

## Electronic Supplementary Information

### Highly Diastereoselective Synthesis of Borylcyclopropanes by Copper-Catalyzed Borylcyclopropanation of Alkenes with Enynones

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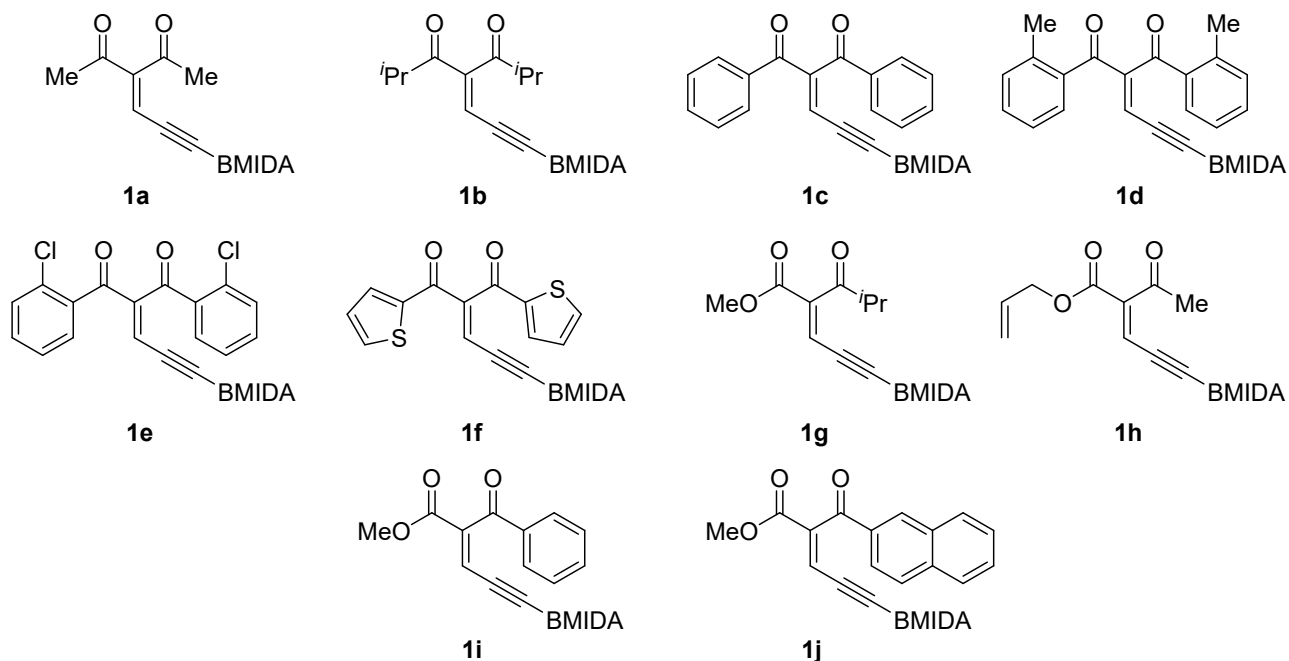
## 1. General Information

**General.** Unless otherwise noted, all reactions were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen with magnetic stirring. The oil bath acts as heat source for reactions that require heating. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230-400 mesh silica gel containing a fluorescent indicator. Visualization was accomplished by exposure to a UV lamp. All the products in this article are compatible with standard silica gel chromatography. Column chromatography was performed on silica gel (200-300 mesh) using standard methods.

**Structural Analysis.**  $^1\text{H}$  NMR and proton decoupled  $^{13}\text{C}$  NMR and  $^{11}\text{B}$  NMR spectra were recorded on Bruker Avance 500 MHz spectrometers at ambient temperature. NMR standards were used as follows:  $^1\text{H}$  NMR spectroscopy:  $\delta = 7.26$  ppm ( $\text{CDCl}_3$ ).  $^{13}\text{C}$  NMR spectroscopy:  $\delta = 77.16$  ppm ( $\text{CDCl}_3$ );  $^1\text{H}$  NMR spectroscopy:  $\delta = 1.94$  ppm ( $\text{CD}_3\text{CN}$ ).  $^{13}\text{C}$  NMR spectroscopy:  $\delta = 1.32$  ppm ( $\text{CD}_3\text{CN}$ );  $^1\text{H}$  NMR spectroscopy:  $\delta = 2.50$  ppm ( $\text{DMSO}-d_6$ ).  $^{13}\text{C}$  NMR spectroscopy:  $\delta = 39.52$  ppm ( $\text{DMSO}-d_6$ ). All  $^{13}\text{C}$  NMR signals are singlets unless noted otherwise. High-resolution mass spectra were recorded on Thermo Fisher Scientific Ultimate 3000-Q-Exactive instrument or Advion Mass Expression CMS instrument. X-ray diffraction analysis was recorded on a XtaLAB Synergy X-ray single crystal diffractometer. Chiral HPLC chromatography was performed with a Shimadzu LC-2050 HPLC system with Daicel CHIRALPAK AD-H column.

**Materials.** Solvents were distilled under nitrogen from calcium hydride or sodium/benzophenone. Reagents from commercial suppliers (*J&K*, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, Strem Chemicals, TCI, Bidepharm) were used without further purification. BMIDA-terminated Enynones **1** were prepared according to literature procedures. Alkenes **2** are available known compounds from commercial suppliers or prepared.

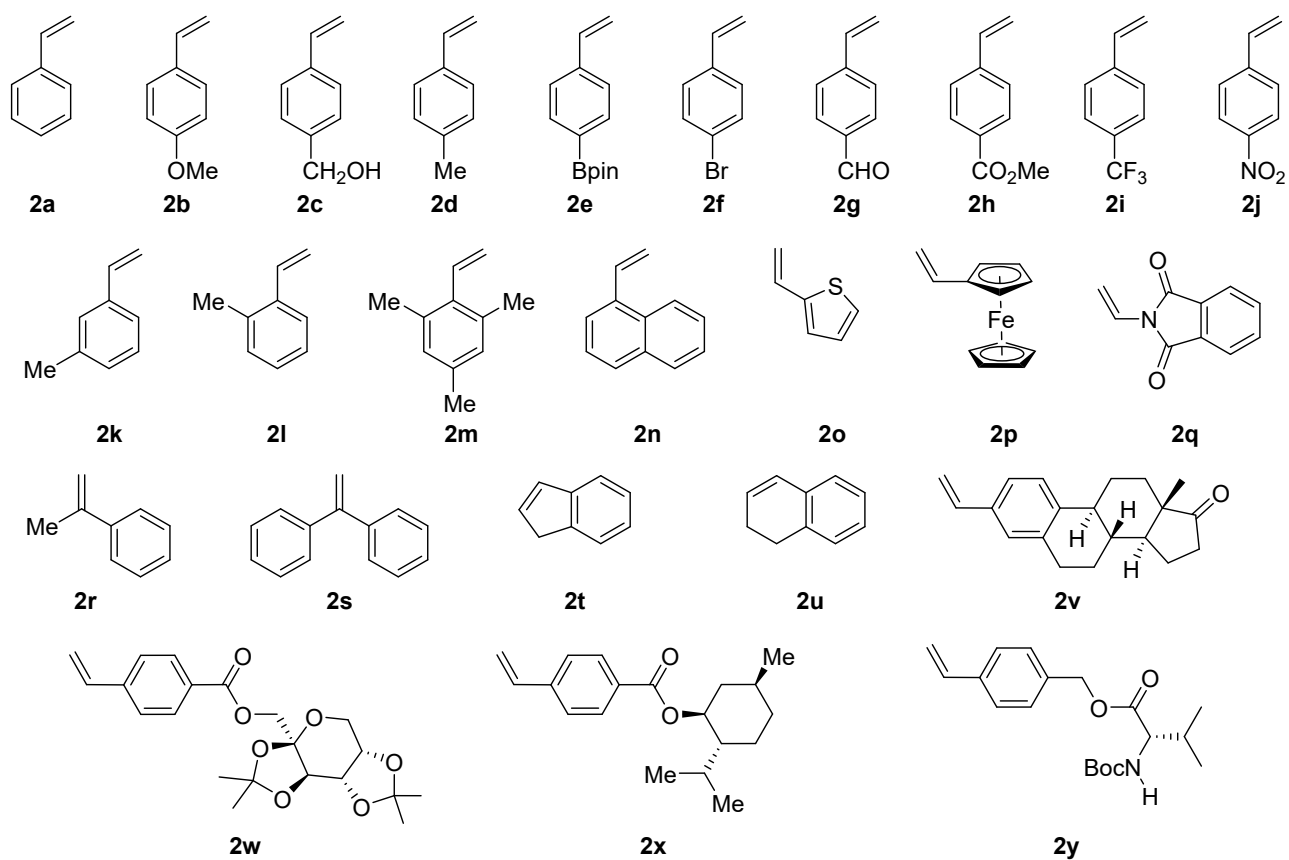
## 2. Structure of Starting BMIDA-terminated Enynes



**Figure S1.** Structure of Starting BMIDA-terminated Enynes

Enynes 1 were prepared according to literature procedures.<sup>[1]</sup>

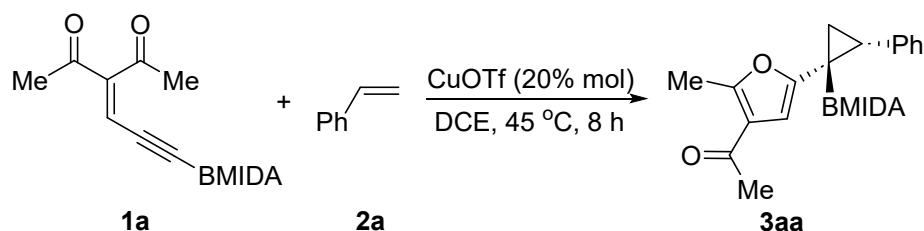
## 3. Structure of Starting Alkenes



**Figure S2.** Structure of Starting Alkenes

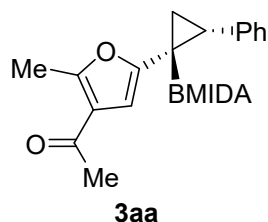
Alkenes **2a-2u** were known and available from commercial suppliers. Compounds **2v**<sup>[2]</sup>, **2w**<sup>[3]</sup>, **2x**<sup>[4]</sup>, **2y**<sup>[2]</sup> were known and prepared according to references.

#### 4. Typical Procedure for (1-(Furan-2-yl)cyclopropyl)borons

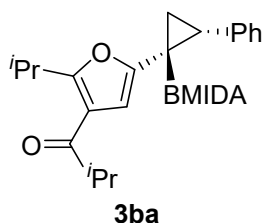


**Typical procedure:** A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, CuOTf (8.5 mg, 0.04 mmol, 0.2 eq.), **1a** (58.2 mg, 0.2 mmol, 1.0 eq.). After evacuation and refill with dry nitrogen for three times, DCE was added and the mixture was stirred at room temperature for 2 minutes. The styrene **2a** (125.0 mg, 1.2 mmol, 6.0 eq.) was injected into the Schlenk. The resulting mixture was stirred at 45 °C for 8 h. When cooled to room temperature, the mixture was concentrated using rotary evaporator. 1,3,5-trimethoxybenzene as the internal reference was added to detect the NMR yields and diastereomeric ratio (d.r.) by <sup>1</sup>H NMR. The product was purified by flash chromatography on silica gel (EA, R<sub>f</sub> = 0.20). The analytical data of the product **3aa** are listed below.

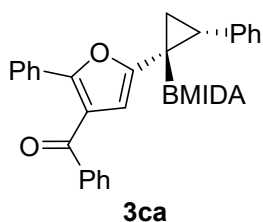
#### 5. Characterization of (1-(Furan-2-yl)cyclopropyl)borons



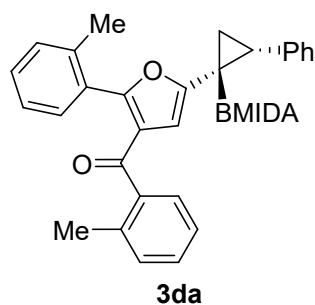
**2-((1R\*,2S\*)-1-(4-acetyl-5-methylfuran-2-yl)-2-phenylcyclopropyl)-6-methyl-1,3,6,2-dioxaboro-cane-4,8-dione (3aa)**, yellow solid, m.p. 172-173 °C (63.2 mg, 80% yield). EA, R<sub>f</sub> = 0.20. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN): δ 7.14-7.10 (m, 2H), 7.10-7.03 (m, 3H), 6.19 (s, 1H), 3.99 (d, J = 17.2 Hz, 1H), 3.94 (d, J = 17.2 Hz, 1H), 3.83 (d, J = 17.2 Hz, 1H), 3.49 (d, J = 17.0 Hz, 1H), 3.04 (s, 3H), 2.55-2.50 (m, 1H), 2.28 (s, 3H), 2.21 (s, 3H), 1.74-1.68 (m, 1H), 1.49-1.45 (m, 1H). <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN): δ 194.8, 169.0, 168.9, 157.2, 154.2, 139.3, 129.0, 128.6, 126.8, 122.9, 118.3, 110.2, 63.7, 63.6, 47.1, 29.4, 28.4, 15.1, 14.3. <sup>11</sup>B NMR (160 MHz, CD<sub>3</sub>CN) δ 11.3 (bs). HRMS (ESI, m/z) Calculated for [C<sub>21</sub>H<sub>26</sub>BN<sub>2</sub>O<sub>6</sub>, M + NH<sub>4</sub>]<sup>+</sup>: 413.1878, found: 413.1871.



**2-((1R\*,2S\*)-1-(4-isobutyryl-5-isopropylfuran-2-yl)-2-phenylcyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3ba)**, yellow solid, m.p. 92-93 °C (87.5 mg, 97% yield). PE/EA = 1:2,  $R_f$  = 0.20.  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.11-7.06 (m, 2H), 7.05-6.97 (m, 3H), 6.20 (s, 1H), 3.99 (d,  $J$  = 17.1 Hz, 1H), 3.95 (d,  $J$  = 17.0 Hz, 1H), 3.74 (d,  $J$  = 17.1 Hz, 1H), 3.46 (d,  $J$  = 6.4 Hz, 1H), 3.45-3.41 (m, 1H), 3.06 (s, 3H), 2.98-2.90 (m, 1H), 2.57-2.49 (m, 1H), 1.80-1.73 (m, 1H), 1.49-1.43 (m, 1H), 1.05 (d,  $J$  = 6.9 Hz, 3H), 0.98 (d,  $J$  = 6.9 Hz, 3H), 0.96 (d,  $J$  = 6.9 Hz, 3H), 0.86 (d,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  201.5, 168.9, 168.7, 165.8, 153.9, 139.4, 128.7, 128.5, 126.6, 119.3, 110.2, 63.5, 63.3, 46.8, 38.9, 28.0, 27.8, 26.0, 21.0, 20.6, 19.0, 18.7, 15.1.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.2 (bs). **HRMS** (ESI,  $m/z$ ) Calculated for  $[\text{C}_{25}\text{H}_{31}\text{BNO}_6, \text{M} + \text{H}]^+$ : 452.2239, found: 452.2234.

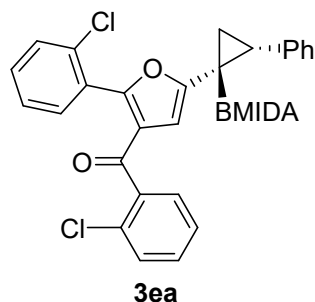


**2-((1R\*,2S\*)-1-(4-benzoyl-5-phenylfuran-2-yl)-2-phenylcyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3ca)**, white solid, m.p. 279-280 °C (61.4 mg, 59% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  7.62-7.02 (m, 15H), 6.02 (s, 1H), 4.31-4.24 (m, 2H), 3.95 (d,  $J$  = 15.9 Hz, 1H), 3.77 (d,  $J$  = 15.7 Hz, 1H), 3.02 (s, 3H), 2.55 (s, 1H), 1.94 (s, 1H), 1.42 (s, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  191.1, 168.7, 168.6, 154.2, 152.3, 138.3, 137.4, 133.1, 129.4, 129.2, 128.6, 128.5, 128.4, 128.3, 127.9, 127.6, 126.4, 125.8, 21.0, 121.0, 112.0, 62.7, 62.6, 27.5, 13.6.  $^{11}\text{B NMR}$  (160 MHz,  $\text{DMSO}-d_6$ )  $\delta$  11.6 (bs). **HRMS** (ESI,  $m/z$ ) Calculated for  $[\text{C}_{31}\text{H}_{27}\text{BNO}_6, \text{M} + \text{H}]^+$ : 520.1926, found: 520.1924.

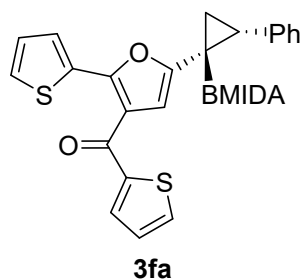


**6-methyl-2-((1R\*,2S\*)-1-(4-(2-methylbenzoyl)-5-(o-tolyl)furan-2-yl)-2-phenylcyclopropyl)-1,3,**

**6,2-dioxaborocane-4,8-dione (3da)**, red solid, m.p. 127-128 °C (85.4 mg, 78% yield). PE/EA = 1:2,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.20-7.12 (m, 5H), 7.10-7.03 (m, 4H), 7.01-6.94 (m, 3H), 6.90 (d,  $J = 7.6$  Hz, 1H), 6.23 (s, 1H), 3.98 (d,  $J = 10.8$  Hz, 1H), 3.95 (d,  $J = 10.6$  Hz, 1H), 3.77 (d,  $J = 17.2$  Hz, 1H), 3.54 (d,  $J = 17.0$  Hz, 1H), 3.03 (s, 3H), 2.63-2.58 (m, 1H), 2.09 (s, 3H), 1.89-1.84 (m, 1H), 1.83 (s, 3H), 1.51-1.45 (m, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  193.7, 168.9, 168.7, 157.8, 156.1, 140.0, 139.2, 138.4, 137.1, 131.5, 131.4, 131.1, 130.8, 130.7, 130.2, 129.2, 128.8, 128.7, 126.9, 125.9, 125.8, 125.2, 117.7, 63.5, 63.4, 47.1, 28.3, 19.9, 14.8.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.3 (bs). **HRMS** (ESI, m/z) Calculated for  $[\text{C}_{33}\text{H}_{31}\text{BNO}_6, \text{M} + \text{H}]^+$ : 548.2239, found: 548.2248.

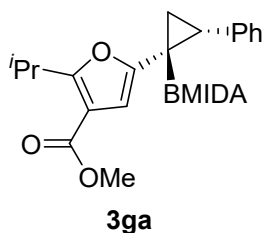


**2-((1R\*,2S\*)-1-(4-(2-chlorobenzoyl)-5-(2-chlorophenyl)furan-2-yl)-2-phenylcyclopropyl)-6-methyl-1,3,6,2-dioxaborocane-4,8-dione (3ea)**, yellow solid, m.p. 140-141 °C (81.2 mg, 69% yield). PE/EA = 1:2,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.21 (d,  $J = 3.7$  Hz, 2H), 7.18-7.05 (m, 10H), 6.99 (d,  $J = 7.8$  Hz, 1H), 6.34 (s, 1H), 3.99 (d,  $J = 7.1$  Hz, 1H), 3.96 (d,  $J = 7.0$  Hz, 1H), 3.80 (d,  $J = 17.2$  Hz, 1H), 3.55 (d,  $J = 17.1$  Hz, 1H), 3.05 (s, 3H), 2.63-2.58 (m, 1H), 1.89-1.84 (m, 1H), 1.54-1.47 (m, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  189.9, 168.8, 168.6, 157.4, 155.2, 139.3, 139.1, 134.5, 132.9, 132.3, 132.0, 131.3, 130.4, 129.9, 129.8, 128.8, 128.7, 127.4, 127.3, 126.9, 125.7, 110.8, 63.6, 63.5, 47.2, 28.4, 26.0, 15.2.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.4 (bs). **HRMS** (ESI, m/z) Calculated for  $[\text{C}_{31}\text{H}_{25}\text{BCl}_2\text{NO}_6, \text{M} + \text{H}]^+$ : 588.1147, found: 588.1138.

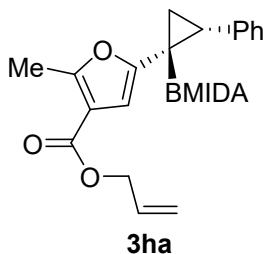


**6-methyl-2-((1R\*,2S\*)-2-phenyl-1-(5-(thiophen-2-yl)-4-(thiophene-2-carbonyl)furan-2-yl)cyclopropyl)-1,3,6,2-dioxaborocane-4,8-dione (3fa)**, yellow solid, m.p. 137-138 °C (82.9 mg, 78% yield). PE/EA = 1:2,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.78 (dd,  $J = 5.0, 1.1$  Hz, 1H), 7.61 (dd,  $J = 3.7, 1.1$  Hz, 1H), 7.41 (dd,  $J = 5.1, 1.1$  Hz, 1H), 7.24 (dd,  $J = 3.8, 1.1$  Hz, 1H), 7.16 (d,  $J = 4.4$  Hz, 4H), 7.16-7.10 (m, 1H), 7.09-7.02 (m, 1H), 7.07-7.00 (m, 1H), 6.30 (s, 1H), 4.03 (d,  $J = 17.3$  Hz, 1H), 3.98 (d,  $J = 17.1$  Hz, 1H), 3.86 (d,  $J = 17.2$  Hz, 1H), 3.64 (d,  $J = 17.1$  Hz, 1H), 3.09 (s, 3H),

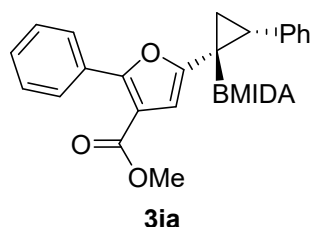
2.72-2.66 (m, 1H), 1.99-1.92 (m, 1H), 1.56-1.50 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  182.5, 169.0, 168.9, 155.2, 150.6, 145.3, 139.2, 135.5, 135.4, 132.4, 129.4, 129.2, 128.8, 128.6, 128.1, 127.0, 120.7, 112.7, 63.7, 47.3, 28.9, 26.0, 14.7.  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.5 (bs). HRMS (ESI,  $m/z$ ) Calculated for  $[\text{C}_{27}\text{H}_{23}\text{BNO}_6\text{S}_2, \text{M} + \text{H}]^+$ : 532.1055, found: 532.1050.



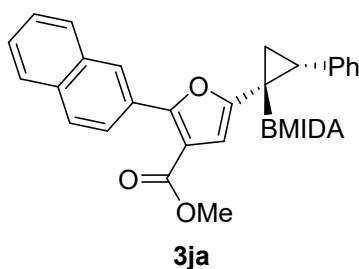
**Methyl-2-isopropyl-5-((1R\*,2S\*)-1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-phenylcyclopropyl)furan-3-carboxylate (3ga)**, red solid, m.p. 91-92 °C (86.1 mg, 98% yield). PE/EA = 1:2,  $R_f$  = 0.20.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.12-7.06 (m, 2H), 7.07-7.03 (m, 1H), 7.01 (d,  $J$  = 7.0 Hz, 2H), 6.12 (s, 1H), 3.98 (d,  $J$  = 17.2 Hz, 1H), 3.94 (d,  $J$  = 17.0 Hz, 1H), 3.73 (d,  $J$  = 17.1 Hz, 1H), 3.67 (s, 3H), 3.53-3.46 (m, 1H), 3.45 (d,  $J$  = 17.0 Hz, 1H), 3.03 (s, 3H), 2.52-2.47 (m, 1H), 1.77-1.70 (m, 1H), 1.49-1.42 (m, 1H), 1.08 (d,  $J$  = 7.0 Hz, 3H), 0.90 (d,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  168.9, 168.7, 166.6, 164.9, 154.3, 139.5, 128.8, 128.6, 126.7, 112.3, 110.1, 63.5, 63.3, 51.7, 46.8, 28.0, 27.6, 26.0, 21.0, 20.7, 15.1.  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.5 (bs). HRMS (ESI,  $m/z$ ) Calculated for  $[\text{C}_{23}\text{H}_{30}\text{BN}_2\text{O}_7, \text{M} + \text{NH}_4]^+$ : 457.2140, found: 457.2127.



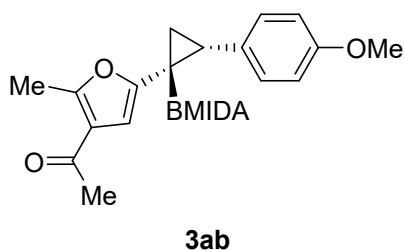
**Allyl-2-methyl-5-((1R\*,2S\*)-1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-phenylcyclopropyl)furan-3-carboxylate (3ha)**, yellow solid, m.p. 203-204 °C (53.3 mg, 61% yield). PE/EA = 1:3,  $R_f$  = 0.20.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.15-7.10 (m, 2H), 7.09-7.02 (m, 3H), 6.10 (s, 1H), 6.00-5.93 (m, 1H), 5.29 (dd,  $J$  = 17.2, 1.6 Hz, 1H), 5.21 (dd,  $J$  = 10.6, 1.4 Hz, 1H), 4.63-4.60 (m, 2H), 3.98 (d,  $J$  = 17.2 Hz, 1H), 3.94 (d,  $J$  = 17.0 Hz, 1H), 3.82 (d,  $J$  = 17.2 Hz, 1H), 3.48 (d,  $J$  = 17.0 Hz, 1H), 3.01 (s, 3H), 2.56-2.51 (m, 1H), 2.30 (s, 3H), 1.77-1.70 (m, 1H), 1.48-1.42 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  169.0, 168.9, 164.1, 158.6, 154.5, 139.3, 133.7, 128.9, 128.6, 126.8, 118.1, 114.3, 109.8, 65.3, 63.6, 63.5, 47.0, 28.4, 26.0, 14.9, 13.8.  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.4 (bs). HRMS (ESI,  $m/z$ ) Calculated for  $[\text{C}_{23}\text{H}_{28}\text{BNO}_7\text{Na}, \text{M} + \text{NH}_4]^+$ : 455.1984, found: 455.1973.



**Methyl-5-((1R\*,2S\*)-1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-phenylcyclopropyl)-2-phenylfuran-3-carboxylate (3ia)**, green solid, m.p. 116-117 °C (80.4 mg, 85% yield). PE/EA = 1:2,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.65-7.59 (m, 2H), 7.45-7.30 (m, 3H), 7.16-7.01 (m, 5H), 6.37 (s, 1H), 3.98 (d,  $J = 17.2$  Hz, 1H), 3.94 (d,  $J = 17.0$  Hz, 1H), 3.78 (d,  $J = 17.2$  Hz, 1H), 3.70 (s, 3H), 3.54 (d,  $J = 17.0$  Hz, 1H), 3.04 (s, 3H), 2.64-2.58 (m, 1H), 1.90-1.83 (m, 1H), 1.54-1.49 (m, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  168.9, 168.8, 164.6, 156.4, 155.7, 139.3, 130.6, 129.0, 128.9, 128.8, 128.6, 126.9, 114.9, 112.6, 63.6, 63.5, 52.1, 47.1, 28.4, 15.0.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.5 (bs). **HRMS** (ESI,  $m/z$ ) Calculated for  $[\text{C}_{26}\text{H}_{28}\text{BN}_2\text{O}_7, \text{M} + \text{NH}_4]^+$ : 491.1984, found: 491.1974.

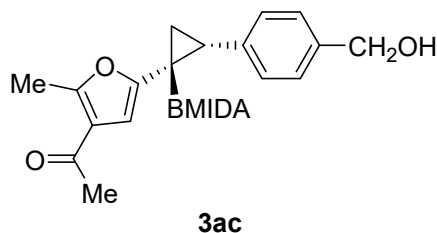


**Methyl-5-((1R\*,2S\*)-1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-phenylcyclopropyl)-2-(naphthalen-2-yl)furan-3-carboxylate (3ja)**, white solid, m.p. 134-135 °C (99.4 mg, 95% yield). PE/EA = 1:2,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  8.20 (s, 1H), 7.92-7.89 (m, 1H), 7.89-7.83 (m, 2H), 7.82-7.76 (m, 1H), 7.58-7.50 (m, 2H), 7.14 (d,  $J = 4.4$  Hz, 4H), 7.08-7.03 (m, 1H), 6.44 (s, 1H), 3.99 (d,  $J = 17.2$  Hz, 1H), 3.96 (d,  $J = 17.1$  Hz, 1H), 3.78 (d,  $J = 17.2$  Hz, 1H), 3.73 (s, 3H), 3.57 (d,  $J = 17.1$  Hz, 1H), 3.05 (s, 3H), 2.70-2.63 (m, 1H), 1.93-1.88 (m, 1H), 1.57-1.52 (m, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  169.0, 168.9, 164.6, 156.4, 156.0, 139.3, 134.1, 133.7, 129.4, 128.9, 128.7, 128.5, 128.4, 128.3, 128.0, 127.9, 127.6, 126.9, 126.2, 118.3, 115.3, 112.8, 63.6, 63.5, 52.1, 47.1, 28.5, 15.1.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.4 (bs). **HRMS** (ESI,  $m/z$ ) Calculated for  $[\text{C}_{30}\text{H}_{30}\text{BN}_2\text{O}_7, \text{M} + \text{NH}_4]^+$ : 541.2140, found: 541.2138.

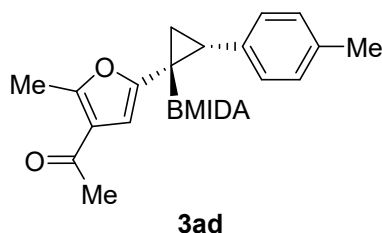


**2-((1R\*,2S\*)-1-(4-acetyl-5-methylfuran-2-yl)-2-(4-methoxyphenyl)cyclopropyl)-6-methyl-1,3,6,**

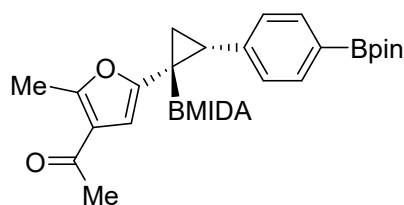
**2-dioxazaborocane-4,8-dione (3ab)**, yellow solid, m.p. 111-112 °C (56.1 mg, 66% yield). EA,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  6.97 (d,  $J = 8.7$  Hz, 2H), 6.68 (d,  $J = 8.7$  Hz, 2H), 6.18 (s, 1H), 3.99 (d,  $J = 17.2$  Hz, 1H), 3.96 (d,  $J = 17.0$  Hz, 1H), 3.83 (d,  $J = 17.2$  Hz, 1H), 3.68 (s, 3H), 3.49 (d,  $J = 17.0$  Hz, 1H), 3.03 (s, 3H), 2.50-2.45 (m, 1H), 2.30 (s, 3H), 2.22 (s, 3H), 1.67-1.62 (m, 1H), 1.46-1.40 (m, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.8, 169.0, 168.9, 158.9, 157.2, 154.5, 131.1, 130.0, 122.9, 114.0, 110.0, 63.7, 63.6, 55.7, 47.1, 29.3, 27.8, 15.1, 14.3.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.2 (bs). **HRMS** (ESI,  $m/z$ ) Calculated for  $[\text{C}_{22}\text{H}_{25}\text{BNO}_7, \text{M} + \text{H}]^+$ : 426.1719, found: 426.1712.



**2-((1R\*,2S\*)-1-(4-acetyl-5-methylfuran-2-yl)-2-(4-(hydroxymethyl)phenyl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3ac)**, yellow solid, m.p. 125-126 °C (66.3 mg, 78% yield). EA,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.09 (d,  $J = 8.1$  Hz, 2H), 7.02 (d,  $J = 8.2$  Hz, 2H), 6.21 (s, 1H), 4.44 (d,  $J = 5.1$  Hz, 2H), 3.99 (d,  $J = 17.2$  Hz, 1H), 3.95 (d,  $J = 17.1$  Hz, 1H), 3.83 (d,  $J = 17.1$  Hz, 1H), 3.49 (d,  $J = 17.2$  Hz, 1H), 3.13-3.07 (m, 1H), 3.04 (s, 3H), 2.54-2.49 (m, 1H), 2.29 (s, 3H), 2.21 (s, 3H), 1.73-1.68 (m, 1H), 1.50-1.45 (m, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.9, 169.0, 168.9, 157.2, 154.2, 140.6, 138.0, 128.9, 127.1, 110.1, 64.4, 63.7, 63.6, 47.1, 29.3, 28.2, 15.3, 14.3.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.1 (bs). **HRMS** (ESI,  $m/z$ ) Calculated for  $[\text{C}_{22}\text{H}_{28}\text{BN}_2\text{O}_7, \text{M} + \text{NH}_4]^+$ : 443.1984, found: 443.1982.

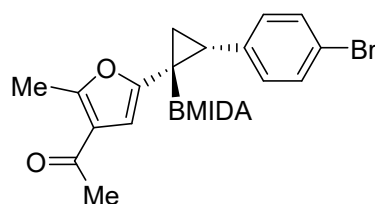


**2-((1R\*,2S\*)-1-(4-acetyl-5-methylfuran-2-yl)-2-(p-tolyl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3ad)**, yellow solid, m.p. 116-117 °C (76.9 mg, 94% yield). EA,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  6.94 (s, 4H), 6.20 (s, 1H), 4.01 (d,  $J = 17.2$  Hz, 1H), 3.96 (d,  $J = 17.1$  Hz, 1H), 3.84 (d,  $J = 17.2$  Hz, 1H), 3.51 (d,  $J = 17.1$  Hz, 1H), 3.05 (s, 3H), 2.52-2.47 (m, 1H), 2.30 (s, 3H), 2.22 (s, 3H), 2.20 (s, 3H), 1.70-1.65 (m, 1H), 1.49-1.43 (m, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.8, 169.0, 168.9, 157.2, 154.3, 136.2, 136.1, 129.3, 128.9, 122.9, 110.0, 63.7, 63.6, 47.1, 29.4, 28.2, 21.0, 15.1, 14.3.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.2 (bs). **HRMS** (ESI,  $m/z$ ) Calculated for  $[\text{C}_{22}\text{H}_{25}\text{BNO}_6, \text{M} + \text{H}]^+$ : 410.1770, found: 410.1773.



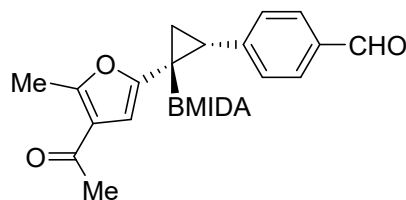
**3ae**

**2-((1R\*,2S\*)-1-(4-acetyl-5-methylfuran-2-yl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3ae)**, yellow solid, m.p. 146-147 °C (80.3 mg, 77% yield). EA,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.46 (d,  $J = 8.1$  Hz, 2H), 7.05 (d,  $J = 8.1$  Hz, 2H), 6.21 (s, 1H), 3.99 (d,  $J = 17.2$  Hz, 1H), 3.95 (d,  $J = 17.1$  Hz, 1H), 3.82 (d,  $J = 17.2$  Hz, 1H), 3.50 (d,  $J = 17.1$  Hz, 1H), 3.03 (s, 3H), 2.57-2.52 (m, 1H), 2.23 (s, 3H), 2.22 (s, 3H), 1.79-1.73 (m, 1H), 1.52-1.46 (m, 1H), 1.28 (s, 12H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.8, 169.0, 168.9, 157.3, 154.0, 143.0, 134.8, 128.4, 122.9, 110.3, 84.6, 63.7, 63.6, 47.1, 29.4, 28.6, 25.2, 25.1, 15.3, 14.3.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  31.0, 11.2 (bs). **HRMS** (ESI, m/z) Calculated for  $[\text{C}_{27}\text{H}_{37}\text{B}_2\text{N}_2\text{O}_8, \text{M} + \text{NH}_4]^+$ : 539.2730, found: 539.2730.



**3af**

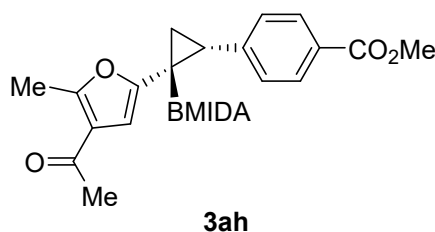
**2-((1R\*,2S\*)-1-(4-acetyl-5-methylfuran-2-yl)-2-(4-bromophenyl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3af)**, yellow solid, m.p. 125-126 °C (71.9 mg, 76% yield). EA,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.26 (d,  $J = 8.4$  Hz, 2H), 6.96 (d,  $J = 8.4$  Hz, 2H), 6.23 (s, 1H), 4.00 (d,  $J = 17.2$  Hz, 1H), 3.95 (d,  $J = 17.1$  Hz, 1H), 3.83 (d,  $J = 17.2$  Hz, 1H), 3.47 (d,  $J = 17.1$  Hz, 1H), 3.02 (s, 3H), 2.53-2.48 (m, 1H), 2.29 (s, 3H), 2.23 (s, 3H), 1.73-1.68 (m, 1H), 1.51-1.46 (m, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.8, 169.0, 168.9, 157.4, 153.7, 138.8, 131.5, 130.8, 122.8, 120.0, 110.4, 63.6, 63.5, 47.0, 29.4, 27.8, 15.2, 14.3.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.3 (bs). **HRMS** (ESI, m/z) Calculated for  $[\text{C}_{21}\text{H}_{22}\text{BBrNO}_6, \text{M} + \text{H}]^+$ : 474.0718, found: 474.0718.



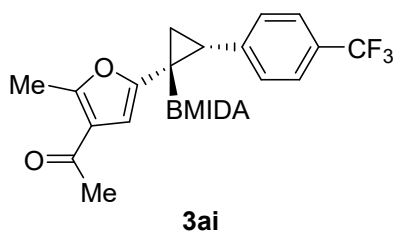
**3ag**

**4-((1S\*,2R\*)-2-(4-acetyl-5-methylfuran-2-yl)-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)cyclopropyl)benzaldehyde (3ag)**, yellow solid, m.p. 125-126 °C (46.5 mg, 55% yield). EA,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  9.85 (s, 1H), 7.63 (d,  $J = 8.2$  Hz, 2H), 7.22 (d,  $J = 8.2$  Hz, 2H), 6.28 (s, 1H), 4.01 (d,  $J = 17.2$  Hz, 1H), 3.96 (d,  $J = 17.1$  Hz, 1H), 3.83 (d,  $J = 17.2$  Hz, 1H),

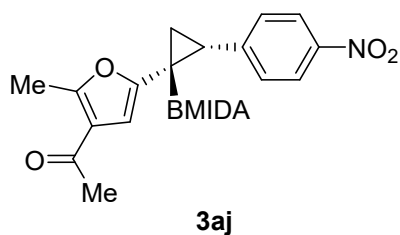
3.47 (d,  $J = 17.1$  Hz, 1H), 3.03 (s, 3H), 2.65-2.60 (m, 1H), 2.26 (s, 3H), 2.22 (s, 3H), 1.87-1.82 (m, 1H), 1.60-1.53 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.8, 193.1, 169.0, 168.8, 157.6, 153.4, 147.2, 135.5, 129.8, 129.3, 122.8, 110.7, 63.6, 47.0, 29.4, 28.6, 15.9, 14.3.  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.1 (bs). HRMS (ESI,  $m/z$ ) Calculated for  $[\text{C}_{22}\text{H}_{23}\text{BNO}_7, \text{M} + \text{H}]^+$ : 424.1562, found: 424.1569.



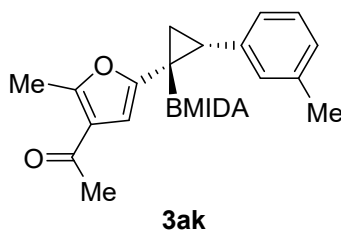
**Methyl-4-((1S\*,2R\*)-2-(4-acetyl-5-methylfuran-2-yl)-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)cyclopropyl)benzoate (3ah)**, yellow solid, m.p. 124-125 °C (61.6 mg, 68% yield). EA,  $R_f = 0.20$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.73 (d,  $J = 8.2$  Hz, 2H), 7.13 (d,  $J = 8.2$  Hz, 2H), 6.26 (s, 1H), 4.01 (d,  $J = 17.2$  Hz, 1H), 3.95 (d,  $J = 17.1$  Hz, 1H), 3.84 (d,  $J = 17.2$  Hz, 1H), 3.79 (s, 3H), 3.48 (d,  $J = 17.1$  Hz, 1H), 3.03 (s, 3H), 2.62-2.57 (m, 1H), 2.26 (s, 3H), 2.21 (s, 3H), 1.84-1.79 (m, 1H), 1.59-1.52 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.8, 168.9, 168.8, 167.6, 157.5, 153.5, 145.3, 129.5, 128.8, 128.7, 122.8, 110.6, 63.6, 52.5, 47.0, 29.4, 28.4, 15.7, 14.2.  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.1 (bs). HRMS (ESI,  $m/z$ ) Calculated for  $[\text{C}_{23}\text{H}_{25}\text{BNO}_8, \text{M} + \text{H}]^+$ : 454.1668, found: 454.1667.



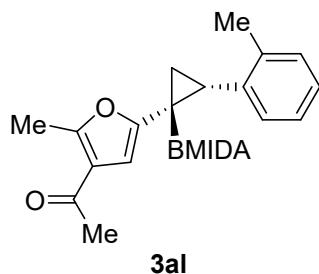
**2-((1R\*,2S\*)-1-(4-acetyl-5-methylfuran-2-yl)-2-(4-(trifluoromethyl)phenyl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3ai)**, yellow solid, m.p. 116-117 °C (50.0 mg, 54% yield). EA,  $R_f = 0.20$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.95 (d,  $J = 8.8$  Hz, 2H), 7.22 (d,  $J = 8.8$  Hz, 2H), 6.31 (s, 1H), 4.00 (d,  $J = 17.2$  Hz, 1H), 3.95 (d,  $J = 17.1$  Hz, 1H), 3.83 (d,  $J = 17.2$  Hz, 1H), 3.46 (d,  $J = 17.1$  Hz, 1H), 3.02 (s, 3H), 2.69-2.64 (m, 1H), 2.26 (s, 3H), 2.22 (s, 3H), 1.89-1.84 (m, 1H), 1.64-1.57 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.8, 169.0, 157.5, 153.4, 129.3, 128.2 (q,  $J = 32.2$  Hz), 125.6 (q,  $J = 271.2$  Hz), 125.3 (q,  $J = 3.7$  Hz), 110.7, 63.4, 47.0, 29.4, 28.1, 15.6, 14.2.  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.2 (bs). HRMS (ESI,  $m/z$ ) Calculated for  $[\text{C}_{22}\text{H}_{22}\text{BF}_3\text{NO}_6, \text{M} + \text{H}]^+$ : 464.1487, found: 464.1489.



**2-((1R\*,2S\*)-1-(4-acetyl-5-methylfuran-2-yl)-2-(4-nitrophenyl)cyclopropyl)-6-methyl-1,3,6,2-dioxaborocane-4,8-dione (3aj)**, yellow solid, m.p. 137-138 °C (27.3 mg, 31% yield). EA,  $R_f$  = 0.20.  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.95 (d,  $J$  = 8.2 Hz, 2H), 7.22 (d,  $J$  = 8.2 Hz, 2H), 6.31 (s, 1H), 4.01 (d,  $J$  = 17.2 Hz, 1H), 3.95 (d,  $J$  = 17.1 Hz, 1H), 3.75 (d,  $J$  = 17.2 Hz, 1H), 3.46 (d,  $J$  = 17.1 Hz, 1H), 3.02 (s, 3H), 2.68-2.63 (m, 1H), 2.26 (s, 3H), 2.22 (s, 3H), 1.87-1.83 (m, 1H), 1.62-1.58 (m, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.8, 169.0, 168.8, 157.8, 153.0, 148.2, 147.1, 129.4, 123.6, 122.8, 110.1, 63.7, 63.6, 47.0, 29.4, 28.3, 16.3, 14.2.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.0 (bs). **HRMS** (ESI,  $m/z$ ) Calculated for  $[\text{C}_{21}\text{H}_{22}\text{BN}_2\text{O}_8, \text{M} + \text{H}]^+$ : 441.1464, found: 441.1464.

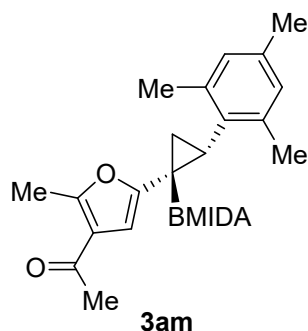


**2-((1R\*,2S\*)-1-(4-acetyl-5-methylfuran-2-yl)-2-(m-tolyl)cyclopropyl)-6-methyl-1,3,6,2-dioxaborocane-4,8-dione (3ak)**, yellow solid, m.p. 105-106 °C (70.4 mg, 86% yield). EA,  $R_f$  = 0.20.  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.04-6.97 (m, 1H), 6.89 (s, 2H), 6.83 (d,  $J$  = 7.6 Hz, 1H), 6.20 (s, 1H), 4.00 (d,  $J$  = 17.2 Hz, 1H), 3.96 (d,  $J$  = 17.0 Hz, 1H), 3.84 (d,  $J$  = 17.2 Hz, 1H), 3.50 (d,  $J$  = 17.0 Hz, 1H), 3.04 (s, 3H), 2.53-2.48 (m, 1H), 2.30 (s, 3H), 2.22 (s, 3H), 2.20 (s, 3H), 1.74-1.69 (m, 1H), 1.49-1.43 (m, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.8, 169.0, 168.9, 157.1, 154.2, 139.1, 138.1, 129.7, 128.5, 127.5, 125.9, 122.8, 110.1, 63.7, 63.6, 47.1, 29.4, 28.5, 21.4, 17.6, 15.1, 14.3.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.2 (bs). **HRMS** (ESI,  $m/z$ ) Calculated for  $[\text{C}_{22}\text{H}_{25}\text{BNO}_6, \text{M} + \text{H}]^+$ : 410.1760, found: 410.1766.

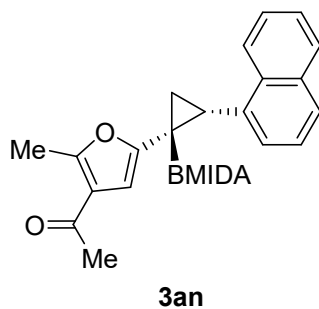


**2-((1R\*,2S\*)-1-(4-acetyl-5-methylfuran-2-yl)-2-(o-tolyl)cyclopropyl)-6-methyl-1,3,6,2-dioxaborocane-4,8-dione (3al)**, yellow solid, m.p. 220-221 °C (72.0 mg, 88% yield). EA,  $R_f$  = 0.20.  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.04 (d,  $J$  = 7.3 Hz, 1H), 7.02-6.96 (m, 1H), 6.94 (d,  $J$  = 4.3 Hz, 2H),

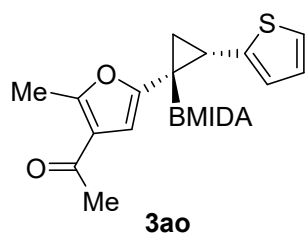
6.04 (s, 1H), 4.04 (d,  $J = 17.5$  Hz, 1H), 3.94-3.89 (m, 2H), 3.34 (d,  $J = 16.9$  Hz, 1H), 2.91 (s, 3H), 2.52-2.47 (m, 1H), 2.43 (s, 3H), 2.25 (s, 3H), 2.14 (s, 3H), 1.89-1.84 (m, 1H), 1.39-1.33 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.7, 169.5, 168.7, 156.9, 154.3, 139.8, 137.1, 130.0, 128.2, 127.1, 125.8, 122.8, 108.8, 63.9, 63.4, 46.9, 29.3, 27.8, 19.9, 14.3, 13.3.  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.1 (bs). HRMS (ESI,  $m/z$ ) Calculated for  $[\text{C}_{22}\text{H}_{25}\text{BNO}_6, \text{M} + \text{H}]^+$ : 410.1770, found: 410.1767.



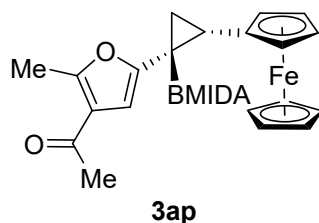
**2-((1R\*,2S\*)-1-(4-acetyl-5-methylfuran-2-yl)-2-mesitylcyclopropyl)-6-methyl-1,3,6,2-dioxaborocane-4,8-dione (3am)**, yellow solid, m.p. 118-119 °C (37.6 mg, 43% yield). EA,  $R_f = 0.20$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  6.67 (s, 2H), 5.81 (s, 1H), 4.04 (d,  $J = 17.4$  Hz, 1H), 3.97 (d,  $J = 16.9$  Hz, 1H), 3.90 (d,  $J = 17.4$  Hz, 1H), 3.53 (d,  $J = 16.9$  Hz, 1H), 2.85 (s, 3H), 2.37-2.32 (m, 7H), 2.29 (s, 3H), 2.12 (s, 6H), 1.79-1.73 (m, 1H), 1.58-1.52 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.7, 169.5, 169.0, 156.5, 155.4, 136.2, 132.6, 129.4, 123.0, 107.2, 64.2, 63.8, 47.2, 29.3, 27.8, 20.8, 18.8, 14.3.  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.2 (bs). HRMS (ESI,  $m/z$ ) Calculated for  $[\text{C}_{24}\text{H}_{29}\text{BNO}_6, \text{M} + \text{H}]^+$ : 438.2083, found: 438.2078.



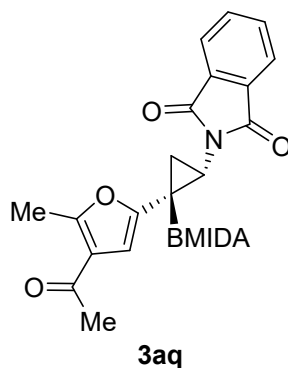
**2-((1R\*,2S\*)-1-(4-acetyl-5-methylfuran-2-yl)-2-(naphthalen-1-yl)cyclopropyl)-6-methyl-1,3,6,2-dioxaborocane-4,8-dione (3an)**, yellow solid, m.p. 135-136 °C (72.1 mg, 81% yield). EA,  $R_f = 0.20$ .  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  8.40 (d,  $J = 8.0$  Hz, 1H), 7.82 (d,  $J = 7.7$  Hz, 1H), 7.65 (d,  $J = 7.7$  Hz, 1H), 7.58 (d,  $J = 7.0$  Hz, 1H), 7.49 (d,  $J = 7.2$  Hz, 1H), 7.31-7.26 (m, 1H), 7.20 (d,  $J = 5.9$  Hz, 1H), 5.89 (s, 1H), 4.43 (d,  $J = 17.4$  Hz, 1H), 4.21 (d,  $J = 17.0$  Hz, 1H), 4.12 (d,  $J = 17.4$  Hz, 1H), 3.57 (d,  $J = 17.0$  Hz, 1H), 2.90 (s, 3H), 2.83 (s, 1H), 2.08 (s, 3H), 1.99 (s, 4H), 1.51 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  193.1, 169.2, 168.5, 155.2, 153.0, 134.1, 133.0, 132.9, 128.1, 126.6, 125.7, 125.5, 125.2, 124.9, 124.4, 121.5, 107.4, 62.9, 62.5, 28.7, 26.0, 13.8, 12.7.  $^{11}\text{B}$  NMR (160 MHz,  $\text{DMSO}-d_6$ )  $\delta$  11.1 (bs). HRMS (ESI,  $m/z$ ) Calculated for  $[\text{C}_{25}\text{H}_{25}\text{BNO}_6, \text{M} + \text{H}]^+$ : 446.1770, found: 446.1763.



**2-((1R\*,2S\*)-1-(4-acetyl-5-methylfuran-2-yl)-2-(thiophen-2-yl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3ao)**, yellow solid, m.p. 108-109 °C (68.2 mg, 85% yield). EA,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.04 (dd,  $J = 5.1, 1.1$  Hz, 1H), 6.83-6.76 (m, 1H), 6.72 (d,  $J = 3.4$  Hz, 1H), 6.28 (s, 1H), 4.00 (d,  $J = 17.1$  Hz, 1H), 3.96 (d,  $J = 17.2$  Hz, 1H), 3.87 (d,  $J = 17.2$  Hz, 1H), 3.54 (d,  $J = 17.1$  Hz, 1H), 3.06 (s, 3H), 2.68-2.63 (m, 1H), 2.34 (s, 3H), 2.24 (s, 3H), 1.58 (d,  $J = 6.9$  Hz, 2H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.8, 168.9, 157.5, 154.1, 143.5, 127.4, 126.0, 124.4, 123.0, 110.3, 63.8, 63.6, 47.2, 29.4, 23.9, 17.8, 14.4.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.2 (bs). **HRMS** (ESI,  $m/z$ ) Calculated for  $[\text{C}_{19}\text{H}_{24}\text{BN}_2\text{O}_6\text{S}, \text{M} + \text{NH}_4]^+$ : 419.1442, found: 419.1435.

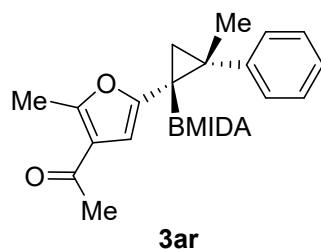


**2-((1R\*,2S\*)-1-(4-acetyl-5-methylfuran-2-yl)-2-(ferrocen-2-yl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3ap)**, yellow solid, m.p. 131-132 °C (74.5 mg, 74% yield). EA,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  6.21 (s, 1H), 4.17-4.12 (m, 6H), 3.98-3.92 (m, 3H), 3.86 (s, 1H), 3.80 (d,  $J = 17.6$  Hz, 2H), 3.49 (d,  $J = 17.0$  Hz, 1H), 3.00 (s, 3H), 2.32 (s, 3H), 2.25 (s, 3H), 2.22-1.17 (m, 1H), 1.44-1.38 (m, 1H), 1.35-1.30 (m, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.8, 169.0, 157.0, 155.1, 122.9, 109.8, 68.6, 68.2, 67.6, 67.4, 63.7, 63.5, 29.4, 24.6, 16.4, 14.4.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.1 (bs). **HRMS** (ESI,  $m/z$ ) Calculated for  $[\text{C}_{25}\text{H}_{27}\text{BFeNO}_6, \text{M} + \text{H}]^+$ : 504.1276, found: 504.1270.

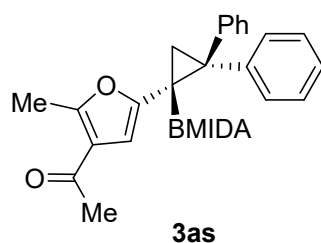


**2-((1R\*,2S\*)-1-(4-acetyl-5-methylfuran-2-yl)-2-(1,3-dioxoisindolin-2-yl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3aq)**, yellow solid, m.p. 140°C-141 °C (66.8 mg, 72% yield). EA,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.69 (d,  $J = 1.9$  Hz, 4H), 6.13 (s, 1H), 4.11-4.03 (m,

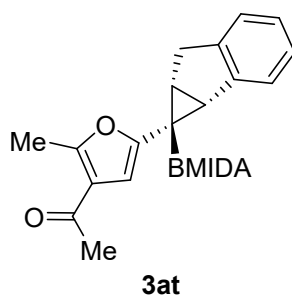
2H), 3.99 (d,  $J = 17.2$  Hz, 1H), 3.72 (d,  $J = 17.1$  Hz, 1H), 3.16 (s, 3H), 3.14-3.09 (m, 1H), 2.29 (s, 3H), 2.24-2.19 (m, 1H), 2.05 (s, 3H), 1.67-1.62 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.6, 169.6, 169.1, 169.0, 157.5, 153.0, 135.2, 132.3, 123.7, 122.9, 109.0, 64.1, 63.8, 47.7, 33.0, 29.2, 14.5, 14.2.  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.5 (bs). HRMS (ESI,  $m/z$ ) Calculated for  $[\text{C}_{23}\text{H}_{25}\text{BN}_3\text{O}_8, \text{M} + \text{NH}_4]^+$ : 482.1729, found: 482.1728.



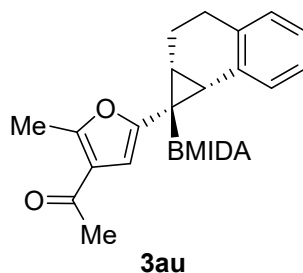
**2-((1R\*,2S\*)-1-(4-acetyl-5-methylfuran-2-yl)-2-methyl-2-phenylcyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3ar)**, yellow solid, m.p. 119-120 °C (52.4 mg, 64% yield). EA,  $R_f = 0.20$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.11 (d,  $J = 7.4$  Hz, 2H), 7.07-7.02 (m, 2H), 6.99-6.94 (m, 1H), 5.57 (s, 1H), 3.92 (d,  $J = 16.9$  Hz, 1H), 3.85 (d,  $J = 16.2$  Hz, 1H), 3.74 (d,  $J = 16.9$  Hz, 1H), 3.09 (d,  $J = 16.2$  Hz, 1H), 2.97 (s, 3H), 2.30 (s, 3H), 2.10 (s, 3H), 1.86 (d,  $J = 4.3$  Hz, 1H), 1.68 (s, 3H), 1.36 (d,  $J = 4.4$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  194.2, 168.1, 167.5, 156.2, 155.0, 144.2, 128.7, 127.6, 126.0, 122.9, 121.9, 107.8, 62.7, 45.7, 35.0, 29.4, 29.1, 23.2, 20.7, 14.1.  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ )  $\delta$  11.9 (bs). HRMS (ESI,  $m/z$ ) Calculated for  $[\text{C}_{22}\text{H}_{25}\text{BNO}_6, \text{M} + \text{H}]^+$ : 410.1770, found: 410.1764.



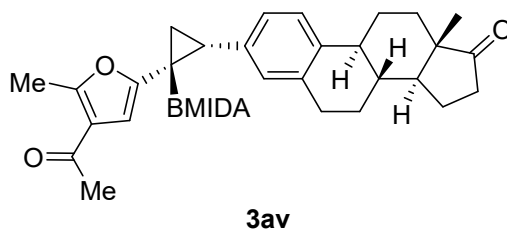
**(R\*)-2-(1-(4-acetyl-5-methylfuran-2-yl)-2,2-diphenylcyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3as)**, yellow solid, m.p. 145-146 °C (55.6 mg, 59% yield). EA,  $R_f = 0.20$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.58 (d,  $J = 7.5$  Hz, 2H), 7.26-7.18 (m, 4H), 7.12-7.07 (m, 1H), 7.02-6.97 (m, 2H), 6.94-6.89 (m, 1H), 5.95 (s, 1H), 3.60 (d,  $J = 16.1$  Hz, 1H), 3.55 (d,  $J = 17.0$  Hz, 1H), 3.44 (d,  $J = 17.0$  Hz, 1H), 2.84 (d,  $J = 16.1$  Hz, 1H), 2.77 (s, 3H), 2.41 (s, 3H), 2.17 (s, 3H), 2.14 (d,  $J = 4.2$  Hz, 1H), 1.85 (d,  $J = 3.9$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  194.1, 167.7, 167.4, 156.7, 153.9, 143.5, 143.0, 129.8, 129.4, 128.2, 127.8, 126.4, 126.2, 122.2, 108.4, 62.5, 62.1, 45.7, 44.6, 29.2, 19.8, 14.3.  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ )  $\delta$  15.5 (bs). HRMS (ESI,  $m/z$ ) Calculated for  $[\text{C}_{27}\text{H}_{27}\text{BNO}_6, \text{M} + \text{H}]^+$ : 472.1926, found: 472.1935.



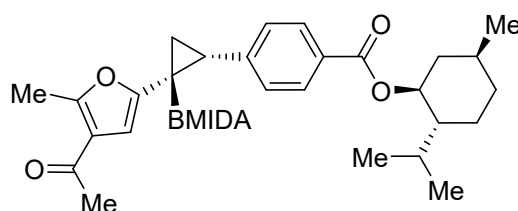
**2-((1R\*,1aS\*,6aR\*)-1-(4-acetyl-5-methylfuran-2-yl)-1,1a,6,6a-tetrahydrocyclopropa[a]inden-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3at)**, yellow solid, m.p. 246-247 °C (66.8 mg, 82% yield). EA,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  7.35 (d,  $J = 7.4$  Hz, 1H), 7.08-7.03 (m, 1H), 6.96-6.91 (m, 1H), 6.85 (d,  $J = 7.4$  Hz, 1H), 5.71 (s, 1H), 4.22 (d,  $J = 17.3$  Hz, 1H), 4.17 (d,  $J = 17.2$  Hz, 1H), 3.76 (d,  $J = 17.2$  Hz, 1H), 3.56 (d,  $J = 17.3$  Hz, 1H), 3.10 (s, 3H), 3.06 (d,  $J = 6.7$  Hz, 1H), 2.92 (d,  $J = 5.7$  Hz, 1H), 2.75 (d,  $J = 17.5$  Hz, 1H), 2.29-2.24 (m, 1H), 2.20 (s, 3H), 2.08 (s, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  193.2, 168.4, 168.2, 155.3, 150.7, 142.9, 142.6, 125.4, 125.3, 124.2, 123.6, 120.9, 109.4, 62.1, 62.0, 13.5.  $^{11}\text{B NMR}$  (160 MHz,  $\text{DMSO}-d_6$ )  $\delta$  14.1 (bs). **HRMS** (ESI, m/z) Calculated for  $[\text{C}_{22}\text{H}_{23}\text{BNO}_6, \text{M} + \text{H}]^+$ : 408.1613, found: 408.1612.



**2-((1R\*,1aR\*,7bS\*)-1-(4-acetyl-5-methylfuran-2-yl)-1a,2,3,7b-tetrahydro-1H-cyclopropa[a]naphthalen-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3au)**, yellow solid, m.p. 132-133 °C (52.3 mg, 68% yield). EA,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.40 (d,  $J = 7.4$  Hz, 1H), 7.17-7.12 (m, 1H), 7.08-7.03 (m, 1H), 6.84 (d,  $J = 7.4$  Hz, 1H), 5.39 (s, 1H), 3.92 (d,  $J = 17.0$  Hz, 1H), 3.87 (d,  $J = 16.9$  Hz, 1H), 3.62 (d,  $J = 17.0$  Hz, 1H), 3.38 (d,  $J = 16.9$  Hz, 1H), 3.14 (s, 3H), 2.51 (d,  $J = 8.0$  Hz, 1H), 2.45-2.40 (m, 1H), 2.38 (s, 3H), 2.04 (s, 3H), 2.01-1.93 (m, 3H), 1.34-1.27 (m, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.5, 168.9, 168.6, 157.1, 153.1, 137.1, 135.6, 130.6, 128.8, 126.7, 126.6, 123.2, 109.9, 63.2, 46.5, 29.2, 26.6, 25.2, 23.8, 19.6, 14.4.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.0 (bs). **HRMS** (ESI, m/z) Calculated for  $[\text{C}_{23}\text{H}_{25}\text{BNO}_6, \text{M} + \text{H}]^+$ : 422.1770, found: 422.1775.

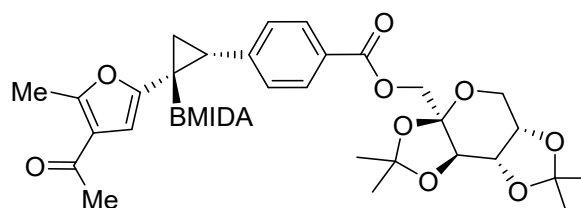


2-((1R\*,2S\*)-1-(4-acetyl-5-methylfuran-2-yl)-2-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**3av**), yellow solid, m.p. 161-162 °C (99.4 mg, 87% yield). EA,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.02 (d,  $J = 8.1$  Hz, 1H), 6.83-6.72 (m, 2H), 6.21 (s, 1H), 4.01 (d,  $J = 17.2$  Hz, 1H), 3.96 (d,  $J = 17.1$  Hz, 1H), 3.85 (d,  $J = 17.2$  Hz, 1H), 3.38 (dd,  $J = 17.1, 2.1$  Hz, 1H), 3.04 (s, 3H), 2.81-2.67 (m, 2H), 2.45-2.38 (m, 2H), 2.31 (d,  $J = 2.5$  Hz, 4H), 2.23 (s, 3H), 2.15 (s, 1H), 2.08-1.97 (m, 2H), 1.82-1.76 (m, 1H), 1.68-1.62 (m, 1H), 1.60-1.26 (m, 8H), 0.83 (s, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.7, 169.0, 168.9, 157.1, 154.4, 154.3, 138.4, 136.8, 136.7, 136.4, 129.5, 129.4, 126.5, 126.2, 125.6, 125.5, 122.9, 110.2, 110.1, 63.7, 63.6, 51.1, 48.6, 47.1, 45.0, 39.0, 36.3, 32.5, 30.0, 29.4, 28.2, 27.2, 26.5, 26.4, 22.1, 17.8, 15.4, 15.3, 14.4, 14.2.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.6 (bs). **HRMS** (ESI, m/z) Calculated for  $[\text{C}_{33}\text{H}_{39}\text{BNO}_7, \text{M} + \text{H}]^+$ : 572.2814, found: 572.2809.



**3aw**

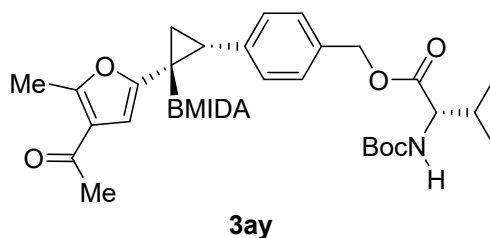
(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl-4-((1S\*,2R\*)-2-(4-acetyl-5-methylfuran-2-yl)-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)cyclopropyl)benzoate (**3aw**), yellow solid, m.p. 108-109 °C (91.2 mg, 79% yield). EA,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.74 (d,  $J = 8.3$  Hz, 2H), 7.13 (d,  $J = 8.3$  Hz, 2H), 6.24 (d,  $J = 8.1$  Hz, 1H), 4.90-4.78 (m, 1H), 3.99 (d,  $J = 17.1$  Hz, 1H), 3.94 (d,  $J = 17.1$  Hz, 1H), 3.82 (dd,  $J = 17.1, 2.6$  Hz, 1H), 3.48 (d,  $J = 17.0$  Hz, 1H), 3.03 (s, 3H), 2.62-2.55 (m, 1H), 2.27 (s, 3H), 2.21 (d,  $J = 4.9$  Hz, 3H), 2.16 (s, 1H), 2.02-1.96 (m, 1H), 1.89-1.78 (m, 2H), 1.74-1.69 (m, 2H), 1.60-1.44 (m, 3H), 1.21-1.05 (m, 2H), 0.93-0.85 (m, 6H), 0.76-0.71 (m, 3H).  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.4 (bs).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.8, 194.7, 168.9, 168.8, 166.6, 157.5, 157.4, 153.6, 153.5, 145.3, 129.5, 129.3, 128.9, 128.8, 122.8, 110.7, 110.6, 75.3, 63.7, 63.6, 48.1, 47.1, 41.7, 35.0, 32.2, 29.4, 28.5, 27.4, 24.4, 22.3, 20.9, 16.9, 15.8, 15.7, 14.3. **HRMS** (ESI, m/z) Calculated for  $[\text{C}_{32}\text{H}_{44}\text{BN}_2\text{O}_8, \text{M} + \text{NH}_4]^+$ : 595.3185, found: 595.3179.



**3ax**

((3aR,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl-4-((1S\*,2R\*)-2-(4-acetyl-5-methylfuran-2-yl)-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxo-

**azaborocan-2-yl)cyclopropyl)benzoate (3ax)**, yellow solid, m.p. 126-127 °C (64.0 mg, 47% yield). EA,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.79 (d,  $J = 7.6$  Hz, 2H), 7.14 (d,  $J = 8.3$  Hz, 2H), 6.25 (s, 1H), 4.65-4.53 (m, 2H), 4.42 (d,  $J = 2.5$  Hz, 1H), 4.22 (d,  $J = 8.0$  Hz, 1H), 4.19-4.11 (m, 1H), 3.99 (d,  $J = 17.2$  Hz, 1H), 3.95 (d,  $J = 17.0$  Hz, 1H), 3.88 (dd,  $J = 13.0, 1.3$  Hz, 1H), 3.83 (d,  $J = 17.2$  Hz, 1H), 3.63 (d,  $J = 13.0$  Hz, 1H), 3.44 (dd,  $J = 17.0, 2.1$  Hz, 1H), 3.02 (s, 3H), 2.62-2.57 (m, 1H), 2.25 (s, 3H), 2.21 (s, 3H), 1.84-1.79 (m, 1H), 1.57-1.51 (m, 1H), 1.46 (s, 3H), 1.34 (d,  $J = 5.5$  Hz, 3H), 1.30 (s, 3H), 1.21 (d,  $J = 12.3$  Hz, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.7, 169.0, 168.8, 166.5, 166.4, 157.5, 153.5, 153.4, 145.7, 145.6, 129.8, 128.8, 128.3, 128.2, 122.8, 122.7, 110.7, 119.6, 109.5, 102.5, 102.4, 71.5, 71.4, 70.9, 70.8, 65.7, 65.6, 63.6, 62.0, 47.0, 29.4, 28.4, 26.7, 26.2, 25.7, 24.2, 15.7, 15.6, 14.2.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.3 (bs). **HRMS** (ESI,  $m/z$ ) Calculated for  $[\text{C}_{34}\text{H}_{44}\text{BN}_2\text{O}_{13}, \text{M} + \text{NH}_4]^+$ : 699.2931, found: 699.2916.



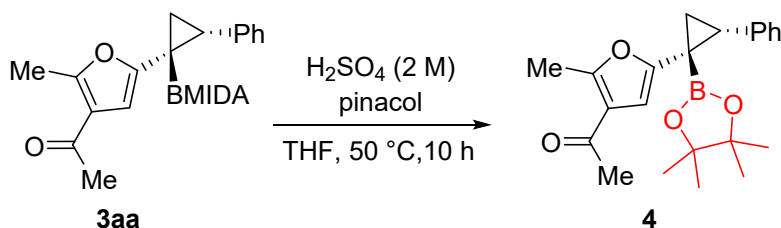
**4-((1S\*,2R\*)-2-(4-acetyl-5-methylfuran-2-yl)-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)cyclopropyl)benzyl (tert-butoxycarbonyl)-L-valinate (3ay)**, yellow solid, m.p. 97-98 °C (103.6 mg, 83% yield). EA,  $R_f = 0.20$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.14 (d,  $J = 7.9$  Hz, 2H), 7.05 (d,  $J = 7.9$  Hz, 2H), 6.22 (s, 1H), 5.54 (d,  $J = 8.0$  Hz, 1H), 5.06 (d,  $J = 12.5$  Hz, 1H), 4.99 (d,  $J = 12.3$  Hz, 1H), 4.02-3.94 (m, 3H), 3.83 (d,  $J = 17.2$  Hz, 1H), 3.50 (d,  $J = 17.1$  Hz, 1H), 3.04 (s, 3H), 2.55-2.50 (m, 1H), 2.28 (s, 3H), 2.22 (s, 3H), 2.05-1.98 (m, 1H), 1.73-1.68 (m, 1H), 1.52-1.46 (m, 1H), 1.39 (s, 9H), 0.85 (d,  $J = 6.8$  Hz, 3H), 0.80 (d,  $J = 6.7$  Hz, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  194.7, 173.0, 169.0, 168.9, 157.3, 156.7, 154.0, 139.6, 134.6, 129.0, 128.7, 122.8, 110.3, 79.8, 67.1, 63.7, 63.6, 60.1, 47.1, 31.4, 29.4, 28.5, 28.2, 19.3, 18.2, 15.4, 14.3.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  11.5 (bs). **HRMS** (ESI,  $m/z$ ) Calculated for  $[\text{C}_{32}\text{H}_{42}\text{BN}_2\text{O}_{10}, \text{M} + \text{H}]^+$ : 625.2927, found: 625.2923.

## 6. Large-Scale Experiments and Late-stage Transformations

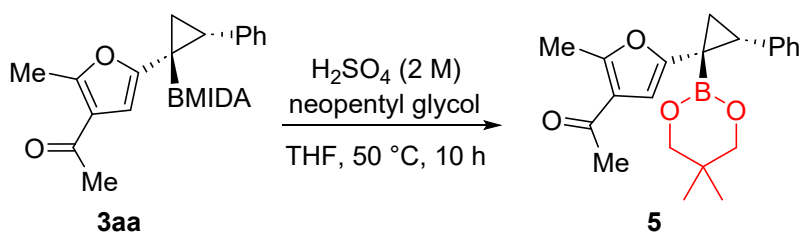
### (a) 10-Fold Scale Experiment

Under argon atmosphere, a pre-dried 10.0 mL Schlenk tube was charged with stirring bar, CuOTf (85.0 mg, 4.0 mmol, 0.2 eq.) was introduced into a Schlenk tube. Then 10.0 mL DCE solution of **1a** (582.1 mg, 2.0 mmol, 1.0 eq.) and styrene **2a** (1249.8 mg, 12.0 mmol, 6.0 eq.) was injected into the Schlenk tube in one portion. The resulting mixture was stirred at 45 °C for 16 h. The product was purified by flash chromatography on silica gel to give the analytical pure product **3aa** (595.5 mg, 76.1% yield).

### (b) Synthetic transformation of product **3aa**

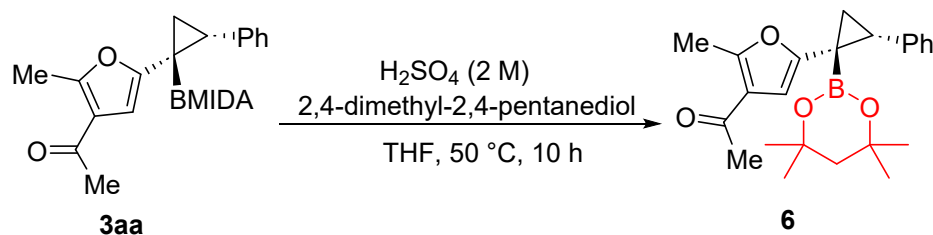


A flame-dried Schlenk flask with stir bar under  $\text{N}_2$  was charged with **3aa** (78.2 mg, 0.2 mmol, 1.0 eq.) and THF (1.5 mL), 2 M  $\text{H}_2\text{SO}_4$  in  $\text{H}_2\text{O}$  (2.0 eq, 22.0  $\mu\text{L}$ , 0.2 mL) was added into mixture slowly, then pinacol (29.0 mg, 0.24 mmol, 1.2 eq.) in THF (0.5 mL) was added subsequently. The solution was stirred at 50 °C for 10 h. Finally, the mixture was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 10:1,  $R_f$  = 0.20) to give product **4** (yellow oil 59.3 mg, 81% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.15-7.10 (m, 2H), 7.09-7.04 (m, 1H), 7.02 (d,  $J$  = 7.1 Hz, 2H), 6.13 (s, 1H), 2.73-2.68 (m, 1H), 2.30 (s, 3H), 2.24 (s, 3H), 1.86-1.80 (m, 1H), 1.65-1.58 (m, 1H), 1.28 (s, 12H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  194.6, 156.5, 152.0, 137.5, 128.6, 127.7, 126.3, 122.0, 108.4, 84.0, 30.4, 29.2, 24.9, 24.7, 16.6, 14.3.  $^{11}\text{B NMR}$  (160 MHz,  $\text{CDCl}_3$ )  $\delta$  32.6 (bs). **HRMS** (ESI,  $m/z$ ) Calculated for  $[\text{C}_{22}\text{H}_{28}\text{BO}_4, \text{M} + \text{H}]^+$ : 367.2075, found: 367.2072.

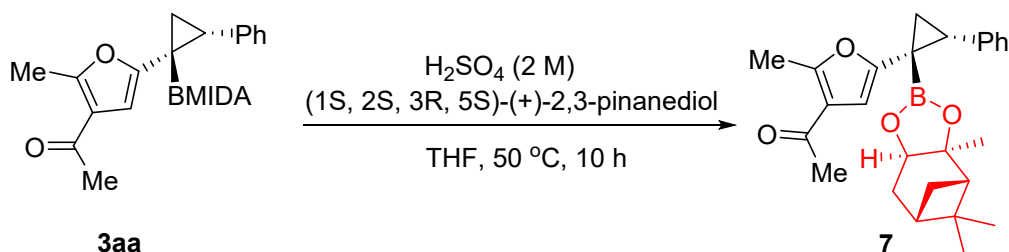


A flame-dried Schlenk flask with stir bar under  $\text{N}_2$  was charged with **3aa** (78.2 mg, 0.2 mmol, 1.0 eq.) and THF (1.5 mL), 2 M  $\text{H}_2\text{SO}_4$  in  $\text{H}_2\text{O}$  (2.0 eq, 22.0  $\mu\text{L}$ , 0.2 mL) was added into mixture slowly, then neopentyl glycol (25.0 mg, 0.24 mmol, 1.2 eq.) in THF (0.5 mL) was added subsequently. The solution was stirred at 50 °C for 10 h. Finally, the mixture was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 10:1,  $R_f$  = 0.20) to give product **5** (yellow oil, 63.1 mg, 83% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.14-7.03 (m, 3H), 6.99 (d,  $J$  = 7.1 Hz, 2H), 6.05 (s,

1H), 3.63 (s, 4H), 2.69-2.64 (m, 1H), 2.31 (s, 3H), 2.23 (s, 3H), 1.75-1.69 (m, 1H), 1.61-1.56 (m, 1H), 0.99 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 194.6, 156.5, 153.1, 138.1, 128.3, 127.6, 126.1, 122.0, 108.3, 72.5, 31.9, 29.6, 29.2, 21.9, 16.6, 14.3. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 28.5 (bs). HRMS (ESI, m/z) Calculated for [C<sub>21</sub>H<sub>26</sub>BO<sub>4</sub>, M + H]<sup>+</sup>: 353.1919, found: 353.1914.

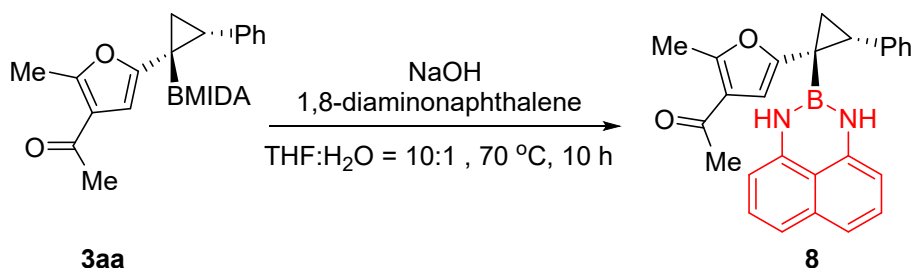


A flame-dried Schlenk flask with stir bar under N<sub>2</sub> was charged with **3aa** (78.2 mg, 0.2 mmol, 1.0 eq.) and THF (1.5 mL), 2 M H<sub>2</sub>SO<sub>4</sub> in H<sub>2</sub>O (2.0 eq, 22.0 μL, 0.2 mL) was added into mixture slowly, then 2,4-dimethyl-2,4-pentanediol (31.7 mg, 0.24 mmol, 1.2 eq.) in THF (0.5 mL) was added subsequently. The solution was stirred at 50 °C for 10 h. Finally, the mixture was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 10:1, R<sub>f</sub> = 0.20) to give product **6** (yellow oil, 59.2 mg, 84% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.13-7.08 (m, 2H), 7.07-6.99 (m, 3H), 6.11 (s, 1H), 2.65-2.60 (m, 1H), 2.30 (s, 3H), 2.25 (s, 3H), 1.83 (s, 2H), 1.74-1.69 (m, 1H), 1.57-1.51 (m, 1H), 1.33 (d, *J* = 2.4 Hz, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 194.8, 156.1, 153.3, 138.6, 128.5, 127.6, 126.0, 121.8, 108.1, 71.0, 48.8, 31.8, 29.7, 29.1, 16.5, 14.2. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 27.8 (bs). HRMS (ESI, m/z) Calculated for [C<sub>23</sub>H<sub>30</sub>BO<sub>4</sub>, M + H]<sup>+</sup>: 381.2232, found: 381.2225.

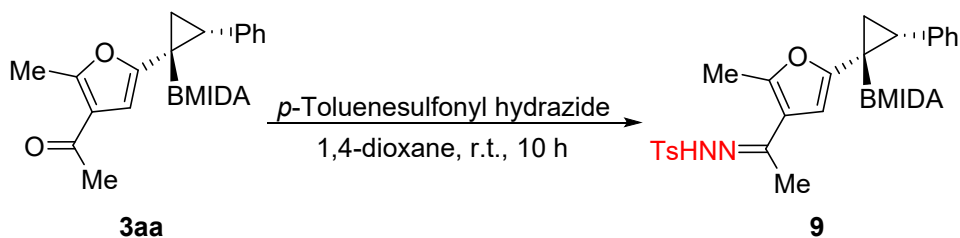


A flame-dried Schlenk flask with stir bar under N<sub>2</sub> was charged with **3aa** (78.2 mg, 0.2 mmol, 1.0 eq.) and THF (1.5 mL), 2 M H<sub>2</sub>SO<sub>4</sub> in H<sub>2</sub>O (2.0 eq, 22.0 μL, 0.2 mL) was added into mixture slowly, then (1S, 2S, 3R, 5S)-(+)-2,3-pinandediol (40.9 mg, 0.24 mmol, 1.2 eq.) in THF (0.5 mL) was added subsequently. The solution was stirred at 50 °C for 10 h. Finally, the mixture was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 10:1, R<sub>f</sub> = 0.20) to give product **7** (yellow oil, 77.0 mg, 92% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.16-6.98 (m, 5H), 6.13 (d, *J* = 10.9 Hz, 1H), 4.34 (d, *J* = 7.5 Hz, 1H), 2.72 (s, 1H), 2.29-2.24 (m, 8H), 2.07 (s, 1H), 1.91-1.86 (m, 3H), 1.67 (s, 1H), 1.42 (d, *J* = 6.6 Hz, 3H), 1.30 (s, 3H), 1.26-1.21 (m, 1H), 0.85 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 194.6, 194.5, 156.7, 156.6, 152.1, 152.0, 137.5, 128.5, 127.7, 127.6, 126.3, 122.0, 121.9, 108.5, 108.4, 86.4, 51.5, 39.6, 38.4, 38.3, 35.7, 35.6, 30.5, 30.4, 29.1, 28.7, 28.6, 27.2,

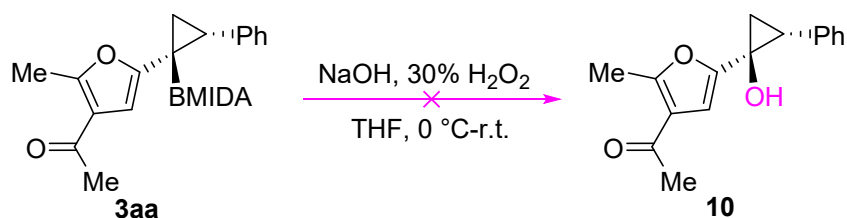
26.6, 26.5, 24.1, 16.9, 16.6, 14.3. **<sup>11</sup>B NMR** (160 MHz, CDCl<sub>3</sub>) δ 32.4 (bs). **HRMS** (ESI, m/z) Calculated for [C<sub>26</sub>H<sub>32</sub>BO<sub>4</sub>, M + H]<sup>+</sup>: 419.2388, found: 419.2387.



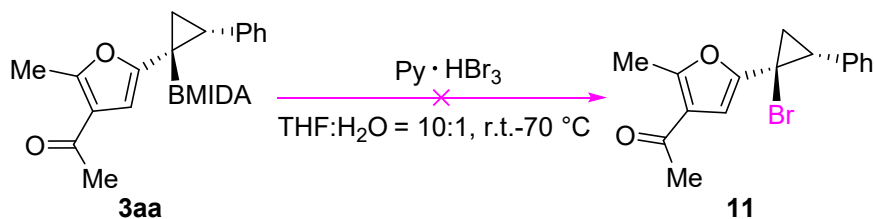
A flame-dried Schlenk flask with stir bar under N<sub>2</sub> was charged with **3aa** (78.2 mg, 0.2 mmol, 1.0 eq.) and NaOH (24.0 mg, 0.6 mmol, 3.0 eq.), THF (2.0 mL), H<sub>2</sub>O (0.2 mL) was added into mixture slowly, then 1,8-diaminonaphthalene (47.5 mg, 0.3 mmol, 1.5 eq.) was added subsequently. The solution was stirred at 70 °C for 10 h. Finally, the mixture was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 10:1, R<sub>f</sub> = 0.20) to give product **8** (red-brown solid, m.p. 100-101 °C, 52.8 mg, 65% yield). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.17-7.10 (m, 5H), 7.06-7.01 (m, 4H), 6.32 (d, *J* = 7.2 Hz, 2H), 6.04 (s, 1H), 6.59 (s, 2H), 2.64-2.59 (m, 1H), 2.41 (s, 3H), 2.27 (s, 3H), 1.89-1.84 (m, 1H), 1.62-1.55 (m, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 194.3, 157.4, 152.8, 140.7, 137.1, 136.4, 128.2, 127.9, 127.7, 126.5, 121.9, 119.6, 118.0, 106.1, 29.9, 29.2, 16.5, 14.5. **<sup>11</sup>B NMR** (160 MHz, CDCl<sub>3</sub>) δ 30.9 (bs). **HRMS** (ESI, m/z) Calculated for [C<sub>26</sub>H<sub>24</sub>BN<sub>2</sub>O<sub>2</sub>, M + H]<sup>+</sup>: 407.1926, found: 407.1919.



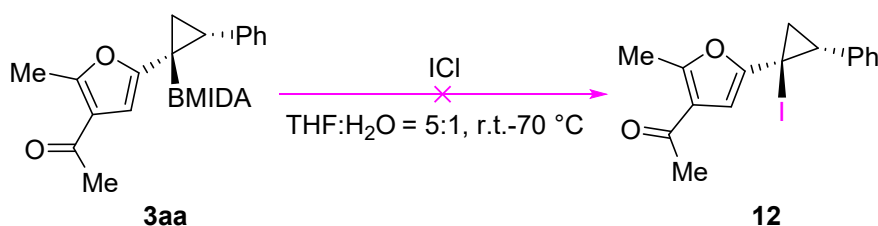
A flame-dried Schlenk flask with stir bar under N<sub>2</sub> was charged with **3aa** (78.2 mg, 0.2 mmol, 1.0 eq.) and *p*-Toluenesulfonyl hydrazide (74.5 mg, 0.4 mmol, 2.0 eq.), dioxane (2.0 mL) was added into mixture slowly. The solution was stirred at 25 °C for 10 h. Finally, the mixture was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 1:4, R<sub>f</sub> = 0.20) to give product **9** (yellow solid, m.p. 162-163 °C, 107.0 mg, 95% yield). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.96 (s, 1H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.05-6.98 (m, 3H), 6.89 (d, *J* = 7.0 Hz, 2H), 5.80 (s, 1H), 3.93-3.88 (m, 2H), 3.72 (d, *J* = 16.7 Hz, 1H), 3.33 (d, *J* = 16.4 Hz, 1H), 3.01 (s, 3H), 2.55-2.50 (m, 1H), 2.38 (s, 3H), 2.05 (s, 3H), 1.79 (s, 3H), 1.69-1.61 (s, 1H), 1.48-1.40 (s, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 168.2, 168.0, 151.8, 150.4, 149.9, 144.3, 138.2, 135.3, 129.7, 128.3, 127.9, 127.7, 126.0, 119.5, 109.3, 62.8, 46.1, 27.9, 21.7, 15.4, 14.8, 14.3. **<sup>11</sup>B NMR** (160 MHz, CDCl<sub>3</sub>) δ 10.7 (bs). **HRMS** (ESI, m/z) Calculated for [C<sub>28</sub>H<sub>31</sub>BN<sub>3</sub>O<sub>7</sub>S, M + H]<sup>+</sup>: 564.1971, found: 564.1964.



A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, **3aa** (78.2 mg, 0.2 mmol, 1.0 eq.), NaOH (57.0 mg, 1.5 mmol, 7.5 eq), and THF (2.0 mL) were introduced to a Schlenk tube. Then, 0.5 mL of 30% H<sub>2</sub>O<sub>2</sub> was added dropwise at 0 °C, and the reaction mixture was allowed to react at room temperature. During the reaction, the consumption of the starting material was monitored by thin-layer chromatography (TLC) until the reaction reached completion. After that, the solvent was removed under reduced pressure, and the residue was purified by silica gel flash chromatography. The target product **10** was not detected by <sup>1</sup>H NMR.



A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, **3aa** (78.2 mg, 0.2 mmol, 1.0 eq.) and pyridinium tribromide (191.8 mg, 0.6 mmol, 3.0 eq.). Then, the solution (THF:H<sub>2</sub>O = 10:1, 2.0 mL) was added and the reaction mixture was stirred from room temperature to 70 °C. During the reaction, the consumption of the starting material was monitored by thin-layer chromatography (TLC) until the reaction reached completion. After that, the solvent was removed under reduced pressure, and the residue was purified by silica gel flash chromatography. The target product **11** was not detected by <sup>1</sup>H NMR.

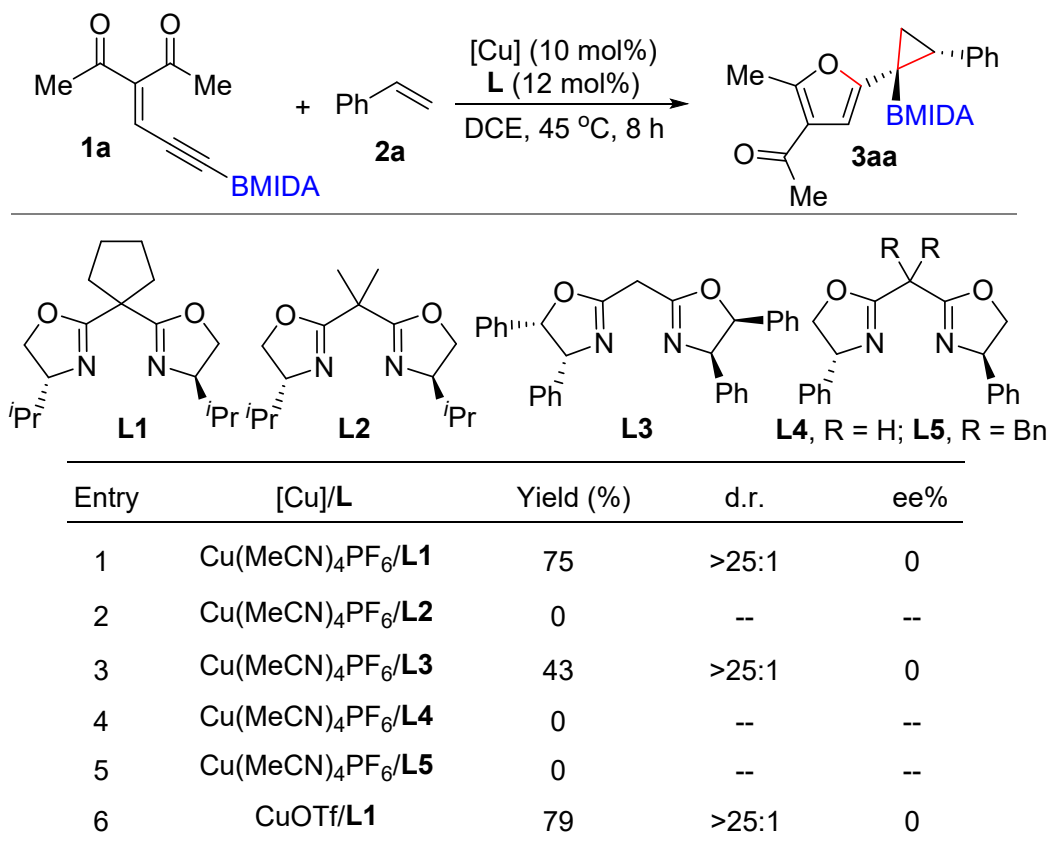


A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, **3aa** (78.2 mg, 0.2 mmol, 1.0 eq.), ICl (97.4 mg, 0.6 mmol, 3.0 eq.). Then, the solution (THF:H<sub>2</sub>O = 5:1, 2.0 mL) was added and the reaction mixture was stirred from room temperature to 70 °C. During the reaction, the consumption of the starting material was monitored by thin-layer chromatography (TLC) until the reaction reached completion. After that, the solvent was removed under reduced pressure, and the residue was purified by silica gel flash chromatography. The target product **12** was not detected by <sup>1</sup>H NMR.

## 7. Preliminary Investigation of Enantioselective Reaction

### 7.1 Results for enantioselective reaction

**Table S1** Investigation of chiral bis(oxazoline) ligands with copper catalyst

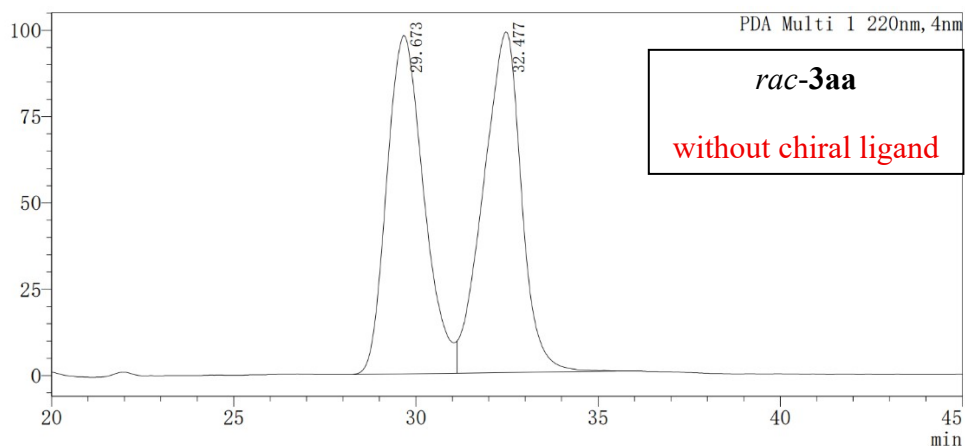


### 7.2 Procedure for enantioselective reaction

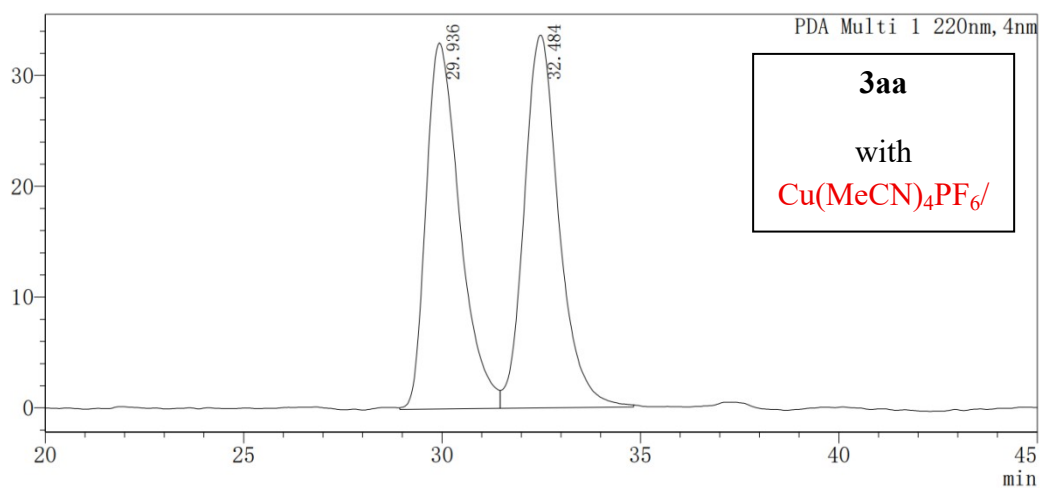
A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, copper salt (0.02 mmol, 0.1 eq.), chiral ligand (0.024 mmol, 0.12 eq.). After evacuation and refill with dry nitrogen for three times, DCE (1.0 mL) was added and the mixture was stirred at room temperature for 1 h. Then **1a** (58.2 mg, 0.2 mmol, 1.0 eq.) and **2a** (125.0 mg, 1.2 mmol, 6.0 eq.) were added successively into the Schlenk tube under N<sub>2</sub> atmosphere. The resulting mixture was stirred at 45 °C for 8 h. When cooled to room temperature, the mixture was concentrated using rotary evaporator. The product was purified by flash chromatography on silica gel (EA, R<sub>f</sub> = 0.20). Diastereomeric ratio (d.r.) and enantio-selectivity (e.e.) were detected respectively by <sup>1</sup>H NMR and chiral HPLC.

### 7.3 HPLC Chromatograms of 3aa

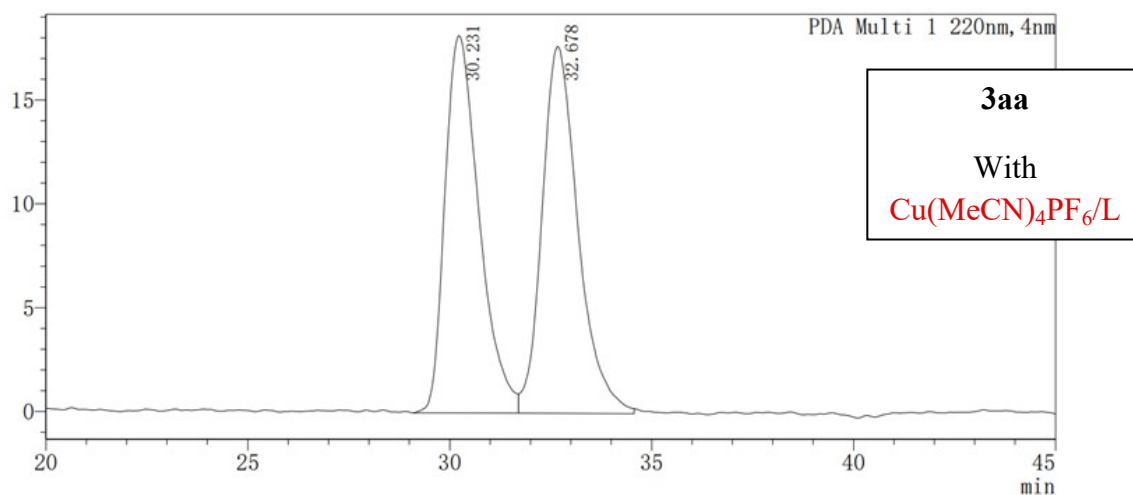
HPLC (AD-H, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)



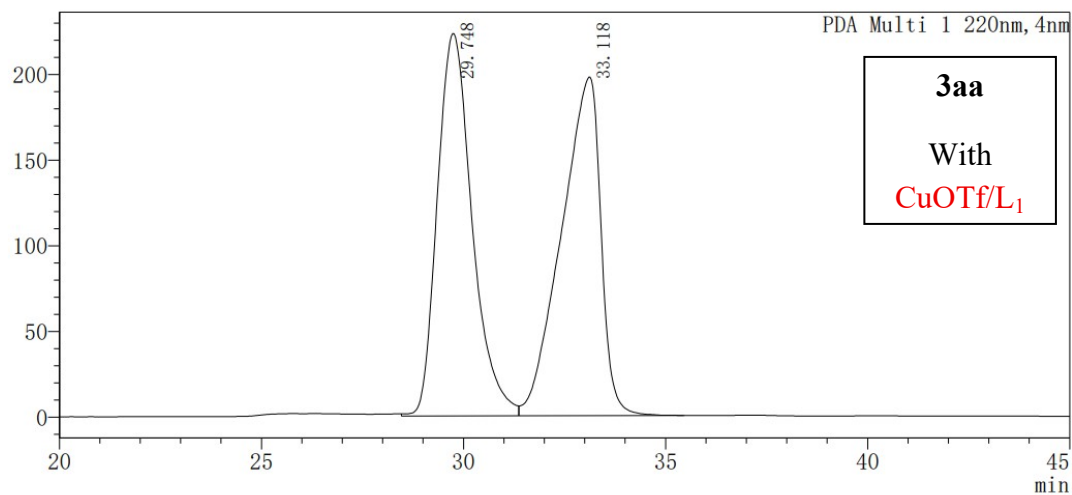
Peak	Retime	Height	Height%	Area	Area%
1	29.673	97987	49.836	6945964	49.276
2	32.477	98633	50.164	7150145	50.724
Total		196620	100.000	14096109	100.000



Peak	Retime	Height	Height%	Area	Area%
1	29.936	33065	49.565	1962502	48.855
2	32.484	33645	50.435	2054511	51.145
Total		66710	100.000	4017013	100.000



Peak	Retime	Height	Height%	Area	Area%
1	30.231	18187	50.707	1074508	49.467
2	32.678	17680	49.293	1097646	50.533
Total		35867	100.000	2172154	100.000

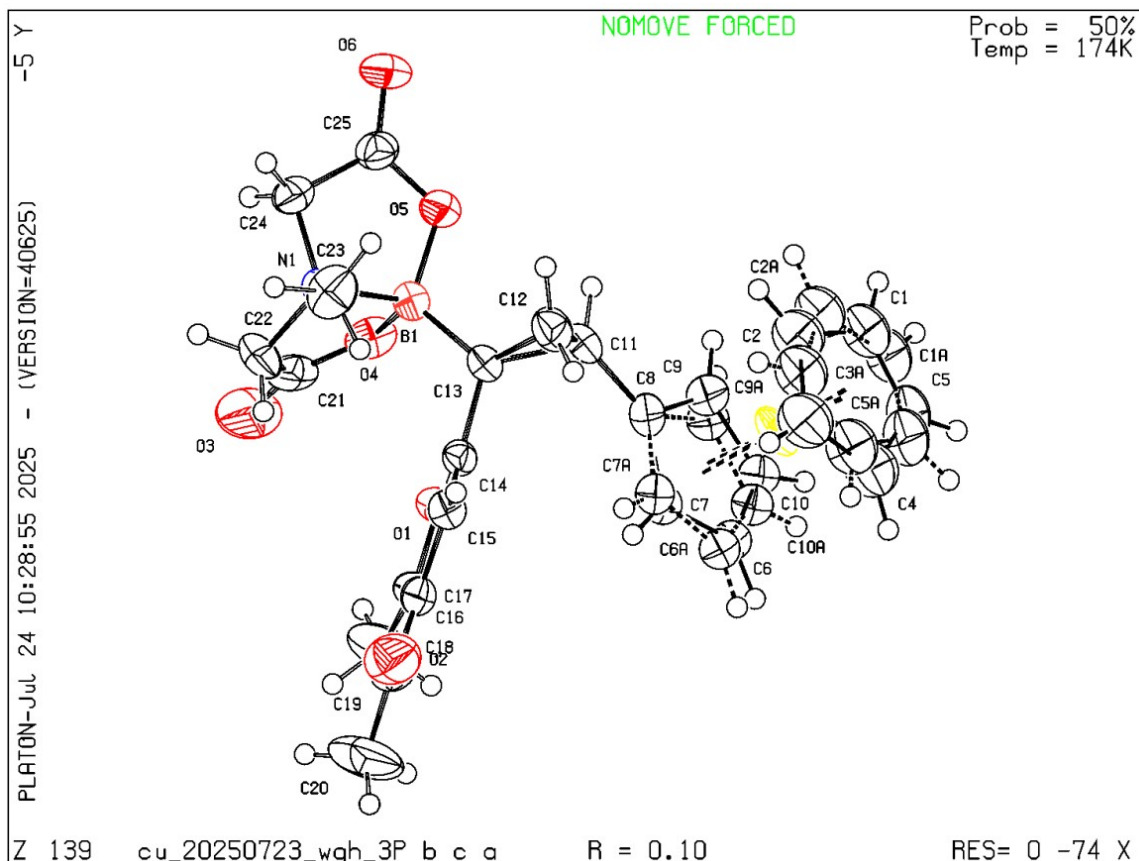


Peak	Retime	Height	Height%	Area	Area%
1	29.748	223188	53.036	13376309	49.960
2	33.118	197638	46.964	13397740	50.040
Total		420826	100.000	26774048	100.000

## 8. References

- [1] D. Song, X. Zhao, F. Lu, X. Sun, G. Wang, L. Xu and X. Zhao, *Org. Biomol. Chem.*, 2025, **24**, 1440-1446.
- [2] A. Herraiz and M. Suero, *Chem. Sci.*, 2019, **10**, 9374.
- [3] J. Tu, J. Liu, W. Tang, M. Su and F. Liu, *Org. Lett.*, 2020, **22**, 3, 1222–1226.
- [4] M. Zhang, M. Chen, X. Ding, J. Kang, Y. Gao, X. He, Z. Wang, A. Lu and Q. Wang, *Chem. Commun.*, 2021, **57**, 9140-9143.

## 9. Crystal Data and Structure Refinement of 3ap



Bond precision: C-C = 0.0103 Å

Wavelength=1.54178

Cell: a=13.3287 (4)

b=11.5160 (4)

c=30.4997 (9)

alpha=90

beta=90

gamma=90

Temperature: 174 K

	Calculated	Reported
Volume	4681.5(3)	4681.5(3)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C25 H26 B Fe N O6	C25 H26 B Fe N O6
Sum formula	C25 H26 B Fe N O6	C25 H26 B Fe N O6
Mr	503.13	503.13
Dx, g cm <sup>-3</sup>	1.428	1.428
Z	8	8
Mu (mm <sup>-1</sup> )	5.520	5.520
F000	2096.0	2096.0
F000'	2093.11	
h, k, lmax	15, 13, 36	15, 13, 36
Nref	4129	4039
Tmin, Tmax	0.618, 0.718	0.501, 0.753
Tmin'	0.491	

Correction method= # Reported T Limits: Tmin=0.501 Tmax=0.753

AbsCorr = MULTI-SCAN

Data completeness= 0.978

Theta(max)= 66.588

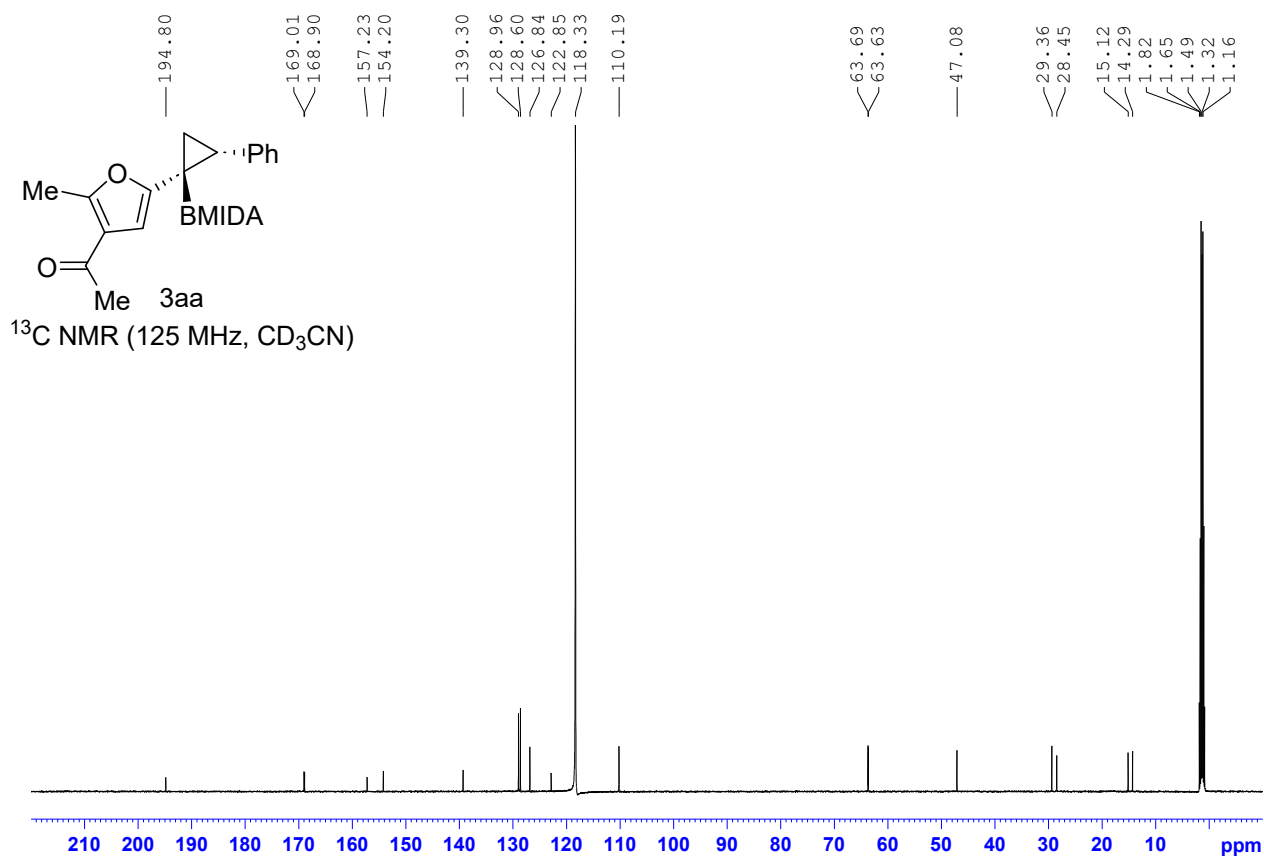
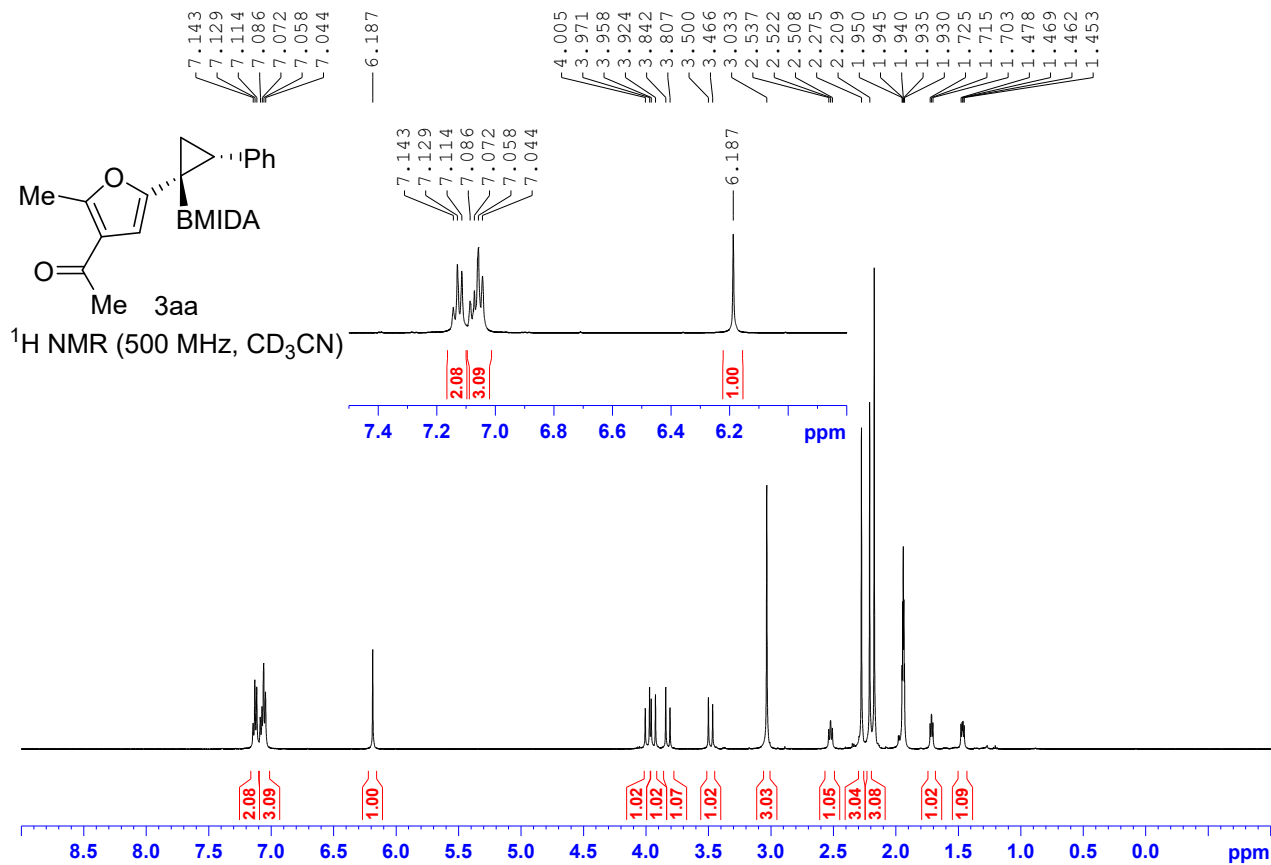
R(reflections)= 0.0977( 2986)

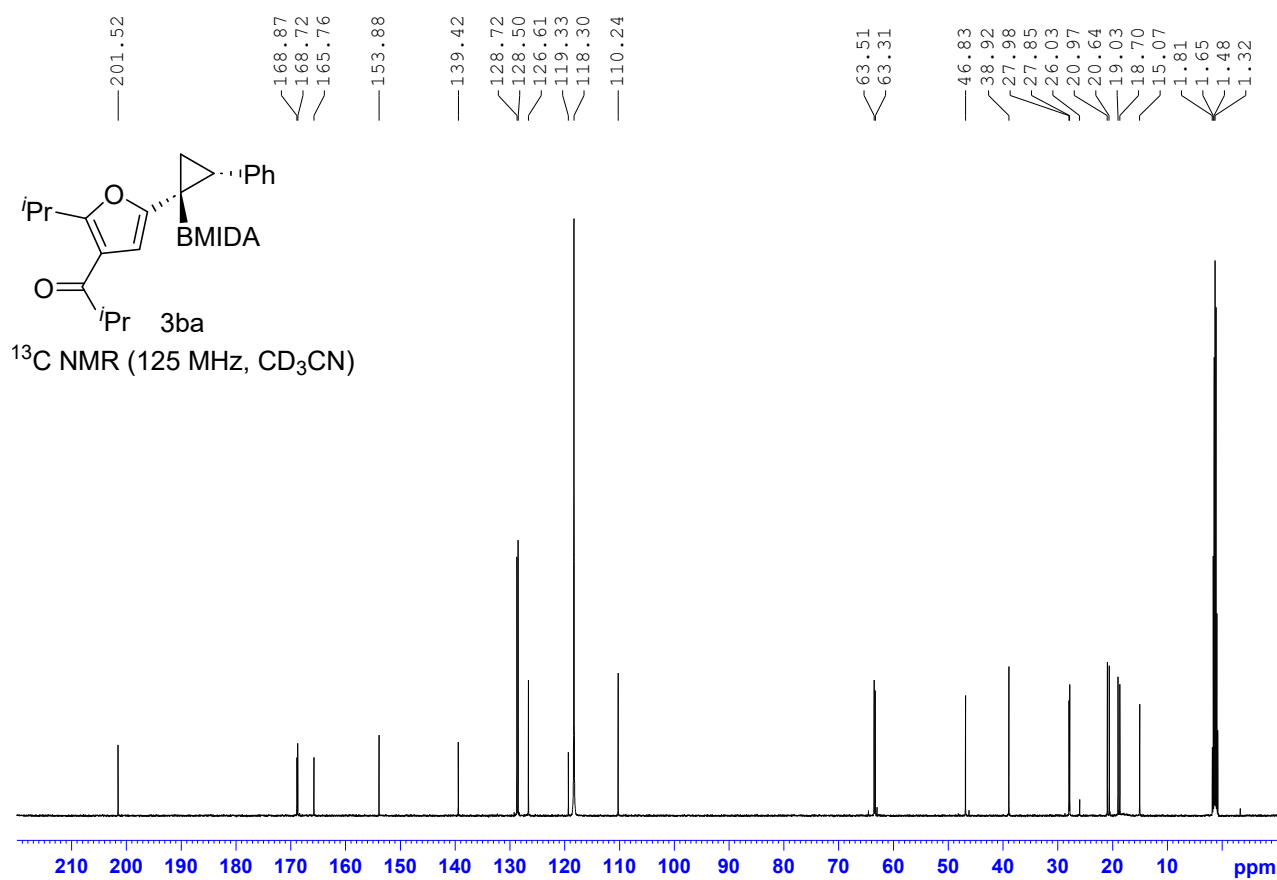
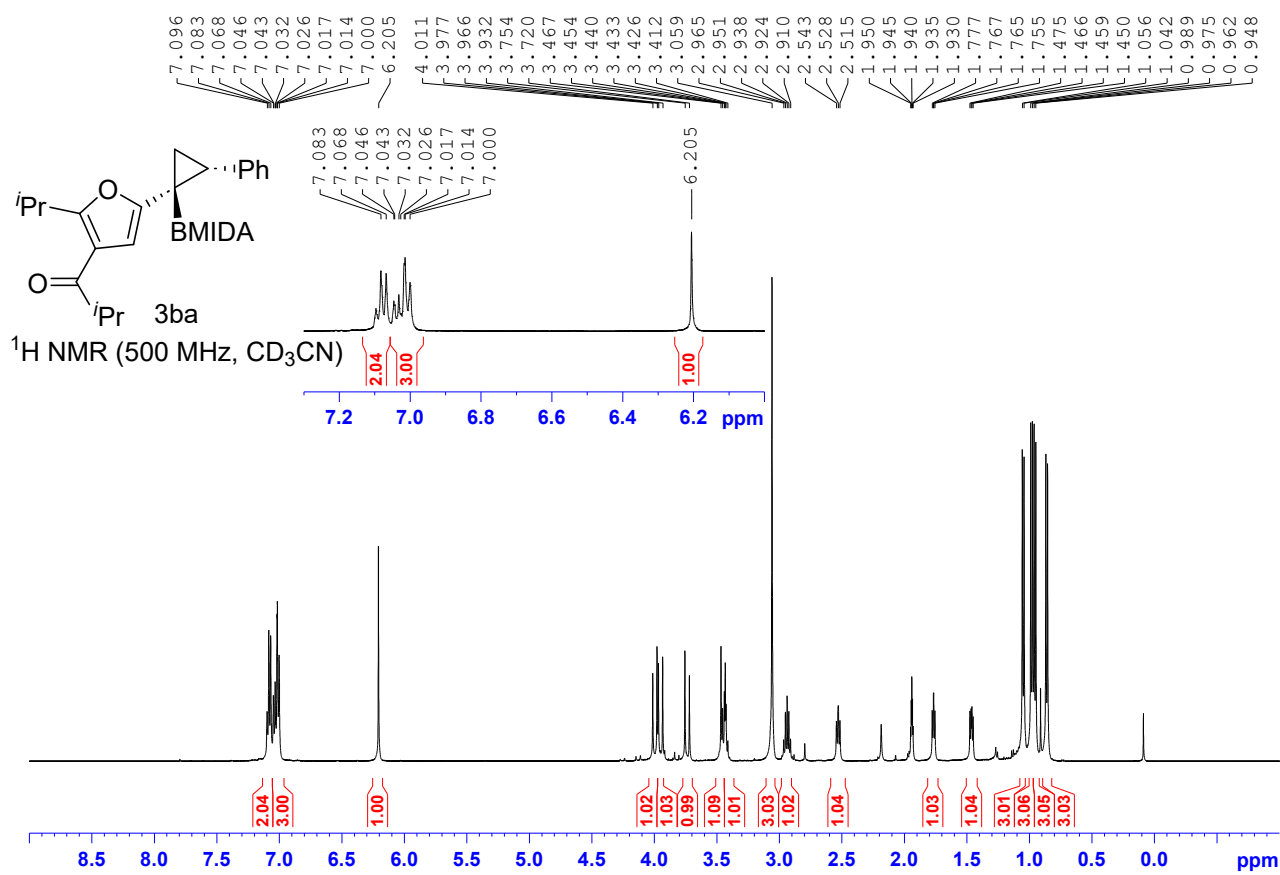
wR2(reflections)=  
0.1982( 4039)

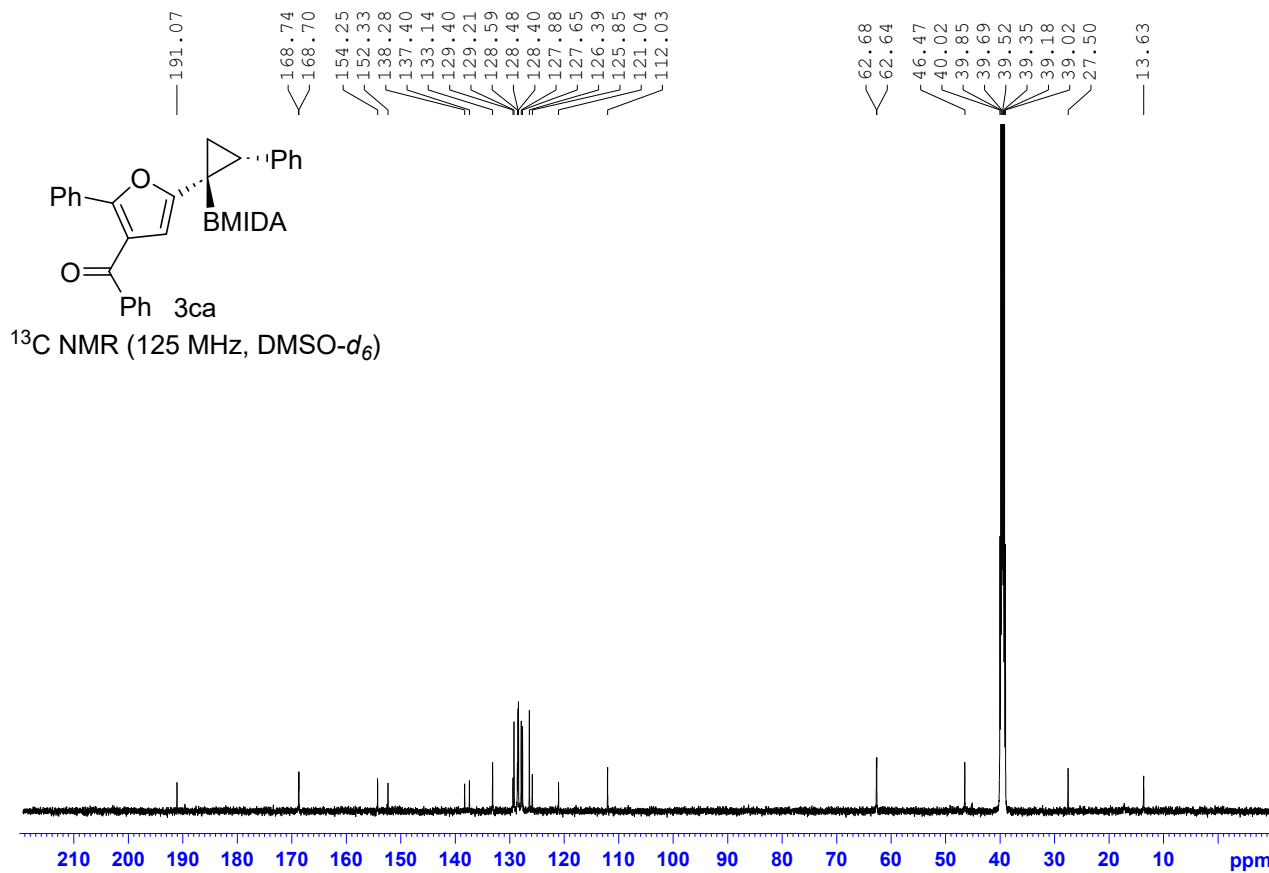
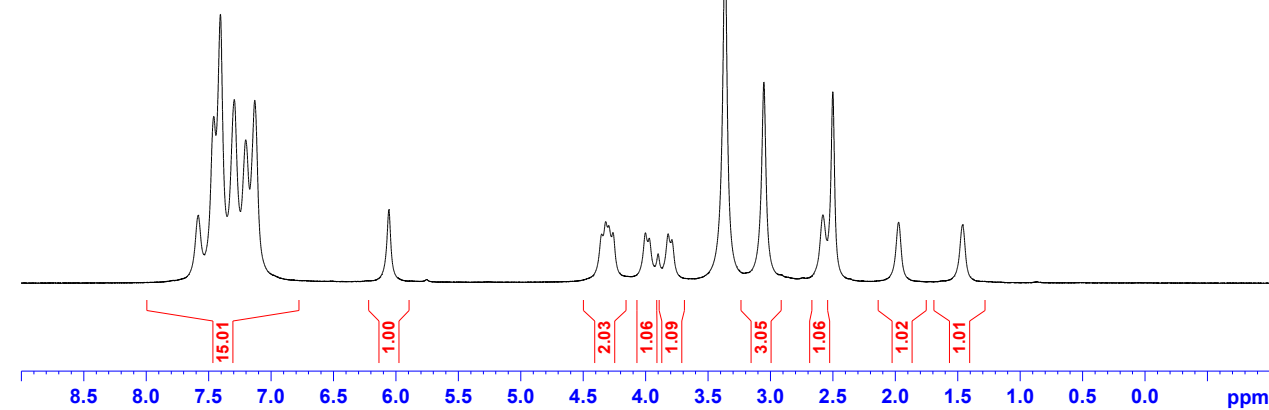
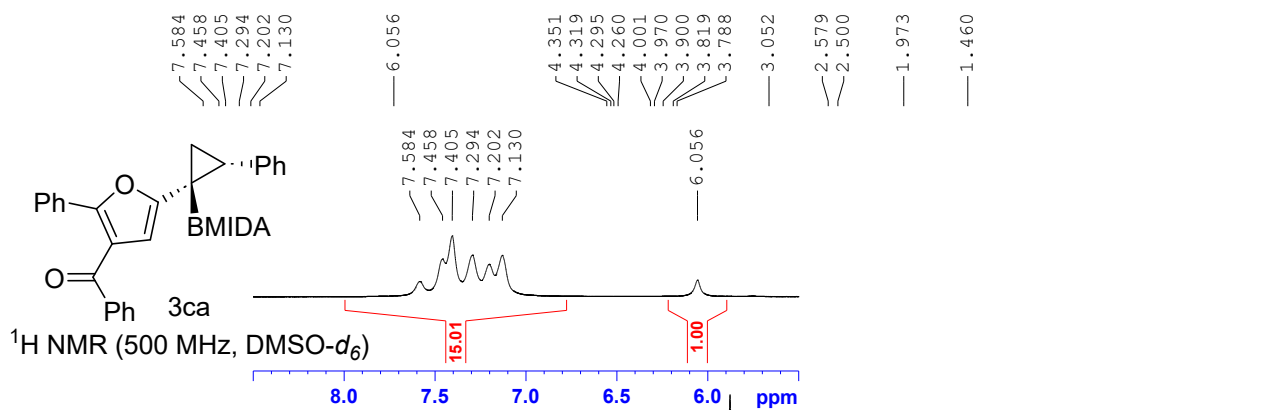
S = 1.151

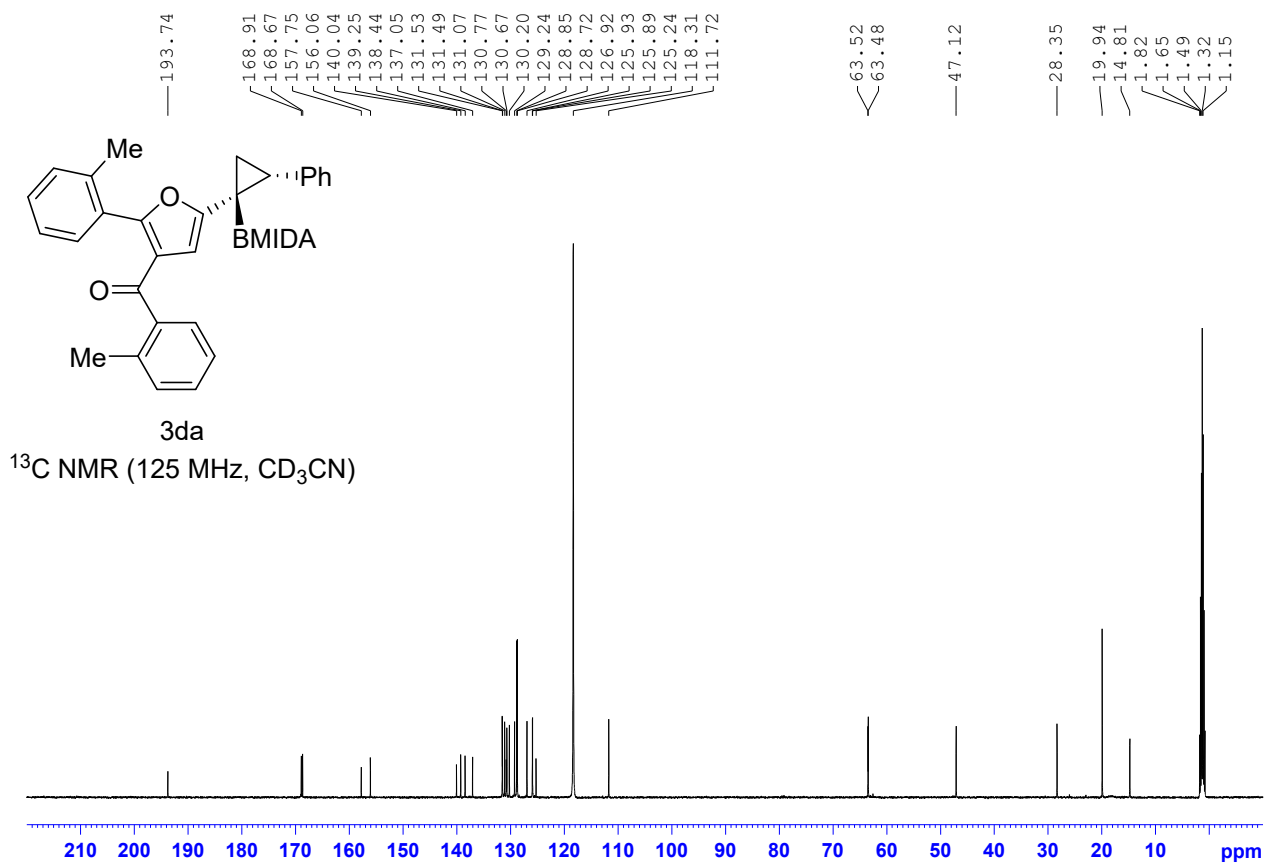
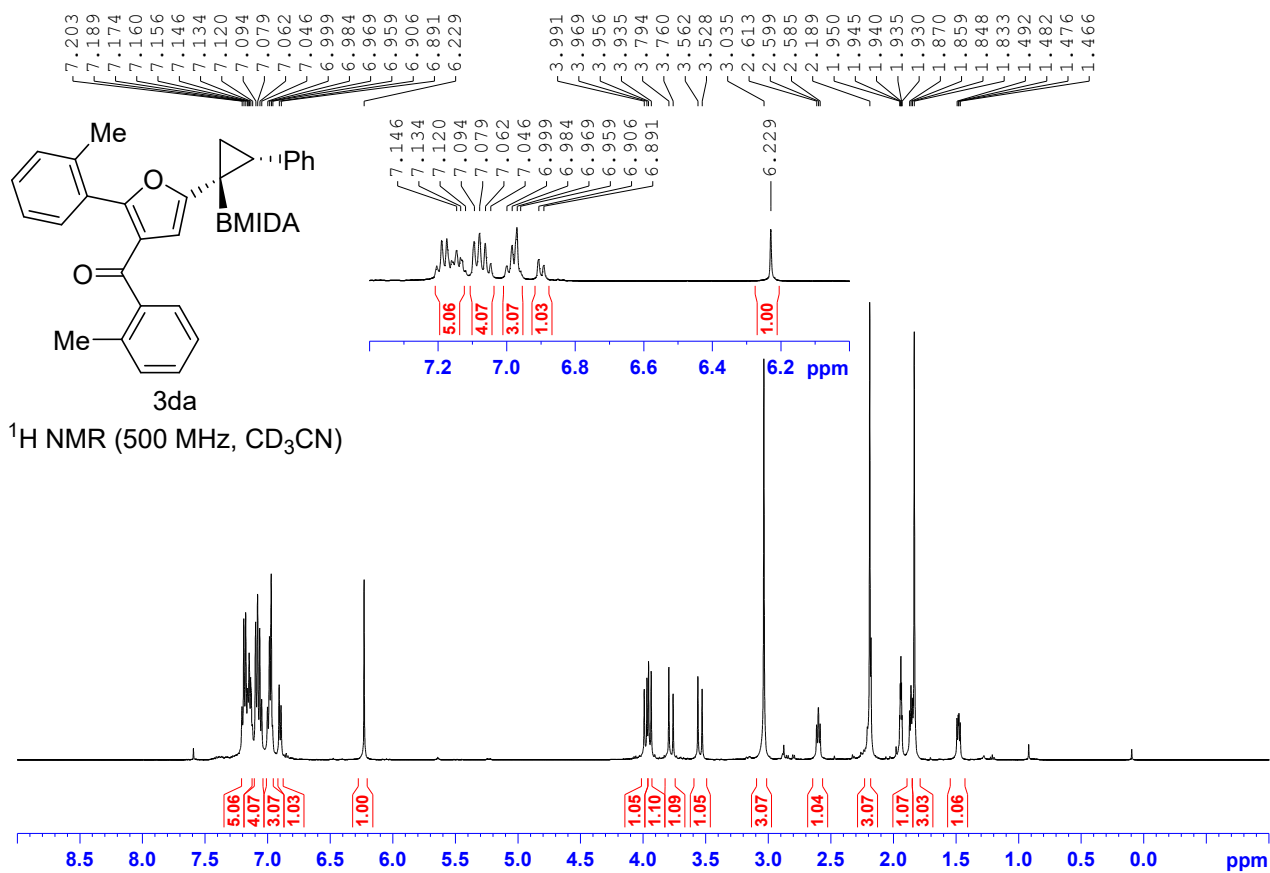
Npar= 401

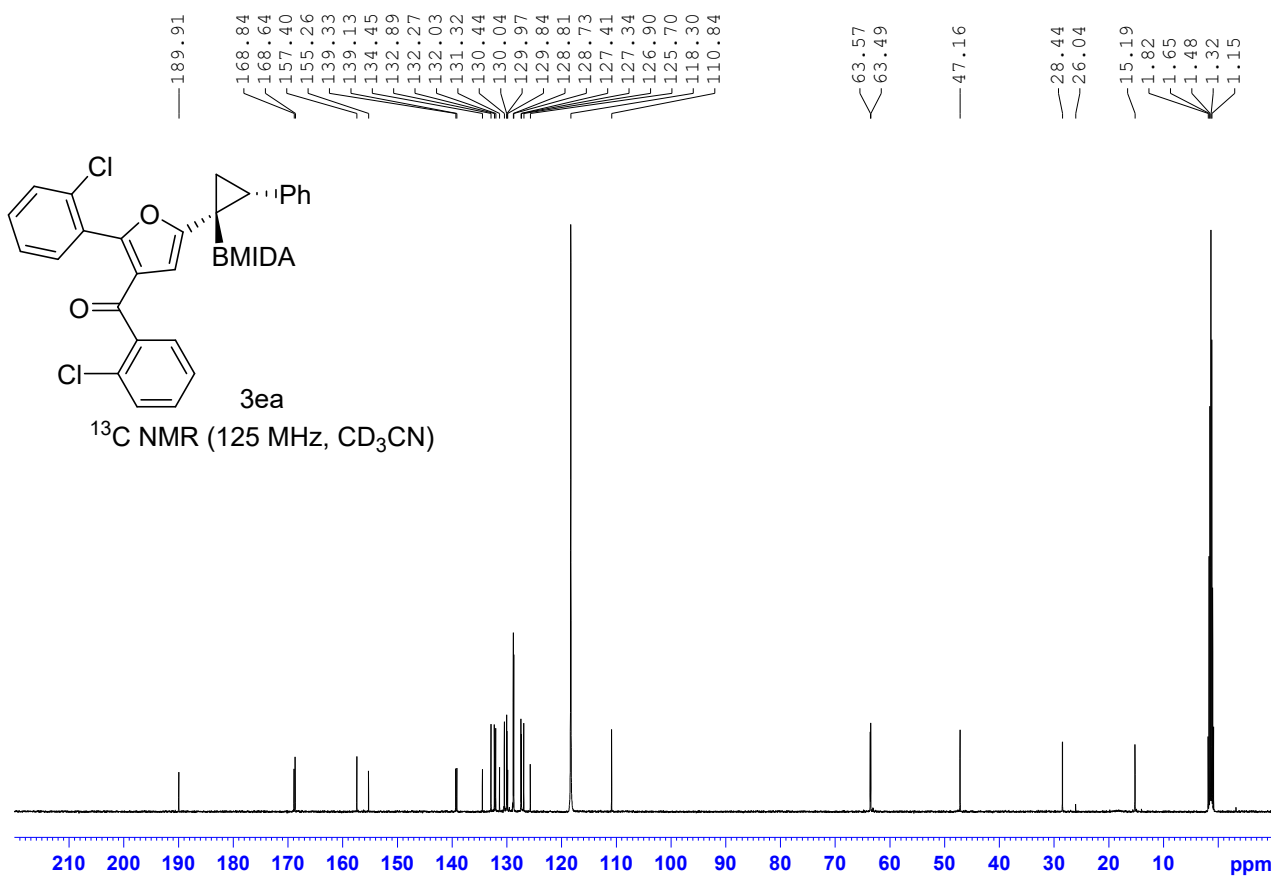
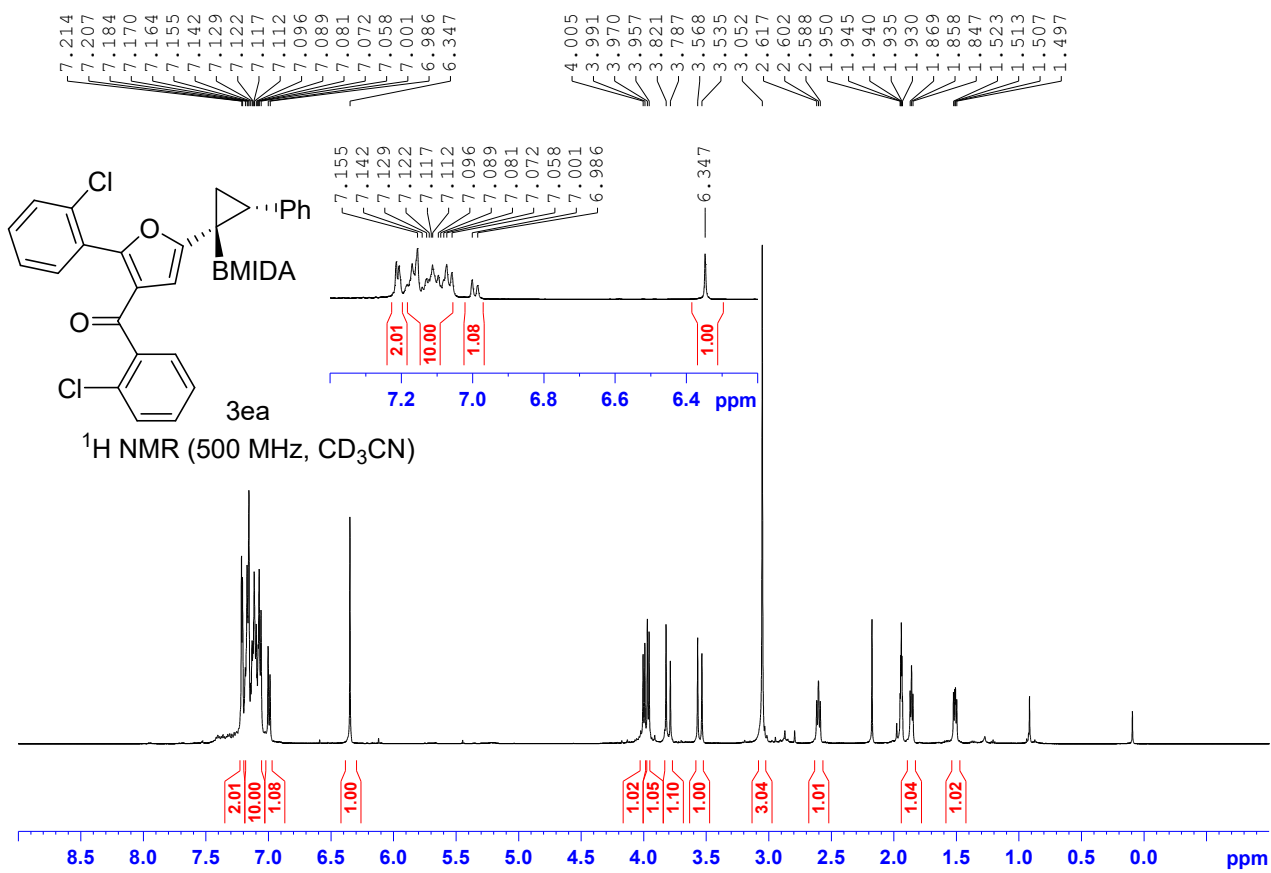
# 10. NMR Spectra

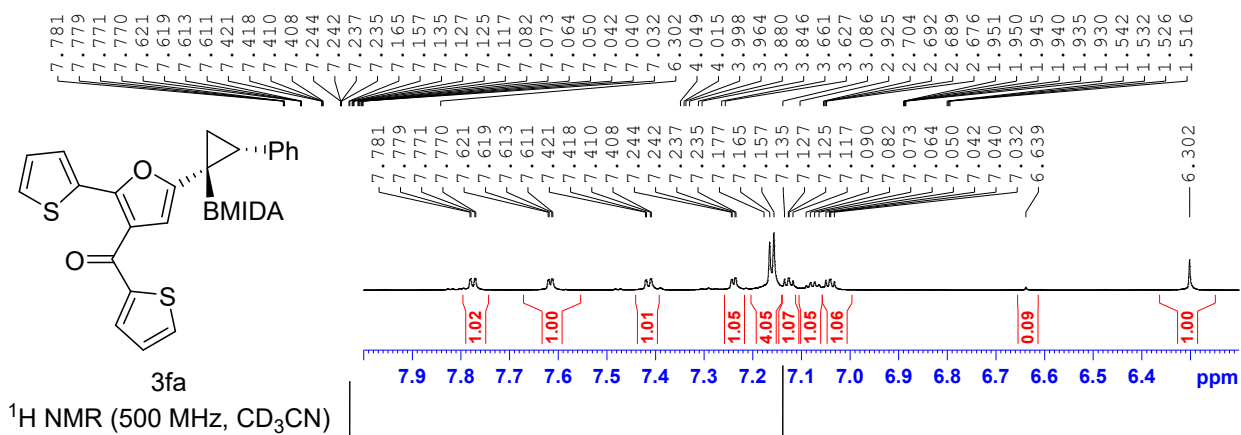




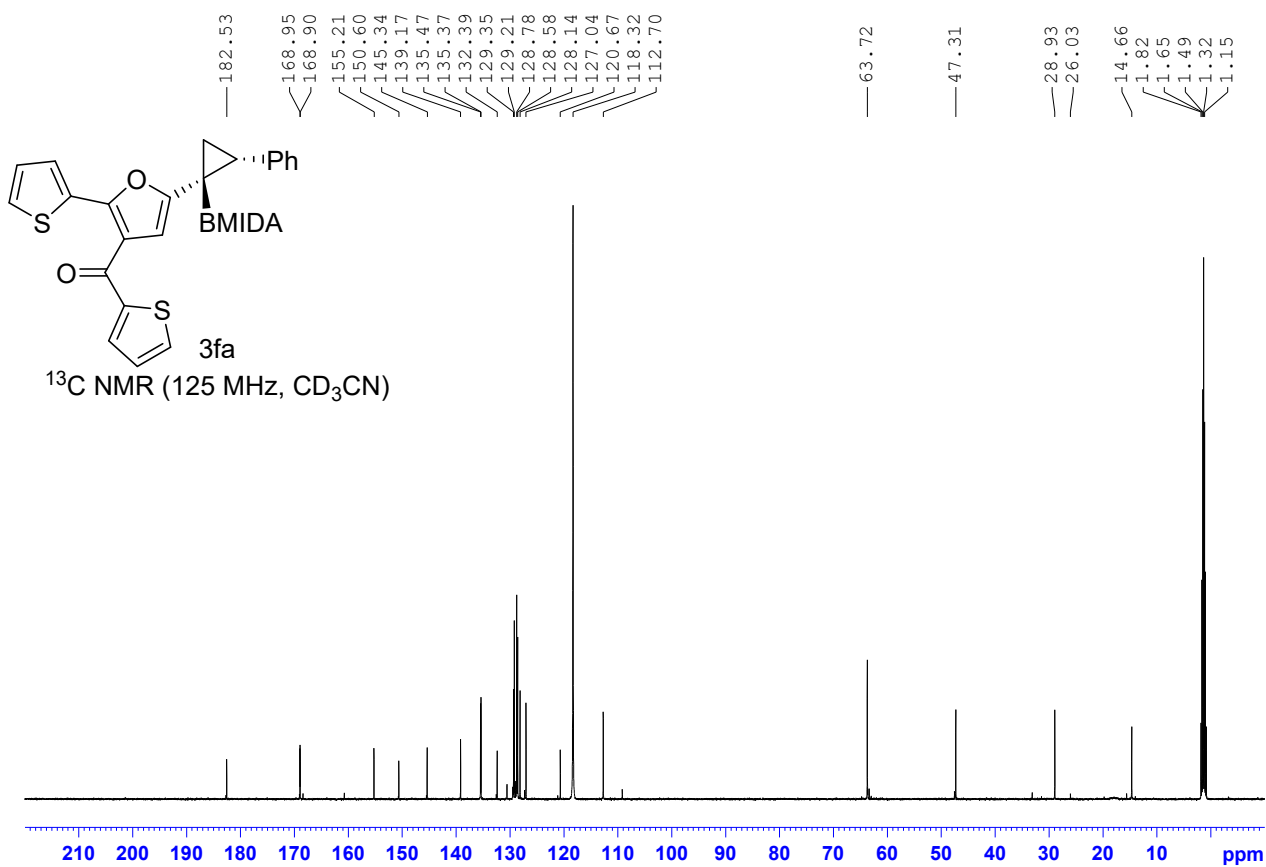








**3fa**  
<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN)



**3fa**  
<sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN)

