Supporting Information

Grubbs Metathesis Enabled by a Light-Driven gem-Hydrogenation of Internal Alkynes

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anie_202007030_sm_miscellaneous_information.pdf
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1. General Remarks

All reactions were carried out in flame-dried glassware under argon, ensuring rigorously inert conditions. The solvents were purified by distillation over the indicated drying agents and were stored and handled under argon: CH₂Cl₂ (CaH₂), MeCN (CaH₂), pentane (Na/K alloy), THF (Na/K alloy).

NMR spectra were recorded on Bruker AV400 or AV500 spectrometers at 298 K unless otherwise indicated, with the chemical shift (δ) given in ppm relative to TMS and the coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CD₂Cl₂: δ_H = 5.32 ppm, δ_C = 53.8 ppm; [D₃]-acetonitrile: δ_H = 1.94 ppm, δ_C = 118.26 ppm; [D₆]-acetone: δ_H = 2.05 ppm, δ_C = 29.8 ppm; C₆D₆: δ_H = 7.16 ppm, δ_C = 128.06 ppm).

Unless stated otherwise, all commercially available compounds (abcr, Acros, TCI, Aldrich, Alfa Aesar) were used without further purification.

Hydrogen gas (N50, ≥99.999 Vol.%) was purchased from AirLiquide and was used without further purification. Deuterium gas (99.8 atom% D, 99.995% purity) was purchased from SigmaAldrich. Both hydrogen and deuterium were handled with standard balloon techniques.

IR spectra were recorded on Alpha Platinum ATR spectrometer (Bruker) at room temperature, wavenumbers (ν) are given in cm⁻¹.

Mass spectrometric samples were analyzed using the following instruments: MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Bruker ESQ3000, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan).

GC-MS was performed with a Shimadzu GCMS-QP2010 Ultra instrument.

Headspace GC-FID samples were measured on an Agilent Technology 6890 or 7890 instrument with a 30 m HP-plot Al₂O₃ column (0.25 mm Ø, 5 µm film) using H₂ as the carrier gas. Headspace GC/MS samples were analyzed on an Agilent Technology 7890A instrument with AT 5975C MSD detection.

Photolysis experiments were performed in a self-made apparatus (Figure S-1), consisting of an aluminum box with a circular arrangement of 8 UV-A lamps (Philips Fluorescent lamps TUV PL-S 9W/2P, λ = 340-380 nm (Figure S-2) at 6 cm distance to the quartz-Schlenk tube. The temperature in the apparatus typically rises to 45 ºC over the course of 1 h.
Figure S-1. Reaction set-up

Figure S-2. Emission spectrum of the UV lamps
2. Mechanistic Studies

2.1 Synthesis of a Hoveyda-Grubbs Carbene by gem-Hydrogenation

1-Isopropoxy-2-(prop-1-yn-1-yl)benzene (19)

1-Ethynyl-2-isopropoxybenzene (250 mg, 1.56 mmol) was dissolved in THF (5 mL) and the resulting solution cooled to –78 °C. n-BuLi (1.6 M in hexanes, 1.07 mL, 1.71 mmol) was added dropwise over 5 min and the mixture was stirred for 30 min. Methyl iodide (147 µL, 2.35 mmol) was added and stirring was continued at room temperature for 15 h. Sat. aq. NH₄Cl (4 mL), tert-butyl methyl ether (10 mL) and water (2 mL) were added and the layers were separated. The aqueous layer was extracted with tert-butyl methyl ether (3 × 20 mL) and the combined organic layers were washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, pentane/tert-butyl methyl ether 100:1) to provide the title compound as a colorless oil (200 mg, 74%). ¹H NMR (400 MHz, CDCl₃) δ 7.36 (dd, J = 7.9, 1.8 Hz, 1H), 7.22 – 7.12 (m, 1H), 6.93 – 6.83 (m, 2H), 4.55 (hept, J = 6.1 Hz, 1H), 2.09 (s, 3H), 1.37 (d, J = 6.1 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 158.8, 133.8, 128.8, 120.9, 115.5, 89.7, 76.3, 72.1, 22.3, 4.8. IR (film) ν 2977, 1594, 1482, 1444, 1383, 1372, 1262, 1102, 974, 748 cm⁻¹. HRMS (ESI⁺) for C₁₂H₁₄O [M⁺]: calcd. 174.10388; found: 174.10392.

Complex 20.

A flame-dried quartz Schlenk tube was charged under argon with [(IMes)(ρ-cymene)RuCl₂] (102 mg, 167 µmol), alkyne 19 (28.2 mg, 167 µmol) and THF (6 mL). The Schlenk tube was closed with a septum and then transferred into the photolysis apparatus (Figure S-1). A hydrogen-filled balloon was connected to a needle which was pierced through the septum. The Schlenk tube was flushed with hydrogen for 2 min through an outlet cannula (the cannula did not reach into the solution to ensure that only the head space of the tube was flushed). After the first 10 seconds of flushing with hydrogen, the light source was switched on and the reaction mixture was stirred for 30 min under hydrogen atmosphere. After cooling to room temperature, all volatile components were removed under high vacuum. The remaining crude material was suspended in pentane (10 mL) and the suspension was vigorously stirred for
5 min. The supernatant was removed via a filter canula and the dark green filtrate was collected. This trituration procedure was repeated twice and the combined filtrates were evaporated. The remaining material was purified by flash chromatography (silica, CH$_2$Cl$_2$ → CH$_2$Cl$_2$/MeOH 25:1). The green band was collected and the solvent evaporated to provide the title compound (34.1 mg, 31%) as a dark green oil. Dark green needle-shaped crystals suitable for X-ray diffraction were grown by slow evaporation of CH$_2$Cl$_2$/pentane solutions in a constant stream of argon.

$^1$H NMR (600 MHz, C$_6$D$_6$) δ 7.35 (dd, $J = 7.7$, 1.6 Hz, 1H), 7.10 (ddd, $J = 8.5$, 7.3, 1.6 Hz, 1H), 6.88 (s, 4H), 6.60 (td, $J = 7.7$, 7.3, 0.9 Hz, 1H), 6.43 (d, $J = 8.3$ Hz, 1H), 6.17 (s, 2H), 4.57 (hept, $J = 6.2$ Hz, 1H), 2.62 (q, $J = 7.5$ Hz, 2H), 2.40 (s, 12H), 2.20 (s, 6H), 1.12 (d, $J = 6.2$ Hz, 6H), 0.97 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 314.5, 174.9, 154.6, 146.7, 138.9, 138.5, 136.0, 129.0, 128.5, 124.6, 121.0, 114.3, 112.4, 74.3, 51.5, 21.2, 20.8, 19.5, 6.2. IR (film) $\tilde{\nu}$ 2961, 2921, 2865, 1573, 1483, 1450, 1395, 1304, 1259, 1224, 1160, 1078, 1012, 936, 922, 850, 791, 751, 698, 665, 614, 593, 579 cm$^{-1}$. HRMS (ESI$^+$) for C$_{33}$H$_{40}$Cl$_2$N$_2$O$_2$Ru [M$^+$]: calcd. 652.15553; found: 652.15557.

A second fraction collected during flash chromatography consisted of compound 21 (colorless oil, 16.1 mg, 55%). $^1$H NMR (600 MHz, CDCl$_3$) δ 7.30 (dd, $J = 7.5$, 1.8 Hz, 1H), 7.21 (td, $J = 7.7$, 1.8 Hz, 1H), 6.97 (td, $J = 7.5$, 1.1 Hz, 1H), 6.93 (dd, $J = 8.2$, 1.2 Hz, 1H), 6.86 (s, 1H), 4.50 (hept, $J = 6.0$ Hz, 1H), 2.14 (s, 2H), 1.36 (d, $J = 6.1$ Hz, 5H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 156.1, 138.3, 131.0, 129.4, 127.6, 123.2, 120.3, 114.8, 71.3, 22.3, 15.9. IR (film) $\tilde{\nu}$ 2975, 2931, 1594, 1481, 1449, 1383, 1372, 1287, 1238, 1120, 957, 749 cm$^{-1}$. HRMS (ESI$^+$) for C$_{24}$H$_{30}$O$_2$Na [M$^+$]: calcd. 373.21349; found: 373.21380.
Figure S-3. Structure of complex 20 in the solid state in two different orientation; hydrogen atoms (except on the ethyl substituent) are omitted for clarity.
Supporting Information

X-ray Crystal Structure Analysis of Complex 20: C\textsubscript{33}H\textsubscript{40}Cl\textsubscript{2} N\textsubscript{2} O Ru, M\textsubscript{r} = 652.64 g · mol\textsuperscript{-1}, green plate, crystal size 0.127 x 0.067 x 0.013 mm\textsuperscript{3}, triclinic, space group P\textoverline{1} [2], a = 8.5880(5) Å, b = 11.2933(6) Å, c = 17.1714(9) Å, α = 99.455(2)°, β = 92.749(2)°, γ = 107.076(2)°, V = 1562.16(15) Å\textsuperscript{3}, T = 100(2) K, Z = 2, D\textsubscript{calc} = 1.387 g · cm\textsuperscript{-3}, λ = 0.71073 Å, μ(Mo-K\textsubscript{α}) = 0.701 mm\textsuperscript{-1}, analytical absorption correction (T\textsubscript{min} = 0.95, T\textsubscript{max} = 0.99), Bruker-AXS Kappa Mach3 diffractometer with APEX-II detector and μS micro focus X-ray source, 1.208 < θ < 33.141°, 67324 measured reflections, 11891 independent reflections, 10420 reflections with I > 2σ(I), R\textsubscript{int} = 0.0411. S = 1.046, 361 parameters, residual electron density +1.5 (0.83 Å from Si3) / -0.7 (0.72 Å from Si3) e · Å\textsuperscript{-3}. The structure was solved by SHELXT and refined by full-matrix least-squares (SHELXL) against F\textsuperscript{2} to R\textsubscript{1} = 0.032 [I > 2σ(I)], wR\textsubscript{2} = 0.073. CCDC-2004044.
$^{13}$C NMR (151 MHz, DMSO-d$_6$) δ 314.51, 174.86, 154.58, 146.73, 138.90, 138.45, 136.02, 129.01, 128.50, 124.57, 121.02, 114.45, 112.36, 74.33, 51.54, 21.16, 20.76, 19.50, 6.18.

$^1$H NMR (600 MHz, DMSO-d$_6$) δ 7.35 (dd, J = 7.7, 1.6 Hz, 1H); 7.10 (dd, J = 8.5, 7.3, 1.6 Hz, 1H); 6.88 (s, 1H); 6.43 (s, 1H); 5.73 (s, 1H); 4.57 (dd, J = 6.2 Hz, 1H); 2.62 (s, 1H); 2.20 (s, 1H); 1.25 - 0.87 (m, 6H); 0.97 - 1.6 Hz (7.5 Hz, 3H).
Side product 21

After analysis the NMR data supports the following structure:

Due to the high symmetry and flexibility of the molecule, no information could be obtained about the double bond geometry. It is either all-cis or all-trans. A X-ray structure could solve that problem. Maybe EIMS can also help to solve that question.

P-10: H240200
Material: 1020102020
Controlled by: H240200
Class: Yellow Blob
Gross: 7.23
Sample: 7.23
Prepared by: 7.23
Sample: 7.23
Analysed by: 7.23
Method: 7.23
Amount: 7.23
Software: 7.23
Reference: 7.23
Temperature: 298 K
Speed of rotation: 6000 rpm
Prep: 74459_0247 EPC 74459_0247 H-Q20-04-22
Experiment: epc310, cpc1093, [13C, 13C-label]_journal.jpg, [13C, 13C-label]_journal.png, [13C, 13C-15N]_journal.png, [13C, 13C-15N]_journal.png
2.2 Kinetic Profiling of Complex 20

In order to characterize complex 20 further, we made use of a standard method to assess the catalytic performance of olefin metathesis catalyst developed by Grubbs et al.\textsuperscript{3} To this end, the ring closing metathesis of diallylmalonate (22) was carried out with complex 20 and the commercially available Grubbs II and Hoveyda-Grubbs II catalysts for comparison.

In an argon-filled glovebox, an NMR tube with a screw cap septum top was charged with a stock solution of the corresponding complex in CD\textsubscript{2}Cl\textsubscript{2} (1 mol\%, 0.5 mL). The sample was brought out of the glovebox and equilibrated at 30°C in the NMR machine before diallylmalonate 22 (12.8 µL, 53.5 µmol) was added via a Hamilton syringe. The NMR tube was quickly shaken and inserted in the NMR probe. Data points were collected over 20 mins and the acquired raw data were processed in MestReNova with the ReactionMonitoring-plugin (Figure S-4).

Figure S-4. RCM of diallylmalonate 22 with formation of product 23 ([Ru-1] = complex 20)
All tested catalysts exhibit similar rates at 1 mol% catalyst loading up to 60% conversion. Figure S-4 shows that after this point the Grubbs II and the Hoveyda-Grubbs II catalyst convert the substrate quantitatively into the product, whereas the reaction catalyzed by 20 stalled at \( \approx 60\% \) conversion. However, this catalysts fully converts the substrate into product without losing activity at a loading of 3 mol%.

### 2.3 Hydrogenative Metathesis with H\(_2\)/D\(_2\) mixtures

A 1:1 mixture of H\(_2\) and D\(_2\) was prepared by using a gas-tight 10 mL Hamilton syringe: a gas volume of 5 mL was taken out of a balloon filled with H\(_2\) and of a second balloon filled with D\(_2\); the Hamilton syringe was then shaken to ensure mixing of the two gases.

A flame-dried quartz Schlenk tube was charged with \([\text{I} \text{Pr}(\text{p}-\text{cymene})\text{RuCl}_2]\) (13.8 mg, 200 \( \mu \)mol, 10 mol%), enyne 1b (44.1 mg, 0.2 mmol) and toluene (2.0 mL, 0.1 M). The Schlenk tube was closed with a septum and then transferred into the photolysis apparatus. The total volume of 10 mL H\(_2\)/D\(_2\) was then flushed through the quartz Schlenk tube using an outlet canula. This procedure was repeated nine times to fully exchange the argon atmosphere for a H\(_2\)/D\(_2\) atmosphere. At this point, the light source was switched on and the mixture was stirred for 60 min. For work-up, the mixture was diluted with pentane (5 mL) and filtered through a short silica pad. The filtrate was evaporated and the remaining crude material was purified by flash chromatography (silica, pentane/tert-butyl methyl ether 50:1) to provide product 2 (28.1 mg, 72%) as a colorless oil. The identity and composition of the different isotopomers was established by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy.

The isotopomer ratio was determined to be [D\(_0\)]:[D\(_1\)]:[D\(_2\)] = 42:34:24. The formation of significant quantities of an [D\(_1\)] isotopomer is suggestive of a non-concerted hydrogen transfer mechanism.
2.4 Headspace Analysis

A flame-dried quartz Schlenk tube was charged with [(IPr)(p-cymene)RuCl₂] (13.8 mg, 0.02 mmol, 10 mol%), the corresponding enyne 1a or 1b (200 µmol) [for the crossover experiment, enyne 1a and 1b (100 µmol, each)] and toluene (2 mL, 0.1 M). The Schlenk tube was closed with a septum and then transferred into the photolysis apparatus. A hydrogen-filled balloon was equipped with a needle which was pierced through the septum and the Schlenk tube was flushed with hydrogen for 2 min through an outlet cannula (the cannula did not reach into the solution to ensure that only the head space of the tube was flushed). After the first 10 seconds of flushing with hydrogen, the light source was switched on and the mixture was stirred for 60 min under hydrogen atmosphere. At this point, a gas-tight 1 mL Hamilton Syringe was used to take 500 µL aliquots of the gas in the headspace of the Schlenk tube and the samples were analyzed by GC. Retention times and fragmentation patterns of authentic samples of various gases (Phillips No.40 + methane, ethane and ethylene) were used to unambiguously assign the structure of the volatile compounds formed during the hydrogenative metathesis reaction.

The presence of alkanes in the headspace is explained by reduction of the alkenes primarily formed by the same catalyst system. Terminal alkenes tend to be reduced (much) faster than more hindered internal alkenes, which likely explains why ethane is by far the major component of the C₂ fraction.
Figure S-5. Possible explanation for the formation of products with odd carbon numbers in the headspace

Hydrogenative metathesis of enyne 1b yields 95% (NMR) of cyclopentene 2. Analysis of the headspace by GC shows that the major species are C₄-products, namely butenes and butane. Interestingly, significant amounts of C₃- and C₅-products are detected as well: their formation is attributed to an isomerization/carbene formation/cross dimerization sequence (see Figure S-5). It has previously been shown that the 12e-fragment [(IPr)RuCl₂] generated under the reaction conditions is an effective catalyst for alkene isomerization. Moreover, DFT calculations suggested that [(IPr)RuCl₂] is able to activate a terminal alkene to generate, via a bimolecular transition state, two new ruthenium carbenes. Cross-dimerization of these “tertiary” ruthenium carbenes with the “secondary” ruthenium carbene explains the observation of C₃- and C₅-products.
The model reaction was also run with 5 mol% and 20 mol% catalyst loading. Headspace GC analysis showed that the proportion of C₄ and C₃ compounds is essentially independent of the loading. However, the ratio between unsaturated and saturated compounds does change in that the proportion of alkanes is significantly increased at higher loading; this finding is again in line with a secondary hydrogenation process.

It is of note that Fogg, Jensen and coworkers have recently studied a pyridine-stabilized ruthenium ethylidene complex, which decomposes via bimolecular coupling to give a mixture of butene,
pentene and propene in a 2:1:1 ratio.\textsuperscript{5} Whilst this observation is qualitatively similar to our observations, we note that pentenes and pentane are underrepresented (relative to propane/propene) in our study. The difference might be explained by the fact that different analytical tools were used (GC/MS versus NMR); since pentenes/pentane are less volatile than propene/propane, they might be underrepresented in the gas phase. Efforts to quantify the pentenes by NMR spectroscopy in the liquid phase were unsuccessful due to severe signal overlap with product 2. Moreover, one might conceive that dimerization of a propylidene complex with an ethylidene complex is (somewhat) slower than the dimerization of a propylidene complex with a methylidene complex.

Hydrogenative metathesis with a 1:1 mixture of enynes 1a\textsuperscript{6} and 1b confirms the bimolecular decomposition of the secondary carbene complex. The increased amount of C\textsubscript{3}-products and concomitant decrease of C\textsubscript{4}- and C\textsubscript{2}-products strongly supports the notion that bimolecular alkylidene coupling is operative. The fact that the C\textsubscript{2}:C\textsubscript{3}:C\textsubscript{4} ratio is not 1:2:1, as statistically expected from such a crossover experiment, is ascribed to different rates of alkylidene coupling and to the necessary isomerization events discussed above.
Headspace analysis (GC) @ 10 mol% catalyst loading

| No. | Ret.Time (min) | area-% (%) | Peak Name       |
|-----|----------------|------------|-----------------|
| 1   | 0.94           | 0.06       | Methan          |
| 2   | 1.01           | 1.31       | Ethan           |
| 3   | 1.26           | 29.19      | Propan          |
| 5   | 1.62           | 1.22       | Propan          |
| 7   | 2.18           | 35.52      | n-Butan         |
| 8   | 3.37           | 10.50      | trans-2-Buten   |
| 9   | 3.51           | 0.51       | 1-Buten         |
| 10  | 3.88           | 0.02       | iso-Buten       |
| 11  | 4.19           | 3.82       | cis-2-Buten     |
| 12  | 4.98           | 0.07       |                 |
| 13  | 5.21           | 0.01       | iso-Pentan      |
| 14  | 5.77           | 6.04       |                 |
| 16  | 6.57           | 0.02       |                 |
| 17  | 9.51           | 3.28       | trans-2-Penten  |
| 18  | 10.76          | 0.20       | 1-Penten        |
| 19  | 11.28          | 0.01       |                 |
| 20  | 11.91          | 0.81       | cis-2-Penten    |
| 25  | 14.09          | 0.01       |                 |
| 26  | 15.13          | 0.96       |                 |
| 28  | 16.45          | 0.01       |                 |
| 30  | 17.45          | 0.24       |                 |
| 31  | 17.62          | 0.07       |                 |
| 32  | 17.73          | 0.01       |                 |
| 33  | 17.76          | 0.01       |                 |
| 34  | 17.88          | 0.04       |                 |
| 36  | 18.17          | 0.04       |                 |
| 38  | 18.57          | 0.01       |                 |
### Supporting Information

| No. | Ret.Time min | area-% % | Peak Name |
|-----|--------------|----------|-----------|
| 39  | 18.67        | 0.01     |           |
| 40  | 18.75        | 0.04     |           |
| 41  | 19.17        | 0.18     |           |
| 44  | 20.00        | 0.01     |           |
| 47  | 21.57        | 0.14     |           |
| 48  | 23.13        | 0.09     |           |
| 49  | 23.39        | 4.20     |           |
| 50  | 24.14        | 0.02     |           |
| 51  | 24.55        | 0.03     |           |
| 52  | 24.67        | 0.01     |           |
| 53  | 24.80        | 0.01     |           |
| 54  | 24.91        | 0.01     |           |
| 57  | 25.32        | 0.01     |           |
| 58  | 25.55        | 0.03     |           |
| 59  | 25.68        | 0.02     |           |
| 60  | 25.89        | 0.03     |           |
| 61  | 26.01        | 0.01     |           |
| 63  | 26.69        | 0.44     |           |
| 64  | 26.99        | 0.01     |           |
| 66  | 27.96        | 0.02     |           |

19 peaks out of 66 (total area percentage = 0.08 %) are below threshold.

**Instrument parameters:**
- **Column:** 29.5 m HP-Plot Al2O3 0.25/5.0 df 0.425
- **Temperature:** 220°C 80°C 10 min iso 88°C 180°C 5 min iso 350°C
- **Gas:** 0.80 bar H2
- **Sample size:** 450.0 μL

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*Signature*
[Manually integrated] BIU-BB-623-02

Sample: BIU-BB-623-02
Instrument: GC_212

Sequenz: 7200 BIU-BB VD
Measured: 25.02.20 14:35

Sequenz date: 25.02.20
Processing M.: Übersicht BIU-BB
Report-File: 623-02

Auswertung ohne Lösungsmittel (Toluol-d8)
Zuordnung mit Vergleichssubstanzen (Gasmischung Phillips No. 40 und Methan, Ethan, Ethen)

| No. | Ret. Time min | area-% | Peak Name |
|-----|---------------|--------|-----------|
| 1   | 0,94          | 0,08   | Methan    |
| 2   | 1,01          | 63,30  | Ethan     |
| 3   | 1,07          | 1,77   | Ethen     |
| 4   | 1,26          | 3,27   | Propan    |
| 5   | 1,62          | 1,71   | Propen    |
| 7   | 2,04          | 0,02   | iso-Butan |
| 8   | 2,20          | 2,32   | n-Butan   |
| 9   | 3,38          | 3,08   | trans-2-Buten |
| 10  | 3,51          | 0,26   | 1-Buten   |
| 11  | 3,69          | 0,08   | iso-Buten |
| 12  | 4,20          | 1,27   | cis-2-Buten |
| 13  | 4,69          | 0,10   |           |
| 14  | 5,22          | 0,01   | iso-Pentan |
| 15  | 5,82          | 1,26   |           |
| 16  | 8,60          | 0,26   |           |
| 17  | 9,57          | 1,17   | trans-2-Penten |
| 18  | 10,77         | 0,16   | 1-Penten  |
| 19  | 11,28         | 0,02   |           |
| 20  | 11,94         | 0,32   | cis-2-Penten |
| 21  | 13,09         | 0,01   |           |
| 22  | 13,45         | 0,01   |           |
| 23  | 14,13         | 0,02   |           |
| 24  | 15,16         | 0,50   |           |
| 25  | 15,96         | 0,01   |           |
| 26  | 16,48         | 0,01   |           |
| 27  | 17,48         | 0,17   |           |
| 28  | 17,65         | 0,23   |           |
| No. | Ret.Time min | area-% % | Peak Name |
|-----|-------------|----------|-----------|
| 29  | 17.79       | 0,03     |           |
| 30  | 17.88       | 0,45     |           |
| 31  | 18.19       | 0,13     |           |
| 32  | 18.47       | 0,02     |           |
| 33  | 18.60       | 0,04     |           |
| 34  | 18.69       | 0,02     |           |
| 35  | 18.77       | 0,03     |           |
| 36  | 19.19       | 0,13     |           |
| 37  | 19.75       | 0,02     |           |
| 38  | 19.83       | 0,03     |           |
| 39  | 20.03       | 0,05     |           |
| 40  | 21.59       | 0,17     |           |
| 41  | 23.15       | 0,11     |           |
| 42  | 23.40       | 15,14    |           |
| 43  | 24.15       | 0,02     |           |
| 44  | 24.57       | 0,04     |           |
| 45  | 24.69       | 0,02     |           |
| 46  | 24.84       | 0,04     |           |
| 47  | 24.93       | 0,04     |           |
| 48  | 25.12       | 0,02     |           |
| 49  | 25.17       | 0,01     |           |
| 50  | 25.35       | 0,06     |           |
| 51  | 25.58       | 0,14     |           |
| 52  | 25.70       | 0,05     |           |
| 53  | 25.91       | 0,09     |           |
| 54  | 26.02       | 0,04     |           |
| 55  | 26.70       | 1,81     |           |
| 56  | 27.00       | 0,02     |           |
| 57  | 27.62       | 0,04     |           |

2 peaks out of 88 (total area percentage = 0,00 %) are below threshold.

Instrument parameters:
- Column: 29.5 m HP-Plot/A203 0,25/5,0df G/425
- Temperature: 220/80, 10 min iso 6/min 180, 5 min iso 350
- Gas: 0,80 bar H2
- Sample size: 450,0 µL
Auswertung ohne Lösungsmittel (Toluol-d8)
Zuordnung mit Vergleichssubstanzen (Gasmischung Phillips No 40 und Methan, Ethan, Ethen)

| No. | Ret. Time (min) | area-% (%) | Peak Name       |
|-----|-----------------|------------|----------------|
| 1   | 0,94            | 0,06       | Methan         |
| 2   | 1,00            | 17,01      | Ethan          |
| 3   | 1,06            | 0,05       | Ethan          |
| 4   | 1,25            | 34,99      | Propan         |
| 5   | 1,62            | 9,83       | Propen         |
| 6   | 2,04            | 0,01       | iso-Butan      |
| 7   | 2,19            | 6,68       | n-Butan        |
| 8   | 3,36            | 14,29      | trans-2-Buten  |
| 9   | 3,51            | 0,98       | 1-Buten        |
| 10  | 3,88            | 0,06       | iso-Buten      |
| 11  | 4,19            | 5,43       | cis-2-Buten    |
| 12  | 4,98            | 0,04       |                |
| 13  | 5,23            | 0,01       | iso-Pentan     |
| 14  | 5,82            | 1,03       |                |
| 15  | 6,61            | 0,08       |                |
| 16  | 9,56            | 2,55       | trans-2-Penten |
| 17  | 10,81           | 0,24       | 1-Penten       |
| 18  | 11,31           | 0,02       |                |
| 19  | 11,95           | 0,69       | cis-2-Penten   |
| 21  | 14,13           | 0,01       |                |
| 22  | 15,17           | 0,10       |                |
| 23  | 15,97           | 0,01       |                |
| 25  | 16,48           | 0,01       |                |
| 27  | 17,49           | 0,13       |                |
| 28  | 17,65           | 0,11       |                |
| 29  | 17,74           | 0,01       |                |
| 30  | 17,79           | 0,01       |                |
Supporting Information

| No. | Ret Time | area-% | Peak Name |
|-----|----------|--------|-----------|
| 31  | 17.89    | 0.37   |           |
| 32  | 18.20    | 0.05   |           |
| 34  | 18.60    | 0.02   |           |
| 35  | 18.70    | 0.02   |           |
| 36  | 18.78    | 0.02   |           |
| 37  | 19.20    | 0.11   |           |
| 40  | 20.03    | 0.01   |           |
| 44  | 21.00    | 0.02   |           |
| 45  | 23.16    | 0.04   |           |
| 46  | 23.41    | 4.40   |           |
| 47  | 24.17    | 0.01   |           |
| 48  | 24.58    | 0.01   |           |
| 50  | 24.94    | 0.01   |           |
| 51  | 25.12    | 0.01   |           |
| 52  | 25.36    | 0.01   |           |
| 54  | 25.58    | 0.02   |           |
| 55  | 25.71    | 0.01   |           |
| 56  | 25.92    | 0.01   |           |
| 57  | 26.04    | 0.01   |           |
| 59  | 28.72    | 0.35   |           |
| 61  | 27.65    | 0.01   |           |
| 62  | 28.01    | 0.01   |           |

13 peaks out of 62 (total area percentage = 0.04 %) are below threshold.

Instrument parameters:
- Column: 29.5 m HP-Plot/Al2O3 0.25/5.0, df G/425
- Temperature: 220/80, 10 min iso, 6 min 180, 5 min iso, 350
- Gas: 0.80 bar H2
- Sample size: 450.0 µL
2.5 VT NMR Studies of [(NHC)(p-cymene)RuCl₂] Complexes

A flame-dried pressure NMR tube was charged with a solution of the corresponding complex [(NHC)(p-cymene)RuCl₂] (15 µmol) in [D₆]-benzene (500 µL). The NMR tube was inserted into the NMR probe head and spectra were acquired in a temperature range from 25 °C to 100 °C (10 °C increments).

Figure S-6. Exchange of the p-cymene ligand in [(IPr)(η₆-cymene)RuCl₂] by C₆D₆ under thermal conditions in the dark
Figure S-7. Exchange of the p-cymene ligand in [(IMes)(η⁶-cymene)RuCl₂] by C₆D₆ under thermal conditions in the dark.

We infer that ligand exchange with [(IPr)(p-cymene)RuCl₂] is more efficient compared to [(IMes)(p-cymene)RuCl₂] as evidenced by the higher NMR yield. In both cases, the ligand displacement starts at 60-70 °C.
2.6 The Impact of the UV Irradiation on the Reaction Outcome

Figure S-8. Comparison of the $^1$H NMR spectra of the crude reaction mixture formed with photochemical (top) or thermal (100°C, bottom) activation: region of the olefinic signals

Figure S-9. Comparison of the $^1$H NMR spectra of the crude reaction mixture formed with photochemical (top) or thermal (100°C, bottom) activation: region of the –OMe signal
2.7 Control Experiment: Orthogonal Entry via a Grubbs Ethylidene Complex

[1,3-Bis(2,6-diisopropyl-phenyl)-2-imidazolidinylidene]dichloro(benzylidene)bis(pyridine)-ruthenium

(1,3-Bis(2,6-diisopropylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene)-(tricyclohexylphosphine)ruthenium (1.00 g, 1.93 mmol) was weighed into a Schlenk tube and neat pyridine (3.90 mL, 48.3 mmol) was added at room temperature, causing an immediate color change from purple to dark green. After 15 min, pentane (20 mL) were carefully layered onto the solution and the Schlenk tube was sealed and stored in a fridge for 18 h. The precipitated light green crystals were filtered off with a filter canula, washed with pentane (3 x 15 mL) and dried under high vacuum to provide the compound as a light green powder (830 mg, 95%).

$^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 19.82 (s, 1H), 8.70 (d, $J = 4.9$ Hz, 2H), 8.36 (d, $J = 5.4$ Hz, 2H), 7.99 – 7.86 (m, 2H), 7.33 – 7.22 (m, 2H), 7.21 – 7.10 (m, 5H), 6.93 – 6.82 (m, 3H), 6.73 (s, 2H), 6.55 (t, $J = 6.5$ Hz, 2H), 6.38 (t, $J = 7.7$ Hz, 1H), 6.05 (t, $J = 6.7$ Hz, 2H), 3.66 (s, 4H), 1.46 (s, 12H), 1.10 (d, $J = 6.8$ Hz, 12H).

$^{13}$C NMR (101 MHz, C$_6$D$_6$) $\delta$ 314.0, 186.9, 153.2, 152.7, 150.6, 147.9, 137.7, 135.5, 135.0, 130.4, 130.2, 129.6, 124.3, 123.2, 122.9, 28.8, 26.5, 23.3.

[1,3-Bis(2,6-diisopropyl-phenyl)-2-imidazolidinylidene]dichloro(ethylidene)bis(pyridine)-ruthenium (24).$^7$

[1,3-Bis(2,6-diisopropyl-phenyl)-2-imidazolidinylidene]dichloro(benzylidene)bis(3-bromopyridine)ruthenium (50 mg, 61.7 µmol) was dissolved in C$_6$D$_6$ (1.5 mL) and the resulting solution was cooled to 5 °C (just above the melting point of benzene).

(2Z)-Butene was bubbled through the mixture for 1 min, causing a color change from dark green to dark yellow within 3 min. The solution was then cooled to 0 °C to freeze the benzene, which was then sublimed off under high vacuum. The residue was then redissolved in cold pentane and the pentane was again removed under high vacuum to azeotropically remove traces of residual methyl styrene that was formed during the reaction. Drying under high vacuum afforded the compound as a yellow-brown solid (42 mg, 93%). The complex decomposes readily at ambient temperature. $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 19.70 (q, $J = 6.0$ Hz, 1H), 8.75 (d, $J = 5.1$ Hz, 4H), 7.28 – 7.06 (m, 12H), 6.72 (s, 2H), 3.89 – 3.49 (m, 4H), 1.89 (d, $J = 6.0$ Hz, 3H), 1.58 (d, $J = 6.5$ Hz, 12H), 1.08 (d, $J = 7.0$ Hz, 12H). Due to the thermal instability of the sample, a $^{13}$C NMR spectrum could not be recorded.
A flame-dried quartz Schlenk tube was charged with enyne 1a (66.0 mg, 0.31 mmol) and toluene (1 mL). The Schlenk tube was closed with a septum and then transferred into the photolysis apparatus. A hydrogen-filled balloon was connected to a needle which was pierced through the septum and the Schlenk tube was flushed with hydrogen for 2 min through an outlet cannula (the cannula did not reach into the solution to make sure that only the head space of the tube was flushed). The ethylidene complex 24 (42.0 mg, 20 mol%) in toluene (2 mL) was added via syringe and the resulting mixture was stirred for 60 min under H₂ atmosphere. The mixture was diluted with pentane (5 mL) and then filtered through a short pad of silica. The filtrate was evaporated and the residue was analyzed by ¹H NMR spectroscopy, which showed the formation of product 2 in 64% NMR yield; the analytical data of this compound are compiled below.
3. Synthesis of Substrates and Precatalysts

3.1 Synthesis of the Substrates

The alkynes S1,13 S2,13 S3,13 S48 and (E)-6-bromohex-2-ene (S5)9 were prepared according to literature procedures.

(E)-7-Bromohept-2-ene (S6)

A solution of (E)-hept-5-en-1-ol (498 mg, 4.36 mmol)10 and CBr4 (1.60 g, 4.82 mmol) in CH2Cl2 (25 mL) was cooled to 0 °C before PPh3 (1.26 g, 4.82 mmol) was added in portions over a period of 30 min under vigorous stirring. Once the addition was complete, stirring was continued for another 2.5 h at ambient temperature. The mixture was concentrated to half of the volume under reduced pressure and then slowly added to hexanes (250 mL) with vigorous stirring. After 5 min, the precipitate was filtered off and the filtrate was concentrated under reduced pressure. Purification of the residue by flash chromatography (silica, pentane) provided the title compound as colorless oil (328 mg, 42%). 1H NMR (400 MHz, CDCl3) δ 5.71 – 5.20 (m, 2H), 3.41 (t, J = 6.8 Hz, 2H), 2.05 – 1.96 (m, 2H), 1.90 – 1.81 (m, 2H), 1.64 (dq, J = 4.3, 1.2 Hz, 3H), 1.56 – 1.44 (m, 2H). 13C NMR (101 MHz, CDCl3) δ 130.7, 125.6, 34.0, 32.4, 31.8, 28.2, 18.1. IR (film) ν 2961, 2933, 2855, 1452, 1438, 1250, 964, 645, 562 cm⁻¹. HRMS (EI) for C7H13Br [M]+: calcd. 176.01958; found: 176.01953.

1-Methoxy-1-(prop-1-yn-1-yl)cyclohexane (S7)

Sodium hydride (381 mg, 15.9 mmol) was added in portions over 5 min to a solution of 1-(1-propynyl)cyclohexanol (2.00 g, 14.5 mmol) in THF (72 mL) at 0 °C. The suspension was stirred for 30 min before dimethyl sulfate (1.53 mL, 16.2 mmol) was added dropwise and stirring was continued overnight at room temperature. Water (100 mL) was carefully added and the mixture was extracted with pentane (3 x 50 mL). The combined organic fractions were washed with brine, dried over Na₂SO₄ and concentrated under reduced
pressure (40 °C, 100 mbar). The residue was dissolved in pentane/diethyl ether (50:1) and the turbid solution filtered through a short silica plug. After evaporation of all volatile materials, the compound was purified by vacuum distillation (34 mbar, bath temperature: 135 °C, head temperature 100 °C) which yields the title compound as a colorless liquid (2.10 g, 95%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.34 (s, 3H), 1.87 (s, 3H), 1.84 – 1.78 (m, 2H), 1.67 – 1.41 (m, 8H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 81.6, 80.3, 74.0, 50.5, 37.0, 25.6, 22.9, 3.6. IR (film) \(\tilde{\nu}\) 2933, 2856, 1447, 1294, 1185, 1172, 1145, 1091, 1086, 925 cm\(^{-1}\). HRMS (ESI\(^+\)) for C\(_{10}\)H\(_{16}\)O\(_{\text{Na}}\) [M+Na\(^+\)]: calcd. 175.10935; found: 175.10935.

1-Bromo-2-(3-methoxy-3-methylbut-1-yn-1-yl)benzene (S8)

Sodium hydride (141 mg, 5.89 mmol) was added to a solution of 4-(2-bromophenyl)-2-methylbut-3-yn-2-ol (880 mg, 3.68 mmol)\(^1\) in DMF (15 mL) at 0 °C and the resulting mixture was stirred for 30 min at this temperature. Methyl iodide (791 mg, 0.34 mL, 5.52 mmol) was added and stirring was continued for 15 h at ambient temperature. Water (20 mL) was introduced and the mixture was extracted with tert-butyl methyl ether (3 x 20 mL). The combined organic layers were washed with brine, dried over Na\(_2\)SO\(_4\) and concentrated under reduced pressure. Purification of the residue was achieved by flash chromatography (silica, pentane/tert-butyl methyl ether 50:1) to yield the title compound (727 mg, 78%) as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.61 – 7.55 (m, 1H), 7.47 – 7.43 (m, 1H), 7.28 – 7.22 (m, 1H), 7.16 (ddd, \(J = 8.0, 7.5, 1.7\) Hz, 1H), 3.48 (s, 3H), 1.57 (s, 6H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 133.4, 129.5, 127.0, 125.8, 125.1, 96.0, 83.0, 71.2, 52.1, 28.4. IR (film) \(\tilde{\nu}\) 2983, 1467, 1433, 1360, 1289, 1266, 1186, 1171, 1146, 1072, 870, 794, 750, 679, 520 cm\(^{-1}\). HRMS (GC-ESI) for C\(_{12}\)H\(_{13}\)OBr [M\(^+\)]: calcd. 252.01453; found: 252.01444.

2-Ethynyl-2-methoxyadamantane (S9)

Prepared analogously from 2-ethynyladamantan-2-ol\(^1\) as a colorless oil (169 mg, 72%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.37 (s, 3H), 2.52 (s, 1H), 2.16 – 2.09 (m, 2H), 2.08 – 2.02 (m, 4H), 1.88 – 1.75 (m, 4H), 1.71 – 1.67 (m, 2H), 1.57 – 1.48 (m, 2H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 85.4, 77.9, 74.4, 50.1, 37.7, 35.5, 35.1, 31.5, 27.2, 26.7. IR (film) \(\tilde{\nu}\) 3304, 2900, 2848, 2104, 1450, 1228, 616, 511 cm\(^{-1}\). HRMS (GC-ESI) for C\(_{13}\)H\(_{18}\)O [M\(^+\)]: calcd. 190.13516; found: 190.13522.
Mestranol methyl ether (S10)

Prepared analogously from commercially available mestranol as a colorless oil (266 mg, 55%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.21 (dd, $J$ = 8.7, 1.1 Hz, 1H), 6.71 (dd, $J$ = 8.6, 2.8 Hz, 1H), 6.63 (d, $J$ = 2.5 Hz, 1H), 3.78 (s, 3H), 3.42 (s, 3H), 2.95 – 2.77 (m, 2H), 2.61 (s, 1H), 2.44 – 2.17 (m, 3H), 2.01 (tt, $J$ = 13.6, 4.9 Hz, 2H), 1.90 – 1.66 (m, 3H), 1.55 (s, 2H), 1.51 – 1.27 (m, 3H), 0.88 (d, $J$ = 0.7 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.5, 138.0, 132.7, 126.5, 113.9, 111.6, 85.8, 84.8, 75.8, 55.3, 53.4, 49.6, 47.6, 43.6, 39.3, 36.7, 34.2, 30.0, 27.4, 26.7, 22.8, 12.8. IR (film) $\tilde{\nu}$ 2933, 1612, 1504, 1465, 1447, 1290, 1252, 1240, 1134, 1109, 1021, 904, 833 cm$^{-1}$. HRMS (GC-El) for C$_{22}$H$_{28}$O$_2$ [M$^+$]: calcd. 324.20838; found: 324.20849.

(E)-1-Methoxy-1-(oct-6-en-1-yn-1-yl)cyclohexane (1b)

Prepared according to a literature procedure.$^{13}$ The analytical data matched those previously reported.

(E)-1-(But-2-en-1-yl)-2-(3-methoxy-3-methylbut-1-yn-1-yl)benzene (S11)

$n$-BuLi (1.55 M in hexanes, 1.91 mL, 2.96 mmol) was added to a solution of S8 (500 mg, 1.97 mmol) in THF (10 mL) at −78 °C. The mixture stirred for 20 min before TMEDA (0.29 mL, 1.97 mmol) was added. After stirring at −78 °C for another 20 min, crotyl bromide (mixture of (E/Z)-isomers, 0.30 mL, 2.96 mmol) was introduced and stirring was continued for 15 h. Water (20 mL) was added and the mixture was extracted with tert-butyl methyl ether (3 x 20 mL). The combined organic fractions were dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The purification of the residue was achieved by flash chromatography (silica, pentane/tert-butyl methyl ether 100:1) to yield the title compound as a colorless oil (mixture of isomers, 420 mg, 93%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 (m, 1H), 7.28 – 7.22 (m, 1H), 7.20 (m, 1H), 7.14 (m, 1H), 5.68 – 5.44 (m, 2H), 3.58 – 3.47 (m, 2H), 3.45 (m, 3H), 1.75 – 1.66 (m, 3H), 1.56 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.0, 132.4, 129.1, 128.7, 128.5, 126.7, 125.9, 122.3, 83.1, 71.2, 51.9, 37.7, 28.6, 18.0. IR (film) $\tilde{\nu}$ 2983, 2934, 1483, 1447, 1377, 1359, 1279, 1171, 1146, 1074, 966, 755 cm$^{-1}$. HRMS (GC-Cl) for C$_{16}$H$_{21}$O [M+H$^+$]: calcd. 229.15847; found: 229.15869.
(E)-Oct-6-en-1-yn-1-ylbenzene (S12a)

Prepared analogously from commercially available phenyl acetylene and bromide S5 as a colorless oil (266 mg, 74%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40 (dt, \(J = 6.9, 1.8\) Hz, 2H), 7.27 (ddd, \(J = 6.3, 2.6, 1.0\) Hz, 3H), 5.57 – 5.37 (m, 2H), 2.40 (td, \(J = 7.1, 1.1\) Hz, 2H), 2.15 (dtd, \(J = 7.6, 5.8, 1.4\) Hz, 2H), 1.72 – 1.62 (m, 5H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 131.6, 130.4, 128.3, 127.6, 125.8, 124.2, 90.3, 80.8, 31.8, 28.7, 18.9, 18.1. IR (film) \(\nu\) 2934, 1598, 1490, 1441, 1330, 1070, 1027, 965, 912, 754, 690, 525 cm\(^{-1}\). HRMS (GC-EI) for \(\text{C}_{14}\text{H}_{16}\) [M\(^+\)]: calcd. 184.12461; found: 184.12465.

(E)-1-methyl-4-(oct-6-en-1-yn-1-yl)benzene (S12b)

Prepared analogously from commercially available 1-ethynyl-4-methylbenzene and bromide S5 as a slightly yellow oil (318 mg, 80%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.31 – 7.27 (m, 2H), 7.11 – 7.06 (m, 2H), 5.55 – 5.38 (m, 2H), 2.39 (t, \(J = 7.2\) Hz, 2H), 2.33 (s, 3H), 2.18 – 2.10 (m, 2H), 1.70 – 1.62 (m, 5H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 137.6, 131.5, 130.5, 129.1, 121.1, 89.5, 80.9, 31.8, 28.8, 21.5, 19.0, 18.1. IR (film) 2932, 2857, 1509, 1452, 1437, 965, 815, 526, 412 cm\(^{-1}\).

(E)-1-methoxy-4-(oct-6-en-1-yn-1-yl)benzene (S12c)

Prepared analogously from commercially available 1-ethynyl-4-methoxybenzene and bromide S5 as a slightly yellow oil (468 mg, 96%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 – 7.30 (m, 2H), 6.84 – 6.78 (m, 2H), 5.55 – 5.38 (m, 2H), 3.80 (s, 3H), 2.38 (t, \(J = 7.2\) Hz, 2H), 2.19 – 2.09 (m, 2H), 1.72 – 1.61 (m, 5H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 159.1, 133.0, 130.6, 125.8, 116.4, 113.9, 88.7, 80.6, 55.4, 31.8, 28.8, 18.9, 18.1. IR (film) 2933, 2836, 1606, 1508, 1288, 1243, 1171, 1034, 965, 829, 534 cm\(^{-1}\). HRMS (ESI\(^+\)) for \(\text{C}_{15}\text{H}_{18}\text{O}\) [M+H\(^+\)]\(^+\): calcd. 215.14304; found: 215.14304.

(Z)-1-Chloro-4-(oct-6-en-1-yn-1-yl)benzene (S12d)

Prepared analogously from commercially available 1-ethynyl-4-methylbenzene and (Z)-6-bromohex-2-ene\(^1\) as a slightly yellow oil (297 mg, 63%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.35 – 7.28 (m, 2H), 7.27 – 7.22 (m, 2H), 5.51 (ddddd, \(J = 9.4, 7.9, 6.5, 4.7, 3.3\) Hz, 1H), 5.44 – 5.35 (m, 1H), 2.41 (t, \(J = 7.1\) Hz, 2H), 2.21 (qt, \(J = 7.2, 1.2\) Hz, 2H), 1.71 – 1.62 (m, 5H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 133.6, 132.9, 129.6, 128.6, 125.1, 122.7, 91.4, 79.8, 28.6, 26.1,
Supporting Information

19.0, 13.0. IR (film) 3013, 2933, 2861, 1488, 1454, 1397, 1345, 1090, 1014, 825, 699, 524 cm\(^{-1}\). HRMS (GC-El) for C\(_{14}\)H\(_{15}\)Cl [M\(^{+}\)]: calcd. 218.08568, found: 218.08575.

\((E)\)‐Triisopropyl(oct-6-en-1-yn-1-yl)silane (S13)

Prepared analogously from commercially available TIPS-acetylene and bromide S5 as a colorless oil (351 mg, 81%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\ 5.51 – 5.35 (m, 2H), 2.24 (t, \(J = 7.0 \) Hz, 2H), 2.15 – 2.07 (m, 2H), 1.66 – 1.62 (m, 3H), 1.61 – 1.53 (m, 2H), 1.13 – 1.01 (m, 21H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\ 130.5, 125.8, 94.8, 80.3, 31.6, 28.9, 19.4, 18.7, 18.6, 11.4. IR (film) \(\tilde{\nu}\) 2941, 2892, 2864, 2171, 1462, 1017, 995, 964, 924, 882, 674, 619, 492 cm\(^{-1}\). HRMS (GC-Cl) for C\(_{14}\)H\(_{33}\)Si [M\(^{+}\)]: calcd. 265.23436; found: 265.23460.

1-((E)-Oct-6-en-1-yn-1-yl)adamantine (S14)

Prepared analogously from compounds S4 and S5 as a colorless oil (185 mg, 62%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\ 5.51 – 5.34 (m, 2H), 2.14 (t, \(J = 7.1 \) Hz, 2H), 2.10 – 2.02 (m, 2H), 1.96 – 1.89 (m, 3H), 1.83 (d, \(J = 2.9 \) Hz, 6H), 1.71 – 1.62 (m, 8H), 1.56 – 1.47 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\ 130.6, 125.3, 89.3, 78.6, 43.4, 36.4, 31.5, 29.4, 29.1, 28.1, 25.8, 18.1, 17.9. IR (film) \(\tilde{\nu}\) 2902, 2850, 1451, 1437, 1344, 1100, 964, 507 cm\(^{-1}\). HRMS (GC-Cl) for C\(_{18}\)H\(_{26}\) [M\(^{+}\)]: calcd. 242.20276; found: 242.20290.

2-Methoxy-2-((E)-oct-6-en-1-yn-1-yl)adamantine (S15)

Prepared analogously from alkyne S9 and bromide S5 as a colorless oil (231 mg, 96%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\ 5.54 – 5.44 (m, 1H), 5.37 (tddd, \(J = 9.0, 7.3, 3.3, 1.6 \) Hz, 1H), 3.34 (s, 3H), 2.27 (t, \(J = 7.0 \) Hz, 2H), 2.22 – 1.98 (m, 8H), 1.81 (p, \(J = 3.2 \) Hz, 1H), 1.75 (ddddd, \(J = 11.4, 3.9, 2.6, 1.4 \) Hz, 3H), 1.68 (ddd, \(J = 4.3, 2.6, 1.6 \) Hz, 2H), 1.64 – 1.55 (m, 5H), 1.53 – 1.46 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\ 129.7, 124.8, 86.8, 81.8, 78.0, 49.8, 37.8, 35.9, 35.3, 31.7, 29.0, 27.4, 26.8, 26.1, 18.4, 12.9. IR (film) \(\tilde{\nu}\) 294, 2854, 1448, 1164, 1101, 1085, 877, 923, 699 cm\(^{-1}\). HRMS (GC-El) for C\(_{19}\)H\(_{29}\)O [M+H\(^{+}\)]: calcd. 273.22129; found: 273.22129.

Mestranol derived enyne (S16)
Prepared analogously from alkyne S10 and bromide S5 as a colorless oil (212 mg, 83%). ¹H NMR (400 MHz, CDCl₃) δ 7.21 (dd, J = 8.6, 1.0 Hz, 1H), 6.71 (dd, J = 8.6, 2.8 Hz, 1H), 6.63 (d, J = 2.7 Hz, 1H), 5.54 – 5.44 (m, 1H), 5.39 (dddd, J = 10.8, 7.2, 4.3, 1.6 Hz, 1H), 3.78 (s, 3H), 3.40 (s, 3H), 2.92 – 2.80 (m, 2H), 2.31 (t, J = 7.0 Hz, 3H), 2.26 – 2.10 (m, 4H), 2.07 – 1.93 (m, 2H), 1.91 – 1.82 (m, 1H), 1.81 – 1.71 (m, 3H), 1.68 – 1.57 (m, 5H), 1.52 – 1.27 (m, 4H), 0.87 (d, J = 0.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.5, 138.1, 132.8, 129.7, 126.5, 124.8, 113.9, 111.6, 88.1, 81.0, 75.8, 55.3, 53.4, 53.2, 49.7, 47.6, 43.7, 39.3, 37.0, 34.4, 30.0, 29.0, 27.4, 26.7, 26.1, 22.8, 18.5, 12.9. IR (film) ṽ 2933, 1496, 1453, 1255, 1238, 1102, 1086, 1039, 726, 694, 464 cm⁻¹. HRMS (GC-El) for C₂₈H₃₈O₂ [M⁺]: calcd. 406.28702; found: 406.28663.

(E)-2-(Dec-8-en-3-yn-2-yloxy)tetrahydro-2H-pyran (S17)

Prepared analogously from 2-(but-3-yn-2-yloxy)tetrahydro-2H-pyran (mixture of diastereoisomers)¹⁵ and bromide S5 as a colorless oil (mixture of diastereoisomers, 119 mg, 39%). ¹H NMR (400 MHz, CDCl₃) δ 5.52 – 5.32 (m, 2H), 5.00 – 4.72 (m, 1H), 4.59 – 4.40 (m, 1H), 4.08 – 3.76 (m, 1H), 3.60 – 3.39 (m, 1H), 2.25 – 2.13 (m, 2H), 2.10 – 2.00 (m, 2H), 1.92 – 1.68 (m, 2H), 1.66 – 1.63 (m, 3H), 1.62 – 1.49 (m, 5H), 1.45 – 1.37 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 130.4, 130.3, 125.7, 125.6, 96.8, 95.8, 85.0, 81.0, 80.0, 62.6, 62.5, 62.3, 61.1, 31.6, 31.6, 30.6, 28.5, 28.5, 25.5, 25.5, 22.6, 22.2, 19.6, 19.3, 18.2, 18.1, 17.9. IR (film) ṽ 2937, 1440, 1335, 1116, 1073, 1019, 967, 873, 814 cm⁻¹. HRMS (GC-Cl) for C₁₅H₂₄O₂ [M+H⁺]: calcd. 237.18491; found: 237.18459.

(E)-1-(1-Methoxycyclohexyl)oct-6-en-1-yn-3-ol (S18)

n-BuLi (1.55 M in hexanes, 4.67 mL, 7.24 mmol) was added dropwise to a solution of alkyne S1 (1.00 g, 7.24 mmol) in THF (20 mL) at 0 °C. After stirring for 30 min, the mixture was cooled to −78 °C before a solution of (E)-hex-4-enal (923 mg, 9.41 mmol)¹⁶ in THF (10 mL) was added dropwise. After warming to room temperature, the solution was stirred overnight before the reaction was quenched with sat. aq. NH₄Cl (10 mL), EtOAc (50 mL) and water (30 mL). The aqueous layer was extracted with EtOAc (3 x 50 mL) and the combined organic phases were washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, pentane/tert-butyl methyl
ether 3:1) to provide the title compound as colorless oil (1.01 g, 59%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.56 – 5.35 (m, 2H), 4.44 (t, $J = 6.5$ Hz, 1H), 3.35 (s, 3H), 2.17 (tq, $J = 7.5$, 3.8, 3.1 Hz, 2H), 1.92 – 1.83 (m, 2H), 1.83 – 1.61 (m, 8H), 1.52 (dtd, $J = 19.7$, 12.3, 9.6 Hz, 5H), 1.38 – 1.20 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 130.2, 126.1, 87.1, 86.1, 74.0, 62.2, 50.8, 37.9, 36.9, 36.8, 28.5, 25.6, 22.9, 18.1. IR (film) $\tilde{\nu}$ 2934, 2875, 1444, 1291, 1184, 1162, 1079, 1055, 1030, 965, 923, 734, 522 cm$^{-1}$. HRMS (ESI$^+$) for C$_{15}$H$_{24}$O$_2$ [M+Na$^+$]: calcd. 259.16685; found: 259.16677.

$^{(E)}$-Oct-6-en-1-yne (S19)

Trimethylsilylacetylene (1.61 mL, 11.4 mmol) was dissolved in THF (50 mL) and the solution cooled to 0°C before $n$-BuLi (1.59 M in hexanes, 8.60 mL, 13.7 mmol) was added dropwise. After stirring for 30 min, a solution of bromide S5 (3.00 g, 14.7 mmol) in DMPU (6.89 mL, 57.0 mmol) and THF (3 mL) was added dropwise. The mixture was stirred at ambient temperature overnight. Sat. aq. NH$_4$Cl (30 mL), tert-butyl methyl ether (100 mL) and water (50 mL) were introduced, the aqueous layer was extracted with tert-butyl methyl ether (3 × 75 mL) and the combined organic phases were washed with brine and dried over Na$_2$SO$_4$. The residue was filtered through a short plug of silica, eluting with pentane/tert-butyl methyl ether (20:1, 100 mL). All volatile compounds were removed under reduced pressure and the residue was directly used in the next step without further purification.

K$_2$CO$_3$ (764 mg, 5.47 mmol) was added in one portion to a solution of the crude silyl alkyne (900 mg, 4.99 mmol) in MeOH (50 mL). After stirring overnight, water (20 mL) was added and the mixture was extracted with pentane (3 × 20 mL). Purification by distillation of the combined organic phases at atmospheric pressure provided the title compound as colorless oil (369 mg, 68%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.52 – 5.34 (m, 2H), 2.18 (td, $J = 7.2$, 2.7 Hz, 2H), 2.08 (dtt, $J = 7.6$, 6.5, 1.2 Hz, 2H), 1.94 (t, $J = 2.7$ Hz, 1H), 1.67 – 1.62 (m, 3H), 1.58 (dt, $J = 14.3$, 7.2 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 130.3, 126.0, 84.7, 68.4, 31.6, 28.5, 18.1, 17.9. IR (film) $\tilde{\nu}$ 2956, 2748, 2379, 1439, 1355, 921, 802 cm$^{-1}$. HRMS (ESI$^+$) for C$_{9}$H$_{13}$ [M+H$^+$]: calcd. 109.10110; found: 109.10118.

$(E)$-(2-Methoxydec-8-en-3-yn-2-yl)benzene (S20)

$n$-BuLi (1.59 M in hexanes, 330 µL, 525 µmol) was added dropwise to a solution of S19 (73.3 mg, 573 µmol) in THF (2 mL) at 0°C. After stirring for 30 min, the mixture was cooled to –78 °C and a solution of acetophenone (43.4 µL, 372 µmol) in THF (0.5 mL) was added. After stirring at –78 °C for 90 min, the mixture was stirred overnight at ambient
temperature. Water (10 mL) was introduced and the mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue purified by flash chromatography (silica, pentane/tert-butyl methyl ether 3:1) to provide an inseparable mixture of the desired alcohol and remaining starting material.

A solution of this crude material (42.3 mg, 185 µmol) in THF (0.5 mL) was added dropwise to a suspension of NaH (13.3 mg, 556 µmol) in THF (1 mL) at 0 °C. After warming to ambient temperature, the mixture was stirred for additional 15 min, before it was cooled to 0 °C and methyl iodide (60 µL, 964 µmol) was added. The mixture was stirred overnight at ambient temperature before the reaction was quenched with water (10 mL) and tert-butyl methyl ether (20 mL). The aqueous layer was extracted with tert-butyl methyl ether (3 × 20 mL), the combined organic phases were washed with brine and dried over Na₂SO₄, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, pentane/tert-butyl methyl ether 15:1) to provide the title compound as colorless oil (37 mg, 82%).

**1H NMR (400 MHz, CDCl₃)**

δ 7.63 – 7.57 (m, 2H), 7.39 – 7.32 (m, 2H), 7.31 – 7.25 (m, 1H), 5.57 – 5.35 (m, 2H), 3.19 (s, 3H), 2.34 (t, J = 7.1 Hz, 2H), 2.14 (dtd, J = 7.7, 6.2, 1.4 Hz, 2H), 1.69 (s, 3H), 1.68 – 1.62 (m, 5H).

**13C NMR (101 MHz, CDCl₃)**

δ 143.4, 130.4, 128.3, 127.7, 126.3, 126.0, 88.1, 80.3, 76.7, 52.4, 33.1, 31.9, 28.8, 18.3, 18.1. IR (film) ν 2985, 2933, 1446, 1366, 1234, 1178, 1097, 975, 763, 699, 608 cm⁻¹. HRMS (ESI⁺) for C₁₇H₂₂O [M+Na⁺]: calcd. 265.15628; found: 265.15624.

(E)-1-Chloro-4-(2-methoxydec-8-en-3-yn-2-yl)benzene (S21)

Prepared analogously from 1-(4-chlorophenyl)ethan-1-one as a colorless oil (205 mg, 79%). ¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.49 (m, 2H), 7.34 – 7.29 (m, 2H), 5.61 – 5.32 (m, 2H), 3.18 (s, 3H), 2.33 (t, J = 7.1 Hz, 2H), 2.18 – 2.09 (m, 2H), 1.69 – 1.60 (m, 8H). ¹³C NMR (101 MHz, CDCl₃) δ 142.1, 133.5, 130.3, 128.4, 127.7, 126.0, 88.5, 79.9, 76.3, 52.4, 33.0, 31.9, 28.8, 18.3, 18.1. IR (film) ν 2988, 2934, 1446, 1366, 1234, 1178, 1097, 975, 763, 699, 606 cm⁻¹. HRMS (ESI⁺) for C₁₇H₂₂ClO [M+Na⁺]: calcd. 299.11731; found: 299.11693.

(E)-1-(2-Methoxydec-8-en-3-yn-2-yl)-4-(trifluoromethyl)benzene (S22)

Prepared analogously from 1-(4-(trifluoromethyl)phenyl)ethan-1-one as colorless oil (335 mg, 87%). ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.67 (m, 2H), 7.65 – 7.57 (m, 2H), 5.56 – 5.34 (m, 2H), 3.21 (s, 3H), 2.34 (t, J = 7.1 Hz, 2H), 2.19 –
2.08 (m, 2H), 1.70 – 1.61 (m, 8H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.7, 130.3, 129.9 (q, $J = 32.1$ Hz), 126.6, 126.1, 125.3 (q, $J = 3.8$ Hz), 123.0, 88.9, 79.6, 76.4, 52.6, 33.0, 31.9, 28.7, 18.3, 18.1. $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ –62.5. IR (film) $\tilde{\nu}$ 2936, 1619, 1409, 1323, 1163, 1124, 1097, 1078, 1066, 968, 622 cm$^{-1}$. HRMS (ESI$^+$) for C$_{18}$H$_{23}$FeO [M+Na]$^+$: calcd. 333.14367; found: 333.14350.

**Methyl (E)-4-(2-methoxydec-8-en-3-yn-2-yl)benzoate (S23)**

![Methyl (E)-4-(2-methoxydec-8-en-3-yn-2-yl)benzoate](image)

Prepared analogously from methyl 4-acetylbenzoate as colorless oil (66.5 mg, 36%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.06 – 7.98 (m, 2H), 7.73 – 7.58 (m, 2H), 5.53 – 5.36 (m, 2H), 3.92 (s, 3H), 3.20 (s, 3H), 2.34 (t, $J = 7.1$ Hz, 2H), 2.21 – 2.08 (m, 2H), 1.70 – 1.61 (m, 8H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.1, 148.8, 130.3, 129.7, 129.6, 126.3, 126.0, 88.7, 79.7, 76.6, 52.6, 52.3, 32.9, 31.9, 28.7, 18.3, 18.1. IR (film) 2989, 2935, 1722, 1610, 1435, 1274, 1234, 1094, 965, 773, 708 cm$^{-1}$. HRMS (ESI$^+$) for C$_{19}$H$_{24}$O$_3$ [M+Na]$^+$: calcd. 323.16176; found: 323.16216.

**(E)-Oct-6-en-1-yn-1-ylferrocene (S24)**

![Oct-6-en-1-yn-1-ylferrocene](image)

$n$-BuLi (1.57 m in hexanes, 906 µL, 1.42 mmol) was added dropwise to a solution of ethynylferrocene (249 mg, 1.19 mmol) in THF (5 mL) at 0 °C. The mixture was stirred at this temperature for 20 min before a solution of bromide S5 (232 mg, 1.42 mmol) in DMPU (716 µL) and THF (3 mL) was added dropwise. After stirring overnight at ambient temperature, the reaction was quenched with sat. aq. NH$_4$Cl (2 mL), tert-butyl methyl ether (10 mL) and water (2 mL). The aqueous layer was extracted with tert-butyl methyl ether (3 × 20 mL) and the combined organic phases were washed with brine and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure and the residue purified by flash chromatography (silica, pentane tert-butyl methyl ether 50:1) to provide the title compound as orange oil (254 mg, 73%). $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 5.52 – 5.23 (m, 2H), 4.40 (s, 2H), 4.10 (s, 5H), 3.89 (s, 2H), 2.21 (t, $J = 7.1$ Hz, 2H), 2.12 – 2.05 (m, 2H), 1.65 – 1.49 (m, 5H). $^{13}$C NMR (101 MHz, C$_6$D$_6$) $\delta$ 130.8, 125.8, 86.4, 79.2, 71.6, 70.1, 68.5, 67.4, 32.0, 29.2, 19.3, 18.0. IR (film) $\tilde{\nu}$ 3096, 2931, 2856, 1452, 1436, 1412, 1326, 1257, 1106, 1001, 965, 817, 488 cm$^{-1}$. HRMS (ESI$^+$) for C$_{18}$H$_{20}$Fe [M$^+$]: calcd. 292.09089; found: 292.09091.

**(E)-1-Methoxy-1-(non-7-en-1-yn-1-yl)cyclohexane (S25)**

![1-Methoxy-1-(non-7-en-1-yn-1-yl)cyclohexane](image)

$n$-BuLi (1.55 m in hexanes, 390 µL, 605 µmol) was added dropwise to a solution of alkyne S1 (83.7 mg, 606 µmol) in THF (2 mL) at 0 °C. The mixture was stirred at this temperature for
30 min before a solution of bromide S6 (123 mg, 696 µmol) in DMPU (300 µL) and THF (1.7 mL) was added dropwise. After warming to ambient temperature, the mixture was stirred overnight. Sat. aq. NH₄Cl (2 mL), tert-butyl methyl ether (20 mL) and water (10 mL) were added, the aqueous layer was extracted with tert-butyl methyl ether (3 × 20 mL) and the combined organic phases were washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, pentane/tert-butyl methyl ether 30:1) to provide the title compound as colorless oil (109 mg, 77%). ¹H NMR (400 MHz, CDCl₃) δ 5.60 – 5.25 (m, 2H), 3.35 (s, 3H), 2.23 (t, J = 6.8 Hz, 2H), 1.99 (tdt, J = 6.7, 5.3, 1.6 Hz, 2H), 1.92 – 1.77 (m, 2H), 1.66 – 1.62 (m, 5H), 1.55 – 1.41 (m, 9H), 1.34 – 1.12 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 131.1, 124.9, 86.3, 81.0, 74.0, 37.0, 32.1, 28.8, 28.3, 25.5, 23.3, 18.7, 18.0. IR (film) ν 2932, 2856, 1447, 1292, 1184, 1092, 1081, 925, 906 cm⁻¹. HRMS (GC-Cl) for C₁₅H₂₆O [M+H]^+; calcd. 235.20532; found: 235.20532.

(E)-1-(Methoxymethoxy)-1-(non-7-en-1-yn-1-yl)cyclohexane (S26)

Prepared analogously from alkyne S2 and bromide S6 as a colorless oil (109 mg, 82%). ¹H NMR (400 MHz, CDCl₃) δ 5.48 – 5.35 (m, 2H), 4.93 (s, 2H), 3.39 (s, 3H), 2.23 (t, J = 6.9 Hz, 2H), 2.04 – 1.95 (m, 2H), 1.91 (dt, J = 11.0, 3.7 Hz, 2H), 1.75 – 1.41 (m, 14H), 1.37 – 1.18 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 131.2, 125.1, 92.8, 87.4, 80.9, 75.4, 55.8, 55.1, 54.9, 32.1, 28.8, 28.3, 25.5, 23.3, 18.7, 18.0. IR (film) ν 2931, 2857, 1448, 1294, 1177, 1149, 1097, 1068, 1026, 965 cm⁻¹. HRMS (ESI⁺) for C₁₇H₂₆O [M+Na]^+: calcd. 287.19815; found: 287.19781.

1-(4-(But-2-en-1-xyloxy)but-1-yn-1-yl)-1-methoxycyclohexane (S27)

NaH (98.8 mg, 4.12 mmol) was added in portions to a solution of 4-(1-methoxycyclohexyl)but-3-yn-1-ol (500 mg, 2.74 mmol) in DMF (14 mL) at 0 °C and the resulting suspension was stirred for 30 min. Crotyl bromide (mixture of (E/Z)-isomers, 423 µL, 4.12 mmol). was added and stirring continued at ambient temperature overnight. Water (20 mL) was introduced and the mixture was extracted with tert-butyl methyl ether (3 × 50 mL). The combined organic phases were washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue purified by flash chromatography (silica, pentane/tert-butyl methyl ether 25:1) to provide the title compound as colorless oil (mixture of (E/Z)-isomers, 453 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ 5.78 – 5.61 (m, 1H), 5.56 (dddd, J = 15.2, 7.9, 4.6, 1.6 Hz, 1H), 4.19 – 3.85 (m, 2H), 3.66 – 3.45 (m, 2H), 3.33 (s, 3H), 2.58 – 2.45 (m, 2H), 1.95 – 1.78 (m, 2H), 1.76 – 1.41 (m, 10H), 1.26 (tt, J = 9.4, 4.9 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 129.8, 128.1, 127.5, 126.8, 83.1, 82.2, 74.1,
Supporting Information

71.7, 68.9, 68.6, 66.3, 50.6, 37.0, 25.7, 23.0, 20.3, 17.9, 13.3. IR (film) \( \tilde{\nu} \) 2933, 2856, 1447, 1293, 1184, 1135, 1092, 1086, 1027, 966, 925, 819 cm\(^{-1}\). HRMS (ESI\(^+\)) for C\(_{15}\)H\(_{24}\)O\(_2\) [M+Na\(^+\)]\(^{\ddagger}\): calcd. 259.16685; found: 259.16676.

**Dimethyl (E)-2-(but-2-en-1-yl)-2-(4-(1-hydroxycyclohexyl)but-3-yn-1-yl)malonate (S28)**

![Dimethyl (E)-2-(but-2-en-1-yl)-2-(4-(1-hydroxycyclohexyl)but-3-yn-1-yl)malonate (S28)](image)

A solution of LiHMDS (674 mg, 4.03 mmol) in THF (4 mL) was added dropwise at \(-78 \, ^\circ\text{C}\) to a solution of dimethyl (E)-2-(but-2-en-1-yl)-2-(but-3-yn-1-yl)malonate (mixture of (E/Z)-isomers, 800 mg, 3.36 mmol)\(^{18}\) in THF (30 mL). After stirring for 30 min at this temperature, cyclohexanone (522 \(\mu\)L, 5.04 mmol) was added dropwise and the mixture was warmed to ambient temperature. The reaction was quenched with sat. aq. NH\(_4\)Cl (2 mL), EtOAc (50 mL) and water (20 mL), the aqueous phase was extracted with EtOAc (3 \(\times\) 50 mL) and the combined organic layers were dried over Na\(_2\)SO\(_4\). The solvent was removed under reduced pressure and the residue purified by flash chromatography (silica, pentane/tert-butyl methyl ether 15:1 – 10:1 – 3:1) to provide the title compound as colorless oil (mixture of (E/Z)-isomers, 439 mg, 39%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 5.68 – 5.48 (m, 1H), 5.25 (dddd, \( J = 16.5, 8.9, 4.4, 2.1 \) Hz, 1H), 3.72 (s, 6H), 2.73 – 2.54 (m, 2H), 2.25 – 2.07 (m, 4H), 1.87 – 1.77 (m, 3H), 1.71 – 1.59 (m, 5H), 1.59 – 1.44 (m, 5H), 1.33 – 1.17 (m, 1H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 171.6, 130.2, 128.4, 124.4, 123.4, 84.6, 83.2, 68.8, 57.5, 57.2, 52.6, 52.6, 40.3, 36.2, 31.8, 31.8, 30.3, 25.4, 23.5, 18.2, 14.4, 14.3, 13.0. IR (film) \( \tilde{\nu} \) 2933, 1720, 1447, 1293, 1132, 1126, 1199, 1178, 1132, 1066, 964, 904 cm\(^{-1}\). HRMS (ESI\(^+\)) for C\(_{15}\)H\(_{24}\)O\(_2\) [M+Na\(^+\)]\(^{\ddagger}\): calcd. 359.18289; found: 359.18247.

**Dimethyl (E)-2-(but-2-en-1-yl)-2-(4-(1-methoxycyclohexyl)but-3-yn-1-yl)malonate (S29)**

![Dimethyl (E)-2-(but-2-en-1-yl)-2-(4-(1-methoxycyclohexyl)but-3-yn-1-yl)malonate (S29)](image)

A solution of S28 (mixture of (E/Z)-isomers, 389 mg, 1.16 mmol) in THF (2 mL) was added dropwise to a suspension of NaH (85.1 mg, 3.55 mmol) in THF (4.5 mL) at 0 \(^\circ\text{C}\). After 5 min, the mixture was warmed to ambient temperature and stirred for additional 10 min. It was then cooled to 0\(^\circ\text{C}\) before MeI (370 \(\mu\)L, 5.95 mmol) was added dropwise. The mixture was stirred at ambient temperature overnight. Water (20 mL) was introduced and the aqueous layer was extracted with tert-butyl methyl ether (3 \(\times\) 50 mL). The combined organic phases were washed with brine and dried over Na\(_2\)SO\(_4\). The solvent was removed under reduced pressure and the residue purified by flash chromatography (silica, pentane/tert-butyl methyl ether 20:1) to provide the title compound as colorless oil (mixture of (E/Z)-isomers, 318 mg, 79%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 5.69 – 5.46 (m, 1H), 5.26 (ddddd, \( J = 14.7, 7.5, 5.6, 3.9, 1.9 \) Hz, 1H), 3.72 (s, 6H), 3.33 (s, 3H), 2.76 – 2.52 (m, 2H), 2.26 – 2.06 (m,
(E)-N-(But-2-en-1-yl)-N-(4-(1-methoxycyclohexyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (S30)

N-(4-(1-Methoxycyclohexyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (S3) (270 mg, 805 µmol) and K₂CO₃ (412 mg, 2.98 mmol) were suspended in MeCN (3 mL). Crotyl bromide (mixture of (E/Z)-isomers, 300 µL, 2.92 mmol) was added and the mixture was stirred at 60 °C overnight. After cooling to room temperature, the mixture was filtered through a pad of cotton wool and the residue in the filter was washed with MeCN (15 mL). The combined filtrates was concentrated and the crude material was purified by flash chromatography (silica, pentane/tert-butyl methyl ether 10:1 – 3:1) to provide the title compound as colorless oil (mixture of (E/Z)-isomers, 269 mg, 86%). ¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.68 (m, 2H), 7.34 – 7.28 (m, 2H), 5.68 – 5.55 (m, 1H), 5.33 – 5.23 (m, 1H), 3.83 (ddt, J = 46.8, 6.6, 1.1 Hz, 2H), 3.31 (s, 3H), 3.30 – 3.24 (m, 2H), 2.57 – 2.46 (m, 2H), 2.43 (s, 3H), 1.88 – 1.77 (m, 2H), 1.71 – 1.43 (m, 10H), 1.35 – 1.22 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 143.3, 143.2, 137.2, 137.1, 130.6, 129.7, 129.7, 128.8, 127.1, 125.6, 124.8, 82.9, 82.6, 73.9, 50.5, 50.5, 46.5, 46.1, 44.8, 36.8, 25.5, 22.7, 21.5, 19.7, 19.6, 17.7, 12.9. IR (film) ν 2935, 1449, 1341, 1202, 1157, 1081, 928, 816, 743, 655, 548 cm⁻¹. HRMS (ESI⁺) for C₂₂H₃₁NO₅S [M+H]⁺: calcd. 412.19169; found: 412.19197.
3.2 Synthesis of the Precatalysts

Since preliminary results showed that the purity of the catalyst has a significant impact on the outcome of the catalytic transformation, a modified and optimized synthesis procedure for [(IPr)(cymene)RuCl₂] was developed. In our hands, literature protocols for the synthesis of this complex did not provide material of acceptable quality.¹⁹

[(IPr)(η⁶-cymene)RuCl₂] (3c)

[(p-Cymene)RuCl₂]₂ (487 mg, 795 µmol) was suspended in THF (15 mL) and a solution of IPr (607 mg, 1.55 mmol) in THF (15 mL) was added dropwise within 5 min. The resulting mixture was stirred for 1 h at ambient temperature in the dark. All volatile components were removed under high vacuum. The residue was redissolved in a minimum amount of CH₂Cl₂ and the turbid solution was filtered through a pad of neutral aluminium oxide. Eluting with CH₂Cl₂/MeOH (50:1, 50 mL) provided an orange solution, which was concentrated under high vacuum. The residue was redissolved in a minimum amount of benzene and filtered through a short pad of Celite, which was eluted with benzene (80 mL). The orange solution was concentrated under high vacuum until the product started to precipitate. At this point, the solution was cooled to 0 °C before pentane (150 mL) was added until an orange solid precipitated from the mixture. The supernatant was siphoned off and the resulting solid was washed with pentane (2 × 25 mL) and dried under high vacuum. The title compound was obtained as orange solid (715 mg, 66%). ¹H NMR (400 MHz, C₆D₆) δ 7.24 (dd, J = 8.4, 7.0 Hz, 2H), 7.15 – 7.11 (m, 4H), 6.49 (s, 2H), 4.86 (d, J = 5.8 Hz, 2H), 4.52 (d, J = 5.8 Hz, 2H), 3.38 (hept, J = 6.7 Hz, 2H), 2.65 (hept, J = 6.8 Hz, 1H), 1.77 (s, 3H), 1.49 (d, J = 6.7 Hz, 12H), 1.07 (d, J = 7.0 Hz, 6H), 1.02 (d, J = 6.8 Hz, 12H). ¹³C NMR (101 MHz, C₆D₆) δ 173.7, 146.4, 140.2, 129.8, 126.5, 123.8, 105.4, 96.9, 86.5, 84.3, 30.4, 28.9, 26.4, 23.5, 22.9, 18.8. The spectroscopic data are consistent with those reported in the literature.¹⁹

During this study, the authors used several batches of 3c and did not notice any significant decomposition or change in the catalytic performance when the material was stored in the dark at −20 °C.

Complexes of the type [(NHC)(p-cymene)RuCl₂] are moderately light-sensitive in solution. Solutions of such complexes should therefore be handled in the dark; the light of the fume-hood should be switched off during any manipulations.
Supporting Information

[(IMes)(η⁶-cymene)RuCl₂] (3b). Prepared analogously; the spectroscopic data are consistent with those reported in the literature.¹⁹

4. Hydrogenative Metathesis Reactions

General Procedure: Intramolecular Hydrogenative Enyne Metathesis

A flame-dried quartz Schlenk tube was charged with [(IPr)(p-cymene)RuCl₂] (13.8 mg, 0.02 mmol, 10 mol%), the substrate (0.2 mmol) and toluene (2 mL, 0.1 M). The Schlenk tube was closed with a septum and then transferred into the photolysis apparatus. A hydrogen-filled balloon was connected to a needle which was pierced through the septum and the Schlenk tube was flushed with hydrogen for 2 min through an outlet cannula (the cannula did not reach into the solution to make sure that only the head space of the tube was flushed). After the first 10 seconds of flushing with hydrogen, the light source was switched on and the reaction mixture was stirred for 60 min under hydrogen atmosphere. The reaction mixture was diluted with pentane (5 mL) and then filtered through a short pad of silica. The filtrate was evaporated and the residue purified by flash chromatography.

1-(Cyclopent-1-en-1-ylmethyl)-1-methoxycyclohexane (2)

Prepared according to the General Procedure from enyne 1b (44.1 mg, 200 µmol); colorless oil (36.9 mg, 95%). When the reaction was carried out on a 1 mmol scale (220 mg of 1b), a yield of 88% (172 mg) was obtained.

When the same reaction was performed in ordinary laboratory glassware (instead of the quartz Schlenk-tube), a yield of 75% was obtained.

The analytical data of 2 matched those previously reported in the literature.²¹

The following compounds were prepared analogously:

2-((1-Methoxycyclohexyl)methyl)cyclopent-2-en-1-ol (5)

Prepared from substrate S18; colorless oil (29.5 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ 5.60 (s, 1H), 4.57 – 4.49 (m, 1H), 4.06 (s, 1H), 3.25 (s, 3H), 2.59 – 2.43 (m, 1H), 2.42 – 2.30 (m, 2H), 2.25 – 2.06 (m, 2H), 1.91 – 1.65 (m, 4H), 1.61 – 1.22 (m, 7H). ¹³C NMR (101 MHz, CDCl₃) δ 141.9, 132.9, 78.4, 76.3, 48.2, 36.3, 34.4, 33.6, 33.5, 30.1, 25.8, 22.5, 22.1. IR (film) ν 3423, 2930, 2853, 1456, 1146, 1131, 1079, 951 cm⁻¹. HRMS (ESI⁺) for C₁₃H₂₂O₂ [M+Na]⁺: calcd. 233.15120; found: 233.15141.
Supporting Information

2-(Cyclopent-1-ylmethyl)-2-methoxyadamantane (6)

Prepared from substrate S15; colorless oil (37.1 mg, 75%). 1H NMR (400 MHz, CDCl3) δ 5.44 (td, J = 2.3, 1.2 Hz, 1H), 3.19 (s, 3H), 2.51 (s, 2H), 2.41 – 2.24 (m, 4H), 2.11 (dd, J = 12.7, 3.2 Hz, 2H), 1.94 – 1.76 (m, 8H), 1.74 – 1.62 (m, 4H), 1.50 – 1.41 (m, 2H). 13C NMR (101 MHz, CDCl3) δ 140.5, 127.3, 79.4, 47.2, 38.6, 36.6, 34.6, 34.0, 32.9, 32.4, 31.5, 27.8, 27.4, 23.8. IR (film) ν 2905, 2846, 1455, 1115, 1083, 1061, 993 cm⁻¹. HRMS (ESI⁺) for C17H26ONa [M⁺]: calcd. 269.18767; found: 269.18758.

3-(2-Methoxy-2-methylpropyl)-1H-indene (7)

Prepared from substrate S11; colorless oil (27.0 mg, 66%). 1H NMR (400 MHz, CDCl3) δ 7.46 (dt, J = 7.4, 1.0 Hz, 1H), 7.42 (dt, J = 7.7, 0.9 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.19 (td, J = 7.4, 1.2 Hz, 1H), 6.40 – 6.35 (m, 1H), 3.39 – 3.34 (m, 2H), 3.31 (s, 3H), 2.77 (d, J = 1.4 Hz, 2H), 1.24 (s, 6H). 13C NMR (101 MHz, CDCl3) δ 146.4, 144.1, 140.7, 131.7, 126.0, 124.4, 123.7, 119.6, 75.5, 49.5, 38.1, 37.5, 25.3. IR (film) ν 2972, 2937, 1717, 1462, 1383, 1366, 1241, 1161, 1070, 1020, 879, 764 cm⁻¹. HRMS (GC-ESI) for C14H19O [M⁺]: calcd. 202.13490; found: 202.13522.

(1-(Cyclopent-1-yl)-2-methoxypropan-2-yl)benzene (8a)

Prepared from substrate S20; colorless oil (36.8 mg, 85%). 1H NMR (400 MHz, CDCl3) δ 7.40 – 7.23 (m, 4H), 7.23 – 7.09 (m, 1H), 5.27 – 5.22 (m, 1H), 3.00 (s, 3H), 2.60 – 2.43 (m, 2H), 2.23 – 2.11 (m, 2H), 2.06 – 1.94 (m, 1H), 1.83 – 1.49 (m, 3H), 1.47 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 145.2, 140.7, 128.4, 128.0, 126.9, 126.5, 79.3, 50.4, 45.0, 36.4, 32.5, 23.9, 22.4. IR (film) ν 2977, 2934, 2846, 2824, 1445, 1371, 1155, 1098, 1072, 764 cm⁻¹. HRMS (ESI⁺) for C15H17O [M+Na]⁺: calcd. 217.15847; found: 217.15847.

1-Chloro-4-(1-(cyclopent-1-yl)-2-methoxypropan-2-yl)benzene (8b)

Prepared from substrate S21; colorless oil (42.0 mg, 85%). 1H NMR (400 MHz, CDCl3) δ 7.29 (s, 4H), 5.34 – 5.26 (m, 1H), 3.06 (s, 3H), 2.60 – 2.46 (m, 2H), 2.26 – 2.16 (m, 2H), 2.12 – 2.00 (m, 1H), 1.89 – 1.78 (m, 1H), 1.77 – 1.65 (m, 2H), 1.51 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 143.9, 140.3, 132.7, 128.8, 128.2, 128.0, 79.0, 50.5, 45.0, 36.5, 32.5, 24.0, 22.5. IR (film) ν 2932, 1842, 1489, 1398, 1153, 1114, 1085, 1055, 1013, 829 cm⁻¹. HRMS (ESI⁺) for C16H19ClO [M+Na]⁺: calcd. 273.10166; found: 273.10150.
1-(1-(Cyclopent-1-en-1-yl)-2-methoxypropan-2-yl)-4-(trifluoromethyl)benzene (8c)

Prepared from substrate S22; colorless oil (48.0 mg, 85%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.62 – 7.55 (m, 2H), 7.53 – 7.43 (m, 2H), 5.35 – 5.23 (m, 1H), 3.09 (s, 3H), 2.63 – 2.50 (m, 2H), 2.26 – 2.18 (m, 2H), 2.14 – 2.02 (m, 1H), 1.92 – 1.80 (m, 1H), 1.79 – 1.65 (m, 2H), 1.55 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 149.7, 140.1, 129.0, 126.8, 129.2 (q, $J$ = 32.2 Hz), 125.1 (q, $J$ = 3.7 Hz), 124.4 (q, $J$ = 272.2 Hz), 79.2, 50.6, 44.8, 36.5, 32.5, 24.0, 22.6. $^{19}$F NMR (282 MHz, CDCl$_3$) δ −62.4. IR (film) $\tilde{\nu}$ 2937, 1619, 1410, 1324, 1163, 1119, 1075, 1016, 844 cm$^{-1}$. HRMS (APPI$^+$) for C$_{16}$H$_{19}$F$_3$O $[M+Na]^+$: calcd. 284.13825; found: 284.13788.

Methyl 4-(1-(cyclopent-1-en-1-yl)-2-methoxypropan-2-yl)benzoate (8d)

Prepared from substrate S23; colorless oil (42.6 mg, 80%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.04 – 7.94 (m, 2H), 7.49 – 7.41 (m, 2H), 5.37 – 5.21 (m, 1H), 3.91 (s, 3H), 3.08 (s, 3H), 2.64 – 2.49 (m, 2H), 2.27 – 2.13 (m, 2H), 2.09 – 1.96 (m, 1H), 1.86 – 1.75 (m, 1H), 1.75 – 1.61 (m, 2H), 1.55 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.2, 150.8, 140.2, 129.5, 128.9, 128.8, 126.6, 79.4, 52.2, 50.6, 44.9, 36.5, 32.5, 24.0, 22.5. IR (film) $\tilde{\nu}$ 2948, 1723, 1435, 1277, 1109, 1087, 1056, 775, 711 cm$^{-1}$. HRMS (GC-Cl) for C$_{17}$H$_{22}$O$_3$ [M+H]$^+$: calcd. 275.16417; found: 275.16440.

2-((1-(Cyclopent-1-en-1-yl)propan-2-yl)oxy)tetrahydro-2H-pyran (9)

Prepared from substrate S17; colorless oil (mixture of diastereoisomers, 25.4 mg, 60%). $^1$H NMR (400 MHz, CDCl$_3$) δ 5.45 – 5.36 (m, 1H), 4.77 – 4.61 (m, 1H), 4.00 – 3.81 (m, 2H), 3.48 (dddd, $J$ = 9.7, 8.3, 4.2, 2.9 Hz, 1H), 2.50 – 2.09 (m, 6H), 1.90 – 1.78 (m, 3H), 1.74 – 1.45 (m, 5H), 1.22 – 1.06 (m, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 141.7, 141.4, 126.2, 126.1, 98.3, 95.8, 72.2, 70.1, 62.9, 62.2, 39.5, 38.5, 35.7, 35.6, 32.6, 32.6, 31.3, 31.3, 25.8, 25.7, 23.8, 23.7, 21.8, 20.1, 19.7, 19.2. IR (film) $\tilde{\nu}$ 2928, 2846, 1372, 1121, 1076, 1020, 995, 869 cm$^{-1}$. HRMS (GC-Cl) for C$_{13}$H$_{20}$O$_2$ [M+H]$^+$: calcd. 211.16926; found: 211.16921.
Compound 10

Prepared from substrate S16; white solid (52.0 mg, 68%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.20 (dd, $J = 8.7, 1.1$ Hz, 1H), 6.71 (dd, $J = 8.6, 2.8$ Hz, 1H), 6.63 (d, $J = 2.7$ Hz, 1H), 5.61 – 5.50 (m, 1H), 3.78 (s, 3H), 3.26 (s, 3H), 2.89 – 2.83 (m, 2H), 2.75 (d, $J = 15.9$ Hz, 1H), 2.48 – 2.23 (m, 4H), 2.22 – 2.08 (m, 2H), 2.08 – 1.93 (m, 1H), 1.93 – 1.79 (m, 3H), 1.74 (td, $J = 12.6, 4.0$ Hz, 1H), 1.69 – 1.52 (m, 3H), 1.52 – 1.21 (m, 6H), 0.97 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.5, 140.8, 138.1, 132.8, 127.2, 126.3, 113.9, 111.6, 88.0, 55.3, 51.5, 50.9, 47.5, 43.7, 39.6, 34.5, 34.0, 32.6, 31.8, 30.0, 27.5, 26.7, 23.6, 23.4, 13.9. IR (film) $\tilde{\nu}$ 2933, 1504, 1245, 1158, 1093, 1081, 1063, 1036, 843, 451 cm$^{-1}$. HRMS (GC-EI) for C$_{26}$H$_{36}$O$_2$ [M+Na]$^+$: calcd. 403.26099; found: 403.26075.

(Cyclopent-1-en-1-ylmethyl)triisopropylsilane (11)

Prepared from substrate S13; colorless oil (39.5 mg, 84%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.22 (q, $J = 1.5$ Hz, 1H), 2.26 (t, $J = 7.4$ Hz, 4H), 1.82 (p, $J = 7.4$ Hz, 2H), 1.66 (s, 2H), 1.05 (s, 21H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.0, 122.6, 38.0, 32.6, 24.1, 18.8, 13.5, 11.6. IR (film) $\tilde{\nu}$ 2940, 2891, 2865, 1463, 1015, 998, 882, 745, 663 cm$^{-1}$. HRMS (GC-EI) for C$_{15}$H$_{30}$Si [M]$^+$: calcd. 238.21074; found: 238.21113.

1-(Cyclopent-1-en-1-ylmethyl)adamantine (12)

Prepared from substrate S14; colorless oil (42.1 mg, 95%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.29 (tt, $J = 2.1, 1.0$ Hz, 1H), 2.34 – 2.22 (m, 4H), 1.96 – 1.90 (m, 3H), 1.88 – 1.79 (m, 4H), 1.73 – 1.58 (m, 6H), 1.48 (d, $J = 2.8$ Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.7, 127.2, 46.0, 43.0, 38.3, 37.2, 33.4, 32.6, 29.0, 24.3. IR (film) $\tilde{\nu}$ 2896, 2844, 1449, 1345, 1315, 1101, 1036, 956, 820, 802, 467 cm$^{-1}$. HRMS (GC-EI) for C$_{16}$H$_{24}$ [M]$^+$: calcd. 216.18734; found: 216.18725.

(Cyclopent-1-en-1-ylmethyl)ferrocene (13)

Prepared from substrate S24; orange oil (41.5 mg, 84%). The isolated product is only modestly stable and decomposes upon storage. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.26 – 5.22 (m, 1H), 4.10 (s, 5H), 4.07 (t, $J = 1.8$ Hz, 2H), 4.06 – 4.04 (m, 2H), 3.12 (q, $J = 1.3$ Hz, 4H), 2.31 – 2.17 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.5, 124.1, 68.7, 68.6, 67.2, 35.1, 32.3, 31.9, 23.4. IR (film) $\tilde{\nu}$ 2922, 2843, 1105, 1038, 1022, 1009, 959, 814, 480 cm$^{-1}$. HRMS (El) for C$_{16}$H$_{18}$Fe [M]$^+$: calcd. 266.07579; found: 266.07570.
(Cyclopent-1-en-1-ylmethyl)benzene (14a) and 1-Phenylcyclohexene (14’a)

Prepared from substrate S12a; colorless oil (14a:14’a = 2:1, 21.0 mg, 66%). The analytical data of 14b matched those reported in the literature, as well as those of a commercial sample. Spectral data of 14a: 1H NMR (400 MHz, CDCl₃) δ 7.41 – 7.37 (m, 2H), 7.35 – 7.27 (m, 2H), 7.23 – 7.17 (m, 1H), 5.38 – 5.31 (m, 1H), 3.40 (d, J = 2.2 Hz, 2H), 2.36 – 2.29 (m, 2H) 2.26 – 2.17 (m, 2H), 1.93 – 1.84 (m, 2H). 13C NMR (101 MHz, CDCl₃) δ 143.9, 140.3, 128.9, 125.9, 125.6, 125.0, 38.1, 34.9, 32.5, 23.6. HRMS (GC-EI) for C₁₂H₁₅ [M+H]⁺: calcd. 159.11663; found: 159.11683.

1-(Cyclopent-1-en-1-ylmethyl)-4-methylbenzene (14b) and 4’-Methyl-2,3,4,5-tetrahydro-1,1’-biphenyl (14’b)

Prepared from substrate S12b; colorless oil (14b:14’b = 2:1, 27.0 mg, 78%). The analytical data of the compounds matched those reported in the literature. 1H NMR (400 MHz, CDCl₃) δ 7.09 (d, J = 3.2 Hz, 4H), 5.34 (hept, J = 1.9 Hz, 1H), 3.36 (s, 2H), 2.33 (s, 3H), 2.31 – 2.28 (m, 2H), 2.20 (tdd, J = 7.1, 3.6, 1.8 Hz, 2H), 1.90 – 1.83 (m, 2H).

1-(Cyclopent-1-en-1-ylmethyl)-4-methoxybenzene (14c) and 4’-Methoxy-2,3,4,5-tetrahydro-1,1’-biphenyl (14’c)

Prepared from substrate S12c; colorless oil (14c:14’c = 2:1, 23.0 mg, 61%). The analytical data matched those reported in the literature. 1H NMR (400 MHz, CDCl₃) δ 7.14 – 7.05 (m, 2H), 6.91 – 6.79 (m, 2H), 5.35 – 5.30 (m, J = 2.3 Hz, 1H), 3.79 (s, 3H), 3.33 (s, 2H), 2.31 (tq, J = 5.8, 1.9 Hz, 2H), 1.86 (tt, J = 8.2, 6.7 Hz, 2H).
1-Chloro-4-(cyclopent-1-en-1-ylmethyl)benzene (14d) and 4'-Chloro-2,3,4,5-tetrahydro-1,1'-biphenyl (14'd)

Prepared from substrate S12d; colorless oil (14d:14’d = 2:1, 31.7 mg, 41%; NMR yield with tetramethylbenzene as internal standard). In this case, flash chromatography did not allow trace amounts of by-products to be separated; however, the product structure could be confirmed by comparison of the NMR data with those reported in the literature.23 1H NMR (400 MHz, CDCl3) (characteristic signals only): δ 7.26 – 7.24 (m, 2H), 7.13 – 7.09 (m, 2H), 5.35 – 5.32 (m, 1H), 3.35 (s, 2H), 2.35 – 2.28 (m, 2H), 2.24 – 2.15 (m, 2H), 1.92 – 1.82 (m, 2H).

1-((1-Methoxycyclohexyl)methyl)cyclohex-1-ene (15a)

Prepared from substrate S25; colorless oil (32.0 mg, 77%). 1H NMR (400 MHz, CDCl3) δ 5.44 – 5.34 (m, 1H), 3.17 (s, 3H), 2.08 – 1.94 (m, 5H), 1.73 – 1.67 (m, 2H), 1.65 – 1.50 (m, 5H), 1.48 – 1.36 (m, 5H), 1.33 – 1.19 (m, 2H). 13C NMR (101 MHz, CDCl3) δ 134.4, 125.5, 90.7, 78.1, 55.8, 46.5, 35.4, 30.7, 25.8, 25.6, 23.3, 22.4, 22.4. IR (film) v 2926, 2856, 1448, 1157, 1085, 1032, 922 cm⁻¹. HRMS (ESI⁺) for C14H24O [M+Na]⁺: calcd. 231.17193; found: 231.17224.

1-((1-Methoxymethoxy)cyclohexyl)methyl)cyclohex-1-ene (15b)

Prepared from substrate S26 using 20 mol% of catalyst; colorless oil (24.6 mg, 79%). 1H NMR (400 MHz, CDCl3) δ 5.44 – 5.37 (m, 1H), 4.73 (s, 2H), 3.41 (s, 3H), 2.18 – 2.10 (m, 2H), 2.03 – 1.98 (m, 4H), 1.75 – 1.67 (m, 2H), 1.65 – 1.50 (m, 5H), 1.48 – 1.36 (m, 5H), 1.33 – 1.19 (m, 2H). 13C NMR (101 MHz, CDCl3) δ 134.4, 125.5, 90.7, 78.1, 55.8, 46.5, 35.4, 30.7, 25.8, 25.6, 23.3, 22.4. IR (film) v 2926, 2856, 1448, 1157, 1140, 1085, 1032, 922 cm⁻¹. HRMS (ESI⁺) for C15H26O2 [M⁺]: calcd. 261.18250; found: 261.18268.

4-((1-Methoxycyclohexyl)methyl)-1-tosyl-1,2,3,6-tetrahydropyridine (16)

Prepared from substrate S30; colorless oil (49.0 mg, 75%). 1H NMR (400 MHz, CDCl3) δ 7.68 – 7.64 (m, 2H), 7.33 – 7.28 (m, 2H), 5.32 (tdt, J = 3.4, 1.7, 0.8 Hz, 1H), 3.56 (dd, J = 3.5, 1.3 Hz, 2H), 3.15 – 3.11 (m, 5H), 2.42 (s, 3H), 2.24 (tq, J = 4.6, 2.1 Hz, 2H), 2.06 (d, J = 1.5 Hz, 2H), 1.67 – 1.55 (m, 2H), 1.55 – 1.31
Supporting Information

(m, 5H), 1.25 – 1.09 (m, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.5, 133.5, 133.4, 129.6, 127.8, 119.9, 75.6, 48.1, 45.0, 43.1, 42.6, 34.3, 29.9, 25.8, 21.9, 21.6. IR (film) $\tilde{\nu}$ 2931, 1685, 1342, 1292, 1162, 1132, 1071, 949, 814, 708, 687, 644 cm$^{-1}$. HRMS (ESI$^+$) for C$_{26}$H$_{29}$NO$_3$S [M+Na$^+$]: calcd. 386.17604; found: 386.17615.

4-((1-Methoxycyclohexyl)methyl)-3,6-dihydro-2H-pyran (17)

Prepared from substrate S27; colorless oil (31.6 mg, 76%). $^1$H NMR (400 MHz, CDCl$_3$) δ 5.43 (tt, $J = 2.9, 1.4$ Hz, 1H), 4.13 (tt, $J = 2.7, 1.4$ Hz, 2H), 3.75 (t, $J = 5.5$ Hz, 2H), 3.18 (s, 3H), 2.20 – 2.15 (m, 2H), 2.12 (d, $J = 1.6$ Hz, 2H), 1.74 – 1.66 (m, 2H), 1.61 – 1.37 (m, 4H), 1.33 – 1.15 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 132.6, 123.6, 75.8, 65.7, 64.7, 48.2, 43.1, 34.5, 30.3, 26.0, 22.1. IR (film) $\tilde{\nu}$ 2932, 2854, 2826, 1725, 1456, 1166, 1135, 1080, 912, 732 cm$^{-1}$. HRMS (ESI$^+$) for C$_{13}$H$_{22}$O$_2$ [M+Na$^+$]: calcd. 233.15120; found: 233.15108.

Dimethyl 4-((1-methoxycyclohexyl)methyl)cyclohex-3-ene-1,1-dicarboxylate (18)

Prepared from substrate S29 using 20 mol% of the catalyst; colorless oil (48.5 mg, 79%). $^1$H NMR (400 MHz, CDCl$_3$) δ 5.39 – 5.33 (m, 1H), 3.69 (s, 6H), 3.13 (s, 3H), 2.63 – 2.45 (m, 2H), 2.11 (s, 4H), 2.04 (s, 2H), 1.64 – 1.56 (m, 2H), 1.55 – 1.33 (m, 4H), 1.27 – 1.13 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.3, 134.1, 121.6, 75.8, 52.9, 52.7, 48.1, 43.1, 34.3, 31.1, 28.3, 26.9, 25.9, 22.0. IR (film) $\tilde{\nu}$ 2932, 1731, 1434, 1253, 1072, 911, 729 cm$^{-1}$. HRMS (ESI$^+$) for C$_{18}$H$_{28}$O$_5$ [M+Na$^+$]: calcd. 347.18289; found: 347.18293.

5. Copies of Spectra
Supporting Information

![Chemical Structure](image)

**NMR Spectrum**

- **A (m)**: 7.31 ppm
- **B (m)**: 7.25 ppm
- **C (dddd)**: 5.51 ppm
- **D (m)**: 5.40 ppm
- **E (d)**: 2.41 ppm
- **F (qu)**: 2.21 ppm
- **G (m)**: 1.05 ppm

**1H NMR**

- **δ 11.25**
- **δ 7.98**
- **δ 7.81**
- **δ 7.72**
- **δ 7.64**

**13C NMR**

- **δ 123.0**
- **δ 128.9**
- **δ 128.1**
- **δ 127.1**

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