Electronic Supplementary Information

F_{10}BINOL-derived Chiral Phosphoric Acid-Catalyzed Enantioselective Carbonyl-Ene Reactions: Theoretical Elucidation of Stereochemical Outcomes

Jun Kikuchi[a], Hiromu Aramaki[a], Hiroshi Okamoto[a], Masahiro Terada*[a]

e-mail: mterada@m.tohoku.ac.jp

[a] *Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan*

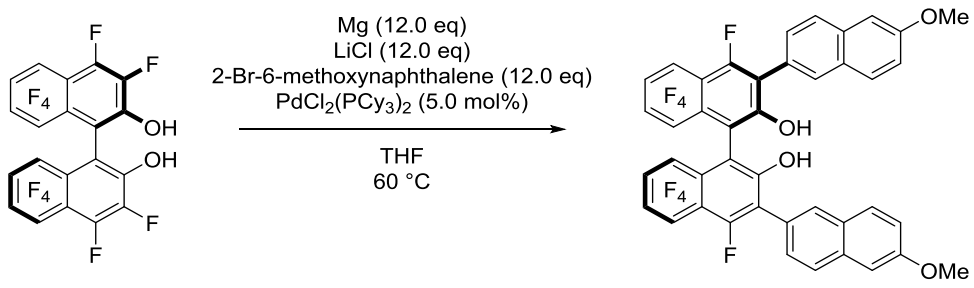
Contents:

1. General Information

All reactions were carried out under nitrogen atmosphere in flame-dried glassware. 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. Purification of reaction products was carried out by flash column chromatography using silica gel 60 N ((Merck 40-63 μm). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm). ^{1}H NMR spectra were recorded on a JEOL ECA-600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane or solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm, TMS: 0.00 ppm). ^{13}C NMR spectra were recorded on a JEOL 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 ECA-600 (243 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the PPh_3 (-6 ppm) resonance as the external standard. ^{19}F NMR spectra were recorded on JEOL ECA-600 (565 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the $C_6H_5CF_3$ (-67.2 ppm) resonance as the external standard. Optical rotations were measured on a Jasco P-1020 digital polarimeter with a sodium lamp and reported as follows; $[\alpha]^{T\ ^{\circ}C}_{D}$ (*c* = g/100 mL, solvent, % ee). Infrared spectra were recorded on a Jasco FT/IR-4100 spectrometer. Chiral stationary phase HPLC analysis was performed on a Jasco LC-2000 Plus Series system with DACIEL chiral analytical column (4.6 mmΦ* 250 mm length). Mass spectra analysis using ESI ionization method was performed on a Bruker Daltonics solariX 9.4T spectrometer at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

2. Preparation of Catalysts

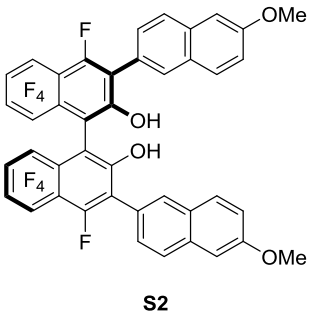
2.1 Preparation of **S2**



S1 **S2**

In a flame dried, nitrogen-flushed three-necked round-bottom flask, equipped with a reflux condenser and two dropping funnels, magnesium (145.8 mg, 6.0 mmol) and LiCl (254.3 mg, 6.0 mmol) was suspended in THF (2.0 ml). A small amount of 2-bromo-6-methoxynaphthalene (1.42 g, 6.0 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 2-Br-6-methoxynaphthalene solution was added slowly. After complete addition of the 2-Br-6-methoxynaphthalene, the mixture was stirred for 30 minutes at room temperature. To a mixture of $PdCl_2(PCy_3)_2$ (18.5 mg, 0.025 mmol) and **S1** (251 mg, 0.50 mmol) in THF (1.5 ml) was added the 6-methoxy-2-naphthylmagnesium 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. (5.0 mL) 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/AcOEt = 5/1) to afford **S2** (317.2 mg, 0.40 mmol, 80%) as a white solid.



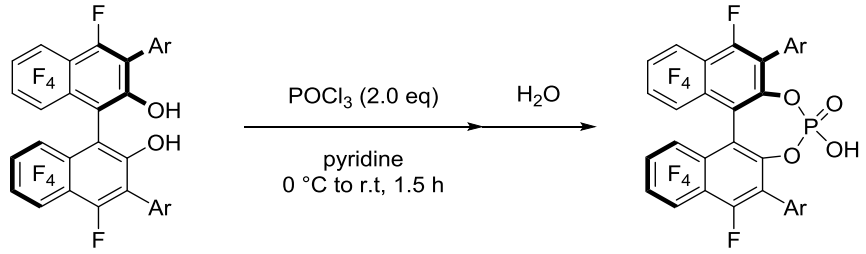
S2

(*R*)-4,4',5,5',6,6',7,7',8,8'-Decafluoro-3,3'-bis(6-methoxy-2-naphthyl)-1,1'-binaphthyl-2,2'-diol ((*R*)-3,3'-(6-MeO-2-naphthyl)$_2$-F$_{10}$BINOL) (S2)

S2: White solid; (317.2mg, 0.4 mmol, 80% yield); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.93 (s, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 9.0 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.22–7.18 (m, 4H), 5.60 (s, 2H), 3.94 (s, 6H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 158.7, 154.4 (d, *J* = 259 Hz), 150.9, 142.5 (dm, *J* = 253 Hz), 142.1 (dm, *J* = 246 Hz), 139.9 (dm, *J* = 254 Hz) , 136.9 (dm, *J* = 251 Hz), 134.8, 129.7, 129.6, 128.8, 128.1, 127.9, 123.3, 120.2, 119.8, 118.2 (d, *J* = 17 Hz), 107.3, 106.8 (t, *J* = 8.8 Hz), 105.7, 55.4; ^{19}F NMR ($CDCl_3$, 565 MHz) δ -115.1 (d, *J* = 74.0 Hz, 2F), -144.4 (dt, *J* = 74.0 Hz, 16.4 Hz, 2F), -146.6 (t, *J* = 15.5 Hz, 2F), -155.2 (t, *J* = 18.9 Hz, 2F), -160.7 (t, *J* = 19.2 Hz, 2F); IR (ATR) 3518, 3006, 2941, 2908, 2842, 1665, 1629, 1604, 1520, 1484, 1466, 1441, 1407, 1386, 1349, 1334, 1272, 1219, 1197, 1186, 1163, 1127, 1110, 1087, 1021, 973, 950, 900, 855 cm^{-1}; HRMS (ESI) calcd. for $C_{42}H_{19}F_{10}O_4$ [M-H]$^-$: 777.1124, found: 777.1128; $[\alpha]^{22}_D$ = -76.9 (*c* = 1.00, $CHCl_3$, >99% ee).

2.2 Preparation of 3d-3f

Reprsentative procedure

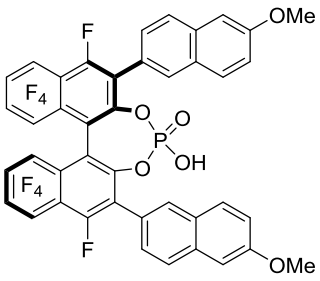


S2
(Ar = 6-MeO-2-naphthyl)

(*R*)-**3e**

To a solution of **S2** (185 mg, 0.24 mmol) in pyridine (2.4 ml) was added $POCl_3$ (73.6 mg, 0.48 mmol) dropwise at 0 °C. The reaction mixture was stirred at room temperature for 1.5 h. The resulting mixture was quenched with H_2O at 0 ºC, and the product was extracted with Et_2O. The combined organic layer was washed with 6.0 M HCl aq., dried over Na_2SO_4 and evaporated. The residual crude was purified by silica gel column chromatography (hexane/AcOEt = 1:1 to AcOEt) to afford the desired product as a salt. Acidification in Et_2O with 3.0 M HCl aq. followed by drying under reduced pressure afforded the desired product as a free acid (*R*)-**3e** (168 mg, 0.20 mmol, 84% yield) as a white solid.

(*R*)-3,3'-(6-MeO-2-naphthyl)$_2$-F$_{10}$BINOL-derived phosphoric acid ((*R*)-3e)

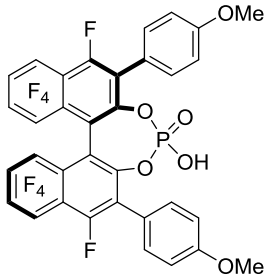


(*R*)-**3e**

(*R*)-**3e**: White solid; (168 mg, 0.20 mmol, 84% yield); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.77 (brm, 2H), 7.53 (brm, 4H), 7.29 (brm, 2H), 6.91 (brm, 2H), 6.76 (brm, 2H), 3.77 (s, 6H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 158.1, 154.9 (d, *J* = 262 Hz), 145.3, 142.8 (dm, *J* = 244 Hz), 142.1 (dm, *J* = 252 Hz), 140.2 (dm, *J* = 246 Hz), 138.5 (dm, *J* = 256 Hz), 134.3, 130.1, 129.7, 128.4, 127.9 (d, *J* = 15.9 Hz), 126.7, 123.1, 122.1 (d, *J* = 16 Hz), 119.6, 118.8, 114.6, 109.5 (m), 105.4 (m), 55.2; ^{19}F NMR ($CDCl_3$, 565 MHz) δ -111.3 (m, 2F), -140.3 (s, 2F), -142.4 (d, *J* = 76.3 Hz, d), -152.7 (d, *J* = 14.1 Hz, 2F), -155.4 (d, *J* = 14.1 Hz, 2F); ^{31}P NMR ($CDCl_3$, 243 MHz) δ 2.61 (s); IR (ATR); 3005, 2941, 2844, 1663, 1632, 1604, 1523, 1505, 1484, 1441, 1380, 1334, 1262, 1222, 1181, 1164, 1126, 1115, 1092, 1024, 973, 950, 854 cm^{-1}; HRMS (ESI) calcd. for $C_{42}H_{18}F_{10}O_6P$ [M-H]$^-$: 839.0681, found: 839.0686; $[\alpha]^{21}_D$ = -154.34 (*c* = 1.00, $CHCl_3$, >99% ee).

(*R*)-3,3'-(4-MeOC_6H_4)$_2$-F$_{10}$BINOL-derived phosphoric acid ((*R*)-3b)

(*R*)-**3b** was synthesized according to the same procedure of (*R*)-**3e**

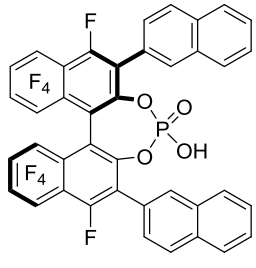


(*R*)-**3b**

White solid; (51.8 mg, 0.07 mmol, 92% yield); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.90 (brs, 1H), 7.36 (d, *J* = 8.4 Hz, 4H), 6.82 (d, *J* = 8.4 Hz, 4H), 3.65 (s, 6H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 159.9, 154.9 (d, *J* = 262 Hz), 145.4, 142.7 (dm, *J* = 253 Hz), 142.1 (dm, *J* = 253 Hz), 140.1 (dm, *J* = 253 Hz) , 138.5 (dm, *J* = 254 Hz), 131.8, 121.7 (d, *J* = 17.4 Hz), 120.1, 119.5, 114.6, 113.9, 109.6 (m), 55.1; ^{19}F NMR ($CDCl_3$, 565 MHz) δ -111.6 (d, *J* = 76.3 Hz, 2F), -140.3 (t, *J* = 17.0 Hz, 2F), -142.4 (dt, *J* = 79.1 Hz, 15.5 Hz, 2F), -152.9 (t, *J* = 16.4, 2F), -155.5 (t, *J* = 17.0, 2F); ^{31}P NMR ($CDCl_3$, 243 MHz) δ 2.68 (s); IR (ATR) 2939, 2841, 1664, 1609, 1519, 1478, 1380, 1295, 1252, 1209, 1178, 1120. 1096, 1021, 1011, 944, 876 cm^{-1}; HRMS (ESI) calcd. for $C_{34}H_{14}F_{10}O_6P$ [M-H]$^-$: 739.0368, found: 739.0373; $[\alpha]^{20}_D$ = -117.2 (*c* = 1.00, $CHCl_3$, >99% ee).

(*R*)-3,3'-(2-naphthyl)$_2$-F$_{10}$BINOL-derived phosphoric acid ((*R*)-3c)

(*R*)-**3c** was synthesized according to the same procedure of (*R*)-**3e**

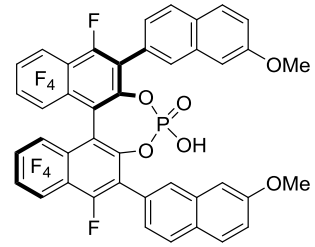


(*R*)-**3c**

White solid; (139 mg, 0.18 mmol, 89% yield); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.81 (s, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 9.0 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 2H), 5.46 (brs, 1H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 155.0 (d, *J* = 265 Hz), 145.3, 142.8 (dm, *J* = 247 Hz), 142.2 (dm, *J* = 252 Hz), 140.3 (dm, *J* = 256 Hz) , 138.5 (dm, *J* = 253 Hz), 133.0, 132.8, 130.3, 128.1, 127.8, 127.42, 127.38, 126.4, 126.0, 125.6, 122.0 (d, *J* = 17.4 Hz), 119.8, 114.7, 109.6 (m); ^{19}F NMR ($CDCl_3$, 565 MHz) δ -111.8 (d, *J* = 76.3 Hz, 2F), -140.2 (t, *J* = 15.5 Hz, 2F), -141.8 (dt, *J* = 15.5, 78.5 Hz, 2F), -152.7 (t, *J* = 17.9 Hz, 2F), -155.5 (t, *J* = 17.8 Hz, 2F); ^{31}P NMR ($CDCl_3$, 243 MHz) δ 1.23 (s); IR (ATR) 3058, 1664, 1618, 1600, 1523, 1482, 1456, 1381, 1337, 1277, 1208, 1179, 1117, 1092, 1025, 970, 934, 889 cm^{-1}; HRMS (ESI) calcd. for $C_{40}H_{14}F_{10}O_4P$ [M-H]$^-$ 779.0470, found: 779.0475; $[\alpha]^{25}_D$ = -121.29 (*c* = 1.00, $CHCl_3$, >99% ee).

(*R*)-3,3'-(7-MeO-2-naphthyl)$_2$-F$_{10}$BINOL-derived phosphoric acid ((*R*)-3d)

(*R*)-**3d** was synthesized according to the same procedure of (*R*)-**3e**



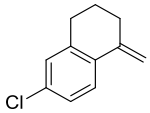
(*R*)-**3d**

White solid; (84 mg, 0.10mmol, 79% yield); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 10.75 (1H, bs), 7.75 (2H, bs), 7.50-7.40 (4H, m), 7.14 (2H, bs), 6.92 (2H, bs), 6.67 (2H, bs), 3.60 (6H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 157.6, 155.0 (d, *J* = 263 Hz), 145.2, 142.7 (dm, *J* = 253 Hz), 142.2 (dm, *J* = 263 Hz), 140.3 (dm, *J* = 254 Hz), 138.6 (dm, *J* = 251 Hz), 134.1, 129.1, 128.9, 128.6, 127.7, 126.0, 125.3, 122.1 (d, *J* = 18.7 Hz), 119.7, 119.3, 114.5, 109.6 (m), 105.9, 55.0; ^{19}F NMR ($CDCl_3$, 565 MHz) δ -111.2 (d, *J* = 76.8 Hz, 2F), -140.3 (s, 2F), -142.2 (dt, *J* = 76.3 Hz, 17.0 Hz, 2F), -152.6 (t, *J* = 19.2 Hz, 2F), -155.4 (t, *J* = 17.8 Hz, 2F); ^{31}P NMR ($CDCl_3$, 243 MHz) δ 2.94 (s); IR (ATR) ; 3006, 2939, 2842, 1663, 1631, 1603, 1522, 1479, 1380, 1331, 1248, 1217, 1176, 1117, 1093, 1023, 976, 866 cm^{-1}; HRMS (ESI) calcd. for $C_{42}H_{18}F_{10}O_6P$ [M-H]$^-$: 839.0681, found: 839.0686; $[\alpha]^{24}_D$ = -107.026 (*c* = 1.00, $CHCl_3$, >99% ee).

3. Preparation of substrates

Novel 1,1-disubstituted olefins were prepared by following the literature procedure[1]

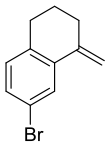
6-chloro-1-methylene-1,2,3,4-tetrahydronaphthalene (4d)



4d

4d: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.55 (d, *J* = 8.4 Hz, 1H), 7.12–7.06 (m, 2H), 5.44 (s, 1H), 4.96 (s, 1H), 2.81 (t, *J* = 6.0 Hz, 2H), 2.55–2.50 (m, 2H), 1.88-1.83 (m, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 142.4, 139.0, 133.2, 133.0, 128.8, 126.1, 125.6, 108.4, 32.9, 30.3, 23.4; IR (ATR) 3086, 3030, 2937, 2866, 2837, 1687, 1626, 1592, 1478, 1454, 1440, 1406, 1344, 1299, 1263, 1241, 1194, 1180, 1112, 1046, 972, 881 cm^{-1}; HRMS (APCI) calcd. for $C_{11}H_{11}Cl$ [M]$^+$: 178.0549, found: 178.0544.

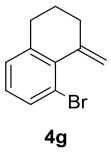
7-bromo-1-methylene-1,2,3,4-tetrahydronaphthalene (4f)



4f

4f: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.75 (s, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 5.45 (s, 1H), 4.99 (s, 1H), 2.77 (t, *J* = 6.2 Hz, 2H), 2.54–2.50 (m, 2H), 1.88–1.83 (m, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 142.2, 136.8, 136.1, 130.8, 130.3, 127.1, 119.6, 109.2, 32.7, 29.9, 23.4; IR (ATR) 3086, 2936, 2863, 2835, 1626, 1588, 1556, 1474, 1454, 1433, 1407, 1345, 1290, 1276, 1263, 1239, 1180, 1135, 1085, 968, 884, 867 cm^{-1}; HRMS (APCI) calcd. for $C_{11}H_{11}Br$ [M]$^+$: 222.0044, found: 222.0044.

8-bromo-1-methylene-1,2,3,4-tetrahydronaphthalene (4g)



4g

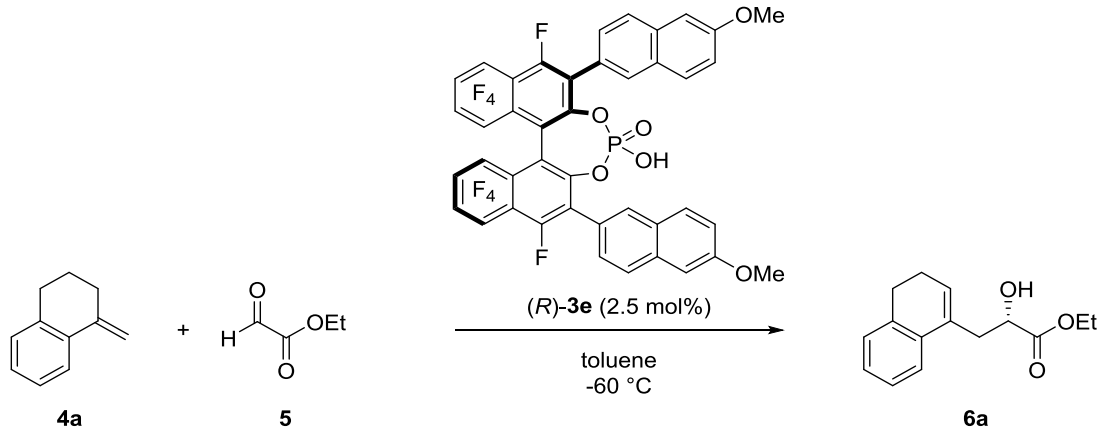
4g: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.46 (d, *J* = 7.8 Hz, 1H), 7.04 (dd, *J* = 7.2 Hz, 1.2 Hz, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 5.65 (d, *J* = 0.6 Hz, 1H), 5.36 (q, *J* = 1.8 Hz, 1H), 2.71 (t, *J* = 6.6 Hz, 2H), 2.50 (tt, *J* = 7.2 Hz, 1.2 Hz, 2H), 1.88-1.82 (m, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 141.8, 141.6, 137.2, 131.8, 127.7, 127.1, 120.6, 116.3, 108.4, 32.4, 30.2, 23.2; IR (ATR) 3051, 2940, 2865, 2844, 1630, 1553, 1439, 1290,

[1] T. W. Liwosz, S. R. Chemler, *Chem. Eur. J.* **2013**, *19*, 12771.

1180, 1109, 968, 905 cm^{-1}; HRMS (APCI) calcd. for $C_{11}H_{11}Br$ $[M]^+$: 222.0044, found: 222.0045.

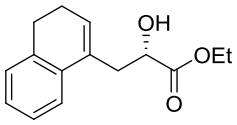
4. Enantioselective Carbonyl-Ene Reaction

Reprsentative procedure:



To a solution of (*R*)-**3e** (4.2 mg, 0.005 mmol) in toluene (1.0 mL) was added freshly distilled ethyl glyoxylate **5** (40.8 mg, 0.4 mmol) and α-methylene-tetraline **4a** (28.8 mg, 0.2 mmol) at -60 °C, and the resulting solution was stirred for 3 h at this temperature. The mixture was directly passed through flash colum chromatography (Hexane/AcOEt =3/1) to give **6a** (41.4 mg, 0.17 mmol, 84% yield) as a colorless oil. The enantiomeric excess was determined by chiral stationary phase HPLC analysis.

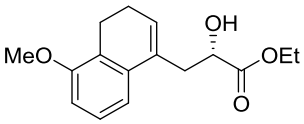
ethyl (*S*)-3-(3,4-dihydronaphthalen-1-yl)-2-hydroxypropanoate (6a)



6a

6a: Colorless oil: (41.4 mg, 84% yield); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.28 (d, *J* = 7.8 Hz, 1H), 7.22–7.18 (m, 1H), 7.16-7.14 (m, 2H), 5.99 (t, *J* = 4.2 Hz, 1H), 4.38–4.35 (m, 1H), 4.21–4.10 (m, 2H), 3.03 (dd, *J* = 14.4 Hz, 4.5 Hz, 1H), 2.80–2.71 (m, 3H), 2.69 (dd, *J* = 6.3 Hz, 0.9 Hz, 1H), 2.29–2.26 (m, 2H), 1.26 (dt, *J* = 7.2 Hz, 0.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 174.6, 136.7, 134.1, 131.7, 128.7, 127.7, 127.0, 126.3, 122.6, 69.5, 61.6, 38.0, 28.3, 23.2, 14.1; IR (ATR) 3474, 3058, 2980, 2934, 2885, 2830, 1732, 1488, 1447, 1369, 1268, 1208, 1096, 1025, 941, 864 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{18}NaO_3$ $[M+Na]^+$: 269.1154, found: 269.1149; HPLC analysis CHIRALPAK AS-H (Hexane/IPA = 90/10, 1.0 mL/min, 254 nm, 30 °C) 8.4 min (major), 11.7 min (minor), 87% ee; $[\alpha]^{23}_D$ = -12.56 (*c* = 1.00, C_6H_6, 87% ee), $[\alpha]^{22}_D$ = 0.979 (*c* = 1.00, $CHCl_3$, 87% ee). **Configuration Assignment:** The absolute configuration was assigned as (*S*) by comparison with (*R*) isomer.; $[\alpha]^{25}_D$ = 13.7 (*c* = 1.94, C_6H_6, 96% ee), Yuan, Y.; Zhang, X.; Ding, K. *Angew. Chem. Int. Ed.* **2003**, *42*, 5478-5480.

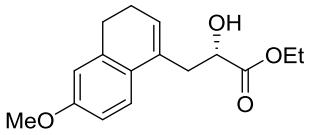
ethyl (*S*)-2-hydroxy-3-(5-methoxy-3,4-dihydronaphthalen-1-yl)propanoate (6b)



6b

6b: Colorless oil: (42.6 mg, 77% yield); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.17 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 5.99 (t, *J* = 4.2 Hz, 1H), 4.36–4.33 (m, 1H), 4.20–4.11 (m, 2H), 3.83 (s, 3H), 3.01 (dd, *J* = 14.4 Hz, 3.6 Hz, 1H), 2.83–2.77 (m, 1H), 2.74–2.67 (m, 3H), 2.24–2.22 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 174.6, 156.2, 135.1, 131.5, 128.9, 126.3, 124.6, 115.5, 109.7, 69.5, 61.5, 55.5,

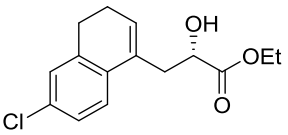
38.5, 22.5, 19.8, 14.1; IR (ATR) 3471, 3072, 2937, 2886, 2835, 1733, 1597, 1573, 1473, 1461, 1440, 1368, 1345, 1261, 1208, 1141, 1091, 1046, 926 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{20}NaO_4$ $[M+Na]^+$: 299.1259, found: 299.1254; HPLC analysis CHIRALPAK AS-H (Hexane/IPA = 85/15, 1.0 mL/min, 254 nm, 30 °C) 10.2 min (major), 11.3 min (minor), 86% ee; $[\alpha]^{22}_D$ = -1.61 (*c* = 1.00, $CHCl_3$, 86% ee). **Configuration Assignment:** The absolute configuration was assigned as (*S*) by analogy.



6c

ethyl (*S*)-2-hydroxy-3-(6-methoxy-3,4-dihydronaphthalen-1-yl)propanoate(6c)

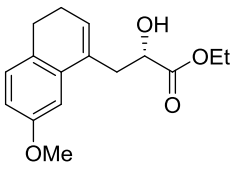
6c: Colorless oil: (48.1 mg, 87% yield); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.21 (d, *J* = 9.0 Hz, 1H), 6.74–6.70 (m, 2H), 5.86 (t, *J* = 4.2 Hz, 1H), 4.37–4.34 (m, 1H), 4.20–4.11 (m, 2H), 3.80 (s, 3H), 3.00 (dd, *J* = 14.4 Hz, 4.2 Hz, 1H), 2.76–2.65 (m, 4H), 2.28–2.24 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 174.5, 158.5, 138.6, 131.3, 127.2, 126.1, 123.8, 114.0, 110.8, 69.5, 61.5, 55.2, 38.2, 28.8, 23.1, 14.2; IR (ATR) 3481, 2979, 2935, 2833, 1733, 1607, 1569, 1499, 1444, 1429, 1372, 1303, 1281, 1252, 1205, 1165, 1142, 1096, 1080, 1031, 865 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{20}NaO_4$ $[M+Na]^+$: 299.1259, found: 299.1254; HPLC analysis CHIRALPAK AS-H (Hexane/IPA = 85/15, 1.0 mL/min, 254 nm, 30 °C) 9.4 min (major), 16.4 min (minor), 63% ee; $[\alpha]^{21}_D$ = 3.82 (*c* = 1.00, $CHCl_3$, 63% ee). **Configuration Assignment:** The absolute configuration was assigned as (*S*) by analogy.



6d

ethyl (*S*)-2-hydroxy-3-(6-chloro-3,4-dihydronaphthalen-1-yl)propanoate (6d)

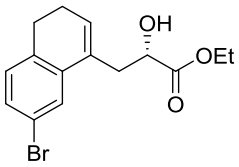
6d: Colorless oil: (37.1 mg, 66% yield); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.20 (d, *J* = 8.4 Hz, 1H), 7.16 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 7.13–7.12 (m, 1H), 5.99 (t, *J* = 4.2 Hz, 1H), 4.35–4.31 (m, 1H), 4.22–4.12 (m, 2H), 2.98 (dd, *J* = 15.0 Hz, 4.8 Hz, 1H), 2.77–2.68 (m, 4H), 2.28–2.25 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 174.5, 138.6, 132.7, 132.2, 131.1, 128.8, 127.7, 126.2, 123.9, 69.5, 61.7, 37.9, 28.1, 22.9, 14.1; IR (ATR) 3464, 2981, 2937, 2887, 2832, 1733, 1592, 1559, 1486, 1442, 1407, 1369, 1274, 1208, 1098, 1024 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{17}ClNaO_3$ $[M+Na]^+$: 303.0764, found: 303.0758; HPLC analysis CHIRALPAK AS-H (Hexane/IPA = 85/15, 1.0 mL/min, 254 nm, 30 °C) 6.6 min (major), 9.6 min (minor), 86% ee; $[\alpha]^{21}_D$ = 2.97 (*c* = 1.00, $CHCl_3$, 86% ee). **Configuration Assignment:** The absolute configuration was assigned as (*S*) by analogy.



6e

ethyl (*S*)-2-hydroxy-3-(7-methoxy-3,4-dihydronaphthalen-1-yl)propanoate (eb)

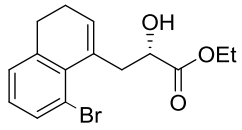
6e: Colorless oil: (47.5 mg, 86% yield); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.06 (d, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 2.4 Hz, 1H), 6.69 (dd, *J* = 7.8 Hz, 2.4 Hz, 1H), 6.01 (t, *J* = 4.2 Hz, 1H), 4.39–4.35 (m, 1H), 4.21–4.11 (m, 2H), 3.80 (s, 3H), 3.00 (dd, *J* = 15.0 Hz, 4.2 Hz, 1H), 2.74–2.65 (m, 4H), 2.27–2.24 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 174.6, 158.3, 135.1, 131.6, 129.3, 128.9, 128.3, 111.2, 109.6, 69.4, 61.6, 55.3, 38.1, 27.3, 23.5, 14.1; IR (ATR) 3469, 2980, 2934, 2884, 2832, 1733, 1604, 1572, 1492, 1466, 1444, 1422, 1369, 1300, 1279, 1252, 1203, 1096, 1045, 866 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{20}NaO_4$ $[M+Na]^+$: 299.1259, found: 299.1254; HPLC analysis CHIRALPAK AS-H (Hexane/IPA = 85/15, 1.0 mL/min, 254 nm, 30 °C) 8.4 min (major), 15.7 min (minor), 92% ee; $[\alpha]^{21}_D$ = 3.65 (*c* = 1.00, $CHCl_3$, 92% ee). **Configuration Assignment:** The absolute configuration was assigned as (*S*) by analogy.



6f

ethyl (*S*)-2-hydroxy-3-(7-bromo-3,4-dihydronaphthalen-1-yl)propanoate (6f)

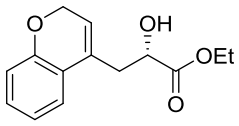
6f: Colorless oil: (41.6 mg, 64% yield); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.39 (d, *J* = 1.2 Hz, 1H), 7.28–7.24 (m, 1H), 7.01 (d, *J* = 8.4 Hz, 1H) , 6.05 (t, *J* = 4.5 Hz, 1H), 4.37–4.34 (m, 1H), 4.24–4.10 (m, 2H), 2.94 (dd, *J* = 15.0 Hz, 4.8 Hz, 1H), 2.77–2.67 (m, 4H), 2.28–2.25 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 174.5, 136.3, 135.5, 130.8, 129.9, 129.6, 129.2, 125.6, 120.0, 69.3, 61.8, 37.6, 27.7, 23.0, 14.1; IR (ATR) 3462, 2980, 2935, 2886, 2832, 1733, 1590, 1555, 1479, 1442, 1397, 1369, 1270, 1233, 1207, 1097, 1024, 876 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{17}BrNaO_3$ $[M+Na]^+$: 347.0259, found: 347.0254; HPLC analysis CHIRALPAK AS-H (Hexane/IPA = 85/15, 1.0 mL/min, 254 nm, 30 °C) 6.9 min (major), 14.5 min (minor), 88% ee; $[\alpha]^{22}_D$ = 12.20 (*c* = 1.00, $CHCl_3$, 88% ee). **Configuration Assignment:** The absolute configuration was assigned as (*S*) by analogy.



6g

ethyl (*S*)-3-(8-bromo-3,4-dihydronaphthalen-1-yl)-2-hydroxypropanoate (6g)

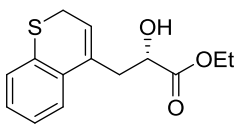
6g: Colorless oil: (24.1 mg, 37% yield); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.43 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.13 (dd, *J* = 7.2 Hz, 1.2 Hz, 1H), 6.95 (t, *J* = 7.8 Hz, 1H), 6.28 (t, *J* = 5.4 Hz, 1H), 4.29–4.25 (m, 1H), 4.11–4.05 (m, 1H), 3.95-3.89 (m, 1H), 3.50 (ddd, *J* = 14.4 Hz, 4.8 Hz, 1.2 Hz, 1H), 3.28 (dd, *J* = 15.0 Hz, 7.8 Hz, 1H), 2.68–2.58 (m, 3H), 2.11–2.06 (m, 2H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 174.7, 142.5, 134.5, 133.6, 133.0, 132.7, 127.6, 126.6, 119.6, 69.7, 61.5, 39.6, 30.6, 22.7, 14.0; IR (ATR) 3479, 2980, 2938, 2893, 2834, 1731, 1439, 1271, 1208, 1097, 1028 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{17}BrNaO_3$ $[M+Na]^+$: 347.0259, found: 347.0254; HPLC analysis CHIRALPAK AS-H (Hexane/IPA = 75/25, 1.0 mL/min, 254 nm, 30 °C) 7.02 min (major), 17.4 min (minor), 60% ee; $[\alpha]^{20}_D$ = 5.46 (*c* = 0.95, $CHCl_3$, 60% ee). **Configuration Assignment:** The absolute configuration was assigned as (*S*) by analogy.



6h

ethyl (*S*)-3-(2H-chromen-4-yl)-2-hydroxypropanoate (6h)

6h: Colorless oil: (37.2 mg, 75% yield); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.20 (dd, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.13 (dt, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1.8 Hz, 1H), 6.91 (dt, *J* = 7.2 Hz, 1.2 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 5.75 (t, *J* = 3.9 Hz, 1H), 4.76 (d, *J* = 3.0 Hz, 2H), 4.40–4.36 (m, 1H), 4.25-4.15 (m, 2H), 2.95 (dd, *J* = 14.4 Hz, 4.2 Hz, 1H) 2.80 (d, *J* = 6.6 Hz, 1H), 2.70 (dd, *J* = 15.5 Hz, 7.8 Hz, 1H), 1.28 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 174.3, 154.4, 129.6, 129.2, 123.2, 123.0, 121.1, 121.0, 116.2, 69.2, 65.1, 61.8, 36.4, 14.1; IR (ATR) 3470, 2980, 2937, 2905, 2837, 1731, 1651, 1605, 1577, 1487, 1449, 1369, 1299, 1219, 1128, 1097, 1028, 937, 862 cm^{-1}; HRMS (ESI) calcd. for $C_{14}H_{16}NaO_4$ $[M+Na]^+$: 271.2678, found: 271.2673; HPLC analysis CHIRALPAK AS-H (Hexane/IPA = 90/10, 1.0 mL/min, 254 nm, 30 °C) 10.6 min (major), 12.2 min (minor), 91% ee; $[\alpha]^{22}_D$ = -5.50 (*c* = 1.00, $CHCl_3$, 91% ee). **Configuration Assignment:** The absolute configuration was assigned as (*S*) by analogy.

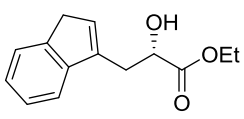


6i

ethyl (*S*)-2-hydroxy-3-(2H-thiochromen-4-yl)propanoate (6i)

6i: Colorless oil: (31.2 mg, 59% yield); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.36 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.17-7.10 (m, 2H), 6.01 (t, *J* = 5.4 Hz, 1H), 4.32–4.27 (m, 1H), 4.19–4.09 (m, 2H), 3.33 (dd, *J* = 15.6 Hz, 6.0 Hz, 1H), 3.29 (dd, *J* = 15.0 Hz, 6.0 Hz, 1H), 3.01 (dd, *J* = 14.4 Hz, 4.8 Hz, 1H), 2.79 (dd, *J* = 14.4 Hz, 7.8 Hz, 1H), 2.71 (d, *J* = 6.6 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR

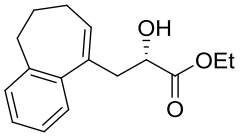
($CDCl_3$, 151 MHz) δ 174.3, 133.8, 133.6, 133.1, 127.9, 127.6, 125.6, 124.8, 122.5, 69.5, 61.7, 39.1, 24.8, 14.1; IR (ATR) 3448, 2978, 2934, 1734, 1633, 1588, 1471, 1446, 1368, 1219, 1152, 1099, 1024 cm^{-1}; HRMS (ESI) calcd. for $C_{14}H_{16}NaO_3S$ $[M+Na]^+$: 287.0718, found: 287.0714; HPLC analysis CHIRALPAK AS-H (Hexane/IPA = 90/10, 1.0 mL/min, 254 nm, 30 °C) 15.8 min (major), 17.5 min (minor), 83% ee; $[\alpha]^{22}_D$ = +6.94 (*c* = 1.00, $CHCl_3$, 83% ee). **Configuration Assignment:** The absolute configuration was assigned as (*S*) by analogy.



6j

ethyl (*S*)-2-hydroxy-3-(1H-inden-3-yl)propanoate (6j)

6j: Colorless oil: (22.3 mg, 48% yield); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.46 (d, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.39 (brs, 1H), 4.55–4.51 (m, 1H), 4.25–4.16 (m, 2H), 3.37 (brs, 2H), 3.10 (dd, *J* = 14.4 Hz, 2.1 Hz, 1H), 2.95 (dd, *J* = 15.0 Hz, 7.2 Hz, 1H), 2.84 (d, *J* = 6.0 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 174.4, 145.0, 144.2, 139.2, 131.2, 126.0, 124.7, 123.8, 119.0, 69.7, 61.8, 38.0, 32.7, 14.1; IR (ATR) 3486, 3065, 2981, 2904, 1732, 1462, 1395, 1259, 1206, 1096, 1055, 1028 cm^{-1}; HRMS (ESI) calcd. for $C_{14}H_{16}NaO_3$ $[M+Na]^+$: 255.0997, found: 255.0992; HPLC analysis CHIRALPAK AS-H (Hexane/IPA = 85/15, 1.0 mL/min, 254 nm, 30 °C) 6.5 min (major), 8.0 min (minor), 62% ee; $[\alpha]^{20}_D$ = 1.21 (*c* = 1.00, $CHCl_3$, 62% ee). **Configuration Assignment:** The absolute configuration was assigned as (*S*) by analogy.



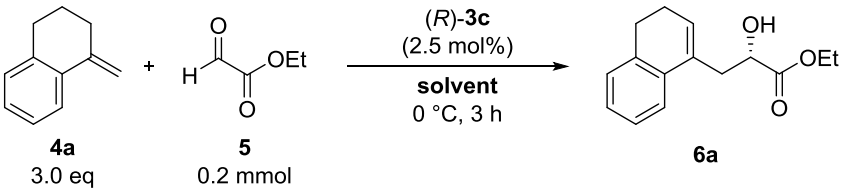
6k

ethyl (*S*)-3-(6,7-dihydro-5H-benzo[7]annulen-9-yl)-2-hydroxypropanoate (6k)

6k: Colorless oil: (39.0 mg, 75% yield); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.26–7.15 (m, 4H), 6.08 (t, *J* = 7.2 Hz, 1H), 4.17–4.14 (m, 1H), 4.03–3.98 (m, 1H), 3.86–3.80 (m, 1H), 3.01 (dd, *J* = 13.8 Hz, 4.2 Hz, 1H), 2.86 (dd, *J* = 14.4 Hz, 6.6 Hz, 1H), 2.65 (d, *J* = 6.0 Hz, 1H), 2.62–2.57 (m, 2H), 2.12-2.07 (m, 2H), 1.86-1.77 (m, 2H), 1.18 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 174.6, 141.8, 139.6, 136.0, 130.2, 129.0, 126.8, 126.2, 125.8, 69.4, 61.4, 41.4, 34.7, 32.1, 24.6, 14.0; IR (ATR) 3482, 3015, 2980, 2932, 2856, 1731, 1486, 1448, 1368, 1259, 1208, 1097, 1037 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{20}NaO_3$ $[M+Na]^+$: 283.1310, found: 283.1305; HPLC analysis CHIRALPAK AS-H (Hexane/IPA = 85/15, 1.0 mL/min, 254 nm, 30 °C) 5.9 min (major), 7.0 min (minor), 93% ee; $[\alpha]^{24}_D$ = 14.47 (*c* = 1.04, $CHCl_3$, 93% ee). **Configuration Assignment:** The absolute configuration was assigned as (*S*) by analogy.

5. Additional Screening

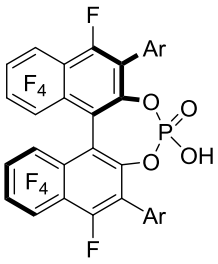
Screening of solvents



4a
3.0 eq

5
0.2 mmol

6a



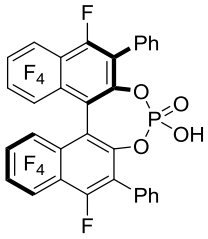
(*R*)-**3c**
Ar = 2-naphthyl

entry	**solvent**	yield (%)[a]	ee (%)
1[b]	benzene	73	62
2	toluene	97	71
3	*o*-xylene	92	72
4	*m*-xylene	59	74
5[b]	*p*-xylene	90	69
6	CF_3-benzene	54	59
7[b]	cyclohexane	67	74
8	CH_2Cl_2	76	43

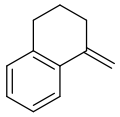
[a] NMR yield (isolated yield in parentheses), [b] 15 °C

6. Computational Studies

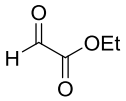
6-1. Model system: As the preliminary computational study, the mechanism of the carbonyl-ene reaction using the model system of F_{10}BINOL-derived phosphoric acid catalyst (*R*)-**3a** and the standard substrates (**4a** and **5**) were investigated. Geometries were optimized and characterized using frequency calculations at the M06-2X/6-31G(d,p) level. Energies in the solution phase were calculated using single-point energy calculations at the same level according to the CPCM solvation model (toluene: ε=2.379) for the optimized structures.



(*R*)-**3a**



4a



5

A variety of initial structures were thoughly explored to identify the transition state of carbonyl ene reaction, and it was found that the reaction proceeds through a stepwise mechanism via **INT-1** (Figure S1). Initially, catalyst forms hydrogen bonds with **4a** and **5** (association or association'). C-C bond formation through transition state **TS-1** yields the **INT-1** respectively. The following abstraction of proton proceeds via transition state **TS-2** or **TS-2'** (**TS-2**: Phosphorous oxygen of catalyst abstracts the proton., **TS-2'**: Alcohol oxygen abstracts the proton.). The energy profile indicates that **TS-2** is more energetically favored pathway than **TS-2'**.

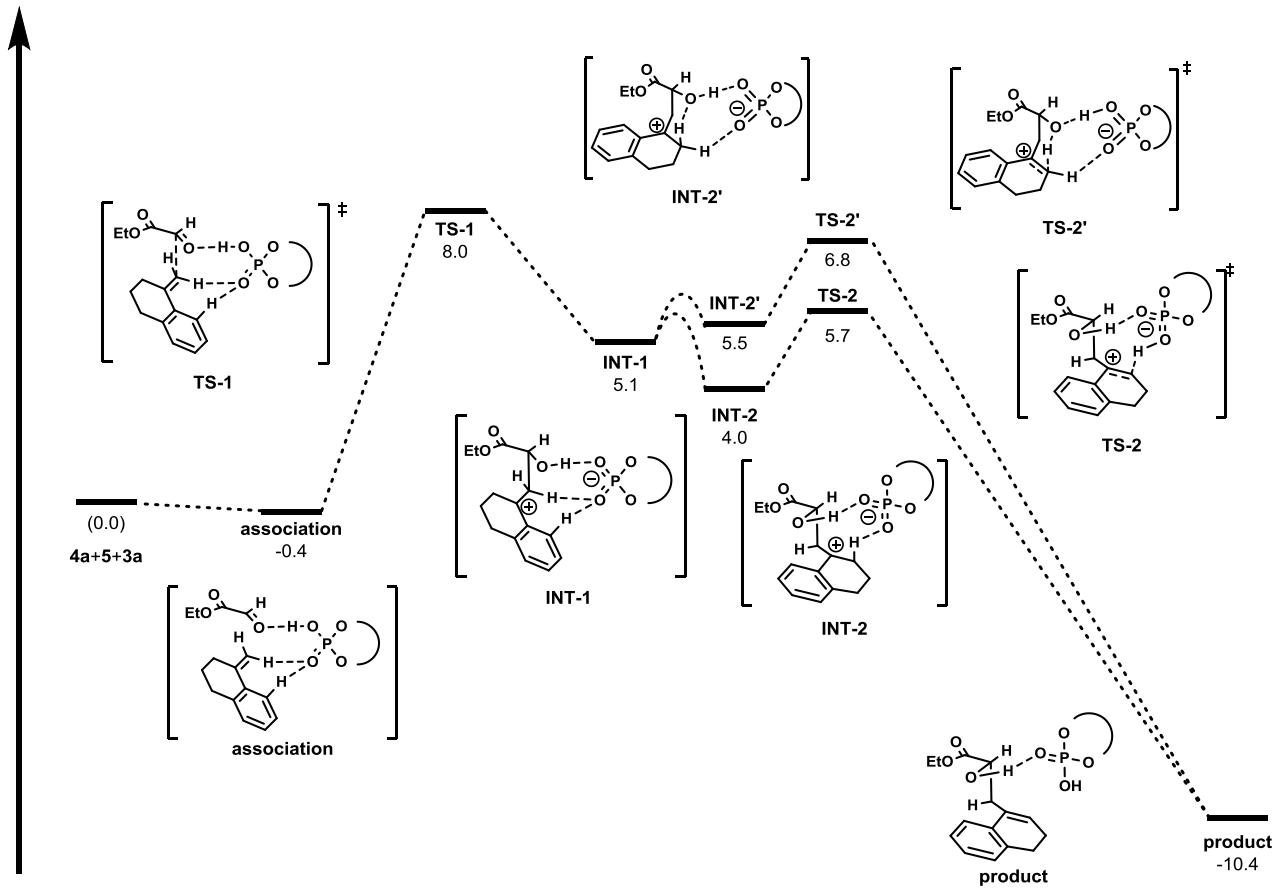


Figure S1. Energy profile of the carbonyl-ene reaction for the model reaction. The potential energy for the sum of **4a**, **5** and **3** was set to zero. Geometries were optimized and characterized using frequency calculations at the M06-2X/6-31G(d,p) level. Gibbs free energies (kcal/mol) in solution phase were calculated using single-point energy calculations at the same level as those for the optimized structures according to the SCRF method based on CPCM (toluene).

A summary of calculated values including solvent corrected single point energy values, as well as enthalpic and entropic corrections at 298.15 K are provided (**Table S1**).

	G_{CPCM} (kcal/mol)	E_{CPCM} (kcal/mol)	Enthalpic correction(kcal/mol)	S (cal/mol K)	ΔG (kcal/mol)
4a+**5**+**3a**	-2304858.6	-	-	-	0.0
association	-2304859.0	-2305223.0	458.1	315.5	-0.4
TS-1	-2304850.6	-2305214.9	456.8	310.5	8.0
INT-1	-2304853.5	-2305220.4	459.3	310.3	5.1
INT-2	-2304854.6	-2305221.7	459.3	309.3	4.0
INT-2’	-2304853.1	-2305244.2	458.2	306.7	5.5
TS-2	-2304852.9	-2305218.4	456.7	306.0	5.7
TS-2’	-2304851.8	-2305217.2	455.7	303.1	6.8
product	-2304869.0	-2305235.4	459.6	312.4	-10.4

Table S1. Summary of calculated values in model system

6-2. Real system: In order to conduct rigorous conformational analysis of these transition states, we systematically generated initial structures of the transition states by changing the dihedral angles of C^2-C^1-C^a-C^b and $C^{2'}$-$C^{1'}$-$C^{a'}$-$C^{b'}$ (for each dihedral angle: -135º, -45º, 45º, and 135º) as well as the orientation of the methoxy group (dihedral angle: 0º and 180º to the naphthyl ring) (Fiugre S2a). This procedure generates eight conformers for each naphthyl ring and hence totally 64 conformers were considered for the initial structures of the catalyst. In addition, on the basis of the model studies of the transition states, conformationally different transition states of the real system were considered by changing the relative orientation of ene-component **4a** and the conformation of the six-membered ring of **4a** for each enantiomeric pathway. Thus, nearly 200 initial structures were calculated to identify the energetically favored transition states accurately. Figure S2b presents the relative Gibbs free energy distribution of 10 TSs for (*S*)-**6a** and 7 TSs for (*R*)-**6a** within 3.0 kcal/mol. Although there are many energetically similar TSs, a comparison between the lowest TSs for each enantiomer clearly shows that the (*S*)-**6a** is the main product in this reaction in agreement with the experiment. The lowest TS for the (*R*)-**6a** (**TS-r (e)**) is 1.1 kcal/mol higher in energy than the lowest TS for the (*S*)-**6a** (**TS-s (a)**).

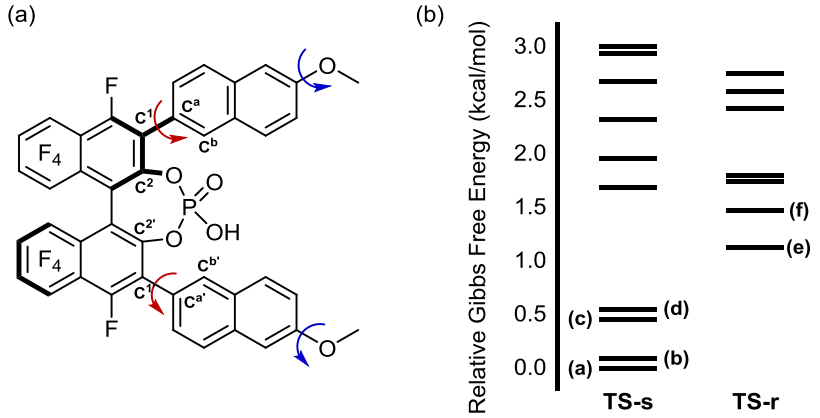


Figure S2. (a) Bond rotation of catalyst substituents. (b) Gibbs free-energy distribution of TSs for (*S*)-**6a** and TSs for (*R*)-**6a** within 3.0 kcal/mol.

The 6 lowest TS structures were listed (Figure S3) and the following key geometric parameters in each structures of (*R*)-**3PA$_{TS}$** were extracted (Table 2): dihedral angle (C^{2}-C^{3}-$C^{3'}$-$C^{2'}$), dihedral angles (C^{2}-C^{1}-C^{a}-C^{b}, $C^{2'}$-$C^{1'}$-$C^{a'}$-$C^{b'}$), interior bond angles (A and A'), and exterior bond angles (B and B').

In all TS sturctures, similar structural distortion of the catalyst was observed.

*In the main text, **TS-s (a)** and **TS-r (e)** are shown in **TS-s** and **TS-r**, respectively.

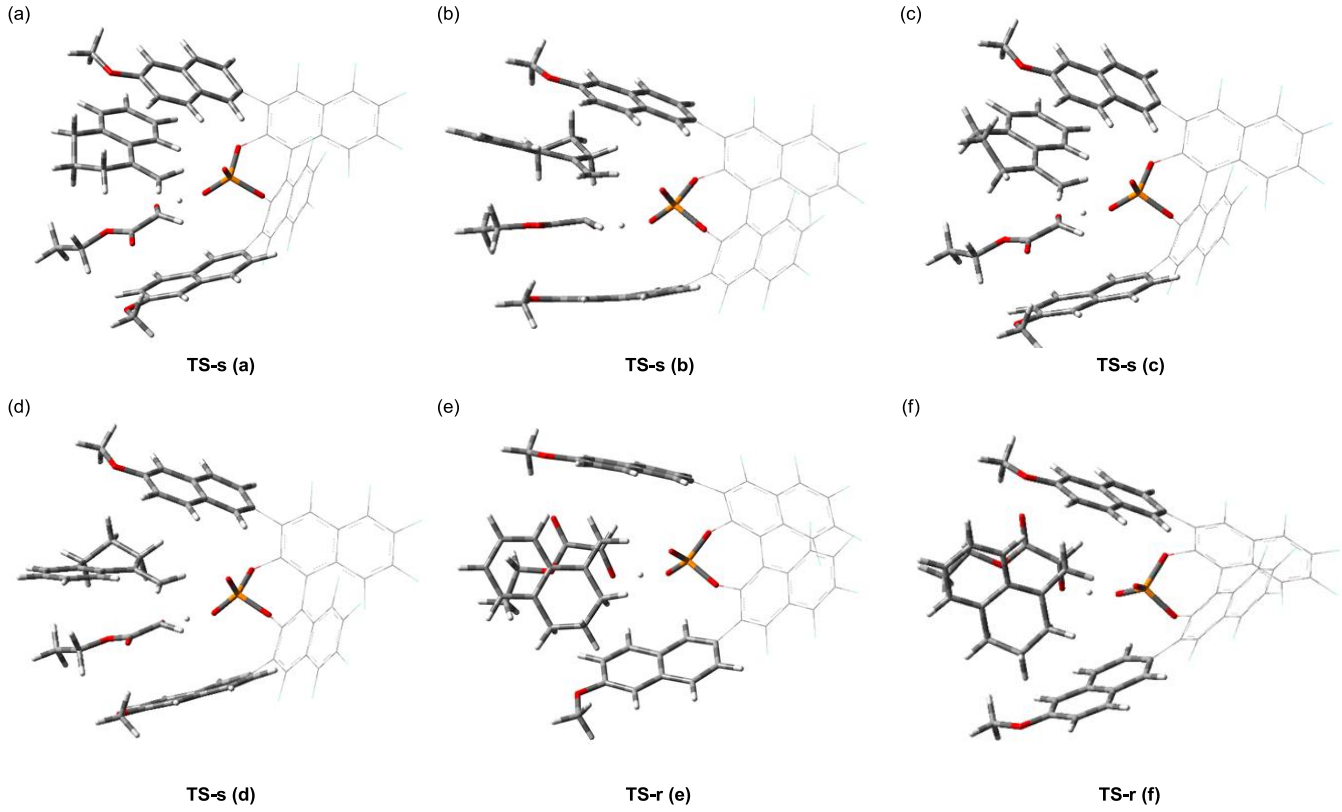
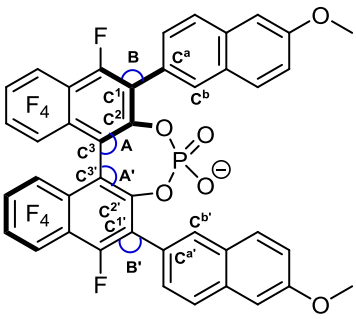


Figure S3. The 6 lowest TS structures



	C^{2}-C^{1}-C^{a}-C^{b}	$C^{2'}$-$C^{1'}$-$C^{a'}$-$C^{b'}$	C^{2}-C^{3}-$C^{3'}$-$C^{2'}$	A	A'	B	B'
(*R*)-**3PA$_{TS\text{-}s\ (a)}$***	76.4°	115.7°	-52.2°	118.0°	117.4°	122.8°	123.6°
(*R*)-**3PA$_{TS\text{-}s\ (b)}$**	96.4°	116.2°	-51.5°	117.4°	116.9°	123.7°	124.2°
(*R*)-**3PA$_{TS\text{-}s\ (c)}$**	75.1°	117.1°	-52.2°	118.0°	117.4°	122.8°	123.5°
(*R*)-**3PA$_{TS\text{-}s\ (d)}$**	76.5°	115.8°	-52.1°	117.8°	117.3°	123.0°	123.5°
(*R*)-**3PA$_{TS\text{-}r\ (e)}$**	77.8°	121.3°	-51.9°	118.0°	117.4°	124.3°	123.3°
(*R*)-**3PA$_{TS\text{-}r\ (f)}$**	121.9°	124.8°	-51.8°	116.8°	116.9°	123.2°	122.9°

Table S2. Selected geometric parameters for structures of (*R*)-**3PA$_{TS}$**. *In the main text, (*R*)-**3PA$_{TS\text{-}s\ (a)}$** is shown in (*R*)-**3PA$_{TS\text{-}s}$**.

A summary of calculated values in the lowest TS for the (*S*)-**6a** (**TS-s (a)**) and the lowest TS for the (*R*)-**6a** (**TS-r (e)**) including solvent corrected single point energy values, as well as enthalpic and entropic corrections associated with vibrational energy at 298.15 K are provided (**Table S3**). These result indicates that the enantiorecognition of this carbonyl-ene reaction contains a large enthoropic contribution.

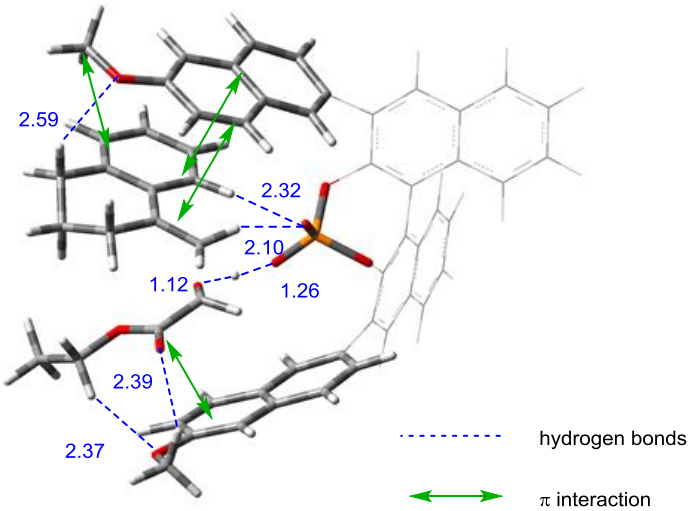
	G_{CPCM} (kcal/mol)	E_{CPCM} (kcal/mol)	Enthalpy correction(kcal/mol)	S (cal/mol K)	ΔG (kcal/mol)
TS-s (a)	-2641191.3	-2641652.5	563.9	344.6	0.0
TS-r (e)	-2641190.2	-2641649.7	563.0	347.1	1.1

Table S3. Summary of calculated values in real system

6-3. Transition state in the carbonyl-ene reaction catalyzed by BINOL-derived phosphoric acid (*R*)-**1**

The transition state in the major pathway of the carbonyl-ene reaction catalyzed by (*R*)-**1** (Ar = 6-methoxy-2-naphthyl) was identified by performing calculation after replacing the fluorine atoms of **TS-s (a)** with hydrogen atoms (Figure S4). In obtained **TS-s** ((*R*)-**1**), it was confirmed that multi-point C−H···O hydrogen bonds and the π interactions were formed between the catalyst and the substrates, as likely shown in transition state **TS-s (a)**.*

*In the main text, **TS-s (a)** is shown in **TS-s**.



TS-s ((*R*)-**1**)

Figure S4. Transition state in the carbonyl-ene reaction of **4a** with **5** catalyzed by (*R*)-**1**. Geometries were optimized and characterized using frequency calculations at the M06-2X/6-31G(d,p) level. Relative Gibbs free energies (kcal/mol) obtained by single-point energy calculations at the same level for the optimized structures with the SCRF method based on CPCM (toluene) are shown.

6-4. Second-Perturbation Energy (kcal/mol) of Donor-acceptor Interaction

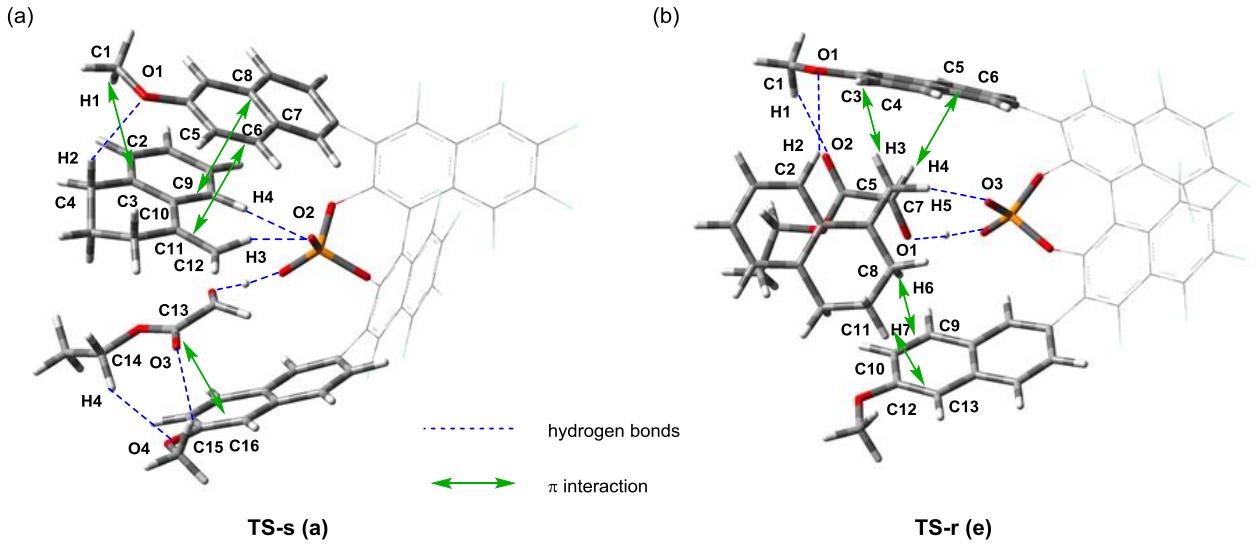
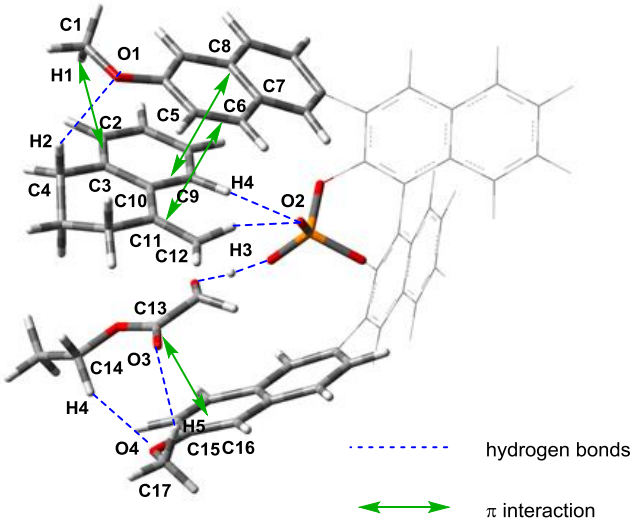


Figure S5. Donor-acceptor Interaction with Respect to (a) **TS-s (a)** and (b) **TS-r (e)**.

*In the main text, **TS-s (a)** and **TS-r (e)** are shown in **TS-s** and **TS-r**, respectively.

TS-s (a)				**TS-r (e)**			
donor	acceptor	Interaction	E (kcal/mol)	donor	acceptor	Interaction	E (kcal/mol)
BD C2-C3	BD* C1-H1	π→σ*	0.56	LP O1	BD* C2-H2	n→σ*	2.73
LP O1	BD* C4-H2	n→σ*	0.60	LP(2) O2	BD* C1-H1	n→σ*	0.61
BD C11-C12	BD* C5-C6	π→π*	0.53	BD C3-C4	BD* C5-H3	π→σ*	1.96
BD C7-C8	BD* C9-C10	π→π*	0.95	BD C5-C6	BD* C7-H4	π→σ*	0.55
LP O2	BD* C12-H3	n→σ*	3.47	LP O3	BD* C5-H5	n→σ*	5.75
LP O2	BD* C12-H3	n→σ*	3.22	LP(2) O3	BD* C5-H5	n→σ*	4.09
LP O2	BD* C9-H4	n→σ*	1.14	BD C9-C10	BD* C8-H6	π→σ*	0.69
LP O2	BD* C9-H4	n→σ*	1.24	BD C12-C13	BD* C11-H7	π→σ*	0.91
BD C15-C16	BD* C13-O3	π→π*	0.74				
LP O4	BD* C14-H4	n→σ*	1.17				
LP(2) O4	BD* C14-H4	n→σ*	1.38				

Table S4. Second-Perturbation Energy (kcal/mol)



TS-s ((*R*)-**1**)

Figure S6. Donor-acceptor Interaction with Respect to **TS-s** ((*R*)-**1**)

TS-s ((*R*)-**1**)							
donor	acceptor	Interaction	E (kcal/mol)	donor	acceptor	Interaction	E (kcal/mol)
BD C2-C3	BD* C1-H1	π→σ*	0.53	LP(3) O2	BD* C9-H4	n→σ*	1.66
LP O1	BD* C4-H2	n→σ*	0.53	BD C13-O3	BD*C15-H16	π→σ*	0.69
BD C12-C13	BD* C5-C6	π→π*	0.99	LP O3	BD* C17-H5	n→σ*	1.15
BD C7-C8	BD* C9-C10	π→π*	0.89	LP O4	BD* C14-H4	n→σ*	1.14
LP O2	BD* C12-H3	n→σ*	3.65				
LP(2) O2	BD* C12-H3	n→σ*	3.26				
LP(2) O2	BD* C9-H4	n→σ*	0.99				

Table S5. Second-Perturbation Energy (kcal/mol)

6-5. Structural analysis of BINOL-derived phosphate anion

The structural analysis of BINOL-derived phosphate anions (**PA**s) was conducted as follows: (i) The catalyst structure of BINOL-derived phosphate anion (*R*)-**1PA$_{TS-s}$** was extracted from **TS-s** ((*R*)-**1**) (Figure S7b). (ii) the structure of BINOL-derived phosphate anion (*R*)-**1PA$_{opt}$** was optimized from (*R*)-**1PA$_{TS-s}$** as the initial structure (Figure S7d) (The obtained structure of (*R*)-**1PA$_{opt}$** was identical to the structure which was optimized after replacing the fluorine atoms of (*R*)-**3PA$_{opt}$** with hydrogen atoms.)

As shown in Table S6, the dihedral angles C^2-C^1-C^a-C^b and $C^{2'}$-$C^{1'}$-$C^{a'}$-$C^{b'}$ in (*R*)-**1PA$_{TS-s}$** are markedly different from those in (*R*)-**1PA$_{opt}$**. These angle differences indicate that 6-methoxy-2-naphthyl substituents rotate to meet the requirements for the noncovalent bond interactions and the steric exclusion with the substrates in the transition state, as observed in (*R*)-**3PA** similarly. In both (*R*)-**1PA** and (*R*)-**3PA**, the dihedral angle C^2-C^3-$C^{3'}$-$C^{2'}$ in transition structures is smaller than that in the optimized structures. These angle differences imply that the binaphthyl (or perfluoro-binaphthyl) axis twists to interact with the substrates and lead to structural distortion of the catalyst framework.

The interior bond angles A and A' of (*R*)-**1PA$_{TS-s}$** are almost identical to those of (*R*)-**1PA$_{opt}$** and larger than those of (*R*)-**3PA**. In contrast, the exterior bond angles B and B' of (*R*)-**1PA$_{TS-s}$** are larger than those of (*R*)-**3PA$_{TS-s\ (a)}$**, although these angles of (*R*)-**1PA$_{opt}$** are smaller than those of (*R*)-**3PA**. The total bond angle differences of B and B' (ΔB + ΔB') between (*R*)-**1PA$_{TS-s}$** and (*R*)-**1PA$_{opt}$** is 7.2° (Between (*R*)-**3PA$_{TS-s\ (a)}$** and (*R*)-**3PA$_{opt}$**: 4.5°). In the case of BINOL-derived phosphoric acid, the more significant distortion of the catalyst fragment is enforced than that of F_{10}BINOL-derived one, because BINOL-derived phosphoric acid has the wider reaction space than that of F_{10}BINOL-derived one.

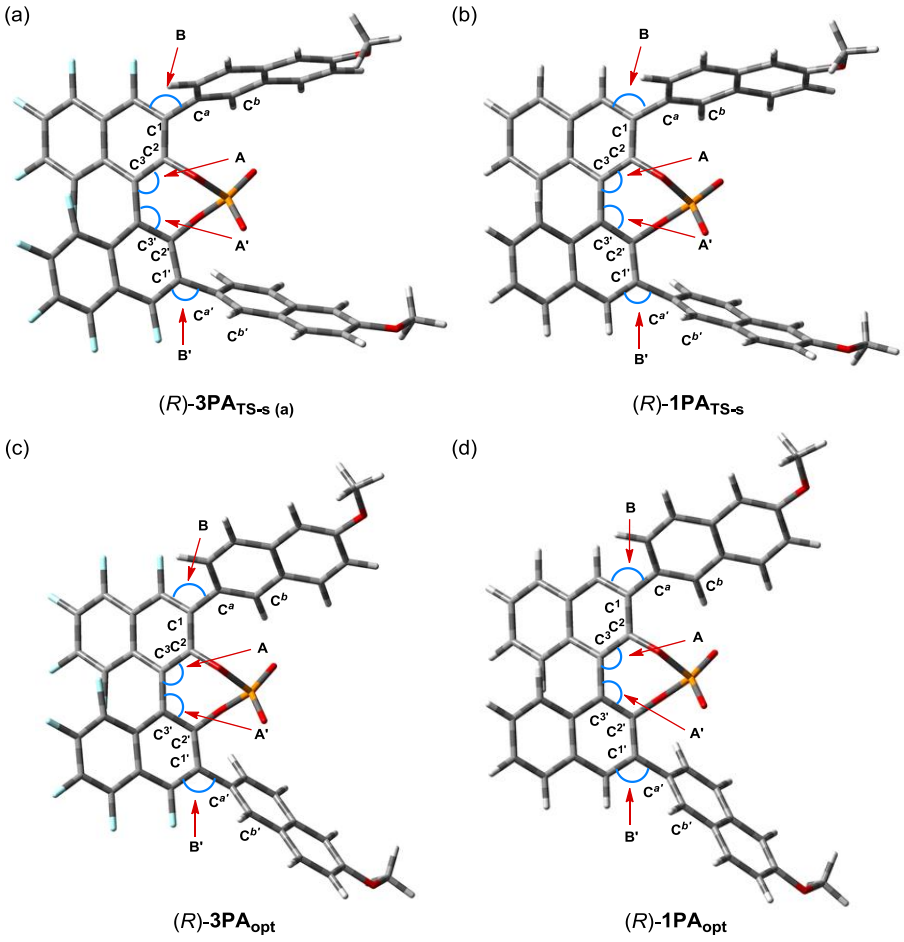


Figure S7. Structural analysis of the catalysts. (a) F_{10}BINOL-derived phosphate anion extracted from **TS-s (a)**. (b) BINOL-derived phosphate anion extracted from **TS-s** ((*R*)-**1**). (c) F_{10}BINOL-derived phosphate anion optimized from (*R*)-**3PA$_{TS-s}$**. (d) BINOL-derived phosphate anion optimized from (*R*)-**1PA$_{TS-s}$**

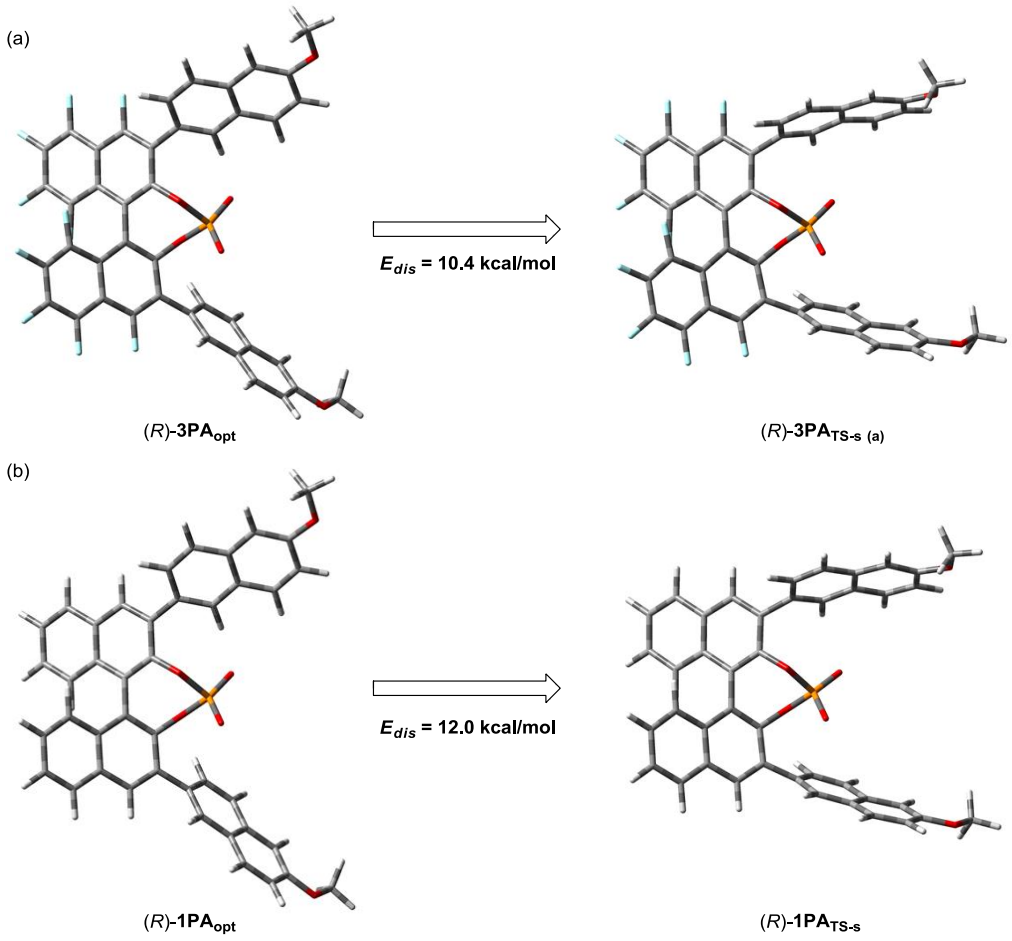
Table S6. Selected geometric parameters for catalyst structures.

	$C^{2}\text{-}C^{1}\text{-}C^{a}\text{-}C^{b}$	$C^{2'}\text{-}C^{1'}\text{-}C^{a'}\text{-}C^{b'}$	$C^{2}\text{-}C^{3}\text{-}C^{3'}\text{-}C^{2'}$	A	A’	B	B’
(*R*)-**3PA**$_{\text{TS-s (a)}}$	76.4°	115.7°	-52.2°	118.0°	117.4°	122.8°	123.6°
(*R*)-**1PA**$_{\text{TS-s}}$	69.4°	114.8°	-50.3°	119.5°	118.8°	123.4°	123.8°
(*R*)-**3PA**$_{\text{opt}}$	50.3°	134.4°	-55.6°	117.8°	117.2°	120.2°	121.7°
(*R*)-**1PA**$_{\text{opt}}$	46.0°	139.7°	-53.3°	119.1°	118.6°	119.5°	120.5°

6-6. The distortion energy of catalysts

The analysis of the distortion energy in caralyst frameworks was conducted (Figure S8). The E_{dis} is the energy required to distort the catalyst framework from their optimized structures to their transition structures. As a result, it was found that the distortion energy difference between (*R*)-**1PA**$_{\text{opt}}$ and (*R*)-**1PA**$_{\text{TS-s}}$ (E_{dis} = 12.0 kcal/mol) is larger than the difference between (*R*)-**3PA**$_{\text{opt}}$ and (*R*)-**3PA**$_{\text{TS-s (a)}}$ (E_{dis} = 10.4 kcal/mol). These results clearly indicate that the energetic destabilization of the BINOL-derived phosphoric acid framework is more significant than that of the F_{10}BINOL-derived one in the transition state.

Figure S8. Energy for the catalyst distortion

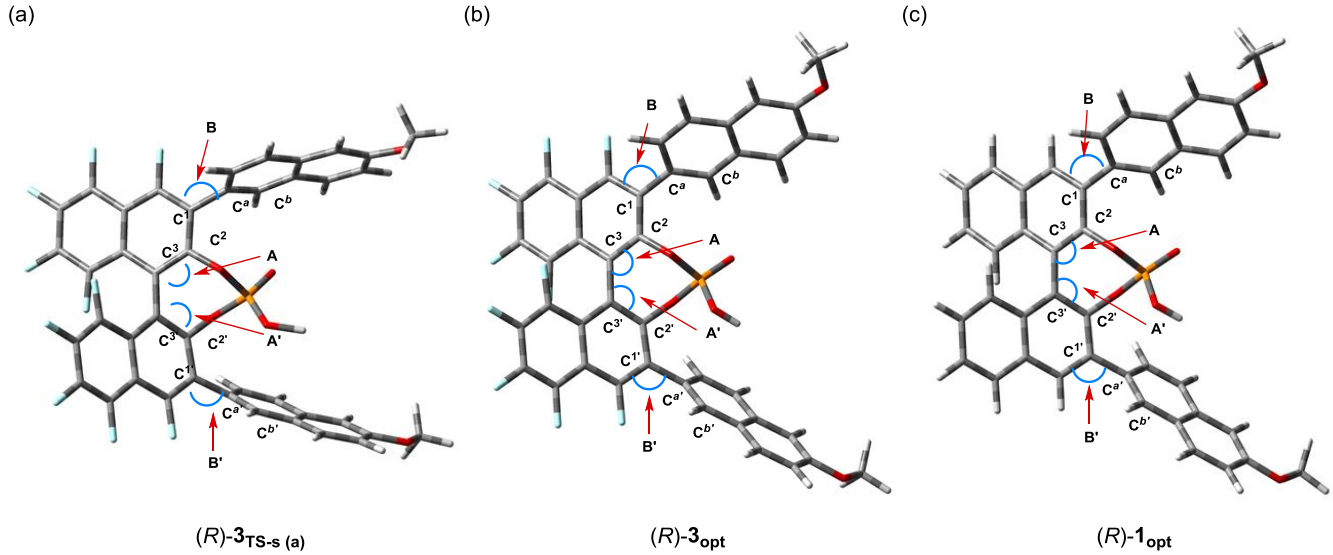


	$E_{TS\text{-}S}$ (a.u.)	E_{opt} (a.u.)	E_{dis} (a.u.)	E_{dis} (kcal/mol)
(*R*)-**3PA**	-3401.451913	-3401.468532	0.016619	10.42858869
(*R*)-**1PA**	-2409.466063	-2409.485134	0.019071	11.96724321

6-7. The optimization of the catalyst structure as phosphoric acid

DFT calculations for the structural analysis of chiral phosphoric acids were carried out in the following order: (i) the structure of F_{10}BINOL-derived phosphoric acid (*R*)-**3**$_{\textbf{TS-s (a)}}$ was extracted from **TS-s (a)** (Figure S9a); (ii) the structure of F_{10}BINOL-derived phosphoric acid (*R*)-**3**$_{\textbf{opt}}$ was optimized based on the (*R*)-**3**$_{\textbf{TS-s (a)}}$ (Figure S9b); and (iii) the structure of BINOL-derived phosphoric acid (*R*)-**1**$_{\textbf{opt}}$ was optimized by replacing the fluorine atoms of (*R*)-**3**$_{\textbf{opt}}$ with hydrogen atoms (Figure S9c).

Figure S9. Structural analysis for Catalyst. (a) F_{10}BINOL-derived phosphoric acid from **TS-s (a)**. (b) Optimized structure of F_{10}BINOL-derived phosphoric acid (*R*)-**3**$_{\textbf{opt}}$. (c) Optimized structure of BINOL-derived phosphoric acid (*R*)-**1**$_{\textbf{opt}}$.

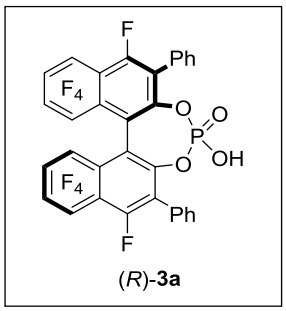


(*R*)-**3**$_{\textbf{TS-s (a)}}$ (*R*)-**3**$_{\textbf{opt}}$ (*R*)-**1**$_{\textbf{opt}}$

	C^{2}-C^{1}-C^{a}-C^{b}	$C^{2'}$-$C^{1'}$-$C^{a'}$-$C^{b'}$	C^{2}-C^{3}-$C^{3'}$-$C^{2'}$	∠A	∠A’	∠B	∠B’
(*R*)-**3**$_{\textbf{TS-s (a)}}$	76.4°	115.7°	-52.2°	118.0°	117.4°	122.8°	123.6°
(*R*)-**3**$_{\textbf{opt}}$	56.5°	129.2°	-55.2°	118.9°	118.2°	120.5°	122.2°
(*R*)-**1**$_{\textbf{opt}}$	51.6°	131.8°	-53.3°	120.0°	119.5°	120.1°	121.6°

Table S7. Selected geometric parameters for catalyst structures.

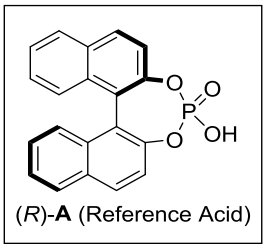
6-8. Theoretical Study on the aciditiy of (*R*)-**3a**



(*R*)-**3a**

The p*K*a value of (*R*)-**3a** in DMSO was calculated with the SMD/M06-2x/6-311++G(2df,2p)//B3LYP/6-31+G(d) method[2]. The geometries were fully optimized using the B3LYP/6-31+G(d) methods in gas-phase. The nature of the stationary points and thermal corrections to Gibbs free energy (**ZPG**) were obtained by frequency calculations at the same level of theory. The energies in solution phase (**E**) were obtained with thermal corrections to the Gibbs free energies (**G**) by performing SMD calculation (M06-2x/6-311++G(2df,2p)) with the gas-phase optimized geometries. In the proton exchange method, (*R*)-**A** (p*K*a exp 3.37) was chosen as the reference acid.

Reference Acid **A**

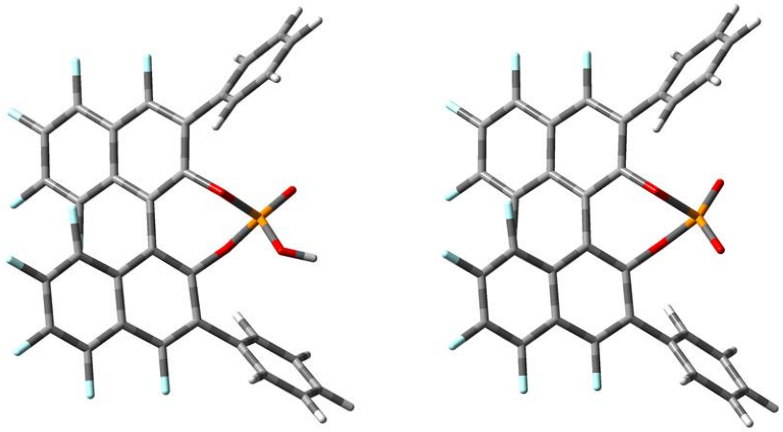


(*R*)-**A** (Reference Acid)

	G
(*R*)-**A** (Phosphoric Acid)	-1412.07198721
(*R*)-**A-PA** (PhosphateAnion)	-1411.63352682

[2] a) C. Yang, X.-S. Xue, X. Li, J.-P. Cheng. *J. Org. Chem.* 2013, **78**, 7076-7085; b) C. Yang, X.-S. Xue, X. Li, J.-P. Cheng, *J. Org. Chem.* 2014, **79**, 4340-4351.

Figure S10. Structures of 3,3'-Ph-F_{10}BINOL-derived Phosphoric Acid ((*R*)-**3a**) and Phosphate Anion ((*R*)-**3a-PA**)



(*R*)-3a (*R*)-3a-PA

	ZPG (hartree)	**E** (hartree)	**G** (hartree)
(*R*)-3a	0.290558	-2866.756485	-**2866.465927**
(*R*)-3a-PA	0.278222	-2866.310306	-**2866.032084**

・Direct method

$\Delta G^*_{soln} = \Delta G^*_{gas} + \Delta G^*_{solv}(A^-) + \Delta G^*_{solv,}(H^+) - \Delta G^*_{solv}(HA)$

$= G^*_{gas}(A^-) + G^*_{gas}(H^+) - G^*_{gas}(HA) + \Delta G^*_{solv}(A^-) + \Delta G^*_{solv}(H^+) - \Delta G^*_{solv}(HA)$

$= [G^*_{gas}(A^-) + \Delta G^*_{solv}(A^-)] + [G^*_{gas}(H^+) + \Delta G^*_{solv}(H^+)] - [G^*_{gas}(HA) + \Delta G^*_{solv}(HA)]$

$= G^*_{soln}(A^-) + G^*_{soln}(H^+) - G^*_{son}(HA)$

$G^*_{soln}(H^+) = G^*_{gas}(H^+) + G^*_{solv}(H^+) = -4.39 + (-268.34 + 1.89) = -270.84$ (kcal/mol)

$G^*_{soln}(HA) = ZPG + E^*_{solv}(HA) = 0.290558 + (-2866.756485) = -2866.465927$ (hartree)

$G^*_{soln}(A^-) = ZPG + E^*_{solv}(A^-) = 0.278222 + (-2866.310306) = -2866.032084$ (hartree)

$\Delta G^*_{soln} = 627.5095 \times \{-2866.032084 - (-2866.465927)\} - 270.84 = (1.40$ kcal/mol)

p*K*a $= \Delta G^*_{soln} \div 2.303RT =$ **1.03**

・Proton Exchange Method

$\Delta G^*_{exchange} = \Delta G^*_{gas,exchange} + \Delta G^*_{solv}(A^-) + \Delta G^*_{solv,}(HRef) - \Delta G^*_{solv}(HA) - \Delta G^*_{solv}(Ref^-)$

$= 627.51 \times \{-2866.032084 - (-2866.465927) + 1411.63352682 - 1412.07198721\}$

$= (-2.90$ kcal/mol)

p*K*a $= \Delta G^*_{exchange} \div 2.303RT +$ p*K*a(HRef) = **1.24**

6-9. Cartesian coordinates

Ethylglyoxylate (5)
M062X/6-31g(d,p); E(RM062X) = -381.538086 hartree
Sum of electronic and thermal Free Energies= -381.469415 hartree
Thermal correction to Gibbs Free Energy= 0.068671 hartree
cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -381.542279 hartree
Gibbs Free Energy in toluene = -381.473608 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.021809	-0.200841	-0.000227
2	1	0	2.886599	0.487939	-0.000808
3	8	0	2.114981	-1.395943	0.000315
4	6	0	0.683311	0.542211	-0.000109
5	6	0	-1.644776	0.366308	0.000052
6	1	0	-1.711368	1.008551	-0.883025
7	1	0	-1.710949	1.008187	0.883426
8	8	0	0.640331	1.747283	0.000245
9	8	0	-0.357005	-0.278182	-0.000351
10	6	0	-2.691015	-0.724569	0.000056
11	1	0	-3.689029	-0.280668	-0.000227
12	1	0	-2.588661	-1.354083	-0.886047
13	1	0	-2.589026	-1.353841	0.886368

Methylenetetraline (4a)
M062X/6-31g(d,p); E(RM062X) = -426.210003 hartree
Sum of electronic and thermal Free Energies= -426.042973 hartree
Thermal correction to Gibbs Free Energy= 0.167030 hartree
cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -426.212039 hartree
Gibbs Free Energy in toluene = -426.045009 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.618841	2.231138	0.288268
2	6	0	0.138099	0.508740	-0.049863
3	6	0	0.406903	-0.870781	0.005950
4	6	0	-0.703785	-1.901649	-0.010324
5	6	0	-2.070828	-1.316886	0.335162
6	6	0	-2.298806	-0.033345	-0.467473
7	1	0	-0.749362	-2.341601	-1.016262
8	1	0	-0.448915	-2.721066	0.670027
9	1	0	-2.856530	-2.049252	0.127222
10	1	0	-2.116981	-1.080730	1.404483
11	1	0	-2.201817	-0.263794	-1.537603
12	1	0	-3.304531	0.363721	-0.305742
13	6	0	2.527987	0.960013	-0.047333
14	6	0	2.791403	-0.406887	0.031054
15	6	0	1.734156	-1.305584	0.052889
16	6	0	1.215860	1.405376	-0.090527
17	1	0	1.015965	2.468168	-0.181899
18	1	0	3.344208	1.674199	-0.083681
19	1	0	3.814338	-0.767559	0.067668
20	1	0	1.932764	-2.373287	0.107559
21	6	0	-1.267513	0.994055	-0.072201
22	1	0	-2.658409	2.541417	0.260734
23	1	0	-0.898543	2.964644	0.633881

3a
M062X/6-31g(d,p); E(RM062X) = -2865.793909 hartree
Sum of electronic and thermal Free Energies= -2865.495807 hartree
Thermal correction to Gibbs Free Energy= 0.298102 hartree
cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -2865.802318 hartree
Gibbs Free Energy in toluene = -2865.504216 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.134118	-3.549999	-1.975477
2	6	0	-0.538313	-2.496671	-1.333858
3	6	0	-1.288800	-1.506481	-0.655026
4	6	0	-2.712516	-1.624361	-0.711809
5	6	0	-3.304019	-2.728574	-1.375953
6	6	0	-2.532513	-3.674746	-1.993241
7	6	0	-0.695932	-0.403444	0.048041
8	6	0	-3.499791	-0.597826	-0.126885
9	6	0	-2.962258	0.501334	0.486735
10	6	0	-1.545484	0.544616	0.567396
11	6	0	0.775230	-0.176311	0.180397
12	6	0	1.672122	-1.109658	0.796498
13	6	0	1.311900	1.002322	-0.302218
14	6	0	1.233563	-2.274450	1.471811
15	6	0	3.078966	-0.875382	0.756304
16	6	0	2.705533	1.265423	-0.388501
17	6	0	2.110497	-3.155556	2.044726
18	6	0	3.967561	-1.803758	1.355809
19	6	0	3.540685	0.305771	0.121619
20	6	0	3.494979	-2.922531	1.984980
21	8	0	0.468527	1.973035	-0.820127
22	8	0	-0.994325	1.651258	1.188792
23	9	0	4.857043	0.496838	0.043319
24	9	0	5.282998	-1.609562	1.333683
25	9	0	4.321169	-3.792047	2.553950
26	9	0	1.667579	-4.235774	2.675918
27	9	0	-0.068303	-2.553953	1.585458
28	9	0	0.794749	-2.438421	-1.387476
29	9	0	-0.399541	-4.460523	-2.601127
30	9	0	-3.082756	-4.706005	-2.621739
31	9	0	-4.625274	-2.873065	-1.428630
32	9	0	-4.826900	-0.698089	-0.214602
33	15	0	-0.454591	2.812051	0.201987
34	8	0	0.126971	3.923861	0.954001
35	8	0	-1.642466	3.138517	-0.802252
36	1	0	-2.239601	3.815975	-0.453179
37	6	0	3.262541	2.473937	-1.052991
38	6	0	4.143971	2.312074	-2.126443
39	6	0	2.935701	3.760425	-0.617886
40	6	0	4.684553	3.422599	-2.764020
41	1	0	4.400801	1.311866	-2.461246
42	6	0	3.480727	4.868579	-1.259589
43	1	0	2.264386	3.899578	0.223055
44	6	0	4.352162	4.704065	-2.332328
45	1	0	5.364908	3.286069	-3.598145
46	1	0	3.222274	5.864112	-0.914183
47	1	0	4.773894	5.571611	-2.829562
48	6	0	-3.805012	1.620013	0.979084
49	6	0	-3.618130	2.158406	2.256576
50	6	0	-4.776399	2.176122	0.138430
51	6	0	-4.388976	3.235182	2.683218
52	1	0	-2.864020	1.735545	2.911344
53	6	0	-5.542709	3.254808	0.567422
54	1	0	-4.921402	1.764019	-0.854873
55	6	0	-5.350028	3.787350	1.840305
56	1	0	-4.235060	3.643999	3.676161
57	1	0	-6.290823	3.679279	-0.093976
58	1	0	-5.947180	4.629565	2.173945

Association
M062X/6-31g(d,p); E(RM062X) = -3673.594294 hartree
Sum of electronic and thermal Free Energies= -3673.014183 hartree
Thermal correction to Gibbs Free Energy= 0.580111 hartree
cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -3673.603666 hartree
Gibbs Free Energy in toluene = -3673.023555 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.906293	2.257868	-1.029638
2	6	0	3.938233	-0.445015	-1.234680
3	6	0	4.181471	2.009808	1.328667
4	6	0	4.382632	1.279486	2.515357
5	6	0	5.678688	0.548231	2.792291
6	6	0	6.491633	0.259953	1.534443
7	6	0	6.578911	1.516025	0.660734
8	1	0	6.275591	1.171237	3.473451
9	1	0	5.466136	-0.379530	3.333635
10	1	0	7.496895	-0.076041	1.810919
11	1	0	6.020286	-0.545214	0.964560
12	1	0	7.066819	2.316392	1.234678
13	1	0	7.189938	1.332920	-0.230028
14	6	0	2.032013	2.776634	2.179271
15	6	0	2.213023	2.007699	3.328894
16	6	0	3.381461	1.277454	3.490974
17	6	0	3.009059	2.772503	1.194733
18	1	0	2.860735	3.369933	0.302228
19	1	0	1.132599	3.371724	2.048033
20	1	0	1.448326	1.988258	4.098753
21	1	0	3.534850	0.693498	4.395211
22	6	0	5.199507	1.971600	0.248201
23	1	0	5.676291	2.222670	-1.795753
24	1	0	3.902560	2.529514	-1.344807
25	1	0	3.157419	0.114878	-1.769816
26	8	0	3.814509	-0.859333	-0.099435
27	6	0	5.194300	-0.689248	-2.058824
28	6	0	7.417470	-1.411258	-2.049592
29	1	0	7.683034	-0.479642	-2.558015
30	1	0	7.254810	-2.174367	-2.817291
31	8	0	5.238288	-0.422264	-3.233317
32	6	0	-4.469094	-2.697039	2.229326
33	6	0	-3.842312	-1.729931	1.489480
34	6	0	-2.646293	-1.984566	0.776820
35	6	0	-2.084434	-3.292694	0.901136
36	6	0	-2.757447	-4.278037	1.667270
37	6	0	-3.926291	-3.988913	2.316838
38	6	0	-1.976595	-0.998981	-0.023168
39	6	0	-0.839335	-3.558276	0.271087
40	6	0	-0.133155	-2.614225	-0.426149
41	6	0	-0.753802	-1.341689	-0.554402
42	6	0	-2.486388	0.384434	-0.274848
43	6	0	-3.755263	0.665931	-0.884279
44	6	0	-1.689552	1.463832	0.056835
45	6	0	-4.599012	-0.338059	-1.420212
46	6	0	-4.218295	2.013713	-0.981676
47	6	0	-2.101429	2.818109	-0.048168
48	6	0	-5.816849	-0.047413	-1.974013
49	6	0	-5.485316	2.288453	-1.555290
50	6	0	-3.361840	3.049053	-0.526182
51	6	0	-6.272308	1.279844	-2.038663
52	8	0	-0.443713	1.260943	0.612679
53	8	0	-0.045075	-0.377004	-1.237074
54	9	0	-3.794487	4.306992	-0.603861
55	9	0	-5.940815	3.534796	-1.649533
56	9	0	-7.456724	1.531900	-2.583521
57	9	0	-6.580177	-1.013075	-2.471220
58	9	0	-4.229158	-1.622270	-1.419731
59	9	0	-4.407884	-0.519824	1.477263
60	9	0	-5.589679	-2.424584	2.886215
61	9	0	-4.553445	-4.906938	3.042762
62	9	0	-2.267687	-5.508987	1.791081

63	9	0	-0.327875	-4.784478	0.397337
64	15	0	0.761019	0.672920	-0.289327
65	8	0	1.517022	1.595744	-1.150299
66	8	0	1.502142	-0.166898	0.795666
67	1	0	2.446554	-0.417211	0.555186
68	8	0	6.181900	-1.208223	-1.340617
69	6	0	8.452246	-1.827672	-1.029717
70	1	0	9.407871	-2.015414	-1.524150
71	1	0	8.593065	-1.039745	-0.285969
72	1	0	8.140161	-2.738445	-0.514249
73	6	0	-1.218846	3.945670	0.355458
74	6	0	-1.563681	4.744819	1.447861
75	6	0	-0.052431	4.221922	-0.362910
76	6	0	-0.744785	5.804558	1.826246
77	1	0	-2.472569	4.529191	2.001281
78	6	0	0.755950	5.291709	0.011240
79	1	0	0.228100	3.597146	-1.204632
80	6	0	0.415895	6.080190	1.107670
81	1	0	-1.015667	6.416152	2.680556
82	1	0	1.656313	5.506369	-0.555771
83	1	0	1.053306	6.907753	1.401265
84	6	0	1.211293	-2.897313	-0.995408
85	6	0	1.543445	-2.505438	-2.297893
86	6	0	2.169937	-3.570080	-0.226924
87	6	0	2.801603	-2.795145	-2.822829
88	1	0	0.815040	-1.976528	-2.902286
89	6	0	3.422013	-3.865886	-0.755774
90	1	0	1.929610	-3.860011	0.790179
91	6	0	3.739203	-3.486718	-2.056634
92	1	0	3.048986	-2.479054	-3.831204
93	1	0	4.152997	-4.384213	-0.144606
94	1	0	4.716282	-3.716946	-2.471164

TS1

M062X/6-31g(d,p); E(RM062X) = -3673.577763 hartree
Sum of electronic and thermal Free Energies= -3672.997275 hartree
Thermal correction to Gibbs Free Energy= 0.580488 hartree
cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -3673.590632 hartree
Gibbs Free Energy in toluene = -3673.010144 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.350608	-1.098154	-1.759904
2	6	0	-3.945163	0.679018	-0.981358
3	6	0	-5.077045	-2.008315	0.432717
4	6	0	-6.132968	-2.252674	1.347695
5	6	0	-7.569925	-2.003442	0.959959
6	6	0	-7.674373	-0.893467	-0.079249
7	6	0	-6.793572	-1.242320	-1.277532
8	1	0	-7.994675	-2.928884	0.545272
9	1	0	-8.152342	-1.765195	1.854490
10	1	0	-8.710719	-0.756868	-0.400806
11	1	0	-7.326214	0.048677	0.358819
12	1	0	-7.158123	-2.174186	-1.737107
13	1	0	-6.835119	-0.481033	-2.063879
14	6	0	-3.461678	-2.732794	2.101874
15	6	0	-4.505459	-2.969393	2.994461
16	6	0	-5.825246	-2.732403	2.615515
17	6	0	-3.745969	-2.258526	0.831566
18	1	0	-2.926475	-2.101342	0.137719
19	1	0	-2.431171	-2.918703	2.385972
20	1	0	-4.292418	-3.337426	3.993283
21	1	0	-6.631210	-2.913824	3.320891
22	6	0	-5.360076	-1.482413	-0.887917
23	1	0	-4.642670	-0.786134	-2.759103
24	1	0	-3.339094	-1.482532	-1.658658
25	1	0	-3.082814	0.772888	-1.654521
26	8	0	-3.748161	0.656137	0.286224
27	6	0	-5.164089	1.429661	-1.487292
28	6	0	-7.087130	2.617950	-0.893980
29	1	0	-7.742734	1.924330	-1.432624
30	1	0	-6.799779	3.409307	-1.592191
31	8	0	-5.427910	1.553964	-2.659933
32	6	0	4.890787	2.421231	2.300926
33	6	0	4.208060	1.526522	1.520897
34	6	0	3.001490	1.865695	0.861440
35	6	0	2.498678	3.186757	1.081386
36	6	0	3.228679	4.095866	1.887895
37	6	0	4.401254	3.723966	2.485492
38	6	0	2.267470	0.953851	0.030141
39	6	0	1.253329	3.541711	0.498853
40	6	0	0.510872	2.677662	-0.256766
41	6	0	1.061247	1.386938	-0.473229
42	6	0	2.666746	-0.461654	-0.246740
43	6	0	3.888741	-0.838058	-0.893522
44	6	0	1.793857	-1.472954	0.116601
45	6	0	4.792817	0.100908	-1.447975
46	6	0	4.237291	-2.217123	-1.013525
47	6	0	2.124393	-2.856935	0.057662
48	6	0	5.954372	-0.281328	-2.062335
49	6	0	5.446383	-2.588085	-1.654690
50	6	0	3.338922	-3.179357	-0.486420
51	6	0	6.289574	-1.641807	-2.167794
52	8	0	0.575016	-1.158839	0.659926
53	8	0	0.298011	0.504206	-1.198039
54	9	0	3.697050	-4.464308	-0.543615
55	9	0	5.791401	-3.867163	-1.786398
56	9	0	7.420772	-1.984327	-2.775926
57	9	0	6.778255	0.625073	-2.577083
58	9	0	4.538395	1.411939	-1.395635
59	9	0	4.733270	0.302953	1.413615
60	9	0	6.020433	2.067664	2.903658
61	9	0	5.084719	4.571831	3.246920
62	9	0	2.792043	5.336396	2.096137
63	9	0	0.780779	4.770199	0.722496
64	15	0	-0.602023	-0.503650	-0.273006
65	8	0	-1.274438	-1.459159	-1.188369
66	8	0	-1.417683	0.299724	0.718145
67	1	0	-2.677604	0.479745	0.521870
68	8	0	-5.903411	1.907522	-0.490368
69	6	0	-7.732862	3.162206	0.359737
70	1	0	-8.634118	3.721667	0.099552
71	1	0	-8.010701	2.352064	1.037943
72	1	0	-7.046632	3.830014	0.884484
73	6	0	1.242266	-3.910709	0.627616
74	6	0	1.757192	-4.782658	1.591946
75	6	0	-0.089265	-4.045255	0.223306
76	6	0	0.951689	-5.767109	2.154037
77	1	0	2.791810	-4.682020	1.904429
78	6	0	-0.890978	-5.033172	0.788550
79	1	0	-0.493973	-3.383656	-0.535819
80	6	0	-0.376631	-5.892533	1.756355
81	1	0	1.362764	-6.434731	2.904283
82	1	0	-1.924031	-5.129378	0.467620
83	1	0	-1.005911	-6.660829	2.194449
84	6	0	-0.816702	3.058146	-0.803242
85	6	0	-1.087018	2.932418	-2.170441
86	6	0	-1.812298	3.540761	0.049916
87	6	0	-2.325124	3.313474	-2.678324
88	1	0	-0.322137	2.536470	-2.830609
89	6	0	-3.052465	3.916261	-0.458329
90	1	0	-1.613295	3.606295	1.114382
91	6	0	-3.305735	3.817522	-1.824370
92	1	0	-2.527920	3.217158	-3.739852
93	1	0	-3.822110	4.279547	0.215144
94	1	0	-4.268095	4.117241	-2.228188

INT1

M062X/6-31g(d,p); E(RM062X) = -3673.583310 hartree
Sum of electronic and thermal Free Energies= -3672.998724 hartree
Thermal correction to Gibbs Free Energy= 0.584586 hartree
cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -3673.599393 hartree
Gibbs Free Energy in toluene = -3673.014807 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.072591	-0.122992	-1.420191
2	6	0	-3.958055	0.872256	-0.174910
3	6	0	-5.423420	-1.958105	-0.360261
4	6	0	-6.706367	-2.555234	-0.133057
5	6	0	-7.897298	-2.191203	-0.982019
6	6	0	-7.762316	-0.806779	-1.604332
7	6	0	-6.401531	-0.684866	-2.288815
8	1	0	-7.976125	-2.938995	-1.785024
9	1	0	-8.810331	-2.276812	-0.386224
10	1	0	-8.560034	-0.631431	-2.329907
11	1	0	-7.832993	-0.027478	-0.838871
12	1	0	-6.313127	-1.460766	-3.069010
13	1	0	-6.270176	0.287114	-2.760098
14	6	0	-4.464472	-3.312829	1.419679
15	6	0	-5.724665	-3.856512	1.654527
16	6	0	-6.831185	-3.486215	0.881977
17	6	0	-4.305598	-2.369107	0.418886
18	1	0	-3.313253	-1.991644	0.193915
19	1	0	-3.607191	-3.622957	2.006452
20	1	0	-5.854854	-4.589696	2.445265
21	1	0	-7.801554	-3.930386	1.081772
22	6	0	-5.278173	-0.943675	-1.339032
23	1	0	-4.076573	0.493917	-2.320158
24	1	0	-3.150589	-0.716096	-1.359007
25	1	0	-3.045776	1.448908	-0.389955
26	8	0	-3.877217	0.243470	1.039983
27	6	0	-5.128441	1.850233	-0.177837
28	6	0	-6.059800	3.704151	0.902931
29	1	0	-7.045827	3.231427	0.931365
30	1	0	-6.002180	4.292599	-0.019594
31	8	0	-6.008160	1.888374	-1.012727
32	6	0	5.066792	2.507585	1.862867
33	6	0	4.290756	1.538143	1.285586
34	6	0	3.057644	1.837155	0.655652
35	6	0	2.629530	3.200294	0.689266
36	6	0	3.454224	4.184720	1.289947
37	6	0	4.649849	3.848318	1.862391
38	6	0	2.229751	0.849696	0.026622
39	6	0	1.365372	3.522007	0.129762
40	6	0	0.518870	2.587000	-0.402480
41	6	0	0.990895	1.244876	-0.428642
42	6	0	2.605734	-0.587363	-0.129267
43	6	0	3.778163	-1.016287	-0.832734
44	6	0	1.776532	-1.556865	0.408434
45	6	0	4.611980	-0.136724	-1.568239
46	6	0	4.149177	-2.394839	-0.822832
47	6	0	2.118906	-2.939875	0.444407
48	6	0	5.738148	-0.570728	-2.214116
49	6	0	5.321026	-2.818850	-1.499002
50	6	0	3.299591	-3.305192	-0.144889
51	6	0	6.104213	-1.926334	-2.176822
52	8	0	0.622575	-1.193463	1.040994
53	8	0	0.148199	0.292309	-0.934194
54	9	0	3.665193	-4.589807	-0.110381
55	9	0	5.690252	-4.098350	-1.502902
56	9	0	7.200708	-2.319590	-2.818342
57	9	0	6.494118	0.279928	-2.900942
58	9	0	4.319501	1.163316	-1.680477

59	9	0	4.745586	0.284029	1.357624
60	9	0	6.217616	2.193251	2.447712
61	9	0	5.421741	4.767616	2.433704
62	9	0	3.086078	5.464186	1.328670
63	9	0	0.986718	4.804229	0.143702
64	15	0	-0.661851	-0.578091	0.212012
65	8	0	-1.417898	-1.625563	-0.532944
66	8	0	-1.347732	0.346994	1.170423
67	1	0	-2.894781	0.233755	1.268221
68	8	0	-5.055169	2.680608	0.854401
69	6	0	-5.785512	4.537555	2.134363
70	1	0	-6.522640	5.339534	2.215371
71	1	0	-5.838233	3.919846	3.032958
72	1	0	-4.789092	4.982654	2.083475
73	6	0	1.273901	-3.958797	1.122486
74	6	0	1.829005	-4.759031	2.125477
75	6	0	-0.059404	-4.150345	0.750089
76	6	0	1.062476	-5.734490	2.753664
77	1	0	2.865524	-4.612084	2.412410
78	6	0	-0.818508	-5.135223	1.375563
79	1	0	-0.498094	-3.531919	-0.026424
80	6	0	-0.264345	-5.926588	2.378410
81	1	0	1.503714	-6.346463	3.533650
82	1	0	-1.847687	-5.290949	1.065056
83	1	0	-0.860630	-6.693741	2.862568
84	6	0	-0.809393	2.963675	-0.948855
85	6	0	-1.229500	2.488944	-2.198348
86	6	0	-1.651604	3.822508	-0.233777
87	6	0	-2.459831	2.875801	-2.721872
88	1	0	-0.586866	1.817620	-2.756961
89	6	0	-2.879246	4.209879	-0.762255
90	1	0	-1.341666	4.182194	0.740919
91	6	0	-3.290025	3.739169	-2.007656
92	1	0	-2.765091	2.510390	-3.697765
93	1	0	-3.517546	4.880656	-0.195159
94	1	0	-4.250496	4.037567	-2.416740

INT2

M062X/6-31g(d,p); E(RM062X) = -3673.586115 hartree
Sum of electronic and thermal Free Energies= -3673.001165 hartree
Thermal correction to Gibbs Free Energy= 0.584950 hartree
cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -3673.601527 hartree
Gibbs Free Energy in toluene = -3673.016577 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.209904	1.506042	-0.581525
2	6	0	4.673037	0.014828	-0.683096
3	6	0	3.801377	2.575764	1.222301
4	6	0	2.685602	3.397105	1.571141
5	6	0	1.961379	4.216582	0.547143
6	6	0	2.817161	4.514019	-0.675923
7	6	0	3.475690	3.234941	-1.182729
8	1	0	1.066059	3.662124	0.230769
9	1	0	1.602686	5.136950	1.014201
10	1	0	2.191919	4.932913	-1.467202
11	1	0	3.589836	5.251843	-0.428312
12	1	0	2.668826	2.566052	-1.555402
13	1	0	4.149600	3.411055	-2.025598
14	6	0	3.990067	1.824944	3.527171
15	6	0	2.882726	2.618373	3.851384
16	6	0	2.243878	3.391718	2.889277
17	6	0	4.445367	1.801366	2.227993
18	1	0	5.280157	1.164581	1.969614
19	1	0	4.478609	1.229311	4.289121
20	1	0	2.519701	2.635397	4.874860
21	1	0	1.383093	3.998022	3.153034
22	6	0	4.170236	2.455758	-0.139091
23	1	0	5.581430	1.770625	-1.572373
24	1	0	6.046953	1.481321	0.121330
25	1	0	3.882394	-0.012508	-1.444717
26	8	0	4.251074	-0.483987	0.527631
27	6	0	5.869372	-0.751718	-1.241694
28	6	0	7.509399	-2.368034	-0.866126
29	1	0	8.303797	-1.680151	-1.170160
30	1	0	7.185825	-2.910906	-1.760840
31	8	0	6.312718	-0.542037	-2.345902
32	6	0	-3.537737	-3.357095	2.462846
33	6	0	-3.193651	-2.307874	1.654916
34	6	0	-2.020479	-2.320062	0.861714
35	6	0	-1.188396	-3.476795	0.954053
36	6	0	-1.569450	-4.552982	1.796378
37	6	0	-2.717877	-4.495777	2.536249
38	6	0	-1.637874	-1.238551	0.006065
39	6	0	0.009632	-3.503381	0.195024
40	6	0	0.437386	-2.457466	-0.582068
41	6	0	-0.420341	-1.321716	-0.640970
42	6	0	-2.422892	0.019653	-0.183405
43	6	0	-3.733883	0.079842	-0.759570
44	6	0	-1.795669	1.211669	0.127795
45	6	0	-4.442030	-1.062525	-1.209012
46	6	0	-4.379637	1.342649	-0.933939
47	6	0	-2.417125	2.480899	-0.010278
48	6	0	-5.691567	-0.976842	-1.760815
49	6	0	-5.675847	1.404745	-1.505053
50	6	0	-3.682786	2.508558	-0.527933
51	6	0	-6.321087	0.270008	-1.910955
52	8	0	-0.504411	1.193802	0.581970
53	8	0	-0.013283	-0.261196	-1.401856
54	9	0	-4.296817	3.687523	-0.659001
55	9	0	-6.298731	2.569886	-1.672949
56	9	0	-7.533742	0.323081	-2.452998
57	9	0	-6.326006	-2.069637	-2.171732
58	9	0	-3.910347	-2.284318	-1.112784
59	9	0	-4.019493	-1.257237	1.641282
60	9	0	-4.645143	-3.313893	3.196524
61	9	0	-3.072983	-5.498485	3.334160
62	9	0	-0.815657	-5.645599	1.906233
63	9	0	0.750869	-4.614380	0.256641
64	15	0	0.651846	1.021500	-0.600655
65	8	0	0.634779	2.177970	-1.533420
66	8	0	1.897320	0.608405	0.118682
67	1	0	3.288264	-0.286759	0.568054
68	6	0	-1.773005	3.742565	0.438110
69	6	0	-1.539551	4.781038	-0.466553
70	6	0	-1.483640	3.935114	1.792037
71	6	0	-1.060539	6.008642	-0.017702
72	1	0	-1.741007	4.618733	-1.520228
73	6	0	-1.019557	5.168715	2.241130
74	1	0	-1.654197	3.122524	2.491913
75	6	0	-0.817949	6.211701	1.339036
76	1	0	-0.893045	6.812657	-0.727175
77	1	0	-0.835874	5.322530	3.300720
78	1	0	-0.469064	7.177354	1.691784
79	6	0	1.705730	-2.532071	-1.351066
80	6	0	1.761533	-2.098643	-2.683129
81	6	0	2.853528	-3.082139	-0.771752
82	6	0	2.936231	-2.223733	-3.416046
83	1	0	0.880405	-1.665444	-3.141783
84	6	0	4.021216	-3.223972	-1.514533
85	1	0	2.832697	-3.402319	0.263483
86	6	0	4.068552	-2.795599	-2.838361
87	1	0	2.964322	-1.883353	-4.445860
88	1	0	4.896779	-3.663191	-1.046956
89	1	0	4.983574	-2.891604	-3.414391
90	8	0	6.398008	-1.606166	-0.368803
91	6	0	7.943504	-3.300251	0.242431
92	1	0	8.788744	-3.907066	-0.089853
93	1	0	8.246775	-2.733090	1.124964
94	1	0	7.126221	-3.966949	0.526829

TS2

M062X/6-31g(d,p); E(RM062X) = -3673.582906 hartree
Sum of electronic and thermal Free Energies= -3673.000483 hartree
Thermal correction to Gibbs Free Energy= 0.582423 hartree
cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -3673.596207 hartree
Gibbs Free Energy in toluene = -3673.013784 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.116224	1.181964	-0.912036
2	6	0	4.619806	-0.297396	-0.742267
3	6	0	4.029658	2.589867	0.923314
4	6	0	3.125179	3.619290	1.297319
5	6	0	2.265057	4.314101	0.277461
6	6	0	2.899858	4.326356	-1.107084
7	6	0	3.411288	2.932745	-1.459724
8	1	0	1.302215	3.786308	0.225335
9	1	0	2.043555	5.328442	0.617233
10	1	0	2.159083	4.636498	-1.847650
11	1	0	3.732447	5.039933	-1.144509
12	1	0	2.379593	2.294693	-1.455226
13	1	0	3.807436	2.822002	-2.469668
14	6	0	4.632731	2.260971	3.252430
15	6	0	3.748621	3.279824	3.611637
16	6	0	3.004827	3.946643	2.643739
17	6	0	4.774921	1.920038	1.920430
18	1	0	5.436278	1.108915	1.646002
19	1	0	5.204447	1.738568	4.010799
20	1	0	3.641364	3.557431	4.655915
21	1	0	2.314510	4.734584	2.929018
22	6	0	4.171449	2.247505	-0.470075
23	1	0	5.349939	1.310920	-1.969886
24	1	0	6.047028	1.272874	-0.342932
25	1	0	3.738643	-0.443493	-1.384039
26	8	0	4.369482	-0.652496	0.569621
27	6	0	5.744578	-1.136026	-1.346465
28	6	0	7.373457	-2.772646	-1.000169
29	1	0	8.133485	-2.129028	-1.452418
30	1	0	6.957970	-3.398790	-1.797300
31	8	0	6.094277	-1.019757	-2.497975
32	6	0	-3.957719	-3.103516	2.460202
33	6	0	-3.490531	-2.106340	1.647508
34	6	0	-2.281420	-2.229878	0.921291
35	6	0	-1.546915	-3.443587	1.089067
36	6	0	-2.054686	-4.463394	1.933964
37	6	0	-3.234050	-4.298659	2.606461
38	6	0	-1.767594	-1.202103	0.065786
39	6	0	-0.314599	-3.584423	0.399911
40	6	0	0.227051	-2.599615	-0.383692
41	6	0	-0.531600	-1.404122	-0.511629
42	6	0	-2.431264	0.115083	-0.181089
43	6	0	-3.706103	0.273744	-0.816740
44	6	0	-1.729531	1.257078	0.152092
45	6	0	-4.474195	-0.813063	-1.301532
46	6	0	-4.245902	1.581580	-1.012350
47	6	0	-2.249082	2.573508	0.010886
48	6	0	-5.687183	-0.634478	-1.910103
49	6	0	-5.505811	1.740206	-1.643368
50	6	0	-3.489115	2.691429	-0.558056
51	6	0	-6.213377	0.656289	-2.084232
52	8	0	-0.461431	1.140379	0.664157
53	8	0	0.014881	-0.391452	-1.259665
54	9	0	-4.025540	3.907790	-0.689551

55	9	0	-6.032514	2.947660	-1.836882
56	9	0	-7.391264	0.800192	-2.682250
57	9	0	-6.381004	-1.676441	-2.353988
58	9	0	-4.038116	-2.070048	-1.183868
59	9	0	-4.229455	-0.995934	1.565787
60	9	0	-5.095521	-2.954482	3.129683
61	9	0	-3.708429	-5.248659	3.405792
62	9	0	-1.394403	-5.606030	2.110167
63	9	0	0.341988	-4.739664	0.533982
64	15	0	0.744378	0.807599	-0.408005
65	8	0	0.914440	1.942332	-1.383692
66	8	0	1.905494	0.322983	0.384037
67	1	0	3.425869	-0.441838	0.724303
68	6	0	-1.539041	3.766835	0.535628
69	6	0	-1.397449	4.919335	-0.243614
70	6	0	-1.077953	3.776347	1.856890
71	6	0	-0.834409	6.070598	0.298477
72	1	0	-1.742959	4.912065	-1.271815
73	6	0	-0.525863	4.932198	2.399440
74	1	0	-1.172842	2.879858	2.460660
75	6	0	-0.411362	6.085233	1.625629
76	1	0	-0.738738	6.961413	-0.313948
77	1	0	-0.202092	4.934969	3.435795
78	1	0	0.008319	6.990552	2.053794
79	6	0	1.512558	-2.795369	-1.098561
80	6	0	1.616591	-2.481924	-2.460115
81	6	0	2.616653	-3.342227	-0.439609
82	6	0	2.796040	-2.734278	-3.150487
83	1	0	0.766700	-2.046747	-2.974347
84	6	0	3.792650	-3.603512	-1.135978
85	1	0	2.552220	-3.566998	0.619236
86	6	0	3.883216	-3.308233	-2.493657
87	1	0	2.865170	-2.491251	-4.205546
88	1	0	4.640840	-4.028244	-0.608925
89	1	0	4.800792	-3.503930	-3.039519
90	8	0	6.323104	-1.952385	-0.467938
91	6	0	7.919958	-3.596642	0.144198
92	1	0	8.723904	-4.244469	-0.212447
93	1	0	8.315799	-2.948326	0.928689
94	1	0	7.136001	-4.221197	0.578492

INT2'

M062X/6-31g(d,p); E(RM062X) = -3673.582510 hartree
Sum of electronic and thermal Free Energies= -3672.998033 hartree
Thermal correction to Gibbs Free Energy= 0.584477 hartree
cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -3673.598637 hartree
Gibbs Free Energy in toluene = -3673.014160 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.674064	-0.194461	1.026356
2	6	0	-3.778874	-1.248685	-0.247303
3	6	0	-5.996686	0.806016	1.190552
4	6	0	-6.978929	1.541380	0.474678
5	6	0	-6.579576	2.361791	-0.722617
6	6	0	-5.197949	2.972334	-0.512338
7	6	0	-4.202174	1.859284	-0.234396
8	1	0	-6.542425	1.696654	-1.598271
9	1	0	-7.340023	3.121621	-0.921558
10	1	0	-4.884028	3.535231	-1.393746
11	1	0	-5.223190	3.671627	0.331153
12	1	0	-4.039576	1.200823	-1.132772
13	1	0	-3.170043	2.174286	-0.026771
14	6	0	-7.709989	-0.061641	2.676260
15	6	0	-8.671605	0.657446	1.964108
16	6	0	-8.308819	1.440827	0.870793
17	6	0	-6.384311	0.000591	2.283237
18	1	0	-5.639039	-0.560785	2.833590
19	1	0	-7.997489	-0.669449	3.526245
20	1	0	-9.713411	0.608503	2.265362
21	1	0	-9.067360	1.990891	0.321780
22	6	0	-4.625234	0.855472	0.738404
23	1	0	-2.644757	0.170133	1.005599
24	1	0	-3.889297	-0.813844	1.895151
25	1	0	-3.041205	-2.002613	0.055105
26	8	0	-3.528209	-0.693509	-1.455263
27	6	0	-5.177887	-1.830702	-0.131327
28	6	0	-7.388321	-1.737172	-0.880659
29	1	0	-7.723166	-1.448043	0.121712
30	1	0	-7.437188	-2.827506	-0.946377
31	8	0	-5.509062	-2.579232	0.759061
32	6	0	5.722657	-2.326319	-1.515035
33	6	0	4.829793	-1.397211	-1.054683
34	6	0	3.558028	-1.757765	-0.547163
35	6	0	3.231508	-3.148841	-0.553915
36	6	0	4.176871	-4.092787	-1.030376
37	6	0	5.395515	-3.692430	-1.503804
38	6	0	2.604661	-0.802593	-0.065772
39	6	0	1.949840	-3.540385	-0.088138
40	6	0	0.998602	-2.648979	0.330082
41	6	0	1.362003	-1.273086	0.314358
42	6	0	2.807941	0.681340	-0.031065
43	6	0	3.797193	1.357368	0.755216
44	6	0	1.898295	1.458005	-0.723662
45	6	0	4.733386	0.683994	1.577809
46	6	0	3.855202	2.785697	0.751814
47	6	0	1.908811	2.880383	-0.737956
48	6	0	5.670391	1.352224	2.317851
49	6	0	4.840847	3.454593	1.522113
50	6	0	2.895968	3.494837	-0.015482
51	6	0	5.729288	2.755425	2.290789
52	8	0	0.907479	0.836855	-1.435905
53	8	0	0.398383	-0.373631	0.681771
54	9	0	2.956069	4.829979	-0.010298
55	9	0	4.925188	4.784007	1.530227
56	9	0	6.649186	3.379414	3.020586
57	9	0	6.534065	0.686807	3.078078
58	9	0	4.739028	-0.649501	1.660960
59	9	0	5.211633	-0.117942	-1.096414
60	9	0	6.908485	-1.953061	-1.984468
61	9	0	6.280214	-4.574219	-1.959282
62	9	0	3.903508	-5.396412	-1.044262
63	9	0	1.665205	-4.846396	-0.071373
64	15	0	-0.406427	0.343098	-0.577108
65	8	0	-1.179620	1.466157	0.009541
66	8	0	-1.050961	-0.720268	-1.422810
67	1	0	-2.498837	-0.682350	-1.560674
68	6	0	0.883740	3.659711	-1.476808
69	6	0	0.203581	4.700836	-0.839070
70	6	0	0.578523	3.360010	-2.807782
71	6	0	-0.764757	5.429570	-1.520116
72	1	0	0.430761	4.929471	0.196659
73	6	0	-0.388243	4.092425	-3.487708
74	1	0	1.096678	2.547074	-3.304500
75	6	0	-1.062887	5.127985	-2.846318
76	1	0	-1.286581	6.234910	-1.012960
77	1	0	-0.613995	3.852389	-4.521653
78	1	0	-1.816314	5.699507	-3.379474
79	6	0	-0.337569	-3.099947	0.795962
80	6	0	-0.874991	-2.611586	1.992891
81	6	0	-1.064260	-4.045858	0.064543
82	6	0	-2.103729	-3.075512	2.454592
83	1	0	-0.321725	-1.872461	2.562155
84	6	0	-2.294646	-4.503887	0.526742
85	1	0	-0.661579	-4.417303	-0.871312
86	6	0	-2.818466	-4.024520	1.725705
87	1	0	-2.499044	-2.700118	3.394035
88	1	0	-2.848593	-5.233933	-0.054379
89	1	0	-3.785338	-4.368980	2.074781
90	8	0	-6.017798	-1.328964	-1.037943
91	6	0	-8.192443	-1.062566	-1.968530
92	1	0	-9.234633	-1.385543	-1.912138
93	1	0	-8.164699	0.024175	-1.854226
94	1	0	-7.799824	-1.319843	-2.954268

TS2'

M062X/6-31g(d,p); E(RM062X) = -3673.580250 hartree
Sum of electronic and thermal Free Energies= -3672.997997 hartree
Thermal correction to Gibbs Free Energy= 0.582253 hartree
cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -3673.594394 hartree
Gibbs Free Energy in toluene = -3673.012141 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.729232	-0.139165	1.187956
2	6	0	-3.775136	-1.162620	-0.067820
3	6	0	-6.076020	0.869661	1.133126
4	6	0	-6.998116	1.524075	0.281587
5	6	0	-6.500141	2.215038	-0.961307
6	6	0	-5.145826	2.872820	-0.712017
7	6	0	-4.182270	1.837336	-0.172688
8	1	0	-6.379217	1.453380	-1.746576
9	1	0	-7.243800	2.934608	-1.314073
10	1	0	-4.750373	3.303434	-1.634470
11	1	0	-5.248179	3.691258	0.010970
12	1	0	-3.969118	0.907841	-0.943034
13	1	0	-3.125488	2.111607	-0.057671
14	6	0	-7.895649	0.115690	2.546496
15	6	0	-8.802481	0.759623	1.705769
16	6	0	-8.355322	1.447763	0.579714
17	6	0	-6.540563	0.158416	2.252875
18	1	0	-5.837300	-0.344937	2.906050
19	1	0	-8.244398	-0.421167	3.421281
20	1	0	-9.864355	0.725287	1.927920
21	1	0	-9.069106	1.938715	-0.075656
22	6	0	-4.655960	0.928998	0.805009
23	1	0	-2.700257	0.221719	1.252702
24	1	0	-4.013179	-0.727406	2.058757
25	1	0	-3.008201	-1.905609	0.179011
26	8	0	-3.523235	-0.539997	-1.265369
27	6	0	-5.150936	-1.810004	-0.018242
28	6	0	-7.327524	-1.809861	-0.865581
29	1	0	-7.716570	-1.477768	0.103608
30	1	0	-7.341862	-2.903005	-0.876065
31	8	0	-5.490589	-2.561151	0.865660
32	6	0	5.657022	-2.366719	-1.598227
33	6	0	4.787647	-1.428974	-1.111020
34	6	0	3.524077	-1.776297	-0.574888
35	6	0	3.178869	-3.162841	-0.582797
36	6	0	4.099860	-4.115987	-1.087878
37	6	0	5.312207	-3.728468	-1.587602
38	6	0	2.595346	-0.811795	-0.063916
39	6	0	1.903475	-3.540972	-0.089375
40	6	0	0.974157	-2.640069	0.357129
41	6	0	1.356500	-1.269788	0.341692
42	6	0	2.820829	0.668877	-0.023574
43	6	0	3.839884	1.325537	0.741291
44	6	0	1.907617	1.464451	-0.688351
45	6	0	4.784954	0.632947	1.536940
46	6	0	3.920283	2.752734	0.743167
47	6	0	1.940939	2.886031	-0.699088
48	6	0	5.750532	1.282347	2.256859
49	6	0	4.934872	3.401937	1.492403
50	6	0	2.954848	3.481298	0.002018

51	6	0	5.830831	2.684599	2.235376
52	8	0	0.884793	0.863053	-1.375610
53	8	0	0.412179	-0.360665	0.741037
54	9	0	3.036502	4.814744	0.010603
55	9	0	5.040012	4.729573	1.505030
56	9	0	6.778040	3.289991	2.945017
57	9	0	6.621697	0.599376	2.992071
58	9	0	4.770825	-0.700843	1.612835
59	9	0	5.184740	-0.154510	-1.154999
60	9	0	6.835737	-2.005760	-2.093722
61	9	0	6.173951	-4.618604	-2.069254
62	9	0	3.808677	-5.415494	-1.103679
63	9	0	1.601579	-4.842677	-0.074868
64	15	0	-0.406574	0.389871	-0.480169
65	8	0	-1.158629	1.510886	0.132690
66	8	0	-1.097247	-0.648987	-1.331934
67	1	0	-2.458649	-0.562561	-1.394442
68	6	0	0.912175	3.683185	-1.413381
69	6	0	0.255995	4.728025	-0.757070
70	6	0	0.579432	3.394602	-2.740274
71	6	0	-0.716828	5.471018	-1.416065
72	1	0	0.504174	4.947721	0.275777
73	6	0	-0.391569	4.141283	-3.398097
74	1	0	1.080022	2.579404	-3.251314
75	6	0	-1.042915	5.180201	-2.738081
76	1	0	-1.220866	6.278478	-0.894697
77	1	0	-0.638504	3.910299	-4.429265
78	1	0	-1.799953	5.762940	-3.253619
79	6	0	-0.357638	-3.075580	0.849527
80	6	0	-0.861681	-2.589645	2.062016
81	6	0	-1.114559	-4.002929	0.124893
82	6	0	-2.088023	-3.037524	2.545179
83	1	0	-0.284872	-1.864858	2.626318
84	6	0	-2.342410	-4.444904	0.608855
85	1	0	-0.737201	-4.372858	-0.822158
86	6	0	-2.832629	-3.968430	1.823129
87	1	0	-2.458569	-2.662918	3.494699
88	1	0	-2.920868	-5.160226	0.033351
89	1	0	-3.797750	-4.299923	2.188681
90	8	0	-5.963081	-1.366618	-0.979078
91	6	0	-8.097012	-1.216200	-2.023424
92	1	0	-9.131990	-1.565145	-1.996267
93	1	0	-8.102703	-0.124686	-1.965779
94	1	0	-7.653086	-1.514332	-2.975453

product

M062X/6-31g(d,p); E(RM062X) = -3673.612402 hartree
Sum of electronic and thermal Free Energies=-3673.028458 hartree
Thermal correction to Gibbs Free Energy= 0.583944 hartree
cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -3673.623434 hartree
Gibbs Free Energy in toluene = -3673.039490 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.199741	1.036490	-1.036344
2	6	0	4.667289	-0.407751	-0.873129
3	6	0	4.258278	2.424996	0.956463
4	6	0	3.386777	3.429792	1.421173
5	6	0	2.462932	4.134444	0.458902
6	6	0	3.066922	4.280418	-0.935597
7	6	0	3.777190	3.026062	-1.372860
8	1	0	1.520236	3.571352	0.393277
9	1	0	2.191115	5.114153	0.856766
10	1	0	2.284292	4.551645	-1.651851
11	1	0	3.796736	5.102917	-0.948451
12	1	0	2.052209	1.937721	-1.250487
13	1	0	3.941520	2.880162	-2.439349
14	6	0	5.010123	2.057147	3.234376
15	6	0	4.151389	3.051712	3.688617
16	6	0	3.343625	3.728538	2.779246
17	6	0	5.062881	1.746582	1.879433
18	1	0	5.712123	0.947384	1.544553
19	1	0	5.640767	1.517304	3.932930
20	1	0	4.108546	3.299570	4.744491
21	1	0	2.664891	4.505855	3.121759
22	6	0	4.342605	2.160455	-0.503701
23	1	0	5.362320	1.193786	-2.105994
24	1	0	6.183769	1.079502	-0.552719
25	1	0	3.713495	-0.506126	-1.415551
26	8	0	4.548953	-0.821197	0.453370
27	6	0	5.664394	-1.284519	-1.623776
28	6	0	7.411742	-2.831587	-1.481418
29	1	0	8.100018	-2.138708	-1.975239
30	1	0	6.958692	-3.448590	-2.264026
31	8	0	5.827595	-1.211590	-2.819713
32	6	0	-4.372506	-2.825091	2.383963
33	6	0	-3.779620	-1.887453	1.581919
34	6	0	-2.542739	-2.123075	0.935989
35	6	0	-1.914439	-3.383952	1.176775
36	6	0	-2.551594	-4.339662	2.008278
37	6	0	-3.754815	-4.068000	2.600144
38	6	0	-1.898525	-1.158201	0.092877
39	6	0	-0.652872	-3.637139	0.575710
40	6	0	0.002275	-2.720467	-0.201928
41	6	0	-0.657489	-1.483063	-0.403404
42	6	0	-2.432824	0.203528	-0.216424
43	6	0	-3.656765	0.445068	-0.923995
44	6	0	-1.671779	1.299400	0.135846
45	6	0	-4.467548	-0.591282	-1.446512
46	6	0	-4.092354	1.784836	-1.153343
47	6	0	-2.090974	2.648233	-0.021806
48	6	0	-5.628759	-0.334500	-2.124742
49	6	0	-5.299758	2.025306	-1.857134
50	6	0	-3.291938	2.843311	-0.653399
51	6	0	-6.053428	0.988180	-2.333994
52	8	0	-0.427140	1.108004	0.713030
53	8	0	0.030515	-0.520800	-1.128067
54	9	0	-3.746188	4.088402	-0.802186
55	9	0	-5.727213	3.263631	-2.088274
56	9	0	-7.179459	1.207591	-3.001385
57	9	0	-6.364590	-1.328879	-2.604560
58	9	0	-4.124919	-1.873267	-1.298306
59	9	0	-4.421023	-0.725185	1.431190
60	9	0	-5.533219	-2.572142	2.975546
61	9	0	-4.351161	-4.958249	3.383626
62	9	0	-1.994880	-5.523800	2.245966
63	9	0	-0.080298	-4.820297	0.791275
64	15	0	0.789150	0.562372	-0.203605
65	8	0	1.102520	1.671916	-1.273434
66	8	0	1.903933	0.085143	0.624032
67	1	0	3.663285	-0.556880	0.751284
68	6	0	-1.343685	3.793223	0.557322
69	6	0	-1.116737	4.952953	-0.190737
70	6	0	-0.941337	3.754811	1.897392
71	6	0	-0.528130	6.066080	0.400889
72	1	0	-1.419787	4.985475	-1.231901
73	6	0	-0.357122	4.870778	2.486698
74	1	0	-1.104740	2.854522	2.480572
75	6	0	-0.161189	6.032897	1.744043
76	1	0	-0.365570	6.963615	-0.186852
77	1	0	-0.066746	4.834200	3.531708
78	1	0	0.285382	6.906810	2.208045
79	6	0	1.322171	-3.005969	-0.815838
80	6	0	1.486116	-2.887167	-2.200480
81	6	0	2.401950	-3.394597	-0.022115
82	6	0	2.710755	-3.184865	-2.784714
83	1	0	0.648740	-2.567364	-2.812982
84	6	0	3.630714	-3.681514	-0.608133
85	1	0	2.281478	-3.454165	1.054712
86	6	0	3.779764	-3.593081	-1.989048
87	1	0	2.836074	-3.095257	-3.858468
88	1	0	4.477637	-3.943889	0.016094
89	1	0	4.735095	-3.819455	-2.451567
90	8	0	6.386144	-2.074945	-0.824596
91	6	0	8.098134	-3.667122	-0.423821
92	1	0	8.900080	-4.256500	-0.874334
93	1	0	8.526527	-3.027992	0.350928
94	1	0	7.387903	-4.350215	0.047743

TS-s (a): *In the main text this is shown in **TS-s**

M062X/6-31g(d,p); E(RM062X) = -4209.724159 hartree
Sum of electronic and thermal Free Energies= -4208.989191 hartree
Thermal correction to Gibbs Free Energy= 0.734968 hartree
cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -4209.737746 hartree
Gibbs Free Energy in toluene = -4209.002778 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.783626	0.733849	-1.407116
2	6	0	3.487880	-1.137182	-0.725451
3	6	0	3.950379	1.703026	0.873898
4	6	0	4.766635	2.200013	1.922275
5	6	0	6.254802	2.344710	1.728187
6	6	0	6.784143	1.256536	0.799987
7	6	0	6.037169	1.326141	-0.528973
8	1	0	6.454281	3.327476	1.276693
9	1	0	6.759040	2.322318	2.698730
10	1	0	7.858467	1.374081	0.632729
11	1	0	6.616320	0.275545	1.257307
12	1	0	6.254966	2.292115	-1.012573
13	1	0	6.361399	0.551069	-1.233450
14	6	0	1.977897	1.973346	2.273934
15	6	0	2.786230	2.446545	3.302453
16	6	0	4.166082	2.563933	3.120817
17	6	0	2.558295	1.618210	1.065853
18	1	0	1.922446	1.317289	0.243473
19	1	0	0.901729	1.898575	2.389135
20	1	0	2.345226	2.729983	4.253404
21	1	0	4.788638	2.932373	3.932306
22	6	0	4.541408	1.266448	-0.375244
23	1	0	4.300943	0.495388	-2.333446
24	1	0	2.720734	0.946338	-1.497215
25	1	0	2.869833	-1.339956	-1.608077
26	8	0	2.960755	-1.170706	0.437655
27	6	0	4.917600	-1.622934	-0.864146
28	6	0	6.842640	-2.325972	0.262940
29	1	0	7.483544	-1.572213	-0.208907
30	1	0	6.841356	-3.221643	-0.363829
31	8	0	5.456782	-1.774627	-1.937115
32	6	0	-5.930953	-1.739593	2.548015
33	6	0	-5.147650	-1.038225	1.671018
34	6	0	-4.079939	-1.638261	0.960894
35	6	0	-3.822055	-3.018709	1.237506
36	6	0	-4.653850	-3.724515	2.142828
37	6	0	-5.687539	-3.101335	2.786076
38	6	0	-3.249920	-0.926456	0.028418
39	6	0	-2.701688	-3.637117	0.620176
40	6	0	-1.864828	-2.972159	-0.229077
41	6	0	-2.183964	-1.614949	-0.510881
42	6	0	-3.378996	0.525979	-0.318410
43	6	0	-4.544481	1.131619	-0.897490
44	6	0	-2.277857	1.341844	-0.120512
45	6	0	-5.688453	0.391461	-1.284843
46	6	0	-4.588045	2.542621	-1.124293

47	6	0	-2.280268	2.745634	-0.348504
48	6	0	-6.795422	0.985538	-1.827481
49	6	0	-5.748374	3.135153	-1.682599
50	6	0	-3.435050	3.308239	-0.808090
51	6	0	-6.831416	2.375468	-2.028091
52	8	0	-1.114246	0.821763	0.382514
53	8	0	-1.318103	-0.949705	-1.345984
54	9	0	-3.470972	4.626985	-1.002945
55	9	0	-5.812186	4.447655	-1.897580
56	9	0	-7.918506	2.925803	-2.558960
57	9	0	-7.849341	0.257858	-2.180677
58	9	0	-5.728815	-0.935235	-1.131847
59	9	0	-5.435319	0.257250	1.514750
60	9	0	-6.925658	-1.140537	3.193837
61	9	0	-6.463858	-3.760041	3.640297
62	9	0	-4.448922	-5.014376	2.402421
63	9	0	-2.433223	-4.909385	0.922213
64	15	0	-0.150714	-0.098688	-0.581776
65	8	0	0.624302	0.654514	-1.595888
66	8	0	0.575414	-0.971523	0.422014
67	1	0	1.836618	-1.088367	0.422297
68	8	0	5.495974	-1.813055	0.313376
69	6	0	7.258540	-2.622405	1.685968
70	1	0	8.270558	-3.033416	1.696712
71	1	0	7.244398	-1.718836	2.300166
72	1	0	6.581061	-3.351695	2.134899
73	6	0	-1.045257	3.536389	-0.092166
74	6	0	-0.008562	3.483270	-0.992553
75	6	0	-0.881974	4.252562	1.121655
76	6	0	1.244445	4.067734	-0.691261
77	1	0	-0.114842	2.921420	-1.914392
78	6	0	0.319928	4.838297	1.430171
79	1	0	-1.714355	4.308233	1.816782
80	6	0	1.429653	4.727083	0.552139
81	6	0	2.355629	3.932773	-1.568895
82	1	0	0.447929	5.361318	2.374001
83	6	0	2.725337	5.183385	0.919686
84	6	0	3.593363	4.377745	-1.202139
85	1	0	2.206979	3.438648	-2.525070
86	6	0	3.787189	4.980785	0.071356
87	1	0	2.854236	5.643098	1.892924
88	1	0	4.457532	4.268574	-1.849878
89	6	0	-0.596584	-3.542831	-0.747301
90	6	0	0.374230	-3.952800	0.136727
91	6	0	-0.297339	-3.488732	-2.133613
92	6	0	1.684871	-4.247775	-0.305855
93	1	0	0.165911	-3.961636	1.202874
94	6	0	0.956446	-3.796445	-2.592172
95	1	0	-1.067312	-3.165216	-2.826143
96	6	0	1.992455	-4.155776	-1.690278
97	6	0	2.733149	-4.560499	0.604468
98	1	0	1.180095	-3.739081	-3.653550
99	6	0	3.325247	-4.374524	-2.134295
100	6	0	4.009503	-4.762501	0.164052
101	1	0	2.505580	-4.616744	1.664755
102	6	0	4.311938	-4.669727	-1.222917
103	1	0	3.541748	-4.280413	-3.192067
104	1	0	4.821521	-4.993148	0.845767
105	8	0	5.081488	5.299632	0.351546
106	6	0	5.333838	5.896448	1.605847
107	1	0	6.407659	6.078084	1.648756
108	1	0	4.798509	6.847662	1.706871
109	1	0	5.038119	5.226949	2.424158
110	8	0	5.619421	-4.871666	-1.530715
111	6	0	5.987680	-4.754996	-2.893102
112	1	0	5.778225	-3.747128	-3.264537
113	1	0	7.059587	-4.946666	-2.932479
114	1	0	5.462349	-5.499076	-3.502865

TS-r (e): *In the main text this is shown in **TS-r**
M062X/6-31g(d,p); E(RM062X) = -4209.720448 hartree
Sum of electronic and thermal Free Energies= -4208.988174 hartree
Thermal correction to Gibbs Free Energy= 0.732274 hartree
cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -4209.733231 hartree
Gibbs Free Energy in toluene = -4209.000957 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.404882	-1.234672	0.267461
2	6	0	3.172671	-0.248863	-1.428398
3	6	0	5.679340	-0.435171	0.912936
4	6	0	6.459393	0.703725	1.220641
5	6	0	5.783934	2.002393	1.583144
6	1	0	6.475648	2.642272	2.138976
7	1	0	5.516464	2.544375	0.664388
8	6	0	7.699252	-1.729277	0.540740
9	6	0	8.466895	-0.601787	0.832060
10	6	0	7.848072	0.600196	1.167638
11	6	0	6.314947	-1.645655	0.577575
12	1	0	5.729155	-2.534893	0.366465
13	1	0	8.174183	-2.672536	0.293261
14	1	0	9.550590	-0.661505	0.809595
15	1	0	8.450767	1.473412	1.402188
16	6	0	4.219467	-0.327468	0.926551
17	1	0	2.345326	-1.249571	0.518717
18	1	0	3.823611	-2.149620	-0.138026
19	1	0	2.514178	-1.057514	-1.773421
20	8	0	2.703335	0.936438	-1.296447
21	6	0	4.590745	-0.372314	-1.947221
22	6	0	6.641603	0.712367	-2.239369
23	1	0	6.689302	0.353418	-3.271265
24	1	0	7.153598	-0.014763	-1.601104
25	8	0	5.047791	-1.409032	-2.371262
26	6	0	-6.885145	1.050648	-2.055184
27	6	0	-5.817572	0.457945	-1.437138
28	6	0	-4.743271	1.205818	-0.897117
29	6	0	-4.811248	2.626582	-1.047567
30	6	0	-5.930543	3.216622	-1.686102
31	6	0	-6.947617	2.448068	-2.181310
32	6	0	-3.619187	0.597364	-0.242395
33	6	0	-3.723824	3.408280	-0.571900
34	6	0	-2.603753	2.852005	-0.029550
35	6	0	-2.575124	1.435582	0.107616
36	6	0	-3.468326	-0.870040	0.034889
37	6	0	-4.355056	-1.663902	0.840131
38	6	0	-2.326655	-1.489750	-0.428837
39	6	0	-5.514987	-1.146971	1.465553
40	6	0	-4.063990	-3.046506	1.070925
41	6	0	-1.969524	-2.844191	-0.179976
42	6	0	-6.351812	-1.926737	2.218004
43	6	0	-4.952349	-3.834323	1.846027
44	6	0	-2.859467	-3.585749	0.544587
45	6	0	-6.073452	-3.289269	2.408653
46	8	0	-1.418372	-0.748102	-1.141959
47	8	0	-1.441286	0.926840	0.684558
48	9	0	-2.568302	-4.861292	0.810850
49	9	0	-4.718854	-5.128131	2.057527
50	9	0	-6.903959	-4.025205	3.139845
51	9	0	-7.433287	-1.404725	2.785984
52	9	0	-5.843050	0.142414	1.346312
53	9	0	-5.827313	-0.875970	-1.359402
54	9	0	-7.873819	0.315126	-2.551748
55	9	0	-7.994289	2.998284	-2.788116
56	9	0	-6.018385	4.536984	-1.833656
57	9	0	-3.788530	4.734299	-0.693223
58	15	0	-0.363824	0.086830	-0.211063
59	8	0	0.452827	-0.725636	0.712642
60	8	0	0.322139	0.976161	-1.243586
61	1	0	1.519268	0.967399	-1.246187
62	8	0	5.258009	0.769810	-1.840629
63	6	0	7.209853	2.104915	-2.090443
64	1	0	8.258130	2.110158	-2.398320
65	1	0	6.660597	2.815445	-2.712125
66	1	0	7.155705	2.433060	-1.049586
67	6	0	4.503069	1.732051	2.368841
68	1	0	4.743195	1.213813	3.304639
69	1	0	4.003928	2.670576	2.622930
70	6	0	3.575593	0.879204	1.512091
71	1	0	2.645525	0.592248	2.012529
72	1	0	3.247191	1.468765	0.625582
73	6	0	-0.634929	-3.348432	-0.594706
74	6	0	0.221426	-3.873316	0.345949
75	6	0	-0.170640	-3.166951	-1.924886
76	6	0	1.564141	-4.182013	0.023242
77	1	0	-0.110584	-3.993384	1.373168
78	6	0	1.121059	-3.474687	-2.267878
79	1	0	-0.847337	-2.757999	-2.667420
80	6	0	2.484436	-4.643840	1.005979
81	6	0	2.036562	-3.969252	-1.300299
82	1	0	1.464962	-3.328030	-3.288294
83	6	0	3.795309	-4.864440	0.693164
84	1	0	2.129785	-4.805638	2.019730
85	6	0	3.403637	-4.209880	-1.614801
86	6	0	4.265970	-4.636362	-0.630592
87	1	0	4.511785	-5.205677	1.432695
88	1	0	3.751496	-3.997471	-2.619018
89	6	0	-1.408905	3.627244	0.408375
90	6	0	-0.304050	3.661530	-0.406695
91	6	0	-1.321616	4.152442	1.722802
92	6	0	0.946117	4.109230	0.080464
93	1	0	-0.355931	3.247933	-1.407421
94	6	0	-0.132286	4.640943	2.202059
95	1	0	-2.202413	4.136844	2.357346
96	6	0	2.128721	3.992942	-0.701305
97	6	0	1.046527	4.592061	1.411709
98	1	0	-0.070060	5.028828	3.214873
99	6	0	3.347448	4.321270	-0.180119
100	1	0	2.054531	3.596492	-1.709536
101	6	0	2.320368	4.957496	1.930828
102	6	0	3.444690	4.808909	1.152431
103	1	0	4.261687	4.215416	-0.755401
104	1	0	2.378915	5.320292	2.950862
105	8	0	5.599190	-4.842498	-0.792275
106	8	0	4.717440	5.067758	1.563132
107	6	0	4.883021	5.561369	2.874157
108	1	0	5.952163	5.723462	3.008037
109	1	0	4.349175	6.508813	3.011914
110	1	0	4.526988	4.839159	3.620184
111	6	0	6.140150	-4.581470	-2.076191
112	1	0	7.203608	-4.808929	-2.005698
113	1	0	5.682196	-5.230341	-2.831754
114	1	0	5.995753	-3.532214	-2.353787

TS-s ((*R*)-1)
M062X/6-31g(d,p); E(RM062X) = -3217.745324 hartree
Sum of electronic and thermal Free Energies= -3216.917116 hartree
Thermal correction to Gibbs Free Energy= 0.828208 hartree
cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -3217.760611 hartree
Gibbs Free Energy in toluene = -3216.9324 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.843366	0.527144	-1.435933
2	6	0	2.597868	-1.191144	-0.535623

3	6	0	2.966653	1.830188	0.675633
4	6	0	3.759605	2.493463	1.648541
5	6	0	5.246921	2.640655	1.449862
6	6	0	5.809343	1.448251	0.683220
7	6	0	5.072715	1.318186	-0.647087
8	1	0	5.432419	3.556175	0.869285
9	1	0	5.740167	2.762424	2.418720
10	1	0	6.882277	1.567215	0.508078
11	1	0	5.659090	0.534131	1.267998
12	1	0	5.266166	2.217230	-1.254926
13	1	0	5.423493	0.465253	-1.239722
14	6	0	0.969267	2.259418	1.998944
15	6	0	1.754875	2.896494	2.953833
16	6	0	3.135423	3.016132	2.773114
17	6	0	1.573262	1.742184	0.863156
18	1	0	0.954812	1.312944	0.085850
19	1	0	-0.107121	2.180433	2.110672
20	1	0	1.294912	3.309656	3.846621
21	1	0	3.738259	3.513972	3.528470
22	6	0	3.579387	1.237325	-0.491397
23	1	0	3.377269	0.193341	-2.322902
24	1	0	1.779204	0.712646	-1.569386
25	1	0	1.991944	-1.556721	-1.374290
26	8	0	2.060329	-1.086371	0.624743
27	6	0	4.034198	-1.676872	-0.593542
28	6	0	5.955943	-2.194933	0.633723
29	1	0	6.591395	-1.498113	0.074592
30	1	0	5.977179	-3.163891	0.127790
31	8	0	4.593395	-1.959139	-1.629826
32	6	0	-6.800012	-1.616249	2.782542
33	6	0	-6.024399	-0.992030	1.838446
34	6	0	-4.969477	-1.683437	1.183637
35	6	0	-4.701998	-3.027208	1.575839
36	6	0	-5.532536	-3.648632	2.544940
37	6	0	-6.564746	-2.965543	3.132058
38	6	0	-4.134445	-1.069461	0.188321
39	6	0	-3.580192	-3.713532	1.039767
40	6	0	-2.743445	-3.114087	0.135276
41	6	0	-3.065780	-1.793995	-0.290792
42	6	0	-4.308415	0.340538	-0.264587
43	6	0	-5.546712	0.833935	-0.795596
44	6	0	-3.238439	1.214061	-0.194959
45	6	0	-6.652574	-0.017640	-1.066219
46	6	0	-5.676453	2.220131	-1.093569
47	6	0	-3.344006	2.597492	-0.523853
48	6	0	-7.827045	0.486967	-1.563151
49	6	0	-6.909906	2.713651	-1.594106
50	6	0	-4.560800	3.081337	-0.926430
51	6	0	-7.966135	1.871034	-1.819535
52	8	0	-2.025681	0.790256	0.296278
53	8	0	-2.213149	-1.199514	-1.200020
54	15	0	-1.070185	-0.240634	-0.547716
55	8	0	-0.294281	0.392861	-1.644224
56	8	0	-0.326015	-0.975230	0.552381
57	1	0	0.930193	-1.045955	0.584789
58	8	0	4.602371	-1.702987	0.605337
59	6	0	6.359847	-2.297234	2.087260
60	1	0	7.378450	-2.684751	2.162220
61	1	0	6.322169	-1.321794	2.578365
62	1	0	5.688398	-2.974049	2.619761
63	6	0	-2.119097	3.438342	-0.422629
64	6	0	-1.095000	3.244555	-1.320623
65	6	0	-1.942536	4.362848	0.638758
66	6	0	0.152474	3.888491	-1.154828
67	1	0	-1.206035	2.526984	-2.126924
68	6	0	-0.742865	5.008466	0.815960
69	1	0	-2.761180	4.526608	1.333778
70	6	0	0.352929	4.755953	-0.049172
71	6	0	1.248268	3.611312	-2.019240
72	1	0	-0.605202	5.688845	1.652237
73	6	0	1.652593	5.274710	0.209142
74	6	0	2.487911	4.120969	-1.760028
75	1	0	1.085233	2.952906	-2.868089
76	6	0	2.699989	4.933280	-0.611508
77	1	0	1.796083	5.893810	1.087482
78	1	0	3.341809	3.904199	-2.394463
79	6	0	-1.451767	-3.697497	-0.309443
80	6	0	-0.483540	-3.979153	0.626255
81	6	0	-1.127963	-3.796426	-1.689069
82	6	0	0.840530	-4.297552	0.239153
83	1	0	-0.705048	-3.849623	1.682294
84	6	0	0.137108	-4.133391	-2.092524
85	1	0	-1.891688	-3.566648	-2.424817
86	6	0	1.166633	-4.365983	-1.142014
87	6	0	1.882457	-4.470886	1.192182
88	1	0	0.376487	-4.194037	-3.150497
89	6	0	2.509949	-4.608867	-1.540260
90	6	0	3.169734	-4.695565	0.795044
91	1	0	1.641638	-4.398820	2.248679
92	6	0	3.489739	-4.767521	-0.588498
93	1	0	2.739810	-4.637622	-2.599088
94	1	0	3.976921	-4.819481	1.509594
95	8	0	3.999110	5.296250	-0.411161
96	6	0	4.268379	6.091729	0.722787
97	1	0	5.342337	6.278629	0.719494
98	1	0	3.732081	7.046689	0.674218
99	1	0	3.986349	5.566728	1.645063
100	8	0	4.806647	-4.977574	-0.854089
101	6	0	5.191239	-5.013214	-2.215745
102	1	0	4.963932	-4.061751	-2.706314
103	1	0	6.267899	-5.181796	-2.220403
104	1	0	4.692072	-5.836580	-2.739992
105	1	0	-4.665449	4.135535	-1.169998
106	1	0	-6.992432	3.775870	-1.807291
107	1	0	-8.902777	2.257612	-2.207545
108	1	0	-8.655628	-0.183090	-1.768385
109	1	0	-7.597846	-1.066004	3.270765
110	1	0	-6.208458	0.046817	1.590536
111	1	0	-6.553170	-1.081799	-0.882672
112	1	0	-7.190482	-3.449545	3.874708
113	1	0	-5.321274	-4.678192	2.820498
114	1	0	-3.365618	-4.722437	1.382924

(*R*)-3PA(TS-s (a))

cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -3401.451913 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.582308	-1.985469	2.248047
2	6	0	-3.758611	-1.203161	1.483769
3	6	0	-2.607759	-1.717394	0.839229
4	6	0	-2.312915	-3.100272	1.061417
5	6	0	-3.187118	-3.890606	1.849323
6	6	0	-4.299381	-3.348008	2.431639
7	6	0	-1.733253	-0.919556	0.024489
8	6	0	-1.116833	-3.636167	0.512824
9	6	0	-0.240589	-2.889663	-0.221112
10	6	0	-0.594904	-1.532106	-0.455168
11	6	0	-1.897079	0.544392	-0.252162
12	6	0	-3.034324	1.135877	-0.898159
13	6	0	-0.854888	1.390603	0.087057
14	6	0	-4.106210	0.374575	-1.425441
15	6	0	-3.121532	2.554877	-1.050133
16	6	0	-0.900712	2.804123	-0.062848
17	6	0	-5.187838	0.954729	-2.030642
18	6	0	-4.254846	3.132275	-1.675732
19	6	0	-2.035673	3.346105	-0.591415
20	6	0	-5.268824	2.351477	-2.157052
21	8	0	0.283203	0.888844	0.661945
22	8	0	0.308971	-0.784988	-1.172445
23	9	0	-2.113885	4.671515	-0.716002
24	9	0	-4.358799	4.451522	-1.823150
25	9	0	-6.329716	2.888104	-2.751186
26	9	0	-6.173605	0.207471	-2.515286
27	9	0	-4.099955	-0.959359	-1.349684
28	9	0	-4.089659	0.086715	1.373964
29	9	0	-5.654911	-1.465527	2.835054
30	9	0	-5.116080	-4.086148	3.176225
31	9	0	-2.947581	-5.184245	2.054863
32	9	0	-0.818512	-4.912206	0.767175
33	15	0	1.366685	0.065739	-0.262200
34	8	0	2.191629	0.907457	-1.160734
35	8	0	2.042038	-0.834720	0.752576
36	6	0	0.270806	3.627212	0.344983
37	6	0	1.382617	3.668431	-0.461511
38	6	0	0.296462	4.276955	1.605975
39	6	0	2.577440	4.283832	-0.018701
40	1	0	1.381582	3.157785	-1.418589
41	6	0	1.439742	4.891158	2.051509
42	1	0	-0.594418	4.258477	2.226580
43	6	0	2.624921	4.876037	1.270533
44	6	0	3.765104	4.245058	-0.800455
45	1	0	1.462245	5.362652	3.030252
46	6	0	3.862265	5.361420	1.775985
47	6	0	4.945350	4.716871	-0.301549
48	1	0	3.721816	3.802286	-1.791720
49	6	0	5.001342	5.251489	1.015290
50	1	0	3.885970	5.768078	2.780580
51	1	0	5.866185	4.680476	-0.875142
52	6	0	1.091977	-3.377841	-0.655409
53	6	0	2.000383	-3.799802	0.287358
54	6	0	1.506917	-3.230659	-2.004667
55	6	0	3.356233	-4.015718	-0.052818
56	1	0	1.701512	-3.879434	1.328741
57	6	0	2.808131	-3.460616	-2.366472
58	1	0	0.785773	-2.898132	-2.743920
59	6	0	3.777606	-3.830509	-1.397378
60	6	0	4.335098	-4.339125	0.928305
61	1	0	3.119666	-3.332245	-3.399089
62	6	0	5.152201	-3.969420	-1.732832
63	6	0	5.652459	-4.463798	0.592348
64	1	0	4.019705	-4.466472	1.959552
65	6	0	6.068893	-4.277873	-0.755158
66	1	0	5.454660	-3.804892	-2.760480
67	1	0	6.412209	-4.701376	1.329670
68	8	0	6.251018	5.604829	1.426193
69	6	0	6.367191	6.136703	2.728789
70	1	0	7.424061	6.358276	2.876627
71	1	0	5.782942	7.058206	2.834021
72	1	0	6.032395	5.409106	3.479673
73	8	0	7.405796	-4.409014	-0.956457
74	6	0	7.884548	-4.198064	-2.272367
75	1	0	7.662823	-3.179332	-2.605021
76	1	0	8.963384	-4.344108	-2.227028
77	1	0	7.447726	-4.925519	-2.966221

(*R*)-3PA(opt)

cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -3401.423846 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.582308	-1.985469	2.248047
2	6	0	-3.758611	-1.203161	1.483769
3	6	0	-2.607759	-1.717394	0.839229

4	6	0	-2.312915	-3.100272	1.061417
5	6	0	-3.187118	-3.890606	1.849323
6	6	0	-4.299381	-3.348008	2.431639
7	6	0	-1.733253	-0.919556	0.024489
8	6	0	-1.116833	-3.636167	0.512824
9	6	0	-0.240589	-2.889663	-0.221112
10	6	0	-0.594904	-1.532106	-0.455168
11	6	0	-1.897079	0.544392	-0.252162
12	6	0	-3.034324	1.135877	-0.898159
13	6	0	-0.854888	1.390603	0.087057
14	6	0	-4.106210	0.374575	-1.425441
15	6	0	-3.121532	2.554877	-1.050133
16	6	0	-0.900712	2.804123	-0.062848
17	6	0	-5.187838	0.954729	-2.030642
18	6	0	-4.254846	3.132275	-1.675732
19	6	0	-2.035673	3.346105	-0.591415
20	6	0	-5.268824	2.351477	-2.157052
21	8	0	0.283203	0.888844	0.661945
22	8	0	0.308971	-0.784988	-1.172445
23	9	0	-2.113885	4.671515	-0.716002
24	9	0	-4.358799	4.451522	-1.823150
25	9	0	-6.329716	2.888104	-2.751186
26	9	0	-6.173605	0.207471	-2.515286
27	9	0	-4.099955	-0.959359	-1.349684
28	9	0	-4.089659	0.086715	1.373964
29	9	0	-5.654911	-1.465527	2.835054
30	9	0	-5.116080	-4.086148	3.176225
31	9	0	-2.947581	-5.184245	2.054863
32	9	0	-0.818512	-4.912206	0.767175
33	15	0	1.366685	0.065739	-0.262200
34	8	0	2.191629	0.907457	-1.160734
35	8	0	2.042038	-0.834720	0.752576
36	6	0	0.270806	3.627212	0.344983
37	6	0	1.382617	3.668431	-0.461511
38	6	0	0.296462	4.276955	1.605975
39	6	0	2.577440	4.283832	-0.018701
40	1	0	1.381582	3.157785	-1.418589
41	6	0	1.439742	4.891158	2.051509
42	1	0	-0.594418	4.258477	2.226580
43	6	0	2.624921	4.876037	1.270533
44	6	0	3.765104	4.245058	-0.800455
45	1	0	1.462245	5.362652	3.030252
46	6	0	3.862265	5.361420	1.775985
47	6	0	4.945350	4.716871	-0.301549
48	1	0	3.721816	3.802286	-1.791720
49	6	0	5.001342	5.251489	1.015290
50	1	0	3.885970	5.768078	2.780580
51	1	0	5.866185	4.680476	-0.875142
52	6	0	1.091977	-3.377841	-0.655409
53	6	0	2.000383	-3.799802	0.287358
54	6	0	1.506917	-3.230659	-2.004667
55	6	0	3.356233	-4.015718	-0.052818
56	1	0	1.701512	-3.879434	1.328741
57	6	0	2.808131	-3.460616	-2.366472
58	1	0	0.785773	-2.898132	-2.743920
59	6	0	3.777606	-3.830509	-1.397378
60	6	0	4.335098	-4.339125	0.928305
61	1	0	3.119666	-3.332245	-3.399089
62	6	0	5.152201	-3.969420	-1.732832
63	6	0	5.652459	-4.463798	0.592348
64	1	0	4.019705	-4.466472	1.959552
65	6	0	6.068893	-4.277873	-0.755158
66	1	0	5.454660	-3.804892	-2.760480
67	1	0	6.412209	-4.701376	1.329670
68	8	0	6.251018	5.604829	1.426193
69	6	0	6.367191	6.136703	2.728789
70	1	0	7.424061	6.358276	2.876627
71	1	0	5.782942	7.058206	2.834021
72	1	0	6.032395	5.409106	3.479673
73	8	0	7.405796	-4.409014	-0.956457
74	6	0	7.884548	-4.198064	-2.272367
75	1	0	7.662823	-3.179332	-2.605021
76	1	0	8.963384	-4.344108	-2.227028
77	1	0	7.447726	-4.925519	-2.966221

(*R*)-1PA(TS-s)

cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -2409.466063 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.091751	-2.865501	2.358478
2	6	0	-4.401924	-2.007040	1.540110
3	6	0	-3.161444	-2.386605	0.959748
4	6	0	-2.624830	-3.663085	1.296989
5	6	0	-3.370720	-4.533269	2.134571
6	6	0	-4.581270	-4.151092	2.649630
7	6	0	-2.407146	-1.520481	0.096172
8	6	0	-1.331270	-4.032404	0.841828
9	6	0	-0.579982	-3.187471	0.067724
10	6	0	-1.161226	-1.943558	-0.310316
11	6	0	-2.863204	-0.153638	-0.287546
12	6	0	-4.130200	0.089895	-0.915401
13	6	0	-2.036031	0.929821	-0.053797
14	6	0	-4.979422	-0.963816	-1.351134
15	6	0	-4.551615	1.430858	-1.142091
16	6	0	-2.430649	2.276092	-0.308804
17	6	0	-6.190223	-0.697816	-1.937783
18	6	0	-5.816648	1.673096	-1.739182
19	6	0	-3.685979	2.504637	-0.807479
20	6	0	-6.623884	0.635553	-2.124300
21	8	0	-0.806420	0.751362	0.536047
22	8	0	-0.392980	-1.099474	-1.087749
23	15	0	0.433419	0.035379	-0.262829
24	8	0	1.134877	0.915446	-1.231906
25	8	0	1.227443	-0.600492	0.863593
26	6	0	-1.448618	3.360158	-0.029352
27	6	0	-0.332095	3.476729	-0.824654
28	6	0	-1.586514	4.210160	1.097995
29	6	0	0.711834	4.369409	-0.490485
30	1	0	-0.201428	2.821407	-1.679545
31	6	0	-0.590288	5.092760	1.438561
32	1	0	-2.479078	4.127445	1.711620
33	6	0	0.606415	5.165778	0.679912
34	6	0	1.914206	4.418423	-1.249893
35	1	0	-0.689178	5.715513	2.323787
36	6	0	1.721787	5.941091	1.103937
37	6	0	2.973478	5.171298	-0.831830
38	1	0	1.984527	3.812316	-2.148954
39	6	0	2.888337	5.913222	0.379048
40	1	0	1.639056	6.502210	2.027873
41	1	0	3.907139	5.205517	-1.384773
42	6	0	0.846097	-3.426106	-0.272752
43	6	0	1.766441	-3.558244	0.741068
44	6	0	1.304968	-3.335689	-1.614119
45	6	0	3.157200	-3.537047	0.477009
46	1	0	1.428214	-3.569282	1.773803
47	6	0	2.644346	-3.344469	-1.901722
48	1	0	0.577038	-3.224261	-2.411052
49	6	0	3.611347	-3.416378	-0.863825
50	6	0	4.122218	-3.548840	1.522247
51	1	0	2.984045	-3.262372	-2.930386
52	6	0	5.004185	-3.316617	-1.132415
53	6	0	5.456450	-3.444129	1.249953
54	1	0	3.778601	-3.620054	2.549977
55	6	0	5.905719	-3.328061	-0.094091
56	1	0	5.327330	-3.205636	-2.161026
57	1	0	6.203752	-3.441246	2.036730
58	8	0	4.044524	6.541945	0.736176
59	6	0	4.019979	7.281618	1.937596
60	1	0	5.017044	7.705409	2.058396
61	1	0	3.282903	8.091789	1.889997
62	1	0	3.787099	6.632529	2.792119
63	8	0	7.253594	-3.213291	-0.231817
64	6	0	7.755041	-3.049209	-1.545177
65	1	0	7.357226	-2.136432	-1.999256
66	1	0	8.837459	-2.969795	-1.446666
67	1	0	7.509367	-3.917922	-2.167203
68	1	0	-4.010754	3.524481	-0.997341
69	1	0	-6.124553	2.703216	-1.896079
70	1	0	-7.586551	0.831621	-2.584866
71	1	0	-6.818859	-1.518189	-2.268620
72	1	0	-6.035653	-2.551323	2.792081
73	1	0	-4.799662	-1.019640	1.336673
74	1	0	-4.652093	-1.989576	-1.222000
75	1	0	-5.140666	-4.823082	3.292156
76	1	0	-2.951242	-5.507795	2.368867
77	1	0	-0.919375	-4.991692	1.144809

(*R*)-1PA(opt)

cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -2409.433005 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.212885	-2.658188	2.481817
2	6	0	-4.504625	-1.848531	1.634806
3	6	0	-3.274671	-2.246164	1.057374
4	6	0	-2.773650	-3.531586	1.438586
5	6	0	-3.531046	-4.354337	2.309842
6	6	0	-4.725979	-3.929901	2.822307
7	6	0	-2.517577	-1.419050	0.158598
8	6	0	-1.497678	-3.932500	0.959094
9	6	0	-0.732603	-3.146304	0.146512
10	6	0	-1.288185	-1.896380	-0.243743
11	6	0	-2.900624	-0.039771	-0.285680
12	6	0	-4.102028	0.289249	-0.999028
13	6	0	-2.009638	0.992072	-0.043299
14	6	0	-5.031564	-0.685287	-1.438104
15	6	0	-4.405047	1.650574	-1.314045
16	6	0	-2.270976	2.354731	-0.355505
17	6	0	-6.177136	-0.354049	-2.109455
18	6	0	-5.600813	1.968704	-2.005494
19	6	0	-3.464913	2.648874	-0.946487
20	6	0	-6.471095	0.989320	-2.396492
21	8	0	-0.819821	0.743144	0.589062
22	8	0	-0.496263	-1.103366	-1.039765
23	15	0	0.397367	0.000175	-0.230653
24	8	0	1.100463	0.853072	-1.217875
25	8	0	1.182749	-0.662391	0.883294
26	6	0	-1.250111	3.391916	-0.041915
27	6	0	-0.141464	3.514756	-0.844453
28	6	0	-1.352013	4.176597	1.135716
29	6	0	0.933896	4.355790	-0.472075
30	1	0	-0.043197	2.904909	-1.736186
31	6	0	-0.327433	5.008700	1.510785
32	1	0	-2.242077	4.089533	1.751643
33	6	0	0.861881	5.090641	0.740317
34	6	0	2.129348	4.414825	-1.240577
35	1	0	-0.398878	5.585953	2.428622
36	6	0	1.998087	5.817876	1.190053
37	6	0	3.211402	5.119069	-0.795947
38	1	0	2.176073	3.861078	-2.174230
39	6	0	3.156146	5.801885	0.450537
40	1	0	1.937342	6.334640	2.141057
41	1	0	4.138575	5.162321	-1.358753

42	6	0	0.668372	-3.466068	-0.224549
43	6	0	1.611235	-3.630873	0.763332
44	6	0	1.083696	-3.409938	-1.580532
45	6	0	2.991005	-3.669180	0.454404
46	1	0	1.306537	-3.637523	1.806049
47	6	0	2.412134	-3.473027	-1.909487
48	1	0	0.335385	-3.280469	-2.355378
49	6	0	3.406686	-3.574201	-0.901283
50	6	0	3.987369	-3.721910	1.469219
51	1	0	2.721598	-3.415581	-2.949085
52	6	0	4.792928	-3.533487	-1.214353
53	6	0	5.314885	-3.676240	1.153834
54	1	0	3.673965	-3.779111	2.507326
55	6	0	5.725639	-3.581666	-0.204877
56	1	0	5.087716	-3.441422	-2.253216
57	1	0	6.086641	-3.706730	1.915917
58	8	0	4.326995	6.390763	0.821636
59	6	0	4.331903	7.078687	2.054470
60	1	0	5.338281	7.478243	2.178898
61	1	0	3.609726	7.903330	2.050881
62	1	0	4.098314	6.397690	2.883320
63	8	0	7.070632	-3.523993	-0.385699
64	6	0	7.538391	-3.391527	-1.715728
65	1	0	7.168384	-2.464483	-2.164414
66	1	0	8.625631	-3.360854	-1.650613
67	1	0	7.234341	-4.252396	-2.322272
68	1	0	-3.689732	3.671109	-1.168731
69	1	0	-5.845251	2.982316	-2.245790
70	1	0	-7.371623	1.225231	-2.924031
71	1	0	-6.859752	-1.113088	-2.430074
72	1	0	-4.862210	-1.725726	-1.254512
73	1	0	-4.924804	-0.886580	1.427442
74	1	0	-6.140881	-2.328859	2.900464
75	1	0	-5.295827	-4.547796	3.484410
76	1	0	-3.183185	-5.325358	2.594467
77	1	0	-1.107153	-4.875453	1.280388

(*R*)-3(TS-s (a))

cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -3401.875918 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.584732	-1.993460	2.248024
2	6	0	-3.763086	-1.209269	1.483468
3	6	0	-2.611485	-1.720948	0.838234
4	6	0	-2.313605	-3.103243	1.060006
5	6	0	-3.185728	-3.895570	1.848215
6	6	0	-4.298833	-3.355433	2.431210
7	6	0	-1.739088	-0.921111	0.023193
8	6	0	-1.116679	-3.636506	0.510692
9	6	0	-0.242394	-2.888014	-0.223556
10	6	0	-0.599697	-1.531165	-0.457171
11	6	0	-1.906150	0.542540	-0.253095
12	6	0	-3.044976	1.131743	-0.898390
13	6	0	-0.865572	1.390886	0.085745
14	6	0	-4.115525	0.368279	-1.425262
15	6	0	-3.135260	2.550585	-1.050049
16	6	0	-0.914460	2.804335	-0.063868
17	6	0	-5.198690	0.946261	-2.029792
18	6	0	-4.270115	3.125706	-1.674951
19	6	0	-2.050837	3.344018	-0.591744
20	6	0	-5.282691	2.342859	-2.155894
21	8	0	0.273874	0.891424	0.659947
22	8	0	0.302226	-0.782003	-1.174774
23	9	0	-2.131913	4.669283	-0.716038
24	9	0	-4.376931	4.444758	-1.822065
25	9	0	-6.345022	2.877356	-2.749377
26	9	0	-6.183127	0.197014	-2.514067
27	9	0	-4.106413	-0.965653	-1.349761
28	9	0	-4.096914	0.079925	1.374080
29	9	0	-5.658126	-1.475896	2.835685
30	9	0	-5.113585	-4.095437	3.176079
31	9	0	-2.943353	-5.188739	2.053385
32	9	0	-0.815531	-4.911960	0.764646
33	15	0	1.358613	0.070784	-0.264915
34	8	0	2.181311	0.914412	-1.163717
35	8	0	2.036392	-0.828438	0.749339
36	1	0	3.297038	-0.891964	0.854345
37	6	0	0.255529	3.629819	0.343512
38	6	0	1.366832	3.673539	-0.463550
39	6	0	0.280466	4.279377	1.604614
40	6	0	2.560582	4.291379	-0.021242
41	1	0	1.366379	3.163073	-1.420724
42	6	0	1.422677	4.895909	2.049673
43	1	0	-0.610051	4.258900	2.225677
44	6	0	2.607480	4.883439	1.268080
45	6	0	3.747919	4.255261	-0.803619
46	1	0	1.444692	5.367265	3.028493
47	6	0	3.844058	5.371339	1.772983
48	6	0	4.927425	4.729472	-0.305235
49	1	0	3.705053	3.812586	-1.794945
50	6	0	4.982970	5.263958	1.011677
51	1	0	3.867425	5.777856	2.777643
52	1	0	5.848037	4.695130	-0.879312
53	6	0	1.090975	-3.373294	-0.658636
54	6	0	2.000759	-3.793514	0.283579
55	6	0	1.504903	-3.224981	-2.008081
56	6	0	3.356885	-4.006501	-0.057340
57	1	0	1.702597	-3.873974	1.325102
58	6	0	2.806412	-3.452121	-2.370604
59	1	0	0.782675	-2.893839	-2.746897
60	6	0	3.777169	-3.820148	-1.402083
61	6	0	4.336940	-4.328025	0.923214
62	1	0	3.117140	-3.322897	-3.403358
63	6	0	5.151880	-3.956092	-1.738276
64	6	0	5.654387	-4.449852	0.586551
65	1	0	4.022351	-4.456233	1.954600
66	6	0	6.069728	-4.262793	-0.761135
67	1	0	5.453458	-3.790731	-2.766049
68	1	0	6.415019	-4.685964	1.323434
69	8	0	6.232110	5.619859	1.421999
70	6	0	6.347835	6.151731	2.724636
71	1	0	7.404311	6.375508	2.871968
72	1	0	5.761695	7.071978	2.830346
73	1	0	6.014966	5.423287	3.475555
74	8	0	7.406801	-4.391072	-0.963152
75	6	0	7.884424	-4.178862	-2.279270
76	1	0	7.660375	-3.160538	-2.611615
77	1	0	8.963589	-4.322636	-2.234518
78	1	0	7.448779	-4.907107	-2.973036

(*R*)-3(opt)

cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = 3401.927839 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.584732	-1.993460	2.248024
2	6	0	-3.763086	-1.209269	1.483468
3	6	0	-2.611485	-1.720948	0.838234
4	6	0	-2.313605	-3.103243	1.060006
5	6	0	-3.185728	-3.895570	1.848215
6	6	0	-4.298833	-3.355433	2.431210
7	6	0	-1.739088	-0.921111	0.023193
8	6	0	-1.116679	-3.636506	0.510692
9	6	0	-0.242394	-2.888014	-0.223556
10	6	0	-0.599697	-1.531165	-0.457171
11	6	0	-1.906150	0.542540	-0.253095
12	6	0	-3.044976	1.131743	-0.898390
13	6	0	-0.865572	1.390886	0.085745
14	6	0	-4.115525	0.368279	-1.425262
15	6	0	-3.135260	2.550585	-1.050049
16	6	0	-0.914460	2.804335	-0.063868
17	6	0	-5.198690	0.946261	-2.029792
18	6	0	-4.270115	3.125706	-1.674951
19	6	0	-2.050837	3.344018	-0.591744
20	6	0	-5.282691	2.342859	-2.155894
21	8	0	0.273874	0.891424	0.659947
22	8	0	0.302226	-0.782003	-1.174774
23	9	0	-2.131913	4.669283	-0.716038
24	9	0	-4.376931	4.444758	-1.822065
25	9	0	-6.345022	2.877356	-2.749377
26	9	0	-6.183127	0.197014	-2.514067
27	9	0	-4.106413	-0.965653	-1.349761
28	9	0	-4.096914	0.079925	1.374080
29	9	0	-5.658126	-1.475896	2.835685
30	9	0	-5.113585	-4.095437	3.176079
31	9	0	-2.943353	-5.188739	2.053385
32	9	0	-0.815531	-4.911960	0.764646
33	15	0	1.358613	0.070784	-0.264915
34	8	0	2.181311	0.914412	-1.163717
35	8	0	2.036392	-0.828438	0.749339
36	1	0	3.297038	-0.891964	0.854345
37	6	0	0.255529	3.629819	0.343512
38	6	0	1.366832	3.673539	-0.463550
39	6	0	0.280466	4.279377	1.604614
40	6	0	2.560582	4.291379	-0.021242
41	1	0	1.366379	3.163073	-1.420724
42	6	0	1.422677	4.895909	2.049673
43	1	0	-0.610051	4.258900	2.225677
44	6	0	2.607480	4.883439	1.268080
45	6	0	3.747919	4.255261	-0.803619
46	1	0	1.444692	5.367265	3.028493
47	6	0	3.844058	5.371339	1.772983
48	6	0	4.927425	4.729472	-0.305235
49	1	0	3.705053	3.812586	-1.794945
50	6	0	4.982970	5.263958	1.011677
51	1	0	3.867425	5.777856	2.777643
52	1	0	5.848037	4.695130	-0.879312
53	6	0	1.090975	-3.373294	-0.658636
54	6	0	2.000759	-3.793514	0.283579
55	6	0	1.504903	-3.224981	-2.008081
56	6	0	3.356885	-4.006501	-0.057340
57	1	0	1.702597	-3.873974	1.325102
58	6	0	2.806412	-3.452121	-2.370604
59	1	0	0.782675	-2.893839	-2.746897
60	6	0	3.777169	-3.820148	-1.402083
61	6	0	4.336940	-4.328025	0.923214
62	1	0	3.117140	-3.322897	-3.403358
63	6	0	5.151880	-3.956092	-1.738276
64	6	0	5.654387	-4.449852	0.586551
65	1	0	4.022351	-4.456233	1.954600
66	6	0	6.069728	-4.262793	-0.761135
67	1	0	5.453458	-3.790731	-2.766049
68	1	0	6.415019	-4.685964	1.323434
69	8	0	6.232110	5.619859	1.421999
70	6	0	6.347835	6.151731	2.724636
71	1	0	7.404311	6.375508	2.871968
72	1	0	5.761695	7.071978	2.830346
73	1	0	6.014966	5.423287	3.475555
74	8	0	7.406801	-4.391072	-0.963152
75	6	0	7.884424	-4.178862	-2.279270
76	1	0	7.660375	-3.160538	-2.611615
77	1	0	8.963589	-4.322636	-2.234518
78	1	0	7.448779	-4.907107	-2.973036

(*R*)-1(TS-s)

cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) =-2409.902847 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.091365	-2.875399	2.358353
2	6	0	-4.403863	-2.015392	1.539652
3	6	0	-3.162945	-2.392271	0.958477
4	6	0	-2.623424	-3.667651	1.295244
5	6	0	-3.366953	-4.539501	2.133193
6	6	0	-4.577988	-4.159940	2.649046
7	6	0	-2.411016	-1.524461	0.094528
8	6	0	-1.329370	-4.034186	0.839239
9	6	0	-0.580351	-3.187582	0.064761
10	6	0	-1.164457	-1.944859	-0.312780
11	6	0	-2.870200	-0.158543	-0.288755
12	6	0	-4.138098	0.082380	-0.915796
13	6	0	-2.045173	0.926637	-0.055400
14	6	0	-4.985361	-0.973076	-1.351118
15	6	0	-4.562487	1.422474	-1.142076
16	6	0	-2.442794	2.272098	-0.310014
17	6	0	-6.197086	-0.709571	-1.936985
18	6	0	-5.828400	1.662103	-1.738354
19	6	0	-3.698914	2.498044	-0.807883
20	6	0	-6.633680	0.622898	-2.123085
21	8	0	-0.814822	0.750712	0.533660
22	8	0	-0.398480	-1.099068	-1.090597
23	15	0	0.426031	0.037439	-0.266065
24	8	0	1.125025	0.919092	-1.235481
25	8	0	1.222097	-0.596876	0.859793
26	1	0	2.452042	-0.382457	1.019075
27	6	0	-1.462883	3.358207	-0.031052
28	6	0	-0.347103	3.477224	-0.827035
29	6	0	-1.601875	4.207793	1.096474
30	6	0	0.695144	4.372072	-0.493416
31	1	0	-0.215583	2.822273	-1.682079
32	6	0	-0.607305	5.092459	1.436519
33	1	0	-2.493880	4.123124	1.710645
34	6	0	0.588770	5.168089	0.677134
35	6	0	1.896938	4.423710	-1.253565
36	1	0	-0.706960	5.714905	2.321875
37	6	0	1.702764	5.945711	1.100552
38	6	0	2.954876	5.178777	-0.836077
39	1	0	1.967981	3.817851	-2.152737
40	6	0	2.868919	5.920387	0.374935
41	1	0	1.619421	6.506553	2.024601
42	1	0	3.888118	5.215029	-1.389596
43	6	0	0.846018	-3.423165	-0.276627
44	6	0	1.767269	-3.553468	0.736606
45	6	0	1.303863	-3.331632	-1.618269
46	6	0	3.157816	-3.529303	0.471686
47	1	0	1.429708	-3.565334	1.769550
48	6	0	2.643077	-3.337550	-1.906705
49	1	0	0.575204	-3.221656	-2.414737
50	6	0	3.610873	-3.407528	-0.869417
51	6	0	4.123506	-3.539171	1.516323
52	1	0	2.981963	-3.254623	-2.935571
53	6	0	5.003330	-3.304794	-1.138861
54	6	0	5.457344	-3.431610	1.243211
55	1	0	3.780679	-3.611223	2.544258
56	6	0	5.905531	-3.314446	-0.101099
57	1	0	5.325600	-3.193018	-2.167660
58	1	0	6.205127	-3.427234	2.029524
59	8	0	4.023997	6.551513	0.731414
60	6	0	3.998635	7.291002	1.932931
61	1	0	4.994877	7.716886	2.053158
62	1	0	3.259819	8.099618	1.885880
63	1	0	3.767659	6.641329	2.787527
64	8	0	7.253075	-3.196813	-0.239649
65	6	0	7.753358	-3.031528	-1.553302
66	1	0	7.353332	-2.119544	-2.007033
67	1	0	8.835666	-2.949837	-1.455455
68	1	0	7.509134	-3.900690	-2.175272
69	1	0	-4.025962	3.517220	-0.997431
70	1	0	-6.138578	2.691587	-1.894946
71	1	0	-7.597045	0.816982	-2.583031
72	1	0	-6.824192	-1.531235	-2.267522
73	1	0	-6.035660	-2.563264	2.792577
74	1	0	-4.803813	-1.028813	1.336571
75	1	0	-4.655785	-1.998156	-1.222300
76	1	0	-5.135563	-4.833180	3.291845
77	1	0	-2.945271	-5.513164	2.367121
78	1	0	-0.915260	-4.992634	1.141858

(*R*)-1(opt)

cpcm(toluene)/M062X/6-31g(d,p); E(RM062X) = -2409.954590 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.513512	5.512652	2.535015
2	6	0	-0.055989	4.560540	1.663084
3	6	0	-0.907780	3.572548	1.112500
4	6	0	-2.268173	3.575049	1.551782
5	6	0	-2.717815	4.576212	2.449657
6	6	0	-1.860817	5.528423	2.929604
7	6	0	-0.467022	2.575728	0.177451
8	6	0	-3.127925	2.540152	1.098100
9	6	0	-2.715088	1.531889	0.268256
10	6	0	-1.370316	1.603680	-0.182013
11	6	0	0.921673	2.485397	-0.365901
12	6	0	1.553100	3.540562	-1.102789
13	6	0	1.643760	1.325000	-0.161669
14	6	0	0.871135	4.708586	-1.522532
15	6	0	2.931787	3.433559	-1.454198
16	6	0	3.021846	1.178746	-0.480905
17	6	0	1.500937	5.708133	-2.213869
18	6	0	3.562525	4.483888	-2.168422
19	6	0	3.622228	2.250172	-1.090255
20	6	0	2.863924	5.599955	-2.538481
21	8	0	1.038427	0.252571	0.474420
22	8	0	-0.944959	0.586157	-1.019301
23	15	0	-0.089569	-0.588309	-0.311665
24	8	0	0.314217	-1.613193	-1.275620
25	8	0	-0.927152	-1.059780	0.953583
26	1	0	-1.542136	-1.775335	0.737123
27	6	0	3.809554	-0.032033	-0.136886
28	6	0	3.420134	-1.282116	-0.560592
29	6	0	4.994030	0.104152	0.635700
30	6	0	4.173371	-2.429899	-0.222118
31	1	0	2.530959	-1.410209	-1.170177
32	6	0	5.741281	-0.994218	0.970143
33	1	0	5.300528	1.092262	0.963786
34	6	0	5.354196	-2.294976	0.554527
35	6	0	3.772077	-3.730151	-0.640425
36	1	0	6.643547	-0.879439	1.564089
37	6	0	6.110838	-3.449084	0.893876
38	6	0	4.508470	-4.828552	-0.305954
39	1	0	2.861953	-3.829110	-1.225434
40	6	0	5.693958	-4.688700	0.469410
41	1	0	7.009420	-3.323431	1.486825
42	1	0	4.221537	-5.828589	-0.611876
43	6	0	-3.596584	0.396100	-0.095679
44	6	0	-4.292260	-0.278733	0.885478
45	6	0	-3.712099	-0.033841	-1.445673
46	6	0	-5.108742	-1.390473	0.572862
47	1	0	-4.211738	0.037052	1.921986
48	6	0	-4.499113	-1.107088	-1.772119
49	1	0	-3.166744	0.496098	-2.218636
50	6	0	-5.217308	-1.820690	-0.777300
51	6	0	-5.825944	-2.103902	1.575288
52	1	0	-4.580433	-1.425722	-2.807180
53	6	0	-6.029188	-2.941253	-1.099451
54	6	0	-6.601200	-3.177709	1.250425
55	1	0	-5.748356	-1.777339	2.608332
56	6	0	-6.706781	-3.604876	-0.103724
57	1	0	-6.096643	-3.249737	-2.136174
58	1	0	-7.155940	-3.733032	1.998587
59	8	0	6.332602	-5.856637	0.731057
60	6	0	7.515826	-5.787656	1.495711
61	1	0	7.875612	-6.810945	1.595639
62	1	0	8.277536	-5.179184	0.993778
63	1	0	7.321438	-5.369306	2.490502
64	8	0	-7.506805	-4.681333	-0.289584
65	6	0	-7.656852	-5.156103	-1.610799
66	1	0	-6.694133	-5.472372	-2.029146
67	1	0	-8.327501	-6.012160	-1.552854
68	1	0	-8.096600	-4.389134	-2.258991
69	1	0	4.663347	2.184900	-1.328395
70	1	0	4.595489	4.425165	-2.441254
71	1	0	3.333770	6.392552	-3.082480
72	1	0	0.962223	6.578755	-2.524844
73	1	0	-0.170911	4.841330	-1.319018
74	1	0	0.986280	4.590801	1.422959
75	1	0	0.152795	6.247804	2.935624
76	1	0	-2.196264	6.281612	3.611572
77	1	0	-3.734544	4.606674	2.781670
78	1	0	-4.138461	2.537978	1.449828

(*R*)-3a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.536095	3.378980	2.098463
2	6	0	-0.821359	2.392980	1.458276
3	6	0	-1.450274	1.347492	0.735510
4	6	0	-2.890465	1.329481	0.744270
5	6	0	-3.601799	2.365400	1.406578
6	6	0	-2.940762	3.371763	2.069041
7	6	0	-0.733102	0.311678	0.042523
8	6	0	-3.550234	0.249781	0.100801
9	6	0	-2.890066	-0.804917	-0.490676
10	6	0	-1.469869	-0.735425	-0.485839
11	6	0	0.758614	0.270402	-0.088715
12	6	0	1.534306	1.279036	-0.757535
13	6	0	1.437083	-0.824032	0.424008
14	6	0	0.964821	2.364862	-1.469753
15	6	0	2.971369	1.187859	-0.754148
16	6	0	2.851949	-0.955141	0.461462
17	6	0	1.733721	3.320041	-2.093338
18	6	0	3.739775	2.192786	-1.400265
19	6	0	3.569572	0.074009	-0.108704
20	6	0	3.135996	3.239170	-2.055467
21	8	0	0.695745	-1.873928	0.964713
22	8	0	-0.790944	-1.799086	-1.070603
23	9	0	4.910250	0.015435	-0.070876
24	9	0	5.077519	2.145306	-1.408363
25	9	0	3.861750	4.176697	-2.670332
26	9	0	1.158148	4.326345	-2.756227
27	9	0	-0.368787	2.500693	-1.577862
28	9	0	0.517657	2.458737	1.560982
29	9	0	-0.905009	4.345627	2.769490

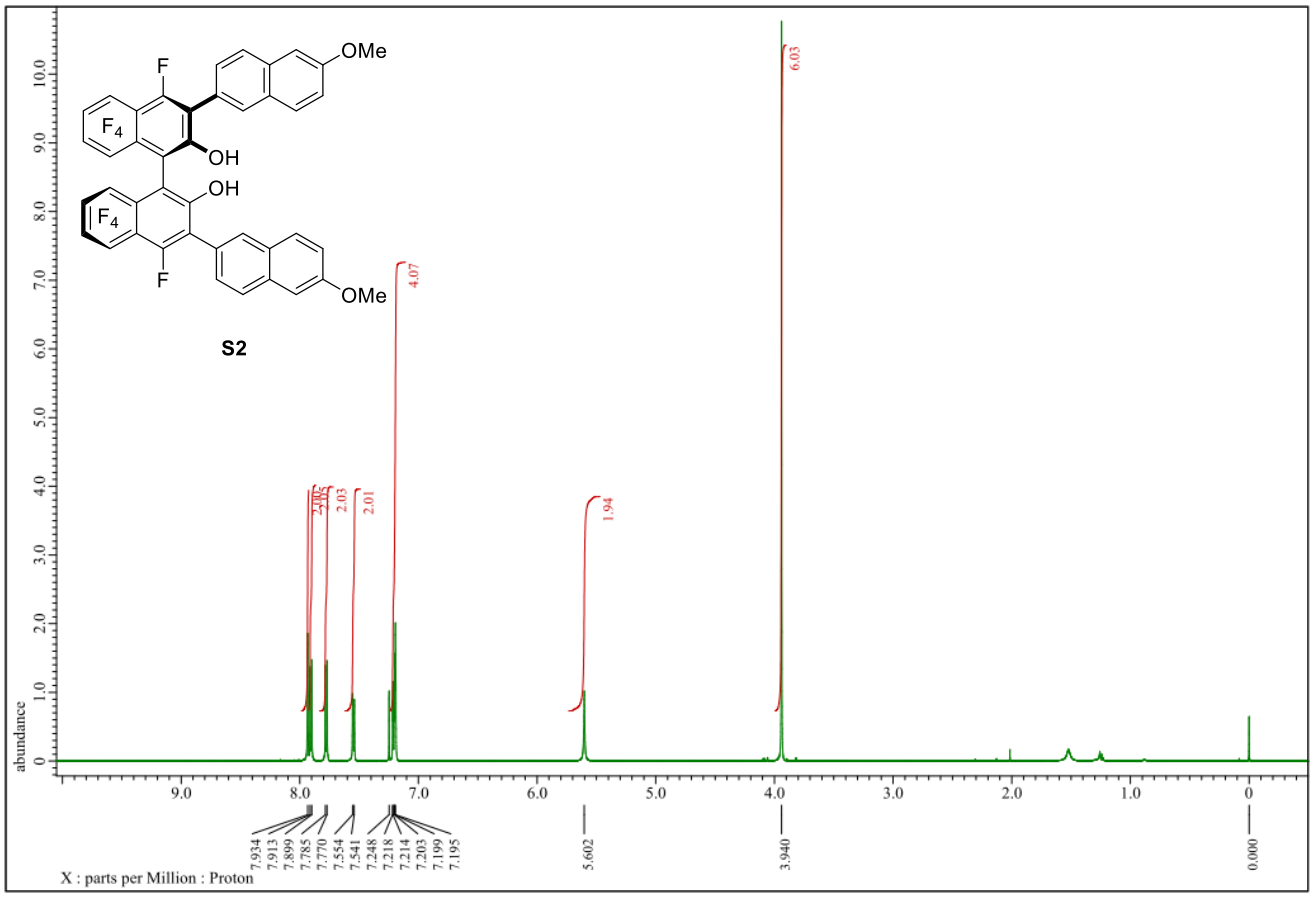
30	9	0	-3.613241	4.338669	2.698734
31	9	0	-4.940336	2.387299	1.422877
32	9	0	-4.893427	0.248914	0.092374
33	15	0	-0.037229	-2.865463	-0.094837
34	8	0	0.751351	-3.839202	-0.863178
35	8	0	-1.149922	-3.450766	0.905153
36	1	0	-1.412577	-4.345229	0.629735
37	6	0	-3.629408	-1.948004	-1.092838
38	6	0	-3.362482	-2.369656	-2.404962
39	6	0	-4.613518	-2.622410	-0.352570
40	6	0	-4.063380	-3.438904	-2.961026
41	1	0	-2.606003	-1.857996	-2.990717
42	6	0	-5.310428	-3.693443	-0.910001
43	1	0	-4.829114	-2.307994	0.663630
44	6	0	-5.038205	-4.104894	-2.215979
45	1	0	-3.846498	-3.750356	-3.979011
46	1	0	-6.067672	-4.205433	-0.322445
47	1	0	-5.582783	-4.938612	-2.650748
48	6	0	3.531083	-2.118457	1.094442
49	6	0	4.498200	-2.847791	0.386916
50	6	0	3.228413	-2.492842	2.412707
51	6	0	5.145380	-3.928279	0.983565
52	1	0	4.735785	-2.573074	-0.635735
53	6	0	3.880815	-3.570650	3.008515
54	1	0	2.484585	-1.935056	2.972864
55	6	0	4.840302	-4.292042	2.295914
56	1	0	5.886954	-4.487471	0.419898
57	1	0	3.639164	-3.845546	4.031606
58	1	0	5.346336	-5.133932	2.760581

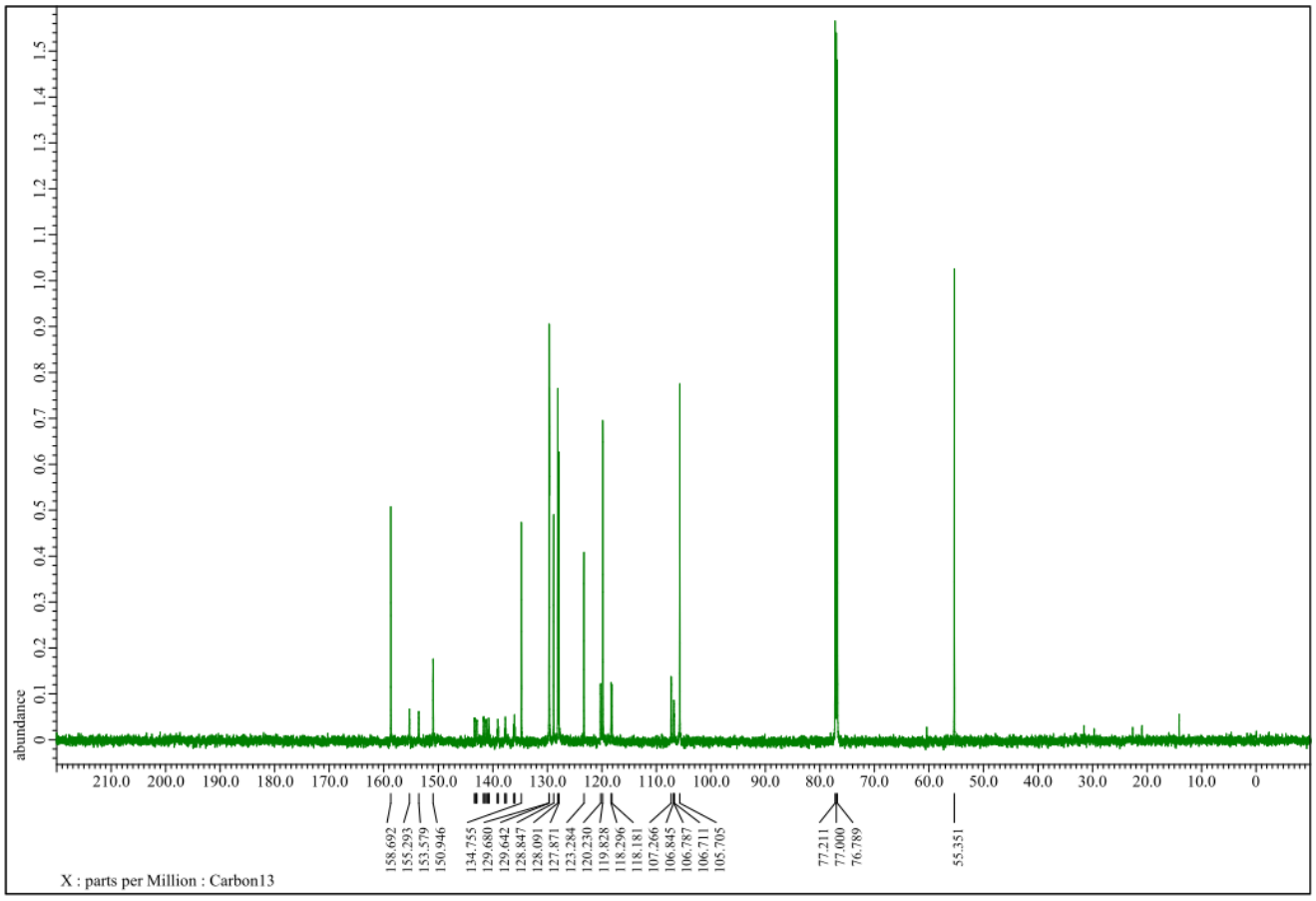
(*R*)-3a-PA

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.636738	3.326520	-2.117250
2	6	0	0.894558	2.365787	-1.472557
3	6	0	1.489253	1.289669	-0.759909
4	6	0	2.930126	1.225539	-0.783342
5	6	0	3.668743	2.236936	-1.452691
6	6	0	3.039901	3.268143	-2.105432
7	6	0	0.745461	0.278699	-0.068998
8	6	0	3.552687	0.128521	-0.134745
9	6	0	2.862512	-0.900974	0.462029
10	6	0	1.433711	-0.813938	0.460333
11	6	0	-0.745477	0.278685	0.068991
12	6	0	-1.489267	1.289644	0.759907
13	6	0	-1.433703	-0.813975	-0.460352
14	6	0	-0.894573	2.365754	1.472566
15	6	0	-2.930141	1.225521	0.783335
16	6	0	-2.862519	-0.900981	-0.462058
17	6	0	-1.636750	3.326482	2.117271
18	6	0	-3.668754	2.236908	1.452696
19	6	0	-3.552695	0.128510	0.134715
20	6	0	-3.039913	3.268107	2.105453
21	8	0	-0.733598	-1.814896	-1.036199
22	8	0	0.733579	-1.814867	1.036202
23	9	0	-4.904503	0.101902	0.116690
24	9	0	-5.013138	2.216084	1.486066
25	9	0	-3.744467	4.217865	2.744088
26	9	0	-1.032676	4.325488	2.780933
27	9	0	0.443566	2.490193	1.560242
28	9	0	-0.443577	2.490228	-1.560238
29	9	0	1.032667	4.325534	-2.780902
30	9	0	3.744453	4.217908	-2.744056
31	9	0	5.013125	2.216109	-1.486061
32	9	0	4.904494	0.101905	-0.116738
33	15	0	0.000054	-2.985848	0.000063
34	8	0	-1.043352	-3.631994	0.836329
35	8	0	1.043462	-3.631954	-0.836237
36	6	0	3.577304	-2.034516	1.107925
37	6	0	3.252511	-2.434868	2.413324
38	6	0	4.606155	-2.710204	0.434930
39	6	0	3.946002	-3.474656	3.029925
40	1	0	2.445369	-1.936614	2.938337
41	6	0	5.295355	-3.752877	1.051111
42	1	0	4.854852	-2.425236	-0.581734
43	6	0	4.971069	-4.137195	2.352853
44	1	0	3.677178	-3.772329	4.040417
45	1	0	6.082076	-4.270961	0.508064
46	1	0	5.506283	-4.953350	2.832522
47	6	0	-3.577312	-2.034521	-1.107960
48	6	0	-4.606192	-2.710185	-0.434985
49	6	0	-3.252494	-2.434895	-2.413347
50	6	0	-5.295393	-3.752856	-1.051171
51	1	0	-4.854914	-2.425200	0.581668
52	6	0	-3.945986	-3.474677	-3.029953
53	1	0	-2.445328	-1.936661	-2.938343
54	6	0	-4.971080	-4.137195	-2.352899
55	1	0	-6.082136	-4.270921	-0.508137
56	1	0	-3.677142	-3.772367	-4.040435
57	1	0	-5.506295	-4.953346	-2.832573

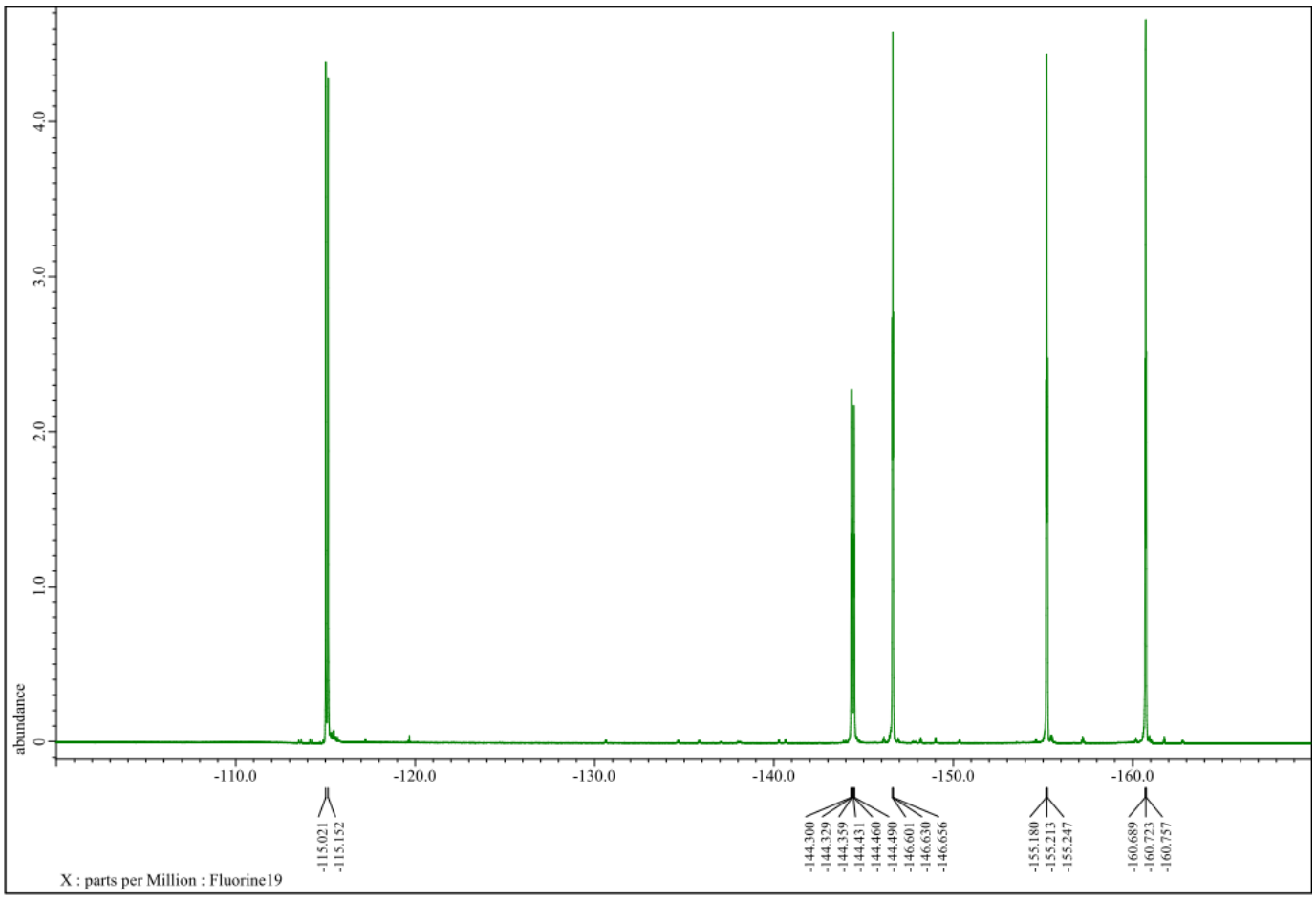
7. NMR Spectra Data

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

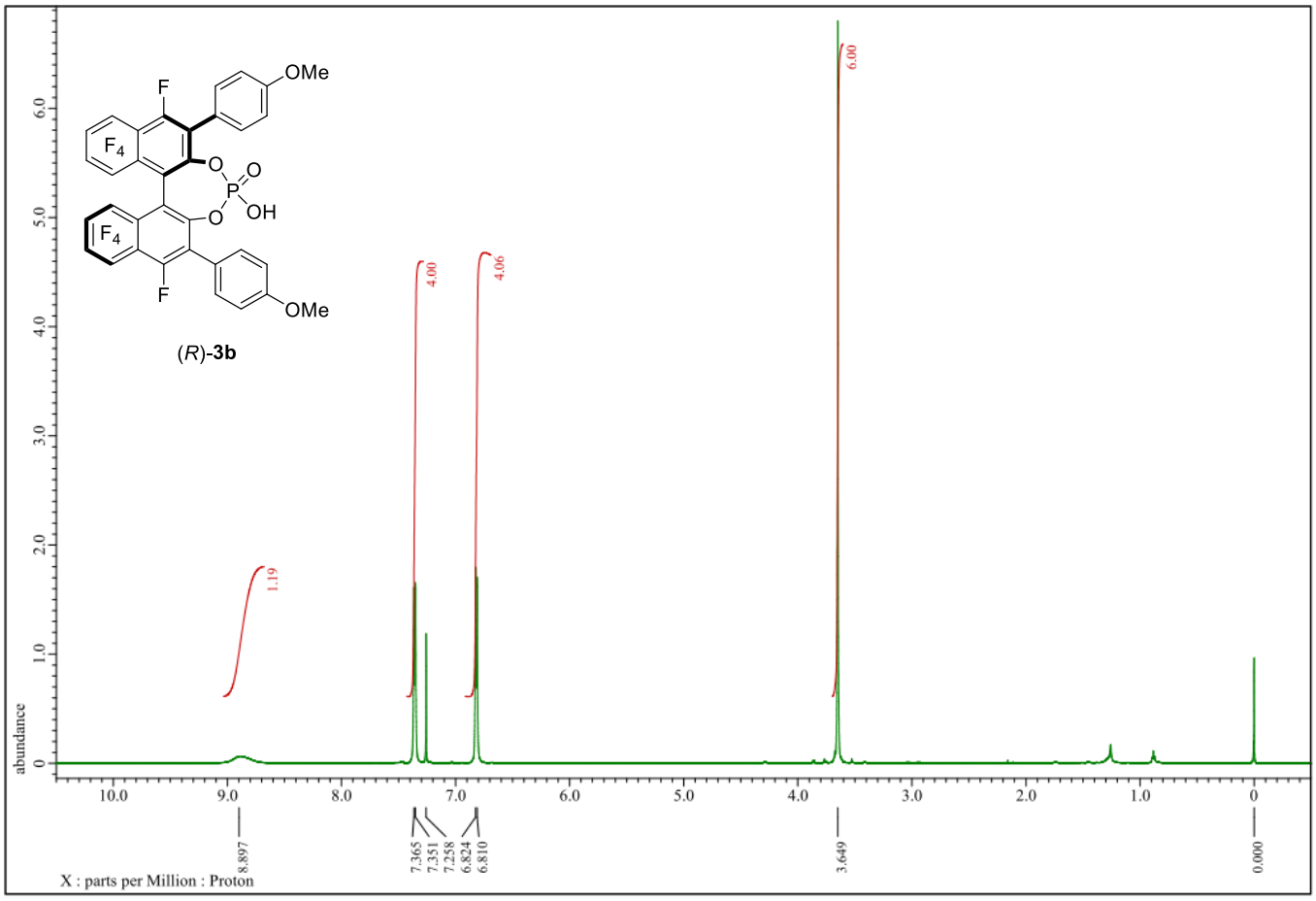


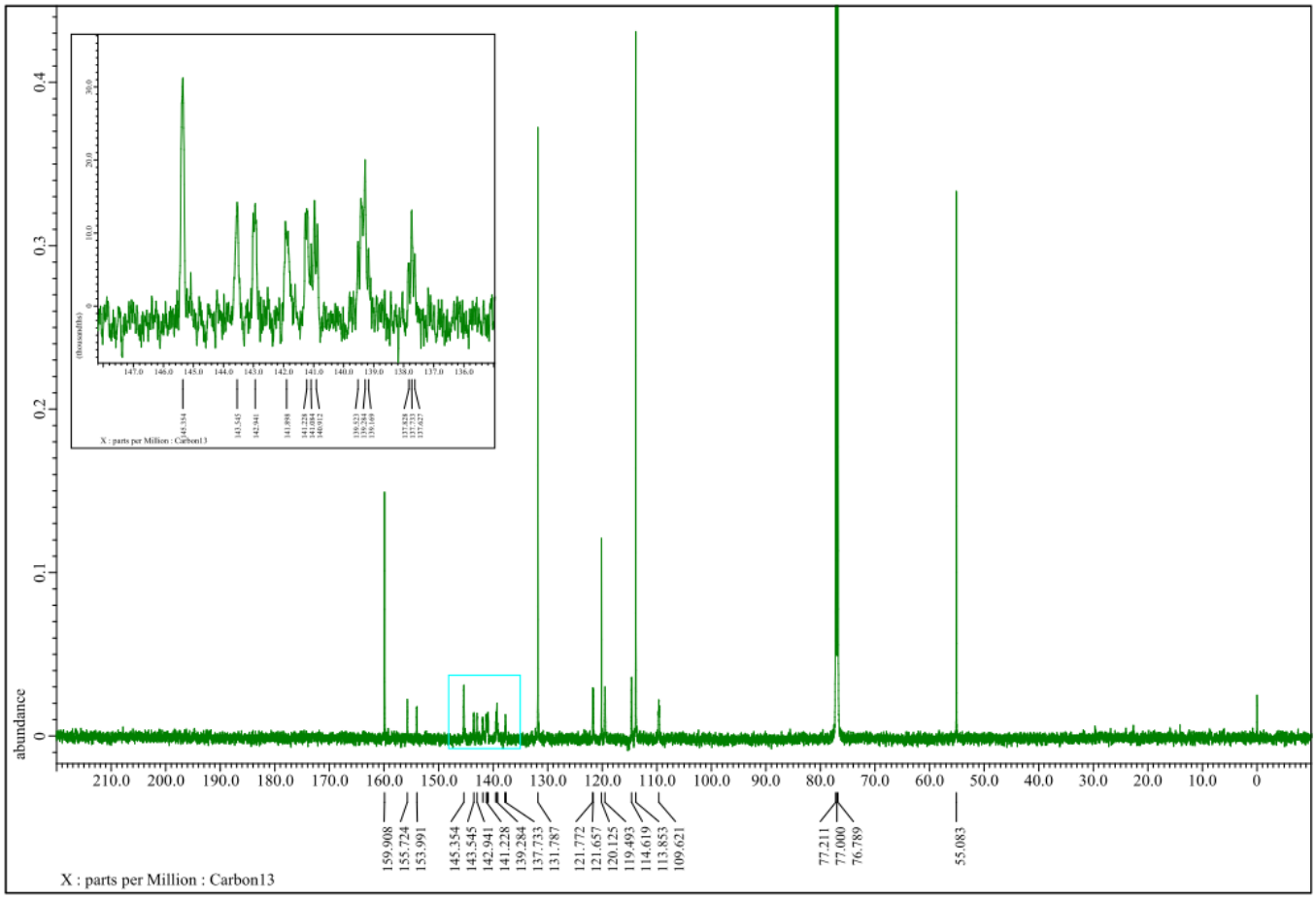


^{19}F NMR (565 MHz) spectra of **S2**

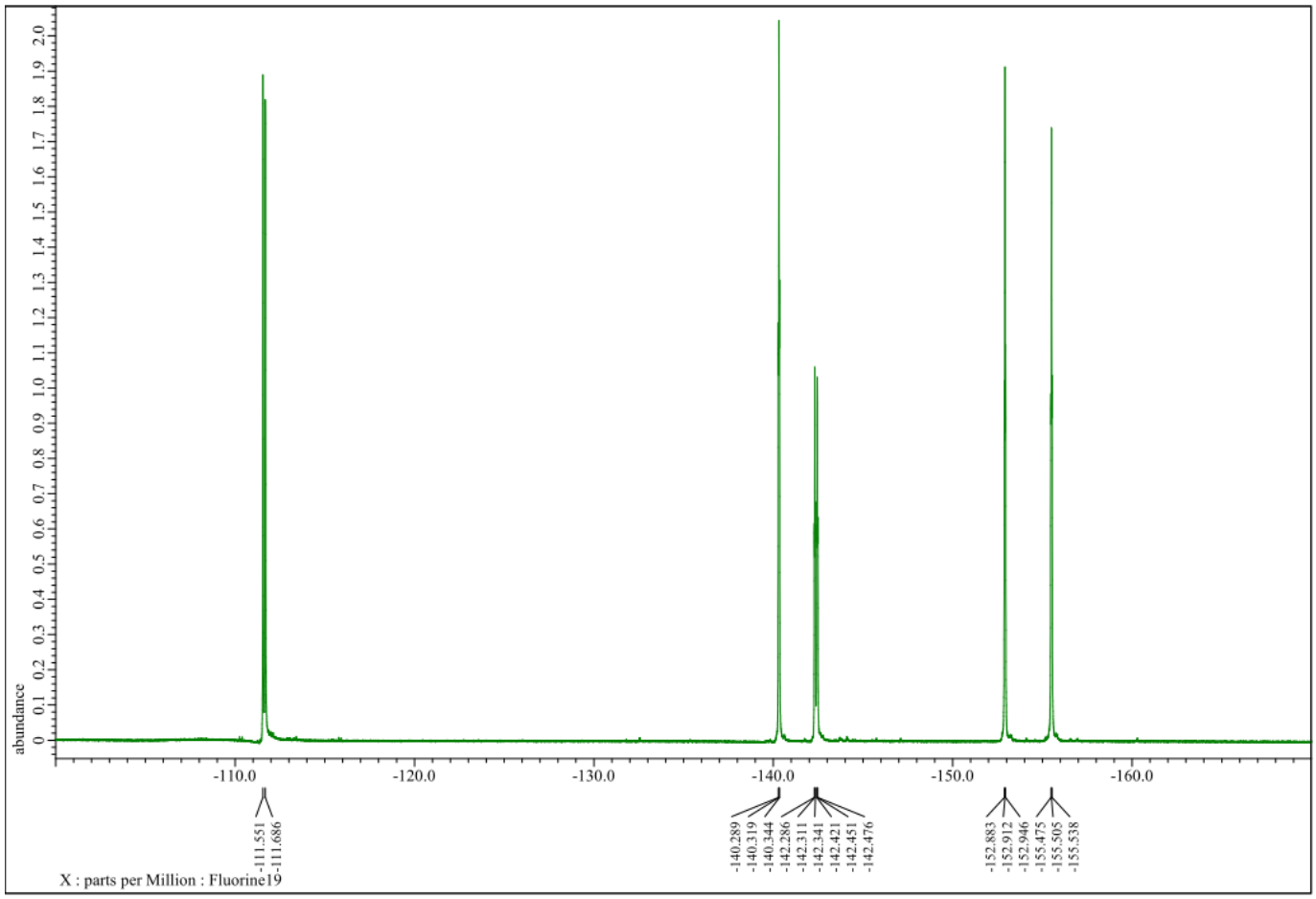


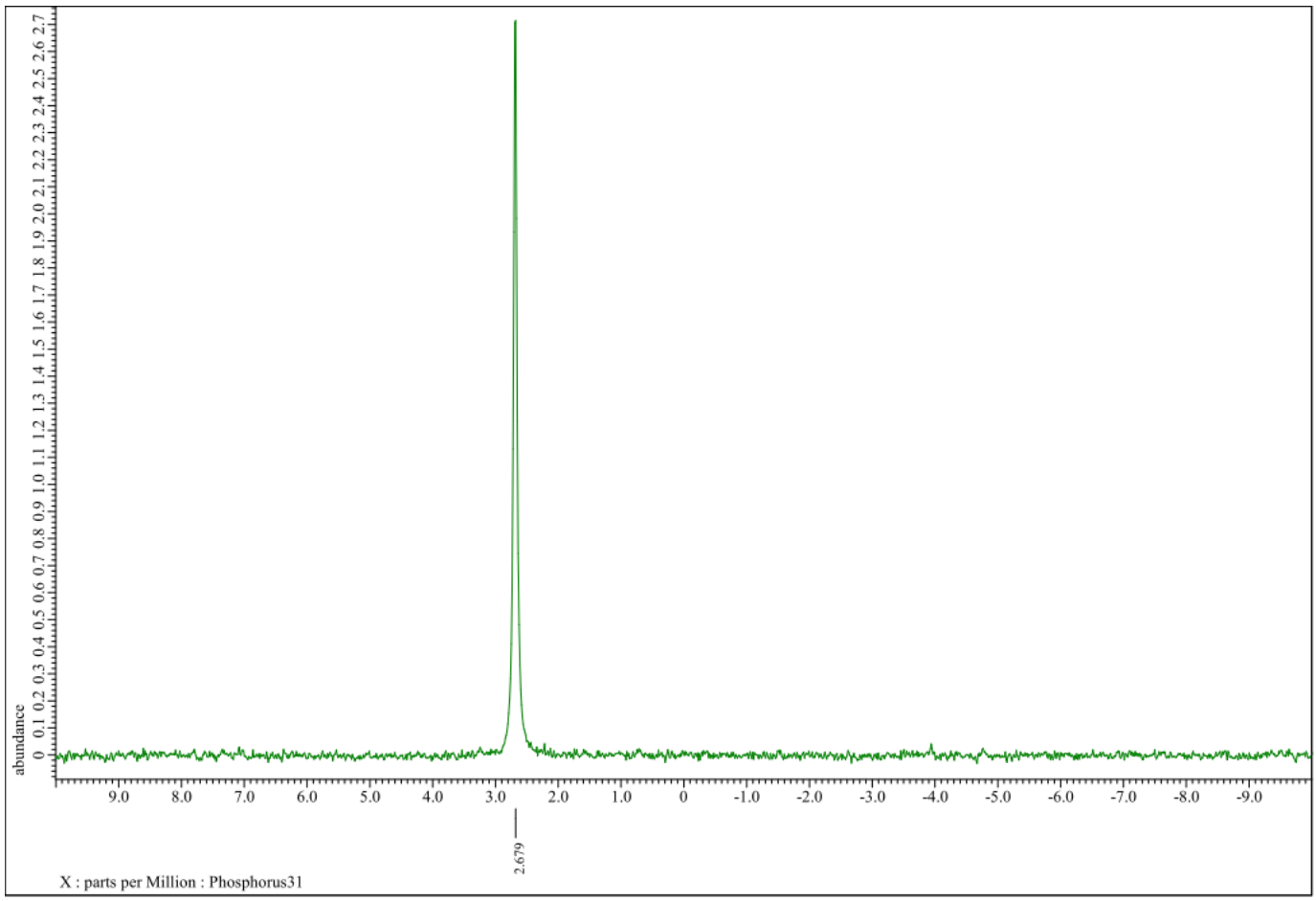
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of (*R*)-**3b**



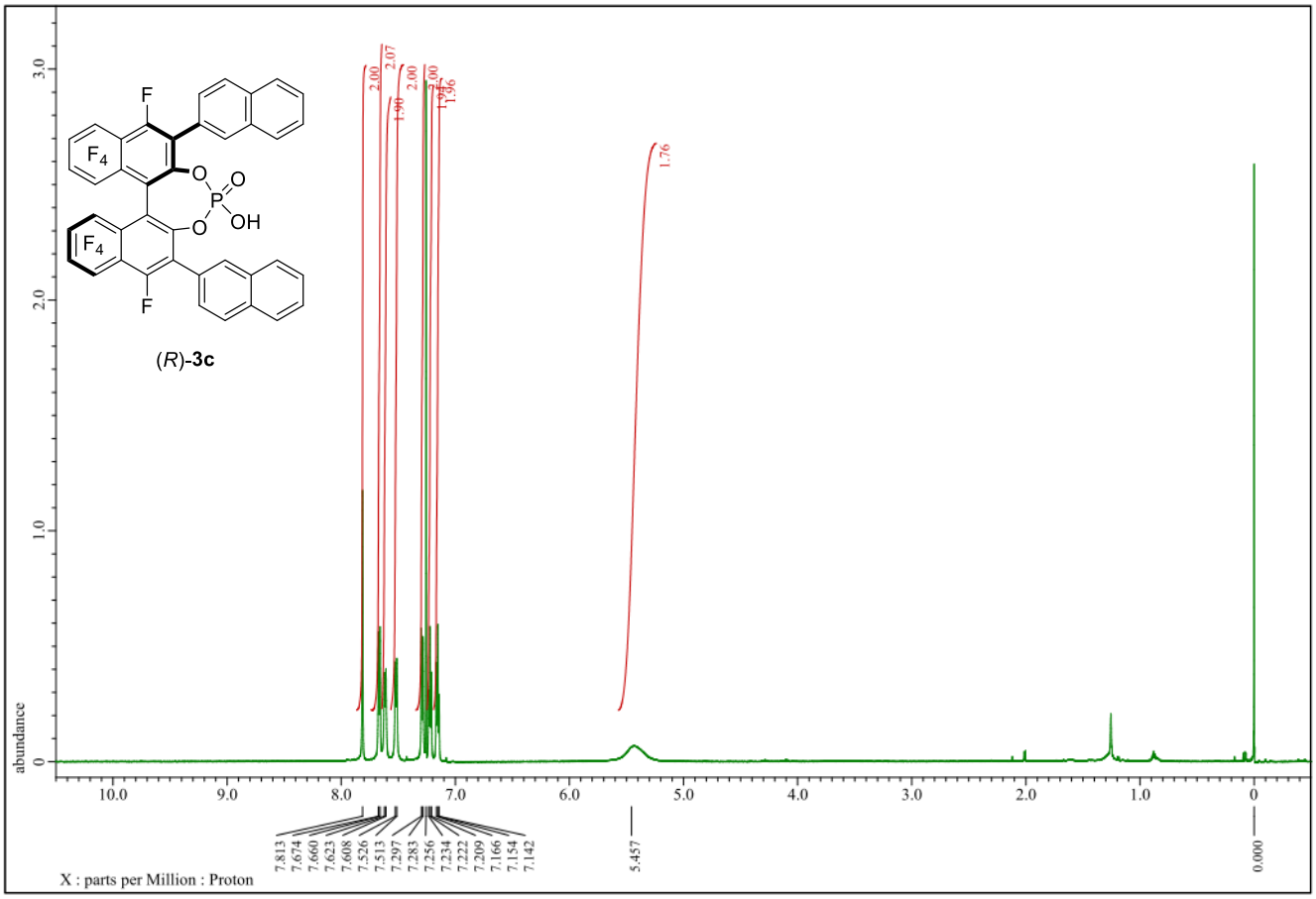


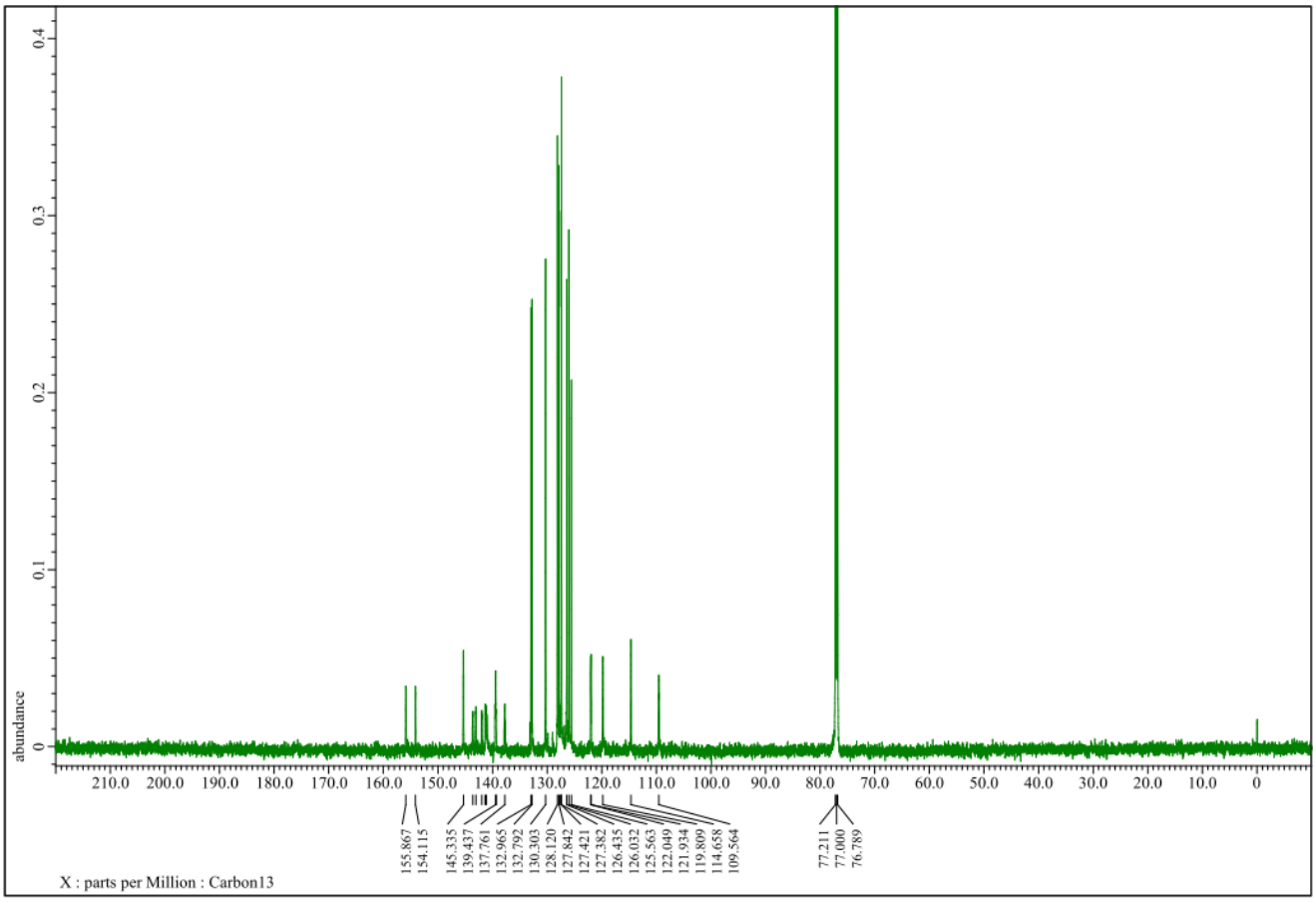
^{19}F NMR (565 MHz) and ^{31}P NMR (243 MHz) spectra of (*R*)-**3b**



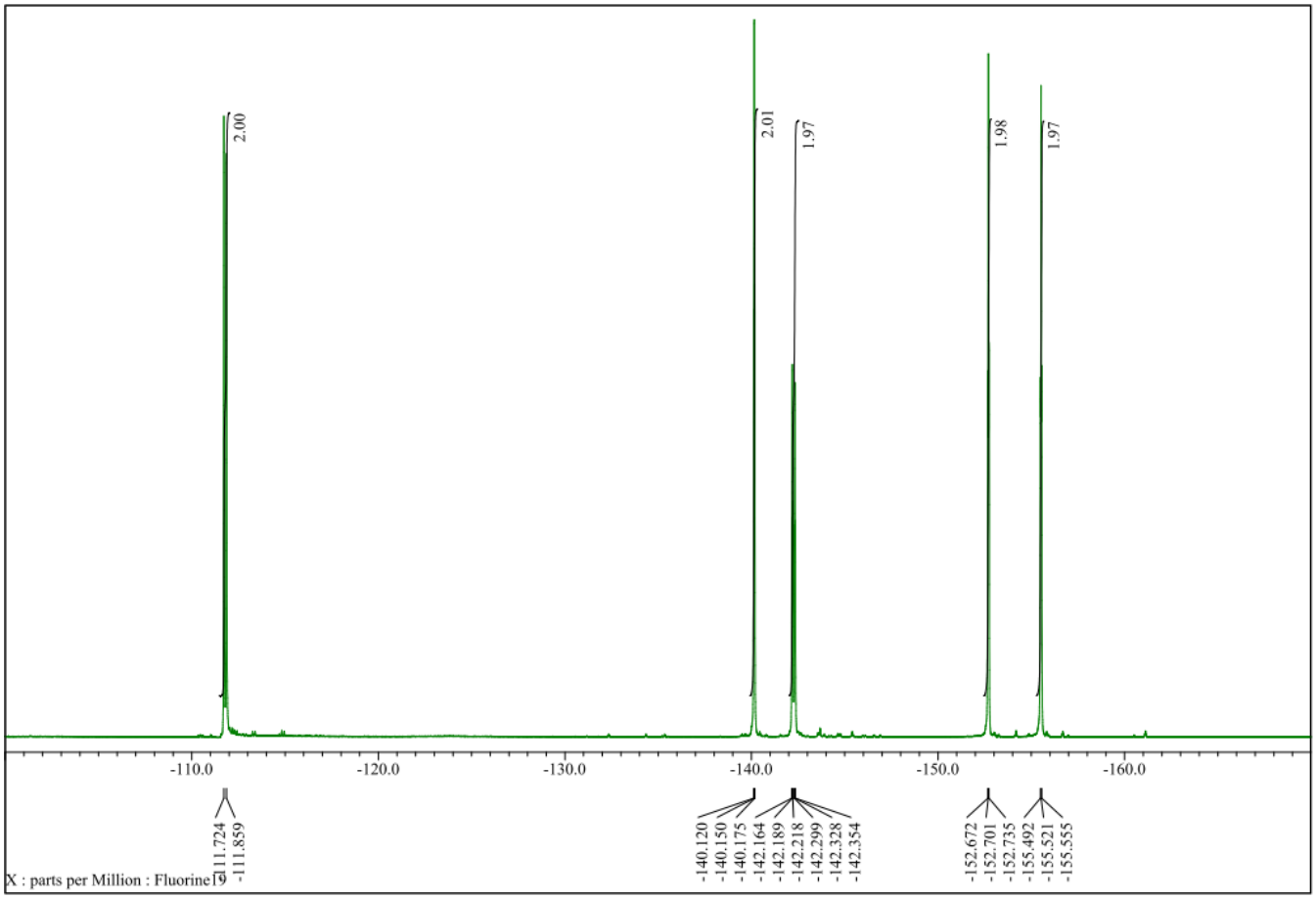


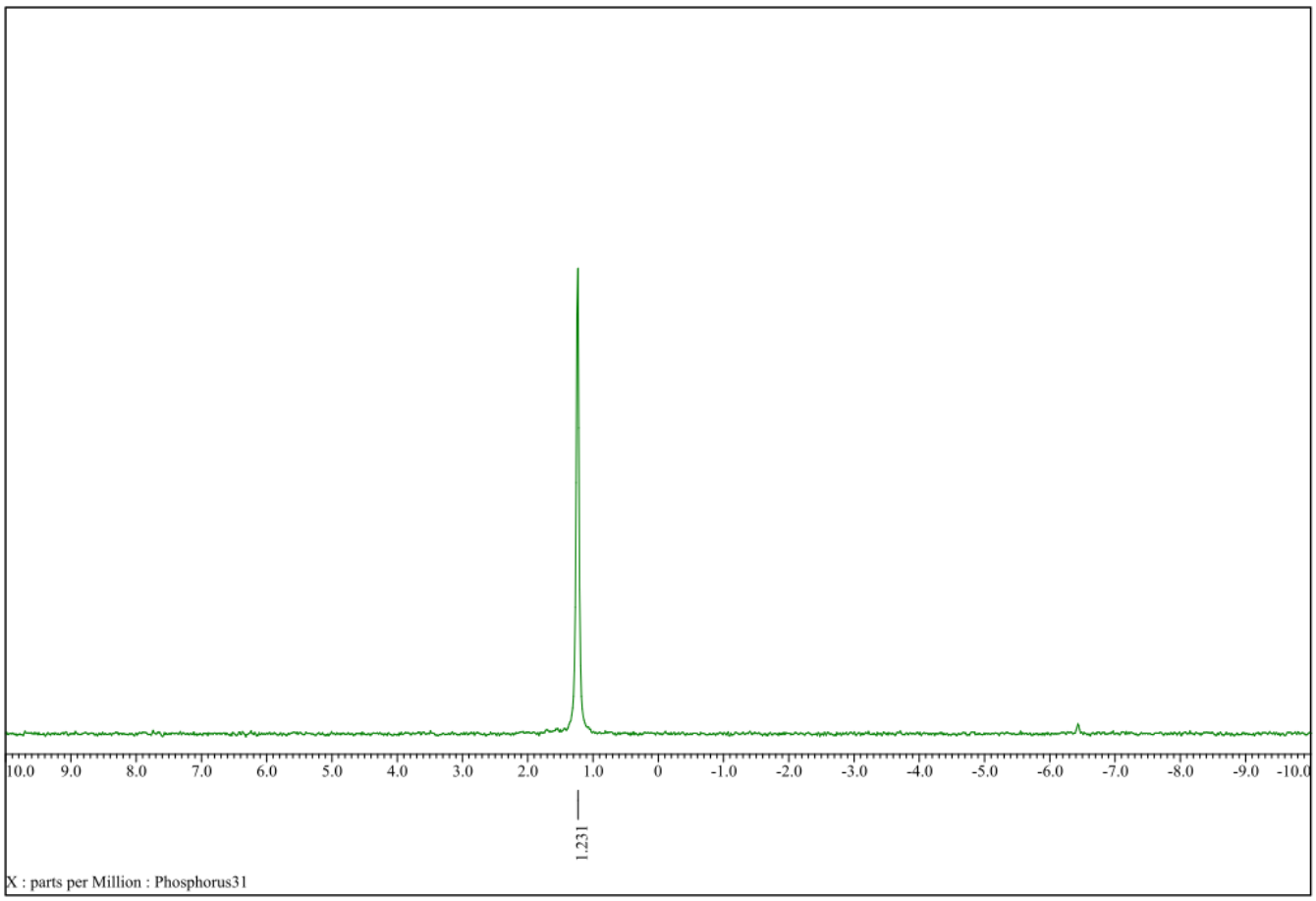
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of (*R*)-**3c**



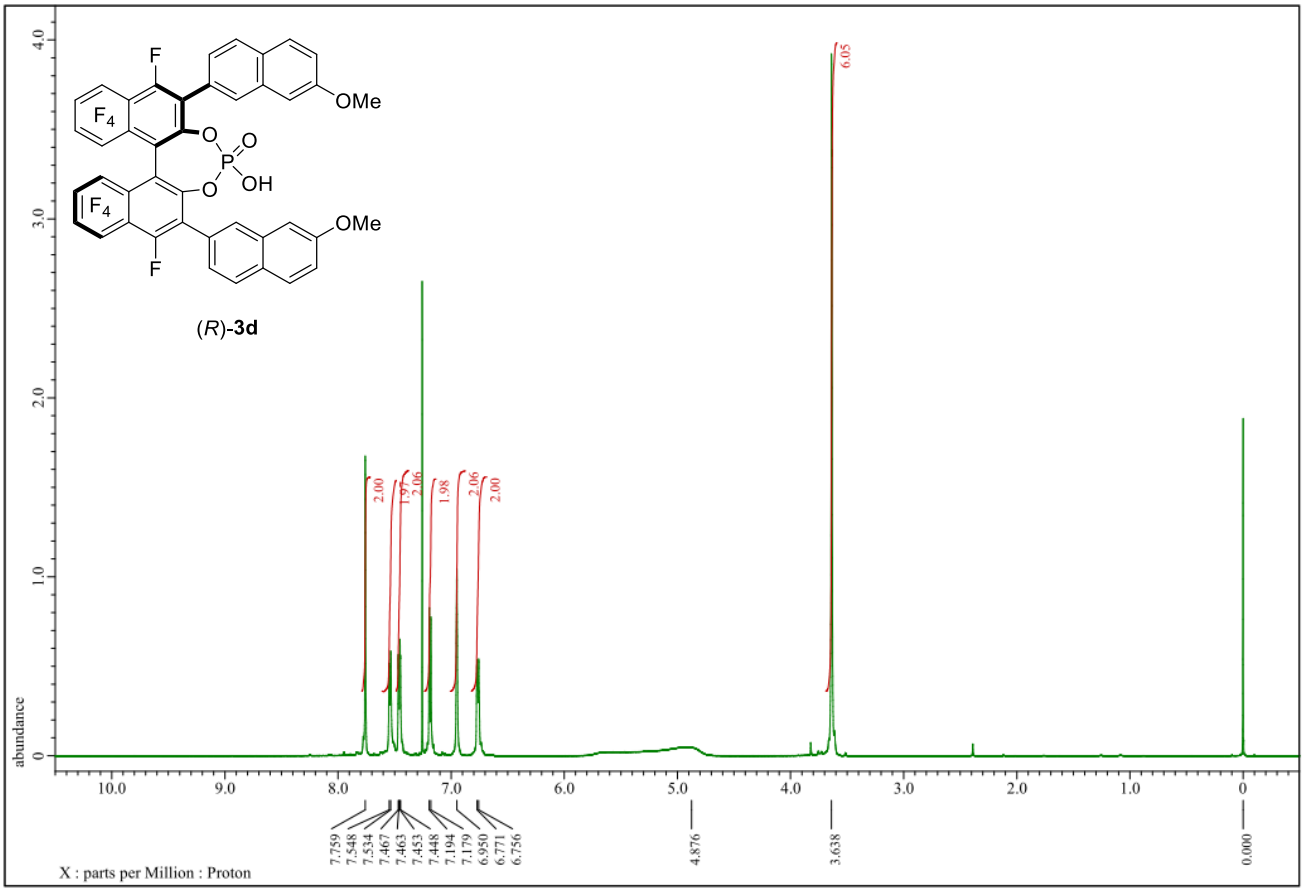


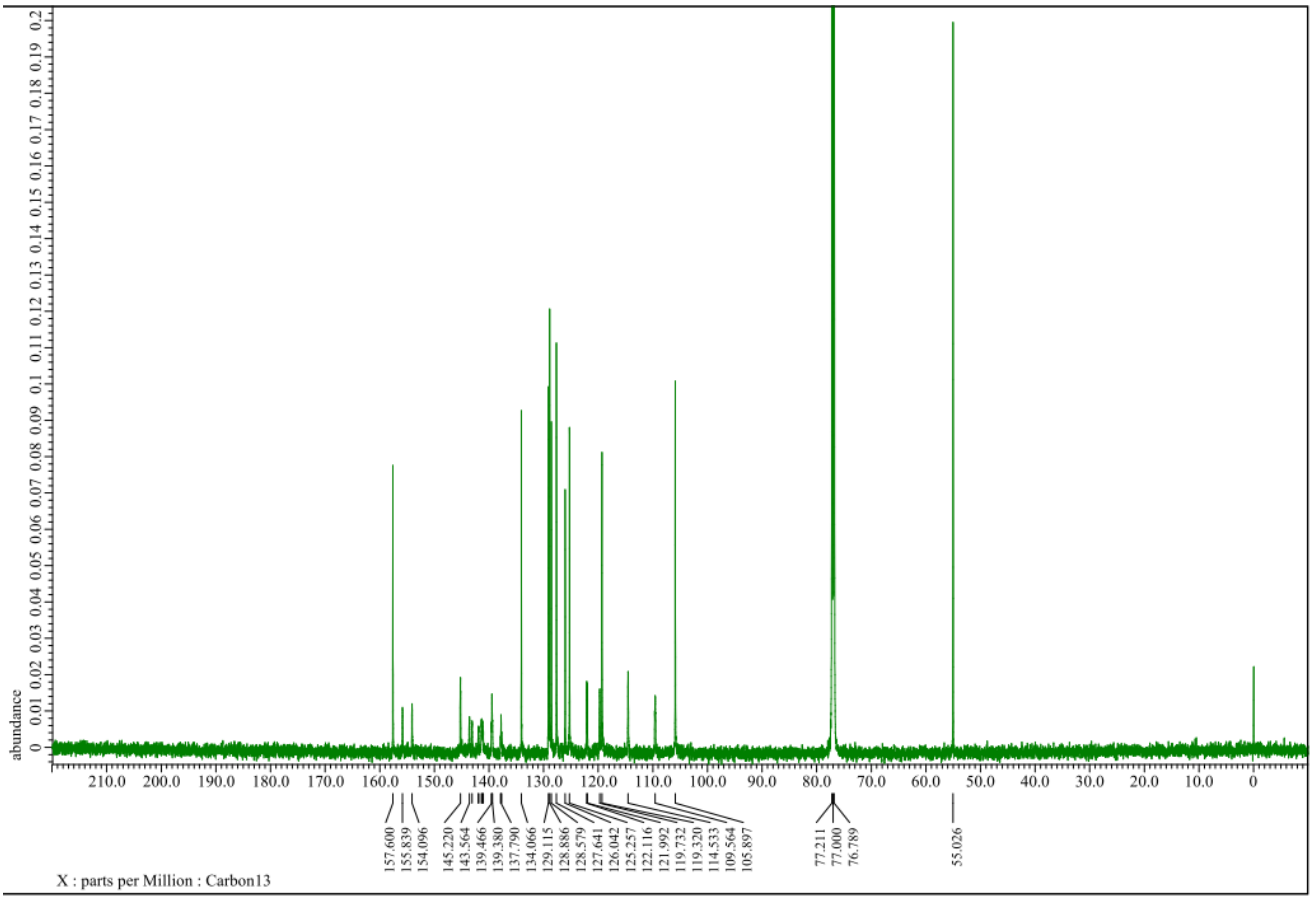
^{19}F NMR (565 MHz) and ^{31}P NMR (243 MHz) spectra of (*R*)-**3c**



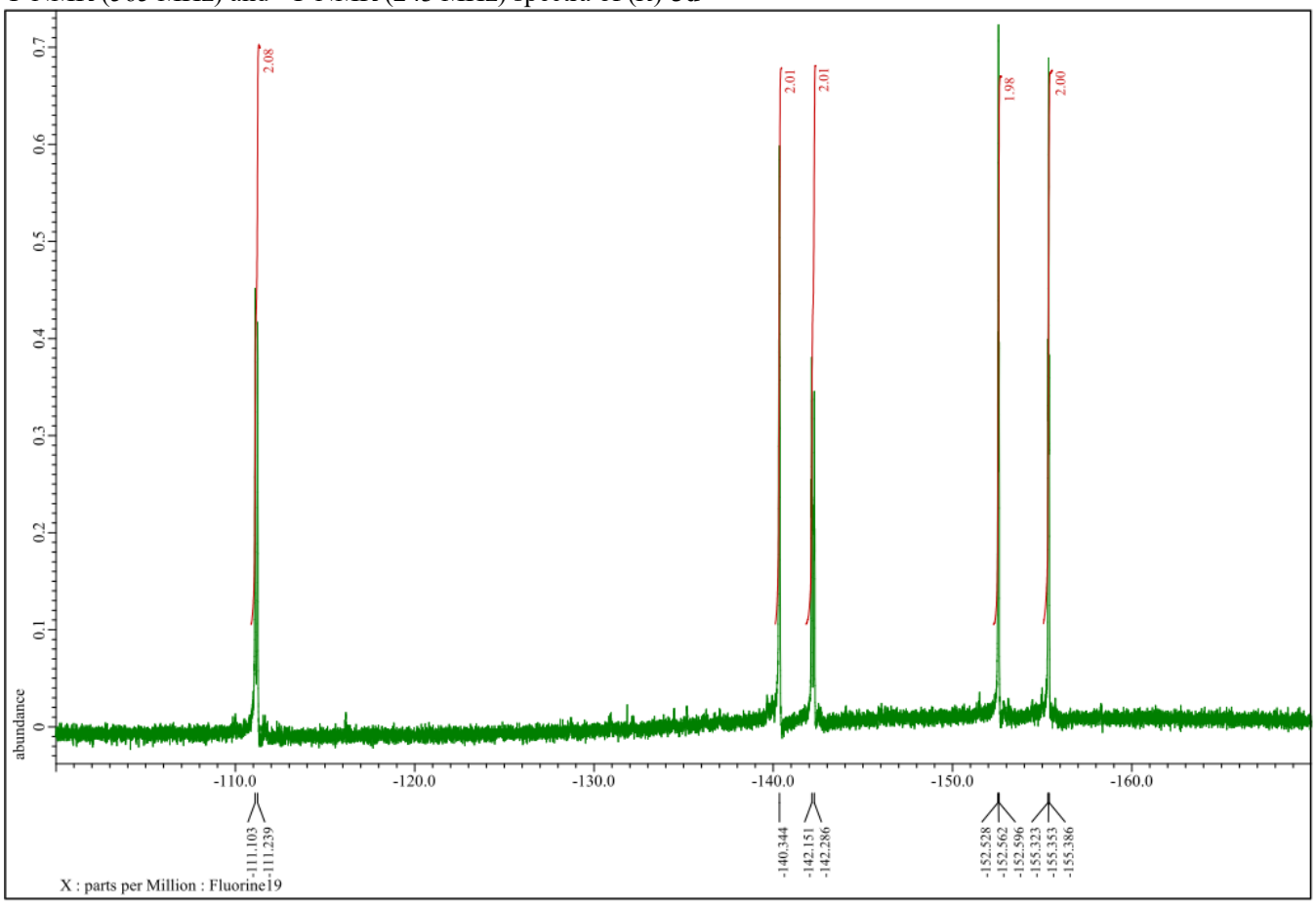


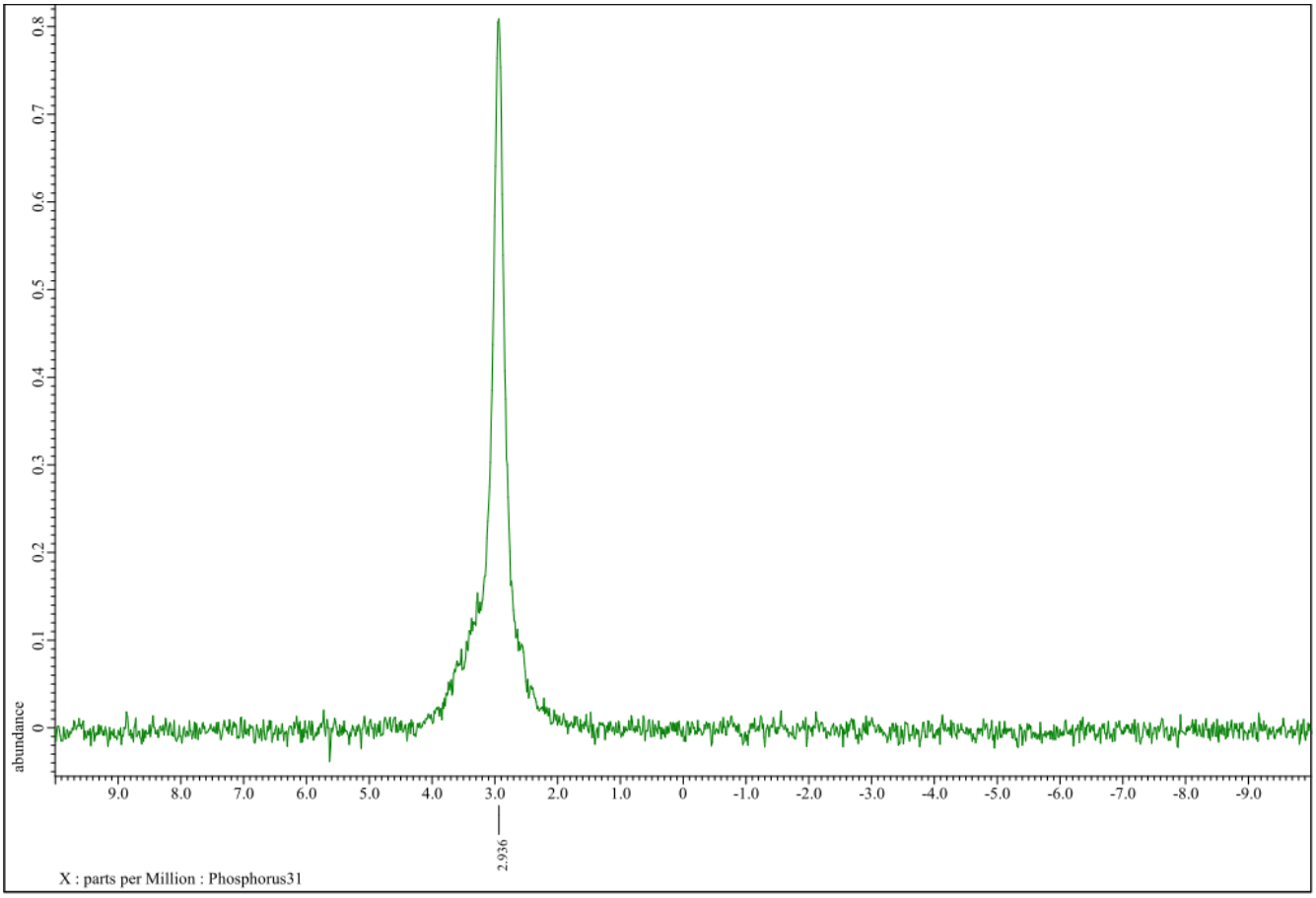
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of (*R*)-**3d**



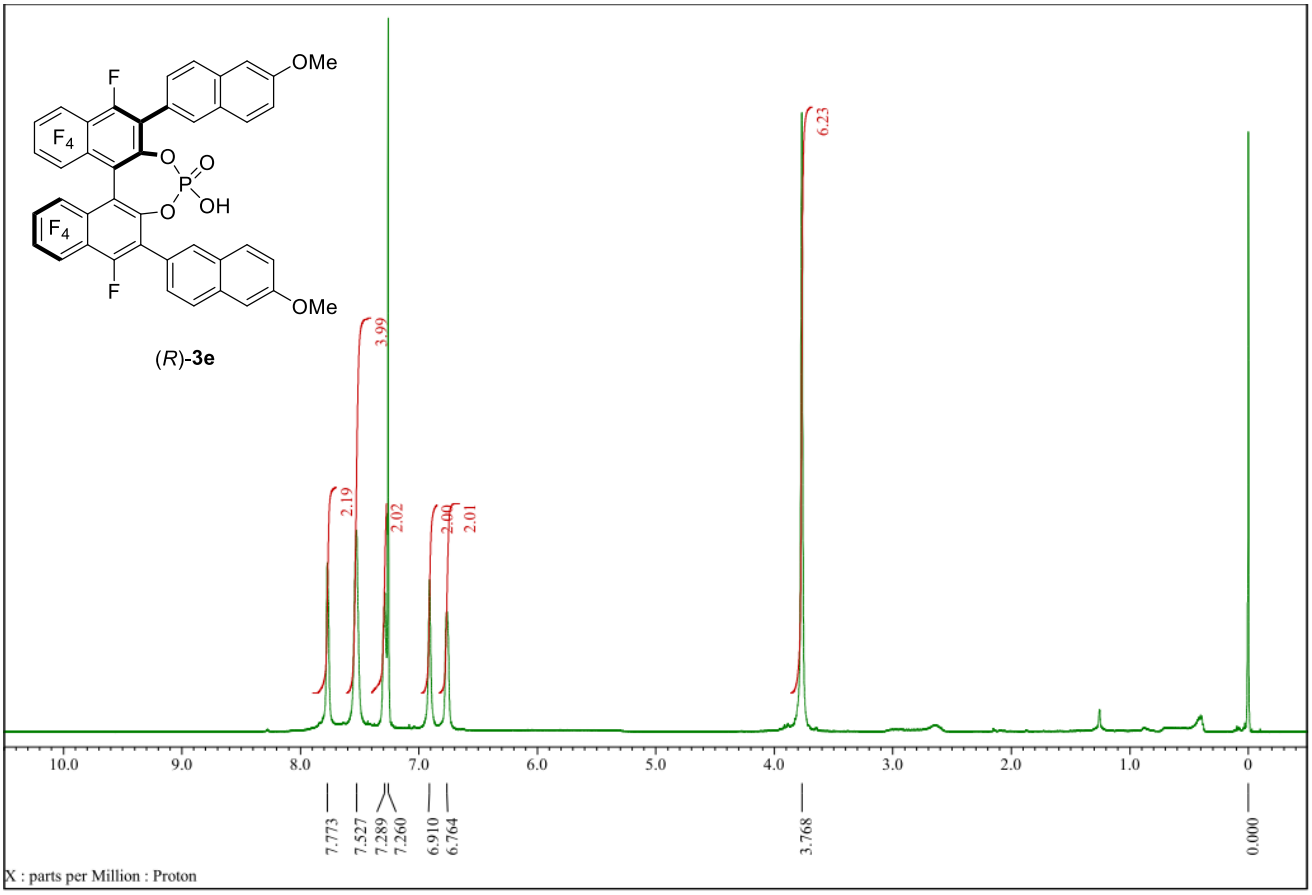


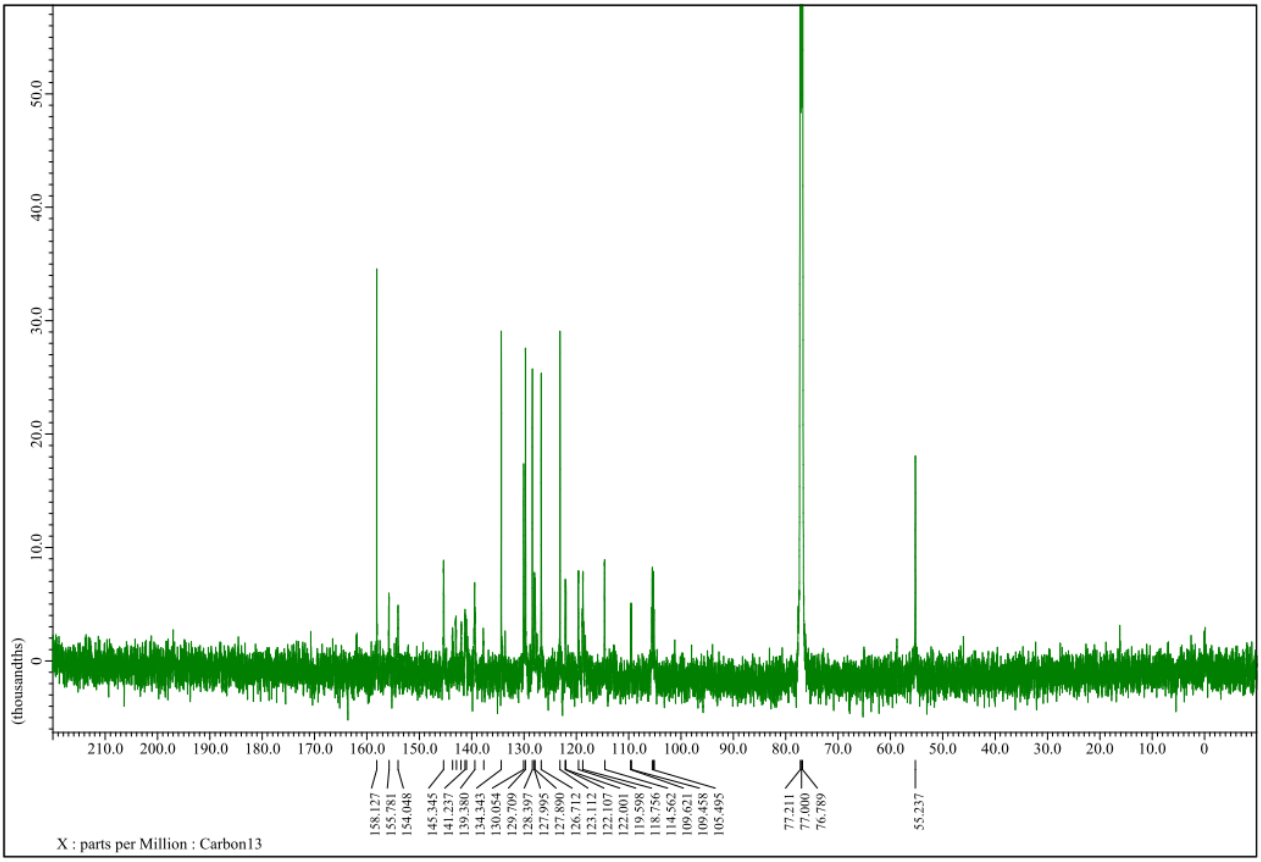
^{19}F NMR (565 MHz) and ^{31}P NMR (243 MHz) spectra of (*R*)-**3d**



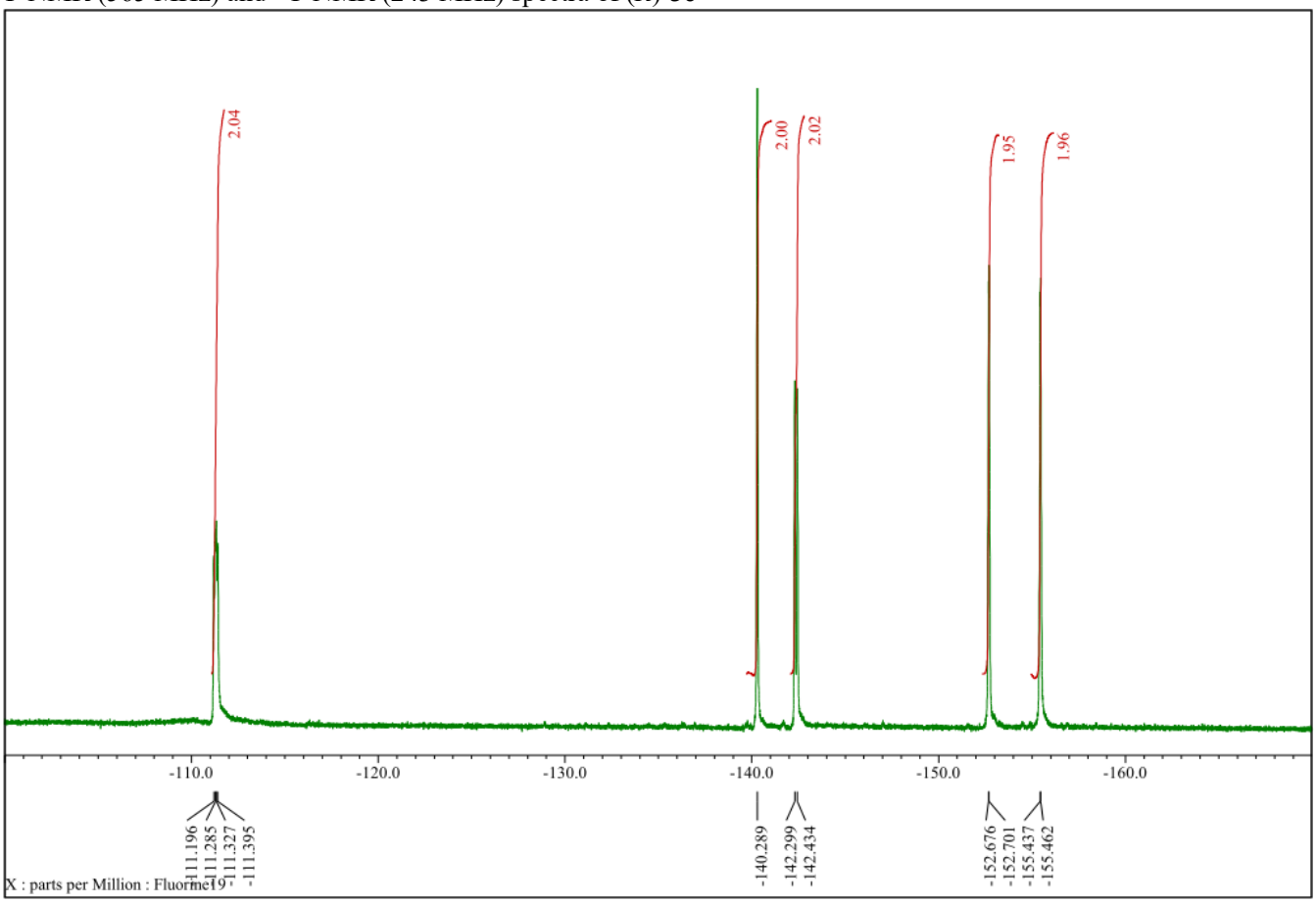


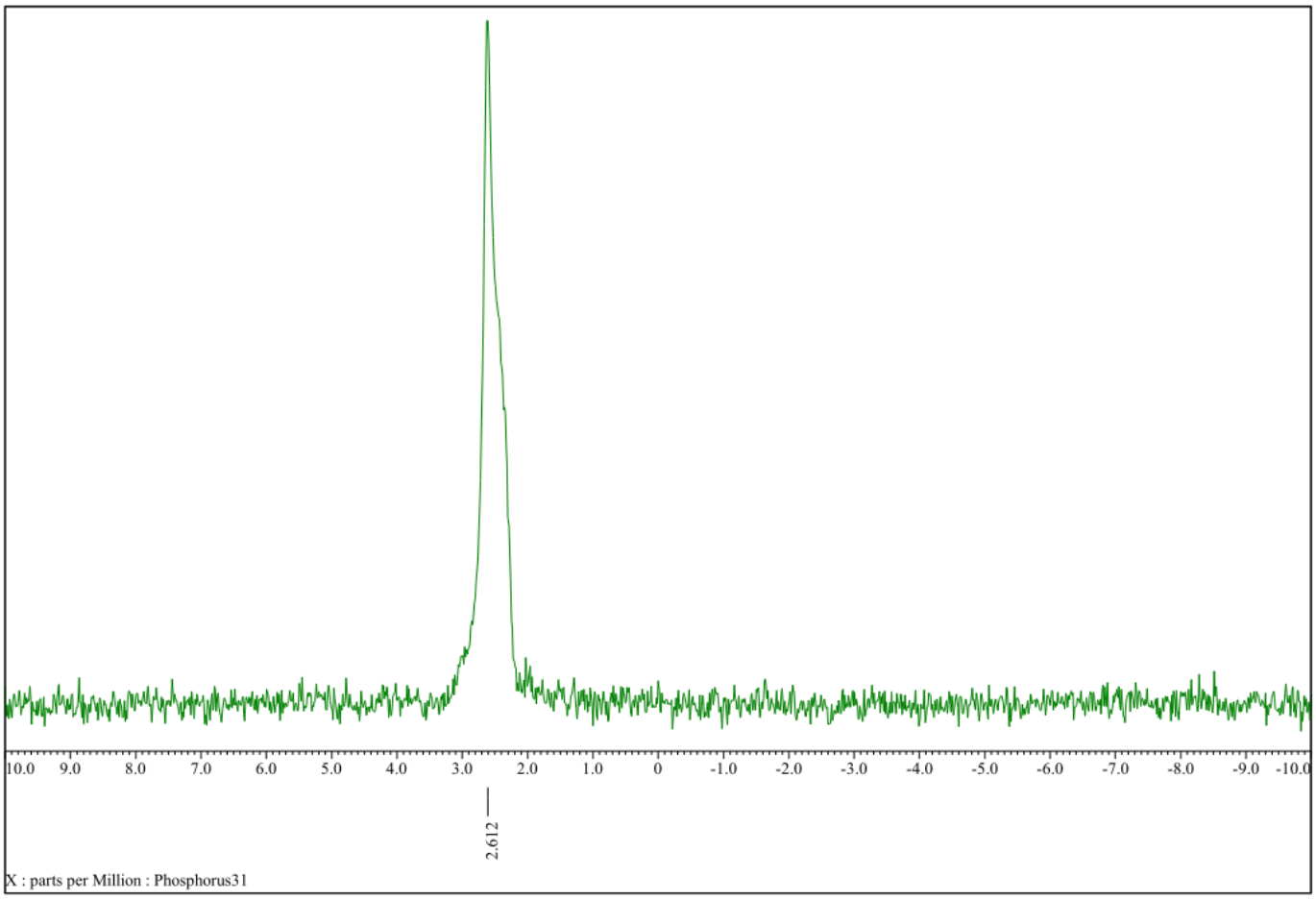
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of (*R*)-**3e**



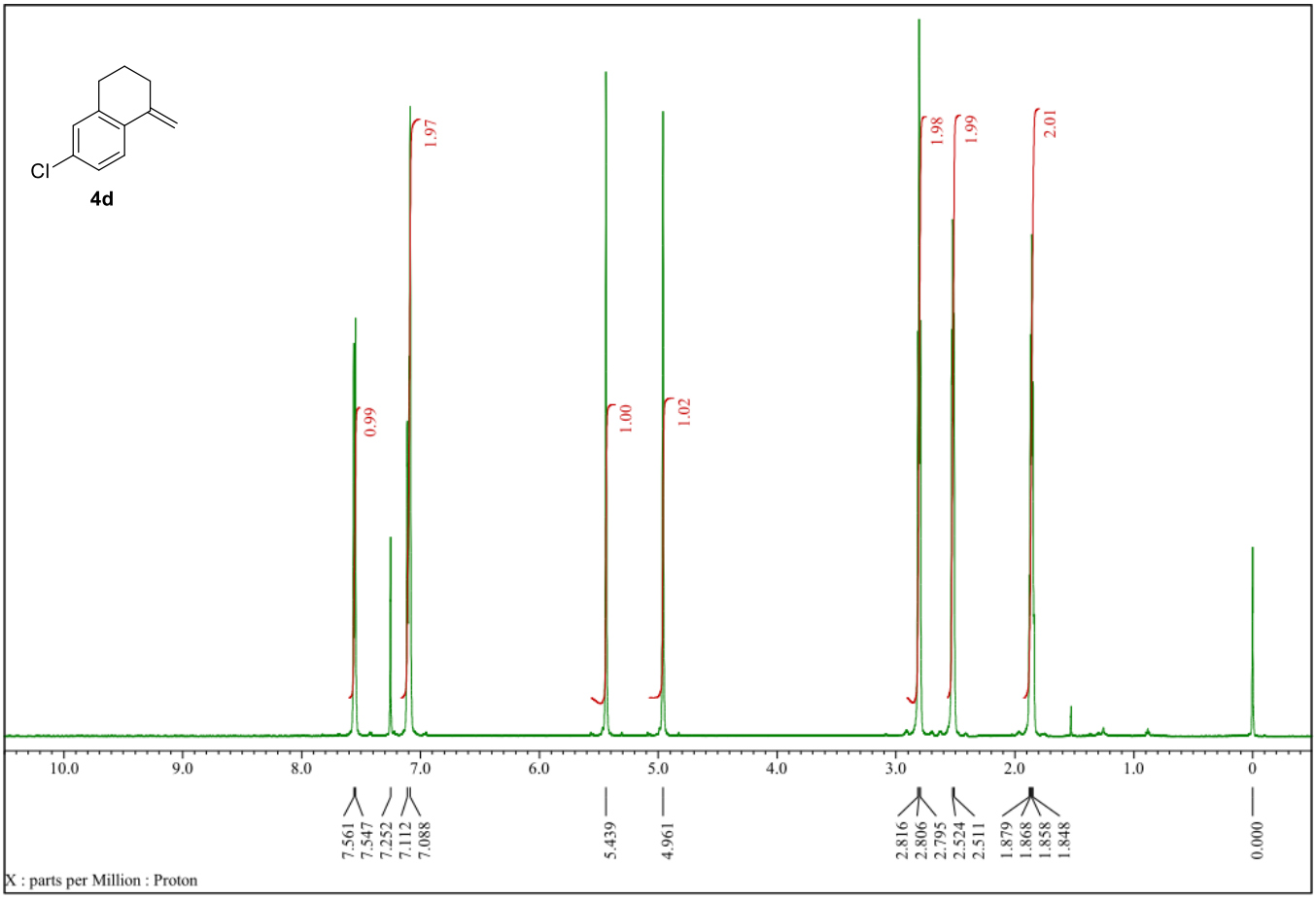


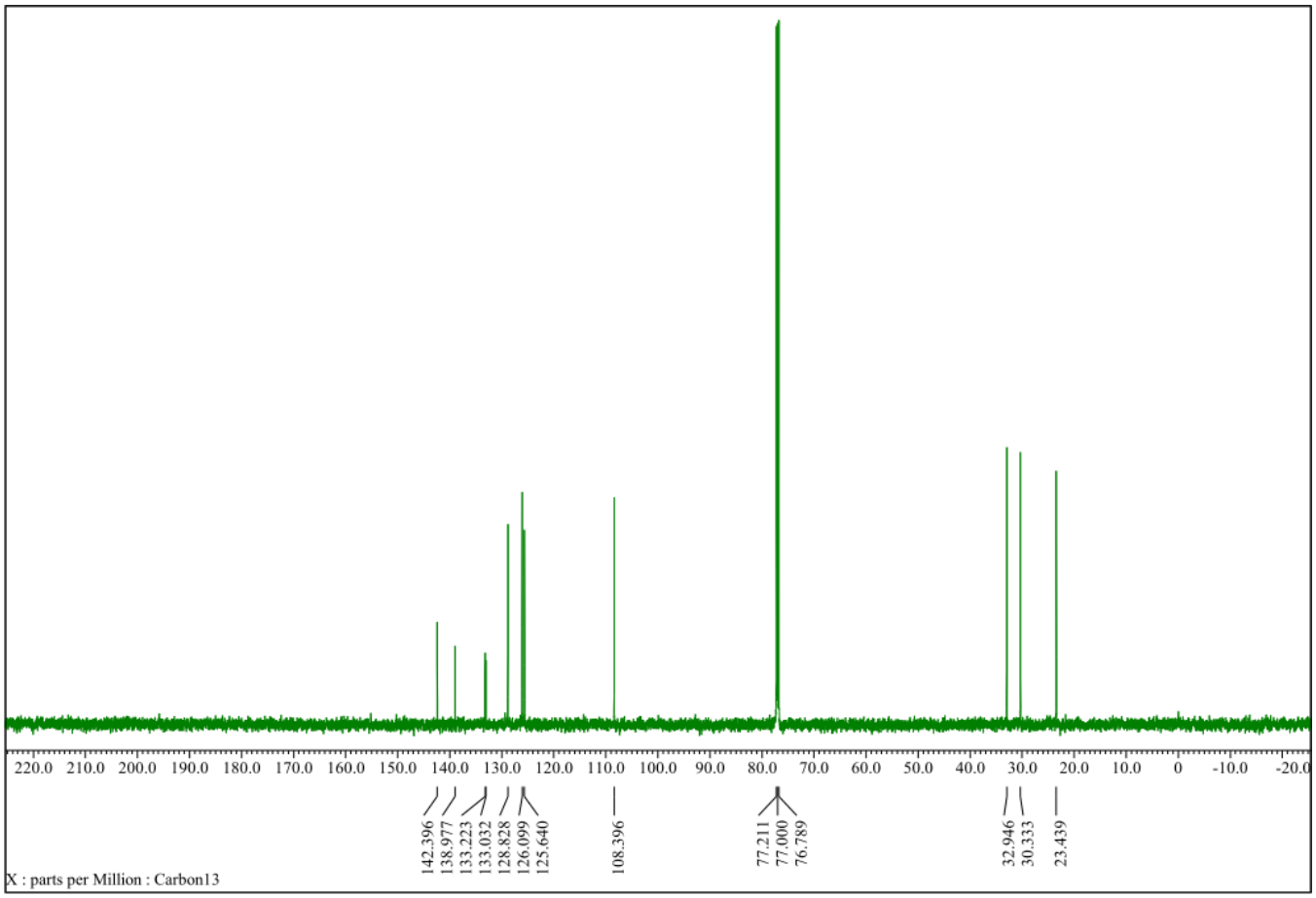
^{19}F NMR (565 MHz) and ^{31}P NMR (243 MHz) spectra of (*R*)-**3e**



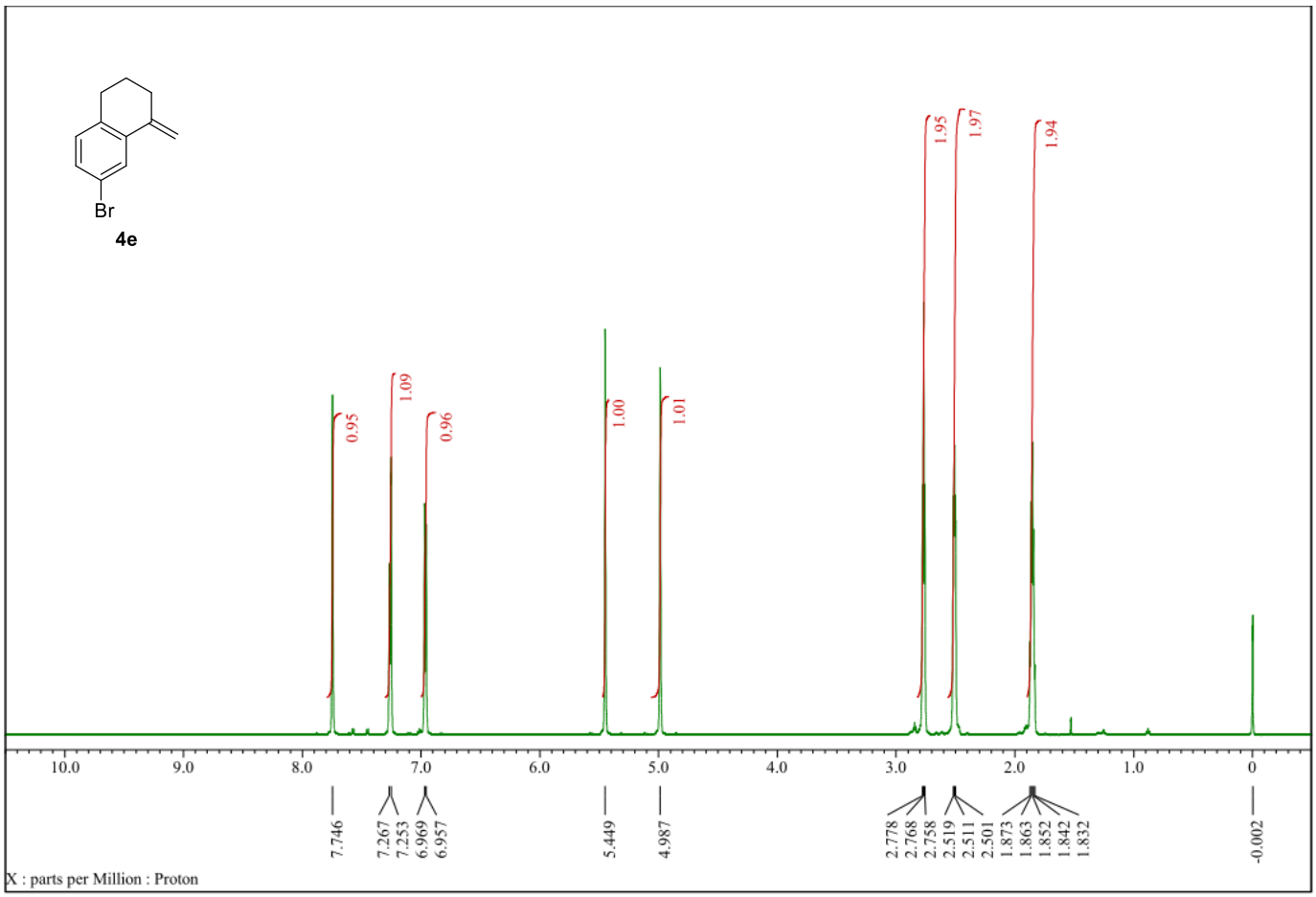


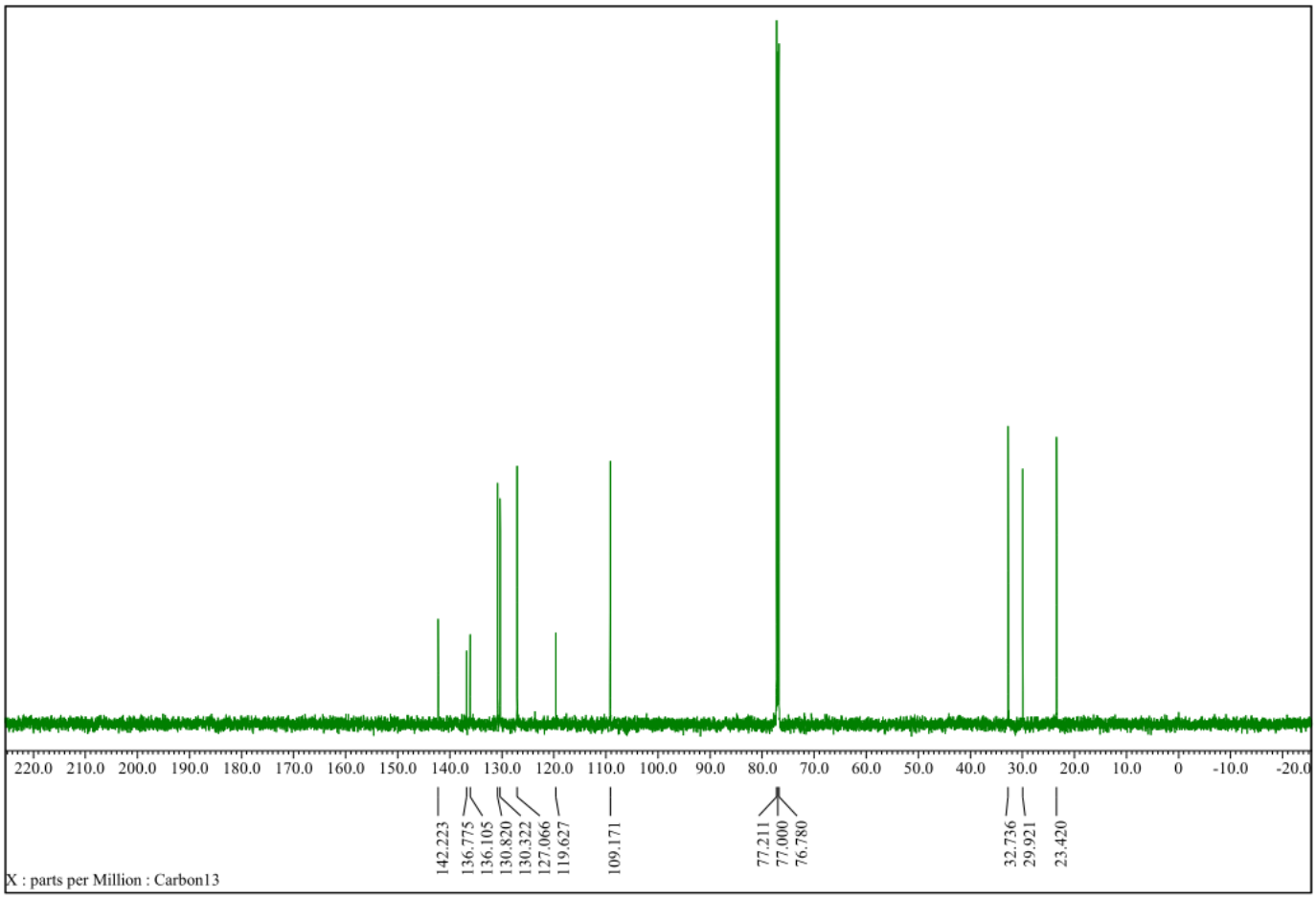
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **4d**



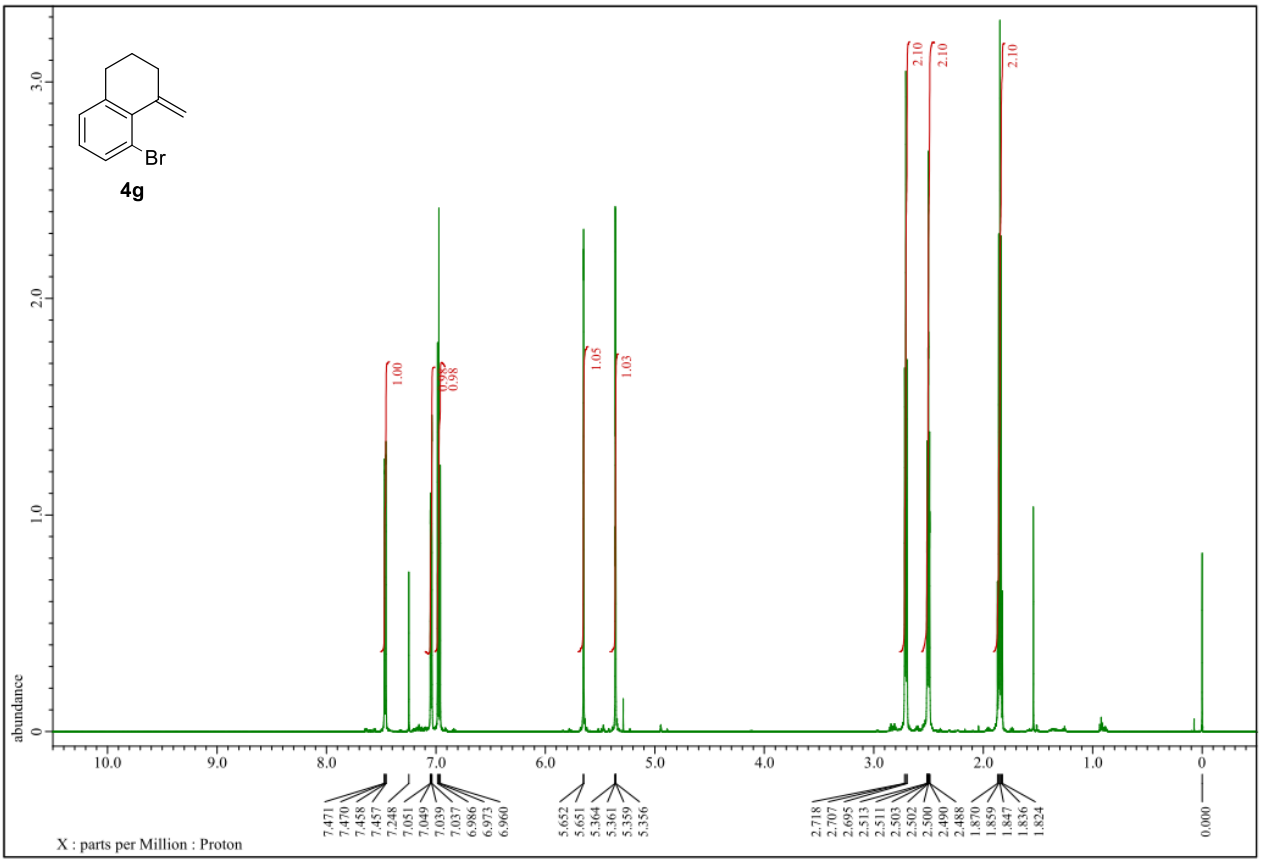


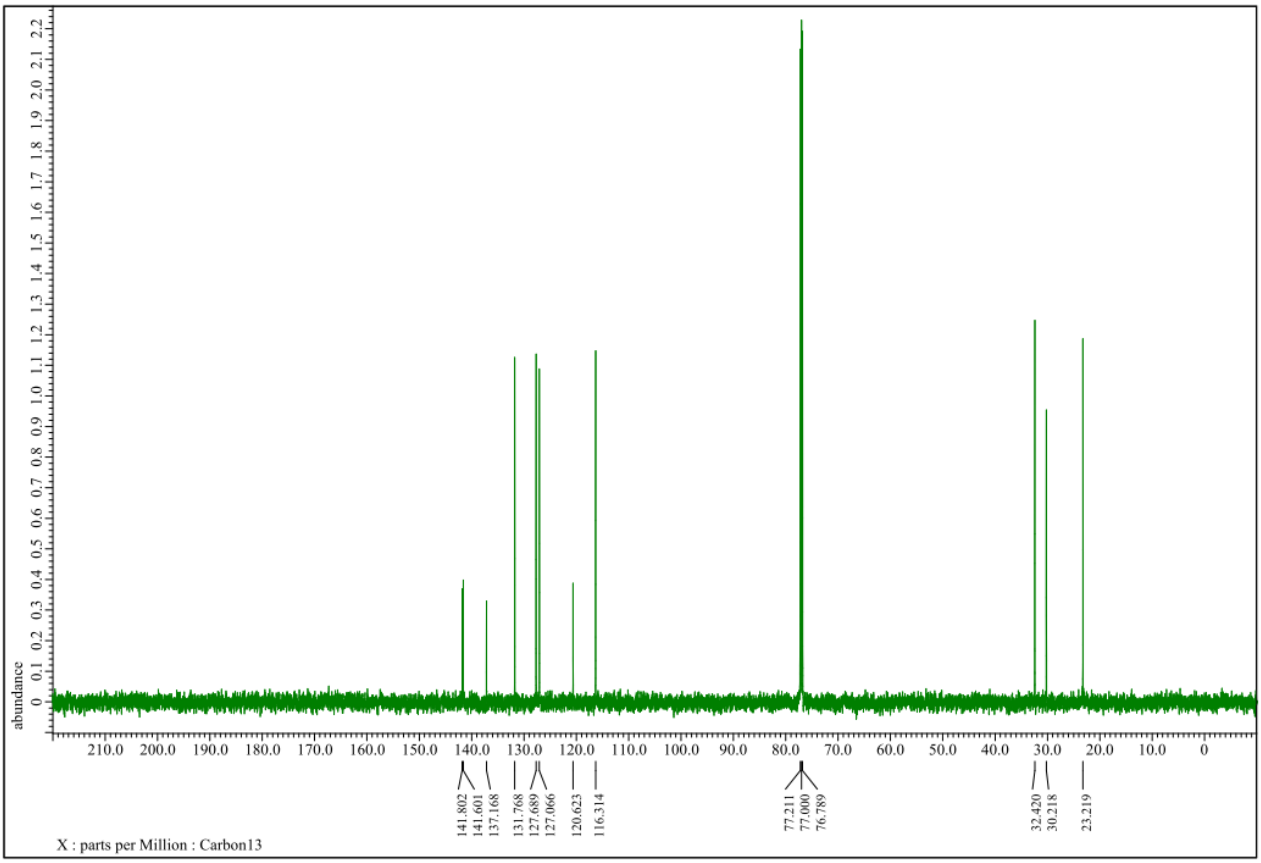
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **4e**



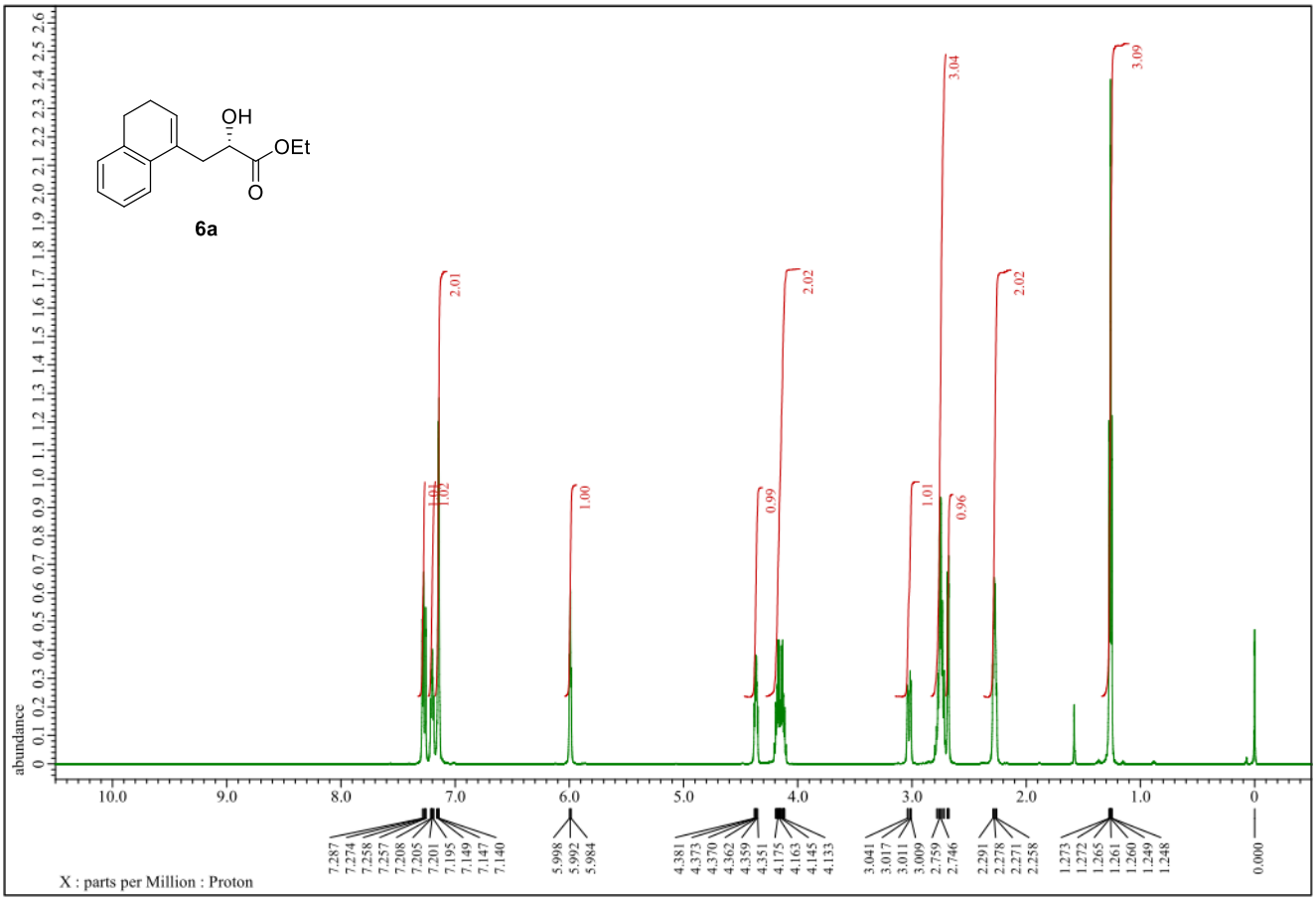


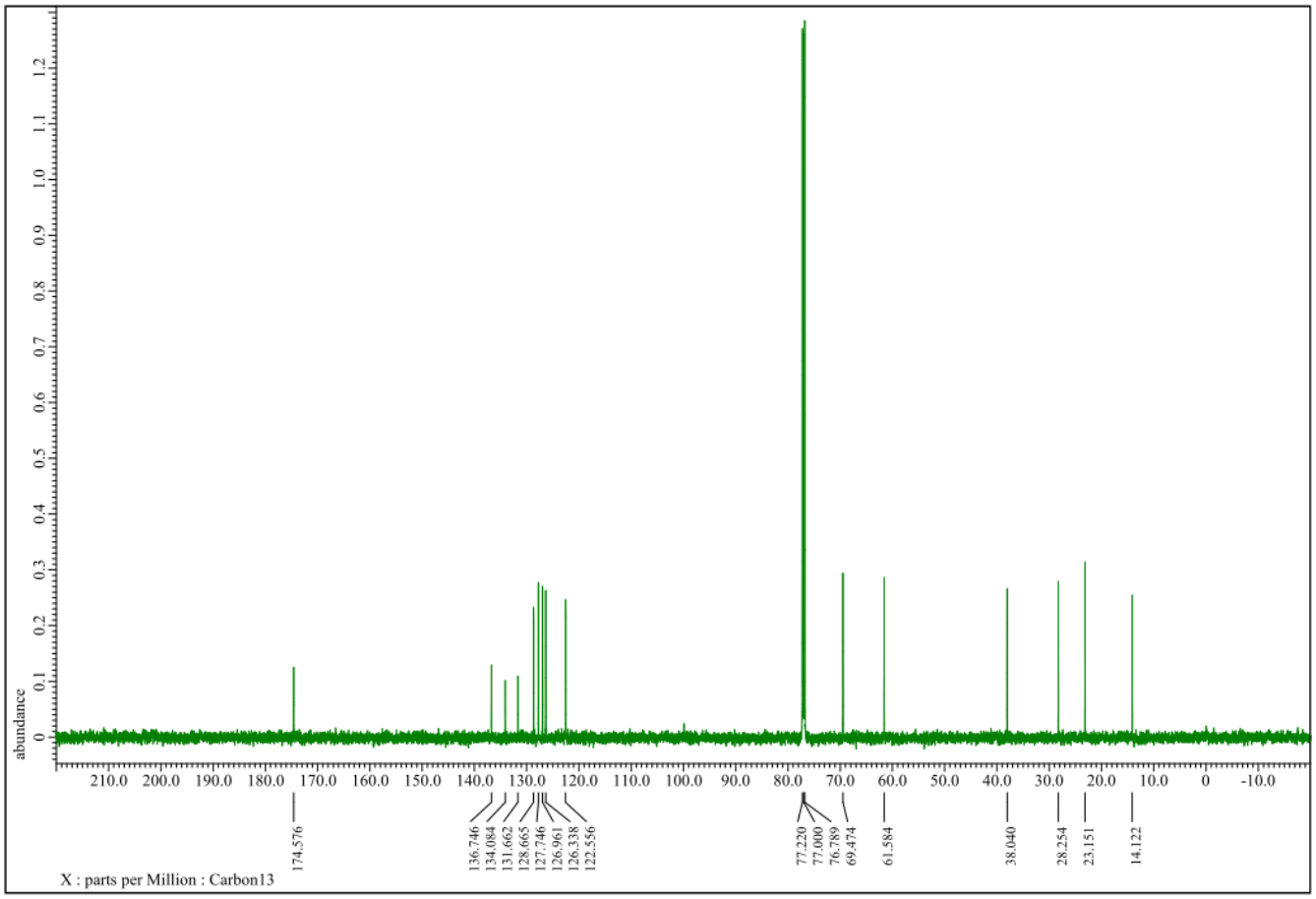
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **4g**



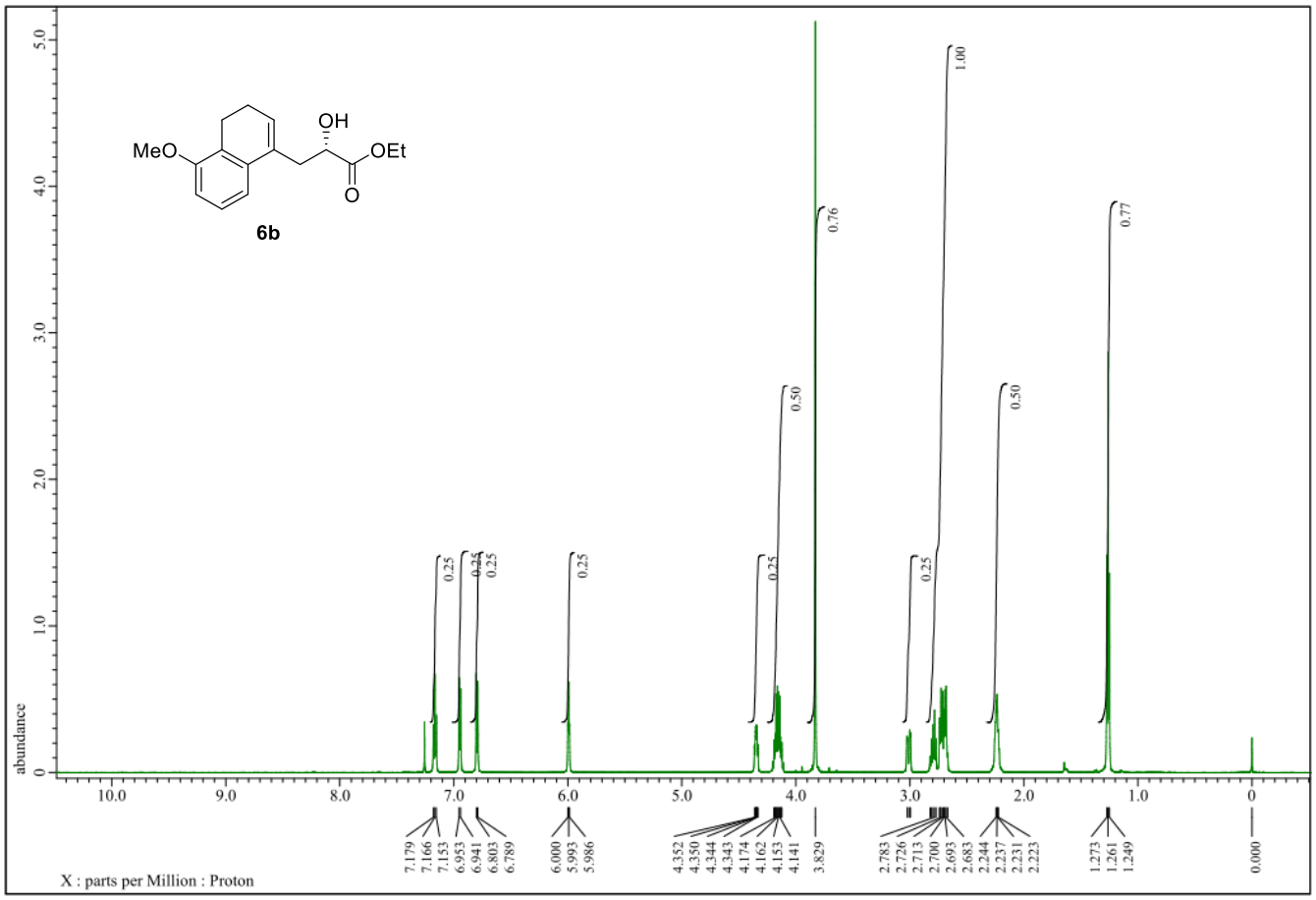


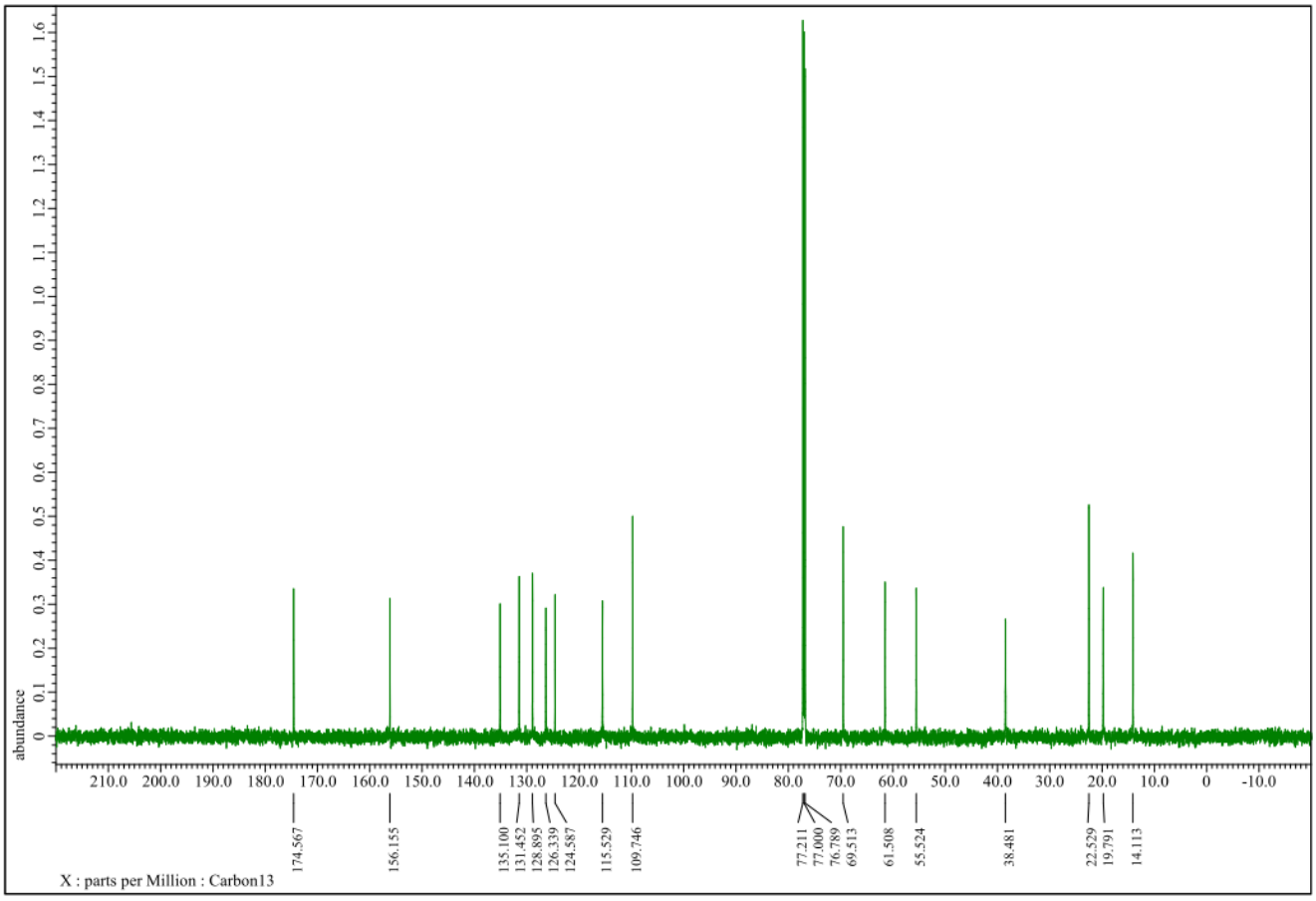
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **6a**





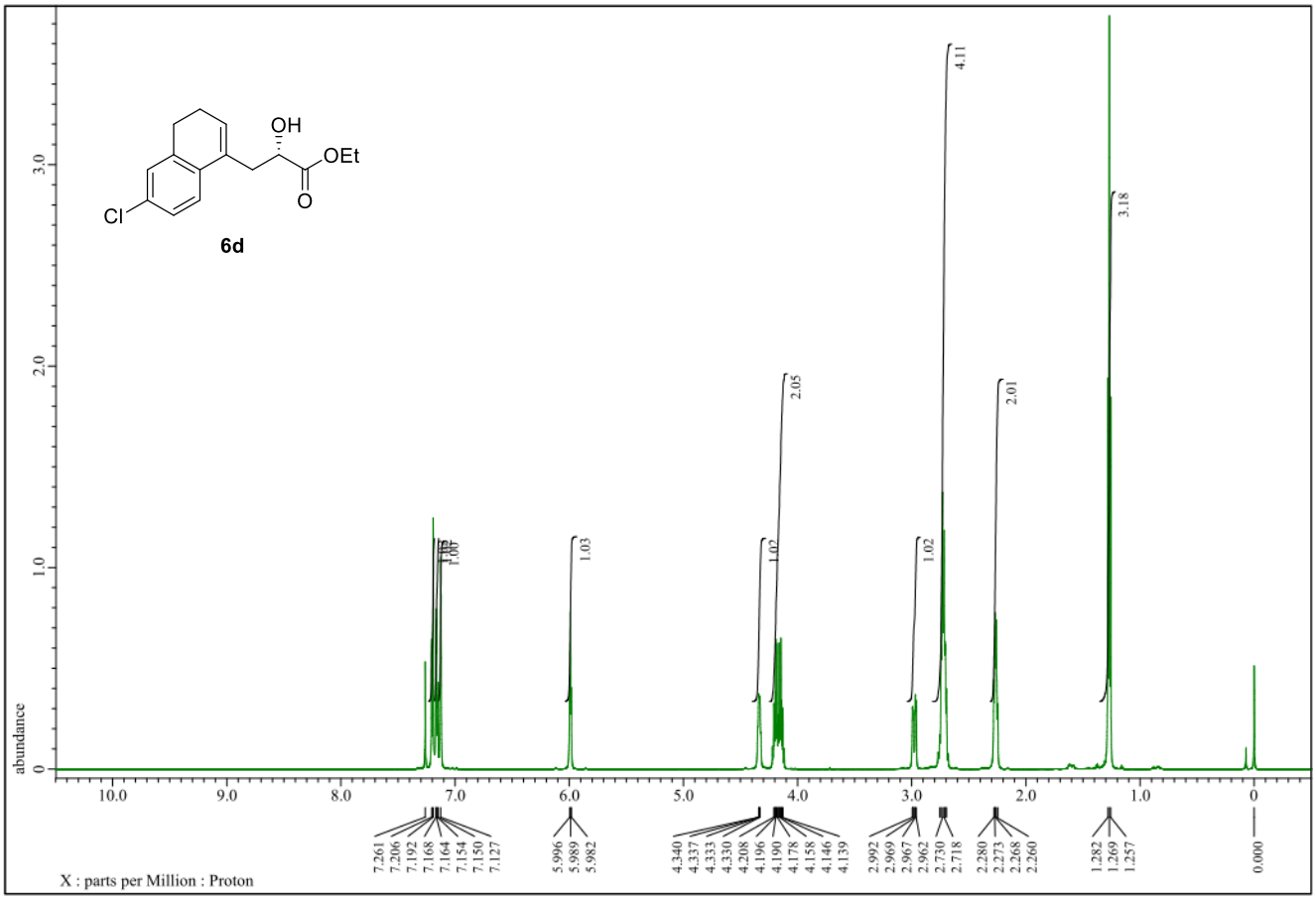
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **6b**

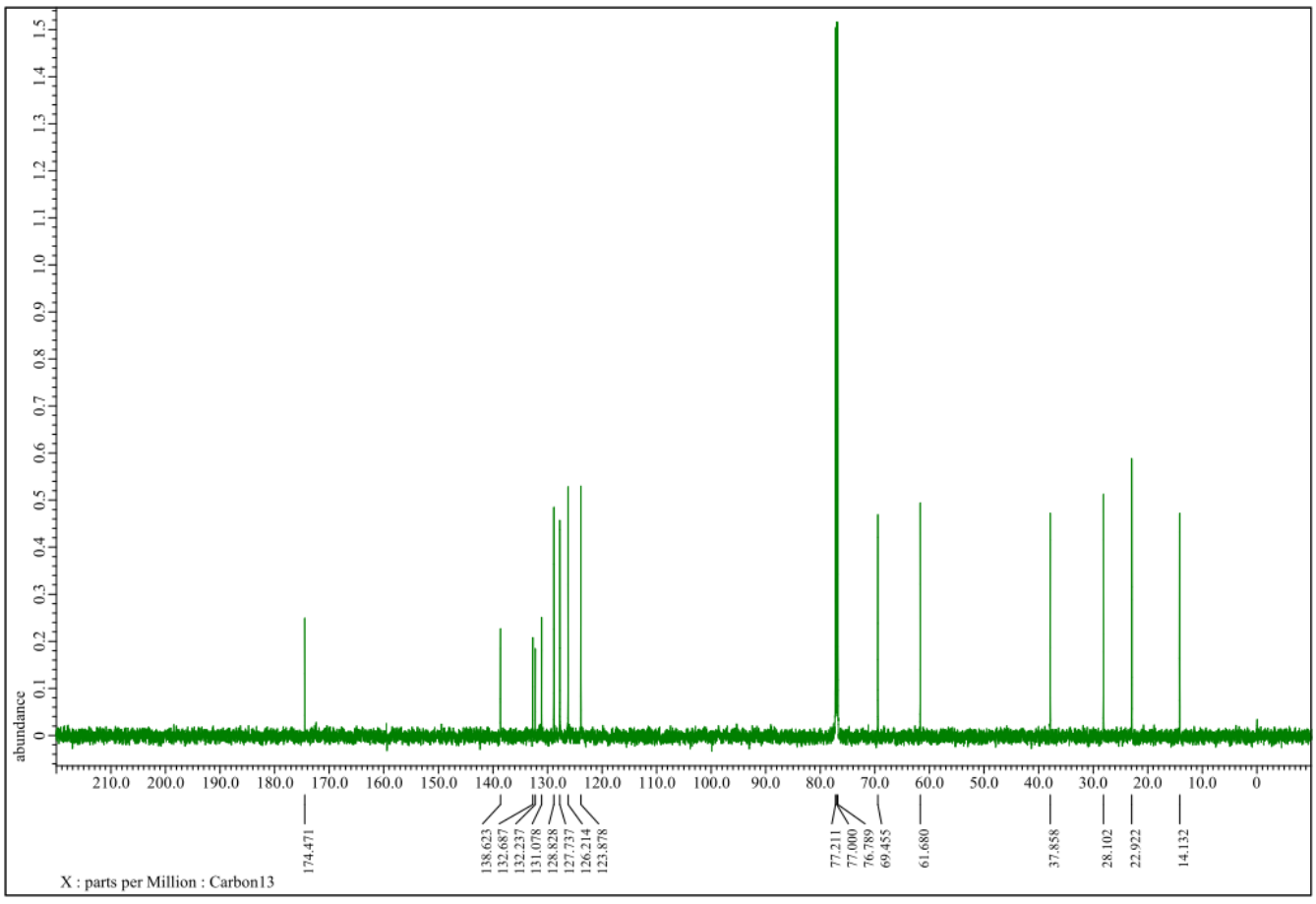




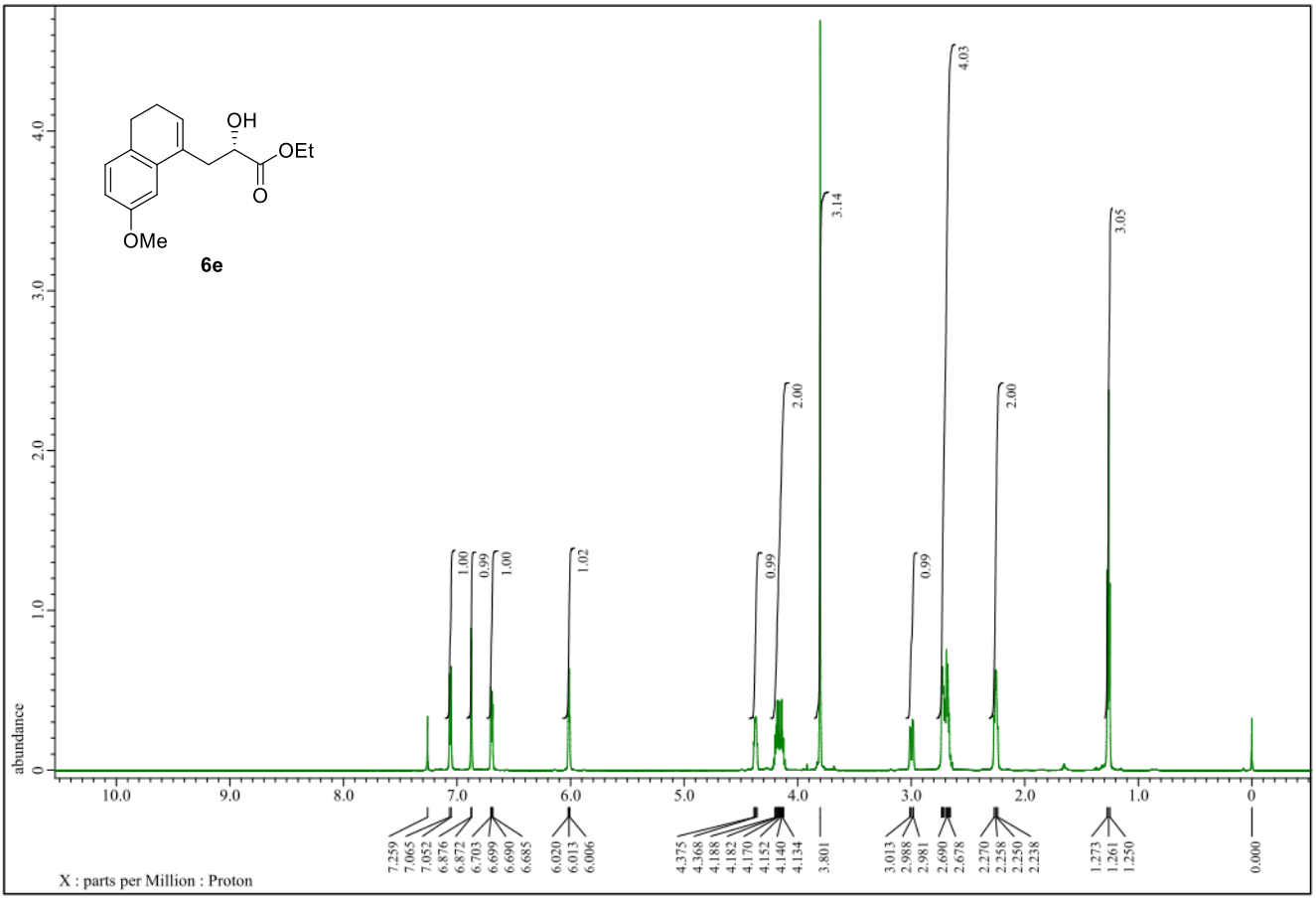
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **6c**

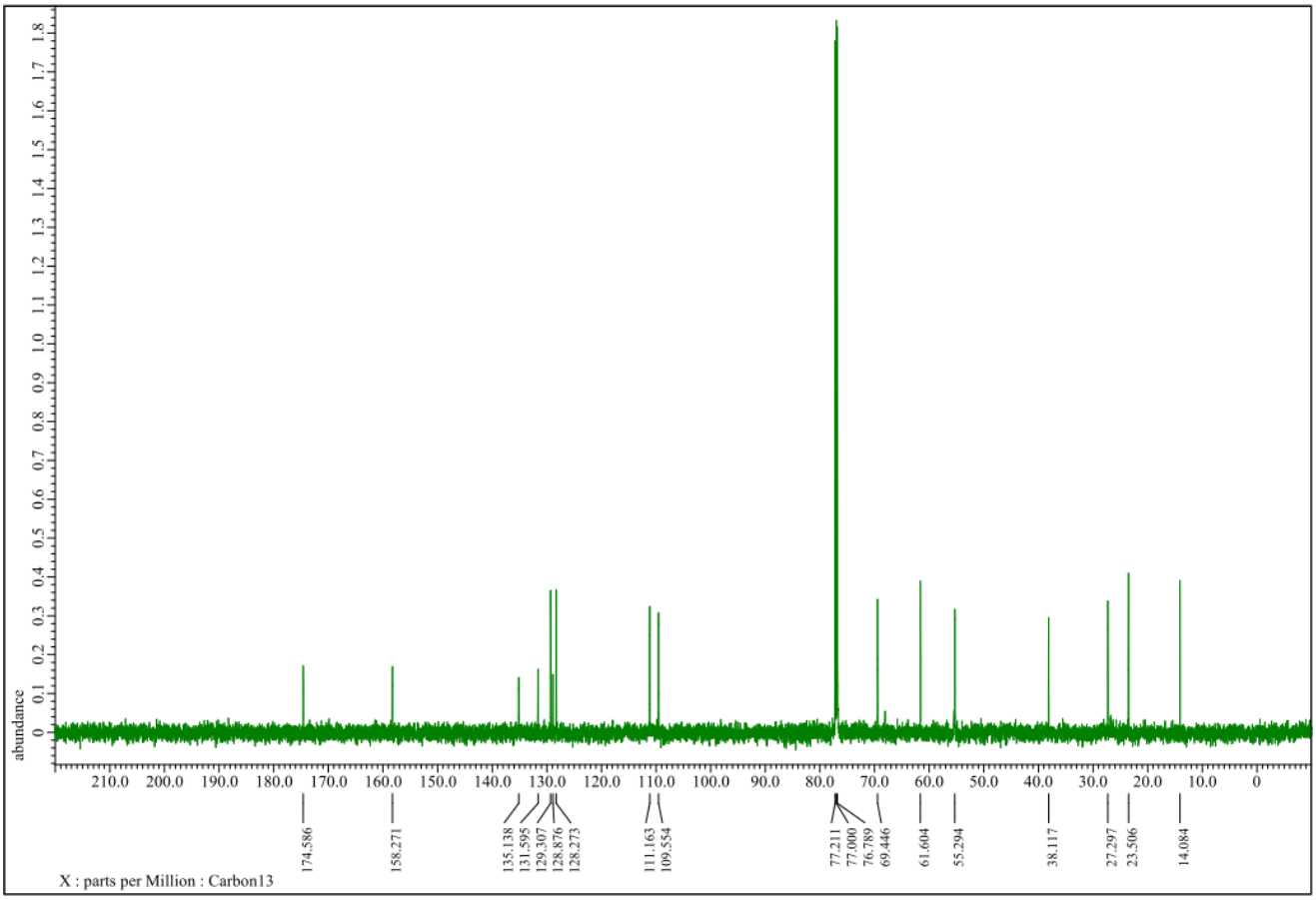
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **6d**



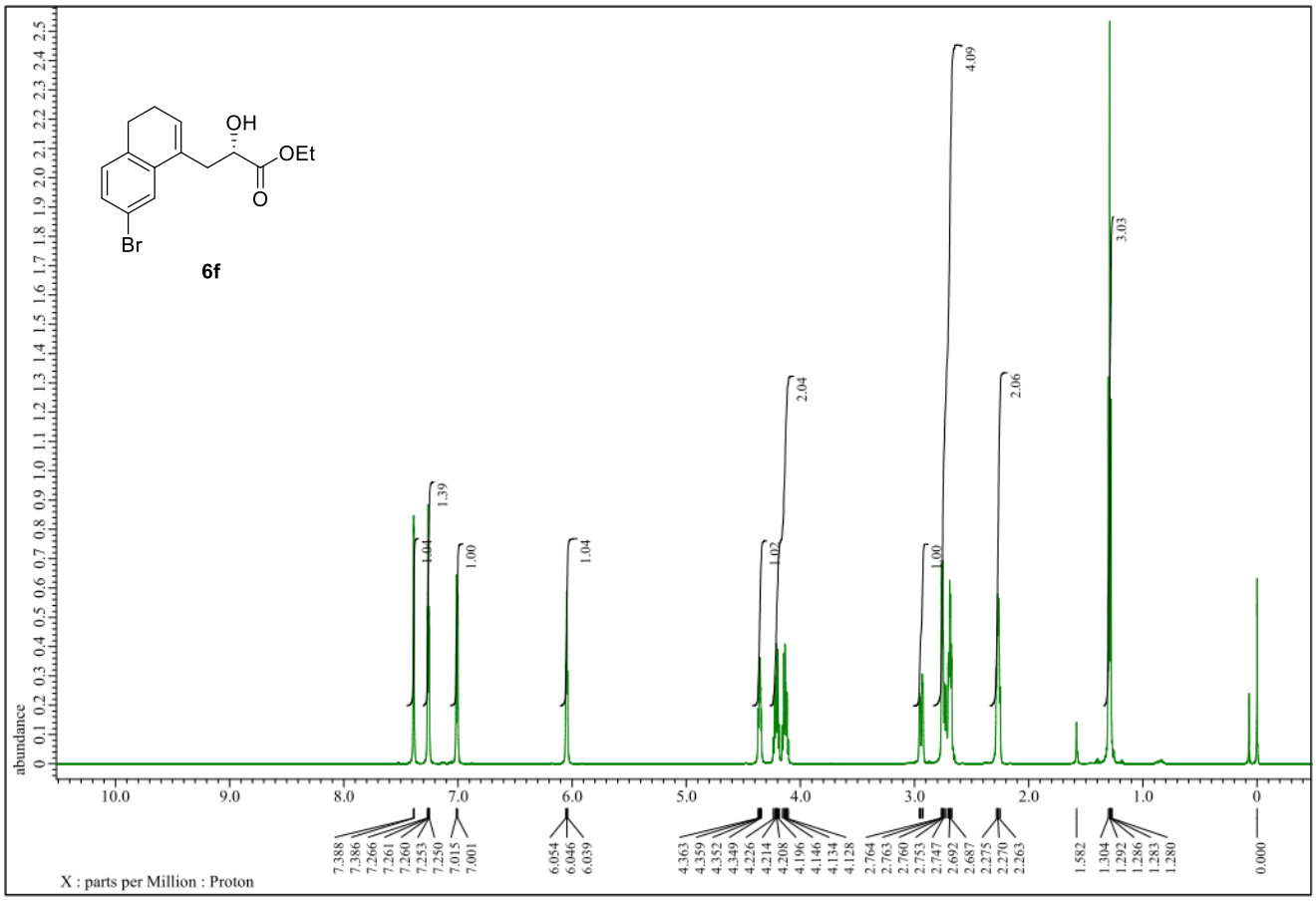


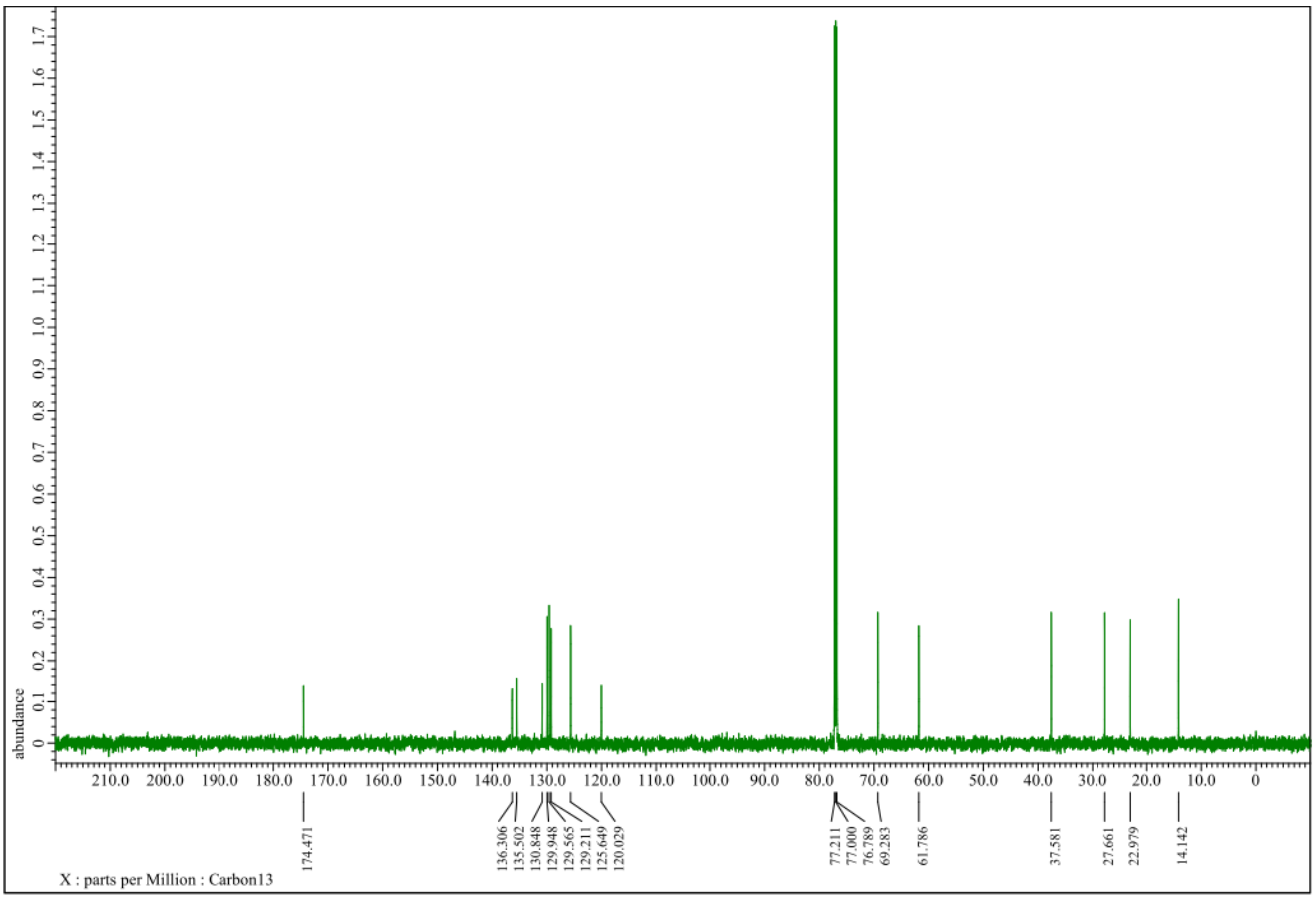
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **6e**



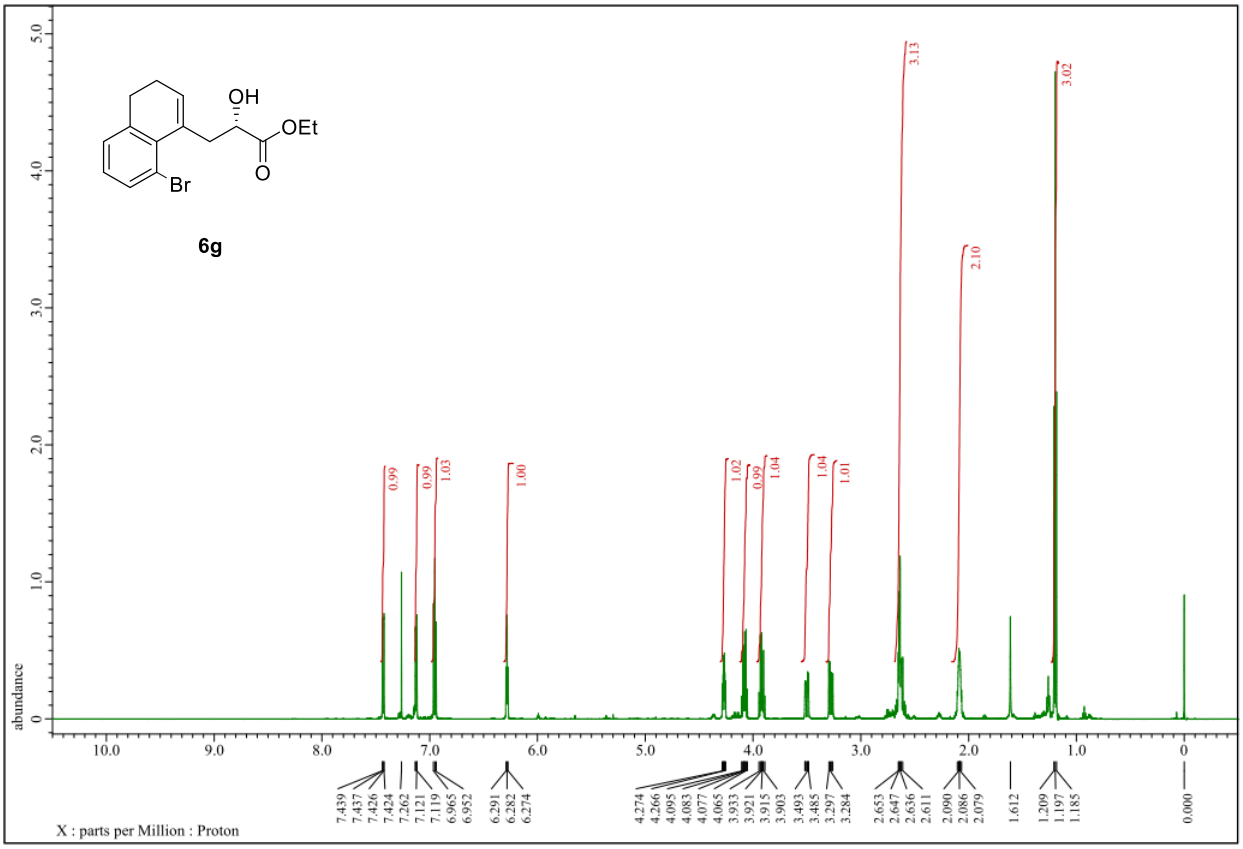


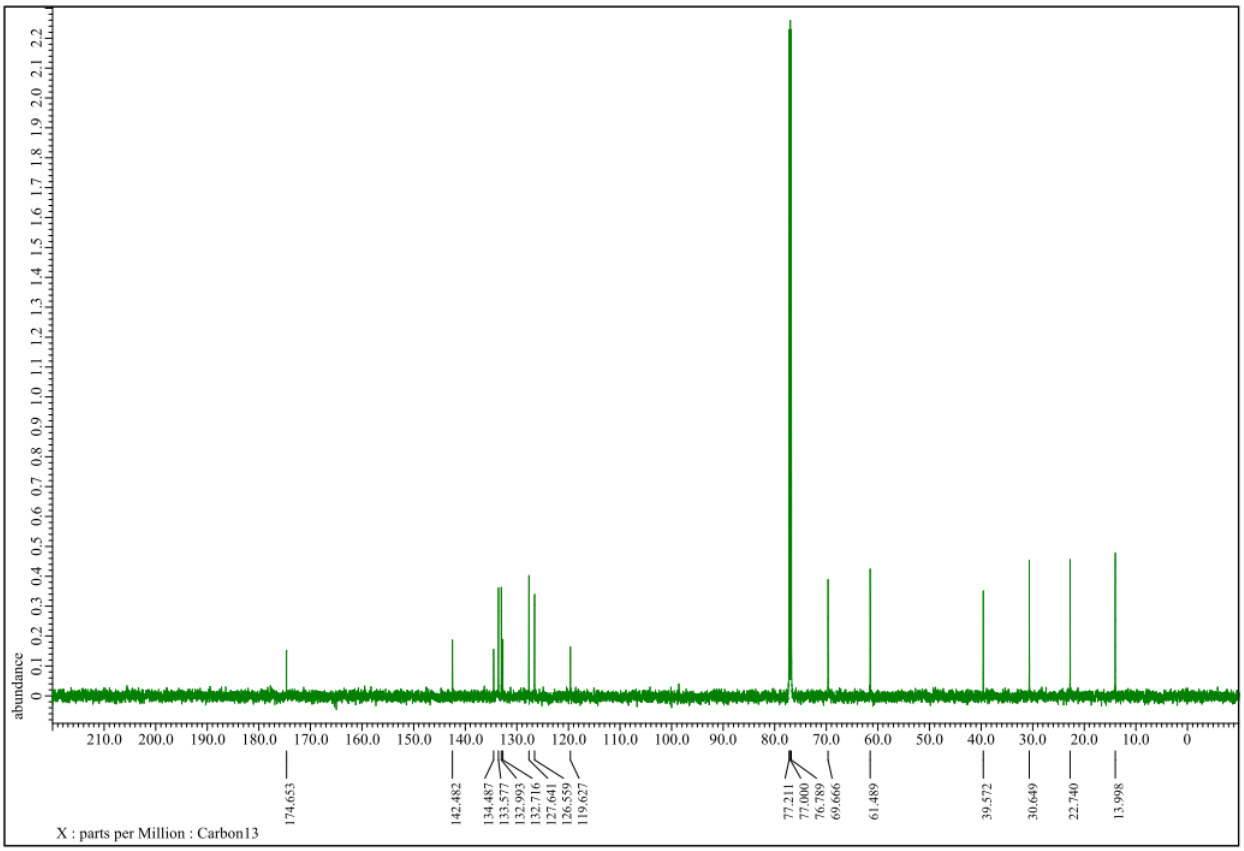
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **6f**



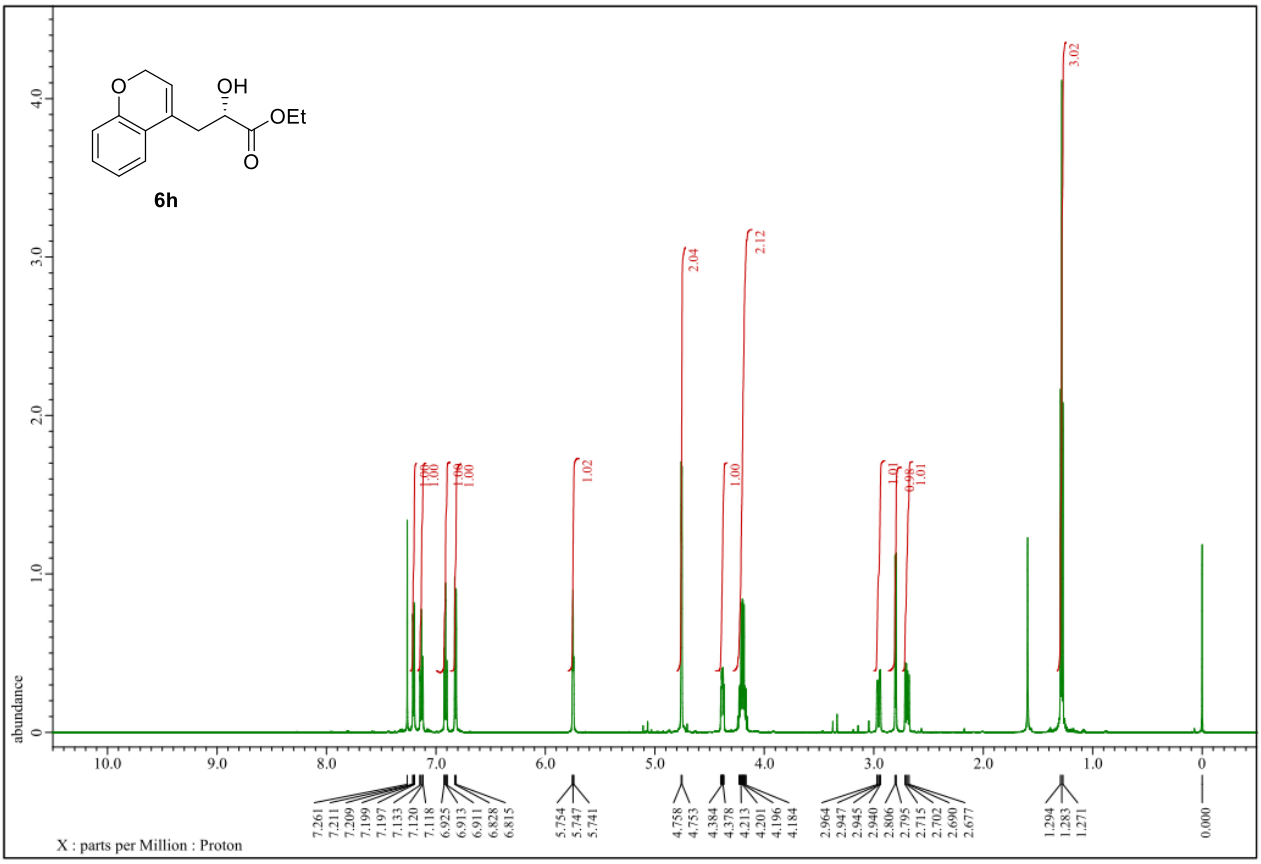


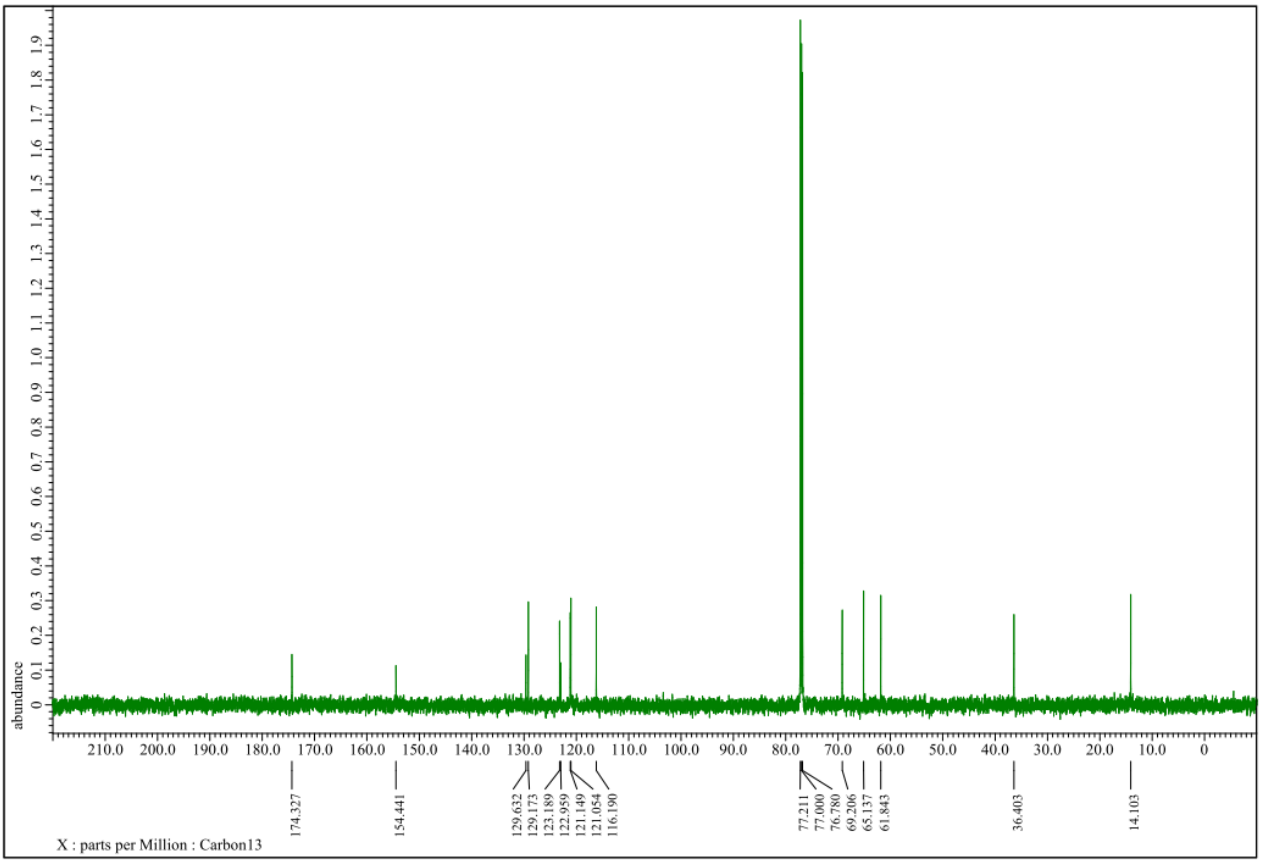
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **6g**



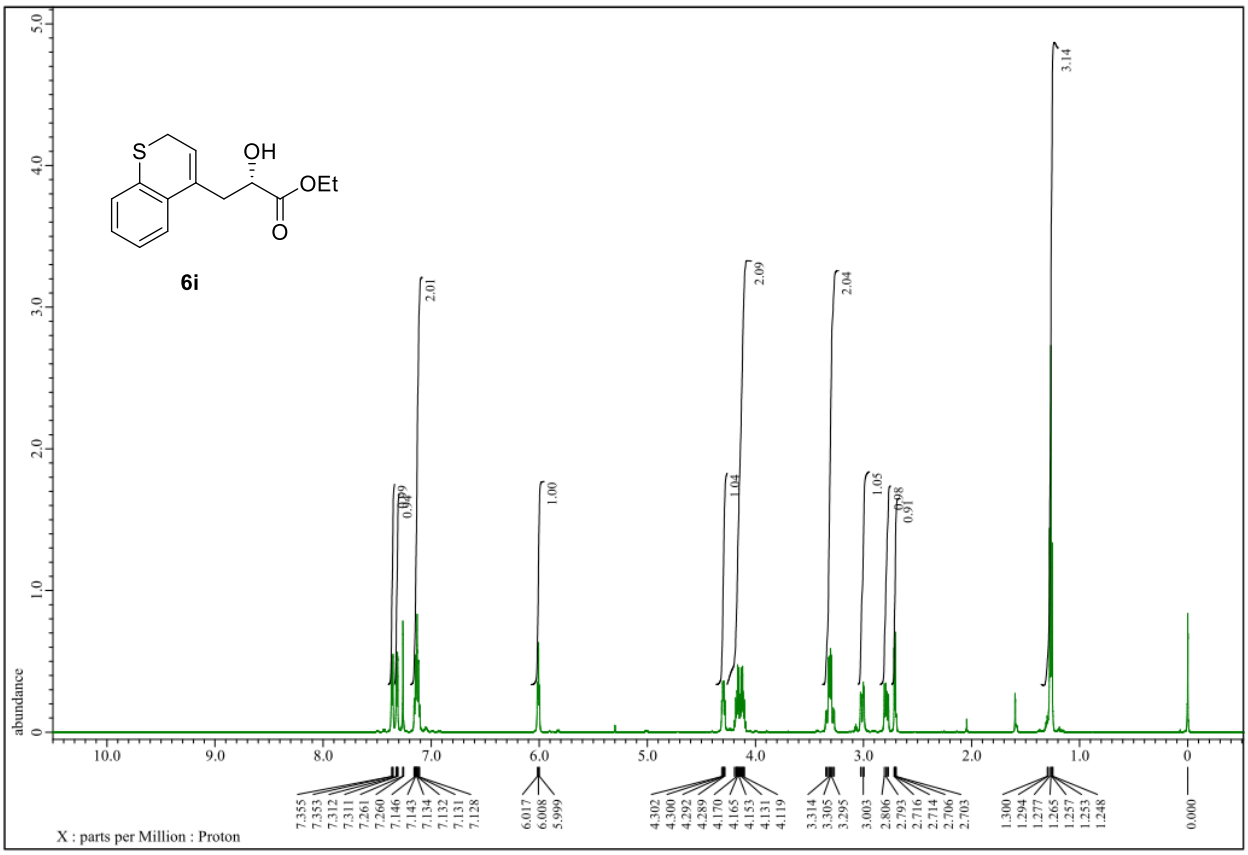


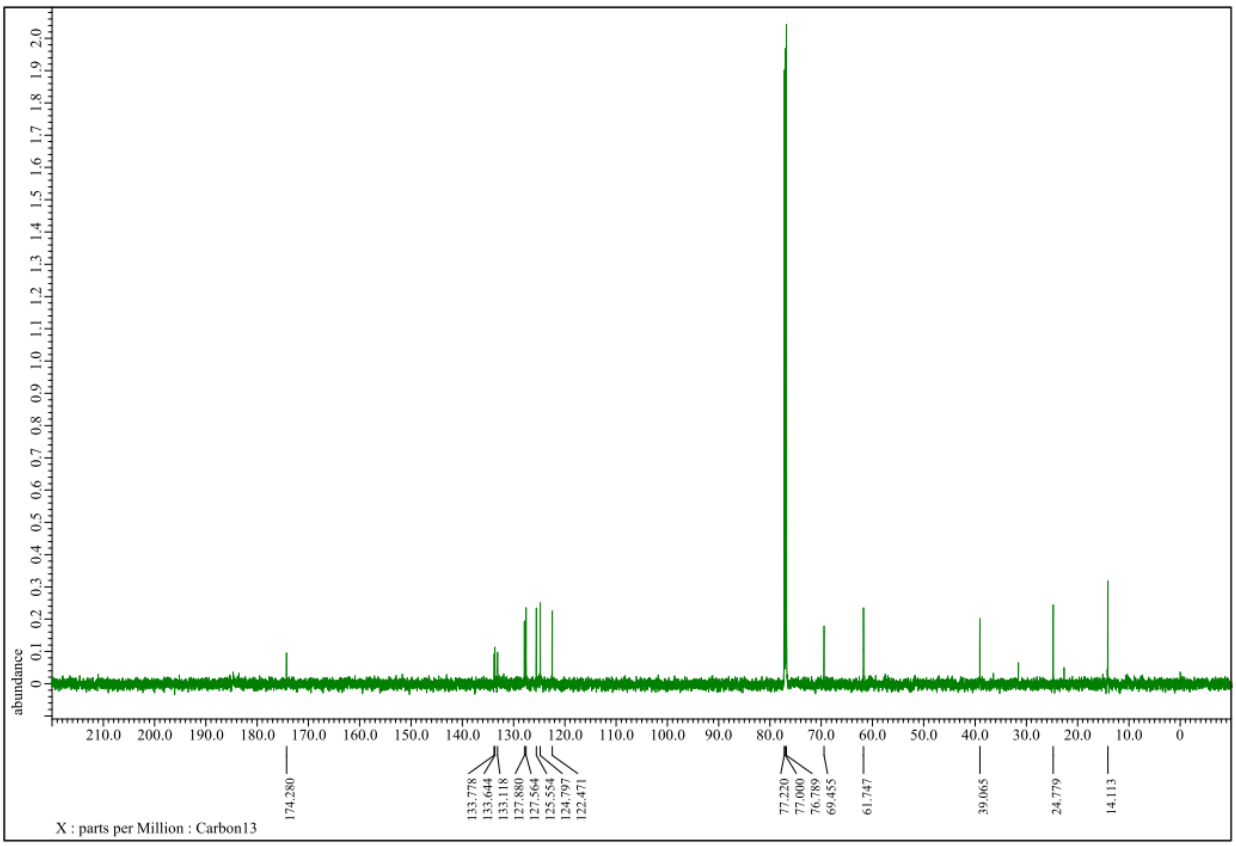
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **6h**



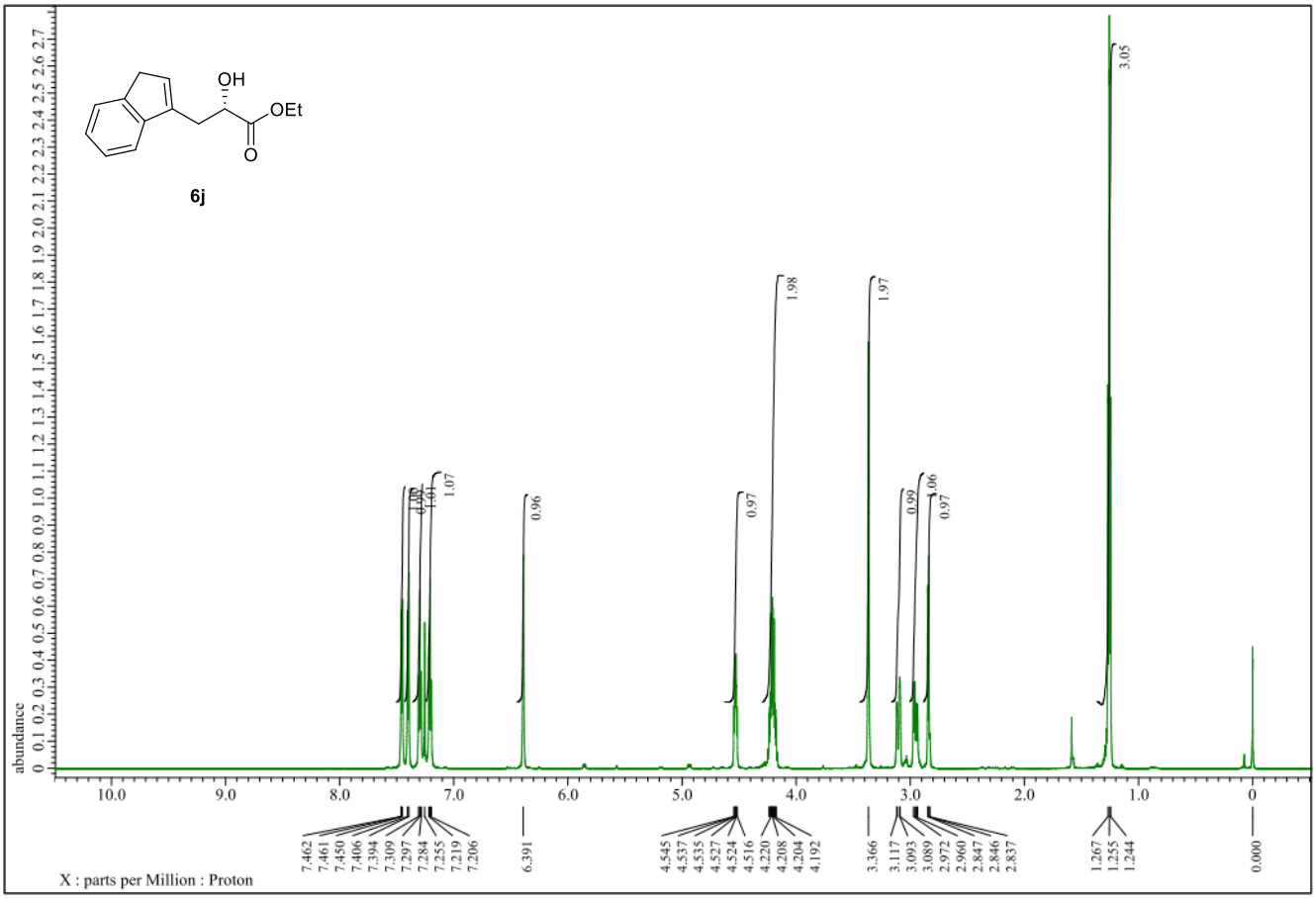


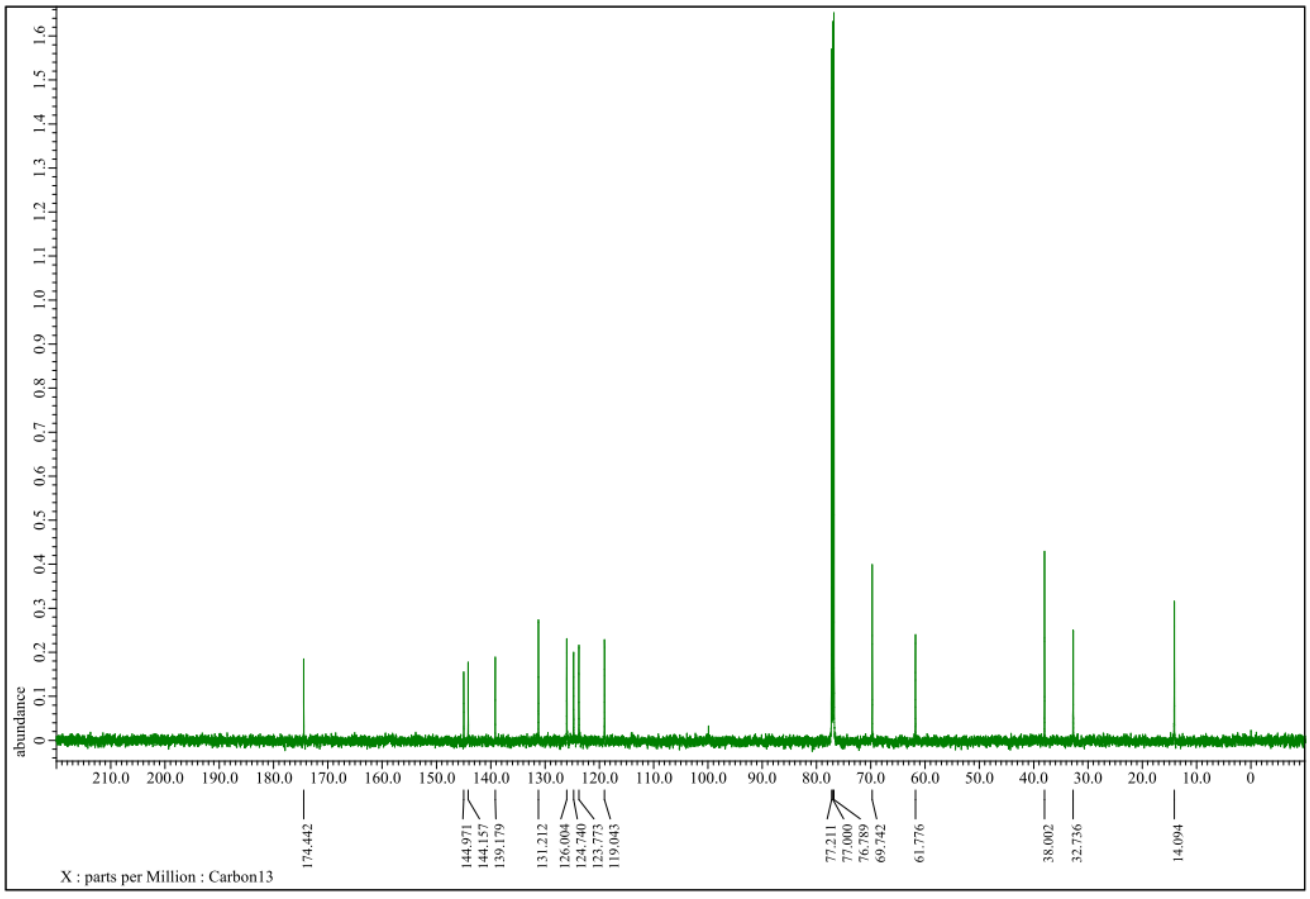
H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **6i**



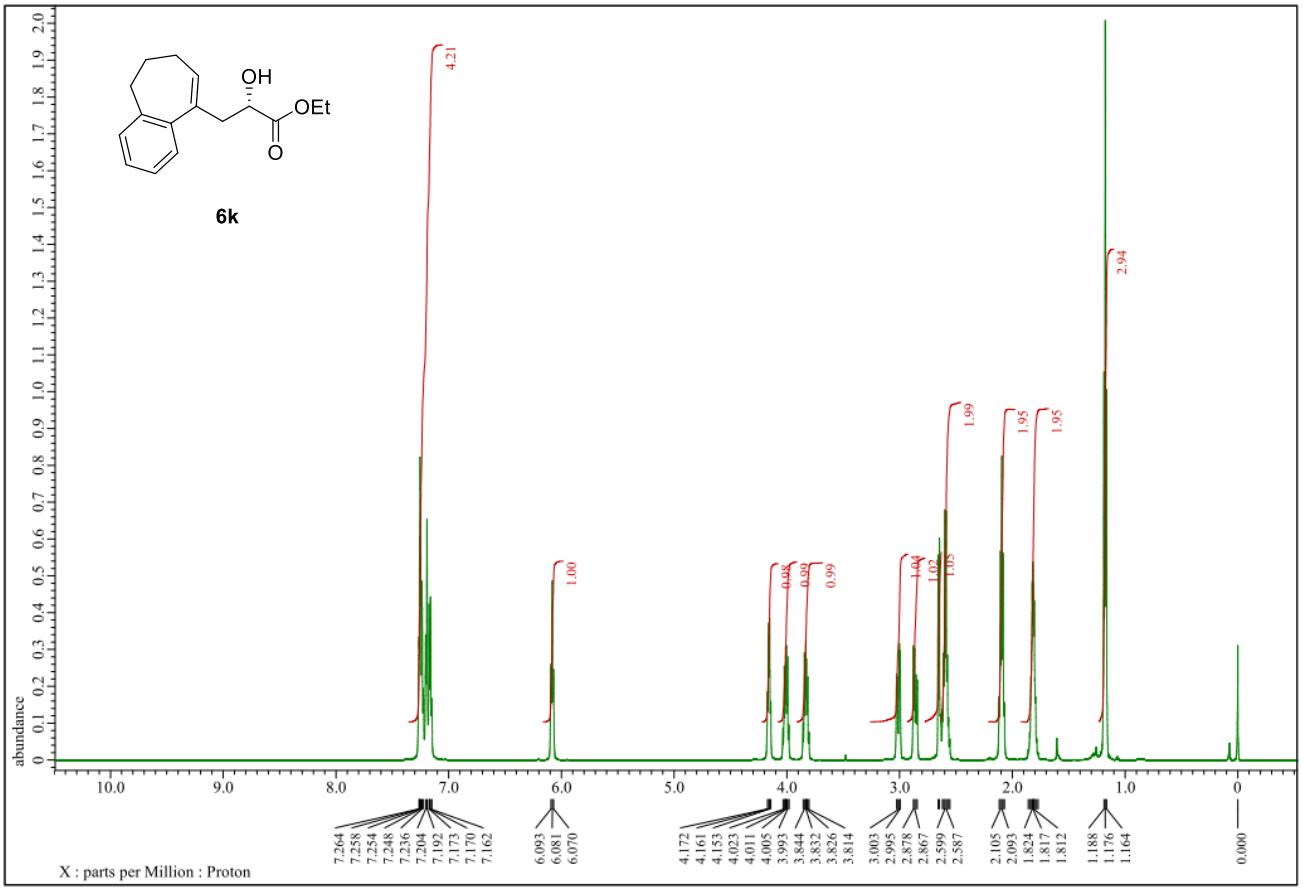


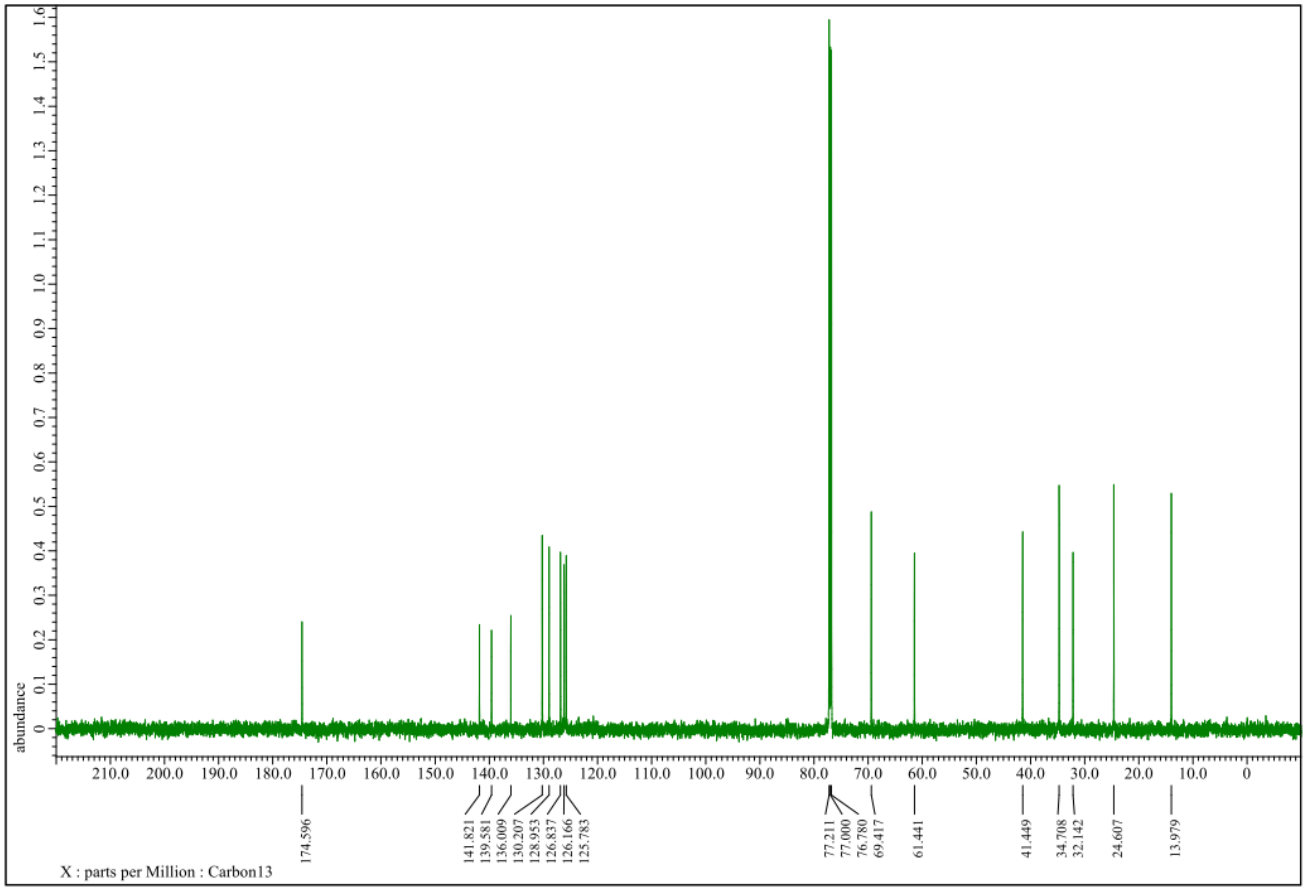
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **6j**



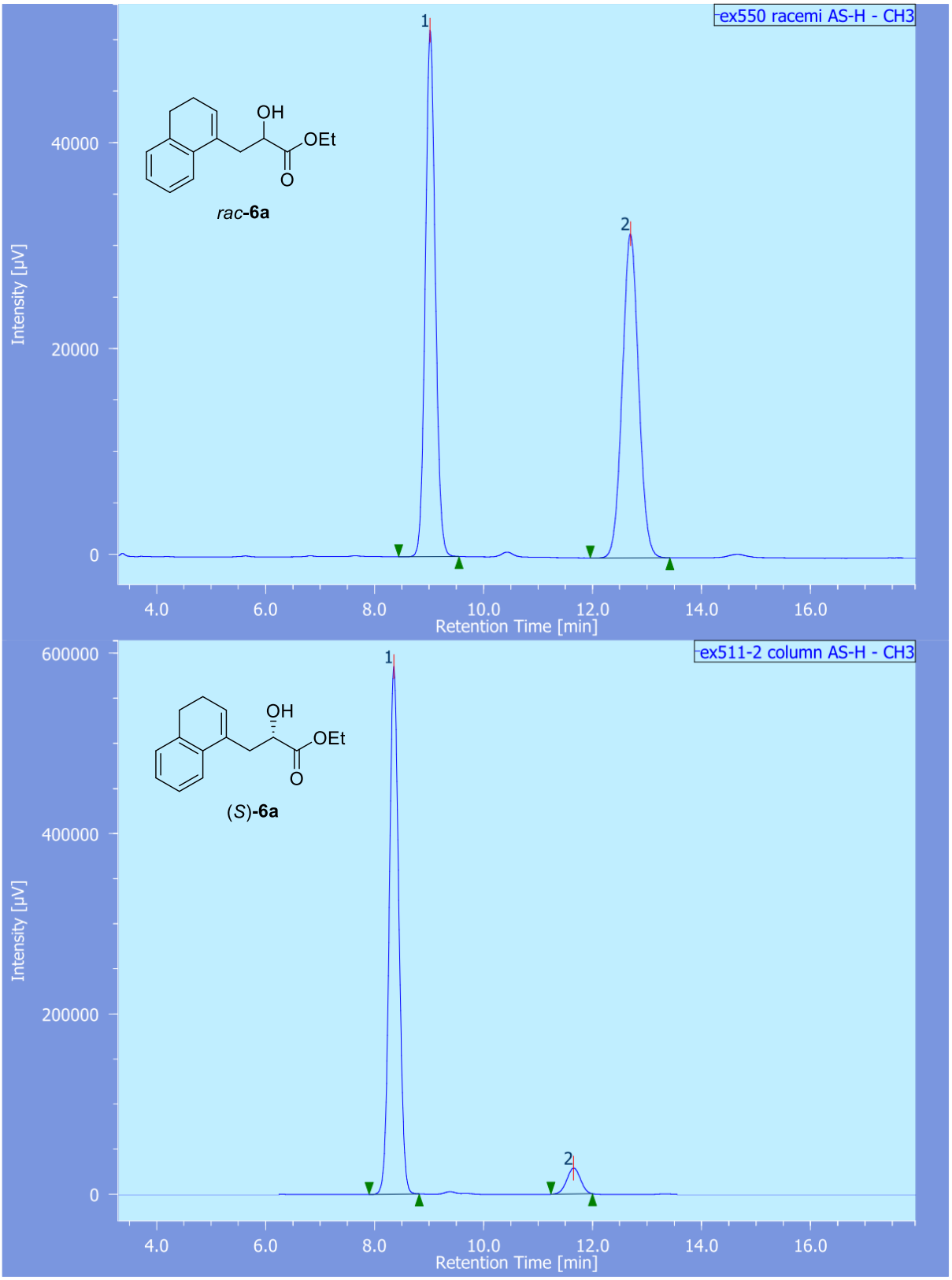


^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **6k**

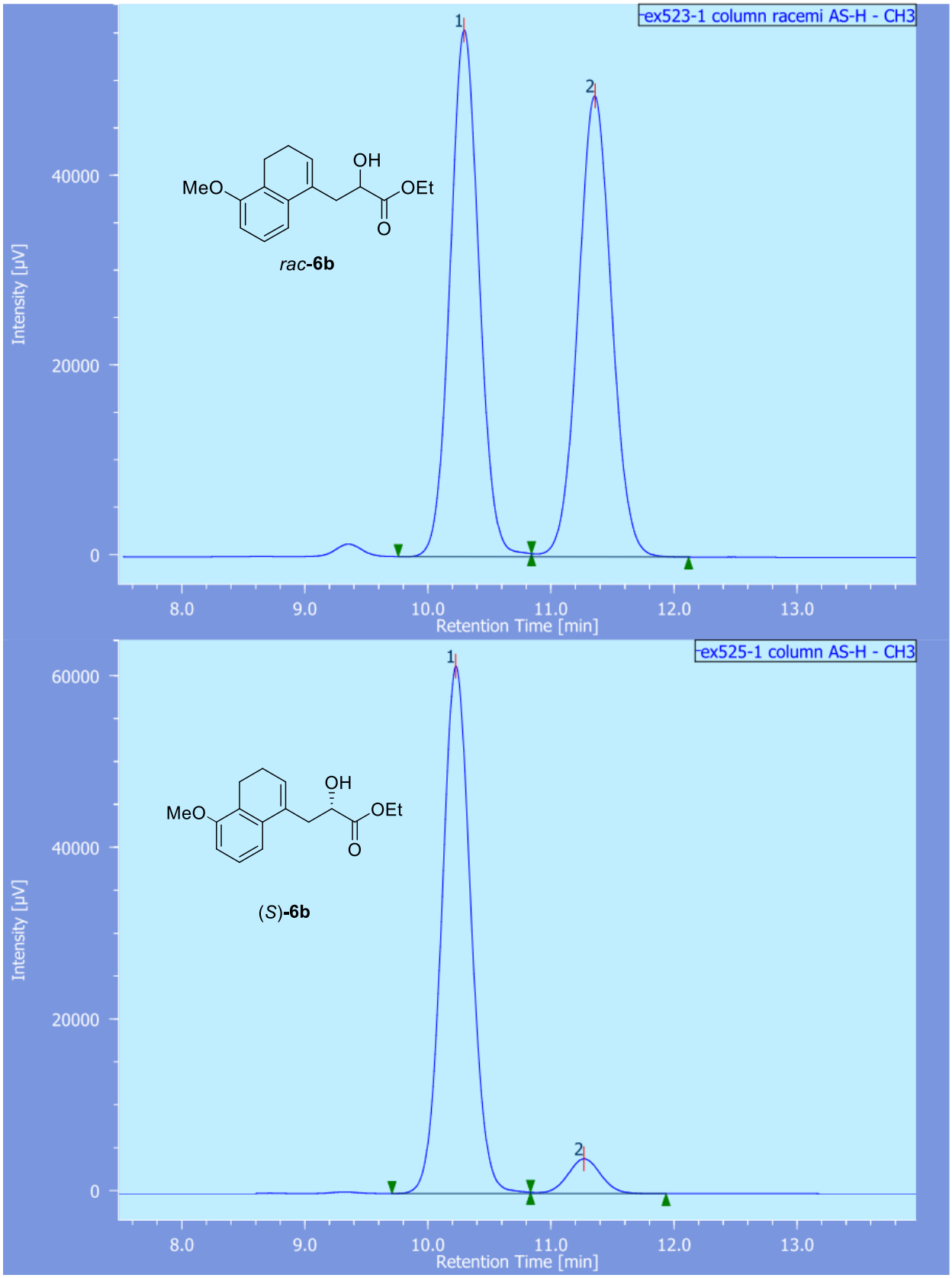




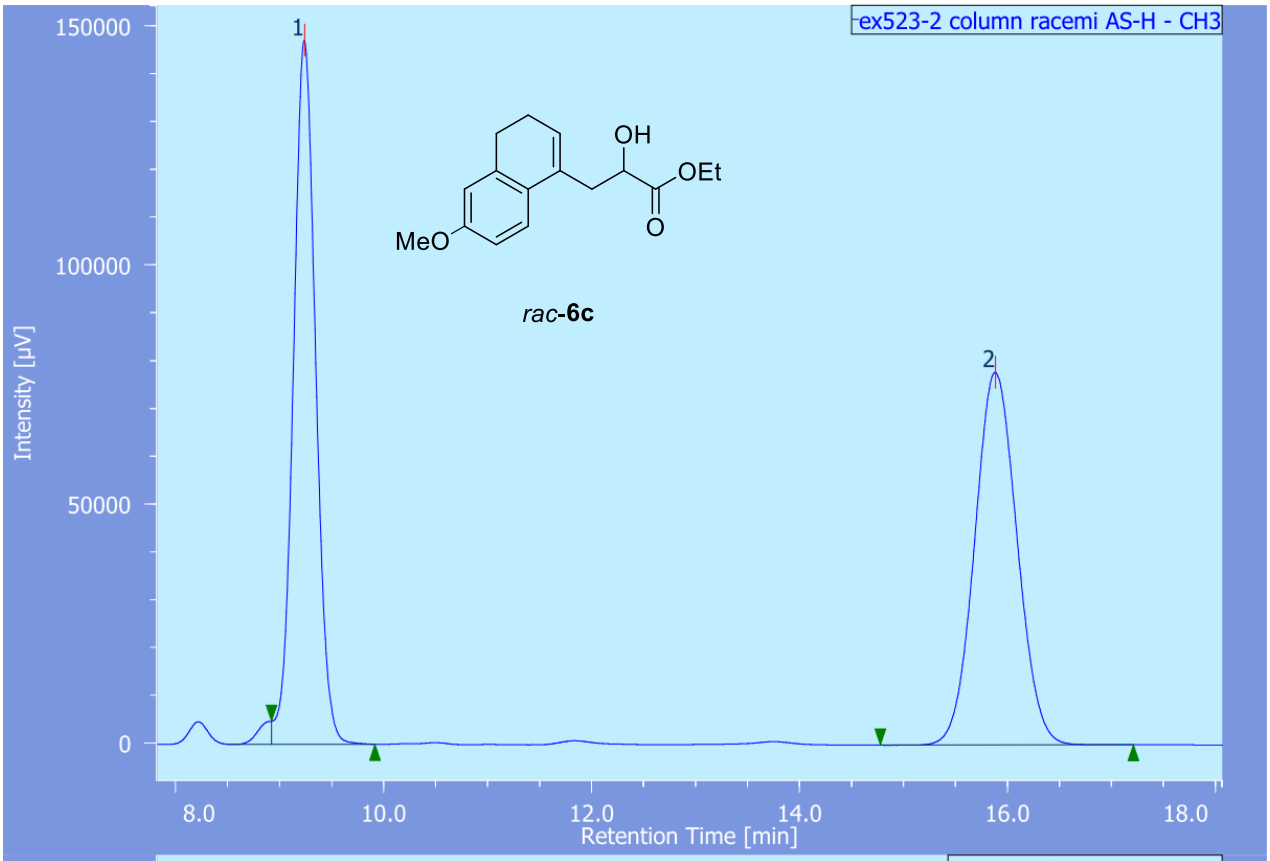
8. HPLC charts



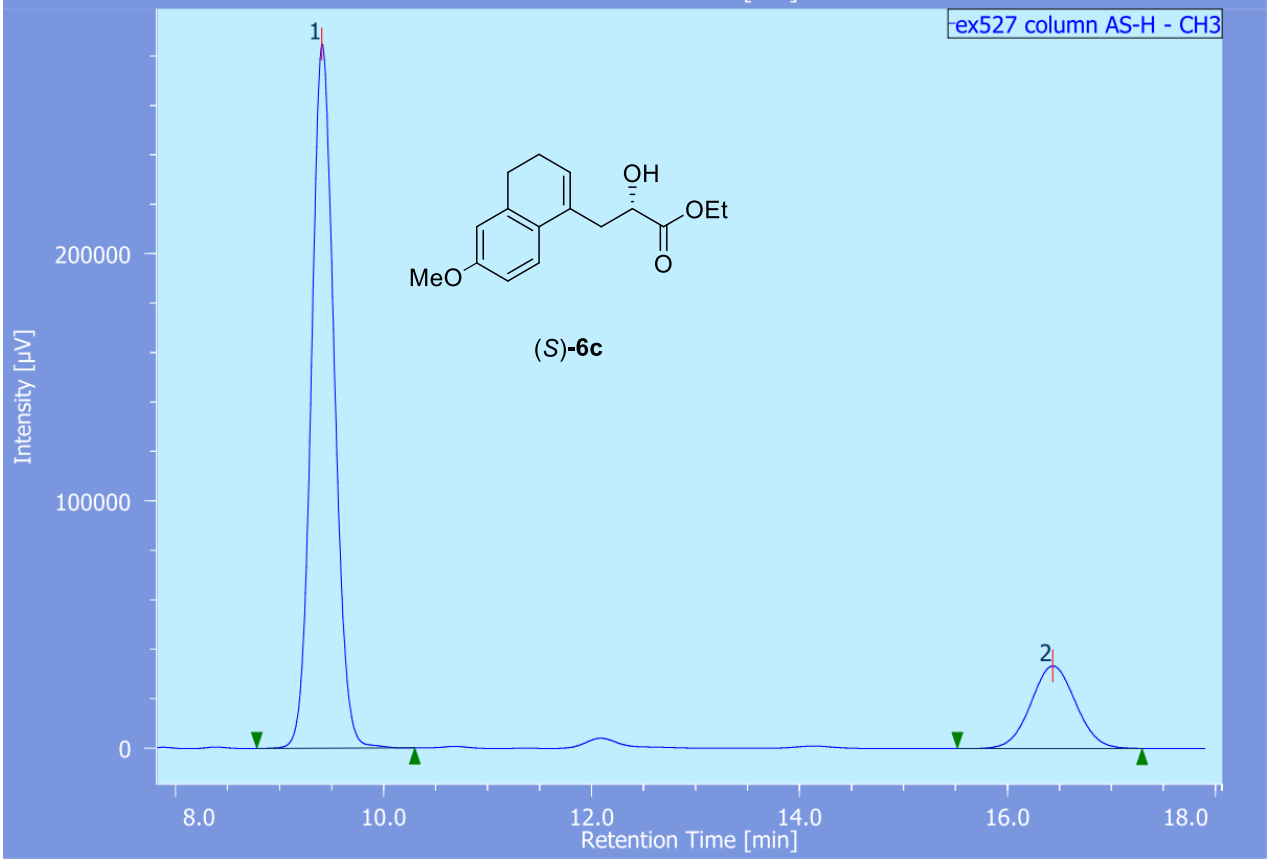
	Retention Time (1)	Retention Time (2)	Area (1)	Area (2)	%Area (1)	%Area (2)
rac-**6a**	9.02	12.69	653236	651596	50.06	49.94
(*S*)-**6a**	8.35	11.65	7169347	504319	93.43	6.57



	Retention Time (1)	Retention Time (2)	Area (1)	Area (2)	%Area (1)	%Area (2)
rac-**6b**	10.29	11.36	910634	922917	49.67	50.33
(*S*)-**6b**	10.23	11.27	1009897	76729	92.94	7.06

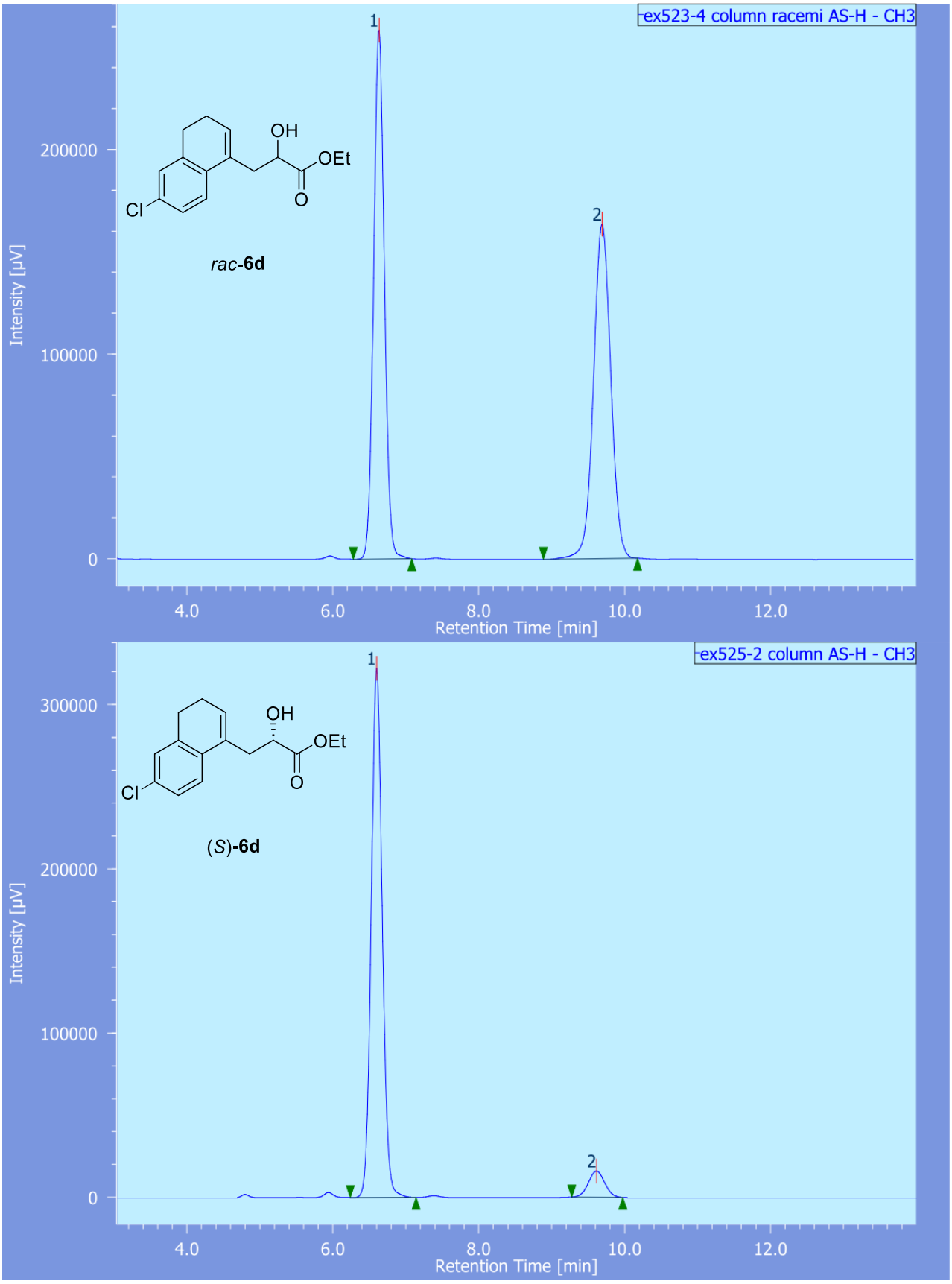


rac-**6c**

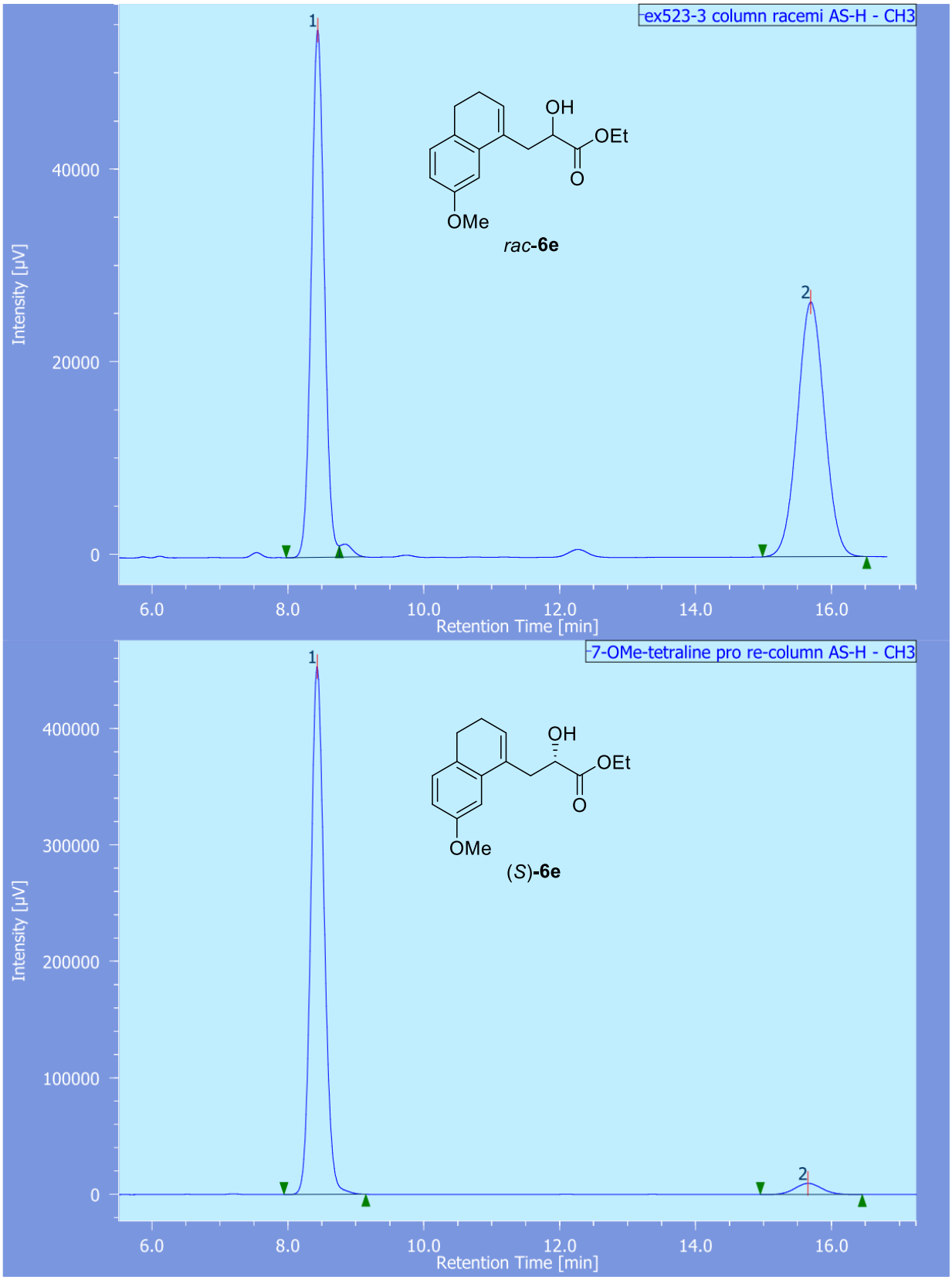


(*S*)-**6c**

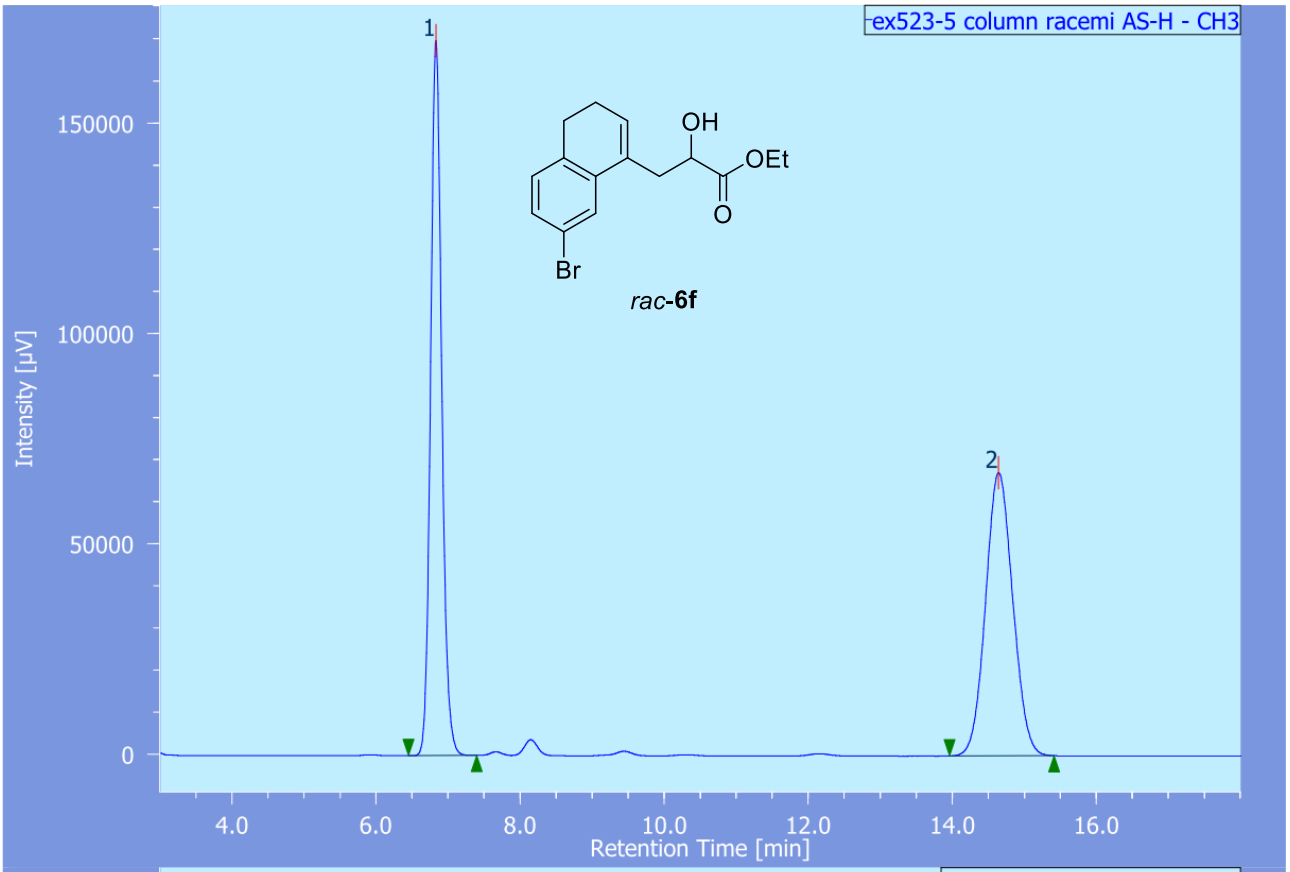
	Retention Time (1)	Retention Time (2)	Area (1)	Area (2)	%Area (1)	%Area (2)
rac-**6c**	9.24	15.88	2199884	2198497	50.02	49.98
(*S*)-**6c**	9.41	16.43	4316582	999712	81.20	18.80

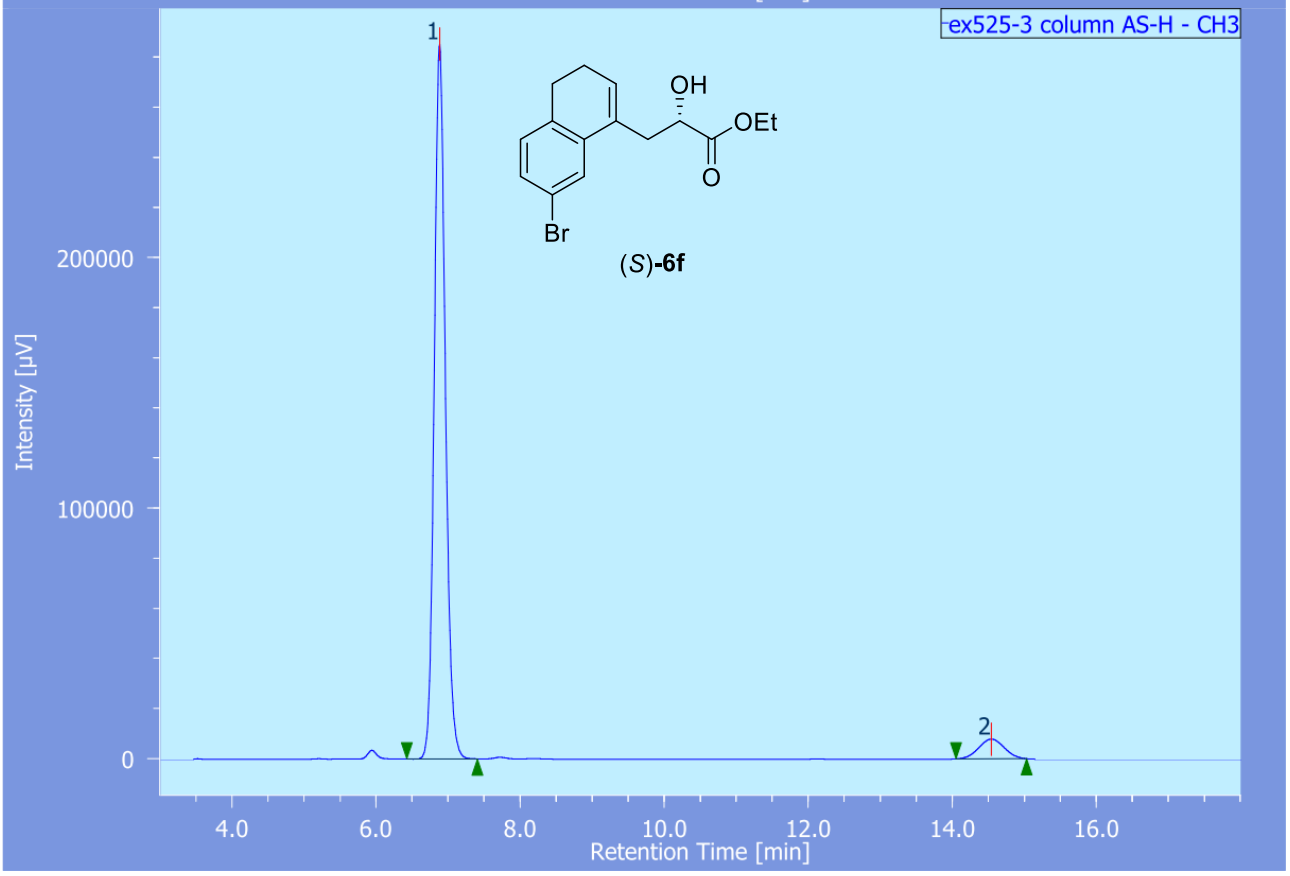


	Retention Time (1)	Retention Time (2)	Area (1)	Area (2)	%Area (1)	%Area (2)
rac-**6d**	6.63	9.69	2624371	2696846	49.32	50.68
(*S*)-**6d**	6.60	9.62	3331082	247448	93.09	6.91

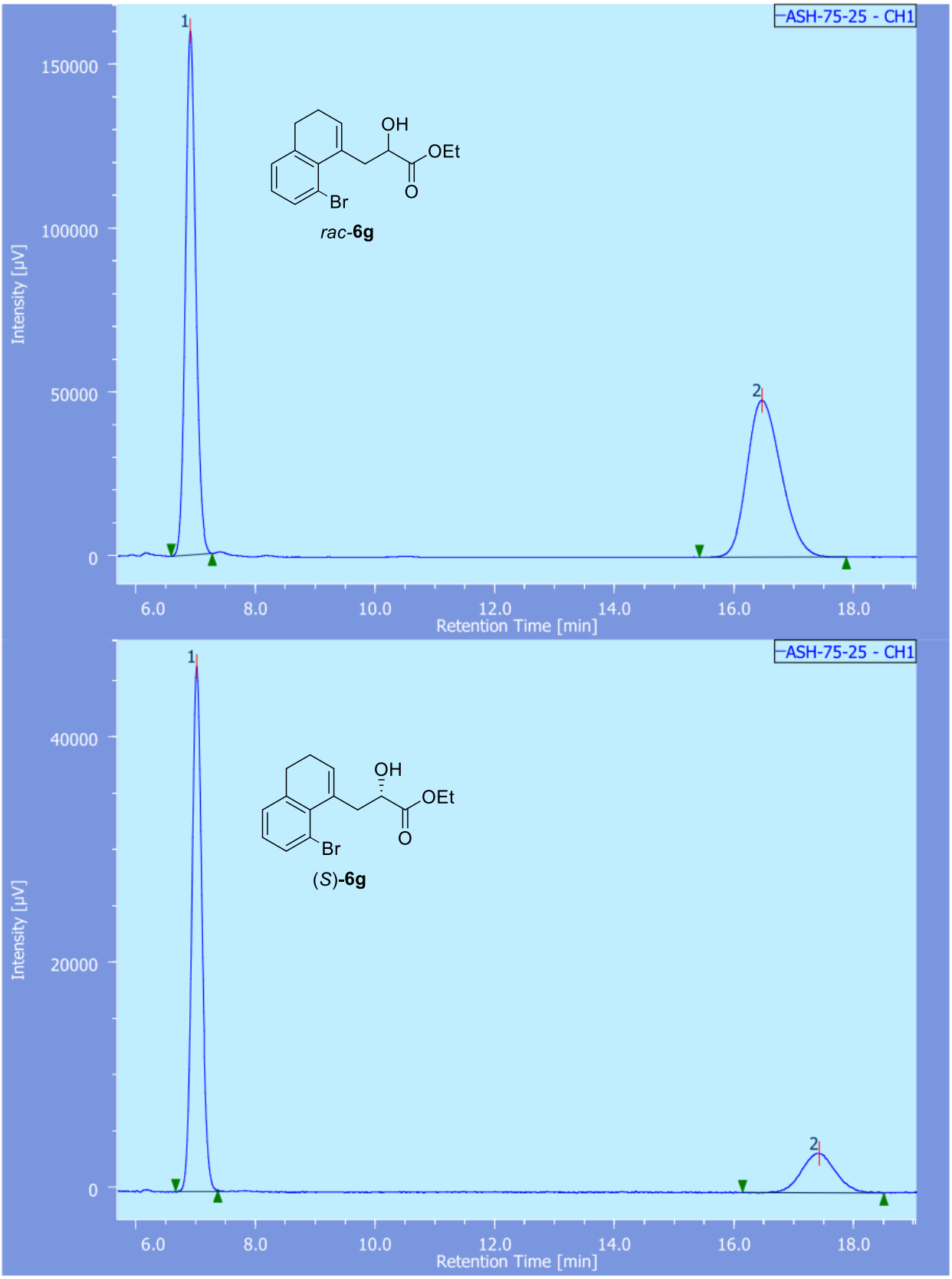


	Retention Time (1)	Retention Time (2)	Area (1)	Area (2)	%Area (1)	%Area (2)
rac-**6e**	8.44	15.69	730716	732529	49.94	50.06
(*S*)-**6e**	8.43	15.65	6222514	264688	95.92	4.08

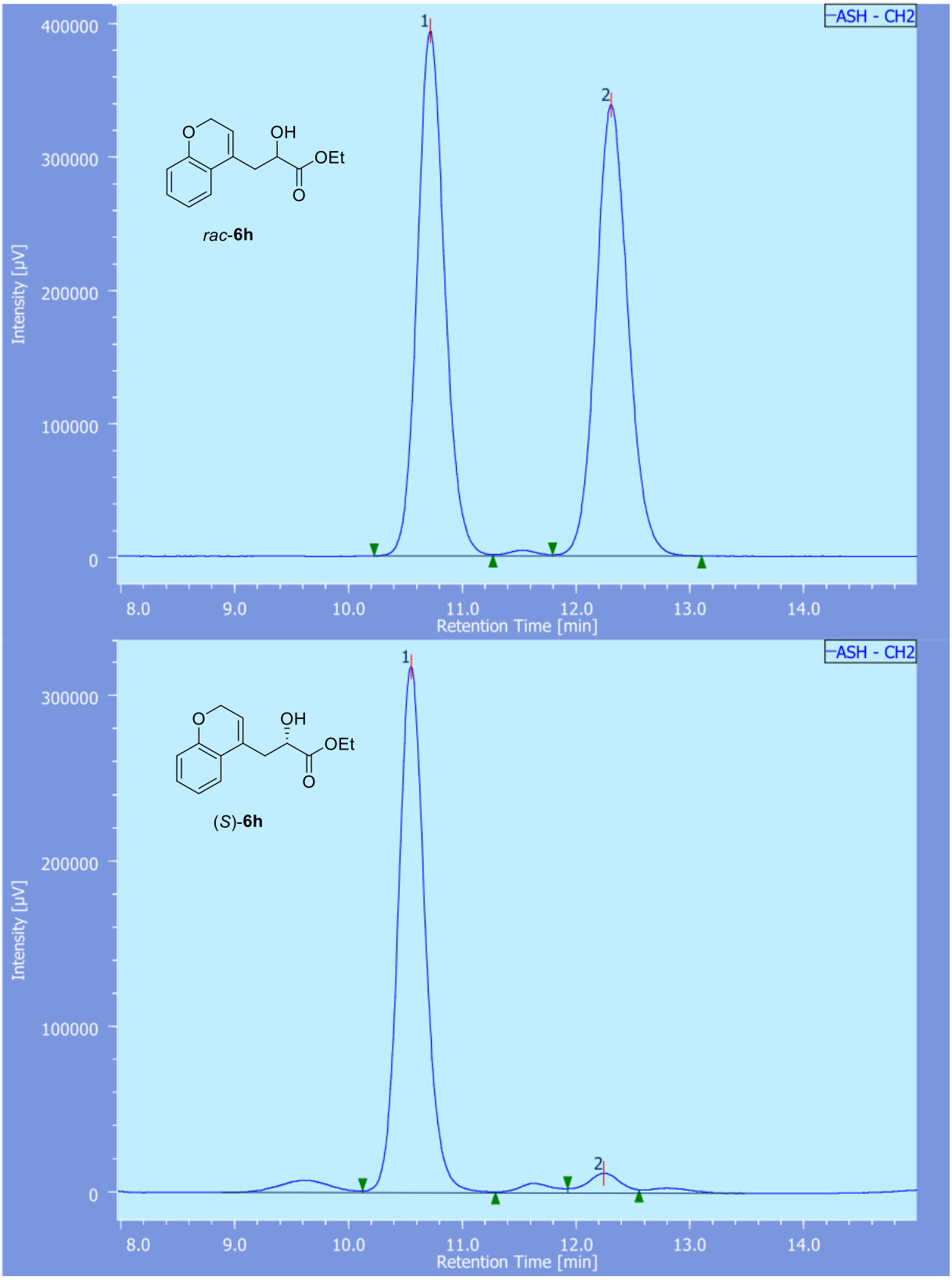




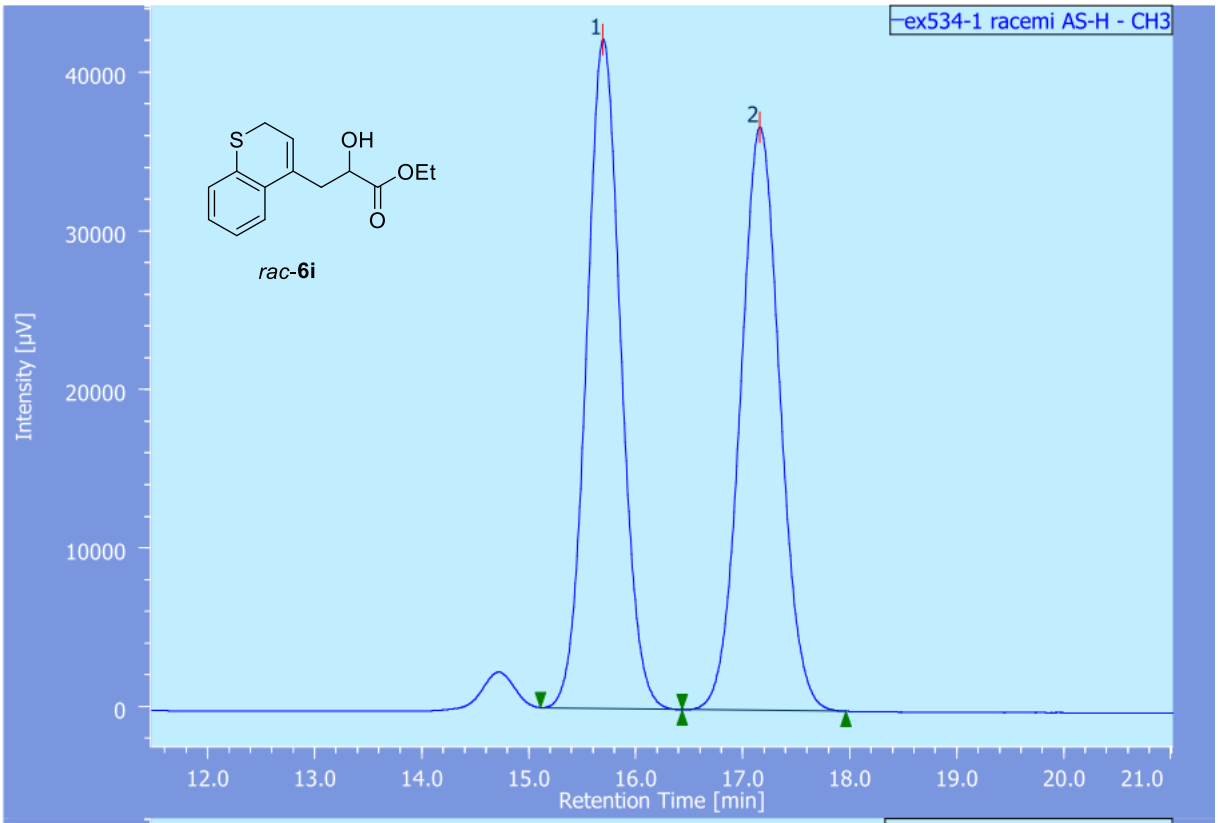
	Retention Time (1)	Retention Time (2)	Area (1)	Area (2)	%Area (1)	%Area (2)
rac-**6f**	6.83	14.64	1827455	1759401	50.95	49.05
(*S*)-**6f**	6.88	14.5	3077119	193503	94.08	5.92

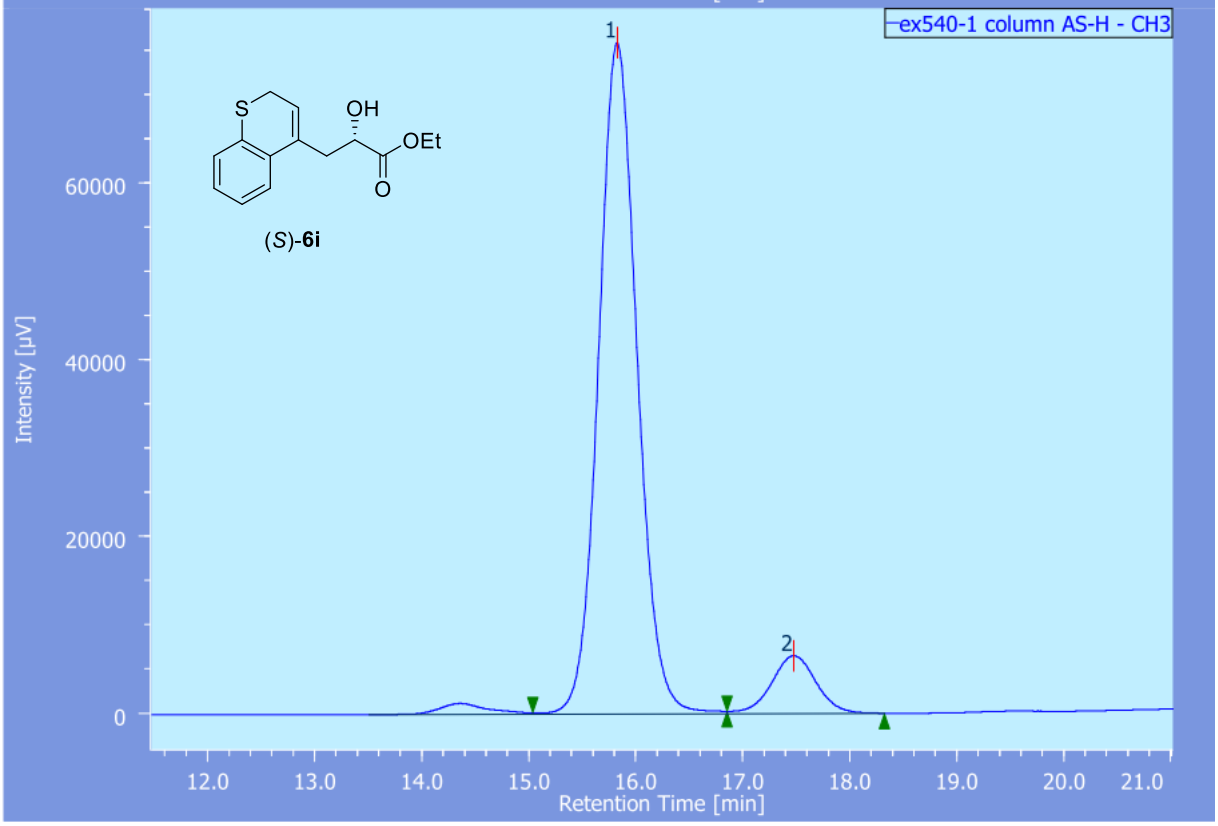


	Retention Time (1)	Retention Time (2)	Area (1)	Area (2)	%Area (1)	%Area (2)
rac-**6g**	6.91	16.48	1918922	1892939	50.34	49.66
(*S*)-**6g**	7.02	17.42	545778	137692	79.85	20.15

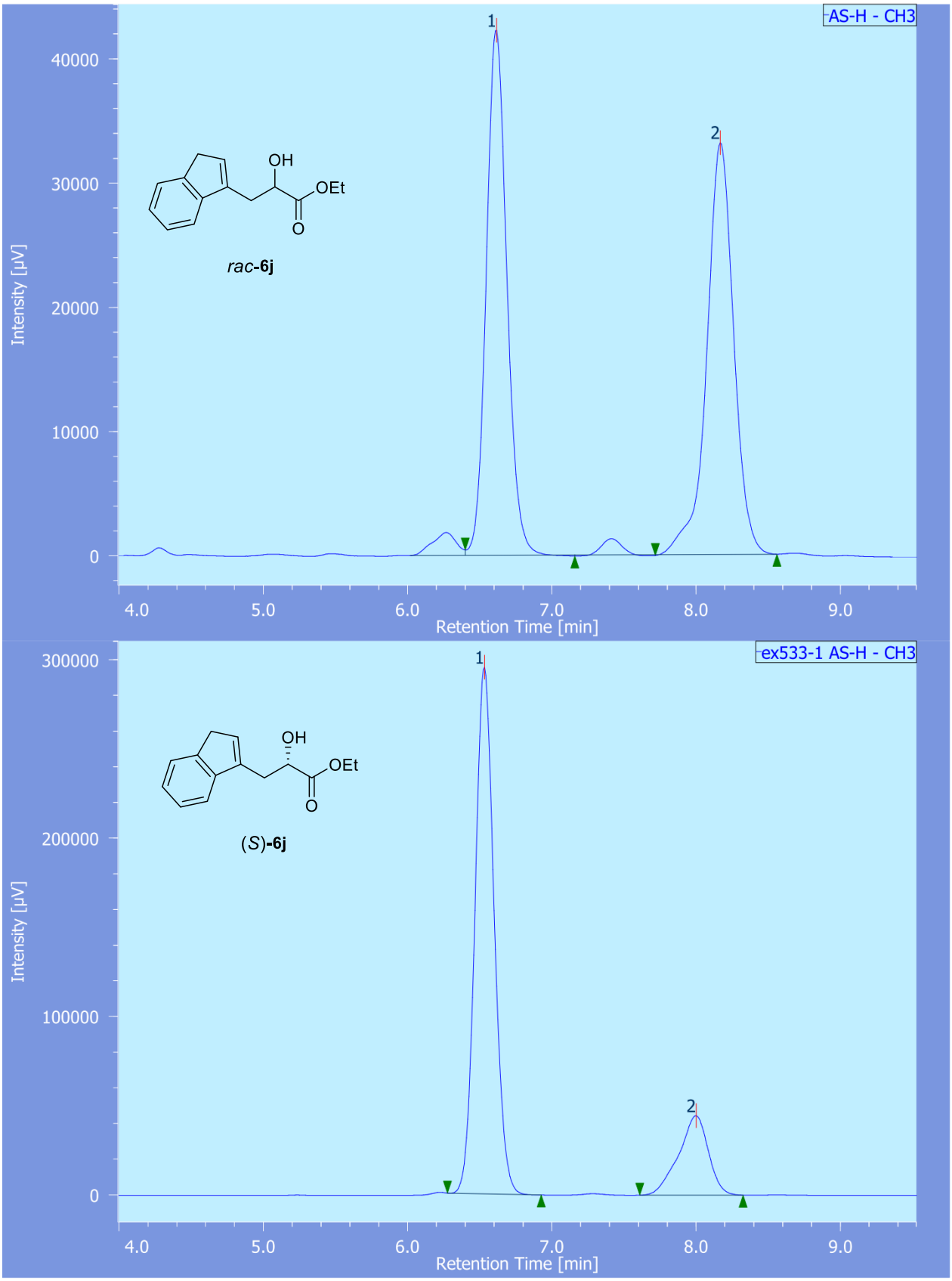


	Retention Time (1)	Retention Time (2)	Area (1)	Area (2)	%Area (1)	%Area (2)
rac-**6h**	10.72	12.31	6571418	6616825	49.83	50.17
(*S*)-**6h**	10.55	12.24	5172358	246307	95.45	4.55

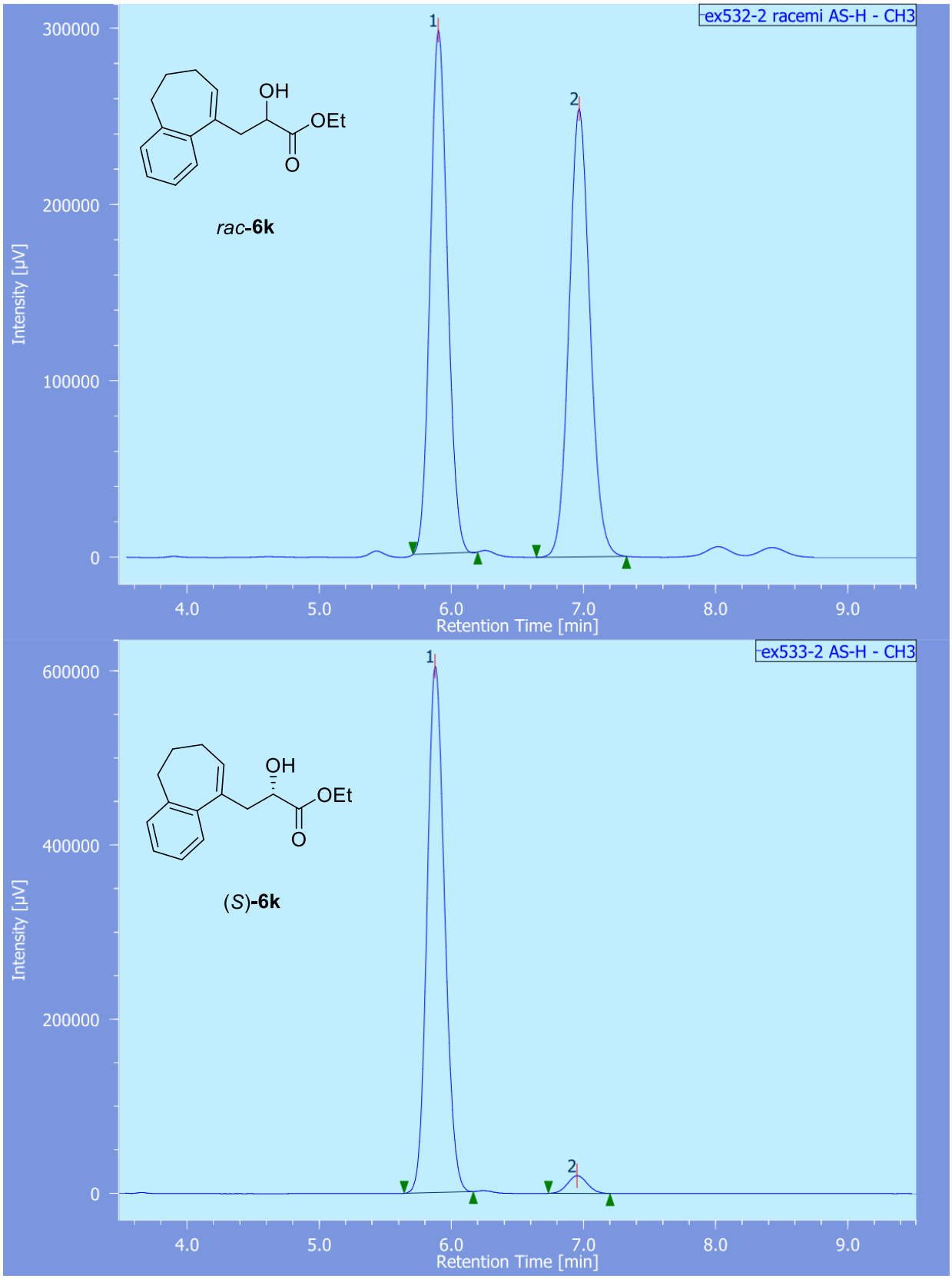




	Retention Time (1)	Retention Time (2)	Area (1)	Area (2)	%Area (1)	%Area (2)
rac-**6i**	15.69	17.16	940063	940252	49.99	50.01
(*S*)-**6i**	15.83	17.48	1895098	187383	91.00	9.00



	Retention Time (1)	Retention Time (2)	Area (1)	Area (2)	%Area (1)	%Area (2)
rac-**6j**	6.62	8.17	415013	430149	49.11	50.89
(*S*)-**6j**	6.53	8.00	2708200	638423	80.92	19.08



	Retention Time (1)	Retention Time (2)	Area (1)	Area (2)	%Area (1)	%Area (2)
rac-**6k**	5.90	6.97	2707995	2797543	49.19	50.81
(*S*)-**6k**	5.88	6.95	5578569	212968	96.32	3.68