Supporting Information

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Title : Catalytic Transformation of Aldimine to Ketimine by Wilkinson's Complex through Transimination

Alkylation of imine through transimination. (Scheme 1) A mixture of imine **1a** (117.4 mg, 0.649 mmol) and 1-hexene (**2a**) (272 mg, 3.24 mmol) in a screw-capped pressure vial (1 mL) was heated at 130 °C for 24 h with [chlorotris(triphenylphosphine)rhodium(I)] (**3**) (3 mg, 0.00324 mmol) and 2-amino-3-picoline (**4**) (7.0 mg, 0.0649 mmol). The reaction mixture was cooled to room temperature, and purified by column chromatography (*n*-hexane:ethylacetate = 5:2) to give 144.5 mg (84 %) of *N*-(1-phenylheptylidene)aniline (**5a**) and 7.4 mg (6 %) of heptanophenone (**11a**).

5a: ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.9 (m, 2H), 7.4-6.8 (m, 8H), 2.6 (t, J = 7.9 Hz, 2H, α-CH_2 to C=N), 1.4-1.1 (m, 8H), 0.8 (t, J = 6.8 Hz, 3H, -CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm) 169.7 (C=N), 150-120 (C_s in phenyl group), 31.4 (α-CH_2 to C=N), 30.1 (δ-CH_2 to C=N), 29.1 (γ-CH_2 to C=N), 27.8 (ε-CH_2 to C=N), 22.3 (β-CH_2 to C=N), 13.8 (CH_3- in hexyl group); MS: *m/z* (%): 265 (9) [M^+], 208 (42), 193 (30), 173 (34), 129 (35), 117 (100), 115 (70), 93 (31), 77 (42); IR (neat): 3054, 3027, 2952, 2924, 2854, 1685, 1625, 1588, 1485, 1443, 1313, 1206, 1024, 768, 689 cm^{-1}; HRMS calcd for $C_{19}H_{23}N_1$ (M^+) 265.183 050, found 265.183 044.

N-{1-[4-(trifluoromethyl)phenyl]heptylidene}aniline (**5b**): ^{1}H NMR (250 MHz, $CDCl_3$)

δ (ppm) 8.0 (d, J = 7.9 Hz, 2H), 7.7 (d, J = 8.2 Hz, 2H), 7.4-7.1 (m, 3H), 6.8 (d, J = 7.8 Hz, 2H), 2.6 (t, J = 7.8 Hz, 2H, α-CH_2 to C=N), 1.4-1.1 (m, 8H), 0.8 (t, J = 6.7 Hz, 3H, -CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm) 168.7 (C=N), 150-120 (C_s in phenyl group & Carbon in -CF_3), 31.1 (α-CH_2 to C=N), 30.1 (δ-CH_2 to C=N), 29.1 (γ-CH_2 to C=N), 27.7 (ε-CH_2 to C=N), 22.3 (β-CH_2 to C=N), 13.8 (CH_3- in hexyl group); MS: *m/z* (%): 333 (7) [M^+], 276 (34), 262 (100), 248 (33), 172 (23), 92 (21), 77 (83); IR (neat): 3052, 2957, 2929, 2854, 1690, 1629, 1592, 1480, 1401, 1322, 1206, 1164, 1127, 1066, 1015, 847, 698 cm^{-1}; HRMS calcd for $C_{20}H_{22}N_1F_3$ (M^+) 333.170 435, found 333.170 366.

N-{1-[4-(dimethylamino)phenyl]heptylidene}aniline (**5c**): ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.9 (m, 2H), 7.3-6.6 (m, 7H), 3.0 (s, 6H, Hs in -$N(CH_3)_2$), 2.6 (t, J = 8.0 Hz, 2H, α-CH_2 to C=N), 1.4-1.1 (m, 8H), 0.8 (t, J = 6.8 Hz, 3H, -CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm) 168.7 (C=N), 152-111 (C_s in phenyl group), 40.1 (Cs in –$N(CH_3)_2$), 31.2 (δ-CH_2 to C=N), 29.7 (α-CH_2 to C=N), 29.3 (γ-CH_2 to C=N), 28.4 (ε-CH_2 to C=N), 22.3 (β-CH_2 to C=N), 13.9 (CH_3- in hexyl group); MS: *m/z* (%): 308 (13) [M^+], 307 (14), 265 (7), 251 (25), 237 (100), 223 (55), 216 (30), 147 (73), 118 (23), 77 (43); IR (neat): 3050, 2952, 2924, 2859, 2803, 1592, 1550, 1522, 1476, 1439, 1359, 1313, 1192, 1164, 1108, 1061, 940, 819, 759, 693 cm^{-1}; HRMS calcd for $C_{21}H_{28}N_2$ (M^+) 308.225 249, found 308.225 189.

2-methyl-*N*-(1-phenylheptylidene)aniline (**5d**): ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.9 (m, 2H), 7.4 (m, 3H), 7.2 (m, 2H), 7.0 (m, 1H), 6.6 (m, 1H), 2.6 (t, J = 7.9 Hz, 2H, α-CH_2 to C=N), 2.1 (s, 3H), 1.4-1.1 (m, 8H), 0.8 (t, J = 6.7 Hz, -CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm) 169.1 (C=N), 151-117 (C_s in phenyl group), 31.6 (α-CH_2 to C=N), 30.1 (δ-CH_2 to C=N), 28.9 (γ-CH_2 to C=N), 27.4 (ε-CH_2 to C=N), 22.5 (β-CH_2 to

C=N), 17.8 (-CH_3), 13.8 (CH_3- in hexyl group); MS: *m/z* (%): 279 (7) [M^+], 264 (3), 222 (14), 209 (13), 194 (100), 107 (6), 91 (30); IR (neat): 3055, 3017, 2952, 2924, 2859, 1681, 1625, 1499, 1443, 1373, 1308, 1205, 1108, 1019, 823, 693 cm^{-1}; HRMS calcd for $C_{20}H_{25}N_1$ (M^+) 279.198 700, found 279.198 422.

N-(1-phenylheptylidene)cyclohexanamine (**5e**): ^1H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.9 (d, J = 6.9 Hz, 2H), 7.6-7.4 (m, 3H), 3.5 (m, 1H, -CH in cyclohexyl group), 2.7 (t, J = 7.7 Hz, 2H, α-CH_2 to C=N), 1.7-1.2 (m, 18H), 0.9 (t, J = 5.9 Hz, -CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm) 166.7 (C=N), 141-126 (C_s in phenyl group), 59.6 (-CH in cyclohexyl group), 34.0 (2, 6-Cs in cyclohexyl group), 31.4 (α-CH_2 to C=N), 29.4 (δ-CH_2 to C=N), 28.9 (γ-CH_2 to C=N), 27.7 (ε-CH_2 to C=N), 25.7 (4-C in cyclohexyl group), 24.7 (3, 5-Cs in cyclohexyl group), 22.5 (β-CH_2 to C=N), 13.9 (CH_3- in hexyl group); MS: *m/z* (%): 271 (4) [M^+], 270 (11), 201 (61), 214 (29), 200 (51), 186 (50), 144 (11), 120 (81), 104 (100), 91 (14), 77 (15); IR (neat): 3059, 3017, 2929, 2854, 1690, 1624, 1574, 1443, 1280, 1229, 1066, 1024, 884, 754, 693 cm^{-1}; HRMS calcd for $C_{19}H_{29}N_1$ (M^+) 271.230 000, found 271.229 626.

Intermolecular hydroacylation through transimination. (Scheme 3) A mixture of imine **1a** (117.4 mg, 0.649 mmol) and 1-hexene (**2a**) (272 mg, 3.24 mmol) in a screw-capped pressure vial (1 mL) was heated at 130 °C for 24 h with [chlorotris(triphenylphosphine)rhodium(I)] (**3**) (3 mg, 0.00324 mmol) and 2-amino-3-picoline (**4**) (7.0 mg, 0.0649 mmol). The reaction mixture was cooled to room temperature, and without isolation of ketimine, hydrolyzed with 1 N HCl 10 ml. Then the organic was extracted with CH_2Cl_2, and dried with anhydrous $MgSO_4$. The mixture was purified by column chromatography (*n*-hexane:ethylacetate = 5:2) to give 108.5 mg

(88 %) of heptanophenone (**11a**).