Experimental procedures and characterization data

General remarks

Unless otherwise indicated, all reactions were performed under either an argon or nitrogen atmosphere in flame-dried glassware equipped with a Teflon coated magnetic stir bar and a rubber septum. Where no temperature is specified, the reactions were run at ambient temperature (23 °C). Reagent quantities (mmol) were calculated based on their reported purities. Anhydrous THF and Et₂O were obtained by distillation over sodium/benzophenone under nitrogen and used as freshly distilled. Et₃N and CH₂Cl₂ were distilled from CaH₂. Commercially available reagents were used as received unless otherwise stated. n-Butyllithium and tert-butyllithium were titrated using 2,6-di-tert-butyl-4-methylphenol and fluorene. Grignard reagents were titrated according to Love’s protocol. Microwave reactions were performed...
using a CEM Model ESP-1500 Plus microwave oven equipped with a pressure monitoring device and an EST-300 Plus fiber optic temperature probe. The reaction vessel was a quartz tube to which was added the reaction mixture as well as a carboflonTM to aid in the absorption of microwave radiation. Reactions were monitored by TLC analysis using glass plates pre-coated (250 μm thickness) with ultra pure silica gel (60A, SiliCycle). TLC plates were viewed using UV light and stained with either p-anisaldehyde, potassium permanganate, or phosphomolybdic acid staining solutions. Flash chromatography was carried out on 230–400 mesh silica gel (60A, SiliCycle). When mentioned, triethylamine was added to the slurry of silica gel until a persistent odor was maintained. Once the basified slurry was loaded on the column, an equal volume of eluent (without triethylamine) was passed through prior to substrate loading.

¹H and ¹³C NMR, spectra were recorded on either Bruker Avance 300 MHz, Bruker Avance 500 MHz, Bruker AMX 500 or Varian INOVA 500 MHz spectrometers in the specified deuterated solvents. IR spectra were recorded on a Bomen Michaelson 100 FTIR spectrometer. HRMS spectra were obtained using a Kratos Analytical Concept spectrometer. Melting points were recorded using a Gallenkamp P1106G Melting Point Apparatus.

Experimental procedures

\[
\begin{align*}
\text{4-Allyl-3-methylcyclohex-2-enone (8)}
\end{align*}
\]

A solution of methyllithium (1.0 M in hexanes, 139.5 mL, 139.5 mmol) was added dropwise to a solution of 6-allyl-3-methoxycyclohex-2-enone (19.31 g, 116.2 mmol) in dry ether at −78 °C for 30 min. The mixture was then stirred at rt for 1 h. An aqueous solution of 1 N HCl was added. After stirring for 1 h at rt, water was added. The
aqueous layer was extracted with ethyl acetate (3x), and the combined organic phases were dried over anhydrous magnesium sulphate, filtered and concentrated. The crude oil was distilled under reduced pressure and purified by chromatography (10% EtOAc:hexanes) to give 14.48 g (83%) of 8 as a clear yellow oil. Spectral data is in accordance with reported data and full characterization is available through the literature [1].

![4-Allyl-3,6-dimethylcyclohex-2-enone](image)

4-Allyl-3,6-dimethylcyclohex-2-enone

A solution of n-BuLi (1.6 M in hexanes, 21.8 mL, 34.95 mmol) was added slowly to diisopropylamine (5.17 mL, 36.61 mmol) in THF(150 mL) at −78 °C for 45 min. 4-Allyl-3-methylcyclohex-2-enone (8) (5 g, 33.28 mmol) was added at −78 °C for 60 min and then iodomethane (2.49 mL, 39.94 mmol). The mixture was stirred at rt for 3 h. An aqueous saturated solution of NH₄Cl was added and the aqueous layers were extracted with ethyl acetate (3x). The combined organic phases were dried over anhydrous magnesium sulfate, filtered and the solvent was evaporated. The crude residue was purified by flash chromatography (10% EtOAc:hexanes) to give 4.92 g (90%) of a yellow-orange oil of 4-allyl-3,6-dimethylcyclohex-2-enone. IR (neat, cm⁻¹) v_max: 3077, 2964, 2930, 2872, 1673, 1639, 1443, 1378; ¹H NMR, (400 MHz, CDCl₃) δ 5.81(m, 1H), 5.79(s, 1H), 5.11(m,2H), 2.43 (m,2H), 2.27 (m,2H), 1.99 (ddd, J = 13.5 Hz, 4.8 Hz, 2.8 Hz, 1H), 1.95(s, 3H), 1.76(m, 1H), 1.09 (d, J = 6.9 Hz, 3H); ¹³C NMR (400 MHz, CDCl₃) δ 201.9 (C), 164.0 (C), 136.5(CH), 126.4 (CH), 117.1 (CH₂), 39.2 (CH), 35.9 (CH), 35.6 (CH₂), 34.5 (CH₂), 22.9 (CH₃), 15.4 (CH₃); HRMS (EI) m/z calcd for C₁₁H₁₆O [M⁺] 164.1201, found: 164.1205.
4-Allyl-3,6-dimethyl-6-(prop-2-ynyl)cyclohex-2-enone (9)

A solution of n-BuLi (1.6 M in hexanes, 1.59 mL, 2.55 mmol) was added slowly to a solution of diisopropylamine (0.38 mL, 2.67 mmol) in THF(15 mL) at −78 °C for 45 min. 4-Allyl-3,6-dimethylcyclohex-2-enone (0.4 g, 2.44 mmol) was added at −78 °C. After stirring for 60 min, propargyl bromide (0.33 mL, 2.92 mmol) was added and the mixture was stirred at rt for 3 h. The resulting mixture was quenched with a saturated solution of NH₄Cl. The aqueous layer was extracted with ethyl acetate (3x). The combined organic phases were dried over anhydrous magnesium sulfate, filtered and concentrated. The crude residue was purified by chromatography (10% EtOAc:hexanes) to give 9 0.31 g (62%) as a yellow-orange oil. IR (neat, cm⁻¹) νₘₐₓ 3305, 3077, 2976, 2930, 1674; ¹H NMR, (400 MHz, CDCl₃) δ 5.78 (s,1H), 5.69 (m,1H), 5.10 (m,2H), 2.49 (m,2H), 2.35 (m, 1H), 2.15 (m,3H), 2.01 (t, J = 2.6 Hz, 1H), 1.93 (s, 3H), 1.57 (dd, J = 13.8, 10.3 Hz, 1H), 1.16 (s, 3H); ¹³C NMR (400 MHz, CDCl₃) δ 202.6 (C), 162.9 (C), 135.3 (CH), 126.5 (CH), 118.1 (CH₂), 80.5 (C), 71.4 (CH), 43.9 (C), 38.5 (CH₂), 36.9 (CH), 36.7 (CH₂), 26.8 (CH₂), 22.3 (2xCH₃); HRMS (EI) m/z calcd for C₁₄H₁₈O [M⁺] 202.1358, found: 202.1379.

4-Allyl-2,5,5-trimethyl-2-(prop-2-ynyl)cyclohexanone

To a solution of CuI (63 mg, 0.33 mmol) and 9 (306.7 mg, 1.52 mmol) in THF (15 mL) and Me₂S (1.5 mL) at 0 °C was slowly added a solution of MeMgBr (1.11 mL, 3.0 M in Et₂O, 3.33 mmol) over 1 h. The mixture was then stirred for 1 h at 0 °C. An
aqueous saturated solution of NH₄Cl was added. The mixture was extracted with Et₂O (3x). The organic phase was dried over MgSO₄ and concentrated in vacuo. The residue was purified by column chromatography (10% EtOAc:hexanes) to provide the desired ketone (175.9 mg, 53%) as a dark orange oil (mixture of two conformers). IR (neat, cm⁻¹) ν max 3310, 3076, 2965, 2931, 2871, 2124, 1716, 1640, 1436; ¹H NMR, (400 MHz, CDCl₃) δ 5.76 (m, 1H), 5.02 (m, 2H), 2.49 (0.5H), 2.45 (m, 1H), 2.37 (m, 2H), 2.33 (m, 0.5H), 2.00 (m, 2.5), 1.70 (m, 2.5 H), 1.26 (t, 1H), 1.09 (s,3H), 1.04 (s, 3H), 0.96 (m, 1H), 0.73 (m, 3H); ¹³C NMR (400 MHz, CDCl₃) δ 213.2 (C), 137.6 (CH), 116.3 (CH₂), 79.5 (C), 71.5 (CH), 52.9 (CH₂), 48.0 (C), 41.5 (CH), 40.0 (CH₂), 39.3 (C), 34.2 (CH₂), 29.8 (CH₃), 27.8 (CH₂), 22.2 (CH₃), 20.1 (CH₃); HRMS (El) m/z calcd for C₁₅H₂₂O [M⁺] 218.1671, found: 218.1659.

(4-Allyl-3,3,6-trimethyl-6-(prop-2-ynyl)cyclohex-1-enyloxy)(tert-butyl)dimethylsilane (10)

4-Allyl-2,5,5-trimethyl-2-(prop-2-ynyl)cyclohexanone (300 mg, 1.37 mmol) was dissolved in acetonitrile (30 mL), and Et₃N (0.383 mL, 2.74 mmol) was added. Then flame-dried NaI (0.309 g, 2.04 mmol) and TBSCl (310 mg, 2.04 mmol) were added. The reaction mixture was allowed to reflux overnight and was then quenched with NaHCO₃ saturated solution, and the aqueous phase was extracted with DCM (3x). The organic phases were then combined and concentrated. The resulting mixture was filtered through a small silica pad and washed with solution of 7% EtOAc in hexanes and concentrated again. The crude enol ether 10 (209 mg, 46%) was then directly used for the next reaction.
7-Allyl-5,8,8-trimethylbicyclo[3.3.1]non-2-en-9-one (11)

A solution of silyl enol ether 10 (20 mg, 0.060 mmol) and (acetonitrile)[(2-biphenyl)di-tert-butylphosphine]gold(I) (0.92 mg, 0.0012 mmol) in DCM (1 mL) was stirred for 6 h at rt. The solvent was evaporated and the residue was purified by flash column chromatography on silica (10% EtOAc:hexanes) to give 88% of 11 as a white solid. IR (neat, cm\(^{-1}\)) \(\nu_{\max} \) 3081, 3 039, 2967, 2921, 1709; \(^1\)H NMR, (400 MHz, CDCl\(_3\)) \(\delta\) 5.82 (m, 1H), 5.76 (m, 1H), 5.63 (dddd, \(J = 9.5, 6, 1.9 \) Hz, 1.9 Hz, 1H), 5.03 (m, 1H), 2.41 (m, 3H), 2.25 (m, 1H), 2.03 (m, 1H), 1.82 (dd, \(J = 13.9\) Hz, 4.5 Hz, 1H), 1.59 (ddd, \(J = 13.7, 10.8, 8.6\) Hz, 2H), 1.28 (m, 4H), 1.02 (s, 3H), 0.99 (s, 3H), 0.79 (s, 3H); \(^{13}\)C NMR (400 MHz, CDCl\(_3\)) \(\delta\) 216.50 (C), 138.03 (CH), 129.80 (CH), 126.55 (CH), 115.96 (CH\(_2\)), 60.27 (CH), 45.96 (CH\(_2\)), 45.61 (CH\(_2\)), 42.35 (C), 38.09 (CH), 34.09 (C), 29.71 (CH\(_2\)), 26.09 (CH\(_3\)), 23.50 (CH\(_3\)), 20.79 (CH\(_3\)); HRMS (El) \(m/z\) calcd for \(C_{15}H_{22}O\) [M+] 218.1671, found: 218.1652.

4-Methylenenon-1-en-8-yn-5-one (B)

To a solution of homoallylphosphonate (5 g, 26 mmol) in THF (50 mL) at -78 °C, under an argon atmosphere, was added dropwise a solution of \(n\)-BuLi (2.45 M in hexanes, 12.74 mL, 31.2 mmol). The reaction mixture was stirred for 3 h and then a solution of methyl pent-4-ynoate (4.38 g, 39 mmol) in THF (10mL) was added to the prepared mixture. After 1 h, the temperature was raised to rt. The reaction was quenched with a saturated solution of \(NH_4\)Cl. The mixture was extracted three times with Et\(_2\)O, washed with water and concentrated at reduced pressure to furnish the
diethyl 5-oxonon-1-en-8-yn-4-ylphosphonate (A) as a brown oil. The crude product was taken into the next step without further purification.

A mixture of diethyl 5-oxonon-1-en-8-yn-4-ylphosphonate A (7.0 g, 24.4 mmol), water (100 mL), potassium carbonate (10.1 g, 73.3 mmol) and aqueous 37% formaldehyde (2.18 mL, 29.3 mmol) was stirred at rt for 3 h. The mixture was then extracted with Et$_2$O, washed with water, saturated solution of NaCl and concentrated under reduced pressure to furnish a yellow oil. Purification by flash chromatography over silica gel (hexanes/EtOAc in gradient 5–10% of EtOAc) gave the 4-methylenenon-1-en-8-yn-5-one B (2.6 g, 72%) as a colorless oil. IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3300, 2919, 2120, 1642, 1628, 1415. ¹H NMR (300 MHz, CDCl$_3$) $\delta$ 6.06 (s, 1 H), 5.87 - 5.70 (m, 2 H), 5.09 - 5.05 (m, 1 H), 5.05 - 4.99 (m, 1 H), 3.04 - 2.98 (m, 2 H), 2.97 - 2.90 (m, 2 H), 2.52 - 2.42 (m, 2 H), 1.94 (t, $J = 2.7$ Hz, 1 H). ¹³C NMR (75 MHz, CDCl$_3$) $\delta$ 198.8, 146.8, 135.3, 125.2, 117.0, 83.4, 68.8, 36.7, 34.9, 13.4. HRMS (ESI) $m/z$ cald for C$_{10}$H$_{12}$ONa$^+$ 148.0888, found: 148.1206.

9-Methyl-6-methylenedec-8-en-1-yn-5-one (E)

To a solution of diethyl 4-methylpent-3-enylphosphonate [2] C (2.43 g, 11.03 mmol) in THF (20 mL) at $-78$ °C, under an argon atmosphere, was added dropwise $n$-BuLi (1.7 M in hexanes, 7.79 mL, 13.24 mmol). The reaction mixture was stirred for 3 h and then a solution of methyl pent-4-ynoate (1.86 g, 16.5 mmol) in THF (5 mL) was added. After stirring for 1 h, the temperature was raised to rt. The reaction was quenched with a saturated solution of NH$_4$Cl. The mixture was extracted three times with Et$_2$O, washed with water and concentrated at reduced pressure to furnish the diethyl 5-oxonon-1-en-8-yn-4-ylphosphonate D as a brown oil. The crude product was taken into the next step without further purification.
A mixture of diethyl 2-methyl-6-oxodec-2-en-9-yn-5-ylphosphonate **D** (1.7 g, 5.66 mmol, 1 equiv), water (25 mL), potassium/carbonate (2.35 g, 17 mmol, 3 equiv) and aqueous 37% formaldehyde (0.46 mL, 6.23 mmol, 1.1 equiv) was stirred at rt for 3 h. The mixture was then extracted with Et₂O, washed with water and a sat. solution of NaCl and concentrated at reduced pressure to furnish a yellow oil. Purification by flash chromatography over silica gel (Hexanes/EtOAc in gradient 5 - 10% of EtOAc) gave the 9-methyl-6-methylenedec-8-en-1-yn-5-one **E** (0.63 g, 63%) as colorless oil.

**IR** (neat, cm⁻¹) νmax 3295, 2968, 2918, 2124, 1680, 1623. ¹H NMR (300 MHz, CDCl₃) δ 6.01 (s, 1 H), 5.75 (dt, J = 1.6 Hz, 0.3, 1 H), 5.12 (sptt, J = 1.4, 7.3 Hz, 1 H), 2.95 (d, J = 7.6 Hz, 2 H), 2.97 (t, J = 6.4 Hz, 2 H), 2.56 - 2.43 (m, 2 H), 1.95 (t, J = 2.7 Hz, 1H), 1.73 (s, 3 H), 1.61 (s, 3 H). ¹³C NMR (75 MHz, CDCl₃) δ 199.4, 147.6, 134.4, 124.4, 120.7, 83.6, 68.8, 36.9, 29.3, 25.9, 17.8, 13.5. HRMS (ESI) m/z calcd for C₁₂H₁₆ONa⁺ 176.1201, found: 176.1196.

1-Morpholinopent-4-yn-1-one (**F**)  

Pent-4-ynoic acid (17.5 g, 176 mmol), morpholine (12.9 mL, 149 mmol) and DMAP (1.82 g, 149 mmol) were dissolved in DCM (325 mL). The solution was cooled to 0 °C and DCC (36.8 g, 178 mmol) was added slowly and the solution warmed up to rt. The reaction was stirred overnight. The resulting mixture is filtered over silica to remove 1,3-dicyclohexylurea, which was insoluble in DCM, and then washed with DCM. The filtrate was concentrated and the residue was purified by flash chromatography (40% EtOAc/hexanes). The yellow solid was then recrystallized from
diisopropyl ether to afford 1-morpholinopent-4-yn-1-one F (19 g, 0.114 mol) a fluffy white solid in 85% yield. IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3250, 2925, 2857, 1644, 1436; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 2.0 (m, 1 H), 2.5 (d, $J = 1.2$ Hz, 4 H), 3.5 (m, 2 H), 3.6 (m, 6 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm 169.6(C), 83.4(C), 68.9 (CH), 67.0 (CH$_2$), 66.6 (CH$_2$), 45.9 (CH$_2$), 42.1(CH$_2$), 32.0 (CH$_2$), 14.5 (CH$_2$); HRMS (EI) $m/z$ calculated for C$_9$H$_{13}$NO$_2$ [M+] 167.0946, found: 167.0934. mp = 81–82 °C.

2-Bromo-4-(methoxymethoxy)butene

Methoxymethyl chloride (7.21 mL, 95 mmol) was added to 3-bromobut-3-en-1-ol (3.14 mL, 31.7 mmol) in DCM (150 mL). N,N-diisopropylethylamine (22.6 mL, 158 mmol) was added to the mixture. The resulting mixture was stirred at rt for 3 h after which all the starting material was consumed. The solution was concentrated and the residue was purified by chromatography using 10% EtOAc in hexanes to afford 2-bromo-4-(methoxymethoxy)but-1-ene as a clear oil in 92% yield. IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 2925, 2852, 2336, 1729, 1279; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 2.69 (td, $J = 6.3$, 0.8 Hz, 2 H) 3.36 (s, 3 H) 3.72 (t, $J = 6.3$ Hz, 2 H) 4.63 (s, 2 H) 5.49 (d, $J = 1.6$ Hz, 1 H) 5.68 (q, $J = 1.2$ Hz, 1 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm 41.7 (CH$_2$), 55.3 (CH$_3$), 65.1 (CH$_2$), 96.5 (CH$_2$), 118.5 (CH$_2$), 130.7 (C); HRMS (EI) $m/z$ calcd for C$_4$H$_4$OBr [M+ (-CH$_2$OCH$_3$)] 148.9602, found: 149.0249.

Hept-1-en-6-yn-3-one (I)

A solution of 1-morpholinopent-4-yn-1-one (4.0 g, 23.92 mmol) in THF (159 mL) was cooled to 0 °C and vinylmagnesium bromide 1 M in THF (60 mL, 59.8 mmol) was added dropwise. The solution was warmed to 23 °C and stirred overnight. The
resulting mixture was quenched with a saturated solution of NH₄Cl. The aqueous phase was extracted with Et₂O (3x), the combined organic phases were dried over MgSO₄ and concentrated at 25 °C. The crude was purified by flash chromatography at 10% Et₂O in hexanes to afford hept-1-en-6-yn-3-one I (0.7 g, 27%) as a clear oil. IR (neat, cm⁻¹) ν_max 3524, 3296, 3091, 2925, 2121 1934, 1688; ¹H NMR (400 MHz, CDCl₃) δ ppm 1.95 (t, J = 2.7 Hz, 1 H) 2.51 (m, 2 H) 2.85 (m, 2 H) 5.87 (dd, J = 10.4, 1.2 Hz, 1 H) 6.24 (dd, J=17.7, 1.1 Hz, 1 H) 6.35 (dd, J = 20.7, 7.3 Hz, 1 H); ¹³C NMR (101 MHz, CDCl₃) δ ppm 12.9 (CH₂), 38.3 (CH₂), 68.7 (CH), 83.1 (C), 128.7 (CH₂), 136.2 (CH), 198.2 (C); HRMS (El) m/z calcd for C₇H₈O [M+] 108.0575, found: 108.0545.

2-Methylhept-1-en-6-yn-3-one (J)

A solution of 1-morpholinopent-4-yn-1-one (4 g, 23.92 mmol) in THF (159 mL) was cooled to 0 °C and a solution of isopropenylmagnesium bromide 0.5 M in THF (120 mL, 59.8 mmol) was added dropwise. The solution was stirred overnight at rt. The resulting mixture was quenched with a saturated solution of NH₄Cl, extracted with Et₂O (3x), dried over MgSO₄ and concentrated. The crude was purified by flash chromatography (10% EtOAc/hexanes) to afford 2-methylhept-1-en-6-yn-3-one J (3 g, 85%) as a clear oil. IR (neat, cm⁻¹) ν_max 3303, 3098, 2963, 2925, 2114, 1688; ¹H NMR (400 MHz, CDCl₃) δ ppm 1.85 (dd, J = 1.4, 0.9 Hz, 3 H), 1.93 (t, J = 2.6 Hz, 1H), 2.47 (ddd, J = 8.2, 6.6, 2.6 Hz, 2 H), 2.93 (m, 2 H), 5.78 (d, J = 1.1 Hz, 1H), 5.96 (s, 1 H); ¹³C NMR (101 MHz, CDCl₃) δ ppm 13.3 (CH₃), 17.4 (CH₂), 36.4 (CH₂), 68.6 (CH), 83.3(C), 124.9(CH₂), 144.1 (C), 199.3 (C); HRMS (El) m/z calcd for C₉H₁₀O [M+] 122.0732, found: 122.0695.
2-Phenylhept-1-en-6-yn-3-one (G)

A solution of (1-bromovinyl)benzene (90%, 3.83 g, 18.84 mmol) in THF (90 mL) was cooled to −78 °C followed by the addition of t-BuLi 1.7 M in pentane (21.2 mL, 37.7 mmol). The mixture was stirred for 30 min which after a solution of 1-morpholinopent-4-yn-1-one (3 g, 17.9 mmol) in THF (10 mL) was added through a cannula to the reaction mixture. After stirring for 2 h, the resulting mixture was quenched with a saturated solution of NH₄Cl and then extracted with Et₂O (3x). The combined organic phases were dried over MgSO₄ and concentrated. The residue was purified by flash chromatography (10% EtOAc/hexanes) to afford 2-phenylhept-1-en-6-yn-3-one G (2 g, 60%) as a pale yellow oil. IR (neat, cm⁻¹) νmax 3295, 3057, 3026, 2921, 2119, 1686; ¹H NMR (400 MHz, CDCl₃) δ ppm 1.96 (t, J = 2.7 Hz, 1 H), 2.54 (m, 2 H), 3.00 (m, 2H), 5.92 (s, 1 H), 6.15 (s, 1 H), 7.25 (dt, J = 5.3, 2.1 Hz, 2 H), 7.34 (m, 3 H); ¹³C NMR (101 MHz, CDCl₃) δ ppm 13.4 (CH₂), 38.5 (CH₂), 68.8 (CH), 83.1 (C), 125.0 (CH₂), 128.2 (CH), 128.3 (CH x 2), 128.4 (CH x 2), 136.9 (C), 149.0 (C), 199.4 (C); HRMS (EI) m/z calculated for C₁₃H₁₂O [M⁺] 184.0888, found: 184.0845.

1-(Methoxymethoxy)-3-methyleneoct-7-yn-4-one (H)

A solution of 2-bromo-4-(methoxymethoxy)but-1-ene (0.392 g, 2 mmol) in THF (5 mL) was cooled to −78 °C followed by the addition of t-BuLi 1.7 M in pentane (2.41 mL, 4.11 mmol). After stirring for 30 min, a solution of 1-morpholinopent-4-yn-1-one (0.16 g, 0.957 mmol) in THF (3 mL) was added through a cannula and the mixture was stirred for 2 h. The reaction was quenched with a saturated solution of NH₄Cl. The mixture was extracted with Et₂O (3x), dried over MgSO₄ and then concentrated. The crude residue was purified by flash chromatography (10–15% EtOAc/hexanes) to afford 1-(methoxymethoxy)-3-methyleneoct-7-yn-4-one H (0.645 g, 34%) as a
clear oil. IR (neat, cm\(^{-1}\)) \(\nu_{\text{max}}\) 3287, 2932, 2885, 2114, 1679; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm 1.94 (t, \(J = 2.7\) Hz, 1 H), 2.50 (ddd, \(J = 8.2, 6.5, 2.7\) Hz, 2 H), 2.59 (td, \(J = 6.5, 0.9\) Hz, 2 H), 3.96 (m, 2 H), 3.33 (s, 3 H), 3.61 (t, \(J = 6.6\) Hz, 2 H), 4.58 (s, 2 H), 5.89 (t, \(J = 1.2\) Hz, 1 H), 6.09 (s, 1 H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) ppm 13.3 (CH\(_2\)), 31.3 (CH\(_2\)), 36.6 (CH\(_2\)), 55.2 (CH\(_3\)), 66.1 (CH\(_2\)), 68.7 (CH), 83.3 (C), 96.4 (CH\(_2\)), 126.0 (CH\(_2\)), 145.4 (C), 199.0 (C); HRMS (El) \(m/z\) calcd for C\(_9\)H\(_{11}\)O\(_2\) [M+ (-CH\(_2\)OCH\(_3\))] 151.0759, found: 151.0758.

**General procedure for the formation of dienes 16, 19–22 and 32–35**

To a solution of enone (1 mmol) in DCM (5 mL) was added Et\(_3\)N (3 mmol) and TIPSOTf (2 mmol). The solution was then heated at reflux overnight. The reaction was quenched with a saturated solution of NaHCO\(_3\). The aqueous phase was extracted with DCM (2x), the organic phases were combined and dried over MgSO\(_4\). The solution was concentrated and the residue was purified by flash chromatography (1% EtOAc:hexanes or 5% Et\(_2\)O:hexanes) to give the corresponding diene as a mixture of Z/E isomers ranging from 4 to 9:1.

(Y)-(Hepta-1,3-dien-6-yn-3-yloxy)triisopropylsilane (19)

Yield 24%; IR (neat, cm\(^{-1}\)) \(\nu_{\text{max}}\) 3313, 2946, 2868, 2121, 1647; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm 1.10 (d, \(J = 6.66\) Hz, 18 H), 1.20 (m, 3 H), 1.94 (t, \(J = 2.7\) Hz, 1 H), 3.06 (dd, \(J = 7.1, 2.7\) Hz, 2 H), 4.82 (t, \(J = 7.1\) Hz, 1 H), 5.03 (dd, \(J = 10.8, 1.0\) Hz, 1 H), 5.38 (dd, \(J = 17.2, 1.0\) Hz, 1 H), 6.14 (dd, \(J = 17.2, 10.8\) Hz, 1 H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) ppm 13.7 (CH x 3), 15.9 (CH\(_2\)), 18.0 (CH\(_3\) x 6), 67.7 (CH), 82.9 (C), 106.9 (CH), 113.7 (CH\(_2\)), 135.3 (CH), 150.5 (C); HRMS (El) \(m/z\) calcd for C\(_{16}\)H\(_{28}\)OSi [M+] 264.1909, found: 264.1921
(Z)-Triisopropyl(2-methylhepta-1,3-dien-6-yn-3-yloxy)silane (20)

Yield 78%; IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3314, 2947, 2866, 2124, 1612, 1464; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 1.10 (d, $J = 6.6$ Hz, 18H), 1.20 (m, 3H), 1.87 (m, 3H), 1.95 (t, $J = 2.7$ Hz, 1H), 3.07 (dd, $J = 6.9$, 2.74 Hz, 2H), 4.89 (t, $J = 6.9$ Hz, 1H), 4.92 (m, 1H), 5.26 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm 13.9 (CH x 3), 15.9 (CH$_2$), 18.0 (CH$_3$ x 6), 20.3 (CH$_3$), 67.7 (CH), 83.1 (C), 104.7 (CH), 113.0 (CH$_2$), 140.7 (C), 152.0 (C); HRMS (EI) $m/z$ calcd for C$_{17}$H$_{30}$OSi [M+] 278.2066, found: 278.2066.

(Z)-Triisopropyl(2-phenylhepta-1,3-dien-6-yn-3-yloxy)silane (22)

Yield 18%; IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3311, 3082, 3060, 3026, 2945, 2867, 2120, 1948, 1875, 1799, 1720; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 1.00 (d, $J = 6.1$ Hz, 18 H), 1.09 (m, 3 H), 1.93 (t, $J = 2.7$ Hz, 1 H), 3.09 (dd, $J = 6.9$, 2.7 Hz, 2 H), 4.86 (t, $J = 6.9$ Hz, 1 H), 5.25 (d, $J = 1.6$ Hz, 1 H), 5.42 (d, $J = 1.6$ Hz, 1 H), 7.31 (m, 3 H), 7.37 (m, 2 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm 13.5 (CH  x 3), 15.7 (CH$_2$), 17.9 (CH$_3$ x 6), 67.7 (CH), 83.0 (C), 108.3 (CH), 114.2 (CH$_2$), 127.7 (CH), 128.1 (CH x 2), 128.1 (CH x 2), 139.3 (C), 147.9 (C), 151.7 (C); HRMS (EI) $m/z$ calcd for C$_{22}$H$_{32}$OSi 340.2222 [M+], found: 340.2225.
(Z)-8-(But-3-ynylidene)-10,10-diisopropyl-11-methyl-7-methylene-2,4,9-trioxa-10-siladodecane (23)

Yield 64%; IR (neat, cm⁻¹) ν_max 3400, 3311, 2945, 2868, 2100, 1698, 1618, 1464; 
¹H NMR (300 MHz, CDCl₃) δ ppm 1.09 (d, J = 6.1 Hz, 18 H), 1.18 (m, 3 H), 1.94 (t, J = 2.7 Hz, 1 H), 2.52 (td, J = 7.1, 0.9 Hz, 2 H), 3.05 (dd, J = 6.9, 2.8 Hz, 2 H), 3.36 (s, 3 H), 3.65 (t, J = 7.2 Hz, 2 H), 4.62 (s, 2 H), 4.91 (t, J = 6.9 Hz, 1 H), 4.97 (d, J = 1.2 Hz, 1 H), 5.32 (d, J = 1.4 Hz, 1 H); 
¹³C NMR (101 MHz, CDCl₃) δ ppm 13.8 (CH₃ x 3), 15.8 (CH₂), 18.0 (CH₃ x 6), 33.6 (CH₂), 55.2 (CH₃), 66.6 (CH₂), 67.8 (CH), 83.0 (C), 96.5 (CH₂), 104.8 (CH), 113.7 (CH₂), 142.5 (C), 151.3 (C); HRMS (El) m/z calcd for C₂₀H₃₆O₃Si [M+ (CH(CH₃)₂)] 309.1886, found: 309.1993.

![TIPSOTf](image)

(Z)-Triisopropyl(9-methyl-6-methylenedeca-4,8-dien-1-yn-5-yloxy)silane (21)

To a solution of 9-methyl-6-methylenedec-8-en-1-yn-5-one E (560 mg, 3.18 mmol) in DCE (30 mL) at rt, under an argon atmosphere, was added Et₃N (2.23 mL, 15.9 mmol) and then TIPSOTf (2.56 mL, 9.53 mmol). The reaction mixture was stirred for 8h at reflux. The reaction was quenched with a saturated solution of NaHCO₃. The mixture was extracted two times with DCM, washed with water, dried over MgSO₄ and concentrated at reduced pressure to furnish a brown oil. Purification by flash chromatography over silica gel (hexanes/EtOAc in gradient 1 - 5% of EtOAc) gave 21 (962 mg, 91%) as yellow oil. IR (neat, cm⁻¹) ν_max 3315, 2962, 2945, 2868, 2121, 1549; 
¹H NMR (300 MHz,CDCl₃) δ 5.29 (d, J = 1.6 Hz, 1 H), 5.23 - 5.14 (m, 1H), 4.95 - 4.86 (m, 1 H), 4.90 (t, J = 7.1 Hz, 1 H), 3.07 (dd, J = 2.7, 6.9 Hz, 2 H), 2.97 - 2.83 (m, 2 H), 1.95 (t, J = 2.7 Hz, 1 H), 1.72 (d, J = 1.1 Hz, 3 H), 1.62 (d, J = 0.9 Hz, 3 H); 
¹³C NMR (75 MHz, CDCl₃) δ 151.8, 144.6, 133.3, 121.8, 112.5, 104.7, 83.4, 67.8, 32.1, 25.9, 18.3 16.0; HRMS (El) m/z calcd for C₁₈H₂₉OSi [M+ (-C₃H₇)] 289.1988, found: 289.2169.
To a solution of 4-methylenenon-1-en-8-yn-5-one B (300 mg, 2.02 mmol) in DCE (20 mL) at rt, under an argon atmosphere, was added Et₃N (1.42 mL, 10.1 mmol) and then TIPSOTf (1.63 mL, 6.07 mmol). The reaction mixture was stirred for 8 h at reflux. The reaction was quenched with a saturation of solution of NaHCO₃. The mixture was extracted two times with DCM, washed with water, dried over MgSO₄ and concentrated at reduced pressure to furnish a brown oil. Purification by flash chromatography over silica gel (hexanes/EtOAc in gradient 1–5% of EtOAc) gave 16 (469 mg, 76%) as a yellow oil. IR (neat, cm⁻¹) νmax 3314, 2945, 2868, 2121; ¹H NMR (400 MHz, CDCl₃) δ 5.85 (ddt, J = 16.9, 10.1, 6.9 Hz, 1 H), 5.34 (d, J = 1.3 Hz, 1 H), 5.12 - 5.03 (m, 2 H), 4.96 (d, J = 1.2 Hz, 1 H), 4.92 (t, J = 6.9 Hz, 1 H), 3.07 (dd, J = 6.9, 2.7 Hz, 2 H), 2.96 (dd, J = 6.8, 0.9 Hz, 2 H), 1.95 (t, J = 2.7 Hz, 1 H), 1.25 - 1.15 (m, 3 H), 1.12 - 1.09 (m, 18 H). ¹³C NMR (75 MHz, CDCl₃) δ 151.5, 144.0, 136.2, 116.5, 113.2, 105.0, 83.2, 67.9, 37.8, 18.3, 18.2, 16.0, 14.0, 13.6; HRMS m/z calcd for C₁₆H₂₅OSi [M+ (-C₃H₇)] 261.1675, found: 261.1695.

**General procedure for the Diels–Alder reaction/gold cyclization process**

Diene (1 equiv) was charged into a microwave quartz tube (the tube was washed in a base bath and dried). N-phenylmaleimide (2 equiv) was added and then toluene (0.1 M) was added. The mixture was heated to 150 °C at 300 W in the microwave for 2 h. After cooling down to rt, catalyst 6 (5 mol%) was added to the mixture with a minimal amount of acetone to solubilize the catalyst. After stirring overnight, the
solution was concentrated and purified by flash chromatography (25–40% EtOAc in hexanes) to afford the desired ketone.

4-Phenyl-4-azatricyclo[6.3.1.0²,6]dodec-9-ene-3,5,12-trione (24)

Yield 93% (35 mg); IR (neat, cm⁻¹) νmax 3483, 3074, 3036, 2930, 2864, 1711; ¹H NMR (400 MHz, CDCl₃) δ ppm 2.33 (ddd, J = 14.5, 7.9, 4.2 Hz, 1 H), 2.64 (t, J = 3.1 Hz, 2 H), 2.95 (m, J = 2.5 Hz, 1 H), 3.03 (m, 3 H), 3.68 (t, J = 8.9 Hz, 1 H), 5.72 (m, 1 H), 5.82 (dt, J = 9.6, 3.4 Hz, 1 H), 7.27 (m, 2 H), 7.39 (m, 1 H), 7.50 (m, 2 H); ¹³C NMR (101 MHz, CDCl₃) δ ppm 31.0 (CH₂), 32.6 (CH₂), 36.3 (CH), 44.0 (CH), 45.7 (CH), 47.5 (CH), 126.1 (CH x2), 127.0 (CH), 128.8 (CH), 129.3 (CH x2), 130.2 (CH), 131.7 (C), 175.6 (C), 177.4 (C), 212.1 (C); HRMS (El) m/z calcd for C₁₇H₁₅NO₃ [M+] 281.1052, found: 281.1061; mp = 155–160 °C.

4-Oxatricyclo[6.3.1.0²,6]dodec-9-ene-3,5,12-trione (25)

Yield 51% (11 mg); IR (neat, cm⁻¹) νmax 2926, 2854, 1857, 1700, 1447; ¹H NMR (400 MHz, CDCl₃) δ ppm 2.36 (ddd, J=14.6, 7.5, 4.2 Hz, 1 H), 2.57 (m, 1 H), 2.70 (m, 1 H), 2.87 (dd, J = 14.6, 2.1 Hz, 1 H), 2.97 (m, 2 H), 3.18 (ddd, J = 9.9, 7.7, 1.0 Hz,
8-Methyl-4-phenyl-4-azatricyclo[6.3.1.0²,6]dodec-9-ene-3,5,12-trione (26)

Yield 88% (75 mg); IR (neat, cm⁻¹) νmax 2960, 2924, 2854, 1709, 1377; ¹H NMR (400 MHz, CDCl₃) δ ppm 1.17 (s, 3 H), 2.4 (dd, J = 14.4, 7.7 Hz, 1 H), 2.62 (m, 2 H), 2.90 (d, J = 14.3 Hz, 1 H), 3.00 (ddd, J = 9.0, 7.8, 0.9 Hz, 1 H), 3.11 (m, 1 H), 3.68 (t, J = 9.0 Hz, 1 H), 5.50 (ddd, J = 9.5, 2.1, 1.1 Hz, 1 H), 5.75 (m, 1 H), 7.26 (m, 2 H), 7.42 (m, 1 H), 7.50 (m, 2 H); ¹³C NMR (101 MHz, CDCl₃) δ ppm 20.5 (CH₃), 32.6 (CH₂), 37.7 (CH), 38.4 (CH₂), 44.4 (CH), 46.1 (C), 47.4 (CH), 125.8 (CH), 126.1 (CH x2), 128.8 (CH), 129.3 (CH x2), 131.7 (C), 135.8 (CH), 175.7 (C), 177.4 (C), 212.8 (C); HRMS (EI) m/z calcd for C₁₈H₁₇NO₃ [M⁺] 295.1208, found: 295.1228; mp = 189–192 °C.

8-Methyl-4-oxatricyclo[6.3.1.0²,6]dodec-9-ene-3,5,12-trione (27)

Yield, 50% (30 mg); IR (neat, cm⁻¹) νmax 2928, 2866, 2138, 1860, 1455; ¹H NMR (400 MHz, CDCl₃) δ ppm 1.13 (s, 3 H), 2.06 (dd, J = 14.5, 7.6 Hz, 1 H), 2.59 (ddd, J = 19.1, 4.9, 1.9 Hz, 1 H), 2.68 (m, 1 H), 2.71 (d, J = 14.5 Hz, 1 H), 3.03 (m, 1 H), 3.19
(ddd, $J = 9.9, 7.5, 1.0$ Hz, 1 H), 3.73 (dd, $J = 9.7, 8.9$ Hz, 1 H), 5.46 (dd, $J = 9.4, 2.9$ Hz, 1 H), 5.76 (m, 1 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm 20.2 (CH$_3$), 33.0 (CH$_2$), 38.0 (CH), 38.2 (CH$_2$), 43.5 (CH), 45.9 (C), 47.9 (CH), 126.4 (CH), 135.3 (CH), 170.2 (C), 172.5 (C), 210.9 (C); HRMS (EI) $m/z$ calculated for C$_{12}$H$_{12}$O$_4$ [M$^+$] 220.0736, found: 220.0717; mp = 101–105 °C.

![Diagram of 4,8-Diphenyl-4-azatricyclo[6.3.1.0$_{2,6}$]dodec-9-ene-3,5,12-trione (30)]

4,8-Diphenyl-4-azatricyclo[6.3.1.0$_{2,6}$]dodec-9-ene-3,5,12-trione (30)

Yield 77% (24 mg); IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3061, 3030, 2926, 2855, 1781; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 2.80 (m, 3 H) 3.26 (m, 3 H) 3.80 (t, $J = 9.2$ Hz, 1 H) 5.71 (dd, $J = 9.6, 2.5$ Hz, 1 H) 5.98 (m, 1 H) 7.21 (m, 2 H) 7.32 (m, 3 H) 7.38 (m, 3 H) 7.52 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm 32.0 (CH$_2$) 34.9 (CH$_2$) 37.9 (CH) 45.3 (CH) 47.2 (C) 54.5 (C) 126.1 (CH$_2$) 126.5 (CH) 127.4 (CH$_2$) 127.6 (CH) 128.4 (CH$_2$) 128.8 (CH) 129.4 (CH$_2$) 131.8 (C) 135.2 (CH) 138.7 (C) 175.5 (C) 177.3 (C) 210.5 (C); HRMS (EI) $m/z$ calculated for C$_{23}$H$_{19}$NO$_3$ 357.1365, found 357.1358; mp = 221–224 °C

![Diagram of 8-Phenyl-4-oxatricyclo[6.3.1.0$_{2,6}$]dodec-9-ene-3,5,12-trione (31)]

8-Phenyl-4-oxatricyclo[6.3.1.0$_{2,6}$]dodec-9-ene-3,5,12-trione (31)

Yield 48% (18 mg); IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 2980, 2928, 2901, 2859, 1851, 1778, 1724; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 2.71 (ddd, $J = 19.1, 5.3, 1.9$ Hz, 1 H), 2.83 (dd, $J =
14.2, 7.5 Hz, 1 H), 2.90 (m, 1 H), 3.10 (d, J = 13.7 Hz, 1 H), 3.18 (m, 1 H), 3.40 (ddd, J = 10.1, 7.5, 0.8 Hz, 1 H), 3.85 (m, 1 H), 5.71 (dd, J = 9.6, 3.1 Hz, 1 H), 6.02 (m, 1 H), 7.18 (m, 2 H), 7.33 (m, 1 H), 7.38 (m, 2 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm 32.4 (CH$_2$), 34.9 (CH$_2$), 38.3 (CH), 44.5 (CH), 47.7 (CH), 54.3 (C), 127.2 (CH), 127.3 (CH x2), 127.9 (CH), 128.5 (CH x2), 134.9 (CH), 137.9 (C), 170.1 (C), 172.5 (C), 208.8 (C); HRMS (EI) m/z calcd for C$_{17}$H$_{14}$O$_4$ [M+] 282.0892, found: 282.0892; mp = 205–208 °C.

9-Hydroxy-5,10-dioxatetracyclo[6.4.3.0$_1$9.0$_3$7]pentadec-3-ene-4,6-dione (32)

Yield 56% (10 mg); IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 3493, 2927, 1852, 1774, 1716; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 1.79 (dd, J = 11.9, 6.9 Hz, 1 H), 2.08 (m, 2 H), 2.23 (m, 2 H), 2.45 (d, J = 13.7 Hz, 2 H), 2.66 (m, 1 H), 3.18 (m, 1 H), 3.60 (dd, J = 9.9, 8.3 Hz, 1 H), 3.79 (ddd, J = 10.1, 8.0, 7.2 Hz, 1 H), 4.06 (m, 1 H), 5.22 (dd, J = 9.6, 2.9 Hz, 1 H), 5.65 (m, 1 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm 27.1 (CH$_2$), 29.4 (CH$_2$), 32.1 (CH$_2$), 37.4 (CH), 39.0 (CH), 45.4 (CH), 45.5 (C), 66.9 (CH$_2$), 102.7 (C), 126.8 (CH), 132.3 (CH), 172.9 (C), 173.9 (C); HRMS (EI) m/z calcd for C$_{13}$H$_{14}$O$_5$ [M+] 250.0841, found: 250.0831; mp=63-65°C.

8-(2-Methyl-2-butene)-allyl-4-phenyl-4-azatricyclo[6.3.1.0$_2$6]dodec-9-ene-3,5,12-trione (28)
Yield: 81% (17 mg); IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 2967, 2941, 1713, 1529; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.56 - 7.36 (m, 3 H), 7.30 - 7.25 (m, 2 H), 5.85 - 5.75 (m, 1 H), 5.54 (dd, $J = 1.6$, 9.4 Hz, 1 H), 5.14 - 5.04 (m, 1 H), 3.69 (t, $J = 9.0$ Hz, 1 H), 3.14 - 3.00 (m, 2 H), 2.93 (d, $J = 14.4$ Hz, 1 H), 2.70 - 2.52 (m, 2 H), 2.38 (dd, $J = 7.6$, 14.8 Hz, 1 H), 2.19 (dd, $J = 7.5$, 14.7 Hz, 1 H), 2.04 (dd, $J = 7.9$, 14.4 Hz, 1 H), 1.71 (d, $J = 0.9$ Hz, 3 H), 1.63 (s, 3 H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 212.8, 177.6, 175.9, 135.0, 134.2, 131.9, 129.4, 128.9, 126.4, 126.2, 118.6, 49.9, 47.7, 44.9, 37.7, 37.0, 32.5, 32.4, 26.2, 18.1; HRMS (ESI) m/z calcd for C$_{22}$H$_{23}$NO$_3$ [M+] 349.1678, found: 349.1678.

8-(2-Methylbutenyl)-4-oxatricyclo[6.3.1.0$^{2,6}$]dodec-9-ene-3,5,12-trione (29)

Yield: 78% (67 mg); IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 2946, 2869, 1751, 1731, 1715, 1464; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.27 (ddd, $J = 1.2$, 7.3, 8.4 Hz, 1 H), 6.20 (dd, $J = 7.7$, 7.9 Hz, 1 H), 4.98 (dd, $J = 1.4$, 7.2 Hz, 1 H), 3.48 (dd, $J = 5.8$, 7.0 Hz, 1 H), 3.34 (dd, $J = 3.7$, 5.5 Hz, 1 H), 3.21 (dd, $J = 3.7$, 5.7 Hz, 1 H), 2.86 (d, $J = 7.3$ Hz, 1 H), 2.54 (dd, $J = 6.2$, 14.9 Hz, 1 H), 2.26 (dd, $J = 8.0$, 14.8 Hz, 1 H), 2.04 (dd, $J = 4.4$, 13.1 Hz, 1 H), 1.85 (d, $J = 13.1$ Hz, 1 H), 1.67 (s, 3 H), 1.63 (s, 3 H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 209.9, 169.6, 135.6, 133.1, 131.5, 118.5, 55.9, 55.2, 51.6, 51.4, 49.4, 38.0, 30.7, 26.1, 17.9, 17.8. HRMS (EI) m/z calcd for C$_{15}$H$_{18}$O$_3$[M+ (-CO)] 246.1256, found: 246.1378.
8-Allyl-4-phenyl-4-azatricyclo[6.3.1.0^2,6]dodec-9-ene-3,5,12-trione (18)

Yield: 80% (211 mg); IR (neat, cm⁻¹) ν_max 3078, 2921, 1712; \(^1\)H NMR (300 MHz, CDCl₃) δ 7.54 - 7.35 (m, 3 H), 7.30 - 7.22 (m, 2 H), 5.87 - 5.64 (m, 2 H), 5.53 (d, J = 9.8 Hz, 1 H), 5.11 (d, J = 3.9 Hz, 1 H), 5.06 (s, 1 H), 3.66 (t, J = 8.9 Hz, 1 H), 3.14 - 2.97 (m, 2 H), 2.87 (d, J = 14.3 Hz, 1 H), 2.59 (br. s., 2 H), 2.47 (dd, J = 6.9, 14.0 Hz, 1 H), 2.20 (dd, J = 7.6, 14.0 Hz, 1 H), 2.03 (dd, J = 7.8, 14.4 Hz, 1 H). \(^{13}\)C NMR (75 MHz, CDCl₃) δ 212.1, 177.5, 175.8, 133.8, 133.2, 131.8, 129.4, 128.8, 126.6, 126.2, 118.7, 49.1, 47.6, 44.8, 38.5, 37.6, 37.0, 32.3; HRMS (EI) m/z calcd C₂₀H₁₉NO₃ [M+] 321.1365, found: 321.1364.

4,9-Diphenyl-8-allyl-4-azatricyclo[6.3.1.0^2,6]dodec-9-ene-3,5,12-trione (37)

Yield: 68% (178 mg); IR (neat, cm⁻¹) ν_max 3072, 2931, 1777, 1713, 1636, 1500, 1445. \(^1\)H NMR (500 MHz, CDCl₃) δ 7.49 - 7.40 (m, 4 H), 7.40 - 7.34 (m, 1 H), 7.34 - 7.27 (m, 3 H), 7.23 - 7.16 (m, 2 H), 5.86 (dd, J = 2.7, 4.4 Hz, 1 H), 5.56 (tdd, J = 6.8, 10.3, 17.1 Hz, 1 H), 4.85 (d, J = 10.3 Hz, 1 H), 4.63 (dd, J = 2.0, 17.1 Hz, 1 H), 3.76 (t, J = 9.0 Hz, 1 H), 3.39 (d, J = 14.9 Hz, 1 H), 3.28 - 3.13 (m, 2 H), 2.79 - 2.65 (m, 2 H), 2.30 - 2.12 (m, 3 H). \(^{13}\)C NMR (101MHz, CDCl₃) δ 211.4, 176.7, 175.8, 143.8, 139.9, 133.6, 131.8, 129.4, 129.1, 128.9, 128.1, 127.8, 127.6, 126.3, 118.4, 51.2, 47.6,
8-Allyl-9-(4-methylphenyl)-4-phenyl-4-azatricyclo[6.3.1.0²,6]dodec-9-ene-3,5,12-trione (38)

Yield: 91% (237 mg); IR (neat, cm⁻¹) ν_max 3072, 2924, 1714, 1593, 1500. ¹H NMR (500 MHz, CDCl₃) δ 7.47 - 7.39 (m, 2 H), 7.39 - 7.29 (m, 3 H), 7.19 (d, J = 7.6 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2 H), 5.84 (t, J = 3.9 Hz, 1 H), 5.56 (ddt, J = 7.1, 10.3, 16.9 Hz, 1 H), 4.86 (dd, J = 1.2, 10.3 Hz, 1 H), 4.67 (dd, J = 1.2, 17.1 Hz, 1 H), 3.74 (t, J = 9.0 Hz, 1 H), 3.37 (d, J = 15.1 Hz, 1 H), 3.25 - 3.12 (m, 2 H), 2.78 - 2.63 (m, 2H), 2.34 (s, 3 H), 2.30 - 2.24 (m, 2 H), 2.20 (dd, J = 7.8, 14.9 Hz, 1 H); ¹³C NMR (126 MHz, CDCl₃) δ 211.5, 176.6, 175.9, 143.6, 137.4, 137.0, 133.7, 131.7, 129.4, 128.9, 128.8, 128.7, 127.2, 126.2, 118.3, 51.3, 47.5, 44.0, 37.6, 37.5, 36.4, 31.4, 21.3; HRMS (El) m/z calcd for C₉₇H₂₅NO₃ [M+] 411.1834, found: 411.1807.

8-Allyl-9-(4-methoxyphenyl)-4-phenyl-4-azatricyclo[6.3.1.0²,6]dodec-9-ene-3,5,12-trione (39)

Yield: 74% (192 mg); IR (neat, cm⁻¹) ν_max 2939, 2254, 1780, 1714, 1605, 1512; ¹H NMR (400 MHz, CDCl₃) δ 7.46 - 7.40 (m, 2 H), 7.39 - 7.33 (m, 3 H), 7.24 - 7.15
(m, 2 H), 6.84 (d, $J = 8.8$ Hz, 2 H), 5.83 (t, $J = 3.2$ Hz, 1 H), 5.55 (ddt, $J = 6.9$, 10.3, 17.1 Hz, 1 H), 4.85 (dd, $J = 2.0$, 10.2 Hz, 1 H), 4.66 (dd, $J = 2.0$, 17.1 Hz, 1 H), 3.80 (s, 3 H), 3.75 (t, $J = 8.8$ Hz, 1 H), 3.36 (d, $J = 14.9$ Hz, 1 H), 3.26 - 3.13 (m, 2 H), 2.78 - 2.59 (m, 2 H), 2.34 - 2.14 (m, 3 H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 211.5, 176.7, 175.9, 159.2, 143.4, 133.7, 132.5, 131.8, 130.2, 129.4, 128.8, 127.2, 126.3, 118.3, 113.4, 55.3, 51.4, 47.6, 44.1, 37.7, 37.5, 36.5, 31.4; HRMS (EI) $m/z$ calcd for C$_{27}$H$_{25}$NO$_4$ [M+] 427.1784, found: 427.1795.

8- Allyl-9- (1-phenylethenyl)-4-phenyl-4-azatricyclo[6.3.1.0$^{2,6}$]dodec-9-ene-3,5,12-trione (37)

Yield: 79% (259 mg); IR (neat, cm$^{-1}$) $\nu_{\text{max}}$ 2957, 2922, 2855, 1712; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 - 7.38 (m, 4 H), 7.33 - 7.27 (m, 4 H), 7.25 - 7.22 (m, 2 H), 5.78 (tdd, $J = 7.4$, 10.5, 18.4 Hz, 1 H), 5.70 (dd, $J = 2.1$, 4.9 Hz, 1 H), 5.68 (s, 1 H), 5.53 (s, 1 H), 5.02 - 4.92 (m, 2 H), 3.70 (t, $J = 8.8$ Hz, 1 H), 3.24 - 3.12 (m, 2 H), 2.76 (ddd, $J = 2.3$, 5.9, 19.5 Hz, 1 H), 2.59 (ddd, $J = 1.2$, 4.7, 19.1 Hz, 1 H), 2.48 (dd, $J = 6.6$, 14.1 Hz, 1 H), 2.24 (dt, $J = 8.2$, 15.2 Hz, 3 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 211.5, 176.6, 175.9, 146.5, 142.7, 141.9, 134.2, 131.8, 129.5, 129.3, 129.0, 128.4, 127.8, 127.5, 126.4, 118.8, 117.0, 51.1, 47.4, 43.9, 37.3, 37.0, 34.6, 31.8; HRMS (EI) $m/z$ calcd for C$_{28}$H$_{26}$NO$_3$ [M+] 423.1834, found: 423.1840.
References

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2. Savignac, P.; Bréque, A. Synth. Comm. 1979, 9, 487. doi:10.1080/00397917908060952
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
\[^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{)}\]

\[^{13}\text{C} \text{NMR (101 MHz, CDCl}_3\text{)}\]
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

Compound F – $^1$H NMR (400 MHz, CDCl$_3$)
13C NMR (101 MHz, CDCl₃)

Compound B – 1H NMR (400 MHz, CDCl₃)
$^{13}$C NMR (101 MHz, CDCl$_3$)

Compound E – $^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

Compound 21 – $^1$H NMR (400 MHz, CDCl$_3$)
\(^{13}\text{C}\) NMR (101 MHz, CDCl\(_3\))

Compound 16 – \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\))
$^{13}$C NMR (101 MHz, CDCl$_3$)
Compound 28 – $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
Compound 29 – $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
Compound 18 – $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
Compound 37 – $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
Compound 39 – $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) – Compound 40
$^{13}$C NMR (101 MHz, CDCl$_3$)