Electronic Supplementary Information

Chiral Strong Brønsted Acid-Catalyzed Enantioselective Addition Reaction of Simple Olefins with Ethyl Glyoxylate

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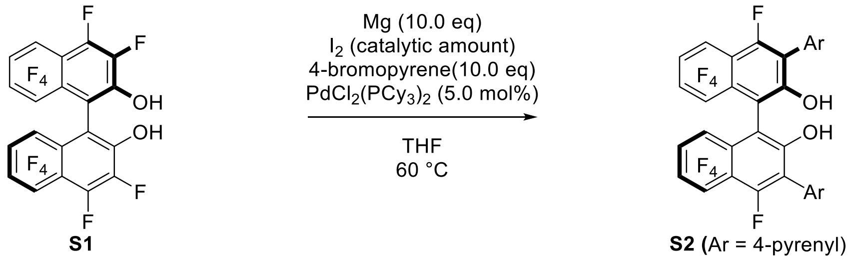
Contents:

1. General Information

Unless otherwise noted, all reactions were carried out under an atmosphere of standard grade nitrogen gas in flame-dried glassware equipped with a magnetic stir bar. Toluene and tetrahydrofuran (THF) were supplied from KANTO Chemical Co., Inc. as “Dehydrated solvent system”. Other solvents and reagents were purchased from commercial suppliers and used without further purification. Flash column chromatography was performed on silica gel 60N (spherical, neutral, 40-50 μm; Kanto Chemical Co., Inc.). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm). ^1H NMR spectra were recorded on a JEOL JNM-ECA600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance or tetramethylsilane (TMS) as the internal standard ($CDCl_3$: 7.26 ppm, TMS: 0.00 ppm, CD_3OD: 3.31 ppm, acetone-d_6: 2.05 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, br = broad, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on a JEOL JNM-ECA600 (151 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$ 77.0 ppm). ^{31}P NMR spectra were recorded on JEOL JNM-ECA-600 (243 MHz) spectrometer with complete proton decoupling. ^{19}F NMR spectra were recorded on JEOL JNM-ECA-600 (565 MHz) spectrometer. Optical rotations were measured on a Jasco P-1020 digital polarimeter with a sodium lamp and reported as follows; $[\alpha]^{T\ °C}_{D}$ (c = g/100 mL, solvent, % ee). Infrared spectra were recorded on a Jasco FT/IR-4100 spectrometer. HPLC analysis was performed on a Jasco LC-2000 Plus system with UV and CD detectors. High resolution mass spectra analysis was performed on a Bruker Daltonics solariX 9.4T FT-ICR-MS spectrometer at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

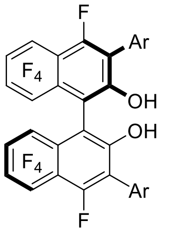
2. Preparation of Catalysts

Preparation of **S2**



In a flame dried, nitrogen-flushed two-necked round-bottom flask, equipped with a reflux condenser, magnesium (121.5 mg, 5.0 mmol) and a catalytic amount of I_2 were suspended in THF (2.0 mL). A small amount of 4-bromopyrene (1.4 g, 5.0 mmol) in THF (5.0 mL) was added to the mixture. The reaction was started by short heating to reflux. In order to keep the solution at reflux, further 4-bromopyrene solution was added dropwise. After complete addition of the 4-bromopyrene, the mixture was stirred for 30 minutes at 40 °C. To a mixture of $PdCl_2(PCy_3)_2$ (18.5 mg, 0.025 mmol) and **S1** (251.1 mg, 0.5 mmol) in THF (1.5 mL) was added the 4-pyrenylmagnesium bromide solution at −78 ºC under argon atmosphere. After evacuated and refilled with argon twice, the reaction mixture was stirred at 60 ºC for 36 h. After the resulting mixture was cooled to room temperature, 3.0 M HCl aq. was added. The resulting mixture was extracted with Et_2O. The combined organic layer was dried over Na_2SO_4, and concentrated under reduced pressure after filtration. The residual crude was purified by silica gel column chromatography (hexane to hexane/EtOAc = 4/1) to afford **S2** (190.7 mg, 0.22 mmol, 44%) as a white solid.

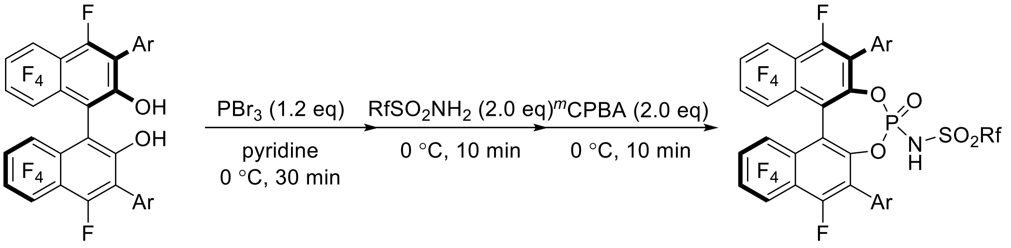
(*R*)-3,3'-(4-pyrenyl)$_2$-F$_{10}$BINOL (S2)



S2 (Ar = 4-pyrenyl)

S2: White solid; (190.7 mg, 0.22 mmol, 44% yield); $R_f = 0.45$ (hexane/EtOAc = 4/1); $[\alpha]^{21.3}_D = 27.4$ ($c = 0.7$, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ: 8.40–8.00 (m, 14H), 7.90–7.60 (m, 4H), Due to the presence of the several rotamers, the integrations are non-integer and have been rounded to best account for the overall number of protons.; ^{13}C NMR (151 MHz, $CDCl_3$) δ: 155.1 (dm, J = 267.4 Hz), 151.5, 142.8 (dm, J = 250.1 Hz), 142.2 (dm, J = 260.2 Hz), 140.2 (dm, J = 250.1 Hz), 136.9 (dt, J = 253.1 Hz, 15.9 Hz), 131.5, 131.3, 131.2, 131.1, 130.1, 130.0, 129.2, 129.1, 127.7 , 127.6, 127.5, 127.3, 126.7, 126.4, 126.3, 126.1, 125.8, 125.6, 125.14, 125.08, 124.89, 124.86, 124.6, 122.5, 120.8, 116.6, 116.5, 107.6, 106.8, ^{13}C signals could not be assigned due to the presence of the several rotamers and multiple ^{13}C-^{19}F couplings; ^{19}F NMR (565 MHz, $CDCl_3$): -112.2 to -112.8 (2F, m), -144.0 to -144.4 (2F, m), -146.2 to -147.1 (2F, m), -154.8 to -155.1 (2F, m), -160.5 to -160.8 (2F, m), Due to the presence of the several rotamers, the integrations are non-integer and have been rounded to best account for the overall number of fluorines.; IR (ATR): 3727, 3705, 3693, 3680, 3648, 3623, 3599 3566, 2939, 1541, 1522, 1508, 1488, 1397, 1339, 1218, 1054, 1032, 1007, 772 cm^{-1}; HRMS(ESI) Calcd for $C_{52}H_{19}F_{10}O_2$ [M-H]$^-$ 865.1225, Found 865.1230.

2.2 Preparation of catalyst

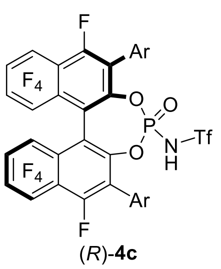


S3

(*R*)-**4**

To a solution of **S3** (0.1 mmol, 1.0 eq) in pyridine (2.0 mL) was added PBr_3 (0.12 mmol, 1.2 eq). The resulting mixture was stirred at 0 °C for 30 min. After stirring, $RfSO_2NH_2$ (0.2 mmol, 2.0 eq) was added at -78 °C. The reaction mixture was warmed to 0 °C, and stirred for 10 min. To the reaction mixture, ^{m}CPBA (0.2 mmol, 2.0 eq) was added. The resulting mixture was stirred at 0 °C for 10 min. The reaction mixture was quenched by 1M HCl aq. (1.0 mL). The resulting mixture was extracted with EtOAc, dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The residual crude product was purified by column chromatography on silica gel (hexane/EtOAc = 3:1 to hexane/EtOAc = 1:1). The resultant solid was dissolved in Et_2O, and the solution was washed with 6M HCl aq. (3 mLx3). Organic layer was dried over Na_2SO_4 and concentrated under reduced pressure after filtration to give (*R*)-**4**.

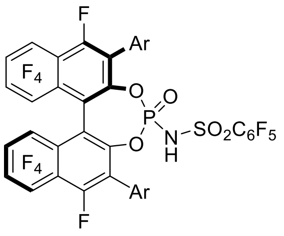
(*R*)-3,3'-(4-pyrenyl)$_2$-F$_{10}$BINOL-derived *N*-Tf Phosphoramide (4c)



(*R*)-**4c**
(Ar = 4-pyrenyl)

Brown solid; (38.2 mg, 0.04 mmol, 40% yield); $R_f = 0.30$ (hexane/EtOAc = 1/1); $[\alpha]^{19.6}_{D} = 26.2$ ($c = 0.6$, $CHCl_3$); ^{1}H NMR (CD_3OD, 600 MHz) δ: 7.65–7.58 (m, 4H), 7.48–7.39 (m, 6H), Due to the presence of the several rotamers, the integrations are non-integer and have been rounded to best account for the overall number of protons.; ^{13}C NMR (151 MHz, $CDCl_3$): ^{13}C signals could not be assigned due to the presence of the several rotamers and multiple ^{13}C-^{19}F couplings; ^{31}P NMR (243 MHz, $CDCl_3$): 5.64, 5.33, 4.07, 3.67; ^{19}F NMR (565 MHz, $CDCl_3$): -79.6 to -80.8 (3F), -103.3 to -110.5 (2F), -139.8 to -143.0 (4F), -151.9 to -153.2 (2F), -155.2 to -156.5 (2F) Due to the presence of the several rotamers, the integrations are non-integer and have been rounded to best account for the overall number of fluorines.; IR (ATR): 3723, 3705, 3680, 3648, 3632, 3623, 3599, 3565, 3526, 3503, 2972, 2938, 2865, 2843, 1670, 1624, 1564, 1541, 1339, 1218, 1054, 1032, 1014, 795 cm^{-1}; HRMS(ESI) Calcd for $C_{53}H_{18}F_{13}NO_5PS$ [M-H$^-$]: 1058.0436 Found: 1058.0440.

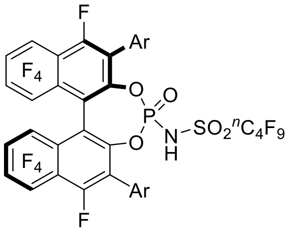
(***R***)-3,3’-(4-pyrenyl)$_2$-F$_{10}$BINOL-derived ***N***- C$_6$F$_5$SO$_2$ Phosphoramide (4d)



(*R*)-**4d**
(Ar = 4-pyrenyl)

Brown solid; (33 mg, 0.03 mmol, 24% yield); R$_f$ = 0.34 (hexane/EtOAc = 1/1); $[\alpha]^{18.0}_{D}$ = 33.2 (*c* = 1.0, CHCl$_3$); ^{1}H NMR (acetone-*d*$_6$, 600 MHz) δ: 8.70-7.93 (m, 16H), 7.90-7.50 (m, 2H), Due to the presence of the several rotamers, the integrations are non-integer and have been rounded to best account for the overall number of protons.; ^{13}C NMR (151 MHz, CDCl$_3$): ^{13}C signals could not be assigned due to the presence of the several rotamers and multiple ^{13}C-^{19}F couplings; ^{31}P NMR (243 MHz, CDCl$_3$): 5.48, 4.24, 3.49; ^{19}F NMR (565 MHz, CDCl$_3$): -106.3 to -112.3 (2F), -136.1 to -146.9 (6F), -150.9 to -152.1 (1F), -153.1 to -160.9 (5F), Due to the presence of the several rotamers, the integrations are non-integer and have been rounded to best account for the overall number of fluorines.; IR (ATR): 3705, 3680, 3648, 3632, 3623, 3503, 2962, 2927, 1716, 1698, 1650, 1619, 1558, 1540, 1519, 1508, 1471, 1339, 1218, 1062, 1025 cm^{-1}; HRMS(ESI) Calcd for $C_{58}H_{18}F_{15}NO_5PS$ [M-H$^-$]: 1156.0404, Found: 1156.0408.

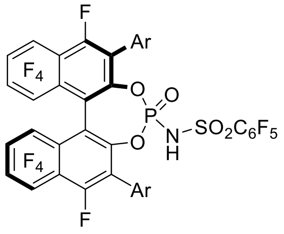
(***R***)-3,3’-(4-pyrenyl)$_2$-F$_{10}$BINOL-derived ***N***-^{n}C$_4$F$_9$SO$_2$ Phosphoramide (4e)



(*R*)-**4e**
(Ar = 4-pyrenyl)

Brown solid; (36.3 mg, 0.03 mmol, 32% yield); R$_f$ = 0.32 (hexane/EtOAc = 1/1); $[\alpha]^{25.0}_{D}$ = 28.7 (*c* = 0.6, CHCl$_3$); ^{1}H NMR (CD$_3$OD, 600 MHz) δ: 8.67–7.82 (m, 15H), 7.76–7.29 (m, 3H), Due to the presence of the several rotamers, the integrations are non-integer and have been rounded to best account for the overall number of protons.; ^{13}C NMR (151 MHz, CDCl$_3$): ^{13}C signals could not be assigned due to the presence of the several rotamers and multiple ^{13}C-^{19}F couplings; ^{31}P NMR (243 MHz, CDCl$_3$): 5.43, 3.79, 3.49; ^{19}F NMR (565 MHz, CDCl$_3$): -80.9 to -81.0 (3F), -106.4 to -109.6 (2F), -113.2 to -114.7 (2F), -121.0 to -122.6 (2F), -126.2 to -126.5 (2F), -139.7 to -140.8 (2F), -142.1 to -142.7 (2F), -152.1 to -152.9 (2F), -155.4 to -156.2 (2F) Due to the presence of the several rotamers, the integrations are non-integer and have been rounded to best account for the overall number of fluorines.; IR (ATR): 3731, 3722, 3705, 3692, 3680, 3649, 3622, 3598, 2973, 2921, 2864, 1564, 1540, 1508, 1489, 1374, 1053, 1032, 1011, 795 cm^{-1}; HRMS(ESI) Calcd for $C_{56}H_{18}F_{19}NO_5PS$ [M-H$^-$]: 1208.0340, Found: 1208.0342.

(***R***)-3,3’-(9-phenanthryl)$_2$-F$_{10}$BINOL-derived ***N***-C$_6$F$_5$SO$_2$ Phosphoramide (4f)

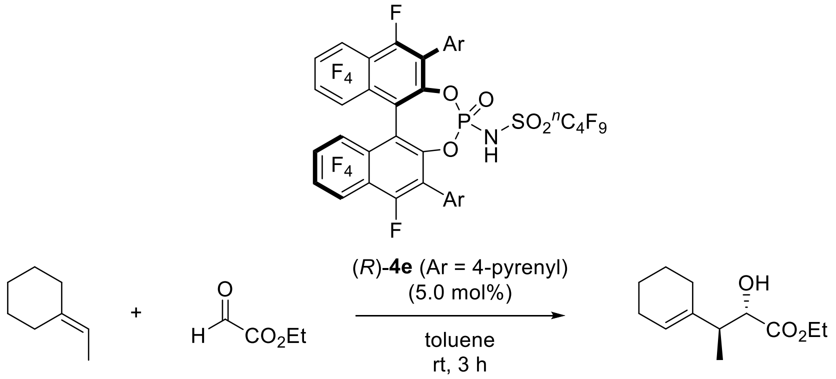


(*R*)-**4f**
(Ar = 9-phenanthryl)

Brown solid; (36.6 mg, 0.03 mmol, 37% yield); R$_f$ = 0.34 (hexane/EtOAc = 1/1); $[\alpha]^{25.0}_{D}$ = -6.36 (*c* = 0.73, CHCl$_3$); ^{1}H NMR (600 MHz, CD$_3$OD) δ: 8.90–8.69 (m, 4H), 8.38–7.31 (m, 18H), Due to the presence of the several rotamers, the integrations are non-integer and have been rounded to best account for the overall number of protons.; ^{13}C NMR (151 MHz, CDCl$_3$): ^{13}C signals could not be assigned due to the presence of the several rotamers and multiple ^{13}C-^{19}F couplings; ^{31}P NMR (243 MHz, $CDCl_3$): 3.94, 3.00, 2.75, 2.29; ^{19}F NMR (565 MHz, $CDCl_3$): -104.9 to -110.7 (2F), -138.0 to -142.9 (6F), -148.0 to -151.0 (1F), -151.9 to -153.4 (2F), -155.3 to -156.9 (2F), -159.6 to -161.4 (2F), Due to the presence of the several rotamers, the integrations are non-integer and have been rounded to best account for the overall number of fluorines.; IR (ATR): 3731, 3704, 3693, 3680, 3648, 3623, 3599, 2972, 2940, 2863, 2843, 1647, 1564, 1540, 1523, 1508, 1032, 1008, 795 cm^{-1}; HRMS(ESI) Calcd for $C_{54}H_{18}F_{15}NO_5PS$ [M-H$^-$]: 1108.0404, Found: 1108.0407.

3. Enantioselective Addition Reaction of Simple Olefins with Ethyl Glyoxylate

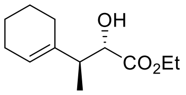
Reprsentative procedure for the enantioselective addition reaction of 1,1,2-trisubstituted olefins with ethyl glyoxylate



1a **2** **3a**

To a solution of (*R*)-**4e** (6.0 mg, 0.005 mmol) in toluene (0.5 mL) was added a **1a** (33.1 mg, 0.3 mmol) and freshly distilled ethyl glyoxylate **2** (10.2 mg, 0.1 mmol) at room temperature, and the resulting solution was stirred for indicated time at this temperature. The mixture was directly passed through flash colum chromatography (Hexane/AcOEt =6/1) to give **3a** (12.1 mg, 0.06 mmol, 57% yield) as a colorless oil. The enantiomeric excess was determined by chiral stationary phase HPLC analysis.

ethyl (2*S*,3*S*)-3-(cyclohex-1-en-1-yl)-2-hydroxybutanoate (3a)



3a

57% yield; colorless liquid: $R_f = 0.49$ (Hexane/EtOAc = 4/1); Diastereomers could be separated by flash column chromatography (Hexane/AcOEt =9/1).; $[\alpha]^{22.4}_D = -3.5$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 5.55-5.52 (m, 1H), 4.24 (q, $J = 7.2$ Hz, 2H), 4.20 (dd, $J = 6.0$ Hz, 4.2 Hz, 1H), 2.56 (d, $J = 6.0$ Hz, 1H), 2.45-2.40 (m, 1H), 2.09-1.92 (m, 4H), 1.69-1.52 (m, 4H), 1.30 (t, $J = 7.2$ Hz, 3H), 1.01 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ; 174.8, 138.02, 123.0, 73.0, 61.5, 45.0, 26.8, 25.3, 23.0, 22.4, 14.2, 12.7; IR (ATR): 3525, 2977, 2929, 2836, 1729, 1541, 1508, 1456, 1374, 1258, 1198, 1099, 1028 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{20}NaO_3$ $[M+Na]^+$ 235.1310, Found: 235.1305.; HPLC analysis CHIRALPAK AS-H (hexane/^{i}PrOH= 99/1, 1.0mL/min, 220 nm, 30 ˚C) 8.8 min (major), 14.1 min (minor). Configuration Assignment: The relative and absolute configurations were assigned as (2*S*,3*S*) by comparison with the reported literature.[1]

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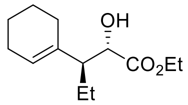
[1] B.-C. Hong, S.-H. Chen, E. S. Kumar, G.-H. Lee and K.-J. Lin, *J. Chin. Chem. Soc.*, 2003, **50**, 917–926.

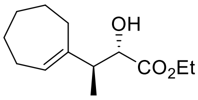
ethyl (2*S*,3*S*)-3-(cyclohex-1-en-1-yl)-2-hydroxypentanoate (3b)



3b

67% yield; colorless liquid: $R_f = 0.47$ (Hexane/EtOAc = 4/1); Diastereomers could be separated by flash column chromatography (Hexane/AcOEt =9/1).; $[\alpha]^{23.8}_{D}$ = 1.8 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 5.51-5.48 (m, 1H), 4.25-4.16 (m, 2H), 4.07 (dd, *J* = 7.8 Hz, 6.0 Hz, 1H), 2.52 (d, *J* = 7.8 Hz, 1H), 2.14-2.09 (m, 1H), 2.06-1.95 (m, 2H), 1.95-1.91 (m, 2H), 1.63-1.45 (m, 6H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.82 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 174.9, 136.0, 125.1, 73.8, 61.3, 54.4, 25.8, 25.4, 22.9, 22.5, 20.5, 14.2, 11.9; IR (ATR): 2961, 2927, 2874, 2837, 1728, 1455, 1260, 1191, 1106, 1064, 1027 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{22}NaO_3$ $[M+Na]^+$ 249.1467, Found: 249.1461.; HPLC analysis CHIRALPAK AS-H (hexane/^{i}PrOH= 99/1, 1.0mL/min, 220 nm, 30 ˚C) 8.6 min (major), 11.6 min (minor). Configuration Assignment: The relative and absolute configuration was assigned as (2*S*,3*S*) by analogy with compound **3a**.

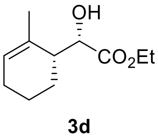
ethyl (2*S*,3*S*)-3-(cyclohept-1-en-1-yl)-2-hydroxybutanoate (3c)



3c

98% yield; colorless liquid: $R_f = 0.47$ (Hexane/EtOAc = 4/1); Diastereomers could be separated by flash column chromatography (Hexane/AcOEt =9/1).; $[\alpha]^{22.6}_{D}$ = 5.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 5.67 (t, *J* = 6.0 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 4.15 (dd, *J* = 6.6 Hz, 4.8 Hz, 1H), 2.52-2.47 (m, 2H), 2.19-2.15 (m, 2H), 2.14-2.07 (m, 2H), 1.82-1.75 (m, 1H), 1.74-1.67 (m, 1H), 1.59-1.46 (m, 2H), 1.45-1.38 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.00 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 174.7, 144.8, 128.1, 72.7, 61.4, 46.6, 32.7, 31.2, 28.3, 27.0, 26.9, 14.2, 12.8; IR (ATR): 2972, 2920, 2849, 1728, 1445, 1256, 1198, 1096, 1024, 784, 759 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{22}NaO_3$ $[M+Na]^+$ 249.1467, Found: 249.1461.; HPLC analysis CHIRALPAK AS-H (hexane/^{i}PrOH= 99/1, 1.0mL/min, 220 nm, 30 ˚C) 7.8 min (major), 11.1 min (minor). Configuraation Assignment: The relative and absolute configuration was assigned as (2*S*,3*S*) by analogy with compound **3a**.

ethyl (*S*)-2-hydroxy-2-((*R*)-2-methylcyclohex-2-en-1-yl)acetate (3d)

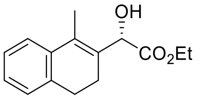


3d

69% yield; colorless liquid: $R_f = 0.42$ (Hexane/EtOAc = 4/1); Diastereomers could not be separated.; $[\alpha]^{23.2}_{D}$ = -9.2 (*c* = 0.6, $CHCl_3$); Major Diastereomer (*syn*): ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 5.68-5.65 (m, 1H), 4.53 (dd, *J* = 4.8 Hz, 3.0 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.72 (d, *J* = 4.8 Hz, 1H), 2.54-2.49 (m, 1H), 2.04-1.93 (m, 2H), 1.79 (s, 3H), 1.83-1.74 (m, 1H), 1.60-1.41 (m, 3H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 175.0, 132.2, 126.6, 70.6, 61.8, 42.4, 25.2, 22.7, 21.5, 21.3, 14.3; Minor diastereomer (*anti*): ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 5.58-5.55 (m, 1H), 4.32-4.18 (m, 3H), 2.84 (d, *J* = 5.4 Hz, 1H), 2.64-2.59 (m, 1H), 2.04-1.93 (m, 2H), 1.69 (s, 3H), 1.69-1.63 (m, 1H), 1.60-1.41 (m, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 175.0, 132.1, 126.1, 72.5, 61.6, 43.3, 26.3, 25.3, 22.3, 20.6, 14.1; IR (ATR):

2969, 2929, 2861, 1727, 1249, 1215,1110, 1093, 1065, 1024 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{18}NaO_3$ $[M+Na]^+$ 221.1154, Found: 221.1148.; HPLC analysis CHIRALPAK AS-H (hexane/^{i}PrOH= 99/1, 1.0mL/min, 220 nm, 30 ˚C) 9.4 min (major), 15.3 min (minor). Configuration Assignment: The relative configuration was determined by comparison with the reported literature.[2] The absolute configuration was assigned as (1*R*,2*S*) by analogy with compound **3a**.

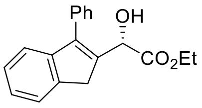
ethyl (*S*)-2-hydroxy-2-(1-methyl-3,4-dihydronaphthalen-2-yl)acetate (3'e)



3'e

51% yield; colorless liquid: R_f = 0.20 (Hexane/EtOAc = 4/1); $[\alpha]^{22.8}_D$ = 89.8 (*c* = 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 600 MHz) δ: 7.34 (d, *J* = 7.8 Hz, 1H), 7.23 (dt, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.17 (dt, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.13 (dd, *J* = 7.2 Hz, 0.6 Hz, 1H), 5.29 (d, *J* = 4.8 Hz, 1H), 4.23 (dq, *J* = 7.2 Hz, 1.2 Hz, 2H), 3.26 (d, *J* = 4.8 Hz, 1H), 2.79-2.67 (m, 2H), 2.39-2.32 (m, 1H), 2.19 (t, *J* = 1.2 Hz, 3H), 2.04-1.97 (m, 1H); ^{13}C NMR (CDCl$_3$, 150 MHz) δ: 174.3, 136.3, 136.2, 131.5, 130.8, 127.1, 127.0, 126.4, 123.7, 70.0, 62.1, 28.4, 22.2, 14.3, 14.1; IR (ATR): 3502, 2986, 2930, 2901, 2835, 1727, 1487, 1450, 1394, 1382, 1253, 1208, 1080, 1065, 1051, 1018, 759 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{18}NaO_3$ $[M+Na]^+$ 269.1154, Found: 269.1148.; HPLC analysis CHIRALPAK AS-H (hexane/^{i}PrOH= 99/1, 1.0mL/min, 254 nm, 30 ˚C) 21.5 min (major), 26.7 min (minor). Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy with compound **3'j**.

ethyl (*S*)-2-hydroxy-2-(3-phenyl-1H-inden-2-yl)acetate (3'f)



3'f

91% yield; yellow liquid: R_f = 0.26 (Hexane/EtOAc = 4/1); $[\alpha]^{23.9}_D$ = 115.7 (*c* = 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 600 MHz) δ: 7.54-7.46 (m, 5H), 7.41 (tt, *J* = 9.0 Hz, 1.8 Hz, 1H), 7.31-7.23 (m, 3H), 5.18 (d, *J* = 4.8 Hz, 1H), 4.30-4.18 (m, 2H), 3.73 (d, *J*= 22.8 Hz, 1H), 3.29 (dd, *J* = 13.8 Hz, 9.0 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz) δ: 174.0, 145.1, 144.1, 142.5, 138.6, 133.9, 129.2, 128.5, 127.9, 126.4, 125.6, 124.0, 120.8, 67.7, 62.4, 36.6, 14.1; IR (ATR): 3058, 3019, 2982, 2900, 1730, 1272, 1208, 1070 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{18}NaO_3$ $[M+Na]^+$ 317.1154, Found: 317.1148.; HPLC analysis CHIRALPAK AS-H (hexane/^{i}PrOH= 98/2, 1.0mL/min, 254 nm, 30 ˚C)) 27.9 min (major), 38.2 min (minor). Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy with compound **3'j**.

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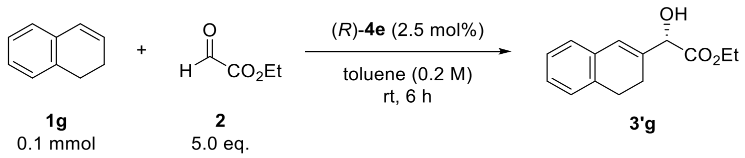
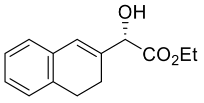
[2] D. A. Evans, S. W. Tregay, C. S. Burgey, N. A. Paras and T. Vojkovsky, *J. Am. Chem. Soc.* 2000, **122**, 7936−7943.

Reprsentative procedure for the enantioselective addition reaction of 1,1-disubstituted olefins with ethyl glyoxylate



To a solution of (*R*)-**4e** (3.0 mg, 0.0025 mmol) in toluene (0.5 mL) was added freshly distilled ethyl glyoxylate **2** 51.0 mg, 0.5 mmol) and **1g** (13.0 mg, 0.1 mmol) at room temperature, and the resulting solution was stirred for indicated time at this temperature. The mixture was directly passed through flash colum chromatography (Hexane/AcOEt =3/1) to give **6a** (17.0 mg, 0.073 mmol, 73% yield) as a colorless oil. The enantiomeric excess was determined by chiral stationary phase HPLC analysis.

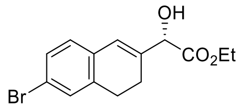
ethyl (*S*)-2-(3,4-dihydronaphthalen-2-yl)-2-hydroxyacetate (3'g)



3'g

73% yield; colorless liquid: R_f = 0.26 (Hexane/EtOAc = 4/1); $[\alpha]^{21.6}_{D}$ = 16.8 (*c* = 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 600 MHz) δ: 7.18-7.12 (m, 2H), 7.11 (d, *J* = 6.6 Hz, 1H), 7.07 (dd, *J* = 7.2 Hz, 2.4 Hz, 1H), 6.59 (s, 1H), 4.73 (d, *J* = 4.8 Hz, 1H), 4.31-4.23 (m, 2H), 3.23 (d, *J* = 5.4 Hz, 1H), 2.84 (t, *J* = 8.4 Hz, 2H), 2.47-2.40 (m, 1H), 2.22-2.15 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz) δ: 173.4, 136.9, 135.2, 133.6, 127.4, 127.3, 126.5, 126.4, 74.1, 62.2, 27.9, 23.0, 14.2; IR (ATR): 2930, 1747, 1480, 1317, 1263, 1104 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{16}NaO_3$ [M+Na]$^+$, Found 255.0992.; HPLC analysis CHIRALPAK AS-H (hexane/^{i}PrOH= 99/1, 1.0mL/min, 254 nm, 30 ˚C) 27.4 min (major), 38.2 min (minor). Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy with compound **3'j**.

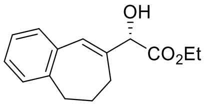
ethyl (*S*)-2-(6-bromo-3,4-dihydronaphthalen-2-yl)-2-hydroxyacetate (3'h)



3'h

44% yield; colorless liquid: R_f = 0.24 (Hexane/EtOAc = 4/1); $[\alpha]^{23.6}_{D}$ = 242.4 (*c* = 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 600 MHz) δ: 7.30-7.24 (m, 2H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.54 (s, 1H), 4.71 (d, *J* = 4.2 Hz, 1H), 4.31-4.23 (m, 2H), 3.26 (d, *J* = 4.8 Hz, 1H), 2.81 (t, *J* = 8.4 Hz, 2H), 2.46-2.38 (m, 1H), 2.21-2.13 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz) δ: 173.2, 137.5, 137.2, 132.4, 130.3, 129.5, 127.9, 125.3, 120.8, 73.9, 62.3, 27.7, 22.8, 14.1; IR (ATR): 2932, 1733, 1480, 1263, 1113, 1074, 882, 802 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{15}BrNaO_3$ [M+Na]$^+$ 333.0102, Found: 335.0096.; HPLC analysis CHIRALPAK AS-H (hexane/^{i}PrOH= 99/1, 1.0mL/min, 254 nm, 30 ˚C) 18.9 min (major), 27.2 min (minor). Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy with compound **3'j**.

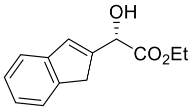
ethyl (*S*)-2-(6,7-dihydro-5H-benzo[7]annulen-8-yl)-2-hydroxyacetate (3’i)



3'i

60% yield; colorless liquid: R_f = 0.29 (Hexane/EtOAc = 4/1); $[\alpha]^{22.6}_D$ = 53.5 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.18 (dd, *J*= 1.2 Hz, 4.8 Hz, 2H), 7.16-7.10 (m, 2H), 6.63 (s, 1H), 4.69 (d, *J* = 3.0 Hz, 1H), 4.33-4.25 (m, 2H), 3.30 (d, *J* = 4.2 Hz, 1H), 2.81-2.72 (m, 2H), 2.41 (dt, *J* = 6.0 Hz, 13.2 Hz, 1H), 2.14 (dt, *J* = 7.2 Hz, 16.8 Hz, 1H), 2.06-2.00 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 174.0, 141.6, 139.4, 135.6, 130.8, 130.6, 129.0, 127.1, 126.0, 62.2, 34.8, 29.1, 28.6, 14.1; IR (ATR): 2981, 2929, 2857, 1730, 1258, 1198, 1105, 1075, 1023 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{18}NaO_3$ $[M+Na]^+$ 269.1154, Found: 269.1148.; HPLC analysis CHIRALPAK AS-H (hexane/^{i}PrOH= 96/4, 1.0mL/min, 254 nm, 30 ˚C) 22.1 min (major), 26.7 min (minor). Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy with compound **3’j**.

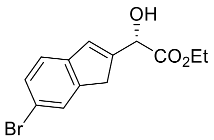
ethyl (*S*)-2-hydroxy-2-(1H-inden-2-yl)acetate (3’j)



3'j

39% yield; colorless liquid: R_f = 0.22 (Hexane/EtOAc = 4/1); $[\alpha]^{24.3}_D$ = 47.2 (*c* = 0.85, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.43 (d, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.19 (dt, *J* = 7.8 Hz, 1.2 Hz, 1H), 6.91 (s, 1H), 5.12 (d, *J* = 6.0 Hz, 1H), 4.34-4.22 (m, 2H), 3.55 (d, *J* = 22.8 Hz, 1H), 3.36 (d, *J* = 20.4 Hz, 1H), 3.23 (d, *J* = 5.4 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 173.0, 145.0, 143.9, 143.2, 129.9, 126.5, 125.0, 123.8, 121.2, 70.3, 62.3, 38.2, 14.2; IR (ATR): 2980, 2923, 1730, 1460, 1394, 1255, 1195, 1131, 1096, 1066, 1017, 751, 716 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{14}NaO_3$ $[M+Na]^+$ 241.0841, Found: 241.0835.; HPLC analysis CHIRALPAK AS-H (hexane/^{i}PrOH= 98/2, 1.0mL/min, 254 nm, 30 ˚C) 34.2 min (major), 56.3 min (minor). Configuration Assignment: The absolute configuration was assigned as (*S*) by the Mosher’s method after the derivatization.

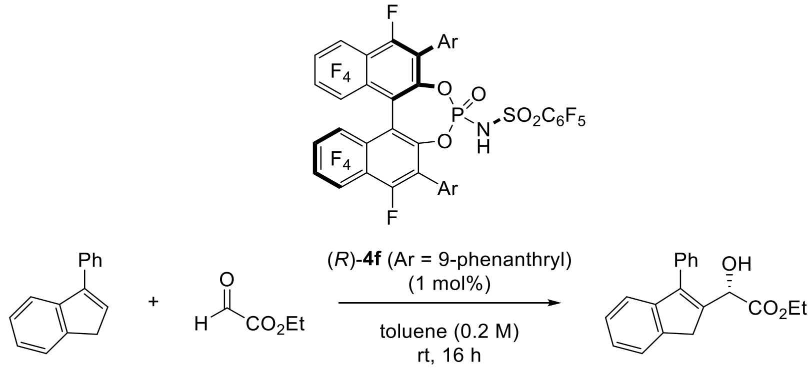
ethyl (*S*)-2-(6-bromo-1H-inden-2-yl)-2-hydroxyacetate (3’k)



3'k

51% yield; white solid: R_f = 0.27 (Hexane/EtOAc = 4/1); $[\alpha]^{21.2}_D$ = 41.9 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.56 (s, 1H), 7.39 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 6.86 (s, 1H), 5.09 (d, *J* = 4.8 Hz, 1H), 4.34-4.24 (m, 2H), 3.54 (d, *J* = 22.8 Hz, 1H), 3.35 (d, *J* = 22.8 Hz, 1H), 3.26 (d, *J* = 6.0 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 172.8, 145.5, 145.2, 142.8, 129.6, 129.1, 127..1, 122.4, 119.0, 70.1, 62.5, 38.3, 14.2; IR (ATR): 3524, 2972, 2928, 1729, 1260, 1210, 1066 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{13}BrNaO_3$ $[M+Na]^+$ 318.9946, Found: 318.9941.; HPLC analysis CHIRALPAK AS-H (hexane/^{i}PrOH= 99/1, 1.0mL/min, 254 nm, 30 ˚C)) 17.9 min (major), 26.7 min (minor). Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy with compound **3’j**.

Experimental procedure for the enantioselective addition reaction of **1f** with **2** on a large scale



1f
3.0 mmol

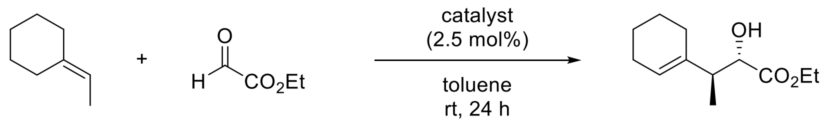
2
1.0 mmol

3'f

To a solution of (*R*)-**4f** (11.1 mg, 0.01 mmol) in toluene (5.0 mL) was added a **1f** (0.58 g, 3.0 mmol) and freshly distilled ethyl glyoxylate **2** (0.10 g, 1.0 mmol) at room temperature, and the resulting solution was stirred for indicated time at this temperature. The mixture was directly passed through flash colum chromatography (Hexane/AcOEt =6/1) to give **3'f** (0.24 g, 0.82 mmol, 82% yield) as a colorless oil. The enantiomeric excess was determined by chiral stationary phase HPLC analysis.

4. Additional Screening

4-1. Screening of catalysts

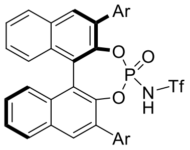


1a **2** **3a**

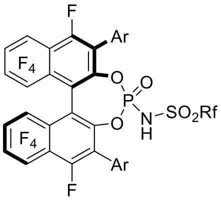
Table S1.

entry	catalyst	yield^{a} (%)	dr	ee (%)	note
1	(*R*)-**7** (Ar = 9-phenanthryl)	26	89/11	55	Table 1, entry 3
2	(*R*)-**7b** (Ar = 2,4,6-$^{i}Pr_3C_6H_2$)	27	76/24	18	
3	(*R*)-**4a** (Ar = 9-phenanthryl, Rf = CF_3)	62	87/13	58	Table 1, entry 4
4	(*R*)-**4g** (Ar = 9-phenanthryl, Rf = $^{n}C_4F_9$)	67	88/12	70	
5	(*R*)-**4b** (Ar = 1-pyrenyl, Rf = CF_3)	72	89/11	55	Table 1, entry 5
6	(*R*)-**4h** (Ar = 1-pyrenyl, Rf = $^{n}C_4F_9$)	43	90/10	68	
7	(*R*)-**4c** (Ar = 4-pyrenyl, Rf = CF_3)	58	90/10	69	Table 1, entry 6
8	(*R*)-**4i** (Ar = 4-pyrenyl, Rf = C_2F_5)	29	88/12	59	
9	(*R*)-**4e** (Ar = 4-pyrenyl, Rf = $^{n}C_4F_9$)	47	90/10	80	Table 1, entry 8
10	(*R*)-**4j** (Ar = Ph, Rf = CF_3)	43	89/11	54	
11	(*R*)-**4k** (Ar = 2-naphthyl, Rf = CF_3)	48	91/9	57	
12	(*R*)-**4l** (Ar = 6-methoxy-2-naphthyl, Rf = CF_3)	48	87/13	42	
13	(*R*)-**8** (Ar = 2-naphthyl, X = S)	<1	--	--	
14	(*R*)-**9** (Ar = 3,5-$(CF_3)_2C_6H_3$)	48	62/38	30	

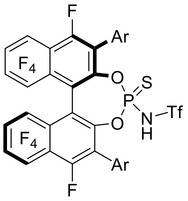
^{a}NMR yield.



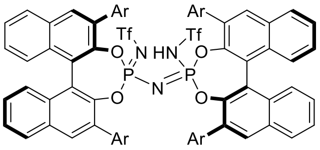
(*R*)-**7**



(*R*)-**4**



(*R*)-**8**



(*R*)-**9**

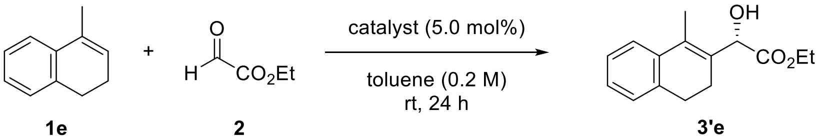


Table S2.

entry	catalyst	yield[a] (%)	ee (%)	note
1	(*R*)-**4a** (G = 9-phenanthryl,Rf = CF_3)	26	63	
2	(*R*)-**4f** (G = 9-phenanthryl, Rf = C_6F_5)	49	81	Table 2, entry 5
3	(*R*)-**4g** (G = 9-phenanthryl, Rf = $^nC_4F_9$)	29	67	
4	(*R*)-**4h** (G = 9-phenanthryl, Rf = $C_{10}F_7$)	35	75	
5	(*R*)-4**m** (G = 9-phenanthryl, Rf = 4-$CF_3C_6F_4$)	20	62	
6	(*R*)-**4b** (G = 1-pyrenyl,Rf = CF_3)	69	47	
7	(*R*)-**4c** (G = 4-pyrenyl,Rf = CF_3)	42	60	
8	(*R*)-**4d** (G = 4-pyrenyl, Rf = C_6F_5)	43	71	
9	(*R*)-**4e** (G = 4-pyrenyl, Rf = $^nC_4F_9$)	38	67	Table 2, entry 4

[a]Isolated yield

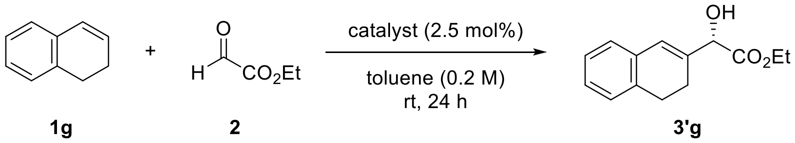
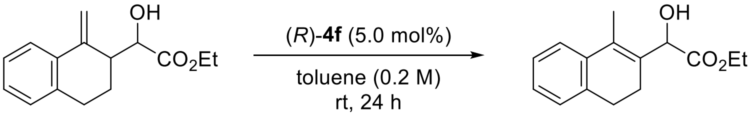


Table S3.

entry	catalyst	yield[a] (%)	ee (%)	note
1	(*R*)-**4a** (G = 9-phenanthryl, Rf = CF_3)	30	66	
2	(*R*)-**4f** (G = 9-phenanthryl, Rf = C_6F_5)	< 1	-	
3	(*R*)-**4g** (G = 9-phenanthryl, Rf = $^nC_4F_9$)	41	74	
4	(*R*)-**4b** (G = 1-pyrenyl, Rf = CF_3)	48	52	
5	(*R*)-**4c** (G = 4-pyrenyl, Rf = CF_3)	57	66	
6	(*R*)-**4e** (G = 4-pyrenyl, Rf = $^nC_4F_9$)	67	72	
7[b]	(*R*)-**4e** (G = 4-pyrenyl, Rf = $^nC_4F_9$)	73	72	Table 3, entry 1

[a]Isolated yield, [b]**2**: 5.0 eq.

4-2. Control experiment

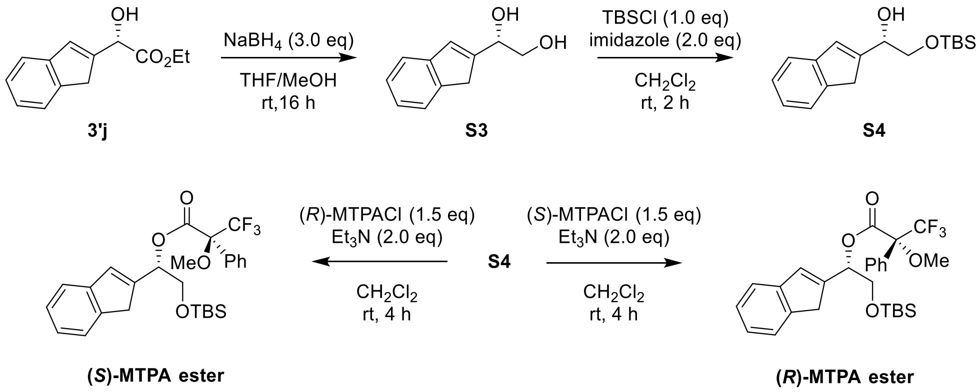


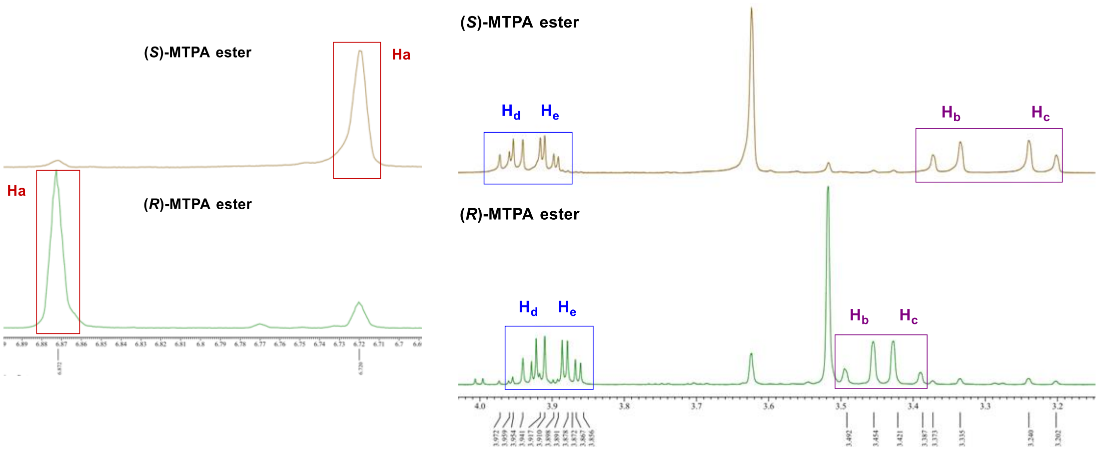
3e
0.1 mmol

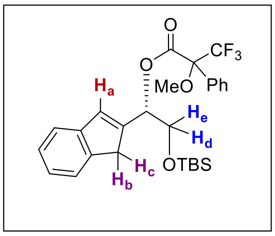
3'e
<1% yield

5. Determination of absolute configuration

The absolute configuration of **3'j** was determined by the Mosher's method after the derivatization of **3'j** to **S4**. **S4** were converted into the **(*S*)-** and **(*R*)-MTPA ester**s by treatment with (*R*)- and (*S*)-MTPA chloride, respectively. The Δδ values (δ^S–δ^R (ppm)) calculated for the two esters (Figure S1) indicated that **3'j** had an *S* configuration.







entry	compound	δHa (ppm)	δHb (ppm)	δHc (ppm)	δHd (ppm)	δHe (ppm)
1	**(*S*)-MTPA ester**	6.72	3.35	3.22	3.95	3.90
2	**(*R*)-MTPA ester**	6.87	3.47	3.40	3.92	3.87
δ^S–δ^R		-0.15	-0.12	-0.18	+0.03	+0.03

Figure S1. NMR spectra and Chemical shifts of MTPA esters

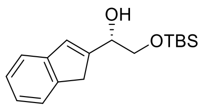
Experimental procedure of 3'j to S4

To a solution of **3'j** (21.8 mg, 0.1 mmol, 86% ee) in THF (0.5 mL) and MeOH (0.1 mL) was added $NaBH_4$ (11.3 mg, 0.3 mmol) in one portion at 0 °C. After stirring for 16 h at the ambient temperature, H_2O was added. The aqueous layer was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration to give **S3**. To a solution of **S3** in CH_2Cl_2 (1.7 mL) was added TBSCl (15.1 mg, 0.1 mmol) and imidazole (13.6 mg, 0.2 mmol) at ambient temperature. After stirring for 2 h at the ambient temperature, the reaction mixture was quenched with H_2O and the resulting mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc = 8/1) to afford the corresponding alcohol **S4** (80% yield, 2teps).

Experimental procedure of S4 to MTPA ester

To a solution of **S4** (11.6 mg, 0.04 mmol), Et_3N (4.0 mg, 0.04 mmol) and DMAP (0.5 mg, 0.004 mmol) in CH_2Cl_2 (0.4 mL) was added (*R*)- or (*S*)-MTPACl (15.2 mg, 0.06 mmol) at room temperature, and the resulting solution was stirred for 4 h at this temperature. The mixture was directly passed through column chromatography (Hexane/EtOAc/Et_3N = 10/1/0.1) to give the (*R*)- or (*S*)-**MTPA ester**.

(*S*)-2-((tert-butyldimethylsilyl)oxy)-1-(1H-inden-2-yl)ethan-1-ol (S4)

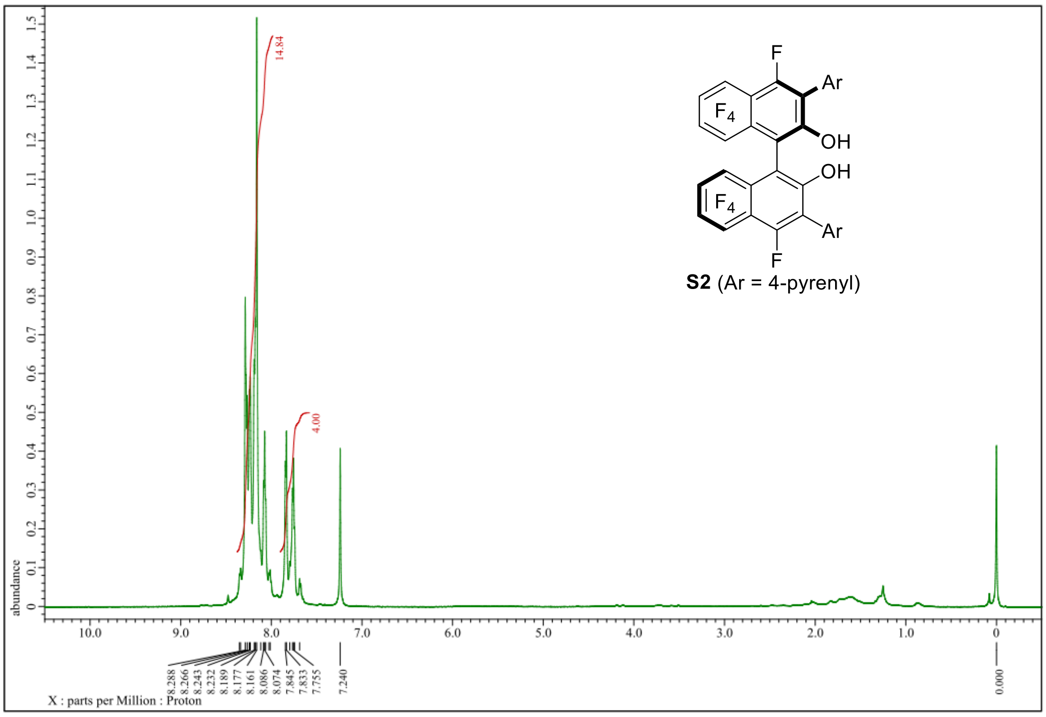


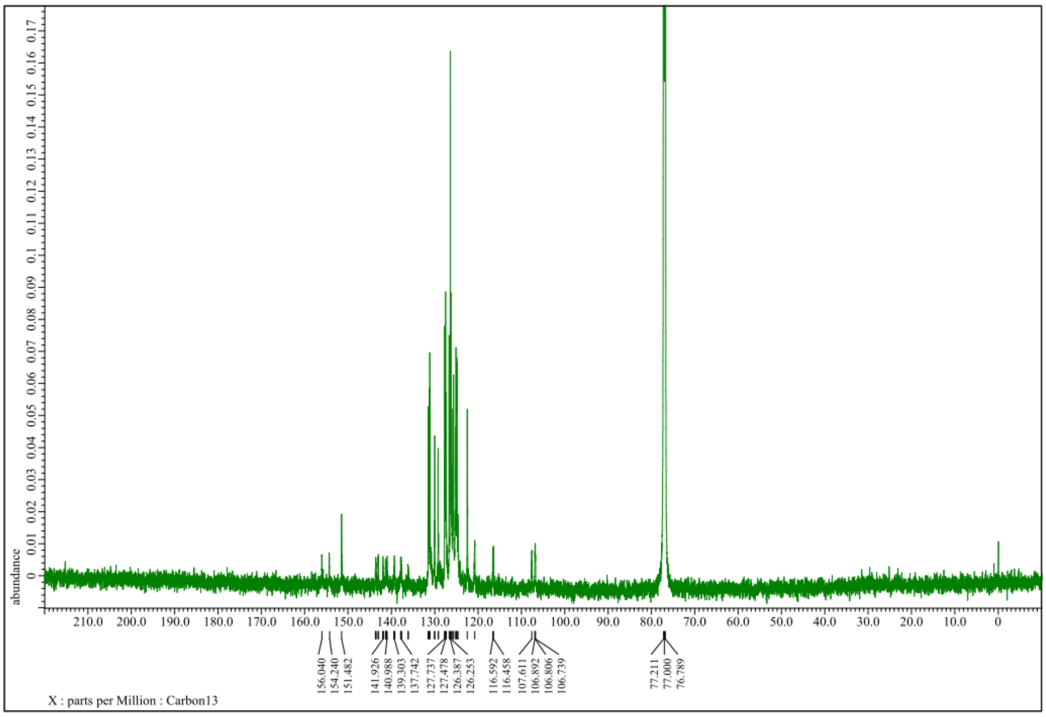
3'j

colorless oil: R_f = 0.62 (Hexane/EtOAc = 4/1); $[\alpha]^{17.7}_D$ = 2.46 (*c* = 0.4, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz) δ: 7.42 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.16 (dt, *J* = 7.8 Hz, 0.6 Hz, 1H), 6.80 (s, 1H), 4.71-4.67 (m, 1H), 3.84 (dd, *J* = 10.2 Hz, 4.2 Hz, 1H), 3.65 (dd, *J*= 9.6 Hz, 7.8 Hz, 1H), 3.46 (d, *J* = 22.8 Hz, 1H), 3.39 (d, *J* = 22.8 Hz, 1H), 2.83 (d, *J* = 3.0 Hz, 1H), 0.93 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 147.8, 144.5, 143.1, 127.9, 126.3, 124.4, 123.6, 120.8, 71.4, 67.3, 38.4, 25.9, 18.3, -5.36, -5.38; IR (ATR): 2956, 2928, 2857, 1099, 1056, 836, 802, 777 cm^{-1}.

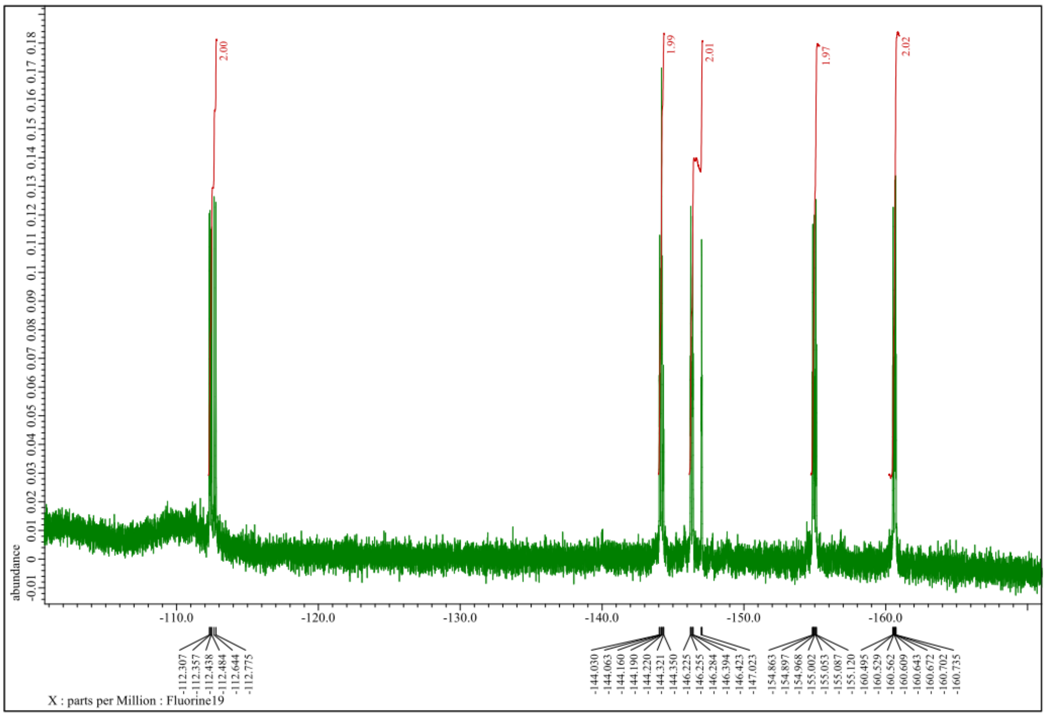
6. NMR Spectra

^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **S2**

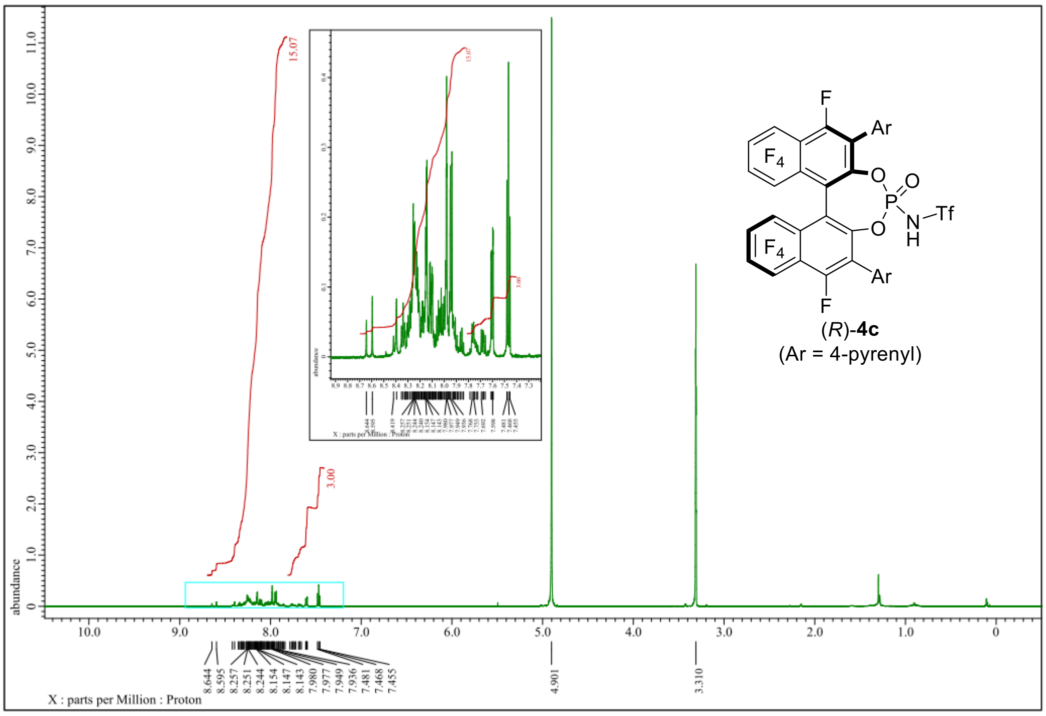


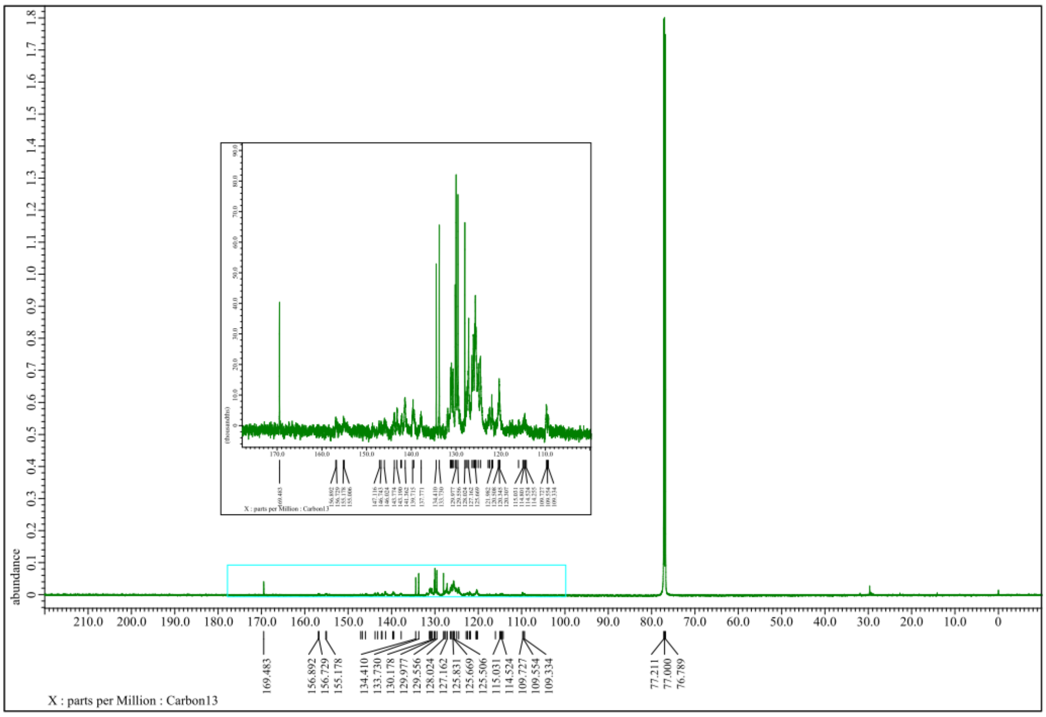


^{19}F NMR (565 MHz) spectra of **S2**

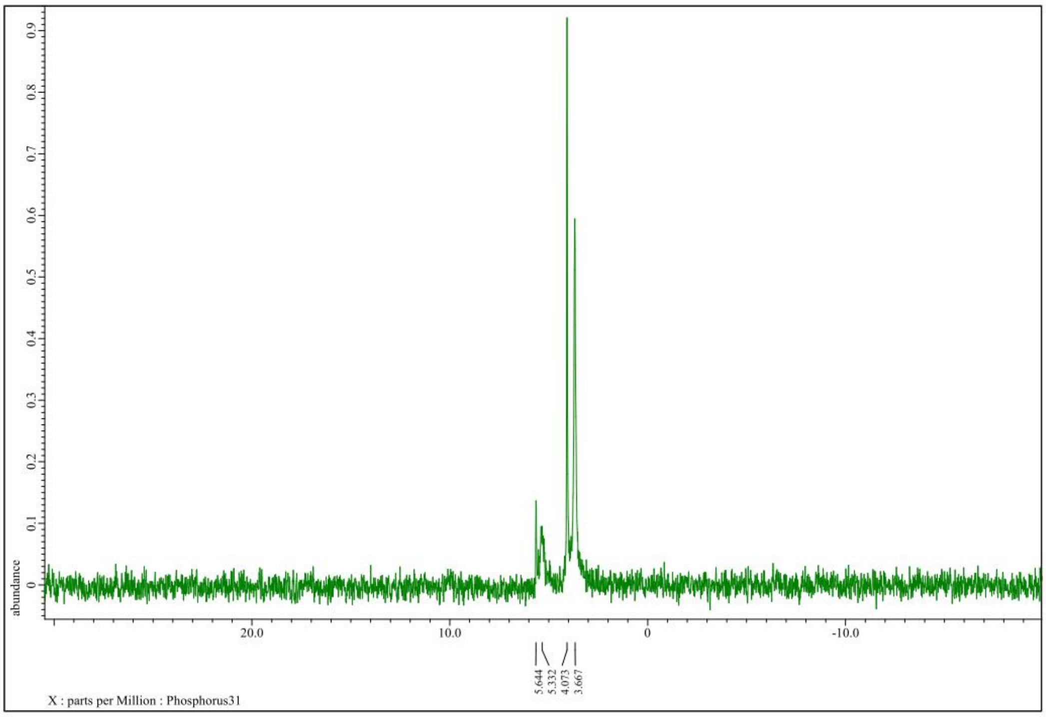


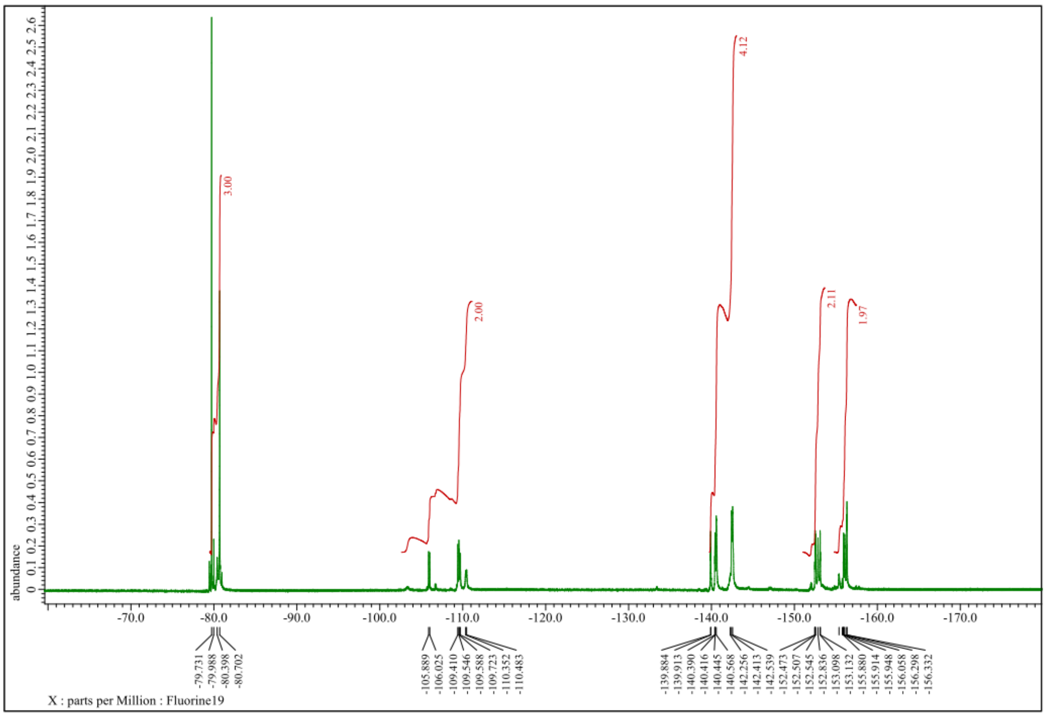
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of (*R*)-**4c**



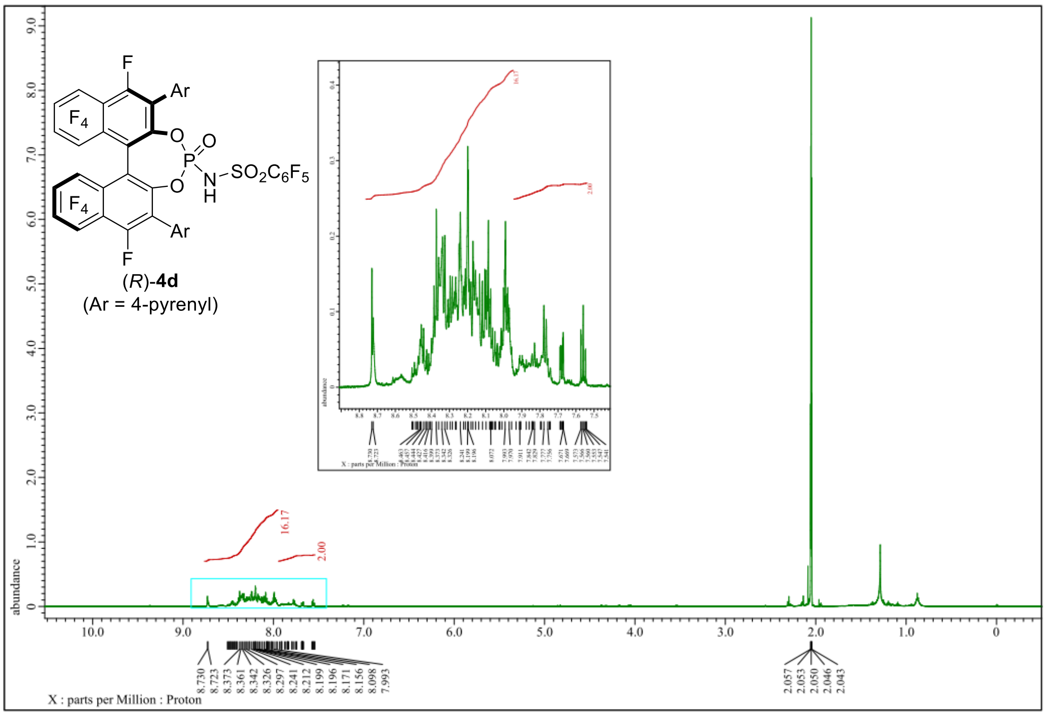


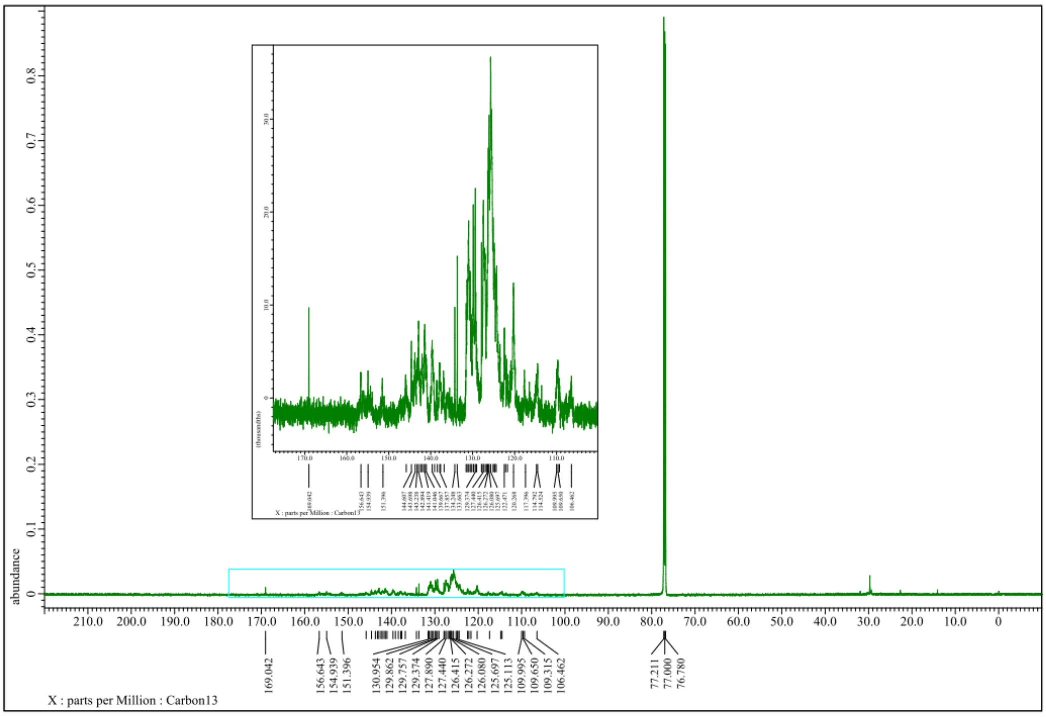
^{31}P NMR (565 MHZ) and ^{19}F NMR (243 MHz) spectra of (*R*)-**4c**



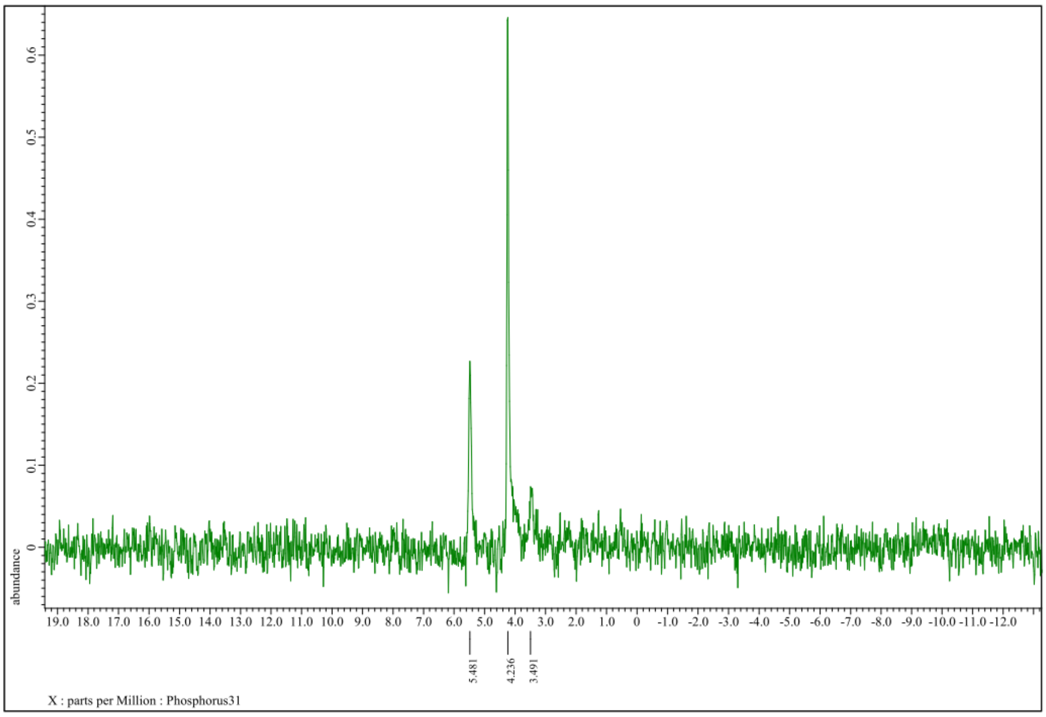


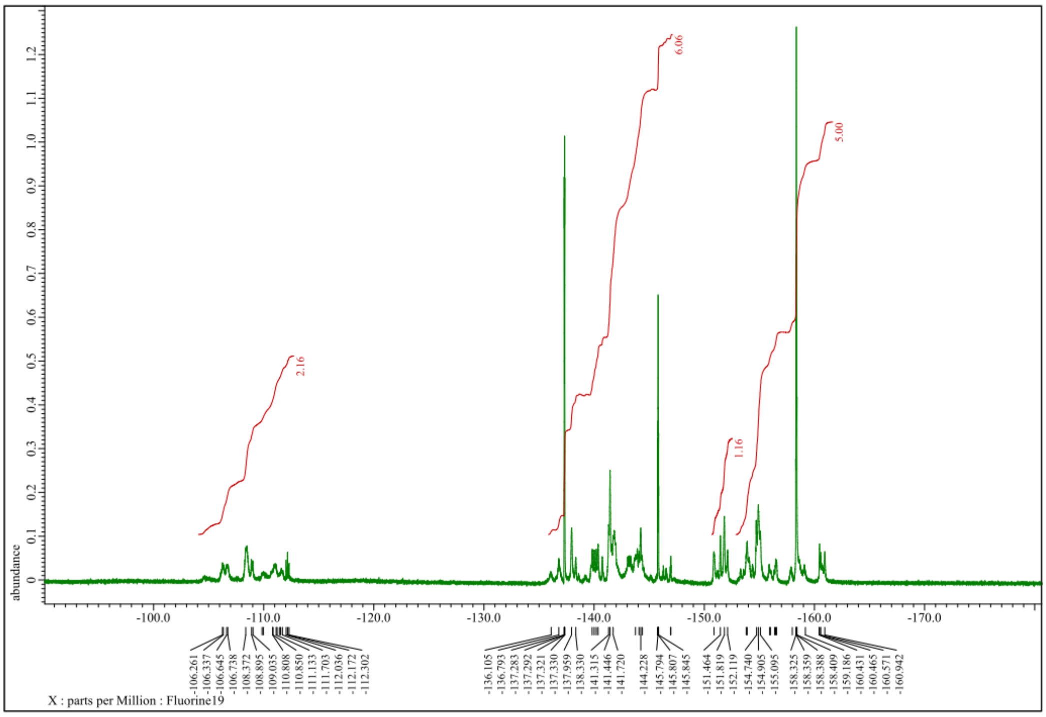
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of (*R*)-**4d**



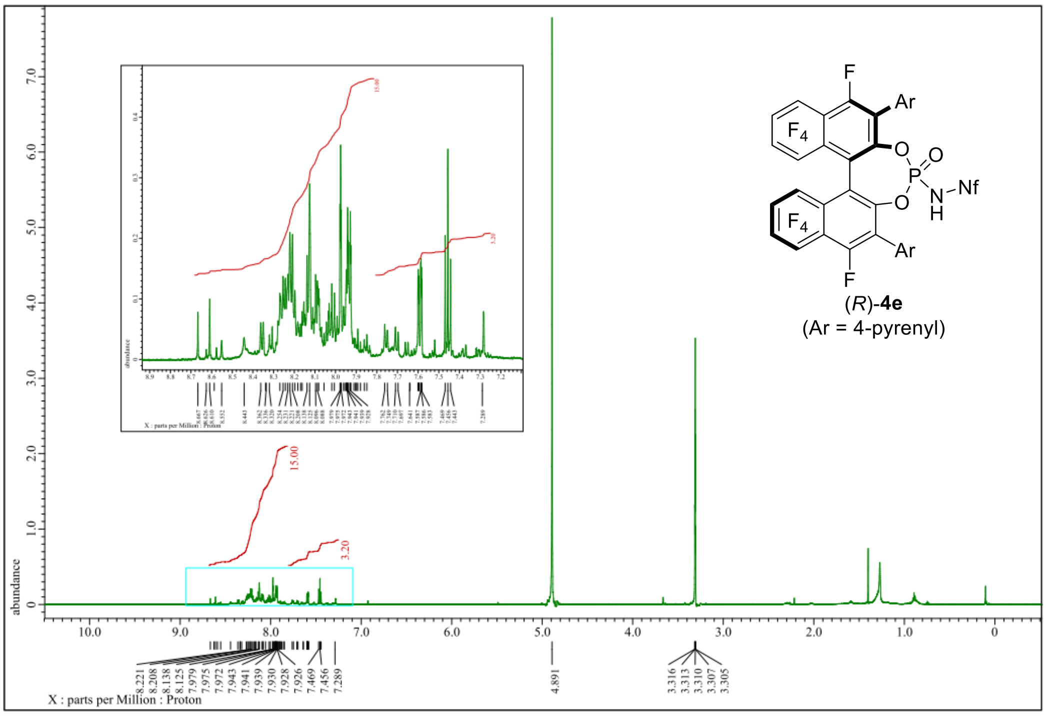


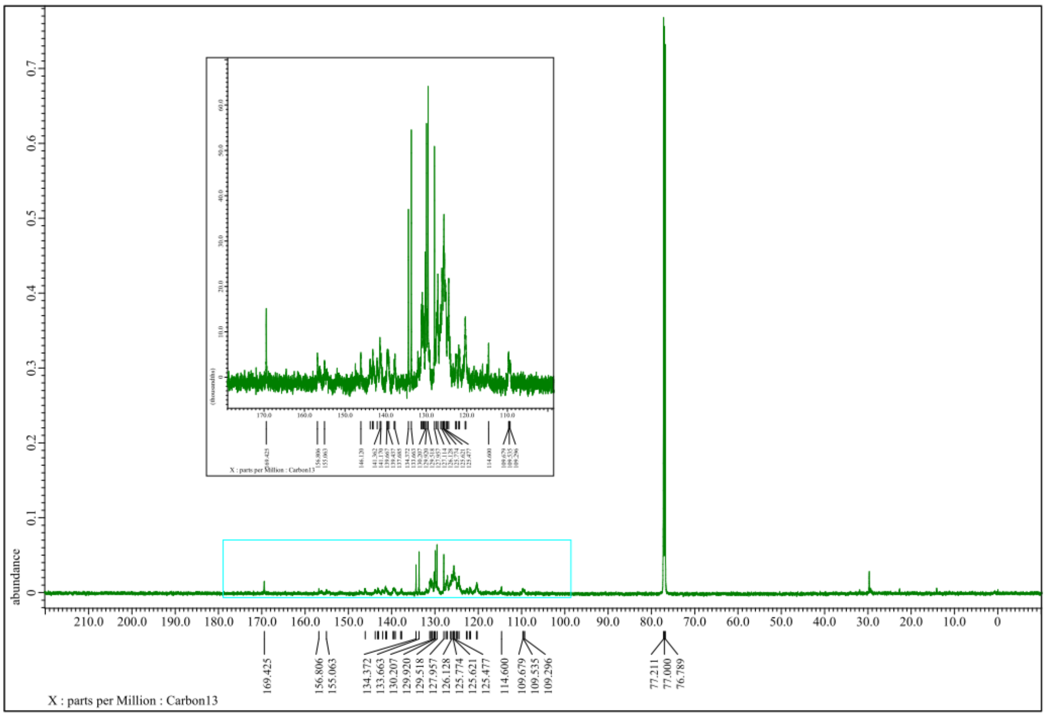
^{31}P NMR (565 MHZ) and ^{19}F NMR (243 MHz) spectra of (*R*)-**4d**



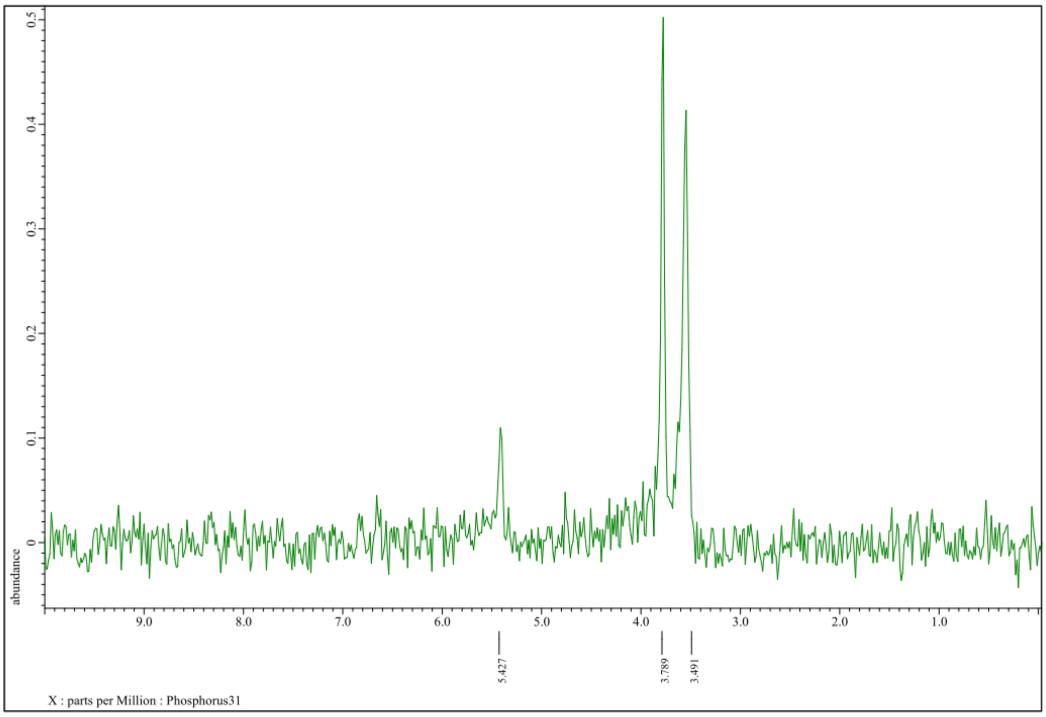


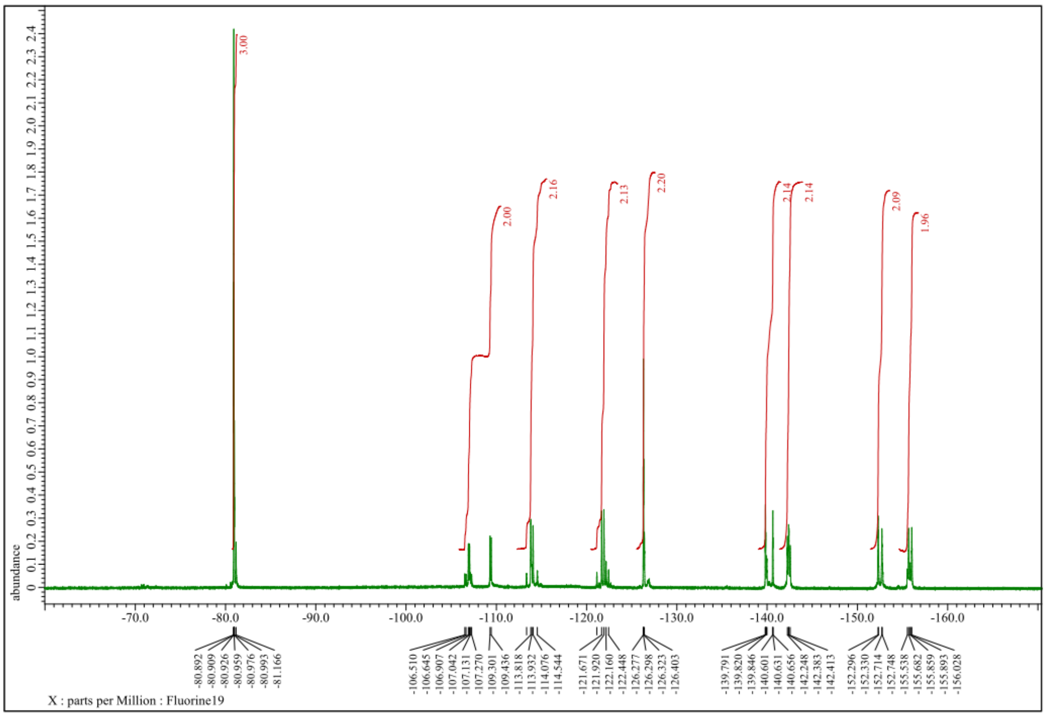
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of (*R*)-**4e**



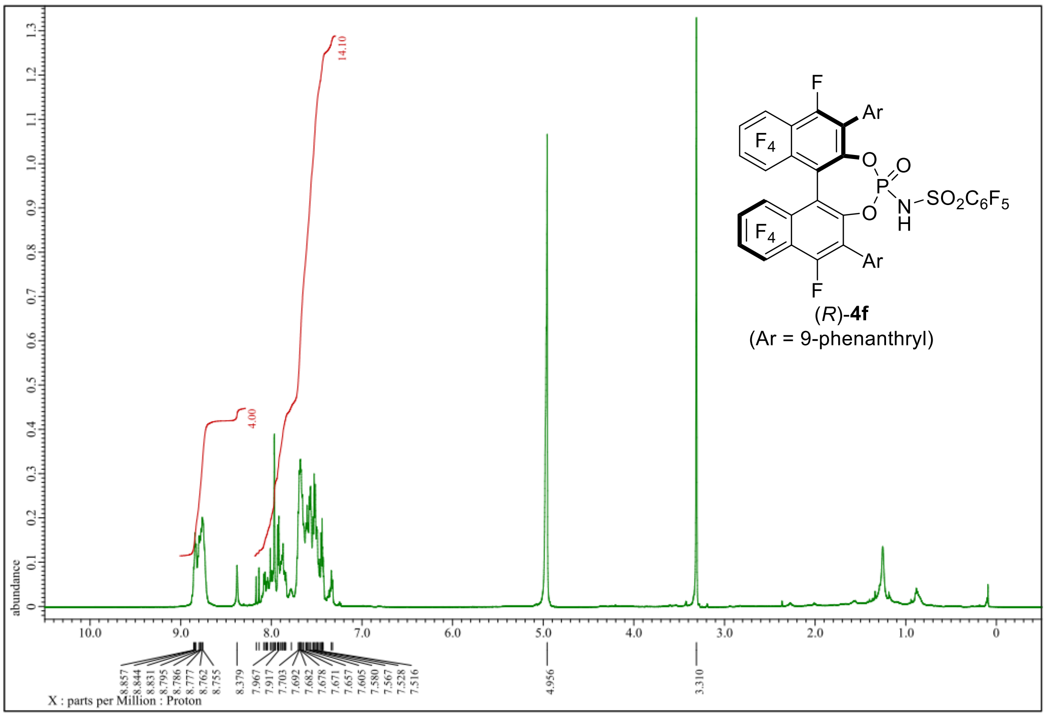


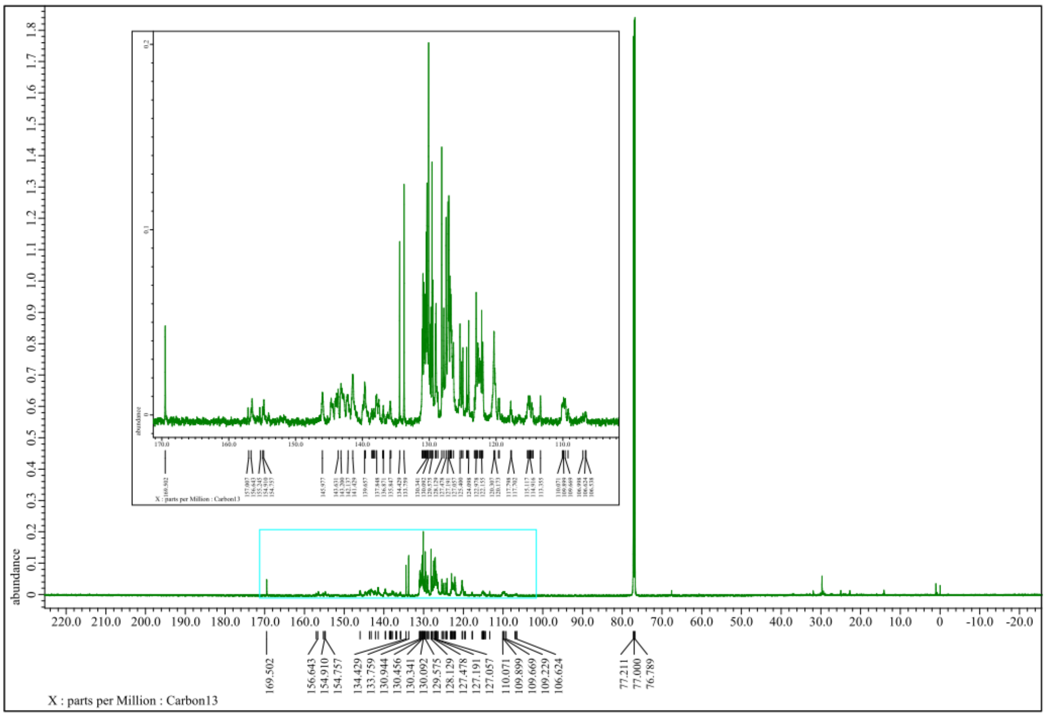
^{31}P NMR (565 MHZ) and ^{19}F NMR (243 MHz) spectra of (*R*)-**4e**



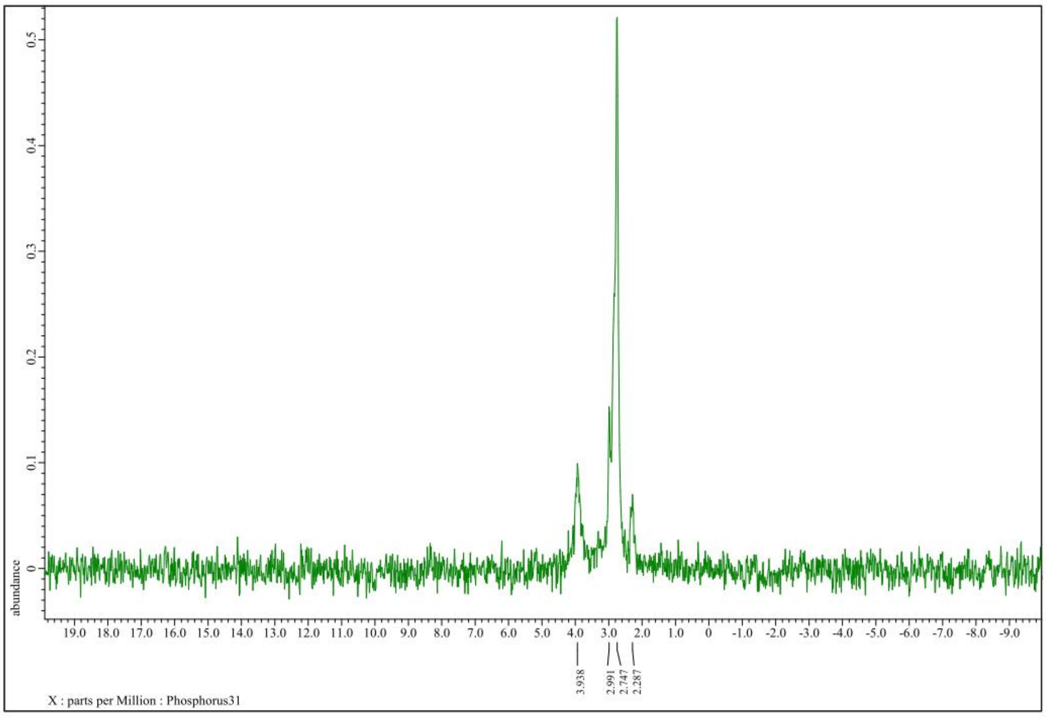


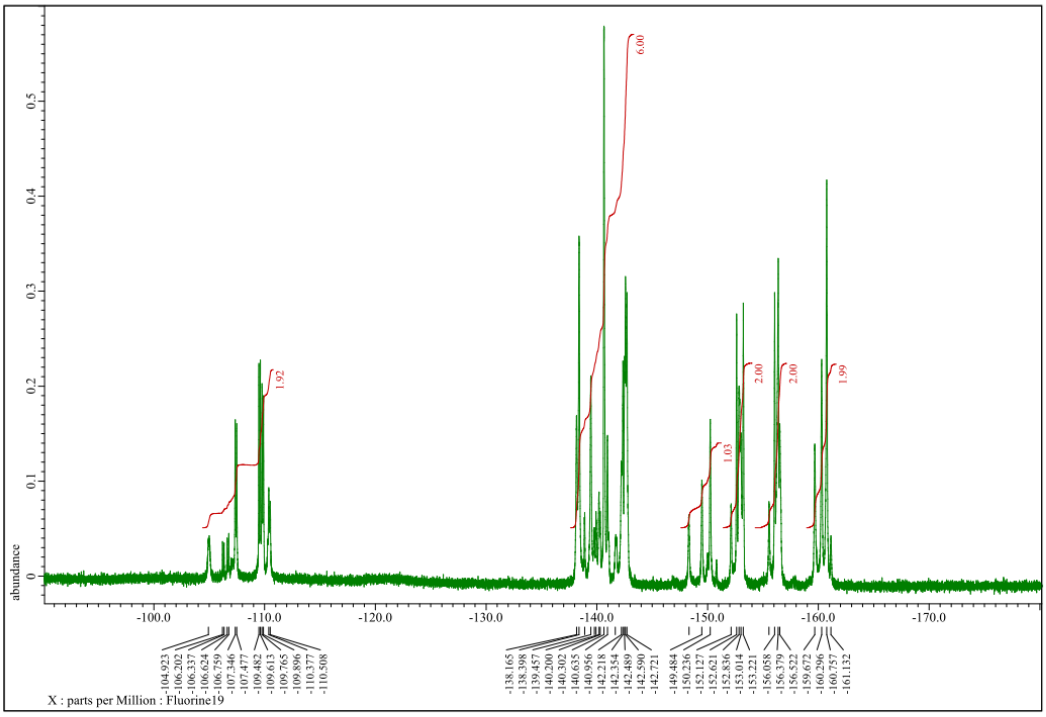
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of (*R*)-**4f**



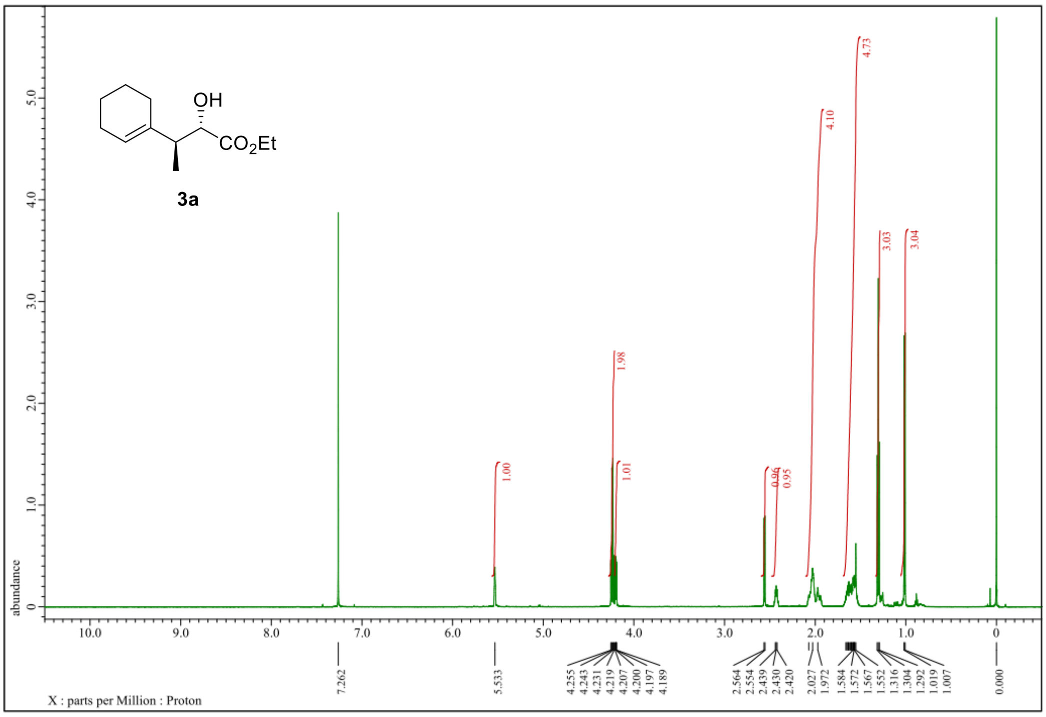


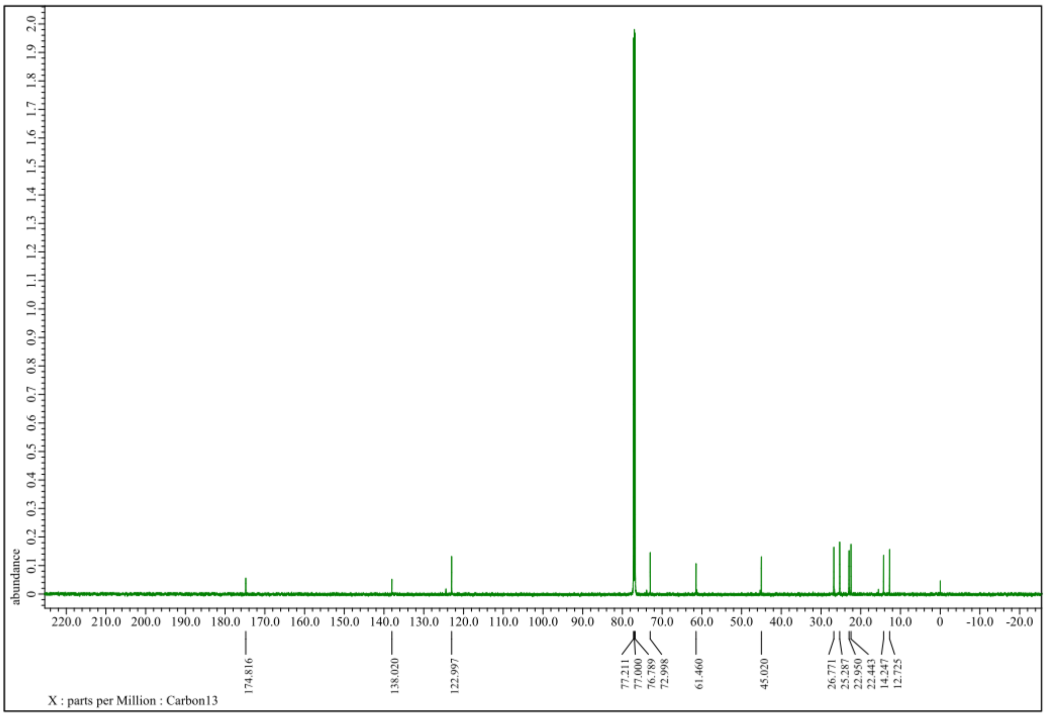
^{31}P NMR (565 MHZ) and ^{19}F NMR (243 MHz) spectra of (*R*)-**4f**



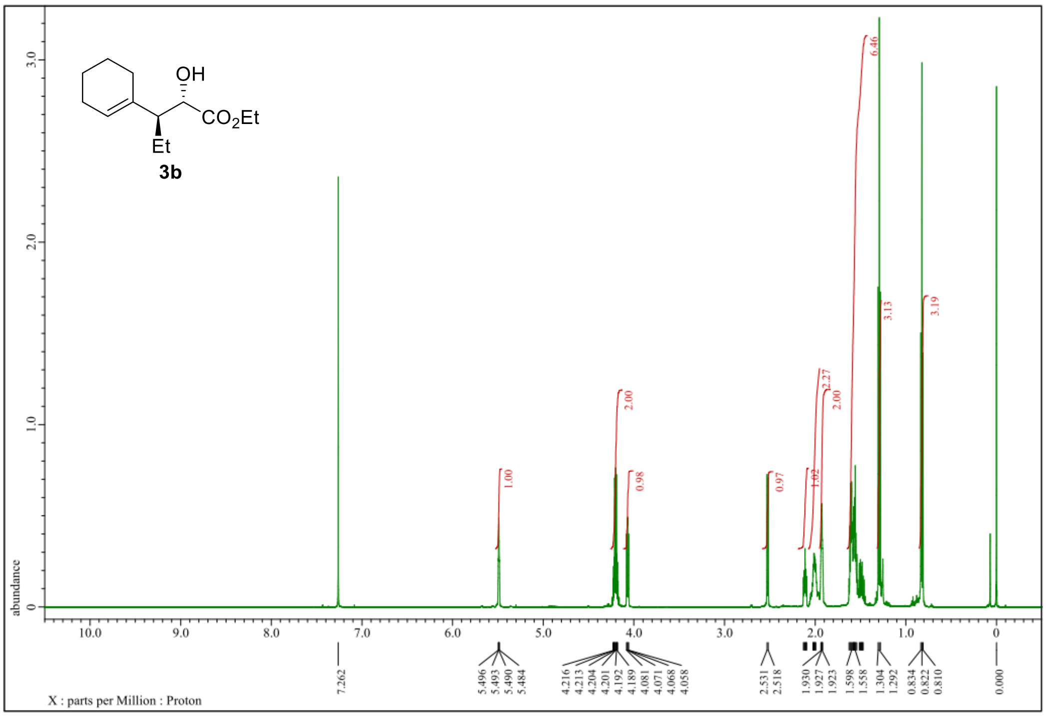


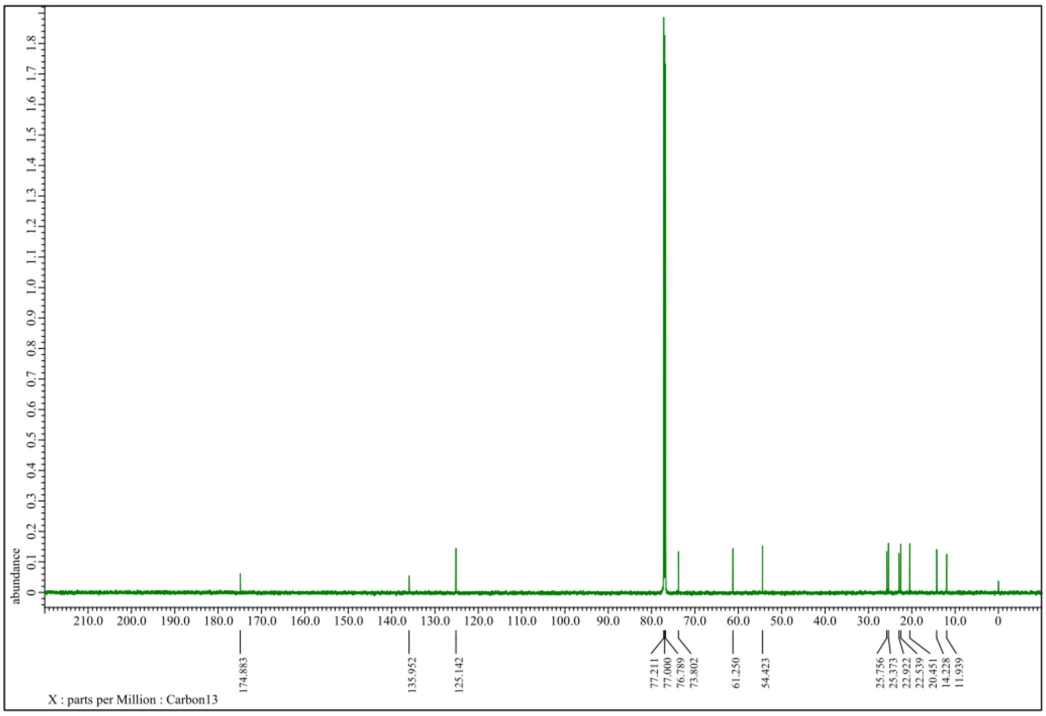
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **3a**



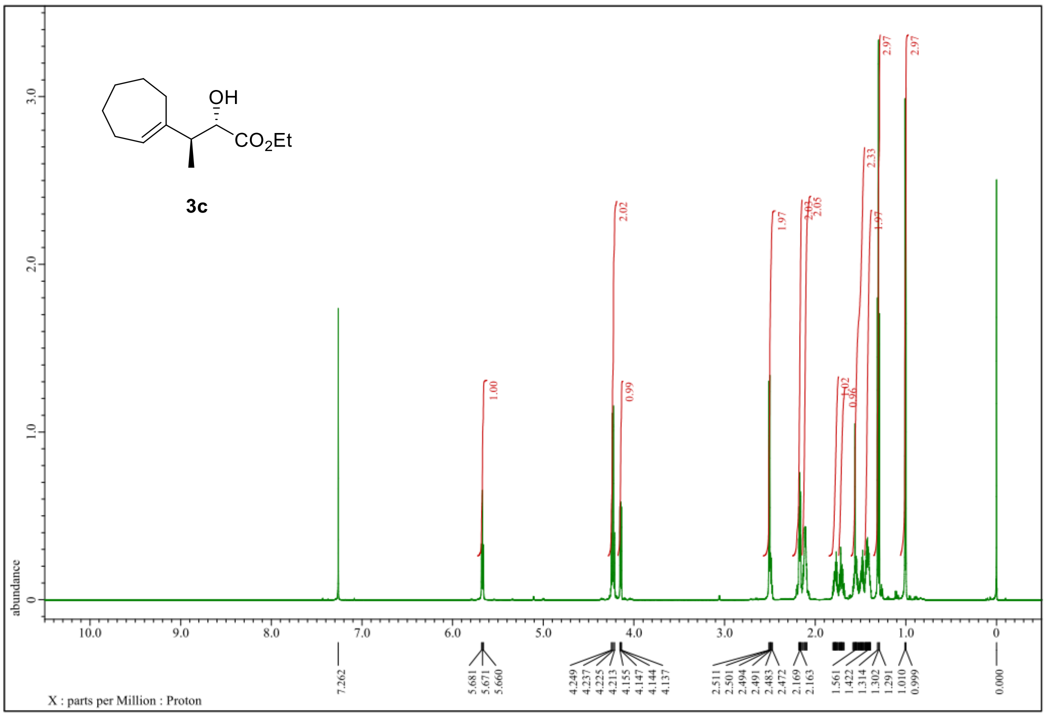


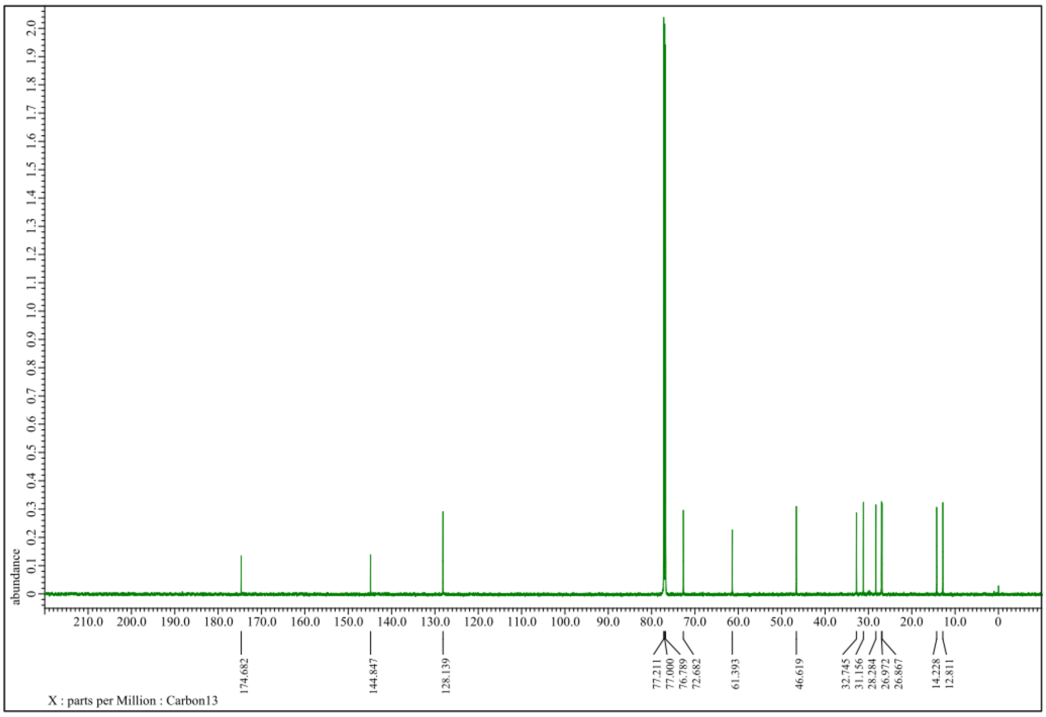
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **3b**



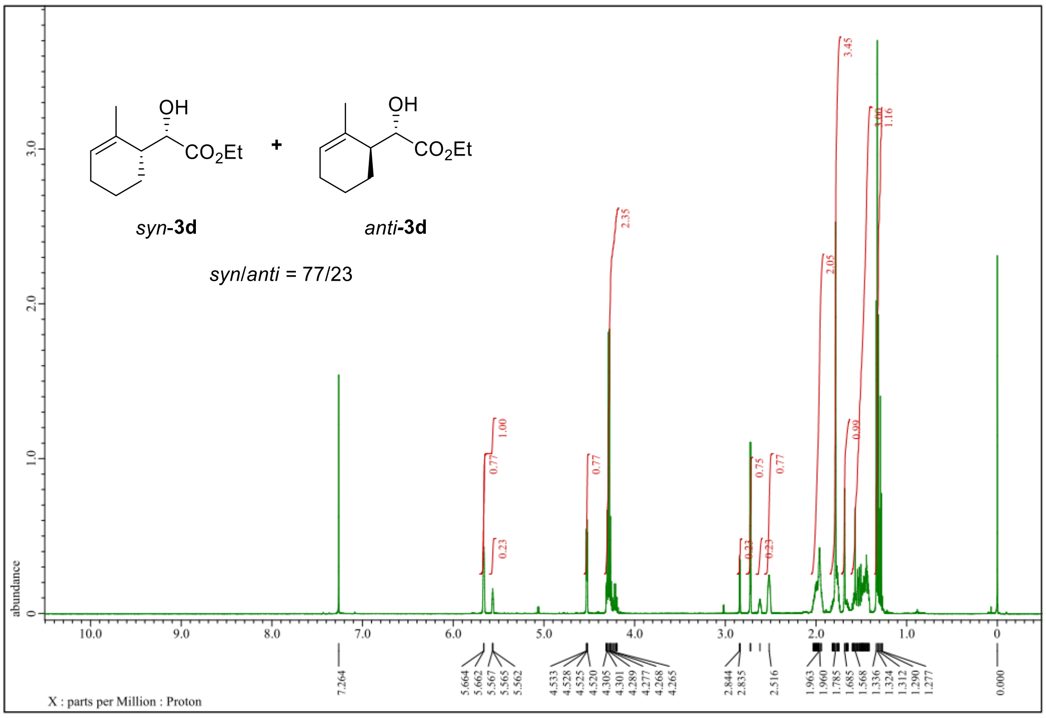


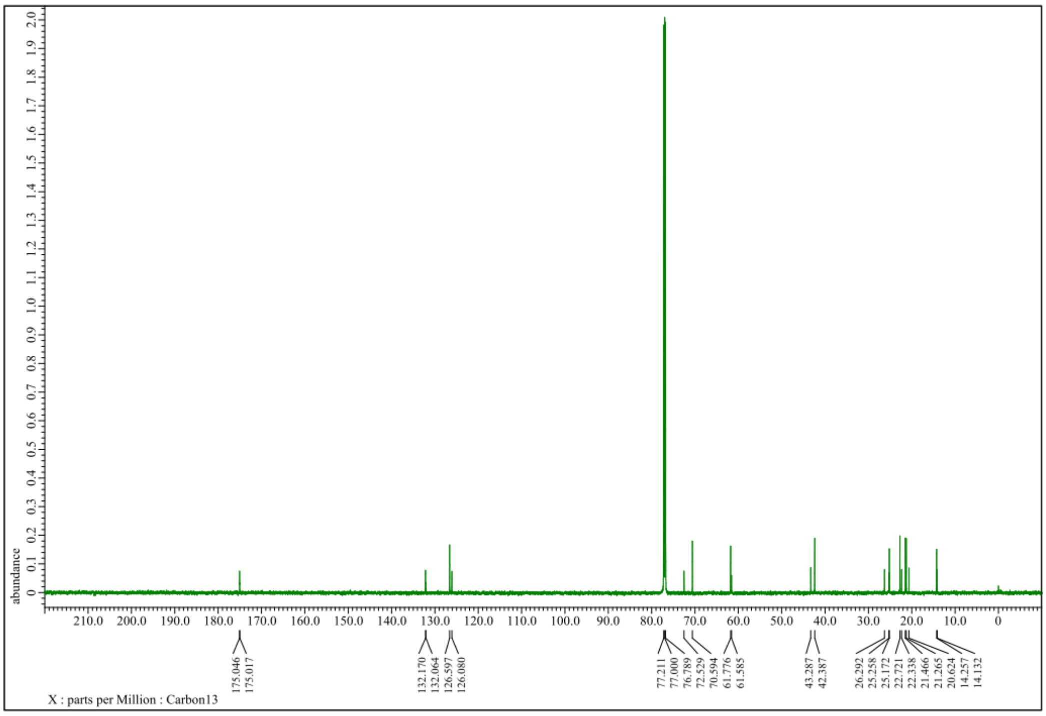
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **3c**



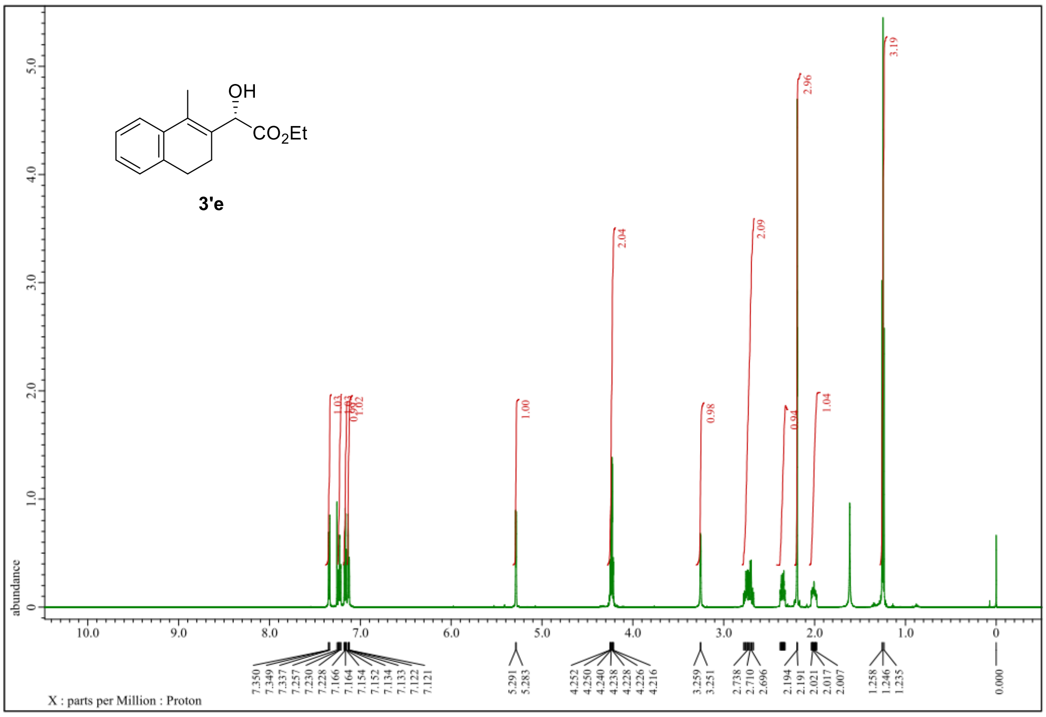


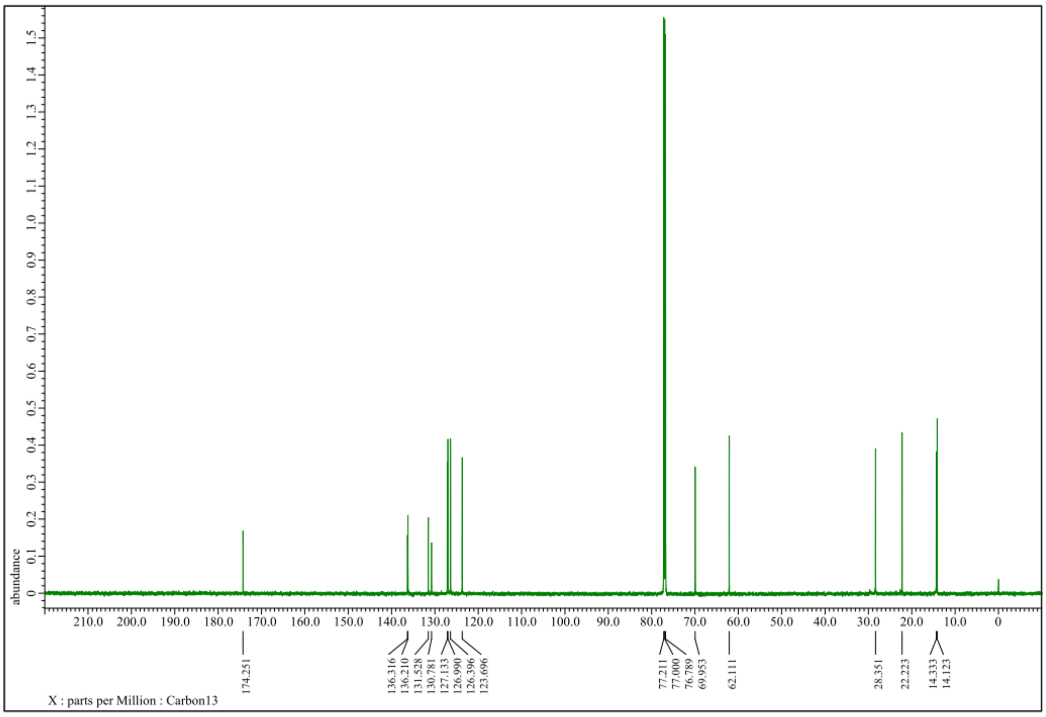
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **3d**



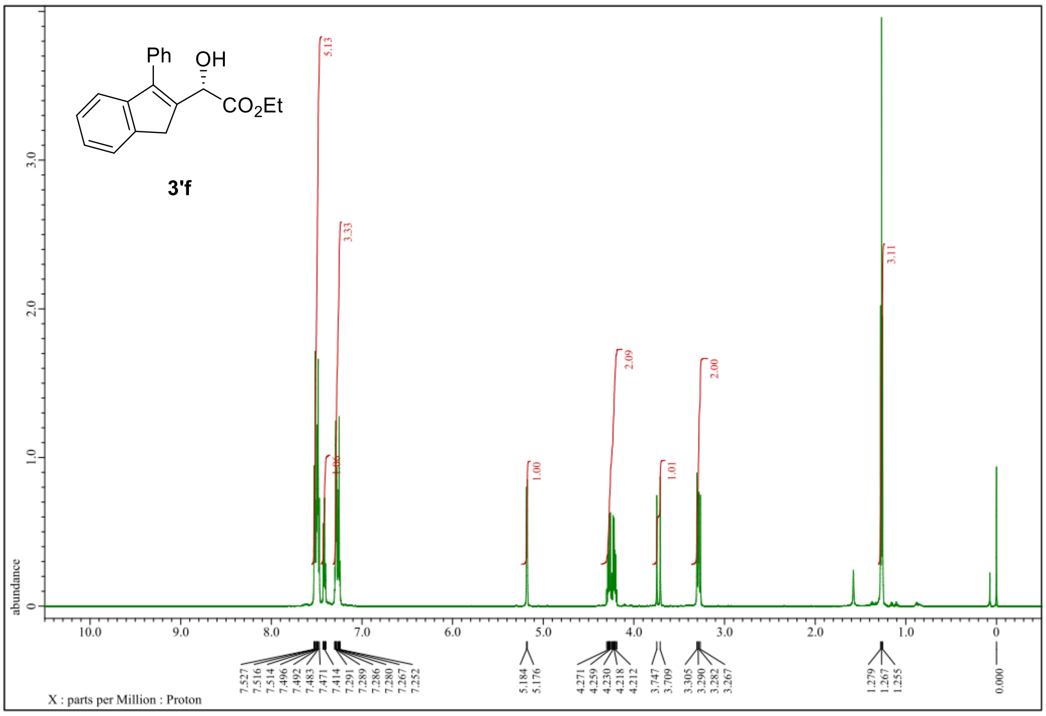


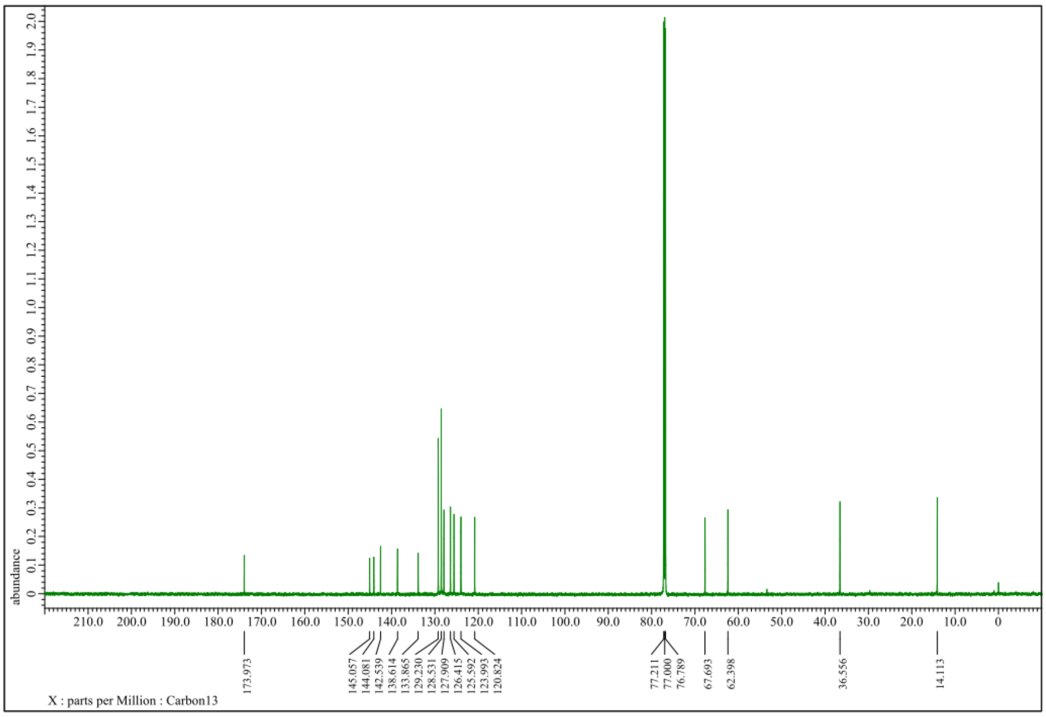
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **3’e**



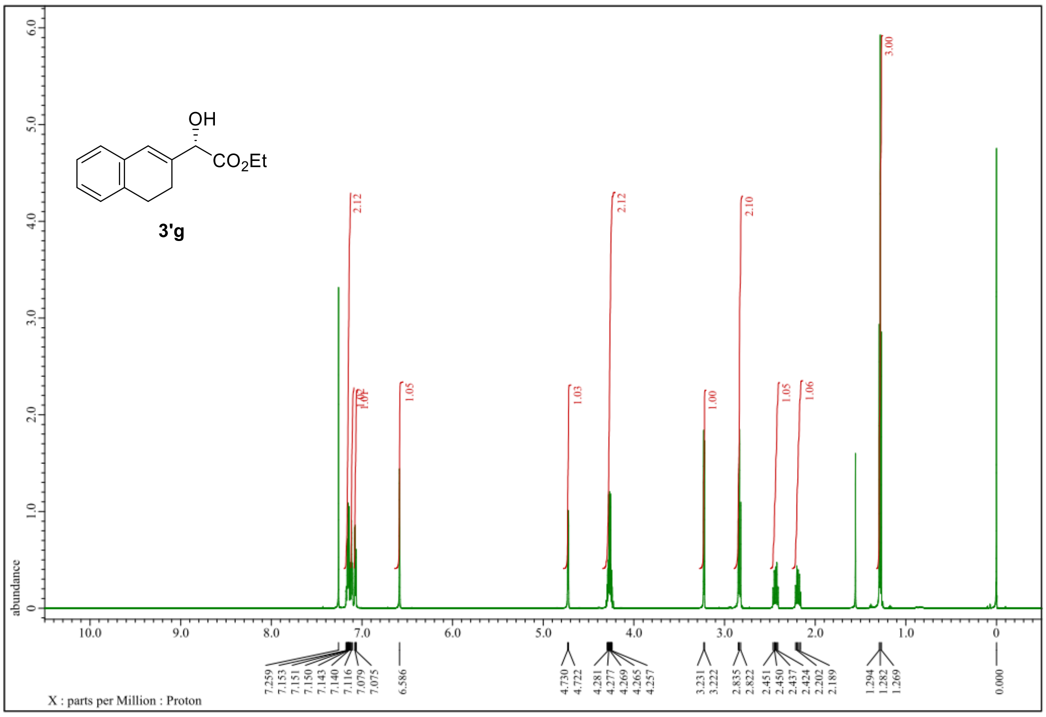


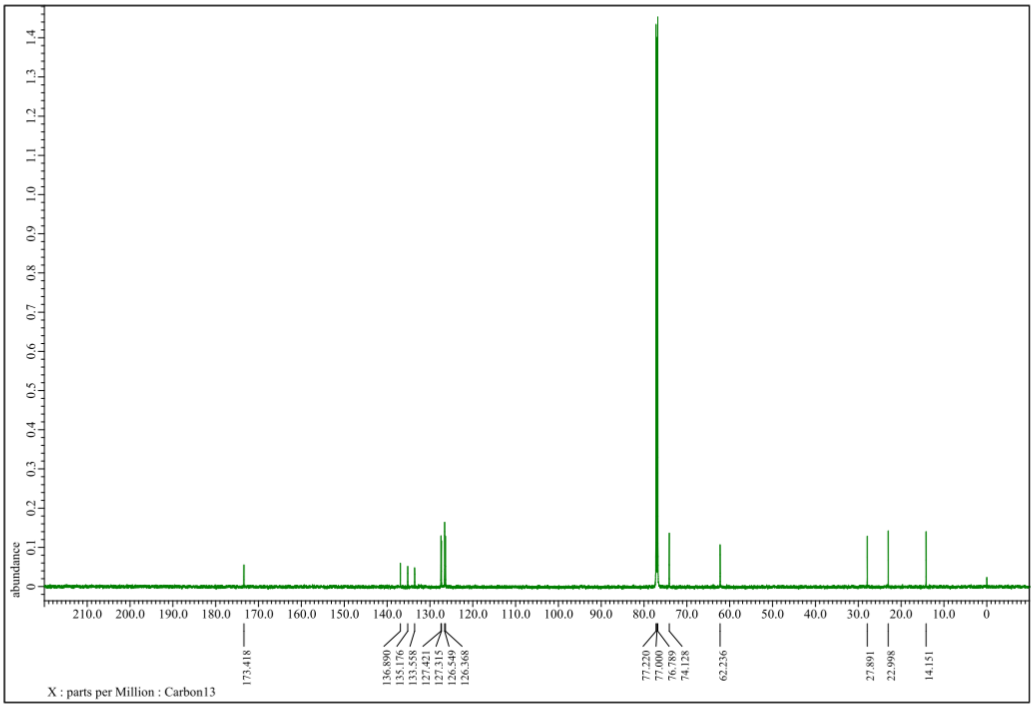
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **3'f**



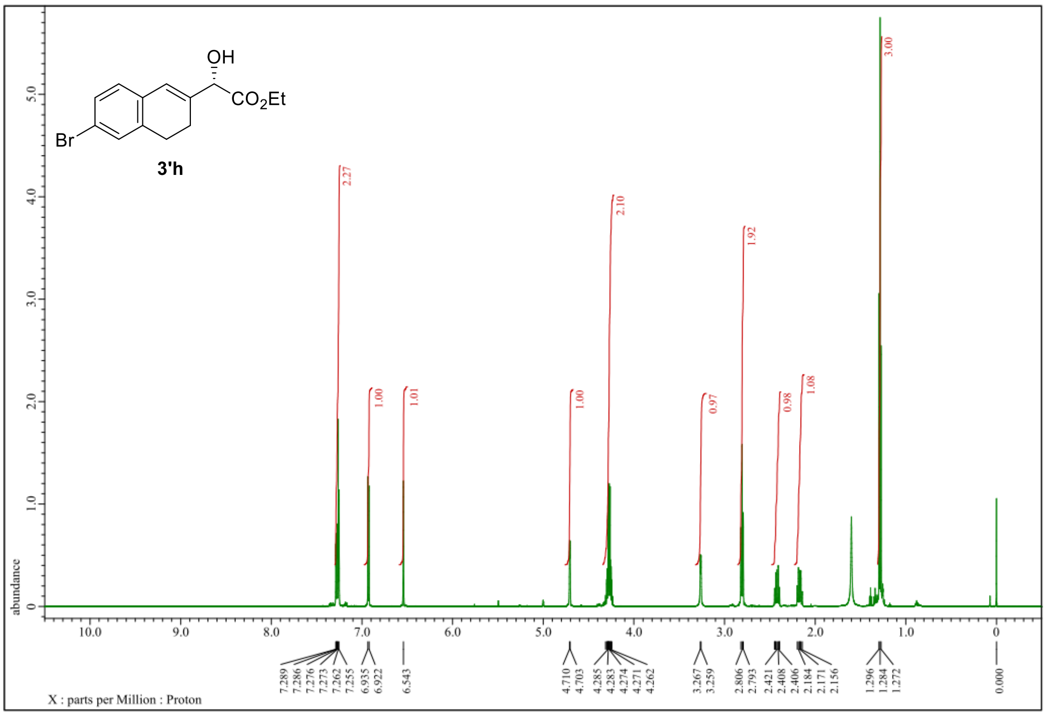


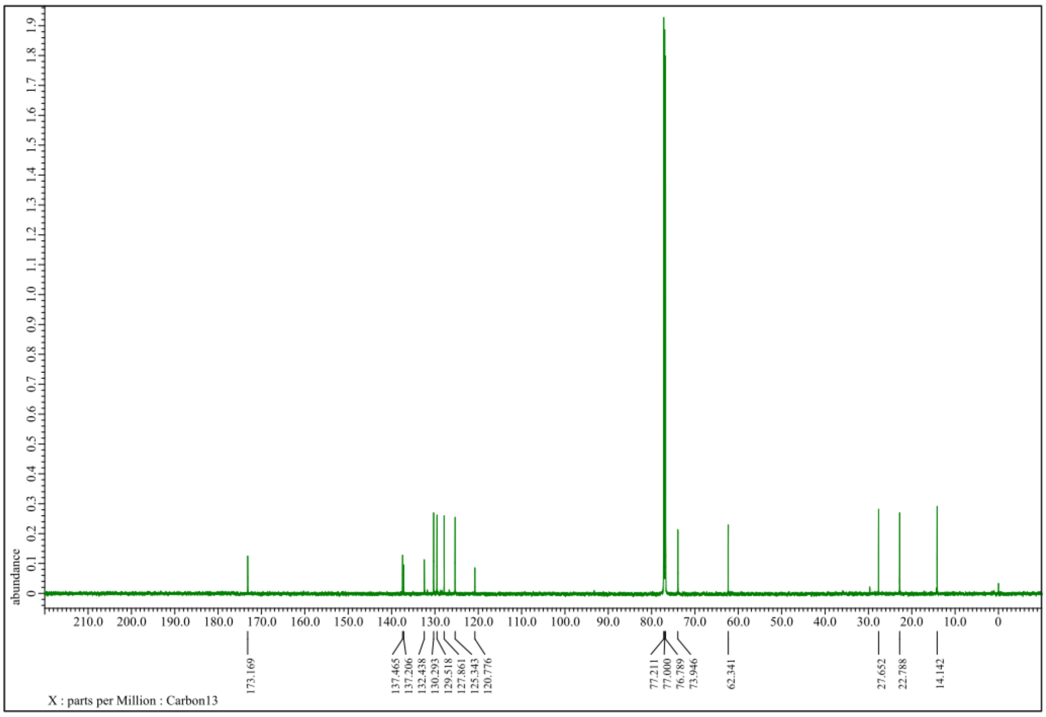
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **3’g**



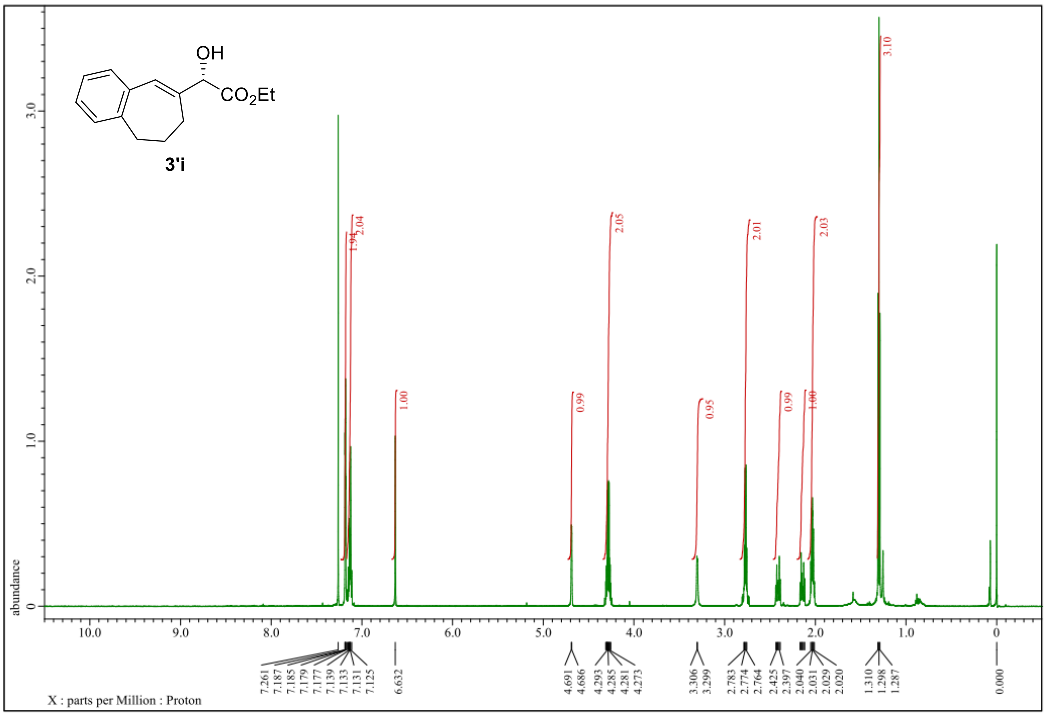


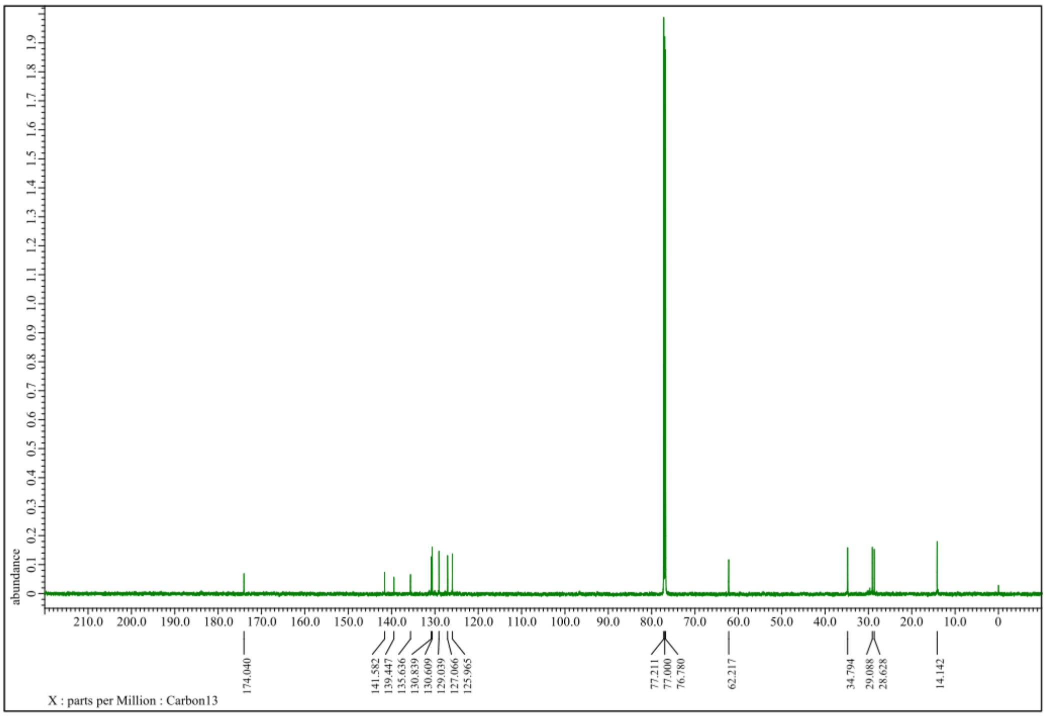
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **3'h**



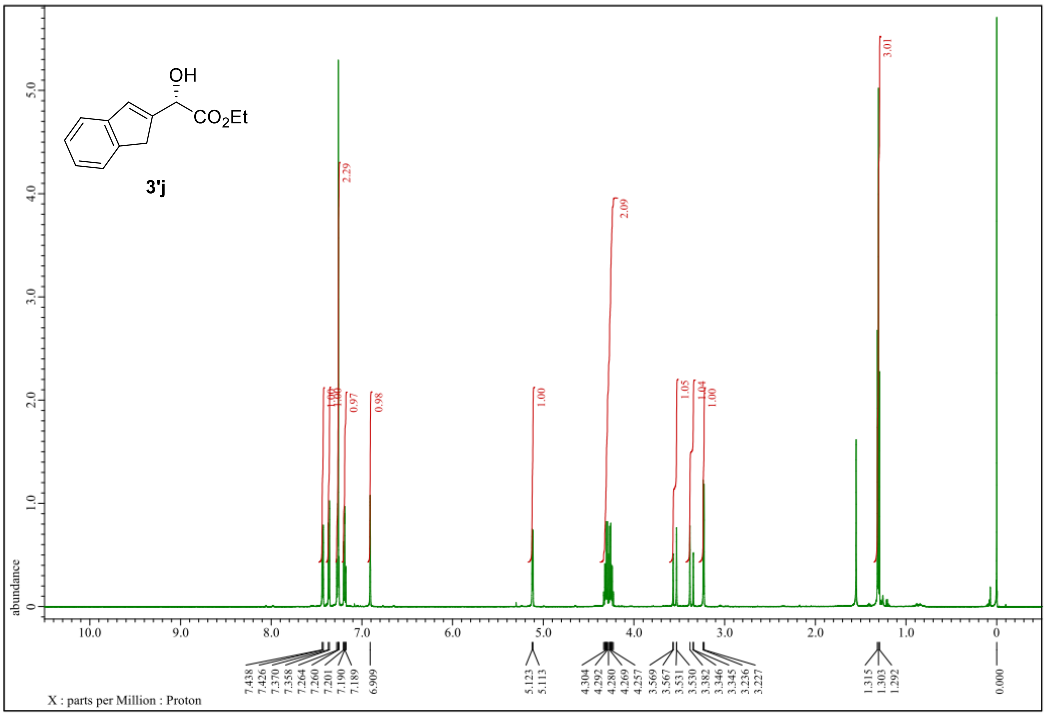


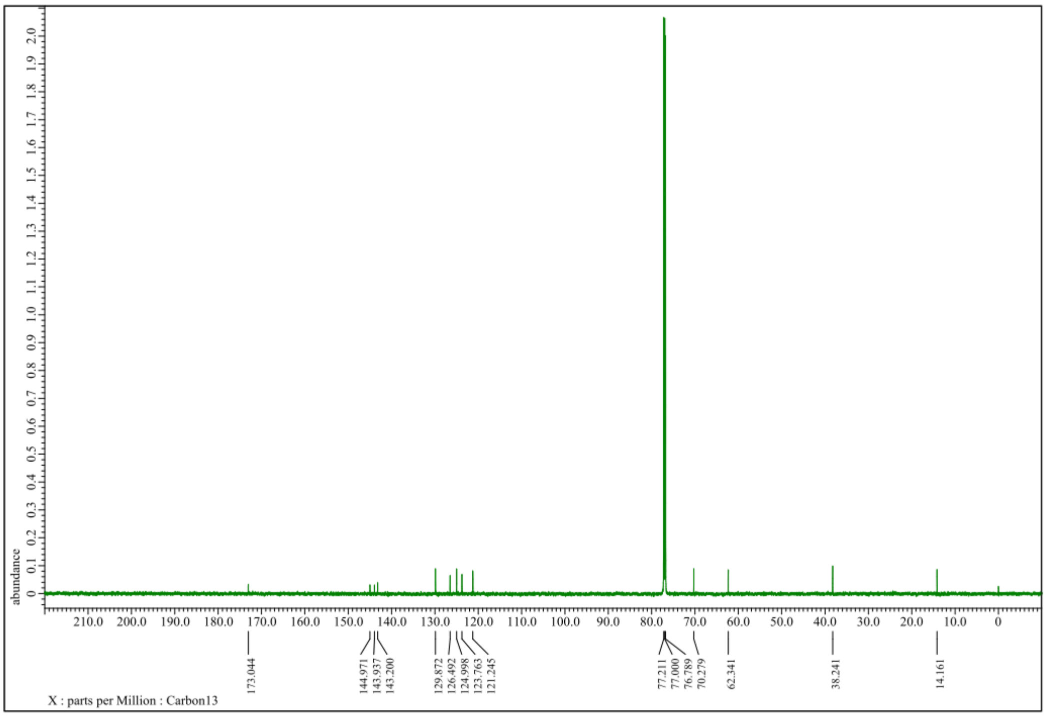
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **3’i**



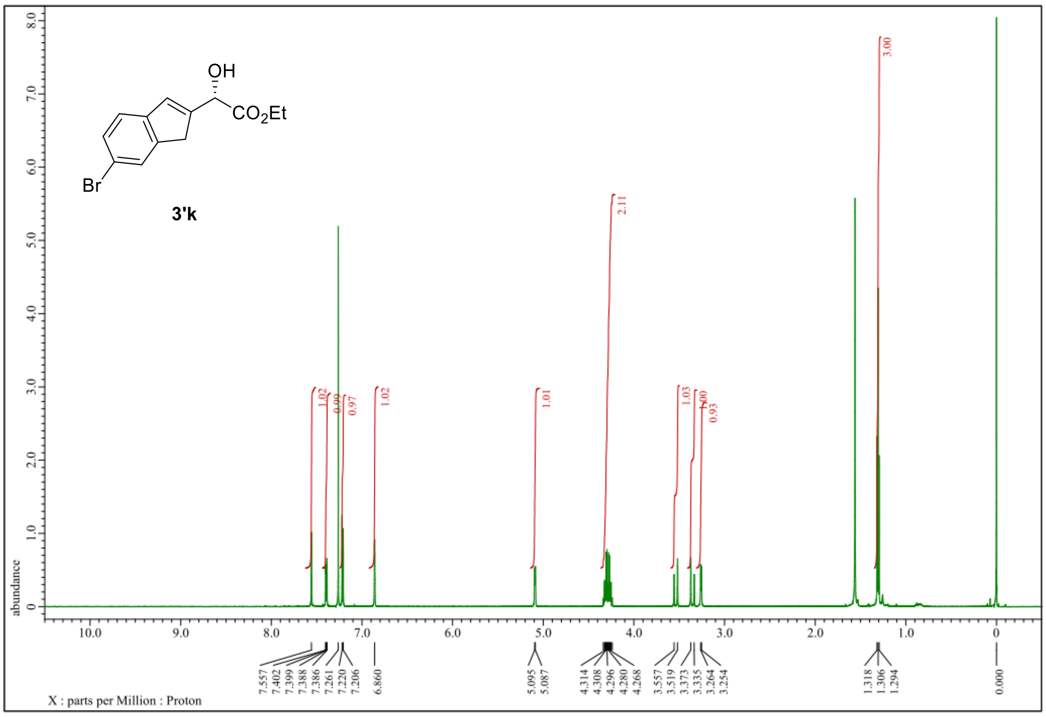


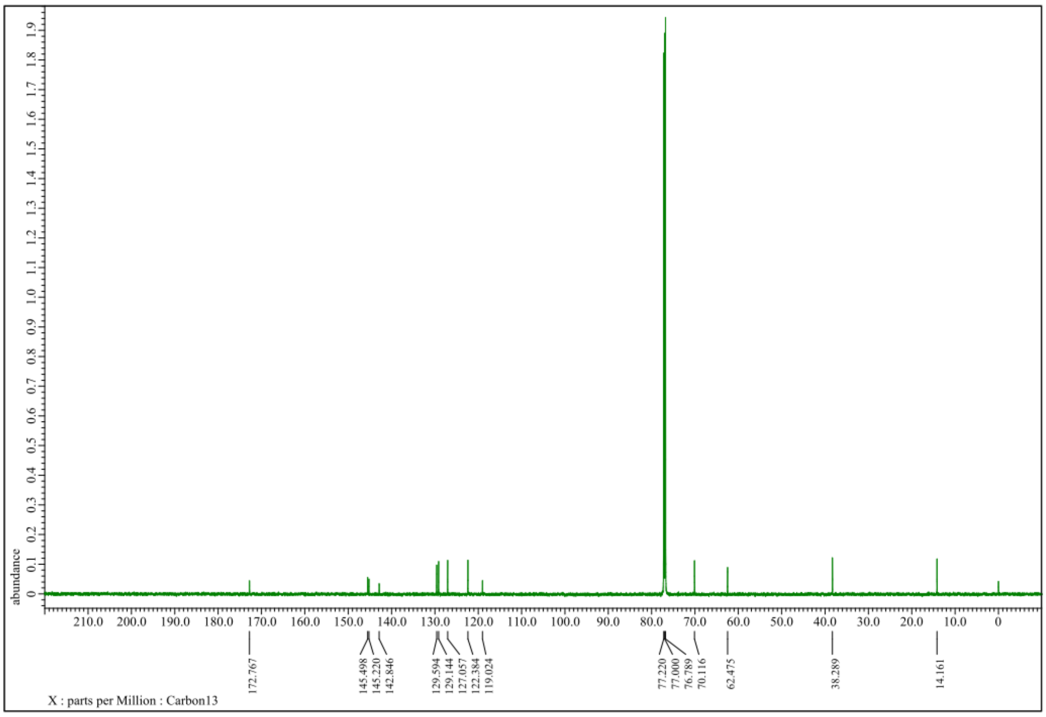
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **3'j**



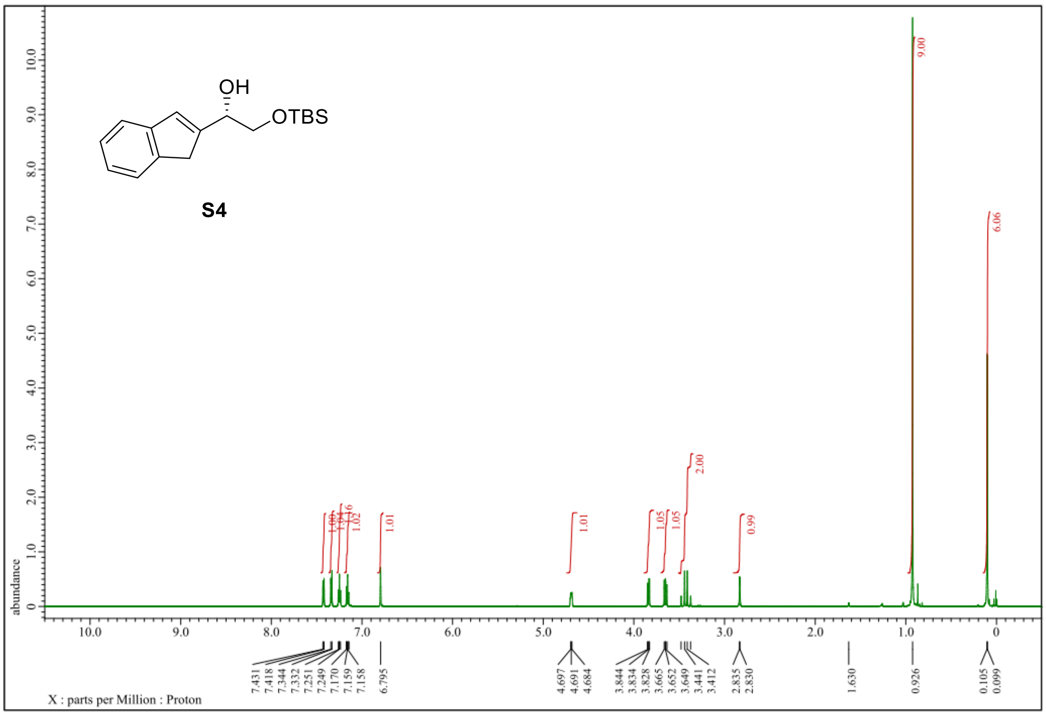


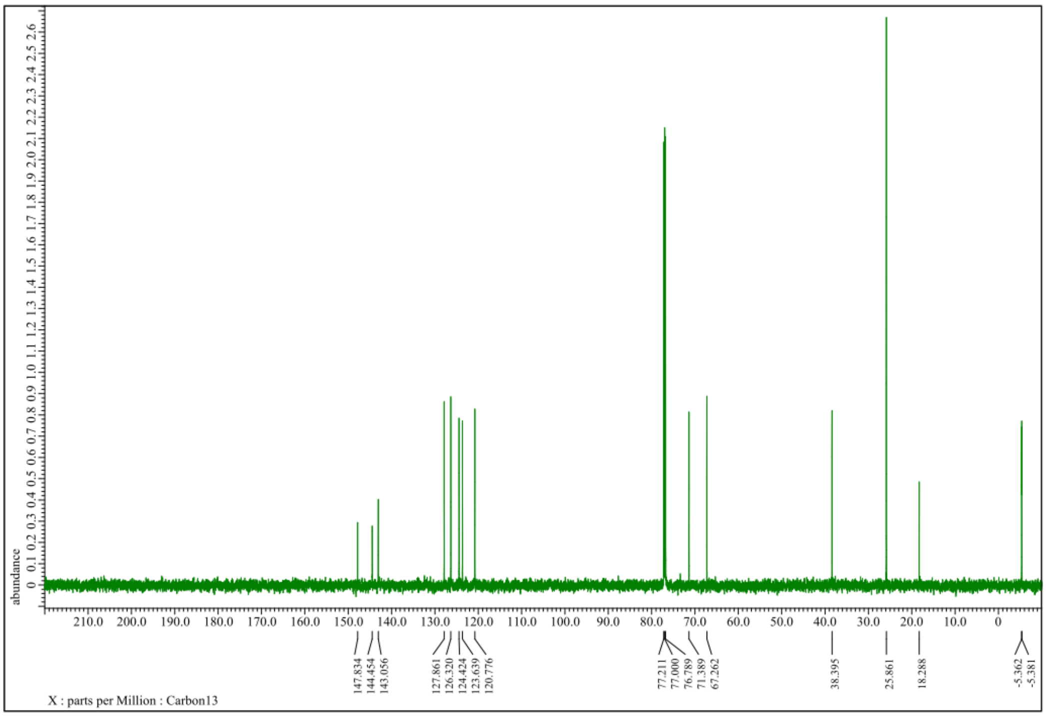
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **3’k**



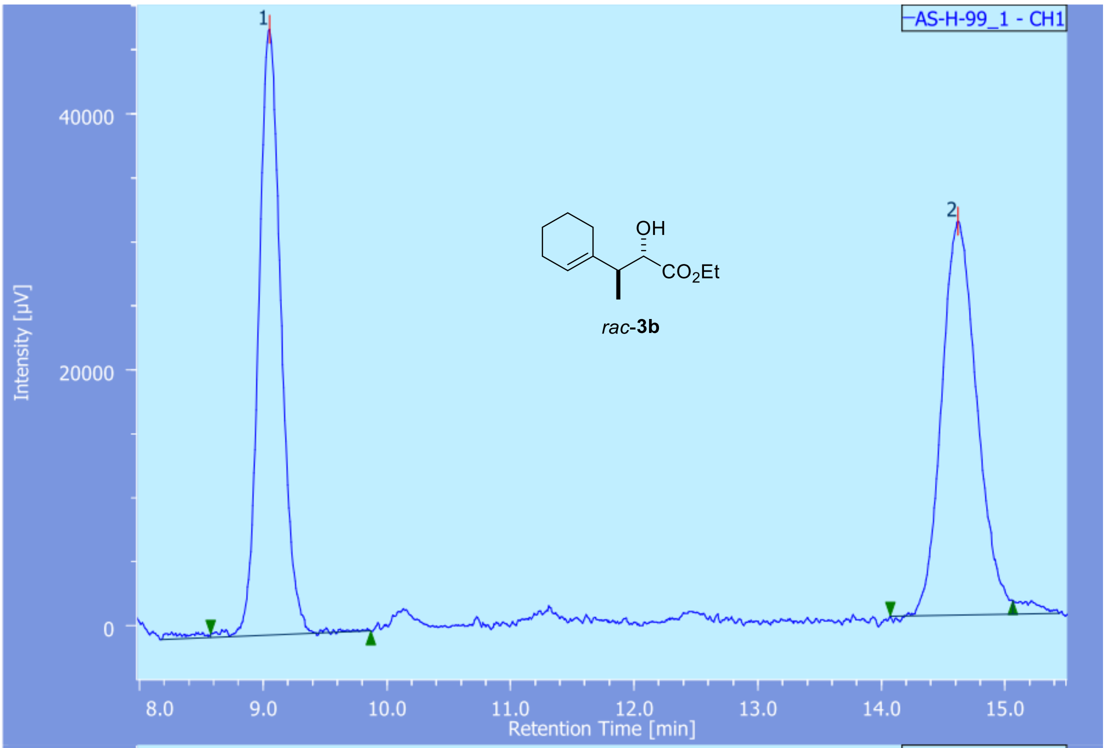


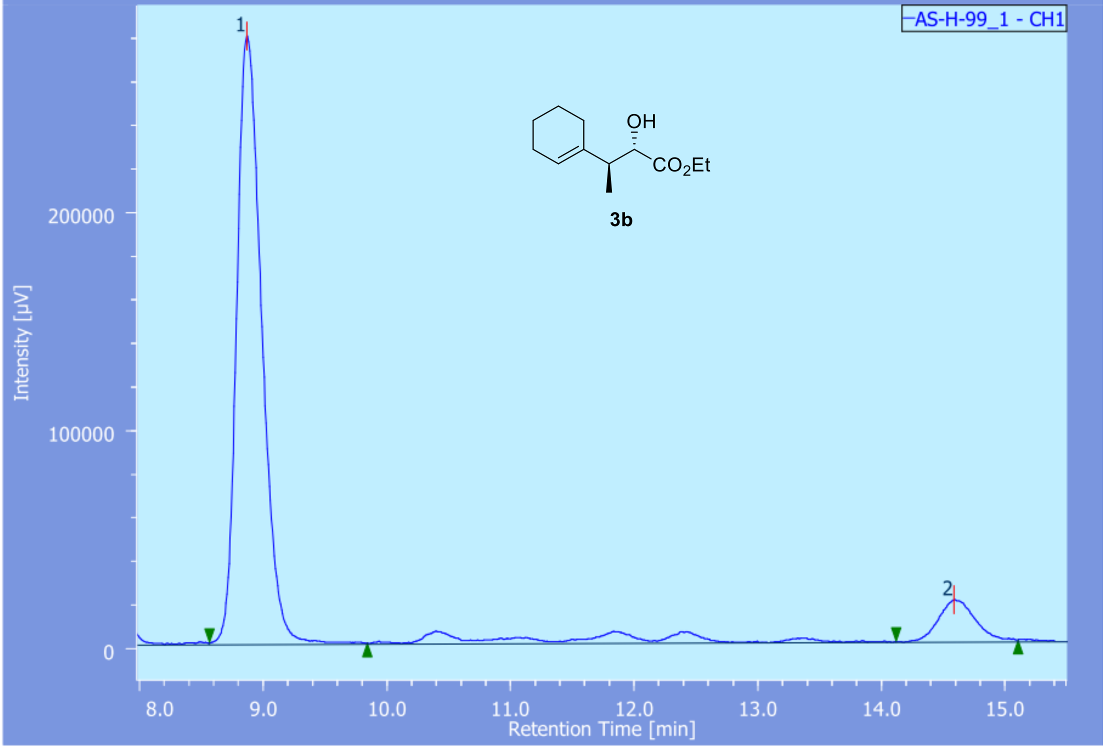
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **S4**



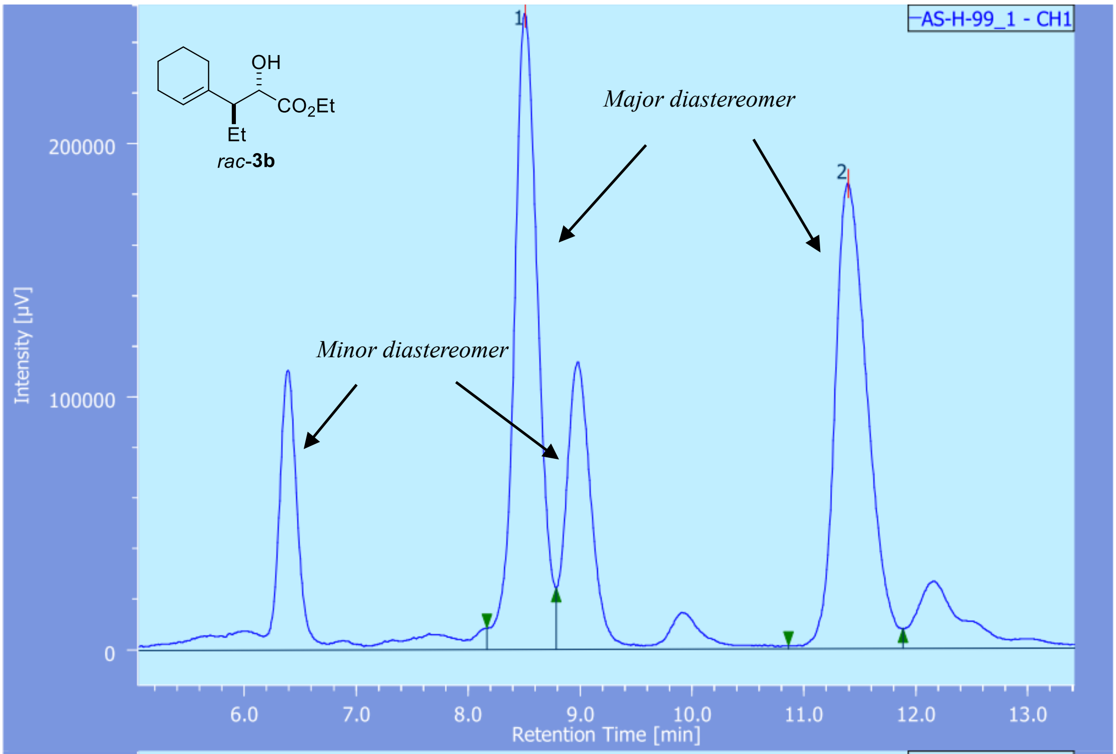


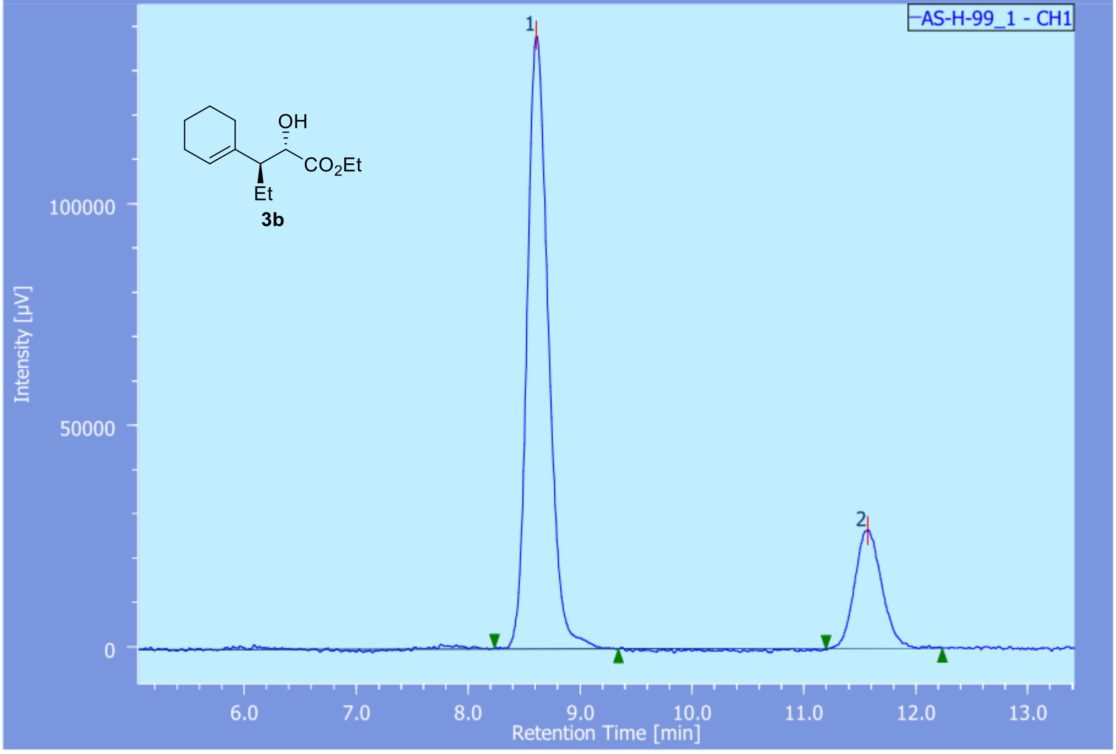
7. HPLC charts



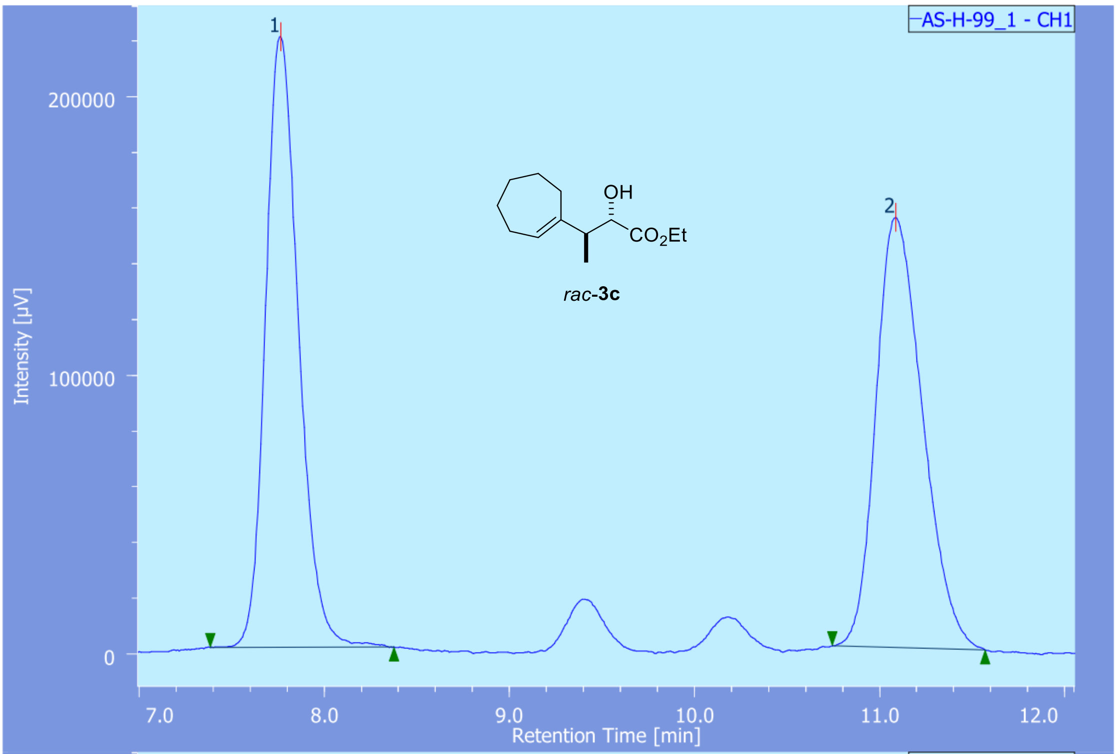


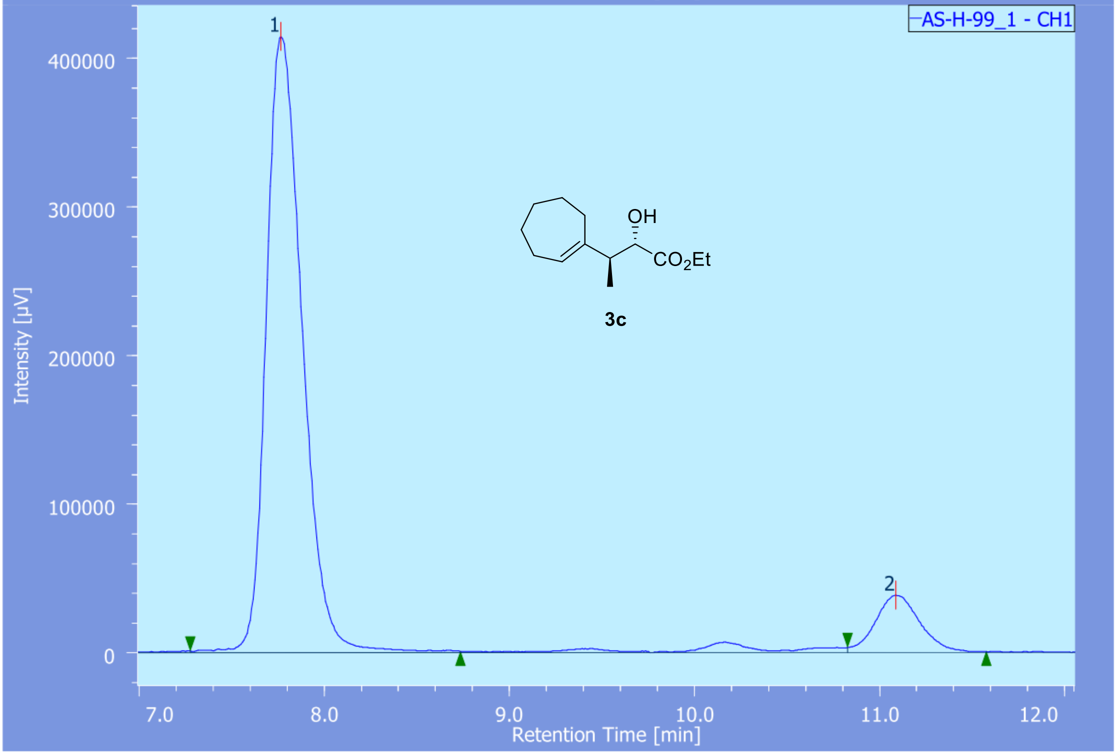
	Retention time (1)	Retention time (2)	Area (1)	Area (2)	% Area (1)	% Area (2)
rac-**3a**	9.1	14.6	597638	609057	49.5	50.5
3a	8.9	14.6	3938391	410594	90.6	9.4



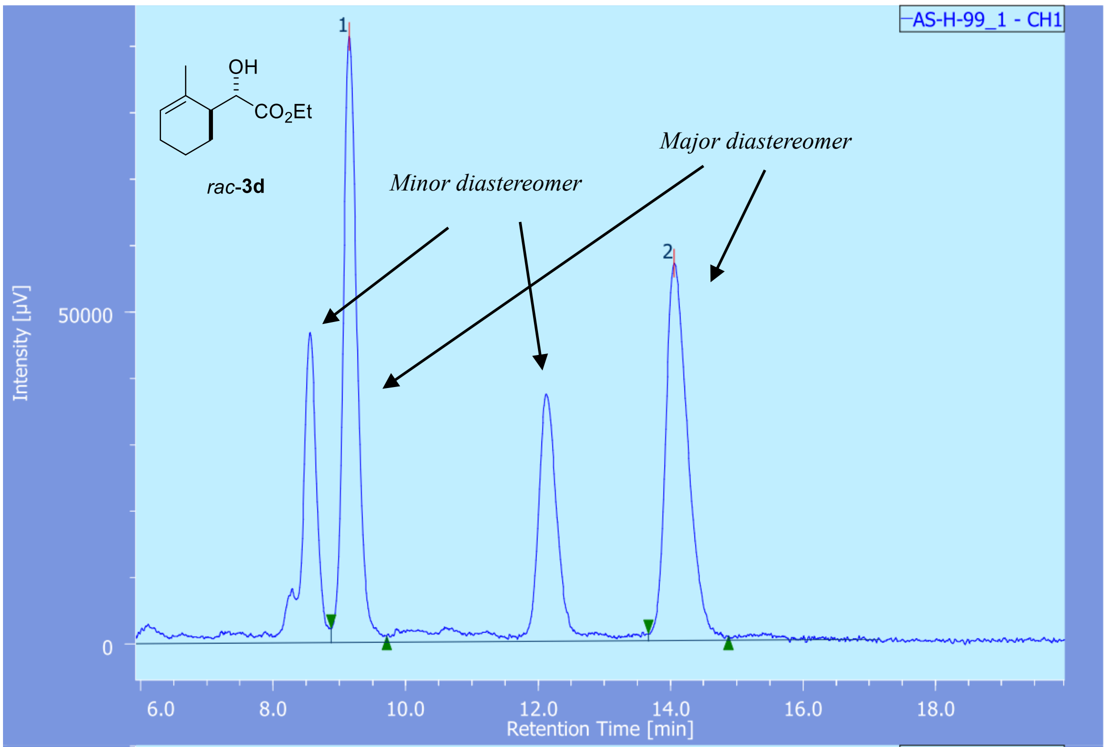


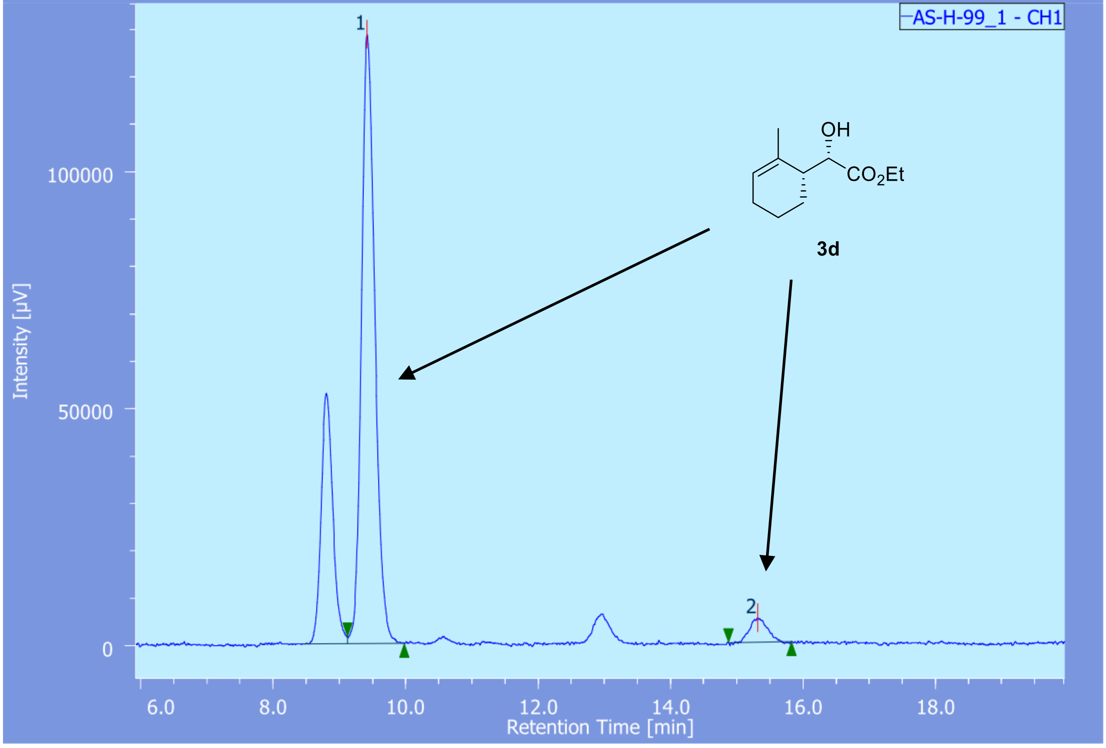
	Retention time (1)	Retention time (2)	Area (1)	Area (2)	% Area (1)	% Area (2)
rac-**3b**	8.5	11.4	3710039	3705847	50.0	50.0
3b	8.6	11.6	1815433	444113	80.3	19.7





	Retention time (1)	Retention time (2)	Area (1)	Area (2)	% Area (1)	% Area (2)
rac-**3c**	7.8	11.1	2718633	2706062	50.1	49.9
3c	7.8	11.1	5605263	643648	89.7	10.3





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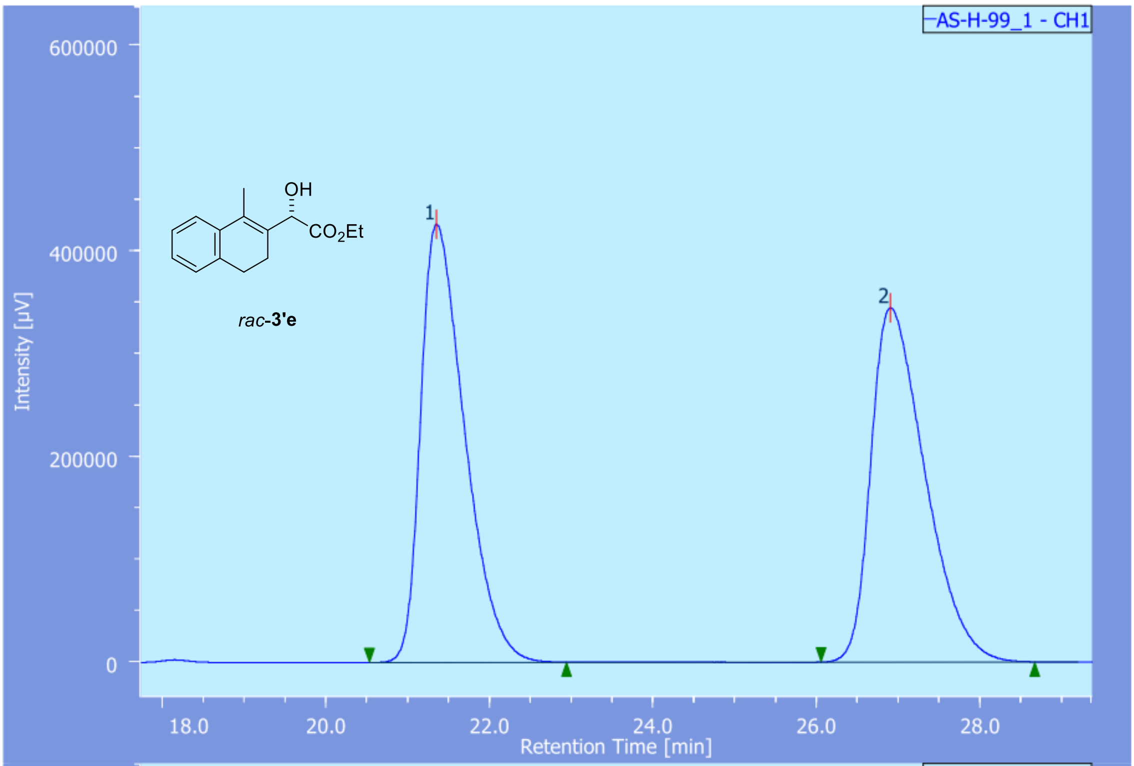
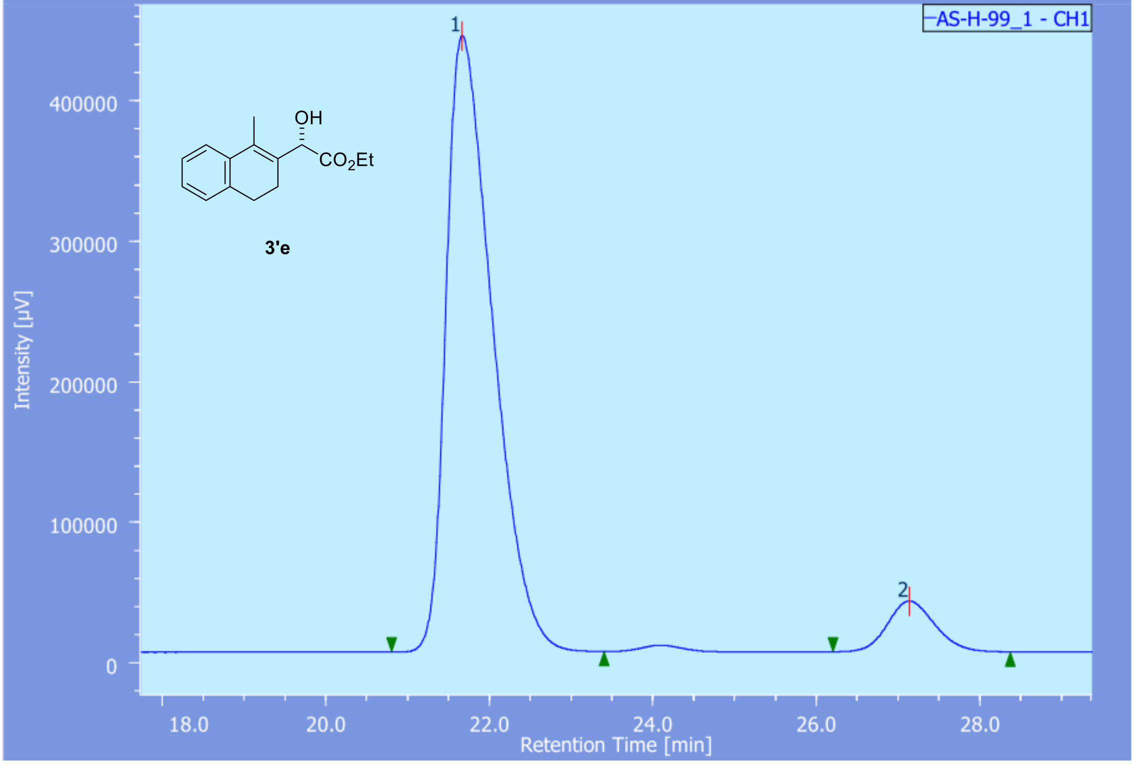
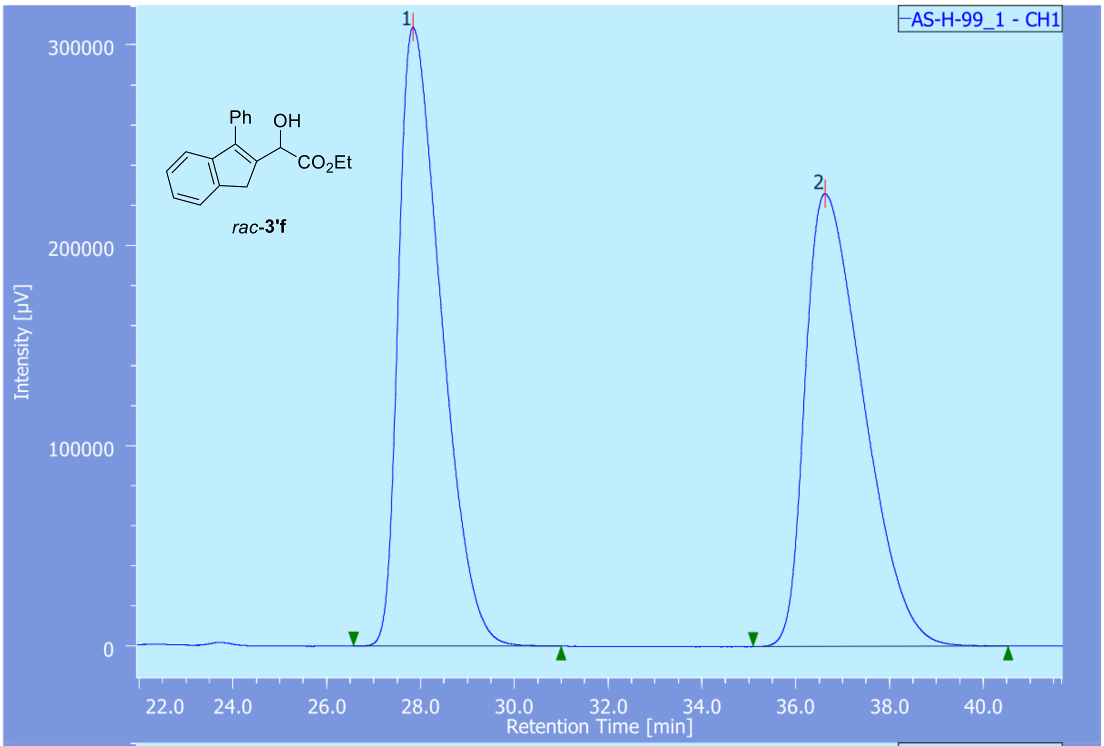
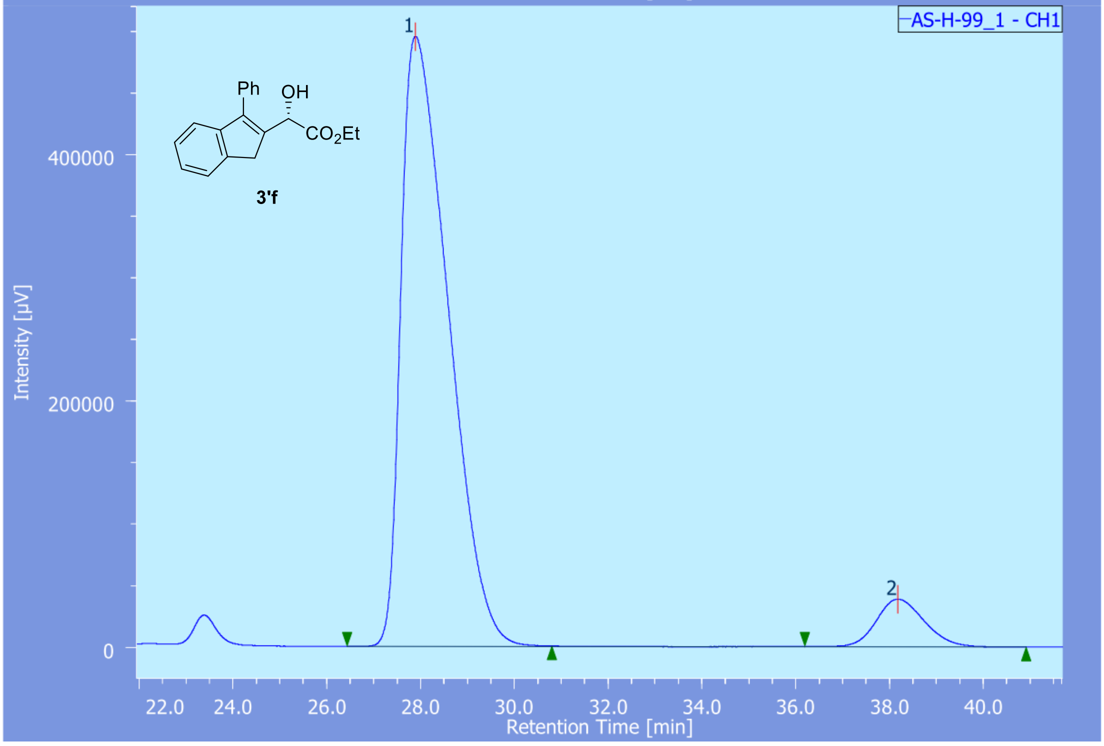
rac-**3d**	9.1	14.1	1317089	1325345	49.8	50.2
3d	9.4	15.3	1802997	96311	94.9	5.1



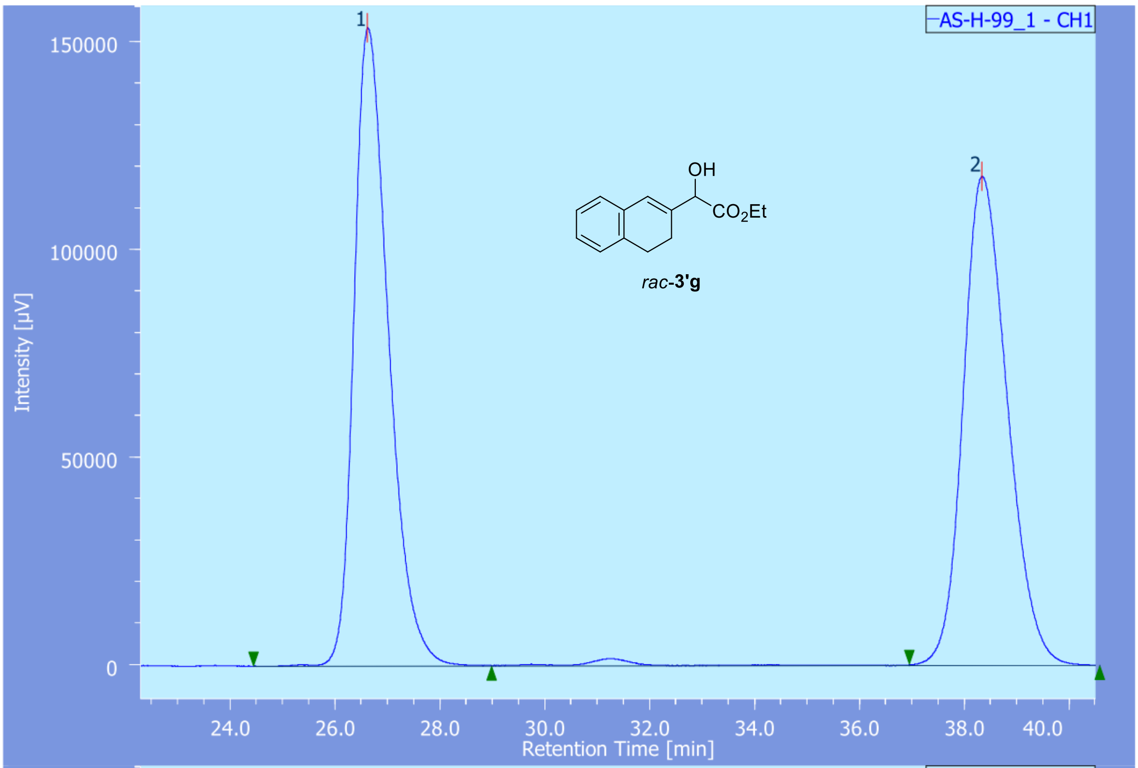


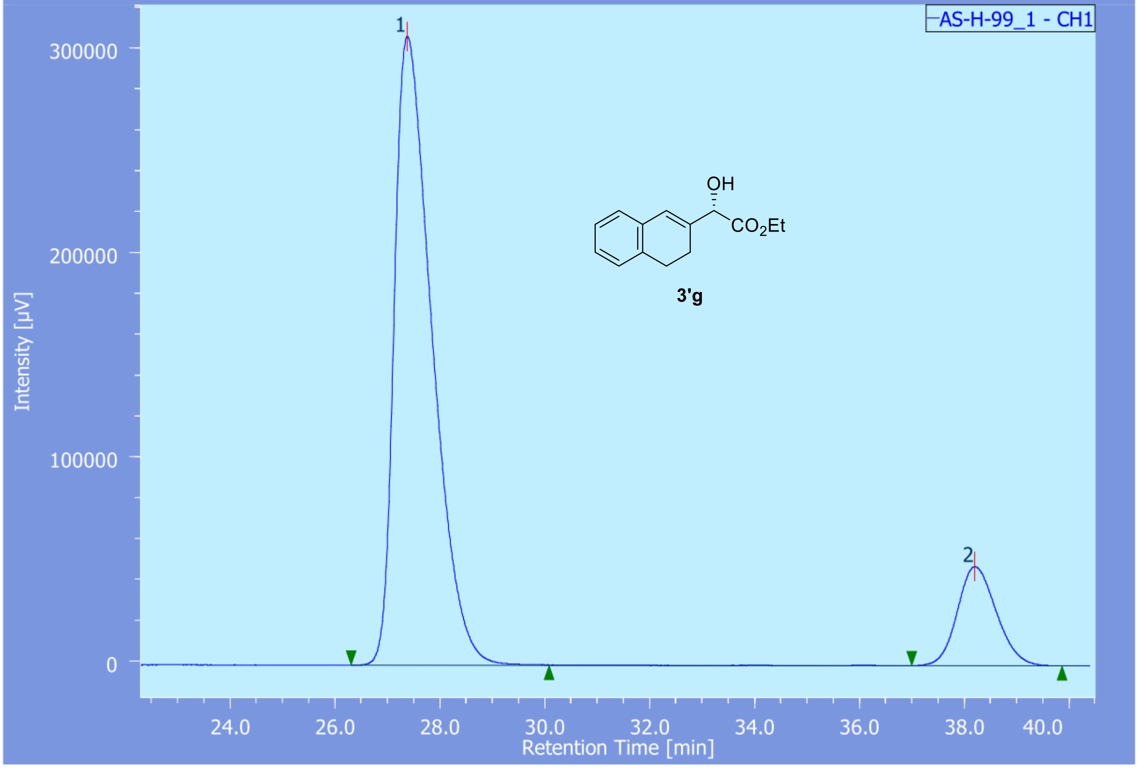
	Retention time (1)	Retention time (2)	Area (1)	Area (2)	% Area (1)	% Area (2)
rac-**3’e**	21.4	26.9	15957340	15913035	50.0	50.0
3’e	21.7	27.1	17358285	1468132	92.2	7.8



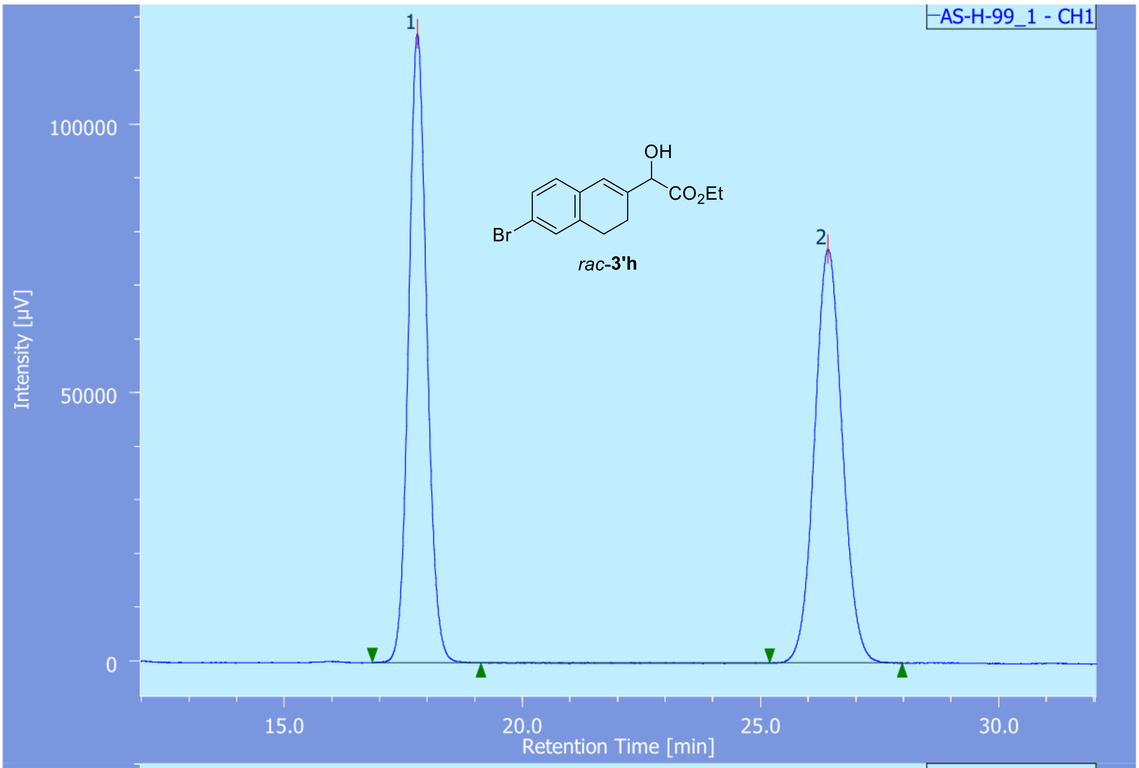


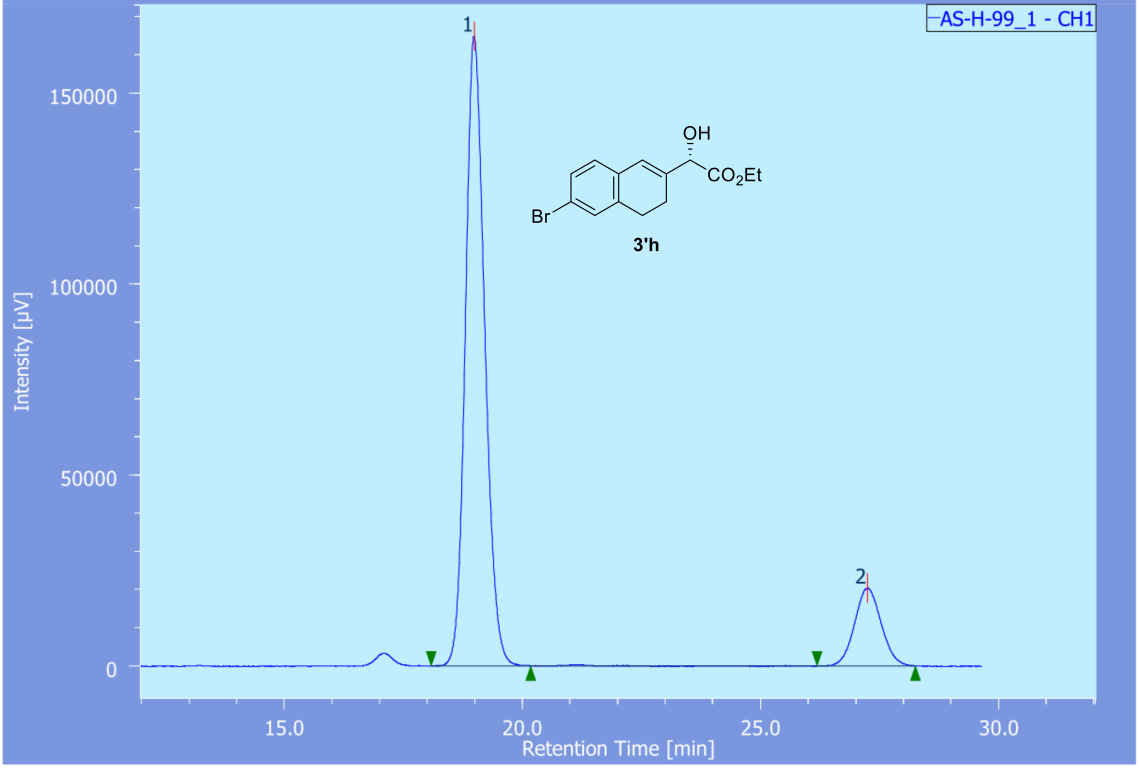
	Retention time (1)	Retention time (2)	Area (1)	Area (2)	% Area (1)	% Area (2)
rac-**3’f**	27.8	36.6	19532278	19487740	50.1	49.9
3’f	27.9	38.2	34671443	2769387	92.6	7.4



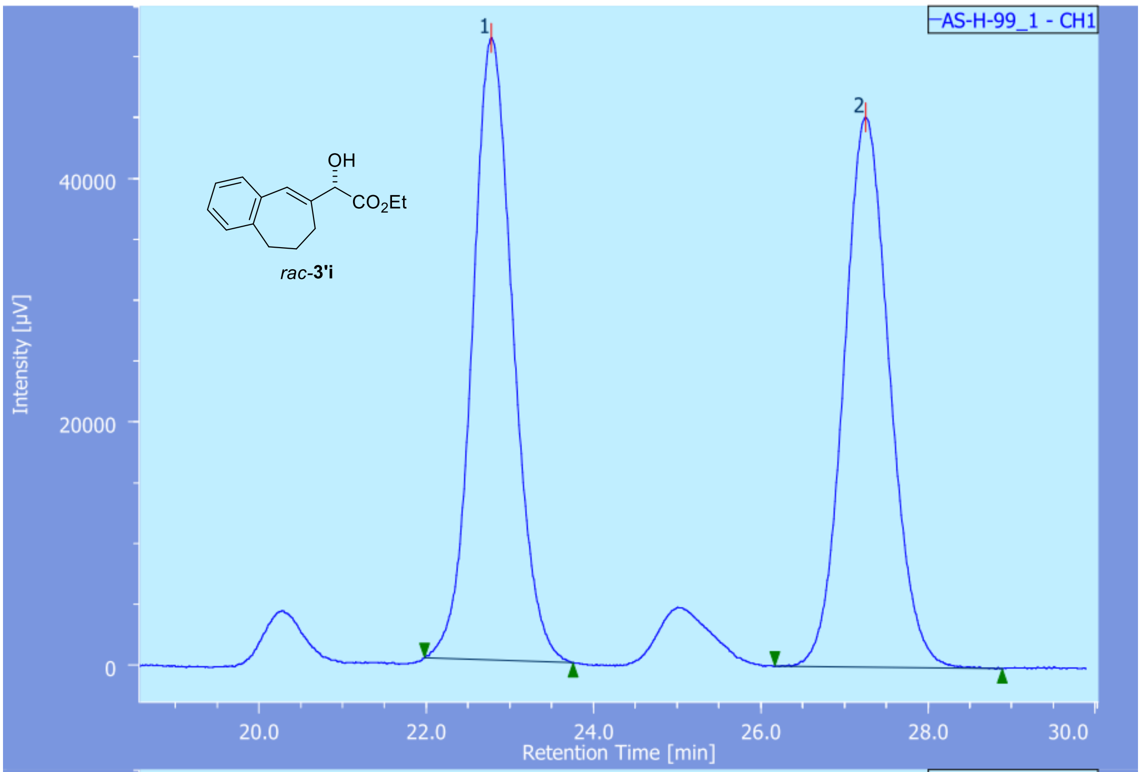


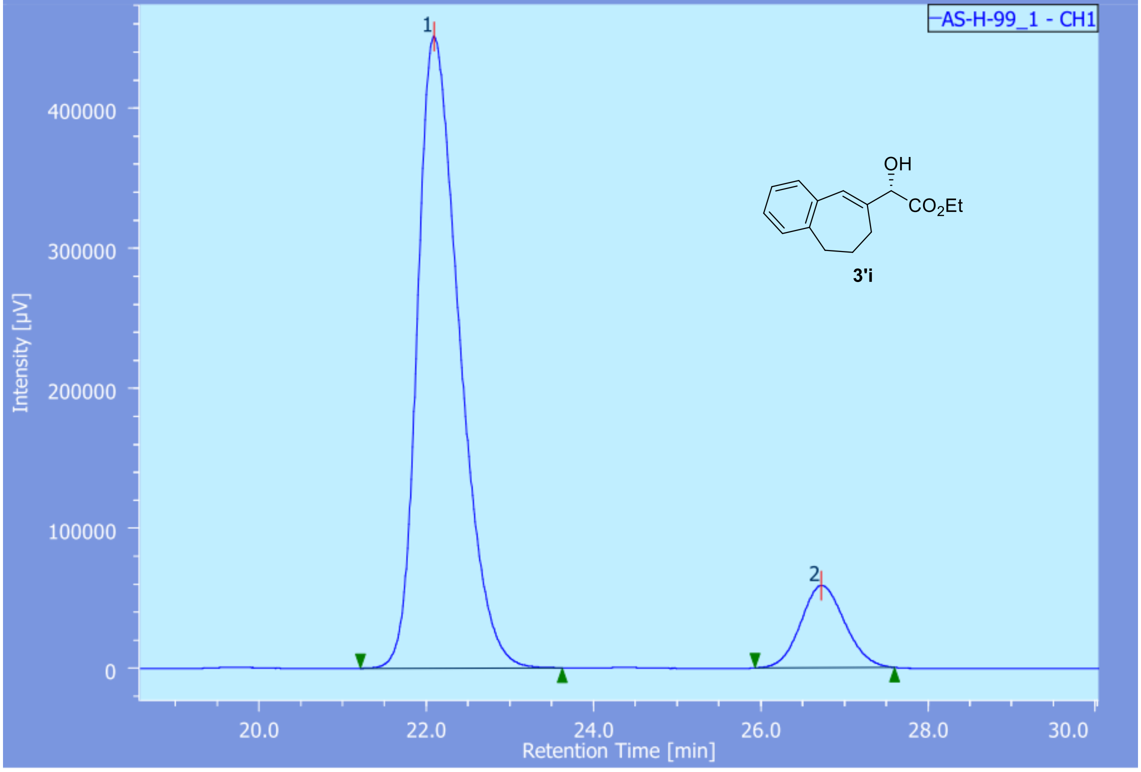
	Retention time (1)	Retention time (2)	Area (1)	Area (2)	% Area (1)	% Area (2)
rac-**3’g**	26.6	38.3	6993023	6914226	50.3	49.7
3’g	27.4	38.2	15334990	2510944	85.9	14.1



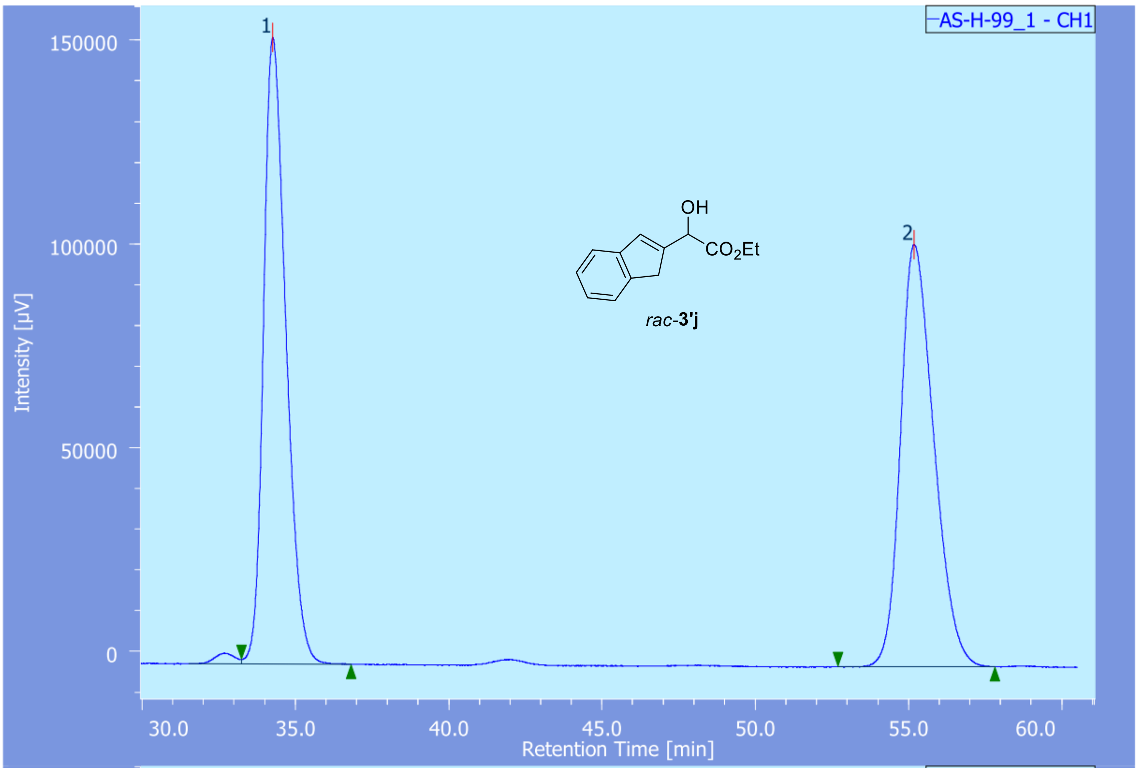


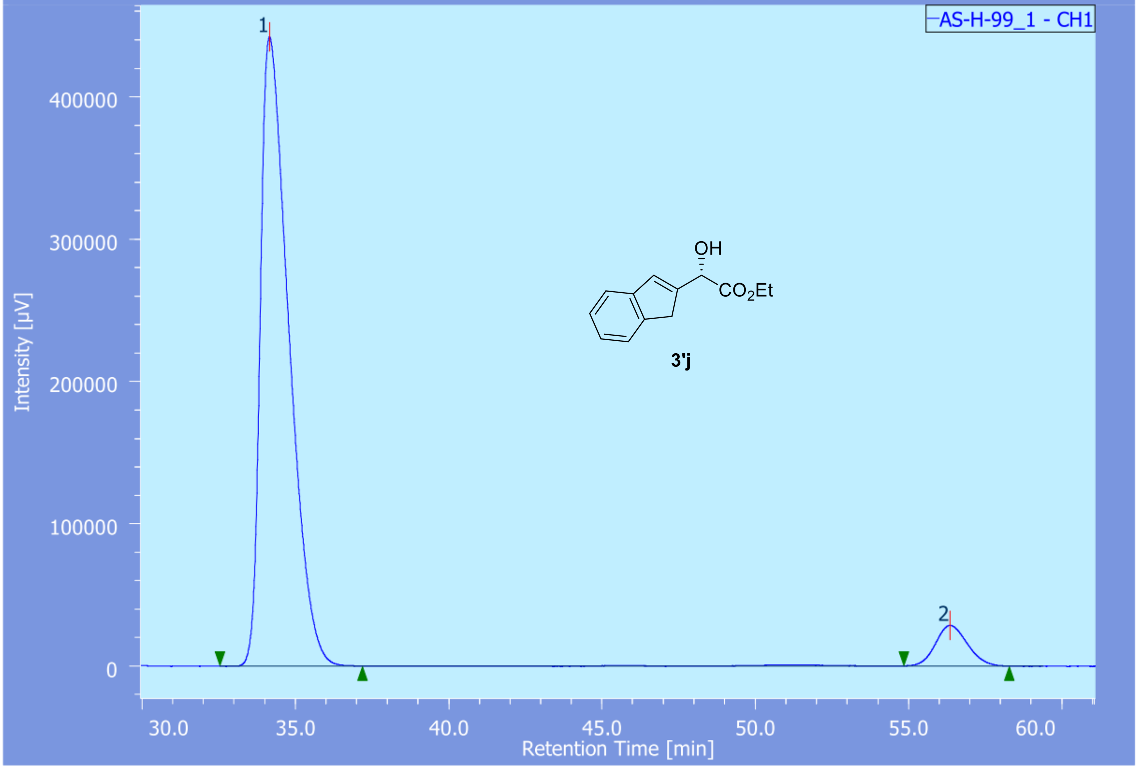
	Retention time (1)	Retention time (2)	Area (1)	Area (2)	% Area (1)	% Area (2)
rac-**3’h**	17.8	26.4	3125272	3125360	50.0	50.0
3’h	19.0	27.2	4654914	788503	85.5	14.5



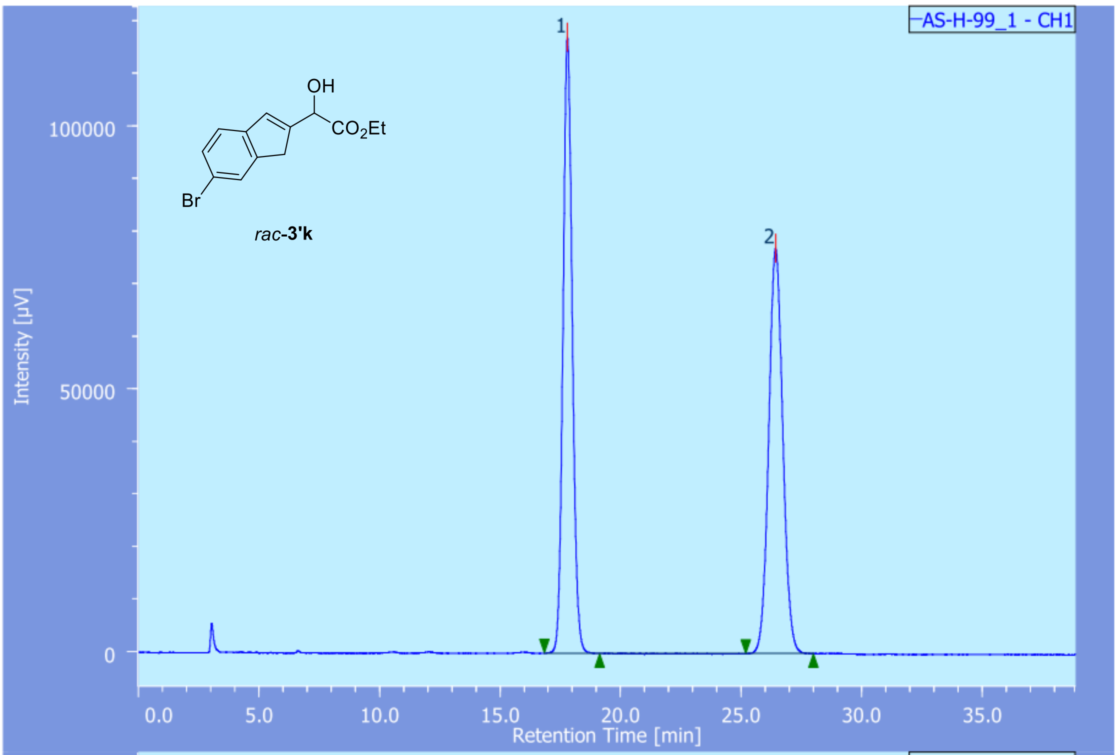


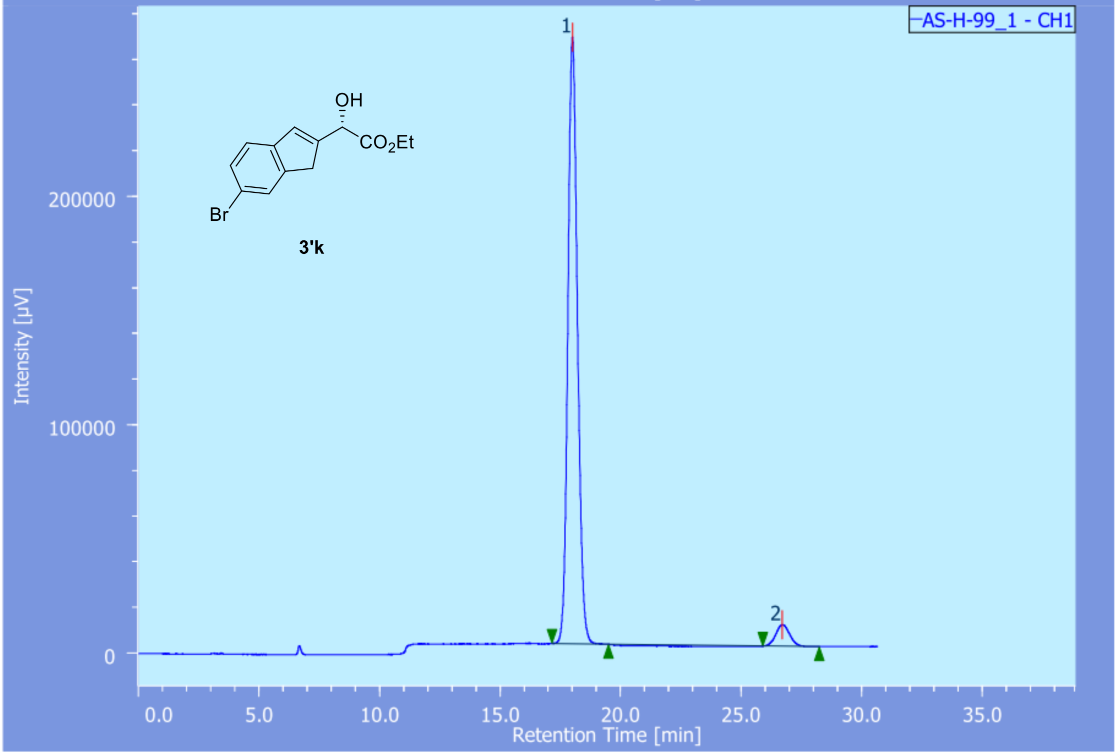
	Retention time (1)	Retention time (2)	Area (1)	Area (2)	% Area (1)	% Area (2)
rac-**3'i**	22.7	27.2	1730811	1722753	50.1	49.9
3'i	22.1	26.7	15699141	2147896	88.0	12.0





	Retention time (1)	Retention time (2)	Area (1)	Area (2)	% Area (1)	% Area (2)
rac-**3’j**	34.2	55.2	7800559	7834443	49.9	50.1
3’j	34.2	56.3	28499751	2109903	93.1	6.9





	Retention time (1)	Retention time (2)	Area (1)	Area (2)	% Area (1)	% Area (2)
rac-**3’k**	17.8	26.4	3125272	3125360	50.0	50.0
3’k	18.0	26.7	7316440	378935	95.1	4.9