Supporting Information for "Cycloheptadiene Ring Synthesis by Tandem Intermolecular Enyne Metathesis" by Amol A. Kulkarni and Steven T. Diver.*

General Information

All reactions were conducted under an argon atmosphere unless otherwise noted. Dichloromethane (CH_2CI_2) and benzene were drawn from a solvent purifier (alumina) immediately prior to use. Ruthenium [1,3-bis-(2,4,6-trimethylphenyl)-2-

imidazolidinylidine]dichloro(phenylmethylene)(tricylohexylphosphine) (Grubbs' second generation catalyst) was obtained from Materia (Pasadena, CA). Cyclopentene was distilled from sodium prior to use and the alkynes were purified by flash column chromatography using silica gel. Column chromatography was carried out on Merck silica gel 60 (230-400 mesh). ¹H-NMR spectra were recorded at 500 MHz and ¹³C-NMR spectra at 125 MHz in CDCl₃.¹H-NMR spectra were referenced on the TMS signal for CDCl₃. The ¹³C-NMR spectra were referenced at 77.0 ppm for CDCl₃. The syringe pump (kd scientific, model 210) was used for the tandem enyne metathesis studies. A 450 W UV immersion lamp (Ace glass catalog no. 7825-34) was used for photolysis studies.

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General Procedure for the Tandem Cyclopentene-Alkyne Metathesis

Into an oven-dried 100 mL Schlenk tube equipped with magnetic stirbar and a cold finger condenser, was added dichloromethane (50 mL) followed by Grubbs' second generation catalyst (42.4 mg, 5 mol %) and the solution was heated to reflux. Alkyne (1.0 mmol) and cyclopentene (4.0 mmol) were dissolved in 2.0 mL of CH₂Cl₂ and this solution was then added to the catalyst solution in CH₂Cl₂ at 45 °C over a period of 16 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 small plug of silica gel (2.5 cm), eluted with CH_2CI_2 to remove the catalyst and the solvent removed in vacuo. The crude oil thus obtained was further purified by silica gel flash chromatography using silica gel (using the indicated eluent) to provide the corresponding dienes as pale yellow oils. The product was redissolved in ca. 5 mL CH₂Cl₂ and DMSO (177 µL, 2.5 mmol) was added.¹ This solution was stirred at room temperature for a period of 18 h after which the solvent was removed in vacuo and the yellow oil was further purified by flash column chromatography using silica gel. Elution with the indicated eluent yielded the corresponding dienes.



Benzoic acid 1-cyclohepta-1,6-dienyl-methyl ester (6A):

As the general experimental, but the reaction conducted on 2.5 mmole scale. The cycloheptadiene (**6A**) was obtained as colorless oil (571 mg, 76 % yield) after purification of the crude reaction mixture using silica gel flash column chromatography (elution with 4 % ethyl acetate in hexanes). Analytical tlc: R_r 0.35 (7 % ethyl acetate in hexanes). ¹H-NMR (500 MHz, CDCl₃, ppm) δ 8.05 (m, 2H), 7.54 (t, J = 7.0 Hz, 1H), 7.42 (t, 8.0 Hz, 2H), 6.01 (t, J = 5.0 Hz, 1H), 5.92 (m, 1H), 5.83 (dd, J = 12, 2 Hz, 1H), 4.75 (s, 2H), 2.35 (d, J = 4.5 Hz, 4H), 1.87 (m, 2H); ¹³C-NMR (125 MHz, CDCl₃, ppm) δ 166.5, 134.8, 133.5, 132.8, 131.6, 130.3, 129.6, 128.2, 125.6, 70.7, 31.7, 30.4, 25.9; FT-IR (thin film, cm⁻¹) 2926, 1717, 1451, 1313, 1111, 711; High-resolution MS (EI⁺, m/z) molecular ion calcd for C₁₅H₁₆O₂ 228.1145, found 228.1147, error 0.9 ppm.



Naphthalene-2-carboxylic acid cyclohepta-1,6-dienyl methyl ester (8):

As the general experimental, but the reaction conducted on 0.4 mmole scale. The cycloheptadiene derivative (**8**) was obtained as colorless oil (63 mg, 57 % 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 0.40 (7% ethyl acetate in hexanes). ¹H-NMR (500 MHz, CDCl₃, ppm) δ 8.62 (s, 1H), 8.08 (dd, J = 8.0,1.5 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.59-7.51 (m, 2H), 6.05 (t, J = 5.5 Hz, 1H), 5.98-5.93 (m, 1H), 5.89 (dd, J = 12.0, 1.0 Hz, 1H), 4.82 (s, 2H), 2.37 (q, J= 5.5 Hz, 4H), 1.91-1.86 (m, 2H); ¹³C-NMR (125 MHz, CDCl₃, ppm) δ 166.7, 135.5, 134.9, 133.7, 132.4, 131.7, 131.0, 129.3, 128.1, 128.0, 127.7, 127.6, 126.5, 125.6, 125.3, 70.4, 31.8, 30.5, 25.9; FT-IR (thin film, cm⁻¹) 2921, 1721, 1627, 1276, 1074, 778; High-resolution MS (El⁺, m/z) molecular ion calcd for C₁₉H₁₈O₂Na 301.1199, found 301.1200, error 0.2 ppm.



Benzoic acid 1-cyclohepta-1,6-dienyl-methyl ester (6B):

As the general experimental, but the reaction conducted on 2.5 mmole scale. The cycloheptadiene derivative (**6B**) was obtained as colorless oil (453 mg, 75 % yield) after purification of the crude reaction mixture with silica gel flash column chromatography (elution with 4 % ethyl acetate in hexanes). Analytical tlc: R_f 0.36 (7% ethyl acetate in hexanes). ¹H-NMR (500 MHz, CDCl₃, ppm) δ 8.04 (t, J = 8.5 Hz, 2H), 7.54 (t, J = 15 Hz, 1H) 7.43 (t, J = 15 Hz, 2H), 6.00-5.92 (m, 3H), 5.53 (q, J = 7.0 Hz, 1H), 2.31 (m, 4H), 1.85 (m, 2H), 1.45 (d, J = 7.0 Hz, 3H); ¹³C-NMR (125 MHz, CDCl₃, ppm) δ 165.7, 136.6, 135.0, 132.7, 130.8, 130.7, 129.6,

128.3, 124.1, 75.9, 31.5, 29.9, 26.6, 20.4; FT-IR (thin film, cm⁻¹) 2929, 1716, 1330, 1314, 1110, 712; High–resolution MS (EI⁺, m/z) molecular ion calcd for $C_{16}H_{18}O_2$ 242.1301 found 242.1304, error 1.2 ppm.



Acetic acid 1-cyclohepta-1,6-dienyl-2-phenyl-ethyl ester (10):

As the general experimental, but the reaction conducted on 0.25 mmole scale. The cycloheptadiene derivative (**10**) was obtained as colorless oil (40 mg, 62 % yield) after purification of the crude reaction mixture using silica gel flash chromatography (elution with 4 % ethyl acetate in hexanes). Analytical tlc: R_r 0.43 (7% ethyl acetate in hexanes). ¹H-NMR (500 MHz, CDCl₃, ppm) δ 7.25 (t, J = 8.0 Hz, 2H), 7.18 (m, 3H), 5.98 (m, 1H), 5.90 (m, 1H), 5.72 (t, J = 6.0 Hz, 1H), 5.31 (t, J = 6 Hz, 1H), 2.97 (dd, J = 13.5, 7.0 Hz, 1H), 2.87 (dd, J = 13.5, 7.0 Hz, 1H), 2.30 (q, J = 5.5 Hz), 2.21-2.17 (m, 2H), 1.99 (s, J = 6 Hz, 3H), 1.84-1.70 (m, 2H); ¹³C-NMR (125 MHz, CDCl₃, ppm) δ 170.1, 137.5, 135.1, 134.3, 132.4, 129.5, 128.1, 126.3, 124.0, 79.7, 40.5, 31.6, 29.8, 26.5, 21.3; FT-IR (thin film, cm⁻¹) 2926, 1739, 1454, 1369, 1019, 699; High-resolution MS (EI⁺, m/z) molecular ion calcd for C₁₇H₂₀O₂ 256.1458, found 256.1452, error 2.4 ppm.



2-Benzyloxymethyl-cyclohepta-1,3-diene (12):

As the general experimental, but the reaction conducted on 2.5 mmole scale. The cycloheptadiene derivative (**12**) was isolated as colorless oil (120 mg, 56 % 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 0.4 (3% ethyl acetate in hexanes). ¹H-NMR (500 MHz, CDCl₃, ppm) δ 7.34-7.25 (m, 5H), 5.93-5.89 (m, 1H), 5.87-5.82 (m, 2H), 4.48 (s, 2H), 3.94 (s, 2H), 2.36-2.31 (m, 4H), 1.88-1.83 (m, 2H); ¹³C-NMR (125 MHz, CDCl₃, ppm) δ 138.5, 134.4, 133.3, 132.2, 128.3, 127.8, 127.4, 126.1, 76.1, 71.4, 31.8, 30.4, 26.1; FT-IR (thin film, cm⁻¹) 2924, 2855, 1453, 1104, 1073, 735; High-resolution MS (EI⁺, m/z) molecular ion calcd for C₁₅H₁₈ONa 237.1250, found 237.1244, error 2.4 ppm.



tert-Butyl-(cyclohepta-1,6-dienylmethoxy)-diphenyl-silane (14):

As the general experimental, but the reaction conducted on 0.3 mmole scale. The cyloheptadiene derivative (**14**) was obtained as colorless oil (61 mg, 56 % yield) after purification of the crude reaction mixture using silica gel flash column chromatography (elution with 3% ethyl acetate in hexanes). Analytical tlc: R_f 0.68 (5% ethyl acetate in hexanes). ¹H-NMR (500 MHz, CDCl₃, ppm) δ 7.68 (dd, J = 7.5, 1 Hz, 4H), 7.42 - 7.35 (m, 6H), 5.85 (m, 2H), 5.69 (d, J = 12.5 Hz, 1H), 4.10 (d, J = 1.5 Hz, 2H), 2.31 (m, 4H), 1.83 (m, 2H), 1.06 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃, ppm) δ 135.6, 135.1, 133.8, 133.7, 129.5, 128.2, 127.6, 125.6, 68.7, 31.8, 30.2, 26.9, 26.2, 19.3; FT-IR (thin film, cm⁻¹) 3048, 2929, 2856, 1427, 1111, 824,

738; High-resolution MS (EI⁺, m/z) molecular ion calcd for $C_{24}H_{30}OSi$ 362.2060, found 362.2056, error 0.1 ppm.



2-Phenyl-1,3-cycloheptadiene (16):

As general experimental, but the reaction done on 0.25 mmole scale. The cycloheptadiene derivative (**16**) was obtained as pale yellow oil (25 mg, 58 % yield) after purification of the crude reaction mixture using silica gel flash column chromatography (elution with 0.5% ethyl acetate in hexanes). Analytical tlc: R_r 0.58 (1% ethyl acetate in hexanes). ¹H-NMR (500 MHz, CDCl₃, ppm) δ 7.35-7.28 (m, 4H), 7.25-7.21 (m, 1H), 6.22 (t, J = 6.0 Hz, 1H), 6.14-6.10 (m, 2H), 2.34 (m, 4H), 2.00 (m, 2H); ¹³C-NMR (125 MHz, CDCl₃, ppm) δ 143.6, 138.7, 135.0, 131.7, 128.4, 128.1, 126.5, 126.4, 30.5, 30.0, 29.5; FT-IR (thin film, cm⁻¹) 3021, 2925, 2856, 1489, 1444, 764, 739, 668; High-resolution MS (EI⁺, m/z) molecular ion calcd for C₁₃H₁₄ 170.1096, found 170.1181, error 4.9 ppm.



2-(3-Chloro-propyl)-cyclohepta-1,3-diene (18):

As general experimental. Crude NMR analysis versus mesitylene internal standard revealed 73% yield. Further purification by column chromatography

resulted in some decomposition. The cycloheptadiene derivative (**18**) was obtained as colorless oil (36 mg, 21 % yield) after purification by means of silica gel flash column chromatography (elution with hexanes). Analytical tlc: $R_f 0.37$ (hexanes). ¹H-NMR (500 MHz, CDCl₃, ppm) δ 5.88-5.84 (m, 1H), 5.69-5.65 (m, 2H), 3.53 (t, J = 6.5 Hz, 2H), 2.29 (q, J= 5.5 Hz, 2H), 2.23 (q, J = 5.5 Hz, 2H), 2.17 (t, J = 6.5 Hz, 2H), 1.90-1.81 (m, 4H); ¹³C-NMR (125 MHz, CDCl₃, ppm) δ 135.0, 134.1, 129.9, 128.2, 44.4, 36.3, 32.0, 31.6, 29.9, 27.5; FT-IR (thin film, cm⁻¹) 2919, 2836, 1437, 661; High-resolution MS (EI⁺, m/z) molecular ion calcd for C₁₀H₁₅Cl 170.0862, found 170.0861, error 0.9 ppm.



Benzoic acid 2-cyclohepta-1,6-dienyl-ethyl ester (20):

As general experimental, but reaction done on 0.2 mmole scale. The cycloheptadiene derivative (**20**) was obtained as colorless oil (22 mg, 57 % yield) after silica gel flash column chromatography (elution with 5% ethyl acetate in hexanes). Analytical tlc: R_f 0.40 (7% ethyl acetate in hexanes). ¹H-NMR (500 MHz, CDCl₃, ppm) δ 8.04 (dd, J= 8.0, 1.0 Hz, 2H), 7.55 (m, 1H), 7.44 (t, J = 8.0 Hz, 2H), 5.88 (m, 1H), 5.76 (m, 2H), 4.36 (t, J = 7.0 Hz, 2H), 2.48 (t, J = 7.0 Hz, 2H), 2.30 (q, J = 5.5 Hz, 2H), 2.24 (q, J = 5.5 Hz, 2H), 1.83 (m, 2H); ¹³C-NMR (125 MHz, CDCl₃, ppm) δ 166.8, 134.5, 133.0, 132.9, 131.6, 130.7, 129.8, 128.5, 128.4, 64.8, 38.9, 31.8, 30.3, 27.6; FT-IR (thin film, cm⁻¹) 2936, 1740, 1369,

1019, 699; High-resolution MS (EI⁺, m/z) molecular ion calcd for $C_{16}H_{18}O_2$ 242.1301, found 242.1310, error 0.4 ppm.



tert-Butyl-(2-cyclohepta-1,6-dienyl-ethoxy)-diphenyl-silane (22):

As the general experimental, but the reaction conducted on 0.2 mmole scale. The cycloheptadiene derivative (**22**) was obtained as colorless oil (40 mg, 53 % yield) after purification of the crude reaction mixture using silical gel flash chromatography (elution with 1% ethyl acetate in hexanes). Analytical tlc: $R_f 0.47$ (2% ethyl acetate in hexanes). ¹H-NMR (500 MHz, CDCl₃, ppm) δ 7.67 (dd, J= 7.5, 1.5 Hz, 4H), 7.43-7.35 (m, 6H), 5.78-5.74 (m, 1H), 5.63 (t, J = 12.0 Hz, 1H), 5.58 (d, J = 12.0 Hz, 1H), 3.70 (t, J = 7.0 Hz, 2H), 2.29-2.26 (m, 4H), 2.21 (q, J = 7.0 Hz, 2H), 1.83-1.78 (m, 2H), 1.04 (m, 9H); ¹³C-NMR (125 MHz, CDCl₃, ppm) δ 135.6, 134.1, 133.4, 133.3, 130.8, 129.5, 128.9, 127.5, 63.9, 42.8, 31.6, 30.2, 27.1, 26.8, 19.2; FT-IR (thin film, cm⁻¹) 2929, 2956, 1427, 1110, 737; High-resolution MS (EI⁺, m/z) molecular ion calcd for C₂₅H₃₂OSiNa₁ 399.2115, found 399.2099, error 3.8 ppm



N-Butyl-N-cyclohepta-1,6-dienylmethyl-4-methyl-benzenesulfonamide (24): As general experimental, but reaction done on 0.22 mmole scale. The cycloheptadiene derivative (**24**) was obtained as colorless oil (48 mg, 65 % yield) after purification of the reaction mixture through silica gel column chromatography (elution with 5 % ethyl acetate in hexanes). Analytical tlc: R_r 0.32 (10% ethyl acetate in hexanes). ¹H-NMR (500 MHz, CDCl₃, ppm) δ 7.68 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.90-5.86 (m, 1H), 5.79 (dd, J = 12.0, 1.0 Hz, 1H), 5.71 (t, J = 5.5 Hz, 1H), 3.67 (s, 2H), 3.04 (t, J = 7.5 Hz, 2H), 2.42 (s, 3H), 2.31 (q, J = 5.5 Hz, 2H), 2.26 (q, J = 5.5 Hz, 2H), 1.81 (m, 2H), 1.44 (m, 2H), 1.21 (m, 2H), 0.84 (t, J = 7 Hz, 3H); ¹³C-NMR (125 MHz, CDCl₃, ppm) δ 142.9, 137.1, 134.6, 132.5, 131.8, 129.5, 127.1, 125.9, 56.3, 47.2, 31.8, 30.4, 30.3, 26.1, 21.5, 20.0, 13.7; FT-IR (thin film, cm⁻¹) 2926, 1337, 1159, 655; High-resolution MS (EI⁺, m/z) molecular ion calcd for C₁₉H₂₇O₂NSNa 356.1655, found 356.1665, error 2.9 ppm



Benzoic acid 6,7-dioxa-bicyclo[3.2.2]non-8-en-8-yl methyl ester (30):

Under ambient atmosphere, diene (6A) (240 mg, 1.05 mmol) was dissolved in 45 mL of CH₂Cl₂ in a 80 mL pyrex test tube equipped with a magnetic stirbar. To this solution was added a catalytic amount (1 mg) of the photosensitive dye, 5,10,15,20-tetraphenyl-21H,23H-porphine (TPP). Oxygen gas was bubbled slowly through the solution. The resultant pale violet solution was then photolyzed with a 450 W UV immersion lamp for 1 h. TLC analysis at this stage showed complete conversion of the diene (6A) and concurrent appearance of a lower moving spot. The crude reaction mixture was concentrated in vacuo and purified by flash column chromatography (elution with 15% hexanes) to afford 152 mg (67 % yield) of the endoperoxide (30) as pale yellow oil. Analytical tlc: R_f 0.54 (40% ethyl acetate in hexanes). ¹H-NMR (500 MHz, CDCl₃, ppm) δ 8.01 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 8.0 Hz 1H), 7.43 (t, J = 8.0 Hz, 2H), 6.38 (d, J = 8 Hz, 1H), 4.90 (s, 2H), 4.79-4.77 (m, 2H), 2.00-1.86 (m, 4H), 1.60-1.55 (m, 1H), 1.38-1.28 (m, 1H); ¹³C-NMR (125 MHz, CDCl₃, ppm) δ 166.0, 135.7, 133.3, 129.6, 129.5, 128.5, 124.5, 78.7, 76.5, 65.0, 31.7, 31.6, 18.4; FT-IR (thin film, cm⁻¹) 2935, 1721, 1451, 1269, 1110, 712; High-resolution MS (EI⁺, m/z) molecular ion calcd for C₁₅H₁₆O₄Na₁ 283.0941, found 283.0940, error 0.1 ppm.



Benzoic acid 3,7-dihydroxy-cyclohept-1-enylmethyl ester (31):

To an oven-dried 25 mL round bottom flask was added endoperoxide (30) (19 mg, 0.073 mmol, 1 eq.) dissolved in 500 μ L of CH₂Cl₂. Zinc dust (19 mg, 0.29 mmol, 4 eq.) was added to this solution. To the resultant suspension was added acetic acid (7.0 µL, 0.12 mmol, 1.7 eq.) dissolved in 500 µL of CH₂Cl₂ in three portions over 30 min time interval. The reaction was stirred at room temperature for a further 15 min. The suspension was passed through a celite plug and eluted with methanol. Concentration of the methanolic extract in vacuo yielded yellow oil which was further purified by passing through a plug of silica gel. Elution with ethyl acetate yielded a pale yellow solution which upon concentration in vacuo afforded 18 mg (92 % yield) of the allylic diol (31) as a pale yellow oil. Analytical tlc: R_f 0.07 (3:1 ethyl acetate in hexanes). ¹H-NMR (500 MHz, CDCl₃, ppm) δ 8.04 (dd, J= 8.0, 1.0 Hz, 2H), 7.56 (m, 1H), 7.43 (m, 2H), 6.10 (d, J = 5.5 Hz, 1H), 4.89-4.83 (m, 2H), 4.36 (s, 2H), 3.35 (br s, 1H), 2.82 (br s, 1H), 2.29-2.21 (m, 1H), 1.91-1.82 (m, 2H), 1.75-1.69 (m, 3H); ¹³C-NMR (125 MHz, CDCl₃, ppm) δ 166.4, 142.0, 135.0, 133.2, 130.0, 129.6, 128.4, 70.4, 68.5, 67.5, 34.2, 34.0, 20.5; FT-IR (thin film, cm⁻¹) 3401, 2927, 1719, 1273, 1070, 712; High-resolution MS (EI⁺, m/z) molecular ion calcd for $C_{15}H_{18}O_4Na$ 285.1097, found 285.1096, error 0.1 ppm.



Benzoic acid 7-hydroxy-3-oxo-cyclohept-1-enyl methyl ester (32):

To an oven-dried 10 mL round bottom flask was added a solution of 9 mg (0.035 mmol, 1 eq.) of the endoperoxide (30) in 200 μ L of CH₂Cl₂. The solution was stirred at room temperature for 1 min and 63 µL (0.35 mmol, 10 eq.) of 1,2,2,6,6pentamethylpiperidine was added to this solution. TLC analysis after 45 min indicated complete conversion of the endoperoxide (30). The reaction was quenched by adding 2 mL of 1N HCl and extracted with 2 mL of CH₂Cl₂. The organic layer was dried over anhydrous K₂CO₃ for a period of 10 min and the solvent removed *in vacuo*. The γ -hydroxcycloheptenone derivative (**32**) was obtained as colorless oil (6 mg, 67% yield) after purification of the crude reaction mixture using a plug of silica gel (elution with 50% ethyl acetate in hexanes). Analytical tlc: R_f 0.16. ¹H-NMR (500 MHz, CDCl₃, ppm) δ 8.03 (d, J= 7.5 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 6.10 (s, 1H), 5.12-5.02 (m, 2H), 4.64-4.60 (m, 1H), 2.94 (d, J = 5.5 Hz, 1H), 2.71-2.65 (m, 1H), 2.52-2.46 (m, 1H), 2.16-2.10 (m, 1H), 1.98-1.89 (m, 1H), 1.89-1.79 (m, 2H); ¹³C-NMR (125 MHz, CDCl₃, ppm) & 203.8, 166.1, 153.0, 133.5, 129.7, 129.3, 128.5, 127.0, 70.2, 65.0, 42.4, 33.9, 17.6; FT-IR (thin film, cm⁻¹) 3435, 2941, 1723, 1660, 1268, 1113, 712; High-resolution MS (EI⁺, m/z) molecular ion calcd for $C_{15}H_{16}O_4Na$ 283. 0941, found 283.0933, error 2.9 ppm.



Naphthalene-2-carboxylic acid 1,1-diphenyl-2,7-dihydro-1H-silepin-4-yl methyl ester (35):

To an oven-dried 50 mL Schlenk tube equipped with magnetic stirbar and a cold finger condenser was added 21 mg (0.1 mmol, 1 eq.) of alkyne (7), 94 mg of the silacyclopentene derivative (34) followed by 10 mL of benzene. Grubbs' second generation catalyst (8.5 mg, 0.01 mmol, 10 mol %) was added to this reaction mixture. The reaction mixture was then immersed in an oil bath maintained at 80 °C. After 2 h, tlc analysis revealed unreacted alkyne and the reaction appeared to have stalled and additional Grubbs' second generation catalyst was added (4.3 mg, 0.005 mmol, 5 mol%). The reaction was complete after 30 min of adding the extra catalyst. The crude reaction mixture was then cooled to room temperature and concentrated. Further purification of the crude reaction mixture by flash column chromatography using silica gel (elution with 7 % ethyl acetate in hexanes) afforded 14 mg (30 % yield) of the silepin (35) as pale yellow oil. Analytical tlc: R_f 0.35 (25 % ethyl acetate in hexanes). ¹H-NMR (500 MHz, CDCl₃, ppm) δ 8.60 (s, 1H), 8.05 (dd, J= 8.0, 1.5 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.60-7.52 (m, 6H), 7.43-7.36 (m, 6H), 6.32-6.22 (m, 2H), 5.94 (d, J = 10 Hz, 1H), 4.85 (s, 2H), 2.09 (d, J = 7.0 Hz, 4H); ¹³C-NMR (125 MHz, CDCl₃, ppm) δ 166.9, 136.0, 135.7, 134.6, 132.8, 132.7, 131.5, 131.3, 130.0, 129.6, 129.3, 128.4, 128.3, 128.2, 128.0, 126.8, 126.1, 125.6, 123.2, 69.0, 16.8, 16.5; FT-IR (thin film, cm⁻¹) 3043, 2921, 1708, 1660, 1283, 1189, 703; High-resolution MS (EI⁺, m/z) molecular ion calcd for C₃₀H₂₆O₂SiNa 469.1594, found 469.1596, error 0.4 ppm.

Reference

¹ Ahn, Y. M.; Yang, K.; Georg, G. I. *Org. Lett.* **2001**, *3*, 1411-1413.