Catalytic asymmetric aromatizing inverse electron-demand [4+2] cycloaddition of 1-thioaurones and 1-azaaurones

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Supporting Information

Table of Contents

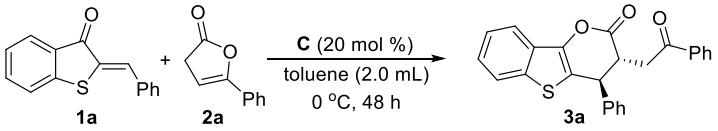
1. General Information

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. ^{1}H NMR and ^{13}C NMR 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. 13C 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-10AVP 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. The substrates **1**[1] and **6**[2] were prepared following the procedures reported in literatures. Among them, **1a-1b**, **1d-1j** were prepared from the same reference[1a]. While **1c**, **1l-1n** were synthesized according to precedent literature report[1b]. Furthermore, **1k** was obtained by the other way[1c].

[1] (a) T. B. Nguyen and P. Retailleau, *Org. Lett*. 2018, **20**, 186-189; (b) B. Maerz, S. Wiedbrauk, S. Oesterling, E. Samoylova, A. Nenov, P. Mayer, R. Vivie-Riedle, W. Zinth and H. Dube, *Chem. Eur. J*. 2014, **20**, 13984-13992; (c) P. Xiao, S.-K. Su, W. Wang, W.-G. Cao, J. Chen, J. Li and Y.-L. Chen, *RSC Advances*. 2019, **9**, 39119-39123.

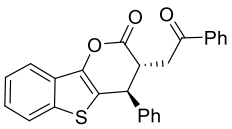
[2] X.-H. Fei, Y.-L. Zhao, F.-F. Yang, X. Guan, Z.-Q. Li, D.-P. Wang, M. Zhou, Y.-Y. Yang and B. He, *Adv. Synth. Catal*. 2021, **363**, 3018-3024.

2. General procedures for the asymmetric synthesis of compounds 3



In an ordinary vial equipped with a magnetic stirring bar, the solution of 1-Thioaurones **1** (0.12 mmol, 1.2 equiv), γ-Deconjugated Butenolides **2** (0.1 mmol, 1.0 equiv) and catalyst **C** (20 mol %) in toluene (2.0 mL) was cooled to 0 ℃. And then, the mixture was stirred at the same temperature for the specified time. After completion of the reaction, as indicated by TLC, the products **3** were isolated by flash chromatography on silica gel (PE/EA = 21/1 ~ 10/1).

(3R,4S)-3-(2-oxo-2-phenylethyl)-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3a)

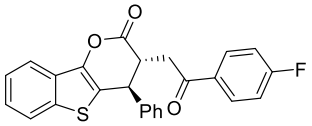


The major diastereomer **3a** was purified by flash column chromatography (petroleum ether/ethyl acetate = 15:1);

White solid; 35.0 mg, 88% yield; 92:8 dr, 99% ee; $[\alpha]_D^{20}$ = +27.9 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 159.3-160.5 ℃;

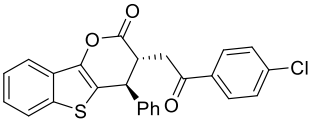
The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 0.6 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 19.7 min, t_{major} = 17.9 min);
^{1}H NMR (300 MHz, $CDCl_3$) δ (major diastereomer) 7.94-7.86 (m, 2H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.58-7.49 (m, 1H), 7.46-7.37 (m, 3H), 7.37-7.26 (m, 6H), 4.55 (d, *J* = 11.6 Hz, 1H), 3.91-3.67 (m, 1H), 3.43 (dd, *J* = 18.0, 6.0 Hz, 1H), 3.23 (dd, *J* = 18.0, 4.2 Hz, 1H);
^{13}C NMR (75 MHz, $CDCl_3$) δ (major diastereomer) 196.7, 169.5, 141.4, 139.8, 136.8, 136.4, 133.5, 129.9, 129.3, 128.7, 128.6, 128.4, 128.2, 125.5, 124.9, 122.8, 120.2, 120.0, 43.4, 43.3, 36.7;
HRMS (ESI-TOF) calcd. for $C_{25}H_{19}O_3S$ $[M + H]^+$ 399.1049; found: 399.1052.

(3R,4S)-3-(2-(4-fluorophenyl)-2-oxoethyl)-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3b)



The major diastereomer **3b** was purified by flash column chromatography (petroleum ether/ethyl acetate = 15:1);
Yellow solid; 32.5 mg, 78% yield; 84:16 dr, 99% ee; $[\alpha]_D^{20}$ = +4.8 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 106.5-107.3 ℃;
The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 23.0 min, t_{major} = 13.5 min);
^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.96-7.89 (m, 2H), 7.82 (d, *J* = 7.3 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.46-7.33 (m, 5H), 7.33-7.27 (m, 2H), 7.14-7.06 (m, 2H), 4.55 (d, *J* = 11.7 Hz, 1H), 3.86-3.70 (m, 1H), 3.41 (dd, *J* = 17.8, 6.1 Hz, 1H), 3.19 (dd, *J* = 17.8, 4.2 Hz, 1H);
^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 195.2, 169.5, 166.0 (d, *J* = 255.4 Hz, 1C), 141.4, 139.7, 136.8, 132.9 (d, *J* =3.0 Hz, 1C), 130.9 (d, *J* = 9.5 Hz, 1C), 129.9, 129.4, 128.6, 128.4, 125.5, 124.9, 122.8, 120.2, 120.0, 115.8 (d, *J* = 21.9 Hz, 1C), 43.4, 43.3, 36.6;
HRMS (ESI-TOF) calcd. for $C_{25}H_{18}FO_3S$ $[M + H]^+$ 417.0955; found: 417.0956.

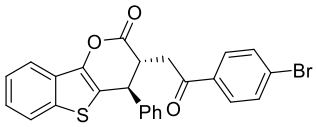
(3R,4S)-3-(2-(4-chlorophenyl)-2-oxoethyl)-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3c)



The major diastereomer **3c** was purified by flash column chromatography (petroleum ether/ethyl acetate = 15:1);
Yellow solid; 32.0 mg, 74% yield; 87:13 dr, 98% ee; $[\alpha]_D^{20}$ = +18.0 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 128.7-129.9 ℃;
The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 20.5 min, t_{major} = 12.9 min);
^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.83 (dd, *J* = 8.4, 6.5 Hz, 3H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.47-7.39 (m, 3H), 7.39-7.26 (m, 6H), 4.55 (d, *J* = 11.7 Hz, 1H), 3.85-3.67 (m, 1H), 3.41 (dd, *J* = 17.8, 6.1 Hz, 1H), 3.18 (dd, *J* = 17.8, 4.1 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 195.6, 169.5, 141.4, 140.1, 139.7, 136.8, 134.8, 129.9, 129.6, 129.4, 129.1, 128.7, 128.5, 125.5, 125.0, 122.9, 120.3, 120.0, 43.5, 43.4, 36.7; **HRMS (ESI-TOF)** calcd. for $C_{25}H_{18}ClO_3S$ $[M + H]^+$ 433.0660; found: 433.0659.

(3R,4S)-3-(2-(4-bromophenyl)-2-oxoethyl)-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3d)



The major diastereomer **3d** was purified by flash column chromatography (petroleum ether/ethyl acetate = 15:1);

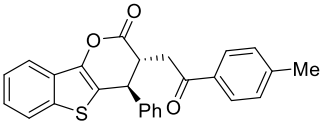
Yellow solid; 37.2 mg, 78% yield; 87:13 dr, 99% ee; $[\alpha]_D^{20}$ = +25.1 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 114.5-115.2 ℃;

The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 18.0 min, t_{major} = 11.1 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.82 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.47-7.33 (m, 5H), 7.34-7.29 (m, 2H), 4.55 (d, *J* = 11.8 Hz, 1H), 3.84-3.71 (m, 1H), 3.40 (dd, *J* = 17.9, 6.2 Hz, 1H), 3.17 (dd, *J* = 17.9, 4.1 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 195.8, 169.5, 141.4, 139.7, 136.9, 135.3, 132.1, 129.9, 129.7, 129.4, 128.8, 128.7, 128.5, 125.5, 125.0, 122.9, 120.3, 120.0, 43.5, 43.4, 36.7; **HRMS (ESI-TOF)** calcd. for $C_{25}H_{18}BrO_3S$ $[M + H]^+$ 477.0155; found: 477.0157.

(3R,4S)-3-(2-oxo-2-(p-tolyl)ethyl)-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3e)



The major diastereomer **3e** was purified by flash column chromatography (petroleum ether/ethyl acetate = 20:1);

Yellow solid; 32.3 mg, 78% yield; 89:11 dr, 99% ee; $[\alpha]_D^{20}$ = +26.5 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 177.2-177.8 ℃;

The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 15.1 min, t_{major} = 11.9 min);

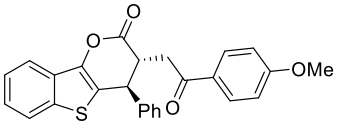
^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.83 (dd, *J* = 10.4, 7.9 Hz, 3H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.46-7.40 (m, 1H), 7.40-7.29 (m, 6H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.57 (d, *J* = 11.2 Hz, 1H), 3.82-3.69 (m, 1H), 3.42 (dd, *J* = 17.9, 5.8 Hz, 1H), 3.25 (dd, *J* = 17.9, 4.5 Hz, 1H), 2.40 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 196.2, 169.6, 144.5, 141.5, 140.0, 136.9, 134.1, 130.0, 129.4, 129.3, 128.6, 128.5, 128.4, 125.5, 124.9, 122.9, 120.3, 119.9, 43.5, 43.4, 36.7, 21.8;

HRMS (ESI-TOF) calcd. for $C_{26}H_{21}O_3S$ $[M + H]^+$ 413.1206; found: 413.1209.

(3R,4S)-3-(2-(4-methoxyphenyl)-2-oxoethyl)-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-

b]pyran-2-one (3f)



The major diastereomer **3f** was purified by flash column chromatography (petroleum ether/ethyl acetate = 18:1);

Yellow solid; 35.6 mg, 83% yield; 81:19 dr, 98% ee; $[\alpha]_D^{20}$ = +55.7 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 164.3-165.2 ℃;

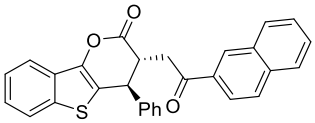
The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 22.6 min, t_{major} = 18.2 min);

^{1}H NMR (300 MHz, $CDCl_3$) δ (major diastereomer) 7.94-7.84 (m, 2H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.45-7.39 (m, 1H), 7.39-7.26 (m, 6H), 6.90 (d, *J* = 8.9 Hz, 2H), 4.56 (d, *J* = 11.1 Hz, 1H), 3.85 (s, 3H), 3.82-3.67 (m, 1H), 3.39 (dd, *J* = 17.7, 5.6 Hz, 1H), 3.23 (dd, *J* = 17.7, 4.5 Hz, 1H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (major diastereomer) 195.1, 169.6, 163.9, 141.5, 140.0, 136.9, 130.5, 130.0, 129.6, 129.3, 128.5, 128.4, 125.5, 124.9, 122.9, 120.3, 119.9, 113.9, 55.6, 43.5, 43.4, 36.5;

HRMS (ESI-TOF) calcd. For $C_{26}H_{20}NaO_4S$ $[M + Na]^+$ 451.0975; found: 451.0955.

(3R,4S)-3-(2-(naphthalen-2-yl)-2-oxoethyl)-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3g)



The major diastereomer **3g** was purified by flash column chromatography (petroleum ether/ethyl acetate = 15:1);

Yellow solid; 36.7 mg, 82% yield; 92:8 dr, 99% ee; $[\alpha]_D^{20}$ = +37.9 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 211.4-212.5 ℃;

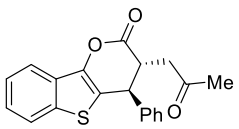
The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 16.3 min, t_{major} = 12.4 min);

^{1}H NMR (300 MHz, $CDCl_3$) δ (major diastereomer) 8.41 (s, 1H), 8.02-7.94 (m, 1H), 7.94-7.81 (m, 4H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.65-7.48 (m, 2H), 7.46-7.39 (m, 1H), 7.39-7.30 (m, 6H), 4.61 (d, *J* = 11.3 Hz, 1H), 3.92-3.75 (m, 1H), 3.59 (dd, *J* = 17.8, 5.8 Hz, 1H), 3.39 (dd, *J* = 17.8, 4.4 Hz, 1H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6, 169.6, 141.5, 139.9, 136.9, 135.9, 133.9, 132.5, 130.0, 129.7, 129.4, 128.8, 128.6, 128.5, 127.9, 127.0, 125.5, 125.0, 123.8, 122.9, 120.3, 120.0, 43.6, 43.5, 36.9;

HRMS (ESI-TOF) calcd. for $C_{29}H_{21}O_3S$ $[M + H]^+$ 449.1206; found: 449.1207.

(3R,4S)-3-(2-oxopropyl)-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3h)



The product **3h** was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1);

Pink solid; 13.7 mg, 41% yield; 52:48 dr, 91% ee for major diastereomer, 90% ee for minor

diastereomer; $[\alpha]_D^{20}$ = +82.7 (*c* 1.00, CH_2Cl_2); m.p. 168.7-169.9 ℃;

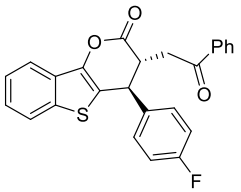
The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 12.7 min, t_{major} = 11.5 min; minor diastereomer: t_{minor} = 10.2 min, t_{major} = 9.2 min);

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 12.0, 7.3 Hz, 1.0H), 7.67 (dd, *J* = 16.5, 7.6 Hz, 1.0H), 7.46-7.34 (m, 3.0H), 7.34-7.22 (m, 3.0H), 7.07-6.99 (m, 1.0H), 4.52-4.36 (m, 1.0H), 4.02-3.91 (m, 0.5H), 3.64-3.53 (m, 0.5H), 3.00 (dd, *J* = 18.5, 5.9 Hz, 0.5H), 2.85 (dd, *J* = 17.8, 6.7 Hz, 0.5H), 2.63 (dd, *J* = 17.8, 3.9 Hz, 0.5H), 2.34 (dd, *J* = 18.5, 7.1 Hz, 0.5H), 2.17 (s, 1.5H), 2.15 (s, 1.5H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.8, 205.4, 169.5, 169.2, 141.6, 141.3, 139.5, 137.9, 137.1, 136.7, 129.8, 129.7, 129.4, 129.3, 128.6, 128.4, 128.3, 127.6, 125.7, 125.5, 124.9, 124.8, 123.0, 122.8, 120.3, 120.2 (2C), 119.5, 43.3, 43.1, 42.0, 41.3, 40.9 (2 C), 30.4 (2 C);

HRMS (ESI-TOF) calcd. for $C_{20}H_{17}O_3S$ $[M + H]^+$ 337.0893; found: 337.0896.

(3R,4S)-4-(4-fluorophenyl)-3-(2-oxo-2-phenylethyl)-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3i)



The major diastereomer **3i** was purified by flash column chromatography (petroleum ether/ethyl acetate = 15:1);

Yellow solid; 29.9 mg, 72% yield; 89:11 dr, 99% ee; $[\alpha]_D^{20}$ = +26.1 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 96.2-97.3 ℃;

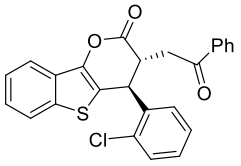
The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 15.7 min, t_{major} = 13.4 min);

^{1}H NMR (300 MHz, $CDCl_3$) δ (major diastereomer) 7.94-7.86 (m, 2H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.60-7.51 (m, 1H), 7.47-7.23 (m, 6H), 7.09-6.99 (m, 2H), 4.56 (d, *J* = 11.3 Hz, 1H), 3.84-3.59 (m, 1H), 3.43 (dd, *J* = 17.9, 5.7 Hz, 1H), 3.24 (dd, *J* = 17.9, 4.5 Hz, 1H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (major diastereomer) 196.6, 169.3, 162.7 (d, *J* = 247.8 Hz, 1C), 141.5, 136.8, 136.4, 135.6 (d, *J* = 3.2 Hz, 1C), 133.6, 130.1 (d, *J* = 8.1 Hz, 1C), 129.9, 128.8, 128.2, 125.6, 125.0, 122.9, 120.3, 119.6, 116.3 (d, *J* = 21.7 Hz, 1C), 43.6, 42.7, 36.7;

HRMS (ESI-TOF) calcd. for $C_{25}H_{18}FO_3S$ $[M + H]^+$ 417.0955; found: 417.0959.

(3R,4S)-4-(2-chlorophenyl)-3-(2-oxo-2-phenylethyl)-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3j)



The major diastereomer **3j** was purified by flash column chromatography (petroleum ether/ethyl acetate = 15:1);

Yellow solid; 30.7 mg, 71% yield; 90:10 dr, 99% ee; $[\alpha]_D^{20}$ = +54.6 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 171.5-172.7 ℃;

The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ

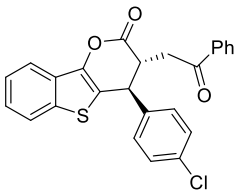
= 254 nm, major diastereomer: t_{minor} = 14.4 min, t_{major} = 12.9 min);

^{1}H NMR (300 MHz, $CDCl_3$) δ (major diastereomer) 7.97-7.88 (m, 2H), 7.83 (d, *J* = 7.4 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.61-7.52 (m, 1H), 7.48-7.40 (m, 3H), 7.38-7.31 (m, 5H), 4.57 (d, *J* = 11.4 Hz, 1H), 3.88-3.70 (m, 1H), 3.45 (dd, *J* = 17.9, 5.8 Hz, 1H), 3.26 (dd, *J* = 17.9, 4.4 Hz, 1H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (major diastereomer) 196.7, 169.6, 141.5, 139.9, 136.9, 136.5, 133.6, 130.0, 129.4, 128.8, 128.6, 128.5, 128.2, 125.5, 125.0, 122.9, 120.3, 120.0, 43.5, 43.4, 36.8;

HRMS (ESI-TOF) calcd. for $C_{25}H_{18}ClO_3S$ $[M + H]^+$ 433.0660; found: 433.0662.

(3R,4S)-4-(4-chlorophenyl)-3-(2-oxo-2-phenylethyl)-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3k)



The major diastereomer **3k** was purified by flash column chromatography (petroleum ether/ethyl acetate = 15:1);

Yellow solid; 29.7 mg, 69% yield; 89:11 dr, 99% ee; $[\alpha]_D^{20}$ = +42.4 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 80.5-81.2 ℃;

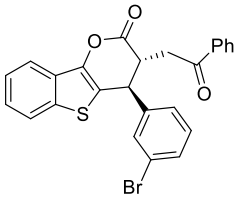
The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 0.8 mL/min, *λ* = 254 nm, major diastereomer: t_{minor} = 16.5 min, t_{major} = 13.8 min);

^{1}H NMR (300 MHz, $CDCl_3$) δ (major diastereomer) 7.96-7.87 (m, 2H), 7.87-7.81 (m, 1H), 7.74-7.66 (m, 1H), 7.62-7.54 (m, 1H), 7.48-7.32 (m, 6H), 7.28-7.24 (m, 2H), 4.58 (d, *J* = 10.9 Hz, 1H), 3.78-3.67 (m, 1H), 3.43 (dd, *J* = 18.0, 5.5 Hz, 1H), 3.27 (dd, *J* = 18.0, 4.7 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 196.5, 169.2, 141.7, 138.4, 136.9, 136.4, 134.5, 133.7, 129.9, 129.8, 129.6, 128.8, 128.2, 125.7, 125.1, 122.9, 120.4, 119.1, 43.5, 42.9, 36.8;

HRMS (ESI-TOF) calcd. for $C_{25}H_{18}ClO_3S$ $[M + H]^+$ 433.0660; found: 433.0662.

(3R,4S)-4-(3-bromophenyl)-3-(2-oxo-2-phenylethyl)-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3l)



The major diastereomer **3l** was purified by flash column chromatography (petroleum ether/ethyl acetate = 15:1);

Yellow solid; 34.2 mg, 72% yield; 89:11 dr, 97% ee; $[\alpha]_D^{20}$ = +47.5 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 109.2-110.6 ℃;

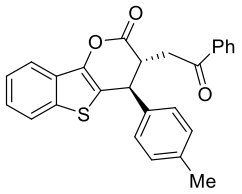
The ee was determined by HPLC (Chiralpak IC, EtOH/hexane = 20/80, flow rate 1.0 mL/min, *λ* = 254 nm, major diastereomer: t_{minor} = 12.1 min, t_{major} = 9.1 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.92 (d, *J* = 7.7 Hz, 2H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.62-7.53 (m, 1H), 7.51-7.41 (m, 5H), 7.41-7.35 (m, 1H), 7.28-7.22 (m, 2H), 4.56 (d, *J* = 10.9 Hz, 1H), 3.79-3.68 (m, 1H), 3.43 (dd, *J* = 18.0, 5.5 Hz, 1H), 3.30 (dd, *J* = 18.0, 4.8 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 196.5, 169.1, 142.3, 141.7, 136.9, 136.4, 133.7, 131.8, 131.5, 130.9, 129.8, 128.8, 128.2, 127.1, 125.7, 125.1, 123.4, 122.9, 120.4, 118.7, 43.5, 43.1, 36.9;

HRMS (ESI-TOF) calcd. for $C_{25}H_{18}BrO_3S$ $[M + H]^+$ 477.0155; found: 477.0168.

(3R,4S)-3-(2-oxo-2-phenylethyl)-4-(p-tolyl)-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3m)



The major diastereomer **3m** was purified by flash column chromatography (petroleum ether/ethyl acetate = 12:1);

Yellow solid; 36.2 mg, 88% yield; 89:11 dr, 99% ee; $[\alpha]_D^{20}$ = +47.0 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 98.3-99.2 ℃;

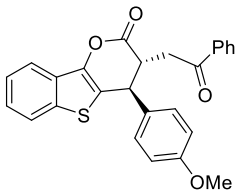
The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 13.2 min, t_{major} = 11.3 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.83 (d, *J* = 7.3 Hz, 2H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.52-7.44 (m, 1H), 7.38-7.31 (m, 3H), 7.30-7.23 (m, 1H), 7.18-7.06 (m, 4H), 4.45 (d, *J* = 11.7 Hz, 1H), 3.74-3.63 (m, 1H), 3.37 (dd, *J* = 17.9, 6.1 Hz, 1H), 3.15 (dd, *J* = 17.9, 4.1 Hz, 1H), 2.27 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 196.8, 169.7, 141.3, 138.4, 136.9, 136.8, 136.6, 133.5, 130.1, 130.0, 128.7, 128.3, 128.2, 125.4, 124.9, 122.9, 120.4, 120.3, 43.5, 43.0, 36.8, 21.3;

HRMS (ESI-TOF) calcd. for $C_{26}H_{21}O_3S$ $[M + H]^+$ 413.1206; found: 413.1208.

(3R,4S)-4-(4-methoxyphenyl)-3-(2-oxo-2-phenylethyl)-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3n)



The major diastereomer **3n** was purified by flash column chromatography (petroleum ether/ethyl acetate = 11:1);

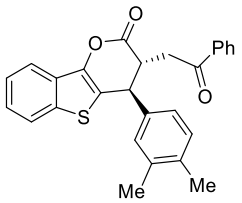
White solid; 34.4 mg, 80% yield; 90:10 dr, 98% ee; $[\alpha]_D^{20}$ = +55.3 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 95.2-96.1 ℃;

The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 19.9 min, t_{major} = 17.1 min);

^{1}H NMR (300 MHz, $CDCl_3$) δ (major diastereomer) 7.97-7.89 (m, 2H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.63-7.52 (m, 1H), 7.52-7.33 (m, 4H), 7.27-7.20 (m, 2H), 6.94-6.84 (m, 2H), 4.52 (d, *J* = 11.8 Hz, 1H), 3.80 (s, 3H), 3.77-3.68 (m, 1H), 3.46 (dd, *J* = 17.9, 6.0 Hz, 1H), 3.24 (dd, *J* = 17.9, 4.1 Hz, 1H);

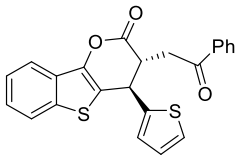
^{13}C NMR (75 MHz, $CDCl_3$) δ (major diastereomer) 196.8, 169.7, 159.7, 141.3, 136.8, 136.6, 133.6, 131.7, 130.0, 129.6, 128.7, 128.2, 125.4, 124.9, 122.9, 120.7, 120.3, 114.7, 55.4, 43.6, 42.6, 36.7;
HRMS (ESI-TOF) calcd. for $C_{26}H_{21}O_4S$ $[M + H]^+$ 429.1155; found: 429.1158.

(3R,4S)-4-(3,4-dimethylphenyl)-3-(2-oxo-2-phenylethyl)-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3o)



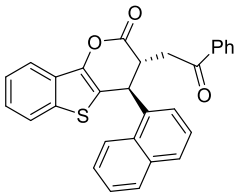
The major diastereomer **3o** was purified by flash column chromatography (petroleum ether/ethyl acetate = 17:1);
Yellow solid; 35.6 mg, 83% yield; 81:19 dr, 99% ee; $[\alpha]_D^{20}$ = +61.0 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 97.6-98.3 ℃;
The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 15.4 min, t_{major} = 13.3 min);
^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.92 (d, *J* = 7.2 Hz, 2H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.60-7.52 (m, 1H), 7.46-7.40 (m , 3H), 7.39-7.32 (m, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.09-6.99 (m, 2H), 4.48 (d, *J* = 11.7 Hz, 1H), 3.84-3.71 (m, 1H), 3.46 (dd, *J* = 17.9, 6.2 Hz, 1H), 3.23 (dd, *J* = 17.9, 4.1 Hz, 1H), 2.25 (s, 3H), 2.23 (s, 3H);
^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 196.9, 169.8, 141.3, 137.7, 137.2, 137.1, 136.9, 136.7, 133.5, 130.5, 130.0, 129.6, 128.7, 128.2, 125.8, 125.4, 124.9, 122.9, 120.6, 120.3, 43.5, 43.0, 36.8, 20.0, 19.6;
HRMS (ESI-TOF) calcd. for $C_{27}H_{23}O_3S$ $[M + H]^+$ 427.1362; found: 427.1367.

(3R,4S)-3-(2-oxo-2-phenylethyl)-4-(thiophen-2-yl)-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3p)



The major diastereomer **3p** was purified by flash column chromatography (petroleum ether/ethyl acetate = 15:1);
White solid; 25.6 mg, 63% yield; 86:14 dr, 94% ee; $[\alpha]_D^{20}$ = +16.0 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 174.3-175.2 ℃;
The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 16.0 min, t_{major} = 14.6 min);
^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.94 (d, *J* = 7.3 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.63-7.54 (m, 1H), 7.51-7.40 (m, 3H), 7.40-7.34 (m, 1H), 7.31 (d, *J* = 5.1 Hz, 1H), 7.05 (d, *J* = 3.5 Hz, 1H), 7.02-6.96 (m, 1H), 4.98 (d, *J* = 11.4 Hz, 1H), 3.84-3.68 (m, 1H), 3.55-3.36 (m, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 196.6, 168.9, 142.9, 140.9, 136.8, 136.5, 133.6, 129.9, 128.8, 128.3, 127.3, 127.2, 126.0, 125.7, 125.0, 122.9, 120.4, 119.8, 44.4, 38.8, 36.8;
HRMS (ESI-TOF) calcd. for $C_{23}H_{17}O_3S_2$ $[M + H]^+$ 405.0614; found: 405.0616.

(3R,4S)-4-(naphthalen-1-yl)-3-(2-oxo-2-phenylethyl)-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3q)



The major diastereomer **3q** was purified by flash column chromatography (petroleum ether/ethyl acetate = 15:1);

Yellow solid; 29.7 mg, 66% yield; 94:6 dr, 99% ee; $[\alpha]_D^{20}$ = +61.5 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 161.1-161.9 ℃;

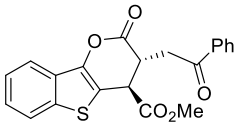
The ee was determined by HPLC (Chiralpak IC, EtOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 12.7 min, t_{major} = 10.5 min);

^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ (major diastereomer) 8.30-8.10 (m, 1H), 8.06-7.91 (m, 2H), 7.91-7.78 (m, 4H), 7.62-7.51 (m, 5H), 7.50-7.39 (m, 4H), 5.66 (d, *J* = 7.2 Hz, 1H), 4.27-4.12 (m, 1H), 3.50 (dd, *J* = 18.2, 6.5 Hz, 1H), 3.16 (dd, *J* = 18.2, 4.0 Hz, 1H);

^{13}C NMR (75 MHz, DMSO-*d*$_6$) δ (major diastereomer) 197.3, 169.1, 140.5, 136.1, 136.0, 135.7, 133.7, 133.5, 131.3, 129.3, 129.1, 128.7 (2 C), 127.9 (2 C), 126.8, 126.1, 125.8, 125.4, 125.1, 123.3, 123.0, 120.7, 119.5, 42.2, 36.9 (2 C);

HRMS (ESI-TOF) calcd. for $C_{29}H_{21}O_3S$ $[M + H]^+$ 449.1206; found: 449.1209.

Methyl (3R,4S)-2-oxo-3-(2-oxo-2-phenylethyl)-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b] pyran-4-carboxylate (3r)



The product **3r** was purified by flash column chromatography (petroleum ether/ethyl acetate= 10:1);

Yellow solid; 13.0 mg, 34% yield; 72:28 dr, 84% ee for major diastereomer, 52% ee for minor diastereomer; $[\alpha]_D^{20}$ = +39.5 (*c* 1.00, CH_2Cl_2); m.p. 67.5-68.3 ℃;

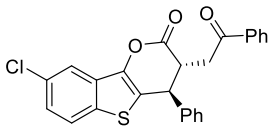
The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 13.4 min, t_{major} = 11.4 min; minor diastereomer: t_{minor} = 14.5 min, t_{major} = 17.0 min);

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.05-7.99 (m, 0.4H), 7.99-7.92 (m, 1.7H), 7.83-7.77 (m, 1.0H), 7.76-7.69 (m, 1.0H), 7.61-7.54 (m, 1.0H), 7.51-7.44 (m, 1.8H), 7.44-7.35 (m, 2.4H), 4.36 (d, *J* = 9.1 Hz, 0.8H), 4.28 (d, *J* = 5.9 Hz, 0.2H), 4.04 (dd, *J* = 18.3, 5.3 Hz, 0.2H), 3.99-3.96 (m, 0.2H), 3.95-3.88 (m, 0.8H), 3.83 (s, 2.4H), 3.75 (dd, 18.3, 5.7 Hz, 0.8H), 3.69 (s, 0.6H), 3.51 (dd, *J* = 18.3, 4.0 Hz, 0.8H), 3.20 (dd, *J* = 18.3, 6.8 Hz, 0.2H);

^{13}C NMR (75 MHz, CDCl$_3$) δ 196.5, 196.3, 170.4, 170.0, 168.5, 168.1, 141.9, 141.7, 137.0, 136.8, 136.2, 136.1, 133.8, 133.7, 129.7, 129.6, 128.8 (2C), 128.3, 128.2, 126.1, 126.0, 125.1, 125.0, 122.9, 122.7, 120.5, 120.4, 112.2, 111.0, 53.1, 53.0, 43.1, 42.5, 38.1, 37.7, 37.4, 36.9;

HRMS (ESI-TOF) calcd. for $C_{21}H_{17}O_5S$ $[M + H]^+$ 381.0791; found: 381.0794.

(3R,4S)-8-chloro-3-(2-oxo-2-phenylethyl)-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3s)



The major diastereomer **3s** was purified by flash column chromatography (petroleum ether/ethyl acetate = 15:1);

Pink solid; 35.4 mg, 82% yield; 90:10 dr, 99% ee; $[\alpha]_D^{20}$ = +13.6 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 103.3-104.3 ℃;

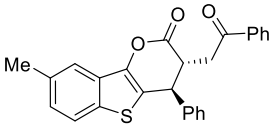
The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 17.9 min, t_{major} = 15.8 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.93-7.88 (m, 2H), 7.80 (d, *J* = 2.0 Hz, 1H), 7.61-7.53 (m, 2H), 7.47-7.41 (m, 2H), 7.41-7.34 (m, 3H), 7.34-7.28 (m, 3H), 4.59 (d, *J* = 11.7 Hz, 1H), 3.83-3.71 (m, 1H), 3.43 (dd, *J* = 18.0, 5.9 Hz, 1H), 3.26 (dd, *J* = 18.0, 4.2 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 196.7, 169.1, 140.7, 139.5, 136.4, 134.9, 133.6, 131.4, 131.0, 129.5, 128.8, 128.7, 128.5, 128.2, 126.0, 124.0, 122.3, 120.0, 43.4, 43.3, 36.7;

HRMS (ESI-TOF) calcd. for $C_{25}H_{18}ClO_3S$ $[M + H]^+$ 433.0660; found: 433.0661.

(3R,4S)-8-methyl-3-(2-oxo-2-phenylethyl)-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3t)



The major diastereomer **3t** was purified by flash column chromatography (petroleum ether/ethyl acetate = 15:1);

White solid; 34.2 mg, 83% yield; 88:12 dr, 99% ee; $[\alpha]_D^{20}$ = +25.6 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 181.1-182.3 ℃;

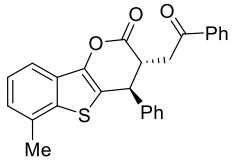
The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 13.0 min, t_{major} = 10.0 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.99-7.87 (m, 2H), 7.64 (s, 1H), 7.59-7.52 (m, 2H), 7.47-7.40 (m, 2H), 7.40-7.29 (m, 5H), 7.18 (dd, *J* = 8.4, 1.6 Hz, 1H), 4.55 (d, *J* = 11.4 Hz, 1H), 3.87-3.67 (m, 1H), 3.44 (dd, *J* = 18.0, 5.9 Hz, 1H), 3.24 (dd, *J* = 18.0, 4.3 Hz, 1H), 2.48 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 196.7, 169.6, 141.2, 139.9, 136.5, 134.9, 134.1, 133.6, 130.2, 129.3, 128.8, 128.6, 128.5, 128.2, 127.2, 122.5, 120.2, 120.1, 43.4, 43.3, 36.8, 21.6;

HRMS (ESI-TOF) calcd. for $C_{26}H_{21}O_3S$ $[M + H]^+$ 413.1206; found: 413.1210.

(3R,4S)-6-methyl-3-(2-oxo-2-phenylethyl)-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (3u)



The major diastereomer **3u** was purified by flash column chromatography (petroleum ether/ethyl acetate = 15:1);

Yellow solid; 34.3 mg, 83% yield; 90:10 dr, 99% ee; $[\alpha]_D^{20}$ = +5.8 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 189.7-190.9 ℃;

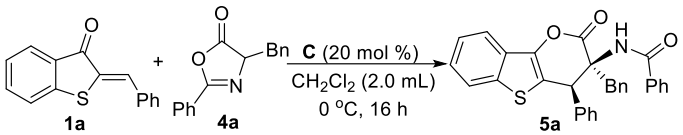
The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 11.9 min, t_{major} = 11.0 min);

^{1}H NMR (300 MHz, $CDCl_3$) δ (major diastereomer) 7.97-7.87 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.61-7.52 (m, 1H), 7.49-7.41 (m, 2H), 7.41-7.29 (m, 6H), 7.17 (d, *J* = 7.2 Hz, 1H), 4.58 (d, *J* = 11.4 Hz, 1H), 3.87-3.72 (m, 1H), 3.46 (dd, *J* = 17.9, 5.9 Hz, 1H), 3.25 (dd, *J* = 17.9, 4.3 Hz, 1H), 2.42 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 196.7, 169.6, 142.0, 140.0, 136.9, 136.5, 133.6, 132.2, 129.8, 129.4, 128.8, 128.6, 128.5, 128.2, 125.8, 125.4, 119.6, 118.0, 43.5, 43.4, 36.8, 19.4;

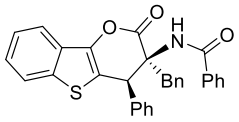
HRMS (ESI-TOF) calcd. for $C_{26}H_{21}O_3S$ $[M + H]^+$ 413.1206; found: 413.1207.

3. General procedures for the asymmetric synthesis of compounds 5



In an ordinary vial equipped with a magnetic stirring bar, the solution of 1-Thioaurones **1** (0.12 mmol, 1.2 equiv), Azlactones **4** (0.1 mmol, 1.0 equiv) and catalyst **C** (20 mol %) in CH_2Cl_2 (2.0 mL) was cooled to 0 ℃. And then, the mixture was stirred at the same temperature for the specified time. After completion of the reaction, as indicated by TLC, the products **5** were isolated by flash chromatography on silica gel (PE/EA = 21/1 ~ 15/1).

N-((3S,4R)-3-benzyl-2-oxo-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-3-yl)benzamide (5a)



The major diastereomer **5a** was purified by flash column chromatography (petroleum ether/ethyl acetate = 15:1);

Yellow solid; 40.7 mg, 93% yield; 89:11 dr, 93% ee; $[\alpha]_D^{20}$ = +267.4 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 186.5-187.3 ℃;

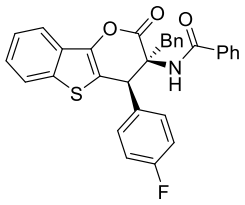
The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 7.4 min, t_{major} = 13.3 min);

^{1}H NMR (300 MHz, $CDCl_3$) δ (major diastereomer) 8.00-7.95 (m, 1H), 7.83-7.76 (m, 1H), 7.57-7.49 (m, 1H), 7.48-7.38 (m, 3H), 7.37-7.29 (m, 3H), 7.24-7.15 (m, 8H), 7.15-7.06 (m, 2H), 6.74 (s, 1H), 5.57 (s, 1H), 4.34 (d, *J* = 13.9 Hz, 1H), 3.38 (d, *J* = 13.9 Hz, 1H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (major diastereomer) 168.4, 168.2, 140.1, 137.7, 137.4, 135.2, 134.7, 131.7, 130.1, 129.1, 129.0, 128.7, 128.5, 128.3, 127.9, 127.6, 126.8, 125.9, 125.3, 123.3, 120.2, 119.7, 66.8, 47.8, 39.2;

HRMS (ESI-TOF) calcd. for $C_{31}H_{24}NO_3S$ $[M + H]^+$ 490.1471; found: 490.1469.

N-((3S,4R)-3-benzyl-4-(4-fluorophenyl)-2-oxo-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-3-yl)benzamide (5b)



The major diastereomer **5b** was purified by flash column chromatography (petroleum ether/ethyl acetate = 16:1);

Light yellow solid; 42.8 mg, 84% yield; 91:9 dr, 97% ee; $[\alpha]_D^{20}$ = +220.5 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 215.8-216.3 ℃;

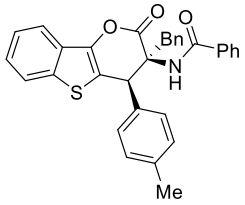
The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 8.5 min, t_{major} = 11.5 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.97 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.57-7.50 (m, 1H), 7.50-7.40 (m, 4H), 7.39-7.32 (m, 2H), 7.26-7.15 (m, 5H), 7.12-7.06 (m, 2H), 6.92-6.83 (m, 2H), 6.78 (s, 1H), 5.59 (s, 1H), 4.30 (d, *J* = 13.9 Hz, 1H), 3.36 (d, *J* = 13.9 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 168.3, 168.1, 162.5 (d, *J* = 247.4 Hz), 140.0, 137.6, 134.9, 134.5, 133.2 (d, *J* = 3.3 Hz), 131.9, 130.1, 129.6 (d, *J* = 8.2 Hz), 129.0, 128.8, 128.6, 127.7, 126.7, 126.1, 125.3, 123.3, 120.2, 119.4, 115.9 (d, *J* = 21.6 Hz), 66.8, 47.0, 39.1;

HRMS (ESI-TOF) calcd. for $C_{31}H_{23}FNO_3S$ $[M + H]^+$ 508.1377; found: 508.1374.

N-((3S,4R)-3-benzyl-2-oxo-4-(p-tolyl)-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-3-yl)benzamide (5c)



The major diastereomer **5c** was purified by flash column chromatography (petroleum ether/ethyl acetate = 16:1);

White solid; 47.0 mg, 93% yield; 89:11 dr, 96% ee; $[\alpha]_D^{20}$ = +231.3 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 192.9-193.2 ℃;

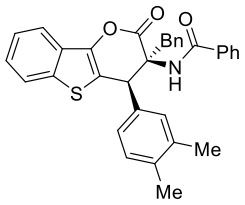
The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 7.6 min, t_{major} = 21.1 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.97 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.55-7.49 (m, 1H), 7.48-7.38 (m, 4H), 7.38-7.30 (m, 2H), 7.24-7.18 (m, 3H), 7.14-7.05 (m, 4H), 6.99 (d, *J* = 7.9 Hz, 2H), 6.75 (s, 1H), 5.54 (s, 1H), 4.33 (d, *J* = 13.9 Hz, 1H), 3.37 (d, *J* = 13.9 Hz, 1H), 2.21 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 168.5, 168.1, 140.0, 138.0, 137.7, 135.2, 134.7, 134.3, 131.7, 130.1, 129.7, 129.1, 128.7, 128.5, 127.7, 127.6, 126.8, 125.9, 125.2, 123.3, 120.1, 119.9, 66.9, 47.4, 39.1, 21.2;

HRMS (ESI-TOF) calcd. for $C_{32}H_{26}NO_3S$ $[M + H]^+$ 504.1628; found: 504.1630.

N-((3S,4R)-3-benzyl-4-(3,4-dimethylphenyl)-2-oxo-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-3-yl)benzamide (5d)



The major diastereomer **5d** was purified by flash column chromatography (petroleum ether/ethyl acetate = 16:1);

Light yellow solid; 45.6 mg, 88% yield; 94:6 dr, 97% ee; $[\alpha]_D^{20}$ = +241.7 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 127.3-128.0 ℃;

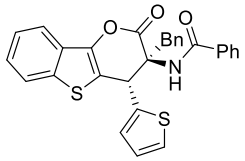
The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 6.8 min, t_{major} = 13.7 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.97 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.57-7.49 (m, 1H), 7.49-7.39 (m, 4H), 7.37-7.31 (m, 2H), 7.24-7.19 (m, 3H), 7.10 (dd, *J* = 6.7, 2.9 Hz, 2H), 6.99-6.85 (m, 3H), 6.72 (s, 1H), 5.50 (s, 1H), 4.33 (d, *J* = 14.0 Hz, 1H), 3.36 (d, *J* = 14.0 Hz, 1H), 2.11 (s, 3H), 2.07 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 168.5, 168.2, 140.1, 137.7, 137.2, 136.7, 135.4, 134.8, 134.5, 131.7, 130.2, 130.1, 129.2, 129.1, 128.7, 128.5, 127.6, 126.8, 125.8, 125.2, 125.1, 123.3, 120.2, 119.9, 67.0, 47.2, 39.0, 19.8, 19.5;

HRMS (ESI-TOF) calcd. for $C_{33}H_{28}NO_3S$ $[M + H]^+$ 518.1784; found: 518.1788.

N-((3S,4R)-3-benzyl-2-oxo-4-(thiophen-2-yl)-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-3-yl)benzamide (5e)



The major diastereomer **5e** was purified by flash column chromatography (petroleum ether/ethyl acetate = 21:1);

Light yellow solid; 38.4 mg, 77% yield; 79:21 dr, 94% ee; $[\alpha]_D^{20}$ = +232.6 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 204.9-205.5 ℃;

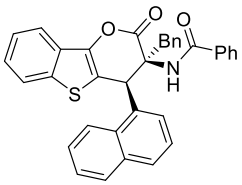
The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 7.3 min, t_{major} = 12.6 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.97 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.58-7.42 (m, 5H), 7.42-7.35 (m, 2H), 7.25-7.19 (m, 3H), 7.15-7.04 (m, 3H), 6.90-6.85 (m, 2H), 6.84-6.79 (m, 1H), 5.95 (s, 1H), 4.25 (d, *J* = 13.9 Hz, 1H), 3.33 (d, *J* = 13.9 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 168.2, 168.0, 139.9, 139.8, 137.6, 135.0, 134.6, 131.9, 130.1, 129.0, 128.8, 128.6, 127.7, 127.2, 127.0, 126.2, 125.9, 125.3, 123.3, 120.4, 119.4, 67.4, 42.4, 38.9;

HRMS (ESI-TOF) calcd. for $C_{29}H_{22}NO_3S_2$ $[M + H]^+$ 496.1036; found: 496.1037.

N-((3S,4R)-3-benzyl-4-(naphthalen-1-yl)-2-oxo-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-3-yl)benzamide (5f)



The major diastereomer **5f** was purified by flash column chromatography (petroleum ether/ethyl acetate = 17:1);

White solid; 49.5 mg, 92% yield; >99:1 dr, 99% ee; $[\alpha]_D^{20}$ = +245.2 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 179.9-180.6 ℃;

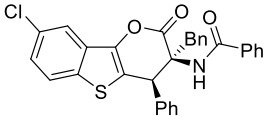
The ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 40/60, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 17.2 min, t_{major} = 39.1 min);

^{1}H NMR (400 MHz, DMSO-d_6) δ (major diastereomer) 8.57 (d, *J* = 8.7 Hz, 1H), 7.95-7.84 (m, 3H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.71-7.64 (m, 1H), 7.56-7.49 (m, 2H), 7.49-7.43 (m, 2H), 7.40-7.33 (m, 2H), 7.26-7.19 (m, 5H), 7.16-7.08 (m, 5H), 6.45 (s, 1H), 4.42 (d, *J* = 13.9 Hz, 1H), 3.51 (d, *J* = 13.9 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ (major diastereomer) 169.0, 167.9, 139.5, 137.3, 135.0, 134.6, 134.5, 134.2, 131.4, 131.3, 130.3, 129.2, 128.9, 128.7, 128.6, 128.5, 127.7, 126.6, 126.5, 126.1, 125.9, 125.5, 125.2, 124.7, 124.0, 123.2, 120.7, 120.2, 66.1, 43.2, 39.4;

HRMS (ESI-TOF) calcd. for $C_{35}H_{26}NO_3S$ $[M + H]^+$ 540.1628; found: 540.1633.

_N_-((3S,4R)-3-benzyl-8-chloro-2-oxo-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-3-yl)benzamide (5g)



The major diastereomer **5g** was purified by flash column chromatography (petroleum ether/ethyl acetate = 16:1);

Red solid; 49.3 mg, 94% yield; >99:1 dr, 98% ee; $[\alpha]_D^{20}$ = +280.9 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 152.3-153.4 ℃;

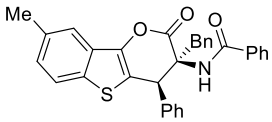
The ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 40/60, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 7.9 min, t_{major} = 11.4 min);

^{1}H NMR (400 MHz, DMSO-d_6) δ (major diastereomer) 8.06 (d, *J* = 8.7 Hz, 1H), 7.97 (d, *J* = 2.1 Hz, 1H), 7.53 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.51-7.45 (m, 1H), 7.41-7.35 (m, 4H), 7.27-7.17 (m, 7H), 7.16-7.11 (m, 2H), 7.11-7.04 (m, 2H), 5.59 (s, 1H), 4.21 (d, *J* = 13.8 Hz, 1H), 3.32 (d, *J* = 13.8 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ (major diastereomer) 168.2, 168.0, 139.3, 137.1, 135.7, 135.1, 134.5, 131.8, 131.7, 130.2, 130.1, 129.1, 128.7, 128.6, 128.4, 127.8, 127.7, 126.8, 126.5, 124.3, 121.8, 120.0, 66.7, 47.8, 39.2;

HRMS (ESI-TOF) calcd. for $C_{31}H_{23}ClNO_3S$ $[M + H]^+$ 524.1082; found: 524.1088.

N-((3S,4R)-3-benzyl-8-methyl-2-oxo-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-3-yl)benzamide (5h)



The major diastereomer **5h** was purified by flash column chromatography (petroleum ether/ethyl acetate = 17:1);

Yellow solid; 41.8 mg, 83% yield; 89:11 dr, 96% ee; $[\alpha]_D^{20}$ = +253.8 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 192.3-193.5 ℃;

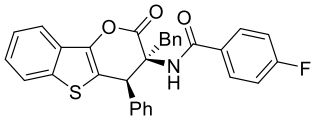
The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 6.4 min, t_{major} = 7.8 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.78 (s, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.46-7.35 (m, 3H), 7.35-7.25 (m, 3H), 7.24-7.15 (m, 8H), 7.13-7.06 (m, 2H), 6.74 (s, 1H), 5.55 (s, 1H), 4.34 (d, *J* = 13.9 Hz, 1H), 3.37 (d, *J* = 13.9 Hz, 1H), 2.55 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 168.5, 168.1, 139.7, 137.4, 135.3, 135.2, 134.8, 134.7, 131.7, 130.1, 129.3, 129.0, 128.7, 128.5, 128.2, 127.8, 127.7, 127.6, 126.7, 122.9, 120.0, 119.7, 66.8, 47.8, 39.1, 21.6;

HRMS (ESI-TOF) calcd. for $C_{32}H_{26}NO_3S$ $[M + H]^+$ 504.1628; found: 504.1629.

***N*-((3S,4R)-3-benzyl-2-oxo-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-3-yl)-4-fluorobenzamide (5i)**



The major diastereomer **5i** was purified by flash column chromatography (petroleum ether/ethyl acetate = 16:1);

Light yellow solid; 42.2 mg, 83% yield; 90:10 dr, 94% ee; $[\alpha]_D^{20}$ = +200.7 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 186.1-186.9 ℃;

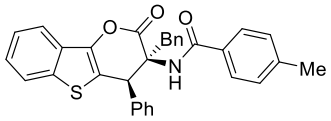
The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 8.7 min, t_{major} = 12.5 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.97 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.55-7.50 (m, 1H), 7.48-7.42 (m, 1H), 7.42-7.36 (m, 2H), 7.24-7.20 (m, 3H), 7.20-7.14 (m, 5H), 7.08 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.03-6.95 (m, 2H), 6.69 (s, 1H), 5.55 (s, 1H), 4.31 (d, *J* = 14.0 Hz, 1H), 3.38 (d, *J* = 14.0 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 168.5, 167.0, 164.9 (d, *J* = 252.2 Hz, 1C), 140.0, 137.7, 137.3, 134.6, 131.2 (d, *J* = 3.1 Hz, 1C), 130.1, 129.2 (d, *J* = 9.1 Hz, 1C), 129.1, 129.0, 128.6, 128.3, 127.8, 127.7, 126.0, 125.3, 123.3, 120.2, 119.5, 115.8 (d, *J* = 21.9 Hz, 1C), 66.8, 47.8, 39.2;

HRMS (ESI-TOF) calcd. for $C_{31}H_{23}FNO_3S$ $[M + H]^+$ 508.1377; found: 508.1381.

***N*-((3S,4R)-3-benzyl-2-oxo-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-3-yl)-4-methylbenzamide (5j)**



The major diastereomer **5j** was purified by flash column chromatography (petroleum ether/ethyl acetate = 16:1);

Light yellow solid; 45.0 mg, 89% yield; 90:10 dr, 96% ee; $[\alpha]_D^{20}$ = +221.4 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 150.1-150.9 ℃;

The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 20/80, flow rate 1.0 mL/min, λ

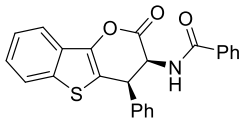
= 254 nm, major diastereomer: t_{minor} = 10.5 min, t_{major} = 14.7 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.97 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.58-7.49 (m, 1H), 7.49-7.41 (m, 1H), 7.30 (d, *J* = 7.7 Hz, 2H), 7.23-7.15 (m, 8H), 7.15-7.06 (m, 4H), 6.72 (s, 1H), 5.57 (s, 1H), 4.34 (d, *J* = 13.8 Hz, 1H), 3.36 (d, *J* = 13.8 Hz, 1H), 2.34 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 168.5, 168.1, 142.2, 140.1, 137.7, 137.4, 134.7, 132.3, 130.2, 129.4, 129.2, 129.0, 128.5, 128.2, 127.9, 127.6, 126.8, 125.9, 125.2, 123.3, 120.2, 119.7, 66.8, 47.8, 39.2, 21.6;

HRMS (ESI-TOF) calcd. for $C_{32}H_{26}NO_3S$ $[M + H]^+$ 504.1628; found: 504.1629.

***N*-((3S,4R)-2-oxo-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-3-yl)benzamide (5k)**



The major diastereomer **5k** was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1);

White solid; 25.2 mg, 63% yield; >99:1 dr, 96% ee; $[\alpha]_D^{20}$ = +267.8 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 232.3-233.4 ℃;

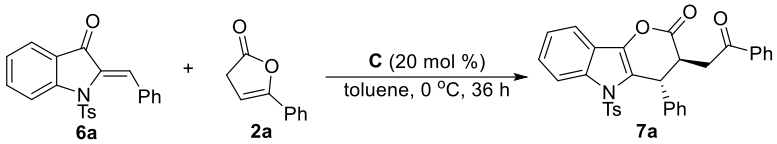
The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 50/50, flow rate 1.0 mL/min, *λ* = 220 nm, major diastereomer: t_{minor} = 7.6 min, t_{major} = 11.2 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.80 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 2H), 7.51-7.32 (m, 5H), 7.21 (s, 3H), 7.00 (s, 2H), 6.58 (d, *J* = 6.3 Hz, 1H), 5.55 (t, *J* = 6.9 Hz, 1H), 4.99 (d, *J* = 7.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 167.4, 167.2, 141.5, 137.6, 135.6, 133.4, 132.3, 129.3, 129.2, 128.9, 128.7, 128.2, 127.2, 126.0, 125.2, 123.2, 120.3, 117.9, 54.3, 42.1.

HRMS (ESI-TOF) calcd. for $C_{24}H_{18}NO_3S$ $[M + H]^+$ 400.1002; found: 400.1012.

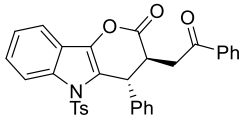
4. General procedures for the asymmetric synthesis of compounds 7



6a **2a** **7a**

In an ordinary vial equipped with a magnetic stirring bar, the solution of 1-Azaaurones **6** (0.12 mmol, 1.2 equiv), *γ*-Deconjugated Butenolides **2** (0.1 mmol, 1.0 equiv) and catalyst **C** (20 mol %) in toluene (2.0 mL) was cooled to 0 ℃. And then, the mixture was stirred at the same temperature for the specified time. After completion of the reaction, as indicated by TLC, the products **7** were isolated by flash chromatography on silica gel (PE/EA = 9/1 ~ 8/1).

(3S,4R)-3-(2-oxo-2-phenylethyl)-4-phenyl-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (7a)



The major diastereomer **7a** was purified by flash column chromatography (petroleum ether/ethyl

acetate = 8:1);

Yellow solid; 40.0 mg, 75% yield; 90:10 dr, 99% ee; $[\alpha]_D^{20}$ = -12.6 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 73.3-74.2 ℃;

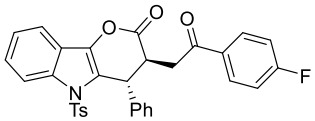
The ee was determined by HPLC (Chiralpak IC, *i*-PrOH/hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 15.1 min, t_{major} = 10.6 min);

^{1}H NMR (600 MHz, $CDCl_3$) δ (major diastereomer) 8.23 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 6.9 Hz, 2H), 7.69-7.60 (m, 2H), 7.52-7.47 (m, 2H), 7.47-7.42 (m, 1H), 7.40-7.35 (m, 1H), 7.34-7.27 (m, 3H), 7.26-7.21 (m, 4H), 6.65 (d, *J* = 8.2 Hz, 2H), 4.96 (d, *J* = 1.6 Hz, 1H), 3.82-3.75 (m, 1H), 3.31 (dd, *J* = 18.0, 2.6 Hz, 1H), 3.22 (dd, *J* = 18.0, 10.6 Hz, 1H), 2.06 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ (major diastereomer) 195.2, 168.8, 145.1, 140.4, 137.8, 136.0, 135.1, 135.0, 134.0, 129.8, 129.4, 129.0, 128.3, 127.8, 127.3, 126.4, 126.3, 124.4, 120.7, 118.6, 117.7, 115.2, 44.8, 42.5, 39.6, 21.5;

HRMS (ESI-TOF) calcd. for $C_{32}H_{26}NO_5S$ $[M + H]^+$ 536.1526; found: 536.1535.

(3S,4R)-3-(2-(4-fluorophenyl)-2-oxoethyl)-4-phenyl-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (7b)



The major diastereomer **7b** was purified by flash column chromatography (petroleum ether/ethyl acetate = 9:1);

Yellow solid; 40.5 mg, 73% yield; 93:7 dr, 99% ee; $[\alpha]_D^{20}$ = -13.8 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 76.1-76.5 ℃;

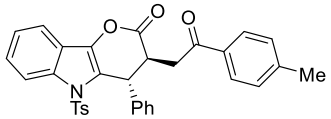
The ee was determined by HPLC (Chiralpak IC, *i*-PrOH/hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 13.7 min, t_{major} = 9.7 min);

^{1}H NMR (300 MHz, $CDCl_3$) δ (major diastereomer) 8.22 (d, *J* = 8.2 Hz, 1H), 8.03-7.85 (m, 2H), 7.66 (d, *J* = 6.8 Hz, 1H), 7.50-7.34 (m, 2H), 7.34-7.27 (m, 3H), 7.24-7.10 (m, 6H), 6.71 (d, *J* = 8.1 Hz, 2H), 4.95 (d, *J* = 1.6 Hz, 1H), 3.83-3.70 (m, 1H), 3.38-3.11 (m, 2H), 2.11 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ (major diastereomer) 193.7, 168.7, 166.3 (d, *J* = 256.6 Hz, 1C), 145.0, 140.3, 137.7, 135.1, 135.0, 132.5 (d, *J* = 2.9 Hz, 1C), 131.0 (d, *J* = 9.4 Hz, 1C), 129.7, 129.4, 127.9, 127.4, 126.5, 126.3, 124.3, 120.6, 118.6, 117.7, 116.2 (d, *J* = 22.1 Hz, 1C), 115.1, 44.8, 42.4, 39.6, 21.5;

HRMS (ESI-TOF) calcd. for $C_{32}H_{25}FNO_5S$ $[M + H]^+$ 554.1432; found: 554.1431.

(3S,4R)-3-(2-oxo-2-(p-tolyl)ethyl)-4-phenyl-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (7c)



The major diastereomer **7c** was purified by flash column chromatography (petroleum ether/ethyl acetate = 9:1);

Yellow solid; 44.3 mg, 81% yield; >99:1 dr, 99% ee; $[\alpha]_D^{20}$ = -65.5 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 188.3-189.2 ℃;

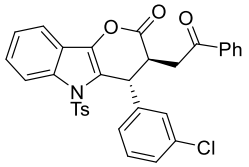
The ee was determined by HPLC (Chiralpak IC, *i*-PrOH/hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 15.1 min, t_{major} = 12.7 min);

^{1}H NMR (300 MHz, $CDCl_3$) δ (major diastereomer) 8.23 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.46-7.33 (m, 2H), 7.30-7.24 (m, 7H), 7.24-7.19 (m, 2H), 6.63 (d, *J* = 8.1 Hz, 2H), 4.96 (d, *J* = 1.5 Hz, 1H), 3.86-3.71 (m, 1H), 3.37-3.07 (m, 2H), 2.42 (s, 3H), 2.04 (s, 3H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (major diastereomer) 194.8, 168.8, 145.0, 140.4, 137.8, 135.1, 135.0, 133.6, 129.8, 129.6, 129.3, 128.4, 127.7, 127.3, 126.3, 126.2, 124.3, 120.7, 118.6, 117.6, 115.1, 44.8, 42.4, 39.5, 21.8, 21.4;

HRMS (ESI-TOF) calcd. for $C_{33}H_{28}NO_5S$ $[M + H]^+$ 550.1683; found: 550.1686.

(3S,4R)-4-(3-chlorophenyl)-3-(2-oxo-2-phenylethyl)-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (7d)



The major diastereomer **7d** was purified by flash column chromatography (petroleum ether/ethyl acetate = 8:1);

Yellow solid; 41.9 mg, 74% yield; 95:5 dr, 99% ee; $[\alpha]_D^{20}$ = -127.9 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 107.3-107.9 ℃;

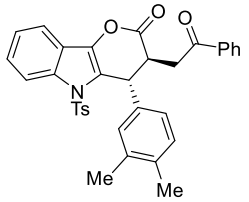
The ee was determined by HPLC (Chiralpak IC, *i*-PrOH/hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 20.0 min, t_{major} = 23.7 min);

^{1}H NMR (300 MHz, $CDCl_3$) δ (major diastereomer) 8.27 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 7.3 Hz, 2H), 7.70-7.59 (m, 2H), 7.53-7.38 (m, 4H), 7.28-7.23 (m, 4H), 7.21-7.15 (m, 1H), 7.11 (s, 1H), 6.68 (d, *J* = 8.1 Hz, 2H), 4.95 (d, *J* = 1.5 Hz, 1H), 3.82-3.67 (m, 1H), 3.39-3.09 (m, 2H), 2.07 (s, 3H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (major diastereomer) 195.2, 168.4, 145.3, 142.4, 138.1, 135.9, 135.3, 135.2, 135.0, 134.1, 130.6, 129.8, 129.1, 128.3, 128.1, 127.3, 126.6, 126.3, 125.7, 124.5, 120.6, 117.8, 117.5, 115.2, 44.7, 42.0, 39.5, 21.5;

HRMS (ESI-TOF) calcd. for $C_{32}H_{24}ClNNaO_5S$ $[M + Na]^+$ 592.0956; found: 592.0963.

(3S,4R)-4-(3,4-dimethylphenyl)-3-(2-oxo-2-phenylethyl)-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (7e)



The major diastereomer **7e** was purified by flash column chromatography (petroleum ether/ethyl acetate = 8:1);

Yellow solid; 44.9 mg, 80% yield; >99:1 dr, 99% ee; $[\alpha]_D^{20}$ = -23.5 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 87.8-88.3 ℃;

The ee was determined by HPLC (Chiralpak IC, *i*-PrOH/hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 38.0 min, t_{major} = 26.9 min);

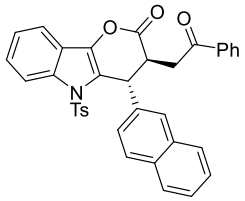
^{1}H NMR (600 MHz, $CDCl_3$) δ (major diastereomer) 8.24 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 6.8 Hz, 2H), 7.68-7.60 (m, 2H), 7.51-7.46 (m, 2H), 7.46-7.42 (m, 1H), 7.40-7.35 (m, 1H), 7.27-7.22 (m,

2H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 6.5 Hz, 2H), 6.63 (d, *J* = 8.1 Hz, 2H), 4.89 (d, *J* = 1.6 Hz, 1H), 3.79-3.73 (m, 1H), 3.28 (dd, *J* = 18.0, 2.6 Hz, 1H), 3.19 (dd, *J* = 18.0, 10.6 Hz, 1H), 2.23 (s, 3H), 2.18 (s, 3H), 2.05 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ (major diastereomer) 195.3, 169.0, 144.9, 137.7, 137.6, 137.5, 136.1, 136.0, 135.1, 135.0, 134.0, 130.5, 129.6, 129.0, 128.3, 128.2, 126.4, 126.2, 124.6, 124.3, 120.7, 118.9, 117.7, 115.2, 45.0, 42.1, 39.6, 21.5, 20.0, 19.6;

HRMS (ESI-TOF) calcd. for $C_{34}H_{30}NO_5S$ $[M + H]^+$ 564.1839; found: 564.1835.

(3S,4R)-4-(naphthalen-2-yl)-3-(2-oxo-2-phenylethyl)-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (7f)



The major diastereomer **7f** was purified by flash column chromatography (petroleum ether/ethyl acetate = 8:1);

Yellow solid; 50.2 mg, 86% yield; 94:6 dr, 99% ee; $[\alpha]_D^{20}$ = -110.2 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 144.9-145.3 ℃;

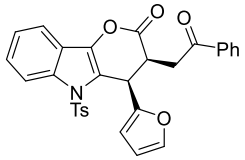
The ee was determined by HPLC (Chiralpak IC, *i*-PrOH/hexane = 25/75, flow rate 1.0 mL/min, *λ* = 254 nm, major diastereomer: t_{minor} = 17.8 min, t_{major} = 12.9 min);

^{1}H NMR (600 MHz, $CDCl_3$) δ (major diastereomer) 8.29 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 2H), 7.87-7.80 (m, 2H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.66-7.60 (m, 1H), 7.57 (dd, *J* = 14.2, 8.3 Hz, 2H), 7.53-7.38 (m, 6H), 7.34 (s, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.42 (d, *J* = 7.9 Hz, 2H), 5.12 (s, 1H), 3.96-3.81 (m, 1H), 3.44-3.25 (m, 2H), 1.89 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ (major diastereomer) 195.4, 168.8, 145.0, 137.9, 137.6, 136.0, 135.3, 134.9, 134.1, 133.6, 133.0, 129.5, 129.4, 129.0, 128.3, 128.1, 127.7, 126.4, 126.3, 126.2, 125.8, 125.7, 124.4, 120.6, 118.4, 117.8, 115.2, 44.8, 42.4, 39.6, 21.3;

HRMS (ESI-TOF) calcd. for $C_{36}H_{28}NO_5S$ $[M + H]^+$ 586.1683; found: 586.1682.

(3S,4R)-4-(furan-2-yl)-3-(2-oxo-2-phenylethyl)-5-tosyl-4,5-dihydropyrano[3,2-b]indol-2(3H)-one (7g)



The major diastereomer **7g** was purified by flash column chromatography (petroleum ether/ethyl acetate = 8:1);

Yellow solid; 43.2 mg, 82% yield; >99:1 dr, 99% ee; $[\alpha]_D^{20}$ = -92.0 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 115.5-116.1 ℃;

The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 10/90, flow rate 1.0 mL/min, *λ* = 254 nm, major diastereomer: t_{minor} = 25.8 min, t_{major} = 20.4 min);

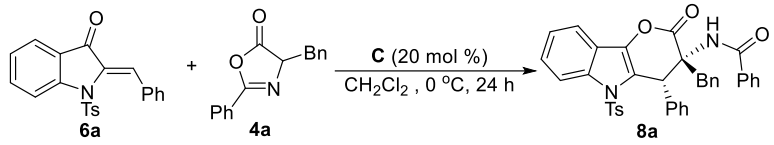
^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ (major diastereomer) 8.13 (d, *J* = 8.4 Hz, 1H), 8.00-7.93 (m, 2H), 7.75-7.67 (m, 1H), 7.67-7.59 (m, 2H), 7.58-7.47 (m, 3H), 7.45-7.37 (m, 3H), 6.86 (d, *J* = 8.1

Hz, 2H), 6.45 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.26 (d, *J* = 3.3 Hz, 1H), 5.07 (d, *J* = 1.8 Hz, 1H), 3.77-3.64 (m, 1H), 3.51 (dd, *J* = 18.4, 4.4 Hz, 1H), 3.43 (dd, *J* =18.4, 8.9 Hz, 1H), 2.08 (s, 3H);

^{13}C NMR (75 MHz, DMSO-d_6) δ (major diastereomer) 196.0, 167.4, 152.3, 145.6, 143.2, 137.4, 135.6, 134.2, 133.9, 133.7, 130.1, 128.8, 128.3, 126.5, 126.0, 124.6, 120.3, 117.6, 116.3, 114.8, 110.8, 107.0, 41.5, 38.5, 35.9, 20.9;

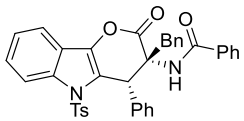
HRMS (ESI-TOF) calcd. for $C_{30}H_{24}NO_6S$ $[M + H]^+$ 526.1319; found: 526.1310.

5. General procedures for the asymmetric synthesis of compounds 8



In an ordinary vial equipped with a magnetic stirring bar, the solution of 1-Azaaurones **6** (0.12 mmol, 1.2 equiv), Azlactones **4** (0.1 mmol, 1.0 equiv) and catalyst **C** (20 mol %) in CH_2Cl_2 (2.0 mL) was cooled to 0 ℃. And then, the mixture was stirred at the same temperature for the specified time. After completion of the reaction, as indicated by TLC, the products **8** were isolated by flash chromatography on silica gel (PE/EA = 15/1 ~ 12/1).

_N_-((3R,4S)-3-benzyl-2-oxo-4-phenyl-5-tosyl-2,3,4,5-tetrahydropyrano[3,2-b]indol-3-yl)benzamide (8a)



The major diastereomer **8a** was purified by flash column chromatography (petroleum ether/ethyl acetate = 12:1);

Yellow solid; 45.2 mg, 72% yield; 88:12 dr, 99% ee; $[\alpha]_D^{20}$ = -156.4 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 219.5-220.4 ℃;

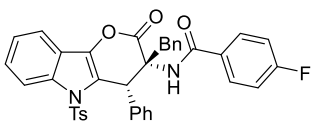
The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 16.8 min, t_{major} = 7.0 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 8.24 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.50-7.38 (m, 3H), 7.39-7.30 (m, 4H), 7.26 (dd, *J* = 14.2, 7.4 Hz, 4H), 7.23-7.15 (m, 6H), 7.10-6.91 (m, 4H), 6.58 (s, 1H), 6.14 (s, 1H), 4.24 (d, *J* = 13.9 Hz, 1H), 3.11 (d, *J* = 13.9 Hz, 1H), 2.23 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 168.1, 145.3, 136.8, 135.8, 135.3, 135.0, 134.9, 134.6, 131.7, 130.1, 129.8, 128.9, 128.7, 128.5, 128.1, 127.6, 127.0, 126.7, 126.4, 124.4, 121.1, 120.1, 117.5, 115.2, 66.7, 46.5, 38.9, 21.6;

HRMS (ESI-TOF) calcd. for $C_{38}H_{31}N_2O_5S$ $[M + H]^+$ 627.1948; found: 627.1944.

_N_-((3R,4S)-3-benzyl-2-oxo-4-phenyl-5-tosyl-2,3,4,5-tetrahydropyrano[3,2-b]indol-3-yl)-4-fluorobenzamide (8b)



The major diastereomer **8b** was purified by flash column chromatography (petroleum ether/ethyl acetate = 12:1);

Yellow solid; 52.2 mg, 81% yield; 89:11 dr, 99% ee; $[\alpha]_D^{20}$ = -96.0 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 225.4-226.5 ℃;

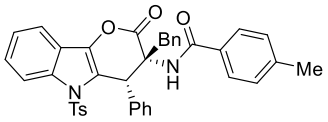
The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 20.1 min, t_{major} = 7.3 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ (major diastereomer) 8.14 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.56-7.43 (m, 4H), 7.34-7.23 (m, 6H), 7.22-7.15 (m, 7H), 7.15-7.07 (m, 2H), 7.02-6.94 (m, 2H), 6.05 (s, 1H), 4.20 (d, *J* = 13.8 Hz, 1H), 3.11 (d, *J* = 13.8 Hz, 1H), 2.22 (s, 3H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (major diastereomer) 168.2, 166.9, 164.9 (d, *J* = 252.1 Hz, 1C), 145.3, 136.8, 135.8, 134.9 (d, *J* = 7.8 Hz, 1C), 134.5, 131.4 (d, *J* = 2.9 Hz, 1C), 130.0, 129.8, 129.1, 129.0, 128.9, 128.7, 128.5, 128.2, 127.7, 127.0, 126.4, 124.5, 121.0, 120.1, 117.5, 115.8 (d, *J* = 21.9 Hz, 1C), 115.2, 66.7, 46.5, 38.9, 21.6;

HRMS (ESI-TOF) calcd. for $C_{38}H_{30}FN_2O_5S$ $[M + H]^+$ 645.1854; found: 645.1851.

N-((3R,4S)-3-benzyl-2-oxo-4-phenyl-5-tosyl-2,3,4,5-tetrahydropyrano[3,2-b]indol-3-yl)-4-methylbenzamide (8c)



The major diastereomer **8c** was purified by flash column chromatography (petroleum ether/ethyl acetate = 12:1);

Yellow solid; 55.2 mg, 86% yield; 88:12 dr, 99% ee; $[\alpha]_D^{20}$ = -61.4 (*c* 0.50, CH_2Cl_2) for major diastereomer; m.p. 102.5-103.6 ℃;

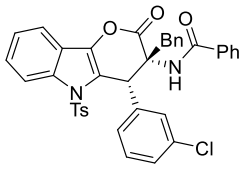
The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 20/80, flow rate 0.8 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 22.2 min, t_{major} = 8.7 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 8.24 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.50-7.36 (m, 2H), 7.32-7.26 (m, 4H), 7.26-7.22 (m, 2H), 7.22-7.15 (m, 6H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.08-7.01 (m, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.56 (s, 1H), 6.14 (s, 1H), 4.25 (d, *J* = 13.9 Hz, 1H), 3.09 (d, *J* = 13.9 Hz, 1H), 2.34 (s, 3H), 2.23 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 168.2, 168.0, 145.3, 142.2, 136.9, 135.8, 135.0, 134.9, 134.7, 132.4, 130.1, 129.8, 129.3, 128.9, 128.7, 128.5, 128.1, 127.6, 127.0, 126.8, 126.3, 124.4, 121.1, 120.1, 117.5, 115.2, 66.7, 46.5, 38.8, 21.6, 21.5;

HRMS (ESI-TOF) calcd. for $C_{39}H_{33}N_2O_5S$ $[M + H]^+$ 641.2105; found: 641.2104.

N-((3R,4S)-3-benzyl-4-(3-chlorophenyl)-2-oxo-5-tosyl-2,3,4,5-tetrahydropyrano[3,2-b]indol-3-yl)benzamide (8d)



The major diastereomer **8d** was purified by flash column chromatography (petroleum ether/ethyl acetate/dichloromethane= 30:1:1);

Yellow solid; 52.9 mg, 80% yield; >99:1 dr, 99% ee; $[\alpha]_D^{20}$ = -60.6 (*c* 0.50, CH_2Cl_2) for major diastereomer; m.p. 100.3-100.9 ℃;

The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 20/80, flow rate 0.8 mL/min, λ

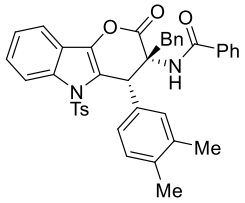
= 254 nm, major diastereomer: t_{minor} = 20.3 min, t_{major} = 8.4 min);

^{1}H NMR (600 MHz, $CDCl_3$) δ (major diastereomer) 8.29 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.52-7.48 (m, 1H), 7.48-7.41 (m, 4H), 7.38-7.32 (m, 4H), 7.22-7.19 (m, 3H), 7.18-7.13 (m, 3H), 7.13-7.08 (m, 1H), 7.07-7.00 (m, 4H), 6.61 (s, 1H), 6.13 (s, 1H), 4.20 (d, *J* = 14.0 Hz, 1H), 3.08 (d, *J* = 14.0 Hz, 1H), 2.25 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ (major diastereomer) 168.2, 167.7, 145.5, 138.7, 136.2, 135.1, 135.0, 134.9, 134.8, 134.3, 131.9, 130.1, 130.0, 129.9, 128.8, 128.6, 128.4, 127.7, 126.9, 126.7, 126.6, 124.6, 120.0, 119.9, 117.6, 115.3, 66.5, 46.1, 38.8, 21.6;

HRMS (ESI-TOF) calcd. for $C_{38}H_{30}ClN_2O_5S$ $[M + H]^+$ 661.1558; found: 661.1553.

***N*-((3R,4S)-3-benzyl-4-(3,4-dimethylphenyl)-2-oxo-5-tosyl-2,3,4,5-tetrahydropyrano[3,2-b]indol-3-yl)benzamide (8e)**



The major diastereomer **8e** was purified by flash column chromatography (petroleum ether/ethyl acetate = 15:1);

Yellow solid; 46.7 mg, 71% yield; >99:1 dr, 99% ee; $[\alpha]_D^{20}$ = -104.8 (*c* 1.00, CH_2Cl_2) for major diastereomer; m.p. 221.5-222.7 ℃;

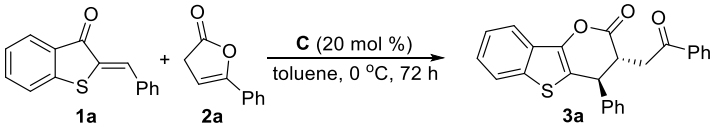
The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 20/80, flow rate 0.8 mL/min, *λ* = 254 nm, major diastereomer: t_{minor} = 15.4 min, t_{major} = 7.8 min);

^{1}H NMR (600 MHz, $CDCl_3$) δ (major diastereomer) 8.27 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.50-7.38 (m, 5H), 7.37-7.29 (m, 4H), 7.22-7.16 (m, 3H), 7.05 (dd, *J* = 6.7, 2.9 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.95-6.89 (m, 3H), 6.55 (s, 1H), 6.05 (s, 1H), 4.21 (d, *J* = 14.0 Hz, 1H), 3.07 (d, *J* = 14.0 Hz, 1H), 2.24 (s, 3H), 2.15 (s, 3H), 2.04 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ (major diastereomer) 168.2, 168.1, 145.1, 137.0, 136.4, 135.8, 135.5, 135.1, 134.9, 134.8, 133.8, 131.6, 130.1, 129.7, 128.7, 128.5, 127.6, 127.0, 126.8, 126.3, 125.9, 124.4, 121.3, 120.1, 117.4, 115.2, 66.8, 46.0, 38.7, 21.6, 19.8, 19.5;

HRMS (ESI-TOF) calcd. for $C_{40}H_{35}N_2O_5S$ $[M + H]^+$ 655.2261; found: 655.2259.

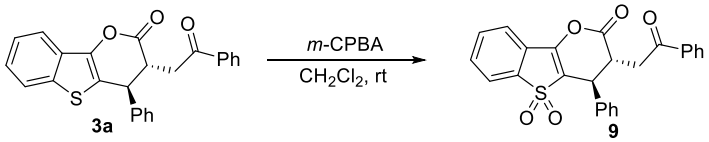
6. Scale-up experiment



In an ordinary vial equipped with a magnetic stirring bar, the solution of 1-Thioaurones **1a** (4.8 mmol, 1.2 equiv), *γ*-Deconjugated Butenolides **2a** (4.0 mmol, 1.0 equiv) and catalyst **C** (20 mol %) in toluene (40 mL) was cooled to 0 ℃. And then, the whole was stirred for 72 h until the completion of the reaction as indicated by TLC. Finally, the reaction mixture was directly concentrated under reduced pressure and purified by flash chromatography on silica gel (PE/EA=30:1-15:1) and acquired the product **3a** (1.11 g, 70% yield, 87:13 dr, 99% ee).

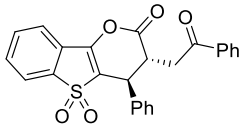
7. Synthetic transformations of products

7.1 The procedure for the synthesis of compound 9



To a flame dried reaction tube was added **3a** (60.0 mg, 0.15 mmol, 1.0 equiv) and meta-chloroperoxybenzoic acid (m-CPBA) (93.0 mg, 0.54 mmol, 3.6 equiv) at room temperature under an argon atmosphere, followed by addition of dry CH_2Cl_2 (1.0 mL). After stirring for 5 h, the mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (PE/EA = 3/1) to afford product **9** (31.8 mg, 49% yield) as a white solid.

(3R,4S)-3-(2-oxo-2-phenylethyl)-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one 5,5-dioxide (9)



White solid; 31.8 mg, 49% yield; >99:1 dr, 99% ee; $[\alpha]_D^{20}$ = +136.7 (*c* 1.00, CH_2Cl_2); m.p. 187.4-188.5 ℃;

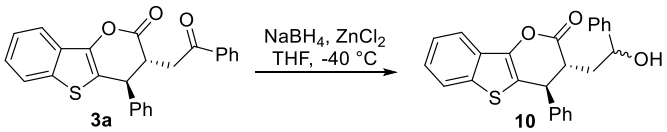
The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 35/65, flow rate 1.0 mL/min, λ = 254 nm, t_{minor} = 39.5 min, t_{major} = 50.1 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ (major diastereomer) 7.96-7.88 (m, 3H), 7.87-7.80 (m, 1H), 7.63-7.53 (m, 3H), 7.46-7.40 (m, 2H), 7.25-7.18 (m, 2H), 7.12-7.00 (m, 3H), 4.72 (d, *J* = 12.6 Hz, 1H), 4.17-4.09 (m, 1H), 3.47 (d, *J* = 4.6 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereomer) 195.4, 188.5, 173.4, 144.4, 137.7, 135.9, 134.7, 133.9, 130.6, 130.1, 129.3, 129.0, 128.9, 128.8, 128.3, 124.7, 122.1, 93.1, 51.1, 40.1, 36.2;

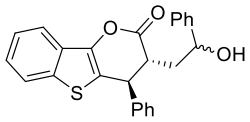
HRMS (ESI-TOF) calcd. for $C_{25}H_{19}O_5S$ $[M + H]^+$ 431.0948; found: 431.0929.

7.2 The procedure for the synthesis of compound 10



In a reaction tube equipped with a magnetic stirring bar, the solution of **3a** (40.0 mg, 0.1 mmol, 1.0 equiv) in THF (1.0 mL) was cooled to -40 ℃, followed by addition of $ZnCl_2$ (27.3 mg, 0.2 mmol, 2.0 equiv) and $NaBH_4$ (7.6 mg, 0.2 mmol, 2.0 equiv). Maintaining the reaction stirring at the same temperature for 96 h until **3a** consumed as monitored by TLC. And then, H_2O (2.0 mL) was added to the reaction tube. The aqueous phase was extracted with ethyl acetate for three times. The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. Then the residue was purified by column chromatography (PE/EA = 7:1) to afford the compound **10** as a white solid (29.4 mg, 74% yield).

(3R,4S)-3-(2-hydroxy-2-phenylethyl)-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-2-one (10)



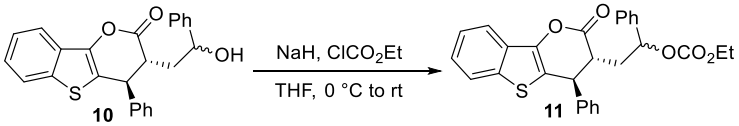
White solid; 29.4 mg, 74% yield; 80:20 dr; $[\alpha]_D^{20}$ = +22.9 (*c* 1.00, CH_2Cl_2); m.p. 200.8-201.9 ℃;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.81 (m, 1.6H), 7.80-7.75 (m, 0.4H), 7.74-7.68 (m, 0.8H), 7.65-7.59 (m, 1.0H), 7.55-7.46 (m, 1.1H), 7.39-7.23 (m, 9.2H), 5.82-5.79 (m, 0.8H), 5.50-5.42 (m, 0.2H), 4.61 (d, *J* = 9.3 Hz, 0.2H), 4.18 (d, *J* = 8.6 Hz, 0.8H), 4.14 (d, *J* = 8.9 Hz, 0.2H), 4.03 (d, *J* = 4.2 Hz, 0.8H), 3.39 (dd, *J* = 18.5, 9.6 Hz, 0.8H), 3.28-3.19 (m, 0.2H), 3.16-3.12 (m, 0.2H), 3.08-2.96 (m, 1.8H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.6, 199.5, 143.6, 142.4, 142.3, 141.7, 137.4, 137.3, 136.6, 136.4, 133.7, 133.5, 131.7, 131.4, 129.1, 129.0, 128.9 (2C), 128.8, 128.7, 128.3, 128.2, 127.9, 127.7, 125.0, 124.8, 124.2, 124.1, 122.8, 122.7, 120.5, 120.2, 116.4, 115.9, 99.1, 93.6, 45.1, 42.9, 42.1, 41.2, 38.3, 37.2;

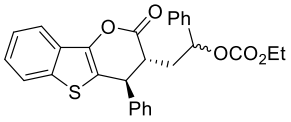
HRMS (ESI-TOF) calcd. for $C_{25}H_{20}NaO_3S$ $[M + Na]^+$ 423.1025; found: 423.1030.

7.3 The procedure for the synthesis of compound 11



In a reaction tube equipped with a magnetic stirring bar, the solution of **10** (50.3 mg, 0.12 mmol, 1.0 equiv) in THF (1.0 mL) was cooled to 0 ℃, followed by addition of NaH (7.2 mg, 0.18 mmol, 1.5 equiv, 60% in mineral oil) and $ClCO_2Et$ (11.3 μL, 0.18 mmol, 1.5 equiv). Subsequently, the whole was stirred for 6 h at room temperature. And then, H_2O (2.0 mL) was added to the reaction tube. The aqueous phase was extracted with ethyl acetate for three times. The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. Then the residue was purified by column chromatography (PE/EA = 13:1) to afford the product **11** as a yellow solid (26.7 mg, 47% yield).

Ethyl (2-((3R,4S)-2-oxo-4-phenyl-3,4-dihydro-2H-benzo[4,5]thieno[3,2-b]pyran-3-yl)-1-phenylethyl) carbonate (11)



Yellow solid; 26.7 mg, 47% yield; 80:20 dr, 99% ee; $[\alpha]_D^{20}$ = +152.6 (*c* 1.00, CH_2Cl_2); m.p. 65.9-66.3 ℃;

The ee was determined by HPLC (Chiralpak IB, EtOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 15.3 min, t_{major} = 16.3 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.87-7.79 (m, 3H), 7.69-7.64 (m, 1H), 7.62-7.55 (m, 1H), 7.50-7.44 (m, 2H), 7.43-7.38 (m, 3H), 7.37-7.29 (m, 4H), 6.57 (d, *J* = 2.1 Hz, 1H), 4.19 (d, *J* = 11.3 Hz, 1H), 4.10 (q, *J* = 7.0 Hz, 2H), 3.35-3.26 (m, 1H), 3.17-3.07 (m, 1H), 2.96 (dd, *J* = 18.4, 3.2 Hz, 1H), 1.15 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (75 MHz, DMSO-d_6) δ 197.6, 153.3, 140.8, 140.5, 136.1, 136.0, 133.5, 130.5, 129.0, 128.8, 128.7, 127.9, 127.8, 125.2, 124.6, 123.1, 119.7, 118.1, 94.7, 64.4, 40.4, 39.5, 36.5, 13.8;

HRMS (ESI-TOF) calcd. for $C_{28}H_{24}NaO_5S$ $[M + Na]^+$ 495.1237; found: 495.1245.

8. X-ray crystal structure of compounds 3a, 5a, 7e and 8b.

Single crystal of compound **3a** was prepared from the mixture solvent of EtOH/ dichloromethane/Petroleum ether (*V* : *V* : *V*= 10/1/1) at room temperature by slow evaporation of solvent. A suitable crystal was selected for structure determination on a Xcalibur, Eos, Gemini diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2[1], the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares minimisation.

Single crystal of compound **5a** was prepared from the single solvent of EtOH at room temperature by slow evaporation of solvent. A suitable crystal was selected for structure determination on a Xcalibur, Eos, Gemini diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2[1], the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares minimisation.

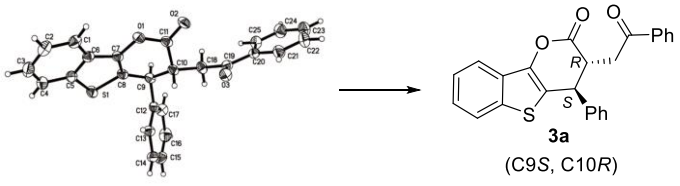
Single crystal of compound **7e** was prepared from the mixture solvent of EtOH/ Petroleum ether (*V* : *V* = 10/1) at room temperature by slow evaporation of solvent. A suitable crystal was selected for structure determination on a Xcalibur, Eos, Gemini diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2[1], the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares minimisation.

Single crystal of compound **8b** was prepared from the mixture solvent of DMSO-d_6/ Petroleum ether (*V* : *V* = 10/1) at room temperature by slow evaporation of solvent. A suitable crystal was selected for structure determination on a Xcalibur, Eos, Gemini diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2[1], the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares minimisation.

[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst*. 2009, **42**, 339-341.

[2] G. M. Sheldrick, *Acta Cryst.* 2008, A64, 112-122.

[3] G. M. Sheldrick, *Acta Cryst.* 2015, C71, 3-8.

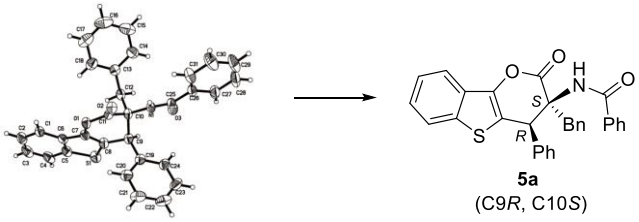


ORTEP of **3a** (at 50% level)

Crystal data and structure refinement for 3a (CCDC-2102386)

Identification code	**3a**
Empirical formula	$C_{25}H_{18}O_3S$
Formula weight	398.45
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$

a/Å	9.1738(2)
b/Å	11.5881(2)
c/Å	18.4905(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1965.66(8)
Z	4
ρ_{calc}g/cm^3	1.346
μ/mm^{-1}	1.657
F(000)	832.0
Crystal size/mm^3	0.17 ×0.12 ×0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/ °	9.006 to 134.13
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -18 ≤ l ≤ 22
Reflections collected	16343
Independent reflections	3499 [R_{int} = 0.0423, R_{sigma} = 0.0298]
Data/restraints/parameters	3499/0/262
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0373, wR_2 = 0.0969
Final R indexes [all data]	R_1 = 0.0403, wR_2 = 0.1001
Largest diff. peak/hole / e Å^{-3}	0.14/-0.24
Flack parameter	-0.006(11)



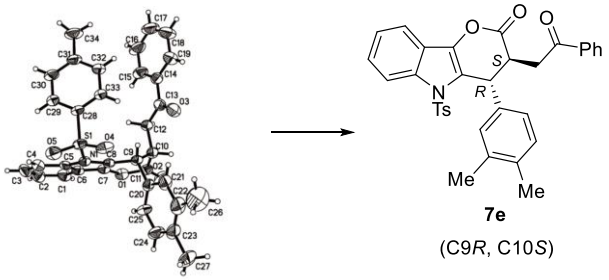
5a
(C9*R*, C10*S*)

ORTEP of **5a** (at 50% level)

Crystal data and structure refinement for 5a (CCDC-2102388)

Identification code	**5a**
Empirical formula	$C_{31}H_{23}NO_3S$
Formula weight	489.56
Temperature/K	293(2)
Crystal system	triclinic
Space group	P1
a/Å	10.0702(4)
b/Å	11.9626(8)
c/Å	12.1903(7)

α/°	117.754(6)
β/°	91.918(4)
γ/°	96.198(4)
Volume/Å^3	1286.10(14)
Z	2
ρ_{calc}g/cm^3	1.264
μ/mm^{-1}	1.377
F(000)	512.0
Crystal size/mm^3	0.13 × 0.11 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.234 to 142.082
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 13, -14 ≤ l ≤ 14
Reflections collected	18465
Independent reflections	8825 [R_{int} = 0.0335, R_{sigma} = 0.0417]
Data/restraints/parameters	8825/4/657
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0494, wR_2 = 0.1247
Final R indexes [all data]	R_1 = 0.0559, wR_2 = 0.1344
Largest diff. peak/hole / e Å^{-3}	0.24/-0.21
Flack parameter	-0.01(2)

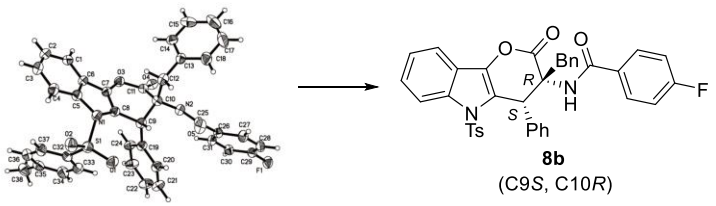


ORTEP of **7e** (at 50% level)

Crystal data and structure refinement for 7e (CCDC-2111474)

Identification code	**7e**
Empirical formula	$C_{34}H_{29}NO_5S$
Formula weight	563.64
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.2382(4)
b/Å	18.0725(7)
c/Å	15.2764(5)
α/°	90
β/°	94.280(4)

γ/°	90
Volume/Å^3	3094.0(2)
Z	4
ρ_{calc}g/cm^3	1.210
μ/mm^{-1}	1.259
F(000)	1184.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.59 to 134.112
Index ranges	-13 ≤ h ≤ 13, -21 ≤ k ≤ 21, -11 ≤ l ≤ 18
Reflections collected	23685
Independent reflections	11060 [R_{int} = 0.0321, R_{sigma} = 0.0441]
Data/restraints/parameters	11060/40/658
Goodness-of-fit on F^2	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.0714, wR_2 = 0.2003
Final R indexes [all data]	R_1 = 0.0855, wR_2 = 0.2200
Largest diff. peak/hole / e Å^{-3}	0.46/-0.30
Flack parameter	0.002(13)



ORTEP of **8b** (at 50% level)

Crystal data and structure refinement for 8b (CCDC-2113255)

Identification code	**8b**
Empirical formula	$C_{38}H_{29}FN_2O_5S$
Formula weight	644.69
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	12.9471(4)
b/Å	19.2285(4)
c/Å	13.9330(4)
α/°	90
β/°	111.418(4)
γ/°	90
Volume/Å^3	3229.15(17)

Z	4
ρ_{calc}g/cm^3	1.326
μ/mm^{-1}	1.334
F(000)	1344.0
Crystal size/mm^3	0.15 × 0.11 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.334 to 142.378
Index ranges	-15 ≤ h ≤ 15, -23 ≤ k ≤ 23, -10 ≤ l ≤ 16
Reflections collected	25310
Independent reflections	12147 [R_{int} = 0.0351, R_{sigma} = 0.0478]
Data/restraints/parameters	12147/1/858
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0482, wR_2 = 0.1233
Final R indexes [all data]	R_1 = 0.0645, wR_2 = 0.1406
Largest diff. peak/hole / e Å^{-3}	0.19/-0.18
Flack parameter	0.011(10)

9. Proposed transition states for the asymmetric aromatizing IED [4+2] cycloaddition.

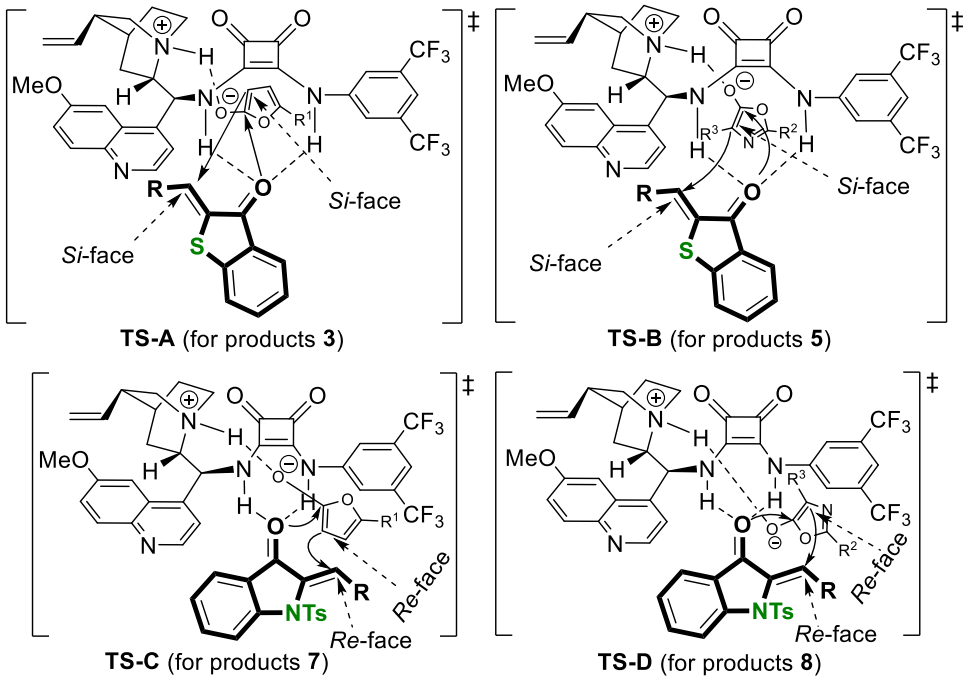


Figure 1

Based on the experimental results and the related literature reports,[1-3] possible transition states were proposed to rationalize the formation of each type of cycloadducts with specific configurations, respectively (Figure 1). Catalyst **C** plays a bifunctional nature to simultaneously activate the electronic dipoles and nucleophilic dienophiles. 1-thioaurones

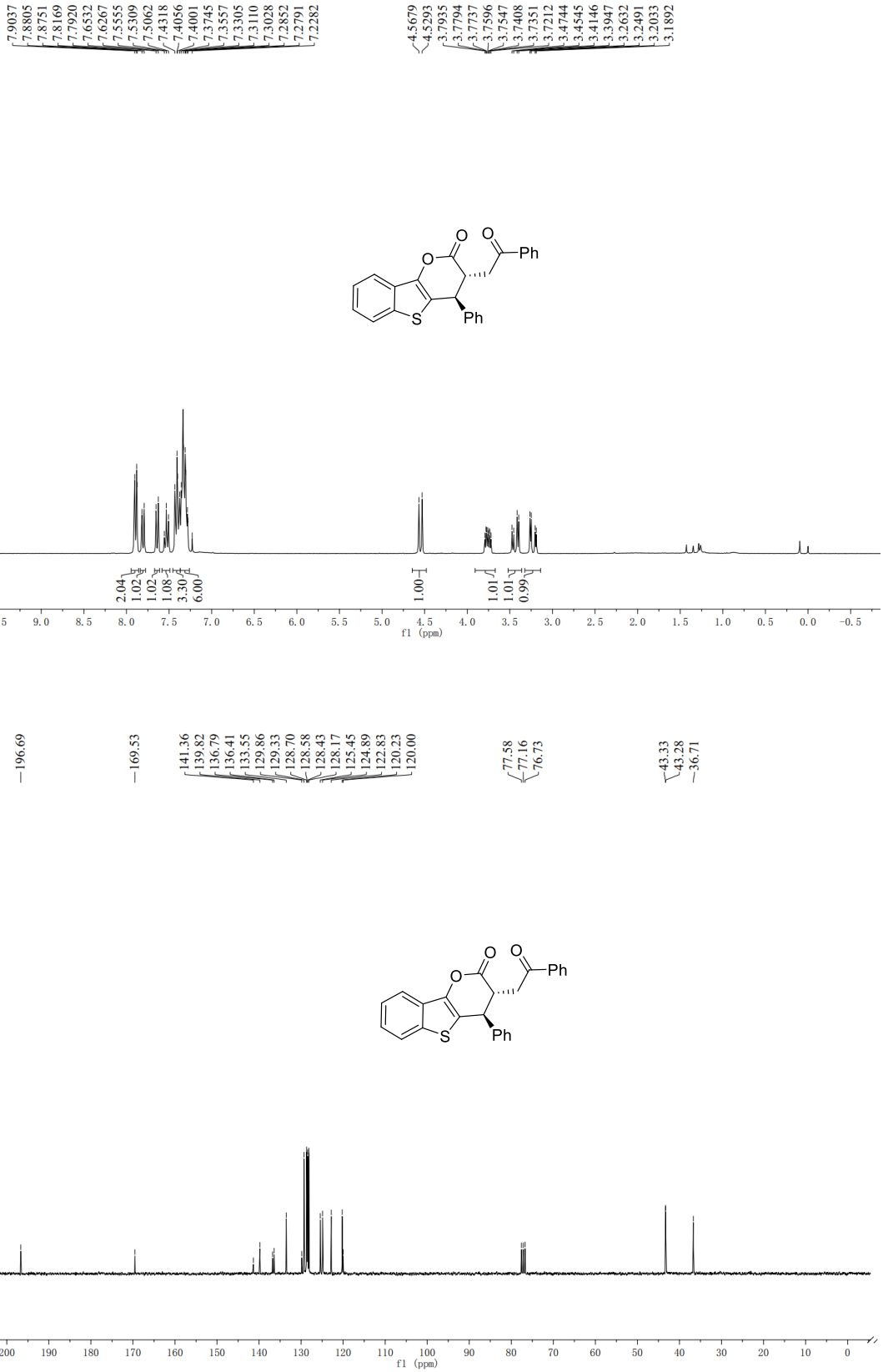
and 1-azaaurones could be oriented and activated by the dual H-bonding from the squaramide NHs to the carbonyl groups, while the γ-deconjugated butenolides and azlactones could be enolized and activated by the tertiary amine of the quinuclidine moiety via deprotonation. And then, under the stereoselective induction of catalyst **C**, the α-position of enolized butenolides attacks the 1-thioaurones in a *Si-Si* fashion (**TS-A**) to construct (*C9S, C10R*)-configuration chiral stereocenters, the subsequent intramolecular transesterification delivers the cycloadduct **3**. Likewise, the addition of enolized azlactones to 1-thioaurones in a *Si-Si* fashion (**TS-B**) generates the (*C9R, C10S*)-configuration chiral stereocenters and further intramolecular transesterification leads to the formation of **5**. In the same manner, the *Re-Re* fashion addition (**TS-C**) and (**TS-D**) involving 1-azaaurones, and the subsequent intramolecular transesterification also results in the formation of products **7** and **8** with (*C9R, C10S*)- and (*C9S, C10R*)-configuration, respectively (Figure 1, below). Notably, the aromatizing trend for the formation of heteroaromatic benzothiophene and indole moieties can be regarded as crucial for the IED [4+2] cycloaddition.

Reference:

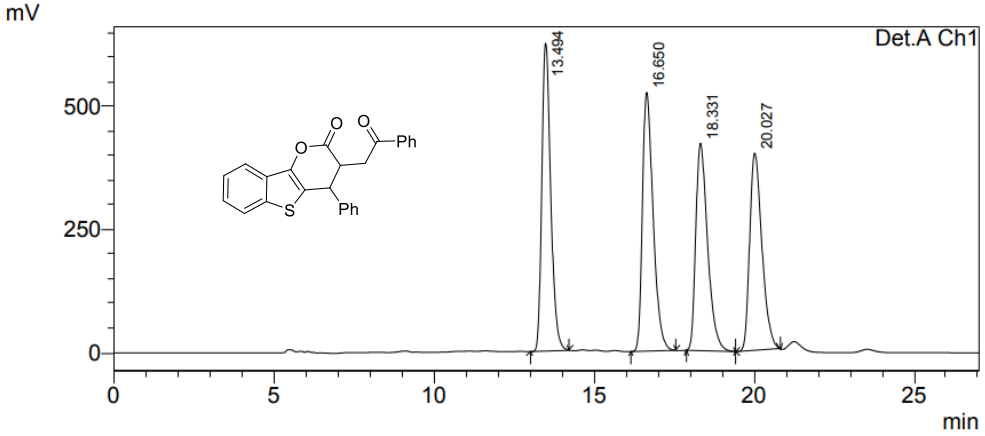
1. (a) A. Skrzyńska, A. Albrecht and Ł. Albrecht, *Adv. Synth. Catal*., 2016, **358**, 2838; (b) M. Saktura, B. Joachim, P. Grzelak and Ł. Albrecht, *Eur. J. Org. Chem.*, 2019, 6592.
2. (a) L. Yang, W. Huang, X.-H. He, M.-C. Yang, X. Li, G. He, C. Peng and B. Han, *Adv. Synth. Catal.*, 2016, **358**, 2970; (b) J. Zhou, B. Wang, X.-H. He, L. Liu, J. Wu, J. Lu, C. Peng, C.-L. Rao and B. Han, *J. Org. Chem.*, 2019, **84**, 5450.
3. (a) B. Wu, Z.-Y. Yu, X. Gao, Y. Lan and Y.-G. Zhou, *Angew. Chem., Int. Ed*., 2017, **56**, 4006; (b) Y.-N. Wang, Q. Xiong, L.-Q. Lu, Q.-L. Zhang, Y. Wang, Y. Lan and W.-J. Xiao, *Angew. Chem., Int. Ed*., 2019, **58**, 11013; (c) Y.-W. Xu and X.-P. Hu, *Org. Lett.*, 2019, **21**, 8091.

10. The copies of ^{1}H NMR, ^{13}C NMR and HPLC spectra for compounds 3, 5, 7-11

^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) of 3a



HPLC spectra of 3a

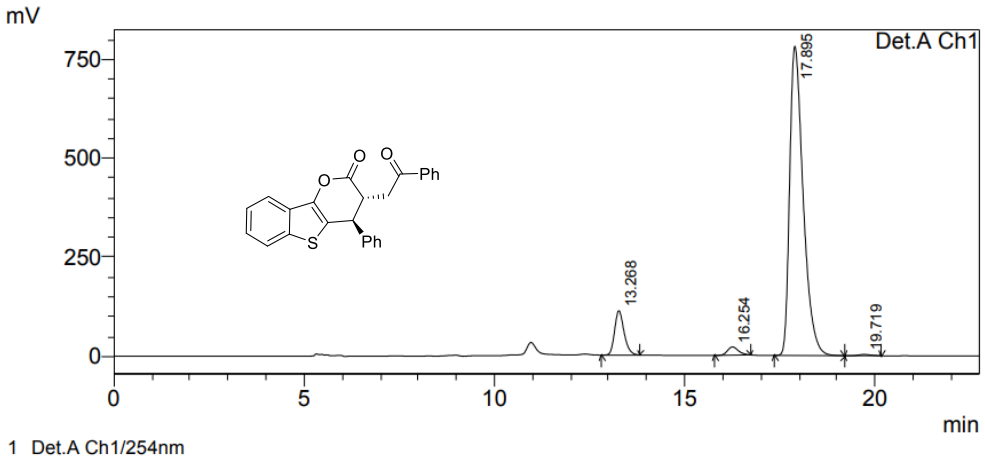


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.494	12045338	624446	26.346
2	16.650	12219180	524842	26.726
3	18.331	10821857	420490	23.670
4	20.027	10633126	399730	23.257
Total		45719502		100.000



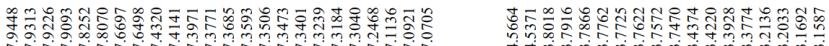
1 Det.A Ch1/254nm

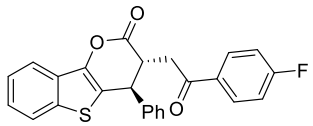
PeakTable

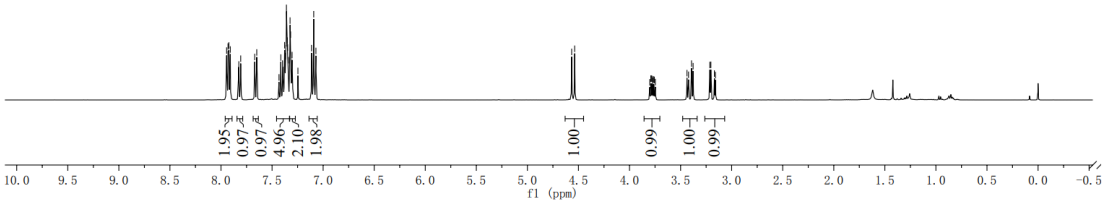
Detector A Ch1 254nm

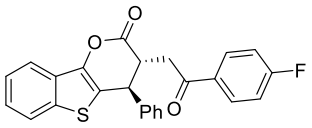
Peak#	Ret. Time	Area	Height	Area %
1	13.268	1940803	112144	8.941
2	16.254	416497	20791	1.919
3	17.895	19279552	781807	88.822
4	19.719	68913	3101	0.317
Total		21705764		100.000

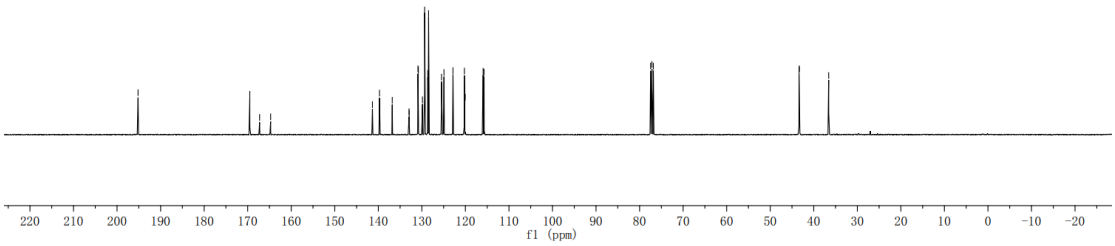
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 3b



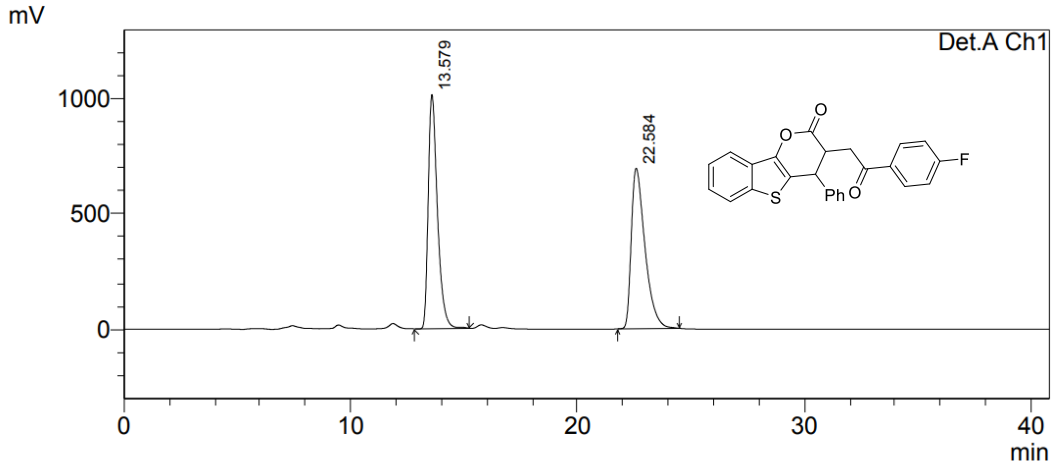








HPLC spectra of 3b

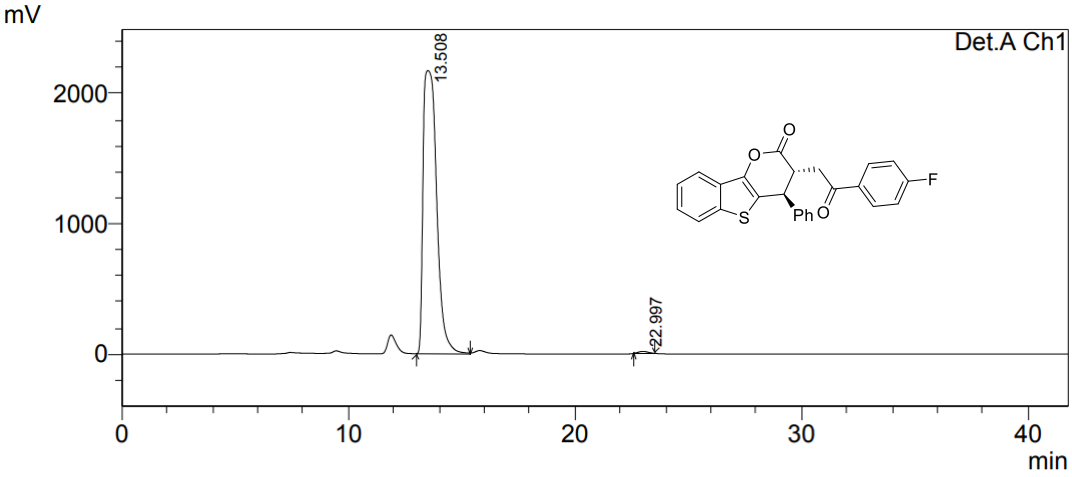


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.579	28670172	1014151	49.608
2	22.584	29122919	694749	50.392
Total		57793090		100.000



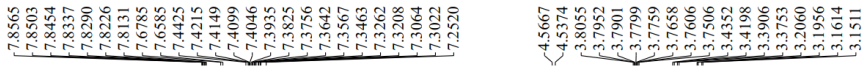
1 Det.A Ch1/254nm

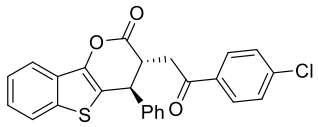
PeakTable

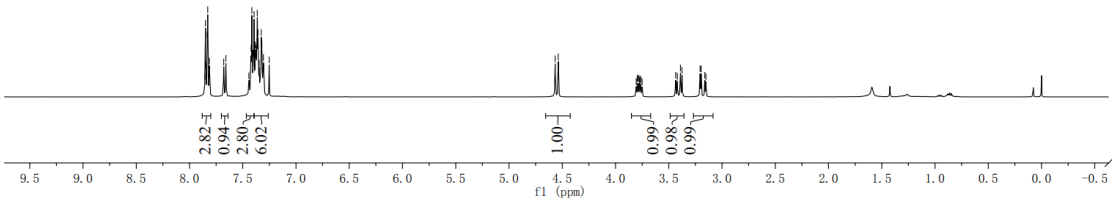
Detector A Ch1 254nm

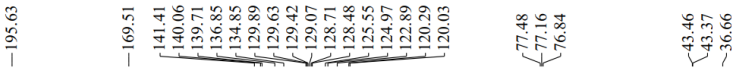
Peak#	Ret. Time	Area	Height	Area %
1	13.508	91053152	2175178	99.465
2	22.997	489506	15890	0.535
Total		91542658		100.000

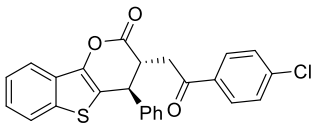
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 3c

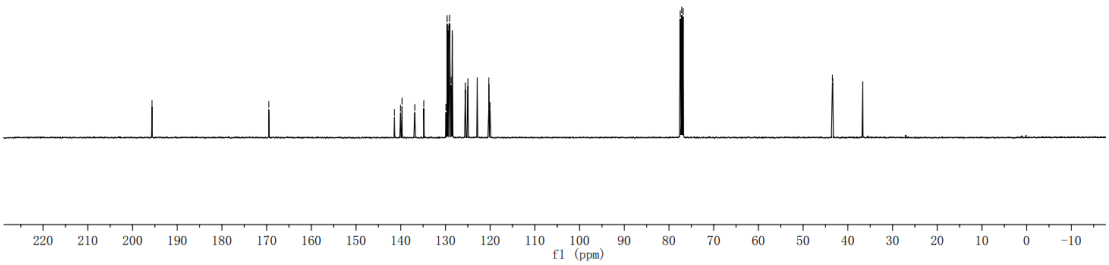




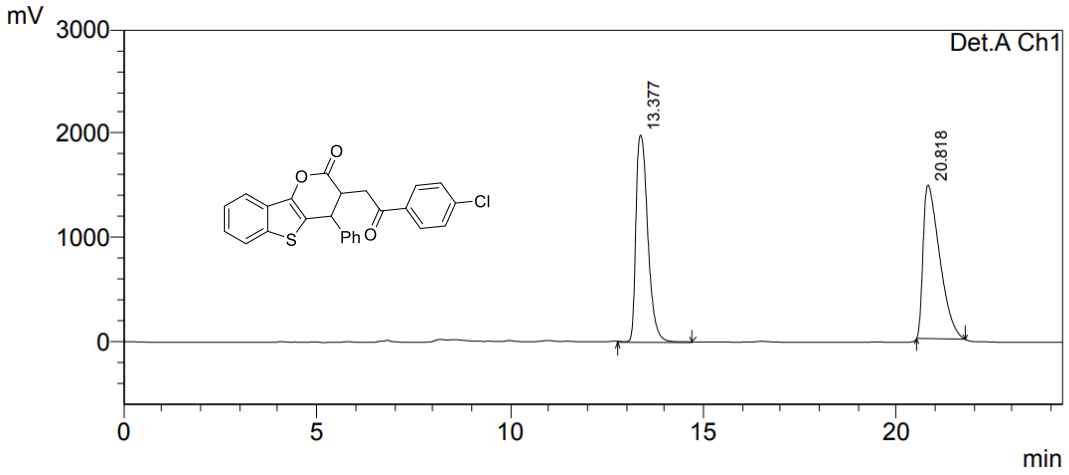








HPLC spectra of 3c

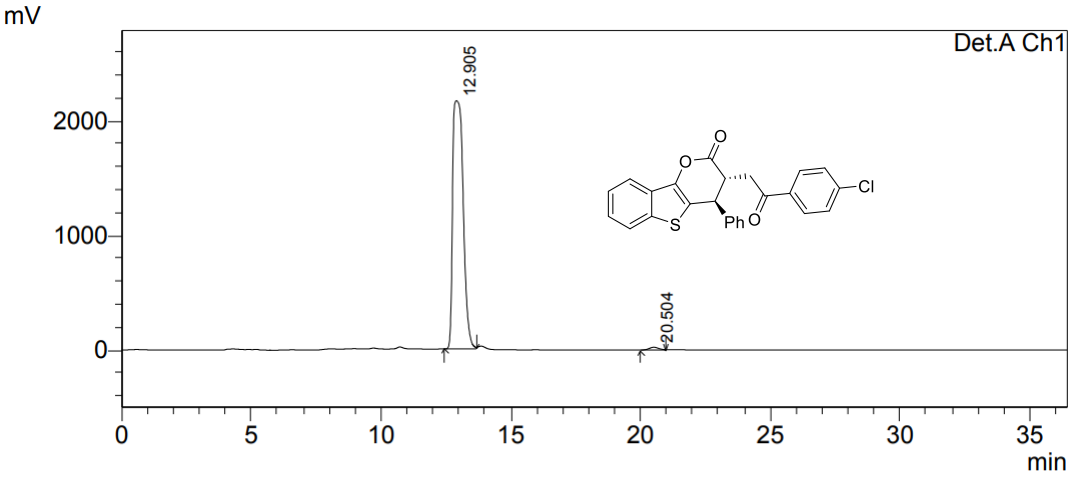


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.377	42726381	1989264	49.242
2	20.818	44040929	1473528	50.758
Total		86767310		100.000



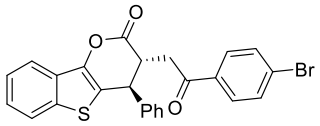
1 Det.A Ch1/254nm

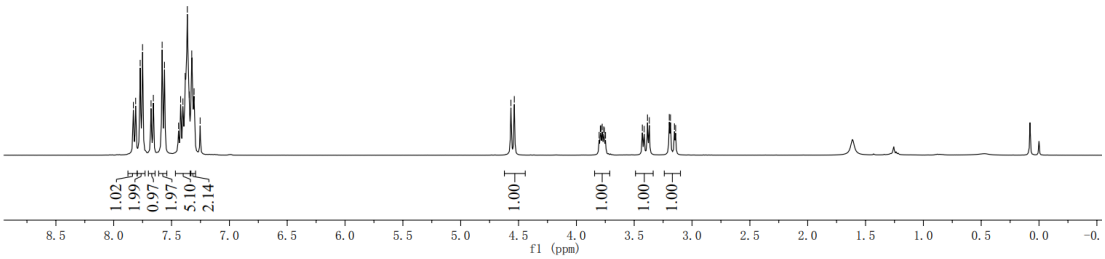
PeakTable

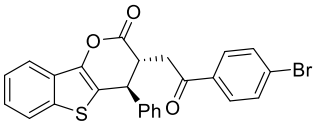
Detector A Ch1 254nm

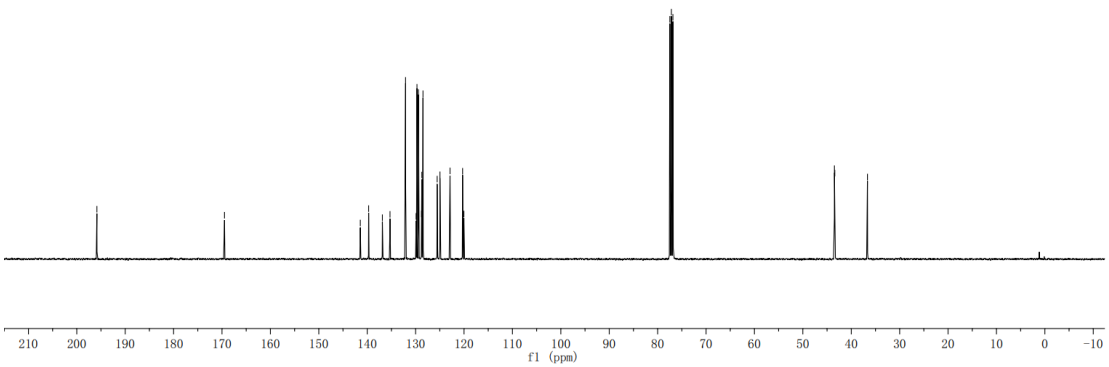
Peak#	Ret. Time	Area	Height	Area %
1	12.905	61382590	2168266	98.998
2	20.504	621495	24087	1.002
Total		62004084		100.000

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 3d

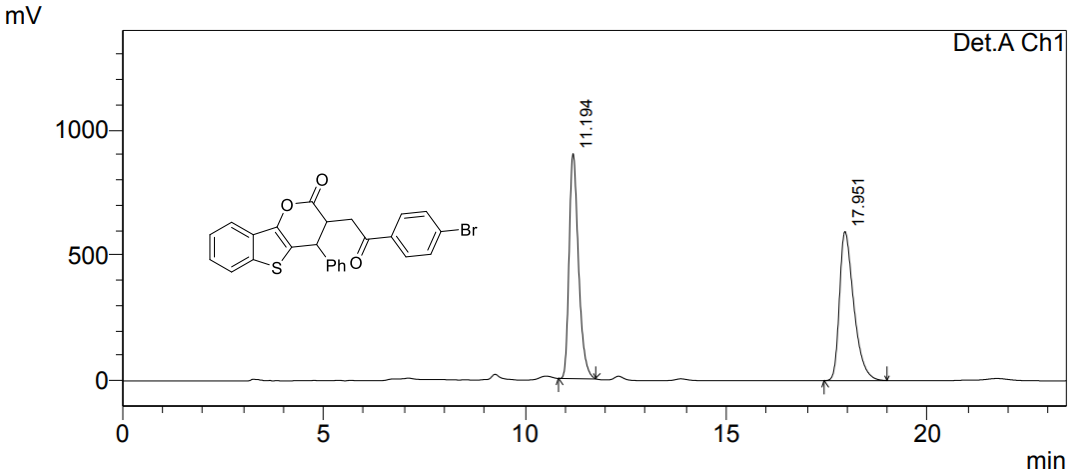








HPLC spectra of 3d

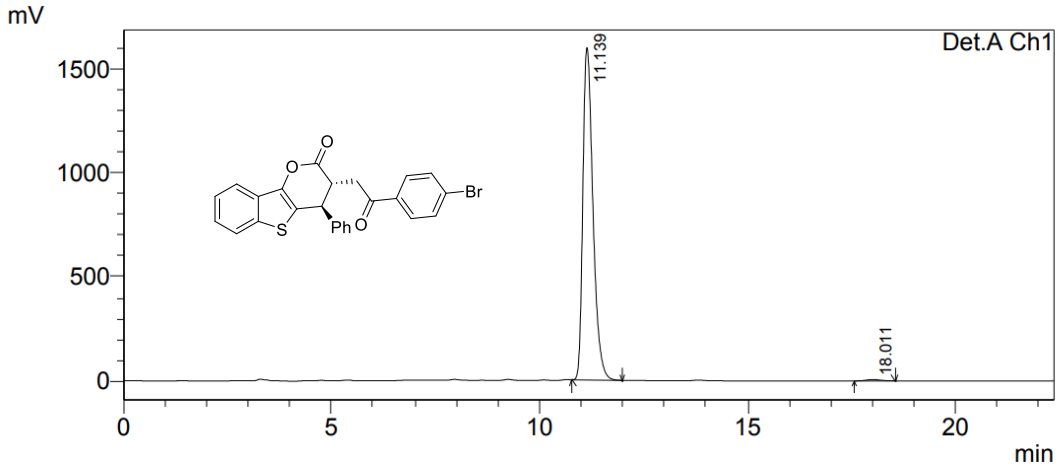


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.194	14582131	896990	49.764
2	17.951	14720157	593659	50.236
Total		29302287		100.000



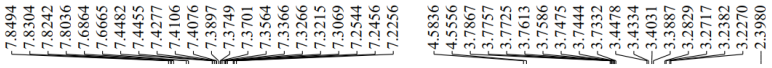
1 Det.A Ch1/254nm

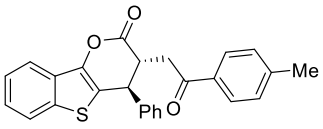
PeakTable

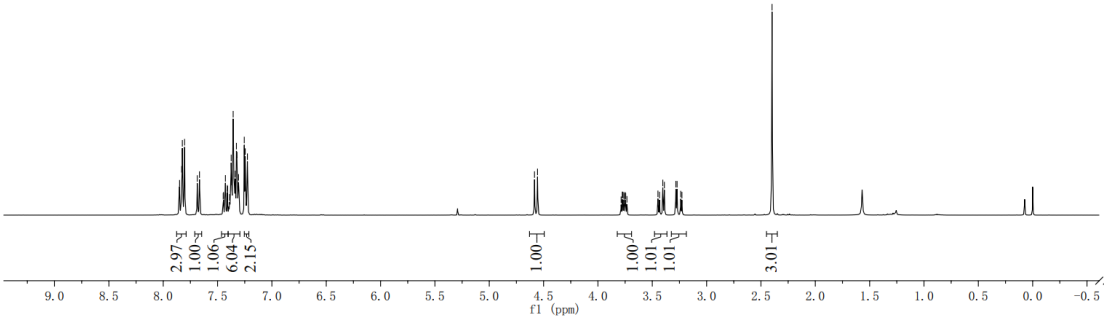
Detector A Ch1 254nm

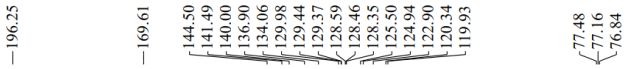
Peak#	Ret. Time	Area	Height	Area %
1	11.139	27069552	1599192	99.438
2	18.011	153083	6596	0.562
Total		27222635		100.000

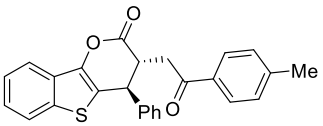
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 3e

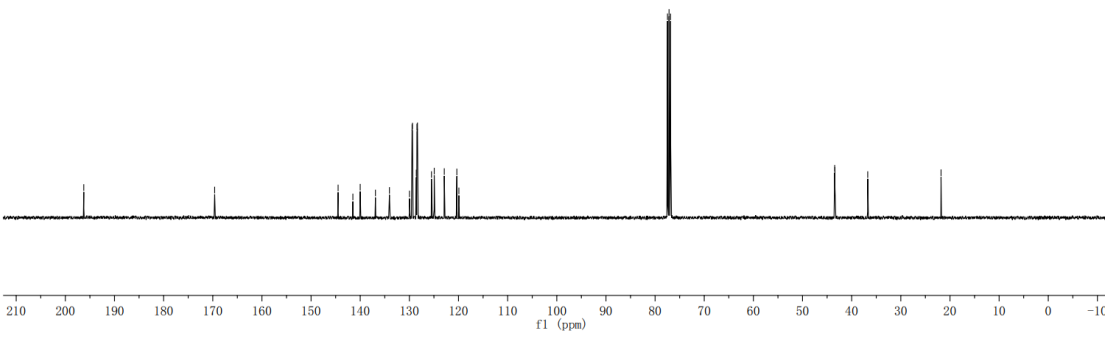




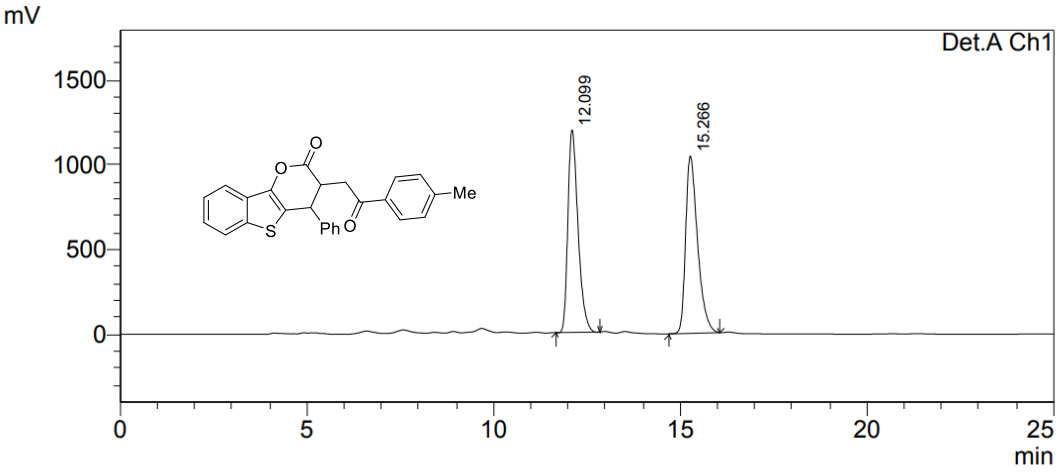








HPLC spectra of 3e

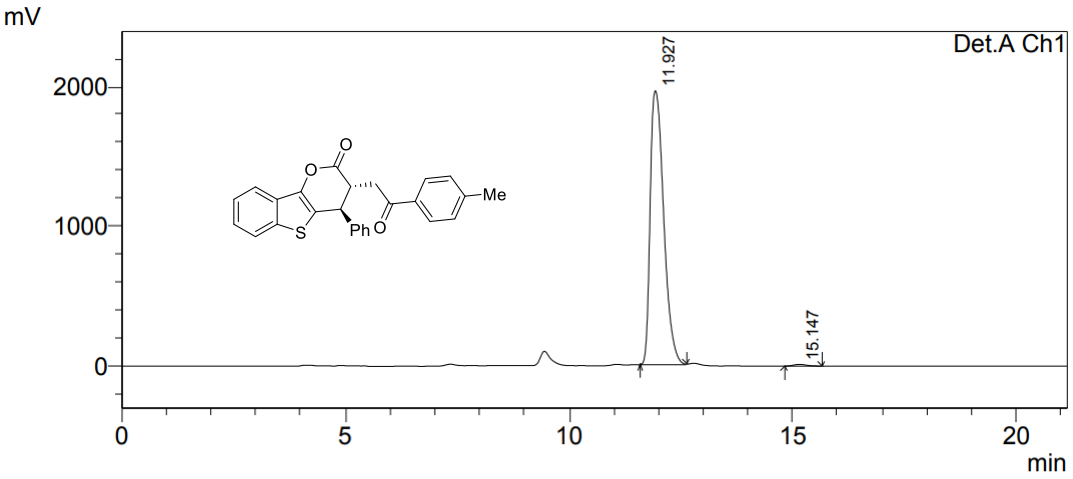


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.099	22529980	1194889	49.166
2	15.266	23294644	1046537	50.834
Total		45824625		100.000



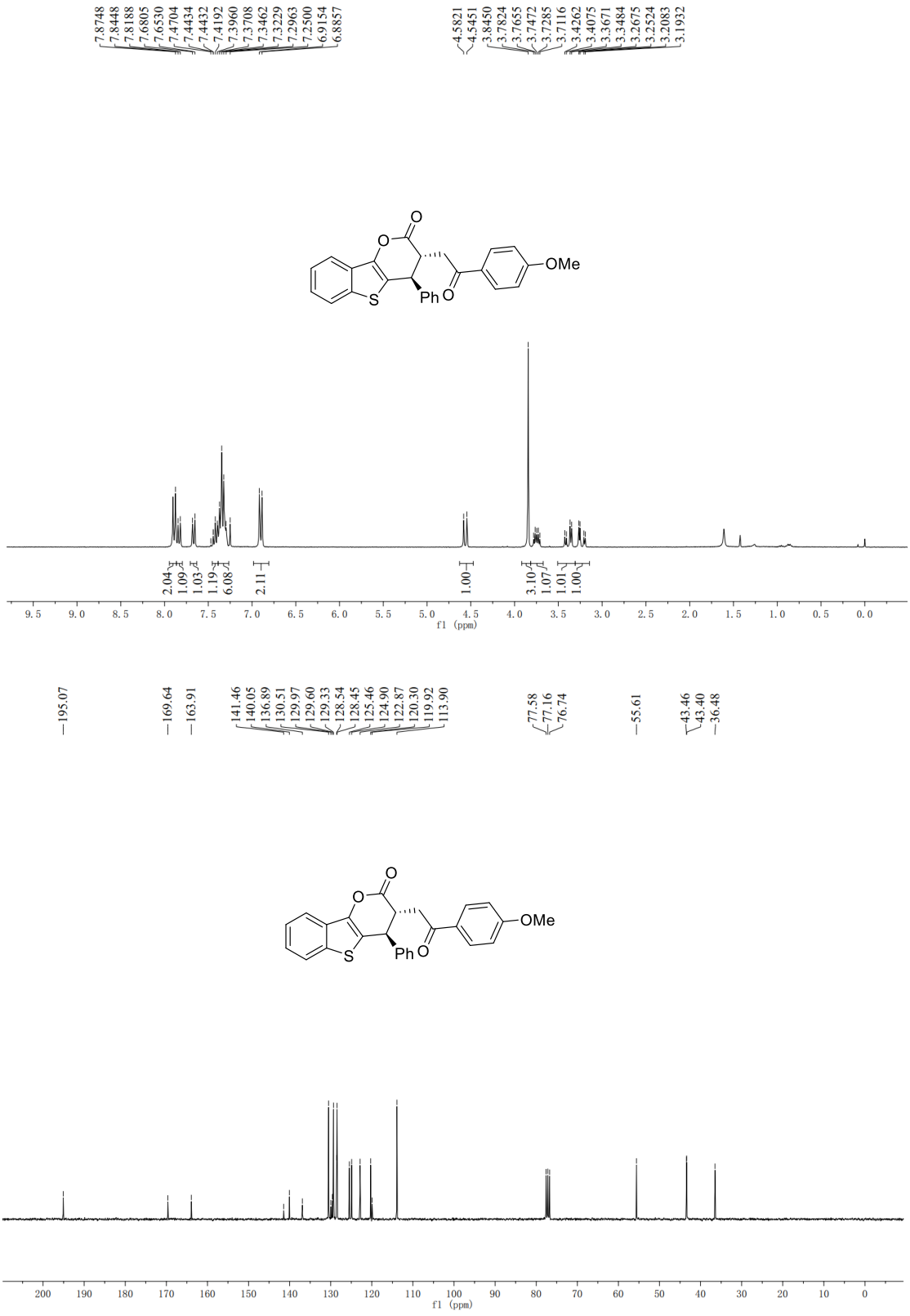
1 Det.A Ch1/254nm

PeakTable

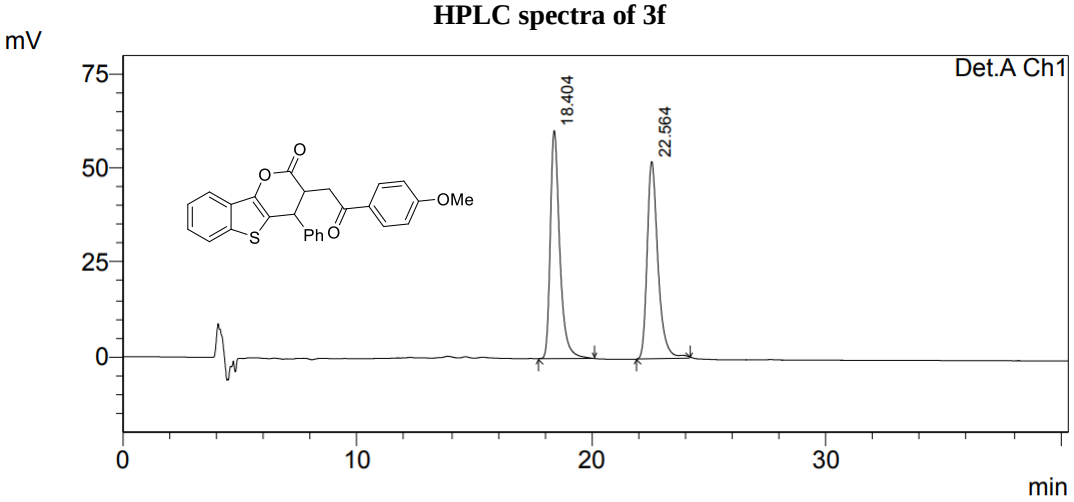
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.927	41428150	1959131	99.397
2	15.147	251175	12398	0.603
Total		41679324		100.000

^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) of 3f



HPLC spectra of 3f

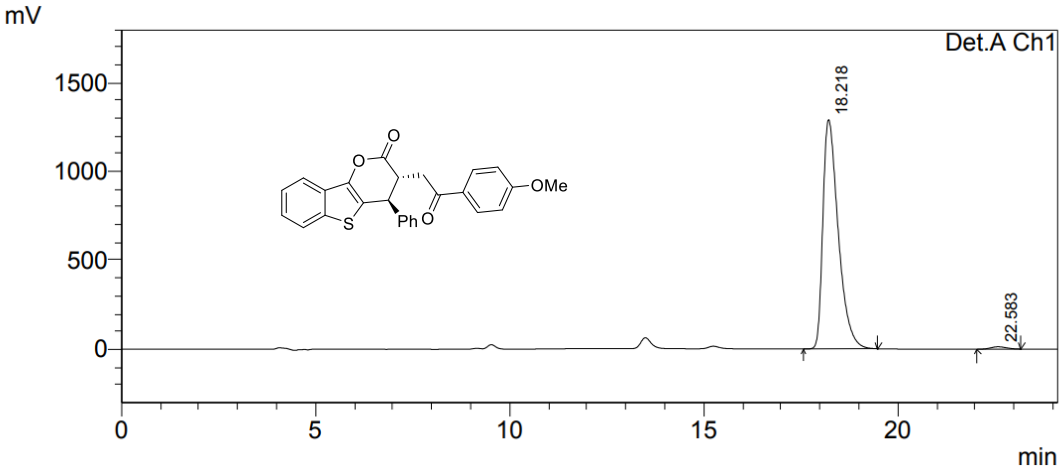


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	18.404	1689527	60437	50.085
2	22.564	1683798	52255	49.915
Total		3373325		100.000



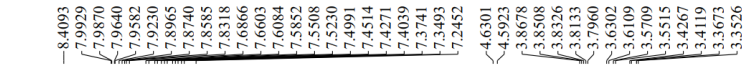
1 Det.A Ch1/254nm

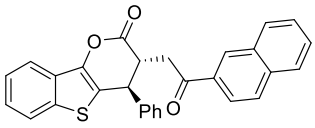
PeakTable

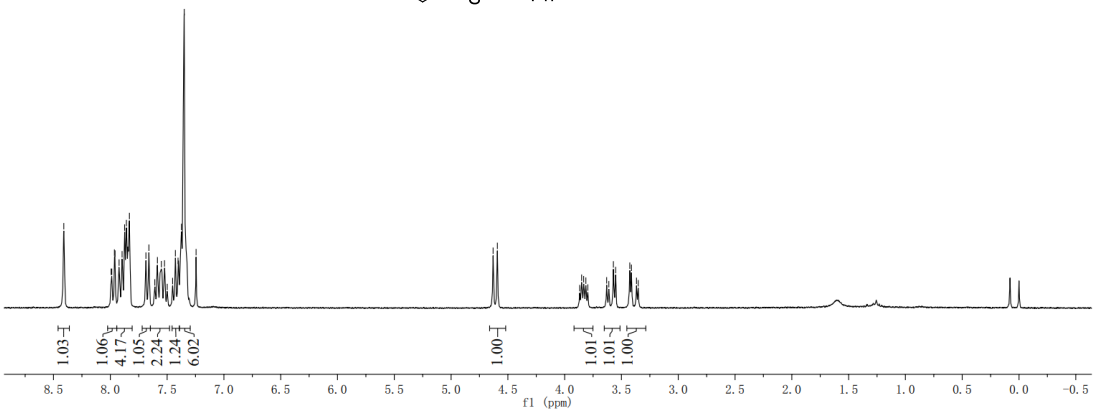
Detector A Ch1 254nm

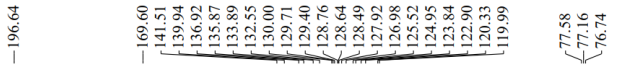
Peak#	Ret. Time	Area	Height	Area %
1	18.218	35490490	1289077	98.914
2	22.583	389648	13572	1.086
Total		35880138		100.000

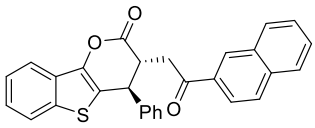
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) of 3g

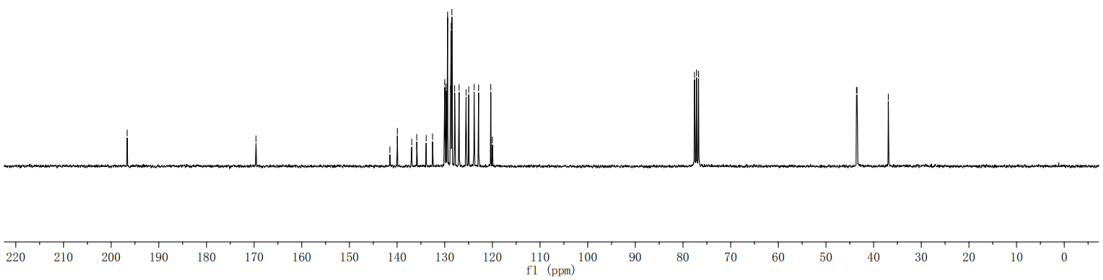




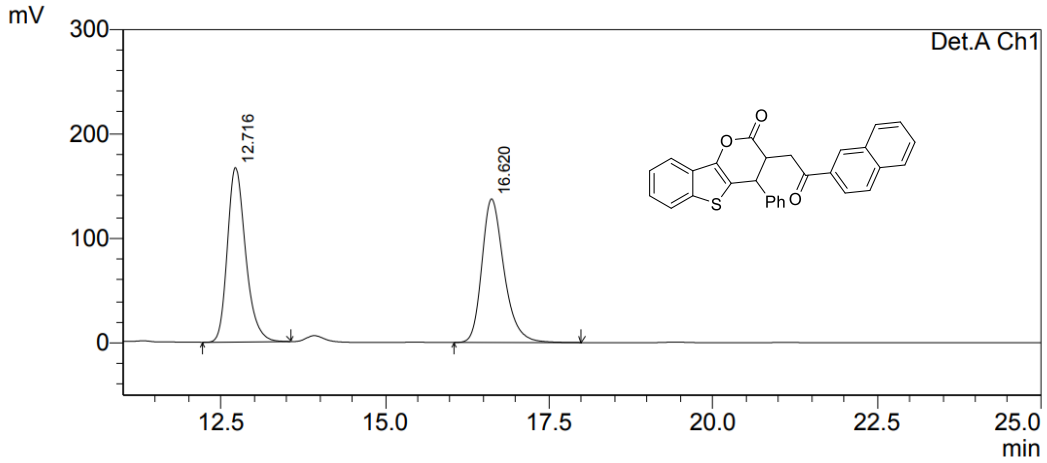








HPLC spectra of 3g

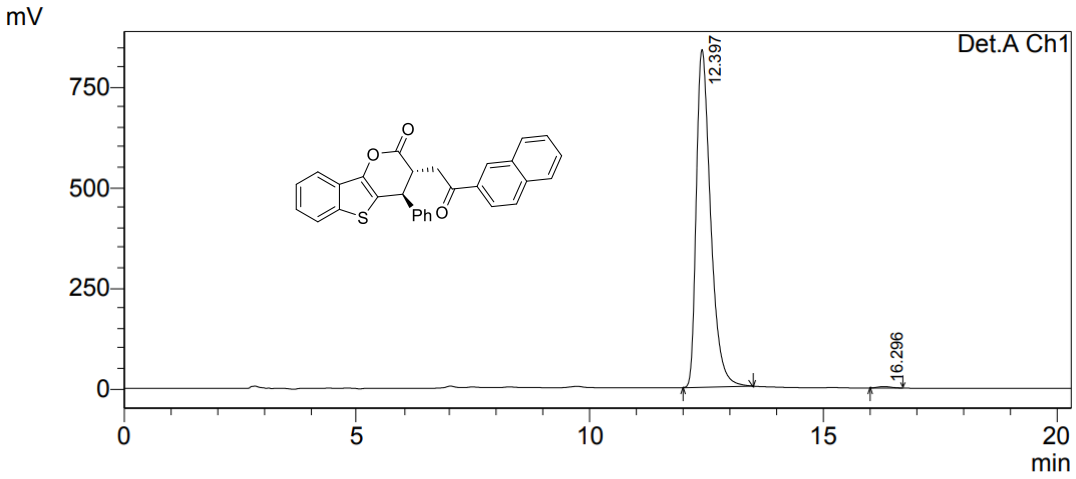


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.716	3197451	166559	49.660
2	16.620	3241279	137159	50.340
Total		6438730		100.000



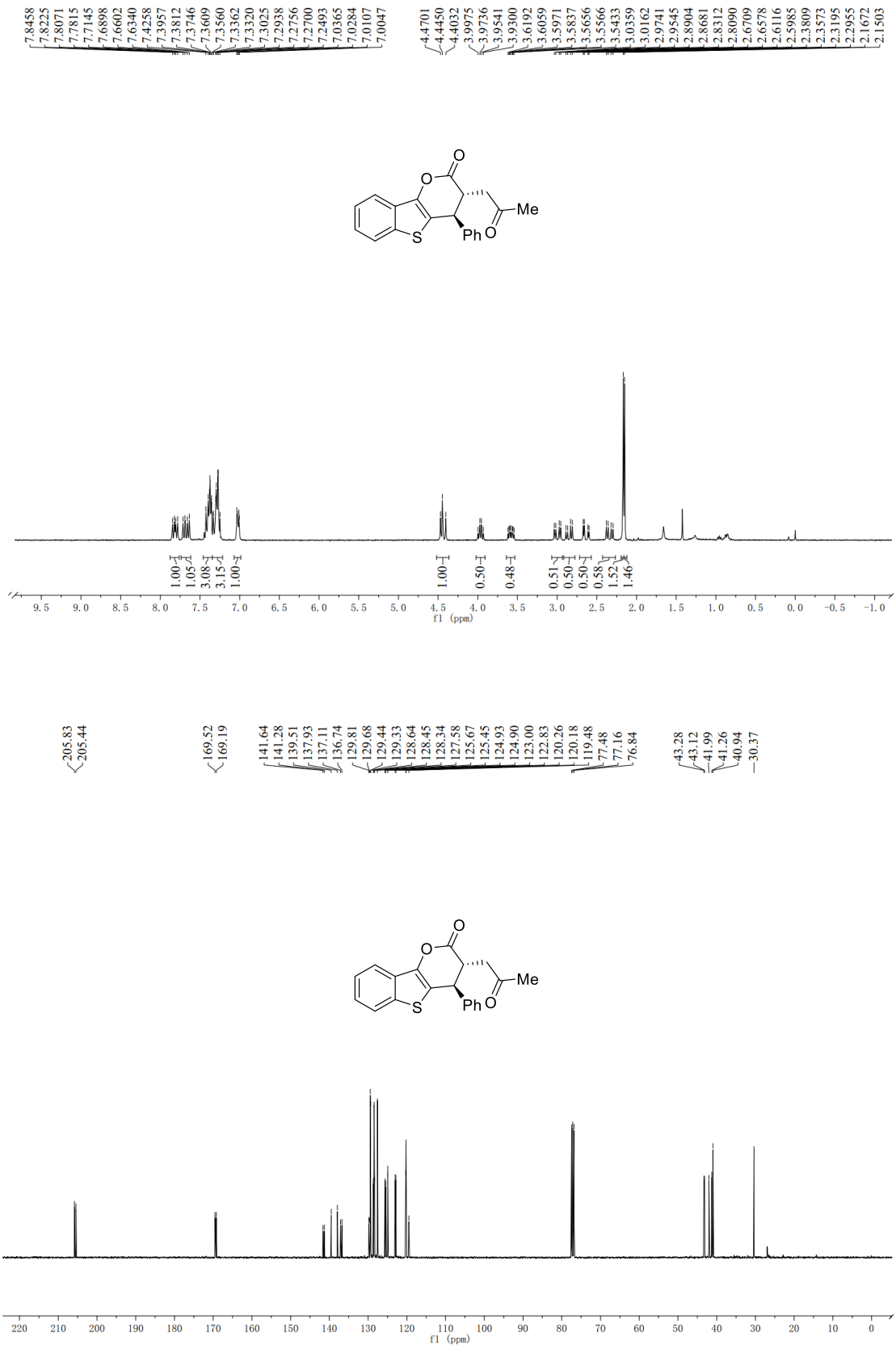
1 Det.A Ch1/254nm

PeakTable

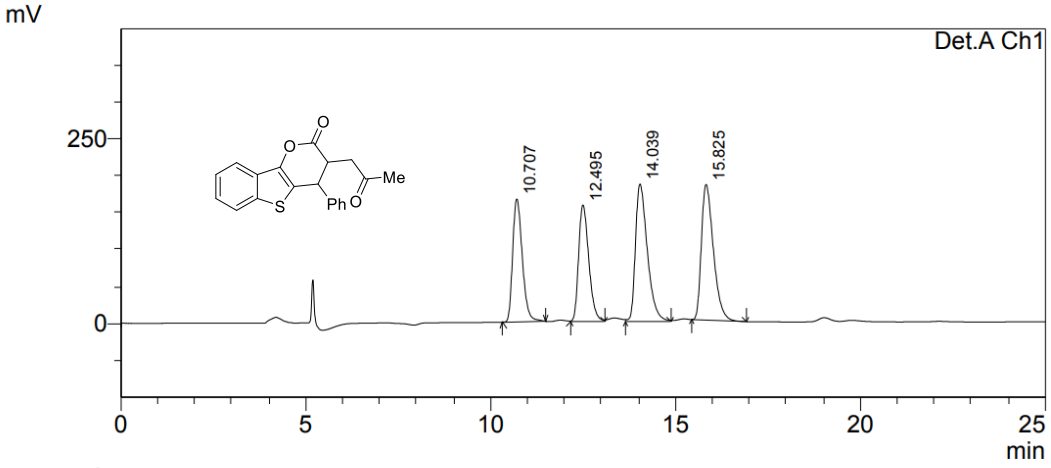
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.397	17948208	841161	99.584
2	16.296	75048	3717	0.416
Total		18023255		100.000

^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 3h



HPLC spectra of 3h

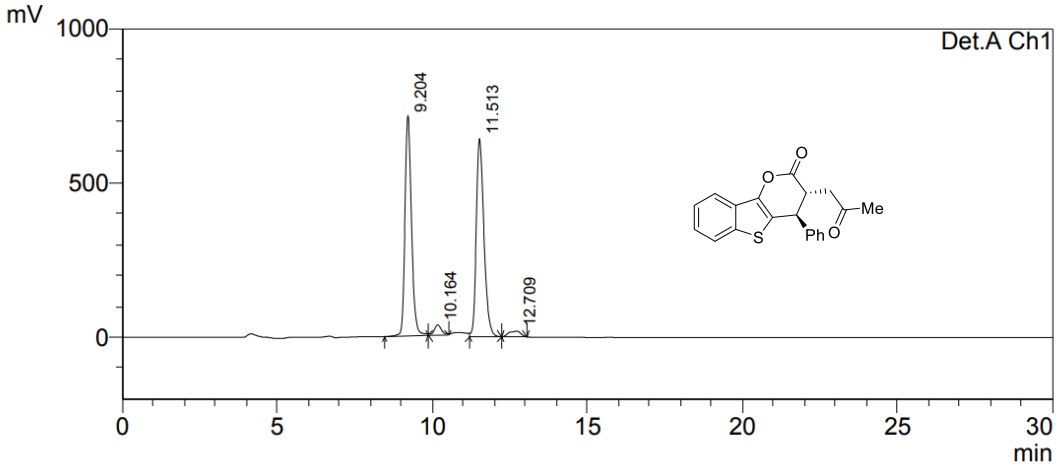


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.707	3023317	166516	21.086
2	12.495	3006277	157605	20.967
3	14.039	4160923	186100	29.020
4	15.825	4147576	183639	28.927
Total		14338093		100.000



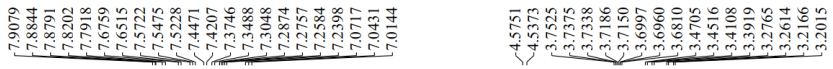
1 Det.A Ch1/254nm

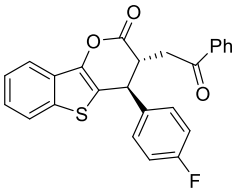
PeakTable

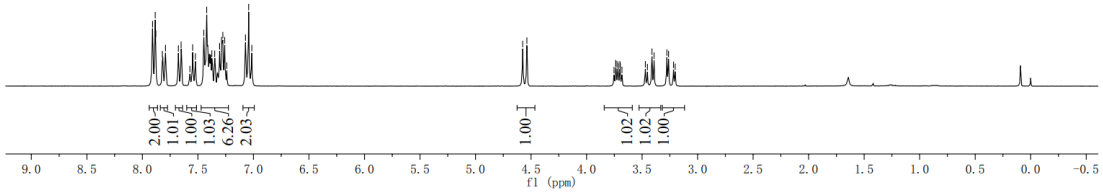
Detector A Ch1 254nm

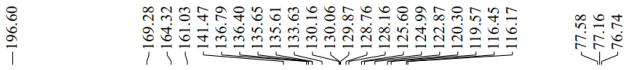
Peak#	Ret. Time	Area	Height	Area %
1	9.204	10435826	712592	46.481
2	10.164	550070	33889	2.450
3	11.513	10996159	640675	48.977
4	12.709	469672	18109	2.092
Total		22451728		100.000

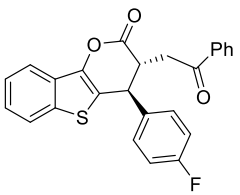
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) of 3i

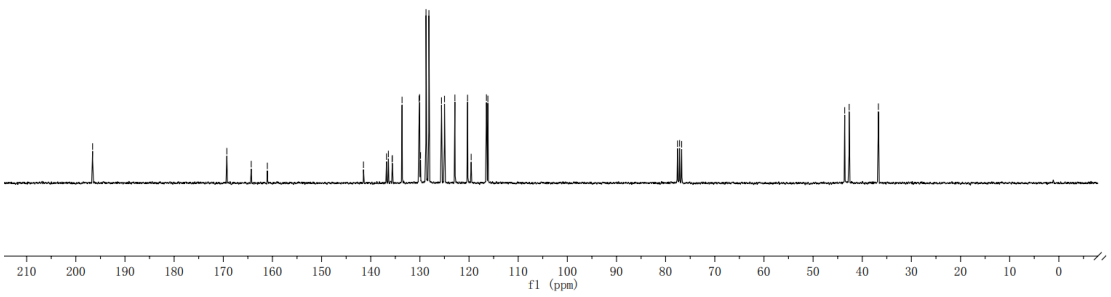




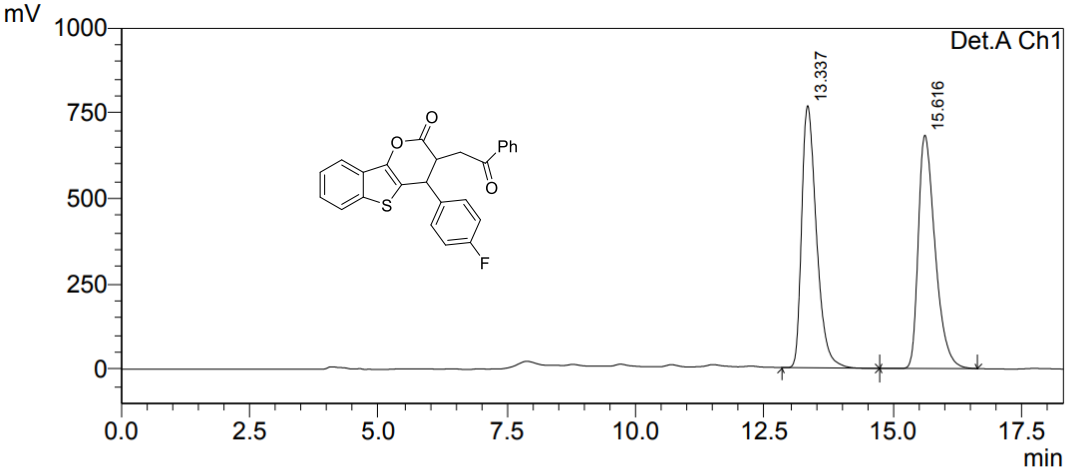








HPLC spectra of 3i

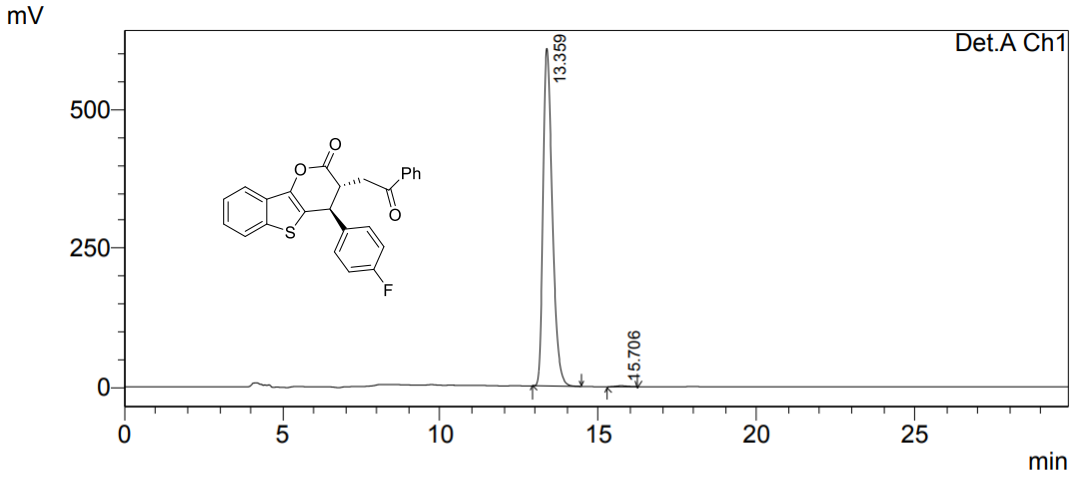


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.337	15338507	767052	49.700
2	15.616	15523949	682913	50.300
Total		30862456		100.000



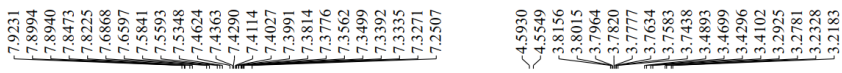
1 Det.A Ch1/254nm

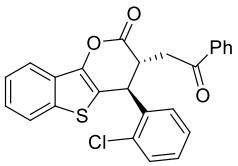
PeakTable

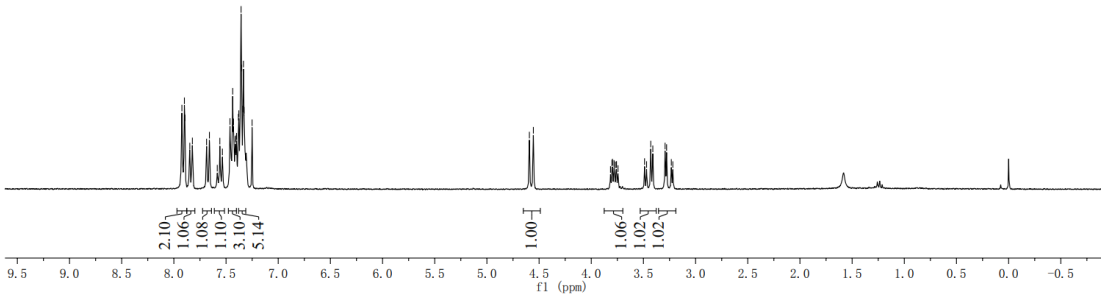
Detector A Ch1 254nm

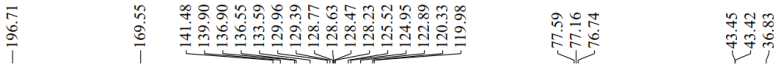
Peak#	Ret. Time	Area	Height	Area %
1	13.359	12429805	610230	99.651
2	15.706	43545	1759	0.349
Total		12473349		100.000

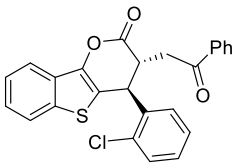
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) of 3j

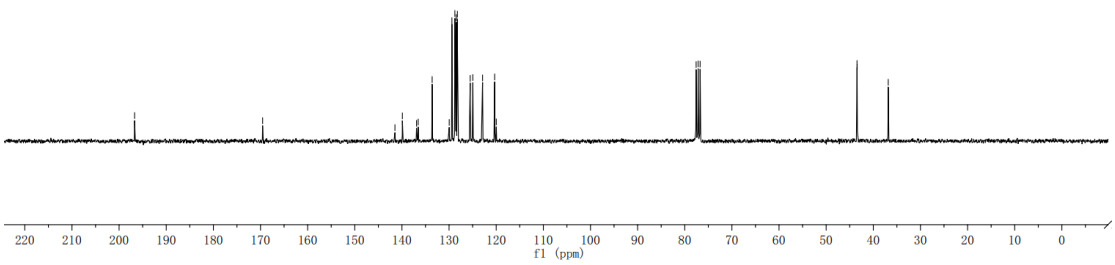




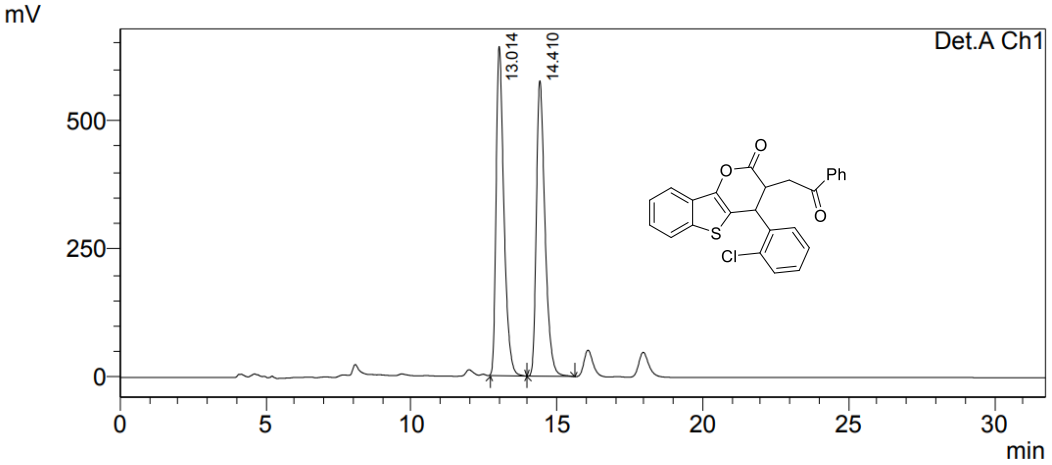








HPLC spectra of 3j

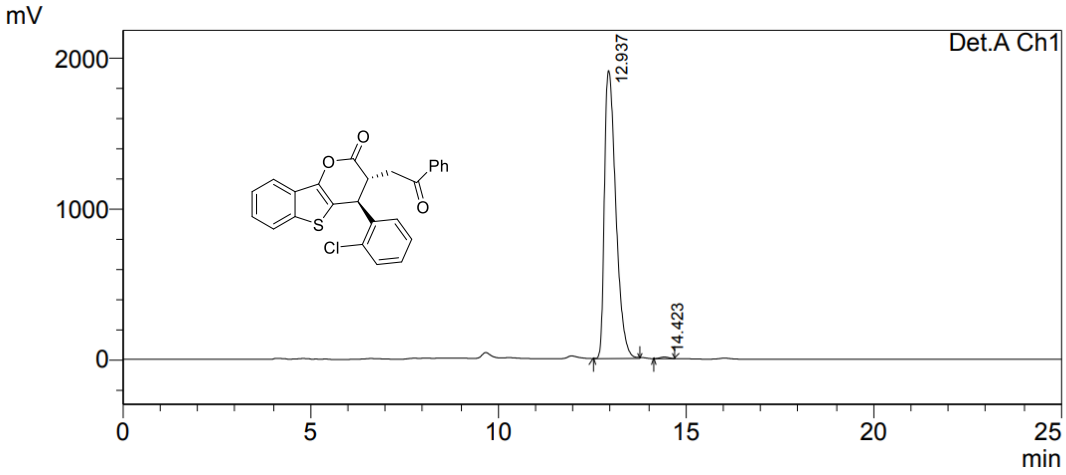


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.014	11937485	641576	50.106
2	14.410	11886875	575637	49.894
Total		23824360		100.000



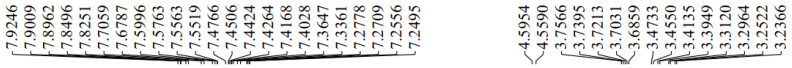
1 Det.A Ch1/254nm

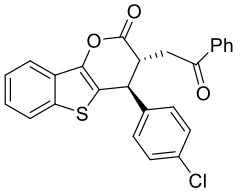
PeakTable

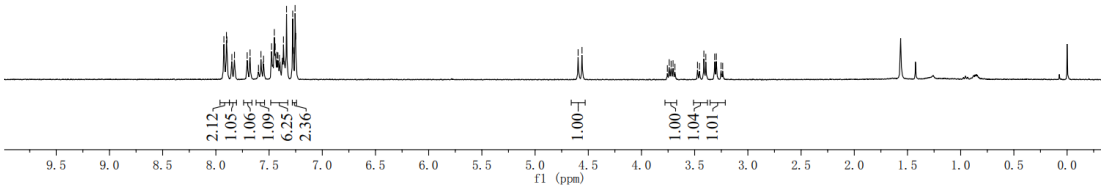
Detector A Ch1 254nm

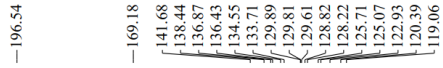
Peak#	Ret. Time	Area	Height	Area %
1	12.937	40607884	1921424	99.556
2	14.423	181180	11168	0.444
Total		40789064		100.000

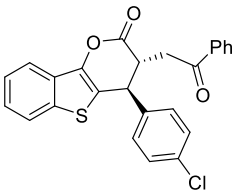
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 3k

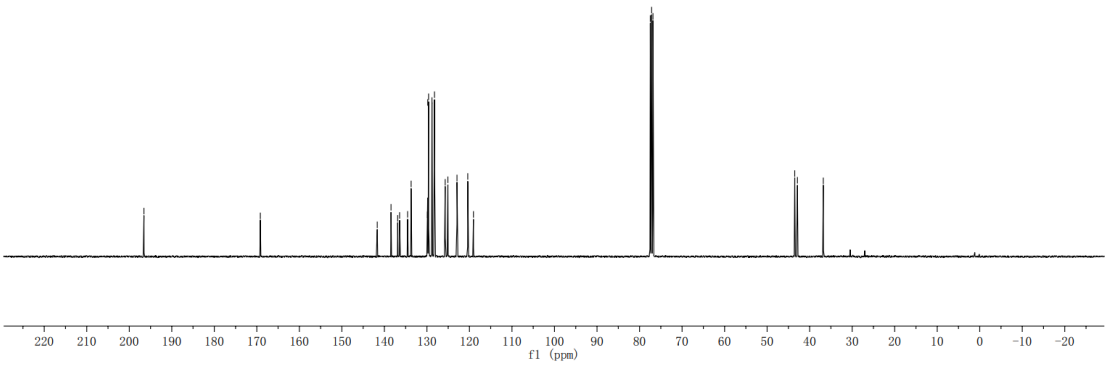




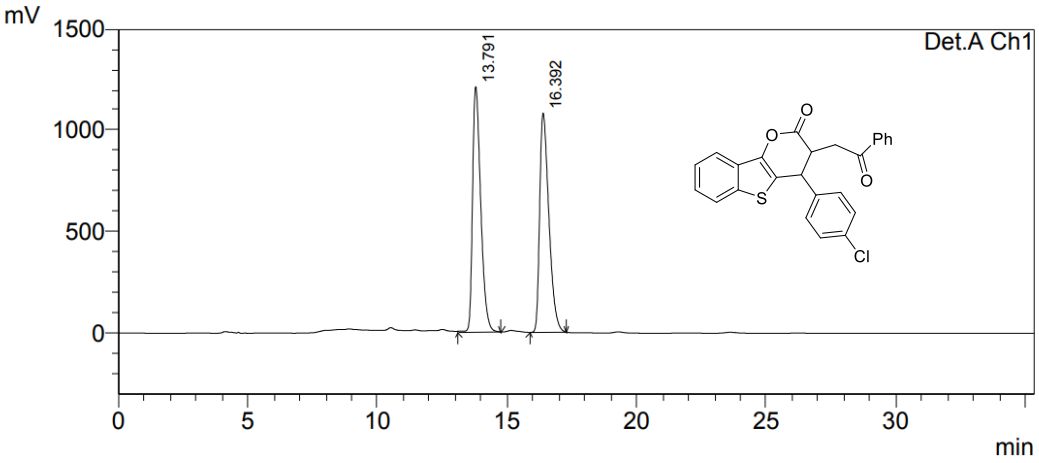








HPLC spectra of 3k

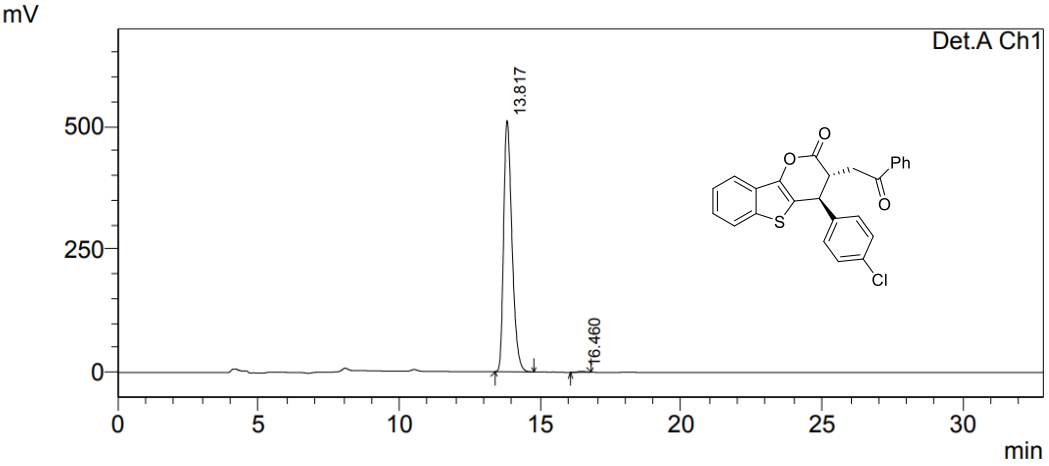


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.791	26633974	1210250	49.860
2	16.392	26783526	1080030	50.140
Total		53417499		100.000



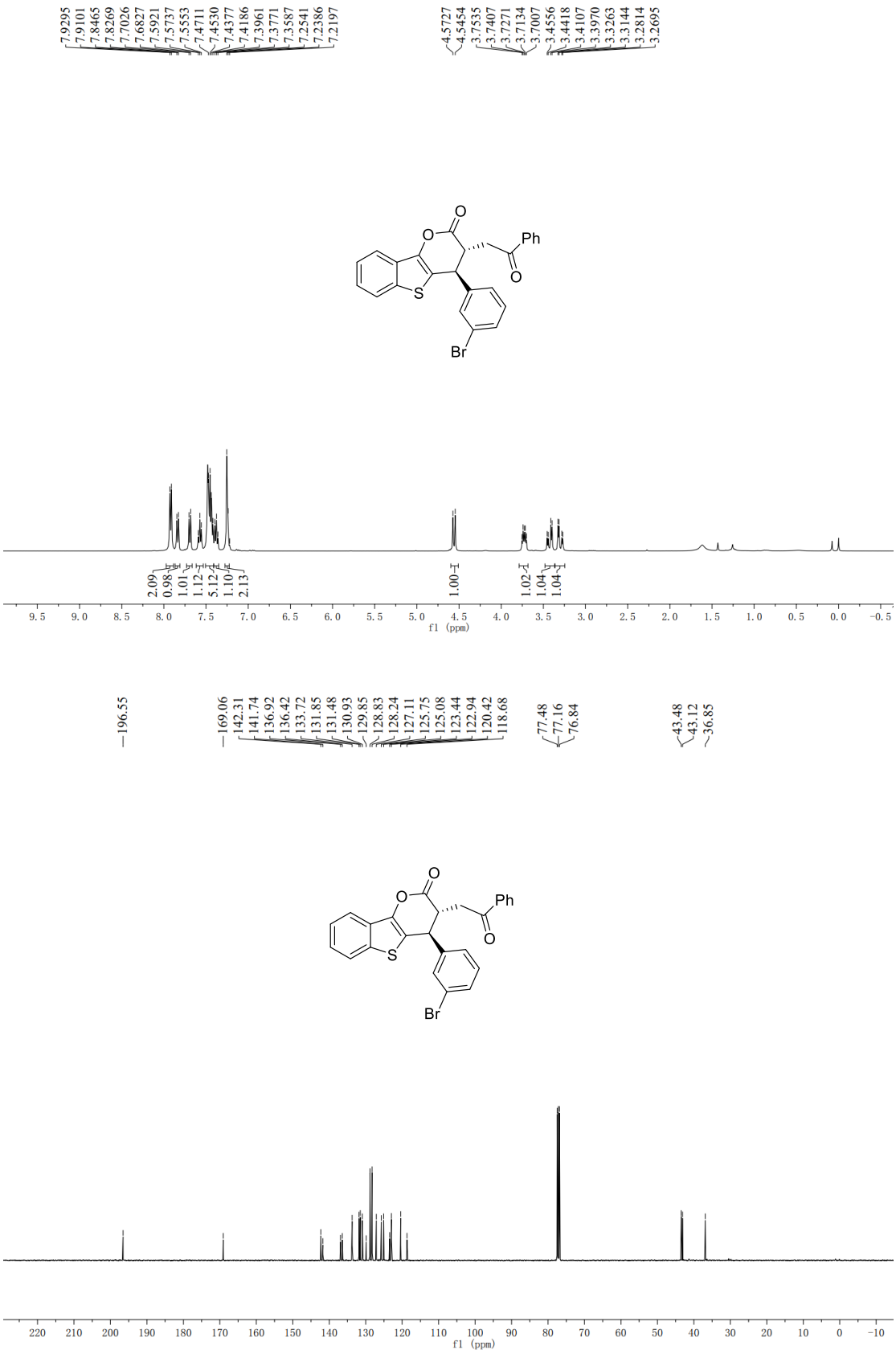
1 Det.A Ch1/254nm

PeakTable

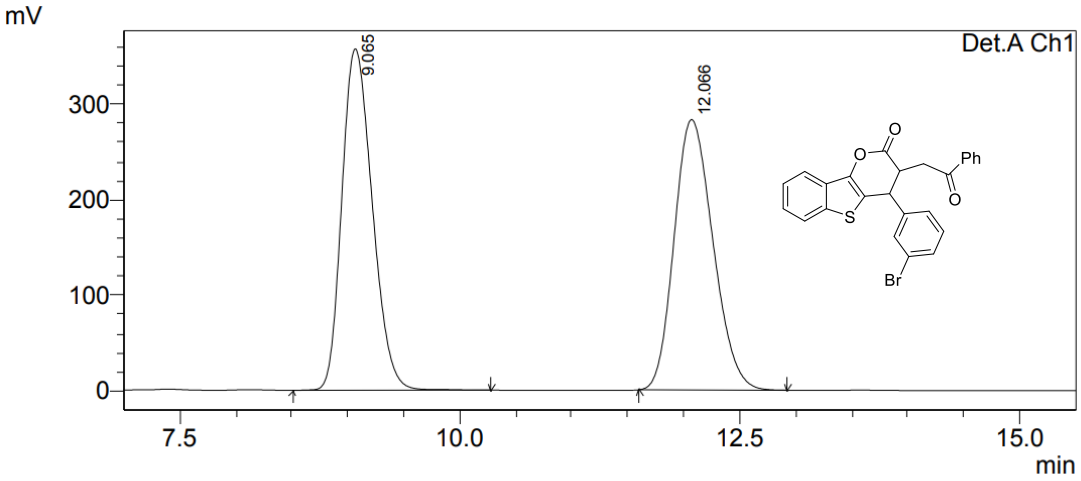
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.817	10531901	510411	99.623
2	16.460	39819	2004	0.377
Total		10571721		100.000

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 3l



HPLC spectra of 3l

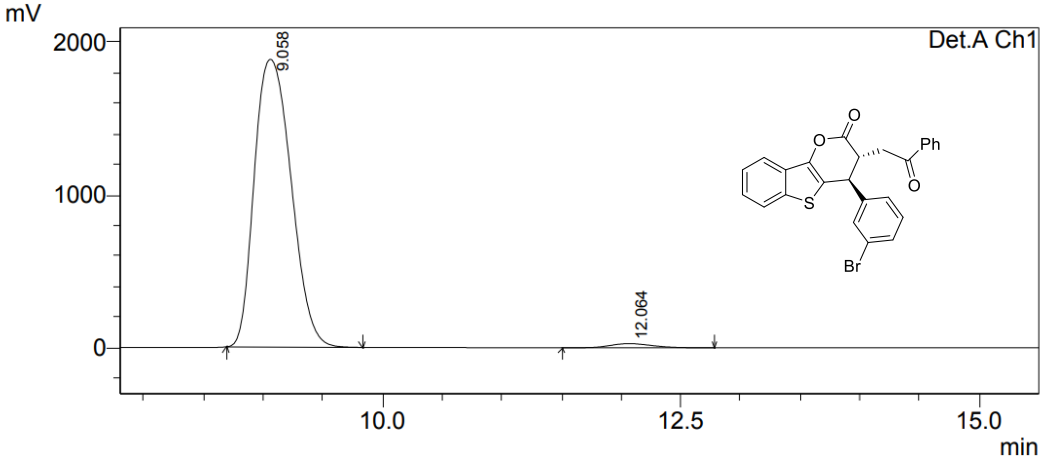


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.065	6754905	357340	49.776
2	12.066	6815701	282834	50.224
Total		13570606		100.000



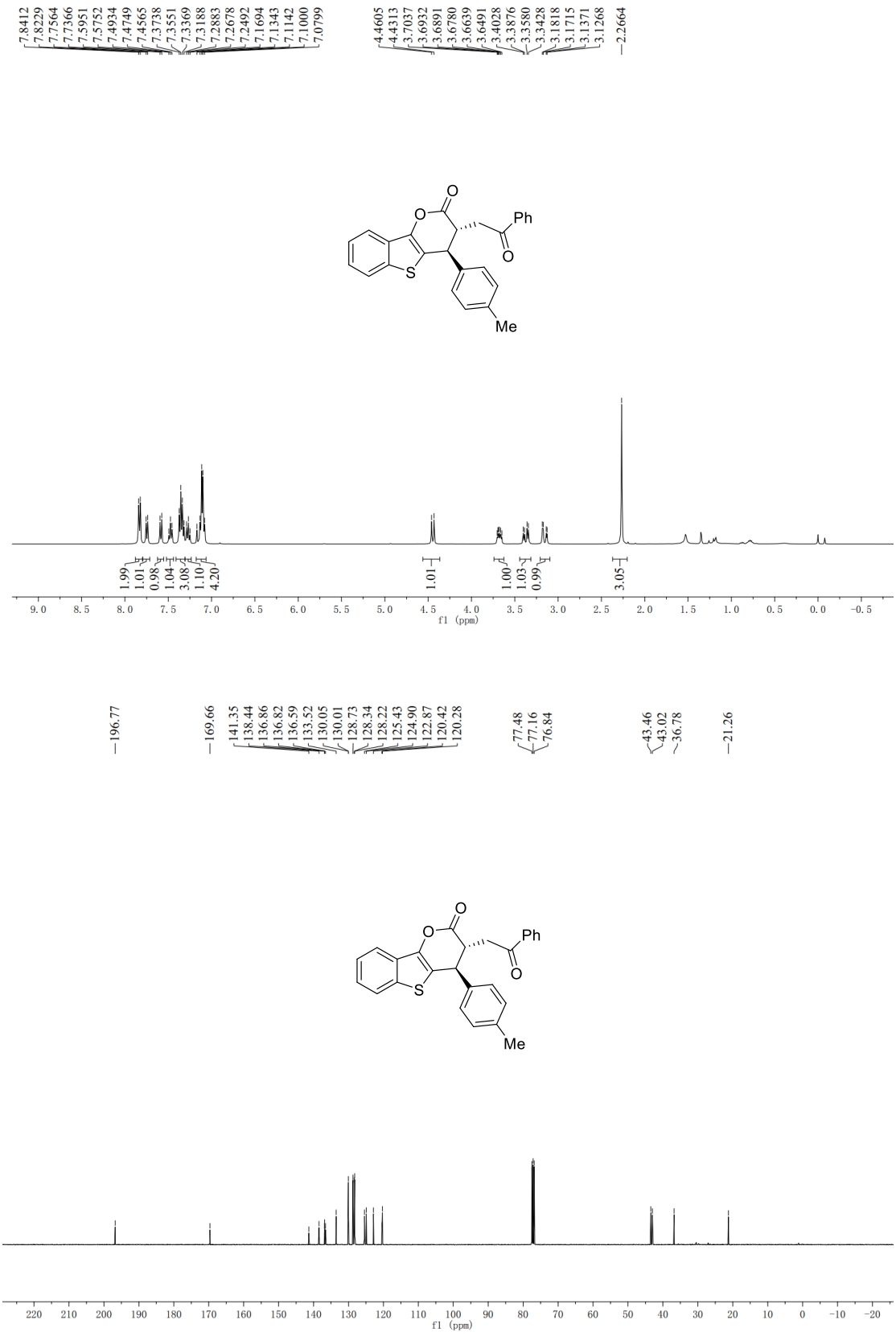
1 Det.A Ch1/254nm

PeakTable

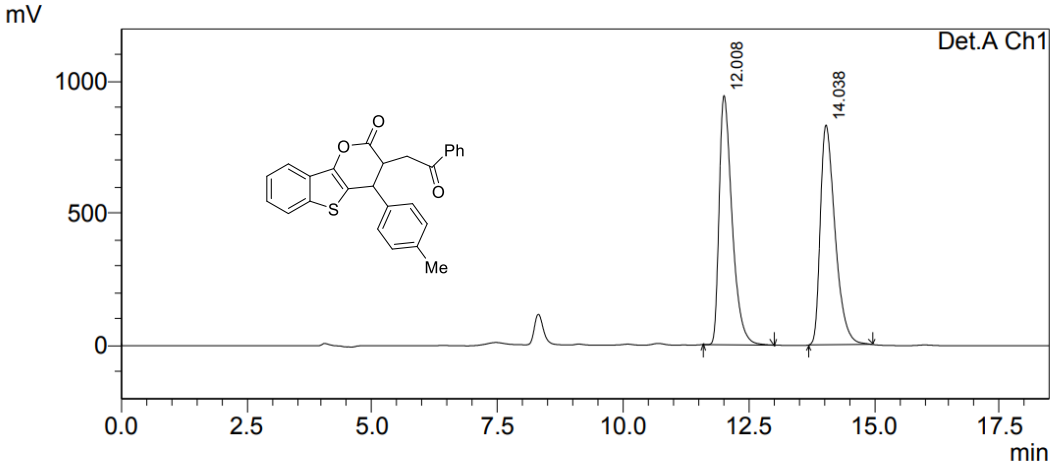
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.058	40480377	1882159	98.421
2	12.064	649615	27051	1.579
Total		41129991		100.000

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 3m



HPLC spectra of 3m

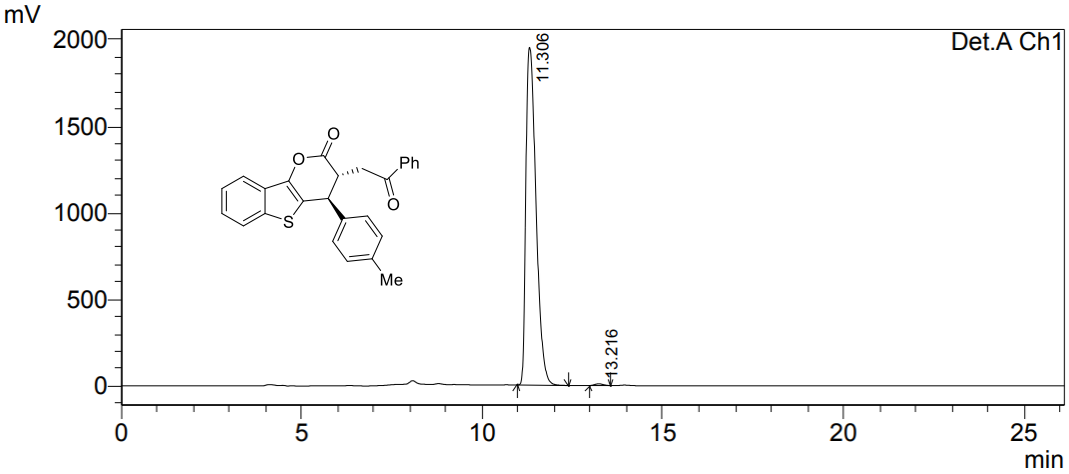


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.008	16845620	941347	49.761
2	14.038	17007348	830290	50.239
Total		33852968		100.000



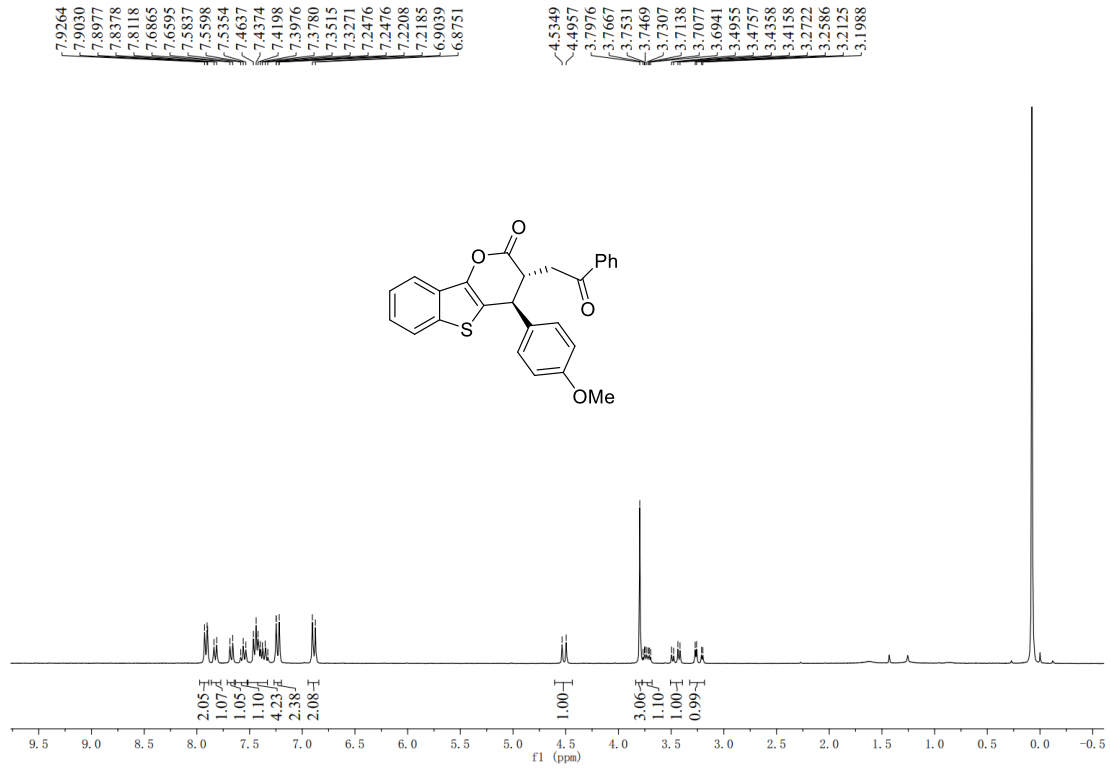
1 Det.A Ch1/254nm

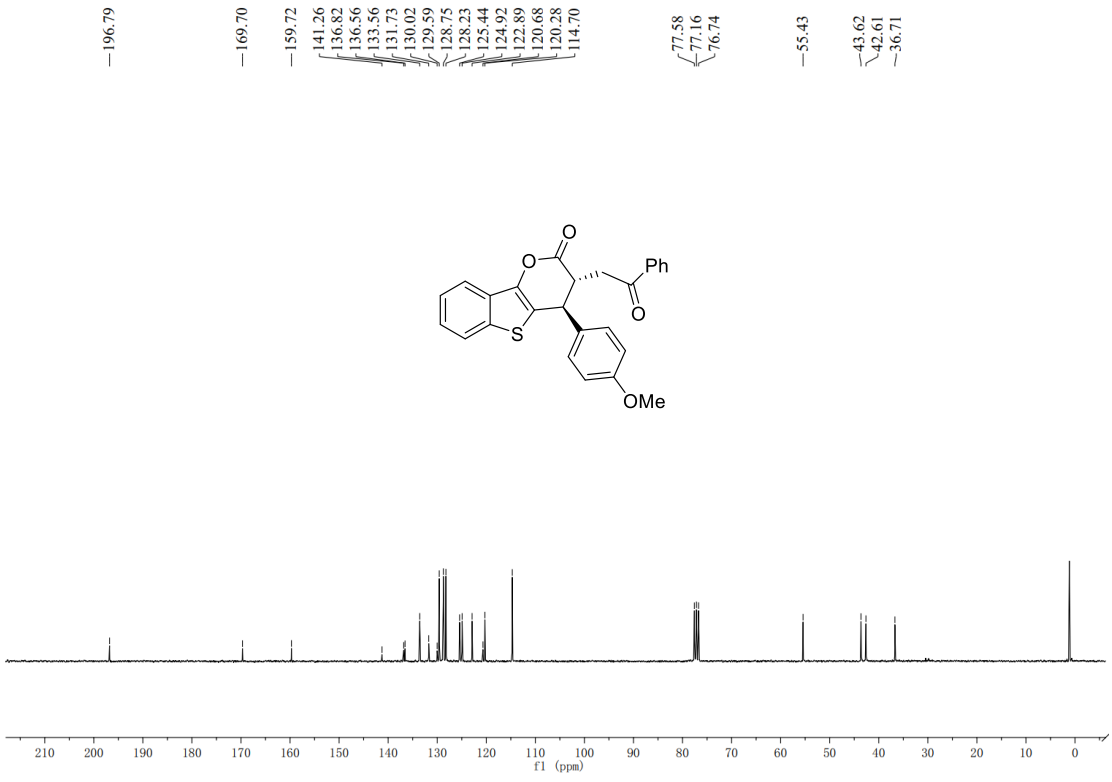
PeakTable

Detector A Ch1 254nm

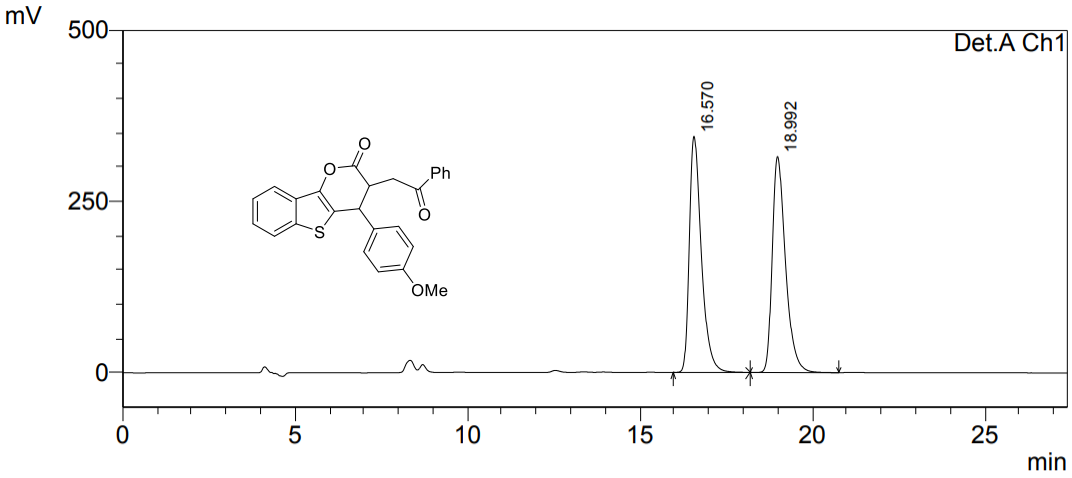
Peak#	Ret. Time	Area	Height	Area %
1	11.306	38106474	1952505	99.564
2	13.216	166946	10165	0.436
Total		38273419		100.000

^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) of 3n





HPLC spectra of 3n

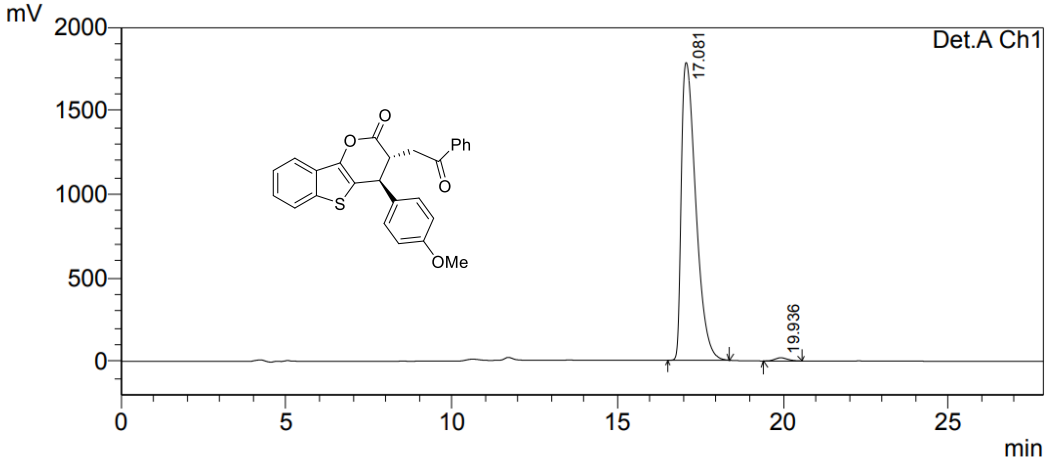


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.570	8364986	343766	49.733
2	18.992	8454933	314617	50.267
Total		16819919		100.000



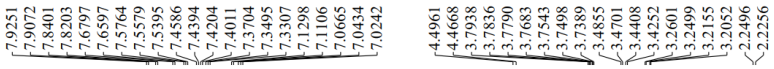
1 Det.A Ch1/254nm

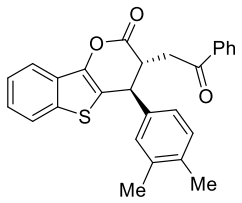
PeakTable

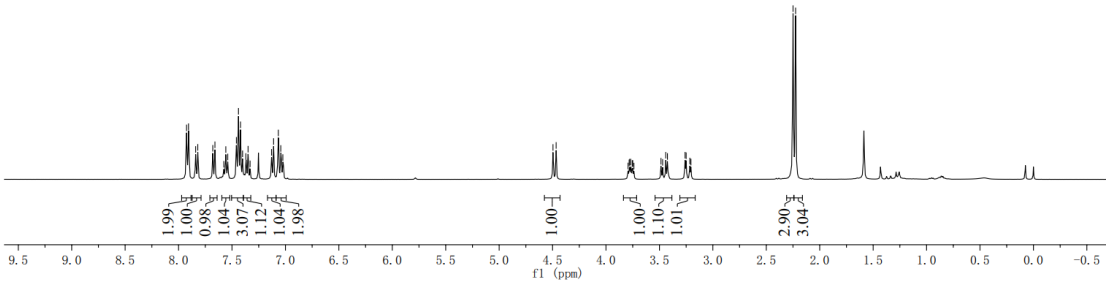
Detector A Ch1 254nm

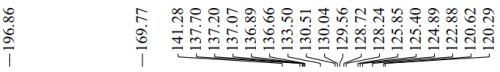
Peak#	Ret. Time	Area	Height	Area %
1	17.081	53738096	1779074	99.077
2	19.936	500470	19034	0.923
Total		54238566		100.000

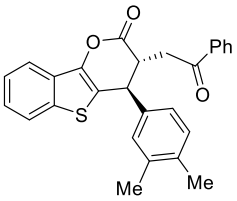
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 3o

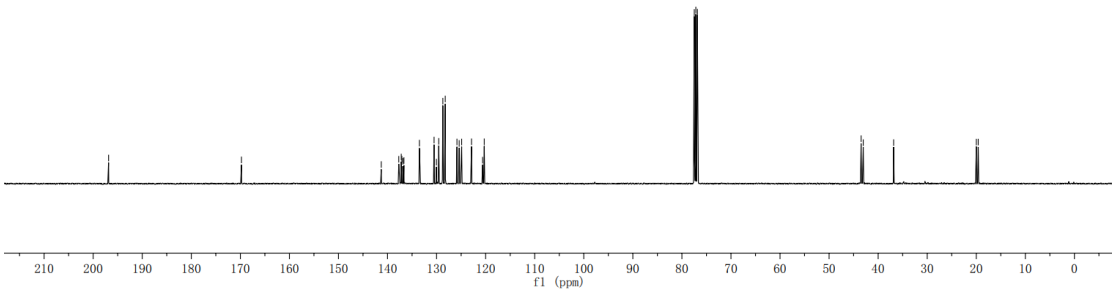




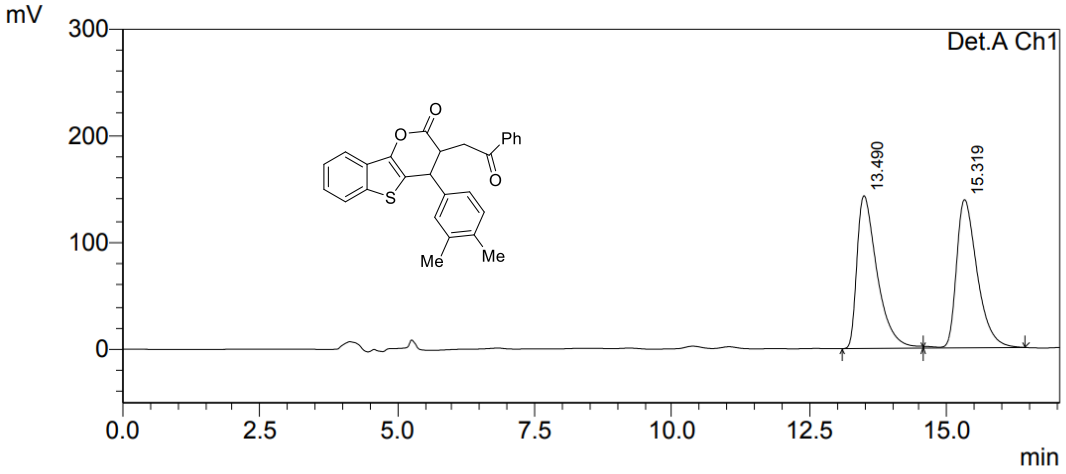








HPLC spectra of 3o

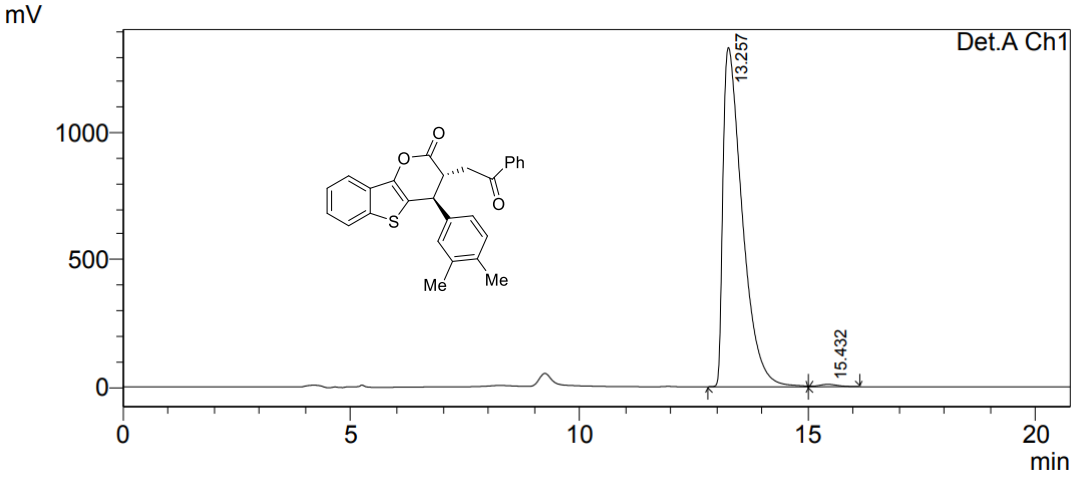


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.490	3650379	142878	50.032
2	15.319	3645672	138672	49.968
Total		7296051		100.000



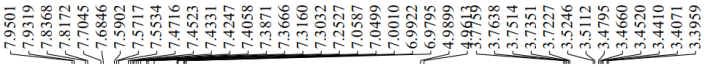
1 Det.A Ch1/254nm

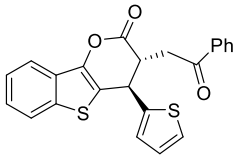
PeakTable

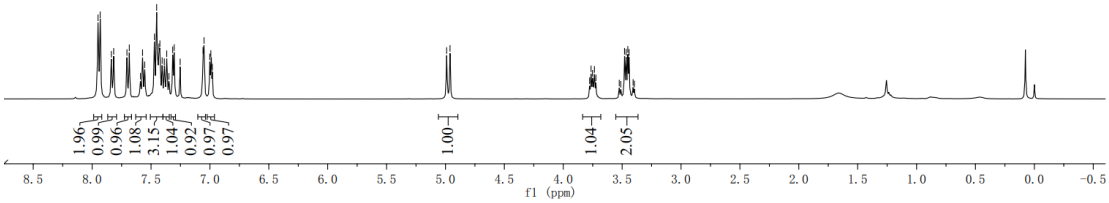
Detector A Ch1 254nm

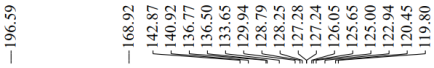
Peak#	Ret. Time	Area	Height	Area %
1	13.257	39356719	1336143	99.308
2	15.432	274297	9416	0.692
Total		39631016		100.000

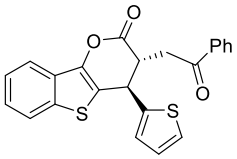
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 3p

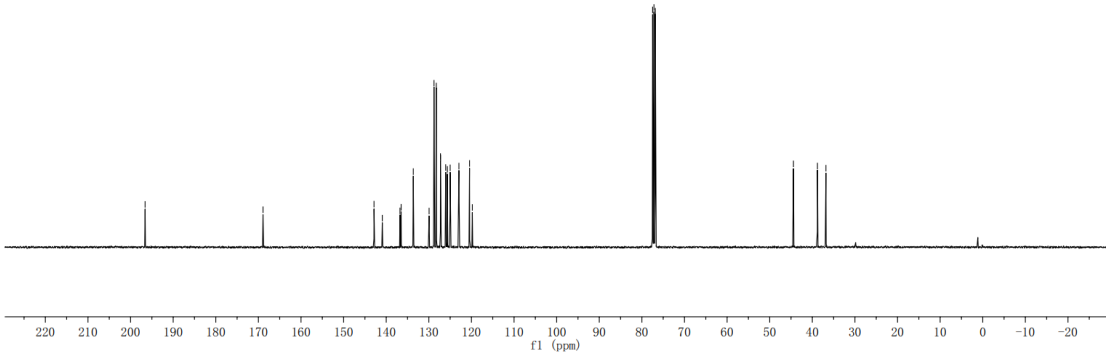




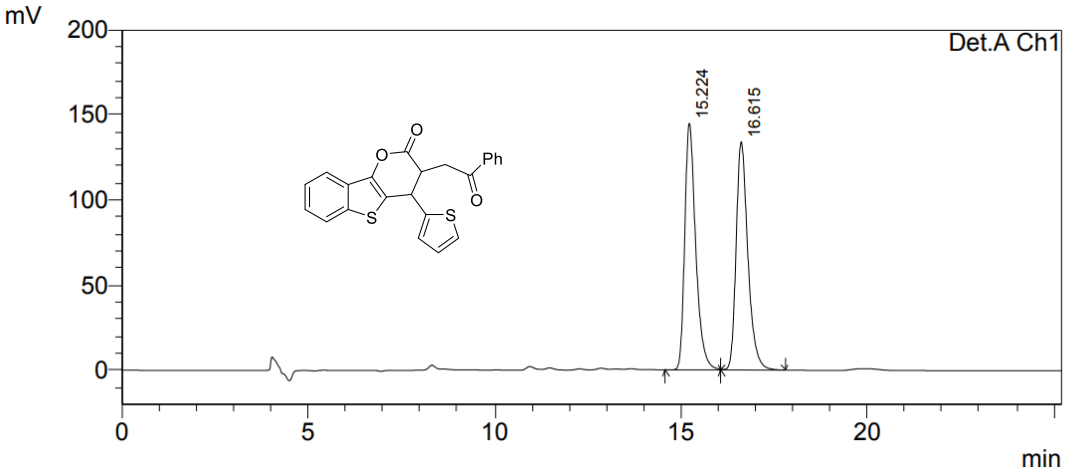








HPLC spectra of 3p

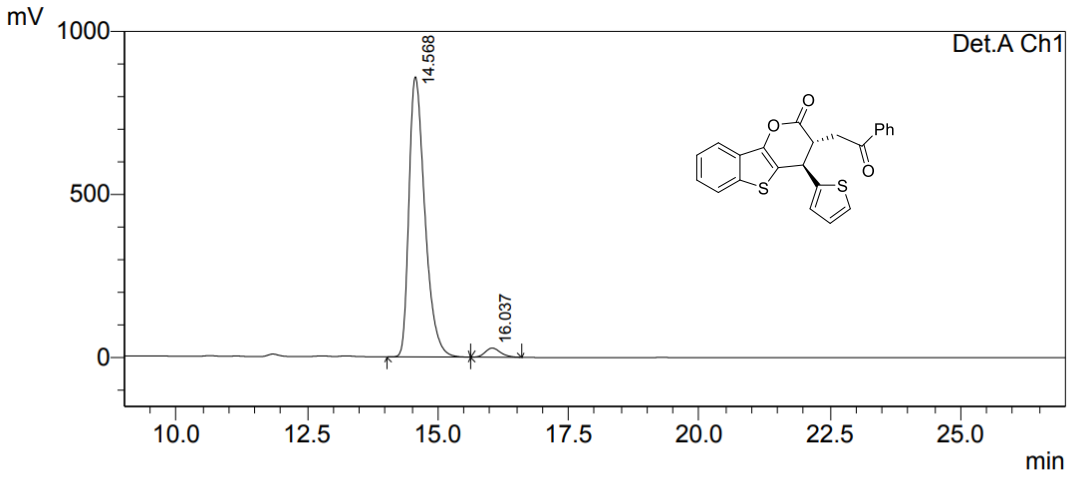


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	15.224	2962293	144720	50.177
2	16.615	2941393	133927	49.823
Total		5903686		100.000



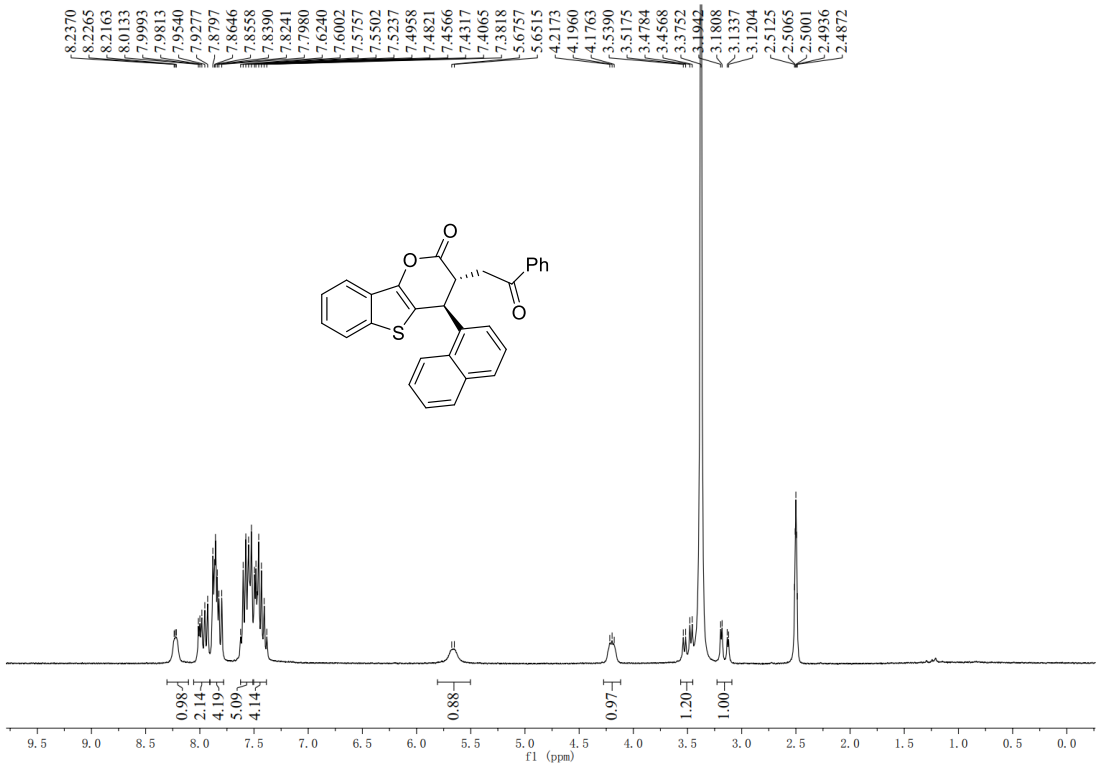
1 Det.A Ch1/254nm

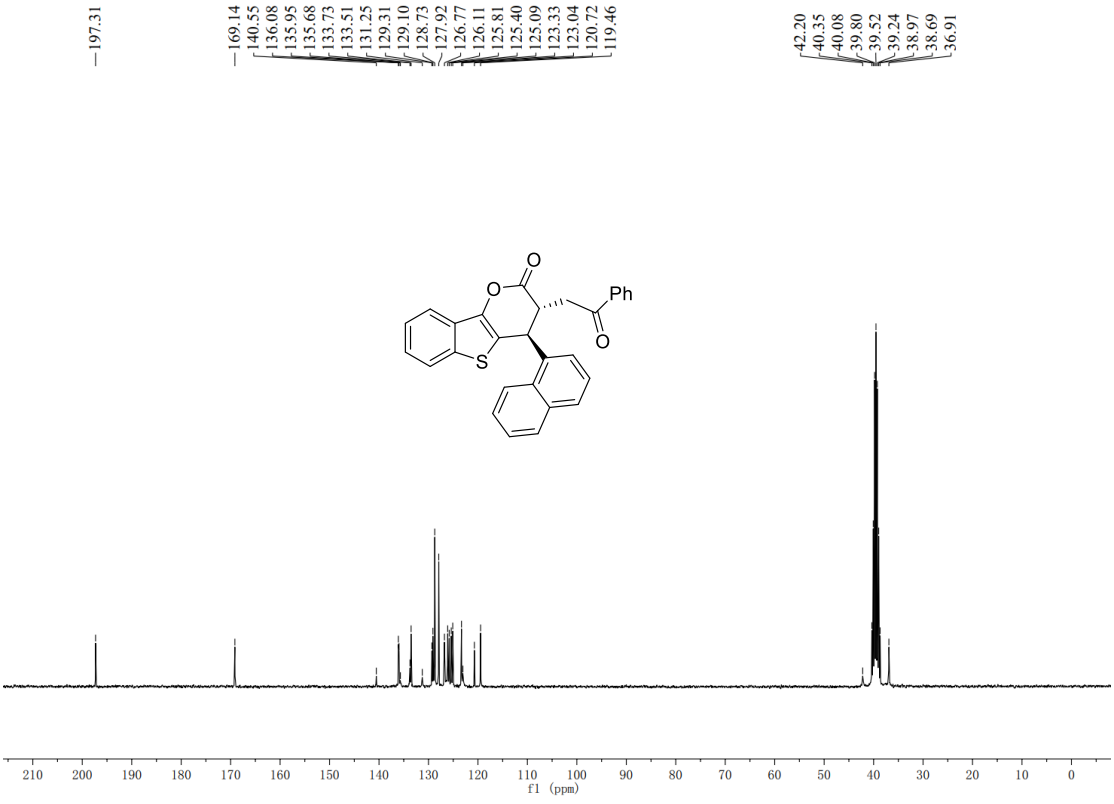
PeakTable

Detector A Ch1 254nm

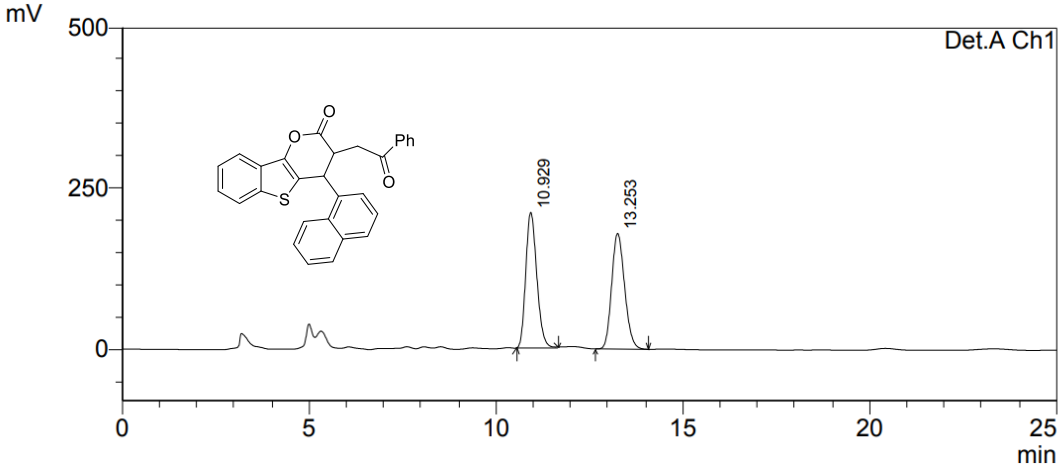
Peak#	Ret. Time	Area	Height	Area %
1	14.568	18093110	856859	96.932
2	16.037	572747	27962	3.068
Total		18665857		100.000

^{1}H NMR (300 MHz, DMSO-d_6) and ^{13}C NMR (75 MHz, DMSO-d_6) of 3q





HPLC spectra of 3q

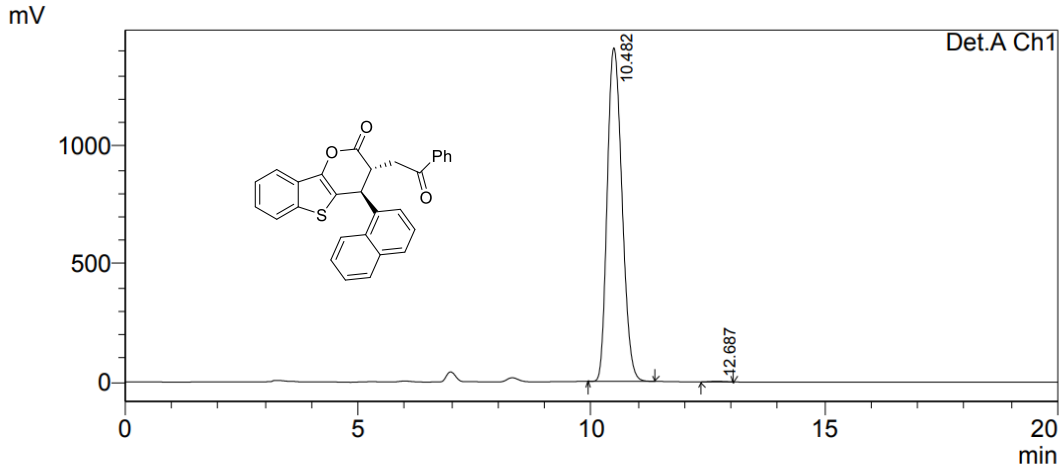


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.929	4349125	211072	50.060
2	13.253	4338645	179880	49.940
Total		8687769		100.000



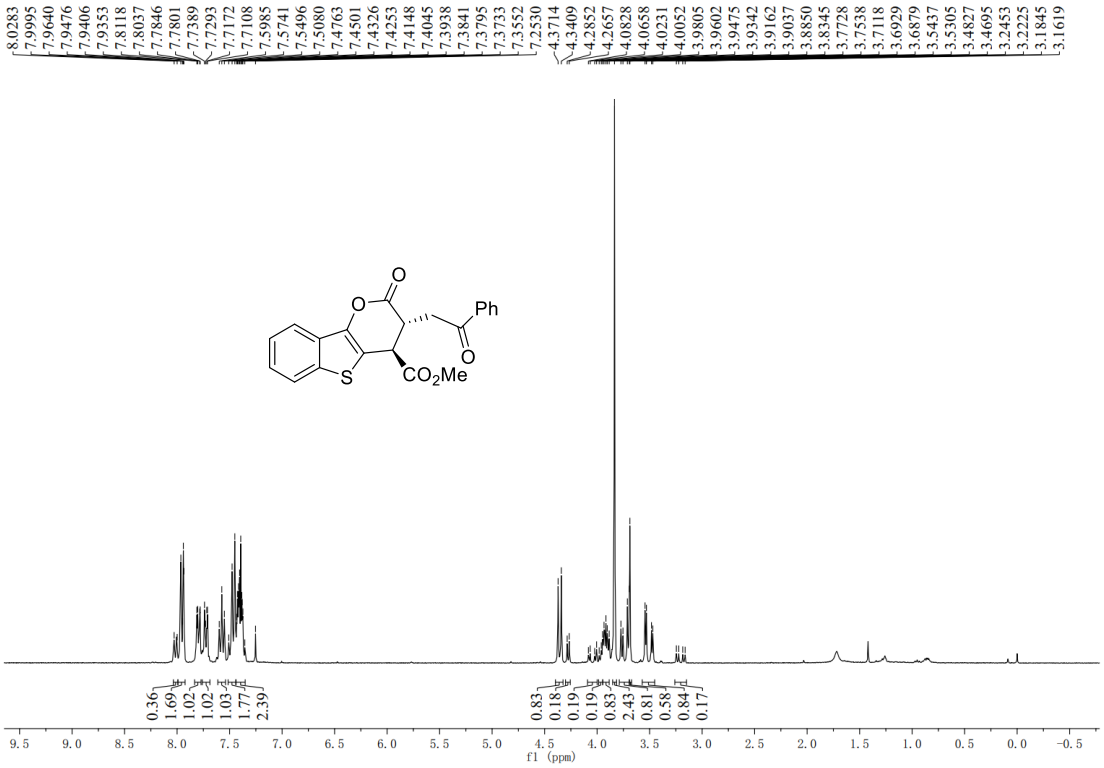
1 Det.A Ch1/254nm

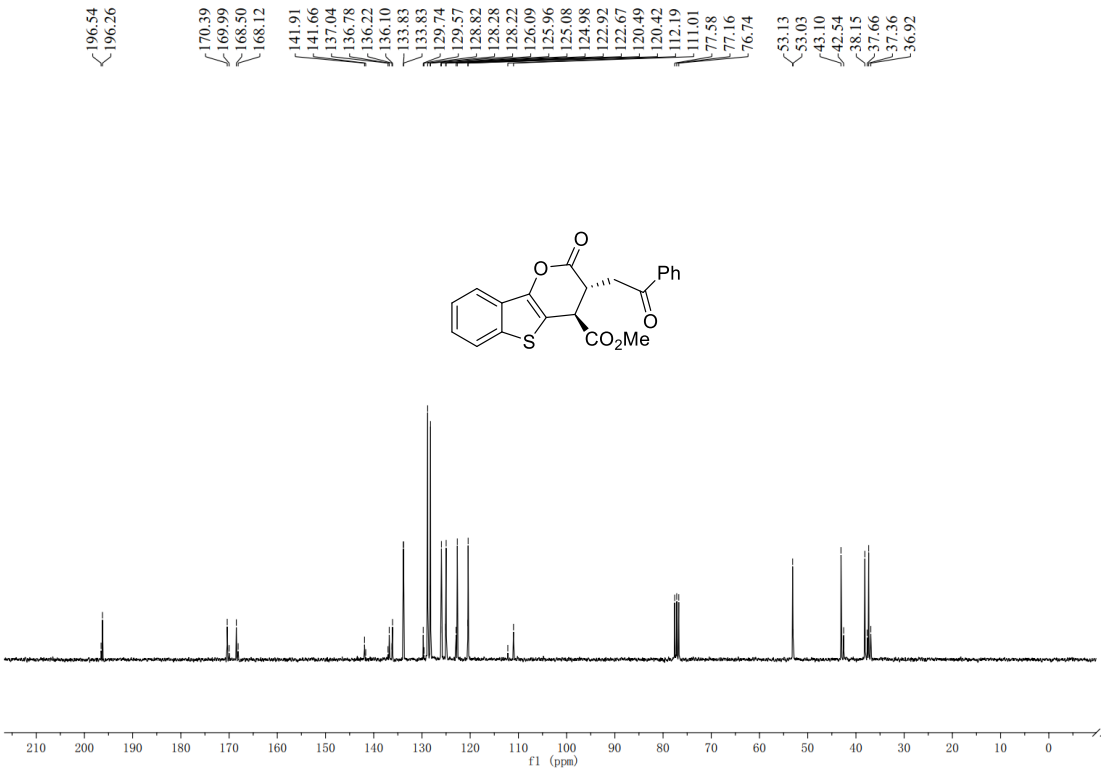
PeakTable

Detector A Ch1 254nm

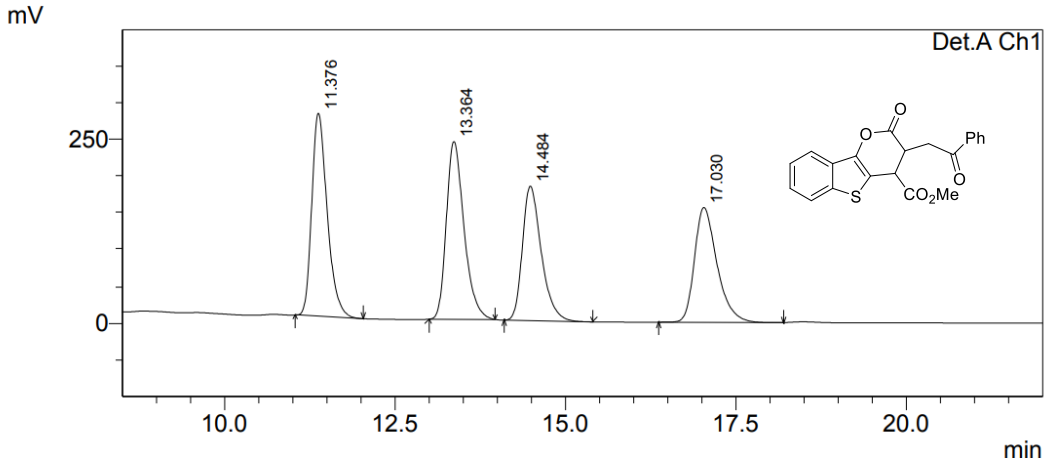
Peak#	Ret. Time	Area	Height	Area %
1	10.482	31132246	1414701	99.820
2	12.687	56140	2623	0.180
Total		31188386		100.000

^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) of 3r





HPLC spectra of 3r

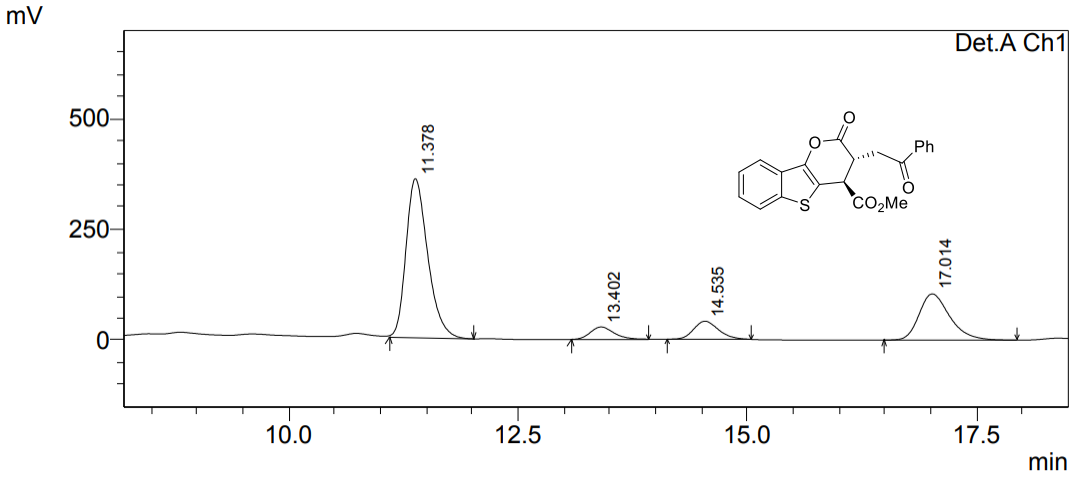


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.376	4338540	275611	27.396
2	13.364	4370141	241835	27.596
3	14.484	3534034	183083	22.316
4	17.030	3593497	156086	22.692
Total		15836212		100.000



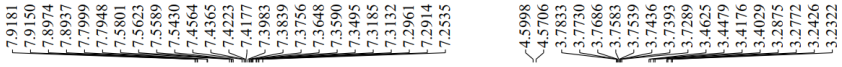
1 Det.A Ch1/254nm

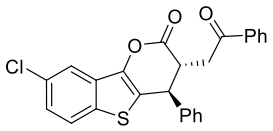
PeakTable

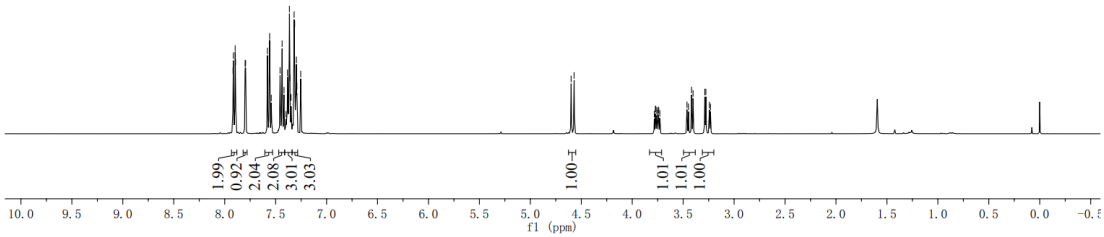
Detector A Ch1 254nm

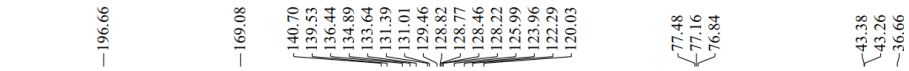
Peak#	Ret. Time	Area	Height	Area %
1	11.378	5924481	358233	61.585
2	13.402	510775	28019	5.310
3	14.535	760242	40560	7.903
4	17.014	2424525	104026	25.203
Total		9620022		100.000

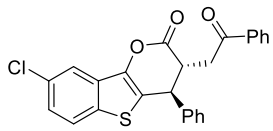
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 3s

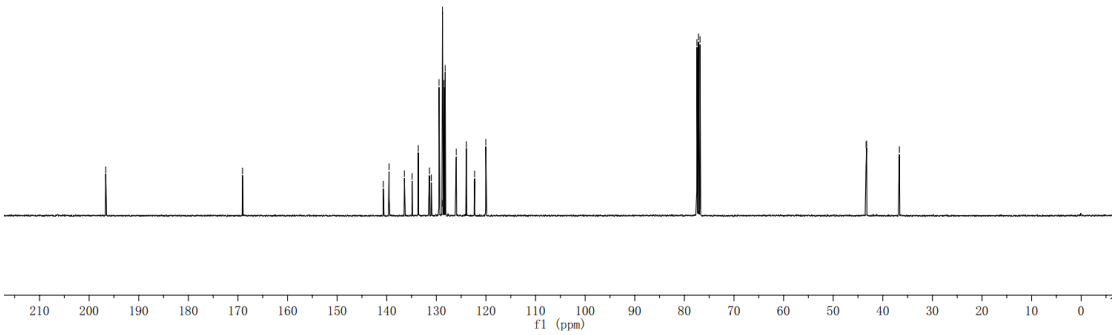




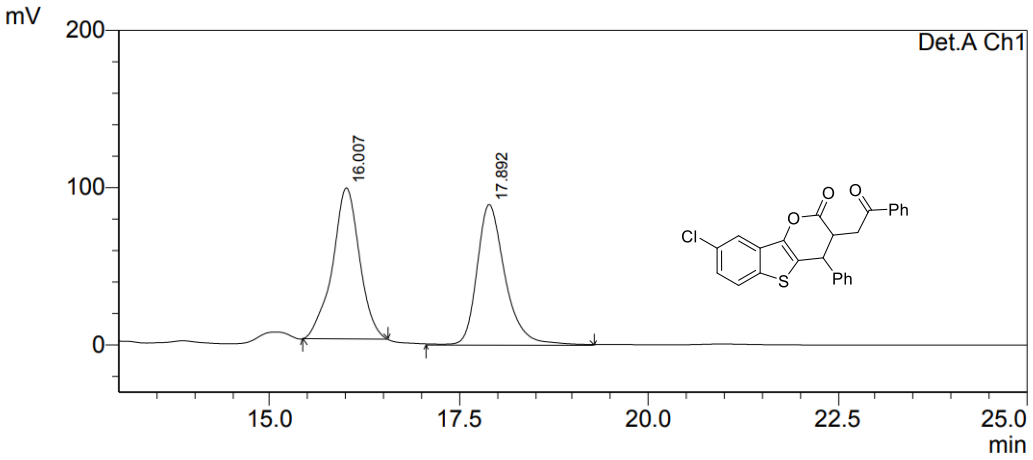








HPLC spectra of 3s

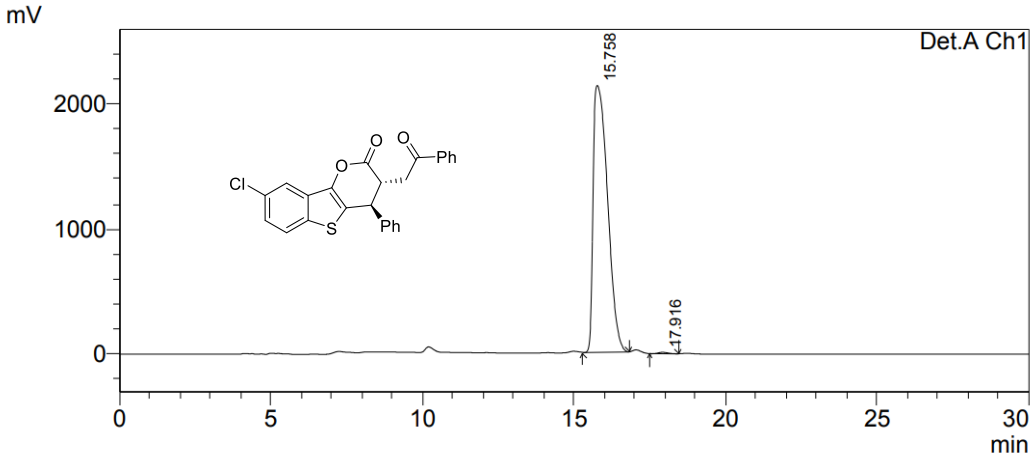


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.007	2380985	95719	50.538
2	17.892	2330268	89248	49.462
Total		4711253		100.000



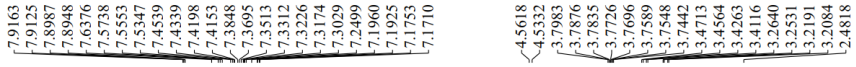
1 Det.A Ch1/254nm

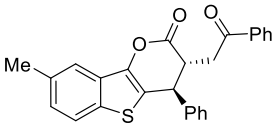
PeakTable

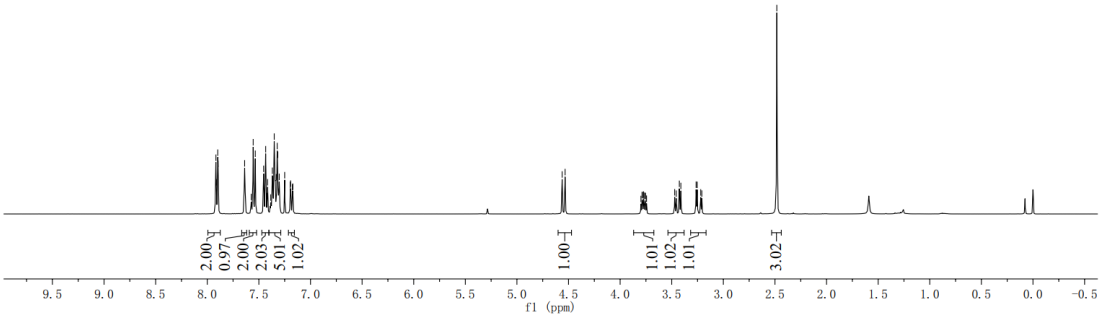
Detector A Ch1 254nm

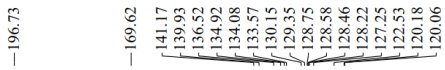
Peak#	Ret. Time	Area	Height	Area %
1	15.758	70424601	2128970	99.676
2	17.916	229197	11171	0.324
Total		70653798		100.000

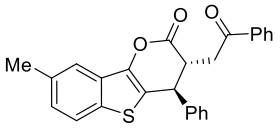
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 3t

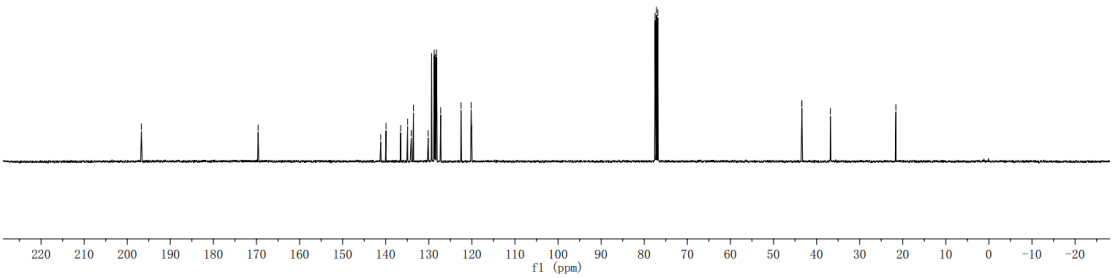




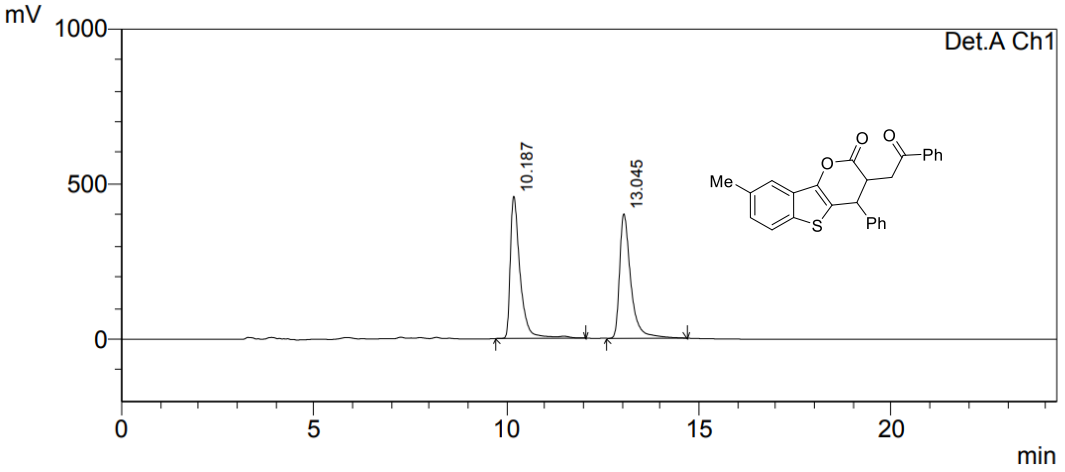








HPLC spectra of 3t

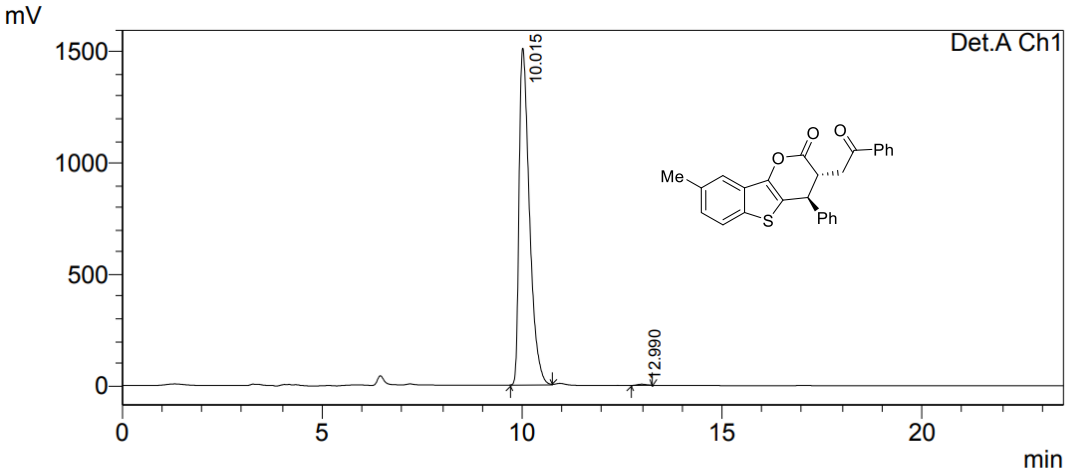


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.187	8093273	457039	49.980
2	13.045	8099618	399715	50.020
Total		16192891		100.000



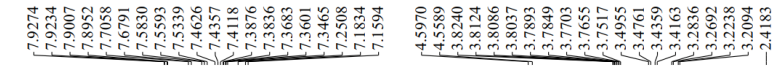
1 Det.A Ch1/254nm

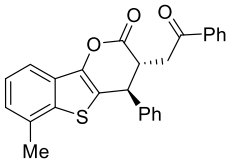
PeakTable

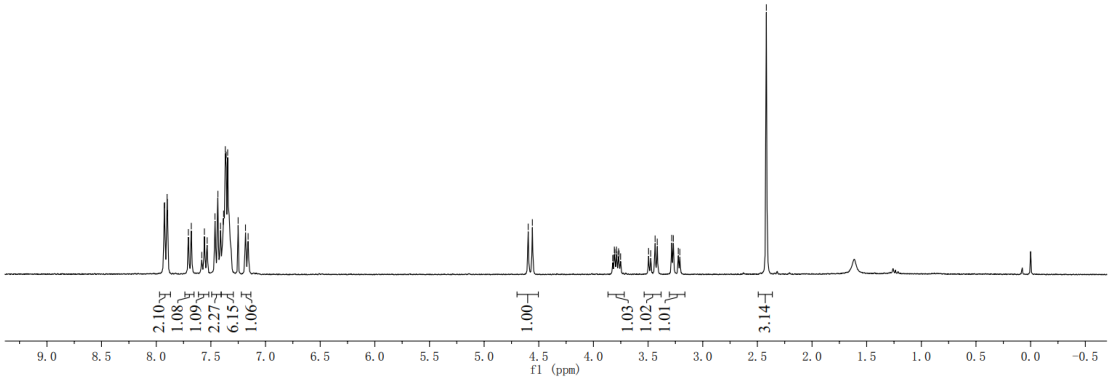
Detector A Ch1 254nm

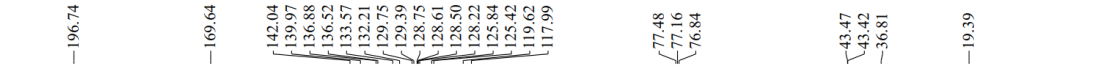
Peak#	Ret. Time	Area	Height	Area %
1	10.015	27318507	1514240	99.692
2	12.990	84375	5395	0.308
Total		27402882		100.000

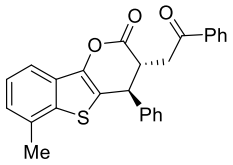
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 3u

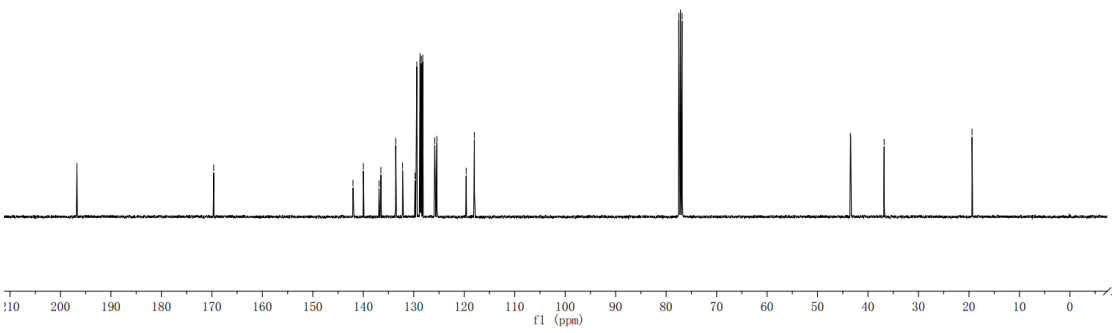




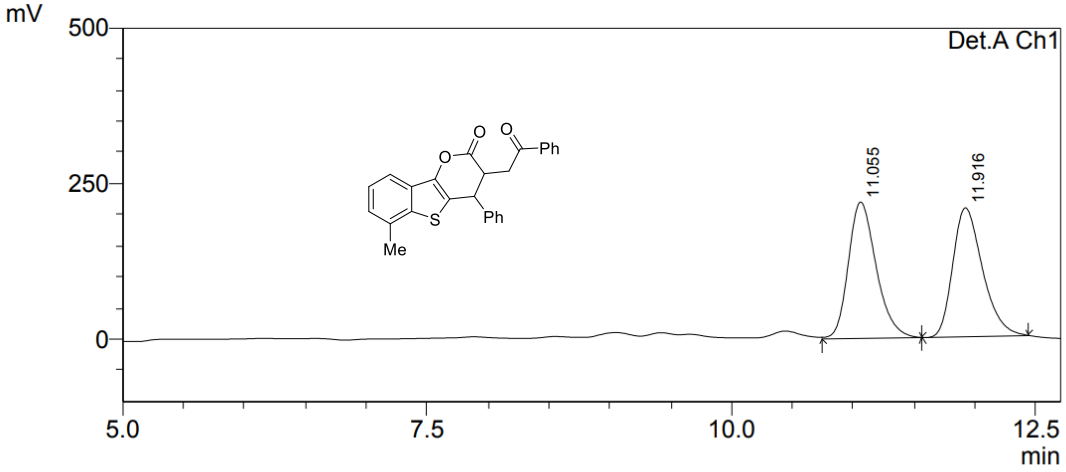








HPLC spectra of 3u

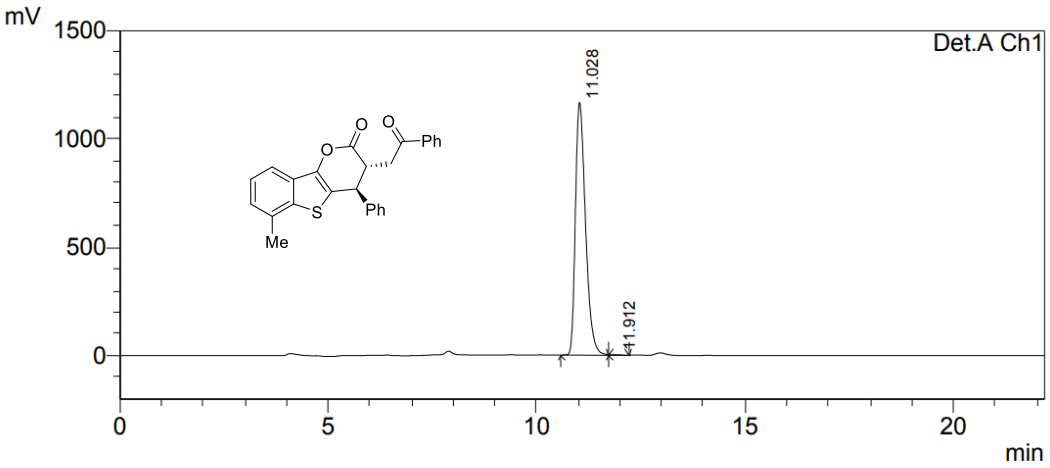


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.055	3484187	218695	49.762
2	11.916	3517549	206450	50.238
Total		7001735		100.000



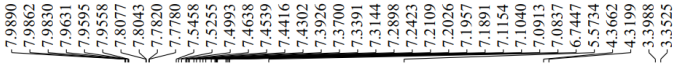
1 Det.A Ch1/254nm

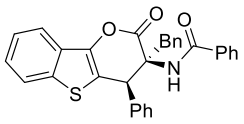
PeakTable

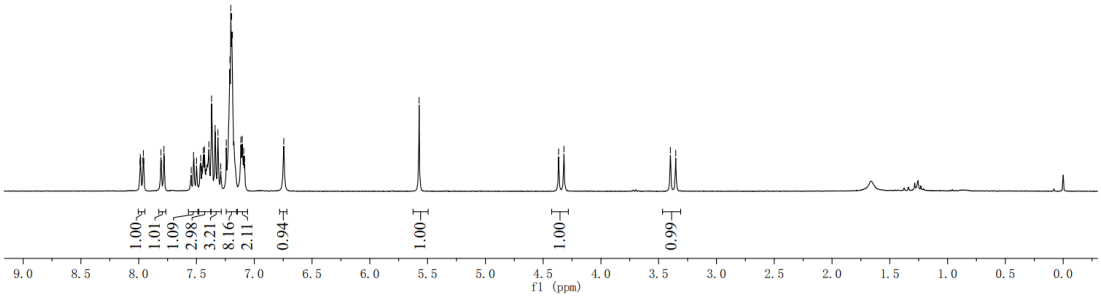
Detector A Ch1 254nm

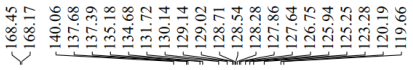
Peak#	Ret. Time	Area	Height	Area %
1	11.028	19579363	1163108	99.812
2	11.912	36925	2229	0.188
Total		19616288		100.000

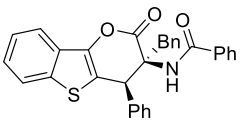
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) of 5a

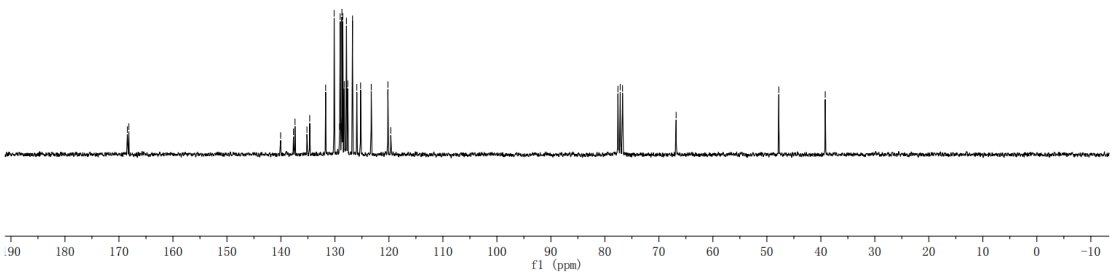




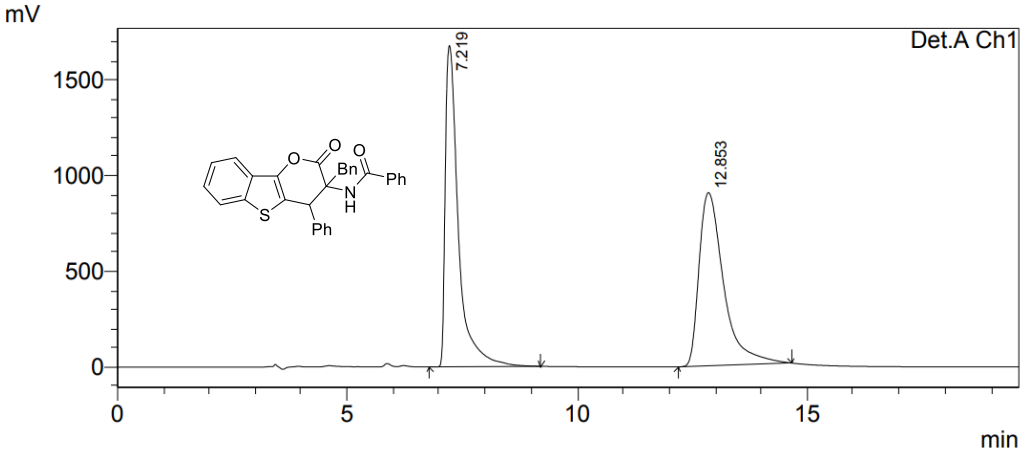








HPLC spectra of 5a

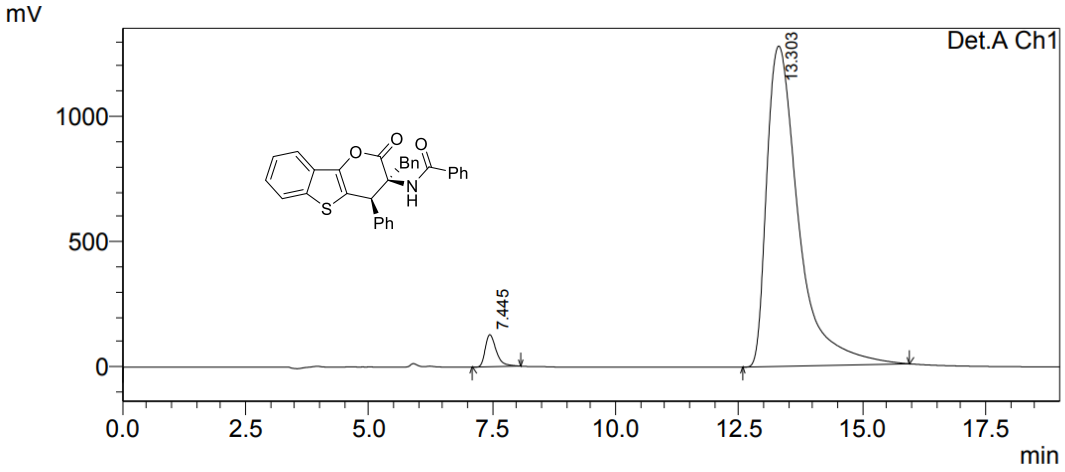


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.219	33236113	1680440	49.703
2	12.853	33633657	905325	50.297
Total		66869770		100.000



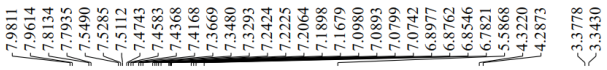
1 Det.A Ch1/254nm

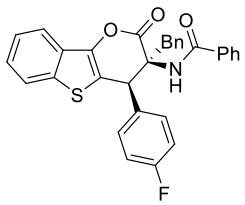
PeakTable

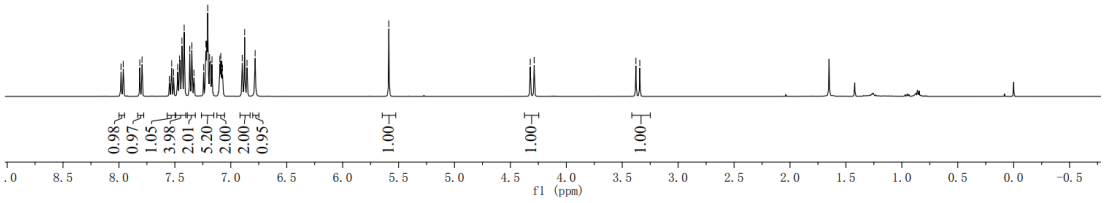
Detector A Ch1 254nm

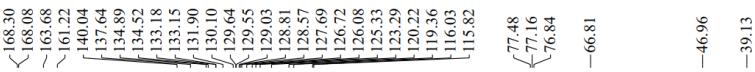
Peak#	Ret. Time	Area	Height	Area %
1	7.445	1998960	128098	3.368
2	13.303	57357314	1277525	96.632
Total		59356274		100.000

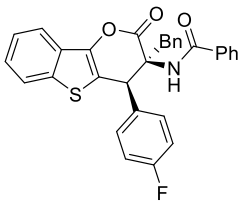
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 5b

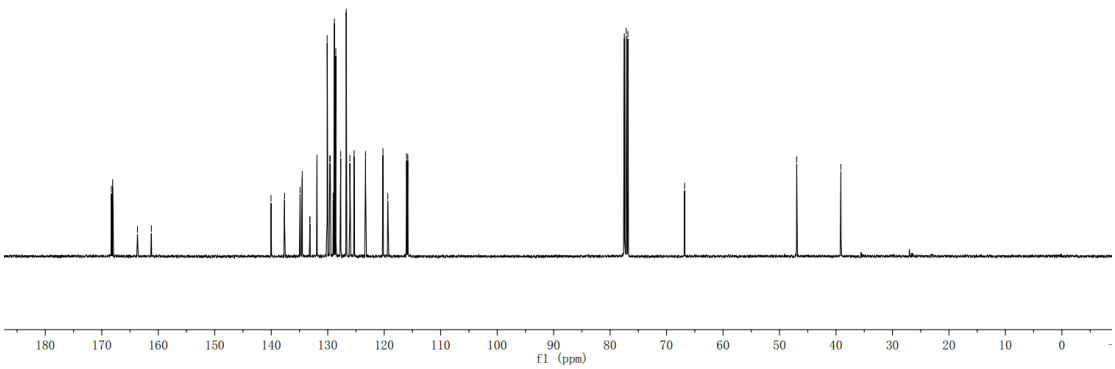




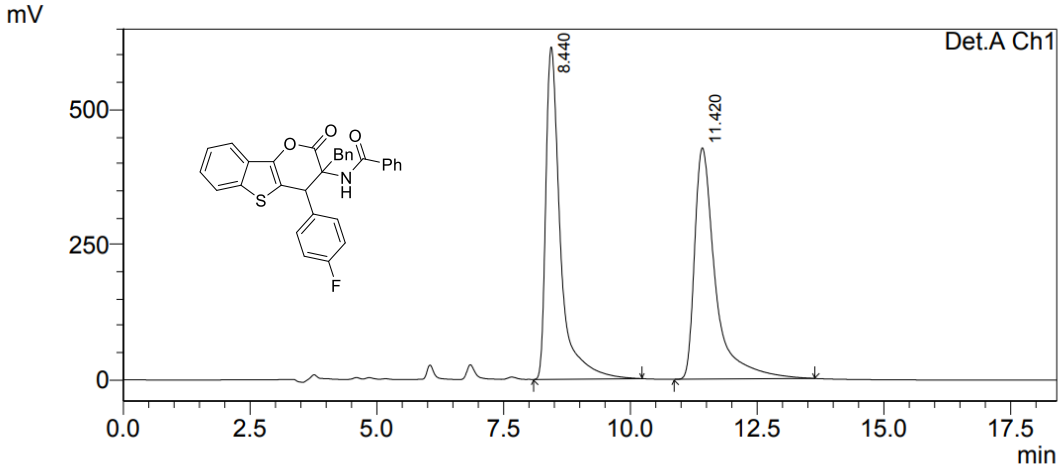








HPLC spectra of 5b

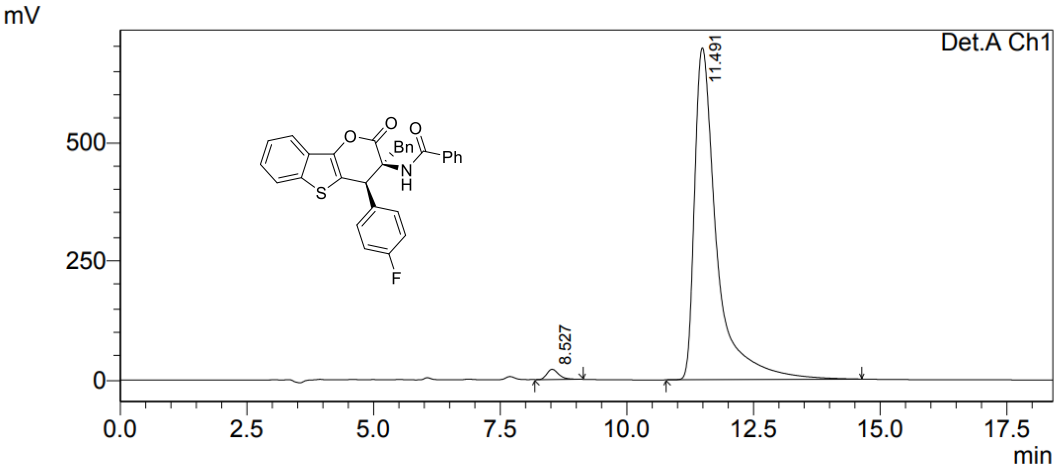


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.440	12288384	614822	50.010
2	11.420	12283284	427864	49.990
Total		24571668		100.000



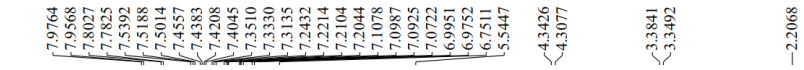
1 Det.A Ch1/254nm

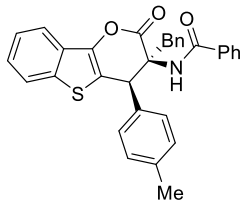
PeakTable

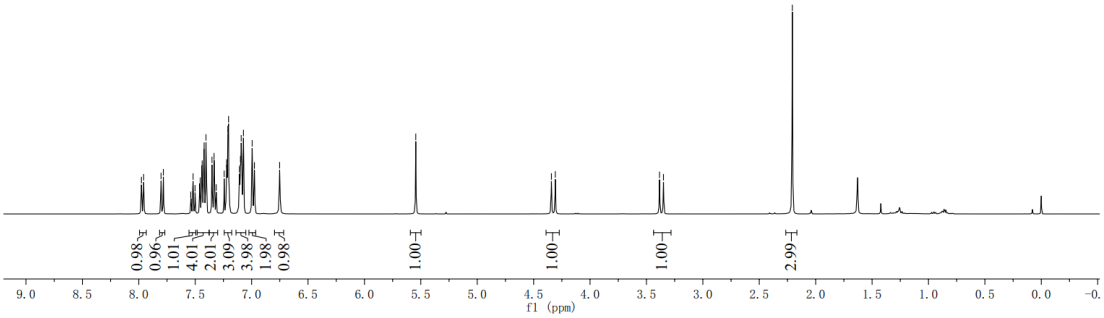
Detector A Ch1 254nm

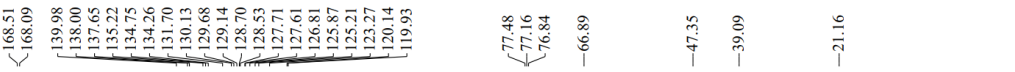
Peak#	Ret. Time	Area	Height	Area %
1	8.527	351465	21382	1.625
2	11.491	21277643	697767	98.375
Total		21629108		100.000

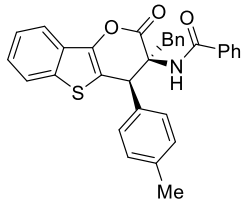
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 5c

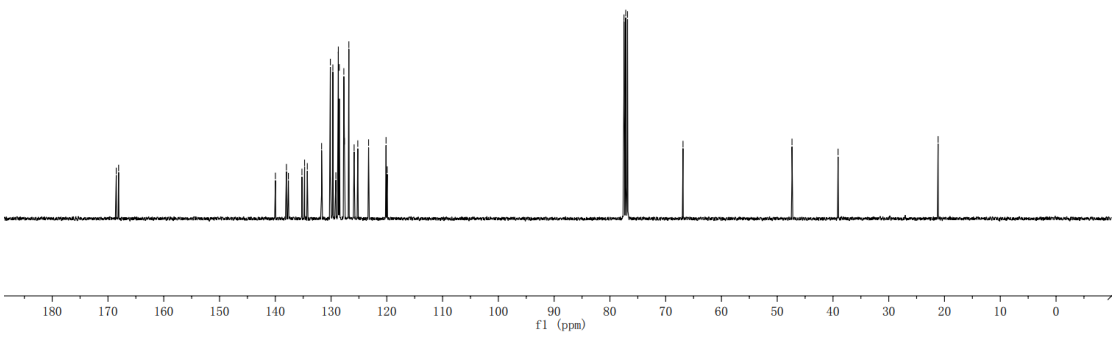




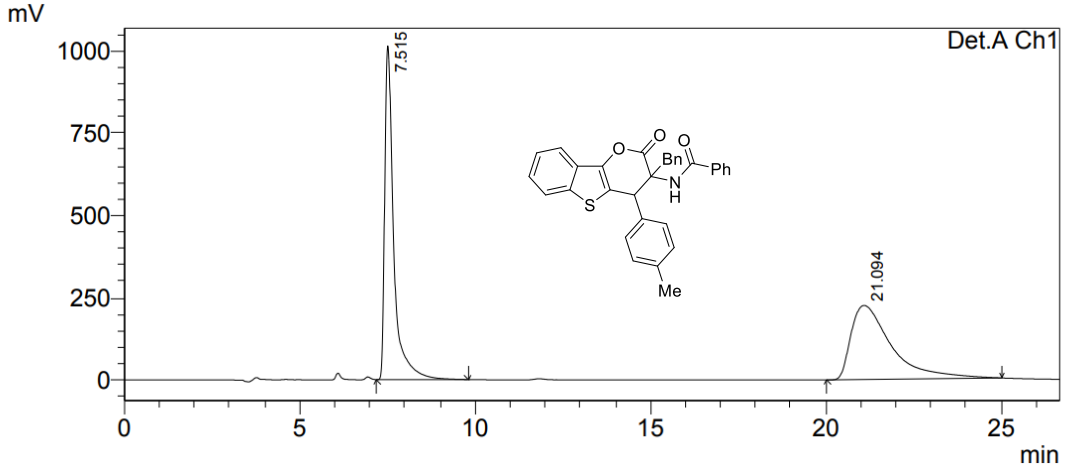








HPLC spectra of 5c

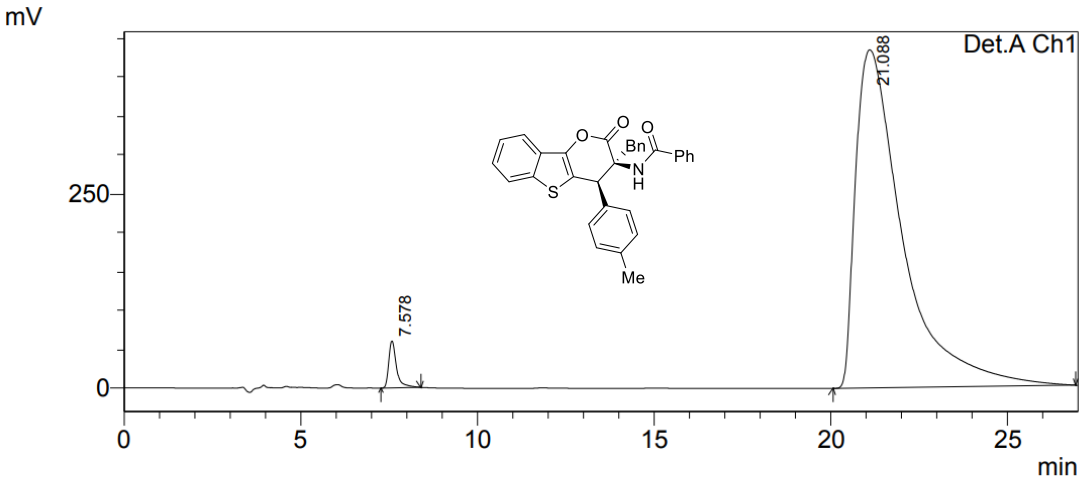


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.515	18102447	1014337	49.963
2	21.094	18129107	225466	50.037
Total		36231554		100.000



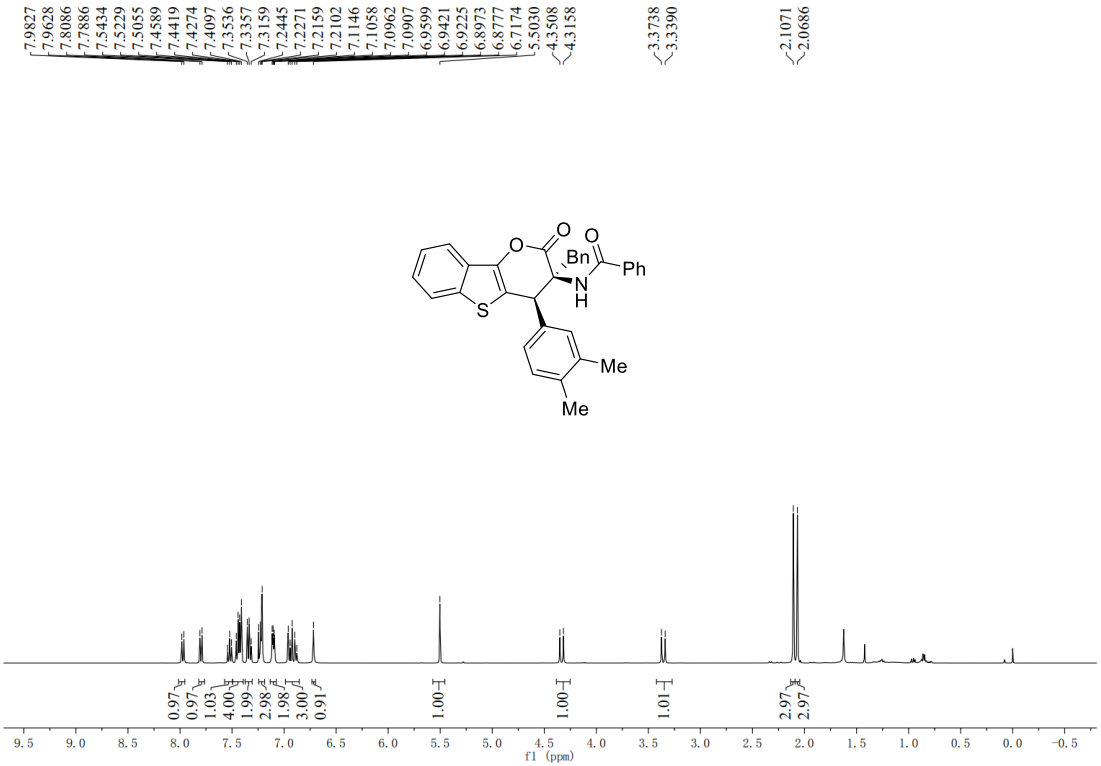
1 Det.A Ch1/254nm

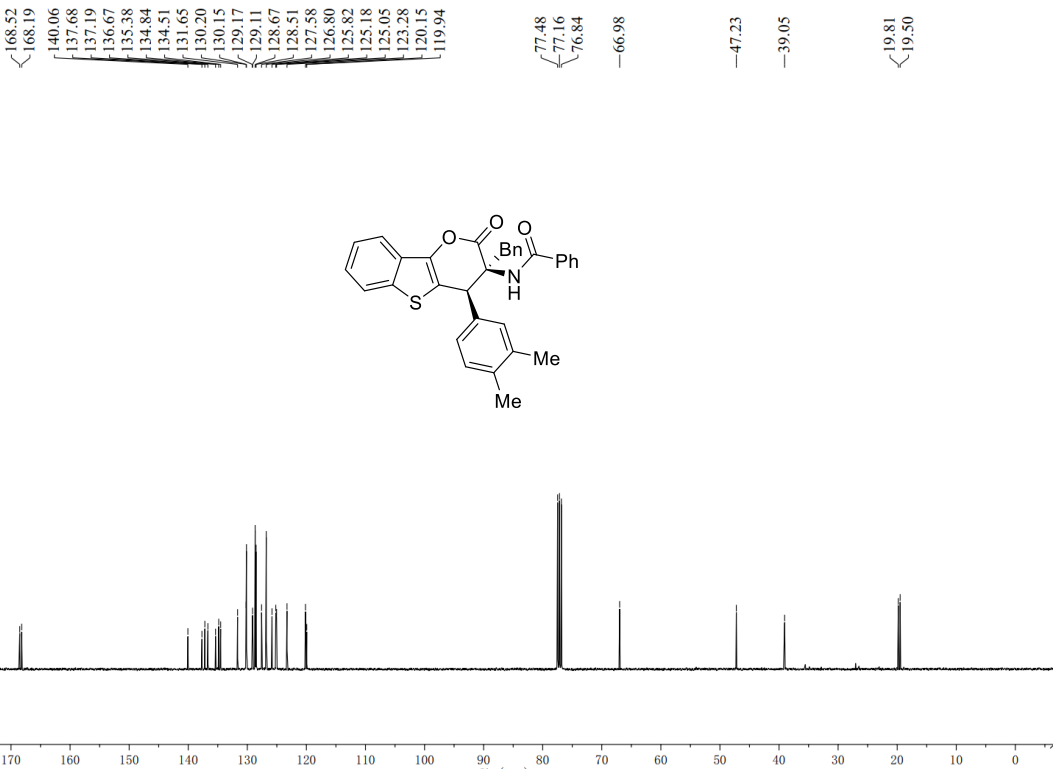
PeakTable

Detector A Ch1 254nm

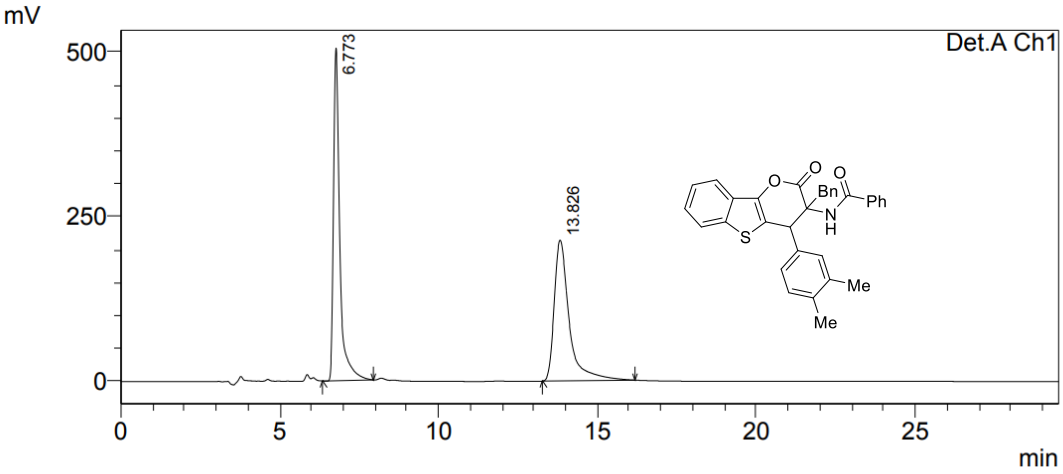
Peak#	Ret. Time	Area	Height	Area %
1	7.578	926274	60519	2.238
2	21.088	40454123	436244	97.762
Total		41380397		100.000

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 5d





HPLC spectra of 5d

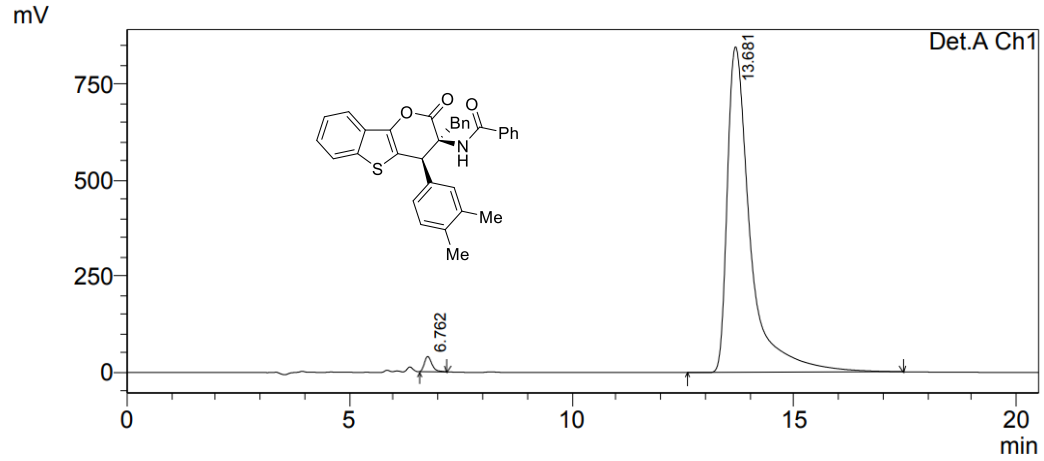


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	6.773	6939470	504785	49.806
2	13.826	6993625	213501	50.194
Total		13933094		100.000



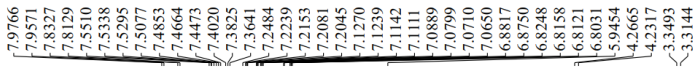
1 Det.A Ch1/254nm

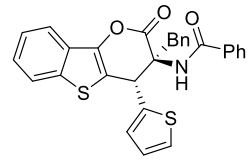
PeakTable

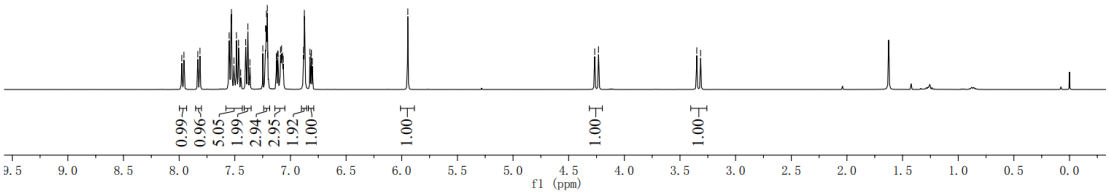
Detector A Ch1 254nm

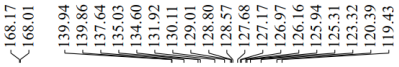
Peak#	Ret. Time	Area	Height	Area %
1	6.762	462956	39619	1.492
2	13.681	30565962	847897	98.508
Total		31028918		100.000

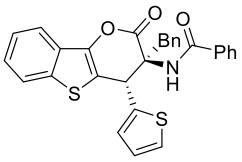
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 5e

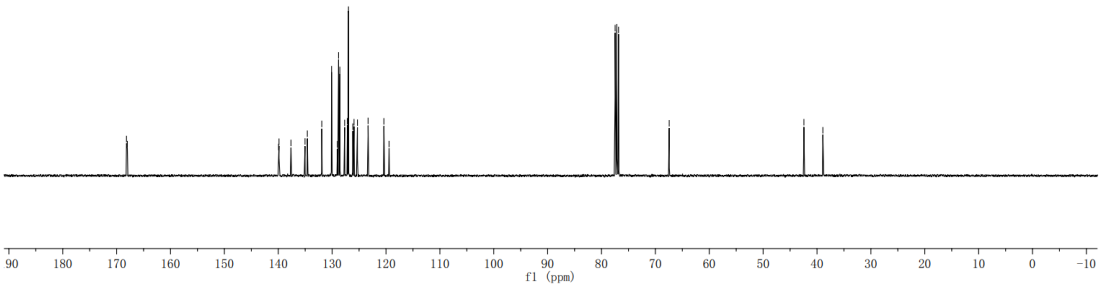




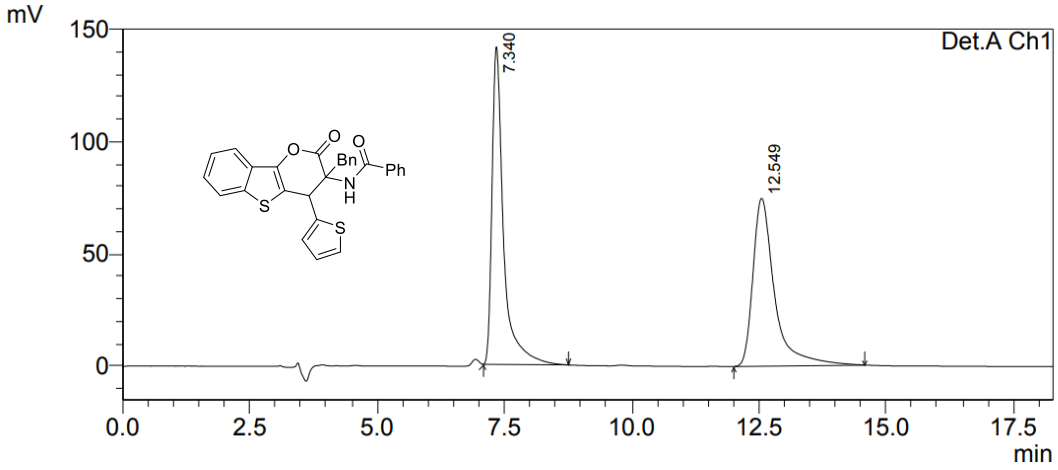








HPLC spectra of 5e

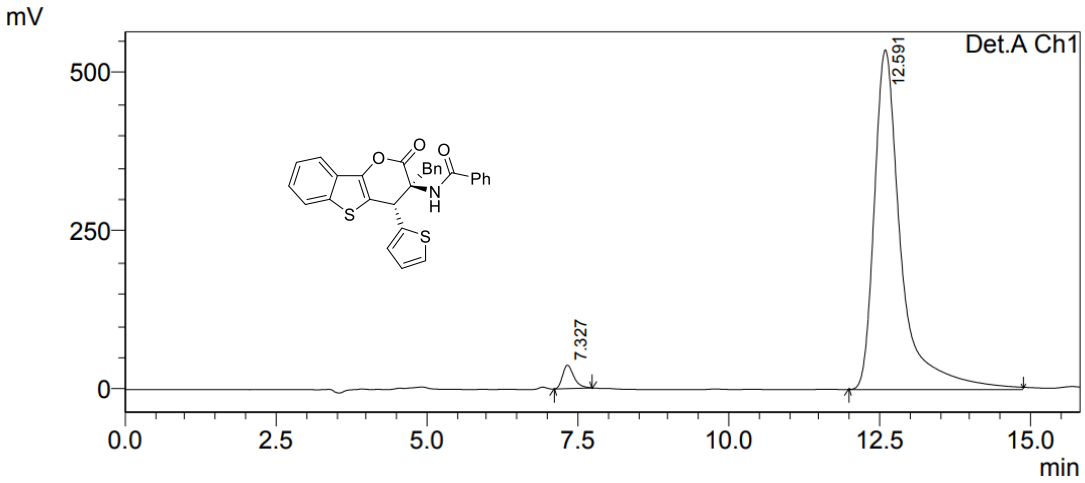


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.340	2220039	141486	50.054
2	12.549	2215229	74745	49.946
Total		4435268		100.000



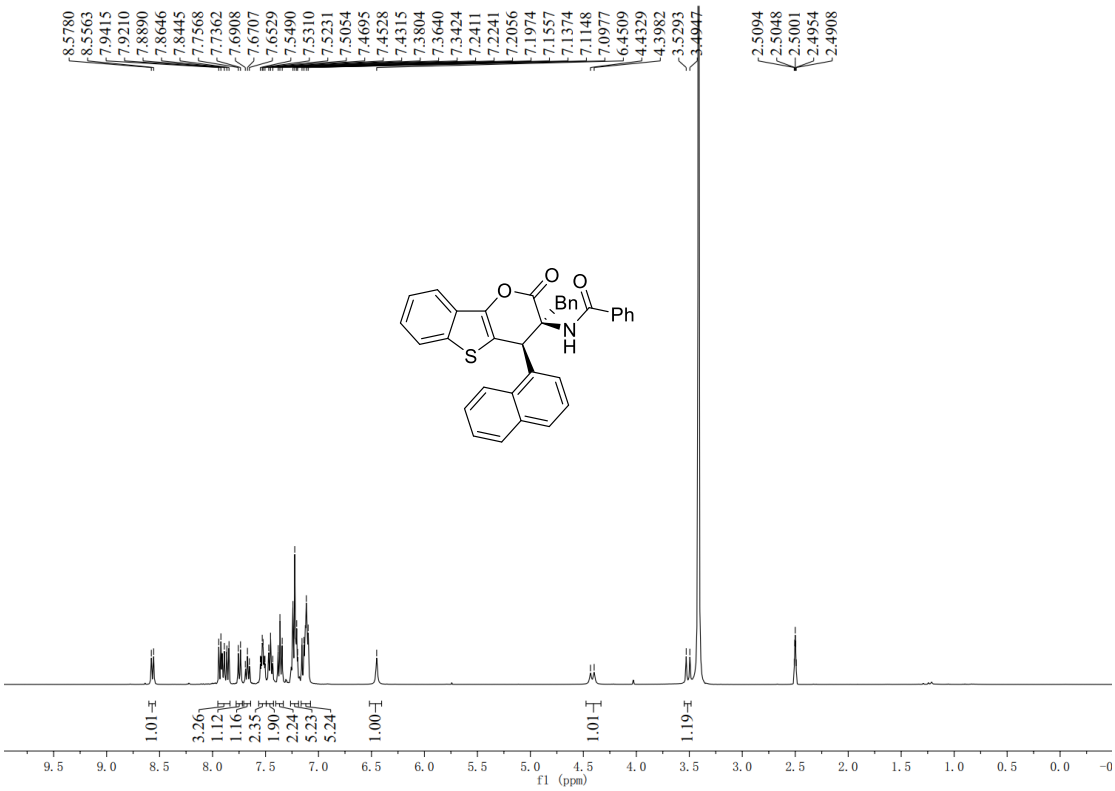
1 Det.A Ch1/254nm

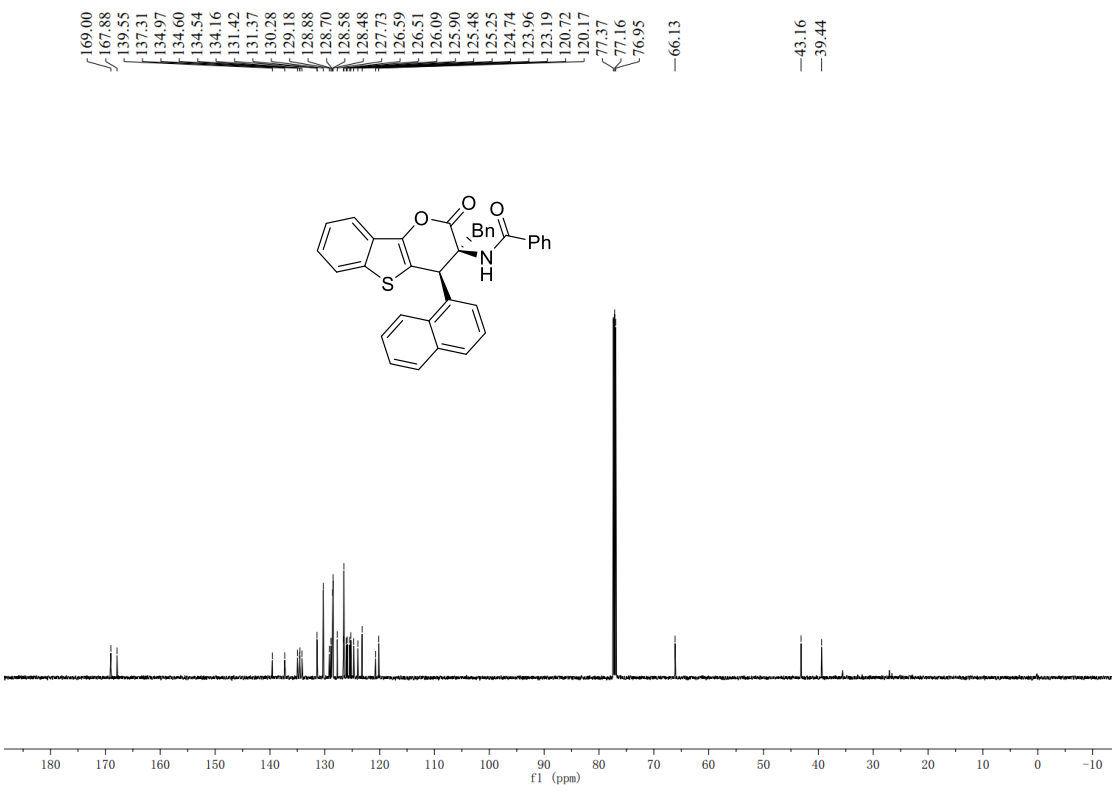
PeakTable

Detector A Ch1 254nm

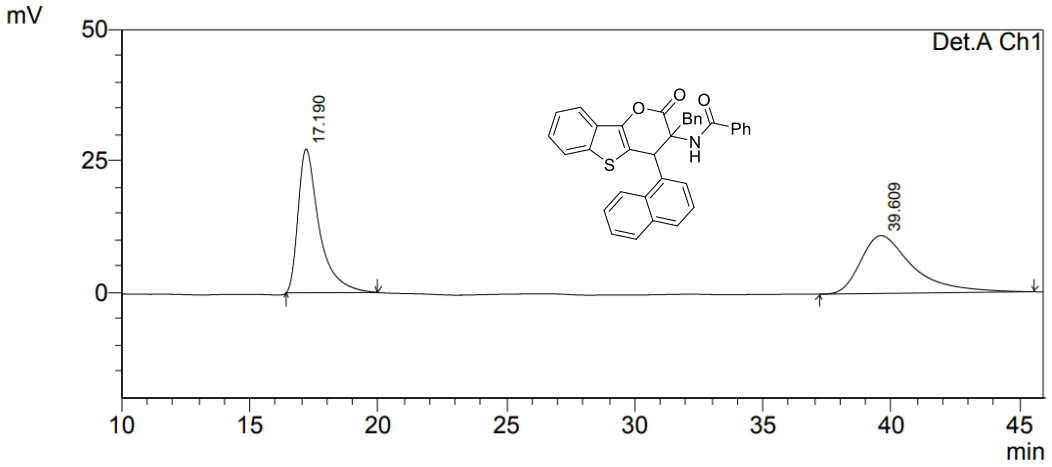
Peak#	Ret. Time	Area	Height	Area %
1	7.327	491655	37044	2.883
2	12.591	16564033	535882	97.117
Total		17055688		100.000

^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (151 MHz, $CDCl_3$) of 5f





HPLC spectra of 5f

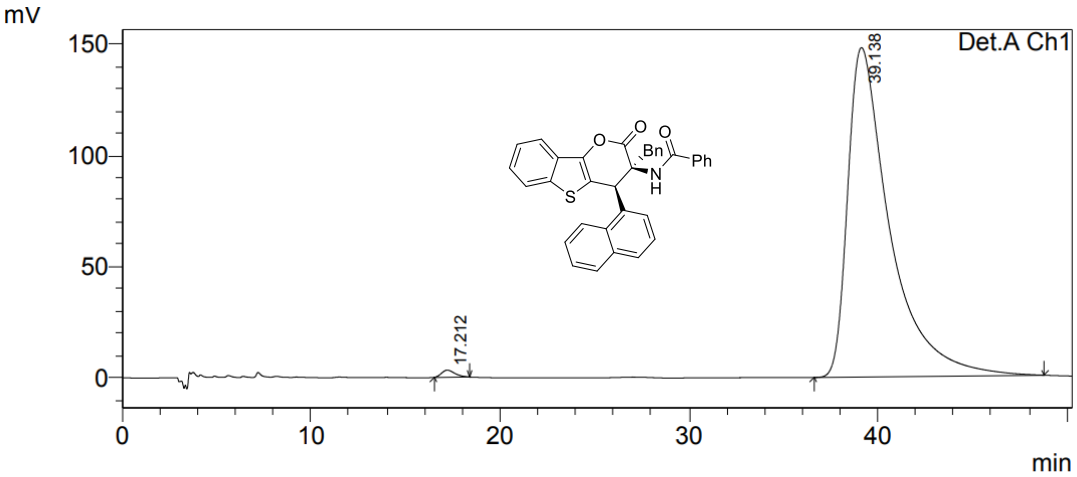


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	17.190	1561224	27290	50.090
2	39.609	1555614	10978	49.910
Total		3116838		100.000



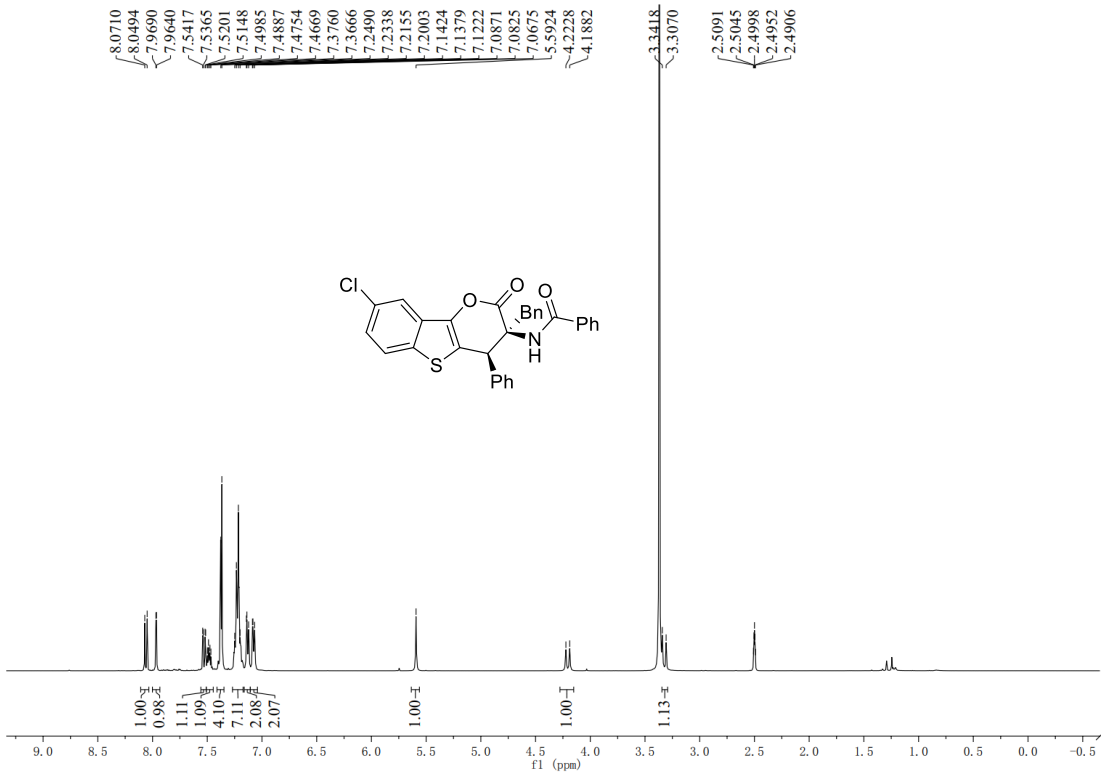
1 Det.A Ch1/254nm

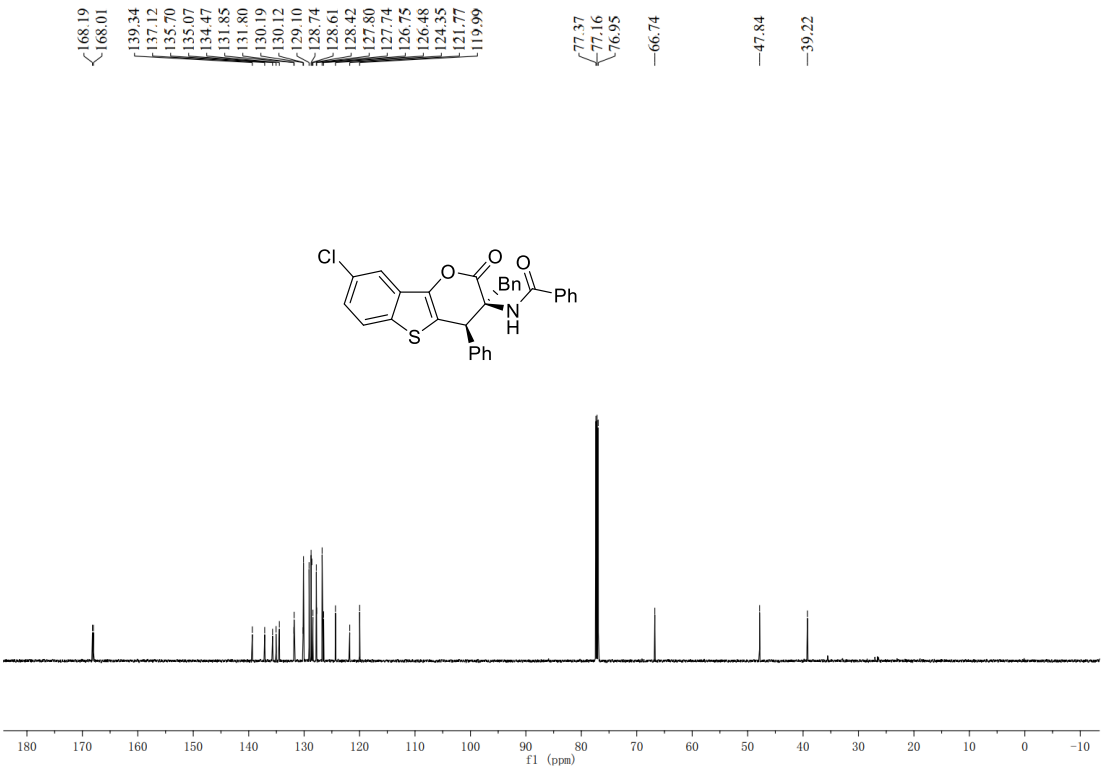
PeakTable

Detector A Ch1 254nm

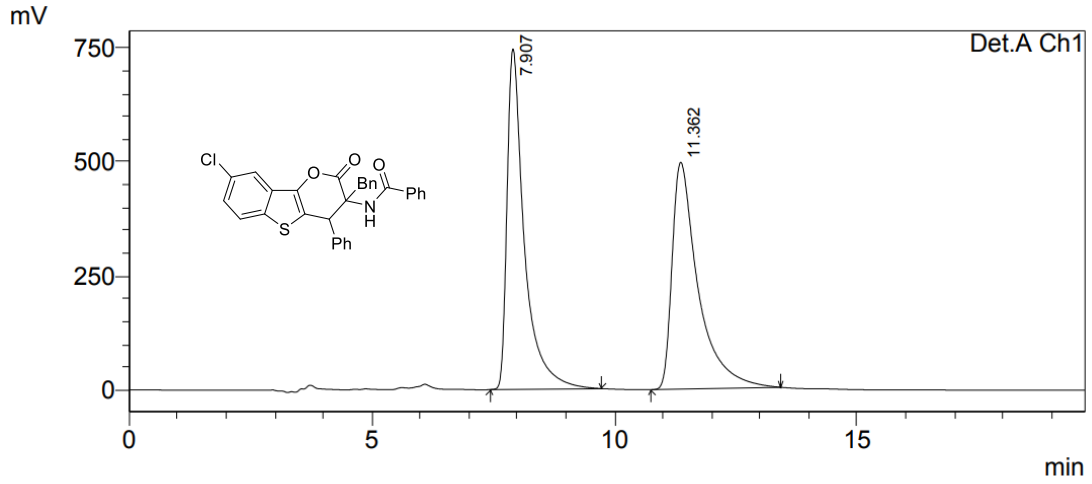
Peak#	Ret. Time	Area	Height	Area %
1	17.212	156968	3203	0.681
2	39.138	22907184	148120	99.319
Total		23064152		100.000

^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (151 MHz, $CDCl_3$) of 5g





HPLC spectra of 5g

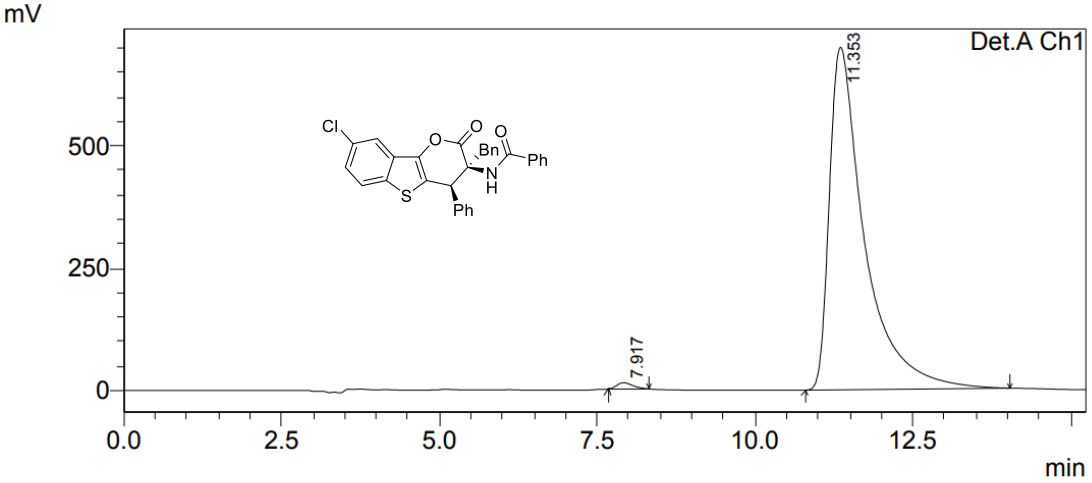


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.907	18517733	746260	49.961
2	11.362	18546774	497014	50.039
Total		37064507		100.000



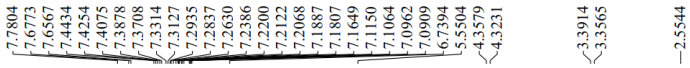
1 Det.A Ch1/254nm

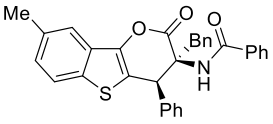
PeakTable

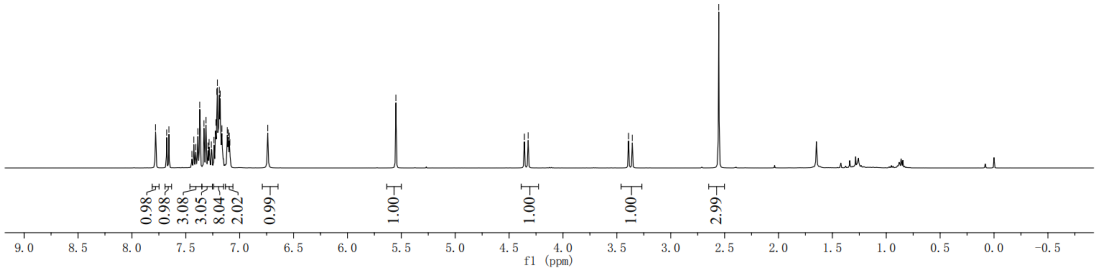
Detector A Ch1 254nm

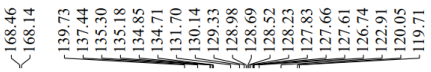
Peak#	Ret. Time	Area	Height	Area %
1	7.917	231740	12928	0.846
2	11.353	27148350	700872	99.154
Total		27380090		100.000

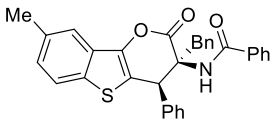
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 5h

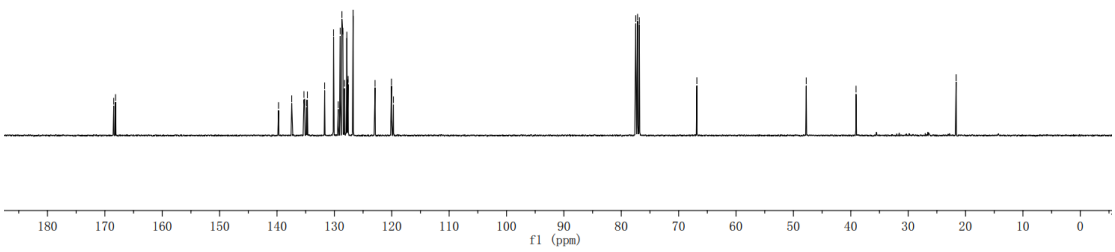




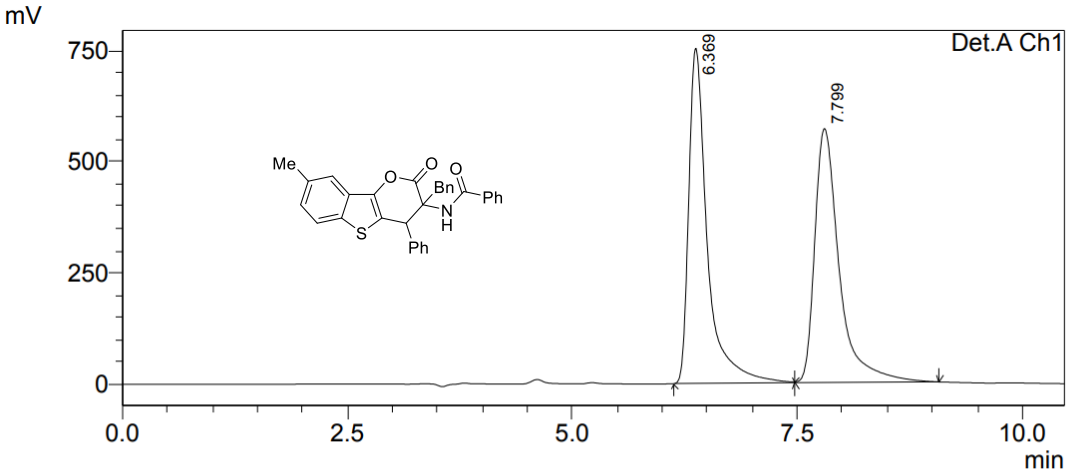








HPLC spectra of 5h

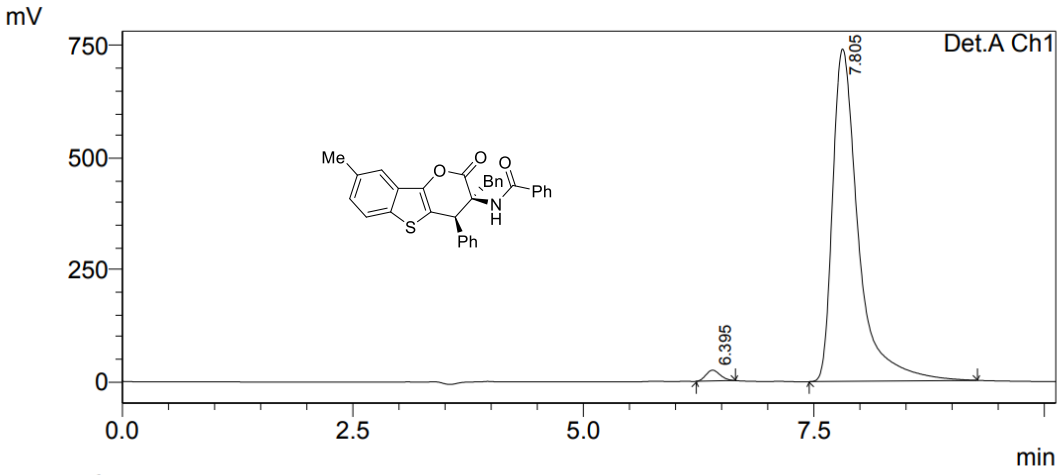


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	6.369	10773736	752137	49.968
2	7.799	10787561	570302	50.032
Total		21561297		100.000



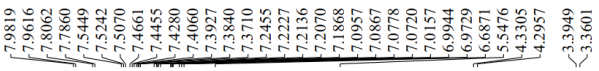
1 Det.A Ch1/254nm

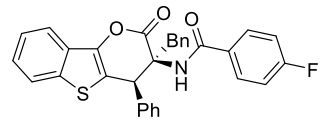
PeakTable

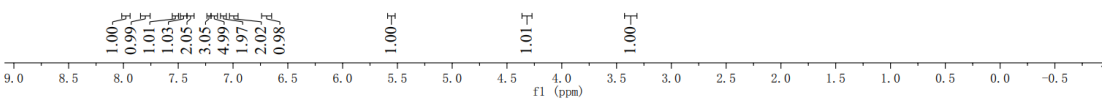
Detector A Ch1 254nm

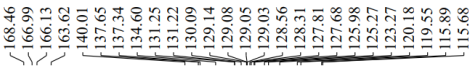
Peak#	Ret. Time	Area	Height	Area %
1	6.395	264014	24481	1.799
2	7.805	14411275	743813	98.201
Total		14675289		100.000

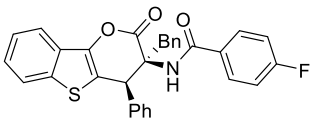
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 5i

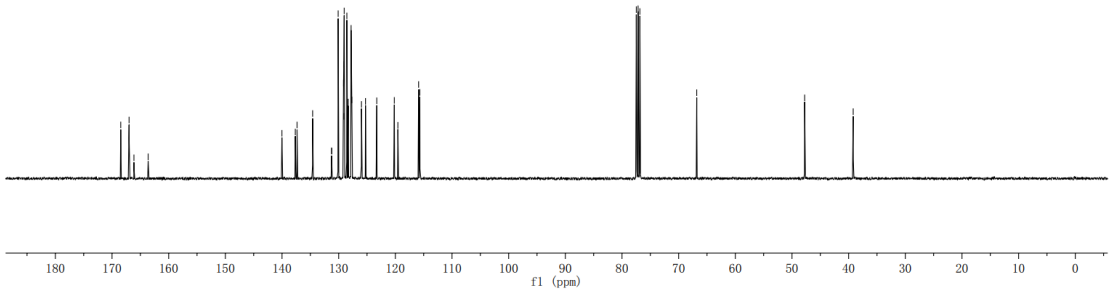




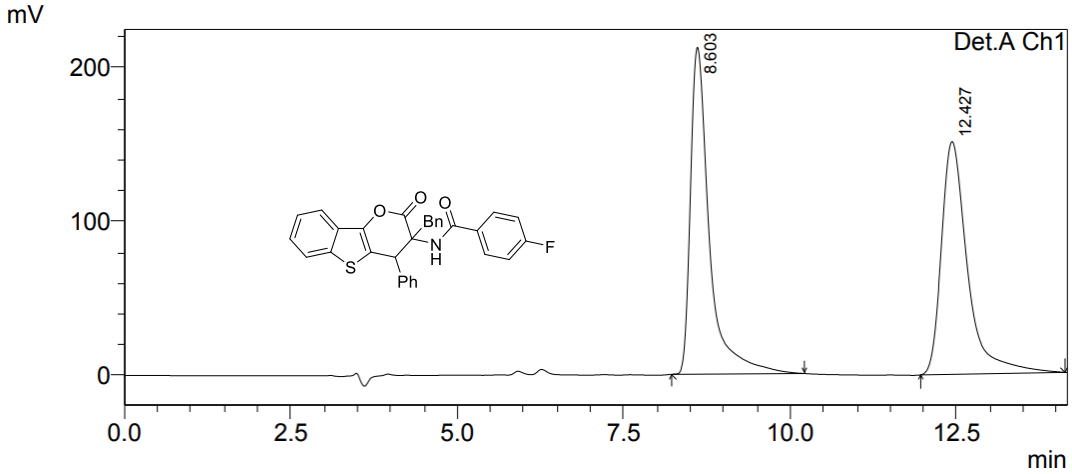








HPLC spectra of 5i

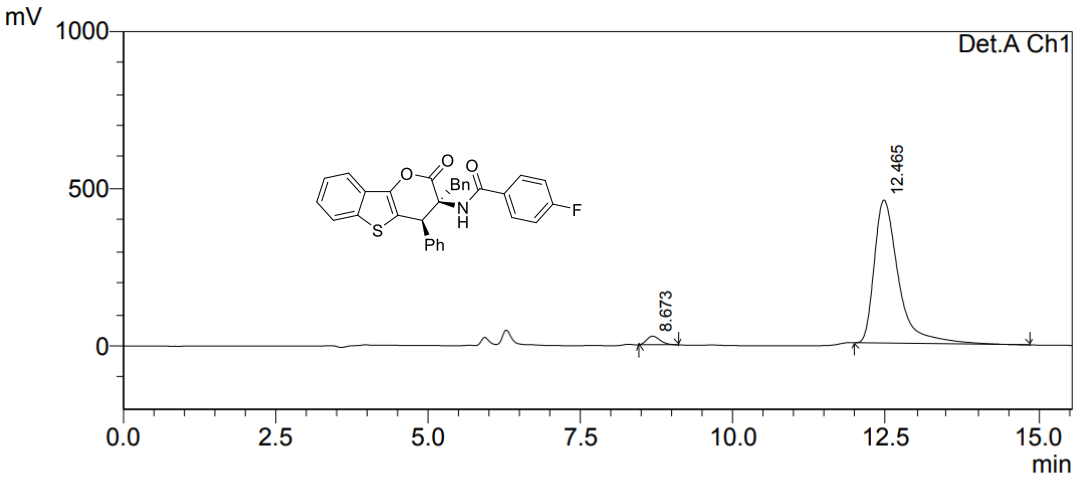


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.603	4173134	212279	50.363
2	12.427	4113029	151168	49.637
Total		8286164		100.000



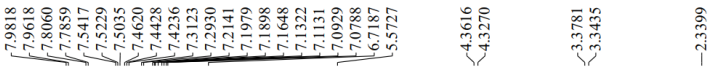
1 Det.A Ch1/254nm

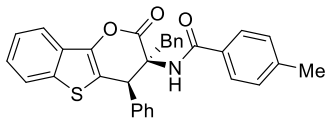
PeakTable

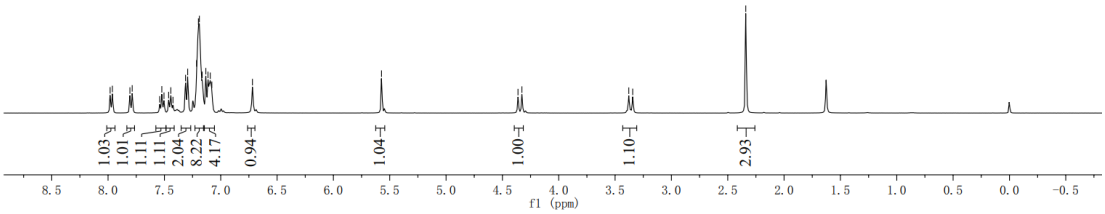
Detector A Ch1 254nm

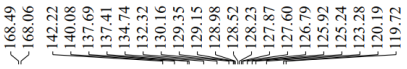
Peak#	Ret. Time	Area	Height	Area %
1	8.673	411185	27384	3.183
2	12.465	12506441	453138	96.817
Total		12917626		100.000

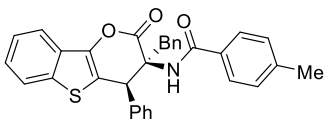
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 5j

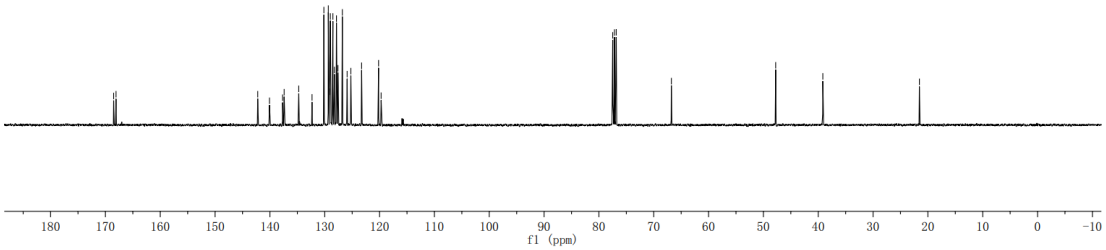




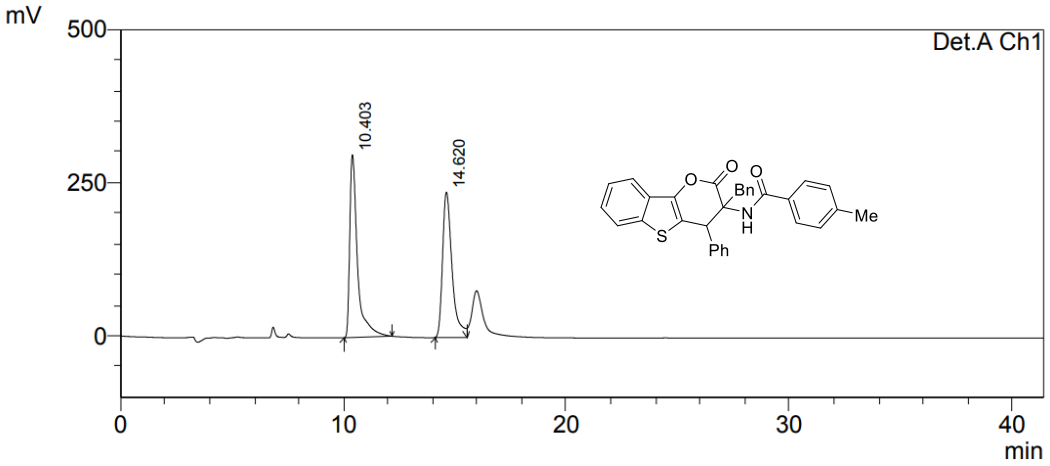








HPLC spectra of 5j

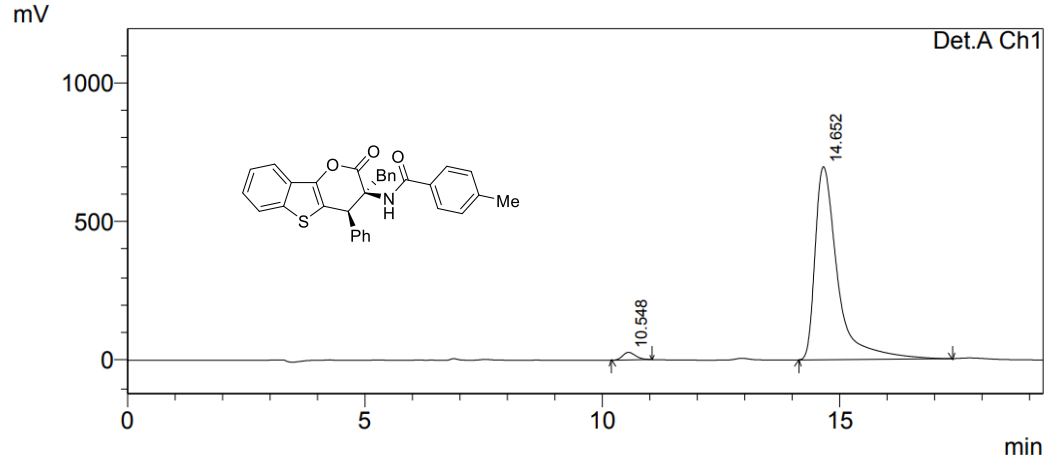


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.403	7202891	297661	50.773
2	14.620	6983477	236734	49.227
Total		14186367		100.000



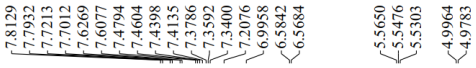
1 Det.A Ch1/254nm

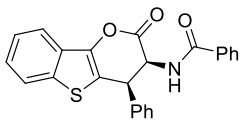
PeakTable

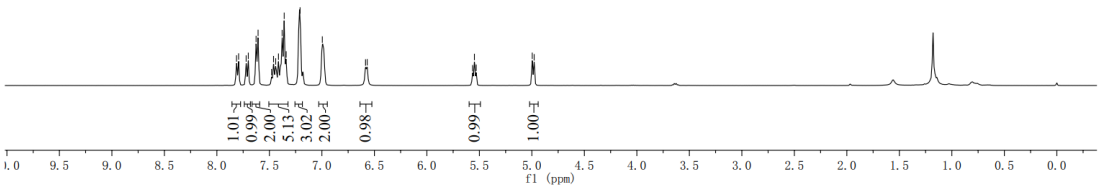
Detector A Ch1 254nm

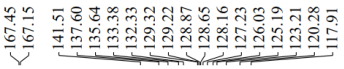
Peak#	Ret. Time	Area	Height	Area %
1	10.548	520791	27326	2.209
2	14.652	23050745	696649	97.791
Total		23571536		100.000

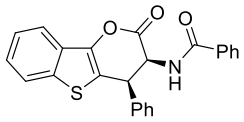
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 5k

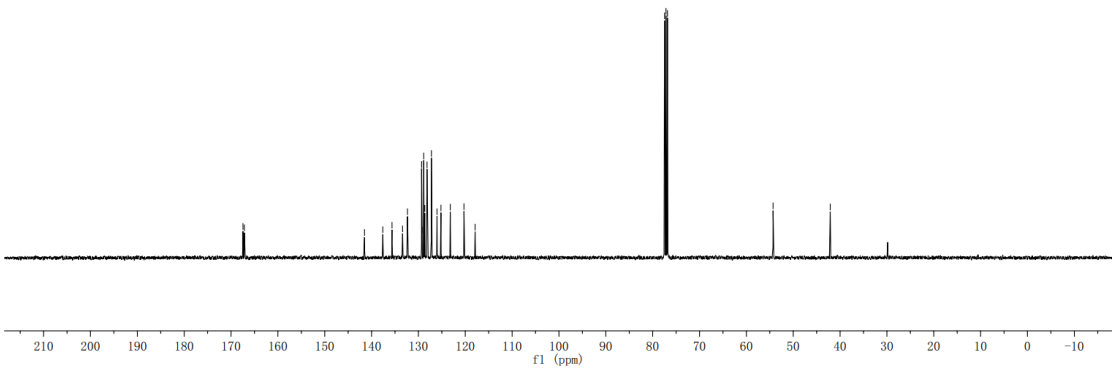




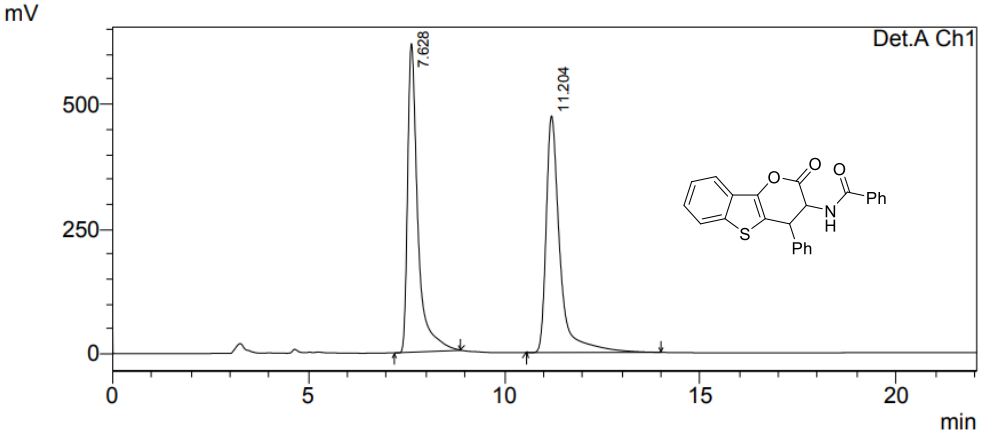








HPLC spectra of 5k

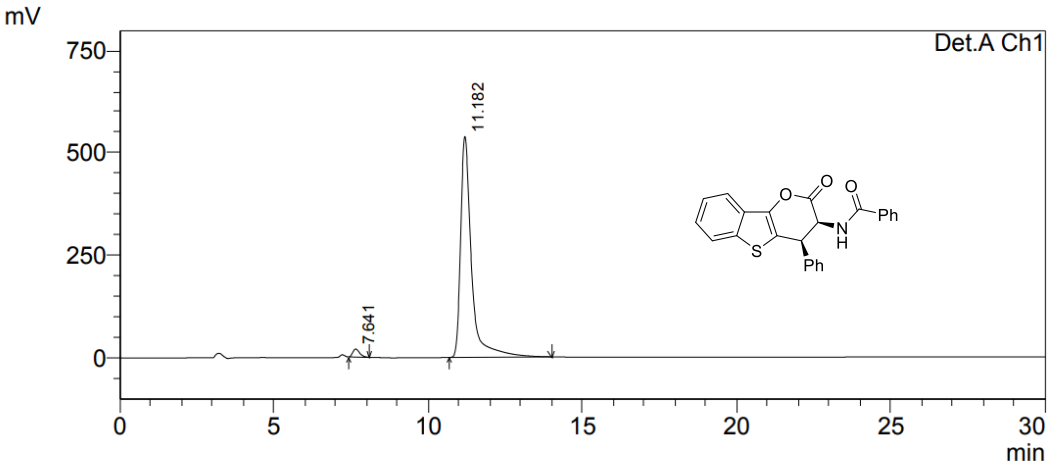


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	7.628	11243034	619446	49.036
2	11.204	11685094	475131	50.964
Total		22928129		100.000



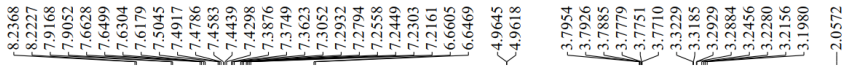
1 Det.A Ch1/220nm

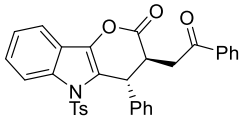
PeakTable

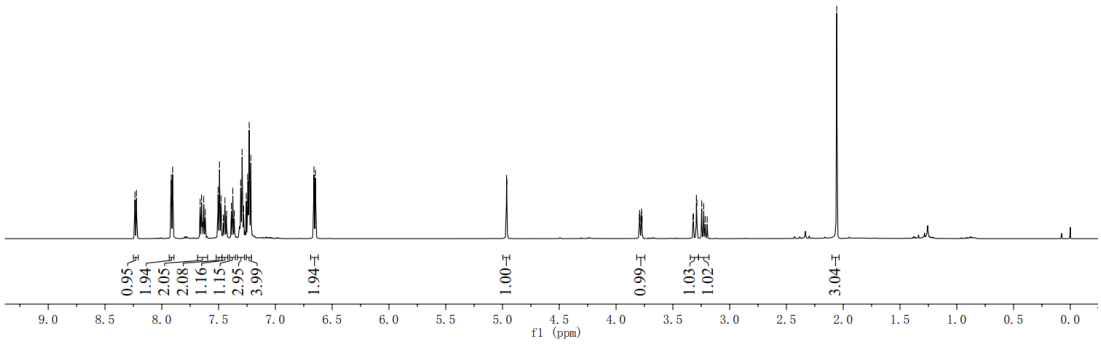
Detector A Ch1 220nm

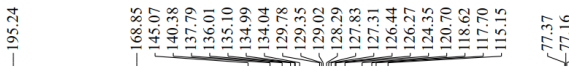
Peak#	Ret. Time	Area	Height	Area %
1	7.641	301532	19675	2.227
2	11.182	13236296	538751	97.773
Total		13537828		100.000

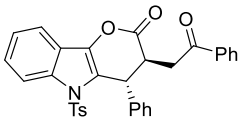
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of 7a

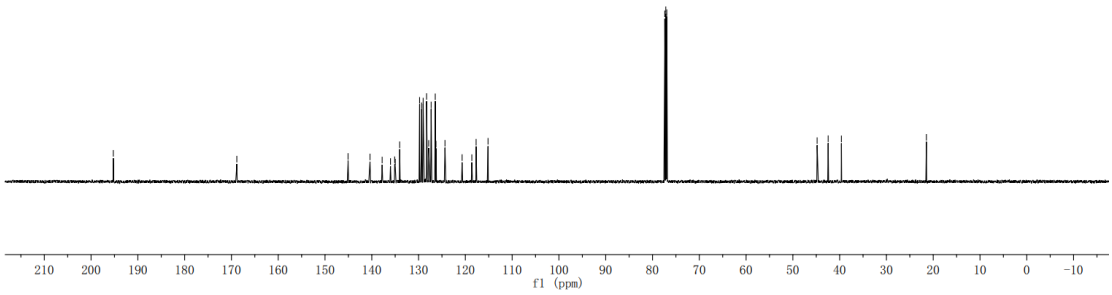




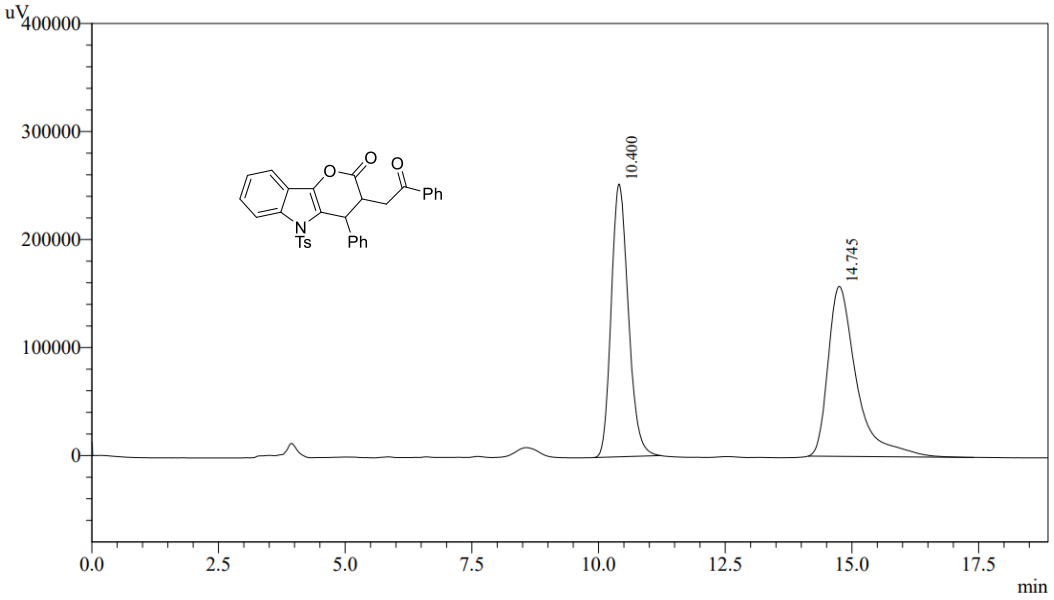








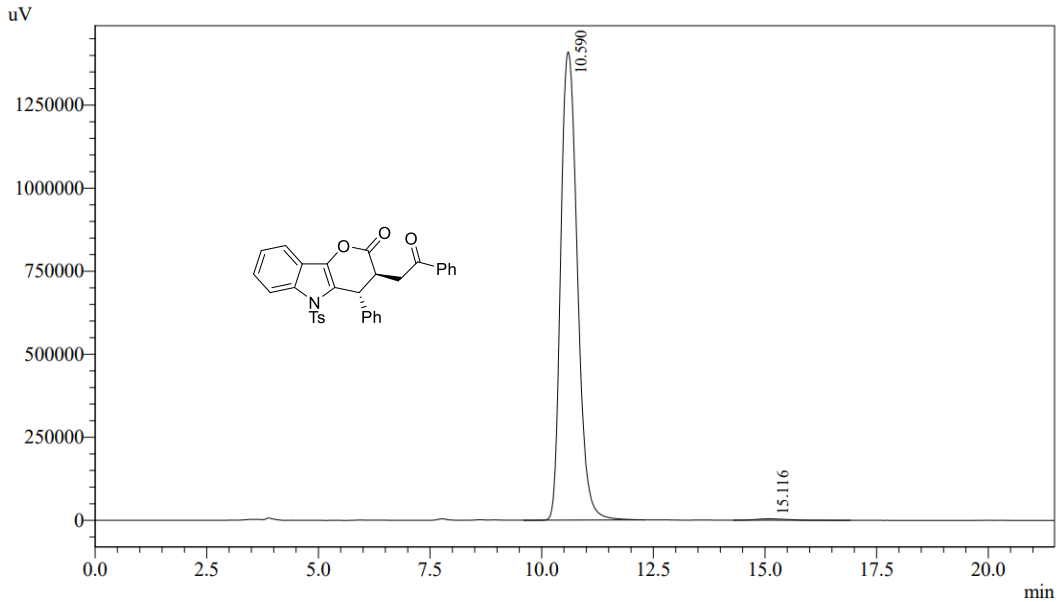
HPLC spectra of 7a



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.400	5932062	252570	49.147	61.620
2	14.745	6137912	157316	50.853	38.380
Total		12069974	409886	100.000	100.000

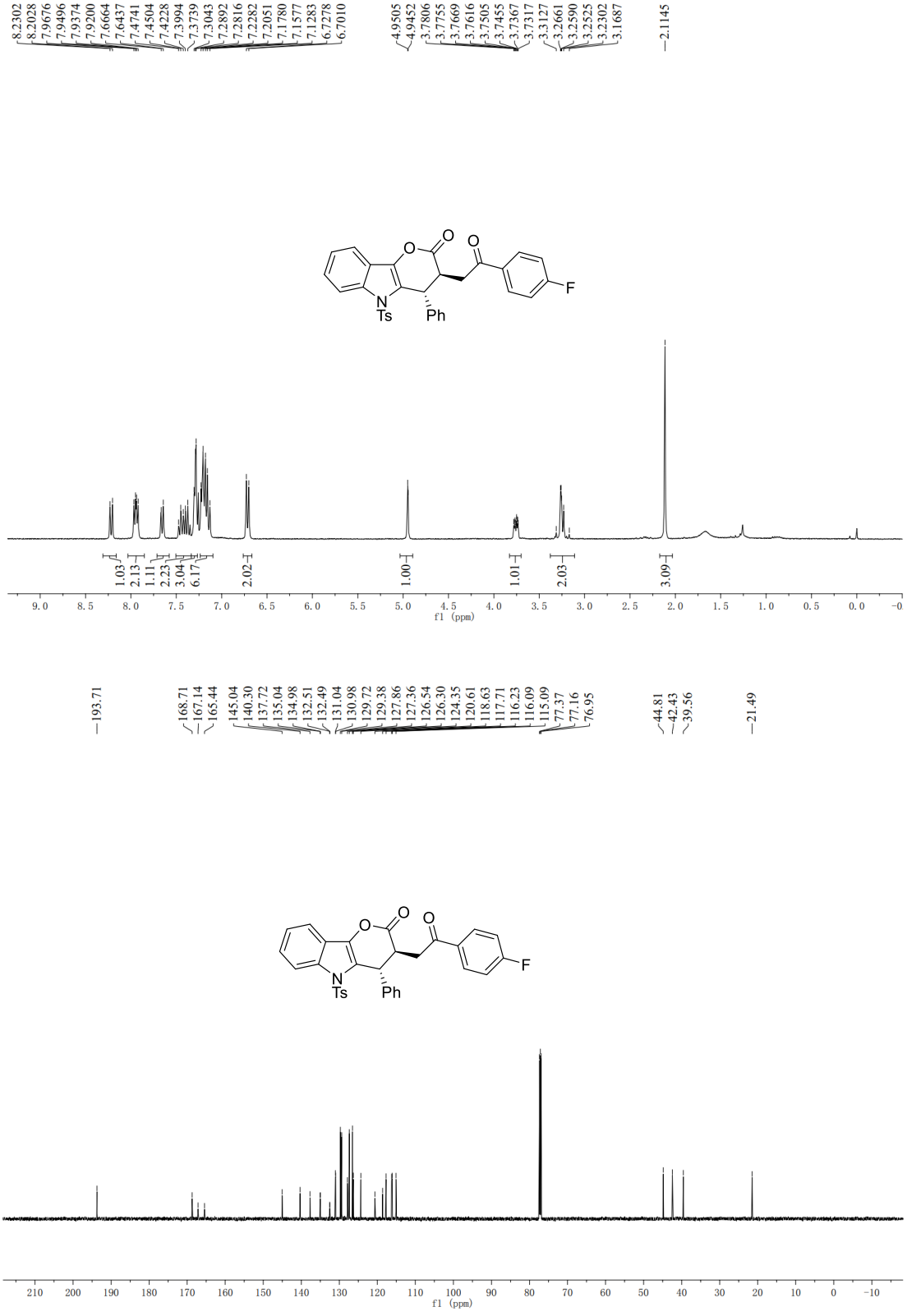


1 Det.A Ch1 / 254nm

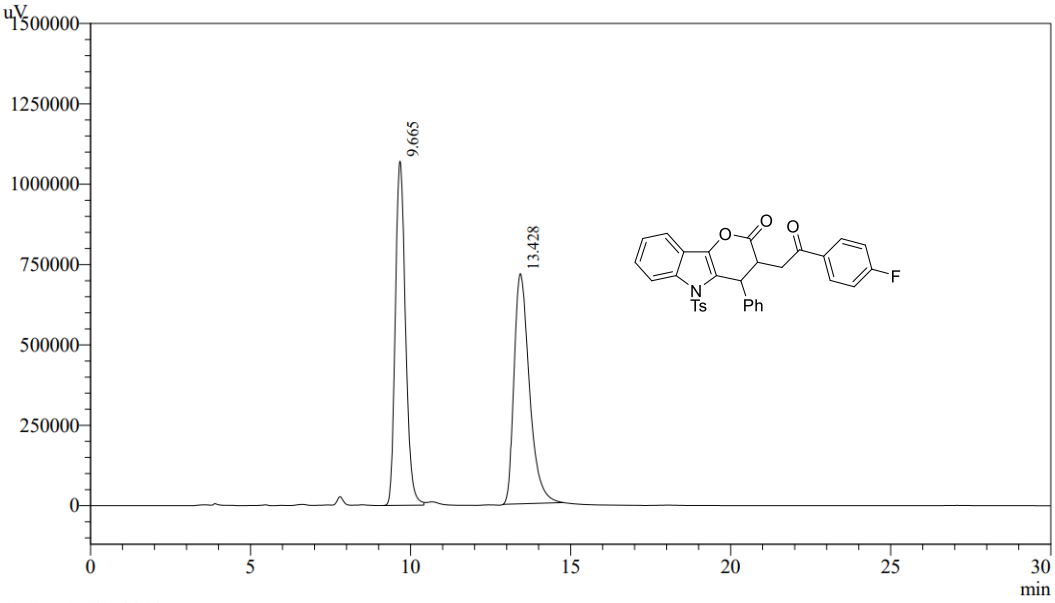
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.590	36541004	1410004	99.425	99.684
2	15.116	211440	4474	0.575	0.316
Total		36752444	1414478	100.000	100.000

^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of 7b



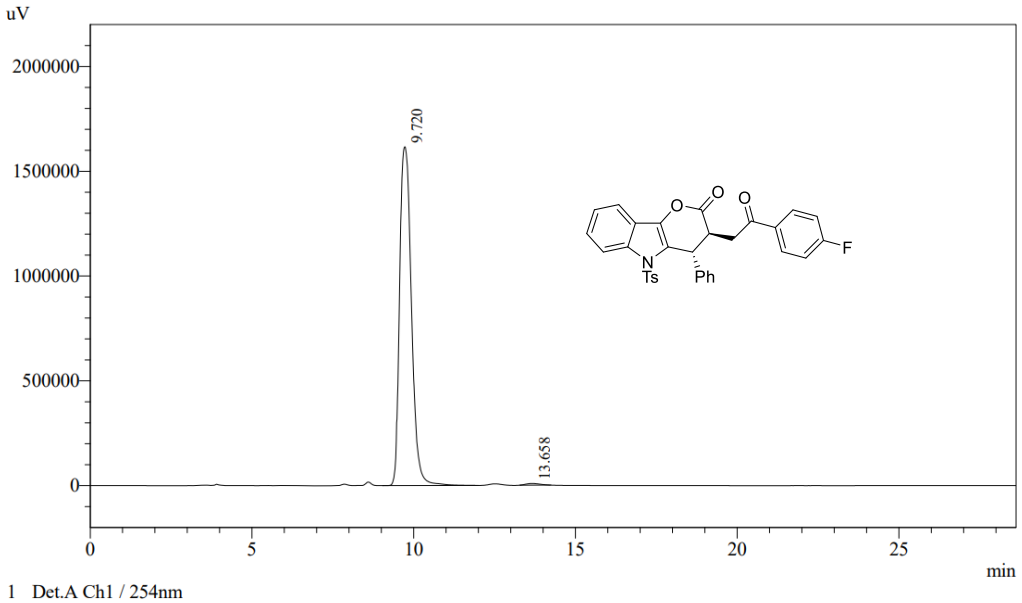
HPLC spectra of 7b



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.665	23771688	1070349	49.882	59.920
2	13.428	23883805	715959	50.118	40.080
Total		47655493	1786309	100.000	100.000

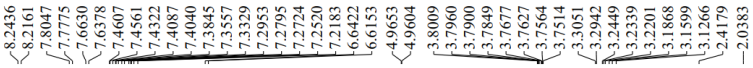


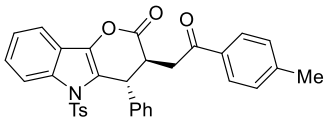
1 Det.A Ch1 / 254nm

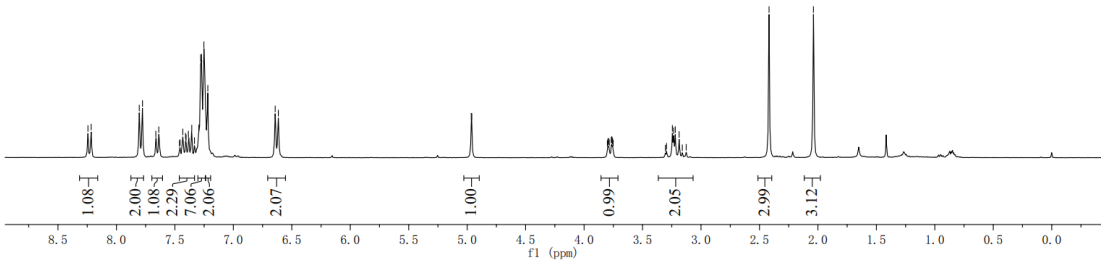
Detector A Ch1 254nm

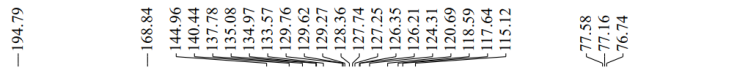
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.720	40980112	1616703	99.437	99.516
2	13.658	231975	7866	0.563	0.484
Total		41212087	1624568	100.000	100.000

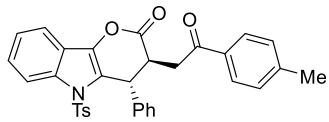
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) of 7c

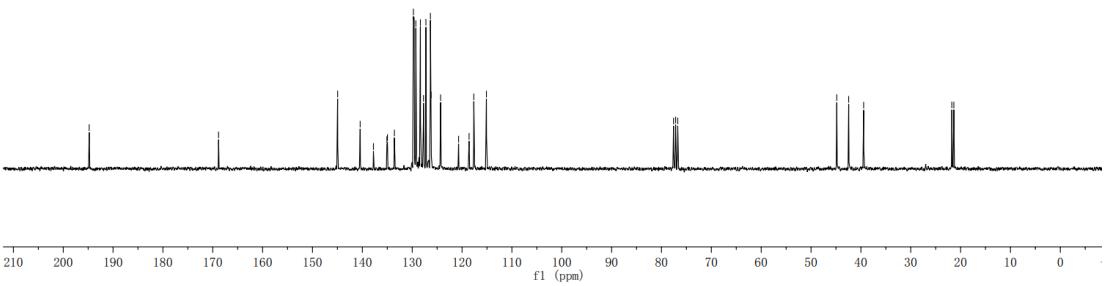




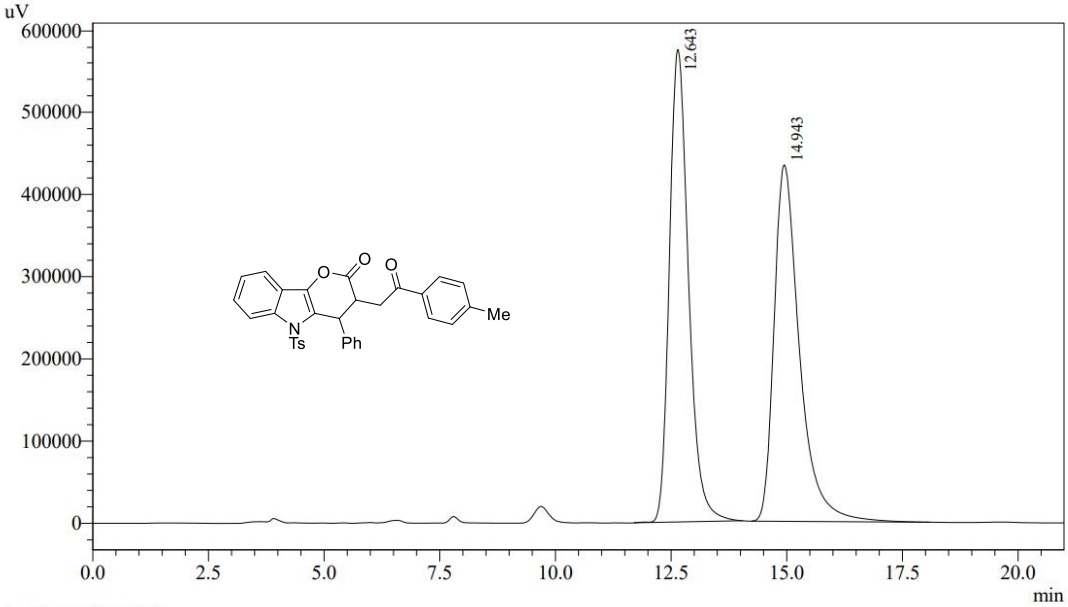








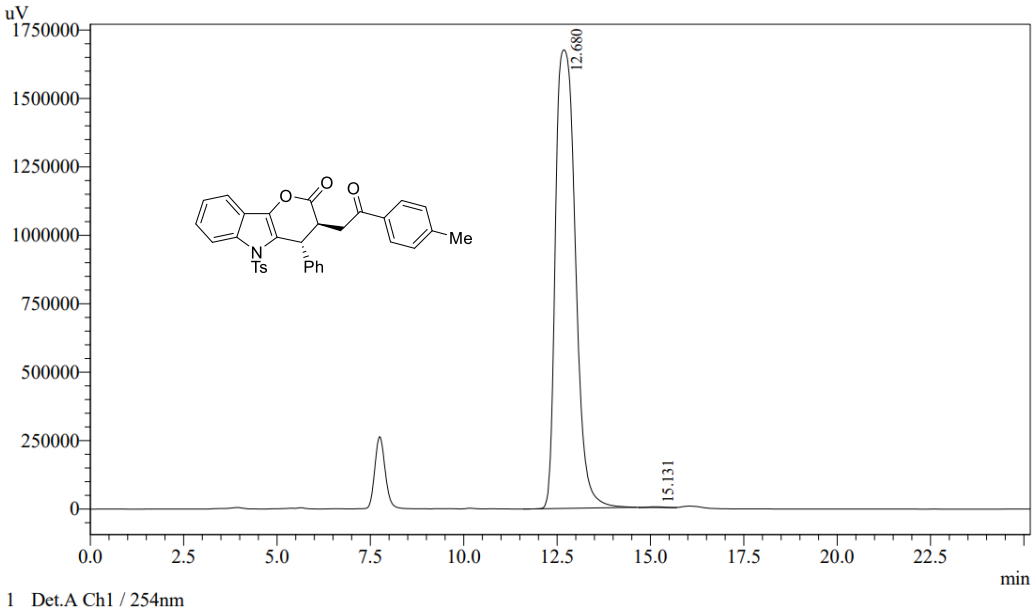
HPLC spectra of 7c



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.643	16538489	575710	49.887	57.043
2	14.943	16613293	433538	50.113	42.957
Total		33151782	1009248	100.000	100.000

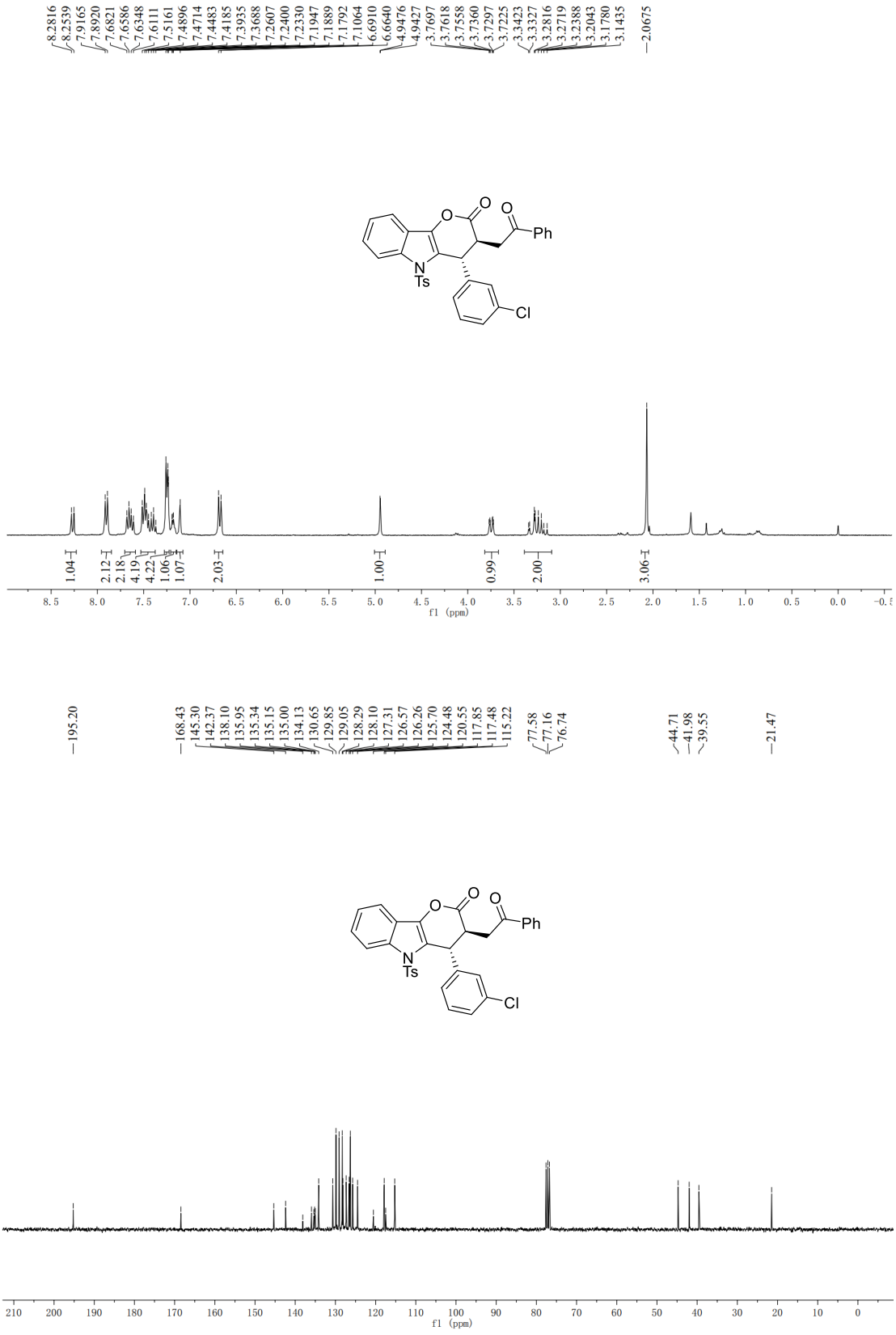


1 Det.A Ch1 / 254nm

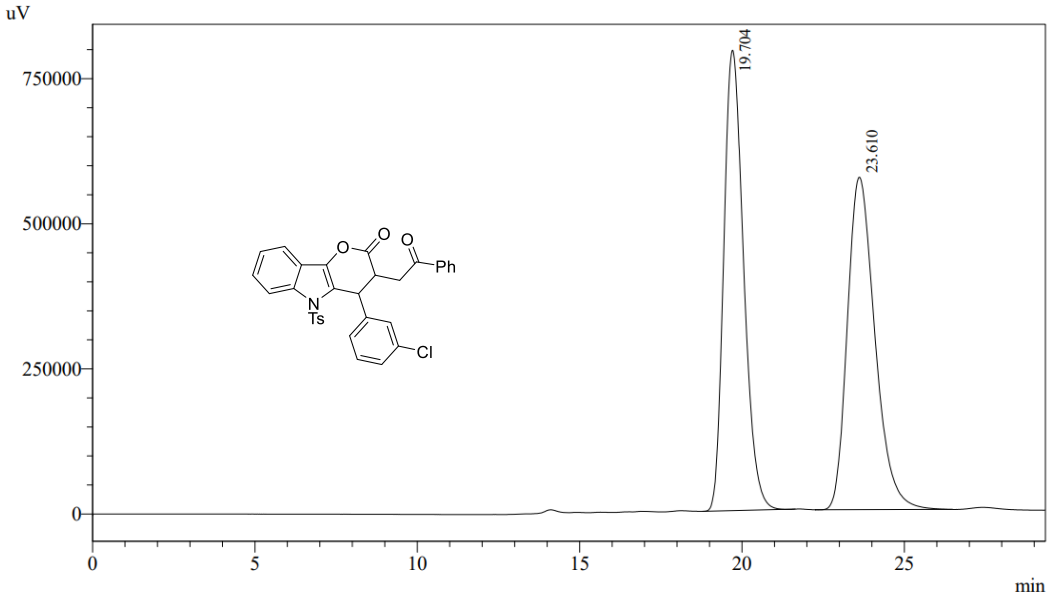
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.680	62247283	1675449	99.893	99.837
2	15.131	66918	2733	0.107	0.163
Total		62314201	1678182	100.000	100.000

^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) of 7d



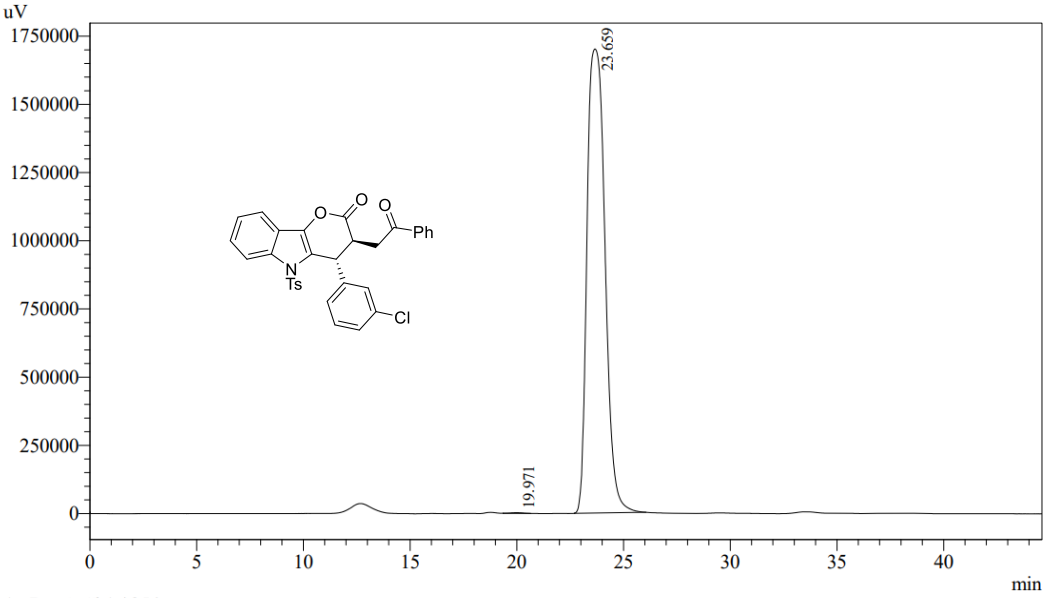
HPLC spectra of 7d



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.704	33700458	793264	49.891	58.067
2	23.610	33847216	572846	50.109	41.933
Total		67547673	1366110	100.000	100.000

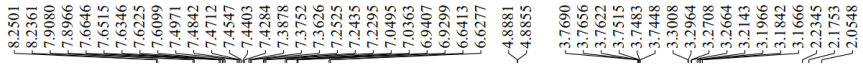


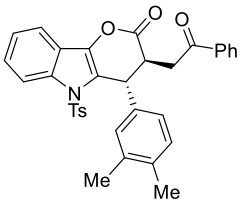
1 Det.A Ch1 / 254nm

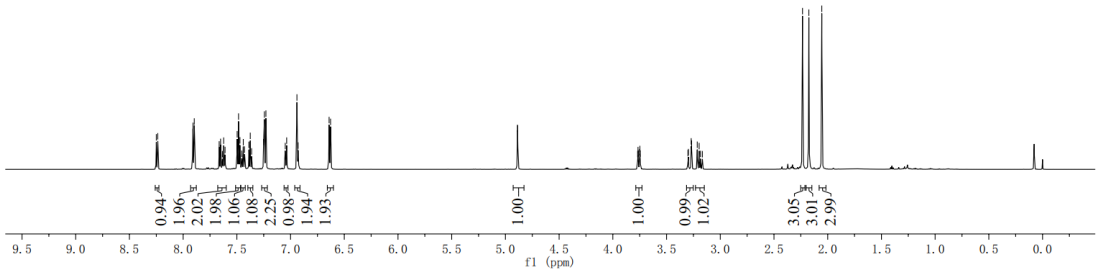
Detector A Ch1 254nm

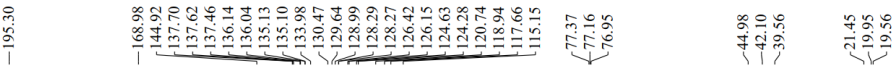
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.971	99362	2455	0.100	0.144
2	23.659	99600453	1701073	99.900	99.856
Total		99699815	1703528	100.000	100.000

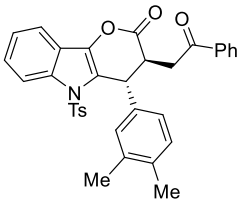
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of 7e

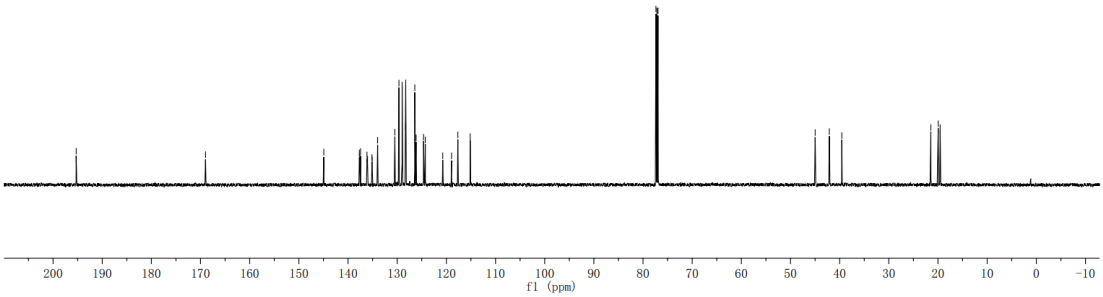




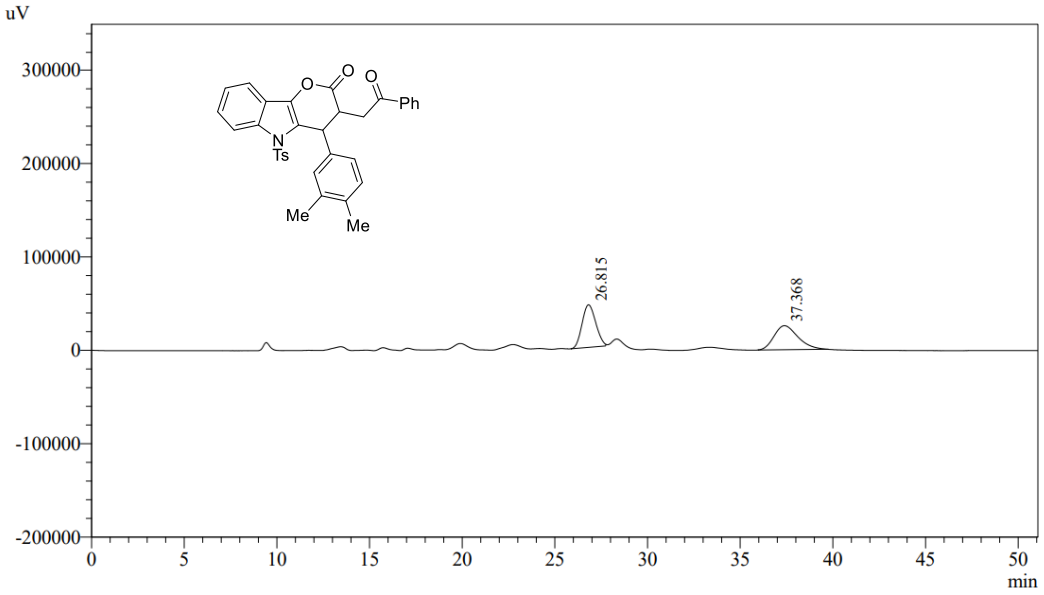








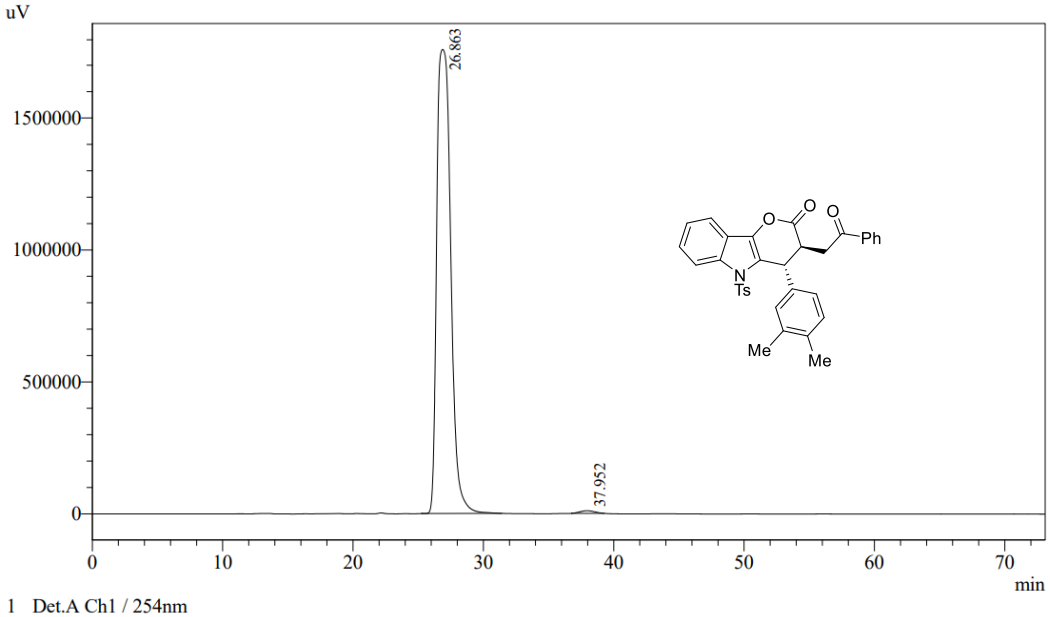
HPLC spectra of 7e



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.815	2332904	45553	50.260	63.883
2	37.368	2308755	25753	49.740	36.117
Total		4641659	71306	100.000	100.000

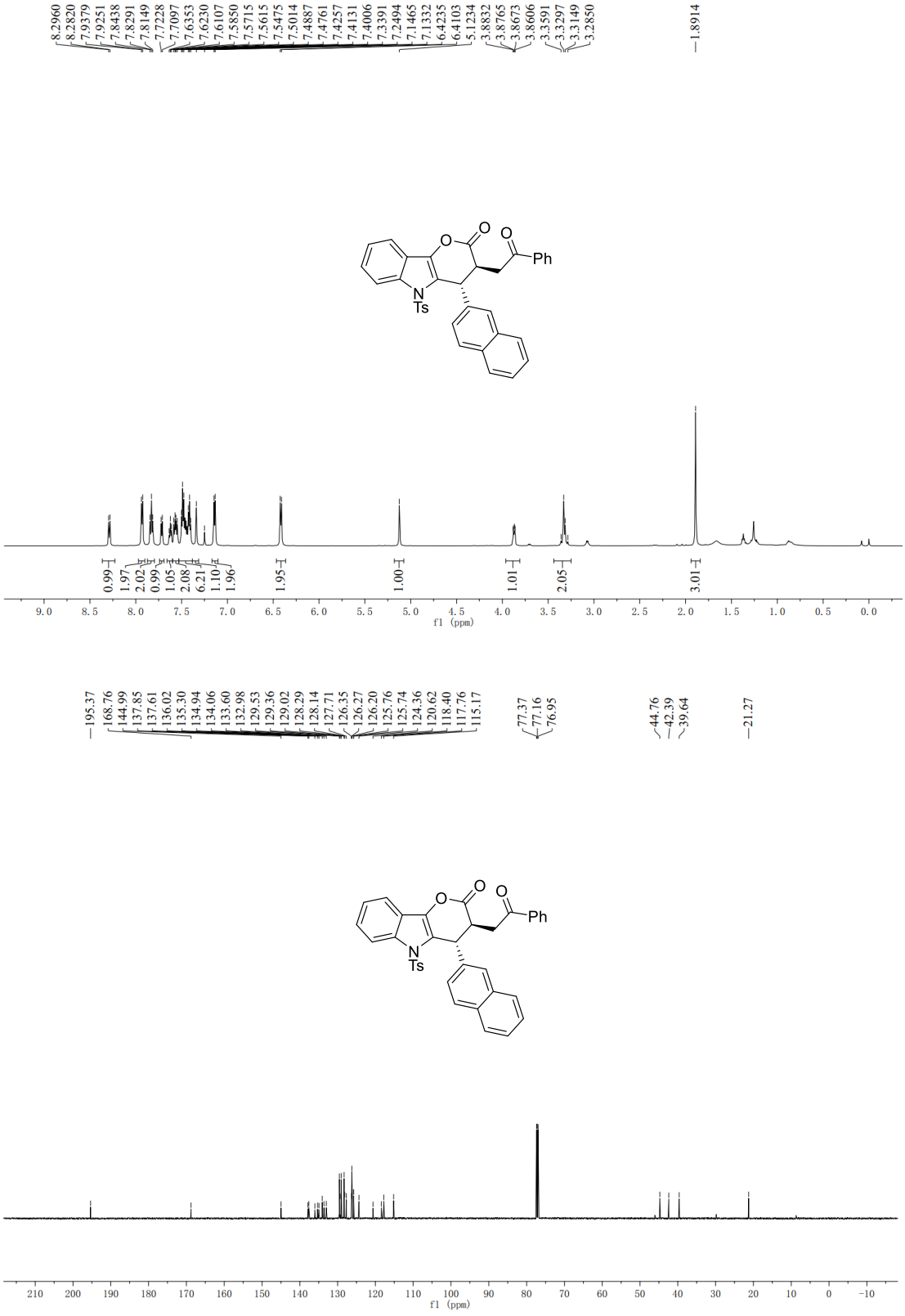


1 Det.A Ch1 / 254nm

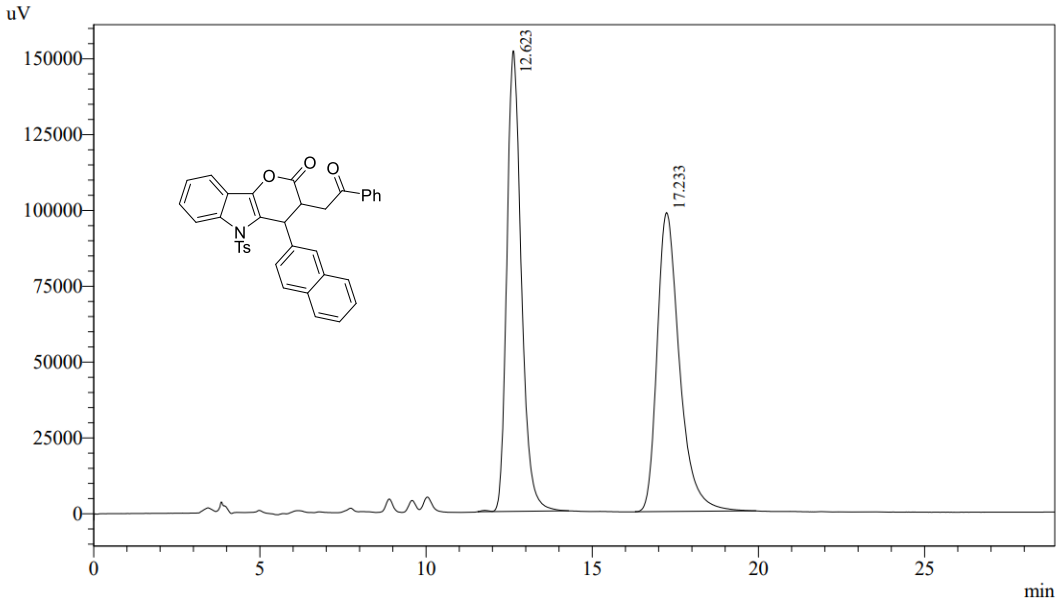
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.863	131708238	1762044	99.414	99.441
2	37.952	776347	9907	0.586	0.559
Total		132484585	1771950	100.000	100.000

^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of 7f



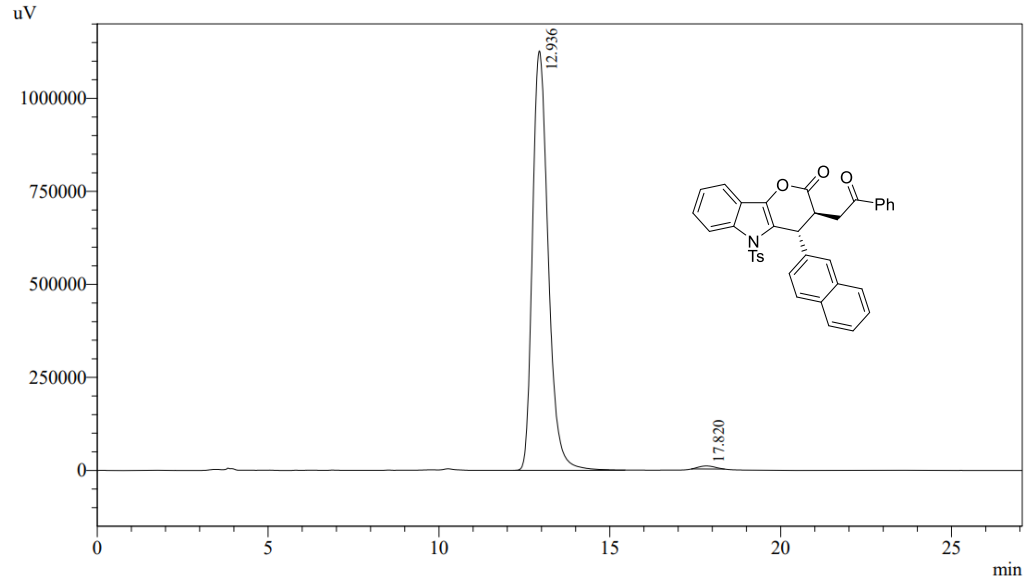
HPLC spectra of 7f



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.623	4612633	151831	50.028	60.639
2	17.233	4607475	98554	49.972	39.361
Total		9220108	250385	100.000	100.000

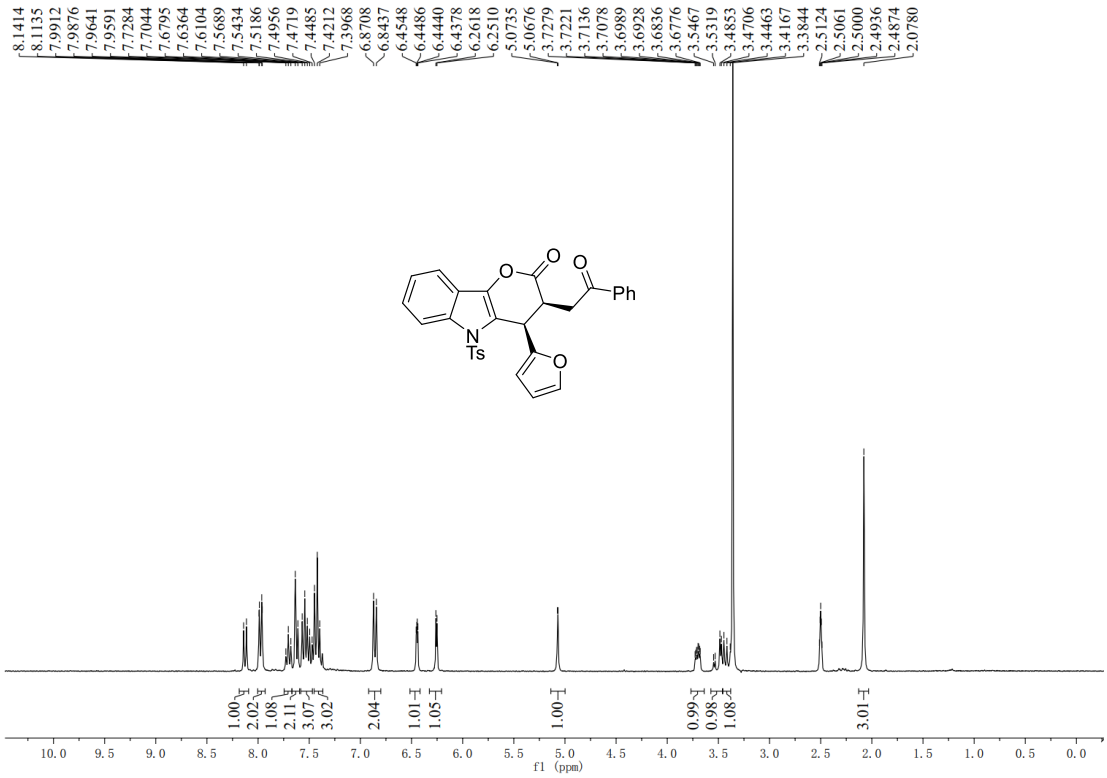


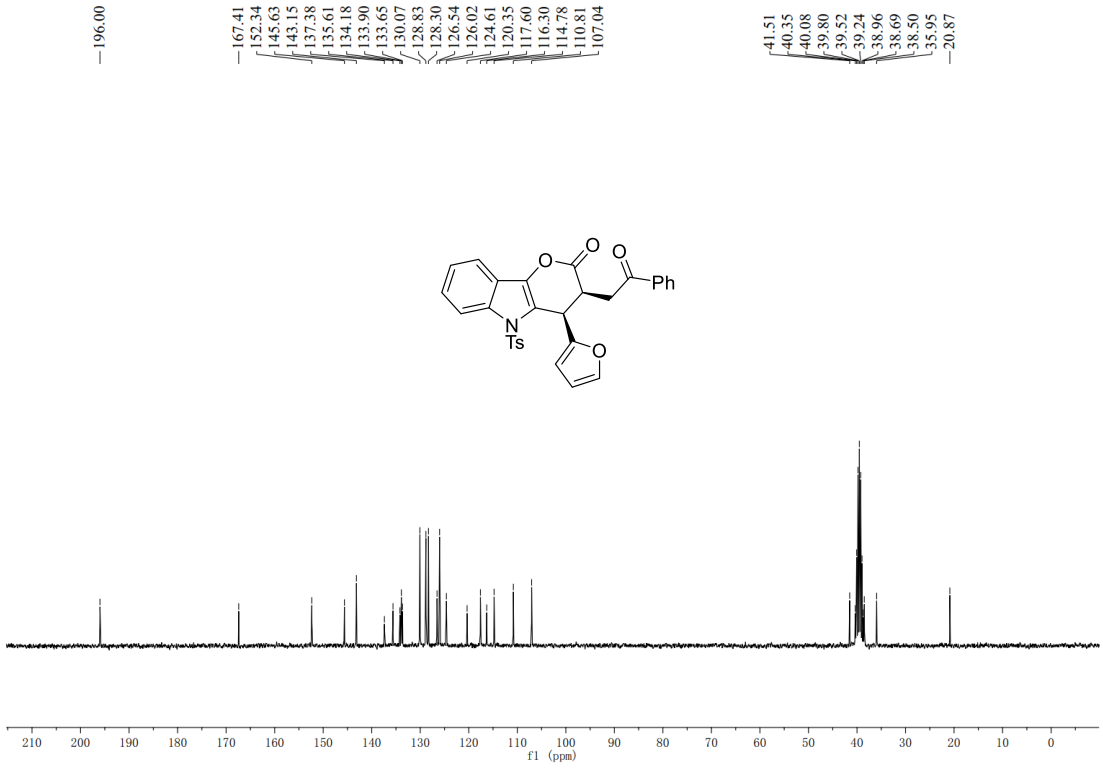
1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

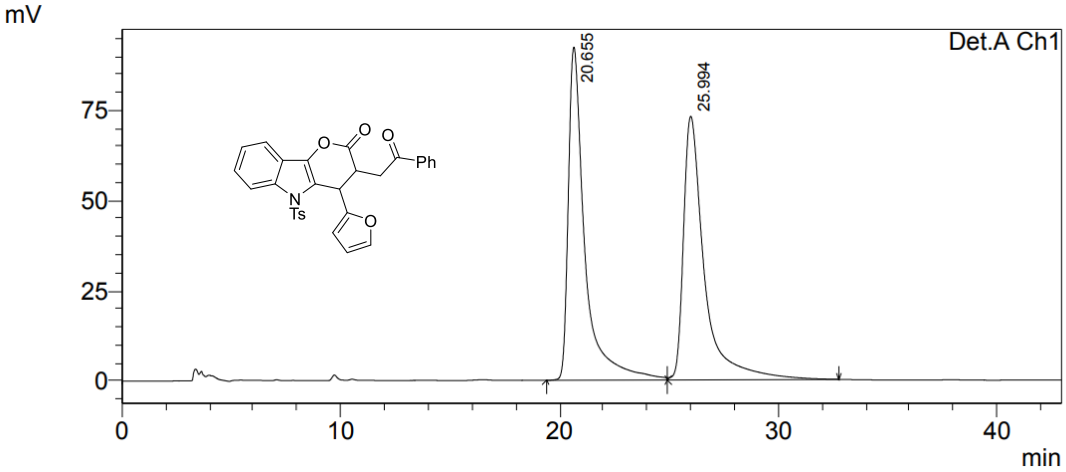
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.936	36148375	1127383	99.276	99.288
2	17.820	263648	8085	0.724	0.712
Total		36412023	1135468	100.000	100.000

^{1}H NMR (300 MHz, DMSO-d_6) and ^{13}C NMR (75 MHz, DMSO-d_6) of 7g





HPLC spectra of 7g

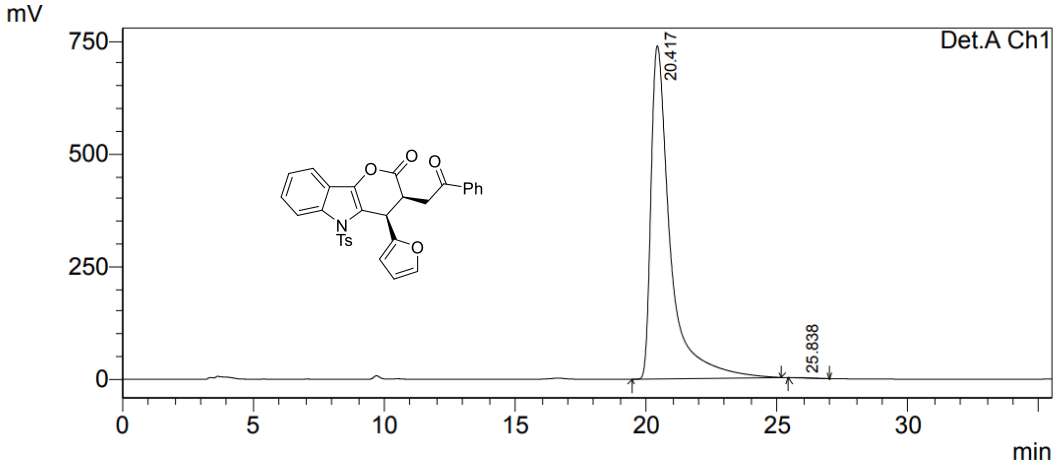


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	20.655	4851060	92248	49.978
2	25.994	4855300	72983	50.022
Total		9706360		100.000



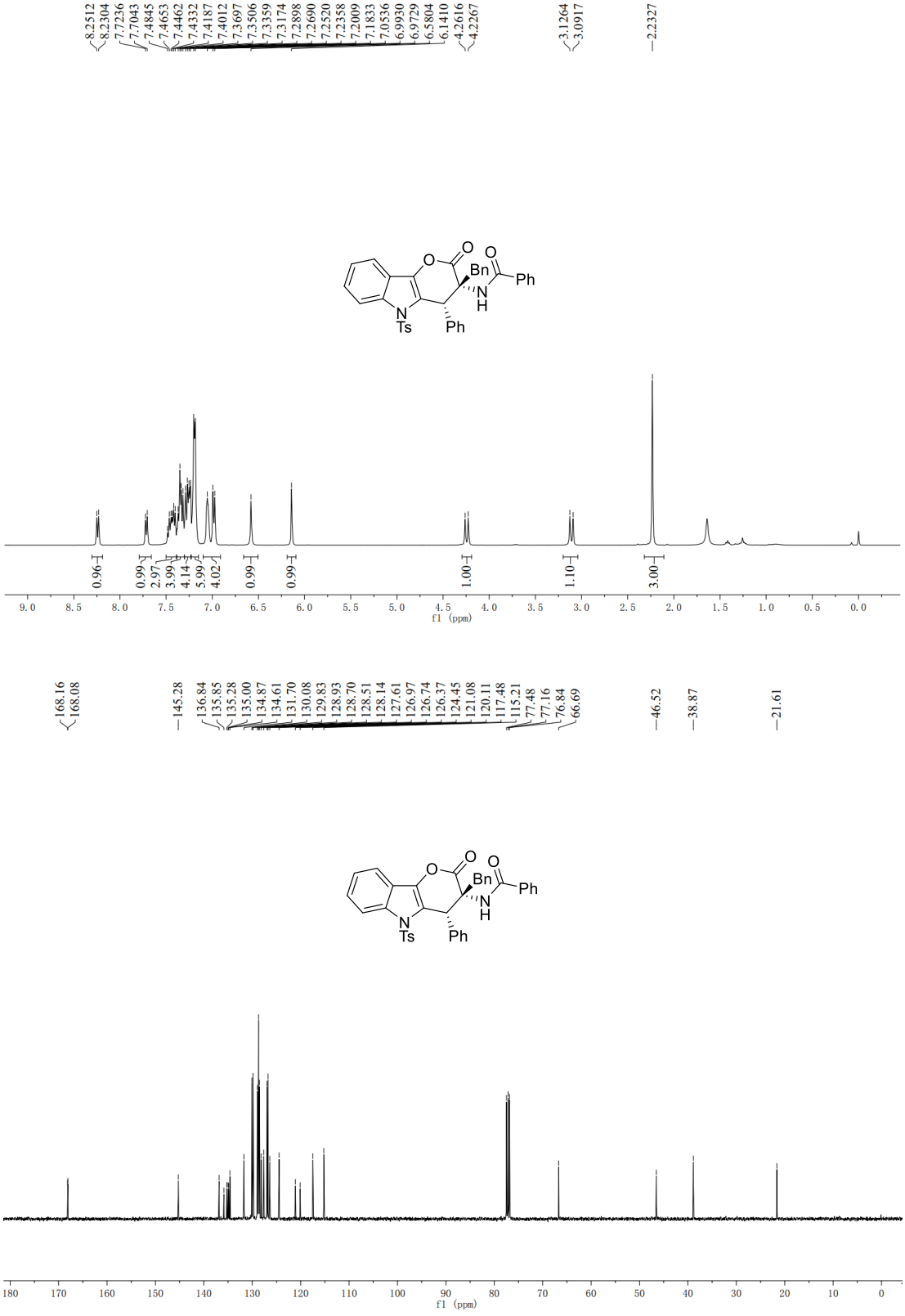
1 Det.A Ch1/254nm

PeakTable

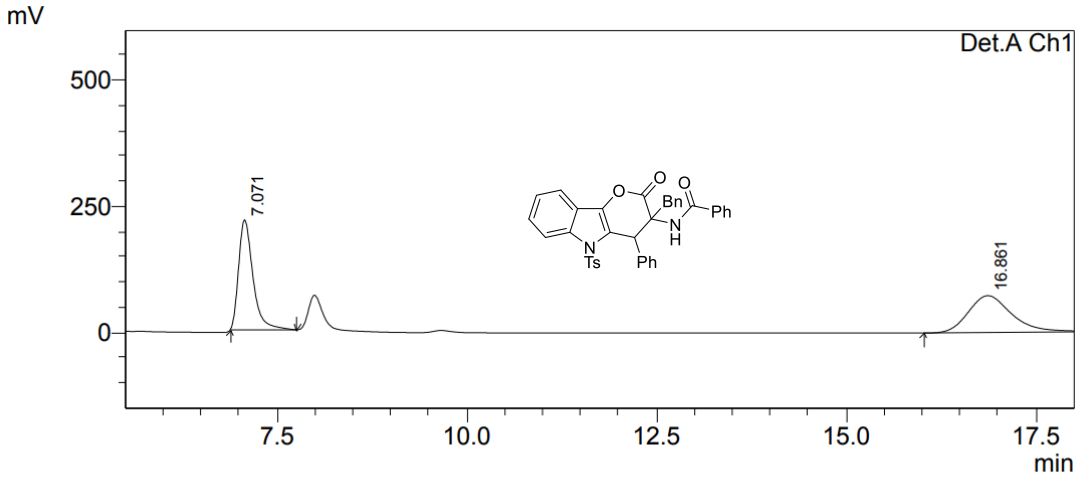
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	20.417	37846293	738805	99.925
2	25.838	28251	640	0.075
Total		37874544		100.000

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 8a



HPLC spectra of 8a

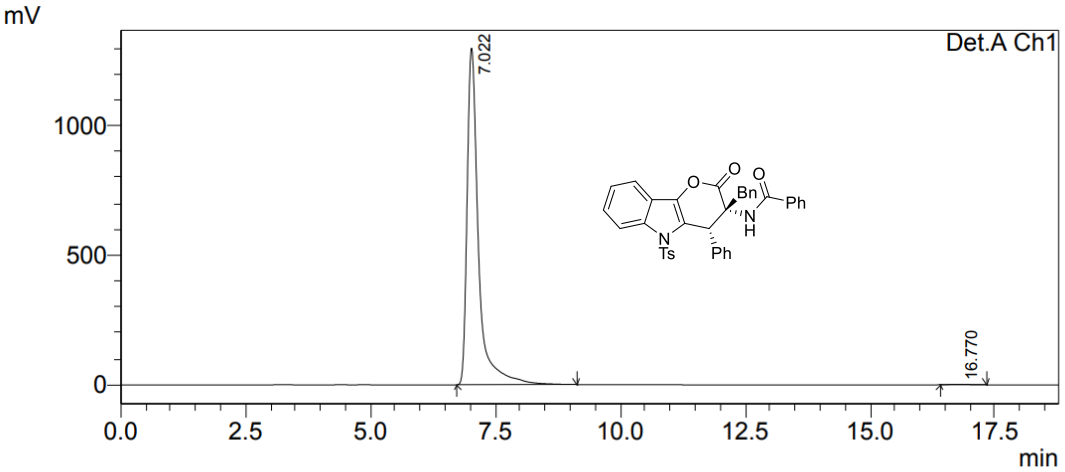


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.071	2880865	217832	49.827
2	16.861	2900827	72944	50.173
Total		5781692		100.000



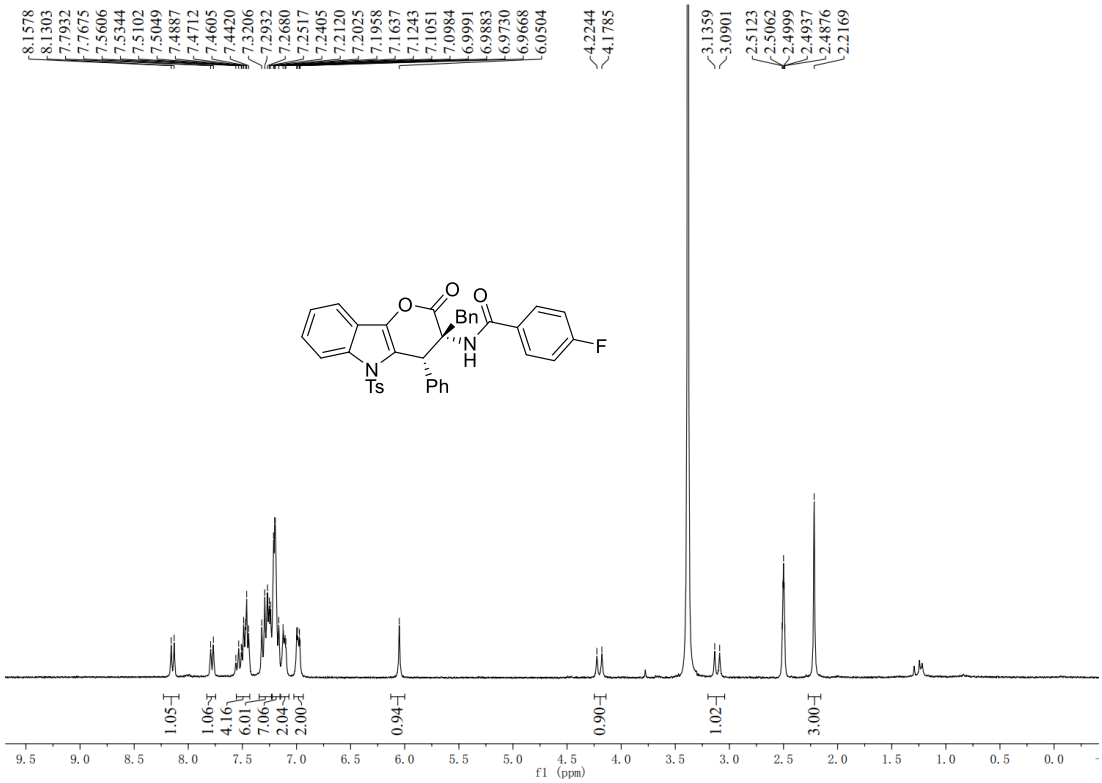
1 Det.A Ch1/254nm

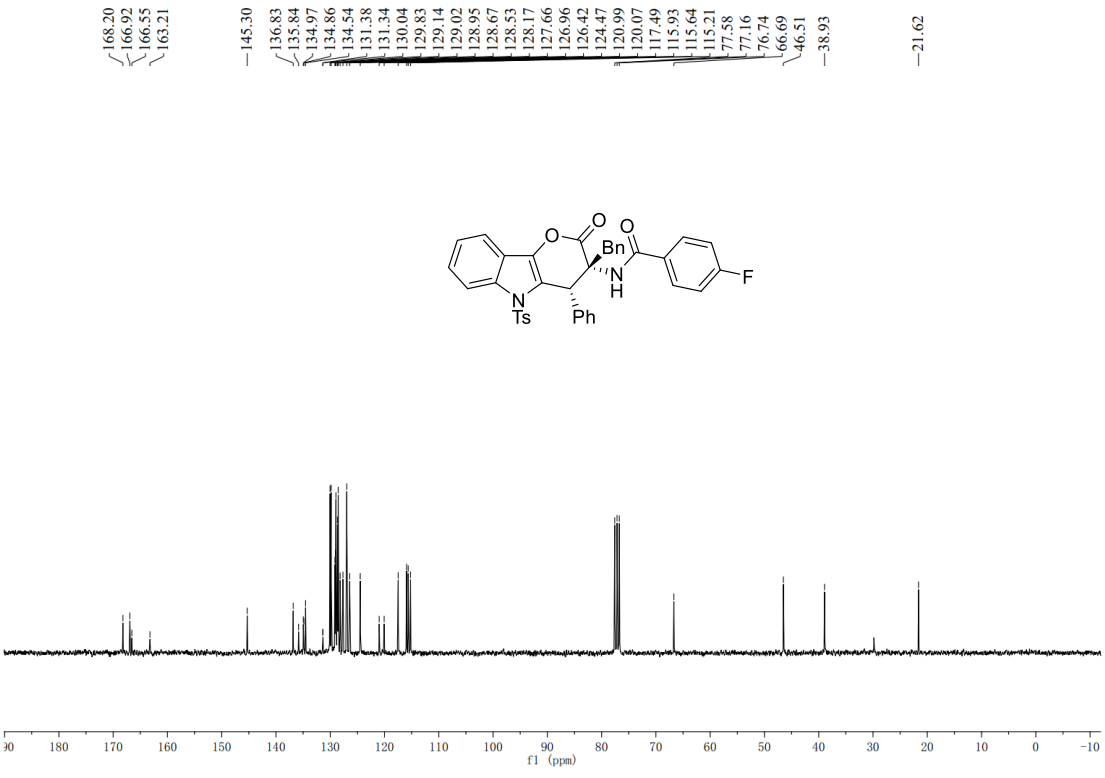
PeakTable

Detector A Ch1 254nm

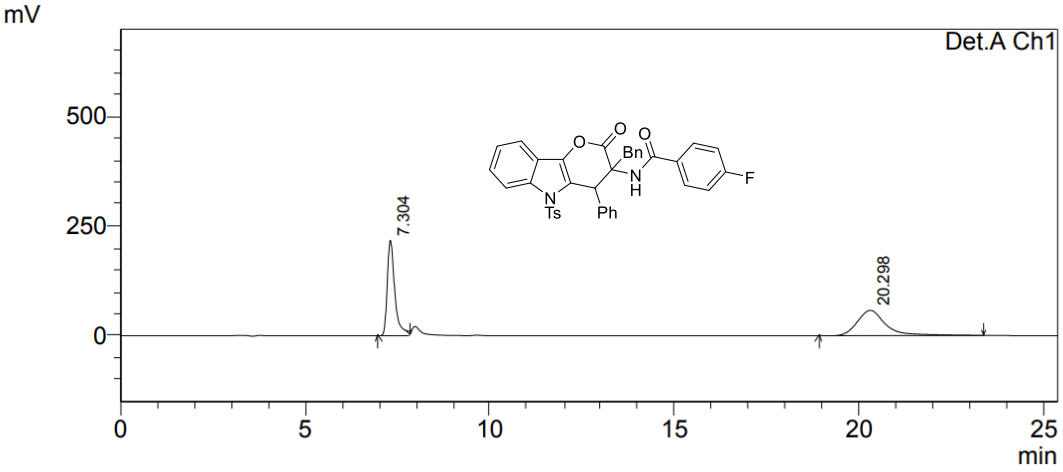
Peak#	Ret. Time	Area	Height	Area %
1	7.022	20561716	1298538	99.751
2	16.770	51365	1713	0.249
Total		20613081		100.000

^{1}H NMR (300 MHz, DMSO-d_6) and ^{13}C NMR (75 MHz, $CDCl_3$) of 8b





HPLC spectra of 8b

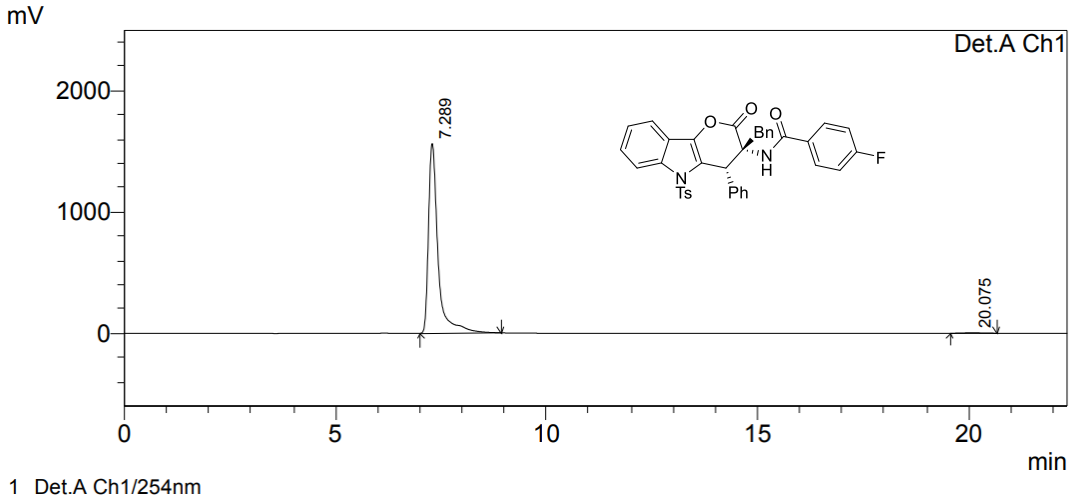


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.304	3096006	217613	49.878
2	20.298	3111132	57738	50.122
Total		6207139		100.000



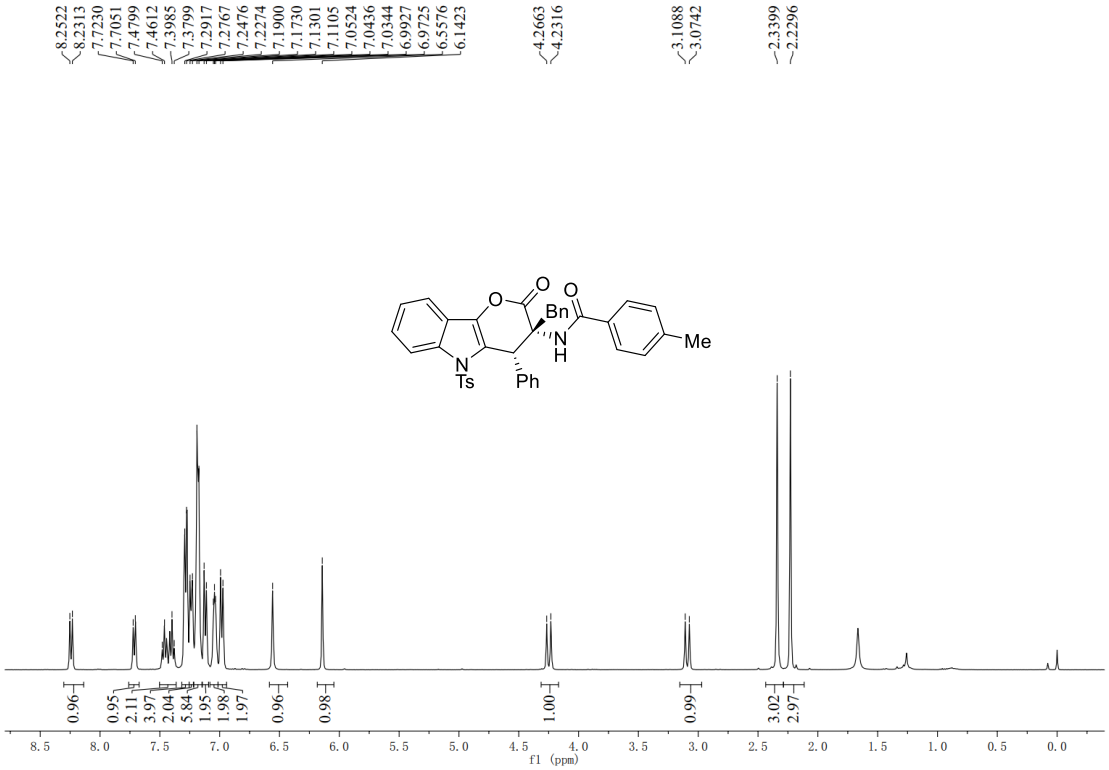
1 Det.A Ch1/254nm

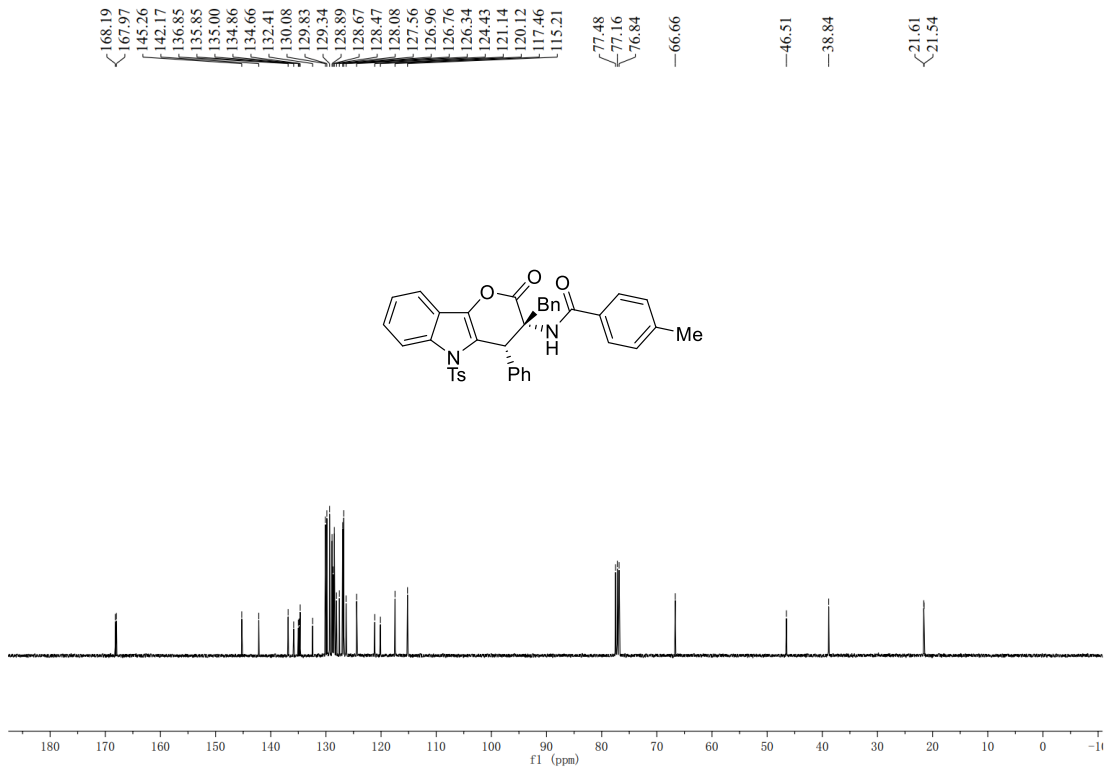
PeakTable

Detector A Ch1 254nm

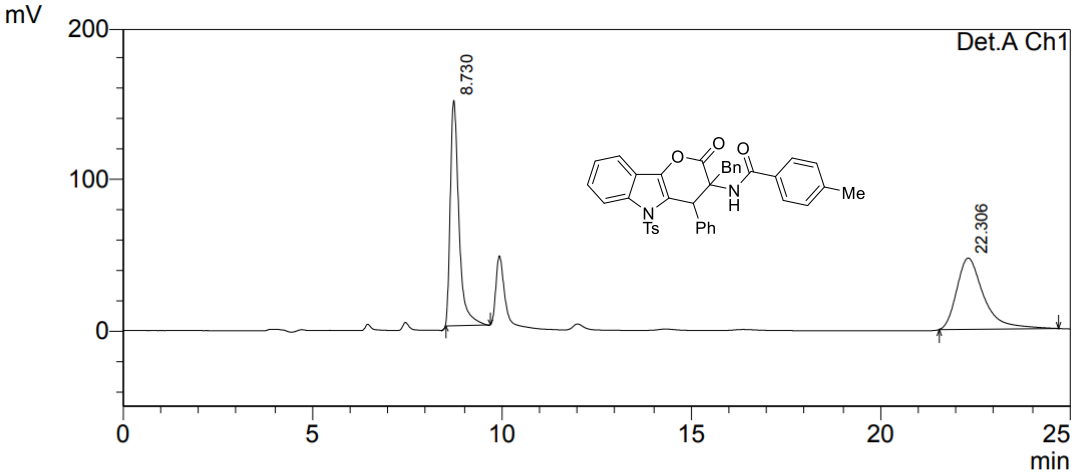
Peak#	Ret. Time	Area	Height	Area %
1	7.289	24862480	1563135	99.475
2	20.075	131182	3644	0.525
Total		24993662		100.000

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 8c





HPLC spectra of 8c

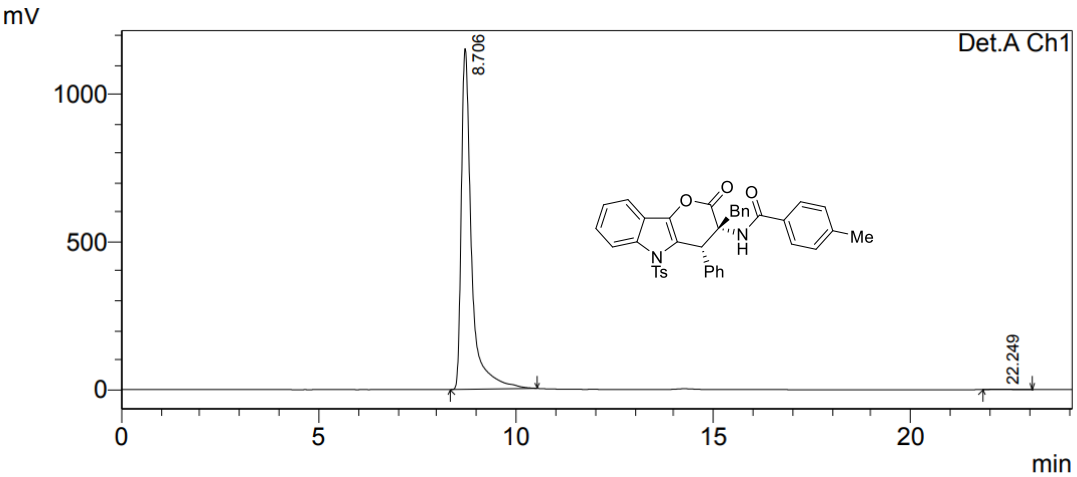


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.730	2372750	149374	50.328
2	22.306	2341810	47206	49.672
Total		4714560		100.000



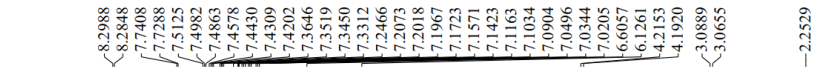
1 Det.A Ch1/254nm

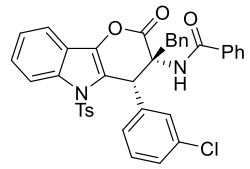
PeakTable

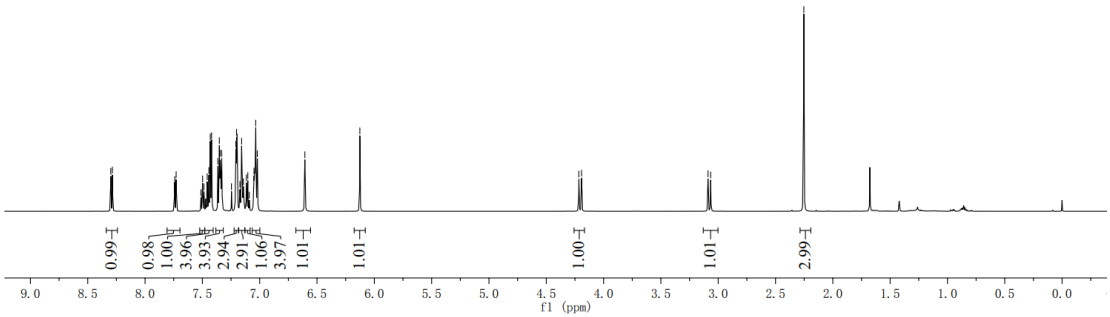
Detector A Ch1 254nm

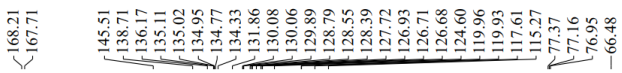
Peak#	Ret. Time	Area	Height	Area %
1	8.706	20808960	1154635	99.764
2	22.249	49143	1299	0.236
Total		20858103		100.000

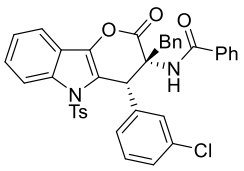
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of 8d

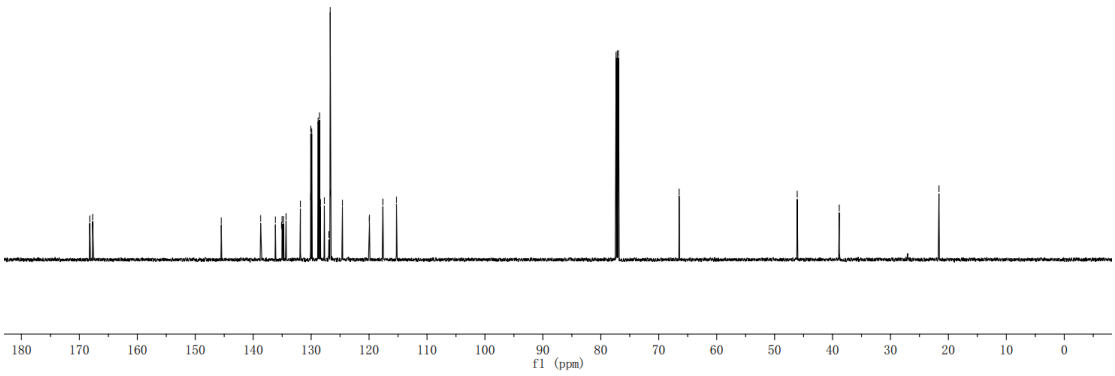




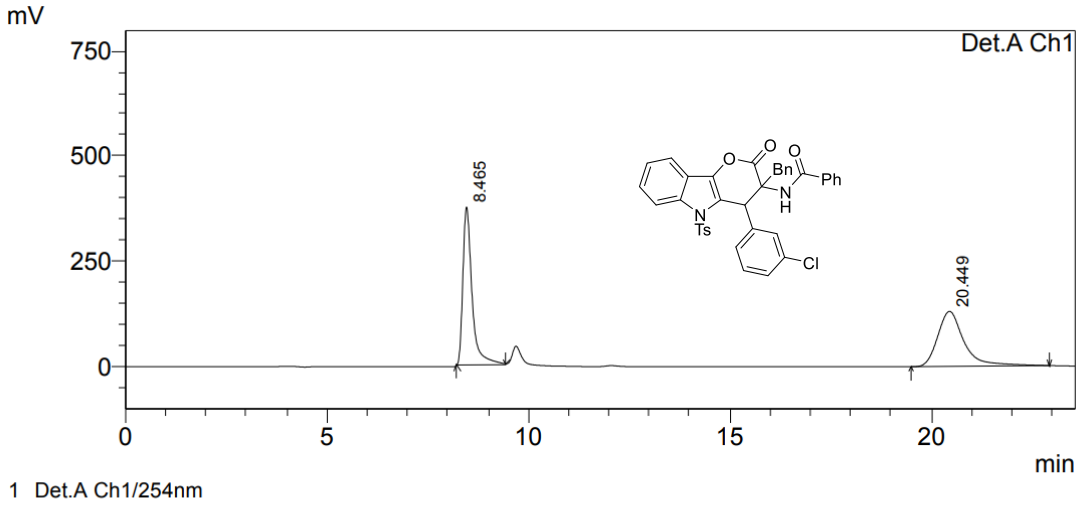








HPLC spectra of 8d

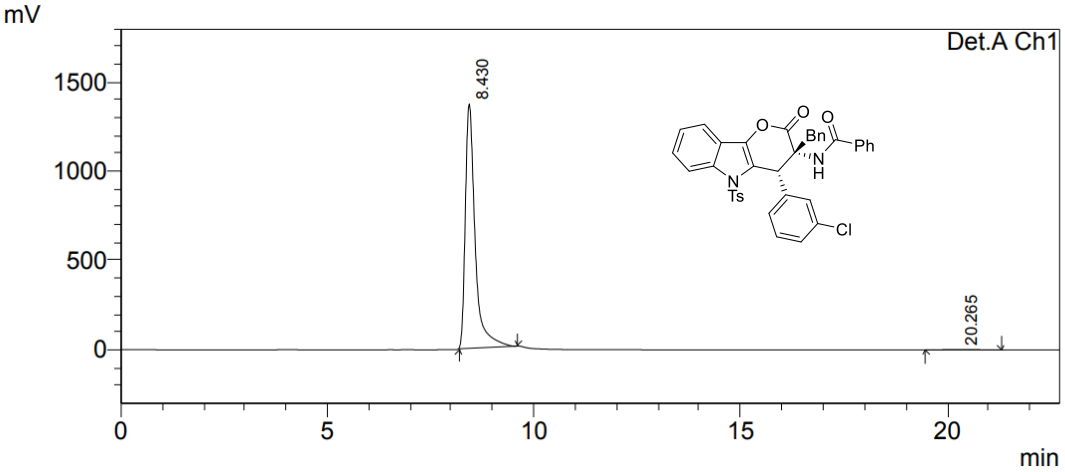


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.465	5952757	374521	50.021
2	20.449	5947730	130652	49.979
Total		11900487		100.000



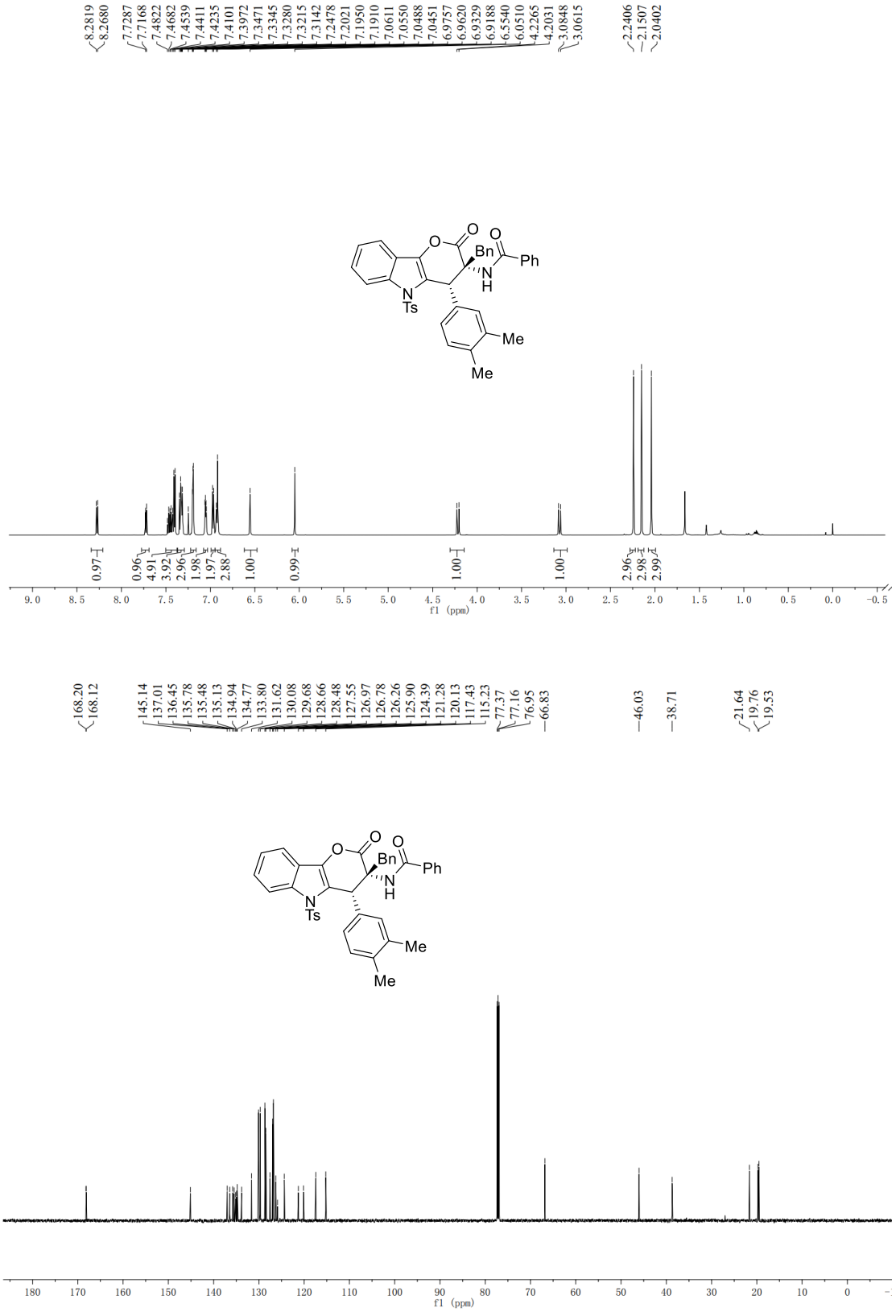
1 Det.A Ch1/254nm

PeakTable

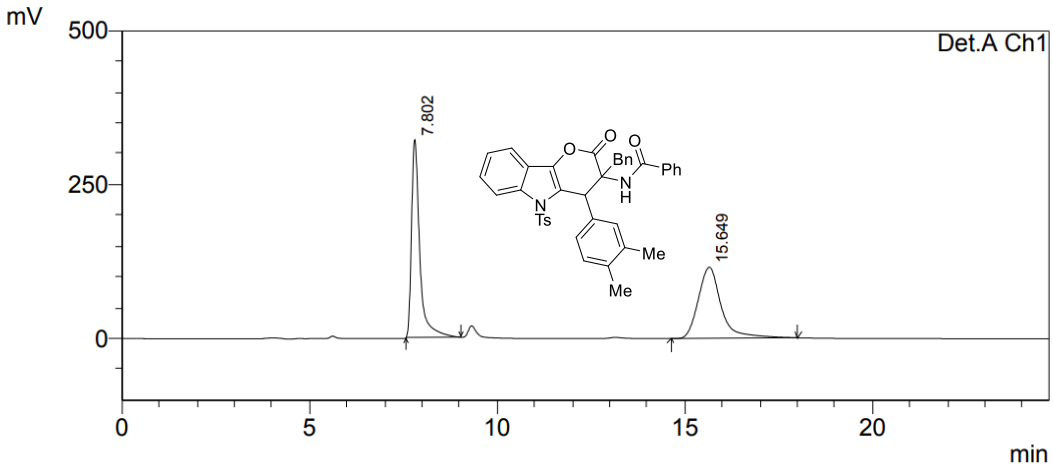
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.430	22541409	1369085	99.773
2	20.265	51303	1295	0.227
Total		22592712		100.000

^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of 8e



HPLC spectra of 8e

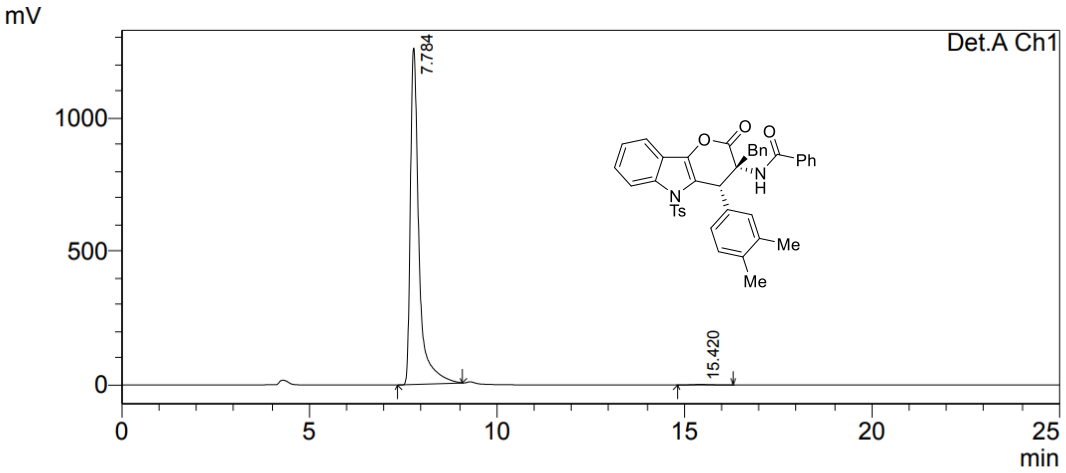


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.802	4902039	320579	50.010
2	15.649	4900028	115318	49.990
Total		9802068		100.000



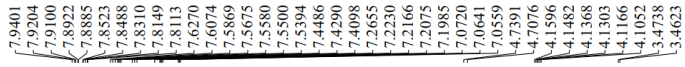
1 Det.A Ch1/254nm

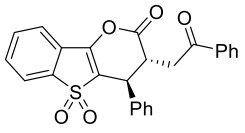
PeakTable

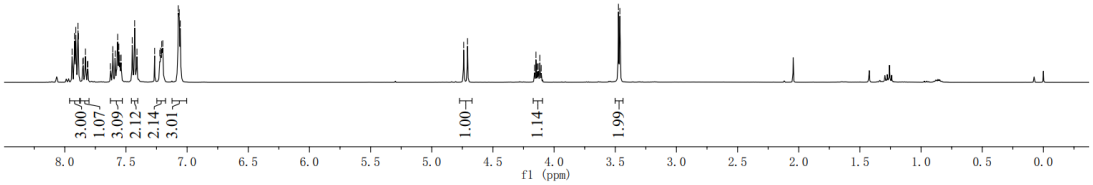
Detector A Ch1 254nm

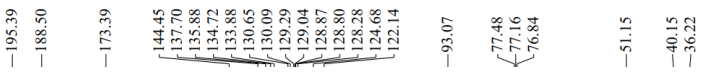
Peak#	Ret. Time	Area	Height	Area %
1	7.784	20047673	1260525	99.662
2	15.420	67942	2018	0.338
Total		20115614		100.000

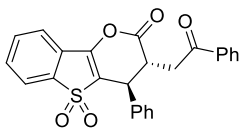
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 9

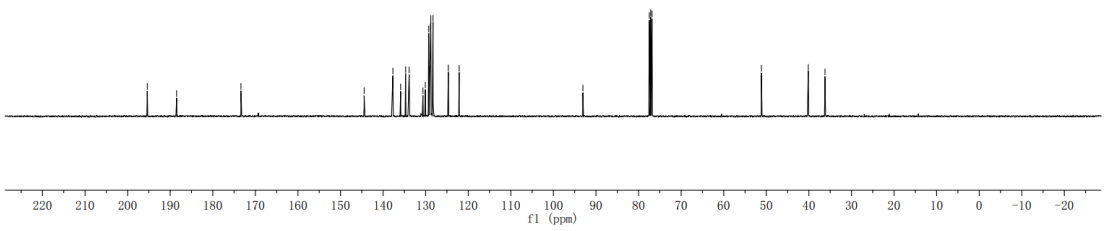




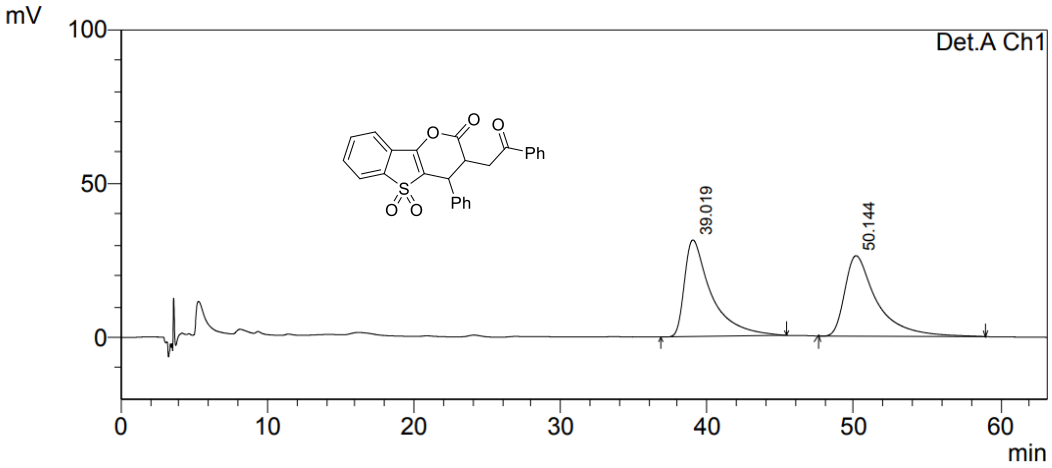








HPLC spectra of 9

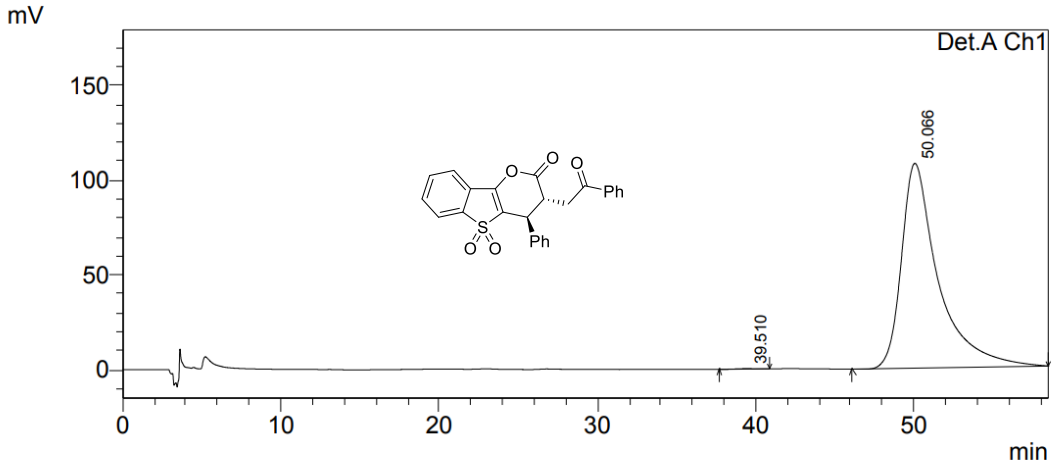


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	39.019	3986223	31320	50.086
2	50.144	3972582	26102	49.914
Total		7958804		100.000



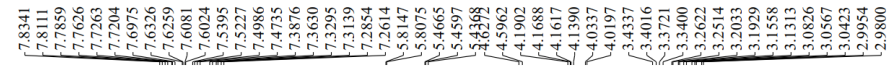
1 Det.A Ch1/254nm

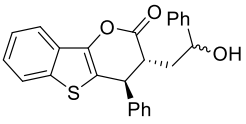
PeakTable

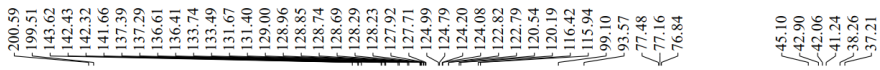
Detector A Ch1 254nm

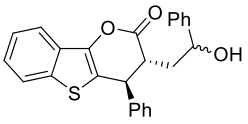
Peak#	Ret. Time	Area	Height	Area %
1	39.510	23234	258	0.133
2	50.066	17452194	108220	99.867
Total		17475427		100.000

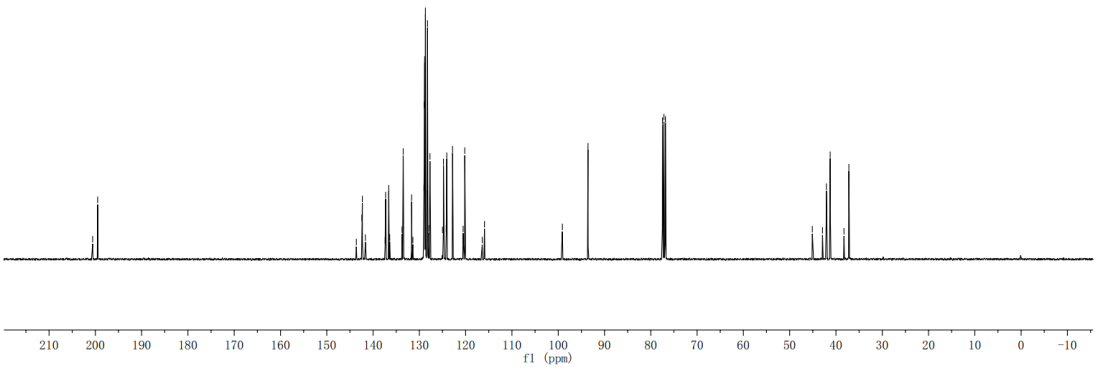
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 10



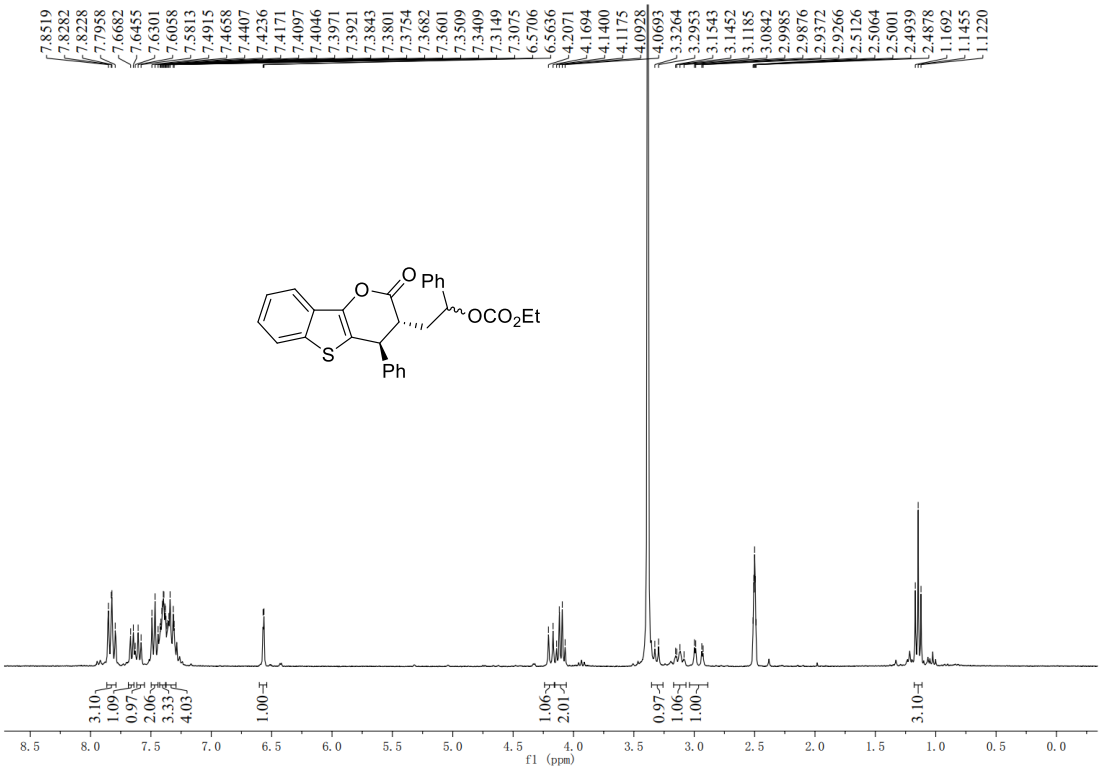


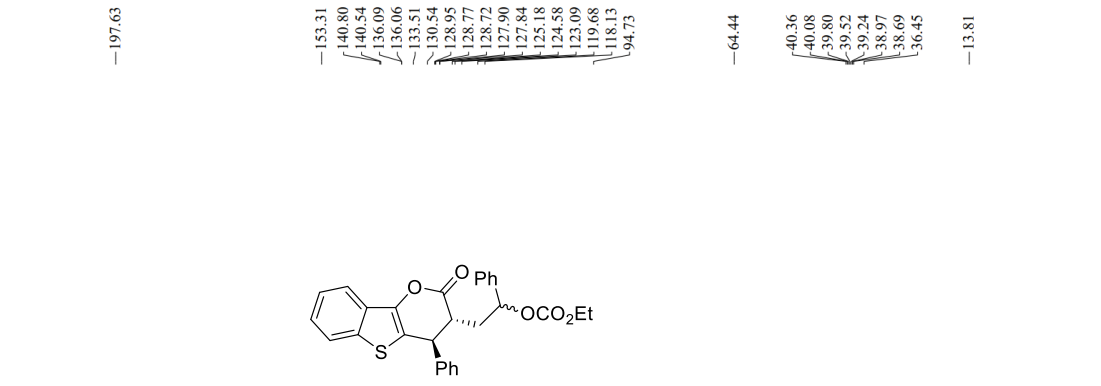


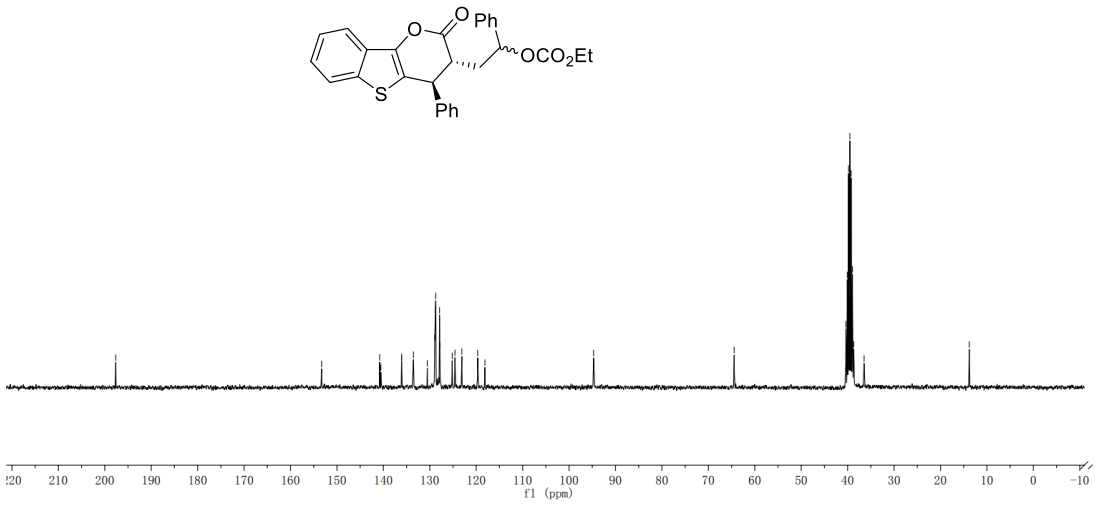




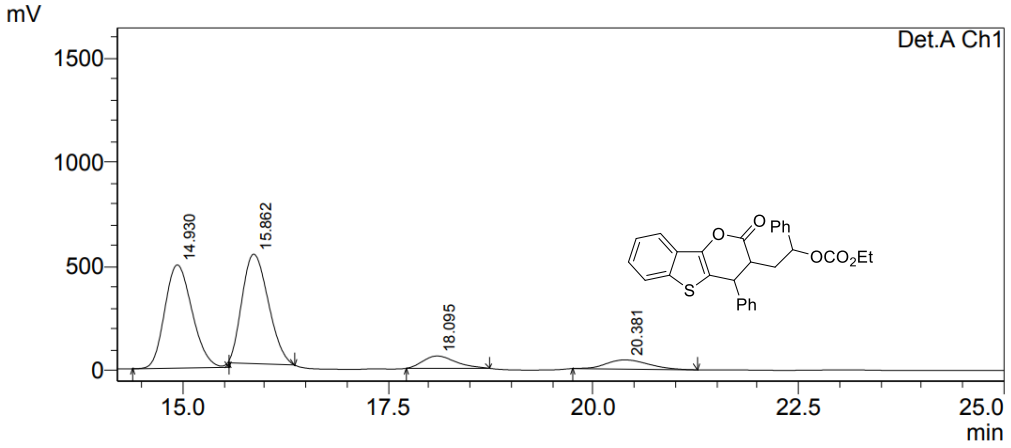
^{1}H NMR (300 MHz, DMSO-d_6) and ^{13}C NMR (75 MHz, DMSO-d_6) of 11







HPLC spectra of 11

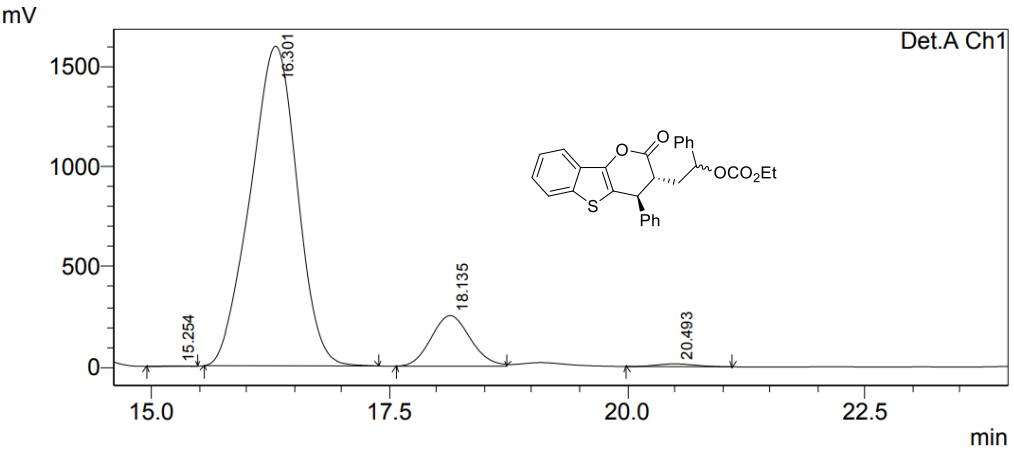


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	14.930	11519768	495683	43.565
2	15.862	11707522	525653	44.275
3	18.095	1624385	58852	6.143
4	20.381	1591012	44172	6.017
Total		26442687		100.000



1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	15.254	31041	1885	0.050
2	16.301	54596209	1593112	87.632
3	18.135	7272798	252734	11.674
4	20.493	401407	14095	0.644
Total		62301455		100.000