Supplementary Information

Photoassisted Oxidation of Ruthenium(II)-Photocatalysts Ru(bpy)$_3^{2+}$ and Ru(bpz)$_3^{2+}$ to RuO$_4$: Orthogonal Tandem Photoredox and Oxidation Catalysis

Dirk Alpers, Malte Gallhof, Christian B. W. Stark and Malte Brasholz*

University of Hamburg, Department of Chemistry – Institute of Organic Chemistry
Martin-Luther-King-Platz 6, 20146 Hamburg, Germany.
email: malte.brasholz@chemie.uni-hamburg.de

Contents:

1 General information and synthesis of substrates S 2 – S 4

2 General procedures S 5
   GP 1: Photoredox-initiated radical cationic Diels-Alder (RCDA) reaction
   GP 2: Oxidative cyclisation of 1,5-dienes with RuCl$_3$/NaIO$_4$
   GP 3: Tandem RCDA/oxidative cleavage reactions
   GP 4: Tandem RCDA/1,5-diene cyclisation reactions

3 Synthesis and characterization of products S 6 – S 19

4 Structural assignment S 20

5 Analysis of cyclisation modes of dienes 8d and 8i S 21

6 UV-Vis experiments S 22 – S 23

7 NMR spectra of new compounds S 24 – S 45
1 General information and synthesis of substrates

- General information:

All reactions were performed in anhydrous solvents using commercial-grade reagents. Reactions were performed under an atmosphere of N\textsubscript{2} unless otherwise stated. Products were purified by flash chromatography on silica gel (230-400 mesh, Machery-Nagel). NMR spectra were recorded on Bruker instruments (Fourier 300, Avance 400 or AvanceII 600). Chemical shifts are reported in ppm relative to the following solvent resonances: \(\delta^{1\text{H}}\) [ppm] = 7.26 (CHCl\textsubscript{3}), 2.50 (DMSO-d\textsubscript{6}) and \(\delta^{13\text{C}}\) [ppm] = 77.00 (CHCl\textsubscript{3}), 39.50 (DMSO-d\textsubscript{6}). Coupling constants are reported in Hz. \(^{13}\text{C}\) NMR spectra were acquired with proton decoupling. NMR peak assignments are based on DEPT and 2D experiments, stereochemical assignments are based on 1D and 2D NOESY experiments. IR spectra were recorded on an ALPHA Platinum ATR-IR instrument by Bruker. Mass spectra were recorded on an Agilent 6224 ESI-TOF instrument.

- Irradiation apparatus:

![Image](image1.png)

**Figure S1**: Irradiation setup 1. Blue LED, 5.4 W / 0.87 cd / 450 ± 25 nm.

![Image](image2.png)

**Figure S2**: Irradiation setup 2. Blue CFL, 2 × 18 W / 2 × 2.73 cd / 450 ± 50 nm.
- Ruthenium catalysts $1a,b$:

$\text{Ru(bpy)}_3\text{Cl}_2\cdot6\text{H}_2\text{O}$ was purchased from Sigma Aldrich. $\text{Ru(bpz)}_3(\text{PF}_6)_2$ and $\text{Ru(bpz)}_3(\text{BArF})_2$ were prepared according to literature procedures.[1],[2]

- Alkenes $6b$-$e$:

$\text{Prepared according to ref.}[3]$  

$\text{Prepared according to ref.}[4]$ followed by standard silylation (TIPSCI, DMAP, Imidazole). Analytical data:

Colorless oil. 

$R_f = 0.35$ (petrol ether/ethyl acetate 5:1).

$^1\text{H-NMR}$ (300 MHz, $\text{CDCl}_3$): $\delta$ 1.05-1.15 (m, 21 H, TIPS), 3.81 (s, 3 H, OMe), 4.41 (dd, $J = 1.8$, 5.0 Hz, 2 H, 1-H), 6.17 (td, $J = 5.0$, 15.9 Hz, 1 H, 2-H), 6.58 (td, $J = 1.8$ Hz, 15.9 Hz, 1 H 3-H), 6.85 (d, $J = 8.8$ Hz, 2 H, Ar), 7.32 (d, $J = 8.8$ Hz, 2 H, Ar) ppm.

$^{13}\text{C-NMR}$ (75 MHz, $\text{CDCl}_3$): $\delta$ 12.1 (d, TIPS), 18.0 (q, TIPS), 55.3 (q, OMe), 64.1 (t, C-1), 113.9 (d, Ar), 127.2 (d, C-2), 127.5 (d, Ar), 128.7 (d, C-3), 130.2 (s, Ar), 159.1 (s, Ar) ppm.

IR: $\tilde{\nu}$ 2940, 2865 (-C-H, =C-H), 1510, 1245.

HRMS (ESI) for $\text{C}_{19}\text{H}_{32}\text{NaO}_2\text{Si}^+$ (M + Na)$^+$ calc. 343.2064, found 343.2027.

$\text{Prepared according to ref.}[5]$  

$\text{Prepared according to ref.}[6]$  

---

Compound 7f:

Compound 7f was synthesized in four steps: Allylic alcohol S1 was prepared according to literature.\[7\] Oxidation with MnO₂\[8\] gave α,β-unsaturated aldehyde S2, which was subjected to Wittig reaction to furnish triene 7f\[9\].

Analytical data:

![7f]

Colorless liquid.

Rᵣ = 0.90 (pentane).

\(^1\)H-NMR (400 MHz, CDCl₃): δ 1.63 (s, 3 H, Me), 1.72 (s, 3 H, Me), 2.78 (t, J = 6.9 Hz, 2 H, 5-H), 4.96 (d, J = 10.3 Hz, 1 H, 1-H), 5.10 (d, J = 17.0 Hz, 1 H, 1-H'), 5.15 (m, 1 H, 6-H), 5.68 (td, J = 6.5, 15.2 Hz, 1 H, 4-H), 6.05 (dd, J = 10.3, 15.2 Hz, 1 H, 3-H), 6.32 (td, J = 10.3 Hz, 17.0 Hz, 1 H, 2-H ppm.

\(^{13}\)C-NMR (100 MHz, CDCl₃): δ 17.6 (q, Me), 25.7 (q, Me), 31.2 (t, C-5), 114.8 (t, C-1), 121.4 (d, C-6), 130.7 (d, C-3), 132.9 (s, C-7), 133.8 (d, C-4), 137.2 (d, C-2) ppm.

---

2 General procedures

- **GP 1: Photoredox-initiated radical cationic Diels-Alder (RCDA) reaction**

In a 10 mL reaction vial, alkene 6 (1 equiv.) and 1,3-diene 7 (3, 10 or 15 equiv.) were dissolved in CH₂Cl₂ (c = 0.02 or 0.08 M in 6) and 0.5 or 2 mol-% Ru(bpz)₃(BArF)₂ [≡ 1b-(BArF)₂] was added. The mixture was stirred open to air for the indicated time, under irradiation with a blue LED reactor (5.4 W / 0.87 cd / 450 ± 25 nm, Figure S1). After conversion was judged complete by TLC, the mixture was evaporated and chromatographed to furnish cycloadduct 8.

- **GP 2: Oxidative cyclisation of 1,5-dienes with RuCl₃/NaIO₄**

In a 25 mL round bottom flask, purified cycloadduct 8 (1 equiv.) was dissolved in 9:1 THF/CH₂Cl₂ (c = 0.05 M). 1 mol-% RuCl₃ (as a 0.1 M stock solution in H₂O) and NaIO₄ on wet silica (0.64 mmol NaIO₄ per 1 g SiO₂, 2.2 equiv.) were added and the mixture was stirred under air (stopped flask) until conversion was judged complete by TLC. The reaction was quenched with i-PrOH, stirred for 60 min, then filtered through a short pad of silica gel with the aid of EtOAc. The filtrate was evaporated and the crude product was chromatographed to furnish tetrahydrofuran derivative.

- **GP 3: Tandem RCDA/oxidative cleavage reactions**

In a 10 mL reaction vial, alkene 6 (1 equiv.) and 1,3-diene 7 (3 equiv.) were dissolved in CH₂Cl₂ (c = 0.08 M in 6) and 1 mol-% Ru(bpz)₃(PF₆)₂ [≡ 1b-(PF₆)₂] was added. The mixture was stirred open to air for 3 h, under irradiation with a blue LED reactor (5.4 W / 0.87 cd / 450 ± 25 nm, Figure S1). After conversion was judged complete by TLC, the mixture was evaporated in the same reaction vial. After drying in vacuum, the crude residue was re-dissolved in 2:1 H₂O/EtOAc (c = 0.04 M). Solid NaIO₄ (3-8 equiv.) was added and the mixture was irradiated under air (stopped vial) with blue CFL lamps (2 × 18 W / 2 × 2.73 cd / 450 ±50 nm, Figure S2), with rapid stirring. After conversion was complete by TLC, the reaction was quenched with i-PrOH, stirred for 60 min, then transferred into a separation funnel. The mixture was extracted with EtOAc (3×) and the organic layer was dried with Na₂SO₄, filtered and evaporated. Column chromatography provided C,C-cleavage product.

- **GP 4: Tandem RCDA/1,5-diene cyclisation reactions**

In a 25 mL round bottom flask, alkene 6 (1 equiv.) and 1,3-diene 7 (3, 10 or 15 equiv.) were dissolved in CH₂Cl₂ (c = 0.02 or 0.08 M in 6) and 0.5 mol-% or 2.0 mol-% Ru(bpz)₃(BArF)₂ [≡ 1b-(BArF)₂] was added. The mixture was stirred open to air for the indicated time, under irradiation with a blue LED reactor (5.4 W / 0.87 cd / 450 ± 25 nm, Figure S1). After conversion was judged complete by TLC, the mixture was evaporated in the same reaction flask. After drying in vacuum, the crude residue was re-dissolved in 9:1 THF/CH₂Cl₂ (c = 0.05 M). NaIO₄ on wet silica (0.64 mmol NaIO₄ per 1 g SiO₂, 5 equiv.) was added and the mixture was irradiated under air (stopped flask) with blue CFL lamps (2 × 18 W / 2 × 2.73 cd / 450 ±50 nm, Figure S2), with rapid stirring. After conversion was complete by TLC, the reaction was quenched with i-PrOH, stirred for 60 min, then filtered through a short pad of silica gel with the aid of EtOAc. The filtrate was evaporated and the crude product was chromatographed to furnish tetrahydrofuran derivative.

Note: in case of some of the cis-THF diol products 10a-e, isolated samples contained trace amounts of a trans-THF byproduct (up to 5%).

---

3 Synthesis and characterization of products

1-[(1S*,6R*)-6-Benzyl-4-(4-methylpent-3-enyl)cyclohex-3-enyl]-4-methoxybenzene (8e)

Photoredox-initiated radical cationic Diels-Alder (RCDA) reaction according to GP 1:

Alkene 6b (56.1 mg, 0.25 mmol), myrcene (7d, 128 μL, 102 mg, 0.75 mmol) and Ru(bpz)$_3$(BArF)$_2$ (2.9 mg, 1.35 μmol) in CH$_2$Cl$_2$ (3.00 mL) gave cycloadduct 8e after 6 h reaction time. After evaporation of solvent, column chromatography (silica gel, petrol ether/dichloromethane 5:1) furnished product 8e as colorless oil (58.6 mg, 65%).

R$_f$ = 0.28 (petrol ether/dichloromethane 5:1).

$^1$H-NMR (400 MHz, CDCl$_3$): δ 1.61 (s, 3 H, Me), 1.71 (s, 3 H, Me), 1.74-1.85 (m, 1 H, 5-H), 1.89-2.04 (m, 3 H, 5-H', 1'-H), 2.02-2.17 (m, 3 H, 6-H, 2'-H), 2.20-2.31 (m, 1 H, 2-H), 2.31-2.43 (m, 1 H, 2'-H), 2.57 (m, 1 H, 1-H), 2.69 (m, 2 H, CH$_2$Ph), 3.83 (s, 3 H, OMe), 5.12 (m, 1 H, 3'-H), 5.49 (br. s, 1 H, 3-H), 6.91 (d, J = 8.5 Hz, 2 H, Ar), 7.10 (d, J = 7.5 Hz, 2 H, Ar), 7.14-7.23 (m, 3 H, Ar), 7.26 (t, J = 7.5 Hz, 2 H, Ar) ppm.

$^{13}$C-NMR (100 MHz, CDCl$_3$): δ 17.7 (q, Me), 25.7 (q, Me), 26.4 (t, C-2'), 34.3 (t, C-5), 34.5 (t, C-2), 37.5 (t, C-1'), 40.8 (t, CH$_2$Ph), 41.9 (d, C-6), 45.3 (d, C-1), 55.2 (q, OMe), 113.9 (d, Ar), 120.0 (d, C-3), 124.4 (d, C-3'), 125.5 (d, Ar), 128.0 (d, Ar), 128.5 (d, Ar), 128.9 (d, Ar), 131.3 (s, C-4'), 137.1 (s, C-4), 138.0 (s, Ar), 141.4 (s, Ar), 158.0 (s, Ar) ppm.

IR: ν 2910 (-C-H, =C-H), 1510, 1245 cm$^{-1}$.

HRMS (ESI) for C$_{26}$H$_{33}$O$^+$ (M + H)$^+$ calc. 361.2526, found 361.2440.

Triisopropyl[(1S*,6S*)-6-(4-methoxyphenyl)-3-(4-methylpent-3-enyl)cyclohex-3-enyl]-methoxy)silane (8f)

Photoredox-initiated radical cationic Diels-Alder (RCDA) reaction according to GP 1:

Alkene 6c (32.1 mg, 0.10 mmol), myrcene (7d, 255 μL, 204 mg, 1.50 mmol) and Ru(bpz)$_3$(BArF)$_2$ (1.2 mg, 0.50 μmol) in CH$_2$Cl$_2$ (1.20 mL) gave cycloadduct 8f after 6 h reaction time. After evaporation of solvent, column chromatography (silica gel, petrol ether/diethylether 50:1) furnished product 8f as colorless oil (30.7 mg, 67%).
\[ R_f = 0.41 \text{ (petrol ether/diethyl ether 50:1).} \]

\[ ^{1}H\text{-NMR (300 MHz, CDCl}_3\text{): } \delta 0.91-1.05 \text{ (m, 21 H, TIPS), 1.64 \text{ (s, 3 H, Me), 1.72 \text{ (s, 3 H, Me), 1.87-2.35 \text{ (m, 9 H, 1-H, 2-H, 5-H, 1'-H, 2'-H), 2.60-2.75 \text{ (m, 1 H, 6-H), 3.34 \text{ (dd, }J = 6.3 \text{ Hz, 9.6 Hz, 1 H, CH}_2\text{OTIPS), 3.48 \text{ (dd, }J = 3.5, 9.6 \text{ Hz, 1 H, CH}_2\text{OTIPS), 3.80 \text{ (s, 3 H, OMe), 5.16 (m, } \text{c, 1 H, 3'-H), 5.42-5.49 \text{ (m, 1 H, 4-H), 6.83 (d, }J = 8.7 \text{ Hz, Ar), 7.12 (d, }J = 8.7 \text{ Hz, 2 H, Ar)} \text{ ppm.} \]

\[ ^{13}C\text{-NMR (75 MHz, CDCl}_3\text{): } \delta 11.9 \text{ (q, TIPS), 17.7 \text{ (q, Me), 18.0 \text{ (d, TIPS), 25.7 \text{ (q, Me), 26.5 \text{ (t, C-1')}, 32.1 \text{ (t, C-2'), 34.5 \text{ (t, C-5), 37.7 \text{ (t, C-2), 41.2 \text{ (d, C-6), 41.7 \text{ (d, C-1), 55.3 \text{ (q, OMe), 65.6 \text{ (t, CH}_2\text{OTIPS), 113.7 \text{ (d, Ar), 119.8 \text{ (d, C-5), 124.4 \text{ (d, C-3'), 128.5 \text{ (d, Ar), 131.4 \text{ (s, C-4'), 137.6 \text{ (s, Ar), 137.6 (s, C-4), 157.9 (s, Ar) ppm.} \]

IR: \[ \tilde{\nu} 2940, 2865 \text{ (-C-H, }=C\text{-H), 1510, 1245 \text{ cm}^{-1}.} \]

HRMS (ESI) for \( \text{C}_{29}\text{H}_{48}\text{NaO}_2\text{Si}^+ \text{ (M + Na)}^+ \text{ calc. 479.3316, found 479.3226.} \]

\[ [(1S*,6S*)-6-(4-Methoxyphenyl)-3-(4-methylpent-3-enyl)cyclohex-3-enyl]methyl acetate (8g) \]

\[ \text{Photoredox-initiated radical cationic Diels-Alder (RCDA) reaction according to GP 1:} \]

Alkene \( 6d \) (20.6 mg, 0.10 mmol), myrcene \( 7d \), 51.1 μL, 40.9 mg, 0.30 mmol) and Ru(bpz)_3(BArF)_2 \( 4.6 \text{ mg, 2.0 } \mu\text{mol) in CH}_2\text{Cl}_2 \) (5.00 mL) gave cycloadduct \( 8g \) after 6 h reaction time. After evaporation of solvent, column chromatography (silica gel, petrol ether/diethyl ether 10:1) furnished product \( 8g \) as colorless oil (22.3 mg, 65%).

\[ R_f = 0.24 \text{ (petrol ether/diethyl ether 10:1).} \]

\[ ^{1}H\text{-NMR (400 MHz, CDCl}_3\text{): } \delta 1.63 \text{ (s, 3 H, Me), 1.71 \text{ (s, 3 H, Me), 1.91-2.05 \text{ (m, 6 H, 3-H, 1'-H, OAc), 2.07-2.33 \text{ (m, 6 H, 2-H, 3'-H, 6-H, 2'-H), 2.59 (dt, }J = 5.9, 10.1 \text{ Hz, 1 H, 1-H), 3.68 (dd, }J = 7.0, 10.9 \text{ Hz, 1 H, CH}_2\text{OAc), 3.78 (s, 3 H, OMe), 3.90 (dd, }J = 3.8, 10.9 \text{ Hz, 1 H, CH}_2\text{OAc), 5.13 (m, 1 H, 3'-H), 5.43-5.51 \text{ (m, 1 H, 5-H), 6.83 (d, }J = 8.7 \text{ Hz, 2 H, Ar), 7.10 (d, }J = 8.7 \text{ Hz, 2 H, Ar) ppm.} \]

\[ ^{13}C\text{-NMR (100 MHz, CDCl}_3\text{): } \delta 17.7 \text{ (q, Me), 20.8 \text{ (q, OAc), 25.7 \text{ (q, Me), 26.4 \text{ (t, C-2'), 32.3 \text{ (t, C-3), 34.4 \text{ (t, C-6), 37.5 \text{ (t, C-1'), 38.4 (d, C-2), 42.0 \text{ (d, C-1), 55.2 \text{ (q, OMe), 67.4 \text{ (t, CH}_2\text{OAc), 113.9 (d, Ar), 120.3 (d, C-5), 124.2 (d, C-3'), 128.3 (d, Ar), 131.5 (s, C-4'), 136.5 \text{ (s, Ar), 136.5 (s, C-4), 158.1 (s, Ar), 171.1 \text{ (s, OAc) ppm.}} \]

IR: \[ \tilde{\nu} 2905 \text{ (-C-H, }=C\text{-H), 1740 \text{ (C=O), 1515, 1245 cm}^{-1.} \]

HRMS (ESI) for \( \text{C}_{22}\text{H}_{30}\text{NaO}_3\text{Si}^+ \text{ (M + Na)}^+ \text{ calc. 365.2087, found 365.2095.} \]
Photoredox-initiated radical cationic Diels-Alder (RCDA) reaction according to GP 1:

Alkene 6e (17.4 mg, 0.10 mmol), myrcene (7d, 170 μL, 136.2 mg, 1.00 mmol) and Ru(bpz)_3(BArF)_2 (4.6 mg, 2.0 μmol) in CH_2Cl_2 (2.00 mL) gave cycloadduct 8h after 24 h reaction time. After evaporation of solvent, column chromatography (silica gel, petrol ether/dichloromethane 5:1) furnished product 8h as colorless oil (14.2 mg, 46%).

R_f = 0.32 (petrol ether/dichloromethane 5:1).

^1^H-NMR (600 MHz, CDCl_3): δ 1.51-1.56 (m, 1 H, 1-H), 1.58 (s, 3 H, Me), 1.67 (s, 3 H, Me), 1.71-1.88 (m, 5 H, 1-H', 2-H, 3-H, 7-H'), 1.89-2.08 (m, 6 H, 1-H, 4-H', 2', 3', 7', 1'-H), 2.13-2.25 (m, 2 H, 4-H, 7a-H), 2.31 (dd, J = 4.7, 18.2 Hz, 1 H, 4-H'), 3.79 (s, 3 H, OMe), 5.05 (t, J = 6.9 Hz, 1 H, 3'-H), 5.42 (m, 1 H, 5-H), 6.82 (d, J = 8.8 Hz, 2 H, Ar), 7.28 (d, J = 8.8 Hz, 2 H, Ar) ppm.

^13^C-NMR (150 MHz, CDCl_3): δ 17.7 (q, Me), 20.6 (t, C-2), 25.7 (q, Me), 26.4 (t, C-2'), 29.2 (t, C-7), 30.7 (t, C-1), 32.7 (t, C-4), 37.7 (t, C-1'), 40.1 (t, C-3), 44.0 (d, C-7a), 45.7 (s, C-3a), 55.2 (q, OMe), 113.2 (d, Ar), 119.0 (d, C-5), 124.4 (d, C-3'), 127.1 (d, Ar), 131.2 (s, C-4'), 135.3 (s, C-6), 140.7 (s, Ar), 157.2 (s, Ar) ppm.

IR: ν 2955, 2925 (-C-H, =C-H), 1515, 1250, 1185, 1040 cm⁻¹.

HRMS (ESI) for C_{22}H_{31}O^+ (M + H)^+ calc. 311.2369, found 311.2346.

Photoredox-initiated radical cationic Diels-Alder (RCDA) reaction according to GP 1:

Alkene 6a (37.1 mg, 0.25 mmol), β-ocimene (7e, 178 μL, 146 mg, 1.07 mmol, (E)/(Z) 7:3, equivalent of 0.75 mmol of (E)-isomer) and Ru(bpz)_3(BArF)_2 (11.5 mg, 5.0 μmol) in CH_2Cl_2 (12.5 mL) gave cycloadduct 8i after 4 h reaction time (endo/exo 9:1 by crude ^1^H NMR). After evaporation of solvent, column chromatography (silica gel, petrol ether/ethyl acetate 30:1) furnished product 8i as colorless oil (50.2 mg, 71%).
$R_f = 0.63$ (petrol ether/ethyl acetate 30:1).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 0.85 (d, $J = 6.4$ Hz, 3 H, Me), 1.39 (s, 3 H, Me), 1.59 (s, 3 H, Me), 1.73 (s, 3 H, Me), 1.75-1.82 (m, 1 H, 3-H), 1.94-2.23 (m, 4 H, 2-H, 6-H, 1'-H), 2.23-2.40 (m, 1 H, 3-H'), 2.64 (dd, $J = 5.0$, 10.5 Hz, 1 H, 1-H), 3.80 (s, 3 H, OMe), 4.89 (m, 1 H, 2'-H), 5.43 (m, 1 H, 4-H), 6.84 (d, $J = 8.7$ Hz, 2 H, Ar), 7.08 (d, $J = 8.7$ Hz, 2 H, Ar) ppm.

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ 17.8 (q, Me), 20.9 (q, Me), 22.9 (q, Me), 25.8 (q, Me), 27.0 (d, C-2), 27.6 (t, C-1'), 34.3 (t, C-3), 45.0 (d, C-6), 50.8 (d, C-1), 55.2 (q, OMe), 113.2 (d, Ar), 121.4 (d, C-4), 124.2 (d, C-2'), 130.2 (d, Ar), 130.5 (s, C-3'), 135.4 (s, Ar), 137.5 (s, C-5), 157.6 (s, Ar) ppm.

IR: $\tilde{\nu}$ 2960, 2910, 2835 (-C-H, =C-H), 1510, 1245 cm$^{-1}$.

HRMS: ESI repeatedly failed for peak match of this compound.

1-Methoxy-4-[(1$R^{*}$,2$S^{*}$,6$S^{*}$)-6-methyl-2-(3-methylbut-2-enyl)cyclohex-3-enyl]benzene (8j)

In the tandem RCDA/1,5-diene cyclisation experiment to furnish product 10g (see below), synthetic triene 7f was employed in the first RCDA step with threefold excess as by GP 4. In order to prepare an analytical sample of intermediate cycloadduct 8j, the RCDA reaction described here was performed with only one equivalent of 7f vs. alkene 6a.

Alkene 6a (20.3 mg, 0.14 mmol), (E)-7-Methylocta-1,3,6-triene (7f, 16.8 mg, 0.14 mmol) and Ru(bpz)$_3$(BArF)$_2$ (6.3 mg, 2.7 μmol) in CH$_2$Cl$_2$ (5.00 mL) gave cycloadduct 8j after 16 h reaction time (endo/exo 9:1 by crude $^1$H NMR). After evaporation of solvent, column chromatography (silica gel, petrol ether/dichloromethane 5:1) furnished product 8j as colorless oil (9.4 mg, 25%).

$R_f = 0.54$ (petrol ether/ethyl dichloromethane 5:1).

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 0.92 (d, $J = 6.6$ Hz, 3 H, Me), 1.37 (s, 3 H, Me), 1.63 (s, 3 H, Me), 1.72-1.94 (m, 3 H, 3-H, 1'-H), 2.10 (m, 1 H, 2-H), 2.19-2.35 (m, 2 H, 3-H', 6-H), 2.70 (dd, $J = 5.5$, 9.0 Hz, 1 H, 1-H), 3.79 (s, 3 H, OMe), 5.01 (m, 1 H, 2'-H), 5.63-5.73 (m, 1 H, C-4), 5.74-5.82 (m, 1 H, C-5), 6.82 (d, $J = 8.7$ Hz, 2 H, Ar), 7.10 (d, $J = 8.7$ Hz, 2 H, Ar) ppm.

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 17.7 (q, Me), 20.8 (q, Me), 25.8 (q, Me), 28.6 (d, C-2), 30.2 (t, C-1'), 33.1 (t, C-3), 39.4 (d, C-6), 49.9 (d, C-1), 55.2 (q, OMe), 113.2 (d, Ar), 123.1 (d, C-2'), 125.7 (d, C-4), 130.1 (d, Ar), 131.4 (d, C-5), 135.9 (s, C-3'), 135.6 (s, Ar), 157.6 (s, Ar) ppm.

IR: $\tilde{\nu}$ 2960, 2910, 2835 (-C-H, =C-H), 1510, 1245 cm$^{-1}$.

HRMS: ESI repeatedly failed for peak match of this compound.
(4R*,5R*)-4-(4-Methoxyphenyl)-5-methyloctane-2,7-dione (9a)

![Chemical structure of 9a](image)

Tandem RCDA/oxidative cleavage according to GP 3:

Alkene 6a (37.1 mg, 0.25 mmol), 2,3-dimethyl-1,3-butadiene (7a, 84.9 μL, 61.6 mg, 0.75 mmol) and Ru(bpz)$_3$(BArF)$_2$ (2.9 mg, 1.25 μmol) in CH$_2$Cl$_2$ (3.00 mL) gave intermediate cycloadduct 8a after 3 h reaction time. After evaporation of solvent, crude cycloadduct 8a (max. 0.25 mol) and NaIO$_4$ (160 mg, 0.75 mmol) in 2:1 H$_2$O/EtOAc (6.00 mL) gave 9a after 3 h reaction time. Column chromatography (silica gel, petrol ether/ethyl acetate 3:1) furnished product 9a as colorless oil (36.0 mg, 55%).

R$_f$ = 0.21 (petrol ether/ethyl acetate 3:1).

$^1$H-NMR (300 MHz, CDCl$_3$): δ 0.75 (d, $J = 6.6$ Hz, 3 H, Me), 1.99 (s, 3 H, 1-H), 2.10 (s, 3 H, 8-H), 2.11-2.19 (m, 1 H, 6-H), 2.26 (m, $J = 6.3$ Hz, 1 H, 5-H), 2.42 (dd, $J = 4.8$, 16.0 Hz, 1 H, 6-H’), 2.69 (dd, $J = 5.9$ Hz, 16.0 Hz, 1 H, 3-H), 2.81 (dd, $J = 8.8$ Hz, 16.0 Hz, 1 H, 3-H’), 3.07 (td, $J = 5.9$, 8.8 Hz, 1 H, 4-H), 3.77 (s, 3H, OMe), 6.81 (d, $J = 8.7$ Hz, 2 H, Ar), 7.03 (d, $J = 8.7$ Hz, 2 H, 10-H, Ar) ppm.

$^{13}$C-NMR (75 MHz, CDCl$_3$): δ 16.7 (q, Me), 30.4 (q, C-1), 30.5 (q, C-8), 33.6 (d, C-5), 44.5 (d, C-4), 47.5 (t, C-3), 48.9 (t, C-6), 55.1 (q, OMe), 113.6 (d, Ar), 129.3 (d, Ar), 133.4 (s, Ar), 158.2 (s, Ar), 207.9 (s, C-2), 208.4 (s, C-7) ppm.

IR: ν 2960, 2930 (C-H), 1710 (C=O), 1510, 1245 cm$^{-1}$.

HRMS (ESI) for C$_{16}$H$_{22}$NaO$_3$ (M + Na)$^+$ calc. 285.1461, found 285.1385.

(3R*,4R*)-3-(4-Methoxyphenyl)-4-methyl-6-oxoheptanoic acid (9b)

![Chemical structure of 9b](image)

Tandem RCDA/oxidative cleavage according to GP 3:

Alkene 6a (37.1 mg, 0.25 mmol), isoprene (7b, 75.1 μL, 51.1 mg, 0.75 mmol) and Ru(bpz)$_3$(PF$_6$)$_2$ (2.2 mg, 2.5 μmol) in CH$_3$NO$_2$ (3.00 mL) gave intermediate cycloadduct 8b after 3 h reaction time. After evaporation of solvent, crude cycloadduct 8b (max. 0.25 mol) and NaIO$_4$ (428 mg, 2.00 mmol) in 2:1 H$_2$O/EtOAc (6.00 mL) gave 9b after 3 h reaction time. Column chromatography (silica
gel, petrol ether/ethyl acetate/acetic acid 75:25:1) furnished product 9b as colorless oil (39.2 mg, 59%).

\[ R_f = 0.15 \text{ (petrol ether/ethyl acetate/acetic acid 75:25:1).} \]

\[ ^1H-NMR \text{ (300 MHz, CDCl}_3\text{): } \delta \text{ 0.77 (d, } J = 6.7 \text{ Hz, 3 H, 7-H), 2.09 (s, 3 H, Ac), 2.13 (t, } J = 8.3 \text{ Hz, 1 H, 5-H), 2.31 (m, 1 H, 4-H), 2.41 (dd, } J = 4.9, 16.0 \text{ Hz, 1 H, 5'-H), 2.60-2.76 (m, 2 H, 2-H), 3.04 \text{ (dd, } J = 6.1, 8.7 \text{ Hz, 1 H, 3-H), 3.78 (s, 3 H, OMe), 6.82 (d, } J = 8.7 \text{ Hz, 2 H, Ar), 7.04 (d, } J = 8.7 \text{ Hz, 2 H, Ar), 9.32 (br s, 1 H, OH) ppm.} \]

\[ ^13C-NMR \text{ (100 MHz, CDCl}_3\text{): } \delta \text{ 16.4 (q, Me), 30.4 (t, C-7), 33.5 (d, C-4), 37.8 (d, C-2), 45.0 (d, C-3), 48.7 (d, C-5), 55.1 (q, OMe), 113.6 (d, Ar), 129.3 (d, Ar), 132.7 (s, Ar), 158.3 (s, Ar), 178.0 (s, C-1), 208.4 (s, C-6) ppm.} \]

IR: \nu 2960 (O-H), 1705 (C=O), 1510, 1245, 1180 cm\(^{-1}\).

HRMS (ESI) for C\(_{15}\)H\(_{20}\)NaO\(_4\)\(^{+}\) (M + Na)\(^{+}\) calc. 287.1254, found 287.1243.

\( (1R,3S,4R,5R)-4-(4-Methoxyphenyl)-5-methylcyclopentane-1,3-dicarboxylic acid (9c) \)

\[ \text{Tandem RCDA/oxidative cleavage according to GP 3:} \]

Alkene 6a (37.1 mg, 0.25 mmol), cyclopentadiene (7c, 63.1 \mu L, 49.6 mg, 0.75 mmol) and Ru(bpz)_3(PF_6)_2 (2.2 mg, 2.5 \mu mol) in CH\(_3\)NO\(_2\) (3.00 mL) gave intermediate cycloadduct 8c (endo/exo 6:1 by crude NMR)\(^{[2]}\) after 3 h reaction time. After evaporation of solvent, crude cycloadduct 8c (max. 0.25 mol) and NaIO\(_4\) (428 mg, 2.00 mmol) in 2:1 H\(_2\)O/EtOAc (6.00 mL) gave 9c after 3 h reaction time. Column chromatography (silica gel, petrol ether/ethyl acetate/acetic acid 75:25:1) furnished product 9c as colorless oil (40.2 mg, 58%). \textbf{Trace signals resulting from C,C-cleavage of the exo-isomer of 8c are detectable in NMR spectra.}

\[ R_f = 0.15 \text{ (petrol ether/ethyl acetate/acetic acid 75:25:1).} \]

\[ ^1H-NMR \text{ (300 MHz , DMSO-\text{d}_6): } \delta \text{ 0.89 (d, } J = 6.0 \text{ Hz, 3 H, Me), 2.09-2.26 (m, 2 H, 2-H), 2.32-2.48 (m, 2 H, 1-H, 5-H), 2.93 (t, } J = 10.2 \text{ Hz, 1 H, 4-H), 2.99-3.12 (m, 1 H, 3-H), 3.33 \text{ (br. s, OH), 3.71 (s, 3 H, OMe), 6.83 (d, } J = 8.7 \text{ Hz, 2 H, Ar), 7.08 (d, } J = 8.7 \text{ Hz, 2 H, Ar), 12.00 (br. s, OH) ppm.} \]

\[ ^13C-NMR \text{ (100 MHz, DMSO-\text{d}_6): } \delta \text{ 17.2 (q, Me), 31.7 (t, C-2), 42.3 (d, C-4), 48.1 (d, C-1), 50.3 (d, C-3), 54.4 (d, C-5), 54.9 (q, OMe), 113.4 (d, Ar), 129.4 (d, Ar), 131.9 (s, Ar), 157.8 (s, Ar), 175.0 (s, CO_2H), 175.7 (s, CO_2H) ppm.} \]

IR: \nu 2960 (O-H), 2670 (C-H) 1705 (C=O), 1515, 1245, 1180.

HRMS (ESI) for C\(_{15}\)H\(_{18}\)NaO\(_5\)\(^{+}\) (M + Na)\(^{+}\) calc. 301.1046, found 301.0889.
(2R*,5R*,6S*,8S*,9S*)-2-(2-Hydroxypropan-2-yl)-8-(4-methoxyphenyl)-9-methyl-1-oxaspiro[4.5]decan-6-ol (10a)

and

(2R*,5R*,6S*,8R*,9R*)-2-(2-Hydroxypropan-2-yl)-8-(4-methoxyphenyl)-9-methyl-1-oxaspiro[4.5]decan-6-ol (10a’)

Cyclisation according to GP 2:

Cycloadduct 8d[3] (175 mg, 0.62 mmol), RuCl₃ (1.3 mg, 6.2 μmol) and NaIO₄ on wet silica (2.11 g, 1.35 mmol) in 9:1 THF/CH₂Cl₂ (12.2 mL) gave 10a,a’ after 2 h reaction time (dr 1:1.2 by crude ¹H NMR). Column chromatography (silica gel, petrol ether/ethyl acetate 5:1) furnished separable products 10a (37.4 mg) and 10a’ (58.3 mg) as colorless oils, combined yield 47%.

Tandem RCDA/1,5-diene cyclisation according to GP 4:

Alkene 6a (37.1 mg, 0.25 mmol), myrcene (7d, 128 μL, 102 mg, 0.75 mmol) and Ru(bpz)₃(BArF)₂ (2.9 mg, 1.25 μmol) in CH₂Cl₂ (3.00 mL) gave intermediate cycloadduct 8d[3] after 2 h reaction time. After evaporation of solvent, crude cycloadduct 8d (max. 0.25 mmol) and NaIO₄ on wet silica (1.95 g, 1.25 mmol) in 9:1 THF/CH₂Cl₂ (5.00 mL) gave 10a,a’ after 18 h reaction time (dr 1:1.2 by crude ¹H NMR). Column chromatography (silica gel, petrol ether/ethyl acetate 5:1) furnished separable products 10a (18.1 mg) and 10a’ (17.1 mg) as colorless oils, combined yield 42%.

10a:

Rᵧ = 0.24 (petrol ether/ethyl acetate 1:1).

¹H-NMR (400 MHz, CDCl₃): δ 0.69 (d, 3 H, J = 6.2 Hz, Me), 1.15 (s, 3 H, Me), 1.26 (s, 3H, Me), 1.50-1.69 (m, 3 H, 7-H, 9-H, 10-H), 1.78-2.10 (m, 7 H, 3-H, 4-H, 7-H’, 10-H’, OH), 2.53 (ddd, J = 3.9, 11.0, 12.8 Hz, 1 H, 8-H), 2.66 (br. s, 1 H, OH), 3.66 (m, 1 H, 6-H), 3.78 (s, 3 H, OMe), 3.87-3.93 (m, 1 H, 2-H), 6.82 (d, J = 8.7 Hz, 2 H, Ar), 7.07 (d, J = 8.6 Hz, 2 H, Ar) ppm.

¹³C-NMR (100 MHz, CDCl₃): δ 20.4 (q, Me), 24.5 (q, Me), 27.0 (t, C-3), 27.3 (q, Me), 34.3 (t, C-4), 35.3 (d, C-9), 38.6 (t, C-7), 40.8 (t, C-10), 43.5 (d, C-8), 55.2 (q, OMe), 71.0 (s, C-2’). 72.9 (d, C-6), 85.3 (s, C-5), 85.4 (d, C-2), 113.9 (d, Ar), 128.6 (d, Ar), 137.2 (s, Ar), 158.0 (s, Ar) ppm.

10a’:

Rᵧ = 0.51 (petrol ether/ethyl acetate 1:1).

¹H-NMR (300 MHz, CDCl₃): δ 0.62 (d, 3 H, J = 6.3 Hz, Me), 1.12 (s, 3 H, Me), 1.17-1.23 (m, 1 H, 10-H) 1.36 (s, 3 H, Me), 1.61 (td, J = 8.8, 12.2 Hz, 1 H, 4-H), 1.77-2.14 (m, 7 H, 3-H, 7-H, 8-H, 9-H, 10-H’), 2.24 (ddd, J = 3.9, 9.3, 12.2 Hz, 1 H, 4-H’), 3.00 (br. s, 2H, OH), 3.48 (dd, J = 5.2, 10.8 Hz, 1 H, 6-H), 3.77 (s, 3 H, OMe), 3.84 (dd, J = 6.6, 8.3 Hz, 1 H, 2-H), 6.82 (d, J = 8.6 Hz, 2 H, Ar), 7.06 (d, J = 8.6 Hz, 2 H, Ar) ppm.

¹³C-NMR (75 MHz, CDCl₃): δ 19.5 (q, Me), 25.7 (q, Me), 26.5 (t, C-3), 28.0 (q, Me), 33.5 (d, C-9), 35.6 (t, C-4), 40.6 (t, C-7), 46.2 (t, C-10), 49.4 (d, C-8), 55.2 (q, OMe), 72.2 (s, C-2’), 75.4 (d, C-6), 84.4 (s, C-5), 85.2 (d, C-2), 113.7 (d, Ar), 128.3 (d, Ar), 137.3 (s, Ar), 157.8 (s, Ar) ppm.
10a,a':

IR: ð 3335 (O-H), 2925, 2865 (–C-H, =C-H), 1510, 1245 cm⁻¹.

HRMS (ESI) for C20H30NaO₄⁺ (M + Na)⁺ calc. 357.2036, found 357.2021.

(2R⁺,5R⁺,6S⁺,8S⁺,9S⁺)-9-Benzyl-2-(2-hydroxypropan-2-yl)-8-(4-methoxyphenyl)-1-
oxaspiro[4.5]decan-6-ol (10b)

and

(2R⁺,5R⁺,6S⁺,8R⁺,9R⁺)-9-Benzyl-2-(2-hydroxypropan-2-yl)-8-(4-methoxyphenyl)-1-
oxaspiro[4.5]decan-6-ol (10b')

Cyclisation according to GP 2:

Cycloadduct 8e (32.9 mg, 0.09 mmol), RuCl₃ (0.2 mg, 0.9 μmol) and NaIO₄ on wet silica (314 mg, 0.20 mmol) in 9:1 THF/CH₂Cl₂ (2.00 mL) gave 10b,b' after 3 h reaction time (dr 1:1.4 by crude ¹H NMR). Column chromatography (silica gel, petrol ether/ethyl acetate 5:2 → 1:1) furnished separable products 10b (9.4 mg) and 10b' (13.0 mg) as colorless oils, combined yield 60%.

Tandem RCDA/1,5-diene cyclisation according to GP 4:

Alkene 6b (56.1 mg, 0.25 mmol), myrcene (7d, 128 μL, 102 mg, 0.75 mmol) and Ru(bpz)₃(BArF)₂ (2.9 mg, 1.25 μmol) in CH₂Cl₂ (3.00 mL) gave intermediate cycloadduct 8e after 6 h reaction time. After evaporation of solvent, crude cycloadduct 8e (max. 0.25 mmol) and NaIO₄ on wet silica (1.95 g, 1.25 mmol) in 9:1 THF/CH₂Cl₂ (5.00 mL) gave 10b,b' after 18 h reaction time (dr 1:1.4 by crude ¹H NMR). Column chromatography (silica gel, petrol ether/ethyl acetate 5:2 → 1:1) furnished separable products 10b (12.2 mg) and 10b' (17.1 mg) as colorless oils, combined yield 29%.

10b:

Rf = 0.27 (petrol ether/ethyl acetate 1:1).

¹H-NMR (600 MHz, CDCl₃): δ 1.11 (s, 3 H, Me), 1.21 (s, 3 H, Me), 1.43-1.51 (m, 1 H, 10-H), 1.63-1.71 (m, 1 H, 4-H, 7-H), 1.72-1.90 (m, 5 H, 3-H, 4'-H, 9-H, 10'-H), 2.00-2.13 (m, 2 H, 7-H, CH₂Ph), 2.56-2.63 (m, 1 H, CH₂Ph), 2.68-2.76 (m, 1 H, 8-H), 3.63 (m, 1 H, 6-H), 3.76 (t, J = 7.6 Hz, 1 H, 2-H), 3.81 (s, 3 H, OMe), 6.89 (d, J = 8.5 Hz, 2 H, Ar), 6.99 (d, J = 7.3 Hz, 2 H, Ar), 7.14 (t, J = 7.3 Hz, 1 H, Ar), 7.18 (d, J = 8.5 Hz, 2 H, Ar), 7.22 (t, J = 7.3 Hz, 2 H, Ar) ppm.

¹³C-NMR (150 MHz, CDCl₃): δ 24.5 (q, Me), 26.9 (t, C-3), 27.3 (q, Me), 34.2 (t, C-4), 37.2 (t, C-10), 38.9 (t, C-7), 40.4 (t, CH₂Ph), 42.4 (d, C-8), 42.5 (d, C-9), 55.2 (q, OMe), 71.0 (s, C-2'), 72.6 (d, C-6), 85.2 (s, C-5), 85.4 (d, C-2'), 114.0 (d, Ar), 125.6 (d, Ar), 128.1 (d, Ar), 128.2 (d, Ar), 129.0 (d, Ar), 136.8 (s, Ar), 140.7 (s, Ar), 158.0 (s, Ar) ppm.
10b':

R_7 = 0.38 (petrol ether/ethyl acetate 1:1).

^1^H-NMR (600 MHz, CDCl\textsubscript{3}): \( \delta \) 1.08 (dd, \( J = 12.1, 13.9 \) Hz, 1 H, 10-H), 1.10 (s, 3 H, Me), 1.33 (s, 3 H, Me), 1.55 (td, \( J = 9.0, 12.0 \) Hz, 1 H, 4-H), 1.71-1.78 (m, 2 H, 3-H, 10-H'), 1.86-1.92 (m, 2 H, 7-H), 1.94-2.05 (m, 2 H, 3-H, CH\textsubscript{2}Ph), 2.15-2.23 (m, 2 H, 4-H, 9-H), 2.26-2.33 (m, 1 H, 8-H), 2.58 (dd, \( J = 3.2, 13.7 \) Hz, 1 H, CH\textsubscript{2}Ph), 3.48 (dd, \( J = 6.4, 9.7 \) Hz, 1 H, 6-H), 3.69 (dd, \( J = 6.8, 8.6 \) Hz, 1 H, 2-H), 3.81 (s, 3 H, OMe), 6.88 (d, \( J = 8.7 \) Hz, 2 H, Ar), 6.98 (d, \( J = 7.5 \) Hz, 2 H, Ar), 7.14 (t, \( J = 7.5 \) Hz, 1 H, Ar), 7.17 (t, \( J = 8.7 \) Hz, 2 H, Ar), 7.21 (t, \( J = 7.5 \) Hz, 2 H, Ar) ppm.

^1^3^C-NMR (150 MHz, CDCl\textsubscript{3}): \( \delta \) 25.7 (q, Me), 26.3 (t, C-3), 28.0 (q, Me), 35.4 (t, C-4), 39.5 (d, C-9), 39.8 (t, CH\textsubscript{2}Ph), 41.0 (t, C-7), 42.2 (t, C-10), 47.9 (d, C-8), 55.2 (q, OMe), 72.1 (s, C-2'), 75.2 (d, C-6), 83.9 (s, C-5), 85.0 (d, C-2), 113.9 (d, Ar), 125.5 (d, Ar), 128.0 (d, Ar), 128.5 (d, Ar), 129.1 (d, Ar), 137.0 (s, Ar), 140.8 (s, Ar), 158.1 (s, Ar) ppm.

IR: \( \tilde{\nu} \) 3330 (O-H), 2930 (C-H, =C-H), 1510, 1250 cm\textsuperscript{-1}.

HRMS (ESI) for C\textsubscript{26}H\textsubscript{34}NaO\textsubscript{4} (M + Na\textsuperscript{+}) calc. 433.2349, found 433.2353.

\((\text{2R,5R,6S,8S,9S})\)-2-(2-Hydroxypropan-2-yl)-8-(4-methoxyphenyl)-9-[(triisopropylsilyl-oxymethyl]-1-oxaspiro[4.5]decan-6-ol (10c)

and

\((\text{2R,5R,6S,8R,9R})\)-2-(2-Hydroxypropan-2-yl)-8-(4-methoxyphenyl)-9-[(triisopropylsilyl-oxymethyl]-1-oxaspiro[4.5]decan-6-ol (10c')

Cyclisation according to GP 2:

Cycloadduct 8f (35.6 mg, 0.078 mmol), RuCl\textsubscript{3} (0.16 mg, 0.8 \mu mol) and NaIO\textsubscript{4} on wet silica (268 mg, 0.17 mmol) in 9:1 THF/CH\textsubscript{2}Cl\textsubscript{2} (2.00 mL) gave 10c,c' after 6 h reaction time (\( dr \) 1:1 by crude \( ^1^H \) NMR). Column chromatography (silica gel, petrol ether/ethyl acetate 2:1) furnished separable products 10c (6.3 mg) and 10c' (7.1 mg) as colorless oils, combined yield 34%.

Tandem RCDA/1,5-diene cyclisation according to GP 4:

Alkene 6c (80.1 mg, 0.25 mmol), myrcene (7d, 639 \mu L, 511 mg, 3.75 mmol) and Ru(bpz)\textsubscript{3}(BARF)\textsubscript{2} (11.5 mg, 5.0 \mu mol) in CH\textsubscript{2}Cl\textsubscript{2} (3.00 mL) gave intermediate cycloadduct 8f after 6 h reaction time. After evaporation of solvent, crude cycloadduct 8f (max. 0.25 mmol) and NaIO\textsubscript{4} on wet silica (1.95 g, 1.25 mmol) in 9:1 THF/CH\textsubscript{2}Cl\textsubscript{2} (5.00 mL) gave 10c,c' after 18 h reaction time (\( dr \) 1:1 by crude \( ^1^H \) NMR). Column chromatography (silica gel, petrol ether/ethyl acetate 5:1 \( \rightarrow \) 1:1) furnished separable products 10c (16.0 mg) and 10c' (16.0 mg) as colorless oils, combined yield 25 %.
10c:

R<sub>f</sub> = 0.38 (petrol ether/ethyl acetate 1:1).

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ 0.92-0.99 (m, 21 H, TIPS), 1.16 (s, 3 H, Me), 1.27 (s, 3 H, Me), 1.61-1.69 (m, 2 H, 7-H, 9-H), 1.82-2.00 (m, 7 H, 3-H, 4-H, 10-H, OH), 2.04 (td, J = 3.6, 14.5 Hz, 1 H, 7-H<sup>1</sup>), 2.56 (br. s, 1 H, OH), 2.79 (dt, J = 4.0, 12.4 Hz, 1 H, 8-H), 3.24 (dd, J = 7.3, 9.7 Hz, 1 H, CH<sub>3</sub>OTIPS), 3.37 (dd, J = 3.0, 9.7 Hz, 1 H, CH<sub>3</sub>OTIPS), 3.65 (m, 1 H, 6-H), 3.78 (s, 3 H, OMe), 3.89-3.95 (m, 1 H, 2-H), 6.81 (d, J = 8.5 Hz, 2 H, Ar), 7.08 (d, J = 8.5 Hz, 2 H, Ar) ppm.

<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>): δ 11.9 (d, TIPS), 18.0 (q, TIPS), 24.5 (q, TIPS), 27.0 (t, C-3), 27.3 (q, Me), 34.3 (t, C-4), 35.2 (t, C-10), 37.8 (t, C-7), 43.4 (d, C-9), 55.3 (q, OMe), 65.6 (t, CH<sub>3</sub>OTIPS), 71.1 (s, C-2'), 72.7 (d, C-6), 85.3 (s, C-5), 85.4 (d, C-2), 113.8 (d, Ar), 128.4 (d, Ar), 136.4 (s, Ar), 157.9 (s, Ar) ppm.

10c':

R<sub>f</sub> = 0.47 (petrol ether/ethyl acetate 2:1).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 0.93-1.01 (m, 21 H, TIPS), 1.15 (s, 3 H, Me), 1.36 (s, 3 H, Me), 1.55 (t, J = 13.3 Hz, 1 H, 7-H), 1.68 (td, J = 8.9, 12.2 Hz, 1 H, 4-H), 1.81-2.13 (m, 6 H, 3-H, 7-H, 9-H, 10-H), 2.29 (ddd, J = 3.8, 9.3, 12.2 Hz, 1 H, 4-H<sup>1</sup>), 2.51 (dt, J = 5.0, 11.4 Hz, 1 H, 8-H), 2.79 (br. s, 2 H, OH), 3.26 (dd, J = 5.2, 9.8 Hz, 1 H, CH<sub>3</sub>OTIPS), 3.37 (dd, J = 2.5, 9.8 Hz, 1 H, CH<sub>3</sub>OTIPS), 3.51 (dd, J = 5.6, 10.4 Hz, 1 H, 6-H), 3.78 (s, 3 H, OMe), 3.85 (dd, J = 6.7, 8.7 Hz, 1 H, 2-H), 6.81 (d, J = 8.7 Hz, 2 H, Ar), 7.10 (d, J = 8.7 Hz, 2 H, Ar) ppm.

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 11.9 (d, TIPS), 25.6 (q, TIPS), 26.5 (t, C-3), 28.0 (q, Me), 35.6 (t, C-4), 40.5 (2 × t, C-7, C-10), 41.4 (d, C-9), 43.0 (d, C-8), 55.2 (q, OMe), 64.8 (t, CH<sub>3</sub>OTIPS), 72.1 (s, C-11), 75.1 (d, C-6), 84.3 (s, C-5), 85.1 (d, C-2), 113.7 (d, Ar), 128.4 (d, Ar), 136.7 (s, Ar), 158.1 (s, Ar) ppm.

10c,c':

IR: ν 3355 (O-H), 2940, 2865 (C-H, =C-H), 1510, 1250, 1070 cm<sup>-1</sup>. HRMS (ESI) for C<sub>29</sub>H<sub>50</sub>NaO<sub>5</sub>Si<sup>+</sup> (M + Na)<sup>+</sup> calc. 529.3320, found 529.3271.

[(2R*,5R*,7S*,8S*,10S*)-10-Hydroxy-2-(2-hydroxypropan-2-yl)-8-(4-methoxyphenyl)-1-oxaspiro[4.5]decan-7-yl]methyl acetate (10d)

and

[(2R*,5R*,7R*,8R*,10S*)-10-Hydroxy-2-(2-hydroxypropan-2-yl)-8-(4-methoxyphenyl)-1-oxaspiro[4.5]decan-7-yl]methyl acetate (10d')
Cyclisation according to GP 2:

Cycloadduct 8g (27.4 mg, 0.08 mmol), RuCl₃ (0.2 mg, 0.8 μmol) and NaIO₄ on wet silica (274 mg, 0.18 mmol) in 9:1 THF/CH₂Cl₂ (2.00 mL) gave 10d,d' after 4 h reaction time (dr 1:1 by crude ¹H NMR). Column chromatography (silica gel, petrol ether/ethyl acetate 1:1) furnished separable products 10d (6.0 mg) and 10d' (6.1 mg) as colorless oils, combined yield 39%.

Tandem RCDA/1,5-diene cyclisation according to GP 4:

Alkene 6d (51.6 mg, 0.25 mmol), myrcene (7d, 128 μL, 102 mg, 0.75 mmol) and Ru(bpz)₃(BArF)₂ (11.5 mg, 5.0 μmol) in CH₂Cl₂ (12.5 mL) gave intermediate cycloadduct 8g after 6 h reaction time. After evaporation of solvent, crude cycloadduct 8g (max. 0.25 mmol) and NaIO₄ on wet silica (1.95 g, 1.25 mmol) in 9:1 THF/CH₂Cl₂ (5.00 mL) gave 10d,d' after 18 h reaction time (dr 1:1 by crude ¹H NMR). Column chromatography (silica gel, petrol ether/ethyl acetate 4:1 → 3:1) furnished separable products 10d (7.5 mg) and 10d' (8.0 mg) as colorless oils, combined yield 16%.

10d:

Rᵣ = 0.39 (petrol ether/ethyl acetate 1:2).

¹H-NMR (400 MHz, CDCl₃): δ 1.16 (s, 3 H, Me), 1.27 (s, 3 H, Me), 1.59 (br. s, 1 H, OH), 1.64-1.74 (m, 2 H, 6-H, 9-H), 1.78-2.02 (m, 9 H, 3-H, 4-H, 6-H, 7-H, OAc), 2.07 (td, J = 3.6, 14.5 Hz, 1 H, 9-H'), 2.61 (br. s, 1 H OH), 2.81 (dt, J = 3.9, 12.0 Hz, 1 H, 8-H), 3.63 (dd, J = 6.8, 11.0 Hz, 1 H, CH₂OAc), 3.67 (m, 1 H, 10-H), 3.78 (s, 3 H, OMe), 3.82 (dd, J = 3.6, 11.0 Hz, 1 H, CH₂OAc), 3.89-3.94 (m, 1 H, 2-H), 6.82 (d, J = 8.6 Hz, 2 H, Ar), 7.07 (d, J = 8.6 Hz, 2 H, Ar) ppm.

¹³C-NMR (100 MHz, CDCl₃): δ 21.0 (q, OAc), 24.8 (q, Me), 27.1 (t, C-3), 27.5 (q, Me), 34.4 (t, C-4), 35.2 (t, C-6), 38.6 (d, t, C-8, C-9), 40.0 (d, C-7), 55.4 (q, OMe), 67.2 (t, CH₂OAc), 71.2 (s, C-2'), 72.7 (d, C-10), 85.1 (s, C-5), 85.6 (d, C-2'), 114.2 (d, Ar), 128.5 (d, Ar), 135.6 (s, Ar), 158.4 (s, Ar), 171.2 (s, CO) ppm.

10d':

Rᵣ = 0.23 (petrol ether/ethylacetate 1:1).

¹H-NMR (400 MHz, CDCl₃): δ 1.16 (s, 3 H, Me), 1.32-1.36 (m, 6-H), 1.39 (s, 3 H, Me), 1.68 (td, J = 9.0, 12.3 Hz, 1 H, 4-H), 1.83-1.96 (m, 4 H, 3-H, 6-H', 9-H), 1.98 (s, 3 H, OAc), 2.05-2.12 (m, 1 H, 3-H'), 2.12-2.24 (m, 1 H, 7-H), 2.29 (ddd, J = 3.8, 9.3, 12.3 Hz, 1 H, 4-H'), 2.42 (dt, J = 4.6, 11.5 Hz, 1 H, 7-H), 2.67 (br. s, 2 H, OH), 3.51 (dd, J = 5.3, 11.0 Hz, 1 H, 10-H), 3.62 (dd, J = 6.2, 11.0 Hz, 1 H, CH₂OAc), 3.78 (s, 3 H, OMe), 3.82 (dd, J = 3.5, 11.0 Hz, 1 H, CH₂OAc), 3.89 (dd, 6.8, 8.6 Hz, 1 H, 2-H), 6.82 (d, J = 8.6 Hz, 2 H, Ar), 7.07 (d, J = 8.6 Hz, 2 H, Ar) ppm.

¹³C-NMR (100 MHz, CDCl₃): δ 20.8 (q, OAc), 25.8 (q, Me), 26.6 (t, C-3), 28.1 (q, Me), 35.6 (t, C-4), 38.2 (d, C-7), 40.3 (t, C-9), 40.5 (t, C-6), 43.9 (d, C-8), 55.2 (q, OMe), 66.7 (t, CH₂OAc), 72.3 (s, C-11), 74.9 (d, C-10), 84.0 (s, C-5), 85.3 (d, C-2'), 114.0 (d, Ar), 128.2 (d, Ar), 135.7 (s, Ar), 158.2 (s, Ar), 171.1 (s, CO) ppm.

10d,d':

IR: ʋ 3360 (O-H), 2935 (-C-H, =C-H), 1735 (C=O), 1510, 1245, 1040 cm⁻¹.

HRMS (ESI) for C₂₂H₂₂NaO₆⁺ (M + Na)⁺ calc. 415.2091, found 415.2098.
(2R*,3a'S*,5R*,6'S*,7a'S*)-5-(2-Hydroxypropan-2-yl)-7a'-(4-methoxyphenyl)decahydro-3H-spiro[furan-2,5'-inden]-6'-ol (10e)

and

(2R*,3a'R*,5R*,6'S*,7a'R*)-5-(2-Hydroxypropan-2-yl)-7a'-(4-methoxyphenyl)decahydro-3H-spiro[furan-2,5'-inden]-6'-ol (10e')

Cyclisation according to GP 2:
Cycloadduct 8h (13.0 mg, 0.042 mmol), RuCl₃ (0.1 mg, 0.4 μmol) and NaIO₄ on wet silica (144 mg, 0.09 mmol) in 9:1 THF/CH₂Cl₂ (1.00 mL) gave 10e,e' after 2 h reaction time (dr 1:1 by crude ¹H NMR). Column chromatography (silica gel, petrol ether/ethyl acetate 2:1 → 1:1) furnished products 10e,e' as an inseparable mixture (7.2 mg), colorless oil, combined yield 48%.

Tandem RCDA/1,5-diene cyclisation according to GP 4:
Alkene 6e (43.6 mg, 0.25 mmol), myrcene (7d, 426 μL, 341 mg, 2.5 mmol) and Ru(bpz)₃(BArF)₂ (11.5 mg, 5.0 μmol) in CH₂Cl₂ (3.00 mL) gave intermediate cycloadduct 8h after 24 h reaction time. After evaporation of solvent, crude cycloadduct 8h (max. 0.25 mol) and NaIO₄ on wet silica (1.95 g, 1.25 mmol) in 9:1 THF/CH₂Cl₂ (5.00 mL) gave 10e,e' after 18 h reaction time (dr 1:1 by crude ¹H NMR). Column chromatography (silica gel, petrol ether/ethyl acetate 5:1 → 1:1) furnished inseparable products 10e,e' (24.8 mg) as colorless oil, combined yield 28%.

10e,e':
¹H-NMR (300 MHz, CDCl₃): δ 1.14 (s, 3 H, Me), 1.15 (s, 3 H, Me), 1.19-1.22 (m, 1 H, CH), 1.24-1.27 (m, 1 H, CH), 1.33 (s, 3 H, Me) 1.35-1.41 (m, 4 H, CH, Me), 1.49-1.82 (m, 13 H, CH), 1.82-1.99 (m, 7 H, CH), 1.99-2.13 (m, 4 H, CH), 2.27 (ddd, J = 3.5, 9.2, 12.0 Hz, 1 H, CH), 2.32-2.60 (m, 7 H, 3×CH, 4×OH), 3.21 (dd, J = 3.9, 11.2 Hz, 1 H, 6'-H), 3.66 (dd, J = 7.6, 9.0 Hz, 1 H, 6'-H), 3.79 (s, 6 H, 2×OMe), 3.82 (dd, J = 6.1, 9.4 Hz, 1 H, 2-H), 3.88 (dd, J = 6.7, 8.8 Hz, 1 H, 2-H), 6.84 (d, J = 8.9 Hz, 4 H, Ar), 7.28 (d, J = 8.9 Hz, 2 H, Ar), 7.32 (d, J = 8.9 Hz, 2 H, Ar) ppm.

¹³C-NMR (150 MHz, CDCl₃): δ = 20.8 (t, CH₂), 21.4 (t, CH₂) 25.6 (q, Me), 25.6 (q, Me), 26.2 (t, CH₂), 26.5 (t, CH₂), 27.9 (q, Me), 28.0 (q, Me), 28.8 (t, CH₂), 29.6 (t, CH₂), 30.8 (t, CH₂), 35.4 (t, CH₂), 36.1 (t, CH₂), 36.8 (t, CH₂), 38.7 (t, CH₂), 41.0 (d, C-7a), 41.39 (t, CH₂), 41.6 (d, C-7a), 42.9 (t, CH₂), 43.3 (t, CH₂), 48.9 (s, C-3a), 50.7 (s, C-3a), 55.2 (q, OMe), 55.2 (q, OMe), 71.7 (s, C-2''), 72.2 (d, C-6'), 72.2 (s, C-2''), 72.5 (d, C-6'), 84.5 (s, C-5), 84.6 (s, C-5), 85.1 (d, C-2), 85.1 (d, C-2), 113.4 (d, Ar), 113.5 (d, Ar), 126.8 (d, Ar), 127.0 (d, Ar), 140.0 (s,Ar), 141.1 (s, Ar), 157.3 (s, Ar), 157.4 (s, Ar) ppm.

IR: ν 3330 (O-H), 2955, 2875 (-C-H, =C-H), 1510, 1250, 1070, 1035 cm⁻¹.

HRMS (ESI) for C₉₃H₈₂NaO₄⁺ (M + Na)⁺ calc. 383.2193, found 383.2206.
(2R*,3aR*,4R*,5S*,7aS*)-2-(2-Hydroxypropan-2-yl)-4-(4-methoxyphenyl)-5,7a-dimethylhexa-hydrobenzofuran-7(7aH)-one (10f)

Cyclisation according to GP 2:
Cycloadduct 8i (67.0 mg, 0.235 mmol, endo/exo 9:1), RuCl₃ (0.5 mg, 2.4 μmol) and NaIO₄ on wet silica (808 mg, 0.52 mmol) in 9:1 THF/CH₂Cl₂ (4.00 mL) gave 10f after 2 h reaction time. Column chromatography (silica gel, petrol ether/ethyl acetate 5:1 → 1:1) furnished product 10f as colorless oil (15.9 mg) in 20% yield.

Tandem RCDA/1,5-diene cyclisation according to GP 4:
Alkene 6a (37.1 mg, 0.25 mmol), β-ocimene (7e, 178 µL, 146 mg, 1.07 mmol, (E)/(Z) 7:3, equivalent of 0.75 mmol of (E)-isomer) and Ru(bpz)₃(BArF)₂ (11.5 mg, 5.0 μmol) in CH₂Cl₂ (12.5 mL) gave intermediate cycloadduct 8i after 4 h reaction time (endo/exo 9:1 by crude NMR). After evaporation of solvent, crude cycloadduct 8i (max. 0.25 mol) and NaIO₄ on wet silica (1.95 g, 1.25 mmol) in 9:1 THF/CH₂Cl₂ (5.0 mL) gave 10f after 18 h reaction time. Column chromatography (silica gel, petrol ether/ethyl acetate 5:1 → 1:1) furnished product 10f as colorless oil (21.6 mg) in 26% yield.

10f:
Rf = 0.31 (petrol ether/ethyl acetate 3:1).

1H-NMR (300 MHz, CDCl₃): δ 0.86 (d, J = 5.8 Hz, 3 H, Me), 0.97 (s, 3 H, Me), 1.32 (s, 3 H, Me), 1.35-1.46 (m, 1 H, 3-H), 1.57 (s, 3 H, Me), 1.80 (m, 1 H, 3-H'), 2.34-2.57 (m, 4 H, 3a-H, 5-H, 6-H, 6'-H), 2.95 (dd, J = 4.7, 10.8 Hz, 1 H, 4-H), 3.47 (br. s, 1 H, OH), 3.70 (dd, J = 5.4, 10.4 Hz, 1 H, 2-H), 3.81 (s, 3 H, OMe), 6.88 (d, J = 8.8 Hz, 2 H, Ar), 7.08 (d, J = 8.8 Hz, 2 H, Ar) ppm.

13C-NMR (75 MHz, CDCl₃) δ 20.6 (q, Me), 22.9 (q, Me), 24.2 (q, Me), 27.1 (t, C-3), 28.5 (q, Me), 33.0 (d, C-5), 47.2 (t, C-6), 49.1 (d, C-4), 55.2 (q, OMe), 56.5 (d, C-3a), 69.7 (s, C-2'), 85.3 (d, C-2), 86.6 (s, C-7a), 114.0 (d, Ar), 128.9 (d, Ar), 133.2 (s, Ar), 158.3 (s, Ar), 213.6 (s, C-7) ppm.

IR: ν 3475 (O-H), 2975, 2935 (-C-H, =C-H), 1715 (C=O), 1515, 1250 cm⁻¹.

HRMS (ESI) for C₂₀H₂₈NaO₄⁺ (M + Na)⁺ calc. 355.1880, found 355.1888.
**Tandem RCDA/1,5-diene cyclisation according to GP 4:**

Alkene 6a (18.2 mg, 0.12 mmol), triene 7f (E/Z 1:0, 45.2 mg, 0.37 mmol) and Ru(bpz)₃(BArF)₂ (5.7 mg, 2.5 μmol) in CH₂Cl₂ (6.00 mL) gave intermediate cycloadduct 8j after 16 h reaction time (endo/exo 9:1 by crude NMR). After evaporation of solvent, crude cycloadduct 8j (max. 0.12 mmol) and NaIO₄ on wet silica (960 mg, 0.62 mmol) in 9:1 THF/CH₂Cl₂ (2.50 mL) gave 10g after 18 h reaction time. Column chromatography (silica gel, petrol ether/ethyl acetate 5:1 → 1:1) furnished product 10g as colorless oil (7.2 mg) in 18% yield.

**10g:**

R_f = 0.33 (petrol ether/ethyl acetate 2:1).

**¹H-NMR (600 MHz, CDCl₃):** δ 0.87 (d, J = 6.2 Hz, 3 H, Me), 0.98 (s, 3 H, Me), 1.33 (s, 3 H, Me), 1.34-1.37 (m, 1 H, 3-H), 1.70 (m, 1 H, 3-H'), 2.33 (t, J = 12.4 Hz, 1 H, 6-H), 2.36-2.45 (m, 1 H, 5-H), 2.51 (dd, J = 2.8, 12.4 Hz, 1 H, 6-H'), 2.94-3.04 (m, 2 H, 3a-H, 4-H), 3.71 (br. s, 1 H, OH), 3.73 (dd, J = 5.3, 10.4 Hz, 1 H, 2-H), 3.81 (s, 3 H, OMe), 4.50 (d, J = 8.0 Hz, 1 H, 7a-H), 6.88 (d, J = 8.6 Hz, 2 H, Ar), 7.08 (d, J = 8.6 Hz, 2 H, Ar) ppm.

**¹³C-NMR (150 MHz, CDCl₃):** δ 20.6 (q, Me), 24.4 (q, Me), 25.9 (t, C-3), 28.4 (q, Me), 33.4 (d, C-5), 47.7 (t, C-6), 49.9 (d, C-4), 50.8 (d, C-3a), 55.2 (q, OMe), 69.6 (s, C-2'), 82.8 (d, C-7a), 87.2 (d, C-2), 114.1 (d, Ar), 129.0 (d, Ar), 133.0 (s, Ar), 158.4 (s, Ar), 211.1 (s, C-7) ppm.

IR: v 3465 (O-H), 2975, (C-H, =C-H), 1715 (C=O), 1515, 1250 cm⁻¹.

HRMS (ESI) for C₁₉H₂₆NaO₄⁺ (M + Na)⁺ calc. 341.1723, found 341.1708.
4 Structural assignment

- Comparison of 10a to known compounds:

![Figure S3: Comparison of $^{13}$C NMR shifts of compound 10a with earlier reported compound S3.][11]

- Relative stereochemistry of compounds 10a and 10a*:

![Figure S4: Key NOE contacts in 10a' and comparison with 10a.][11]

Following NOE-based assignments of 10a and 10a* as shown in Figure S4, compounds 10b-d, 10b-d' could be assigned accordingly using $^1$H and $^{13}$C NMR data (Table S1).

**Table S1**

<table>
<thead>
<tr>
<th>R</th>
<th>#</th>
<th>2-H</th>
<th>6-H</th>
<th>8-H</th>
<th>C-6</th>
<th>C-8</th>
<th>C-10</th>
<th>#</th>
<th>2-H</th>
<th>6-H</th>
<th>8-H</th>
<th>C-6</th>
<th>C-8</th>
<th>C-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>10a</td>
<td>3.90</td>
<td>3.66</td>
<td>2.53</td>
<td>72.9</td>
<td>43.5</td>
<td>40.8</td>
<td>10a*</td>
<td>3.84</td>
<td>3.48</td>
<td>2.08</td>
<td>75.4</td>
<td>49.4</td>
<td>46.2</td>
</tr>
<tr>
<td>Bn</td>
<td>10b</td>
<td>3.76</td>
<td>3.65</td>
<td>2.72</td>
<td>72.6</td>
<td>42.4</td>
<td>37.2</td>
<td>10b*</td>
<td>3.69</td>
<td>3.48</td>
<td>2.29</td>
<td>75.2</td>
<td>47.9</td>
<td>42.2</td>
</tr>
<tr>
<td>OTIPS</td>
<td>10c</td>
<td>3.93</td>
<td>3.65</td>
<td>2.72</td>
<td>72.7</td>
<td>37.8</td>
<td>35.2</td>
<td>10c*</td>
<td>3.85</td>
<td>3.51</td>
<td>2.53</td>
<td>75.1</td>
<td>43.0</td>
<td>40.5</td>
</tr>
<tr>
<td>OAc*</td>
<td>10c</td>
<td>3.92</td>
<td>3.67</td>
<td>2.81</td>
<td>72.6</td>
<td>38.5</td>
<td>35.5</td>
<td>10d*</td>
<td>3.89</td>
<td>3.51</td>
<td>2.42</td>
<td>74.9</td>
<td>43.9</td>
<td>40.5</td>
</tr>
</tbody>
</table>

*Position numbering adjusted for comparison in this table.

5 Analysis of cyclisation modes of dienes 8d and 8i

- RuO$_4$-mediated cyclisation of substrate 8d:

  ![](image)

  **Figure S5**: Possible cyclisation modes of cycloadduct 8d with RuO$_4$. The shown four reaction pathways all appear conformationally accessible and productive.

- RuO$_4$-mediated cyclisation of substrate 8i:

  ![](image)

  **Figure S6**: Possible cyclisation modes of cycloadduct 8i with RuO$_4$. Out of four conceivable reaction pathways, only two appear possible and productive.
6 UV-Vis experiments

Figure S7: Bleaching of a solution of Ru(bpy)$_3$Cl$_2$·6H$_2$O (c = 1.534·10$^{-4}$ mol·l$^{-1}$) and NaIO$_4$ (c = 8.626·10$^{-3}$ mol·l$^{-1}$) in H$_2$O under irradiation with blue LED light (5.4 W / 0.87 cd / 450 ±25 nm, setup in Figure S1).

Figure S8: Comparison of irradiated and dark bleaching experiment, plot of 453 nm absorption maximum.
Figure S9: UV-Vis spectrum of RuO$_4$ after partitioning of the irradiated aqueous reaction mixture of Figure S7 between brine and MeCN/CCl$_4$ 1:1 (organic phase spectrum). For reference spectra see refs.$^{[12],[13]}$
7 NMR spectra of new compounds

\begin{center}
\includegraphics[width=\textwidth]{nmr_spectra.png}
\end{center}

$^1$H NMR (300 MHz in CDCl$_3$), $^{13}$C NMR (75 MHz in CDCl$_3$)
$^1$H NMR (400 MHz in CDCl$_3$), $^{13}$C NMR (100 MHz in CDCl$_3$)
$^1$H NMR (400 MHz in CDCl$_3$), $^{13}$C NMR (100 MHz in CDCl$_3$)
$^1$H NMR (300 MHz in CDCl$_3$), $^{13}$C NMR (75 MHz in CDCl$_3$)
$^1$H NMR (400 MHz in CDCl$_3$), $^{13}$C NMR (100 MHz in CDCl$_3$)
$^{1}$H NMR (600 MHz in CDCl$_3$), $^{13}$C NMR (150 MHz in CDCl$_3$)
\textsuperscript{1}H NMR (300 MHz in CDCl$_3$), \textsuperscript{13}C NMR (75 MHz in CDCl$_3$)
$^1$H NMR (400 MHz in CDCl$_3$), $^{13}$C NMR (100 MHz in CDCl$_3$)
$^{1}H$ NMR (300 MHz in CDCl$_3$), $^{13}C$ NMR (75 MHz in CDCl$_3$)
$^1$H NMR (300 MHz in CDCl$_3$), $^{13}$C NMR (100 MHz in CDCl$_3$)
$^1$H NMR (300 MHz in DMSO-$d_6$), $^{13}$C NMR (100 MHz in DMSO-$d_6$)

Spectra show traces of diastereoisomer from C,C-cleavage of exo-8c
$^{1}$H NMR (400 MHz in CDCl$_3$), $^{13}$C NMR (100 MHz in CDCl$_3$)
$^{1}H$ NMR (300 MHz in CDCl$_3$), $^{13}C$ NMR (75 MHz in CDCl$_3$)
$^1$H NMR (600 MHz in CDCl$_3$), $^{13}$C NMR (150 MHz in CDCl$_3$)
$^1$H NMR (600 MHz in CDCl$_3$), $^{13}$C NMR (150 MHz in CDCl$_3$)
$^{1}H$ NMR (600 MHz in CDCl$_3$), $^{13}C$ NMR (150 MHz in CDCl$_3$)
$^1$H NMR (400 MHz in CDCl$_3$), $^{13}$C NMR (100 MHz in CDCl$_3$)
$^1$H NMR (400 MHz in CDCl$_3$), $^{13}$C NMR (100 MHz in CDCl$_3$)
$^{1}H$ NMR (400 MHz in CDCl$_3$), $^{13}$C NMR (100 MHz in CDCl$_3$)

[Chemical structure and spectra images]
$^1$H NMR (300 MHz in CDCl$_3$)
$^{13}$C NMR (150 MHz in CDCl$_3$)
\(^1\)H NMR (300 MHz in CDCl\(_3\)), \(^{13}\)C NMR (75 MHz in CDCl\(_3\))
\[ \text{H NMR (600 MHz in CDCl}_3\text{), } \text{C NMR (150 MHz in CDCl}_3\text{)} \]