**Supporting Information**

# Direct Functionalization of Arenes by Primary Alcohol Sulfonate Esters Catalyzed by Gold(III)

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**General.** All reagents were obtained commercially and used without further purification unless otherwise noted. All reactions were performed under nitrogen atmosphere. The starting materials were synthesized by following previous procedures.[1,2] Flash chromatographic purification of products was accomplished by using forced-flow chromatography on EM Science Geduran silica gel 60 (35-75μm). Thin layer chromatography was performed on EM Science silica gel 60 F254 plates (250 μm). Proton nuclear magnetic resonance (NMR) spectra were acquired on Varian XL-400/500 and carbon nuclear magnetic resonance (NMR) spectra were acquired on a Varian XL-400. All the spectra are referenced internally to residual protio solvent signals or internal TMS standard. Data for $^{1}$H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, tiplet; m, multiplet), integration, coupling constant (Hz). Data for $^{13}$C NMR are reported in terms of chemical shift (δ, ppm). Different carbon atoms were determined by $^{13}$C NMR DEPT 135 spectra. Low-resolution mass spectra were obtained from the Mass Spectrometry Facility at the University of Chicago.

The regiochemistry of all adducts (in Tables 1) were unambiguously established on the basis of chemical shifts, coupling constants in $^{1}$H NMR spectra, and by comparison with the known compounds.[3-5]

**Intermolecular reaction of arenes with sulfonates .** To a mixture of gold(III) chloride (5.0 mol%) and silver triflate (3 equiv based on $AuCl_3$) in dry dichloroethane (3.0 mL) were added arene (0.5 mmol) and sulfonate (1.0 mmol) with stirring in a sealed tube. After the addition, the reaction was heated to 120 $^{o}$C, monitored by TLC or GC-Ms till completion. The product distribution was determined by GC-Ms analysis. All products were assigned based on comparison to the standard compounds purchased from commercial sources. For electron rich arenes, the products were also isolated by flash chromatography.

***n*-Butyl-pentamethylbezene** (entry 1, **Table 1**). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.4 Hz, 3H, $CH_3$), 1.45 (m, 4H, $2CH_2$), 2.23 (s, 9H, $CH_3$), 2.30 (s, 6H, $CH_3$), 2.65 (t, *J* = 7.3 Hz, 2H, $CH_2$). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 14.0, 16.9, 16.3, 20.6, 23.3 ($CH_2$), 32.2 ($CH_2$), 33.3 ($CH_2$), 128.4, 128.9, 129.7, 130.2. MS of $C_{15}H_{24}$: (m/z, EI): 204 ($M^+$).

***n*-Butyl-2,3,5,6-tetramethylbezene** (entry 2, **Table 1**). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 1.04 (t, *J* = 7.4 Hz, 3H, $CH_3$), 1.52 (m, 4H, $2CH_2$), 2.26 (s, 6H, $2CH_3$), 2.30 (s, 6H, $2CH_3$), 2.71 (t, *J* = 7.3 Hz, 2H, $CH_2$), 6.90 (s, 1H, Aryl ). $^{13}$C NMR (100 MHz, $CDCl_3$) δ

14.0, 15.3, 20.6 ($CH_2$), 23.3 ($CH_2$), 30.0 ($CH_2$), 31.9 ($CH_2$), 128.5, 129.2, 131.8, 133.6. MS of $C_{14}H_{22}$: (m/z, EI): 190 ($M^+$).

**2-Phenethyl-pentamethylbezene** (entry 6, **Table 1**) $^1$H NMR (500 MHz, $CDCl_3$) δ 2.25 (s, 9H, $CH_3$), 2.33(s, 6H, $CH_3$), 2.74 (t, *J* = 7.4 Hz, 2H, $CH_2$), 2.98 (t, *J* = 7.4 Hz, 2H, $CH_2$), 7.22 (m, 2H, aryl), 7.32 (m, 3H, aryl). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 16.4, 16.9, 16.9, 33.1 ($CH_2$), 36.1 ($CH_2$), 125.9, 128.2, 128.5, 131.7, 132.7, 132.8, 135.5, 142.4. MS of $C_{19}H_{24}$: (m/z, EI): 252 ($M^+$).

**General Procedure for preparation of the starting materials.**[1] To a suspension of 2-naphthenol in water was added NaOH in small portions and the reaction mixture was stirred until the solution become clear. Then 3-Bromo-1-propanol was added by syringe at room temperature. The mixture was stirred and monitored by TLC until the starting material disappeared. The mixture was extracted with $CH_2Cl_2$, the combined organic layer was washed 3 times with water and dried over anhydrous sodium sulfate. The crude products were obtained by removing the solvent under reduce pressure and used directly as the starting material for the next step.

To a solution of 3-(2-Naphthylenoxy)-1-propanol and 1.1 equiv of $Et_3N$ in $CH_2Cl_2$ was slowly added 1.1 equiv of methanesulfonyl chloride by syringe under $N_2$ at 0 $^oC$. The reaction mixture was warmed to room temperature and stirred for an extra 2 h. After the reaction was completed, water was added and the product was extracted with $CH_2Cl_2$. The combined organic layer was dried over anhydrous sodium sulfate. The residue was purified by flash chromatography to afford **Methanesulfonic acid 3-(naphthen-2-yloxy)-propyl ester**. (Starting material of entry 2, **Table 2**). $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 2.31 (m, 2H, $CH_2$), 3.01 (s, 3H, $CH_3$), 4.23 (t, *J* = 6.1 Hz, 2H, $CH_2$), 4.51 (t, *J* = 6.1 Hz, 2H, $CH_2$), 7.16 (m, 2H, aryl), 7.36 (t, *J* = 7.4 Hz, 1H, aryl), 7.48 (t, *J* = 7.4 Hz, 1H, aryl), 7.77 (m, 3H, aryl). $^{13}$C NMR (100 MHz, $CD_2Cl_2$) δ 29.0, 37.2, 63.1, 66.8, 106.6, 118.6, 123.8, 126.5, 126.7, 127.6, 129.0, 129.5, 134.4, 156.4.

**Trifluoromethanesulfonic acid 3-(naphthen-2-yloxy)-propyl ester**. (Starting material of entry 1, **Table 2**). $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 2.38 (m, 2H, $CH_2$), 4.23 (t, *J* = 6.1 Hz, 2H, $CH_2$), 4.83 (t, *J* = 6.1 Hz, 2H, $CH_2$), 7.16 (m, 2H, aryl), 7.38 (t, *J* = 7.4 Hz, 1H, aryl), 7.48 (t, *J* = 7.4 Hz, 1H, aryl), 7.78 (m, 3H, aryl).

**Methanesulfonic acid 3-(6-bromo-naphthen-2-yloxy)-propyl ester**. (Starting material of entry 4, **Table 2**). $^1$H NMR (400 MHz, $CDCl_3$) δ 2.24 (m, 2H, $CH_2$), 2.98 (s, 3H, $CH_3$), 4.13 (t, *J* = 5.8 Hz, 2H, $CH_2$), 4.46 (t, *J* = 6.1 Hz, 2H, $CH_2$), 7.06 (s, 1H, aryl), 7.12 (d, *J* = 8.9 Hz, 1H, aryl), 7.48 (d, *J* = 7.5 Hz, 1H, aryl), 7.59 (m, 2H, aryl), 7.88 (s, 1H, aryl). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 28.7, 36.9, 63.0, 66.7, 106.4, 116.9, 119.5, 128.2, 128.4, 129.3, 129.4, 129.8, 132.7, 156.5.

**Methanesulfonic acid 3-(3.5-dimethoxy-phenoxy)-propyl ester**. (Starting material of entry 5, **Table 2**). $^1$H NMR (400 MHz, $CDCl_3$) δ 2.22 (m, 2H, $CH_2$), 3.00 (s, 3H, $CH_3$), 3.78 (s, 6H, $2OCH_3$), 4.06 (t, *J* = 5.9 Hz, 2H, $CH_2$), 4.44 (t, *J* = 5.9 Hz, 2H, $CH_2$), 6.08 (d,

*J* = 2.1 Hz, 2H, aryl), 6.10 (d, *J* = 2.1 Hz, 1H, aryl). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 29.0, 37.2, 55.3, 63.1, 66.7, 93.1, 93.2, 93.3, 160.3, 161.5.

**Methanesulfonic acid 3-(4-methoxy-phenoxy)-propyl ester**. (Starting material of entry 6, **Table 2**). $^1$H NMR (400 MHz, $CDCl_3$) δ 2.15 (m, 2H, $CH_2$), 2.95 (s, 3H, $CH_3$), 3.73 (s, 3H, $OCH_3$), 3.99 (t, *J* = 5.9 Hz, 2H, $CH_2$), 4.39 (t, *J* = 5.9 Hz, 2H, $CH_2$), 6.82 (s, 4H, aryl). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 29.1, 37.0, 55.6, 63.8, 67.1, 114.7, 115.4, 152.6, 154.0.

**Trifluoromethanesulfonic acid 3-(3.5-dimethyl-phenoxy)-propyl ester**. (Starting material of entry 7, **Table 2**). $^1$H NMR (500 MHz, $CDCl_3$) δ 2.31 (m, 2H, $CH_2$), 2.34 (s, 6H, $2CH_3$), 4.10 (t, *J* = 6.0 Hz, 2H, $CH_2$), 4.78 (t, *J* = 6.0 Hz, 2H, $CH_2$), 6.58 (s, 2H, aryl), 6.68 (s, 1H, aryl).

**Methanesulfonic acid 3-(4-*tert*-butylphenoxy)-propyl ester**. (Starting material of entry 8, **Table 2**). $^1$H NMR (500 MHz, $CDCl_3$) δ 1.33 (s, 9H, $CH_3$), 2.22 (m, 2H, $CH_2$), 2.99 (s, 3H, $CH_3$), 4.08 (t, *J* = 5.8 Hz, 2H, $CH_2$), 4.44 (t, *J* = 6.2 Hz, 2H, $CH_2$), 6.86 (d, *J* = 6.8 Hz, 2H, aryl), 7.33 (d, *J* = 6.8 Hz, 2H, aryl).

**Trifluoromethanesulfonic acid 3-phenoxy-propyl ester**. (Starting material of entry 9, **Table 2**). $^1$H NMR (400 MHz, $CDCl_3$) δ 2.36 (m, 2H, $CH_2$), 4.12 (t, *J* = 5.8 Hz, 2H, $CH_2$), 4.81 (t, *J* = 5.8 Hz, 2H, $CH_2$), 6.93 (d, *J* = 7.7 Hz, 2H, aryl), 7.03 (t, *J* = 7.6 Hz, 1H, aryl), 7.35 (t, *J* = 7.7 Hz, 2H, aryl).

**3-Methanesulfonyloxy-propionic acid naphthen-2-yl ester**. (Starting material of entry 11, **Table 2**). Yield, 53% based on 2-naphthenol. $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 3.07 (s, 3H, $CH_3$), 3.09 (t, *J* = 5.9 Hz, 2H, $CH_2$), 4.59 (t, *J* = 5.9 Hz, 2H, $CH_2$), 7.30 (d, *J* = 8.7 Hz, 1H, aryl), 7.54 (m, 2H, aryl), 7.63 (s, 1H, aryl), 7.91 (m, 3H, aryl). $^{13}$C NMR (100 MHz, $CD_2Cl_2$) δ 34.1, 37.15, 65.3, 118.5, 121.0, 126.0, 126.8, 127.6, 127.8, 129.5, 131.5, 133.63, 148.1, 168.9.

**3-Methanesulfonyloxy-propionic acid (6-bromo-maphthen-2-yl) ester**. (Starting material of entry 12, **Table 2**). $^1$H NMR (400 MHz, $CDCl_3$) δ 3.06 (s, 3H, $CH_3$), 3.07 (t, *J* = 5.9 Hz, 2H, $CH_2$), 4.59 (t, *J* = 5.9 Hz, 2H, $CH_2$), 7.24 (d, *J* = 8.9 Hz, 1H, aryl), 7.54 (m, 2H, aryl), 7.66 (d, *J* = 8.0 Hz, 1H, aryl), 7.75 (d, *J* = 8.9 Hz, 1H, aryl), 7.99 (s, 1H, aryl). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 34.1, 37.2, 64.8, 118.5, 119.8, 121.8, 128.6, 129.2, 129.7, 130.0, 132.4, 148.0, 168.5, 182.6.

**3-Methanesulfonyloxy-propionic acid 3.5-dimethoxy-phenyl ester**. (Starting material of entry 13, **Table 2**). $^1$H NMR (400 MHz, $CDCl_3$) δ 3.01 (t, *J* = 5.9 Hz, 2H, $CH_2$), 3.07 (s, 3H, $CH_3$), 3.78 (s, 6H, $2OCH_3$), 4.56 (t, *J* = 5.9 Hz, 2H, $CH_2$), 6.29 (d, *J* = 2.2 Hz, 2H, aryl), 6.41 (d, *J* = 2.2 Hz, 1H, aryl). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 33.9, 37.1, 55.4, 64.8, 98.3, 99.9, 151.6, 161.1, 168.3.

**3-Methanesulfonyloxy-propionic acid 3.5-dimethyl-phenyl ester**. (Starting material of entry 14, **Table 2**). $^1$H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 6H, $2CH_3$), 2.97 (t, *J* = 5.7 Hz, 2H, $CH_2$), 3.02 (s, 3H, $CH_3$), 4.52 (t, *J* = 5.7 Hz, 2H, $CH_2$), 6.71 (s, 2H, aryl), 6.86 (s, 1H,

aryl). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 20.9, 33.7, 36.8, 64.5, 118.7, 127.6, 139.1, 149.9, 168.5.

**General procedure for cyclialkylation of aryloxypropyl esters.** To a mixture of gold(III) chloride (5.0 mol%) and silver triflate (3 equiv based on $AuCl_3$) in dry dichloroethane (6.0 mL) was added the sulfonate ester substrate (0.5 mmol) with stirring in a sealed tube. The reaction was heated to 120 $^{o}$C, monitored by TLC till completion. The product was purified by flash chromatography.

**2,3-Dihydro-1H-naphtho[*2,1-b*]pyran** (Product of entry 1 and 2, **Table 2**).
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.20 (m, 2H, $CH_2$). 3.09 (t, *J* = 6.5 Hz, 2H, $CH_2$), 4.29 (t, *J* = 5.2 Hz, 2H, $CH_2$), 7.10 (d, *J* = 8.9 Hz, 1H, aryl), 7.41 (t, *J* = 7.0 Hz, 1H, aryl), 7.53 (t, *J* = 7.0 Hz, 1H, aryl), 7.66 (d, *J* = 8.9 Hz, 1H, aryl), 7.83 (m, 2H, aryl). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.2, 28.6, 66.0, 115.5, 117.4, 122.8, 125.1, 125.7, 127.2, 128.9, 129.0, 130.8, 131.1. MS of $C_{13}H_{12}O$: (m/z, EI): 184 ($M^+$).

**2,3-Dihydro-1H-6-bromonaphtho[*2,1-b*]pyran** (Product of entry 4, **Table 2**).
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.16 (m, 2H, $CH_2$). 2.98 (t, *J* = 6.5 Hz, 2H, $CH_2$), 4.26 (t, *J* = 5.3 Hz, 2H, $CH_2$), 7.08 (d, *J* = 8.9 Hz, 1H, aryl), 7.53 (m, 2H, aryl), 7.63 (d, *J* = 9.0 Hz, 1H, aryl), 7.90 (d, *J* = 1.8 Hz, 1H, aryl). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.0, 21.9, 66.0, 114.0, 116.7, 120.1, 123.5, 126.5, 129.2, 129.9, 130.1, 131.6, 152.7. MS of $C_{13}H_{11}BrO$: (m/z, EI): 262 ($M^+$, $^{79}$Br, 100), 264 ($M^+$, $^{81}$Br, 97.5).

**3,4-Dihydro-5,7-dimethoxy-2H-1-benzopyran** (Product of entry 5, **Table 2**).
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.08 (m, 2H, $CH_2$), 2.76 (t, *J* = 6.5 Hz, 2H, $CH_2$), 4.18 (t, *J* = 5.8 Hz, 2H, $CH_2$), 3.78 (s, 3H, $CH_3$), 3.81 (s, 3H, $CH_3$), 6.24 (d, *J* = 2.3 Hz, 1H, aryl), 6.26 (d, *J* = 2.3 Hz, 1H, aryl). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 20.0, 28.8, 55.5, 55.6, 65.3, 91.0, 93.8, 94.6, 103.3, 117.4, 153.1. MS of $C_{11}H_{14}O_3$: (m/z, EI): 194 ($M^+$).

**3,4-Dihydro-6-methoxy-2H-1-benzopyran** (Product of entry 6, **Table 2**).
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.04 (m, 2H, $CH_2$), 2.79 (t, *J* = 5.1 Hz, 2H, $CH_2$), 3.77 (s, 3H, $OCH_3$), 4.16 (t, *J* = 5.1 Hz, 2H, $CH_2$), 6.60 (s, 1H, aryl), 6.70 (d, *J* = 8.0 Hz, 1H, aryl), 6.78 (d, *J* = 8.0 Hz, 1H, aryl). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 22.5, 25.1, 55.6, 66.3, 113.2, 114.2, 117.2, 122.7, 148.9, 153.1. MS of $C_{10}H_{12}O_2$: (m/z, EI): 164 ($M^+$).

**3,4-Dihydro-5,7-dimethyl-2H-1-benzopyran** (Product of entry 7, **Table 2**).
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.05 (m, 2H, $CH_2$), 2.08 (s, 3H, $CH_3$), 2.26 (s, 3H, $CH_3$), 2.64 (t, *J* = 5.8 Hz, 2H, $CH_2$), 4.17 (t, *J* = 6.1 Hz, 2H, $CH_2$), 6.61 (s, 2H, aryl). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 19.1, 22.2, 22.6, 29.4, 65.6, 113.6, 114.8, 116.5, 122.8, 123.1, 154.8. MS of $C_{11}H_{14}O$: (m/z, EI): 162 ($M^+$).

**3,4-Dihydro-6-*tert*-butyl-2H-1-benzopyran** (Product of entry 8, **Table 2**). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 9H, $CH_3$), 2.00 (m, 2H, $CH_2$), 2.78 (t, *J* = 6.5 Hz, 2H, $CH_2$), 4.16 (t, *J* = 5.2 Hz, 2H, $CH_2$), 6.74 (d, *J* = 7.5 Hz, 1H, aryl), 7.04 (d, *J* = 2.4 Hz, 1H, aryl), 7.12 (d d, *J* = 6.8 and 2.4 Hz, 1H, aryl). $^{13}$C NMR (100 MHz, $CDCl_3$) δ22.5, 25.1,

31.5, 34.0, 66.4, 121.3, 124.2, 126.5, 130.4, 142.7, 152.6. MS of $C_{13}H_{18}O$: (m/z, EI): 190 ($M^+$).

**3,4-Dihydro-2H-1-benzopyran** (Product of entry 9 an 10, **Table 2**). $^1$H NMR (400 MHz, $CDCl_3$) δ 2.06 (m, 2H, $CH_2$), 2.76 (t, *J* = 6.3 Hz, 2H, $CH_2$), 4.17 (t, *J* = 5.6 Hz, 2H, $CH_2$), 7.07 (d, *J* = 7.7 Hz, 2H, aryl), 7.13 (m, 2H, aryl). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 20.5, 25.3, 66.5, 121.3, 124.3, 126.5, 130.8, 142.7, 152.6. MS of $C_9H_{10}O$: (m/z, EI): 134 ($M^+$).

**1,2-Dihydro-3H-naphtho[*2,1-b*]pyran-3-one.** (Product of entry 11, **Table 2**). $^1$H NMR (400 MHz, $CDCl_3$) δ 2.91 (t, *J* = 7.4 Hz, 2H, $CH_2$), 3.35 (t, *J* = 7.4 Hz, 2H, $CH_2$), 7.23 (d, *J* = 8.9 Hz, 1H, aryl), 7.49 (t, *J* = 6.0 Hz, 1H, aryl), 7.57 (t, *J* = 6.2 Hz, 1H, aryl), 7.76 (d, *J* = 8.9 Hz, 1H, aryl), 7.86 (m, 2H, aryl). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 19.8, 28.6, 115.5, 117.4, 122.7, 125.1, 125.9, 127.1, 128.7, 128.9, 130.7, 131.0, 168.4. MS of $C_{13}H_{10}O_2$: (m/z, EI): 198 ($M^+$).

**1,2-Dihydro-3H-6-bromo-naphtho[*2,1-b*]pyran-3-one.** (Product of entry 12, **Table 2**). $^1$H NMR (400 MHz, $CDCl_3$) δ 2.91 (t, *J* = 7.8 Hz, 2H, $CH_2$), 3.32 (t, *J* = 7.6 Hz, 2H, $CH_2$), 7.23 (d, *J* = 8.9 Hz, 1H, aryl), 7.62 (m, 2H, aryl), 7.73 (d, *J* = 9.0 Hz, 1H, aryl), 7.97 (d, *J* = 1.9 Hz, 1H, aryl). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 19.8, 28.4, 115.8, 118.6, 119.0, 124.5, 128.0, 129.6, 130.4, 130.6, 131.8, 149.8, 167.9. MS of $C_{13}H_9BrO_2$: (m/z, EI): 276 ($M^+$, $^{79}$Br, 100), 278 ($M^+$, $^{81}$Br, 97.7).

**3,4-Dihydro-5,7-dimethoxy-2H-1-benzopyran-2-one**. (Product of entry 13, **Table 2**). $^1$H NMR (400 MHz, $CDCl_3$) δ 2.73 (t, *J* = 6.6 Hz, 2H, $CH_2$), 2.89 (t, *J* = 6.6 Hz, 2H, $CH_2$), 3.79 (s, 3H, $CH_3$), 3.82 (s, 3H, $CH_3$), 6.24 (d, *J* = 2.3 Hz, 1H, aryl), 6.26 (d, *J* = 2.3 Hz, 1H, aryl). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 17.0, 28.8, 55.5, 55.6, 91.0, 93.8, 94.6, 103.3, 117.4, 153.1, 169.7. MS of $C_{11}H_{12}O_4$: (m/z, EI): 208 ($M^+$).

**3,4-Dihydro-5,7-dimethyl-2H-1-benzopyran-2-one**. (Product of entry 14, **Table 2**). $^1$H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H, $CH_3$), 2.30 (s, 3H, $CH_3$), 2.74 (t, *J* = 7.6 Hz, 2H, $CH_2$), 2.87 (t, *J* = 7.6 Hz, 2H, $CH_2$), 6.73 (s, 1H, aryl), 6.80 (s, 1H, aryl). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 19.0, 20.8, 20.9, 29.0, 115.1, 115.8, 125.9, 126.7, 137.8, 151.2, 162.1. MS of $C_{11}H_{12}O_2$: (m/z, EI): 176 ($M^+$).

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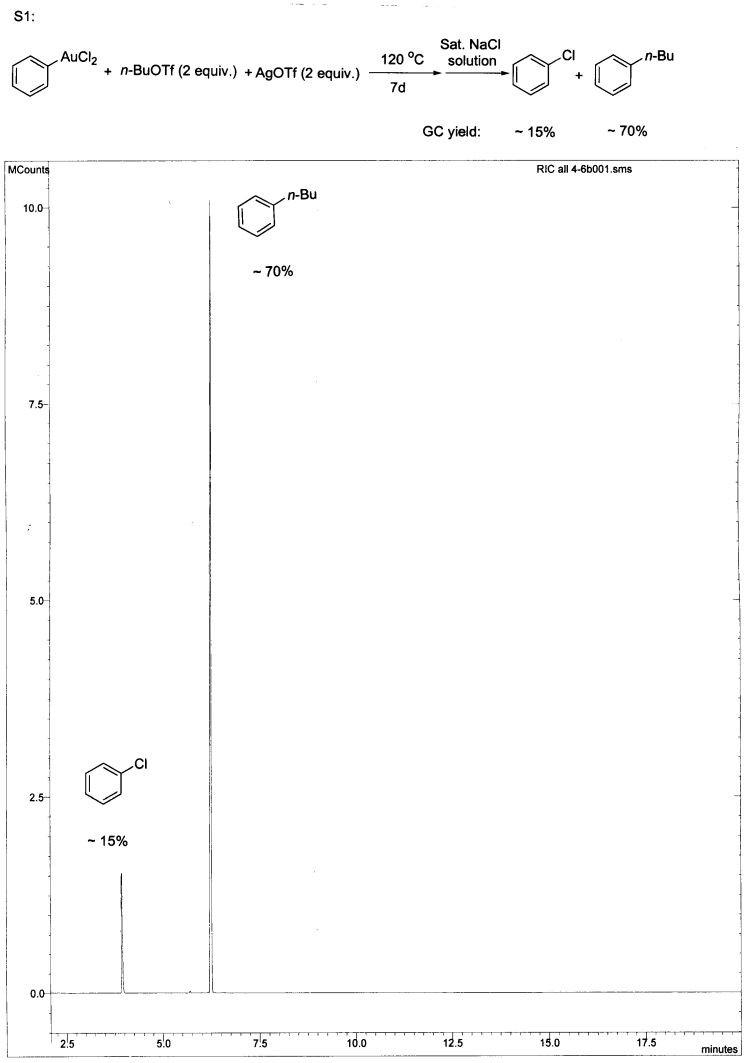


**Figure S1**. GC spectrum of the reaction mixture of dicholophenylgold(III) (0.2 mmol) with *n*-butyl triflate (0.4 mmol) and AgOTf (0.4 mmol) after the reaction was quenched with saturated aqueous NaCl solution (after 7 days at 120 °C). The quantity of the product was determined by comparing the GC peak intensity to that of the standard compound.

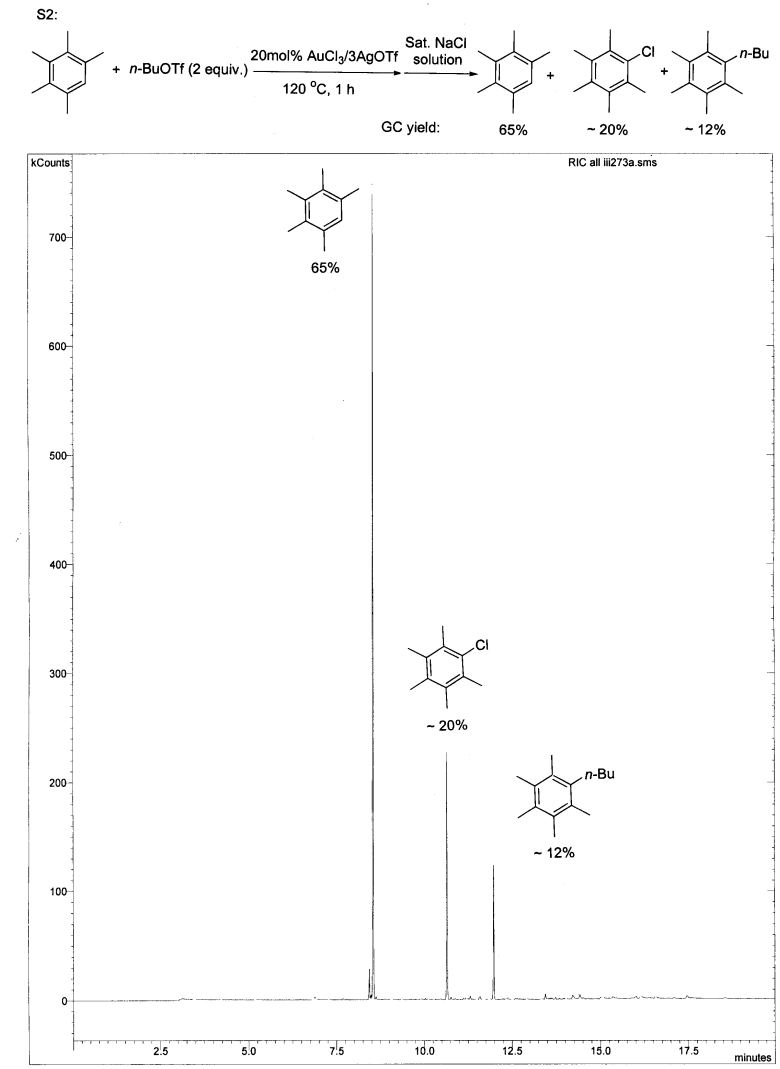


**Figure S2**. GC spectrum of the reaction mixture of pentamethylbenzene (0.5 mmol) with *n*-butyl triflate (1.0 mmol) and 20 mol% of $AuCl_3$/3AgOTf. The reaction was run for 1 h and was quenched by adding saturated aqueous NaCl solution. The GC peak intensity (compared to the standard compound) was used to estimate the quantity of each compound.