Supporting information

Conjugated Enynes as a New Type of Substrates for Olefin Metathesis

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General. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 300 (300 MHz) and Bruker AMX 500 (500 MHz) spectrometer. Chemical shift are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane, or in ppm relative to the singlet at 7.26 ppm of chloroform- d_1 . Splitting patterns are designated as follows: s; singlet, d; doublet, t; triplet, q; quartet, m; multiplet, dd; doublet of doublet, td; doublet of triplet, dt; triplet of doublet, qd; doublet of quintet, b; broad. Column chromatography was carried out using silica gel 60 (230-400 mesh, ASTM, Merck). Catalyst **1** and **2** were purchased from Aldrich Co. and Strem Co., and used without further purification.

Representative procedure for the synthesis of conjugated enynes. To a stirred solution of vinyl bromide (1.0 M solution in THF, 15 mL, 15.0 mmol), $\text{Pd}(\text{PPh}_3)_4$ (173 mg, 0.15 mmol), CuI (76 mg, 0.4 mmol), and triethylamine (2.0 g, 20.0 mmol) was added a solution of phenylacetylene (1.0 g, 10.0 mmol) in THF (5 mL) via a syringe pump for 1 h. The reaction mixture was stirred at room temperature for 3 h and then it was filtered through Celite. The filtrate was evaporated under the reduced pressure and the resulting residue was subjected to column chromatography on silica gel with *n*-pentane to yield 1.1 g (85%) of 4-phenyl-1-buten-3-yne (**4**): ^1H NMR (300 MHz, CDCl_3) δ 7.48 (m, 2H), 7.33 (m, 3H), 6.05 (dd, 1H, $J = 17.5, 11.0$ Hz), 5.77 (dd, 1H, $J = 17.5, 1.9$ Hz), 5.57 (dd, 1H, $J = 11.0, 1.9$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 131.5, 128.2, 126.8, 123.1, 117.1, 89.9, 88.0.

General Procedure of Conjugated Enyne Cross Metathesis with Catalyst 3. To a solution of enyne **4** (51.2 mg, 0.40 mmol) in benzene (2 mL) was added catalyst **3** (35.4

mg, 0.10 equiv) followed by allyltrimethylsilane (**5**, 137.1mg, 3.0 equiv). The reaction mixture was stirred for 18 hr at 70 °C under nitrogen atmosphere. After removal of organic solvent under reduced pressure, the residue was purified by a column chromatography on silica gel with *n*-pentane to afford (**Z/E**)-1-phenyl-5-trimethylsilyl-3-penten-1-yne (Table 1, entry 1). *Z*-isomer; ¹H NMR (300 MHz, CDCl₃) δ 7.39-7.20 (m, 5H), 6.01 (dt, 1H, *J* = 10.7, *J* = 8.7 Hz), 5.51 (d, 1H, *J* = 10.7 Hz), 1.90 (d, 2H, *J* = 8.7 Hz), 0.03 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 141.5, 131.2, 128.2, 127.6, 124.0, 106.0, 93.2, 87.2, 23.0, -1.5; *E*-isomer; ¹H NMR (300 MHz, CDCl₃) δ 7.21-7.48 (m, 5H), 6.21 (dt, 1H, *J* = 15.6, 8.5 Hz), 5.42 (d, 1H, *J* = 15.6 Hz), 1.61 (d, 2H, *J* = 8.5 Hz), 0.0 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 142.5, 132.4, 128.4, 127.5, 123.8, 107.2, 89.1, 86.9, 24.9, -1.9; HRMS (EI) calcd for C₁₄H₁₈Si [M⁺] 214.1178, found 214.1182.

(Z)-1-Trimethylsilyl-2-tridecen-4-yne (Table 1, entry 2); ¹H NMR (300 MHz, CDCl₃) δ 5.82 (dt, 1H, *J* = 10.4, *J* = 8.7 Hz), 5.27 (d, 1H, *J* = 10.6 Hz), 2.28 (m, 2H), 1.76 (d, 2H, *J* = 8.4 Hz), 1.23-1.53 (m, 12H), 0.83 (m, 3H), 0.0 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 139.3, 106.6, 94.1, 77.9, 31.8, 29.2, 29.1, 28.9, 22.6, 22.3, 19.5, 14.0, -1.6; HRMS (EI) calcd for C₁₆H₃₀Si [M⁺] 250.2117, found 250.2127.

(1-Methoxymethyl)-[1,1-dimethyl-6-trimethylsilyl-(Z)-4-hexen-2-ynyl] ether (Table 1, entry 3); ¹H NMR (300 MHz, CDCl₃) δ 5.82 (dt, 1H, *J* = 10.6, 8.7 Hz), 5.31 (d, 1H, *J* = 10.6 Hz), 4.86 (s, 2H), 3.34 (s, 3H), 1.77 (d, 2H, *J* = 8.7 Hz), 1.49 (s, 6H), 0.0 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 141.4, 105.4, 94.6, 93.1, 82.3, 71.6, 55.4, 30.4, 22.8, -1.6; HRMS (EI) calcd for C₁₃H₂₄O₂Si [M⁺] 240.1546, found 240.1554.

(1-Methoxymethyl)-[1,1-dimethyl-6-phenyl-(Z/E)-4-hexen-2-ynyl] ether (Table 1, entry 4); *Z*-isomer; ¹H NMR (300 MHz, CDCl₃) δ 7.17-7.32 (m, 5H), 6.06 (dt, 1H, *J* = 10.6, 7.5 Hz), 5.60 (d, 1H, *J* = 10.6 Hz), 4.92 (s, 2H), 3.63 (d, 2H, *J* = 7.4 Hz), 3.38 (s, 3H), 1.57 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 141.9, 139.5, 128.5, 128.4, 126.2, 109.2, 93.1, 81.3, 71.5, 55.4, 36.4, 30.2; *E*-isomer; ¹H NMR (300 MHz, CDCl₃) δ 7.17-7.32 (m, 5H), 6.27 (dt, 1H, *J* = 15.7, 7.5 Hz), 5.52 (d, 1H, *J* = 15.7 Hz), 4.88 (s, 2H), 3.42 (d, 2H, *J* = 8.1 Hz), 3.35 (s, 3H), 1.51 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 143.0, 138.7, 128.7, 128.6, 126.3, 110.2, 95.3, 83.0, 71.3, 55.4, 39.2, 30.1; HRMS (EI) calcd for C₁₆H₂₀O₂ [M⁺] 244.1463, found 244.1467.

(1-Methoxymethyl)-[1,1-dimethyl-(Z/E)-4-hepten-2-ynyl] ether (Table 1, entry 5). *Z*-isomer; ¹H NMR (300 MHz, CDCl₃) δ 5.90 (dt, 1H, *J* = 10.7, 7.3 Hz), 5.44 (d, 1H, *J* =

10.8 Hz), 4.92 (s, 2H), 3.39 (s, 3H), 2.29 (qd, 2H, $J = 7.5, 1.3$ Hz), 1.54 (s, 6H), 1.01 (t, 3H, $J = 7.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 145.6, 107.9, 93.1, 81.4, 71.4, 55.3, 30.2, 23.5, 13.1: *E*-isomer; ^1H NMR (300 MHz, CDCl_3) δ 6.18 (dt, 1H, $J = 15.8, 6.6$ Hz), 5.49 (d, 1H, $J = 15.8$ Hz), 4.90 (s, 2H), 3.39 (s, 3H), 2.12 (qd, 2H, $J = 6.6, 1.6$ Hz), 1.52 (s, 6H), 1.00 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 146.3, 108.1, 95.1, 83.4, 71.3, 55.3, 30.2, 25.9, 12.7; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{18}\text{O}_2$ [M^+] 182.1307, found 182.1314.

(*Z/E*)-5-Phenyl-2-penten-4-yn-1-ol (Table 1, entry 6); ^1H NMR (300 MHz, CDCl_3) δ 7.27-7.46 (m, 5H), 6.14 (dt, 1H, $J = 10.8, 6.4$ Hz), 5.82 (d, 1H, $J = 10.8$ Hz), 4.50 (t, 2H, $J = 5.5$ Hz), 1.80 (b, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.2, 131.4, 128.4, 128.3, 122.9, 110.6, 95.2, 84.9, 61.0: *E*-isomer; ^1H NMR (300 MHz, CDCl_3) δ 7.27-7.46 (m, 5H), 6.34 (dt, 1H, $J = 15.8, 5.1$ Hz), 5.97 (d, 1H, $J = 15.8$ Hz), 4.25 (t, 2H, $J = 5.1$ Hz), 1.68 (b, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.7, 131.4, 128.2, 128.1, 122.9, 110.6, 90.0, 87.5, 62.9; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{10}\text{O}$ [M^+] 158.0732, found 158.0735.

[(*Z*)-8-Trimethylsilyl-6-octen-4-ynyl] acetate (Table 1, entry 9); ^1H NMR (300 MHz, CDCl_3) δ 5.85 (dt, 1H, $J = 10.5, 8.7$ Hz), 5.27 (d, 1H, $J = 10.7$ Hz), 4.14 (t, 2H, $J = 6.3$ Hz), 2.41 (td, 2H, $J = 7.0, 2.0$ Hz), 2.0 (s, 3H), 1.82 (quintet, 2H, $J = 6.6$ Hz), 1.76 (d, 2H, $J = 8.8$ Hz), 0.0 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 171.0, 139.9, 106.2, 92.1, 78.6, 63.2, 27.9, 22.4, 20.9, 16.3, -1.6; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{22}\text{O}_2\text{Si}$ [M^+] 238.1389, found 238.1385.

***N*-Methyl-*N*-[6-trimethylsilyl-(*Z*)-4-hexen-2-ynyl]-(4-methyl)benzenesulfonamide** (Table 1, entry 10); ^1H NMR (300 MHz, CDCl_3) δ 7.71 (d, 2H, $J = 8.2$ Hz), 7.29 (d, 2H, $J = 7.9$ Hz), 5.90 (dt, 1H, $J = 10.7, 8.7$ Hz), 5.11 (d, 1H, $J = 10.6$ Hz), 4.17 (s, 2H), 2.82 (s, 3H), 2.42 (s, 3H), 1.64 (d, 2H, $J = 8.7$ Hz), 0.0 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 143.3, 141.6, 129.4, 127.9, 105.2, 85.5, 83.4, 40.8, 34.3, 22.8, 21.4, -1.7; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_2\text{SSi}$ [M^+] 335.1375, found 335.1379.

***N*-Methyl-*N*-[(*Z*)-4-hepten-2-ynyl]-(4-methyl)benzenesulfonamide** (Table 1, entry 11); ^1H NMR (300 MHz, CDCl_3) δ 7.68 (d, 2H, $J = 6.2$ Hz), 7.26 (d, 2H, $J = 6.2$ Hz), 5.78 (dt, 1H, $J = 8.0, 5.5$ Hz), 5.16 (d, 1H, $J = 8.0$ Hz), 4.14 (s, 2H), 2.79 (s, 3H), 2.37 (s, 3H), 2.02 (qd, 2H, $J = 5.6, 1.0$ Hz), 0.88 (t, 3H, $J = 5.7$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 145.9, 143.4, 134.1, 129.3, 127.8, 107.3, 85.5, 82.5, 40.6, 34.3, 23.4, 21.4, 13.2; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2\text{S}$ [M^+] 277.1136, found 277.1135.

General Procedure of Conjugated Enyne Ring Closing Metathesis with Catalyst 3.

To a solution of alkenyl enyne **9** (100 mg, 0.34 mmol) in benzene (17 mL) was added catalyst **3** (30.1 mg, 10 mol %). The reaction mixture was stirred for 18 hr at 70 °C. After removal of organic solvent, the residue was purified by column chromatography on silica gel with Et₂O/*n*-pentane (1:10) to give a cyclized triene **10**; ¹H NMR (300 MHz, CDCl₃) δ 6.33 (dd, 1H, *J* = 17.5, 10.7 Hz), 5.94 (t, 1H, *J* = 6.5 Hz), 5.17 (d, 1H, *J* = 17.5 Hz), 5.10 (d, 1H, *J* = 10.5 Hz), 4.96 (d, 2H, *J* = 6.3 Hz), 4.17-4.03 (m, 4H), 2.95 (s, 2H), 2.26-2.17 (m, 4H), 1.75 (m, 2H), 1.20 (t, 6H, *J* = 7.1 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 171.6, 150.8, 137.4, 132.7, 116.1, 113.3, 60.9, 54.9, 36.4, 35.0, 27.8, 21.9, 13.9; HRMS (EI) calcd for C₁₇H₂₄O₄ [M⁺] 292.1675, found 292.1686.

Compound **12a**. ¹H NMR (500 MHz, CDCl₃) δ 7.06-6.94 (m, 4H), 6.44 (dd, 1H, *J* = 10.4, 6.4 Hz), 5.92 (t, 1H, *J* = 4.4 Hz), 5.36 (d, 1H, *J* = 10.4 Hz), 5.22 (d, 2H, *J* = 15.5 Hz), 5.17 (d, 1H, *J* = 6.4 Hz), 4.65 (s, 2H), 4.19-4.15 (m, 4H), 3.90 (t, 2H, *J* = 3.7 Hz), 1.90 (t, 2H, *J* = 3.2 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 151.2, 149.7, 148.2, 140.1, 136.8, 130.4, 123.4, 122.5, 120.5, 117.0, 116.6, 116.0, 70.1, 67.2, 65.7, 65.4, 28.7; HRMS (EI) calcd for C₁₇H₂₀O₃ [M⁺] 272.1412, found 272.1410.

Compound **12b**. ¹H NMR (300 MHz, CDCl₃) δ 7.11-6.91 (m, 4H), 6.41 (dd, 1H, *J* = 17.4, 10.6 Hz), 5.90 (t, 1H, *J* = 7.1 Hz), 5.31 (d, 1H, *J* = 17.4 Hz), 5.14 (d, 2H, *J* = 6.6 Hz), 5.13 (d, 1H, *J* = 10.6 Hz), 4.53 (s, 2H), 4.12 (t, 2H, *J* = 5.6 Hz), 3.91 (d, 2H, *J* = 7.1 Hz), 3.61 (t, 2H, *J* = 5.6 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 151.9, 150.9, 145.1, 141.0, 137.3, 129.1, 124.2, 123.1, 121.8, 119.0, 117.2, 115.3, 78.4, 66.4, 64.5, 61.3, 29.2; HRMS (EI) calcd for C₁₇H₂₀O₃ [M⁺] 272.1412, found 272.1411.

Compound **14**. ¹H NMR (300 MHz, CDCl₃) δ 7.66 (d, 2H, *J* = 8.0 Hz), 7.27 (d, 2H, *J* = 8.9 Hz), 6.34 (dd, 1H, *J* = 17.4, 10.4 Hz), 5.79 (t, 1H, *J* = 5.9 Hz), 5.29 (d, 1H, *J* = 17.4 Hz), 5.15 (d, 1H, *J* = 10.6 Hz), 5.07 (d, 2H, *J* = 6.3 Hz), 3.94 (s, 2H), 3.39 (t, 2H, *J* = 6.2 Hz), 2.41 (s, 3H), 2.25 (m, 2H), 1.82 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 148.4, 143.0, 138.0, 137.0, 136.0, 131.4, 129.5, 127.1, 116.9, 114.6, 50.1, 48.9, 26.6, 26.4, 21.4; HRMS (EI) calcd for C₁₇H₂₄O₄ [M⁺] 303.1293, found 303.1288.

Compound **15**. ¹H NMR (300 MHz, CDCl₃) δ 7.67 (d, 2H, *J* = 8.3 Hz), 7.34 (d, 2H, *J* = 8.0 Hz), 6.82 (dd, 1H, *J* = 17.1, 11.1 Hz), 5.49 (d, 1H, *J* = 11.2 Hz), 5.39 (d, 1H, *J* = 17.4 Hz), 4.47 (d, 1H, *J* = 16.8 Hz), 3.80 (d, 1H, *J* = 16.9 Hz), 3.74 (td, 1H, *J* = 13.6,

4.2 Hz), 3.20 (m, 3H), 2.97 (m, 1H), 2.43 (s, 3H), 2.31 (m, 1H), 2.11-1.87 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 144.1, 135.6, 130.7, 130.1, 127.0, 124.9, 119.1, 111.2, 111.0, 110.0, 109.2, 50.5, 48.7, 45.0, 44.7, 38.0, 32.8, 29.8, 28.8, 21.5; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{21}\text{N}_5\text{O}_2\text{S}$ [M^+] 431.1416, found 431.1431.

Compound **16**. ^1H NMR (300 MHz, CDCl_3) δ 7.64 (d, 2H, $J = 8.3$ Hz), 7.31 (d, 2H, $J = 8.0$ Hz), 6.20 (m, 1H), 5.96 (t, 1H, $J = 6.3$ Hz), 4.00 (s, 2H), 3.43 (t, 2H, $J = 5.6$ Hz), 3.29 (t, 2H, $J = 1.8$ Hz), 3.22 (d, 2H, $J = 1.6$ Hz) 2.43 (s, 3H), 2.32 (m, 2H), 1.71 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 143.6, 137.5, 132.9, 129.8, 127.0, 115.8, 110.5, 111.4, 51.2, 47.0, 38.0, 37.1, 33.4, 32.9, 26.9, 26.0, 21.5; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{21}\text{N}_5\text{O}_2\text{S}$ [M^+] 431.1416, found 431.1424.

Crystal data of compound **15**.

Empirical formula	$\text{C}_{23}\text{H}_{21}\text{N}_5\text{O}_2\text{S}$	
Formula weight	431.51	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic,	P2(1)/c
Unit cell dimensions	$a = 14.209(4)$ Å	$\alpha = 90$ deg.
	$b = 12.367(3)$ Å	$\beta = 99.104(5)$ deg.
	$c = 12.819(3)$ Å	$\gamma = 90$ deg.
Volume	$2224.3(9)$ Å ³	
Z, Calculated density	4,	1.289 Mg/m^3
Absorption coefficient	0.175 mm^{-1}	
F(000)	904	
Theta range for data collection	2.20 to 28.09 deg.	
Limiting indices	$-17 \leq h \leq 10$, $-14 \leq k \leq 15$, $-16 \leq l \leq 16$	
Reflections collected / unique	13504 / 5000 [$R(\text{int}) = 0.0302$]	
Completeness to $\theta = 28.09$	92.1 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5000 / 0 / 354	
Goodness-of-fit on F^2	0.908	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0398$, $wR_2 = 0.0920$	
R indices (all data)	$R_1 = 0.0835$, $wR_2 = 0.1062$	
Extinction coefficient	$0.0027(6)$	

Largest diff. peak and hole

0.187 and -0.265 e. Å⁻³

(Z)-1-Phenyl-5-trimethylsilyl-3-penten-1-yne (Table 1, entry 1)

(E)-1-Phenyl-5-trimethylsilyl-3-penten-1-yne (Table 1, entry 1)

(Z)-1-Trimethylsilyl -2-tridecene-4-yne (Table 1, entry 2)

(1-Methoxymethyl)-[1,1-dimethyl-6-trimethylsilyl-(Z)-4-hexen-2-ynyl] ether

(Table 1, entry 3)

(1-Methoxymethyl)-[1,1-dimethyl-6-phenyl-(Z/E)-4-hexen-2-ynyl] ether (Table 1, entry 4)

(1-Methoxymethyl)-[1,1-dimethyl-(Z/E)-4-hepten-2-ynyl] ether (Table 1, entry 5)

(Z/E)-5-Phenyl-2-penten-4-yn-1-ol (Table 1, entry 6)

[(Z)-8-Trimethylsilyl-6-octen-4-ynyl] acetate (Table 1, entry 9)

***N*-Methyl-*N*-[6-trimethylsilyl-(*Z*)-4-hexen-2-ynyl]-(4-methyl)benzenesulfonamide**

(Table 1, entry 10)

***N*-Methyl-*N*-[(*Z*)-4-hepten-2-ynyl]-(4-methyl)benzenesulfonamide (Table 1, entry 11)**

Compound 10

Compound 12a

Compound 12b

Compound 14

Compound 15

Compound 16