

## Supplementary Information

### Hydrogen-bonding catalysis of sulfonium salts

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and Seiji Shirakawa\*<sup>a</sup>

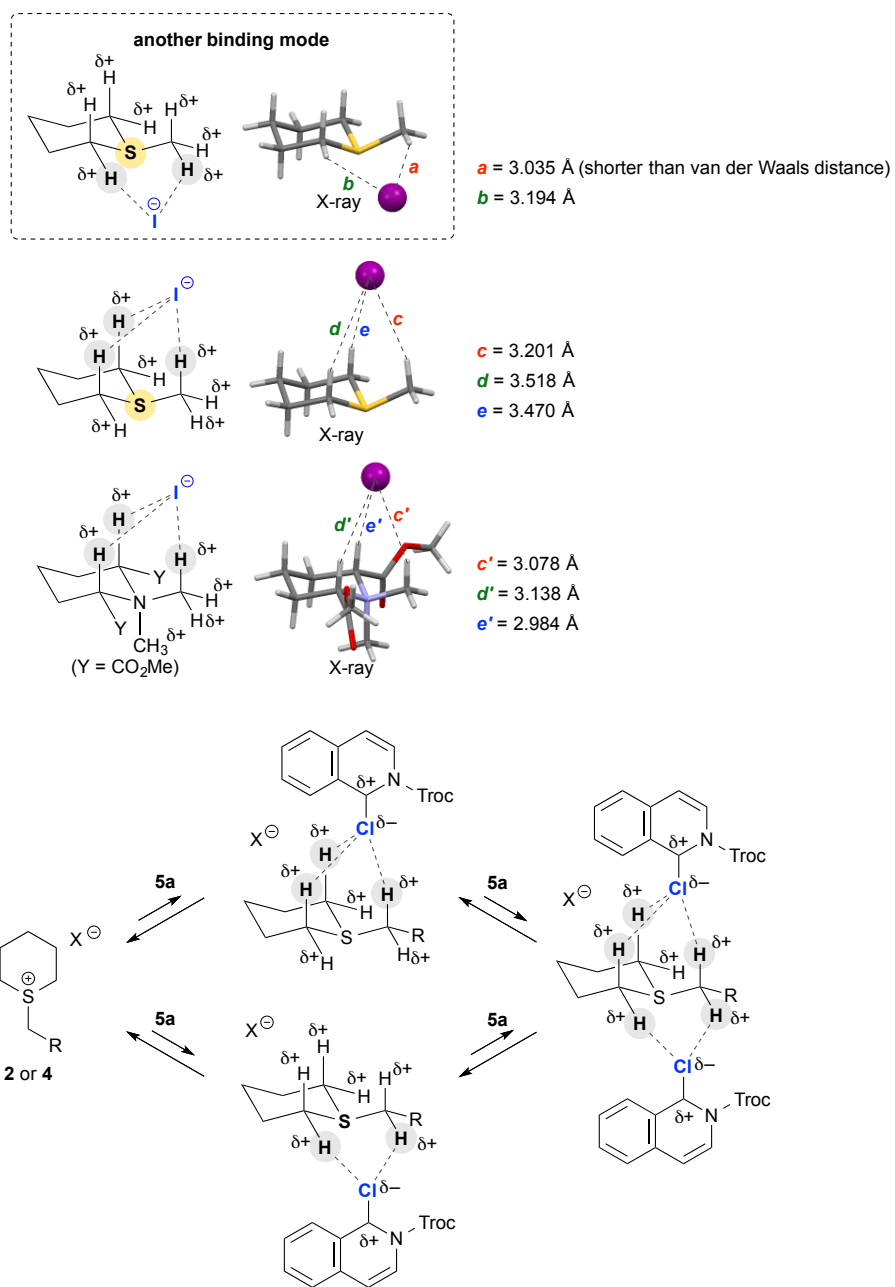
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#### General Information

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a JEOL JNM-AL 400 NMR instrument (400 MHz for <sup>1</sup>H NMR and 100 MHz for <sup>13</sup>C NMR). Tetramethylsilane (TMS) served as the internal standard (0 ppm) for <sup>1</sup>H NMR, and CDCl<sub>3</sub> served as the internal standard (77.0 ppm) for <sup>13</sup>C NMR. The following abbreviations were used to express the multiplicities: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-700N. Infrared spectra (IR) were measured on a JASCO FT/IR-4200 spectrometer. All reactions were monitored by thin-layer chromatography using Merck precoated TLC plates (silica gel 60GF-254, 0.25 mm), with visualization by the use of UV lamp (254 nm), or dyes such as KMnO<sub>4</sub>. The products were purified by flash column chromatography on silica gel. Dehydrated tetrahydrofuran and dichloromethane was purchased from Kanto Chemical.



**Fig. S1** Another binding mode of catalyst **2a** and possible activation modes with *N*-acylisoquinoline **5a**.

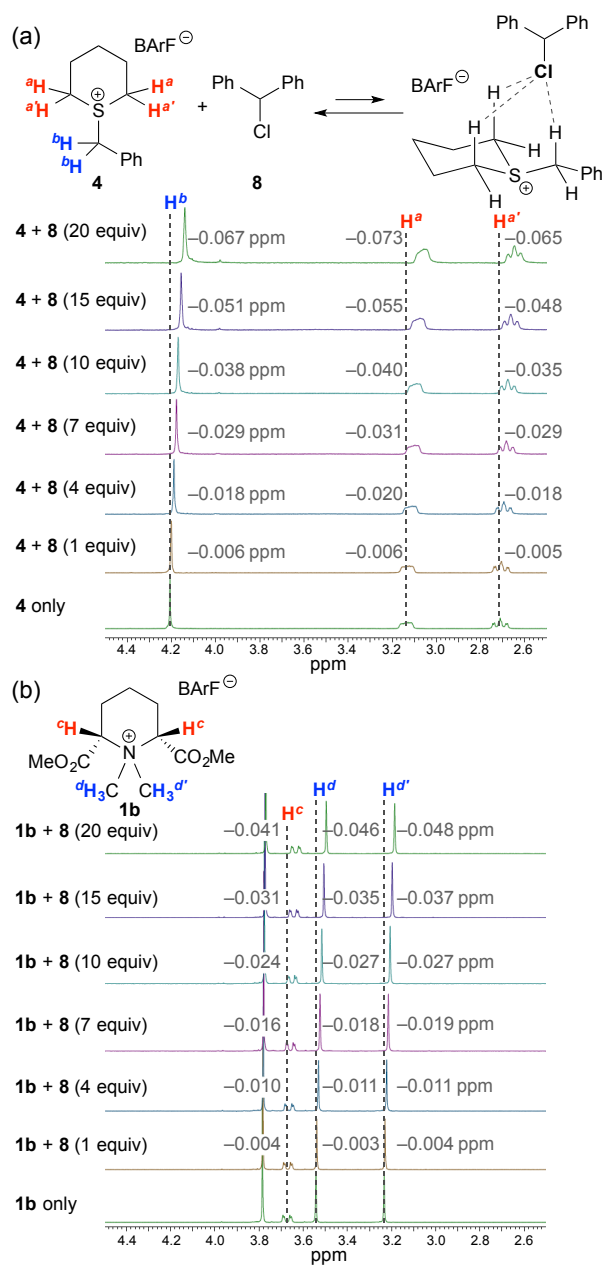
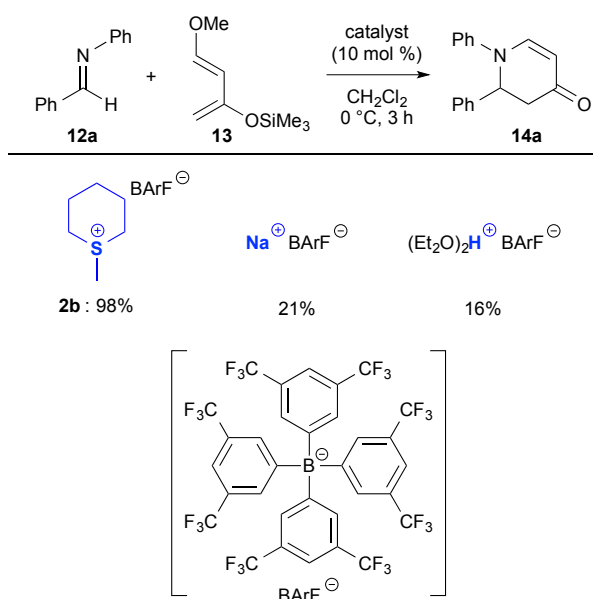


Fig. S2  $^1\text{H}$  NMR titration studies of **4** and **1b** (see also page S-11).



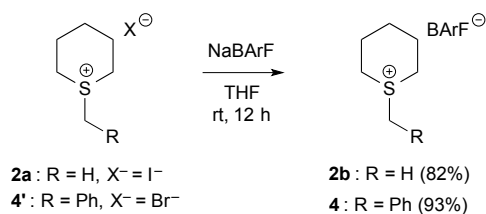
**Scheme S1** Control experiments in the aza Diels-Alder reaction of imine **12a**.

## Experimental Section

### Synthesis of catalyst **2a**.

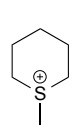
Catalyst **2a**<sup>1</sup> was prepared according to the literature.

### Synthesis of catalysts **2b** and **4**.

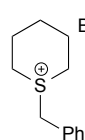


To a solution of **2a**<sup>1</sup> or **4**<sup>2</sup> (0.50 mmol) in THF (10 mL) was added sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBArF) (0.50 mmol), and the reaction mixture was stirred at room temperature for 12 h. The resulting solution was evaporated,

and the residue was purified by column chromatography on silica gel (hexane/CH<sub>2</sub>Cl<sub>2</sub> = 1/0–0/1 as eluent) to give catalysts **2b** or **4** in 82 and 93% yields, respectively.



**2b**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.70 (s, 8H), 7.56 (s, 4H), 3.18–3.24 (m, 2H), 2.68–2.75 (m, 2H), 2.51 (s, 3H), 2.04–2.13 (m, 2H), 1.76–1.87 (m, 3H), 1.23–1.41 (m, 1H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD): δ = 162.9 (q, *J* = 49.7 Hz), 135.8, 130.4 (q, *J* = 31.6 Hz); 125.8 (q, *J* = 270 Hz), 118.5 (m), 38.6, 23.8, 22.2, 21.6; IR (neat): 1276, 1120, 913, 744 cm<sup>-1</sup>; HRMS (FAB) calcd for C<sub>6</sub>H<sub>13</sub>S: 117.0738 ([M]<sup>+</sup>), found 117.0740.

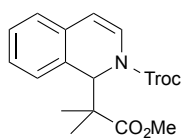


**4**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.70 (s, 8H), 7.54 (s, 4H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 7.2 Hz, 2H), 4.21 (s, 2H), 3.10–3.17 (m, 2H), 2.67–2.75 (m, 2H), 2.08–2.17 (m, 2H), 1.71–1.82 (m, 3H), 1.38–1.48 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 161.7 (q, *J* = 49.7 Hz), 134.8, 131.7, 130.6, 129.8, 129.0 (q, *J* = 31.3 Hz); 124.5 (q, *J* = 271 Hz), 123.4, 117.5 (m), 45.8, 36.7, 22.4, 21.2; IR (neat): 1353, 1273, 1114, 887, 839, 713, 682, 670 cm<sup>-1</sup>; HRMS (FAB) calcd for C<sub>12</sub>H<sub>17</sub>S: 193.1051 ([M]<sup>+</sup>), found 193.1051.

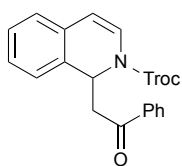
### General procedure for Mannich-type reactions of *N*-acylisoquinolines **5**.

To a solution of isoquinoline derivative (0.20 mmol) in dehydrated THF (2.0 mL) was added 2,2,2-trichloroethyl chloroformate (TrocCl, 0.21 mmol) at 0 °C under N<sub>2</sub> atmosphere, and stirred for 0.5 h at 0 °C. The resulting solution of *N*-acylisoquinoline **5** was cooled to the reaction temperature (–78 or 0 °C). The solution of catalyst **4** (0.020 mmol, 10 mol %) in dehydrated THF (1.0 mL) was then added to a solution of *N*-acylisoquinoline **5** at the reaction temperature (–78 or 0 °C). The flask of the initial catalyst solution was washed with additional dehydrated THF (1.0 mL) to complete transfer of the catalyst to the reaction solution. The reaction mixture was stirred for 5 min at the reaction temperature (–78 or 0 °C), and then silyl ether **6** (0.30 mmol) was added to the reaction mixture. The mixture was stirred for several hours (3–8 h) at the reaction temperature (–78 or 0 °C). The reaction mixture was quenched by saturated aqueous NaHCO<sub>3</sub> at the reaction temperature (–78 or 0 °C), and extracted with ethyl acetate for three times at room temperature. The combined extracts were dried

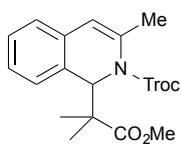
over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 1/0–5/1 as eluent) to give product **7**.



**7a:**<sup>3</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) [observed as a 3:1 mixture of rotamers]:  $\delta$  = 7.18–7.29 (m, 2H), 7.02–7.11 (m, 2H), 6.95–6.97 (m, 1H), 6.05 (d,  $J$  = 7.6 Hz, 0.25H), 5.95 (d,  $J$  = 7.2 Hz, 0.75H), 5.79 (s, 0.25H), 5.74 (s, 0.75H), 4.97 (d,  $J$  = 12.0 Hz, 0.75H), 4.88 (d,  $J$  = 11.6 Hz, 0.25H), 4.84 (d,  $J$  = 11.6 Hz, 0.25H), 4.70 (d,  $J$  = 12.0 Hz, 0.75H), 3.64 (s, 2.25H), 3.61 (s, 0.75H), 1.12–1.29 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) [observed as a mixture of rotamers]:  $\delta$  = 175.7, 152.5, 152.1, 131.2, 131.1, 128.3, 128.2, 128.0, 127.8, 127.1, 127.0, 126.4, 125.4, 124.8, 124.7, 112.7, 111.8, 95.0, 94.7, 75.7, 75.4, 61.1, 60.7, 52.1, 52.0, 50.4, 50.1, 23.7, 22.4, 21.4, 20.7; IR (neat): 2979, 2951, 1721, 1382, 1317, 1229, 1122, 714 cm<sup>-1</sup>.



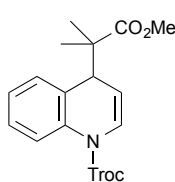
**7b:**<sup>3</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) [observed as a 3:2 mixture of rotamers]:  $\delta$  = 7.89 (d,  $J$  = 7.2 Hz, 1.2H), 7.84 (d,  $J$  = 6.8 Hz, 0.8H), 7.39–7.56 (m, 3H), 7.08–7.26 (m, 4H), 6.96 (d,  $J$  = 8.0 Hz, 0.4H), 6.91 (d,  $J$  = 8.0 Hz, 0.6H), 6.01–6.12 (m, 2H), 4.86 (d,  $J$  = 12.0 Hz, 0.6H), 4.81 (s, 0.8H), 4.72 (d,  $J$  = 11.6 Hz, 0.6H), 3.59 (dd,  $J$  = 8.4, 15.2 Hz, 0.4H), 3.39 (dd,  $J$  = 8.0, 14.8 Hz, 0.6H), 3.28 (dd,  $J$  = 6.0, 14.4 Hz, 0.6H), 3.22 (dd,  $J$  = 5.2, 15.6 Hz, 0.4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) [observed as a mixture of rotamers]:  $\delta$  = 196.8, 196.5, 151.4, 150.9, 136.9, 136.8, 133.3, 133.2, 131.6, 131.4, 129.6, 129.5, 128.6, 128.28, 128.24, 128.19, 128.07, 127.5, 127.4, 126.7, 126.6, 125.2, 125.1, 124.6, 123.5, 110.6, 110.4, 94.9, 94.8, 75.5, 75.2, 53.0, 52.8, 44.2, 43.4; IR (neat): 3062, 2955, 1720, 1682, 1635, 1384, 1321, 1283, 1243, 1124, 779, 754, 716, 691 cm<sup>-1</sup>.



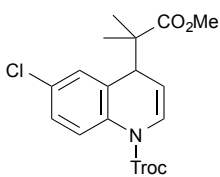
**7c:**<sup>3</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.23–7.27 (m, 1H), 7.16–7.20 (m, 1H), 7.05–7.11 (m, 2H), 6.04 (s, 1H), 5.62 (s, 1H), 5.02 (br, 1H), 4.62 (br, 1H), 3.57 (s, 3H), 2.33 (s, 3H), 1.22 (s, 3H), 1.21 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 175.5, 153.1, 135.3, 131.8, 129.8, 128.0, 127.2, 126.5, 124.3, 117.0, 95.0, 75.7, 63.1, 51.7, 48.1, 22.9, 21.8; IR (neat): 2976, 2951, 1718, 1389, 1308, 1242, 1134, 1050, 755, 714 cm<sup>-1</sup>.

### General procedure for regioselective Mannich-type reactions with quinolines **9**.

To a solution of quinoline derivative **9** (0.20 mmol) in dehydrated THF (2.0 mL) was added 2,2,2-trichloroethyl chloroformate (TrocCl, 0.21 mmol) at 0 °C under N<sub>2</sub> atmosphere, and stirred for 0.5 h at 0 °C. The resulting solution was cooled to the reaction temperature (−78 or 0 °C). To a cooled solution was added a solution of catalyst **4** (0.020 mmol, 10 mol %) in dehydrated THF (1.0 mL) at the reaction temperature (−78 or 0 °C). The flask of the initial catalyst solution was washed with additional dehydrated THF (1.0 mL) to complete transfer of the catalyst to the reaction solution. The reaction mixture was stirred for 5 min at the reaction temperature (−78 or 0 °C), and then ketene silyl acetal **6a** (0.30 mmol) was added to the reaction mixture. The mixture was stirred for 3 h at the reaction temperature (−78 or 0 °C). The reaction mixture was quenched by saturated aqueous NaHCO<sub>3</sub> at the reaction temperature (−78 or 0 °C), and extracted with ethyl acetate for three times at room temperature. The combined extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 1/0–5/1 as eluent) to give product **10**. The regioselectivity of product **10** was determined by <sup>1</sup>H NMR analysis by comparison with literature data.<sup>4</sup>



**10a:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.97 (d,  $J$  = 8.4 Hz, 1H), 7.27–7.31 (m, 1H), 7.14–7.19 (m, 2H), 7.04–7.09 (m, 1H), 5.38–5.42 (m, 1H), 4.86–4.97 (m, 2H), 3.82 (d,  $J$  = 6.0 Hz, 1H), 3.69 (s, 3H), 1.09 (s, 3H), 1.08 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 177.2, 150.6, 137.0, 129.6, 128.1, 127.8, 126.9, 125.1, 122.0, 112.0, 95.0, 75.3, 51.9, 48.9, 45.4, 21.7, 20.8; IR (neat): 2978, 2952, 1723, 1381, 1327, 1236, 1137, 759, 715 cm<sup>−1</sup>; HRMS (FAB) calcd for C<sub>17</sub>H<sub>19</sub>Cl<sub>3</sub>NO<sub>4</sub>: 406.0380 ([M+H]<sup>+</sup>), found 406.0383.

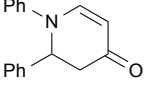


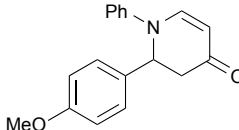
**10b:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.94 (d,  $J$  = 8.8 Hz, 1H), 7.24–7.27 (m, 1H), 7.15 (d,  $J$  = 8.0 Hz, 1H), 7.04 (d,  $J$  = 2.0 Hz, 1H), 5.39 (dd,  $J$  = 6.8, 7.2 Hz, 1H), 4.86–4.96 (m, 2H), 3.78 (d,  $J$  = 6.4 Hz, 1H), 3.71 (s, 3H), 1.09 (s, 3H), 1.08 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 176.8, 150.5, 135.6, 130.4, 130.0, 129.2, 127.8, 127.0, 123.2, 111.5,

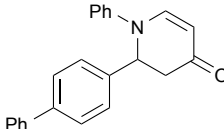
94.8, 75.4, 51.9, 49.0, 45.3, 21.3, 21.1; IR (neat): 2977, 2953, 2878, 1725, 1380, 1332, 1232, 1141, 818, 715  $\text{cm}^{-1}$ ; HRMS (FAB) calcd for  $\text{C}_{17}\text{H}_{18}\text{Cl}_4\text{NO}_4$ : 439.9990 ( $[\text{M}+\text{H}]^+$ ), found 439.9983.

### General procedure for aza Diels-Alder reactions.

To a solution of imine **12** (0.10 mmol) and catalyst **2b** (0.010 mmol, 10 mol %) in dehydrated  $\text{CH}_2\text{Cl}_2$  (2.0 mL) was added Danishefsky diene **13** (0.15 mmol) at 0 °C under  $\text{N}_2$  atmosphere, and stirred for 3 h at 0 °C. Then, aqueous 1N HCl (50  $\mu\text{L}$ ) was added to the reaction mixture, and further stirred for 5 min at 0 °C. The reaction mixture was quenched by  $\text{H}_2\text{O}$  at 0 °C, and extracted with  $\text{CH}_2\text{Cl}_2$  for three times at room temperature. The combined extracts were dried over  $\text{Na}_2\text{SO}_4$ , and concentrated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 1/0–0/1 as eluent) to give product **14**.

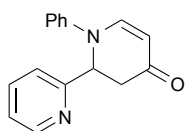
 **14a:**  $^5$   $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.68 (d,  $J$  = 8.0 Hz, 1H), 7.26–7.35 (m, 7H), 7.11 (t,  $J$  = 7.4 Hz, 1H), 7.02 (d,  $J$  = 7.6 Hz, 2H), 5.27–5.30 (m, 2H), 3.30 (dd,  $J$  = 7.0, 16.2 Hz, 1H), 2.80 (dd,  $J$  = 2.8, 16.8 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 190.2, 148.2, 144.7, 137.9, 129.5, 129.0, 127.8, 126.1, 124.4, 118.5, 103.0, 61.7, 43.4; IR (neat): 3060, 2894, 1642, 1566, 1493, 1277, 1202, 755, 694  $\text{cm}^{-1}$ .

 **14b:**  $^5$   $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.65 (dd,  $J$  = 1.0, 8.0 Hz, 1H), 7.30 (t,  $J$  = 7.8 Hz, 2H), 7.18 (d,  $J$  = 8.8 Hz, 2H), 7.11 (t,  $J$  = 7.4 Hz, 1H), 7.03 (d,  $J$  = 8.0 Hz, 2H), 6.85 (d,  $J$  = 8.8 Hz, 2H), 5.23–5.29 (m, 2H), 3.78 (s, 3H), 3.27 (dd,  $J$  = 7.6, 16.4 Hz, 1H), 2.76 (dd,  $J$  = 4.0, 16.8 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 190.4, 159.1, 148.2, 144.7, 129.8, 129.5, 127.3, 124.4, 118.6, 114.3, 102.7, 61.2, 55.2, 43.6; IR (neat): 3064, 2959, 2931, 2836, 1643, 1569, 1494, 1204, 1032, 829, 757, 731, 693  $\text{cm}^{-1}$ .

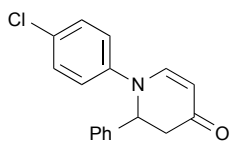
 **14c:**  $^5$   $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.71 (dd,  $J$  = 1.0, 7.8 Hz, 1H), 7.53–7.57 (m, 4H), 7.43 (t,  $J$  = 7.6 Hz, 2H), 7.29–7.37 (m, 5H), 7.13 (t,  $J$  = 7.4 Hz, 1H), 7.07 (d,  $J$  = 8.0 Hz, 2H), 5.30–5.35 (m, 2H), 3.35 (dd,  $J$  = 7.2, 16.4 Hz, 1H), 2.83 (dd,  $J$  = 3.2, 15.2 Hz, 1H);  $^{13}\text{C}$  NMR (100



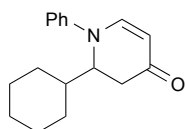
MHz, CDCl<sub>3</sub>):  $\delta$  = 190.2, 148.1, 144.6, 140.8, 140.4, 136.8, 129.6, 128.7, 127.7, 127.4, 127.0, 126.5, 124.4, 118.5, 103.0, 61.4, 43.3; IR (neat): 3055, 3030, 2923, 1643, 1571, 1491, 1207, 757, 730, 694 cm<sup>-1</sup>.



**14d:**<sup>5</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.63 (dd,  $J$  = 0.8, 4.8 Hz, 1H), 7.71 (dd,  $J$  = 1.4, 8.0 Hz, 1H), 7.62 (dt,  $J$  = 2.0, 8.0 Hz, 1H), 7.27–7.36 (m, 3H), 7.19–7.23 (m, 1H), 7.13 (t,  $J$  = 7.4 Hz, 1H), 7.04 (d,  $J$  = 7.6 Hz, 2H), 5.36 (d,  $J$  = 5.6 Hz, 1H), 5.30 (d,  $J$  = 8.0 Hz, 1H), 3.29 (dd,  $J$  = 7.6, 16.8 Hz, 1H), 3.13 (ddd,  $J$  = 1.2, 2.6, 16.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 190.5, 157.4, 150.2, 147.6, 144.5, 136.8, 129.6, 124.3, 122.7, 120.4, 118.0, 103.5, 63.0, 41.4; IR (neat): 3064, 3010, 1641, 1568, 1495, 1212, 756, 694 cm<sup>-1</sup>.



**14e:**<sup>5</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.61 (dd,  $J$  = 1.0, 7.8 Hz, 1H), 7.21–7.36 (m, 7H), 6.94 (d,  $J$  = 9.2 Hz, 2H), 5.30 (dd,  $J$  = 1.0, 7.2 Hz, 1H), 5.24 (dd,  $J$  = 3.2, 6.8 Hz, 1H), 3.28 (dd,  $J$  = 7.2, 16.4 Hz, 1H), 2.80 (ddd,  $J$  = 1.2, 3.2, 16.4 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 190.1, 147.8, 143.2, 137.5, 129.7, 129.5, 129.1, 128.0, 126.0, 119.8, 103.4, 61.8, 43.5; IR (neat): 3061, 2921, 2897, 1645, 1568, 1492, 1320, 1295, 1205, 1094, 824, 786, 744, 699 cm<sup>-1</sup>.

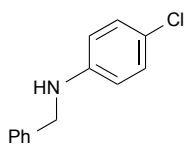


**14f:**<sup>5</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.45 (d,  $J$  = 7.6 Hz, 1H), 7.39 (t,  $J$  = 7.8 Hz, 2H), 7.14–7.20 (m, 3H), 5.15 (d,  $J$  = 8.0 Hz, 1H), 4.05–4.10 (m, 1H), 2.92 (dd,  $J$  = 7.2, 16.4 Hz, 1H), 2.62 (d,  $J$  = 16.4 Hz, 1H), 1.54–1.96 (m, 6H), 0.98–1.20 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 192.0, 148.5, 145.1, 129.7, 124.5, 120.3, 101.3, 62.7, 39.5, 37.7, 30.2, 28.9, 26.2, 26.03, 25.97; IR (neat): 2925, 2851, 1642, 1571, 1495, 1321, 1273, 1204, 756, 695 cm<sup>-1</sup>.

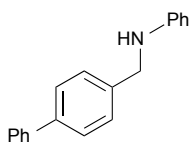
### General procedure for reductions of imines **12**.

To a solution of imine **12** (0.10 mmol) and catalyst **2b** (0.010 mmol, 10 mol %) in dehydrated CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) was added Hantzsch ester **15** (0.12 mmol) at 25 °C under N<sub>2</sub> atmosphere, and stirred for 6 h at 25 °C. The reaction mixture was then

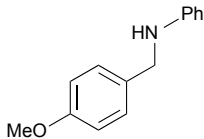
directly charged into silica gel, and purified (hexane/ethyl acetate = 1/0–5/1 as eluent) to give product **16**.



**16a:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.34–7.35 (m, 4H), 7.27–7.31 (m, 1H), 7.11 (d,  $J$  = 8.8 Hz, 2H), 6.55 (d,  $J$  = 8.8 Hz, 2H), 4.30 (s, 2H), 4.09 (br, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 146.0, 138.5, 129.1, 128.7, 127.5, 127.4, 122.7, 114.4, 48.6; IR (neat): 3426, 3062, 3029, 2922, 2850, 1600, 1497, 815, 733, 698  $\text{cm}^{-1}$ .



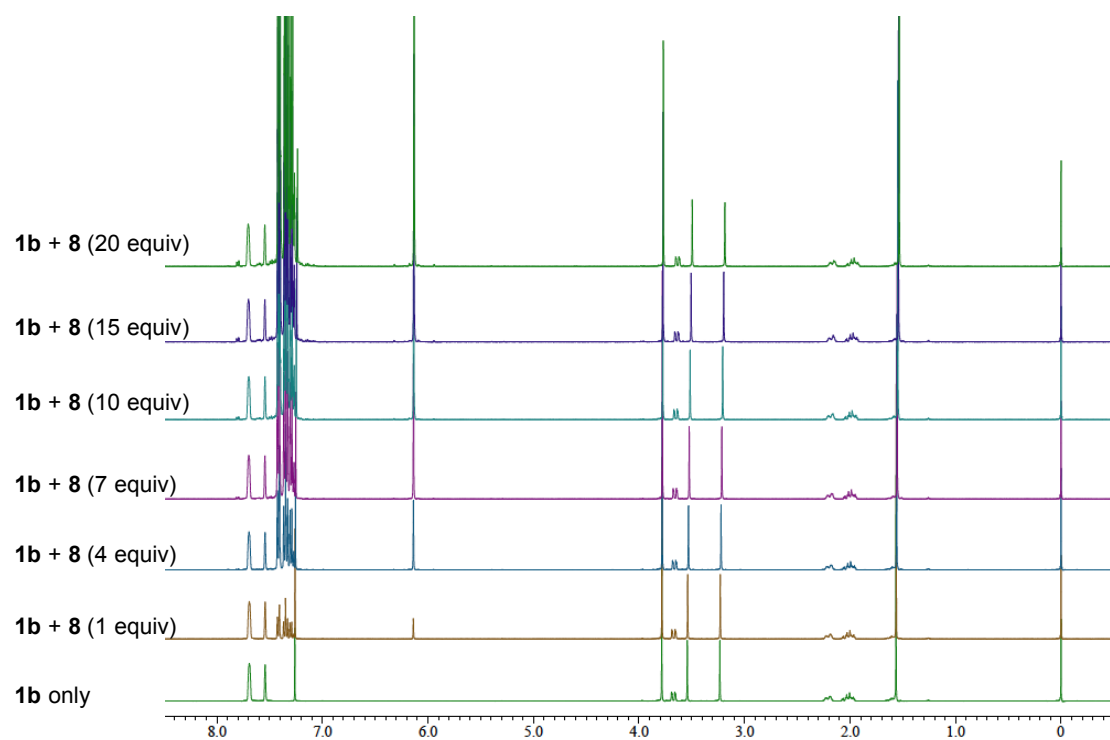
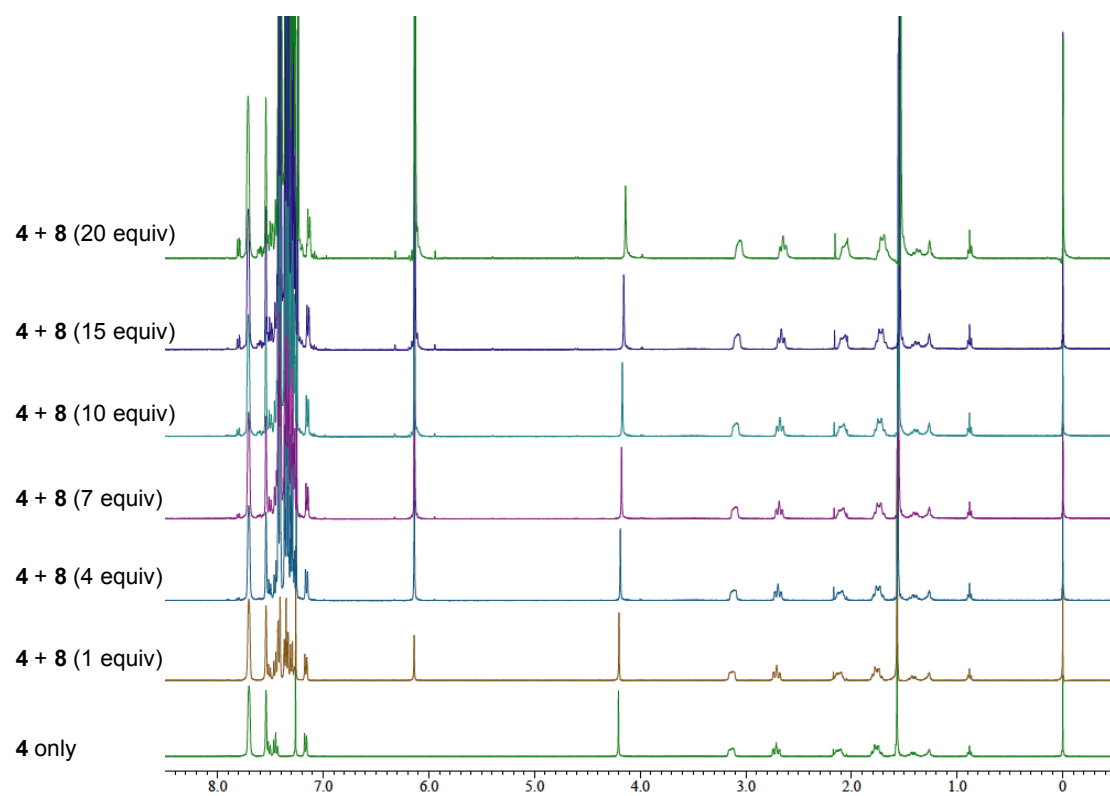
**16b:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.55–7.60 (m, 4H), 7.41–7.46 (m, 4H), 7.34 (t,  $J$  = 8.0 Hz, 1H), 7.19 (t,  $J$  = 7.6 Hz, 2H), 6.73 (t,  $J$  = 7.6 Hz, 1H), 6.67 (d,  $J$  = 8.4 Hz, 2H), 4.38 (s, 2H), 4.08 (br, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.1, 140.8, 140.2, 138.5, 129.3, 128.8, 127.9, 127.4, 127.2, 127.0, 117.6, 112.9, 48.0; IR (neat): 3396, 3050, 3029, 2958, 2926, 2853, 2826, 1601, 1498, 748, 689  $\text{cm}^{-1}$ .



**16c:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.30 (d,  $J$  = 8.8 Hz, 2H), 7.18 (t,  $J$  = 7.6 Hz, 2H), 6.88 (d,  $J$  = 8.4 Hz, 2H), 6.71 (t,  $J$  = 6.8 Hz, 1H), 6.64 (d,  $J$  = 8.8 Hz, 2H), 4.26 (s, 2H), 3.95 (br, 1H), 3.81 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.8, 148.2, 131.4, 129.2, 128.8, 117.5, 114.0, 112.8, 55.3, 47.8; IR (neat): 3417, 3050, 3019, 2954, 2932, 2907, 2835, 1602, 1508, 1245, 1176, 1033, 823, 749, 692  $\text{cm}^{-1}$ .

### NMR titration studies.

To an NMR tube was added **4** (0.0050 mmol) followed by  $\text{CDCl}_3$  (0.50 mL). To the solution was added appropriate amount of chlorodiphenylmethane **8** (1M solution in  $\text{CDCl}_3$ ) via syringe, and measured  $^1\text{H}$  NMR. After the measurement, additional amount of **8** (1M solution in  $\text{CDCl}_3$ ) was added to the NMR tube, and the  $^1\text{H}$  NMR measurement was repeated. The  $^1\text{H}$  NMR titration study of **1b** with **8** was also performed in the same manner.



## References

- 1 Z. Polívka, J. Holubek, M. Budesínský, O. Matousová, E. Svátek, J. Metys and M. Protiva, *Collect. Czech. Chem. Commun.*, 1987, **52**, 2758.
- 2 S. M. Date, R. Singh and S. K. Ghosh, *Org. Biomol. Chem.*, 2005, **3**, 3369.
- 3 S. Shirakawa, S. Liu, S. Kaneko, Y. Kumatabara, A. Fukuda, Y. Omagari and K. Maruoka, *Angew. Chem., Int. Ed.*, 2015, **54**, 15767.
- 4 H. Rudler, B. Denise, Y. Xu, A. Parlier and J. Vaissermann, *Eur. J. Org. Chem.*, 2005, 3724.
- 5 (a) Y. Takeda, D. Hisakuni, C.-H. Lin and S. Minakata, *Org. Lett.*, 2015, **17**, 318; (b) Y. Kumatabara, S. Kaneko, S. Nakata, S. Shirakawa and K. Maruoka, *Chem.–Asian J.*, 2016, **11**, 2126.
- 6 (a) P. A. Champagne, J. Pomarole, M.-È. Thérien, Y. Benhassine, S. Beaulieu, C. Y. Legault and J.-F. Paquin, *Org. Lett.*, 2013, **15**, 2210; (b) I. Chatterjee, M. Oestreich, *Org. Lett.*, 2016, **18**, 2463; (c) V. Fasano, J. E. Radcliffe and M. J. Ingleson, *ACS Catal.*, 2016, **6**, 1793.

