Spectral data for "Generation of Molecular Complexity from Cyclooctatetraene Using Dienyliron and Olefin Metathesis"

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**Electronic Supporting Information**

**Generation of molecular complexity from cyclooctatetraene using dienyliron and olefin metathesis methodology**

Mohamed F. El-Mansy, Anobick Sar, Subhabrata Chaudhury, Nathaniel J. Wallock and William A. Donaldson*

### Experimental procedures

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**Tricarbonyl[1,3-dimethyl 2-[(3,4,6,7-η⁴)-8-benzoylbicyclo[3.2.1]octa-3,6-dien-2-yl]-2-(2-propen-1-yl)propanedioate]iron.** To a solution of sodium dimethyl allylmalonate, freshly prepared from dimethyl allylmalonate (0.157 g, 0.809 mmol) and excess NaH in THF (15 ml), at 0 °C under N₂ was added solid cation 2 (0.200 g, 0.404 mmol) and the reaction mixture stirred for 1 h. Water (15 mL) was added and the mixture was extracted several times with ethyl acetate. The combined extracts were dried (MgSO₄), concentrated, and the residue was purified by column chromatography (SiO₂, hexane-ethyl acetate = 10:1 to 5:1...
gradient elution) to afford a golden-yellow oil (0.200 g, 95%). IR (Neat) 2954, 2033, 1715, 1681 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 2.61 (dd, J = 8.6, 14.8 Hz, 1H), 2.73 (m, 1H), 2.80 (dd, J = 6.8, 14.8 Hz, 1H), 3.26 (m, 4H), 3.41 (m, 2H), 3.74 (br m, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 5.08 (d, J = 17.4 Hz, 1H), 5.14 (d, J = 10.2 Hz, 1H), 5.68 (dtd, J = 7.4, 8.6, 15.4 Hz, 1H), 7.49 (m, 2H), 7.59 (m, 1H), 7.87 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 28.0, 36.5, 37.9, 38.9, 42.8, 52.7, 52.9, 53.5, 57.4, 62.4 (2 signals overlapping), 69.7, 119.8, 128.4, 128.9, 131.9, 133.3, 136.1, 170.9, 172.0, 199.0, 215.0. FAB-HRMS m/z 521.0903 (calcd for C₂₆H₂₅O₈Fe (M + H⁺) m/z 521.0899).

**Dimethyl 2-[(3,4,6,7-η⁴)-8-benzoyle bicyclo[3.2.1]octa-3,6-dien-2-yl]-2-(2-propen-1-yl)propanedioate (7).** To a solution of the above iron complex (0.160 g, 0.307 mmol) in methanol was added cerium ammonium nitrate (0.336 g, 0.614 mmol) in one portion. The reaction mixture was stirred for 1 h at room temperature. Water (20 mL) was added and the mixture was extracted several times with ethyl acetate. The combined organic extracts were dried (MgSO₄) and concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂, hexane-ethyl acetate = 10:1) to afford 7 (0.096 g, 82%) as a colorless oil. IR (Neat) 3058, 3005, 1712, 1362 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 2.79 (t, J = 2.8 Hz, 1H), 2.84 (m, 2H), 3.17 (m, 2H), 3.31 (s, 1H), 3.63 (s, 3H), 3.71 (s, 3H), 5.09 (m, 2H), 5.52 (td, J = 2.6, 9.8 Hz, 1H), 5.67 (dtd, J = 7.6, 10.1, 17.6 Hz, 1H), 5.88 (dd, J = 3.1, 5.5 Hz, 1H), 5.99 (dd, J = 2.9, 5.6 Hz, 1H), 6.28 (ddd, J = 2.8, 6.5, 9.8 Hz, 1H), 7.43 (m, 2H), 7.52 (m, 1H), 7.91 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 38.1, 41.3, 42.1, 43.7, 52.4 (two signals overlapped), 55.1, 60.9, 119.4, 125.2, 128.5, 128.7, 131.2, 132.3, 132.9, 134.9, 136.1, 136.5, 170.9, 171.1, 199.7. This material was used in the next step without further characterization.

**N-(8-Benzoyle bicyclo[3.2.1]octa-3,6-dien-2-yl)-4-methyl-N-2-propen-1-yl-benzenesulfonylamide (8).** To a solution of 2 (0.20 g, 0.40 mmol) in acetonitrile (15 mL) under N₂, was added the potassium salt of tosyl allylamine (0.250 g, 1.00 mmol). The mixture was stirred at room temperature for 3 h, at which time monitoring by TLC indicated the disappearance of 2. The reaction mixture was filtered under vacuum and the filter bed washed with acetonitrile. To the combined filtrates was added cerium ammonium nitrate (0.42 g, 0.77 mmol). The mixture was stirred under nitrogen for 2 h, and then filtered through a short column of silica gel, using
CH₂Cl₂ to complete the elution. The combined filtrates were concentrated and the residue purified by column chromatography (SiO₂, hexanes–ethyl acetate = 4:1) to give 8 (0.117 g, 70%) as a colorless solid. mp 137-138 °C; IR (CH₂Cl₂) 1676, 1330, 1157 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 2.43 (s, 3H), 3.11 (br s, 1H), 3.22 (dd, J = 3.0, 6.6 Hz, 1H), 3.88 (s, 1H), 3.98 (dd, J = 6.4, 16.8 Hz, 1H), 4.13 (br dd, J = 5.0, 16.8 Hz, 1H), 4.27-4.30 (m, 1H), 5.04-5.11 (m, 2H), 5.23 (dd, J = 1.2, 17.6 Hz, 1H), 5.86-5.93 (m, 2H), 6.18 (dd, J = 3.2, 5.6 Hz, 1H), 6.39 (ddd, J = 2.5, 6.4, 9.2 Hz, 1H), 7.30 (d, J = 7.6 Hz, 2H), 7.45 (t, J = 7.8 Hz, 2H), 7.55 (tt, J = 1.6, 7.6 Hz, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.89 (dd, J = 1.6, 8.4 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 42.9, 47.3, 48.9, 55.3, 57.2, 117.5, 124.6, 127.3, 128.5, 128.8, 129.9, 130.0, 133.1, 135.9, 136.2, 137.9, 138.5, 140.4, 143.6, 199.4. Anal. Calcd for C₂₉H₂₅NO₃S·½ H₂O: C, 70.07; H, 6.11. Found: C, 70.29; H, 5.90.

**Dimethyl 2-(bicyclo[5.1.0]octa-3,5-dien-2-yl)-2-(2-propen-1-yl)propanedioate (9):** To a cold solution of dimethyl allylmalonate (0.25 mL, 1.5 mmol) in dry ether (10 mL) was added a solution of methyl lithium (1.0 mL, 1.6 M in ether, 1.6 mmol). The mixture was stirred for 15 min at room temperature, at which time cation 3 (0.573 g, 1.01 mmol) was added in one portion. After 1 h, the reaction mixture was quenched with water (15 mL). The biphasic solution was extracted several times with ethyl acetate, and the combined extracts were dried (MgSO₄) and concentrated to ca. 15 mL. (Complete concentration resulted in spontaneous decomposition of the crude complex to give (COT)Fe(CO)₂PPh₃ and dimethyl allylmalonate). The solution of the crude complex was diluted with acetonitrile (10 mL) and CAN (1.186 g, 2.131 mmol) was added in one portion. The solution was stirred for 30 min, poured onto water (25 mL) and extracted several times with ethyl acetate. The combined extractions were washed with water, followed by brine, dried (MgSO₄), and concentrated. The residue was purified by column chromatography (SiO₂, hexanes–ethyl acetate = 30:1) to give 9 (0.186 g, 67%) as a pale yellow oil. IR (neat) 3017, 2954, 1731, 1640, 1435, 1220 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.64 (dddd, J = 0.8, 4.4, 8.2, 8.8 Hz, 1H), 1.11-1.22 (m, 1H), 1.85 (dddd, J = 0.5, 4.4, 5.3, 5.9 Hz, 1H), 1.96-2.06 (m, 1H), 2.70-2.86 (m, 2H), 3.33-3.80 (m, 1H), 3.74 (s, 3H), 3.75 (s, 3H), 5.03-5.14 (m, 2H), 5.30 (tdd, J = 0.8, 5.0, 10.9 Hz, 1H), 5.57 (tdd, J = 0.9, 5.3, 11.6 Hz, 1H), 5.74-5.89 (m, 2H), 6.14 (tdd, J = 0.5, 7.7, 11.5 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 6.4, 15.9,
39.6, 42.4, 42.5, 52.67, 52.71, 61.8, 118.4, 123.1, 126.9, 127.6, 132.8, 134.6, 170.4, 170.5. 
GC/MS m/z 276. El-HRMS m/z 276.1357 (calcd for C_{16}H_{20}O_4 m/z 276.1362).

**N-(Bicyclo[5.1.0]octa-3,5-dien-2-yl)-4-methyl-N-2-propen-1-yl-benzene-sulfonamide (10):** To a stirring suspension of 3 (1.00 g, 1.77 mmol) in water-saturated ether (60 mL) was added the potassium salt of N-tosyl allylamine (2.76 g, 11.1 mmol). After 30 min the orange ethereal layer was decanted from any solid and additional moist ether (60 mL) was added to the solid and the mixture stirred for 10 min. This was repeated until the mother liquor was colorless. The collected ethereal layers were combined and concentrated to give a yellow solid (1.10 g, 90%): mp 108-109 °C. To a stirring solution of complex (0.30 g, 0.44 mmol) in dry acetonitrile (20 mL) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.11 g, 0.48 mmol). After 1 h, the starting material had been consumed as indicated by TLC monitoring. The reaction mixture was passed through short column of silica gel and the column flushed with CH_2Cl_2 until no further product appeared by TLC monitoring. These fractions were combined and concentrated, and the residue was purified by column chromatography (SiO_2, hexanes-ethyl acetate = 4:1) to give 10 (81 mg, 58%) as a faint yellow oil. IR (CH_2Cl_2) 1346, 1162 cm^{-1}; ^1H NMR (CDCl_3, 400 MHz) δ 0.77 (dt, J = 4.5, 8.4 Hz, 1H), 1.11-1.19 (m, 1H), 1.71 (dt, J = 4.8, 5.6 Hz, 1H), 1.79 (q, J = 8.4 Hz, 1H), 2.35 (s, 3H), 3.75 (dd, J = 6.2, 16.2 Hz, 1H), 3.95 (dd, J = 5.8, 16.2 Hz, 1H), 4.96 (br d, J = 11.6 Hz, 1H), 5.07 (dd, J = 2.0, 10.4 Hz, 1H), 5.08-5.12 (br s, 1H), 5.21 (dd, J = 1.6, 18.8 Hz, 1H), 5.44 (dd, J = 6.0, 11.6 Hz, 1H), 5.60 (ddd, J = 2.8, 6.4, 11.6 Hz, 1H), 5.93 (tdd, J = 6.2, 10.0, 17.2 Hz, 1H), 6.10 (dd, J = 7.2, 12.0 Hz, 1H), 7.25 and 7.70 (ABq, J = 8.4 Hz, 4H total); ^13C NMR (CDCl_3, 100 MHz) δ 8.4, 14.8, 21.7, 44.1, 48.1, 57.6, 117.1, 122.6, 126.6, 127.5, 127.9, 129.8, 135.3, 136.1, 137.7, 143.3. ESI-HRMS m/z 338.1180 (calcd for C_{18}H_{21}NO_2SNa (M+Na^+) m/z 338.1191).

**Dimethyl (6-styryl-2,4-cycloheptadien-1-yl)propandioate (11):** To a cold solution of dimethyl allylmalonate (1.00 mL, 6.16 mmol) in freshly distilled dry ether (120 mL) was added dropwise a solution of n-butyl lithium (4.5 mL, 1.6 M in hexanes, 7.1 mmol). The mixture was stirred for 1 h and warmed to room temperature. Solid cation 4 (2.00 g, 4.74 mmol) was added and the mixture stirred for 3 h. The reaction mixture was quenched with water and extracted several times with ether. The combined ether extracts were washed with brine, dried
(Na₂SO₄), concentrated and the residue purified by column chromatography (SiO₂, hexanes–ethyl acetate = 4:1) to give a yellow oil which was used in the next step without further characterization. The mixture (2.608 gm) was dissolved in methanol (100 mL) and cerium ammonium nitrate (7.50 gm, 13.7 mmol) was added. The mixture was stirred for 1 h, then concentrated and the residue was partitioned between water and ether. The combined ether extracts were washed with brine, dried (Na₂SO₄), and concentrated. The residue was purified by column chromatography (SiO₂, hexanes–ethyl acetate = 20:1) to give 11 (1.17 gm, 67%) as a colorless oil. ¹H NMR (CDCl₃, 400 MHz) δ 1.55-1.68 (m, 1H), 2.09 (dd, J = 13.3, 5.4 Hz, 1H), 2.60-2.78 (dd, J = 10.4, 8.2 Hz, 2H), 3.11 (br d, J = 8.7 Hz, 1H), 3.38-3.48 (m, 1H), 3.72 (s, 6H), 5.05 (br s, 1H), 5.08 (d, J = 7.5 Hz, 1H), 5.69-5.87 (br m, 5H), 6.11 (ddd, J = 15.7, 8.1, 1.1 Hz, 1H), 6.41 (d, J = 15.9 Hz, 1H), 7.15-7.34 (m, 5H, Ar); ¹³C NMR (CDCl₃, 100 MHz) δ 37.9, 38.8, 43.0, 47.4, 52.5, 61.7, 119.1, 124.4, 124.7, 126.3, 127.3, 128.7, 129.6, 132.8, 133.2, 134.3, 137.0, 137.6, 171.4. ESI-HRMS m/z 389.1728 (calcd for C₂₃H₂₆O₄Na m/z 389.1729).  

N-(6-styryl-2,4-cycloheptadien-1-yl)-4-methyl-N-2-propen-1-yl-benzenesulfonamide (12). To a solution of 4 (0.10 g, 0.24 mmol) in acetonitrile (10 mL), under N₂, was added the potassium salt of tosyl allylamine (0.140 g, 0.562 mmol). The mixture was stirred for 2 h, at which time TLC indicated the disappearance of 4. The reaction mixture was dried under reduced pressure and the solid residue was purified by column chromatography (SiO₂, hexanes–ethyl acetate = 4:1) to give the product (0.113 g, 86%) as a yellow foam. mp 47-48 °C; IR (CH₂Cl₂) 2047, 1965, 1338, 1157 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.14 (q, J = 12.4 Hz, 1H), 1.55 (br d, J = 13.2 Hz, 1H), 1.91 (d, J = 7.2 Hz, 1H), 2.40 (s, 3H), 2.82-2.92 (m, 2H), 3.68 (dd, J = 6.0, 16.8 Hz, 1H), 3.93 (dd, J = 5.2, 16.8 Hz, 1H), 4.38 (dd, J = 3.6, 12.0 Hz, 1H), 5.14 (d, J = 10.4 Hz, 1H), 5.22-5.33 (m, 3H), 5.80-5.94 (m, 2H), 6.33 (d, J 15.2 Hz, 1H), 7.20-7.38 (m, 7H), 7.77 (d, J = 8.0 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.6, 36.4, 44.0, 46.2, 57.1, 58.6, 61.5, 88.3, 88.6, 117.0, 126.3, 127.3, 127.6, 128.8, 129.1, 130.1, 135.2, 136.5, 137.1, 137.9, 143.8. This compound was utilized in the next step without further characterization. To the prior complex (0.277 g, 0.509 mmol) in acetonitrile (15 mL), under N₂, was added cerium ammonium nitrate (0.47 g, 0.858 mmol). The mixture was stirred at room temperature for 1 h, at which time TLC indicated complete disappearance of starting material. The reaction mixture was filtered through a short column of silica gel, which was washed with CH₂Cl₂ until all of the product was eluted.
These fractions were combined, concentrated, and the residue was purified by column chromatography (SiO\(_2\), hexanes−ethyl acetate = 17:3) to give 12 (0.106 g, 51%) as a faint yellow oil. IR (CH\(_2\)Cl\(_2\)) 1336, 1162 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 1.96 (br d, \(J = 12.6\) Hz, 1H), 2.08 (td, \(J = 10.9\), 12.6 Hz, 1H), 2.42 (s, 3H), 3.30-3.42 (m, 1H), 3.73 (dd, \(J = 6.0\), 16.5 Hz, 1H), 3.85 (dd, \(J = 6.0\), 16.5 Hz, 1H), 4.85-4.94 (m, 1H), 5.13 (dd, \(J = 0.9\), 8.7 Hz, 1H), 5.23 (dd, \(J = 1.5\), 16.8 Hz, 1H), 5.39 (br d, \(J = 11.1\) Hz, 1H), 5.64-5.75 (m, 3H), 5.91 (tdd, \(J = 6.0\), 10.5, 17.1 Hz, 1H), 6.11 (dd, \(J = 8.4\), 15.9 Hz, 1H), 6.39 (d, \(J = 15.9\) Hz, 1H), 7.20-7.38 (m, 7H), 7.77 (d, \(J = 8.0\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 21.7, 39.0, 43.2, 47.9, 59.1, 117.6, 123.9, 125.1, 126.3, 127.4, 127.5, 128.8, 129.8, 129.9, 132.6, 134.4, 136.1, 137.3, 137.6, 137.9, 143.5. ESI-HRMS m/z 428.1657 (calcd for C\(_{25}\)H\(_{27}\)N\(_2\)SNa (M+Na\(^+\)) m/z 428.1660).

4-Benzoyl-5-[5',5'-bis(methoxycarbonyl)-2'-cyclopenten-1'-yl]-3-ethenylcyclopentene (13). To a solution of 8 (0.096 g, 0.25 mmol) in dichloromethane (18 mL) was added Grubbs' 1st generation catalyst (0.011 g, 0.013 mmol, 5 mol%) and the mixture was stirred for 5 h. Monitoring by \(^1\)H NMR spectroscopy showed the completion of the reaction during this time. The reaction mixture was filtered through a pad of silica and the filtrate was collected and concentrated under reduced pressure. The residue was purified by column chromatography (SiO\(_2\), hexane-ethyl acetate = 10:1 to 5:1, gradient elution) to afford 13 (0.060 g, 62%) as a brown oil. IR (Neat) 3059, 2954, 1731, 1683, 1266 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.75 (dt, \(J = 2.2\), 18.0 Hz, 1H), 3.05-3.09 (br m, 1H), 3.23 (dd, \(J = 2.5\), 17.8 Hz, 1H), 3.38 (s, \(J = 4.1\) Hz, 1H), 3.69 (s, 3H), 3.75-3.77 (m, 1H), 4.82 (d, \(J = 16.9\) Hz, 1H), 4.98 (dd, \(J = 1.6\), 10.0 Hz, 1H), 5.42 (dt, \(J = 2.4\), 5.6 Hz, 1H), 5.54-5.58 (m, 1H), 5.72-6.02 (m, 3H), 7.44 (t, \(J = 7.4\) Hz, 2H), 7.54 (t, \(J = 7.6\) Hz, 1H), 7.91 (t, \(J = 7.6\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 41.4, 48.6, 51.3, 52.9, 53.1, 53.7, 56.9, 62.1, 115.9, 128.5, 128.9, 129.1, 130.6, 131.4, 132.9, 134.5, 136.5, 140.1, 170.5, 172.9, 200.7. FAB-HRMS m/z 381.1701 (calcd for C\(_{23}\)H\(_{25}\)O\(_5\) (M + H\(^+\)) m/z 381.1702).

H\(_2\)-(5-Benzoyl-4-ethenyl-2-cyclopenten-1-yl)-2,5-dihydro-1-[((4-methylphenyl)sulfonyl]-1H-pyrrole (14): To a solution of 11 (45 mg, 0.11 mmol) in freshly distilled dichloromethane (25 mL), under N\(_2\), was added Grubbs' 1st generation catalyst (5 mg, 0.006 mmol, 5 mol%). The reaction progress was monitored by \(^1\)H NMR spectroscopy, which revealed that no starting material was
left after 90 min. The whole reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography (SiO₂, hexanes–ethyl acetate = 4:1) to give 14 (36 mg, 80%) as a colorless oil. IR (CH₂Cl₂) 1678, 1340, 1162 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 2.37 (s, 3H), 3.39-3.46 (br m, 1H), 3.76 (tdd, J = 2.4, 4.8, 15.2 Hz, 1H), 3.80-3.85 (m, 1H), 4.02-4.10 (m, 2H), 4.63-4.68 (m, 1H), 4.93 (d, J = 16.8 Hz, 1H), 5.01 (dd, J = 1.4, 9.4 Hz, 1H), 5.54 (qd, J = 2.0, 6.2 Hz, 1H), 5.59 (td, J = 2.2, 6.0 Hz, 1H), 5.65-5.70 (m, 2H), 5.91 (ddd, J = 8.8, 10.2, 17.0 Hz, 1H), 7.22 (t, J = 8.0 Hz, 2H), 7.46 (t, J = 7.4 Hz, 2H), 7.56 (qd, J = 1.4, 9.4 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 8.00 (dd, J = 2.0, 7.6 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 52.1, 55.0, 56.0, 56.3, 69.5, 115.9, 126.7, 127.7, 128.6, 128.7, 129.2, 129.8, 129.9, 133.1, 133.9, 134.5, 137.4, 140.3, 143.7, 202.3. ESI-HRMS mlz 442.1451 (calcd for C₂₅H₂₅N₃O₃S (M+Na⁺) mlz 442.1453).

2-[2-(1Z,3-Butadien-1-yl)cyclopropyl]-3-cyclopentene-1,1-dicarboxylic acid dimethyl ester (15). To a solution of 9 (0.1301 g, 0.4708 mmol) in CH₂Cl₂ (35 mL) was added Grubbs' 1st generation catalyst (19.6 mg, 0.0238 mmol). The solution was heated at reflux for 22 h, during which time additional Grubbs' catalyst (38.5 mg, 0.0468 mmol) was added in portions when product conversion ceased, as indicated by ¹H NMR spectroscopic monitoring. The dark reaction solution was cooled to room temperature, filtered through a bed of silica gel and the filter bed washed with ethyl acetate. The combined filtrate and washings were concentrated and the residue was purified by preparative TLC (SiO₂, hexanes–ethyl acetate = 10:1) to give 15 (96.0 mg, 74%) as a white solid. mp 52-55 °C; IR (KBr) 3090, 3038, 2954, 1727, 1640, 1452, 1433, 1266 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.34-0.41 (m, 1H), 0.92 (dddd, J = 6.2, 7.9, 8.5, 11.1 Hz, 1H), 1.09 (dt, J = 4.7, 8.5 Hz, 1H), 1.77-1.90 (m, 1H), 2.78-2.87 (m, 1H), 3.33 (br d, J = 11.2 Hz, 1H), 3.37-3.47 (m, 1H), 3.60 (s, 3H), 3.73 (s, 3H), 5.05-5.31 (m, 3H), 5.61-5.70 (m, 2H), 6.04 (dt, J = 0.9, 10.9 Hz, 1H), 6.71 (dddt, J = 0.9, 10.2, 11.3, 16.7 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 13.6, 16.9, 20.9, 41.0, 50.8, 53.1, 53.2, 62.9, 116.5, 126.8, 128.4, 131.4, 132.1, 132.5, 170.1, 171.9. Anal. Calcd for C₁₆H₂₀O₄: C, 69.55; H, 7.29. Found: C, 69.27; H, 7.37.

Self metathesis dimer (16): To a solution of 10 (248 mg, 0.786 mmol) in freshly distilled CH₂Cl₂ (100 mL) under N₂ was added Grubbs' 1st generation catalyst (39 mg, 0.047 mmol, 6 mol%). The mixture was heated at reflux and the
reaction progress was monitored by NMR spectroscopy. After 6 h additional Grubbs’ I (39 mg, 0.047 mmol, 6 mol %) was added and heating continued for 12 h. A final portion of Grubbs’ catalyst (20 mg, 0.024 mmol, 3 mol %) was added and heating continued for 12 h. The reaction mixture was concentrated and purified by column chromatography (SiO₂, hexanes–ethyl acetate = 7:3) to afford a mixture of diastereomeric dimers 16 (180 mg, 76%) as a colorless solid. mp 162-163 °C; IR (CH₂Cl₂) 1336, 1161 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 0.81-0.87 (m, 2H), 1.12-1.22 (m, 2H), 1.73-1.85 (m, 4H), 2.42 (s, 6H), 3.73 (dd, J = 2.4, 16.0 Hz, 2H), 3.92 (br d, J = 14.8 Hz, 2H), 4.94 (dt, J = 2.8, 12.0 Hz, 2H), 5.05-5.10 (br s, 2H), 5.46 (dd, J = 6.2, 11.4 Hz, 2H), 5.61 (dt, J = 2.8, 6.0, 12.0 Hz, 2H), 5.83 (q, J = 3.2 Hz, 2H), 6.14 (dd, J = 7.4, 11.4 Hz, 2H), 7.29 and 7.72 (ABq, J = 8.0 Hz, 8H total); ¹³C NMR (CDCl₃, 100 MHz) δ 25.5, 44.1, 46.9, 57.6, 122.6, 126.7, 127.5, 127.7, 129.9, 130.5, 135.3, 137.5, 143.4. Anal. Calcd for C₃₄H₅₈N₂O₄S₂: C, 67.75; H, 6.35. Found: C, 67.29; H, 5.92.

**Bicyclo[4.4.1]undeca-5,7,9-triene-2,2-dicarboxylic acid dimethyl ester (17):** To a stirring solution of 11 (30 mg, 0.082 mmol) in CH₂Cl₂ (2 mL) at room temperature was added Grubbs 1st generation catalyst (3 mg, 5 mol%). The reaction mixture was stirred for 45 min, concentrated and the residue purified by column chromatography (SiO₂, hexanes–ethyl acetate = 20:1) to give 17 (19 mg, 88%) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ 2.27 (dd, J = 1.2, 14.2 Hz, 1H), 2.55 (dd, J = 14.2, 1.5 Hz, 1H), 2.85-2.75 (m, 1H), 2.96-2.89 (m, 2H), 3.33-3.25 (dq, J = 17.3, 2 Hz, 1H), 3.66 (s, 3H), 3.75 (s, 3H), 3.84-3.76 (m, 1H), 5.66-5.57 (m, 2H), 6.21-6.18 (m, 1H), 6.31-6.26 (m, 1H), 6.44-6.39 (m, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 32.8, 40.3, 43.6, 50.6, 52.5, 52.9, 63.0, 127.4, 128.4, 131.4, 132.5, 132.9, 146.8, 171.1, 173.0. ESI-HRMS m/z 262.1198 (calcd for C₁₅H₁₈O₄ m/z 262.1205).

**N-Toluenesulfonyl-2-Azabicyclo[4.4.1]undeca-5,7,9-triene (18):** To a solution of 12 (60 mg, 0.15 mmol) in freshly distilled dichloromethane (20 mL), was added Grubbs’ 2nd generation catalyst (7 mg, 0.008 mmol, 5 mol %). The reaction mixture was stirred under N₂ and the reaction progress was monitored by ¹H NMR spectroscopy. After 4 h all signals for the starting material had disappeared. The reaction mixture was concentrated under a flow of N₂, and the residue purified by column chromatography (SiO₂, hexanes–ethyl acetate = 4:1) to afford 18 as a colorless oil (37 mg, 82%). ¹H NMR (CDCl₃, 400 MHz) δ 2.43 (s, 3H), 2.81 (ddd, J = 1.2, 8.8, 14.4 Hz, 1H), 2.97-2.99 (narrow m, 2H), 3.06, ddd,
$J = 1.2, 3.6, 14.4$ Hz, 1H), 4.06-4.09 (narrow m, 2H), 4.59 (td, $J = 4.0, 8.4$ Hz, 1H), 5.56-5.60 (narrow m, 2H), 6.20-6.24 (m, 1H), 6.30 (qd, $J = 1.2, 5.4$ Hz, 1H), 6.43 (qd, $J = 2.0, 5.4$ Hz, 1H), 7.31 and 7.73 (ABq, $J_{AB} = 8.2$ Hz, 4H total); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 21.7, 38.0, 44.6, 55.9, 67.6, 125.0, 127.6, 129.5, 130.0, 130.1, 131.9, 132.6, 134.8, 143.7, 144.5. This compound decomposed upon standing and thus a satisfactory HRMS was not obtained.
(±)-7

$^1$H NMR
(400 MHz, CDCl$_3$)
$^{1}$H NMR
$(400 \text{ MHz}, \text{CDCl}_3)$
(±)-8

$^{13}$C NMR

(100 MHz, CDCl$_3$)
(±)-9

1H NMR
(300 MHz, CDCl₃)
\[ ^{13}\text{C NMR} \]
\[ (75\text{ MHz, CDCl}_3) \]
(±)-10

$^1$H NMR
(400 MHz, CDCl$_3$)

PPM
(±)-10

$^{13}$C NMR

(100 MHz, CDCl$_3$)

Nuts - $\text{dmtofreece}.\text{fid}$
\((\pm)-11\) 

$^1$H NMR 

(300 MHz, CDCl$_3$)
(±)-11
13C NMR
(75 MHz, CDCl₃)
(±)-12
1H NMR
(300 MHz, CDCl₃)
$^{13}$C NMR
(75 MHz, CDCl$_3$)

(a)-12
(±)-13

$^{1}$H NMR

(400 MHz, CDCl$_3$)
STANDARD 1H OBSERVE - profile
F1: 100.527  F2: 399.751  SW1: 24510  OF1: 10546.3  PTSid: 31875  32768
EX: s2pul  PW: 7.5 us  PD: 1.0 sec  NA: 500  LB: 0.0  Nuts - $sc725-13c.fid

(±)-13
13C NMR
(100 MHz, CDCl₃)
(±)-14

$^1$H NMR

(400 MHz, CDCl$_3$)
"(±)-14

$^{13}$C NMR

(100 MHz, CDCl$_3$)

F1: 100.526  F2: 399.745  SW1: 24510  OF1: 10571.1  PTS1d: 31875, 32768
EX: s2pul  PW: 5.8 us  PD: 1.0 sec  NA: 256  LB: 1.5

Nuts - Sm181c.fid
(±)-15

$^1$H NMR

(300 MHz, CDCl$_3$)

STANDARD 1H OBSERVE: blank line

F1: 300.151  F2: 75.480  SW1: 4810  OF1: 1806.2  PTS1d: 14430  16384

EX: s2pul  PW: 6.0 us  PD: 1.0 sec  NA: 8  LB: 0.0  Nuts - $nw256product.fid
$(\pm)-15$

$^{13}\text{C NMR}$

$(75 \text{ MHz}, \text{CDCl}_3)$
(±)-16

$^1$H NMR

(400 MHz, CDCl$_3$)
(±)-16

$^{13}$C NMR

(100 MHz, CDCl$_3$)
(±)-17

$^1$H NMR

(300 MHz, CDCl$_3$)
\( (\pm) - 17 \)

\( ^{13}C \) NMR

(750 MHz, CDCl\(_3\) )
(±)-18

$^{13}$H NMR

(100 MHz, CDCl$_3$)