Supporting Information for
Efficient Functionalization of Aromatic C–H Bonds Catalyzed by Gold(III) under
Mild and Solvent Free Conditions

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General. All reagents were obtained commercially and used without further purification unless otherwise noted. All reactions were performed under air atmosphere. Chromatographic purification of products was accomplished using forced-flow chromatography on EM Science Geduran silica gel 60 (35-75 μ m). Thin layer chromatography was performed on EM Science silica gel 60 F254 plates (250 μ m). Proton nuclear magnetic resonance (NMR) spectra were referenced internally according to residual protio solvent signals. Data for ^1H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet), integration, coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift (δ , ppm).

The regio- and stereochemistry of all adducts (in Tables 1.2) were unambiguously established on the basis of chemical shifts, coupling constants in ^1H NMR spectra, and comparing with the known compounds¹.

General procedure for alkyne hydroarylation. To a suspension of gold(III) chloride (0.5-5 mol%) and silver triflate (3 equivalents based on AuCl_3) in dichloroethane (0.5 mL) were added arene (1.0 mmol) and alkyne (0.5 mmol) substrates with stirring. The reaction was monitored by TLC till completion. The products were purified by flash chromatography.

An example for solvent-free alkyne hydroarylation procedure. A mixture of pentamethylbenzene (296.0 mg, 2.0 mmol), ethyl propiolate (196.0 g, 2.0 mmol), AuCl_3 (15.2 mg, 0.05 mmol), and AgOTf (38.4 mg, 0.15 mmol) in a test tube was stirred for 60 min until the mixture turned into solid. Then the product was filtered through a short silica gel column with 10/1 hexane/ EtOAc as eluent. Removal of solvents yielded white crystals: (2Z)-ethyl 3-(pentamethylphenyl)propenoate in quantity.

General procedure for the preparation of coumarins. A portion of aryl alkynoate (0.5 mmol) was mixed with AuCl_3 (5 mol%) and AgOTf (15 mol%) in 2.0 mL of dichloroethane and stirred at 50 $^\circ\text{C}$ or 70 $^\circ\text{C}$. Stirring continued until the disappearance of the alkynoate as monitored by TLC. The final product was purified by flash chromatography.

Isotope experiment 1: reaction of mesitylene- d_{12} with ethyl propiolate. A mixture of $(\text{CD}_3)_3\text{C}_6\text{D}_3$ (132.0 mg, 1.0 mmol), $\text{HC}\equiv\text{CCO}_2\text{Et}$ (49 mg, 0.5 mmol), AuCl_3 (7.6 mg, 0.025 mmol) and AgOTf (19.2 mg, 0.075 mmol) in 0.5 mL dichloroethane was stirred for 48 h at room temperature. Standard workup gave oil products (114.7 mg in 99% yield). ^1H NMR (400 MHz, CDCl_3): δ 1.08 (t, J = 6.9 Hz, 3H, CH_3), 4.01 (q, J = 6.9 Hz, OCH_2), 6.10 (d, J = 12.0 Hz, 0.12H, vinyl), 7.00 (s, 0.88H, vinyl). MS of $\text{C}_{14}\text{H}_6\text{D}_{12}\text{O}_2$ (m/e, ACPI): 231.2 ($\text{M}+1^+$).

Isotope experiment 2: H/D exchange reaction of phenyl- D_5 2-butynoate and (4-methoxyphenyl) 3-phenylpropiolate. Substrates phenyl- d_5 2-butynoate (42 mg, 0.25 mmol) and (4-methoxyphenyl) 3-phenylpropiolate (63 mg, 0.25 mmol) were dissolved in 2 mL of dichloroethane in one pot containing AuCl_3 (7.6 mg, 0.025 mmol) and AgOTf (19.2 mg, 0.075 mmol). The mixture was stirred at 70 $^\circ\text{C}$ for 12 h. Four products were

observed by GC/MS: m/e M^+ for $C_{10}H_4D_4O_2$: 164; M^+ for $C_{10}H_3D_5O_2$: 165; M^+ for $C_{16}H_{12}O_3$: 252; and $C_{16}H_{11}DO_3$: 253. Standard workup afforded two mixtures: **4-methyl-coumarin-d₄/d₃** (35.5 mg, 86%) 1H NMR (400 MHz, $CDCl_3$) δ 2.45 (d, J = 1.2 Hz, 3H, Me), 6.29 (s, 0.52 H, vinyl); **4-phenyl-6-methoxycoumarin-d₁/d₀** (65.0 mg, 99%) 1H NMR (500 MHz, $CDCl_3$) δ 3.74 (s, 3H, CH_3), 6.38 (s, 0.48 H, vinyl), 6.94 (d, J = 2.4 Hz, 1H, aryl), 7.13 (dd, J = 2.1, 8.6 Hz, 1H, aryl), 7.34 (d, J = 8.8 Hz, 1H, aryl), 7.46 (m, 2H, aryl), 7.54 (m, 3H, aryl).

Product characterization data (1H NMR spectra for unknown compounds were provided).

(2Z)-Ethyl 3-(pentamethylphenyl)propenoate (entries 1 and 2 in Table 1).¹ 1H NMR (400 MHz, $CDCl_3$): δ 1.09 (t, J = 7.2 Hz, 3H, CH_3), 2.14 (s, 6H, 2 CH_3), 2.19 (s, 6H, 2 CH_3), 2.22 (s, 3H, CH_3), 4.01 (q, J = 7.2 Hz, 2H, OCH_2), 6.12 (d, J = 12.0 Hz, 1H, vinyl), 7.12 (d, J = 12.0 Hz, 1H, vinyl). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 16.2, 16.6, 17.5, 59.6, 122.0, 129.6, 131.7, 133.1, 133.8, 146.3, 165.2. MS of $C_{16}H_{22}O_2$ (m/e , EI): 246 (M^+).

(3E)-4-(Pentamethylphenyl)-3-buten-2-one (entry 3 in Table 1).¹ 1H NMR (400 MHz, $CDCl_3$): δ 2.20 (s, 12H, 4 CH_3), 2.23 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 6.16 (d, J = 16.5 Hz, 1H, vinyl), 7.71 (d, J = 16.5 Hz, 1H, vinyl). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 16.2, 16.7, 17.7, 27.1, 130.9, 132.4, 132.6, 133.7, 135.1, 144.9, 197.9. MS of $C_{15}H_{20}O$ (m/e , EI): 216 (M^+).

(3Z)-3-(Pentamethylphenyl)propenoic acid (entry 4 in Table 1).¹ 1H NMR (400 MHz, $CDCl_3$): δ 2.20 (s, 12H, 4 CH_3), 2.23 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 6.16 (d, J = 16.5 Hz, 1H, vinyl), 7.71 (d, J = 16.5 Hz, 1H, vinyl), 10.20 (bs, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 16.2, 16.7, 17.7, 27.1, 130.9, 132.4, 132.6, 133.7, 135.1, 144.9, 197.9. MS of $C_{14}H_{18}O_2$ (m/e , EI): 218 (M^+).

(2Z)-Ethyl 3-mesitylpropenoate (entry 5 in Table 1).¹ 1H NMR (400 MHz, $CDCl_3$): δ 1.08 (t, J = 6.9 Hz, 3H, CH_3), 2.14 (s, 6H, 2 CH_3), 3.25 (s, 3H, CH_3), 4.01 (q, J = 6.9 Hz, OCH_2), 6.10 (d, J = 12.0 Hz, 1H, vinyl), 6.82 (s, 2H, aryl), 7.00 (d, J = 12.0 Hz, 1H, vinyl). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 19.9, 20.8, 59.7, 122.6, 127.6, 132.6, 134.2, 136.4, 143.9, 165.2. MS of $C_{14}H_{18}O_2$ (m/e , EI): 218 (M^+).

(2Z)-Ethyl 3-(2,4,6-trimethyl-3-bromophenyl)propenoate (entry 6 in Table 1).¹ 1H NMR (400 MHz, $CDCl_3$): δ 1.09 (t, J = 7.2 Hz, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 4.02 (q, J = 7.2 Hz, 2H, OCH_2), 6.13 (d, J = 12.0 Hz, 1H, vinyl), 6.93 (s, 1H, aryl), 7.02 (d, J = 12.0 Hz, 1H, vinyl). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.9, 19.9, 21.2, 23.9, 60.0, 123.2, 125.0, 129.2, 133.1, 134.3, 134.6, 136.9, 143.6, 165.1. MS of $C_{14}H_{17}^{79}BrO_2$ (m/e , ACPI): 297 ($C_{14}H_{17}^{79}BrO_2$, $M+1^+$), 299 ($C_{14}H_{17}^{81}BrO_2$, $M+1^+$).

(2Z)-Ethyl 3-(2,3,5,6-tetramethylphenyl)propenoate (entry 7 in Table 1).¹ 1H NMR ($CDCl_3$, 400 MHz): δ 0.95 (t, J = 6.9 Hz, 3H, CH_3), 1.97 (s, 6H, 2 CH_3), 2.10 (s, 6H, 2 CH_3), 3.88 (q, J = 6.9 Hz, 2H, OCH_2), 6.01 (d, J = 11.7 Hz, 1H, vinyl), 6.77 (s, 1H,

aryl), 6.94 (d, $J = 11.7$ Hz, vinyl). ^{13}C NMR (CDCl_3 , 100 MHz): δ 13.6, 16.2, 19.7, 59.5, 122.3, 123.0, 130.3, 132.7, 135.5, 145.2, 165.1. MS of $\text{C}_{15}\text{H}_{20}\text{O}_2$ (m/e, EI): 232 (M^+).

(2Z)-Ethyl 3-(1-naphthyl)propenoate (entry 8 in Table 1). ^1H NMR (400 MHz, CDCl_3): δ 0.95 (t, $J = 7.2$ Hz, 3H, CH_3), 3.96 (q, $J = 7.2$ Hz, 2H, OCH_2), 6.19 (d, $J = 12.3$ Hz, 1H, vinyl), 7.42 (m, 4H, aryl), 7.48 (d, $J = 12.3$ Hz, 1H, vinyl), 7.8 (m, 3H, aryl). ^{13}C NMR (100 MHz, CDCl_3): δ 12.6, 60.0, 122.6, 124.2, 124.8, 125.7, 126.1, 126.4, 128.4, 128.5, 130.9, 132.9, 133.1, 141.6, 165.7. MS of $\text{C}_{15}\text{H}_{14}\text{O}_2$ (m/e, EI): 226 (M^+).

(2E)-Ethyl 3-(2,4,6-trimethoxyphenyl)propenoate (entry 9 in Table 1).

^1H NMR (400 MHz, CDCl_3): δ 1.32 (t, $J = 7.1$ Hz, 3H, CH_3), 3.85 (s, 3H, CH_3), 3.87 (s, 3H, CH_3), 4.24 (q, $J = 7.1$ Hz, 2H, OCH_2), 6.11 (s, 2H, aryl), 6.75 (d, $J = 16.2$ Hz, 1H, vinyl), 8.09 (d, $J = 16.2$ Hz, 1H, vinyl). ^{13}C NMR (CDCl_3 , 100 MHz): δ 14.1, 55.3, 55.5, 59.9, 90.3, 117.5, 135.4, 152.2, 161.2. MS of $\text{C}_{14}\text{H}_{18}\text{O}_5$ (m/e, EI): 266 (M^+).

(2Z)-Ethyl 3-phenyl-3-(2,4,6-trimethoxyphenyl)propenoate (entry 10 in Table 1).

^1H NMR (400 MHz, CDCl_3): δ 1.17 (t, $J = 7.1$ Hz, 3H, CH_3), 3.66 (s, 6H, CH_3), 3.86 (s, 3H, CH_3), 4.09 (q, $J = 7.1$ Hz, 2H, OCH_2), 6.23 (s, 2H, aryl), 6.54 (s, 1H, vinyl), 7.30 (m, 3H, aryl), 7.45 (m, 2H, aryl). ^{13}C NMR (CDCl_3 , 100 MHz): δ 14.0, 55.0, 55.6, 59.4, 90.6, 109.3, 119.1, 126.1, 128.0, 128.6, 140.2, 149.1, 157.7, 161.1, 165.6. MS of $\text{C}_{20}\text{H}_{22}\text{O}_5$ (m/e, ACPI): 343 ($\text{M}+1^+$).

Methyl 3-(2,4,6-trimethoxyphenyl)propanoate (entry 11 in Table 1).

^1H NMR (400 MHz, CDCl_3): δ 2.45 (t, $J = 7.9$ Hz, 2H, CH_2), 2.90 (t, $J = 7.9$ Hz, 2H, CH_2), 3.67 (s, 3H, CH_3), 3.78 (s, 6H, CH_3), 3.80 (s, 3H, CH_3), 6.11 (s, 2H, aryl). ^{13}C NMR (CDCl_3 , 100 MHz): δ 18.3, 33.6, 51.3, 55.1, 55.4, 90.2, 109.0, 158.6, 159.5, 174.2. MS of $\text{C}_{13}\text{H}_{18}\text{O}_4$ (m/e, ACPI): 238 (M^+).

3-(2,4,6-Trimethoxyphenyl)-cyclohexanone (entry 12 in Table 1).

^1H NMR (400 MHz, CDCl_3): δ 1.70 (m, 2H, CH_2), 2.03 (m, 1H, CH), 2.26 (m, 2H, CH_2), 2.36 (m, 2H, CH_2), 3.10 (t, $J = 12.3$ Hz, 1H, CH_2), 3.62 (m, 1H, CH_2), 3.76 (s, 6H, CH_3), 3.78 (s, 3H, CH_3), 6.12 (s, 2H, aryl). ^{13}C NMR (CDCl_3 , 100 MHz): δ 25.4, 28.8, 33.8, 41.2, 45.3, 55.0, 55.3, 90.7, 112.2, 158.8, 159.4, 212.4. MS of $\text{C}_{15}\text{H}_{20}\text{O}_4$ (m/e, ACPI): 265.0 ($\text{M}+1^+$).

Characterization of coumarins

Coumarin (1a).

^1H NMR (400 MHz, CDCl_3) δ 6.44 (d, $J = 9.5$ Hz, 1H, vinyl), 7.32 (m, 2H, aryl), 7.50 (m, 2H, aryl), 7.73 (d, $J = 9.5$ Hz, 1H, vinyl); ^{13}C NMR (CDCl_3 , 100 MHz) δ 116.7, 116.9, 118.8, 124.5, 127.9, 134.8, 143.5, 154.0, 160.8. MS of $\text{C}_9\text{H}_6\text{O}_2$ (m/e, EI): 146 (M^+).

4-Methyl-coumarin (1b).

^1H NMR (400 MHz, CDCl_3) δ 2.45 (d, $J = 1.2$ Hz, 3H, Me), 6.29 (q, $J = 1.2$ Hz, 1H, vinyl), 7.31 (m, 2H, aryl), 7.54 (t, $J = 8.6$ Hz, 1H, aryl), 7.61 (d, $J = 7.8$ Hz, 1H, aryl); ^{13}C NMR (CDCl_3 , 100 MHz) δ 18.7, 115.0, 117.0, 119.9, 124.2, 124.60, 131.8, 152.4, 153.4, 160.8. MS of $\text{C}_{10}\text{H}_8\text{O}_2$ (m/e, EI): 160 (M^+).

4-Phenyl-coumarin (1c).

^1H NMR (400 MHz, CDCl_3) δ 6.38 (s, 1H, vinyl), 7.24 (m, 2H, aryl), 7.50 (m, 7H, aryl); ^{13}C NMR (CDCl_3 , 100 MHz) δ 115.2, 115.4, 117.3, 119.0, 124.2, 127.0, 127.9, 128.9, 129.1, 129.5, 132.0, 135.2, 154.2, 155.7, 160.8. MS of $\text{C}_{15}\text{H}_{10}\text{O}_2$ (m/e, EI): 222 (M^+).

6-tert-Butylcoumarin (2a). ^1H NMR (400 MHz, CDCl_3): δ 1.37 (s, 9H, 3 CH_3), 6.41 (d, $J = 9.6$ Hz, 1H, vinyl), 7.27 (d, $J = 8.7$ Hz, 1H, aryl), 7.45 (d, $J = 2.7$ Hz, 1H, aryl), 7.60 (dd, $J = 2.7$ and 8.7 Hz, 1H, aryl), 7.71 (d, $J = 9.6$ Hz, 1H, vinyl). ^{13}C NMR (CDCl_3 , 100

MHz): δ 31.3, 34.5, 116.3, 116.4, 118.2, 124.1, 129.5, 143.9, 147.5, 152.0, 161.1. MS of $C_{13}H_{14}O_2$ (m/e, EI): 203 ($M+1^+$).

4-Phenyl-6-tert-butylcoumarin (2b). 1H NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 9H, *tert*-butyl), 6.36 (s, 1H, vinyl), 7.35 (d, $J = 8.4$ Hz, 1H, aryl), 7.54 (m, 6H, aryl), 7.60 (dd, $J = 2.4, 8.4$ Hz, 1H, aryl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.2, 34.6, 115.0, 116.8, 118.2, 123.2, 128.4, 128.8, 129.5, 129.6, 135.4, 147.2, 152.2, 155.9, 161.0. MS of $C_{19}H_{18}O_2$ (m/e, ACPI): 279 ($M+1^+$).

4-Phenyl-6-methoxycoumarin (3). 1H NMR (500 MHz, $CDCl_3$) δ 3.74 (s, 3H, CH_3), 6.38 (s, 1H, vinyl), 6.94 (d, $J = 2.4$ Hz, 1H, aryl), 7.13 (d d, $J = 2.1, 8.6$ Hz, 1H, aryl), 7.34 (d, $J = 8.8$ Hz, 1H, aryl), 7.46 (m, 2H, aryl), 7.54 (m, 3H, aryl); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 103.7, 109.9, 115.6, 118.2, 119.0, 119.4, 128.3, 128.9, 129.7, 135.2, 148.5, 155.8, 161.0. MS of $C_{16}H_{12}O_3$ (m/e, ACPI): 253 ($M+1^+$).

1-Phenyl-3H-naphtho[2,1-b]pyran-3-one (4). 1H NMR (400 MHz, $CDCl_3$) δ 2.91 (s, 3H, CH_3), 6.37 (s, 1H, vinyl), 7.44 (d, $J = 9.0$ Hz, 1H, aryl), 7.54 (t, $J = 8.1$ Hz, 1H, aryl), 7.64 (t d, 1H, $J = 2.1, 8.1$ Hz, aryl), 7.91 (d, $J = 8.1$ Hz, 1H, aryl), 7.93 (d, $J = 8.1$ Hz, 1H, aryl), 8.58 (d, 1H, $J = 9.0$ Hz, aryl); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.4, 114.4, 116.5, 117.8, 125.0, 125.4, 127.8, 129.7, 130.2, 131.3, 133.6, 154.1, 154.6, 160.3. MS of $C_{19}H_{12}O_2$ (m/e, EI): 272 (M^+).

4, 6-Diphenylcoumarin (5).

1H NMR (500 MHz, $CDCl_3$) δ 6.39 (s, 1H, vinyl), 7.28 (m, 2H, aryl), 7.40 (m, 2H, aryl), 7.48 (m, 2H), 7.60 (m, 3H, aryl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 115.2, 119.4, 124.0, 126.4, 127.9, 128.8, 129.1, 129.1, 129.6, 130.7, 133.3, 135.6, 135.9, 150.9, 156.0, 160.4. MS of $C_{21}H_{14}O_2$ (m/e, EI): 298 (M^+).

4-Phenyl-6-bromocoumarin (6).

^1H NMR (400 MHz, CDCl_3) δ 6.39 (s, 1H, vinyl), 7.28 (d, $J = 8.8$ Hz, 1H, aryl), 7.44 (m, 2H, aryl), 7.56 (m, 3H, aryl), 7.63 (m, 2H, aryl); ^{13}C NMR (75 MHz, CDCl_3) δ 116.0, 117.0, 119.0, 120.6, 126.8, 128.3, 128.7, 129.0, 130.0, 134.4, 134.7, 153.0, 154.5, 160.0. MS of $\text{C}_{15}\text{H}_9\text{BrO}_2$ (m/e, EI): 300 (M^+ , $\text{C}_{15}\text{H}_9^{79}\text{BrO}_2$), 302 (M^+ , $\text{C}_{15}\text{H}_9^{81}\text{BrO}_2$).

Reference:

1. Jia, C. G. Piao, D. G.; Oyamada, J. Z.; Lu, W. J.; Kitamura, T.; Fujiwara, Y. *Science* **2000**, 287, 1992-1995.

Figure S1

Figure S1. ^1H NMR spectrum of the crude product obtained from reacting equal molar amounts of pentamethylbenzene with $\text{HC}\equiv\text{CCO}_2\text{Et}$ (1 h, 2.5 mol% catalyst) at room temperature under solvent free conditions. The product was filtered through a short column of silica gel to rid of the catalyst.

Figure S2a

Figure S2b

Figure S2: (a) ^1H NMR spectrum of pentamethylbenzene (0.1 mmol) in dichloroethane- d_4 . (b) ^1H NMR spectrum of the same solution taken immediately after addition of 0.1 mmol of AuCl_3 and 0.3 mmol of AgOTf . Note the spectrum change and the disappearance of the aromatic proton signal.