Supporting Information

Direct Synthesis of Dialkylaryl-vinylsilane Derivatives: Metathesis of Dialkylaryl-isopropenylsilane and Its Application to Tetracyclic Silacycle Dye Synthesis

Shohei Yoshioka, Tsunayoshi Takehara, Tsuyoshi Matsuzaki, Takeyuki Suzuki, Hirofumi Tsujino, Tadayuki Uno, Yasuo Tsutsumi, Kenichi Murai, Hiromichi Fujioka, Mitsuhiro Arisawa*

Graduate School of Pharmaceutical Sciences, Osaka University
1-6 Yamada-oka, Suita, Osaka 565-0871, Japan
arisaw@phs.osaka-u.ac.jp

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General

$^1$H-NMR spectra were recorded in CDCl$_3$ at 25 °C unless otherwise noted, at 300, 400 or 500 MHz, with TMS as an internal standard. $^{13}$C-NMR spectra were recorded in CDCl$_3$ at 25 °C unless otherwise noted, at 300, 400 or 500MHz with TMS or CDCl$_3$ as an internal standard. $^{19}$F NMR spectra were recorded in CDCl$_3$ at 25 °C unless otherwise noted, at 470 MHz, with C$_6$F$_6$ as an internal standard.
1. Synthesis of Cross metathesis substrate 1

![Chemical Reaction Diagram]

To a solution of 2-bromonaphtalene (5.0 mmol, 1.035 g) in THF (0.5 M) was added dropwise 2.76 M n-BuLi (1.1 eq.) in n-hexane at -78 °C. After the mixture was stirred at -78 °C for 1 h, Me₂SiCl₂ (1.2 eq.) was added dropwise to the mixture. The reaction mixture was warmed to room temperature over 2 h. We call this reaction mixture, solution α.

On the other hand, to a solution of magnesium (3.0 eq.) in THF (0.2 M) was added dropwise a solution of 1-bromopropene in THF (0.2 M) at 50 °C for 3 h. We call this reaction mixture, solution β.

To a solution α was dropwisely added solution β at room temperature and heated to 50 °C for 3 h. After that, the reaction was quenched by the addition of 1M HCl aq. to the reaction mixture. The organic compound was extracted with CHCl₃. The organic layer was dried over Na₂SO₄, and the solvent was evaporated. The residue was subjected to column chromatography (only n-hexane) on silica gel 60N to give compound 1b (a colorless oil, E/Z = 7/2: 0.550 mmol, 124.6 mg, 11%).

1H-NMR (CDCl₃, 400 MHz) δ: 8.02 (1H, s), 7.86-7.81 (3H, m), 7.64-7.62 (1H, m), 7.49-7.46 (2H, m), 6.58 (1H, ddd, J = 14.0, 6.8, 1.8 Hz), 5.73 (1H, d, J = 14.0 Hz), 1.73 (3H, dd, J = 6.8, 1.8 Hz), 0.43 (6H, s).

13C-NMR (CDCl₃, 125 MHz) δ: 144.45, 136.83, 134.49, 133.79, 133.07, 130.37, 129.34, 128.18, 127.83, 127.01, 126.36, 125.96, 22.89. HRMS (MALDI-TOF) calcd for C₁₅H₁₈NaSi: 249.1070 ([M + Na]⁺), found 249.1074 ([M + Na]⁺).

1a (a yellow oil, quant. 1.06 g, 5.00 mmol) was prepared from 2-bromonaphtalene (1.04 g, 5.00 mmol) by the same procedure with 1b using dimethylvinylchlorosilane instead of dimethyldichlorosilane and Grignard reagent.

1H-NMR (CDCl₃, 300 MHz) δ: 8.04 (1H, s), 7.89-7.82 (3H, m), 7.62 (1H, dd, J = 8.0, 1.1 Hz), 7.52-7.48 (2H, m), 6.39 (1H, dd, J = 20.2, 14.7 Hz), 6.12 (1H, dd, J = 14.7, 3.7 Hz), 5.83 (1H, dd, J = 20.2, 3.7 Hz), 0.46 (6H, s).

13C-NMR (75 MHz, CHCl₃) δ: 137.98, 135.90, 134.54, 133.76, 133.14, 132.97, 130.18, 128.12, 127.77, 127.04, 126.39, 125.97. -2.79. HRMS (ESI) calcd for C₁₄H₁₈Si: 213.1100 ([M+H]⁺), found 213.1092 ([M+H]⁺).
1c (a colorless oil, 43%, 0.486 g, 0.215 mmol) was prepared from 2-bromonaphtalene (1.04 mg, 0.500 mmol) by the same procedure with 1b using 2-bromopropene instead of 1-bromopropene.

\[ \text{1H-NMR (CDCl}_3\text{, 500 MHz)} \delta: 8.12 \text{ (1H, s), } 7.94-7.91 \text{ (3H, m), } 7.69 \text{ (1H, dd, } J = 8.0, 1.1 \text{ Hz), } 7.57-7.56 \text{ (2H, m), } 5.83 \text{ (1H, s), } 5.50 \text{ (1H, s), } 0.55 \text{ (6H, s).} \]

\[ \text{13C-NMR (CDCl}_3\text{, 125 MHz)} \delta: 146.10, 135.56, 134.62, 133.81, 133.02, 130.28, 128.14, 127.79, 127.03, 126.82, 126.38, 125.94, 22.70, -3.35 \]

HRMS (ESI) calcd for C\text{15}H\text{18}NaSi: 249.1070 ([M+Na]\text{+}) found 249.1066 ([M+Na]\text{+})

2. Cross metathesis of compound 1b (general procedure A)

To a solution of 1b (1.0 mmol) in toluene (0.2 M) was added Grubbs II (3 x 3 mol%, every hour) and the mixture was refluxed for 3 h. The solvent was evaporated and the residue was subjected to column chromatography on neutral flash silica gel 60N to give 2a.

2a (a colorless oil, 85%, 24.5 mg, 0.850 mmol) was prepared from 1b (22.6 mg, 0.100 mmol) and styrene (104.2 mg, 1.00 mmol) by a general procedure A.

\[ \text{1H-NMR (CDCl}_3\text{, 400 MHz)} \delta: 8.07 \text{ (1H, s), } 7.86-7.82 \text{ (3H, m), } 7.65 \text{ (1H, dd, } J = 8.5, 1.2 \text{ Hz), } 7.50-7.46 \text{ (4H, m), } 7.37-7.32 \text{ (2H, m), } 7.29-7.26 \text{ (1H, m), } 6.99 \text{ (1H, d, } J = 19.5 \text{ Hz), } 6.66 \text{ (1H, d, } J = 19.5 \text{ Hz), } 0.52 \text{ (6H, s).} \]

\[ \text{13C-NMR (CDCl}_3\text{, 125 MHz)} \delta: 145.5, 138.2, 136.1, 134.6, 133.8, 133.0, 128.6, 128.3, 128.1, 127.8, 127.1, 126.61, 126.58, 126.4, 126.00, -2.4 \]

HRMS (ESI) calcd for C\text{20}H\text{20}Si: 311.1232 ([M+Na]\text{+}) found 311.1221 ([M+Na]\text{+})

2d (a colorless oil, 97%, 30.8 mg, 0.967 mmol) was prepared from 1b (22.6 mg, 0.100 mmol) and 2-vinylanisole (134.2 mg, 1.00 mmol) by a general procedure A.

\[ \text{1H-NMR (CDCl}_3\text{, 400 MHz)} \delta: 7.91 \text{ (1H, s), } 7.69-7.64 \text{ (3H, m), } 7.49 \text{ (1H, dd, } J = 8.1, 1.1 \text{ Hz), } 7.42 \text{ (1H, dd, } J = 7.8, 1.8 \text{ Hz), } 7.32-7.29 \text{ (3H, m), } 7.08-7.05 \text{ (1H, m), } 6.79 \text{ (1H, d, } J = 7.8 \text{ Hz), } 6.70 \text{ (1H, dd, } J = 8.1, 0.9 \text{ Hz), } 6.47 \text{ (1H, d, } J = 19.2 \text{ Hz), } 3.66 \text{ (3H, s), } 0.36 \text{ (6H, s).} \]

\[ \text{13C-NMR (CDCl}_3\text{, 125 MHz)} \delta: 156.8, 139.9, 136.6, 134.7, 133.8, 133.1, 130.4, 129.4, 128.2, 127.8, 127.4, 127.1, 126.5, 126.4, 126.0, 120.7, 111.1, 55.6, -2.2 \]

HRMS (MALDI-TOF) calcd for C\text{21}H\text{20}ONaSi: 341.1332 ([M+Na]\text{+}), found 341.1329 ([M+Na]\text{+}).
2c (a colorless oil, 84%, 26.8 mg, 0.842 mmol) was prepared from 1b (22.6 mg, 0.100 mmol) and 3-vinylanisole (134.2 mg, 1.00 mmol) by a general procedure A.

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 8.08 (1H, s), 7.88-7.84 (3H, m), 7.66 (1H, dd, $J = 8.2, 0.9$ Hz), 7.52-7.49 (2H, m), 7.27 (1H, dd, $J = 8.2, 8.2$ Hz), 7.08 (1H, d, $J = 8.0$ Hz), 7.02 (1H, dd, $J = 2.1, 2.1$ Hz), 6.97 (1H, d, $J = 19.0$ Hz), 6.84 (1H, dt, $J = 8.0, 1.4$ Hz), 6.66 (1H, d, $J = 19.0$ Hz), 3.83 (3H, s), 0.54 (6H, s).

$^{13}$C-NMR (CDCl$_3$, 125 MHz) $\delta$: 156.0, 145.4, 139.7, 136.0, 133.8, 132.9, 131.2, 130.4, 128.2, 127.9, 127.1, 126.5, 126.0, 119.4, 114.3, 111.4, 55.3. -2.4 HRMS (MALDI-TOF) calcd for C$_{21}$H$_{22}$OSi: 318.1434 ([M+H]$^+$), found 318.1435 ([M+H]$^+$).

2d (a colorless oil, 90%, 28.7 mg, 0.901 mmol) was prepared from 1b (22.6 mg, 0.100 mmol) and 4-vinylanisole (134.2 mg, 1.00 mmol) by a general procedure A.

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 8.09 (1H, s), 7.89-7.84 (3H, m), 7.67 (1H, dd, $J = 8.2, 0.9$ Hz), 7.52-7.49 (2H, m), 7.45-7.42 (2H, m), 6.96 (1H, d, $J = 19.2$ Hz), 6.91-6.87 (2H, m), 6.51 (1H, d, $J = 19.2$ Hz), 3.83 (3H, s), 0.53 (6H, s). $^{13}$C-NMR (CDCl$_3$, 125 MHz) $\delta$: 159.8, 145.0, 136.4, 134.6, 133.8, 133.0, 131.2, 130.4, 128.2, 127.9, 127.1, 126.4, 126.0, 124.2, 114.0, 55.4. -2.2 HRMS (MALDI-TOF) calcd for C$_{21}$H$_{22}$OSi: 318.1434 ([M+H]$^+$), found 318.1432 ([M+H]$^+$).

2e (a colorless oil, 52%, 16.9 mg, 0.0523 mmol) was prepared from 1b (22.6 mg, 0.100 mmol) and 4-chlorostyrene (138.6 mg, 1.00 mmol) by a general procedure A.

$^1$H-NMR (CDCl$_3$, 500 MHz) $\delta$: 8.09 (1H, s), 7.88-7.83 (3H, m), 7.68-7.65 (2H, m), 7.51-7.49 (2H, m), 7.45 (1H, d, $J = 18.9$ Hz), 7.37 (1H, d, $J = 7.8$ Hz), 7.25 (1H, dd, $J = 7.8, 7.8$ Hz), 7.22-7.19 (1H, m), 6.67 (1H, d, $J = 18.9$ Hz), 0.56 (6H, s). $^{13}$C-NMR (CDCl$_3$, 125 MHz) $\delta$: 141.3, 136.3, 135.8, 134.6, 133.8, 133.3, 133.0, 130.8, 130.2, 129.8, 129.1, 128.2, 127.8, 127.2, 126.9, 126.5, 126.3, 126.0, -2.4 HRMS (MALDI-TOF) calcd for C$_{20}$H$_{19}$NaSiCl: 345.0837 ([M+Na]$^+$), found 345.0823 ([M+Na]$^+$).

2f (a colorless oil, 63%, 20.2 mg, 0.0626 mmol) was prepared from 1b (22.6 mg, 0.100 mmol) and 4-chlorostyrene (138.6 mg, 1.00 mmol) by a general procedure A.

$^1$H-NMR (CDCl$_3$, 500 MHz) $\delta$: 8.06 (1H, s), 7.85-7.84 (3H, m), 7.64-7.62 (1H, m), 7.51-7.49 (2H, m), 7.47-7.45 (1H, m), 7.32-7.31 (1H, m), 7.28-7.22 (2H, m), 6.90
(1H, d, J = 19.5 Hz), 6.68 (1H, d, J = 18.9 Hz), 0.53 (6H, s). $^{13}$C-NMR (CDCl$_3$, 125 MHz \(\delta\): 144.0, 140.1, 135.6, 134.7, 133.8, 133.0, 130.2, 129.8, 129.2, 128.15, 128.13, 127.8, 127.2, 126.5, 126.1, 124.9, -2.5. HRMS (MALDI-TOF) calcd for C$_{20}$H$_{19}$SiCl: 322.0939 ([M+H$^+$]), found 322.0934 ([M+H$^+$]).

2g (a colorless oil, 69%, 22.3 mg, 0.0691 mmol) was prepared from 1b (22.6 mg, 0.100 mmol) and 4-chlorostyrene (138.6 mg, 1.00 mmol) by a general procedure A.

$^1$H-NMR (CDCl$_3$, 400 MHz \(\delta\): 8.08 (1H, s), 7.89-7.84 (3H, m), 7.65 (1H, d, \(J = 7.9\) Hz), 7.52-7.50 (2H, m), 7.40 (2H, d, \(J = 8.6\) Hz), 7.31 (2H, d, \(J = 8.6\) Hz), 6.93 (1H, d, \(J = 19.2\) Hz), 6.64 (1H, d, \(J = 19.2\) Hz), 0.54 (6H, s). $^{13}$C-NMR (CDCl$_3$, 100 MHz \(\delta\): 144.1, 136.7, 135.7, 134.6, 133.9, 133.8, 133.0, 130.2, 128.8, 128.14, 128.09, 127.80, 127.76, 127.2, 126.5, 126.1, -2.4. HRMS (ESI) calcd for C$_{20}$H$_{19}$ClSi: 345.0842 ([M+Na$^+$]), found 345.0833 ([M+Na$^+$]).

2h (a colorless oil, 88%, 30.5 mg) was prepared from 1b (22.6 mg, 0.100 mmol) and 4-acetoxy styrene (162.2 mg, 1.00 mmol) by a general procedure A.

$^1$H-NMR (CDCl$_3$, 400 MHz \(\delta\): 8.06 (1H, s), 7.85-7.84 (3H, m), 7.64 (1H, d, \(J = 8.0\) Hz), 7.49-7.48 (4H, m), 7.07 (2H, d, \(J = 8.7\) Hz), 6.96 (1H, d, \(J = 19.0\) Hz), 6.61 (1H, d, \(J = 19.0\) Hz), 2.30 (3H, s), 0.52 (6H, s). $^{13}$C-NMR (CDCl$_3$, 100 MHz \(\delta\): 197.76, 144.21, 142.54, 136.51, 135.42, 134.69, 133.85, 133.00, 131.24, 130.17, 128.82, 128.14, 127.81, 127.21, 126.69, 126.57, 126.10, 26.75, -2.5. HRMS (ESI) calcd for C$_{22}$H$_{22}$NaO$_2$Si: 369.1281 ([M+Na$^+$]) found 369.1281 ([M+Na$^+$]).

2i (a pale yellow oil, 43%, 14.2 mg) was prepared from 1b (22.6 mg, 0.100 mmol) and 4-acetylstyrene (146.2 mg, 1.00 mmol) by a general procedure A.

$^1$H-NMR (CDCl$_3$, 400 MHz \(\delta\): 8.06 (1H, s), 7.94-7.91 (2H, m), 7.85-7.84 (4H, m), 7.07 (2H, d, \(J = 8.4\) Hz), 7.54-7.48 (4H, m), 7.00 (1H, d, \(J = 19.0\) Hz), 6.81 (1H, d, \(J = 19.0\) Hz), 2.60 (3H, s), 0.53 (6H, s). $^{13}$C-NMR (CDCl$_3$, 100 MHz \(\delta\): 197.76, 144.21, 142.54, 136.51, 135.42, 134.69, 133.85, 133.00, 131.24, 130.17, 128.82, 128.14, 127.81, 127.21, 126.69, 126.57, 126.10, 26.75, -2.5. HRMS (ESI) calcd for C$_{22}$H$_{22}$NaO$_2$Si: 353.1332 ([M+Na$^+$]) found 353.1331 ([M+Na$^+$]).
2j (a pale yellow oil, 51%, 17.7 mg) was prepared from 1b (22.6 mg, 0.100 mmol) and 4-(Methoxycarbonyl)styrene (162.2 mg, 1.00 mmol) by a general procedure A.

$^{1}$H-NMR (CDCl$_3$, 500 MHz) $\delta$: 8.07 (1H, s), 8.02-8.00 (2H, m), 7.86-7.85 (3H, m), 7.64 (1H, d, $J = 8.2$ Hz), 7.52-7.49 (4H, m), 7.00 (1H, d, $J = 18.9$ Hz), 6.80 (1H, d, $J = 18.9$ Hz), 3.92 (3H, s), 0.54 (6H, s).

$^{13}$C-NMR (CDCl$_3$, 125 MHz) $\delta$: 166.97, 144.35, 142.40, 135.47, 134.68, 133.85, 133.00, 130.87, 130.18, 129.99, 129.54, 128.15, 127.81, 127.20, 126.55, 126.50, 126.08, 52.18, -2.50 HRMS (ESI) calcd for C$_{22}$H$_{22}$NaO$_2$Si: 369.1276 ([M+Na$^+$]$^+$) found 369.1278 ([M+Na$^+$]$^+$)

2k (a pale yellow oil, 35%, 11.7 mg) was prepared from 1b (22.6 mg, 0.100 mmol) and 4-nitrostyrene (162.2 mg, 1.00 mmol) by a general procedure A.

$^{1}$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 8.21-8.18 (2H, m), 8.06 (1H, s), 7.86-7.84 (3H, m), 7.63 (1H, dd, $J = 8.3$, 0.9 Hz), 7.58-7.56 (2H, m), 7.52-7.49 (2H, m), 7.00 (1H, d, $J = 18.8$ Hz), 6.87 (1H, d, $J = 18.8$ Hz), 0.55 (6H, s).

$^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$: 147.32, 144.19, 142.96, 134.90, 134.74, 133.94, 133.90, 133.00, 130.06, 128.14, 127.83, 127.33, 127.16, 126.68, 126.18, 124.06, -2.61 HRMS (ESI) calcd for C$_{20}$H$_{19}$NNaO$_2$Si: 356.1075 ([M+Na$^+$]$^+$) found 356.1075 ([M+Na$^+$]$^+$)

2l (a pale yellow oil, 59%, 23.8 mg) was prepared from 1b (22.6 mg, 0.100 mmol) and 4-((tert-butoxycarbonylamino)styrene (219.3 mg, 1.00 mmol) by a general procedure A.

$^{1}$H-NMR (CDCl$_3$, 500 MHz) $\delta$: 8.06 (1H, s), 7.84-7.83 (3H, m), 7.64 (1H, d, $J = 8.3$ Hz), 7.50-7.47 (2H, m), 7.40 (2H, d, $J = 8.6$ Hz), 7.33 (2H, d, $J = 8.6$ Hz), 6.92 (1H, d, $J = 19.2$ Hz), 6.53 (1H, d, $J = 19.2$ Hz), 6.53 (1H, br s), 0.51 (6H, s).

$^{13}$C-NMR (CDCl$_3$, 125 MHz) $\delta$: 152.62, 144.88, 138.37, 136.22, 134.61, 133.79, 133.21, 133.00, 130.32, 128.15, 127.78, 127.34, 127.06, 126.39, 125.96, 125.22, 118.33, 80.74, 28.41, -2.33 HRMS (ESI) calcd for C$_{25}$H$_{30}$NNaO$_2$Si: 426.1865 ([M+Na$^+$]$^+$) found 426.1850 ([M+Na$^+$]$^+$)
3. Synthesis of ring-closing metathesis substrate 3 (general procedure B)

To a solution of MePPh$_3$Br (1.0 eq.) in THF (0.5 M) was dropwise 2.76 M solution of n-BuLi (1.0 eq.) in n-hexane at 0 °C to room temperature over a period of 2 h. After that, a solution of an o-bromobenzaldehyde derivative (1.0 eq.) was added to the reaction mixture at 0 °C and warmed to room temperature. After stirring for 2 h, the reaction was stopped by the addition of 1 M HCl aq. to the reaction mixture. The organic compound was extracted with CHCl$_3$. The organic layer was dried over Na$_2$SO$_4$, and the solvent was evaporated. The residue was subjected to column chromatography (only n-hexane) on silica gel 60N to give an o-bromostyrene derivative.

To a solution of the o-bromostyrene derivative in THF (0.5 M) was added dropwise 2.76 M solution of n-BuLi (1.1 eq.) in n-hexane at -78 °C. After the mixture was stirred at -78 °C for 1 h, the mixture was added dropwise to a solution of Me$_2$SiCl$_2$ (1.2 eq.) in THF (2 M). The reaction mixture was warmed to room temperature over 2 h. We call this reaction mixture, solution $\alpha$.

On the other hand, to a mixture of magnesium (3.0 eq.) in THF (0.2 M) was added dropwise a solution of 1-bromopropene in THF (0.2 M) at 50 °C for 3 h. We call this reaction mixture, solution $\beta$.

To the solution $\alpha$ was dropped added the solution $\beta$ at room temperature and the reaction mixture was heated to 50 °C for 3 h. After that, the reaction was stopped by the addition of 1M HCl aq. to the reaction mixture. The organic compound was extracted with CHCl$_3$. The organic layer was dried over Na$_2$SO$_4$, and the solvent was evaporated. The residue was subjected to column chromatography (only n-hexane) on silica gel to give compound 3.

3a (a colorless oil, $E/Z = 4/1$, 64%, 743 mg, 3.20 mmol) was prepared from 2-bromo-5-methoxybenzaldehyde (1.08 g, 5.00 mmol) by a general procedure B.

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 7.48 (1H, d, $J = 7.9$ Hz), 7.11 (1H, dd, $J = 2.4$, 2.4 Hz), 7.05 (1H, dd, $J = 17.1$, 11.0 Hz), 6.82 (1H, dd, $J = 7.9$, 2.4 Hz), 6.48 (1H, dq, $J = 14.0$, 7.0 Hz), 5.70 (1H, dq, $J = 14.0$, 1.5 Hz), 5.63 (1H, dd, $J = 17.1$, 1.2 Hz), 5.25 (1H, dd, $J = 10.4$, 1.2 Hz), 3.84 (3H, s), 1.66 (3H, dd, $J = 7.0$, 1.5 Hz), 0.40 (6H, s). $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$: 160.7, 145.4, 144.4, 138.1, 136.1, 130.2, 129.1, 114.9, 112.6, 110.7, 55.1, 19.1, 0.0. HRMS (ESI) calcd for C$_{14}$H$_{20}$OSi: 255.1181 ([M+Na$^+$]) found 255.1170 ([M+Na$^+$]).
3b (a colorless oil, $E/Z = 18/1$, a colorless oil, 23%, 268 mg, 1.15 mmol) was prepared from 2-bromo-6-methoxybenzaldehyde (1.08 g, 5.00 mmol) by a general procedure B.

$^1$H-NMR (CDCl$_3$, 400 MHz) δ: 7.22 (1H, dd, $J = 9.0, 7.3$ Hz), 7.15 (1H, dd, $J = 7.3, 1.2$ Hz), 6.94 (1H, dd, $J = 9.0, 1.2$ Hz), 6.89 (1H, dd, $J = 17.7, 11.6$ Hz), 6.11 (1H, dq, $J = 18.3, 6.1$ Hz), 5.84 (1H, dd, $J = 18.3, 1.8$ Hz), 5.77 (1H, dd, $J = 17.7, 2.4$ Hz), 5.47 (1H, dd, $J = 11.6, 2.4$ Hz), 5.34 (3H, s), 1.84 (3H, dd, $J = 6.1, 1.8$ Hz), 0.36 (6H, s).

$^{13}$C-NMR (CDCl$_3$, 100 MHz) δ: 157.5, 143.4, 139.9, 134.8, 132.6, 130.4, 127.5, 127.3, 119.6, 112.1, 55.4, 22.8, -0.7.

HRMS (ESI) calcd for C$_{14}$H$_{20}$OSi: 255.1181 ([M+Na]$^+$) found 255.1174 ([M+Na]$^+$)

3c (a colorless oil, $E/Z = 1.8/1$, 46%, 533 mg, 2.29 mmol) was prepared from 2-bromo-4-methoxybenzaldehyde (1.08 g, 5.00 mmol) by a general procedure B.

$^1$H-NMR (CDCl$_3$, 400 MHz) δ: 7.55 (1H, d, $J = 8.5$ Hz), 7.12 (1H, d, $J = 2.7$ Hz), 7.01 (1H, dd, $J = 17.4, 11.0$ Hz), 6.90 (1H, dd, $J = 8.5, 2.7$ Hz), 6.51 (1H, dq, $J = 13.8, 6.8$ Hz), 5.71 (1H, dd, $J = 13.8, 1.2$ Hz), 5.54 (1H, dd, $J = 17.4, 1.2$ Hz), 5.14 (1H, dd, $J = 11.0, 1.2$ Hz), 3.8 (3H, s), 1.68 (3H, dd, $J = 6.8, 1.6$ Hz), 0.44-0.38 (6H, m). $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ: 158.6, 144.9, 139.6, 137.7, 136.5, 128.7, 126.5, 120.4, 114.4, 112.4, 55.4, 19.4, -0.1.

HRMS (ESI) calcd for C$_{14}$H$_{20}$OSi: 233.1362 ([M+H]$^+$) found 233.1358 ([M+H]$^+$)

3d (a colorless oil, $E/Z = 11/5$, 40%, 158 mg, 0.679 mmol) was prepared from 2-bromo-3-methoxybenzaldehyde (538 mg, 2.50 mmol) by a general procedure B (2-bromo-3-methoxybenzaldehyde was synthesized from 2-bromo-3-hydroxybenzaldehyde by method of previous report$^1$).

$^1$H-NMR (CDCl$_3$, 500 MHz) δ: 7.31 (1H, dd, $J = 8.0, 7.6$ Hz), 7.15 (1H, d, $J = 7.6$ Hz), 7.11 (1H, dd, $J = 16.0, 10.7$ Hz), 6.77 (1H, d, $J = 8.0$ Hz), 6.09 (1H, dq, $J = 18.3, 6.1$ Hz), 5.94 (1H, d, $J = 18.3$ Hz), 5.53 (1H, dd, $J = 16.0, 1.5$ Hz), 5.20 (1H, dd, $J = 10.7, 1.5$ Hz), 3.79 (3H, s), 1.84 (3H, dd, $J = 6.1, 1.6$ Hz), 0.42 (6H, s). $^{13}$C-NMR (CDCl$_3$, 125 MHz) δ: 164.79, 146.29, 141.51, 139.80, 132.33, 131.45, 130.53, 125.00, 119.55, 115.02, 109.25, 55.28, 22.69, 0.90. HRMS (APCI) calcd for C$_{14}$H$_{20}$OSi: 233.1356 ([M+H]$^+$) found 233.1352 ([M+H]$^+$)

Ref. 1) Guoqing Zhao, Guangqing Xu, Chao Qian and Wenjun Tan J. Am. Chem. Soc. 2017, 139, 3360-3363
3e (a colorless oil, E/Z = 12/1, 15%, 178 mg, 0.753 mmol) was prepared from 2-bromo-6-chlorobenzaldehyde (1.10 g, 5.00 mmol) by a general procedure B. 

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 7.43 (1H, d, $J = 7.3$ Hz), 7.38 (1H, d, $J = 8.0$ Hz), 7.17 (1H, dd, $J = 8.0, 7.3$ Hz), 6.65 (1H, dd, $J = 17.1, 11.5$ Hz), 6.07 (1H, dq, $J = 18.3, 6.1$ Hz), 5.80 (1H, dq, $J = 18.3, 1.3$ Hz), 5.56 (1H, dd, $J = 11.5, 1.3$ Hz), 5.45 (1H, dd, $J = 17.1, 1.3$ Hz), 1.84 (3H, dd, $J = 6.1, 1.3$ Hz), 0.33 (6H, s).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 143.7, 140.5, 135.9, 133.6, 133.1, 130.4, 130.4, 130.2, 127.5, 121.5, 22.8, -0.7.

HRMS (ESI) calcd for C$_{13}$H$_{17}$ClSi: 259.0686 ([M+Na$^+$]$^+$) found 259.0685 ([M+Na$^+$]$^+$)

3f (a colorless oil, E/Z = 1/1, 21%, 250 mg, 1.05 mmol) was prepared from 2-bromo-5-chlorobenzaldehyde (1.10 g, 5.00 mmol) by a general procedure B.

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 7.53 (1H, d, $J = 2.3$ Hz), 7.48 (1H, d, $J = 8.0$ Hz), 7.22 (1H, dd, $J = 8.0, 2.3$ Hz), 7.05 (1H, dd, $J = 8.0, 8.0$ Hz), 6.50 (1H, dq, $J = 14.0, 6.7$ Hz), 5.69 (1H, dq, $J = 14.0, 1.4$ Hz), 5.66 (1H, dd, $J = 4.0, 1.3$ Hz), 1.65 (3H, dd, $J = 6.7, 1.4$ Hz), 0.36 (6H, s). $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$: 145.5, 145.1, 137.1, 136.3, 136.0, 135.8, 128.2, 126.8, 125.2, 116.0, 22.8, -0.3. HRMS (ESI) calcd for C$_{13}$H$_{17}$ClSi: 259.0686 ([M+Na$^+$]$^+$) found 259.0681 ([M+Na$^+$]$^+$)

3g (a colorless oil, only E, 20%, 234mg, 0.99 mmol) was prepared from 2-bromo-4-chlorobenzaldehyde (1.10 g, 5.00 mmol) by a general procedure B.

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 7.51 (1H, d, $J = 1.8$ Hz), 7.41 (1H, d, $J = 7.9$ Hz), 7.20 (1H, dd, $J = 7.9, 1.8$ Hz), 7.02 (1H, dd, $J = 17.4, 11.0$ Hz), 6.12 (1H, dq, $J = 18.3, 6.1$ Hz), 5.81 (1H, dq, $J = 18.3, 1.8$ Hz), 5.63 (1H, d, $J = 17.4$ Hz), 5.29 (1H, d, $J = 11.0$ Hz), 1.85 (3H, dd, $J = 6.1, 1.8$ Hz), 0.34 (6H, s). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 145.7, 144.4, 137.2, 136.3, 135.8, 135.5, 129.3, 126.8, 125.2, 116.0, 22.8, -1.3. HRMS (ESI) calcd for C$_{13}$H$_{17}$ClSi: 259.0686 ([M+Na$^+$]$^+$) found 259.0681 ([M+Na$^+$]$^+$)

3h (a colorless oil, E/Z = 1.8/1, 34%, 378 mg, 1.72 mmol) was prepared from 2-bromo-6-fluorobenzaldehyde (1.01 g, 5.00 mmol) by a general procedure B.

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 7.30-7.28 (1H, m), 7.19-7.17 (1H, m), 7.10-7.05 (1H, m), 6.80 (1H, dd, $J = 18.0, 11.9$ Hz), 6.16-6.10 (1H, m), 5.85-5.77 (2H, m), 5.55-5.52 (1H, m), 1.85 (3H, dd, $J = 6.4, 1.5$ Hz), 0.37 (6H, s). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 161.1 ($J = 251$ Hz), 144.5 ($J = 60$ Hz), 132.1, 130.6 ($J = 20$ Hz), 130.6 ($J = 7$ Hz), 129.5, 128.4, 127.8 ($J = 3$ Hz), 120.6 ($J = 11$ Hz), 117.1 ($J = 23$ Hz), 22.8, -1.1 $^{19}$F-NMR (CDCl$_3$, 376 MHz) $\delta$: -110.2 (m) HRMS (ESI) calcd for C$_{13}$H$_{17}$FSi: 243.0981 ([M+Na$^+$]$^+$) found 243.0971 ([M+Na$^+$]$^+$)
3i (a colorless oil, E/Z = 20/1, 49%, 542 mg, 2.46 mmol) was prepared from 2-bromo-5-fluorobenzaldehyde (1.01 g, 5.00 mmol) by a general procedure B.

\[ \text{H-NMR (CDCl}_3, 400 \text{ MHz}) \delta: 7.29 (1\text{H, d, } J = 7.6 \text{ Hz}), 7.21-7.17 (1\text{H, m}), 7.07 (1\text{H, dd, } J = 11.6, 7.6 \text{ Hz}), 6.80 (1\text{H, dd, } J = 17.8, 12.3 \text{ Hz}), 6.13 (1\text{H, dq, } J = 12.0, 6.1 \text{ Hz}), 5.81 (2\text{H, dd, } J = 17.8, 12.3 \text{ Hz}), 5.53 (1\text{H, dq, } J = 12.0, 1.8 \text{ Hz}), 1.85 (3\text{H, dd, } J = 6.1, 1.8 \text{ Hz}), 0.39 (6\text{H, s}). \]

\[ \text{C-NMR (CDCl}_3, 100 \text{ MHz}) \delta: 162.3 (J = 250 \text{ Hz}), 144.2, 141.1, 132.1, 130.6 (J = 20 \text{ Hz}), 130.6 (J = 7 \text{ Hz}), 129.5, 127.8 (J = 8 \text{ Hz}), 120.6 (J = 11 \text{ Hz}), 117.1 (J = 23 \text{ Hz}), 22.8, -1.1 \text{F-NMR (CDCl}_3, 376 \text{ MHz}) \delta: -110.2 \text{ (m). HRMS (ESI) calcd for C}_{13}\text{H}_{17}\text{FSi: 243.0981 ([M+Na]}^+ \text{ found 243.0973 ([M+Na]}^+ \text{).} \]

3j (a colorless oil, E/Z = 4/1, 49%, 542 mg, 2.46 mmol) was prepared from 2-bromo-4-fluorobenzaldehyde (1.01 g, 5.00 mmol) by a general procedure B.

\[ \text{H-NMR (CDCl}_3, 400 \text{ MHz}) \delta: 7.73-7.71 (1\text{H, m}), 7.44-7.36 (1\text{H, m}), 7.26-7.19 (2\text{H, m}), 6.34 (1\text{H, dq, } J = 18.3, 6.1 \text{ Hz}), 6.02 (1\text{H, dd, } J = 18.3, 1.5 \text{ Hz}), 5.75 (1\text{H, d, } J = 18.3 \text{ Hz}), 5.42 (1\text{H, d, } J = 11.0 \text{ Hz}), 2.06 (3\text{H, dd, } J = 6.1, 1.5 \text{ Hz}), 0.56 (6\text{H, d, } J = 3.7 \text{ Hz}). \]

\[ \text{C-NMR (CDCl}_3, 100 \text{ MHz}) \delta: 162.0 (J = 247 \text{ Hz}), 144.6, 140.2 (J = 4 \text{ Hz}), 137.2, 129.1, 127.9, 127.0 (J = 7 \text{ Hz}), 121.1 (J = 19 \text{ Hz}), 116.2 (J = 21 \text{ Hz}), 114.5, 22.8, -1.5 \text{F-NMR (CDCl}_3, 376 \text{ MHz}) \delta: -110.0 \text{ (m). HRMS (ESI) calcd for C}_{13}\text{H}_{17}\text{FSi: 243.0981 ([M+Na]}^+ \text{ found 243.0973 ([M+Na]}^+ \text{).} \]

4. Ring-closing metathesis of 3 (general procedure C)

To a solution of 14 in CHCl\text{3} (0.005 M) was added Grubbs II (5 mol\%) and the mixture was refluxed for 2 h. The solvent was evaporated and the residue was subjected to column chromatography on neutral flash silica gel 60N to give 15.

4a (a colorless oil, quant, 19.0 mg, 0.0998 mmol) was prepared from 3a (23.2 mg, 0.100 mmol) by a general procedure C.

\[ \text{H-NMR (CDCl}_3, 400 \text{ MHz}) \delta: 7.47 (1\text{H, d, } J = 7.8 \text{ Hz}), 7.32 (1\text{H, d, } J = 10.1 \text{ Hz}), 6.88 (1\text{H, s}), 6.80 (1\text{H, dd, } J = 7.8, 1.0 \text{ Hz}), 6.36 (1\text{H, dd, } J = 10.1, 1.0 \text{ Hz}), \]
3.84 (3H, s), 0.35 (6H, s). $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ: 161.6, 151.4, 148.8, 134.2, 132.7, 129.0, 111.9, 110.9, 55.3, -3.7. HRMS (ESI) calcd for C$_{11}$H$_{14}$OSi: 213.0712 ([M+Na]$^+$) found 213.0703 ([M+Na]$^+$)

4b: (a colorless oil, 35%, 6.6 mg, 0.0348 mmol) was prepared from 3b (23.2 mg, 0.100 mmol) by a general procedure C.

$^1$H-NMR (CDCl$_3$, 500 MHz) δ: 7.67 (1H, d, J = 10.3 Hz), 7.22 (1H, dd, J = 8.0, 6.9 Hz), 7.12 (1H, d, J = 6.9 Hz), 6.87 (1H, d, J = 8.0 Hz), 6.19 (1H, d, J = 10.3 Hz), 3.85 (3H, s), 0.31 (6H, s). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ: 154.31, 143.93, 140.55, 137.02, 130.66, 128.51, 123.88, 112.49, 55.43, -3.96.

HRMS (APCI) calcd for C$_{11}$H$_{14}$OSi: 191.0887 ([M+H]$^+$) found 191.0885 ([M+H]$^+$)

4c: (a colorless oil, quant, 19.0 mg, 0.100 mmol) was prepared from 3c (23.2 mg, 0.100 mmol) by a general procedure C.

$^1$H-NMR (CDCl$_3$, 400 MHz) δ: 7.32 (1H, d, J = 10.3 Hz), 7.19 (1H, d, J = 8.1 Hz), 7.12 (1H, d, J = 2.4 Hz), 6.83 (1H, dd, J = 8.1, 2.4 Hz), 6.12 (1H, d, J = 10.3 Hz), 3.84 (3H, s), 0.33 (6H, s). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ: 159.1, 148.8, 142.2, 140.8, 129.7, 124.8, 118.4, 113.8, 55.5, -3.7. HRMS (APCI) calcd for C$_{11}$H$_{14}$OSi: 191.0887 ([M+H]$^+$) found 191.0885 ([M+H]$^+$)

4d: (a colorless oil, 63%, 14.6 mg, 0.0626 mmol) was prepared from 3d (23.3 mg, 0.100 mmol) by a general procedure C.

$^1$H-NMR (CDCl$_3$, 500 MHz) δ: 7.28 (1H, dd, J = 7.5, 7.5 Hz), 7.23 (1H, d, J = 10.8 Hz), 6.86 (1H, d, J = 7.5 Hz), 6.70 (1H, d, J = 7.5 Hz), 6.22 (1H, d, J = 10.8 Hz), 3.79 (3H, s), 0.32 (6H, s). $^{13}$C-NMR (CDCl$_3$, 125 MHz) δ: 163.15, 151.04, 148.31, 133.44, 132.00, 117.49, 109.41, 55.37, -4.41. HRMS (APCI) calcd for C$_{11}$H$_{14}$OSi: 191.0887 ([M+H]$^+$) found 191.0885 ([M+H]$^+$)

4e: (a colorless oil, 25%, 4.9 mg, 0.0252 mmol) was prepared from 3e (23.7 mg, 0.100 mmol) by a general procedure C.

$^1$H-NMR (CDCl$_3$, 300 MHz) δ: 7.65 (1H, d, J = 10.6 Hz), 7.37 (1H, d, J = 6.9 Hz), 7.29 (1H, dd, J = 7.8, 0.9 Hz), 7.14 (1H, dd, J = 7.8, 6.9 Hz), 6.38 (1H, d, J = 10.6 Hz), 0.32 (7H, s). $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ: 145.76, 145.68, 141.34, 134.12, 130.41, 130.15, 129.75, 128.37, -4.08. HRMS (APCI) calcd for C$_{10}$H$_{11}$ClSi: 195.0391 ([M+H]$^+$) found 195.0387 ([M+H]$^+$)

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4f (a colorless oil, 62%, 12.1 mg, 0.0621 mmol) was prepared from 3f (23.7 mg, 0.100 mmol) by a general procedure C.

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 7.42 (1H, d, $J$ = 7.3 Hz), 7.26 (1H, d, $J$ = 10.4 Hz), 7.23 (1H, d, $J$ = 2.3 Hz), 7.19 (1H, dd, $J$ = 7.3, 2.3 Hz), 6.35 (1H, d, $J$ = 10.4 Hz), 0.32 (6H, s). $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$: 151.1, 148.0, 136.5, 135.9, 134.6, 132.6, 126.7, 124.3, -4.1. HRMS (ESI) calcd for C$_{10}$H$_{11}$ClSi: 195.0397 ([M+H]$^+$) found 195.0391 ([M+H]$^+$)

4g (a colorless oil, 80%, 15.6 mg, 0.0801 mmol) was prepared from 3g (23.7 mg, 0.100 mmol) by a general procedure C.

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 7.42 (1H, d, $J$ = 2.1 Hz), 7.25 (1H, d, $J$ = 10.3 Hz), 7.23 (1H, dd, $J$ = 8.0, 2.1 Hz), 7.11 (1H, d, $J$ = 8.0 Hz), 6.23 (1H, d, $J$ = 10.3 Hz), 0.29 (6H, s). $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$: 148.3, 147.5, 141.1, 133.2, 132.9, 131.8, 129.5, 125.1, -4.1. LRMS (EI) calcd for C$_{10}$H$_{11}$ClSi: 217.0216 ([M+Na]$^+$) found 217.0211 ([M+Na]$^+$)

4j (a colorless oil, 42%, 7.4 mg, 0.0415 mmol) was prepared from 3j (20.2 mg, 0.100 mmol) by a general procedure C.

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 7.29 (1H, d, $J$ = 10.5 Hz), 7.19 (1H, dd, $J$ = 7.8, 0.9 Hz), 7.19 (1H, dd, $J$ = 8.6, 7.8 Hz), 6.97 (1H, d, $J$ = 8.6, 6.4, 0.9 Hz), 6.21 (1H, d, $J$ = 10.5 Hz), 0.31 (6H, s). $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$: 162.6 ($J$ = 246 Hz), 148.3, 145.1, 141.7, 131.8, 125.1, 118.8 ($J$ = 20 Hz), 115.9 ($J$ = 22 Hz), -4.0. $^{19}$F-NMR (CDCl$_3$, 376 MHz) $\delta$: -111.6 (m). HRMS (APCI) calcd for C$_{10}$H$_{11}$FSi: 179.0687 ([M+H]$^+$) found 179.0684 ([M+H]$^+$)

5. Synthesis of enyne metathesis substrate 5 (general procedure D)

To a solution of PdCl$_2$(PPh$_3$)$_2$ (3 mol%), Cul (3 mol%) and an o-bromoiodobenze derivative (1.0 eq.) in Et$_3$N/THF=1/1 (0.5 M) was added trimethylsilylacetylene (1.1 eq.) at room temperature. After the mixture was stirred at room temperature for 2 h, the mixture was filtrated through celite cake and the solvent was evaporated under reduced pressure. The residue was subjected to column
chromatography on neutral flash silica gel 60N to give an o-bromotrimethylsilylacetylene derivative.

To a solution of compound o-bromotromethylsilylacetylene derivative in THF (0.5 M) was added dropwise 2.76 M n-BuLi in n-hexane (1.1 eq.) at -78 °C, After the mixture was stirred at -78 °C for 1 h, allylchlorodimethylsilane (1.2 eq.) was added dropwise to the mixture. The reaction mixture was stirred at -78 °C for 1 h, and warmed to room temperature. The reaction was stopped with the addition of 1M HCl aq. to the reaction mixture and organic compound was extracted with CHCl₃. The organic layer was dried over Na₂SO₄, and the solvent was evaporated. The residue was subjected to column chromatography on neutral flash silica gel 60N to give compound o-trimethylsilylacetylene-dimethylallylsilybenzene derivative.

To a solution of compound o-trimethylsilylacetylenedimethylallylsilybenzene derivative in toluene (0.2 M) was added RuHCl(CO)(PPh₃)₃ (5 mol%) and the mixture was refluxed for 3 h. After cooled to room temperature, saturated KOH in MeOH was added to the reaction mixture and stirred for 10 minutes. The reaction was stopped with 1M HCl aq. and organic compound was extracted with CHCl₃. The organic layer was dried over Na₂SO₄, and the solvent was evaporated. The residue was subjected to column chromatography on neutral flash silica gel 60N to give compound 5.

**5a** (a colorless oil, E/Z = 10/1, 40%, 397 mg, 1.98 mmol) was prepared from o-bromoiriodobenzene (1.41 g, 5.00 mmol) by a general procedure D.

**1H-NMR** (CDCl₃, 400 MHz) δ: 7.55-7.54 (2H, m), 7.33-7.33 (2H, m), 6.19 (1H, dq, J = 20.0, 6.4 Hz), 5.99 (1H, d, J = 20.0 Hz), 3.24 (1H, s), 1.90 (3H, d, J = 6.4 Hz), 0.46 (6H, s). **13C-NMR** (100 MHz, CHCl₃) δ: 147.1, 145.2, 137.6, 136.4, 131.9, 131.8, 131.0, 130.4, 88.3, 83.3, 25.8, 0.6. HRMS (EI) calcd for C₁₃H₁₆Si: 223.0919 ([M+Na]⁺) found 223.0912 ([M+Na]⁺)

**5b** (a colorless oil, E/Z = 10/1, 32%, 327 mg, 1.42 mmol) was prepared from 3-bromo-2-iodoanisole (1.37 g, 4.39 mmol) by a general procedure D.

**1H-NMR** (CDCl₃, 400 MHz) δ: 7.49 (1H, dd, J = 8.5, 5.3 Hz), 7.17 (1H, dd, J = 8.8, 2.7 Hz), 6.97 (1H, ddd, J = 8.8, 8.5, 2.7 Hz), 6.18 (1H, dq, J = 18.3, 6.2 Hz), 5.90 (1H, dq, J = 18.3, 1.6 Hz), 3.80 (3H, s), 3.17 (1H, s), 1.87 (3H, dd, J = 6.2, 1.6 Hz), 0.43 (6H, s). **13C-NMR** (100 MHz, CHCl₃) δ: 163.0, 146.8, 139.2, 136.3, 132.4, 131.8, 121.6, 117.6, 88.2, 83.2, 58.2, 25.9, 0.9. HRMS (ESI) calcd for C₁₄H₁₅OSi: 231.1205 ([M+H]⁺) found 231.1197 ([M+H]⁺)
5c (a yellow oil, $E/Z = 10/1$, 44%, 505 mg, 2.19 mmol) was prepared from 2-bromo-3-iodoanisole (1.56 g, 5.00 mmol) by a general procedure D.

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 7.47 (1H, d, $J = 8.2$ Hz), 7.03 (1H, d, $J = 2.7$ Hz), 6.81 (1H, dd, $J = 8.2$, 2.7 Hz), 6.18 (1H, dq, $J = 18.4$, 6.1 Hz), 5.94 (1H, dq, $J = 18.4$, 1.2 Hz), 3.81 (3H, s), 3.13 (1H, s), 1.87 (3H, dd, $J = 6.1$, 1.2 Hz), 0.43 (6H, s).

$^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$: 159.0, 144.3, 144.2, 135.1, 128.7, 120.9, 119.4, 113.4, 85.2, 78.8, 55.2, 22.8, -2.5. HRMS (ESI) calcd for C$_{14}$H$_{18}$OSi: 231.1205 ([M+H]$^+$) found 231.1198 ([M+H]$^+$)

5d (a pale yellow oil, $E/Z = 10/1$, 44%, 476 mg, 2.22 mmol) was prepared from 3-bromo-4-iodoluene (1.57 g, 5.00 mmol) by a general procedure D.

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 7.42 (1H, d, $J = 7.3$ Hz), 7.39 (1H, s), 7.16 (1H, d, $J = 7.3$ Hz), 6.20 (1H, dq, $J = 19.1$, 6.1 Hz), 5.98 (1H, d, $J = 19.1$ Hz), 3.21 (1H, s), 2.34 (3H, s), 1.90 (3H, d, $J = 6.0$ Hz), 0.46 (6H, s).

$^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$: 143.9, 138.7, 138.6, 134.8, 134.1, 129.2, 129.0, 127.4, 85.4, 80.1, 22.9, 21.2, -2.3. HRMS (ESI) calcd for C$_{14}$H$_{18}$Si: 237.1075 ([M+Na]$^+$) found 237.1068 ([M+Na]$^+$)

5e (a yellow oil, $E/Z = 10/1$, 52%, 560 mg, 2.61 mmol) was prepared from 2-bromo-3-iodoluene (1.57 g, 5.00 mmol) by a general procedure D.

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 7.44 (1H, d, $J = 7.8$ Hz), 7.31 (1H, s), 7.16 (1H, d, $J = 7.3$ Hz), 6.20 (1H, dq, $J = 19.1$, 6.1 Hz), 5.98 (1H, d, $J = 19.1$ Hz), 3.18 (1H, s), 2.35 (3H, s), 1.89 (3H, d, $J = 6.0$, 1.6 Hz), 0.45 (6H, s).

$^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$: 143.9, 134.8, 134.1, 129.2, 129.0, 127.4, 85.4, 80.1, 22.9, 21.2, -2.3. HRMS (ESI) calcd for C$_{14}$H$_{18}$Si: 241.0825 ([M+Na]$^+$) found 241.0819 ([M+Na]$^+$)

5f (a pale yellow oil, $E/Z = 10/1$, 17%, 186 mg, 0.851 mmol) was prepared from 2-bromo-5-fluoriodobenzene (1.50 g, 5.00 mmol) by a general procedure D.

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 7.47 (1H, dd, $J = 8.2$, 6.4 Hz), 7.22 (1H, dd, $J = 9.6$, 2.3 Hz), 7.02 (1H, ddd, $J = 8.2$, 8.2, 2.3 Hz), 6.18 (1H, dq, $J = 19.2$, 6.0 Hz), 5.92 (1H, dd, $J = 19.2$, 1.8 Hz), 3.26 (1H, s), 1.88 (3H, dd, $J = 6.0$, 1.8 Hz), 0.44 (6H, s).

$^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$: 162.0 ($J = 248$ Hz), 144.3, 137.9 ($J = 4$ Hz), 136.7 ($J = 9$ Hz), 129.4 ($J = 8$ Hz), 128.7, 120.2 ($J = 22$ Hz), 115.4 ($J = 19$ Hz), 84.1, 81.2, 22.8, -2.4. $^{19}$F-NMR (CDCl$_3$, 283 MHz) $\delta$: -108.1 (m). HRMS (ESI) calcd for C$_{13}$H$_{13}$FSi: 241.0825 ([M+Na]$^+$) found 241.0819 ([M+Na]$^+$)
5g (a pale yellow oil, $E/Z = 3/1$, 13%, 143 mg, 0.655 mmol) was prepared from 2-bromo-4-fluoriodobenzene (1.50 g, 5.00 mmol) by a general procedure D. 

$^1$H-NMR (CDCl$_3$, 300 MHz) δ: 7.49 (1H, dd, $J = 8.6, 5.3$ Hz), 7.17 (1H, dd, $J = 8.6, 2.8$ Hz), 7.00-6.94 (1H, m), 6.19 (1H, dq, $J = 18.4, 6.2$ Hz), 5.91 (1H, dq, $J = 18.4, 1.6$ Hz), 3.18 (1H, s), 1.88 (3H, dd, $J = 6.2, 1.6$ Hz), 0.43 (6H, s). 

$^{13}$C-NMR (CDCl$_3$) δ: 161.9 (J = 250 Hz), 145.8 (J = 5 Hz), 144.8, 135.5 (J = 8 Hz), 128.0, 123.1, 121.4 (J = 20 Hz), 115.7 (J = 22 Hz), 84.2, 80.0, 22.7, -2.8. 

$^{19}$F-NMR (CDCl$_3$, 283 MHz) δ: -107.7 (m). 

HRMS (ESI) calcd for C$_{13}$H$_{15}$FSi: 241.0825 ([M+Na$^+$]$^+$) found 241.0818 ([M+Na$^+$]$^+$)

6. Synthesis of enyne metathesis compound 6a 

To a solution of 5a (20.0 mg, 0.100 mmol) in CHCl$_3$ (2 mL, 0.05 M) was added Grubbs II (4.2 mg, 5 mol%) and the mixture was refluxed for 2 h. The solvent was evaporated and the residue was subjected to column chromatography on neutral flash silica gel 60N to give 6a (a pale yellow oil, 60%, 12.1 mg, 0.0604 mmol, $E/Z = 4:1$). 

$^1$H-NMR (CDCl$_3$, 400 MHz) δ: 7.53 (1H, dd, $J = 6.6, 1.2$ Hz), 7.45 (1H, d, $J = 7.3$ Hz), 7.35 (1H, ddd, $J = 7.8, 7.3, 1.2$ Hz), 7.24 (1H, dd, $J = 7.8, 6.6$ Hz), 6.54 (1H, dq, $J = 15.6, 1.2$ Hz), 6.31 (1H, dq, $J = 15.6, 6.5$ Hz), 6.21 (1H, s), 1.91 (3H, dd, $J = 6.5, 1.2$ Hz), 0.30 (6H, s). 

$^{13}$C-NMR (CDCl$_3$, 100 MHz) δ: 156.34, 148.95, 140.18, 131.81, 130.11, 129.60, 127.19, 126.81, 125.15, 121.47, 18.82, -3.79 HRMS (APCI) calcd for C$_{13}$H$_{16}$Si: 201.1094 ([M+H$^+$]$^+$) found 201.1090 ([M+H$^+$]$^+$)

7. Synthesis of polycyclic compound 7 (general procedure E) 

To a solution of 5 in CHCl$_3$ (0.005 M) was added Grubbs II (5 mol%) and the mixture was reflux for 2 h. After the solvent was evaporated, the residue was dissolved in toluene (0.2 M). Then maleic anhydride (3.0 eq.) was added to the mixture and the mixture was reflux for 3 h. 2,3-dichloro-5,6-dicyano-p-benzoquinone (3.0 eq.) was added to the reaction mixture and the mixture was reflux for 3 h. The solvent was evaporated and the residue was subjected to column chromatography on neutral
flash silica gel 60N to give 7.

7a (a white solid, 52%, 15.3 mg, 0.0520 mmol) was prepared from 5a (20.0 mg, 0.100 mmol) by a general procedure E.

$^1$H-NMR (CDCl$_3$, 400 MHz) δ: 7.98 (1H, s), 7.92 (1H, d, $J$ = 7.9 Hz), 7.73 (1H, d, $J$ = 7.0 Hz), 7.52 (1H, dd, $J$ = 7.9, 7.0 Hz), 7.43 (1H, dd, $J$ = 7.0, 7.0 Hz), 2.78 (3H, s), 0.56 (6H, s). $^{13}$C-NMR (100 MHz, CHCl$_3$) δ: 164.7, 163.8, 156.3, 145.0, 142.6, 141.4, 136.9, 136.6, 133.5, 130.7, 129.8, 128.7, 126.5, 122.4, 18.4, -4.3 HRMS (MALDI-TOF) calcd for C$_{17}$H$_{15}$O$_3$Si: 295.0785 ([M+H]$^+$), found 295.0785 ([M+H]$^+$). m.p. >250 °C (recrystallized from CHCl$_3$, a white column).

7b (a yellow solid, 35%, 15.3 mg, 0.0520 mmol) was prepared from 5b (23.0 mg, 0.100 mmol) by a general procedure E.

$^1$H-NMR (CDCl$_3$, 400 MHz) δ: 7.92 (1H, s), 7.64 (1H, d, $J$ = 7.8 Hz), 7.42 (1H, d, $J$ = 2.3 Hz), 6.99 (1H, dd, $J$ = 7.8, 2.3 Hz), 3.92 (3H, s), 2.78 (3H, s), 0.53 (6H, s). $^{13}$C-NMR (100 MHz, CHCl$_3$) δ: 164.6, 163.7, 162.1, 155.9, 146.9, 142.4, 138.0, 136.4, 134.5, 132.0, 128.6, 126.5, 115.4, 108.4, 55.4, 18.3, -4.1 HRMS (MALDI-TOF) calcd for C$_{18}$H$_{16}$O$_4$Si: 324.0812 ([M+H]$^+$), found 324.0805 ([M+H]$^+$). m.p. 241.0-242.0 °C (recrystallized from CHCl$_3$, a pale yellow column).

7c (an orange solid, 48%, 15.7 mg, 0.0484 mmol) was prepared from 5c (23.0 mg, 0.100 mmol) by a general procedure E.

$^1$H-NMR (CDCl$_3$, 500 MHz) δ: 7.85 (1H, s), 7.84 (1H, d, $J$ = 8.6 Hz), 7.22 (1H, d, $J$ = 2.6 Hz), 7.02 (1H, dd, $J$ = 8.6, 2.6 Hz), 3.90 (3H, s), 0.55 (6H, s). $^{13}$C-NMR (125 MHz, CHCl$_3$) δ: 164.8, 163.8, 161.1, 156.3, 143.6, 142.6, 137.6, 136.5, 135.9, 127.6, 125.2, 123.8, 118.2, 116.2, 55.5, 18.3, -4.4 HRMS (MALDI-TOF) calcd for C$_{18}$H$_{17}$O$_3$Si: 324.0812 ([M+H]$^+$), found 324.0820 ([M+H]$^+$). m.p. >250 °C (recrystallized from CHCl$_3$, an orange needle).

7d (an orange solid, 24%, 7.3 mg, 0.0237 mmol) was prepared from 5d (21.8 mg, 0.100 mmol) by a general procedure E.

$^1$H-NMR (CDCl$_3$, 400 MHz) δ: 7.98 (1H, s), 7.75 (1H, s), 7.62 (1H, d, $J$ = 7.3 Hz), 7.26 (1H, d, $J$ = 7.3 Hz), 2.78 (3H, s), 2.47 (3H, s), 0.53 (6H, s). $^{13}$C-NMR (100 MHz, CHCl$_3$) δ: 164.7, 163.8, 163.8, 162.2, 156.0, 156.0, 147.0, 142.5, 138.1, 136.5, 134.6, 132.1, 128.7, 126.6, 115.5, 108.5, 55.5, 18.4, -4.0. HRMS (MALDI-TOF) calcd for C$_{18}$H$_{17}$O$_3$Si: 309.0942 ([M+H]$^+$), found 309.0940 ([M+H]$^+$).
7e (an orange solid, 21%, 6.5 mg, 0.0211 mmol) was prepared from 5e (21.8 mg, 0.100 mmol) by a general procedure E.

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 7.93 (1H, s), 7.80 (1H, d, $J = 7.8$ Hz), 7.54 (1H, d, $J = 1.4$ Hz), 7.33 (1H, ddd, $J = 7.8, 1.4$ Hz), 7.27 (3H, s), 2.43 (3H, s), 0.54 (6H, s). $^{13}$C-NMR (100 MHz, CHCl$_3$) $\delta$: 164.7, 163.8, 156.4, 142.5, 142.4, 141.4, 139.9, 136.5, 134.1, 131.4, 128.2, 126.0, 122.2, 21.5, 18.3, -4.4. HRMS (MALDI-TOF) caleld for C$_{18}$H$_{16}$O$_3$Si: 308.0863 ([M+H$^+$]), found 308.0863 ([M+H$^+$]). m.p. >250 °C (recrystallized from CHCl$_3$, a yellow column).

7f (a white solid, 39%, 12.2 mg, 0.0391 mmol) was prepared from 5f (21.8 mg, 0.100 mmol) by a general procedure E.

$^1$H-NMR (CDCl$_3$, 500 MHz) $\delta$: 7.91 (1H, s), 7.68 (1H, ddd, $J = 7.9, 5.5$ Hz), 7.58 (1H, ddd, $J = 10.5, 2.3$ Hz), 7.14 (1H, ddd, $J = 9.0, 7.9, 2.3$ Hz), 2.79 (3H, s), 0.55 (6H, s). $^{13}$C-NMR (125 MHz, CHCl$_3$) $\delta$: 165.1 ($J = 247$ Hz), 164.4, 163.5, 154.9, 147.6 ($J = 8$ Hz), 142.7, 137.5, 136.5, 135.4, 135.0 ($J = 8$ Hz), 128.9, 126.9, 116.8 ($J = 20$ Hz), 109.7 ($J = 21$ Hz), 18.3, -4.4 $^{19}$F-NMR (376 MHz, CHCl$_3$) $\delta$: -105.1 (ddd, $J = 10.5, 9.0, 5.5$) HRMS (MALDI-TOF) caleld for C$_{17}$H$_{14}$O$_3$FSi: 313.0691 ([M+H$^+$]), found 313.0689 ([M+H$^+$]). m.p. 249.0-250.0 °C (recrystallized from CHCl$_3$, a white column).

7g (a white solid, 38%, 11.8 mg, 0.0379 mmol) was prepared from 5g (21.8 mg, 0.100 mmol) by a general procedure E.

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 7.91 (1H, s), 7.89 (1H, ddd, $J = 8.7, 4.6$ Hz), 7.39 (1H, ddd, $J = 7.6, 2.5$ Hz), 7.19 (1H, ddd, $J = 8.7, 8.7, 2.5$ Hz), 2.78 (3H, s), 0.56 (6H, s). $^{13}$C-NMR (100 MHz, CHCl$_3$) $\delta$: 164.3 ($J = 201$ Hz), 164.6, 163.6, 155.3, 144.5 ($J = 5$ Hz), 142.8, 140.8, 136.6, 136.2, 128.4, 126.1, 124.1 ($J = 6$ Hz), 120.0 ($J = 16$ Hz), 117.6 ($J = 18$ Hz), 18.3, -4.5 $^{19}$F-NMR (376 MHz, CHCl$_3$) $\delta$: -106.5 (ddd, $J = 8.7, 7.6, 4.6$ Hz) HRMS (MALDI-TOF) caleld for C$_{17}$H$_{14}$O$_3$FSi: 313.0691 ([M + H$^+$]), found 313.0700 ([M + H$^+$]). m.p. >250 °C (recrystallized from CHCl$_3$, a yellow column).
8. Synthesis of carbide complex

To a solution of 1b (63.7 mg, 0.300 mmol) in CHCl₃ (2 mL, 0.05 M) was added Grubbs II (84.9 mg, 0.100 mmol) and the mixture was heated for 2 h at 45 °C. The solvent was evaporated and the residue was subjected to column chromatography (n-hexane/AcOEt = 20/1) on neutral flash silica gel 60N to give carbide complex (an orange solid, 34%, 26.4 mg, 0.0343 mmol).

¹H-NMR (CDCl₃, 400 MHz) δ: 6.95 (2H, s), 6.89 (2H, s), 4.10-4.04 (4H, m), 2.54 (6H, s), 2.49 (6H, s), 2.34-2.29 (3H, m), 2.29 (3H, s), 2.24 (3H, s), 1.88-1.86 (6H, m), 1.67-1.60 (6H, m), 1.19-1.12 (12H, m).

9. NMR chart

1b
1b

single pulse decoupled gated NOE

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1a

single pulse

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1a
single pulse decoupled gated NOE

1c
single pulse
single pulse decoupled gated NOE

2c

single pulse
### 2d

**Single Pulse Decoupled Gated NOE**

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### 2e

**Single Pulse**

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2f

single pulse decoupled gated NOE

2g

single pulse
2j

single pulse decoupled gated NOE

2k

single pulse
single pulse decoupled gated NOE

single pulse
single pulse decoupled gated NOE

S44
5c

single pulse decoupled gated NOE

5d

single pulse
single pulse decoupled gated NOE

7a