A Convenient and Efficient Route for the Allylation of Aromatic Amines and α -Aryl Aldehydes with Alkynes in the Presence of a Pd(0)/PhCOOH Combined Catalyst System

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General Procedure for the allylation of aromatic amines. The reaction of *N*-methylaniline **1a** with 1-phenyl-1-propyne **2a** is representative. To a mixture of *N*-methylaniline **1a** (0.092 g, 0.859 mmol), 1-phenyl-1-propyne **2a** (0.100 g, 0.859 mmol), tetrakis(triphenylphosphine)palladium (0.050 g, 0.043 mmol) in dry 1,4-dioxane (2 mL) was added benzoic acid (0.010 g, 0.086 mmol), and the mixture was stirred at 100 °C for 8h. The reaction mixture was then filtered through a short silica gel column using ether as an eluent, and the filtrate was concentrated. The residue was purified by a silica gel column chromatography (hexane/AcOEt, 9:1) to give the allylated product **3a** (0.194 g, 93%) as an oil.

Structure of **3a**,¹ **3b**,² **3c**,³ **3d**,⁴ **3e**,⁴ **3h**,⁵ **3i**,⁵ **6e**,⁶ **6g**,⁷ **6j**,⁸ **6k**,⁹ **6l**,¹⁰ **6m**,⁹ **6o**,⁹ **6q**¹¹ are known in the literature. The characterization data for the newly synthesized compounds **6a**, **6b**, **6c**, **6f**, **6h**, **6i**, **6n**, **6p**, **10** as well as the copies of the ¹H NMR spectra of all monoallylation products are given below.

***N*-Cinnamyl-2,4-dimethoxybenzenamine (6a).** IR (neat) 3412 cm⁻¹, ¹H NMR (CDCl₃, 400 MHz) δ 7.38-7.18 (m, 5H), 6.60 (d, *J* = 15.2 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 1H), 6.45 (d, *J* = 2.8 Hz, 1H), 6.40 (d, *J* = 2.8 Hz, 1H), 6.35 (dt, *J* = 15.2, 5.6 Hz, 1H), 3.89 (d, *J* = 5.6 Hz, 2H), 3.82 (s, 3H), 3.74 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 151.9, 147.8, 136.8, 132.1, 131.0, 128.6, 127.9, 127.4, 126.1, 110.5, 103.6, 99.0, 55.6, 55.3, 46.6; HRMS calcd for C₁₇H₁₉NO₂ (M⁺) 269.1416, found 269.1410.

***N*-(4-chlorocinnamyl)-2,4-Dimethoxybenzenamine (6b).** IR (neat) 3406 cm⁻¹, ¹H NMR (CDCl₃, 400 MHz) δ 7.31-7.21 (m, 4H), 6.58 (d, *J* = 8.8 Hz, 1H), 6.55 (d, *J* = 15.6 Hz, 1H), 6.45 (d, *J* = 2.4 Hz, 1H), 6.38 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.31 (dt, *J* = 15.6, 6.0 Hz, 1H), 3.88 (dd, *J* = 6.0, 1.2 Hz, 2H), 3.82 (s, 3H), 3.74 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 151.9, 147.9, 135.4, 132.8, 132.0, 129.8, 128.5, 128.2, 127.4, 110.5, 103.7, 99.1, 55.7, 55.4, 46.6; HRMS calcd for C₁₇H₁₈ClNO₂ (M⁺) 303.1026, found 303.1025.

***N*-(4-methoxycinnamyl)-2,4-Dimethoxybenzenamine (6c).**

IR (neat) 3455 cm⁻¹, ¹H NMR (CDCl₃, 400 MHz) δ 7.30 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 8.4 Hz, 1H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.44 (d, *J* = 2.4 Hz, 1H), 6.38 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.21 (dt, *J* = 16.0, 6.0 Hz, 1H), 3.86 (dd, *J* = 6.0, 1.2 Hz, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 3.74 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 158.9, 151.9, 147.9, 133.1, 132.1, 130.7, 129.9,

129.6, 128.2, 127.3, 125.1, 113.8, 110.8, 103.7, 99.0, 55.7, 55.4, 55.2, 46.9; HRMS calcd for $C_{18}H_{21}NO_3$ (M^+) 299.1521, found 299.1525.

***N*-Cinnamyl-2,3-dimethylbenzenamine (6f).** IR (neat) 3442 cm^{-1} , ^1H NMR ($CDCl_3$, 400 MHz) δ 7.39-7.16 (m, 5H), 7.01 (broad triplet, $J = 8.0\text{ Hz}$, 1H), 6.65-6.58 (m, 2H), 6.57 (d, $J = 8.4\text{ Hz}$, 1H), 6.36 (ddd, $J = 16.0, 5.6, 2.0\text{ Hz}$, 1H), 3.95 (d, $J = 5.6\text{ Hz}$, 2H), 3.68 (bs, 1H), 2.28 (s, 3H), 2.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.8, 136.8, 136.4, 131.4, 128.5, 127.4, 127.2, 126.1, 120.3, 119.5, 108.3, 46.5, 20.7, 12.6; HRMS calcd for $C_{17}H_{19}N$ (M^+) 237.1517, found 237.1512.

***N*-Cinnamyl-2-cyanobenzenamine (6h).** IR (neat) 3448 cm^{-1} , ^1H NMR ($CDCl_3$, 400 MHz) δ 7.41-7.20 (m, 7H), 6.70 (d, $J = 8.4\text{ Hz}$, 1H), 6.68 (t, $J = 7.6\text{ Hz}$, 1H), 6.60 (d, $J = 16.0\text{ Hz}$, 1H), 6.24 (dt, $J = 16.0, 5.6\text{ Hz}$, 1H), 4.80 (bs, 1H), 4.01 (dd, $J = 5.6, 1.2\text{ Hz}$, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.8, 136.2, 134.0, 132.5, 131.9, 128.4, 127.6, 126.2, 126.1, 125.1, 117.7, 116.5, 110.8, 95.7, 45.2; HRMS calcd for $C_{16}H_{14}N_2$ (M^+) 234.1157, found 234.1159.

***N*-Cinnamyl-2-methoxy-4-nitrobenzenamine (6i).** IR (neat) 3413 cm^{-1} , ^1H NMR ($CDCl_3$, 400 MHz) δ 7.88 (dd, $J = 8.8, 2.4\text{ Hz}$, 1H), 7.62 (d, $J = 2.4\text{ Hz}$, 1H), 7.36-7.21 (m, 5H), 6.60 (d, $J = 16.0\text{ Hz}$, 1H), 6.54 (d, $J = 8.8\text{ Hz}$, 1H), 6.25 (dt, $J = 16.0, 5.6\text{ Hz}$, 1H), 5.23 (bt, 1H), 4.04 (dt, $J = 5.6, 1.6\text{ Hz}$, 2H), 3.93 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.9, 143.8, 136.9, 136.1, 132.2, 128.4, 127.6, 126.2, 124.7, 119.6, 106.8, 104.5, 55.7, 44.9; HRMS calcd for $C_{16}H_{16}N_2O_3$ (M^+) 284.1161, found 284.1155.

***N*-Cinnamyl-3-acetylbenzenamine (6n).** IR (neat) $3421, 1698\text{ cm}^{-1}$, ^1H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.18 (m, 8H), 6.85 (d, $J = 7.6\text{ Hz}$, 1H), 6.61 (d, $J = 16.0\text{ Hz}$, 1H), 6.28 (dt, $J = 16.0, 5.6\text{ Hz}$, 1H), 3.97 (d, $J = 5.6\text{ Hz}$, 2H), 2.55 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.5, 147.9, 137.9, 136.5, 133.2, 131.5, 129.1, 12.6, 126.2, 126.1, 117.7, 117.5, 111.7, 45.9, 26.6; HRMS calcd for $C_{17}H_{17}NO$ (M^+) 251.1310, found 251.1315.

***N*-Cinnamyl-4-phenylbenzenamine (6p).** IR (neat) 3434 cm^{-1} , ^1H NMR ($CDCl_3$, 400 MHz) δ 7.45-7.11 (m, 12H), 6.78 (d, $J = 7.6\text{ Hz}$, 1H), 6.75 (d, $J = 7.6\text{ Hz}$, 1H), 6.54 (d, $J = 15.6\text{ Hz}$, 1H), 6.25 (dt, $J = 15.6, 5.6\text{ Hz}$, 1H), 4.15 (bs, 1H), 3.90 (bs, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.7,

139.3, 136.7, 131.0, 130.0, 129.2, 128.5, 128.4, 127.6, 127.3, 127.0, 126.6, 126.2, 117.0, 110.7, 46.1; HRMS calcd for C₂₁H₁₉N (M⁺) 285.1517, found 285.1512.

2-(cinnamylamino)Phenol (10).

IR (neat) 3426-3450 (br) cm⁻¹, ¹H NMR (CDCl₃, 400 MHz) δ 7.55-7.14 (m, 5H), 6.79 (d, *J* = 7.2 Hz, 1H), 6.70 (t, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 7.6 Hz, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.29 (dt, *J* = 16.0, 6.0 Hz, 1H), 3.87 (bd, *J* = 5.2 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 171.6, 144.0, 136.7, 136.2, 133.5, 131.8, 128.7, 128.5, 127.4, 126.0, 121.5, 118.7, 114.8, 113.5, 46.9; HRMS calcd for C₁₅H₁₅NO (M⁺) 225.1154, found 225.1156.

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 CDCl3
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General Procedure for the α -allylation of aldehydes: The reaction of the aldehyde **11a** with 1-phenyl-1-propyne **2a** is representative. To a mixture of **11a** (0.100 g, 0.745 mmol), 1-phenyl-1-propyne **2a** (0.087 g, 0.745 mmol), and Pd(PPh₃)₄ (0.043 g, 0.037 mmol) in dry 1,4-dioxane (2 mL) was added benzoic acid (0.009 g, 0.075 mmol), and the mixture was stirred at 100 °C for 15h. The reaction mixture was then filtered through a short silica gel column using ether as an eluent, and the filtrate was concentrated. The residue was purified by silica gel column chromatography (hexane/AcOEt, 9:1) to give **12a** (0.179 g, 96%).

Structures of **12a**,¹ **12i**² are known in the literature. The characterization data for **12a**, **12i** along with the newly synthesized compounds **12b**, **12c**, **12d**, **12e**, **12f**, **12g**, **12h**, **12j** and the copies of their ¹H NMR spectra given below.

(E)-2-methyl-2,5-diphenylpent-4-enal (12a). Oil; IR (neat) 1724, 1598 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 9.56 (s, 1H), 7.42-7.18 (m, 10H), 6.39 (dt, J = 15.5, 1.1 Hz, 1H), 5.93 (dt, J = 15.5, 7.5 Hz, 1H), 2.82 (ddd, J = 13.2, 7.5, 1.1 Hz, 1H), 2.76 (ddd, J = 13.2, 7.5, 1.1 Hz, 1H), 1.49 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 201.7, 139.4, 137.2, 133.6, 128.9, 128.4, 127.4, 127.2, 127.1, 126.9, 126.1, 54.1, 40.0, 19.0; HRMS calcd for C₁₈H₁₈O (M⁺) 250.1358, found 250.1352.

(E)-5-(4-chlorophenyl)-2-methyl-2-phenylpent-4-enal (12b). Oil; IR (neat) 1716, 1598 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 9.59 (s, 1H), 7.46-7.18 (m, 9H), 6.37 (d, J = 16.0 Hz, 1H), 5.94 (dt, J = 16.0, 8.0 Hz, 1H), 2.85 (dd, J = 14.0, 8.0 Hz, 1H), 2.79 (dd, J = 14.0, 8.0 Hz, 1H), 1.52 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 201.7, 139.2, 135.6, 132.7, 132.3, 128.9, 128.5, 127.4, 127.2, 127.1, 125.6, 54.1, 39.9, 18.9; HRMS calcd for C₁₈H₁₇ClO (M⁺) 284.0968, found 284.0962.

(E)-5-(4-methoxyphenyl)-2-methyl-2-phenylpent-4-enal (12c). Oil; IR (neat) 1724, 1606 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 9.56 (s, 1H), 7.41-7.16 (m, 7H), 6.80 (m, 2H), 6.33 (dt, J = 15.6, 1.1 Hz, 1H), 5.80 (dt, J = 15.6, 7.5 Hz, 1H), 3.78 (s, 3H), 2.78 (ddd, J = 13.4, 7.5, 1.1 Hz, 1H), 2.76 (ddd, J = 13.4, 7.5, 1.1 Hz, 1H), 1.48 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 201.2, 158.8, 139.5, 132.9, 129.9, 128.8, 127.3, 127.1, 127.0, 122.5, 113.8, 55.3, 54.2, 39.9, 19.1; HRMS calcd for C₁₉H₂₂O₂ (M⁺) 280.1463, found 280.1458.

(E)-ethyl 5-formyl-5-phenylhex-2-enoate (12d). Oil; IR (neat) 1724, 1720, 1610 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 9.47 (s, 1H), 7.41-7.22 (m, 5H), 6.67 (dt, $J = 15.2, 8.0$ Hz, 1H), 5.81 (d, $J = 15.2$ Hz, 1H), 4.13 (q, $J = 7.2$ Hz, 2H), 2.80 (dd, $J = 14.0, 8.0$ Hz, 1H), 2.73 (dd, $J = 14.0, 8.0$ Hz, 1H), 1.48 (s, 3H), 1.23 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 200.6, 165.5, 143.5, 132.0, 129.0, 128.5, 125.8, 124.2, 61.8, 60.3, 42.2, 26.6, 18.17; HRMS calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3$ (M^+) 246.1256, found 246.1253.

(E)-5-(4-(trifluoromethyl)phenyl)-2-methyl-2-phenylpent-4-enal (12e). Oil; IR (neat) 1724, 1614 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 9.48 (s, 1H), 7.42 (d, $J = 8.4$ Hz, 2H), 7.36-7.18 (m, 7H), 6.33 (d, $J = 15.6$ Hz, 1H), 5.96 (dt, $J = 15.6, 7.6$ Hz, 1H), 2.77 (dd, $J = 14.4, 7.6$ Hz, 1H), 2.71 (dd, $J = 14.4, 7.6$ Hz, 1H), 1.43 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 201.5, 139.0, 132.2, 129.2, 128.9, 127.9, 127.5, 127.1, 126.2, 125.4, 125.3, 54.1, 40.0, 19.0; HRMS calcd for $\text{C}_{19}\text{H}_{17}\text{F}_3\text{O}$ (M^+) 318.1231, found 318.1226.

(E)-2-methyl-5-phenyl-2-*p*-tolylpent-4-enal (12f). Oil; IR (neat) 1724, 1610 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 9.46 (s, 1H), 7.18-7.08 (m, 9H), 6.32 (d, $J = 16.0$ Hz, 1H), 5.87 (dt, $J = 16.0, 7.6$ Hz, 1H), 2.73 (dd, $J = 14.0, 7.6$ Hz, 1H), 2.68 (dd, $J = 14.0, 7.6$ Hz, 1H), 2.28 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 201.8, 137.2, 137.1, 136.3, 133.4, 129.6, 128.4, 127.1, 126.9, 126.0, 125.0, 53.8, 39.9, 21.0, 19.0; HRMS calcd for $\text{C}_{19}\text{H}_{20}\text{O}$ (M^+) 264.1514, found 264.1509.

(E)-2-(4-methoxyphenyl)-2-methyl-5-phenylpent-4-enal (12g). Oil; IR (neat) 1716, 1608 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 9.50 (s, 1H), 7.25-7.18 (m, 7H), 6.92 (d, $J = 8.4$ Hz, 2H), 6.39 (d, $J = 15.6$ Hz, 1H), 5.93 (dt, $J = 15.6, 7.6$ Hz, 1H), 3.82 (s, 3H), 2.80 (dd, $J = 14.0, 7.6$ Hz, 1H), 2.73 (dd, $J = 14.0, 7.6$ Hz, 1H), 1.46 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 201.7, 158.7, 137.2, 133.4, 131.1, 128.4, 128.3, 127.1, 126.0, 125.0, 114.3, 55.3, 53.4, 40.0, 19.0; HRMS calcd for $\text{C}_{19}\text{H}_{20}\text{O}_2$ (M^+) 280.1463, found 280.1458.

(E)-2-(4-chlorophenyl)-2-methyl-5-phenylpent-4-enal (12h). Oil; IR (neat) 1717, 1609 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 9.50 (s, 1H), 7.36 (d, $J = 8.4$ Hz, 2H), 7.28 (m, 7H), 6.40 (d, $J = 15.6$ Hz, 1H), 5.89 (dt, $J = 15.6, 7.2$ Hz, 1H), 2.80 (dd, $J = 14.4, 7.2$ Hz, 1H), 2.74 (dd, $J = 14.4, 7.2$ Hz,

1H), 1.45 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 201.2, 137.9, 136.9, 133.9, 133.4, 128.9, 128.5, 128.4, 127.3, 126.0, 124.2, 53.8, 40.0, 19.1; HRMS calcd for $\text{C}_{18}\text{H}_{17}\text{ClO}$ (M^+) 284.0968, found 284.0962.

(E)-2,2,5-triphenylpent-4-enal (12i). Oil; IR (neat) 1724, 1598 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 9.86 (s, 1H), 7.38-7.13 (m, 15H), 6.26 (d, J = 16.0 Hz, 1H), 5.93 (dt, J = 16.0, 7.2 Hz, 1H), 3.22 (broad doublet, J = 6.8 Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 198.2, 139.6, 137.3, 133.3, 129.9, 129.2, 129.1, 128.6, 128.3, 128.2, 128.1, 127.4, 126.9, 125.9, 125.3, 63.9, 37.9; HRMS calcd for $\text{C}_{23}\text{H}_{20}\text{O}$ (M^+) 312.1514, found 312.1509.

(E)-5-(4-chlorophenyl)-2,2-diphenylpent-4-enal (12j). Oil; IR (neat) 1724, 1597 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 9.85 (s, 1H), 7.38-7.16 (m, 12H), 7.05 (d, J = 8.4 Hz, 2H), 6.18 (d, J = 15.6 Hz, 1H), 5.90 (dt, J = 15.6, 7.2 Hz, 1H), 3.21 (broad doublet, J = 7.6 Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 198.0, 139.5, 135.8, 132.6, 132.2, 129.5, 129.4, 129.0, 128.7, 128.4, 128.2, 127.4, 127.1, 126.1, 64.0, 37.9; HRMS calcd for $\text{C}_{23}\text{H}_{19}\text{ClO}$ (M^+) 346.1124, found 346.1121.

References:

1. Kimura, M.; Horino, Y.; Mukai, R.; Tanaka, S.; Tamaru Y. *J. Am. Chem. Soc.* **2001**, *123*, 10401-10402.
2. Ciganek, E.; Read, J. M.; Calabrese, J. C. *J. Org. Chem.* **1995**, *60*, 5795-5802.

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