Supporting Information

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Title : Catalytic Activation of C-H and C-C Bonds of Allylamines *via* Olefin Isomerization by Transition metal Complexes

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Preparation of allylamine derivatives 1a, 1b, 1c, 8 and 9. Allylamine **1a** was prepared by the reaction of cinnamyl chloride and *N*-lithium-2-amino-3-picoline, generated from 2-amino-3-picoline and *n*-BuLi in THF. Other allylamines (**1b** and **1c**) and homoallylamine (**9**) were prepared by the same method. Tertiaryamine (**8**) was prepared by the reaction of **1a** and CH_3I using *n*-BuLi. In **1a**, *trans*-form was determined by H-H NOESY NMR experiment. In **1b**, two isomers were observed in a 95:5 ratio. Major isomer was the *trans*-isomer as shown by H-H NOESY NMR experiment. **1a**: ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 8.04 (d, J = 5.0 Hz, 1H, 6-**H** in picoline group), 7.39-7.18 (m, 6Hs, 4-**H** in picoline group and 2,3,4,5,6-**H**s in phenyl group), 6.60 (d, J = 15.49, 1H, (*trans*)-CH_2-CH=C**H**-Ph), 6.55-6.51 (m, 1H, 5-**H** in picoline group), 6.46-6.35 (m, 1H, (*trans*)-CH_2-C**H**=CH-Ph), 4.30 (d, J = 5.46, 2Hs, -CH_2-NH-), 4.27 (br, 1H, -N**H**-), 2.10 (s, 3Hs, CH_3- in picoline group); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm) 156.42, 145.43, 136.93, 136.81, 131.32, 128.48, 127.39, 126.29,

116.57, 112.79, 43.68, 16.93; MS, m/e 224(M^+, 6%), 133(47), 105(87), 91(100%), 77(9), 65(12); IR spectrum (neat) 3062, 3028, 2927, 1713, 1602, 1496, 1453, 1408, 1362, 1069, 1030, 748, 699 cm^{-1}; HRMS calcd for $C_{15}H_{16}N_2$ (M^+) 224.1316, found 224.1313. **1b**: ^1H NMR (250 MHz, $CDCl_3$) δ (ppm) 8.01 (d, J = 4.6 Hz, 1H, 6-**H** in picoline group), 7.19 (d, J = 7.0 Hz, 1H, 4-**H** in picoline group), 6.51 (dd, J = 6.9 Hz, J = 5.28 Hz, 1H, 5-**H** in picoline group), 5.76-5.59 (m, 2Hs, -C**H**=C**H**-CH_3), 4.11 (s, 1H, -N**H**-), 4.04 (br, 2Hs, -C$\mathbf{H_2}$-NH), 2.05 (s, 3Hs, -C$\mathbf{H_3}$ in picoline group), 1.69 (d, J = 4.6 Hz, 3Hs, (*trans*)-CH=CH-C$\mathbf{H_3}$); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm) 156.46, 145.23, 136.50, 128.31, 127.27, 116.32, 112.35, 43.42, 17.59, 16.73; MS, m/e 162(M^+, 27%), 147(31), 133(100%), 121(7), 108(8), 92(18); IR spectrum (neat) 3447, 3022, 2964, 2916, 2857, 1601, 1581, 1499, 1471, 1410, 1380. 1333, 1281, 1247, 1180, 1118, 965, 774 cm^{-1}; HRMS calcd for $C_9H_{12}N_2$ (M^+) 162.1154, found 162.1157. **1c**: ^1H NMR (250 MHz, $CDCl_3$) δ (ppm) 8.01 (d, J = 4.6 Hz, 1H, 6-**H** in picoline group), 7.19 (d, J = 7.0 Hz, 1H, 4-**H** in picoline group), 6.51 (dd, J = 6.9 Hz, J = 5.28 Hz, 1H, 5-**H** in picoline group), 6.11-5.96 (m, 1H, -C**H**=CH_2), 5.23 (d, J = 18.0, 1H, CH=C**H**H), 5.12 (d, J = 10.1, 1H, CH=CH**H**), 4.20 (s, 1H, -N**H**-), 4.12 (br, 2Hs, C$\mathbf{H_2}$-NH), 2.07 (s, 3Hs, C$\mathbf{H_3}$- in picoline group); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm) 156.38, 145.29, 136.65, 135.83, 116.37, 115.36, 112.59, 43.86, 16.78; MS, m/e 148(M^+, 29%), 133(100%), 121(8), 107(5), 92(22); IR spectrum (neat) 3455, 3019, 2987, 2924, 1607, 1500, 1475, 1411, 1336, 1285, 1190, 1000, 931, 785 cm^{-1}; HRMS calcd for $C_9H_{12}N_2$ (M^+) 148.0998, found 148.1001. **8**: ^1H NMR (250 MHz, $CDCl_3$) δ (ppm) 8.15 (dd, J = 4.9 Hz, J = 1.3 Hz, 1H, 6-**H** in picoline group), 7.42-7.11 (m, 6Hs, 4-**H** in picoline group and 2,3,4,5,6-**H**s in phenyl group), 6.81 (dd, J = 7.3, J = 4.9, 1H, 5-**H** in picoline group), 6.64 (d, J = 15.87, 1H, (*trans*)-CH_2-CH=C**H**-Ph), 6.33 (td, J = 15.9, J = 6.0, 1H, (*trans*)-CH_2-C**H**=CH-Ph),

3.87 (d, J = 6, 2Hs, -C**H**$_2$-NH-), 2.86 (s, 3Hs, (C**H**$_3$)N-), 2.32 (s, 3Hs, C**H**$_3$- in picoline group); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm) 162.25, 144.94, 139.37, 137.06, 131.90, 128.51, 127.36, 126.31, 124.09, 117.04, 56.25, 38.51, 29.68, 16.93; MS, m/e 238(M^+, 64%), 223(20), 208(54), 196(17), 147(68), 121(31), 115(100%), 107(12), 92(39); IR spectrum (neat) 3025, 2926, 1588, 1471, 1451, 1405, 1356, 1221, 1121, 1099, 966, 933, 785, 746, 693 cm^{-1}; HRMS calcd for $C_{16}H_{18}N_2$ (M^+) 238.1466, found 238.1469. **9**: ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 8.01 (d, J = 4.9 Hz, 1H, 6-**H** in picoline group), 7.19 (dd, J = 7.1 Hz, J = 0.8 Hz, 1H, 4-**H** in picoline group), 6.50 (dd, J = 7.1 Hz, J = 5.2 Hz, 1H, 5-**H** in picoline group), 5.92-5.81 (m, 1H, -C**H**=CH$_2$), 5.23 (d, J = 18.0, 1H, CH=C**H**H), 5.17-5.08 (m, 2Hs, CH=C**H**$_2$), 4.17 (s, 1H, -N**H**-), 3.54 (dd, J = 12.0 Hz, J = 6.6 Hz, 2Hs, C**H**$_2$-NH), 2.45-2.37 (m, 2Hs, C**H**$_2$-CH=CH$_2$), 2.05 (s, 3Hs, C**H**$_3$- in picoline group); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm) 156.81, 145.40, 136.62, 136.21, 116.80, 116.51, 112.43, 40.34, 33.93, 16.79; MS, m/e 162(M^+, 19%), 147(3), 121(100%), 108(14), 92(28); IR spectrum (neat) 3444, 3073, 2975, 2928, 2863, 1601, 1503, 1470, 1411, 1335, 1281, 1180, 1116, 1070, 992, 915, 774 cm^{-1}; HRMS calcd for $C_9H_{12}N_2$ (M^+) 162.1154, found 162.1159.

Catalytic C-H bond activation of 1a with 1-hexene (2a) by $Ru_3(CO)_{12}$ (3a). A screw-capped pressure vial (1 mL) was charged with 117 mg (0.522 mmol) of **1a**, 129 mg (1.54 mmol) of 1-hexene (**2a**), 10 mg (0.0156 mmol) of $Ru_3(CO)_{12}$ (**3a**), and 207 mg (2.25 mmol) of toluene. It was stirred at 130 °C for 6 h. After the reaction, ketimine (**4a**) was isolated in 90 % yield by column chromatography. Ketimine (**4a**) was hydrolyzed by 1N HCl solution and purified by column chromatography (*n*-hexane:ethylacetate = 5:2) to give 95.6 mg (84 %) of 1-phenyl-3-nonanone (**5a**). For the reaction of other

allylamines (**1b** and **1c**) and 1-alkenes in Table 2, the products were obtained by same procedure. All ketone compounds are already known except **5b** and **5e**. **4a**: ((*E*)-, (*Z*)-isomers are inseparable) ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 8.22 (br, 1H, 6-**H** in picoline group), 7.42 (d, J = 7.4 Hz, 1H, 4-**H** in picoline group), 7.28-7.26 (m, 2Hs, 3,5-**H**s in phenyl group), 7.20-7.19 (m, 2Hs, 2,6-**H**s in phenyl group), 7.00-6.97 (d, 1H, 4-**H** in phenyl group), 6.90 (dd, J = 7.1 Hz, J = 5.15 Hz, 1H, 5-**H** in picoline group), 3.11-2.08 (m, 6Hs), 2.01 (s, 3Hs, C**H**$_3$- in picoline group), 1.75-0.79 (m, 11Hs); MS, m/e 308(M^+, 5%), 251(8), 237(35), 217(57), 183(18), 147(100%), 133(5), 108(7), 92(37); IR spectrum (neat) 3061, 3026, 2927, 2857, 1663, 1585, 1496, 1464, 1415, 1377, 1180, 1110, 990, 747 cm^{-1}; HRMS calcd for $C_{21}H_{28}N_2$ (M^+) 308.2246, found 308.2250. **5b** (6,6-dimethyl-1-phenyl-3-heptanone): ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.29-7.26 (m, 2Hs, 3,5-**H**s in phenyl group), 7.20-7.17 (m, 3Hs, 2,4,6-**H**s in phenyl group), 2.90 (t, J = 7.6, 2Hs, α-CH_2 to CO in phenethyl group), 2.75 (t, J = 7.6, 2Hs, β-C**H**$_2$ to CO in phenethyl group), 2.34 (t, J = 8.2, 2Hs, α-C**H**$_2$ to CO in *t*-butylethyl group), 1.45 (t, J = 8.2, 2Hs, β-C**H**$_2$ to CO in *t*-butylethyl group), 0.86 (s, 9Hs, C**H**$_3$- in *t*-butyl group); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 210.54, 141.11, 128.40 (**C**$_3$, **C**$_5$ in phenyl group), 128.25 (**C**$_2$, **C**$_6$ in phenyl group), 125.99, 44.19, 38.69, 37.26, 29.82, 29.29, 29.03 (-C(**C**H$_3$)$_3$); MS, m/e 218(M^+, 21%), 203(12%), 133(55%), 105(91%), 91(100%), 85(13%); IR spectrum (neat) 3028, 2955, 2866, 1714, 1603, 1453, 1366, 1093, 747, 699 cm^{-1}; HRMS calcd for $C_{15}H_{22}O$ (M^+) 218.1665, found 218.1673. **5e** (7,7-dimethyl-4-octanone): ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 2.40 (t, J = 7.3 Hz, 2Hs, α-C**H**$_2$ to CO in propyl group), 2.35 (t, J = 8.2 Hz, 2Hs, α-C**H**$_2$ to CO in *t*-butylethyl group), 1.64-1.57 (m, 2Hs, β-C**H**$_2$ to CO in propyl group), 1.47 (t, J = 8.2 Hz, 2Hs, β-C**H**$_2$ to CO in *t*-butylethyl group), 0.91 (t, J = 7.5 Hz, 3Hs, C**H**$_3$ in propyl group), 0.88(s, 9Hs, C**H**$_3$ in *t*-

butyl group); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 211.79, 44.67, 38.46, 37.38, 29.30, 29.08 (-C(**C**H_3)$_3$), 17.32, 13.73; MS, m/e 156(M^+, 3%), 141(17), 113(100%), 99(13), 85(17), 71(97); IR spectrum (neat) 2958, 2872, 2044, 1991, 1964, 1715, 1469, 1412, 1393, 1366, 1294, 1248, 1184, 1125, 1082, 1030 cm^{-1}; HRMS calcd for $C_{10}H_{20}O$ (M^+) 156.1509, found 156.1512.

Catalytic C-H bond activation of 1a with 1-hexene (2a) adding H_2O by $Ru_3(CO)_{12}$ (3a). A screw-capped pressure vial (1 mL) was charged with 52.3 mg (0.233 mmol) of **1a**, 61.4 mg (0.730 mmol) of 1-hexene (**2a**), 4.6 mg (0.0072 mmol) of $Ru_3(CO)_{12}$ (**3a**), 203 mg (2.21 mmol) of toluene and 4.3 mg (0.239mmol). It was stirred at 130 °C for 6 h. After the reaction, the reaction mixture was purified by column chromatography (*n*-hexane:ethylacetate = 5:2) to give 37.5 mg (74 %) of 1-phenyl-3-nonanone (**5a**).

Catalytic C-H bond and C-C bond activation of 1a with 1-hexene (2a) by $[Rh(C_8H_{14})_2Cl]_2$ (3b) and PCy_3. A screw-capped pressure vial (1 mL) was charged with 48 mg (0.216 mmol) of **1a**, 181 mg (2.16 mmol) of 1-hexene (**2a**), 2.3 mg (0.0065 mmol) of $[Rh(C_8H_{14})_2Cl]_2$ (**3b**), 3.6 mg (0.013mmol) of tricyclohexylphosphine without solvent. It was stirred at 170 °C for 30 min. After the reaction, **1a** was completely transformed to a mixture of ketimine **4a** and **10a** in a 4 : 96 ratio measured by gas chromatography detector (GCD). The reaction mixture was hydrolyzed by 1N HCl solution and purified by column chromatography (*n*-hexane:ethylacetate = 5:2) to give 1.2 mg (3 %) of 1-henyl-3-nonanone (**5a**) and 39 mg (91%) of 7-tridecanone (**11a**). For the reaction of other 1-alkenes in Table 1, the products were obtained by same procedure. All ketone compounds are already known. **10a**: ^1H NMR (500 MHz,

$CDCl_3$) δ (ppm) 8.20 (d, J = 4.0 Hz, 1H, 6-**H** in picoline group), 7.41 (d, J = 7.1 Hz, 1H, 4-**H** in picoline group), 6.87 (dd, J = 6.9 Hz, J = 5.3 Hz, 1H, 5-**H** in picoline group), 2.45 (t, J = 7.3 Hz, 2Hs), 2.09 (m, 2Hs), 2.07 (s, 3Hs, C**H**$_3$- in picoline group), 1.73 (m, 2Hs), 1.42 (m, 4Hs), 1.33 (m, 4Hs), 1.27-1.18 (m, 2Hs), 1.14 (m, 4Hs), 0.90 (m, 3Hs), 0.82 (t, J = 6.8, 3Hs); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 177.22, 162.05, 145.93, 137.92, 122.89, 118.56, 38.62, 34.40, 31.70, 31.20, 29.23, 26.27, 26.04, 22.54, 22.29, 17.26, 13.93; MS, m/e 288(M^+, 1.5%), 287(2.4), 245(2.2), 231(13), 217(100%), 203(16), 147(79), 133(57%), 120(4), 108(21), 92(50); IR spectrum (neat) 2956, 2928, 2858, 1664, 1586, 1461, 1415, 1378, 1268, 1108, 779, 726 cm^{-1}; HRMS calcd for $C_{19}H_{32}N_2$ (M^+) 288.2556, found 288.2552.