Synthesis of Unsymmetrical Diarylmethanols via C-Si bond Bifunctionalization Enabled by Sequential [1,4]-Csp2 to O-Silyl Migration

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1. General Methods

Commercial reagents were used without any purification. All reactions were performed using common anhydrous, inert atmosphere techniques. Reactions were monitored by TLC which was performed on glass-backed silica plates and visualized using UV, KMnO$_4$ stains, H$_3$PO$_4$·12MoO$_3$/EtOH stains, H$_2$SO$_4$ (conc.)/anisaldehyde/ EtOH stains. Column chromatography was performed using silica gel (200-300 mesh) eluting with EtOAc/petroleum ether. $^1$H NMR spectra were recorded at 400 MHz (Varian and Bruker) and 600 MHz (Agilent), $^{13}$C NMR spectra were recorded at 100 MHz (Bruker) and 150 MHz (Agilent) using CDCl$_3$ (except where noted) with TMS as standard. Infrared spectra were obtained using KCl plates on a VECTOR22. High-resolution mass spectral analyses performed on Waters Q-TOF. CH$_2$Cl$_2$ were distilled from CaH$_2$. THF were distilled from Na. All spectral data obtained for new compounds are reported here.

2. Experimental Procedures and Spectral Data of Products

2.1. Synthesis of 1

To a solution of 2-bromo-iodobenzene 6 (14 g, 50 mmol, 6.3 mL) in THF (500 mL) at -78 °C under argon was added $i$-PrMgCl (27 mL, 2.0 M in THF). The reaction stirred for 30 min before adding 2-bromobenzaldehyde (9.25 g, 50 mmol, 6.1 mL) at -78 °C. The mixture was warmed to room temperature and reacted overnight. The reaction was quenched with sat. aq. HCl (15 mL, 1 N) and extracted with EtOAc (3 × 100 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure to afford bis(2-bromophenyl)methanol 7 (17 g) as a colorless solid, which was used for the next step without purification.

A solution of bis(2-bromophenyl)methanol 7 (17 g, 50 mmol), hexamethyldisilazane...
(7.3 mL, 35 mmol) and ten crystals of iodine in CH₂Cl₂ (100 mL) was stirred at room temperature for 15 min. The reaction was quenched with Na₂S₂O₃ (20 g). After stirring for 30 min, the mixture was passed through a short pad of silica and concentrated under reduced pressure to give the crude silyl ether, which was used for the next step without purification.

To a solution of the crude silyl ether and chlorotrimethylsilane (38 mL, 300 mmol) in dry THF (500 mL) was added n-butyllithium (2.5 M in hexanes, 60 mL, 150 mmol) over 30 min dropwise at −78 °C. The resulting mixture was warmed to room temperature overnight. The reaction was quenched with H₂O (100 mL) and extracted with EtOAc (3 × 100 mL). The combined organic layers were dried over Na₂SO₄, concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 500:1 → 100:1) to afford 1 as a colorless liquid (10.3 g, 63% from 6).

¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.61 (m, 2H), 7.31 – 7.25 (m, 4H), 6.99 (d, J = 7.2 Hz, 2H), 6.23 (d, J = 4.8 Hz, 1H), 2.16 (d, J = 4.8 Hz, 1H), 0.32 (s, 18H);

¹³CNMR (100 MHz, CDCl₃) δ 149.0, 139.2, 135.0, 128.9, 127.8, 126.9, 75.1, 0.9;

IR (neat) cm⁻¹ 3350, 3054, 2952, 2897, 1433, 1246, 1121, 835;

HRMS (ESI-TOF, m/z) calcd for C₁₉H₂₈OSi₂ (M+Na⁺): 351.1576, found 351.1570.

2.2. Preparation of 3a-3f

Preparation of 3a

\[
\begin{align*}
\text{3a} & : \text{To a solution of CuI (10 mg, 0.05 mmol) and phenanthroline (12 mg, 0.05 mmol)} \\
& \text{in DMF (1.0 mL) was slowly added } \text{t-BuOLi (0.15 mL, 1.0 M in THF) at 0 °C under argon atmosphere. The reaction mixture was stirred at room temperature for 10 min. 1}
\end{align*}
\]
(33 mg, 0.1 mmol) was added with stirring for 5 min before adding 3-chloroprop-1-ene (15 μL, 0.15 mmol). The mixture was stirred at room temperature for 30 min before quenching with aq. HCl (0.2 mL, 1 N) and extracting with EtOAc (3 × 5 mL). The combined organic layers were washed with H2O (3 × 2 mL), dried over Na2SO4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 300:1 → 100:1) to afford 3a (27 mg, 90% yield) as a colorless liquid.

1H NMR (400 MHz, CDCl3) δ 7.60 (t, J = 4.8 Hz, 1H), 7.35 – 7.20 (m, 6H), 7.13 (t, J = 3.6 Hz, 1H), 6.25 (d, J = 3.6 Hz, 1H), 5.93 – 5.83 (m, 1H), 5.04 (d, J = 10 Hz, 1H), 4.96 (d, J = 17.2 Hz, 1H), 3.38 (dd, J = 6.0, 6.4 Hz, 1H), 3.28 (dd, J = 6.0, 6.4 Hz, 1H), 2.08 (d, J = 4.4 Hz, 1H), 0.33 (s, 9H);

13C NMR (100 MHz, CDCl3) δ 148.1, 140.9, 139.0, 137.5, 137.1, 135.2, 129.9, 129.3, 127.7, 127.3, 127.2, 127.1, 126.2, 116.1, 72.5, 36.6, 0.8;

IR (neat) cm⁻¹ 3391, 3057, 2953, 1248, 1010, 834, 751;

HRMS (ESI-TOF, m/z) calcd for C19H24OSi (M+Na)⁺: 319.1489, found 319.1487.

**Preparation of 3b**

3b: Using the same procedure as that used for 3a: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in THF); 1 (33 mg, 0.1 mmol), 3-chloro-2-methylpropene (15 μL, 0.15 mmol) at room temperature for 0.5 h afforded 3b (28 mg, 89% yield) as a colorless liquid.

1H NMR (400 MHz, CDCl3) δ 7.61 – 7.59 (m, 1H), 7.30 – 7.14 (m, 7H), 6.24 (d, J = 4 Hz, 1H), 4.86 (s, 1H), 4.57 (s, 1H), 3.33 (d, J = 16 Hz, 1H), 3.24 (d, J = 16 Hz, 1H), 2.17 (d, J = 4 Hz, 1H), 1.67 (s, 3H), 0.31 (s, 9H);
\(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.1, 145.2, 141.5, 138.9, 137.1, 135.2, 130.2, 129.2, 127.6, 127.3, 127.1, 126.3, 112.6, 72.5, 40.8, 22.7, 0.7;

IR (neat) cm\(^{-1}\) 3436, 3005, 1275, 1260, 837, 764, 750;

HRMS (ESI-TOF, m/z) calcd for C\(_{20}\)H\(_{26}\)OSi (M+Na): 333.1645, found 333.1647.

**Preparation of 3c**

![3c](image)

3c: Using the same procedure as that used for 3a: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); \(t\)-BuOLi (0.15 mL, 1.0 M in THF); 1 (33 mg, 0.1 mmol), iodoethane (36 \(\mu\)L, 0.15 mmol) at room temperature for 0.5 h afforded 3c (25 mg, 88% yield) as a colorless liquid.

\(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.62 – 7.60 (m, 1H), 7.45 – 7.43 (m, 1H), 7.30 – 7.20 (m, 5H), 7.08 – 7.06 (m, 1H), 6.26 (d, \(J = 3.6\) Hz, 1H), 2.61(ddd, \(J = 7.6, 15.2, 15.2\) Hz, 1H), 2.46 (ddd, \(J = 7.6, 15.2, 15.2\) Hz, 1H), 2.01 (d, \(J = 4.4\) Hz, 1H), 1.11 (t, \(J = 7.6\) Hz, 3H), 0.37 (s, 9H);

\(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.5, 141.5, 140.5, 139.1, 135.3, 129.3, 128.4, 127.6, 127.3, 127.2, 126.7, 125.7, 72.4, 25.0, 14.7, 0.8;

IR (neat) cm\(^{-1}\) 3361, 2962, 1452, 1275, 1249, 837, 751;

HRMS (ESI-TOF, m/z) calcd for C\(_{18}\)H\(_{24}\)OSi (M+Na): 307.1489, found 307.1485.

**Preparation of 3d**

![3d](image)

3d: Using the same procedure as that used for 3a: CuI (10 mg, 0.05 mmol),
phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in THF); 1 (33 mg, 0.1 mmol), (bromomethyl)benzene (18 μL, 0.15 mmol) at room temperature for 0.5 h afforded 3d (27 mg, 77% yield) as a colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.60 – 7.58 (m, 1H), 7.38 – 7.35 (m, 1H), 7.31 – 7.28 (m, 2H), 7.25 – 7.14 (m, 6H), 7.06 – 7.03 (m, 3H), 6.23 (d, $J$ = 3.2 Hz, 1H), 3.97 (d, $J$ = 4.4 Hz, 1H), 0.24 (s, 9H);

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.1, 141.1, 140.2, 139.3, 138.6, 135.3, 130.5, 129.3, 129.0, 128.5, 127.7, 127.3, 127.2, 126.3, 126.1, 72.7, 38.4, 0.7;

IR (neat) cm$^{-1}$ 3403, 3058, 2953, 1723, 1451, 1249, 1009, 837;

HRMS (ESI-TOF, m/z) calcd for C$_{23}$H$_{26}$OSi (M+Na)$^+$: 369.1645, found 369.1642.

**Preparation of 3e**

![Chemical Structure of 3e](image)

3e: Using the same procedure as that used for 3a: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in THF); 1 (33 mg, 0.1 mmol), 1-(p-Tosyloxy)-3-phenyl-2-propyne (43 mg, 0.15 mmol) at room temperature for 0.5 h afforded 3e (30 mg, 80% yield) as a colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.63 – 7.61 (m, 2H), 7.40 – 7.26 (m, 10H), 7.16 – 7.14 (m, 1H), 6.31 (d, $J$ = 4 Hz, 1H), 3.83 (d, $J$ = 18.8 Hz, 1H), 3.65 (d, $J$ = 18.8 Hz, 1H), 2.17 (d, $J$ = 4.4 Hz, 1H), 0.34 (s, 9H);

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 147.6, 140.5, 139.3, 135.3, 134.4, 131.6, 129.5, 129.2, 128.2, 128.0, 127.8, 127.4, 127.2, 126.8, 123.5, 87.2, 83.4, 72.5, 23.3, 0.8;

IR (neat) cm$^{-1}$ 3407, 2920, 2850, 1275, 1260, 764, 750;

HRMS (ESI-TOF, m/z) calcd for C$_{23}$H$_{26}$OSi (M+Na)$^+$: 393.1645, found 393.1649.
Preparation of 3f

3f: Using the same procedure as that used for 3a: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in THF); 1 (33 mg, 0.1 mmol), 3-bromo-1-(trimethylsilyl)-1-propyne (25 μL, 0.15 mmol) at room temperature for 0.5 h afforded 3f (27 mg, 70% yield) as a colorless liquid.

1H NMR (400 MHz, CDCl3) δ 7.63 – 7.54 (m, 2H), 7.35 – 7.26 (m, 5H), 7.14 – 7.10 (m, 1H), 6.23 (d, J = 4 Hz, 1H), 3.68 (d, J = 18.8 Hz, 1H), 3.43 (d, J = 19.2 Hz, 1H), 2.21 (d, J = 4.4 Hz, 1H), 0.35 (s, 9H), 0.16 (s, 9H);

13C NMR (100 MHz, CDCl3) δ 147.5, 140.6, 139.2, 135.3, 134.0, 129.4, 129.0, 127.9, 127.3, 127.2, 127.1, 126.8, 103.9, 87.8, 72.4, 23.8, 0.9, 0.0;

IR (neat) cm⁻¹ 3366, 3056, 2956, 2174, 1248, 1122, 834, 757;

HRMS (ESI-TOF, m/z) calcd for C22H30OSi2 (M+Na)+: 389.1727, found 389.1725.

2.3. Synthesis of 3g-3i

Preparation of 3g

3g: To a solution of CuI (10 mg, 0.05 mmol) and tetrakis(triphenylphosphine) palladium (6 mg, 5 mol%) in DMF (1.0 mL) was slowly added t-BuOLi (0.15 mL, 1.0 M in THF) at 0 °C under argon atmosphere. The reaction mixture was stirred at room
temperature for 10 min. 1 (33 mg, 0.1 mmol), 4-iodoanisole (35 mg, 0.15 mmol) was added successively and kept stirring at room temperature for 1 h. The reaction was quenched with aq. HCl (0.2 mL, 1 N) solution, extracted with EtOAc (3 × 5 mL) and washed with H₂O (3 × 2 mL). The combined organic layers were then dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 300:1 → 100:1) to afford 3g (33 mg, 92% yield) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, J = 7.2 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.35 – 7.32 (m, 4H), 7.29 – 7.23 (m, 2H), 7.14 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8 Hz, 2H), 6.05 (d, J = 4.0 Hz, 1H), 3.08 (s, 3H), 2.11 (d, J = 4.4 Hz, 1H), 0.06 (s, 9H);

¹³C NMR (100 MHz, CDCl₃) δ 158.9, 148.6, 141.3, 140.6, 139.0, 135.2, 133.2, 130.7, 130.5, 128.9, 127.8, 127.5, 127.6, 127.4, 127.2, 126.9, 113.5, 72.3, 55.3, 0.37;

IR (neat) cm⁻¹ 3460, 2953, 1611, 1515, 1479, 1244, 1178, 835, 764;

HRMS (ESI-TOF, m/z) calcd for C₂₃H₂₆O₂Si (M+Na)⁺: 385.1594, found 385.1601.

**Preparation of 3h**

3h: Using the same procedure as that used for 3g: Cul (10 mg, 0.05 mmol), tetrakis(triphenylphosphine) palladium (6 mg, 5 mol%), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in THF); 1 (33 mg, 0.1 mmol), 4-iodotoluene (33 mg, 0.15 mmol) at room temperature for 1 h afforded 3h (28 mg, 80% yield) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.27 (m, 8H), 7.14 – 7.08 (m, 4H), 6.05 (d, J = 4.0 Hz, 1H), 2.36 (s, 3H), 2.06 (d, J = 4.0 Hz, 1H), 0.06 (s, 9H);

¹³C NMR (100 MHz, CDCl₃) δ 148.6, 141.6, 140.6, 139.0, 137.9, 136.9, 135.2, 130.5,
129.2, 128.9, 128.7, 127.8, 127.7, 127.4, 127.2, 126.9, 72.3, 21.1, 0.4;

IR (neat) cm⁻¹ 3443, 2953, 2853, 1724, 1249, 1006, 837, 821, 759;

HRMS (ESI-TOF, m/z) calcd for C₂₃H₂₆O₃Si (M+Na)⁺: 369.1645, found 369.1649.

\textbf{Preparation of 3i}

\begin{center}
\includegraphics[width=0.5\textwidth]{3i.png}
\end{center}

3i: Using the same procedure as that used for 3g: CuI (10 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium (6 mg, 5 mol%), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in THF); 1 (33 mg, 0.1 mmol), 2-bromopropene (14 μL, 0.15 mmol) at room temperature for 1 h afforded 3i (27 mg, 90% yield) as a colorless liquid.

\(^1\)H NMR (400 MHz, CDCl₃) δ 7.59 (t, \(J = 4.8\) Hz, 1H), 7.40 (t, \(J = 4.8\) Hz, 1H), 7.29 – 7.25 (m, 4H), 7.16 – 7.11 (m, 2H), 6.28 (d, \(J = 3.6\) Hz, 1H), 5.12 (s, 1H), 4.72 (s, 1H), 2.25 (d, \(J = 4.4\) Hz, 1H), 1.93 (s, 3H), 0.34 (s, 9H);

\(^13\)C NMR (100 MHz, CDCl₃) δ 148.8, 144.9, 143.0, 139.8, 139.2, 135.2, 129.1, 128.3, 127.7, 127.6, 127.3, 126.9, 126.8, 115.9, 72.5, 25.2, 0.8;

IR (neat) cm⁻¹ 3436, 2954, 1433, 1249, 1121, 1006, 838, 763;

HRMS (ESI-TOF, m/z) calcd for C₁₉H₂₄O₃Si (M+Na)⁺: 319.1489, found 319.1488.

\textbf{2.4. Synthesis of 5a – 5m}

\textbf{Preparation of 5a}

\begin{center}
\includegraphics[width=0.5\textwidth]{5a.png}
\end{center}

5a: To a solution of CuI (10 mg, 0.05 mmol) and phenanthroline (12 mg, 0.05 mmol)
in DMF (1.0 mL) was slowly added t-BuOLi (0.15 mL, 1.0 M in THF) at 0 °C under argon atmosphere. The reaction mixture was stirred at room temperature for 10 min. 1 (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol) was added successively and kept stirring at room temperature for 0.5 h. Then TBAF (0.15 mL, 1.0 M in THF), t-BuOLi (0.2 mL, 1.0 M in THF), 3-chloro-2-methylpropene (15 μL, 0.15 mmol) were added successively. The resulted mixture was stirred at room temperature for 1 h. The reaction was quenched with sat. aq. NaCl (2 mL), extracted with EtOAc (3 × 5 mL) and washed with H₂O (3 × 3 mL). The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 100:1 → 20:1) to afford 5a (21 mg, 77% yield) as a colorless liquid.

**1H NMR (400 MHz, CDCl₃)** δ 7.36 (dd, J = 1.6, 2 Hz, 1H), 7.26 – 7.17 (m, 7H), 6.25 (d, J = 4 Hz, 1H), 5.98 – 5.87 (m, 1H), 5.07 – 5.03 (m, 1H), 5.01 – 4.95 (m, 1H), 4.87 (s, 1H), 4.58 (s, 1H), 3.40 – 3.26 (m, 4H), 2.17 (d, J = 4 Hz, 1H), 1.73 (s, 3H);

**13C NMR (100 MHz, CDCl₃)** δ 145.6, 141.2, 140.7, 137.4, 137.2, 137.1, 130.6, 129.9, 127.7, 127.7, 127.2, 126.9, 126.7, 126.5, 115.9, 112.1, 69.3, 41.0, 36.7, 22.8;

**IR (neat) cm⁻¹** 3347, 2928, 2850, 1260, 1016, 764, 750;

**HRMS (ESI-TOF, m/z)** calcd for C₂₀H₂₂O (M+Na)⁺: 301.1563, found 301.1560.

**Preparation of 5b**

![5b](attachment:image.png)

**5b:** Using the same procedure as that used for 5a: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in THF); 1 (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), t-BuOLi (0.2 mL, 1.0 M in THF), 2-phenylallyl-4-methylbenzenesulfonate (43 mg, 0.15 mmol) at room temperature for...
1 h afforded **5b** (24 mg, 70% yield) as a white solid. (mp. 56.9 °C – 57.6 °C)

**1H NMR** (400 MHz, CDCl₃) δ 7.38 – 7.26 (m, 8H), 7.25 – 7.18 (m, 5H), 6.26 (s, 1H), 5.97 - 5.83 (m, 1H), 5.49 (s, 1H), 5.00 – 4.92 (m, 2H), 4.82 (s, 1H), 3.77 (s, 2H), 3.41 – 3.25 (m, 2H), 2.12 (s, 1H);

**13C NMR** (100 MHz, CDCl₃) δ 146.9, 140.9, 140.8, 140.6, 137.7, 137.3, 136.9, 130.5, 130.0, 128.3, 127.9, 127.7, 127.6, 127.2, 127.0, 126.7, 126.6, 125.9, 116.0, 114.4, 69.5, 37.9, 36.7;

**IR** (neat) cm⁻¹ 3336, 3059, 2919, 2850, 1485, 1451, 1260, 1014, 751;

**HRMS** (ESI-TOF, m/z) calcd for C₂₅H₂₄O (M+Na)⁺: 363.1719, found 363.1713.

**Preparation of 5c**

![Structure of 5c](image)

**5c**: Using the same procedure as that used for **5a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), t-BuOLi (0.2 mL, 1.0 M in THF), 3-chloro-2-chloromethyl-1-propene (18 μL, 0.15 mmol) at room temperature for 1 h afforded **5c** (21 mg, 66 % yield) as a colorless liquid.

**1H NMR** (400 MHz, CDCl₃) δ 7.32 – 7.27 (m, 3H), 7.24 – 7.17 (m, 5H), 6.26 (d, J = 4 Hz, 1H), 5.98 – 5.87 (m, 1H), 5.22 (s, 1H), 5.07 – 4.96 (m, 2H), 4.81 (s, 1H), 3.99 (d, J = 3.2 Hz, 2H), 3.51 (d, J = 3.2 Hz, 2H), 3.44 – 3.28 (m, 2H), 2.15 (d, J = 4.4 Hz, 1H);

**13C NMR** (100 MHz, CDCl₃) δ 144.6, 141.1, 140.6, 137.5, 137.3, 135.9, 130.6, 130.0, 127.9, 127.9, 127.4, 127.0, 126.5, 116.1, 69.3, 47.9, 36.6, 36.2;
IR (neat) cm\(^{-1}\) 3337, 3072, 2922, 1602, 1451, 1260, 1013, 913, 751;

HRMS (ESI-TOF, m/z) calcd for C\(_{20}\)H\(_{21}\)OCl (M+Na\(^+\)) : 335.1179, found 335.1176.

**Preparation of 5d**

\[
\begin{align*}
5d: & \text{ Using the same procedure as that used for 5a: CuI (10 mg, 0.05 mmol),} \\
& \text{ phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in} \\
& \text{THF); 1 (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 \mu L, 0.1 mmol). Then TBAF (0.15} \\
& \text{mL, 1.0 M in THF), t-BuOLi (0.2 mL, 1.0 M in THF), cinnamyl chloride (21 \mu L,} \\
& \text{0.15 mmol) at room temperature for 1 h afforded 5d (20 mg, 60\% yield) as a colorless} \\
& \text{liquid.}
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 – 7.28 (m, 5H), 7.25 – 7.17 (m, 8H), 6.36 – 6.21 (m, 3H), 5.98 – 5.87 (m, 1H), 5.06 – 4.93 (m, 2H), 3.57 – 3.34(m, 4H), 2.13 (s, 1H);

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 140.7, 140.7, 137.8, 137.6, 137.3, 137.3, 131.1, 130.1, 128.8, 128.5, 128.4, 127.9, 127.9, 127.2, 127.1, 127.1, 126.6, 126.6, 126.1, 116.1, 69.5, 36.7, 35.9;

IR (neat) cm\(^{-1}\) 3337, 3025, 2920, 2850, 1450, 1260, 914, 750;

HRMS (ESI-TOF, m/z) calcd for C\(_{25}\)H\(_{24}\)O (M+Na\(^+\)) : 363.1719, found 363.1716.

**Preparation of 5e**

\[
\begin{align*}
5e: & \text{ Using the same procedure as that used for 5a: CuI (10 mg, 0.05 mmol),} \\
& \text{ phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in} \\
& \text{THF); 1 (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 \mu L, 0.1 mmol). Then TBAF (0.15} \\
& \text{mL, 1.0 M in THF), t-BuOLi (0.2 mL, 1.0 M in THF), cinnamyl chloride (21 \mu L,} \\
& \text{0.15 mmol) at room temperature for 1 h afforded 5e (20 mg, 60\% yield) as a colorless} \\
& \text{liquid.}
\end{align*}
\]
5e: Using the same procedure as that used for 5a: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in THF); I (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), t-BuOLi (0. 2 mL, 1.0 M in THF), 1-chloro-3-methyl-2-butene (17 μL, 0.15mmol) at room temperature for 1 h afforded 5e (20 mg, 70% yield) as a colorless liquid.

^1^H NMR (400 MHz, CDCl3) δ 7.37 – 7.17 (m, 8H), 6.27(d, J = 2.8 Hz, 1H), 6.00 – 5.88 (m, 1H), 5.23 (t, J = 7.2 Hz, 1H), 5.08 – 4.96 (m, 2H), 3.42 – 3.27 (m, 4H), 2.13 (d, J = 4.4 Hz, 1H), 1.72 (s, 3H), 1.66 (s, 3H);

^13^C NMR (100 MHz, CDCl3) δ 140.7, 139.5, 137.4, 137.2, 133.0, 130.0, 129.9, 129.4, 127.9, 127.7, 127.1, 127.0, 126.9, 126.5, 126.2, 123.0, 116.0, 69.3, 36.7, 31.4, 25.7, 17.9;

IR (neat) cm⁻¹ 3313, 2918, 2851, 1638, 1451, 1276, 1014, 913, 750;

HRMS (ESI-TOF, m/z) calcd for C_{21}H_{24}O (M+Na)^+: 315.1719, found 315.1715.

**Preparation of 5f**

![5f](image)

5f: Using the same procedure as that used for 5a: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in THF); I (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), t-BuOLi (0. 2 mL, 1.0 M in THF), geranyl chloride (28 μL, 0.15 mmol) at room temperature for 1 h afforded 5f (22 mg, 60% yield) as a colorless liquid.

^1^H NMR (400 MHz, CDCl3) δ 7.35 – 7.33 (m, 1H), 7.25 – 7.15 (m, 7H), 6.27 (d, J = 4.0 Hz, 1H), 5.98 – 5.88 (m, 1H), 5.26 – 5.22 (m, 1H), 5.04 – 4.97 (m, 3H), 3.48 –
3.25 (m, 4H), 2.13 (d, J = 4.4 Hz, 1H), 2.07 – 1.99 (m, 4H), 1.68 (s, 3H), 1.65 (s, 3H), 1.56 (s, 3H);

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 140.7, 139.5, 137.4, 137.2, 133.0, 130.0, 129.9, 129.4, 127.9, 127.7, 127.0, 126.9, 126.5, 126.2, 123.0, 116.0, 69.3, 36.7, 31.4, 25.7, 17.9;

IR (neat) cm\(^{-1}\) 3313, 2966, 2917, 2852, 1638, 1602, 1451, 1014, 913, 751;

HRMS (ESI-TOF, m/z) calcd for C\(_{26}\)H\(_{32}\)O (M+Na\(^+\)): 383.2345, found 383.2344.

**Preparation of 5g**

![Structural formula of 5g](image)

5g: Using the same procedure as that used for 5a: Cul (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); \(t\)-BuOLi (0.15 mL, 1.0 M in THF); 1 (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 \(\mu\)L, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), \(t\)-BuOLi (0.2 mL, 1.0 M in THF), 1-chloro-6,6-dimethyl-2-heptyne-4-alkyne (25 \(\mu\)L, 0.15 mmol) at room temperature for 1 h afforded 5g (21 mg, 62% yield) as a colorless liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.32 – 7.27 (m, 2H), 7.24 – 7.16 (m, 6H), 6.22 (d, J = 4.4 Hz, 1H), 6.15 – 6.08 (m, 1H), 6.02 – 5.92 (m, 1H), 5.43 – 5.38 (m, 1H), 5.10 – 4.98 (m, 2H), 3.45 – 3.33 (m, 4H), 2.10 (d, J = 4.8 Hz, 1H), 1.22 (s, 9H);

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 140.6, 140.6, 140.4, 137.5, 137.3, 136.9, 130.1, 130.1, 127.9, 127.9, 127.1, 127.0, 126.7, 126.6, 116.1, 111.5, 98.1, 77.2, 69.4, 36.7, 35.7, 31.0, 27.8;

IR (neat) cm\(^{-1}\) 3298, 2968, 2923, 1452, 1266, 1015, 915, 759;

HRMS (ESI-TOF, m/z) calcd for C\(_{25}\)H\(_{28}\)O (M+Na\(^+\)): 367.2032, found 367.2031.

**Preparation of 5h**
5h: Using the same procedure as that used for 5a: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in THF); I (33 mg, 0.1 mmol), cinnamyl chloride (14 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), t-BuOLi (0.2 mL, 1.0 M in THF), 3-chloro-2-methylpropene (15 μL, 0.15 mmol) at room temperature for 1 h afforded 5h (30 mg, 84 % yield) as a colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.40 (m, 2H), 7.33 (d, $J = 4.0$ Hz, 4H), 7.29 – 7.26 (m, 2H), 7.24 – 7.15 (m, 5H), 6.34 – 6.28 (m, 1H), 6.25 – 6.18 (m, 1H), 6.06 (s, 1H), 4.86 (s, 1H), 4.54 (s, 1H), 3.50 – 3.30 (m, 4H), 2.19 (s, 1H), 1.72 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 145.4, 143.2, 141.9, 137.3, 136.9, 131.1, 130.6, 129.9, 128.7, 128.4, 128.3, 127.8, 127.4, 127.3, 127.1, 126.8, 126.5, 126.1, 112.1, 72.6, 41.0, 35.9, 22.8;

IR (neat) cm$^{-1}$ 3363, 2918, 2154, 1449, 1264, 1013, 893;

HRMS (ESI-TOF, m/z) calcd for C$_{26}$H$_{26}$O (M+Na)$^+$: 377.1876, found 377.1875.

**Preparation of 5i**

5i: Using the same procedure as that used for 5a: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in THF); I (33 mg, 0.1 mmol), 1-chloro-3-methyl-2-butene (12 μL, 0.1 mmol). Then
TBAF (0.15 mL, 1.0 M in THF), t-BuOLi (0.2 mL, 1.0 M in THF), 3-chloro-2-methylpropene (15 μL, 0.15 mmol) at room temperature for 1 h afforded **5i** (22 mg, 72% yield) as a colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.12 (m, 8H), 6.25 (d, $J = 2.4$ Hz, 1H), 5.24 – 5.19 (m, 1H), 4.85 (s, 1H), 4.57 (d, 1H), 3.40 – 3.20 (m, 4H), 2.22 (d, $J = 4.4$ Hz, 1H), 1.71 (s, 6H), 1.64 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 145.5, 141.2, 140.6, 139.3, 137.1, 133.0, 130.5, 129.3, 127.7, 127.6, 127.1, 126.9, 126.6, 126.2, 122.9, 112.1, 69.3, 41.0, 31.3, 25.7, 22.7, 17.8;

IR (neat) cm$^{-1}$ 3345, 2925, 1484, 1260, 1013, 763;

HRMS (ESI-TOF, m/z) calcd for C$_{22}$H$_{26}$O (M+Na)$^+$: 329.1876, found 329.1875.

**Preparation of 5j**

![Chemical Structure of 5j]

**5j**: Using the same procedure as that used for **5a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in THF); 1 (33 mg, 0.1 mmol), 3-chloro-2-methylpropene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), t-BuOLi (0.2 mL, 1.0 M in THF), 3-bromo-1-(trimethylsilyl)-1-propyne (25 μL, 0.15 mmol) at room temperature for 1 h afforded **5j** (23 mg, 66% yield) as a colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 – 7.46 (m, 1H), 7.39 – 7.36 (m, 1H), 7.32 – 7.28 (m, 2H), 7.25 – 7.18 (m, 4H), 6.28 (d, $J = 4$ Hz, 1H), 4.87 (s, 1H), 4.60 (s, 1H), 3.62 (d, $J = 18.8$ Hz, 1H), 3.45 – 3.30 (m, 3H), 2.4 (d, $J = 4$ Hz, 1H), 1.71 (s, 3H), 0.17 (s, 9H);

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 145.6, 140.6, 140.4, 137.3, 133.8, 130.6, 129.0, 127.9,
127.8, 127.1, 126.9, 126.8, 112.3, 104.1, 87.7, 69.1, 41.0, 23.7, 22.7, 0.01;

IR (neat) cm\(^{-1}\) 3314, 2921, 2174, 1452, 1250, 1017, 842, 759;

HRMS (ESI-TOF, m/z) calcd for C\(_{23}\)H\(_{28}\)OSi (M+Na\(^+\)): 371.1802, found 371.1802.

**Preparation of 5k**

![Structure of 5k](image)

**5k:** Using the same procedure as that used for **5a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); \(t\)-BuOLi (0.15 mL, 1.0 M in THF); \(I\) (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 \(\mu\)L, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), \(t\)-BuOLi (0.2 mL, 1.0 M in THF), iodoethane (36 \(\mu\)L, 0.15 mmol) at room temperature for 1 h afforded **5k** (15 mg, 60% yield) as a colorless liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 – 7.34 (m, 1H), 7.29 – 7.26 (m, 1H), 7.24 – 7.16 (m, 6H), 6.27 (d, \(J = 4.4\) Hz, 1H), 6.02 – 5.92 (m, 1H), 5.10 – 4.98 (m, 2H), 3.45 – 3.43 (m, 2H), 2.68 – 2.50 (m, 2H), 2.03 (d, \(J = 4.4\) Hz, 1H), 1.16 (t, \(J = 7.6\) Hz, 3H);

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 141.6, 141.0, 140.1, 137.5, 137.3, 130.0, 128.6 127.8, 127.8, 127.1, 126.7, 126.6, 125.9, 116.0, 69.3, 36.8, 25.1, 14.9;

IR (neat) cm\(^{-1}\) 3289, 2964, 2924, 1638, 1452, 1260, 1016, 751;

HRMS (ESI-TOF, m/z) calcd for C\(_{18}\)H\(_{20}\)O (M+Na\(^+\)): 275.1406, found 275.1407.

**Preparation of 5l**

![Structure of 5l](image)

**5l:** Using the same procedure as that used for **5a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); \(t\)-BuOLi (0.15 mL, 1.0 M in THF); \(I\) (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 \(\mu\)L, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), \(t\)-BuOLi (0.2 mL, 1.0 M in THF), iodoethane (36 \(\mu\)L, 0.15 mmol) at room temperature for 1 h afforded **5l** (15 mg, 60% yield) as a colorless liquid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 – 7.34 (m, 1H), 7.29 – 7.26 (m, 1H), 7.24 – 7.16 (m, 6H), 6.27 (d, \(J = 4.4\) Hz, 1H), 6.02 – 5.92 (m, 1H), 5.10 – 4.98 (m, 2H), 3.45 – 3.43 (m, 2H), 2.68 – 2.50 (m, 2H), 2.03 (d, \(J = 4.4\) Hz, 1H), 1.16 (t, \(J = 7.6\) Hz, 3H);

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 141.6, 141.0, 140.1, 137.5, 137.3, 130.0, 128.6 127.8, 127.8, 127.1, 126.7, 126.6, 125.9, 116.0, 69.3, 36.8, 25.1, 14.9;
THF); 1 (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), t-BuOLi (0.2 mL, 1.0 M in THF), (bromomethyl)benzene (18 μL, 0.15 mmol) at room temperature for 1 h afforded S1 (20 mg, 59% yield) as a colorless solid. (mp. 64.5 °C – 65.3 °C)

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 7.33 - 7.26 \text{ (m, 4H), 7.23 - 7.09 \text{ (m, 9H), 6.27 \text{ (d, } J = 4.0 \text{ Hz, 1H), 5.87 - 5.76 \text{ (m, 1H), 5.00 - 4.84 \text{ (m, 2H), 4.03 \text{ (d, } J = 16 \text{ Hz, 1H), 3.98 \text{ (d, } J = 16 \text{ Hz, 1H), 3.22 - 3.12 \text{ (m, 2H), 1.93 \text{ (d, } J = 4.4 \text{ Hz, 1H);}} \]

\[ ^13C \text{ NMR (100 MHz, CDCl}_3 \delta 140.9, 140.5, 138.4, 137.5, 137.1, 130.8, 129.9, 128.7, 128.5, 127.8, 127.3, 126.9, 126.8, 126.5, 126.2, 116.0, 69.34, 38.6, 36.5; IR (neat) cm}^{-1} 3335, 2918, 2152, 1452, 1275, 1014, 763; \]

HRMS (ESI-TOF, m/z) calcd for C_{23}H_{22}O (M+Na)\(^+\): 337.1563, found 337.1560.

**Preparation of 5m**

\[
\begin{align*}
\text{Ph} & \\
\text{OH} & \\
\text{5m} & \\
\text{ } & \\
\text{ } & \\
\text{ } & \\
\end{align*}
\]

**5m**: Using the same procedure as that used for 5a: Cul (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in THF); 1 (33 mg, 0.1 mmol), 1-(p-Tosyloxy)-3-phenyl-2-propyne (29 mg, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), t-BuOLi (0.2 mL, 1.0 M in THF), 3-chloroprop-1-ene (15 μL, 0.15 mmol) at room temperature for 1 h afforded 5m (23 mg, 69% yield) as a yellow liquid.

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 7.47 - 7.28 \text{ (m, 7H), 7.23 - 7.08 \text{ (m, 6H), 6.12 \text{ (d, } J = 3.2 \text{ Hz, 1H), 5.79 - 5.69 \text{ (m, 1H), 5.07 \text{ (d, } J = 12.8 \text{ Hz, 1H), 4.93 - 4.90 \text{ (m, 1H), 4.82 - 4.72 \text{ (m, 2H), 3.24 - 3.05 \text{ (m, 2H), 2.04(d, } J = 3.6 \text{ Hz, 1H);}} \]

\[ ^13C \text{ NMR (100 MHz, CDCl}_3 \delta 141.6, 140.8, 137.3, 137.2, 136.0, 134.6, 130.7, 129.5, 128.5, 128.2, 127.9, 127.7, 127.5, 127.1, 127.1, 126.6, 126.4, 115.7, 106.0, 77.8, 69.6, \]
36.6, 29.7;

IR (neat) cm⁻¹ 3366, 2923, 2218, 1969, 1260, 915, 750;

HRMS (ESI-TOF, m/z) calcd for C₂₅H₂₂O (M+Na)⁺: 361.1563, found 361.1561.

2.4. Synthesis of 5n – 5q

**Preparation of 5n**

![Structure of 5n](image)

**5n**: To a solution of CuI (10 mg, 0.05 mmol) and phenanthroline (12 mg, 0.05 mmol) in DMF (1.0 mL) was slowly added t-BuOLi (0.15 mL, 1.0 M in THF) at 0 °C under argon atmosphere. The reaction mixture was stirred at room temperature for 10 min. Then 1 (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol) was added successively and kept stirring at room temperature for 0.5 h. Then TBAF (0.15 mL, 1.0 M in THF), CuI (10 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium (6 mg, 5 mol%), t-BuOLi (0. 2 mL, 1.0 M in THF), iodobenzene (17 μL, 0.15 mmol) were added successively. The resulted mixture was stirred at room temperature for 1 h. The reaction was quenched with sat. aq. NaCl (2 mL), extracted with EtOAc (3 × 5 mL) and washed with H₂O (3 × 3 mL). The combined organic layers were then dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 100:1→20:1) to afford 5n (20 mg, 65% yield) as a colorless liquid.

**¹H NMR (400 MHz, CDCl₃)** δ 7.54 – 7.29 (m, 9H), 7.23 – 7.05 (m, 4H), 6.01 (s, 1H), 5.60 – 5.50(m, 1H), 4.84 – 4.64(m, 2H), 2.95 – 2.85 (m, 2H), 2.09 (s, 1H);

**¹³C NMR (100 MHz, CDCl₃)** δ 141.6, 141.5, 140.7, 140.1, 137.2, 136.9, 130.1, 129.7, 129.3, 128.1, 127.7, 127.5, 127.5, 127.2, 126.7, 126.3, 115.5, 69.5, 36.4;
IR (neat) cm⁻¹ 3330, 2922, 2852, 1450, 1275, 1260, 1007, 750;

HRMS (ESI-TOF, m/z) calcd for C₂₂H₂₀O (M+Na)⁺: 323.1406, found 323.1405.

**Preparation of 5o**

![Structure of 5o](image)

**5o:** Using the same procedure as that used for **5n:** CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in THF); I (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), CuI (10 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium (6 mg, 5 mol%), t-BuOLi (0.2 mL, 1.0 M in THF), 4-iodotoluene (33 mg, 0.15 mmol) at room temperature for 1 h afforded **5o** (22 mg, 70% yield) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.52 (m, 1H), 7.42 – 7.31 (m, 3H), 7.23 – 7.17 (m, 7H), 7.08 – 7.06 (m, 1H), 6.02 (d, J = 3.6 Hz, 1H), 5.60 – 5.50 (m, 1H), 4.84 – 4.65 (m, 2H), 2.97 – 2.86 (m, 2H), 2.40 (s, 3H), 2.07 (d, J = 4.4 Hz, 1H);

¹³C NMR (100 MHz, CDCl₃) δ 141.6, 141.5, 140.2, 137.8, 137.2, 136.9, 136.9, 130.2, 129.6, 129.1, 128.8, 127.5, 127.5, 127.5, 126.6, 126.3, 115.5, 69.6, 36.4, 21.2;

IR (neat) cm⁻¹ 3336, 2922, 2852, 1668, 1450, 1275, 1007, 821, 751;

HRMS (ESI-TOF, m/z) calcd for C₂₃H₂₂O (M+Na)⁺: 337.1563, found 337.1559.

**Preparation of 5p**
5p: Using the same procedure as that used for 5n: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in THF); 1 (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), CuI (10 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium (6 mg, 5 mol%), t-BuOLi (0.2 mL, 1.0 M in THF), 1-(tert-butyl)-4-iodobenzene (27 μL, 0.15 mmol) at room temperature for 1 h afforded 5p (24 mg, 68% yield) as a colorless liquid.

1H NMR (400 MHz, CDCl3) δ 7.54 – 7.28 (m, 7H), 7.24 – 7.20 (m, 4H), 7.06 – 7.04 (m, 1H), 6.02 (s, 1H), 5.58 – 5.48 (m, 1H), 4.81 – 4.58 (m, 2H), 2.90 – 2.87 (m, 2H), 2.06 (s, 1H), 1.36 (s, 9H);

13C NMR (100 MHz, CDCl3) δ 150.1, 141.6, 140.3, 137.7, 137.3, 137.0, 130.1, 129.7, 128.9, 127.5, 127.5, 127.5, 126.7, 126.3, 125.0, 115.3, 69.5, 36.5, 34.5, 31.4, 29.7;

IR (neat) cm⁻¹ 3337, 3005, 2851, 1363, 1275, 1260, 764;

HRMS (ESI-TOF, m/z) calcd for C26H28O (M+Na)⁺: 379.2032, found 379.2030.

Preparation of 5q

5q: Using the same procedure as that used for 5n: CuI (10 mg, 0.05 mmol),
phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in THF); I (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), CuI (10 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium (6 mg, 5 mol%), t-BuOLi (0.2 mL, 1.0 M in THF), 4-iodobiphenyl (42 mg, 0.15 mmol) at room temperature for 1 h afforded 5q (28 mg, 74% yield) as a colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.60 – 7.51 (m, 4H), 7.46 – 7.44 (m, 1H), 7.41 – 7.37 (m, 3H), 7.31 – 7.22 (m, 7H), 7.15 – 7.13 (m, 1H), 7.10 – 6.98 (m, 1H), 5.99 (d, $J$= 4 Hz, 1H), 5.52 – 5.42 (m, 1H), 4.74 – 4.55 (m, 2H), 2.88 – 2.85 (m, 2H), 2.40 (d, $J$ = 4.4 Hz, 1H);

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 141.5, 141.2, 140.7, 140.2, 140.1, 139.7, 137.3, 136.9, 130.1, 129.7, 129.7, 128.8, 127.8, 127.6, 127.6, 127.4, 127.1, 126.8, 126.7, 126.4, 115.5, 69.6, 36.4;

IR (neat) cm$^{-1}$ 3365, 3006, 2920, 1478, 1006, 1260, 764;

HRMS (ESI-TOF, m/z) calcd for C$_{28}$H$_{24}$O (M+Na)$^+$: 399.1719, found 399.1714.

2.6. Synthesis of 5r-5t

**Preparation of 5r**

![Chemical structure of 5r](image)

5r: To a solution of CuI (10 mg, 0.05 mmol) and tetrakis(triphenylphosphine) palladium (6 mg, 5 mol%) in DMF (1.0 mL) was slowly added t-BuOLi (0.15 mL, 1.0 M in THF) at 0 °C under argon atmosphere. The reaction mixture was stirred at room temperature for 10 min. I (33 mg, 0.1 mmol), 4-iodoanisole (24 mg, 0.1 mmol) were added successively and kept stirring at room temperature for 1 h. Then TBAF (0.15 mL, 1.0 M in THF) was added slowly at 0 °C under argon atmosphere. The reaction mixture was stirred at room temperature for 1 h. Then 5r (28 mg, 74% yield) was isolated as a colorless liquid.
mL, 1.0 M in THF), t-BuOLi (0.2 mL, 1.0 M in THF), 3-chloroprop-1-ene (15 μL, 0.15 mmol) were added successively. The resulted mixture was stirred at room temperature for 1 h. The reaction was quenched with sat. aq. NaCl (2 mL), extracted with EtOAc (3 × 5 mL) and washed with H₂O (3 × 3 mL). The combined organic layers were then dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 100:1 → 20:1) to afford 5r (22 mg, 67% yield) as a white solid. (mp. 105.5°C – 106.3°C).

¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, J = 7.2 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.31 (t, J = 4.8 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.07 (d, J = 7.6 Hz, 1H), 6.91 (d, J = 8 Hz, 2H), 6.01 (s, 1H), 5.61 – 5.51 (m, 5H), 4.38 (d, J = 10 Hz, 1H), 4.68 (d, J = 16.8 Hz, 1H), 3.84 (s, 3H), 2.98 – 2.87 (m, 2H), 2.12 (s, 1H);

¹³C NMR (100 MHz, CDCl₃) δ 158.9, 141.5, 141.3, 140.2, 137.2, 136.9, 133.1, 130.4, 130.3, 129.7, 127.6, 127.5, 127.5, 127.4, 126.6, 126.3, 115.5, 113.6, 69.6, 55.3, 36.4;

IR (neat) cm⁻¹ 3367, 2917, 1611, 1515, 1480, 1178, 1036, 750;

HRMS (ESI-TOF, m/z) calcd for C₂₃H₂₂O₂ (M+Na)⁺: 353.1517, found 353.1509.

**Preparation of 5s**

![5s](image)

5s: Using the same procedure as that used for 5r: CuI (10 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium (6 mg, 5 mol%), DMF (1.0 mL); t-BuOLi (0.15 mL, 1.0 M in THF); I (33 mg, 0.1 mmol), 4-iodotoluene (22 mg, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), t-BuOLi (0.2 mL, 1.0 M in THF), 3-chloro-2-methylpropene (15 μL, 0.15 mmol) at room temperature for 1 h afforded 5s (21 mg, 64% yield) as a colorless liquid.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 – 7.17 (m, 11H), 7.06 – 7.03 (m, 1H), 6.01 (d, $J$ = 3.6 Hz, 1H), 4.64 (s, 1H), 4.28 (s, 1H), 2.86 (s, 2H), 2.38 (s, 3H), 2.14 (d, $J$ = 4 Hz, 1H), 1.44 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.3, 141.9, 141.5, 140.2, 137.8, 136.8, 136.8, 130.2, 130.1, 129.1, 128.8, 127.4, 127.4, 127.3, 126.9, 126.4, 111.8, 69.5, 40.3, 22.3, 21.1.

IR (neat) cm$^{-1}$ 3359, 3061, 3023, 2918, 1649, 1480, 1447, 1006, 750;

HRMS (ESI-TOF, m/z) calcd for C$_{24}$H$_{24}$O (M+Na)$^+$: 351.1719, found 351.1720.

**Preparation of 5t**

5t: Using the same procedure as that used for 5r: CuI (10 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium (6 mg, 5 mol%), DMF (1.0 mL); $\tau$-BuOLi (0.15 mL, 1.0 M in THF); 1 (33 mg, 0.1 mmol), 4-iodotoluene (22 mg, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), $\tau$-BuOLi (0.2 mL, 1.0 M in THF), cinnamyl chloride (21 $\mu$L, 0.15 mmol) at room temperature for 1 h afforded 5t (27 mg, 70% yield) as a colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67 – 7.65 (m, 1H), 7.38 – 7.22 (m, 8H), 7.20 – 7.10 (m, 8H), 6.07 (d, $J$ = 4 Hz, 1H), 5.96 – 5.92 (m, 1H), 5.85 – 5.78 (m, 1H), 3.03 – 3.00 (m, 1H), 2.39 (s, 2H), 2.11 (d, $J$ = 4 Hz, 1H);

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.7, 141.6, 140.1, 137.8, 137.4, 137.2, 137.0, 130.4, 130.3 129.8, 129.3, 129.0, 128.6, 128.3, 127.9, 127.6, 127.6, 127.5, 126.9, 126.3, 126.3, 126.0, 69.6, 35.6, 21.2;

IR (neat) cm$^{-1}$ 3359, 3024, 2851, 1516, 1480, 1262, 1007, 759;

HRMS (ESI-TOF, m/z) calcd for C$_{29}$H$_{28}$O (M+Na)$^+$: 413.1876, found 413.1877.
2.7. Synthesis of Diaryketones 8a-8c

**Preparation of 8a**

![Image of 8a]

**8a:** To a solution of 5k (13 mg, 0.05 mmol) in CH₂Cl₂ (1 mL) was added Dess-Martin periodinane (32 mg, 0.075 mmol) at room temperature. The reaction was stirred for 12 h before extraction with EtOAc (3 × 5 mL) and washing with H₂O (3 × 2 mL). The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 500:1→300:1) to afford 8a (12 mg, 94% yield) as a colorless liquid.

**1H NMR (400 MHz, CDCl₃) δ 7.46 – 7.28 (m, 5H), 7.24 – 7.17 (m, 3H), 6.03 – 5.92 (m, 1H), 5.05 – 5.00 (m, 2H), 3.64 – 3.62 (m, 2H), 2.86 – 2.80 (m, 2H), 1.23 (t, J = 7.6 Hz, 3H);**

**13C NMR (100 MHz, CDCl₃) δ 200.6, 144.6, 140.3, 139.0, 138.7, 137.2, 131.3, 131.2, 130.8, 130.7, 130.4, 129.9, 125.7, 125.2, 116.0, 37.6, 26.6, 15.9;**

**IR (neat) cm⁻¹ 3062, 2965, 2871, 1662, 1572, 1483, 1235, 1255, 924;**

**HRMS (ESI-TOF, m/z) calcd for C₁₉H₁₈O (M+Na)⁺: 273.1250, found 273.1240.**

**Preparation of 8b**

![Image of 8b]

**8b:** Using the same procedure as that used for 8a: 5s (17 mg, 0.05 mmol) and
Dess-Martin periodinane (32 mg, 0.075 mmol) in CH₂Cl₂ (1 mL) at room temperature for 12 h afforded 8b (16 mg, 96% yield) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.10 (m, 12H), 4.81 (s, 1H), 4.51 (s, 1H), 3.54 (s, 2H), 2.27 (s, 3H), 1.68 (s, 3H);

¹³C NMR (100 MHz, CDCl₃) δ 200.2, 145.1, 141.9, 140.4, 140.1, 138.2, 137.6, 136.8, 131.4, 131.2, 130.7, 130.6, 130.4, 129.6, 128.8, 128.6, 126.7, 125.3, 112.2, 41.0, 22.7, 21.0;

IR (neat) cm⁻¹ 3020, 2918, 2849, 1661, 1443, 931, 819, 757;

HRMS (ESI-TOF, m/z) calcd for C₂₄H₂₂O (M+Na)⁺: 349.1568, found 349.1560.

**Preparation of 8c**

8c: Using the same procedure as that used for 8a: 5t (20 mg, 0.05 mmol) and Dess-Martin periodinane (32 mg, 0.075 mmol) in CH₂Cl₂ (1 mL) at room temperature for 12 h afforded 8c (19 mg, 98% yield) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.52 (m, 2H), 7.42 – 7.39 (m, 2H), 7.35 – 7.27 (m, 4H), 7.22 – 7.10 (m, 6H), 7.06 – 7.00 (m, 3H), 6.42 (d, J = 16 Hz, 1H), 6.34 – 6.27 (m, 1H), 3.72 (d, J = 6.8 Hz, 2H), 2.23 (s, 3H);

¹³C NMR (100 MHz, CDCl₃) δ 200.4, 141.9, 141.0, 140.1, 137.8, 137.6, 137.6, 136.9, 131.4, 131.1, 130.7, 130.4, 130.3, 129.6, 129.3, 128.6, 128.7, 128.4, 127.0, 126.8, 126.1, 125.4, 36.8, 21.1;

IR (neat) cm⁻¹ 3057, 2850, 1660, 1446, 1107, 819, 766;

HRMS (ESI-TOF, m/z) calcd for C₂₉H₂₄O (M+Na)⁺: 411.1725, found 411.1722.
HTB-5-92_13C_CDCl3_2019-5-14

1

M$_3$Si OH SiMe$_3$

148.989
139.184
135.036
128.912
127.775
126.891

77.212
77.000
76.789
75.089

0.897
Me\[\text{OH SiMe}_3\]

3b

The spectrum shows multiple peaks at different ppm values. The peaks are labeled with corresponding chemical shifts. The structure 3b is indicated in the spectrum.
HTB-6-84_CDCl3_13C_2019-7-2

$\begin{align*}
\text{Me} & \quad \text{OH} & \quad \text{SiMe}_3 \\
\end{align*}$

$3b$
The given text is an NMR spectrum of a compound labeled as 3c. The spectrum shows peaks at various ppm values, corresponding to different chemical shifts. The peaks are labeled with their respective chemical shifts in ppm. The compound structure is also shown with labels for the atoms and functional groups.
HTB-7-113_CDCl3_13C_2019-8-1

Me₃Si

3f
5b

The chemical shifts (in ppm) are as follows:
- 137.270
- 130.471
- 129.958
- 128.292
- 127.746
- 127.904
- 127.615
- 126.598
- 126.654
- 126.992
- 127.156
- 127.746
- 128.292
- 129.958
- 130.471
- 133.293
- 137.270

The downfield regions are marked as follows:
- 36.668
- 37.879

The upfield regions are marked as follows:
- 36.668
- 37.879

The figure shows a spectrum with peaks at various chemical shifts, corresponding to different functional groups in the molecule 5b.
HTB-7-81_CDCi3_1H_2019-10-18

S69
HTB-7-95_CDCl3_1H_2019-10-15
HTB-6-71_CDC13_1H_2019-7-2

The diagram shows a 1H NMR spectrum with peaks at various ppm values. The chemical structure labeled as 3g is also depicted.

Key peaks:
- 9.22 ppm
- 8.01 ppm
- 7.547 ppm
- 7.427 ppm
- 7.414 ppm
- 7.330 ppm
- 7.276 ppm
- 7.254 ppm
- 7.230 ppm
- 7.150 ppm
- 6.853 ppm
- 6.047 ppm

Chemical shifts and integrals for various peaks are indicated on the spectrum.
HTB-7-3_CDCl3_1H_2019-7-12

[Chemical structure image]
HTB-7-1_CDC13_13C_2019-7-15

\[
\begin{array}{c}
\text{158.865} \\
\text{141.531} \\
\text{141.286} \\
\text{140.250} \\
\text{137.235} \\
\text{136.886} \\
\text{133.098} \\
\text{130.367} \\
\text{129.669} \\
\text{127.491} \\
\text{127.472} \\
\text{127.441} \\
\text{127.290} \\
\text{115.501} \\
\text{113.571} \\
\text{77.319} \\
\text{77.000} \\
\text{77.000} \\
\text{76.682} \\
\text{76.918} \\
\text{55.304} \\
\text{36.367}
\end{array}
\]

\[
\begin{array}{c}
\text{5r}
\end{array}
\]
HLY-2-86_CDC13_13C_2019-10-18

8a

[Chemical structure image]