), 4.62 (d, *J* = 6.9 Hz, 1H), 4.24 (d, *J* = 4.8 Hz, 1H), 2.04 (s, 3H), 1.22 (s, 18H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 155.2, 153.8, 152.1, 137.4, 136.7, 134.5, 133.2, 132.2, 130.7, 129.8, 128.6, 128.4, 127.8, 127.5, 126.7, 126.0, 125.6, 122.2, 120.0, 118.0, 116.0, 115.5, 69.1, 49.5, 46.6, 34.2, 30.1, 20.5; HRMS (ESI-TOF) calcd. for $C_{40}H_{42}NaO_3$ $[M + Na]^+$ 593.3026; found: 593.3021.



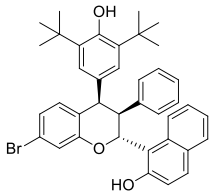
1-((2*R*,3*S*,4*R*)-3-(4-bromophenyl)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)chroman-2-yl)naphthalen-2-ol (5c): Yellow solid; 47.7 mg, 75% yield; >95:5 dr, 80% ee; $[\alpha]_D^{20}$ = -141.9 (*c* 0.80, CH_2Cl_2); mp 124.0-125.8 ℃; The ee was determined by HPLC (Chiralpak IA, *i*-PrOH/hexane = 5/95, flow rate 0.8 mL/min, λ = 254 nm, t_{minor} = 9.7 min, t_{major} = 14.5 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.98 (s, 1H), 8.19 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.27-7.14 (m, 2H), 7.07 (d, *J* = 6.8 Hz, 1H), 7.04-6.84 (m, 5H), 6.77 (s, 1H), 6.67-6.47 (m, 3H), 6.38 (s, 2H), 4.67 (d, *J* = 6.1 Hz, 1H), 4.29 (d, *J* = 4.9 Hz, 1H), 1.24 (s, 18H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 155.1, 153.8, 152.3, 139.3, 137.8, 133.1, 132.0, 130.8, 130.7, 130.1, 129.6, 128.7, 128.5, 127.8, 126.6, 126.1, 125.2, 122.3, 120.2, 119.2, 117.9, 116.1, 115.1, 68.8, 49.1, 46.6, 34.3, 30.2; HRMS (ESI-TOF) calcd. for $C_{39}H_{39}BrNaO_3$ $[M + Na]^+$ 657.1975; found: 657.1984.



1-((2*R*,3*S*,4*R*)-3-(3-chlorophenyl)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)chroman-2-yl)naphthalen-2-ol (5d): Yellow solid; 39.5 mg, 67% yield; >95:5 dr, 86% ee; $[\alpha]_D^{20}$ = -143.3 (*c* 0.57, CH_2Cl_2); mp 119.4-121.1 ℃; The ee was determined by HPLC (Chiralpak IA, *i*-PrOH/hexane = 5/95, flow rate 0.6 mL/min, λ = 254 nm, t_{minor} = 12.5 min, t_{major} = 14.3 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.04 (s, 1H), 8.18 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.26-7.15 (m, 2H), 7.10-6.98 (m, 2H), 6.96-6.81 (m, 4H), 6.74 (s, 1H), 6.60 (d, *J* = 15.0 Hz, 3H), 6.43 (s, 2H), 4.83-4.58 (m, 1H), 4.33 (d, *J* = 4.9 Hz, 1H), 1.25 (s, 18H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 155.0, 153.9, 152.3, 142.2, 137.8, 133.0, 132.0, 131.7, 130.8, 130.1, 128.7, 128.5, 128.4, 127.8, 127.2, 126.4, 126.1, 125.6, 125.3, 122.3, 120.2, 117.8, 116.1, 114.9, 68.8, 49.0, 46.7, 34.3, 30.2; HRMS (ESI-TOF) calcd. for $C_{39}H_{39}ClNaO_3$ $[M + Na]^+$ 613.2480; found: 613.2476.



1-((2*R*,3*S*,4*R*)-6-bromo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-phenylchroman-2-yl)naphthalen-2-ol (5e): Yellow solid; 45.9 mg, 72% yield; >95:5 dr, 90% ee; $[\alpha]_D^{20}$ = -86.2 (*c* 0.61, CH_2Cl_2); mp 127.7-129.4 ℃; The ee was determined by HPLC (Chiralpak IA, *i*-PrOH/hexane = 5/95, flow rate 0.8 mL/min, λ = 254 nm, t_{minor} = 11.4 min, t_{major} = 13.1 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.94 (s, 1H), 8.12 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.39-7.30 (m, 2H), 7.27 (d, *J* = 2.5 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 8.9 Hz, 1H), 6.90 (t, *J* = 8.1 Hz, 2H), 6.86-6.75 (m, 3H), 6.69-6.44 (m, 3H), 6.37 (s, 2H), 4.63 (d, *J* = 9.6 Hz, 1H), 4.31 (d, *J* = 4.6 Hz, 1H), 1.23 (s, 18H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 154.4, 154.0, 152.4, 139.2, 137.7, 133.1, 132.6, 131.4, 130.6, 130.1, 128.7, 128.6, 128.4, 128.3, 126.9, 126.6, 126.1, 125.8, 122.2, 118.4, 117.9, 114.9, 111.3, 69.5, 49.0, 46.3, 34.3, 30.2; HRMS (ESI-TOF) calcd. for $C_{39}H_{39}BrNaO_3$ $[M + Na]^+$ 657.1975; found: 657.1964.



1-((2*R*,3*S*,4*R*)-7-bromo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-phenylchroman-2-yl)naphthalen-2-ol (5f): Yellow solid; 52.5 mg, 83% yield; >95:5 dr, 71% ee; $[\alpha]_D^{20}$ = -103.0 (*c* 0.8, CH_2Cl_2); mp 132.3-134.1 ℃; The ee was determined by HPLC (Chiralpak IA, *i*-PrOH/hexane = 5/95, flow rate 0.6 mL/min, λ = 254 nm, t_{minor} = 11.6 min, t_{major} = 13.5 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.97 (s, 1H), 8.14 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.25-7.17 (m, 1H), 7.16 (s, 1H), 7.05 (s, 2H), 6.99 (d, *J* = 8.9 Hz, 1H), 6.93-6.73 (m, 4H), 6.70-6.51 (m, 3H), 6.37 (s, 2H), 4.65 (d, *J* = 9.3 Hz, 1H), 4.27 (d, *J* = 4.7 Hz, 1H), 1.23 (s, 18H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 156.1, 154.0, 152.3, 139.3, 137.7, 133.1, 132.4, 131.5, 130.1, 128.7, 128.6, 128.4, 126.9, 126.6, 126.2, 125.8, 125.3, 123.0, 122.2, 119.7, 118.6, 118.0, 114.8, 69.7, 48.9, 46.5, 34.3, 30.2; HRMS (ESI-TOF) calcd. for $C_{39}H_{39}BrNaO_3$ $[M + Na]^+$ 657.1975; found: 657.1958.

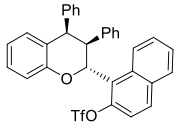
4. Procedure for the gram-scale experiment

In an ordinary vial equipped with a magnetic stirring bar, the *ortho*-hydroxy benzylic alcohols **2a** (3.0 mmol, 0.6 g, 1.2 equiv) were added to a solution of 1-vinylnaphthalen-2-ols **1a** (2.5 mmol, 0.615 g, 1.0 equiv), CPA **D** (5 mol %) and 3 Å MS (0.5 g) in toluene (12.5 mL) at 0 ^{o}C. And then, the mixture was stirred at the same temperature for 18 h. After completion of the reaction, as indicated by TLC, the toluene were removed in vacuo and the residue was purified by column chromatography eluting with petroleum ether/ethyl acetate (15/1～10/1) as eluent affording chromane **3a** (1.05 g, 98% yield, >95:5 dr, 97% ee), as a white spumous solid.

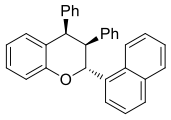
5. Procedure for the synthesis of chromanes 6 and 7

To a mixture of chromane **3a** (128.5 mg, 0.3 mmol) and DMAP (109.9 mg, 0.9 mmol, 3.0 equiv) was added CH_2Cl_2 (3 mL) under the atmosphere of Ar_2, stirring at room temperature for 10 minutes. After that, a solution of N-phenylbis(trifluoromethanesulfonimide) (214.3 mg, 0.6 mmol, 2.0 equiv) in CH_2Cl_2 (2 mL) was added and the mixture was stirred at room temperature for 5 h. After completion of the reaction, as indicated by TLC, H_2O was added (5 mL) and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL) and dried under anhydrous Na_2SO_4. The organic solvents were removed in vacuo and the residue was purified by column chromatography eluting with petroleum ether /EtOAc (petroleum ether/ethyl acetate = 15/1) as eluent affording product **6** (148.5 mg, 88% yield, >95:5 dr, 95% ee),

as a white spumous solid. Under protection of Ar_2, compound **6** (112 mg, 0.2 mmol) was placed with 10% Pd/C (34 mg, 30 wt %) and Et_2NH (30.0 μL, 0.28 mmol, 1.4 equiv) in a 25 mL round bottomed flask, followed by MeOH (4 mL). Then, the reaction vessel was repeatedly purged with H_2 using a balloon and a needle as a vent. Finally, the reaction was stirred at room temperature for 20 h under H_2 (1 atm, balloon). When the reaction was completed, as indicated by TLC, the suspension was passed through a pad of Celite and the organic solvents were removed under vacuum. The residue was purified by column chromatography eluting with petroleum ether /EtOAc (petroleum ether/ethyl acetate = 50/1) as eluent affording product **7** (70.5 mg, 86% yield, >95:5 dr, 96% ee), as a white spumous solid.

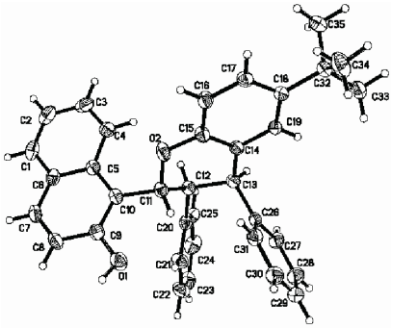


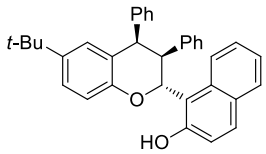
1-((2*R*,3*S*,4*R*)-3,4-diphenylchroman-2-yl)naphthalen-2-yl trifluoromethanesulfonate (6): White solid; 148.5 mg, 88% yield; >95:5 dr, 95% ee; $[\alpha]_D^{20}$ = -270.3 (*c* 2.24, CH_2Cl_2); mp 92.3-94.5 ℃; The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 5/95, flow rate 0.8 mL/min, λ = 254 nm, t_{minor} = 5.8 min, t_{major} = 4.9 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.57 (s, 1H), 8.09-7.80 (m, 2H), 7.72-7.48 (m, 2H), 7.37-7.14 (m, 5H), 7.09 (s, 2H), 7.02-6.92 (m, 1H), 6.92-6.64 (m, 5H), 6.39 (d, *J* = 6.6 Hz, 3H), 4.85-4.61 (m, 1H), 4.55 (d, *J* = 4.1 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 153.7, 145.0, 141.2, 137.2, 132.6, 131.9, 131.4, 130.8, 130.4, 129.1, 128.4, 127.6, 127.2, 126.9, 126.8, 126.7, 125.9, 125.0, 124.4, 121.1, 120.2, 118.8, 116.6, 115.9, 111.7, 70.6, 48.1, 47.1; HRMS (ESI-TOF) calcd. for $C_{32}H_{23}F_3NaO_4S$ $[M + Na]^+$ 583.1161; found: 583.1173.



(2*R*,3*S*,4*R*)-2-(naphthalen-1-yl)-3,4-diphenylchroman (7): White solid; 70.5 mg, 86% yield; >95:5 dr, 96% ee; $[\alpha]_D^{20}$ = -151.1 (*c* 3.14, CH_2Cl_2); mp 99.6-101.3 ℃; The ee was determined by HPLC (Chiralpak IB, DCM/hexane = 5/95, flow rate 0.6 mL/min, λ = 254 nm, t_{minor} = 12.7 min, t_{major} = 11.3 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.28 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.19-7.10 (m, 3H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.95-6.81 (m, 4H), 6.80-6.70 (m, 2H), 6.61 (d, *J* = 6.8 Hz, 2H), 6.40 (d, *J* = 10.6 Hz, 1H), 4.49 (d, *J* = 5.2 Hz, 1H), 4.42 (dd, *J* = 10.7, 5.2 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 154.3, 141.6, 139.0, 134.2, 133.4, 131.4, 130.4, 130.2, 128.8, 128.7, 128.6, 128.2, 127.6, 127.4, 126.6, 126.5, 126.4, 126.2, 125.6, 125.1, 124.8, 123.0, 120.5, 116.2, 72.5, 48.0, 46.4; HRMS (ESI-TOF) calcd. for $C_{31}H_{24}NaO$ $[M + Na]^+$ 435.1719; found: 435.1726.

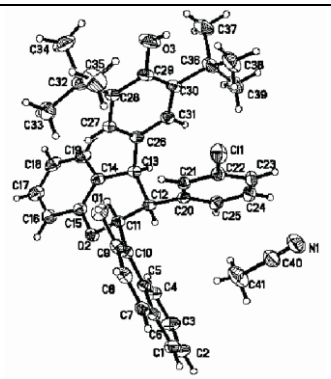
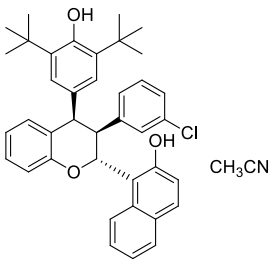
6. X-ray crystal data for compound 3r and 5d





Identification code	**3r**
Empirical formula	$C_{35}H_{32}O_2$
Formula weight	484.63

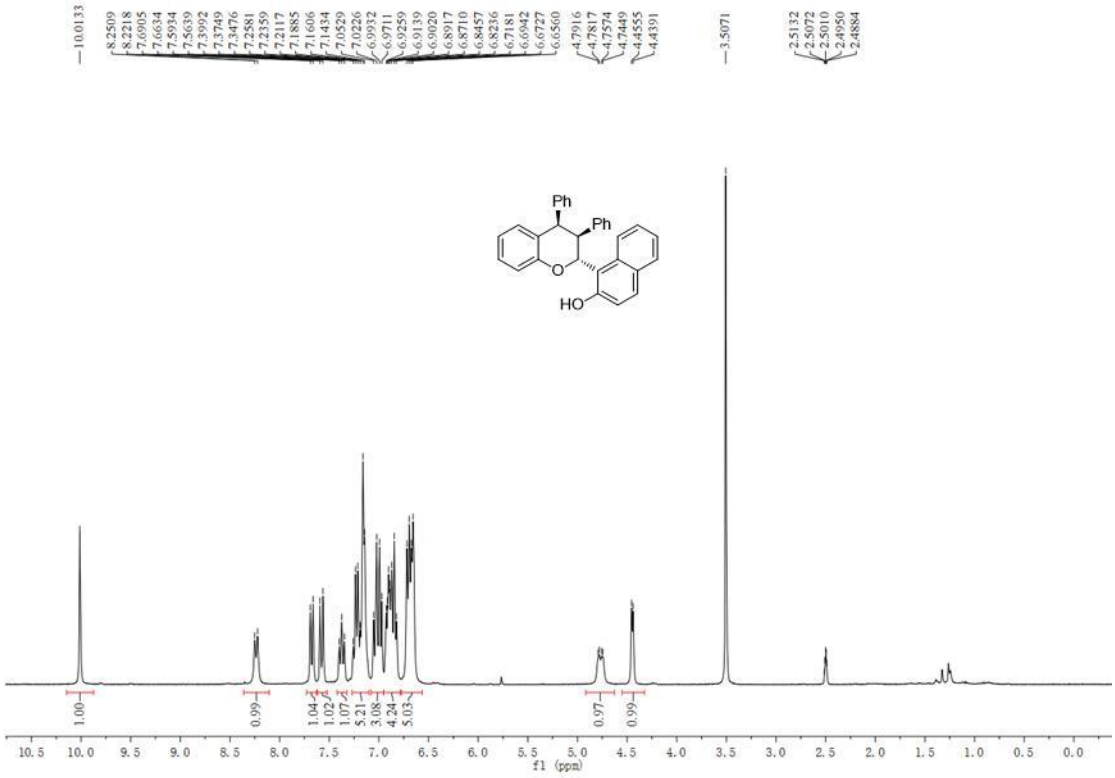
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.43565(16)
b/Å	16.9768(3)
c/Å	19.2055(3)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	3076.49(10)
Z	4
$\rho_{calc}g/cm^3$	1.215
μ/mm^{-1}	1.200
F(000)	1200.0
Crystal size/mm^3	0.19 × 0.1 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.95 to 141.79
Index ranges	$-11 \le h \le 6$, $-17 \le k \le 20$, $-23 \le l \le 23$
Reflections collected	11706
Independent reflections	5806 [R_{int} = 0.0320, R_{sigma} = 0.0437]
Data/restraints/parameters	5806/0/376
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0490, wR_2 = 0.1286
Final R indexes [all data]	R_1 = 0.0567, wR_2 = 0.1375
Largest diff. peak/hole / e $Å^{-3}$	0.34/-0.22
Flack parameter	0.006(15)

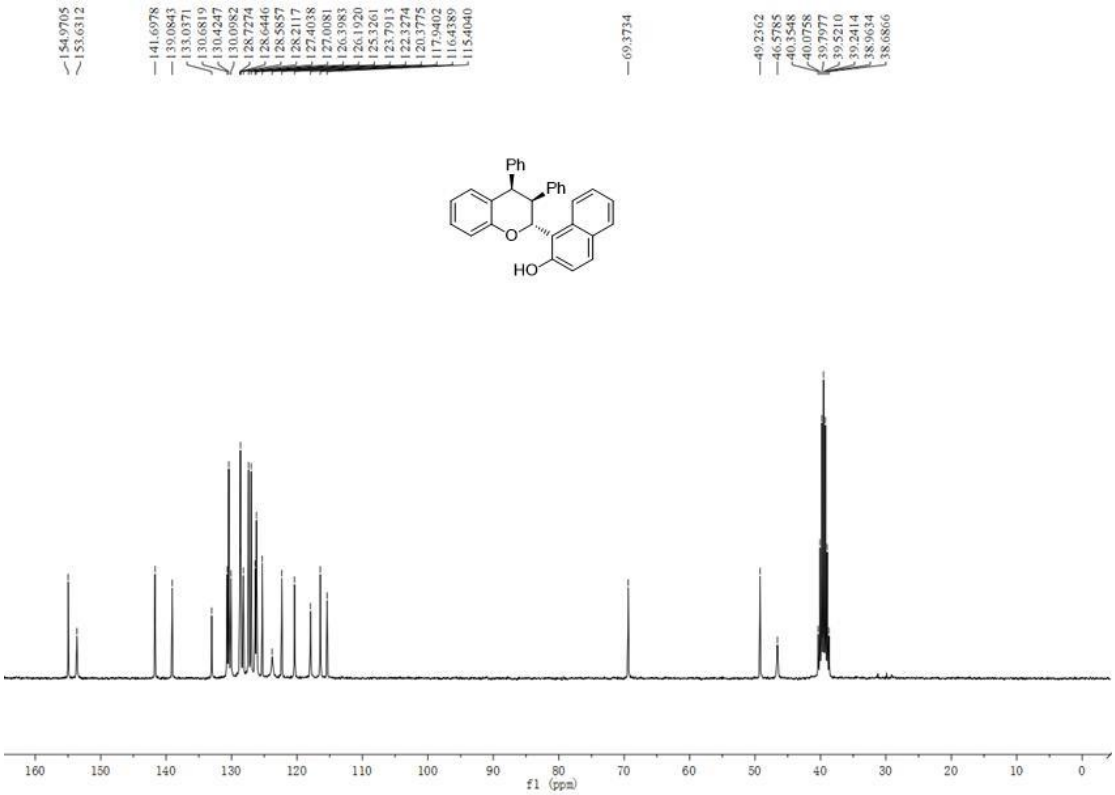
	
Identification code	**5d**
Empirical formula	$C_{41}H_{42}ClNO_3$
Formula weight	632.20
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.8441(7)

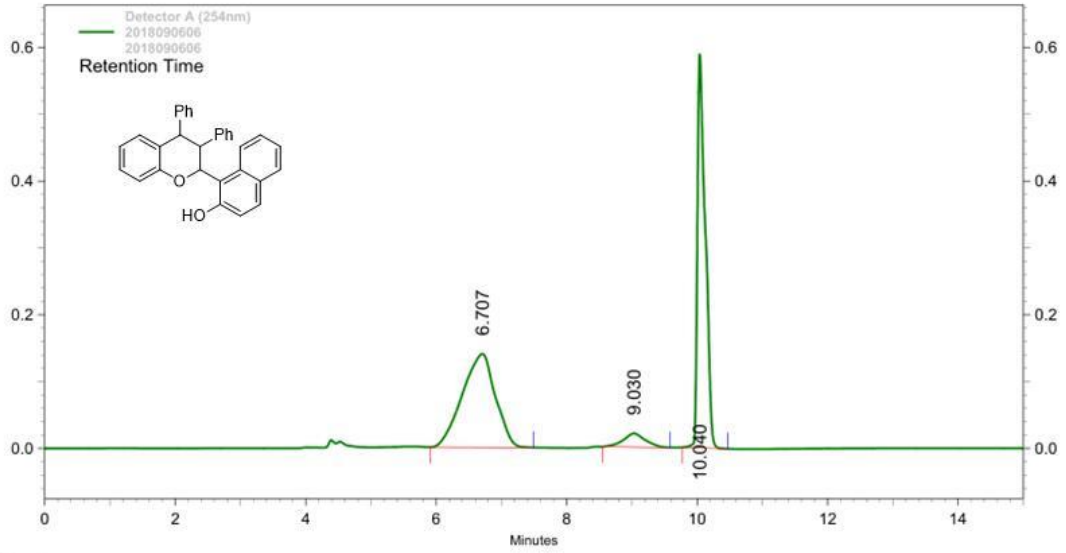
b/Å	10.6009(8)
c/Å	15.1947(9)
α/°	90
β/°	103.393(6)
γ/°	90
Volume/$Å^3$	1855.9(2)
Z	2
$\rho_{calc}g/cm^3$	1.131
μ/mm^{-1}	1.190
F(000)	672.0
Crystal size/mm^3	0.15 × 0.11 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/ °	7.672 to 134.148
Index ranges	$-14 \leq h \leq 14$, $-11 \leq k \leq 12$, $-18 \leq l \leq 18$
Reflections collected	16351
Independent reflections	6064 [R_{int} = 0.0327, R_{sigma} = 0.0380]
Data/restraints/parameters	6064/1/426
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0439, wR_2 = 0.1096
Final R indexes [all data]	R_1 = 0.0544, wR_2 = 0.1199
Largest diff. peak/hole / e $Å^{-3}$	0.11/-0.17
Flack parameter	-0.052(17)

7. The copies of ^{1}H NMR, ^{13}C NMR and HPLC spectra for compounds 3, 5, 6 and 7

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3a

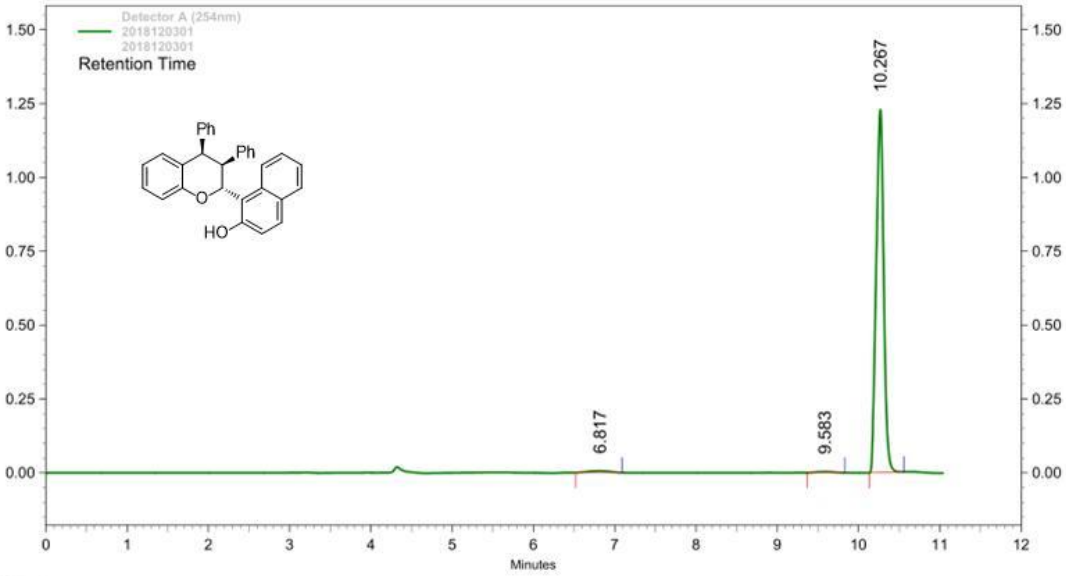






Detector A (254nm)

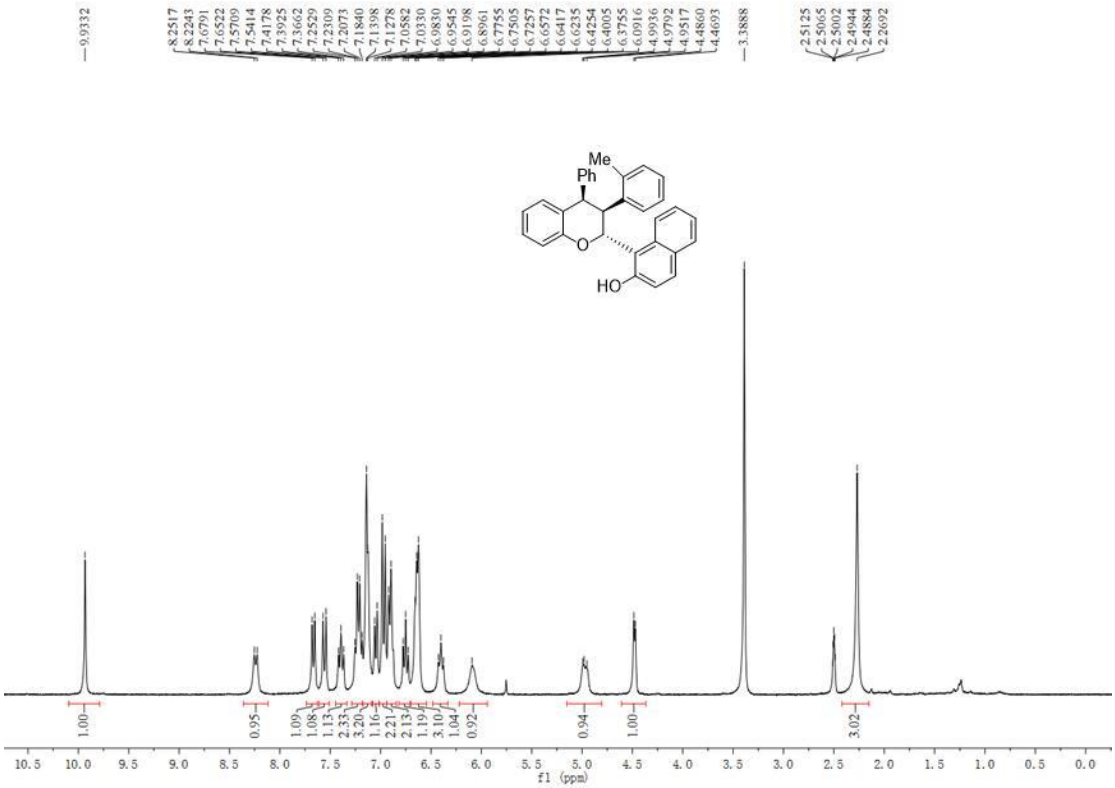
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	6.707	139863	18.66	4935369	47.65
2	9.030	20361	2.72	477583	4.61
3	10.040	589286	78.62	4945210	47.74
Totals		749510	100.00	10358162	100.00

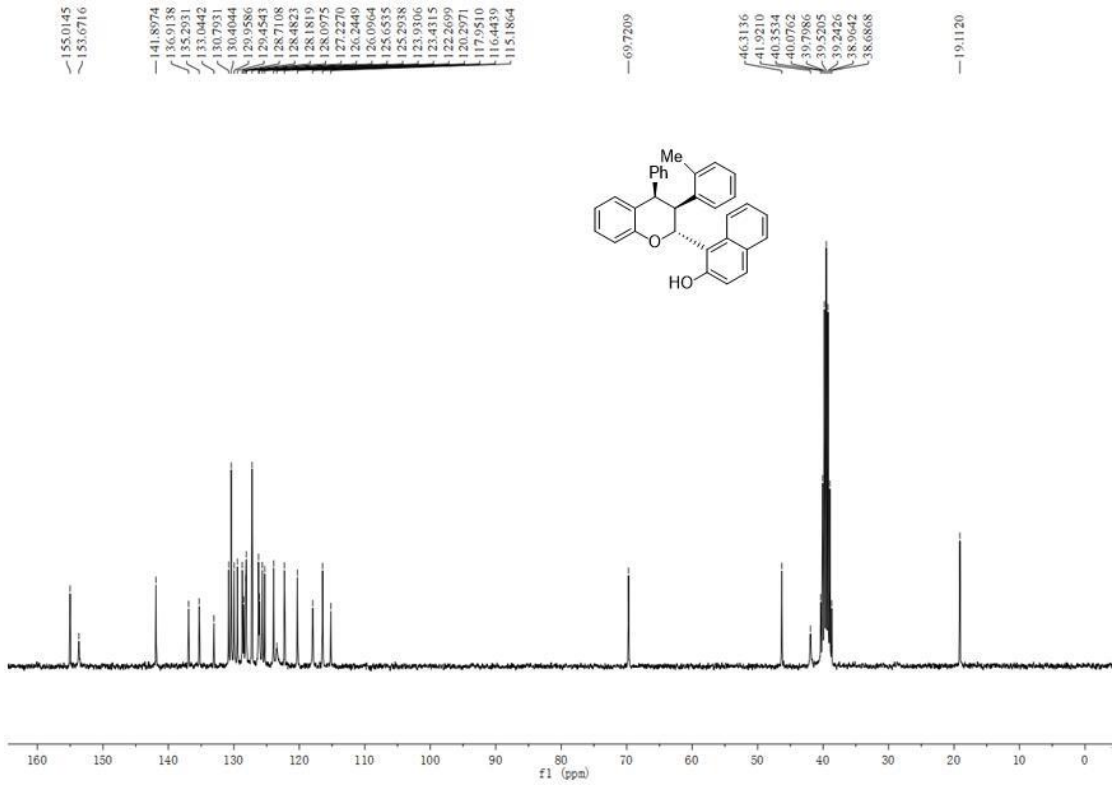


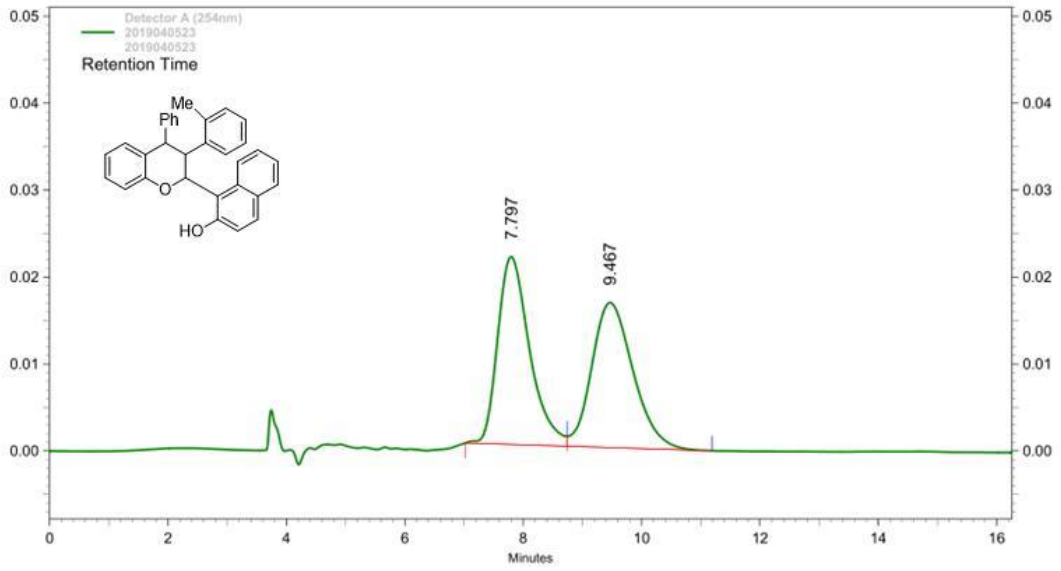
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	6.817	5400	0.44	101257	1.26
2	9.583	3351	0.27	47893	0.60
3	10.267	1228843	99.29	7881407	98.14
Totals		1237594	100.00	8030557	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3b

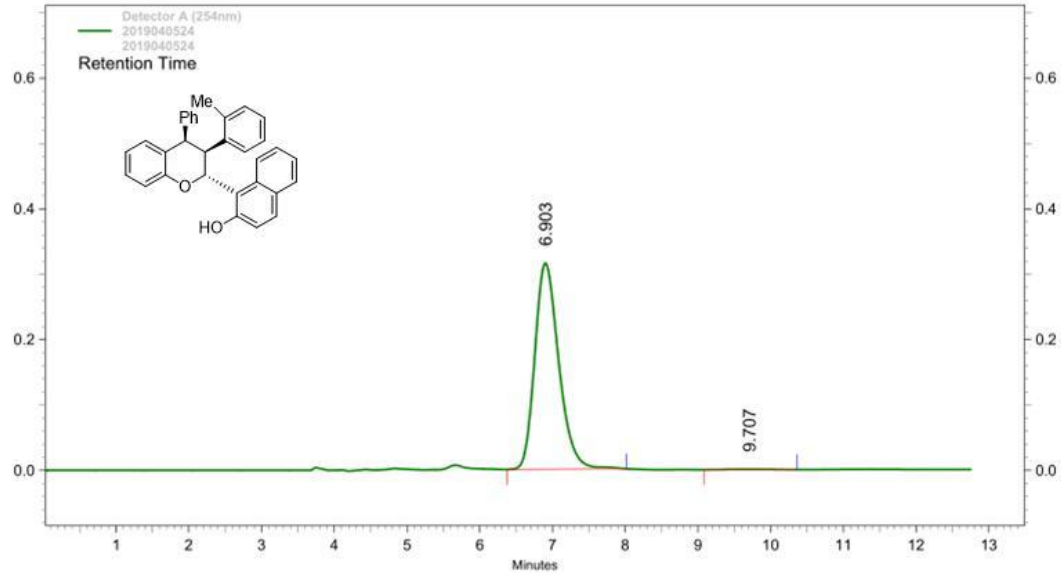






Detector A (254nm)

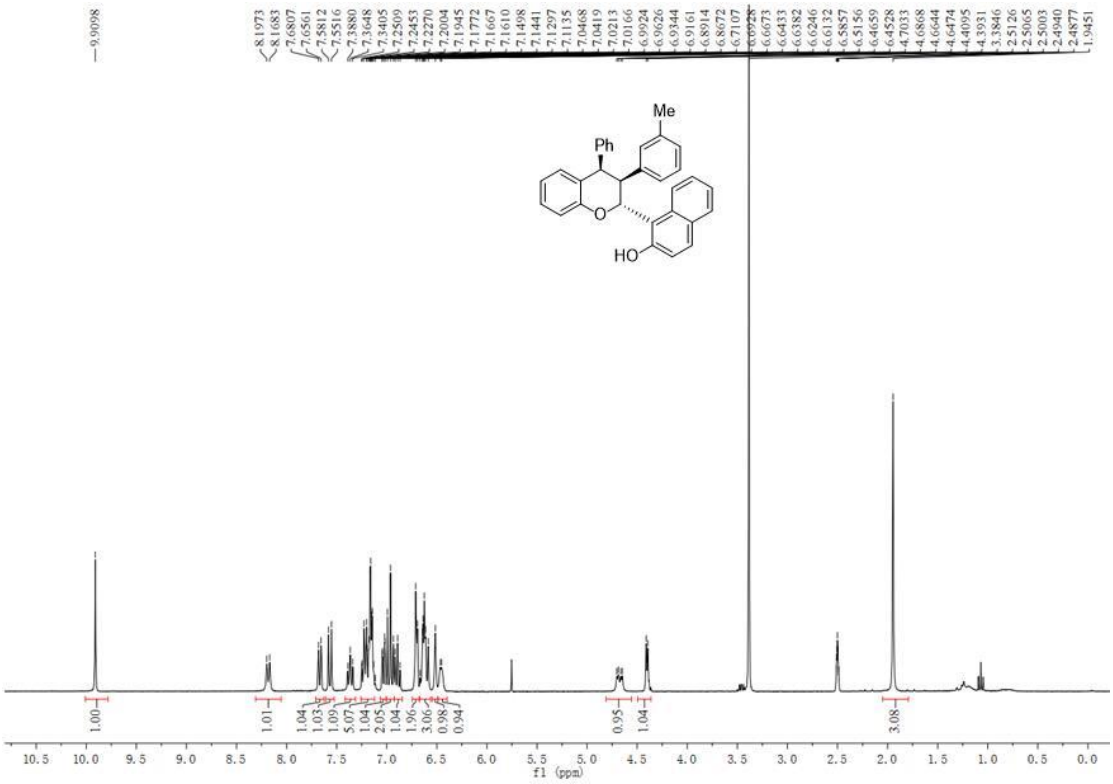
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	7.797	21579	56.44	807554	49.98
2	9.467	16656	43.56	808263	50.02
Totals		38235	100.00	1615817	100.00

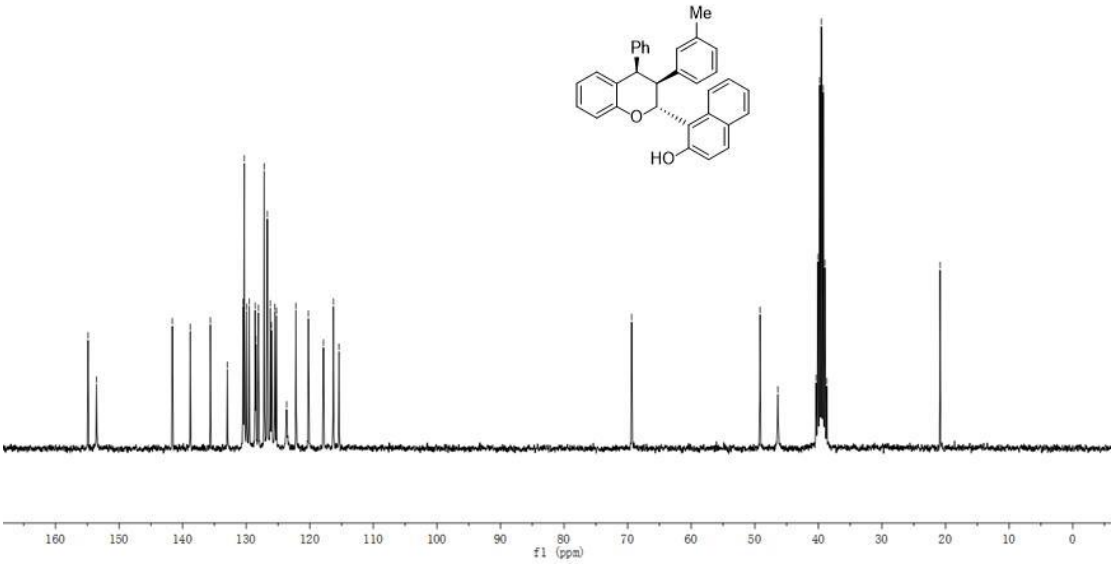


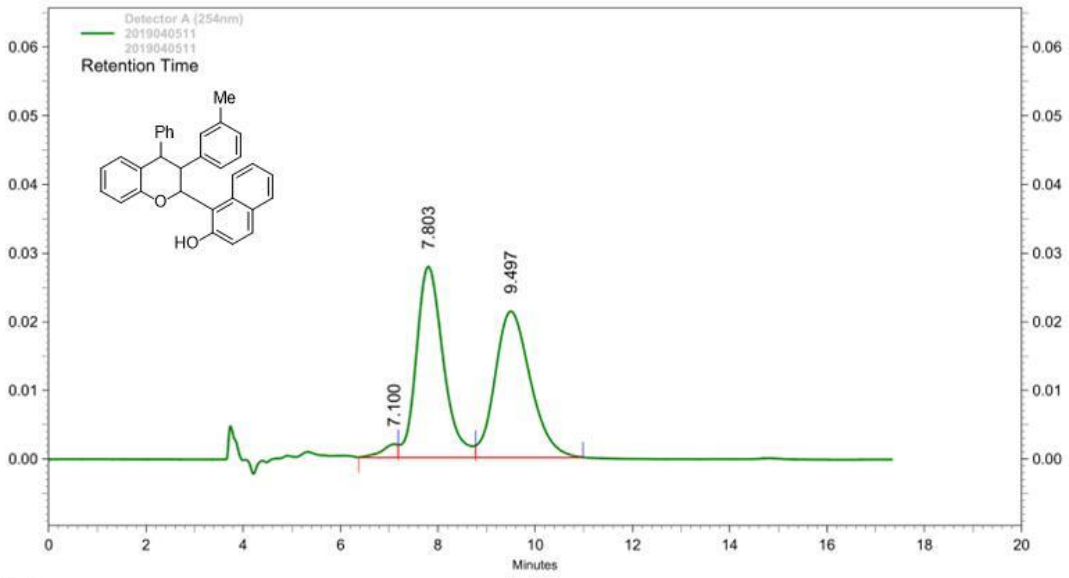
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	6.903	315182	99.79	7228277	99.61
2	9.707	662	0.21	28137	0.39
Totals		315844	100.00	7256414	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3c

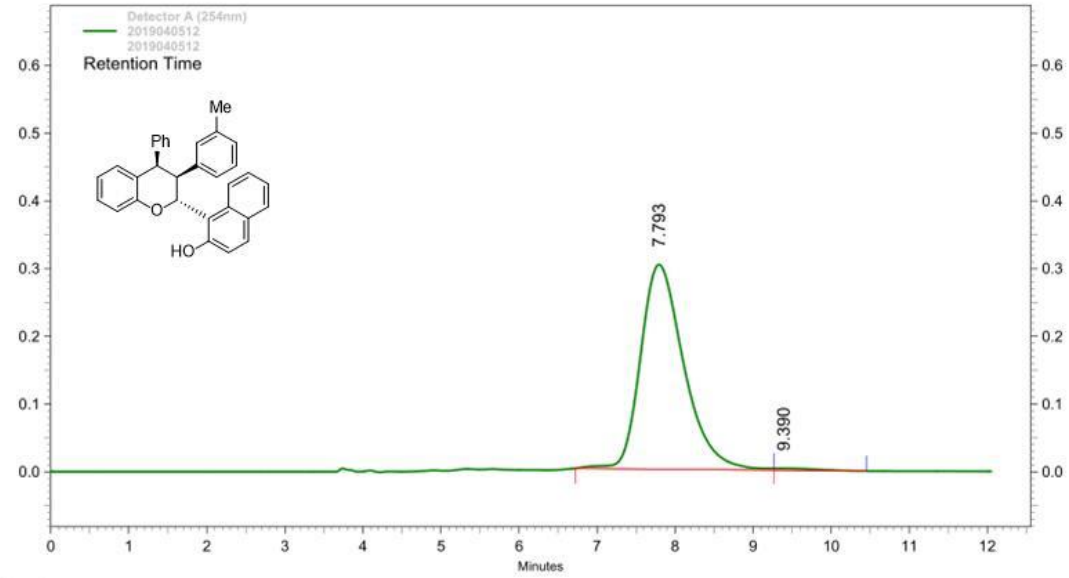






Detector A (254nm)

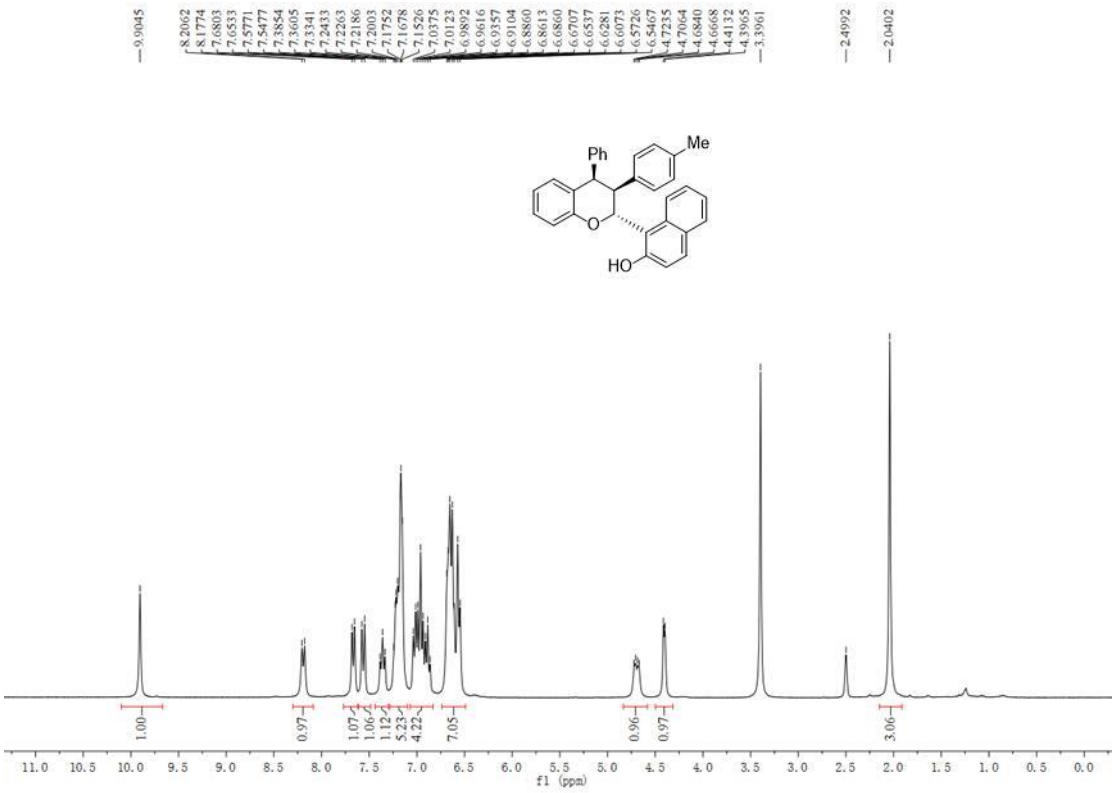
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	7.100	1904	3.74	41963	1.93
2	7.803	27768	54.51	1064837	48.87
3	9.497	21266	41.75	1072100	49.20
Totals		50938	100.00	2178900	100.00

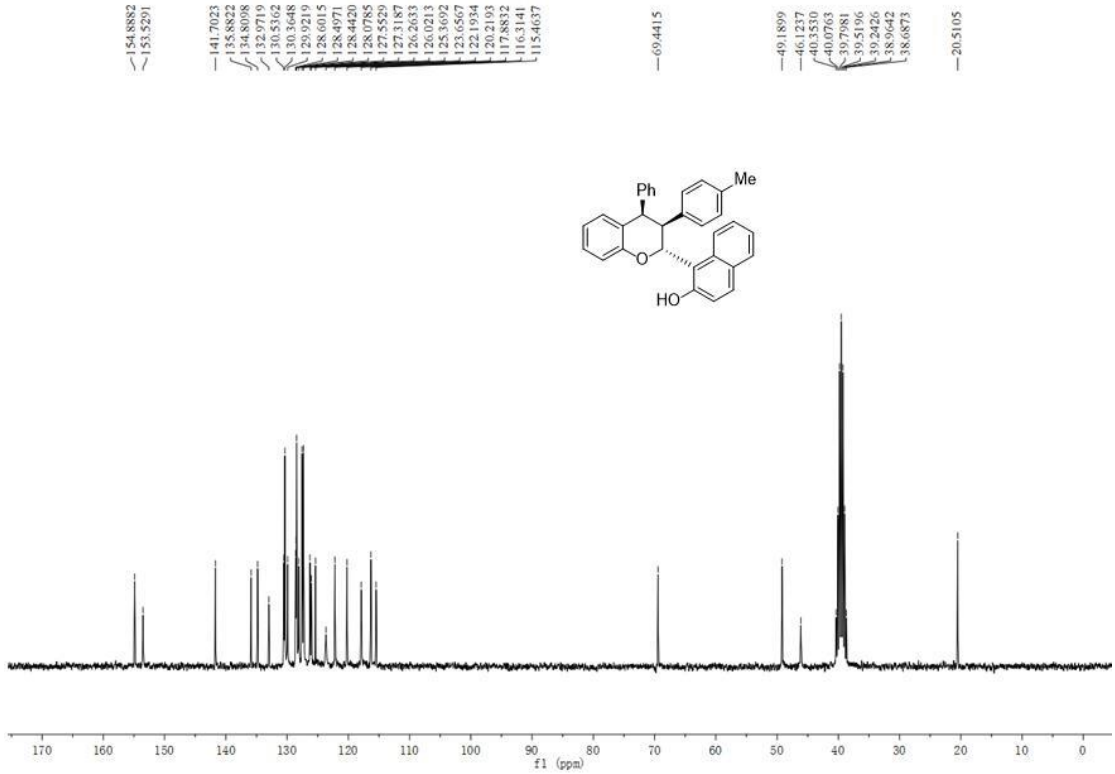


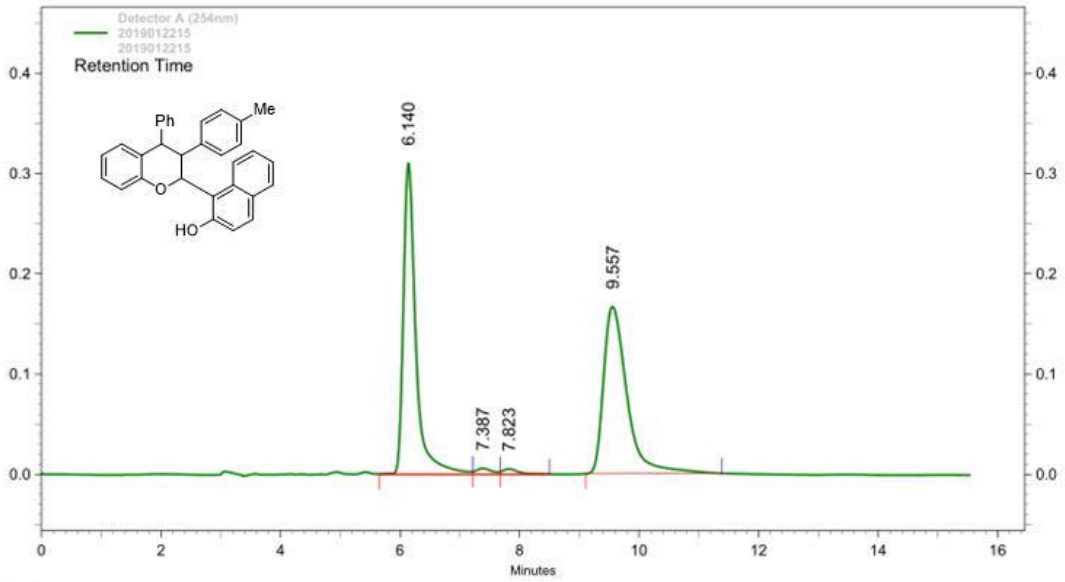
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	7.793	301969	99.10	11643003	99.16
2	9.390	2750	0.90	98054	0.84
Totals		304719	100.00	11741057	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3d

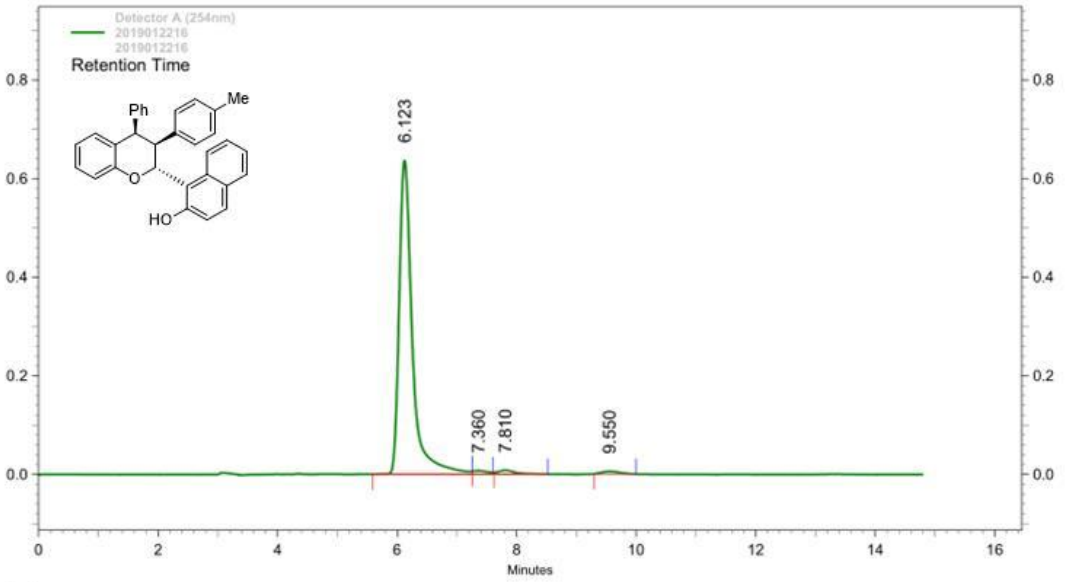






Detector A (254nm)

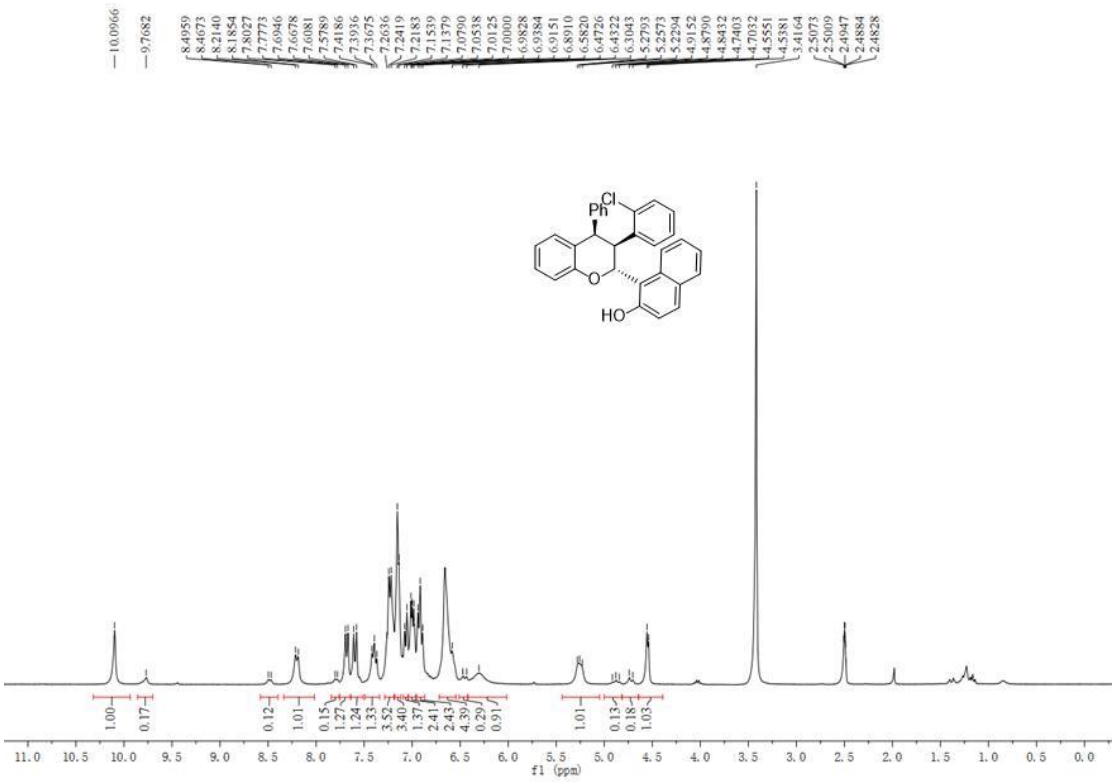
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	6.140	309997	63.57	4476526	48.69
2	7.387	5759	1.18	106264	1.16
3	7.823	5265	1.08	94096	1.02
4	9.557	166648	34.17	4517331	49.13
Totals		487669	100.00	9194217	100.00

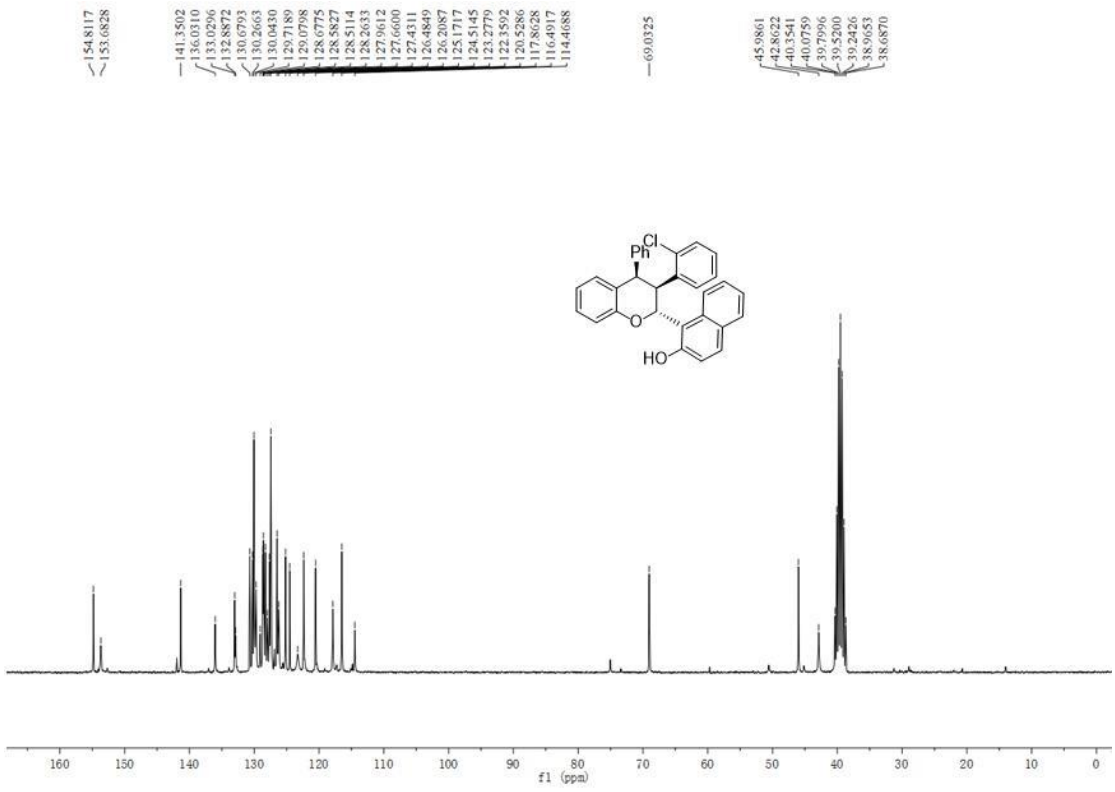


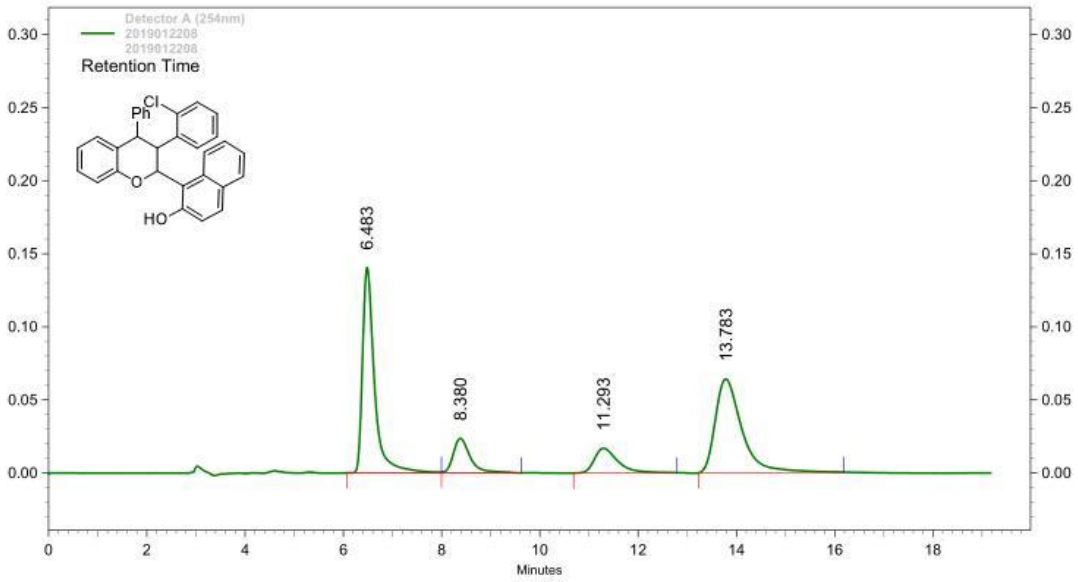
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	6.123	636384	96.98	9724307	96.20
2	7.360	6841	1.04	115003	1.14
3	7.810	7830	1.19	158475	1.57
4	9.550	5171	0.79	110646	1.09
Totals		656226	100.00	10108431	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3e

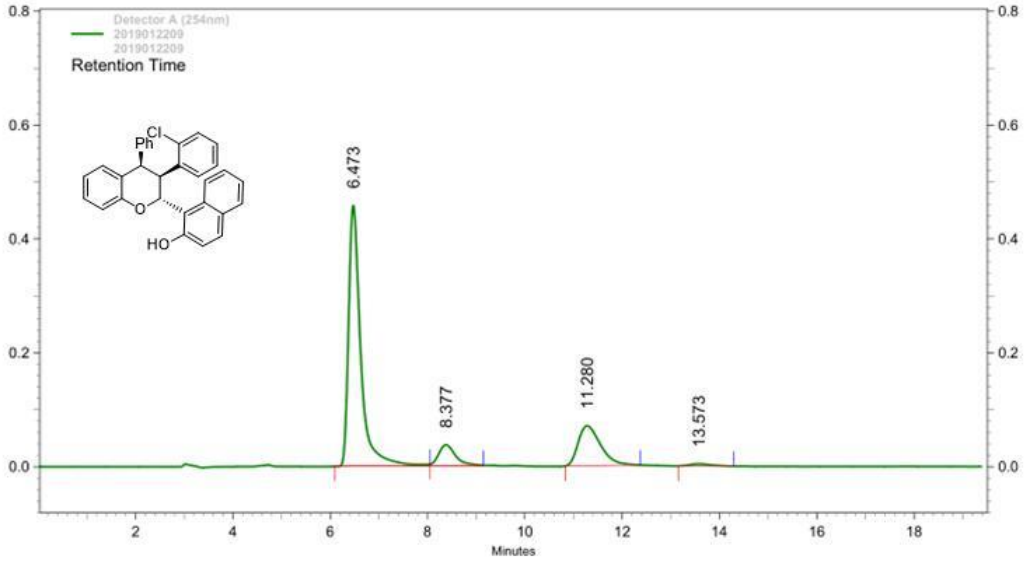






Detector A (254nm)

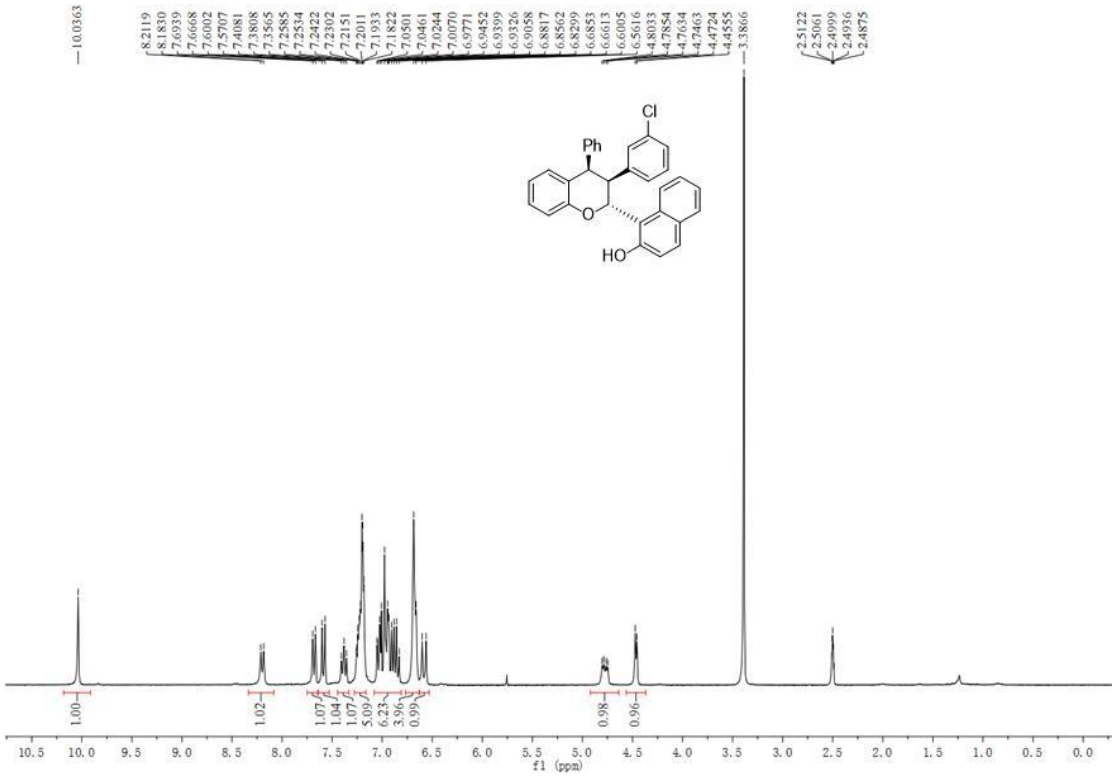
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	6.483	140503	57.33	2381515	40.41
2	8.380	23603	9.63	565799	9.60
3	11.293	16905	6.90	555965	9.43
4	13.783	64083	26.15	2390715	40.56
Totals		245094	100.00	5893994	100.00

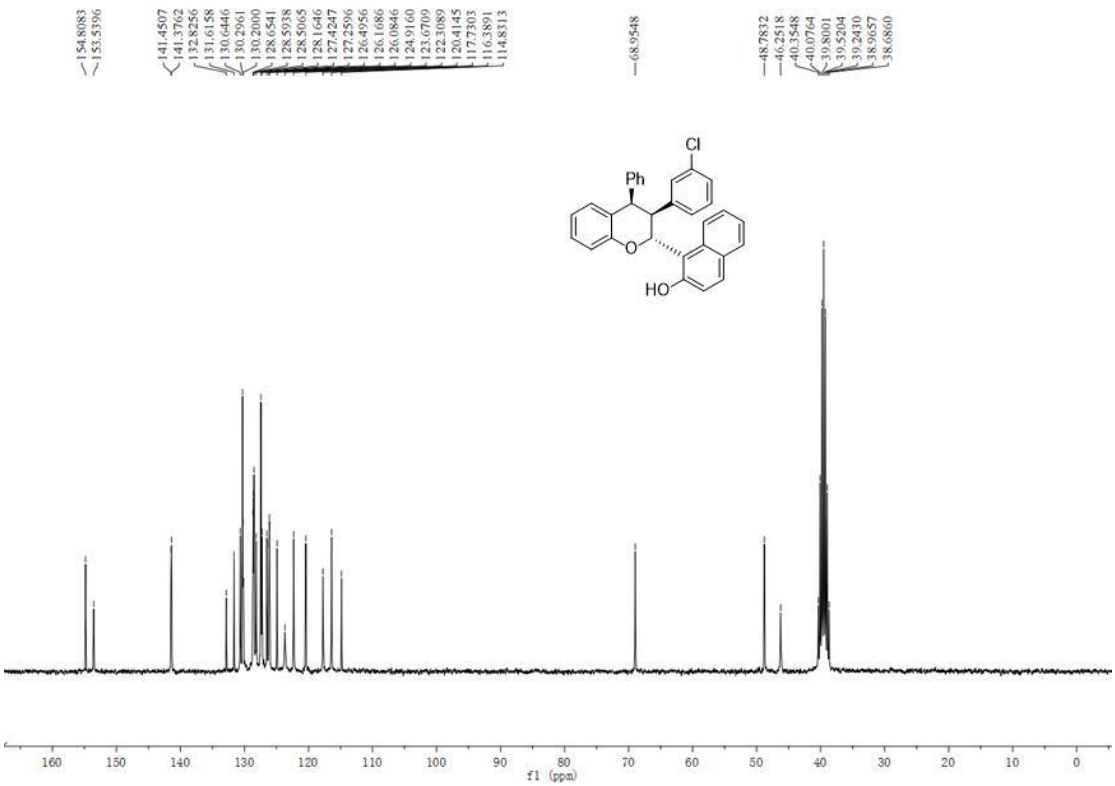


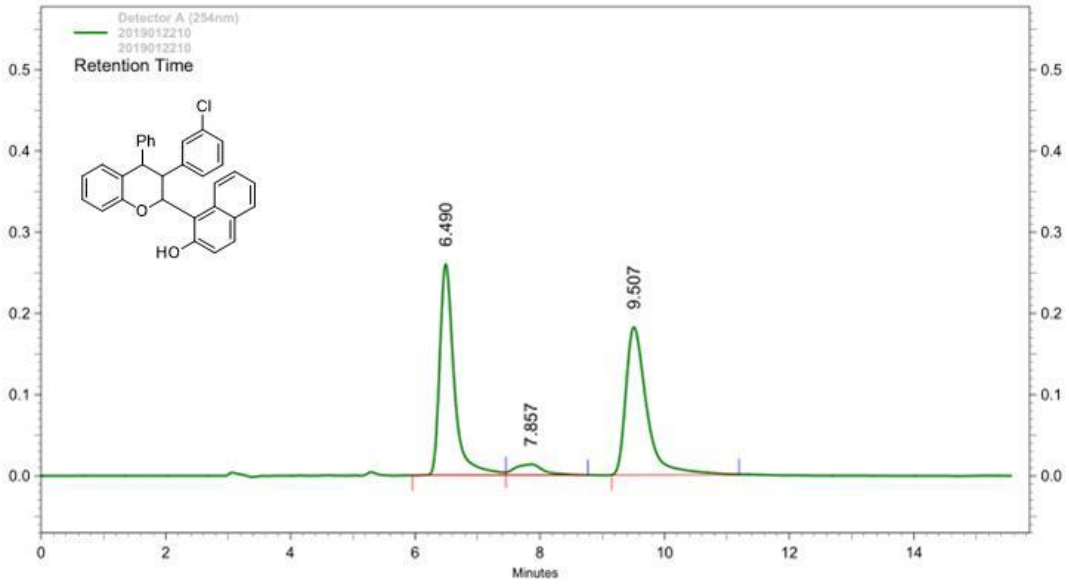
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	6.473	457969	80.59	7938291	71.13
2	8.377	36532	6.43	871259	7.81
3	11.280	69999	12.32	2237139	20.05
4	13.573	3740	0.66	113655	1.02
Totals		568240	100.00	11160344	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3f

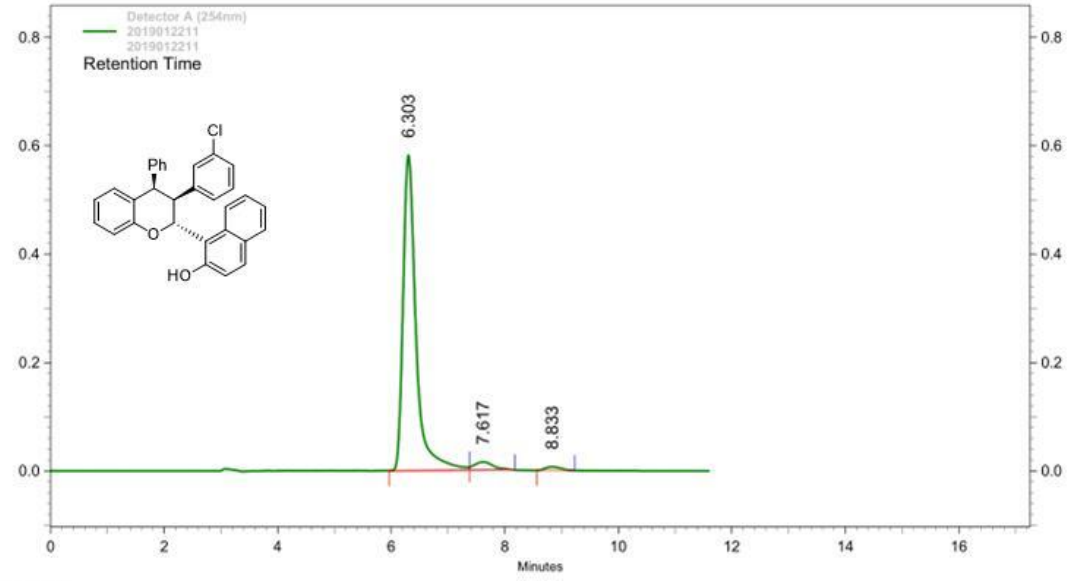






Detector A (254nm)

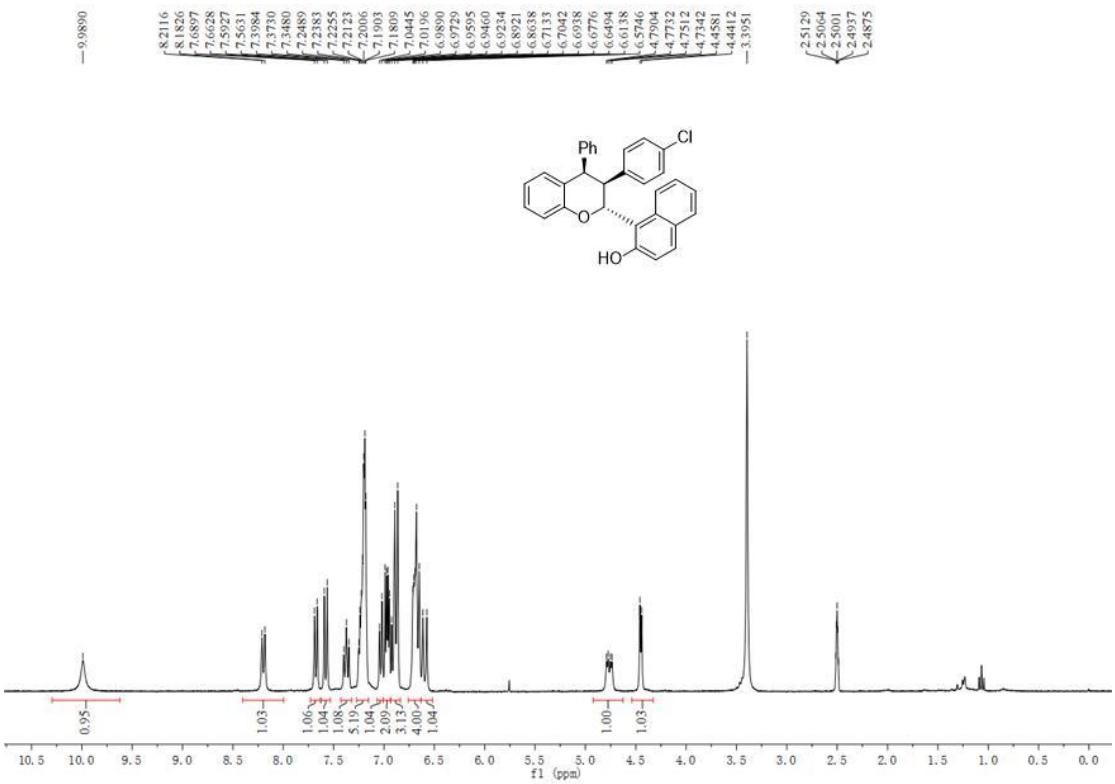
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	6.490	259979	57.12	4215832	47.69
2	7.857	13348	2.93	421109	4.76
3	9.507	181852	39.95	4202689	47.54
Totals		455179	100.00	8839630	100.00

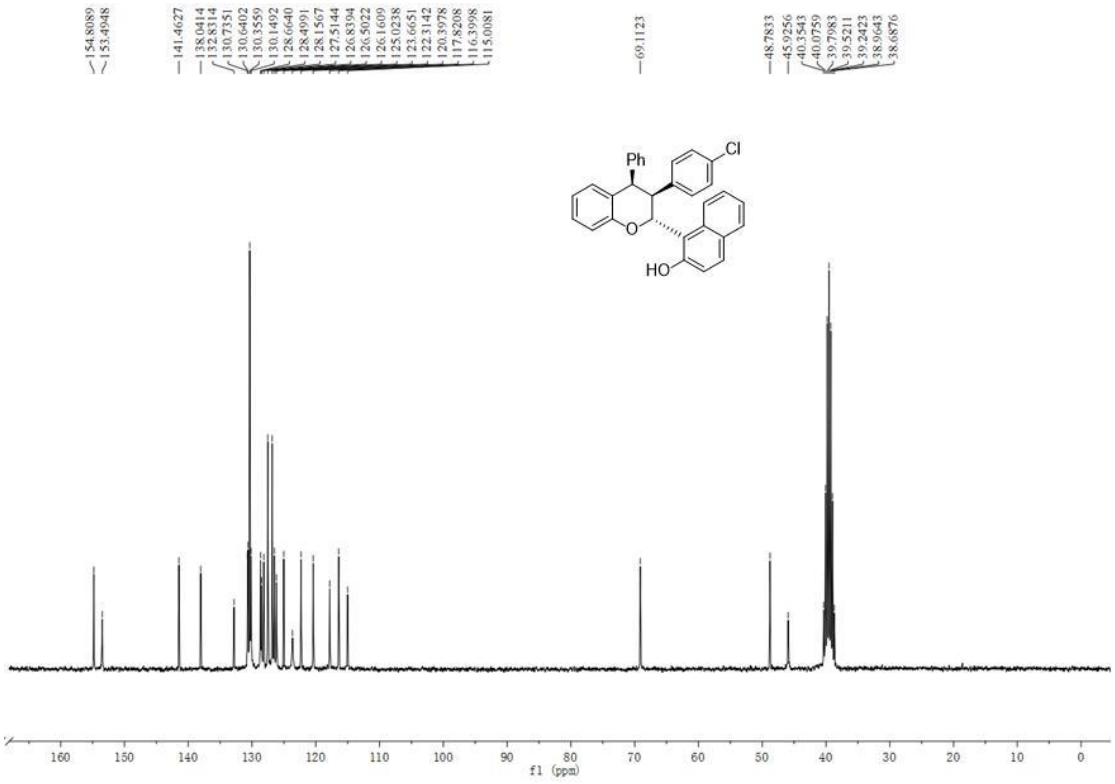


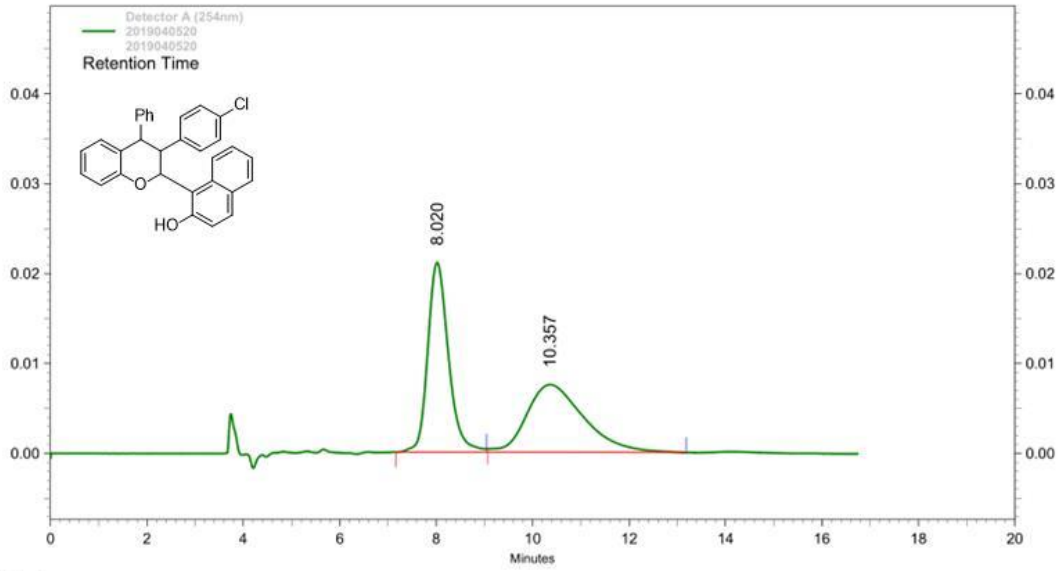
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	6.303	581877	96.42	9217897	95.11
2	7.617	14963	2.48	350204	3.61
3	8.833	6660	1.10	123550	1.27
Totals		603500	100.00	9691651	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3g

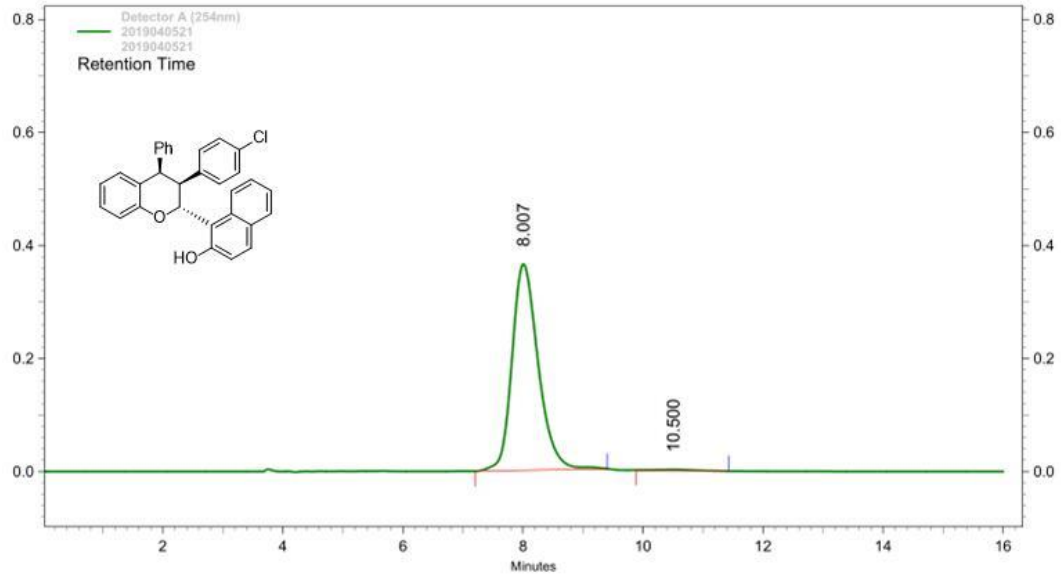






Detector A (254nm)

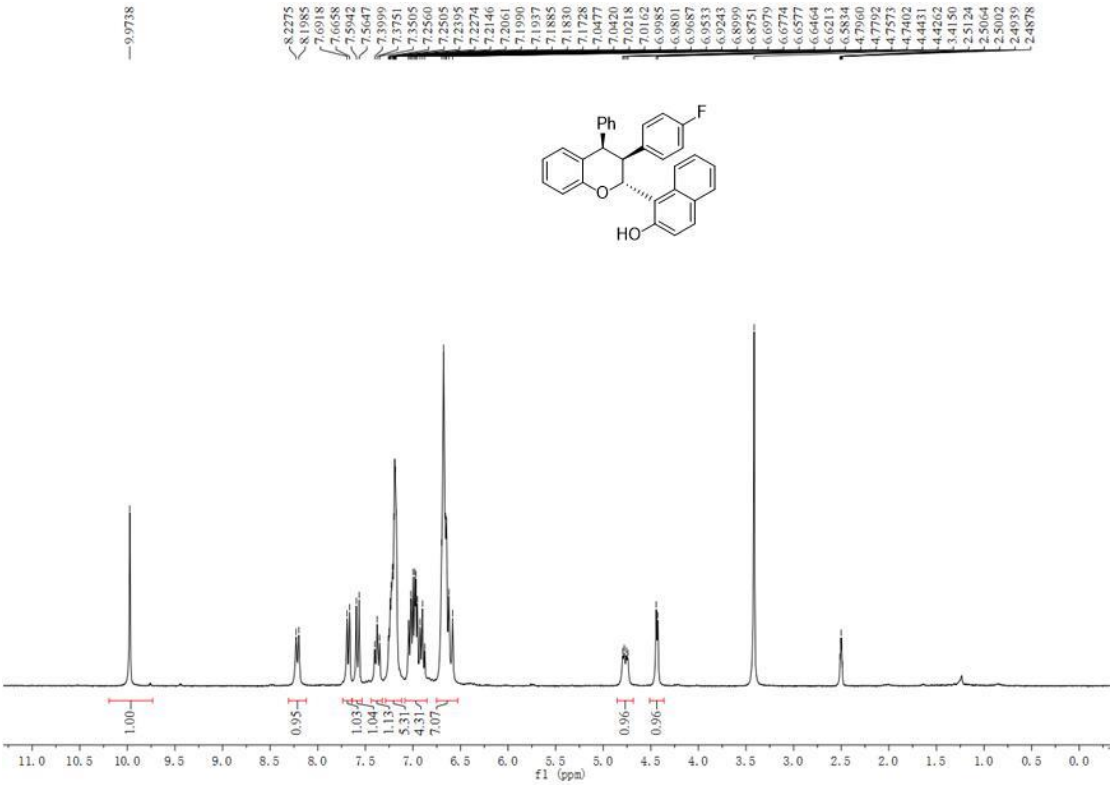
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.020	21083	73.71	628838	50.41
2	10.357	7520	26.29	618594	49.59
Totals		28603	100.00	1247432	100.00

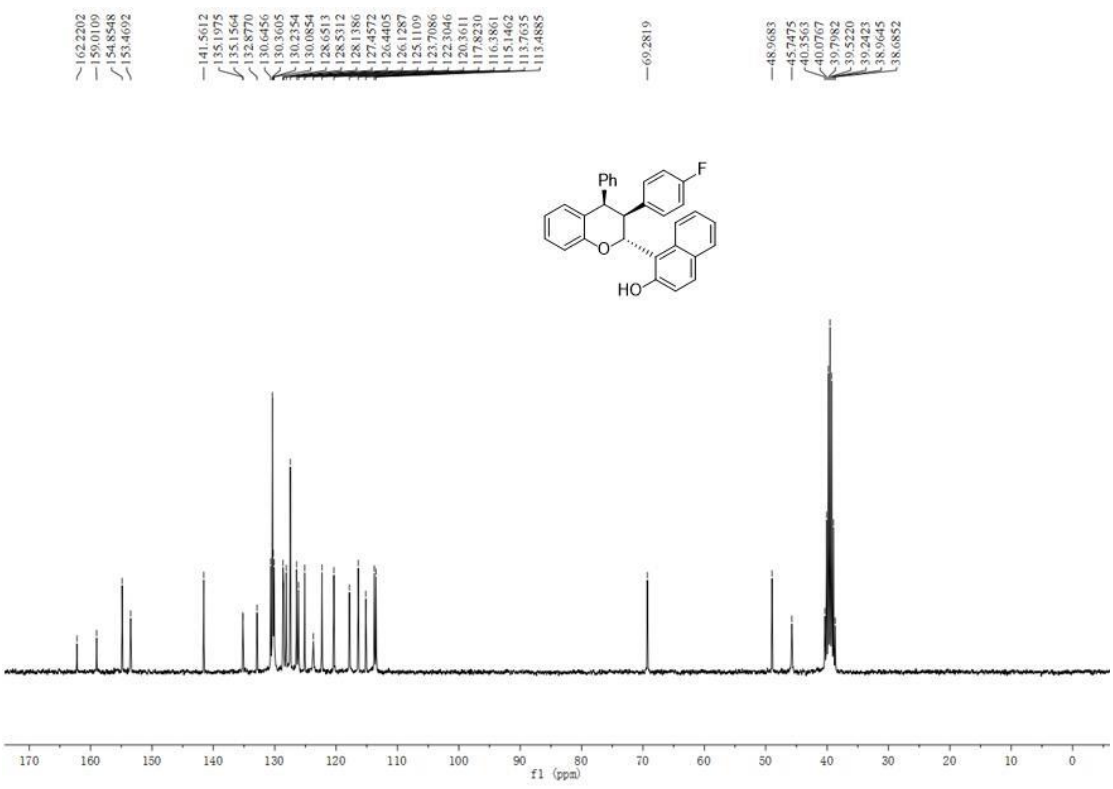


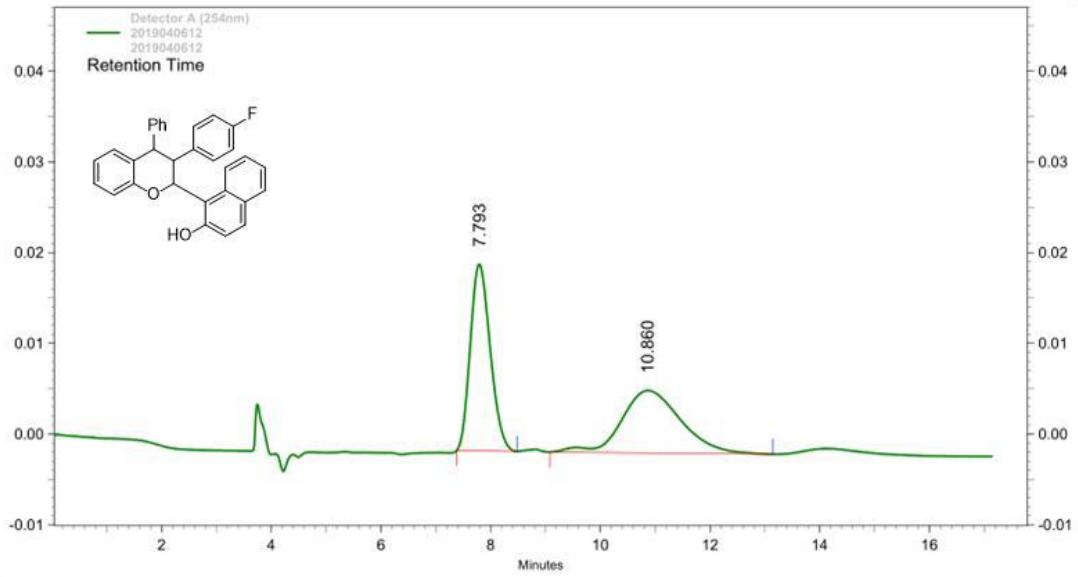
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.007	364983	99.54	11092075	99.41
2	10.500	1684	0.46	65774	0.59
Totals		366667	100.00	11157849	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3h

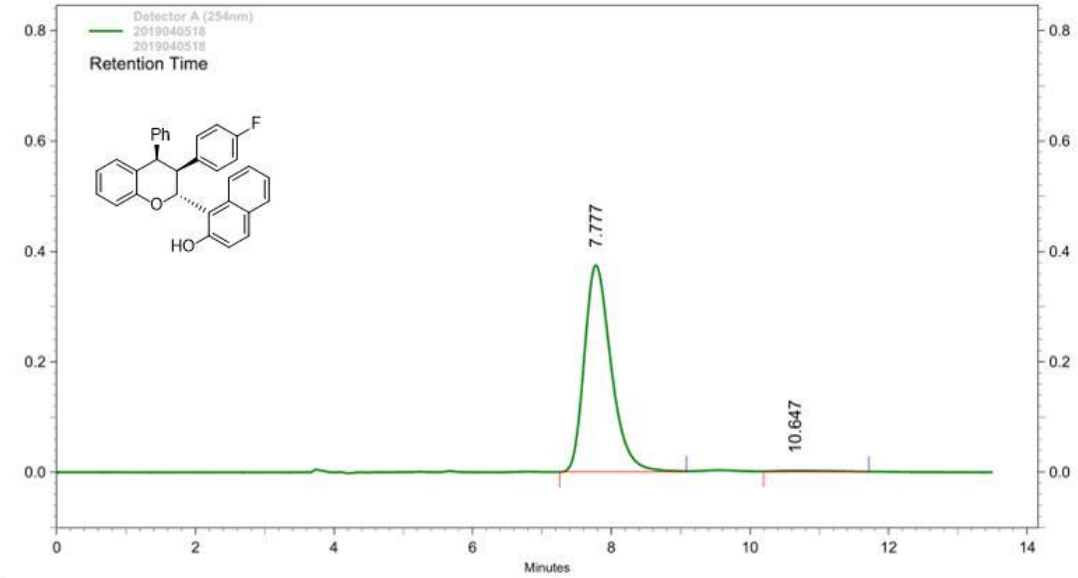






Detector A (254nm)

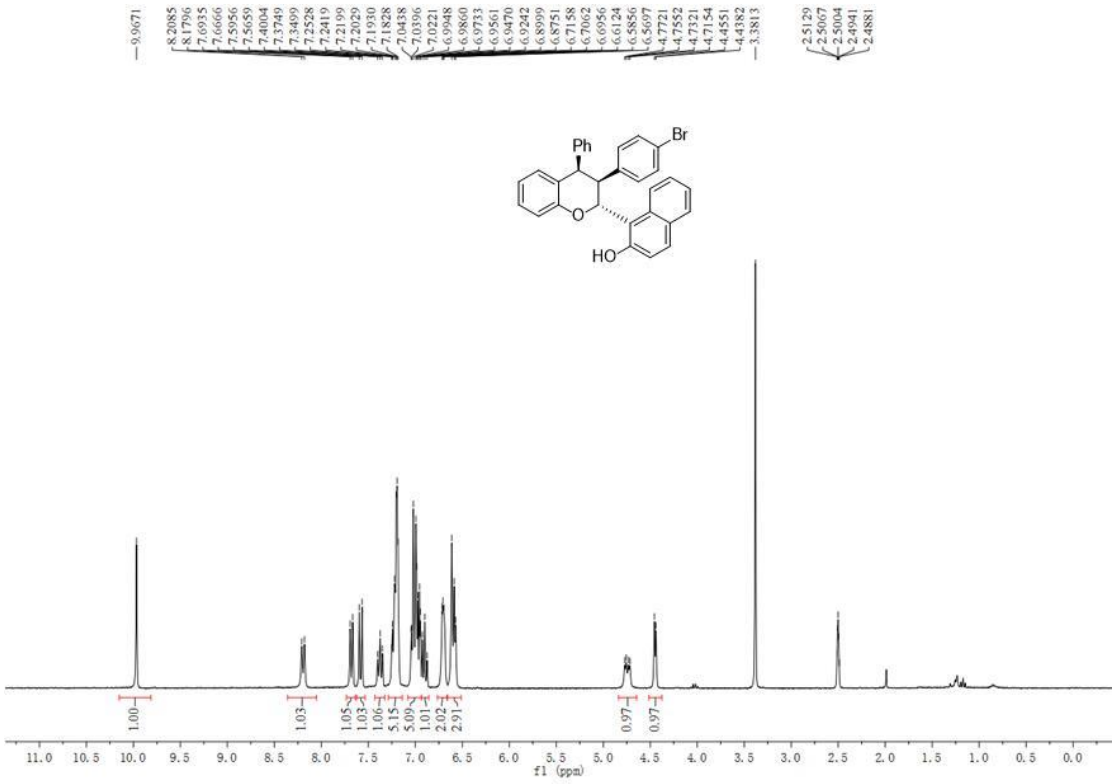
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	7.793	20559	74.93	518767	50.11
2	10.860	6880	25.07	516450	49.89
Totals		27439	100.00	1035217	100.00

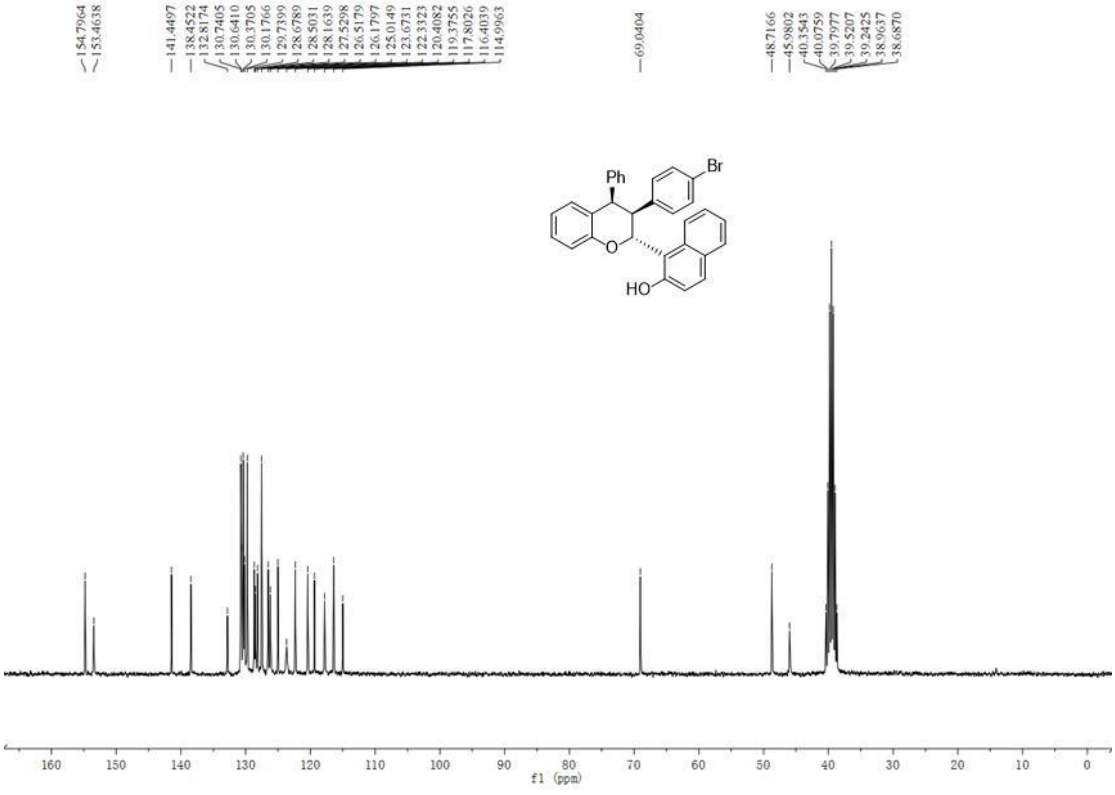


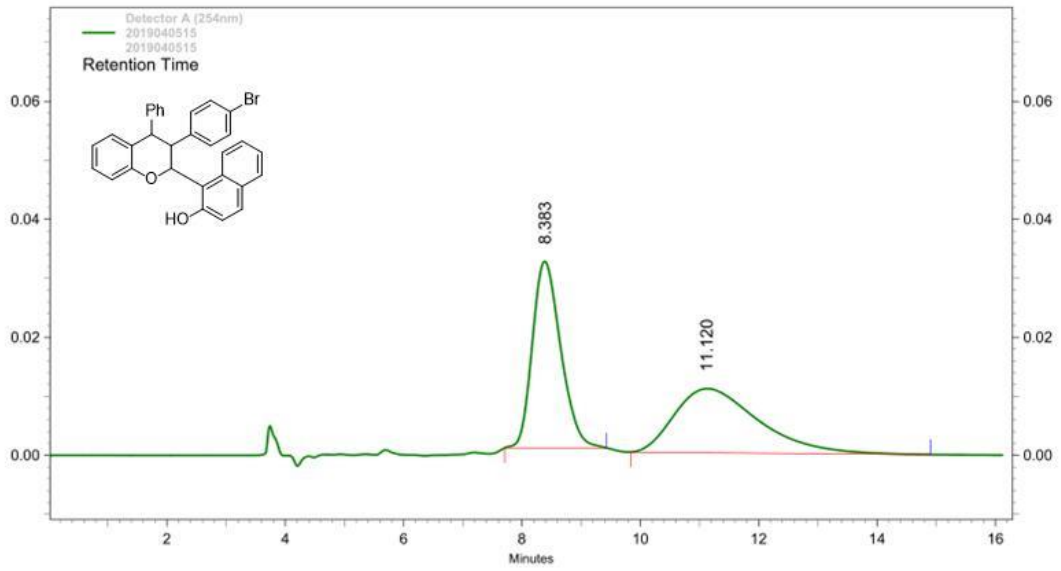
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	7.777	374167	99.58	10031306	99.23
2	10.647	1567	0.42	77513	0.77
Totals		375734	100.00	10108819	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3i

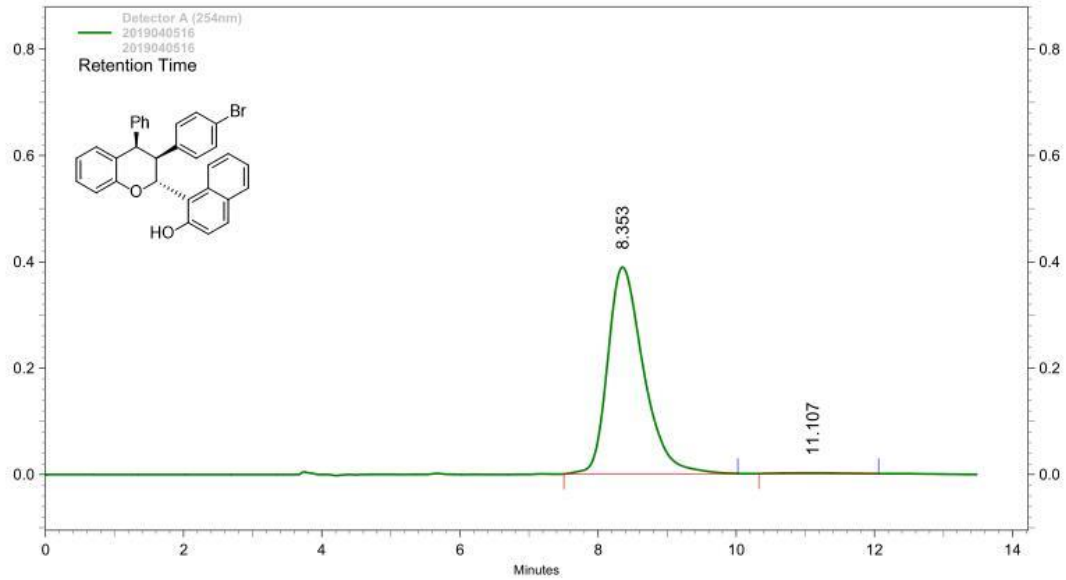






Detector A (254nm)

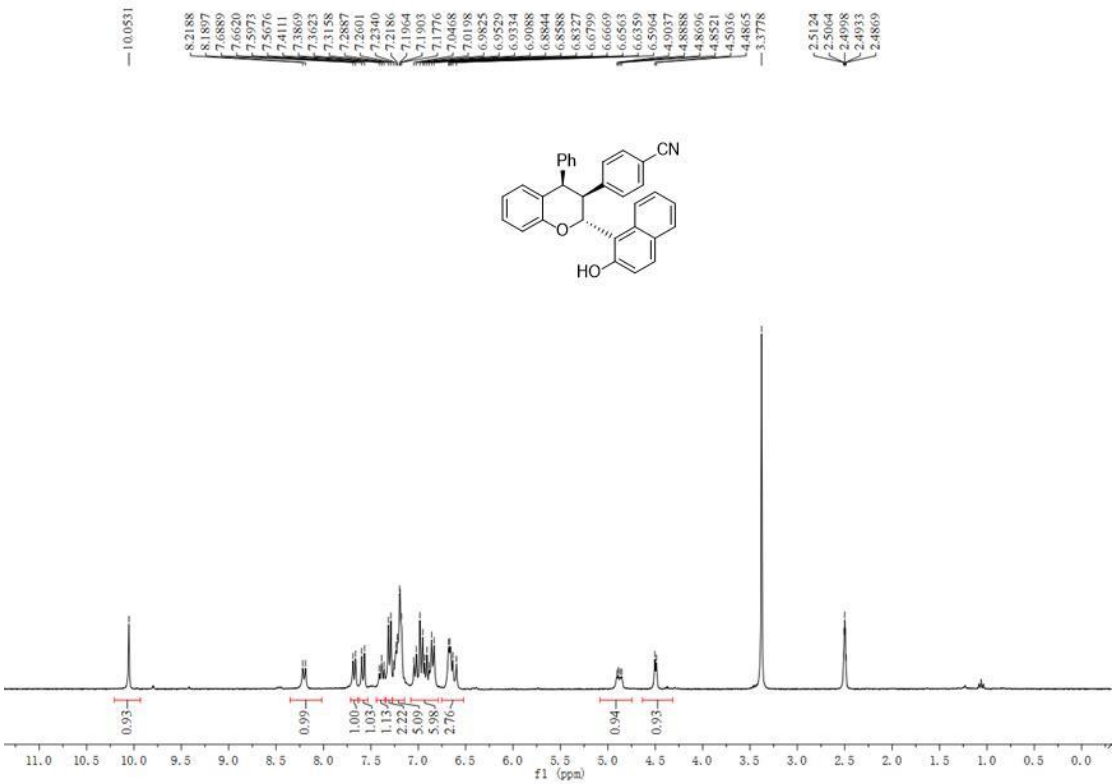
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.383	31601	74.45	1052249	49.62
2	11.120	10845	25.55	1068181	50.38
Totals		42446	100.00	2120430	100.00

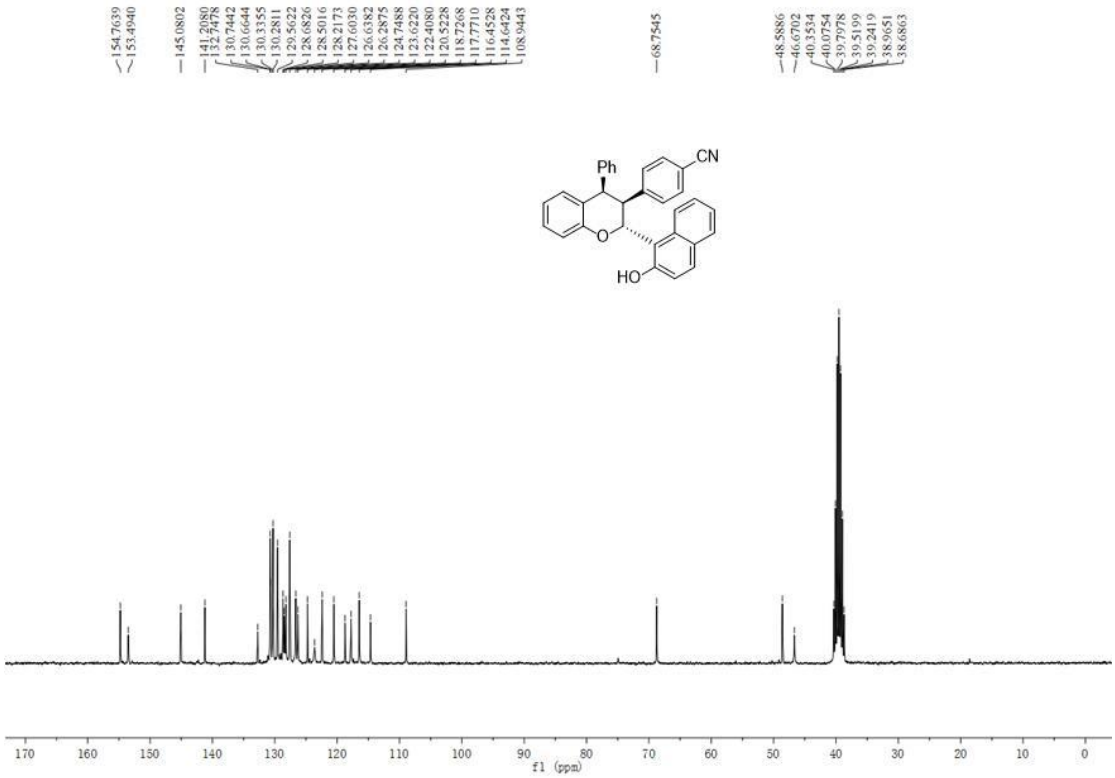


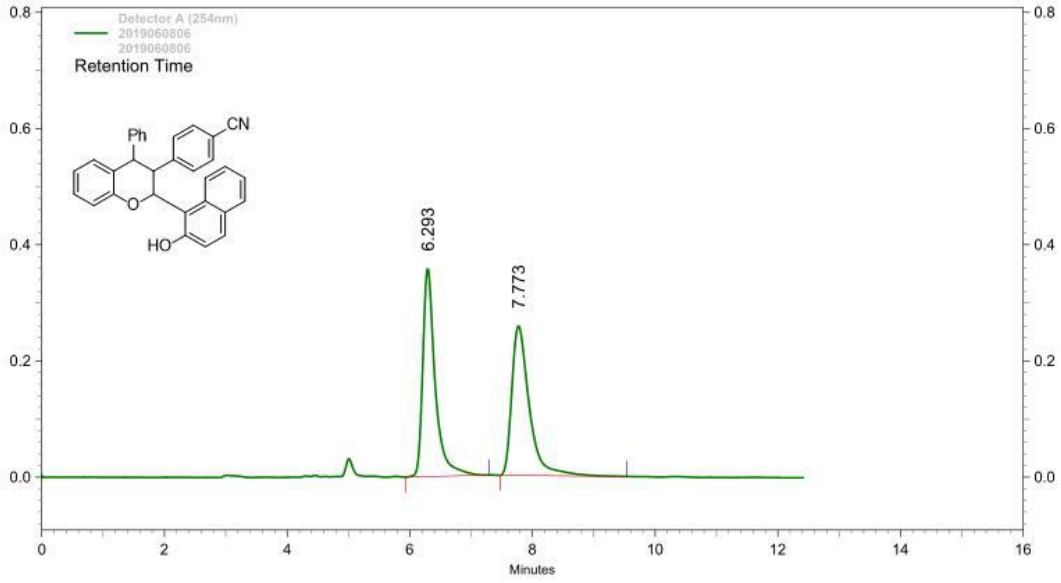
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.353	388674	99.63	13973483	99.36
2	11.107	1450	0.37	89365	0.64
Totals		390124	100.00	14062848	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3j

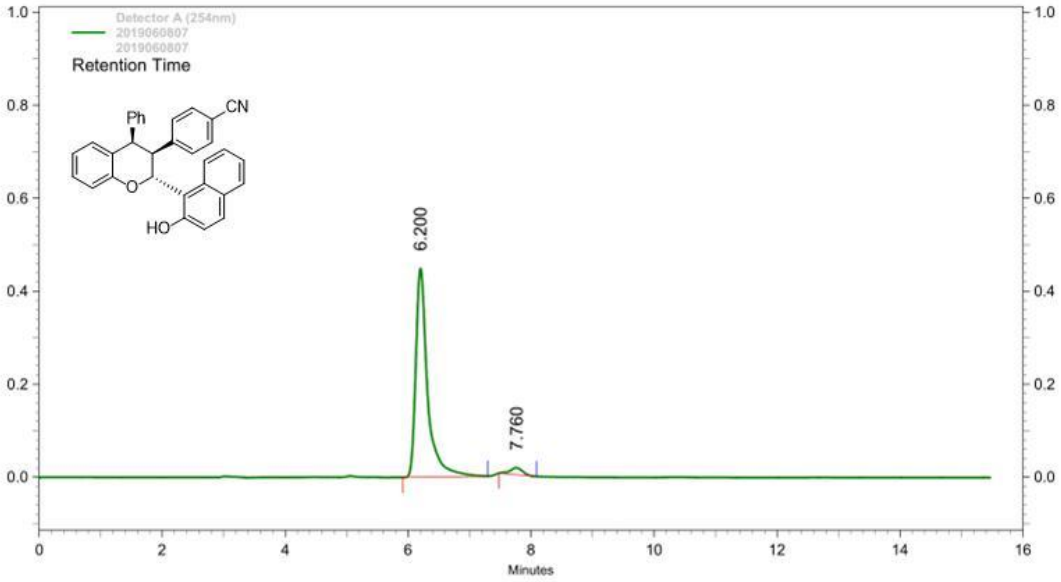






Detector A (254nm)

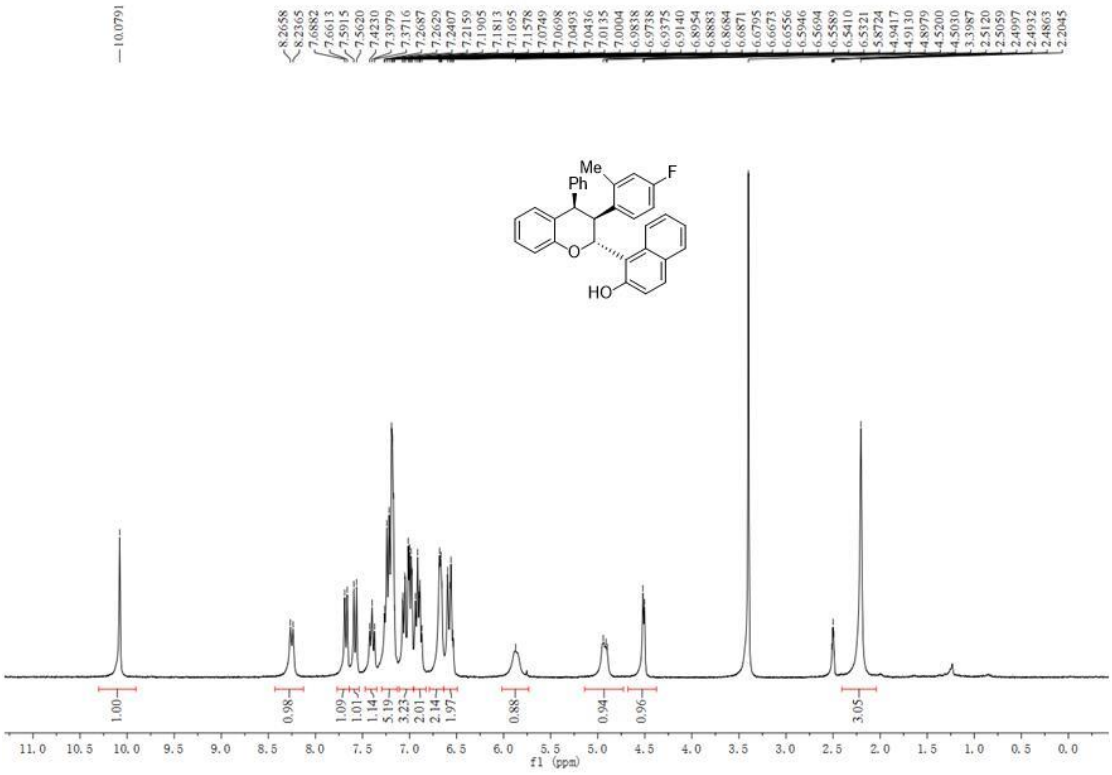
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	6.293	357693	58.20	5036253	49.67
2	7.773	256889	41.80	5103632	50.33
Totals		614582	100.00	10139885	100.00

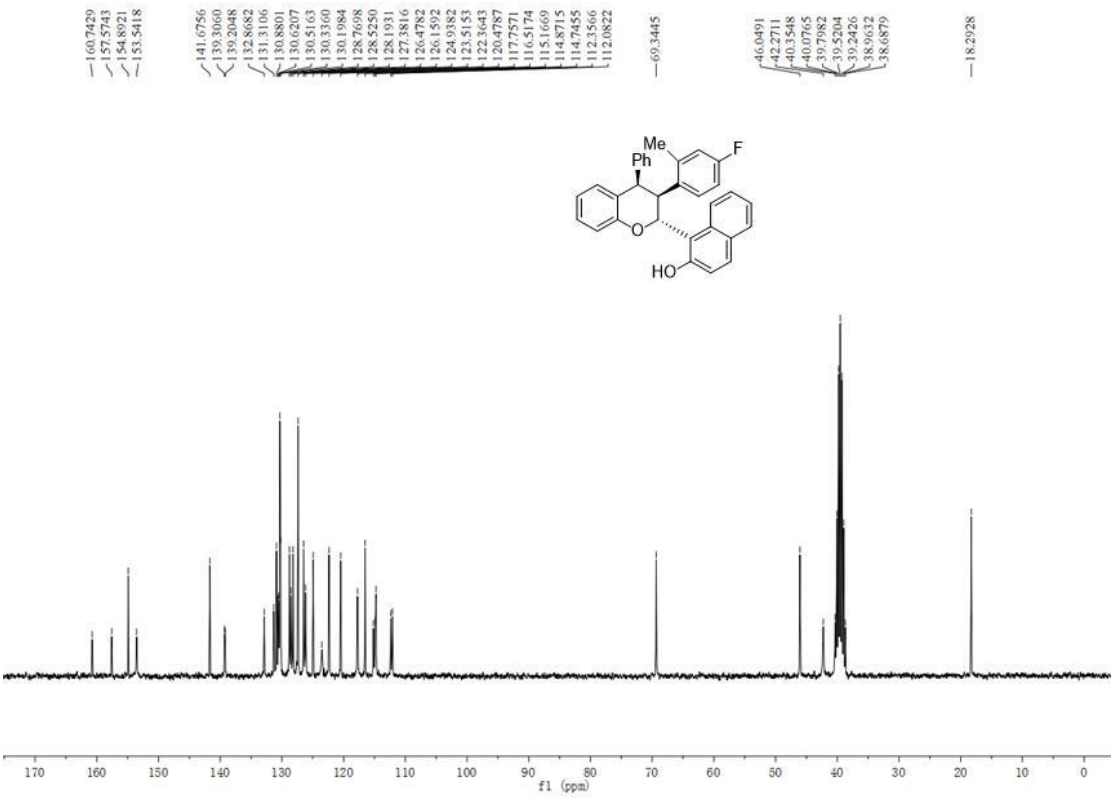


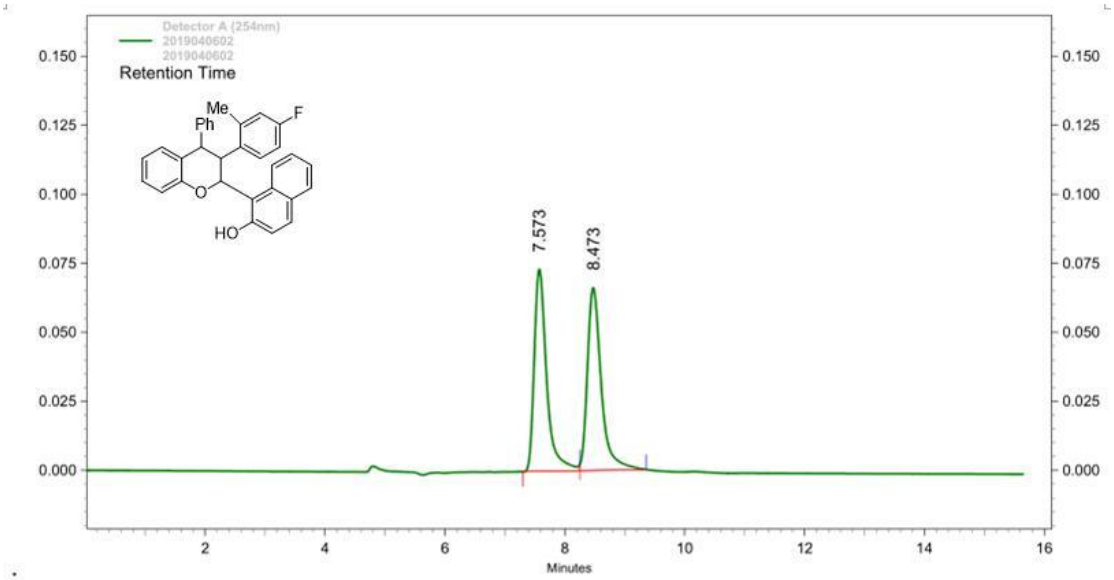
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	6.200	448888	96.81	5961774	96.60
2	7.760	14792	3.19	210043	3.40
Totals		463680	100.00	6171817	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3k

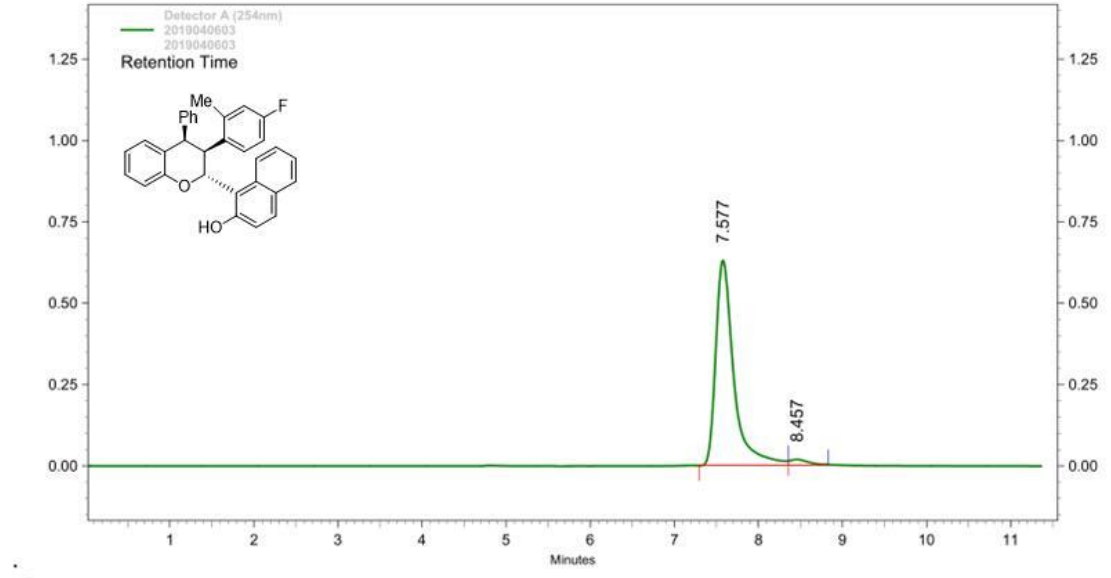






Detector A (254nm)

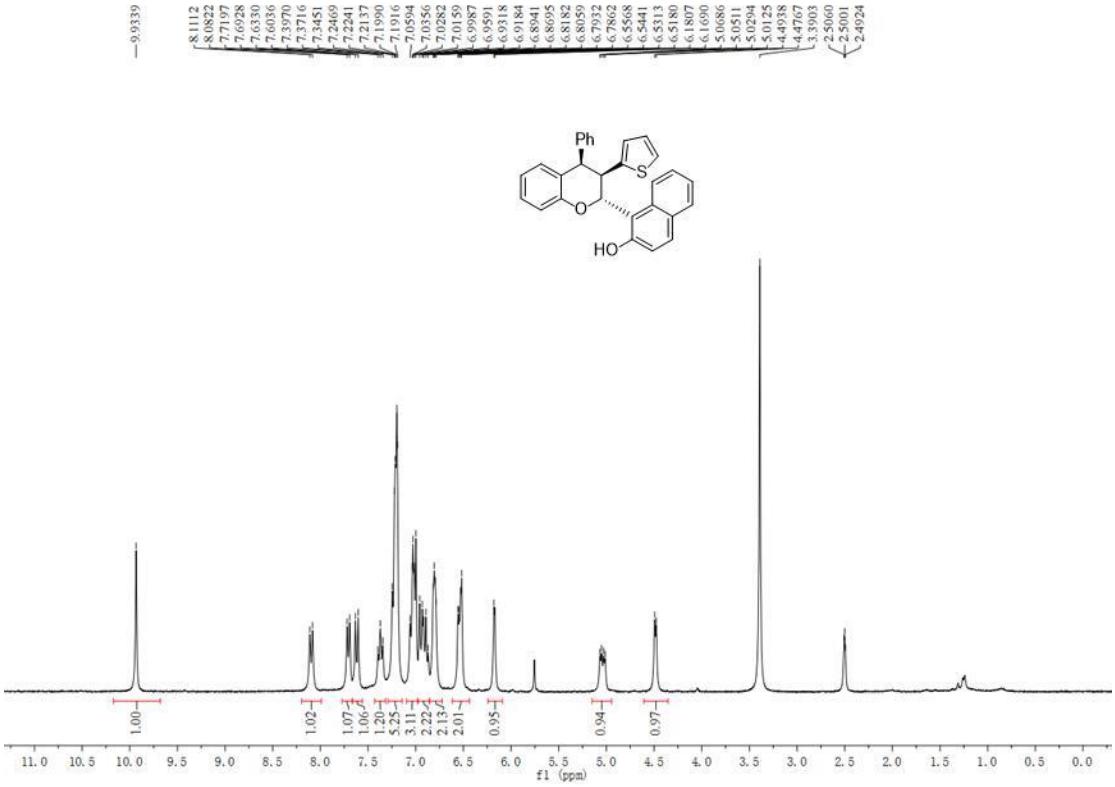
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	7.573	73228	52.51	1056801	49.77
2	8.473	66215	47.49	1066709	50.23
Totals		139443	100.00	2123510	100.00

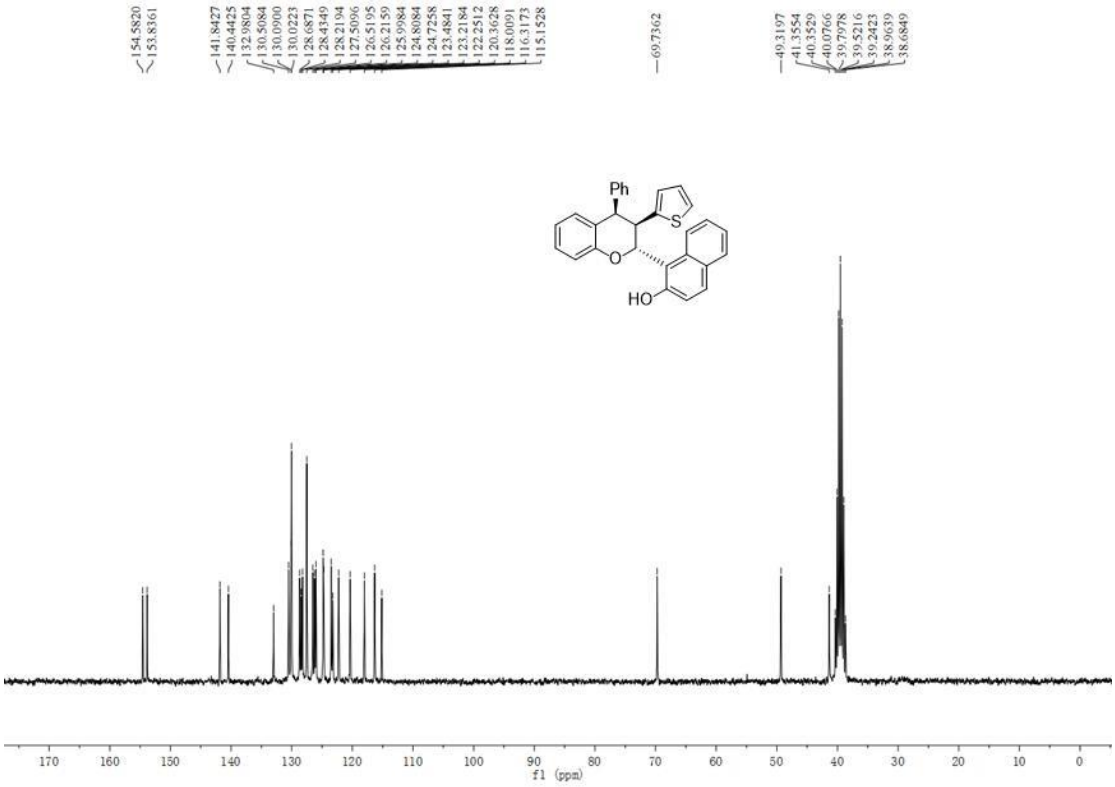


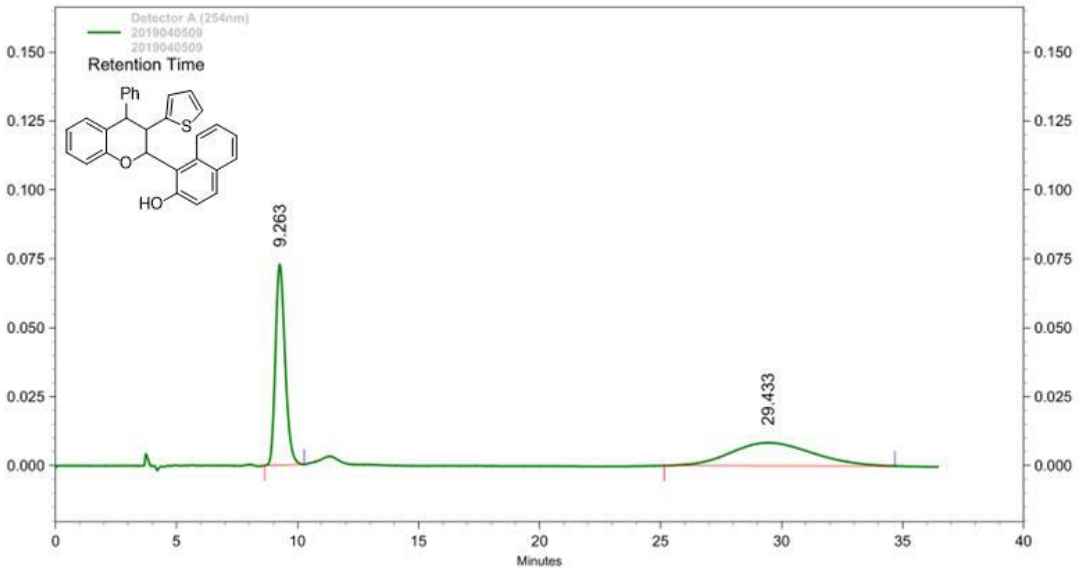
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	7.577	629851	97.42	9377756	97.42
2	8.457	16688	2.58	248158	2.58
Totals		646539	100.00	9625914	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3l

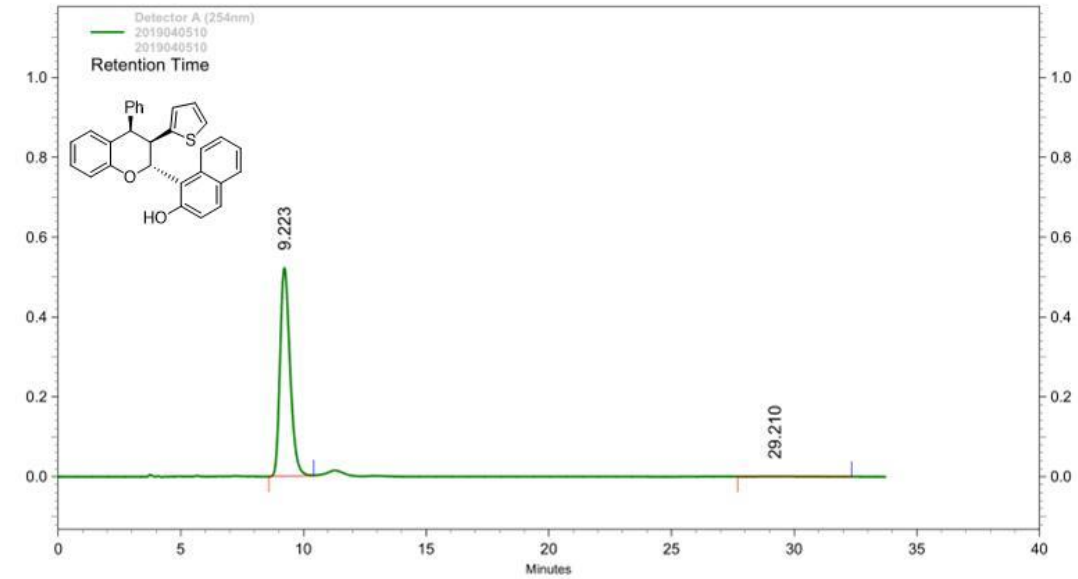






Detector A (254nm)

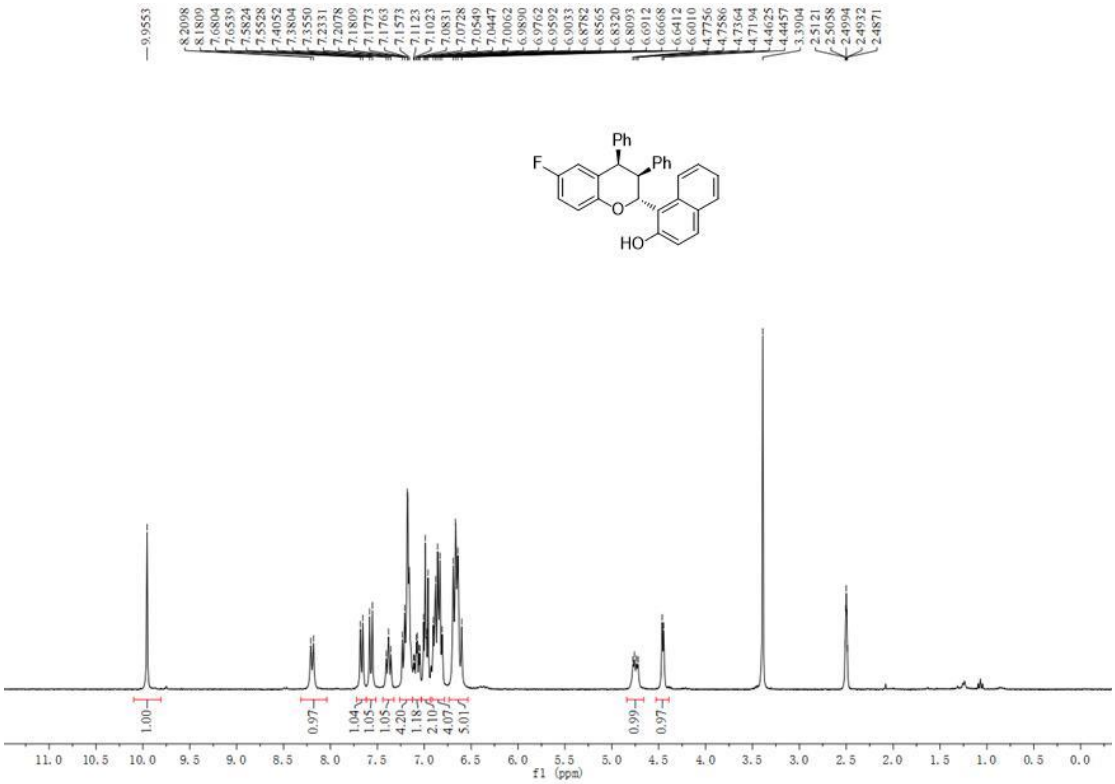
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	9.263	72763	89.71	2013297	50.49
2	29.433	8345	10.29	1973903	49.51
Totals		81108	100.00	3987200	100.00

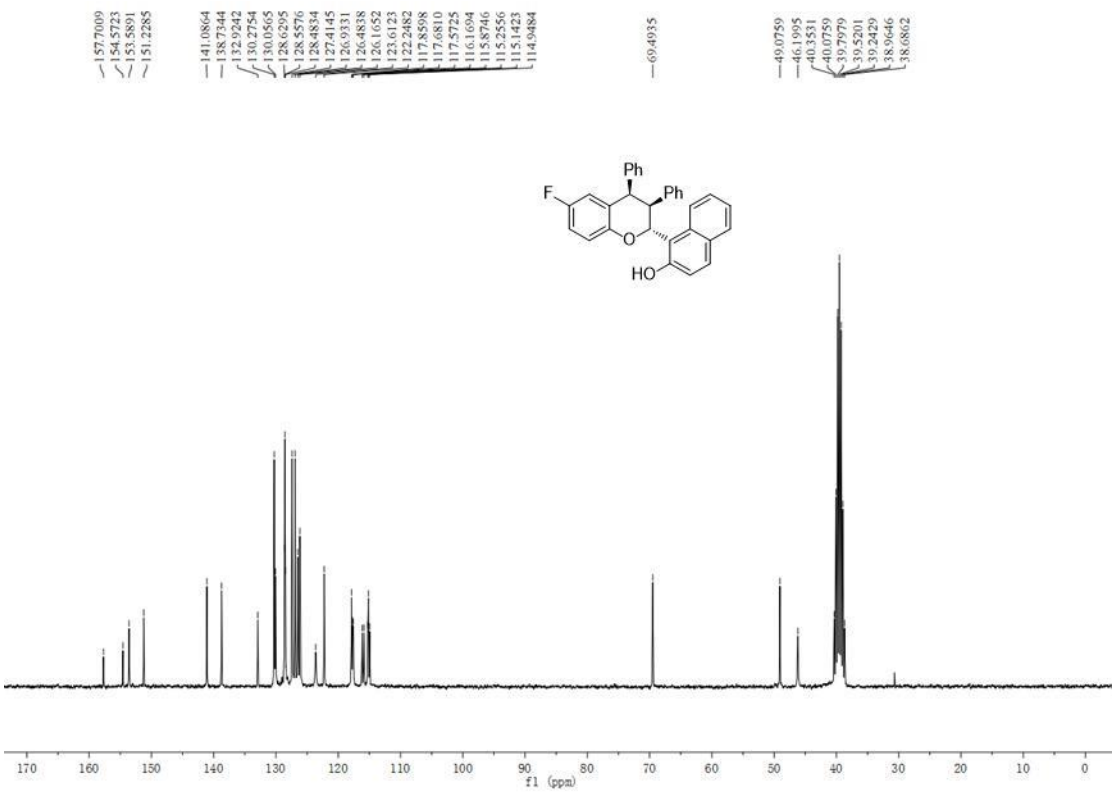


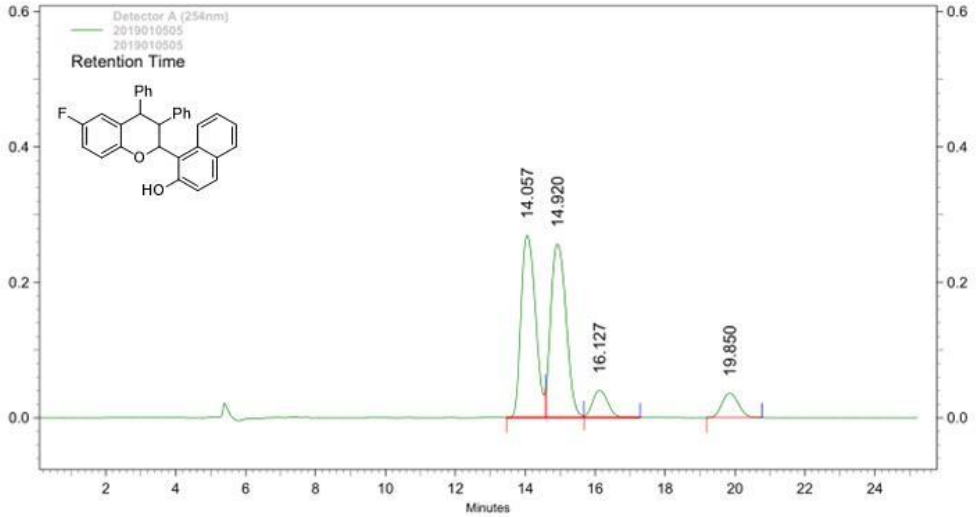
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	9.223	521707	99.93	14804157	99.63
2	29.210	340	0.07	54854	0.37
Totals		522047	100.00	14859011	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3m

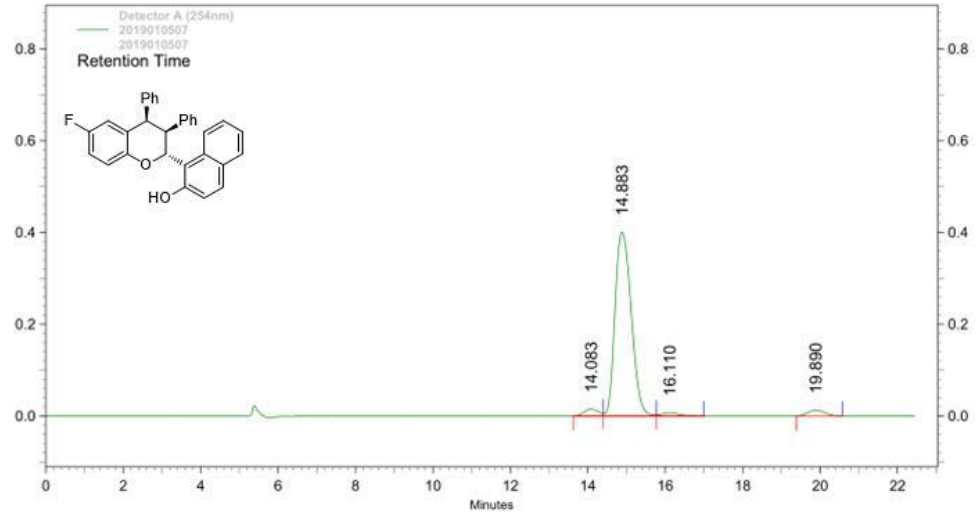






Detector A (254nm)

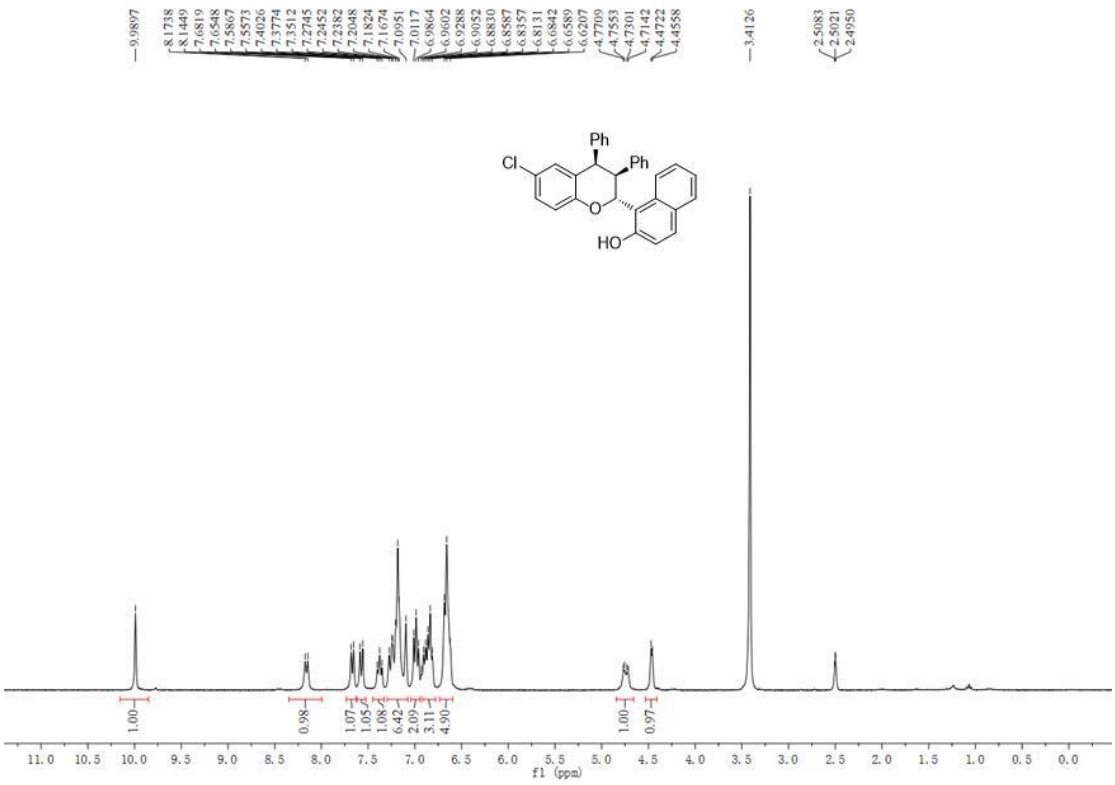
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	14.057	269102	44.74	7777155	43.16
2	14.920	256353	42.62	7815411	43.37
3	16.127	40063	6.66	1235069	6.85
4	19.850	36023	5.99	1191867	6.61
Totals		601541	100.00	18019502	100.00

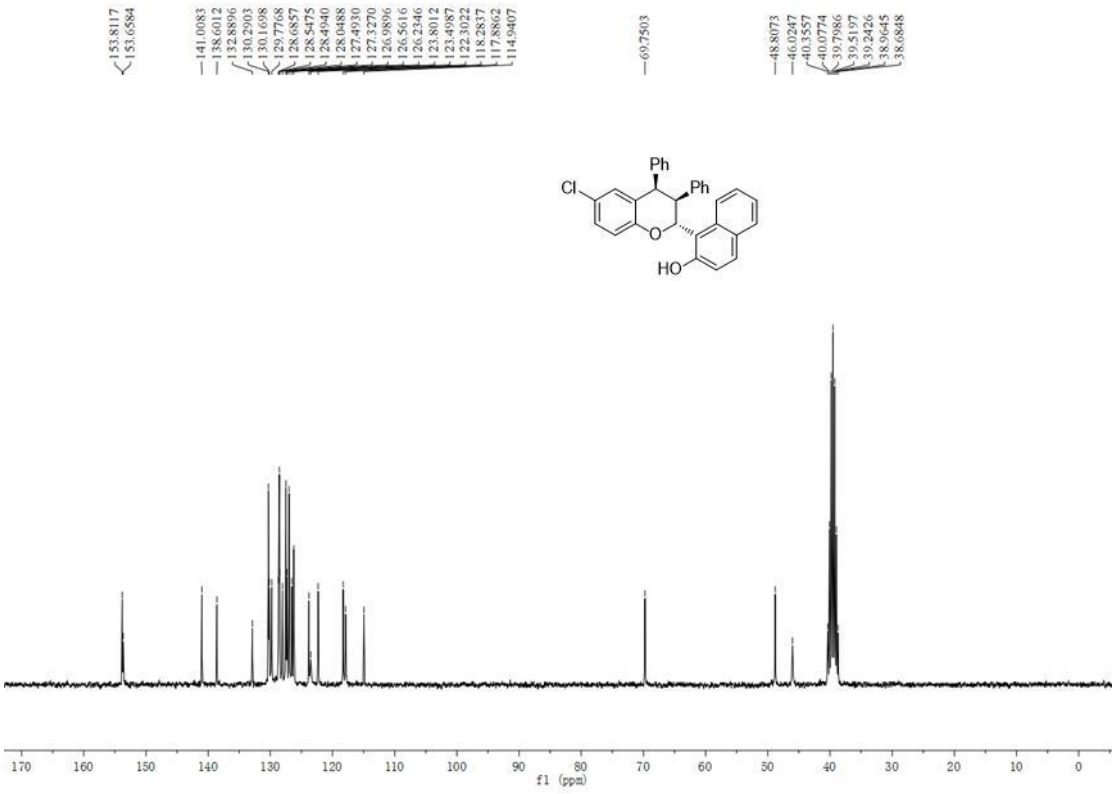


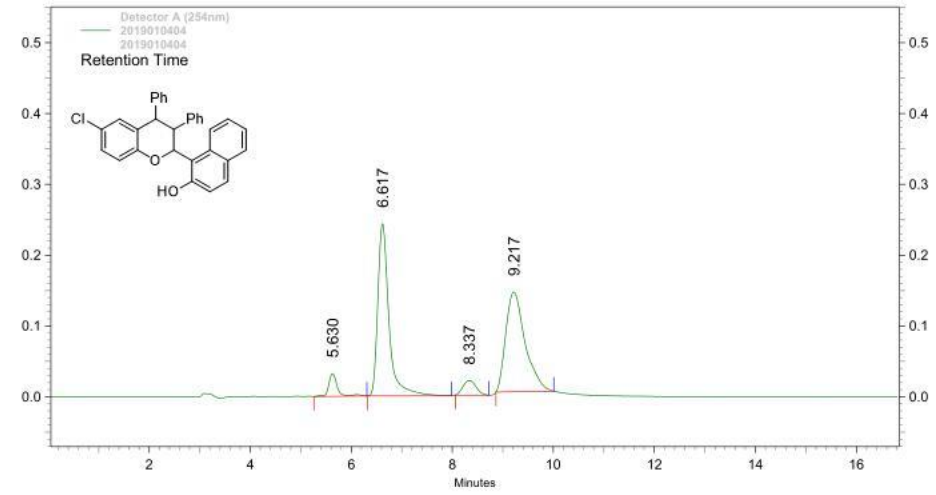
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	14.083	14432	3.33	373927	2.97
2	14.883	399886	92.34	11631555	92.45
3	16.110	6723	1.55	201274	1.60
4	19.890	12025	2.78	374421	2.98
Totals		433066	100.00	12581177	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3n

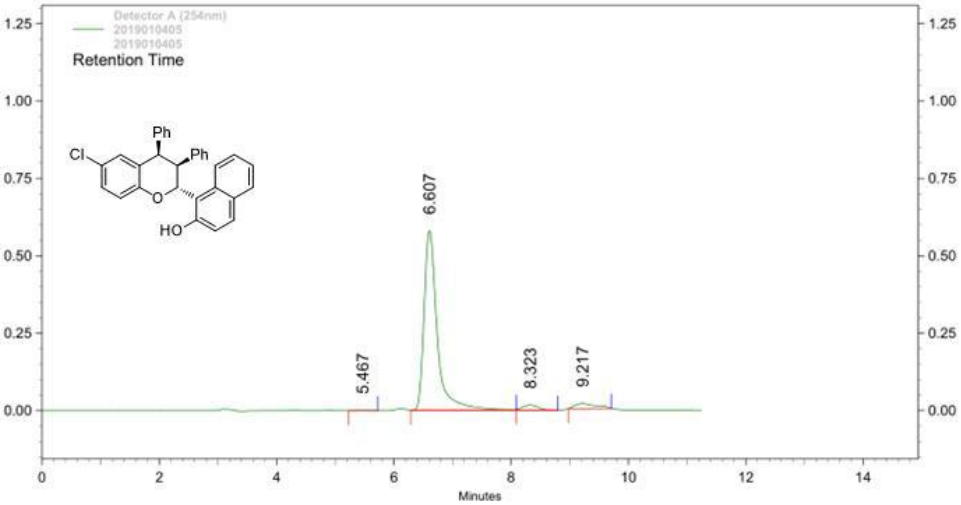






Detector A (254nm)

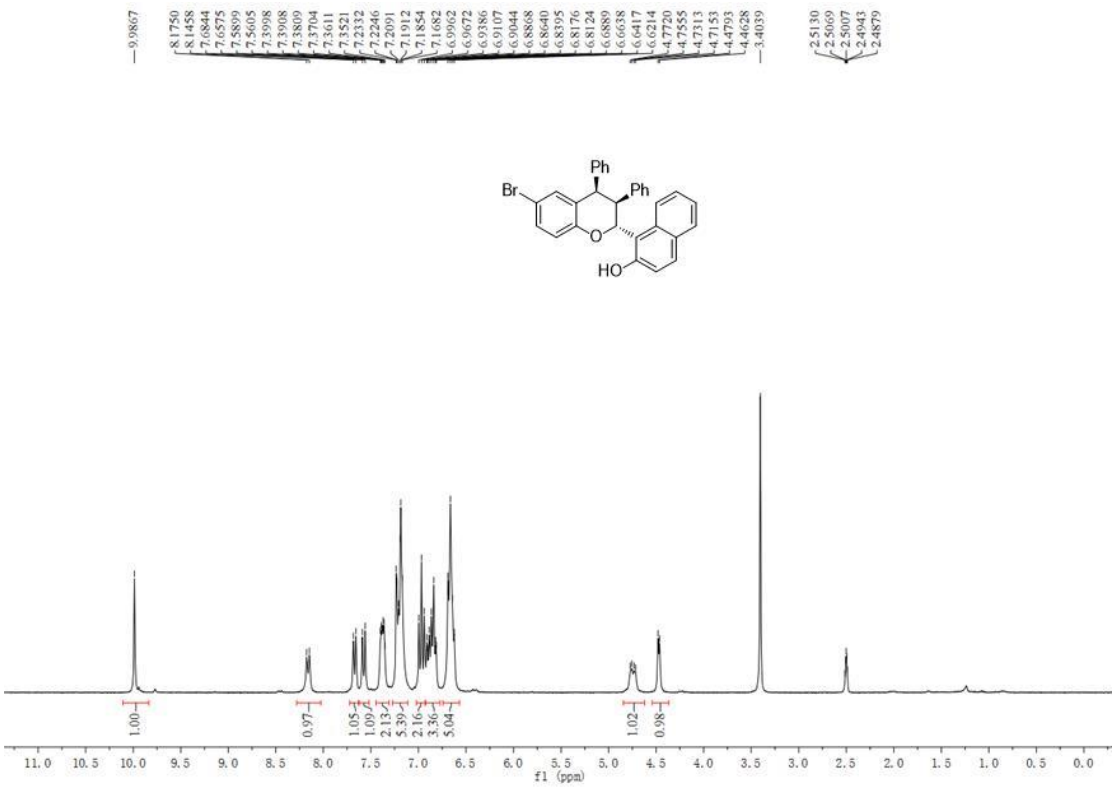
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	5.630	32090	7.34	376962	4.57
2	6.617	243373	55.68	3747752	45.42
3	8.337	20663	4.73	369127	4.47
4	9.217	140960	32.25	3756795	45.53
Totals		437086	100.00	8250636	100.00

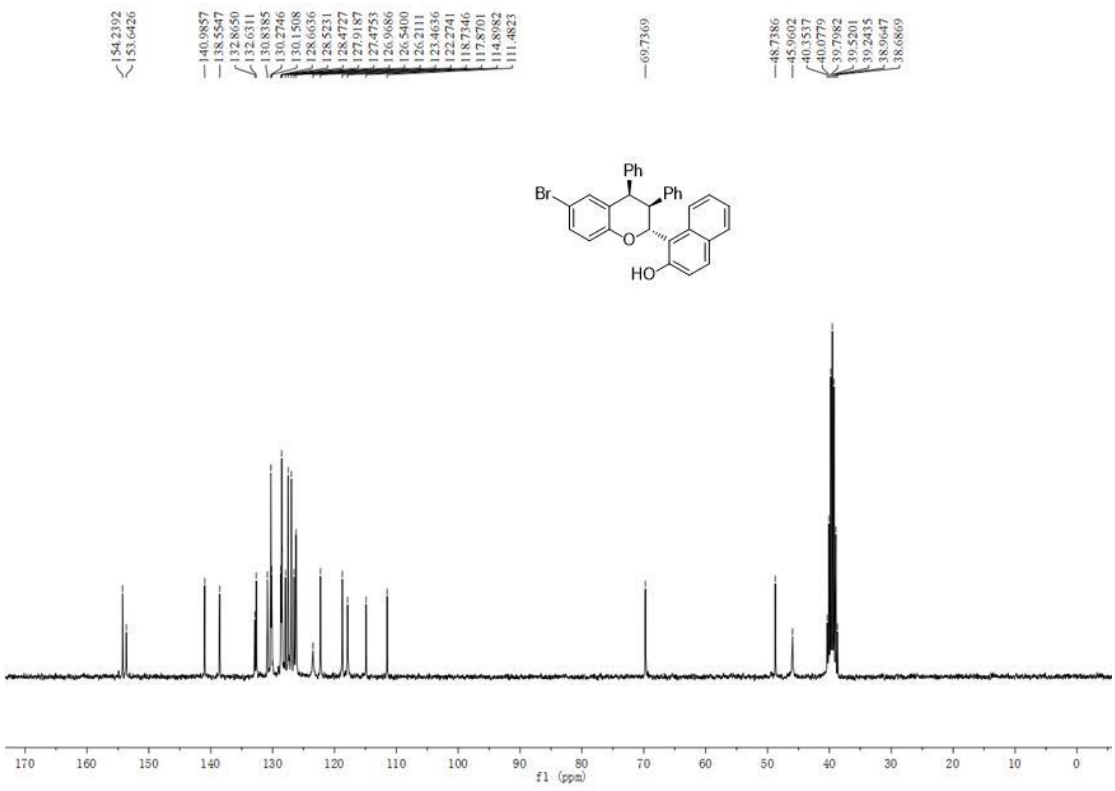


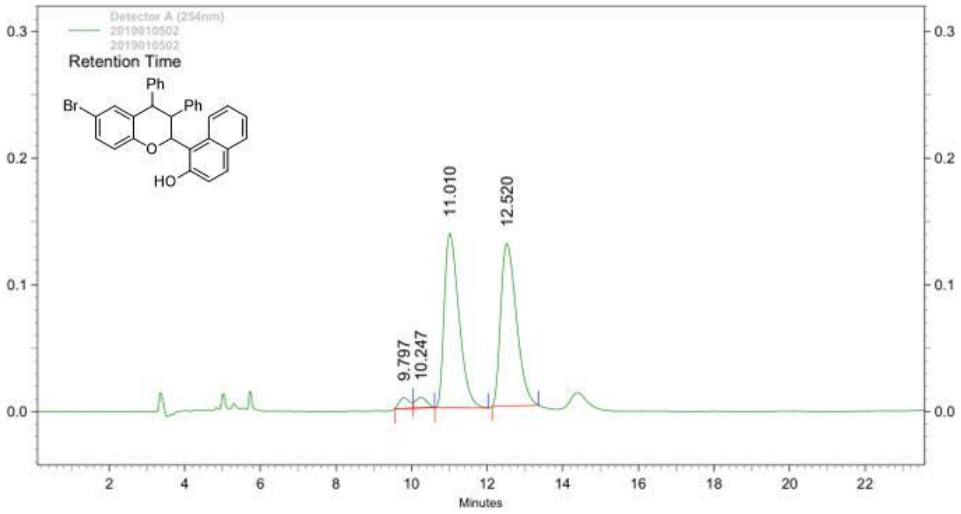
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	5.467	337	0.06	4950	0.05
2	6.607	579772	94.69	9061673	92.70
3	8.323	16499	2.69	307158	3.14
4	9.217	15684	2.56	401588	4.11
Totals		612292	100.00	9775369	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3o

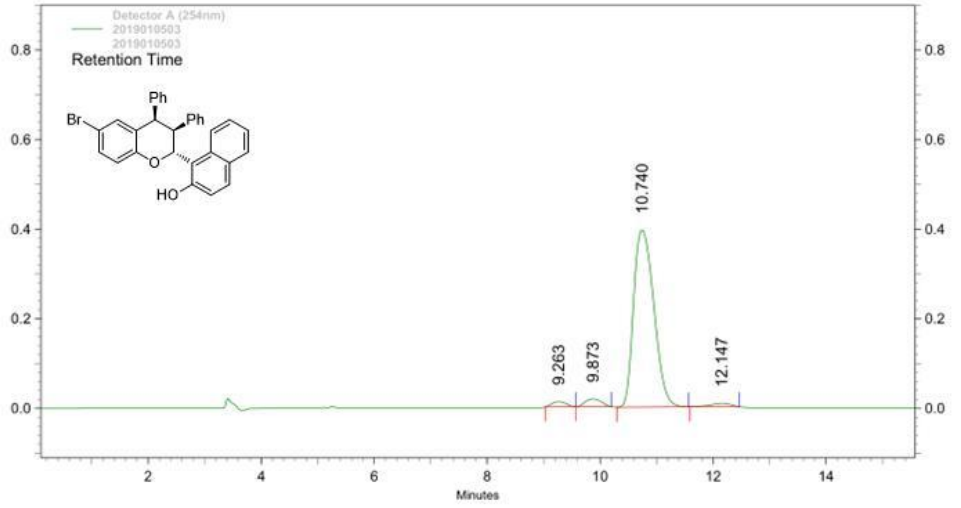






Detector A (254nm)

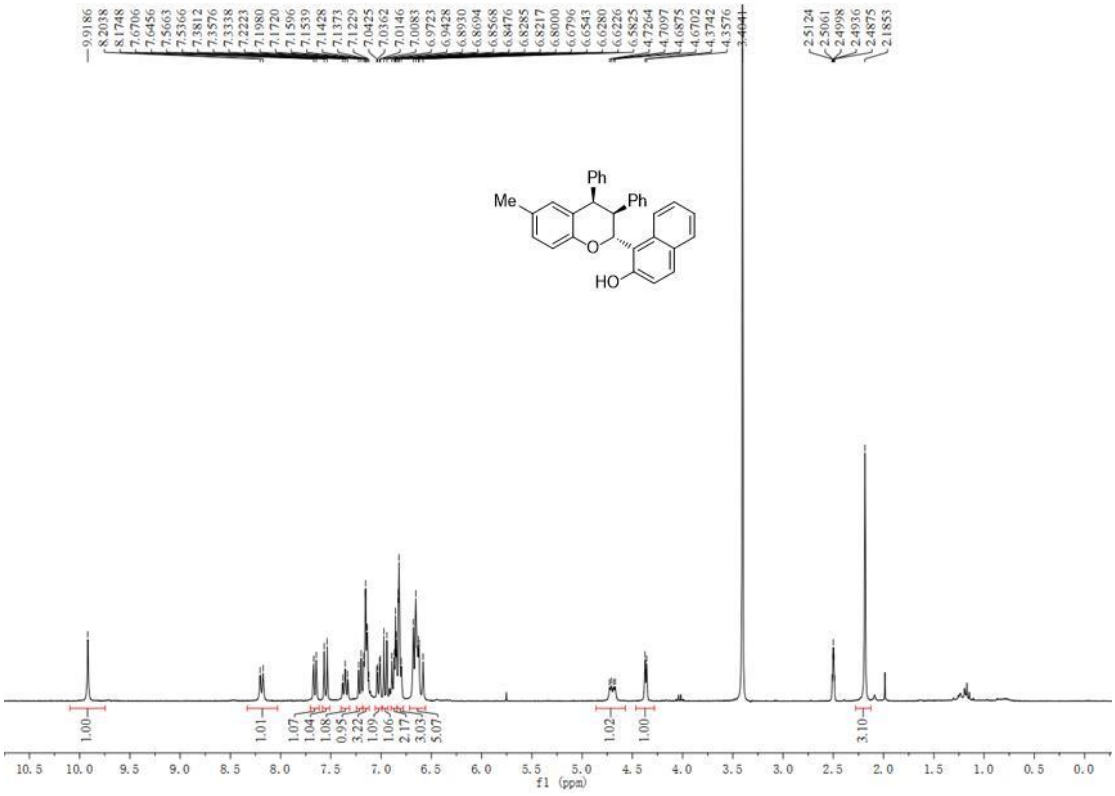
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	9.797	8468	3.00	161149	2.08
2	10.247	8460	2.99	176136	2.27
3	11.010	137442	48.65	3708683	47.82
4	12.520	128113	45.35	3710198	47.84
Totals		282483	100.00	7756166	100.00

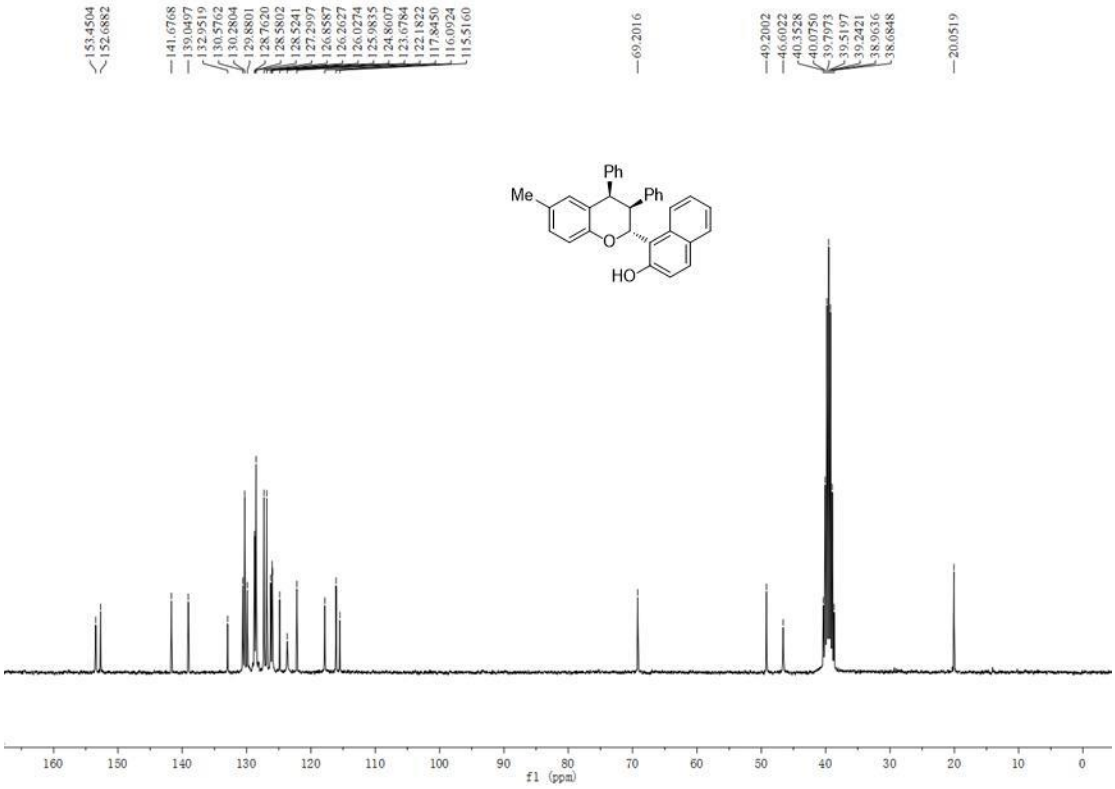


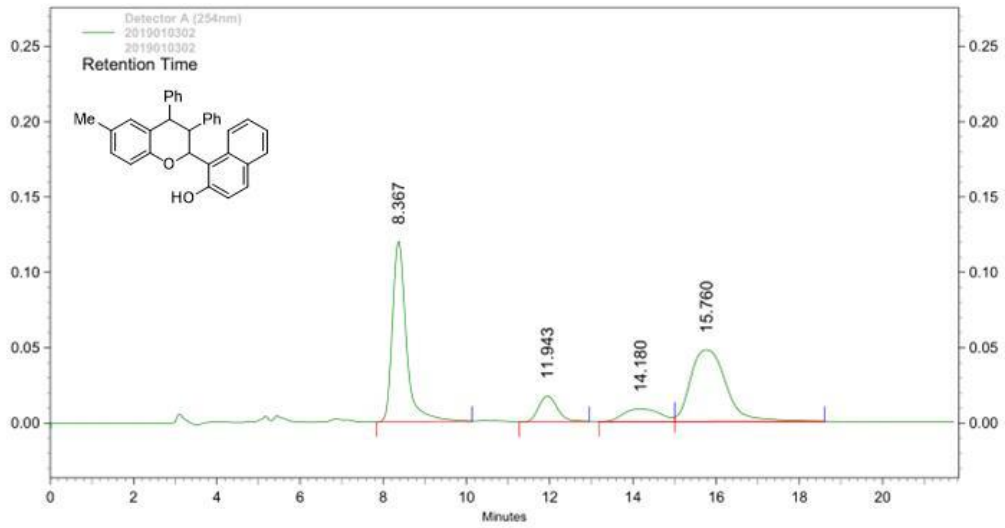
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	9.263	11468	2.66	203230	1.92
2	9.873	17206	3.99	344847	3.25
3	10.740	394932	91.55	9852973	92.98
4	12.147	7783	1.80	196299	1.85
Totals		431389	100.00	10597349	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3p

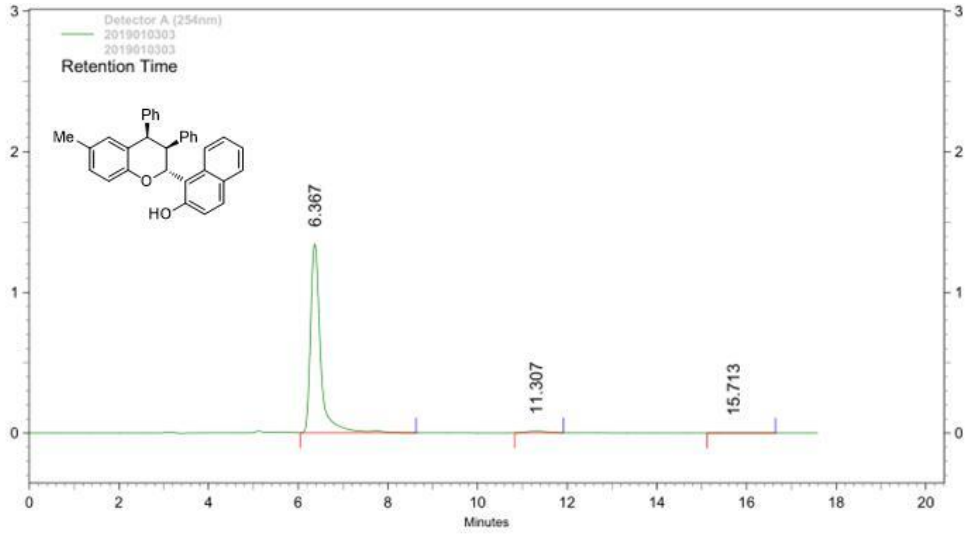






Detector A (254nm)

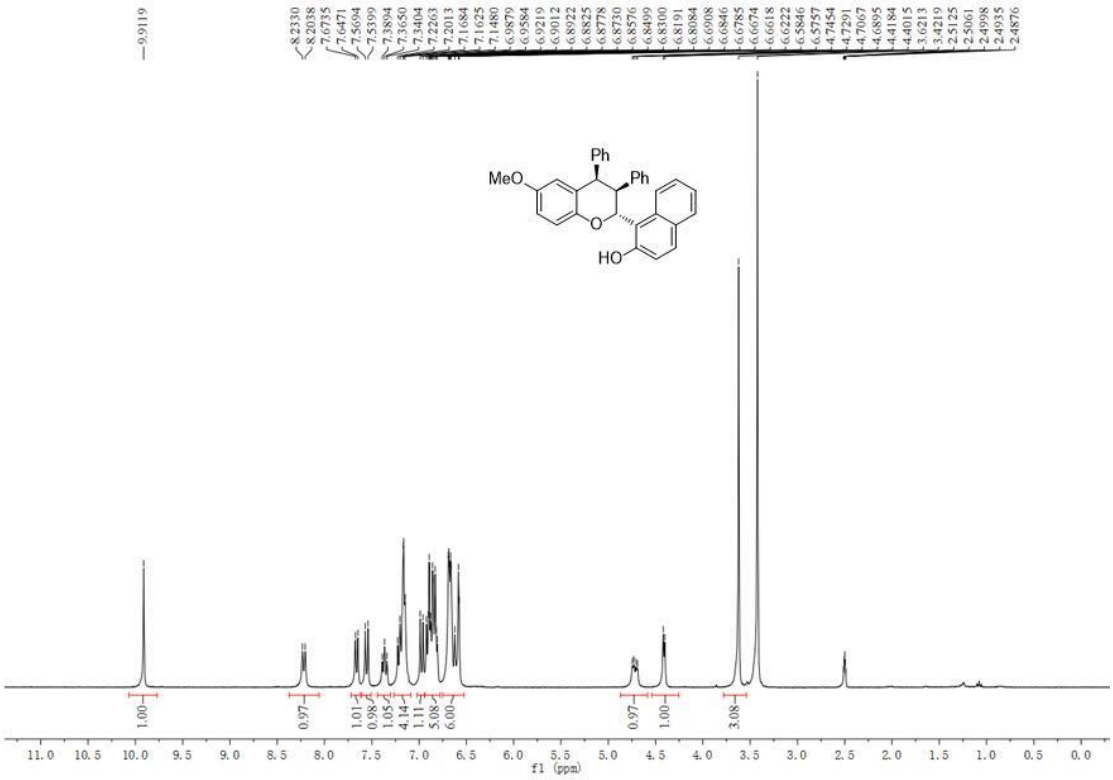
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.367	119553	62.16	2788905	42.00
2	11.943	17046	8.86	529862	7.98
3	14.180	8232	4.28	509838	7.68
4	15.760	47510	24.70	2811942	42.35
Totals		192341	100.00	6640547	100.00

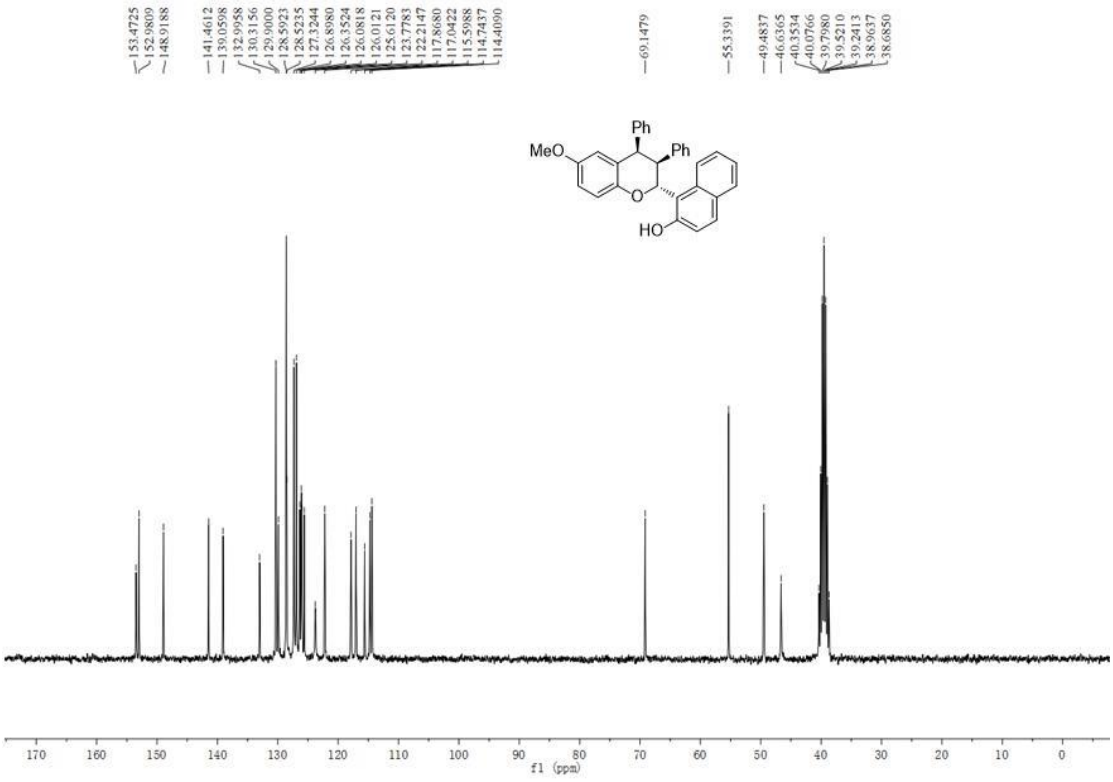


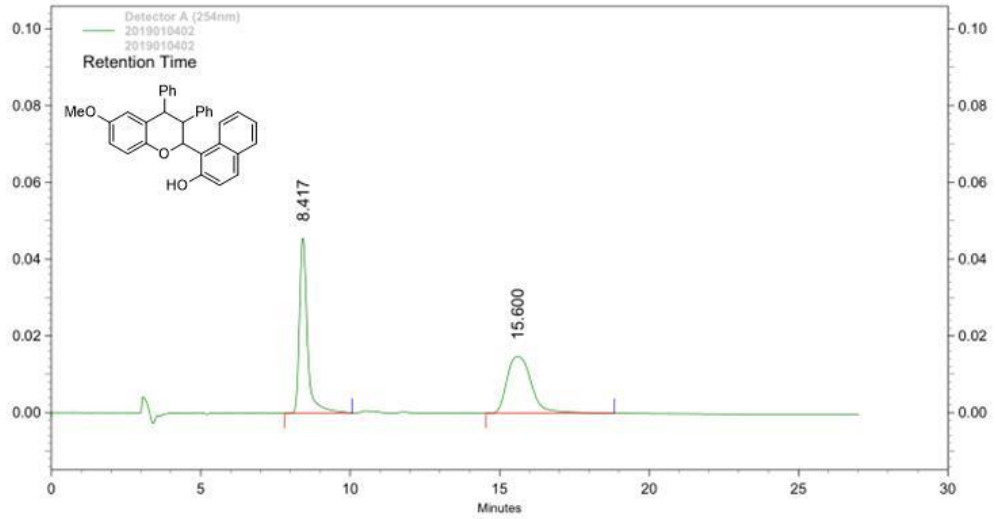
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	6.367	1343122	99.14	21050063	98.25
2	11.307	11430	0.84	366059	1.71
3	15.713	170	0.01	8195	0.04
Totals		1354722	100.00	21424317	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3q

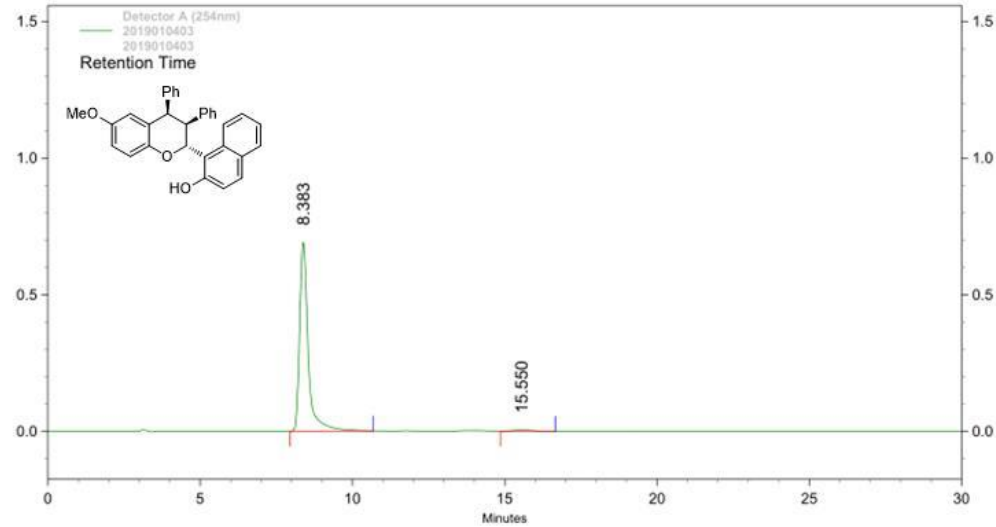






Detector A (254nm)

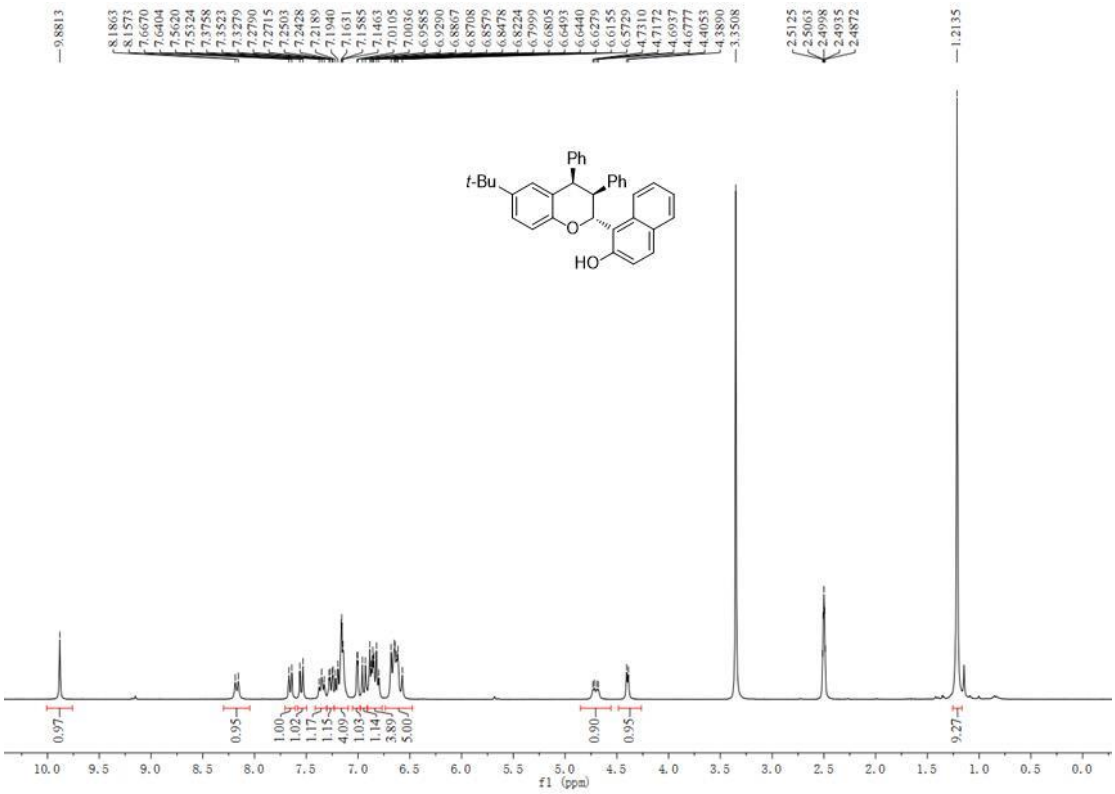
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.417	45644	75.50	847747	49.99
2	15.600	14815	24.50	848127	50.01
Totals		60459	100.00	1695874	100.00

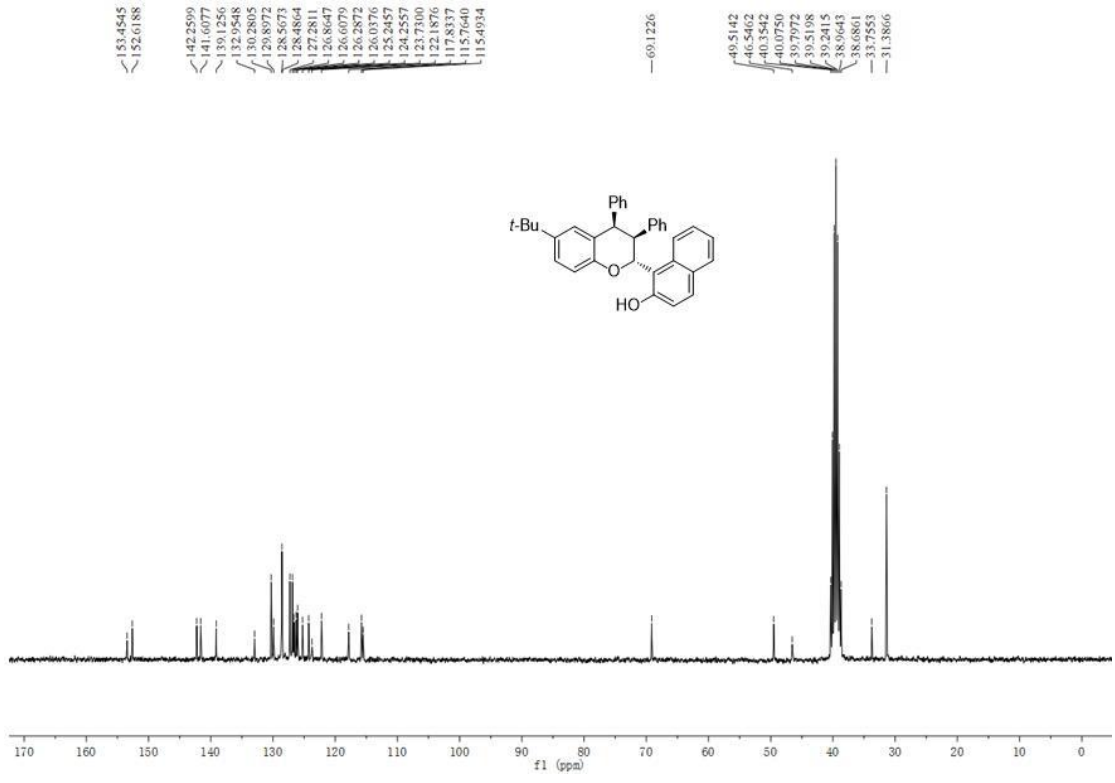


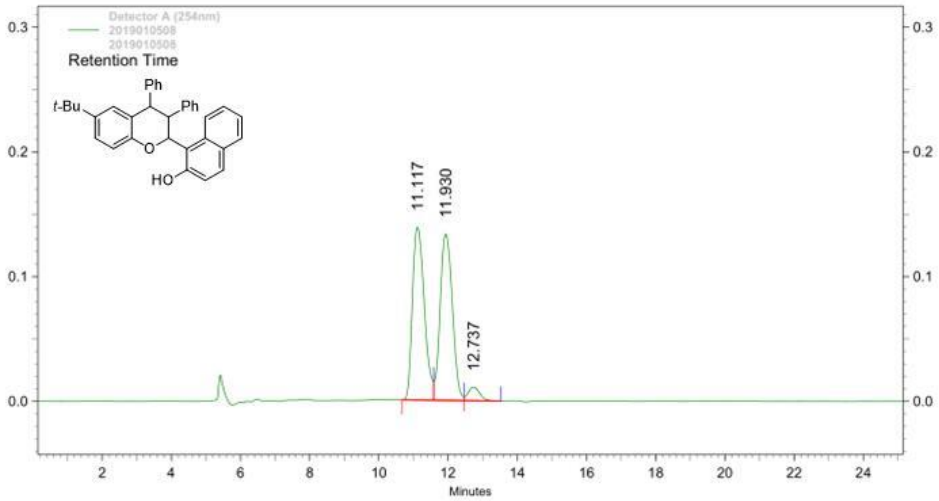
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.383	690732	99.49	13569345	98.70
2	15.550	3510	0.51	178252	1.30
Totals		694242	100.00	13747597	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3r

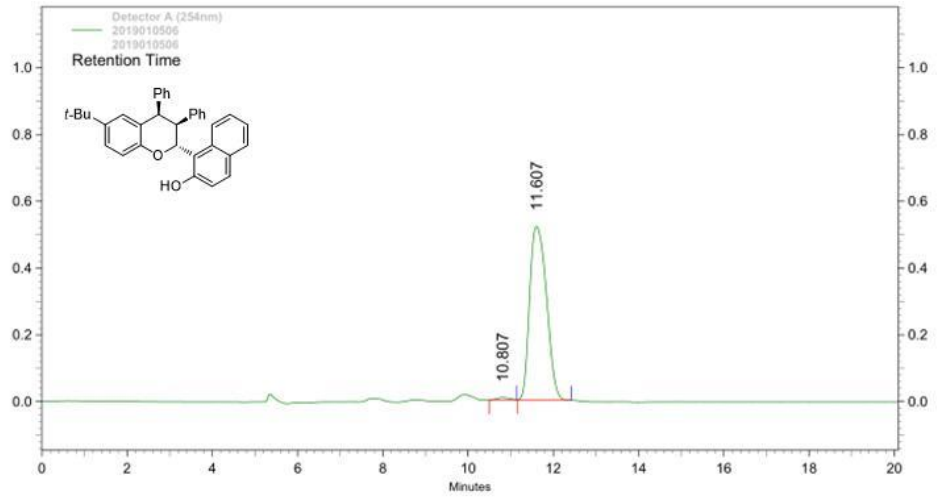






Detector A (254nm)

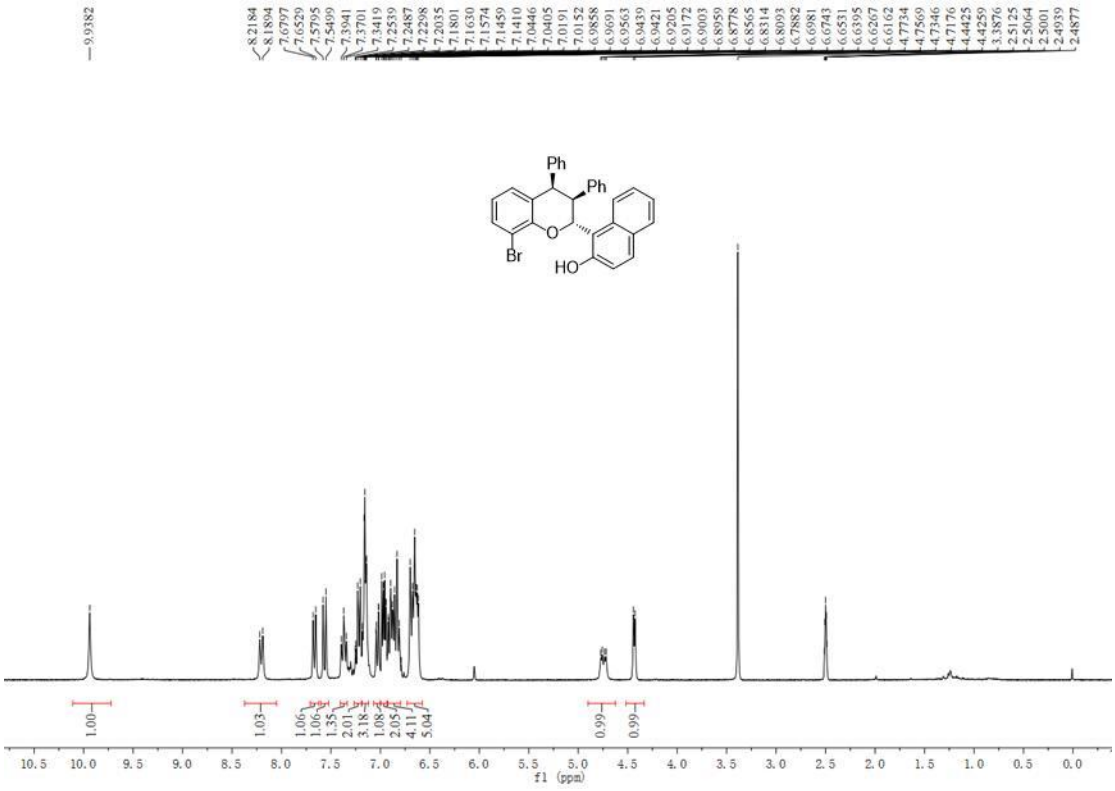
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	11.117	138622	49.04	3315747	48.49
2	11.930	133298	47.16	3276265	47.92
3	12.737	10750	3.80	245587	3.59
Totals		282670	100.00	6837599	100.00

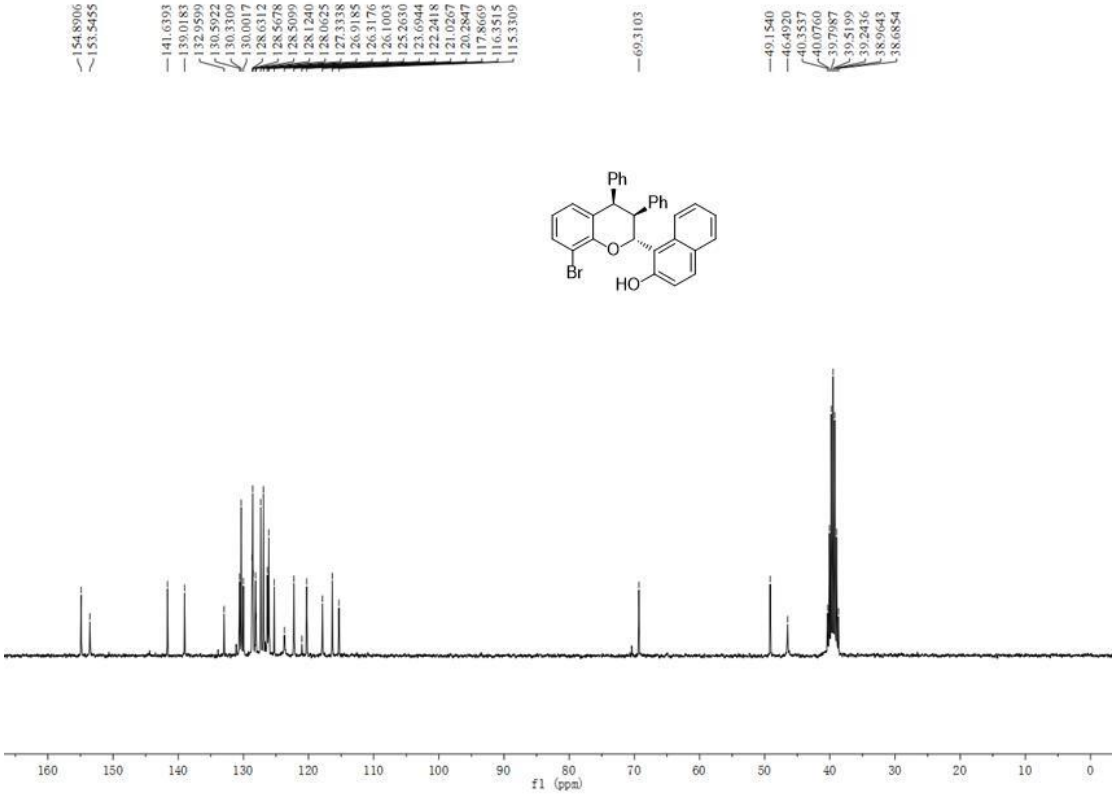


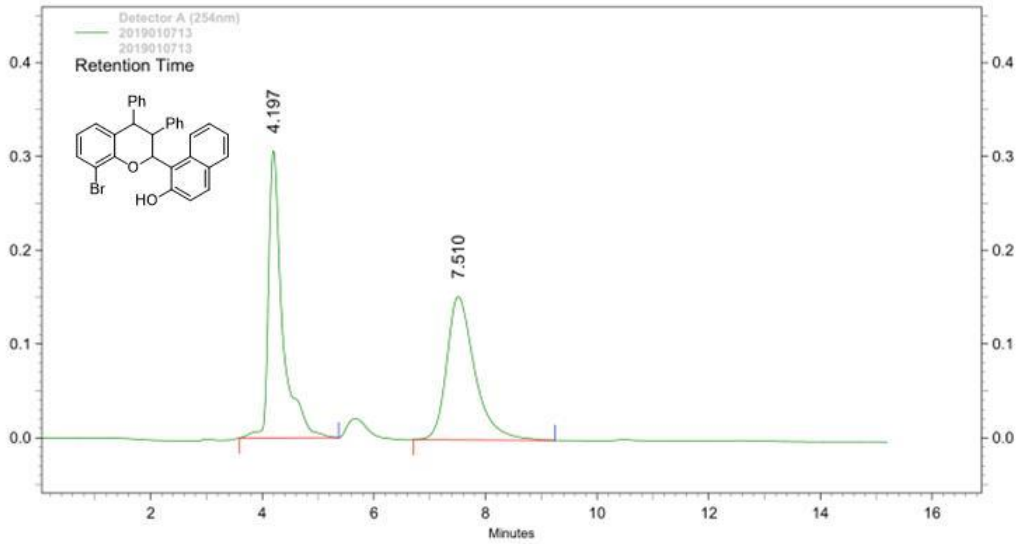
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	10.807	6294	1.20	125179	0.87
2	11.607	519243	98.80	14283015	99.13
Totals		525537	100.00	14408194	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3s

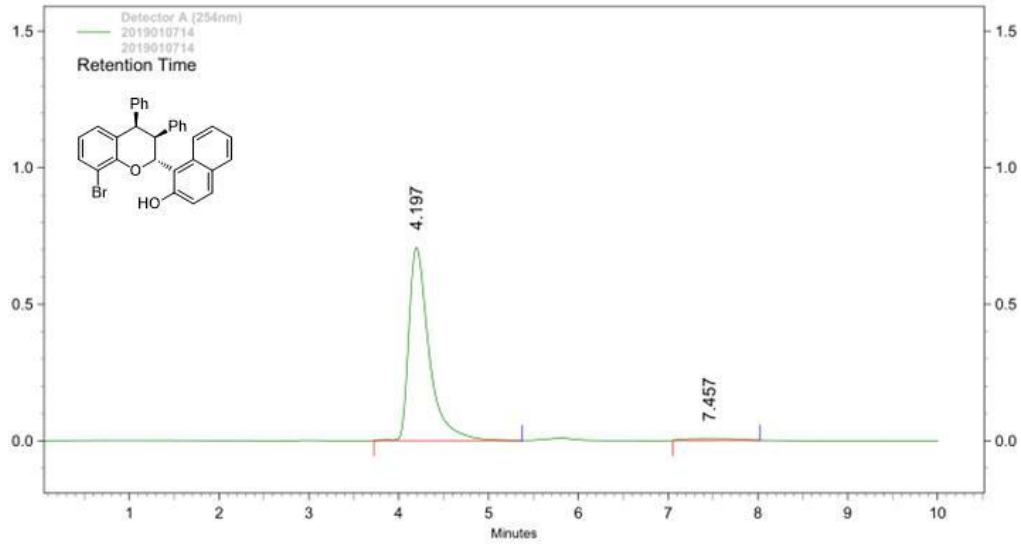






Detector A (254nm)

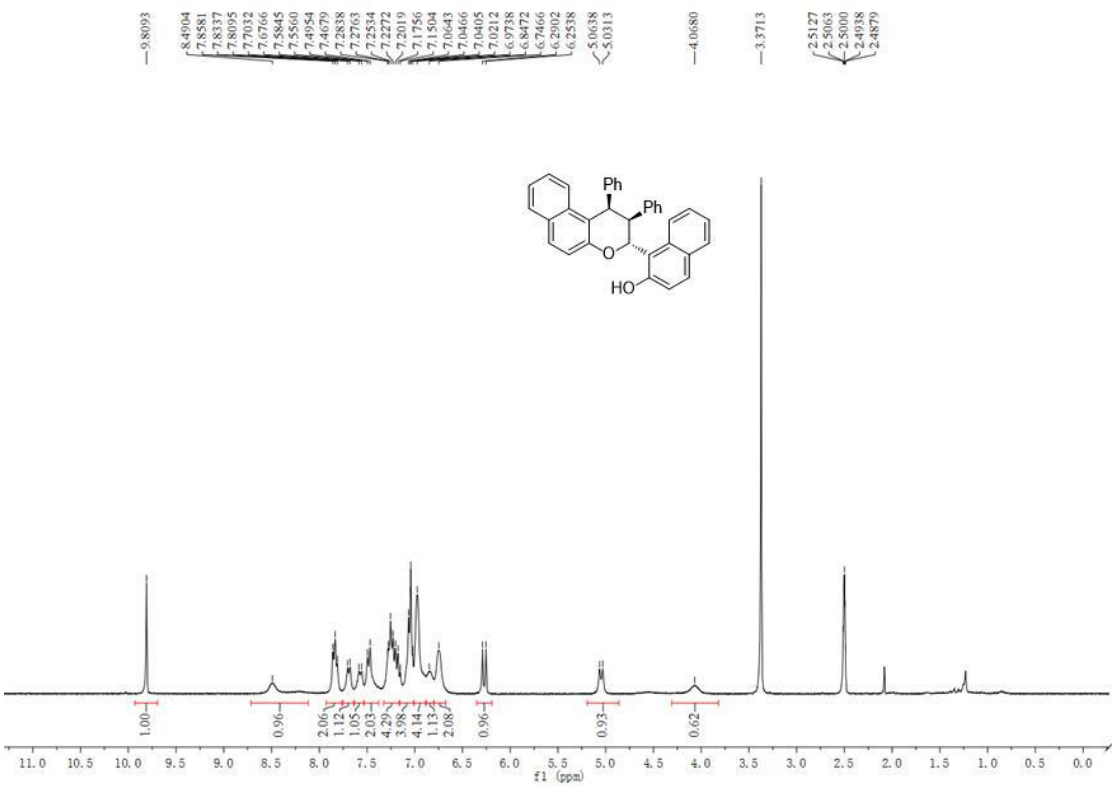
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	4.197	306182	66.71	5348520	50.01
2	7.510	152767	33.29	5346297	49.99
Totals		458949	100.00	10694817	100.00

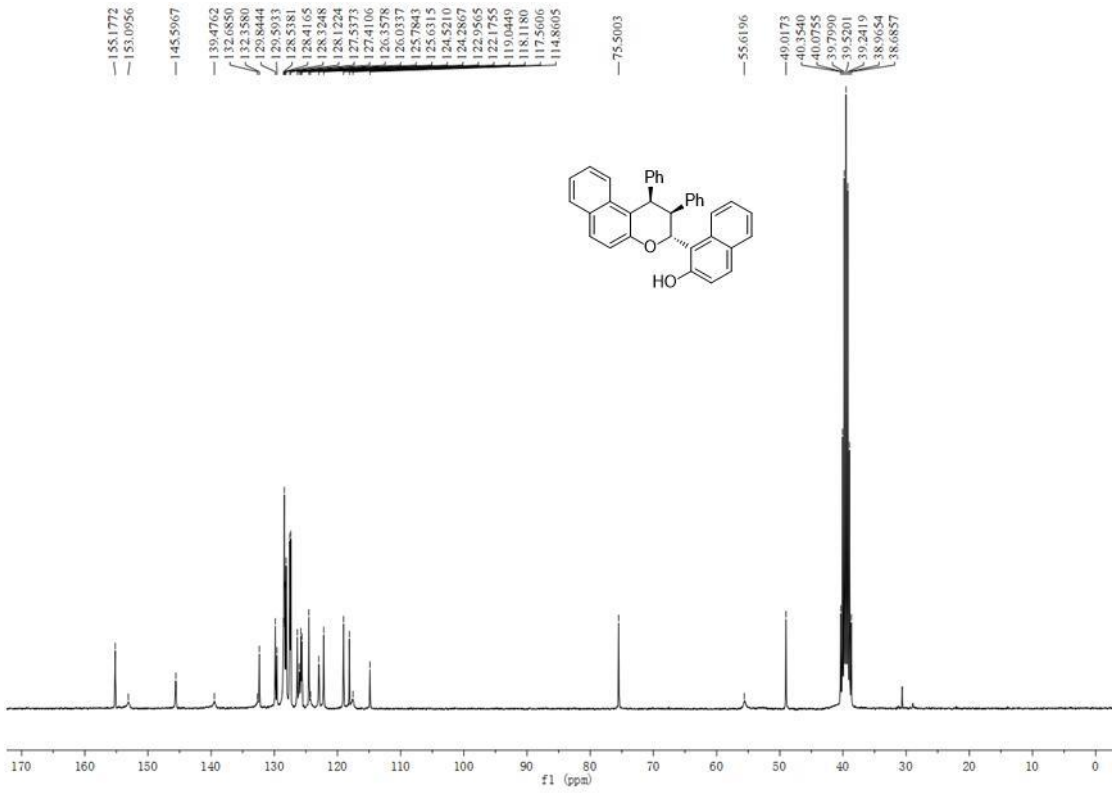


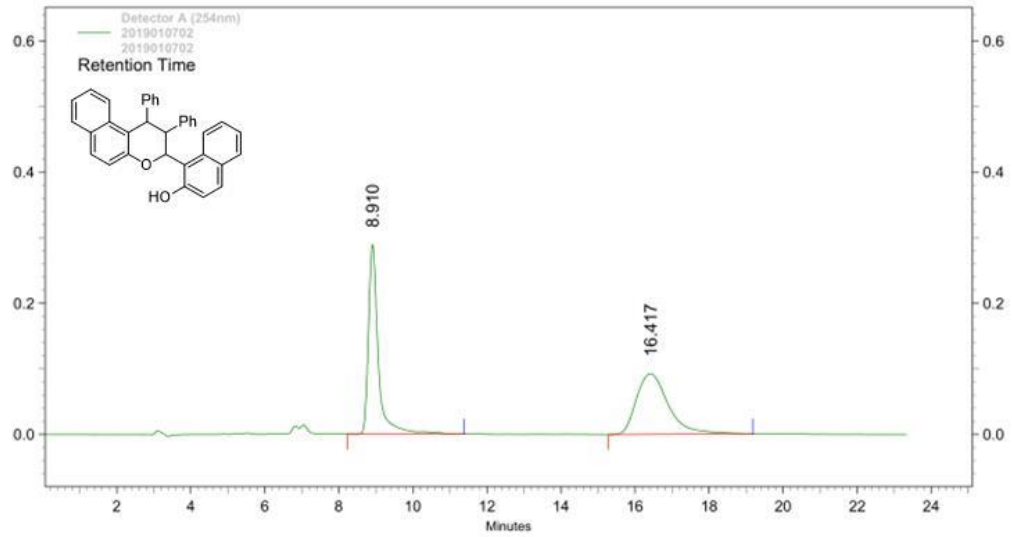
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	4.197	706827	99.20	11044399	98.02
2	7.457	5716	0.80	223070	1.98
Totals		712543	100.00	11267469	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3t

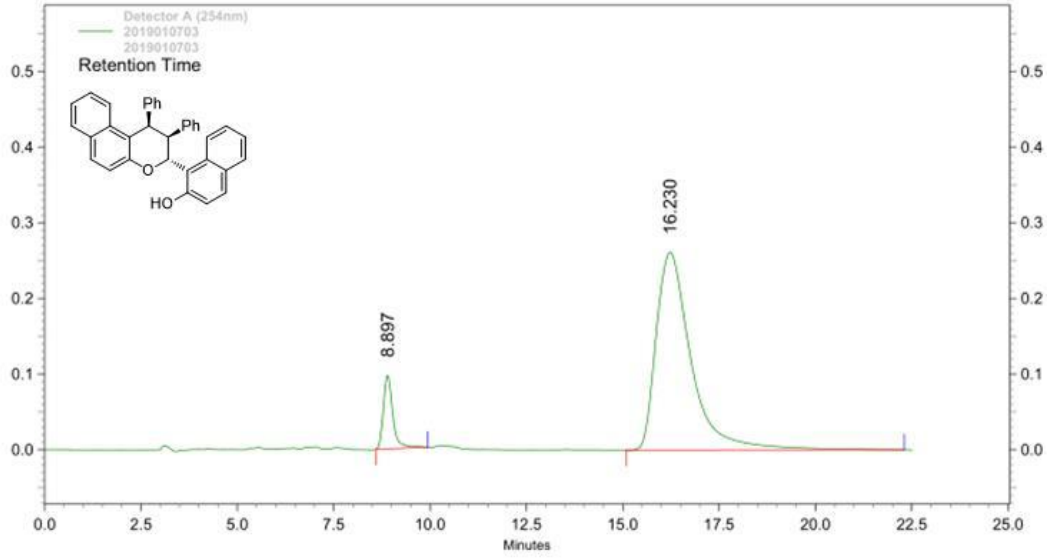






Detector A (254nm)

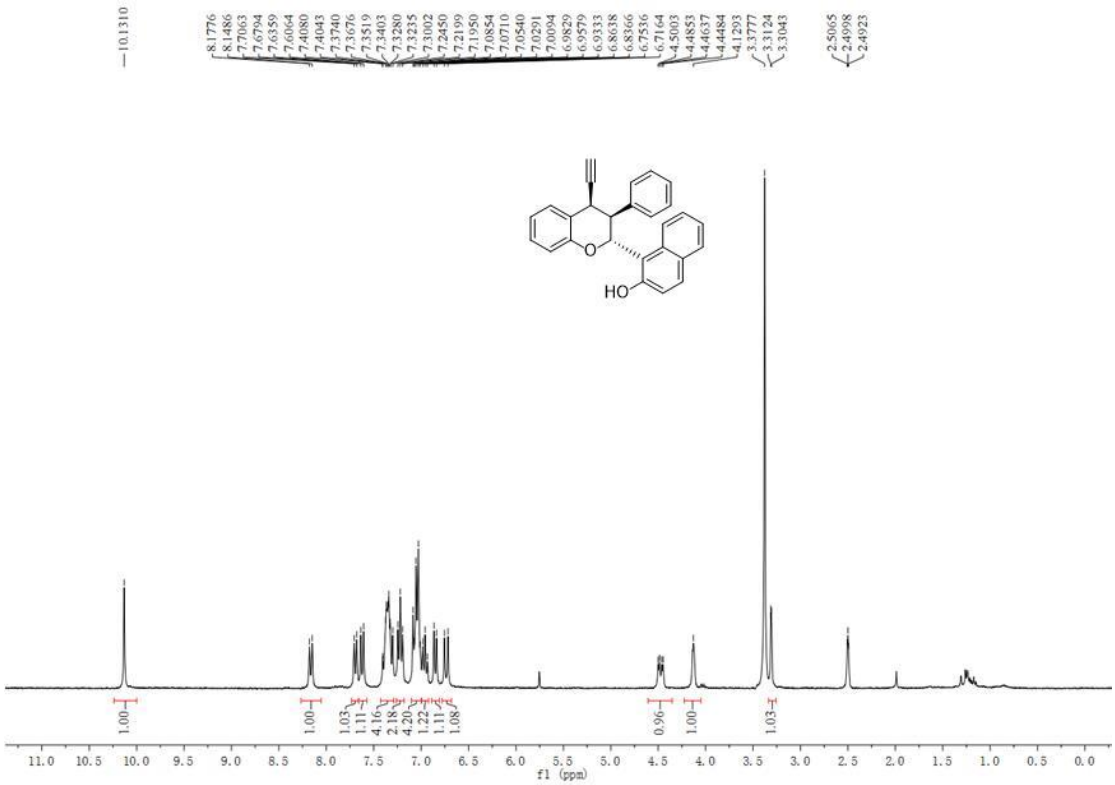
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.910	289059	75.76	5399491	49.32
2	16.417	92499	24.24	5547876	50.68
Totals		381558	100.00	10947367	100.00

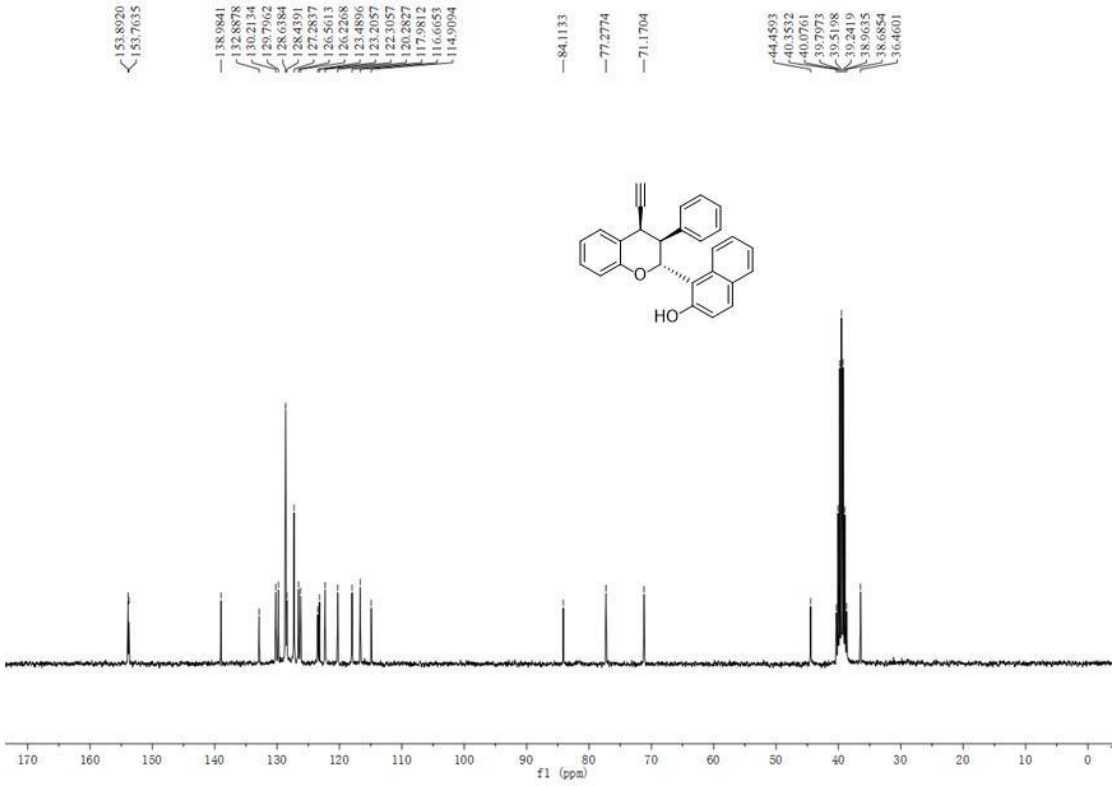


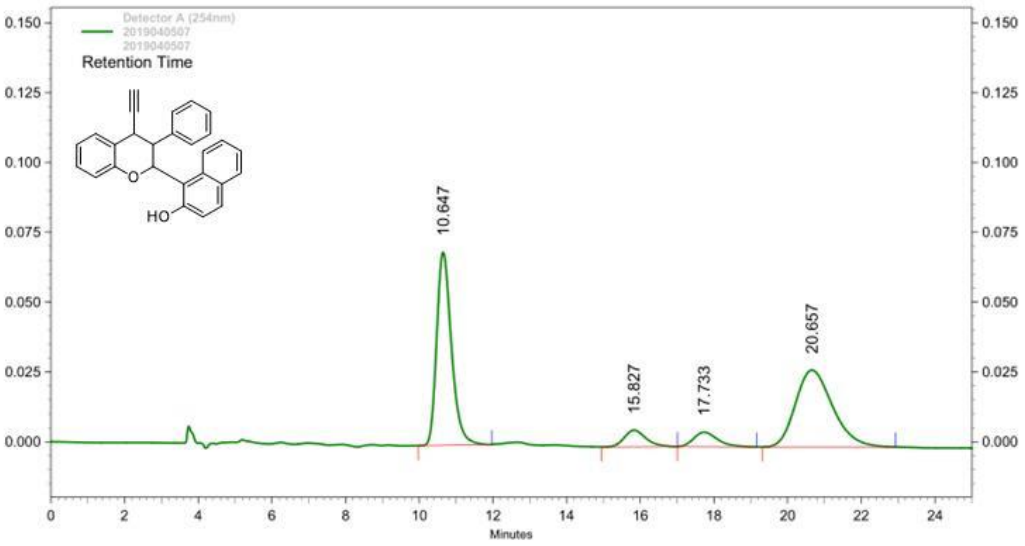
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.897	97061	27.08	1655116	9.13
2	16.230	261356	72.92	16478154	90.87
Totals		358417	100.00	18133270	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3u

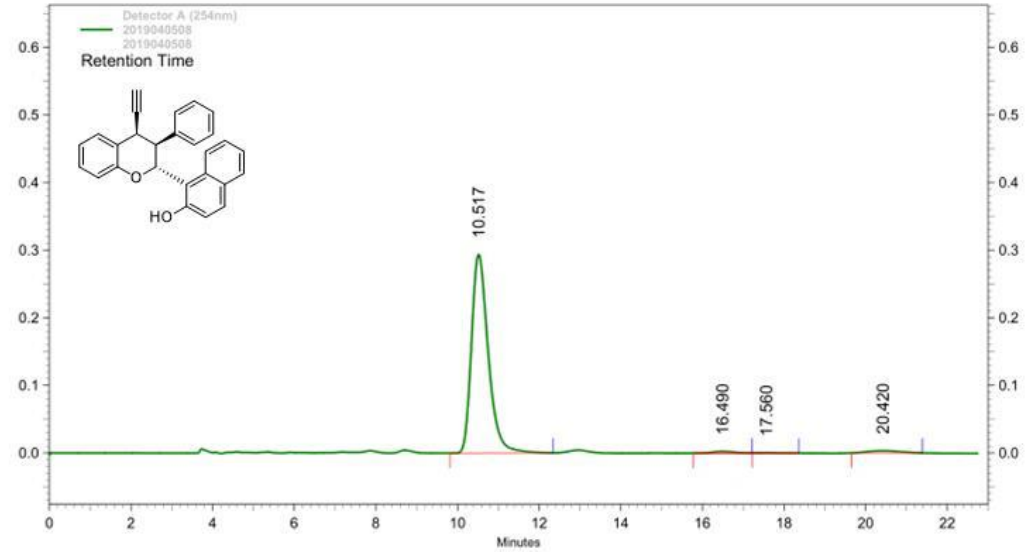






Detector A (254nm)

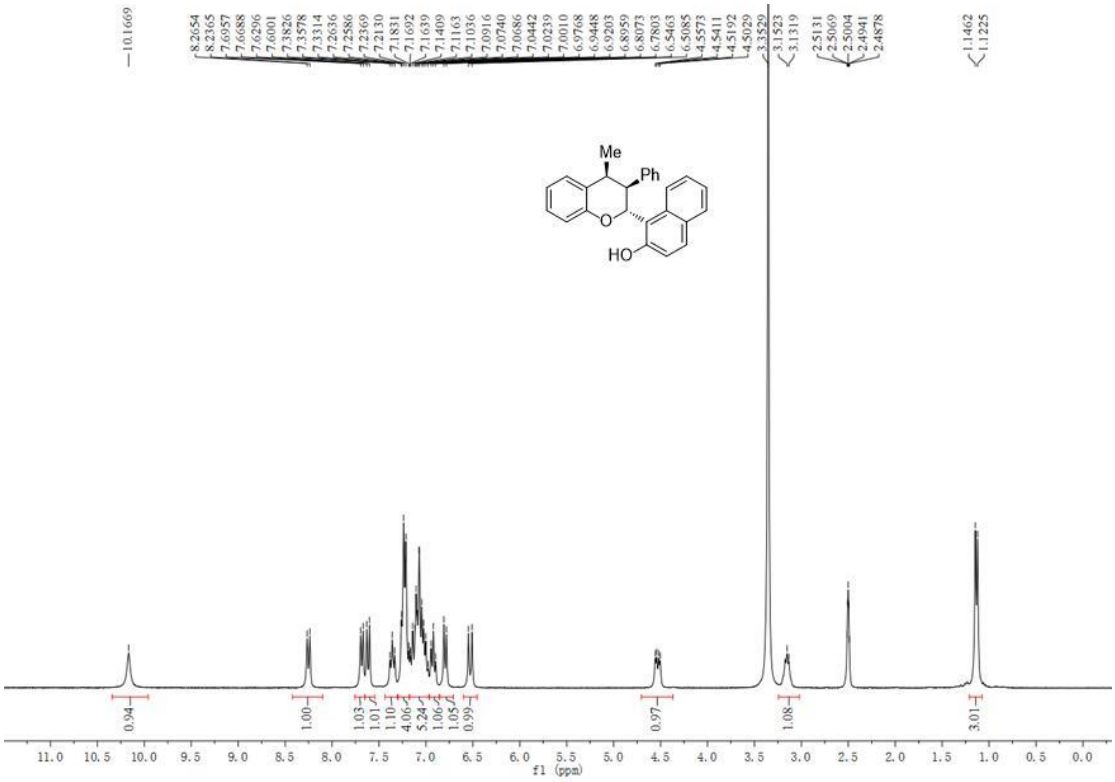
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	10.647	69079	64.15	1929317	44.57
2	15.827	5915	5.49	240008	5.54
3	17.733	5164	4.80	232285	5.37
4	20.657	27525	25.56	1926845	44.52
Totals		107683	100.00	4328455	100.00

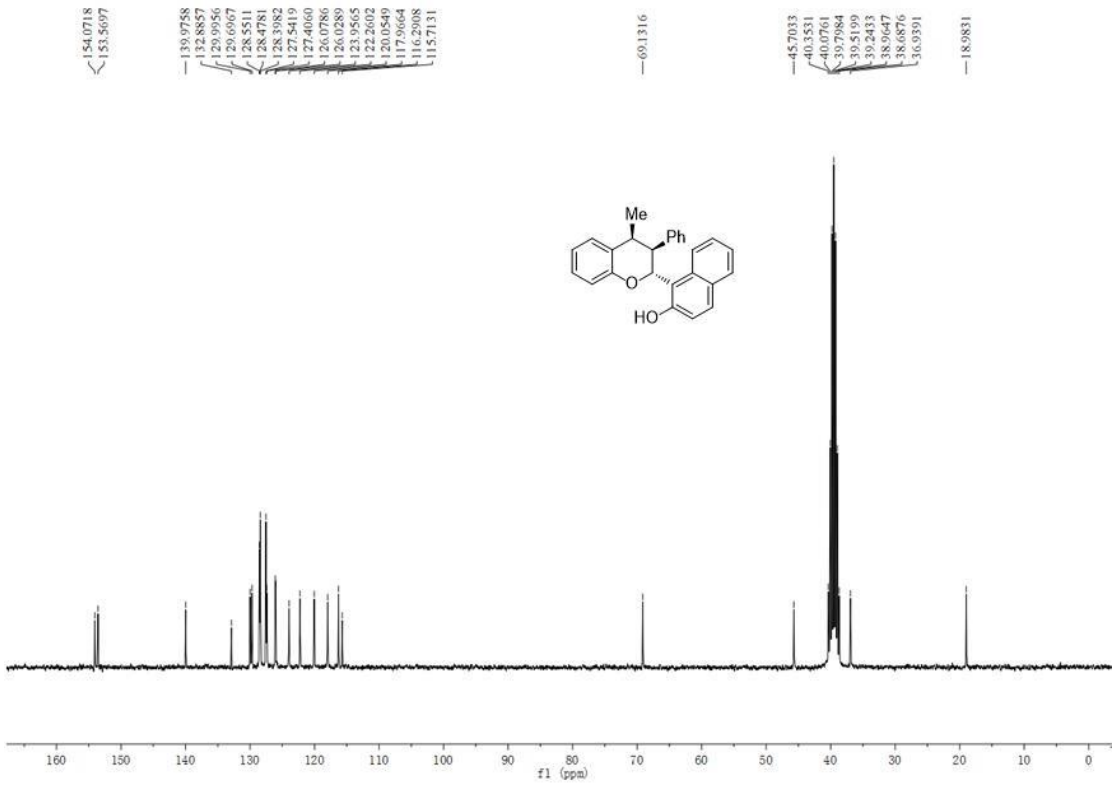


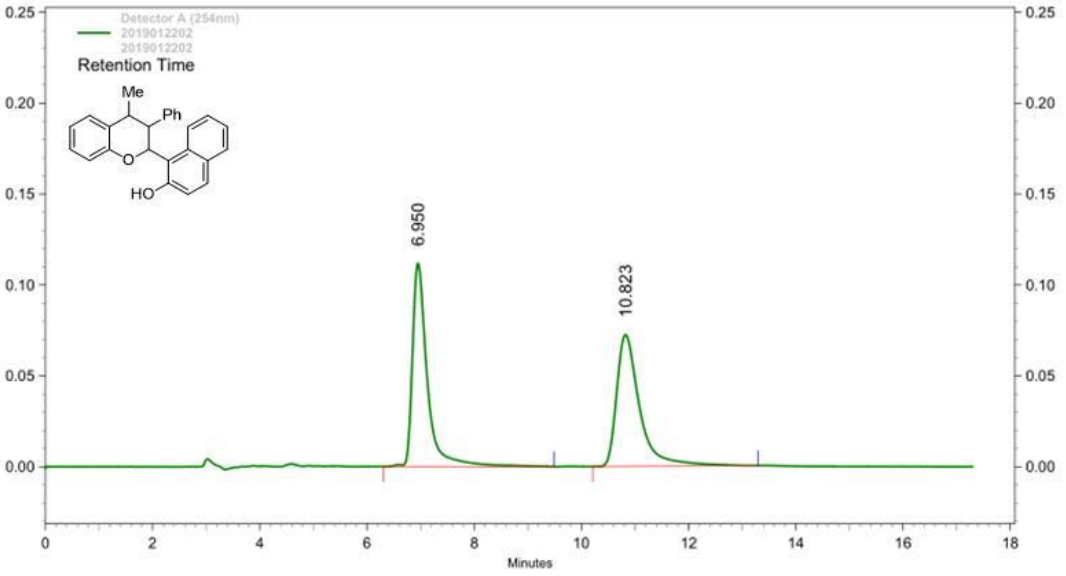
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	10.517	293669	97.82	8377531	96.45
2	16.490	2656	0.88	102093	1.18
3	17.560	620	0.21	24612	0.28
4	20.420	3278	1.09	181831	2.09
Totals		300223	100.00	8686067	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3v

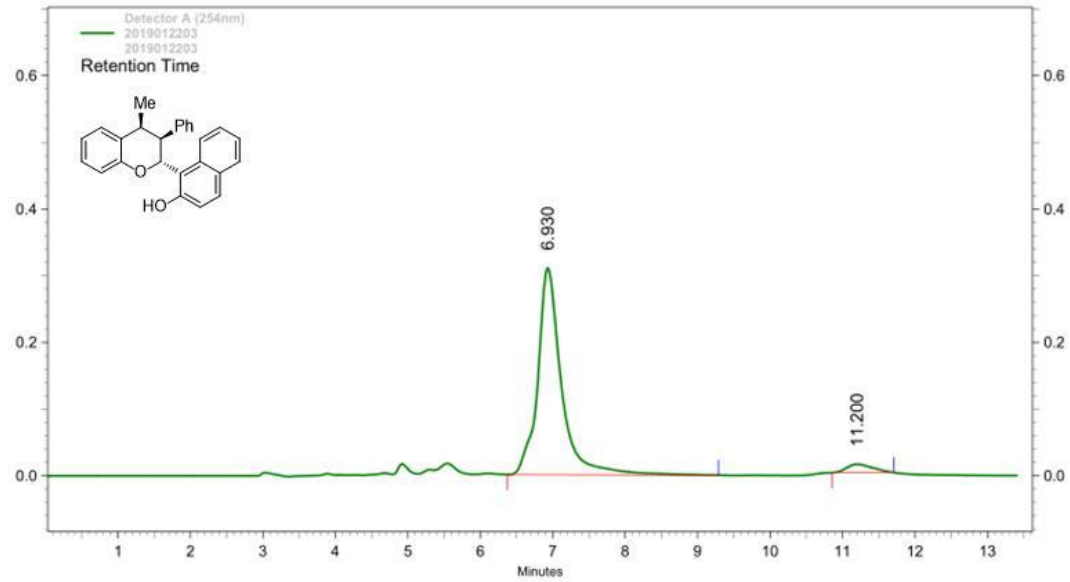






Detector A (254nm)

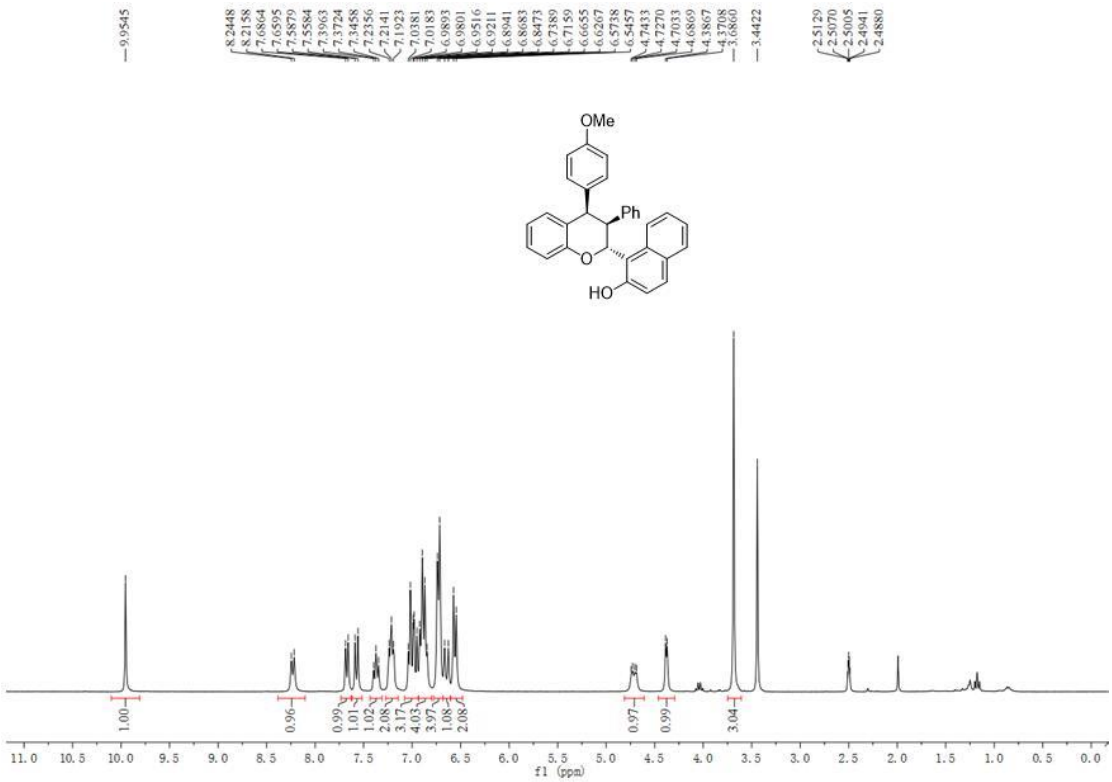
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	6.950	111785	60.67	2167907	50.10
2	10.823	72474	39.33	2159281	49.90
Totals		184259	100.00	4327188	100.00

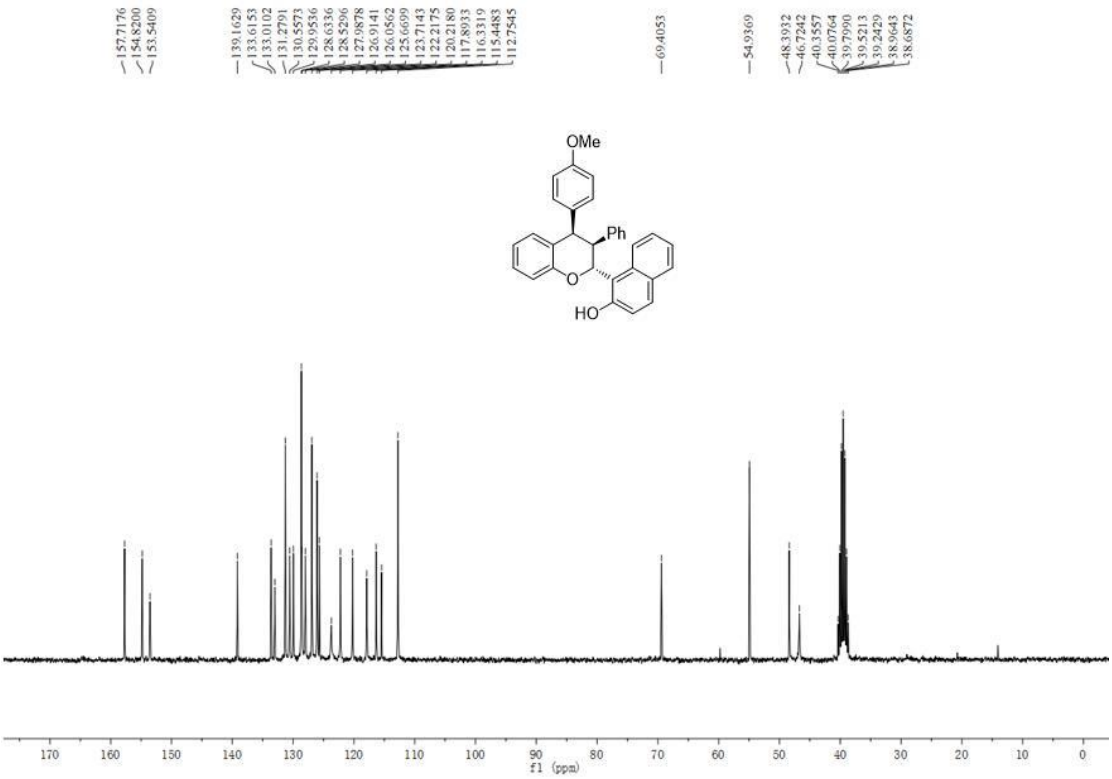


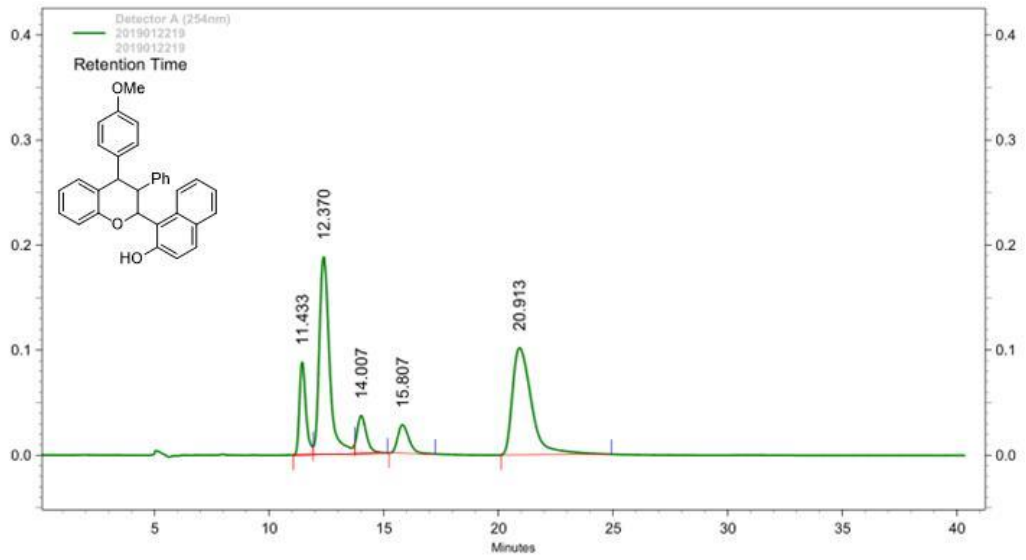
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	6.930	309779	96.11	7040378	95.72
2	11.200	12534	3.89	315039	4.28
Totals		322313	100.00	7355417	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3w

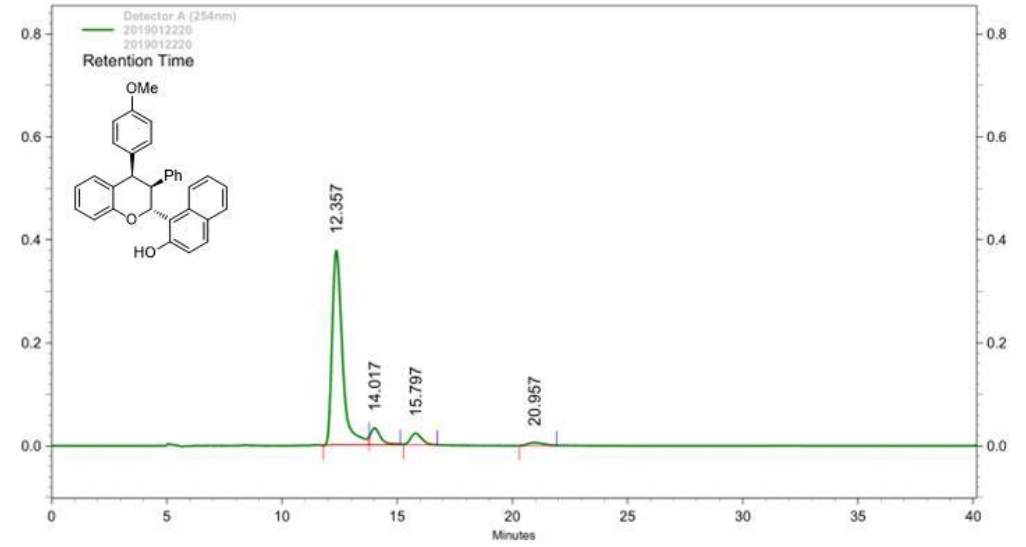






Detector A (254nm)

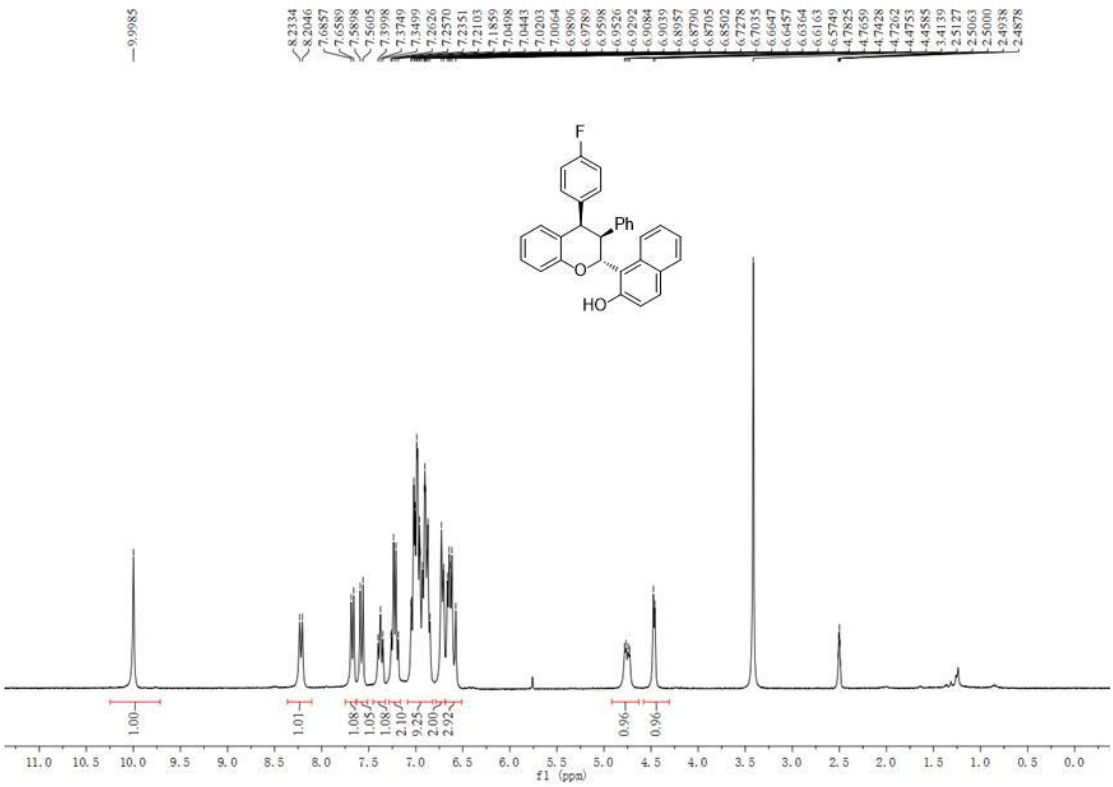
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	11.433	88269	20.00	1734206	11.21
2	12.370	188049	42.61	5897258	38.13
3	14.007	36072	8.17	988767	6.39
4	15.807	27097	6.14	920404	5.95
5	20.913	101828	23.07	5927207	38.32
Totals		441315	100.00	15467842	100.00

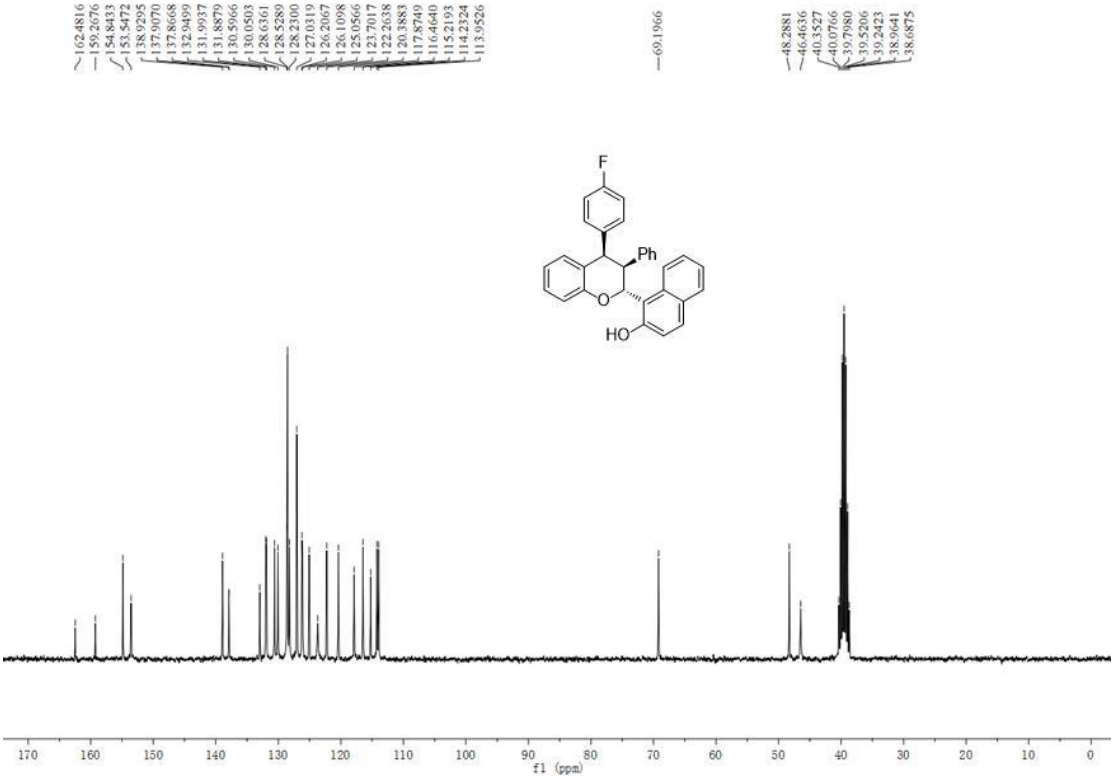


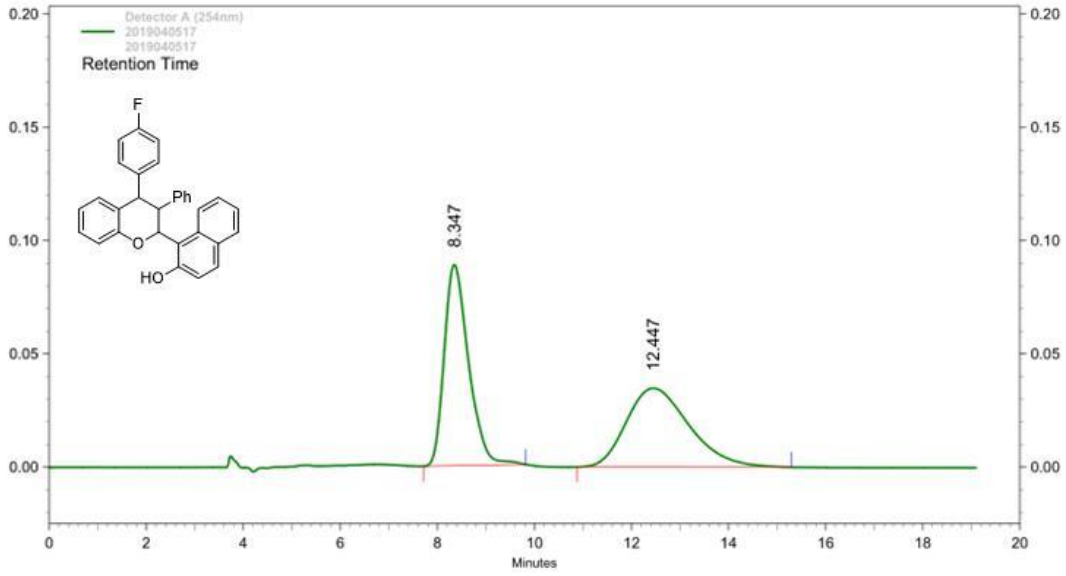
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	12.357	377918	86.38	11806625	86.12
2	14.017	32169	7.35	915945	6.68
3	15.797	21716	4.96	714703	5.21
4	20.957	5681	1.30	271992	1.98
Totals		437484	100.00	13709265	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 3x

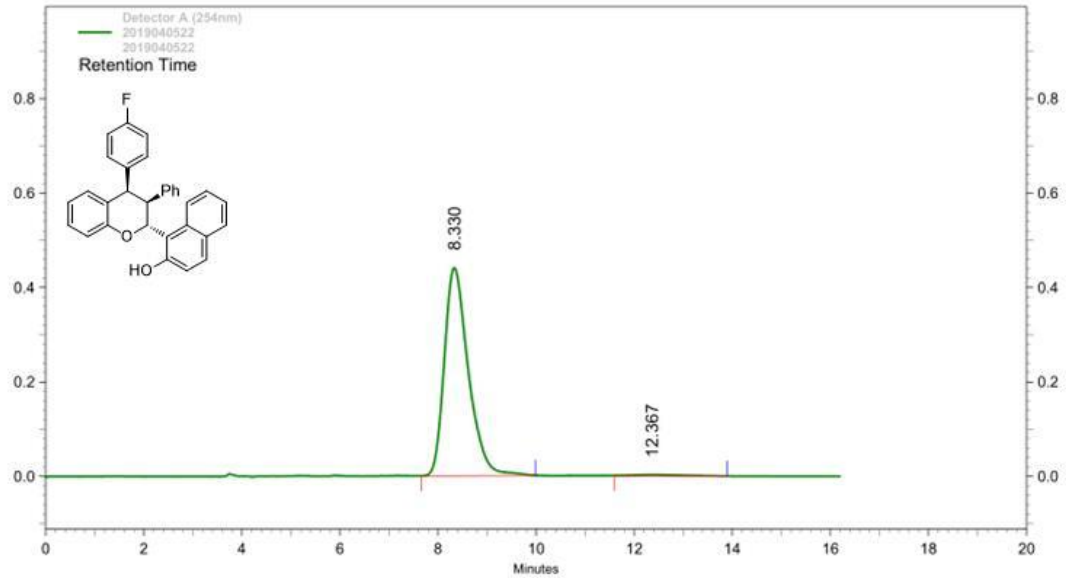






Detector A (254nm)

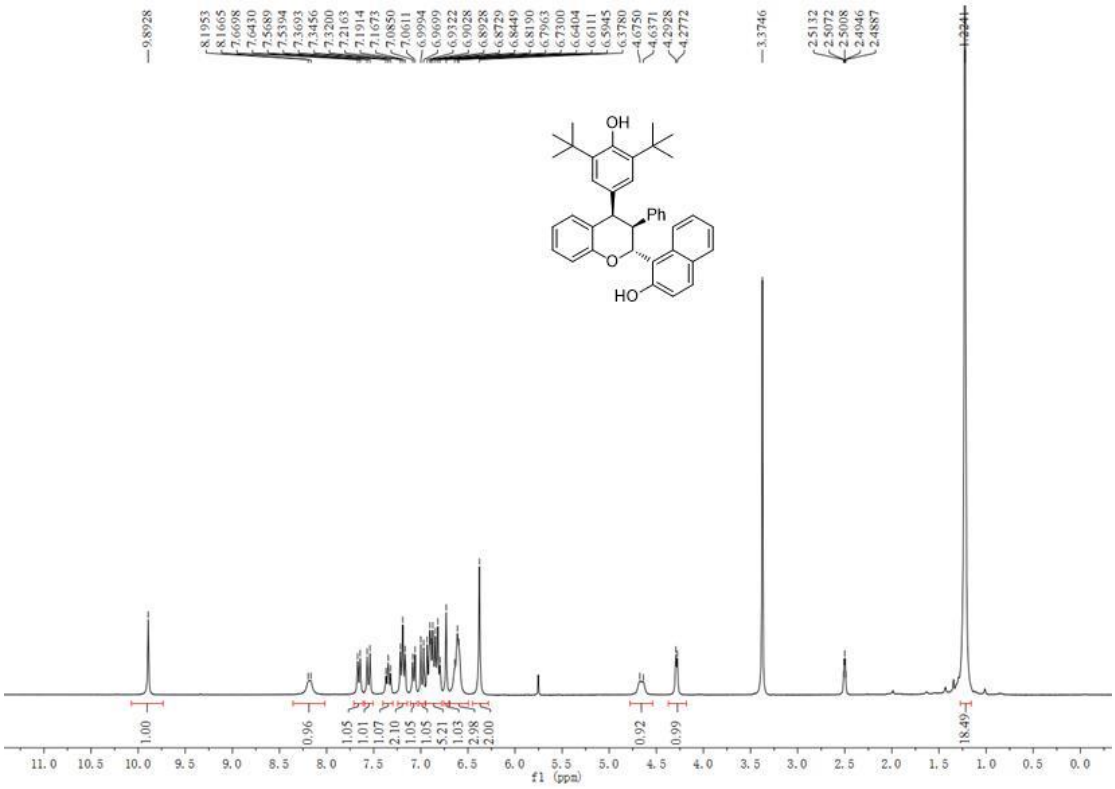
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.347	88708	71.83	3099280	49.80
2	12.447	34785	28.17	3124716	50.20
Totals		123493	100.00	6223996	100.00

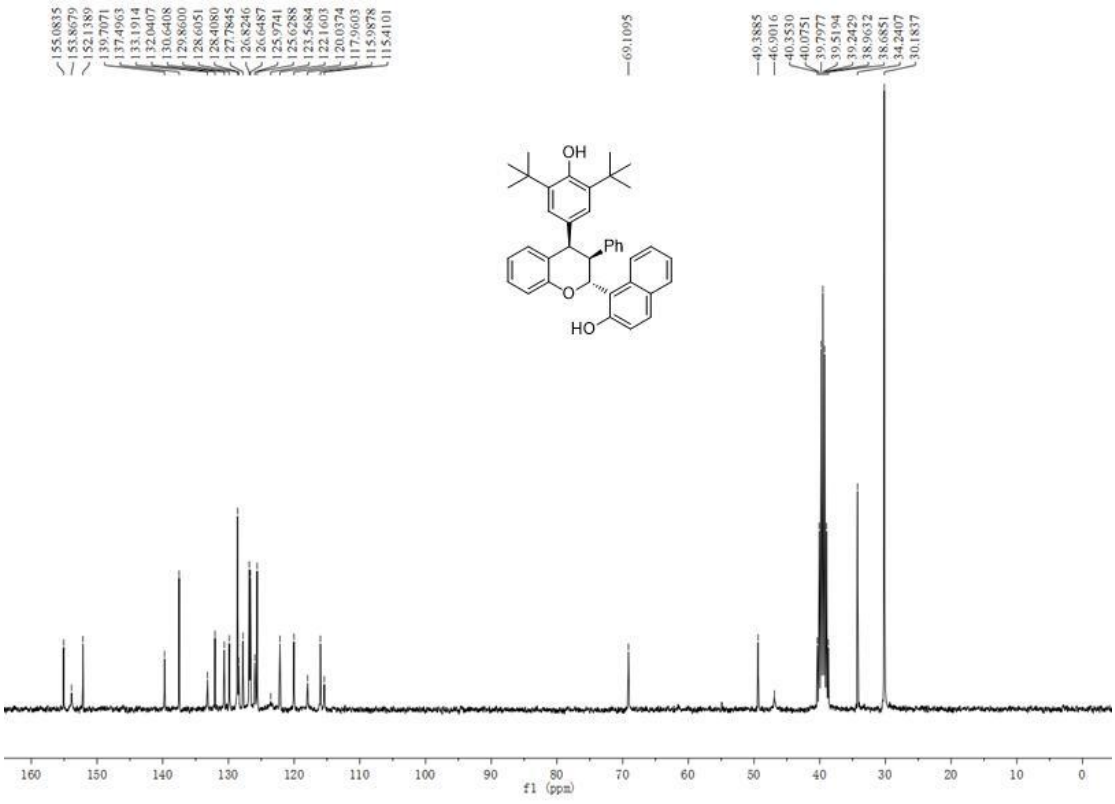


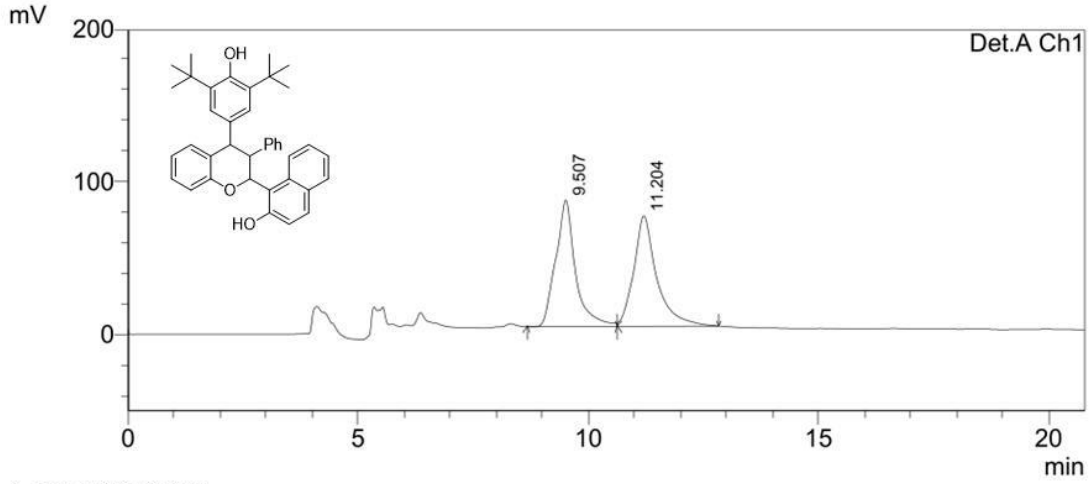
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.330	440494	99.53	14989210	99.03
2	12.367	2070	0.47	146241	0.97
Totals		442564	100.00	15135451	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 5a





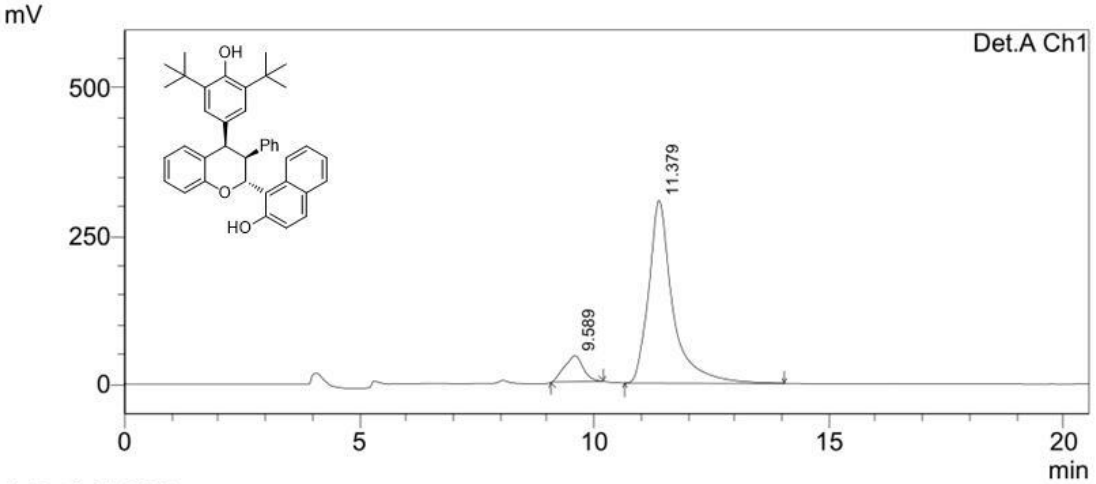


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.507	2488780	82893	49.713
2	11.204	2517547	72351	50.287
Total		5006328		100.000



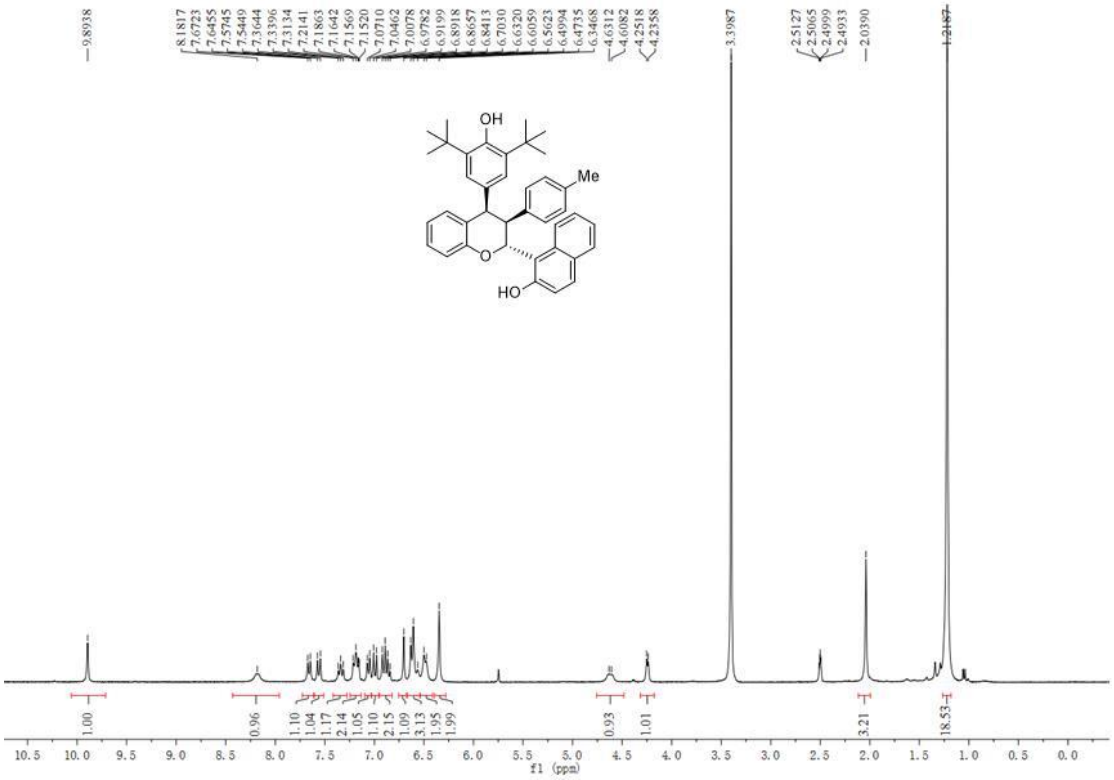
1 Det.A Ch1/254nm

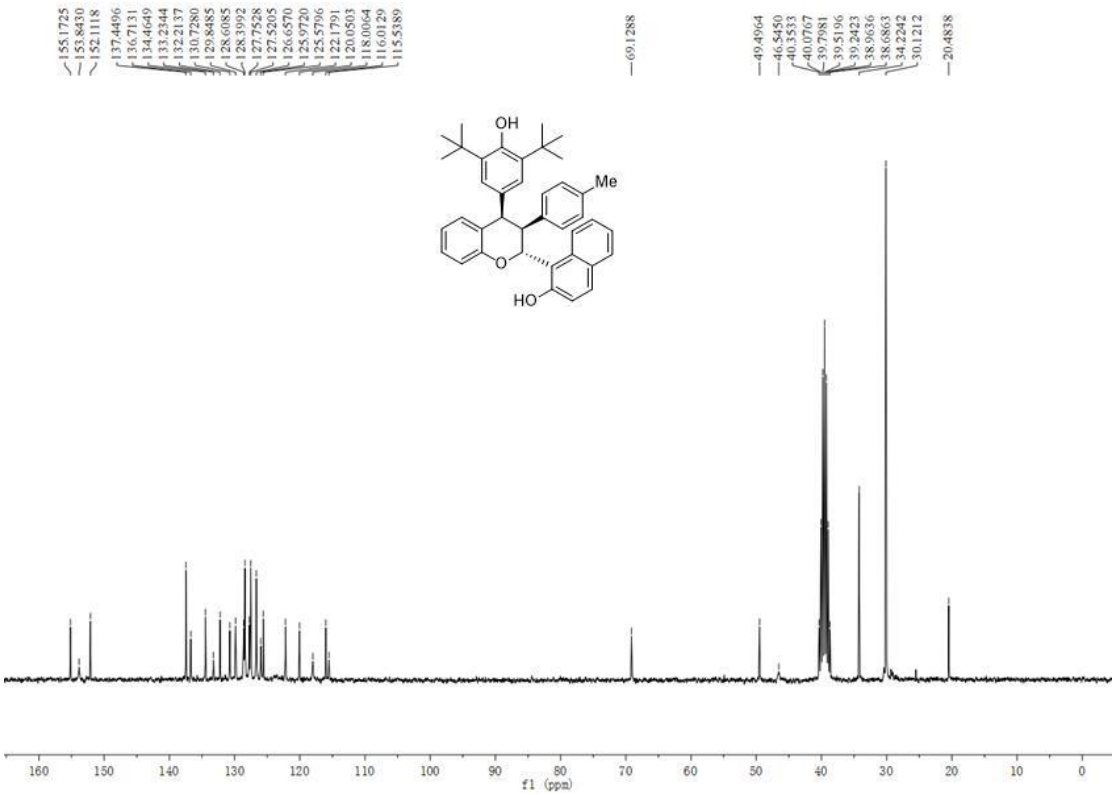
PeakTable

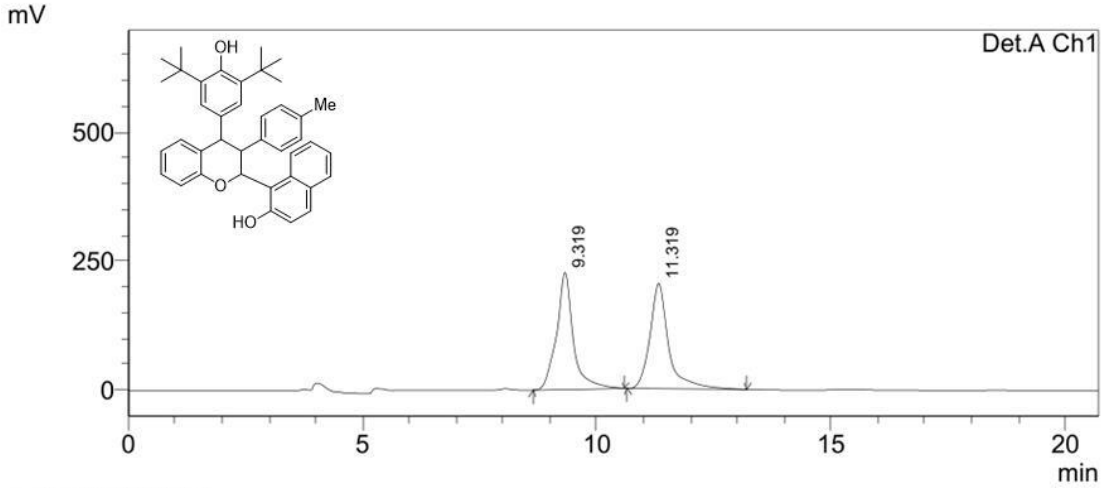
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.589	1214100	44024	9.931
2	11.379	11011075	308588	90.069
Total		12225174		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 5b





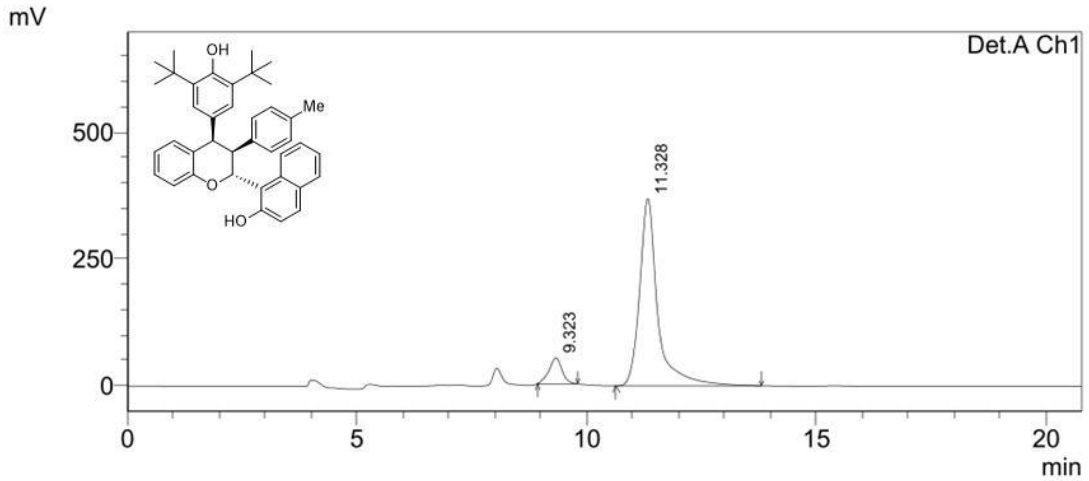


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.319	5679805	227195	50.071
2	11.319	5663761	203876	49.929
Total		11343565		100.000



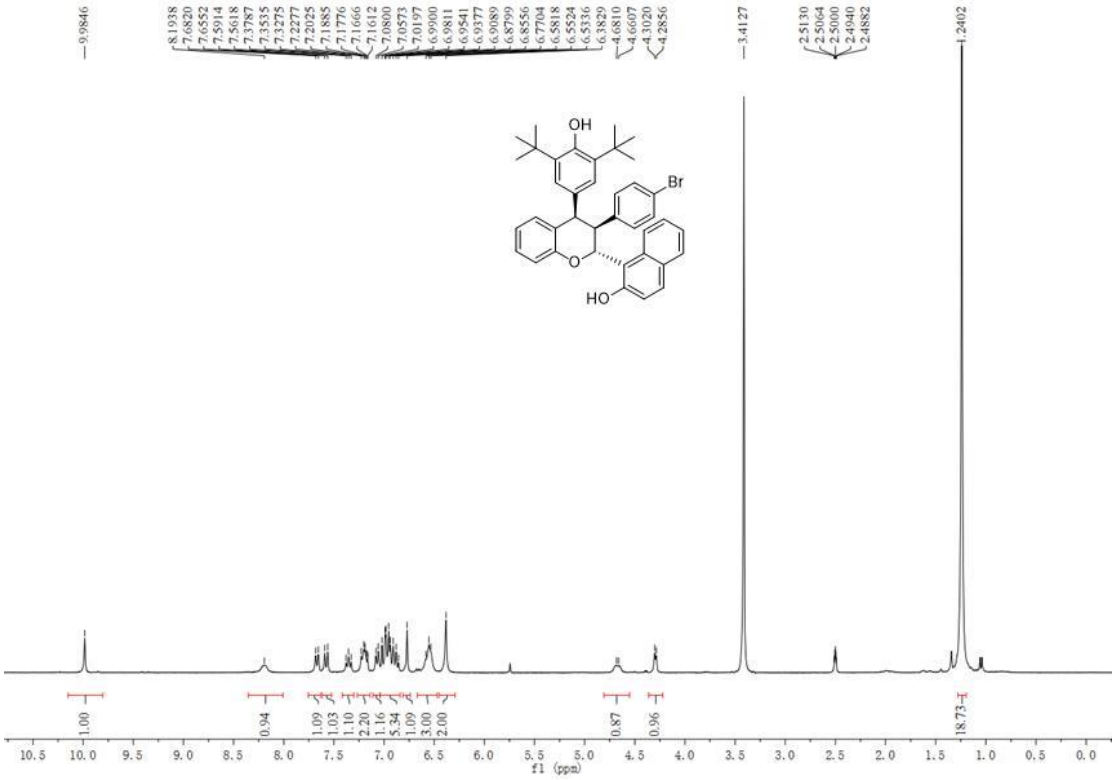
1 Det.A Ch1/254nm

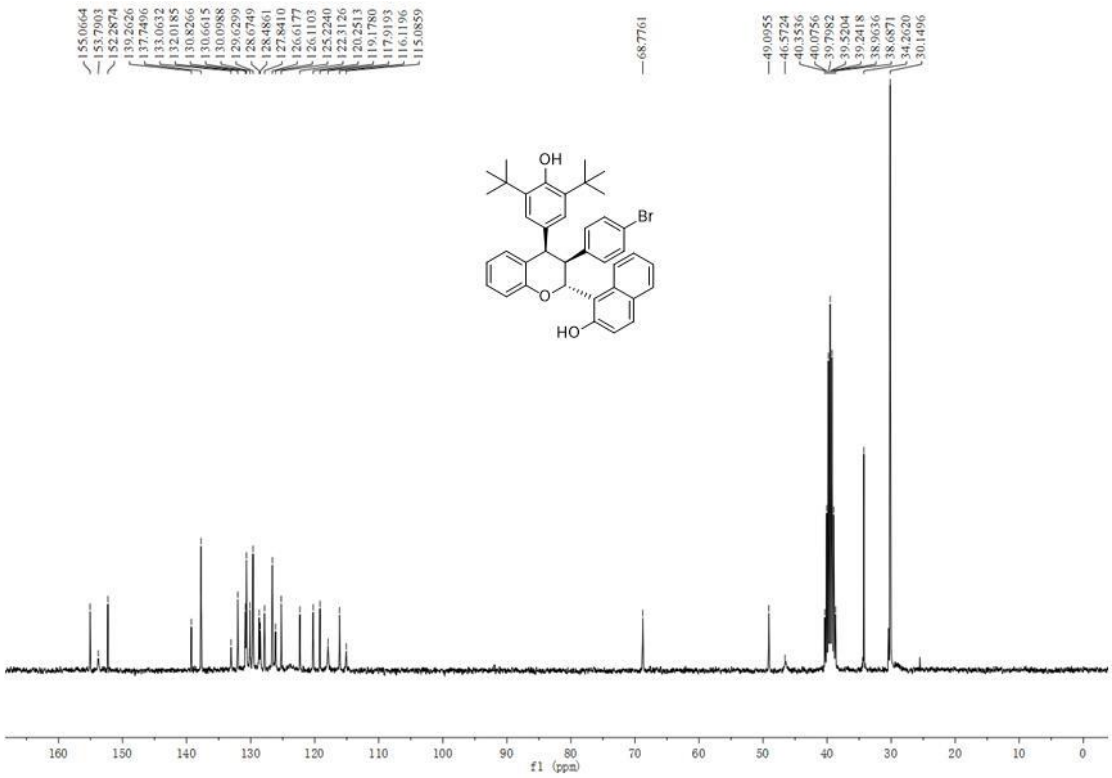
PeakTable

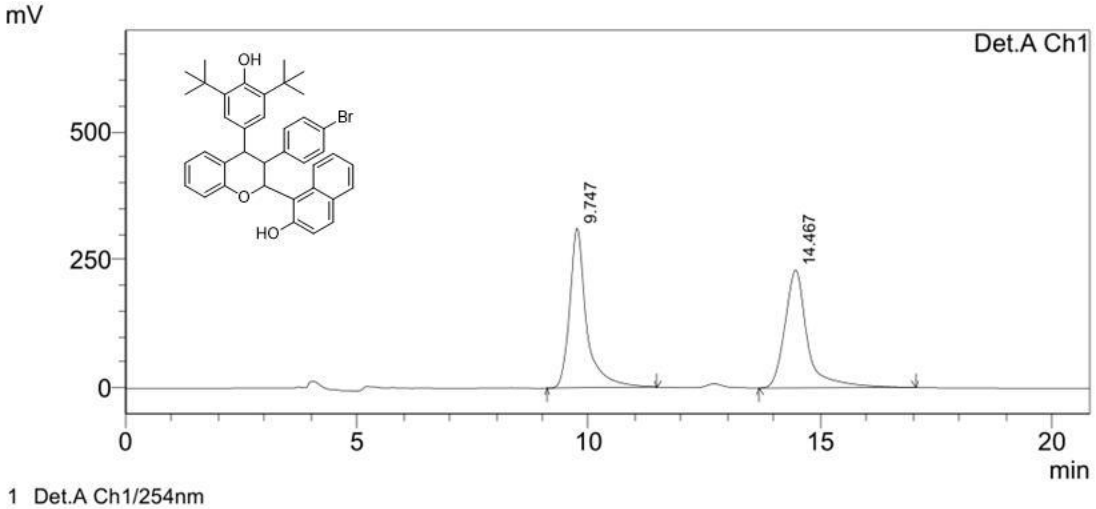
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.323	1008678	50949	9.043
2	11.328	10145617	368819	90.957
Total		11154295		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 5c





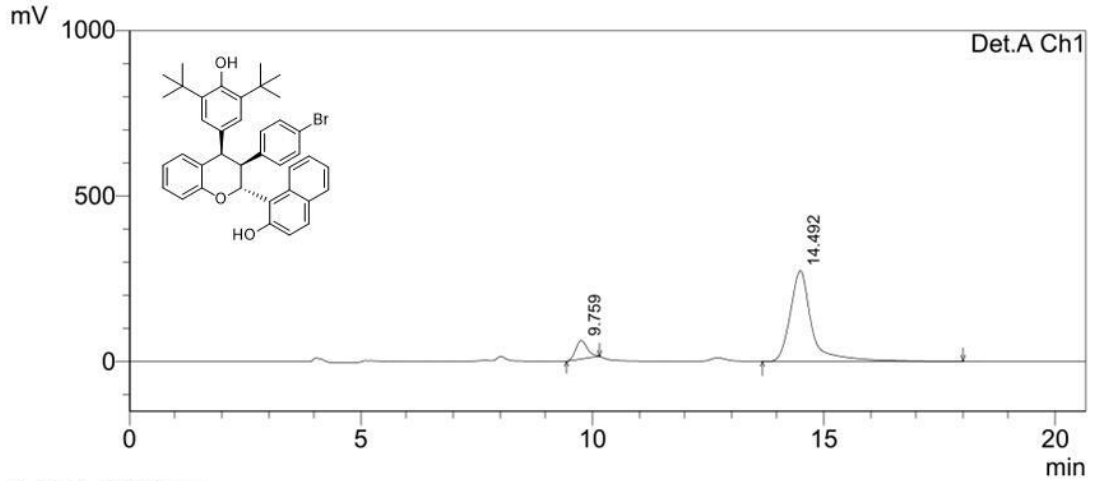


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.747	7896594	311400	50.183
2	14.467	7838925	230010	49.817
Total		15735519		100.000



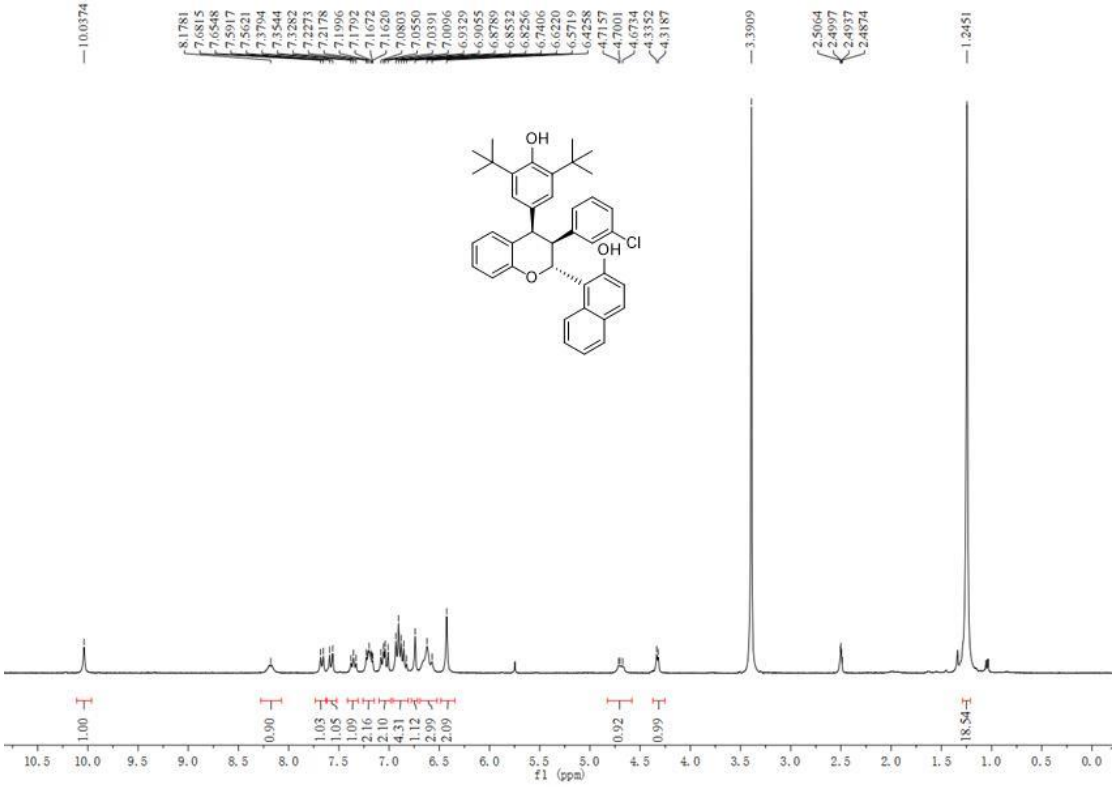
1 Det.A Ch1/254nm

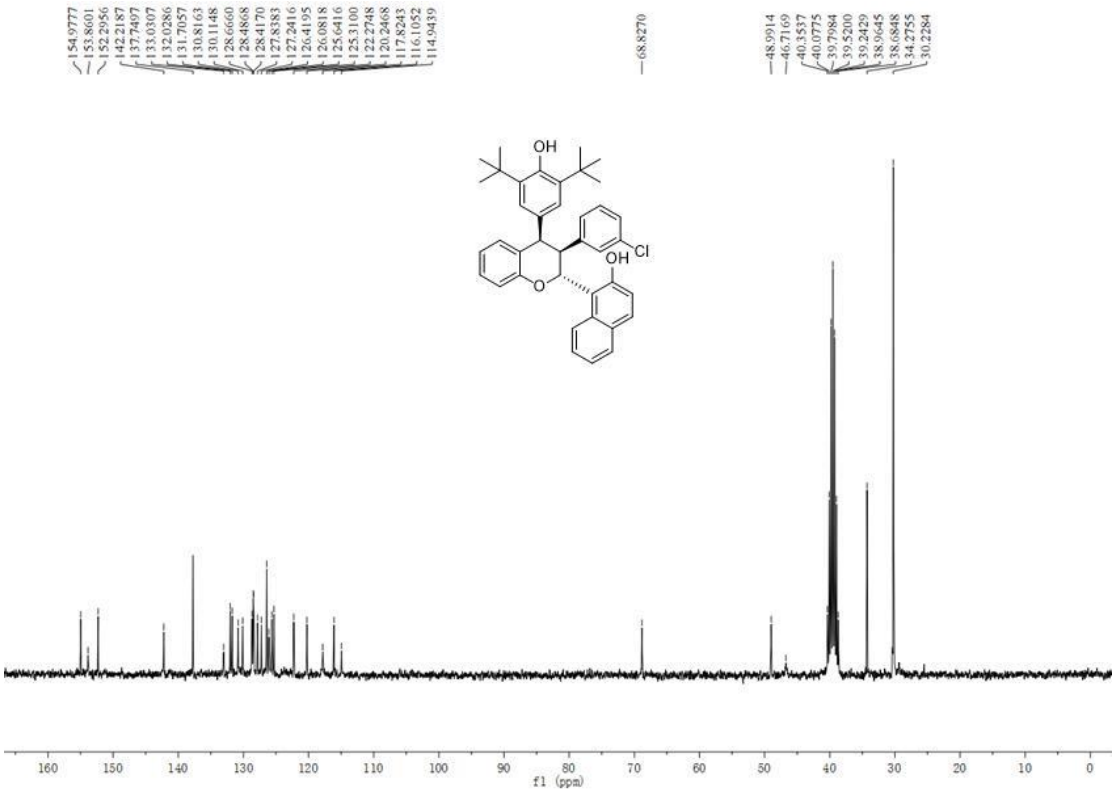
PeakTable

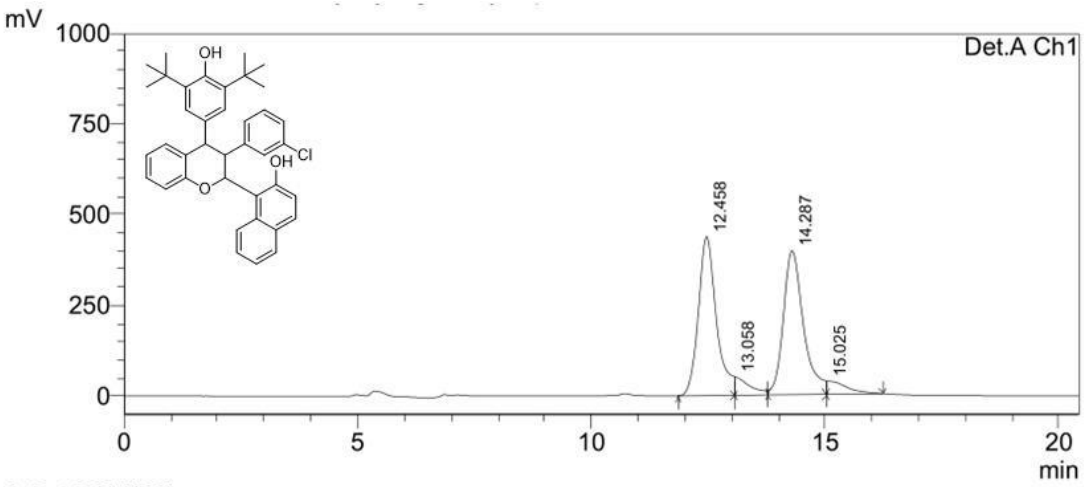
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.759	971331	55718	9.865
2	14.492	8874480	273735	90.135
Total		9845811		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 5d





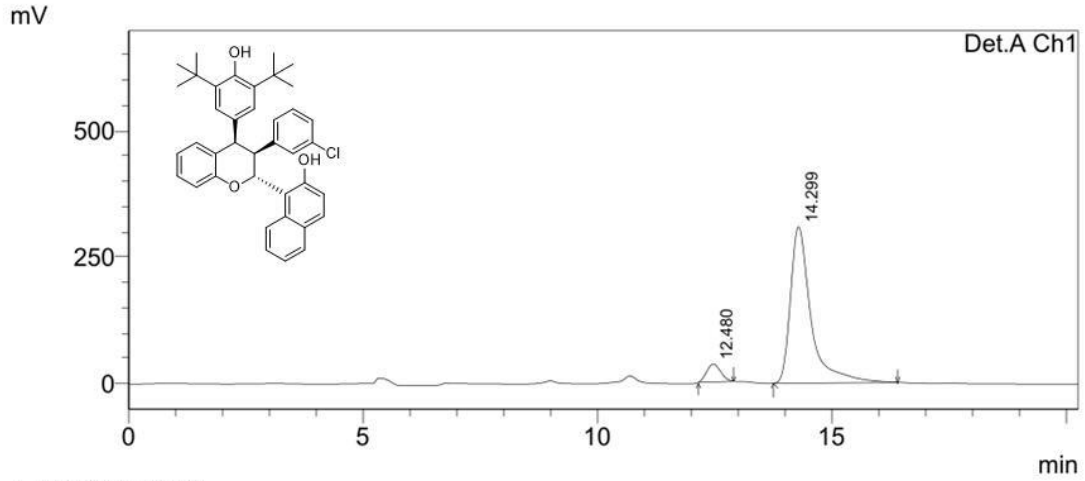


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.458	11714033	437529	45.245
2	13.058	1170056	51839	4.519
3	14.287	11899271	397108	45.961
4	15.025	1106720	37137	4.275
Total		25890079		100.000



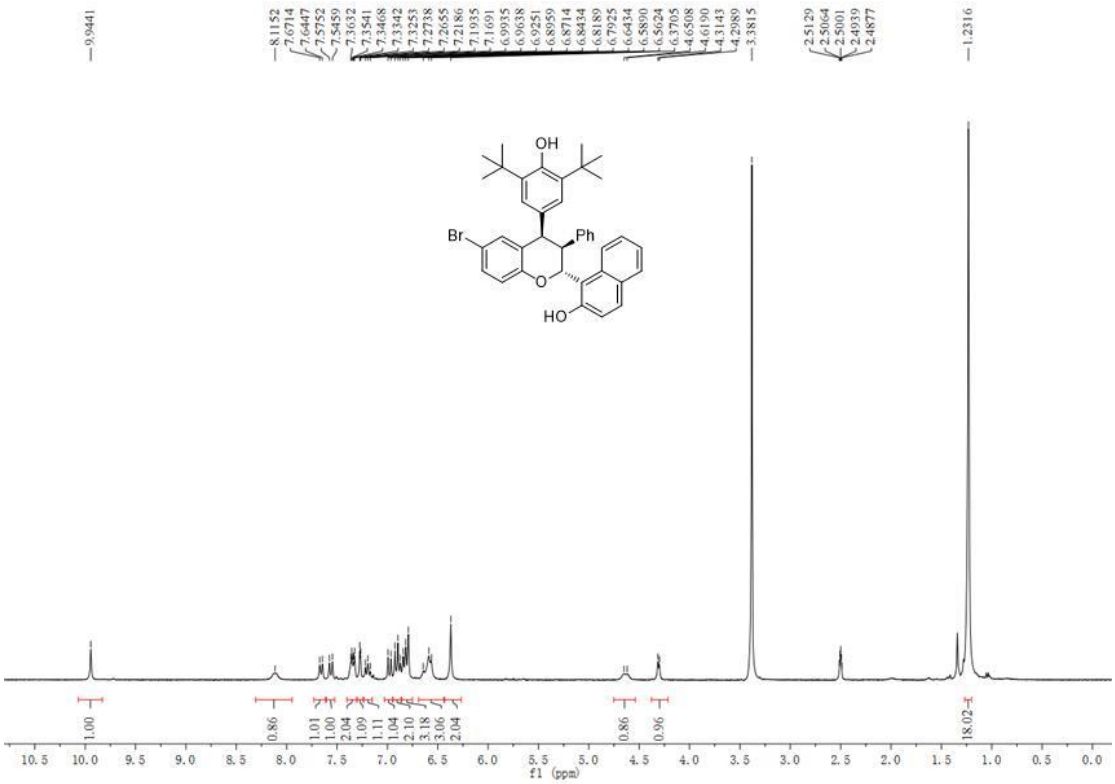
1 Det.A Ch1/254nm

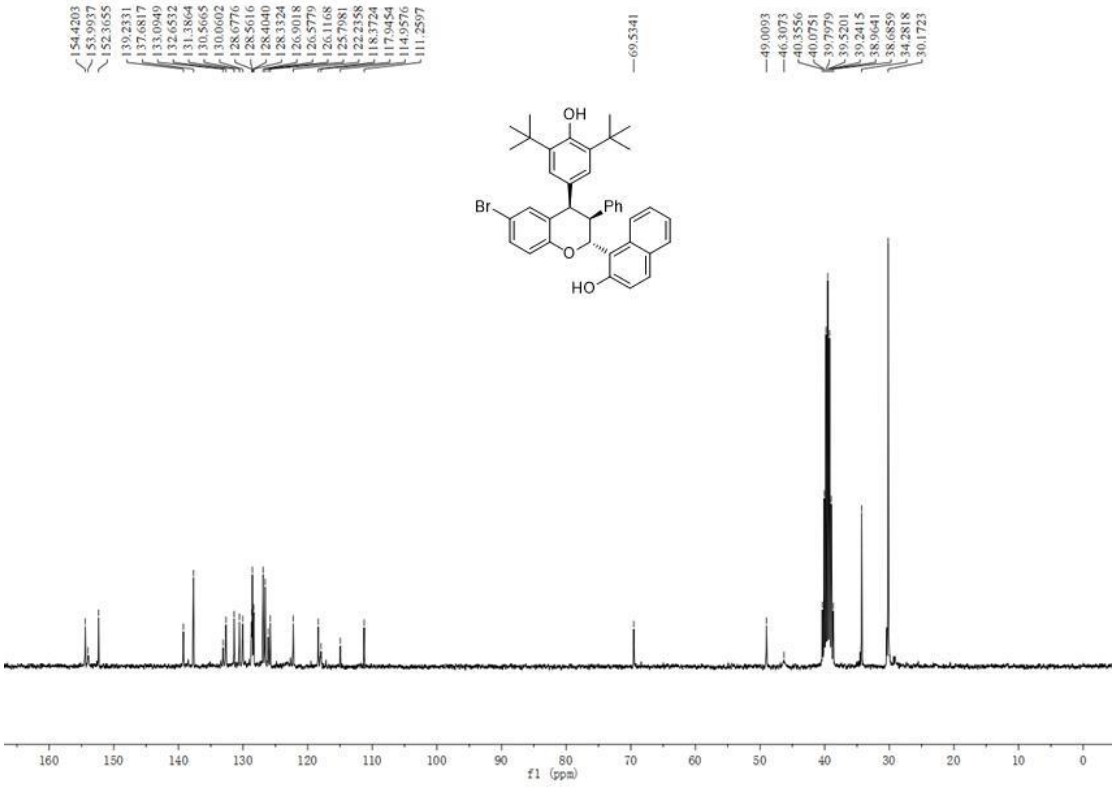
PeakTable

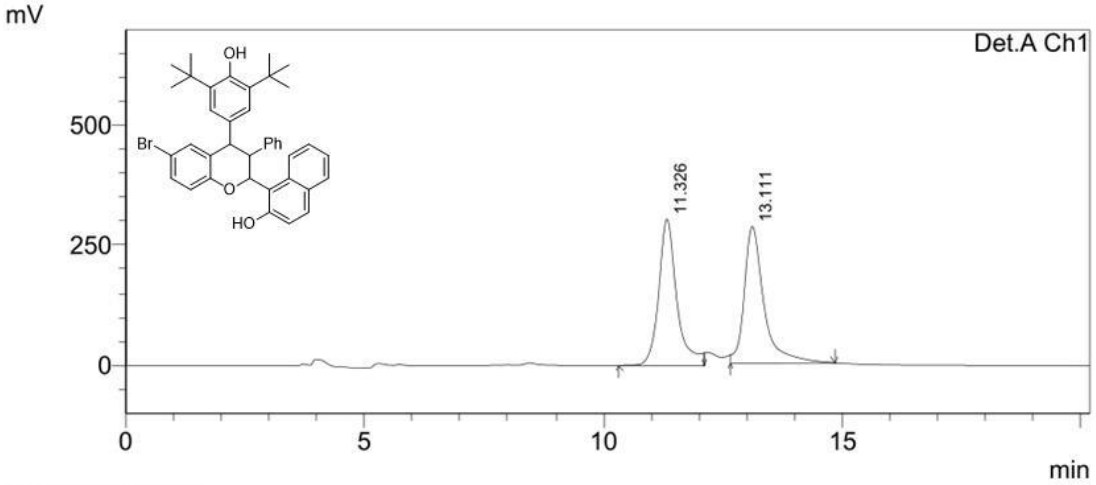
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.480	722022	35142	7.135
2	14.299	9398110	308747	92.865
Total		10120131		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 5e





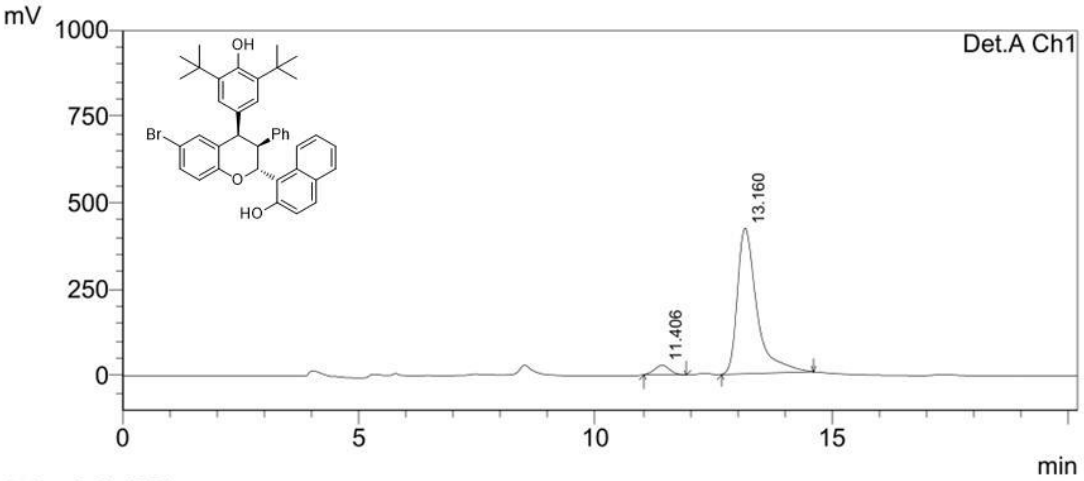


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.326	8045060	304614	49.743
2	13.111	8128123	284557	50.257
Total		16173183		100.000



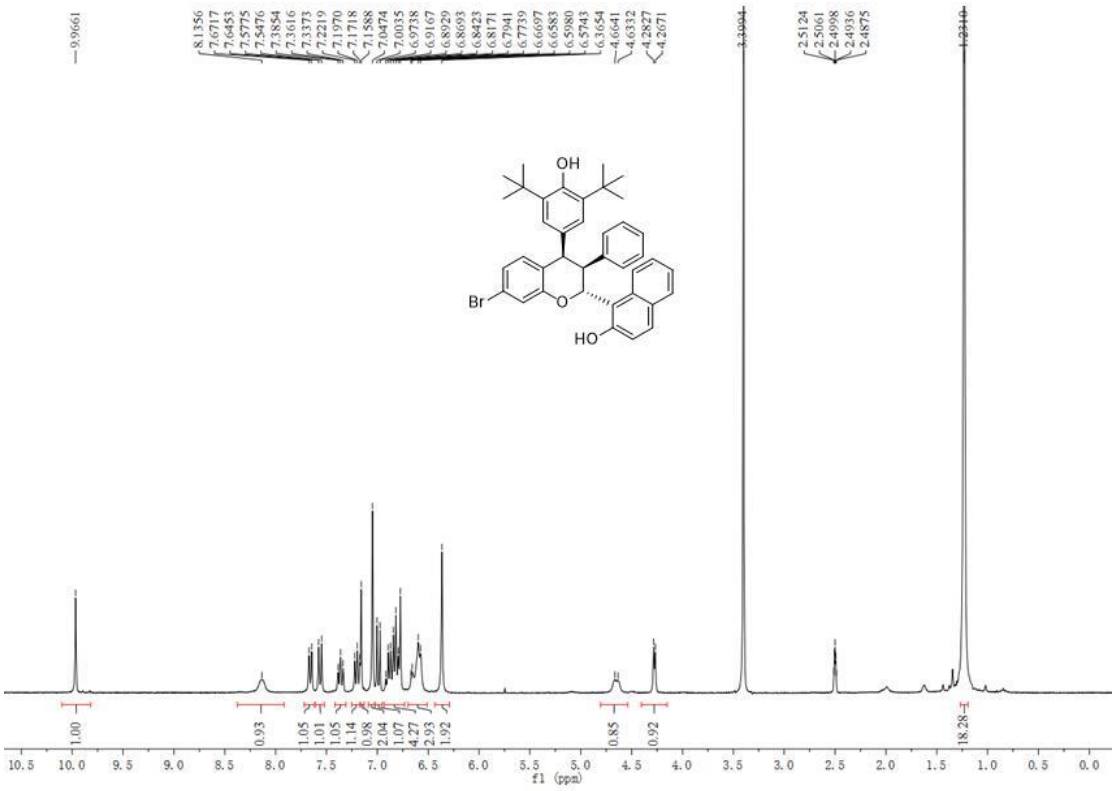
1 Det.A Ch1/254nm

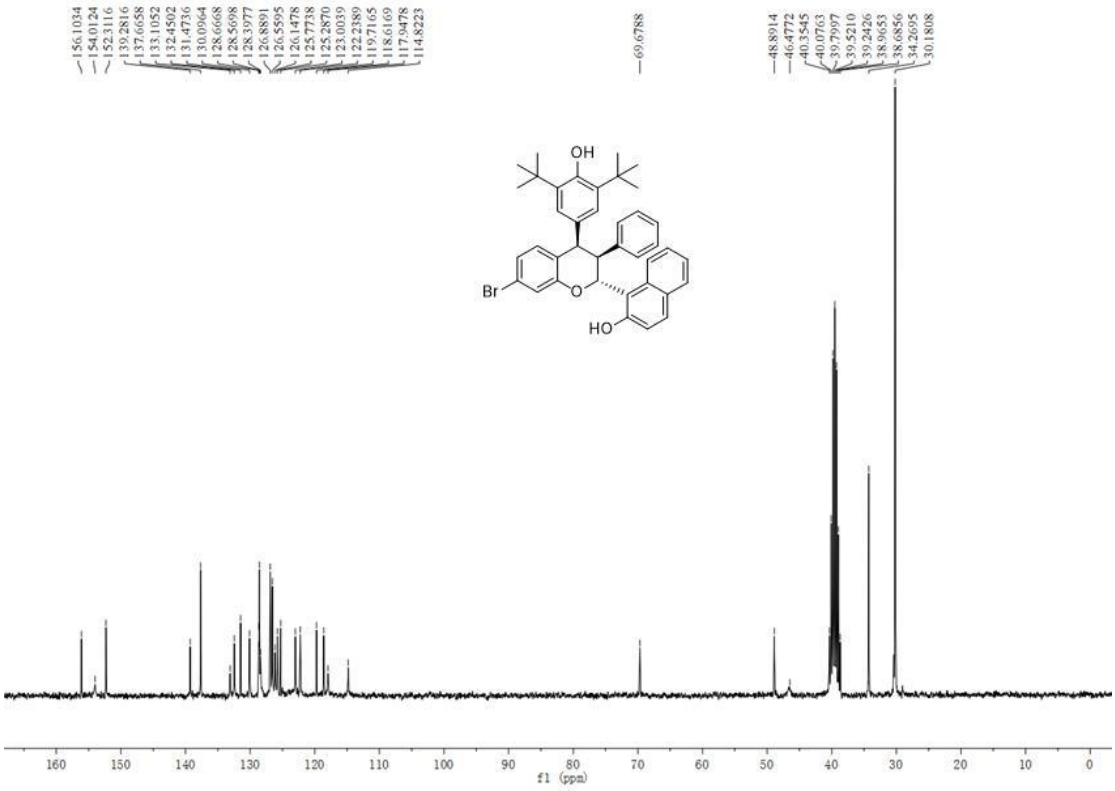
PeakTable

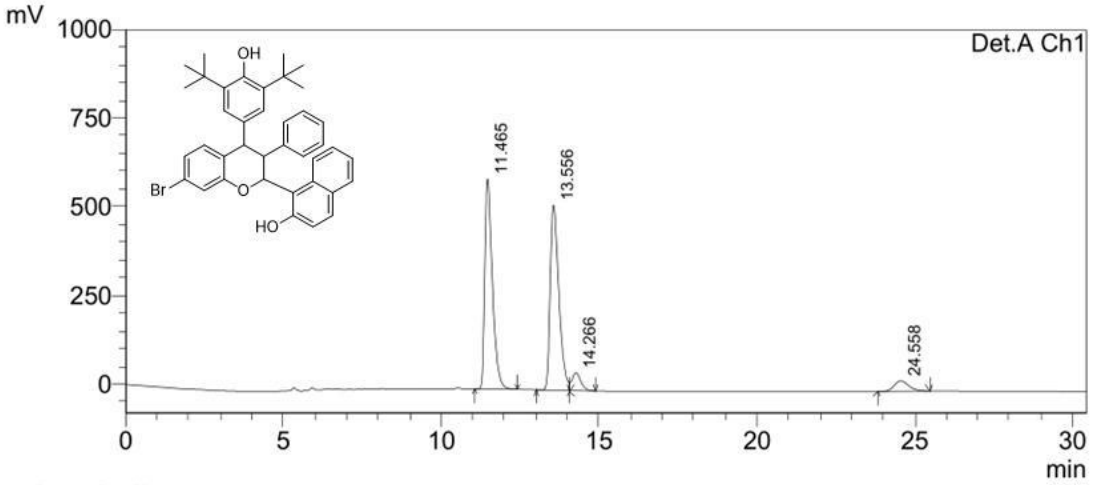
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.406	622859	28126	4.893
2	13.160	12105496	420971	95.107
Total		12728355		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 5f





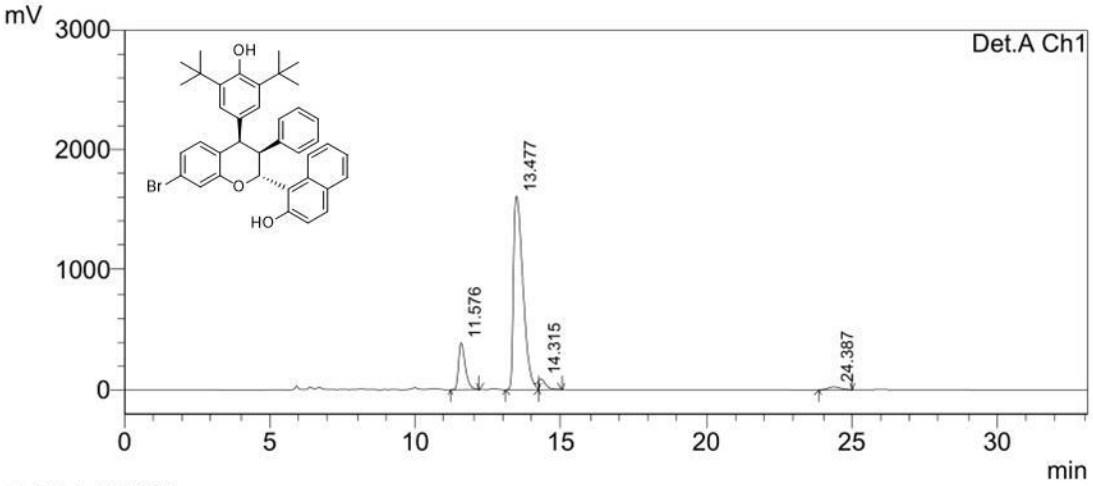


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.465	9945763	592547	45.661
2	13.556	9957213	521033	45.713
3	14.266	939587	50110	4.314
4	24.558	939268	29319	4.312
Total		21781831		100.000



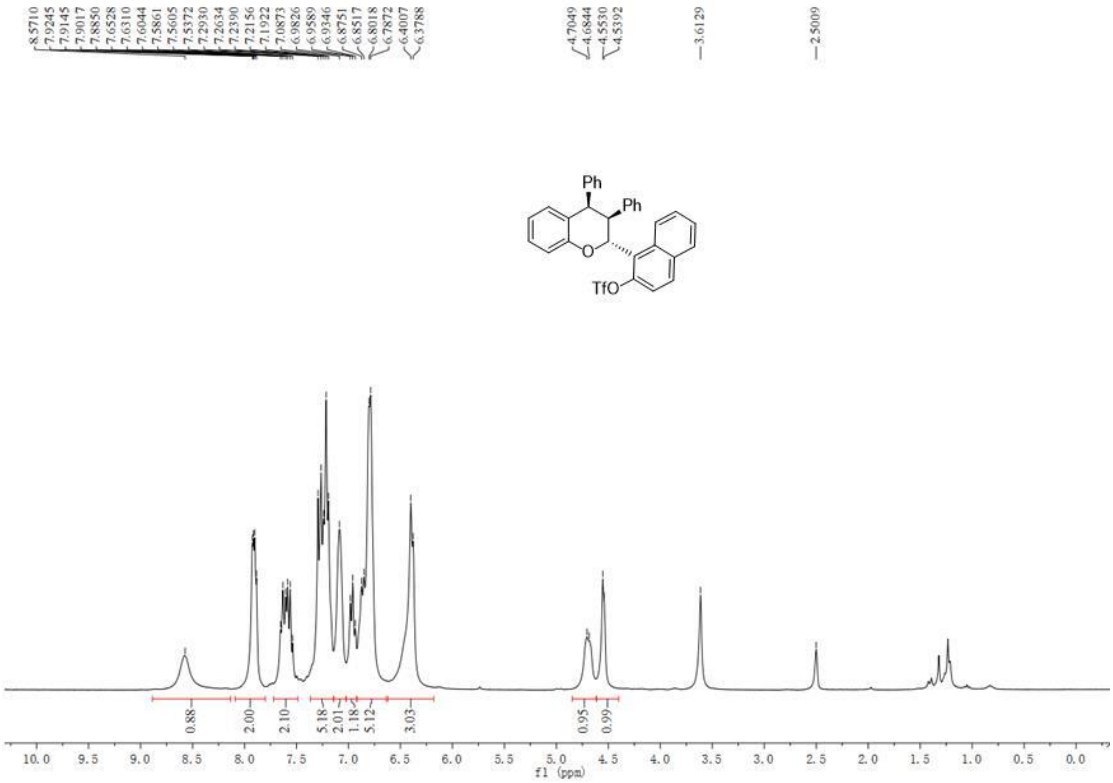
1 Det.A Ch1/254nm

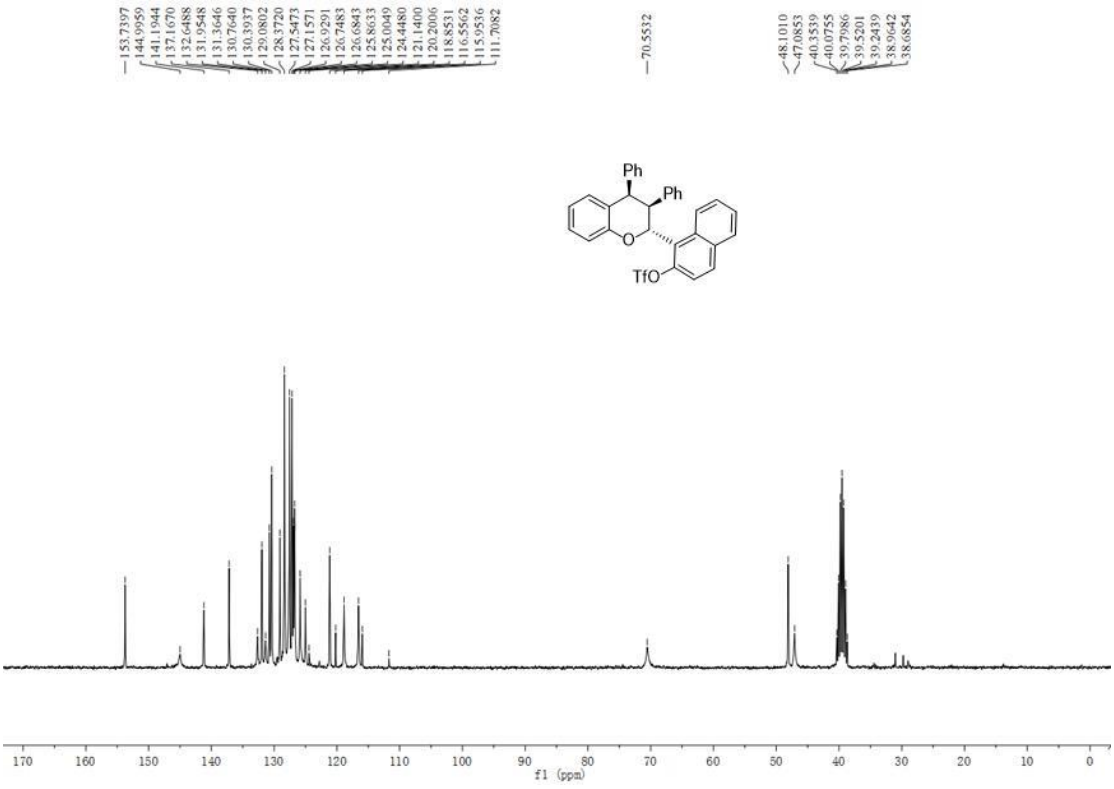
PeakTable

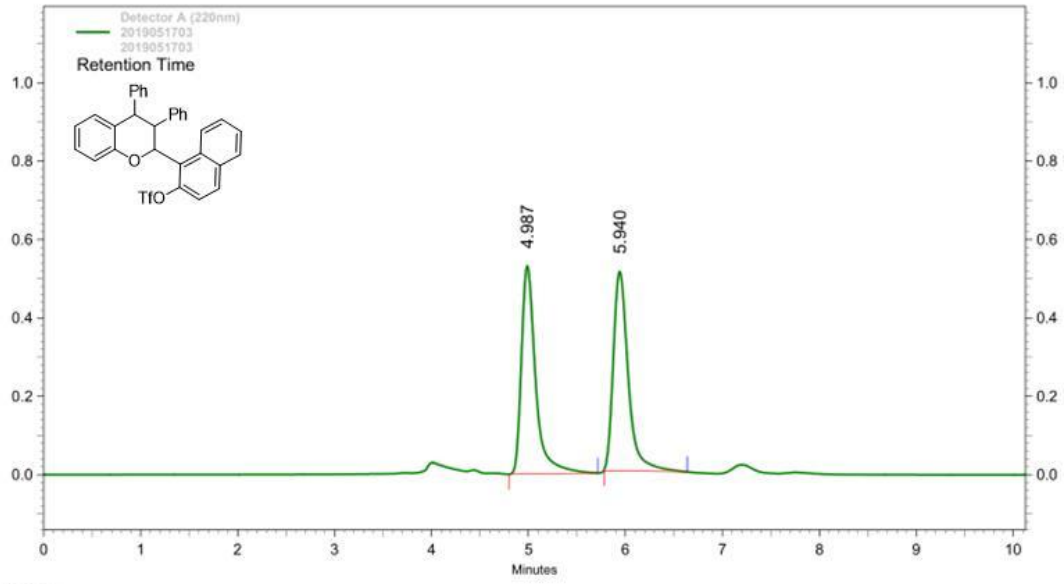
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.576	6203114	389525	13.719
2	13.477	36741906	1611421	81.257
3	14.315	1540058	88112	3.406
4	24.387	731686	24409	1.618
Total		45216764		100.000

^{1}H NMR, ^{13}C NMR and HPLC spectra of 6

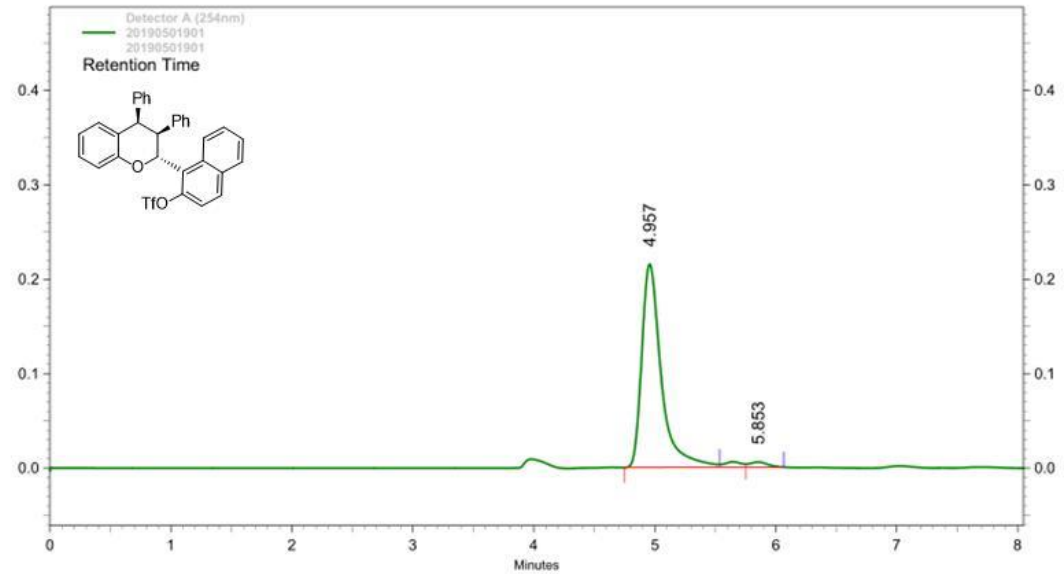






Detector A (220nm)

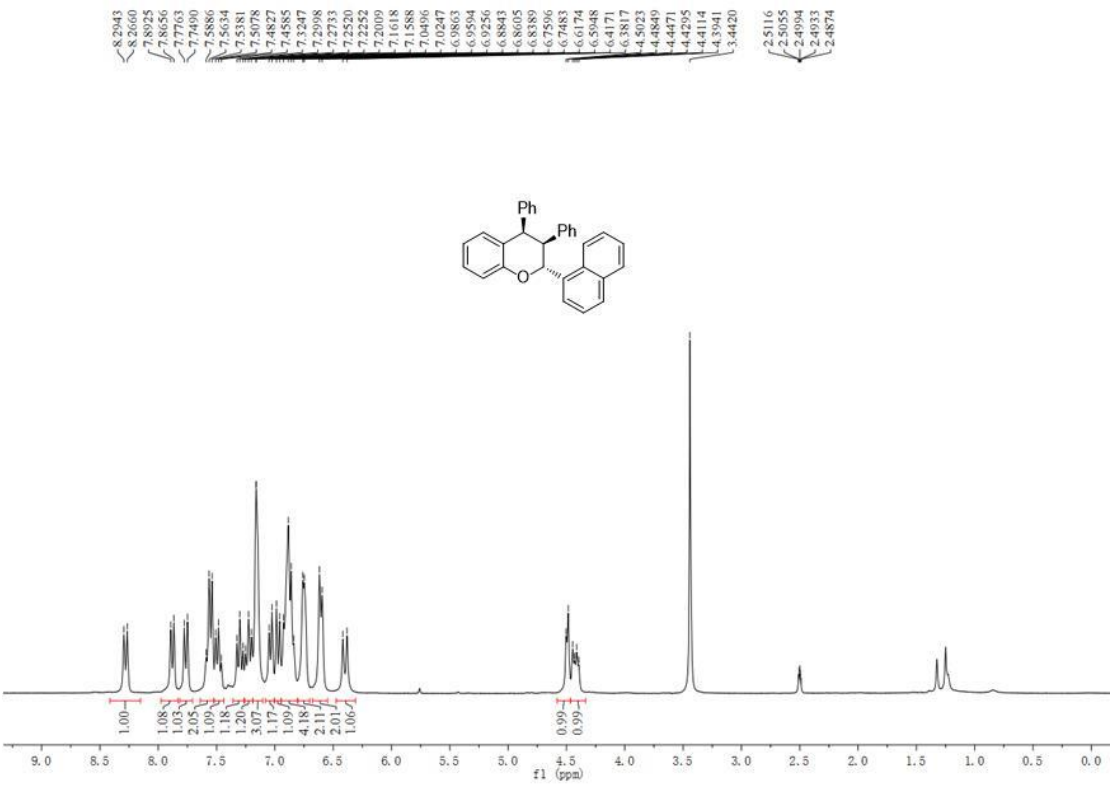
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	4.987	531019	51.08	5411840	49.75
2	5.940	508492	48.92	5465187	50.25
Totals		1039511	100.00	10877027	100.00

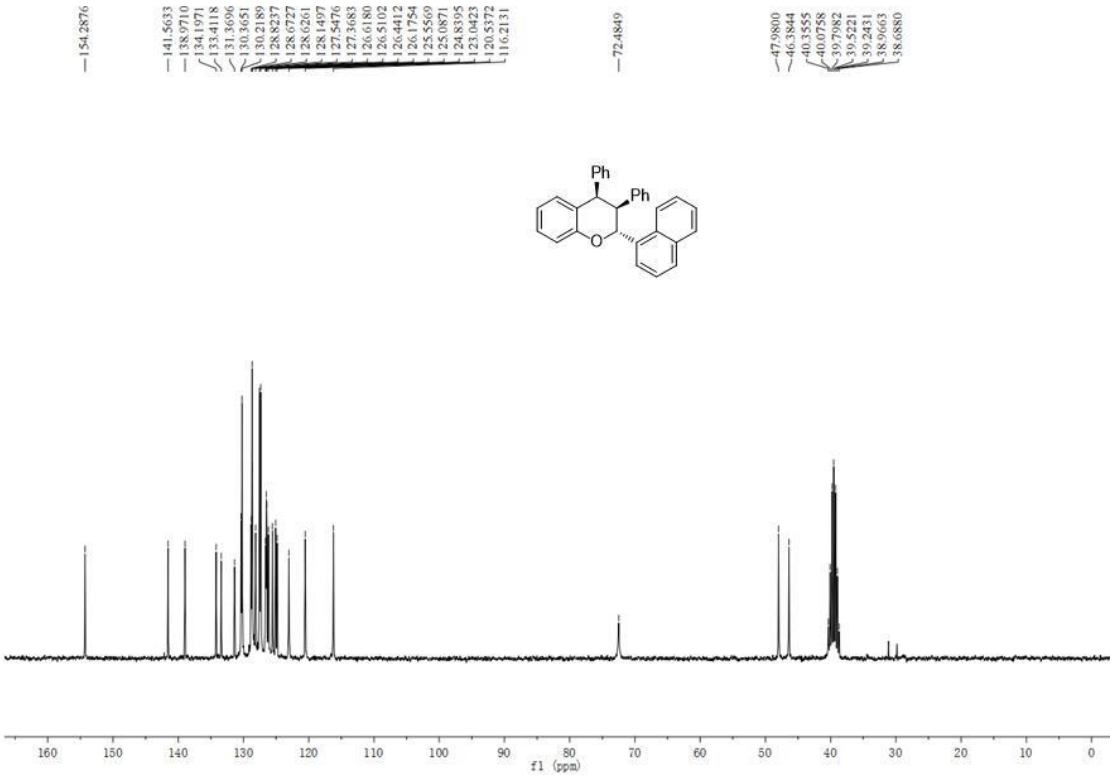


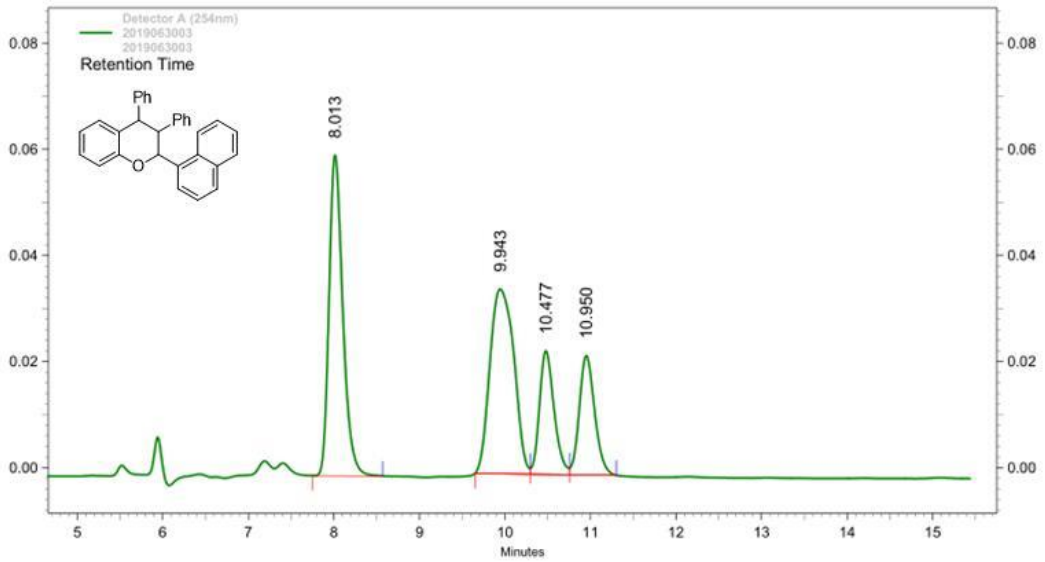
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	4.957	215382	97.54	2422191	97.68
2	5.853	5436	2.46	57403	2.32
Totals		220818	100.00	2479594	100.00

^{1}H NMR, ^{13}C NMR and HPLC spectra of 7

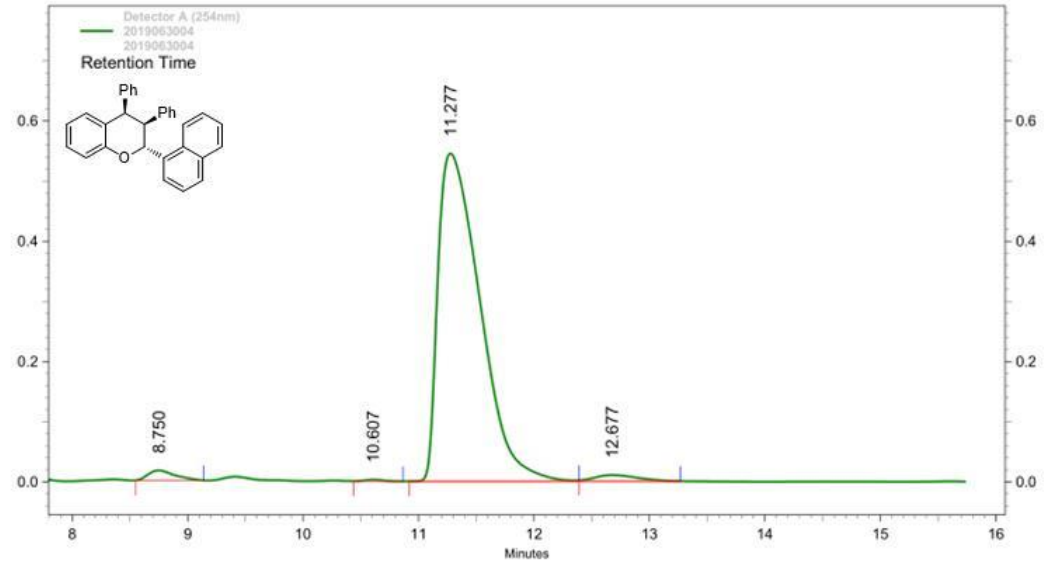






Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.013	60399	42.87	674505	35.28
2	9.943	34778	24.68	678544	35.49
3	10.477	23261	16.51	277474	14.51
4	10.950	22458	15.94	281166	14.71
Totals		140896	100.00	1911689	100.00



Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.750	16511	2.87	267073	1.86
2	10.607	2540	0.44	28348	0.20
3	11.277	545210	94.91	13772418	96.10
4	12.677	10191	1.77	263042	1.84
Totals		574452	100.00	14330881	100.00