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SUPPORTING INFORMATION

Asymmetric three-component reaction of diazo compound with alcohol and seven-membered imine

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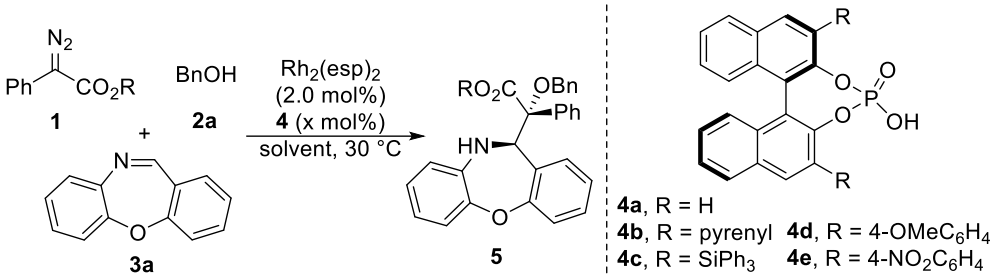
General Information

All reactions were performed in oven-dried glassware under atmosphere of argon. Solvents were dried and distilled followed the standard methods before using. Chiral phosphoric acids (CPAs) and alcohols **2** purchased from chemical vendors and used directly without any treatment. Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). Flash column chromatography was performed using silica gel (300-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on 400/500 MHz spectrometer; chemical shifts are reported in ppm with the solvent signals as reference, and coupling constants (J) are given in Hertz. The peak information is described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. Enantioselectivity was determined on HPLC using Chiralpak IA, AD-H, IF-3 column. High-resolution mass spectra (HRMS) were recorded on a commercial apparatus (ESI Source) and (CI Source). Starting materials **1**[1] and **3**[2] were prepared according to the reported reference.

Table S1. Optimization of the Reaction Conditions[a]

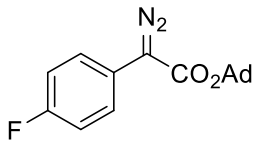


Entry	**4** (x mol %)	R	Solvent	Yield (%)[b]	*dr*[c]	*ee* (%)[d]
1	**4a** (10)	Ad	DCE	61	1:1	30(11)
2	**4b** (10)	Ad	DCE	90	1.5:1	99(95)
3	**4c** (10)	Ad	DCE	79	> 20:1	99
4	**4d** (10)	Ad	DCE	66	3:1	93(80)
5	**4e** (10)	Ad	DCE	56	3:1	86(77)
6	**4c** (10)	Me	DCE	85	2:1	98(99)
7	**4c** (10)	*t*Bu	DCE	79	20:1	86
8	**4c** (10)	Ad	DCM	65	> 20:1	99
9	**4c** (10)	Ad	TBME	trace	> 20:1	99
10	**4c** (10)	Ad	EA	46	> 20:1	99
11	**4c** (10)	Ad	toluene	69	> 20:1	99
12[e]	**4c** (10)	Ad	DCE	85	> 20:1	99
13[f]	**4c** (10)	Ad	DCE	95	> 20:1	99
14[f]	**4c** (5.0)	Ad	DCE	94	> 20:1	99
15[f]	**4c** (2.0)	Ad	DCE	70	> 20:1	99
16[f,g]	**4c** (2.0)	Ad	DCE	96	> 20:1	99

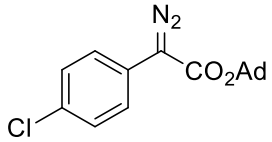
[a]The reaction was carried out on a 0.1 mmol scale: to the mixture of $Rh_2(esp)_2$ (2.0 mol%), **4** (indicated amount), **2a** (0.12 mmol), and 4 Å MS (100 mg) in the indicated solvent (0.5 mL), was added a solution of diazo compound **1a** (0.12 mmol) and imine **3a** (0.1 mmol) in the same solvent (1.5 mL) *via* syringe pump over 2 h under an argon atmosphere at 30 °C, and the reaction mixture was stirred for an additional 1 h under these conditions. [b]Isolated yields. [c]Determined by ^{1}H NMR analysis of the crude reaction mixture. [d]Determined by chiral HPLC analysis, see SI for detail. [e]3 Å MS (100 mg) was used instead of 4 Å MS. [f]5 Å MS (100 mg) was used instead of 4 Å MS. [g]The amount of $Rh_2(esp)_2$ was reduced to 1.0 mol%, and the mixture of **1a** and **3a** in DCE was added *via* syringe pump over 10 h. DCM = dichloromethane. TBME = *tert*-butyl methyl ether. EA = ethyl acetate.

General Procedure for the Synthesis of Diazo Compounds 1:

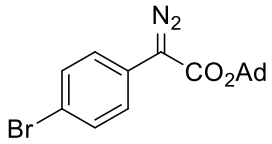
The diazo compounds **1** were prepared according to literature procedures.[1]



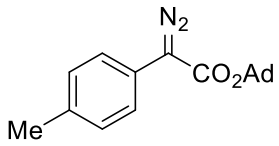
(3*r*)-Adamantan-1-yl 2-diazo-2-(4-fluorophenyl)acetate (1b). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.46 – 7.39 (m, 2H), 7.10 – 7.03 (m, 2H), 2.22 – 2.16 (comp, 9H), 1.71 – 1.65 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.4, 161.0 (d, *J* = 245.9 Hz), 126.0 (d, *J* = 7.9 Hz), 122.08, 116.0 (d, *J* = 21.9 Hz), 82.4, 41.8, 36.3, 31.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -116.8. HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{19}FN_2NaO_2$ $[M+Na]^+$: 337.1323, found 337.1324.



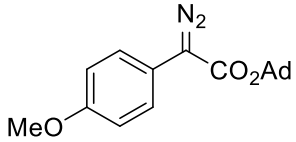
(3*r*)-Adamantan-1-yl 2-(4-chlorophenyl)-2-diazoacetate (1c). Yellow oil; ^{1}H NMR 7.41 – 7.37 (m, 2H), 7.33 – 7.29 (m, 2H), 2.24 – 2.14 (comp, 9H), 1.75 – 1.62 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.0, 131.2, 129.0, 125.1, 125.0, 82.5, 41.8, 36.2, 31.1; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{19}ClN_2NaO_2$ $[M+Na]^+$: 353.1027, found 353.1020.



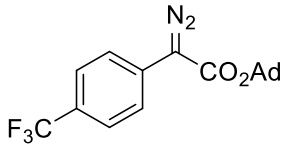
(3*r*)-Adamantan-1-yl 2-(4-bromophenyl)-2-diazoacetate (1d). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.49 – 7.44 (m, 2H), 7.36 – 7.30 (m, 2H), 2.23 – 2.16 (comp, 9H), 1.72 – 1.66 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.8, 132.0, 125.5, 125.4, 119.0, 82.5, 41.8, 36.2, 31.0; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{19}BrN_2NaO_2$ $[M+Na]^+$: 397.0522, found 397.0519.



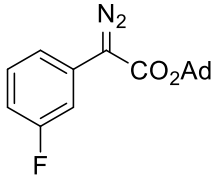
(3*r*)-Adamantan-1-yl 2-diazo-2-(p-tolyl)acetate (1e). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.37 – 7.31 (m, 2H), 7.19 – 7.14 (m, 2H), 2.32 (s, 3H), 2.22 – 2.18 (comp, 9H), 1.73 – 1.66 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.6, 135.4, 129.7, 129.23, 129.20, 124.2, 82.1, 41.8, 36.3, 31.1, 21.1; HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{22}N_2NaO_2$ [M+Na]$^+$: 333.1573, found 333.1574.



(3*r*)-Adamantan-1-yl 2-diazo-2-(4-methoxyphenyl)acetate (1f). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.32 – 7.27 (m, 2H), 6.87 – 6.83 (m, 2H), 3.72 (s, 3H), 2.15 – 2.10 (comp, 9H), 1.65 – 1.59 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.9, 158.0, 126.0, 117.8, 114.6, 82.1, 55.5, 41.9, 36.3, 31.1; HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{22}N_2NaO_3$ [M+Na]$^+$: 349.1523, found 349.1520.

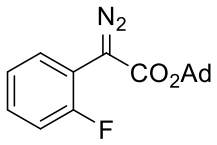


(3*r*)-Adamantan-1-yl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (1g). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.61 – 7.55 (comp, 4H), 2.25 – 2.16 (comp, 9H), 1.75 – 1.64 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.3, 130.8, 127.2 (q, *J* = 32.7 Hz), 125.7 (q, *J* = 3.8 Hz), 124.9 (q, *J* = 271.7 Hz), 123.4, 82.8, 41.7, 36.1, 31.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ = -62.4. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{19}F_3N_2NaO_2$ [M+Na]$^+$: 387.1291, found 387.1290.



(3*r*)-Adamantan-1-yl 2-diazo-2-(3-fluorophenyl)acetate (1h). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.36 – 7.32 (m, 1H), 7.32 – 7.27 (m, 1H), 7.15 – 7.10 (m,

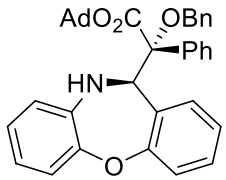
1H), 6.82 (tdd, *J* = 8.3, 2.5, 0.6 Hz, 1H), 2.43 – 2.03 (comp, 9H), 1.81 – 1.54 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.7, 163.3 (d, *J* = 245.1 Hz), 130.2 (d, *J* = 8.8 Hz), 128.9 (d, *J* = 9.5 Hz), 118.9 (d, *J* = 2.8 Hz), 112.2 (d, *J* = 21.4 Hz), 111.1 (d, *J* = 25.4 Hz), 82.6, 41.8, 36.2, 31.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ = -112.0; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{19}FN_2NaO_2$ $[M+Na]^+$: 337.1323, found 337.1333.



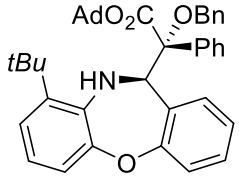
(3*r*)-Adamantan-1-yl 2-diazo-2-(2-fluorophenyl)acetate (1i). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.73 – 7.63 (m, 1H), 7.23 – 7.11 (m, 2H), 7.08 – 6.99 (m, 1H), 2.20 – 2.15 (comp, 9H), 1.73 – 1.63 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.2, 158.4 (d, *J* = 247.1 Hz), 129.5 (d, *J* = 2.2 Hz), 128.2 (d, *J* = 8.2 Hz), 124.5 (d, *J* = 3.4 Hz), 115.6 (d, *J* = 21.4 Hz), 114.5 (d, *J* = 11.8 Hz), 82.3, 41.7, 36.2, 31.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -114.1. HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{19}FN_2NaO_2$ $[M+Na]^+$: 337.1323, found 337.1325.

General Procedure for the Asymmetric Three-component Reaction

To a 10-mL oven-dried vial with a magnetic stirring bar, alcohol **2** (0.12 mmol), $Rh_2(esp)_2$ (0.76 mg, 1.0 mol%), chiral phosphoric acid **4c** (1.73 mg, 2.0 mol%), and 5Å MS (100 mg) in 0.5 mL DCE, a solution of diazo compound **1** (0.12 mmol) and imine **3** (0.1 mmol) in DCE (1.5 mL) was added *via* a syringe pump over 10 h (or 2 h in the cases with **3m**) under argon atmosphere at 30 °C, and the reaction mixture was stirred for additional 1 h under these conditions. The crude reaction mixture was subjected to proton NMR analysis to determine the *dr* values and purified by column chromatography on silica gel without any additional treatment (Hexanes : EtOAc = 50:1) to give the pure products **5** or **6** in generally good to high yields with excellent enantioselectivity.

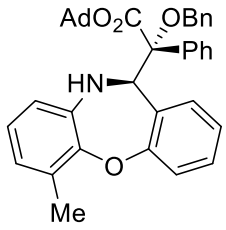


(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-10,11-dihydrodibenzo[*b,f*][1,4] oxazepin-11-yl)-2-phenylacetate (5a) White solid, 54.8 mg, 96% yield, > 20:1 *dr*, 99% *ee*, $[\alpha]_D^{20}$ = - 66.1° (c = 0.30, DCM), mp = 116 – 118 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 2H), 7.34 – 7.30 (comp, 5H), 7.29 – 7.25 (m, 2H), 7.24 (s, 1H), 7.22 – 7.16 (m, 2H), 7.02 – 6.93 (m, 2H), 6.89 – 6.85 (m, 1H), 6.84 – 6.78 (m, 1H), 6.61 – 6.57 (m, 2H), 5.30 (s, 1H), 4.84 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.42 (s, 1H), 2.13 – 2.02 (comp, 9H), 1.65 – 1.60 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 157.7, 145.7, 138.9, 137.9, 136.0, 131.0, 129.1, 129.0, 128.6, 128.3, 128.0, 127.4, 127.2, 126.9, 124.4, 123.3, 121.4, 120.5, 119.04, 119.03, 88.0, 83.3, 67.7, 64.7, 41.3, 36.1, 30.9; HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{38}NO_4$ $[M + H]^+$: 572.2795, found 572.2799; HPLC conditions for determination of enantiomeric excess: Chiral AD-H, λ = 254 nm, hexane : isopropanol = 98:2, flow rate =1.0 mL/min, t_{major} = 14.2 min.

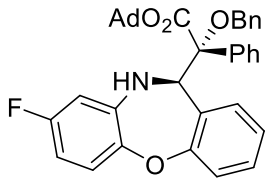


(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-9-(*tert*-butyl)-10,11-dihydro-dibenzo[*b,f*][1,4]oxazepin-11-yl)-2-phenylacetate (5b) Colorless oil, 55.8 mg, 89% yield, > 20:1 *dr*, 99% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.40 – 7.35 (comp, 4H), 7.34 – 7.26 (comp, 4H), 7.26 – 7.23 (m, 1H), 7.20 – 7.15 (m, 1H), 7.05 – 7.00 (m, 1H), 6.97 – 6.92 (m, 1H), 6.88 – 6.84 (m, 1H), 6.67 – 6.59 (m, 2H), 5.30 (s, 1H), 4.89 (d, *J* = 11.9 Hz, 1H), 4.50 (d, *J* = 11.9 Hz, 1H), 4.44 (s, 1H), 2.17 – 2.12 (m, 3H), 2.09 – 1.98 (comp, 6H), 1.67 – 1.62 (comp, 6H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 158.0, 147.4, 144.0, 139.0, 137.1, 136.2, 130.9, 129.2, 129.1, 128.7, 128.4, 128.1, 127.6, 127.3, 127.1, 123.3, 120.9, 120.5, 116.54, 116.49,

88.1, 83.3, 67.9, 65.0, 41.3, 36.2, 34.3, 31.5, 31.0; HRMS (TOF MS ESI$^+$) calculated for $C_{42}H_{46}NO_4$ [M + H]$^+$: 628.3421 found 628.3428; HPLC conditions for determination of enantiomeric excess: Chiral AD-H, λ = 254 nm, hexane : isopropanol = 80:20, flow rate =1.0 mL/min, t_{major} = 3.5 min.

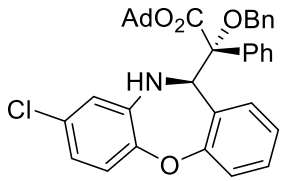


(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-6-methyl-10,11-dihydrodibenzo [*b,f*][1,4]oxazepin-11-yl)-2-phenylacetate (5c) Colorless oil, 53.8 mg, 92% yield, > 20:1 *dr*, 99% *ee*, $[\alpha]_D^{20}$ = - 36.8^o (c = 0.30, DCM); ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) δ 7.39 (d, *J* = 7.6 Hz, 2H), 7.37 – 7.33 (comp, 4H), 7.31 – 7.26 (m, 2H), 7.24 – 7.15 (comp, 4H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.92 (m, 1H), 6.71 (m, 1H), 6.50 (d, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.25 (s, 1H), 4.83 (d, *J* = 11.9 Hz, 1H), 4.49 (d, *J* = 11.9 Hz, 1H), 4.45 (s, 1H), 2.26 (s, 3H), 2.18 – 2.13 (m, 3H), 2.12 – 2.04 (comp, 6H), 1.67 – 1.62 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 169.9, 157.8, 144.5, 139.0, 138.0, 136.1, 131.1, 130.4, 129.2, 129.0, 128.8, 128.4, 128.0, 127.5, 127.3, 127.1, 123.8, 123.2, 121.01, 121.00, 117.1, 88.3, 83.3, 67.8, 65.2, 41.4, 36.2, 31.0, 17.0; HRMS (TOF MS ESI$^+$) calculated for $C_{39}H_{40}NO_4$ [M + H]$^+$: 586.2952, found 586.2959; HPLC conditions for determination of enantiomeric excess: Chiral AD-H, λ = 254 nm, hexane : isopropanol = 98:2, flow rate =1.0 mL/min, t_{major} = 8.7 min.

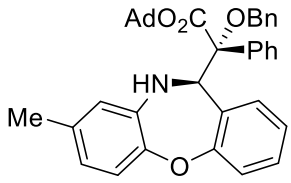


(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-8-fluoro-10,11-dihydrodibenzo [*b,f*][1,4]oxazepin-11-yl)-2-phenylacetate (5d) White solid, 54.2 mg, 92% yield, > 20:1 *dr*, 99% *ee*, mp = 142 – 144^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (comp,

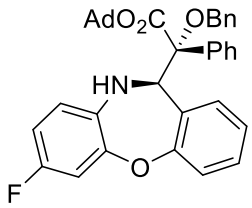
6H), 7.34 – 7.29 (m, 3H), 7.28 – 7.26 (m, 1H), 7.25 – 7.19 (m, 2H), 7.04 – 6.97 (m, 2H), 6.86 – 6.79 (m, 1H), 6.34 – 6.23 (m, 2H), 5.29 (d, *J* = 2.9 Hz, 1H), 4.87 (d, *J* = 12.0 Hz, 1H), 4.55 (s, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 2.19 – 2.14 (m, 3H), 2.13 – 2.04 (comp, 6H), 1.69 – 1.63 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 159.7 (d, *J* = 239.8 Hz), 157.8, 141.7 (d, *J* = 2.1 Hz), 139.2 (d, *J* = 10.9 Hz), 138.8, 135.9, 131.2, 129.5, 128.8, 128.6, 128.4, 128.2, 127.6, 127.4, 127.0, 123.7, 122.2 (d, *J* = 10.2 Hz), 120.5, 105.0 (d, *J* = 26.0 Hz), 104.8 (d, *J* = 23.0 Hz), 88.0, 83.5, 67.9, 64.6, 41.4, 36.2, 31.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.6; HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{37}FNO_4$ $[M + H]^+$: 590.2701, found 590.2696; HPLC conditions for determination of enantiomeric excess: Chiral AD-H, λ = 254 nm, hexane : isopropanol = 80:20, flow rate =1.0 mL/min, t_{major} = 4.9 min.



(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-8-chloro-10,11-dihydrodibenzo [*b,f*][1,4]oxazepin-11-yl)-2-phenylacetate (5e) White solid, 55.1 mg, 91% yield, > 20:1 *dr*, 99% *ee*, $[\alpha]_D^{20}$ = - 68.1° (c = 0.30, DCM); mp = 182 – 184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 3H), 7.33 – 7.29 (comp, 4H), 7.29 – 7.26 (m, 2H), 7.25 – 7.22 (m, 2H), 7.21 – 7.17 (m, 1H), 7.00 – 6.94 (m, 2H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 2.4 Hz, 1H), 6.53 – 6.48 (m, 1H), 5.25 (s, 1H), 4.83 (d, *J* = 12.0 Hz, 1H), 4.55 (s, 1H), 4.49 (d, *J* = 12.0 Hz, 1H), 2.16 – 2.11 (m, 3H), 2.10 – 2.01 (comp, 6H), 1.67 – 1.60 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 157.5, 144.1, 139.0, 138.8, 135.9, 131.3, 129.5, 129.2, 128.6, 128.4, 128.2, 127.6, 127.4, 127.03, 127.01, 123.7, 122.5, 120.5, 118.6, 118.2, 88.0, 83.6, 67.9, 64.7, 41.4, 36.2, 31.0; HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{37}ClNO_4$ $[M + H]^+$: 606.2406, found 606.2407; HPLC conditions for determination of enantiomeric excess: Chiral AD-H, λ = 317 nm, hexane : isopropanol = 80:20, flow rate =1.0 mL/min, t_{major} = 4.4 min.

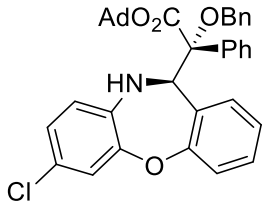


(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-8-methyl-10,11-dihydrodibenzo [*b,f*][1,4]oxazepin-11-yl)-2-phenylacetate (5f) White solid, 52.7 mg, 90% yield, > 20:1 *dr*, 99% *ee*, $[\alpha]_D^{20}$ = - 54.0° (c = 0.43, DCM), mp = 173 – 175 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.40 – 7.34 (comp, 5H), 7.34 – 7.27 (m, 3H), 7.25 – 7.22 (m, 1H), 7.21 – 7.17 (m, 1H), 7.03 – 6.96 (m, 2H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.47 – 6.38 (m, 2H), 5.35 (s, 1H), 4.89 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.39 (s, 1H), 2.18 (s, 3H), 2.16 – 2.04 (comp, 9H), 1.68 – 1.63 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 158.1, 144.0, 139.0, 137.6, 136.1, 134.1, 130.9, 129.3, 129.2, 128.7, 128.4, 128.1, 127.5, 127.3, 127.0, 123.5, 121.2, 120.5, 119.8, 119.7, 88.0, 83.3, 67.8, 64.4, 41.4, 36.2, 31.0, 20.8; HRMS (TOF MS ESI$^+$) calculated for $C_{39}H_{40}NO_4$ $[M + H]^+$: 586.2952, found 586.2943; HPLC conditions for determination of enantiomeric excess: Chiral AD-H, λ = 254 nm, hexane : isopropanol = 80:20, flow rate =1.0 mL/min, t_{major} = 3.9 min.

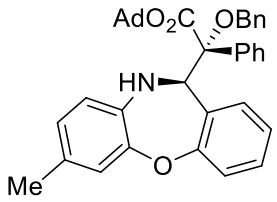


(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-7-fluoro-10,11-dihydrodibenzo [*b,f*][1,4]oxazepin-11-yl)-2-phenylacetate (5g) White solid, 48.3 mg, 82% yield, > 20:1 *dr*, 99% *ee*, mp = 142 – 144 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.37 – 7.30 (comp, 6H), 7.30 – 7.26 (m, 2H), 7.25 – 7.23 (m, 1H), 7.23 – 7.18 (m, 1H), 7.03 – 6.95 (m, 2H), 6.67 – 6.62 (m, 1H), 6.60 – 6.50 (m, 2H), 5.24 (s, 1H), 4.87 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.34 (s, 1H), 2.19 – 2.12 (m, 3H), 2.10 – 2.02 (comp, 6H), 1.69 – 1.62 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 157.3, 156.3 (d, *J* = 238.2 Hz), 146.3 (d, *J* = 10.6 Hz), 139.0, 136.1, 134.2 (d, *J* = 2.7

Hz), 131.0, 129.2, 129.0, 128.7, 128.4, 128.2, 127.6, 127.4, 127.1, 123.6, 120.5, 119.8 (d, *J* = 8.9 Hz), 110.9 (d, *J* = 22.2 Hz), 108.7 (d, *J* = 24.3 Hz), 88.2, 83.4, 67.9, 64.8, 41.4, 36.2, 31.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -124.7; HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{37}FNO_4$ $[M + H]^+$: 590.2701, found 590.2696; HPLC conditions for determination of enantiomeric excess: Chiral AD-H, λ = 266 nm, hexane : isopropanol = 80:20, flow rate =1.0 mL/min, t_{major} = 5.7 min.

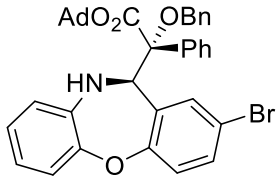


(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-7-chloro-10,11-dihydrodibenzo [*b,f*][1,4]oxazepin-11-yl)-2-phenylacetate (5h) White solid, 50.2 mg, 83% yield, > 20:1 *dr*, 99% *ee*, $[\alpha]_D^{20}$ = - 57.1° (c = 0.30, DCM), mp = 144 - 146 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.34 (comp, 4H), 7.34 – 7.28 (comp, 6H), 7.24 – 7.19 (m, 2H), 7.02 – 6.96 (m, 2H), 6.88 (d, *J* = 2.3 Hz, 1H), 6.82 – 6.77 (m, 1H), 6.50 (d, *J* = 8.5 Hz, 1H), 5.22 (s, 1H), 4.84 (d, *J* = 12.0 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.42 (s, 1H), 2.18 – 2.14 (m, 3H), 2.12 – 2.02 (comp, 6H), 1.68 – 1.62 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 157.3, 145.7, 138.9, 136.7, 136.0, 131.4, 129.5, 128.6, 128.5, 128.4, 128.2, 127.6, 127.4, 127.1, 124.2, 123.6, 122.9, 121.6, 120.6, 119.7, 88.3, 83.5, 67.9, 65.1, 41.4, 36.2, 31.0; HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{37}ClNO_4$ $[M + H]^+$: 606.2406, found 606.2408; HPLC conditions for determination of enantiomeric excess: Chiral AD-H, λ = 217 nm, hexane : isopropanol = 80:20, flow rate =1.0 mL/min, t_{major} = 6.4 min.

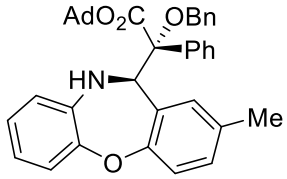


(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-7-methyl-10,11-dihydrodibenzo [*b,f*][1,4]oxazepin-11-yl)-2-phenylacetate (5i) White solid, 49.7 mg, 85% yield, >

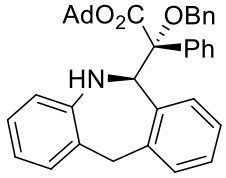
20:1 *dr*, 99% *ee*, mp = 173 - 175 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 2H), 7.36 – 7.33 (comp, 4H), 7.32 – 7.26 (m, 3H), 7.25 – 7.21 (m, 2H), 7.20 – 7.15 (m, 1H), 7.02 – 6.93 (m, 2H), 6.74 (d, *J* = 1.4 Hz, 1H), 6.67 – 6.62 (m, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 5.29 (s, 1H), 4.85 (d, *J* = 11.9 Hz, 1H), 4.47 (d, *J* = 12.0 Hz, 1H), 4.32 (s, 1H), 2.17 (s, 3H), 2.15 – 2.12 (m, 3H), 2.09 – 2.02 (comp, 6H), 1.66 – 1.62 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 157.9, 146.1, 139.1, 136.2, 135.3, 131.0, 129.3, 129.14, 129.10, 128.8, 128.4, 128.1, 127.5, 127.3, 127.1, 125.0, 123.4, 121.9, 120.5, 119.4, 88.2, 83.3, 67.9, 64.8, 41.4, 36.2, 31.0, 20.4; HRMS (TOF MS ESI$^+$) calculated for $C_{39}H_{40}NO_4$ $[M + H]^+$: 586.2952, found 586.2951; HPLC conditions for determination of enantiomeric excess: Chiral AD-H, λ = 254 nm, hexane : isopropanol = 80:20, flow rate =1.0 mL/min, t_{major} = 6.3 min.



(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-2-bromo-10,11-dihydrodibenzo [*b,f*][1,4]oxazepin-11-yl)-2-phenylacetate (5j) White solid, 55.3 mg, 85% yield, > 20:1 *dr*, 99% *ee*, $[\alpha]_D^{20}$ = - 3.5° (c = 0.30, DCM) , mp = 131 - 133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 1H), 7.41 – 7.30 (comp, 9H), 7.26 – 7.22 (m, 2H), 6.93 – 6.80 (m, 3H), 6.67 – 6.55 (m, 2H), 5.24 (d, *J* = 7.1 Hz, 1H), 4.84 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 12.1 Hz, 1H), 4.40 (d, *J* = 7.1 Hz, 1H), 2.22 – 2.16 (m, 3H), 2.15 – 2.04 (comp, 6H), 1.78 – 1.63 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 156.9, 145.6, 138.7, 137.6, 135.4, 134.0, 132.0, 130.9, 128.6, 128.5, 128.3, 127.6, 127.4, 127.0, 124.7, 122.4, 121.4, 119.5, 119.3, 115.9, 88.1, 83.7, 67.9, 64.5, 41.5, 36.2, 31.0; HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{37}BrNO_4$ $[M + H]^+$: 650.1900, found 650.1895; HPLC conditions for determination of enantiomeric excess: Chiral AD-H, λ = 254 nm, hexane : isopropanol = 98:2, flow rate =1.0 mL/min, t_{major} = 13.4 min.

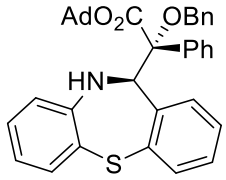


(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-2-methyl-10,11-dihydrodibenzo [*b,f*][1,4]oxazepin-11-yl)-2-phenylacetate (5k) White solid, 48.0 mg, 82% yield, > 20:1 *dr*, 99% *ee*, $[\alpha]_D^{20}$ = - 10.1° (c = 0.30, DCM) ,mp = 138 – 140 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (comp, 6H), 7.32 – 7.28 (m, 2H), 7.25 – 7.20 (m, 2H), 7.14 – 7.10 (m, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.90 – 6.85 (m, 2H), 6.83 – 6.79 (m, 1H), 6.62 – 6.56 (m, 2H), 5.23 (d, *J* = 4.6 Hz, 1H), 4.82 (d, *J* = 12.1 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.44 (s, 1H), 2.23 (s, 3H), 2.19 – 2.15 (m, 3H), 2.13 – 2.07 (comp, 6H), 1.68 – 1.64 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 155.8, 146.2, 139.0, 138.1, 135.9, 132.6, 132.1, 129.7, 128.7, 128.4, 128.1, 128.0, 127.4, 127.3, 127.0, 124.4, 121.4, 120.2, 119.1, 119.0, 88.2, 83.3, 67.7, 65.0, 41.4, 36.2, 31.0, 20.8; HRMS (TOF MS ESI$^+$) calculated for $C_{39}H_{40}NO_4$ $[M + H]^+$: 586.2952, found 586.2958; HPLC conditions for determination of enantiomeric excess: Chiral AD-H, λ = 254 nm, hexane : isopropanol = 90:10, flow rate =1.0 mL/min, t_{major} = 4.8 min.

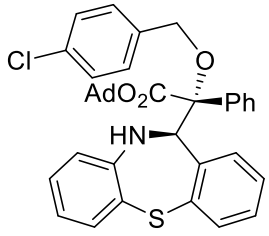


(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-6,11-dihydro-5*H*-dibenzo [*b,e*]azepin-6-yl)-2-phenylacetate (5l) White solid, 53.5 mg, 94% yield, > 20:1 *dr*, 95% *ee*, $[\alpha]_D^{20}$ = - 92.4° (c = 0.30, DCM), mp = 132 – 134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 1H), 7.38 – 7.28 (comp, 8H), 7.25 – 7.20 (m, 2H), 7.14 – 7.05 (m, 2H), 7.00 – 6.94 (m, 2H), 6.89 (d, *J* = 7.2 Hz, 1H), 6.71 – 6.64 (m, 2H), 5.42 (d, *J* = 7.4 Hz, 1H), 4.85 (d, *J* = 12.1 Hz, 1H), 4.51 (d, *J* = 12.2 Hz, 1H), 4.51 (s, 1H), 3.31 (d, *J* = 13.9 Hz, 1H), 3.14 (d, *J* = 13.9 Hz, 1H), 2.23 – 2.18 (m, 3H), 2.17 – 2.11 (comp, 6H), 1.73 – 1.66 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 144.8, 141.2, 139.0, 135.9, 134.1, 131.21, 131.16, 129.5, 128.6, 128.4, 128.2, 127.8, 127.5,

127.3, 127.2, 127.0, 125.7, 122.8, 120.1, 119.8, 88.4, 83.4, 67.8, 65.9, 41.5, 39.1, 36.2, 31.0; HRMS (TOF MS ESI$^+$) calculated for $C_{39}H_{40}NO_3$ [M + H]$^+$: 570.3003, found 570.3002; HPLC conditions for determination of enantiomeric excess: Chiral IA, λ = 254 nm, hexane : isopropanol = 98:2, flow rate =1.0 mL/min, t_{major} = 5.0 min, t_{minor} = 7.8 min.

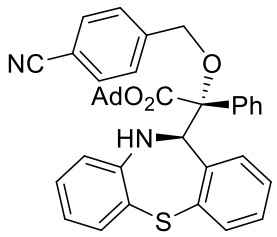


(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-10,11-dihydrodibenzo[*b,f*][1,4] thiazepin-11-yl)-2-phenylacetate (5m) White solid, 55.8 mg, 95% yield, > 20:1 *dr*, 99% *ee*, $[\alpha]_D^{20}$ = - 82.8^o (c = 0.30, DCM), mp = 153 – 155 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 – 7.99 (m, 1H), 7.89 – 7.76 (m, 2H), 7.59 – 7.50 (m, 1H), 7.47 – 7.36 (comp, 6H), 7.37 – 7.27 (m, 3H), 7.25 – 7.22 (m, 1H), 7.12 – 7.08 (m, 1H), 6.90 – 6.82 (m, 1H), 6.78 (d, *J* = 9.2 Hz, 1H), 6.55 – 6.48 (m, 1H), 6.44 – 6.36 (m, 1H), 5.39 (d, *J* = 11.7 Hz, 1H), 4.45 (d, *J* = 11.8 Hz, 1H), 4.41 (s, 1H), 2.10 – 2.04 (m, 3H), 1.95 – 1.88 (m, 3H), 1.77 – 1.71 (m, 3H), 1.61 – 1.54 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 145.5, 145.2, 139.2, 137.2, 135.5, 132.7, 131.9, 129.2, 128.7, 128.6, 128.4, 128.3, 128.2, 128.0, 127.54, 127.46, 125.9, 119.4, 118.6, 117.1, 86.4, 83.1, 68.5, 60.9, 41.1, 36.1, 30.9; HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{38}NO_3S$ [M + H]$^+$: 588.2567, found 588.2574; HPLC conditions for determination of enantiomeric excess: Chiral IA, λ = 304 nm, hexane : isopropanol = 98:2, flow rate =1.0 mL/min, t_{major} = 4.5 min.

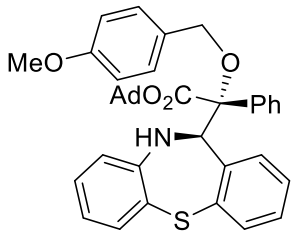


(3*R*)-Adamantan-1-yl (2*R*)-2-((4-chlorobenzyl)oxy)-2-((*R*)-10,11-dihydrodibenzo [*b,f*][1,4]thiazepin-11-yl)-2-phenylacetate (5n) White solid, 59.0 mg, 95% yield, > 20:1 *dr*, 93% *ee*, $[\alpha]_D^{20}$ = - 58^o (c = 0.30, DCM), mp = 114 – 116 ^{o}C; ^{1}H NMR (500

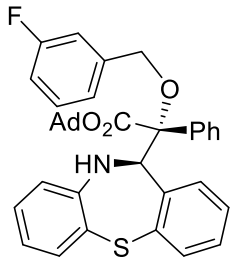
MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 1H), 7.81 – 7.75 (m, 2H), 7.54 – 7.50 (m, 1H), 7.44 – 7.33 (comp, 7H), 7.31 – 7.27 (m, 1H), 7.25 – 7.21 (m, 1H), 7.11 – 7.06 (m, 1H), 6.89 – 6.84 (m, 1H), 6.75 (d, *J* = 9.3 Hz, 1H), 6.55 – 6.49 (m, 1H), 6.44 – 6.38 (m, 1H), 5.29 (d, *J* = 11.8 Hz, 1H), 4.37 (d, *J* = 11.8 Hz, 1H), 4.33 (d, *J* = 9.8 Hz, 1H), 2.09 – 2.01 (m, 3H), 1.92 – 1.83 (m, 3H), 1.74 – 1.66 (m, 3H), 1.57 – 1.52 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm) δ 170.5, 145.4, 145.2, 137.6, 137.1, 135.5, 133.3, 132.7, 132.0, 129.2, 128.9, 128.83, 128.81 128.80, 128.4, 128.2, 128.1, 125.7, 119.5, 118.7, 117.2, 86.5, 83.2, 67.9, 60.8, 41.1, 36.1, 30.9; HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{37}ClNO_3S$ $[M + H]^+$: 622.2177, found 622.2185; HPLC conditions for determination of enantiomeric excess: Chiral IA, λ = 312 nm, hexane : isopropanol = 95:5, flow rate =1.0 mL/min, t_{major} = 4.0 min, t_{minor} = 5.2 min.



(3*R*)-Adamantan-1-yl (2*R*)-2-((4-cyanobenzyl)oxy)-2-((*R*)-10,11-dihydrodibenzo [*b,f*][1,4]thiazepin-11-yl)-2-phenylacetate (5o) White solid, 57.5 mg, 94% yield, > 20:1 *dr*, 99% *ee*, $[\alpha]_D^{20}$ = - 56.2° (c = 0.31, DCM), mp = 126 – 128°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 1H), 7.80 – 7.75 (m, 2H), 7.71 – 7.65 (m, 2H), 7.56 – 7.50 (m, 3H), 7.42 – 7.37 (m, 3H), 7.31 – 7.27 (m, 1H), 7.25 – 7.22 (m, 1H), 7.12 – 7.08 (m, 1H), 6.91 – 6.84 (m, 1H), 6.77 (d, *J* = 9.3 Hz, 1H), 6.58 – 6.51 (m, 1H), 6.47 – 6.41 (m, 1H), 5.37 (d, *J* = 12.9 Hz, 1H), 4.47 (d, *J* = 12.9 Hz, 1H), 4.30 (d, *J* = 9.5 Hz, 1H), 2.08 – 2.02 (m, 3H), 1.91 – 1.83 (m, 3H), 1.73 – 1.66 (m, 3H), 1.59 – 1.51 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 145.2, 145.1, 144.6, 136.8, 135.5, 132.7, 132.5, 132.1, 129.2, 129.0, 128.5, 128.3, 128.23, 128.20, 127.7, 125.5, 119.6, 119.01, 119.00, 117.4, 111.3, 86.6, 83.5, 67.8, 60.8, 41.1, 36.1, 30.9; HRMS (TOF MS ESI$^+$) calculated for $C_{39}H_{37}N_2O_3S$ $[M + H]^+$: 613.2519, found 613.2525; HPLC conditions for determination of enantiomeric excess: Chiral IA, λ = 254 nm, hexane : isopropanol = 95:5, flow rate =1.0 mL/min, t_{major} = 6.8 min.

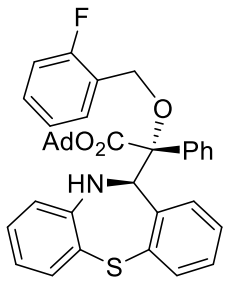


(3*R*)-Adamantan-1-yl (2*R*)-2-((*R*)-10,11-dihydrodibenzo[*b,f*][1,4]thiazepin-11-yl)-2-((4-methoxybenzyl)oxy)-2-phenylacetate (5p) White solid, 58.6 mg, 95% yield, > 20:1 *dr*, 99% *ee*, $[\alpha]_D^{20}$ = - 69.8º (c = 0.31, DCM), mp = 120 – 122 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.99 (m, 1H), 7.85 – 7.78 (m, 2H), 7.54 – 7.48 (m, 1H), 7.43 – 7.34 (comp, 5H), 7.31 – 7.27 (m, 1H), 7.25 – 7.19 (m, 1H), 7.11 – 7.06 (m, 1H), 6.95 – 6.90 (m, 2H), 6.88 – 6.82 (m, 1H), 6.75 (d, *J* = 10.1 Hz, 1H), 6.57 – 6.45 (m, 1H), 6.42 – 6.33 (m, 1H), 5.29 (d, *J* = 11.1 Hz, 1H), 4.39 (d, *J* = 10.1 Hz, 1H), 4.34 (d, *J* = 11.2 Hz, 1H), 3.83 (s, 3H), 2.09 – 2.02 (m, 3H), 1.95 – 1.83 (m, 3H), 1.78 – 1.67 (m, 3H), 1.63 – 1.49 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 159.2, 145.5, 145.2, 137.4, 135.5, 132.7, 131.9, 131.3, 129.2, 128.7, 128.4, 128.3, 128.2, 128.0, 125.9, 119.4, 118.5, 117.0, 113.98, 113.95, 86.3, 83.0, 68.2, 60.8, 55.4, 41.1, 36.1, 30.9; HRMS (TOF MS ESI$^+$) calculated for $C_{39}H_{40}NO_4S$ $[M + H]^+$: 618.2673, found 618.2681; HPLC conditions for determination of enantiomeric excess: Chiral IA, λ = 254 nm, hexane : isopropanol = 95:5, flow rate =1.0 mL/min, t_{major} = 4.4 min.



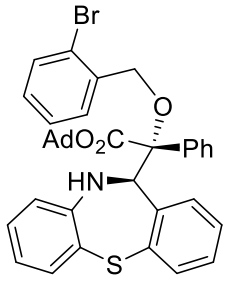
(3*R*)-Adamantan-1-yl (2*R*)-2-((*R*)-10,11-dihydrodibenzo[*b,f*][1,4]thiazepin-11-yl)-2-((3-fluorobenzyl)oxy)-2-phenylacetate (5q) White solid, 55.7 mg, 92% yield, > 20:1 *dr*, 93% *ee*, mp = 130 – 132 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.99 (m, 1H), 7.82 – 7.75 (m, 2H), 7.59 – 7.47 (m, 1H), 7.44 – 7.37 (m, 3H), 7.35 – 7.28 (m, 2H), 7.26 – 7.19 (m, 1H), 7.19 – 7.12 (m, 2H), 7.12 – 7.08 (m, 1H), 7.02 – 6.97 (m, 1H), 6.90 – 6.83 (m, 1H), 6.76 (d, *J* = 9.5 Hz, 1H), 6.55 – 6.49 (m, 1H), 6.44 – 6.41

(m, 1H), 5.33 (d, *J* = 12.1 Hz, 1H), 4.41 (d, *J* = 12.1 Hz, 1H), 4.36 (d, *J* = 9.8 Hz, 1H), 2.09 – 2.02 (m, 3H), 1.93 – 1.86 (m, 3H), 1.75 – 1.69 (m, 3H), 1.59 – 1.52 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 163.1 (d, *J* = 245.7 Hz), 145.3 (d, *J* = 21.4 Hz), 141.8 (d, *J* = 7.3 Hz), 137.0, 135.5, 132.7, 132.0, 130.1, 130.0, 129.3, 128.8, 128.4, 128.3, 128.2, 128.1, 125.7, 122.9 (d, *J* = 2.7 Hz), 119.6, 118.8, 117.2, 114.5 (d, *J* = 10.9 Hz), 114.2 (d, *J* = 11.5 Hz), 86.5, 83.3, 67.9, 60.8, 41.1, 36.1, 30.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.1; HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{37}FNO_3S$ [M + H]$^+$: 606.2473, found 606.2479; HPLC conditions for determination of enantiomeric excess: Chiral IA, λ = 310 nm, hexane : isopropanol = 98:2, flow rate =0.3 mL/min, t_{major} = 14.5 min, t_{minor} = 15.8 min.

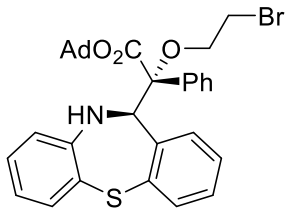


(3*R*)-Adamantan-1-yl (2*R*)-2-((*R*)-10,11-dihydrodibenzo[*b,f*][1,4]thiazepin-11-yl)-2-((2-fluorobenzyl)oxy)-2-phenylacetate (5r) White solid, 54.5 mg, 90% yield, > 20:1 *dr*, 99% *ee*, $[\alpha]_D^{20}$ = - 25.9^o (c = 0.42, DCM), mp = 130 – 132 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 1H), 7.87 – 7.81 (m, 2H), 7.58 – 7.48 (m, 2H), 7.45 – 7.37 (m, 3H), 7.34 – 7.27 (m, 2H), 7.25 – 7.15 (m, 2H), 7.12 – 7.04 (m, 2H), 6.91 – 6.83 (m, 1H), 6.79 (d, *J* = 9.8 Hz, 1H), 6.56 – 6.47 (m, 1H), 6.47 – 6.40 (m, 1H), 5.35 (d, *J* = 11.7 Hz, 1H), 4.55 (d, *J* = 11.6 Hz, 1H), 4.45 (d, *J* = 10.0 Hz, 1H), 2.10 – 2.02 (m, 3H), 1.94 – 1.85 (m, 3H), 1.76 – 1.67 (m, 3H), 1.61 – 1.53 (comp, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 160.9 (d, *J* = 247.1 Hz), 145.3 (d, *J* = 26.0 Hz), 136.9, 135.5, 132.7, 131.9, 130.01, 130.0, 129.4 (d, *J* = 8.2 Hz), 129.2, 128.8, 128.42, 128.40, 128.2, 128.0, 126.1 (d, *J* = 14.5 Hz), 125.8, 124.3 (d, *J* = 3.4 Hz), 119.3, 118.5, 116.9, 115.5 (d, *J* = 21.4 Hz), 86.3, 83.1, 62.8 (d, *J* = 3.6 Hz), 60.8, 41.1, 36.1, 30.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.0. HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{37}FNO_3S$ [M + H]$^+$: 606.2473, found 606.2481; HPLC conditions for

determination of enantiomeric excess: Chiral IA, λ = 330 nm, hexane : ethanol = 95:5, flow rate = 0.3 mL/min, t_{major} = 13.0 min.

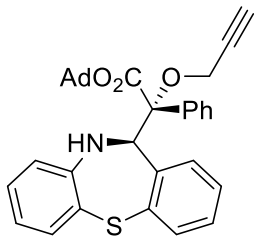


(3*R*)-Adamantan-1-yl (2*R*)-2-((2-bromobenzyl)oxy)-2-((*R*)-10,11-dihydrodibenzo [*b,f*][1,4]thiazepin-11-yl)-2-phenylacetate (5s) White solid, 36.6 mg, 55% yield, > 20:1 *dr*, 97% *ee*, mp = 130 – 132 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 1H), 7.86 – 7.80 (m, 2H), 7.63 – 7.60 (m, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.50 (m, 1H), 7.44 – 7.37 (m, 3H), 7.36 – 7.32 (m, 1H), 7.27 – 7.22 (m, 2H), 7.19 – 7.14 (m, 1H), 7.10 – 7.07 (m, 1H), 6.90 – 6.83 (m, 1H), 6.81 (d, *J* = 9.5 Hz, 1H), 6.53 – 6.47 (m, 1H), 6.43 (d, *J* = 8.1 Hz, 1H), 5.31 (d, *J* = 12.2 Hz, 1H), 4.54 (d, *J* = 9.9 Hz, 1H), 4.51 (d, *J* = 12.2 Hz, 1H), 2.06 – 2.02 (m, 3H), 1.92 – 1.85 (m, 3H), 1.74 – 1.68 (m, 3H), 1.58 – 1.51 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 145.5, 145.1, 138.4, 136.8, 135.6, 132.8, 132.7, 131.9, 129.6, 129.2, 129.1, 128.9, 128.39, 128.38, 128.2, 128.0, 127.7, 125.9, 123.2, 119.2, 118.5, 117.0, 86.3, 83.1, 68.1, 60.9, 41.1, 36.1, 30.9; HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{37}BrNO_3S$ $[M + H]^+$: 666.1672, found 666.1678; HPLC conditions for determination of enantiomeric excess: Chiral IF-3, λ = 254 nm, hexane : isopropanol = 98:2, flow rate =1.0 mL/min, t_{major} = 4.9 min, t_{minor} = 4.6 min.

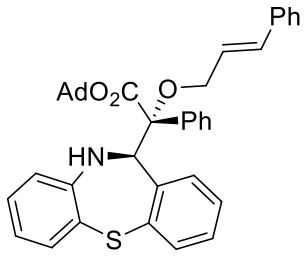


(3*R*)-Adamantan-1-yl (2*R*)-2-(2-bromoethoxy)-2-((*R*)-10,11-dihydrodibenzo [*b,f*][1,4]thiazepin-11-yl)-2-phenylacetate (5t) White solid, 30.2 mg, 50% yield, >

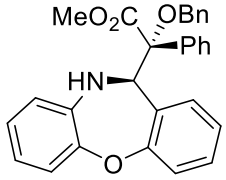
20:1 *dr*, 99% *ee*, mp = 130 – 132 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 1H), 7.87 – 7.80 (m, 2H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.45 – 7.37 (m, 3H), 7.35 – 7.28 (m, 1H), 7.27 – 7.20 (m, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.99 – 6.87 (m, 1H), 6.77 (d, *J* = 9.6 Hz, 1H), 6.58 – 6.49 (m, 2H), 4.61 (d, *J* = 9.9 Hz, 1H), 4.52 – 4.45 (m, 1H), 3.75 – 3.67 (m, 2H), 3.67 – 3.58 (m, 1H), 2.10 – 2.01 (m, 3H), 1.88 – 1.79 (m, 3H), 1.73 – 1.63 (m, 3H), 1.61 – 1.48 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 145.4, 145.1, 136.8, 135.5, 132.8, 131.9, 129.2, 128.9, 128.5, 128.4, 128.3, 128.0, 125.6, 119.5, 118.5, 116.8, 86.0, 83.2, 66.1, 60.6, 41.0, 36.1, 32.4, 30.8; HRMS (TOF MS ESI$^+$) calculated for $C_{33}H_{35}BrNO_3S$ $[M + H]^+$: 604.1516, found 604.1513; HPLC conditions for determination of enantiomeric excess: Chiral IA, λ = 254 nm, hexane : isopropanol = 95:5, flow rate =1.0 mL/min, t_{major} = 4.5 min.



(3*R*)-Adamantan-1-yl (2*R*)-2-((*R*)-10,11-dihydrodibenzo[*b,f*][1,4]thiazepin-11-yl)-2-phenyl-2-(prop-2-yn-1-yloxy)acetate (5u) White solid, 21.4 mg, 40% yield, > 20:1 *dr*, 99% *ee*, $[\alpha]_D^{20}$ = - 73.8º (c = 0.30, DCM), mp = 130 – 132 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 7.95 (d, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 7.4 Hz, 2H), 7.51 (d, *J* = 6.8 Hz, 1H), 7.44 – 7.35 (m, 3H), 7.33 – 7.27 (m, 1H), 7.25 – 7.19 (m, 1H), 7.09 – 7.04 (m, 1H), 6.90 – 6.82 (m, 1H), 6.65 (d, *J* = 10.1 Hz, 1H), 6.52 – 6.44 (m, 2H), 4.90 (dd, *J* = 15.5, 2.3 Hz, 1H), 4.36 (d, *J* = 10.2 Hz, 1H), 4.18 (dd, *J* = 15.5, 2.4 Hz, 1H), 2.51 (t, *J* = 2.3 Hz, 1H), 2.08 – 2.02 (m, 3H), 1.92 – 1.84 (m, 3H), 1.75 – 1.68 (m, 3H), 1.59 – 1.52 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 170.0, 145.5, 145.1, 136.6, 135.5, 132.7, 131.9, 129.2, 128.9, 128.5, 128.2, 128.1, 128.0, 125.7, 119.5, 118.5, 116.9, 87.2, 83.5, 80.9, 74.2, 60.8, 55.7, 41.1, 36.1, 30.9; HRMS (TOF MS ESI$^+$) calculated for $C_{34}H_{34}NO_3S$ $[M + H]^+$: 536.2254, found 536.2246; HPLC conditions for determination of enantiomeric excess: Chiral IF-3, λ = 254 nm, hexane : isopropanol = 95:5, flow rate =1.0 mL/min, t_{major} = 4.4 min.

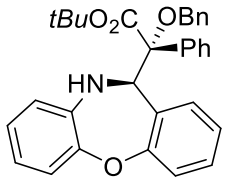


(3*R*)-Adamantan-1-yl (2*R*)-2-(cinnamyloxy)-2-((*R*)-10,11-dihydrodibenzo[*b,f*][1,4] thiazepin-11-yl)-2-phenylacetate (5v) Colorless oil, 52.1 mg, 85% yield, > 20:1 *dr*, 99% *ee*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 7.97 (m, 1H), 7.83 – 7.73 (m, 2H), 7.53 – 7.49 (m, 1H), 7.45 – 7.37 (comp, 5H), 7.36 – 7.28 (m, 3H), 7.27 (d, *J* = 1.2 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.10 – 7.04 (m, 1H), 6.90 – 6.84 (m, 1H), 6.73 – 6.62 (m, 2H), 6.53 – 6.42 (m, 3H), 4.92 – 4.84 (m, 1H), 4.41 (d, *J* = 9.9 Hz, 1H), 4.16 – 4.08 (m, 1H), 2.07 – 2.00 (m, 3H), 1.92 – 1.85 (m, 3H), 1.75 – 1.67 (m, 3H), 1.62 – 1.49 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 145.6, 145.3, 137.4, 137.2, 137.0, 135.6, 132.7, 131.9, 131.7, 129.2, 128.73, 128.7, 128.3, 128.2, 128.0, 127.8, 127.0, 126.7, 125.9, 119.4, 118.5, 117.0, 86.4, 83.1, 68.0, 60.9, 41.1, 36.1, 30.9; HRMS (TOF MS ESI$^+$) calculated for $C_{40}H_{40}NO_3S$ $[M + H]^+$: 614.2723, found 614.2722; HPLC conditions for determination of enantiomeric excess: Chiral IF-3, λ = 254 nm, hexane : isopropanol = 98:2, flow rate =1.0 mL/min, t_{major} = 5.6 min.

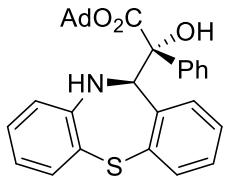


Methyl (*R*)-2-(benzyloxy)-2-((*R*)-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl)-2-phenylacetate (5w) Colorless oil, 38.3 mg, 85% yield, 2 : 1 *dr*, 98% (99%) *ee*; ^{1}H NMR (500 MHz, $CDCl_3$) δ major: 7.39 – 7.36 (m, 2H), 7.35 – 7.31 (comp, 4H), 7.30 – 7.26 (m, 2H), 7.25 – 7.20 (m, 2H), 7.18 – 7.13 (m, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.88 – 6.80 (m, 3H), 6.64 – 6.57 (m, 2H), 5.05 (s, 1H), 4.62 (d, *J* = 11.8 Hz, 1H), 4.62 (s, 1H), 4.45 (d, *J* = 11.8 Hz, 1H), 3.65 (s, 3H); minor: 7.40 – 7.35 (m, 2H), 7.30 – 7.20 (comp, 8H), 7.19 – 7.15 (m, 1H), 7.14 – 7.09 (m, 1H), 6.99 – 6.95 (m, 1H), 6.85 – 6.80 (m, 1H), 6.80 – 6.74 (m, 1H), 6.72 – 6.67 (m, 1H),

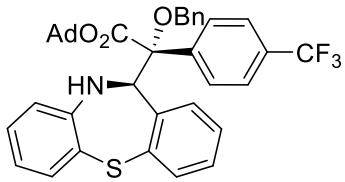
6.65 – 6.58 (m, 1H), 6.58 – 6.53 (m, 1H), 5.18 (s, 1H), 4.87 (d, *J* = 11.8 Hz, 1H), 4.56 (s, 1H), 4.50 (d, *J* = 11.9 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ major: 171.5, 157.7, 145.5, 138.5, 137.7, 135.8, 131.8, 129.6, 128.6, 128.4, 128.3, 127.7, 127.5, 127.2, 126.9, 124.5, 123.1, 121.2, 120.8, 119.2, 119.0, 88.5, 68.0, 67.8, 52.2; minor: 172.5, 157.9, 145.2, 139.1, 137.8, 137.0, 131.9, 129.6, 128.23, 128.20, 128.12, 128.10, 127.6, 127.2, 126.9, 124.5, 123.1, 121.4, 121.1, 119.0, 118.4, 89.3, 69.2, 67.3, 52.5. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{26}NO_4$ $[M + H]^+$: 452.1862, found 452.1860; HPLC conditions for determination of enantiomeric excess: Chiral AD-H, λ = 254 nm, hexane : isopropanol = 90:10, flow rate =1.0 mL/min, t_{major} = 7.3 min, t_{minor} = 13.3 min.



***tert*-Butyl (*R*)-2-(benzyloxy)-2-((*R*)-10,11-dihydrodibenzo[*b,f*][1,4]oxazepin-11-yl) -2-phenylacetate (5x)** Colorless oil, 38.9 mg, 79% yield, > 20:1 *dr*, 86% *ee*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.7 Hz, 2H), 7.27 – 7.25 (m, 3H), 7.24 – 7.20 (m, 3H), 7.19 – 7.09 (comp, 4H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.91 – 6.86 (m, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.77 – 6.73 (m, 1H), 6.56 – 6.50 (m, 2H), 5.23 (s, 1H), 4.78 (d, *J* = 12.1 Hz, 1H), 4.44 (d, *J* = 12.1 Hz, 1H), 4.37 (s, 1H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 157.9, 145.9, 139.0, 138.0, 136.1, 131.1, 129.3, 129.0, 128.7, 128.4, 128.2, 127.6, 127.3, 127.0, 124.5, 123.5, 121.5, 120.7, 119.22, 119.15, 88.3, 83.2, 67.9, 64.9, 28.1. HRMS (TOF MS ESI$^+$) calculated for $C_{32}H_{32}NO_4$ $[M + H]^+$: 494.2331, found 494.2335; HPLC conditions for determination of enantiomeric excess: Chiral AD-H, λ = 254 nm, hexane : isopropanol = 80:20, flow rate =1.0 mL/min, t_{major} = 4.4 min, t_{minor} = 5.8 min.

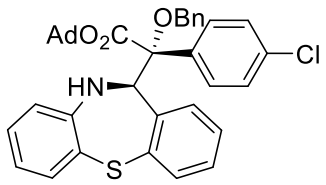


(3*S*,5*S*,7*S*)-Adamantan-1-yl (*R*)-2-((*R*)-10,11-dihydrodibenzo[*b,f*][1,4]thiazepine -11-yl)-2-hydroxy-2-phenylacetate (5y) Colourless oil, 55.1 mg, 55% yield, > 20:1 *dr*, 77% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 2H), 7.21 – 7.16 (m, 2H), 7.08 – 7.04 (m, 1H), 7.01 – 6.96 (m, 1H), 6.94 – 6.89 (m, 1H), 6.62 – 6.58 (m, 1H), 6.49 – 6.44 (m, 1H), 4.72 (s, 1H), 4.27 (d, *J* = 9.2 Hz, 1H), 2.13 – 2.09 (m, 3H), 2.03 – 2.01 (comp, 6H), 1.60 – 1.57 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 145.8, 142.6, 139.5, 136.4, 132.6, 132.1, 128.7, 128.3, 128.2, 127.9, 127.7, 126.1, 119.8, 119.7, 119.1, 117.3, 84.3, 81.1, 58.5, 41.0, 36.0, 31.0; HRMS (TOF MS ESI$^+$) calculated for $C_{31}H_{32}NO_3S$ $[M + H]^+$: 498.2025, found 498.2031; HPLC conditions for determination of enantiomeric excess: Chiral IC, λ = 254 nm, hexane : isopropanol = 70:30, flow rate =1.0 mL/min, t_{major} = 3.7 min, t_{minor} = 4.4 min.

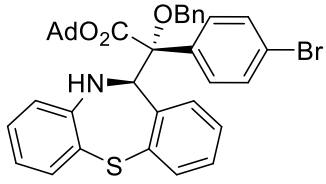


(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-10,11-dihydrodibenzo[*b,f*][1,4] thiazepin-11-yl)-2-(4-(trifluoromethyl)phenyl)acetate (6a) White solid, 55.7 mg, 85% yield, > 20:1 *dr*, 99% *ee*, $[\alpha]_D^{20}$ = - 85.7° (c = 0.30, DCM), mp = 113 – 115 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.69 – 7.61 (m, 2H), 7.55 – 7.48 (m, 1H), 7.45 – 7.37 (comp, 4H), 7.36 – 7.27 (m, 2H), 7.25 – 7.22 (m, 1H), 7.12 – 7.04 (m, 1H), 6.93 – 6.84 (m, 1H), 6.67 (d, *J* = 10.3 Hz, 1H), 6.59 – 6.51 (m, 1H), 6.48 – 6.39 (m, 1H), 5.39 (d, *J* = 11.7 Hz, 1H), 4.40 (d, *J* = 11.7 Hz, 1H), 4.31 (d, *J* = 10.4 Hz, 1H), 2.13 – 2.01 (m, 3H), 1.99 – 1.87 (m, 3H), 1.79 – 1.69 (m, 3H), 1.64 – 1.49 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 145.2, 144.6, 141.2, 138.7, 135.7, 132.8, 130.8 (q, *J* = 32.6 Hz), 130.4, 129.2, 128.8, 128.7, 128.3, 128.2, 127.8, 127.4, 125.9, 125.2 (q, *J* = 3.8 Hz), 123.3(q, *J* = 272.4 Hz), 119.9,

119.2, 117.7, 86.3, 83.7, 68.8, 61.1, 41.1, 36.1, 30.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -69.7; HRMS (TOF MS ESI$^+$) calculated for $C_{39}H_{37}F_3NO_3S$ [M + H]$^+$: 656.2441, found 656.2442; HPLC conditions for determination of enantiomeric excess: Chiral IA, λ = 300 nm, hexane : isopropanol = 98:2, flow rate =1.0 mL/min, t_{major} = 3.8 min, t_{minor} = 4.6 min.

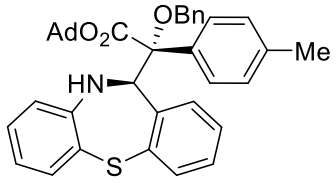


(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-(4-chlorophenyl)-2-((*R*)-10,11-dihydrodibenzo[*b,f*][1,4]thiazepin-11-yl)acetate (6b) White solid, 57.8 mg, 93% yield, > 20:1 *dr*, 95% *ee*, $[\alpha]_D^{20}$ = - 38.0^o (c = 0.30, DCM), mp = 130 – 132 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 1H), 7.76 – 7.70 (m, 2H), 7.54 – 7.49 (m, 1H), 7.42 – 7.36 (comp, 5H), 7.35 – 7.27 (m, 3H), 7.25 – 7.20 (m, 1H), 7.12 – 7.07 (m, 1H), 6.90 – 6.84 (m, 1H), 6.67 (d, *J* = 9.6 Hz, 1H), 6.56 – 6.50 (m, 1H), 6.43 – 6.39 (m, 1H), 5.36 (d, *J* = 11.7 Hz, 1H), 4.39 (d, *J* = 11.7 Hz, 1H), 4.31 (d, *J* = 10.0 Hz, 1H), 2.09 – 2.04 (m, 3H), 1.91 – 1.86 (m, 3H), 1.73 – 1.68 (m, 3H), 1.60 – 1.51 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 145.2, 144.8, 138.9, 135.8, 135.6, 134.7, 132.8, 131.9, 129.9, 129.2, 128.7, 128.4, 128.2, 128.1, 127.7, 127.5, 125.9, 119.8, 119.0, 117.5, 86.0, 83.4, 68.6, 61.0, 41.1, 36.1, 30.9; HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{37}ClNO_3S$ [M + H]$^+$: 622.2177, found 622.2178; HPLC conditions for determination of enantiomeric excess: Chiral IA, λ = 330 nm, hexane : isopropanol = 95:5, flow rate =1.0 mL/min, t_{major} = 3.7 min, t_{minor} = 4.3 min.



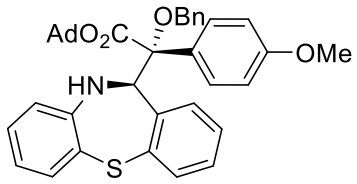
(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-(4-bromophenyl)-2-((*R*)-10,11-dihydrodibenzo[*b,f*][1,4]thiazepin-11-yl)acetate (6c) White solid, 63.2 mg, 95%

yield, > 20:1 *dr*, 95% *ee*, $[\alpha]_D^{20}$ = - 26.5º (c = 0.32, DCM), mp = 85 – 87 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.97 (m, 1H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 3H), 7.45 – 7.36 (comp, 4H), 7.36 – 7.27 (m, 2H), 7.26 – 7.21 (m, 1H), 7.14 – 7.01 (m, 1H), 6.92 – 6.83 (m, 1H), 6.68 (d, *J* = 10.2 Hz, 1H), 6.60 – 6.48 (m, 1H), 6.41 (s, 1H), 5.37 (d, *J* = 11.7 Hz, 1H), 4.40 (d, *J* = 11.7 Hz, 1H), 4.31 (d, *J* = 10.4 Hz, 1H), 2.10 – 2.01 (m, 3H), 1.92 – 1.83 (m, 3H), 1.76 – 1.68 (m, 3H), 1.61 – 1.50 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 145.2, 144.8, 138.9, 136.3, 135.6, 132.8, 131.9, 131.4, 130.2, 129.2, 128.7, 128.2, 128.1, 127.7, 127.4, 125.9, 123.1, 119.8, 119.0, 117.5, 86.1, 83.4, 68.6, 60.9, 41.1, 36.1, 30.9; HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{37}BrNO_3S$ $[M + H]^+$: 666.15672, found 666.15679; HPLC conditions for determination of enantiomeric excess: Chiral IA, λ = 300 nm, hexane : isopropanol = 95:5, flow rate =1.0 mL/min, t_{major} = 3.8 min, t_{minor} = 4.4 min.

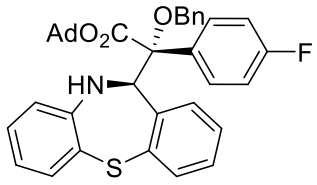


(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-10,11-dihydrodibenzo[*b,f*][1,4] thiazepin-11-yl)-2-(p-tolyl)acetate (6d) White solid, 56.5 mg, 94% yield, > 20:1 *dr*, 99% *ee*, $[\alpha]_D^{20}$ = - 52.0º (c = 0.30, DCM), mp = 90 – 92 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.42 – 7.38 (m, 2H), 7.36 – 7.28 (m, 2H), 7.26 – 7.21 (m, 3H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.90 – 6.85 (m, 1H), 6.79 (d, *J* = 9.6 Hz, 1H), 6.56 – 6.48 (m, 1H), 6.41 (d, *J* = 8.0 Hz, 1H), 5.38 (d, *J* = 11.7 Hz, 1H), 4.45 (d, *J* = 11.6 Hz, 1H), 4.42 (s, 1H), 2.39 (s, 3H), 2.12 – 2.02 (m, 3H), 1.96 – 1.83 (m, 3H), 1.81 – 1.69 (m, 3H), 1.62 – 1.51 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 145.5, 145.4, 139.3, 138.5, 135.5, 134.3, 132.7, 131.9, 129.2, 129.0, 128.6, 128.3, 128.1, 128.0, 127.49, 127.45, 125.8, 119.3, 118.5, 116.9, 86.2, 82.9, 68.4, 60.9, 41.1, 36.1, 30.9, 21.2; HRMS (TOF MS ESI$^+$) calculated for $C_{39}H_{40}NO_3S$ $[M + H]^+$: 602.2723, found 602.2719; HPLC conditions for determination of enantiomeric excess: Chiral IA, λ =

310 nm, hexane : isopropanol = 95:5, flow rate =1.0 mL/min, t_{major} = 3.9 min, t_{minor} = 4.5 min.

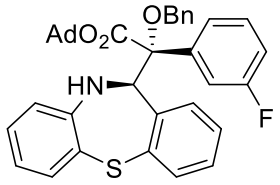


(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-10,11-dihydrodibenzo[*b,f*][1,4] thiazepin-11-yl)-2-(4-methoxyphenyl)acetate (6e) White solid, 42.0 mg, 68% yield, > 20:1 *dr*, 99% *ee*, mp = 90 – 92 °C; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) δ 8.05 – 8.00 (m, 1H), 7.73 (d, *J* = 8.9 Hz, 2H), 7.56 – 7.49 (m, 1H), 7.45 – 7.35 (comp, 4H), 7.33 – 7.28 (m, 2H), 7.24 – 7.18 (m, 1H), 7.13 – 7.05 (m, 1H), 6.94 – 6.82 (m, 3H), 6.75 (d, *J* = 9.0 Hz, 1H), 6.56 – 6.47 (m, 1H), 6.46 – 6.38 (m, 1H), 5.32 (d, *J* = 11.7 Hz, 1H), 4.39 (s, 1H), 4.39 (d, *J* = 11.7 Hz, 1H), 3.83 (s, 3H), 2.10 – 1.98 (m, 3H), 1.91 – 1.81 (m, 3H), 1.76 – 1.65 (m, 3H), 1.63 – 1.53 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm) δ 170.9, 159.7, 145.5, 145.3, 139.3, 135.5, 132.8, 131.9, 130.8, 129.8, 129.4, 129.2, 128.6, 128.2, 128.0, 127.5, 125.9, 119.4, 118.6, 117.1, 113.6, 85.9, 82.9, 68.3, 60.9, 55.4, 41.1, 36.1, 30.9; HRMS (TOF MS ESI$^+$) calculated for $C_{39}H_{40}NO_4S$ $[M + H]^+$: 618.2673, found 618.2674; HPLC conditions for determination of enantiomeric excess: Chiral IA, λ = 330 nm, hexane : isopropanol = 95:5, flow rate =1.0 mL/min, t_{major} = 4.3 min.



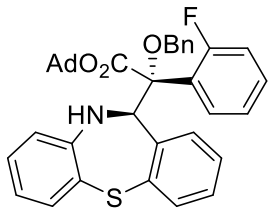
(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-10,11-dihydrodibenzo[*b,f*][1,4] thiazepin-11-yl)-2-(4-fluorophenyl)acetate (6f) White solid, 56.9 mg, 94% yield, > 20:1 *dr*, 97% *ee*, $[\alpha]_D^{20}$ = - 91.7° (c = 0.37, DCM), mp = 116 – 118 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.55 – 7.49 (m, 1H), 7.44 – 7.36 (comp, 4H), 7.35 – 7.27 (m, 2H), 7.26 – 7.20 (m, 1H), 7.13 – 7.05 (m, 3H),

6.89 – 6.85 (m, 1H), 6.70 (d, *J* = 10.3 Hz, 1H), 6.57 – 6.50 (m, 1H), 6.42 (d, *J* = 8.1 Hz, 1H), 5.35 (d, *J* = 11.7 Hz, 1H), 4.38 (d, *J* = 11.7 Hz, 1H), 4.34 (d, *J* = 10.4 Hz, 1H), 2.08 – 2.05 (m, 3H), 1.92 – 1.87 (m, 3H), 1.74 – 1.70 (m, 3H), 1.60 – 1.52 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 162.8 (d, *J* = 248.2 Hz), 145.3, 144.9, 139.0, 135.6, 133.1 (d, *J* = 3.4 Hz), 132.8, 131.9, 130.4 (d, *J* = 8.1 Hz), 129.2, 128.6, 128.2, 128.1, 127.7, 127.5, 125.9, 119.7, 118.9, 117.5, 115.2 (d, *J* = 21.3 Hz), 85.9, 83.3, 68.5, 61.0, 41.1, 36.1, 30.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.3; HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{37}FNO_3S$ [M + H]$^+$: 606.2473, found 606.2472; HPLC conditions for determination of enantiomeric excess: Chiral IA, λ = 300 nm, hexane : isopropanol = 95:5, flow rate =1.0 mL/min, t_{major} = 3.7 min, t_{minor} = 4.3 min.

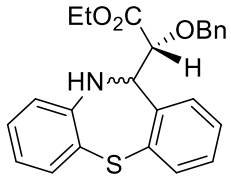


(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-10,11-dihydrodibenzo[*b,f*][1,4] thiazepin-11-yl)-2-(3-fluorophenyl)acetate (6g) White solid, 54.5 mg, 90% yield, > 20:1 *dr*, 98% *ee*, $[\alpha]_D^{20}$ = - 75.8^o (c = 0.30, DCM), mp = 88 – 90 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 1H), 7.62 – 7.51 (m, 3H), 7.46 – 7.40 (m, 3H), 7.39 – 7.34 (m, 2H), 7.32 – 7.21 (m, 3H), 7.14 – 7.06 (m, 2H), 6.92 – 6.84 (m, 1H), 6.71 (d, *J* = 10.1 Hz, 1H), 6.57 – 6.51 (m, 1H), 6.46 – 6.41 (m, 1H), 5.40 (d, *J* = 11.7 Hz, 1H), 4.43 (d, *J* = 11.6 Hz, 1H), 4.33 (d, *J* = 10.3 Hz, 1H), 2.09 – 2.03 (m, 3H), 1.95 – 1.86 (m, 3H), 1.79 – 1.68 (m, 3H), 1.62 – 1.51 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 162.7 (d, *J* = 245.3 Hz), 1453, 144.9, 139.8 (d, *J* = 6.9 Hz), 138.9, 135.6, 132.7, 131.9, 129.6 (d, *J* = 8.1 Hz), 129.2, 128.7, 128.3, 128.1, 127.7, 127.5, 125.9, 124.1 (d, *J* = 2.8 Hz), 119.8, 118.9, 117.4, 115.8 (d, *J* = 23.6 Hz), 115.7 (d, *J* = 21.1 Hz), 86.1 (d, *J* = 1.6 Hz), 83.5, 68.7, 61.0, 41.1, 36.1, 30.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.2; HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{37}FNO_3S$ [M + H]$^+$: 606.2473, found 606.2467; HPLC conditions for determination of enantiomeric excess: Chiral

IA, λ = 300 nm, hexane : isopropanol = 98:2, flow rate =1.0 mL/min, t_{major} = 3.9 min, t_{minor} = 4.5 min.



(3*R*)-Adamantan-1-yl (2*R*)-2-(benzyloxy)-2-((*R*)-10,11-dihydrodibenzo[*b,f*][1,4] thiazepin-11-yl)-2-(2-fluorophenyl)acetate (6h) White solid, 18.2 mg, 30% yield, > 20:1 *dr*, 91% *ee*, mp = 90 – 92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.95 (m, 2H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.39 – 7.34 (m, 3H), 7.31 – 7.27 (m, 1H), 7.25 – 7.23 (m, 1H), 7.21 – 7.14 (m, 2H), 7.14 – 7.06 (m, 2H), 6.93 – 6.85 (m, 1H), 6.83 (d, 1H), 6.54 – 6.50 (m, 1H), 6.44 (d, *J* = 8.1 Hz, 1H), 5.33 (d, *J* = 11.1 Hz, 1H), 4.70 (d, *J* = 9.2 Hz, 1H), 4.45 (d, *J* = 11.2 Hz, 1H), 2.07 – 2.02 (m, 3H), 1.90 – 1.85 (m, 3H), 1.76 – 1.72 (m, 3H), 1.58 – 1.52 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 161.1 (d, *J* = 248.3 Hz), 145.4, 143.4, 138.8, 135.7, 132.7, 131.9, 130.7 (d, *J* = 9.2 Hz), 130.2 (d, *J* = 3.1 Hz), 128.7, 128.5, 128.4, 128.0, 127.7, 127.6, 125.4, 125.3, 124.6 (d, *J* = 3.0 Hz), 119.3, 118.7, 118.2, 116.4 (d, *J* = 25.0 Hz), 84.3, 83.1, 68.2, 61.2, 40.9, 36.1, 30.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -106.4; HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{37}FNO_3S$ $[M + H]^+$: 606.2473, found 606.2480; HPLC conditions for determination of enantiomeric excess: Chiral IA, λ = 254 nm, hexane : isopropanol = 90:10, flow rate =1.0 mL/min, t_{major} = 3.9 min, t_{minor} = 4.5 min.



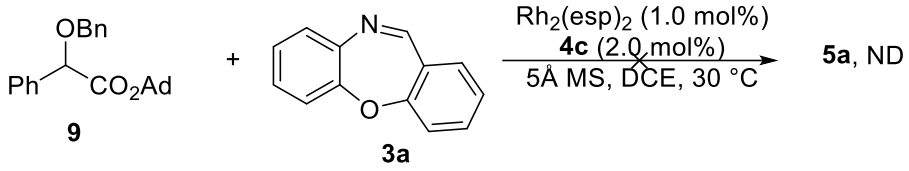
Ethyl (2*R*)-2-(benzyloxy)-2-(10,11-dihydrodibenzo[*b,f*][1,4]thiazepin-11-yl) acetate (6i) Colorless oil, 20.3 mg, 50% yield, 1.5:1 *dr*, 93%/55% *ee*; ^{1}H NMR (500 MHz, $CDCl_3$) δ major: 7.42 (d, *J* = 7.3 Hz, 1H), 7.38 (d, *J* = 5.9 Hz, 1H), 7.31 (d, *J* = 7.3 Hz, 1H), 7.25 – 7.21 (m, 3H), 7.15 – 7.12 (m, 3H), 7.08 – 7.06 (m, 1H), 6.83 –

6.79 (m, 1H), 6.49 – 6.44 (m, 1H), 6.23 (d, *J* = 8.1 Hz, 1H), 4.84 – 4.81 (m, 1H), 4.78 (d, *J* = 11.6 Hz, 1H), 4.36 (d, *J* = 11.6 Hz, 1H), 4.18 (s, 1H), 4.13 – 4.05 (m, 2H), 1.04 (t, *J* = 7.1 Hz, 3H); minor: 7.52 – 7.49 (m, 1H), 7.37 (d, *J* = 7.0 Hz, 1H), 7.35 – 7.33 (m, 2H), 7.24 (d, *J* = 2.7 Hz, 2H), 7.20 (d, *J* = 3.9 Hz, 1H), 6.95 (m, 1H), 6.62 (m, 1H), 6.51 (d, *J* = 8.1 Hz, 1H), 5.59 (d, *J* = 5.3 Hz, 1H), 4.92 (d, *J* = 6.5 Hz, 1H), 4.82 (d, *J* = 11.1 Hz, 1H), 4.65 (s, 1H), 4.56 (d, *J* = 11.1 Hz, 1H), 4.14 – 4.06 (m, 1H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ major: 171.2, 145.9, 141.0, 137.2, 136.1, 132.6, 132.2, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 118.8, 118.5, 117.2, 80.5, 73.7, 61.3, 58.5, 14.2; minor: 171.0, 146.2, 141.0, 137.0, 136.5, 131.9, 131.7, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 127.9, 119.2, 119.1, 117.6, 80.0, 73.0, 61.3, 60.2, 14.1; HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{24}NO_3S$ $[M + H]^+$: 406.1471, found 406.1465; HPLC conditions for determination of enantiomeric excess: Chiral AD-H, λ = 300 nm, hexane : isopropanol = 80:20, flow rate =0.5 mL/min, t_{major} = 23.7 min, t_{minor} = 25.6 min.

Control Experiments:

Synthesis of 9: To a 10-mL oven-dried vial with a magnetic stirring bar, **2a** (21.6 mg, 0.2 mmol), and $Rh_2(esp)_2$ (0.8 mg, 1.0 mol%) in 2.0 mL DCE, a solution of **1a** (71.0 mg, 0.24 mmol) in DCE (2.0 mL) was added *via* a syringe pump over 2 h under argon atmosphere at 30 °C. Then the solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel (Hexanes : EtOAc = 50:1) to give 60.2 mg of pure product **9** as white solid in 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.42 – 7.27 (comp, 8H), 4.81 (s, 1H), 4.61 (q, *J* = 11.9 Hz, 2H), 2.16 – 2.10 (m, 3H), 2.09 – 2.01 (comp, 6H), 1.66 – 1.61 (comp, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 137.7, 137.2, 128.5, 128.52, 128.47, 128.1, 127.9, 127.4, 82.0, 80.4, 71.2, 41.3, 36.2, 31.0; HRMS (TOF MS ESI+) calculated for $C_{25}H_{29}O_3$ $[M + H]^+$: 377.2117, found 377.2115.

Control reaction with **9** and **3a**:



To a 10-mL oven-dried vial containing a magnetic stirring bar, **9** (37.6 mg, 0.10 mmol), **3a** (19.5 mg, 0.10 mmol), **4c** (1.7 mg, 2.0 mol%), 5Å MS (100 mg), $Rh_2(esp)_2$ (0.8 mg, 1.0 mol%), and DCE (2.0 mL) were added in sequence, and the reaction mixture was stirred at 30 °C under argon atmosphere for 10 h. Then the reaction crude mixture was subjected to proton NMR analysis in $CDCl_3$ (see Fig. S1 for detail). All the materials were remained and no product **5a** was formed.

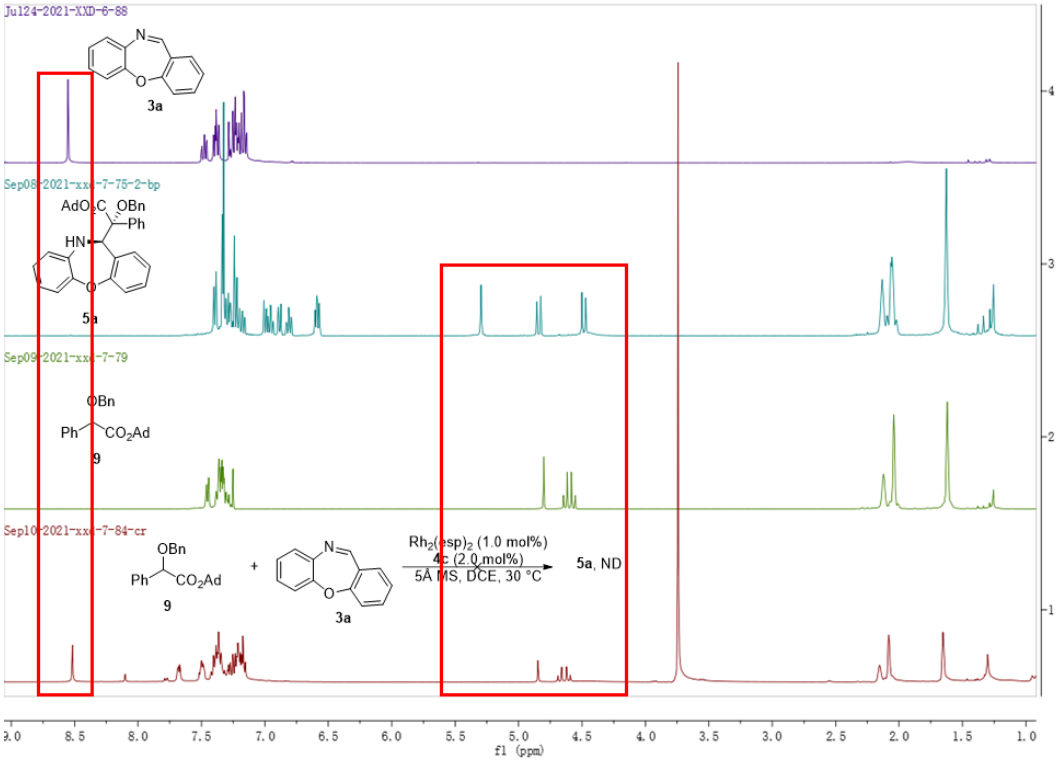
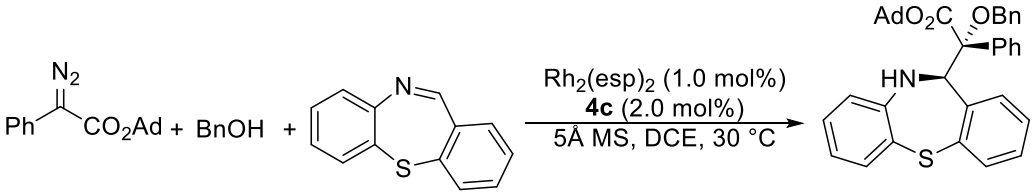


Fig. S1 Proton NMR spectrum of crude reaction mixture of **9** with **3a** under standard conditions.

Procedure of the Scale Up

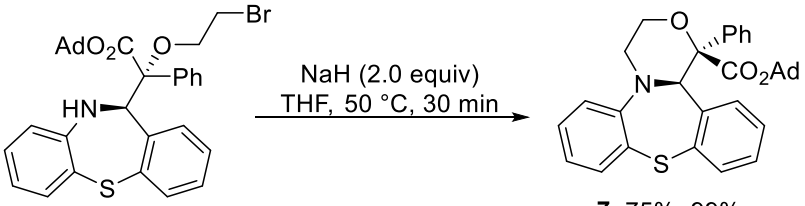


1a, 712 mg, 2.4 mmol | **2a**, 260 mg, 2.4 mmol | **3m**, 422 mg, 2.0 mmol

5m, 1.04 g, 90% yield, > 20:1*dr*, 99% *ee*

To a 10-mL oven-dried vial with a magnetic stirring bar, **2a** (260 mg, 2.4 mmol, 1.2 equiv), $Rh_2(esp)_2$ (16.0 mg, 1.0 mol%), **4c** (34 mg, 2.0 mol%) and 5Å MS (2.0 g) in 10 mL DCE, a solution of **1a** (712 mg, 2.4 mmol, 1.2 equiv) and imine **3m** (422 mg, 2.0 mmol, 1.0 equiv) in DCE (30 mL) was added *via* a syringe pump over 10 h under argon atmosphere at 30 °C, and the reaction mixture was stirred for additional 1 h under these conditions. Then the solvent was evaporated in vacuo, the residue was purified by column chromatography on silica gel (Hexanes : EtOAc = 50:1) to give 1.04 g of pure product **5m** in 90% yield with 99% *ee*.

Synthetic Transformations

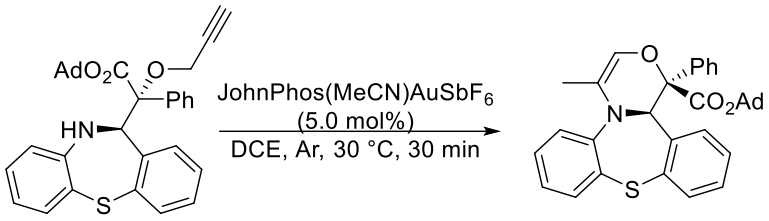


5t (99% *ee*)

7, 75%, 99% *ee*
CCDC: 2126677

Synthesis of 7: To a 10-mL oven-dried round-bottom flask with a magnetic stirring bar, a solution of **5t** (60.3 mg, 0.1 mmol) in THF (2.0 mL), was added NaH (4.8 mg, 0.2 mmol, 2.0 equiv) under stirring at 0 °C, then the reaction mixture was allowed up to 50 °C for stirring 0.5 h. When the reaction was completed (monitored by TLC), the solvent was evaporated under vacuum after filtering through a pad of Celite. The residue was purified by column chromatography on silica gel (Hexanes : EtOAc = 50:1) to give 39.2 mg of pure product **7** as white solid in 75% yield with 99% *ee*, $[\alpha]_D^{20}$ = - 113.1° (c = 0.30, DCM), mp = 270 – 272 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.09 (m, 1H), 7.74 – 7.64 (m, 2H), 7.62 – 7.53 (m, 1H), 7.41 – 7.34 (m, 2H),

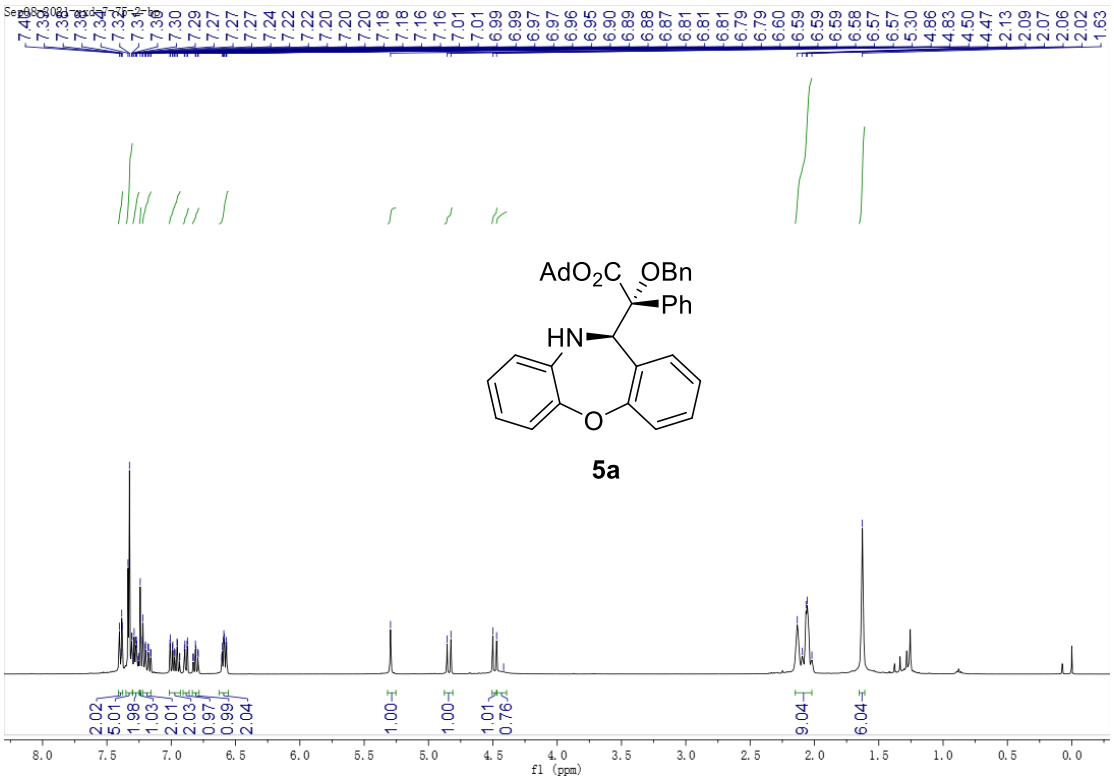
7.33 – 7.23 (comp, 4H), 7.16 (s, 1H), 6.98 – 6.88 (m, 1H), 6.72 – 6.66 (m, 1H), 6.65 – 6.60 (m, 1H), 3.99 – 3.90 (m, 1H), 3.88 – 3.77 (m, 1H), 3.23 – 3.11 (m, 2H), 1.97 – 1.89 (m, 3H), 1.65 – 1.56 (comp, 4H), 1.54 – 1.38 (comp, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 148.1, 141.0, 138.4, 136.8, 131.7, 131.6, 128.8, 128.6, 128.3, 127.9, 127.7, 127.6, 127.5, 123.0, 121.6, 120.6, 81.7, 81.1, 63.3, 56.2, 46.9, 40.6, 36.0, 30.7; HRMS (TOF MS ESI+) calculated for $C_{33}H_{34}NO_3S$ $[M + H]^+$: 524.2254, found 524.2258; HPLC conditions for determination of enantiomeric excess: Chiral IF-3, λ = 254 nm, hexane : isopropanol = 98:2, flow rate =1.0 mL/min, t_{major} = 23.9 min.



5u (99% *ee*)

8, 95%, 99% *ee*

Synthesis of 8: To a 10-mL oven-dried vial containing a magnetic stirring bar, **5u** (53.5 mg, 0.10 mmol), JohnPhos(MeCN)$AuSbF_6$ (3.7 mg, 5.0 mol%), and DCE (2.0 mL) were added in sequence, and the reaction mixture was stirred at 30 °C under argon atmosphere for 0.5 h. When the reaction was completed (monitored by TLC), the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel with any treatment (Hexanes : EtOAc = 50:1) to give 29.4 mg of pure product **8** as white solid in 95% yield with 99% *ee*, mp = 104 – 106 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.64 (m, 1H), 7.61 – 7.53 (m, 2H), 7.49 – 7.43 (m, 1H), 7.29 – 7.23 (m, 3H), 7.22 – 7.13 (m, 3H), 6.84 – 6.72 (m, 2H), 6.33 (s, 1H), 6.08 (d, *J* = 1.1 Hz, 1H), 5.92 – 5.82 (m, 1H), 2.07 – 1.97 (m, 3H), 1.89 – 1.76 (comp, 6H), 1.58 – 1.47 (comp, 6H), 1.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.7, 142.6, 141.0, 137.9, 134.8, 129.7, 128.2, 128.1, 127.8, 127.2, 126.9, 126.6, 126.1, 126.0, 124.9, 122.9, 122.5, 115.2, 82.8, 81.3, 59.2, 40.9, 36.0, 30.8, 15.2; HRMS (TOF MS ESI+) calculated for $C_{34}H_{34}NO_3S$ $[M + H]^+$: 536.2254, found 536.2248; HPLC conditions for determination of enantiomeric excess: Chiral IF-3, λ = 266 nm, hexane : isopropanol = 80:20, flow rate =1.0 mL/min, t_{major} = 6.9 min.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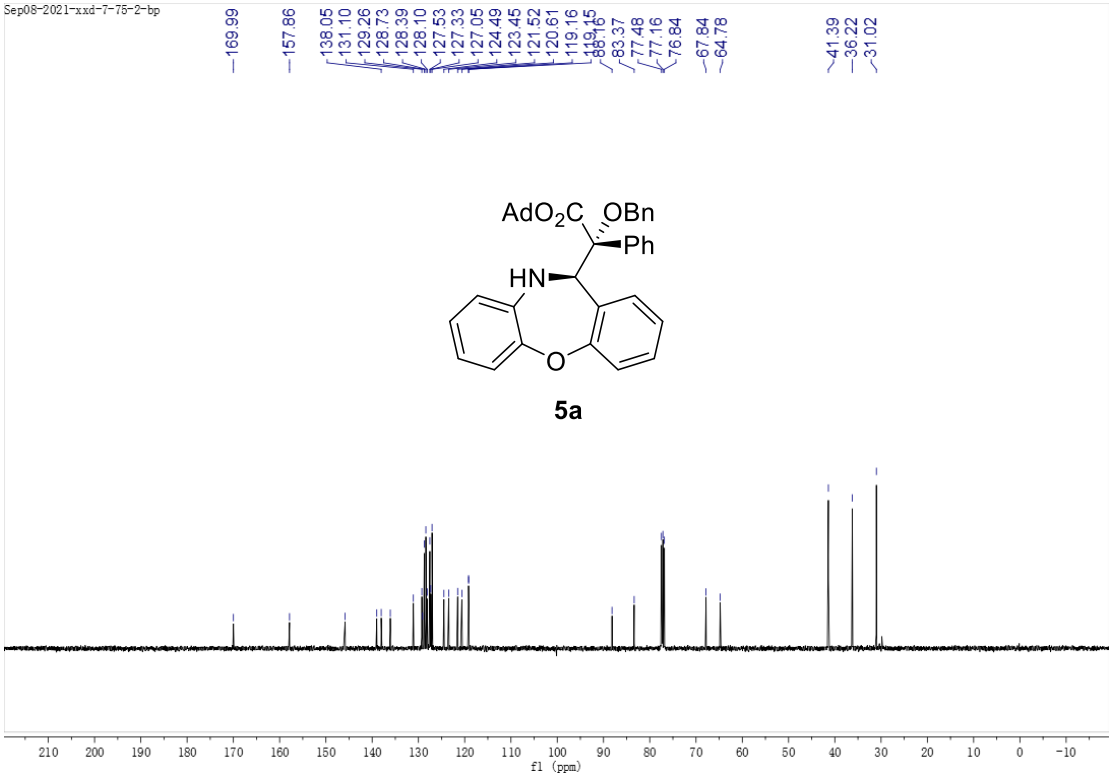
OBn
Ph
HN
O
5a
f1 (ppm)


Sep08-2021-xxd-7-75-2-bp
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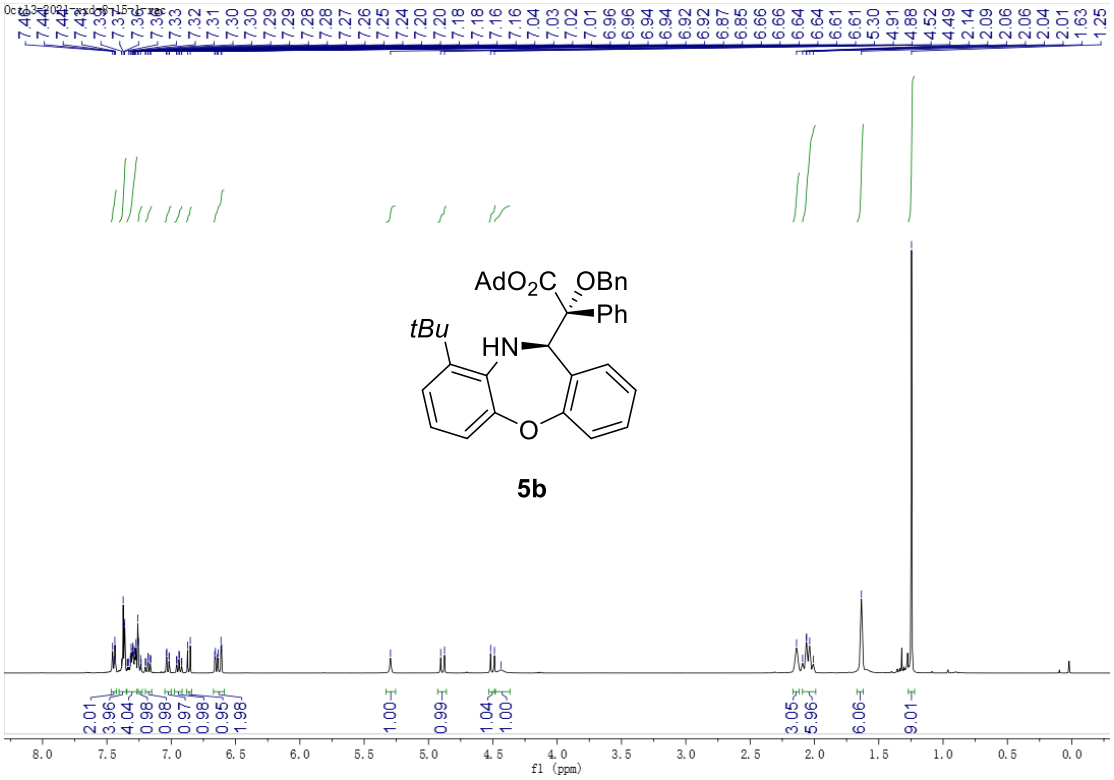
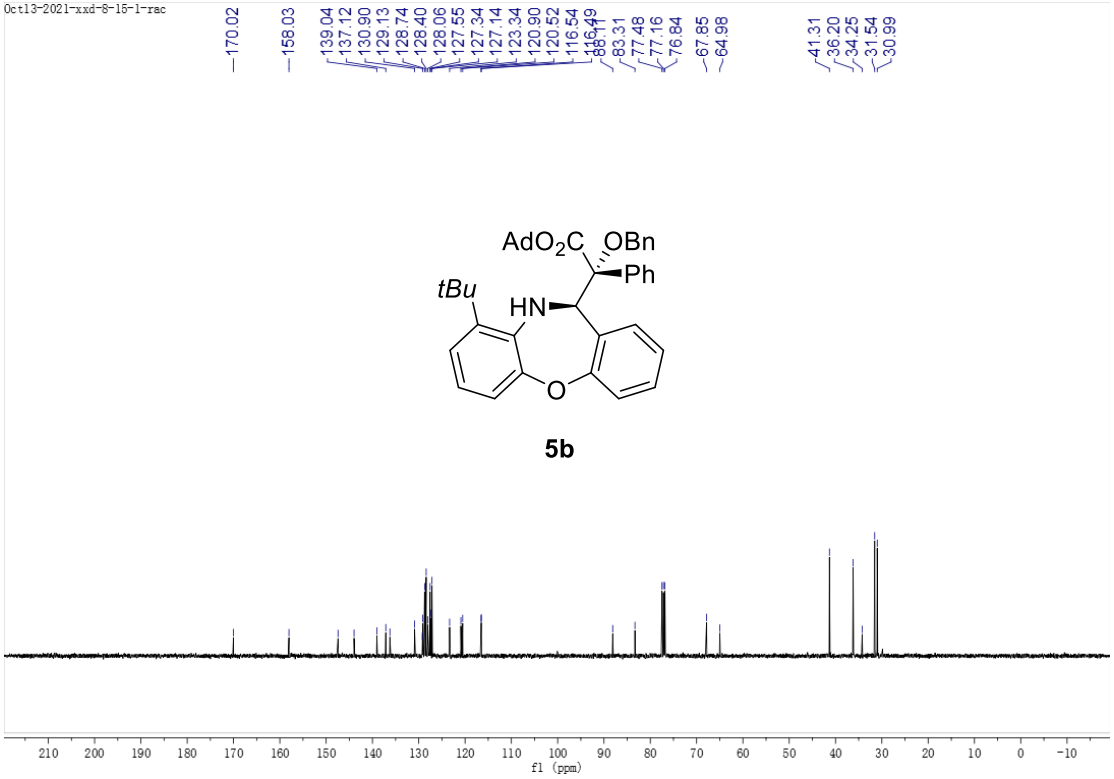
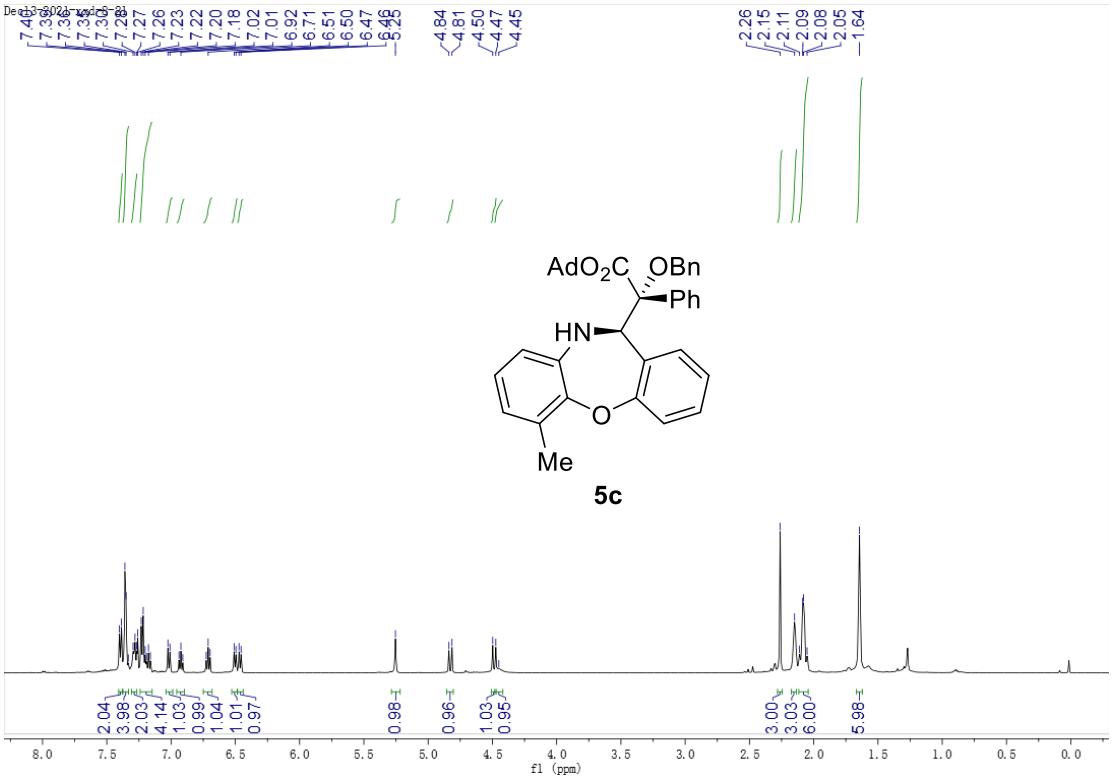
OBn
Ph
HN
O
5a
f1 (ppm)



5b



5b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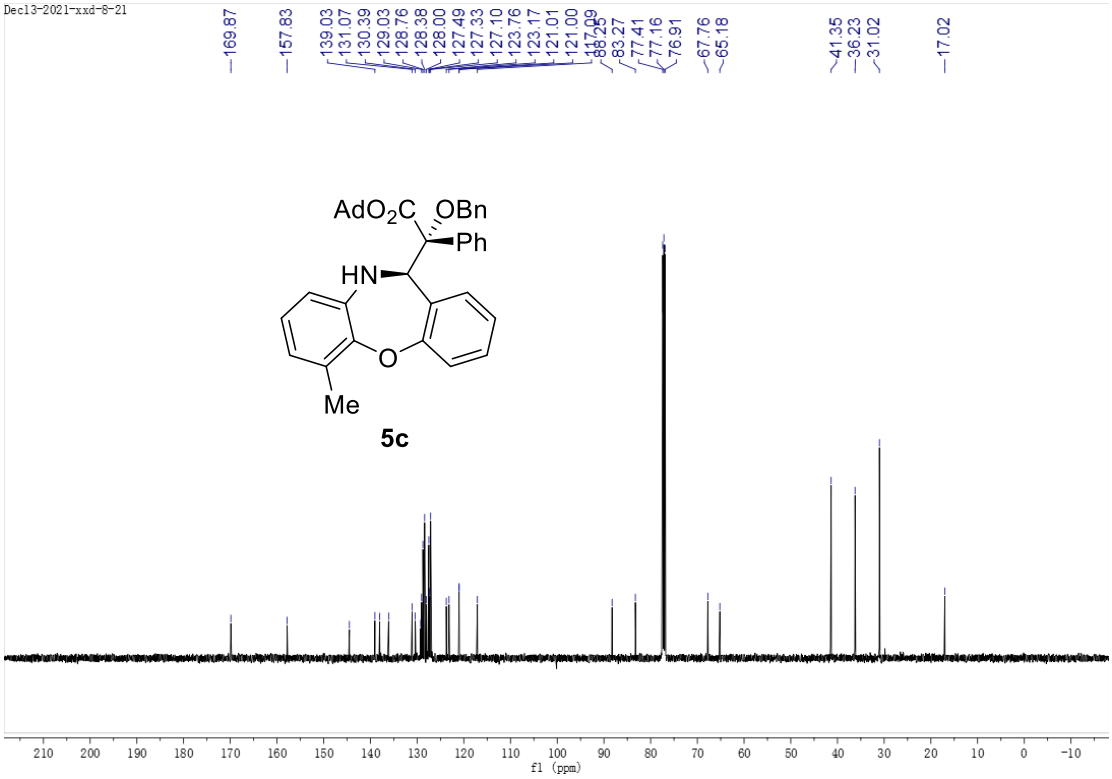
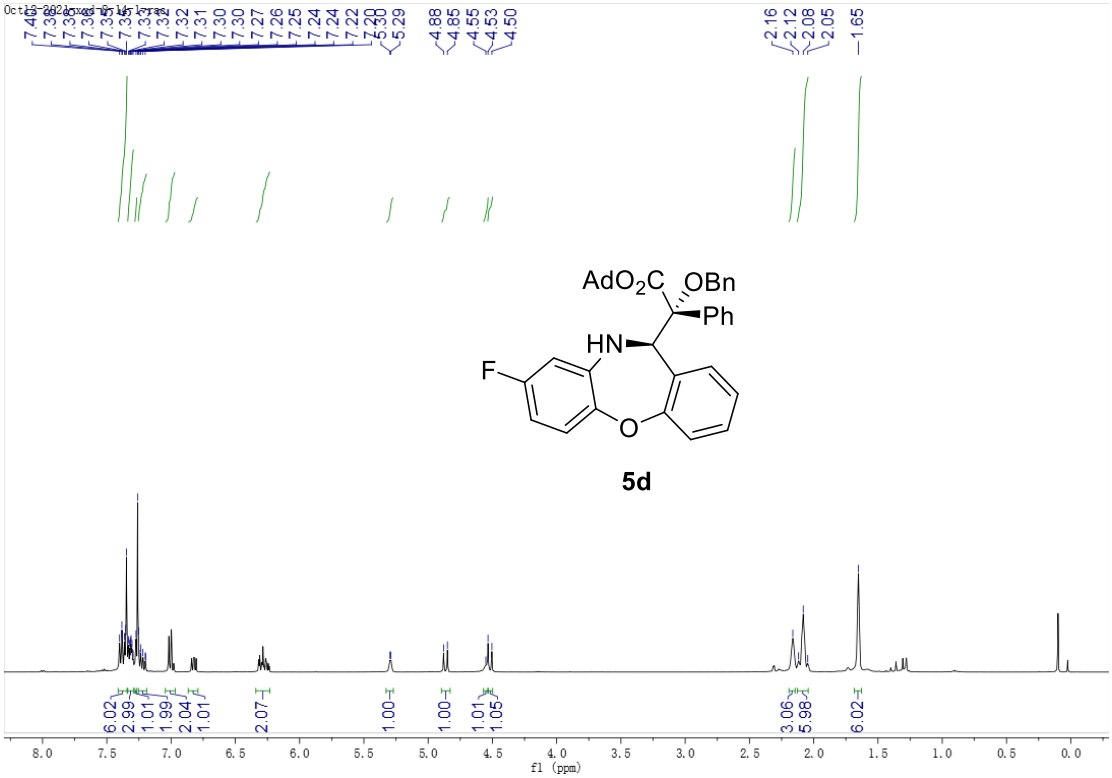
OBn
Ph
HN
O
Me
5c
f1 (ppm)


AdO2C
OBn
Ph
HN
O
Me
5c
f1 (ppm)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7.27
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7.22
5.30
5.29
4.88
4.85
4.55
4.53
4.50
2.16
2.12
2.08
2.05
1.65
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OBn
Ph
HN
F
O
6.02
2.99
1.01
1.99
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1.01
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1.00
1.01
1.05
3.06
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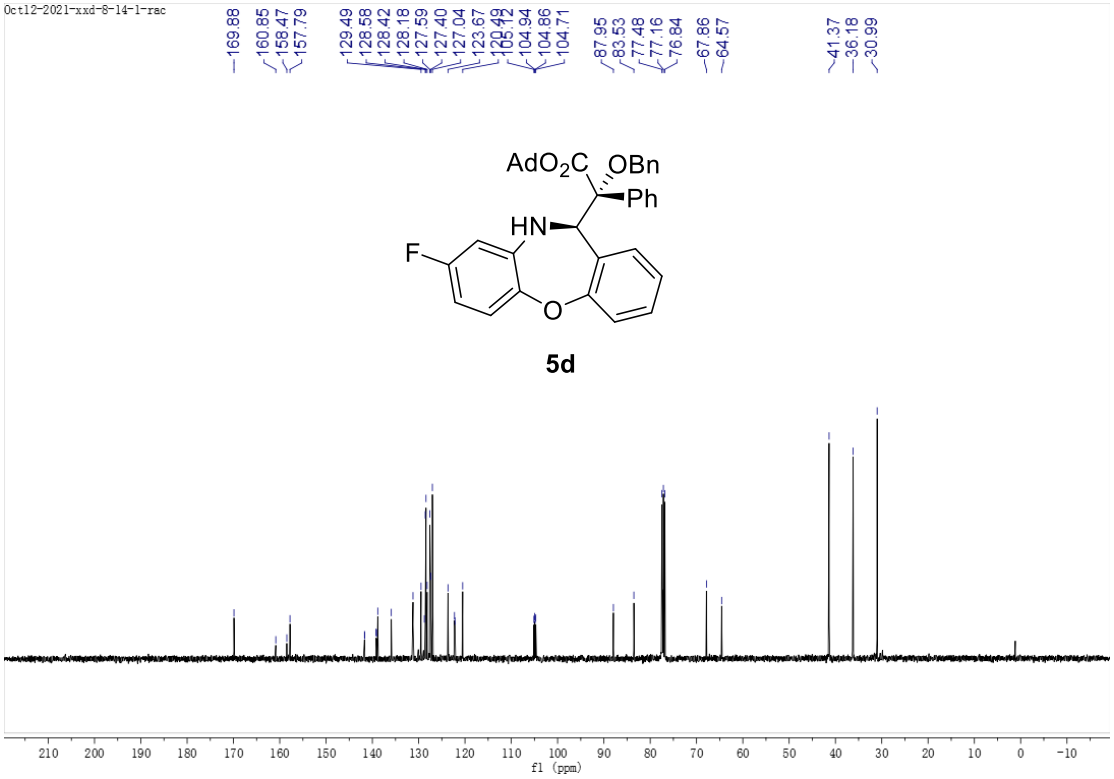
6.02
f1 (ppm)

5d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127.40
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83.53
77.48
77.16
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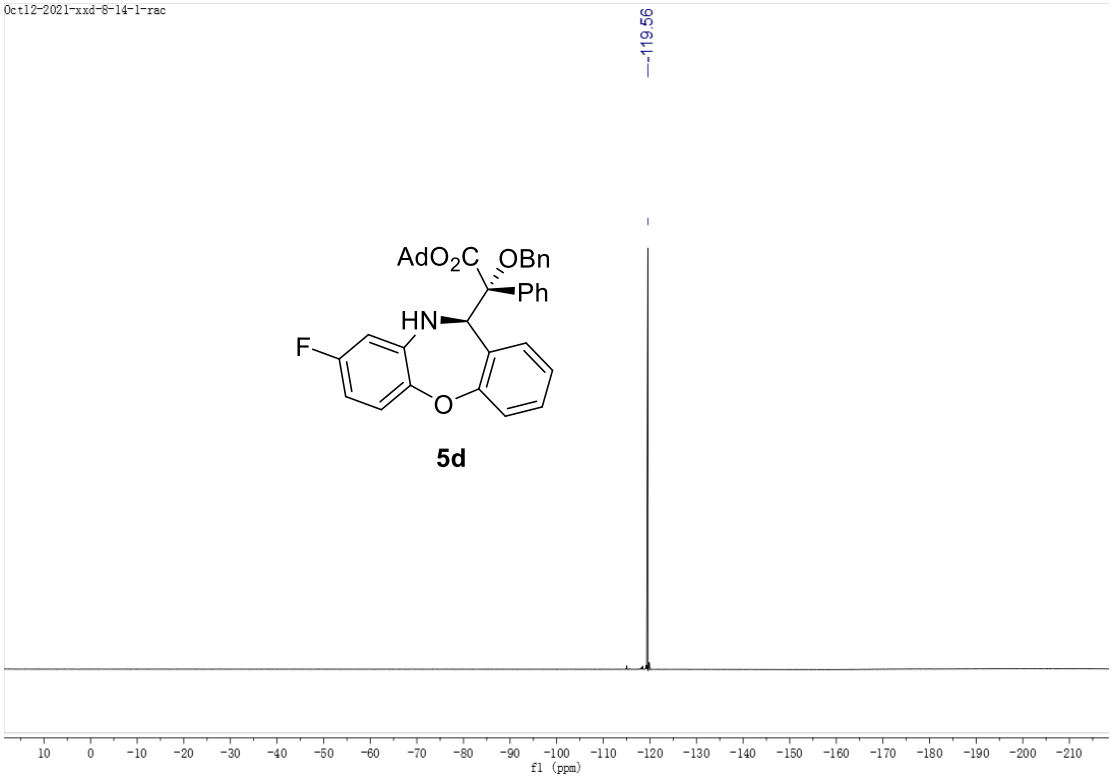
OBn
Ph
HN
F
O
f1 (ppm)

5d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F
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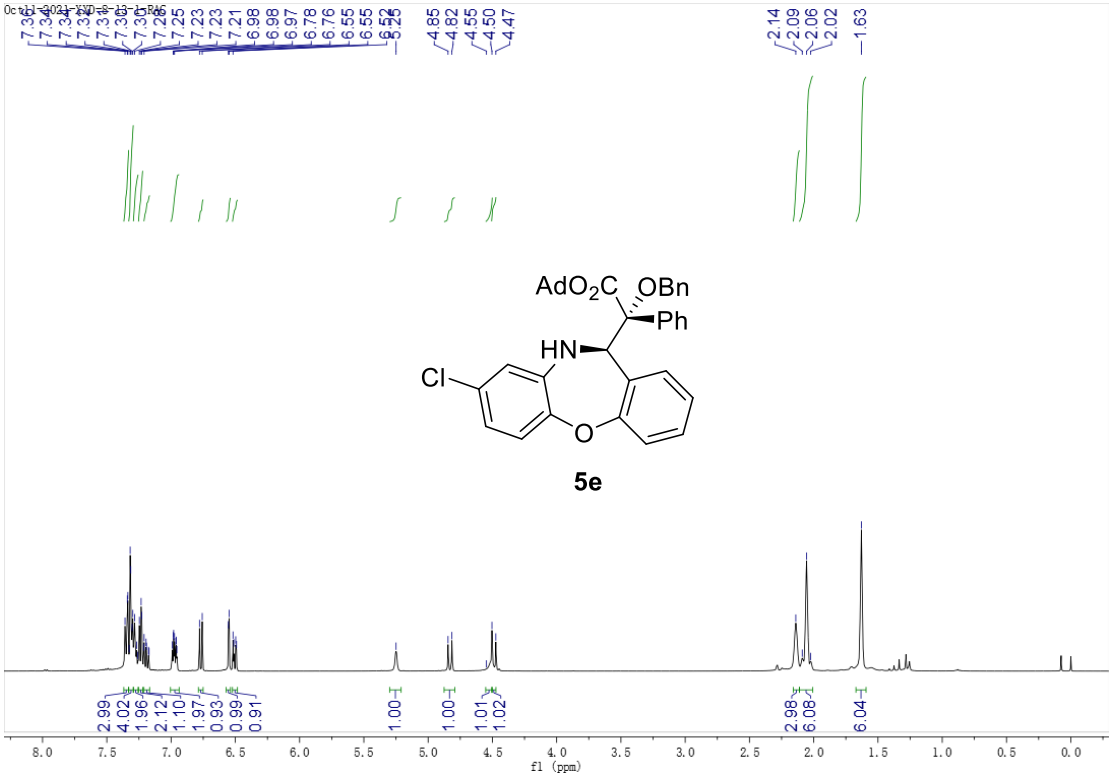
f1 (ppm)

5d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4.50
4.47
2.14
2.09
2.06
2.02
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AdO2C
OBn
Ph
HN
Cl
O
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1.10
1.97
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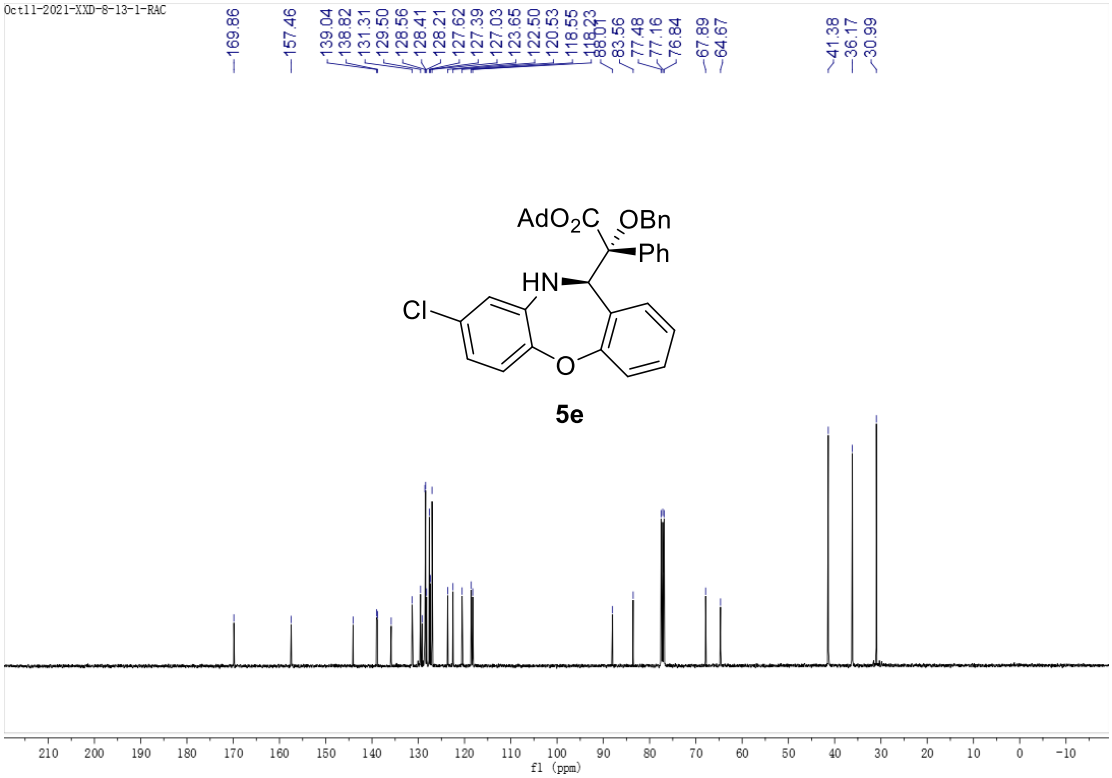
2.98
6.08
6.04
f1 (ppm)

5e


Oct11-2021-XXD-8-13-1-RAC
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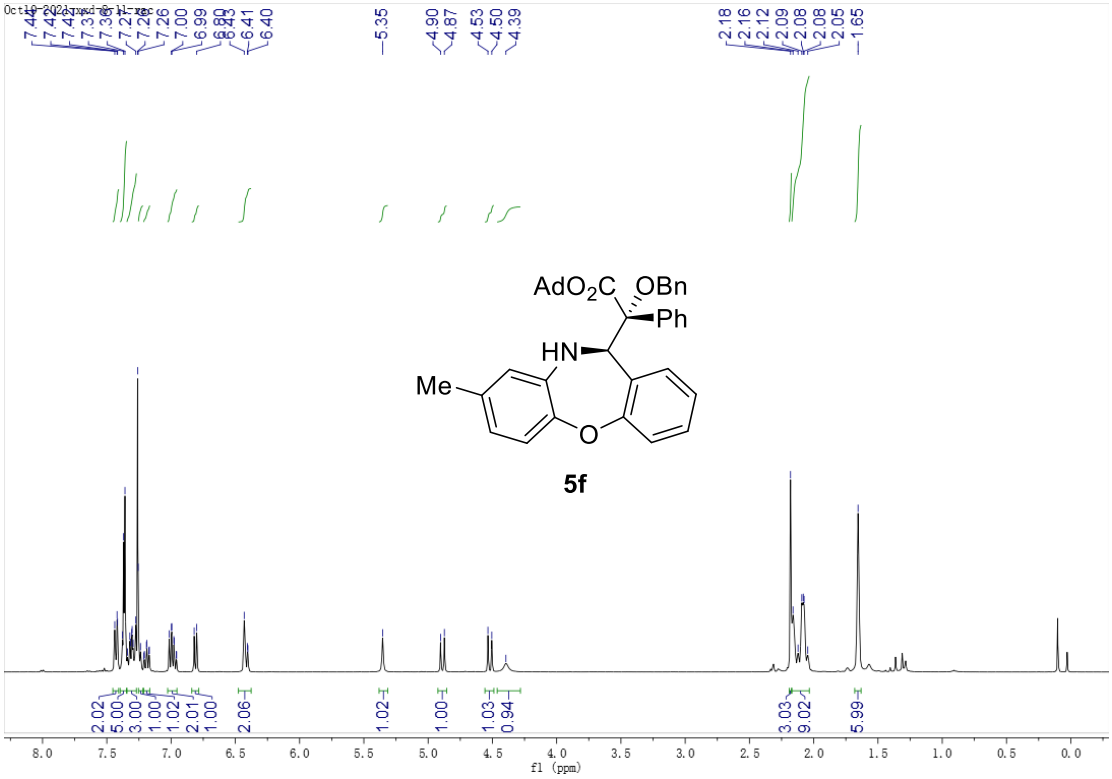
Ph
HN
Cl
O
5e
f1 (ppm)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4.53
4.50
4.39
2.18
2.16
2.12
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2.08
2.08
2.05
1.65
AdO2C
OBn
Ph
HN
Me
O
5f
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3.00
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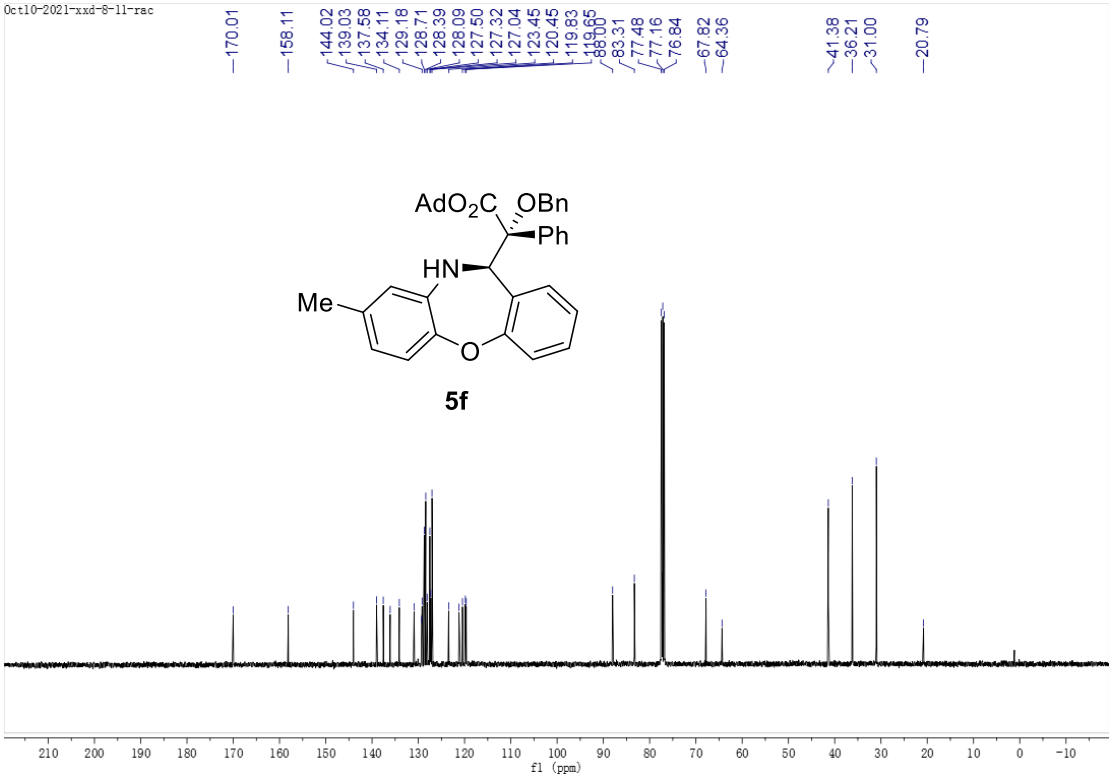
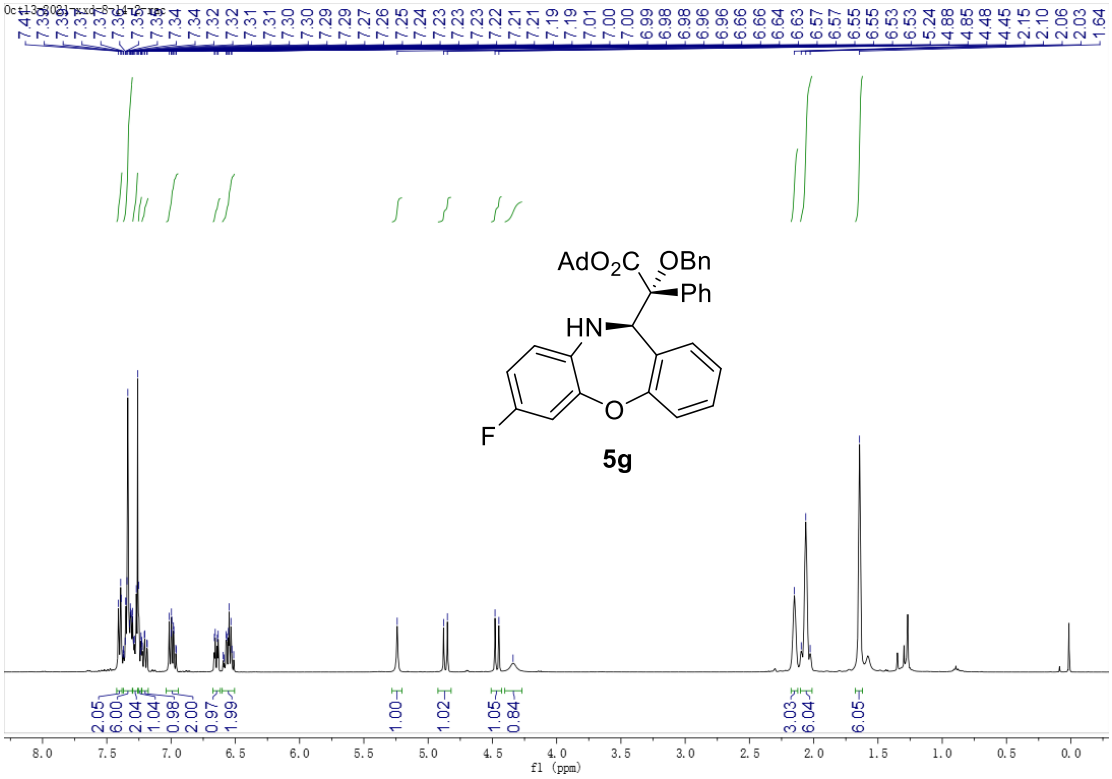
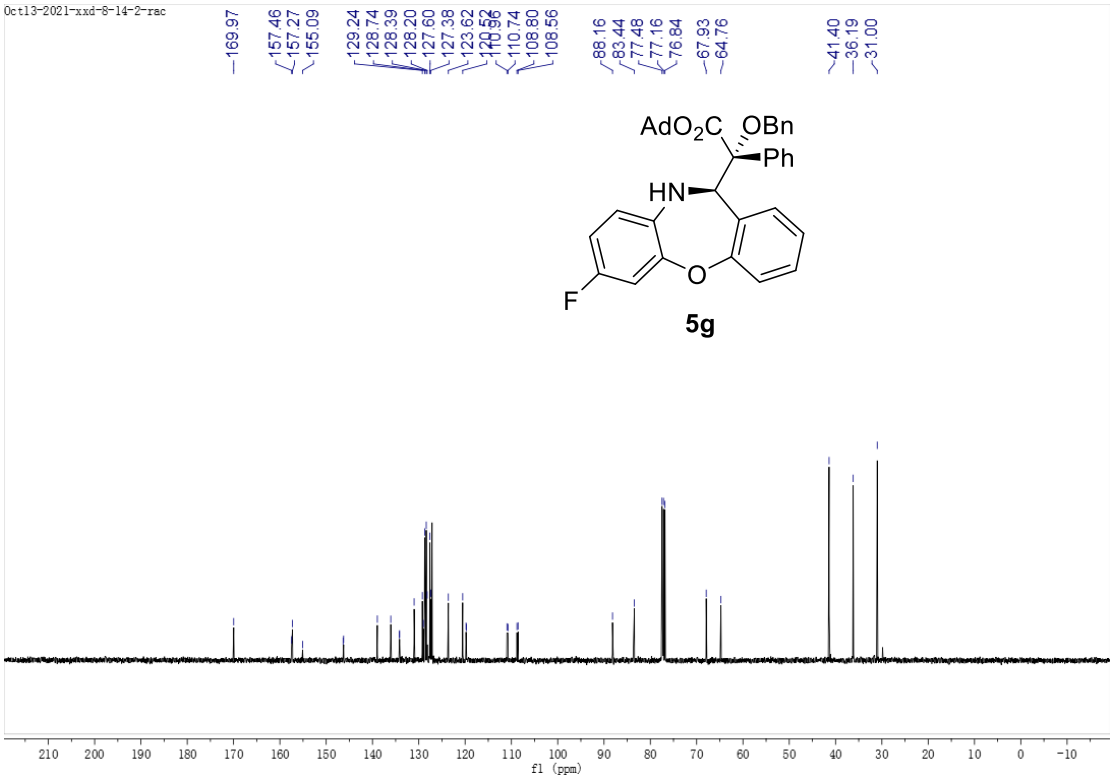
f1 (ppm)


Oct10-2021-xxd-8-11-rac
AdO2C
OBn
Ph
HN
Me
O
5f
f1 (ppm)


AdO2C
OBn
Ph
HN
F
O
5g
f1 (ppm)


Oct13-2021-xxd-8-14-2-rac
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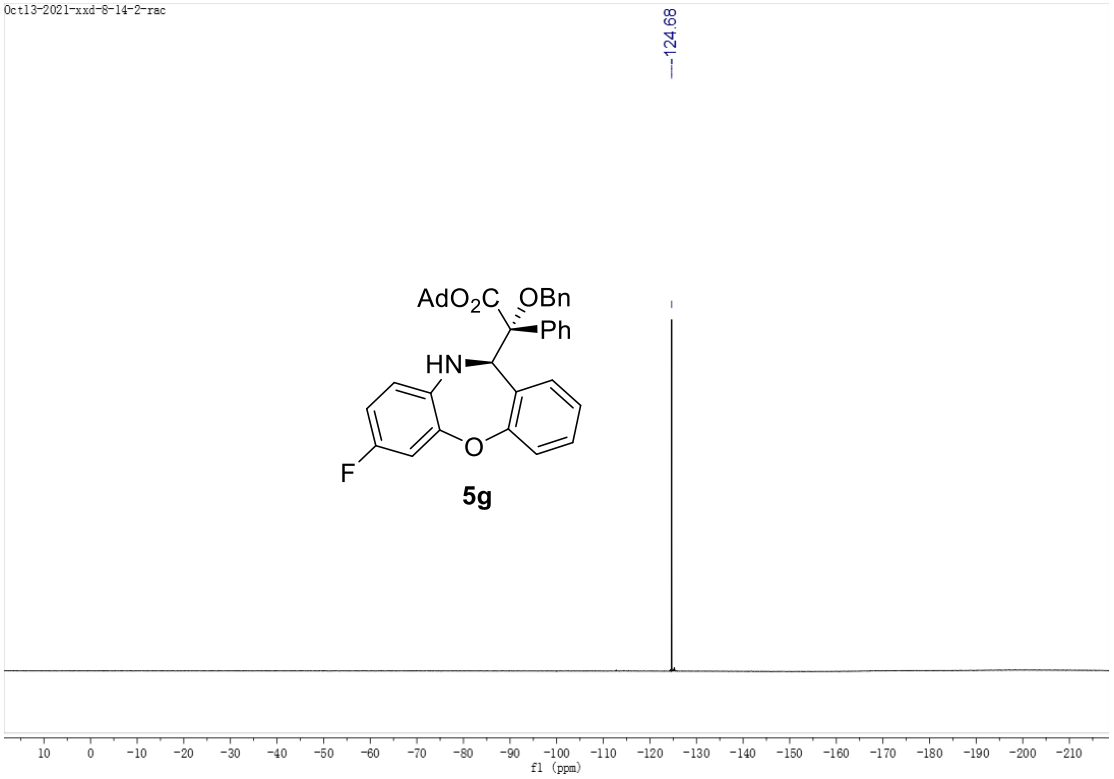
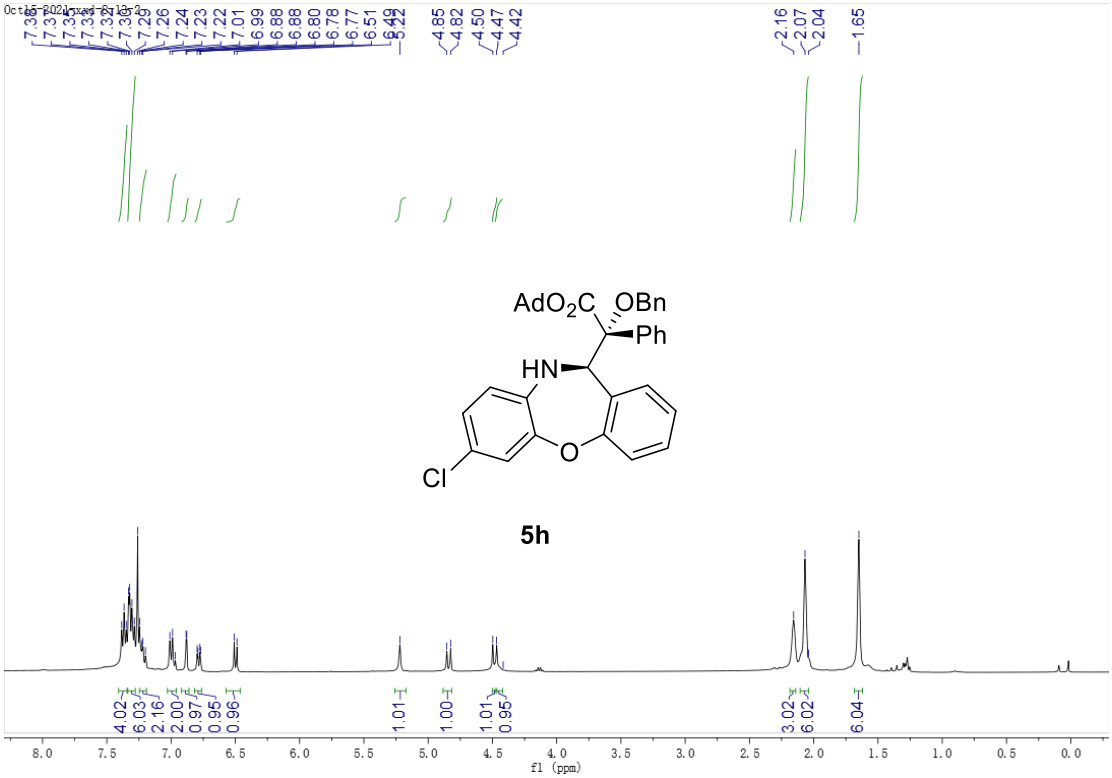
127.60
127.38
123.62
110.74
108.80
108.56
88.16
83.44
77.48
77.16
76.84
67.93
64.76
41.40
36.19
31.00
AdO2C
OBn
Ph
HN
O
F
5g
f1 (ppm)


Oct13-2021-xxd-8-14-2-rac
-124.68
AdO2C
OBn
Ph
HN
O
F
5g
f1 (ppm)


7.36
7.33
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7.30
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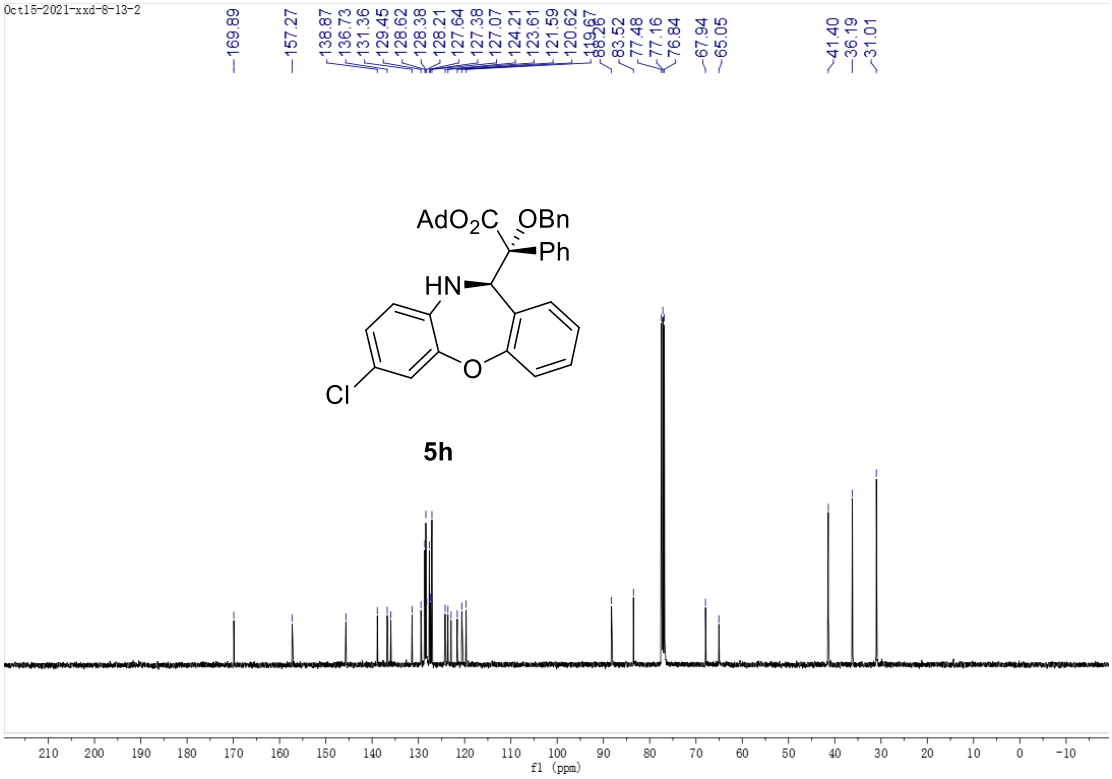
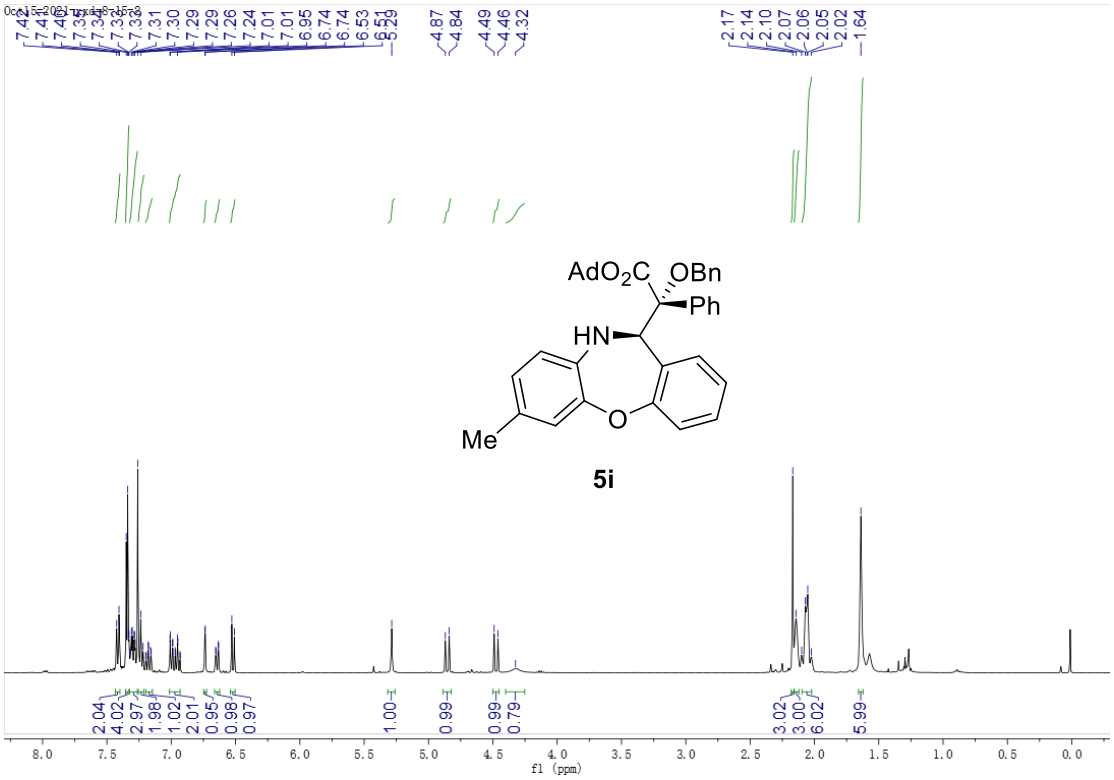
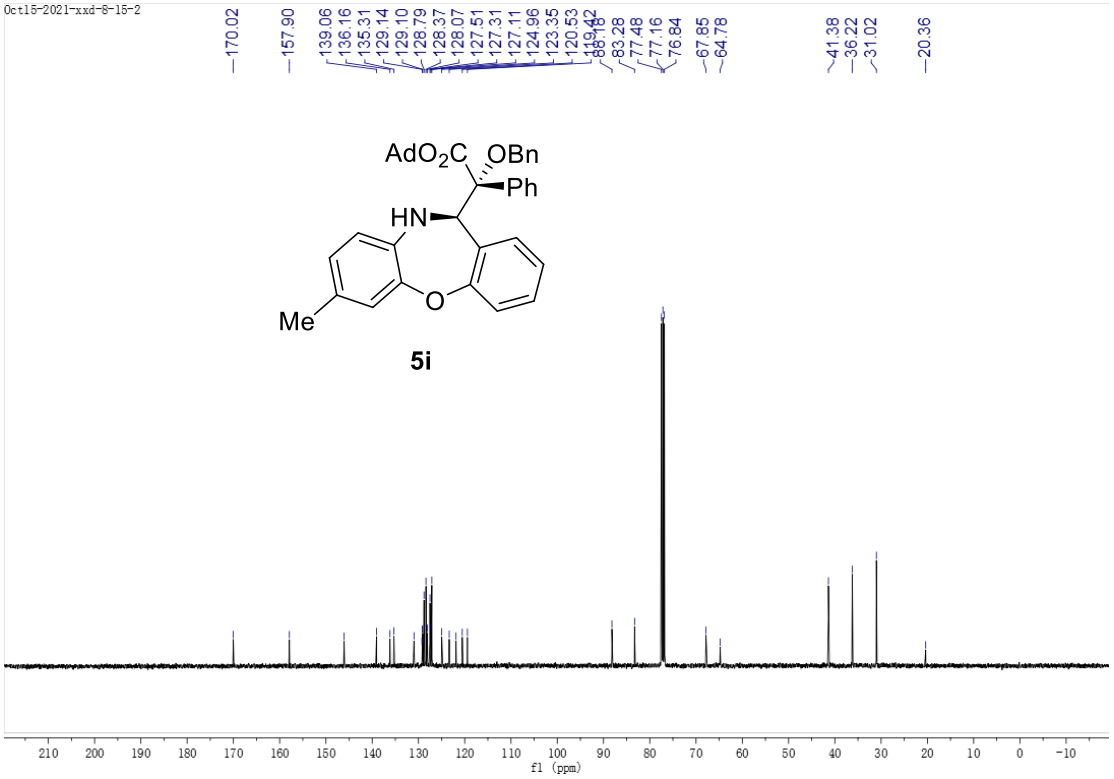
7.26
7.24
7.23
7.22
7.01
6.99
6.88
6.88
6.80
6.78
6.77
6.51
6.49
5.22
4.85
4.82
4.50
4.47
4.42
2.16
2.07
2.04
1.65
AdO2C
OBn
Ph
HN
O
Cl
4.02
6.03
2.16
2.00
0.97
0.95
0.96
1.01
1.00
1.01
0.95
3.02
6.02
6.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

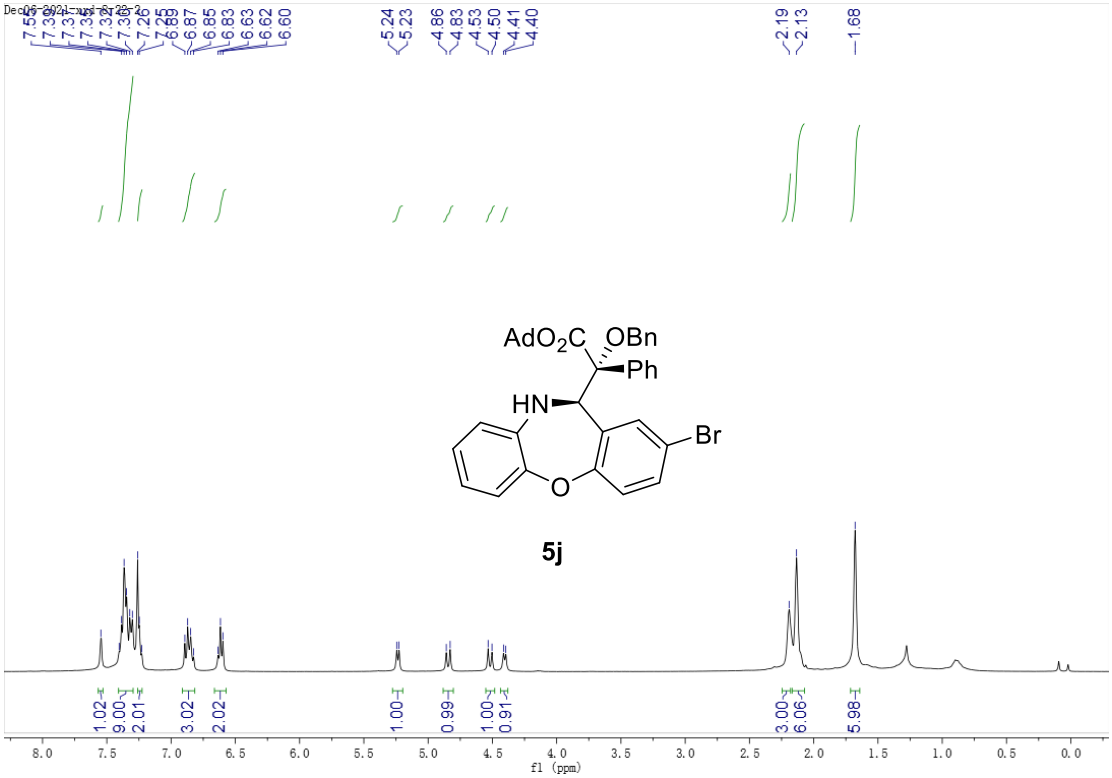
5h


Oct15-2021-xxd-8-13-2
169.89
157.27
138.87
136.73
131.36
129.45
128.62
128.38
128.21
127.64
127.38
127.07
124.21
123.61
121.59
120.62
119.67
88.26
83.52
77.48
77.16
76.84
67.94
65.05
41.40
36.19
31.01
AdO2C
OBn
Ph
HN
O
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

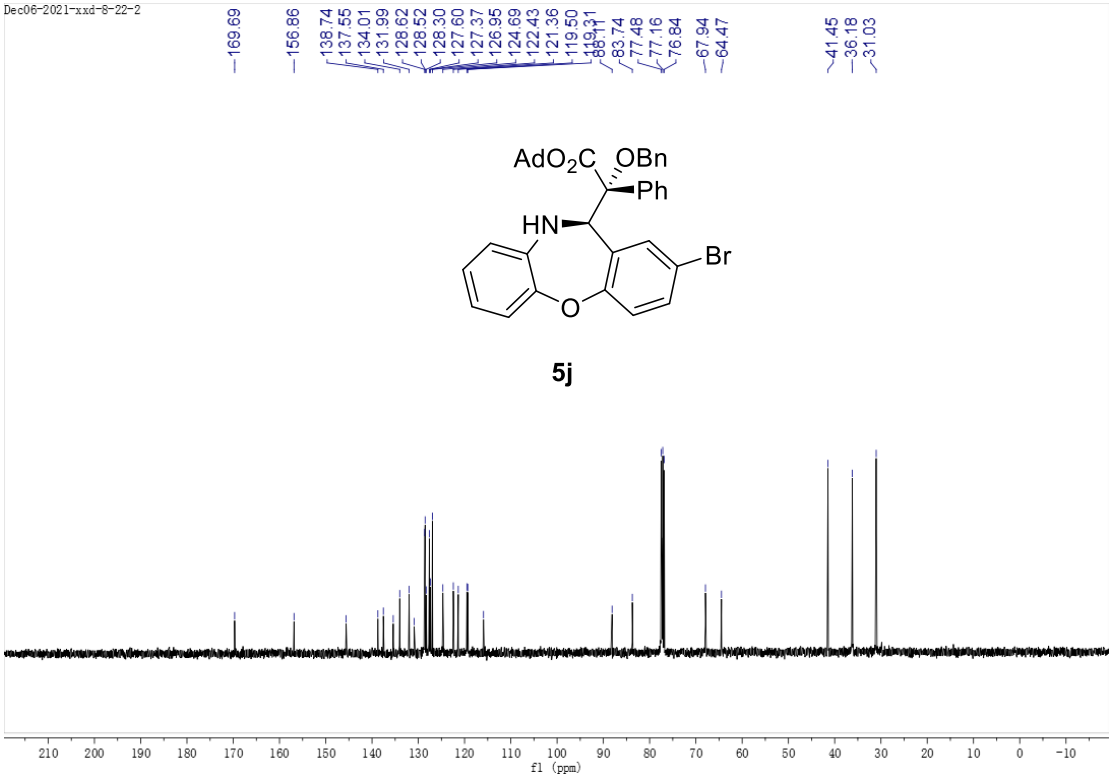
5h


7.42
7.41
7.40
7.34
7.33
7.32
7.31
7.30
7.29
7.29
7.26
7.24
7.01
7.01
6.95
6.74
6.74
6.53
6.51
5.29
4.87
4.84
4.49
4.46
4.32
2.17
2.14
2.10
2.07
2.06
2.05
2.02
1.64
AdO2C
OBn
Ph
HN
O
Me
5i
2.04
4.02
2.97
1.98
1.02
2.01
0.95
0.98
0.97
1.00
0.99
0.99
0.79
3.02
3.00
6.02
5.99
f1 (ppm)

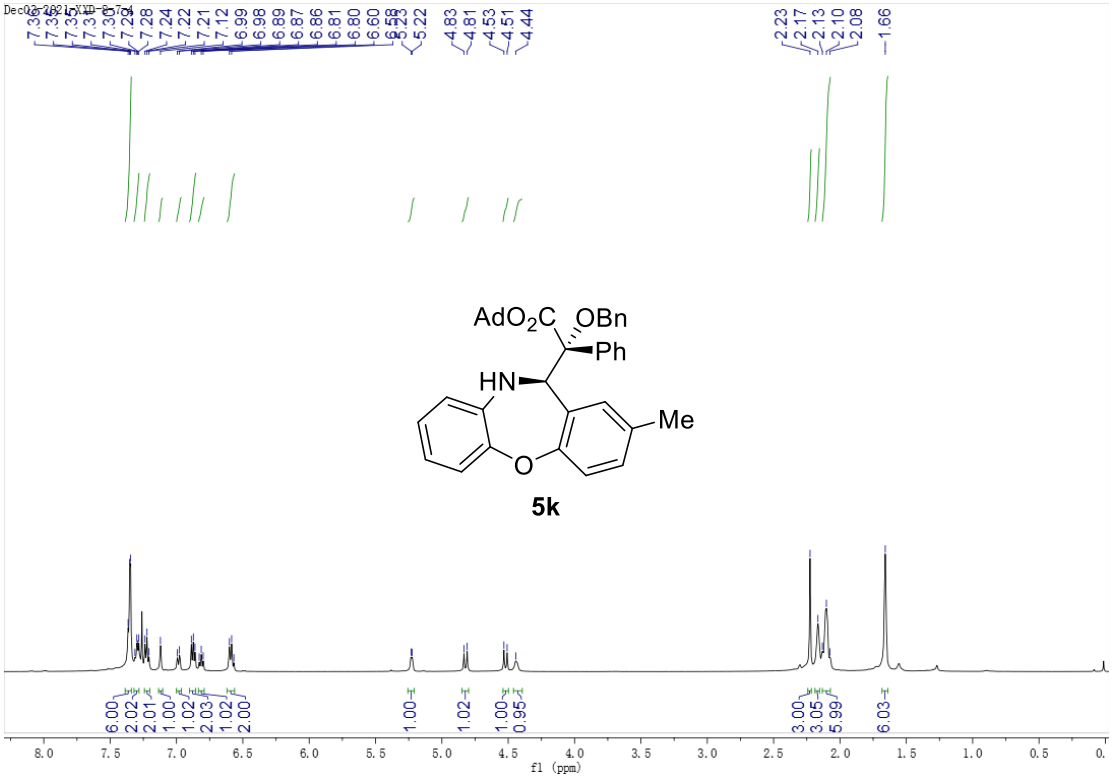

Oct15-2021-xxd-8-15-2
170.02
157.90
139.06
136.16
135.31
129.14
129.10
128.79
128.37
128.07
127.51
127.31
127.11
124.96
123.35
120.53
119.42
83.28
77.48
77.16
76.84
67.85
64.78
41.38
36.22
31.02
20.36
AdO2C
OBn
Ph
HN
O
Me
5i
f1 (ppm)

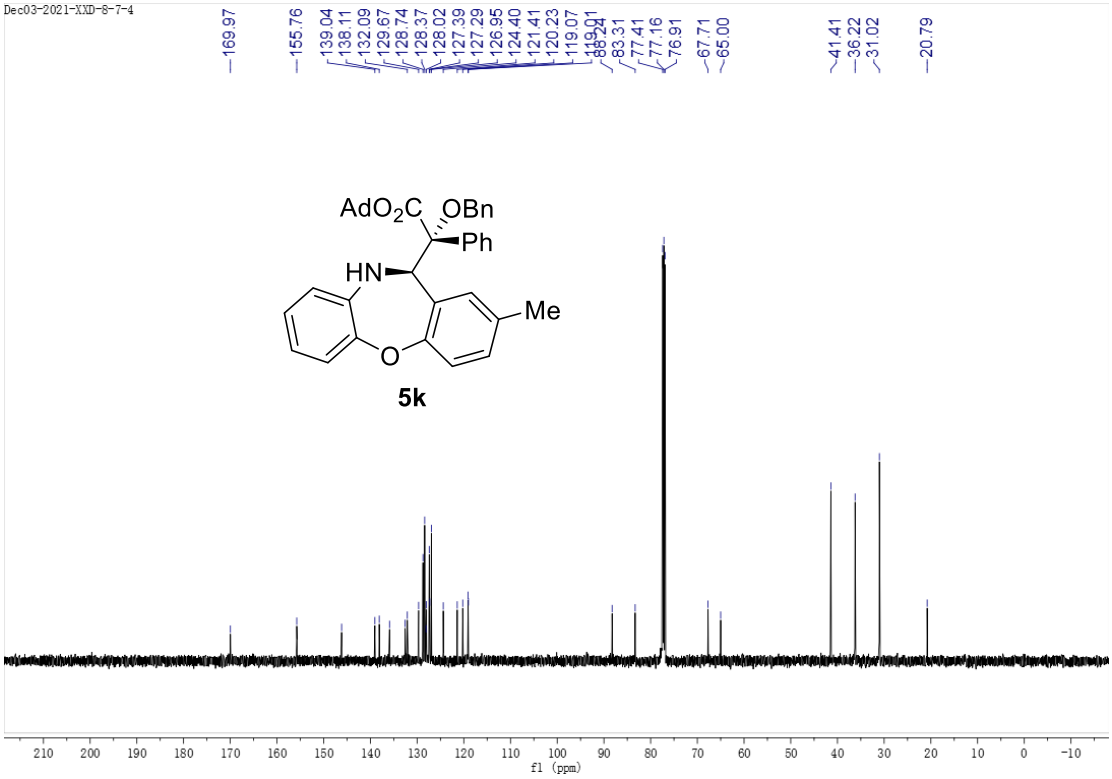

7.55
7.33
7.32
7.26
6.89
6.87
6.85
6.83
6.63
6.62
6.60
5.24
5.23
4.86
4.83
4.53
4.50
4.41
4.40
2.19
2.13
1.68
AdO2C
OBn
Ph
HN
Br
O
1.02
9.00
2.01
3.02
2.02
1.00
0.99
1.00
0.91
3.00
6.06
5.98
f1 (ppm)

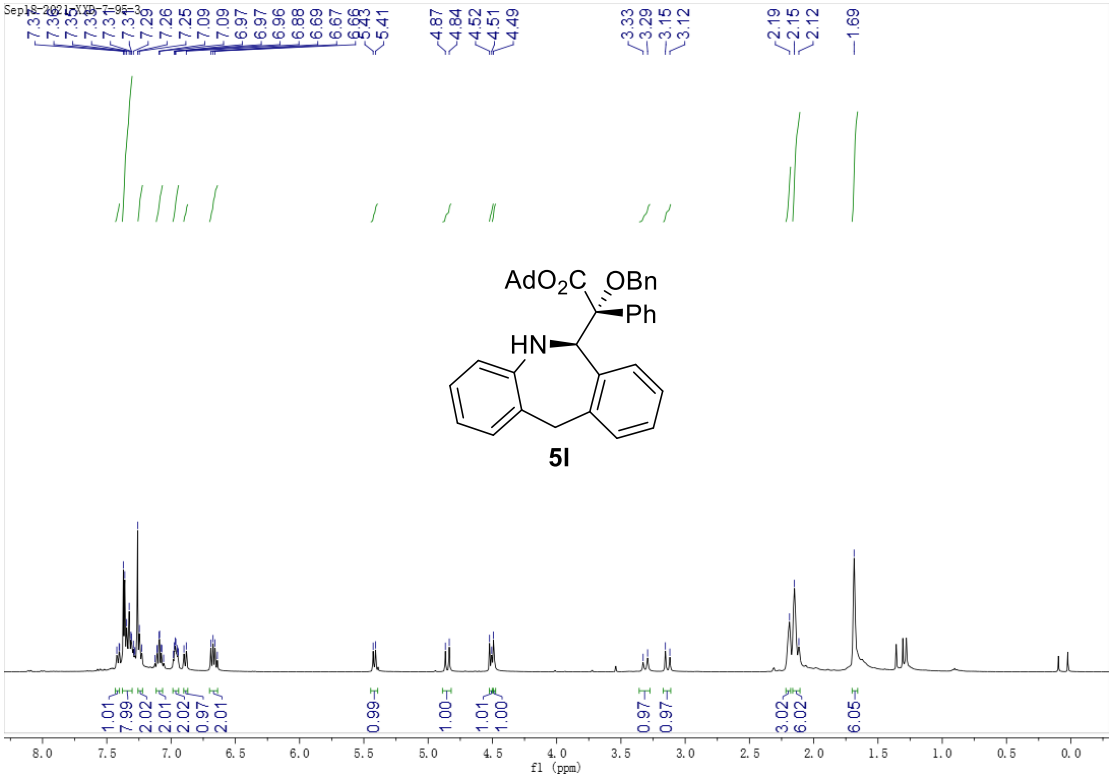
5j

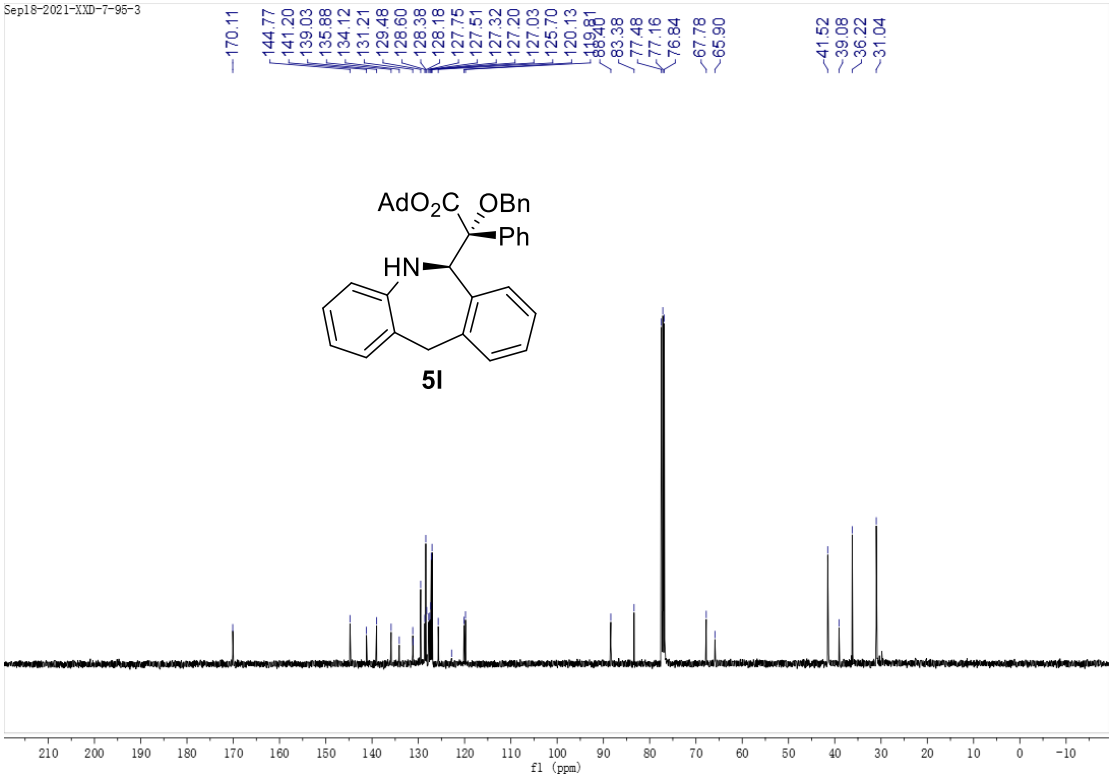

Dec06-2021-xxd-8-22-2
169.69
156.86
138.74
137.55
134.01
131.99
128.62
128.52
128.30
127.60
127.37
126.95
124.69
122.43
121.36
119.50
119.31
88.41
83.74
77.48
77.16
76.84
67.94
64.47
41.45
36.18
31.03
AdO2C
OBn
Ph
HN
Br
O
f1 (ppm)

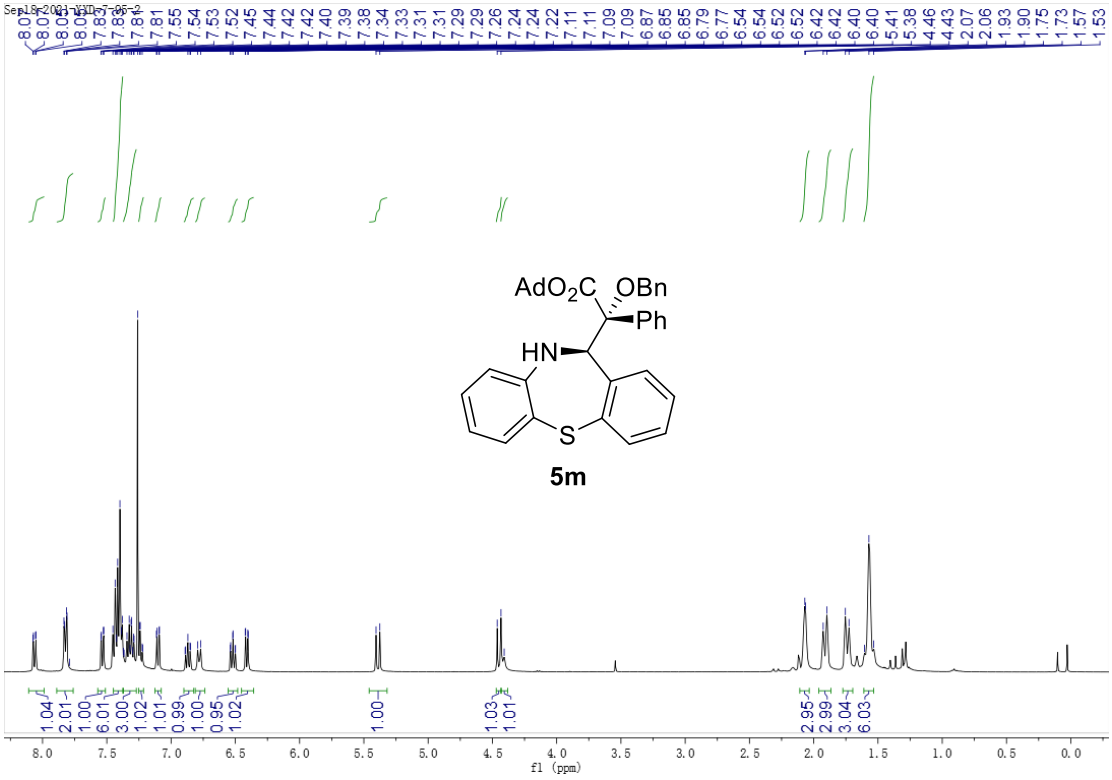
5j

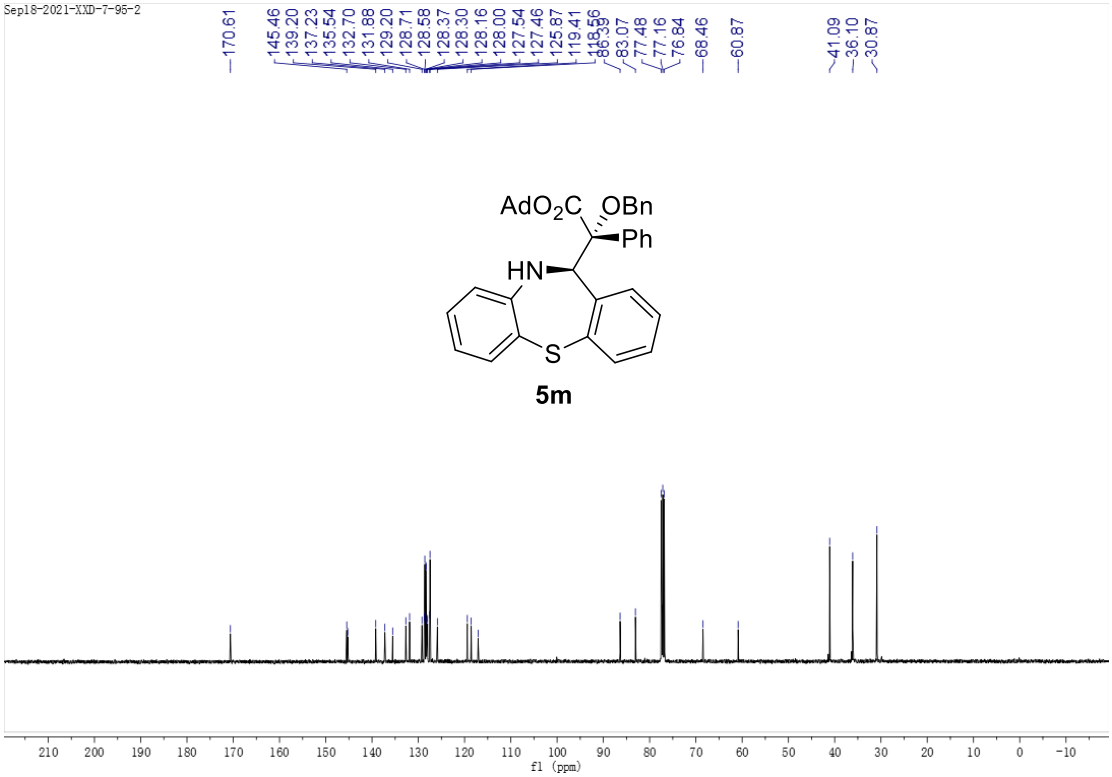

7.36
7.35
7.35
7.31
7.30
7.29
7.28
7.24
7.22
7.21
7.12
6.99
6.98
6.89
6.87
6.86
6.81
6.80
6.60
6.58
6.53
5.22
4.83
4.81
4.53
4.51
4.44
2.23
2.17
2.13
2.10
2.08
1.66
AdO2C
OBn
Ph
HN
Me
O
5k
6.00
2.02
2.01
1.00
1.02
2.03
1.02
2.00
1.00
1.02
1.00
0.95
3.00
3.05
5.99
6.03
f1 (ppm)

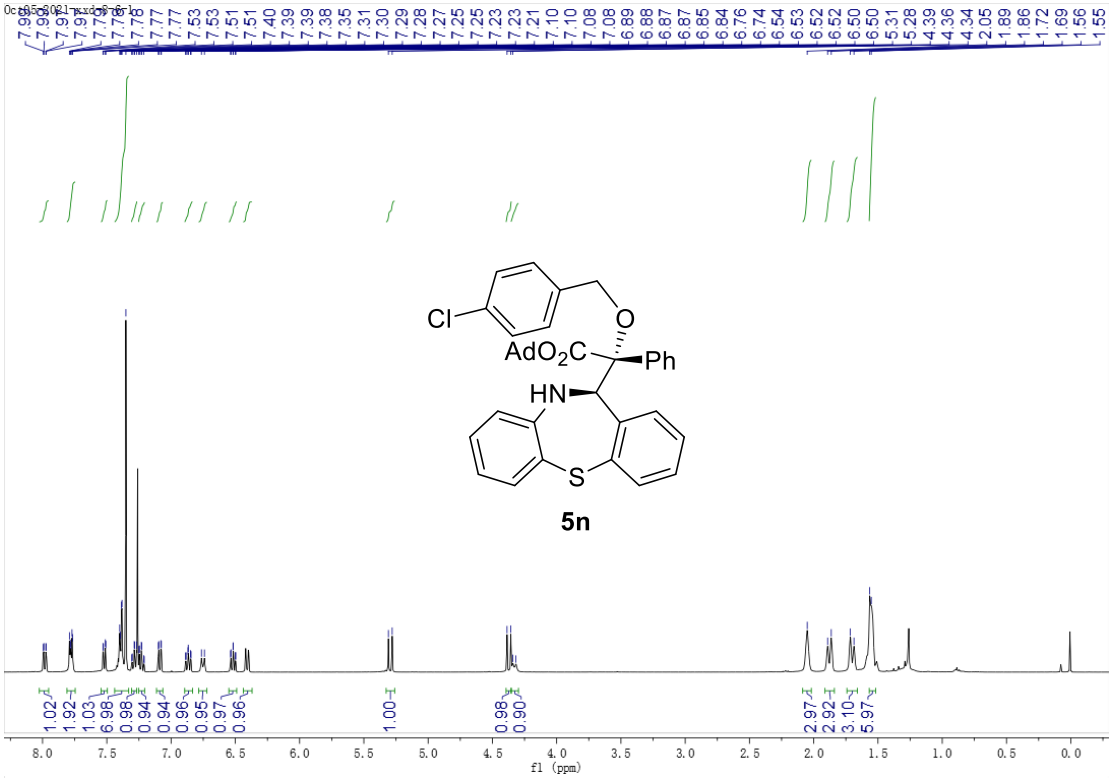

Dec03-2021-XXD-8-7-4
169.97
155.76
139.04
138.11
132.09
129.67
128.74
128.37
128.02
127.39
127.29
126.95
124.40
121.41
120.23
119.07
119.01
88.24
83.31
77.41
77.16
76.91
67.71
65.00
41.41
36.22
31.02
20.79
AdO2C
OBn
Ph
HN
Me
O
5k
f1 (ppm)

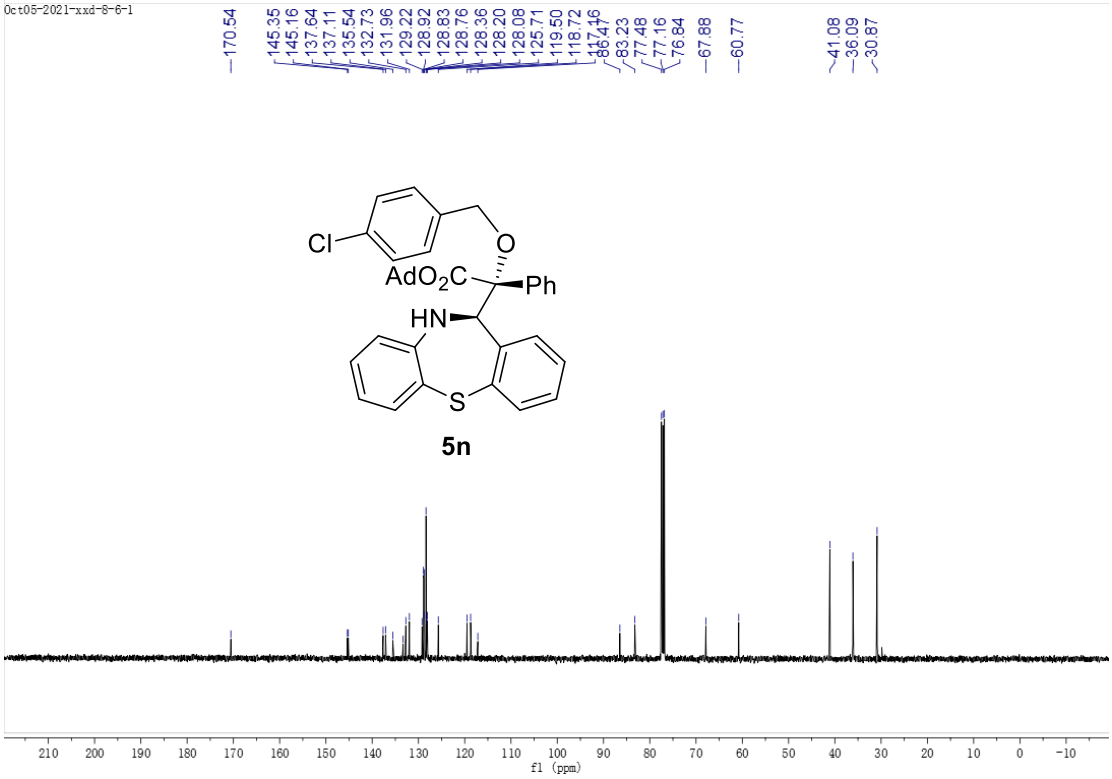

7.36
7.35
7.34
7.31
7.30
7.29
7.26
7.25
7.09
7.09
6.97
6.97
6.96
6.88
6.69
6.67
5.43
5.41
4.87
4.84
4.52
4.51
4.49
3.33
3.29
3.15
3.12
2.19
2.15
2.12
1.69
AdO2C
OBn
Ph
HN
5l
1.01
7.99
2.02
2.01
2.02
0.97
2.01
0.99
1.00
1.01
1.00
0.97
0.97
3.02
6.02
6.05
f1 (ppm)

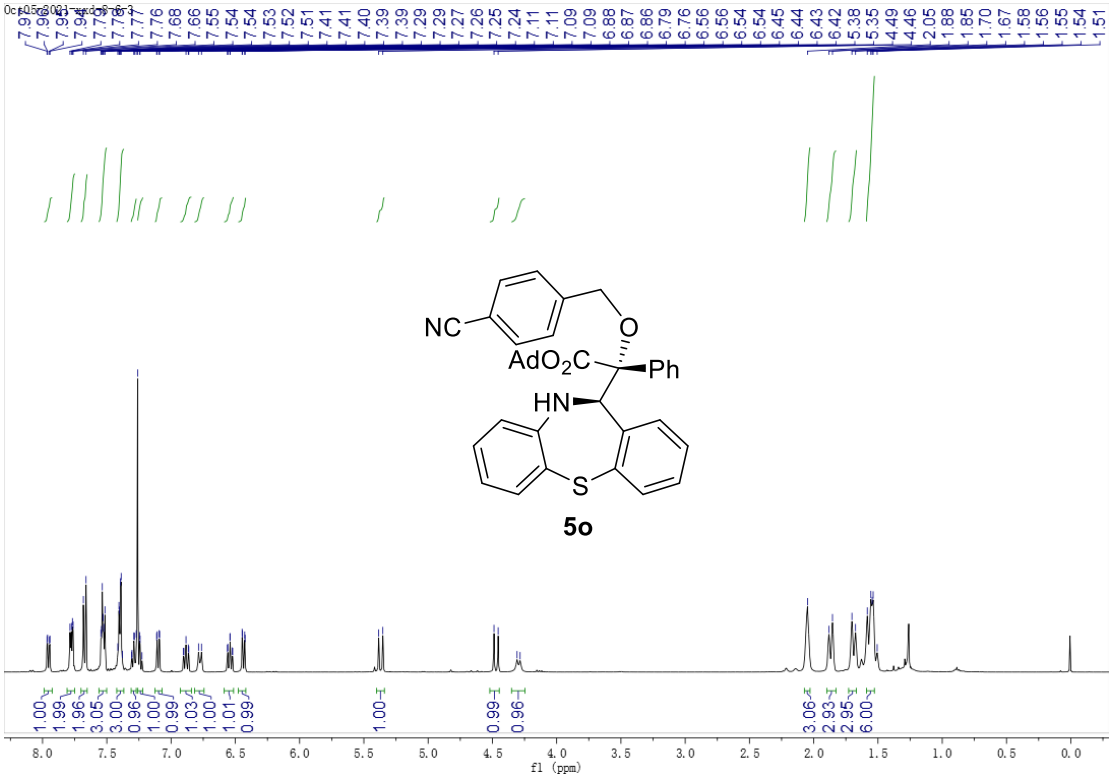

170.11
144.77
141.20
139.03
135.88
134.12
131.21
129.48
128.60
128.38
128.18
127.75
127.51
127.32
127.20
127.03
125.70
120.13
119.81
88.40
83.38
77.48
77.16
76.84
67.78
65.90
41.52
39.08
36.22
31.04
AdO2C
OBn
Ph
HN
5l
f1 (ppm)

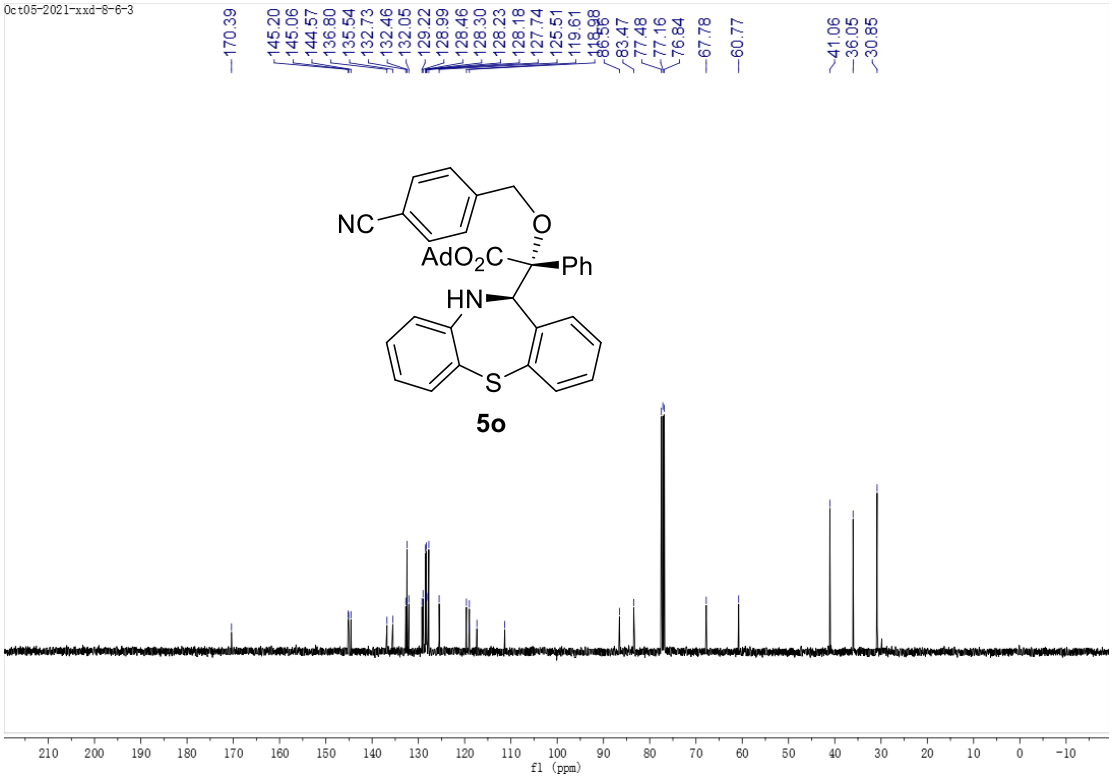

AdO2C
OBn
Ph
HN
S
5m
f1 (ppm)

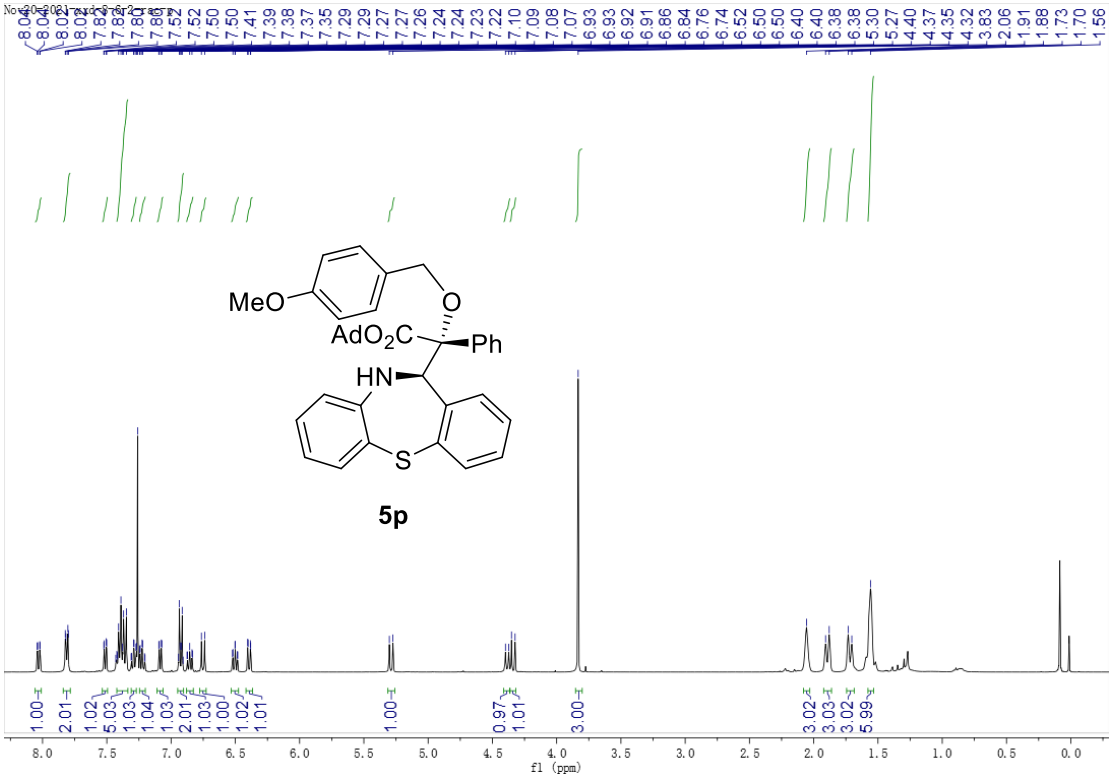

AdO2C
OBn
Ph
HN
S
5m
f1 (ppm)

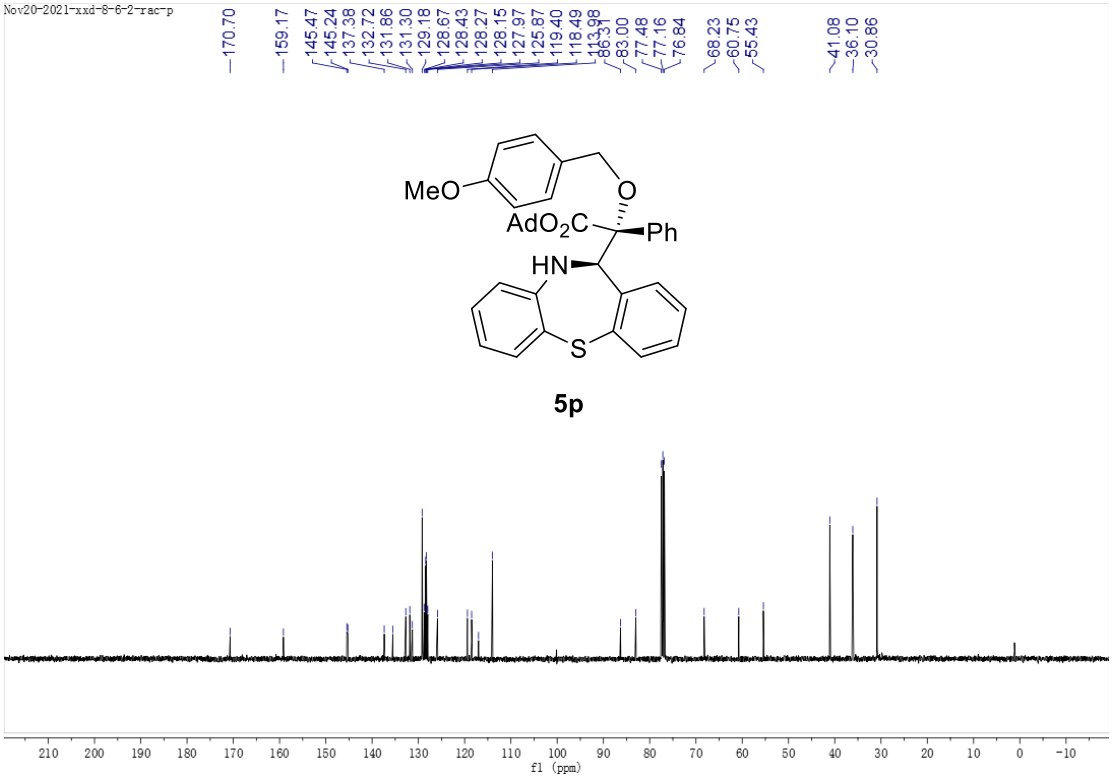

Cl
O
AdO2C
Ph
HN
S
5n
1.02
1.92
1.03
6.98
0.98
0.94
0.94
0.96
0.95
0.97
0.96
1.00
0.98
0.90
2.97
2.92
3.10
5.97
fl (ppm)

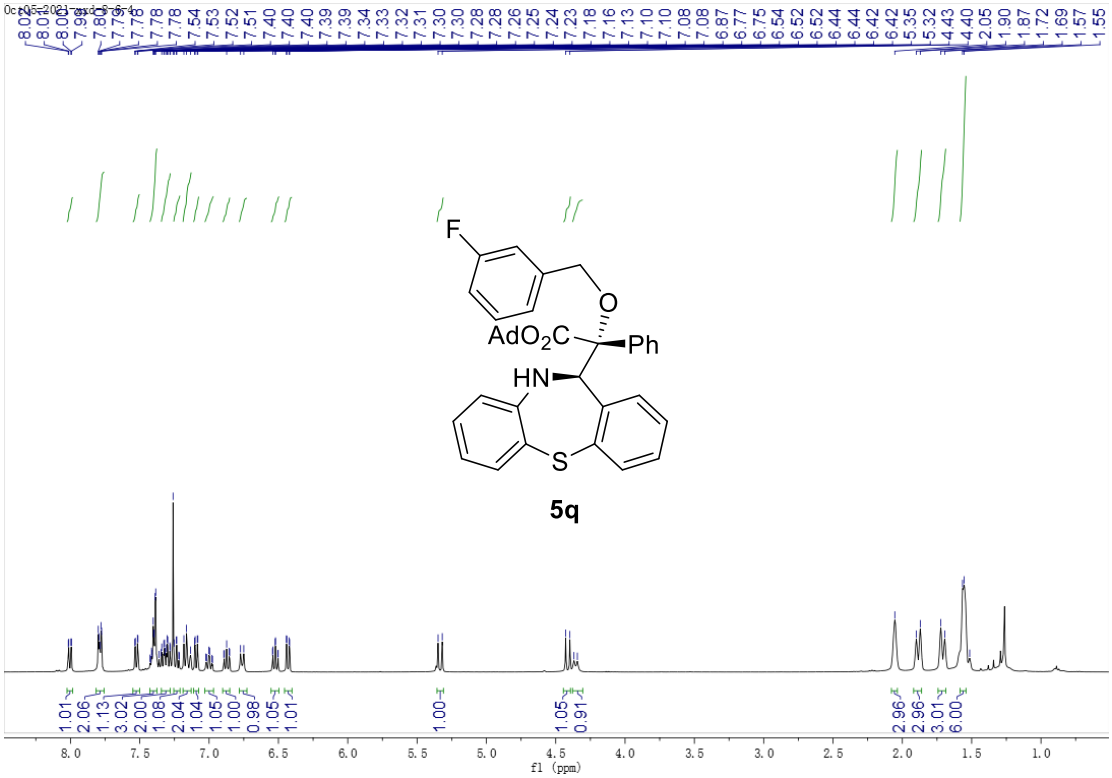

Oct05-2021-xxd-8-6-1
170.54
145.35
145.16
137.64
137.11
135.54
132.73
131.96
129.22
128.92
128.83
128.76
128.36
128.20
128.08
125.71
119.50
118.72
88.47
83.23
77.48
77.16
76.84
67.88
60.77
41.08
36.09
30.87
Cl
O
AdO2C
Ph
HN
S
5n
fl (ppm)

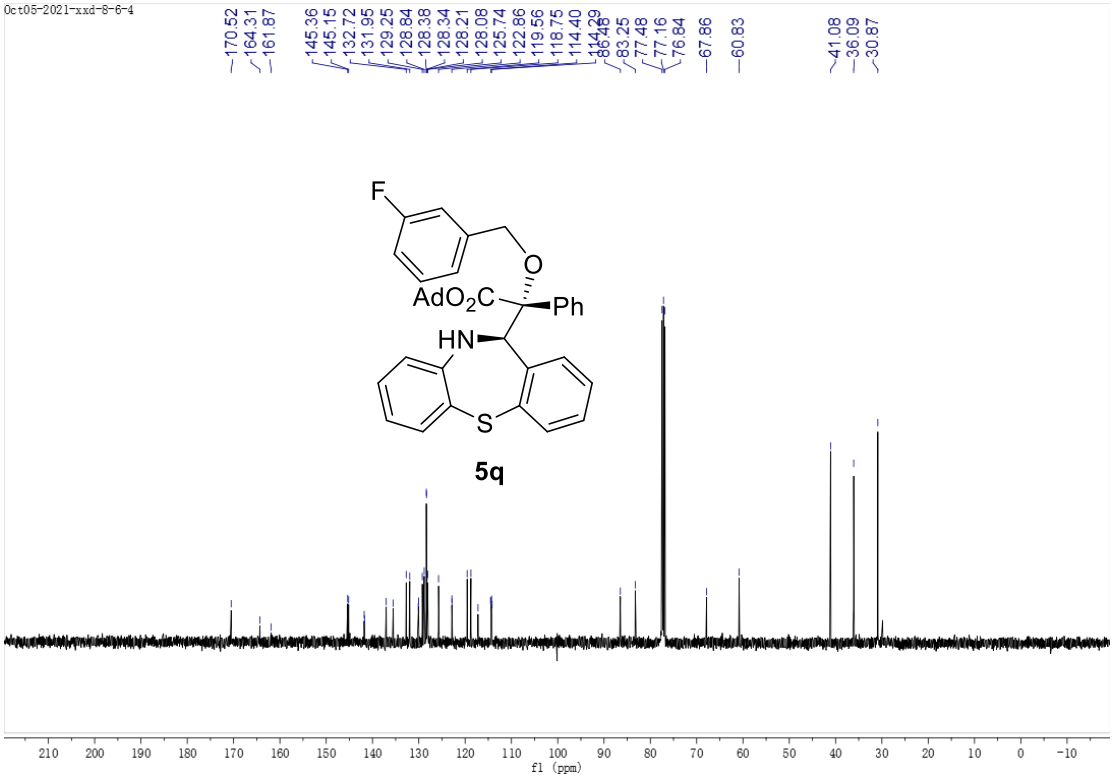

NC
O
AdO2C
Ph
HN
S
5o
fl (ppm)

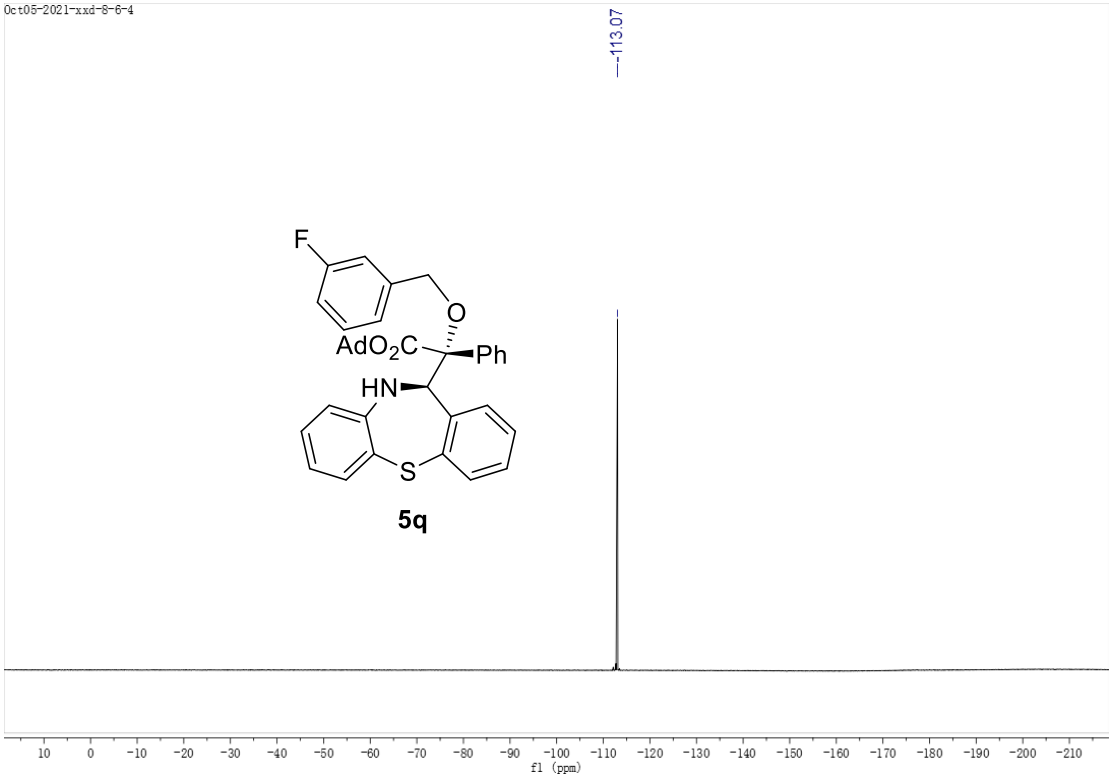

NC
O
AdO2C
Ph
HN
S
5o
fl (ppm)

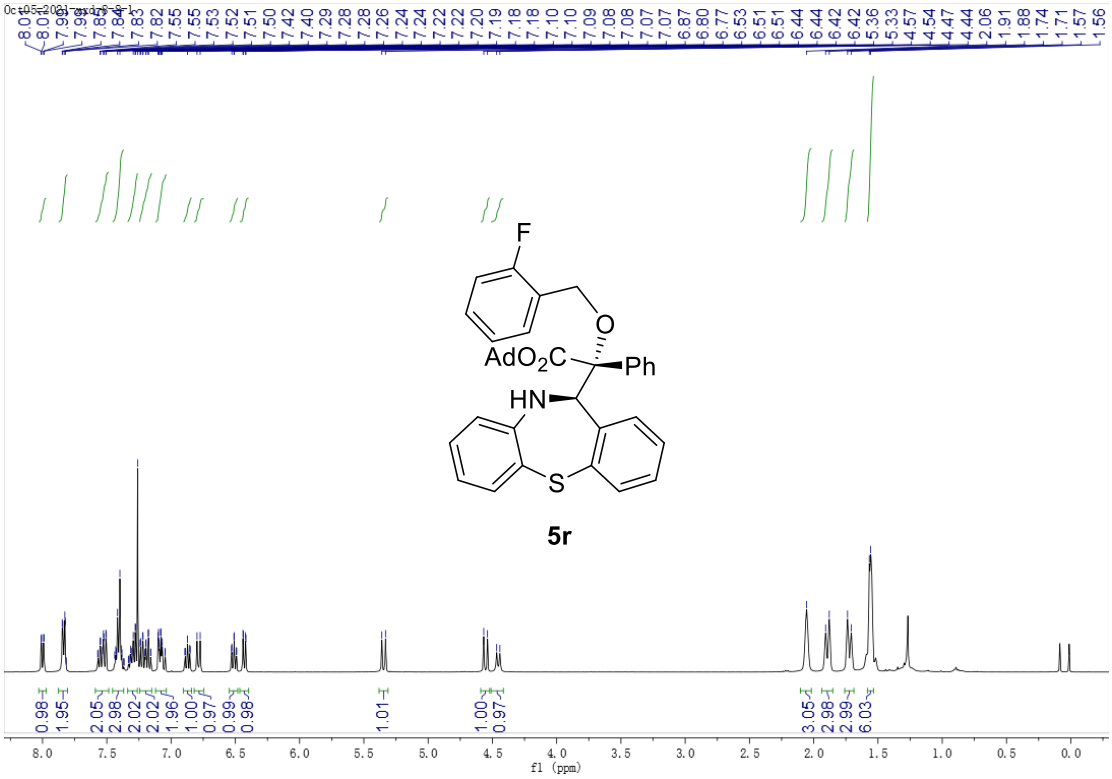

MeO
O
AdO2C
Ph
HN
S
5p

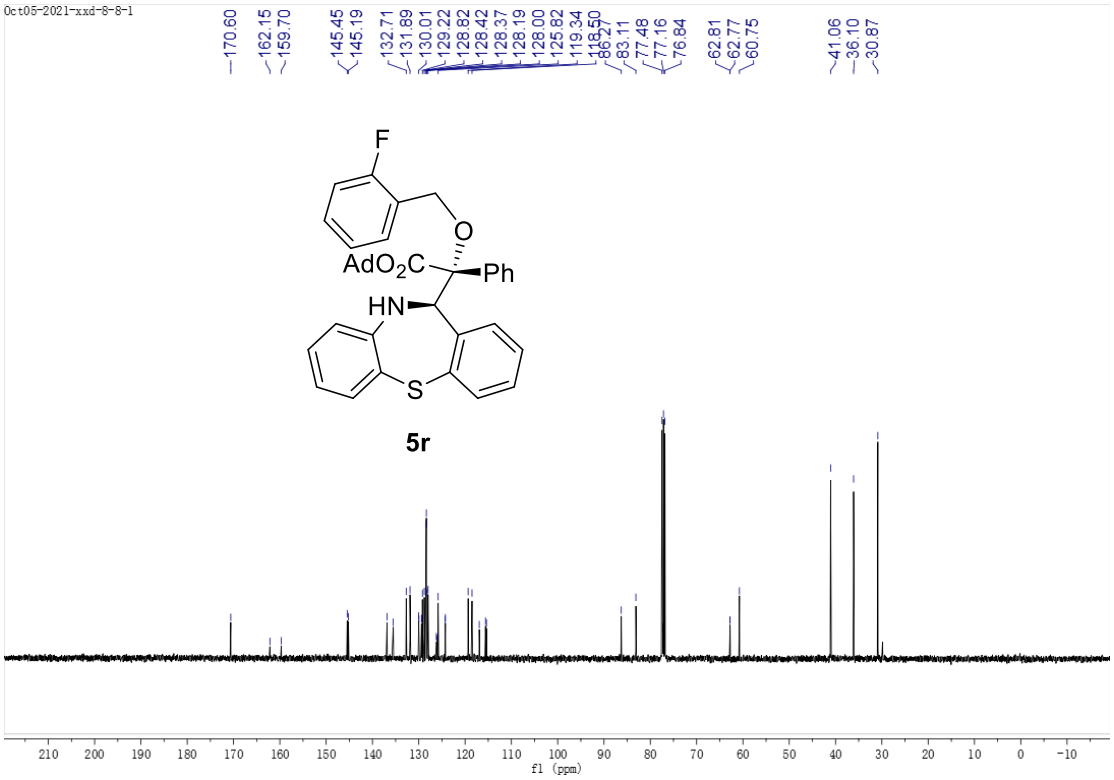

MeO
O
AdO2C
Ph
HN
S
5p

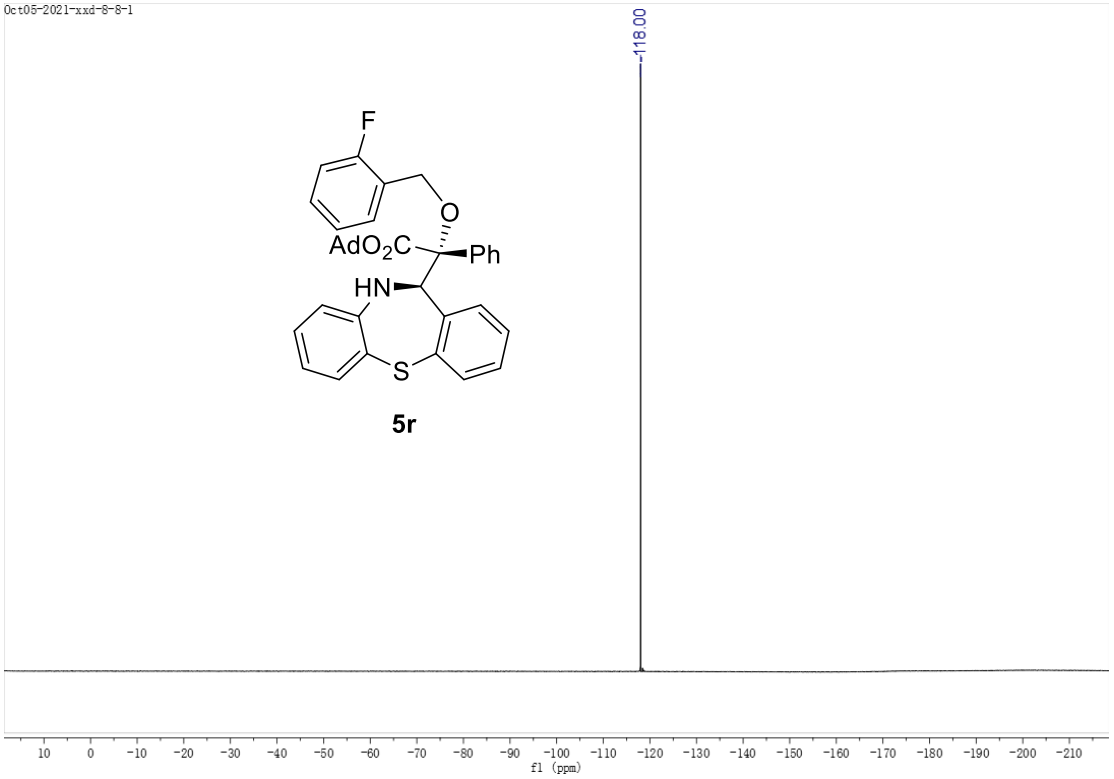

F
O
AdO2C
Ph
HN
S
5q
fl (ppm)

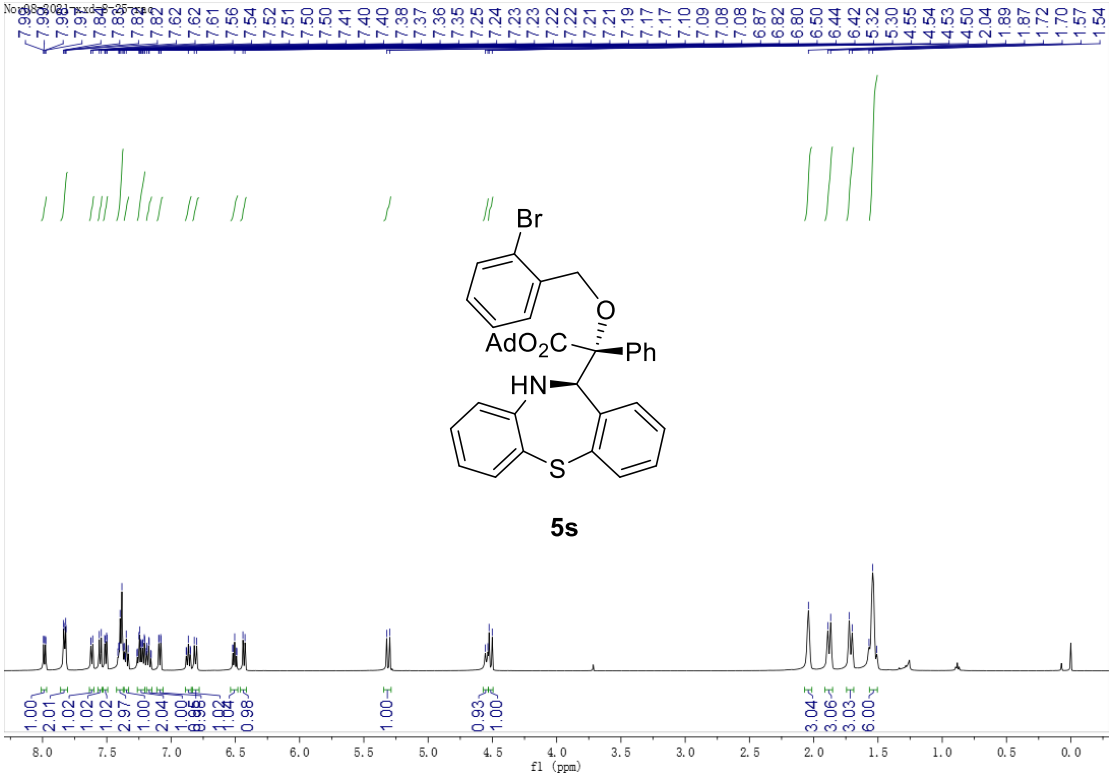

F
O
AdO2C
Ph
HN
S
5q
fl (ppm)

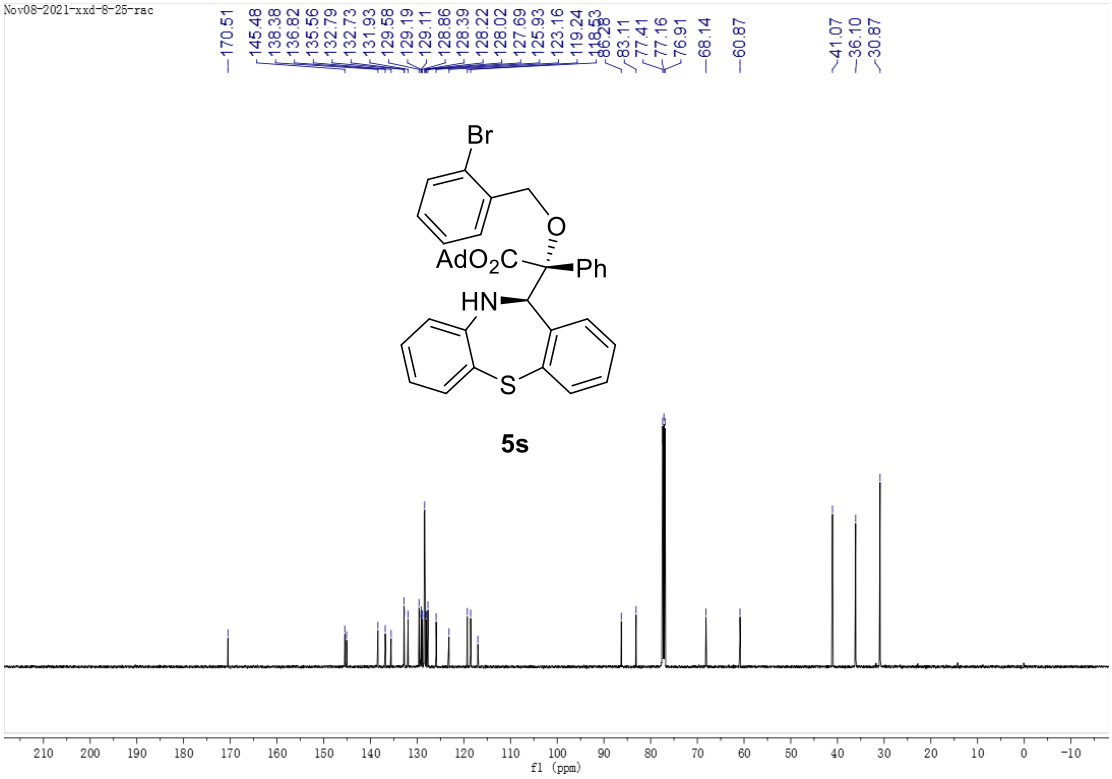

Oct05-2021-xxd-8-6-4
-113.07
F
O
AdO2C
Ph
HN
S
5q
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

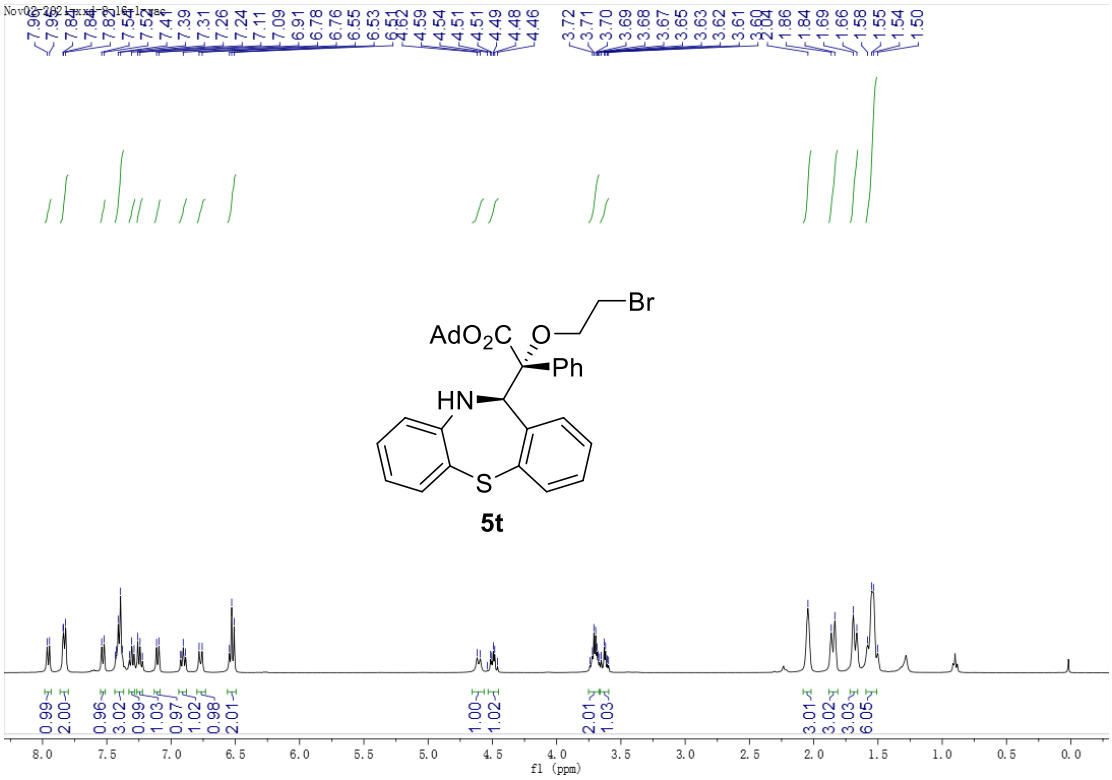

8.01
8.01
7.99
7.99
7.85
7.84
7.83
7.82
7.55
7.55
7.53
7.52
7.51
7.50
7.42
7.40
7.29
7.28
7.28
7.26
7.24
7.24
7.22
7.22
7.20
7.19
7.18
7.18
7.10
7.10
7.09
7.08
7.08
7.07
7.07
6.87
6.80
6.77
6.53
6.51
6.51
6.44
6.44
6.42
6.42
5.36
5.33
4.57
4.54
4.47
4.44
2.06
1.91
1.88
1.74
1.71
1.57
1.56
F
O
AdO2C
Ph
HN
S
5r
0.98
1.95
2.05
2.98
2.02
2.02
1.96
1.00
0.97
0.99
0.98
1.01
1.00
0.97
3.05
2.98
2.99
6.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

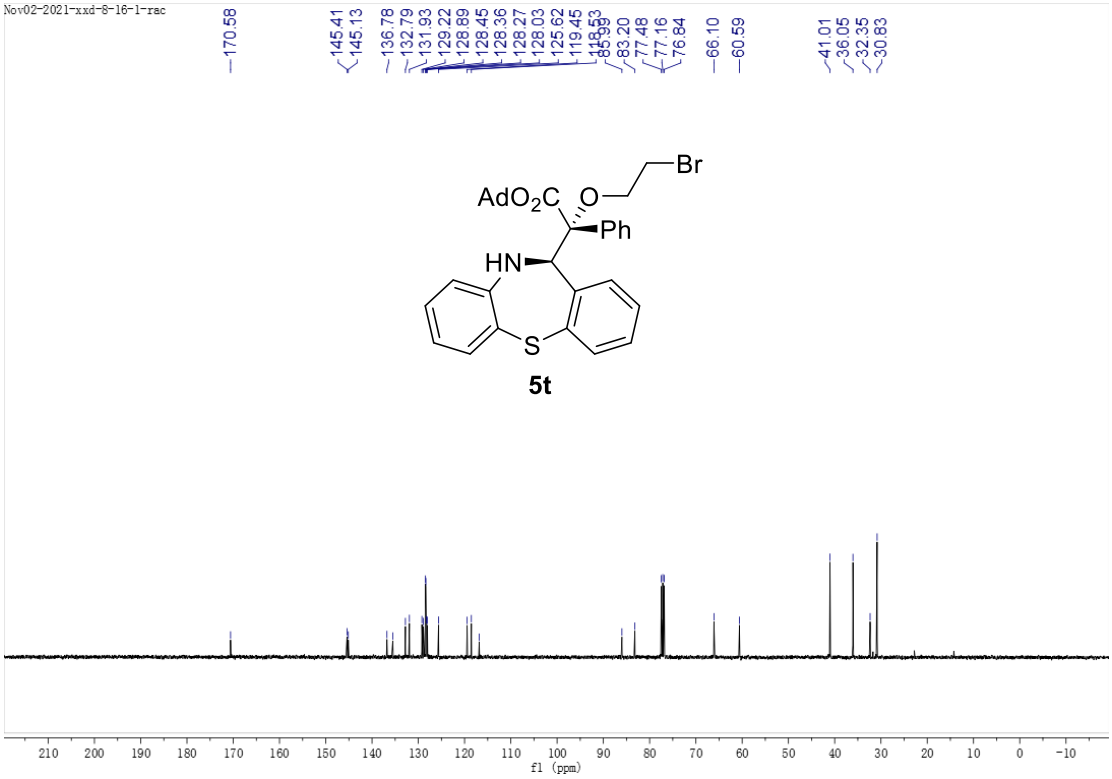

Oct05-2021-xxd-8-8-1
170.60
162.15
159.70
145.45
145.19
132.71
131.89
130.01
129.22
128.82
128.42
128.37
128.19
128.00
125.82
119.34
118.50
86.27
83.11
77.48
77.16
76.84
62.81
62.77
60.75
41.06
36.10
30.87
F
O
AdO2C
Ph
HN
S
5r
f1 (ppm)

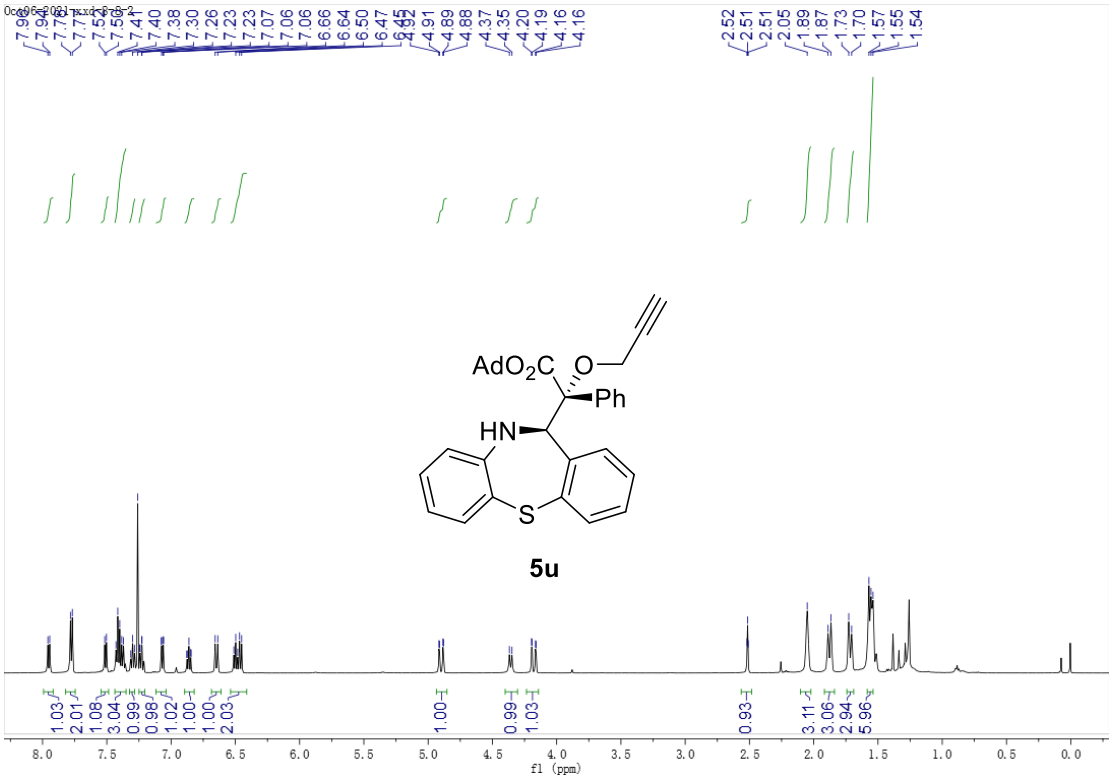

Oct05-2021-xxd-8-8-1
-118.00
F
O
AdO2C
Ph
HN
S
5r
f1 (ppm)

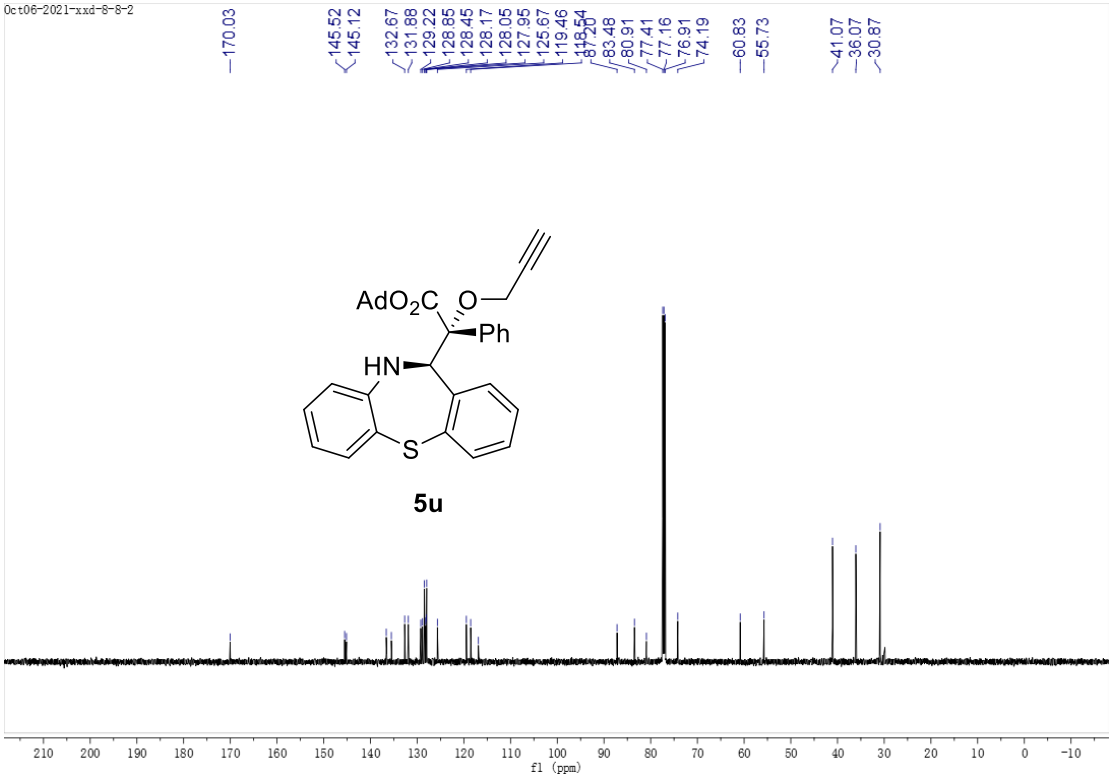

Br
O
AdO2C
Ph
HN
S
5s
fl (ppm)

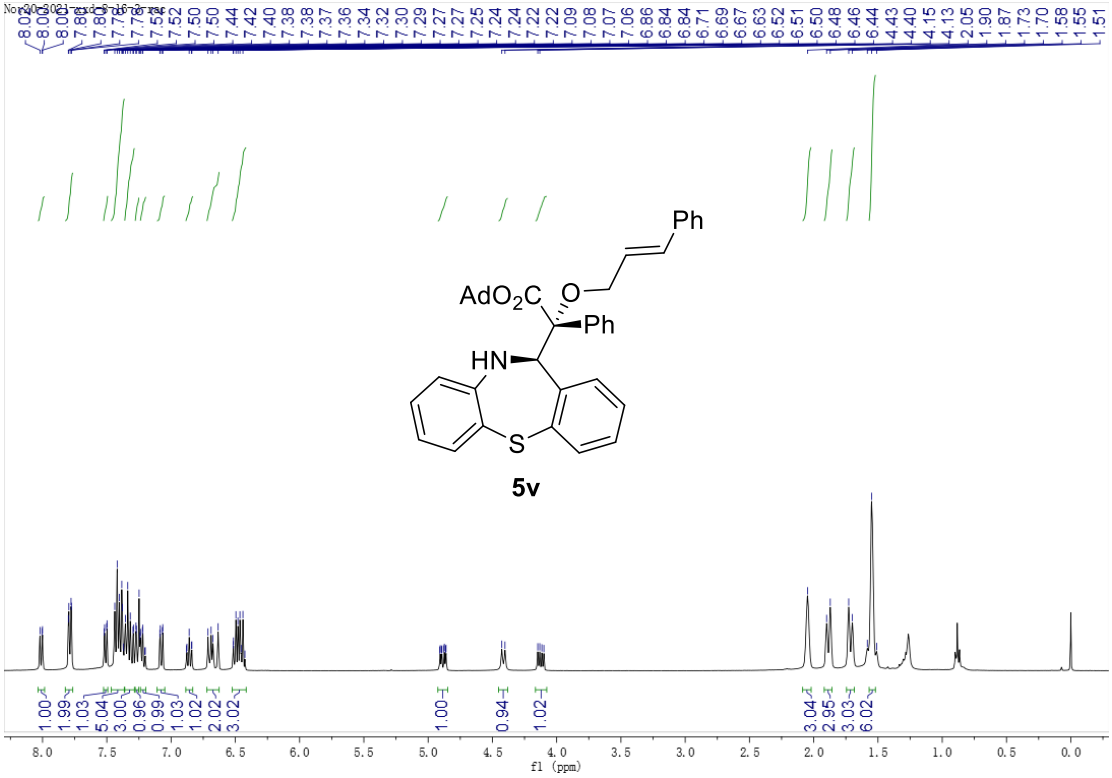

Br
O
AdO2C
Ph
HN
S
5s
fl (ppm)

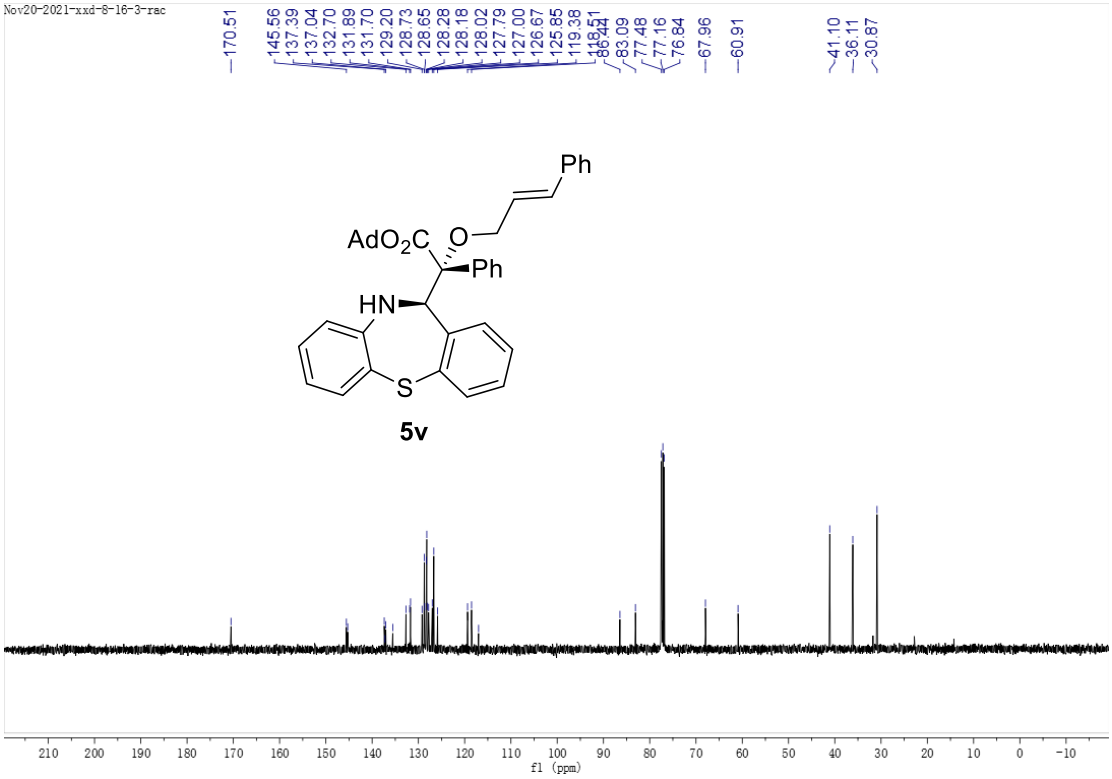

Br
AdO2C
O
Ph
HN
S
5t
fl (ppm)

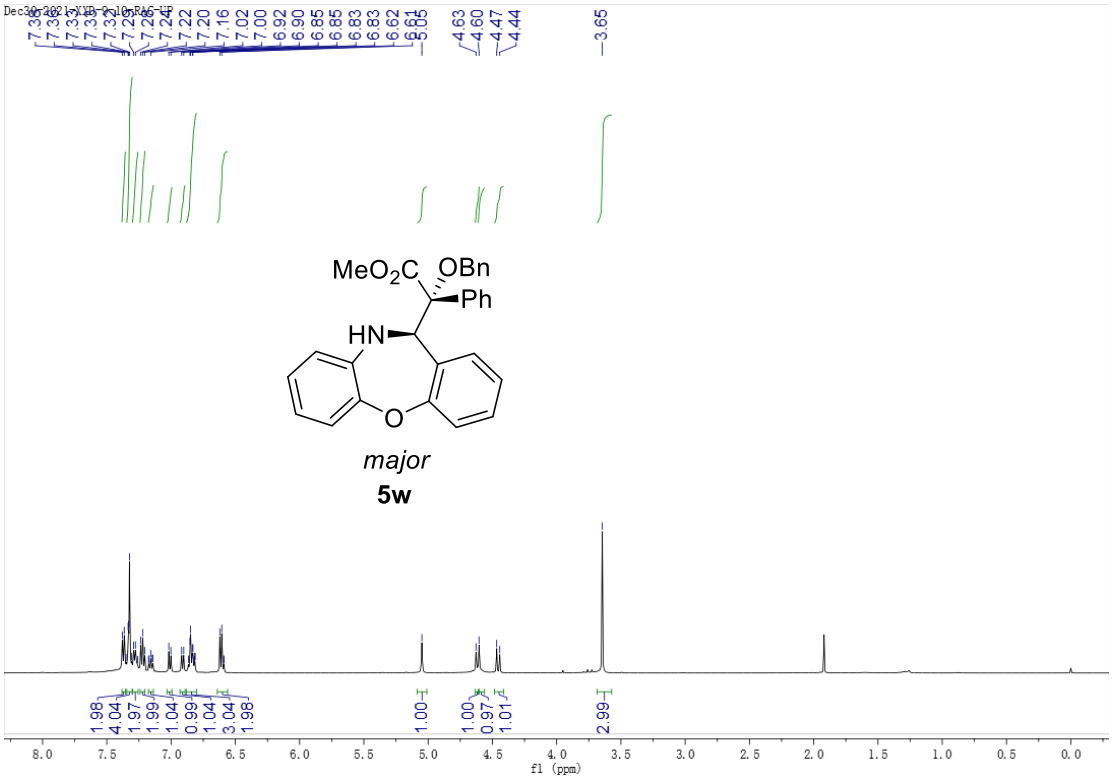

Br
AdO2C
O
Ph
HN
S
5t
fl (ppm)

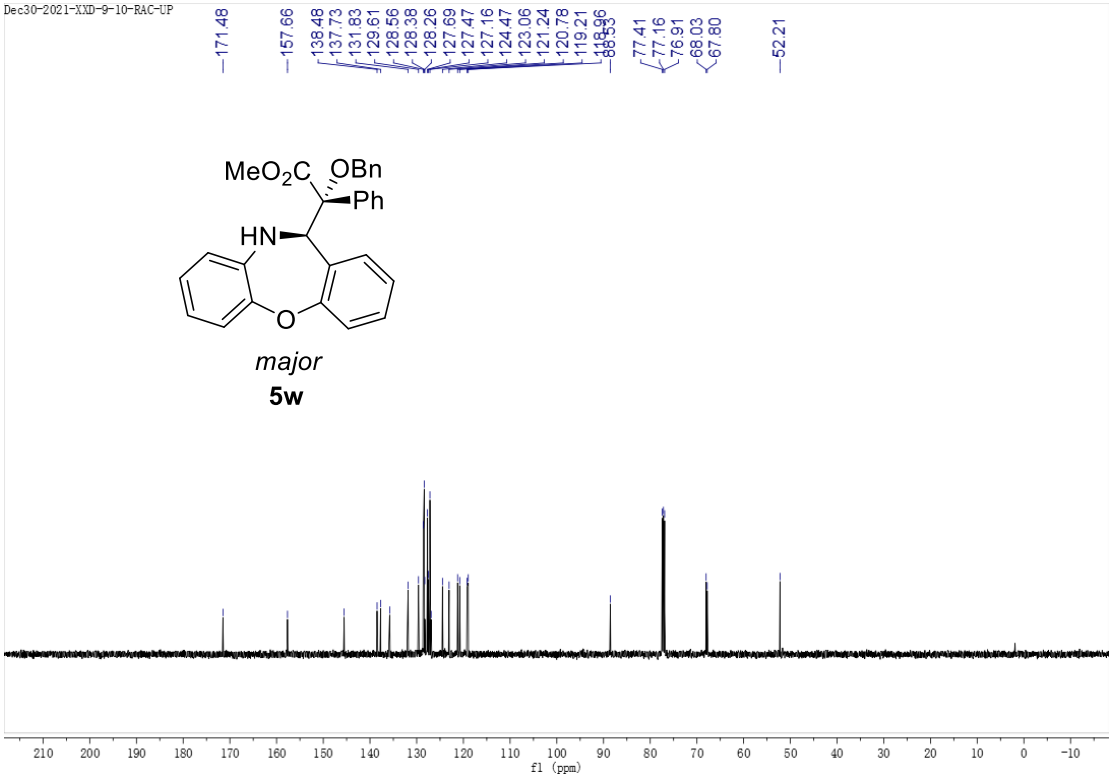

7.99
7.94
7.77
7.75
7.56
7.41
7.40
7.38
7.30
7.26
7.23
7.07
7.06
7.06
6.66
6.64
6.50
6.47
4.92
4.91
4.89
4.88
4.37
4.35
4.20
4.19
4.16
4.16
2.52
2.51
2.51
2.05
1.89
1.87
1.73
1.70
1.57
1.55
1.54
AdO2C
O
Ph
HN
S
5u
1.03
2.01
1.08
3.04
0.99
0.98
1.02
1.00
1.00
2.03
1.00
0.99
1.03
0.93
3.11
3.06
2.94
5.96
f1 (ppm)


Oct06-2021-xxd-8-8-2
170.03
145.52
145.12
132.67
131.88
129.22
128.85
128.45
128.17
128.05
127.95
125.67
119.46
118.54
87.20
83.48
80.91
77.41
77.16
76.91
74.19
60.83
55.73
41.07
36.07
30.87
AdO2C
O
Ph
HN
S
5u
f1 (ppm)


Ph
AdO2C
O
Ph
HN
S
5v
fl (ppm)


Ph
AdO2C
O
Ph
HN
S
5v
fl (ppm)


7.38
7.36
7.34
7.33
7.32
7.29
7.26
7.24
7.22
7.20
7.16
7.02
7.00
6.92
6.90
6.85
6.85
6.83
6.83
6.62
6.61
5.05
4.63
4.60
4.47
4.44
3.65
MeO2C
OBn
Ph
HN
O
major
5w
1.98
4.04
1.97
1.99
1.04
0.99
1.04
3.04
1.98
1.00
1.00
0.97
1.01
2.99
fl (ppm)


171.48
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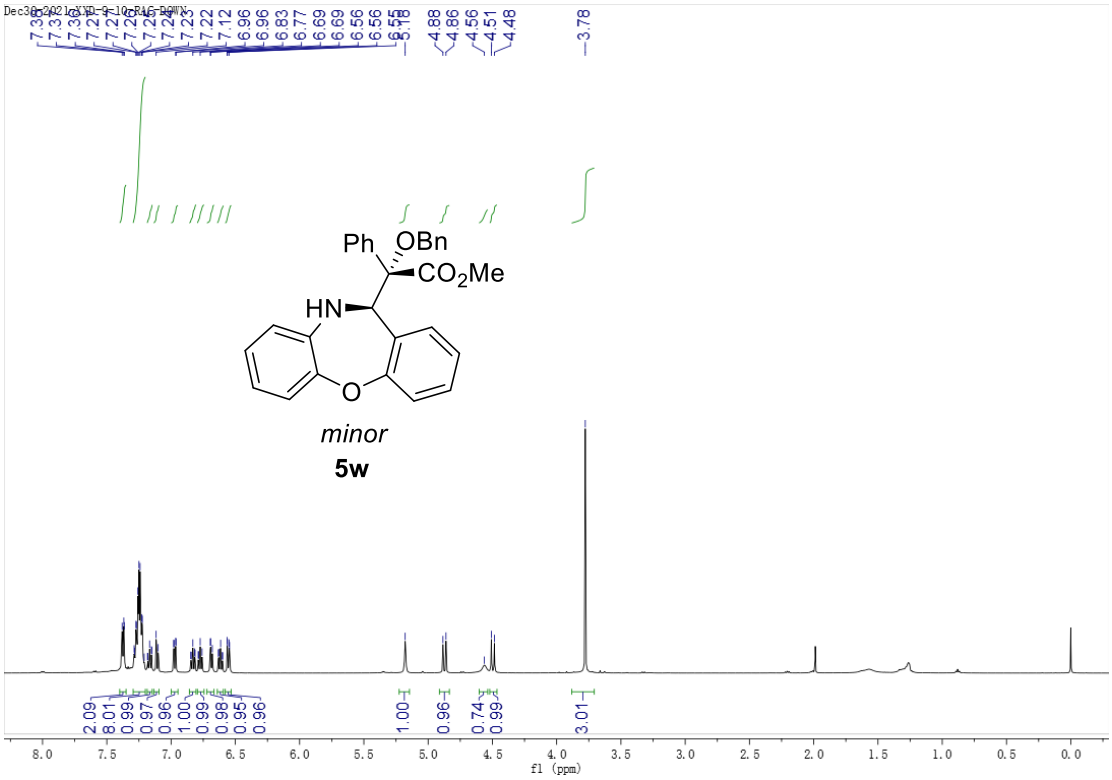
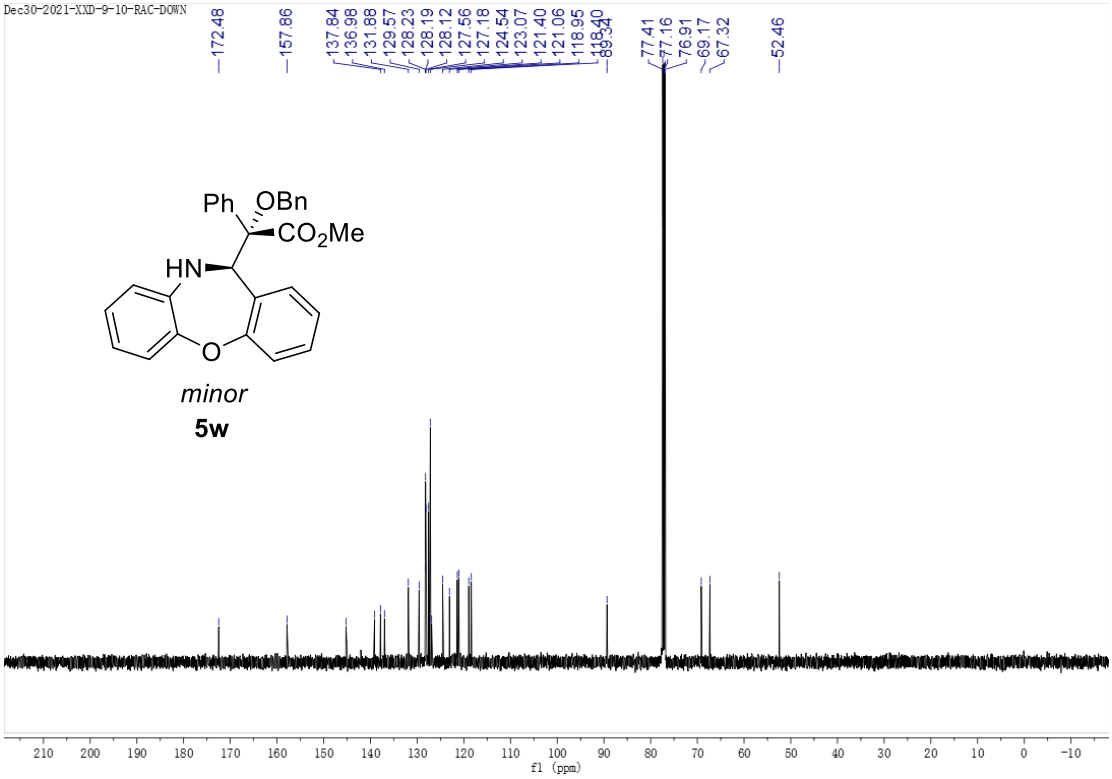
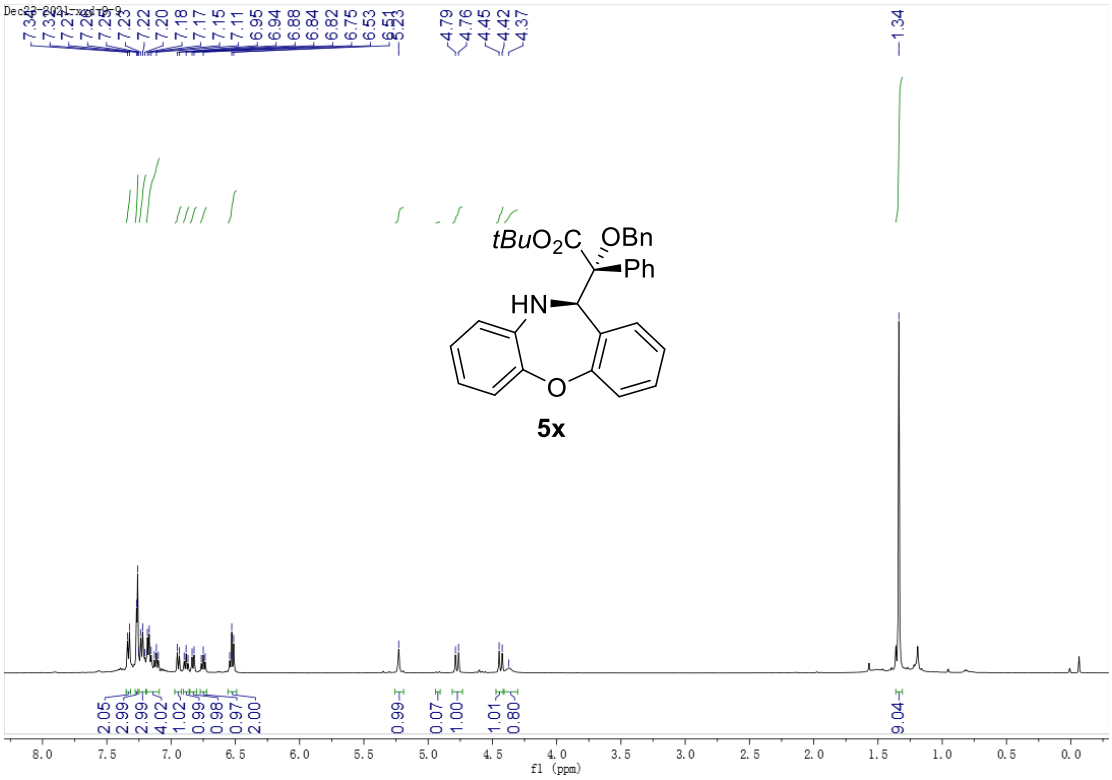
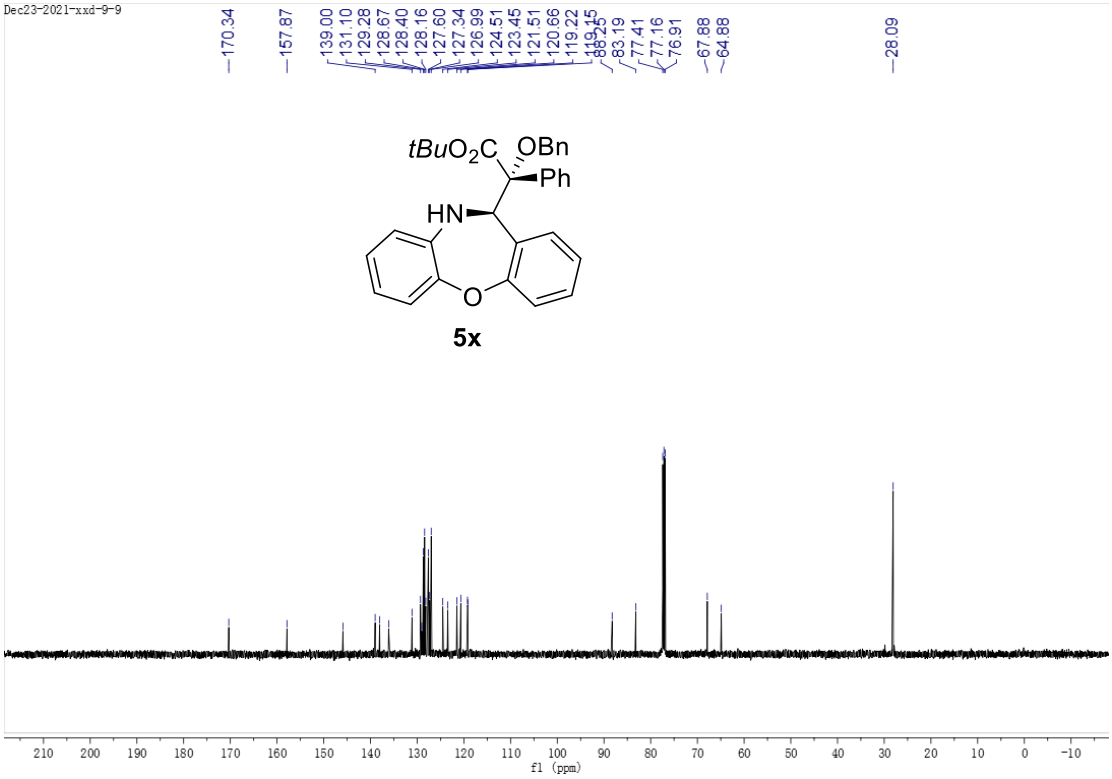
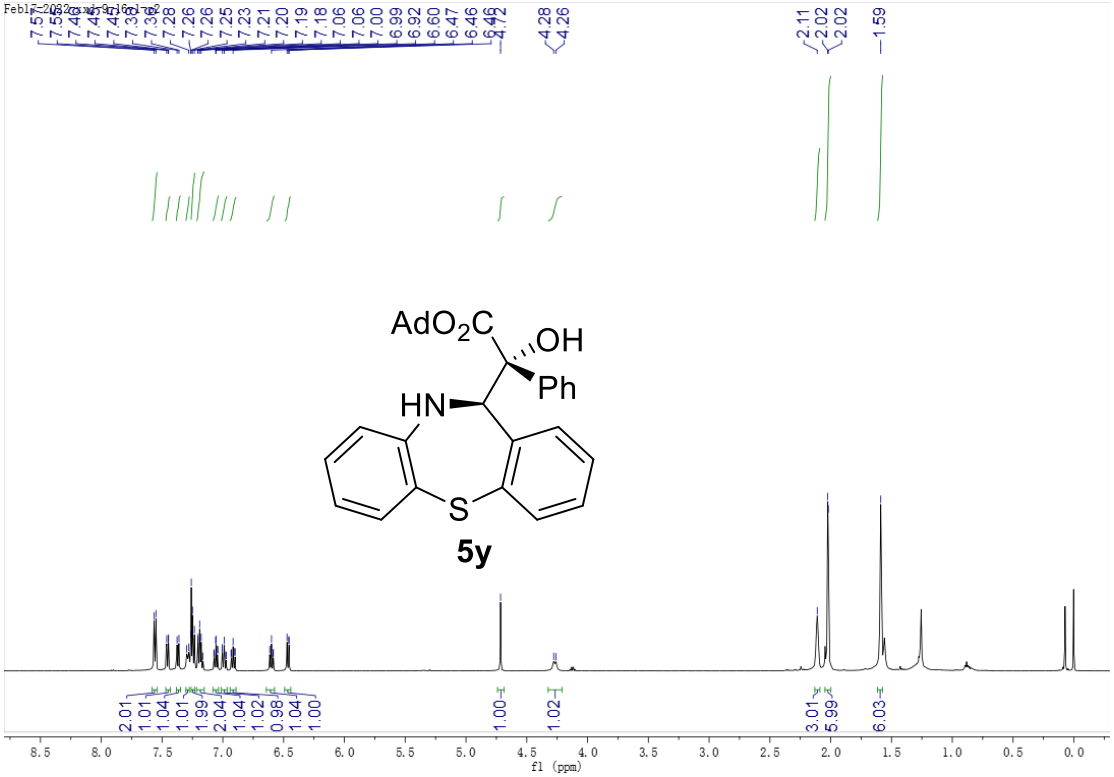
129.61
128.56
128.38
128.26
127.69
127.47
127.16
124.47
123.06
121.24
120.78
119.21
88.53
77.41
77.16
76.91
68.03
67.80
52.21
MeO2C
OBn
Ph
HN
O
major
5w
fl (ppm)

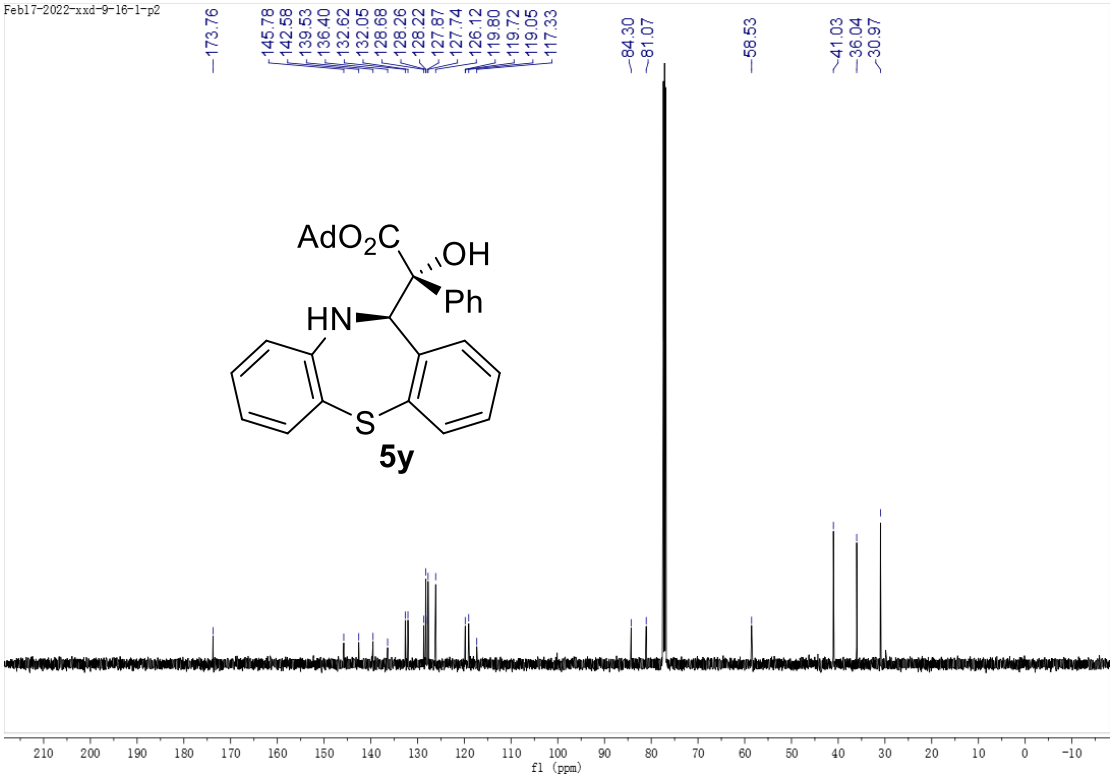

Ph
OBn
CO2Me
HN
O
minor
5w
f1 (ppm)

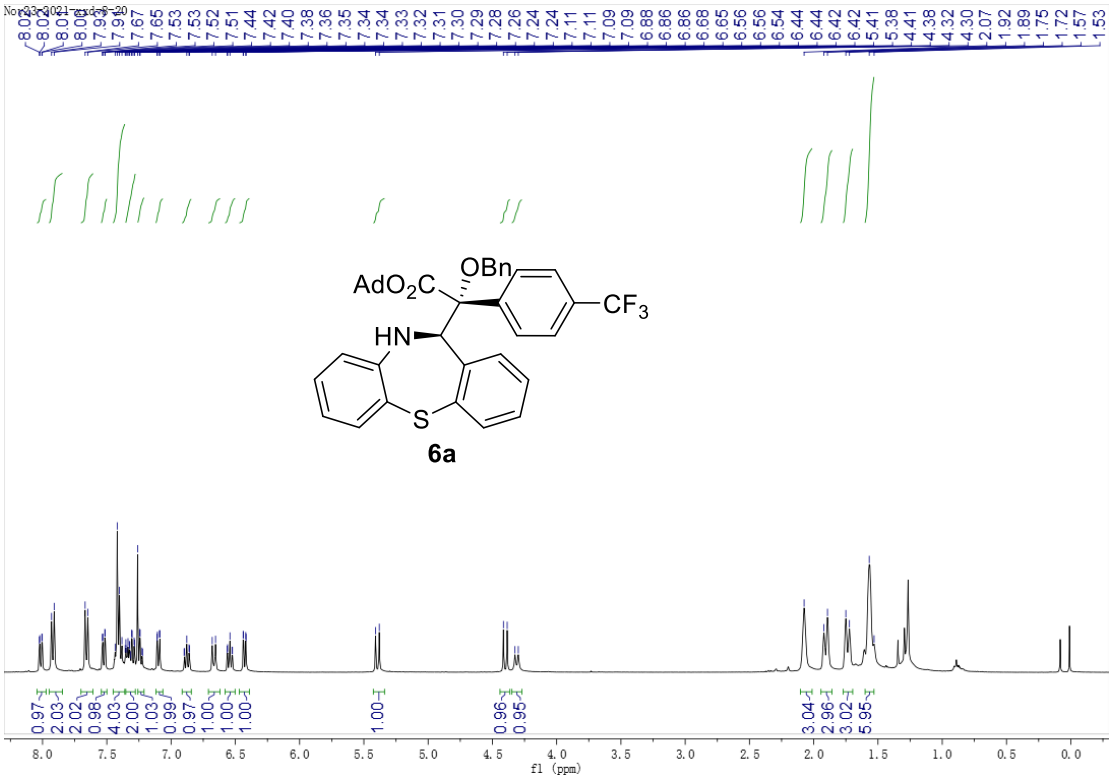

Ph
OBn
CO2Me
HN
O
minor
5w
f1 (ppm)

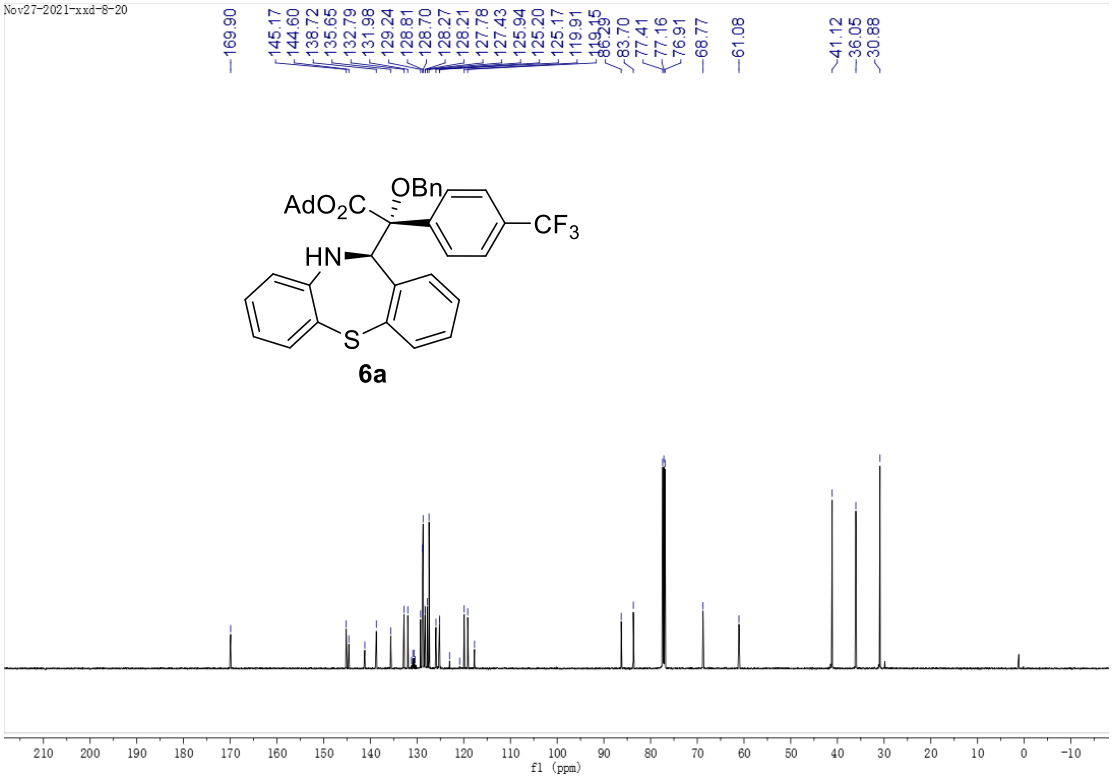

tBuO2C
OBn
Ph
HN
O
5x

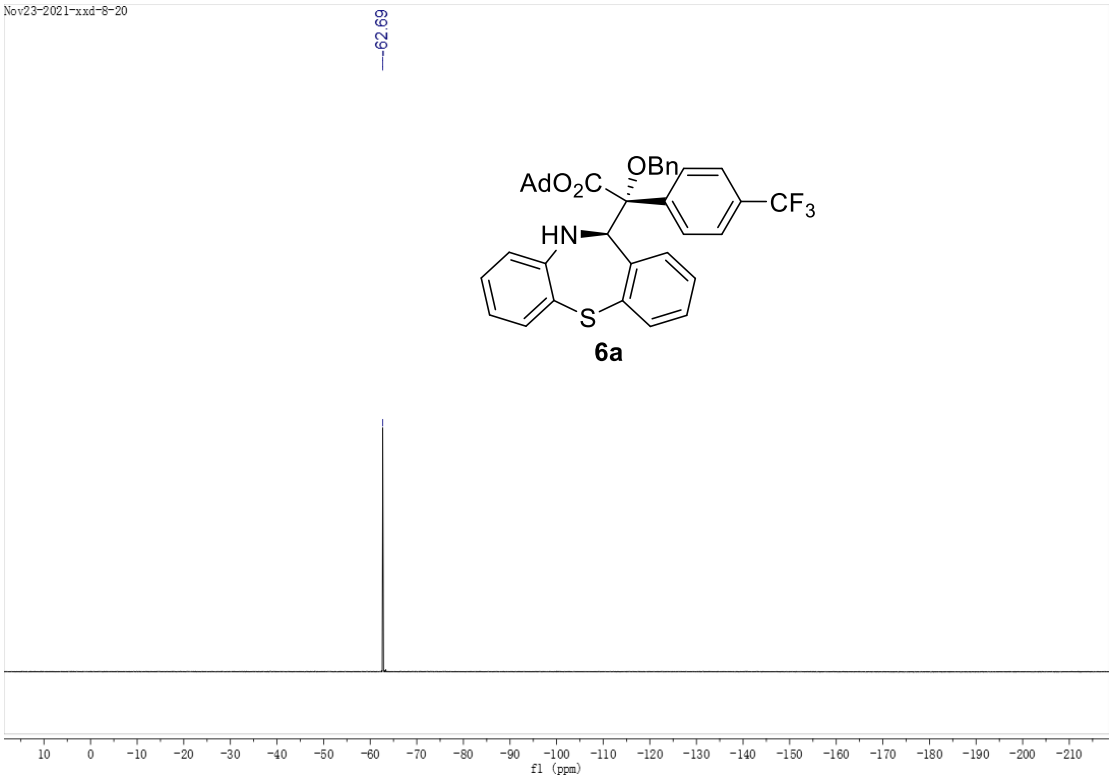

tBuO2C
OBn
Ph
HN
O
5x

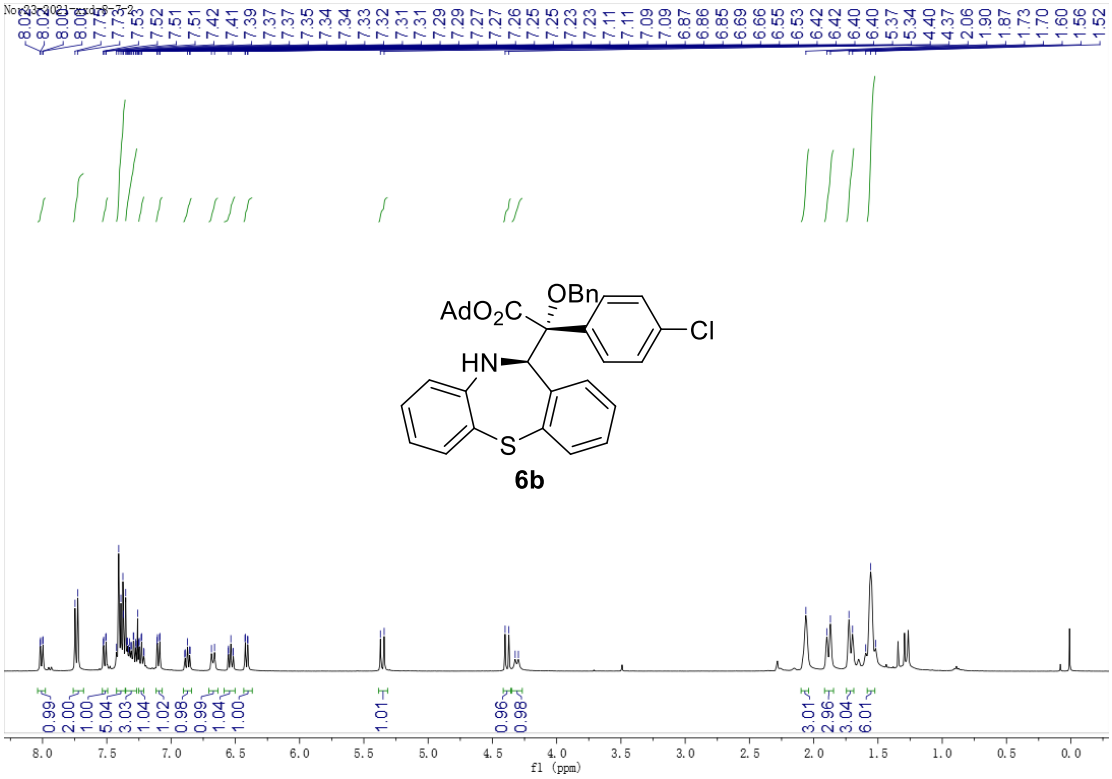

AdO2C
OH
Ph
HN
S
5y
f1 (ppm)

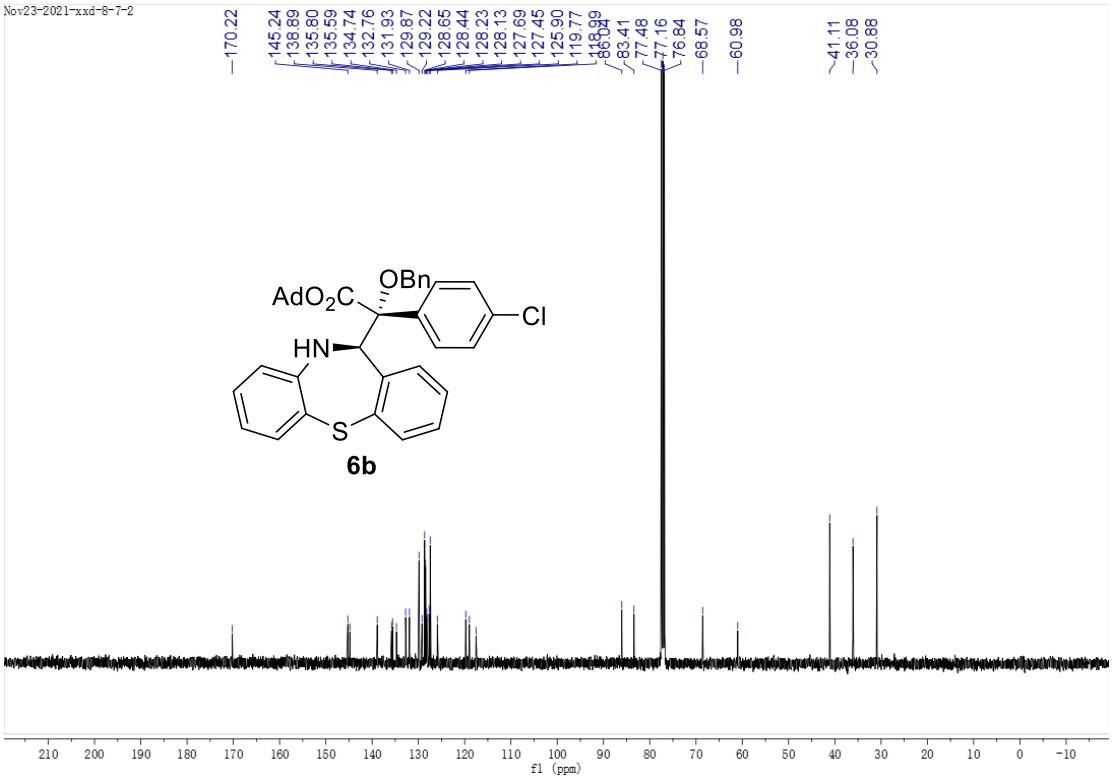

AdO2C
OH
Ph
HN
S
5y
f1 (ppm)


AdO2C
OBn
CF3
HN
S
6a
fl (ppm)


AdO2C
OBn
CF3
HN
S
6a
fl (ppm)


Nov23-2021-xxd-6-20
-62.69
AdO2C
OBn
CF3
HN
S
6a
f1 (ppm)


AdO2C
OBn
Cl
HN
S
6b
f1 (ppm)


Nov23-2021-xxd-6-7-2
170.22
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135.80
135.59
134.74
132.76
131.93
129.87
129.22
128.65
128.44
128.23
128.13
127.69
127.45
125.90
119.77
86.04
83.41
77.48
77.16
76.84
68.57
60.98
41.11
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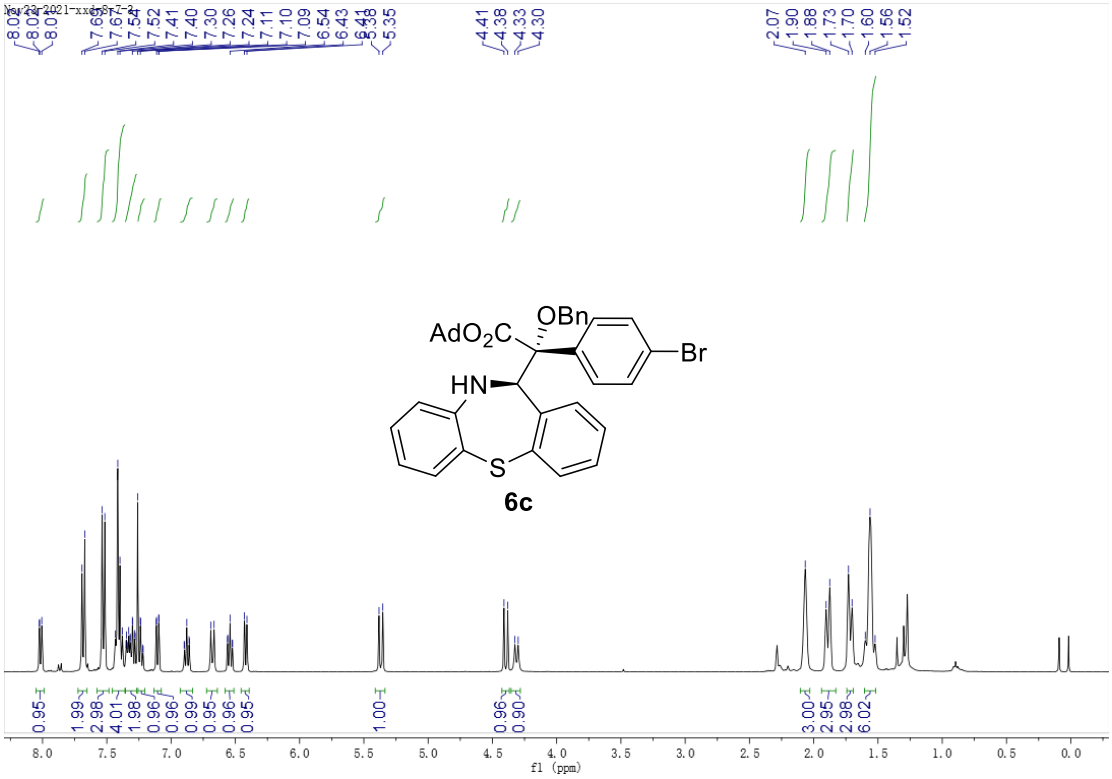
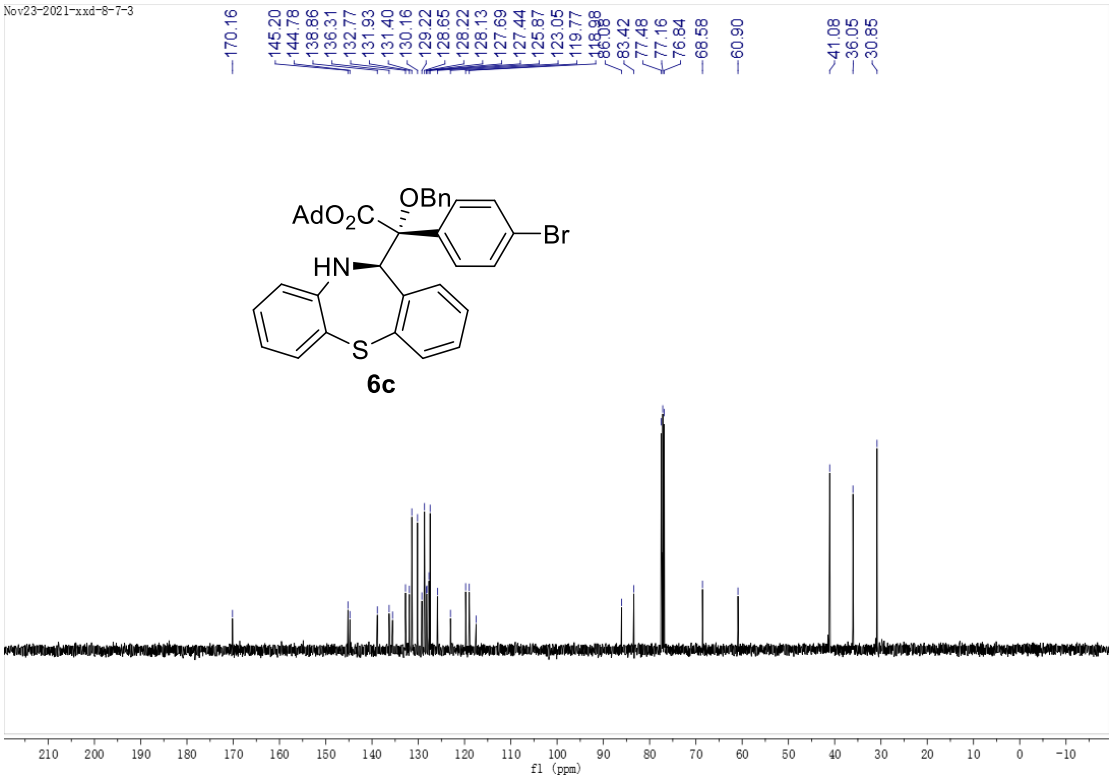
AdO2C
OBn
Cl
HN
S
6b
f1 (ppm)


8.04
8.02
8.01
7.69
7.67
7.54
7.52
7.41
7.40
7.30
7.26
7.24
7.11
7.10
7.09
6.54
6.43
6.41
5.38
5.35
4.41
4.38
4.33
4.30
2.07
1.90
1.88
1.73
1.70
1.60
1.56
1.52
AdO2C
OBn
Br
HN
S
6c
0.95
1.99
2.98
4.01
1.98
0.96
0.96
0.99
0.95
0.96
0.95
1.00
0.96
0.90
3.00
2.95
2.98
6.02
f1 (ppm)


Nov23-2021-xxd-8-7-3
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138.86
136.31
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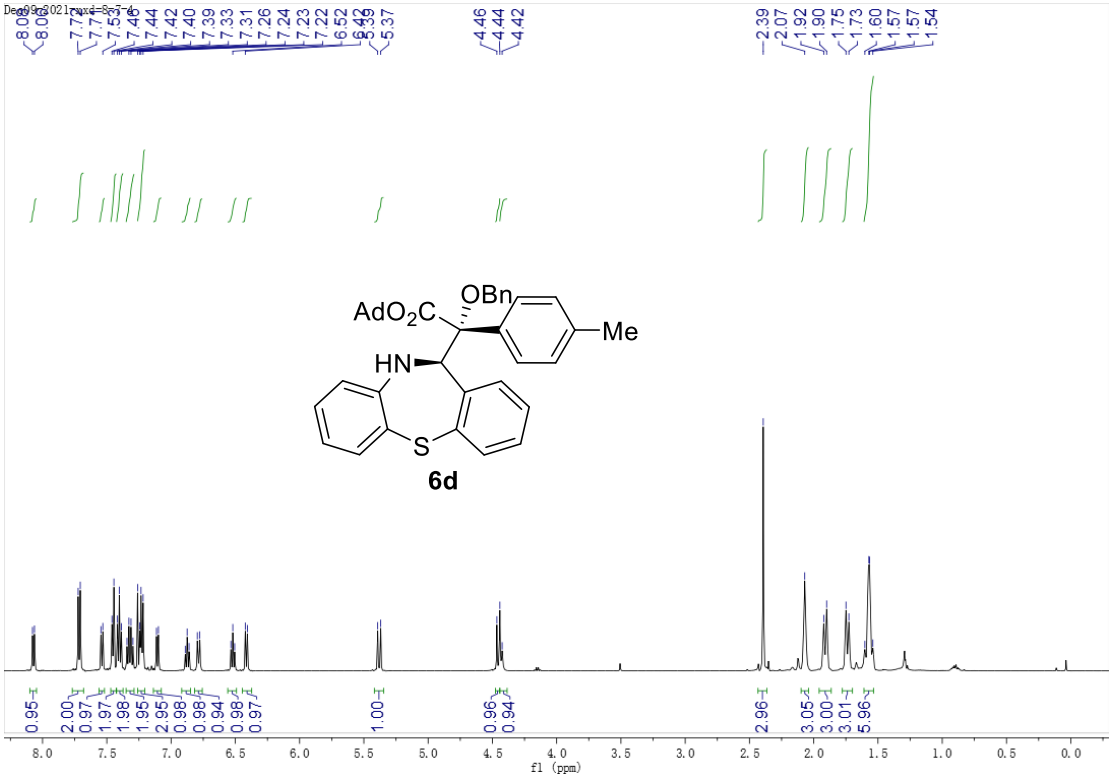
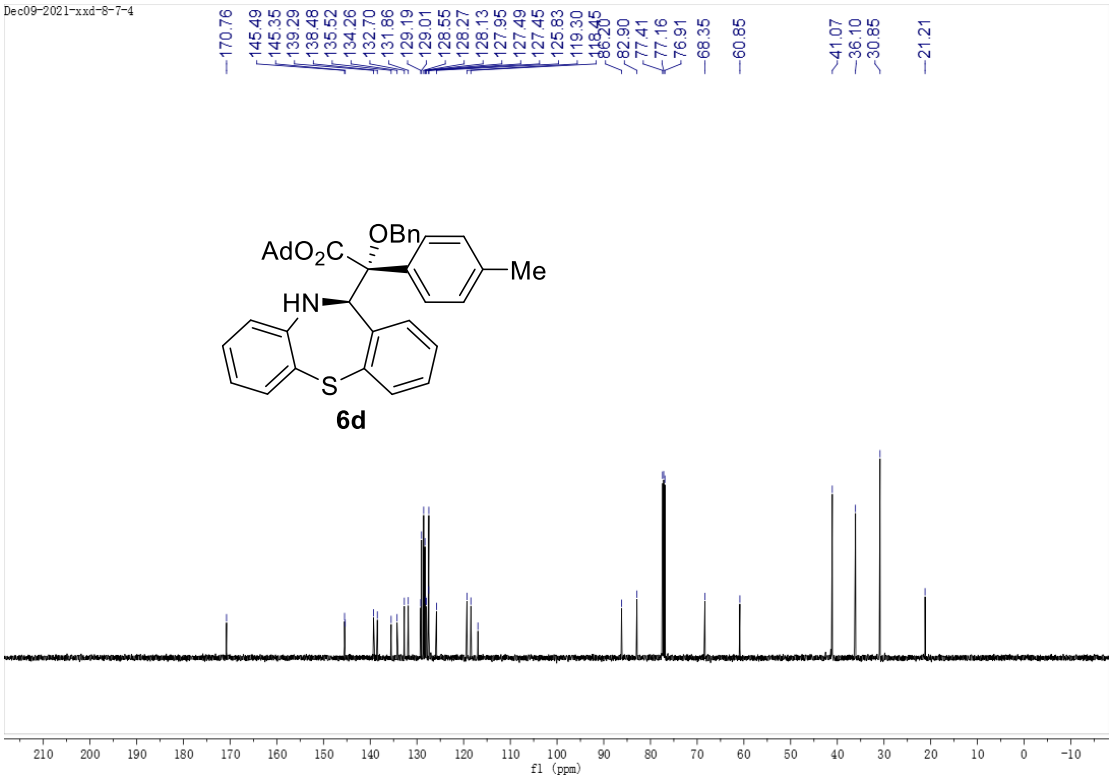
131.93
131.40
130.16
129.22
128.65
128.22
128.13
127.69
127.44
125.87
123.05
119.77
86.08
83.42
77.48
77.16
76.84
68.58
60.90
41.08
36.05
30.85
AdO2C
OBn
Br
HN
S
6c
f1 (ppm)


8.08
8.06
7.79
7.77
7.55
7.46
7.44
7.42
7.40
7.39
7.33
7.31
7.26
7.24
7.23
7.22
6.52
6.42
6.39
5.37
4.46
4.44
4.42
2.39
2.07
1.92
1.90
1.75
1.73
1.60
1.57
1.57
1.54
AdO2C
OBn
Me
HN
S
6d
0.95
2.00
0.97
1.97
1.98
1.95
2.95
0.98
0.98
0.94
0.98
0.97
1.00
0.96
0.94
2.96
3.05
3.00
3.01
5.96
f1 (ppm)


Dec09-2021-xxd-6-7-4
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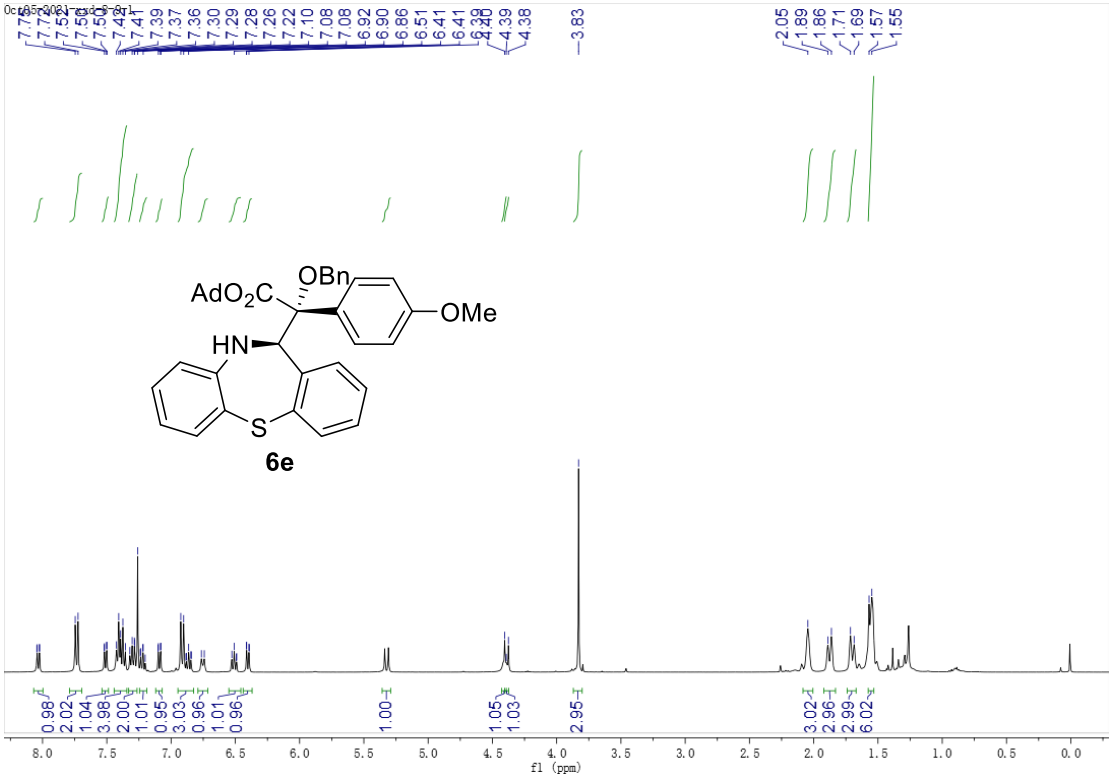
134.26
132.70
131.86
129.19
129.01
128.55
128.27
128.13
127.95
127.49
127.45
125.83
119.30
88.45
86.20
82.90
77.41
77.16
76.91
68.35
60.85
41.07
36.10
30.85
21.21
AdO2C
OBn
Me
HN
S
6d
f1 (ppm)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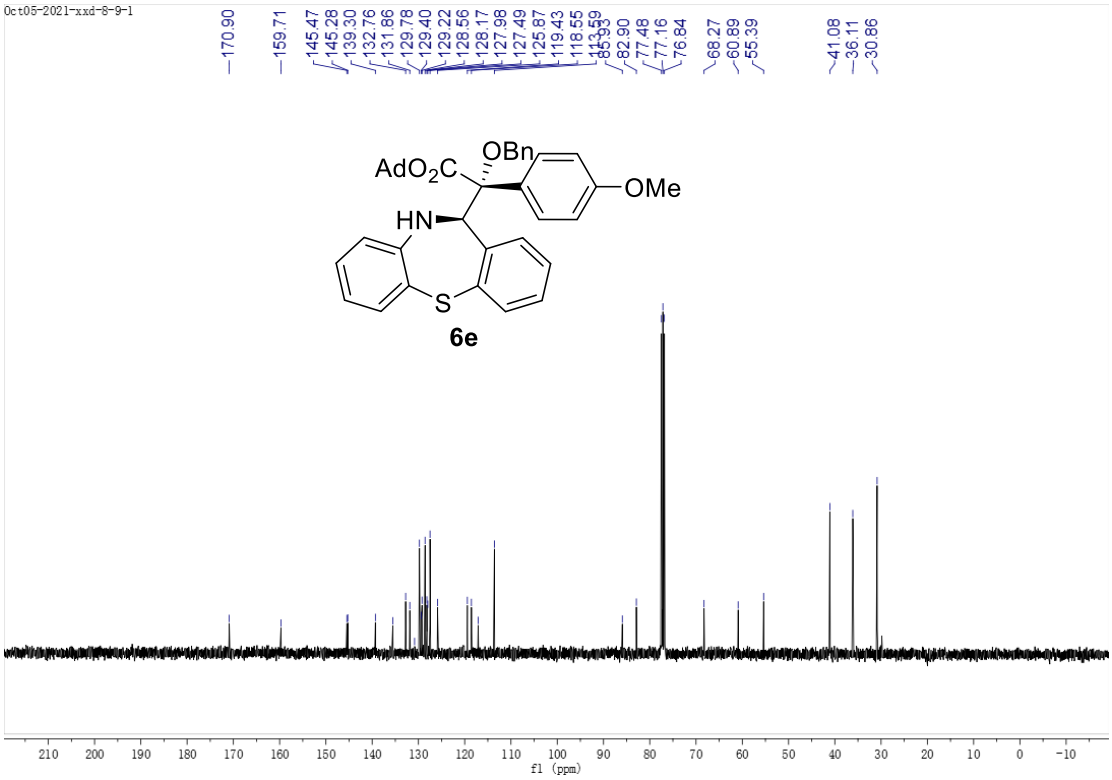
7.37
7.36
7.30
7.29
7.28
7.26
7.22
7.10
7.08
7.08
6.92
6.90
6.86
6.51
6.41
6.41
6.39
4.39
4.38
3.83
2.05
1.89
1.86
1.71
1.69
1.57
1.55
AdO2C
OBn
OMe
HN
S
6e
0.98
2.02
1.04
3.98
2.00
1.01
0.95
3.03
0.96
1.01
0.96
1.00
1.05
1.03
2.95
3.02
2.96
2.99
6.02
f1 (ppm)


Oct05-2021-xxd-8-9-1
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131.86
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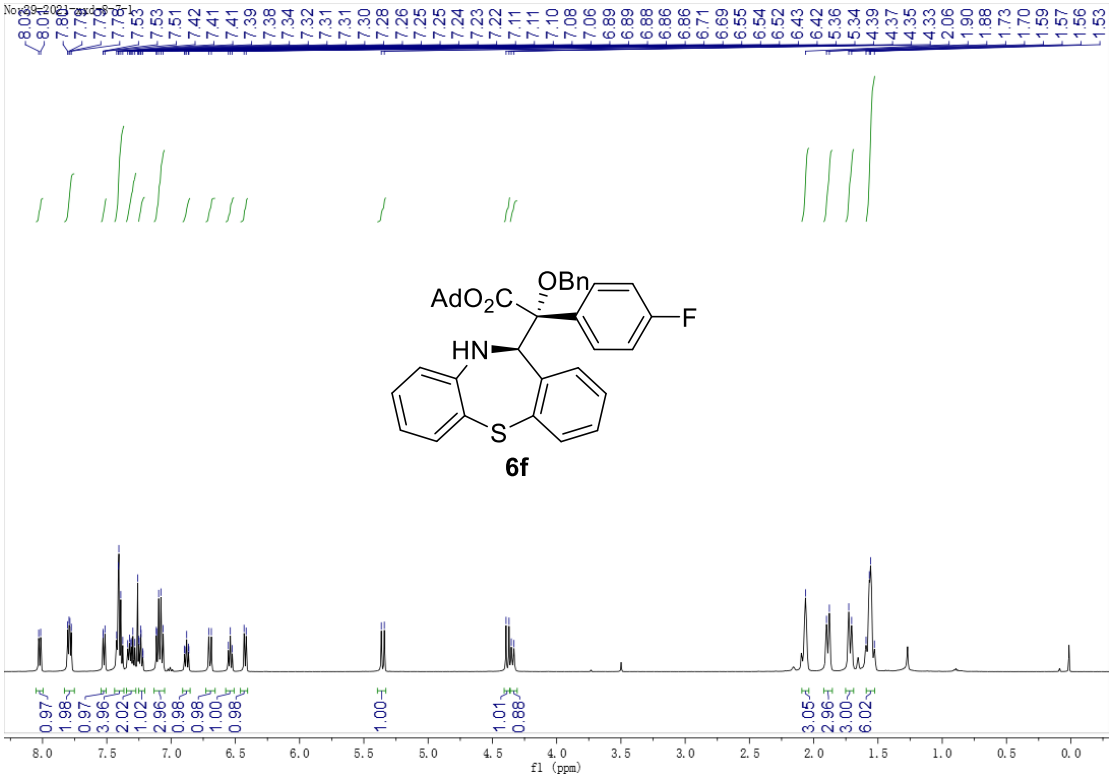
129.40
129.22
128.56
128.17
127.98
127.49
125.87
119.43
118.55
113.59
85.93
82.90
77.48
77.16
76.84
68.27
60.89
55.39
41.08
36.11
30.86
AdO2C
OBn
OMe
HN
S
6e
f1 (ppm)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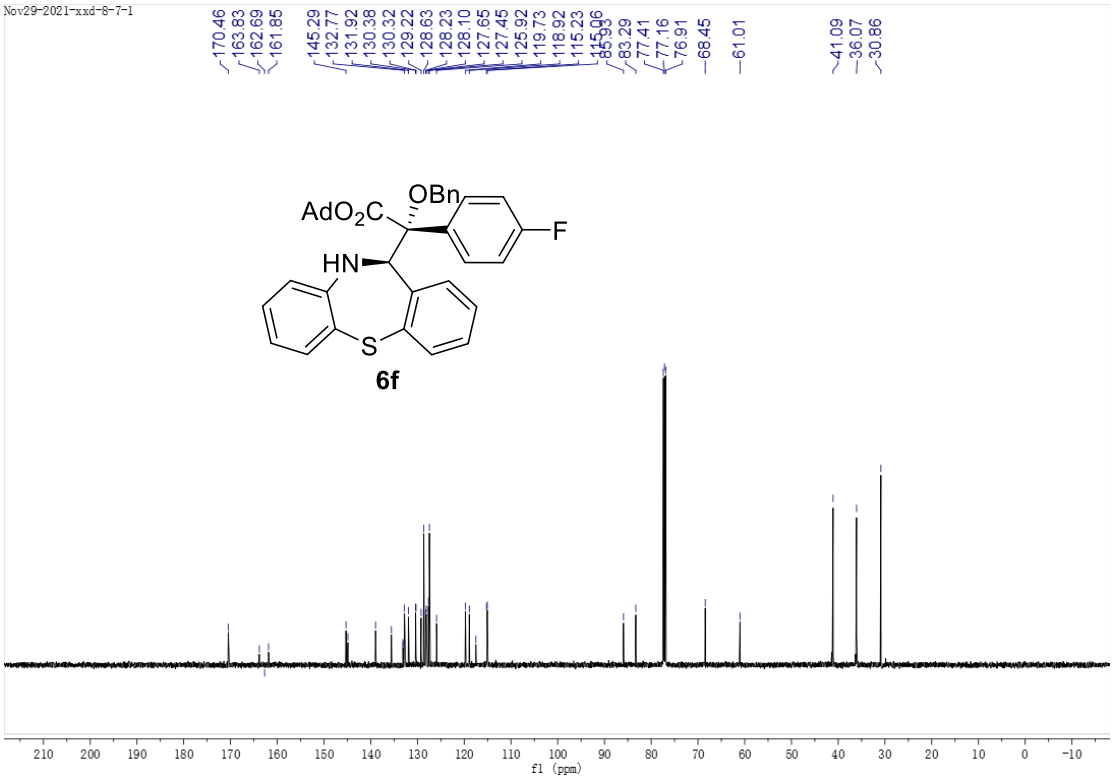
7.51
7.42
7.41
7.41
7.39
7.38
7.34
7.32
7.31
7.31
7.30
7.28
7.26
7.25
7.25
7.24
7.23
7.22
7.11
7.11
7.10
7.08
7.06
6.89
6.89
6.88
6.86
6.86
6.71
6.69
6.55
6.54
6.52
6.43
6.42
5.36
5.34
4.39
4.37
4.35
4.33
2.06
1.90
1.88
1.73
1.70
1.59
1.57
1.56
1.53
AdO2C
OBn
F
HN
S
6f
0.97
1.98
0.97
3.96
2.02
1.02
2.96
0.98
0.98
1.00
0.98
1.00
1.01
0.88
3.05
2.96
3.00
6.02
f1 (ppm)


Nov29-2021-xxd-8-7-1
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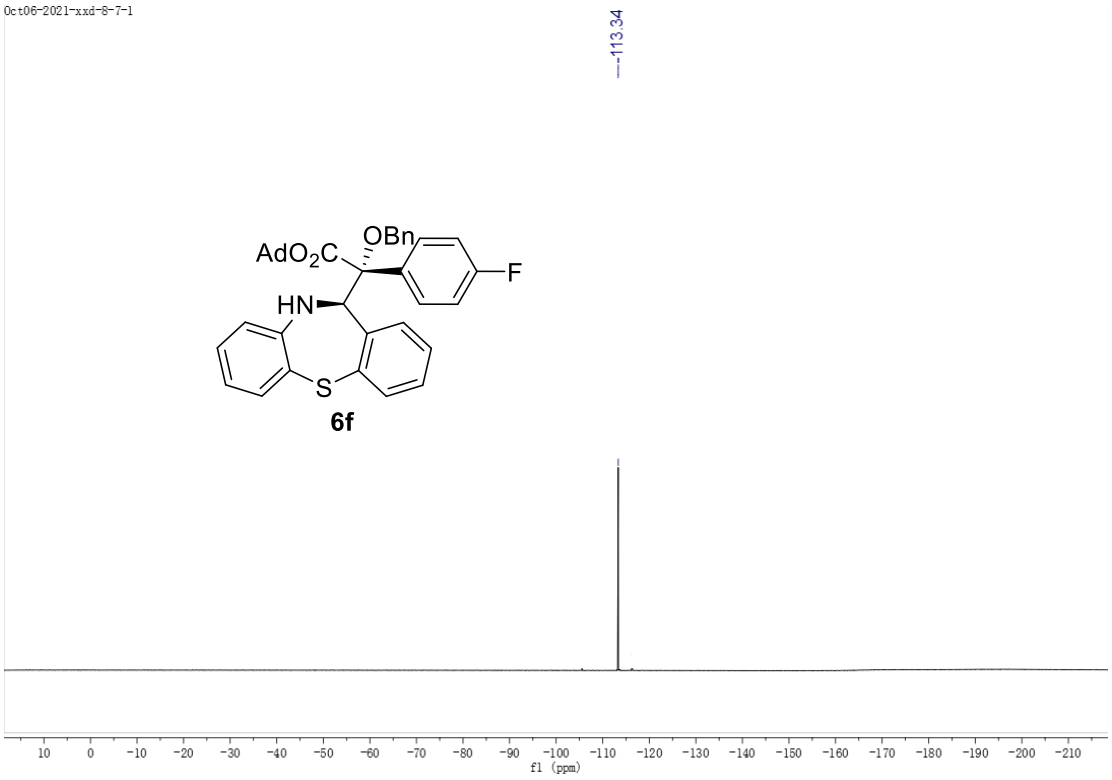
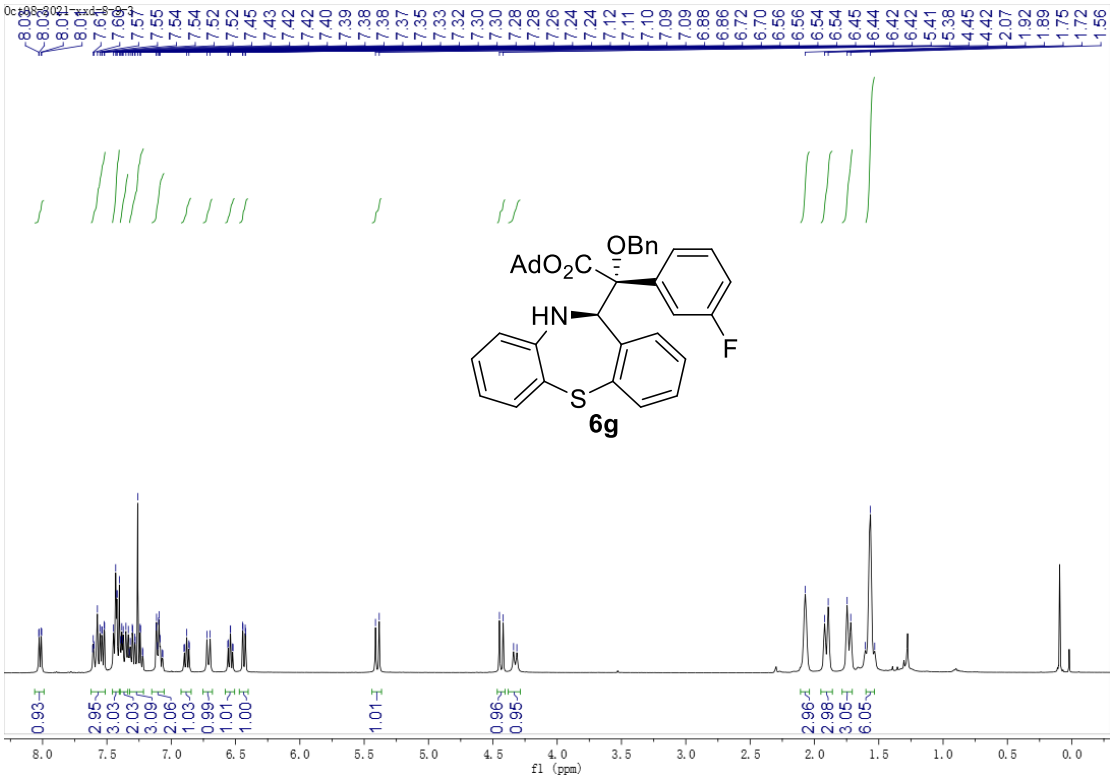
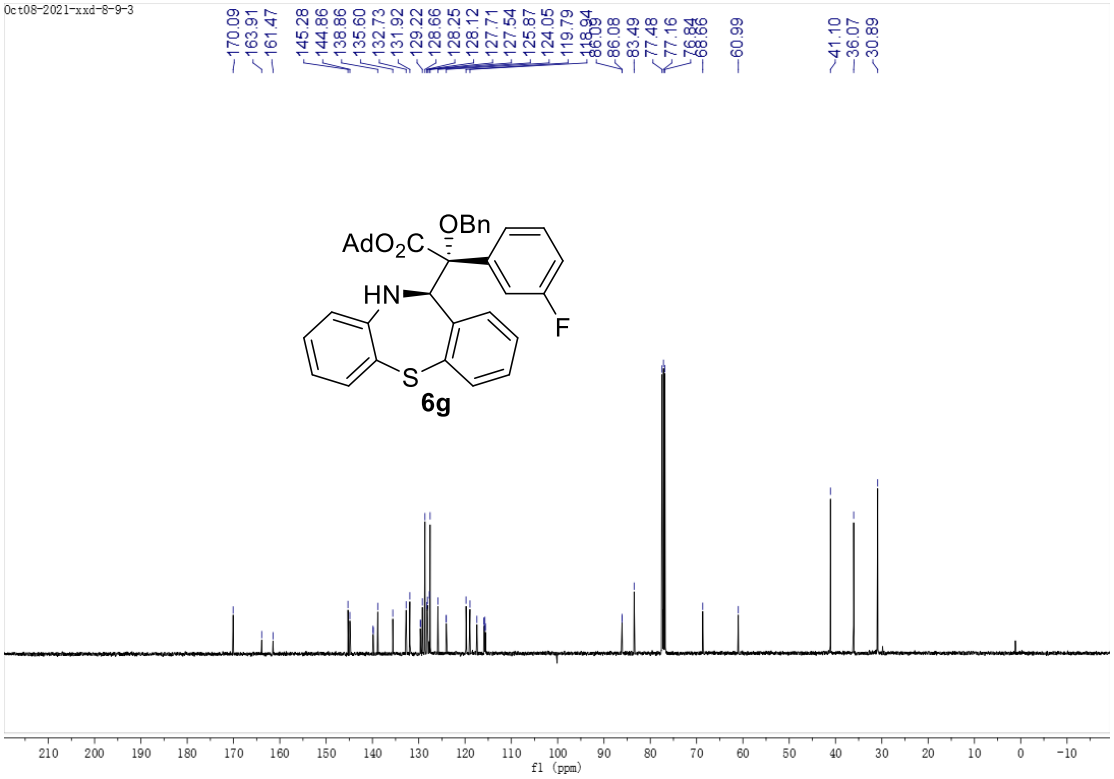
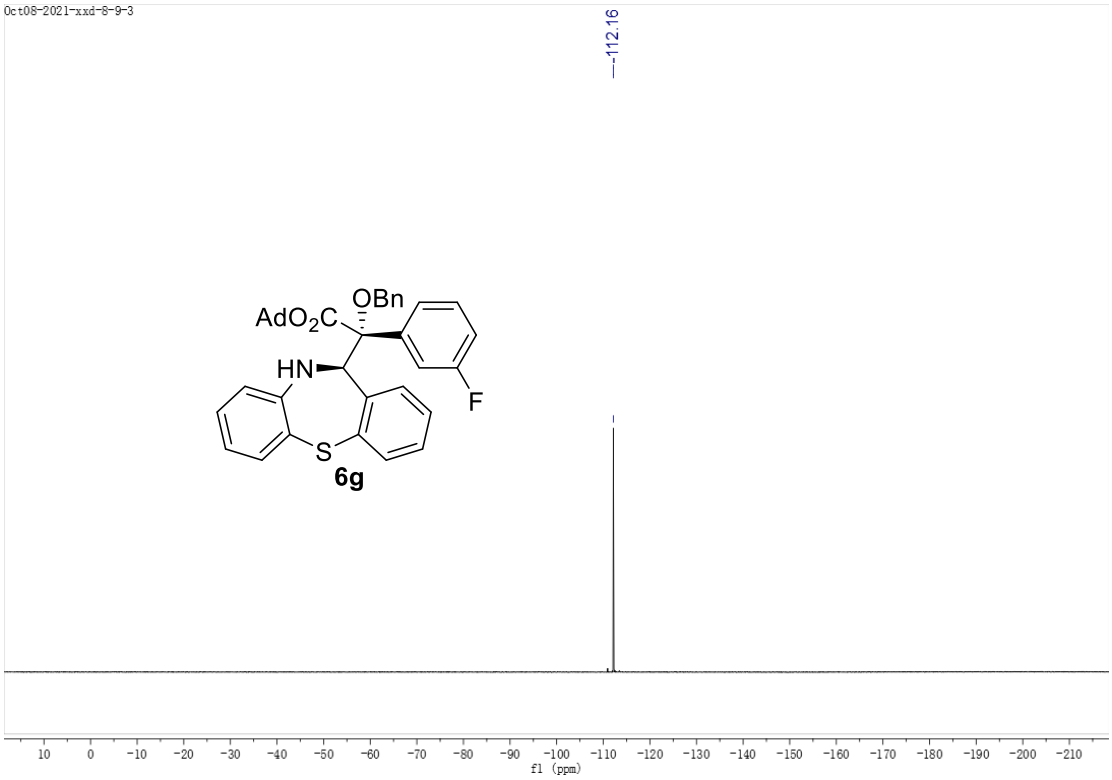
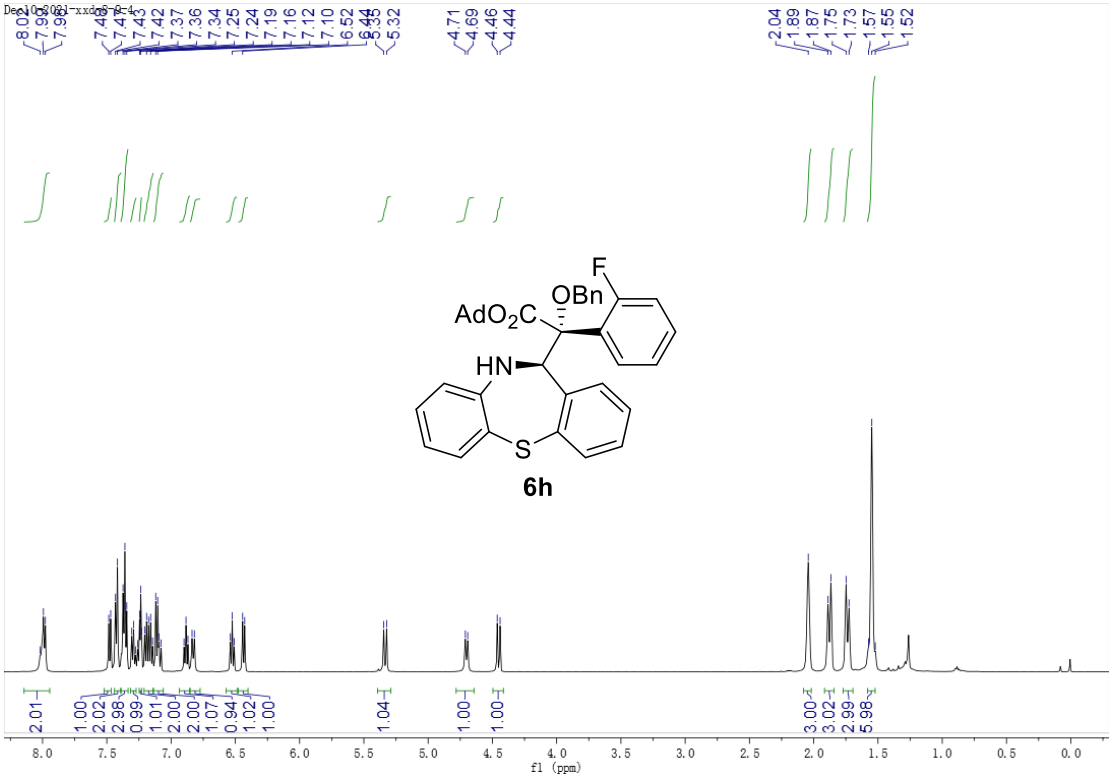
129.22
128.63
128.23
128.10
127.65
127.45
125.92
119.73
118.92
115.23
115.06
85.93
83.29
77.41
77.16
76.91
68.45
61.01
41.09
36.07
30.86
AdO2C
OBn
F
HN
S
6f
f1 (ppm)


Oct06-2021-xxd-8-7-1
-113.34
AdO2C
OBn
F
HN
S
6f
f1 (ppm)


AdO2C
OBn
HN
F
S
6g
fl (ppm)


Oct08-2021-xxd-8-9-3
AdO2C
OBn
HN
F
S
6g
fl (ppm)


Oct08-2021-xxd-8-9-3
-112.16
AdO2C
OBn
HN
F
S
6g
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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7.47
7.43
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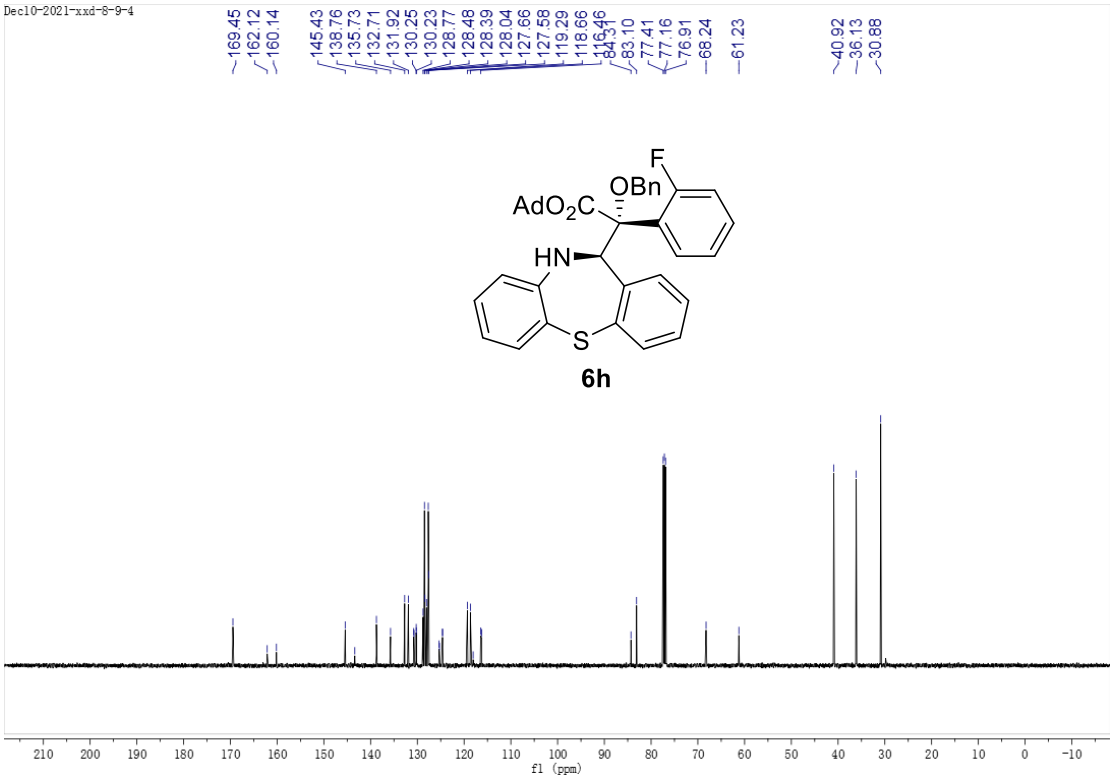
7.37
7.36
7.34
7.25
7.24
7.19
7.16
7.12
7.10
6.52
6.44
6.35
5.32
4.71
4.69
4.46
4.44
2.04
1.89
1.87
1.75
1.73
1.57
1.55
1.52
F
AdO2C
OBn
HN
S
6h
2.01
1.00
2.02
2.98
0.99
1.01
2.00
2.00
1.07
0.94
1.02
1.00
1.04
1.00
1.00
3.00
3.02
2.99
5.98
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Dec10-2021-xxd-8-9-4
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145.43
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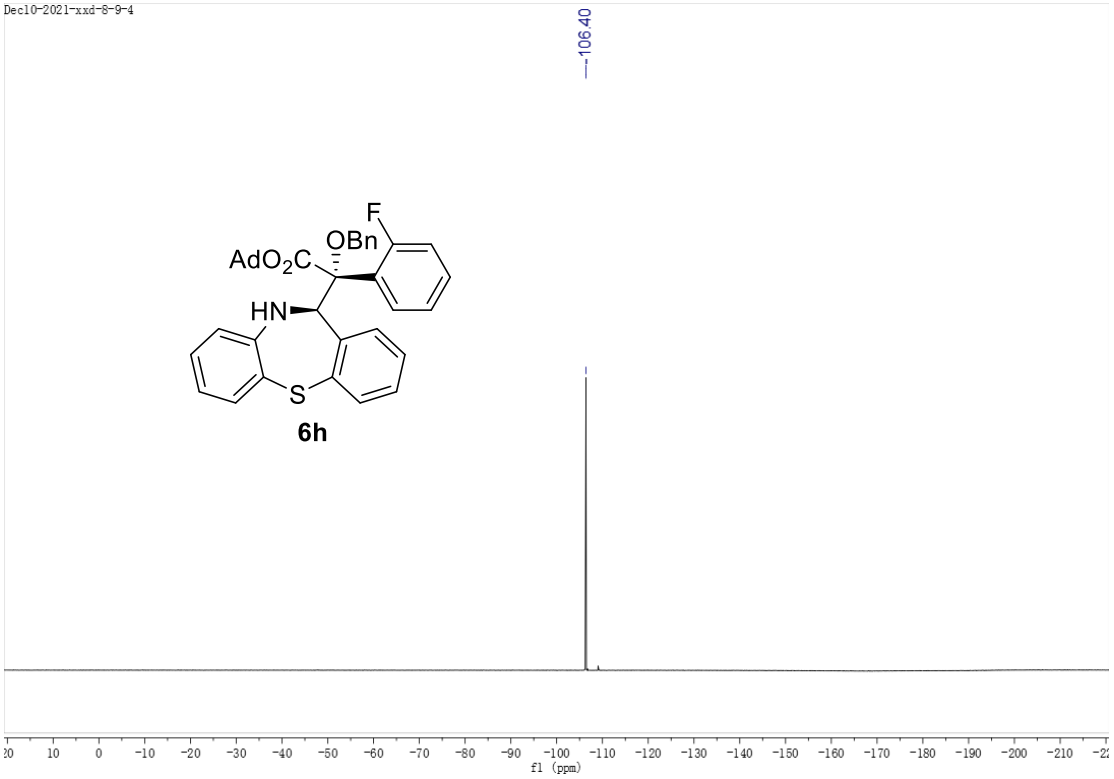
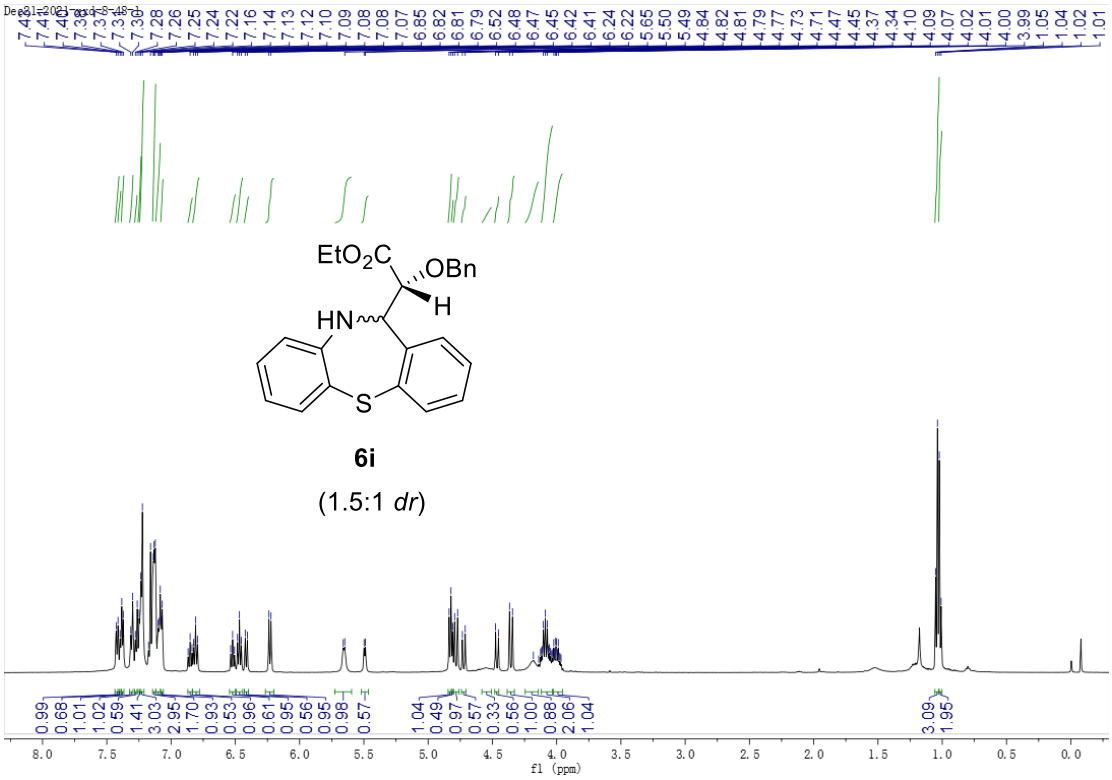
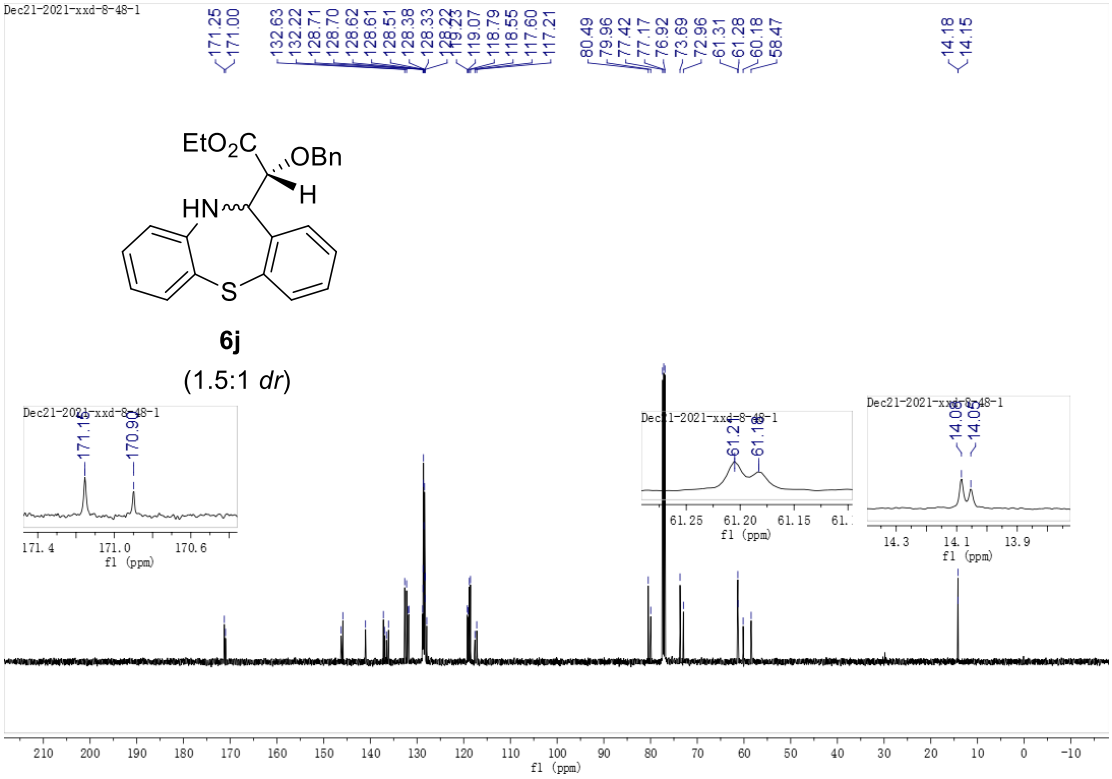
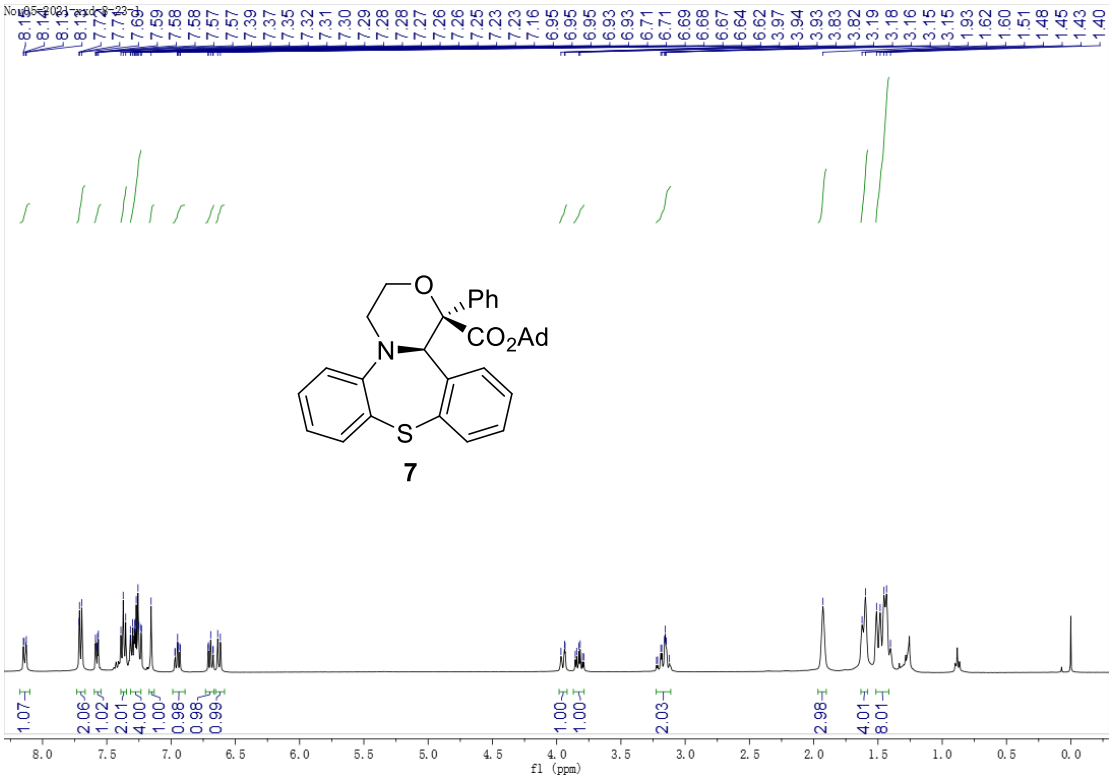
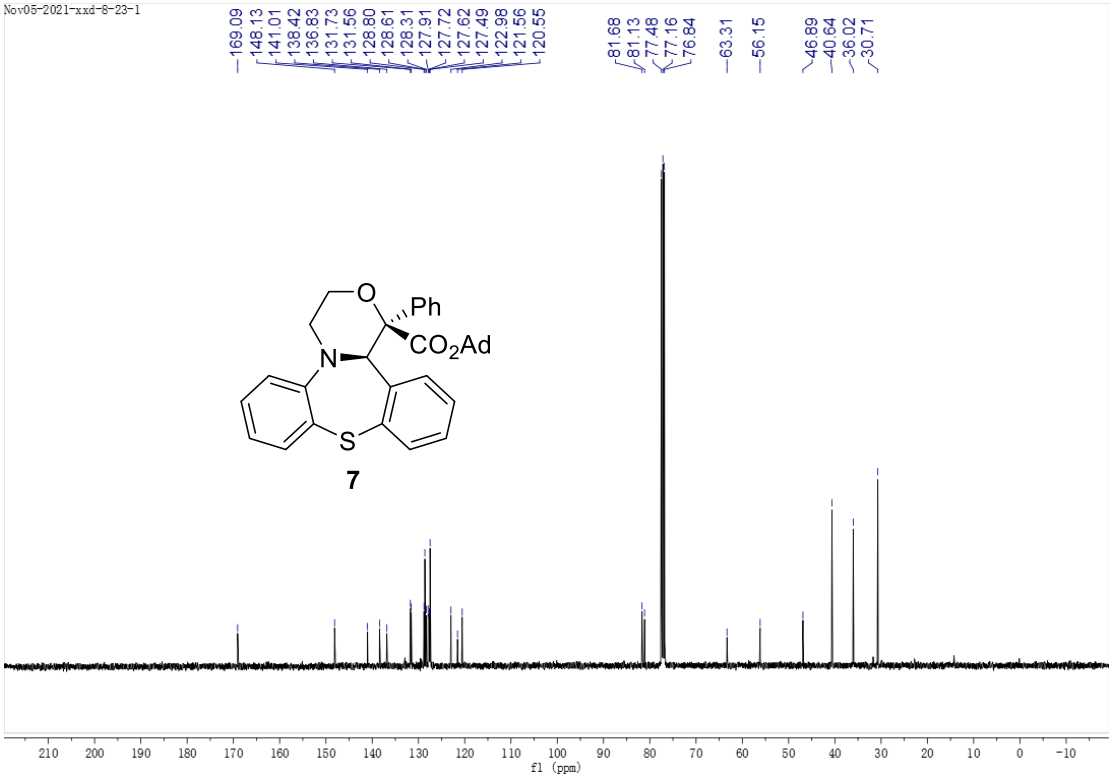
135.73
132.71
131.92
130.25
130.23
128.77
128.48
128.39
128.04
127.66
127.58
119.29
118.66
116.46
84.31
83.10
77.41
77.16
76.91
68.24
61.23
40.92
36.13
30.88
F
OBn
AdO2C
HN
S
6h
f1 (ppm)

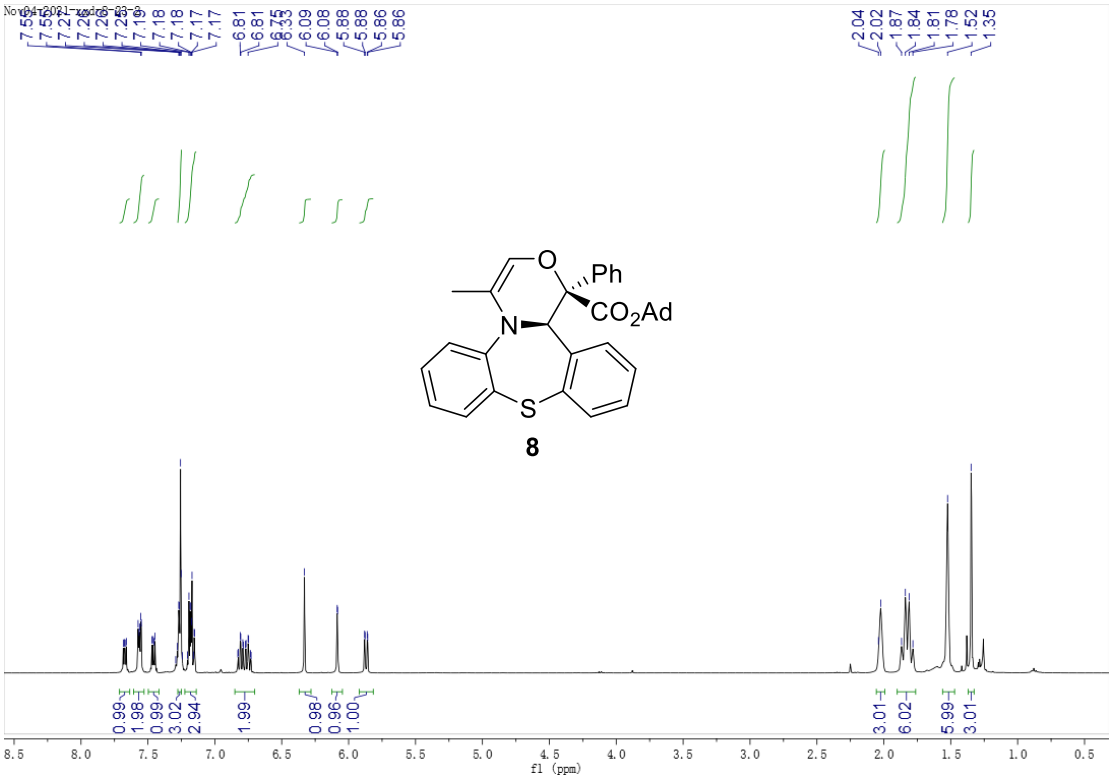

Dec10-2021-xxd-8-9-4
106.40
F
OBn
AdO2C
HN
S
6h
f1 (ppm)

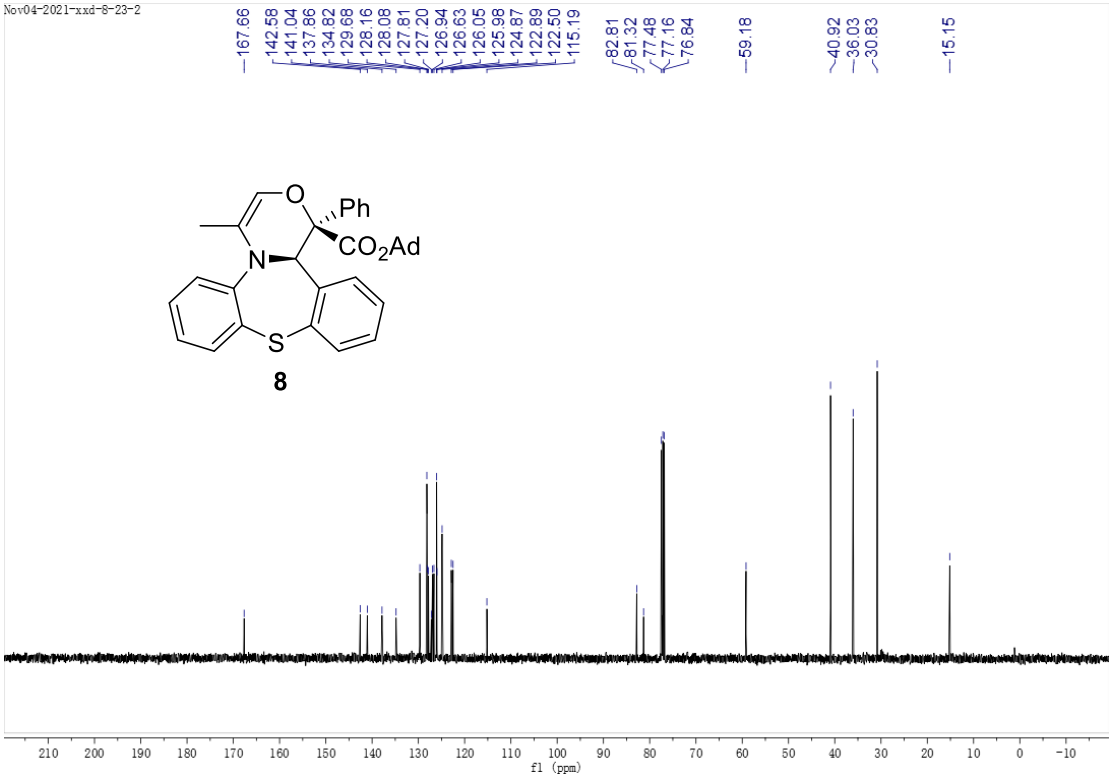

Dec21-2021-xxd-8-48-1
EtO2C
OBn
H
HN
S
6i
(1.5:1 dr)
f1 (ppm)

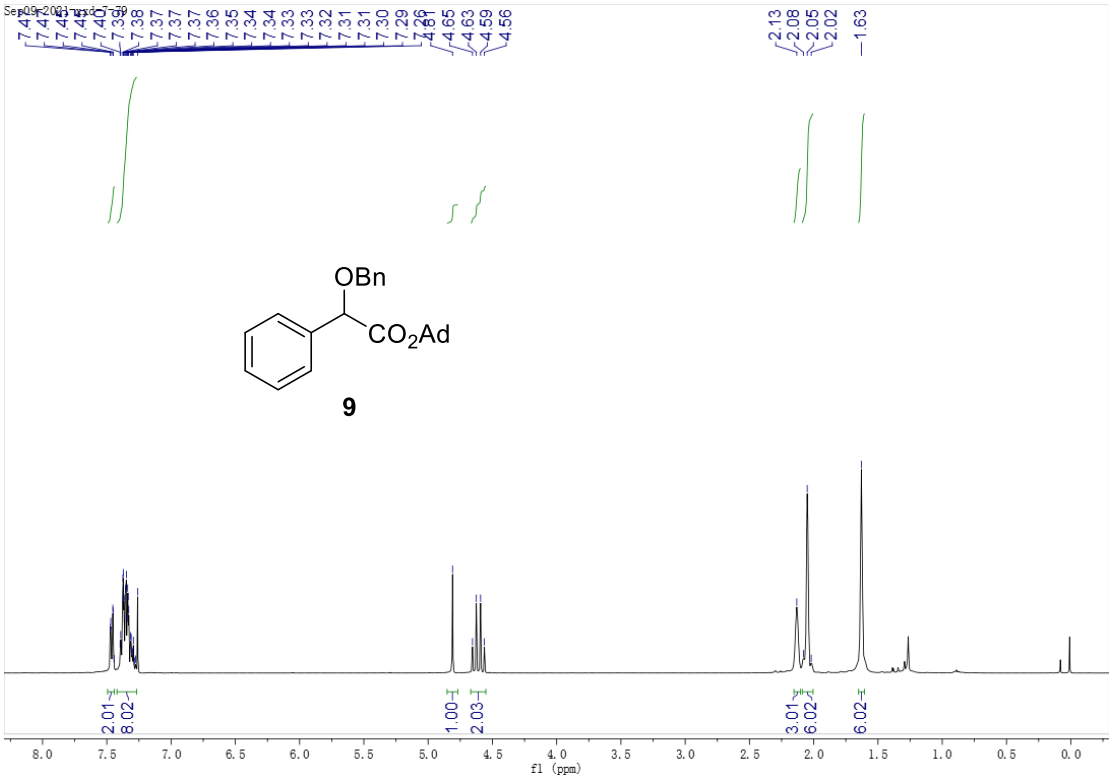

Dec21-2021-xxd-8-48-1
EtO2C
OBn
H
HN
S
6j
(1.5:1 dr)
f1 (ppm)

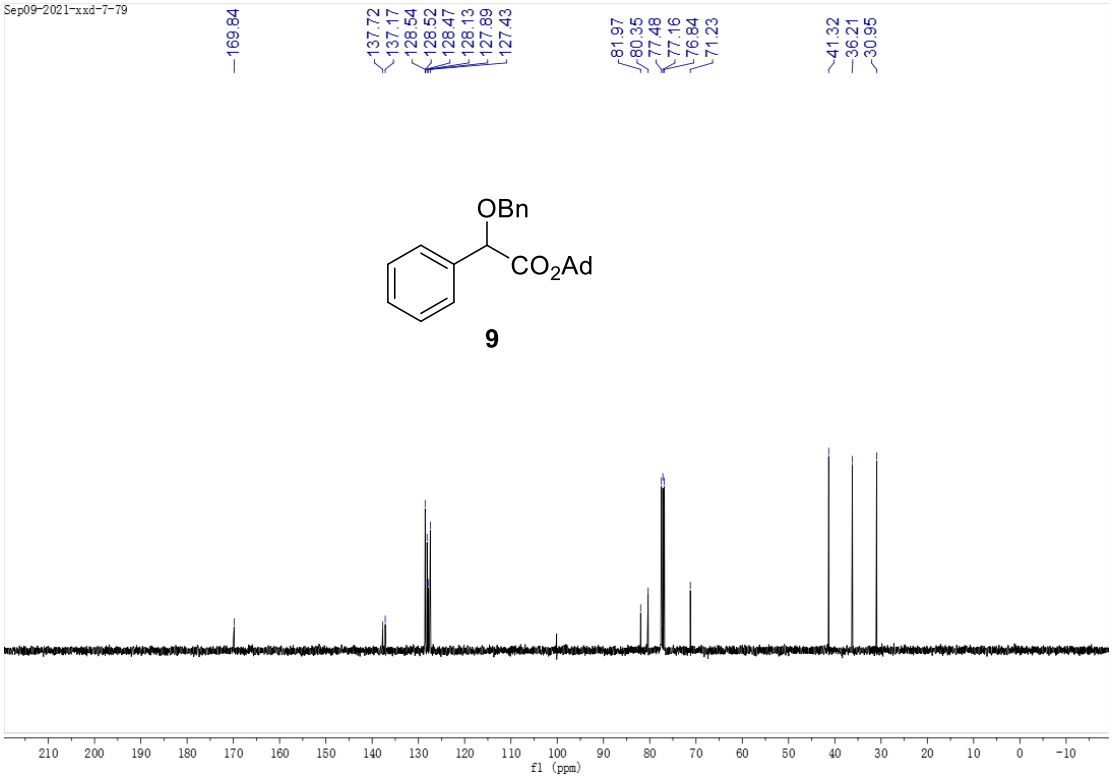

Ph
CO2Ad
N
O
S
7
fl (ppm)


Ph
CO2Ad
N
O
S
7
fl (ppm)


7.59
7.58
7.21
7.20
7.19
7.18
7.18
7.17
7.17
6.81
6.81
6.75
6.33
6.09
6.08
5.88
5.88
5.86
5.86
2.04
2.02
1.87
1.84
1.81
1.78
1.52
1.35
O
Ph
CO2Ad
N
S
8
0.99
1.98
0.99
3.02
2.94
1.99
0.98
0.96
1.00
3.01
6.02
5.99
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

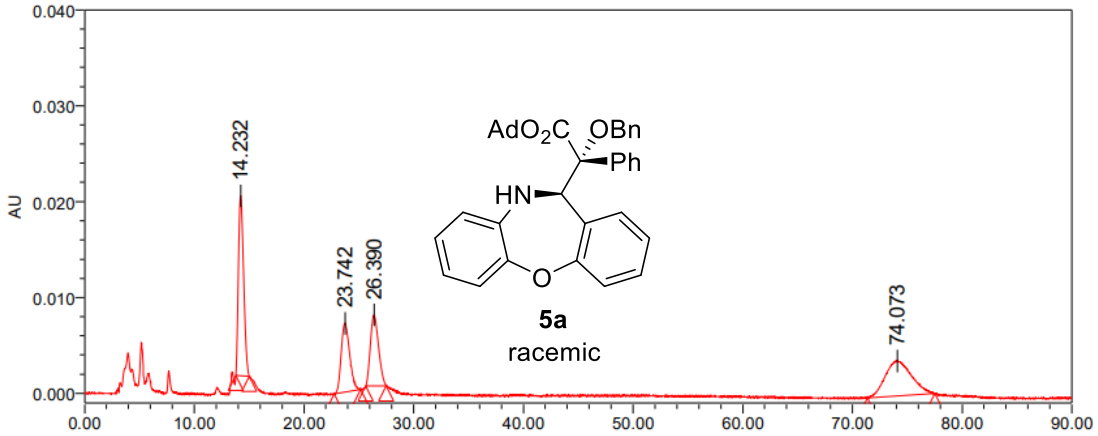

Nov04-2021-xxd-8-23-2
167.66
142.58
141.04
137.86
134.82
129.68
128.16
128.08
127.81
127.20
126.94
126.63
126.05
125.98
124.87
122.89
122.50
115.19
82.81
81.32
77.48
77.16
76.84
59.18
40.92
36.03
30.83
15.15
O
Ph
CO2Ad
N
S
8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Sep09-2021-xxd-7-79
7.47
7.46
7.45
7.44
7.43
7.40
7.39
7.38
7.37
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.26
4.61
4.65
4.63
4.59
4.56
2.13
2.08
2.05
2.02
1.63
OBn
CO2Ad
9
2.01
8.02
1.00
2.03
3.01
6.02
6.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

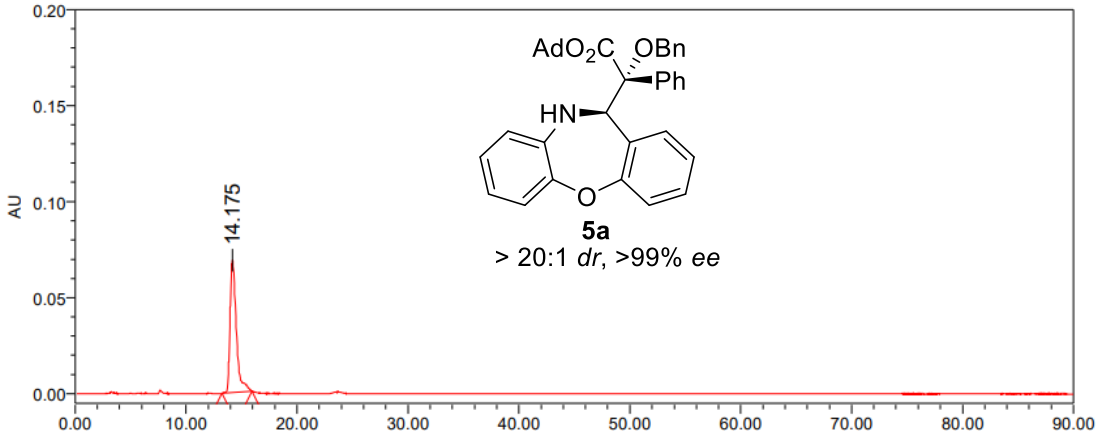

Sep09-2021-xxd-7-79
169.84
137.72
137.17
128.54
128.52
128.47
128.13
127.89
127.43
81.97
80.35
77.48
77.16
76.84
71.23
41.32
36.21
30.95
OBn
CO2Ad
9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Condition：Chrial AD-H, λ = 254 nm, hexane/isopropanol = 98:2

flow rate = 1.0 mL/min



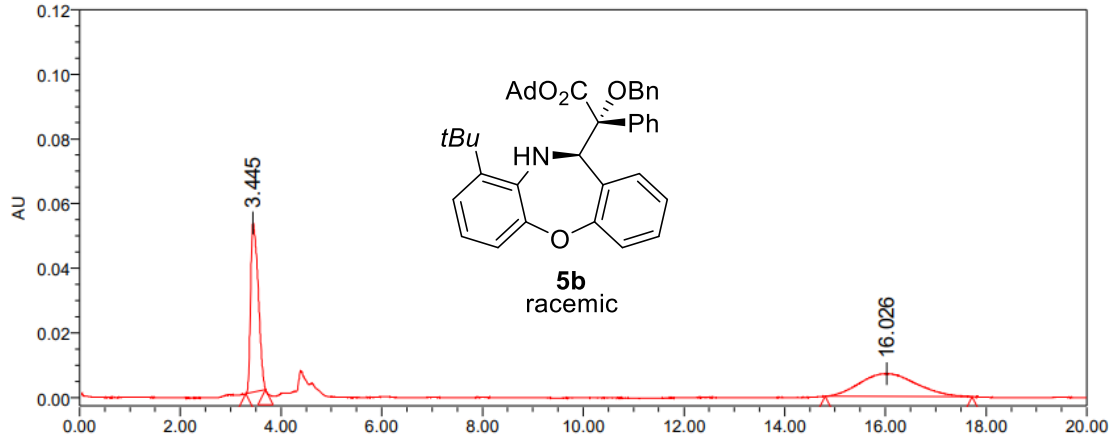
Entry	RT min	Height mV	Area mV.sec	% Area %
1	14.232	18761	612336	30.91
2	23.742	7189	382586	19.31
3	26.391	7404	377648	19.06
4	74.073	3660	608741	30.72



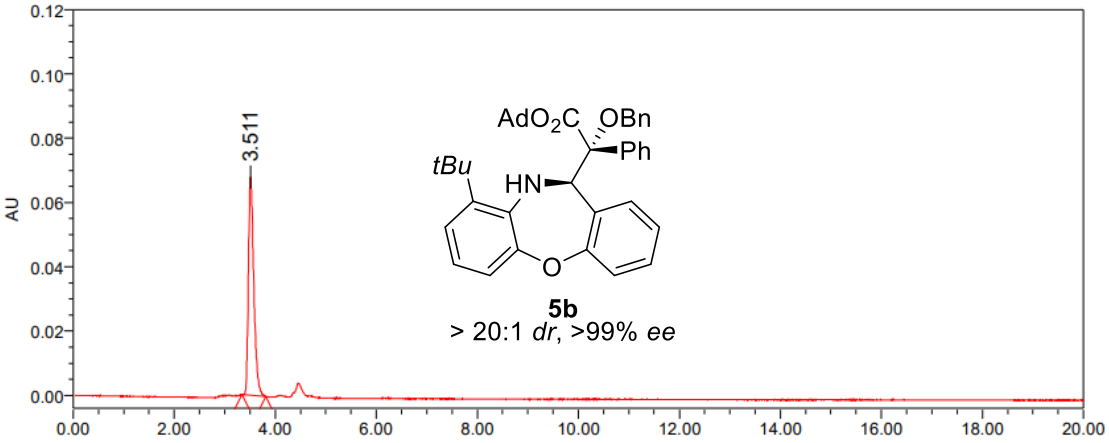
Entry	RT min	Height mV	Area mV.sec	% Area %
1	14.175	69095	2743195	100.00

Condition：Chrial AD-H, λ = 254 nm, hexane/isopropanol = 80:20

flow rate = 1.0 mL/min



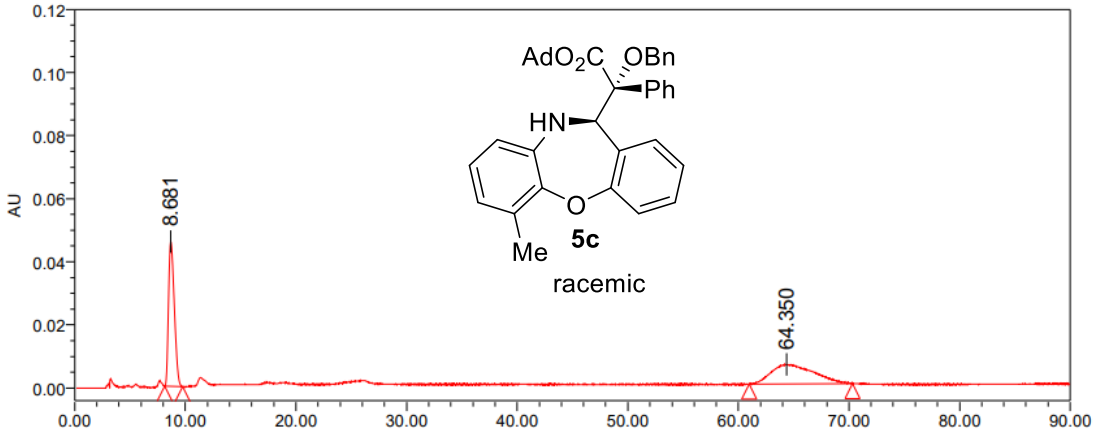
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.445	52305	551371	50.11
2	16.026	7503	549031	49.89



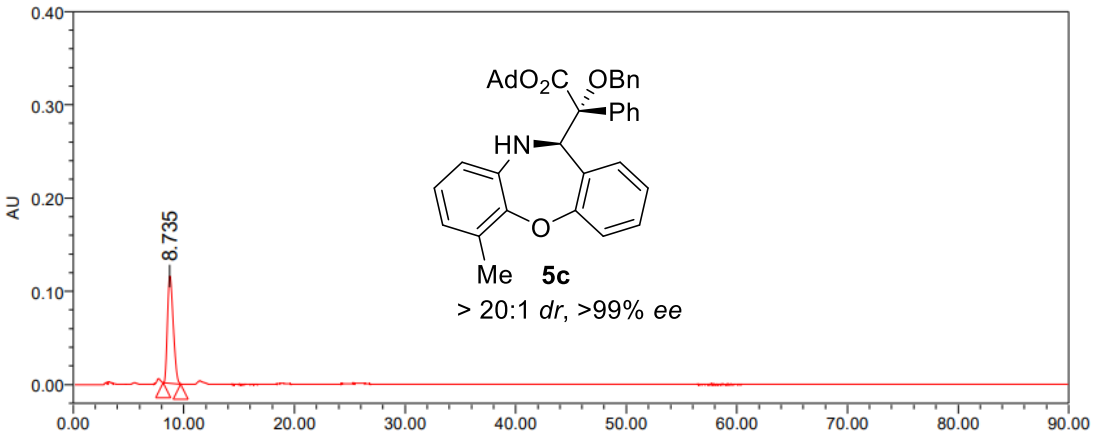
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.511	29123	217847	100.00

Condition：Chrial AD-H, λ = 254 nm, hexane/isopropanol = 98:2

flow rate = 1.0 mL/min



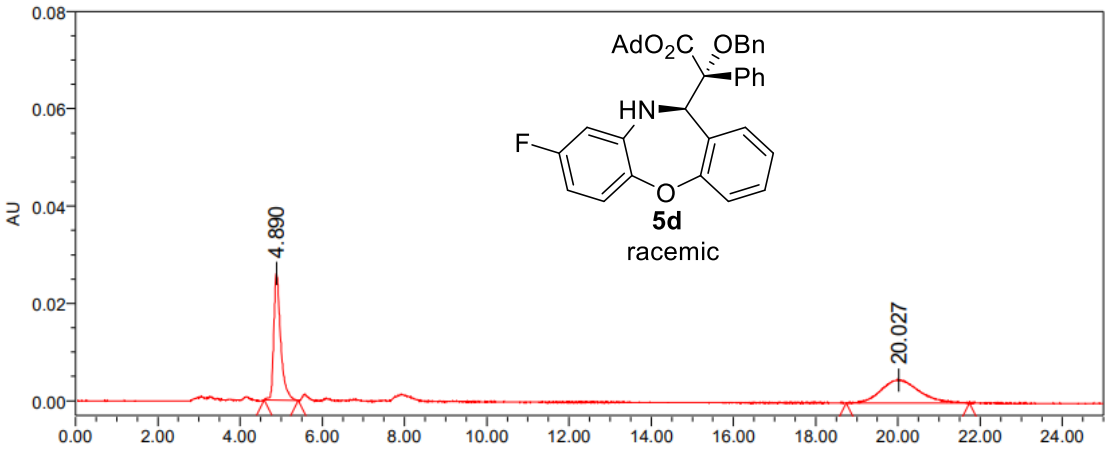
Entry	RT min	Height mV	Area mV.sec	% Area %
1	8.681	45893	1663022	50.44
2	64.350	6188	1634225	49.56



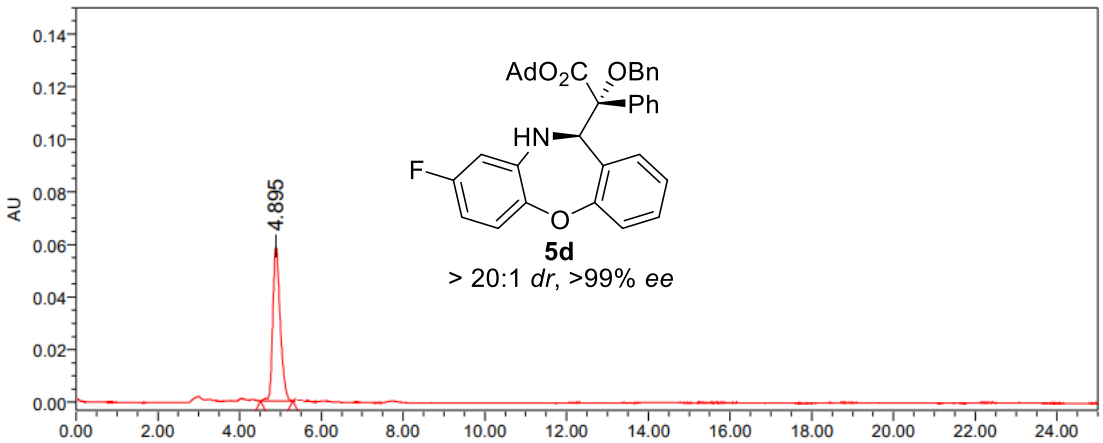
Entry	RT min	Height mV	Area mV.sec	% Area %
1	8.735	114944	4179305	100.00

Condition：Chrial AD-H, λ = 254 nm, hexane/isopropanol = 80:20

flow rate = 1.0 mL/min



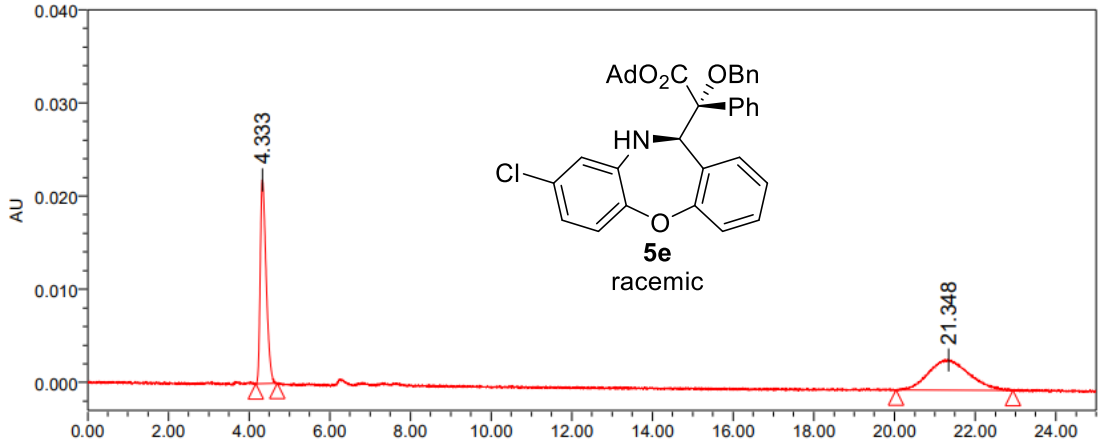
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.890	26024	303827	50.36
2	20.027	4701	299528	49.64



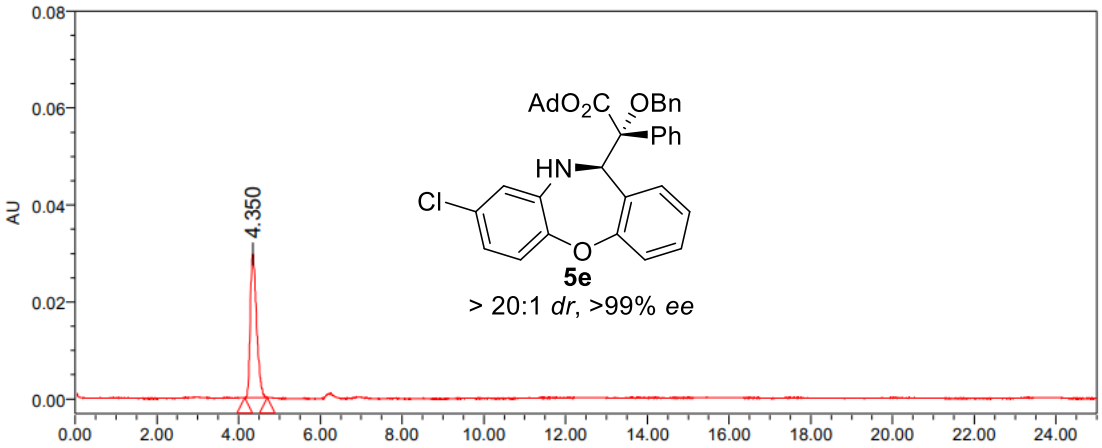
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.895	58931	741141	100.00

Condition：Chrial AD-H, λ = 317 nm, hexane/isopropanol = 80:20

flow rate = 1.0 mL/min



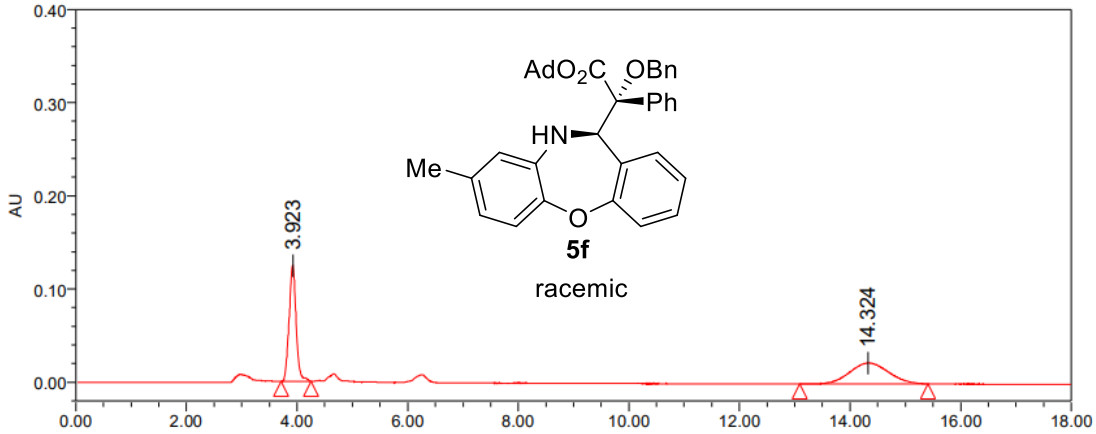
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.333	21866	218672	49.44
2	21.305	3215	50.56	50.56



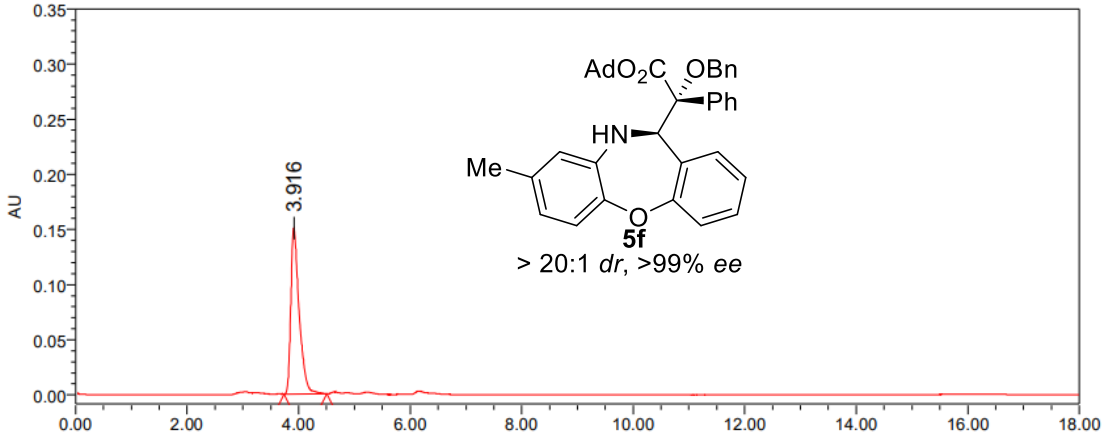
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.350	29603	317698	100.00

Condition：Chrial AD-H, λ = 254 nm, hexane/isopropanol = 80:20

flow rate = 1.0 mL/min



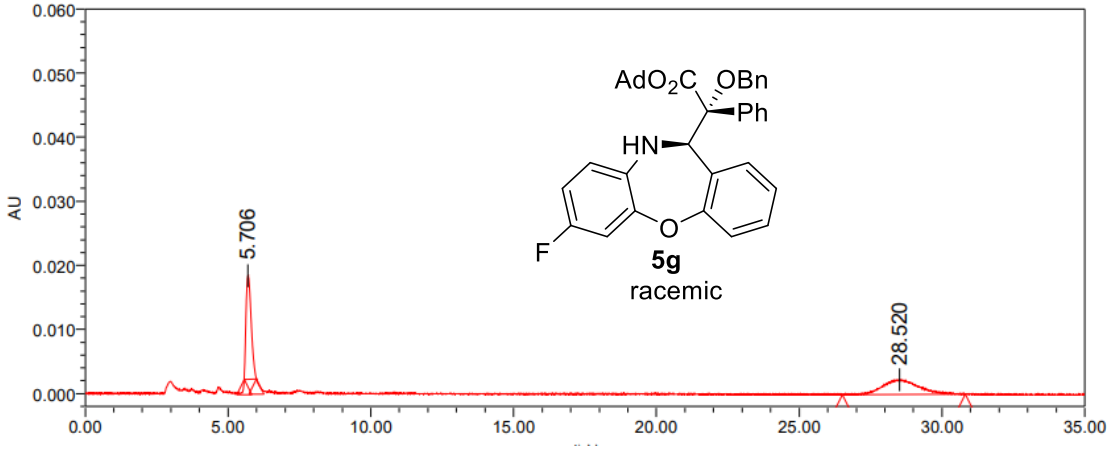
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.923	124297	1099742	50.11
2	14.324	22340	1095046	23.27



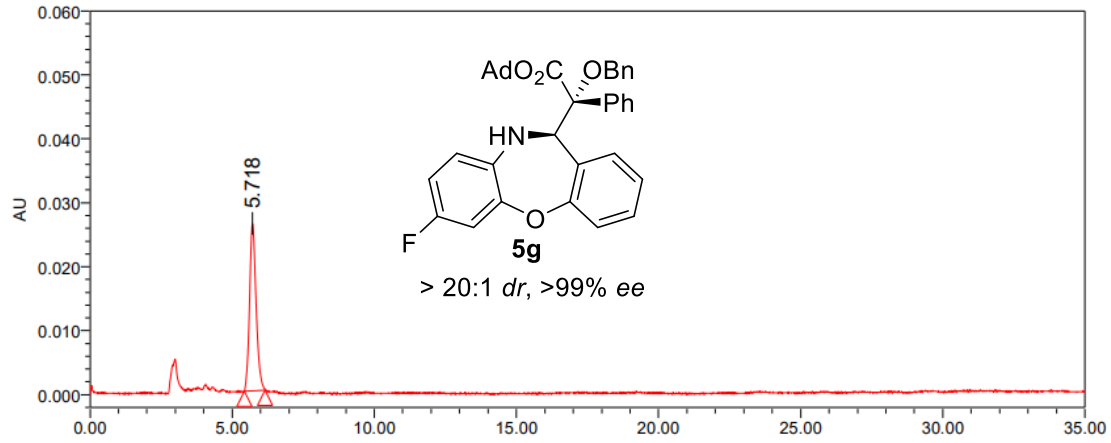
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.916	150693	1574137	100.00

Condition：Chrial AD-H, λ = 266 nm, hexane/isopropanol = 80:20

flow rate = 1.0 mL/min



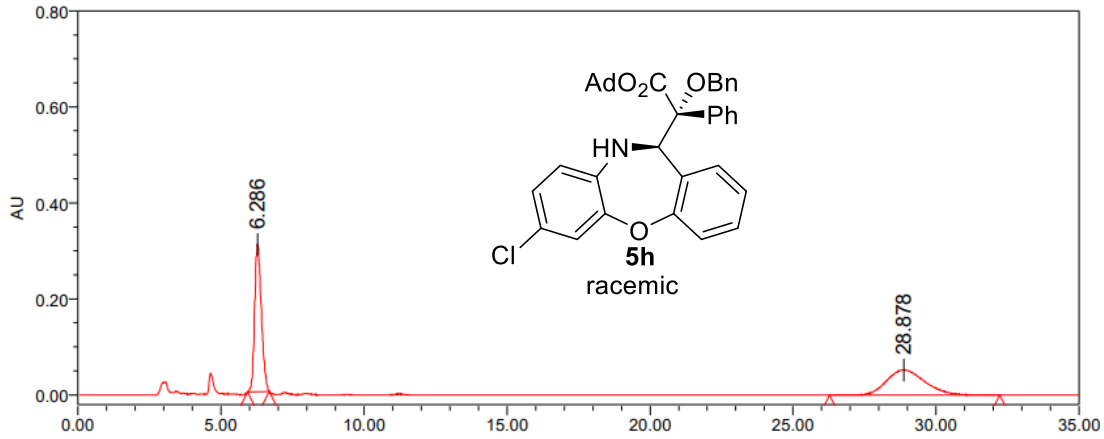
Entry	RT min	Height mV	Area mV.sec	% Area %
1	5.706	16175	201639	50.51
2	28.520	2272	197568	49.49



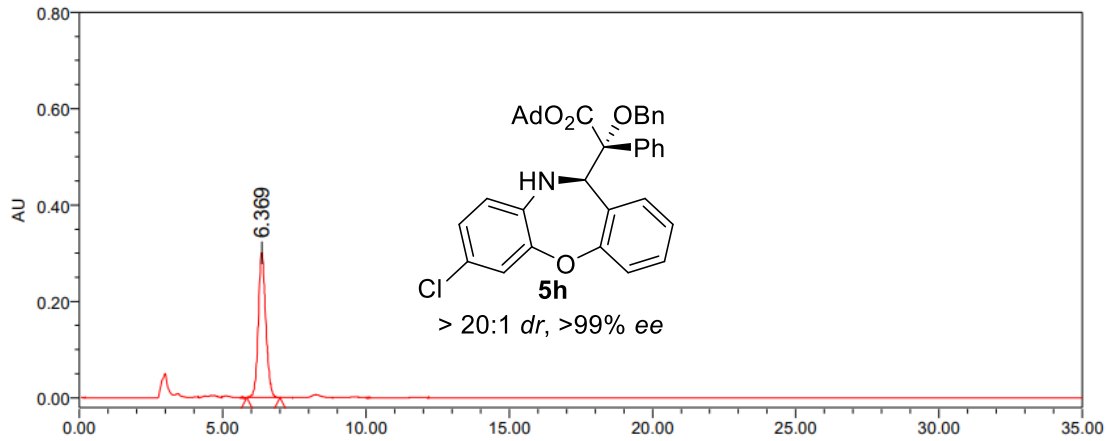
Entry	RT min	Height mV	Area mV.sec	% Area %
1	5.718	26317	411298	100.00

Condition：Chrial AD-H, λ = 217 nm, hexane/isopropanol = 80:20

flow rate = 1.0 mL/min



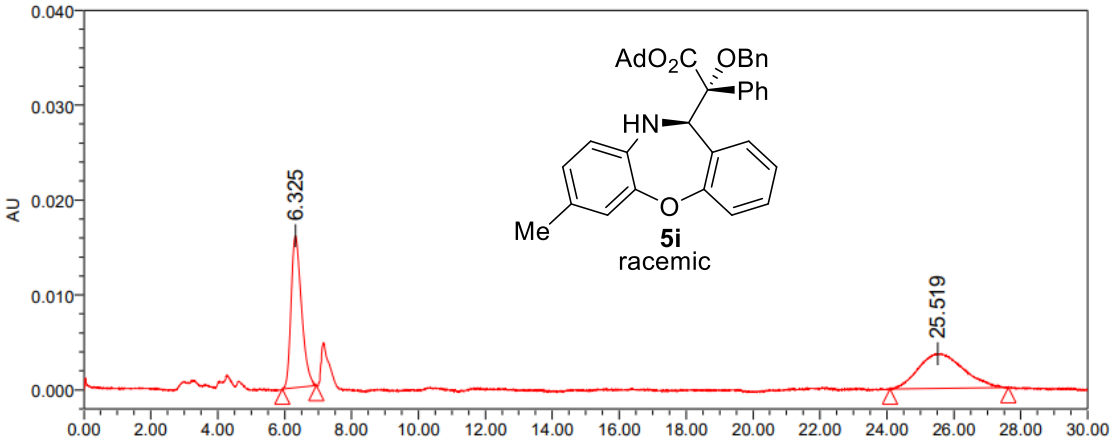
Entry	RT min	Height mV	Area mV.sec	% Area %
1	6.286	307432	5079285	50.79
2	28.878	52533	4921793	49.21s



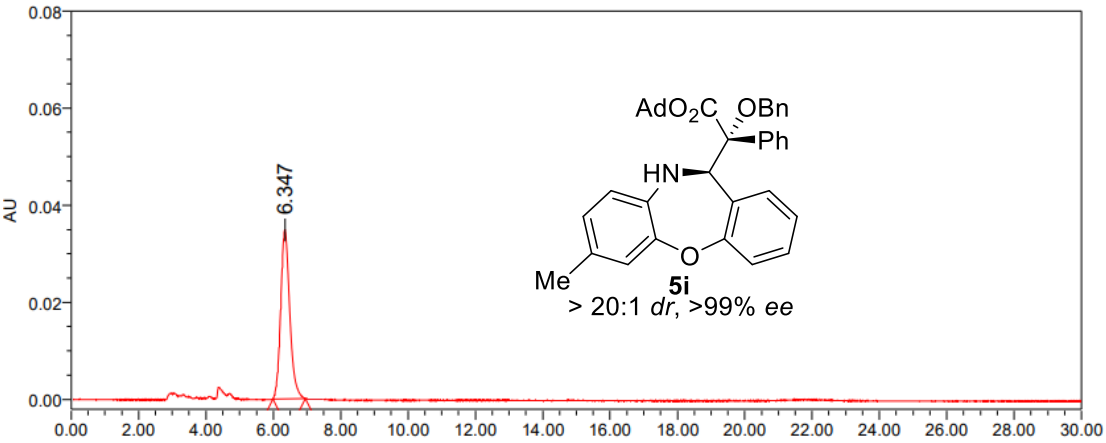
Entry	RT min	Height mV	Area mV.sec	% Area %
1	6.369	300284	5484165	100.00

Condition：Chrial AD-H, λ = 254 nm, hexane/isopropanol = 80:20

flow rate = 1.0 mL/min



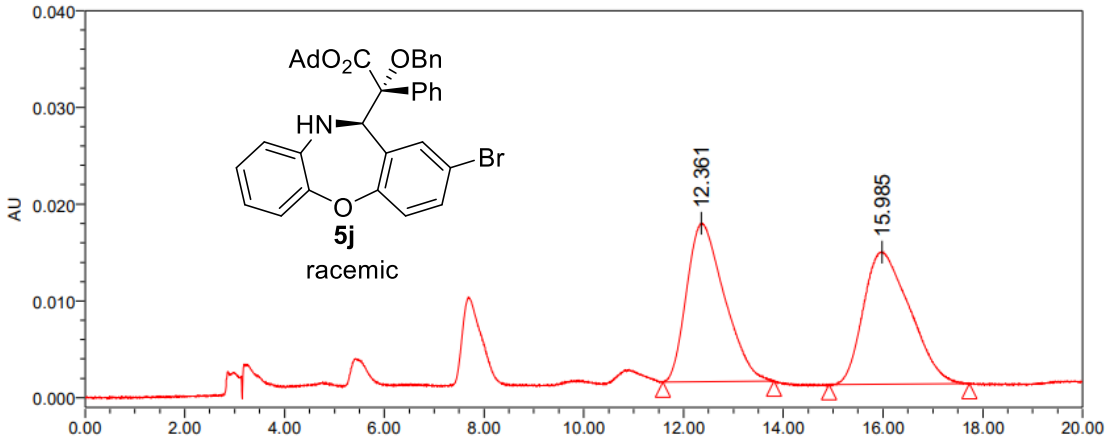
Entry	RT min	Height mV	Area mV.sec	% Area %
1	6.325	16017	341845	49.92
2	25.519	3655	342944	50.02



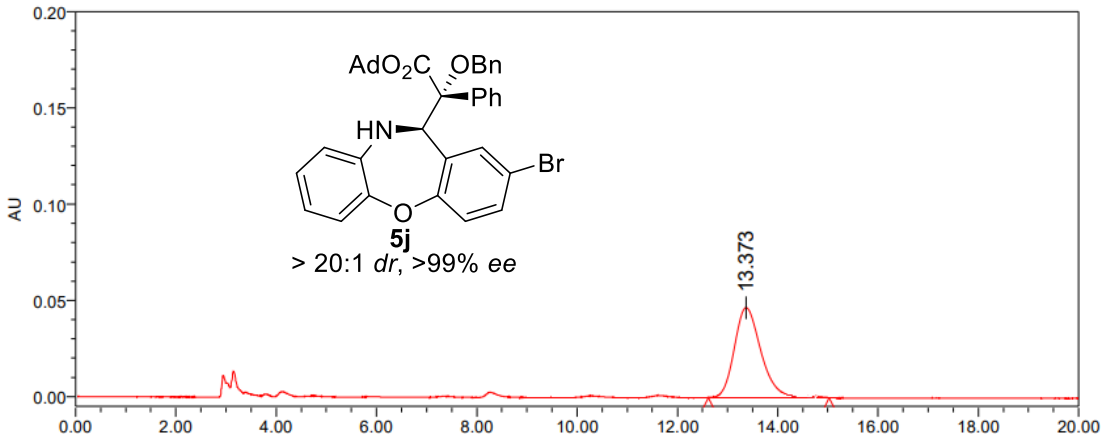
Entry	RT min	Height mV	Area mV.sec	% Area %
1	6.347	34831	655381	100.00

Condition：Chrial AD-H, λ = 254 nm, hexane/isopropanol = 98:2

flow rate = 1.0 mL/min



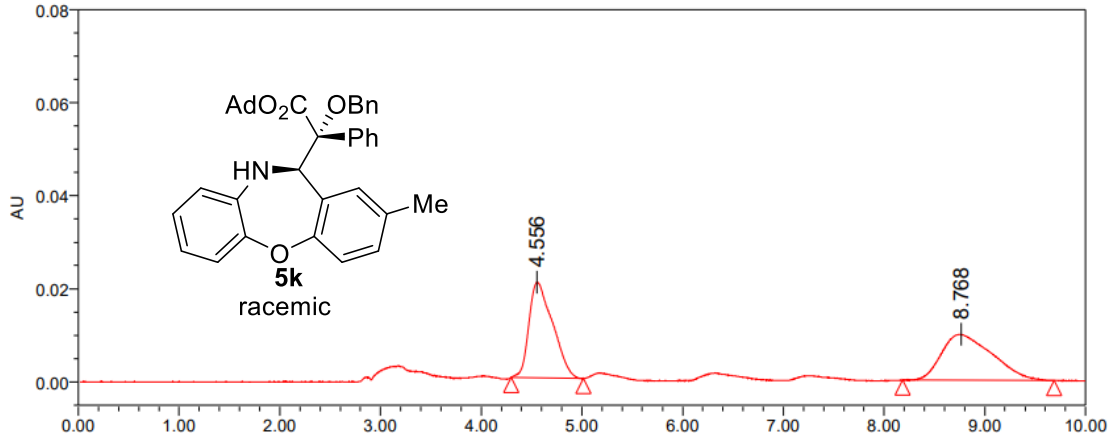
Entry	RT min	Height mV	Area mV.sec	% Area %
1	12.361	16355	858408	49.25
2	15.985	13685	885756	50.75



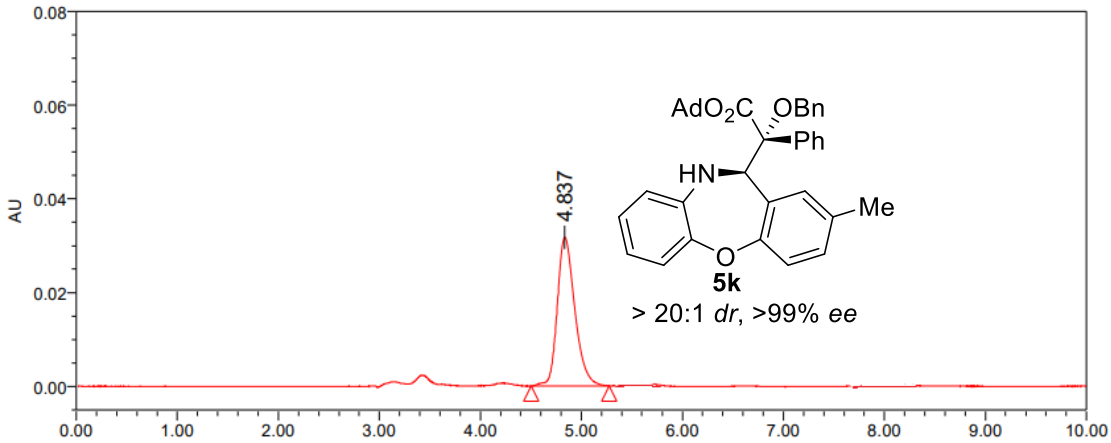
Entry	RT min	Height mV	Area mV.sec	% Area %
1	13.373	46744	176153	100.00

Condition：Chrial AD-H, λ = 254 nm, hexane/isopropanol = 90:10

flow rate = 1.0 mL/min



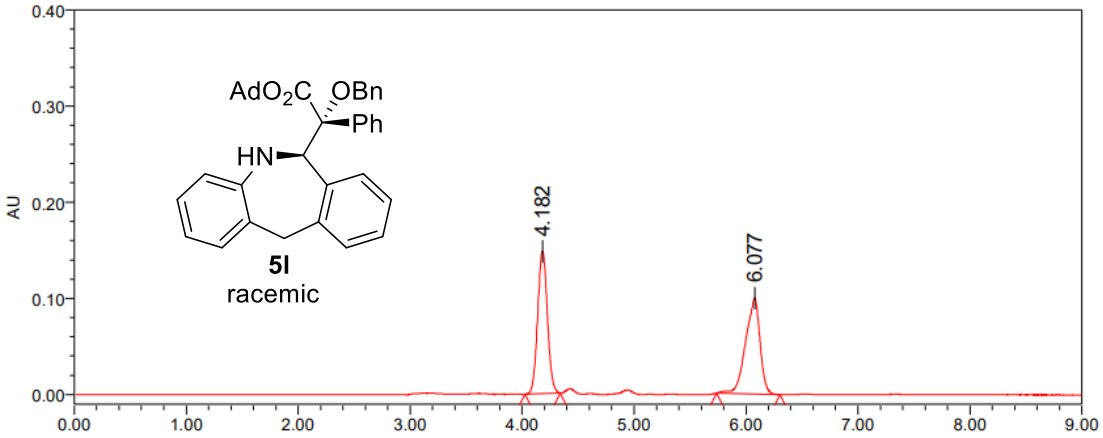
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.556	20587	337314	49.47
2	8.768	9846	344572	50.53



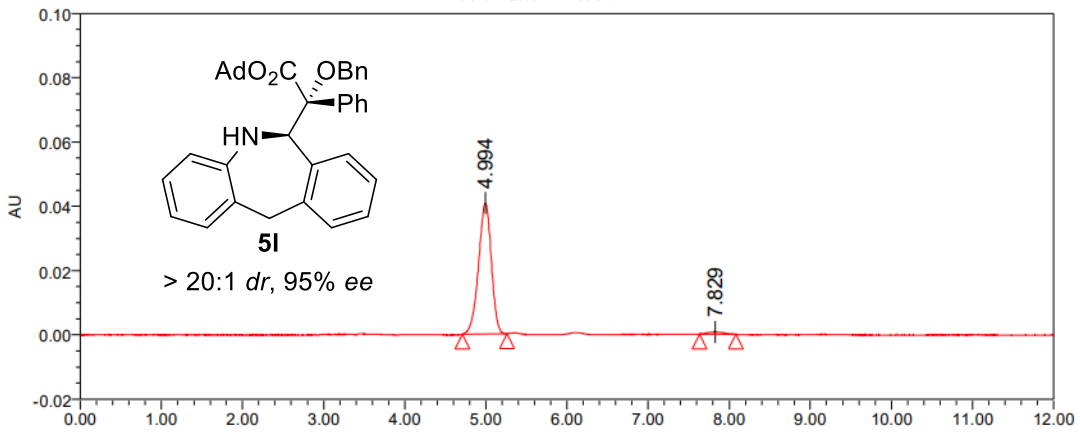
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.837	31695	3822073	100.00

Condition：Chrial IA, λ = 254 nm, hexane/isopropanol = 98:2

flow rate = 1.0 mL/min



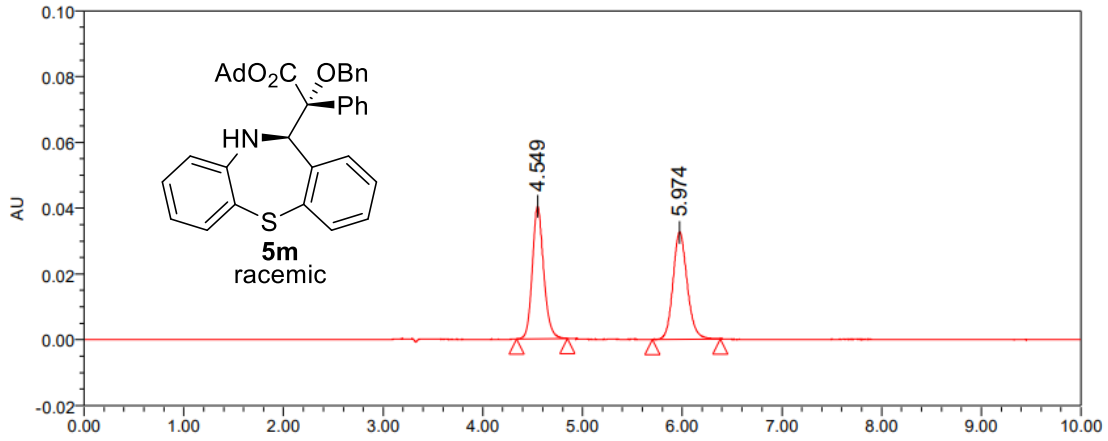
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.182	148027	890600	50.02
2	6.077	99633	889714	49.98



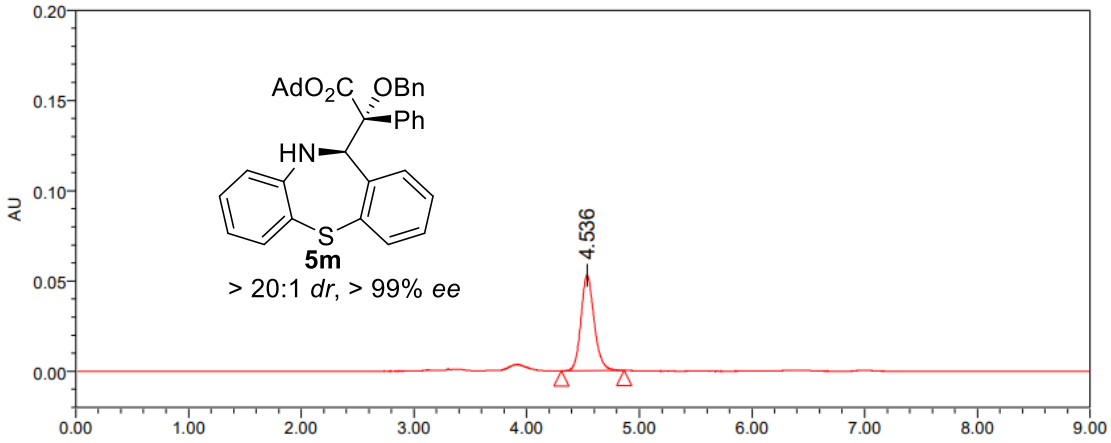
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.994	40692	447766	97.87
2	7.829	703	9738	2.13

Condition：Chrial IA, λ = 304 nm, hexane/isopropanol = 98:2

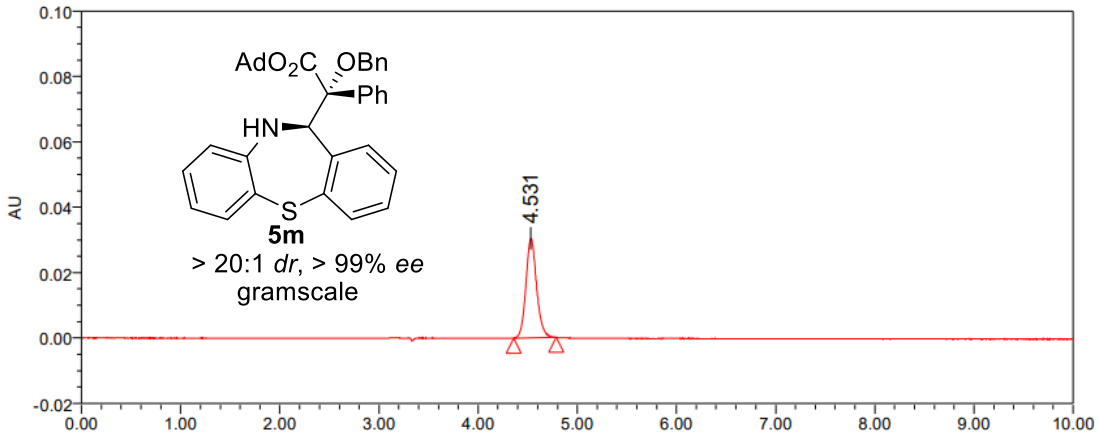
flow rate = 1.0 mL/min



Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.549	40188	318285	49.64
2	5.974	32518	322916	50.36



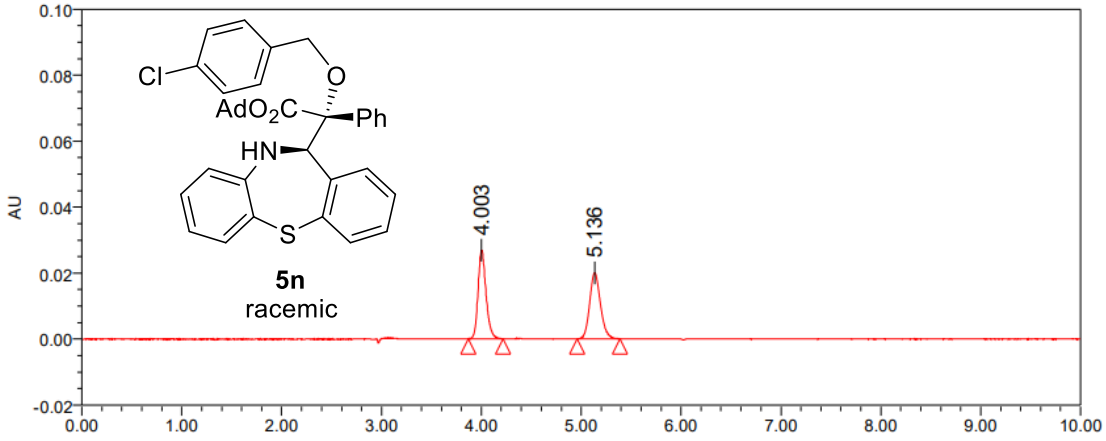
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.536	52971	433363	100.00



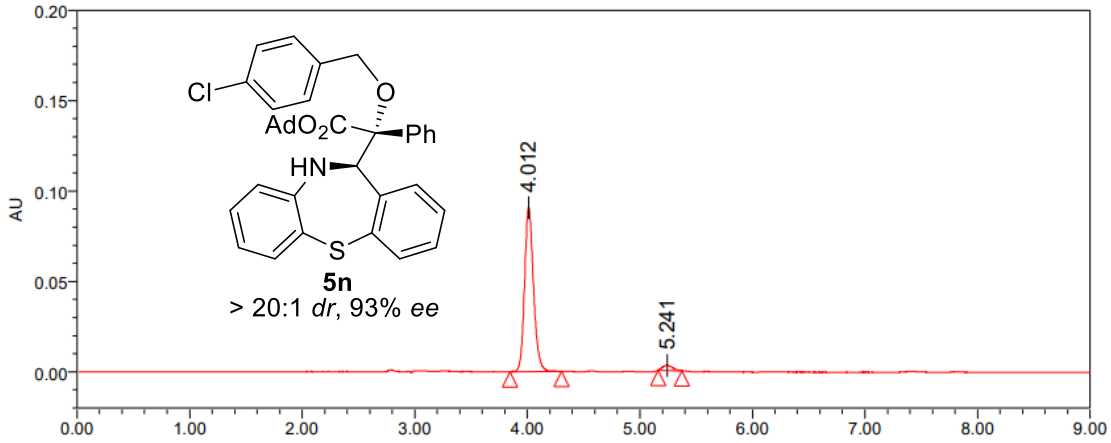
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.531	30423	227628	100.00

Condition：Chrial IA, λ = 312 nm, hexane/isopropanol = 95:5

flow rate = 1.0 mL/min



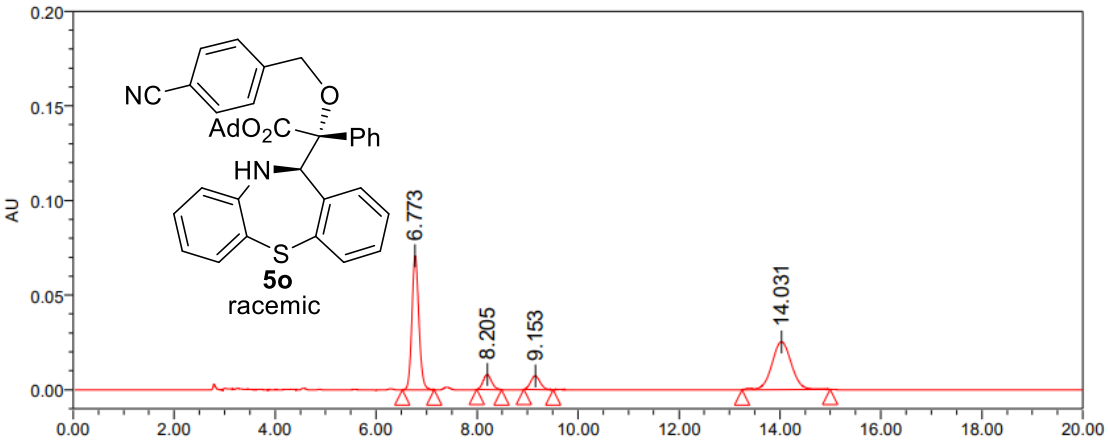
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.003	26874	149490	50.07
2	5.136	20027	149061	49.93



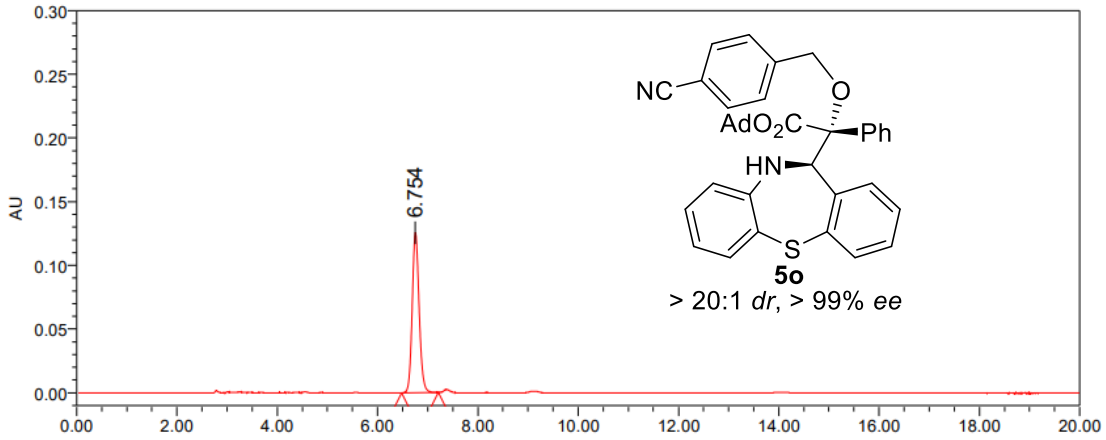
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.012	90778	501477	96.71
2	5.241	2816	17071	3.29

Condition：Chrial IA, λ = 254 nm, hexane/isopropanol = 95:5

flow rate = 1.0 mL/min



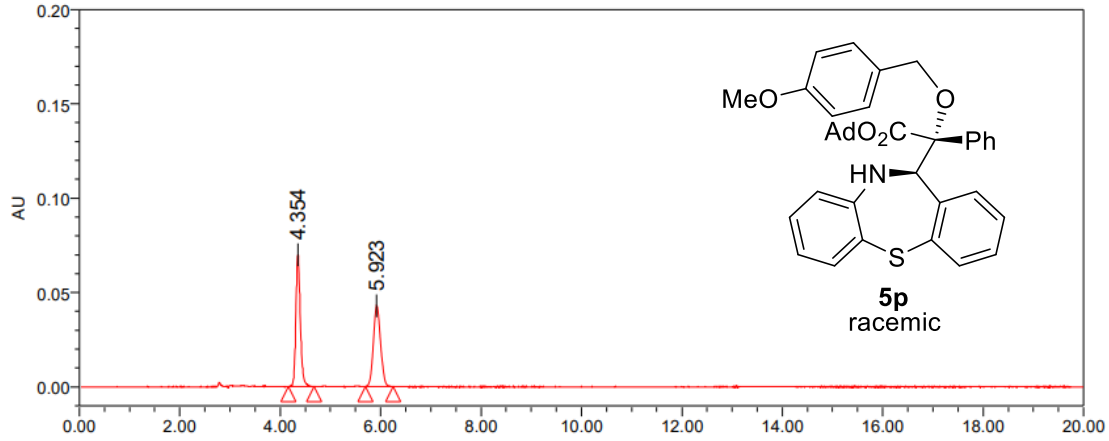
Entry	RT min	Height mV	Area mV.sec	% Area %
1	6.773	70841	676515	44.07
2	8.205	7894	92769	6.04
3	9.153	7201	92912	6.05
4	14.031	25284	672909	43.83



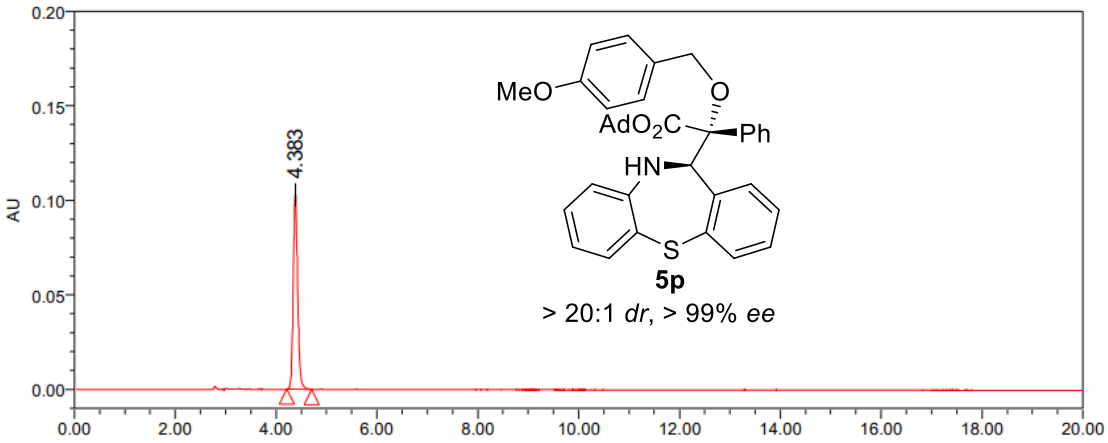
Entry	RT min	Height mV	Area mV.sec	% Area %
1	6.754	125541	1200946	100.00

Condition：Chrial IA, λ = 254 nm, hexane/isopropanol = 95:5

flow rate = 1.0 mL/min



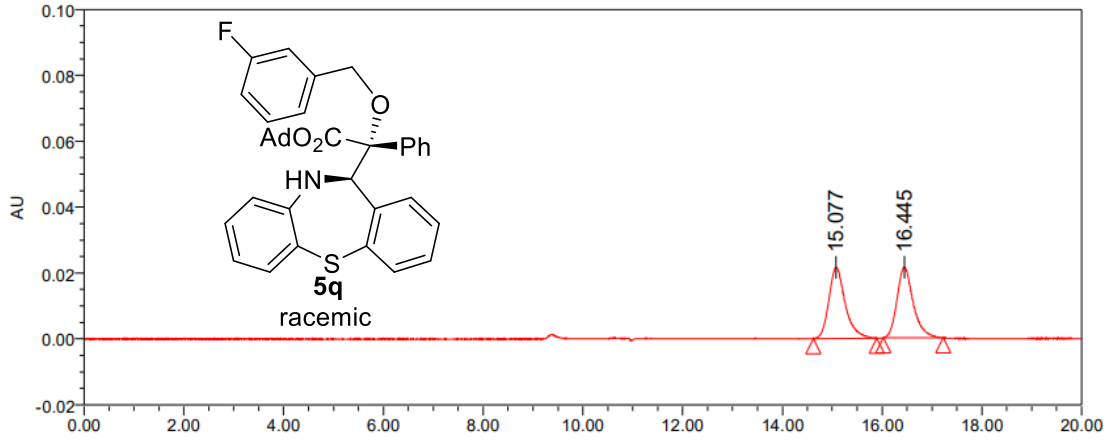
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.354	69924	433980	50.51
2	5.923	42773	425145	49.49



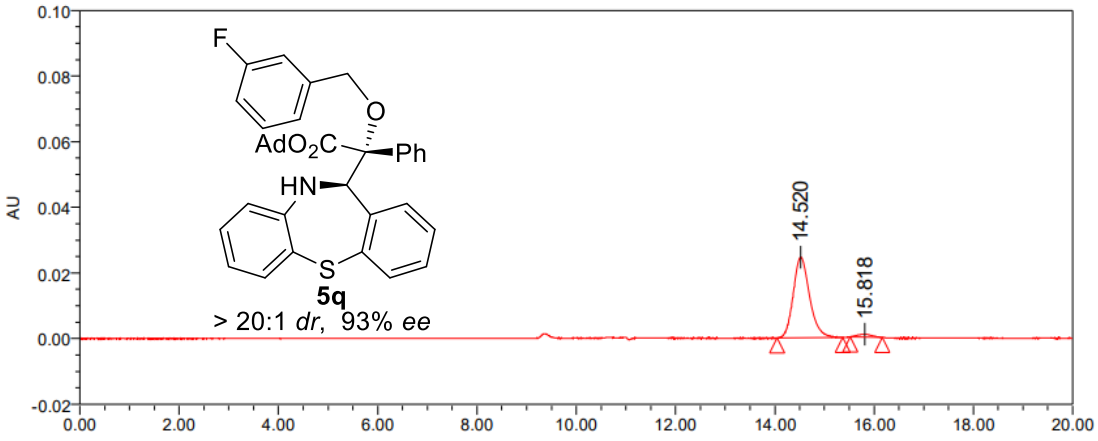
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.383	103052	628456	100.00

Condition：Chrial IA, λ = 310 nm, hexane/isopropanol = 98:2

flow rate = 0.3 mL/min



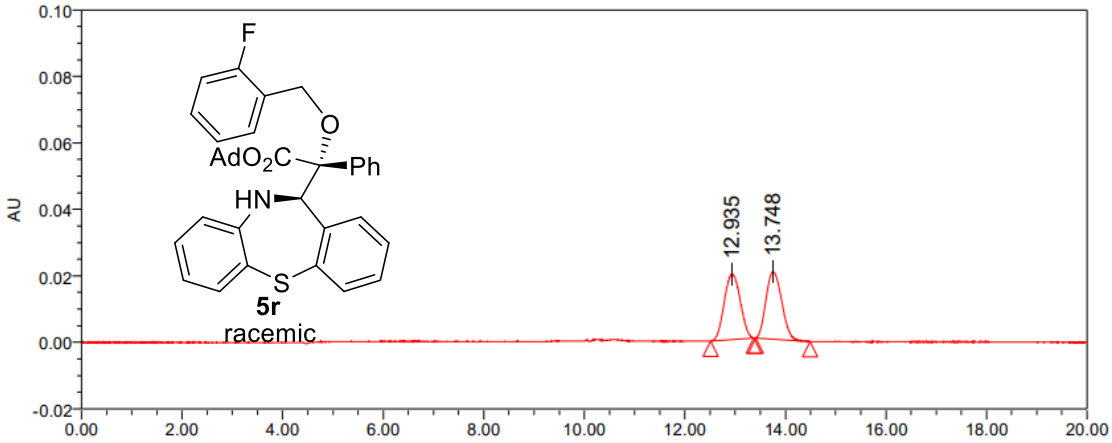
Entry	RT min	Height mV	Area mV.sec	% Area %
1	15.077	21569	493208	50.37
2	16.445	21414	485947	49.63



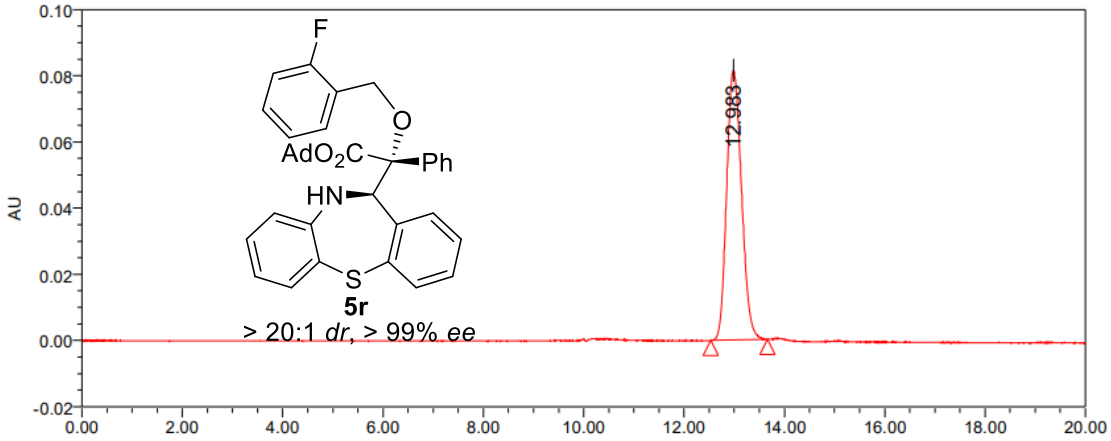
Entry	RT min	Height mV	Area mV.sec	% Area %
1	14.520	24543	558035	96.89
2	15.818	862	17923	3.11

Condition：Chrial IA, λ = 330 nm, hexane/isopropanol = 95:5

flow rate = 0.3 mL/min



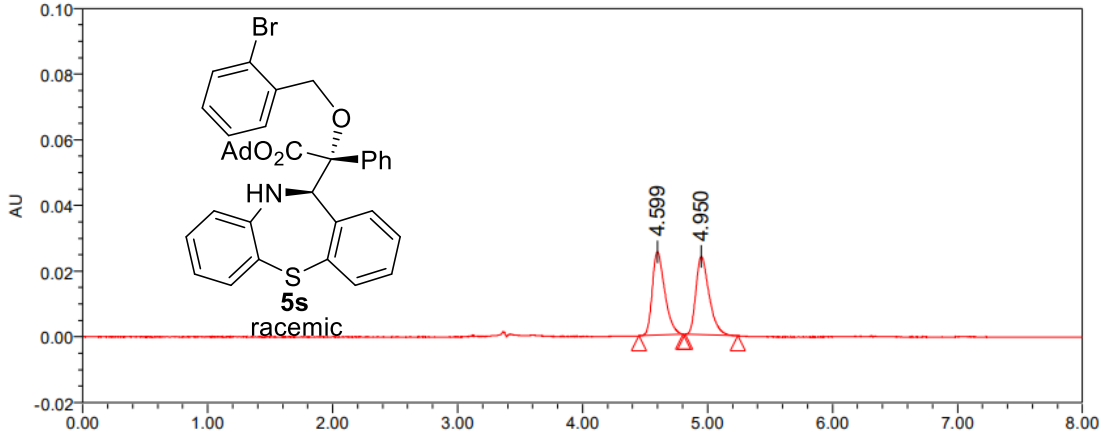
Entry	RT min	Height mV	Area mV.sec	% Area %
1	12.935	19672	440518	50.19
2	13.748	20274	437143	49.81



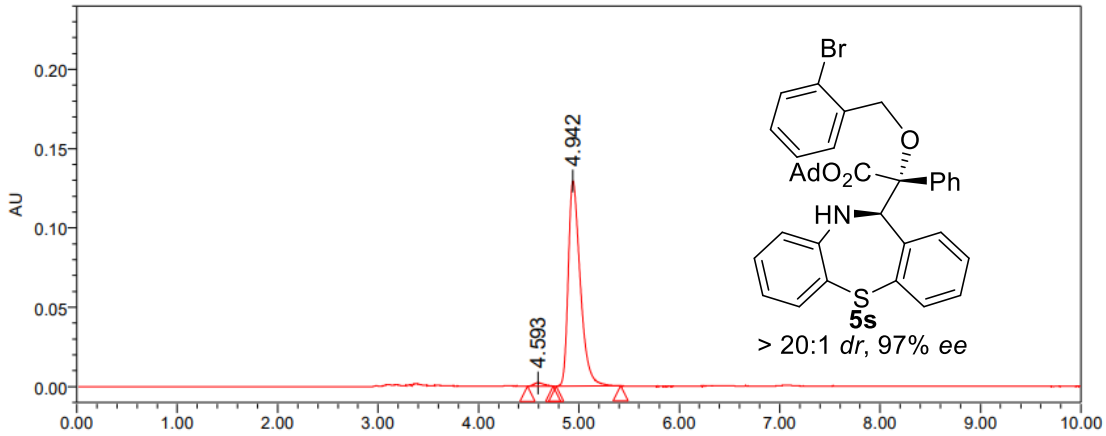
Entry	RT min	Height mV	Area mV.sec	% Area %
1	12.983	81519	1694884	100.00

Condition：Chrial IF-3, λ = 254 nm, hexane/isopropanol = 98:2

flow rate = 1.0 mL/min



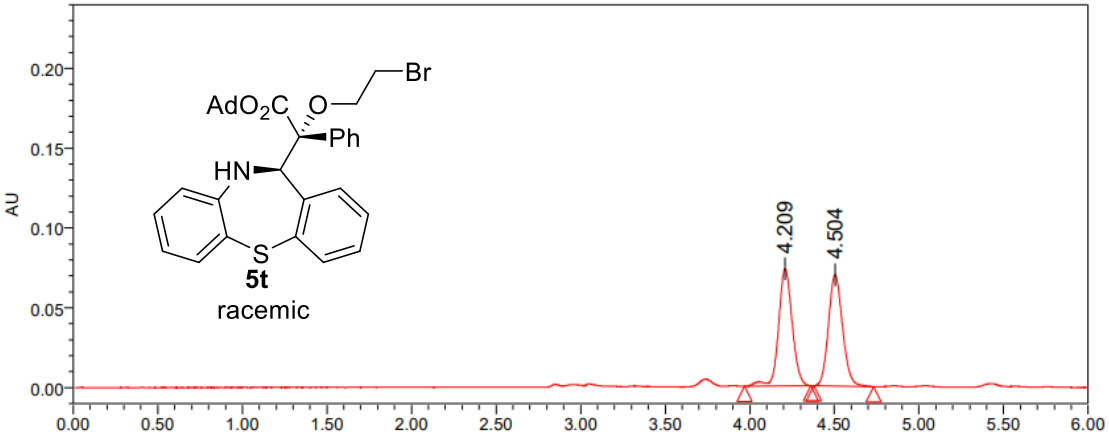
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.599	25395	175768	49.92
2	4.950	23894	176339	50.08



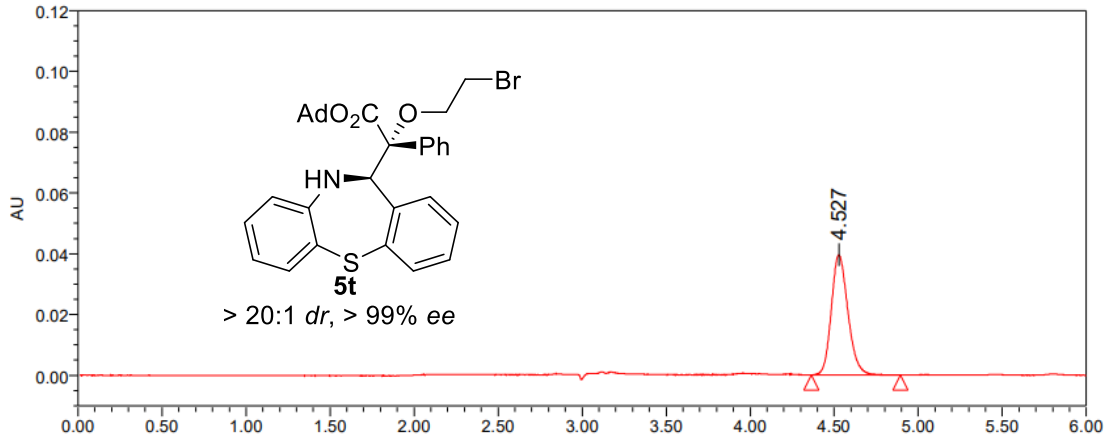
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.593	2097	14457	1.33
2	4.942	129259	1070316	98.63

Condition：Chrial IA, λ = 254 nm, hexane/isopropanol = 95:5

flow rate = 1.0 mL/min



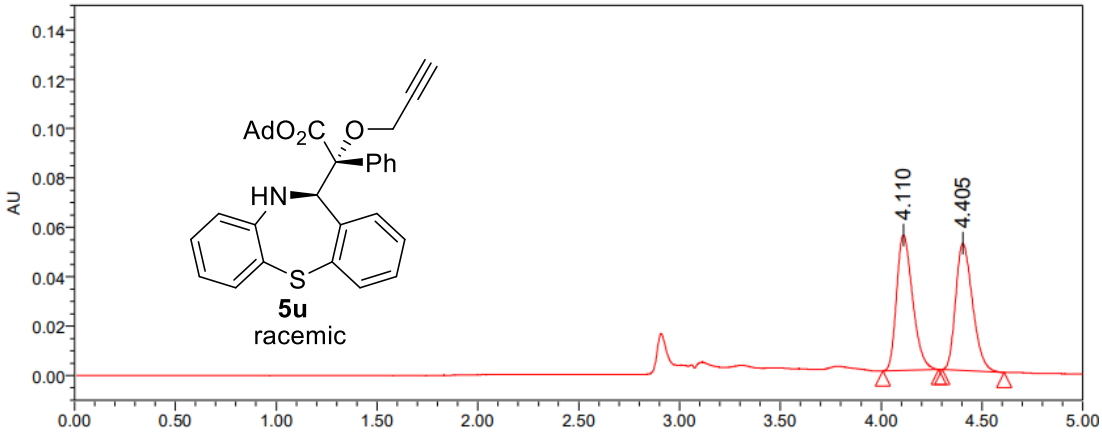
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.209	73638	414935	50.51
2	4.504	69780	406534	49.49



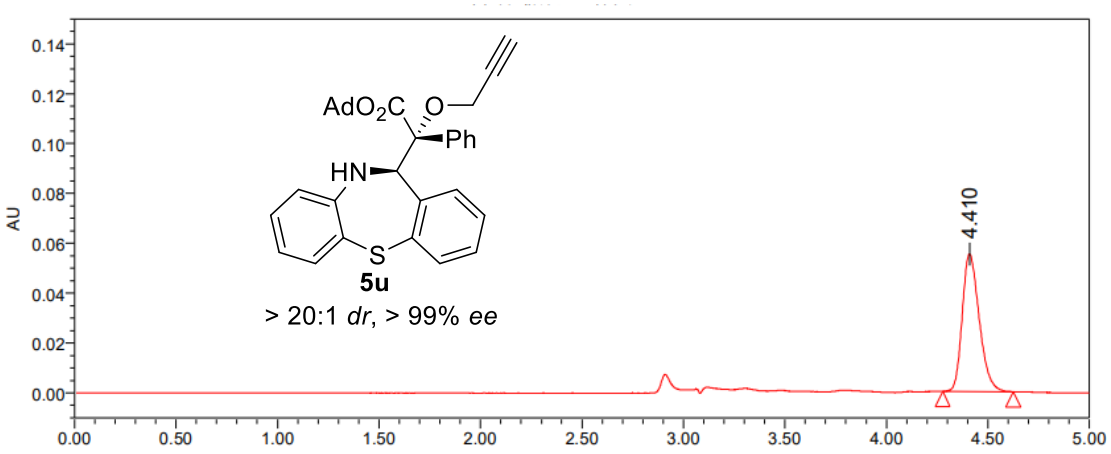
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.527	39474	270401	100.00

Condition：Chrial IF-3, λ = 254 nm, hexane/isopropanol = 95:5

flow rate = 1.0 mL/min



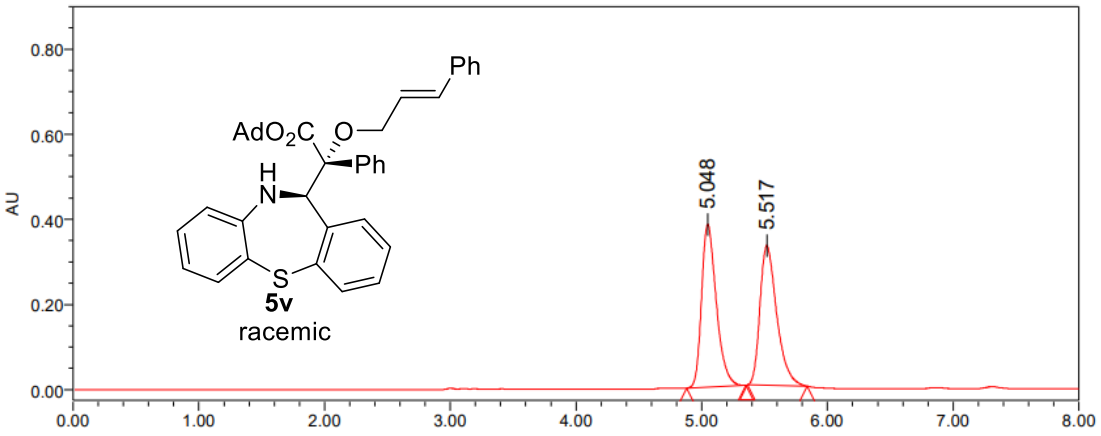
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.110	54941	303847	50.36
2	4.405	51501	299562	49.64



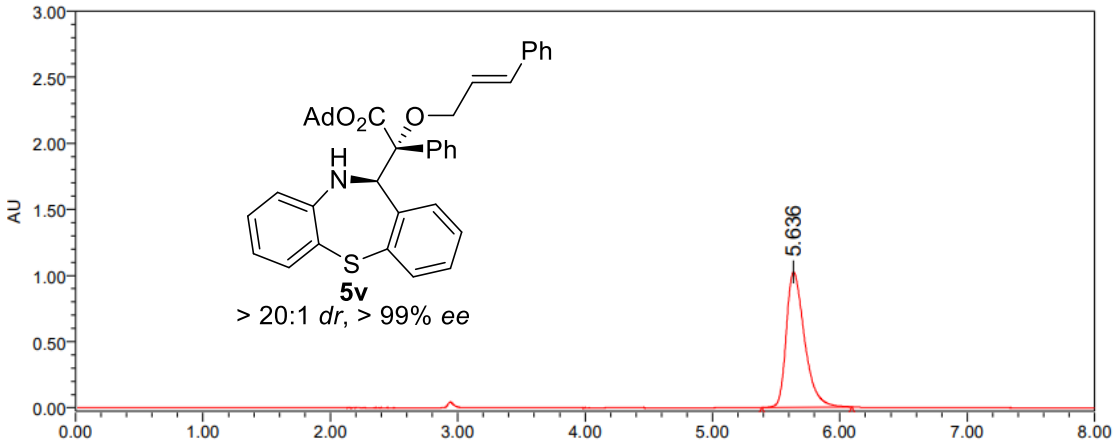
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.410	55230	321535	100.00

Condition：Chrial IF-3, λ = 254 nm, hexane/isopropanol = 98:2

flow rate = 1.0 mL/min



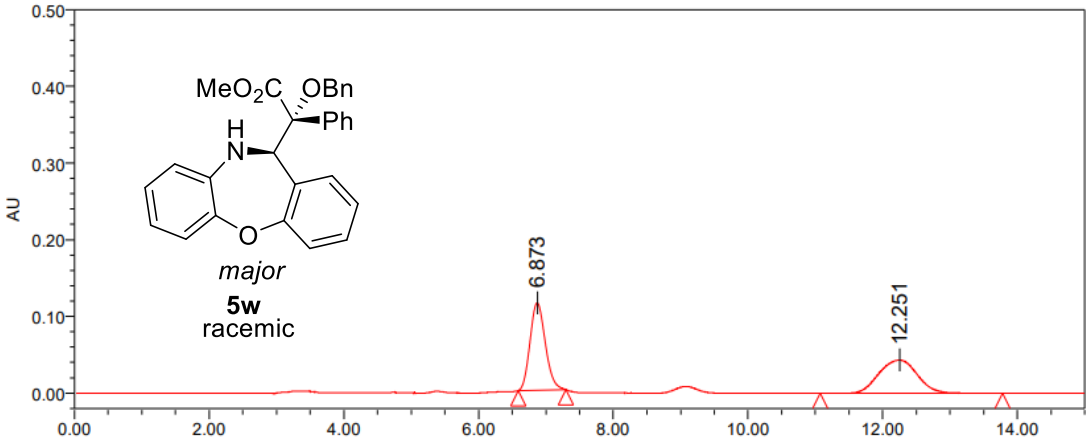
Entry	RT min	Height mV	Area mV.sec	% Area %
1	5.048	382340	3120386	50.53
2	5.517	328359	3054796	49.47



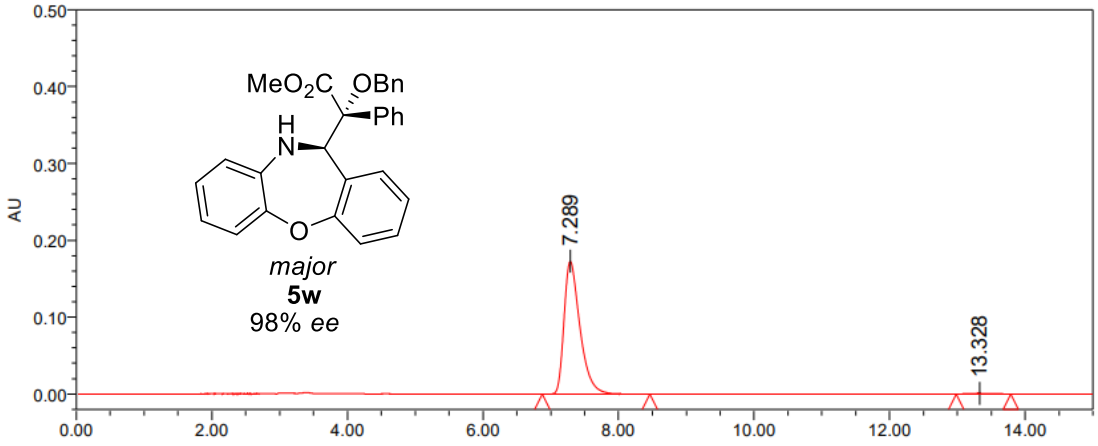
Entry	RT min	Height mV	Area mV.sec	% Area %
1	5.636	1023637	10164931	100.00

Condition：Chrial AD-H, λ = 254 nm, hexane/isopropanol = 90:10

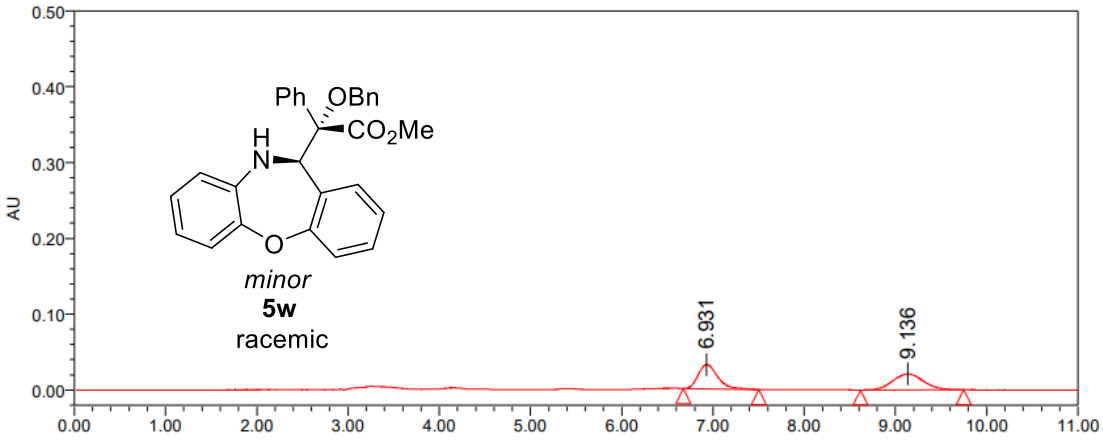
flow rate = 1.0 mL/min



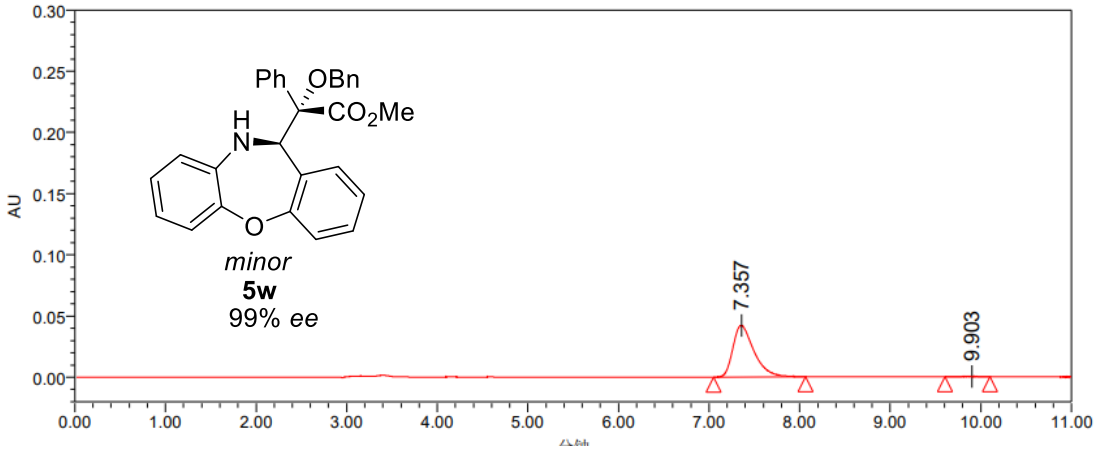
Entry	RT min	Height mV	Area mV.sec	% Area %
1	6.873	113866	1795557	50.78
2	12.251	43517	1740674	49.22



Entry	RT min	Height mV	Area mV.sec	% Area %
1	7.289	172730	2809339	99.15
2	13.328	1021	23996	0.85



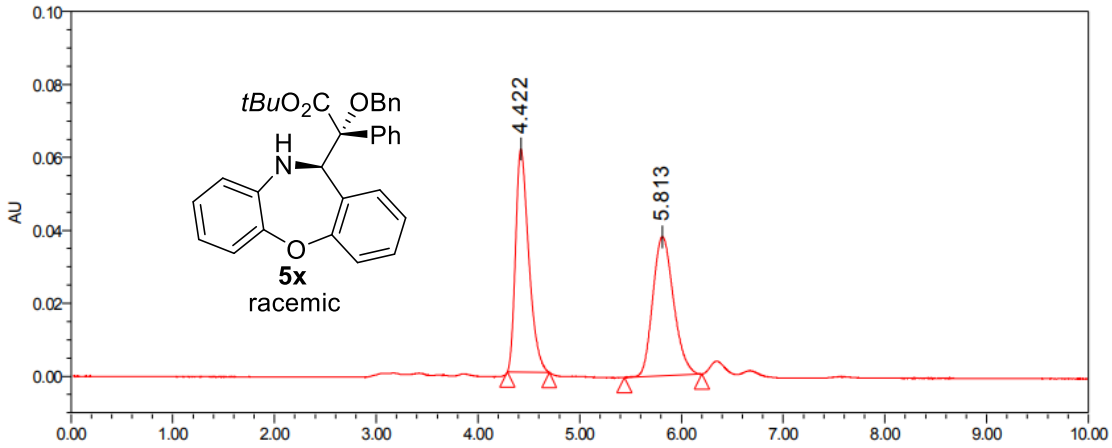
Entry	RT min	Height mV	Area mV.sec	% Area %
1	6.931	32229	484381	49.51
2	9.136	21011	493921	50.29



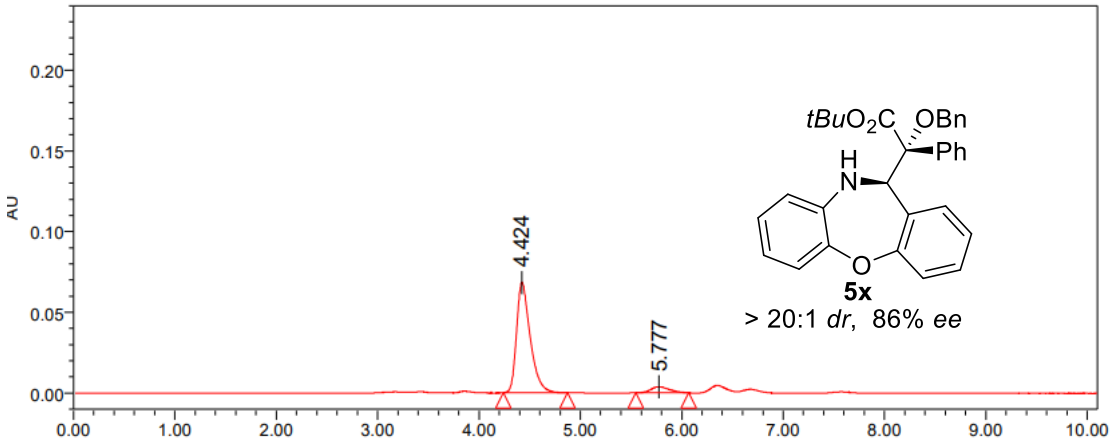
Entry	RT min	Height mV	Area mV.sec	% Area %
1	7.357	42158	675354	99.53
2	9.903	209	3192	0.47

Condition：Chrial AD-H, λ = 254 nm, hexane/isopropanol = 80:20

flow rate = 1.0 mL/min



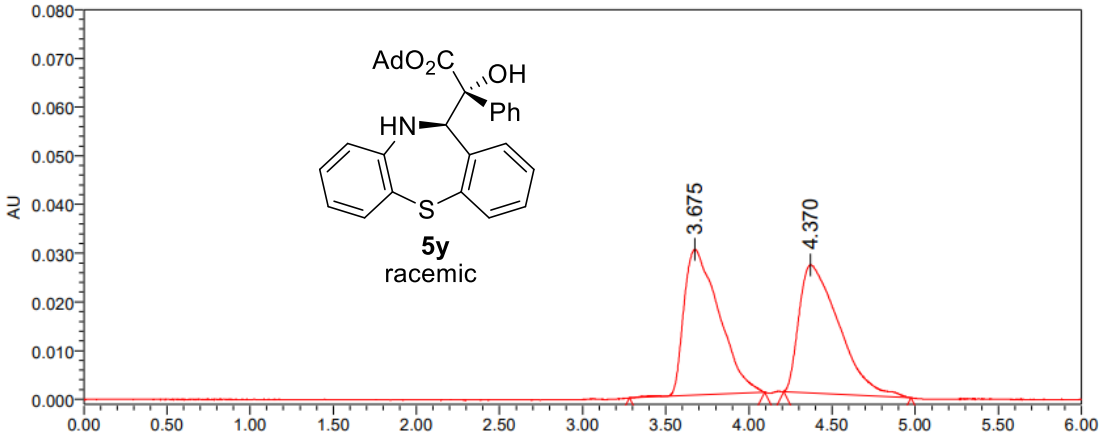
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.422	61156	551901	50.42
2	5.813	38114	542765	49.58



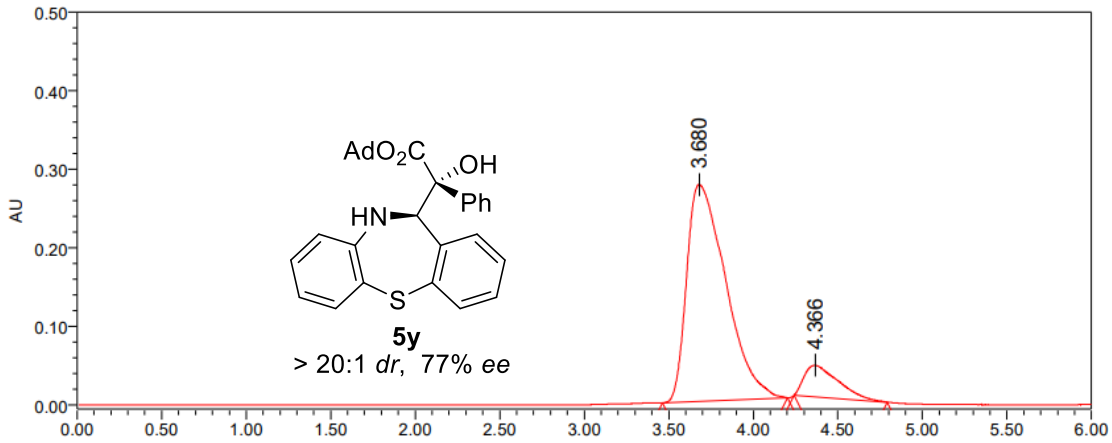
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.424	68374	638433	93.21
2	5.777	3712	46522	6.79

Condition：Chrial IC, λ = 254 nm, hexane/isopropanol = 70:30

flow rate = 1.0 mL/min



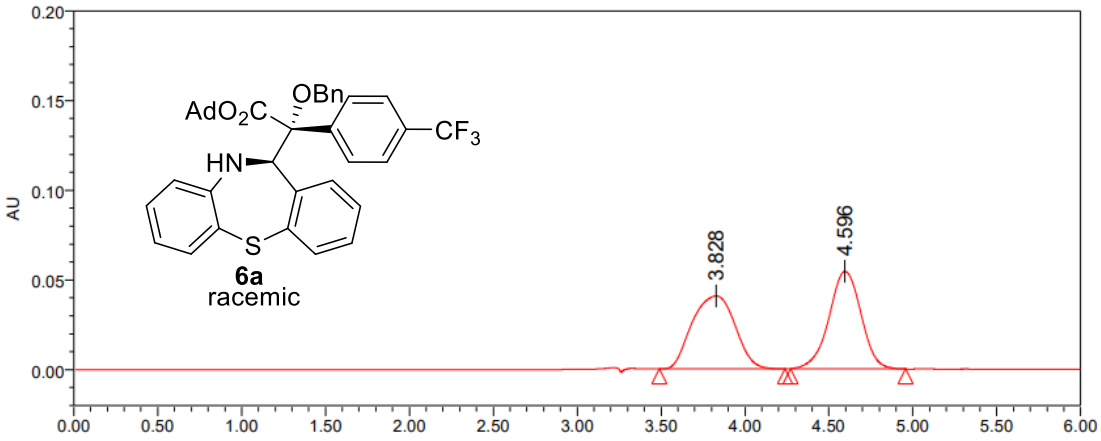
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.675	439443	29886	50.0
2	4.370	439484	26281	50.0



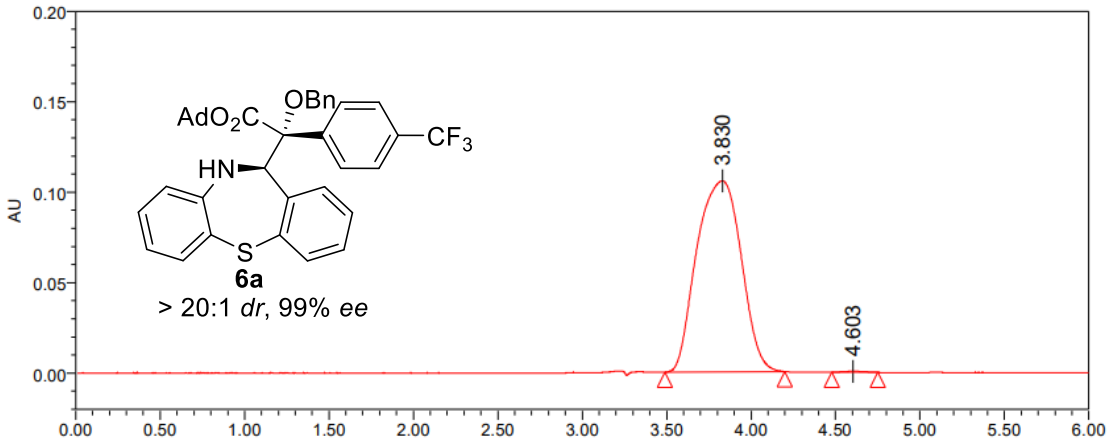
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.680	4438610	275798	88.78
2	4.366	560750	39858	11.22

Condition：Chrial IA, λ = 300 nm, hexane/isopropanol = 98:2

flow rate = 1.0 mL/min



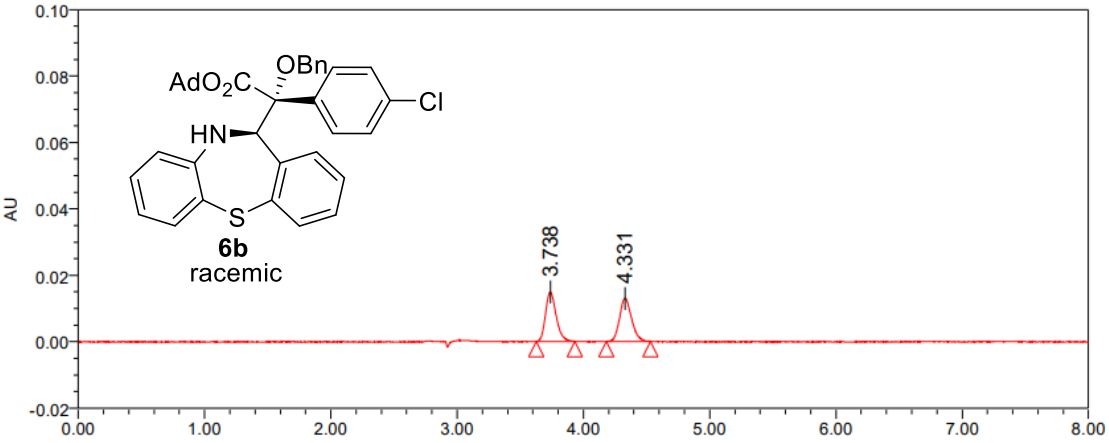
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.838	40746	725294	50.19
2	4.596	54281	719924	49.81



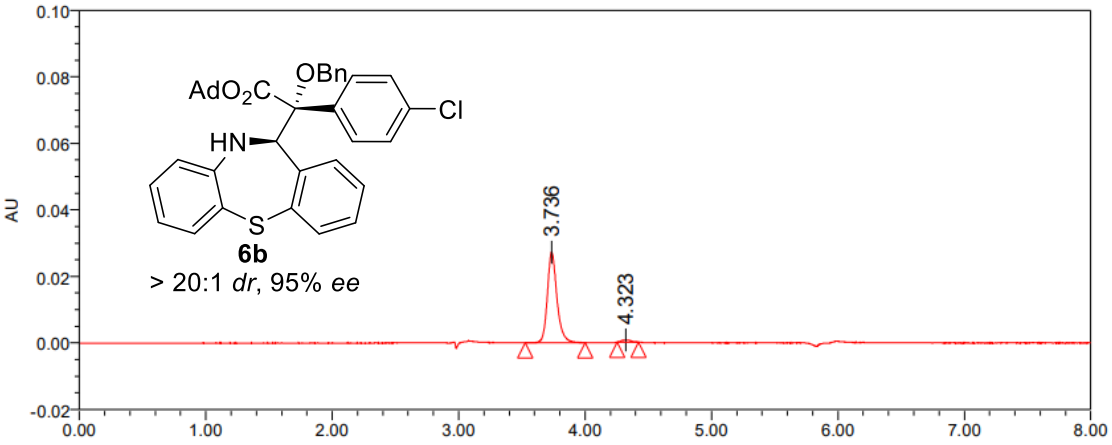
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.830	105622	1941465	99.74
2	4.603	548	5069	0.26

Condition：Chrial IA, λ = 330 nm, hexane/isopropanol = 95:5

flow rate = 1.0 mL/min



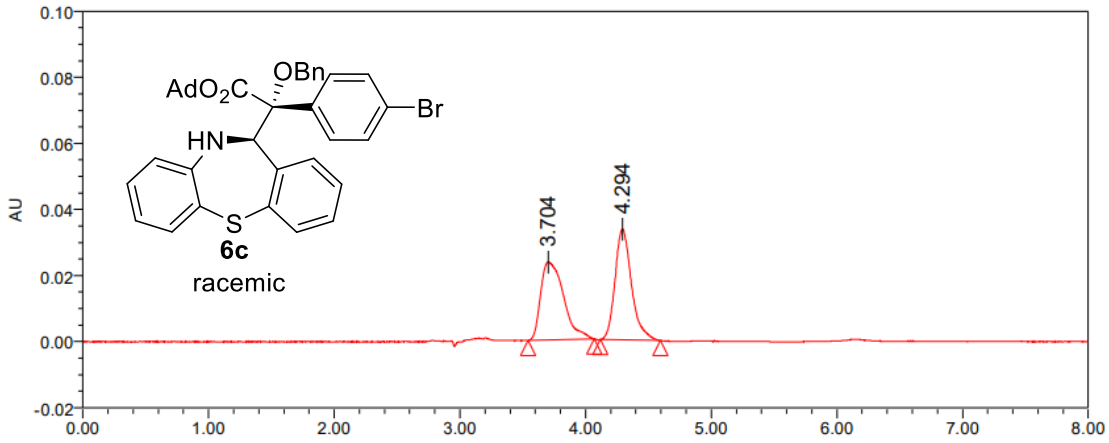
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.738	14900	86896	50.04
2	4.331	13028	86746	49.96



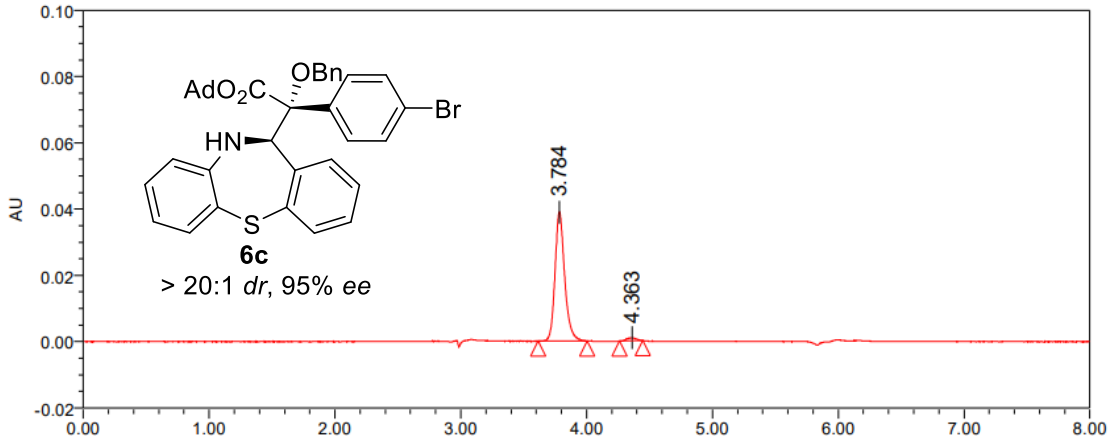
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.736	27211	143026	97.79
2	4.323	654	3231	2.21

Condition：Chrial IA, λ = 300 nm, hexane/isopropanol = 95:5

flow rate = 1.0 mL/min



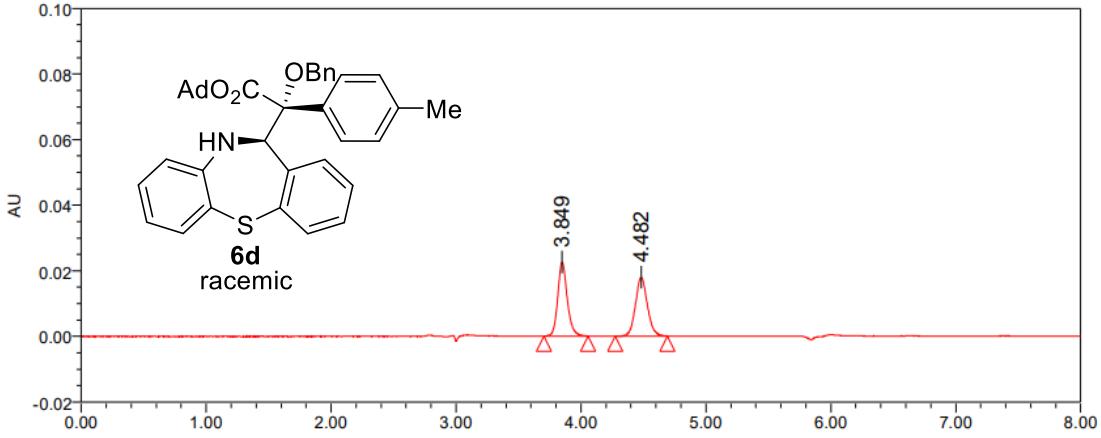
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.704	23594	299335	49.40
2	4,294	33557	306545	50.60



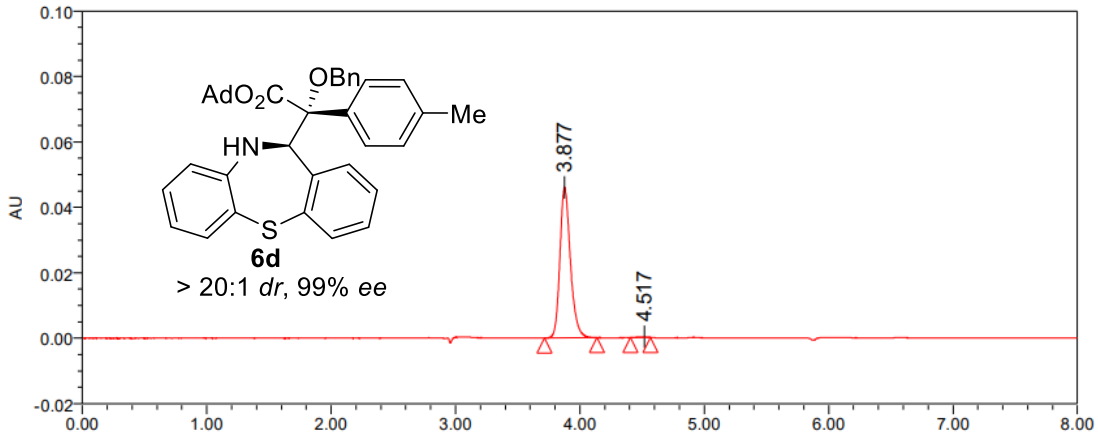
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.784	38969	207591	97.61
2	4.363	940	5073	2.39

Condition：Chrial IA, λ = 310 nm, hexane/isopropanol = 95:5

flow rate = 1.0 mL/min



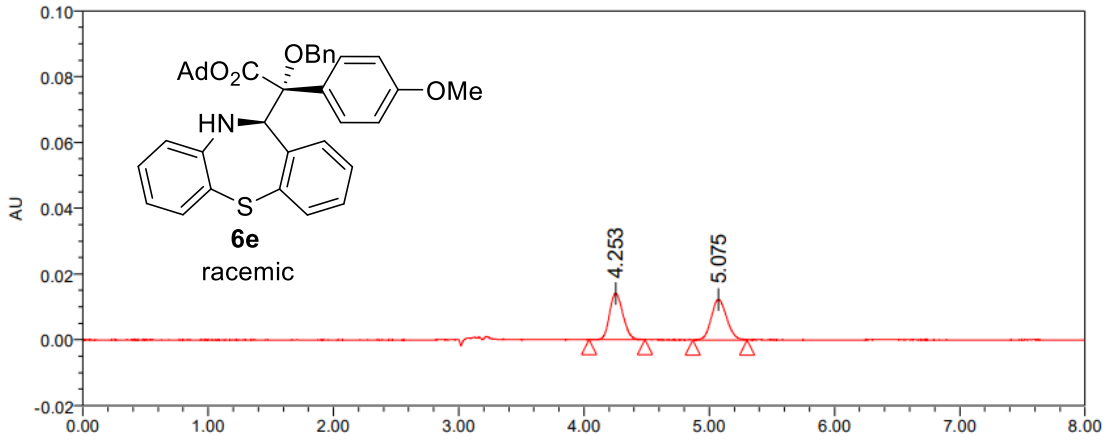
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.849	22529	118945	49.93
2	4.482	17927	119279	50.07



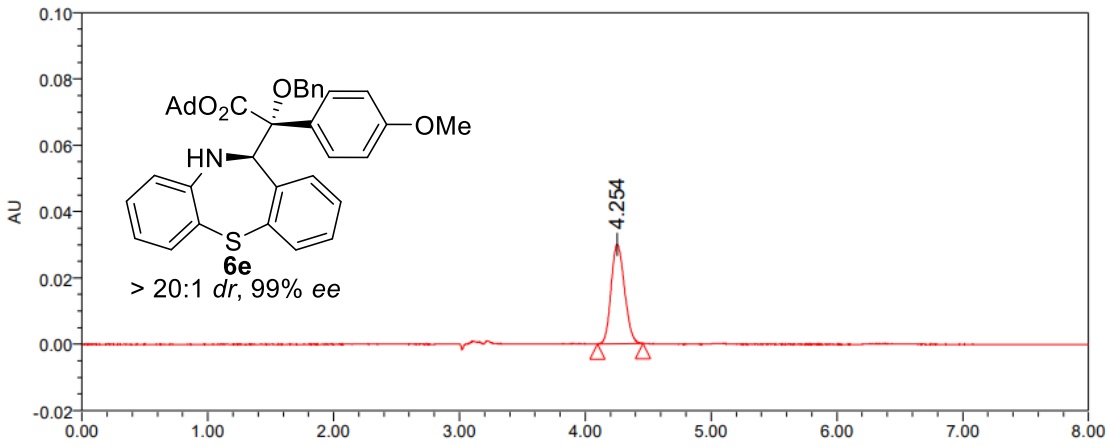
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.877	46051	269187	99.58
2	4.517	234	1143	0.42

Condition：Chrial IA, λ = 330 nm, hexane/isopropanol = 95:5

flow rate = 1.0 mL/min



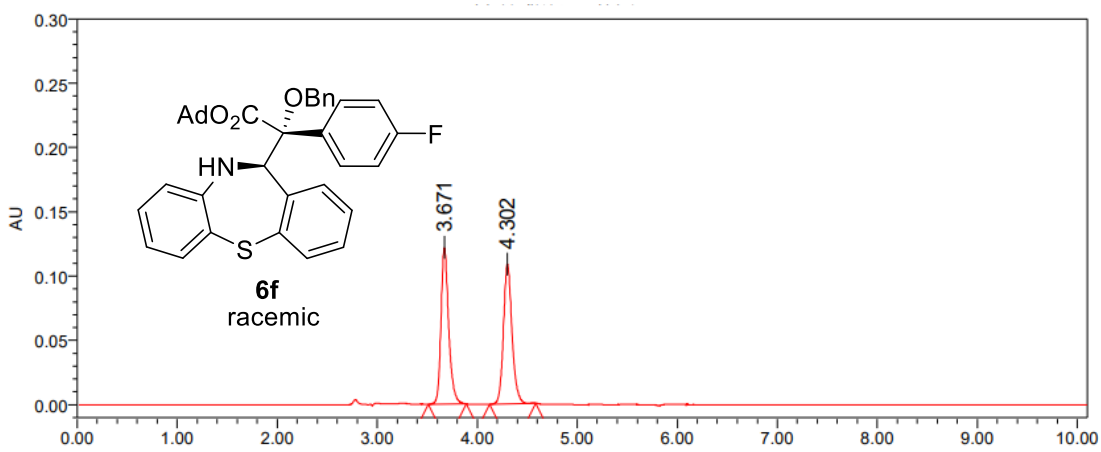
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.253	14016	103555	49.85
2	5.075	12266	104198	50.15



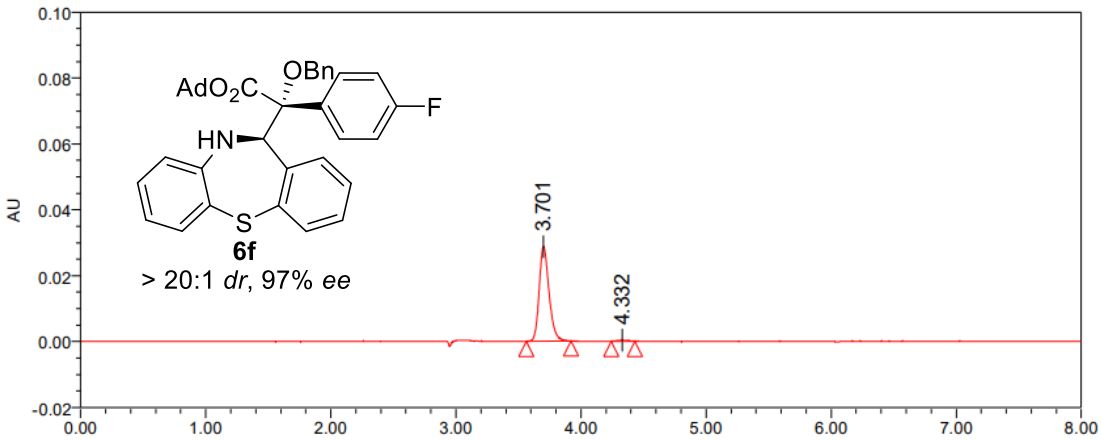
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.254	29965	221794	100.00

Condition：Chrial IA, λ = 300 nm, hexane/isopropanol = 95:5

flow rate = 1.0 mL/min



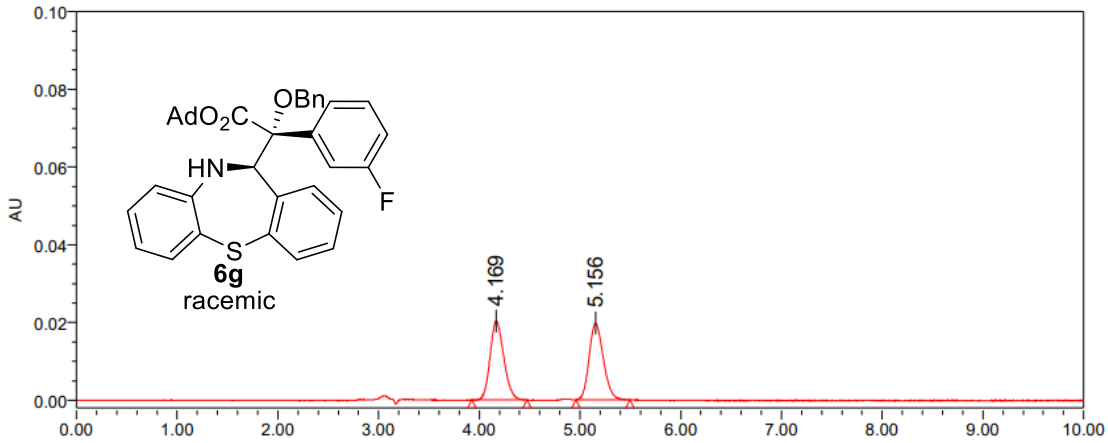
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.671	122053	651878	50.06
2	4.302	108707	650433	49.94



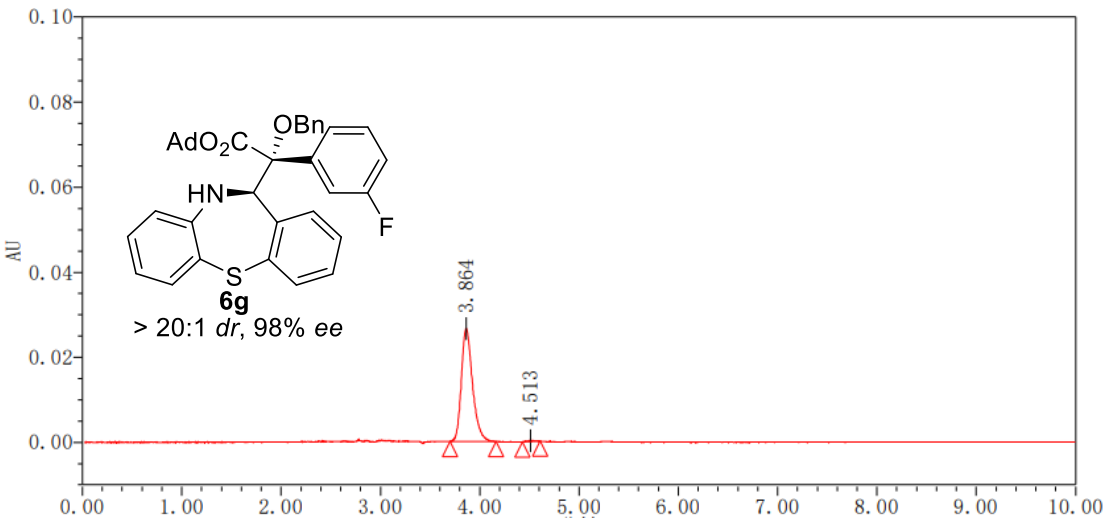
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.701	28774	157658	98.86
2	4.332	331	1815	1.14

Condition：Chrial IA, λ = 300nm, hexane/isopropanol = 98:2

flow rate = 1.0 mL/min



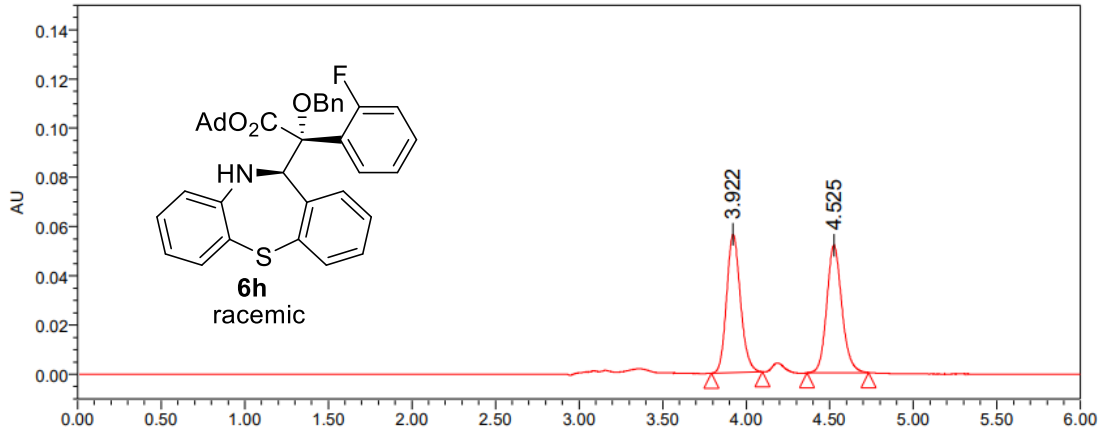
Entry	RT min	Height mV	Area mV.sec	% Area %
1	4.169	20268	192859	50.05
2	5.156	19708	192435	49.95



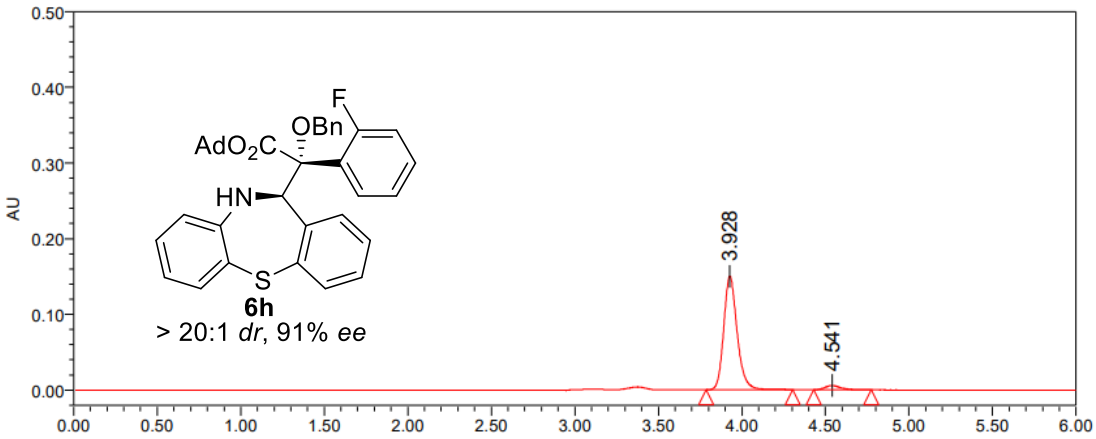
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.864	26507	206421	99.52
2	4.513	220	1169	1.48

Condition：Chrial IA, λ = 254 nm, hexane/isopropanol = 90:10

flow rate = 1.0 mL/min



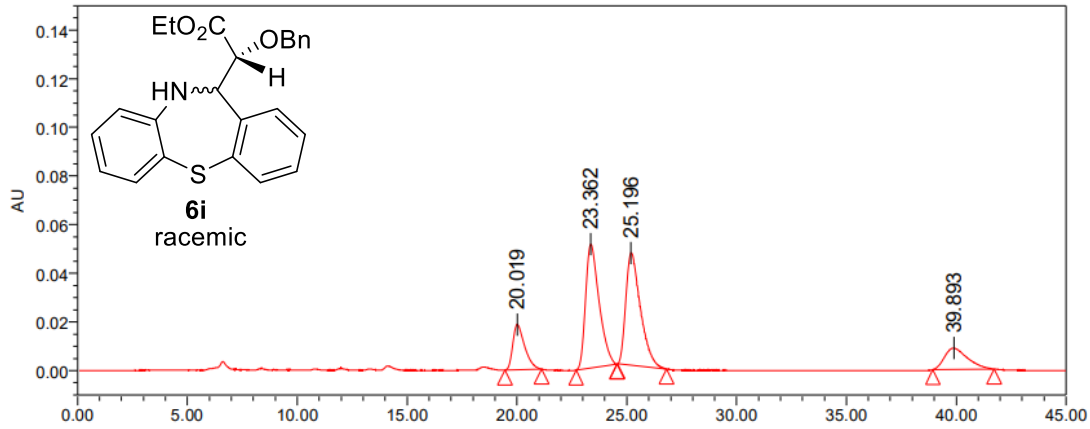
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.922	56287	323758	49.83
2	4.525	51791	325919	50.17



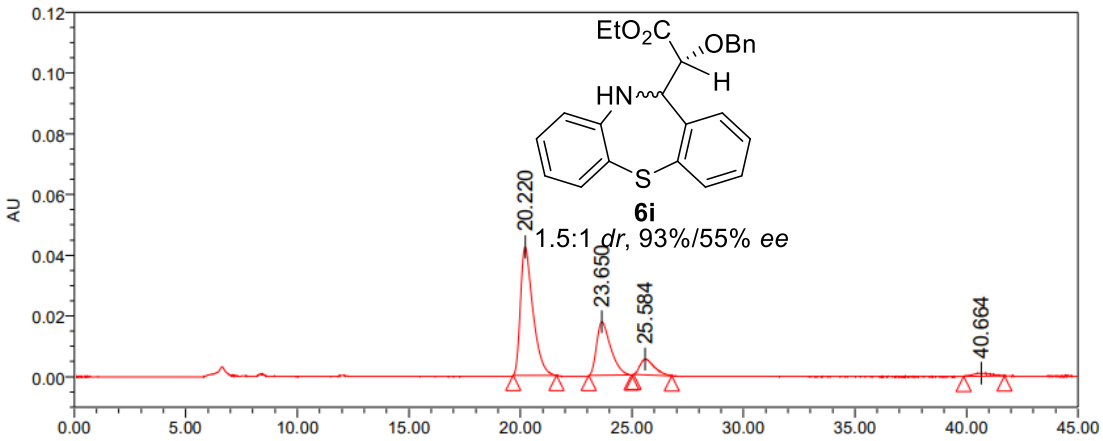
Entry	RT min	Height mV	Area mV.sec	% Area %
1	3.928	150171	840569	95.79
2	4.541	5680	36964	4.21

Condition：Chrial AD-H, λ = 300 nm, hexane/isopropanol = 80:20

flow rate = 0.5 mL/min



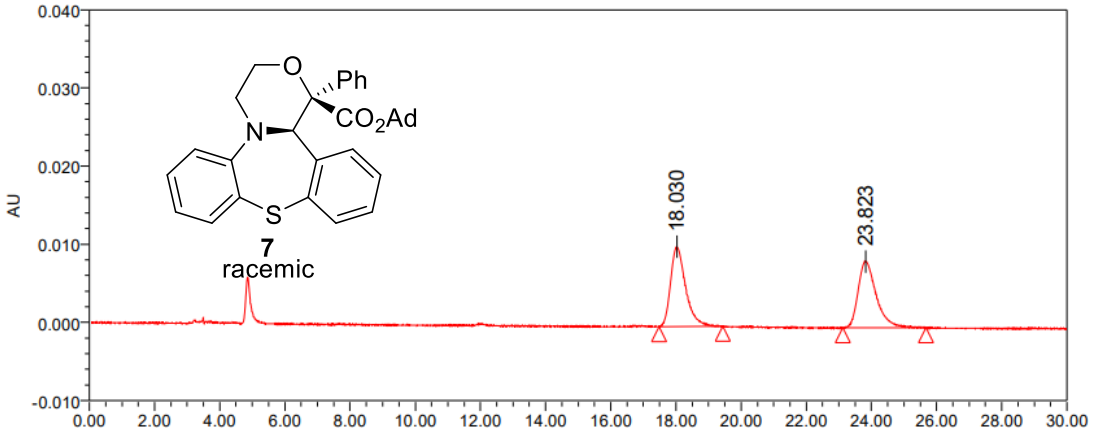
Entry	RT min	Height mV	Area mV.sec	% Area %
1	20.019	18613	694550	12.30
2	23.362	50843	2169930	38.42
3	25.196	46237	2145186	37.98
4	39.893	8798	638334	11.30



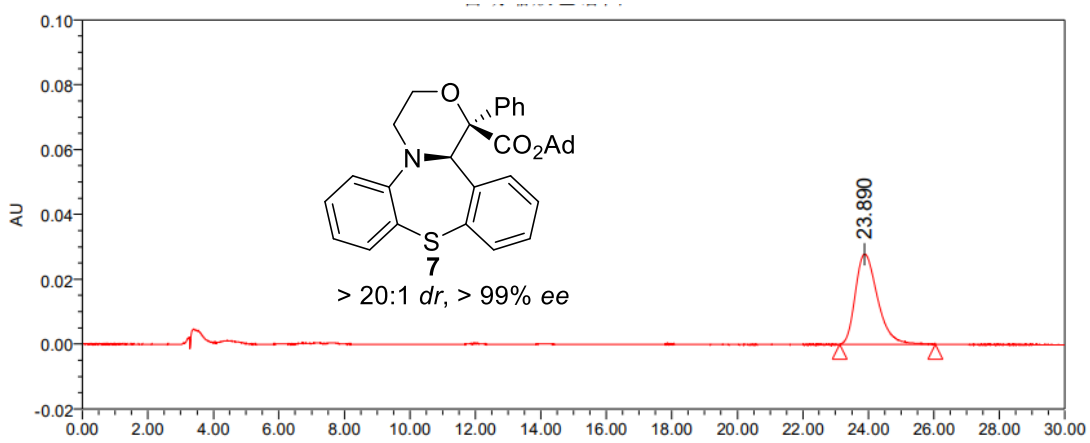
Entry	RT min	Height mV	Area mV.sec	% Area %
1	20.220	42322	1637160	60.90
2	23.650	17667	771070	28.68
3	25.584	5165	229274	8.53
4	40.664	879	50741	1.89

Condition：Chrial IF-3, λ = 254 nm, hexane/isopropanol = 98:2

flow rate = 1.0 mL/min



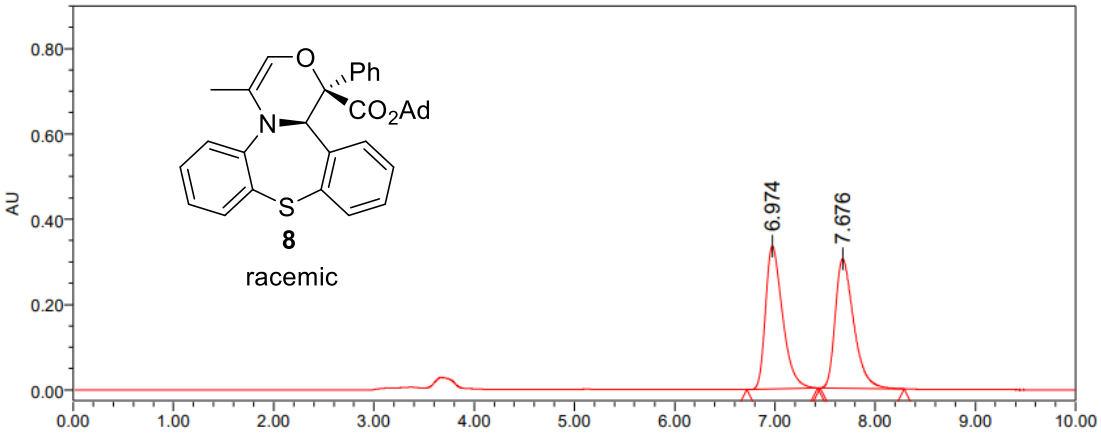
Entry	RT min	Height mV	Area mV.sec	% Area %
1	18.030	10185	323113	49.70
2	28.823	8493	327067	50.30



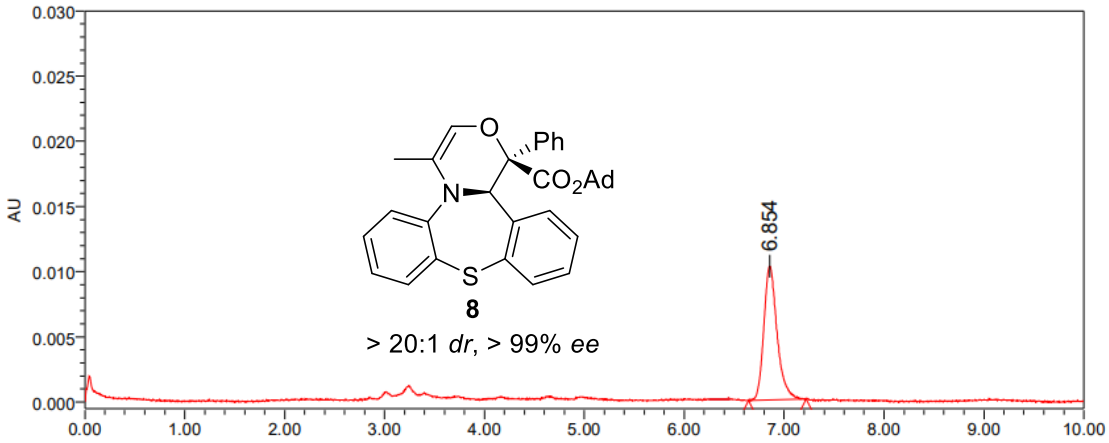
Entry	RT min	Height mV	Area mV.sec	% Area %
1	23.890	27840	1294547	100.00

Condition：Chrial IF-3, λ = 331 nm, hexane/isopropanol = 80:20

flow rate = 1.0 mL/min

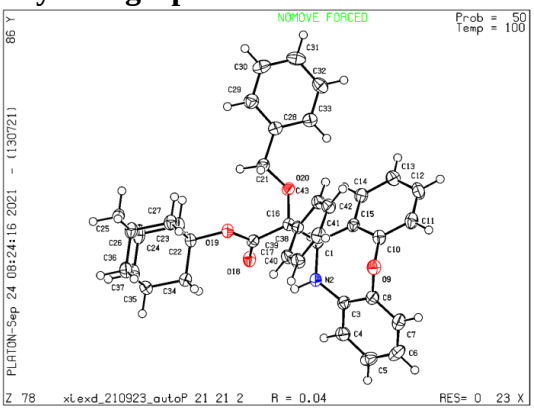


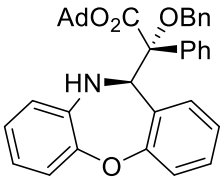
Entry	RT min	Height mV	Area mV.sec	% Area %
1	6.974	335250	3947844	50.42
2	7.676	303130	3882395	49.58



Entry	RT min	Height mV	Area mV.sec	% Area %
1	6.854	10252	94608	100.00

Crystallographic Data for 5a.



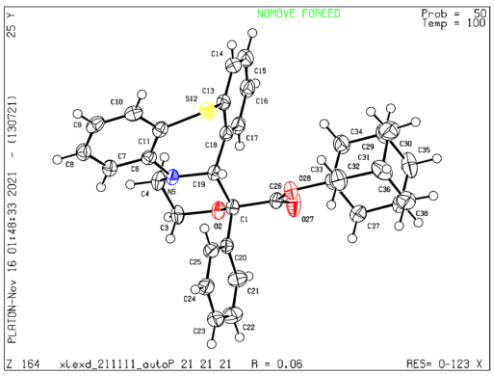


5a

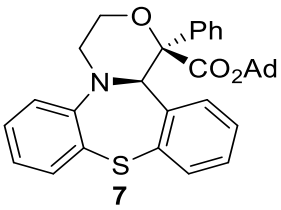
CCDC 2126676

```
Bond precision:   C-C = 0.0034 A          Wavelength=1.54184

Cell:             a=17.3081(2)     b=14.4922(2)     c=11.9555(2)
                  alpha=90         beta=90          gamma=90
Temperature:      100 K

                  Calculated                Reported
Volume            2998.83(7)                2998.83(7)
Space group       P 21 21 2                 P 21 21 2
Hall group        P 2 2ab                   P 2 2ab
Moiety formula    C38 H37 N O4              C38 H37 N O4
Sum formula       C38 H37 N O4              C38 H37 N O4
Mr                571.69                    571.68
Dx,g cm-3         1.266                     1.266
Z                 4                         4
Mu (mm-1)         0.644                     0.644
F000              1216.0                    1216.0
F000'             1219.50
h,k,lmax          22,18,15                  22,17,15
Nref              6491[ 3636]               6219
Tmin,Tmax         0.793,0.879               0.472,1.000
Tmin'             0.773

Correction method= # Reported T Limits: Tmin=0.472 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.71/0.96        Theta(max)= 78.916

R(reflections)= 0.0393( 5670)                wR2(reflections)=
                                             0.1013( 6219)
S = 1.051                  Npar= 388
```

Crystallographic Data for 7.



CCDC 2126677



7

```
Bond precision:   C-C = 0.0067 A          Wavelength=1.54184

Cell:             a=10.8906(1)     b=13.7438(2)     c=18.1534(2)
                  alpha=90         beta=90          gamma=90
Temperature:      100 K

                  Calculated                Reported
Volume            2717.17(6)                2717.17(6)
Space group       P 21 21 21                P 21 21 21
Hall group        P 2ac 2ab                 P 2ac 2ab
Moiety formula    C33 H33 N O3 S            C33 H33 N O3 S
Sum formula       C33 H33 N O3 S            C33 H33 N O3 S
Mr                523.66                    523.66
Dx,g cm-3         1.280                     1.280
Z                 4                         4
Mu (mm-1)         1.331                     1.331
F000              1112.0                    1112.0
F000'             1116.30
h,k,lmax          13,17,23                  13,17,23
Nref              5860[ 3294]               5739
Tmin,Tmax         0.852,0.875               0.780,1.000
Tmin'             0.766

Correction method= # Reported T Limits: Tmin=0.780 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.74/0.98        Theta(max)= 78.786

R(reflections)= 0.0607( 5390)                wR2(reflections)=
                                             0.1609( 5739)
S = 1.043                  Npar= 343
```

Reference

1 Y. Tang, Q. Chen, X. Liu, G. Wang, L. Lin and X. Feng, Direct synthesis of chiral allenoates from the asymmetric C-H insertion of α-diazoesters into terminal alkynes, *Angew. Chem. Int. Ed.*, 2015, **54**, 9512-9516.

2 Y. Ren, Y. Wang, S. Liu and K. Pan, Organocatalysed asymmetric direct Mannich reaction of acetophenone derivatives and dibenzo[*b*,*f*][1,4]oxazepines with azetidine-2-carboxylic acid, *ChemCatChem.*, 2014, **6**, 2985-2992