Supporting Information
for
Acid, silver, and solvent-free gold catalyzed hydrophenoxylation of unactivated internal alkynes.


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Detailed synthetic procedures for the synthesis of the arylgold compounds and vinyl ethers as well as NMR spectra for all new compounds.

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**General considerations**: Unless specified, all solvents were dried using a Grubbs-type solvent purification system. (JohnPhos)AuCl and \((t\text{-BuXPhos})\text{AuCl}\), were prepared by displacement of dimethyl sulfide from \(\text{Me}_2\text{S}\text{AuCl}\) by JohnPhos or \(t\text{-BuXPhos}\) [1,2]. The \((\text{NHC})\text{AuCl}\) (\(\text{NHC} = \text{SIMes}, \text{IMes}, \text{SIPr}, \text{IPr}\)) [3,4] precursors as well as arylgold compounds 1–3 [5] were prepared following literature procedures. The arylboronic acids, alkynes, phenols, and \(\text{Cs}_2\text{CO}_3\) (powder) were obtained from Aldrich and used as received. NMR spectra were collected on a Varian DirectDrive 600 MHz NMR spectrometer (\(^1\text{H}: 599.77\text{ MHz}\) and \(^{13}\text{C}: 150.81\text{ MHz}\)). \(^1\text{H}\) and \(^{13}\text{C}\{^1\text{H}\}\) chemical shifts were determined by reference to residual non-deuterated solvent resonances. The alkene geometry was determined using \(^1\text{H}\text{–}^1\text{H}\) NOESY experiments. All coupling constants are listed in Hertz. Microwave catalyzed reactions carried out in sealed vessels using a CEM Discover equipped with an external IR (surface) temperature sensor. The PowerMax setting on the Discover was off. Conventionally heated reactions were carried out in an oil bath. HRMS data were obtained on a Thermo Scientific Exactive Plus LC/MS system (ESI).

**General method for the arylation reactions: general procedure A**: For a typical reaction, \((\text{NHC})\text{AuCl}\), 2 equiv of the arylboronic acid, 2 equiv of \(\text{Cs}_2\text{CO}_3\), and a magnetic stirring bar were added to a 10 mL reactor vial. After exchanging the air for nitrogen, isopropanol was added by syringe. The mixtures were triturred on a stirring plate for 3 minutes followed by irradiation in the Discover microwave reactor. The following settings were used for each experiment: Temperature = 50 °C, time = 20 min, initial power level = 25 W. The initial power setting listed for each reaction was maintained until the desired temperature was reached. The power was then reduced for the remainder
of the reaction to maintain the temperature. The reaction time listed is the total irradiation time (no ramping periods). Note: High initial high levels of microwave power (to rapidly heat the sample) resulted in significant decomposition (gold metal). After cooling to room temperature, the volatiles were removed, and the title compounds were purified by column chromatography (basic alumina). The arylgold compounds were dissolved in \( \text{CH}_2\text{Cl}_2 \) and dried over molecular sieves. After filtration, they were dried under vacuum to afford white powders.

**Preparation of (IMes)Au(4-C\(_6\)H\(_4\)-Bu) (4).** General procedure A was followed with (IMes)AuCl (0.20 g, 0.37 mmol), 4-\textit{t}-butylphenylboronic acid (0.135 g, 0.76 mmol), cesium carbonate (0.24 g, 0.74 mmol), and isopropanol (1.5 mL). Chromatography: basic alumina (37.5 g), gradient hexane/THF (90:10–50:50). \( R_f \) 0.60 (hexane/THF 50:50), yield = 0.18 g of a white powder (76.1%). HRMS: \([\text{M + Na}^+]\) calcd for C\(_{31}\)H\(_{37}\)AuN\(_2\)Na: 657.2520; found, 657.2509. Spectral data: \(^1\text{H NMR (CDCl}_3, 25 ^\circ\text{C}) \delta 7.07 \text{ (s, 4H, Ar-H)}, 7.04 \text{ (s, 2H, =CH)}, 6.98 \text{ (br s, 4H, Ar-H)}, 2.34 \text{ (s, 6H, -Me)}, 2.16 \text{ (s, 12H, -Me)}, 1.19 \text{ (s, 9H, -Me)}. \(^{13}\text{C}^{\{^1\text{H}\}} \text{NMR (CDCl}_3, 25 ^\circ\text{C}) \delta 196.0 \text{ (s, carbene C)}, 165.4 \text{ (s, quat)}, 146.6 \text{ (s, quat)}, 139.9 \text{ (s, Ar-CH)}, 139.0 \text{ (s, quat)}, 135.4 \text{ (s, quat)}, 134.9 \text{ (s, quat)}, 129.2 \text{ (s, Ar-CH)}, 123.6 \text{ (s, Ar-CH)}, 121.7 \text{ (s, =CH)}, 34.0 \text{ (s, quat)}, 31.4 \text{ (s, -CMe}_3\text{)}, 21.1 \text{ (s, -Me)}, 18.0 \text{ (s, -Me}).

**Preparation of (SIMes)Au(4-C\(_6\)H\(_4\)-Bu) (5).** General procedure A was followed with (SIMes)AuCl (0.20 g, 0.37 mmol), 4-\textit{t}-butylphenylboronic acid (0.135 g, 0.76 mmol), cesium carbonate (0.24 g, 0.74 mmol), and isopropanol (1.5 mL). Chromatography: basic
alumina (37.5 g), gradient hexane/THF (90:10–50:50). $R_f$ 0.62 (hexane/THF 50:50), yield = 0.15 g of a white powder (63.5%). HRMS: [M + Na]$^+$ calcd for $C_{31}H_{39}AuN_2Na$: 659.2676; found, 659.2683. Spectral data: $^1$H (CDCl$_3$, 25 °C) $\delta$ 7.00 (AA′BB′, 4H, Ar-H), 6.94 (s, 4H, Ar-H), 3.93 (s, 4H, -NCH$_2$), 2.37 (s, 12H, -Me), 2.30 (s, 6H, -Me), 1.18 (s, 9H, -Me). $^{13}$C{$_1^H$} NMR (CDCl$_3$, 25 °C) $\delta$ 216.4 (s, carbene C), 165.7 (s, quat), 146.7 (s,quat), 139.9 (s, Ar-CH), 138.2 (s, quat), 135.8 (s, quat), 135.4 (s,quat), 129.4 (s, Ar-CH), 123.5 (s, Ar-CH), 50.8 (s, -NCH$_2$), 34.0 (s,quat), 31.4 (s, -Me), 21.1 (s, -Me), 18.1 (s, -Me).

**Preparation of (SIMes)Au(4-C$_6$H$_4$OMe) (6).** General procedure A was followed with (SIMes)AuCl (0.20 g, 0.37 mmol), 4-methoxyphenylboronic acid (0.115 g, 0.76 mmol), cesium carbonate (0.24 g, 0.74 mmol), and isopropanol (1.5 mL). Chromatography: basic alumina (37.5 g), gradient hexane/THF (90:10–50:50). $R_f$ 0.45 (hexane/THF 50:50), yield = 0.12 g of a white powder (53.0%). HRMS: [M + Na]$^+$ calcd for $C_{28}H_{33}AuN_2ONa$: 633.2156; found, 633.2144. Spectral data: $^1$H NMR (CDCl$_3$, 25 °C) $\delta$ 6.95 (s, 4H, Ar-H), 6.95 (AA′BB′, 2H, Ar-H), 6.63 (AA′BB′, 2H, Ar-H), 3.93 (s, 3H, -NCH$_2$), 3.66 (s, 3H, -OMe), 2.37 (s, 12H, -Me), 2.31 (s, 6H, -Me). $^{13}$C{$_1^H$} NMR (CDCl$_3$, 25 °C) $\delta$ 216.2 (s, carbene C), 160.3 (s, quat), 157.1 (s,quat), 140.7 (s, Ar-CH), 138.2 (s,quat), 135.8 (s,quat), 135.4 (s,quat), 129.4 (s, Ar-CH), 112.7 (s, Ar-CH), 55.0 (s, -OMe), 50.9 (s, -NCH$_2$), 21.1 (s, -Me), 18.2 (s, -Me).

**Preparation of (IPr)Au(4-C$_6$H$_4$t-Bu) (7).** General procedure A was followed with (IPr)AuCl (0.20 g, 0.32 mmol), 4-tert-butylphenylboronic acid (0.115 g, 0.65 mmol),
cesium carbonate (0.21 g, 0.64 mmol), and isopropanol (1.5 mL). Chromatography: basic alumina (37.5 g), gradient hexane/THF (90:10-50:50). $R_t$ 0.69 (hexane/THF 50:50), yield = 0.20 g of a white powder (86.4%). HRMS: [M + Na]$^+$ calcd for C$_{37}$H$_{49}$AuN$_2$Na: 741.3459; found, 741.3418. Spectral data: $^1$H NMR (CDCl$_3$, 25 °C) $\delta$ 7.44 (t, 2H, $J$ = 7.5, Ar-H), 7.25 (d, 4H, $J$ = 7.2, Ar-H), 7.13 (s, 2H, =CH-), 7.05 (s, 4H, Ar-H), 2.67 (sept, 4H, $J$ = 6.9, iPrCH), 1.41 (d, 12H, $J$ = 7.2, iPr-Me), 1.23 (d, 12H, $J$ = 7.2, iPr-Me), 1.18 (s, 9H, -Me). $^{13}$C{$^1$H} NMR (CDCl$_3$, 25 °C) $\delta$ 197.3 (s, carbene C), 166.1 (s, quat), 146.2 (s, quat), 145.7 (s, quat), 140.0 (s, Ar-CH), 134.7 (s, quat), 130.1 (s, Ar-CH), 123.9 (s, Ar-CH), 123.5 (s, Ar-CH), 122.7 (s, =CH-), 34.0 (s, -CMe$_3$), 31.4 (s, -CMe$_3$), 28.8 (s, iPr-CH), 24.5 (s, iPr-Me), 23.9 (s, iPr-Me).

**Preparation of (SIPr)Au(4-C$_6$H$_4$-Bu) (8).** General procedure A was followed with (SIPr)AuCl (0.20 g, 0.32 mmol), 4-tert-butyphenylboronic acid (0.115 g, 0.65 mmol), cesium carbonate (0.21 g, 0.64 mmol), and isopropanol (1.5 mL). Chromatography: basic alumina (37.5 g), gradient hexane/THF (90:10-50:50). $R_t$ 0.70 (hexane/THF 50:50), yield = 0.21 g of a white powder (91%). HRMS: [M + Na]$^+$ calcd for C$_{37}$H$_{51}$AuN$_2$Na: 743.3618; found, 743.3574. Spectral data: $^1$H NMR (CDCl$_3$, 25 °C) $\delta$ 7.34 (t, 2H, $J$ = 7.5, Ar-H), 7.20 (d, 4H, $J$ = 8.4, Ar-H), 7.02 (AA'BB', 2H, Ar-H), 6.96 (AA'BB', 2H, Ar-H), 3.98 (s, 4H, -NCH$_2$-), 3.15 (sept, 4H, $J$ = 6.8, iPr-CH), 1.48 (d, 12H, $J$ = 7.2, iPr-Me), 1.34 (d, 12H, $J$ = 7.2, iPr-Me), 1.16 (s, 9H, -CMe$_3$). $^{13}$C{$^1$H} NMR (CDCl$_3$, 25 °C) $\delta$ 216.7 (s, carbene C), 166.4 (s, quat), 146.7 (s, quat), 146.1 (s, quat), 139.9 (s, Ar-CH), 134.8 (s, quat), 129.4 (s, Ar-CH), 124.3 (s, Ar-CH), 123.4 (s, Ar-CH), 53.7 (s, -NCH$_2$-), 34.0 (s, -CMe$_3$), 31.4 (s, -CMe$_3$), 29.0 (s, iPr-CH), 25.1 (s, iPr-Me), 24.0 (s, iPr-Me).
Preparation of (SIr)Au(4-C₆H₄OMe) (9). General procedure A was followed with (SIr)AuCl (0.20 g, 0.32 mmol), 4-methoxyphenylboronic acid (0.10 g, 0.66 mmol), cesium carbonate (0.21 g, 0.64 mmol), and isopropanol (1.5 mL). Chromatography: basic alumina (37.5 g), gradient hexane/THF (90:10–50:50). Rf 0.65 (hexane/THF 50:50), yield = 0.15 g of a white powder (67.3%). HRMS: [M + Na]⁺ calcd for C₃₄H₄₅AuN₂ONa: 717.3098; found, 717.3055. Spectral data: ᵃ¹H NMR (CDCl₃, 25 °C) δ 7.36 (t, 2H, J = 7.8, Ar-H), 7.21 (d, 4H, J = 7.8, Ar-H), 6.92 (d, 2H, J = 8.4, Ar-H), 6.60 (d, 2H, J = 8.4, Ar-H), 4.00 (s, 4H, -NCH₂-), 3.63 (s, 3H, -OMe), 3.15 (sept, 4H, J = 6.9, iPr-CH), 1.47 (d, 12H, J = 7.2, iPr-Me), 1.35 (d, 12H, J = 7.2, iPr-Me). ᵃ¹³C{⁻¹H} NMR (CDCl₃, 25 °C) δ 216.6 (s, carbene C), 160.9 (s, quat), 156.8 (s, quat), 146.7 (s, quat), 140.6 (s, Ar-CH), 134.8 (s, quat), 129.4 (s, Ar-CH), 124.3 (s, Ar-CH), 112.6 (s, Ar-CH), 54.9 (s, -NCH₂-), 53.7 (s, -OMe), 29.0 (s, iPr-CH), 25.1 (s, iPr-Me), 24.1 (s, iPr-Me).

General method for the catalyst screening reactions: microwave and conventional heating: general procedure B: A reactor vial (10 mL) was charged with the LAuAr species (1–9, 0.014 mmol), alkyne (0.28 mmol), phenol (0.56 mmol), and a magnetic stirring bar. After exchanging the air for nitrogen, the samples were irradiated in a focused microwave reactor or heated in an oil bath. For the reactions carried out in the microwave reactor, the initial power setting listed for each reaction was maintained until the desired temperature was reached. No ramping periods were used in these reactions; thus, the reaction time listed is the total irradiation time (not the time at the desired temperature). After cooling, CDCl₃ was added to the reaction mixtures until
homogeneous solutions were obtained (≈2 mL). Anisole (internal standard, 0.28 mmol) was added to the solutions and the extent of each reaction was determined by $^1$H NMR spectroscopy.

Isolation of the vinyl ethers: The synthesis of the vinyl ethers was carried out following the same general procedure from the catalyst screening reactions using either 1 or 7 as the catalyst. Once cooled, the vinyl ethers were purified by column chromatography, dried using molecular sieves (hexane/EtOAc solution), and isolated as oils or powders following removal of the volatiles.

**Preparation of 1-[[1(Z)-1,2-diphenylethenyl]oxy]-4-nitrobenzene (10),** CAS: 1219621-28-9 [6]. General procedure B was followed (microwave heating) using 1 (0.0088 g, 0.014 mmol), diphenylacetylene (0.050 g, 0.28 mmol), and 4-nitrophenol (0.078 g, 0.56 mmol). Temperature = 130 °C, time = 20 min, initial power level = 50 W. Chromatography: silica gel (19.1 g), hexane/EtOAc (90:10). $R_f$ 0.62 (hexane/EtOAc 90:10), yield = 0.074 g of a white powder (83%).

**Preparation of 1-[[1(Z)-1,2-diphenylethenyl]oxy]-4-trifluoromethylbenzene (11).** CAS: 1219621-27-8 [6]. General procedure B was followed (microwave heating) with 1 (0.0088 g, 0.014 mmol), diphenylacetylene (0.050 g, 0.28 mmol), and 4-(trifluoromethyl)phenol (0.091 g, 0.56 mmol). Temperature = 130 °C, time = 20 min, initial power level = 50 W. Chromatography: silica gel (19.1 g), hexane/EtOAc (95:5). $R_f$ 0.56 (hexane/EtOAc 95:5), yield = 0.086 g of a white powder (91%).
Preparation of 1-[(1Z)-1,2-diphenylethenyl]oxy]-2-nitrobenzene (12). General procedure B was followed (microwave heating) with 1 (0.0088 g, 0.014 mmol), diphenylacetylene (0.050 g, 0.28 mmol), and 2-nitrophenol (0.078 g, 0.56 mmol). Temperature = 130 °C, time = 20 min, initial power level = 50 W. Chromatography: silica gel (19.1 g), hexane/EtOAc (95:5). R_f 0.40 (hexane/EtOAc 95:5), yield = 0.062 g of a pale yellow powder (70%).

Preparation of 1-[(1Z)-1,2-diphenylethenyl]oxy]benzene (13). General procedure B was followed (conventional heating) with 7 (0.010 g, 0.014 mmol) diphenylacetylene (0.050 g, 0.28 mmol), and phenol (0.053 g, 0.56 mmol). Temperature = 130 °C, time = 20 min. Chromatography: silica gel (19.1 g), hexane/EtOAc (93:7). R_f 0.74, hexane/EtOAc (93:7), yield = 0.052 g of a white powder (68%).

Preparation of 1-[(1Z)-1,2-diphenylethenyl]oxy]-4-tert-butylbenzene (14). General procedure B was followed (conventional heating) with 7 (0.010 g, 0.014 mmol), diphenylacetylene (0.050 g, 0.28 mmol), and 4-tert-butylphenol (0.084 g, 0.56 mmol). Temperature = 130 °C, time = 20 min. Chromatography: silica gel (19.1 g), gradient hexane/EtOAc (100:0–98:2). R_f 0.41 (hexane/EtOAc 98:2), yield = 0.067 g of a white powder (73%). HRMS: [M + H]^+ calcd for C_{24}H_{25}O: 329.1907; found, 329.1903. Spectral data: ^1H NMR (CDCl_3, 25 °C) δ 7.64 (d, 2H, J = 7.8, Ar-H), 7.59 (d, 2H, J = 7.2, Ar-H), 7.31–7.17 (m, 8H, Ar-H), 6.93 (AA'BB', 2H, Ar-H), 6.62 (s, 1H, =CH-), 1.23 (s, 9H, -CMe_3). ^13C{^1H} NMR (CDCl_3, 25 °C) δ 154.0 (s, quat), 149.9 (s, quat), 144.5 (s, quat),
136.3 (s, quat), 134.9 (s, quat), 129.0 (s, Ar-CH), 128.52 (s, Ar-CH), 128.50 (s, Ar-CH), 128.3 (s, Ar-CH), 127.3 (s, Ar-CH), 126.4 (s, Ar-CH), 126.1 (s, Ar-CH), 116.7 (s, =CH-), 115.6 (s, Ar-CH), 34.1 (s, -CMe$_3$), 31.5 (s, -CMe$_3$).

Preparation of 1-[[(1Z)-1,2-diphenylethenyl]oxy]-4-methoxybenzene (15), CAS: 1219621-22-3 [6]. General procedure B was followed (microwave heating) with 1 (0.0088 g, 0.014 mmol), diphenylacetylene (0.050 g, 0.28 mmol), and 4-methoxyphenol (0.070 g, 0.56 mmol). Temperature = 130 °C, time = 20 min, initial power level = 50 W. Chromatography: silica gel (19.1 g), hexane/EtOAc (100:0–90:10). $R_f$ 0.51 (hexane/EtOAc 95:5), yield = 0.068 g of a white powder (80%).

Preparation of 4-[[(1Z)-1-butyl-1-hexen-1-yl]oxy]nitrobenzene (16). General procedure B was followed (microwave heating) with 1 (0.0088 g, 0.014 mmol), 5-decyne (50.6 μL, 0.28 mmol), and 4-nitrophenol (0.078 g, 0.56 mmol). Temperature = 130 °C, time = 20 min, initial power level = 50 W. Chromatography: silica gel (19.1 g), gradient hexane/EtOAc (100:0–60:40). $R_f$ 0.67 (hexane/EtOAc 95:5), yield = 0.068 g of a colorless oil (87%). HRMS: [M + H]$^+$ calcd for C$_{16}$H$_{24}$N$_3$: 278.1758; found, 278.1748.

Spectral data: $^1$H NMR (CDCl$_3$, 25 °C) $\delta$ 8.19 (AA'BB', 2H, Ar-H), 6.99 (AA'BB', 2H, Ar-H), 5.12 (t, 1H, $J = 7.2$, -CH-), 2.15 (t, 2H, $J = 7.8$, -CH$_2$-), 1.93 (q, 2H, $J = 7.2$ -CH$_2$-), 1.47 (m, 2H, -CH$_2$-), 1.34–1.25 (m, 6H, -CH$_2$-), 0.89 (t, 3H, $J = 7.2$, -Me), 0.84 (t, 3H, $J = 6.8$, -Me). $^{13}$C{$^1$H} NMR (CDCl$_3$, 25 °C) $\delta$ 162.3 (s, quat), 150.0 (s, quat), 141.9 (s, quat), 126.0 (s, Ar-CH), 117.5 (s, -CH-), 115.5 (s, Ar-CH), 32.2 (s, -CH$_2$-), 31.3 (s, -CH$_2$-), 28.9 (s, -CH$_2$-), 24.9 (s, -CH$_2$-), 22.3 (s, -CH$_2$-), 22.1 (s, -CH$_2$-), 13.8 (s, -CH$_3$).
Preparation of [(1Z)-1-butyl-1-hexen-1-yl]oxy]-4-(trifluoromethyl)benzene (17). General procedure B was followed (microwave heating) with 1 (0.0088 g, 0.014 mmol), 5-decyne (50.6 μL, 0.28 mmol), and 4-(trifloromethyl)phenol (0.091 g, 0.56 mmol). Temperature = 130 °C, time = 20 min, initial power level = 50 W. Chromatography: silica gel (19.1 g), hexane. Rf 0.86 (hexane), yield = 0.080 g of a colorless oil (95%). HRMS: [M + H]^+ calcd for C_{17}H_{24}F_3O: 301.1781; found, 301.1771. Spectral data: \(^1\)H NMR (CDCl₃, 25 °C) δ 7.53 (d, 2H, J = 7.8, Ar-H), 6.98 (d, 2H, J = 8.4, Ar-H), 5.07 (t, 1H, J = 7.2, =CH-), 2.12 (t, 2H, J= 7.5, -CH₂-), 1.96 (q, 2H, J = 7.2, -CH₂-), 1.44 (m, 2H, -CH₂-), 1.35-1.25 (m, 6H, -CH₂-), 0.88 (t, 3H, J= 7.2, -Me), 0.85 (t, 3H, J = 7.2, -Me). \(^{13}\)C\{\(^1\)H\} NMR (CDCl₃, 25 °C) δ 159.5 (s, quat), 150.1 (s, quat), 126.9 (q, J = 3.9, Ar-CH), 124.4 (q, J= 271.3, -CF₃), 123.3 (q, J = 32.4, quat), 117.0 (s, =CH-), 115.6 (s, Ar-CH), 32.0 (s, -CH₂-), 31.5 (s, -CH₂-), 29.0 (s, -CH₂-), 24.9 (s, -CH₂-), 22.3 (s, -CH₂-), 22.1 (s, -CH₂-), 13.8 (s, -Me).

Preparation of 2-[(1Z)-1-butyl-1-hexen-1-yl]oxy]nitrobenzene (18). General procedure B was followed (conventional heating) with 7 (0.010 g, 0.014 mmol), 5-decyne (50.6 μL, 0.28 mmol), and 2-nitrophenol (0.078 g, 0.56 mmol). Temperature = 130 °C, time = 30 min. Chromatography: basic alumina (27.5 g), gradient hexane/THF (100:0–95:5). Rf 0.80 (hexane/THF 95:5), yield = 0.066 g of a pale yellow oil (84%). HRMS: [M + H]^+ calcd for C_{16}H_{24}NO₃: 278.1758 ; found, 278.1747. Spectral data: \(^1\)H NMR (CDCl₃, 25 °C) δ 7.87 (d, 1H, J = 7.0, Ar-H), 7.46 (t, 1H, J = 8.1, Ar-H), 7.04 (d, 1H, J = 7.2, Ar-H), 7.03 (t, 1H, J = 7.8, Ar-H), 5.12 (t, 1H, J = 6.9, =CH-), 2.15 (t, 2H, J = 7.8,
-CH₂-), 1.98 (q, 2H, J = 7.2, -CH₂-), 1.47 (m, 2H, -CH₂-), 1.37 - 1.26 (m, 6H, -CH₂-), 0.88 (t, 3H, J = 7.2, -Me), 0.85 (t, 3H, J = 6.9, -Me). ¹³C{¹H} NMR (CDCl₃, 25 ºC) δ 150.3 (s,quat), 149.8 (s,quat), 139.7 (s,quat), 133.8 (s,Ar-CH), 125.7 (s,Ar-CH), 120.8 (s,Ar-CH), 117.5 (s,=CH-), 116.3 (s,Ar-CH), 32.0 (s,-CH₂-), 31.3 (s,-CH₂-), 28.8 (s,-CH₂-), 24.8 (s,-CH₂-), 22.2 (s,-CH₂-), 22.1 (s,-CH₂-), 13.81 (s,-Me), 13.79 (s,-Me).

Preparation of [[(1Z)-1-butyl-1-hexen-1-yl]oxy]benzene (19). General procedure B was followed (conventional heating) with 7 (0.010 g, 0.014 mmol), 5-decyne (50.6 µL, 0.28 mmol), and phenol (0.053 g, 0.56 mmol). Temperature = 130 ºC, time = 20 min. Chromatography: silica gel (19.1 g), hexane. Rf 0.71 (hexane), yield = 0.048 g of a colorless oil (74%). HRMS: [M + H]⁺ calcld for C₁₆H₂₅O: 233.1907; found, 233.1898. Spectral data: ¹H NMR (CDCl₃, 25 ºC) δ 7.26 (t, 2H, J = 8.4, Ar-H), 6.95 (t, 1H, J = 7.5, Ar-H), 6.92 (d, 2H, J = 7.5, Ar-H), 5.00 (t, 1H, J = 7.2, =CH-), 2.11 (t, 2H, J = 7.2, -CH₂-), 2.01 (q, 2H, J = 7.2, -CH₂-), 1.43 (m, 2H, -CH₂-), 1.29 (m, 6H, -CH₂-), 0.87 (t, 3H, J = 7.2, -CH₃), 0.85 (t, 3H, J = 7.2, -CH₃). ¹³C{¹H} NMR (CDCl₃, 25 ºC) δ 156.8 (s,quat), 150.6 (s,quat), 129.4 (s, Ar-CH), 121.2 (s, Ar-CH), 116.1 (s, =CH-), 115.9 (s, Ar-CH), 32.0 (s, -CH₂-), 31.7 (s, -CH₂-), 29.1 (s, -CH₂-), 24.8 (s, -CH₂-), 22.3 (s, -CH₂-), 22.2 (s, -CH₂-), 13.90 (s, -Me), 13.87 (s, -Me).

Preparation of [[(1Z)-1-butyl-1-hexen-1-yl]oxy]-4-tert-butylbenzene (20). General procedure B was followed (microwave heating) with 1 (0.0088 g, 0.014 mmol), 5-decyne (50.6 µL, 0.28 mmol), and 4-tert-butylphenol (0.084 g, 0.56 mmol). Temperature = 130 ºC, time = 20 min, initial power level = 50 W. Chromatography: silica gel (19.1 g),
hexane. \( R_f \) 0.53 (hexane), yield = 0.057 g of a colorless oil (71%). HRMS: \([M + H]^+\) calcd for \( C_{20}H_{33}O \): 289.2533; found, 289.2524. Spectral data: \(^1H\) NMR (CDCl\(_3\), 25 °C) \( \delta \) 7.27 (AA'BB', 2H, Ar-H), 6.84 (AA'BB', 2H, Ar-H), 4.98 (t, 1H, \( J = 7.2 \), \(-\text{CH}-\)), 2.10 (t, 2H, \( J = 7.5 \), \(-\text{CH}_2\)-), 2.02 (q, 2H, \( J = 7.0 \), \(-\text{CH}_2\)-), 1.43 (m, 2H, \(-\text{CH}_2\)-), 1.34-1.26 (m, 6H, \(-\text{CH}_2\)-), 1.30 (s, 9H, \(-\text{CMe}_3\)), 0.87 (t, 3H, \( J = 7.5 \), \(-\text{CH}_3\)), 0.85 (t, 3H, \( J = 6.9 \), \(-\text{CH}_3\)).

\(^{13}C\)\(^{1H}\) NMR (CDCl\(_3\), 25 °C) \( \delta \) 154.4 (s, quat), 150.8 (s, quat), 143.9 (s, quat), 126.2 (s, Ar-CH), 115.9 (s, \(-\text{CH}-\)), 115.4 (s, Ar-CH), 34.1 (s, \(-\text{CMe}_3\)), 32.0 (s, \(-\text{CH}_2\)-), 31.8 (s, \(-\text{CH}_2\)-), 31.6 (s, \(-\text{CMe}_3\)), 29.1 (s, \(-\text{CH}_2\)-), 24.9 (s, \(-\text{CH}_2\)-), 22.4 (s, \(-\text{CH}_2\)-), 22.2 (s, \(-\text{CH}_2\)-), 14.0 (s, \(-\text{Me}\)), 13.9 (s, \(-\text{Me}\)).

**Preparation of \([[(1Z)-1\text{-butyl-1-hexen-1-yl}][\text{oxy}]-4\text{-methoxybenzene (21).}** General procedure B was followed (microwave heating) with 1 (0.0088 g, 0.014 mmol), 5-decyne (50.6 µL, 0.28 mmol), and 4-methoxyphenol (0.070 g, 0.56 mmol). Temperature = 130 °C, time = 20 min, initial power level = 50 W. Chromatography: silica gel (19.1 g), hexane/EtOAc (95:5). \( R_f \) 0.86 hexane/EtOAc (95:5), yield = 0.066 g of a colorless oil (89%). HRMS: \([M + H]^+\) calcd for \( C_{17}H_{27}O_2 \): 262.2013; found, 263.2011. Spectral data: \(^1H\) NMR (CDCl\(_3\), 25 °C) \( \delta \) 6.85 (AA'BB', 2H, Ar-H), 6.81 (AA'BB', 2H, Ar-H), 4.94 (t, 1H, \( J = 6.9 \), \(-\text{CH}-\)), 3.78 (s, 3H, \(-\text{OMe}\)), 2.07 (t, 2H, \( J = 7.5 \), \(-\text{CH}_2\)-), 2.04 (q, 2H, \( J = 7.0 \), \(-\text{CH}_2\)-), 1.41 (m, 2H, \(-\text{CH}_2\)-), 1.30 (m, 6H, \(-\text{CH}_2\)-), 0.86 (t, 6H, \( J = 7.2 \), \(-\text{Me}\)).

\(^{13}C\)\(^{1H}\) NMR (CDCl\(_3\), 25 °C) \( \delta \) 154.3 (s, quat), 151.1 (s, quat), 150.6 (s, quat), 117.0 (s, Ar-CH), 115.4 (s, \(-\text{CH}-\)), 114.6 (s, Ar-CH), 55.7 (s, \(-\text{OMe}\)), 31.8 (s, \(-\text{CH}_2\)-), 29.1 (s, \(-\text{CH}_2\)-), 24.8 (s, \(-\text{CH}_2\)-), 22.4 (s, \(-\text{CH}_2\)-), 22.1 (s, \(-\text{CH}_2\)-), 13.92 (s, \(-\text{Me}\)), 13.87 (s, \(-\text{Me}\)).
Preparation of [[(1Z)-4-[1-butyl-1-hexen-1-yl]oxy]-1,1'-biphenyl (22). General procedure B was followed (conventional heating) with 7 (0.010 g, 0.014 mmol), 5-decyne (50.6 µL, 0.28 mmol), and 4-phenylphenol (0.096 g, 56 mmol). Temperature = 130 °C, time = 20 min. Chromatography: silica gel (19.1 g), gradient hexane/EtOAc (100:0–95:5). \( R_f \) 0.81 (hexane/EtOAc 95:5), yield = 0.069 g of a colorless oil (80%). HRMS: \([M + H]^+\) calcd for C\(_{22}\)H\(_{29}\)O: 309.2220; found, 309.2211. Spectral data: \(^1\)H NMR (CDCl\(_3\), 25 °C) \( \delta \) 7.54 (d, 2H, \( J = 7.2\), Ar-H), 7.50 (AA'BB', 2H, Ar-H), 7.40 (t, 2H, \( J = 7.5\), Ar-H), 7.29 (t, 1H, \( J = 7.5\), Ar-H), 6.98 (AA'BB', 2H, Ar-H), 5.03 (t, 1H, \( J = 6.9\), =CH), 2.15 (t, 2H, \( J = 7.2\), -CH\(_2\)-), 2.04 (q, 2H, \( J = 7.2\), -CH\(_2\)-), 1.46 (m, 2H, -CH\(_2\)-), 1.36–1.26 (m, 6H, -CH\(_2\)-), 0.88 (t, 3H, \( J = 6.9\), -Me), 0.87 (t, 3H, \( J = 7.2\), -Me). \(^{13}\)C\(^{1}\)H NMR (CDCl\(_3\), 25 °C) \( \delta \) 156.4 (s, quat), 150.6 (s, quat), 140.8 (s, quat), 134.4 (s, quat), 128.7 (s, Ar-CH), 128.2 (s, Ar-CH), 126.8 (s, Ar-CH), 126.7 (s, Ar-CH), 116.3 (s, =CH-), 116.2 (s, Ar-CH), 32.1 (s, -CH\(_2\)-), 31.7 (s, -CH\(_2\)-), 29.1 (s, -CH\(_2\)-), 24.9 (s, -CH\(_2\)-), 22.4 (s, -CH\(_2\)-), 22.2 (s, -CH\(_2\)-), 13.94 (s, -CH\(_3\)), 13.91 (s, -CH\(_3\)).

References
Std proton

Sample Name:  
Archive directory:  
Sample directory:  
FidFile: 400ras032213.006  
Pulse Sequence: Proton (z2pul)  
Solvent: cdcl3  
Data collected on: Mar 27 2013

Temp. 25.0 C / 298.1 K
Operator: ras

Wmnr600 "rum600"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.049 sec
Width 9615.4 Hz
Single scan

Observe E1, 599.7738193 MHz

Data processing
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min 9 sec
Std Carbon

File: home/ras/Desktop/t68ras38813.001.tif

Pulse Sequence: sigpu
Solvent: cmc19
Temp: 295.0 C / 298.1 K
PROTON: 400.133395
PPMREF: 0.0001

VMR8-600 "Pmr680"

Relax, delay 1.000 sec
Pulse 45.0 degrees
Avg. time 1.200 sec
Width 0.0007 Hz
3232 repetitions
Observe 139.13432472 MHz
Decouple 139.730382 MHz
Power 56 dB

Sample size 0.000 cm
VALT7-16 modulated
DATA PROCESSING
Line broadening 8.5 Hz
FT size 321072
Total time 19 hr, 14 min, 43 sec
Sample Name:

Data Collected on:

nmr600-vnmrs600

Archive directory:

Sample directory:

Fidfile: 600raso52913.004

Pulse Sequence: PROTON (xipul)

Solvent: cdcl3

Data collected on: May 28 2013

Temp. 25.0 C / 298.1 K

Operator: ras

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.754 sec

Width 9615.6 Hz

Single scan

OBSERVE - H1, 599.7738340 MHz

DATA PROCESSING

FT size 32768

Total time 0 min 3 sec
Sample Name:
Data Collected on: nmr600-nmr600
Archive directory:
Sample directory:

File: 600ras053913.003

Pulse Sequence: CARRON (a2pul)
Solvent: cdc13
Data collected on: May 28 2013

Temp. 25.0 C / 298.1 K
Operator: rma

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.885 sec
Width 37878.8 Hz
36408 repetitions

OBSERVE C13, 150.8132472 MHz
DMPOLYHE H1, 599.7763882 MHz
Power 40 dB
continuously on

WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
PT size 65536
Total time 129 hr, 31 min
Sample Name:

Data Collected on:

nmr600-nmr600

Archive directory:

Sample directory:

FID File: 606rasa061313.007

Pulse Sequence: PROTON (a2pul)

Solvent: dcd13

Data collected on: Jun 14 2013

Temp. 25.0 C / 298.1 K

Operator: ras

Delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.704 sec

Width 9615.4 Hz

Single scan

OBSERVE: 599.7738340 MHz

DATA PROCESSING

FT size 33768

Total time 0 min 3 sec
Sample Name:

Data Collected on:
mx600-vnmrs600
Archive directory:

Sample directory:

PidFile: 600ras052813.009

Pulse Sequence: CARBON (n2pul)
Solvent: cdc13
Data collected on: May 29 2013

Temp. 25.0 C / 298.1 K
Operator: rax

Relax, delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.865 sec
Width 37878.8 Hz
23360 repetitions

DECOUPLE H1, 599.9768382 MHz
Power 46 dB continuously on

MALTE-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 129 hr, 31 min

ppm
Std proton

Sample Name:

Data Collected on:
mnr600-vnmrs600

Archive directory:

Sample directory:

Fidfile: 600ras061313.001

Pulse Sequence: CARBON (e2pul)

Solvent: cdcl3

Data collected on: Jun 12 2013

Temp. 25.0 C / 298.1 K

Operator: ras

Relax. delay 1.000 sec

Pulse 45.0 degree

Acq. time 0.865 sec

Width 44642.9 Hz

25000 repetitions

OBSERVE C13, 150.8132519 MHz

DECOUPLE sh, 599.7763282 MHz

Power 46 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

PT size 131072

Total time 12 hr, 57 min

220 200 180 160 140 120 100 80 60 40 20 ppm

S23
Sample Name:
Data Collected on:
mnr600-vnmrs600
Archive directory:
Sample directory:
FIDfile: 600ras061413.008
Pulse Sequence: PROTON (z2pul)
Solvent: cdc13
Data collected on: Jun 18 2013

Temp. 35.0°C / 298.1 K
Operator: rae
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.704 sec
Width 6515.4 Hz
Single scan
OBSERVE RL. 599.7738327 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 3 sec
Sample Name:

Data Collected on:

mmr600-vmhrs600

Archive directory:

Sample directory:

FidFile: 600ras061913.001

Pulse Sequence: CARBON (z2ps1)

Solvent: cdc13

Data collected on: Jun 18 2013

Temp. 25.0 C / 298.1 K

Operator: ras

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.885 sec

Width 37878.8 Hz

20576 repetitions

OBSERVE: C13, 150.8132478 MHz

DECOUPLE H1, 599.7760382 MHz

Power 46 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 129 hr, 31 min
Sample Name:

Data Collected on:
mnr600-vnmrs600
Archive directory:

Sample directory:

FidFile: 600ras062613.006

Pulse Sequence: PROTON (a2pul)
Solvent: cdc13
Data collected on: Jun 27 2011

Temp. 29.0 C / 298.1 K
Operator: ras

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.704 sec
Width 9415.4 Hz
Single scan

DATA PROCESSING
FT size 32768
Total time 6 min 3 sec
Sample Name:
Data Collected on:
nmr600-vnmrs600
Archive directory:
Sample directory:
FidFile: 600ras062513.013
Pulse Sequence: CARBON (xipul)
Solvent: cdc13
Data collected on: Jun 25 2013

Temp. 25.0 C / 298.1 K
Operator: ras

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.865 sec
Width 3797.8 Hz
27328 repetitions

CENTERD 13C, 150.8132482 MHz
DECOUPLE X1, 599.7763382 MHz
Power 46 GHz
continuously on

WALYE-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
PT size 65536
Total time 129 hr, 31 min
Sample Name:
Data Collected on:
mnr600-vmnr600
Archive Directory:
Sample directory:
FidFile: 600ras062413.010
Pulse Sequence: CARBON (alipul)
Solvent: ccd13
Data collected on: Jun 24 2013

Temp. 25.0 C / 298.1 K
Operator: ras
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.865 sec
Width 39.979 Hz
21424 repetitions
OBSERVE 1H, 13C, 51.232455 MHz
DECOUPLE 1H, 13C, 59.93768382 MHz
Pwrer 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 129 hr, 31 min
Sample Name:

Data Collected on:
mnr600-vnmrs600
Archive directory:

Sample directory:

PidFile: 600rax062513.000

Pulse Sequence: CARBON (x2pul)
Solvent: cdc13
Data collected on: Jun 25 2013

Temp. 25.0 C / 298.1 K
Operator: ras

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.065 sec
WIDTH 37978.0 Hz
1984 repetitions

GAINMex C13, 150.8133483 MHz
DECOUPLE H1, 599.7768392 MHz
Power 46 dB continually on

DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 129 hr, 31 min
Sample Name:

Data Collected on:
mnr600-vnmrs600

Archive directory:

Sample directory:

FidFile: 600ras022513.019

Pulse Sequence: PROTON (c2pul)

Solvent: cdc13

Data collected on: Jun 26 2013

Temp. 25.0 C / 298.1 K

Operator: ras

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.704 sec

Width 9615.4 Hz

Single scan

ORDERVE NI 599.7738310 MHz

DATA PROCESSING

PT size 32768

Total time 0 min 3 sec
Sample Name:

Data Collected on:
nmr600-vnmrs600
Archive directory:
Sample directory:
FidFile: 600ras002613.002

Pulse Sequence: CARBON (e2pul)
Solvent: cdc13
Data collected on: Jun 27 2013

Temp. 25.0 C / 298.1 K
Operator: ras

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.865 sec
Width 37978.8 Hz
64 repetitions

OBSERVES C13, 150.8132526 MHz
DRCOUPLE H1, 599.7768382 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
PT size 65536
Total time 129 hr, 31 min

160 140 120 100 80 60 40 20 ppm
Sample Name:
Data Collected on:
mmr600-mmrs600
Archive directory:
Sample directory:
FidFile: 600ras062513.004
Pulse Sequence: PHOTON (xlpul)
Solvent: cdcl3
Data collected on: Jun 25 2013

Temp. 25.0 C / 298.1 K
Operator: ras
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.704 sec
Width 9615.4 Hz
Single scan

DATA PROCESSING
FT size 102768
Total time 0 min 3 sec
Sample Name:

Data Collected on:
mmr600-vmr600

Archive Directory:

Sample directory:

FID File: 600msd02513.005

Pulse Sequence: C13C12 (x2pul)

Solvent: dcd3

Data collected on: Jun 25 2013

Temp. 25.0 C / 298.1 K

Operator: ras

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.060 sec

Width 37078.8 Hz

624 repetitions

C13C12 150.8123455 MHz

DECOUPLE H1, 599.7768382 MHz

Power 46 dB
continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz
PT size 65536
Total time 129 hr, 31 min
Sample Name:

Data Collected on:
mmr600-vnmrs600
Archive directory:

Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (x2pul)
Solvent: cdcl3
Data collected on: Jun 27 2013

Temp. 25.0 C / 298.1 K
Operator: ras

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.784 sec
Width 9415.4 Hz
Single scan

REFERENCE "H 599.7738483 MHz
DATA PROCESSING
PT size 32768
Total time 6 min 3 sec

S38
Sample Name:

Data Collected on:
snr600-vmsnr600

Archive directory:

Sample directory:

PfidFile: 600ras062413.002

Pulse Sequence: CARBON (x2pul)

Solvent: cdc13

Data collected on: Jun 24 2013

Temp. 25.0 C / 298.1 K

Operator: ras

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.060 sec

Width 37878.8 Hz

384 repetitions

GAMMA Ve C13, 150.8132510 MHz

DECoupling R1, 599.7768382 MHz

Power 46 GB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 129 hr. 31 min

ppm
Sample Name:

Data Collected on:
nmr600-vnmrs600
Archive directory:

Sample directory:

PidFile: 600ras0062413.005

Pulse Sequence: CARBON (x2pul)
Solvent: cdcl3
Data collected on: Jun 24 2013

Temp. 25.0 C / 298.1 K
Operator: ras

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.885 sec
Width 37978.8 Hz
112 repetitions

OBSERVED 213, 100.612523 Ms
DECOUPLED 1H, 599.7766382 Ms
Power 46 dB
continuously on

DATA PROCESSING
Line broadening 0.5 Hz
PT size 65536
Total time 129 hr, 31 min