Supporting Information for “Ring Synthesis by Stereoselective, Methylene-Free Enyne Cross Metathesis” by Amol A. Kulkarni and Steven T. Diver*

General Information

All reactions were conducted under an argon atmosphere unless otherwise noted. Dichloromethane (CH_2Cl_2) (alumina) and toluene (alumina + Q5) were drawn from a solvent purifier (alumina) immediately prior to use. Ruthenium [1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(phenylmethylene)(tricyclohexylphosphine) (Grubbs' second generation catalyst) was obtained from Materia Inc. (Pasadena, CA). 1,5-Cyclooctadiene (COD) was distilled from sodium prior to use. Alkynes were purified by flash column chromatography using silica gel. All-*cis* polybutadiene was purchased from Aldrich (18137-4). Column chromatography was carried out on Merck silica gel 60 (230 – 400 mesh). ^1H -NMR spectra were recorded at 500 MHz and ^{13}C -NMR spectra at 125 MHz in CDCl_3 . ^1H -NMR spectra were referenced on the TMS signal for CDCl_3 . The ^{13}C -NMR spectra were referenced at 77.0 ppm for CDCl_3 . The syringe pump (kd scientific, model 210) was used for the tandem enyne metathesis studies using a 5 mL glass gas tight syringe.

General Procedure for the 1,5-Cyclooctadiene (COD)-Alkyne Tandem Metathesis

Into an oven-dried 100 mL Schlenk tube equipped with a magnetic stirbar and a cold finger condenser, was added COD (244 μL , 2.0 mmole) dissolved in 40 mL CH_2Cl_2 followed by Grubbs' second generation catalyst (42 mg, 5 mol %) and this solution was

immersed in an oil bath maintained at 45 °C. Alkyne (1 mmole) and COD (244 µL, 2.0 mmole) were dissolved in 2.0 mL of CH₂Cl₂ and this solution was added to the solution of COD and the catalyst in CH₂Cl₂ at 45 °C over a period of 4 h by means of a gas-tight syringe (syringe pump). After the addition was complete, the reaction mixture was stirred at 45 °C for an additional 45 min. If the reaction mixture revealed the presence of unreacted alkyne (tlc), additional catalyst was added (in the portions of 2.5 mol %) until full consumption of the reactant alkyne was observed. After the reaction was complete, the reaction mixture was concentrated, then partially purified by passing through a small plug of silica gel (5.0 cm), eluted with 2 % ethyl acetate in hexanes (100 mL) to remove the catalyst and the solvent removed *in vacuo*. The viscous yellow oil thus obtained was redissolved in 2.0 mL of CH₂Cl₂ and this solution was slowly added to 10.0 mL methanol maintained at 0 °C dropwise with vigorous stirring. The milky suspension thus formed was filtered through a pipette column of silica gel. The filtrate was concentrated *in vacuo*. To the pale yellow oil thus obtained was added freshly distilled mesitylene (46.2 µL, 0.33 mmol) as the internal standard and the yield of the cyclohexadiene derivative was obtained against the internal standard. The crude reaction mixture was finally purified by flash chromatography using silica gel (using the indicated eluent) to provide the corresponding dienes as colorless oils.

Cyclohexa-1,5-dienylmethyl 2-naphthoate (4A):

As the general experimental. The cyclohexadiene derivative (**4A**) was obtained as a colorless oil (171 mg, 65 % yield) after purification of the crude reaction mixture using silica gel flash column chromatography (elution with 2 % ethyl acetate in hexanes).

Analytical tlc: R_f 0.41 (10 % ethyl acetate in hexanes). ^1H -NMR (500 MHz, CDCl_3 , ppm) δ 8.62 (s, 1H), 8.08 (dd, J = 8.5, 1.5 Hz, 1H), 7.98 (d, J = 8.5 Hz, 1H) 7.88 (d, J = 8.5 Hz, 2H), 7.61 – 7.52 (m, 2H), 6.04 (dd, J = 9.5, 1.5 Hz, 1H), 5.96 – 5.91 (m, 2H), 4.84 (s, 2H), 2.26 – 2.19 (m, 4H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 166.7, 135.5, 132.5, 131.2, 131.1, 129.4, 128.2, 128.1, 127.74, 127.72, 127.5, 126.6, 125.3, 125.0, 124.3, 67.2, 22.1, 22.0; FT-IR (thin film, cm^{-1}) 2935, 1717, 1282, 1195, 963, 778; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{18}\text{H}_{16}\text{O}_2$ 264.1145, found 264.1153, error 3.1 ppm.

Cyclohexa-1,5-dienylmethyl benzoate (4B):

As the general experimental. The cyclohexadiene derivative (**4B**) was obtained as a colorless oil (152 mg, 71 % yield) after purification of the crude reaction mixture using silica gel flash column chromatography (elution with 2 % ethyl acetate in hexanes). Analytical tlc: R_f 0.42 (10 % ethyl acetate in hexanes). ^1H -NMR (500 MHz, CDCl_3 , ppm) δ 8.08 - 8.05 (m, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 5.99 (dd, J = 9.5, 1.0 Hz, 1H), 5.93 – 5.88 (m, 2H), 4.78 (s, 2H), 2.23 – 2.17 (m, 4H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) 166.5, 132.9, 131.1, 130.2, 129.6, 128.3, 127.7, 124.9, 124.3, 67.0, 22.1, 22.0; FT-IR (thin film, cm^{-1}) 2935, 1719, 1451, 1270, 1110, 711; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{Na}_1$ 237.0886, found 237.0887, error 0.5 ppm.

***tert*-butyl(cyclohexa-1,5-dienylmethoxy)diphenylsilane (4C):**

As the general experimental. The cyclohexadiene derivative (**4C**) was obtained as a colorless oil (177 mg, 51 % yield) after purification of the crude reaction mixture using silica gel flash column chromatography (elution with 1.5 % ethyl acetate in hexanes).

Analytical tlc: R_f 0.46 (7 % ethyl acetate in hexanes). ^1H -NMR (500 MHz, CDCl_3 , ppm) δ 7.70 – 7.68 (m, 4H), 7.42 – 7.36 (m, 6H), 5.88 – 5.82 (m, 2H), 5.71 (s, 1H), 4.14 (s, 2H), 2.16 – 2.13 (m, 4H), 1.06 (s, 9H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) 135.6, 135.0, 133.8, 129.6, 127.6, 126.8, 124.4, 120.1, 65.9, 26.8, 22.5, 22.0, 19.3; FT-IR (thin film, cm^{-1}) 3053, 2849, 1428, 1107, 698, 501; High-resolution MS (EI^+ , m/z) calcd for $\text{C}_{23}\text{H}_{28}\text{O}_1\text{Si}_1$ 348.1904, found 348.1909, error 1.6 ppm.

1-[(cyclohexa-1,5-dienylmethoxy)methyl]benzene (4D):

As the general experimental. The cyclohexadiene derivative (**4D**) was obtained as a colorless oil (118 mg, 59 % yield) after purification of the crude reaction mixture using silica gel flash column chromatography (elution with 2 % ethyl acetate in hexanes). Analytical tlc: R_f 0.46 (7 % ethyl acetate in hexanes). ^1H -NMR (500 MHz, CDCl_3 , ppm) δ 7.37 – 7.34 (m, 4H), 7.29 – 7.27 (m, 1H), 5.98 (dd, J = 10.0, 1.5 Hz, 1H), 5.91 – 5.87 (m, 1H), 5.74 (s, 1H), 4.48 (s, 2H), 3.96 (s, 2H), 2.19 – 2.15 (m, 4H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 138.5, 132.9, 128.3, 127.8, 127.5, 127.3, 124.9, 123.9, 72.5, 71.6, 22.2, 22.1; FT-IR (thin film, cm^{-1}) 3033, 2853, 1356, 1070, 736; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2$ 200.1196, found 200.1201, error 2.8 ppm.

1-(cyclohexa-1,5-dienyl)ethyl benzoate (5A):

As the general experimental. The cyclohexadiene derivative (**5A**) was obtained as a colorless oil (169 mg, 74 % yield) after purification of the crude reaction mixture using silica gel flash column chromatography (elution with 2 % ethyl acetate in hexanes). Analytical tlc: R_f 0.44 (10 % ethyl acetate in hexanes). ^1H -NMR (500 MHz, CDCl_3 , ppm)

δ 8.05 (d, $J = 7.5\text{ Hz}$, 2H), 7.55 – 7.52 (m, 1H), 7.43 (t, $J = 7.5\text{ Hz}$, 2H), 6.04 (d, $J = 10.0\text{ Hz}$, 1H), 5.92 – 5.89 (m, 1H), 5.83 – 5.81 (m, 1H), 5.58 (q, $J = 6.5\text{ Hz}$, 1H), 2.21 – 2.12 (m, 4H), 1.45 (d, $J = 6.5\text{ Hz}$, 3H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 165.8 135.7, 132.7, 130.7, 129.5, 128.2, 127.7. 123.1, 122.1, 72.8, 22.1, 21.9, 19.6; FT-IR (thin film, cm^{-1}) 2980, 1717, 1450, 1269, 1109, 714; High-resolution MS (EI^+ , m/z) calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2$ 228.1145, found 228.1142, error 1.1 ppm.

1-cyclohexa-1,5-dienyl)-2-phenethyl acetate (5B):

As the general experimental. The cyclohexadiene derivative (**5B**) was obtained as a colorless oil (151 mg, 66 % yield) after purification of the crude reaction mixture using silica gel chromatography (elution with 2 % ethyl acetate in hexanes). Analytical tlc: R_f 0.40 (10% ethyl acetate in hexanes). ^1H -NMR (500 MHz, CDCl_3 , ppm) δ 7.26 (t, $J = 7.0\text{ Hz}$, 2H), 7.20 (m, 1H), 7.16 (t, $J = 7.0\text{ Hz}$, 2H), 6.03 (d, $J = 10.0\text{ Hz}$, 1H), 5.91 (d, $J = 10.0\text{ Hz}$, 1H), 5.57 (s, 1H), 5.38 (t, 7.5 Hz, 1H) 2.96 (dd, $J = 13.5, 7.5\text{ Hz}$, 1H), 2.87 (dd, $J = 13.5, 7.5\text{ Hz}$, 1H), 2.11 – 2.07 (m, 4H), 1.99 (s, 3H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 170.1, 137.2, 133.7, 129.5, 128.1, 127.8, 126.4, 123.9, 123.1, 76.8, 40.0, 22.0, 21.9, 21.2; FT-IR (thin film, cm^{-1}) 2929, 1740, 1494, 1371, 1239, 1019, 714; High-resolution MS (EI^+ , m/z) calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2$ 242.1301, found 242.1295, error 2.6 ppm.

2-(cyclohexa-1,5-dienyl)ethyl 2-naphthoate (6A):

As the general experimental. The reaction showed ca. 50 % conversion after 5h, Additional 2.5 % catalyst was added at $t = 5\text{ h}$ and $t = 8\text{ h}$. The reaction showed complete consumption of the alkyne after 10 h. The cyclohexadiene derivative (**6A**) was obtained

as a colorless oil (133 mg, 41 % yield) after purification of the crude reaction mixture using silica gel flash column chromatography (elution with 2 % ethyl acetate in hexanes). Analytical tlc: R_f 0.42 (10 % ethyl acetate in hexanes) ^1H -NMR (500 MHz, CDCl_3 , ppm) δ 8.60 (s, 1H), 8.06 (dd, J = 8.0, 1.5 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H) 7.88 (d, J = 8.0 Hz, 2H), 7.60 – 7.52 (m, 2H), 5.95 – 5.87 (m, 2H), 5.65 (s, 1H), 4.44 (t, J = 7.0 Hz, 2H), 2.54 (t, J = 7.0 Hz, 2H), 2.17 – 2.11 (m, 4H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 166.7, 135.5, 132.5, 131.9, 131.0, 129.3, 128.2, 128.1, 127.7, 127.6, 127.2, 126.7, 126.6, 125.2, 122.7, 64.1, 34.9, 22.4, 22.1; FT-IR (thin film, cm^{-1}) 2937, 1718, 1227, 1195, 779; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2$ 278.1293, found 278.1301, error 2.9 ppm.

***tert*-butyl 2-(cyclohexa-1,5-dienyl)ethyl(tosyl)carbamate (6B):**

As the general experimental but the reaction done on 0.5 mmole scale. The cyclohexadiene derivative (**6B**) was obtained as a colorless oil (117 mg, 62 % yield) after purification of the crude reaction mixture using silica gel flash column chromatography (elution with 4 % ethyl acetate in hexanes). Analytical tlc: R_f 0.35 (15 % ethyl acetate in hexanes). ^1H -NMR (500 MHz, CDCl_3 , ppm) δ 7.78 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.91 (dd, J = 10.0, 1.5 Hz, 1H), 5.87 – 5.84 (m, 1H), 5.60 (s, 1H), 3.86 (t, J = 8.0 Hz, 2H), 2.46 (t, J = 8.0 Hz, 2H), 2.43 (s, 3H), 2.13 – 2.10 (m, 4H), 1.35 (s, 9H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 150.8, 144.0, 137.5, 132.2, 129.2, 127.8, 127.1, 126.7, 122.7, 84.0, 46.5, 36.3, 27.8, 22.3, 22.1, 21.5; FT-IR (thin film, cm^{-1}) 2982, 1725, 1595, 1353, 1151, 808; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{20}\text{H}_{27}\text{O}_4\text{N}_1\text{S}_1$ 377.1655, found 377.1646, error 2.6 ppm.

Ethyl 3-(cyclohexa-1,5-dienyl)propanoate (6C):

As the general experimental but the reaction done on 2.0 mmole scale. The cyclohexadiene derivative (**6C**) was obtained as a colorless oil (123 mg, 68 % yield) after purification of the crude reaction mixture using silica gel flash column chromatography (elution with 2 % ethyl acetate in hexanes). Analytical tlc: R_f 0.38 (10 % ethyl acetate in hexanes). ^1H -NMR (500 MHz, CDCl_3 , ppm) δ 5.86 – 5.79 (m, 2H), 5.50 (s, 1H), 4.13 (q, J = 7.0 Hz, 2H), 2.42 – 2.39 (m, 2H), 2.36 – 2.33 (m, 2H), 2.10 – 2.08 (m, 4H), 1.25 (t, J = 7.0 Hz, 3H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 173.3, 134.2, 127.1, 126.6, 120.7, 60.3, 33.4, 30.6, 22.24, 22.23, 14.2; FT-IR (thin film, cm^{-1}) 2957, 1736, 1372, 1162, 1042; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$ 180.1145, found 180.1148, error 1.6 ppm.

3-(cyclohexa-1,5-dienyl)propyl 2-naphthoate (7A):

As the general experimental but the reaction done on 0.5 mmole scale. The reaction showed ca. 50 % conversion after 5 h. Additional 2.5 mol % catalyst was added at t = 5h and t = 8h. The reaction showed complete consumption of the alkyne after 10 h. The cyclohexadiene derivative (**7A**) was obtained as a colorless oil (62 mg, 42 % yield) after purification of the crude reaction mixture using silica gel flash column chromatography (elution with 2 % ethyl acetate in hexanes). Analytical tlc: R_f 0.42 (10 % ethyl acetate in hexanes). ^1H -NMR (500 MHz, CDCl_3 , ppm) δ 8.61 (s, 1H), 8.07 (dd, J = 8.0, 1.5 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 2H), 7.60 – 7.53 (m, 2H), 5.88 – 5.85 (m, 2H), 5.55 (s, 1H), 4.38 (t, J = 7.0 Hz, 2H), 2.23 (t, J = 7.0 Hz, 2H), 2.12 – 2.09 (m, 4H), 1.97 – 1.91 (m, 2H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 166.7, 135.5, 134.5,

132.5, 131.0, 129.3, 128.15, 128.08, 127.74, 127.68, 127.2, 126.8, 126.6, 125.2, 120.9, 64.6, 31.9, 27.3, 22.34, 22.30; FT-IR (thin film, cm^{-1}) 3029, 1717, 1285, 1100, 779; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{20}\text{H}_{20}\text{O}_2$ 292.1458, found 292.1460, error 0.8 ppm.

2-(3-chloropropyl)cyclohexa-1,3-diene (7B):

As the general experimental but the reaction done on 0.5 mmole scale. The cyclohexadiene derivative (**7B**) was obtained as a colorless oil (38 mg, 48 % yield) after purification of the crude reaction mixture using silica gel flash column chromatography (elution with 1 % ethyl acetate in hexanes). Analytical tlc: R_f 0.45 (4 % ethyl acetate in hexanes) ^1H -NMR (500 MHz, CDCl_3 , ppm) δ 5.87 – 5.84 (m, 1H), 5.81 – 5.79 (m, 1H), 5.53 (s, 1H), 3.53 (t, $J = 7.0$ Hz, 2H), 2.17 (t, $J = 7.0$ Hz, 2H), 2.12 – 2.09 (m, 4H), 1.90 – 1.85 (m, 2H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 134.1, 127.2, 126.7, 121.3, 44.4, 32.5, 31.1, 22.31, 22.29; FT-IR (thin film, cm^{-1}) 3024, 2860, 1440, 1294, 1055; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_9\text{H}_{13}\text{Cl}$ 156.0700, found 156.0697, error 2.4 ppm.

General Procedure for the Tandem Metathesis / Diels-Alder Cycloaddition Protocol

Into an oven-dried 100 mL Schlenk tube equipped with magnetic stirbar and a cold finger condenser, was added dichloromethane (40 mL) followed by all-*cis* polybutadiene (PB) (433 mg, 8 mmole) cut into small pieces. This mixture was then immersed in an oil bath maintained at 45 °C. The polymer dissolved slowly in the solvent and produced a viscous solution after 45 min. Grubbs' second generation catalyst was added at this stage. Alkyne (1 mmole) was dissolved in 2.0 mL of the CH_2Cl_2 and this

solution was slowly added to the solution of catalyst and the polymer in refluxing CH_2Cl_2 over 4 h by means of a gas-tight syringe (syringe pump). After the addition was complete, the reaction mixture was stirred in the oil bath for additional 45 min. The reaction mixture was concentrated, then partially purified by passing through a plug of silica gel (2.5 cm), eluted with 2 % ethyl acetate in hexanes to remove the catalyst and the solvent removed *in vacuo*. The pale yellow oil thus obtained was redissolved in 4.0 mL of toluene. This solution was then transferred to an oven-dried 25 mL Schlenk tube equipped with magnetic stirrer and a cold finger condenser. *N*-phenylmaleimide (346 mg, 2 mmole) was added and the reaction mixture was immersed in an oil bath maintained at 112 °C for 12 h. After the end of the reaction, the solvent was removed *in vacuo* and the crude oil thus obtained was purified by flash column chromatography using silica gel (using the indicated eluent) to provide the corresponding cycloadduct.

Cycloadduct (10):

As the general experimental. The cycloadduct (**10**) was obtained as a white solid (268 mg, 61 % yield over 2 steps) after purification of the crude reaction mixture using silica gel flash column chromatography (elution with 30 % ethyl acetate in hexanes). mp = 50 – 52 °C Analytical tlc: R_f 0.38 (45 % ethyl acetate in hexanes). ^1H -NMR (500 MHz, CDCl_3 , ppm) δ 8.57 (s, 1H), 8.00 (dd, 9.0, 1.5 Hz, 1H), 7.85 – 7.80 (m, 3H), 7.58 – 7.55 (m, 1H), 7.51 – 7.48 (m, 1H), 7.36 – 7.27 (m, 3H), 7.20 – 7.18 (m, 2H), 6.35 (dd, J = 6.0, 1.5 Hz, 1H), 4.92 (dd, J = 13.5, 1.5 Hz, 1H), 4.84 (dd, J = 13.5, 1.5 Hz, 1H), 3.39 – 3.34 (m, 2H), 3.11 – 3.07 (m, 2H), 1.80 – 1.70 (m, 2H), 1.56 – 1.48 (m, 2H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 177.8, 177.4, 166.5, 140.1, 135.5, 132.4, 131.8, 131.4, 129.5, 129.0,

128.7, 128.6, 128.2, 128.0, 127.6, 126.9, 126.6, 126.5, 125.2, 65.2, 44.7, 44.0, 34.2, 32.4, 24.1, 24.0; FT-IR (thin film, cm^{-1}) 2949, 1711, 1380, 1284, 1196, 780; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{28}\text{H}_{23}\text{O}_4\text{N}_1\text{Na}_1$ 460.1519, found 460.1529, error 2.0 ppm.

Cycloadduct (11):

As the general experimental but the reaction done on 0.5 mmole scale. The cycloadduct (**11**) was obtained as a colorless viscous oil (160 mg, 58 % yield over 2 steps) after purification of the crude reaction mixture using silica gel flash column chromatography (elution with 35 % ethyl acetate in hexanes). Analytical tlc: R_f 0.30 (50 % ethyl acetate in hexanes). ^1H -NMR (500 MHz, CDCl_3 , ppm) δ 7.72 (d, $J = 8.0$ Hz, 2H), 7.45 (t, $J = 8.0$ Hz, 2H), 7.38 – 7.35 (m, 1H), 7.26 (d, $J = 8.0$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 6.01 (dd, $J = 6.5, 1.5$ Hz, 1H), 3.93 – 3.87 (m, 1H), 3.81 – 3.75 (m, 1H), 3.25 – 3.19 (m, 2H), 3.05 – 2.99 (m, 2H) 2.63 – 2.51 (m, 2H), 2.42 (s, 3H), 1.71 – 1.65 (m, 2H), 1.52 – 1.41 (m, 2H), 1.33 (s, 9H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 178.0, 177.8, 150.7, 144.1, 142.0, 137.3, 131.9, 129.2, 129.1, 128.5, 127.8, 126.7, 125.8, 84.3, 45.1, 44.5, 44.1, 36.2, 35.3, 32.6, 27.8, 24.3, 23.7, 21.6; FT-IR (thin film, cm^{-1}) 2871, 1712, 1370, 1156, 915, 731; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{30}\text{H}_{34}\text{O}_6\text{N}_2\text{Na}_1\text{S}_1$ 573.2030, found 573.2045, error 2.8 ppm.