New Catalysts for Asymmetric Hydrosilylation of Keontes Discovered by Mass Spectrometry Screening

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Supporting Information

Note. Amino alcohol component K ($\text{NR}_2 = \text{NMe}_2$) was prepared from the corresponding aminoindanol ($\text{NR}_2 = \text{NH}_2$) by reductive methylation with formaldehyde and formic acid.

Characterization data for ligands.

ABG: ^1H NMR (CDCl_3): 4.51 (d, $J = 6.3$ Hz, 1H), 5.55 (dd, $J = 6.2, 9.8$ Hz, 1H), 6.58 - 7.97 (m, 27H), 7.08 (s, 1H); ^{31}P NMR (CDCl_3): 143.21 (s).

AAG: ^1H NMR (CDCl_3): 4.66 (d, $J = 6.7$ Hz, 1H), 5.77 (dd, $J = 6.2, 9.8$ Hz, 1H), 6.79 - 7.99 (m, 27H), 8.05 (s, 1H); ^{31}P NMR (CDCl_3): 153.37 (s).

CBG: ^1H NMR (CDCl_3): 0.19 (s, 3H), 0.85 (s, 3H), 4.36 (d, $J = 5.9$ Hz, 1H), 4.70 - 4.80 (m, 2H), 5.57 (dd, $J = 5.9, 10.0$ Hz, 1H), 6.77 - 7.72 (m, 35H), 7.90 (s, 1H); ^{31}P NMR (CDCl_3): 137.43 (s).

CAG: ^1H NMR (CDCl_3): 0.21 (s, 3H), 1.02 (s, 3H), 4.38 (d, $J = 5.9$ Hz), 4.76 (d, $J = 4.1$ Hz), 5.02 (dd, $J = 1.0, 4.1$ Hz, 1H), 5.68 (dd, $J = 5.2, 9.8$ Hz, 1H), 7.11 - 7.61 (m, 35H), 7.83 (s, 1H); ^{31}P NMR (CDCl_3): 139.47 (s).

CCF: ^1H NMR (CDCl_3): 0.64 (s, 3H), 0.84 (s, 3H), 1.40 - 1.80 (m, 4H), 2.12 - 2.24 (m, 1H), 2.41 - 2.59 (m, 1H), 2.81 - 2.97 (m, 1H), 3.31 (d, $J = 13.0$ Hz, 1H), 3.48 - 3.65 (m, 1H), 3.72 - 3.84 (m, 1H), 3.90 (d, $J = 13.4$ Hz, 1H), 5.02 (d, $J = 8.3$ Hz, 1H), 5.26 (d, $J = 8.3$ Hz, 1H), 7.24 - 7.57 (m, 25H); ^{31}P NMR (CDCl_3): 132.23 (s); ^{13}C NMR (CDCl_3): 23.18, 26.64, 27.06, 28.69, 54.71, 59.82, 63.56, 65.84, 81.20, 82.40, 82.72, 83.20, 85.20, 112.82, 127.07, 127.31, 127.40, 127.51, 127.83, 128.15, 128.33, 128.41, 129.00, 129.19, 129.31, 129.37, 139.90, 141.92, 146.68.

CCE: ^1H NMR (CDCl_3): 0.59 (s, 3H), 0.91 (s, 3H), 1.41 - 1.78 (m, 4H), 2.10 - 2.22 (m, 2H), 2.32 (s, 3H), 2.98 - 3.09 (m, 1H), 3.57 - 3.68 (m, 1H), 3.86 - 3.99 (m, 1H), 5.03 (dd, $J = 1.7, 8.3$ Hz, 1H), 5.20 (d, $J = 8.3$ Hz, 1H), 7.20 - 7.62 (m, 20H); ^{31}P NMR (CDCl_3): 132.45 (s); ^{13}C NMR (CDCl_3): 23.12, 26.47, 27.17, 28.93, 41.72, 57.83, 65.13, 65.41, 81.41, 82.36, 82.68, 82.91, 84.96, 112.70, 127.26, 127.36, 127.41, 127.48, 127.80, 128.06, 128.30, 128.96, 129.22, 141.74, 146.45.

CBI: ^1H NMR (CDCl_3): 0.21 (s, 3H), 0.93 (s, 3H), 2.02 (s, 6H), 2.12 (s, 3H), 4.28 (d, $J = 6.2$ Hz, 1H), 4.62 - 4.84 (m, 2H), 5.61 (dd, $J = 1.5, 8.3$ Hz, 1H), 6.65 - 7.30 (m, 32H), 8.24 (s, 1H); ^{31}P NMR (CDCl_3): 137.94 (s).

CBH: ^1H NMR (CDCl_3): 0.24 (s, 3H), 0.98 (s, 3H), 4.40 (d, $J = 6.0$ Hz, 1H), 4.78 - 4.98 (m, 2H), 5.8 (dd, $J = 1.6, 8.4$ Hz, 1H), 6.81 - 7.96 (m, 39H), 8.04 (s, 1H); ^{31}P NMR (CDCl_3): 137.47 (s).

CBJ: ^1H NMR (CDCl_3): 0.41 (s, 3H), 1.01 (s, 3H), 3.87 (s, 3H), 4.52 (d, $J = 5.9$ Hz, 1H), 4.89 - 4.06 (m, 2H), 5.80 (dd, $J = 3.8, 10.0$ Hz, 1H), 6.84 - 7.92 (m, 34H), 8.06 (s, 1H); ^{31}P NMR (CDCl_3): 137.47 (s).

CBK: ^1H NMR (CDCl_3): 0.28 (s, 3H), 0.98 (s, 3H), 2.91 (s, 6H), 4.40 (d, $J = 5.9$ Hz, 1H), 4.80 (d, $J = 8.5$ Hz, 1H), 4.88 (dd, $J = 2.3, 8.2$ Hz, 1H), 5.67 (dd, $J = 6.3, 10.3$ Hz, 1H), 6.55 - 7.50 (m, 34H), 7.86 (s, 1H); ^{31}P NMR (CDCl_3): 137.64 (s).

CBL: mp 115 °C (dec.); ^1H NMR (CDCl_3): 0.31 (s, 3H), 0.97 (s, 3H), 4.35 (d, $J = 6.2$ Hz, 1H), 4.85 - 4.95 (m, 2H), 5.70 (dd, $J = 5.9, 10.0$ Hz, 1H), 6.85 - 7.75 (m, 34H), 7.96 (s, 1H); ^{31}P NMR (CDCl_3): 137.44 (s).

CBM: ^1H NMR (CDCl_3): 0.20 (s, 3H), 0.85 (s, 3H), 4.41 (d, $J = 5.3$ Hz, 1H), 4.68 - 4.78 (m, 2H), 5.59 (dd, $J = 6.4, 10.8$ Hz, 1H), 6.76 - 8.06 (m, 35H); ^{31}P NMR (CDCl_3): 137.34 (s).

CBN: mp 100 °C (dec.); ^1H NMR (CDCl_3): 0.51 (s, 3H), 1.3 (s, 3H), 4.76 (d, $J = 5.57$, 1H), 5.05 - 5.12 (m, 2H), 5.96 (dd, $J = 5.9, 9.7$ Hz, 1H), 7.02 - 8.16 (m, 37H), 8.78 (s, 1H); ^{31}P NMR (CDCl_3): 137.24 (s).

CBO: mp 116 °C (dec.); ^1H NMR (CDCl_3): 0.45 (s, 3H), 1.11 (s, 3H), 4.46 (d, $J = 6.4$ Hz, 1H), 4.92 - 5.02 (m, 2H), 5.86 (dd, $J = 5.9, 10.0$ Hz, 1H), 6.98 - 8.10 (m, 37H), 8.29 (s, 1H); ^{31}P NMR (CDCl_3): 137.53 (s).

CBP: mp 113 °C (dec.); ^1H NMR (CDCl_3): 0.40 (s, 3H), 1.05 (s, 3H), 3.92 (s, 2H), 4.59 (d, $J = 6.15$ Hz, 1H), 4.90 - 4.98 (m, 2H), 5.42 (dd, $J = 5.9, 10.0$ Hz, 1H), 6.90 - 7.98 (m, 37H), 8.17 (s, 1H); ^{31}P NMR (CDCl_3): 137.47 (s).

CDA: mp 87-89 °C; ^1H NMR (CDCl_3): 0.54 (s, 3H), 0.63 (d, $J = 6.7$ Hz, 3H), 0.88 (s, 3H), 2.31 (s, 6H), 4.99 - 5.12 (m, 3H), 7.04 - 7.62 (m, 25H); ^{31}P NMR (CDCl_3): 136.97 (s).

CEB: ^1H NMR (CDCl_3): 0.41 (s, 3H), 0.84 (s, 3H), 0.86 (d, $J = 6.4$ Hz, 3H), 0.80 - 1.10 (m, 14H), 2.1 - 2.38 (m, 4H), 2.83 - 3.02 (m, 1H), 4.93 - 5.05 (m, 2H), 5.33 (dd, $J = 8.3, 8.4$ Hz, 1H), 6.97 - 7.62 (m, 25H); ^{31}P NMR (CDCl_3): 138.88 (s); ^{13}C NMR (CDCl_3): 10.68, 14.54, 20.74, 22.98, 26.11, 27.61, 31.47, 31.91, 50.34, 61.25, 61.36, 81.37, 82.12, 82.36, 82.77, 84.65, 84.77, 112.69, 127.13, 127.57, 127.72, 128.01, 128.33, 128.99, 129.27, 129.38, 140.91, 142.02, 142.07, 143.15, 146.02, 146.72. Calcd for $\text{C}_{48}\text{H}_{56}\text{NO}_5\text{P}$: C, 76.06; H, 7.45; N, 1.85. Found: C, 76.33; H, 7.55; N, 1.91.

CBC: ^1H NMR (CDCl_3): 0.22 (s, 3H), 0.93 (s, 3H), 1.25 - 2.30 (m, 10H), 3.46 (d, $J = 7.9$ Hz, 1H), 4.85 (s, 2H), 5.87 (dd, $J = 8.2, 8.2$ Hz, 1H), 6.72 - 7.4 (m, 30H); ^{31}P NMR (CDCl_3): 139.53 (s).

CH: ^1H NMR (CDCl_3): 0.62 (s, 3H), 0.85 (s, 3H), 1.30 (d, $J = 6.6$ Hz, 3H), 4.99 (dd, $J = 1.8, 7.7$ Hz, 1H), 4.98 - 5.38 (m, 2H), 7.02 - 7.82 (m, 25H); ^{31}P NMR (CDCl_3): 133.56 (s).

CFA: ^1H NMR (CDCl_3): 0.46 (s, 3H), 1.06 (d, $J = 6.8$ Hz, 3H), 1.14 (s, 3H), 2.38 (s, 6H), 2.78 - 2.88 (m, 1H), 5.06 (d, $J = 8.2$ Hz, 1H), 5.25 (d, $J = 8.2$ Hz, 1H), 5.51 (dd, $J = 4.7, 9.2$ Hz, 1H), 7.15 - 7.72 (m, 25H); ^{31}P NMR (CDCl_3): 141.76 (s).

DEA: ^1H NMR (CDCl_3): 0.41 (s, 3H), 1.07 (d, $J = 6.4$ Hz, 3H), 1.17 (s, 3H), 2.39 (s, 6H), 2.62 - 2.78 (m, 1H), 5.38 (d, $J = 8.3$ Hz, 1H), 5.43 (d, $J = 8.2$ Hz, 1H), 5.60 - 5.72 (m, 1H), 7.16 - 8.40 (m, 33H); ^{31}P NMR (CDCl_3): 139.29 (s); ^{13}C NMR (CDCl_3): 9.01, 26.44, 27.80, 41.61, 65.77, 81.61, 82.91, 83.00, 85.10, 85.21, 113.18, 125.40, 125.64, 126.24, 126.48, 126.77, 127.62, 128.18, 128.89, 132.65, 132.70, 132.83, 132.96, 133.05, 138.36, 139.19, 2.96, 5.83, 143.49. Calcd for $\text{C}_{58}\text{H}_{52}\text{NO}_5\text{P}$: C, 79.70; H, 6.00; N, 1.60; Found: C, 79.78; H, 6.24; N, 1.58.

CGA: mp 145-147 °C; ^1H NMR (CDCl_3): 0.60 (s, 3H), 0.96 (s, 3H), 2.23 (s, 6H), 2.29 (t, $J = 4.15$, 2H), 3.92 - 4.03 (m, 2H), 5.09 (dd, $J = 2.8, 8.0$, 1H), 5.20 (d, $J = 8.0$, 1H), 7.27 - 7.63 (m, 20H); ^{31}P NMR (CDCl_3): 132.67 (s); ^{13}C NMR (CDCl_3): 26.48, 27.22, 45.93, 46.07, 59.74, 60.69, 81.32, 82.91, 85.20, 112.91, 127.47, 128.20, 128.35, 129.20, 141.76, 141.67, 146.36, 146.46.

CEC: mp 95 °C (dec.); ^1H NMR (CDCl_3): 0.00 (s, 3H), 0.71 (d, $J = 6.4$ Hz, 3H), 0.75 (s, 3H), 0.88 - 1.02 (m, 6H), 2.01 - 2.37 (m, 4H), 2.30 - 2.37 (m, 1H), 4.57 (d, $J = 8.3$ Hz, 1H), 4.67 (dd, $J = 2.2, 8.0$ Hz, 1H), 5.15 (dd, $J = 5.37, 9.2$, 1H), 6.57 - 7.26 (m, 25H); ^{31}P NMR (CDCl_3): 140.26 (s); ^{13}C NMR (CDCl_3): 9.93, 25.16, 26.16, 26.93, 27.79, 50.68, 66.65, 81.42, 84.87, 112.85, 127.65, 127.69, 127.88, 128.14, 128.44, 129.07, 129.34, 140.99, 142.08, 143.12, 145.91, 146.72. Calcd for $\text{C}_{45}\text{H}_{48}\text{NO}_5\text{P}$: C, 75.71; H, 6.78; N, 1.96. Found: C, 75.66; H, 6.84; N, 1.89.

CED: mp 88 °C (dec.); ^1H NMR (CDCl_3): 0.40 (s, 3H), 1.07 (d, $J = 6.3$ Hz, 3H), 1.04 (s, 3H), 1.44 - 1.79 (m, 4H), 2.41 - 2.69 (m, 5H), 5.02 (dd, $J = 1.7, 8.3$ Hz, 1H), 5.12 (d, $J = 8.3$ Hz, 1H), 6.02 (dd, $J = 4.8, 9.4$ Hz, 1H), 7.02 - 7.63 (m, 25H); ^{31}P NMR (CDCl_3): 139.33 (s); ^{13}C NMR (CDCl_3): 11.38, 23.81, 26.4, 27.54, 51.20, 65.18, 80.83, 82.30, 82.62, 82.68, 85.26, 113.01, 127.14, 127.43, 127.71, 127.92, 128.08, 128.35, 129.00, 129.4, 141.24, 141.95, 145.85, 146.52. Calcd for $\text{C}_{44}\text{H}_{46}\text{NO}_5\text{P}$: C, 75.52; H, 6.63; N, 2.00. Found: C, 75.24; H, 6.67; N, 1.94.

CIA: ^1H NMR (CDCl_3): 0.61 (s, 3H), 0.84 (d, $J = 6.8$ Hz, 3H), 0.84 (s, 3H), 2.20 (s, 6H), 2.40 - 2.49 (m, 1H), 3.51 - 3.57 (m, 1H), 3.88 - 3.96 (m, 1H), 5.02 (dd, $J = 1.7, 8.30$ Hz, 1H), 5.24 (d, $J = 8.30$ Hz, 1H), 7.22 - 7.60 (m, 20H); ^{31}P NMR (CDCl_3): 131.95 (s).

CJA: ^1H NMR (CDCl_3): 0.58 (s, 3H), 0.98 (s, 3H), 2.21 (s, 6H), 2.36 (dd, $J = 4.4, 3.8$ Hz, 1H), 2.70 (dd, $J = 7.6, 13.0$ Hz, 1H), 5.08 (d, $J = 8.30$, 1H), 5.20 (d, $J = 8.3$, 1H), 5.22 - 5.48 (m, 1H), 7.02 - 7.68 (m, 25H); ^{31}P NMR (CDCl_3): d 136.79 (s).

CBA: mp 163-165 °C; ^1H NMR (CDCl_3): 0.00 (s, 3H), 0.72 (s, 3H), 1.95 (s, 6H), 3.09 (d, $J = 5.1$ Hz, 1H), 4.60 (s, 2H), 5.60 (dd, $J = 5.8, 9.8$ Hz, 1H), 6.48 - 7.21 (m, 30H); ^{31}P NMR (CDCl_3): 140.16 (s); ^{13}C NMR (CDCl_3): 26.14, 27.71, 43.51, 74.73, 78.04, 80.92, 82.32, 82.69, 85.30, 112.97, 127.3, 127.30, 127.82, 128.15, 128.38, 129.00, 129.46, 130.56, 136.15, 140.85, 141.81, 145.78, 146.51. Calcd for $\text{C}_{47}\text{H}_{46}\text{NO}_5\text{P}$: C, 76.71; H, 6.30; N, 1.90. Found: C, 76.43; H, 6.34; N, 1.96.

CKA: mp 90-91 °C; ^1H NMR (CDCl_3): 0.41 (s, 3H), 1.13 (s, 3H), 2.52 (s, 6H), 2.96 (dd, $J = 6.8, 16.1$ Hz, 1H), 3.1 (dd, $J = 6.3, 11.23$ Hz, 1H), 4.26 (d, $J = 6.3$ Hz, 1H), 5.05 - 5.18 (m, 2H), 5.42 - 5.58 (m, 1H), 7.10 - 7.77 (m, 24H); ^{31}P NMR (CDCl_3): 137.95 (s); ^{13}C NMR (CDCl_3): 26.08, 27.71, 40.09, 42.07, 42.18, 70.39, 76.08, 81.69, 82.50, 84.49, 112.68, 125.05, 126.26, 126.96, 127.56, 128.08, 128.43, 129.20, 140.56, 140.73, 141.57, 141.87, 146.25, 146.56. Calcd for $\text{C}_{42}\text{H}_{42}\text{NO}_5\text{P}$: C, 75.09; H, 6.30; N, 2.09. Found: C, 74.89; H, 6.45; N, 2.08.

Table S1. Addition of silver salts

Entry	Ligand	Equiv. of Ag	Ag salt	ee (%)	Conversion (%)
1	CBG	1.0	AgBF ₄	-16.0	73.4
2	CCE	1.0	AgBF ₄	-14.0	84.7
3	CBN	1.0	AgBF ₄	-26.7	78.3
4	CEA	1.0	AgBF ₄	45.4	53.8
5	CH	1.0	AgBF ₄	-12.9	93.7
6	12	1.0	AgBF ₄	67.0	87.0
7	CBG	2.0	AgBF ₄	-19.3	67.7
8	CCE	2.0	AgBF ₄	-34.5	83.6
9	CBN	2.0	AgBF ₄	-16.3	65.7
10	CEA	2.0	AgBF ₄	-3.1	66.9
11	CH	2.0	AgBF ₄	-12.5	79.3
12	12	2.0	AgBF ₄	63.5	99.2
13	CBG	4.0	AgBF ₄	-16.0	66.6
14	CCE	4.0	AgBF ₄	-32.3	87.0
15	CBN	4.0	AgBF ₄	-12.6	68.6
16	CEA	4.0	AgBF ₄	34.8	59.6
17	CH	4.0	AgBF ₄	-5.0	66.1
18	12	4.0	AgBF ₄	56.1	66.1
19	CBG	4.0	AgPF ₆	-2.0	10.1
20	CCE	4.0	AgPF ₆	-15.4	22.3
21	CBN	4.0	AgPF ₆	-4.1	23.3
22	CEA	4.0	AgPF ₆	18.4	18.6
23	CH	4.0	AgPF ₆	-7.0	38.4
24	12	4.0	AgPF ₆	62.2	26.0
25	CBG	4.0	AgOTf	-70.4	38.9
26	CCE	4.0	AgOTf	-	0.9
27	CBN	4.0	AgOTf	29.1	11.2
28	CEA	4.0	AgOTf	-	0.5
29	CH	4.0	AgOTf	-	0.1
30	12	4.0	AgOTf	-	1.2