Supporting Information

for

Scope and limitations of the dual-gold-catalysed
hydrophenoxylation of alkynes

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1. General considerations

Unless otherwise stated, all solvents and reagents were used as purchased and all reactions were performed under air. Deuterated solvents (CD$_2$Cl$_2$, CDCl$_3$) were filtered through basic alumina in order to remove traces of HCl. NMR spectra were recorded on 500, 400 and 300 MHz spectrometers at room temperature in CD$_2$Cl$_2$ or CDCl$_3$. Chemical shifts (δ) are reported in ppm, relative to the solvent residual peak CD$_2$Cl$_2$ (5.32 ppm for $^1$H and 54.00 ppm for $^{13}$C) and CDCl$_3$ (7.26 ppm for $^1$H and 77.16 ppm for $^{13}$C). Data for $^1$H NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, br = broad signal, m = multiplet), coupling constants (J) in Hz and integration. Flash chromatography was performed on silica gel 60 Å pore diameter and 40–63 μm particle size. Elemental analysis was carried out by the analytical services of London Metropolitan University. High-resolution mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre (Grove Building Ext., Swansea University, Singleton Park, Swansea, SA2 8PP, UK). [{Au(IPr)}$_2$(µ-OH)][BF$_4$] was synthesized following the reported methodologies [1]:

2. Synthesis & characterization of vinyl ether derivatives (6)

**General procedure**

As described in reference [2], [{Au(NH$_2$C$_3$)}$_2$(µ-OH)][BF$_4$] (0.5–1.0 mol %) was added to a solution of alkyne (0.5 mmol) and phenol (0.55 mmol, 1.1 equiv) in toluene (1 mL). The reaction mixture was stirred at 80 or 110 °C. After the reaction was completed, the solvent was concentrated in vacuum. The residue was purified by flash column chromatography on silica gel to give the corresponding product.

**(Z)-4-((1,2-Diphenylvinyl)oxy)benzonitrile (3aa)**

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from diphenylacetylene (1a) (89.0 mg, 0.50 mmol), 4-hydroxybenzonitrile (2a) (65.5 mg, 0.55 mmol) and [{Au(IPr)}$_2$(µ-OH)][BF$_4$] (6.5 mg, 5 µmol, 1.0 mol %) in toluene (1 mL) at 110 °C for 24 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 95/5) to give 6aa (74 mg, 50%, average of two runs) as a white solid.

$^1$H NMR (CDCl$_3$, 500 MHz): δ 7.58-7.55 (m, 4H), 7.54-7.51 (m, 2H), 7.38-7.28 (m, 5H), 7.25-7.22 (m, 1H), 7.11-7.07 (m, 2H), 6.75 (s, 1H).

$^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz): δ 159.94, 148.60, 135.02, 134.36, 134.05, 129.11, 129.03, 128.99, 128.78, 128.03, 125.79, 118.95, 117.43, 117.04, 105.72; HRMS (NIS) calcd for C$_{21}$H$_{16}$NO [(M+H)$^+$] 298.1226, found 298.1233.

**(Z)-1-(4-((1,2-Diphenylvinyl)oxy)phenyl)ethanone (3ab)**

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from diphenylacetylene (1a) (89.0 mg, 0.50 mmol), 4-hydroxyacetophenone (2b) (74.8 mg, 0.55 mmol) and [{Au(IPr)}$_2$(µ-OH)][BF$_4$] (3.2 mg, 2.5 µmol, 0.5 mol %) in toluene (1 mL) at 80 °C for 14 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 95/5) to give 3ab (140 mg, 90%, average of two runs) as a white solid.

$^1$H NMR (CDCl$_3$, 500 MHz): δ 7.88-7.86 (m, 2H), 7.61-7.58 (m, 4H), 7.36-7.28 (m, 5H), 7.24-7.21 (m, 1H), 7.09-7.06 (m, 2H), 6.74 (s, 1H), 2.51 (s, 3H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz): δ 196.75, 160.51, 149.03, 135.46, 134.34, 131.69, 130.85, 129.11, 128.99, 128.78, 128.03, 125.79, 118.95, 117.43, 117.04, 105.72; HRMS (NIS) calcd for C$_{22}$H$_{19}$O$_2$ [(M+H)$^+$] 315.1380, found 315.1385.
(Z)-Methyl 4-[(1,2-diphenylvinyl)oxy]benzoate (3ac)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from diphenylacetylene (1a) (89.0 mg, 0.50 mmol), methyl 4-hydroxybenzoate (2c) (83.7 mg, 0.55 mmol) and [{Au(IPr)}_2(μ-OH)][BF_4] (3.2 mg, 2.5 µmol, 0.5 mol %) in toluene (1 mL) at 80 °C for 3 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 9/1) to give 3ac (140 mg, 85%, average of two runs) as a white solid.

^1H NMR (CDCl_3, 400 MHz) δ 7.97-7.88 (m, 2H), 7.64-7.53 (m, 4H), 7.39-7.17 (m, 6H), 7.09-6.99 (m, 2H), 6.72 (s, 1H), 3.85 (s, 3H); ^13C[^1H] NMR (CDCl_3, 101 MHz) δ 166.7, 160.4, 149.1, 135.5, 134.4, 131.9, 129.1, 128.9, 128.8, 127.8, 125.9, 124.2, 117.1, 116.1, 52.1; HRMS (NIS) calcd for C_{22}H_{19}O\_[(M+H)^+] 331.1329, found 331.1327.

(Z)-4-((1,2-Diphenylvinyl)oxy)benzaldehyde (3ad)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from diphenylacetylene (1a) (89.0 mg, 0.50 mmol), phenol (2d) (67.0 mg, 0.50 mmol) and [{Au(IPr)}_2(μ-OH)][BF_4] (3.2 mg, 2.5 µmol, 0.5 mol %) in toluene (1 mL) at 80 °C for 6 h, was purified by column chromatography on silica gel (CH_2Cl_2), to give 3ad (142 mg, 94%, average of two runs) as a colourless solid.

^1H NMR (CDCl_3, 300 MHz) δ 9.83 (s, 1H), 7.78-7.76 (m, 2H), 7.62-7.59 (m, 4H), 7.36-7.15 (m, 8H), 6.80 (s, 1H); ^13C[^1H] NMR (CDCl_3, 75 MHz) δ 151.6, 150.4, 136.5, 135.3, 129.4, 129.1, 129.0, 127.9, 126.6, 117.6, 117.2; HRMS (APCI) calcd for C_{21}H_{17}O\_[(M+H)^+] 301.1223, found 301.1222.

(Z)-5-((1,2-Diphenylvinyl)oxy)benzo[d][1,3]dioxole (3ae)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from diphenylacetylene (1a) (89.0 mg, 0.50 mmol), sesamol (2e) (70.0 mg, 0.50 mmol) and [Au(IPr)]_2(μ-OH)][BF_4] (3.2 mg, 2.5 µmol, 0.5 mol %) in toluene (1 mL) at 80 °C for 1 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 95/5) to give 3ae (150 mg, 94%, average of two runs) as a white solid.

^1H NMR (CDCl_3, 300 MHz; CDCl_3): δ 7.69-7.67 (m, 2H), 7.62-7.60 (m, 2H), 7.37-7.23 (m, 6H), 6.65 (d, J = 8.5 Hz, 1H; + d, J = 2.5 Hz, 1H; + s, 1H), 6.49 (dd, J = 8.5, 2.5 Hz, 1H), 5.88 (s, 2H).

^13C[^1H] NMR (101 MHz, CDCl_3): δ 151.46, 150.08, 148.47, 142.66, 136.07, 134.85, 129.03, 128.66, 128.52, 127.52, 126.23, 116.82, 108.30, 108.23, 101.40, 99.18. HRMS (APCI) calcd. for C_{21}H_{17}O_3 [(M+H)^+] 317.1172, found 317.1170.

(Z)-2-((1,2-Diphenylvinyl)oxy)naphthalene (3af)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from diphenylacetylene (1a) (89.0 mg, 0.50 mmol), naphthol (2f) (79.3 mg, 0.55 mmol) and [{Au(IPr)}_2(μ-OH)][BF_4] (3.2 mg, 2.5 µmol, 0.5 mol %) in toluene (1 mL) at 80 °C for 3 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 95/5) to give 3af (158 mg, 98%, average of two runs) as a white solid.

^1H NMR (CDCl_3, 300 MHz) δ 7.82-7.72 (m, 2H), 7.71-7.57 (m, 5H), 7.43-7.14 (m, 10H), 6.75 (s, 1H); ^13C[^1H] NMR (CDCl_3, 75 MHz) δ 154.3, 149.7, 135.9, 134.8, 134.5, 130.0, 129.7, 129.1, 128.7, 128.7, 128.6, 127.8, 127.6, 127.1, 126.5, 126.1, 124.3, 118.3, 117.1, 111.1; HRMS (APCI) calcd for C_{24}H_{19}O [(M+H)^+] 323.1430, found 323.1430.
(Z)-[1-(3,5-Dimethylphenoxy)ethene-1,2-diyl]dibenzenes (3ai)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from diphenylacetylene (1a) (89.0 mg, 0.50 mmol), 3,5-dimethylphenol (2i) (67.0 mg, 0.55 mmol) and [{Au(IPr)}2(µ-OH)][BF4]− (3.2 mg, 2.5 µmol, 0.5 mol %) in toluene (1 mL) at 80 °C for 2 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 95/5) to give 3ai (142 mg, 94%, average of two runs) as a white solid.

1H NMR (CDCl3, 400 MHz) δ 7.68-7.62 (m, 2H), 7.62-7.57 (m, 2H), 7.37-7.15 (m, 6H), 6.65 (brs, 2H), 6.64 (s, 1H), 6.59 (brs, 1H), 2.21 (s, 6H); 13C{1H} NMR (CDCl3, 101 MHz) δ 156.4, 149.8, 139.5, 139.5, 136.3, 135.0, 129.1, 128.6, 127.4, 126.1, 124.0, 116.7, 114.1, 21.5; HRMS (APCI) calcd for C22H20O [M+H]+ 300.1509, found 300.1507.

(Z)-(1-(4-Chloro-3,5-dimethylphenoxy)ethene-1,2-diyl)dibenzenes (3aj)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from alkyn 1a (89.0 mg, 0.50 mmol), phenol (2j) (86.0 mg, 0.50 mmol) and [{Au(IPr)}2(µ-OH)][BF4]− (3.2 mg, 2.5 µmol, 0.5 mol %) in toluene (1 mL) at 80 °C for 6 h, was purified by column chromatography on silica gel (pentane/EtOAc = 95/5), to give 3aj (164 mg, 98%, average of two runs) as a colourless solid.

1H NMR (CDCl3, 300 MHz) δ 7.64 (ddd, J = 14.4, 7.7, 1.5 Hz, 4H), 7.38-7.22 (m, 6H), 6.80 (s, 2H), 6.69 (s, 1H), 2.30 (s, 6H); 13C{1H} NMR (CDCl3, 75 MHz) δ 154.2, 149.5, 137.6, 135.9, 134.8, 129.1, 128.7, 128.7, 128.6, 127.6, 126.1, 117.0, 116.2, 21.1; HRMS (APCI) calcd for C22H20ClO [M+H]+ 335.1197, found 335.1195.

(Z)-[1-(2-Chloro-4-fluorophenoxy)ethene-1,2-diyl]dibenzenes (3ak)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from diphenylacetylene (1a) (89.0 mg, 0.50 mmol), 2-chloro-4-fluorophenol (2k) (81.0 mg, 0.55 mmol) and [{Au(IPr)}2(µ-OH)][BF4]− (6.5 mg, 5 µmol, 1.0 mol %) in toluene (1 mL) at 110 °C for 6 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 95/5) to give 3ak (143 mg, 88%, average of two runs) as a white solid whose NMR data were consistent to those reported in the literature [3].

1H NMR (CDCl3, 300 MHz) δ 7.70-7.61 (m, 2H), 7.61-7.54 (m, 2H), 7.39-7.13 (m, 7H), 6.77 (dd, J = 9.1, 5.0 Hz, 1H), 6.73-6.64 (m, 2H); 13C{1H} NMR (CDCl3, 75 MHz) δ 157.3 (d, JCF = 243 Hz), 149.7, 148.1 (d, JCF = 2.8 Hz), 135.2, 134.4, 129.0, 128.88, 128.87, 128.7, 127.8, 126.0, 123.4 (d, JCF = 11 Hz), 117.8 (d, JCF = 26 Hz), 117.2, 116.6 (d, JCF = 8.6 Hz), 114.5 (d, JCF = 23 Hz); 19F NMR (CDCl3, 282 MHz) δ -120.3.

(Z)-[1-(2-Chloro-5-fluorophenoxy)ethene-1,2-diyl]dibenzenes (3al)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from diphenylacetylene (1a) (89.0 mg, 0.50 mmol), 2-chlorophenol (2l) (70.7 mg, 0.55 mmol) and [{Au(IPr)}2(µ-OH)][BF4]− (6.5 mg, 5 µmol, 1.0 mol %) in toluene (1 mL) at 110 °C for 3 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 95/5) to give 3al (141 mg, 92%, average of two runs) as a colourless liquid whose NMR data were consistent to those reported in the literature [3].

1H NMR (CDCl3, 300 MHz) δ 7.72-7.65 (m, 2H), 7.65-7.57 (m, 2H), 7.43 (dd, J = 7.8, 1.7 Hz, 1H), 7.39-7.18 (m, 6H), 6.99 (dt, J = 7.7, 1.7 Hz, 1H), 6.93-6.79 (m, 2H), 6.72 (s, 1H); 13C{1H} NMR (CDCl3, 75 MHz) δ 151.7, 149.5, 135.4, 134.5, 130.6, 129.1, 128.8, 128.8, 128.7, 127.8, 127.7, 125.9, 123.0, 122.9, 117.1, 116.3.
According to the general procedure for hydrophenoxylation, a crude product, which was prepared from diphenylacetylene (1a) (89.0 mg, 0.50 mmol), 2-allylphenol (2m) (74.0 mg, 0.55 mmol) and [{Au(IPr)}_2(µ-OH)][BF_4] (6.5 mg, 5 µmol, 1.0 mol %) in toluene (1 mL) at 110 °C for 3 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 95/5) to give 3am (144 mg, 92%, average of two runs) as a white solid.

^1H NMR (CDCl_3, 300 MHz): δ 7.66-7.59 (m, 2H), 7.58-7.51 (m, 2H), 7.39-7.15 (m, 7H), 7.02-6.84 (m, 2H), 6.73 (dd, J = 7.8, 1.6 Hz, 1H), 6.67 (s, 1H), 6.25-6.06 (m, 1H), 5.25-5.09 (m, 2H); ^13C{^1H} NMR (CDCl_3, 101 MHz) δ 153.8, 149.7, 137.0, 136.1, 134.9, 130.6, 129.0, 128.7, 128.6, 128.5, 128.4, 127.51, 127.45, 126.0, 122.0, 116.9, 116.1, 114.5, 34.3; HRMS (APCI) calcd for C_{23}H_{21}O [(M+H)^+] 313.1587, found 313.1588.

(Z)-[1-(2-Allylphenoxy)ethene-1,2-diyl]dibenzene (3an)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from diphenylacetylene (1a) (89.0 mg, 0.50 mmol), 2,4-di-tert-butylphenol (2o) (103.2 mg, 0.50 mmol) and [{Au(IPr)}_2(µ-OH)][BF_4] (3.2 mg, 2.5 µmol, 0.5 mol %) in toluene (1 mL) at 80 °C for 14 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 95/5) to give 3an (160 mg, 83%, average of two runs) as an off-white solid.

^1H NMR (CDCl_3, 300 MHz): δ 7.62-7.58 (m, 2H), 7.57-7.53 (m, 2H), 7.40 (d, J = 2.5 Hz, 1H), 7.35-7.21 (m, 5H), 7.20-7.15 (m, 1H), 6.93 (dd, J = 8.5, 2.5 Hz, 1H), 6.69 (d, J = 8.7 Hz, 1H), 6.67 (s, 1H), 1.58 (s, 9H), 1.26 (s, 9H); ^13C{^1H} NMR (CDCl_3, 101 MHz) δ 152.7, 149.60, 143.77, 134.95, 129.04, 128.61, 128.30, 127.35, 126.43, 124.51, 123.79, 117.49, 114.69, 35.40, 34.44, 31.72, 30.63; HRMS (APCI) calcd for C_{28}H_{33}O [(M+H)^+] 385.2526, found 385.2519.

(Z)-[1-(2,4-Di-tert-butylphenoxy)ethene-1,2-diyl]dibenzene (3ap)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from diphenylacetylene (1a) (89.0 mg, 0.50 mmol), catechol (2p) (55.1 mg, 0.50 mmol) and [Au(IPr)]_2(µ-OH)][BF_4] (3.2 mg, 2.5 µmol, 0.5 mol %) in toluene (1 mL) at 80 °C for 6 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 95/5) to give 3ap (100 mg, 70%, average of two runs) as a colourless liquid, whose NMR data were consistent to those reported in the literature [4].

^1H NMR (300 MHz; CDCl_3): δ 7.60-7.57 (m, 2H), 7.54-7.50 (m, 2H), 7.36-7.28 (m, 5H), 7.27-7.21 (m, 1H), 7.03 (dd, J = 8.0, 1.5 Hz, 1H), 6.88 (td, J = 7.7, 1.5 Hz, 1H), 6.75 (dd, J = 8.1, 1.5 Hz, 1H), 6.71 (s, 1H), 6.64 (dd, J = 8.1, 7.4, 1.6 Hz, 1H), 5.87 (s, 1H); ^13C{^1H} NMR (101 MHz, CDCl_3): δ 149.27, 145.79, 143.16, 135.41, 134.45, 128.91, 128.84, 128.77, 127.81, 125.79, 123.22, 120.62, 117.44, 115.78, 115.08.
1,2-Bis(((Z)-1,2-diphenylvinyl)oxy)benzene (4ap)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from diphenylacetylene (1a) (178.0 mg, 1 mmol), catechol (2p) (55.1 mg, 0.50 mmol) and [Au(IPr)]2(μ-OH)][BF4] (3.2 mg, 0.25 μmol, 0.5 mol%) in toluene (1 mL) at 80 °C for 18 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 95/5) to give 4ap (256 mg, 55%, average of two runs) as a colourless liquid, whose NMR data were consistent to those reported in the literature [4].

1H NMR (400 MHz; CDCl3): δ 7.82-7.77 (m, 8H), 7.42-7.33 (m, 10H), 7.32-7.27 (m, 2H), 6.90-6.86 (dt, J = 6.0, 3.6 Hz, 2H), 6.76 (s, 2H), 6.69 (dt, J = 6.4, 3.3 Hz, 2H).

13C(1H) NMR (CDCl3, 101 MHz): δ 150.00, 145.53, 136.01, 135.01, 129.19, 128.78, 128.71, 128.66, 127.59, 126.16, 122.60, 117.04, 116.33, 77.48, 77.16, 76.84.

1,3-Bis(((Z)-1,2-diphenylvinyl)oxy)benzene (4aq)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from diphenylacetylene (1a) (89.0 mg, 0.50 mmol), resorcinol (2q) (28.0 mg, 0.25 mmol) and [Au(IPr)]2(μ-OH)][BF4] (3.2 mg, 2.5 μmol, 1.0 mol%) in toluene (1 mL) at 80 °C for 6 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 95/5) to give 4aq (198 mg, 84%, average of two runs) as a white solid, whose NMR data were consistent to those reported in the literature [4].

1H NMR (CDCl3, 300 MHz) δ 7.61-7.53 (m, 4H), 7.52-7.43 (m, 4H), 7.34-7.16 (m, 12H), 7.02 (t, J = 8.2 Hz, 1H), 6.74 (t, J = 2.3 Hz, 1H), 6.60 (brs, 3H), 6.58 (d, J = 2.3 Hz, 1H); 13C(1H) NMR (CDCl3, 75 MHz) δ 157.7, 149.7, 135.9, 134.7, 134.7, 130.4, 129.0, 128.6, 128.6, 128.4, 127.4, 126.1, 126.1, 116.7, 110.2, 105.6.

1,4-Bis(((Z)-1,2-diphenylvinyl)oxy)benzene (4ar)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from alkyne 1a (89.0 mg, 0.50 mmol), hydroquinone (2r) (28.0 mg, 0.25 mmol) and [Au(IPr)]2(μ-OH)][BF4] (3.2 mg, 2.5 μmol, 0.5 mol%) in toluene (1 mL) at 80 °C for 16 h, was purified by trituration in pentane after evaporation of the volatiles, to give 4ar (212 mg, 95%, average of two runs) as a colourless solid, whose NMR data were consistent to those reported in the literature [4].

1H NMR (CD2Cl2, 500 MHz) δ 7.62-7.60 (m, 2H), 7.56-7.54 (m, 2H), 7.33-7.26 (m, 5H), 7.22-7.18 (m, 1H), 6.88 (s, 2H), 6.61 (s, 1H); 13C(1H) NMR (CDCl3, 75 MHz) δ 151.6, 150.7, 136.5, 135.3, 129.4, 129.1, 129.0, 127.9, 126.6, 117.6, 117.2.

1,4-Bis(((Z)-1,2-diphenylvinyl)oxy)-2,5-dichlorobenzene (4as)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from alkyne 1a (89.0 mg, 0.50 mmol), hydroquinone 2s (45.0 mg, 0.25 mmol) and [Au(IPr)]2(μ-OH)][BF4] (3.2 mg, 2.5 μmol, 0.5 mol%) in toluene (1 mL) at 80 °C for 16 h, was purified by trituration in pentane after evaporation of the volatiles, to give 4as (64 mg, 47%, average of two runs) as an off-white solid.

1H NMR (CD2Cl2, 400 MHz): δ 7.61-7.54 (m, 8H), 7.36-7.23 (m, 12H), 6.91 (s, 2H), 6.72 (s, 2H); HRMS (APCI) calcd for C34H26O2Cl2 [(M+H)+] 534.1148, found 534.1140.
(Z)-4,4'-((1-Phenoxyethene-1,2-diyl)bis(methoxybenzene) (3bt)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from alkyne (1b) (119.2 mg, 0.50 mmol), phenol (2t) (52.0 mg, 0.55 mmol) and [[Au(IPr)₂(μ-OH)]BF₄] (6.5 mg, 5 μmol, 1.0 mol %) in toluene (1 mL) at 110 °C for 14 h, was purified by column chromatography on silica gel (pentane/EtOAc = 95/5) to give 2bt (148 mg, 89%, average of two runs) as a off-white solid.

^1H NMR (300 MHz; CDCl₃): δ 7.57 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 7.26-7.18 (m, 2H), 7.03 (d, J = 7.8 Hz, 2H), 6.94 (t, J = 7.3 Hz, 1H), 6.82 (dd, J = 9.0, 2.6 Hz, 4H), 6.53 (s, 1H), 3.65 (s, 6H). ^13C[^1H] NMR (126 MHz, CDCl₃): δ 159.60, 158.68, 156.54, 147.82, 130.16, 129.72, 128.72, 127.85, 127.19, 121.92, 116.26, 114.66, 114.06, 114.03, 55.32, 55.28. HRMS (APCI) calcd for C₂₂H₂₁O₃ [M⁺] 333.1485, found 333.1482.

(Z)-4,4'-(1-Phenoxyethene-1,2-diyl)bis(chlorobenzene) (3ct)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from alkyne 1c (123.5 mg, 0.50 mmol), phenol (2t) (52.0 mg, 0.55 mmol) and [[Au(IPr)₂(μ-OH)]BF₄] (6.5 mg, 5 μmol, 1.0 mol %) in toluene (1 mL) at 110 °C for 14 h, was purified by column chromatography on silica gel (pentane/EtOAc = 9/1) to give 3ct (140 mg, 82%, average of two runs) as a off-white solid.

^1H NMR (300 MHz; CDCl₃): δ 7.56-7.54 (m, 2H), 7.52-7.48 (m, 2H), 7.30-7.21 (m, 6H), 6.99-6.95 (m, 3H), 6.58 (s, 1H). ^13C[^1H] NMR (101 MHz, CDCl₃): δ 156.0, 142.8, 139.1, 137.0, 129.8, 127.9, 127.7, 127.0, 126.6, 125.6, 125.4, 122.6, 116.0, 110.6; HRMS (APCI) calcd for C₁₉H₁₄Cl₂O [M⁺] 341.0494, found 341.0491.

(Z)-[(1,4-Dimethoxybut-2-en-2-yl)oxy]benzene (3dt)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from alkyne 1d [5] (114.0 mg, 1.00 mmol), phenol (2t) (47.0 mg, 0.50 mmol) and [[Au(IPr)₂(μ-OH)]BF₄] (3.2 mg, 2.5 μmol, 0.5 mol %) in toluene (1 mL) at 80 °C for 2 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 10/1) to give 3dt (89 mg, 85%, average of two runs) as a colourless liquid.

^1H NMR (CDCl₃, 300 MHz) δ 7.34-7.23 (m, 2H), 7.08-6.93 (m, 3H), 5.51 (t, J = 6.4, 0.9 Hz, 1H), 4.02 (dt, J = 6.4, 0.9 Hz, 2H), 3.91 (dt, J = 0.9 Hz, 2H), 3.35 (s, 3H), 3.31 (s, 3H); ^13C[^1H] NMR (CDCl₃, 75 MHz) δ 156.3, 149.9, 129.7, 122.5, 116.5, 114.9, 70.6, 66.4, 58.4, 58.2; HRMS (APCI) calcd for C₁₂H₁₈O₃ [M⁺] 208.1094, found 208.1093.

(Z)-2,2'-(1-Phenoxyethene-1,2-diyl)dipheno (3et)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from alkyne 1e [6] (95.0 mg, 0.50 mmol), phenol (2t) (52.0 mg, 0.55 mmol) and [[Au(IPr)₂(μ-OH)]BF₄] (6.5 mg, 5 μmol, 1.0 mol %) in toluene (1 mL) at 110 °C for 1 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 9/1) to give 3et (91 mg, 64%, average of two runs) as a off-white solid.

^1H NMR (CDCl₃, 400 MHz) δ 7.31-7.24 (m, 2H), 7.23-7.20 (m, 1H), 7.19 (ddd, J = 5.0, 1.0, 1.0 Hz, 1H), 7.17-7.13 (m, 1H), 7.10-7.07 (m, 3H), 7.04-6.95 (m, 3H), 6.94-6.90 (m, 1H); ^13C[^1H] NMR (CDCl₃, 101 MHz) δ 156.0, 142.8, 139.1, 137.0, 129.8, 127.9, 127.7, 127.0, 126.6, 125.6, 125.4, 122.6, 116.0, 110.6; HRMS (APCI) calcd for C₁₆H₁₃OS₂ [(M+H)⁺] 285.0402, found 285.0397.
(Z)-2,2'-(1-Phenoxyethene-1,2-diyl)bis(chlorobenzene) (3ft)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from alkyne 1f (123.0 mg, 0.50 mmol), phenol (2t) (47.0 mg, 0.50 mmol) and [{Au(IPr)}2(μ-OH)][BF4] (3.2 mg, 2.5 μmol, 0.5 mol %) in toluene (1 mL) at 80 °C for 6 h, was purified by column chromatography on silica gel (pentane), to give 3ft (148 mg, 87%, average of two runs) as a colourless oil.

1H NMR (CDCl3, 300 MHz) δ 8.18-8.15 (m, 1H), 7.66-7.62 (m, 1H), 7.50-7.47 (m, 1H), 7.44-7.41 (m, 1H), 7.33-7.30 (m, 6H), 7.17-7.13 (m, 2H), 7.05-7.00 (m, 1H), 6.93 (s, 1H); 13C(1H) NMR (CDCl3, 75 MHz) δ 155.7, 148.7, 136.1, 134.9, 133.6, 132.9, 132.6, 131.1, 130.6, 130.0, 129.8, 129.5, 128.5, 126.8, 126.5, 122.8, 117.6, 116.2; HRMS (ESI) calcd. for C20H15ClO5 [(M+H)+] 341.0494, found 341.0495.

(Z)-2-Phenoxybut-1-en-1-ylbenzene and (Z)-(1-phenoxybut-1-en-1-yl)benzene (3it /3it' = 1/0.23)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from 1i (65.0 mg, 0.50 mmol), phenol (2t) (52.0 mg, 0.55 mmol) and [{Au(IPr)}2(μ-OH)][BF4] (3.2 mg, 2.5 μmol, 0.5 mol %) in toluene (1 mL) at 80 °C for 6 h, was purified by column chromatography on silica gel (pentane/EtOAc = 95/5) to give the inseparable mixture of 3it and 3it' (3it /3it' = 1/0.23, 90 mg, 80%, average of two runs) as a colourless liquid.

1H NMR (400 MHz; CDCl3): δ 7.54-7.52 (m, 2H), 7.51-7.48 (m, 0.6H), 7.33-7.21 (m, 6H), 7.17-7.13 (m, 1H), 7.06 (t, J = 1.1 Hz, 0.32H), 7.04-7.01 (m, 3H), 6.98-6.95 (m, 0.5H), 6.93-6.91 (m, 0.15H), 5.94 (s, 1H), 5.87 (t, J = 7.3 Hz, 0.23H), 2.31 (qd, J = 7.4, 0.8 Hz, 2H), 2.23 (quintet, J = 7.5 Hz, 0.48H), 1.14 (t, J = 7.4 Hz, 3H), 1.04 (t, J = 7.5 Hz, 0.74H). 13C(1H) NMR (126 MHz; CDCl3): δ 157.61, 155.50, 154.23, 151.33, 150.17, 150.09, 149.03, 135.75, 114.06, 26.41, 19.47, 13.97, 11.96. HRMS (APCI) calcd. for C16H14O [(M+H)+] 225.1274, found 225.1271.

(Z)-1-Methoxy-4-((1-phenylprop-1-en-2-yl)oxy)benzene and (Z)-1-methoxy-4-((1-phenylprop-1-en-1-yl)oxy)benzene (3ju /3ju' = 1/0.22)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from 1j (58.0 mg, 0.50 mmol), phenol 2u (68.3 mg, 0.55 mmol) and [{Au(IPr)}2(μ-OH)][BF4] (3.2 mg, 2.5 μmol, 0.5 mol %) in toluene (1 mL) at 80 °C for 6 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 95/5) to give the inseparable mixture of 3ju and 3ju' (3ju /3ju' = 1/0.22, 104 mg, 87%, average of two runs) as a colourless liquid.

1H NMR (400 MHz; CDCl3): δ 7.58-7.55 (m, 2H), 7.49-7.46 (m, 0.45), 7.30-7.23 (m, 3H), 7.17-7.13 (m, 1H), 6.99-6.95 (m, 2H), 6.91-6.83 (m, 3H), 6.79-6.76 (m, 0.40), 5.89 (q, J = 7.0 Hz, 0.23), 5.78 (s, 1H), 3.79 (s, 3H), 3.73 (s, 0.62H), 1.93 (s, 3H), 1.77 (d, J = 7.0 Hz, 0.62H). 13C(1H) NMR (126 MHz; CDCl3): δ 155.50, 154.23, 151.33, 150.17, 150.09, 149.03, 135.75, 135.62, 128.50, 128.41, 128.16, 127.84, 126.38, 125.32, 121.65, 119.23, 116.17, 114.77, 114.75, 113.55, 112.35, 110.03, 108.34, 55.75, 55.71, 19.69, 11.52. HRMS (APCI) calcd. for C18H17O2 [(M+H)+] 241.1223, found 241.1223.
(Z)-3-(2-Phenoxyhex-1-en-1-yl)pyridine (3nt) and (Z)-3-(1-phenoxhex-1-en-1-yl)pyridine (3nt') (3nt/3nt' = 1/0.43)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from alkyne 1n (79.0 mg, 0.50 mmol), phenol (2t) (47.0 mg, 0.50 mmol) and [{Au(IPr)}₂(μ-OH)][BF₄] (19.5 mg, 0.34 mmol, 3.0 mol %) in toluene (1 mL) at 110 °C for 24 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 95/5~70/30) to give 3nt and 3nt' (3nt / 3nt' = 1/0.43, 96 mg, 76%, average of two runs) as a pale yellow oil.

^1H NMR (CDCl₃, 300 MHz) δ 8.77 (d, J = 1.8 Hz, 1H), 8.63 (br, 2.25H), 8.45 (dd, J = 4.7, 1.4 Hz, 1H), 8.36 (d, J = 3.7 Hz, 2.33H), 7.94 (dt, J = 8.1, 1.9 Hz, 2.36H), 7.71 (dt, J = 8.0, 2.0 Hz, 1H), 7.34-7.12 (m, 12H), 7.08-6.92 (m, 10H), 5.95-5.89 (m, 1+2.21H), 2.33-2.20 (m, 6.62H), 1.58-1.21 (m, 15.38H), 0.89 (t, J = 7.3 Hz, 10.38H); ^13C{^1H} NMR (CDCl₃, 75 MHz) δ 157.0, 155.7, 155.1, 149.7, 148.7, 147.5, 147.1, 146.4, 134.9, 132.6, 131.3, 129.8, 129.8, 123.5, 123.3, 122.9, 121.9, 120.4, 117.4, 115.6, 111.2, 32.9, 31.4, 29.3, 25.7, 22.6, 22.2, 14.0, 14.0. HRMS (ESI) calcd for C₁₇H₁₉N; ([M+H]+) 254.1539, found 254.1541.

(Z)-[4-(Benzyloxy)but-2-en-2-yl]oxy]benzene (3ot)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from alkyne 1o [7] (160.0 mg, 1.00 mmol), phenol (2t) (47.0 mg, 0.50 mmol) and [{Au(IPr)}₂(μ-OH)][BF₄] (3.2 mg, 0.25 mmol, 0.5 mol %) in toluene (1 mL) at 80 °C for 2 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 95/5) to give 3ot (89 mg, 70%, average of two runs) as a colourless liquid.

^1H NMR (CDCl₃, 300 MHz) δ 7.34-7.18 (m, 7H), 7.03-6.94 (m, 1H), 6.94-6.86 (m, 2H), 5.21 (t, J = 6.8 Hz, 1H), 4.43 (s, 2H), 4.06 (s, 1H), 3.62 (s, 3H); ^13C{^1H} NMR (CDCl₃, 101 MHz) δ 156.1, 150.9, 138.6, 129.7, 128.4, 127.9, 127.6, 122.4, 117.0, 112.6, 72.4, 64.5, 18.6; HRMS (APCI) calcd for C₁₉H₁₉O₂ ([M+H]+) 293.1163, found 293.1167.

(Z)-[5-(Benzyloxy)pent-2-en-2-yl]oxy]benzene (3pt) and (Z)-[5-(benzyloxy)pent-2-en-3-yl]oxy]benzene (3pt') (3pt/3pt' = 1/0.17)

According to the general procedure for hydrophenoxylation, a crude product, which was prepared from alkyne 1p [8] (87.0 mg, 0.50 mmol), phenol (2t) (52.0 mg, 0.55 mmol) and [{Au(IPr)}₂(μ-OH)][BF₄] (3.2 mg, 0.25 mmol, 0.5 mol %) in toluene (1 mL) at 80 °C for 3 h, was purified by column chromatography on silica gel (n-hexane/EtOAc = 95/5) to give 3pt and 3pt' (3pt / 3pt' = 1/0.17, 114 mg, 85%, average of two runs) as a colourless liquid.

^1H NMR (CDCl₃, 300 MHz) δ 7.33-7.14 (m, 7H+1.19H), 6.96-6.80 (m, 3+0.51H), 5.12 (q, J = 6.7 Hz, 0.17H), 5.03 (tq, J = 7.2, 1.1 Hz, 1H), 4.43 (s, 2H), 4.42 (s, 0.34H), 3.51 (t, J = 6.7 Hz, 0.34H), 3.41 (t, J = 7.2 Hz, 2H), 2.45-2.36 (m, 0.34H), 2.31 (dtq, J = 7.2, 7.2, 1.1 Hz, 2H), 1.75 (dt, J = 7.2, 1.1 Hz, 3H), 1.50-1.47 (m, 0.51H); ^13C{^1H} NMR (CDCl₃, 75 MHz) δ 156.6, 156.4, 148.6, 148.4, 138.7, 138.5, 129.6, 129.6, 128.5, 128.4, 127.8, 127.8, 127.7, 127.6, 121.8, 121.6, 116.4, 115.9, 112.7, 112.3, 73.0, 72.8, 69.8, 67.5, 33.5, 26.0, 18.5, 10.9.
3. References

4. NMR Spectra


