

# Supporting Information

## Enantioselective Synthesis of Multi-Substituted Indane Derivatives via Copper-Catalyzed Cascade Reaction

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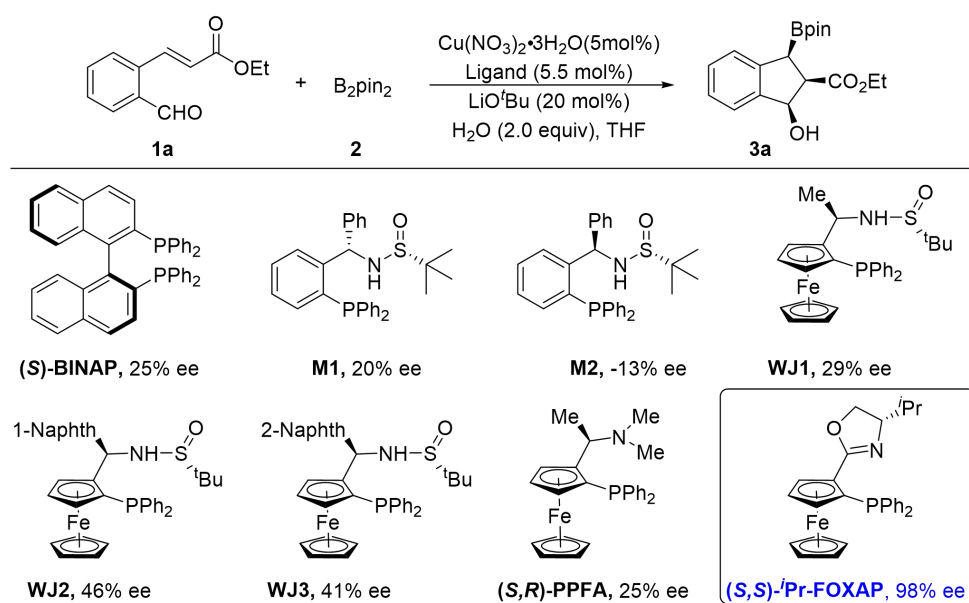
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## 1. General Information

All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring.  $^1\text{H}$  NMR spectra,  $^{19}\text{F}$  NMR spectra,  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 300, 400 and 500 MHz spectrometer in  $\text{CDCl}_3$ . All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. Data for  $^1\text{H}$  NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, coupling constant(s) in Hz, integration), coupling constant (Hz), and intergration. Data for  $^{13}\text{C}$  NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ( $\text{CDCl}_3$ : 77.0 ppm). Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh). Dichloromethane, dichloroethane, toluene were freshly distilled from  $\text{CaH}_2$ ; THF,  $\text{Et}_2\text{O}$ ,  $i\text{Pr}_2\text{O}$  and MTBE were freshly distilled from sodium metal prior to use. The ligands were commercial available. The substrates **1** were synthesized according to the procedure of references.<sup>1</sup>

**Table S1. Screening the Known Ligands<sup>a</sup>**



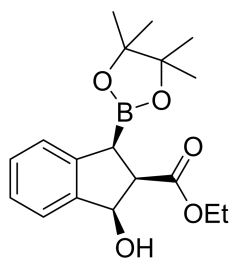
[a] All reactions were carried out with 0.1 mmol of **1a**, 0.15 mmol of **2**, 5 mol% of catalyst ( $[\text{Cu}]$  to Ligand = 1:1.2), 20%  $\text{LiO}^t\text{Bu}$  (1N in THF),  $\text{H}_2\text{O}$  (2.0 equiv) in 1.0 mL THF at rt for 12 h. [b] The ee of the major product were determined by chiral HPLC.

## 2. General Procedure for the Synthesis of products 3-9

### Typical procedure for asymmetric copper-catalyzed boronation cyclization of alkenes with B<sub>2</sub>pin<sub>2</sub>.

The solution of (*S,S*)-*i*-Pr-FOXAP (5.5 mol%) and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (5 mol%) in THF (3 mL) was stirred at room temperature for 30 mins. Alkene **1** (0.3 mmol) and B<sub>2</sub>pin<sub>2</sub> (0.45 mmol) were then added sequentially. After stirring for further 10 mins, LiO<sup>t</sup>Bu (0.06 mmol) and then H<sub>2</sub>O (0.6 mmol) were added to the reaction mixture. After the alkene **1** was consumed completely determined by TLC analysis, the crude product was then purified by flash column chromatography on silica gel to afford the desired product **3**. The enantiomeric excesses of the products were determined by chiral stationary phase HPLC using a Chiralpak column.

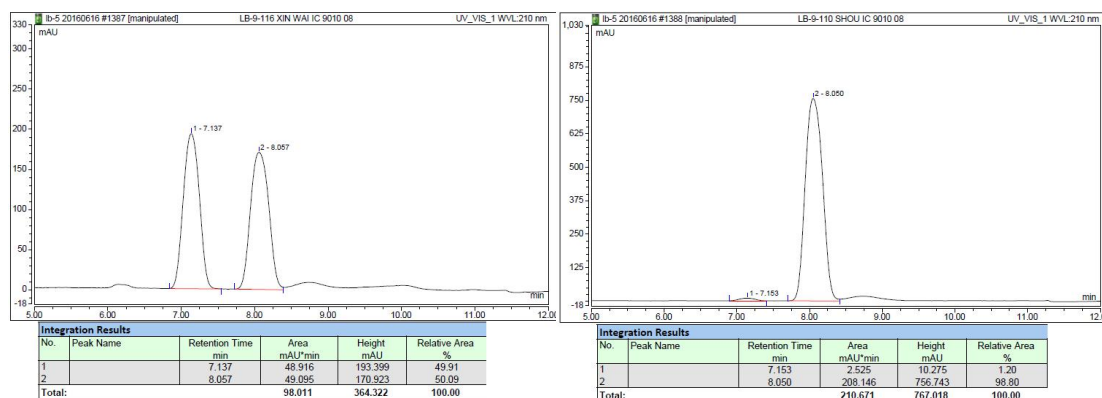
#### 3.1 Synthesis of ethyl (1*R*,2*R*,3*S*)-1-hydroxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate (**3a**).



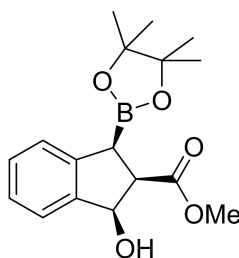
**3a**

The reaction of alkene **1** (40.8 mg, 0.2 mmol) and b<sub>2</sub>pin<sub>2</sub> **2** (76.0 mg, 0.3 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3a** as a roopy liquid (41.8 mg, 63% yield) with 98% ee. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.47 (d, *J* = 6.3 Hz, 1H), 7.28-7.18 (m, 3H), 5.25-5.19 (m, 1H), 4.33-4.21 (m, 2H), 3.98 (d, *J* = 12.2 Hz, 1H), 3.58-3.53 (m, 1H), 2.97 (d, *J* = 8.3 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.21 (d, *J* = 13.8 Hz, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 172.46, 143.90, 143.12, 129.02, 126.60, 125.59, 123.78, 84.38, 76.03, 61.06, 54.50, 24.60, 24.32, 14.32. ESI-MS calculated for C<sub>18</sub>H<sub>25</sub>BNaO<sub>5</sub>: m/z (%): 355.1691 (M+Na<sup>+</sup>), found: 355.1691. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 210 nm); minor enantiomer tr = 7.2 min, major

enantiomer tr = 8.1 min.  $[\alpha]_D^{20} = -6.2$  ( $c = 0.17$ ,  $\text{CHCl}_3$ ).

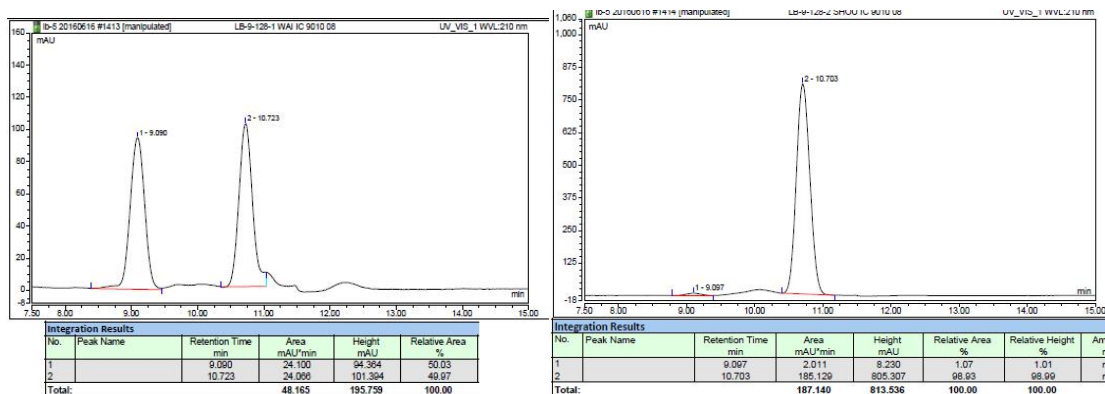


### 3.2 Synthesis of methyl (1*R*,2*R*,3*S*)-1-hydroxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate (**3b**).

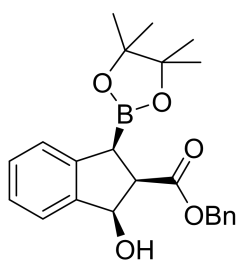


**3b**

The reaction of alkene **1** (57.0 mg, 0.3 mmol) and **2** (114 mg, 0.45 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3b** as a ropy liquid (72.5 mg, 76% yield) with 99% ee.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 7.4$  Hz, 1H), 7.28-7.18 (m, 3H), 5.23-5.19 (m, 1H), 3.98 (d,  $J = 12.2$  Hz, 1H), 3.81 (s, 3H), 3.60-3.56 (m, 1H), 2.98 (d,  $J = 8.4$  Hz, 1H), 1.21 (d,  $J = 14.0$  Hz, 12H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  172.75, 143.72, 142.92, 129.01, 126.60, 125.57, 123.73, 84.37, 75.97, 54.23, 52.09, 24.51, 24.27. ESI-MS calculated for  $\text{C}_{17}\text{H}_{23}\text{BNaO}_5$ :  $m/z$  (%): 341.1534 ( $\text{M}+\text{Na}^+$ ), found: 341.1531. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 210 nm); minor enantiomer tr = 9.1 min, major enantiomer tr = 10.7 min.  $[\alpha]_D^{20} = -6.3$  ( $c = 0.17$ ,  $\text{HCl}_3$ ).

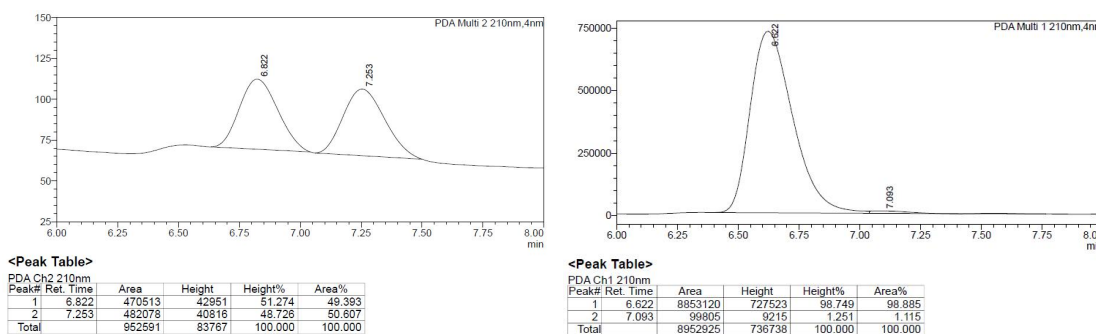


### 3.3 Synthesis of benzyl (1*R*,2*R*,3*S*)-1-hydroxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate (**3c**).

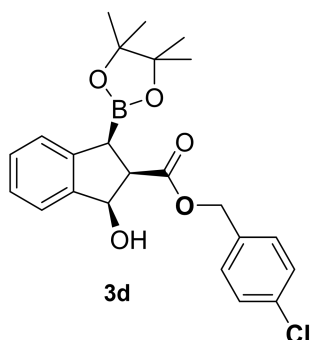


**3c**

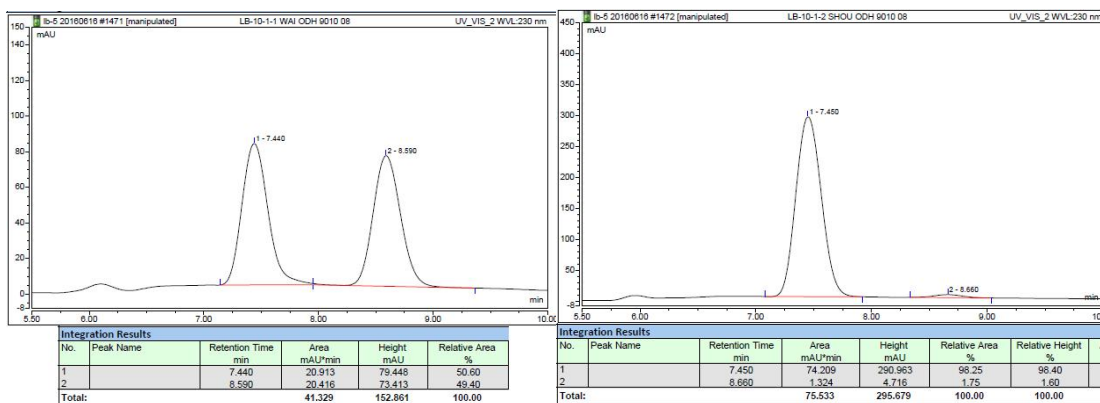
The reaction of alkene **1** (80.0 mg, 0.3 mmol) and **2** (114.0 mg, 0.45 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3c** as a rosy liquid (78 mg, 66% yield) with 98% ee. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39-7.35 (m, 3H), 7.31-7.24 (m, 3H), 7.18-7.10 (m, 3H), 5.20-5.16 (m, 1H), 5.17 (s, 2H), 3.92 (d, *J* = 12.2 Hz, 1H), 3.55-3.52 (m, 1H), 2.91 (d, *J* = 8.2 Hz, 1H), 1.10 (d, *J* = 15.1 Hz, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 172.26, 143.73, 143.02, 135.99, 129.02, 128.44, 128.06, 128.06, 126.62, 125.56, 123.75, 84.41, 76.01, 66.71, 54.41, 24.53, 24.27. ESI-MS calculated for C<sub>23</sub>H<sub>27</sub>BNaO<sub>5</sub>: *m/z* (%): 417.1848 (M+Na<sup>+</sup>), found: 417.1850. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 210 nm); major enantiomer *tr* = 6.6 min, minor enantiomer *tr* = 7.1 min. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = -10.5 (*c* = 0.17, CHCl<sub>3</sub>).



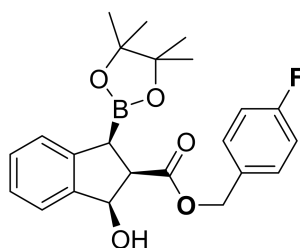
### 3.4 Synthesis of 4-chlorobenzyl (1*R*,2*R*,3*S*)-1-hydroxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate (**3d**).



The reaction of alkene **1** (90.0 mg, 0.3 mmol) and **2** (114.0 mg, 0.45 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3d** as a rosy liquid (93.7 mg, 73% yield) with 96% ee. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.45 (d, *J* = 6.6 Hz, 1H), 7.39-7.29 (m, 5H), 7.24-7.17 (m, 3H), 5.27-5.21 (m, 1H), 5.20 (d, *J* = 14.7 Hz, 2H), 3.99 (d, *J* = 12.3 Hz, 1H), 3.63-3.58 (m, 1H), 1.17 (d, *J* = 9.6 Hz, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 172.19, 143.64, 142.91, 134.55, 133.90, 129.43, 129.08, 128.61, 126.67, 125.57, 123.76, 84.45, 76.01, 65.87, 54.36, 24.53, 24.26. ESI-MS calculated for C<sub>23</sub>H<sub>26</sub>BClNaO<sub>5</sub>: *m/z* (%): 451.1458 (M+Na<sup>+</sup>), found: 451.1463. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 210 nm); minor enantiomer *tr* = 7.5 min, major enantiomer *tr* = 8.7 min. [α]<sub>D</sub><sup>20</sup> = -2.6 (*c* = 0.17, CHCl<sub>3</sub>).



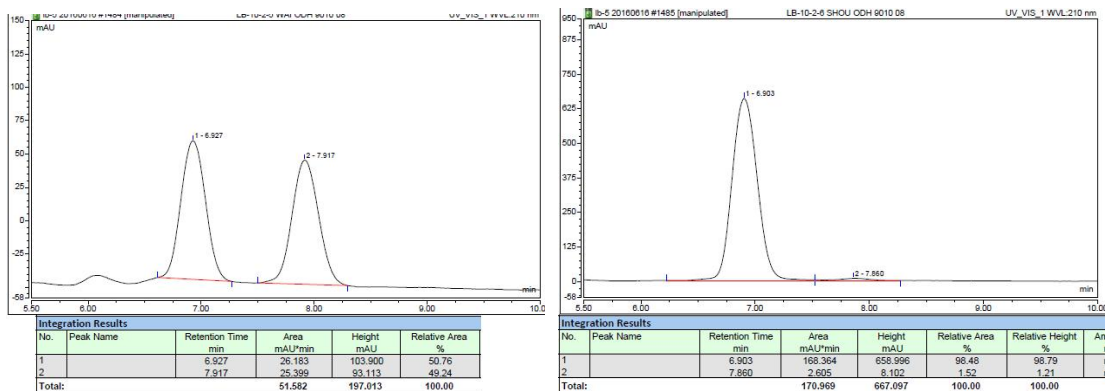
### 3.5 Synthesis of 4-fluorobenzyl (1*R*,2*R*,3*S*)-1-hydroxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate (**3e**).



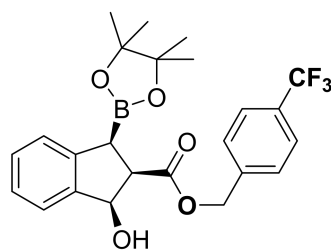
**3e**

The reaction of alkene **1** (81.0 mg, 0.3 mmol) and **2** (114.0 mg, 0.45 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3e** as a rosy liquid (77.9 mg, 63% yield) with 97% ee. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.46-7.39 (m, 3H), 7.28-7.18 (m, 3H), 7.05 (t, *J* = 8.7 Hz, 2H), 5.28-5.15 (m, 1H), 5.21 (d, *J* = 10.7 Hz, 1H), 4.00 (d, *J* = 12.2 Hz, 1H), 3.62-3.57 (m, 1H), 2.98 (d, *J* = 8.2 Hz, 1H), 1.18 (d, *J* = 10.4 Hz, 1H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -108.05--118.44 (m). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 172.17, 162.49 (d, *J* = 246.4 Hz), 143.25 (d, *J* = 92.3 Hz), 131.81 (d, *J* = 3.2 Hz), 129.96 (d, *J* = 8.2 Hz), 129.00, 126.60, 125.50, 123.70, 115.35, 115.18, 84.35, 75.95, 65.92, 54.31, 24.47, 24.20. ESI-MS calculated for C<sub>23</sub>H<sub>26</sub>BFNaO<sub>5</sub>: *m/z* (%): 435.1754 (M+Na<sup>+</sup>), found: 435.1767. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 210 nm); minor enantiomer *tr* = 7.9 min, major enantiomer *tr* = 6.9 min. [α]<sub>D</sub><sup>20</sup> = -54.3 (*c* = 0.17, CHCl<sub>3</sub>).



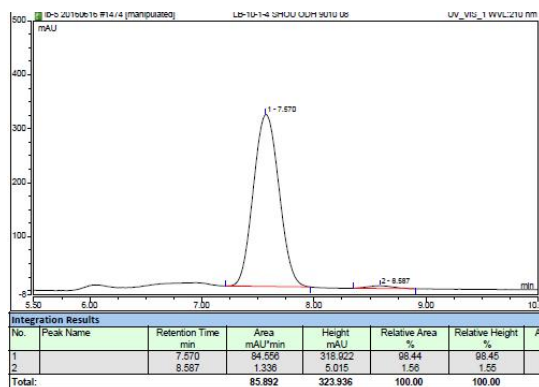
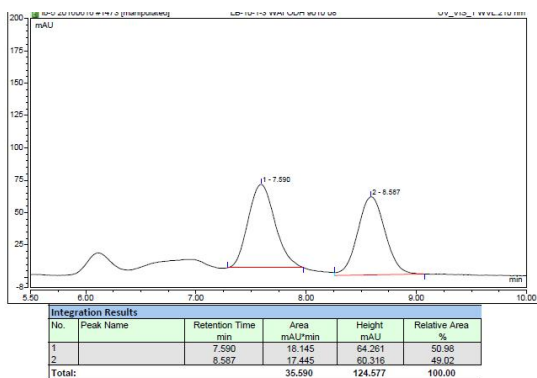


### 3.6 Synthesis of 4-(trifluoromethyl)benzyl (1*R*,2*R*,3*S*)-1-hydroxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate (**3f**).

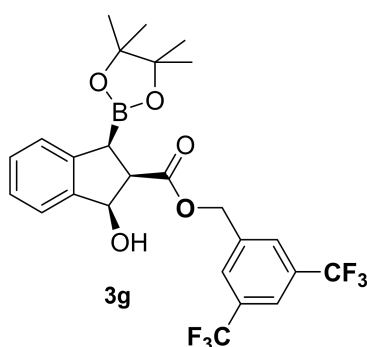


**3f**

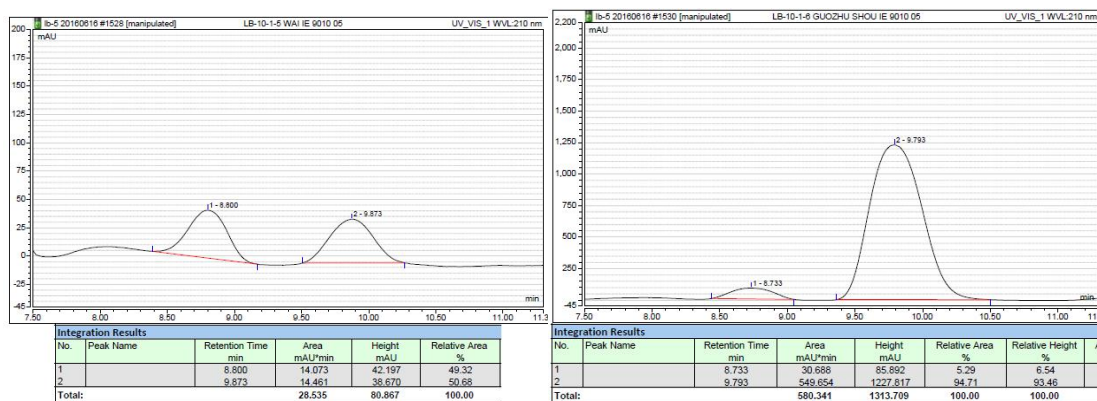
The reaction of alkene **1** (100.2 mg, 0.3 mmol) and **2** (114.0 mg, 0.45 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3f** as a rosy liquid (85.9 mg, 62% yield) with 97% ee. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.54-7.45 (m, 4H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.18-7.08 (m, 3H), 5.27 (d, *J* = 13.1 Hz, 1H), 5.18 (d, *J* = 6.0 Hz, 2H), 5.13 (d, *J* = 13.1 Hz, 1H), 3.56-3.52 (m, 1H), 2.90 (d, *J* = 8.3 Hz, 1H), 1.06 (d, *J* = 9.3 Hz, 12H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -62.59. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 172.13, 143.55, 142.84, 140.09, 130.11 (q, *J*<sub>C-F</sub> = 32.6 Hz), 129.10, 127.93, 127.93, 126.69, 125.55, 125.34 (q, *J* = 3.7 Hz), 123.75, 84.44, 76.00, 65.69, 54.28, 24.46, 24.20. ESI-MS calculated for C<sub>24</sub>H<sub>26</sub>BF<sub>3</sub>NaO<sub>5</sub>: *m/z* (%): 485.1722 (M+Na<sup>+</sup>), found: 485.1721. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 210 nm); minor enantiomer *tr* = 7.6 min, major enantiomer *tr* = 8.6 min. [α]<sub>D</sub><sup>20</sup> = -12.3 (*c* = 0.17, CHCl<sub>3</sub>).



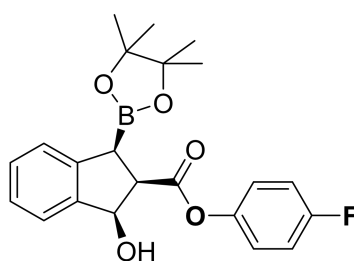
### 3.7 Synthesis of 3,5-bis(trifluoromethyl)benzyl (1*R*,2*R*,3*S*)-1-hydroxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate (**3g**).



The reaction of alkene **1** (80.4 mg, 0.2 mmol) and **2** (76.0 mg, 0.3 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3g** as a ropy liquid (68.9 mg, 65% yield) with 90% ee. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.93 (s, 2H), 7.82 (s, 1H), 7.48 (d, *J* = 6.6 Hz, 1H), 7.42-6.98 (m, 3H), 5.29 (m, 2H), 5.23 (d, *J* = 13.3 Hz, 1H), 3.97 (d, *J* = 12.3 Hz, 1H), 3.66 (m, 1H), 3.00 (d, *J* = 8.2 Hz, 1H), 1.13 (s, 12H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -62.83. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 172.18, 143.44, 142.73, 138.87, 131.76 (q, *J*<sub>C-F</sub> = 33.4 Hz), 129.19, 127.78, 126.75, 125.67, 123.76, 121.82, 84.49, 76.04, 64.95, 54.20, 24.41, 24.14. ESI-MS calculated for C<sub>25</sub>H<sub>25</sub>BF<sub>6</sub>NaO<sub>5</sub>: *m/z* (%): 553.1596 (M+Na<sup>+</sup>), found: 553.1599. Enantiomeric excess was determined by HPLC with a Chiralpak IE column (hexanes: 2-propanol = 90:10, 0.5 mL/min, 210 nm); minor enantiomer *tr* = 8.7 min, major enantiomer *tr* = 9.8 min. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = -8.8 (*c* = 0.17, CHCl<sub>3</sub>).

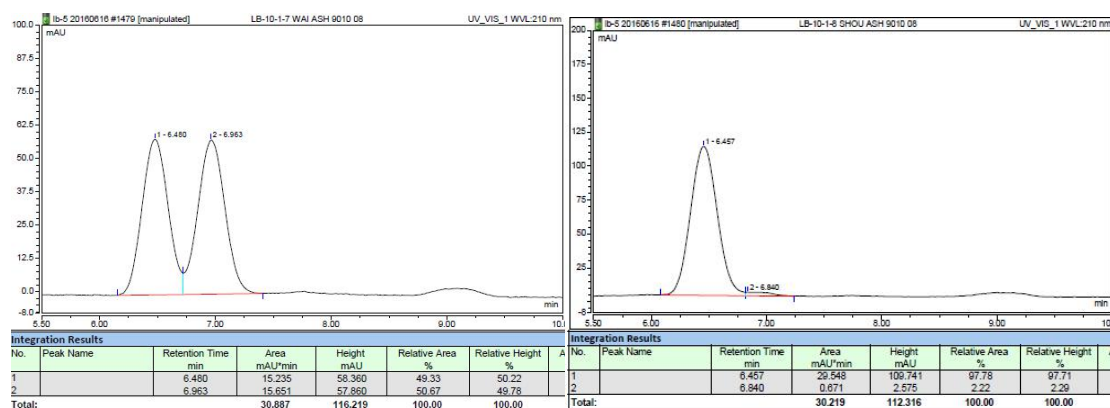


### 3.8 Synthesis of 4-fluorophenyl (1*R*,2*R*,3*S*)-1-hydroxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate (**3h**).

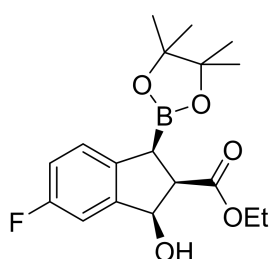


**3h**

The reaction of alkene **1** (81.0 mg, 0.3 mmol) and **2** (114.0 mg, 0.45 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3h** as a roppy liquid (72.8 mg, 61% yield) with 96% ee. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 6.2 Hz, 1H), 7.28-7.20 (m, 3H), 7.17-7.12 (m, 2H), 7.09-7.03 (m, 2H), 5.41-5.35 (m, 1H), 4.10 (d, *J* = 12.3 Hz, 1H), 3.83-3.78 (m, 1H), 3.05 (d, *J* = 8.1 Hz, 1H), 1.15 (d, *J* = 14.7 Hz, 12H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -110.36--124.58 (m). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 171.17, 160.23 (d, *J* = 243.8 Hz), 146.82 (d, *J* = 2.8 Hz), 143.17 (d, *J* = 121.1 Hz), 129.22, 126.79, 125.68, 123.81, 123.10 (d, *J* = 8.5 Hz), 116.07, 115.88, 84.54, 76.32, 54.31, 24.58, 24.27. ESI-MS calculated for C<sub>22</sub>H<sub>24</sub>BFNaO<sub>5</sub>: *m/z* (%): 421.1597 (M+Na<sup>+</sup>), found: 421.1605. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 210 nm); minor enantiomer *tr* = 6.8 min, major enantiomer *tr* = 6.5 min. [α]<sub>D</sub><sup>20</sup> = -54.3 (*c* = 0.17, CHCl<sub>3</sub>).

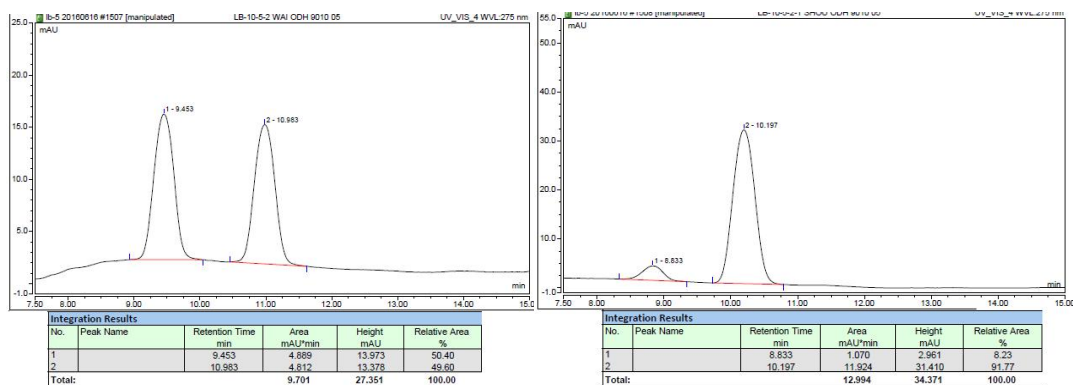


### 3.9 Synthesis of ethyl (1*S*,2*R*,3*R*)-5-fluoro-3-hydroxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate (**3i**).

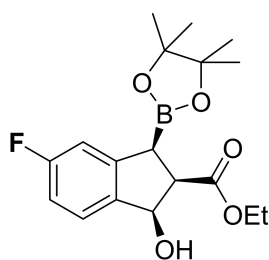


**3i**

The reaction of alkene **1** (66.6 mg, 0.3 mmol) and **2** (114.0 mg, 0.45 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3i** as a rosy liquid (72.5 mg, 69% yield) with 84% ee. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.13-7.08 (m, 2H), 6.96-6.89 (m, 1H), 5.18-5.12 (m, 1H), 4.23 (q, *J* = 69.58 Hz, 2H), 4.02 (d, *J* = 12.2 Hz, 1H), 3.58-3.53 (m, 1H), 2.89 (d, *J* = 8.3 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.18 (d, *J* = 11.7 Hz, 12H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -116.33 (td, *J* = 8.5, 4.9 Hz). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 172.05, 161.76 (d, *J* = 243.9 Hz), 144.83 (d, *J* = 7.3 Hz), 139.14 (d, *J* = 2.5 Hz), 124.69 (d, *J* = 8.4 Hz), 116.00 (d, *J* = 22.6 Hz), 112.45 (d, *J* = 22.0 Hz), 84.41, 75.70, 75.69, 61.07, 54.80, 24.52, 24.26, 14.23. ESI-MS calculated for C<sub>18</sub>H<sub>24</sub>BFNaO<sub>5</sub>: *m/z* (%): 373.1596 (M+Na<sup>+</sup>), found: 373.1586. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 90:10, 0.5 mL/min, 275 nm); minor enantiomer *tr* = 8.8 min, major enantiomer *tr* = 10.2 min. [α]<sub>D</sub><sup>20</sup> = -5.4 (*c* = 0.17, CHCl<sub>3</sub>).

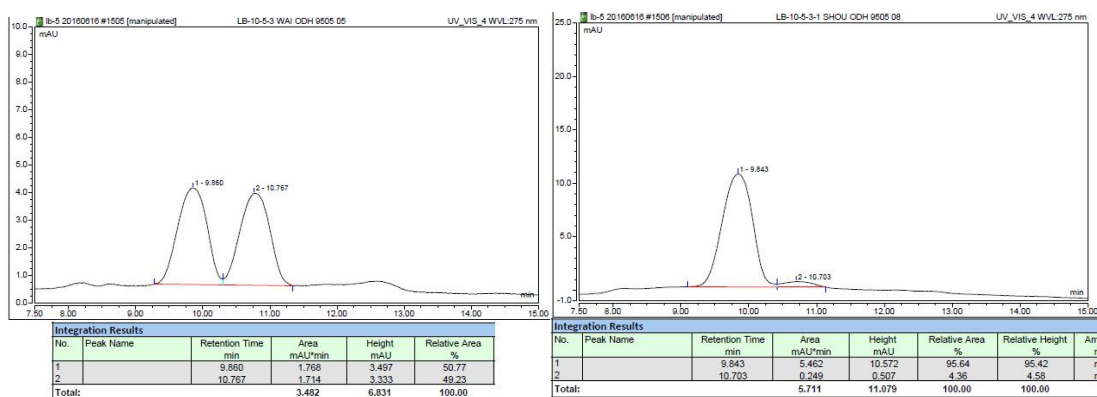


### 3.10 Synthesis of ethyl (1*R*,2*R*,3*S*)-5-fluoro-1-hydroxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate (**3j**).

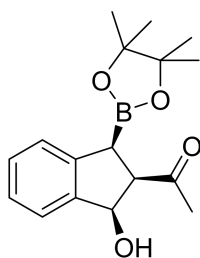


**3j**

The reaction of alkene **1** (66.6 mg, 0.3 mmol) and **2** (114.0 mg, 0.45 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3j** as a rosy liquid (69.3 mg, 66% yield) with 91% ee. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40-7.37 (m, 1H), 6.87 (t, *J* = 9.5 Hz, 2H), 5.17-5.13 (m, 1H), 4.26-4.22 (m, 2H), 3.91 (d, *J* = 12.0 Hz, 1H), 3.55 (t, *J* = 7.1 Hz, 1H), 2.92 (d, *J* = 8.1 Hz, 1H), 1.31 (t, *J* = 2.0 Hz, 3H), 1.19 (d, *J* = 15.7 Hz, 12H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -113.17. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 172.15, 163.49 (d, *J* = 246.3 Hz), 146.44, 138.87, 126.86 (d, *J* = 9.0 Hz), 113.67 (d, *J* = 22.4 Hz), 110.63 (d, *J* = 22.7 Hz), 84.51, 75.16, 61.13, 54.89, 24.58, 24.32, 14.25. ESI-MS calculated for C<sub>18</sub>H<sub>24</sub>BFNaO<sub>5</sub>: *m/z* (%): 373.1596 (M+Na<sup>+</sup>), found: 373.1601. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 9505, 0.8 mL/min, 275 nm); minor enantiomer *tr* = 10.7 min, major enantiomer *tr* = 9.8 min. [α]<sub>D</sub><sup>20</sup> = -0.8 (*c* = 0.17, CHCl<sub>3</sub>).

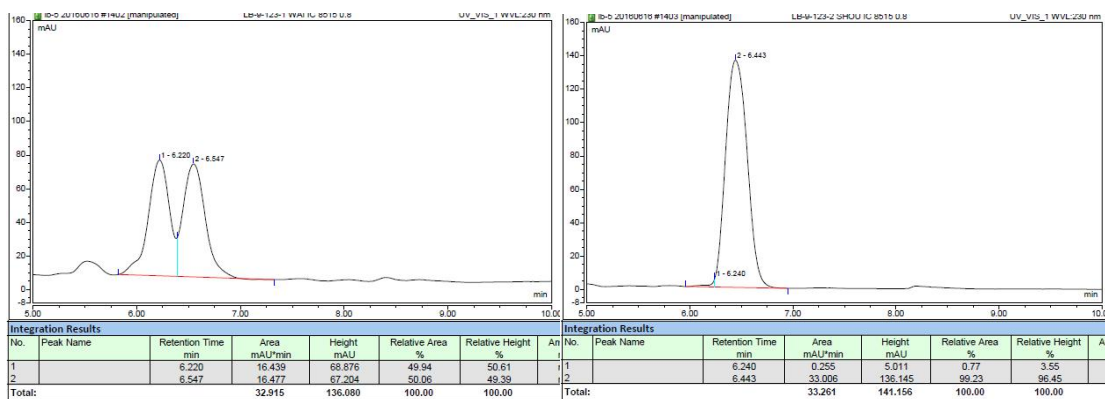


### 3.11 Synthesis of 1-((1*R*,2*R*,3*S*)-1-hydroxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-inden-2-yl)ethan-1-one (**3k**).

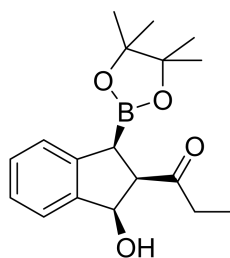


**3k**

The reaction of alkene **1** (52.2 mg, 0.3 mmol) and **2** (114.0 mg, 0.3 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3k** as a white solid (75.2 mg, 83% yield) with 99% *ee*. M.p. = 77-78 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.47 (d, *J* = 7.5 Hz, 1H), 7.28-7.18 (m, 3H), 5.39-5.33 (m, 1H), 3.96 (d, *J* = 12.4 Hz, 1H), 3.70-3.65 (m, 1H), 2.81 (d, *J* = 8.0 Hz, 1H), 2.40 (s, 3H), 1.20 (d, *J* = 10.9 Hz, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 207.70, 144.04, 142.77, 129.06, 126.51, 125.43, 123.86, 84.18, 75.85, 63.65, 27.99, 24.41, 24.29. ESI-MS calculated for C<sub>17</sub>H<sub>23</sub>BNaO<sub>4</sub>: *m/z* (%): 325.1585 (M+Na<sup>+</sup>), found: 325.1588. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 85:15, 0.8 mL/min, 210 nm); minor enantiomer *tr* = 6.2 min, major enantiomer *tr* = 6.4 min. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +9.8 (*c* = 0.17, CHCl<sub>3</sub>).

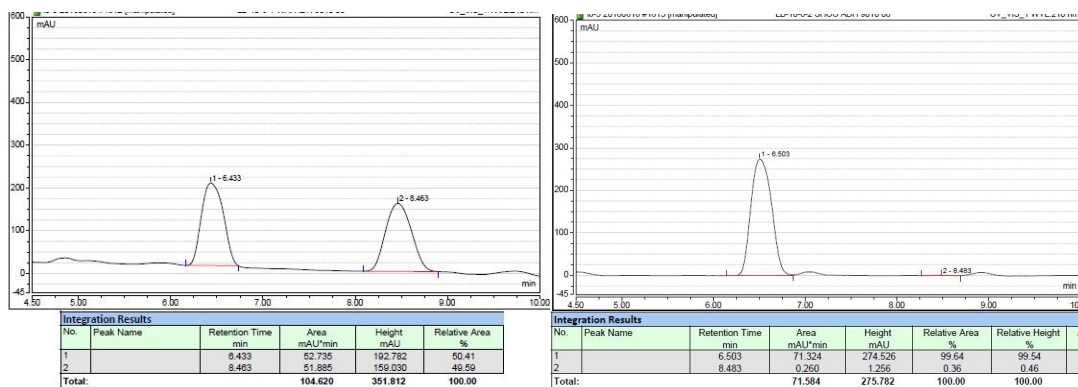


### 3.12 Synthesis of 1-((1*R*,2*R*,3*S*)-1-hydroxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-inden-2-yl)propan-1-one (**3I**).

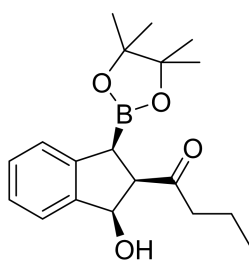


**3I**

The reaction of alkene **1** (56.4 mg, 0.3 mmol) and **2** (114.0 mg, 0.45 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3I** as a colorless ropy liquid (67.3 mg, 71% yield) with 99% ee. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.44 (d, *J* = 7.6 Hz, 1H), 7.26-7.16 (m, 1H), 5.36-5.30 (m, 1H), 3.95 (d, *J* = 12.5 Hz, 1H), 3.68-3.63 (m, 1H), 2.90-2.78 (m, 2H), 2.65-2.54 (m, 1H), 1.18 (d, *J* = 8.4 Hz, 12H), 1.13 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 210.28, 144.08, 142.93, 129.01, 126.45, 125.41, 123.84, 84.14, 75.93, 62.69, 33.65, 24.53, 24.27, 7.67. ESI-MS calculated for C<sub>18</sub>H<sub>25</sub>BNaO<sub>4</sub>: *m/z* (%): 339.1741 (M+Na<sup>+</sup>), found: 339.1734. Enantiomeric excess was determined by HPLC with a Chiralpak ADH column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 210 nm); minor enantiomer *tr* = 8.5 min, major enantiomer *tr* = 6.5 min. [α]<sub>D</sub><sup>20</sup> = +10.6 (*c* = 0.17, CHCl<sub>3</sub>).



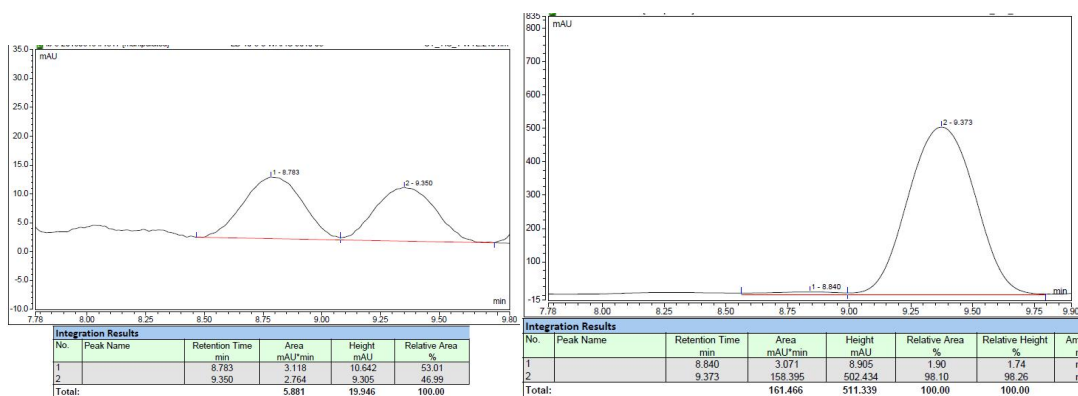
### 3.13 Synthesis of 1-((1*R*,2*R*,3*S*)-1-hydroxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-inden-2-yl)butan-1-one (**3m**)



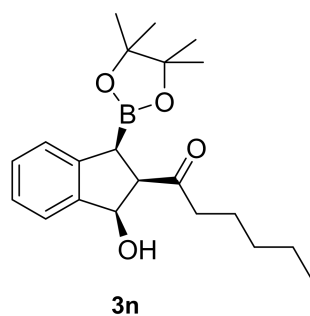
**3m**

The reaction of alkene **1** (60.6 mg, 0.3 mmol) and **2** (114.0 mg, 0.45 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3m** as a rosy liquid (72.9 mg, 73% yield) with 96% ee. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.43 (d, *J* = 7.5 Hz, 1H), 7.26-7.15 (m, 3H), 5.36-5.26 (m, 1H), 3.96 (d, *J* = 12.5 Hz, 1H), 3.65-3.60 (m, 1H), 2.84-2.73 (m, 1H), 2.63-2.52 (m, 1H), 1.75-1.62 (m, 1H), 1.17 (d, *J* = 8.2 Hz, 1H), 0.95 (t, *J* = 7.4 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 209.80, 144.03, 142.94, 128.96, 126.41, 125.36, 123.79, 84.08, 75.87, 62.88, 42.34, 24.51, 24.21, 17.04, 13.72. ESI-MS calculated for C<sub>19</sub>H<sub>27</sub>BNaO<sub>4</sub>: *m/z* (%): 353.1898 (M+Na<sup>+</sup>), found: 353.1894. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 90:10, 0.5 mL/min, 210 nm); minor enantiomer *tr* = 8.8 min, major enantiomer *tr* = 9.4 min. [α]<sub>D</sub><sup>20</sup> = +10.9 (*c* = 0.17, CHCl<sub>3</sub>).

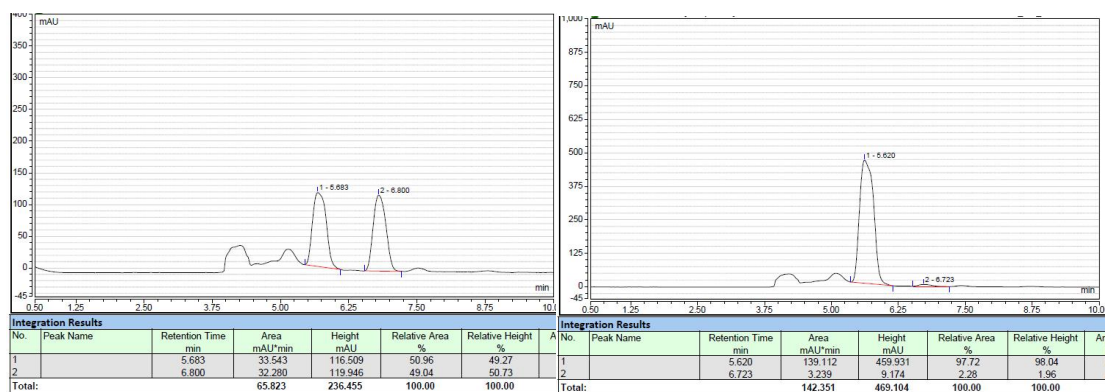




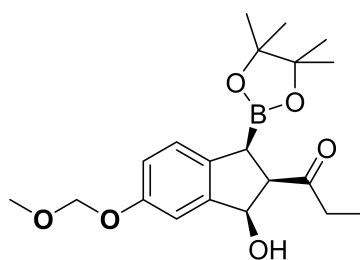
### 3.14 Synthesis of 1-((1*R*,2*R*,3*S*)-1-hydroxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-inden-2-yl)hexan-1-one (**3n**)



The reaction of alkene **1** (69.0 mg, 0.3 mmol) and **2** (114.0 mg, 0.45 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3n** as a rosy liquid (70.0 mg, 65% yield) with 96% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.42 (d, *J* = 7.3 Hz, 1H), 7.23-7.14 (m, 3H), 5.33-5.29 (m, 1H), 3.95 (d, *J* = 12.4 Hz, 1H), 3.63-3.61 (m, 1H), 2.81-2.74 (m, 2H), 2.61-2.55 (m, 1H), 1.67-1.62 (m, 2H) 1.32-1.30 (m, 4H), 1.17 (d, *J* = 14.3 Hz, 12H), 0.88 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 209.94, 143.99, 142.88, 128.92, 126.37, 125.33, 123.75, 84.05, 75.84, 62.82, 40.40, 31.35, 24.47, 24.18, 23.26, 22.38, 13.87. ESI-MS calculated for C<sub>21</sub>H<sub>31</sub>BNaO<sub>4</sub>, *m/z* (%): 381.2208, (M+Na<sup>+</sup>), found: 381.2185. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 210 nm); minor enantiomer *tr* = 6.7 min, major enantiomer *tr* = 5.6 min. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = -11.6 (*c* = 0.17, CHCl<sub>3</sub>).

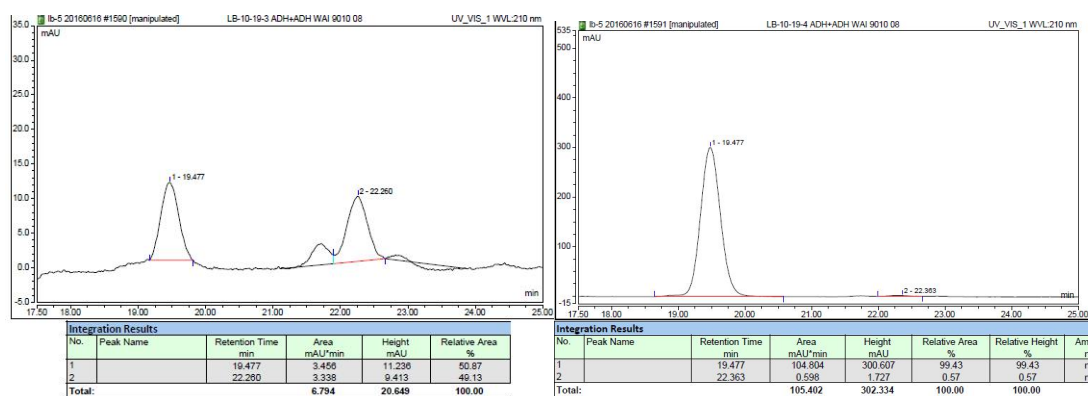


### 3.15 Synthesis of 1-((1*S*,2*R*,3*R*)-3-hydroxy-5-(methoxymethoxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-inden-2-yl)propan-1-one (**3o**)

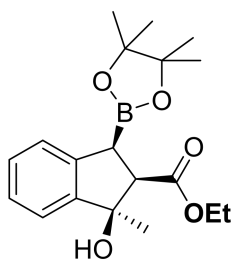


**3o**

The reaction of alkene **1** (74.4 mg, 0.3 mmol) and **2** (114.0 mg, 0.45 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3o** (77.8 mg, 69% yield) with 99% ee. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.09 (dd, *J* = 18.0, 5.3 Hz, 1H), 6.91 (dd, *J* = 8.3, 2.4 Hz, 1H), 5.26 (dd, *J* = 12.4, 6.2 Hz, 1H), 5.14 (dd, *J* = 19.7, 6.7 Hz, 1H), 3.98 (d, *J* = 12.4 Hz, 1H), 3.66-3.62 (m, 1H), 3.47 (s, 3H), 2.87-2.79 (m, 1H), 2.70 (d, *J* = 8.0 Hz, 1H), 2.60-2.52 (m, 1H), 1.18 (d, *J* = 5.2 Hz, 12H), 1.11 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 210.19, 156.20, 144.17, 137.21, 124.51, 117.63, 113.20, 94.80, 84.13, 75.99, 63.14, 55.93, 33.63, 24.55, 24.27, 7.64. ESI-MS calculated for C<sub>20</sub>H<sub>29</sub>BNaO<sub>6</sub>, *m/z* (%): 399.1949 (M+Na<sup>+</sup>), found: 399.1956. Enantiomeric excess was determined by HPLC with a Chiralpak ADH+ADH column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 254 nm); minor enantiomer *tr* = 22.4 min, major enantiomer *tr* = 19.5 min. [α]<sub>D</sub><sup>20</sup> = -14.0 (*c* = 0.17, CHCl<sub>3</sub>).

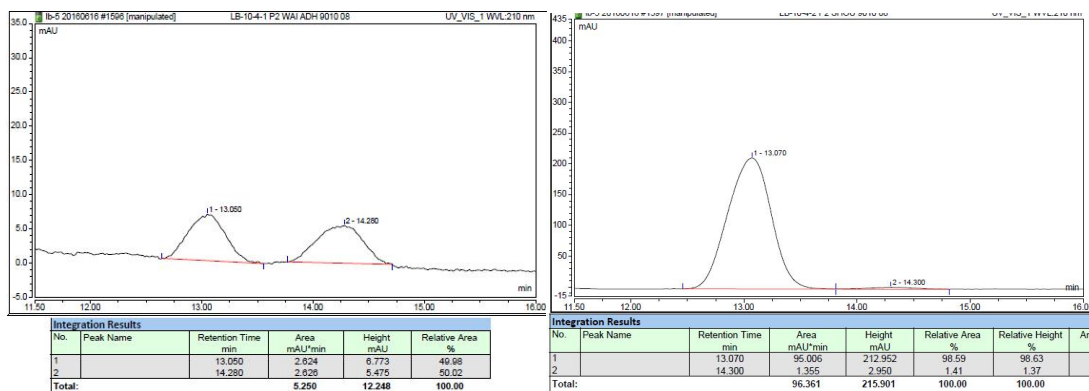


### 3.16 Synthesis of ethyl (1*R*,2*R*,3*S*)-1-hydroxy-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate (**3p**)

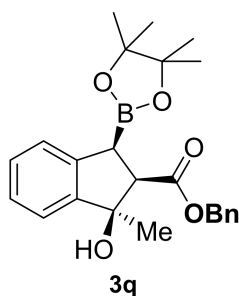


**3p**

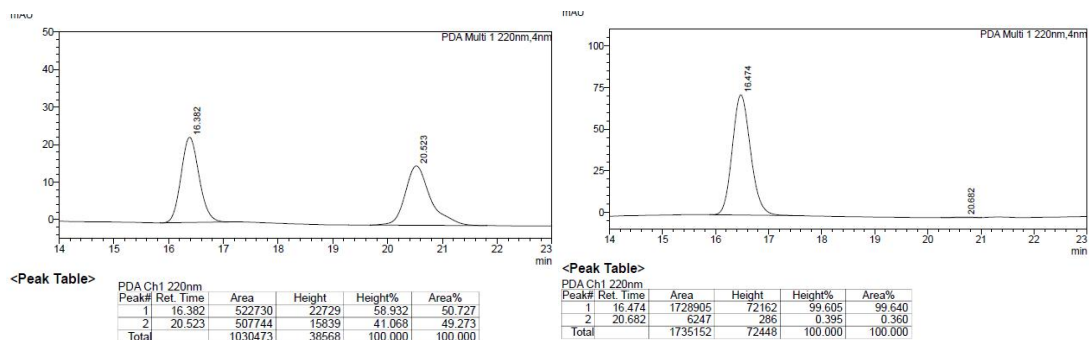
The reaction of alkene **1** (65.4 mg, 0.3 mmol) and **2** (114.0 mg, 0.45 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3p** as a rosy liquid (67 mg, 65% yield) with 97% ee. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.35-7.29 (m, 2H), 7.27-7.21 (m, 2H), 4.27-4.19 (m, 2H), 3.24 (q, *J* = 9.9 Hz, 2H), 2.94 (s, 1H), 1.78 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.25 (d, *J* = 4.3 Hz, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 173.11, 145.85, 142.37, 128.80, 126.69, 124.51, 122.82, 83.78, 80.67, 60.71, 56.65, 26.26, 24.98, 24.43, 14.30. ESI-MS calculated for C<sub>19</sub>H<sub>27</sub>BNaO<sub>5</sub>: *m/z* (%): 369.1847 (M+Na<sup>+</sup>), found: 369.1853. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 210 nm); minor enantiomer *tr* = 14.3 min, major enantiomer *tr* = 13.1 min. [α]<sub>D</sub><sup>20</sup> = -15.5 (*c* = 0.17, CHCl<sub>3</sub>).



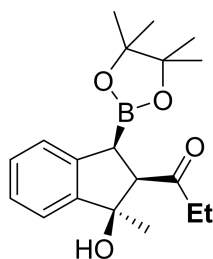
### 3.17 Synthesis of benzyl (1*R*,2*R*,3*S*)-1-hydroxy-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate (**3q**)



The reaction of alkene **1** (56.0 mg, 0.2 mmol) and **2** (76.0 mg, 0.3 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3q** as a white solid (50.6 mg, 62% yield) with 99% ee. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.46-7.33 (m, 2H), 7.31-7.27 (m, 2H), 5.28 (s, 1H), 3.44-3.32 (m, 2H), 2.92 (s, 1H), 1.86 (s, 3H), 1.23 (d, *J* = 2.4 Hz, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 172.71, 145.73, 142.25, 135.85, 128.80, 128.43, 128.08, 128.08, 126.66, 124.48, 122.79, 83.72, 80.78, 66.42, 56.84, 26.24, 24.83, 24.33. Enantiomeric excess was determined by HPLC with a Chiralpak ADH column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 220 nm); minor enantiomer *tr* = 20.7 min, major enantiomer *tr* = 16.5 min. ESI-MS calculated for C<sub>24</sub>H<sub>29</sub>BNaO<sub>5</sub>: *m/z* (%): 431.2000 (M+Na<sup>+</sup>), found: 431.2008. [α]<sub>D</sub><sup>20</sup> = -14.3 (*c* = 0.17, CHCl<sub>3</sub>).

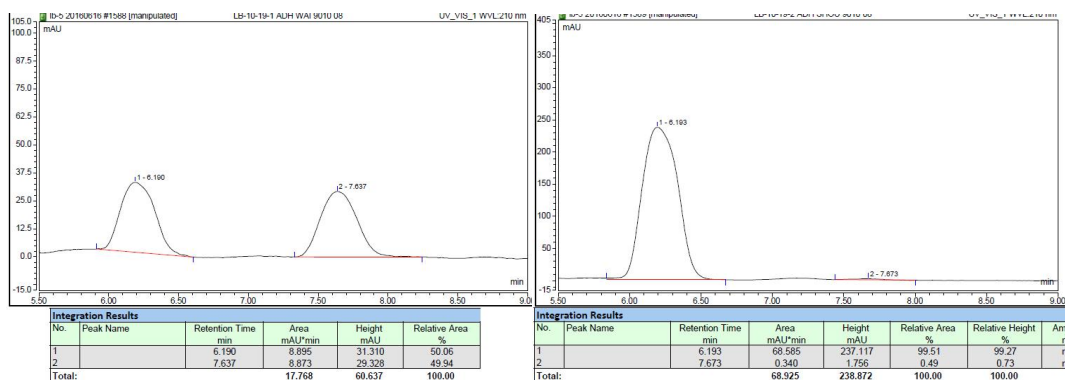


### 3.18 Synthesis of 1-((1*R*,2*R*,3*S*)-1-hydroxy-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-inden-2-yl)propan-1-one (**3r**)

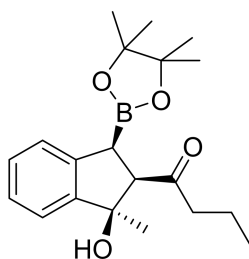


**3r**

The reaction of alkene **1** (60.6 mg, 0.3 mmol) and **2** (114.0 mg, 0.45 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3r** as a colorless ropy liquid (74 mg, 75% yield) with 99% ee. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.35-7.32 (m, 1H), 7.22-7.13 (m, 3H), 4.29 (s, 1H), 3.54 (d, *J* = 8.1 Hz, 1H), 2.86-2.75 (m, 2H), 2.66-2.56 (m, 1H), 1.90 (s, 3H), 1.17 (d, *J* = 11.3 Hz, 12H), 1.16-1.07 (m, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 210.60, 145.99, 142.84, 128.66, 126.41, 123.58, 123.02, 83.79, 79.94, 67.64, 35.54, 26.18, 24.52, 24.31, 7.62. ESI-MS calculated for C<sub>19</sub>H<sub>27</sub>BNaO<sub>4</sub>: *m/z* (%): 353.1898 (M+Na<sup>+</sup>), found: 353.1890. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 210 nm); minor enantiomer *tr* = 7.7 min, major enantiomer *tr* = 6.2 min. [α]<sub>D</sub><sup>20</sup> = -8.3 (*c* = 0.17, CHCl<sub>3</sub>).

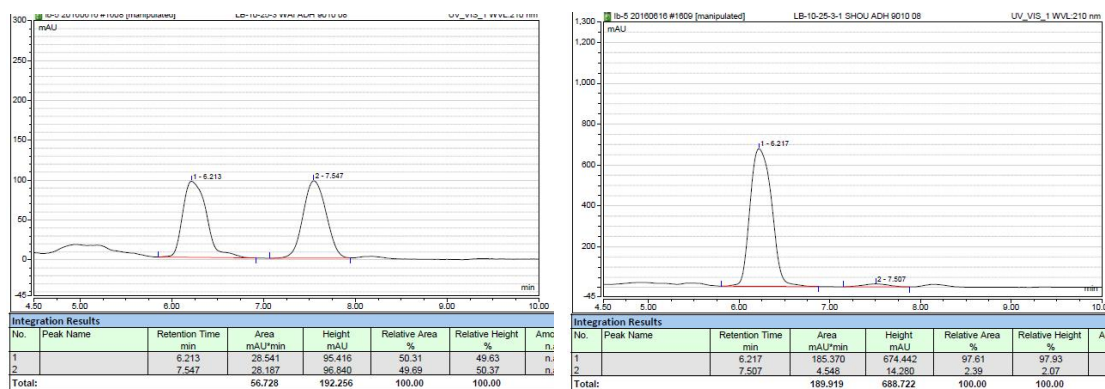


### 3.19 Synthesis of 1-((1*R*,2*R*,3*S*)-1-hydroxy-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-inden-2-yl)butan-1-one (**3s**).

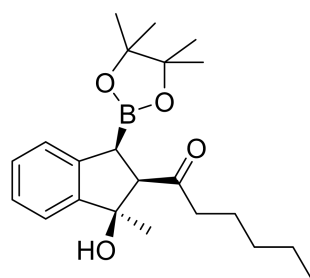


**3s**

The reaction of alkene **1** (64.8 mg, 0.3 mmol) and **2** (76.0 mg, 0.45 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3s** as a white solid (69 mg, 67% yield) with 95% ee. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.34-7.31 (m, 1H), 7.21-7.12 (m, 3H), 4.31 (s, 1H), 3.53 (d, *J* = 8.1 Hz, 1H), 2.81-2.70 (m, 2H), 2.64-2.53 (m, 1H), 1.90 (s, 3H), 1.74-1.59 (m, 2H), 1.16 (d, *J* = 11.8 Hz, 12H), 0.89 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 210.14, 145.95, 142.76, 128.60, 126.34, 123.52, 122.95, 83.7, 79.93, 67.76, 44.20, 26.18, 24.48, 24.24, 16.97, 13.69. ESI-MS calculated for Chemical Formula: C<sub>20</sub>H<sub>29</sub>BNaO<sub>4</sub>, Exact Mass: *m/z* (%): 367.2051 (M+Na<sup>+</sup>), found: 367.2049. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 210 nm); minor enantiomer *tr* = 6.2 min, major enantiomer *tr* = 7.5 min. [α]<sub>D</sub><sup>20</sup> = +8.4 (*c* = 0.17, CHCl<sub>3</sub>).

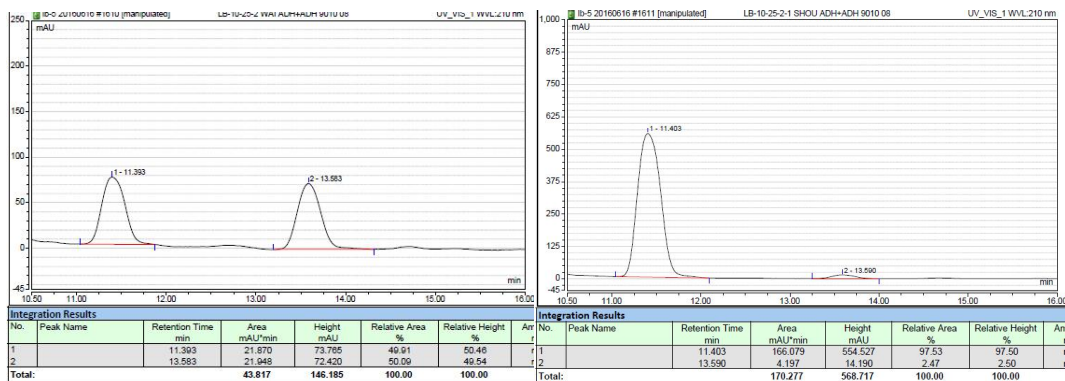


### 3.20 Synthesis of 1-((1*R*,2*R*,3*S*)-1-hydroxy-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-inden-2-yl)hexan-1-one (**3t**).

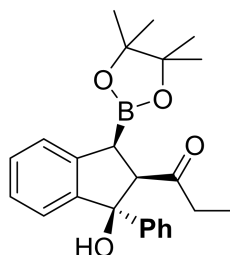


**3t**

The reaction of alkene **1** (73.2 mg, 0.3 mmol) and **2** (114.0 mg, 0.45 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3t** as a white solid (76 mg, 68% yield) with 96% ee. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.37-7.34 (m, 1H), 7.25-7.14 (m, 3H), 4.34 (s, 1H), 3.54 (d, *J* = 8.1 Hz, 1H), 2.83-2.72 (m, 2H), 2.65-2.54 (m, 1H), 1.93 (s, 3H), 1.77-1.65 (m, 3H), 1.27-1.24 (m, 3H), 1.18 (d, *J* = 11.5 Hz, 12H), 0.97 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 210.30, 145.96, 142.79, 128.60, 126.34, 123.52, 122.95, 83.71, 79.93, 67.74, 42.28, 31.34, 26.17, 24.48, 24.24, 23.22, 22.40, 13.87. ESI-MS calculated for C<sub>22</sub>H<sub>33</sub>BNaO<sub>4</sub>: *m/z* (%): 395.2364 (M+Na<sup>+</sup>), found: 395.2372. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H+ADH column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 210 nm); minor enantiomer *tr* = 13.6 min, major enantiomer *tr* = 11.4 min.  $[\alpha]_D^{20} = -70.4$  (*c* = 0.17, CHCl<sub>3</sub>).



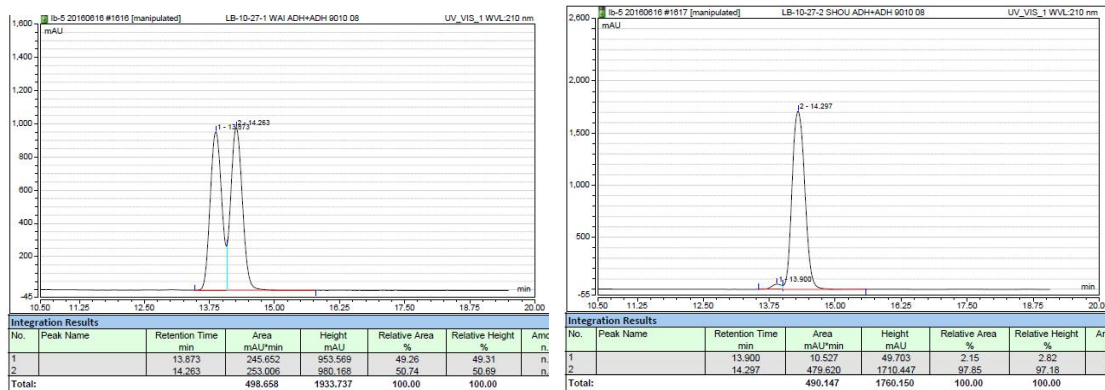
### 3.21 Synthesis of 1-((1*S*,2*R*,3*S*)-1-hydroxy-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-inden-2-yl)propan-1-one (**3u**)



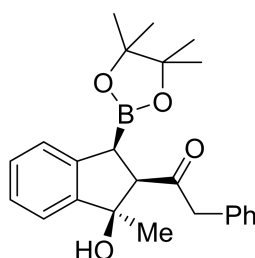
**3u**

The reaction of alkene **1** (79.2 mg, 0.3 mmol) and **2** (114.0 mg, 0.45 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3u** as a white solid (86 mg, 73% yield) with 96% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.49 (d, *J* = 7.3 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.21-7.18 (m, 1H), 7.10 (d, *J* = 3.9 Hz, 2H), 6.98-6.95 (m, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 4.78 (s, 1H), 3.98 (d, *J* = 8.2 Hz, 1H), 2.87 (d, *J* = 8.1 Hz, 1H), 2.15-2.10 (m, 1H), 1.81-1.76 (m, 1H), 1.12 (d, *J* = 23.0 Hz, 12H), 0.77 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 210.20, 147.61, 144.79, 143.15, 128.66, 127.89, 126.91, 126.70, 126.44, 125.15, 123.30, 84.46, 84.05, 70.43, 34.72, 24.50, 24.30, 7.31. ESI-MS calculated for C<sub>24</sub>H<sub>29</sub>BNaO<sub>4</sub>: *m/z* (%): 415.2055 (M+Na<sup>+</sup>), found: 415.2060. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H+ADH column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 210 nm); minor enantiomer *tr* = 13.9 min, major enantiomer *tr* = 14.3 min. [α]<sub>D</sub><sup>20</sup> = -82.8 (*c* = 0.17, CHCl<sub>3</sub>).



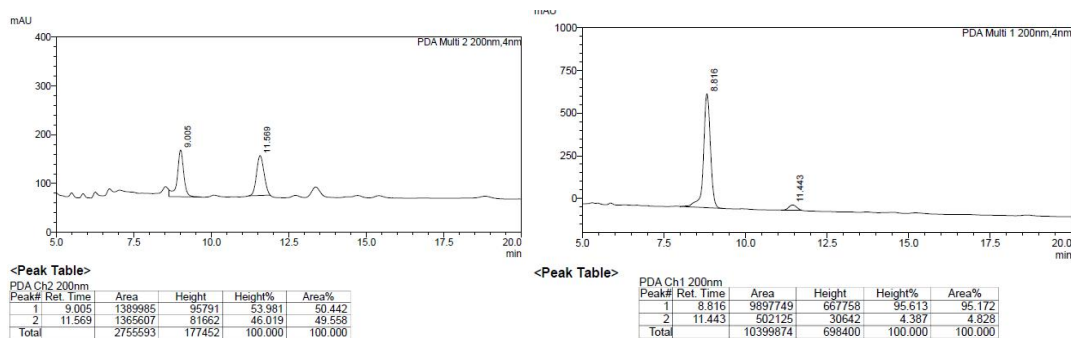


### 3.22 Synthesis of 1-((1*R*,2*R*,3*S*)-1-hydroxy-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-inden-2-yl)-2-phenylethan-1-one (**3v**)

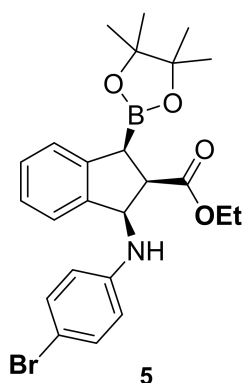


**3v**

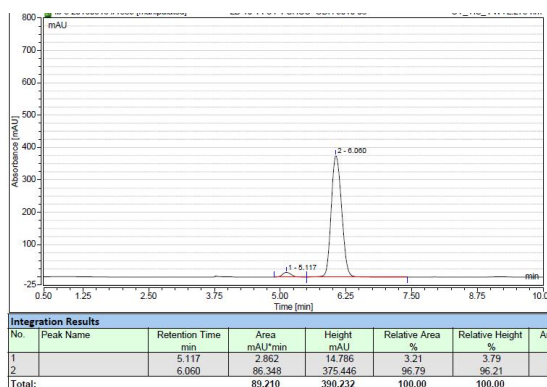
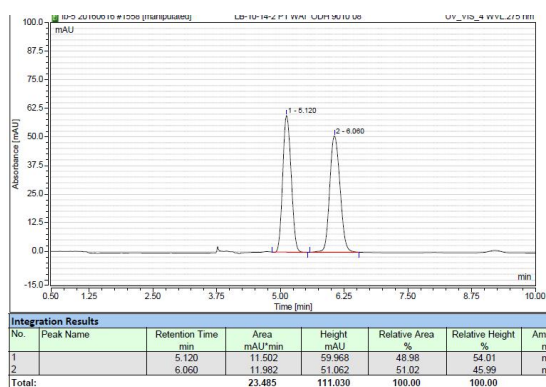
The reaction of alkene **1** (52.8 mg, 0.2 mmol) and **2** (76 mg, 0.3 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **3v** as a colorless ropy liquid (49.4 mg, 63% yield) with 90% ee. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.40-7.32 (m, 4H), 7.29-7.23 (m, 4H), 7.18-7.15 (m, 1H), 4.47 (s, 1H), 4.11 (d, *J* = 16.1 Hz, 1H), 4.00 (d, *J* = 15.9 Hz, 1H), 3.68 (d, *J* = 8.1 Hz, 1H), 2.79 (d, *J* = 8.0 Hz, 1H), 2.01 (s, 3H), 1.18 (d, *J* = 12.5 Hz, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 207.53, 145.87, 142.74, 134.03, 129.69, 128.73, 128.51, 126.84, 126.49, 123.57, 123.05, 83.92, 80.16, 66.56, 49.17, 26.51, 24.99, 24.57, 24.28. ESI-MS calculated for C<sub>24</sub>H<sub>29</sub>BNaO<sub>4</sub>: *m/z* (%): 415.2051 (M+Na<sup>+</sup>), found: 415.2047. Enantiomeric excess was determined by HPLC with a Chiralpak ADH column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 200 nm); minor enantiomer *tr* = 11.4 min, major enantiomer *tr* = +8.8 min. [α]<sub>D</sub><sup>20</sup> = -5.8 (*c* = 0.17, CHCl<sub>3</sub>).



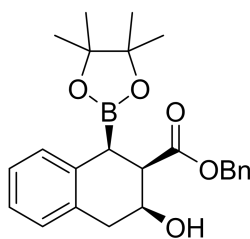
### 3.23 Synthesis of ethyl (1*R*,2*R*,3*S*)-1-((4-bromophenyl)amino)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate (**5**)



The reaction of alkene **4** (71.4 mg, 0.2 mmol) and **2** (76.0 mg, 0.3 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **5** as a ropy liquid (22.3 mg, 23% yield) with 94% ee. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.45–7.20 (m, 2H), 7.19–6.97 (m, 1H), 6.61 (d, *J* = 8.8 Hz, 1H), 5.48–5.08 (m, 1H), 4.00 (dq, *J* = 10.9, 7.1 Hz, 1H), 3.78 (ddd, *J* = 15.4, 9.6, 6.8 Hz, 1H), 2.98 (d, *J* = 8.5 Hz, 1H), 1.28 (d, *J* = 14.1 Hz, 4H), 1.06 (t, *J* = 7.1 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 172.67, 146.67, 143.48, 142.35, 131.72, 128.48, 126.45, 124.58, 124.03, 115.11, 108.30, 83.96, 60.77, 59.53, 52.55, 24.82, 24.60, 13.93. ESI-MS calculated for C<sub>24</sub>H<sub>29</sub>BBrNNaO<sub>4</sub>: *m/z* (%): 508.1265 (M+Na<sup>+</sup>), found: 508.1269. Enantiomeric excess was determined by HPLC with a Chiralpak ODH column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 275 nm); minor enantiomer *tr* = 5.1 min, major enantiomer *tr* = 6.1 min. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +80.1 (*c* = 0.17, CHCl<sub>3</sub>).

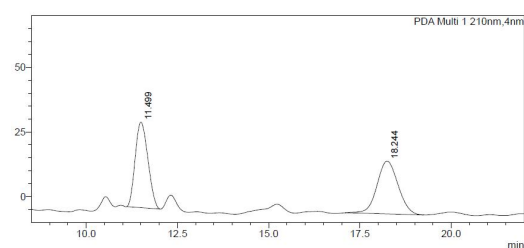


### 3.26 Synthesis of benzyl (1*S*,2*R*,3*S*)-3-hydroxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**7**).



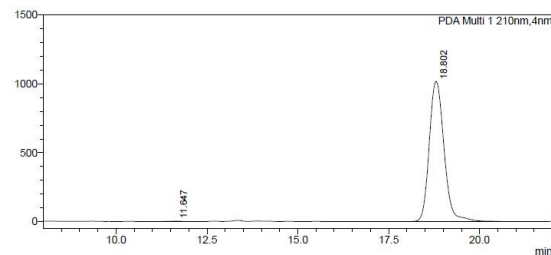
**7**

The reaction of alkene **6** (0.2 mmol) and **2** (0.3 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **7** as a ropy liquid (77% yield) with 99% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.36–7.31 (m, 6H), 7.14–7.07 (m, 3H), 5.21 (q, *J* = 12.4 Hz, 2H), 4.63 (s, 1H), 3.14–3.08 (m, 3H), 2.95–2.91 (m, 1H), 2.45 (d, *J* = 4.9 Hz, 1H), 1.19 (d, *J* = 1.9 Hz, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 174.35, 135.74, 134.33, 131.83, 130.12, 128.51, 128.28, 128.17, 128.04, 126.07, 125.61, 83.71, 66.55, 65.31, 46.42, 36.82, 24.77, 24.30. ESI-MS calculated for C<sub>24</sub>H<sub>29</sub>BNaO<sub>5</sub>: *m/z* (%): 431.2005 (M+Na<sup>+</sup>), found: 431.2006. Enantiomeric excess was determined by HPLC with a Chiralpak ADH column (hexanes: 2-propanol = 85:15, 0.8 mL/min, 210 nm); minor enantiomer *tr* = 11.6 min, major enantiomer *tr* = 18.8 min. [α]<sub>D</sub><sup>20</sup> = +11.5 (*c* = 0.17, CHCl<sub>3</sub>).



Peak Table>

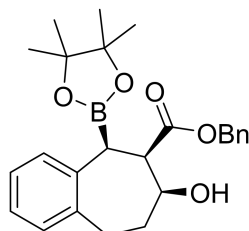
Peak#	Ret. Time	Area	Height	Height%	Area%
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2	18.244	821842	20459	38.196	50.635
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Peak Table>

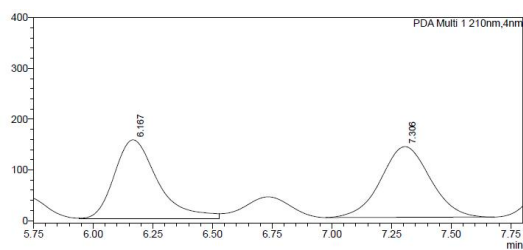
Peak#	Ret. Time	Area	Height	Height%	Area%
1	11.647	54334	3175	0.311	0.188
2	18.802	28788365	1016923	99.689	99.812
Total		28842699	1020098	100.000	100.000

3.28 Synthesis of benzyl (5*S*,6*R*,7*S*)-7-hydroxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene-6-carboxylate (**9**)



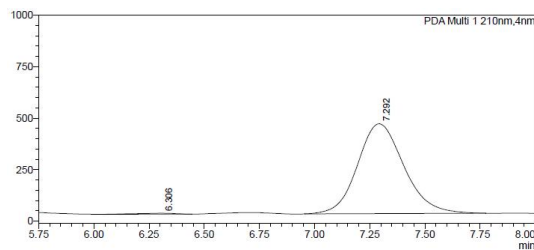
**9**

The reaction of alkene **8** (0.2 mmol) and **2** (76.0 mg, 0.3 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **9** as a ropy liquid (70% yield) with 98% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.36–7.33 (m, 3H), 7.23–7.22 (m, 2H), 7.11–7.09 (m, 2H), 7.03–7.00 (m, 1H), 6.95 (d, *J* = 7.0 Hz, 1H), 5.00 (d, *J* = 12.1 Hz, 1H), 4.86 (d, *J* = 12.1 Hz, 1H), 4.15–4.11 (m, 1H), 3.44 (s, 1H), 3.16 (d, *J* = 4.6 Hz, 2H), 2.77 (d, *J* = 4.6 Hz, 1H), 2.63 (t, *J* = 13.2 Hz, 1H), 2.09 (s, 1H), 1.94 (dd, *J* = 24.0, 12.2 Hz, 1H), 1.23 (d, *J* = 10.8 Hz, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 173.92, 141.69, 138.53, 135.44, 130.98, 129.09, 128.48, 128.47, 128.24, 126.52, 126.22, 83.92, 72.62, 66.27, 48.94, 33.02, 31.35, 24.76, 24.72. ESI-MS calculated for C<sub>19</sub>H<sub>27</sub>BNaO<sub>5</sub>: *m/z* (%): 369.1847 (M+Na<sup>+</sup>), found: 369.1841. Enantiomeric excess was determined by HPLC with a Chiralpak ODH column (hexanes: 2-propanol = 85:15, 0.8 mL/min, 210 nm); minor enantiomer *tr* = 6.2 min, major enantiomer *tr* = 7.2 min. [α]<sub>D</sub><sup>20</sup> = +13.8 (*c* = 0.17, CHCl<sub>3</sub>).



Peak Table>

Peak#	Ret. Time	Area	Height	Height%	Area%
1	6.167	1999698	156251	52.838	49.838
2	7.306	2012737	139465	47.162	50.162
Total		4012435	295716	100.000	100.000



Peak Table>

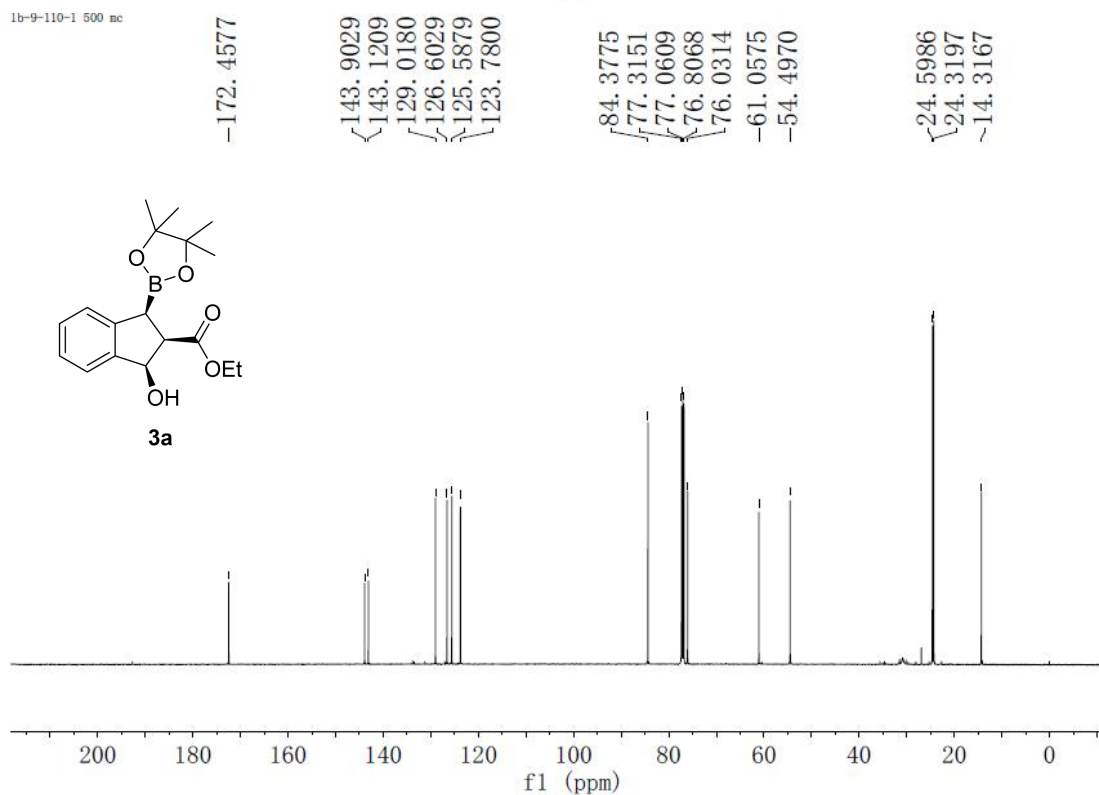
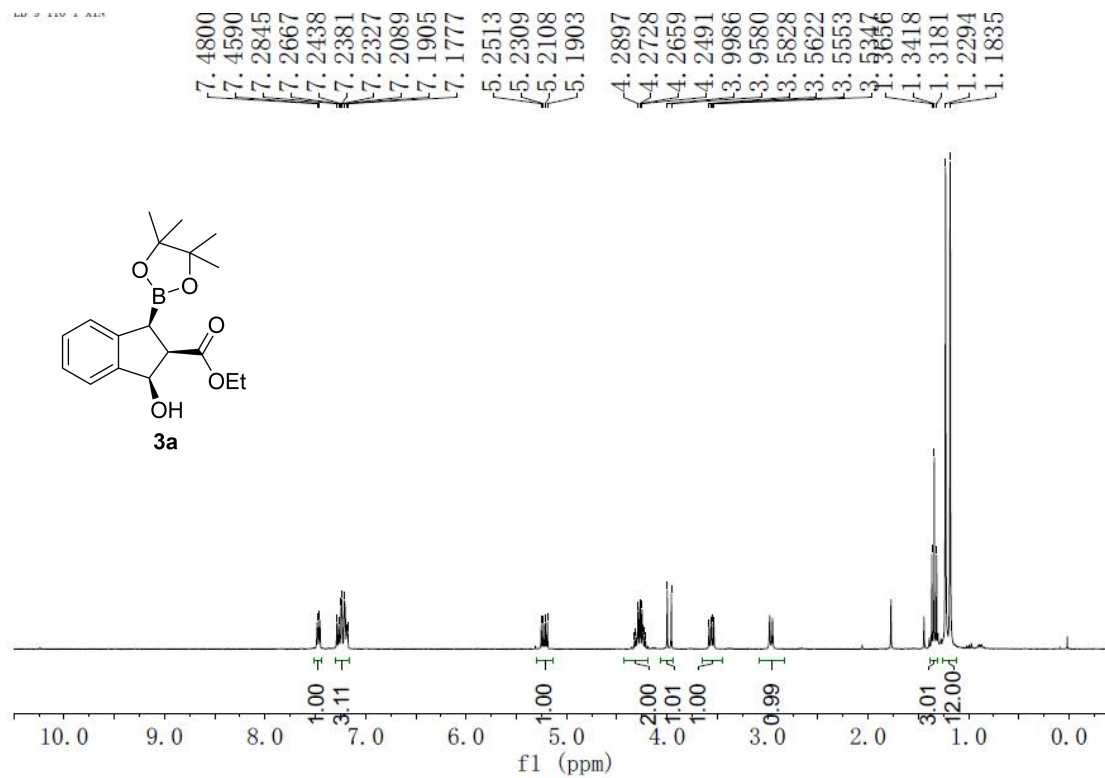
Peak#	Ret. Time	Area	Height	Height%	Area%
1	6.306	55202	4327	0.982	0.855
2	7.292	6402828	436287	99.018	99.145
Total		6458030	440615	100.000	100.000

## References

- (1) (a) M. R. Sk, S. S. Bera, and M. S. Maji, Cp\*Co(III)-Catalyzed C-H Alkenylation of Aromatic Ketones with Alkenes. *Adv. Synth. Catal.* DOI: 10.1002/adsc.201801385 (b) G. Li, L. Wan, G. Zhang, D. Leow, J. Spangler, and J.-Q. Yu, Pd(II)-Catalyzed C-H Functionalizations Directed by Distal Weakly Coordinating Functional Groups. *J. Am. Chem. Soc.* **2015**, *137*, 4391–4397.

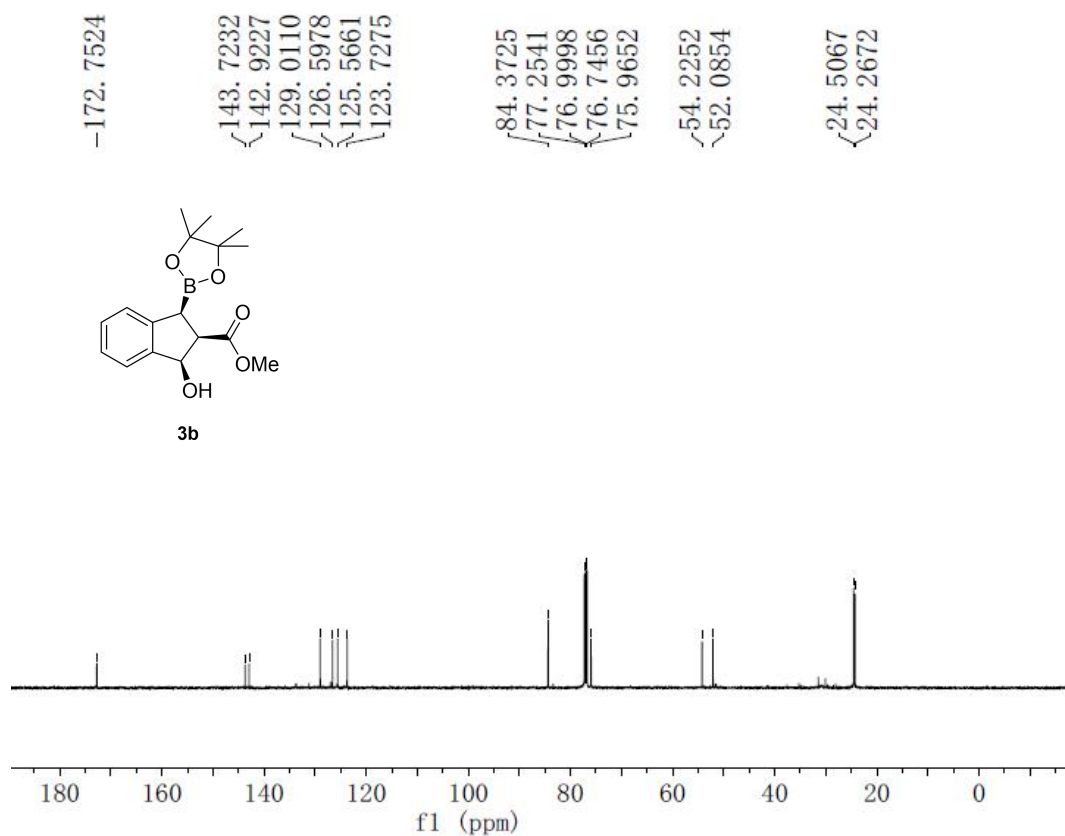
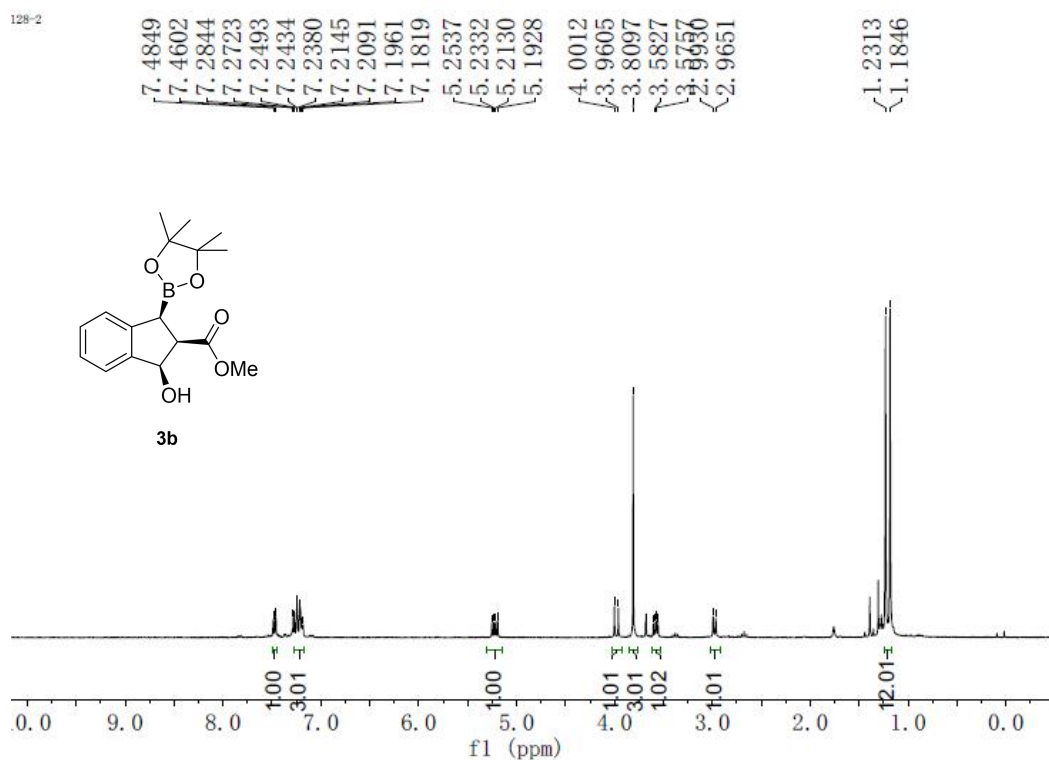
## 4 NMR Spectra for New Compounds

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of **3a**

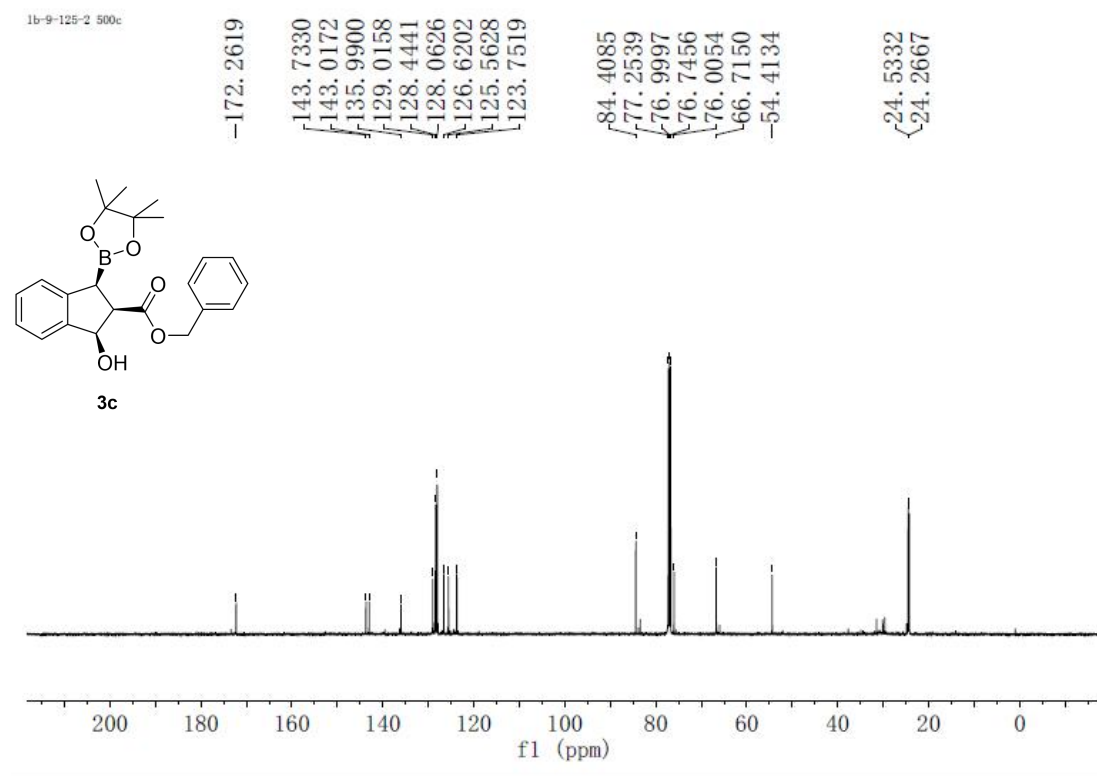
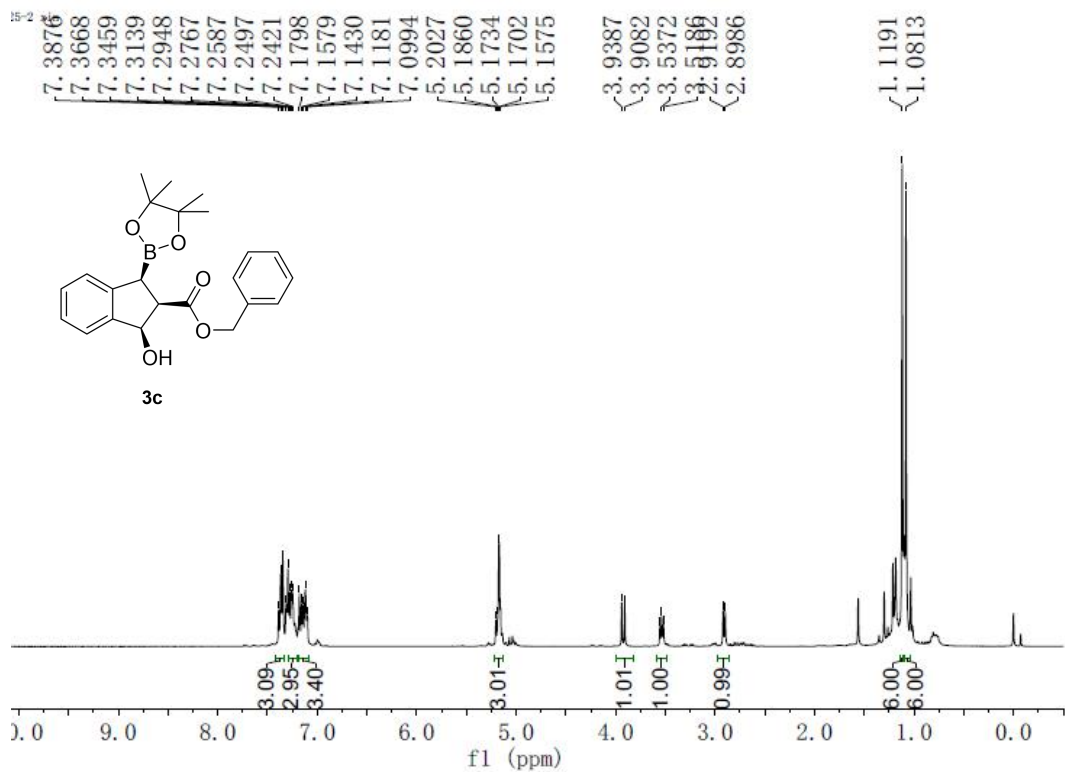


**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 3b**

128-2



**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 3c**



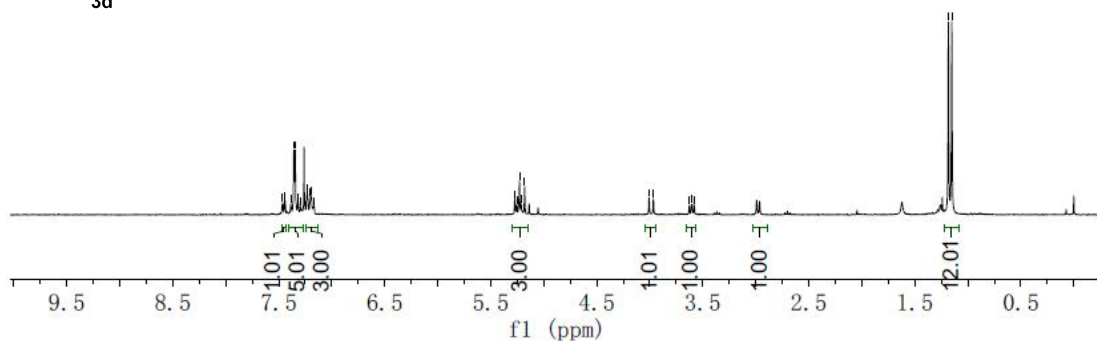
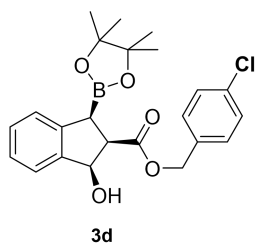


**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 3d**

LB-10-1-2XIN

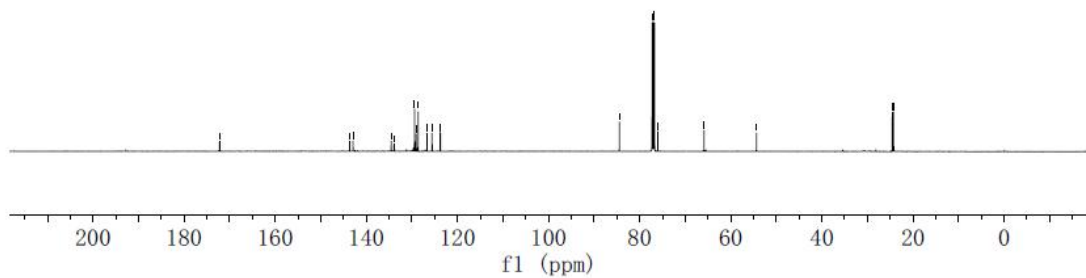
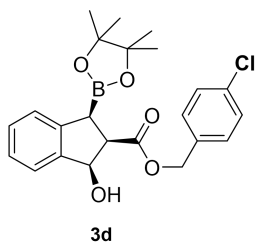
7.4638  
7.4419  
7.3857  
7.3566  
7.3439  
7.3233  
7.3158  
7.2944  
7.2355  
7.2295  
7.2001  
7.1934  
7.1663  
5.2717  
5.2542  
5.2288  
5.2139  
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3.6273  
3.6071  
3.6001  
3.5796

1.1831  
1.1512

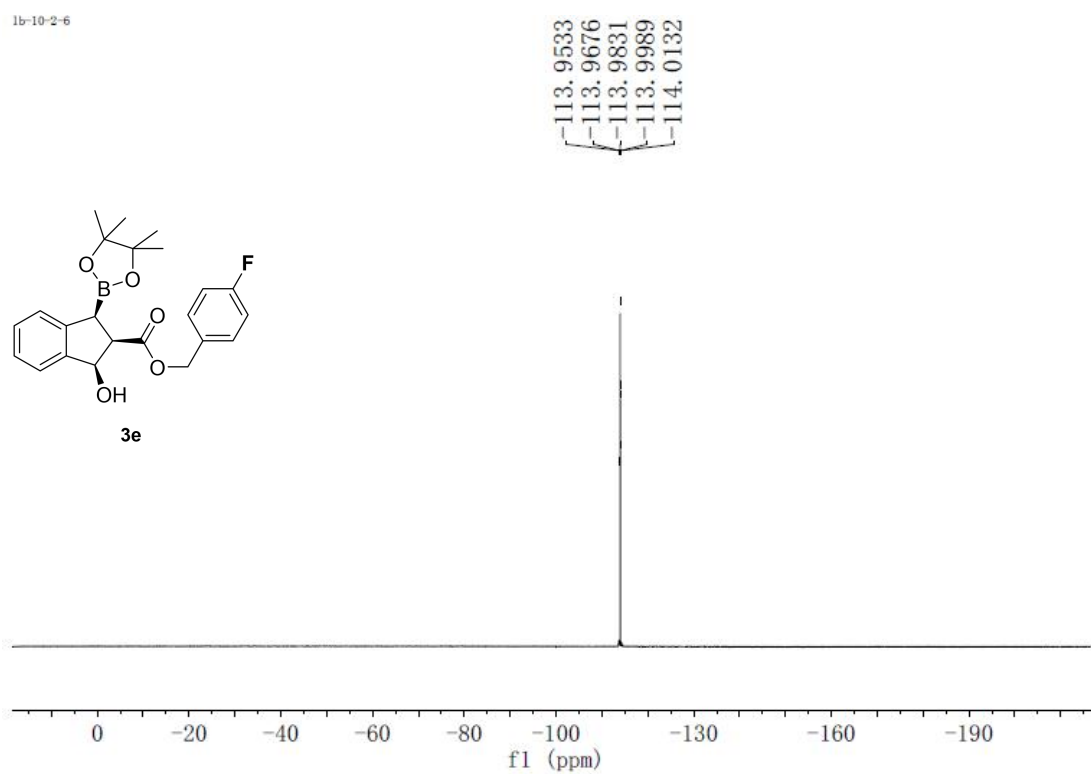
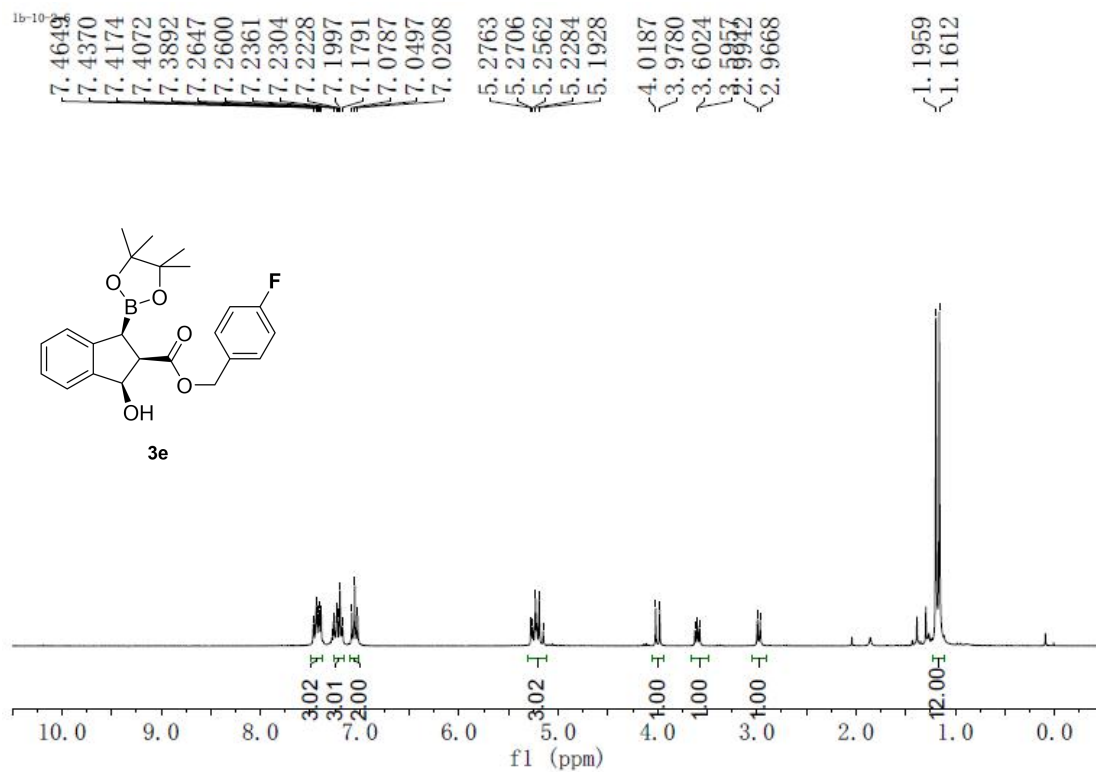


LB-10-1-2 500C

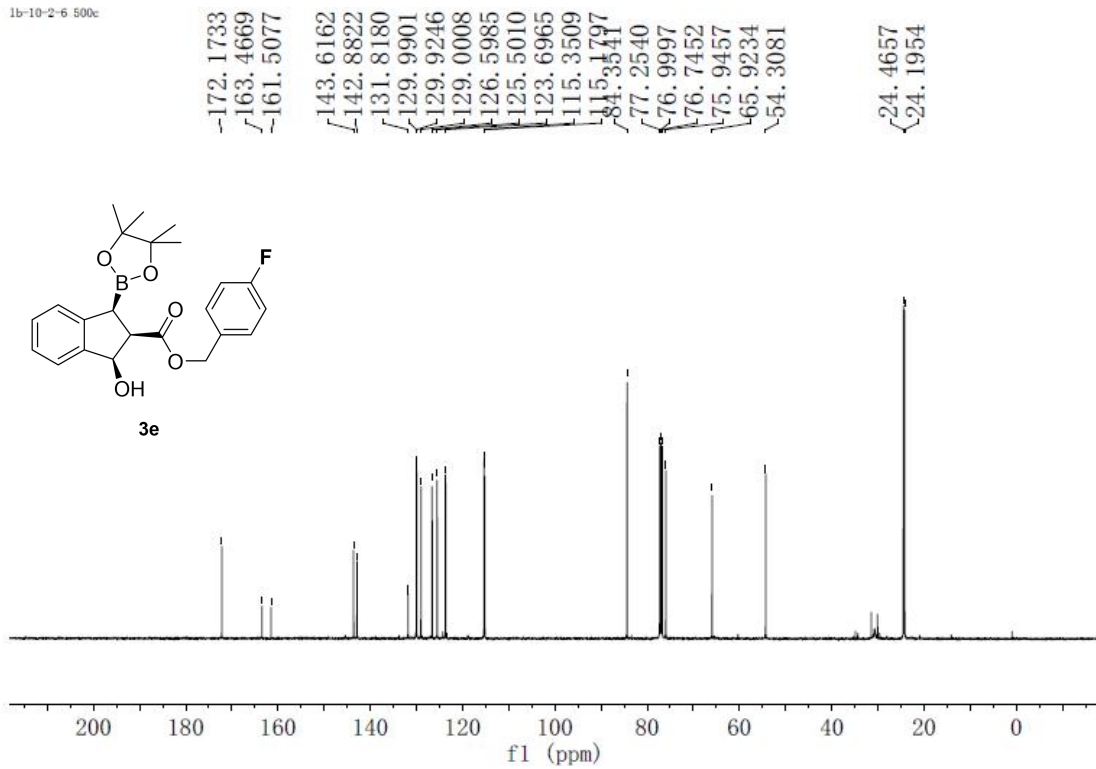
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134.5451  
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123.7606  
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76.0100  
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54.3589  
24.5294  
24.2639



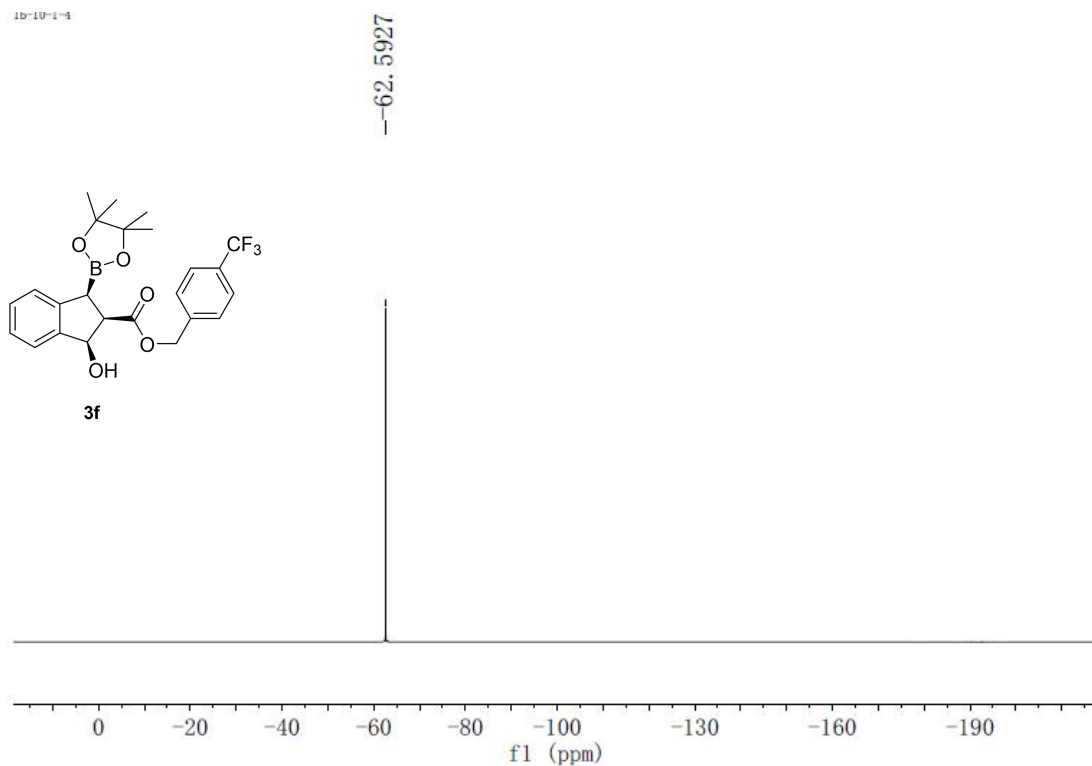
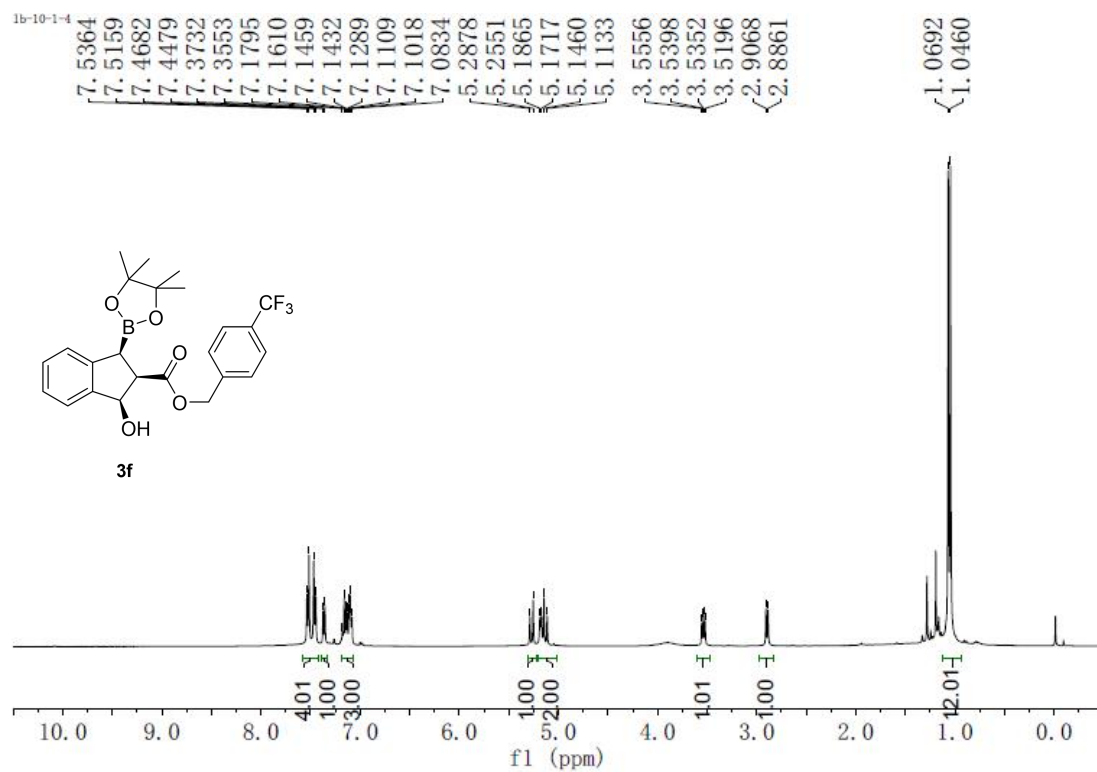
**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>), **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>) and **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) of **3e**

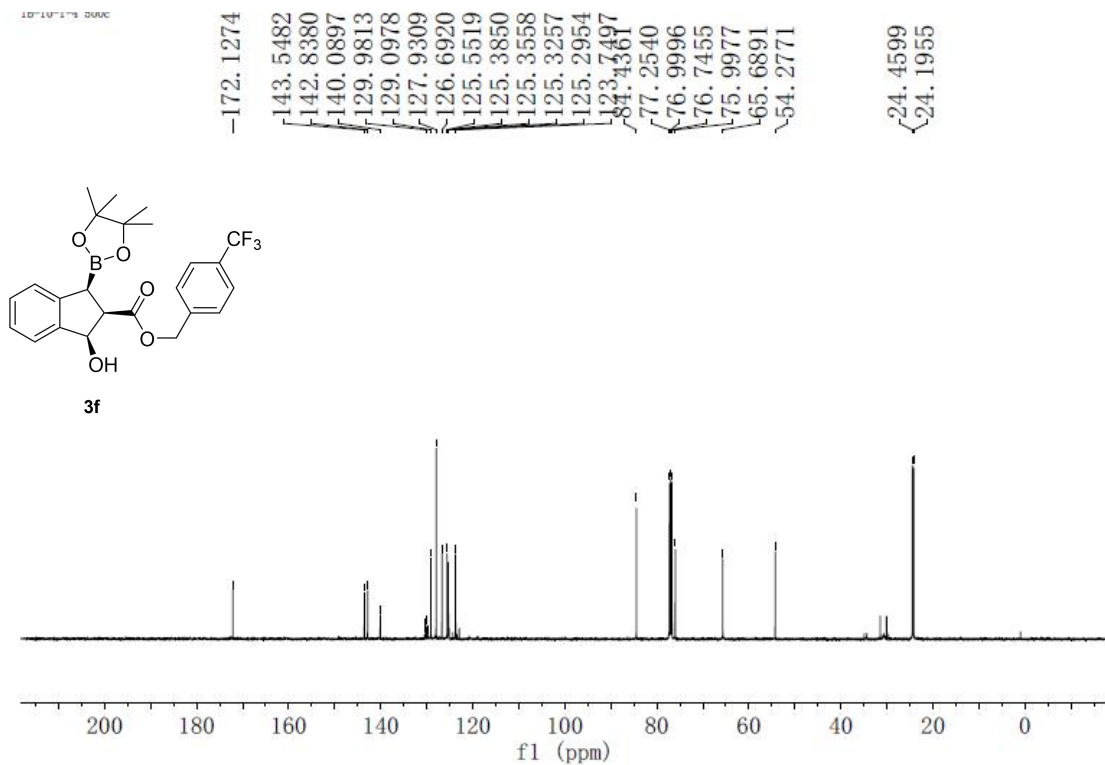


1b-10-2-6 500c

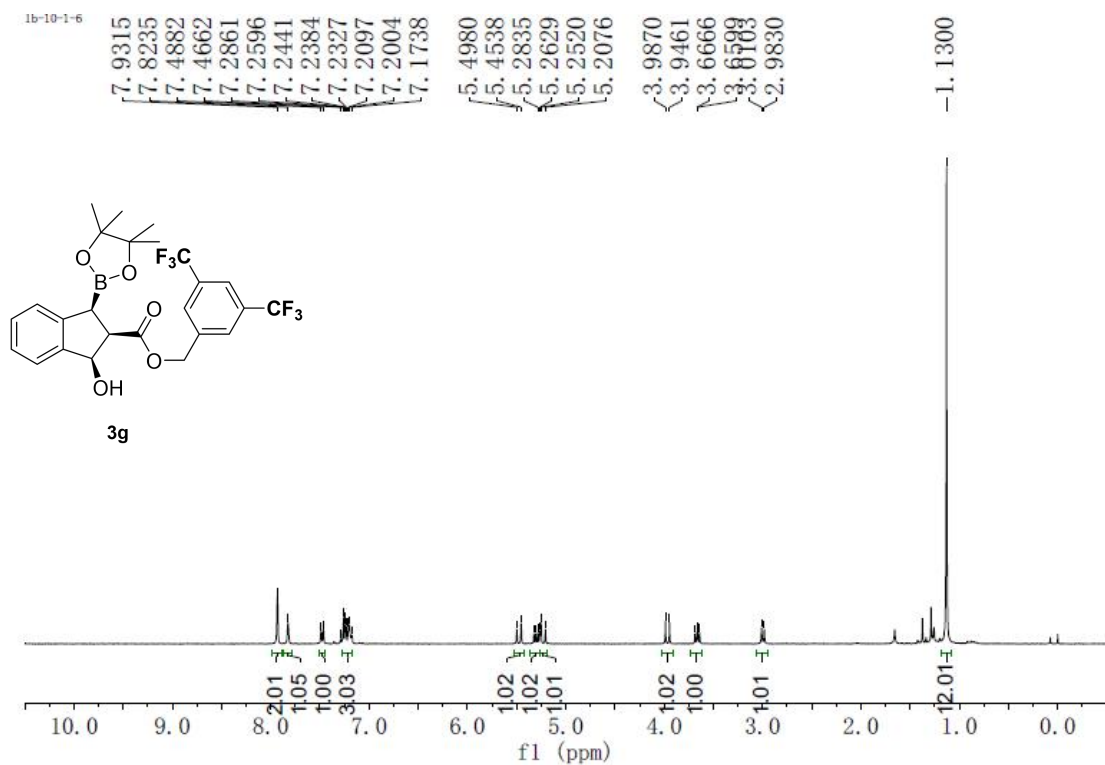


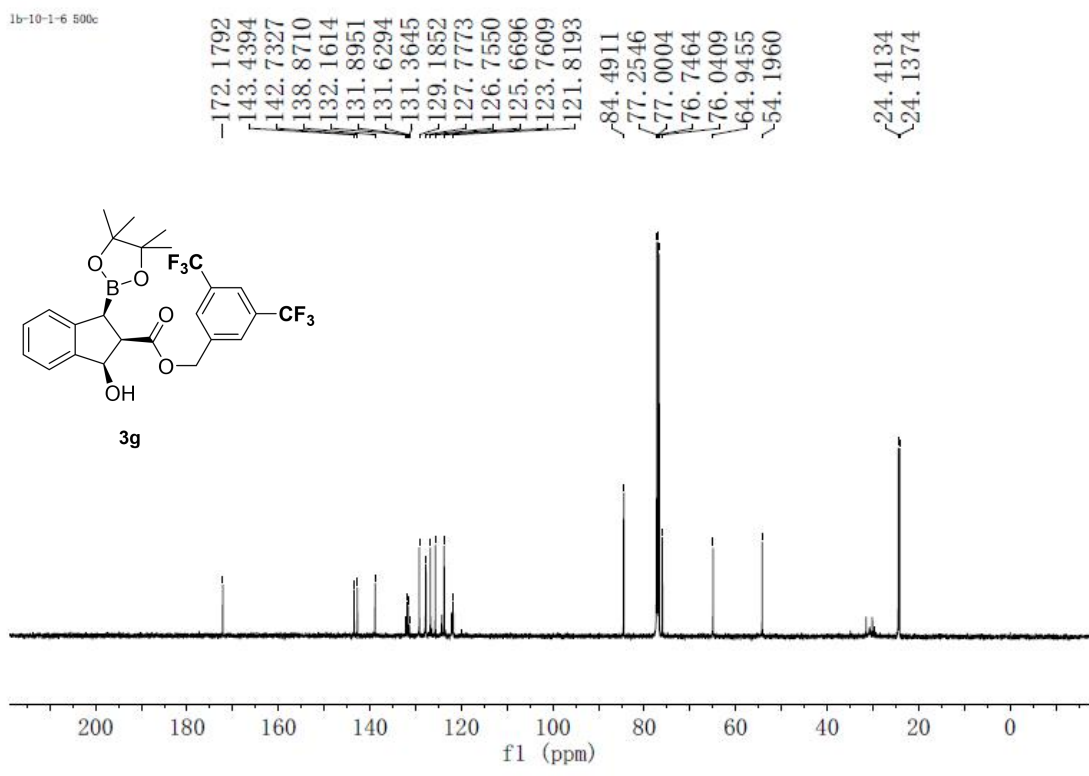
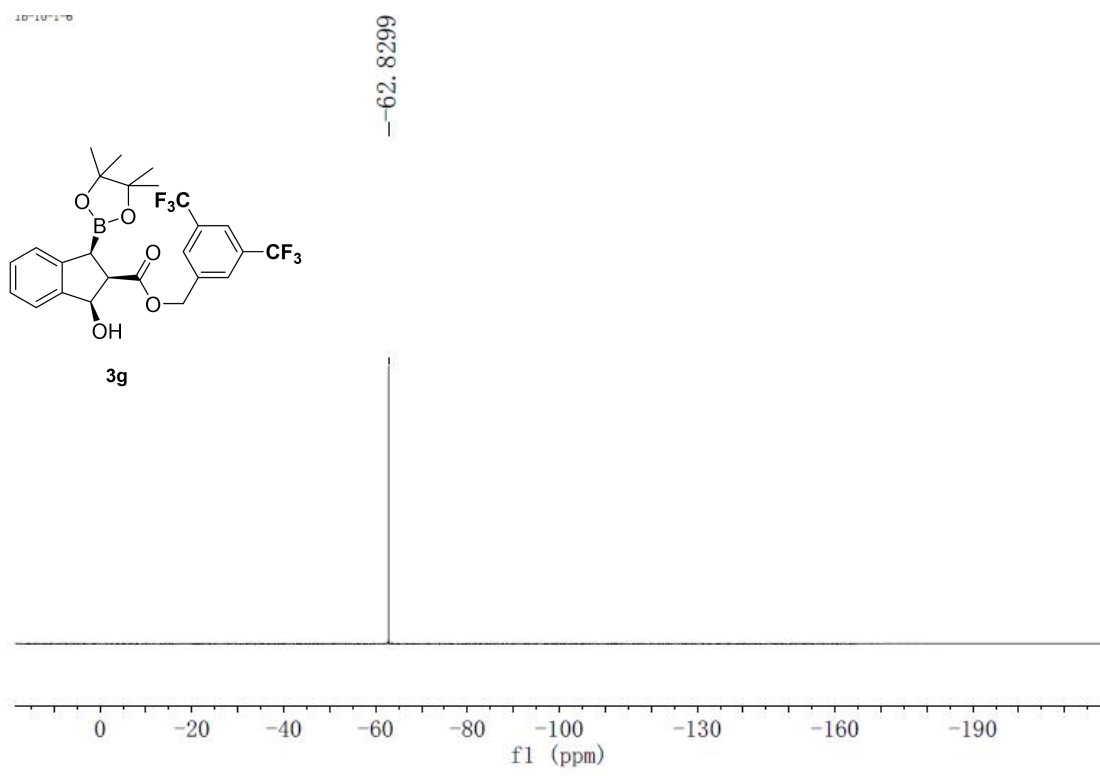
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of **3f**



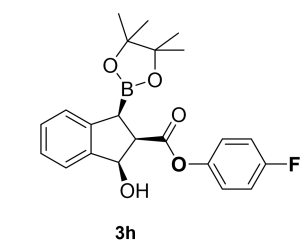
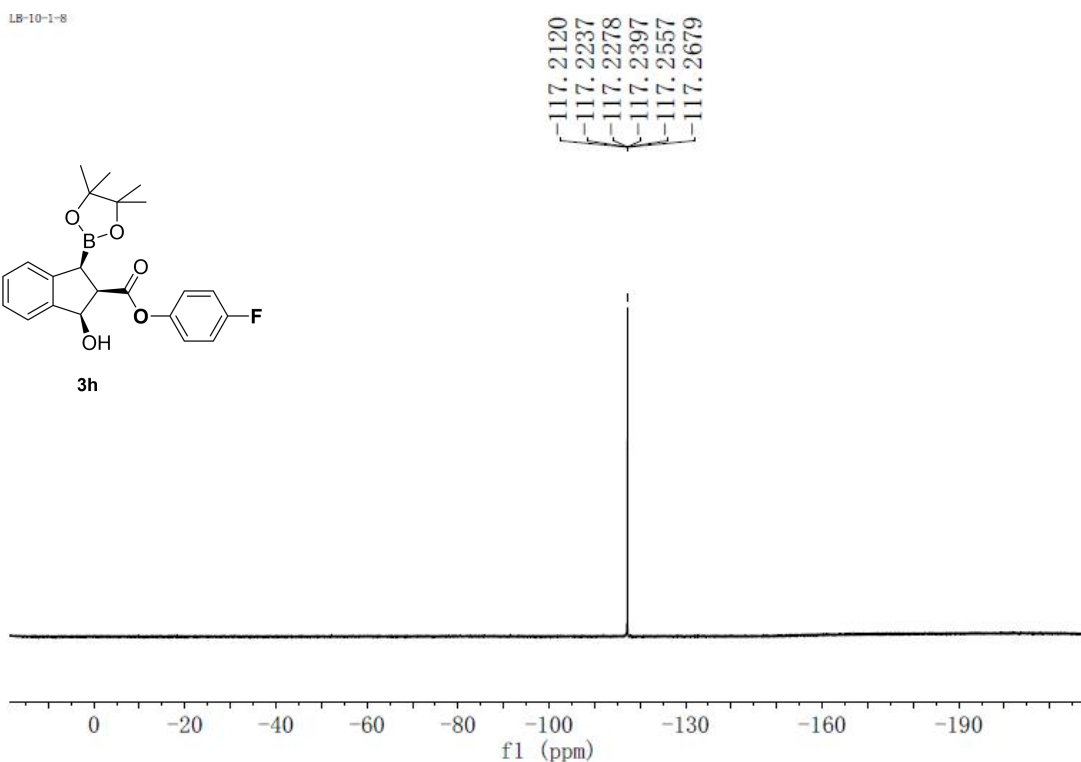
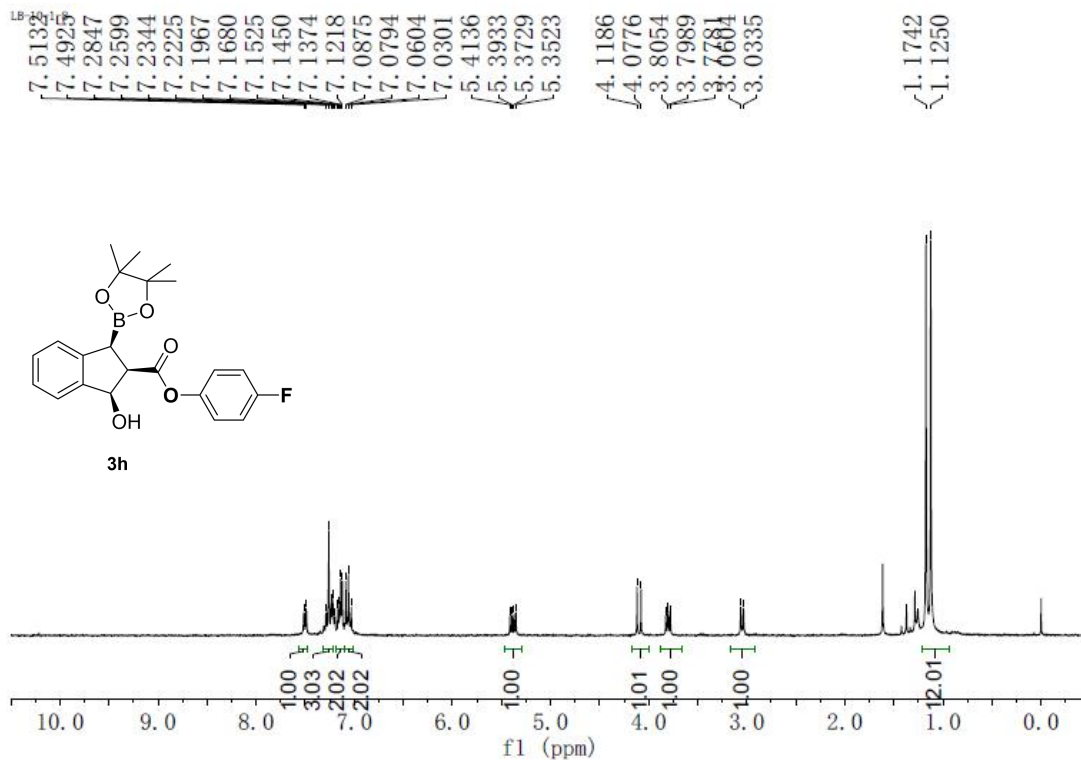


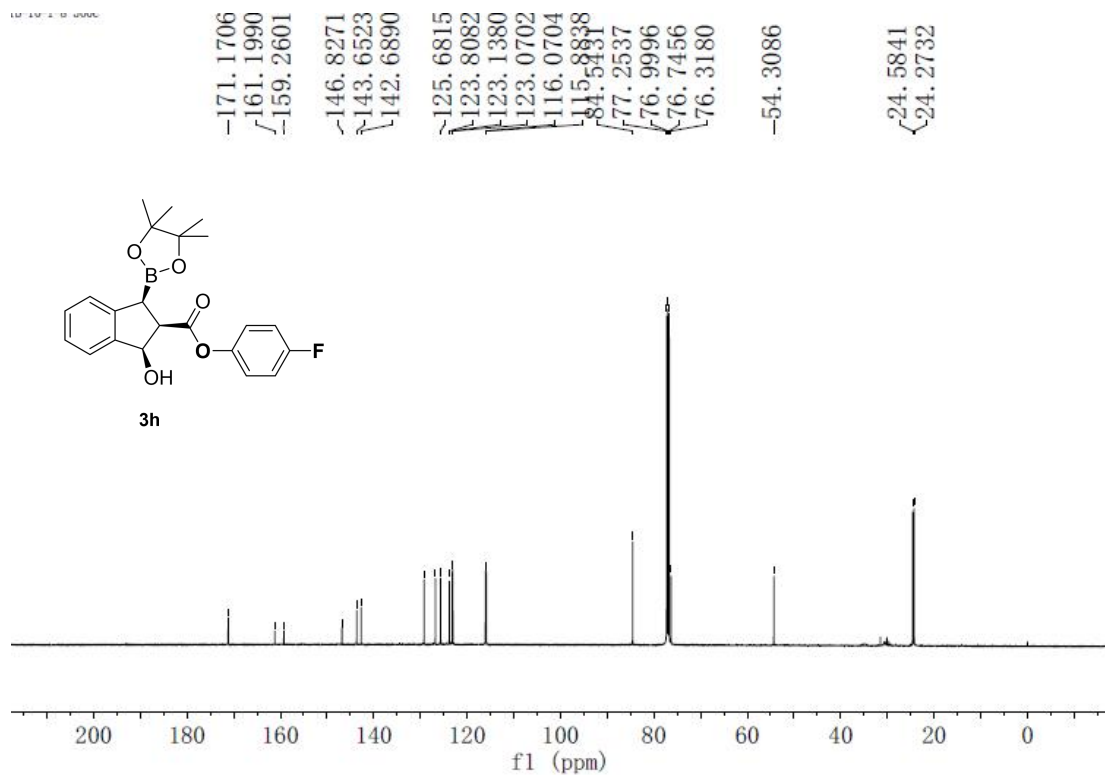
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of **3g**



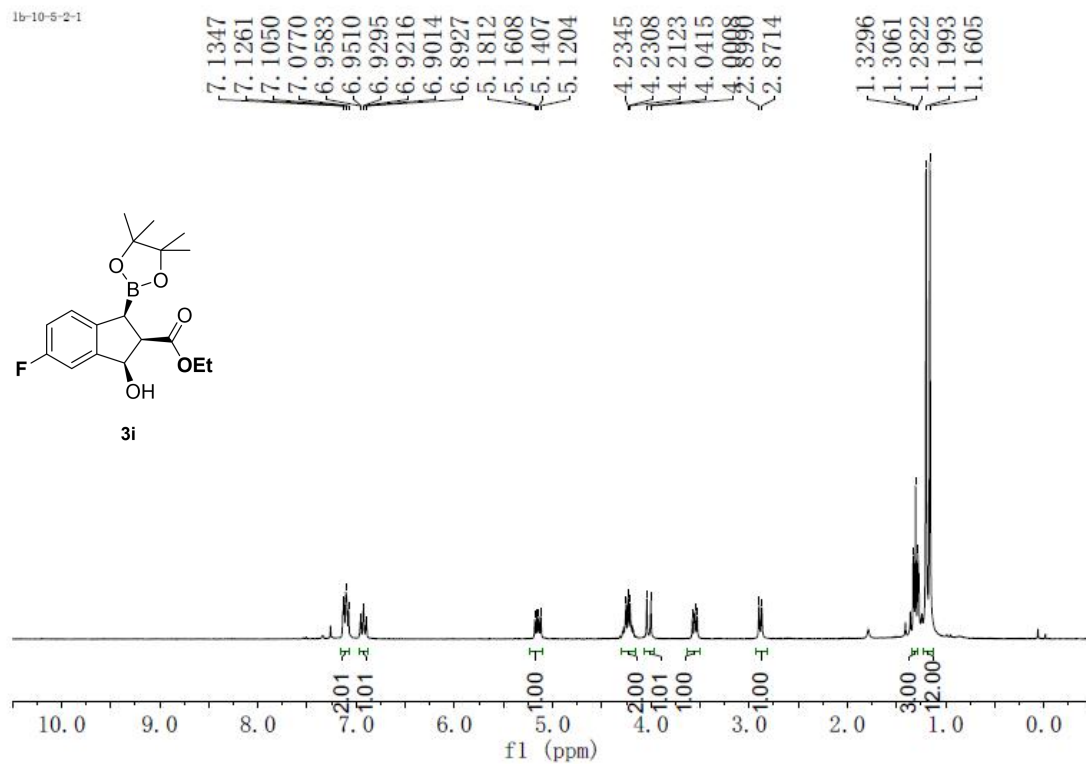


**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>), **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>) and **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) of **3h**



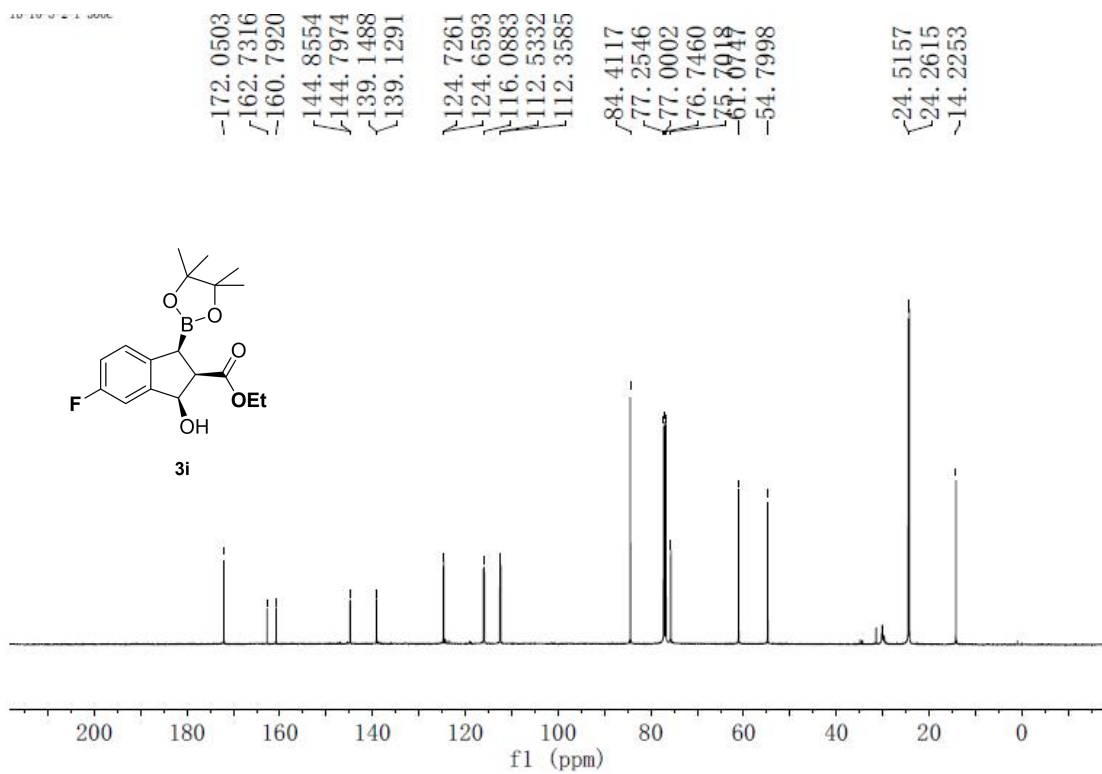
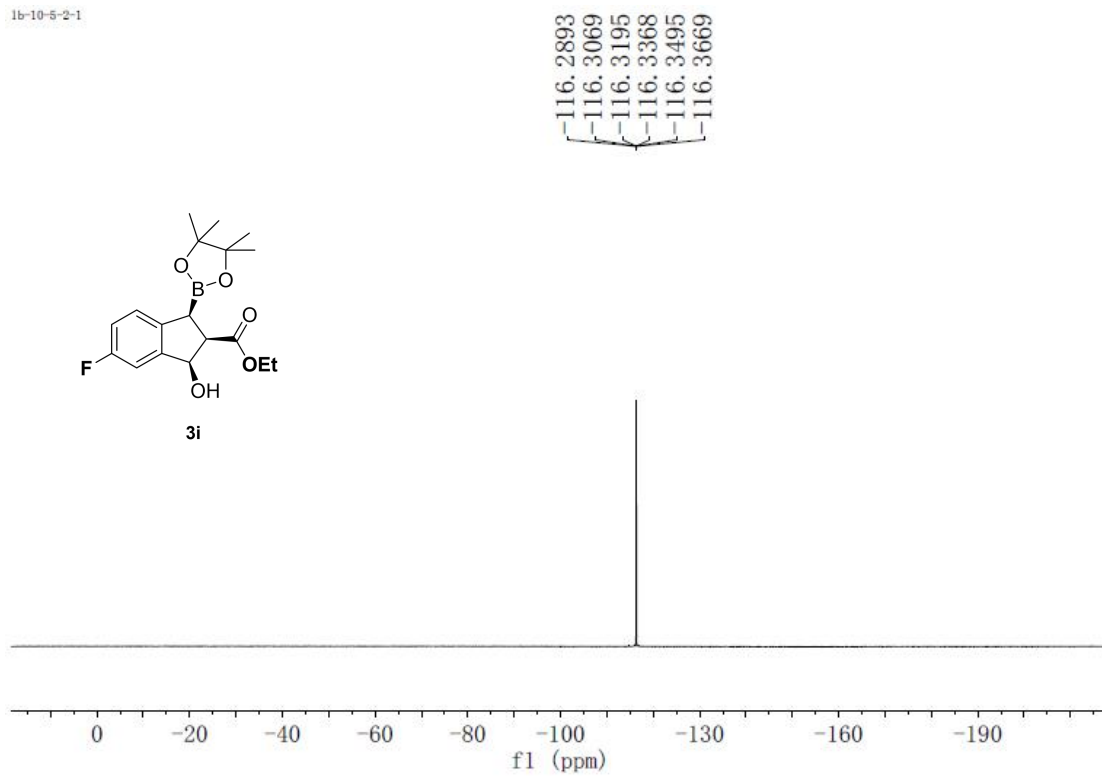


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of **3i**





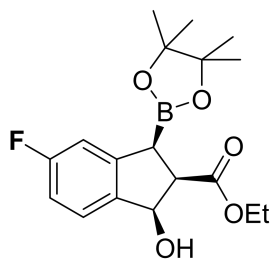
1b-10-5-2-1



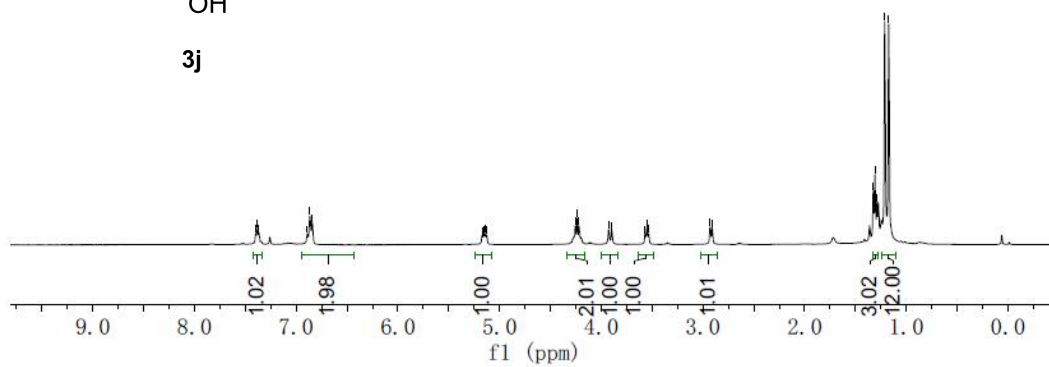
**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>), **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>) and **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) of **3j**

1b-10-5-3-1

7.3988, 7.3798, 7.3663, 6.8899, 6.8656, 6.8426, 5.1720, 5.1569, 5.1427, 5.1278, 4.2558, 4.2376, 4.2197, 3.9277, 3.5306, 3.5101, 2.9101, 1.3263, 1.3091, 1.2913, 1.2132, 1.1739

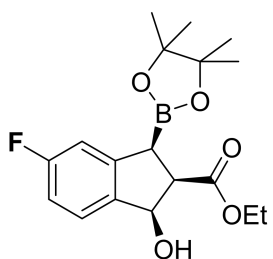


**3j**

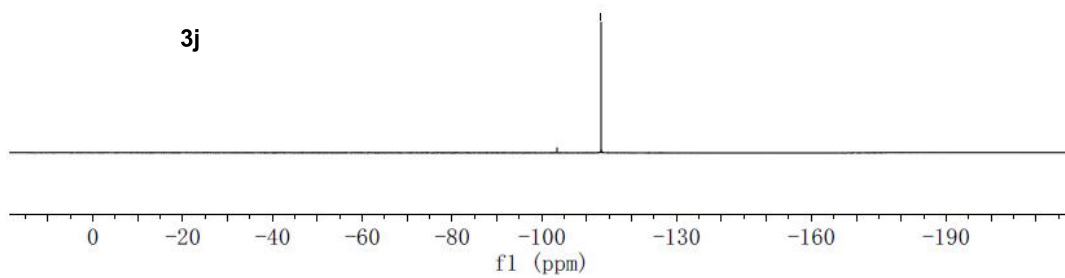


1b-10-5-3-1

--113.1719



**3j**



1b-10-5-3-1 500c

~172.1483  
~164.4721  
~162.5139

-146.4366  
-138.8718

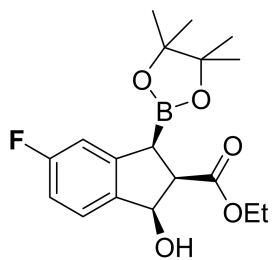
126.8955  
126.8240  
113.7627

113.5848  
110.7168  
110.5363

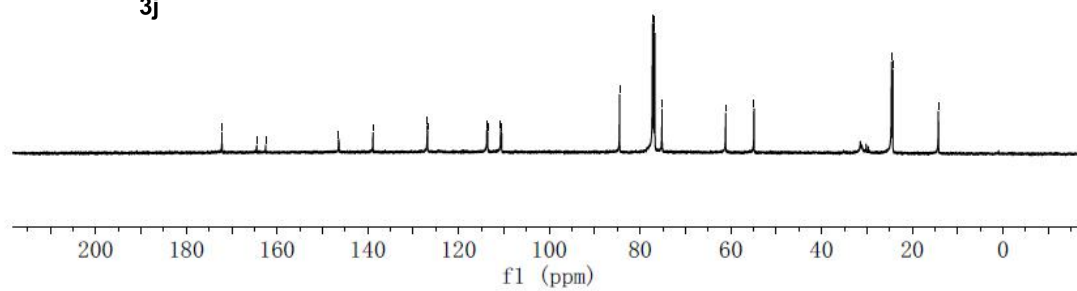
84.5088  
77.2540  
76.9998  
76.7458  
75.1556

-61.1304  
-54.8933

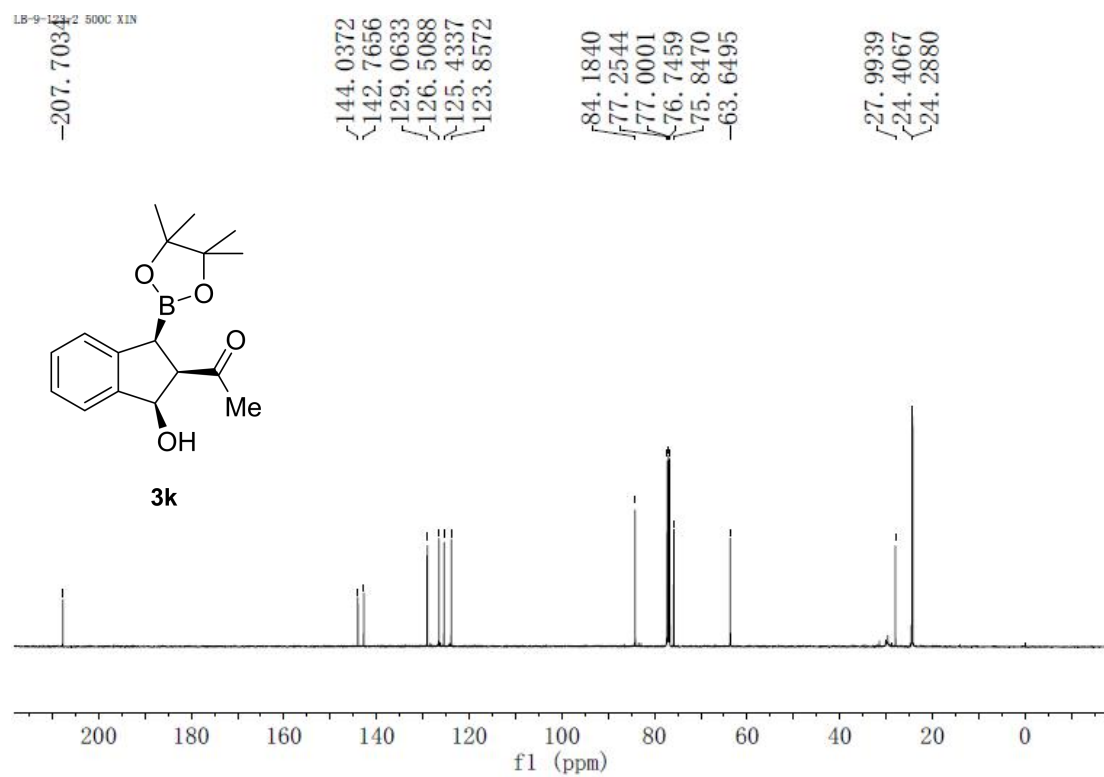
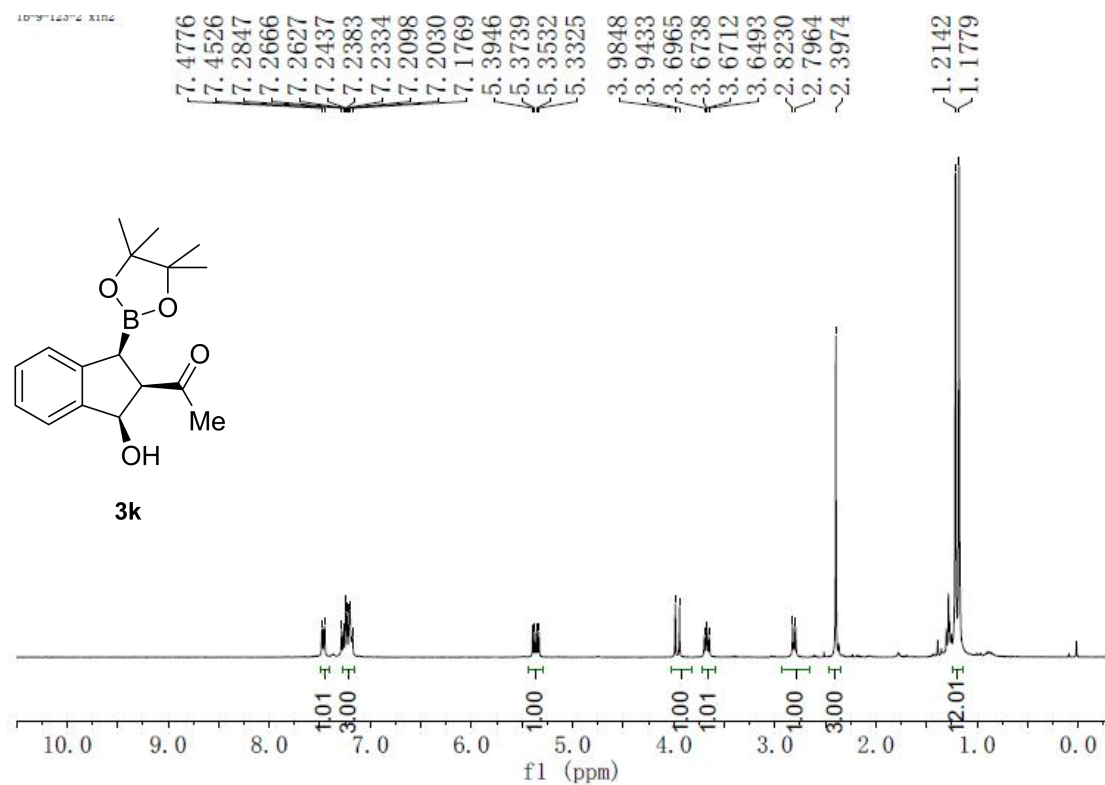
24.5789  
24.3215  
~14.2509



3j

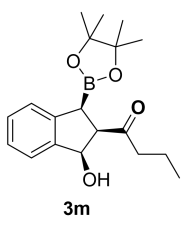
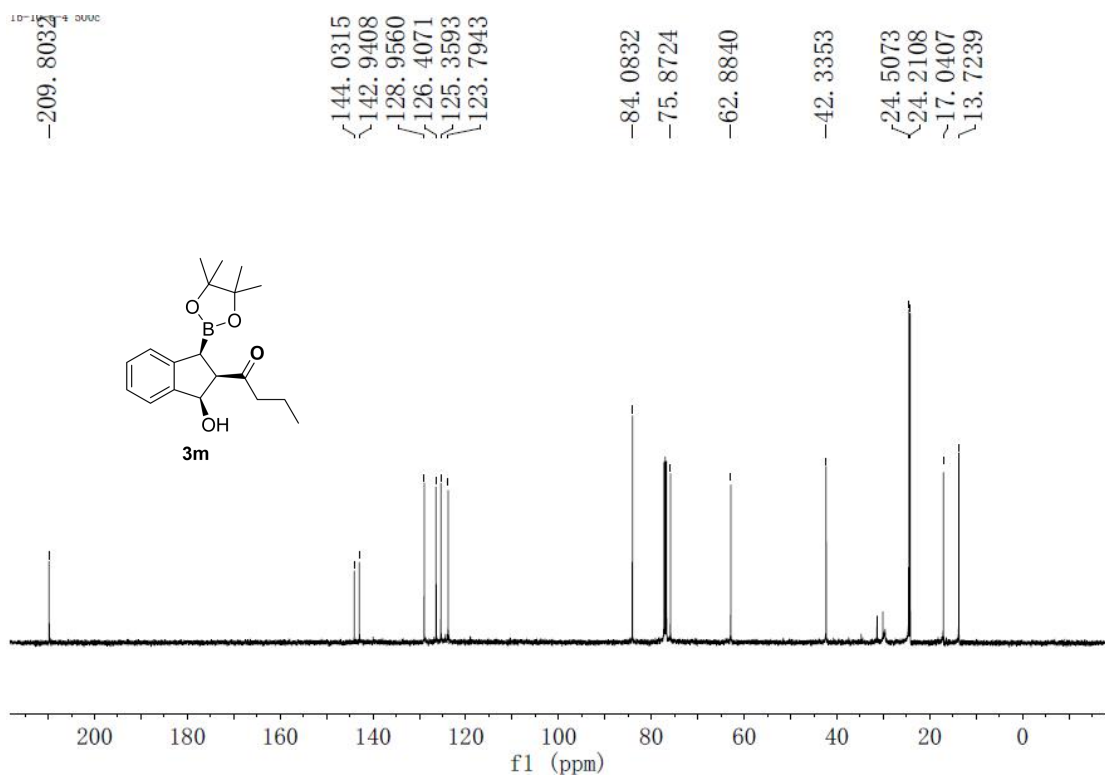
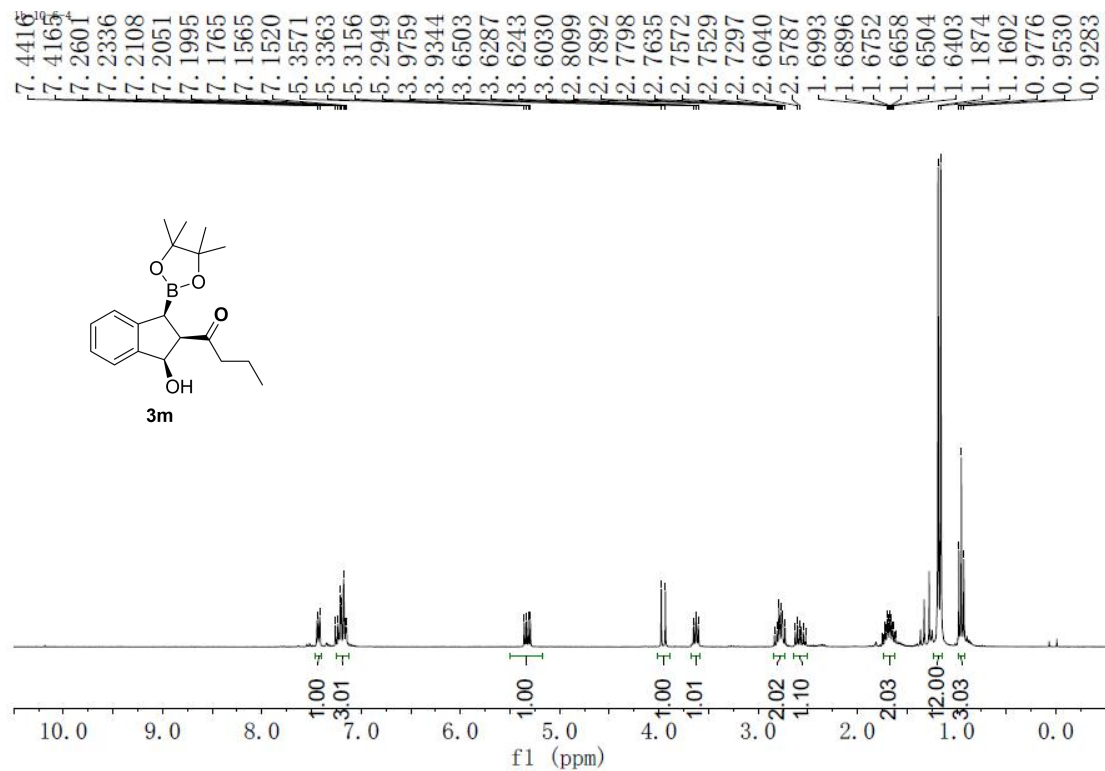


**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 3k**



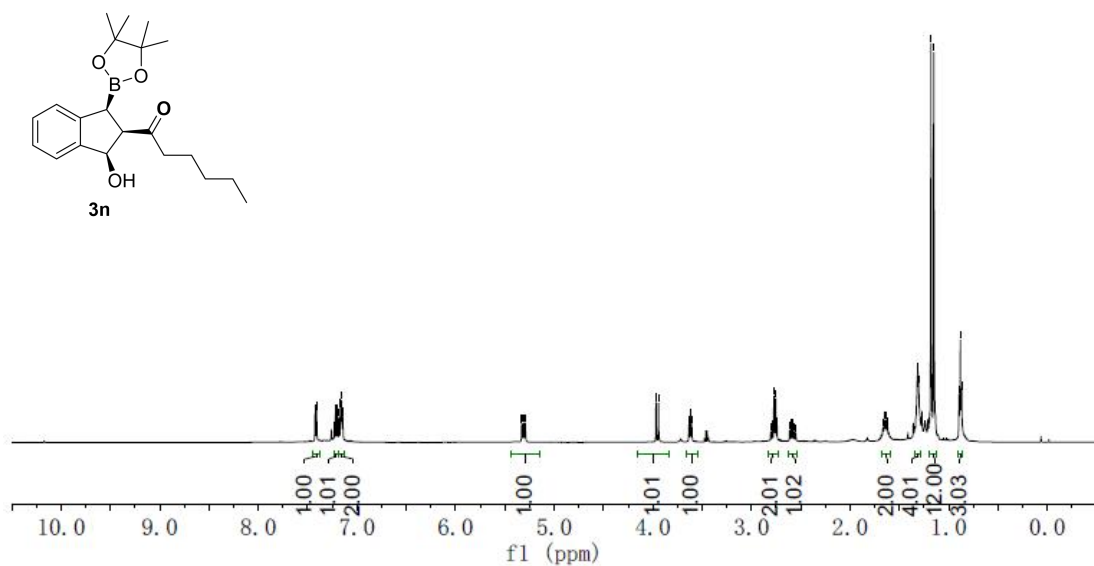


**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 3m**



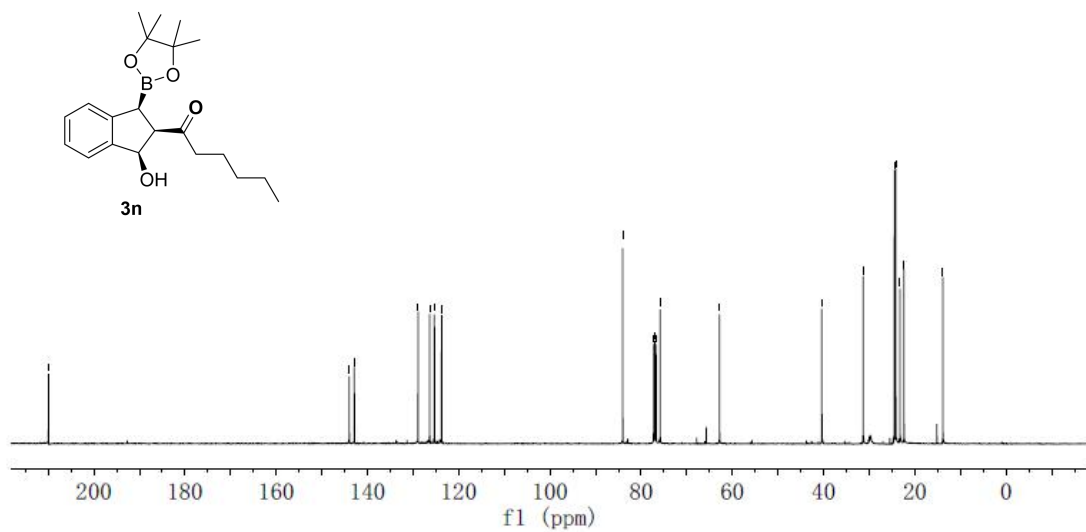
**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 3n**

7.424  
7.409  
7.295  
7.2168  
7.2149  
7.2024  
7.2000  
7.1813  
7.1668  
7.1596  
7.1447  
5.3298  
5.3174  
5.3051  
5.2926  
3.9674  
3.9425  
3.6337  
3.6203  
3.6054  
2.7879  
2.7714  
2.7548  
2.7409  
2.6131  
2.6005  
2.5963  
2.5835  
1.6654  
1.6516  
1.6377  
1.6208  
1.3184  
1.3108  
1.3042  
1.1797  
1.1512  
0.8960  
0.8821  
0.8680

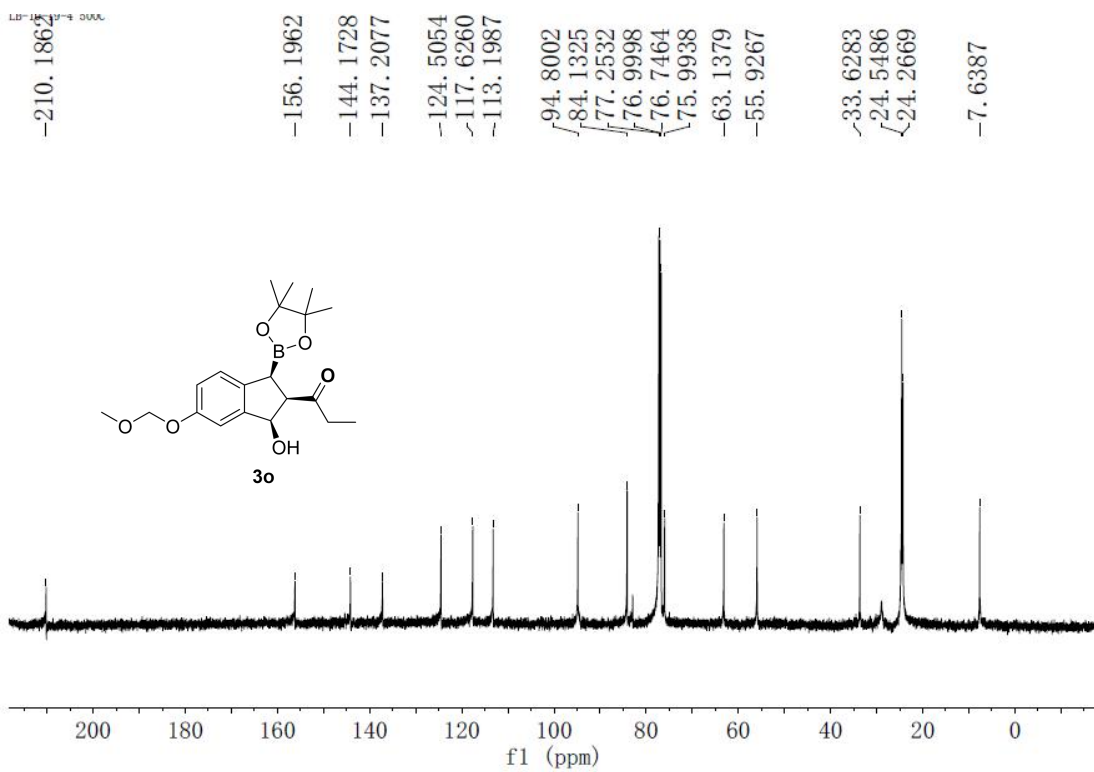
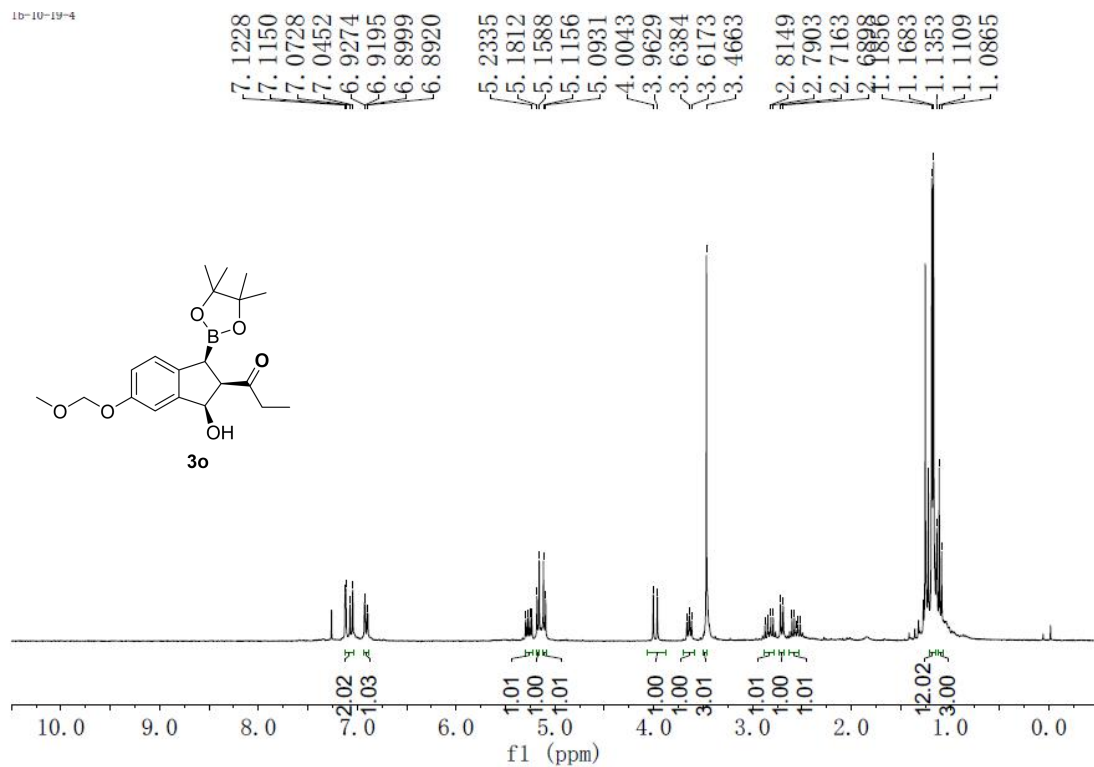


1b-10126-3-1 500c

-209.937  
143.9933  
142.8837  
128.9207  
126.3720  
125.3266  
123.7542  
84.0475  
77.2548  
77.0003  
76.7458  
75.8394  
62.8227  
40.3977  
31.3465  
24.4710  
24.1821  
23.2644  
22.3840  
13.8700

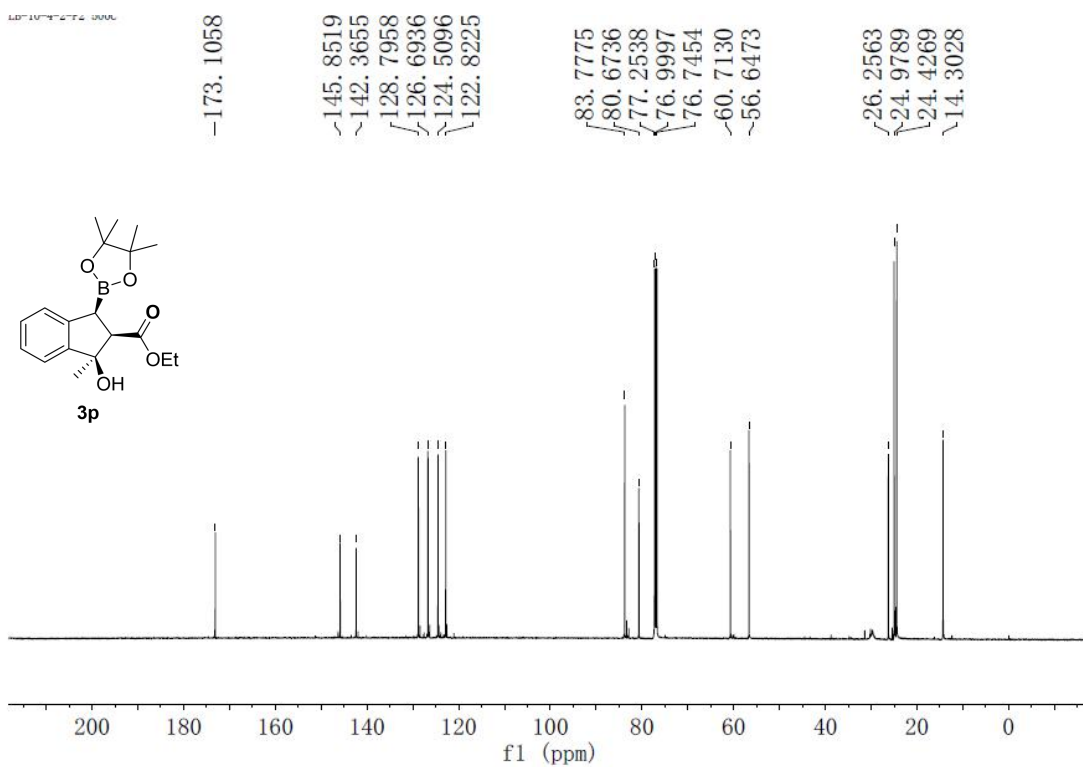
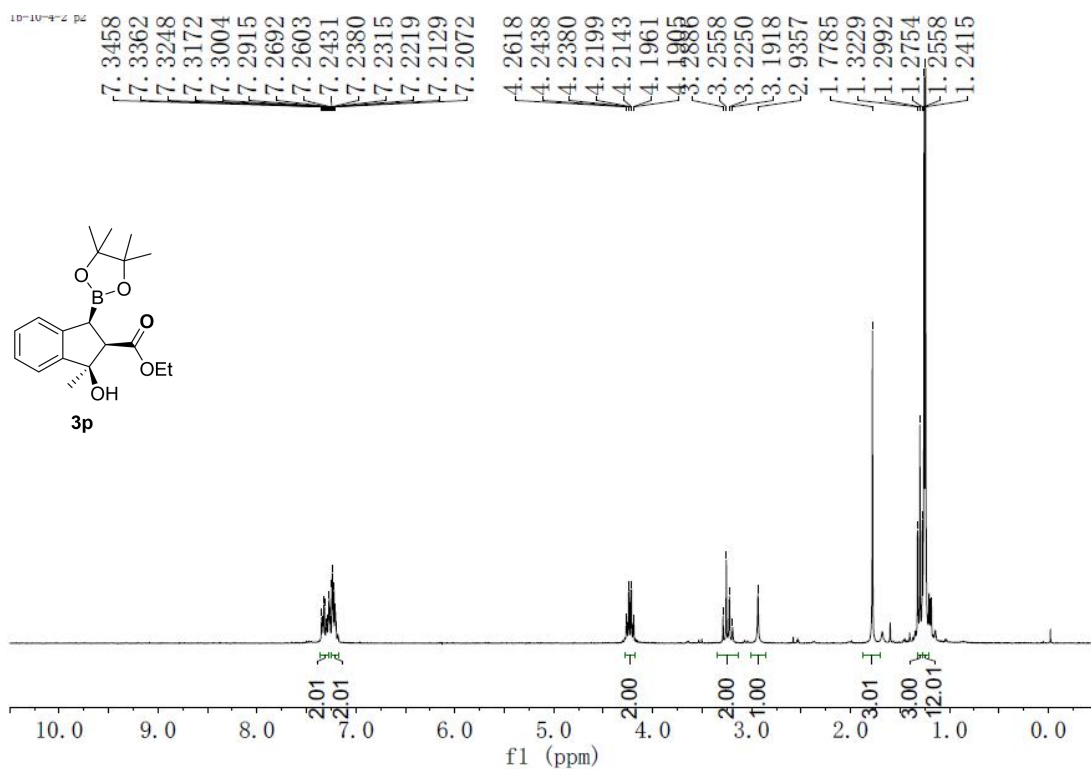


**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of **3o****

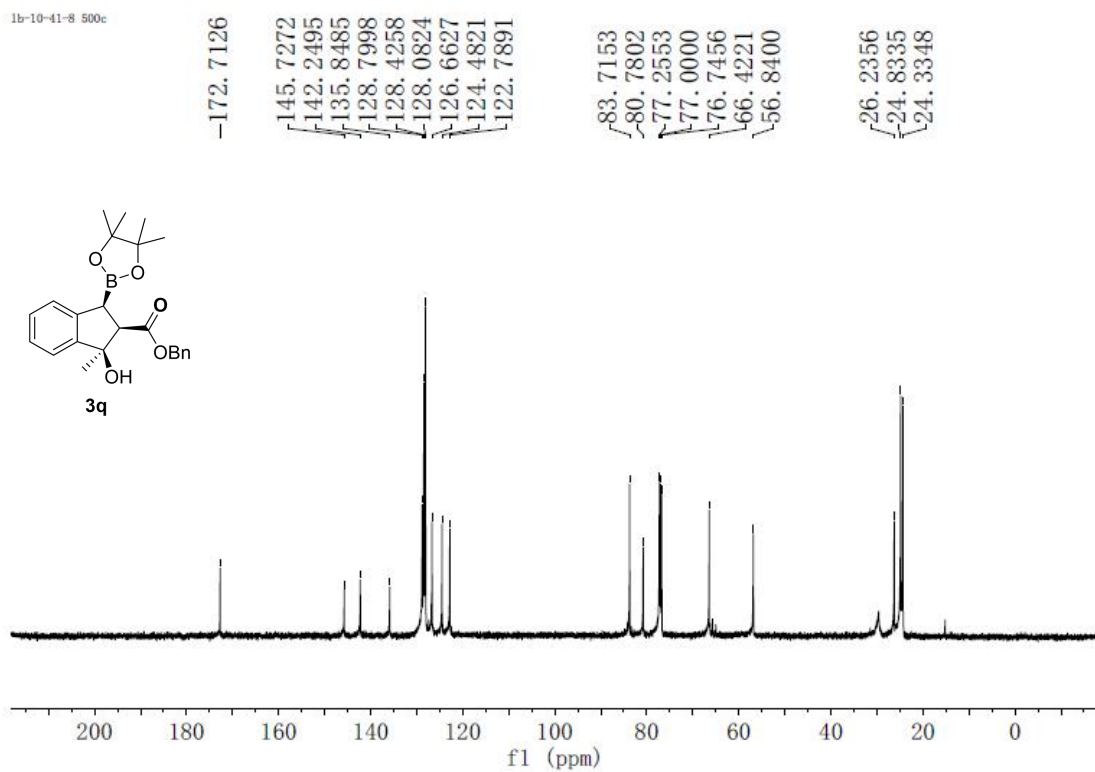
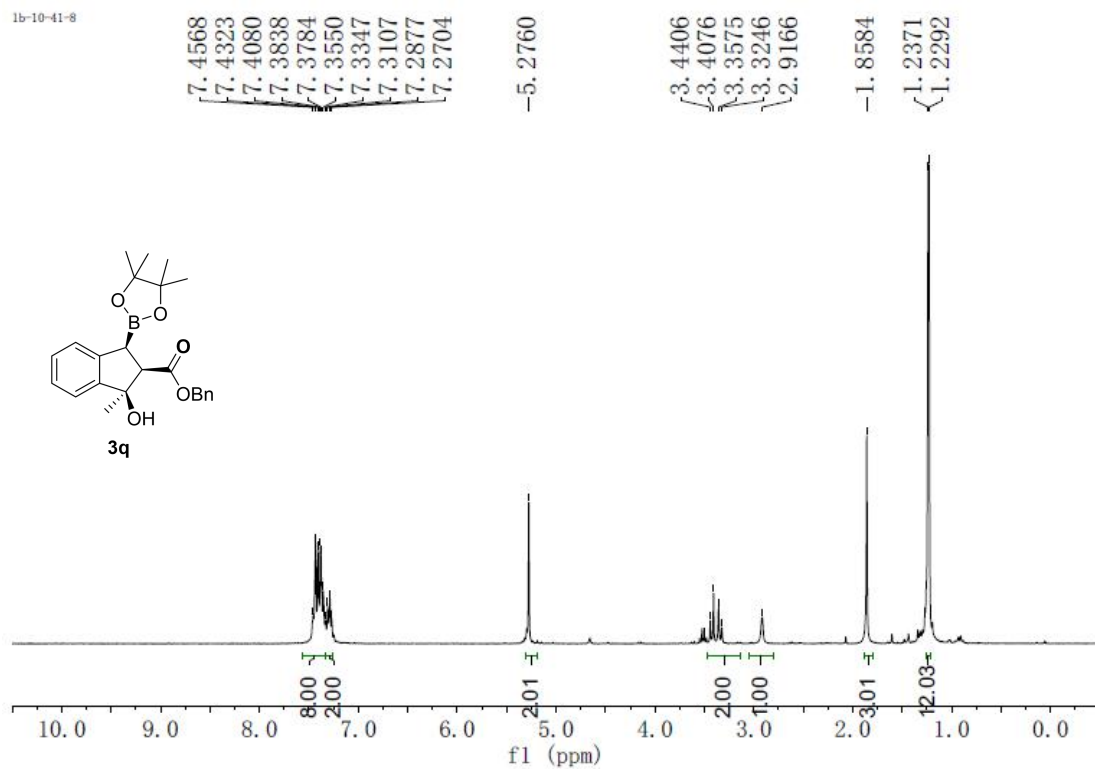




<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of **3p**

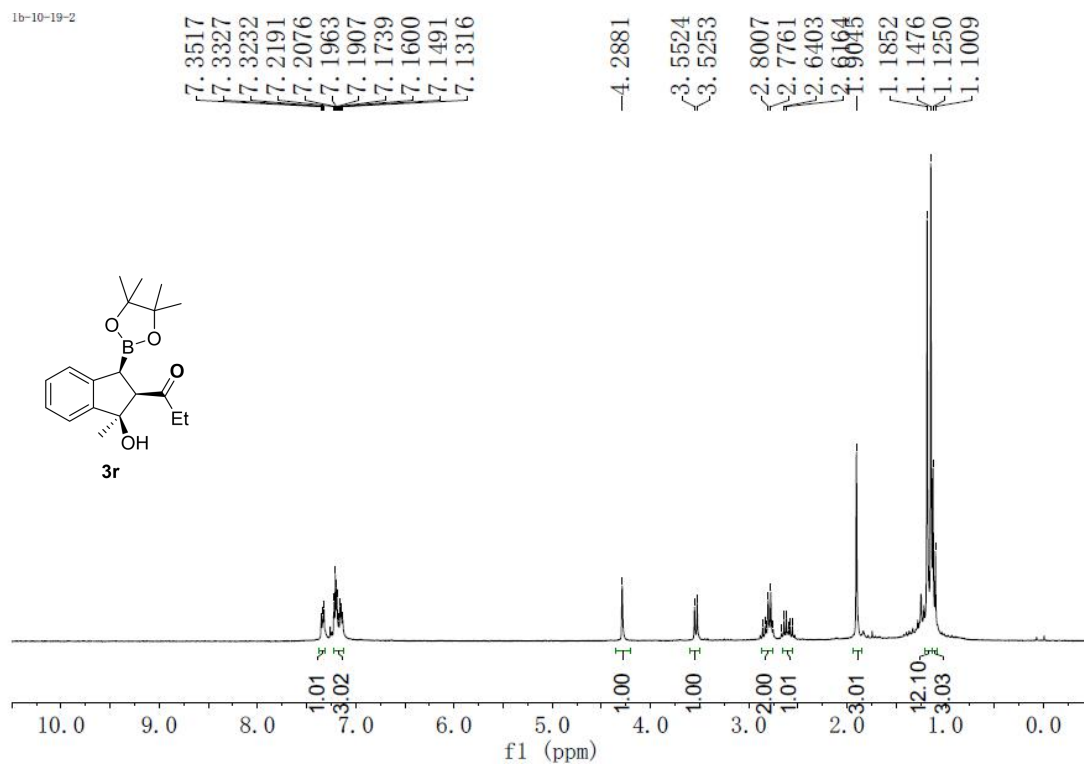


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of **3q**

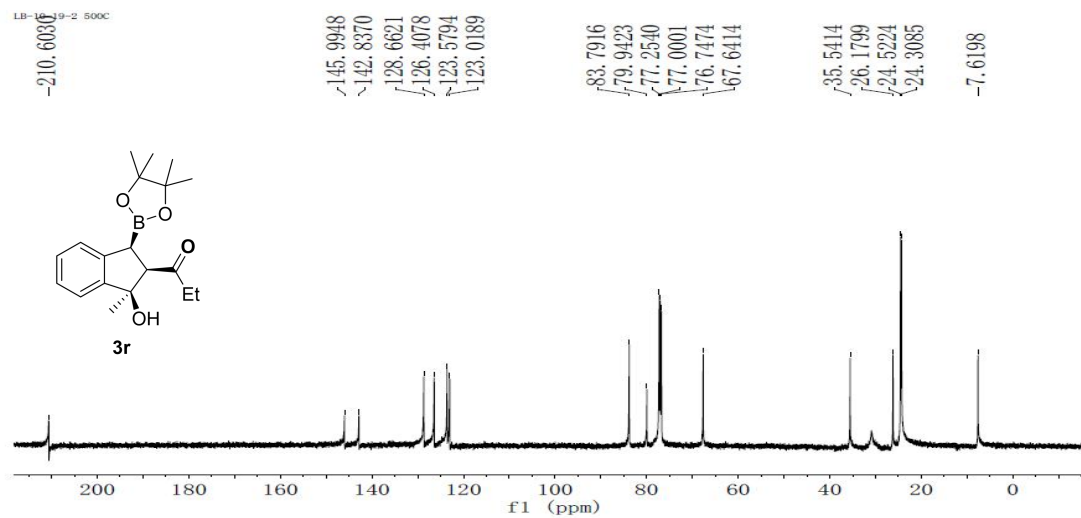


**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 3r**

1b-10-19-2

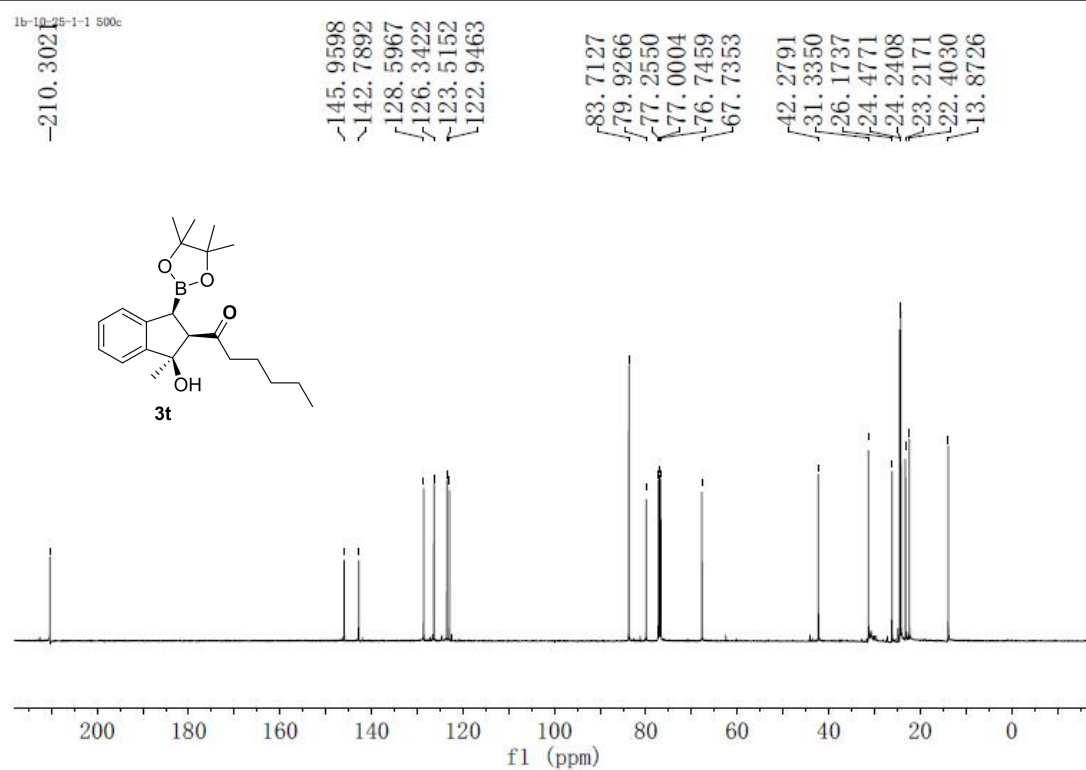
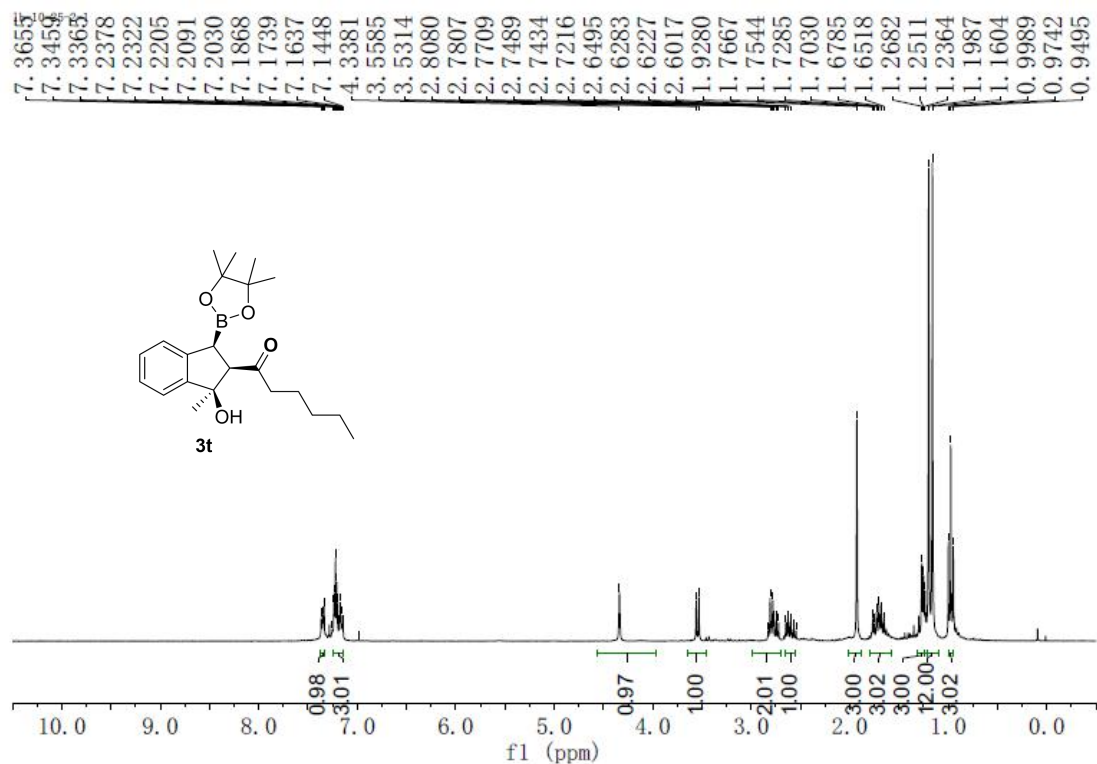


1b-10-19-2: 500C

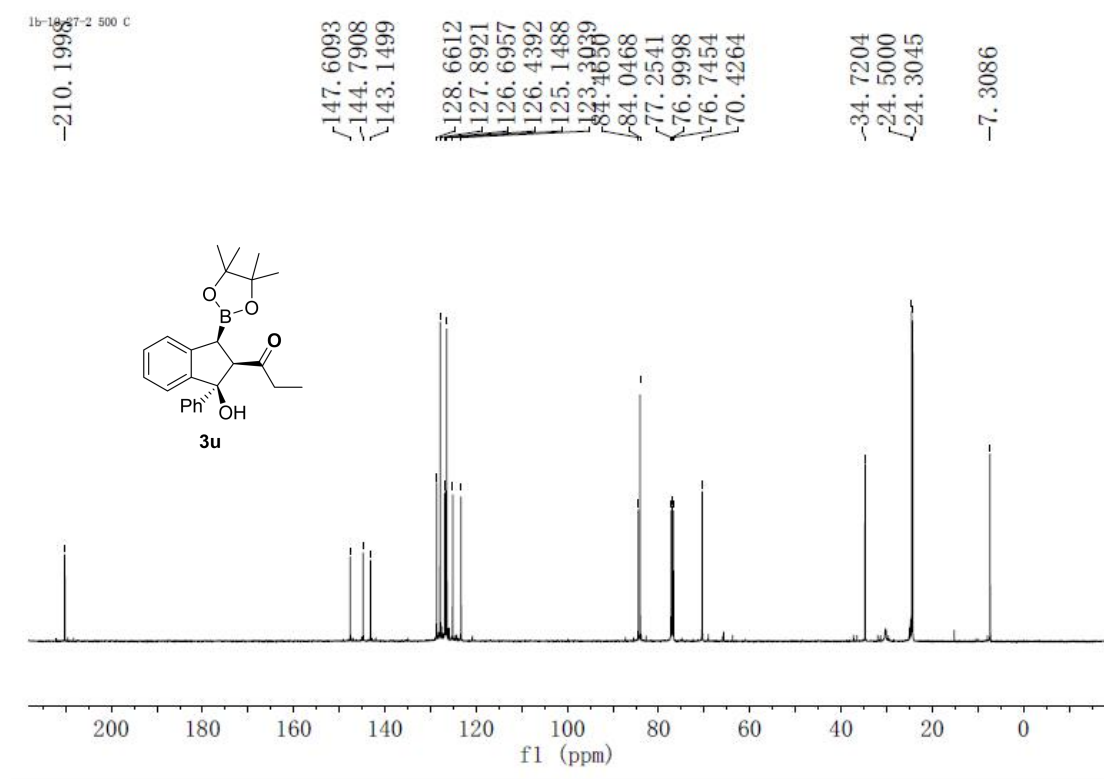
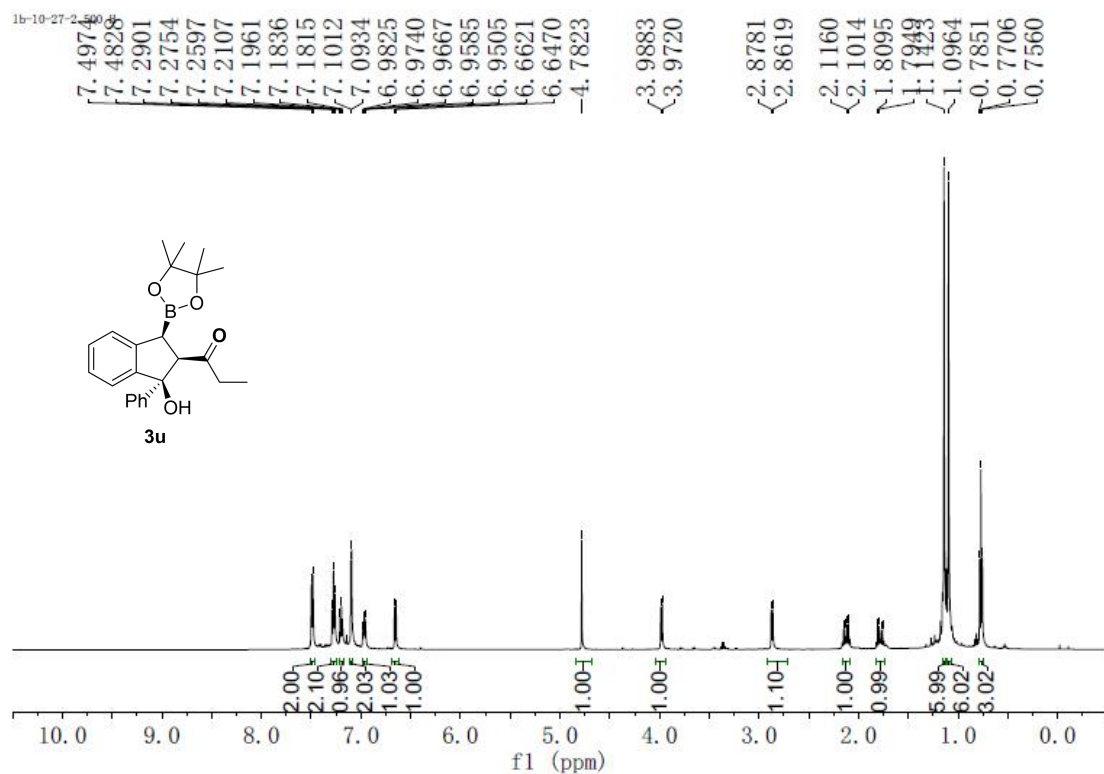




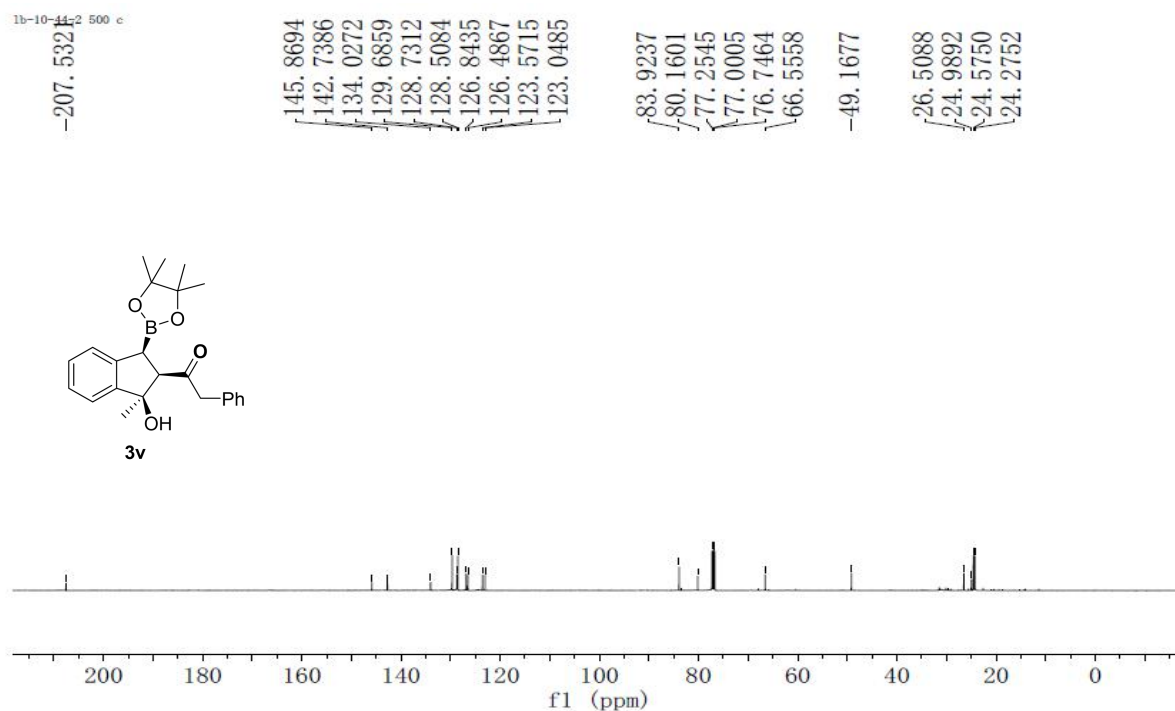
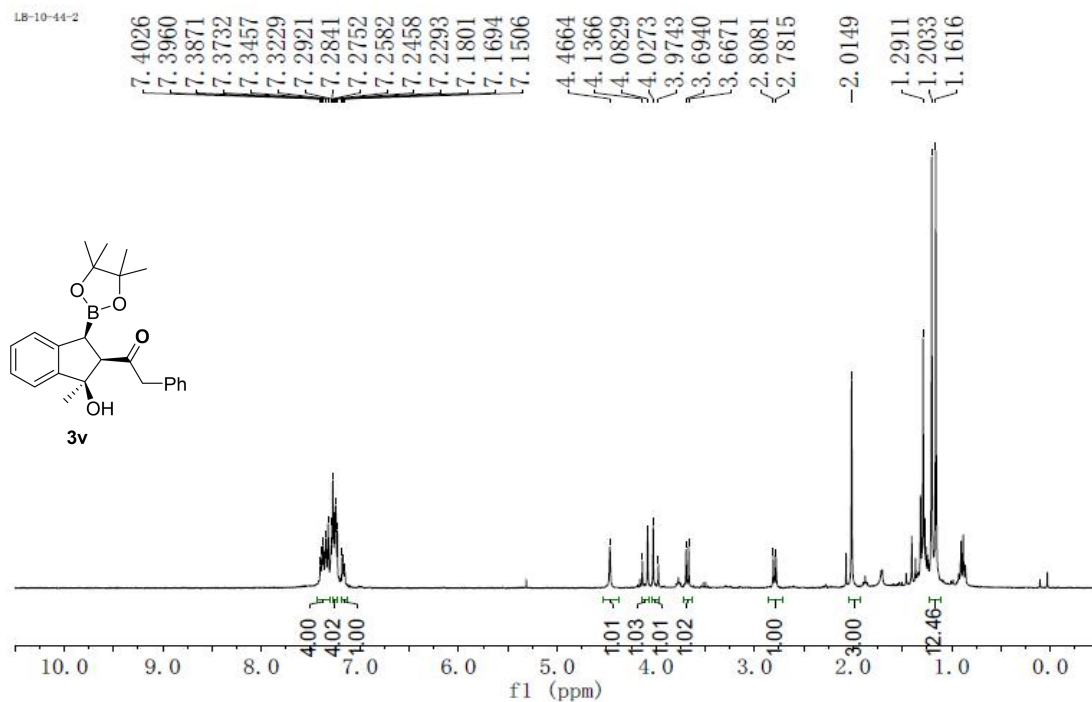
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of **3t**



**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of **3u****

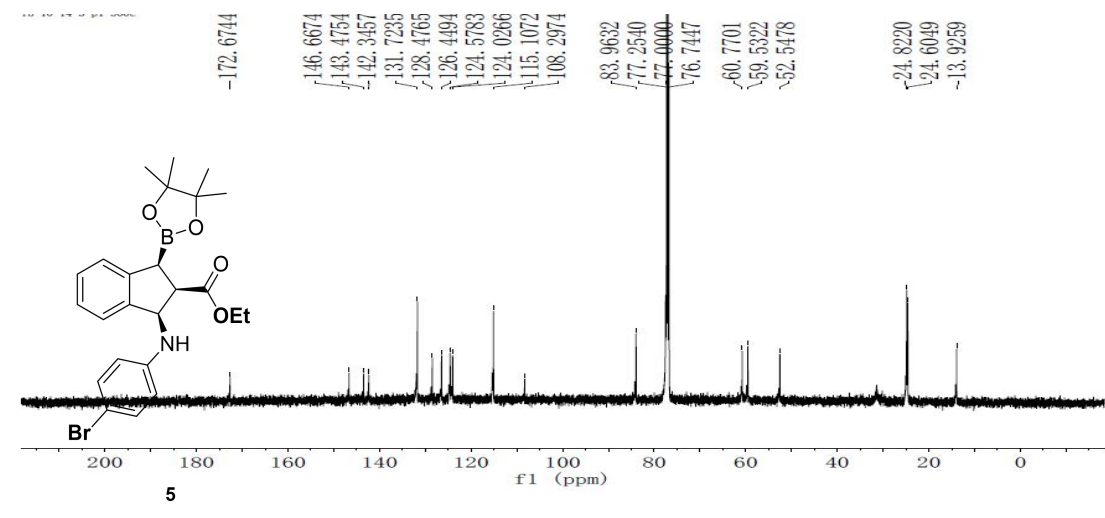
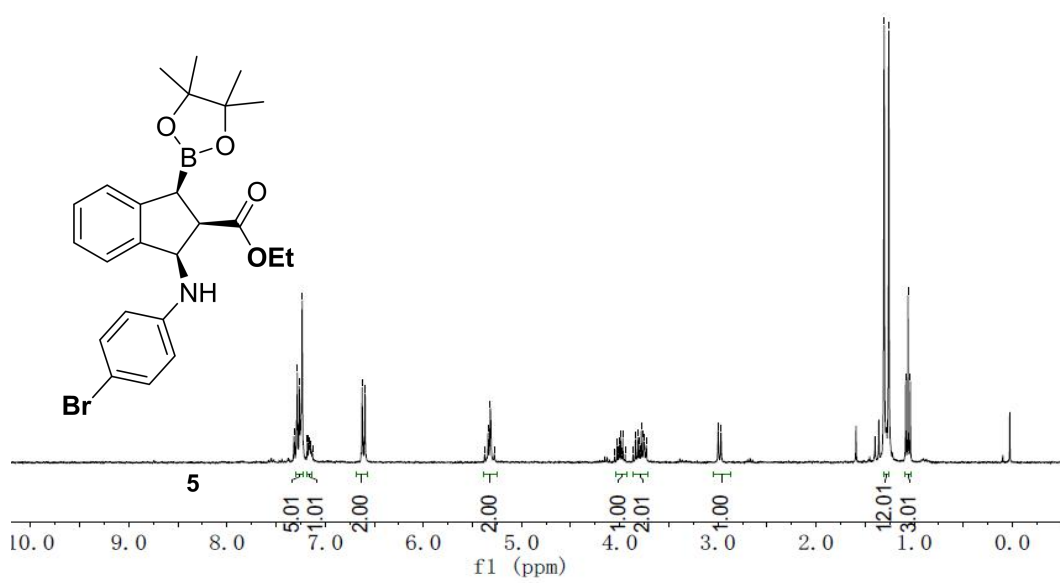


**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 3v**



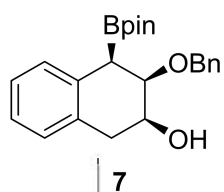
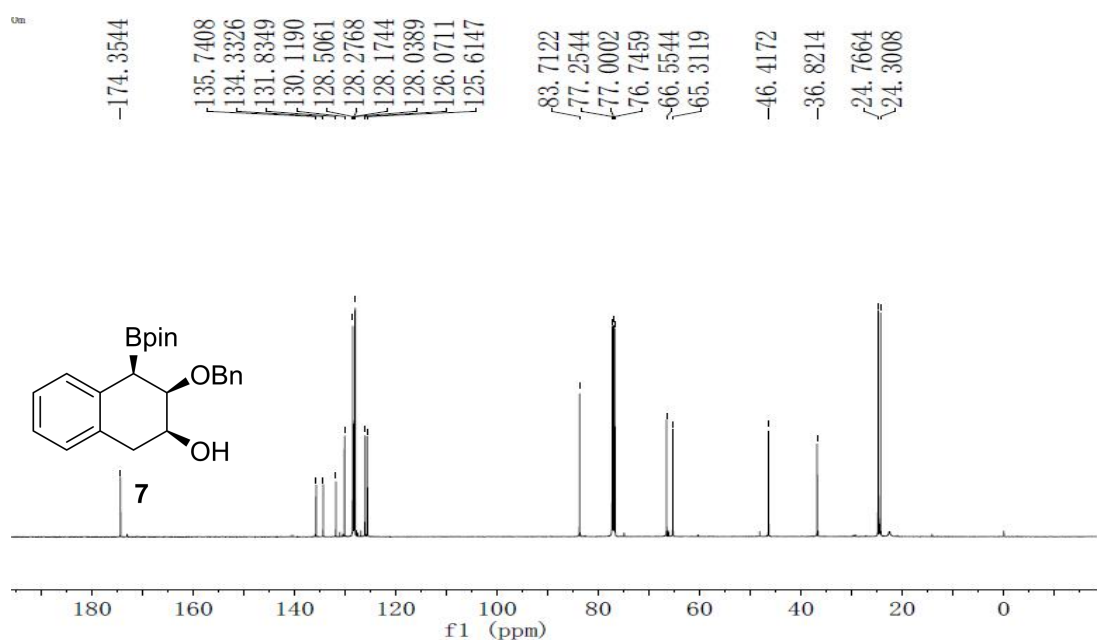
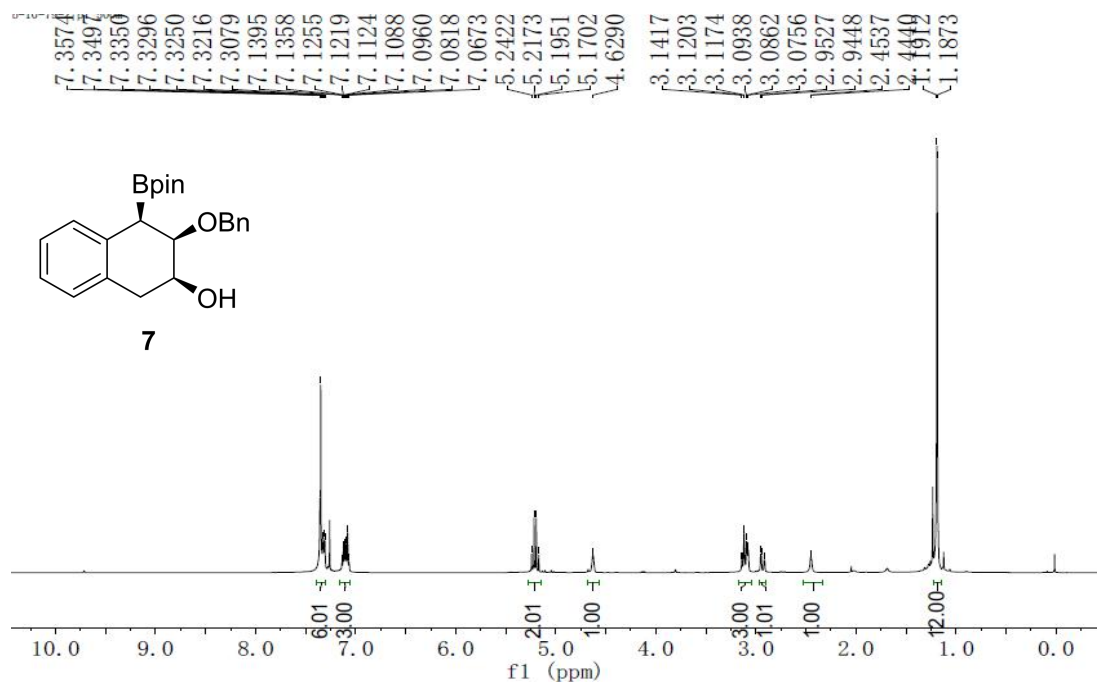
**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 5**

7.2919  
7.2839  
7.2638  
7.2417  
7.2341  
7.1815  
7.1705  
7.1569  
7.1455  
7.1286  
6.6231  
6.5936  
5.3760  
5.3398  
5.3183  
5.2780  
4.0276  
4.0158  
4.0039  
3.9920  
3.9807  
3.9683  
3.9445  
3.8633  
3.8397  
3.8159  
3.8040  
3.7919  
3.7799  
3.7569  
3.7505  
3.7287  
2.9969  
2.9684  
1.3063  
1.2593  
1.0868  
1.0630  
1.0393





<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of **7**



**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of **9****

