Electronic supplementary information (ESI)

Synthesis, structure and catalytic properties of CNN pincer palladium(II) and ruthenium(II) complexes with *N*-substituted-2-aminomethyl-6-phenylpyridines

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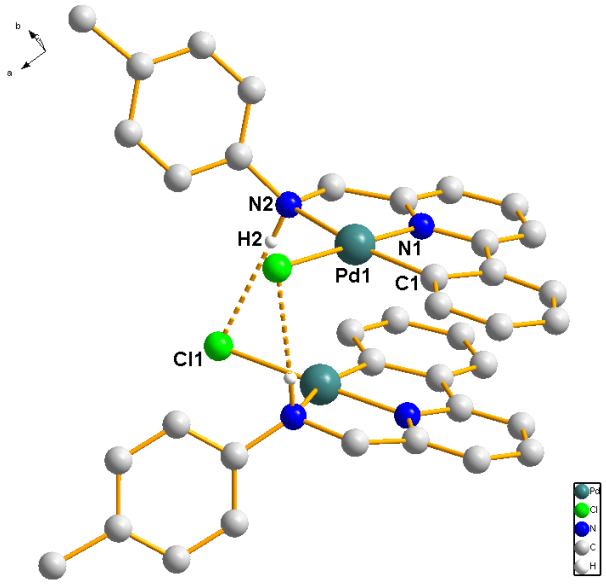

Fig. S1 Dimer of CNN pincer Pd complex **3c** formed by NH···Cl hydrogen bonds [Cl(1)···H(2) 2.470 Å, Cl(1)···N(2) 3.333 Å, N(2)-H(2)···Cl(1) 178°]. Non-hydrogen bonding H atoms have been omitted for clarity.

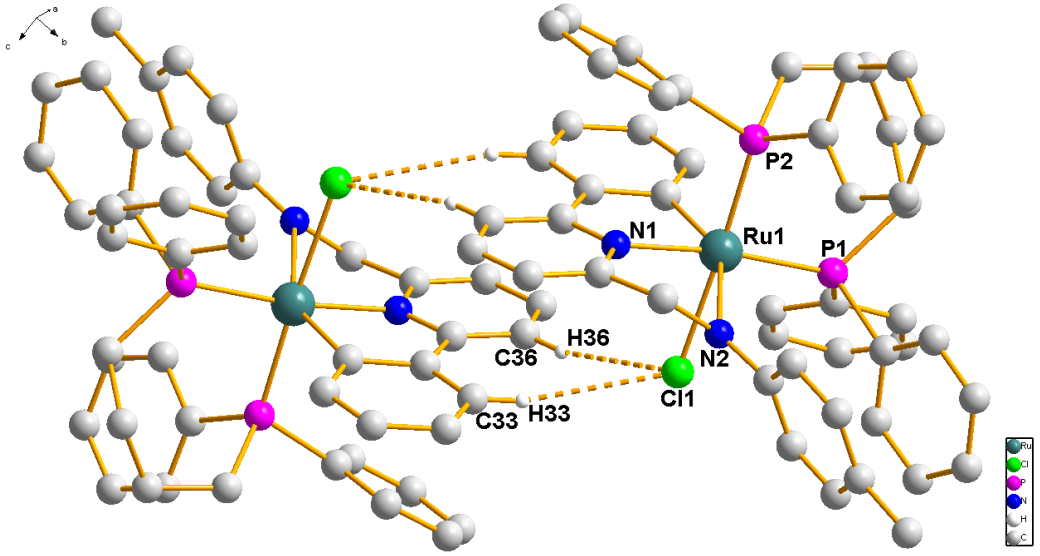

Fig. S2 Dimer of CNN pincer Ru(II) complex **5** formed by CH···Cl hydrogen bonds [Cl(1)···H(36) 2.908 Å, Cl(1)···C(36) 3.820 Å, C(36)-H(36)···Cl(1) 167°; Cl(1)···H(33) 2.881 Å, Cl(1)···C(36) 3.773 Å, C(33)-H(33)···Cl(1) 161°]. Non-hydrogen bonding H atoms have been omitted for clarity.

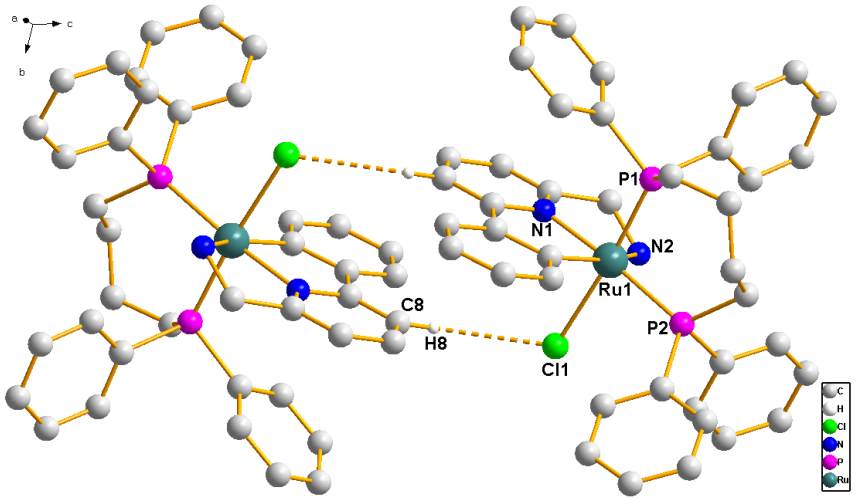

Fig. S3 Dimer of CNN pincer Ru(II) complex **7·CH_2Cl_2** formed by CH···Cl hydrogen bonds [Cl(1)···H(8) 2.831 Å, Cl(1)···C(8) 3.581 Å, C(8)-H(8)···Cl(1) 139°]. CH_2Cl_2 and non-hydrogen bonding H atoms have been omitted for clarity.

Analytical data of the homoallylic alcohol products from allylation of aldehydes with allyltributyltin:

Phenylbut-3-en-1-ol [1-6]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.24 (m, 5H), 5.84-5.74 (m, 1H), 5.17-5.12 (m, 2H), 4.71 (dd, *J* = 5.6, 7.3 Hz, 1H), 2.51-2.46 (m, 2H), 2.18 (br s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 134.5, 128.4, 127.6, 125.8, 118.4, 73.3, 43.8.

1-(4-Nitrophenyl)but-3-en-1-ol [3-6]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 5.79-5.69 (m, 1H), 5.14-5.09 (m, 2H), 4.82 (t, *J* = 6.1 Hz, 1H), 2.75 (br s, 1H, OH), 2.54-2.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 147.1, 133.3, 126.6, 123.6, 119.4, 72.2, 43.8.

1-(4-Bromophenyl)but-3-en-1-ol [5]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.79-5.69 (m, 1H), 5.14-5.11 (m, 2H), 4.64 (dd, *J* = 5.7, 7.3 Hz, 1H), 2.49-2.40 (m, 3H, CH_2 and OH).

1-(2-Bromophenyl)but-3-en-1-ol [4]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.49 (m, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.14-7.11 (m, 1H), 5.90-5.81 (m, 1H), 5.20-5.15 (m, 2H), 5.08 (dd, *J* = 3.7, 8.4 Hz, 1H), 2.65-2.59 (m, 1H), 2.37-2.30 (m, 2H).

1-(4-Fluorophenyl)but-3-en-1-ol [3]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.26 (m, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 5.80-5.72 (m, 1H), 5.16-5.12 (m, 2H), 4.69 (t, *J* = 6.4 Hz, 1H), 2.48-2.43 (m, 2H), 2.37 (br s, 1H, OH).

1-(4-Chlorophenyl)but-3-en-1-ol [1,3.5]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 5.80-5.69 (m, 1H), 5.15-5.11 (m, 2H), 4.66 (dd, *J* = 5.7, 7.2 Hz, 1H), 2.48-2.38 (m, 3H, CH_2 and OH).

1-(3-Phenoxyphenyl)but-3-en-1-ol [7]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.26 (m, 3H), 7.09-7.05 (m, 2H), 7.01-6.98 (m, 3H), 6.90-6.88 (m, 1H), 5.81-5.71 (m, 1H), 5.14-5.10 (m, 2H), 4.66 (dd, *J* = 5.4, 7.4 Hz, 1H), 2.50-2.41 (m, 2H), 2.31 (br s, 1H, OH).

1-(Naphthalen-1-yl)but-3-en-1-ol [4,7]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 7.1 Hz, 1H), 7.47-7.42 (m, 3H), 5.88-5.80 (m, 1H), 5.43 (dd, *J* = 4.0, 8.2 Hz, 1H), 5.18-5.12 (m, 2H), 2.71-2.66 (m, 1H), 2.58-2.52 (m, 1H), 2.39 (br s, 1H, OH).

1-(4-Methylphenyl)but-3-en-1-ol [4,5]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 5.84-5.74 (m, 1H), 5.16-5.10 (m, 2H), 4.67 (t, *J* = 6.5 Hz, 1H), 2.48 (t, *J* = 6.8 Hz, 2H), 2.34 (s, 3H, CH_3), 2.15 (br s, 1H, OH).

1-(2-Methylphenyl)but-3-en-1-ol [4]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.6 Hz, 1H), 7.20-7.07 (m, 3H), 5.85-5.75 (m, 1H), 5.15-5.09 (m, 2H), 4.90 (dd, *J* = 4.5, 8.1 Hz, 1H), 2.48-2.33 (m, 2H), 2.28 (s, 3H, CH_3), 2.08 (br s, 1H, OH).

1-(4-Methoxyphenyl)but-3-en-1-ol [1,3-6]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.84-5.74 (m, 1H), 5.17-5.11 (m, 2H), 4.68 (t, *J* = 6.5 Hz, 1H), 3.80 (s, 3H, OCH_3), 2.49 (t, *J* = 6.8 Hz, 2H), 2.06 (br s, 1H, OH).

Phenyl-5-hexen-3-ol[1,2,5,6]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.21 (m, 5H), 5.89-5.79 (m, 1H), 5.18-5.14 (m, 2H), 3.71-3.66 (m, 1H), 2.87-2.80 (m, 1H), 2.74-2.67 (m, 1H), 2.37-2.31 (m, 1H), 2.24-2.17 (m, 1H), 1.83-1.78 (m, 3H, CH_2 and OH).

(*E*)-Phenyl-1,5-hexadien-3-ol [1-5]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.17 (m, 5H), 6.55 (d, *J* = 15.9 Hz, 1H), 6.18 (dd, *J* = 6.3, 15.9 Hz, 1H), 5.84-5.77 (m, 1H), 5.15-5.10 (m, 2H), 4.32-4.28 (m, 1H), 2.38-2.33 (m, 2H), 1.96 (br s, 1H, OH).

1-(Pyridin-2-yl)but-3-en-1-ol [1]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 4.7 Hz, 1H), 7.64 (dt, *J* = 1.5, 7.2 Hz, 1H), 7.29-7.26 (m, 1H), 7.16-7.13 (m, 1H), 5.84-5.74 (m, 1H), 5.08-5.03 (m, 2H), 4.77 (dd, *J* = 4.8, 7.3 Hz, 1H), 4.28 (br s, 1H, OH), 2.63-2.56 (m, 1H), 2.48-2.41 (m, 1H).

1-(Furan-2-yl)but-3-en-1-ol [1,3,4]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 1.7 Hz, 1H),

6.33 (dd, *J* = 1.8, 3.3 Hz, 1H), 6.25 (d, *J* = 3.2 Hz, 1H), 5.84-5.76 (m, 1H), 5.22-5.14 (m, 2H), 4.75 (t, *J* = 6.5 Hz, 1H), 2.66-2.59 (m, 2H), 2.10 (br s, 1H, OH).

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Analytical data of the homoallylic amine products from three-component reaction of aldehyde, amine and allyltributyltin:

4-Methyl-*N*-[1-(4-chlorophenyl)but-3-enyl]aniline [8]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.24 (m, 4H), 6.89 (d, *J* = 8.1 Hz, 2H), 6.41 (d, *J* = 8.1 Hz, 2H), 5.74-5.67 (m, 1H), 5.18-5.12 (m, 2H), 4.31 (dd, *J* = 5.6, 7.7 Hz, 1H), 2.60-2.55 (m, 1H), 2.51-2.45 (m, 1H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 141.8, 134.1, 132.5, 129.6, 128.7, 127.8, 127.4, 118.6, 114.0, 57.3, 42.9, 20.3.

***N*-(4-Methylphenyl)-α-2-propen-1-ylbenzenepropanamine** [9]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.25-7.18 (m, 3H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.52 (d, *J* = 8.1 Hz, 2H), 5.87-5.77 (m, 1H), 5.11-5.07 (m, 2H), 3.47-3.41 (m, 1H), 2.78-2.72 (m, 2H), 2.34 (t, *J* = 6.7 Hz, 2H), 2.26 (s, 3H), 1.91-1.79 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 142.0, 134.6, 129.8, 128.5, 128.4, 126.7, 125.8, 117.8, 113.9, 52.4, 38.4, 36.0, 32.3, 20.4.

4-Methyl-*N*-[1-(pyridin-2-yl)but-3-enyl]aniline [9-11]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, *J* = 4.7 Hz, 1H), 7.68-7.64 (m, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.22-7.18 (m, 1H), 6.90 (d, *J* = 8.3 Hz, 2H), 6.46 (d, *J* = 8.4 Hz, 2H), 5.77-5.72 (m, 1H), 5.17-5.10 (m, 2H), 4.55 (dd, *J* = 5.4, 7.8 Hz, 1H), 2.79-2.72 (m, 1H), 2.62-2.55 (m, 1H), 2.18 (s, 3H). ^{13}C NMR (100 MHz,

$CDCl_3$): δ 162.1, 147.9, 144.3, 138.1, 134.1, 129.6, 127.1, 122.5, 121.8, 118.6, 113.7, 58.2, 41.2, 20.3.

4-Methyl-*N*-(1-phenylbut-3-enyl)aniline [12-14]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.18 (m, 5H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.48 (d, *J* = 8.0 Hz, 2H), 5.78-5.69 (m, 1H), 5.19-5.12 (m, 2H), 4.35 (t, *J* = 7.2 Hz, 1H), 2.67-2.54 (m, 2H), 2.19 (s, 3H).

4-Methyl-*N*-[1-(4-methoxyphenyl)but-3-enyl]aniline [15]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.47 (d, *J* = 8.0 Hz, 2H), 5.74-5.68 (m, 1H), 5.16-5.08 (m, 2H), 4.28 (t, *J* = 6.9 Hz, 1H), 3.77 (s, 3H), 2.62-2.52 (m, 2H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 134.6, 129.5, 129.3, 127.6, 118.2, 114.5, 114.4, 113.9, 113.6, 57.7, 55.2, 42.8, 20.4.

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Analytical data of the alcohol products from transfer hydrogenation of ketones:

Phenethyl alcohol: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.35 (m, 4H, ArH), 7.32-7.28 (m, 1H, ArH), 4.88 (q, J = 6.4 Hz, 1H, CH), 2.62 (br s, 1H, OH), 1.50 (d, J = 6.4 Hz, 3H, CH_3).

4-Methoxyphenethyl alcohol: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, J = 8.7 Hz, 2H, ArH), 6.82 (d, J = 8.7 Hz, 2H, ArH), 4.75 (q, J = 6.4 Hz, 1H, CH), 3.74 (s, 3H, OCH_3), 2.81 (br s, 1H, OH), 1.40 (d, J = 6.5 Hz, 3H, CH_3).

4-Bromophenethyl alcohol: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 8.4 Hz, 2H, ArH), 7.24 (d, J = 8.2 Hz, 2H, ArH), 4.83 (q, J = 6.4 Hz, 1H, CH), 2.10 (br s, 1H, OH), 1.45 (d, J = 6.4 Hz, 3H, CH_3).

4-Chlorophenethyl alcohol: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, J = 8.4 Hz, 2H, ArH), 7.22 (d, J = 8.4 Hz, 2H, ArH), 4.77 (q, J = 6.2 Hz, 1H, CH), 3.10 (br s, 1H, OH), 1.40 (d, J = 6.4 Hz, 3H, CH_3).

Diphenylmethanol: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.31 (m, 8H, ArH), 7.28-7.25 (m, 2H, ArH), 5.83 (br s, 1H, OH), 2.26-2.22 (m, 1H, CH).

Cyclohexanol: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64-3.58 (m, 1H, CH), 2.48 (br s, 1H, OH), 1.92-1.87 (m, 2H, CH_2), 1.76-1.72 (m, 2H, CH_2), 1.56-1.52 (m, 1H, CH_2), 1.29-1.17 (m, 5H, CH_2).

2-Nonanol: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 (q, 1H, J = 5.9 Hz, CH), 2.44 (br s, 1H, OH), 1.46-1.28 (m, 12H, CH_2), 1.18 (d, J = 6.2 Hz, 3H, $CHCH_3$), 0.88 (t, J = 6.6 Hz, 3H, CH_2CH_3).

4-phenylbut-3-en-2-ol: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.23 (m, 5H, ArH), 6.55 (d, J =

15.9 Hz, 1H, ArC*H*=), 6.25 (dd, *J* = 15.8, 6.4 Hz, 1H, =C*H*CH), 4.49-4.45 (m, 1H, CH), 1.90 (br s, 1H, OH), 1.36 (d, *J* = 6.4 Hz, 3H, CH_3).