Supporting Information for
Iridium-Catalyzed \(\gamma\)-Selective Hydromboration of \(\gamma\)-Substituted Allylic amides

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1. General

All oxygen- and moisture-sensitive manipulations were carried out under an inert atmosphere using standard Schlenk techniques or glovebox. THF, CH$_2$Cl$_2$, CyH, and 1,4-dioxane were purified by passing through a neutral alumina column under argon. All other chemicals and solvents were purchased and used as received.

$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR, and $^{11}$B NMR spectra were recorded on Zhongke-Niujin 400, Bruker DRX400 NMR spectrometer at ambient temperature with CDCl$_3$, C$_6$D$_6$ or d$_6$-toluene as solvent. $^{13}$C shifts were obtained with $^1$H decoupling. Chemical shifts and coupling constants are listed in ppm and Hz, respectively. IR spectra were recorded on a Thermo-Fisher Nicolet 6700 FT-IR Analyzer. High-resolution mass spectroscopy data were obtained on Agilent 6530, Agilent 6224 TOF LC/MS spectrometer. Melting points were determined on an Electrothermal IA9000 Series Digital Melting Point Apparatus.
2. General procedures to prepare γ-substituted allyl amides 1a-v

**Step 1:** The preparation of γ-substituted allyl amide 1 was adapted from the literature procedures\(^1\). To a 250-mL round bottomed flask was charged with malonic acid (2.1 g, 20 mmol, 2.0 equiv), piperidinium acetate (31 mg, 2.0 mol %), and aldehyde hydrocarbon (10 mmol) in DMSO (20 mL). After the reaction mixture was stirred at 40 °C for 2 h, the solution was heated in an oil bath at 100 °C. A rapid evolution of carbon dioxide was observed. Heating was maintained until the evolution of carbon dioxide ceased. The solution was cooled to room temperature, poured into cold water (50 mL), and extracted with diethyl ether 3 times (3 × 20 mL). The combined organic phase was washed with water (30 mL), brine (30 mL), and then dried over anhydrous MgSO\(_4\). After removal of the solvent, the crude β,γ-unsaturated acid S1 was used for the next step without further purification.

**Step 2:** To a solution of the crude acid S1 in toluene (30 mL) was slowly added diphenylphosphoryl azide (DPPA) (2.75 g, 10.0 mmol) followed by addition of Et\(_3\)N (1.12 g, 11.0 mmol). The resulting solution was stirred at 80 °C for 2 h. After cooling to room temperature, 1 M NaOH (20 mL) was added and the mixture was allowed to stir at rt for 2 h. The organic phase was then separated and concentrated. The residue was dissolved in CH\(_2\)Cl\(_2\) (20 mL) followed by sequential addition of RCO\(_2\)H (10.0 mmol), EDCI (1.92 g, 10.0 mmol, 1.0 equiv) and DMAP (1.22 g, 1.0 mmol, 1.0 equiv) at 0 °C. The resulting mixture was allowed to warm to room temperature and stir at this temperature for additional 2 h. The reaction was then quenched by saturated aq. NaHCO\(_3\) (50 mL) and extracted with diethyl ether twice (2 × 50 mL). The combined ethereal solution was dried over anhydrous MgSO\(_4\). After removal of the solvent, the residue was purified by column chromatography on silica using PE/EtOAc as the eluent to afford the corresponding γ-substituted allyl amide 1. The yield is based on RCO\(_2\)H.

**Compound 1a:** R\(_f\) = 0.3 (PE/EtOAc = 6:1), white solid, mp = 45 - 47 °C, 0.79 g, 42% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.79 (d, \(J\) = 6.8 Hz, 2H), 7.59 - 7.32 (m, 3H), 6.33 (s, 1H), 5.82 - 5.64 (m, 1H), 5.62 - 5.46 (m, 1H), 4.02 (s, 2H), 2.06 (t, \(J\) = 6.8 Hz, 2H), 0.99 (t, \(J\) = 7.2 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.2, 135.6, 134.7, 131.3, 128.5, 126.9, 124.6, 41.9, 25.2, 13.3; IR (KBr film) 3309, 3062, 2962, 1637, 1539, 1490, 1308, 966, 803, 694 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{12}\)H\(_{15}\)NNaO ([M+Na]\(^+\)) 212.1046, found 212.1051.

**Compound 1b:** R\(_f\) = 0.4 (PE/EtOAc = 6:1), white solid, mp = 69 - 71 °C, 1.12 g, 55% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.39 - 7.34

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Compound 1c: Rf = 0.2 (PE/EtOAc = 4:1), white solid, mp = 59 - 61 °C, 1.03 g, 47% yield. 1H NMR (400 MHz, CDCl3) δ 7.84 – 7.69 (m, 2H), 6.98 – 6.86 (m, 2H), 6.04 (s, 1H), 5.81 – 5.67 (m, 1H), 5.61 – 5.47 (m, 1H), 4.07 – 3.96 (m, 2H), 3.85 (s, 3H), 2.12 – 1.99 (m, 2H), 1.00 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 166.2, 165.8, 163.3, 135.4, 130.7, 124.3, 115.3 (d, J = 8.8 Hz), 42.1, 25.1, 13.2; IR (KBr film) 3315, 2966, 2918, 1633, 1546, 1488, 1095, 974, 844, 757, 633 cm⁻¹; HRMS (ESI) calcd for C12H14ClNO (M+Na⁺) 290.0151, found 290.0150.

Compound 1f: Rf = 0.3 (PE/EtOAc = 6:1), white solid, mp = 94 - 96 °C, 0.73 g, 33% yield. 1H NMR (400 MHz, CDCl3) δ 7.91 – 7.86 (m, 2H), 7.78 – 7.72 (m, 2H), 7.32 – 7.25 (m, 2H), 6.11 (s, 1H), 5.81 – 5.76 (m, 1H), 5.61 – 5.43 (m, 1H), 4.11 – 4.07 (m, 2H), 2.12 – 2.00 (m, 2H), 1.00 (t, J = 7.6 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 166.1, 137.6, 136.0, 133.0, 128.8, 128.3, 124.3, 42.1, 25.2, 13.3; IR (KBr film) 3315, 2958, 1633, 1546, 1488, 1095, 974, 844, 757, 648 cm⁻¹; HRMS (ESI) calcd for C12H14BrNNaO (M+Na⁺) 290.0151, found 290.0150.

Compound 1f: Rf = 0.3 (PE/EtOAc = 6:1), white solid, mp = 104 - 106 °C, 1.39 g, 52% yield. 1H NMR (400 MHz, CDCl3) δ 7.72 – 7.63 (m, 2H), 7.61 – 7.51 (m, 2H), 6.11 (s, 1H), 5.83 – 5.66 (m, 1H), 5.58 – 5.45 (m, 1H), 4.10 – 3.93 (m, 2H), 2.15 – 1.99 (m, 2H), 1.00 (t, J = 7.6 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 166.2, 135.7, 133.4, 131.6, 128.6, 125.9, 124.3, 42.0, 25.2, 13.2; IR (KBr film) 3330, 2966, 2918, 1633, 1543, 1012, 971, 841, 752, 633 cm⁻¹; HRMS (ESI) calcd for C12H14BrNNaO (M+Na⁺) 290.0151, found 290.0150.
Compound 1g: Rf = 0.3 (PE/EtOAc = 6:1), white solid, mp = 139 - 141 °C, 1.17 g, 37% yield. 1H NMR (400 MHz, CDCl3) δ 7.92 – 7.67 (m, 2H), 7.61 – 7.44 (m, 2H), 6.06 (s, 1H), 5.88 – 5.63 (m, 1H), 5.63 – 5.42 (m, 1H), 4.09 – 3.92 (m, 2H), 2.18 – 1.98 (m, 2H), 1.00 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 166.4, 137.7, 136.0, 134.1, 128.5, 124.3, 98.2, 42.1, 25.2, 13.3; IR (KBr film) 3326, 2963, 2918, 1632, 1543, 1482, 971, 840, 749, 635 cm⁻¹; HRMS (ESI) calcd for C12H18NO ([M+H]+) 280.0919, found 280.0919.

Compound 1h: Rf = 0.3 (PE/EtOAc = 6:1), white solid, mp = 77 - 79 °C, 1.41 g, 55% yield. 1H NMR (400 MHz, CDCl3) δ 7.91 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.15 (s, 1H), 5.85 – 5.62 (m, 1H), 5.62 – 5.36 (m, 1H), 4.08 – 3.83 (m, 2H), 2.11 – 1.92 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 166.2, 137.9, 135.5, 132.9 (q, J = 32.5 Hz), 127.5, 125.3 (d, J = 3.6 Hz), 124.1, 123.6 (q, J = 270.8 Hz), 42.1, 25.1, 13.1; 19F NMR (376 MHz, CDCl3) δ -62.9; IR (KBr film) 3318, 2915, 1637, 1550, 1330, 1169, 857, 773, 651 cm⁻¹; HRMS (ESI) calcd for C13H13F3N3NaO ([M+Na]+) 280.0920, found 280.0926.

Compound 1I: Rf = 0.2 (PE/EtOAc = 6:1), white solid, mp = 45 - 47 °C, 1.57 g, 61% yield. 1H NMR (400 MHz, CDCl3) δ 7.53 (d, J = 2.4 Hz, 1H), 7.46 (d, J = 4.8 Hz, 1H), 7.06 (t, J = 3.6 Hz, 1H), 6.20 (s, 1H), 5.87 – 5.65 (m, 1H), 5.61 – 5.39 (m, 1H), 3.99 (t, J = 5.6 Hz, 2H), 2.15 – 1.96 (m, 2H), 0.99 (t, J = 7.6 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 161.6, 139.0, 135.7, 129.7, 127.9, 127.5, 124.3, 41.9, 25.2, 13.3; IR (KBr film) 3302, 3083, 2962, 1625, 1546, 1420, 1301, 967, 858, 716 cm⁻¹; HRMS (ESI) calcd for C13H13NOS ([M+Na]+) 258.0947, found 258.0955.

Compound 1J: Rf = 0.2 (PE/EtOAc = 6:1), white solid, mp = 50 - 52 °C, 1.36 g, 78% yield. 1H NMR (400 MHz, CDCl3) δ 7.77 (d, J = 7.2 Hz, 2H), 7.54 – 7.35 (m, 3H), 6.25 (s, 1H), 5.78 – 5.64 (m, 1H), 5.61 – 5.46 (m, 1H), 4.00 (t, J = 6.0 Hz, 2H), 1.70 (d, J = 6.0 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 167.2, 134.5, 131.3, 128.7, 128.5, 126.8, 41.9, 17.7; IR (KBr film) 3312, 3061, 2916, 1637, 1577, 1540, 1490, 1310, 964, 694 cm⁻¹; HRMS (ESI) calcd for C13H13NNaO ([M+Na]+) 198.0889, found 198.0899.

Compound 1k: Rf = 0.3 (PE/EtOAc = 6:1), white solid, mp = 119 - 121 °C, 1.58 g, 65% yield. 1H NMR (400 MHz, CDCl3) δ 7.89 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 6.87 (s, 1H), 5.79 – 5.59 (m, 1H), 5.60 – 5.42 (m, 1H), 3.98 (t, J = 6.0 Hz, 2H), 1.68 (dd, J = 6.4, 0.8 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 166.1, 137.9, 133.0 (q, J = 32.6 Hz), 128.8, 127.4, 126.4, 125.4 (d, J = 3.6 Hz), 123.6 (q, J = 270.8 Hz), 42.0, 17.5; 19F NMR (376 MHz, CDCl3) δ -62.9; IR (KBr film) 3320, 2917, 1638, 1549, 1334, 1165, 1125, 965, 859, 773 cm⁻¹; HRMS (ESI) calcd for C12H13F3NO ([M+H]+) 244.0944, found 244.0954.
Compound 11: \( R_i = 0.2 \) (PE/EtOAc = 4:1), white solid, mp = 85 - 87 °C, 1.58 g, 77% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.78 (d, \( J = 8.8 \) Hz, 2H), 6.68 (d, \( J = 8.8 \) Hz, 2H), 6.71 (s, 1H), 5.75 - 5.58 (m, 1H), 5.58 - 5.46 (m, 1H), 3.95 (t, \( J = 6.0 \) Hz, 2H), 3.80 (s, 3H), 1.66 (dd, \( J = 6.0, 1.2 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 166.7, 161.9, 128.7, 127.9, 127.0, 126.8, 113.4, 55.1, 41.7, 17.5; IR (KBr film) 3252, 3061, 1631, 1545, 1284, 840, 766, 678 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{12}\)H\(_{18}\)NO\(_2\) ([M+H]\(^+\)) 206.1176, found 206.1172.

Compound 1m: \( R_i = 0.3 \) (PE/EtOAc = 6:1), white solid, mp = 50 - 52 °C, 1.72 g, 85% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.77 (d, \( J = 7.2 \) Hz, 2H), 7.55 - 7.35 (m, 3H), 6.20 (s, 1H), 5.75 - 5.62 (m, 1H), 5.62 - 5.47 (m, 1H), 4.02 (s, 2H), 2.02 (d, \( J = 6.8 \) Hz, 2H), 1.40 (dd, \( J = 14.4, 7.2 \) Hz, 2H), 0.90 (t, \( J = 7.2 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 167.2, 134.6, 133.8, 131.3, 128.4, 126.9, 125.6, 41.9, 34.2, 22.2, 13.6; IR (KBr film) 3311, 2957, 2927, 1637, 1540, 1489, 1310, 1073, 968, 694 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{13}\)H\(_{18}\)NO ([M+H]\(^+\)) 204.1383, found 204.1388.

Compound 1n: \( R_i = 0.4 \) (PE/EtOAc = 6:1), yellow oil, 1.06 g, 49% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.86 - 7.65 (m, 2H), 7.61 - 7.33 (m, 3H), 6.19 (s, 1H), 5.83 - 5.64 (m, 1H), 5.61 - 5.39 (m, 1H), 4.02 (t, \( J = 5.2 \) Hz, 2H), 2.03 (dd, \( J = 12.8, 6.4 \) Hz, 2H), 1.41 - 1.18 (m, 4H), 0.88 (t, \( J = 7.2 \) Hz, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 167.2, 134.7, 134.2, 131.3, 128.5, 126.9, 125.5, 42.0, 31.9, 31.2, 22.2, 13.8; IR (KBr film) 3312, 2956, 2926, 1638, 1538, 1489, 1309, 968, 802, 694 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{14}\)H\(_{20}\)NO ([M+H]\(^+\)) 218.1539, found 218.1538.

Compound 1o: \( R_i = 0.3 \) (PE/EtOAc = 6:1), white solid, mp = 48 - 50 °C, 1.51 g, 60% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.76 (d, \( J = 7.2 \) Hz, 2H), 7.54 - 7.37 (m, 3H), 7.35 - 7.12 (m, 6H), 6.16 (s, 1H), 5.95 - 5.76 (m, 1H), 5.72 - 5.53 (m, 1H), 4.06 (t, \( J = 5.6 \) Hz, 2H), 3.39 (d, \( J = 6.8 \) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 167.2, 139.8, 134.5, 132.2, 131.3, 128.5, 128.4, 127.1, 126.9, 126.1, 41.7, 38.6; IR (KBr film) 3310, 3026, 2908, 1637, 1537, 1489, 1292, 1074, 969, 696 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{17}\)H\(_{19}\)NO ([M+H]\(^+\)) 252.1383, found 252.1382.

Compound 1p: \( R_i = 0.2 \) (PE/EtOAc = 6:1), white solid, mp = 49 - 51 °C, 0.98 g, 37% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.79 (d, \( J = 7.2 \) Hz, 2H), 7.40 (t, \( J = 7.2 \) Hz, 1H), 7.31 (t, \( J = 7.6 \) Hz, 2H), 7.22 (t, \( J = 7.2 \) Hz, 2H), 7.17 - 7.05 (m, 4H), 5.70 - 5.55 (m, 1H), 5.56 - 5.39 (m, 1H), 3.93 (t, \( J = 5.2 \) Hz, 2H), 2.61 (t, \( J = 7.2 \) Hz, 2H), 2.27 (dd, \( J = 14.4, 6.8 \) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 167.2, 141.3, 134.2, 132.1, 131.0, 128.1, 128.0, 126.8, 126.1, 125.5, 41.6, 35.1, 33.7; IR (KBr film) 3317, 3026, 2922, 1637, 1540, 1490, 1310, 1074, 968, 697 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{18}\)H\(_{20}\)NO ([M+H]\(^+\)) 266.1539, found 266.1538.
Compound 1q: R<sub>1</sub> = 0.2 (PE/EtOAc = 2:1), white solid, mp = 70 - 72 ºC, 1.28 g, 68% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.35 (m, 2H), 7.33 – 7.29 (m, 1H), 7.28 – 7.24 (m, 2H), 5.62 – 5.46 (m, 1H), 5.44 – 5.27 (m, 2H), 3.86 – 3.69 (m, 2H), 3.58 (s, 2H), 1.67 – 1.57 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.6, 134.8, 129.5, 129.0, 128.3, 127.3, 126.6, 43.8, 41.5, 17.7; IR (KBr film) 3292, 3084, 2960, 1637, 1547, 1453, 964, 716, 694, 546 cm<sup>−1</sup>; HRMS (ESI) calcd for C<sub>12</sub>H<sub>15</sub>NNO<sub>4</sub> ([M+Na]<sup>+</sup>) 212.1046, found 212.1037.

Compound 1r: R<sub>1</sub> = 0.3 (PE/EtOAc = 6:1), colorless oil, 0.68 g, 26% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.78 (d, J = 7.2 Hz, 2H), 7.49 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 6.24 (s, 1H), 5.76 – 5.50 (m, 2H), 4.02 (t, J = 6.0 Hz, 2H), 3.66 (s, 3H), 2.32 (t, J = 7.6 Hz, 2H), 2.09 (q, J = 7.2 Hz, 2H), 1.85 – 1.66 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 134.6, 132.6, 131.4, 128.5, 126.9, 126.7, 51.4, 41.8, 33.4, 31.6, 24.2; IR (KBr film) 3319, 2949, 1735, 1639, 1537, 1436, 1293, 1159, 969, 695 cm<sup>−1</sup>; HRMS (ESI) calcd for C<sub>15</sub>H<sub>20</sub>NO<sub>3</sub> ([M+H]<sup>+</sup>) 262.1438, found 262.1436.

Compound 1s: R<sub>1</sub> = 0.3 (PE/EtOAc = 3:1), colorless oil, 2.19 g, 71% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85 – 7.70 (m, 2H), 7.54 – 7.47 (m, 1H), 7.46 – 7.40 (m, 2H), 7.37 – 7.21 (m, 5H), 6.10 (s, 1H), 5.77 – 5.64 (m, 1H), 5.63 – 5.48 (m, 1H), 4.50 (s, 2H), 4.02 (t, J = 5.6 Hz, 2H), 3.48 (t, J = 6.4 Hz, 2H), 2.15 (q, J = 6.8 Hz, 2H), 1.76 – 1.65 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.2, 138.5, 133.6, 133.4, 131.4, 130.5, 128.5, 128.3, 127.6, 127.5, 126.8, 126.0, 72.9, 69.5, 41.9, 29.1, 28.9; IR (KBr film) 3316, 3062, 2935, 2854, 1638, 1538, 1309, 1102, 969, 696 cm<sup>−1</sup>; HRMS (ESI) calcd for C<sub>20</sub>H<sub>22</sub>NO<sub>3</sub> ([M+H]<sup>+</sup>) 310.1802, found 310.1803.

Compound 1t: R<sub>1</sub> = 0.2 (PE/EtOAc = 2:1), white solid, mp = 85 - 87 ºC, 0.91 g, 45% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.07 (s, 1H), 8.29 – 8.18 (m, 1H), 8.17 – 8.08 (m, 1H), 8.08 – 7.98 (m, 1H), 7.64 (t, J = 7.6 Hz, 1H), 6.26 (s, 1H), 5.86 – 5.67 (m, 1H), 5.67 – 5.49 (m, 1H), 4.12 – 3.97 (m, 2H), 1.73 (dd, J = 6.4, 1.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 191.6, 165.8, 136.4, 135.5, 133.1, 132.6, 129.5, 129.5, 127.3, 126.3, 42.1, 17.7; IR (KBr film) 3313, 2930, 1635, 1543, 1505, 1358, 1316, 964, 854, 777 cm<sup>−1</sup>; HRMS (ESI) calcd for C<sub>12</sub>H<sub>13</sub>NO<sub>3</sub> ([M+K]<sup>+</sup>) 242.0578, found 242.0571.

Compound 1u: R<sub>1</sub> = 0.3 (PE/EtOAc = 1:1), white solid, mp = 100 - 102 ºC, 0.42 g, 22% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64 – 7.56 (m, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 7.01 (dd, J = 8.0, 2.0 Hz, 1H), 6.31 (s, 1H), 5.81 – 5.64 (m, 1H), 5.60 – 5.43 (m, 1H), 3.99 (t, J = 6.0 Hz, 2H), 1.69 (dd, J = 6.4, 0.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.9, 157.1, 135.2, 129.7, 129.3, 126.1, 119.2, 117.5, 115.0, 42.1, 17.7; IR (KBr film) 3350, 2919, 1622, 1587, 1541, 1448, 1227, 964, 748, 678 cm<sup>−1</sup>; HRMS (ESI) calcd for C<sub>11</sub>H<sub>13</sub>NNO<sub>2</sub> ([M+Na]<sup>+</sup>) 214.0838, found 214.0847.
1H), 5.79 – 5.65 (m, 1H), 5.64 – 5.49 (m, 1H), 5.36 (dd, J = 10.8, 5.6 Hz, 1H), 4.01 (t, J = 6.0 Hz, 2H), 1.71 (dd, J = 6.4, 1.2 Hz, 3H); \(^1\)H NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.8, 140.5, 135.9, 133.6, 128.9, 127.2, 126.7, 126.3, 115.9, 41.9, 17.7; IR (KBr film) 3311, 2919, 2852, 1701, 1640, 1541, 1207, 966, 814, 685 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{13}\)H\(_{15}\)NNaO ([M+Na\(^{+}\)]\(^{+}\)) 224.1046, found 224.1049.

3. Preparation of homoallylic amide 1w

![Chemical structure](image)

**Step 1:** The preparation of acid S2 was according to literature procedures.\(^2\) To a 100-mL flask charged with allylic alcohol (10 mmol), and triethylorthoacetate (18 mL, 100 mmol, 10 equiv) was added propionic acid (75 μL, 10 mol %). The mixture was refluxed for 12 h. The resulting pale yellow mixture was allowed to cool to room temperature. KOH (1.69 g, 30 mmol, 3.0 equiv) in MeOH (30 mL) was added. The resulting mixture was refluxed for 5 h. After cooled down to room temperature, MeOH was removed under attenuated pressure. The resulting oil was dissolved in Et\(_2\)O (40 mL) and extracted with saturated aq. NaHCO\(_3\) twice (2 × 20 mL). The aqueous layer was acidified to pH = 2 and extracted with DCM 3 times (3 × 30 mL). The combined organic layers were dried over anhydrous Na\(_2\)SO\(_4\). After concentration, the crude acid S2 was used for the next step without further purification.

To a solution of the crude acid S2 in toluene (30 mL) was slowly added diphenylphosphoryl azide (DPPA) (2.75 g, 10.0 mmol) followed by addition of Et\(_3\)N (1.12 g, 11.0 mmol) at 0 \(^\circ\)C. The resulting mixture was allowed to warm to room temperature and stir at this temperature for additional 2 h. The reaction was then quenched by saturated aq. NaHCO\(_3\) (50 mL) and extracted with diethyl ether twice (2 × 50 mL). The combined ethereal solution was dried over anhydrous MgSO\(_4\). After removal of the solvent, the residue was purified by column chromatography on silica using PE/EtOAc as the eluent to afford the corresponding homoallylic amide 1w. \(R_f = 0.2\) (PE/EtOAc = 6:1), white solid, mp = 73 – 75 \(^\circ\)C, 0.62 g, 33% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 – 7.68 (m, 2H), 7.54 – 7.47 (m, 1H), 7.47 – 7.37 (m, 2H), 6.15 (s, 1H), 5.67 – 5.52 (m, 1H), 5.50 – 5.36 (m, 1H), 3.48 (dd, J = 12.4, 6.8 Hz, 2H), 2.31 (q, J = 6.8 Hz, 2H), 1.69 (dd, J = 6.4, 1.2 Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.4, 134.8, 131.3, 128.5, 128.2, 127.7, 126.8, 39.3, 32.6, 18.0; IR (KBr film) 3317, 3024, 2959, 1633, 1547, 1347, 1312, 1076, 963, 696 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{12}\)H\(_{15}\)NNaO ([M+Na\(^{+}\)]\(^{+}\)) 212.1046, found 212.1041.

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4. **Preparation of homoallylic amide 1x**

![Chemical structure of 1x]

To a 50-mL flask charged with homoallylic amine (0.71 g, 10.0 mol) and CH₂Cl₂ (20 mL) were added addition of PhCO₂H (1.22 g, 10.0 mmol), EDCI (1.92 g, 10.0 mmol, 1.0 equiv) and DMAP (1.22 g, 1.0 mmol, 1.0 equiv) at 0 °C. The resulting mixture was allowed to warm to room temperature and stir at this temperature for additional 2 h. The reaction was then quenched by saturated aq. NaHCO₃ (50 mL) and extracted with diethyl ether twice (2 × 50 mL). The combined ethereal solution was dried over anhydrous MgSO₄. After removal of the solvent, the residue was purified by column chromatography on silica using PE/EtOAc as the eluent to afford the corresponding homoallylic amide 1x. 

Rf = 0.3 (PE/EtOAc = 6:1), colorless oil, 1.61 g, 92% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.80 – 7.72 (m, 2H), 7.53 – 7.47 (m, 1H), 7.46 – 7.38 (m, 2H), 6.19 (s, 1H), 5.97 – 5.86 (m, 1H), 5.26 – 5.04 (m, 2H), 3.54 (dd, J = 12.4, 6.4 Hz, 2H), 2.39 (q, J = 6.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 167.5, 135.3, 134.7, 131.4, 128.6, 126.8, 117.5, 38.7, 33.7; IR (KBr film) 3303, 3075, 2932, 1638, 1542, 1311, 1110, 917, 856, 711 cm⁻¹; HRMS (ESI) calcd for C₁₁H₁₃NNaO ([M+Na⁺]⁺) 198.0889, found 198.0886.

5. **The role of 1,1-diphenylethene**

¹H NMR (400 MHz, CDCl₃) of the crude reaction mixture (Table 1, entry 1) shows that the 46% of 1,1-diphenylethene is converted to 1,1-diphenylethane (0.43/(1/2+0.43) = 46%). This result clearly indicates that 1,1-diphenylethene acts as a hydrogen acceptor for the current reaction.
6. General procedure for the catalytic hydroboration

To a 25-mL flame-dried Schlenk tube charged with [IrCp*Cl$_2$]$_2$ (2.0 mg, 1.25 mol %), 1,1-diphenylethene (35.3 μL, 0.2 mmol, 1.0 equiv) was added CyH (1 mL). The solution was allowed to stir for 10 min. Amide (0.20 mmol) and HBpin (46 μL, 0.32 mmol, 1.6 equiv) was added successively. The reaction was allowed to stir at room temperature for 5 h. The regioselectivity was determined by GC analysis or $^1$H NMR of crude materials. After removal of the solvent, the residue was purified by column chromatography on silica gel using PE/EtOAc as the eluent to afford desired borylated product 2.

**Compound 2a:** $R_f = 0.3$ (PE/EtOAc = 4:1), white solid, mp = 70 - 72 °C, 49.5 mg, 78% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.77 (d, $J = 7.2$ Hz, 2H), 7.59 – 7.30 (m, 3H), 6.54 (s, 1H), 3.47 (q, $J = 6.8$ Hz, 2H), 1.79 – 1.64 (m, 2H), 1.55 – 1.41 (m, 2H), 1.23 (s, 12H), 1.07 – 0.99 (m, 1H), 0.93 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.4, 135.0, 131.1, 128.4, 126.9, 83.2, 39.7, 30.2, 24.7, 24.0, 13.4; $^{11}$B NMR (128 MHz, CDCl$_3$) δ 34.3; IR (KBr film) 3320, 2975, 2928, 2870, 1637, 1541, 1312, 1143, 966, 695 cm$^{-1}$; HRMS (ESI) calcd for C$_{18}$H$_{29}$BNO$_3$ ([M+H]$^+$) 318.2235, found 318.2238.

**Compound 2b:** $R_f = 0.4$ (PE/EtOAc = 4:1), white solid, mp = 90 - 92 °C, 43.7 mg, 66% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 (d, $J = 7.6$ Hz, 1H), 7.31 – 7.24 (m, 1H), 7.24 – 7.13 (m, 2H), 6.16 (brs, 1H), 3.54 – 3.34 (m, 2H), 2.44 (s, 3H), 1.75 – 1.64 (m, 2H), 1.55 – 1.41 (m, 2H), 1.19 (s, 6H), 1.18 (s, 6H), 1.04 – 0.98 (m, 1H), 0.93 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.0, 137.0, 135.8, 130.8, 130.0, 126.7, 125.6, 83.2, 39.5, 30.1, 24.7, 24.0, 19.7, 13.4; $^{11}$B NMR (128 MHz, CDCl$_3$) δ 34.3; IR (KBr film) 3278, 2928, 1637, 1540, 1388, 1314, 1144, 966, 852, 741 cm$^{-1}$; HRMS (ESI) calcd for C$_{19}$H$_{31}$BNO$_3$ ([M+H]$^+$) 332.2392, found 332.2392.

**Compound 2c:** $R_f = 0.2$ (PE/EtOAc = 4:1), colorless oil, 54.8 mg, 79% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.74 (d, $J = 8.4$ Hz, 2H), 6.91 (d, $J = 8.4$ Hz, 2H), 6.40 (s, 1H), 3.84 (s, 3H), 3.45 (q, $J = 6.8$ Hz, 2H), 1.71 (q, $J = 7.2$ Hz, 2H), 1.57 – 1.41 (m, 2H), 1.24 (s, 12H), 1.06 – 0.98 (m, 1H), 0.93 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.9, 161.9, 128.6, 127.3, 113.6, 83.2, 55.3, 39.7, 30.3, 24.8, 24.7, 24.1, 13.4; $^{11}$B NMR (128 MHz, CDCl$_3$) δ 35.0; IR (KBr film) 3332, 2923, 1631, 1607, 1506, 1387, 1314, 1255, 1030, 845 cm$^{-1}$; HRMS (ESI) calcd for C$_{19}$H$_{32}$BNaO$_4$ ([M+Na]$^+$) 370.2160, found 370.2163.
Compound 2d: Rt = 0.4 (PE/EtOAc = 4:1), white solid, mp = 62 - 64 °C, 50.3 mg, 75% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.89 - 7.73 (m, 2H), 7.18 - 6.99 (m, 2H), 6.56 (s, 1H), 3.49 (q, \(J = 6.4 \text{ Hz}, 2H\)), 1.81 - 1.67 (m, 2H), 1.59 - 1.42 (m, 2H), 1.26 (s, 12H), 1.08 - 1.00 (m, 1H), 0.96 (t, \(J = 7.2 \text{ Hz}, 3H\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.1 (d, \(J = 58.2 \text{ Hz}\)), 163.3, 131.2, 129.2 (d, \(J = 8.8 \text{ Hz}\)), 115.4 (d, \(J = 21.8 \text{ Hz}\)), 83.3, 39.9, 30.1, 24.8, 24.7, 24.1, 13.4; \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) 34.6; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -108.8; IR (KBr film) 3320, 2928, 2870, 1638, 1504, 1316, 1144, 966, 851, 766 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{18}\)H\(_{27}\)BFNNaO\(_3\) ([M+Na]\(^+\)) 358.1960, found 358.1963.

Compound 2e: Rt = 0.3 (PE/EtOAc = 4:1), white solid, mp = 48 - 50 °C, 45.1 mg, 64% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.72 (d, \(J = 8.4 \text{ Hz}, 2H\)), 7.39 (d, \(J = 8.0 \text{ Hz}, 2H\)), 6.57 (brcs, 1H), 3.46 (q, \(J = 6.8 \text{ Hz}, 2H\)), 1.71 (q, \(J = 7.6 \text{ Hz}, 2H\)), 1.58 - 1.40 (m, 2H), 1.23 (s, 12H), 1.04 - 0.96 (m, 1H), 0.93 (t, \(J = 7.2 \text{ Hz}, 3H\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.3, 137.3, 133.3, 128.6, 128.4, 83.3, 39.9, 30.1, 24.7, 24.7, 24.0, 13.4; \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) 34.5; IR (KBr film) 3320, 2927, 2870, 1636, 1545, 1315, 1144, 848, 797, 669 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{18}\)H\(_{26}\)BrCINO\(_3\) ([M+H]\(^+\)) 352.1845, found 352.1849.

Compound 2f: Rt = 0.4 (PE/EtOAc = 4:1), white solid, mp = 72 - 74 °C, 63.4 mg, 80% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.64 (d, \(J = 8.0 \text{ Hz}, 2H\)), 7.54 (d, \(J = 6.8 \text{ Hz}, 2H\)), 6.49 (brcs, 1H), 3.46 (q, \(J = 6.8 \text{ Hz}, 2H\)), 1.76 - 1.67 (m, 2H), 1.56 - 1.49 (m, 1H), 1.49 - 1.42 (m, 1H), 1.25 (s, 12H), 1.05 - 0.96 (m, 1H), 0.93 (t, \(J = 7.6 \text{ Hz}, 3H\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.4, 133.8, 131.6, 128.6, 125.7, 83.3, 39.9, 30.1, 24.7, 24.7, 24.0, 13.3; \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) 34.9; IR (KBr film) 3311, 2927, 2869, 1636, 1544, 1314, 1143, 1011, 844, 754 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{18}\)H\(_{28}\)BrCINO\(_3\) ([M+Na]\(^+\)) 418.1160, found 418.1163.

Compound 2g: Rt = 0.4 (PE/EtOAc = 4:1), white solid, mp = 100 - 102 °C, 68.2 mg, 77% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.76 (d, \(J = 8.0 \text{ Hz}, 2H\)), 7.50 (d, \(J = 8.0 \text{ Hz}, 2H\)), 6.59 (brcs, 1H), 3.45 (q, \(J = 6.4 \text{ Hz}, 2H\)), 1.70 (q, \(J = 7.6 \text{ Hz}, 2H\)), 1.56 - 1.38 (m, 2H), 1.23 (s, 12H), 1.03 - 0.98 (m, 1H), 0.92 (t, \(J = 7.2 \text{ Hz}, 3H\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.6, 137.6, 134.4, 128.6, 98.0, 83.3, 39.9, 30.1, 24.8, 24.8, 24.1, 13.4; \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) 34.8; IR (KBr film) 3310, 2925, 2856, 1635, 1543, 1388, 1314, 1143, 1007, 797 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{18}\)H\(_{28}\)BINO\(_3\) ([M+H]\(^+\)) 444.1201, found 444.1205.

Compound 2h: Rt = 0.3 (PE/EtOAc = 4:1), white solid, mp = 78 - 80 °C, 56.2 mg, 73% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.89 (d, \(J = 8.0 \text{ Hz}, 2H\)), 7.68 (d, \(J = 7.6 \text{ Hz}, 2H\)),
13C NMR (100 MHz, CDCl₃) δ 166.1, 138.3, 132.9 (q, J = 32.4 Hz), 127.4, 125.4 (d, J = 3.5 Hz), 123.7 (q, J = 270.9 Hz), 83.3, 40.0, 30.0, 24.8, 24.7, 24.1, 13.4; ¹³B NMR (128 MHz, CDCl₃) δ 34.4; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.9; IR (KBr film) 3309, 2977, 2931, 1642, 1551, 1327, 1131, 1069, 1018, 858 cm⁻¹; HRMS (ESI) calcd for C₁₉H₂₇BF₃NaNO₃ ([M+Na⁺]⁺) 408.1928, found 408.1932.

Compound 2l: Rᵢ = 0.3 (PE/EtOAc = 4:1), white solid, mp = 71 - 73 °C, 43.9 mg, 68% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.48 (dd, J = 4.0, 1.2 Hz, 1H), 7.44 (dd, J = 5.2, 1.2 Hz, 1H), 7.06 (dd, J = 4.8, 3.6 Hz, 1H), 2.62 (brs, 1H), 3.55 - 3.33 (m, 2H), 1.70 (q, J = 7.6 Hz, 2H), 1.56 - 1.39 (m, 2H), 1.25 (s, 12H), 1.05 - 0.96 (m, 1H), 0.93 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 161.7, 139.4, 129.5, 127.7, 127.4, 83.2, 39.6, 30.3, 24.8, 24.0, 13.4; ¹¹B NMR (128 MHz, CDCl₃) δ 34.7; IR (KBr film) 3310, 2928, 2970, 1624, 1550, 1311, 1143, 966, 858, 714 cm⁻¹; HRMS (ESI) calcd for C₁₉H₂₇BF₃NaNO₃ ([M+Na⁺]⁺) 436.1619, found 436.1622.

Compound 2j: Rᵢ = 0.3 (PE/EtOAc = 4:1), white solid, mp = 83 - 85 °C, 48.5 mg, 80% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 7.6 Hz, 2H), 7.55 - 7.36 (m, 3H), 6.55 (brs, 1H), 3.61 - 3.36 (m, 2H), 1.82 - 1.70 (m, 1H), 1.70 - 1.59 (m, 1H), 1.15 - 1.10 (m, 1H), 1.04 (d, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.4, 135.0, 131.1, 128.4, 126.9, 83.2, 39.5, 32.4, 24.7, 15.6; ¹¹B NMR (128 MHz, CD₂CN) δ 29.7; IR (KBr film) 3321, 2975, 2928, 1637, 1541, 1313, 1143, 966, 851, 694 cm⁻¹; HRMS (ESI) calcd for C₁₉H₂₆BNNaO₃ ([M+Na⁺]⁺) 326.1898, found 326.1901.

Compound 2k: Rᵢ = 0.3 (PE/EtOAc = 4:1), white solid, mp = 68 - 70 °C, 46.7 mg, 63% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 6.67 (brs, 1H), 3.66 - 3.33 (m, 2H), 1.81 - 1.71 (m, 1H), 1.71 - 1.59 (m, 1H), 1.22 (s, 12H), 1.17 - 1.07 (m, 1H), 1.05 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 138.3, 132.9 (q, J = 32.7 Hz), 127.4, 125.4 (d, J = 3.3 Hz), 123.7 (q, J = 270.9 Hz), 83.3, 39.7, 32.3, 24.7, 15.6; ¹¹B NMR (128 MHz, CDCl₃) δ 34.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.9; IR (KBr film) 3310, 2977, 2930, 1642, 1551, 1327, 1131, 1069, 859, 685 cm⁻¹; HRMS (ESI) calcd for C₁₉H₂₆BF₃NaNO₃ ([M+Na⁺]⁺) 394.1772, found 394.1775.

Compound 2l: Rᵢ = 0.2 (PE/EtOAc = 4:1), colorless oil, 50.0 mg, 75% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 7.2 Hz, 2H), 6.90 (d, J = 7.2 Hz, 2H), 6.36 (brs, 1H), 3.84 (s, 3H), 3.59 - 3.35 (m, 2H), 1.68 - 1.59 (m, 2H), 1.23 (s, 12H), 1.15 - 1.08 (m, 1H), 1.04 (d, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.9, 161.8, 128.6, 127.2, 113.5, 83.2, 55.3, 39.4, 32.5, 24.7, 15.6; ¹¹B NMR (128 MHz, CDCl₃) δ 34.5; IR (KBr film) 3328, 2976, 2931, 1633, 1506, 1255, 1144,
1031, 845, 768 cm⁻¹; HRMS (ESI) calcd for C₁₈H₂₉BNNaO₄ ([M+Na⁺]⁺) 356.0204, found 356.027.

**Compound 2m**: Rₙ = 0.3 (PE/EtOAc = 4:1), white solid, mp = 51 - 53 °C, 46.3 mg, 70% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.82 – 7.70 (m, 2H), 7.52 – 7.45 (m, 1H), 7.45 – 7.38 (m, 2H), 6.46 (brs, 1H), 3.47 (q, J = 6.8 Hz, 2H), 1.71 (q, J = 7.2 Hz, 2H), 1.40 – 1.30 (m, 4H), 1.23 (s, 12H), 1.10 – 1.06 (m, 1H), 0.90 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.4, 135.0, 131.2, 128.4, 126.9, 83.2, 39.8, 33.3, 30.4, 24.7, 22.1, 14.3; ¹¹B NMR (128 MHz, CDCl₃) δ 34.1; IR (KBr film) 3322, 2956, 2925, 1638, 1542, 1314, 1243, 1144, 860, 694 cm⁻¹; HRMS (ESI) calcd for C₁₉H₃₀BNNaO₃ ([M+Na⁺]⁺) 354.2211, found 354.2214.

**Compound 2n**: Rₙ = 0.3 (PE/EtOAc = 4:1), white solid, mp = 65 - 67 °C, 51.1 mg, 74% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 7.2 Hz, 2H), 7.57 – 7.33 (m, 3H), 6.53 (brs, 1H), 3.47 (q, J = 6.4 Hz, 2H), 1.71 (q, J = 6.8 Hz, 2H), 1.53 – 1.36 (m, 2H), 1.29 (brs, 3H), 1.23 (s, 12H), 1.10 – 1.03 (m, 1H), 0.88 (t, J = 5.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.4, 135.0, 131.1, 128.4, 126.9, 83.2, 39.8, 33.3, 30.8, 30.4, 24.7, 22.9, 14.0; ¹¹B NMR (128 MHz, CDCl₃) δ 35.2; IR (KBr film) 3322, 2926, 2857, 1637, 1543, 1313, 1144, 967, 852, 694 cm⁻¹; HRMS (ESI) calcd for C₁₉H₃₂BNNaO₃ ([M+Na⁺]⁺) 368.2367, found 368.2371.

**Compound 2o**: Rₙ = 0.3 (PE/EtOAc = 4:1), yellow oil, 36.1 mg, 45% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.76 – 7.70 (m, 2H), 7.51 – 7.44 (m, 1H), 7.44 – 7.36 (m, 2H), 7.25 – 7.19 (m, 4H), 7.18 – 7.13 (m, 1H), 6.37 (brs, 1H), 3.57 – 3.39 (m, 2H), 2.84 (dd, J = 14.0, 8.0 Hz, 1H), 2.68 (dd, J = 13.6, 8.0 Hz, 1H), 1.72 (q, J = 7.1 Hz, 2H), 1.50 – 1.40 (m, 1H), 1.17 (s, 6H), 1.15 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 167.4, 141.7, 135.0, 131.2, 128.9, 128.4, 128.2, 126.9, 83.5, 39.6, 37.0, 30.2, 24.7, 24.7; ¹¹B NMR (128 MHz, CDCl₃) δ 34.1; IR (KBr film) 3325, 2976, 2927, 1638, 1541, 1490, 1320, 1142, 851, 698 cm⁻¹; HRMS (ESI) calcd for C₂₃H₃₆BNNaO₃ ([M+Na⁺]⁺) 402.2211, found 402.2215.

**Compound 2p**: Rₙ = 0.3 (PE/EtOAc = 4:1), yellow oil, 47.9 mg, 61% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 7.2 Hz, 2H), 7.54 – 7.37 (m, 3H), 7.30 – 7.14 (m, 5H), 6.49 (brs, 1H), 3.49 (q, J = 6.8 Hz, 2H), 2.79 – 2.49 (m, 2H), 1.87 – 1.68 (m, 4H), 1.25 (s, 12H), 1.18 – 1.11 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 167.4, 142.6, 134.9, 131.2, 128.4, 128.4, 128.3, 126.9, 125.7, 83.4, 39.6, 35.2, 33.1, 30.4, 24.8, 24.8; ¹¹B NMR (128 MHz, CDCl₃) δ 34.4; IR (KBr film) 3323, 2976, 2927, 1637, 1541, 1315, 1142, 966, 852, 697 cm⁻¹; HRMS (ESI) calcd for C₂₄H₃₈BNNaO₃ ([M+Na⁺]⁺) 416.2367, found 416.2372.

**Compound 2q**: Rₙ = 0.2 (PE/EtOAc = 2:1), white solid, mp = 88 - 90 °C, 43.2 mg, 68% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.32 (m, 2H), 7.32 – 7.28 (m, 1H), 7.27 – 7.21 (m, 2H), 5.53 (s, 1H), 3.56 (s, 2H), 3.33 – 3.14 (m, 2H), 1.62 – 1.49 (m, 1H), 1.47
−1.36 (m, 1H), 1.21 (s, 12H), 1.05−0.89 (m, 4H); 13C NMR (100 MHz, CDCl3) δ 170.7, 135.0, 129.4, 128.9, 127.2, 83.1, 43.9, 39.1, 32.4, 24.7, 24.7, 15.3; 11B NMR (128 MHz, CDCl3) δ 34.7; IR (KBr film) 3228, 3062, 2922, 1639, 1568, 1234, 1141, 1013, 848, 696 cm−1; HRMS (ESI) calcd for C18H28BNNaO3 ([M+Na]+) 340.2054, found 340.2061.

Compound 2r: Rf = 0.1 (PE/EtOAc = 4:1), yellow oil, 44.3 mg, 57% yield. 1H NMR (400 MHz, CDCl3) δ 7.77 (d, J = 7.2 Hz, 2H), 7.57−7.34 (m, 3H), 6.53 (brs, 1H), 3.66 (s, 3H), 3.47 (q, J = 6.8 Hz, 2H), 2.32 (t, J = 7.2 Hz, 2H), 1.75−1.63 (m, 4H), 1.54−1.38 (m, 2H), 1.24 (s, 12H), 1.12−1.04 (m, 1H); 13C NMR (100 MHz, CDCl3) δ 174.1, 167.4, 134.9, 131.2, 128.4, 126.9, 83.4, 51.4, 39.6, 34.2, 30.5, 30.3, 24.8, 24.7, 24.2; 11B NMR (128 MHz, CDCl3) δ 35.2; IR (KBr film) 3330, 2976, 2930, 1736, 1639, 1541, 1315, 1143, 857, 695 cm−1; HRMS (ESI) calcd for C21H22BNNaO5 ([M+Na]+) 412.2266, found 412.2269.

Compound 2s: Rf = 0.2 (PE/EtOAc = 3:1), colorless oil, 60.3 mg, 69% yield. 1H NMR (400 MHz, CDCl3) δ 7.80−7.72 (m, 2H), 7.52−7.45 (m, 1H), 7.44−7.38 (m, 2H), 7.33 (d, J = 4.4 Hz, 4H), 7.30−7.23 (m, 1H), 6.50 (s, 1H), 4.49 (s, 2H), 3.54−3.37 (m, 4H), 1.75−1.59 (m, 4H), 1.57−1.44 (m, 2H), 1.22 (s, 12H), 1.13−1.04 (m, 1H); 13C NMR (100 MHz, CDCl3) δ 167.4, 138.5, 134.9, 131.2, 128.4, 128.3, 127.6, 127.4, 126.9, 83.3, 72.7, 70.4, 39.7, 30.4, 29.0, 27.5, 24.8, 24.7; 11B NMR (128 MHz, CDCl3) δ 35.4; IR (KBr film) 3327, 2929, 2857, 1638, 1541, 1314, 1143, 1028, 802, 696 cm−1; HRMS (ESI) calcd for C20H21BNO4 ([M+H]+) 348.2111, found 348.2120.

Compound 2t: Rf = 0.2 (PE/EtOAc = 2:1), colorless oil, 40.4 mg, 61% yield. 1H NMR (400 MHz, CDCl3) δ 10.08 (s, 1H), 8.30−8.20 (m, 1H), 8.16−8.06 (m, 1H), 8.04−7.97 (m, 1H), 7.62 (d, J = 7.6 Hz, 1H), 6.64 (s, 1H), 3.67−3.38 (m, 2H), 1.83−1.72 (m, 1H), 1.68 (dd, J = 13.2, 6.4 Hz, 1H), 1.22 (s, 12H), 1.17−1.10 (m, 1H), 1.05 (d, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 191.6, 166.1, 136.3, 135.9, 133.0, 132.2, 129.4, 127.7, 83.3, 39.7, 32.4, 24.7, 24.7, 15.7; 11B NMR (128 MHz, CDCl3) δ 34.0; IR (KBr film) 3327, 2930, 2856, 1701, 1640, 1544, 1208, 1144, 966, 686 cm−1; HRMS (ESI) calcd for C18H17BNO4 ([M+H]+) 332.2028, found 332.2030.

Compound 2u: Rf = 0.2 (PE/EtOAc = 2:1), colorless oil, 42.1 mg, 66% yield. 1H NMR (400 MHz, CDCl3) δ 7.66−7.56 (m, 1H), 7.24 (d, J = 7.6 Hz, 1H), 7.16 (d, J = 7.6 Hz, 1H), 6.99 (dd, J = 8.0, 1.6 Hz, 1H), 6.68 (t, J = 4.0 Hz, 1H), 3.57−3.38 (m, 2H), 1.82−1.58 (m, 2H), 1.22 (s, 12H), 1.16−1.07 (m, 1H), 1.04 (d, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 167.8, 157.0, 135.9, 129.6, 118.8, 117.7, 115.1, 83.4, 39.7, 32.3, 24.7, 24.7, 15.6; 11B NMR (128 MHz, CDCl3) δ 35.0; IR (KBr film) 3332, 2961, 2928, 1638,
1581, 1315, 1143, 1028, 801, 688 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{17}\)H\(_{26}\)BNNaO\(_4\) ([M+Na]\(^+\)) 342.1847, found 342.1846.

Compound 2v: \(R_1 = 0.2\) (PE/EtOAc = 4:1), yellow oil, 60.6 mg, 66% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.67 (d, \(J = 8.4\) Hz, 2H), 7.30 – 7.21 (m, 2H), 6.46 (s, 1H), 3.56 – 3.38 (m, 2H), 2.78 (t, \(J = 8.0\) Hz, 2H), 1.79 – 1.70 (m, 1H), 1.68 – 1.59 (m, 1H), 1.22 (s, 24H), 1.14 (t, \(J = 8.0\) Hz, 3H), 1.04 (d, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.4, 148.0, 132.2, 128.0, 126.8, 83.2, 39.4, 32.5, 29.8, 24.8, 24.7, 15.6; \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) 34.1; IR (KBr film) 3333, 2977, 2930, 1636, 1545, 1371, 1144, 967, 846 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{25}\)H\(_{41}\)B\(_2\)NNaO\(_5\) ([M+Na]\(^+\)) 480.3063, found 480.3069.

Compound 2w: \(R_1 = 0.2\) (PE/EtOAc = 6:1), colorless oil, 40.3 mg, 64% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.84 – 7.71 (m, 2H), 7.51 – 7.46 (m, 1H), 7.45 – 7.39 (m, 2H), 6.33 (s, 1H), 3.56 – 3.26 (m, 2H), 1.71 – 1.50 (m, 3H), 1.46 – 1.34 (m, 1H), 1.23 (s, 12H), 1.10 – 1.02 (m, 1H), 1.00 (d, \(J = 6.8\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.4, 134.9, 131.2, 128.5, 126.8, 83.0, 40.1, 30.3, 28.7, 24.7, 15.6; \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) 35.0; IR (KBr film) 3322, 2976, 2929, 1638, 1541, 1386, 1313, 1144, 858, 695 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{18}\)H\(_{29}\)BNO\(_3\) ([M+H]\(^+\)) 318.2235, found 318.2237.

Compound 2x: \(R_1 = 0.2\) (PE/EtOAc = 6:1), white solid, mp = 79 – 81 °C, 50.1 mg, 83% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.86 – 7.69 (m, 2H), 7.52 – 7.46 (m, 1H), 7.45 – 7.39 (m, 2H), 6.32 (s, 1H), 3.45 (dd, \(J = 12.4, 6.8\) Hz, 2H), 1.69 – 1.59 (m, 2H), 1.58 – 1.46 (m, 2H), 1.24 (s, 14H), 0.85 (t, \(J = 7.6\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.4, 134.9, 131.2, 128.5, 126.8, 83.1, 39.6, 31.8, 24.8, 21.1; \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) 34.0; IR (KBr film) 3323, 2976, 2929, 1638, 1541, 1386, 1313, 1144, 858, 695 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{17}\)H\(_{26}\)BNNaO\(_3\) ([M+Na]\(^+\)) 326.1898, found 326.1909.

7. Gram-scale prepration of 2a

To a 25-mL flame-dried Schlenk tube charged with [IrCp*Cl\(_2\)]\(_2\) (53 mg, 1.25 mol %), 1,1-diphenylethene (936 μL, 5.3 mmol, 1.0 equiv) was added CyH (26 mL). The solution was allowed to stir for 10 min. 1a (1.0 g, 5.3 mmol) and HBpin (1.1 g, 8.48 mmol, 1.6 equiv) was added successively. The reaction was allowed to stir at room temperature for 5 h. The regioselectivity was determined by GC analysis. After removal of the solvent, the residue was
purified by column chromatography on silica gel using PE/EtOAc (4:1) as the eluent to afford desired borylated product 2a (1.05 g, 68% yield, 88% \text{y}).

8. Preparation of compound 4

The preparation of 4 was adapted from literature procedures.\(^3\) To a 25-mL flask charged with 2a (63.4 mg, 0.20 mmol) and THF/H\text{O} (2 : 1, 3 mL) was added NaBO\text{4} \cdot 4\text{H}\text{O} (153.9 mg, 1.0 mmol, 5.0 equiv). The reaction was allowed to stir at room temperature for 3 h. The solution was extracted with Et\text{O} twice (2 × 10 mL). The combined ethereal solution was dried over anhydrous MgSO\text{4}. After removal of the solvent, the residue was purified by column chromatography on silica using PE/EtOAc (2 : 1) as the eluent to afford 4 as white solid (mp = 63 - 65 °C, 39.8 mg, 96% yield). \(^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.85 - 7.71 (m, 2H), 7.53 - 7.47 (m, 1H), 7.46 - 7.37 (m, 2H), 6.84 (brs, 1H), 3.98 - 3.85 (m, 1H), 3.71 - 3.56 (m, 1H), 3.44 - 3.29 (m, 1H), 1.83 - 1.72 (m, 1H), 1.66 - 1.58 (m, 1H), 1.57 - 1.47 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H); \(^13\text{C} \text{NMR} (100 \text{ MHz, CDCl}_3) \delta 168.1, 134.4, 131.5, 128.5, 126.9, 71.4, 37.5, 36.2, 30.3, 10.0; IR (KBr film) 3337, 2968, 2934, 2881, 1639, 1541, 1309, 931, 695 cm\text{⁻¹}; HRMS (ESI) calcd for C\text{12}H\text{16}NO\text{2} ([M+H\text{⁺}] \text{⁺}) 208.1332, found 208.1328.

9. Preparation of compound 5

The preparation of 5 was adapted from literature procedures.\(^4\) To a 25-mL flame-dried Schlenk tube charged with 2a (63.4 mg, 0.20 mmol), AgNO\text{3} (6.8 mg, 0.04 mmol), Selectfluor (212.4 mg, 0.60 mmol, 3.0 equiv), DCM (1.0 mL), H\text{2}O (1.0 mL) and TFA (62 \text{µL}, 0.8 mmol, 4.0 equiv) were then added. The reaction mixture was allowed to stir at 50 °C for 5 h. After cooling to room temperature, the reaction was quenched by slow addition of saturated aq. NaHCO\text{3} (5 mL), and the resulting mixture was extracted with Et\text{O}Ac 3 times (3 × 10 mL). The combined ethereal solution was dried over anhydrous MgSO\text{4}. After removal of the solvent, the residue was purified by column chromatography on silica using PE/EtOAc (6 : 1) as the eluent to afford 5 as colorless oil (33.4 mg, 80% yield). \(^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.86 - 7.70 (m, 2H), 7.53 - 7.47 (m, 1H), 7.46 - 7.37 (m, 2H), 6.50 (brs, 1H), 4.75 - 4.45 (m, 1H), 3.79 - 3.64 (m, 1H), 3.61 - 3.47 (m, 1H), 2.11 - 1.82 (m, 2H), 1.79 - 1.52 (m, 2H), 0.99 (t, J = 7.5 Hz, 3H); \(^13\text{C} \text{NMR} (100 \text{ MHz, CDCl}_3) \delta 167.5, 134.6, 131.4, 128.5, 126.8, 95.1 (d, J = 165.6 Hz), 37.1 (d, J = 2.8 Hz), 34.1 (d, J = 19.8 Hz), 28.2 (d, J = 21.0 Hz), 9.3 (d, J = 6.0 Hz); \(^19\text{F} \text{NMR} (376 \text{ MHz, CDCl}_3) \delta -181.9; IR (KBr film) 3315, 2968, 2934, 2881, 1639, 1541, 1309, 1076, 931, 695 \text{cm} \text{⁻¹}; HRMS (ESI) calcd for C\text{12}H\text{17}F\text{NO} ([M+H\text{⁺}] \text{⁺}) 210.1289, found 210.1286.


10. Preparation of compound 6

The preparation of 6 was adapted from literature procedures. To a 25-mL flame-dried Schlenk tube charged with 1-bromo-3,5-bis(trifluoromethyl)benzene (69 μL, 0.4 mmol, 2.0 equiv) and THF (1 mL) was added nBuLi (160 μL, 0.4 mmol, 2.0 equiv, 2.5 M in hexanes) at -78 °C. The resulting mixture was allowed to stir for 1 h and 2a (63.4 mg, 0.2 mmol) was added dropwise as a solution in THF (1.0 mL). The mixture was allowed to stir at -78 °C for 1 h. A solution of an NBS (71.2 mg, 0.4 mmol, 2.0 equiv) was added dropwise as a solution in THF (1.0 mL). After the mixture was allowed to stir at room temperature for 1 h, saturated aq. Na₂S₂O₃ (5 mL) was added. The reaction mixture was diluted with Et₂O (15 mL) and water (15 mL). The combined ethereal solution was dried over anhydrous MgSO₄. After removal of the solvent, the residue was purified by column chromatography on silica using PE/EtOAc (5:1) as the eluent to afford 7 as colorless oil (41.1 mg, 80% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.62 (m, 2H), 7.50 – 7.44 (m, 1H), 7.43 – 7.35 (m, 2H), 7.32 (dd, J = 1.6, 0.8 Hz, 1H), 1.638, 1541, 1279, 1027, 801, 694 cm⁻¹; HRMS (ESI) calcd for C_{12}H_{17}BrNO ([M+H]^+): 270.0488, found 270.0487.

11. Preparation of compound 7

The preparation of 6 was adapted from literature procedures. To a 25-mL flame-dried Schlenk tube charged with furan (73 μL, 1.0 mmol, 5.0 equiv) and THF (1.0 mL) was added nBuLi (400 μL, 1.0 mmol, 5.0 equiv, 2.5 M in hexanes) at -78 °C. The reaction was then allowed to warm to room temperature and stir at this temperature for additional 1 h. The mixture was then cooled to -78 °C again and 2a (63.4 mg, 0.20 mmol) was added dropwise as a solution in THF (1.0 mL). The mixture was allowed to stir at -78 °C for 1 h. A solution of an NBS (42.7 mg, 0.24 mmol, 1.2 equiv) was added dropwise as a solution in THF (1.0 mL). After 1 h at -78 °C, saturated aq. Na₂S₂O₃ (2 mL) was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with Et₂O (15 mL) and water (15 mL). The combined ethereal solution was dried over anhydrous MgSO₄. After removal of the solvent, the residue was purified by column chromatography on silica using PE/EtOAc (6:1) as the eluent to afford 7 as colorless oil (41.1 mg, 80% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.62 (m, 2H), 7.50 – 7.44 (m, 1H), 7.43 – 7.35 (m, 2H), 7.32 (dd, J = 1.6, 0.8 Hz, 1H), 270.0488, found 270.0487.

6.30 (dd, J = 3.2, 2.0 Hz, 1H), 6.08 – 6.06 (m, 2H), 3.50 – 3.30 (m, 2H), 2.78 – 2.64 (m, 1H), 2.06 – 1.94 (m, 1H), 1.94 – 1.82 (m, 1H), 1.73 – 1.60 (m, 2H), 0.85 (t, J = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.3, 157.9, 141.0, 134.7, 131.3, 128.4, 126.8, 110.1, 105.6, 38.9, 38.5, 33.7, 27.2, 11.7; IR (KBr film) 3307, 2962, 2931, 2873, 1636, 1541, 1307, 1007, 923, 694 cm$^{-1}$; HRMS (ESI) calcd for C$_{16}$H$_{20}$NO$_2$ ([M+H]$^+$) 258.1489, found 258.1489.

12. Preparation of compound 8

![Diagram of reaction](image)

The preparation of 8 was adapted from literature procedures$^7$. To a 25-mL flame-dried Schlenk tube charged with 1-bromo-3,5-dimethoxybenzene (173.6 mg, 0.8 mmol, 4.0 equiv) and THF (1 mL) was added nBuLi (320 μL, 0.8 mmol, 4.0 equiv, 2.5 M in hexanes) at -78 °C. The resulting mixture was allowed to stir for 1 h. and 2a (63.4 mg, 0.2 mmol) was added dropwise as a solution in THF (1.0 mL). A solution of an NBS (142.4 mg, 0.8 mmol, 4.0 equiv) was added dropwise as a solution in THF (1.0 mL). After the mixture was allowed to stir at -78 °C for 1 h, saturated aq. Na$_2$S$_2$O$_3$ (2 mL) was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with Et$_2$O (15 mL) and water (15 mL). The combined ethereal solution was dried over anhydrous MgSO$_4$. After removal of the solvent, the residue was purified by column chromatography on silica using PE/EtOAc (4: 1) as the eluent to afford 8 as white solid (mp = 65 – 67 °C, 54.9 mg, 84% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.61 – 7.52 (m, 2H), 7.48 – 7.43 (m, 1H), 7.40 – 7.33 (m, 2H), 6.36 (d, J = 2.4 Hz, 2H), 6.31 (t, J = 2.4 Hz, 1H), 5.93 (brs, 1H), 3.76 (s, 6H), 3.57 – 3.42 (m, 1H), 3.26 (m, 1H), 2.53 – 2.40 (m, 1H), 2.09 – 1.96 (m, 1H), 1.90 – 1.76 (m, 1H), 1.71 – 1.64 (m, 1H), 1.61 – 1.55 (m, 1H), 0.80 (t, J = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.1, 161.1, 147.6, 134.7, 131.2, 128.4, 126.7, 105.8, 97.9, 55.2, 46.9, 39.0, 35.9, 29.9, 12.1; IR (KBr film) 3320, 2961, 2930, 1637, 1595, 1459, 1153, 1060, 800, 697 cm$^{-1}$; HRMS (ESI) calcd for C$_{20}$H$_{26}$NO$_3$ ([M+H]$^+$) 328.1907, found 328.1910.

13. Preparation of compound 9

![Diagram of reaction](image)

The preparation of 7 was adapted from literature procedures$^2$. To a 25-mL flame-dried Schlenk tube charged with 2a (63.4 mg, 0.20 mmol), THF (1.5 mL), Vinylimagnesium bromide (1.2 mL, 1.0 M in THF, 6.0 equiv) was then added dropwise. The resulted mixture was allowed to stir as room temperature for one hour. To the above solution at -78 °C, iodine (304.8 mg, 1.2 mmol, 6.0 equiv) was added dropwise as a solution in methanol (2.0 mL). The reaction mixture was allowed to stir 30 min. at the same temperature followed by dropwise

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addition of a solution of NaOMe (64.8 mg, 1.2 mmol, 6.0 equiv) in methanol (2.5 mL). After warming to room temperature, the resultant mixture was allowed to stir for 1.5 h. Saturated aq. Na$_2$S$_2$O$_3$ (2 mL) was then added. The reaction mixture was diluted with Et$_2$O (15 mL) and water (15 mL). The combined ethereal solution was dried over anhydrous MgSO$_4$. After removal of the solvent, the residue was purified by column chromatography on silica using PE/EtOAc (6:1) as the eluent to afford colorless oil (39.9 mg, 92% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.93 – 7.66 (m, 2H), 7.64 – 7.34 (m, 3H), 6.27 (brs, 1H), 5.72 – 5.45 (m, 1H), 5.25 – 4.86 (m, 2H), 3.64 – 3.19 (m, 2H), 2.09 – 1.89 (m, 1H), 1.81 – 1.69 (m, 1H), 1.59 – 1.39 (m, 2H), 1.36 – 1.24 (m, 1H), 0.96 – 0.75 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.3, 142.3, 134.9, 131.2, 128.5, 126.8, 115.3, 44.1, 38.5, 34.3, 27.8, 11.5; IR (KBr film) 3310, 2962, 2927, 1637, 1542, 1490, 1307, 912, 802, 694 cm$^{-1}$; HRMS (ESI) calcd for C$_{14}$H$_{20}$NO ([M+H]$^+$) 218.1539, found 218.1538.

14. Preparation of achiral CpIr(cod) (I)

![Diagram](image)

The preparation of I was according to the literature procedures.$^8$ To a flame-dried, N$_2$-filled 10-mL Schlenk tube charged with CpTl (135.0 mg, 0.5 mmol) and THF (1 mL) was added [IrCl(cod)]$_2$ (100.2 mg, 0.15 mmol) at room temperature. The resulting mixture was then allowed to stir at room temperature for additional 2 h. After removal of the solvent, the residue was subjected to column chromatography on neutral Al$_2$O$_3$ using anhydrous Et$_2$O as the eluent to afford CpIr(cod) (I) as the pale white solid (90.1 mg, 82% yield). $^1$H NMR spectrum is consistent with literature reported.$^8$ $^1$H NMR (400 MHz, d$_8$-toluene) δ 5.04 (s, 5H), 4.04 (d, $J$ = 3.6 Hz, 4H), 2.39 – 2.35 (m, 4H), 2.16 – 2.09 (m, 4H).

15. Preparation of chiral CpIr(cod) (II).

![Diagram](image)

The preparation of II was adapted from literature procedures.$^9$ To a N$_2$-filled 10-mL Schlenk tube charged with a mixture of spiro Cp ligands S3 (10.0 mg, 0.027 mmol) and [IrOMe(COD)]$_2$ (10.8 mg, 0.016 mmol) were added toluene (0.5 mL) and MeOH (0.5 mL). The resulting mixture was allowed to stir at 70 °C 3 h. After the removal of the solvent, the residue was purified by column chromatography on silica gel using toluene as the eluent to afford chiral...
Ir-complex II as a pale white solid (12.8 mg, 70% yield). $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 6.86 (d, $J$ = 8.0 Hz, 1H), 6.81 (d, $J$ = 8.0 Hz, 1H), 6.47 (d, $J$ = 8.4 Hz, 1H), 6.32 (d, $J$ = 8.4 Hz, 1H), 5.38 (t, $J$ = 2.0 Hz, 1H), 4.63 (t, $J$ = 2.0 Hz, 1H), 4.38 (t, $J$ = 2.4 Hz, 1H), 3.78 (d, $J$ = 14.0 Hz, 1H), 3.86 (td, $J$ = 8.0, 2.4 Hz, 2H), 3.40 (s, 3H), 3.25 (s, 2H), 3.20 (s, 3H), 3.14 – 3.09 (m, 3H), 2.64 – 2.55 (m, 2H), 2.49 – 2.42 (m, 2H), 2.16 – 2.06 (m, 2H), 1.95 – 1.68 (m, 10H); $^{13}$C NMR (100 MHz, C$_6$D$_6$) $\delta$ 169.7, 157.7, 157.0, 148.9, 148.4, 134.4, 133.4, 128.9, 128.2, 125.3, 124.5, 123.4, 123.0, 122.8, 109.7, 109.6, 104.9, 92.5, 86.4, 82.3, 77.2, 62.3, 59.7, 54.9, 54.8, 47.3, 46.5, 34.7, 33.3, 20.2, 13.8; HRMS (ESI) calcd for C$_{34}$H$_{38}^{191}$IrO$_2$ ([M+H]$^+$) 669.2473, found 669.2464.
16. NMR spectra of all new compounds

$^1$H NMR spectrum of Compound 1a (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 1a (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of Compound 1b (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 1b (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of Compound 1c (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 1c (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of Compound 1d (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 1d (CDCl$_3$, 100 MHz)
\[19F\text{ NMR spectrum of Compound 1d (CDCl}_3, 376 \text{ MHz})\]

\[1H\text{ NMR spectrum of Compound 1e (CDCl}_3, 400 \text{ MHz})\]
$^{13}$C NMR spectrum of Compound 1e (CDCl$_3$, 100 MHz)

$^1$H NMR spectrum of Compound 1f (CDCl$_3$, 400 MHz)
\[^{13}\text{C NMR spectrum of Compound 1f (CDCl}_3, 100 \text{ MHz)}\]

\[^{1}\text{H NMR spectrum of Compound 1g (CDCl}_3, 400 \text{ MHz)}\]
$^{13}$C NMR spectrum of Compound 1g (CDCl$_3$, 100 MHz)

$^1$H NMR spectrum of Compound 1h (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 1h (CDCl$_3$, 100 MHz)

$^{19}$F NMR spectrum of Compound 1h (CDCl$_3$, 376 MHz)
$^1$H NMR spectrum of Compound 1i (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 1i (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of Compound 1j (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 1j (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of Compound 1k (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectra of Compound 1k (CDCl$_3$, 100 MHz)
$^{19}$F NMR spectra of Compound 1k (CDCl$_3$, 376 MHz)

$^1$H NMR spectrum of Compound 1l (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectra of Compound 1l (CDCl$_3$, 100 MHz)

$^{1}$H NMR spectrum of Compound 1m (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 1m (CDCl$_3$, 100 MHz)

$^1$H NMR spectrum of Compound 1n (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 1n (CDCl$_3$, 100 MHz)

$^1$H NMR spectrum of Compound 1o (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 1o (CDCl$_3$, 100 MHz)

$^1$H NMR spectrum of Compound 1p (CDCl$_3$, 400 MHz)
\textsuperscript{13}C NMR spectrum of Compound 1p (CDCl\textsubscript{3}, 100 MHz)

\textsuperscript{1}H NMR spectrum of Compound 1q (CDCl\textsubscript{3}, 400 MHz)
$^{13}$C NMR spectrum of Compound 1q (CDCl$_3$, 100 MHz)

$^1$H NMR spectrum of Compound 1r (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 1r (CDCl$_3$, 100 MHz)

$^1$H NMR spectrum of Compound 1s (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 1s (CDCl$_3$, 100 MHz)

$^1$H NMR spectrum of Compound 1t (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 1t (CDCl$_3$, 100 MHz)

$^1$H NMR spectrum of Compound 1u (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 1u (CDCl$_3$, 100 MHz)

$^1$H NMR spectrum of Compound 1v (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 1v (CDCl$_3$, 100 MHz)

$^1$H NMR spectrum of Compound 1w (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound \textit{1w} (CDCl$_3$, 100 MHz)

$^1$H NMR spectrum of Compound \textit{1x} (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 1x (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of Compound 2a (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectra of Compound 2a (CDCl$_3$, 100 MHz)
$^{11}$B NMR spectrum of Compound 2a (CDCl$_3$, 128 MHz)

$^1$H NMR spectrum of Compound 2b (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 2b (CDCl$_3$, 100 MHz)

$^{11}$B NMR spectra of Compound 2b (CDCl$_3$, 128 MHz)
$^1$H NMR spectrum of Compound 2c (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 2c (CDCl$_3$, 100 MHz)
$^{11}$B NMR spectrum of Compound 2c (CDCl$_3$, 128 MHz)

$^1$H NMR spectrum of Compound 2d (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 2d (CDCl$_3$, 100 MHz)

$^{11}$B NMR spectrum of Compound 2d (CDCl$_3$, 128 MHz)
$^{19}$F NMR spectrum of Compound 2d (CDCl$_3$, 376 MHz)

$^1$H NMR spectrum of Compound 2e (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 2e (CDCl$_3$, 100 MHz)

$^{11}$B NMR spectrum of Compound 2e (CDCl$_3$, 128 MHz)
$^1$H NMR spectrum of Compound 2f (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 2f (CDCl$_3$, 100 MHz)
$^{11}$B NMR spectrum of Compound 2f (CDCl$_3$, 128 MHz)

$^1$H NMR spectrum of Compound 2g (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 2g (CDCl$_3$, 100 MHz)

$^{11}$B NMR spectrum of Compound 2g (CDCl$_3$, 128 MHz)
\[ ^1H \text{ NMR spectrum of Compound 2h (CDCl}_3, 400 \text{ MHz)} \]

\[ ^{13}C \text{ NMR spectrum of Compound 2h (CDCl}_3, 100 \text{ MHz)} \]
$^{11}$B NMR spectrum of Compound 2h (CDCl$_3$, 128 MHz)

$^{19}$F NMR spectrum of Compound 2h (CDCl$_3$, 376 MHz)
$^1$H NMR spectrum of Compound 2i (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 2i (CDCl$_3$, 100 MHz)
\(^{11}\)B NMR spectrum of Compound 2i (CDCl\(_3\), 128 MHz)

\(^1\)H NMR spectrum of Compound 2j (CDCl\(_3\), 400 MHz)
$^{13}$C NMR spectrum of Compound 2j (CDCl$_3$, 100 MHz)

$^{11}$B NMR spectra of Compound 2j (CDCl$_3$, 128 MHz)
$^1$H NMR spectrum of Compound 2k (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 2k (CDCl$_3$, 100 MHz)
$^{11}$B NMR spectrum of Compound 2k (CDCl$_3$, 128 MHz)

$^{19}$F NMR spectrum of Compound 2k (CDCl$_3$, 376 MHz)
$^1$H NMR spectrum of Compound 2l (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 2l (CDCl$_3$, 100 MHz)
$^{11}$B NMR spectrum of Compound 2l (CDCl$_3$, 128 MHz)

$^1$H NMR spectrum of Compound 2m (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 2m (CDCl$_3$, 100 MHz)

$^{11}$B NMR spectrum of Compound 2m (CDCl$_3$, 128 MHz)
$^1$H NMR spectrum of Compound 2n (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 2n (CDCl$_3$, 100 MHz)
$^{11}$B NMR spectrum of Compound 2n (CDCl$_3$, 128 MHz)

$^1$H NMR spectrum of Compound 2o (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 2o (CDCl$_3$, 100 MHz)

$^{11}$B NMR spectrum of Compound 2o (CDCl$_3$, 128 MHz)
$^{1}H$ NMR spectrum of Compound 2p (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 2p (CDCl$_3$, 100 MHz)
$^{11}$B NMR spectrum of Compound 2p (CDCl$_3$, 128 MHz)

$^1$H NMR spectrum of Compound 2q (CDCl$_3$, 400 MHz)
\textbf{\textsuperscript{13}C NMR spectrum of Compound 2q (CDCl\textsubscript{3}, 100 MHz)}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{c_nmr_spectrum}
\end{figure}

\textbf{\textsuperscript{11}B NMR spectrum of Compound 2q (CDCl\textsubscript{3}, 128 MHz)}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{b_nmr_spectrum}
\end{figure}
$^1$H NMR spectrum of Compound 2r (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 2r (CDCl$_3$, 100 MHz)
$^{11}$B NMR spectrum of Compound 2r (CDCl$_3$, 128 MHz)

$^1$H NMR spectrum of Compound 2s (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 2s (CDCl$_3$, 100 MHz)

$^{11}$B NMR spectrum of Compound 2s (CDCl$_3$, 128 MHz)
$^1$H NMR spectrum of Compound 2t (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 2t (CDCl$_3$, 100 MHz)
$^{11}$B NMR spectrum of Compound 2t (CDCl$_3$, 128 MHz)

$^1$H NMR spectrum of Compound 2u (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 2u (CDCl$_3$, 100 MHz)

$^{11}$B NMR spectrum of Compound 2u (CDCl$_3$, 128 MHz)
$^1$H NMR spectrum of Compound 2v (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 2v (CDCl$_3$, 100 MHz)
$^{11}B$ NMR spectrum of Compound 2v (CDCl$_3$, 128 MHz)

$^1H$ NMR spectrum of Compound 2w (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 2w (CDCl$_3$, 100 MHz)

$^{11}$B NMR spectrum of Compound 2w (CDCl$_3$, 128 MHz)
$^1$H NMR spectrum of Compound 2x (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 2x (CDCl$_3$, 100 MHz)
$^{11}B$ NMR spectrum of Compound 2x (CDCl$_3$, 128 MHz)

$^1H$ NMR spectrum of Compound 4 (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 4 (CDCl$_3$, 100 MHz)

$^1$H NMR spectrum of Compound 5 (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of Compound 5 (CDCl$_3$, 100 MHz)

$^{19}$F NMR spectrum of Compound 5 (CDCl$_3$, 376 MHz)
$^1$H NMR spectrum of Compound 6 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 6 (CDCl$_3$, 100 MHz)
$^1H$ NMR spectrum of Compound 7 (CDCl$_3$, 400 MHz)

$^{13}C$ NMR spectrum of Compound 7 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of Compound 8 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 8 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of Compound 9 (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of Compound 9 (CDCl$_3$, 100 MHz)
$^1$H NMR spectrum of Achiral CpIr(cod) (I) ($d_8$-toluene, 400 MHz)

$^1$H NMR spectrum of Chiral CpIr(cod) (II) ($C_6D_6$, 400 MHz)
$^{13}\text{C }\text{NMR spectrum of Chiral }\text{CpIr(cod) (II)}\ (\text{C}_6\text{D}_6, \text{100 MHz})$