Electronic Supplementary Material (ESI) for ChemComm.

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

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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_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, AvanceI 400 or AvanceIII 600). Chemical shifts are reported in ppm relative to the following solvent resonances: δ^{1H} [ppm] = 7.26 ($CHCl_3$), 2.50 (DMSO-d_6) and δ^{13C} [ppm] = 77.00 ($CHCl_3$), 39.50 (DMSO-d_6). Coupling constants are reported in Hz. ^{13}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:

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

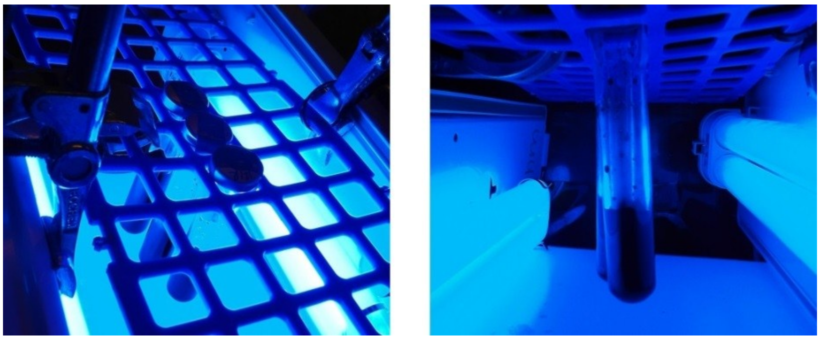
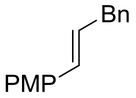


Figure S2: Irradiation setup 2. Blue CFL, 2 × 18 W / 2 × 2.73 cd / 450 ± 50 nm.

- Ruthenium catalysts **1a**,**b**:

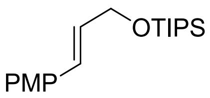
$Ru(bpy)_3Cl_2{\cdot}6H_2O$ was purchased from Sigma Aldrich. $Ru(bpz)_3(PF_6)_2$ and $Ru(bpz)_3(BArF)_2$ were prepared according to literature procedures.[1],[2]

- Alkenes **6b-e**:



6b

Prepared according to ref.[3]



6c

Prepared according to ref.[4] followed by standard silylation (TIPSCl, DMAP, Imidazole). Analytical data:

Colorless oil.

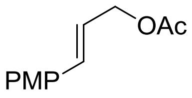
R_f = 0.35 (petrol ether/ethyl acetate 5:1).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 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}C-NMR (75 MHz, $CDCl_3$): δ 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.

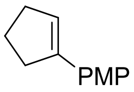
IR: ṽ 2940, 2865 (-C-H, =C-H), 1510, 1245.

HRMS (ESI) for $C_{19}H_{32}NaO_2Si^+$ $(M + Na)^+$ calc. 343.2064, found 343.2027.



6d

Prepared according to ref.[5]



6e

Prepared according to ref.[6]

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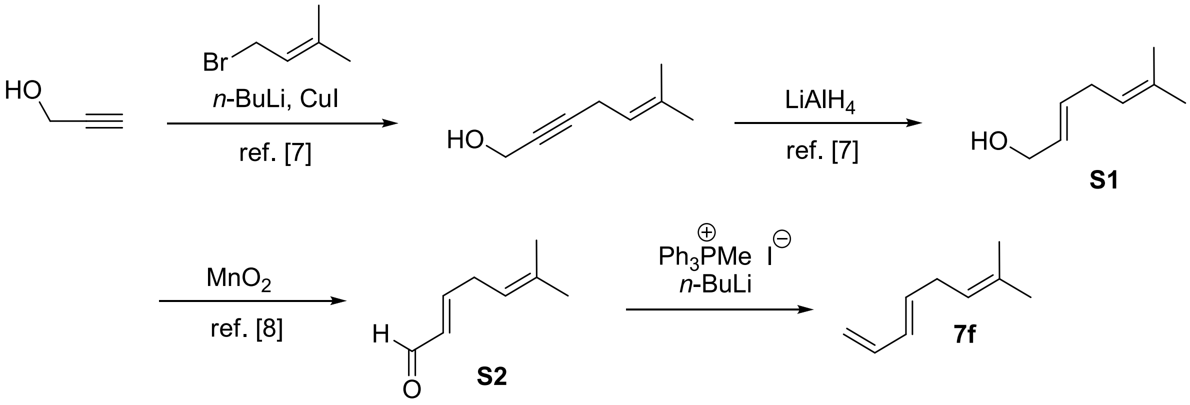
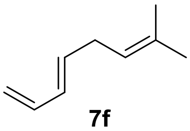
[1] M. A. Ischay, Z. Lu and T. P. Yoon, *J. Am. Chem. Soc.*, 2010, **132**, 8572.
[2] S. Lin, M. A. Ischay, C. G. Fry and T. P. Yoon, *J. Am. Chem. Soc.*, 2011, **133**, 19350.
[3] H. Tsukamoto, T. Uchiyama, T. Suzuki and Y. Kondo, *Org. Biomol. Chem.*, 2008, **6**, 3005.
[4] D. F. Fischer, A. Barakat, Z. Xin, M. E. Weiss and R. Peters, *Chem. Eur. J.*, 2009, **15**, 8722.
[5] A. Serra-Muns, A. Guerinot, S. Reymond and J. Cossy, *Chem. Commun.*, 2010, **46**, 4178.
[6] J. Tallineau, G. Bashiardes, J.-M. Coustard and F. Lecornué, *Synthesis*, 2009, 2761.

- Compound **7f**:

Compound **7f** was synthesized in four steps: Allylic alcohol **S1** was prepared according to literature.[7] Oxidation with MnO_2[8] gave *α,β*-unsaturated aldehyde **S2**, which was subjected to Wittig reaction to furnish triene **7f**.[9]



Analytical data:



7f

Colorless liquid.

R_f = 0.90 (pentane).

^{1}H-NMR (400 MHz, $CDCl_3$): 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_c, 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, $CDCl_3$): 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.

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[7] P. Norcott and C. S. P. McErlean, *Eur. J. Org. Chem.,* 2014, 5056.

[8] R. Schäckel, B. Hinkelmann, F. Sasse and M. Kalesse, *Angew. Chem. Int. Ed.,* 2010, **49**, 1619.

[9] E. W. Underhill, J. G. Millar, R. A. Ring, J. W. Wong, D. Barton and M. Giblin, *J. Chem. Ecol.*, 1987, **13**, 1319.

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 CH_2Cl_2 (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 $RuCl_3/NaIO_4$**

In a 25 mL round bottom flask, purified cycloadduct **8** (1 equiv.) was dissolved in 9:1 THF/CH_2Cl_2 (c = 0.05 M). 1 mol-% $RuCl_3$ (as a 0.1 M stock solution in H_2O) and $NaIO_4$ on wet silica[10] (0.64 mmol $NaIO_4$ per 1 g SiO_2, 2.2 equiv.) were added and the mixture was stirred under air (*stoppered 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 **10**.

- **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 CH_2Cl_2 (c = 0.08 M in **6**) and 1 mol-% $Ru(bpz)_3(PF_6)_2$ [= **1b**·($PF_6)_2$] 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 H_2O/EtOAc (c = 0.04 M). Solid $NaIO_4$ (3-8 equiv.) was added and the mixture was irradiated under air (*stoppered 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 Na_2SO_4, filtered and evaporated. Column chromatography provided C,C-cleavage product **9**.

- **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 CH_2Cl_2 (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/CH_2Cl_2 (c = 0.05 M). $NaIO_4$ on wet silica[10] (0.64 mmol $NaIO_4$ per 1 g SiO_2, 5 equiv.) was added and the mixture was irradiated under air (*stoppered 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 **10.** 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%).

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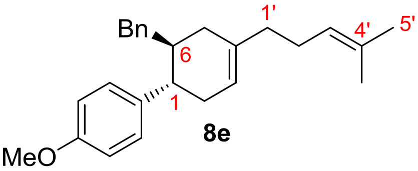
[10] S. Roth, S. Göhler, H. Cheng and C. B. W. Stark, *Eur. J. Org. Chem.*, 2005, 4109.

3 Synthesis and characterization of products

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



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_2Cl_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).

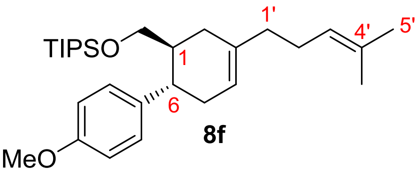
^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.61 (s, 3 H, Me), 1.71 (s, 3 H, Me), 1.74-1.85 (m, 1 H, 5-H), 1.89-2.04 (m, 3 H, 5-H', 1'-H), 2.02-2.17 (m, 3 H, 6-H, 2'-H), 2.20-2.31 (m, 1 H, 2-H), 2.31-2.43 (m, 1 H, 2-H'), 2.57 (m$_c$, 1 H, 1-H), 2.69 (m$_c$, 2 H, CH_2Ph), 3.83 (s, 3 H, OMe), 5.12 (m$_c$, 1 H, 3'-H), 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_2Ph), 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: ṽ 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{[(1*S**,6*S**)-6-(4-methoxyphenyl)-3-(4-methylpent-3-enyl)cyclohex-3-enyl]-methoxy}silane (8f)



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_2Cl_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 (petrol ether/diethyl ether 50:1).

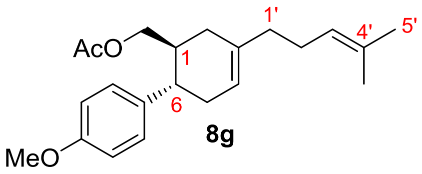
^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.91-1.05 (m, 21 H, TIPS), 1.64 (s, 3 H, Me), 1.72 (s, 3 H, Me), 1.87-2.35 (m, 9 H, 1-H, 2-H, 5-H, 1'-H, 2'-H), 2.60-2.75 (m, 1 H, 6-H), 3.34 (dd, *J* = 6.3 Hz, 9.6 Hz, 1 H, CH_2OTIPS), 3.48 (dd, *J* = 3.5, 9.6 Hz, 1 H, CH'$_2$OTIPS), 3.80 (s, 3 H, OMe), 5.16 (m_c, 1 H, 3'-H), 5.42-5.49 (m, 1 H, 4-H), 6.83 (d, *J* = 8.7 Hz, Ar), 7.12 (d, *J* = 8.7 Hz, 2 H, Ar) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$) δ 11.9 (q, TIPS), 17.7 (q, Me), 18.0 (d, TIPS), 25.7 (q, Me), 26.5 (t, C-1'), 32.1 (t, C-2'), 34.5 (t, C-5), 37.7 (t, C-2), 41.2 (d, C-6), 41.7 (d, C-1), 55.3 (q, OMe), 65.6 (t, CH_2OTIPS), 113.7 (d, Ar), 119.8 (d, C-5), 124.4 (d, C-3'), 128.5 (d, Ar), 131.4 (s, C-4'), 137.6 (s, Ar), 137.6 (s, C-4), 157.9 (s, Ar) ppm.

IR: ṽ 2940, 2865 (-C-H, =C-H), 1510, 1245 cm^{-1}.

HRMS (ESI) for $C_{29}H_{48}NaO_2Si^+$ $(M + Na)^+$ calc. 479.3316, found 479.3226.

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



8g

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 mg, 2.0 µmol) in CH_2Cl_2 (5.00 mL) gave cycloadduct **8g** after 6 h reaction time. After evaporation of solvent, column chromatography (silica gel, petrol ether/ethyl acetate 10:1) furnished product **8g** as colorless oil (22.3 mg, 65%).

R_f = 0.24 (petrol ether/diethyl ether 10:1).

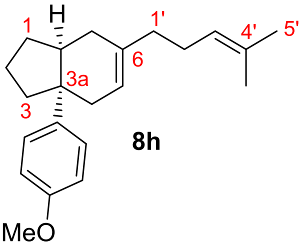
^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.63 (s, 3 H, Me), 1.71 (s, 3 H, Me), 1.91-2.05 (m, 6 H, 3-H, 1'-H, OAc), 2.07-2.33 (m, 6 H, 2-H, 3-H', 6-H, 2'-H), 2.59 (dt, *J* = 5.9, 10.1 Hz, 1 H, 1-H), 3.68 (dd, *J* = 7.0, 10.9 Hz, 1 H, CH_2OAc), 3.78 (s, 3 H, OMe), 3.90 (dd, *J* = 3.8, 10.9 Hz, 1 H, CH'$_2$OAc), 5.13 (m_c, 1 H, 3'-H), 5.43-5.51 (m, 1 H, 5-H), 6.83 (d, *J* = 8.7 Hz, 2 H, Ar), 7.10 (d, *J* = 8.7 Hz, 2 H, Ar) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$): δ 17.7 (q, Me), 20.8 (q, OAc), 25.7 (q, Me), 26.4 (t, C-2'), 32.3 (t, C-3), 34.4 (t, C-6), 37.5 (t, C-1'), 38.4 (d, C-2), 42.0 (d, C-1), 55.2 (q, OMe), 67.4 (t, CH_2OAc), 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 (s, Ar), 136.5 (s, C-4), 158.1 (s, Ar), 171.1 (s, OAc) ppm.

IR: ṽ 2905 (-C-H, =C-H), 1740 (C=O), 1515, 1245 cm^{-1}.

HRMS (ESI) for $C_{22}H_{30}NaO_3^+$ $(M + Na)^+$ calc. 365.2087, found 365.2095.

(3a*S**,7a*S**)-3a-(4-Methoxyphenyl)-6-(4-methylpent-3-enyl)-2,3,3a,4,7,7a-hexahydro-1*H*-indene (8h)



8h

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).

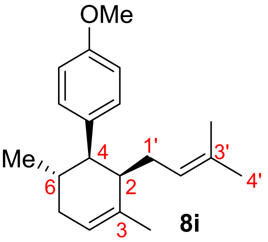
^{1}H-NMR (600 MHz, $CDCl_3$): δ 1.51-1.56 (m, 1 H, 1-H), 1.58 (s, 3 H, Me), 1.67 (s, 3 H, Me), 1.71-1.88 (m, 5 H, 1-H‘, 2-H, 3-H, 7-H’) 1.89-2.08 (m, 6 H, 3-H’, 7-H’, 1’-H, 2’-H) 2.13-2.25 (m, 2 H, 4-H, 7a-H), 2.31 (dd, *J* = 4.7, 18.2 Hz, 1 H, 4-H‘), 3.79 (s, 3 H, OMe), 5.05 (t, *J* = 6.9 Hz, 1 H, 3’-H), 5.42 (m_c, 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: ṽ 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.

1-[(1*R**,2*R**,6*S**)-3,6-dimethyl-2-(3-methylbut-2-enyl)cyclohex-3-enyl]-4-methoxybenzene (8i)



8i

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).

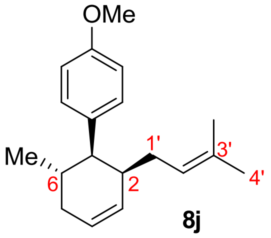
^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.85 (d, *J* = 6.4 Hz, 3 H, Me), 1.39 (s, 3 H, Me), 1.59 (s, 3 H, Me), 1.73 (s, 3 H, Me), 1.75-1.82 (m, 1 H, 3-H), 1.94-2.23 (m, 4 H, 2-H, 6-H, 1'-H), 2.23-2.40 (m, 1 H, 3-H‘), 2.64 (dd, *J* = 5.0, 10.5 Hz, 1 H, 1-H), 3.80 (s, 3 H, OMe), 4.89 (m_c, 1 H, 2'-H), 5.43 (m, 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, $CDCl_3$): δ 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: ṽ 2960, 2910 (-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)



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_2Cl_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).

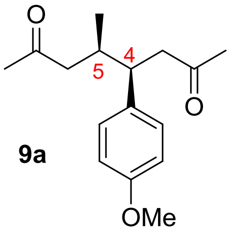
^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.92 (d, *J* = 6.6 Hz, 3 H, Me), 1.37 (s, 3 H, Me), 1.63 (s, 3 H, Me), 1.72-1.94 (m, 3 H, 3-H, 1'-H), 2.10 (m_c, 1 H, 2-H), 2.19-2.35 (m, 2 H, 3-H‘, 6-H), 2.70 (dd, *J* = 5.5, 9.0 Hz, 1 H, 1-H), 3.79 (s, 3 H, OMe), 5.01 (m_c, 1 H, 2'-H), 5.63-5.73 (m, 1 H, C-4), 5.74-5.82 (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, $CDCl_3$): δ 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), 131.9 (s, C-3'), 135.6 (s, Ar), 157.6 (s, Ar) ppm.

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

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

(4*R**,5*R**)-4-(4-Methoxyphenyl)-5-methyloctane-2,7-dione (9a)



9a

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_2Cl_2 (3.00 mL) gave intermediate cycloadduct **8a**[2] 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_2O/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).

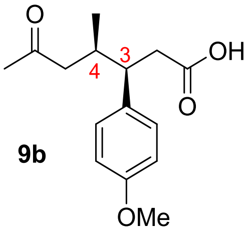
^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.75 (d, *J* = 6.6 Hz, 3 H, Me), 1.99 (s, 3 H, 1-H), 2.10 (s, 3 H, 8-H), 2.11-2.19 (m, 1 H, 6-H), 2.26 (m$_c$, *J* = 6.3 Hz, 1 H, 5-H), 2.42 (dd, *J* = 4.8, 16.0 Hz, 1 H, 6-H'), 2.69 (dd, *J* = 5.9 Hz, 16.0 Hz, 1 H, 3-H), 2.81 (dd, *J* = 8.8 Hz, 16.0 Hz, 1 H, 3-H'), 3.07 (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: ṽ 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.

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



9b

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_3NO_2 (3.00 mL) gave intermediate cycloadduct **8b**[2] 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_2O/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 (petrol ether/ethyl acetate/acetic acid 75:25:1).

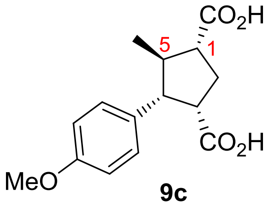
^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.77 (d, *J* = 6.7 Hz, 3 H, 7-H), 2.09 (s, 3 H, Ac), 2.13 (t, *J* = 8.3 Hz, 1 H, 5-H), 2.31 (m, 1 H, 4-H), 2.41 (dd, *J* = 4.9, 16.0 Hz, 1 H, 5'-H), 2.60-2.76 (m, 2 H, 2-H), 3.04 (dd, *J* = 6.1, 8.7 Hz, 1 H, 3-H), 3.78 (s, 3 H, OMe), 6.82 (d, *J* = 8.7 Hz, 2 H, Ar), 7.04 (d, *J* = 8.7 Hz, 2 H, Ar), 9.32 (br s, 1 H, OH) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$): δ 16.4 (q, Me), 30.4 (q, C-7), 33.5 (d, C-4), 37.8 (t, C-2), 45.0 (d, C-3), 48.7 (t, 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: ṽ 2960 (-C-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.

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



9c

Tandem RCDA/oxidative cleavage according to GP 3:

Alkene **6a** (37.1 mg, 0.25 mmol), cyclopentadiene (**7c**, 63.1 µL, 49.6 mg, 0.75 mmol) and $Ru(bpz)_3(PF_6)_2$ (2.2 mg, 2.5 µmol) in CH_3NO_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_2O/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%). *Trace signals resulting from C,C-cleavage of the exo-isomer of* **8c** *are detectable in NMR spectra.*

R$_f$ = 0.15 (petrol ether/ethyl acetate/acetic acid 75:25:1).

^{1}H-NMR (300 MHz , DMSO-*d*$_6$): δ 0.89 (d, *J* = 6.0 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 Hz, 1 H, 4-H), 2.99-3.12 (m, 1 H, 3-H), 3.33 (br. s, OH), 3.71 (s, 3 H, OMe), 6.83 (d, *J* = 8.7 Hz, 2 H, Ar), 7.08 (d, *J* = 8.7 Hz, 2 H, Ar), 12.00 (br. s, OH) ppm.

^{13}C-NMR (100 MHz, DMSO-*d*$_6$) δ 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.

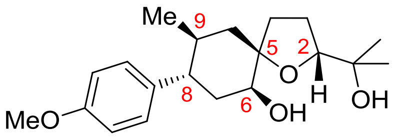
IR: ṽ 2960 (O-H), 2670 (C-H) 1705 (C=O), 1515, 1245, 1180.

HRMS (ESI) for $C_{15}H_{18}NaO_5^+$ $(M + Na)^+$ calc. 301.1046, found 301.0889.

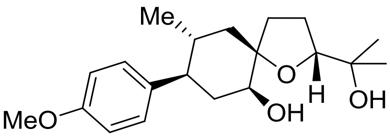
(2*R**,5*R**,6*S**,8*S**,9*S**)-2-(2-Hydroxypropan-2-yl)-8-(4-methoxyphenyl)-9-methyl-1-oxaspiro[4.5]decan-6-ol (10a)

and

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



10a



10a'

Cyclisation according to GP 2:

Cycloadduct **8d**[2] (175 mg, 0.62 mmol), RuCl$_3$ (1.3 mg, 6.2 µmol) and NaIO$_4$ on wet silica (2.11 g, 1.35 mmol) in 9:1 THF/CH$_2$Cl$_2$ (12.2 mL) gave **10a**,**a'** after 2 h reaction time (*dr* 1:1.2 by crude ^{1}H NMR). Column chromatography (silica gel, petrol ether/ethyl acetate 5:1 → 1:1) 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 CH$_2$Cl$_2$ (3.00 mL) gave intermediate cycloadduct **8d**[2] after 2 h reaction time. After evaporation of solvent, crude cycloadduct **8d** (max. 0.25 mmol) and NaIO$_4$ on wet silica (1.95 g, 1.25 mmol) in 9:1 THF/CH$_2$Cl$_2$ (5.00 mL) gave **10a**,**a'** after 18 h reaction time (*dr* 1:1.2 by crude ^{1}H NMR). Column chromatography (silica gel, petrol ether/ethyl acetate 5:1 → 1:1) furnished separable products **10a** (18.1 mg) and **10a'** (17.1 mg) as colorless oils, combined yield 42%.

10a:

R$_f$ = 0.24 (petrol ether/ethyl acetate 1:1).

^{1}H-NMR (400 MHz, CDCl$_3$): 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$_c$, 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.

^{13}C-NMR (100 MHz, CDCl$_3$): 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':

R$_f$ = 0.51 (petrol ether/ethyl acetate 1:1).

^{1}H-NMR (300 MHz, CDCl$_3$): 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.

^{13}C-NMR (75 MHz, CDCl$_3$): 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’:

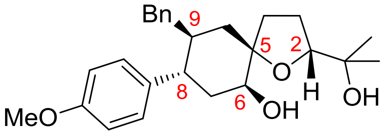
IR: ṽ 3335 (O-H), 2925, 2865 (-C-H, =C-H), 1510, 1245 cm^{-1}.

HRMS (ESI) for $C_{20}H_{30}NaO_4^+$ (M + Na)$^+$ calc. 357.2036, found 357.2021.

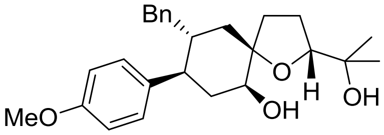
(2*R**,5*R**,6*S**,8*S**,9*S**)-9-Benzyl-2-(2-hydroxypropan-2-yl)-8-(4-methoxyphenyl)-1-oxaspiro[4.5]decan-6-ol (10b)

and

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



10b



10b'

Cyclisation according to GP 2:

Cycloadduct **8e** (32.9 mg, 0.09 mmol), $RuCl_3$ (0.2 mg, 0.9 µmol) and $NaIO_4$ on wet silica (314 mg, 0.20 mmol) in 9:1 THF/CH_2Cl_2 (2.00 mL) gave **10b**,**b’** after 3 h reaction time (*dr* 1:1.4 by crude ^{1}H 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 CH_2Cl_2 (3.00 mL) gave intermediate cycloadduct **8e** after 6 h reaction time. After evaporation of solvent, crude cycloadduct **8e** (max. 0.25 mmol) and $NaIO_4$ on wet silica (1.95 g, 1.25 mmol) in 9:1 THF/CH_2Cl_2 (5.00 mL) gave **10b**,**b’** after 18 h reaction time (*dr* 1:1.4 by crude ^{1}H 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:

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

^{1}H-NMR (600 MHz, $CDCl_3$): 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, 2 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, CH_2Ph), 2.56-2.63 (m, 1 H, CH_2Ph), 2.68-2.76 (m_c, 1 H, 8-H), 3.63 (m_c, 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.

^{13}C-NMR (150 MHz, $CDCl_3$): 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, CH_2Ph), 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_f = 0.38 (petrol ether/ethyl acetate 1:1).

^{1}H-NMR (600 MHz, $CDCl_3$): δ 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_2Ph), 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'_2Ph), 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 (d, J = 8.7 Hz, 2 H, Ar), 7.21 (t, J = 7.5 Hz, 2 H, Ar) ppm.

^{13}C-NMR (150 MHz, $CDCl_3$): δ 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_2Ph), 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.

10b,b':

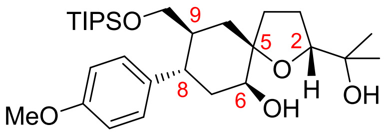
IR: ṽ 3330 (O-H), 2930 (-C-H, =C-H), 1510, 1250 cm $^{-1}$.

HRMS (ESI) for $C_{26}H_{34}NaO_4^+$ $(M + Na)^+$ calc. 433.2349, found 433.2353.

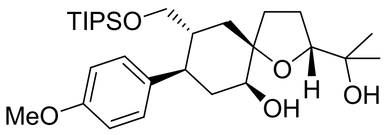
(2*R**,5*R**,6*S**,8*S**,9*S**)-2-(2-Hydroxypropan-2-yl)-8-(4-methoxyphenyl)-9-[(triisopropylsilyloxy)methyl]-1-oxaspiro[4.5]decan-6-ol (10c)

and

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



10c



10c'

Cyclisation according to GP 2:

Cycloadduct **8f** (35.6 mg, 0.078 mmol), $RuCl_3$ (0.16 mg, 0.8 µmol) and $NaIO_4$ on wet silica (268 mg, 0.17 mmol) in 9:1 THF/CH_2Cl_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 µL, 511 mg, 3.75 mmol) and $Ru(bpz)_3(BArF)_2$ (11.5 mg, 5.0 µmol) in CH_2Cl_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 $NaIO_4$ on wet silica (1.95 g, 1.25 mmol) in 9:1 THF/CH_2Cl_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 → 1:1) furnished separable products **10c** (16.0 mg) and **10c'** (16.0 mg) as colorless oils, combined yield 25 %.

10c:

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

^{1}H-NMR (600 MHz, $CDCl_3$): 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'), 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_2OTIPS), 3.37 (dd, *J* = 3.0, 9.7 Hz, 1 H, CH'$_2$OTIPS), 3.65 (m$_c$, 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.

^{13}C-NMR (150 MHz, $CDCl_3$): δ 11.9 (d, TIPS), 18.0 (q, TIPS), 24.5 (q, Me), 27.0 (t, C-3), 27.3 (q, Me), 34.3 (t, C-4), 35.2 (t, C-10), 37.8 (d, C-8), 38.7 (t, C-7), 43.4 (d, C-9), 55.3 (q, OMe), 65.6 (t, CH_2OTIPS), 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_f = 0.47 (petrol ether/ethyl acetate 2:1).

^{1}H-NMR (400 MHz, $CDCl_3$): 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'), 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_2OTIPS), 3.37 (dd, *J* = 2.5, 9.8 Hz, 1 H, CH'$_2$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.

^{13}C-NMR (100 MHz, $CDCl_3$) δ 11.9 (d, TIPS), 18.0(q, TIPS), 25.6 (q, Me), 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_2OTIPS), 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':

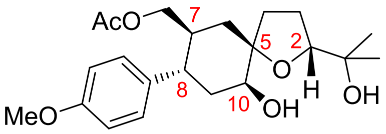
IR: ṽ 3355 (O-H), 2940, 2865 (-C-H, =C-H), 1510, 1250, 1070 cm^{-}1.

HRMS (ESI) for $C_{29}H_{50}NaO_5Si^+$ (M + Na)$^+$ calc. 529.3320, found 529.3271.

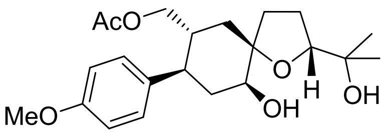
[(2*R,5*R**,7*S**,8*S**,10*S**)-10-Hydroxy-2-(2-hydroxypropan-2-yl)-8-(4-methoxyphenyl)-1-oxaspiro[4.5]decan-7-yl]methyl acetate (10d)**

and

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



10d



10d'

Cyclisation according to GP 2:

Cycloadduct **8g** (27.4 mg, 0.08 mmol), $RuCl_3$ (0.2 mg, 0.8 µmol) and $NaIO_4$ on wet silica (274 mg, 0.18 mmol) in 9:1 THF/CH_2Cl_2 (2.00 mL) gave **10d**,**d'** after 4 h reaction time (*dr* 1:1 by crude ^{1}H 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 CH_2Cl_2 (12.5 mL) gave intermediate cycloadduct **8g** after 6 h reaction time. After evaporation of solvent, crude cycloadduct **8g** (max. 0.25 mmol) and $NaIO_4$ on wet silica (1.95 g, 1.25 mmol) in 9:1 THF/CH_2Cl_2 (5.00 mL) gave **10d**,**d'** after 18 h reaction time (*dr* 1:1 by crude ^{1}H NMR). Column chromatography (silica gel, petrol ether/ethyl acetate 4:1 → 2:3) furnished separable products **10d** (7.5 mg) and **10d'** (8.0 mg) as colorless oils, combined yield 16%.

10d:

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

^{1}H-NMR (400 MHz, $CDCl_3$): 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, CH_2OAc), 3.67 (m_c, 1 H, 10-H), 3.78 (s, 3 H, OMe), 3.82 (dd, *J* = 3.6, 11.0 Hz, 1 H, CH'_2OAc), 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.

^{13}C-NMR (100 MHz, $CDCl_3$): 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, CH_2OAc), 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':

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

^{1}H-NMR (400 MHz, $CDCl_3$): 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, CH_2OAc), 3.78 (s, 3 H, OMe), 3.82 (dd, *J* = 3.5, 11.0 Hz, 1 H, CH'_2OAc), 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.

^{13}C-NMR (100 MHz, $CDCl_3$) 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, CH_2OAc), 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':**

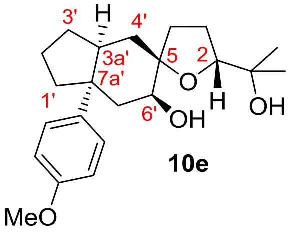
IR: ṽ 3360 (O-H), 2935 (-C-H, =C-H), 1735 (C=O), 1510, 1245, 1040 cm^{-1}.

HRMS (ESI) for $C_{22}H_{32}NaO_6^+$ $(M + Na)^+$ calc. 415.2091, found 415.2098.

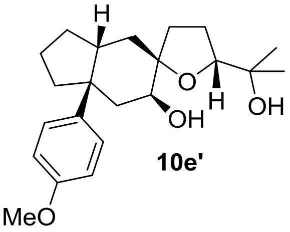
(2*R**,3a'*S**,5*R**,6'*S**,7a'*S**)-5-(2-Hydroxypropan-2-yl)-7a'-(4-methoxyphenyl)decahydro-3*H*-spiro[furan-2,5'-inden]-6'-ol (10e)

and

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



10e



10e'

Cyclisation according to GP 2:

Cycloadduct **8h** (13.0 mg, 0.042 mmol), $RuCl_3$ (0.1 mg, 0.4 µmol) and $NaIO_4$ on wet silica (144 mg, 0.09 mmol) in 9:1 THF/CH_2Cl_2 (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 CH_2Cl_2 (3.00 mL) gave intermediate cycloadduct **8h** after 24 h reaction time. After evaporation of solvent, crude cycloadduct **8h** (max. 0.25 mol) and $NaIO_4$ on wet silica (1.95 g, 1.25 mmol) in 9:1 THF/CH_2Cl_2 (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':

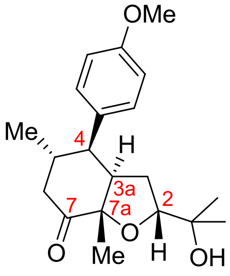
^1H-NMR (300 MHz, $CDCl_3$): δ 1.14 (s, 3 H, Me), 1.15 (s, 3 H, Me), 1.19-1.22 (m, 1 H, CH), 1.24-1.27 (m, 1 H, CH), 1.33 (s, 3 H, Me) 1.35-1.41 (m, 4 H, CH, Me), 1.49-1.82 (m, 13 H, CH), 1.82-1.99 (m, 7 H, CH), 1.99-2.13 (m, 4 H, CH), 2.27 (ddd, *J* = 3.5, 9.2, 12.0 Hz, 1 H, CH), 2.32-2.60 (m, 7 H, 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.

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 20.8 (t, CH_2), 21.4 (t, CH_2) 25.6 (q, Me), 25.6 (q, Me), 26.2 (t, CH_2), 26.5 (t, CH_2), 27.9 (q, Me), 28.0 (q, Me), 28.8 (t, CH_2), 29.6 (t, CH_2), 30.8 (t, CH_2), 35.4 (t, CH_2), 36.1 (t, CH_2), 36.8 (t, CH_2), 38.7 (t, CH_2), 41.0 (d, C-7a), 41.39 (t, CH_2), 41.6 (d, C-7a), 42.9 (t, CH_2), 43.3 (t, CH_2), 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: ṽ 3330 (O-H), 2955, 2875 (-C-H, =C-H), 1510, 1250, 1070, 1035 cm^{-1}.

HRMS (ESI) for $C_{22}H_{32}NaO_4^+$ $(M + Na)^+$ calc. 383.2193, found 383.2206.

(2*R**,3a*R**,4*R**,5*S**,7a*S**)-2-(2-Hydroxypropan-2-yl)-4-(4-methoxyphenyl)-5,7a-dimethylhexahydrobenzofuran-7(7a*H*)-one (10f)



10f

Cyclisation according to GP 2:

Cycloadduct **8i** (67.0 mg, 0.235 mmol, *endo*/*exo* 9:1), $RuCl_3$ (0.5 mg, 2.4 µmol) and $NaIO_4$ on wet silica (808 mg, 0.52 mmol) in 9:1 THF/CH_2Cl_2 (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 CH_2Cl_2 (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 $NaIO_4$ on wet silica (1.95 g, 1.25 mmol) in 9:1 THF/CH_2Cl_2 (5.00 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:

R_f = 0.31 (petrol ether/ethyl acetate 3:1).

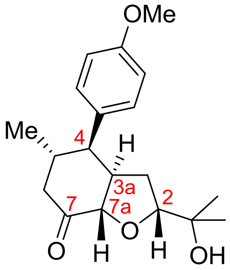
^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.86 (d, *J* = 5.8 Hz, 3 H, Me), 0.97 (s, 3 H, Me), 1.32 (s, 3 H, Me), 1.35-1.46 (m_c, 1 H, 3-H), 1.57 (s, 3 H, Me), 1.80 (m_c, 1 H, 3-H'), 2.34-2.57 (m, 4 H, 3a-H, 5-H, 6-H, 6'-H), 2.95 (dd, *J* = 4.7, 10.8 Hz, 1 H, 4-H), 3.47 (br. s, 1 H, OH), 3.70 (dd, *J* = 5.4, 10.4 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.

^{13}C-NMR (75 MHz, $CDCl_3$) 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: ṽ 3475 (O-H), 2975, 2935 (-C-H, =C-H), 1715 (C=O), 1515, 1250 cm $^{-1}$.

HRMS (ESI) for $C_{20}H_{28}NaO_4^+$ $(M + Na)^+$ calc. 355.1880, found 355.1888.

(2*R**,3a*R**,4*R**,5*S**,7a*S**)-2-(2-Hydroxypropan-2-yl)-4-(4-methoxyphenyl)-5-methylhexahydrobenzofuran-7(7a*H*)-one (10g)



10g

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 CH_2Cl_2 (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 $NaIO_4$ on wet silica (960 mg, 0.62 mmol) in 9:1 THF/CH_2Cl_2 (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).

^{1}H-NMR (600 MHz, $CDCl_3$): 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$_c$, 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.

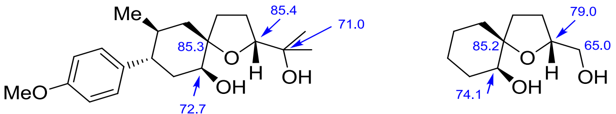
^{13}C-NMR (150 MHz, $CDCl_3$) δ 20.6 (q, Me), 24.4 (q, Me), 25.9 (t, C-3), 28.4 (q, Me), 33.4 (d, C-5), 47.7 (t, C-6), 49.9 (d, C-4), 50.8 (d, C-3a), 55.2 (q, OMe), 69.6 (s, C-2'), 82.8 (d, C-7a), 87.2 (d, C-2), 114.1 (d, Ar), 129.0 (d, Ar), 133.0 (s, Ar), 158.4 (s, Ar), 211.1 (s, C-7) ppm.

IR: ṽ 3465 (O-H), 2975, (-C-H, =C-H), 1715 (C=O), 1515, 1250 cm $^{-1}$.

HRMS (ESI) for $C_{19}H_{26}NaO_4^+$ $(M + Na)^+$ calc. 341.1723, found 341.1708.

4 Structural assignment

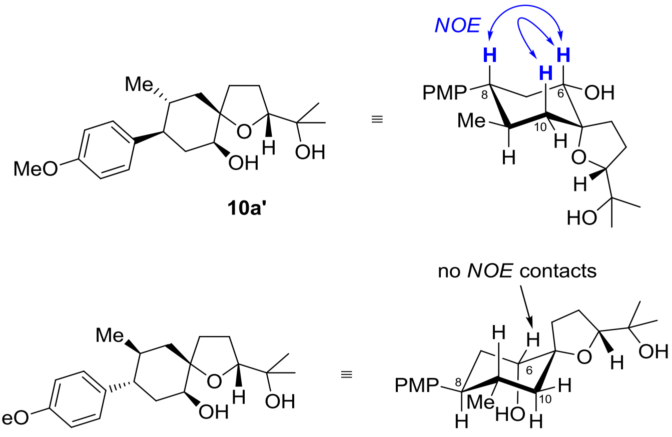
- Comparison of **10a** to known compounds:



10a **S3** ref. [11]

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

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



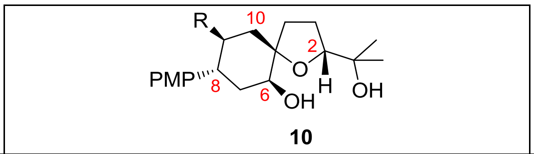
10a'

10a

Figure S4: Key NOE contacts in **10a'** and comparison with **10a**.

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



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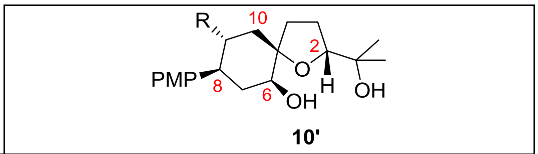

10'

R	#	2-H	6-H	8-H	C-6	C-8	C-10	#	2-H	6-H	8-H	C-6	C-8	C-10
Me	**10a**	3.90 (m)	**3.66 (m$_c$)**	2.53 (ddd)	**72.9**	43.5	40.8	**10a'**	3.84 (dd)	**3.48 (dd)**	2.08 (m)	**75.4**	49.4	46.2
Bn	**10b**	3.76 (t)	**3.63 (m$_c$)**	2.72 (m)	**72.6**	42.4	37.2	**10b'**	3.69 (dd)	**3.48 (dd)**	2.29 (m)	**75.2**	47.9	42.2
OTIPS	**10c**	3.93 (m)	**3.65 (m$_c$)**	2.72 (dt)	**72.7**	37.8	35.2	**10c'**	3.85 (dd)	**3.51 (dd)**	2.53 (dt)	**75.1**	43.0	40.5
OAc*	**10c**	3.92 (m)	**3.67 (m$_c$)**	2.81 (dt)	**72.6**	38.5	35.5	**10d'**	3.89 (dd)	**3.51 (dd)**	2.42 (dt)	**74.9**	43.9	40.5

*Position numbering adjusted for comparison in this table.

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[11] T. J. Donohoe and S. Butterworth, *Angew. Chem. Int. Ed.*, 2003, **42**, 948.

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

- RuO_4-mediated cyclisation of substrate **8d**:

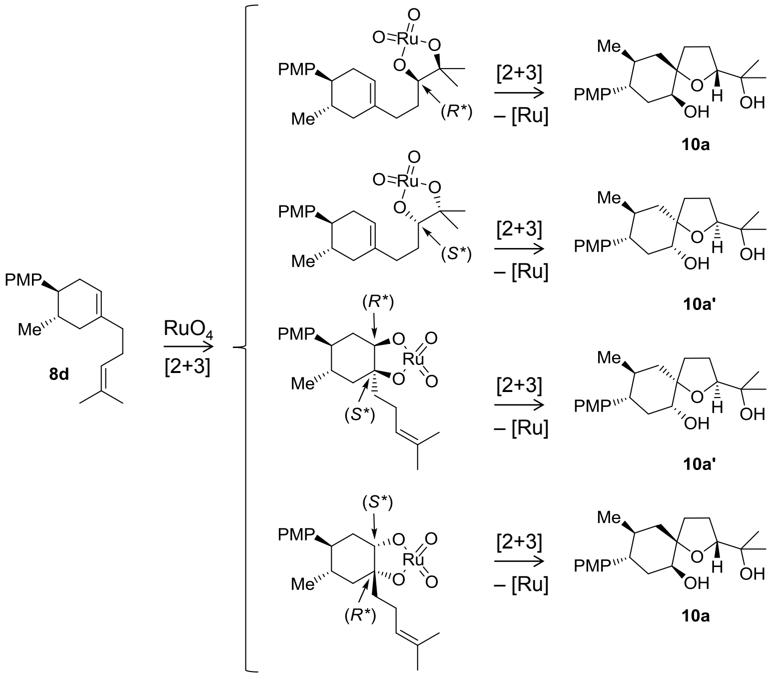

Figure S5: Possible cyclisation modes of cycloadduct **8d** with RuO_4. The shown four reaction pathways all appear conformationally accessible and productive.

- RuO_4-mediated cyclisation of substrate **8i**:

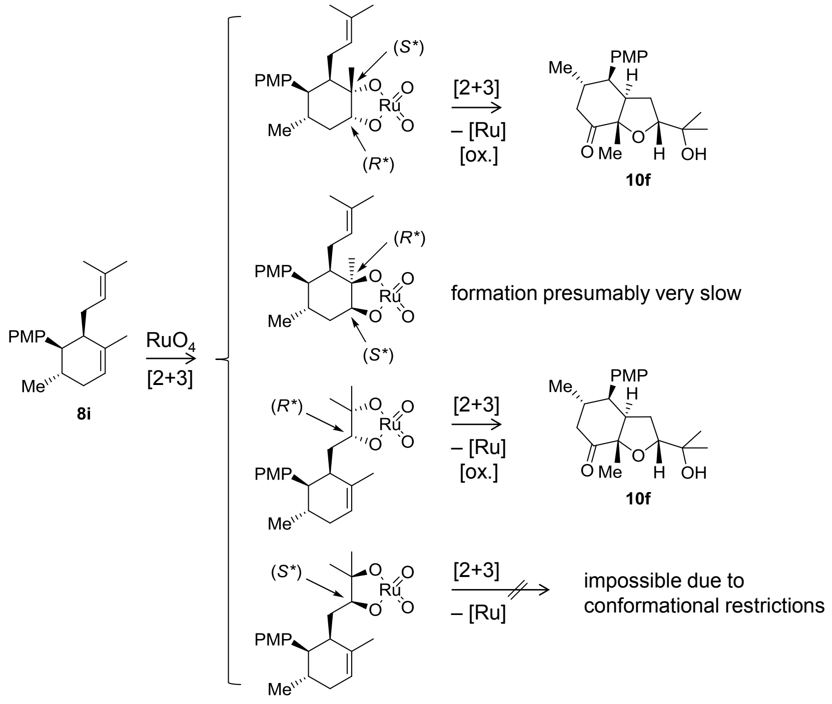

Figure S6: Possible cyclisation modes of cycloadduct **8i** with RuO_4. Out of four conceivable reaction pathways, only two appear possible and productive.

6 UV-Vis experiments

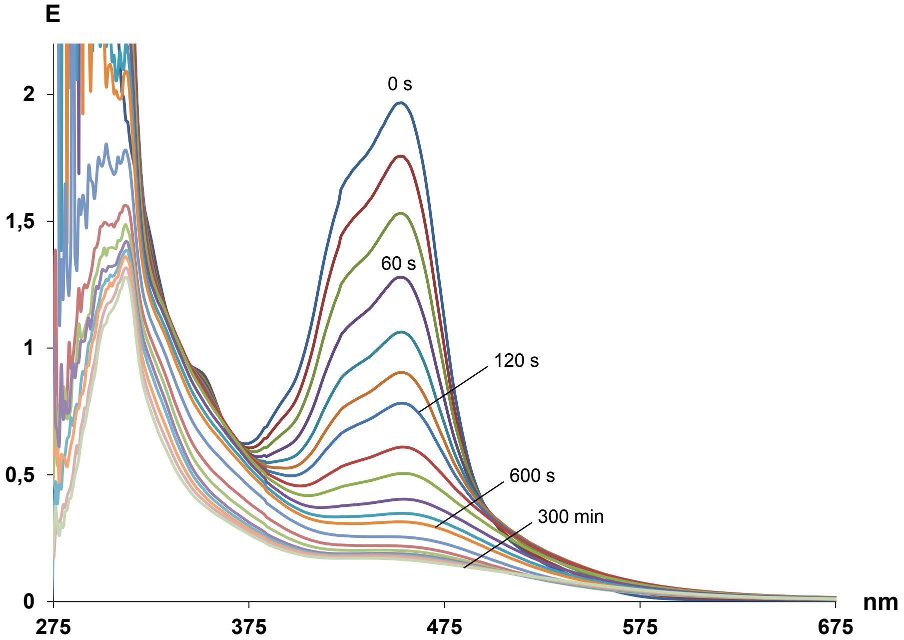

Figure S7: Bleaching of a solution of Ru(bpy)$_3$Cl$_2$·6H$_2$O (c = 1.534·10^{-4} mol·l^{-1}) and NaIO$_4$ (c = 8.626·10^{-3} mol·l^{-1}) in H$_2$O under irradiation with blue LED light (5.4 W / 0.87 cd / 450 ±25 nm, setup in Figure S1).

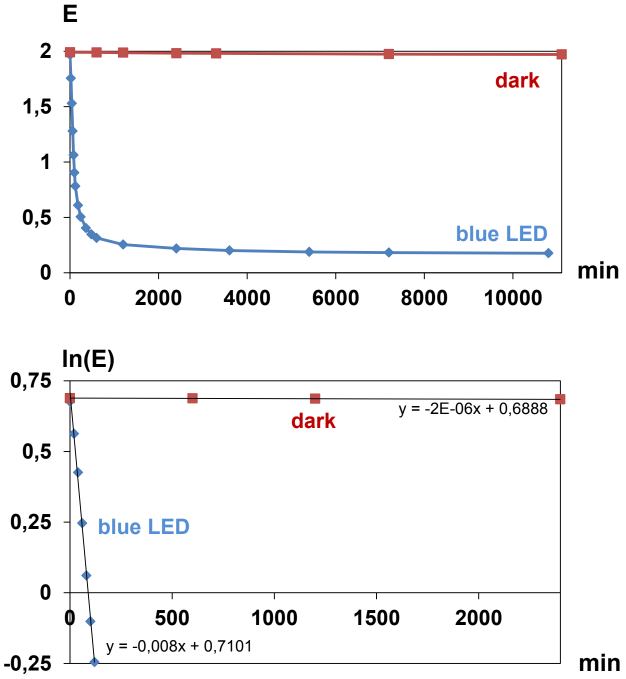

Figure S8: Comparison of irradiated and dark bleaching experiment, plot of 453 nm absorption maximum.

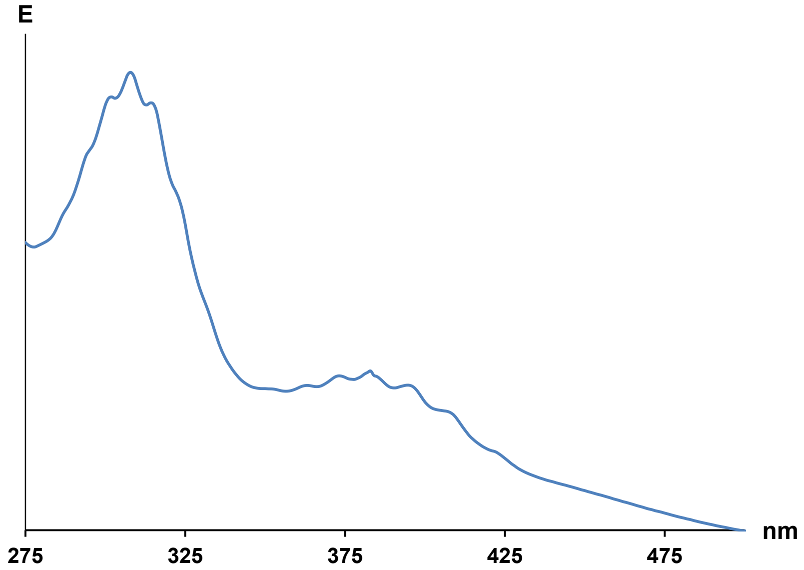

Figure S9: UV-Vis spectrum of RuO_4 after partitioning of the irradiated aqueous reaction mixture of Figure S7 between brine and $MeCN/CCl_4$ 1:1 (organic phase spectrum). For reference spectra see refs.[12],[13]

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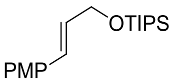
[12] A. G. F. Shoair and R. H. Mohamed, *Synth. Commun.*, 2006, **36**, 59.

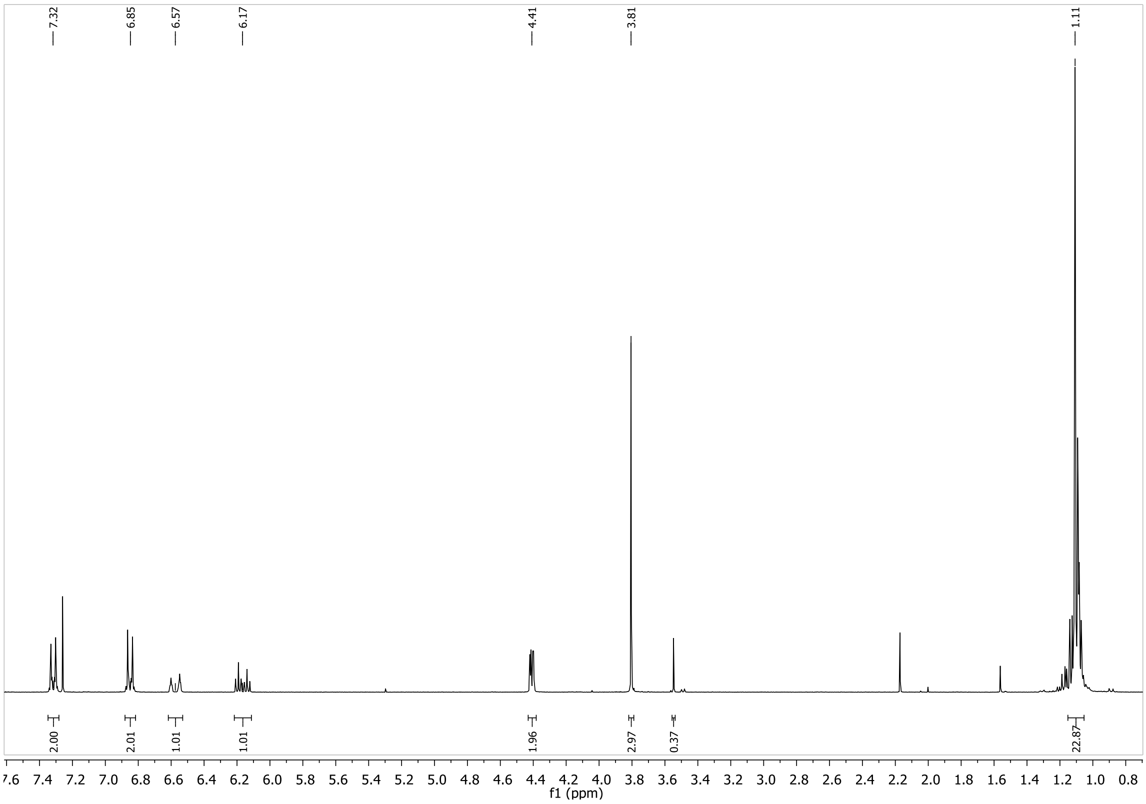
[13] R. E. Connick and C. R. Hurley, *J. Am. Chem. Soc.* **1952**, *74*, 5012.

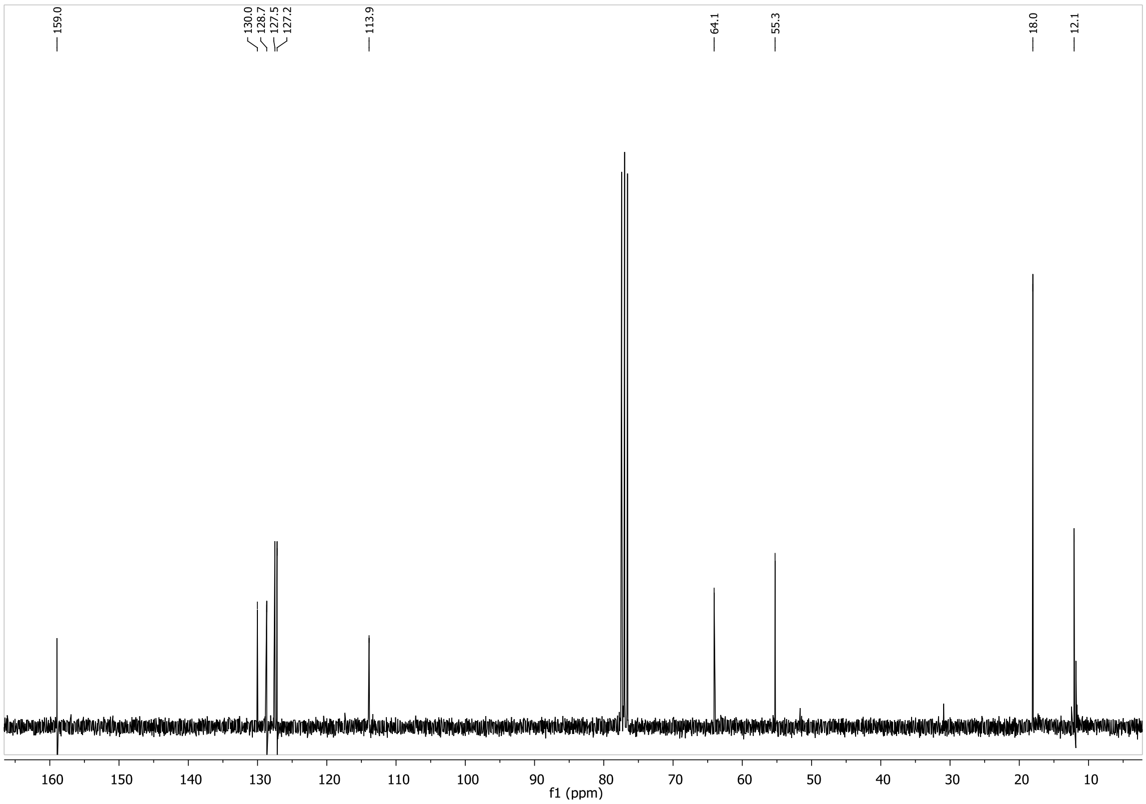
7 NMR spectra of new compounds

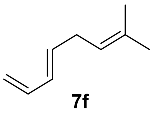


6c

^{1}H NMR (300 MHz in CDCl$_3$), ^{13}C NMR (75 MHz in CDCl$_3$)

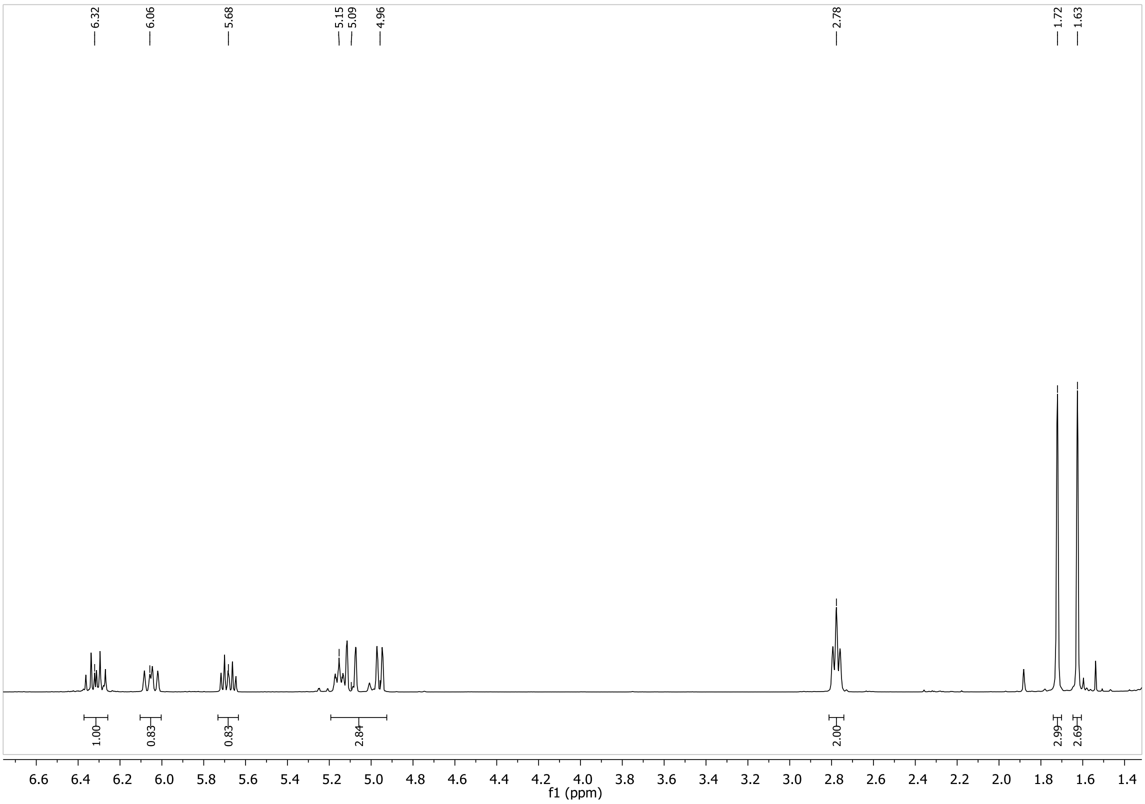


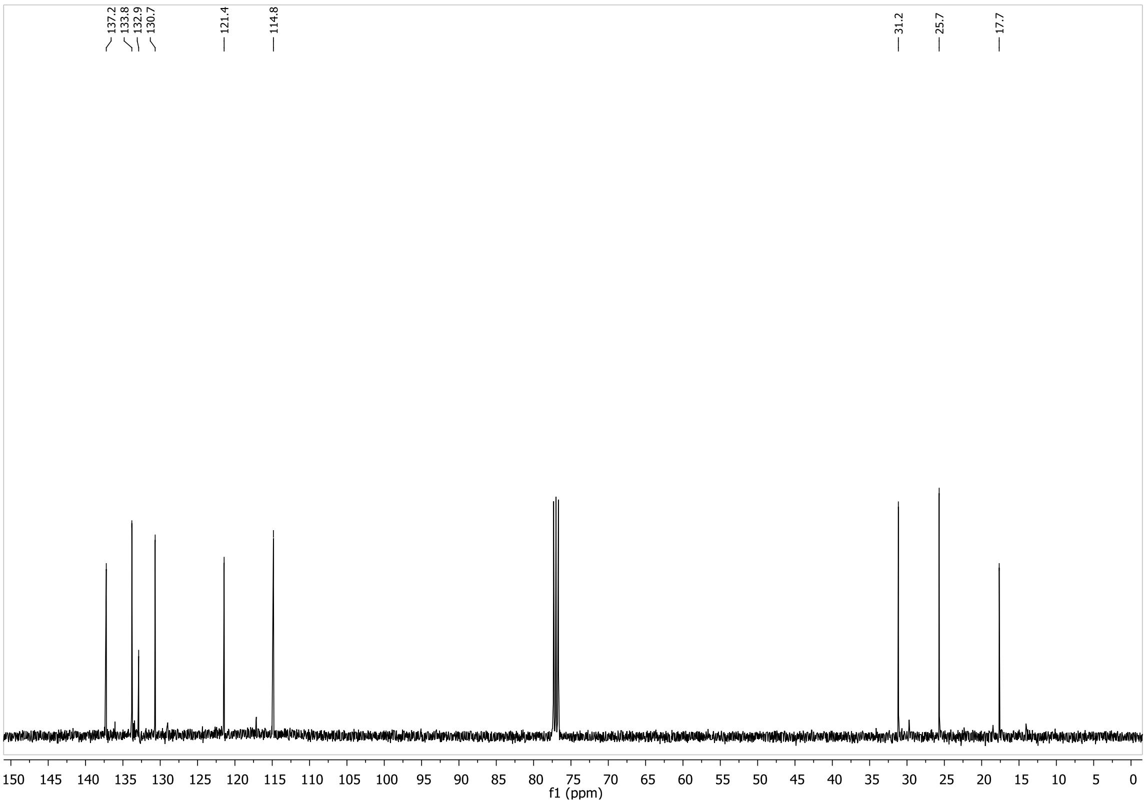


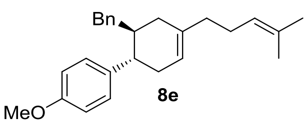


7f

^{1}H NMR (400 MHz in CDCl$_3$), ^{13}C NMR (100 MHz in CDCl$_3$)

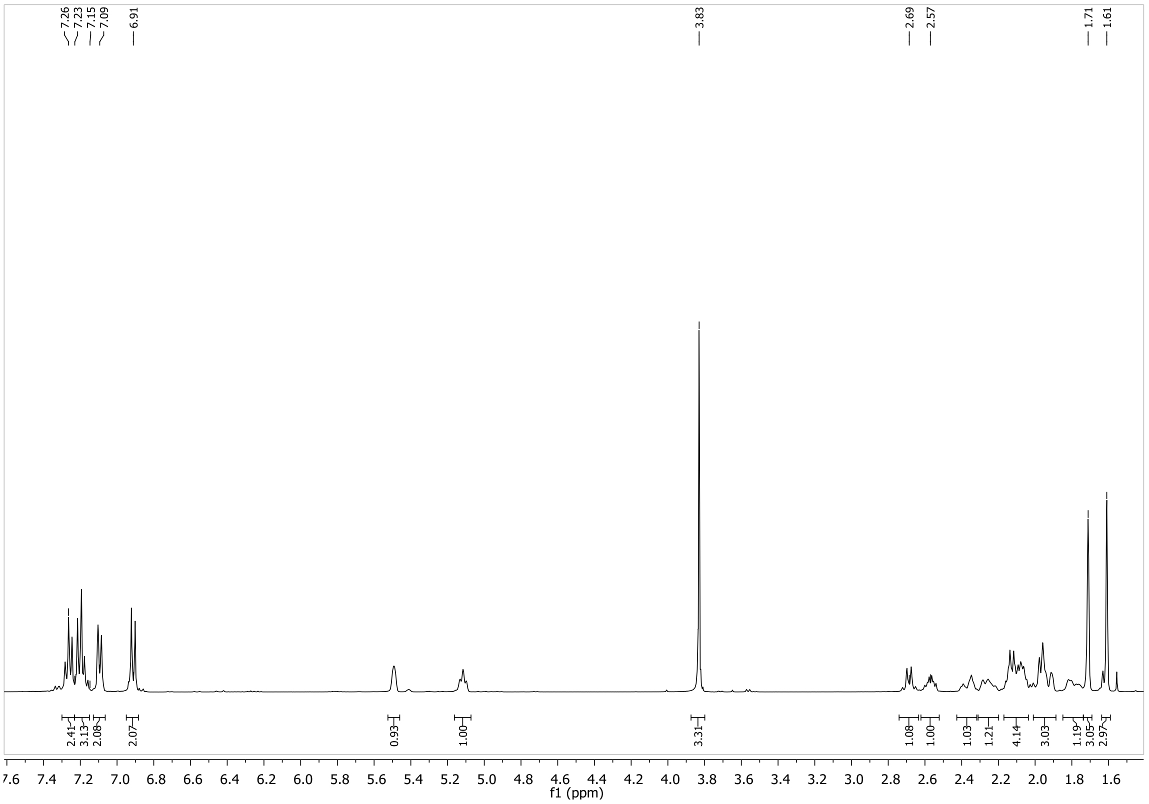


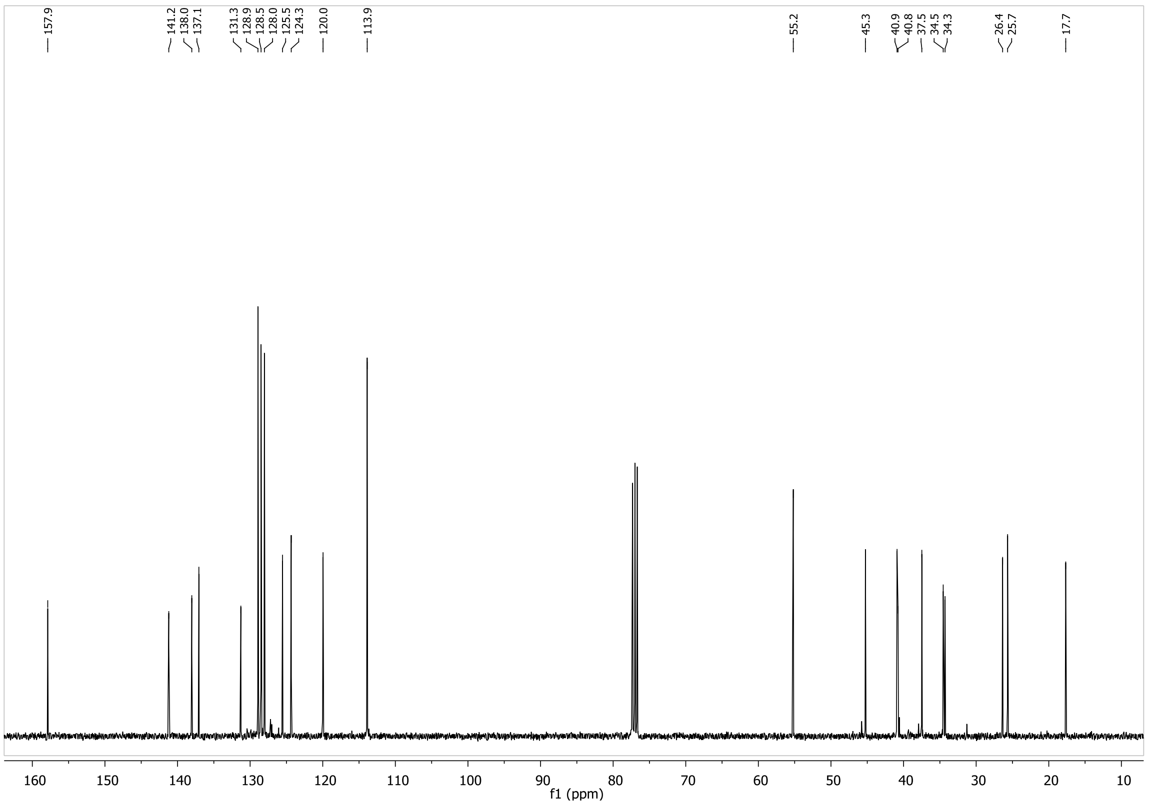


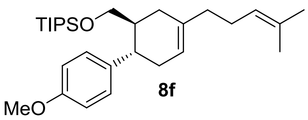


8e

^{1}H NMR (400 MHz in CDCl$_3$), ^{13}C NMR (100 MHz in CDCl$_3$)

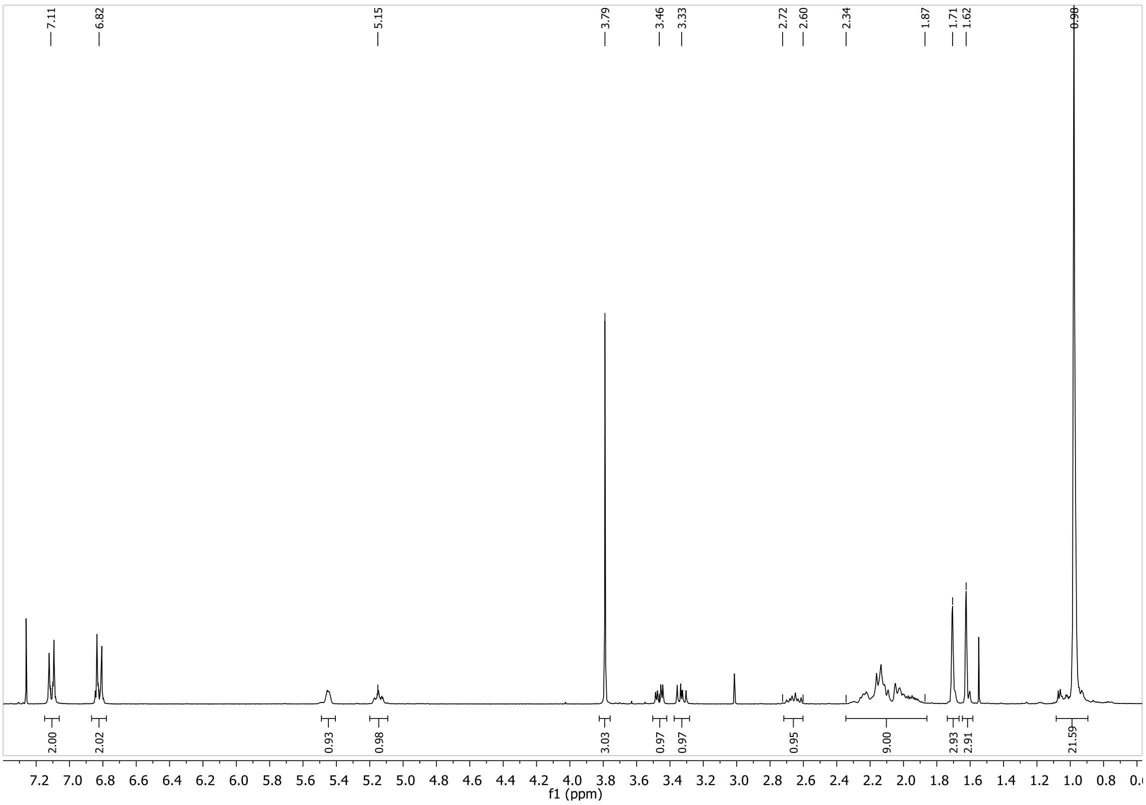


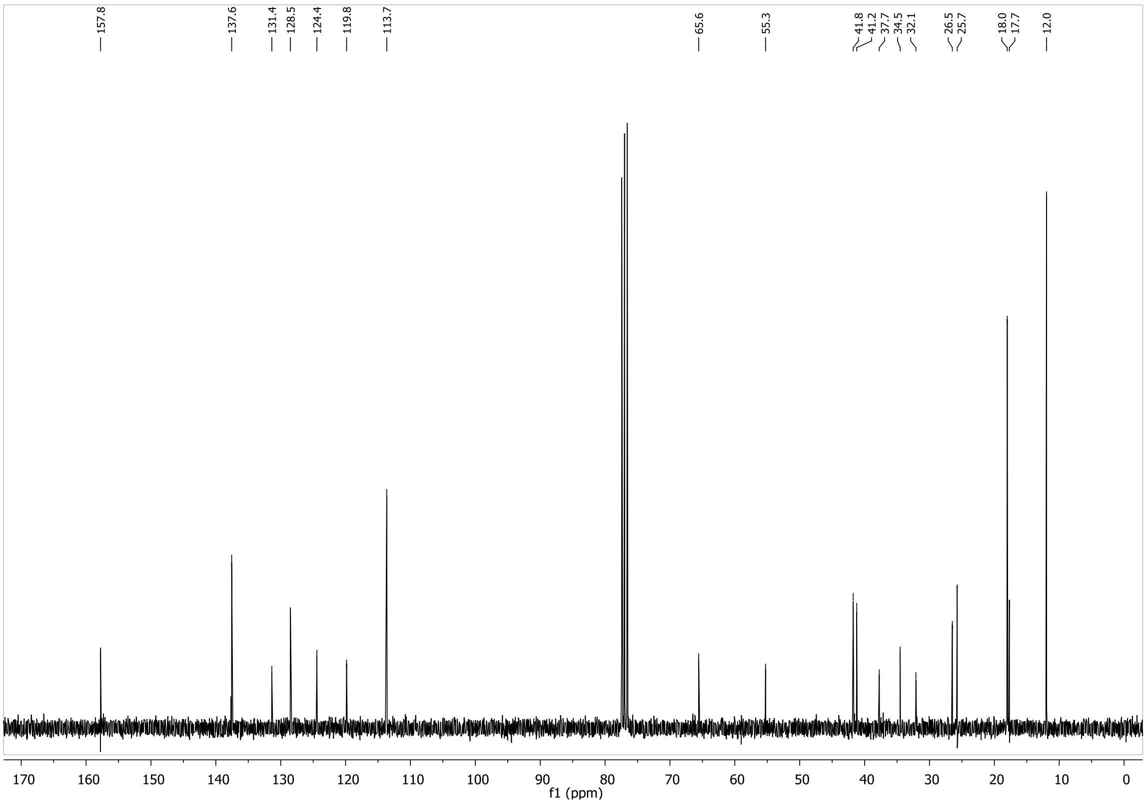


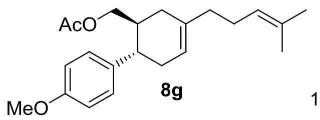


8f

^{1}H NMR (300 MHz in $CDCl_3$), ^{13}C NMR (75 MHz in $CDCl_3$)

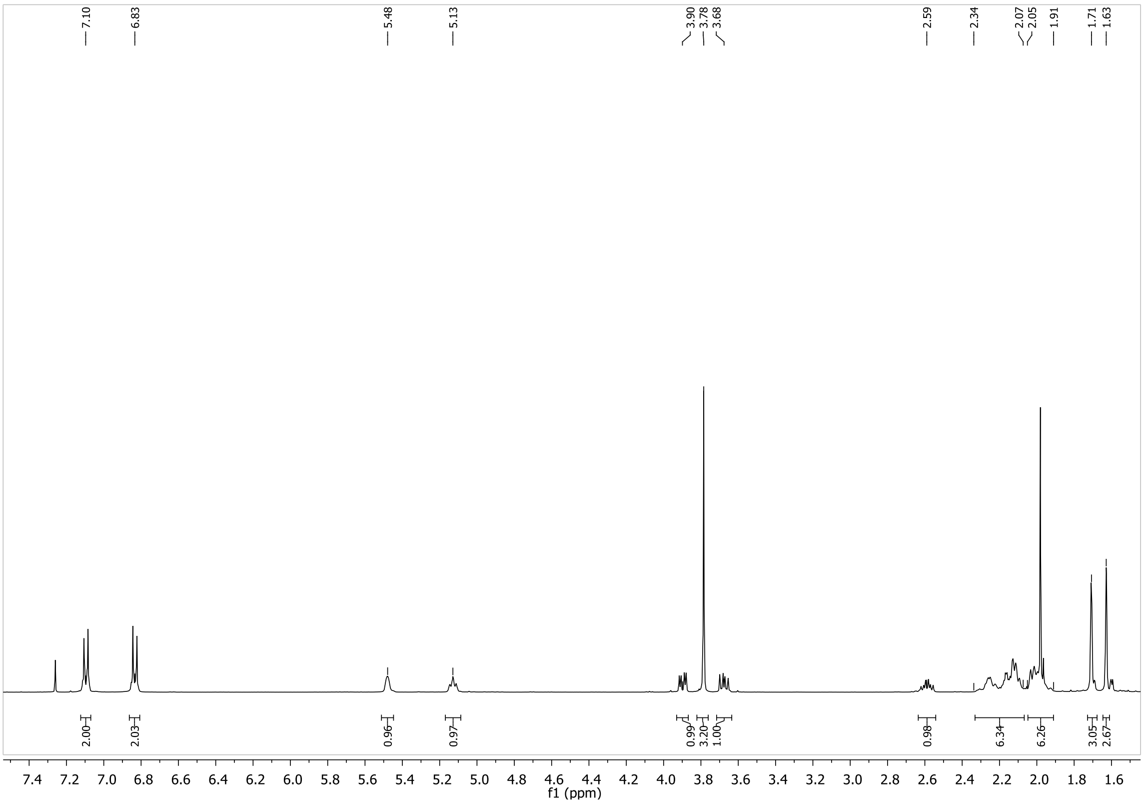


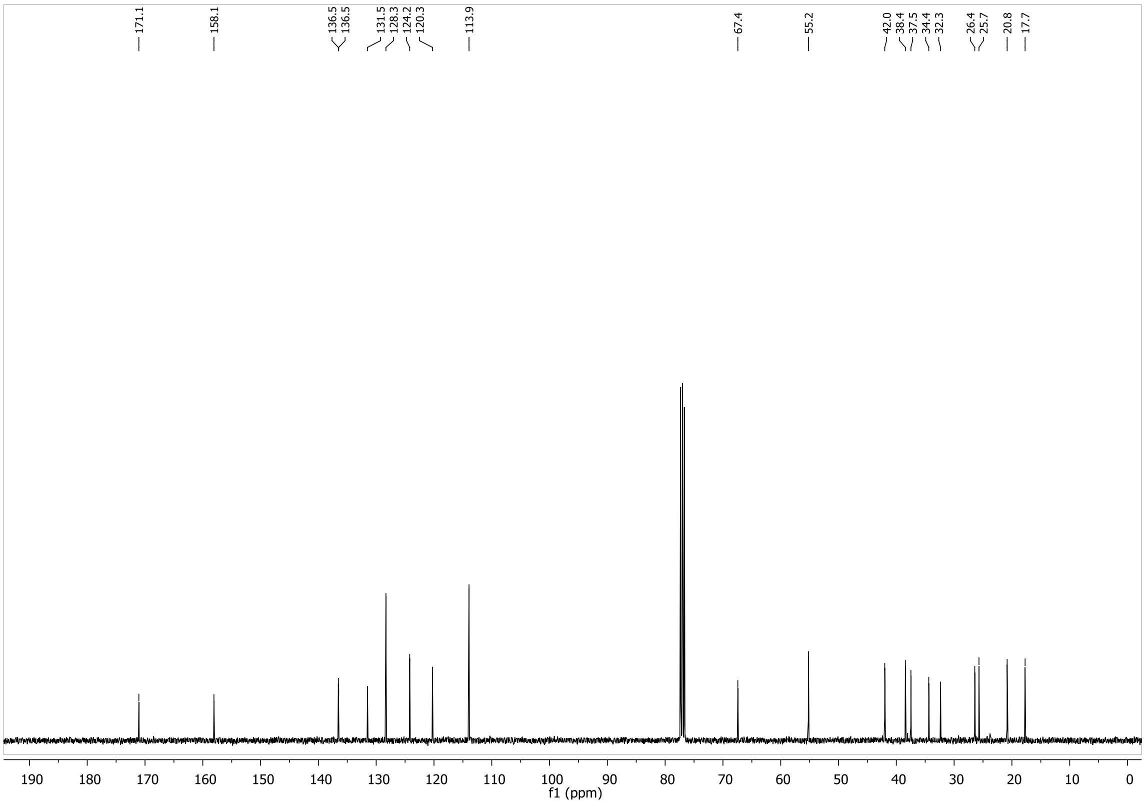


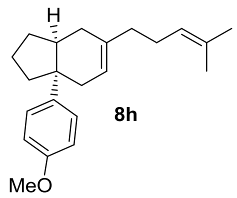


8g

^{1}H NMR (400 MHz in CDCl$_3$), ^{13}C NMR (100 MHz in CDCl$_3$)

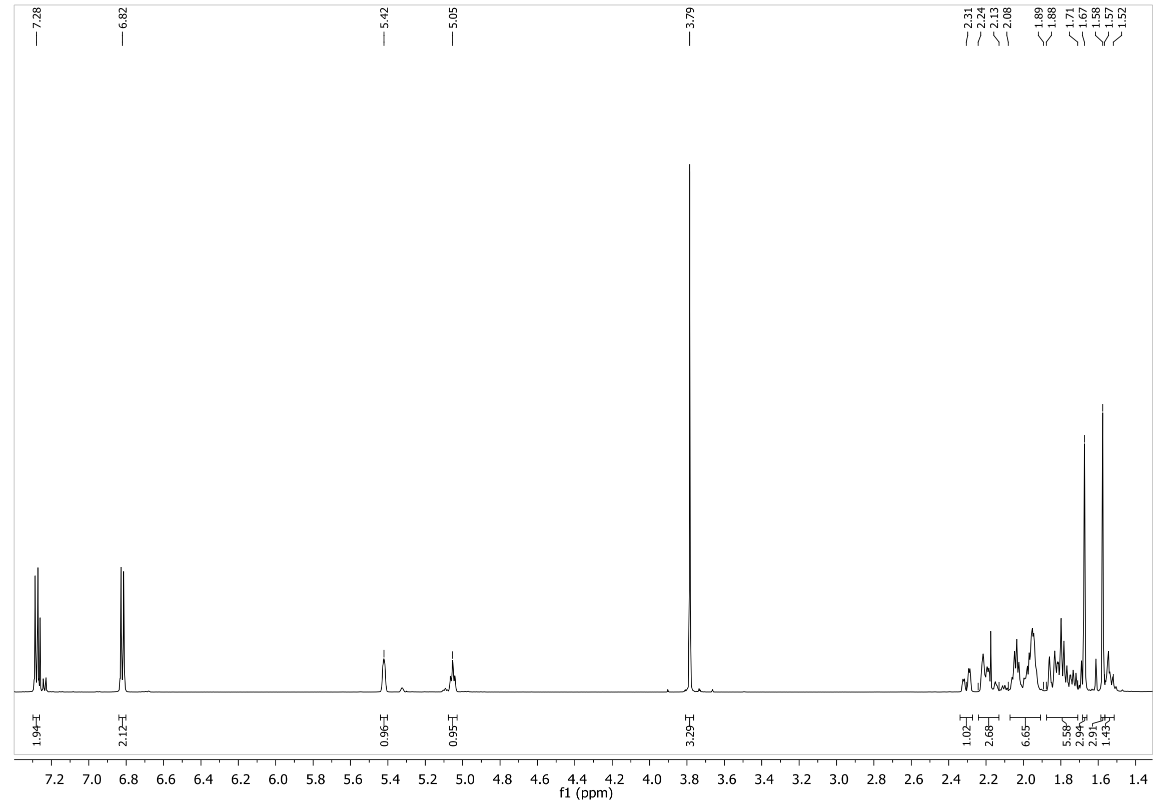


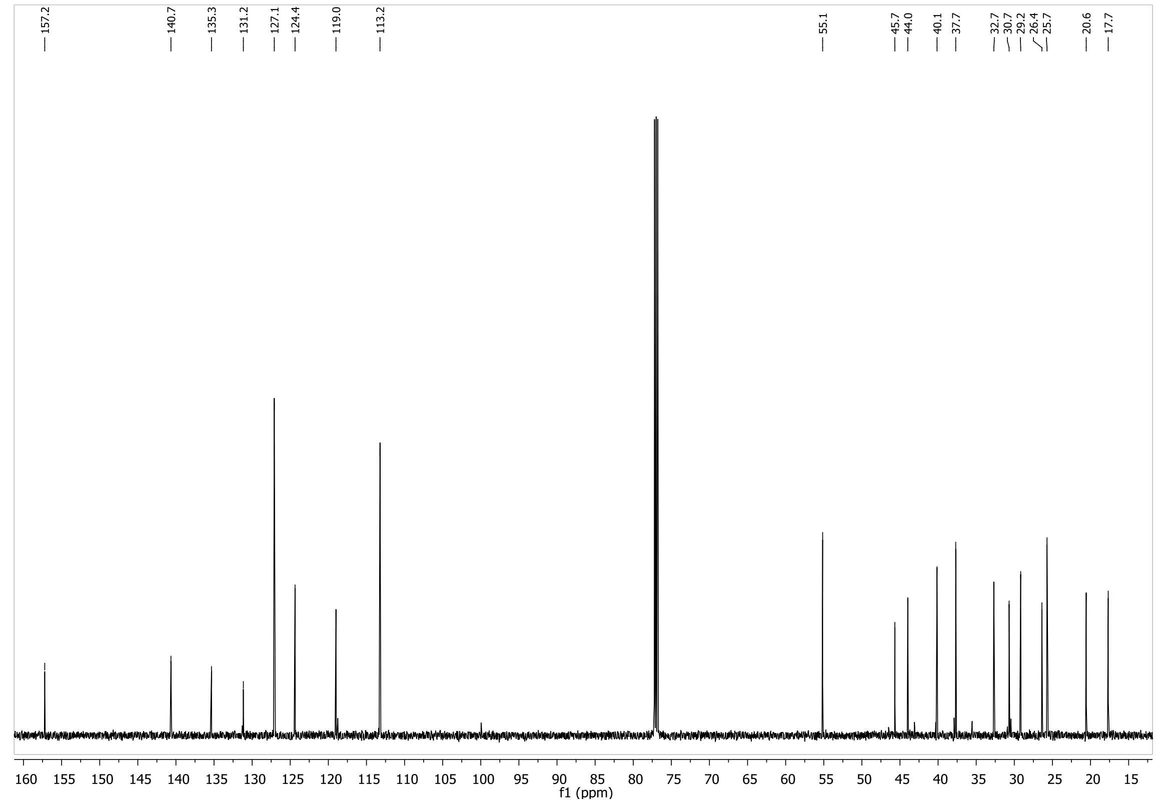


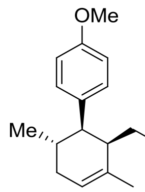


8h

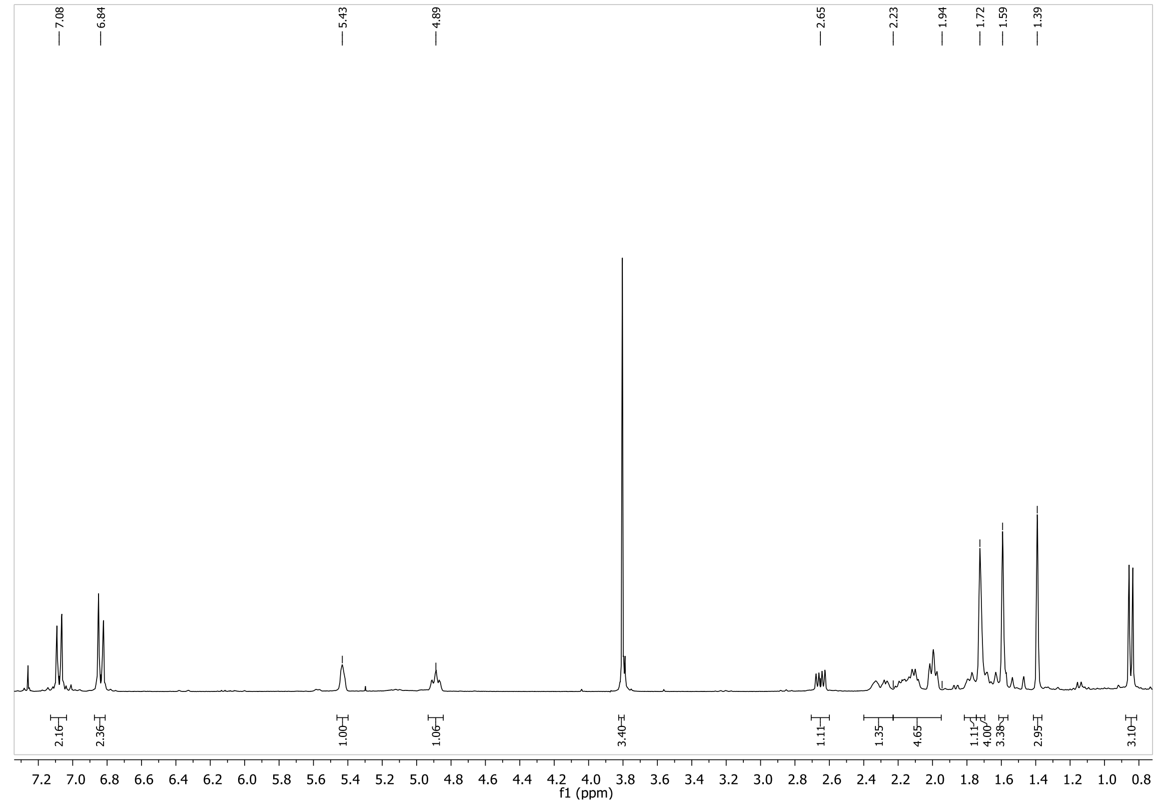
^{1}H NMR (600 MHz in CDCl$_3$), ^{13}C NMR (150 MHz in CDCl$_3$)

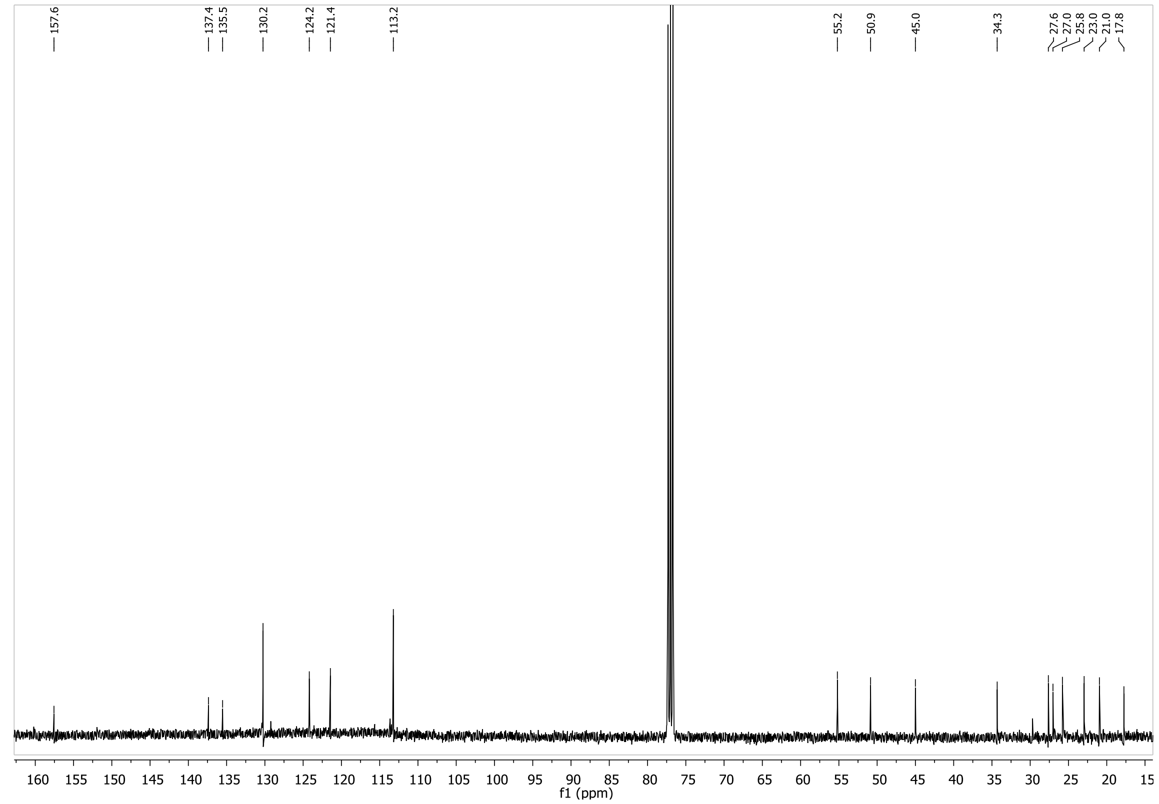


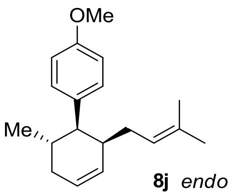




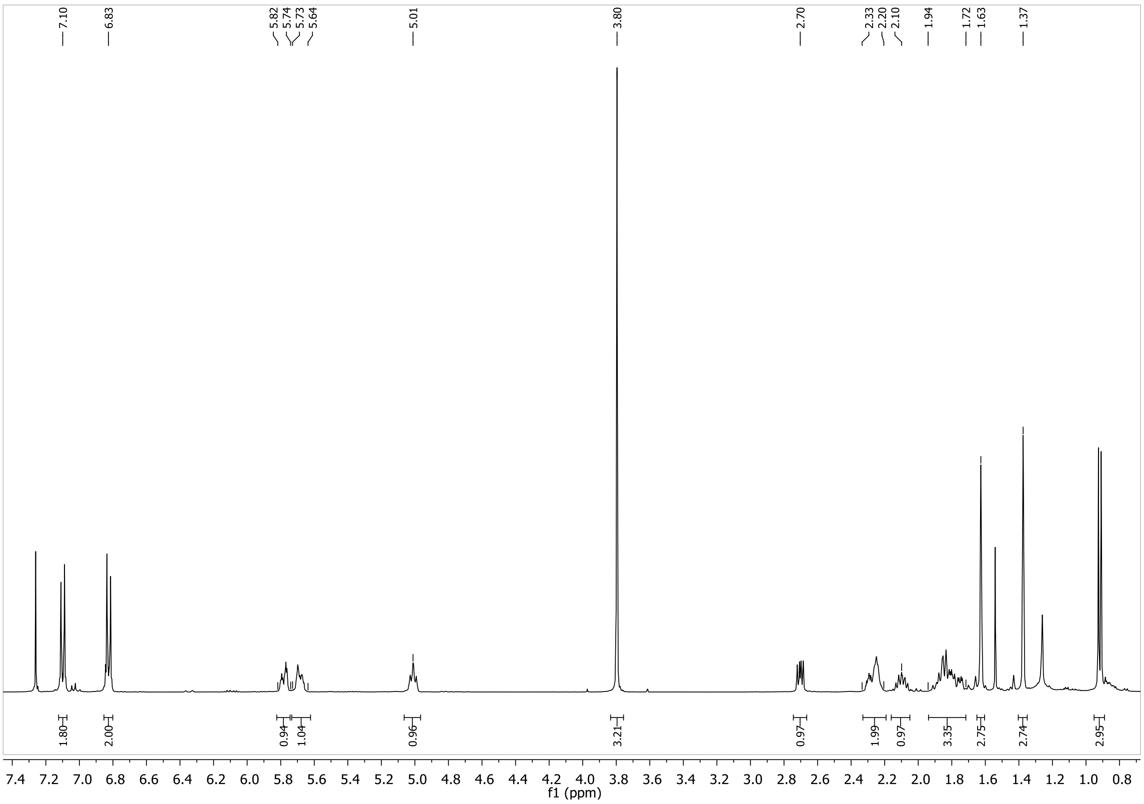
8i *endo*/*exo* 9:1 ^{1}H NMR (300 MHz in $CDCl_3$), ^{13}C NMR (75 MHz in $CDCl_3$)

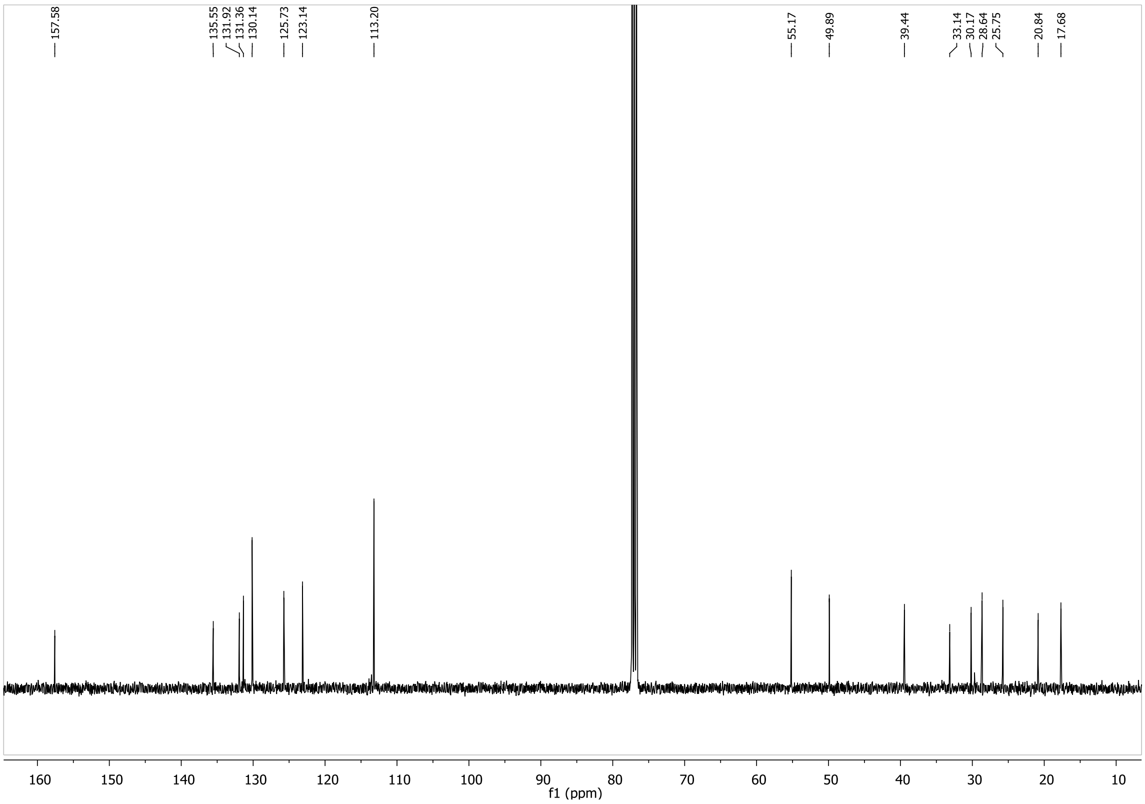


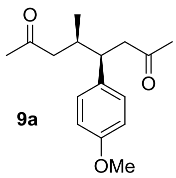




8j *endo*/*exo* 9:1 ^{1}H NMR (400 MHz in CDCl$_3$), ^{13}C NMR (100 MHz in CDCl$_3$)

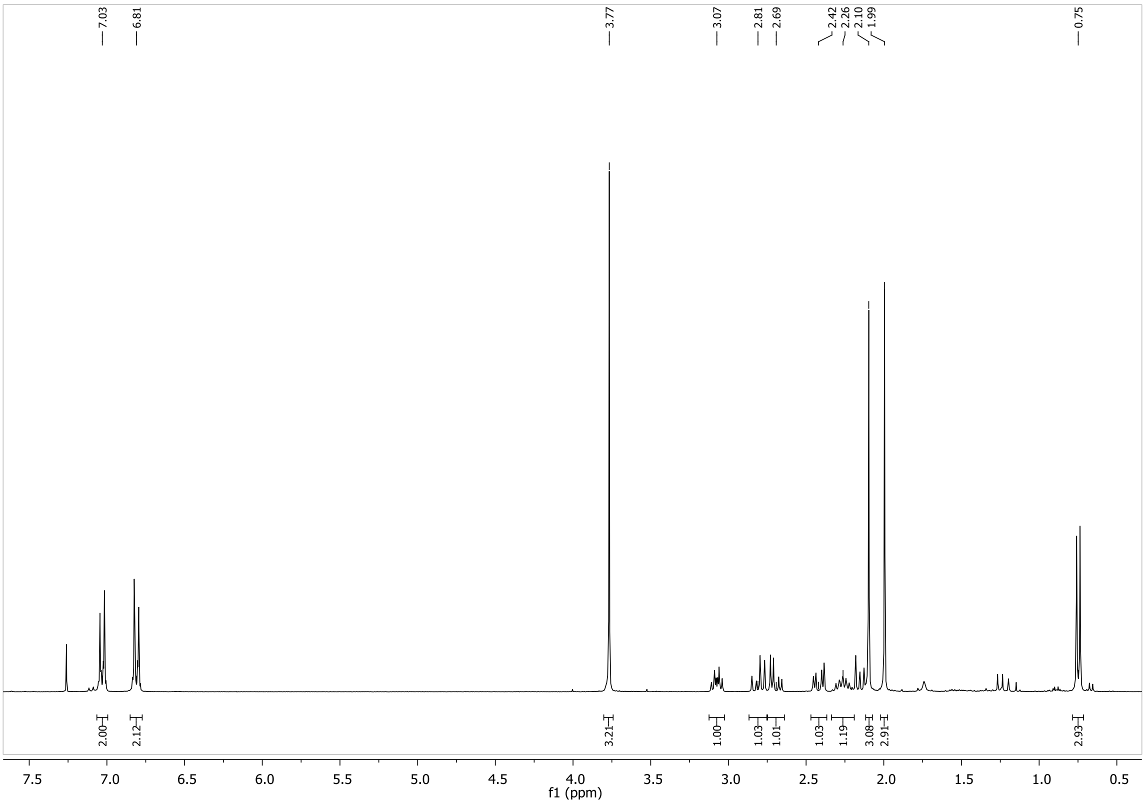


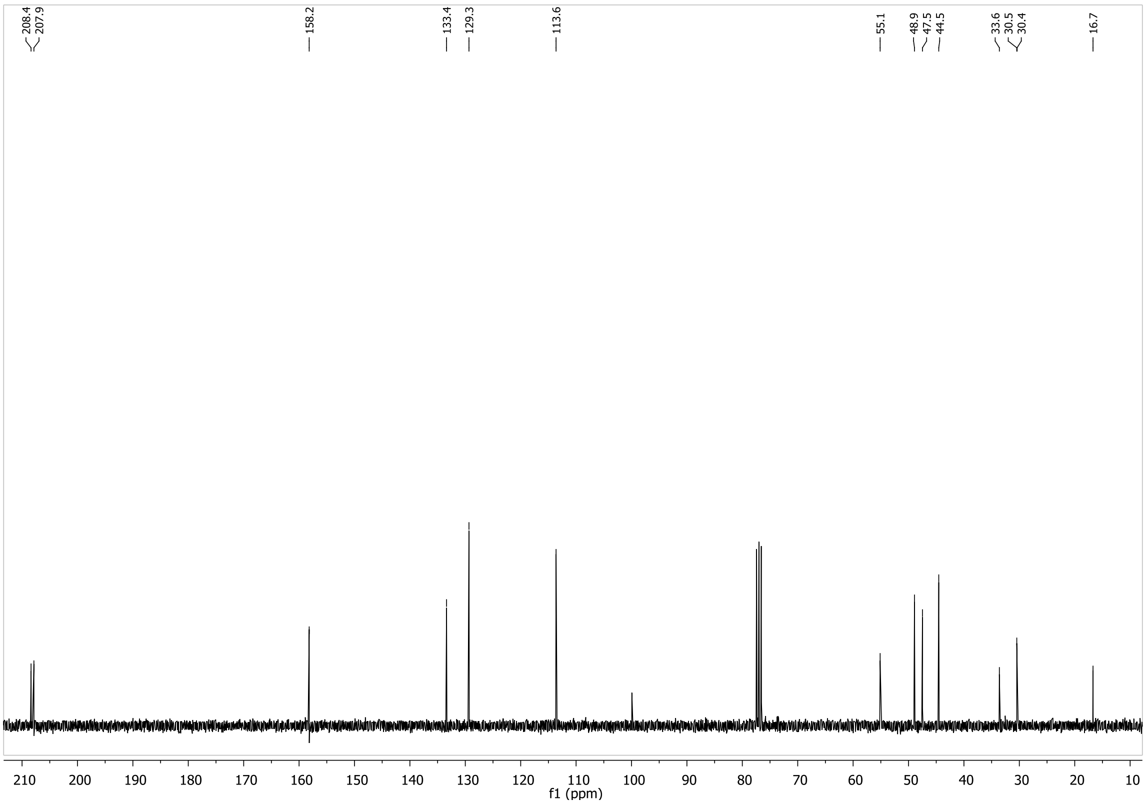


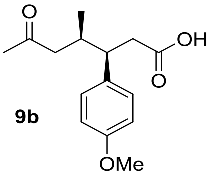


9a

^{1}H NMR (300 MHz in CDCl$_3$), ^{13}C NMR (75 MHz in CDCl$_3$)

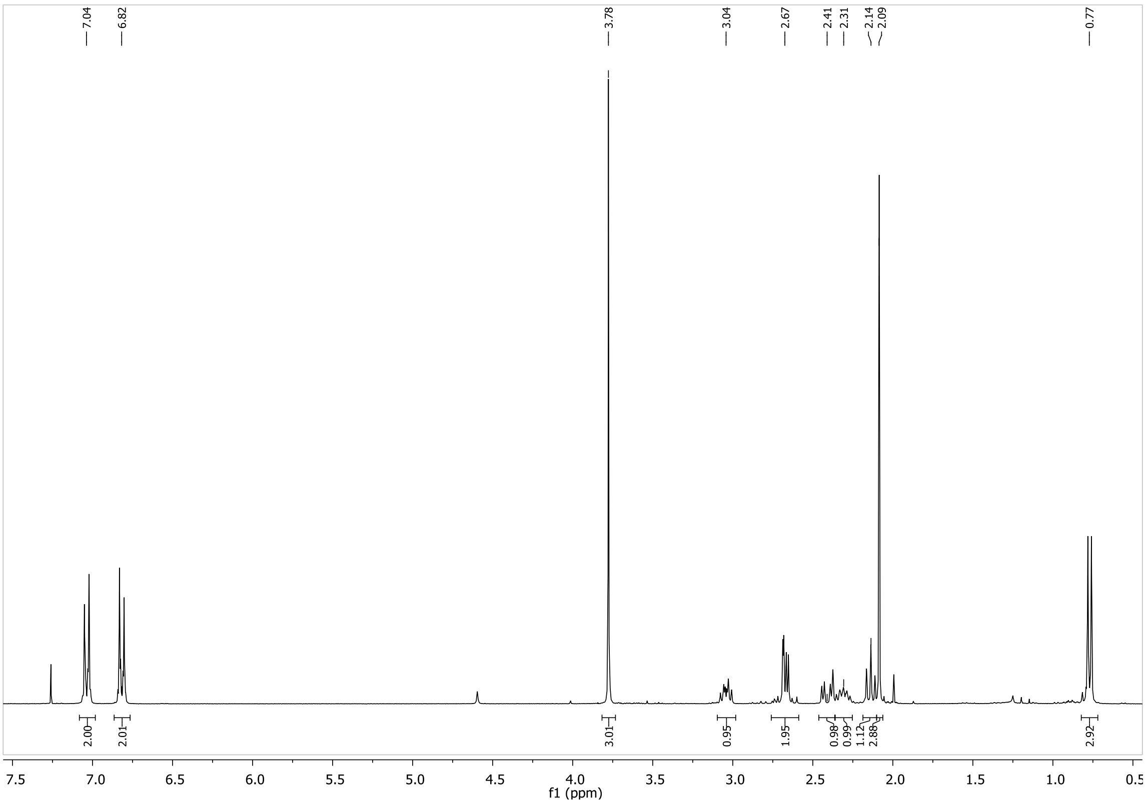


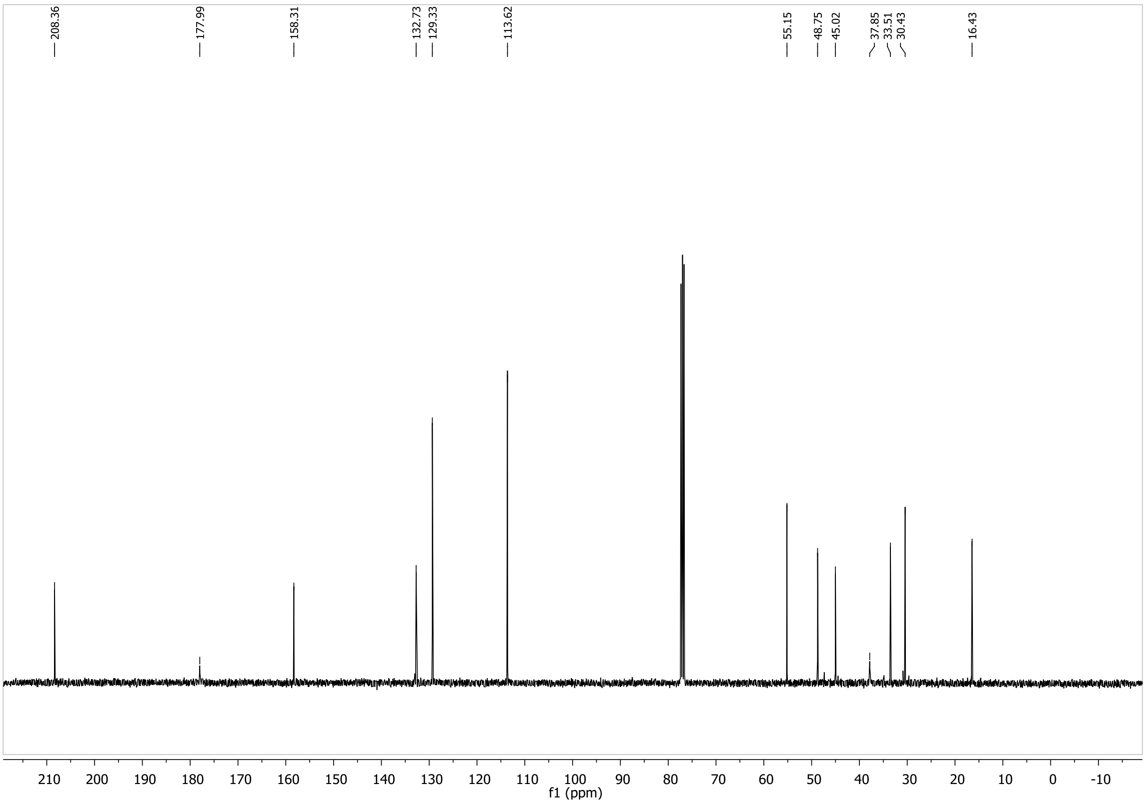


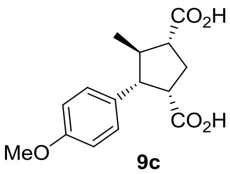


9b

^{1}H NMR (300 MHz in CDCl$_3$), ^{13}C NMR (100 MHz in CDCl$_3$)



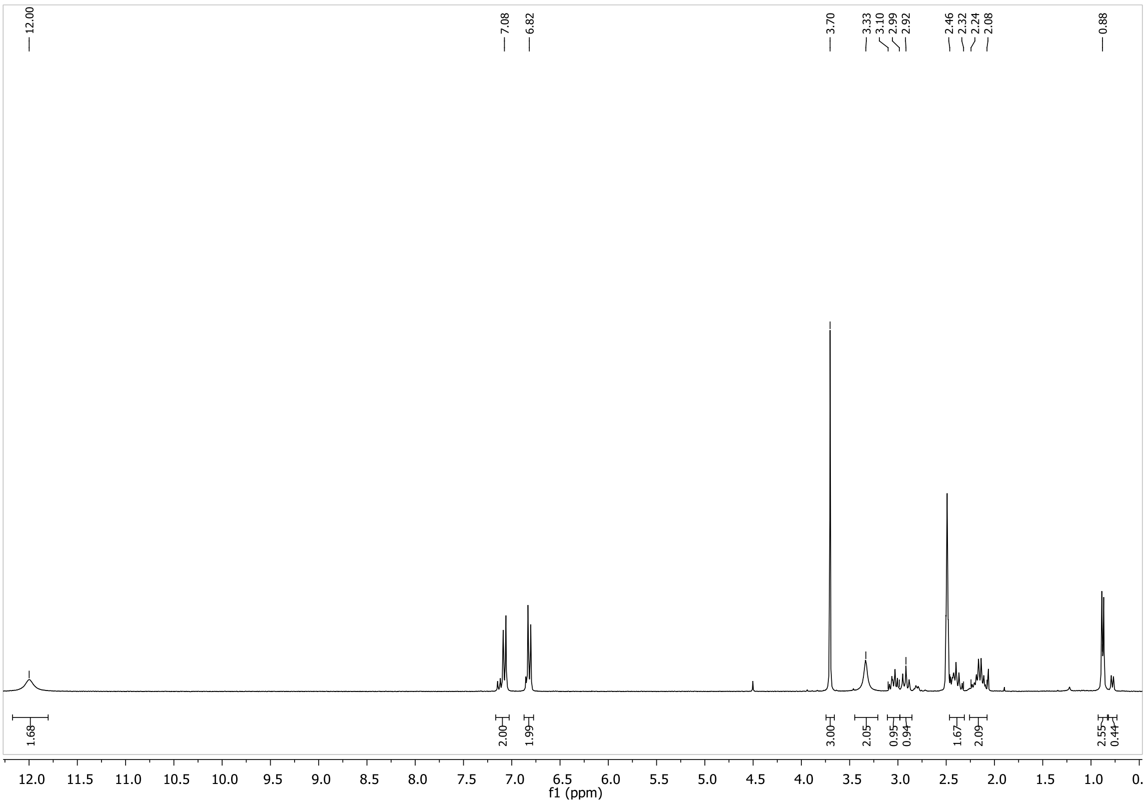


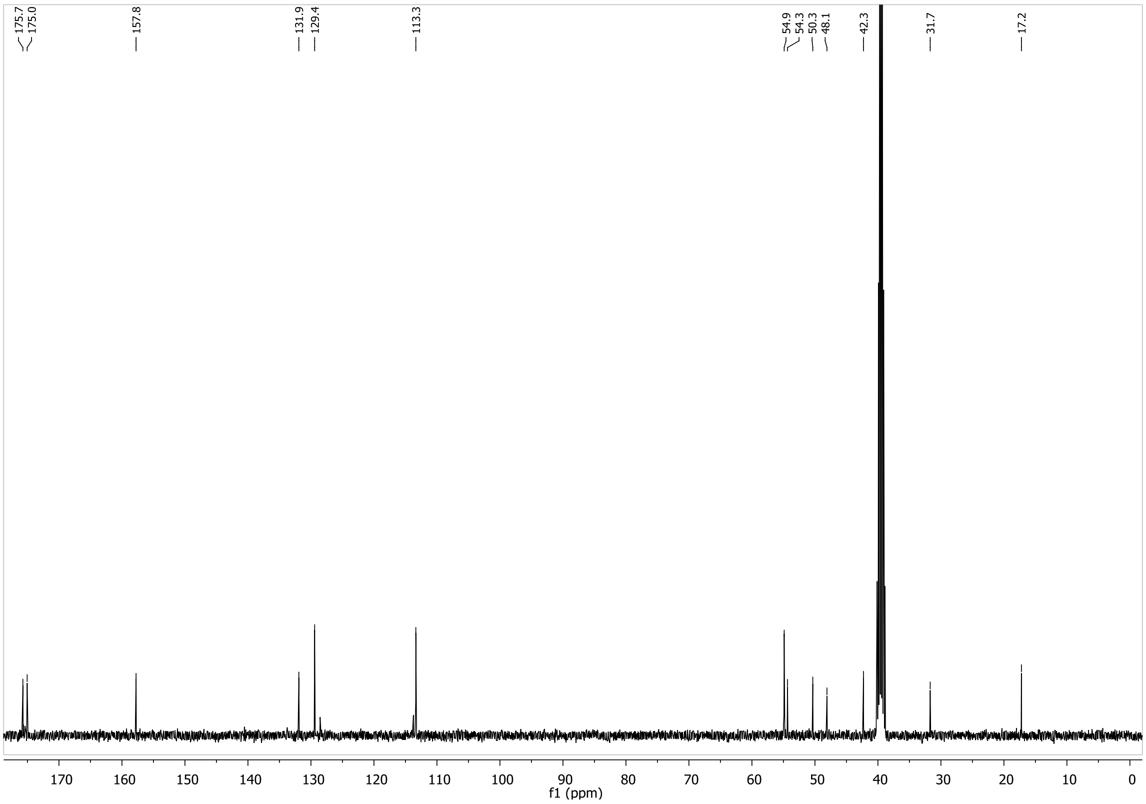


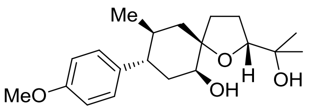
9c

^{1}H NMR (300 MHz in DMSO-d_6), ^{13}C NMR (100 MHz in DMSO-d_6)

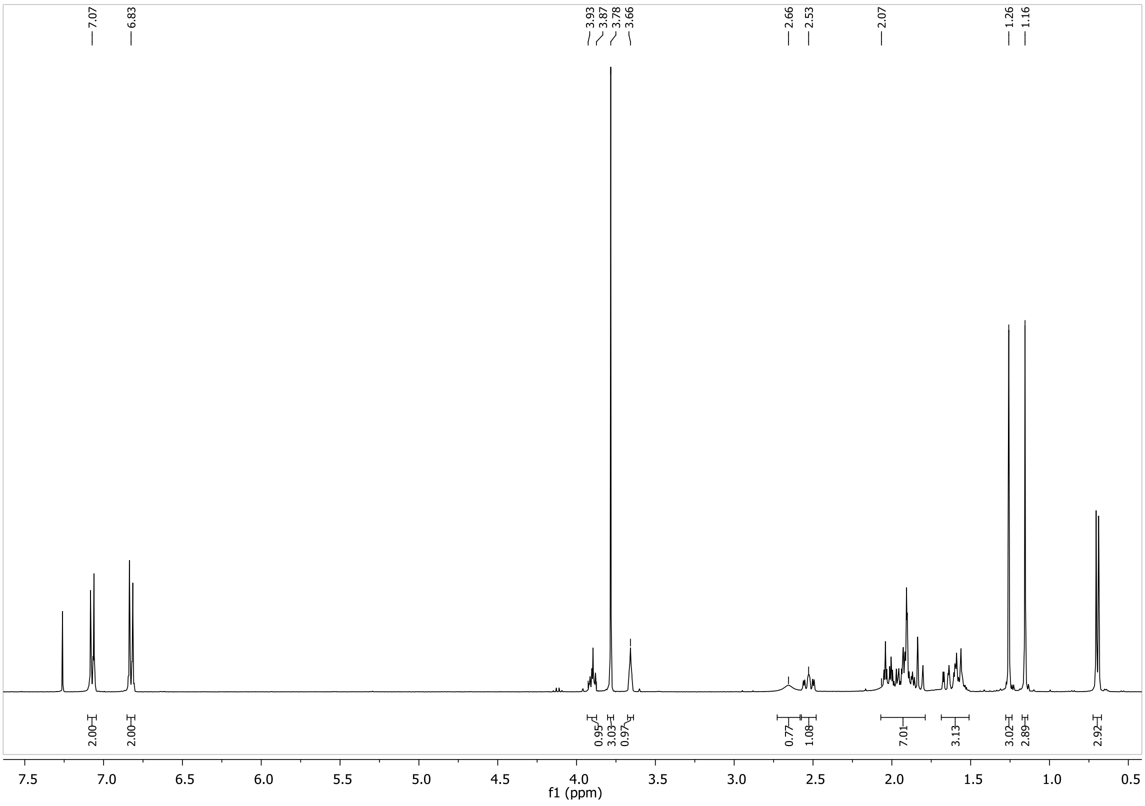
*Spectra show traces of diastereoisomer from C,C-cleavage of exo-***8c**

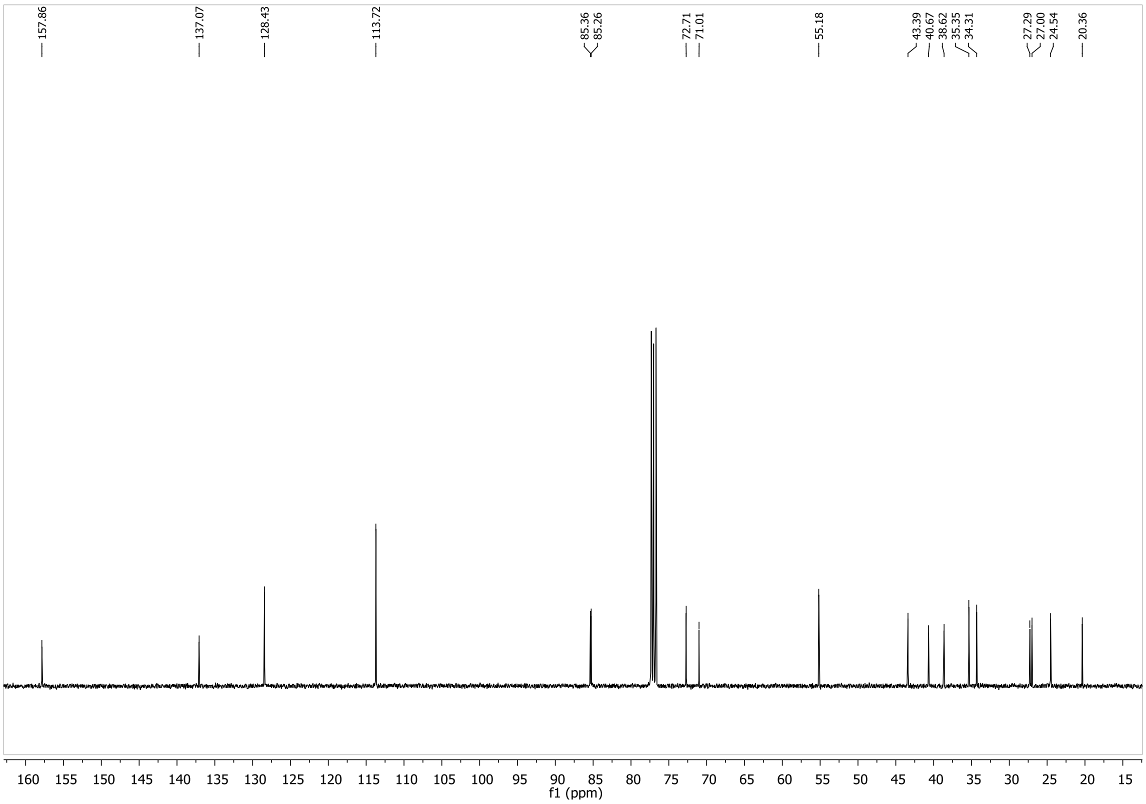


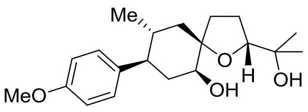




10a ^{1}H NMR (400 MHz in CDCl$_3$), ^{13}C NMR (100 MHz in CDCl$_3$)

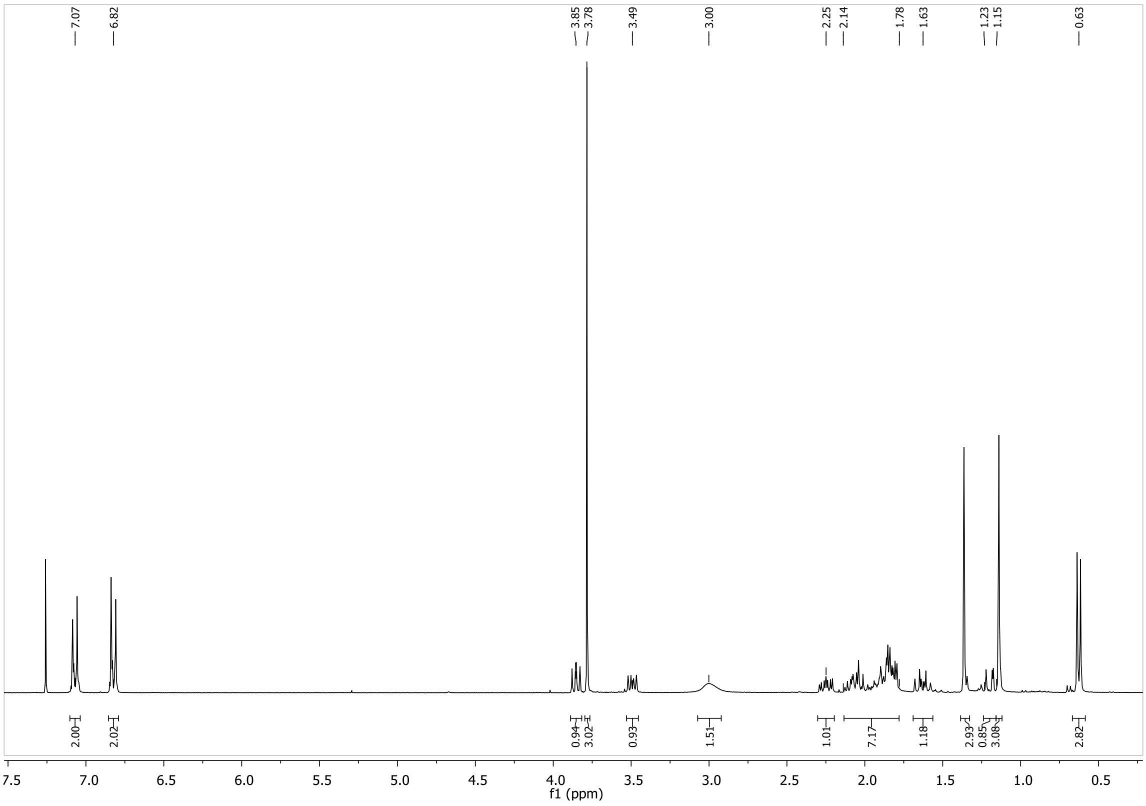


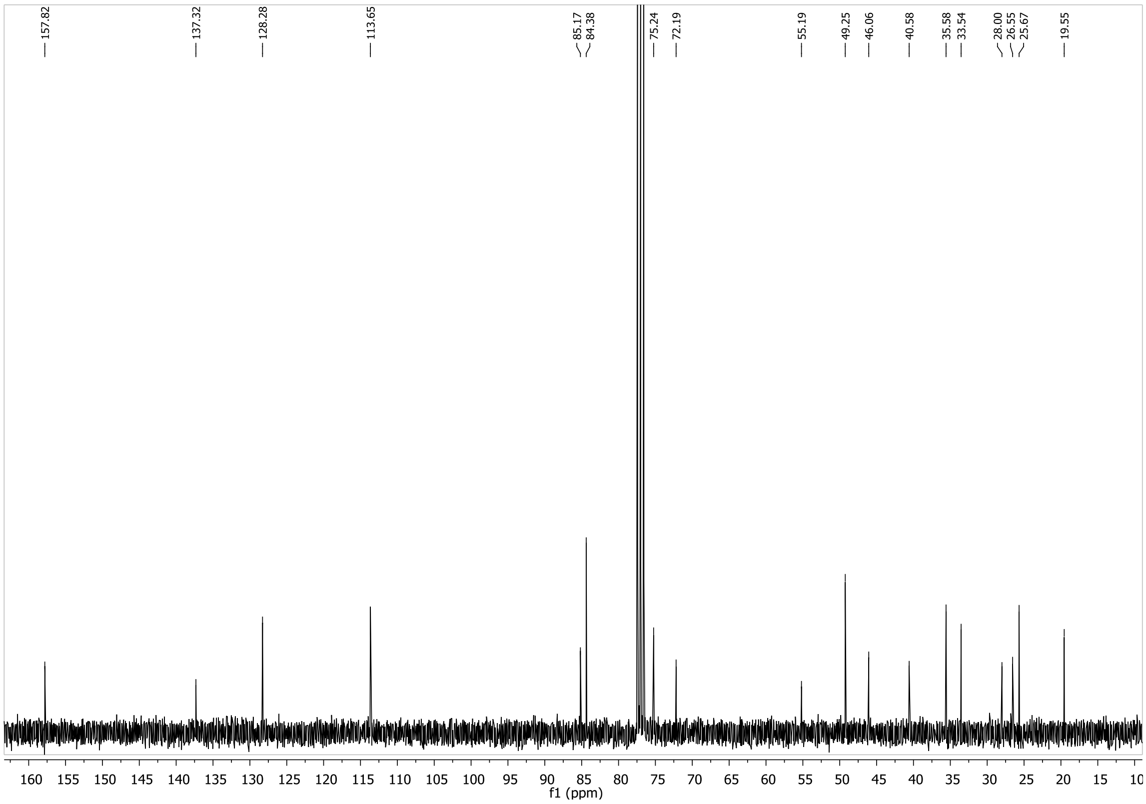


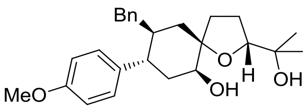


10a'

^{1}H NMR (300 MHz in CDCl$_3$), ^{13}C NMR (75 MHz in CDCl$_3$)







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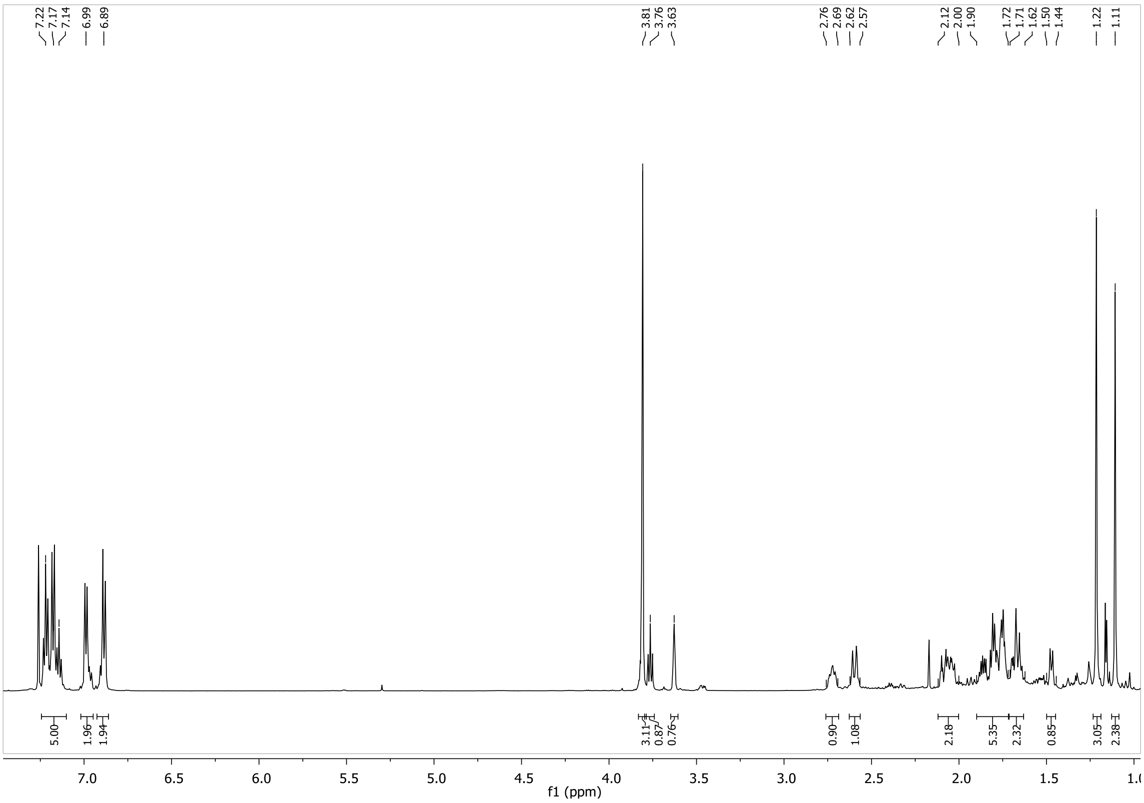
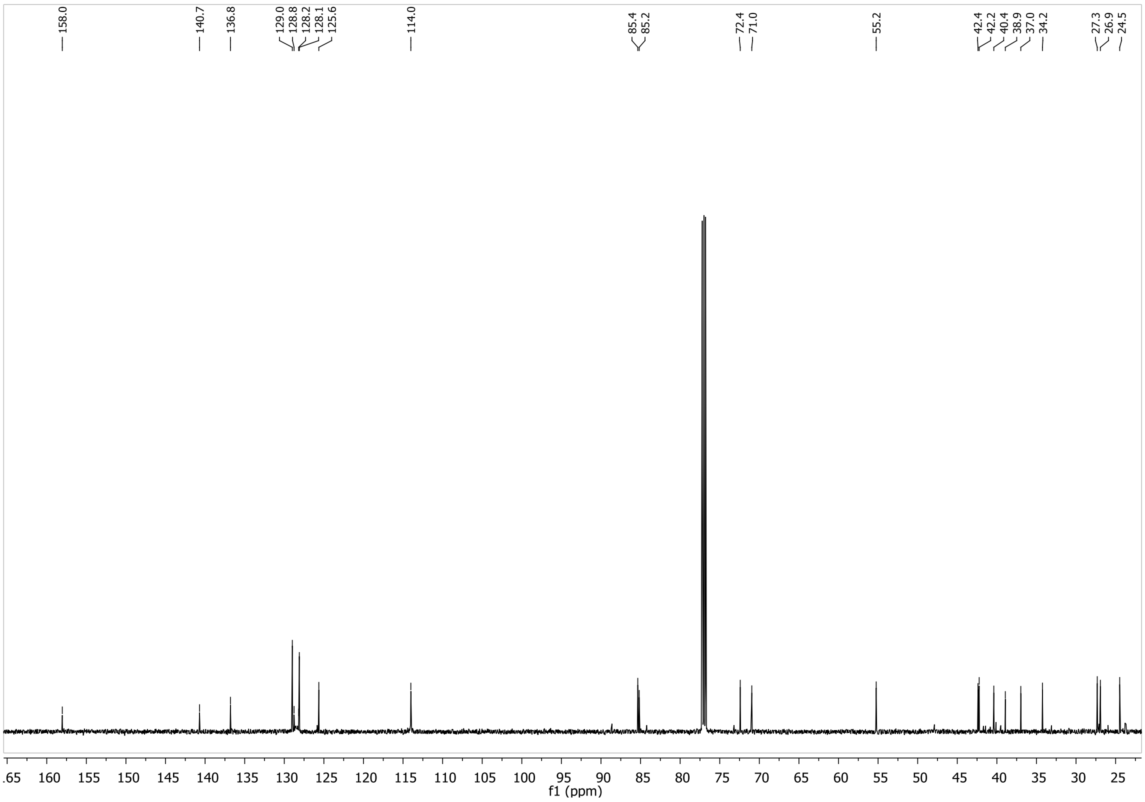
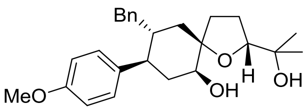
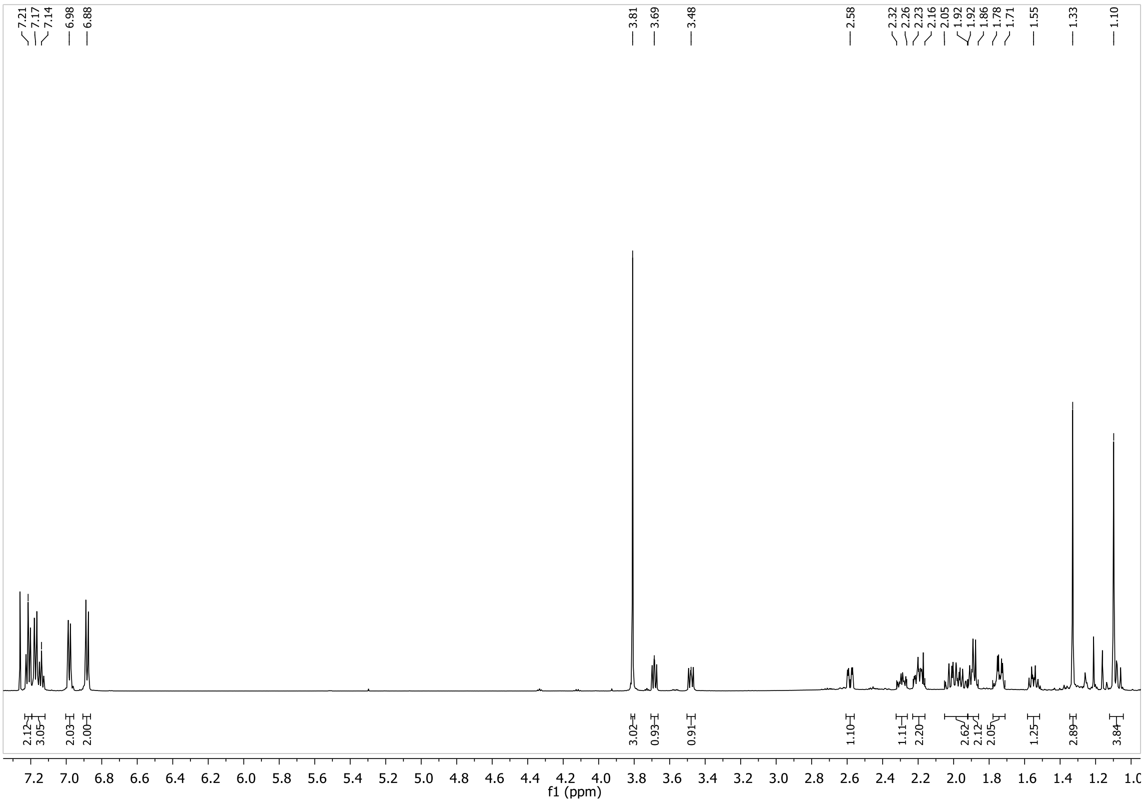
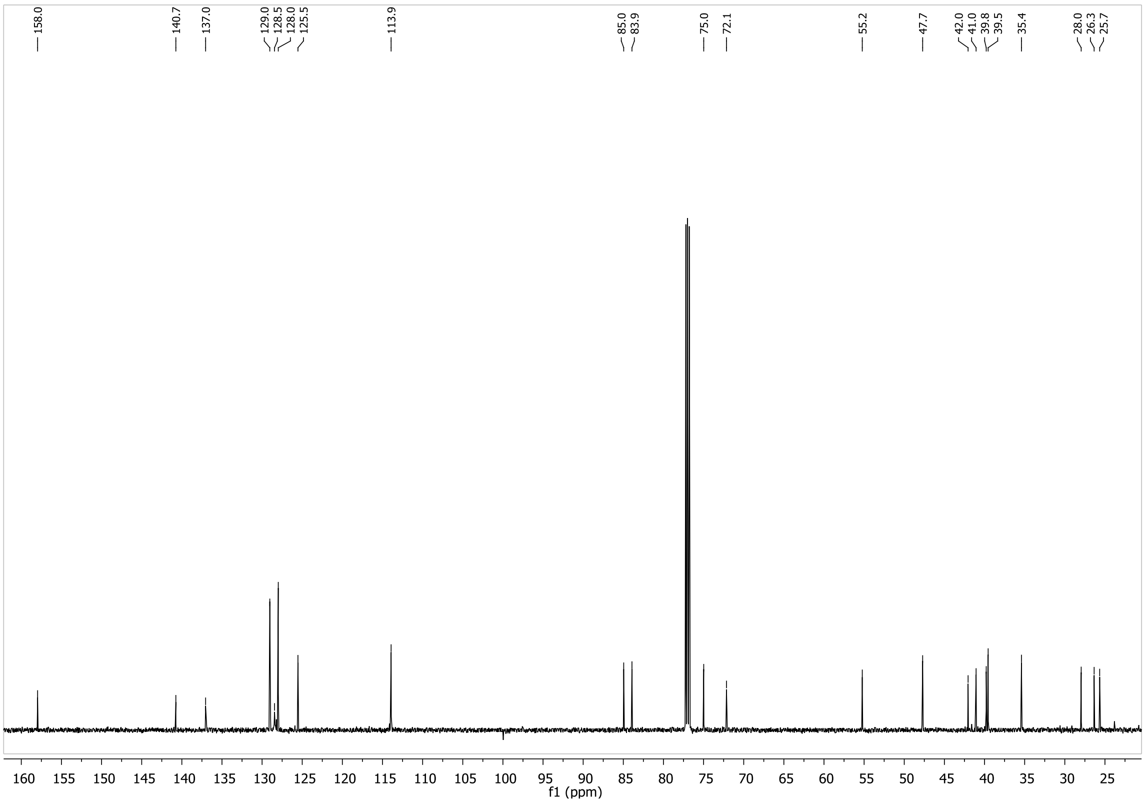


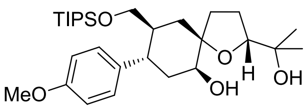




10b' ^{1}H NMR (600 MHz in CDCl$_3$), ^{13}C NMR (150 MHz in CDCl$_3$)

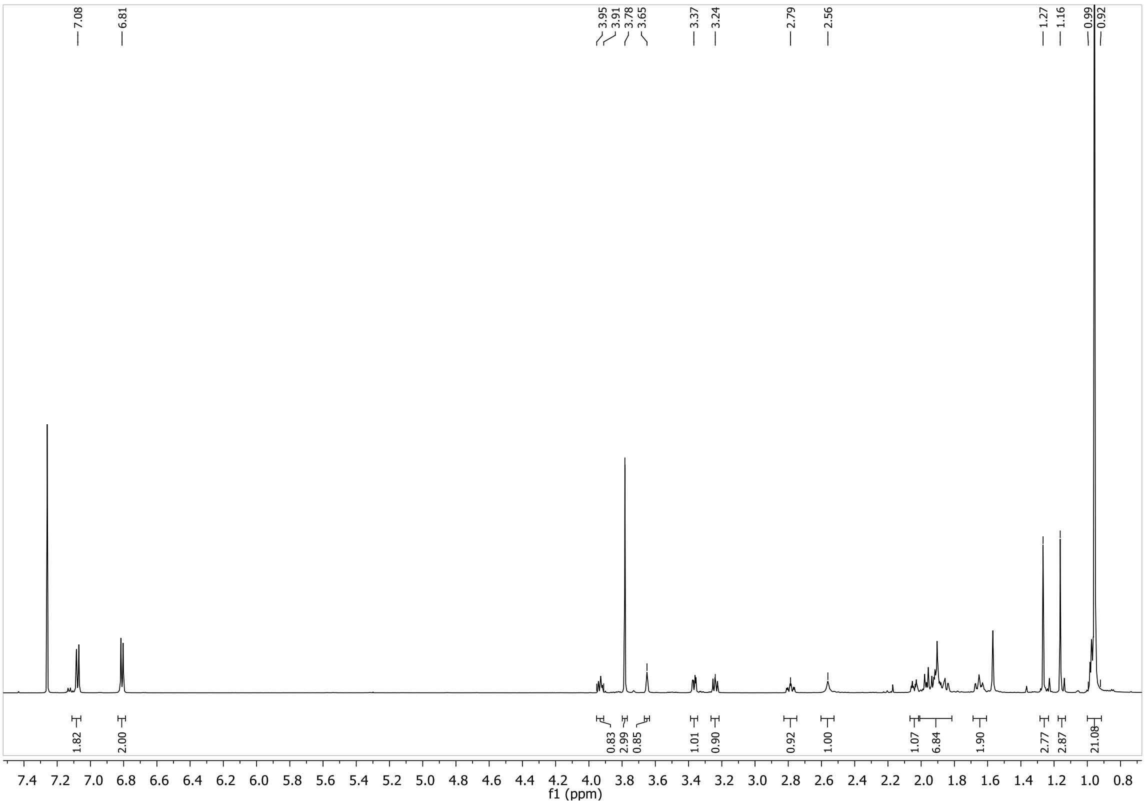


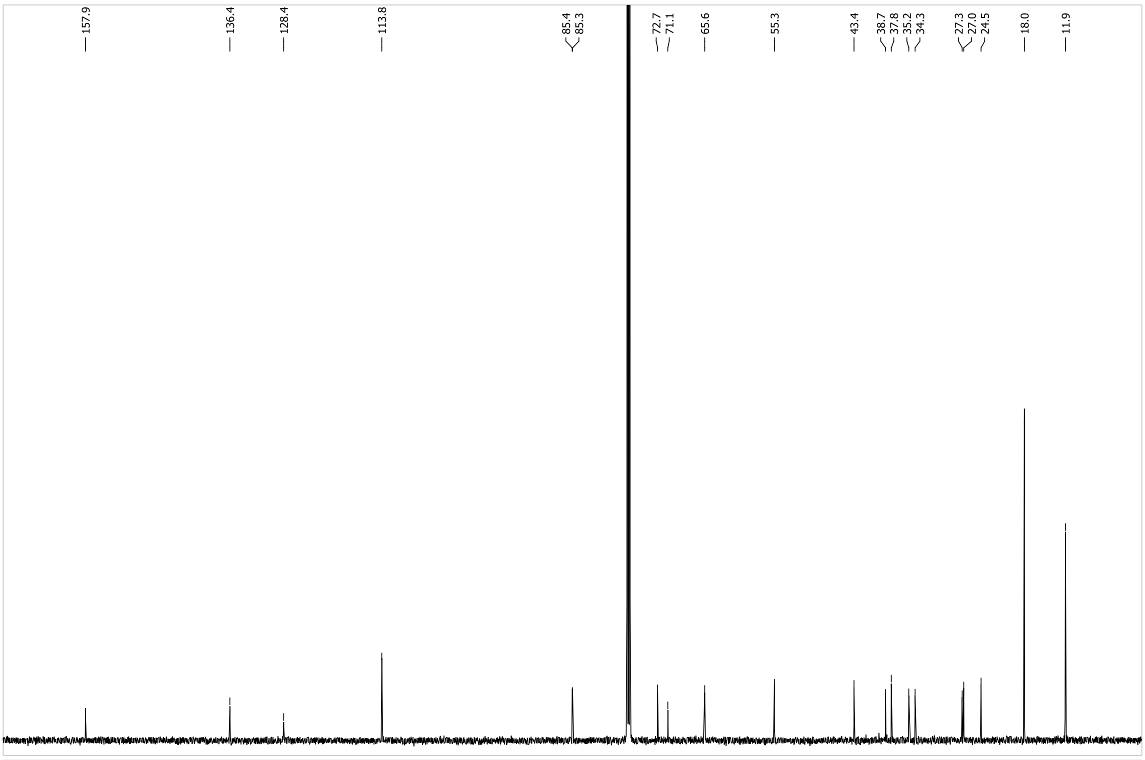


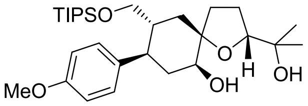


10c

^{1}H NMR (600 MHz in CDCl$_3$), ^{13}C NMR (150 MHz in CDCl$_3$)

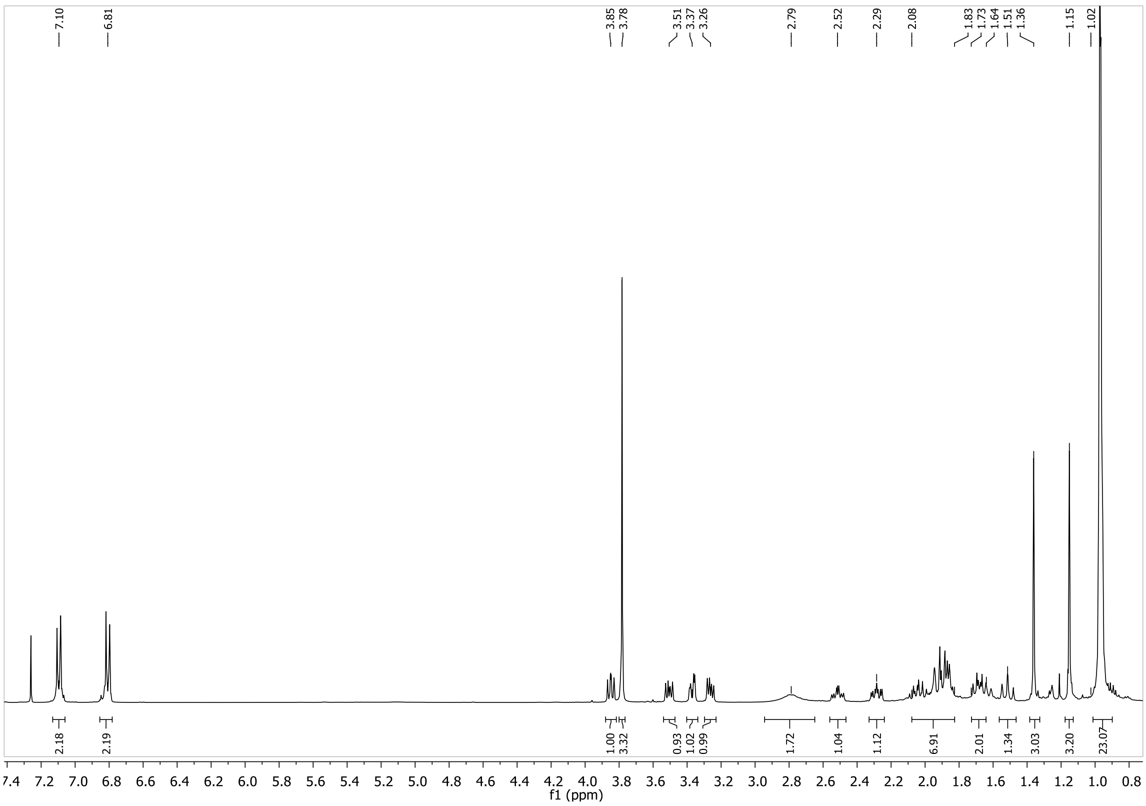


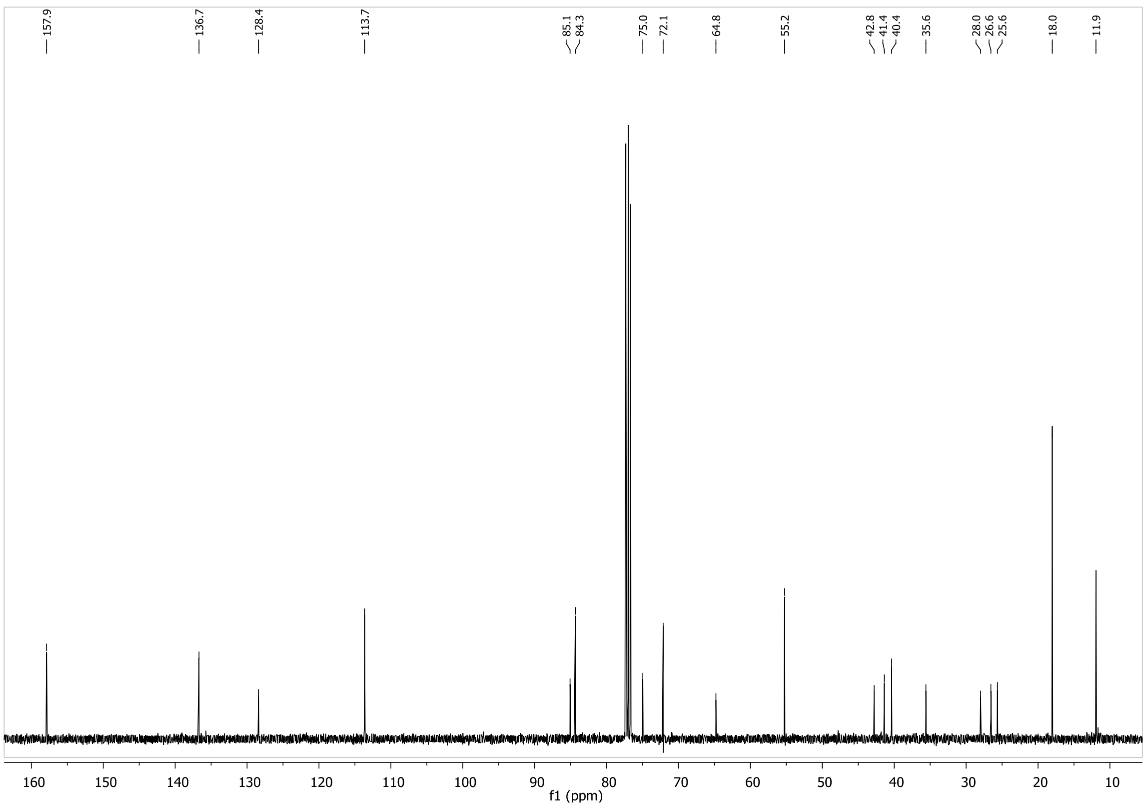


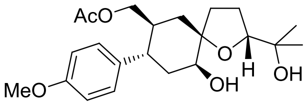


10c'

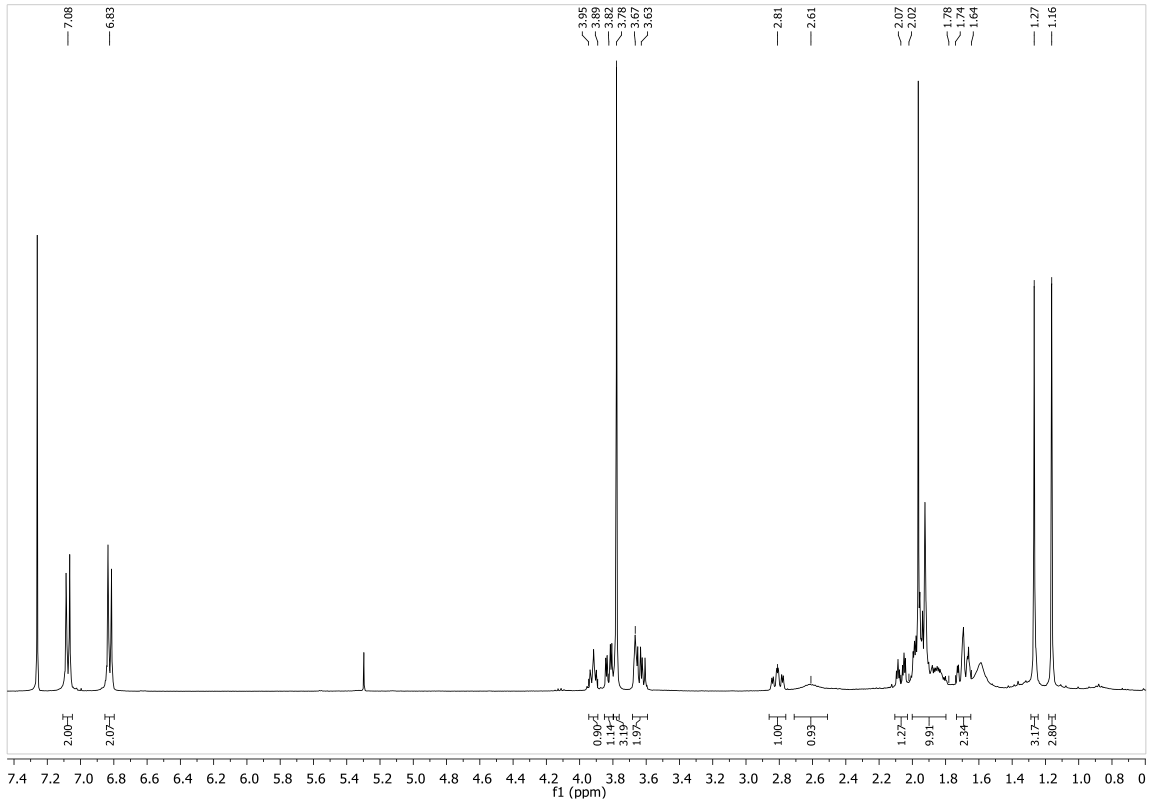
^{1}H NMR (400 MHz in $CDCl_3$), ^{13}C NMR (100 MHz in $CDCl_3$)

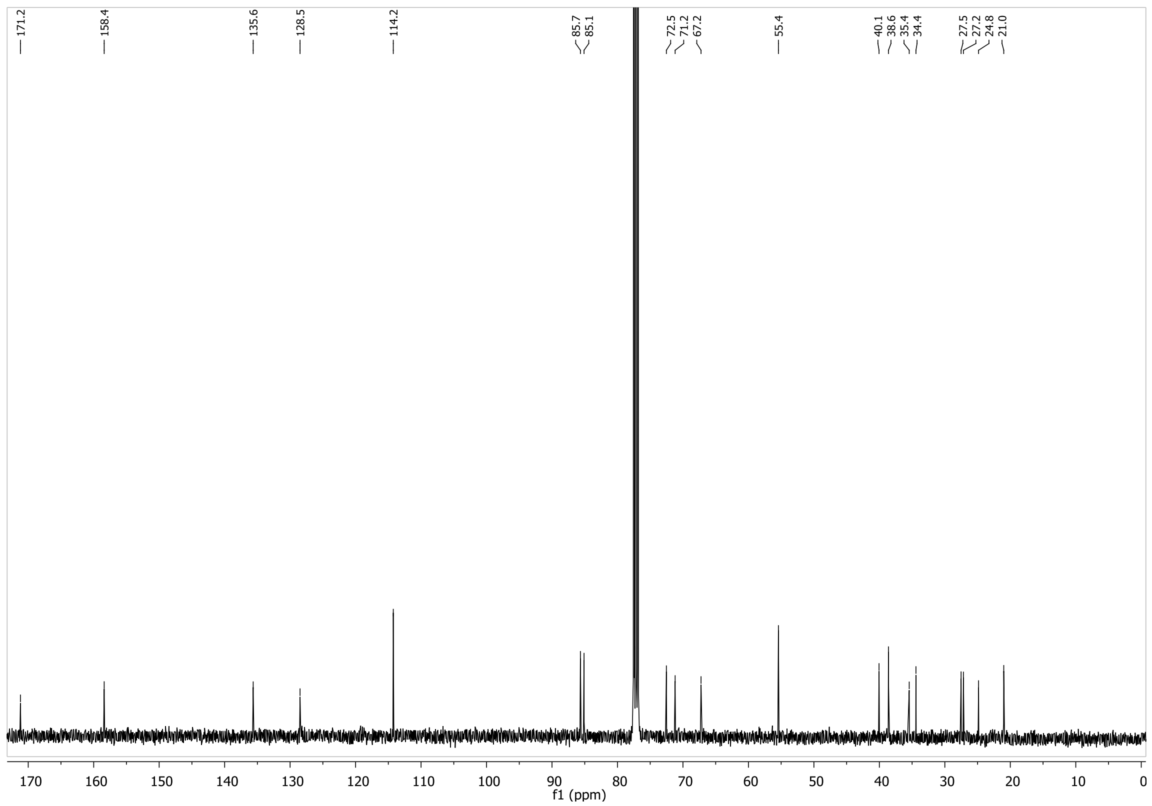


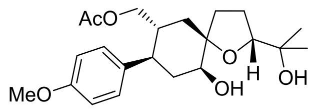




10d ^{1}H NMR (400 MHz in CDCl$_3$), ^{13}C NMR (100 MHz in CDCl$_3$)

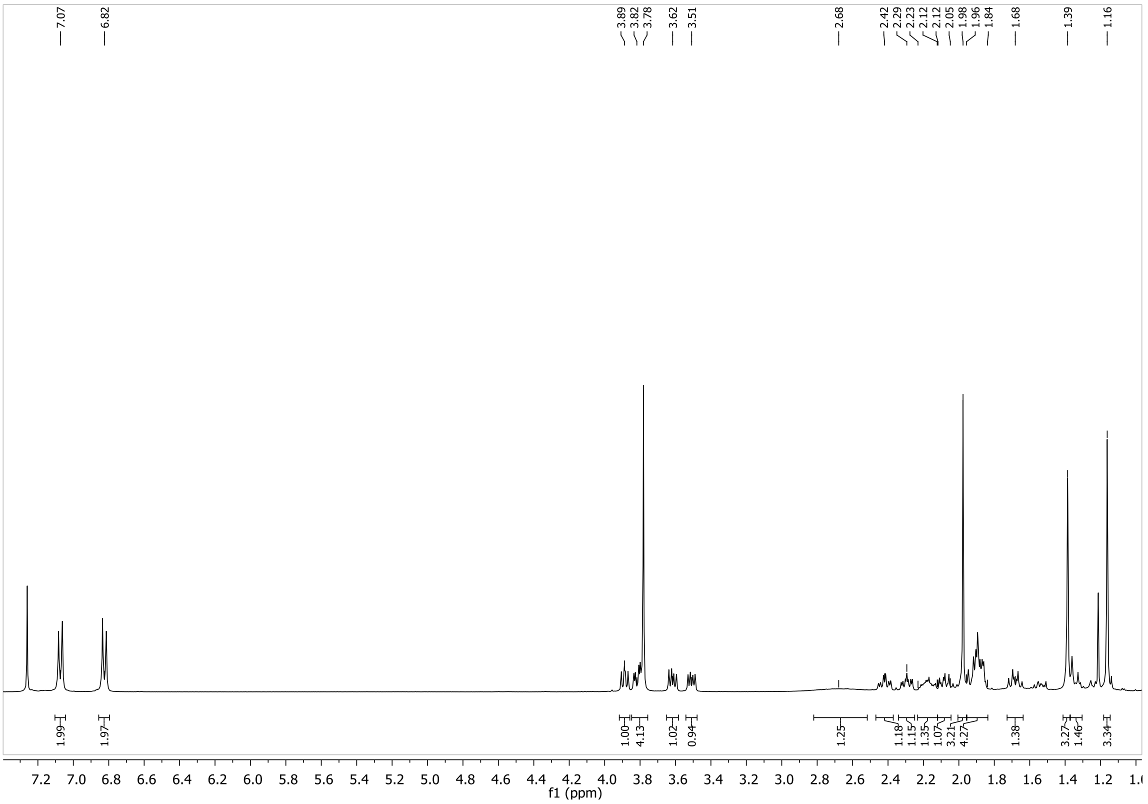


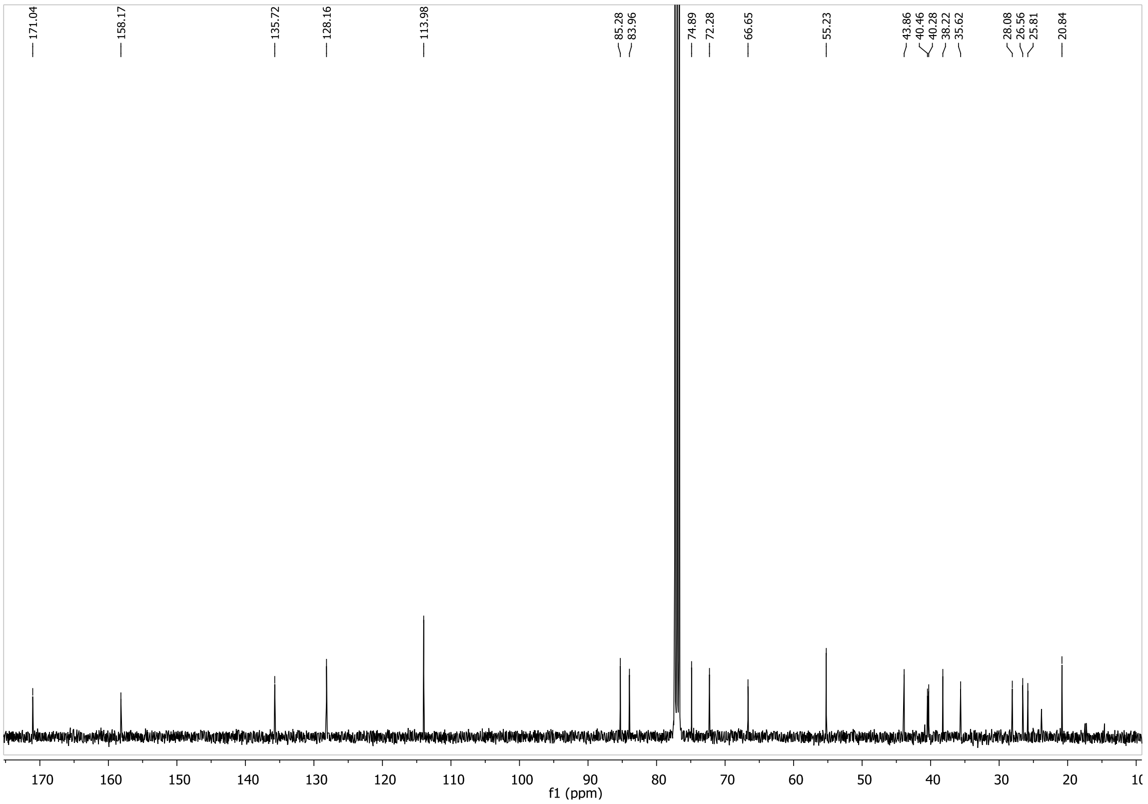


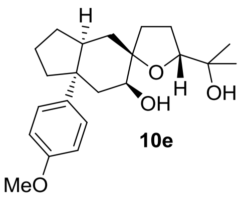


10d'

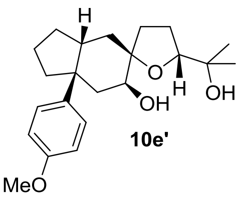
^{1}H NMR (400 MHz in CDCl$_3$), ^{13}C NMR (100 MHz in CDCl$_3$)





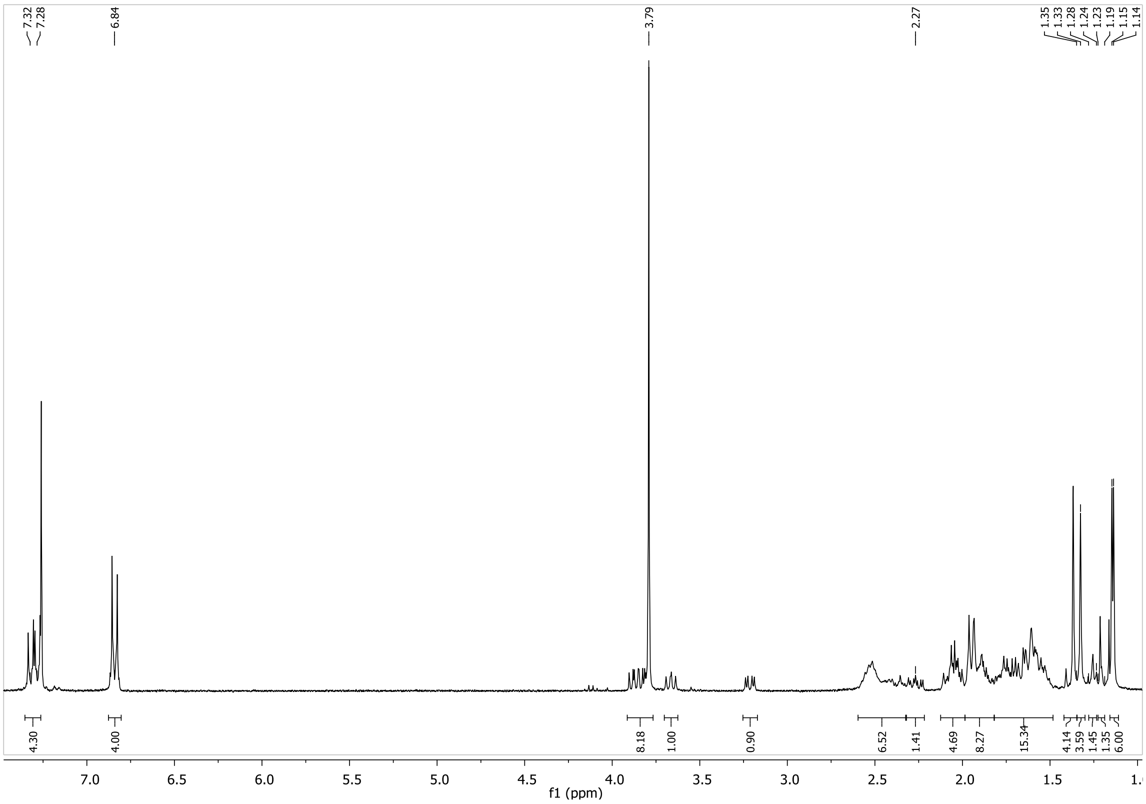


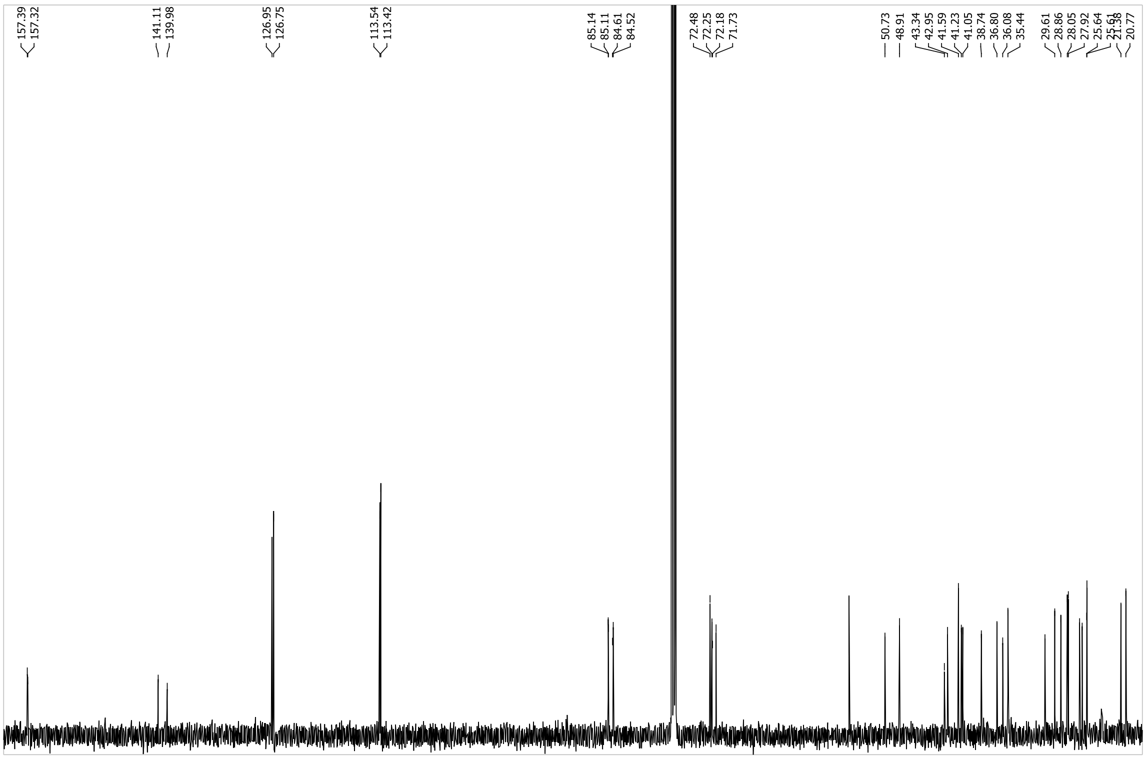
10e

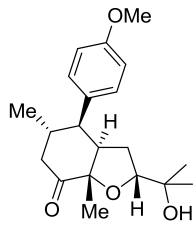


10e'

^{1}H NMR (300 MHz in $CDCl_3$)
^{13}C NMR (150 MHz in $CDCl_3$)

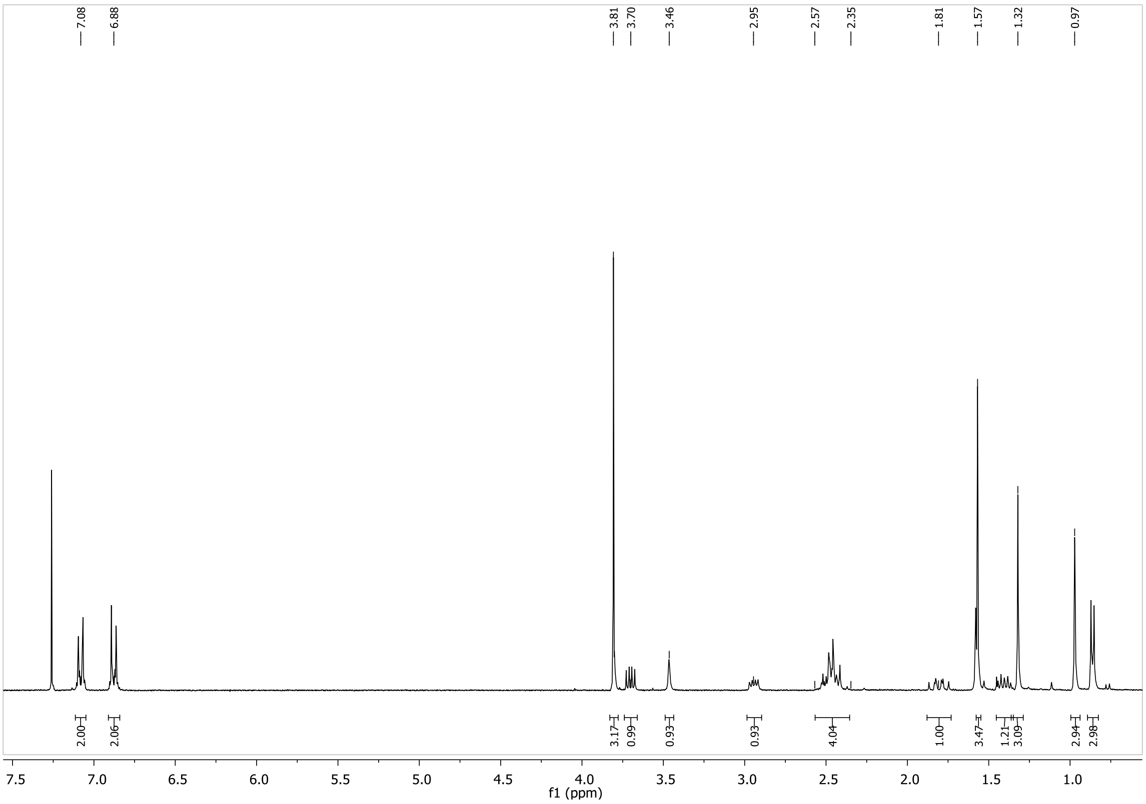


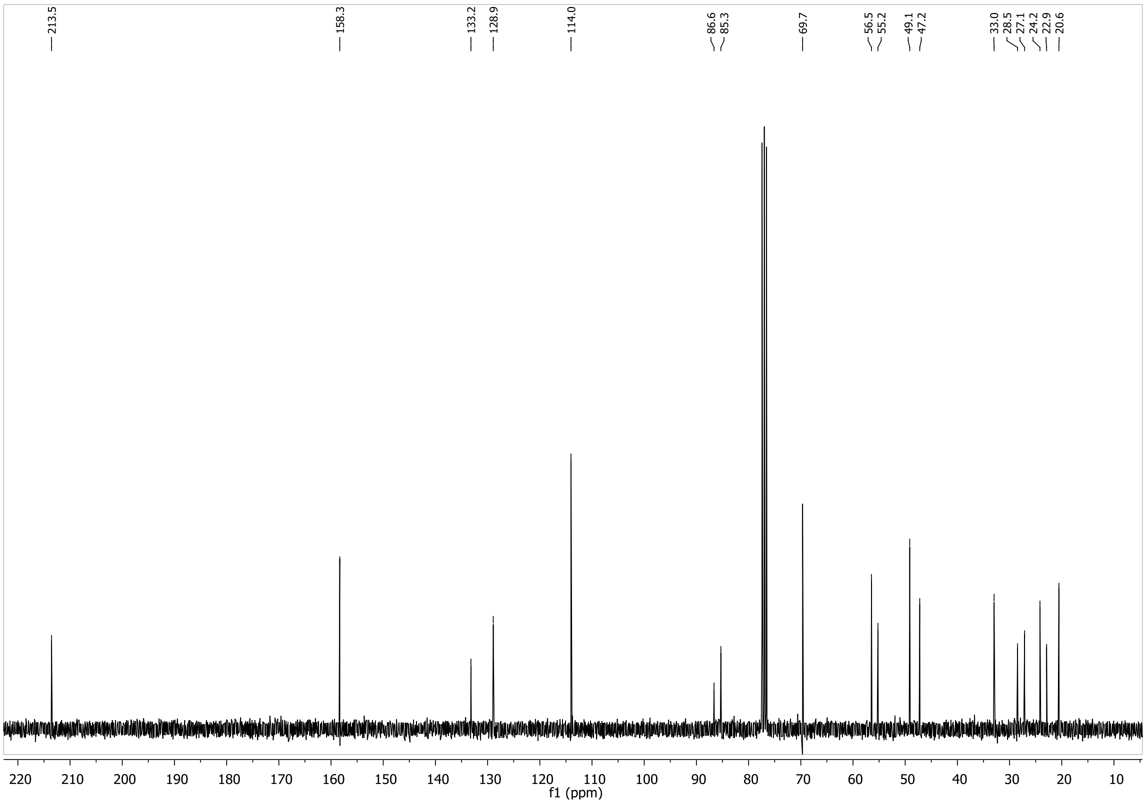


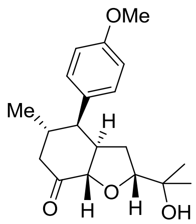


10f

^{1}H NMR (300 MHz in $CDCl_3$), ^{13}C NMR (75 MHz in $CDCl_3$)







10g

^{1}H NMR (600 MHz in CDCl$_3$), ^{13}C NMR (150 MHz in CDCl$_3$)