

Supplementary Information

Iridium/chiral phosphoramidite-olefin complex-catalysed enantioselective [3+2] annulation of *ortho*-ketoarylboron compounds with conjugated dienes

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1. General Information

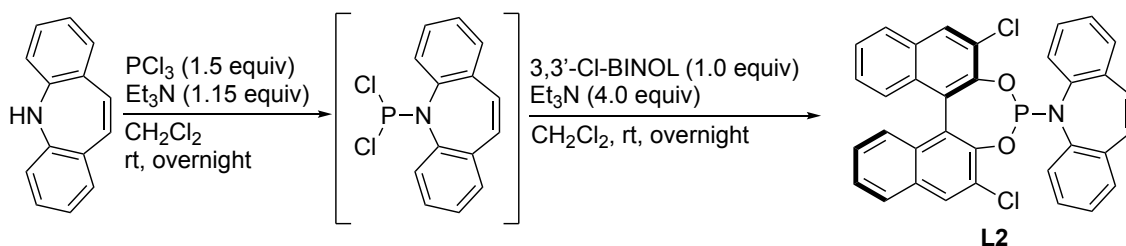
All manipulations of oxygen- and moisture-sensitive materials were carried out using standard Schlenk techniques under a nitrogen atmosphere. NMR spectra were recorded on JEOL JNM ECZ-400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C) or Bruker Avance III HD 400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C , 162 MHz for ^{31}P). Chemical shifts are reported in δ (ppm) referenced to the residual peaks of CDCl_3 (δ 7.26) for ^1H NMR, CDCl_3 (δ 77.00) and CD_3COCD_3 (δ 29.80) for ^{13}C NMR. The following abbreviations are used; s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; br, broad. High-resolution mass spectra were obtained with JEOL AccuTOF LC-plus 4G spectrometer. Preparative thin-layer chromatography was performed with Silica Gel 70 PF₂₅₄ (Wako). Alumina (active 200) for column chromatography was purchased from Nacalai Tesque.

2. Materials

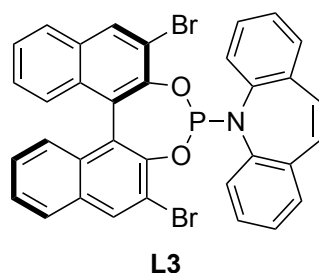
Dehydrated solvents were purchased and used after deoxygenated by bubbling N_2 . $[\text{IrCl}(\text{coe})_2]_2$ was prepared according to the reported procedures.¹ Other solvents and chemicals were purchased from commercial suppliers and used as received.

3. Preparation of Phosphoramidite-Olefin Ligands

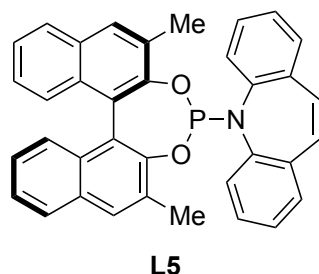
Phosphoramidite-olefine ligands **L2**, **L3** and **L5** were prepared from iminostilbene by typical procedures as shown below.



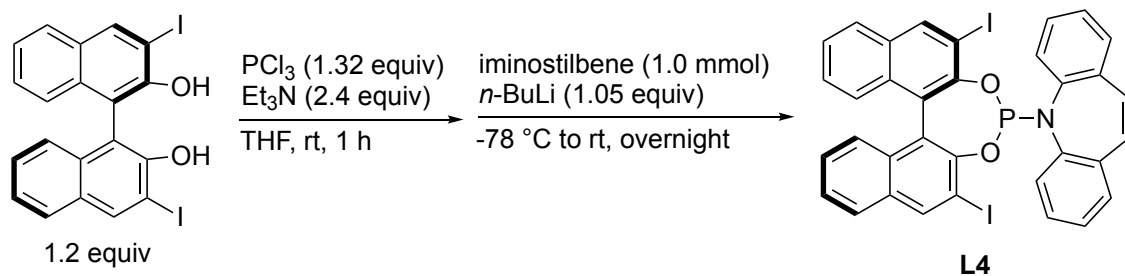
To a solution of PCl_3 (0.21 g, 1.5 equiv) in CH_2Cl_2 (10 mL) was added a mixture of Et_3N (0.12 g, 1.15 equiv) and iminostilbene (0.19 g, 1.0 mmol) in CH_2Cl_2 (5 mL) at $0\text{ }^\circ\text{C}$ under N_2 atmosphere. After completion of the addition, the mixture was stirred at room temperature overnight. The yellow solution was concentrated on a rotary evaporator to remove excess PCl_3 . The yellow residue was redissolved in CH_2Cl_2 (10 mL), and Et_3N (4.1 g, 4.0 equiv) and (1*R*)-3,3'-dichloro[1,1'-binaphthalene]-2,2'-diol (1.0 equiv) were added to the solution at $0\text{ }^\circ\text{C}$ under N_2 atmosphere. After the mixture was stirred at room temperature overnight, the resulting mixture was concentrated on a rotary evaporator, and the residue was subjected to column chromatography on silica gel eluted with a mixture of hexane and CH_2Cl_2 (10:3) containing 3% of Et_3N to give **L2** as a colorless solid (0.18 g, 32% yield). $[\alpha]_D^{25} -492$ (c 1.02, CHCl_3) for 99% ee; ^1H NMR (400 MHz, CDCl_3) δ 8.09 (s, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.73 (t, $J = 8.0$ Hz, 2H), 7.43–7.37 (m, 3H), 7.23–6.89 (m, 12H), 6.58–6.54 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 145.9 (d, $^2J_{\text{P-C}} = 8$ Hz), 144.7, 142.3, 142.1, 142.0 (d, $^2J_{\text{P-C}} = 6$ Hz), 136.02, 135.98, 135.8, 131.9, 131.3, 131.2, 131.1, 130.8, 130.1, 129.5, 129.2, 129.0, 128.8 (d, $^2J_{\text{P-C}} = 6$ Hz), 128.5 (d, $^2J_{\text{P-C}} = 4$ Hz), 128.2, 127.7, 127.6, 127.5, 127.0, 126.77, 126.75, 126.6, 126.4, 126.3, 126.1, 125.9, 125.6, 123.0, 122.0; ^{31}P NMR (162 MHz, CDCl_3) δ 139.1. HRMS (DART) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{33}\text{H}_{21}\text{NO}_2\text{PCl}_2$ 576.0682; Found 576.0660.



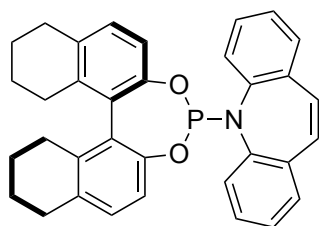
L3 was prepared according to the procedures for **L2** using (1*R*)-3,3'-dibromo[1,1'-binaphthalene]-2,2'-diol. **L3** (0.20 g, 30% yield, colorless solid); $[\alpha]_D^{25} - 492$ (*c* 0.98, CHCl₃) for 99% ee; ¹H NMR (400 MHz, CDCl₃) δ 8.26 (s, 1H), 7.98 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.43–7.38 (m, 2H), 7.26–6.93 (m, 12H), 6.64 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 146.5 (d, ²*J*_{P-C} = 9 Hz), 145.5, 142.2, 142.1 (d, ²*J*_{P-C} = 3 Hz), 142.0, 136.0, 132.9, 132.2, 131.8, 131.7, 131.6, 130.9, 130.6, 129.3, 128.9, 128.7, 128.57, 128.53, 128.3, 127.7 (d, ²*J*_{P-C} = 9 Hz), 127.4, 126.9, 126.83, 126.75, 126.6, 126.5, 126.4, 126.3, 125.8, 125.5, 125.2 (d, ²*J*_{P-C} = 5 Hz), 122.8, 116.3, 116.1; ³¹P NMR (162 MHz, CDCl₃) δ 138.7. HRMS (DART) *m/z*: [M + H]⁺ Calcd for C₃₃H₂₁NO₂PBr₂ 663.9671; Found 663.9683.



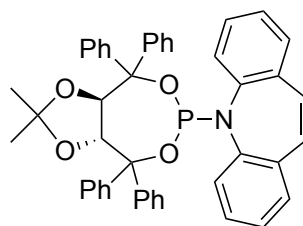
L5 was prepared according to the procedures for **L2** using (1*R*)-3,3'-dimethyl[1,1'-binaphthalene]-2,2'-diol. **L5** (0.19 g, 35% yield, colorless solid); $[\alpha]_D^{25} - 471$ (*c* 0.97, CHCl₃) for 99% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.82–7.80 (m, 2H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.43 (s, 1H), 7.36–7.30 (m, 3H), 7.21–6.95 (m, 10H), 6.90 (s, 2H), 6.51 (t, *J* = 7.2 Hz, 1H), 2.72 (s, 3H), 2.42 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 149.2, 149.1, 148.1 (d, ²*J*_{P-C} = 2 Hz), 143.03, 142.97, 142.9, 142.8, 136.0 (d, ²*J*_{P-C} = 3 Hz), 135.1, 131.7, 131.5, 131.3, 130.4, 130.1, 129.7, 129.0, 128.8, 128.5, 128.35, 128.33, 127.7, 127.6, 127.5, 127.0, 126.8, 126.4, 126.1, 125.1, 124.8, 124.7, 124.3, 124.1, 124.0, 121.4, 18.2, 17.6; ³¹P NMR (162 MHz, CDCl₃) δ 137.0; HRMS (DART) *m/z*: [M + H]⁺ Calcd for C₃₆H₂₇NO₂P 536.1774; Found 536.1773.



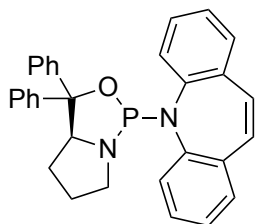
To a solution of PCl_3 (0.18 g, 1.32 equiv) in THF (3 mL) was added a mixture of Et_3N (0.24 g, 2.4 equiv), (1*R*)-3,3'-diiodo[1,1'-binaphthalene]-2,2'-diol (0.65 g, 1.2 equiv), and THF (3 mL) at 0 °C under N_2 atmosphere. After completion of the addition, the mixture was stirred at room temperature for an hour. The resulting mixture was filtered through celite, and the filter cake was washed with THF. The filtrate was concentrated on a rotary evaporator. The resulting solid was dissolved in THF (6 mL) and the solution was used for the further reaction. To a solution of iminostilbene (0.19 g, 1.0 mmol) in THF (5 mL) was slowly added *n*-BuLi (ca. 15% in hexane) (0.66 mL, 1.05 equiv) at -78 °C under N_2 atmosphere, and the mixture was stirred at the same temperature for an hour. To the resulting blue solution was slowly added the THF solution prepared in the previous step. After completion of the addition, the mixture was stirred at room temperature overnight. The resulting orange solution was concentrated on a rotary evaporator, and the residue was subjected to column chromatography on silica gel eluted with a solution of hexane and CH_2Cl_2 (10:3) containing 3% of Et_3N to give **L4** as a colorless solid (0.27 g, 35% yield). $[\alpha]_{\text{D}}^{25} -468$ (*c* 1.02, CHCl_3) for 99% ee; ^1H NMR (400 MHz, CDCl_3) δ 8.49 (s, 1H), 8.29 (s, 1H), 7.78–7.72 (m, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.41–7.35 (m, 2H), 7.24–6.87 (m, 12H), 6.71 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 148.5, 148.4, 147.6 (d, $^2J_{\text{P-C}} = 2$ Hz), 142.4, 142.3, 141.9, 141.8, 136.0, 135.9 (d, $^2J_{\text{P-C}} = 2$ Hz), 132.4, 131.9, 131.3, 131.1, 129.4, 128.8, 128.70, 128.65, 128.5, 128.4, 127.8, 127.7, 127.2, 126.8, 126.73, 126.70, 126.5, 125.6, 125.3, 124.15, 124.09, 121.68, 121.66, 91.4, 91.0; ^{31}P NMR (162 MHz, CDCl_3) δ 138.1; HRMS (DART) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{34}\text{H}_{21}\text{O}_2\text{NPI}_2$ 759.9394; Found 759.9376.



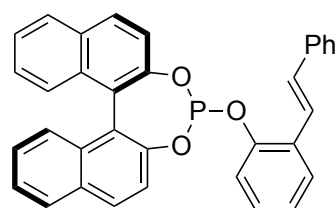
L6



L7



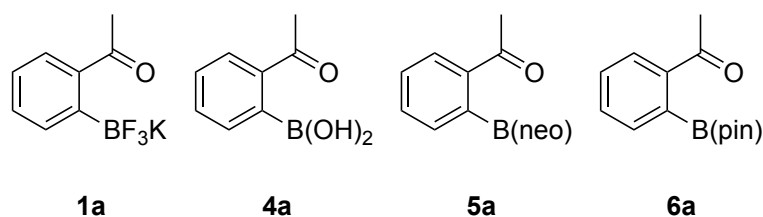
L8



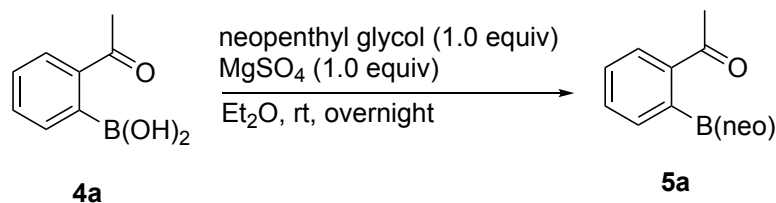
L9

Known P-olefin ligands (*rac*)-**L1** (CAS: 1809289-27-7), (*R*)-**L1** (CAS: 1265884-98-7), **L6** (CAS: 2070926-11-1), **L7** (CAS: 1092695-14-1), **L8** (CAS: 1092695-17-4), and **L9** (CAS: 1638298-36-8) were prepared according to the reported procedures.¹

4. Preparation of Boron Reagents

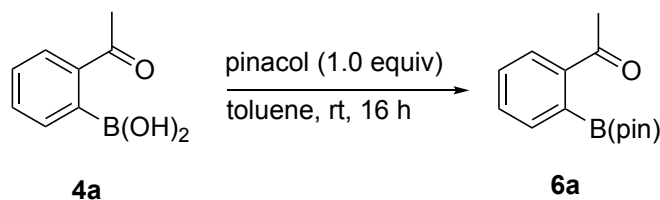


4a was purchased from commercial suppliers and used as received. **1a** (CAS: 1258323-44-2) was prepared from **4a** according to the reported procedures.³ **5a** (CAS: 849412-53-9) was prepared from **4a** by the procedures shown below.

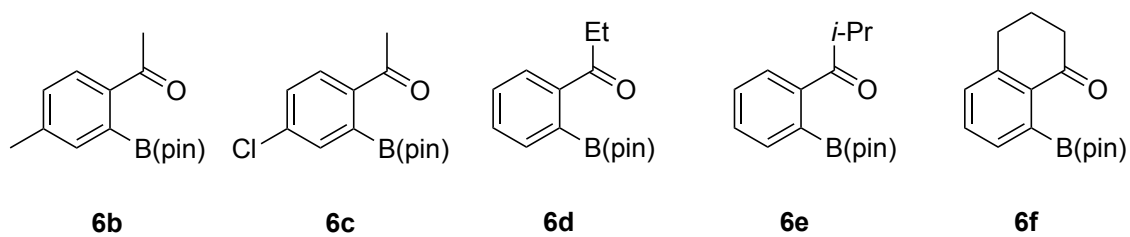


4a (82.0 mg, 0.50 mmol), neopentyl glycol (50.6 mg, 1.0 equiv), MgSO₄ (12.0 mg, 1.0 equiv), and Et₂O (0.3 mL) were placed in a round-bottom flask. The mixture was stirred at room temperature overnight, and the resulting mixture was concentrated on a rotary evaporator. The residue was subjected to preparative TLC on silica gel eluted with EtOAc/hexane (1:5) to give **5a** (57.6 mg, 50% yield).

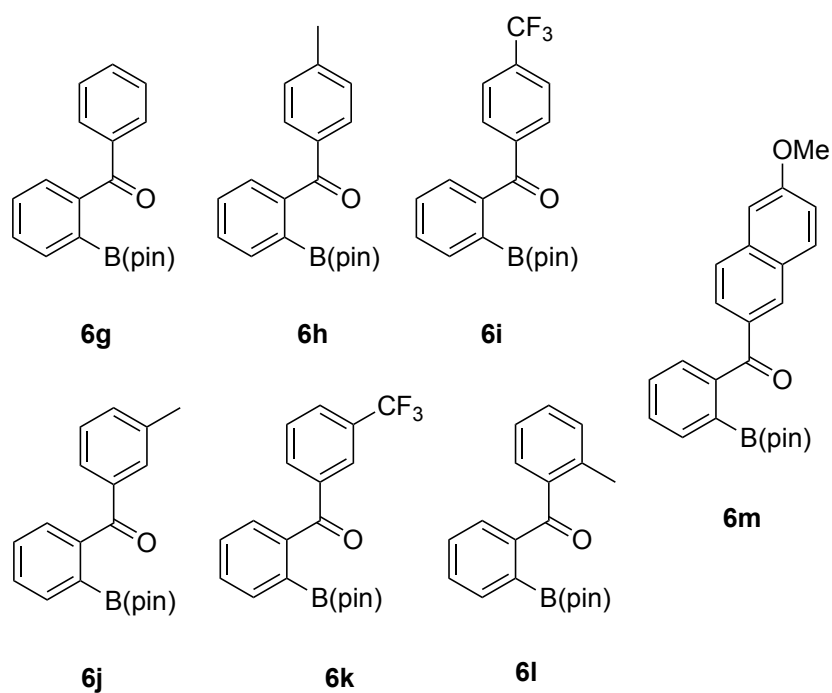
6a (CAS: 325141-75-1) was prepared from **4a** as shown below.



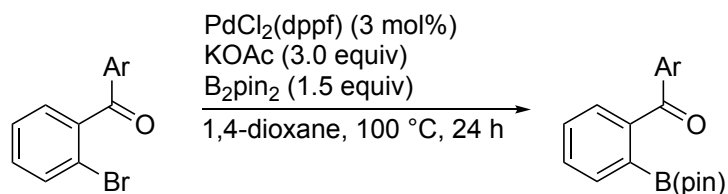
4a (82.0 mg, 0.50 mmol), pinacol (59.1 mg, 1.0 equiv), and toluene (0.3 mL) were placed in a round flask. The mixture was stirred at the room temperature for 16 h, and the resulting mixture was concentrated on a rotary evaporator. The residue was subjected to preparative TLC on silica gel eluted with EtOAc/hexane (1:5) to give **6a** (84.0 mg, 68% yield).



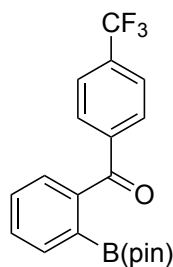
6b (CAS: 1350374-39-8), **6c** (CAS: 1350374-40-1), **6d** (CAS: 1350374-35-4), **6e** (CAS: 1350374-36-5), and **6f** (CAS: 2377067-16-6) were prepared according to the reported procedures.⁴



6g (CAS: 949115-05-3), **6h** (CAS: 1622886-59-2), **6i**, **6j**, **6k**, **6l** (CAS: 2053897-25-7), and **6m** were prepared from the corresponding aryl *o*-bromophenyl ketones according to the typical procedures shown below.

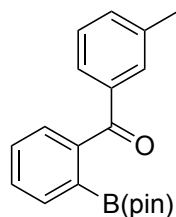


Aryl bromide (1.0–3.0 mmol), PdCl₂(dppf) (3 mol%), KOAc (3.0 equiv), and B₂pin₂ (1.5 equiv) were placed in a Schlenk tube under N₂. 1,4-Dioxane (5 mL/mmol) was added to the mixture. The Schlenk tube was capped with a glass stopper and the mixture was stirred at 100 °C for 24 h. The mixture was extracted with CH₂Cl₂, dried over Na₂SO₄, filtered, and concentrated on a rotary evaporator. The residue was subjected to column chromatography on silica gel eluted with hexane/EtOAc (20:1–10:1) to give **6g–6m**.



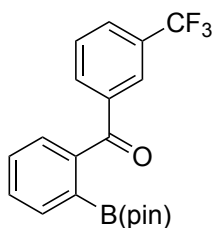
6i

Compound 6i (68% yield, colorless solid). ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 6.8 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.58–7.50 (m, 3H), 1.18 (s, 12H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 197.1, 142.9, 141.1, 134.1, 133.7 (q, ²*J*_{F-C} = 32 Hz), 130.8, 130.1, 129.9, 128.8, 125.1 (q, ³*J*_{F-C} = 4 Hz), 123.7 (q, ¹*J*_{F-C} = 272 Hz), 84.1, 24.4. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. HRMS (DART) *m/z*: [M + H]⁺ Calcd for C₂₀H₂₁BF₃O₃ 377.1530; Found 377.1515.



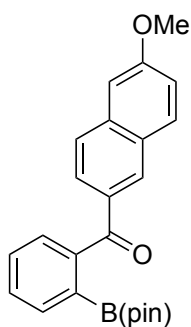
6j

Compound 6j (76% yield, pale yellow oil). ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 6.4$ Hz, 1H), 7.61 (s, 1H), 7.56–7.44 (m, 4H), 7.36–7.29 (m, 2H), 2.38 (s, 3H), 1.19 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 198.2, 143.5, 138.0, 137.9, 133.6, 133.0, 130.32, 130.27, 129.5, 129.0, 128.0, 127.3, 83.9, 24.4, 21.2. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. HRMS (DART) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{24}\text{BO}_3$ 323.1813; Found 323.1825.



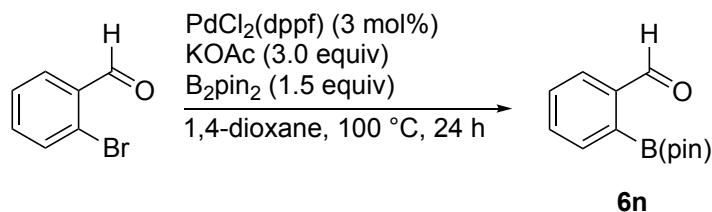
6k

Compound 6k (54% yield, pale yellow solid). ^1H NMR (400 MHz, CDCl_3) δ 8.08 (s, 1H), 7.90 (d, $J = 7.6$ Hz, 1H), 7.81–7.78 (m, 2H), 7.58–7.49 (m, 4H), 1.15 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 196.9, 143.1, 138.9, 134.3, 133.1, 130.9 (q, $^2J_{\text{F-C}} = 33$ Hz), 130.6, 130.1, 128.8, 128.7, 128.6, 126.5 (q, $^3J_{\text{F-C}} = 4\text{Hz}$), 123.7 (q, $^1J_{\text{F-C}} = 270$ Hz), 84.1, 24.4. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. HRMS (DART) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{21}\text{BF}_3\text{O}_3$ 377.1530; Found 377.1542.



6m

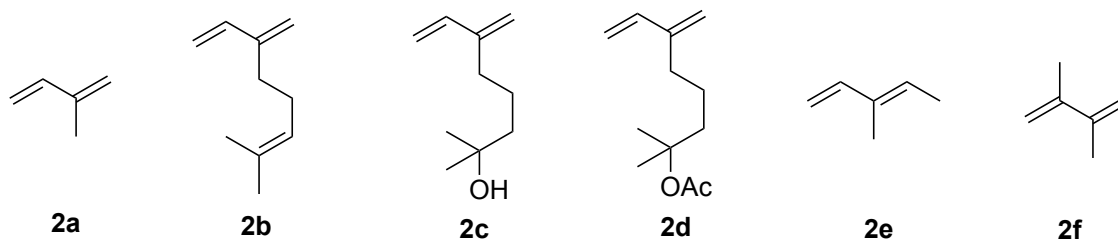
Compound 6m (46% yield, pale yellow solid). ^1H NMR (400 MHz, CDCl_3) δ 8.08 (s, 1H), 7.98 (dd, $J = 8.6$ Hz, 1.4 Hz, 1H), 7.80–7.74 (m, 3H), 7.60–7.49 (m, 3H), 7.18–7.15 (m, 2H), 3.95 (s, 3H), 1.10 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 198.0, 159.6, 133.9, 133.5, 132.1, 131.0, 130.0, 129.8, 128.7, 126.9, 126.2, 119.5, 105.7, 83.9, 55.4, 24.5. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. HRMS (DART) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{26}\text{BO}_4$ 389.1919; Found 389.1920.



6n

6n (CAS: 380151-85-9) was prepared from the aryl *o*-bromophenyl aldehyde same as above procedures.

5. Preparation of 1,3-Dienes



Dienes **2a**, **2b**, **2e**, and **2f** were purchased from commercial suppliers and used as received. **2c** (CAS: 543-39-5) and **2d** (CAS: 118-39-4) were prepared from **2b** according to the reported procedures.⁵

6. Procedure for Tables 1 and 2

$[\text{IrCl}(\text{coe})_2]_2$ (4.5 mg, 0.0050 mmol, 5 mol% of Ir) and (*rac*)- or (*R*)-**L1** (6.1 mg, 0.012 mmol, 6 mol%) were placed in a Schlenk tube under N_2 . Toluene (0.8 mL) was added to the tube, and the resulting mixture was stirred at room temperature for 15 min. To the resulting red solution were added boron reagents **1a**, **4a–6a** (0.20 mmol), Et_3N (36 μL , 0.26 mmol, 1.3 equiv), H_2O (0.8 mL), and isoprene (**2a**) (40.9 mg, 0.60 mmol, 3.0 equiv). The Schlenk tube was capped with a glass stopper and stirred at 80 °C for 24 h. The resulting mixture was extracted with Et_2O , dried over MgSO_4 , filtered, and concentrated on a rotary evaporator. The residue was subjected to preparative TLC on silica gel eluted with EtOAc /hexane (1:4) to give **3aa**.

7. Procedure for Scheme 2

$[\text{IrCl}(\text{coe})_2]_2$ (4.5 mg, 0.0050 mmol, 5 mol% of Ir) and **L2–L9** (0.012 mmol, 6 mol%) were placed in a Schlenk tube under N_2 . Toluene (0.8 mL) was added to the tube, and the resulting mixture was stirred at room temperature for 15 min. To the resulting red solution were added **1a** (0.20 mmol), Et_3N (36 μL , 0.26 mmol, 1.3 equiv), H_2O (0.8 mL), and isoprene (**2a**) (40.9 mg, 0.60 mmol, 3.0 equiv). The Schlenk tube was capped with a glass stopper and the mixture was stirred at 80 °C for 24 h. The resulting mixture was extracted with Et_2O , dried over MgSO_4 , filtered, and concentrated on a rotary evaporator. The residue was subjected to preparative TLC on silica gel eluted with EtOAc /hexane (1:4) to give **3aa**. The ee was measured by chiral HPLC analysis.

8. Procedure for Scheme 3

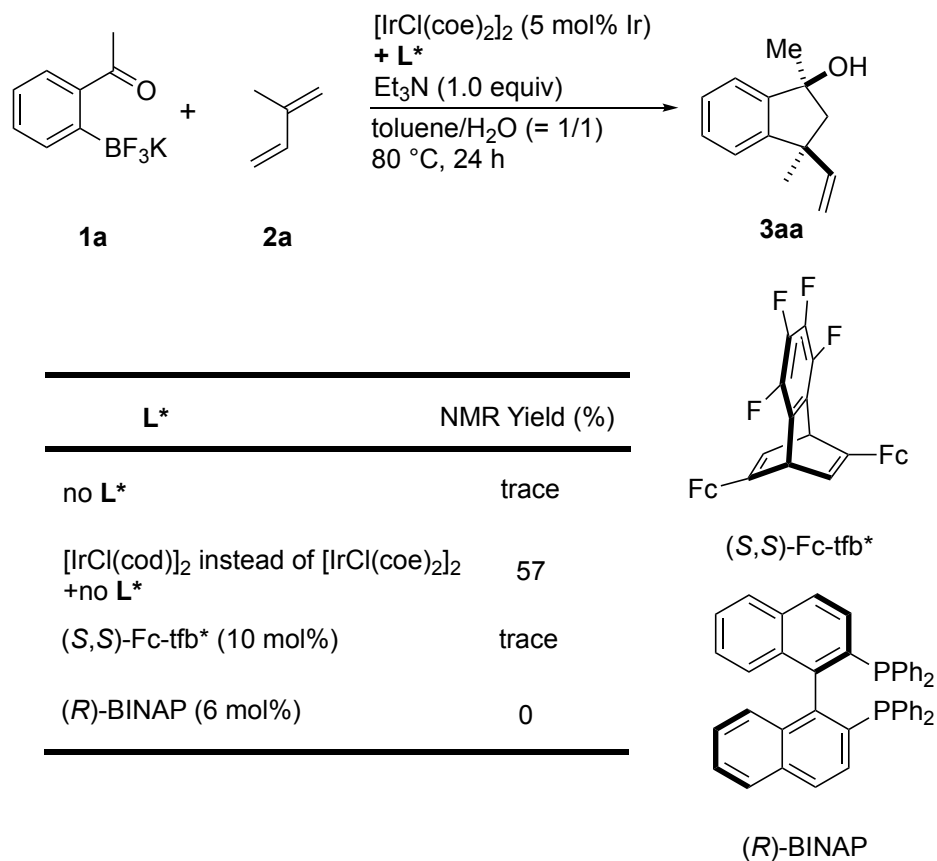
[IrCl(coe)₂]₂ (4.5 mg, 0.0050 mmol, 5 mol% of Ir) and (*R*)-**L3** (8.0 mg, 0.012 mmol, 6 mol%) were placed in a Schlenk tube under N₂. Toluene (0.8 mL) was added to the tube, and the resulting mixture was stirred at room temperature for 15 min. To the resulting red solution were added *o*-benzoylphenyl pinacol boron ester **6a–6n** (0.20 mmol), Et₃N (28 μL, 0.20 mmol, 1.0 equiv), H₂O (0.8 mL), and isoprene **2a** (40.9 mg, 0.60 mmol, 3.0 equiv). The Schlenk tube was capped with a glass stopper and stirred at 80 °C for 24 h. The resulting mixture was extracted with Et₂O, dried over MgSO₄, filtered, concentrated on a rotary evaporator. The residue was subjected to preparative TLC on silica gel eluted with EtOAc/hexane (1:4) to give **3aa–3ma**.

9. Procedure for Scheme 4

[IrCl(coe)₂]₂ (4.5 mg, 0.0050 mmol, 5 mol% of Ir) and (*R*)-**L3** (8.0 mg, 0.012 mmol, 6 mol%) were placed in a Schlenk tube under N₂. Toluene (0.8 mL) was added to the tube, and the resulting mixture was stirred at room temperature for 15 min. To the resulting red solution were added *o*-benzoylphenyl pinacol boron ester **6g** (61.6 mg, 0.20 mmol), Et₃N (28 μL, 0.20 mmol, 1.0 equiv), H₂O (0.8 mL), and 1,3-dienes **2b–2f** (0.60 mmol, 3.0 equiv). The Schlenk tube was capped with a glass stopper and stirred at 80 °C for 24 h or 48 h. The resulting mixture was extracted with Et₂O, dried over MgSO₄, filtered, concentrated on a rotary evaporator. The residue was subjected to preparative TLC on silica gel eluted with EtOAc/hexane (1:4) to give **3gb–3gf**.

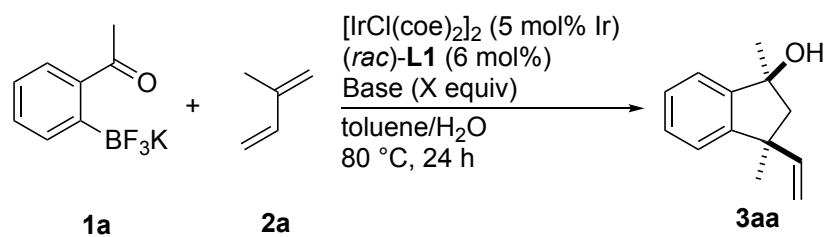
10. Other Experimental Data

Table S-1. Ligand screening^a



^aReaction conditions: **1a** (0.10 mmol), **2a** (0.30 mmol, 3.0 equiv), [IrCl(coe)₂]₂ (0.0025 mmol, 5 mol% of Ir), (*rac*)-**L1** (0.006 mmol, 6 mol%), and Et₃N (0.10 mmol, 1.0 equiv) in toluene (0.4 mL) and H₂O (0.4 mL) at 80 °C for 24 h under N₂ atmosphere. Ratio of diastereomers (dr >99:1).

Table S-2. Screening of base^a

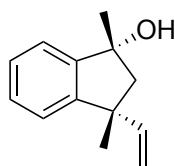


Base	X	Yield (%) ^b	Dr (Cis/Trans) ^b
	1.0	68	>99/1
Et ₃ N	0.5	58	>99/1
	1.3	58	>99/1
	2.5	54	>99/1

DABCO	1.0	29	>99/1
Pyridine	1.0	7	>99/1
KOAc	1.0	41	86/14
None	-	45	73/27

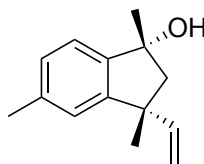
^aReaction conditions: **1a** (0.20 mmol), **2a** (0.60 mmol, 3.0 equiv), [IrCl(coe)₂]₂ (0.0050 mmol, 5 mol% of Ir), (*rac*)-**L1** (0.012 mmol, 6 mol%) and base in toluene (0.8 mL) and H₂O (0.8 mL) at 80 °C for 24 h under N₂ atmosphere. ^bDetermined by ¹H NMR.

11. Characterization of the products



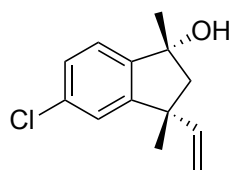
3aa

Compound 3aa (19.8 mg, 53% yield, 99% ee, colorless oil): The ee was measured by HPLC (CHIRALCEL[®] OD-H, hexane/2-propanol = 100:1, flow 1.0 mL/min, 254 nm, $t_1 = 16.9$ min (minor), $t_2 = 20.2$ min (major)); $[\alpha]_D^{25} +13$ (c 0.68, CHCl₃) for 99% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.40–7.29 (m, 3H), 7.18 (dd, $J = 8.0, 1.6$ Hz, 1H), 6.19 (dd, $J = 17.4, 10.6$ Hz, 1H), 4.97 (dd, $J = 10.6, 1.4$ Hz, 1H), 4.78 (dd, $J = 17.4, 1.4$ Hz, 1H), 2.38 (d, $J = 13.6$ Hz, 1H), 2.12 (d, $J = 13.6$ Hz, 1H), 2.02 (br, 1H), 1.63 (s, 3H), 1.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 148.8, 147.8, 147.3, 128.6, 127.6, 124.1, 122.7, 111.8, 79.5, 56.0, 48.4, 27.3, 26.4; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for C₁₃H₁₆ONa 211.1093; Found 211.1092.



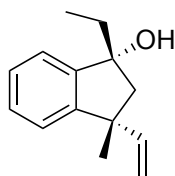
3ba

Compound 3ba (25.4 mg, 63% yield, 99% ee, colorless oil): The ee was measured by HPLC (CHIRALPAK[®] IA, hexane/2-propanol = 100:1, flow 1.0 mL/min, 254 nm, $t_1 = 22.0$ min (minor), $t_2 = 27.7$ min (major)); $[\alpha]_D^{25} +28$ (c 1.27, CHCl₃) for 99% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, $J = 7.8$ Hz, 1H), 7.12 (d, $J = 7.8$ Hz, 1H), 6.98 (s, 1H), 6.18 (dd, $J = 17.4, 10.6$ Hz, 1H), 4.97 (dd, $J = 10.6, 1.2$ Hz, 1H), 4.81 (dd, $J = 17.4, 1.2$ Hz, 1H), 2.38–2.35 (m, 4H), 2.11 (d, $J = 14.0$ Hz, 1H), 1.98 (br, 1H), 1.62 (s, 3H), 1.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 148.8, 148.0, 144.6, 128.5, 124.6, 122.5, 111.6, 79.3, 56.2, 48.3, 27.4, 26.3, 21.5; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for C₁₄H₁₈NaO 225.1250; Found 225.1254.



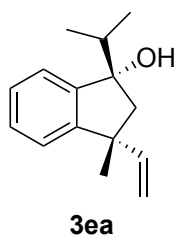
3ca

Compound 3ca (33.2 mg, 75% yield, 99% ee, colorless oil): The ee was measured by HPLC (CHIRALPAK[®] IA, hexane/2-propanol = 100:1, flow 1.0 mL/min, 254 nm, t_1 = 23.7 min (minor), t_2 = 27.3 min (major)); $[\alpha]^{25}_D$ +33 (c 1.66, CHCl₃) for 99% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.25 (m, 2H), 7.18 (d, J = 2.0 Hz, 1H), 6.14 (dd, J = 17.2, 10.4 Hz, 1H), 5.00 (dd, J = 10.4, 1.0 Hz, 1H), 4.80 (dd, J = 17.2, 1.0 Hz, 1H), 2.37 (d, J = 13.8 Hz, 1H), 2.12 (d, J = 13.8 Hz, 1H), 2.04 (br, 1H), 1.60 (s, 3H), 1.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.8, 148.0, 145.9, 134.4, 127.9, 124.4, 124.1, 112.2, 79.1, 56.0, 48.4, 27.4, 26.2; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for C₁₃H₁₅³⁵ClNaO 245.0704; Found 245.0701.

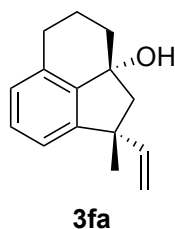


3da

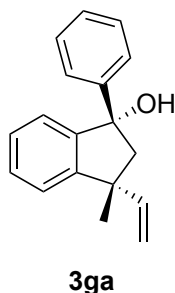
Compound 3da (30.7 mg, 76% yield, 99% ee, colorless oil): The ee was measured by HPLC (CHIRALCEL[®] OD-H, hexane/2-propanol = 100:1, flow 0.6 mL/min, 254 nm, t_1 = 23.3 min (minor), t_2 = 26.6 min (major)); $[\alpha]^{25}_D$ +37 (c 0.41, CHCl₃) for 99% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.27 (m, 3H), 7.19–7.17 (m, 1H), 6.20 (dd, J = 17.2, 10.4 Hz, 1H), 4.96 (dd, J = 10.4, 1.4 Hz, 1H), 4.76 (dd, J = 17.2, 1.4 Hz, 1H), 2.26 (d, J = 13.8 Hz, 1H), 2.14 (d, J = 13.8 Hz, 1H), 2.10 (dt, J = 21.4, 7.4 Hz, 1H), 1.94 (s, 1H), 1.78 (dt, J = 21.4, 7.4 Hz, 1H), 1.42 (s, 3H), 1.01 (t, J = 7.4 Hz, 3H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 149.0, 148.3, 146.7, 128.7, 127.5, 124.2, 123.0, 111.5, 82.5, 52.5, 48.3, 32.5, 26.4, 8.8; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for C₁₄H₁₈ONa 225.1250; Found 225.1261.



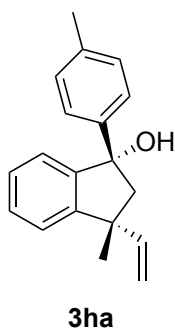
Compound 3ea (23.8 mg, 55% yield, 99% ee, colorless oil): The ee was measured by HPLC (CHIRALCEL[®] OD-H, hexane/2-propanol = 100:1, flow 0.6 mL/min, 254 nm, $t_1 = 19.1$ min (minor), $t_2 = 23.4$ min (major)); $[\alpha]^{25}_D +52$ (c 0.71, CHCl₃) for 99% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.35–7.27 (m, 3H), 7.18–7.16 (m, 1H), 6.20 (dd, $J = 17.2, 10.4$ Hz, 1H), 4.93 (dd, $J = 10.4, 1.2$ Hz, 1H), 4.73 (dd, $J = 17.2, 1.2$ Hz, 1H), 2.38 (m, 1H), 2.14 (d, $J = 14.2$ Hz, 1H), 2.09 (d, $J = 14.2$ Hz, 1H), 1.92 (s, 1H), 1.42 (s, 3H), 1.13 (d, $J = 6.6$ Hz, 3H), 0.75 (d, $J = 6.6$ Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 149.0, 148.3, 146.7, 128.7, 127.5, 123.2, 123.0, 111.5, 82.5, 52.5, 48.3, 32.5, 26.4, 8.75; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for C₁₃H₂₀O₃Na 239.1406; Found 239.1412.



Compound 3fa (30.8 mg, 72% yield, 95% ee, colorless oil): The ee was measured by HPLC (CHIRALCEL[®] OD-H, hexane/2-propanol = 100:1, flow 0.5 mL/min, 254 nm, $t_1 = 17.0$ min (minor), $t_2 = 19.0$ min (major)); $[\alpha]^{25}_D +11$ (c 0.67, CHCl₃) for 95% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.29–7.25 (m, 1H), 7.04–7.02 (m, 2H), 6.38 (dd, $J = 17.4, 10.2$ Hz, 1H), 5.02 (dd, $J = 10.2, 1.2$ Hz, 1H), 4.84 (dd, $J = 17.4, 1.2$ Hz, 1H), 2.93–2.87 (m, 1H), 2.69–2.60 (m, 1H), 2.43 (d, $J = 13.0$ Hz, 1H), 2.32–2.16 (m, 3H), 1.94 (d, $J = 13.0$ Hz, 1H), 1.91–1.84 (m, 1H), 1.49–1.38 (m, 4H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 149.4, 146.8, 143.6, 135.0, 129.0, 126.6, 121.5, 112.7, 76.1, 56.4, 49.8, 34.2, 26.7, 25.9, 18.6; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for C₁₄H₁₆ONa 237.1257; Found 237.1250.

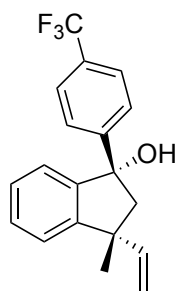


Compound 3ga (42.5 mg, 85% yield, 99% ee, colorless oil): The ee was measured by HPLC (CHIRALPAK[®] IA, hexane/2-propanol = 100:1, flow 1.0 mL/min, 254 nm, the minor product peak was not detected due to quite high enantioselectivity, $t_r = 34.7$ min (major)); $[\alpha]_D^{25} +50$ (c 0.66, CHCl₃) for 99% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.45–7.26 (m, 8H), 7.06 (dd, $J = 7.0, 1.4$ Hz, 1H), 6.30 (dd, $J = 17.4, 10.4$ Hz, 1H), 5.03 (dd, $J = 10.4, 0.6$ Hz, 1H), 4.84 (dd, $J = 17.4, 0.6$ Hz, 1H), 2.62 (d, $J = 14.2$ Hz, 1H), 2.43 (d, $J = 14.2$ Hz, 1H), 2.35 (s, 1H), 1.46 (s, 3H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 148.8, 148.7, 147.5, 146.1, 128.8, 127.9, 127.8, 126.8, 126.0, 124.8, 124.1, 111.9, 84.1, 58.9, 49.0, 26.3; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for C₁₈H₁₈ONa 273.1250; Found 273.1249.



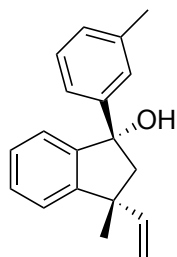
Compound 3ha (37.0 mg, 70% yield, 99% ee, colorless oil): The ee was measured by HPLC (CHIRALCEL[®] OD-H, hexane/2-propanol = 100:1, flow 0.6 mL/min, 254 nm, $t_1 = 28.3$ min (minor), $t_2 = 31.3$ min (major)); $[\alpha]_D^{25} +25$ (c 0.87, CHCl₃) for 99% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.41–7.26 (m, 5H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.08 (d, $J = 7.2$ Hz, 1H), 6.29 (dd, $J = 17.6, 10.4$ Hz, 1H), 5.03 (dd, $J = 10.4, 1.2$ Hz, 1H), 4.85 (dd, $J = 17.6, 1.2$ Hz, 1H), 2.61 (d, $J = 13.8$ Hz, 1H), 2.45 (d, $J = 13.8$ Hz, 1H), 2.37 (s, 3H), 2.34 (s, 1H), 1.45 (s, 3H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 148.8, 148.6, 147.6, 143.2,

136.4, 128.7, 128.6, 127.8, 125.9, 124.8, 124.1, 111.8, 84.0, 58.9, 48.9, 26.2, 21.0. HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{19}H_{20}ONa$ 287.1399; Found 287.1406.



3ia

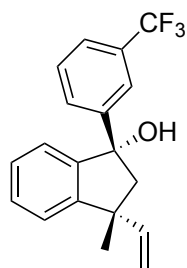
Compound 3ia (54.1 mg, 85% yield, 95% ee, colorless oil): The ee was measured by HPLC (CHIRALPAK[®] IK, hexane/2-propanol = 100:1, flow 0.6 mL/min, 254 nm, t_1 = 8.9 min (minor), t_2 = 10.1 min (major)); $[\alpha]_D^{25} +35$ (c 2.14, $CHCl_3$) for 95% ee; 1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.40 (t, J = 8.0 Hz, 1H), 7.30–7.25 (m, 2H), 6.99 (dd, J = 7.0, 1.8 Hz, 1H), 6.29 (dd, J = 17.2, 10.4 Hz, 1H), 5.03 (dd, J = 10.4, 1.2 Hz, 1H), 4.80 (dd, J = 17.2, 1.2 Hz, 1H), 2.61 (d, J = 13.8 Hz, 1H), 2.43 (s, 1H), 2.38 (d, J = 13.8 Hz, 1H), 1.48 (s, 3H); ^{13}C $\{^1H\}$ NMR (100 MHz, CD_3COCD_3) δ 154.0, 150.9, 148.3, 147.9, 147.8, 129.6, 128.9 (q, $^2J_{F-C}$ = 32 Hz), 128.3, 127.8, 125.6, 125.47 (q, $^3J_{F-C}$ = 4 Hz), 125.46 (q, $^1J_{F-C}$ = 269 Hz), 110.7, 84.2, 59.6, 49.4, 26.1; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{19}H_{17}OF_3Na$ 341.1124; Found 341.1130.



3ja

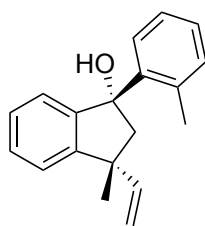
Compound 3ja (32.2 mg, 61% yield, 98% ee, colorless oil): The ee was measured by HPLC (CHIRALPAK[®] IK, hexane/2-propanol = 100:1, flow 0.6 mL/min,

254 nm, $t_1 = 11.4$ min (major), $t_2 = 12.0$ min (minor)); $[\alpha]^{25}_D +37$ (c 0.97, CHCl_3) for 98% ee; ^1H NMR (400 MHz, CDCl_3) δ 7.40 (td, $J = 7.2, 1.6$ Hz, 1H), 7.31–7.20 (m, 5H), 7.12–7.08 (m, 2H), 6.31 (dd, $J = 17.2, 11.0$ Hz, 1H), 5.04 (dd, $J = 11.0, 1.2$ Hz, 1H), 4.86 (dd, $J = 17.2, 1.2$ Hz, 1H), 2.62 (d, $J = 13.8$ Hz, 1H), 2.44 (d, $J = 13.8$ Hz, 1H), 2.373 (s, 3H), 2.367 (s, 1H), 1.47 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 148.8, 148.7, 147.6, 146.0, 137.5, 128.8, 127.84, 127.82, 127.6, 126.6, 124.8, 124.1, 123.1, 111.8, 84.1, 58.9, 49.0, 26.3, 21.61; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{20}\text{ONa}$ 241.1406; Found 287.1407.



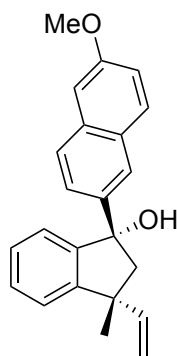
3ka

Compound 3ka (49.3 mg, 77% yield, 99% ee, colorless oil): The ee was measured by HPLC (CHIRALPAK[®] IA, hexane/2-propanol = 100:1, flow 1.0 mL/min, 254 nm, $t_1 = 23.1$ min (major), $t_2 = 25.0$ min (minor)); $[\alpha]^{25}_D +38$ (c 1.62, CHCl_3) for 99% ee; ^1H NMR (400 MHz, CDCl_3) δ 7.81 (s, 1H), 7.55 (t, $J = 7.2$ Hz, 2H), 7.47–7.40 (m, 2H), 7.31–7.26 (m, 2H), 7.01 (d, $J = 7.2$ Hz, 1H), 6.30 (dd, $J = 17.4, 10.2$ Hz, 1H), 5.04 (d, $J = 10.2$ Hz, 1H), 4.83 (d, $J = 17.4$ Hz, 1H), 2.63 (d, $J = 13.8$ Hz, 1H), 2.45 (s, 1H), 2.39 (d, $J = 13.8$ Hz, 1H), 1.49 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 148.7, 147.1, 147.0, 130.3 (q, $^2J_{\text{F-C}} = 32$ Hz), 129.6, 129.2, 128.4, 128.1, 125.6, 124.6, 124.3, 123.9 (q, $^1J_{\text{F-C}} = 249$ Hz), 123.7 (q, $^3J_{\text{F-C}} = 4$ Hz), 122.8 (q, $^3J_{\text{F-C}} = 4$ Hz), 112.3, 83.8, 58.9, 49.2, 26.4; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{17}\text{OF}_3\text{Na}$ 341.1124; Found 341.1135.



3la

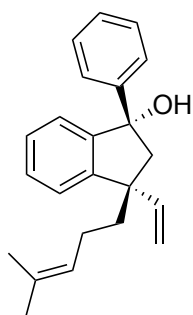
Compound 3la (29.4 mg, 56% yield, 98% ee, colorless oil): The ee was measured by HPLC (CHIRALCEL[®] OD-H, hexane/2-propanol = 100:1, flow 0.6 mL/min, 254 nm, $t_1 = 27.1$ min (major), $t_2 = 31.1$ min (minor)); $[\alpha]^{25}_D +33$ (c 0.85, CHCl₃) for 98% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, $J = 7.6$ Hz, 1H), 7.39 (t, $J = 7.6, 1.2$ Hz, 1H), 7.31–7.25 (m, 2H), 7.22–7.15 (m, 3H), 7.12 (d, $J = 7.6$ Hz, 1H), 6.25 (dd, $J = 17.4, 10.5$ Hz, 1H), 5.03 (dd, $J = 10.5, 1.2$ Hz, 1H), 4.83 (dd, $J = 17.4, 1.2$ Hz, 1H), 2.58 (m, 2H), 2.23 (s, 1H), 2.12 (s, 3H), 1.39 (s, 3H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 148.5, 148.4, 147.4, 143.2, 135.5, 132.1, 128.8, 127.8, 127.2, 126.8, 125.3, 124.4, 124.3, 111.5, 84.5, 55.9, 48.8, 25.8, 21.6; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for C₁₉H₂₀ONa 287.1406; Found 247.1412.



3ma

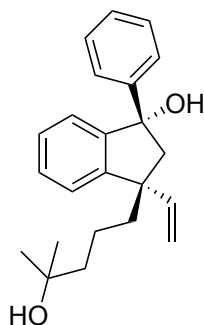
Compound 3ma (47.6 mg, 72% yield, 99% ee, colorless oil): The ee was measured by HPLC (CHIRALPAK[®] IC, hexane/2-propanol = 100:1, flow 1.0 mL/min, 254 nm, $t_1 = 20.7$ min (major), $t_2 = 23.2$ min (minor)); $[\alpha]^{25}_D -6.6$ (c 2.12, CHCl₃) for 99% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, $J = 2.0$ Hz, 1H), 7.74 (d, $J = 8.6$ Hz, 1H), 7.70 (d, $J = 8.6$ Hz, 1H), 7.43–7.37 (m, 2H), 7.31–7.27 (m, 2H), 7.17–7.15 (m, 2H), 7.08 (d, 7.6 Hz, 1H), 6.33 (dd, $J = 17.4, 10.6$ Hz, 1H), 5.05 (dd, $J = 10.6, 1.2$ Hz, 1H), 4.89

(dd, $J = 17.4, 1.2$ Hz, 1H), 3.93 (s, 3H), 2.67 (d, $J = 14.0$ Hz, 1H), 2.53 (d, $J = 14.0$ Hz, 1H), 2.48 (s, 1H), 1.48 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 157.7, 148.9, 148.7, 147.5, 141.1, 133.5, 129.7, 128.9, 128.4, 127.9, 126.6, 125.2, 124.8, 124.3, 124.2, 118.8, 111.8, 105.5, 84.2, 58.7, 55.3, 49.0, 26.3; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{22}\text{ONa}$ 353.1512; Found 353.1515.



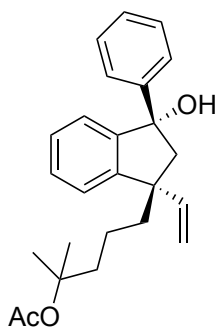
3gb

Compound 3gb (52.8 mg, 83% yield, 99% ee, colorless oil): The ee was measured by HPLC (CHIRALPAK[®] IA, hexane/2-propanol = 100:1, flow 0.6 mL/min, 254 nm, $t_1 = 21.3$ min (major), $t_2 = 24.7$ min (minor)); $[\alpha]_D^{25} +42$ (c 2.29, CHCl_3) for 99% ee; ^1H NMR (400 MHz, CDCl_3) δ 7.45–7.42 (m, 2H), 7.39–7.33 (m, 3H), 7.30–7.25 (m, 3H), 7.04 (d, $J = 7.6$ Hz, 1H), 6.30 (dd, $J = 17.2, 10.4$ Hz, 1H), 5.11–5.07 (m, 2H), 4.94 (dd, $J = 17.2, 1.0$ Hz, 1H), 2.60 (d, $J = 14.2$ Hz, 1H), 2.51 (d, $J = 14.2$ Hz, 1H), 2.33 (s, 1H), 2.08–1.68 (m, 4H), 1.67 (s, 3H), 1.55 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 148.0, 147.8, 147.3, 146.1, 131.8, 128.8, 127.9, 126.8, 126.1, 126.0, 125.0, 124.2, 124.1, 112.8, 84.0, 54.8, 52.8, 39.6, 25.7, 23.5, 17.6; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{26}\text{ONa}$ 341.1876; Found 341.1875.



3gc

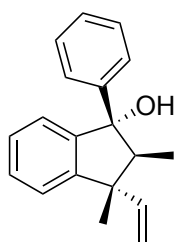
Compound 3gc (37.1 mg, 58% yield, 99% ee, colorless oil): The ee was measured by HPLC (CHIRALPAK[®] IH, hexane/2-propanol = 19:1, flow 0.6 mL/min, 254 nm, t_1 = 22.2 min (minor), t_2 = 27.7 min (major)); $[\alpha]_D^{20}$ +556 (c 0.10, CHCl₃) for 99% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.46–7.25 (m, 8H), 7.05 (dd, J = 7.6, 1.4 Hz, 1H), 6.29 (dd, J = 17.2, 10.4 Hz, 1H), 5.08 (dd, J = 10.4, 1.2 Hz, 1H), 4.91 (dd, J = 17.2, 1.2 Hz, 1H), 2.61 (d, J = 13.8 Hz, 1H), 2.47 (d, J = 13.8 Hz, 1H), 2.35 (s, 1H), 2.17 (br, 1H), 1.94–1.87 (m, 1H), 1.69–1.62 (m, 2H), 1.51–1.42 (m, 2H), 1.34–1.17 (m, 7H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 148.2, 147.6, 147.2, 146.1, 128.8, 127.9, 126.8, 126.0, 125.0, 124.2, 113.0, 83.94, 70.9, 55.1, 52.8, 44.4, 40.4, 29.3, 19.5; HRMS (ESI) m/z : [M + Na]⁺ Calcd for C₂₃H₂₈O₂Na 359.1982; Found 359.1982.



3gd

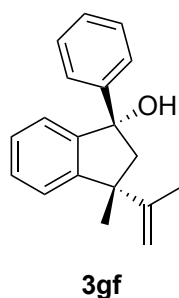
Compound 3gd (45.9 mg, 63% yield, 99% ee, colorless oil): The ee was measured by HPLC (CHIRALPAK[®] IK, hexane/2-propanol = 100:1, flow 0.6 mL/min, 254 nm, t_1 = 30.6 min (minor), t_2 = 32.6 min (major)); $[\alpha]_D^{25}$ +51 (c 1.20, CHCl₃) for 99% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, J = 7.8 Hz, 2H), 7.40–7.34 (m, 3H), 7.30–7.25 (m, 3H), 7.04 (d, J = 7.8 Hz, 1H), 6.28 (dd, J = 17.4, 10.4 Hz, 1H), 5.08 (d, J = 10.4 Hz,

1H), 4.92 (d, $J = 17.4$ Hz, 1H), 2.61 (d, $J = 13.6$ Hz, 1H), 2.45 (d, $J = 13.6$ Hz, 1H), 2.36 (s, 1H), 1.92 (s, 3H), 1.90–1.86 (m, 1H), 1.79–1.62 (m, 3H), 1.43–1.42 (m, 1H), 1.39 (s, 3H), 1.38 (s, 3H), 1.27–1.20 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.4, 148.2, 147.7, 147.1, 146.1, 128.8, 127.9, 126.8, 125.9, 125.0, 124.1, 112.9, 83.9, 82.2, 55.0, 52.8, 41.1, 39.9, 26.04, 25.99, 22.4, 19.0; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{30}\text{O}_3\text{Na}$ 401.2087; Found 401.2093.



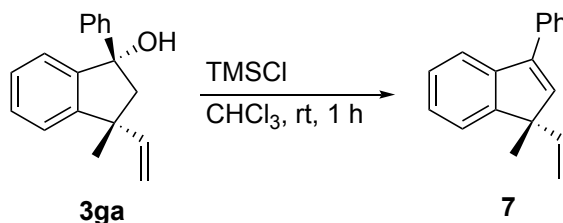
3ge

Compound 3ge (15.5 mg, 29% yield, 99% ee, colorless oil): The ee was measured by HPLC (CHIRALPAK[®] IK, hexane/2-propanol = 100:1, flow 0.6 mL/min, 254 nm, $t_1 = 7.8$ min (minor), $t_2 = 8.2$ min (major)); $[\alpha]^{25}_{\text{D}} +58$ (c 0.52, CHCl_3) for 99% ee; ^1H NMR (400 MHz, CDCl_3) δ 7.43–7.40 (m, 2H), 7.38–7.32 (m, 3H), 7.30–7.24 (m, 3H), 7.05 (d, $J = 8.0$ Hz, 1H), 6.24 (dd, $J = 17.4, 10.4$ Hz, 1H), 5.06 (dd, $J = 10.4, 1.4$ Hz, 1H), 4.64 (dd, $J = 17.4, 1.4$ Hz, 1H), 2.33 (q, $J = 7.0$ Hz, 1H), 2.01 (s, 1H), 1.48 (s, 3H), 1.00 (d, $J = 7.0$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 148.8, 148.1, 146.6, 144.8, 128.6, 127.7, 126.7, 126.4, 125.0, 124.4, 113.8, 84.9, 59.5, 51.4, 24.0, 6.8; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{20}\text{ONa}$ 287.1406; Found 287.1406.



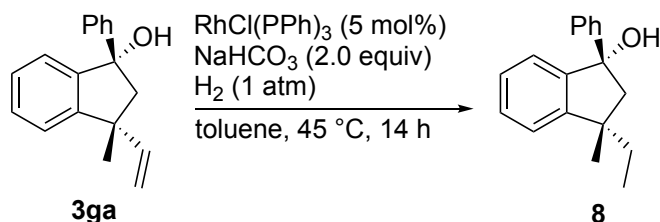
Compound 3gf (17.2 mg, 33% yield, 97% ee, colorless oil): The ee was measured by HPLC (CHIRALPAK[®] ID, hexane/2-propanol = 100:1, flow 0.6 mL/min, 254 nm, $t_1 = 30.4$ min (major), $t_2 = 36.0$ min (minor)); $[\alpha]^{25}_D +23$ (c 0.54, CHCl_3) for 97% ee; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.33 (d, $J = 8.0$ Hz, 2H), 7.39–7.32 (m, 3H), 7.28–7.24 (m, 3H), 7.04 (d, $J = 7.2$ Hz, 1H), 4.85 (s, 1H), 4.42 (s, 1H), 2.74 (d, $J = 13.6$ Hz, 1H), 2.59 (s, 1H), 2.34 (d, $J = 13.6$ Hz, 1H), 1.92 (s, 3H), 1.50 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 154.5, 149.6, 147.4, 146.0, 128.6, 127.9, 127.8, 126.7, 125.9, 124.9, 124.4, 112.1, 84.0, 57.7, 51.7, 26.0, 20.2; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{20}\text{ONa}$ 287.14106; Found 287.1409.

12. Transformation of 3ga (Scheme 5)

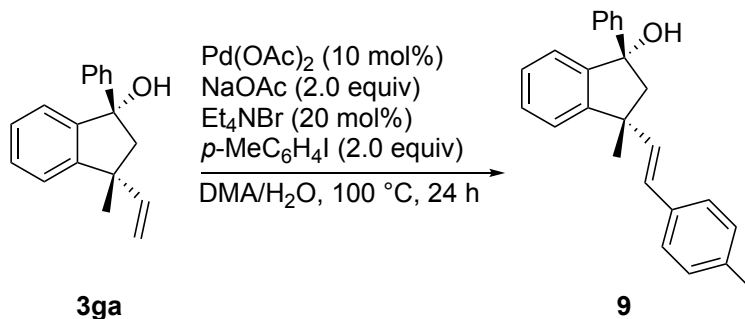


To a solution of **3ga** (6.1 mg, 0.024 mmol) in CHCl_3 (0.12 mL) was added trimethylsilyl chloride (TMSCl, 24.2 mg, 0.22 mmol), and the mixture was stirred at room temperature for an hour. The mixture was concentrated on a rotary evaporator, and the residue was subjected to preparative TLC on silica gel eluted with EtOAc/hexane (1:10) to give **7**. **Compound 7** (5.0 mg, 88% yield, 99% ee, colorless oil): The ee was measured by HPLC (CHIRALPAK[®] IA, hexane, flow 1.0 mL/min, 254 nm, $t_1 = 35.6$ min (minor), $t_2 = 36.9$ min (major)); $[\alpha]^{25}_D +60$ (c 0.32, CHCl_3) for 99% ee; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.61 (d, $J = 7.6$ Hz, 2H), 7.52 (d, $J = 7.6$ Hz, 1H), 7.45 (t, $J = 8.0$ Hz, 2H), 7.39–7.24 (m, 4H), 6.39 (s, 1H), 5.84 (dd, $J = 17.0, 10.4$ Hz, 1H), 5.28 (d, $J = 17.0$ Hz, 1H), 5.06 (d, $J = 10.4$ Hz, 1H), 1.50 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 151.9, 142.4,

142.1, 140.89, 140.85, 135.6, 128.5, 127.7, 126.7, 125.6, 122.8, 120.8, 112.4, 54.6, 21.1;
HRMS (DART) m/z : $[M + H]^+$ Calcd for $C_{18}H_{17}$ 233.1325; Found 233.1328.



$RhCl(PPh_3)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and $NaHCO_3$ (17.0 mg, 0.20 mmol, 2.0 equiv) were placed in a Schlenk tube under H_2 . Toluene (1.0 mL) and alcohol **3ga** (26.6 mg, 0.11 mmol) were added to the tube, and the resulting mixture was stirred at 45 °C for 14 h. The mixture was passed through a short silica gel column eluted with EtOAc and concentrated on a rotary evaporator. The residue was subjected to preparative TLC on silica gel eluted with EtOAc/hexane (1:4) to give **8**. **Compound 8** (17.7 mg, 70% yield, 99% ee, colorless oil): The ee was measured by HPLC (CHIRALPAK[®] IC, hexane/2-propanol = 100/1, flow 1.0 mL/min, 254 nm, t_1 = 16.5 min (major), t_2 = 17.2 min (minor)); $[\alpha]^{20}_D$ -46 (c 0.89, $CHCl_3$) for 99% ee; 1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.31 (m, 5H), 7.27–7.23 (m, 3H), 7.06 (d, J = 7.2 Hz, 1H), 2.55 (d, J = 14.2 Hz, 1H), 2.29 (d, J = 14.2 Hz, 1H), 2.09 (s, 1H), 1.79 (q, J = 7.2 Hz, 2H), 1.26 (s, 3H), 0.95 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.3, 147.8, 146.7, 128.8, 128.0, 127.3, 126.7, 126.0, 124.5, 123.3, 84.3, 56.8, 46.3, 35.6, 26.9, 9.6; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{18}H_{20}ONa$ 275.1406; Found 241.1404.

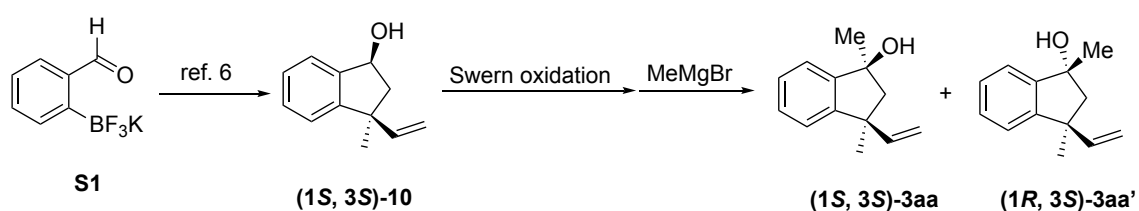


$Pd(OAc)_2$ (0.7 mg, 0.03 mmol, 10 mol%), $NaOAc$ (5.3 mg, 0.066 mmol, 2.0 equiv), Et_4NBr (1.4 mg, 20 mol%), p -iodotoluene (14.2 mg, 0.066 mmol, 2.0 equiv) and

3ga (8.2 mg, 0.033 mmol) were placed in a Schlenk tube under N₂. *N,N*-Dimethylacetamide (DMA, 0.36 mL) and H₂O (0.04 mL) were added to the tube, and the mixture was stirred at 100 °C for 24 h. The resulting mixture was passed through a short silica gel column eluted with EtOAc, and the mixture was concentrated on a rotary evaporator. The residue was subjected to preparative TLC on silica gel eluted with Et₂O/hexane (1:10) to give **9**. **Compound 9** (9.0 mg, 80% yield, 98% ee, colorless oil): The ee was measured by HPLC (CHIRALCEL[®] OD-H, hexane/2-propanol = 200/1, flow 1.0 mL/min, 254 nm, t₁ = 35.6 min (major), t₂ = 88.7 min (minor)); [α]²⁵_D +6.5 (c 0.19, CHCl₃) for 98% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.46–7.22 (m, 10H), 7.10–7.08 (m, 3H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.17 (d, *J* = 16.0 Hz, 1H), 2.71 (d, *J* = 14.2 Hz, 1H), 2.52 (d, *J* = 14.2 Hz, 1H), 2.35 (s, 1H), 2.32 (s, 3H), 1.54 (s, 3H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 149.3, 147.5, 146.2, 139.2, 137.0, 134.2, 129.2, 128.9, 128.0, 127.9, 126.9, 126.8, 126.2, 126.1, 124.8, 124.3, 84.1, 59.5, 48.4, 26.8, 21.1; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₅H₂₄ONa 363.1719; Found 363.1713.

13. Determination of the Absolute Configuration

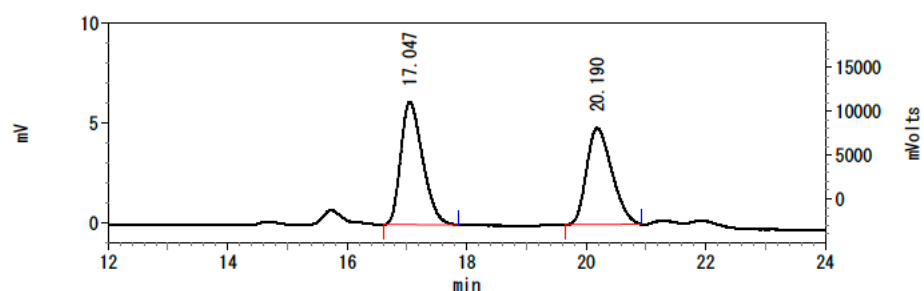
(1*S*,3*S*)-**3aa** and (1*R*,3*S*)-**3aa'** were prepared from (1*S*,3*S*)-**10**, which was derived from aldehyde **S1** by the asymmetric [3+2] annulation with isoprene.⁶



To a solution of (COCl)₂ (18.8 mg, 0.15 mmol, 2.0 equiv) in CH₂Cl₂ (0.4 mL) was added DMSO (17.3 mg, 0.22 mmol, 3.0 equiv) in CH₂Cl₂ (0.4 mL) at -78 °C, and the mixture was stirred for 5 min. To the mixture was added a solution of (1*S*,3*S*)-**10** (12.9 mg, 0.074 mmol) in CH₂Cl₂ (0.4 mL), and the mixture was stirred at -78 °C for 30 min. Then, Et₃N (44.6 mg, 0.44 mmol, 6.0 equiv) was added to the mixture at the same temperature. The mixture was stirred for 10 min and allowed to warm to room temperature. The resulting mixture was quenched with NH₄Cl aq. and extracted with

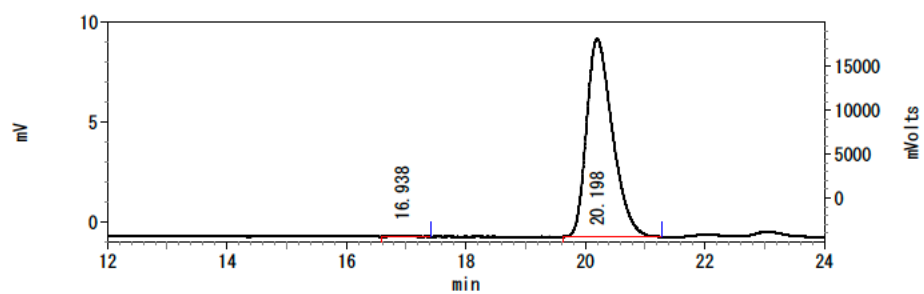
CH₂Cl₂. The organic layer was concentrated on a rotary evaporator, and the residue (5.8 mg) was used for the next reaction step without further purification. The residue (5.8 mg) was dissolved in THF (0.17 mL). To the solution was added MeMgCl in THF (3.0 M solution) (2.0 equiv) at 0 °C, and the mixture was stirred at room temperature for 1 h. The resulting mixture was quenched with NH₄Cl aq., extracted with Et₂O, and organic extract was concentrated on a rotary evaporator. The residue was subjected to preparative TLC on silica gel eluted with Et₂O/hexane (1:8) to give a mixture of (1*S*,3*S*)-**3aa** and (1*R*,3*S*)-**3aa'** (2.2 mg, 4:6). A peak of the prepared (1*S*,3*S*)-**3aa** by HPLC analysis using CHIRALCEL[®] OD-H (hexane/2-propanol = 100:1, flow 1.0 mL/min) was observed at 16.9 min. A major peak of compound **3aa** obtained in Scheme 3 appeared at 20.2 min, indicating that the absolute configuration of **3aa** in Scheme 2 is (1*R*,3*R*).

HPLC chart of (*rac*)-**3aa**



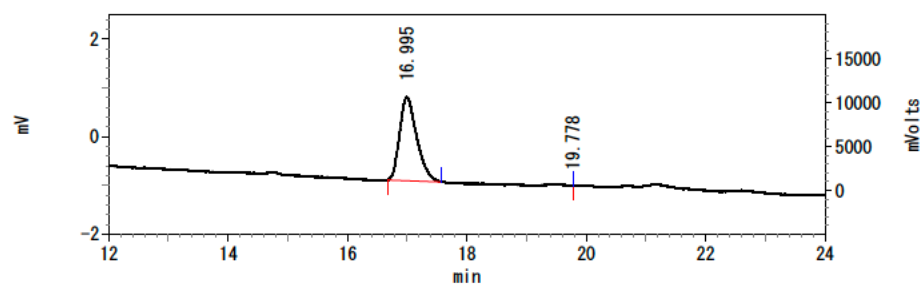
Pk #	Retention Time	Area	Area Percent
1	17.047	156298	52.289
2	20.190	142614	47.711

HPLC chart of **3aa** in Scheme 2



Pk #	Retention Time	Area	Area Percent
1	16.938	485	0.162
2	20.198	299219	99.838

HPLC chart of (1*S*,3*S*)-**3aa**



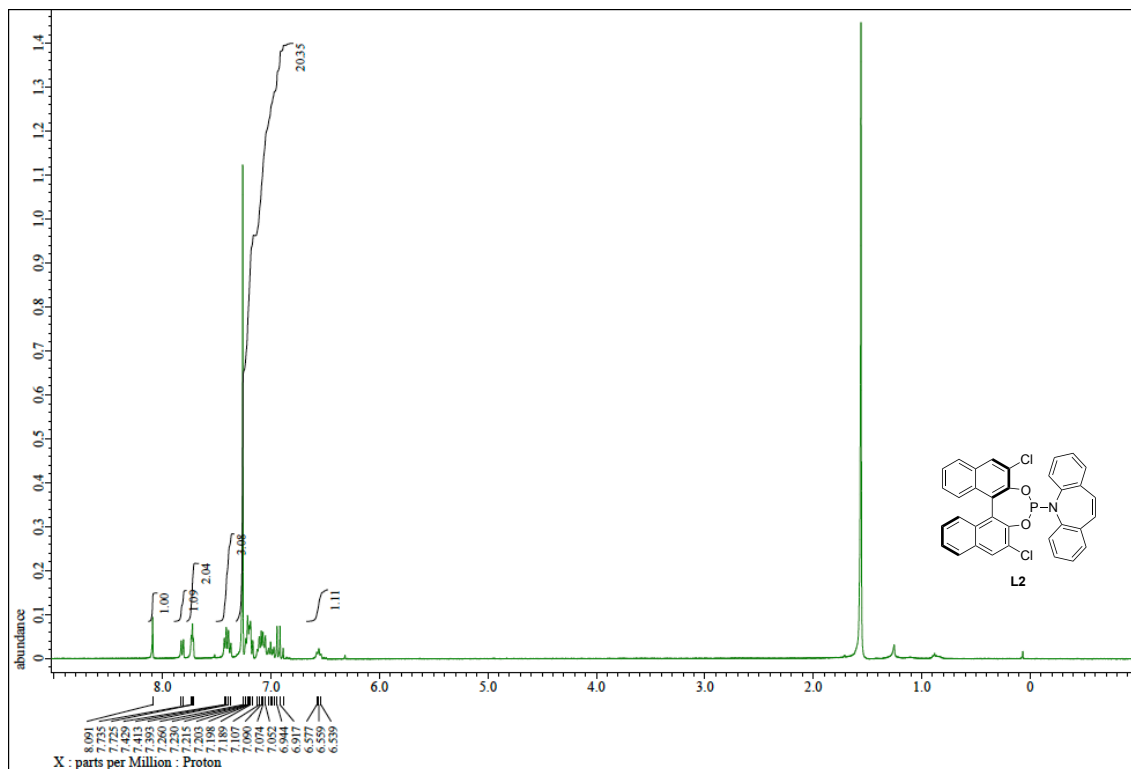
Pk #	Retention Time	Area	Area Percent
1	16.995	34246	99.997
2	19.778	1	0.003

14. References

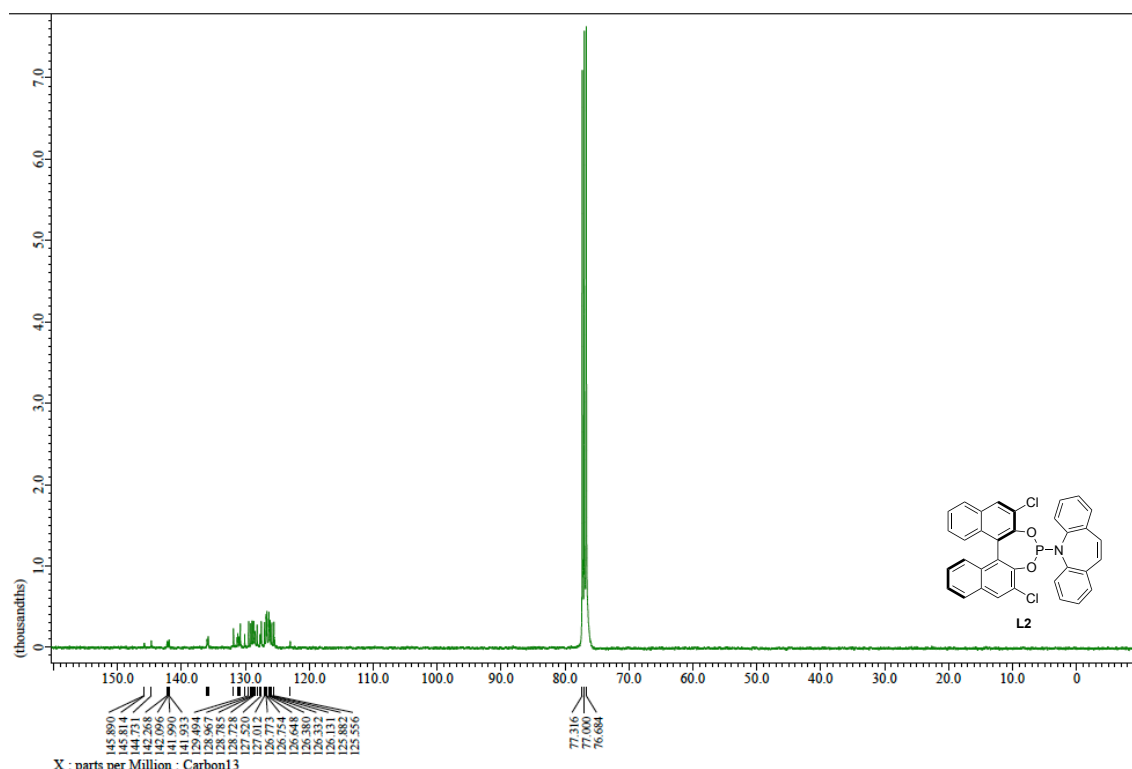
1. R. Uson, L. A. Oro and J. A. Cabeza, *Inorg. Synth.*, 1985, **23**, 129.
2. (a) T. M. Beck and B. Breit, *Angew. Chem., Int. Ed.*, 2017, **56**, 1903; (b) R. Mariz, A. Briceño and R. Dorta, *Organometallics*, 2008, **27**, 6605; (c) Y.-N. Yu and M.-H. Xu, *Org. Chem. Front.*, 2014, **1**, 738.
3. S. Chang, Y. B. Sun, X. R. Zhang, L. L. Dong, H. Y. Zhu, H. W. Lai and D. Wang, *Appl. Organomet. Chem.*, 2018, **32**, e3970.
4. H. Itoh, T. Kikuchi, T. Ishiyama and N. Miyaoura, *Chem. Lett.*, 2011, **40**, 1007.
5. (a) F.-W. Ling, M.-C. Luo, M.-K. Chen, J. Zeng, S.-Q. Li, H.-B. Yin, J.-R. Wu, Y.-X. Xu and G. Huang, *Polymer*, 2019, **178**, 121629; (b) P. A. Wender, M. P. Croatt and B. Witulski, *Tetrahedron*, 2006, **62**, 7505.
6. T. Nishimura, Y. Yasuhara, M. Nagaosa and T. Hayashi, *Tetrahedron: Asymmetry*, 2008, **19**, 1778.

15. ^1H NMR, ^{13}C NMR, ^{31}P NMR spectra, chiral HPLC charts

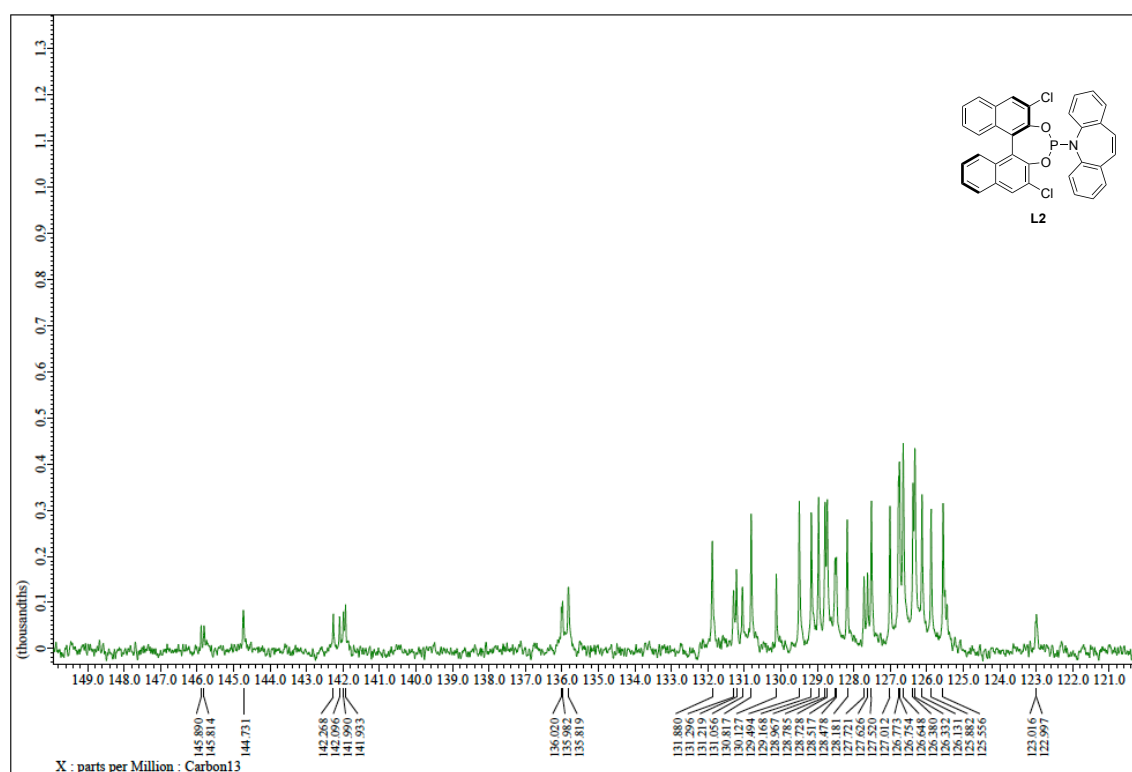
^1H NMR of L2 (400 MHz, CDCl_3)



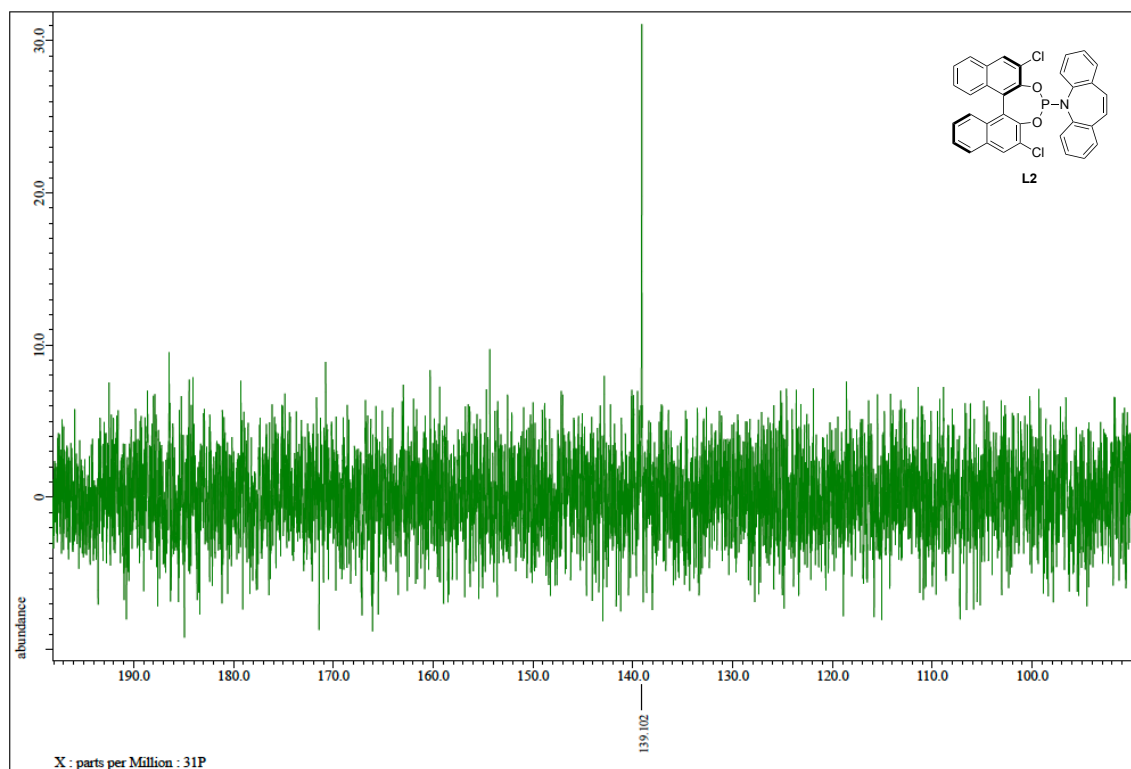
¹³C NMR of L2 (100 MHz, CDCl₃)



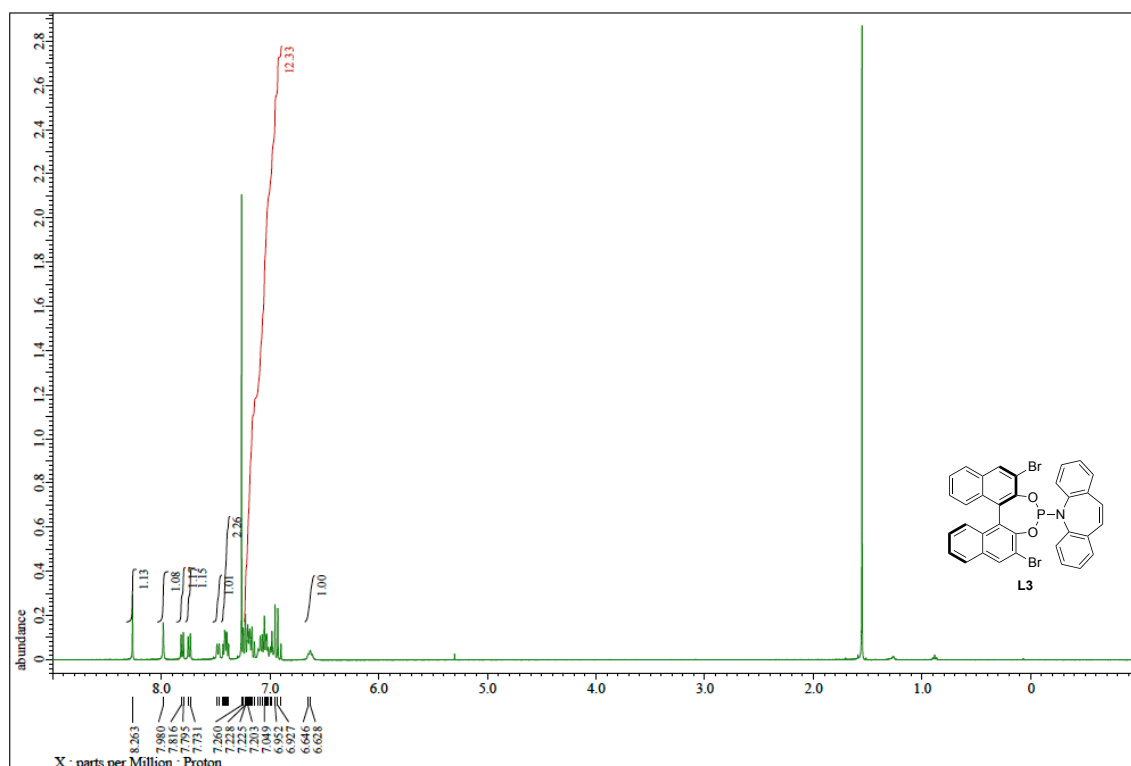
(150-120 ppm)



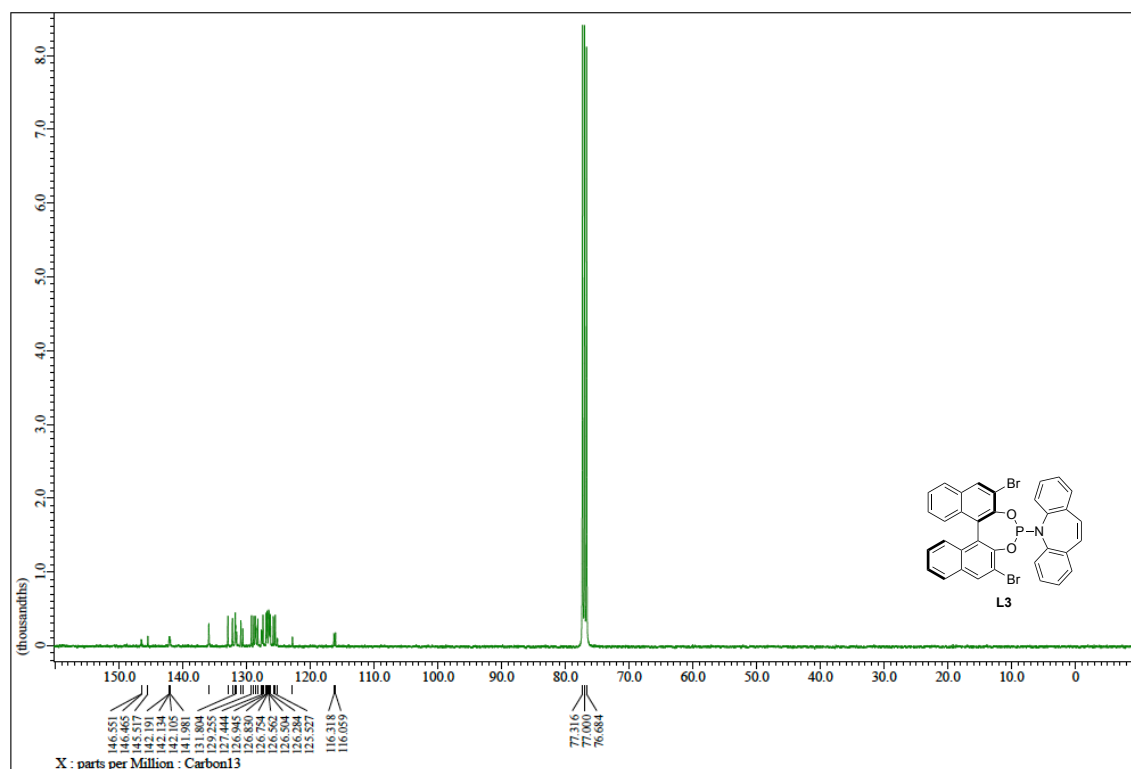
^{31}P NMR of L2 (162 MHz, CDCl_3)



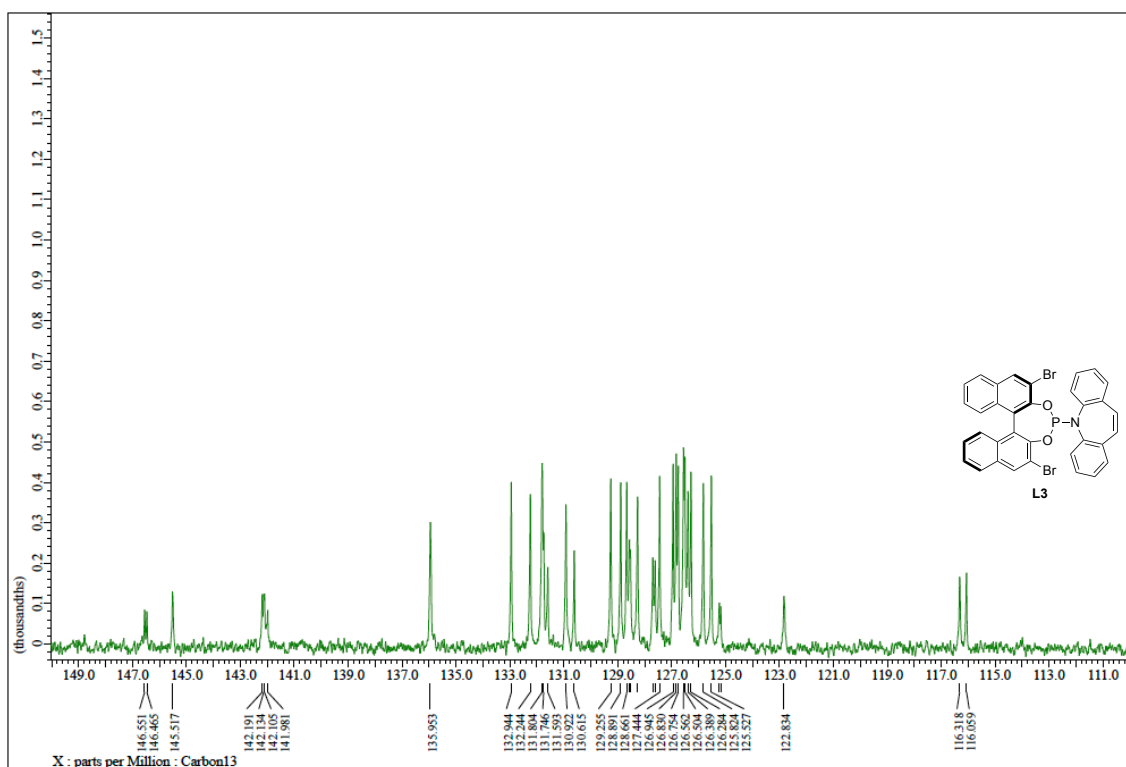
¹H NMR of L3 (400 MHz, CDCl₃)



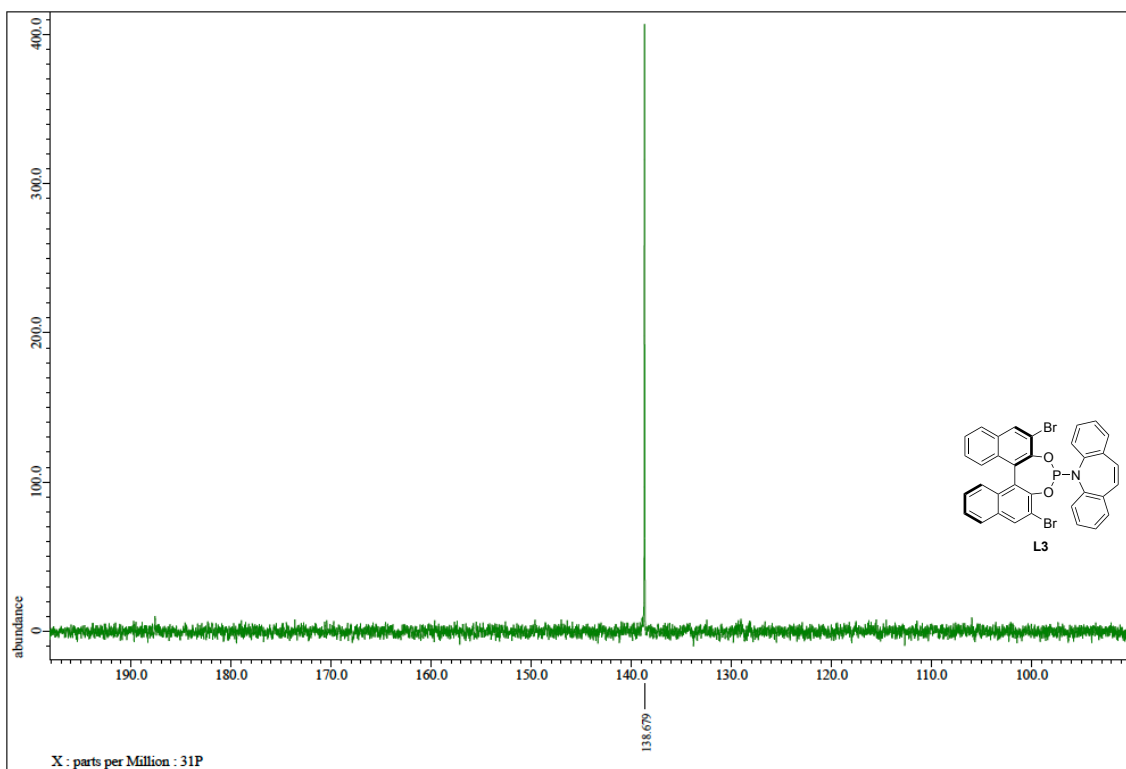
¹³C NMR of L3 (100 MHz, CDCl₃, overview)



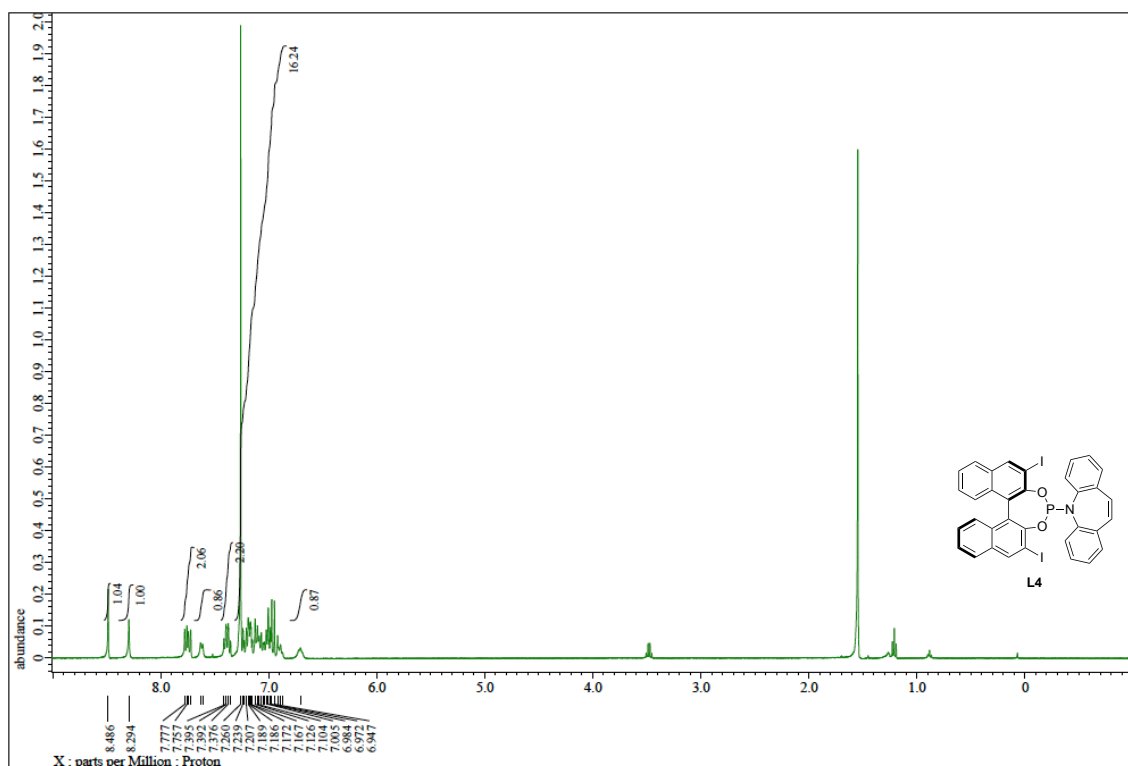
(150-110 ppm)



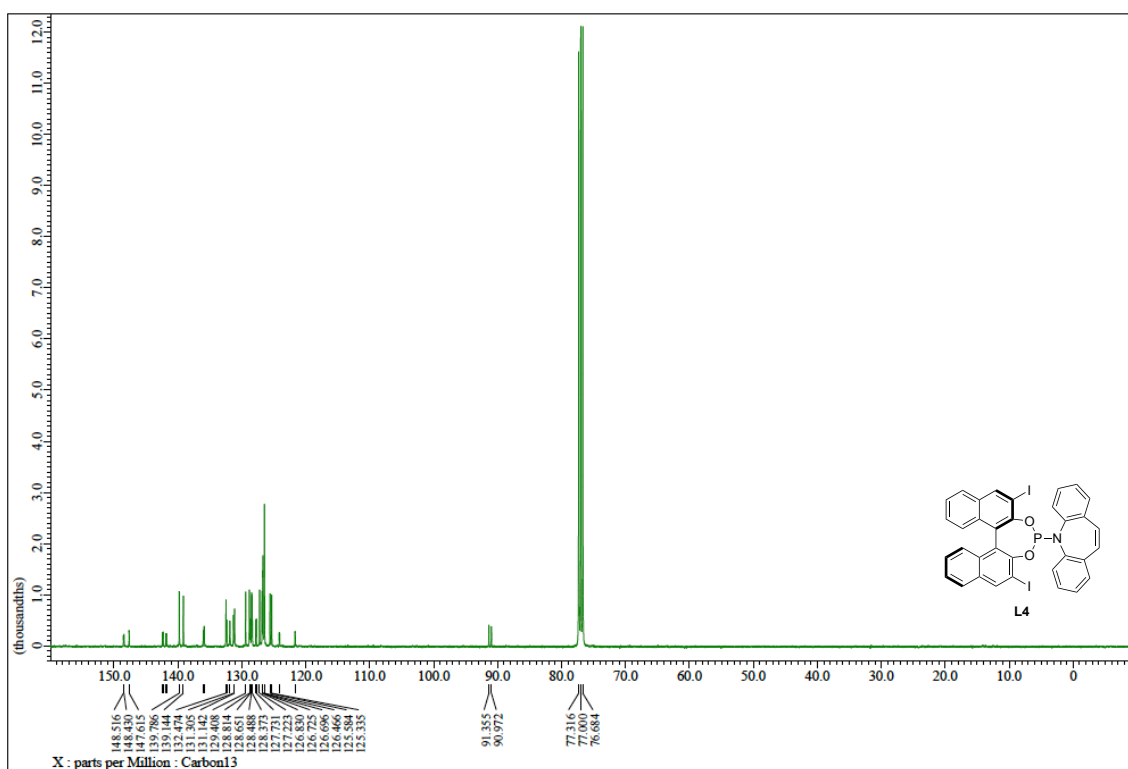
³¹P NMR of L3 (162 MHz, CDCl₃)



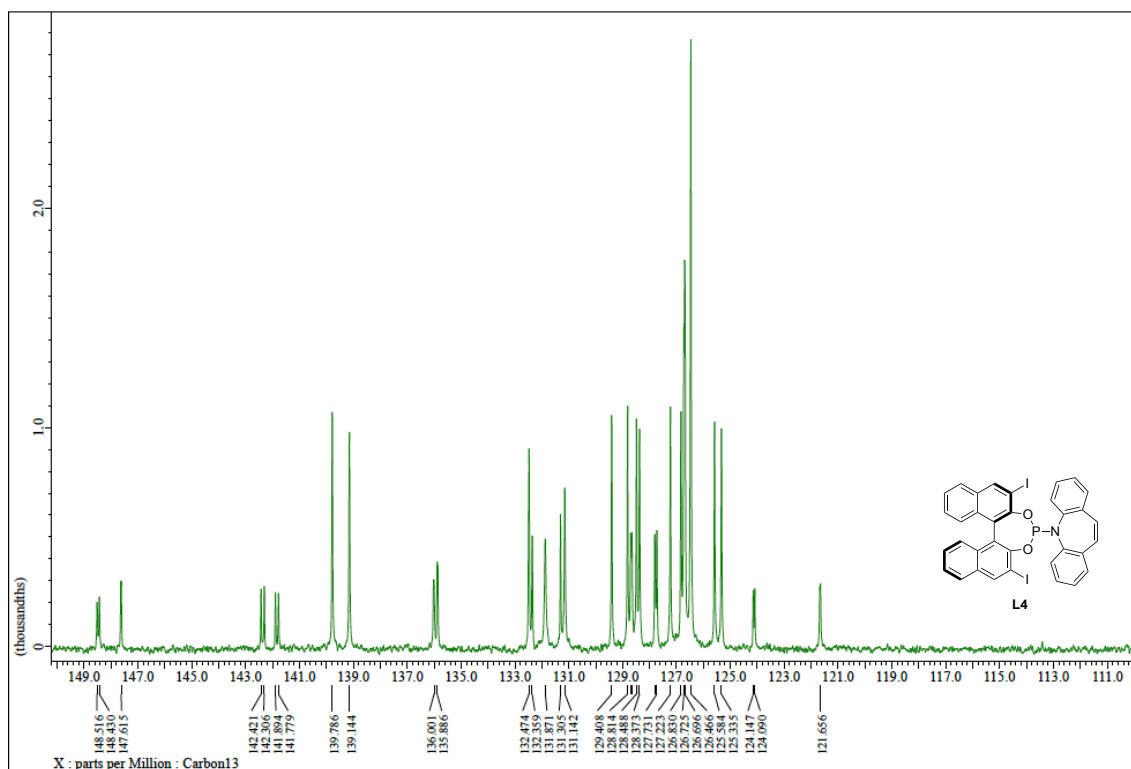
¹H NMR of L4 (400 MHz, CDCl₃)



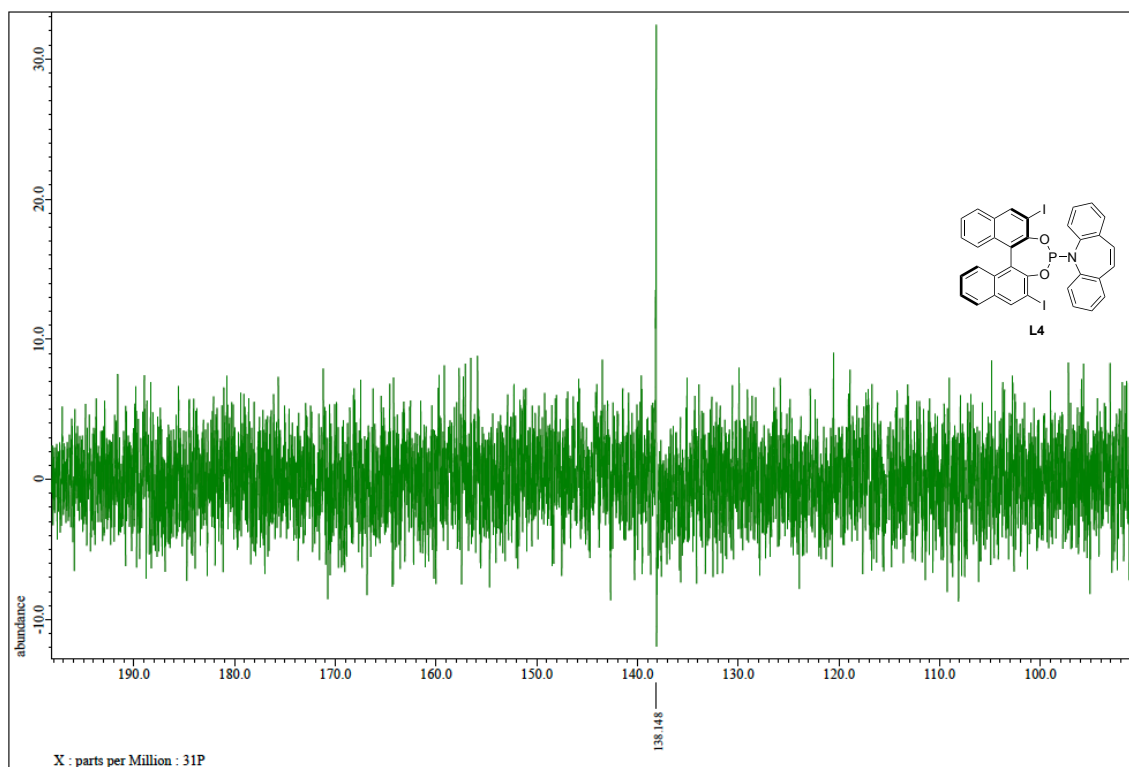
¹³C NMR of L4 (100 MHz, CDCl₃, overview)



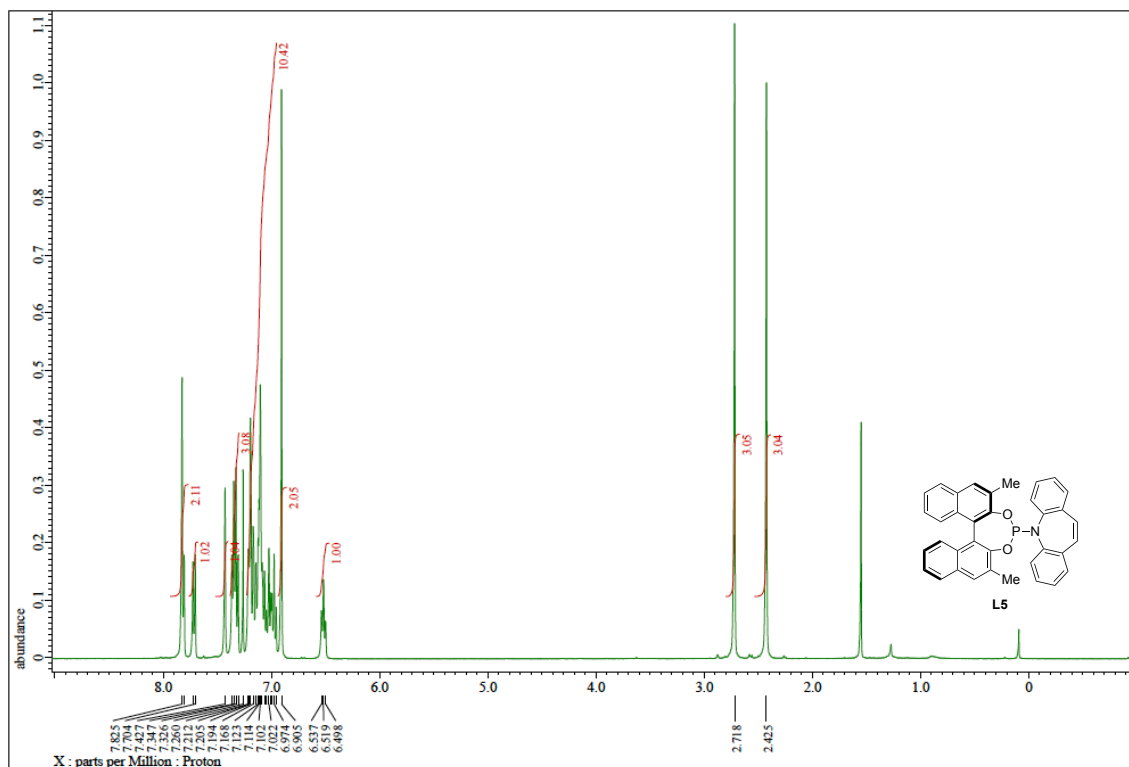
(150-110 ppm)



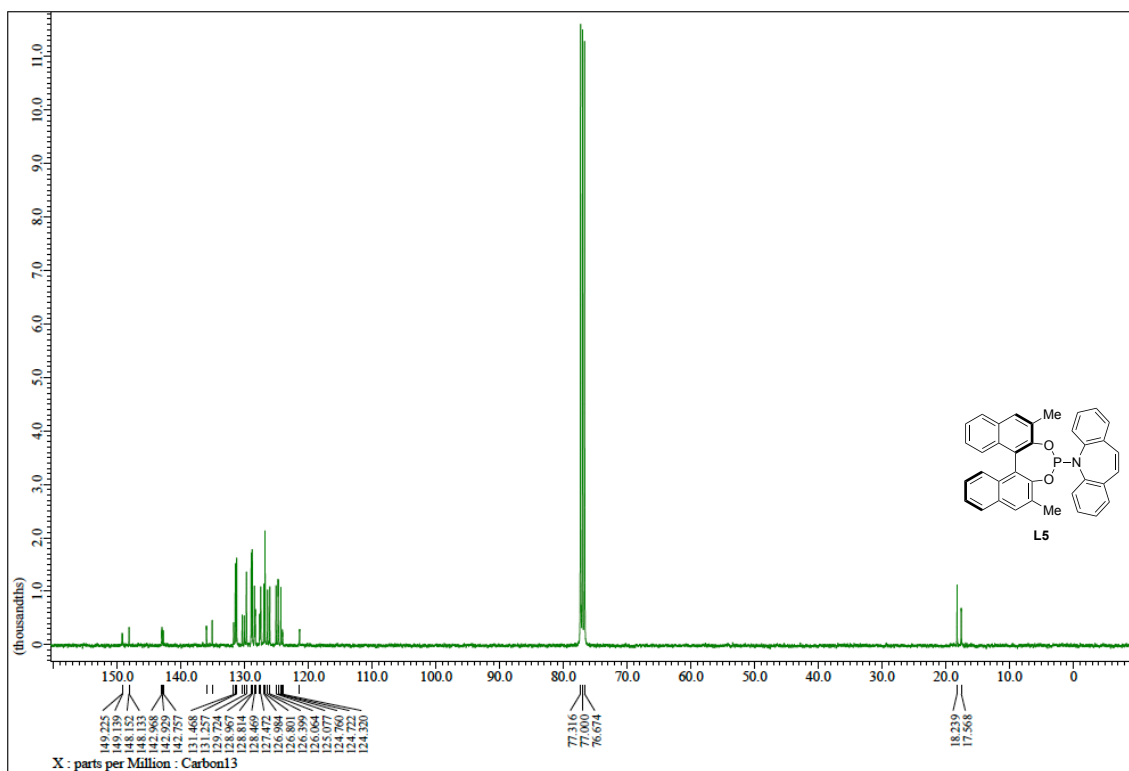
³¹P NMR of L4 (162 MHz, CDCl₃)



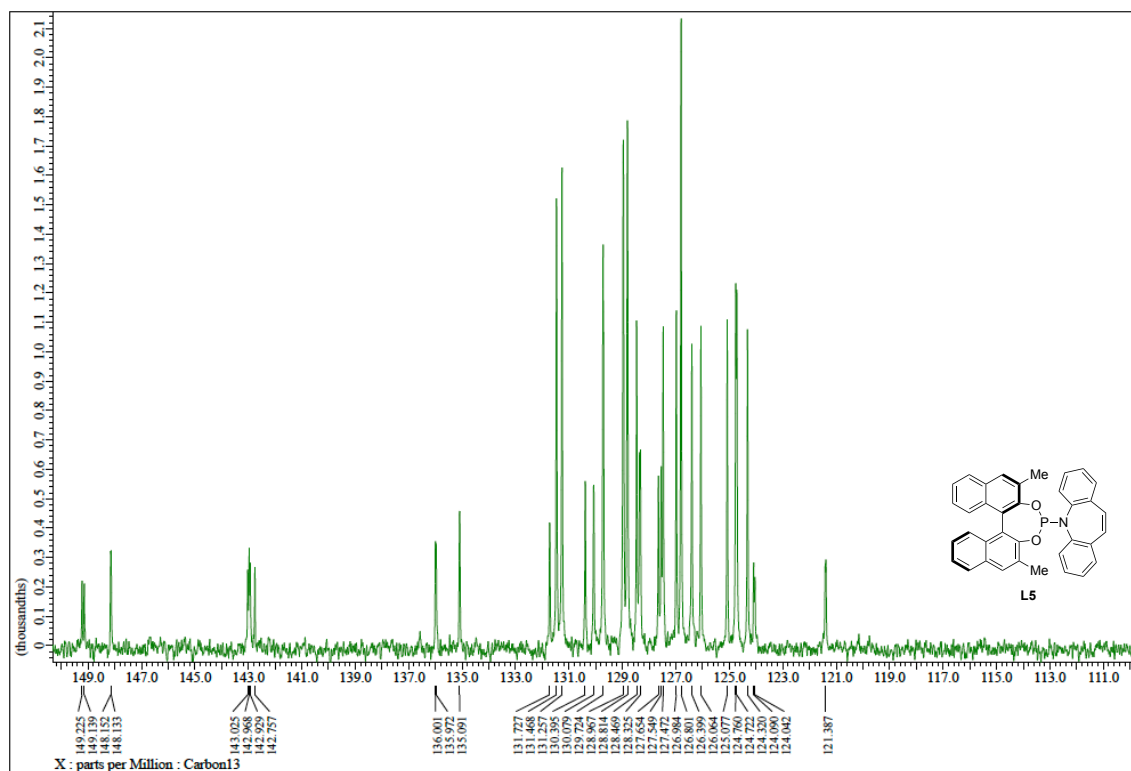
^1H NMR of L5 (400 MHz, CDCl_3)



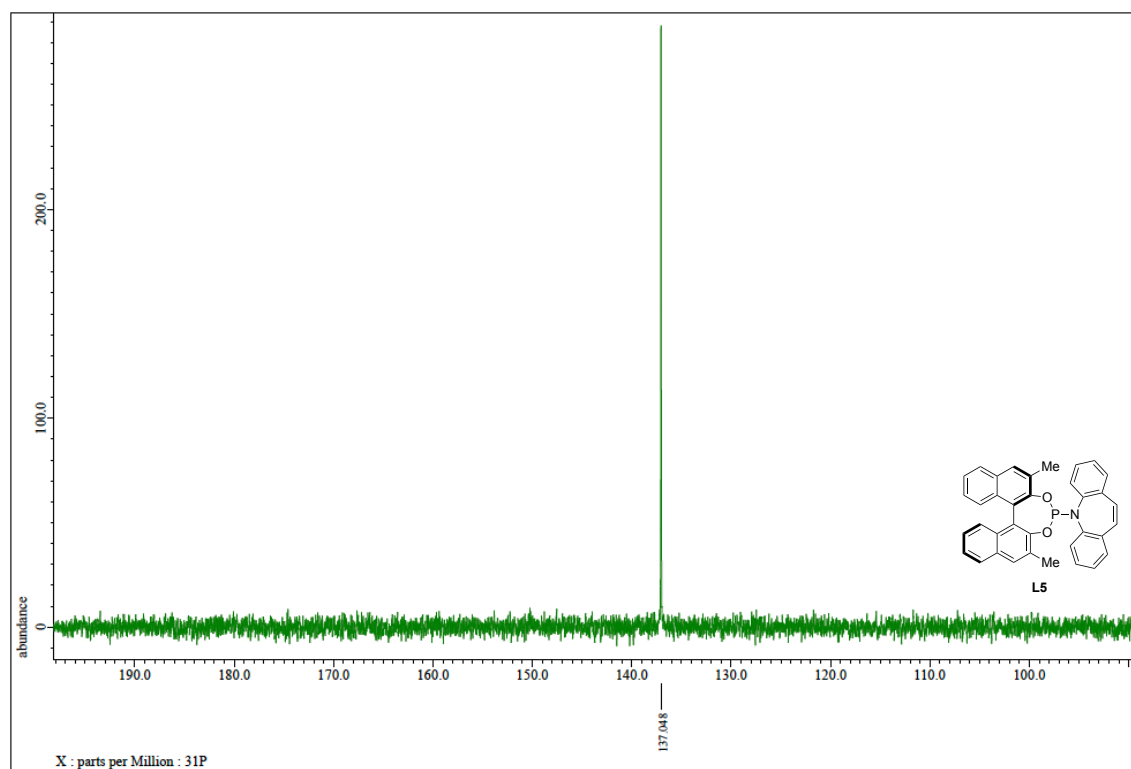
^{13}C NMR of L5 (100 MHz, CDCl_3)



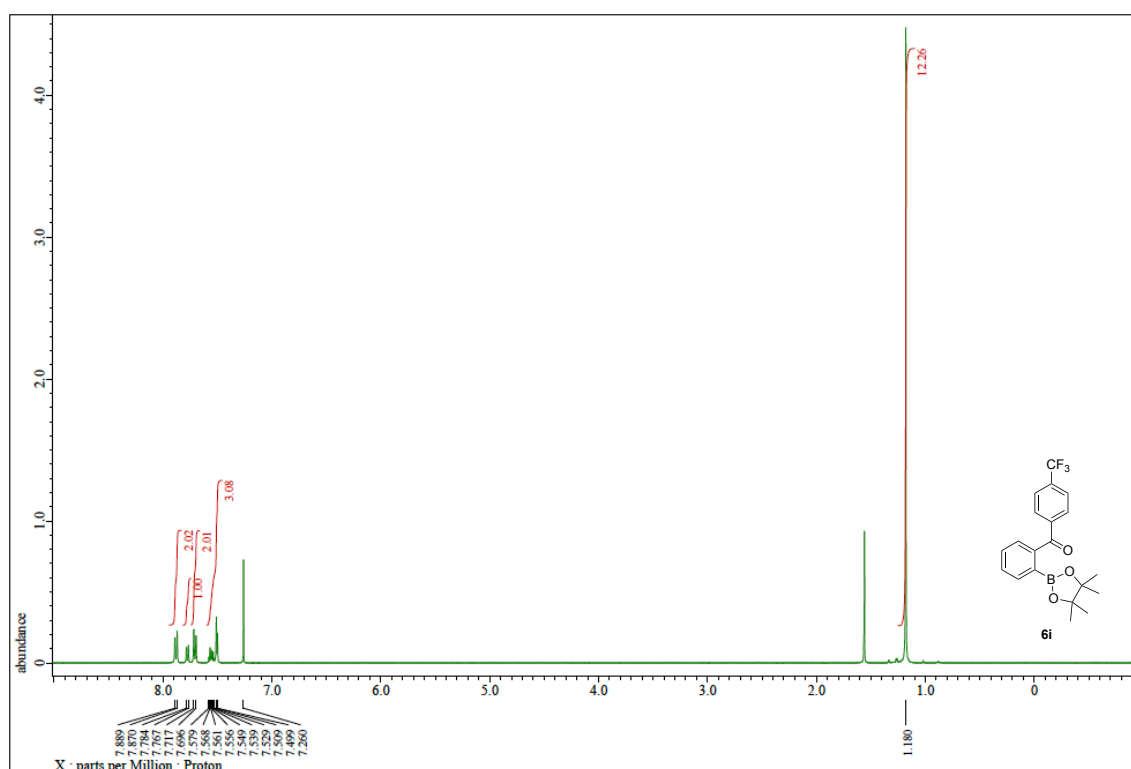
(150-110 ppm)



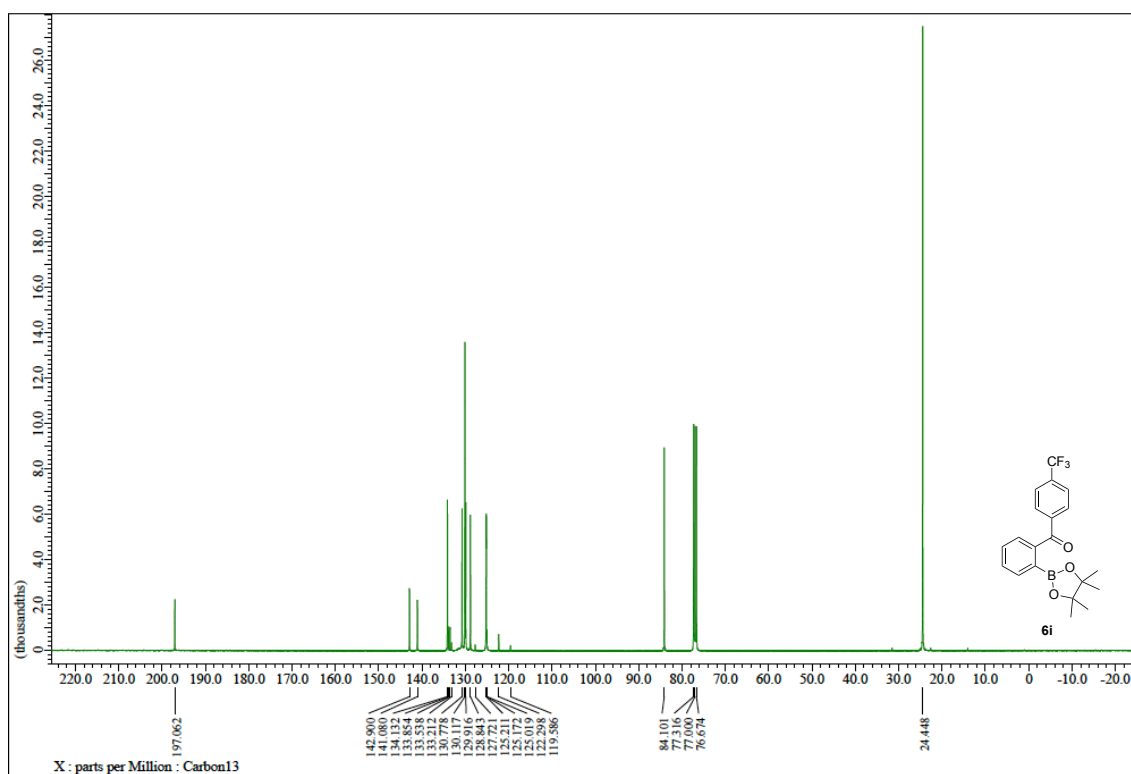
³¹P NMR of L5 (162 MHz, CDCl₃)



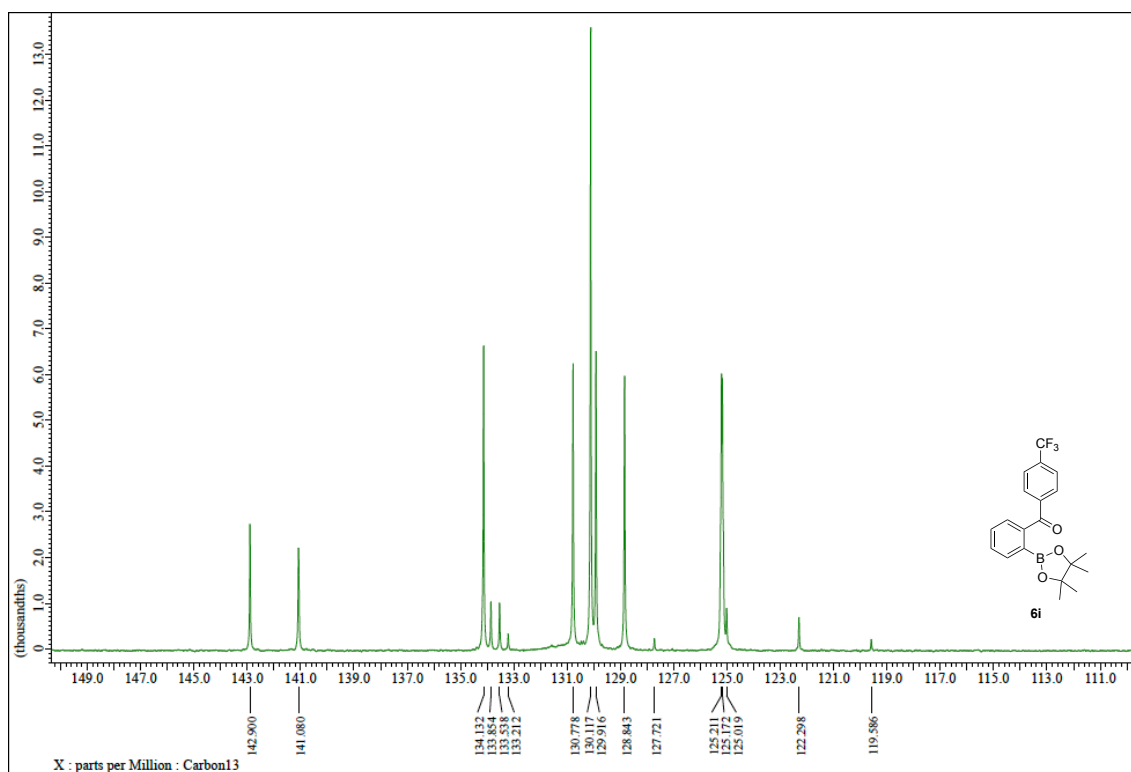
¹H NMR of 6j (400 MHz, CDCl₃)



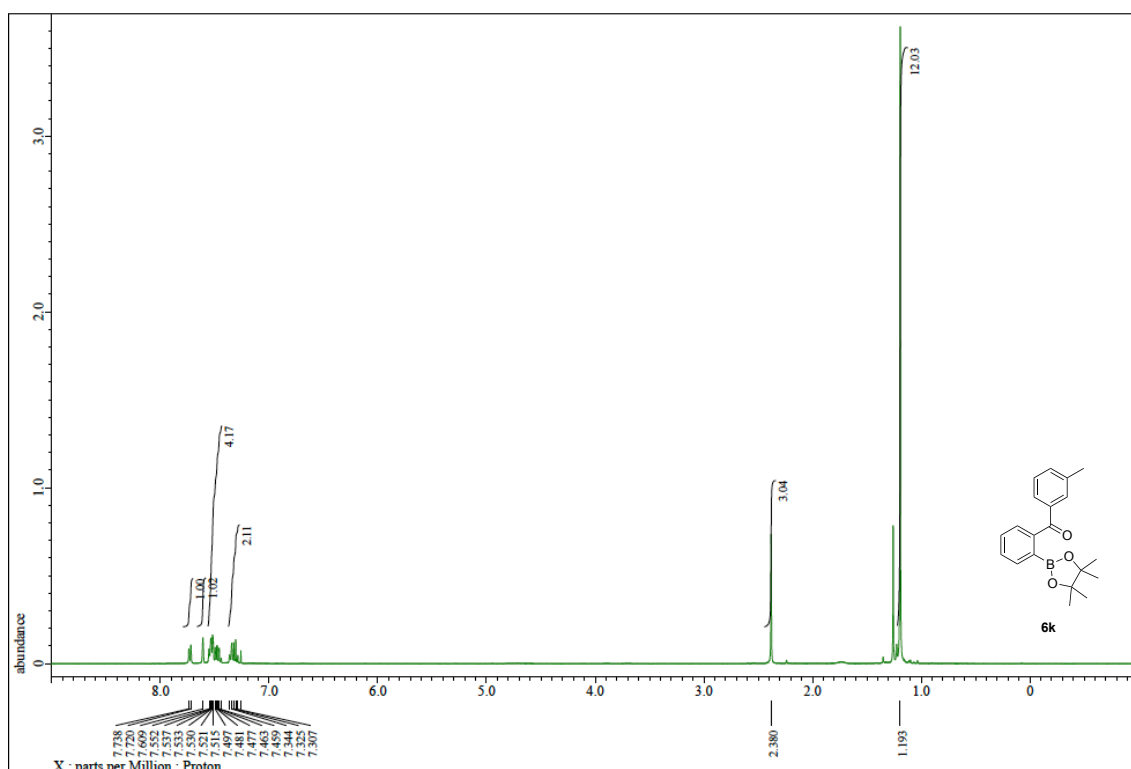
¹³C NMR of 1i (400 MHz, CDCl₃, overview)



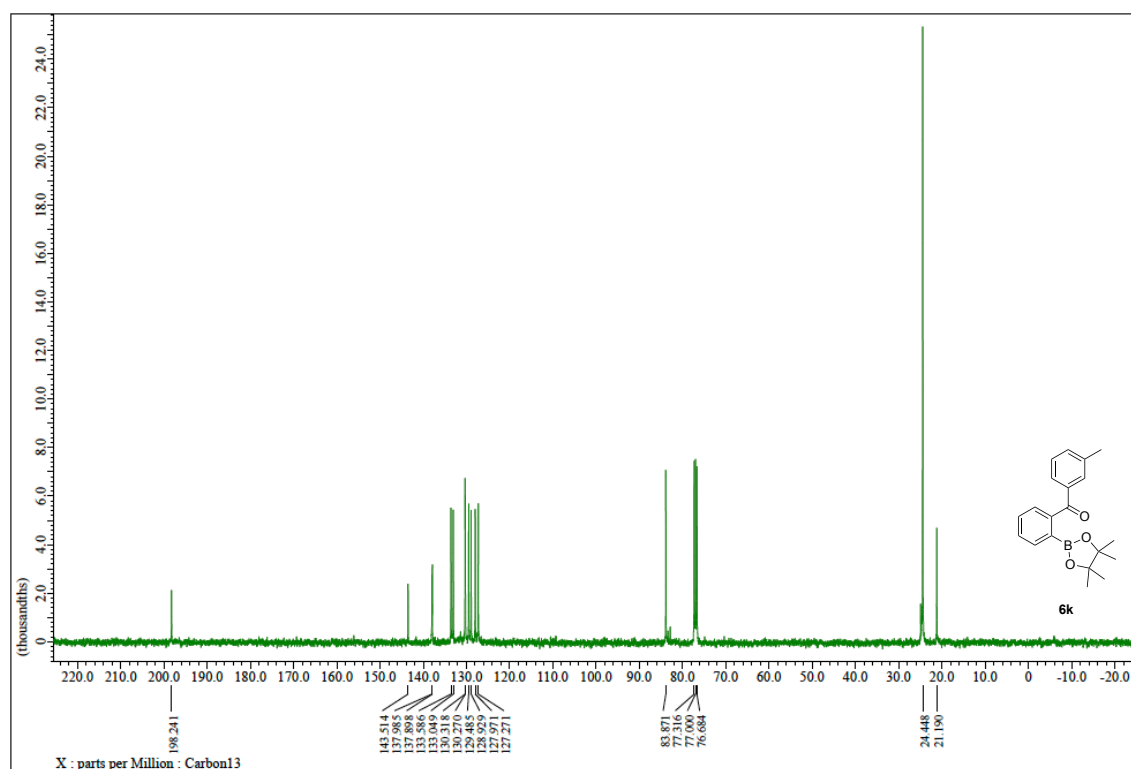
(150-110 ppm)



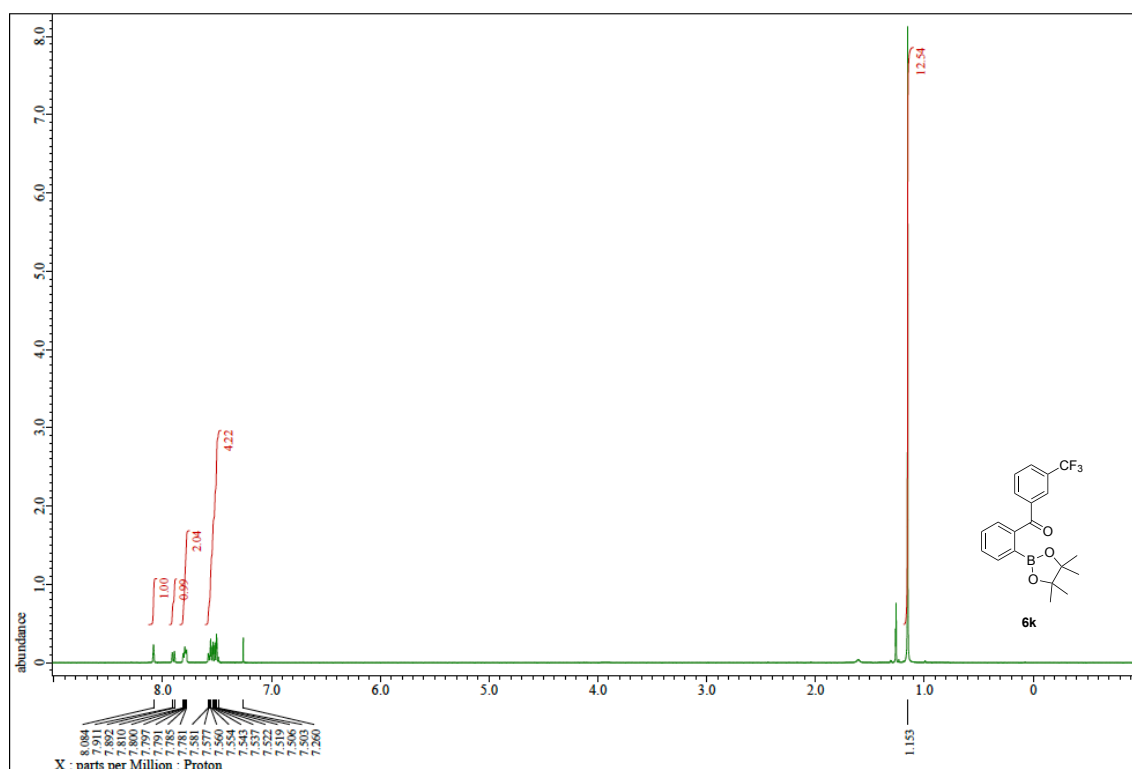
¹H NMR of 6j (400 MHz, CDCl₃)



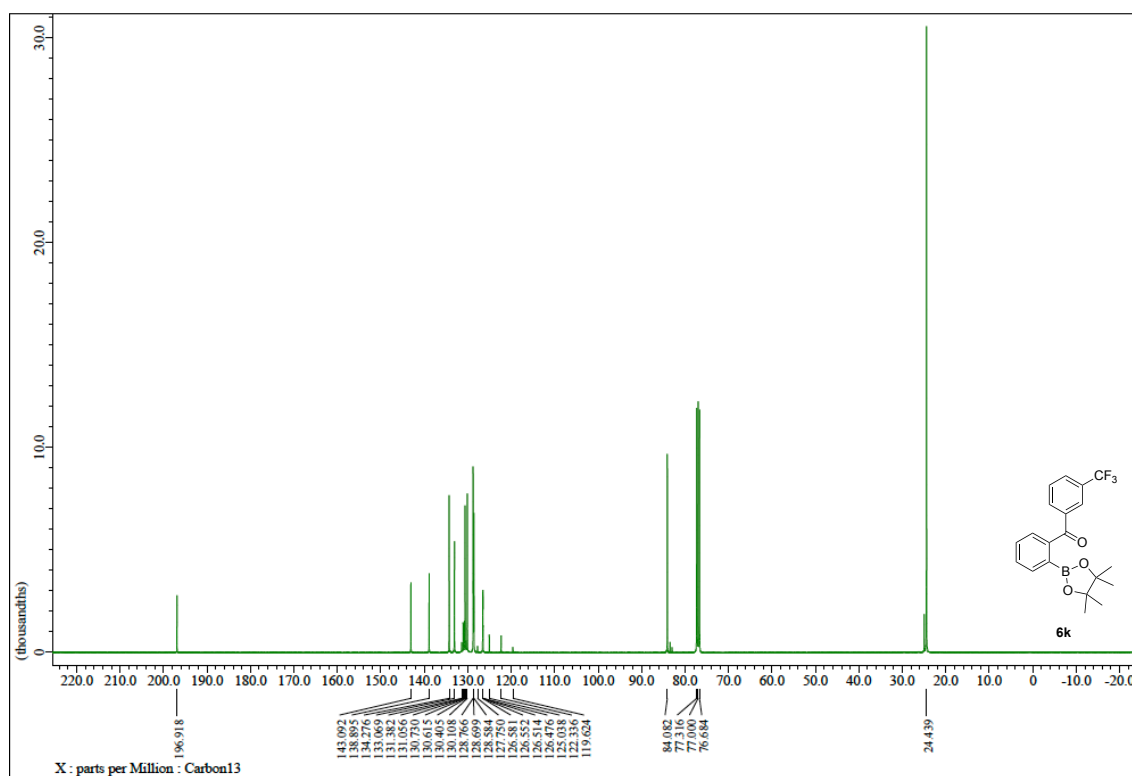
¹³C NMR of 6j (100 MHz, CDCl₃)



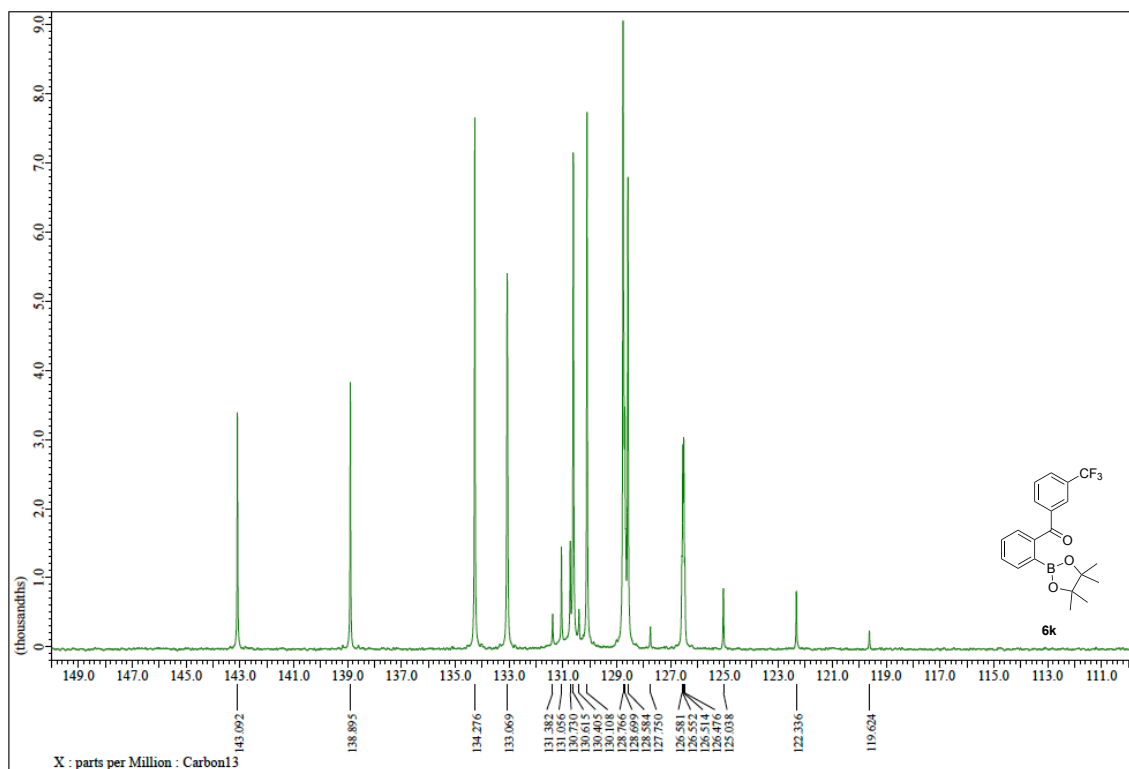
¹H NMR of 6k (400 MHz, CDCl₃)



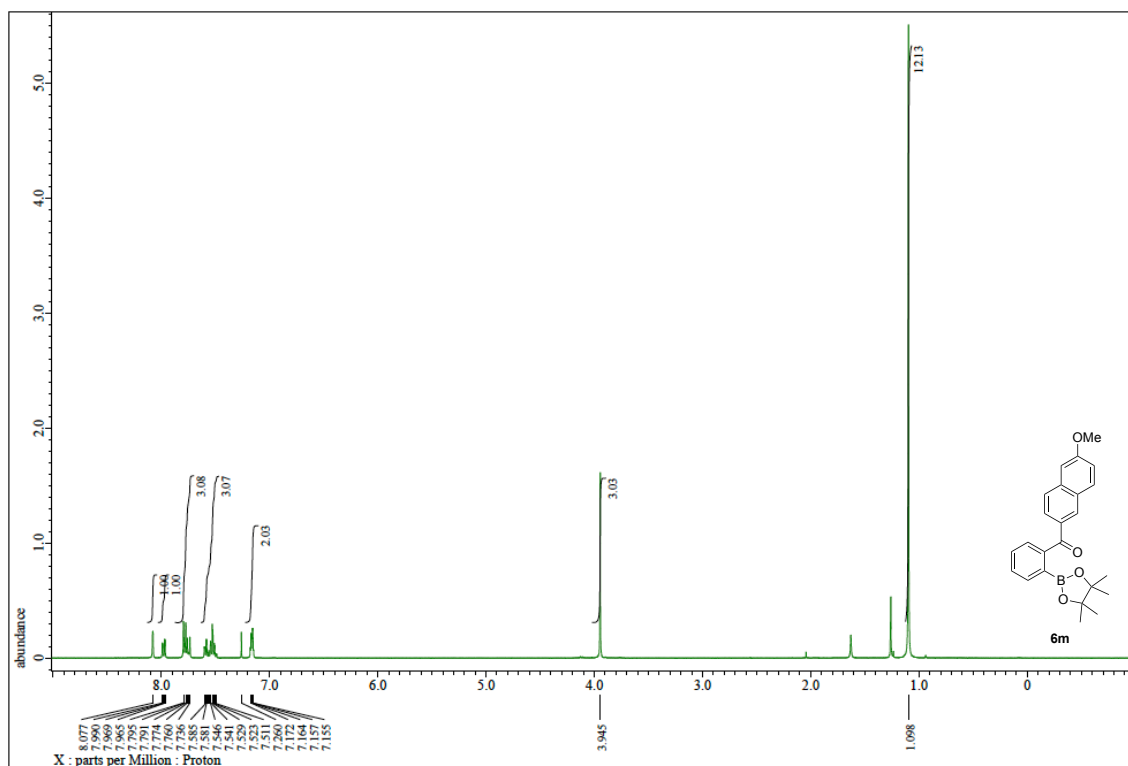
¹³C NMR of 6k (100 MHz, CDCl₃, overview)



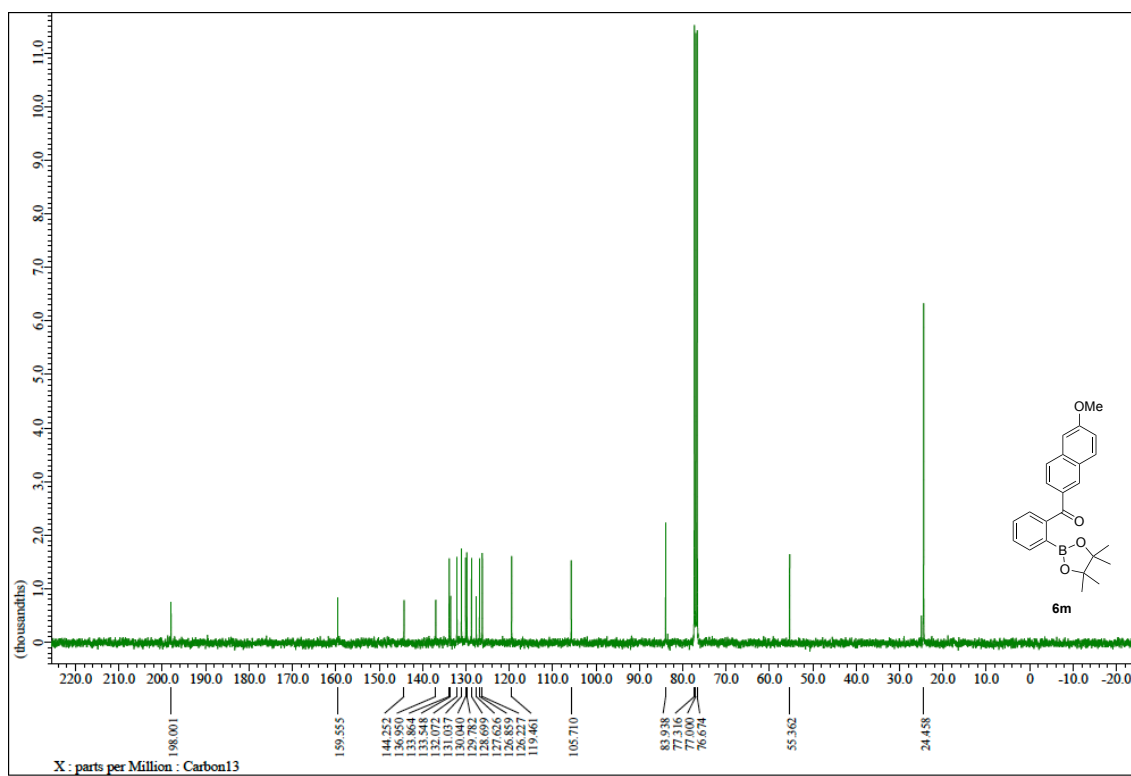
(150-110 ppm)



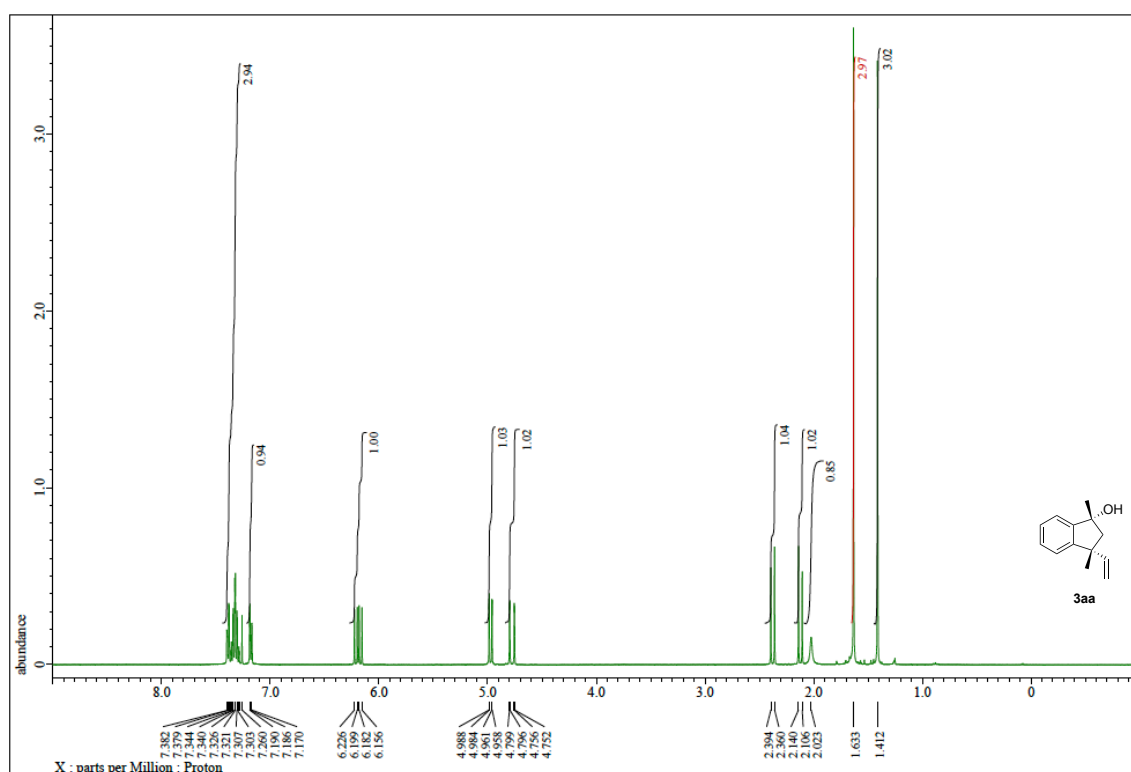
¹H NMR of 6m (400 MHz, CDCl₃)



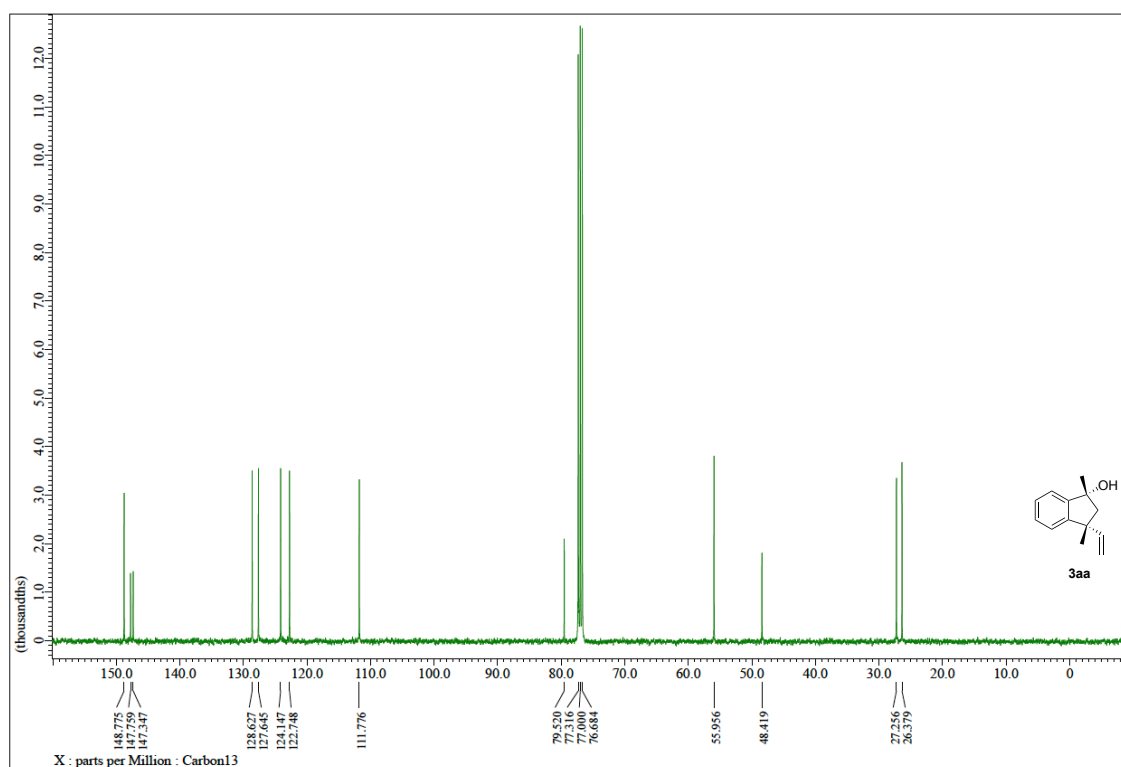
¹³C NMR of 6m (100 MHz, CDCl₃)

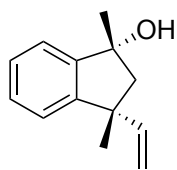


¹H NMR of 3aa (400 MHz, CDCl₃)



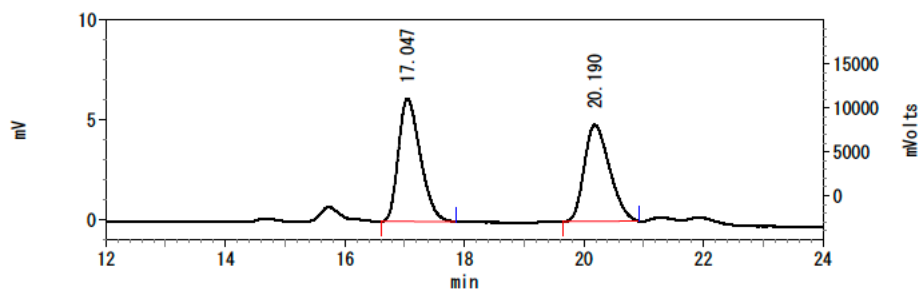
¹³C NMR of 3aa (100 MHz, CDCl₃)





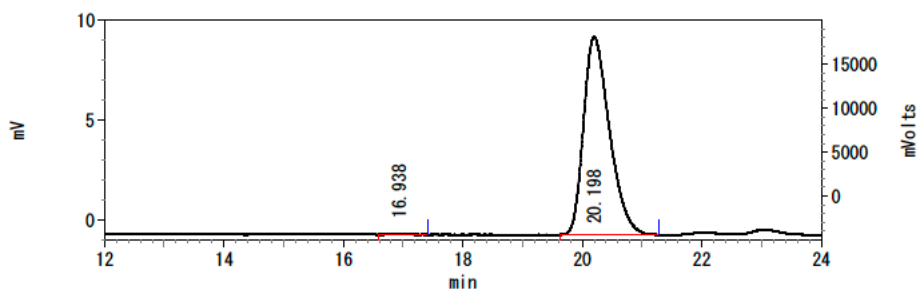
3aa

HPLC chart of (*rac*)-3aa



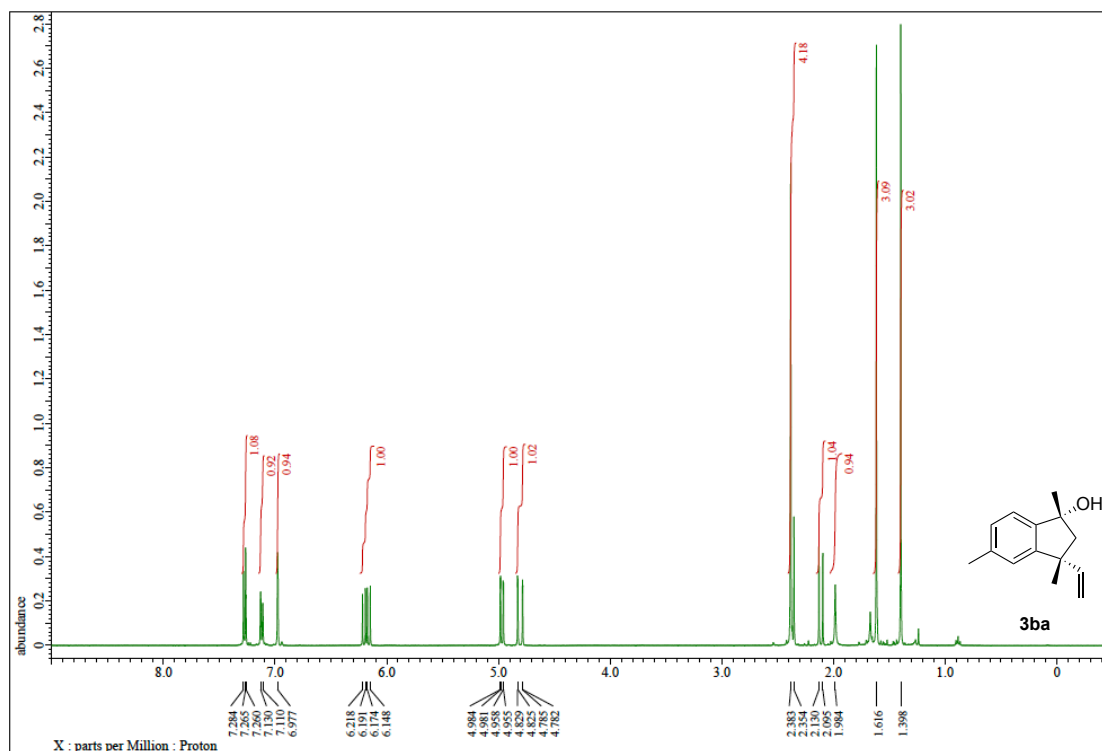
Pk #	Retention Time	Area	Area Percent
1	17.047	156298	52.289
2	20.190	142614	47.711

HPLC chart of (1*R*,3*R*)-3aa

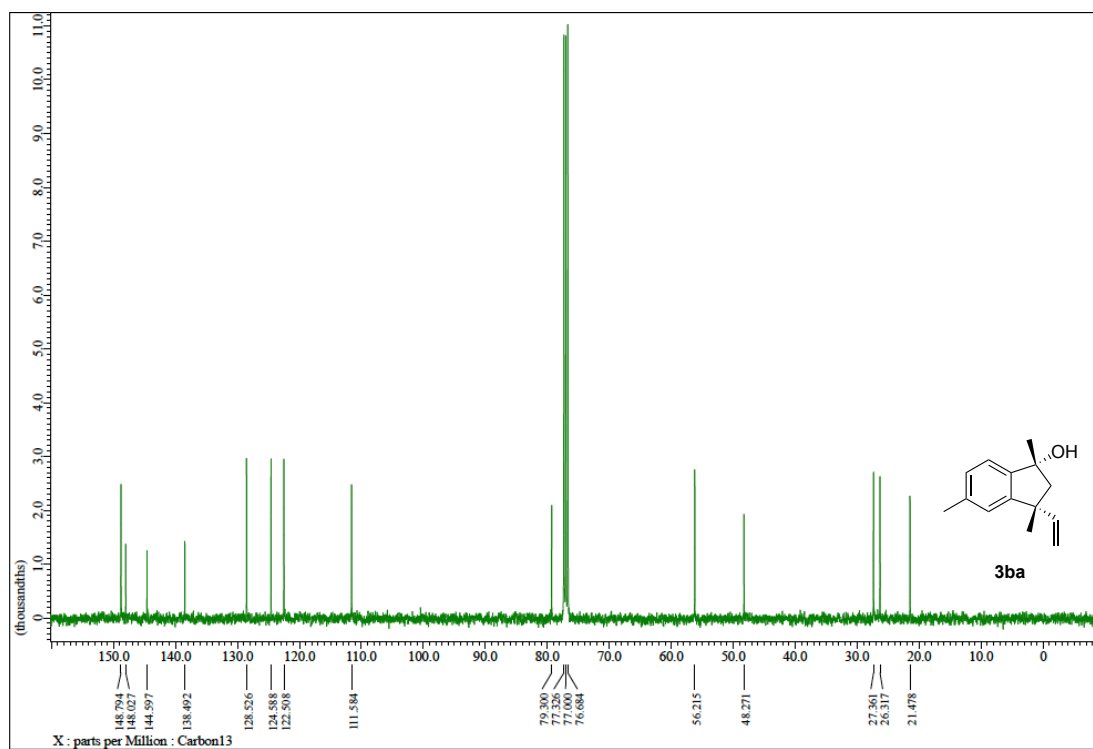


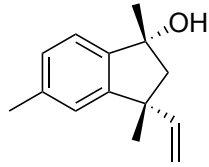
Pk #	Retention Time	Area	Area Percent
1	16.938	485	0.162
2	20.198	299219	99.838

¹H NMR of 3ba (400 MHz, CDCl₃)



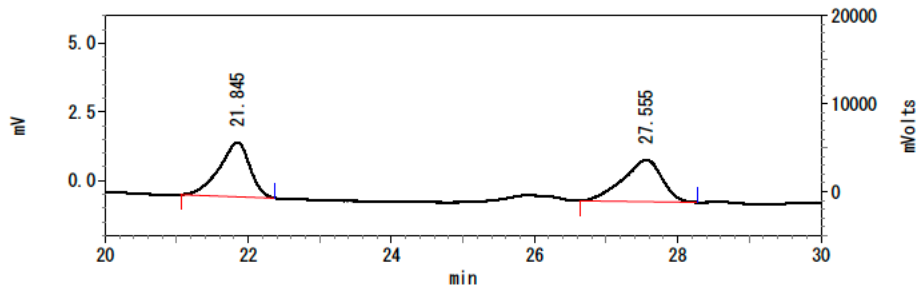
¹³C NMR of 3ca (100 MHz, CDCl₃)





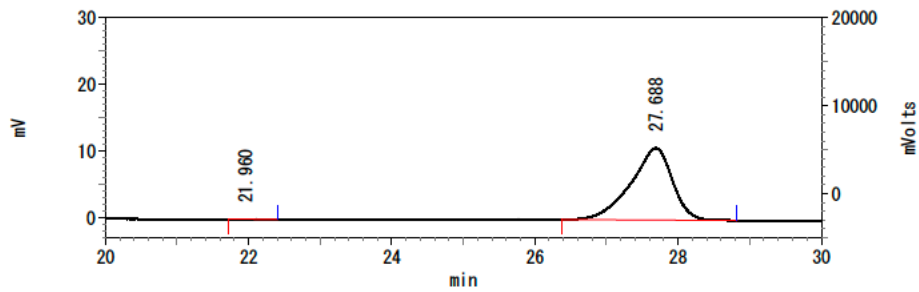
3ba

HPLC chart of (*rac*)-3ba



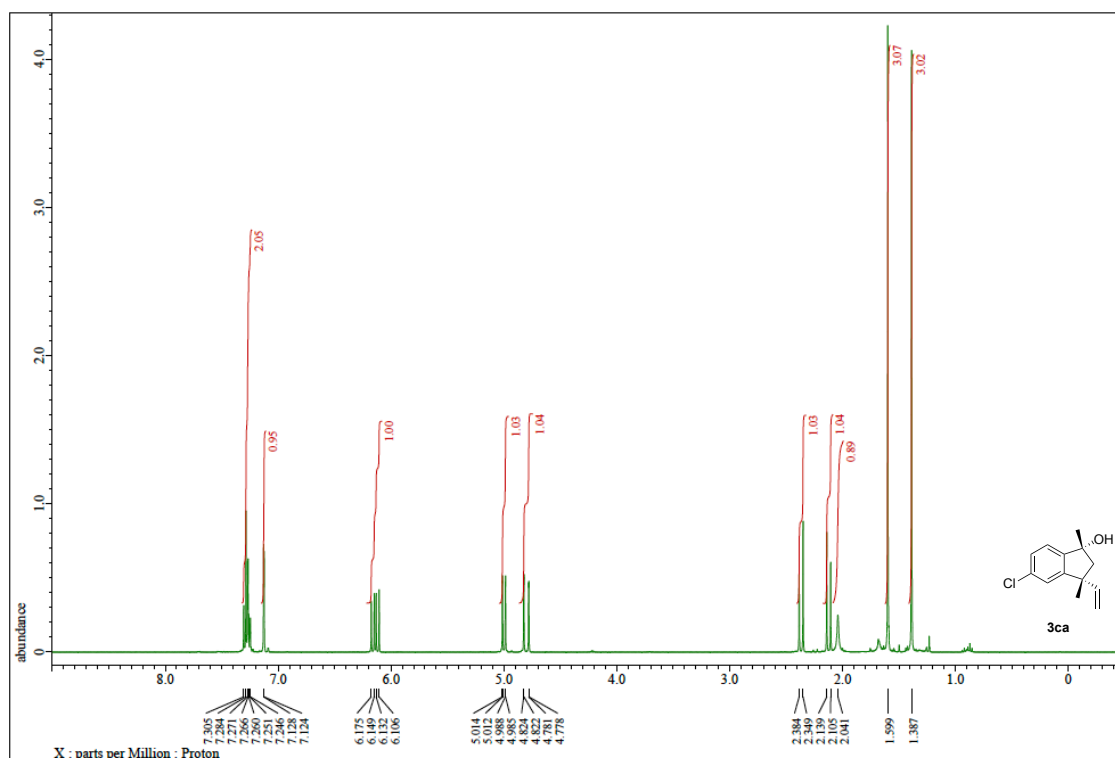
Pk #	Retention Time	Area	Area Percent
1	21.845	59304	50.441
2	27.555	58266	49.559

HPLC chart of (1*R*,3*R*)-3ba

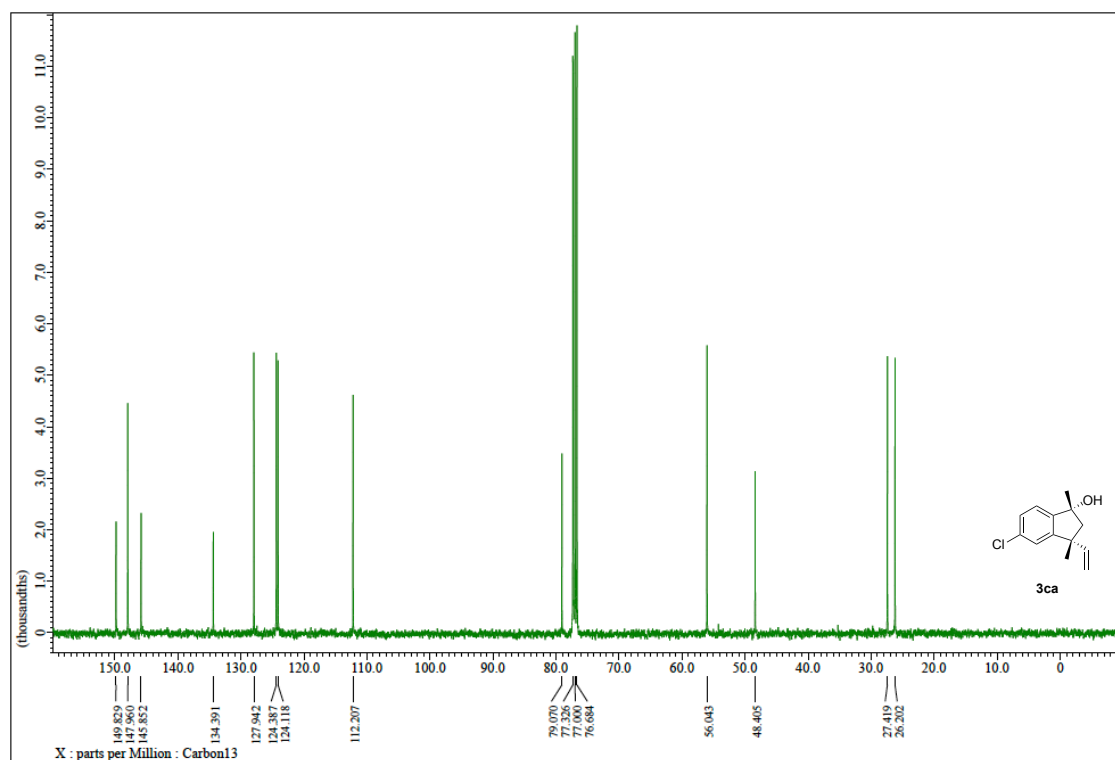


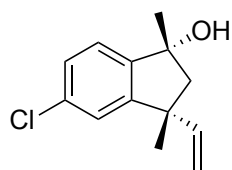
Pk #	Retention Time	Area	Area Percent
1	21.960	509	0.116
2	27.688	438583	99.884

¹H NMR of 3ca (400 MHz, CDCl₃)



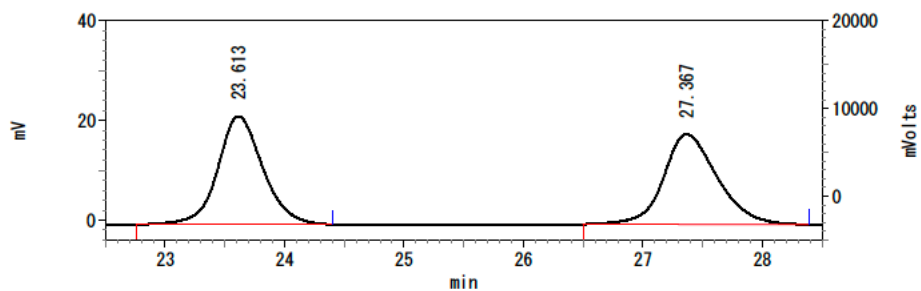
¹³C NMR of 3ca (100 MHz, CDCl₃)





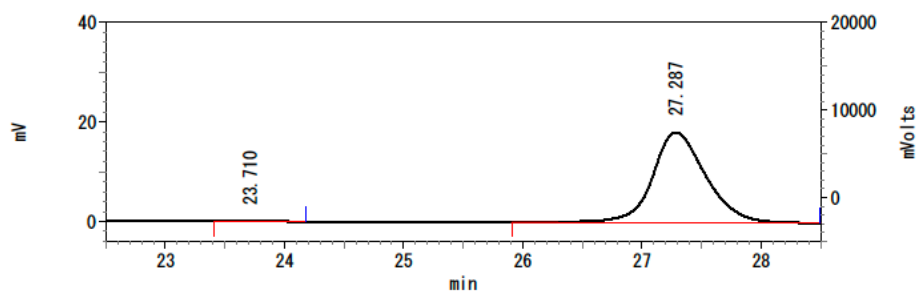
3ca

HPLC chart of (*rac*)-3ca



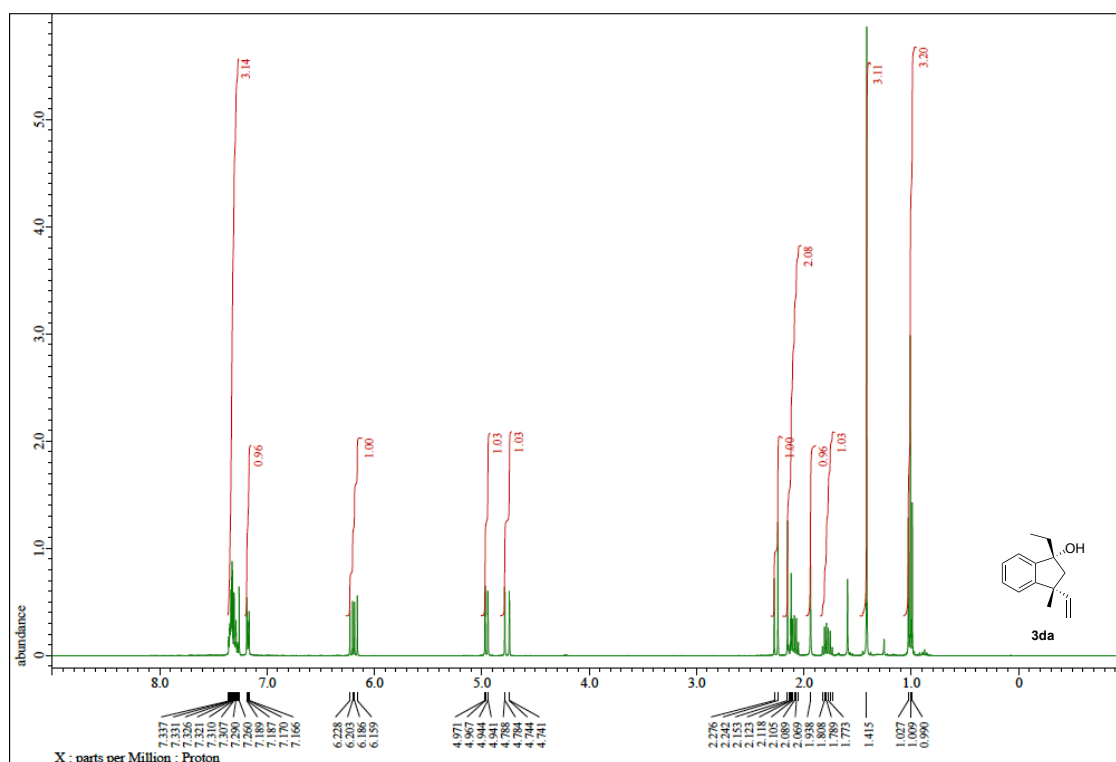
Pk #	Retention Time	Area	Area Percent
1	23.613	570693	50.289
2	27.367	564126	49.711

HPLC chart of (1*R*,3*R*)-3ca

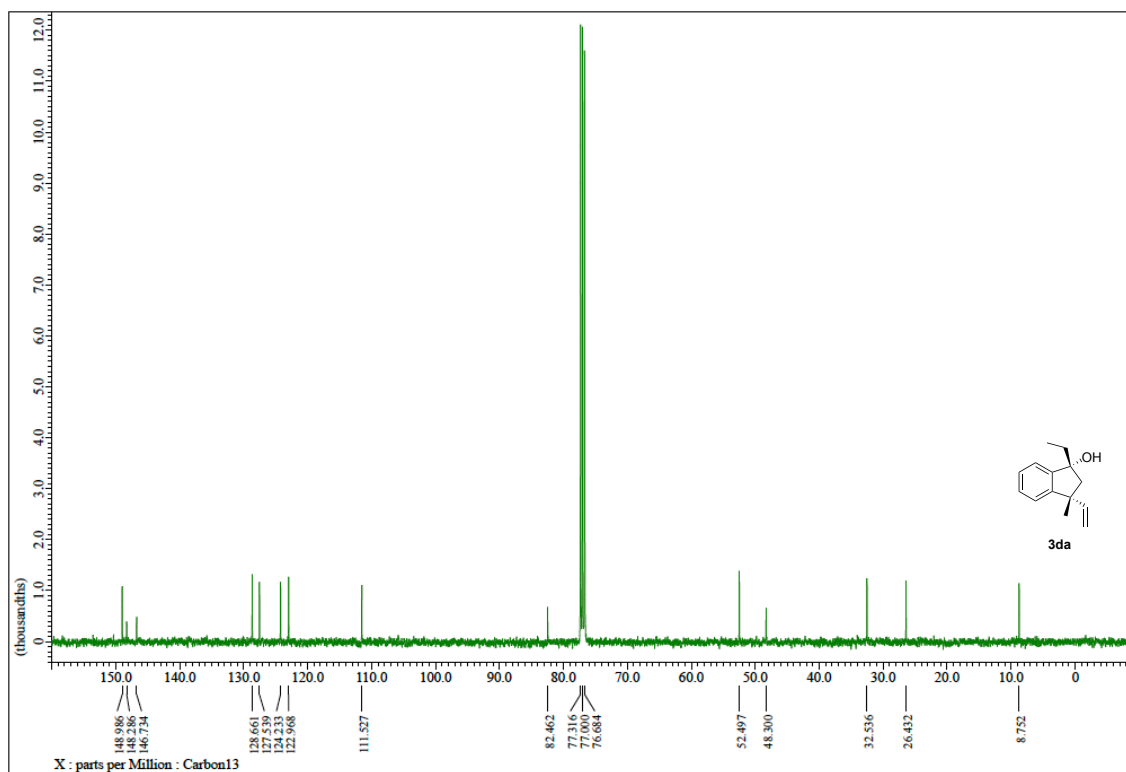


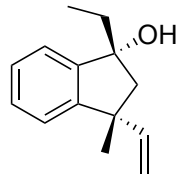
Pk #	Retention Time	Area	Area Percent
1	23.710	1337	0.235
2	27.287	566754	99.765

¹H NMR of 3da (400 MHz, CDCl₃)



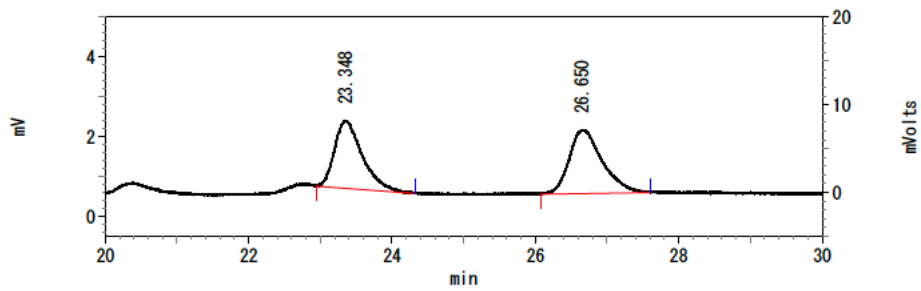
¹³C NMR of 3da (100 MHz, CDCl₃)





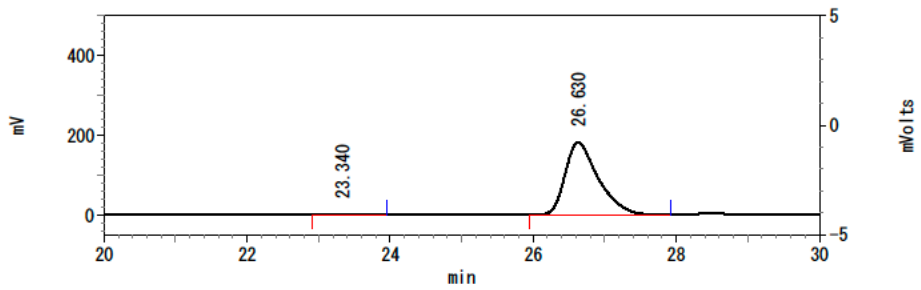
3da

HPLC chart of (*rac*)-3da



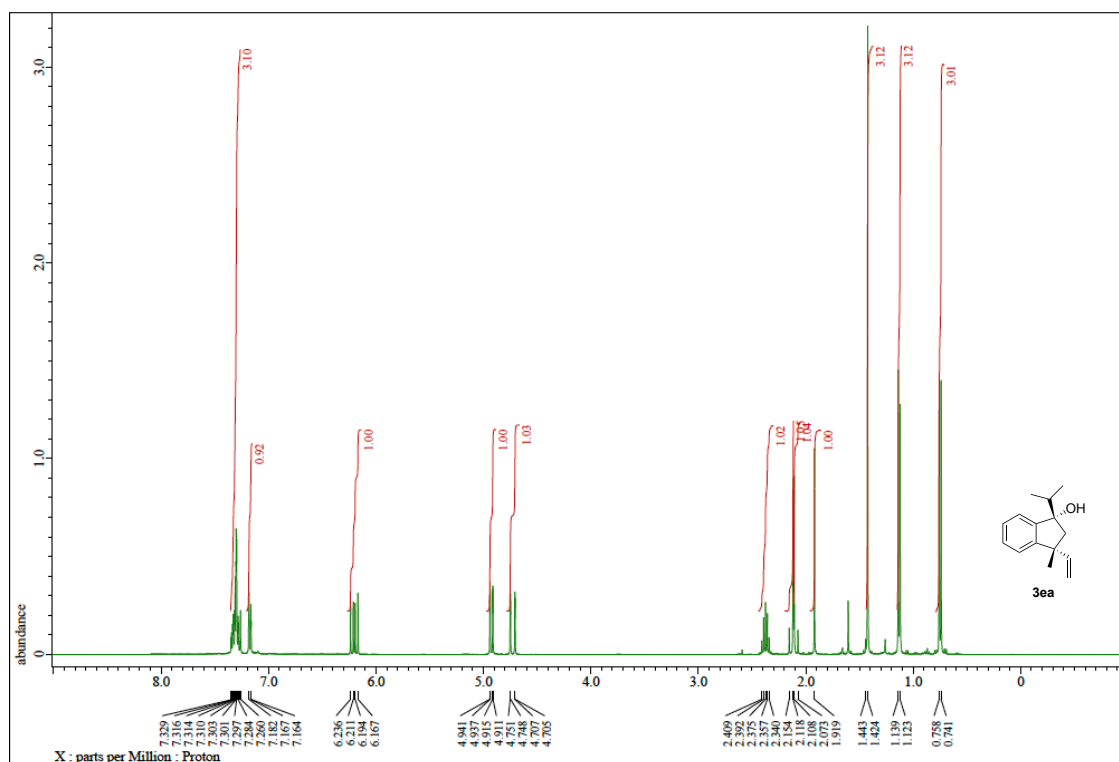
Pk #	Retention Time	Area	Area Percent
1	23.348	45846	47.076
2	26.650	51542	52.924

HPLC chart of (1*R*,3*R*)-3da

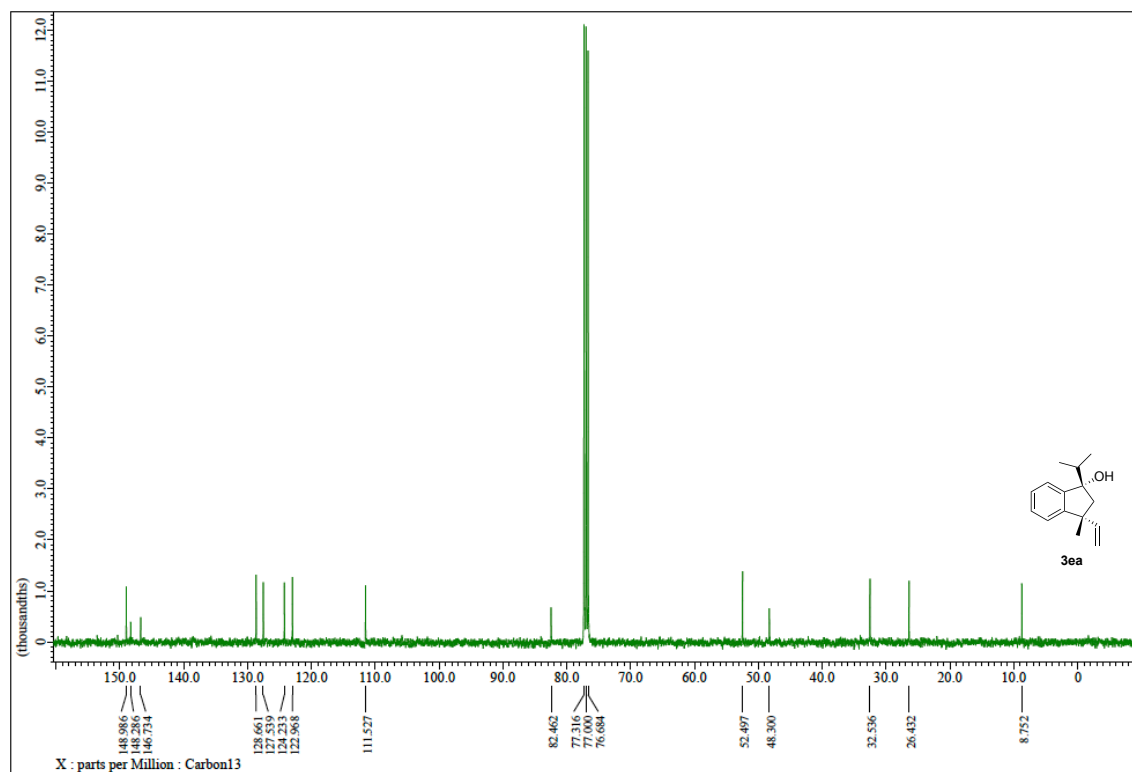


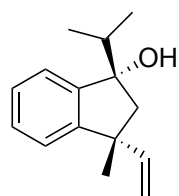
Pk #	Retention Time	Area	Area Percent
1	23.340	16726	0.287
2	26.630	5817702	99.713

¹H NMR of 3ea (400 MHz, CDCl₃)



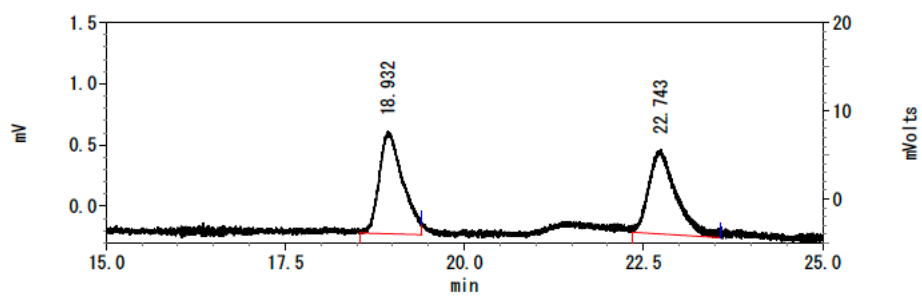
¹³C NMR of 3ea (100 MHz, CDCl₃)





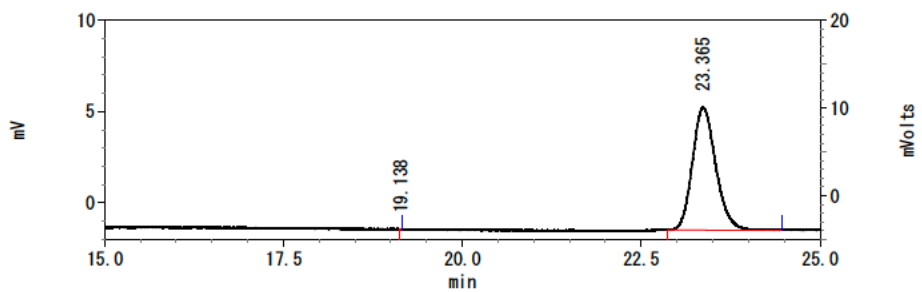
3ea

HPLC chart of (*rac*)-3ea



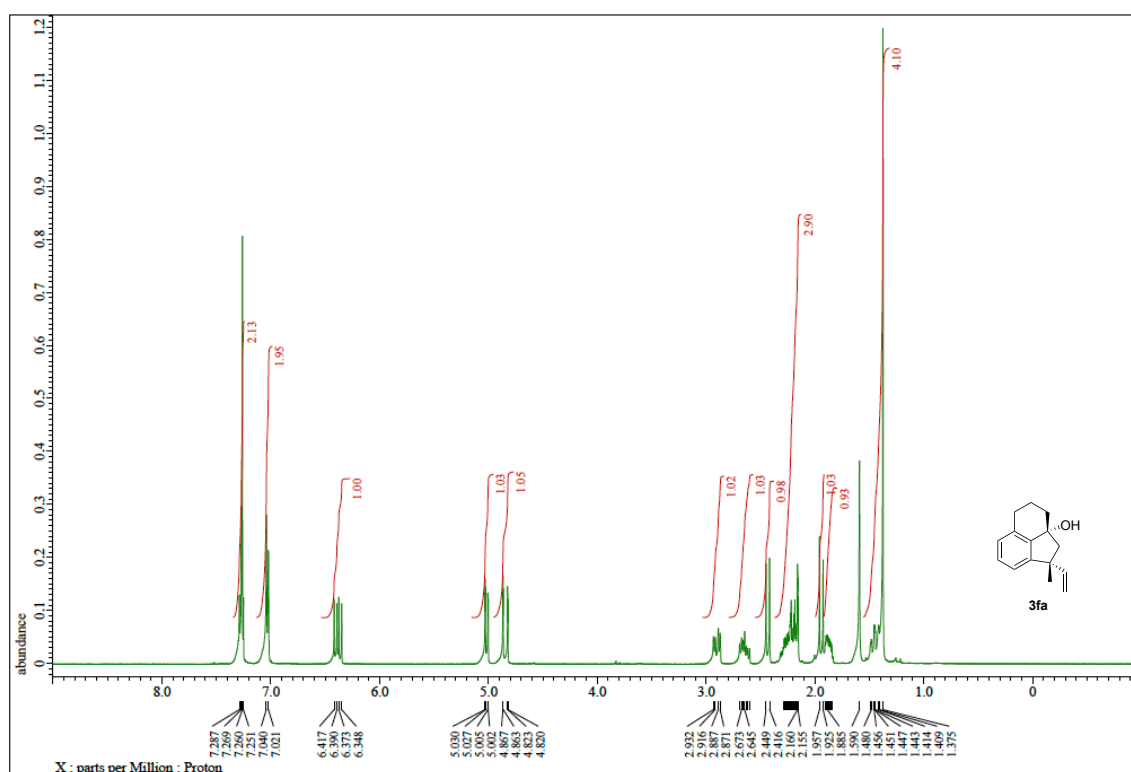
Pk #	Retention Time	Area	Area Percent
1	18.932	18806	51.076
2	22.743	18014	48.924

HPLC chart of (*1S,3R*)-3ea

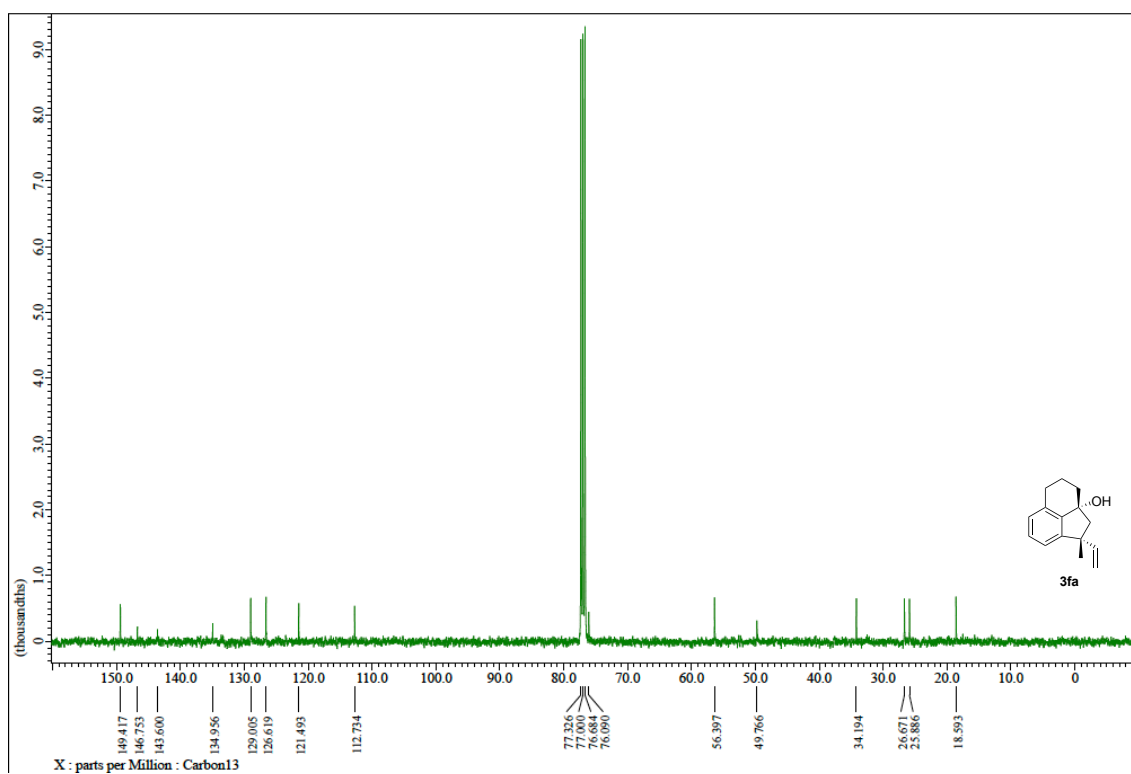


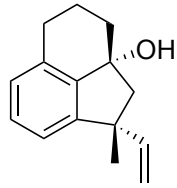
Pk #	Retention Time	Area	Area Percent
1	19.138	21	0.014
2	23.365	153196	99.986

¹H NMR of 3fa (400 MHz, CDCl₃)



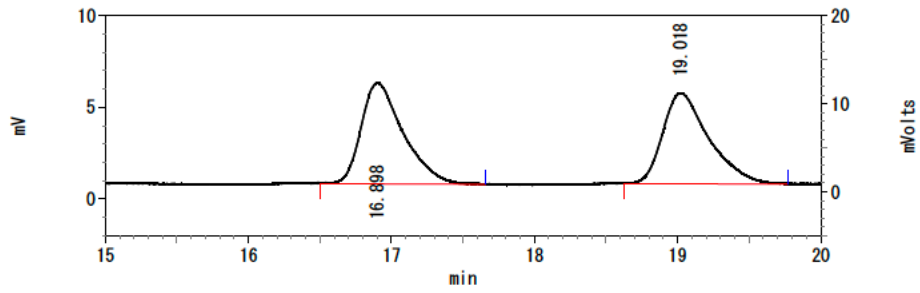
¹³C NMR of 3fa (100 MHz, CDCl₃)





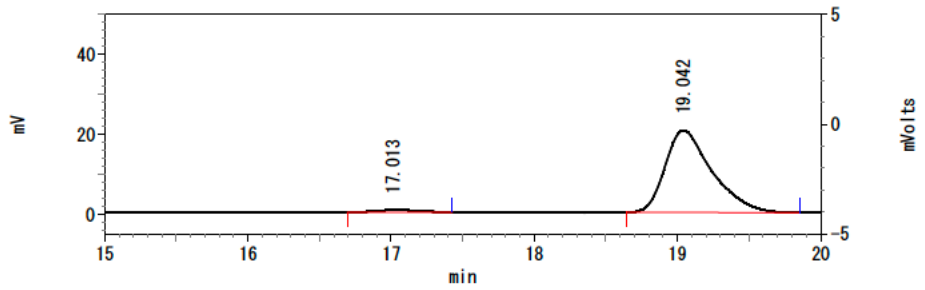
3fa

HPLC chart of (*rac*)-3fa



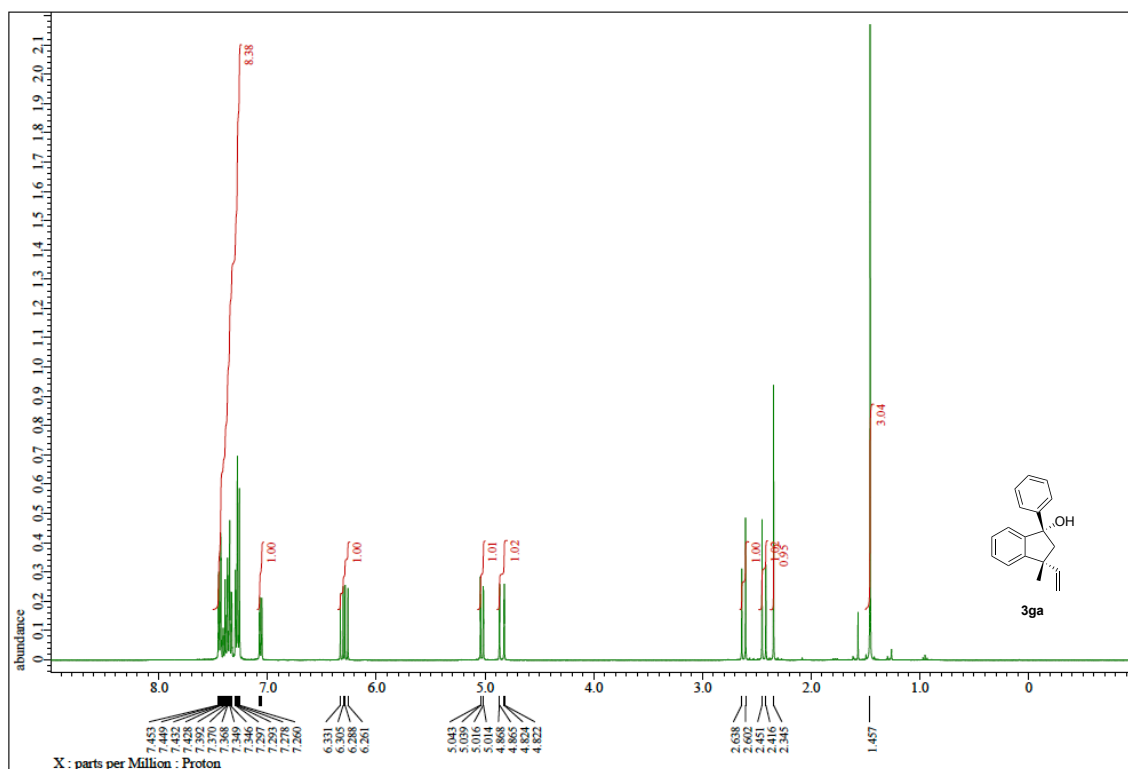
Pk #	Retention Time	Area	Area Percent
1	16.898	112883	50.366
2	19.018	111243	49.634

HPLC chart of (1*R*,3*R*)-3fa

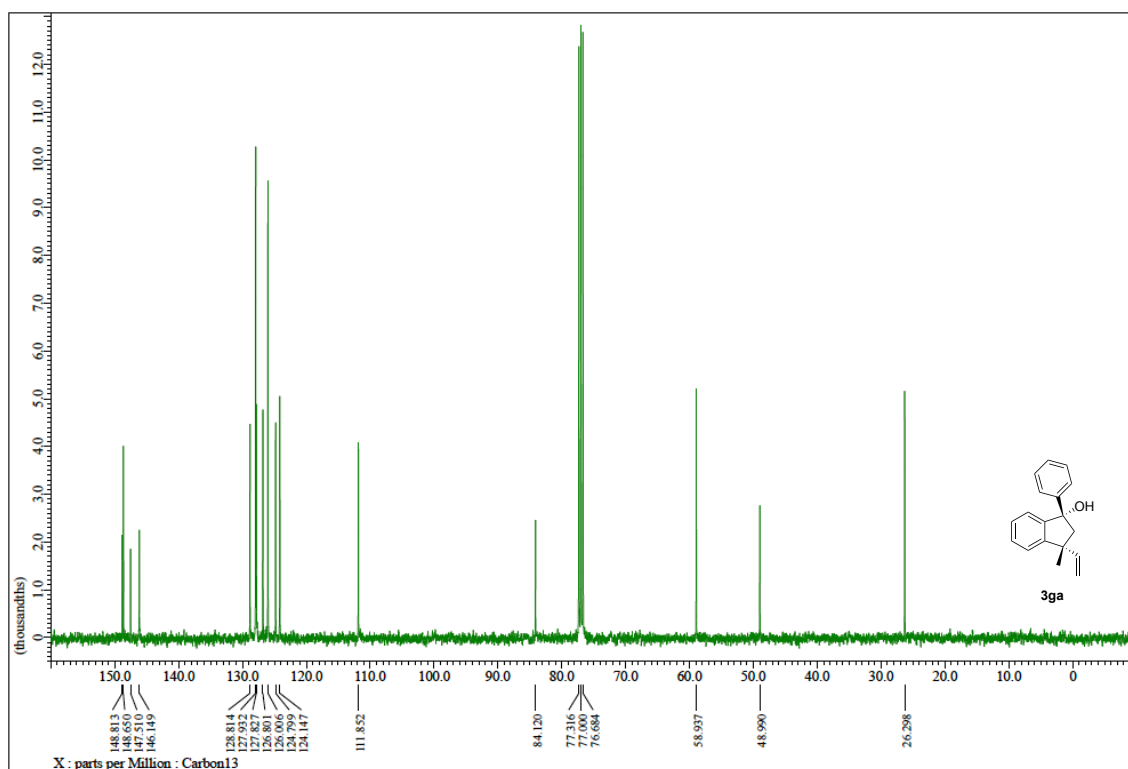


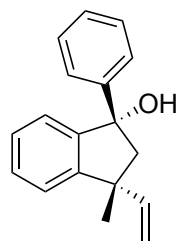
Pk #	Retention Time	Area	Area Percent
1	17.013	12112	2.532
2	19.042	466194	97.468

¹H NMR of 3ga (400 MHz, CDCl₃)



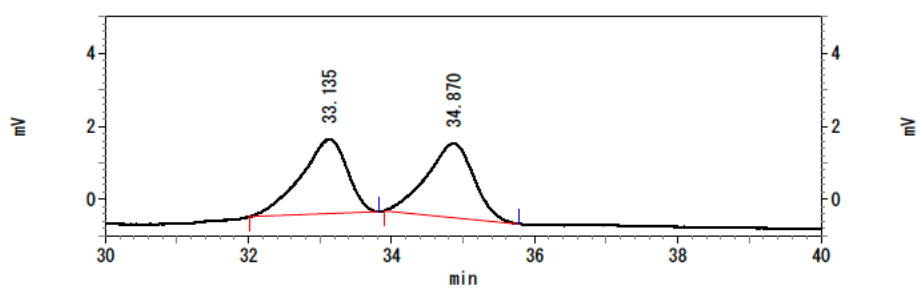
¹³C NMR of 3ga (100 MHz, CDCl₃)





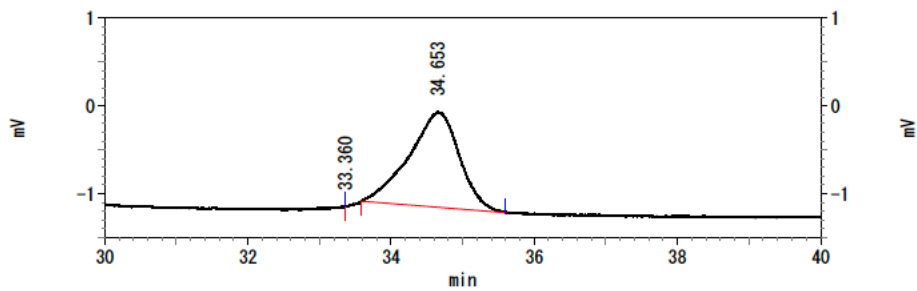
3ga

HPLC chart of (*rac*)-3ga



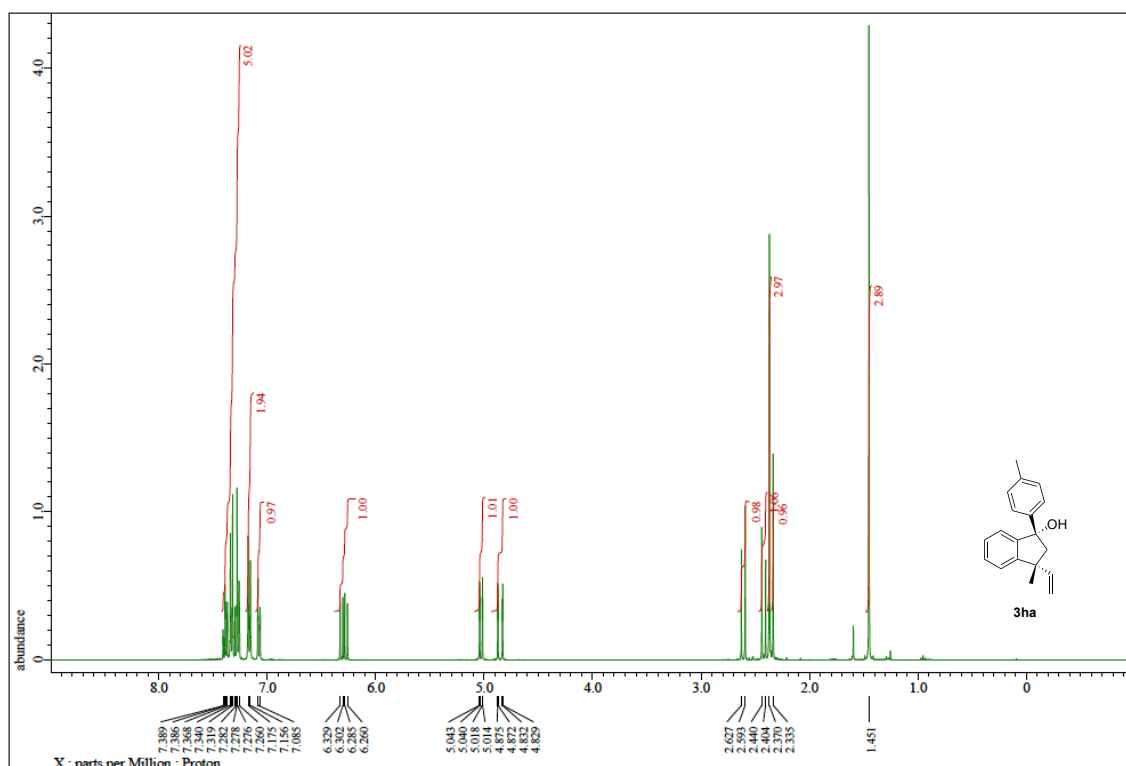
Pk #	Retention Time	Area	Area Percent
1	33.135	91479	49.495
2	34.870	93347	50.505

HPLC chart of (*1S,3R*)-3ga

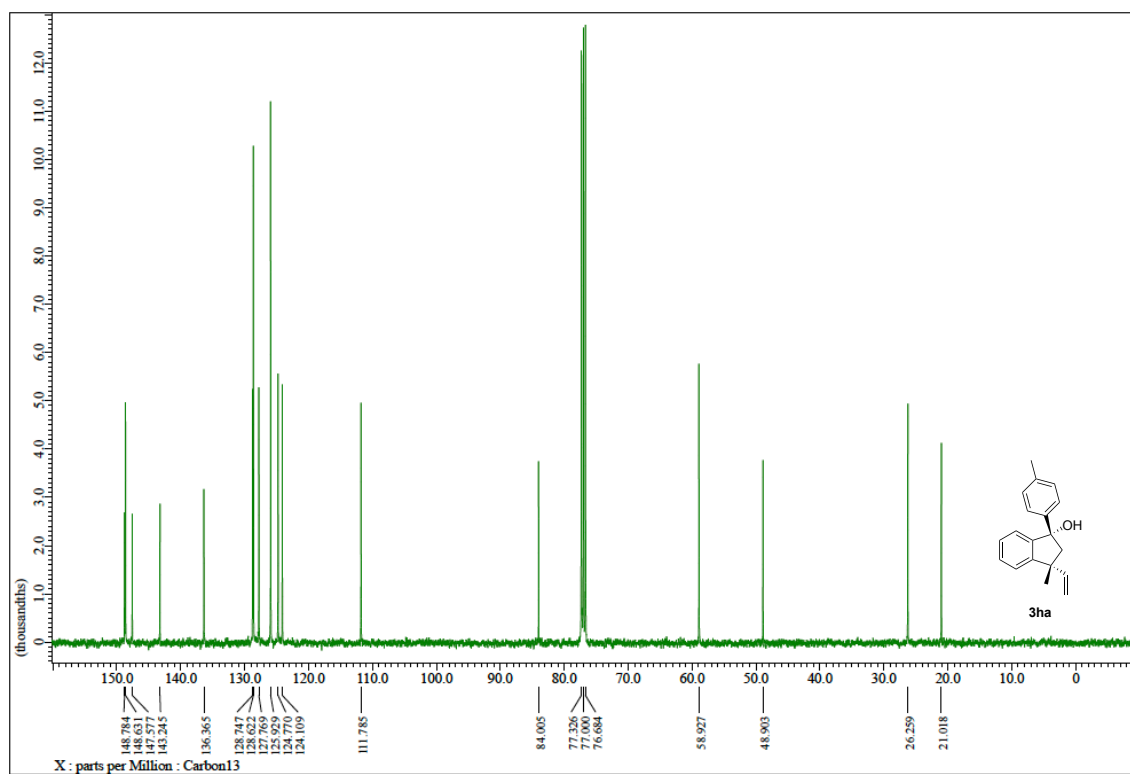


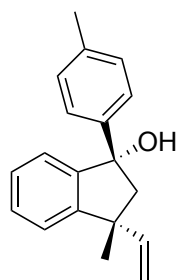
Pk #	Retention Time	Area	Area Percent
1	33.360	0	0.000
2	34.653	52882	100.000

¹H NMR of 3ha (400 MHz, CDCl₃)



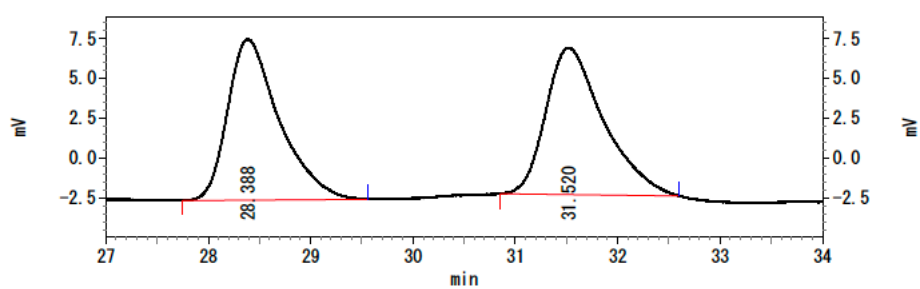
¹³C NMR of 3ha (100 MHz, CDCl₃)





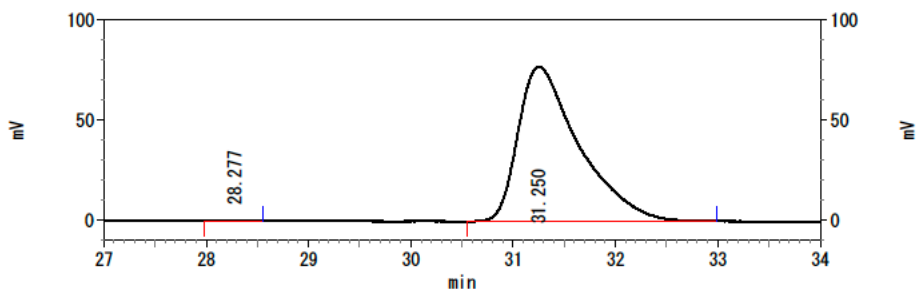
3ha

HPLC chart of (*rac*)-3ha



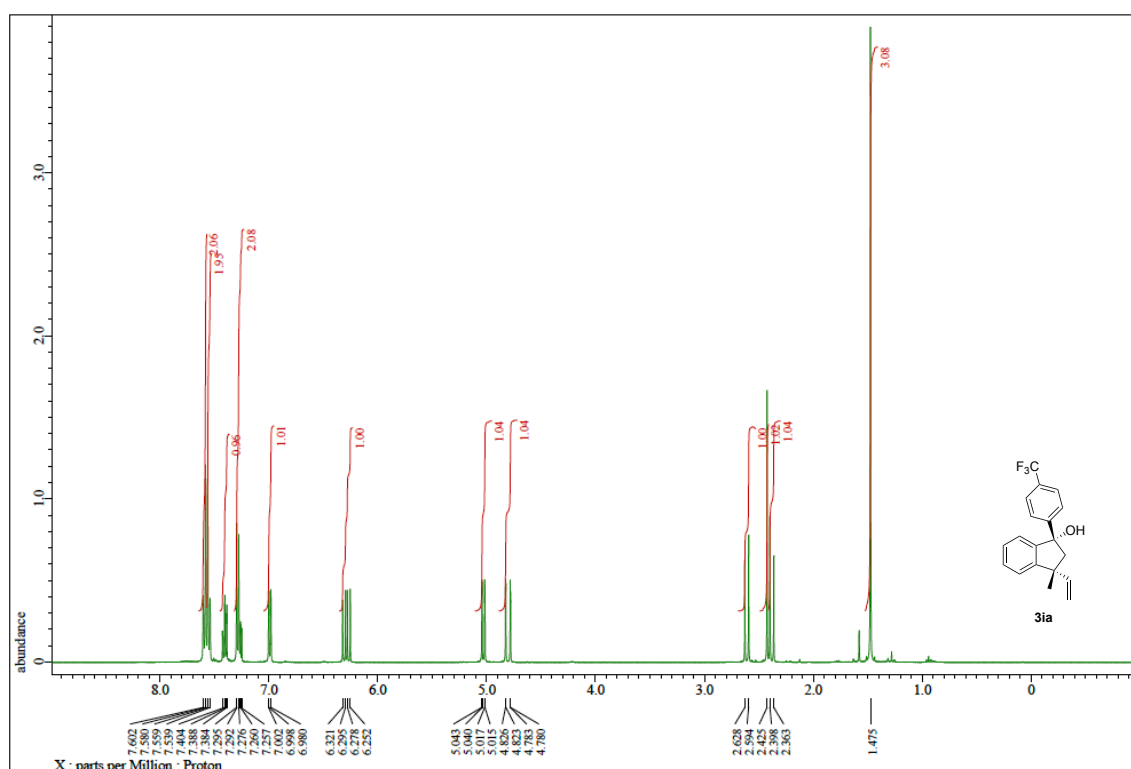
Pk #	Retention Time	Area	Area Percent
1	28.388	353965	49.393
2	31.520	362670	50.607

HPLC chart of (*1S,3R*)-3ha

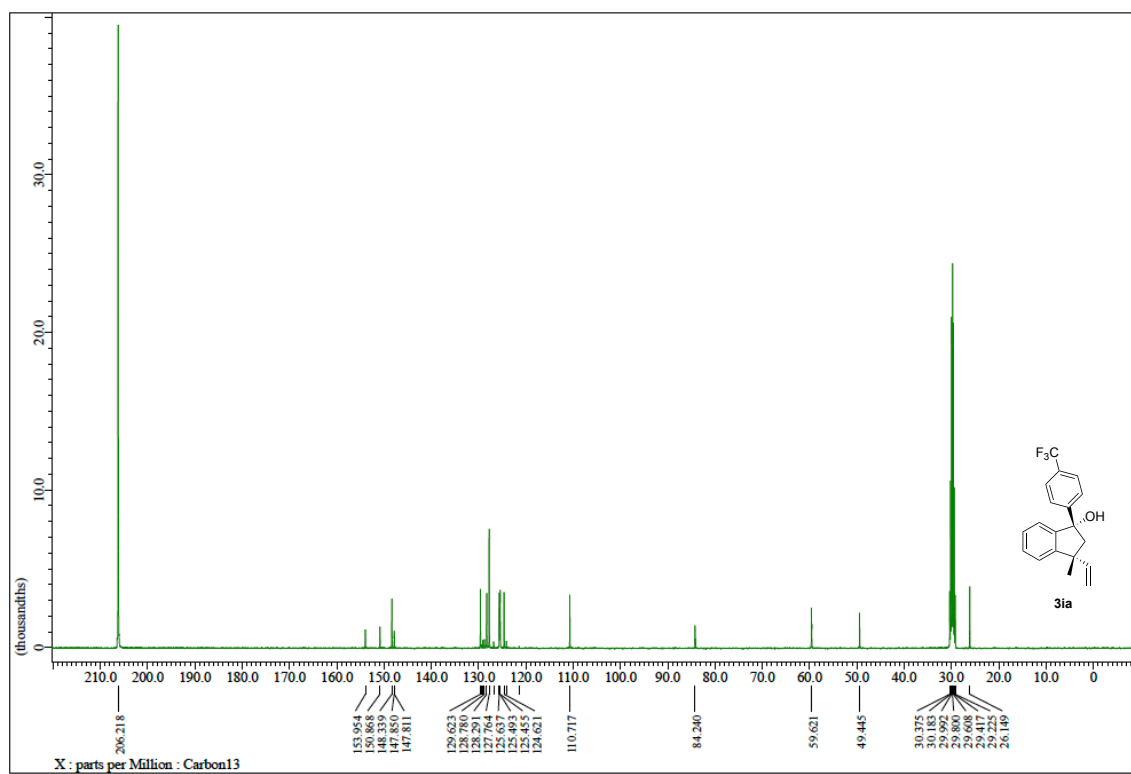


Pk #	Retention Time	Area	Area Percent
1	28.277	3512	0.110
2	31.250	3192909	99.890

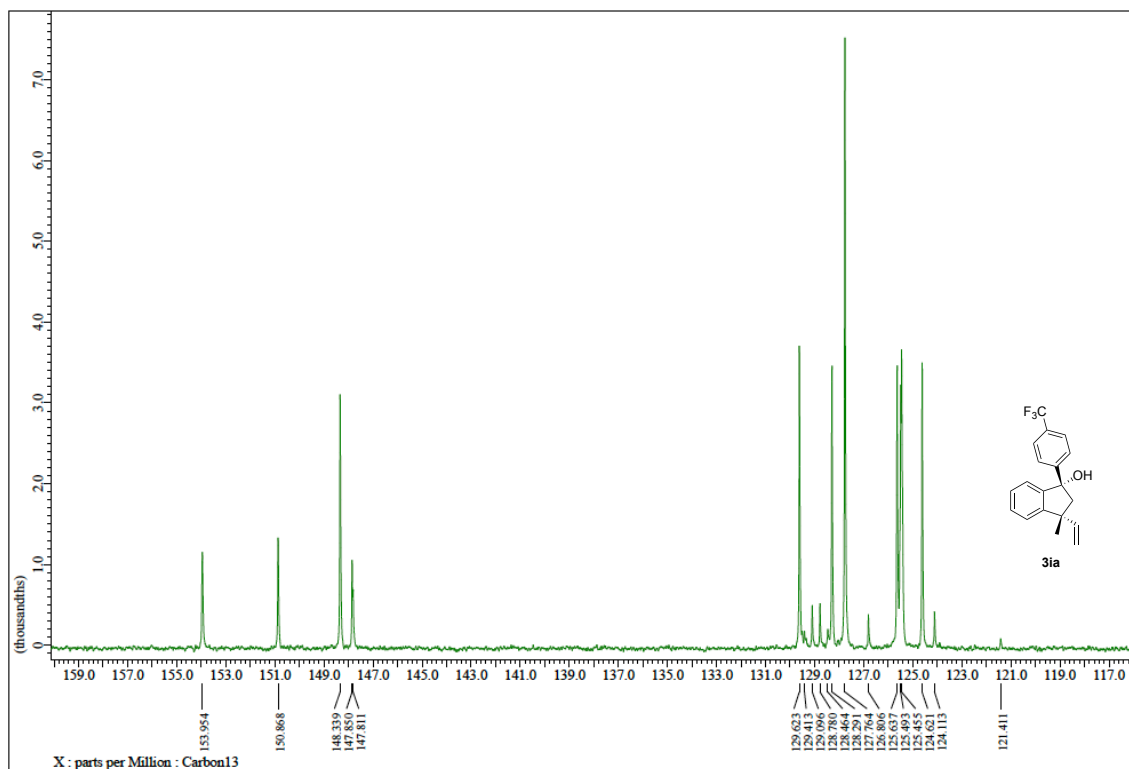
¹H NMR of 3ia (400 MHz, CDCl₃)

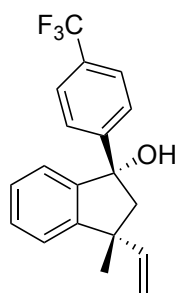


¹³C NMR of 3ia (100 MHz, CD₃COCD₃, overview)



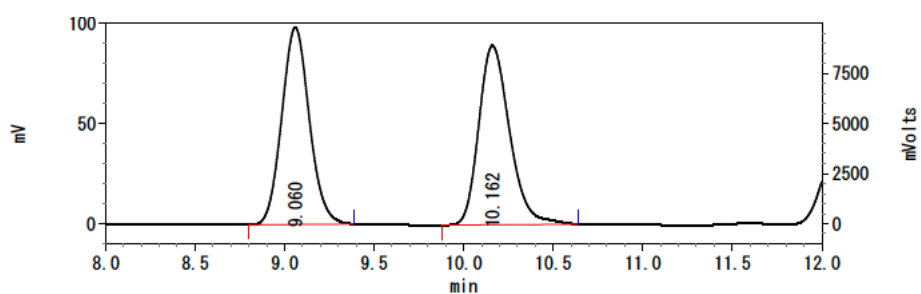
(160 ppm-116 ppm)





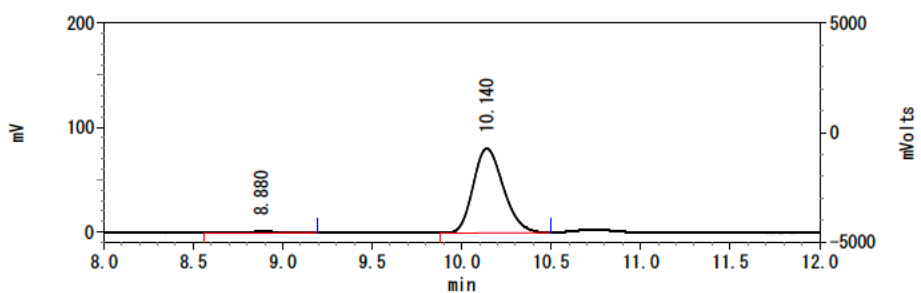
3ia

HPLC chart of (rac)-3ia



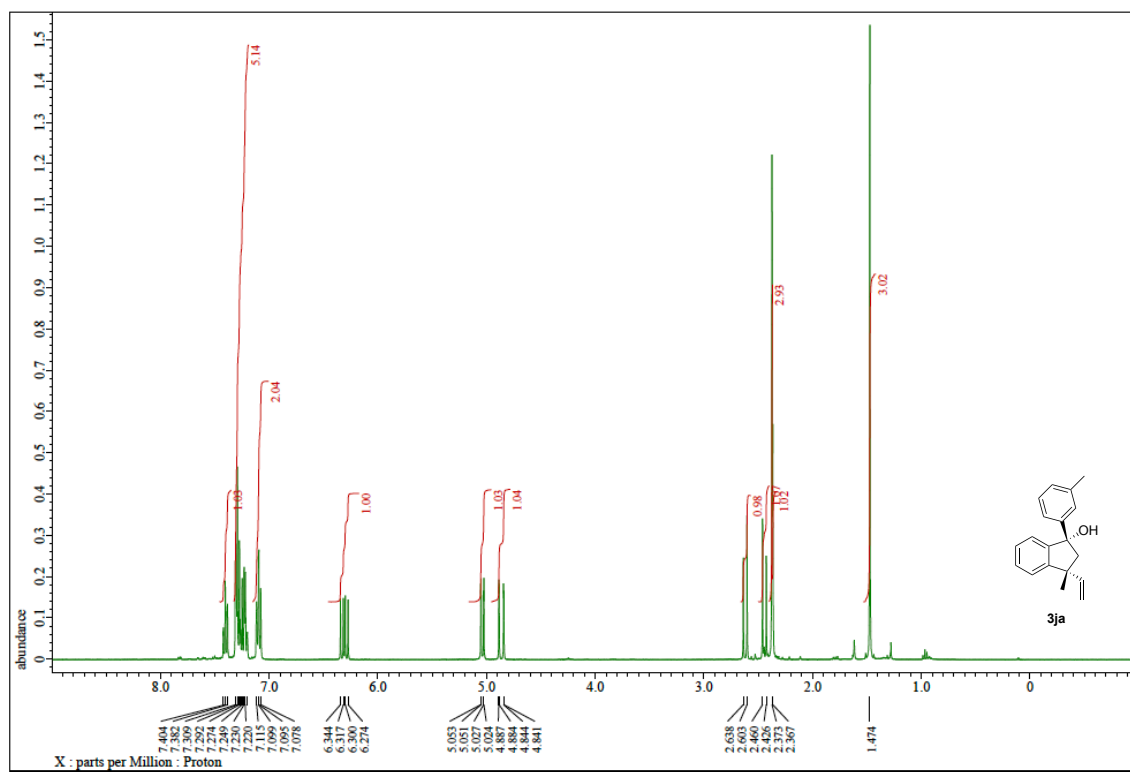
Pk #	Retention Time	Area	Area Percent
1	9.060	1052105	49.556
2	10.162	1070952	50.444

HPLC chart of (1S,3R)-3ia

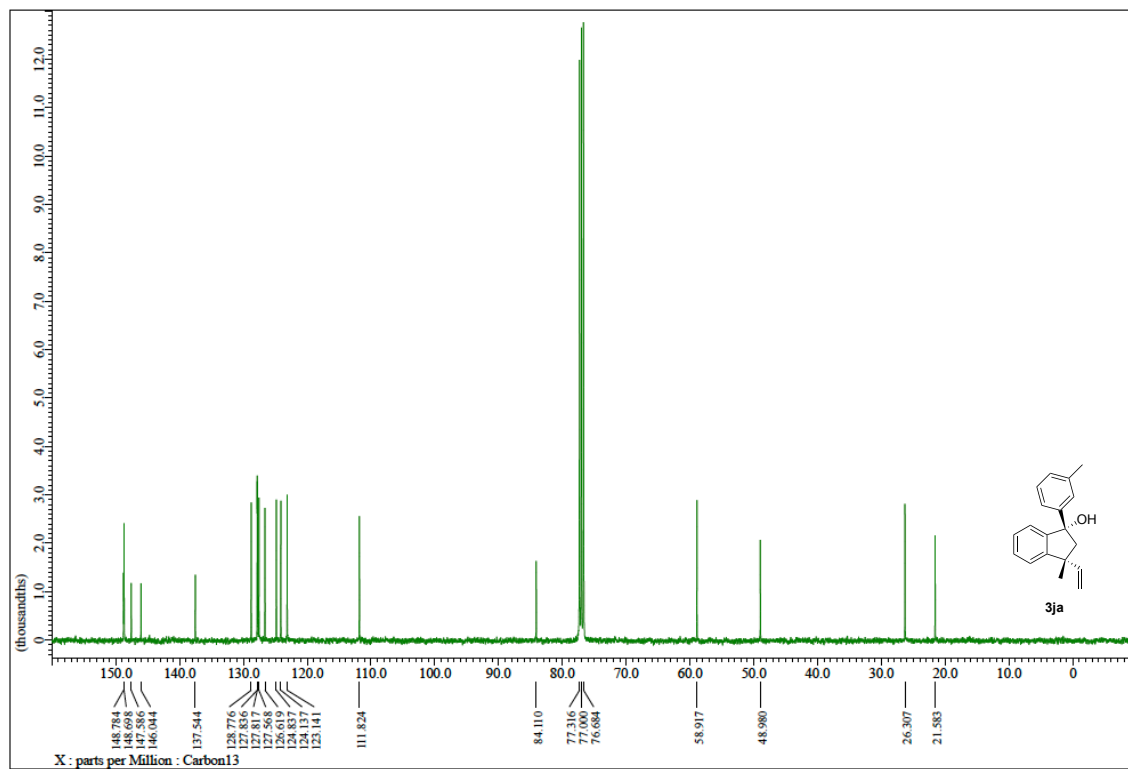


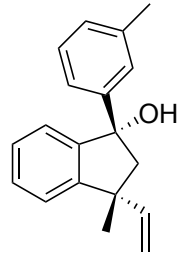
Pk #	Retention Time	Area	Area Percent
1	8.880	24947	2.567
2	10.140	946770	97.433

¹H NMR of 3ja (400 MHz, CDCl₃)



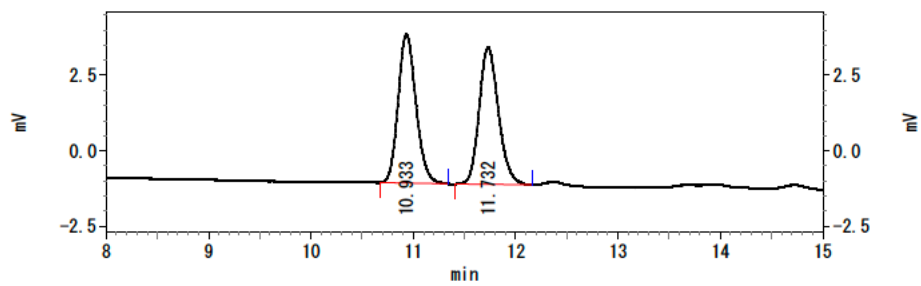
¹³C NMR of 3ja (100 MHz, CDCl₃)





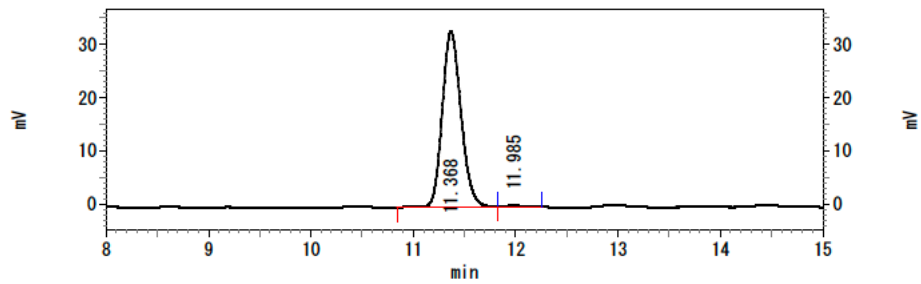
3ja

HPLC chart of (rac)-3ja



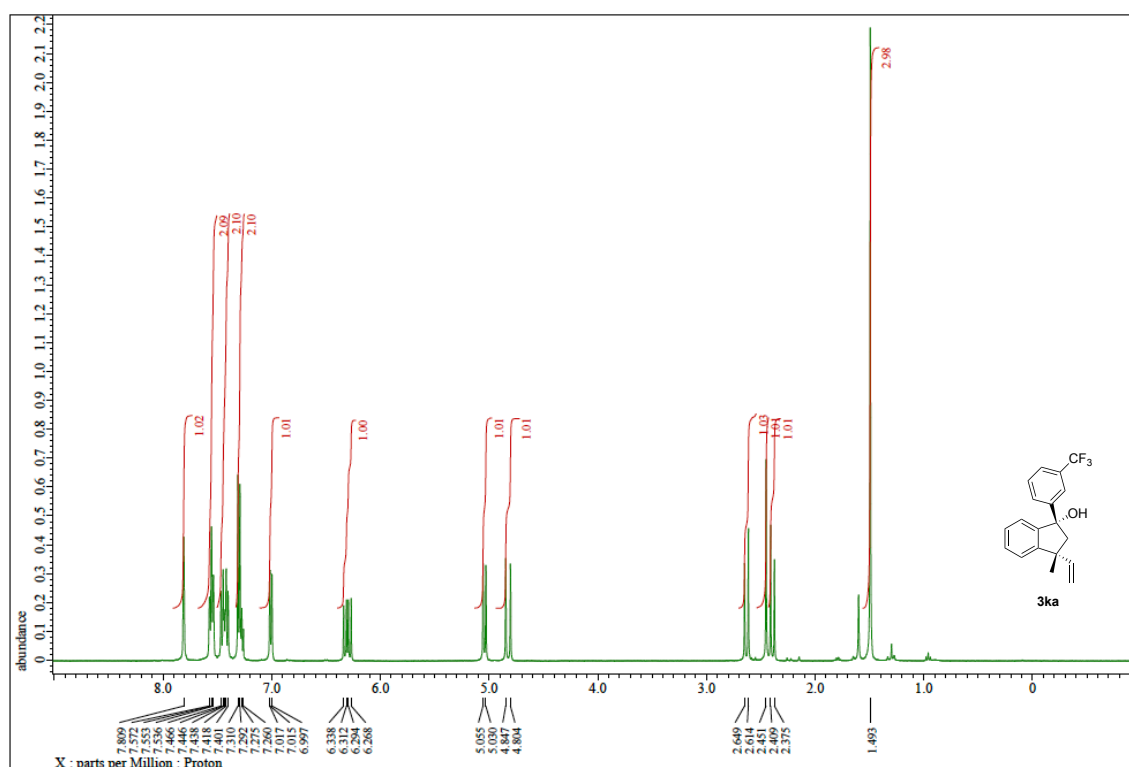
Pk #	Retention Time	Area	Area Percent
1	10.933	59853	50.145
2	11.732	59507	49.855

HPLC chart of (1S,3R)-3ja

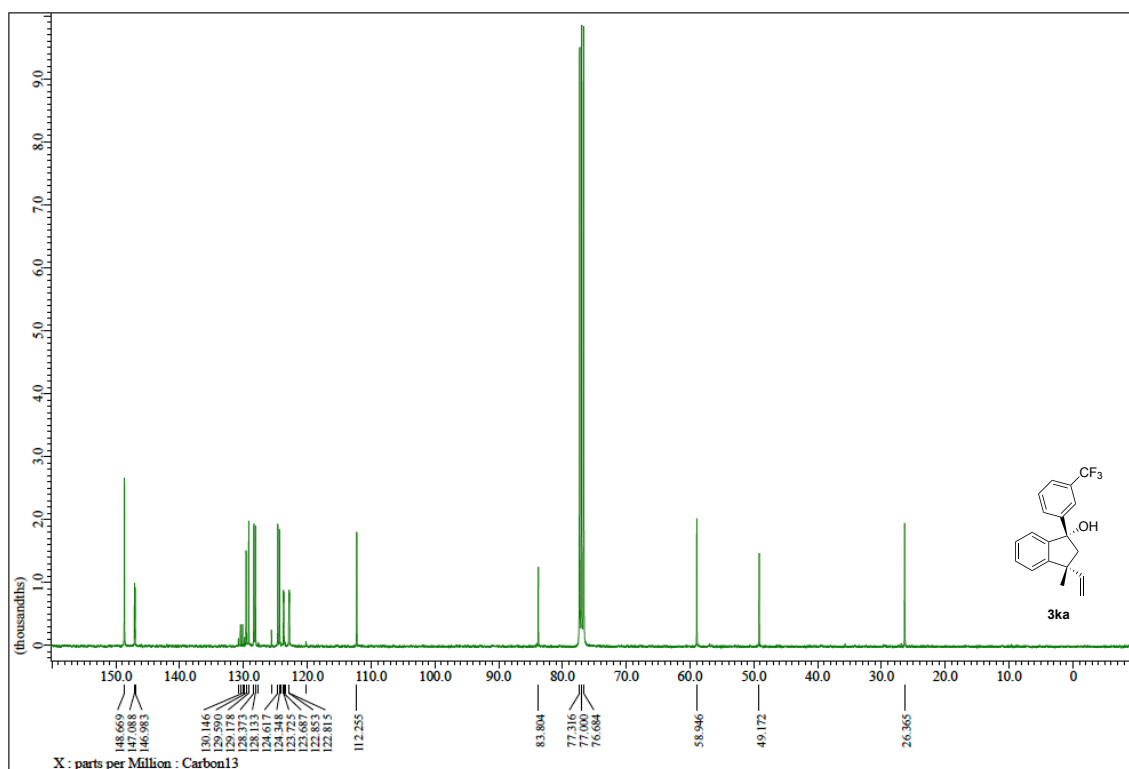


Pk #	Retention Time	Area	Area Percent
1	11.368	421262	99.148
2	11.985	3620	0.852

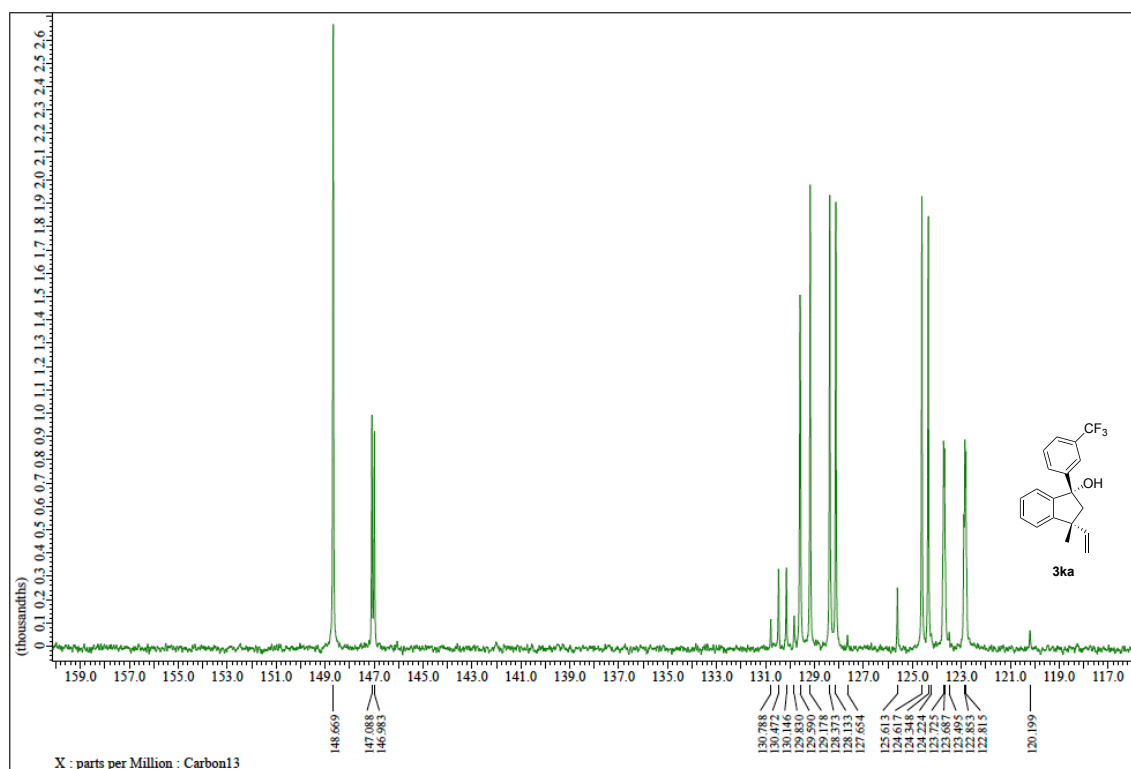
¹H NMR of 3ka (400 MHz, CDCl₃)

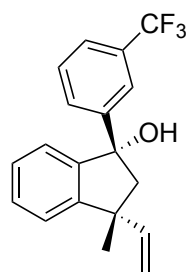


¹³C NMR of 3ka (100 MHz, CDCl₃, overview)



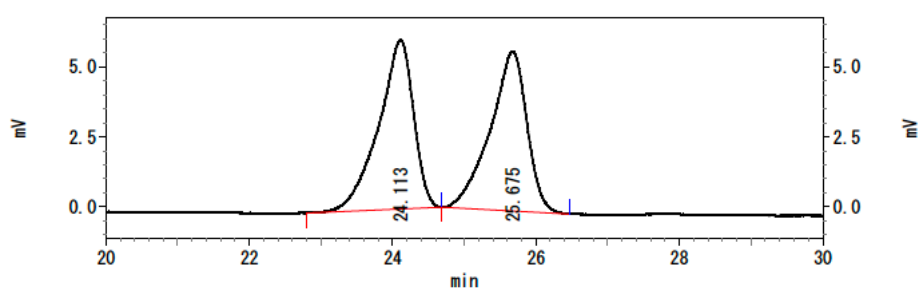
(160 ppm-116 ppm)





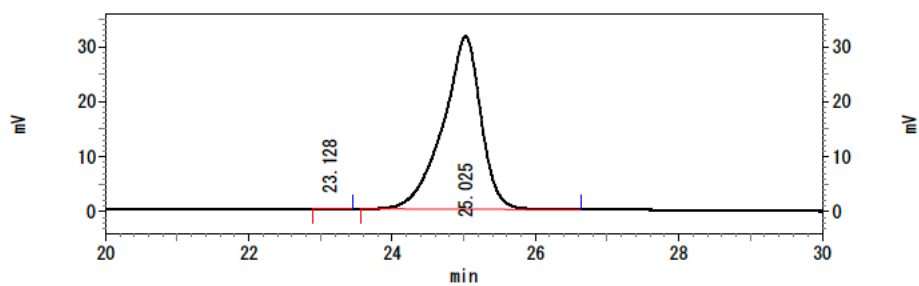
3ka

HPLC chart of (*rac*)-3ka



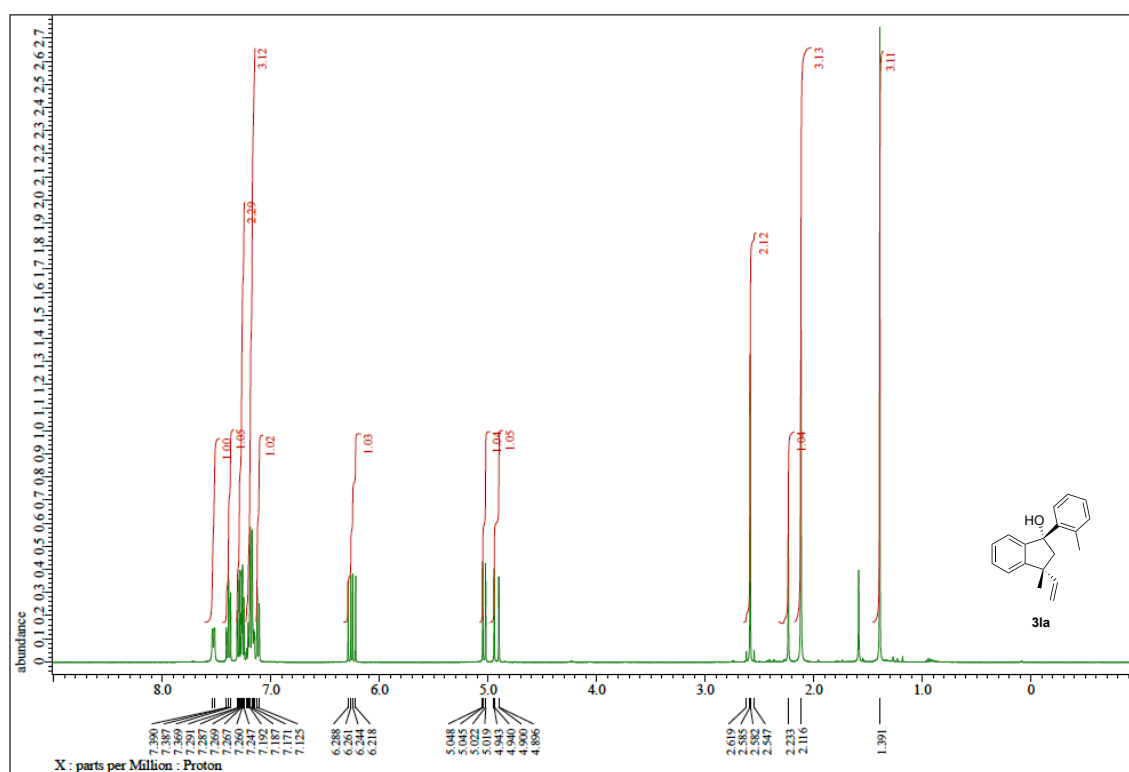
Pk #	Retention Time	Area	Area Percent
1	24.113	203998	50.165
2	25.675	202658	49.835

HPLC chart of (1*S*,3*R*)-3ka

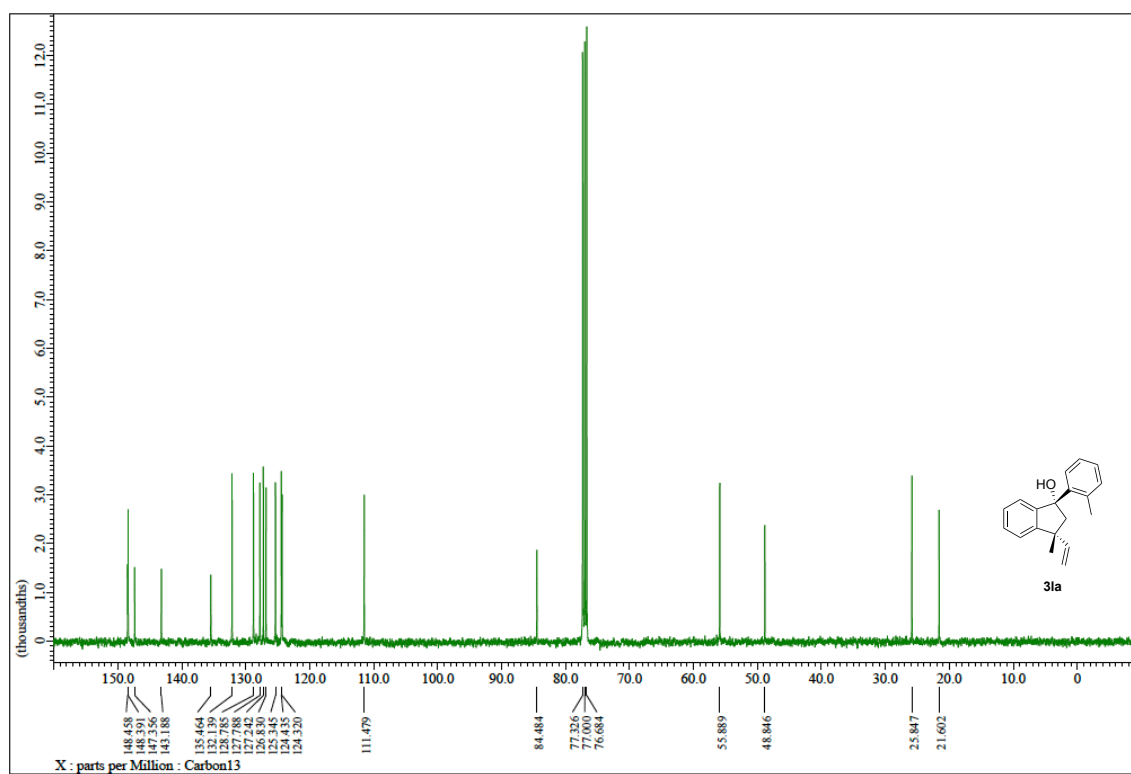


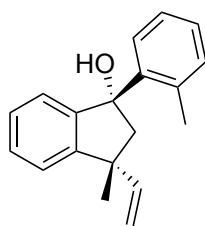
Pk #	Retention Time	Area	Area Percent
1	23.128	462	0.040
2	25.025	1159753	99.960

¹H NMR of 3la (400 MHz, CDCl₃)



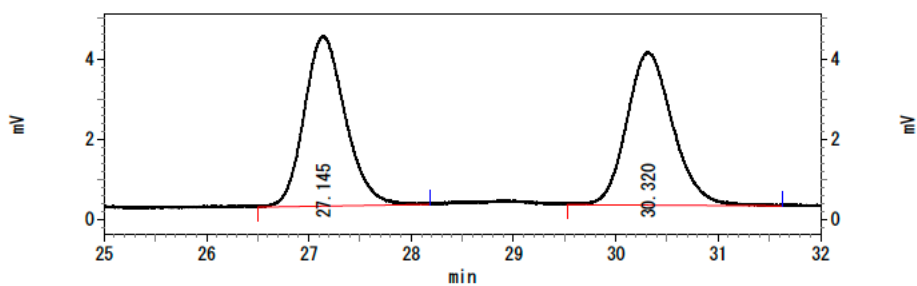
¹³C NMR of 3la (100 MHz, CDCl₃)





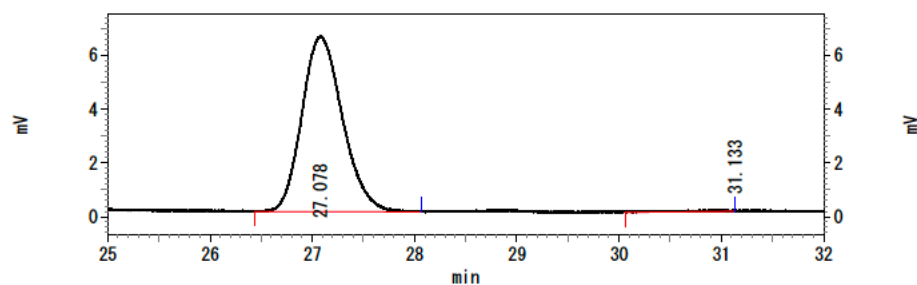
3la

HPLC chart of (*rac*)-3la



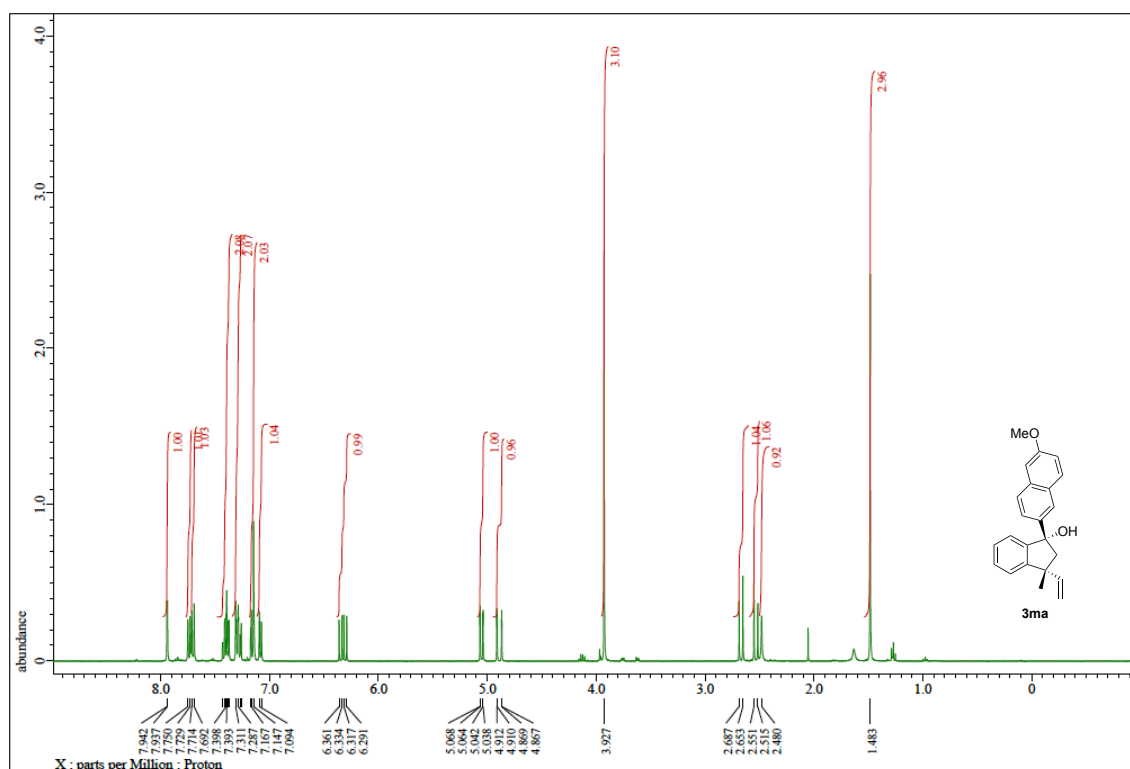
Pk #	Retention Time	Area	Area Percent
1	27.145	118199	49.840
2	30.320	118959	50.160

HPLC chart of (1*S*,3*R*)-3la

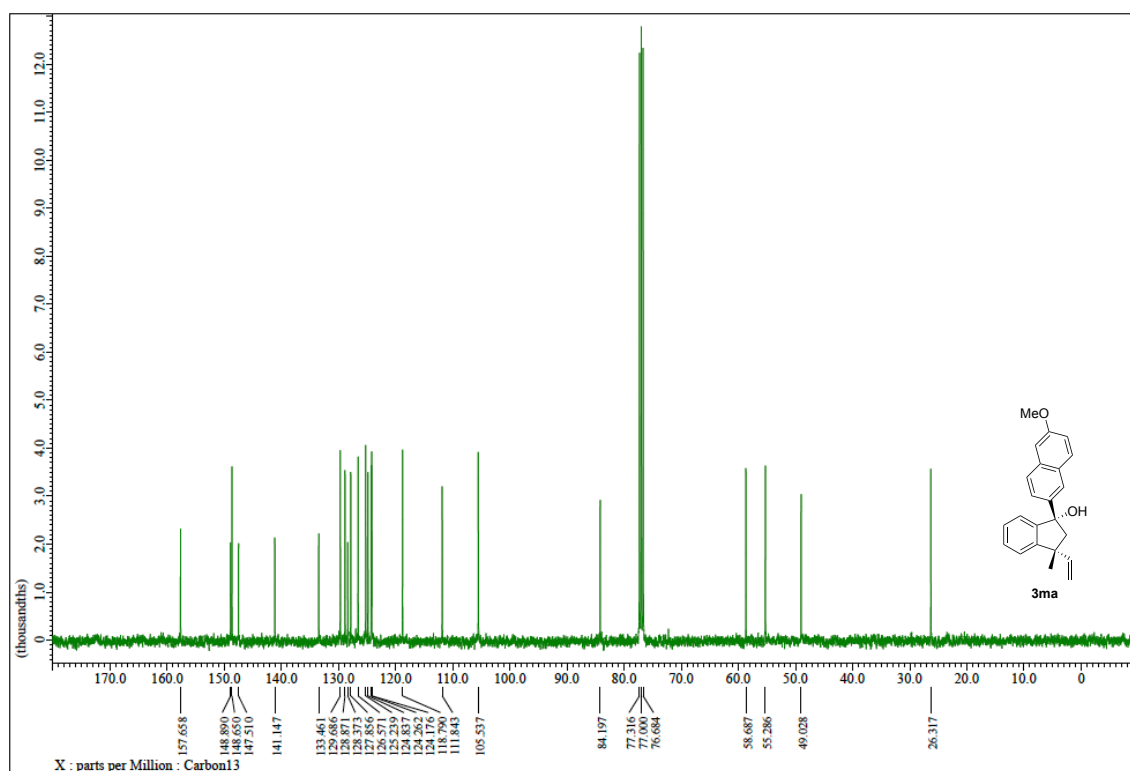


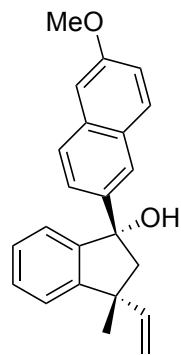
Pk #	Retention Time	Area	Area Percent
1	27.078	180599	99.090
2	31.133	1659	0.910

¹H NMR of 3ma (400 MHz, CDCl₃)



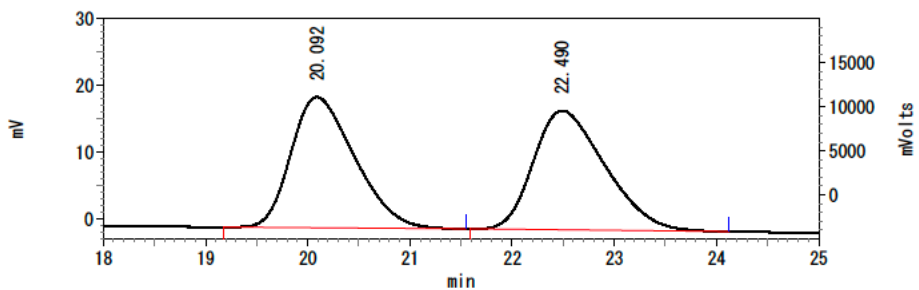
¹³C NMR of 3ma (100 MHz, CDCl₃)





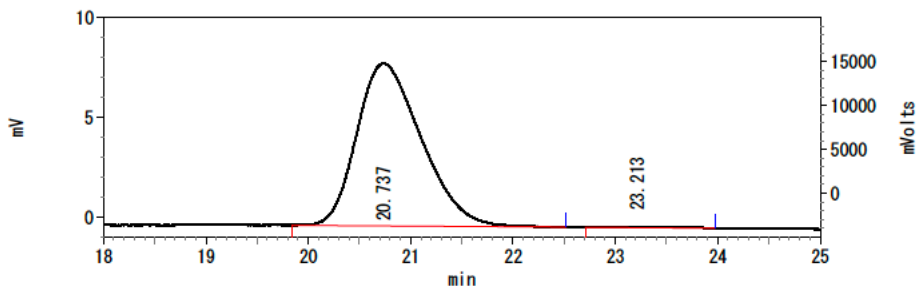
3ma

HPLC chart of (*rac*)-3ma



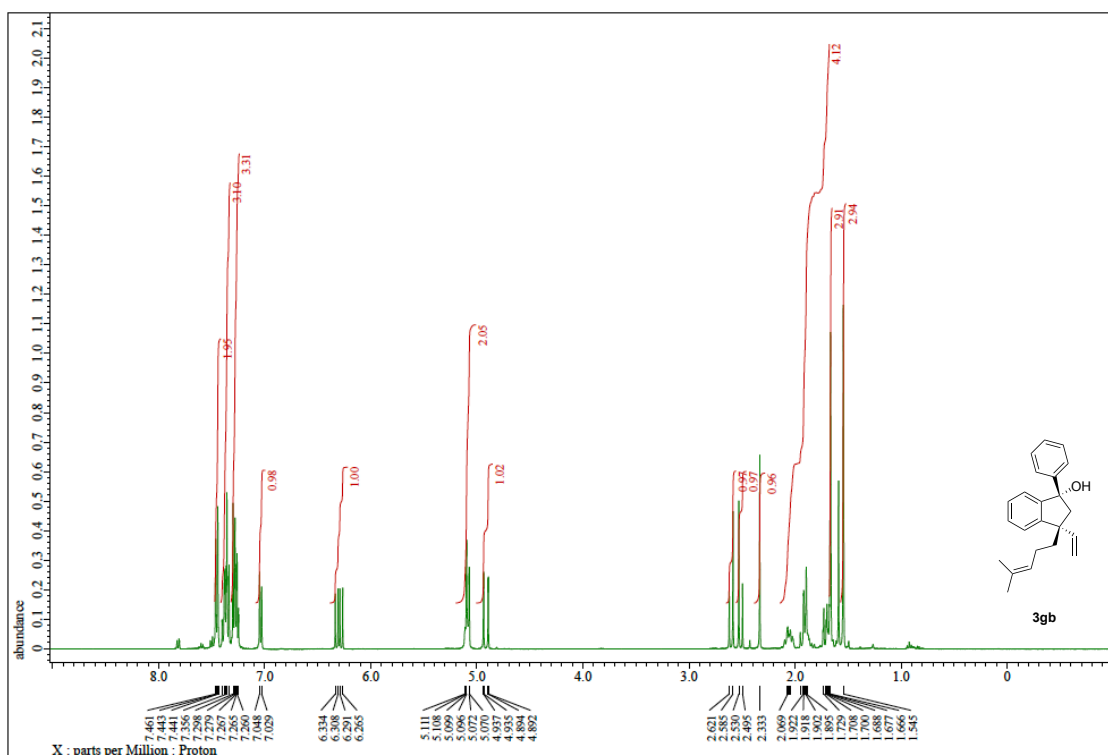
Pk #	Retention Time	Area	Area Percent
1	20.092	848663	49.408
2	22.490	868989	50.592

HPLC chart of (1*S*,3*R*)-3ma

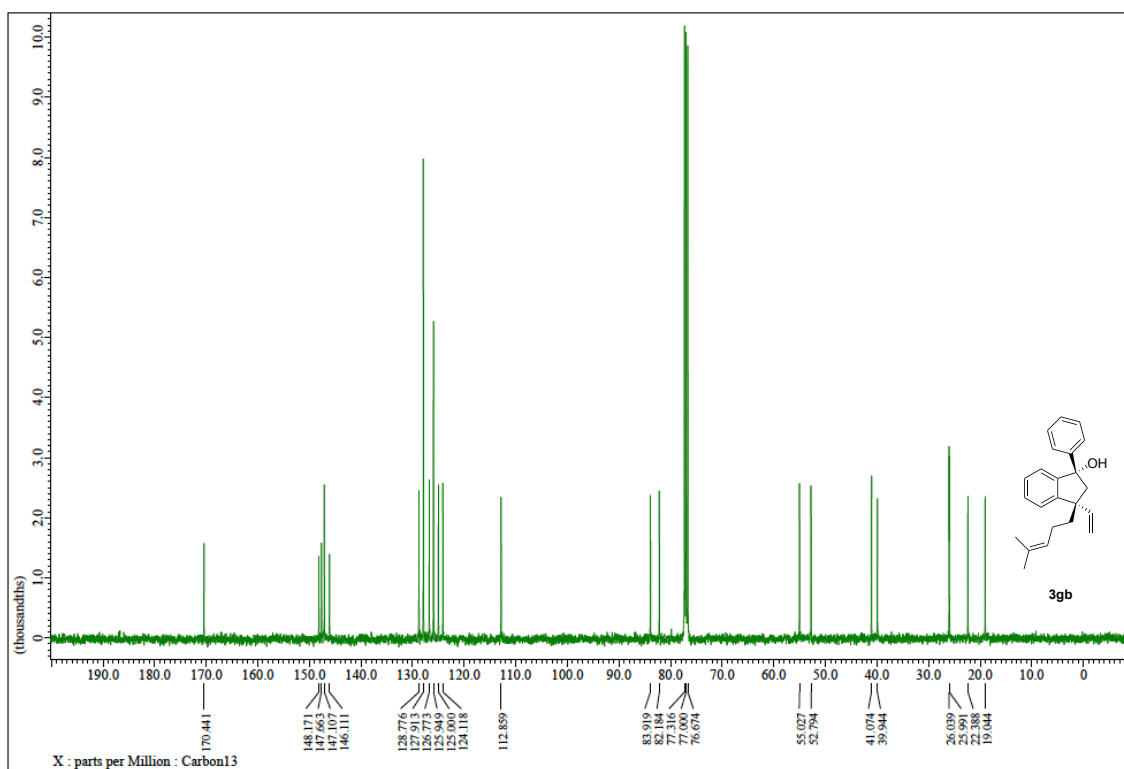


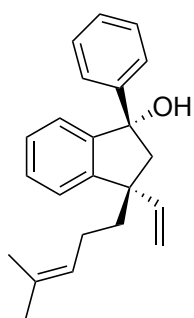
Pk #	Retention Time	Area	Area Percent
1	20.737	356480	99.361
2	23.213	2292	0.639

¹H NMR of 3gb (400 MHz, CDCl₃)



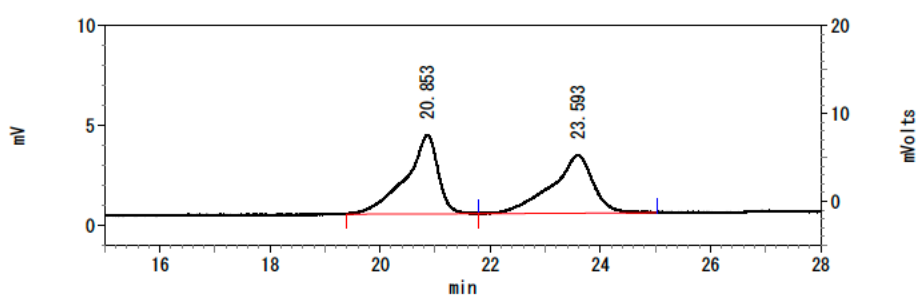
¹³C NMR of 3gb (100 MHz, CDCl₃)





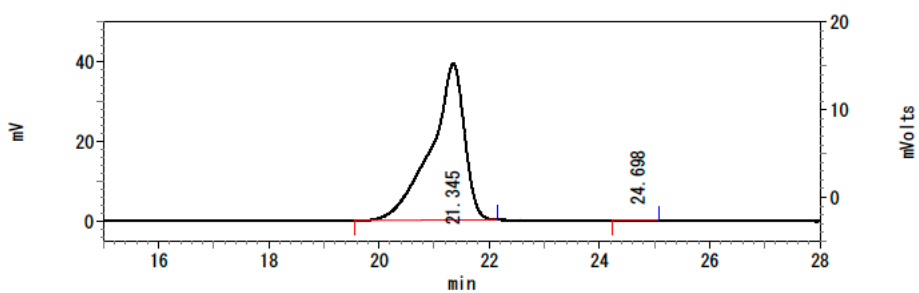
3gb

HPLC chart of (*rac*)-3gb



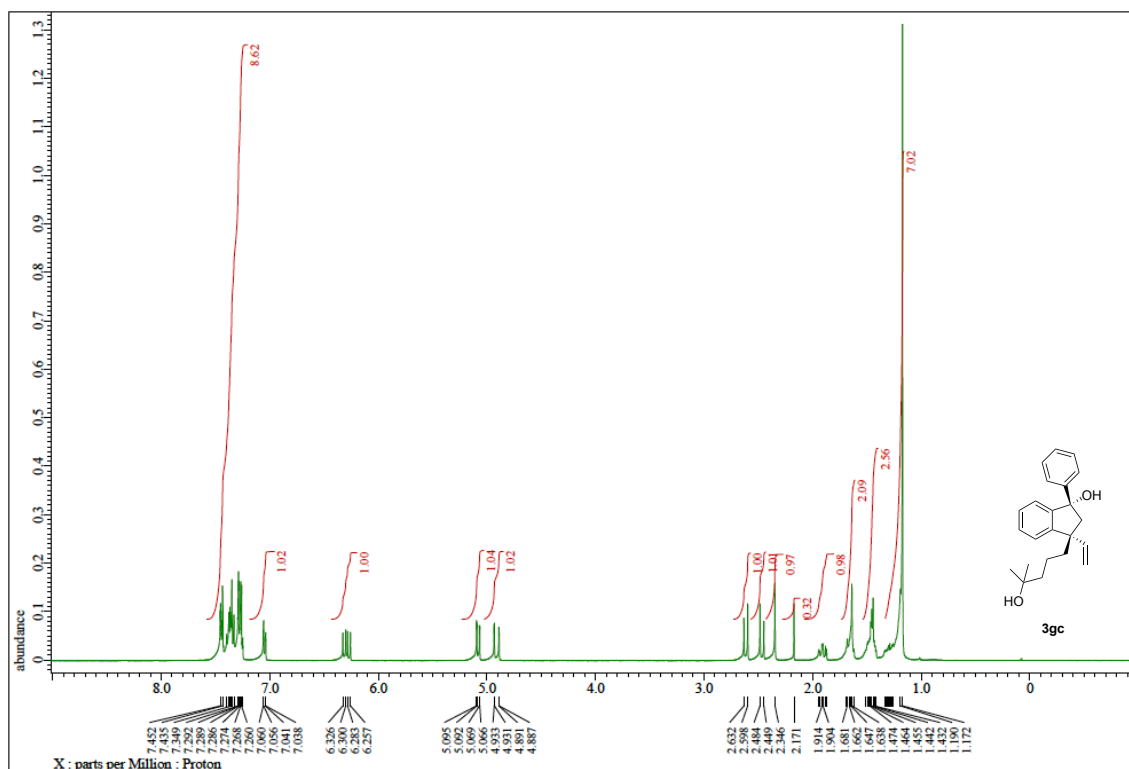
Pk #	Retention Time	Area	Area Percent
1	20.853	162082	51.357
2	23.593	153518	48.643

HPLC chart of (*1S,3R*)-3gb

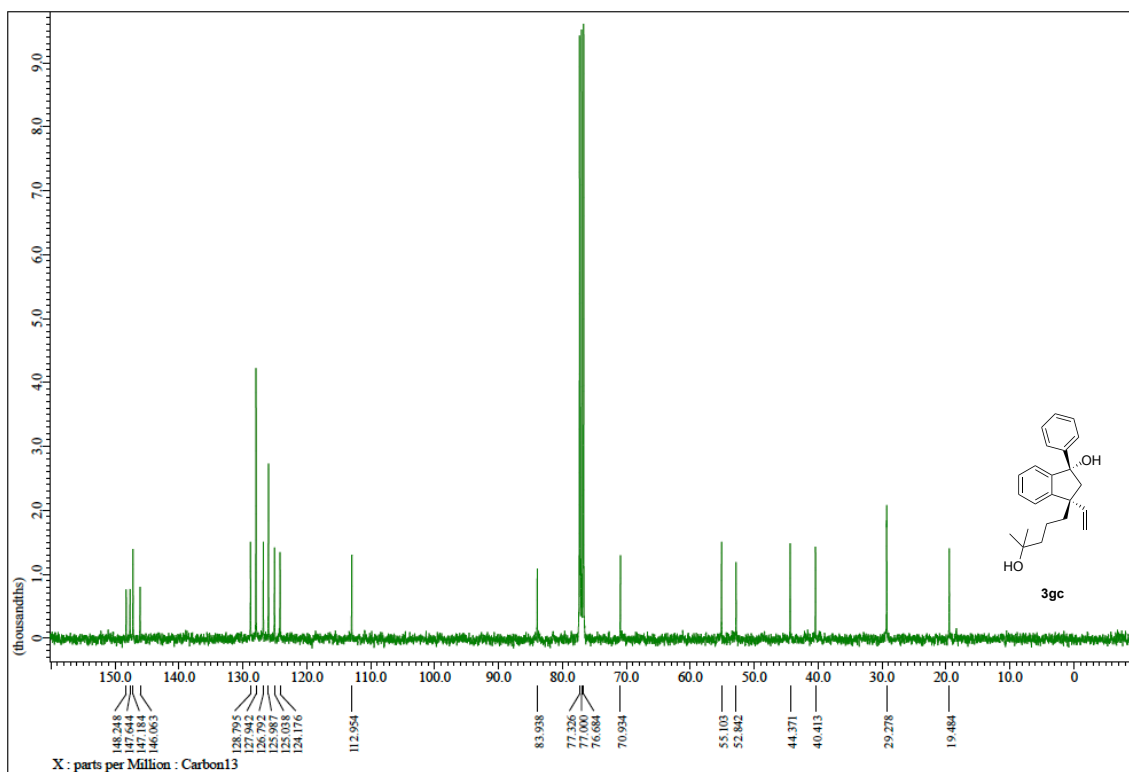


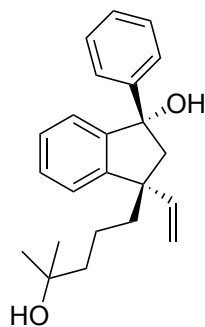
Pk #	Retention Time	Area	Area Percent
1	21.345	1652959	99.911
2	24.698	1475	0.089

¹H NMR of 3gc (400 MHz, CDCl₃)



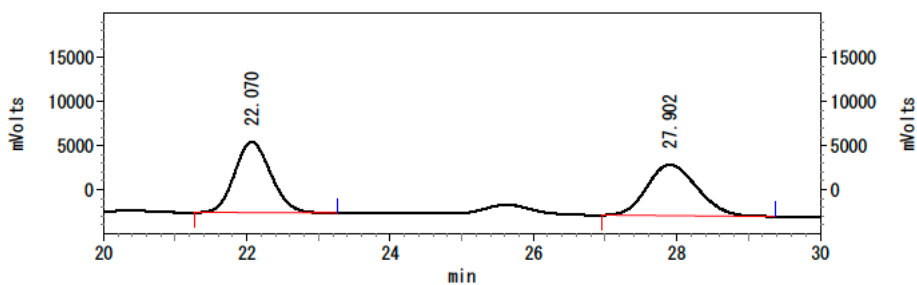
¹³C NMR of 3gc (100 MHz, CDCl₃)





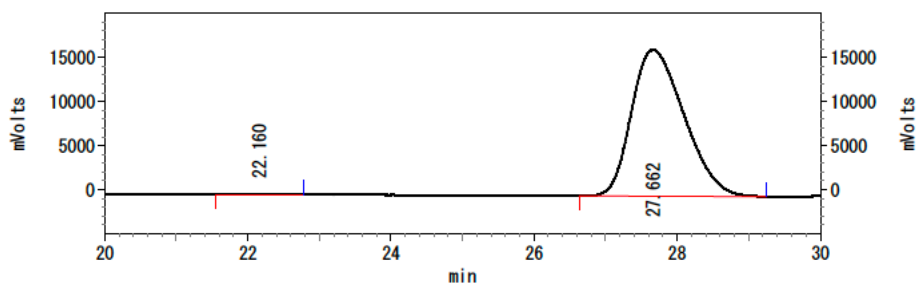
3gc

HPLC chart of (*rac*)-3gc



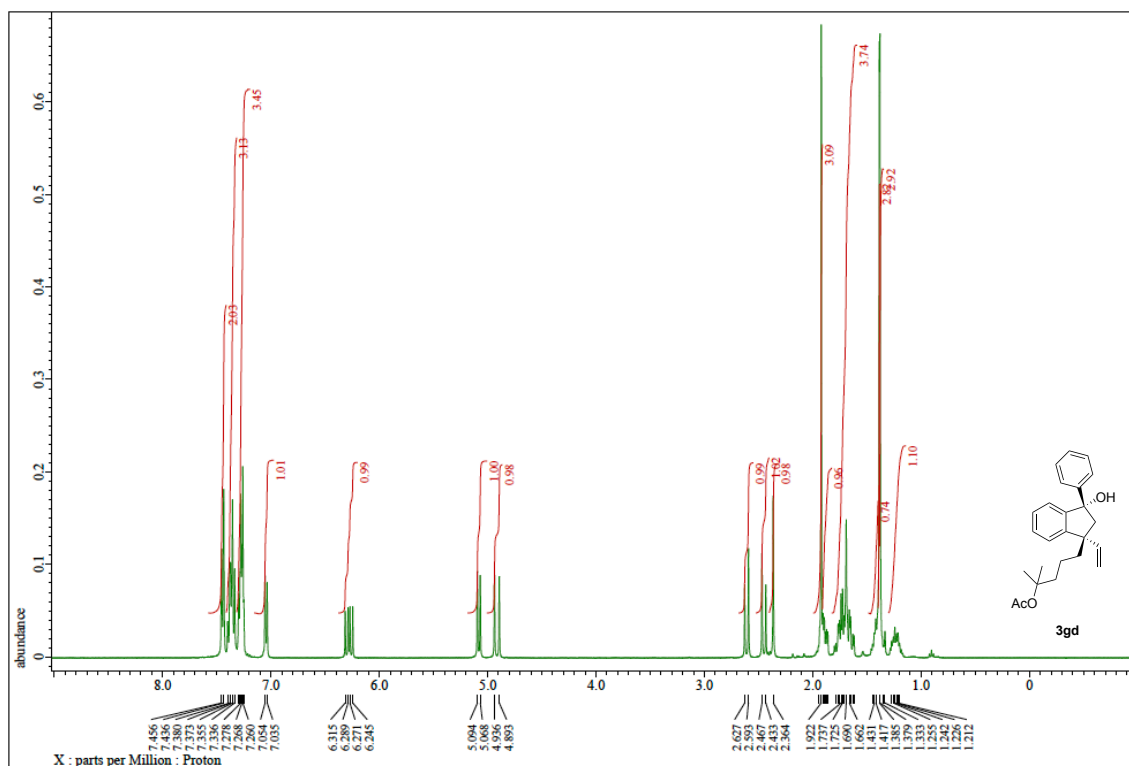
Pk #	Retention Time	Area	Area Percent
1	22.070	282164	50.066
2	27.902	281415	49.934

HPLC chart of (1*R*,3*R*)-3gc

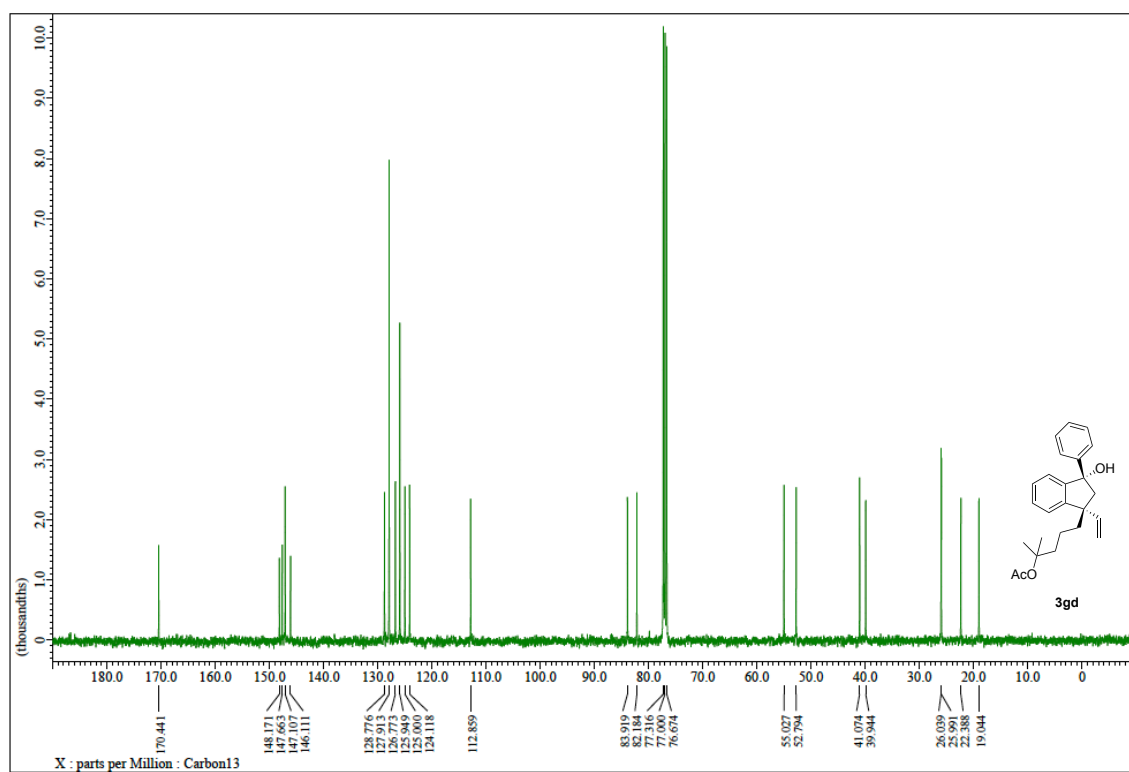


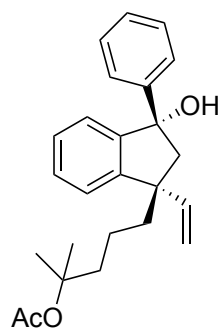
Pk #	Retention Time	Area	Area Percent
1	22.160	1693	0.199
2	27.662	849611	99.801

¹H NMR of 3gd (400 MHz, CDCl₃)



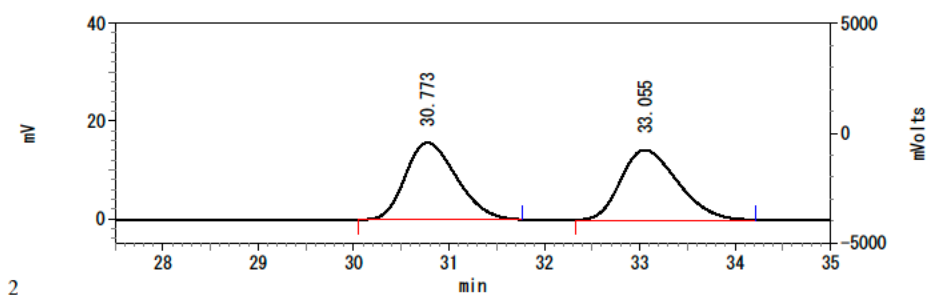
¹³C NMR of 3gd (100 MHz, CDCl₃)





3gd

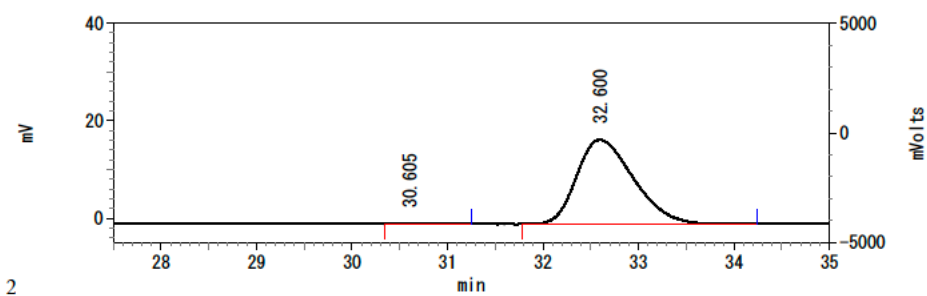
HPLC chart of (*rac*)-3gd



2

Pk #	Retention Time	Area	Area Percent
1	30.773	589013	49.823
2	33.055	593197	50.177

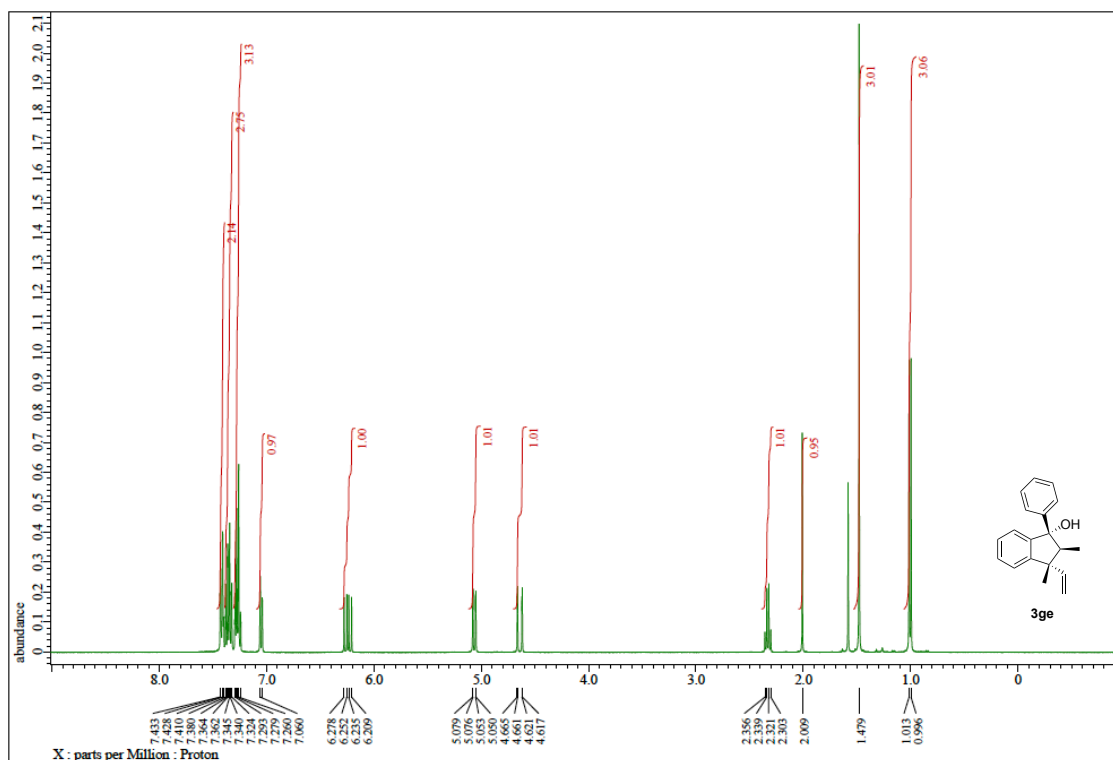
HPLC chart of (1*R*,3*R*)-3gd



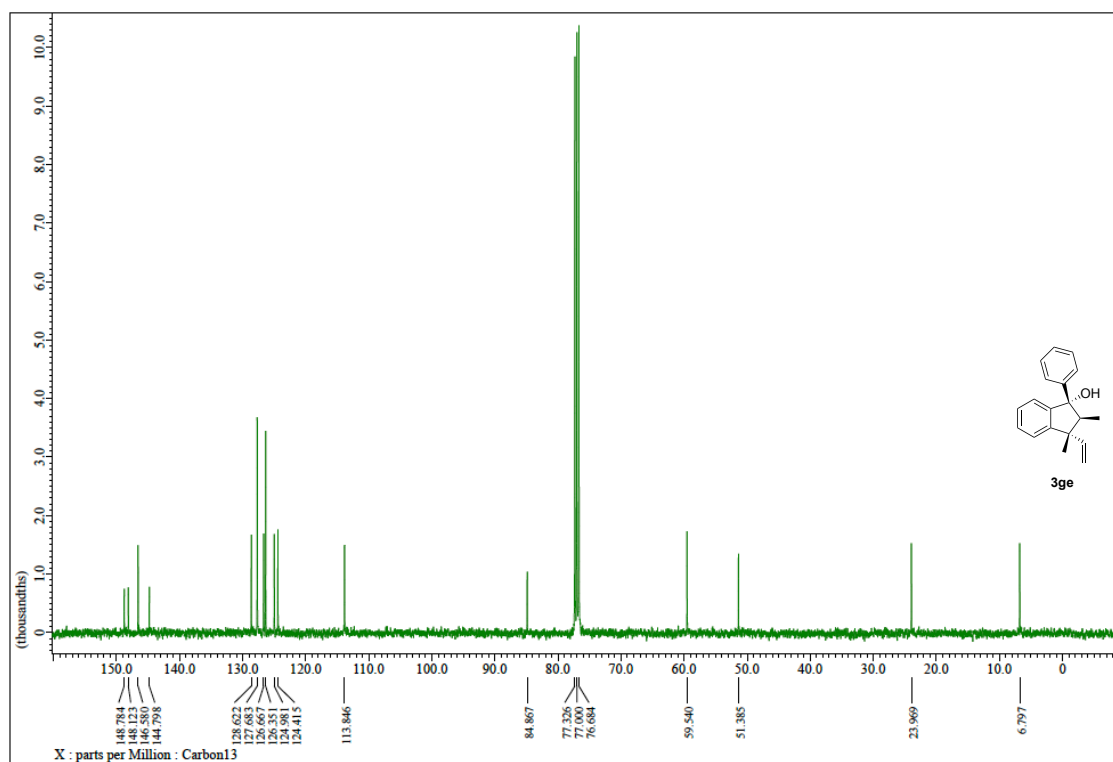
2

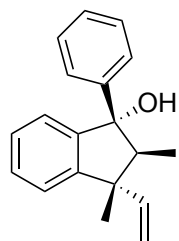
Pk #	Retention Time	Area	Area Percent
1	30.605	1149	0.160
2	32.600	717600	99.840

¹H NMR of 3ge (400 MHz, CDCl₃)



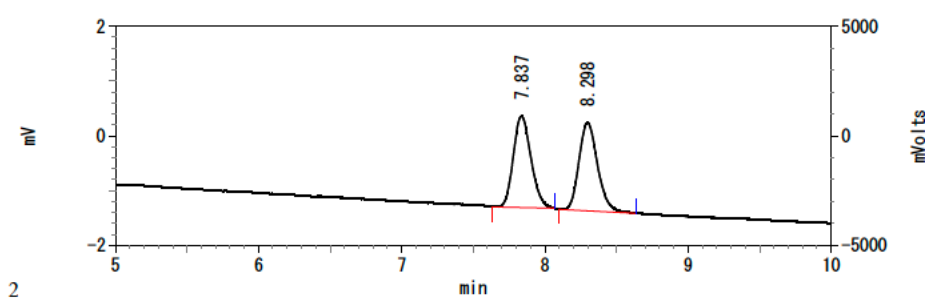
¹³C NMR of 3ge (100 MHz, CDCl₃)





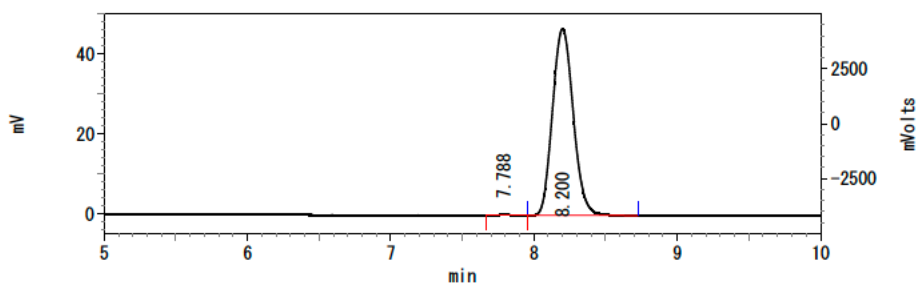
3ge

HPLC chart of (*rac*)-3ge



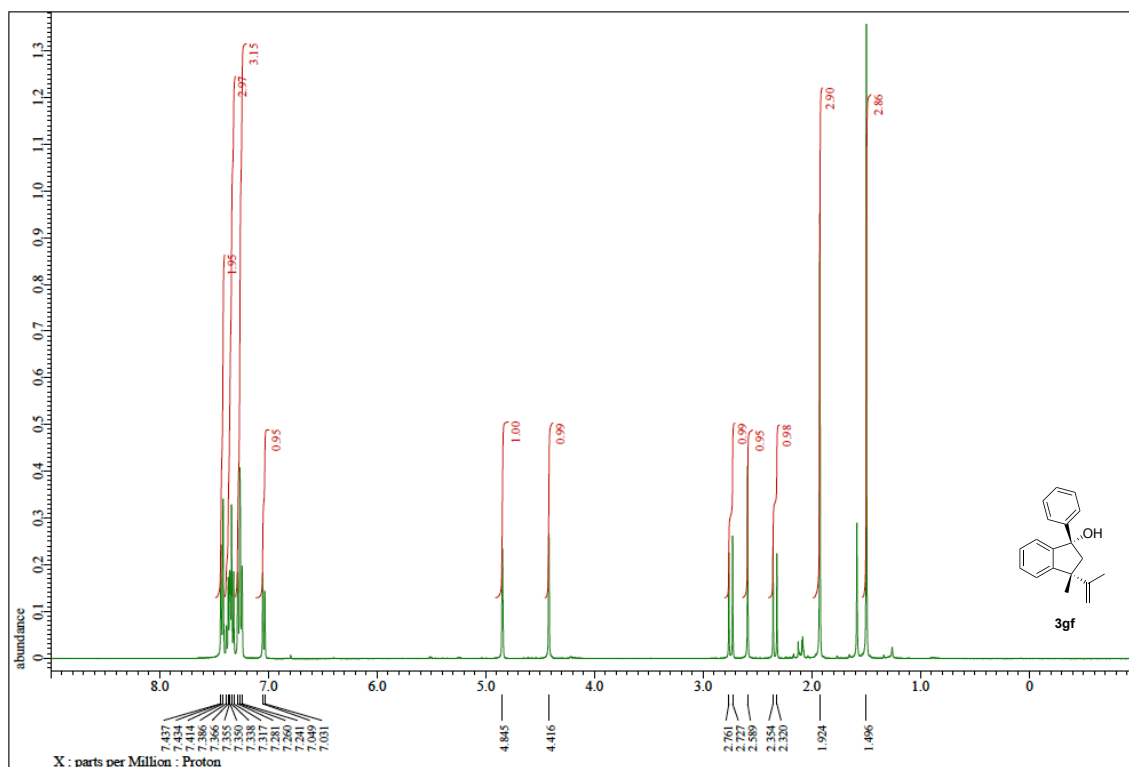
Pk #	Retention Time	Area	Area Percent
1	7.837	14357	49.694
2	8.298	14534	50.306

HPLC chart of (1*R*,2*S*,3*S*)-3ge

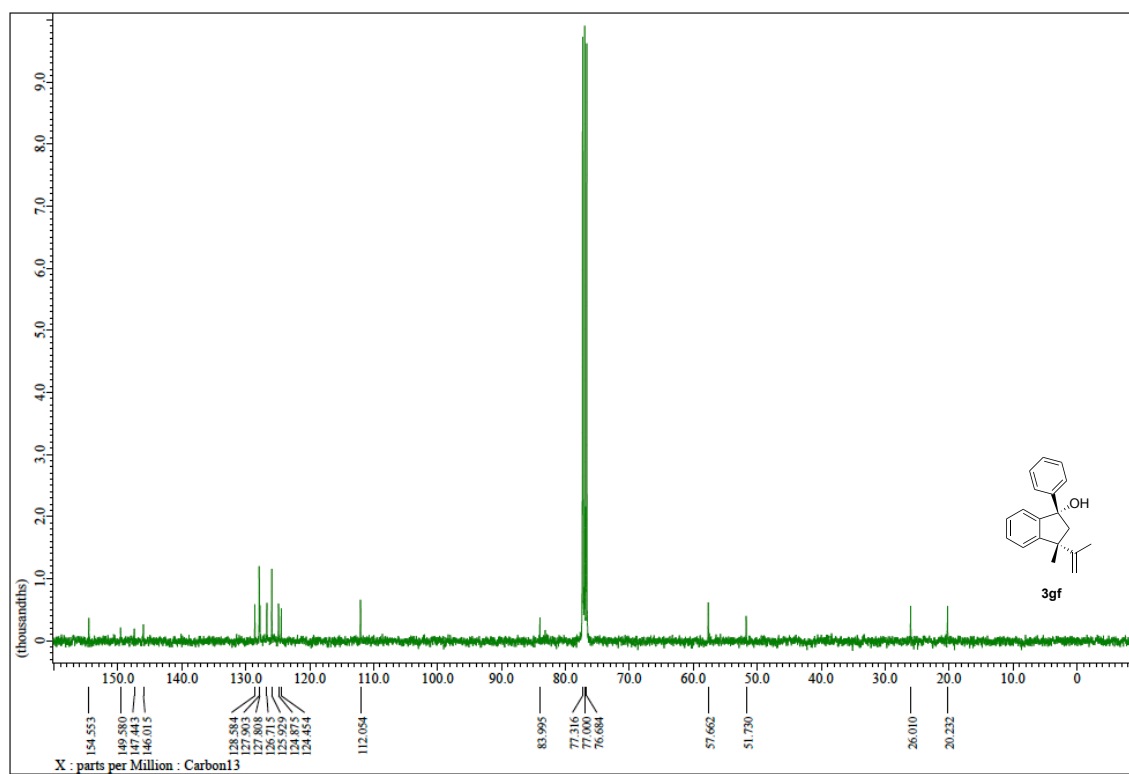


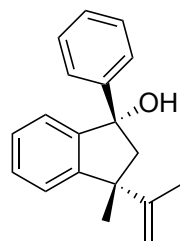
Pk #	Retention Time	Area	Area Percent
1	7.788	945	0.200
2	8.200	470942	99.800

^1H NMR of 3gf (400 MHz, CDCl_3)



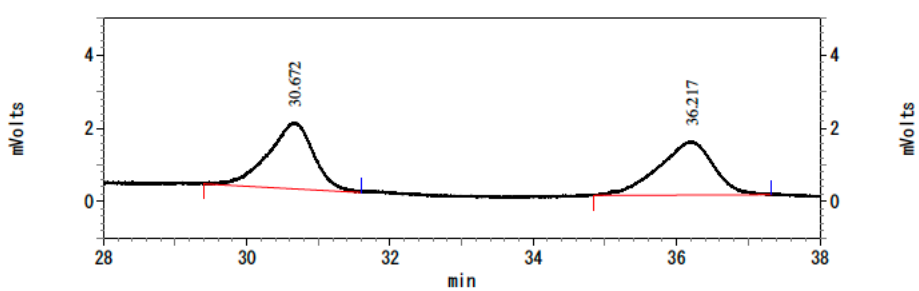
^{13}C NMR of 3gf (100 MHz, CDCl_3)





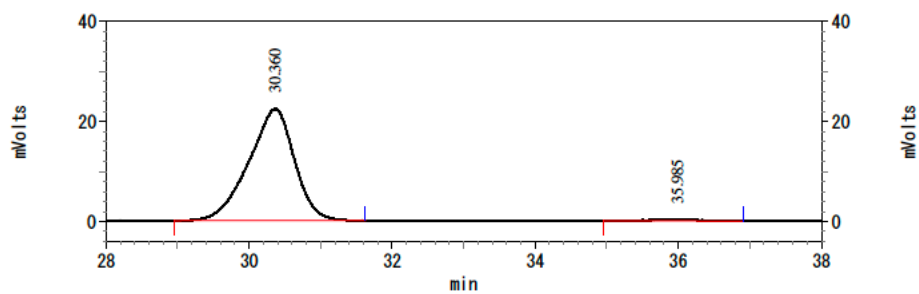
3gf

HPLC chart of (*rac*)-3gf



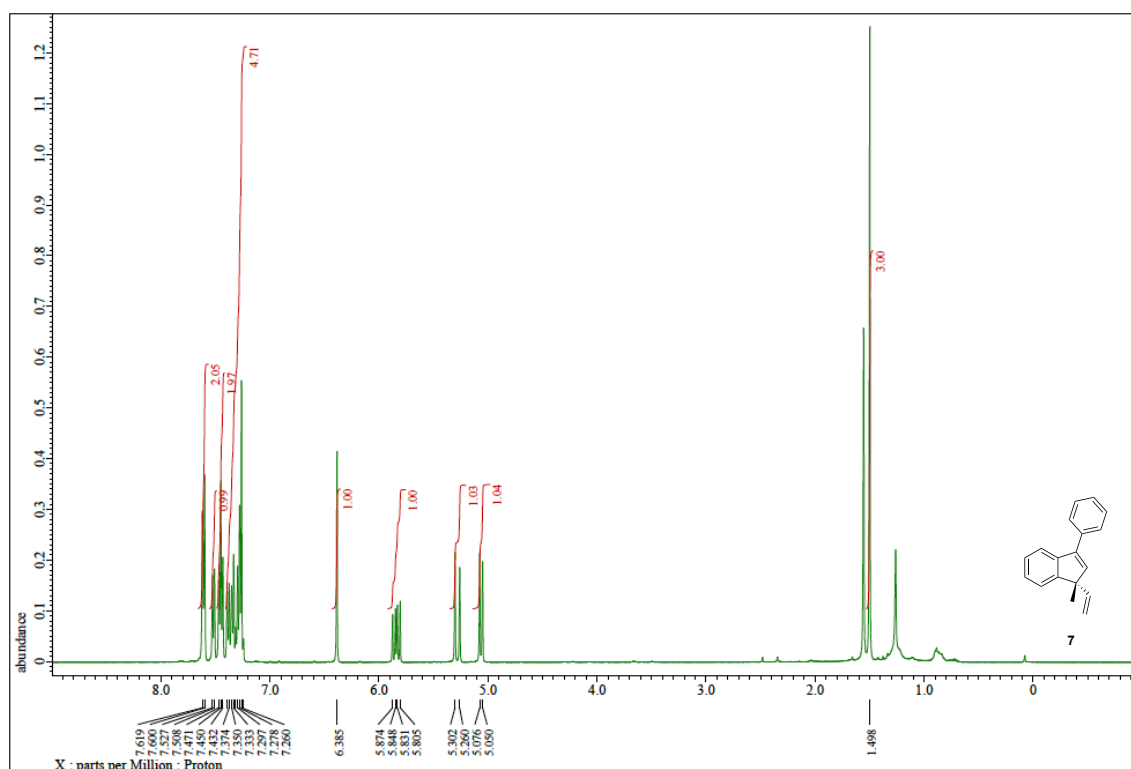
Pk #	Retention Time	Area	Area Percent
1	30.672	80144	50.625
2	36.217	78165	49.375

HPLC chart of (*1R,3R*)-3gf

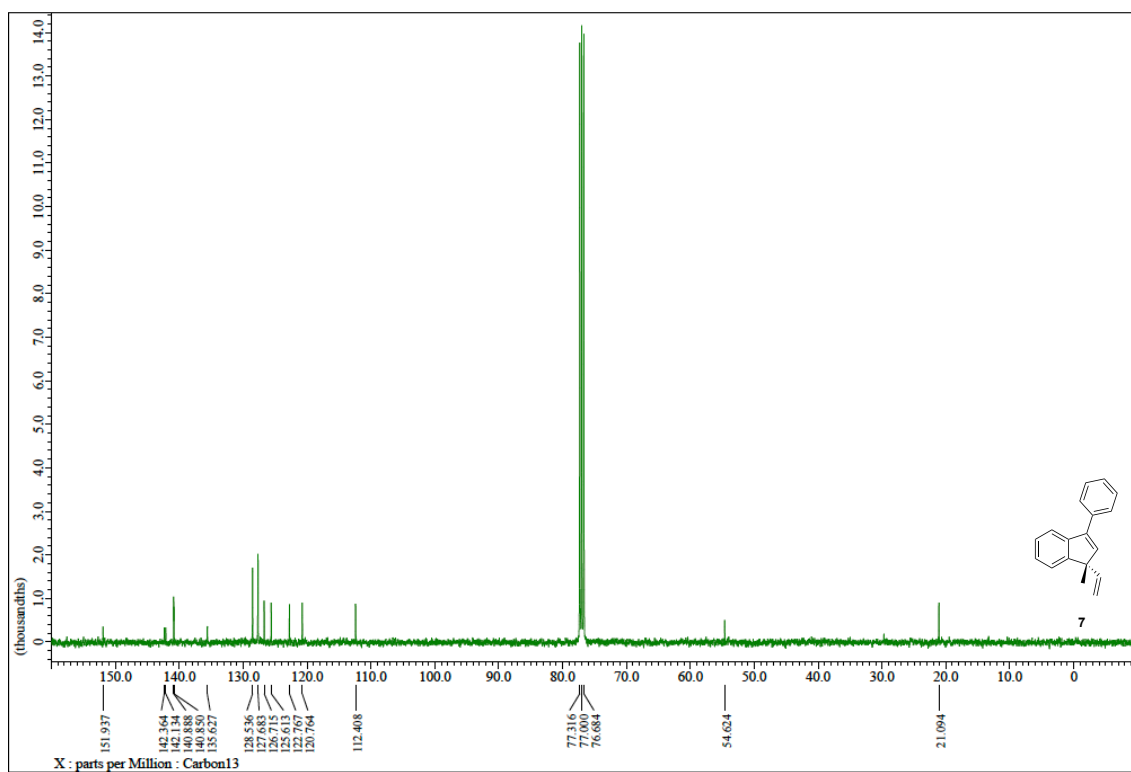


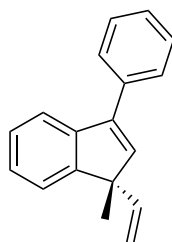
Pk #	Retention Time	Area	Area Percent
1	30.360	991752	98.467
2	35.985	15440	1.533

¹H NMR of 7 (400 MHz, CDCl₃)



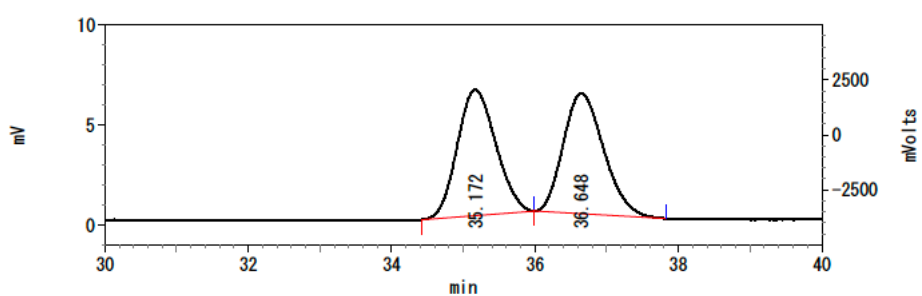
¹³C NMR of 7 (400 MHz, CDCl₃)





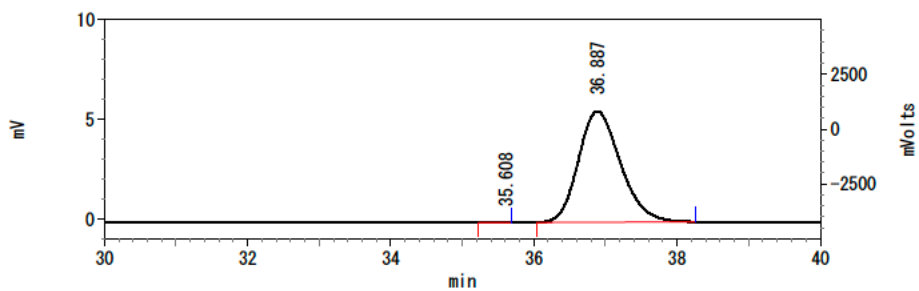
7

HPLC chart of (*rac*)-7



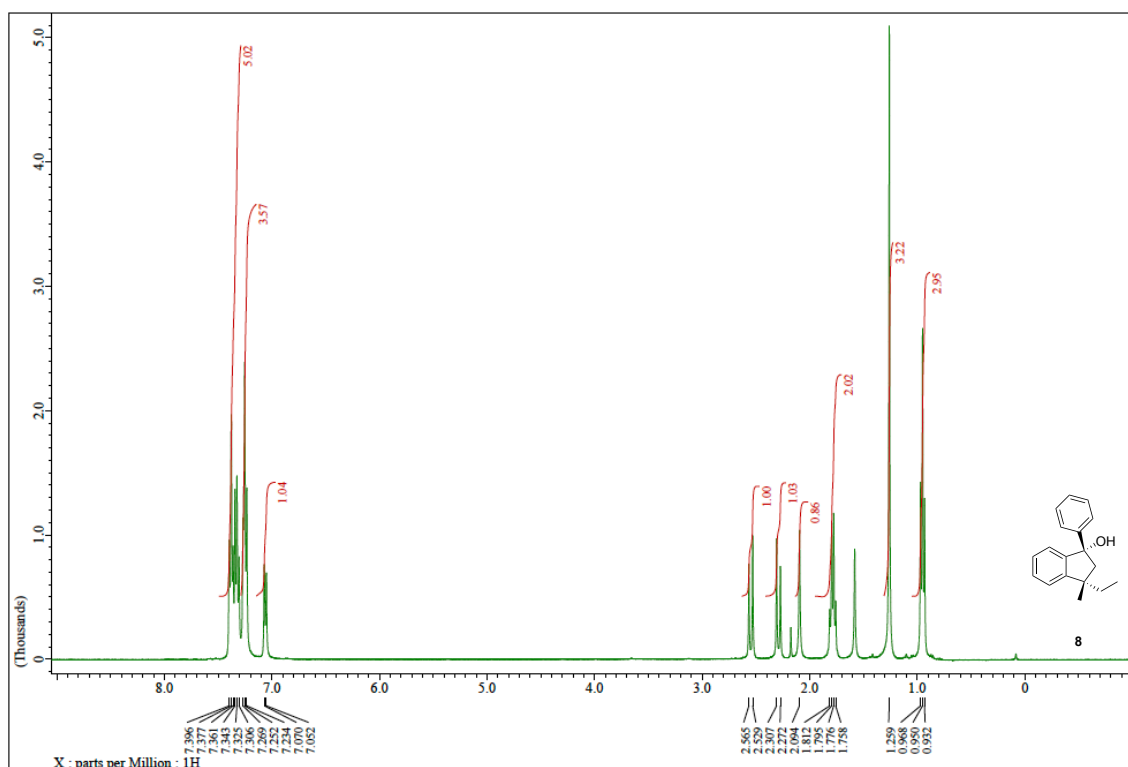
Pk #	Retention Time	Area	Area Percent
1	35.172	235020	49.818
2	36.648	236735	50.182

HPLC chart of (*R*)-7

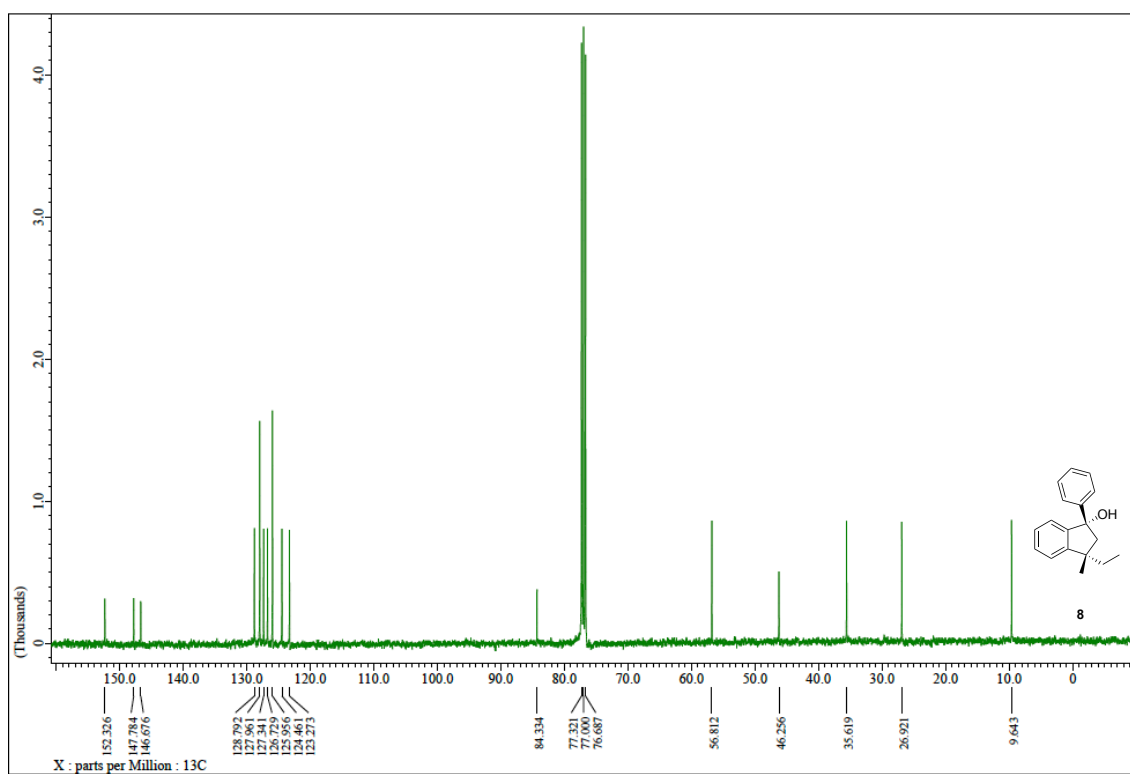


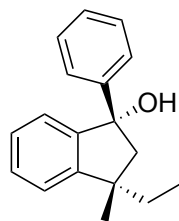
Pk #	Retention Time	Area	Area Percent
1	35.608	155	0.068
2	36.887	227232	99.932

¹H NMR of 8 (400 MHz, CDCl₃)



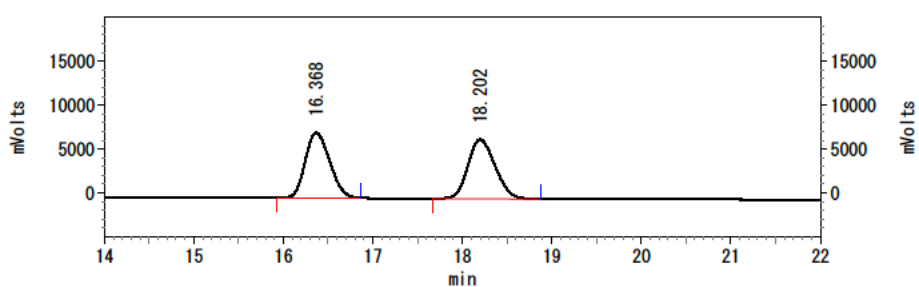
¹³C NMR of 8 (100 MHz, CDCl₃)





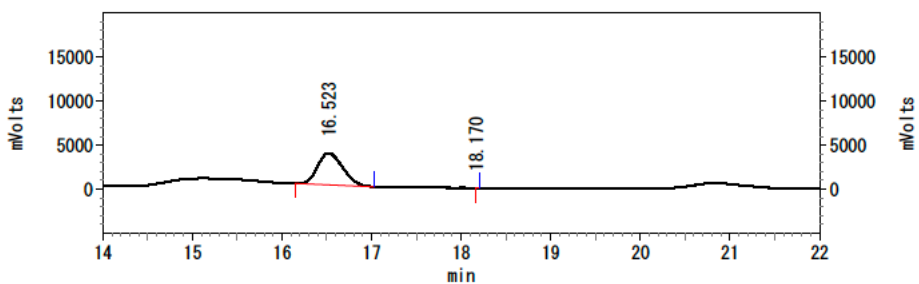
8

HPLC chart of (*rac*)-8



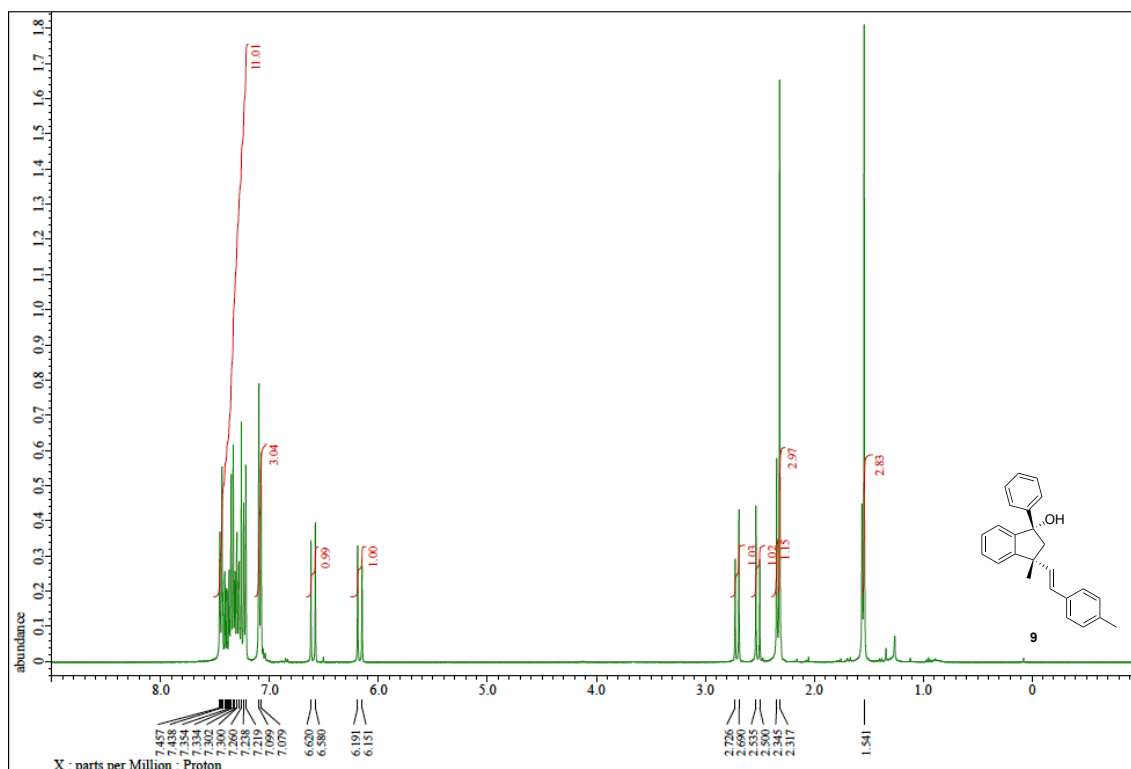
Pk #	Retention Time	Area	Area Percent
1	16.368	140751	49.631
2	18.202	142846	50.369

HPLC chart of (1*R*,3*R*)-8

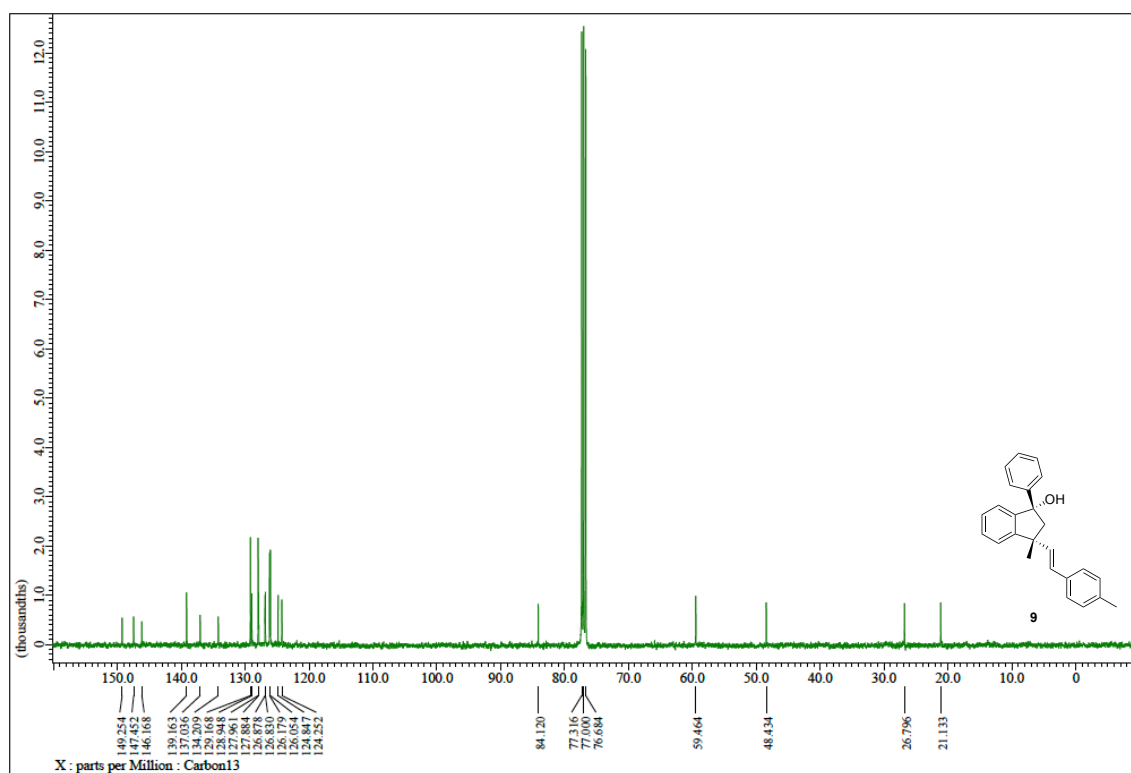


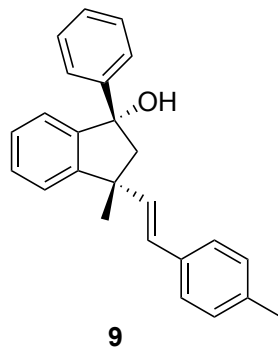
Pk #	Retention Time	Area	Area Percent
1	16.523	70599	99.990
2	18.170	7	0.010

¹H NMR of 9 (400 MHz, CDCl₃)

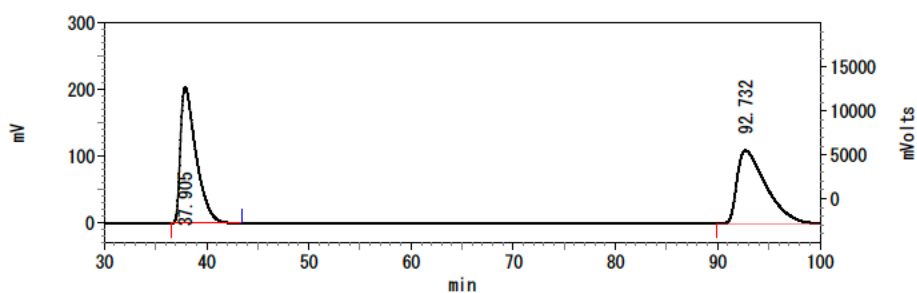


¹³C NMR of 9 (100 MHz, CDCl₃)



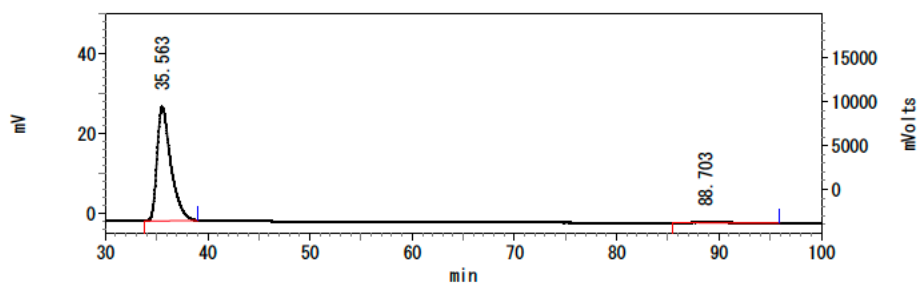


HPLC chart of (rac)-9



Pk #	Retention Time	Area	Area Percent
1	37.905	21660884	50.003
2	92.732	21658622	49.997

HPLC chart of (1R,3R)-9



Pk #	Retention Time	Area	Area Percent
1	35.563	2682423	98.845
2	88.703	31353	1.155