

**Rapid Assembly of Structurally Defined and Highly Functionalized Conjugated Dienes
Via Tethered Enyne Metathesis**

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Supporting Information

Enyne 2a: ^1H NMR (CDCl_3 , 500 MHz) δ : 0.170 (3H, s), 0.174 (3H, s), 1.69 (2H, bd, J = 8.1 Hz), 1.86 (3H, d, J = 2.2 Hz), 1.94–1.99 (2H, m), 2.73–2.77 (2H, m), 4.35 (1H, m), 4.85–4.93 (2H, m), 5.78–5.87 (1H, m), 7.18–7.31 (5H, m). ^{13}C NMR (CDCl_3 , 125 MHz) δ : -1.98, -1.84, 3.52, 24.86, 31.43, 40.27, 62.45, 80.39, 80.77, 113.61, 125.77, 128.30, 128.45, 134.13, 141.74. Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{OSi}$: C, 74.94; H, 8.88. Found: C, 75.06; H, 9.12.

Diene 5a: ^1H NMR (CDCl_3 , 500 MHz) δ : 1.87–2.10 (2H, m), 1.90 (3H, s), 2.69 (1H, m), 2.81 (1H, m), 4.29 (1H, dd, J = 6.8, 13.4 Hz), 4.35 (1H, dd, J = 6.6, 13.4 Hz), 4.63 (1H, dd, J = 4.5, 8.8 Hz), 4.95 (1H, s), 4.96 (1H, s), 5.78 (1H, t, J = 6.7 Hz), 7.16–7.34 (5H, m). ^{13}C NMR (CDCl_3 , 125 MHz) δ : 22.88, 32.44, 37.85, 58.70, 69.85, 113.82, 125.93, 127.73, 128.41, 128.46, 141.62, 143.22, 145.87. Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2 \cdot 0.2\text{H}_2\text{O}$: C, 76.36; H, 8.72. Found: C, 76.67; H, 8.78.

Enyne 2b: ^1H NMR (CDCl_3 , 500 MHz) δ : 0.181 (6H, s), 0.907 (9H, d, J = 6.7 Hz), 1.14 (3H, t, J = 7.5 Hz), 1.49 (1H, dt, J = 6.8, 13.4 Hz), 1.55–1.62 (1H, m), 1.70 (2H, bd, J = 8.1 Hz), 1.80 (1H, sept, J = 13.5 Hz), 2.21 (2H, dq, J = 2.0, 7.6 Hz), 4.40 (1H, ddt, J = 1.9, 6.4, 7.8 Hz), 4.86–4.94 (2H, m), 5.84 (1H, ddt, J = 8.1, 10.1, 17.0 Hz). ^{13}C NMR (CDCl_3 , 125 MHz) δ : -1.94, -1.80,

12.38, 13.79, 22.36, 22.63, 24.94, 24.92, 47.91, 61.55, 81.09, 86.12, 113.52, 134.22. Anal. Calcd for $C_{14}H_{26}OSi$: C, 70.52; H, 10.99. Found: C, 70.47; H, 11.24.

Diene 5b: 1H NMR ($CDCl_3$, 500 MHz) δ : 0.981 (3H, d, $J = 6.4$ Hz), 0.991 (3H, d, $J = 6.4$ Hz), 1.05 (3H, t, $J = 7.4$ Hz), 1.36 (1H, ddd, $J = 4.1, 8.7, 14.0$ Hz), 1.66 (1H, ddd, $J = 5.2, 9.4, 14$ Hz), 1.79 (1H, m), 2.25 (1H, q, $J = 7.4$ Hz), 4.34 (2H, bd, $J = 6.3$ Hz), 4.62 (1H, dd, $J = 4.0, 9.4$ Hz), 4.94 (2H, d, $J = 14.1$ Hz), 5.69 (1H, t, $J = 6.7$ Hz). Anal. Calcd for $C_{12}H_{22}O_2 \cdot 0.25H_2O$: C, 71.07; H, 11.18. Found: 70.87; H, 11.37

Enyne 2c: 1H NMR ($CDCl_3$, 500 MHz) δ : 0.175 (3H, s), 0.179 (3H, s), 1.24 (9H, s), 1.69 (2H, d, $J = 8.0$ Hz), 2.00 (2H, m), 2.75 (2H, ddd, $J = 2.9, 6.6, 9.3$ Hz), 4.41 (1H, $J = 6.4$ Hz), 4.72 (2H, d, $J = 1.7$ Hz), 4.88–4.94 (2H, m), 5.78–5.86 (1H, m), 7.17–7.34 (5H, m). ^{13}C NMR ($CDCl_3$, 125 MHz) δ : -2.00, -1.84, 24.75, 27.05, 31.26, 38.72, 39.72, 52.26, 62.04, 79.13, 113.81, 125.88, 128.34, 128.44, 133.84, 141.36, 177.65. Anal. Calcd for $C_{22}H_{32}O_3Si$: C, 70.92; H, 8.66. Found: 70.62; H, 8.84.

Diene 5c: 1H NMR ($CDCl_3$, 500 MHz) δ : 1.23 (9H, s), 1.86 (1H, m), 2.05 (1H, m), 2.67 (1H, ddd, $J = 6.9, 9.2, 14.0$ Hz), 2.79 (1H, ddd, $J = 5.5, 9.6, 13.8$ Hz), 4.22 (1H, dd, $J = 6.4, 13.5$ Hz), 2.26 (1H, dd, $J = 6.7, 13.5$ Hz), 4.63 (1H, dd, $J = 4.9, 8.7$ Hz), 4.70 (1H, $J = 13.4$ Hz), 4.74 (1H, d, $J = 13.5$ Hz), 5.12 (1H, s), 5.19 (1H, s), 5.68 (1H, t, $J = 6.5$ Hz), 7.18 – 7.31 (5H, m). Anal. Calcd for $C_{20}H_{28}O_4 \cdot 0.5H_2O$: C, 70.35; H, 8.56. Found: 70.71; H, 8.25.

Enyne 2d: 1H NMR ($CDCl_3$, 500 MHz) δ : 0.188 (6H, s), 0.899 (3H, t, $J = 6.9$ Hz), 1.24–1.47 (8H, m), 1.65 – 1.71 (4H, m), 2.40 (1H, d, $J = 2.2$ Hz), 4.36 (1H, dt, $J = 2.1, 6.6$ Hz), 4.87 – 4.94 (2H, m), 5.83 (1H, ddt, $J = 8.1, 10.1, 16.9$ Hz). ^{13}C NMR ($CDCl_3$, 125 MHz) δ : -2.04, -1.90, 14.05, 22.58, 24.78, 25.06, 28.89, 31.75, 38.48, 62.72, 72.25, 85.44, 113.76, 133.96. Anal. Calcd for $C_{14}H_{26}OSi$: C, 70.52; H, 10.99. Found: 70.83; H, 11.33.

Diene 5d: ^1H NMR (CDCl_3 , 500 MHz) δ : 0.892 (3H, t, J = 6.9 Hz), 1.24–1.46 (8H, m), 1.57–1.65 (1H, m), 1.69–1.77 (1H, m), 4.34 (2H, d, J = 6.8 Hz), 4.62 (1H, dd, J = 5.6, 8.0 Hz), 5.09 (1H, d, J = 11.2 Hz), 5.36 (1H, d, J = 17.6 Hz), 5.80 (1H, t, J = 13.5 Hz), 6.30 (1H, dd, J = 11.2, 17.6 Hz). ^{13}C NMR (CDCl_3 , 125 MHz) δ : 14.01, 22.56, 25.93, 29.14, 31.74, 36.12, 58.54, 69.57, 114.43, 129.34, 136.81, 143.08. Anal. Calcd for $\text{C}_{12}\text{H}_{22}\text{O}_2$: C, 72.68; H, 11.18. Found: 72.86; H, 11.07.

Enyne 2e: ^1H NMR (CDCl_3 , 500 MHz) δ : 0.165 (9H, s), 0.871 (3H, t, J = 6.9 Hz), 1.24–1.45 (8H, m), 1.67 (2H, d, J = 8.0 Hz), 2.02–2.14 (2H, m), 4.34 (2H, d, J = 1.7 Hz), 4.84–4.91 (2H, m), 5.07 (1H, bt, J = 8.0 Hz), 5.79 (1H, m), 7.73 (2H, dd, J = 3.1, 5.4 Hz), 7.86 (2H, dd, J = 3.1, 5.4 Hz). ^{13}C NMR (CDCl_3 , 125 MHz) δ : -2.39, 13.97, 22.48, 24.35, 26.27, 28.47, 31.56, 33.27, 41.85, 51.37, 81.66, 81.79, 113.88, 123.88, 131.85, 133.65, 134.01, 167.07. Anal. Calcd for $\text{C}_{23}\text{H}_{31}\text{NO}_3\text{Si}$: C, 69.48; H, 7.86, N, 3.52. Found: C, 69.76%; H, 7.89; N, 3.66.

Diene 5e: ^1H NMR (CDCl_3 , 500 MHz) δ : 0.165 (6H, s), 0.831 (3H, t, J = 6.9 Hz), 1.15–1.34 (8H, m), 1.97 (1H, m), 2.33 (1H, m), 4.17 (2H, d, J = 6.7 Hz), 4.26 (1H, d, J = 12.9 Hz), 4.33 (1H, d, J = 12.9 Hz), 4.98 (1H, dd, J = 5.0, 10.3 Hz), 5.35 (1H, s), 5.40 (1H, s), 5.86 (1H, t, J = 6.7 Hz), 7.22 (2H, dd, J = 3.0, 5.4 Hz), 7.82 (2H, dd, J = 3.1, 5.4 Hz). ^{13}C NMR (CDCl_3 , 125 MHz) δ : 13.98, 22.51, 26.77, 28.92, 29.77, 31.62, 52.04, 58.55, 59.15, 115.40, 123.28, 130.16, 131.58, 134.06, 142.21, 146.27, 168.74. Anal. Calcd for $\text{C}_{21}\text{H}_{27}\text{NO}_4 \cdot 0.5\text{H}_2\text{O}$: C, 68.83; H, 7.70; N, 3.82. Found: C, 68.81; H, 7.61; N, 3.79.

Enyne 2f: ^1H NMR (CDCl_3 , 500 MHz) δ : 0.153 (6H, s), 1.50–1.66 (6H, m), 1.70–1.76 (1H, m), 1.77–1.90 (1H, m), 2.40 (1H, ddt, J = 2.2, 6.4, 16.7 Hz), 2.52 (1H, ddt, J = 2.2, 6.1, 16.7 Hz), 3.46 (1H, dd, J = 5.6, 9.8 Hz), 3.49–3.55 (2H, m), 3.84 (1H, ddd, J = 2.9, 9.1, 11.5 Hz), 3.99 (1H, quint, J = 5.4 Hz), 4.19 (1H, dt, J = 2.1, 15.3 Hz), 4.28 (1H, dt, J = 2.1, 15.3 Hz), 4.55 (2H,

s), 4.80 (1H, t, $J = 3.4$ Hz), 4.85–4.90 (2H, m), 5.80 (1H, m), 7.27–7.37 (5H, m). ^{13}C NMR (CDCl_3 , 125 MHz) δ : -1.87, 19.10, 24.99, 25.38, 30.28, 54.55, 61.95, 70.59, 73.35, 73.54, 77.54, 83.22, 96.68, 113.64, 127.55, 127.59, 128.31, 134.13, 138.24. Anal. Calcd for $\text{C}_{23}\text{H}_{31}\text{NO}_3\text{Si}$: C, 66.82; H, 8.51. Found: C, 68.45, H, 8.57.

Diene 5f: ^1H NMR (CDCl_3 , 500 MHz) δ : 1.56–1.90 (6H, m), 2.47 (1H, dd, $J = 3.3, 14.1$ Hz), 2.58 (1H, m), 3.43 (1H, m), 3.50–3.55 (1H, m), 3.53 (1H, dd, $J = 3.8, 9.5$ Hz), 3.85–3.94 (2H, m), 4.07 (1H, ddd, $J = 1.1, 6.9, 12.2$ Hz), 4.08 (1H, dd, $J = 6.8, 12.2$ Hz), 4.23 (1H, dd, $J = 8.0, 12.3$ Hz), 4.44 (1H, d, $J = 12.7$ Hz), 4.57 (2H, s), 4.64 (1H, s), 5.24 (1H, s), 5.32 (1H, s), 6.10 (1H, dt, $J = 7.5, 10.1$ Hz), 7.27–7.38 (5H, m). Anal. Calcd for $\text{C}_{21}\text{H}_{30}\text{O}_5 \cdot 0.25 \text{H}_2\text{O}$: C, 68.73; H, 8.38. Found: C, 68.54; H, 8.37.

Enyne 2g: ^1H NMR (CDCl_3 , 500 MHz) δ : 0.143 (6H, s), 0.898 (3H, t, $J = 7.0$ Hz), 1.25–1.40 (6H, m), 1.48 (2H, quint, $J = 7.3$ Hz), 1.65 (2H, d, $J = 8.0$ Hz), 2.15 (2H, tt, $J = 2.3, 7.1$ Hz), 2.39 (2H, tt, $J = 2.3, 7.3$ Hz), 3.69 (2H, t, $J = 7.2$ Hz), 4.87–4.94 (2H, m), 5.81 (1H, ddt, $J = 8.1, 10.1, 17.0$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz) δ : -2.53, 14.02, 18.74, 22.53, 23.02, 24.35, 28.53, 28.94, 31.35, 62.06, 76.61, 81.63, 113.69, 133.89. Anal. Calcd for $\text{C}_{15}\text{H}_{28}\text{OSi}$: C, 71.36; H, 11.18. Found: C, 70.99, H, 11.39.

Diene 5g: ^1H NMR (CDCl_3 , 500 MHz) δ : 0.874 (3H, t, $J = 6.8$ Hz), 1.20–1.30 (6H, m), 1.44 (2H, m), 2.22 (2H, t, $J = 7.6$ Hz), 2.56 (2H, t, $J = 5.8$ Hz), 3.63 (2H, t, $J = 5.8$ Hz), 4.15 (2H, d, $J = 7.4$ Hz), 4.95 (1H, s), 5.03 (1H, s), 6.00 (1H, t, $J = 7.4$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz) δ : 14.05, 22.62, 28.55, 29.16, 30.72, 31.69, 34.10, 57.98, 60.17, 112.22, 127.39, 140.23, 148.07. Anal. Calcd for $\text{C}_{13}\text{H}_{24}\text{O}_2$: C, 73.54, H, 11.39. Found: C, 73.80; H, 11.18.

Enyne 2h: ^1H NMR (CDCl_3 , 500 MHz) δ : 0.184 (6H, s), 1.22 (9H, s), 1.69 (2H, d, $J = 8.1$ Hz), 1.87 (2H, m), 2.20 (2H, m), 4.35 (2H, d, $J = 1.6$ Hz), 4.88–4.95 (2H, m), 5.00–5.07 (2H, m), 5.40

(1H, tt, $J = 1.5, 6.6$ Hz), 5.77–5.86 (2H, m). ^{13}C NMR (CDCl_3 , 125 MHz) δ : -2.30, 24.40, 27.04, 29.18, 33.84, 38.73, 51.34, 63.17, 82.64, 83.48, 113.98, 115.53, 133.61, 136.98, 177.26. Anal. Calcd for $\text{C}_{18}\text{H}_{30}\text{O}_3\text{Si}$: C, 67.03; H, 9.38. Found: C, 67.05, H, 9.45.

Diene 5h: ^1H NMR (CDCl_3 , 500 MHz) δ : 1.17 (9H, s), 1.79–1.84 (1H, m), 2.34–2.46 (2H, m), 2.57–2.66 (1H, m), 4.29 (1H, dd, $J = 7.0, 13.2$ Hz), 4.33 (1H, dd, $J = 6.8, 13.3$ Hz), 4.38 (1H, d, $J = 12.2$ Hz), 4.42 (1H, d, $J = 12.1$ Hz), 5.81 (1H, t, $J = 6.9$ Hz), 5.97 (1H, dt, $J = 2.1, 7.6$ Hz), 6.25 (1H, t, $J = 5.1$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz) δ : 27.04, 30.86, 31.14, 38.78, 58.65, 59.02, 78.58, 129.21, 134.23, 136.60, 140.98, 178.65. Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_4 \cdot 0.2\text{H}_2\text{O}$: C, 65.19; H, 8.75. Found: C, 65.44, H, 8.79.