Supporting Information

Palladium-Catalyzed Allylation of Imine with Allyl Alcohols

Masamichi Shimizu, Masanari Kimura,[‡] Toshiya Watanabe, Yoshinao Tamaru*

Department of Applied Chemistry, Faculty of Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki, 852-8521, Japan, and Graduate School of Science and Technology, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki, 852-8521, Japan

General Procedure for the Preparation of Homoallyl Amine by the Reaction of *p*-Anisidine-Benzaldehyde Imine and *trans*-Crotyl Alcohol (run 1, Table 3): A solution of benzaldehyde (1.0 mmol) and *p*-anisidine (1.05 mmol) in dry THF (1 ml) was refluxed for 30 min under N₂ and then the solvent was removed by distillation (azeotropic removal of water, bp 63 °C). THF (1 ml) was added and distilled off under atmospheric pressure of N₂. Over the imine residue were successively added Pd(OAc)₂ (0.1 mmol), Bu₃P (0.2 mmol), crotyl alcohols (1.2 mmol), THF (1ml), and Et₃B (3.6 mmol, 1 M in hexane). The homogeneous mixture was stirred and heated for 24 h at 50 °C under N₂. The mixture was diluted with EtOAc and washed with sat. NaHCO₃ and brine, and then the organic phase was dried (MgSO₄) and concentrated in vacuo to give an yellow oil, which was purified by column chromatography over silica gel (EtOAc/hexane, 1/100 to 1/20 v/v) to give **1n** in 89% yield (*R*_f=0.83, EtOAc/hexane=1/2). The following homoallyl amines were characterized by comparison of spectra in literature: 4-methoxy-*N*-(1-(4-methoxy phenyl)but-3-enyl)aniline (**1c**),¹ *N*-(1-(4-chlorophenyl)but-3-enyl)-4-methoxyaniline (**1e**),² 4-methoxy-*N*-(1-(pyridin-3-yl)but-3-enyl)aniline (**1g**),³ *N*-(1-(furan-2-yl)but-3-enyl)-4-methoxy aniline (**1h**),⁴ 4-methoxy-*N*-(1-phenylhex-5-en-3-yl)aniline (**1m**).³

***N*-(1-(Benzo[d][1,3]dioxol-6-yl)but-3-enyl)-4-methoxyaniline (1a)**: IR (neat) 3402 (w), 2900 (m), 2831 (m), 2777 (w), 1846 (w), 1686 (w), 1638 (w), 1608 (w), 1514 (s), 1485 (s), 1440 (s), 1406 (w), 1373 (w), 1240 (s), 1180 (m), 1097 (m), 993 (w), 929 (m), 818 (s), 754 (w) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.44 (dd, *J* = 14.2, 8.0, 1 H), 2.54 (dd, *J* = 14.2, 5.9, 1 H), 3.69 (s, 3 H), 4.20 (dd, *J* = 8.0, 5.9, 1 H), 5.12 (dd, *J* = 10.1, 1.6, 1 H), 5.16 (dd, *J* = 17.1, 1.6, 1 H), 5.74 (dddd, *J* = 17.1, 10.1, 8.0, 5.9, 1 H), 5.91 (d, *J* = 1.5, 1 H), 5.92 (d, *J* = 1.5, 1 H), 6.46 (d, *J* = 8.8, 2 H), 6.68 (d, *J* = 8.8, 2 H), 6.74 (d, *J* = 7.8, 1 H), 6.81 (dd, *J* = 7.8, 1.7, 1 H), 6.85 (d, *J* = 1.7, 1

H) ; ^{13}C NMR (100 MHz, CDCl_3): δ 43.6, 55.8, 57.8, 100.9, 106.7, 108.2, 114.6, 114.7, 118.2, 119.4, 134.7, 138.0, 141.5, 146.3, 147.8, 151.9; HRMS calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_3$ 297.1365, found m/z (relative intensity): 297.1349 (M^+ , 100), 274 (2).

4-(1-(4-Methoxyphenylamino)but-3-enyl)phenol (1b): IR (neat) 3391(br), 2907 (m), 2833 (m), 1614 (m), 1597 (w), 1514 (s), 1443 (m), 1406 (m), 1238 (s), 1178 (m), 1109 (m), 1036 (m), 997 (w), 920 (m), 822 (s), 752 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 1.21 (s, 1H), 2.42 (dt, J = 14.6, 8.0, 1 H), 2.55 (ddd, J = 14.6, 8.0, 5.2, 1 H), 3.69 (s, 3 H), 5.12 (d, J = 10.2, 1 H), 5.15 (d, J = 17.1, 1H), 5.74 (dddd, J = 17.1, 10.2, 8.0, 6.6, 1H), 6.45 (d, J = 8.8, 2H), 6.72 (d, J = 8.8, 2H), 6.77 (d, J = 8.5, 2 H), 7.21 (d, J = 8.5, 2 H), ^{13}C NMR (100 MHz, CDCl_3) : δ 43.4, 55.7, 57.4, 114.6, 114.6, 115.3, 118.0, 127.4, 134.7, 135.8, 141.5, 151.8, 154.2: HRMS calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_2$ 269.1416 found m/z (relative intensity): 269.1427 (13), 228 (100).

4-Methoxy-*N*-(1-phenylbut-3-enyl)aniline (1d): IR (neat) 3400 (w), 3025 (w), 1640 (w), 1512 (s), 1452 (w), 1440 (w), 1240 (s), 1178 (m), 1038 (m), 995 (w), 920 (w), 820 (m), 756 (m), 702 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.50 (dt, J = 14.3, 8.1, 1 H), 2.59 (ddd, J = 14.3, 6.4, 5.3, 1 H), 3.68 (s, 3 H), 4.30 (dd, J = 8.1, 5.3, 1 H), 5.12 (d, J = 10.3, 1H), 5.16 (d, J = 17.0, 1 H), 5.74 (dddd, J = 17.0, 10.3, 8.1, 6.3, 1 H), 6.47 (d, J = 8.8, 2 H), 6.67 (d, J = 8.8, 2 H) 7.20-7.37 (m, 5 H) ; ^{13}C NMR (100 MHz, CDCl_3): δ 43.2, 55.8, 58.3, 114.8, 115.0, 118.2, 126.5, 127.0, 128.6, 134.7, 141.3, 143.6, 152.3; HRMS calcd for $\text{C}_{17}\text{H}_{19}\text{NO}$ 253.1466, found m/z (relative intensity): 253.1461 (M^+ , 10), 212 (100).

4-Methoxy-*N*-((*E*)-1-phenylhexa-1,5-dien-3-yl)aniline (1f): IR (neat) 3390 (w), 3025 (w), 1676 (m), 1626 (w), 1512 (s), 1448 (w), 1240 (m), 1178 (w), 1038 (m), 970 (m), 918 (m), 820 (m), 748 (m), 694 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.44 (dt, J = 14.1, 7.1, 1 H), 2.46 (dt, J = 14.1, 7.1, 1 H), 3.72 (s, 3 H), 3.97 (dt, J = 6.1, 7.1, 1 H), 5.14 (d, J = 10.0, 1 H), 5.17 (d, J = 17.0, 1 H), 5.85 (ddt, J = 17.0, 10.0, 7.1, 1 H), 6.18 (dd, J = 16.0, 6.1, 1 H), 6.58 (d, J = 16.0, 1 H), 6.62 (d, J = 8.9, 2 H), 6.74 (d, J = 8.9, 2 H) 7.18-7.35 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3): δ 40.5, 55.7, 55.8, 114.7, 115.0, 118.1, 126.2, 127.2, 128.4, 129.0, 130.2, 134.4, 136.9, 141.4, 152.1; HRMS calcd for $\text{C}_{19}\text{H}_{21}\text{NO}$ 279.1623, found m/z (relative intensity): 279.1634 (M^+ , 11), 238 (100)

4-Methoxy-*N*-(2-methylhex-5-en-3-yl)aniline (1i): IR (neat) 3398(w), 2957 (m), 2909 (m), 2872 (w), 2831 (w), 1639 (w), 1618 (w), 1512 (s), 1464 (m), 1441 (w), 1238 (s), 1180 (w), 1041 (s), 995 (w), 914 (m), 817 (s), 754 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 0.93 (d, J = 6.8, 3 H), 0.96 (d, J = 6.8, 3 H), 1.88 (dsept, J = 5.1, 6.8, 1 H), 2.17 (dt, J = 14.1, 7.1, 1 H), 2.30 (dt, J

= 14.1, 7.1, 1 H), 3.15 (dt, $J = 5.1, 7.1, 3$ H), 3.73 (s, 3 H), 5.04 (d, $J = 10.2, 1$ H), 5.06 (d, $J = 17.1, 1$ H), 5.81 (ddt, $J = 17.1, 10.2, 7.1, 1$ H), 6.14 (d, $J = 8.8, 2$ H), 6.75 (d, $J = 8.8, 2$ H); ^{13}C NMR (100 MHz, CDCl_3): δ 18.4, 18.6, 30.7, 35.6, 55.9, 59.1, 114.5, 114.6, 114.7, 114.9, 116.9, 135.7, 142.5, 151.5; HRMS calcd for $\text{C}_{14}\text{H}_{21}\text{NO}$ 219.1623, found m/z (relative intensity): 219.1622 (M^+ , 27), 178 (100).

***N*-(1-(Cyclohex-3-enyl)but-3-enyl)-4-methoxyaniline (1j):** IR (neat) 3396 (w), 3020 (m), 2912 (s), 2833 (m), 2343 (w), 1637 (w), 1618 (w), 1510 (s), 1437 (m), 1408 (w), 1236 (s), 1180 (w), 1042 (m), 997 (w), 914 (m), 818 (m), 731 (w) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 1.24-2.38 (m, 7 H), 3.20-3.29 (m, 2 H), 3.73 (s, 3 H), 5.05 (d, $J = 10.6, 1$ H), 5.06 (d, $J = 17.3, 1.7, 1$ H), 5.67 (s, 2 H), 5.80 (ddt, $J = 17.3, 10.6, 7.3, 1$ H), 6.54 (d, $J = 8.8, 2$ H), 6.75 (d, $J = 8.8, 2$ H); ^{13}C NMR (100 MHz, CDCl_3): δ 25.1, 25.7, 28.6, 35.8, 37.4, 55.8, 57.9, 114.5, 114.9, 118.2, 117.2, 126.2, 127.0, 135.1, 135.2, 134.7, 151.6; HRMS calcd for $\text{C}_{17}\text{H}_{23}\text{NO}$ 257.1780, found m/z (relative intensity): 257.1776 (M^+ , 100), 256 (5), 246 (1), 245 (5), 233 (1).

***N*-(1-Cyclohexenylbut-3-enyl)-4-methoxyaniline (1k):** IR (neat) 3400 (w), 2927 (m), 2833 (m), 1679 (w), 1639 (w), 1618 (w), 1510 (s), 1439 (m), 1406 (w), 1292 (m), 1236 (s), 1178 (m), 1039 (m), 993 (w), 918 (m), 818 (m), 756 (w); ^1H NMR (400 MHz, CDCl_3): δ 1.44-1.65 (m, 2 H), 1.95-2.05 (m, 2 H), 2.31 (dt, $J = 14.3, 7.1, 1$ H), 2.37 (dt, $J = 14.3, 6.3, 1$ H), 3.40-3.62 (br, 1 H), 3.58 (t, $J = 6.3, 1$ H), 3.73 (s, 3 H), 5.08 (dd, $J = 10.2, 1.7, 1$ H), 5.12 (d, $J = 17.0, 1.7, 1$ H), 5.67 (s, 1 H), 5.77 (ddt, $J = 17.0, 10.2, 7.1, 1$ H), 6.53 (dd, $J = 6.9, 2.2, 2$ H), 6.74 (dd, $J = 6.9, 2.2, 2$ H); ^{13}C NMR (100 MHz, CDCl_3): δ 22.7, 22.8, 24.6, 25.0, 39.2, 55.8, 59.8, 114.5, 114.6, 114.8, 114.9, 117.0, 122.9, 135.3, 137.7, 142.0, 151.6; HRMS calcd for $\text{C}_{17}\text{H}_{23}\text{NO}$ 257.1780, found m/z (relative intensity): 257.1784 (M^+ , 100), 256 (7), 246 (1), 245 (3).

4-Methoxy-*N*-(1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-3-yl)but-3-enyl)aniline (1l): IR (neat) 3400 (w), 2986 (s), 2912 (s), 2831 (s), 1678 (w), 1639 (w), 1618 (w), 1512 (s), 1466 (m), 1440 (m), 1364 (w), 1240 (s), 1180 (m), 1041 (s), 991 (w), 916 (m), 817 (s), 758 (w) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ one of isomer 0.67 (s, 3 H), 0.96 (d, $J = 8.5, 1$ H), 1.28 (s, 3 H), 2.01-2.44 (m, 7 H), 3.45-3.65 (br, 1 H), 3.65 (dd, $J = 7.3, 5.1, 1$ H), 3.72 (s, 3 H), 5.09 (d, $J = 10.2, 1$ H), 5.13 (d, $J = 17.3, 1$ H), 5.41 (s, 1 H), 5.80 (dddd, $J = 17.3, 10.2, 7.3, 3.7, 1$ H), 6.51 (d, $J = 8.8, 2$ H), 6.72 (d, $J = 8.8, 2$ H), δ another isomer 0.86 (s, 3 H), 1.18 (d, $J = 8.5, 1$ H), 1.26 (s, 3 H), 2.01-2.44 (m, 7 H), 3.45-3.65 (br, 1 H), 3.59 (t, $J = 6.1, 1$ H), 3.72 (s, 3 H), 5.10 (d, $J = 10.2, 1$ H), 5.14 (d, $J = 17.3, 1$ H), 5.41 (s, 1 H), 5.76 (dddd, $J = 17.3, 10.2, 7.3, 3.7, 1$ H), 6.54 (d, $J = 8.8, 2$ H), 6.71 (d, $J = 8.8, 2$ H); ^{13}C NMR (100 MHz, CDCl_3): δ one of isomer 21.4, 26.4, 31.1, 31.9, 38.1, 38.4, 41.1, 42.8, 55.8, 58.0, 114.5, 114.6, 114.7, 117.4, 117.9, 135.4, 141.9, 148.5,

151.6; δ another isomer 21.6, 26.4, 31.2, 31.7, 38.1, 38.5, 41.1, 43.2, 55.8, 58.1, 114.5, 114.6, 114.7, 117.5, 117.7, 135.3, 141.9, 147.7, 151.7; HRMS calcd for $C_{20}H_{27}NO$ 297.2093, found m/z (relative intensity): 297.2096 (M^+ , 100), 296 (5).

4-Methoxy-*N*-(2-methyl-1-phenylbut-3-enyl)aniline (1n): IR (neat) 3396 (w), 3026 (w), 2930 (m), 1638 (w), 1512 (s), 1452 (m), 1406 (w), 1240 (m), 1178 (w), 1038 (m), 1001 (w), 918 (w), 817 (m), 762 (m), 702 (m) cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ *anti*-isomer 0.99 (d, $J = 7.0$, 3 H), *syn*-isomer 0.95 (d, $J = 7.0$, 3 H), 2.49 (dq, $J = 7.0$, 7.3, 1 H), 3.67 (s, 3 H), 3.98 (d, $J = 7.3$, 1 H), *anti*-isomer 5.16 (d, $J = 10.3$, 1 H), *syn*-isomer 4.88 (d, $J = 10.3$, 1 H), *anti*-isomer 5.19 (d, $J = 17.3$, 1 H), *syn*-isomer 4.91 (d, $J = 17.3$, 1 H), *anti*-isomer 5.76 (ddd, $J = 17.3$, 10.3, 7.0, 1 H), *syn*-isomer 5.62 (ddd, $J = 17.3$, 10.3, 7.0, 1 H), 6.42 (d, $J = 9.0$, 2 H), 6.62 (d, $J = 9.0$, 2 H) 7.20-7.36 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.4, 45.4, 55.7, 63.2, 114.4, 114.6, 116.0, 126.8, 127.2, 128.1, 140.6, 141.8, 142.7, 151.7; HRMS calcd for $C_{18}H_{21}NO$ 267.1623, found m/z (relative intensity): 267.1649 (M^+ , 12), 212 (100).

4-Methoxy-*N*-(1,2-diphenylbut-3-enyl)aniline (1o): IR (neat) 3392 (w), 3028 (w), 1624 (m), 1602 (w), 1512 (s), 1452 (m), 1242 (m), 1180 (m), 1036 (m), 968 (w), 922 (w), 820 (m), 758 (m), 700 (m) cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 3.53 (dd, $J = 8.1$, 9.0, 1 H), 3.67 (s, 3 H), 4.41 (d, $J = 8.1$, 1 H), *anti*-isomer 5.22 (d, $J = 17.1$, 1 H), *syn*-isomer 4.93 (d, $J = 17.1$, 1 H), *anti*-isomer 5.26 (d, $J = 10.2$, 1 H), *syn*-isomer 5.05 (d, $J = 10.2$, 1 H), *anti*-isomer 6.19 (ddd, $J = 9.0$, 10.2, 17.1, 1 H), *syn*-isomer 5.96 (ddd, $J = 9.0$, 10.2, 17.1, 1 H), 6.45 (d, $J = 9.0$, 2 H), 6.66 (d, $J = 9.0$, 2 H) 6.93-7.24 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 58.3, 63.0, 114.3, 114.6, 127.2, 127.8, 128.1, 128.3, 128.6, 140.6, 141.4, 141.9, 144.8, 152.0; HRMS calcd for $C_{23}H_{23}NO$ 329.1780, found m/z (relative intensity): 329.1742 (M^+ , 2), 212 (100).

4-Methoxy-*N*-(3-methyl-1-phenylbut-3-enyl)aniline (1p): IR (neat) 3393 (w), 3026 (w), 2909 (m), 1647 (w), 1512 (s), 1452 (m), 1406 (w), 1238 (s), 1178 (w), 1040 (m), 899 (m), 820 (m), 754 (m), 700 (m) cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 1.76 (s, 3 H), 2.39 (dd, $J = 14.2$, 10.3, 1 H), 2.50 (dd, $J = 14.2$, 4.4, 1 H), 3.69 (s, 1 H), 4.31 (dd, $J = 10.3$, 4.4, 1 H), 4.86 (s, 1 H), 4.92 (s, 1 H), 6.44 (d, $J = 9.0$, 2 H), 6.67 (d, $J = 9.0$, 2 H), 7.22-7.42 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 48.1, 55.7, 56.5, 113.8, 114.6, 126.1, 126.7, 128.5, 141.7, 142.4, 144.4, 151.9; HRMS calcd for $C_{18}H_{21}NO$ 267.123, found m/z (relative intensity): 267.1649 (M^+ , 11), 212 (100)

Preparation of 1-amino-1-phenylbut-3-en **2** ⁵

A solution of ammonium cerium nitrate (15.0 mmol) in water (50 mL) was added slowly to a

stirred solution of homoallyl amine **1n** (3.0 mmol, *anti:syn* = 8:1) in acetonitrile (60 mL) at room temperature. After 2 hours, sat. NaHCO₃ was added to adjust to pH 6 of the solution and then sodium sulfite was added until no brown suspension appear any longer. The mixture was extracted with ethyl acetate and the organic phase was dried (MgSO₄) and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel to give **2** (*anti:syn* = 8:1) in 50% yield. The major anti-isomer showed resonances in 400 MHz ¹H NMR spectrum superimposable to those of an authentic sample.⁶

References

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¹H NMR spectra for new compounds are shown in the following pages.

1o:
anti,syn mixture

Chem3D presentation of **2**