Supporting Information
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Organocuprate Oxidation: Synthesis of Highly Substituted Symmetrical 1,3-Dienes

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Supplementary Information

1 General Experimental

1H NMR spectra were recorded on Bruker DPX, DRX and Avance 400 or Avance 500 spectrometers in deuterochloroform or deuterodimethyl sulfoxide operating at 400 and 500 MHz respectively. 13C NMR spectra were recorded on Bruker DPX, DRX and Avance 400 or Avance 500 spectrometers operating at 100 and 125 MHz respectively. Chemical shifts are quoted relative to residual solvent (7.26 ppm for CHCl3 and 77.0 ppm for 13C of CDCl3, 2.54 ppm for DMSO and 40.45 ppm for 13C of [D6]-DMSO) and coupling constants (J) are given to the nearest 0.1 Hz. The following abbreviations are used singularly or in combination to indicate the multiplicity of signals: s singlet, d doublet, t triplet, q quartet, qn quintet, sex sextet, m multiplet, app apparent and br broad. NMR spectra were acquired at 300 K unless otherwise indicated. Assignments are supported by COSY, HMQC and HMBC correlations and DEPT where appropriate.

High resolution mass spectroscopic (HRMS) analyses were measured on a Micromass Q-TOF or a Micromass LCT Premier spectrometer. Mass values are reported within the error limits of ±5 ppm mass units. Low resolution mass spectroscopic (LCMS) analyses were measured on a Waters ZQ 4000.
Infra-red spectra were recorded on a Perkin-Elmer 1600 FT IR spectrometer. The sample was prepared neat or as a solution in the solvent indicated. Selected absorption maxima ($\nu_{\text{max}}$) are reported in wavenumbers ($\text{cm}^{-1}$).

Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. The quoted solvent system refers to that used in recrystallisation or purification.

Reactions were carried out in oven-dried glassware under an atmosphere of nitrogen with dry, freshly distilled solvents. Tetrahydrofuran was distilled from LiAlH$_4$ with triphenylmethane as indicator. Diethyl ether was distilled from CaH$_2$ and LiAlH$_4$. Dichloromethane, hexane, ethyl acetate, methanol and toluene were distilled from CaH$_2$. Copper(I) bromide-dimethyl sulfide complex was purified before use by crystallisation from dimethyl sulfide/pentane. Grignard reagent solutions were titrated with 1,10-phenanthroline and menthol, $n$-butyllithium reagent solution was titrated with diphenylacetic acid and $t$-butyllithium reagent solution was titrated with $N$-benzylbenzamide before use.

Analytical thin layer chromatography (TLC) was carried out on Merck pre-coated 0.23 mm thick plates of Keiselgel 60 F$_{254}$. Flash column chromatography was carried out using Merck 9385 Keiselgel 60 SiO$_2$ (230-400 mesh) unless otherwise stated.

2 Experimental Details

2.1 Synthesis of alkenyl halides

\[ (3\text{-Bromobut-3-enyloxy})(\text{tert-butyl})\text{diphenylsilane}^{[1]} \] (1)
tert-Butyldiphenylchlorosilane (1.69 mL, 6.50 mmol) was added dropwise to a solution of 3-bromobut-3-en-1-ol (0.58 mL, 5.84 mmol) and imidazole (0.90 g, 13.24 mmol) in CH₂Cl₂ (20 mL) at room temperature and stirred for 3 hours. The solvent was removed in vacuo and the residue purified by flash column chromatography (Pet. ether 40-60:Et₂O, 5:1) to yield the title compound as a clear oil (2.27 g, 100%); Rᵣ = 0.65 (Pet. ether 40-60:Et₂O, 5:1); δₜ (500 MHz, CDCl₃) 7.70 – 7.66 (4H, m, PhH), 7.44 – 7.37 (6H, m, PhH), 5.65 (1H, m, C=CHH), 5.48 (1H, d, J = 1.5 Hz, C=CHH), 3.84 (2H, t, J = 6.2 Hz, OCH₂), 2.65 (2H, td, J = 6.2, 0.7 Hz, OCH₂CH₂), 1.05 (9H, s, C(CH₃)₃); δₙ (125 MHz, CDCl₃) 135.6 (CH), 133.6 (C), 130.8 (C), 129.6 (CH), 127.7 (CH), 118.5 (CH₂), 61.4 (CH₂), 44.5 (CH₂), 26.8 (CH₃), 19.2 (C); νₘₚₓ / cm⁻¹ (CDCl₃) 2922, 2861, 1628 (C=CH), 1426, 1100, 926, 885, 819, 735, 706; LCMS (AP+) 239 (M+H-2xPh)⁺. Spectral data consistent with literature values.[¹] Based on a literature procedure.[²]

**(But-3-ynyloxy)(tert-butyl)diphenylsilane**[^3] ([S1])

![TBDPSO-≡≡](image)

tert-Butyldiphenylchlorosilane (2.31 mL, 8.9 mmol) was added dropwise to a solution of 3-butyne-1-ol (0.61 mL, 8.0 mmol) and imidazole (1.09 g, 16.0 mmol) in CH₂Cl₂ (20 mL) at room temperature and stirred for 3.5 hours. The solvent was removed in vacuo and the residue purified by flash column chromatography (Pet. ether 40-60:Et₂O, 5:1) to yield the title compound as a clear oil (2.47 g, 100%); Rᵣ = 0.54 (Pet. ether 40-60:Et₂O, 5:1); δₜ (400 MHz, CDCl₃) 7.71 – 7.68 (4H, m, PhH), 7.45 – 7.36 (6H, m, PhH), 3.79 (2H, t, J = 7.1 Hz, OCH₂), 2.46 (2H, td, J = 7.1, 2.7 Hz, OCH₂CH₂), 1.95 (1H, t, J = 2.7 Hz, C≡CH), 1.07 (9H, s, C(CH₃)₃); δₙ (125 MHz, CDCl₃) 135.6 (CH), 133.5 (C), 129.7 (CH), 127.7 (CH), 81.5 (C), 69.3 (CH), 62.3 (CH₂), 26.8 (CH₃), 22.6 (CH₂), 19.2 (C); νₘₚₓ / cm⁻¹ (CDCl₃) 3291 (C≡CH), 3068, 2927, 2856, 1590, 1469, 1426, 1108, 701; HRMS ESI [M+Na]⁺ found 331.1482 [C₂₀H₂₄OSiNa]⁺ requires 331.1489. Spectral data consistent with literature values.[³] Based on a literature procedure.[²]
(E)-tert-Butyl(4-iodobut-3-enyloxy)diphenylsilane\textsuperscript{[4]} (2)

Borane-THF complex (1 M solution in THF, 3.05 mL, 3.05 mmol) was added dropwise to a solution of 2,5-dimethylhexa-2,4-diene (0.94 mL, 6.50 mmol) in THF (1.5 mL) and stirred at 0 °C for 3 hours. Alkyne S1 (925 mg, 3.00 mmol) was then added dropwise and the reaction stirred at 0 °C for a further hour. The reaction was quenched by the addition of water (0.44 mL) and aqueous formaldehyde (0.25 mL) was then added and the reaction mixture stirred overnight at room temperature. The reaction mixture was then partitioned between brine (15 mL) and EtOAc (15 mL) and the organic layer separated. The aqueous layer was washed with EtOAc (15 mL), the organic extracts combined and the solvent removed \textit{in vacuo}.

The resulting crude boronic acid was then dissolved in Et\textsubscript{2}O (5 mL) and cooled to 0 °C. Aqueous 3M NaOH (2.8 mL) was added, followed by 0.5 M solution of iodine in Et\textsubscript{2}O (1.02 g, 4.0 mmol) and the reaction stirred for 40 minutes. The reaction was quenched with saturated aqueous Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} solution (20 mL) and the organic layer separated. The aqueous layer was washed with EtOAc (20 mL) and the combined organic extracts washed with water (15 mL), brine (15 mL), dried (MgSO\textsubscript{4}) and the solvent removed \textit{in vacuo}. The residue was purified by flash column chromatography (Pet. ether 40-60:CH\textsubscript{2}Cl\textsubscript{2}, 8:1) to yield the \textit{title compound} as a clear oil (568 mg, 43%); \(R_f = 0.41\) (Pet. ether 40-60:CH\textsubscript{2}Cl\textsubscript{2}, 5:1); \(\delta_H\) (400 MHz, CDCl\textsubscript{3}) 7.66 – 7.64 (4H, m, Ph\textsubscript{H}), 7.43 – 7.37 (6H, m, Ph\textsubscript{H}), 6.53 (1H, dt, \(J = 14.5, 7.3\) Hz, CH\textsubscript{2}CH=CH\textsubscript{I}), 6.06 (1H, dt, \(J = 14.5, 1.3\) Hz, CH\textsubscript{2}CH=CH\textsubscript{I}), 2.28 (2H, app qd, \(J = 7.3, 1.3\) Hz, CH\textsubscript{2}CH=CH\textsubscript{I}), 1.05 (9H, s, C(CH\textsubscript{3})\textsubscript{3}); \(\delta_C\) (125 MHz, CDCl\textsubscript{3}) 143.3 (CH), 135.6 (CH), 133.6 (C), 129.7 (CH), 127.7 (CH), 76.5 (CH), 62.3 (CH\textsubscript{2}), 39.1 (CH\textsubscript{2}), 26.8 (CH\textsubscript{3}), 19.2 (C); \(\nu_{max} / cm^{-1}\) (CDCl\textsubscript{3}) 2930, 2858, 1472, 1427, 1111, 950, 823, 710; HRMS ESI
\([M+Na]^+\) found 459.0612 \([C_{20}H_{25}OSiNa]^+\) requires 459.0612. Spectral data consistent with literature values.\[^4\] Based on literature procedures.\[^5, 6\]

**((Z))-5-(2-Iodoprop-1-enyl)-1,2,3-trimethoxybenzene (3)**

\[
\text{MeO} - \text{I} - \text{MeO}
\]

\(\text{n-Butyllithium (1.6 M in hexanes, 6.25 mL, 10.0 mmol) was added dropwise to a suspension of ethyltriphenylphosphonium bromide (3.71 g, 10.0 mmol) in THF (50 mL) and the mixture stirred until all the solid dissolved. The resultant solution was transferred via cannula onto a pre-cooled solution of iodine (2.25 g, 8.85 mmol) in THF (75 mL) at -78 °C and stirred for 5 minutes. The reaction mixture was warmed to -20 °C, sodium hexamethyldisilazane (1 M in THF, 8.5 mL, 8.5 mmol) added dropwise and the solution allowed to stir for 5 minutes. A solution of 3,4,5-trimethoxybenzaldehyde (1.64 g) in THF (25 mL) was then added and the solution stirred for a further 10 minutes. The reaction was poured onto saturated aqueous NH\(_4\)Cl solution (150 mL) and the organic layer separated. The aqueous layer was extracted with Et\(_2\)O (150 mL) and the combined organic extracts washed with brine (300 mL), dried (MgSO\(_4\)) and the solvents removed \textit{in vacuo}. The residue was purified by flash column chromatography (Pet. ether 40-60:Et\(_2\)O, 1:1) to yield the \textit{title compound} as a pale brown oil (1.72 g, 62%); \(R_f = 0.28\) (Pet. ether 40-60:Et\(_2\)O, 2:1); \(\delta_H\) (500 MHz, CDCl\(_3\)) 6.75 (2H, s, ArH), 6.59 (1H, m, (Ar)CH=CH), 3.88 (6H, s, OCH\(_3\)), 3.86 (3H, s, OCH\(_3\)), 2.72 (3H, d, \(J=1.5\) Hz, CH\(_3\)); \(\delta_C\) (125 MHz, CDCl\(_3\)) 152.7 (C), 137.5 (C), 134.2 (CH), 133.4 (C), 105.7 (CH), 98.9 (C), 60.9 (CH\(_3\)), 56.1 (CH\(_3\)), 35.6 (CH\(_3\)); \(\nu_{max}/cm^{-1}\) (CDCl\(_3\)) 2938, 1581 (C=C), 1505 (C=C), 1453, 1415, 1334, 1237, 1140, 1074, 1005; HRMS ESI \([M+H]^+\) found 335.0151 \([C_{12}H_{10}O_3]^+\) requires 335.0144; stereochemistry assigned \((Z)\) on the basis of NOE correlation between signals at 6.59 and 2.72. Based on a literature procedure.\[^7\]\)
2.2 Alkenyl halide homo-coupling products (Table 1)

**General procedure 1**

Alkenyl halide (1 equiv.) was dissolved in THF (4 mL) and cooled to -78 °C. t-Butyllithium (1.7 M in pentane, 2 equiv.) was added dropwise and the solution stirred at -78 °C for 30 minutes, and then allowed to warm to room temperature over 10 minutes. The resultant solution was transferred via cannula onto a pre-cooled suspension of CuBr.SMe$_2$ (0.5 equiv.) in THF (2 mL) at -78 °C and stirred for 30 minutes. A solution of oxidant 5 (1 equiv.) in THF (4 mL) was then added and the solution stirred at -78 °C for 30 minutes and at room temperature for 1 hour.

**Buta-1,3-diene-2,3-diyl dibenzene**$^8$ (4)

Prepared via general procedure 1. The reaction was quenched with saturated aqueous NH$_4$Cl solution (10 mL), and the organic layer separated. The aqueous layer was washed with Et$_2$O (10 mL), the organic extracts combined, washed with brine (20 mL), dried (MgSO$_4$) and the solvent removed in vacuo. The residue was purified by flash column chromatography (Pet. ether 40-60) to yield the **title compound** as a yellow oil (135 mg, 86%); $R_f = 0.26$ (Pet. ether 40-60); $\delta_H$ (500 MHz, CDCl$_3$) 7.47 – 7.43 (4H, m, PhH), 7.34 – 7.24 (6H, m, PhH), 5.60 (2H, d, $J = 1.7$ Hz, C=CH$_2$), 5.37 (2H, d, $J = 1.7$ Hz, C=CHH); $\delta_C$ (125 MHz, CDCl$_3$) 149.9 (C), 140.2 (C), 128.2 (CH), 127.5 (CH), 127.5 (CH), 116.4 (CH$_2$); $\nu_{max}$ / cm$^{-1}$ (CDCl$_3$) 3022, 2946, 1598 (C=C), 1572 (C=C), 1491, 1441; LCMS (ES+) 206 ($M^+$). Spectral data consistent with literature values.$^8$
2,2,13,13-Tetramethyl-7,8-dimethylene-3,3,12,12-tetraphenyl-4,11-dioxa-3,12-disilatetradecane (6)

Prepared via general procedure 1. The reaction mixture was filtered through a plug of silica eluting with pet. ether 40-60:Et₂O (1:1) and the solvent removed in vacuo. The residue was purified by flash column chromatography (Pet. ether 40-60:EtOAc, 10:1 moving to 5:1) to yield the title compound as a clear oil which solidified to a white amorphous solid on standing (193 mg, 62%); Rᵣ = 0.08 (Pet. ether 40-60:EtOAc, 10:1); δ_H (500 MHz, CDCl₃) 7.67 – 7.65 (8H, m, PhH), 7.45 – 7.37 (12H, m, PhH), 6.08 (2H, m, C=CHH), 5.81 (2H, d, J = 2.5 Hz, C=CHH), 3.56 (4H, t, J = 6.8 Hz, OCH₂), 2.49 (4H, app t, J = 6.8 Hz, OCH₂CH₂), 1.21 (18H, s, C(CH₃)₃); δ_C (125 MHz, CDCl₃) 143.0 (C), 136.1 (CH), 134.2 (C), 131.6 (CH₂), 129.1 (CH), 127.6 (CH), 61.3 (CH₂), 40.0 (CH₂), 28.6 (CH₃), 18.4 (C); ν_max / cm⁻¹ (CDCl₃) 3063, 2927, 2861, 2861, 1464, 1426, 1390, 1363, 1103, 1037, 735, 757; HRMS ESI [M+Na+2H]⁺ found 643.3396 [C₄₀H₅₂O₂Si₂Na]⁺ requires 643.3398.

(7E,9E)-2,2,15,15-Tetramethyl-3,3,14,14-tetraphenyl-4,13-dioxa-3,14-disilahexadeca-7,9-diene (7)

Prepared via general procedure 1. The reaction mixture was filtered through a plug of silica eluting with pet. ether 40-60:Et₂O (1:1) and the solvent removed in vacuo. The residue was purified by flash column chromatography (Pet. ether 40-60:CH₂Cl₂, 5:1 moving to 1:1) to yield the title compound as a clear oil (62 mg, 40%); Rᵣ = 0.13 (Pet. ether 40-60:CH₂Cl₂, 5:1); δ_H (400 MHz, CDCl₃) 7.70 – 7.67 (8H, m, PhH), 7.43 – 7.36 (12H, m, PhH), 6.03 (2H, m, CH₂CH=CHH), 5.57 (2H, m, CH₂CH=CHH), 3.71 (4H, t, J = 6.8 Hz, OCH₂), 2.34
Buta-1,3-diene-1,1,2,3,4,4-hexaylhexabenzene. The reaction mixture was filtered through a plug of silica eluting with pet. ether 40-60:Et₂O (1:1) and the solvent removed in vacuo. The resultant yellow solid was washed with pet. ether 40-60 to yield the title compound as a pale yellow crystalline solid (304 mg, 79%); m.p. 210-213 °C (Pet. ether 40-60) (lit.,[10] 213-214 °C); Rᵣ = 0.40 (Pet. ether 40-60:EtOAc, 10:1); δₜ (400 MHz, CDCl₃) 7.20 – 7.16 (4H, m, PhH), 7.07 – 7.03 (12H, m, PhH), 6.96 – 6.85 (14H, m, PhH); δₑ (125 MHz, CDCl₃) 144.0 (C), 143.8 (C), 143.0 (C), 141.5 (C), 140.5 (C), 131.4 (CH), 131.3 (CH), 129.9 (CH), 127.4 (CH), 127.3 (CH), 127.2 (CH), 126.6 (CH), 126.4 (CH), 125.9 (CH); νₘₐₓ / cm⁻¹ (CDCl₃) 3048, 3018, 1601 (C=C), 1489, 1439, 1072, 1029, 908, 756, 728, 696; HRMS EI [M⁺] found 510.2362 [C₄₀H₃₀]⁺ requires 510.2342. Spectral data consistent with literature values.[9]

1,2-Dicyclohexylideneethane. Prepared via general procedure 1. The reaction mixture was filtered through a plug of silica eluting with pet. ether 40-60:Et₂O (1:1) and the solvent removed...
in vacuo. The residue was purified by flash column chromatography (Pet.
ether 40-60) to yield the title compound as a clear oil (81 mg, 57%); \( R_f = 0.58 \) (Pet.
ether 40-60); \( \delta_H \) (400 MHz, CDCl\(_3\)) 5.99 (2H, s, C=CH), 2.28 (4H, br m,
CH\(_2\)C=CH), 2.15 (4H, br m, CH\(_2\)C=CH), 1.56 (12H, br app s, CH\(_2\)CH\(_2\)CH\(_2\)); \( \delta_c \)
(125 MHz, CDCl\(_3\)) 140.9 (C), 117.2 (CH), 37.7 (CH\(_2\)), 28.9 (CH\(_2\)), 28.6 (CH\(_2\)),
27.7 (CH\(_2\)), 26.9 (CH\(_2\)); \( \nu_{max} / \text{cm}^{-1} \) (CDCl\(_3\)) 2931, 2857, 1719, 1448; LCMS
(AP+) 190 (\( M^+ \)). Spectral data consistent with literature values.\(^{[11]}\)

5,5’-(1Z,3Z)-2,3-Dimethylbuta-1,3-diene-1,4-diylbis(1,2,3-
trimethoxybenzene) (10)

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\text{MeO} \quad \text{OMe}
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\text{MeO} \quad \text{OMe}
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\text{MeO} \quad \text{OMe}
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\( i \)-Propylmagnesium chloride (1.96 M in THF, 1.96 mL, 3.85 mmol) was added
dropwise to a suspension of lithium chloride (163 mg, 3.85 mmol) and alkenyl
iodide 9 (1.17 g, 3.50 mmol) in THF (2 mL) at -40 °C and stirred for 3 hours.
The resultant solution was transferred via cannula onto a pre-cooled
suspension of CuBr.SMe\(_2\) (362 mg, 1.75 mmol) in THF (2 mL) at -40 °C and
stirred for 20 minutes. A solution of oxidant 5 (1.03 g, 3.50 mmol) in THF (4
mL) was then added and the solution stirred at -40 °C for 30 minutes and at
room temperature for 1 hour. The reaction mixture was filtered through a plug
of silica eluting with pet. ether 40-60:EtOAc (1:1) and the solvent removed in
vacuo. The residue was purified by flash column chromatography (Pet.
ether 40-60:EtOAc, 2:1) to yield the title compound as a pale yellow crystalline solid
(460 mg, 63%); m.p. 92-93 °C (Pet. ether 40-60:EtOAc); \( R_f = 0.07 \) (Pet. ether
40-60:EtOAc, 5:1); \( \delta_H \) (400 MHz, CDCl\(_3\)) 6.72 (4H, s, ArH), 6.26 (2H, d, \( J =
1.3 \) Hz, (Ar)CH=C), 3.81 (6H, s, OCH\(_3\)), 3.73 (12H, s, OCH\(_3\)), 1.93 (6H, d, \( J =
1.3 \) Hz, CH\(_3\)); \( \delta_c \) (125 MHz, CDCl\(_3\)) 152.8 (C), 139.5 (C), 136.7 (C), 132.9 (C),
125.8 (CH), 104.5 (CH), 60.8 (CH\(_3\)), 55.8 (CH\(_3\)), 23.7 (CH\(_3\)); \( \nu_{max} / \text{cm}^{-1} \)
(CDCl₃) 2937, 2836, 1578 (C=C), 1413, 1330, 1234, 1130, 1003, 728; HRMS ESI [M+H]+ found 415.2141 [C₂₄H₃₁O₆]+ requires 415.2121. Grignard reagent formation based on a literature procedure.[¹²]

2.3 Synthesis of oxidant

(3,5-Dinitrophenyl)(4-methylpiperazin-1-yl)methanone[^1][°](5)

3,5-Dinitrobenzoic acid (21.2 g, 0.10 mmol) was dissolved in thionyl chloride (100 mL) and heated under reflux overnight. The thionyl chloride was then removed *in vacuo* and by azeotropic distillation with toluene. The residue was dissolved in CHCl₃ (200 mL) and added dropwise to a suspension of 1-methylpiperazine (13.2 mL, 0.12 mmol) and K₂CO₃ (14.0 g, 0.10 mmol) in CHCl₃ (200 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature, washed with water (400 mL x 4), dried (K₂CO₃) and the solvent removed *in vacuo* to yield the title compound as orange crystals (28.6 g, 97%); m.p. 138-139 °C (Hexane) (lit.,[^1][°] 138-141 °C); δₓ (500 MHz, [D₆]DMSO, 120 °C) 8.87 (1H, t, J = 2.1 Hz, ArH), 8.55 (2H, d, J = 2.1 Hz, ArH), 3.55 (4H, m, C(O)NCH₂), 2.41 (4H, t, J = 5.1 Hz, MeNCH₂), 2.28 (3H, s, NCH₃); δₓ (125 MHz, [D₆]DMSO, 120 °C) 164.4 (C), 148.0 (C), 138.8 (C), 126.6 (CH), 118.4 (CH), 53.7 (CH₂ x 2), 44.7 (CH₃); vₓ / cm⁻¹ (THF) 3104, 2937, 2795, 1641 (C=O), 1539 (NO₂), 1345 (NO₂). Spectral data consistent with literature values.[¹³] Based on a literature procedure.[¹³]
3 References


4 $^1$H and $^{13}$C NMR Spectra