

## SUPPORTING INFORMATION

# **Triplet-sensitised di- $\pi$ -methane rearrangement of *N*-substituted 2-azabarrelenones**

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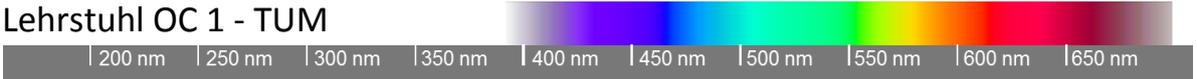
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## 1 General Information

All reactions sensitive to air or moisture were carried out in flame-dried glassware under argon pressure using standard Schlenk techniques. Dry tetrahydrofuran (THF) and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) were obtained from an *MBraun* MB-SPS 800 solvent purification system. Other dry solvents were obtained from *Merck* and *Acros* in the highest purity available and used without further purification. Technical solvents used for aqueous workup and for column chromatography [*n*-hexane (hexane), ethyl acetate (EtOAc), methanol (MeOH), dichloromethane ( $\text{CH}_2\text{Cl}_2$ )] were distilled prior to use. Photochemical experiments were performed in Duran phototubes ( $\varnothing = 1.0$  cm) under argon atmosphere in a positive geometry setup [cylindrical array of 16 fluorescent light tubes,  $\lambda = 420$  nm (*Luzchem* LZC-420, 8 W),  $\lambda = 366$  nm (*Philips Lighting*, Black Light Blue, 8 W)<sup>[1]</sup>]. Flash chromatography was performed on silica 60 (*Merck*, 230-400 mesh) with the indicated eluent mixtures. Thin layer chromatography (TLC) was performed on silica coated glass plates (silica 60 F254) with detection by UV ( $\lambda = 254$  and 366 nm) and/or by staining with a potassiumpermanganate solution [ $\text{KMnO}_4$ ] followed by heat treatment. HPLC analyses were performed using a chiral stationary phase [ChiralPak AD-H (250 x 4.6 mm), Chiralpak AS-H (250 x 4.6 mm), *Daicel Chemical Industries*] with UVD 340 Photodiode Array Detector, P580 Pump and an ASI-100 Automated Sample Injector at 20 °C. Analytical gaschromatography was performed at a HP 6890 Series GC (*Agilent*, achiral stationary phase: HP-5 column, poly-dimethyl/diphenyl-siloxane, 95/5) with a flame ionisation detector. IR spectra were recorded on a *JASCO* IR-4100 (ATR).  $^1\text{H}$  and  $^{13}\text{C}$ -NMR-spectra were recorded at 303 K either on a *Bruker* AVHD400, AVHD500 or a AVHD500cryo spectrometer. NMR spectra were calibrated to the respective residual solvent signals of  $\text{CDCl}_3$   $\delta$  ( $^1\text{H}$ ) = 7.26 ppm,  $\delta$  ( $^{13}\text{C}$ ) = 77.16 ppm, DMSO  $\delta$  ( $^1\text{H}$ ) = 2.50 ppm,  $\delta$  ( $^{13}\text{C}$ ) = 39.52 ppm. Apparent multiplets which occur as a result of accidental equality of coupling constants to those of magnetically non-equivalent protons are marked as virtual (*virt.*). The relative configuration of products and the multiplicity of the  $^{13}\text{C}$  NMR signals were determined by two-dimensional NMR spectra (COSY, HSQC, HMBC, NOESY). Melting points were measured on a *Büchi* M-565 instrument and are not corrected. High resolution mass spectroscopy (HR-MS) was performed on a *Thermo Scientific* LTQ-FT Ultra (ESI) or a *Thermo Scientific* DFS-HRMS spectrometer (EI). Preparative electrolysis was carried out with a KD6005P laboratory compact power supply of the company *KORAD* with constant voltage in an open undivided cell. A platinum spiral cathode (wire diameter 1 mm, height 7 cm, 7 turns) and a platinum anode arranged in a cylindrical shape around the cathode (diameter 3.8 cm, height 5 cm, wire diameter 0.2 cm) were used as electrodes.

Lehrstuhl OC 1 - TUM


 200 nm | 250 nm | 300 nm | 350 nm | 400 nm | 450 nm | 500 nm | 550 nm | 600 nm | 650 nm

## Datasheet FLT022

LZC-420

## Basic Information

Type	<u>Fluorescent light tube</u>
Description Manufacturer / Supplier	<u>Luzchem LZC-420</u>
Order number / Date of purch.	<u>n/a / Luzchem</u>
Internal lot / serial number	<u>n/a / 07/2017</u>
	<u>2017-07/ FLT 022</u>

## Specification Manufacturer

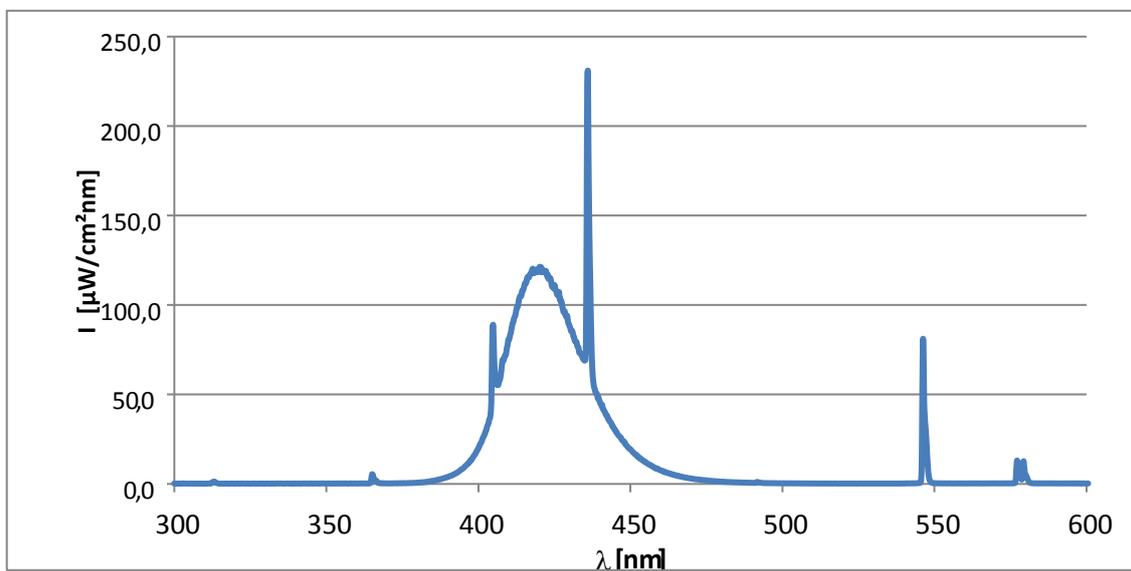
Type / size	<u>T5 tube, G5 socket</u>
Mechanical specification	<u>16mm diameter, 288 mm length</u>
Electrical specification	<u>8 W</u>
Wavelength (range, typ.)	<u>400 - 440 nm</u>
Spectral width (FWHM)	<u>~ 30 nm</u>
	<u>LES-420-016</u>

## Characterization

Description of measurement	Measured with Ocean-optics USB4000 spectrometer using a calibrated setup (cosine corrector/fibre). The cosine corrector was placed at 20 mm distance from a single fluorescent tube at half height.
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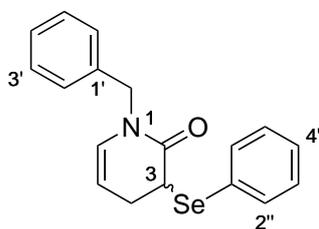
Measured dominant wavelength / Int.	<u>421 nm</u>	<u>121 <math>\mu\text{W}/\text{mm}^2\text{nm}</math></u>
Measured spectral width (FWHM)	<u>30 nm</u>	
Integral Reference intensity / range	<u>4142 <math>\mu\text{W}/\text{cm}^2</math></u>	<u>350-500 nm</u>

## Spectrum



## 2 Synthesis of 2-Azabarrelenones

### (*R*<sup>\*</sup>)-1-Benzyl-3-(phenylselanyl)-3,4-dihydropyridin-2(1*H*)-one (**S1**)



C<sub>18</sub>H<sub>17</sub>NOSe  
M: 342.30 g/mol

According to a literature procedure,<sup>[2]</sup> to a solution of 1-benzyl-3,4-dihydropyridin-2(1*H*)-one<sup>[3]</sup> (1.10 g, 5.87 mmol, 1.0 eq.) in THF (11.8 mL), cooled at  $-78\text{ }^{\circ}\text{C}$  and under argon atmosphere, a solution of LDA (12.3 mmol, 2.1 eq.) in THF (11.8 mL) was added dropwise. After stirring for 30 min, a solution of phenylselenenyl chloride (1.24 g, 6.46 mmol, 1.1 eq.) and *N,N'*-dimethylpropyleneurea (DMPU, 780  $\mu\text{L}$ , 830 mg, 6.46 mmol, 1.1 eq.) in THF (11.8 mL) was slowly added at  $-78\text{ }^{\circ}\text{C}$ . The resulting orange solution was maintained at  $-78\text{ }^{\circ}\text{C}$  for 20 min and left to reach room temperature. The reaction was stopped by the addition of sat.  $\text{NH}_4\text{Cl}$ -solution (10 mL). The mixture was diluted with EtOAc (100 mL) and water (200 mL) and the layers were separated. The aqueous phase was extracted with EtOAc ( $2 \times 50\text{ mL}$ ). The combined organic phases were washed with water (100 mL) and brine (100 mL), dried over  $\text{Na}_2\text{SO}_4$  and concentrated *in vacuo*. Flash chromatography ( $\text{SiO}_2$ , Hex/EtOAc 9:1  $\rightarrow$  8:2) gave the the title compound **S1** as a light yellow liquid (1.10 g, 3.21 mmol, 55%).

**TLC** (Cy/EtOAc = 2:1):  $R_f = 0.50$  [UV].

**<sup>1</sup>H-NMR** ( $\text{CDCl}_3$ , 300 K, 500 MHz):

$\delta$  (ppm) = 7.79-7.62 (m, 2H, 2''), 7.49-7.09 (m, 8H, H-2', H-3', H-4', H-3'', H-4''), 6.08 (dd,  $^3J = 7.8\text{ Hz}$ ,  $^4J = 2.9\text{ Hz}$ , 1H, H-6), 5.22-5.05 (m, 1H, H-5), 4.78 (d,  $^2J = 15.1\text{ Hz}$ , 1H, Ph-CHH), 4.64 (d,  $^2J = 15.1\text{ Hz}$ , 1H, Ph-CHH), 4.22-3.93 (m, 1H, H-3), 2.94 (ddt,  $^2J = 18.1\text{ Hz}$ ,  $^3J = 5.8\text{ Hz}$ ,  $^3J \approx ^4J = 2.9\text{ Hz}$ , 1H, CHH-4), 2.62 (ddd,  $^2J = 18.1\text{ Hz}$ ,  $^3J = 6.1\text{ Hz}$ ,  $^3J = 3.1\text{ Hz}$ , 1H, CHH-4).

**<sup>13</sup>C-NMR** ( $\text{CDCl}_3$ , 300 K, 101 MHz):

168.5 (s, C-2), 137.1 (s, C-1'), 135.2 (d, 2C, C-2''), 130.0 (d, C-6), 129.2 (d, 2C, C-3''), 128.8 (d, 2C, C-3'), 128.3 (d, C-4''), 127.8 (d, 2C, C-2'), 127.7 (d, C-4'), 104.3 (d, C-5), 49.3 (t,  $\text{CH}_2$ ), 42.3 (d, C-3), 28.4 (t, C-4).

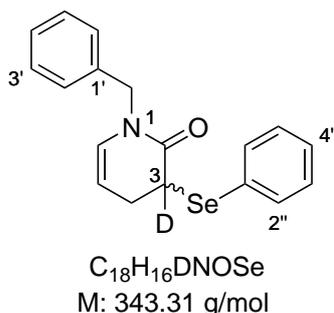
**IR** (ATR):

$\tilde{\nu}$  (cm<sup>-1</sup>) = 3060 (w, C–H), 2929 (w, C–H), 1657 (s, N–C=O), 1405 (m), 1383 (m), 1253 (m), 1188 (m), 1073 (w), 962 (w), 738 (s), 692 (s).

**MS** (EI, 70 eV):

$m/z$  (%) = 343 (28) [M<sup>+</sup>], 239 (40), 186 (29) [M<sup>+</sup>–C<sub>6</sub>H<sub>5</sub>Se], 91 (100) [C<sub>7</sub>H<sub>7</sub><sup>+</sup>].

**(*R*<sup>\*</sup>)-1-Benzyl-3-(phenylselanyl)-3,4-dihydropyridin-2(1*H*)-one-3-*d* (S2)**

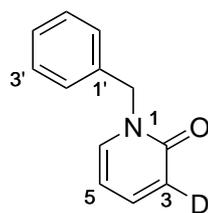


According to a literature procedure,<sup>[4]</sup> to a stirred solution of **S1** (8.17 g, 23.9 mmol, 1.0 eq.) in THF (230 mL) at –78 °C, was added Lithium bis(trimethylsilyl)amide (LHMDS, 1 M in toluene, 47.7 mL, 47.7 mmol, 2.0 eq.) dropwise. After stirring for 30 min at –40 °C, ethanol-*d*<sup>1</sup> (14.0 mL, 239 mmol, 10.0 eq.) was added dropwise and the reaction left to stir at room temperature for 10 min. To the solution was added sat. NH<sub>4</sub>Cl-solution (15 mL) and the solvent removed under reduced pressure. To the residue EtOAc (100 mL) and water (200 mL) was added, the layers were separated and the aqueous phase extracted with EtOAc (2×150 mL). The combined organic layers were washed with water (2 × 150 mL), brine (100 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration and removal of the solvent under reduced pressure provides the dihydropyridone **S2** (8.17 g, 23.9 mmol, quant., 85% D) as a yellow liquid. The selenide was used in the next step without further purification.

**TLC** (Cy/EtOAc = 2:1):  $R_f$  = 0.51 [UV].

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 K, 500 MHz):

$\delta$  (ppm) = 7.78-7.68 (m, 2H, H-2''), 7.39-7.28 (m, 8H, H-2', H-3', H-4', H-3'', H-4''), 6.08 (dd, <sup>3</sup> $J$  = 7.7 Hz, <sup>4</sup> $J$  = 2.9 Hz, 1H, H-6), 5.14-5.10 (m, 1H, H-5), 4.78 (d, <sup>2</sup> $J$  = 15.1 Hz, 1H, Ph–CHH), 4.65 (d, <sup>2</sup> $J$  = 15.1 Hz, 1H, 1H, Ph–CHH), 4.08 (ddd, <sup>3</sup> $J$  = 6.1 Hz, <sup>3</sup> $J$  = 3.2, <sup>4</sup> $J$  = 1.3 Hz, 0.15H, H-3), 2.99-2.90 (m, 1H, CHH-4), 2.62 (ddd, <sup>2</sup> $J$  = 18.0 Hz, <sup>3</sup> $J$  = 6.1 Hz, <sup>3</sup> $J$  = 3.1 Hz, 1H, CHH-4).

**1-Benzylpyridin-2(1H)-one-3-d (6a-d<sup>1</sup>)**

C<sub>12</sub>H<sub>10</sub>DNO  
M: 186.23 g/mol

A solution of *m*-chloroperoxybenzoic acid ( $w_i = 60\%$ , 13.7 g, 47.6 mmol, 2.0 eq.) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was added at  $-40\text{ }^\circ\text{C}$  to a stirred solution of the dihydropyridone **S2** (8.17 g, 23.8 mmol, 1.0 eq.) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL). After stirring for 60 min at room temperature, saturated aqueous NaHCO<sub>3</sub>-solution (150 mL) and NaOH-solution (2 M, 150 mL) were added. After separation of the layers, the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 150 mL) and the organic layers were combined. The organic phase was washed successively with water (100 mL), aqueous NaOH-solution (2 M, 150 mL), brine (150 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration and removal of the solvent under reduced pressure provided the crude material, which was purified via flash chromatography (250 g SiO<sub>2</sub>, EtOAc/MeOH 1:0 → 99:1) to give the pyridone **6a-d<sup>1</sup>** (3.81 g, 20.5 mmol, 86%, 85% D) as colorless solid.

**M.p.:** 95-97 °C.

**TLC** (EtOAc):  $R_f = 0.39$  [UV].

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 K, 500 MHz):

$\delta$  (ppm) = 7.55-7.19 (m, 7H, H-2', H-3', H-4', H-4, H-6), 6.63 (dd,  $^3J = 9.3$  Hz,  $^4J = 1.2$  Hz, 0.15H, H-3), 6.15 (*virt. t.*,  $^3J \approx ^3J = 6.7$  Hz, 1H, H-5), 5.16 (s, 2H, CH<sub>2</sub>).

**<sup>13</sup>C-NMR** (CDCl<sub>3</sub>, 300 K, 126 MHz):

$\delta$  (ppm) = 162.4 (s, C-2), 139.2 (d, C-4), 137.2 (s, C-1'), 136.2 (d, C-6), 128.6 (d, 2C, C-3'), 127.8 (d, 2C, C-2'), 127.7 (d, C-4'), 120.37 (t,  $^1J_{\text{CD}} = 25.5$  Hz, C-3), 106.0 (d, C-5), 51.6 (t, CH<sub>2</sub>).

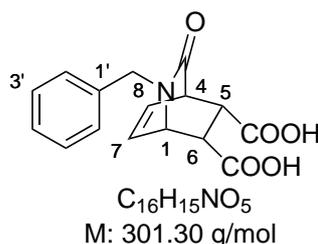
**IR** (ATR):

$\tilde{\nu}$  (cm<sup>-1</sup>) = 3064 (w, C-H), 3031 (w), 1648 (s, N-C=O), 1531 (s), 1455 (m), 1378 (w), 1223 (w), 1060 (w), 766 (m).

**MS** (EI, 70 eV):

$m/z$  (%) = 186 (62) [M<sup>+</sup>], 91 (100) [C<sub>7</sub>H<sub>7</sub><sup>+</sup>], 80 (18), 65 (17).

**HR-MS** (EI): [C<sub>12</sub>H<sub>10</sub>DNO<sup>+</sup>]: 186.0896 [M<sup>+</sup>], calc.: 186.0898.

**(1S\*,4R\*,5S\*,6S\*)-2-Benzyl-3-oxo-2-azabicyclo[2.2.2]oct-7-ene-5,6-dicarboxylic acid (9a)**

A mixture of 1-benzylpyridin-2(1*H*)-one<sup>[5]</sup> (14.7 g, 79.4 mmol, 1.0 eq.) and maleic anhydride (15.6 g, 159 mmol, 2.0 eq.) in PhCH<sub>3</sub> (50.0 mL) was gently refluxed for 2 d. The reaction mixture was concentrated to half of its volume under reduced pressure and CH<sub>2</sub>Cl<sub>2</sub> (60 mL) and water (20 mL) was added. The layers were separated as far as possible and the aqueous phase was basified by the addition of 4 M and 1 M NaOH-solution (pH ≈ 10) to solubilize colorless solid at the phase boundary. The layers were separated completely and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration and removal of the solvent under reduced pressure provided a brown residue, that contains remaining starting material and the *Diels-Alder*-product.

To the crude product PhCH<sub>3</sub> (50 mL) and water (30 mL) was added and the resulting mixture was allowed to reflux with vigorous stirring for four hours. After cooling down to room temperature, EtOAc (60 mL) was added and the aqueous phase was basified by the addition of NaOH-solution (4 M, pH ≈ 8). The layers were separated, and the organic phase was extracted with NaOH-solution (1 M, 40 mL). The organic phase was washed successively with water (200 mL), aqueous NaHCO<sub>3</sub>-solution (200 mL), brine (100 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration and removal of the solvent under reduced pressure provided remaining starting material (5.29 g, 28.5 mmol, 36%) as a beige solid.

The combined aqueous layers were washed with EtOAc (60 mL) and acidified (pH ≈ 1) by adding concentrated hydrochloric acid (12 M). A white precipitate formed, which was purified by recrystallization from the reaction mixture and additional water to give the diacid **9a** (11.9 g, 39.5 mmol, 50%) as colorless crystals.

**M.p.:** 191-193 °C (from H<sub>2</sub>O, decomposition).

**<sup>1</sup>H-NMR** (DMSO-*d*<sub>6</sub>, 300 K, 400 MHz):

δ (ppm) = 12.34 (br. s, 2H, 2 × COOH), 7.38-7.24 (m, 3H, H-2', H-4'), 7.21-7.13 (m, 2H, H-3'), 6.41-6.34 (m, 2H, H-7, H-8), 4.54 (d, <sup>2</sup>J = 15.0 Hz, CHH), 4.34 (*virt.* dt, <sup>3</sup>J = 5.0 Hz, <sup>3</sup>J ≈ <sup>4</sup>J = 2.6 Hz, H-1), 4.27 (d, <sup>2</sup>J = 15.0 Hz, CHH), 3.52 (*virt.* dt, <sup>3</sup>J = 5.5 Hz, <sup>3</sup>J ≈ <sup>4</sup>J = 2.1 Hz, H-4),

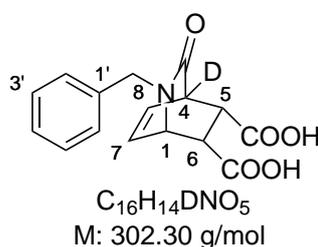
3.26 (dd,  $^3J = 10.4$  Hz,  $^3J = 2.6$  Hz, H-6), 3.21 (dd,  $^3J = 10.4$  Hz,  $^3J = 2.0$  Hz, H-5).

$^{13}\text{C-NMR}$  (DMSO- $d_6$ , 300 K, 101 MHz):

$\delta$  (ppm) = 171.8 (s, C-3), 171.5 (s, COOH), 171.3 (s, COOH), 137.3 (s, C-1'), 132.9 (d, C-7), 130.3 (d, C-8), 128.5 (d, 2C, C-3'), 127.7 (d, 2C, C-2'), 127.3 (d, C-4'), 55.1 (d, C-1), 48.7 (d, C-6), 47.1 (d, C-4), 46.8 (t,  $\text{CH}_2$ ), 43.5 (d, C-5).

The analytical data obtained matched those reported in the literature.<sup>[6]</sup>

**(1S\*,4R\*,5S\*,6S\*)-2-Benzyl-3-oxo-2-azabicyclo[2.2.2]oct-7-ene-5,6-dicarboxylic-4-d acid (9a-d<sup>1</sup>)**



A mixture of **6a-d<sup>1</sup>** (3.75 g, 20.1 mmol, 1.0 eq.) and maleic anhydride (3.95 g, 40.3 mmol, 2.0 eq.) in  $\text{PhCH}_3$  (30.0 mL) was gently refluxed for 2 d. The reaction mixture was concentrated to half of its volume under reduced pressure and  $\text{CH}_2\text{Cl}_2$  (20 mL) and water (10 mL) was added. The layers were separated as far as possible and the aqueous phase was basified by the addition of 4 M and 1 M NaOH-solution (pH  $\approx$  10) to solubilize colorless solid at the phase boundary. The layers were separated completely and the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (2  $\times$  20 mL). The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ . Filtration and removal of the solvent under reduced pressure provided a brown residue.

To the crude product  $\text{PhCH}_3$  (15 mL) and water (15 mL) was added and the resulting mixture was allowed to reflux with vigorous stirring for one hour. After cooling down to room temperature, EtOAc (15 mL) was added and the aqueous phase was basified by the addition of NaOH-solution (4 M, pH  $\approx$  9). The layers were separated, and the organic phase was extracted with NaOH-solution (1 M, 20 mL). The organic phase was washed successively with water (20 mL), aqueous  $\text{NaHCO}_3$ -solution (20 mL), brine (20 mL) and dried over  $\text{Na}_2\text{SO}_4$ . Filtration and removal of the solvent under reduced pressure provided remaining starting material **6a-d<sup>1</sup>** (1.80 g, 9.67 mmol, 48%) as a beige solid.

The combined aqueous layers were washed with EtOAc (40 mL) and acidified (pH  $\approx$  1) by adding concentrated hydrochloric acid (12 M). A white precipitate formed, which was purified by recrystal-

lization from the reaction mixture and additional water to give the diacid **9a-d**<sup>1</sup> (2.12 g, 7.01 mmol, 35%, 84% D) as colorless crystals.

**M.p.:** 170-172 °C (from H<sub>2</sub>O).

**<sup>1</sup>H-NMR** (DMSO-*d*<sub>6</sub>, 300 K, 500 MHz):

δ (ppm) = 12.36 (s, 2H, 2 × COOH), 7.37-7.30 (m, 2H, H-2'), 7.30-7.23 (m, 1H, H-4'), 7.20-7.15 (m, 2H, H-3'), 6.44-6.32 (m, 2H, H-7, H-8), 4.54 (d, <sup>2</sup>J = 15.0 Hz, 1H, CHH), 4.33 (*virt. dt.*, <sup>3</sup>J = 5.1 Hz, <sup>3</sup>J ≈ <sup>4</sup>J = 2.5 Hz, 1H, H-1), 4.27 (d, <sup>2</sup>J = 15.0 Hz, 1H, CHH), 3.51 (*virt. dt.*, <sup>3</sup>J = 5.7 Hz, <sup>3</sup>J ≈ <sup>4</sup>J = 2.1 Hz, 0.16H, H-4), 3.26 (dd, <sup>3</sup>J = 10.4 Hz, <sup>3</sup>J = 2.8 Hz, 1H, H-6), 3.21 (d, <sup>3</sup>J = 10.4 Hz, 1H, H-5).

**<sup>13</sup>C-NMR** (DMSO-*d*<sub>6</sub>, 300 K, 126 MHz):

δ (ppm) = 171.9 (s, COOH), 171.6 (s, COOH), 171.4 (s, C-3), 137.3 (s, C-1'), 132.9 (d, C-7), 130.3 (d, C-8), 128.5 (d, 2C, C-3'), 127.7 (d, 2C, C-2'), 127.3 (d, C-4'), 55.1 (d, C-1), 48.6 (d, C-6), 47.1 (d, C-4), 46.8 (t, CH<sub>2</sub>), 43.4 (d, C-5).

**IR** (ATR):

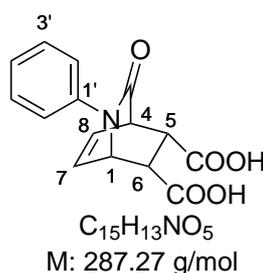
$\tilde{\nu}$  (cm<sup>-1</sup>) = 3166 (br, O-H), 3011 (w), 2495 (w), 1965 (w), 1733 (s, HO-C=O), 1686 (s, N-C=O), 1594 (m), 1409 (w), 1210 (m), 1178 (m), 814 (m), 761 (m).

**MS** (EI, 70 eV):

*m/z* (%) = 284 (16) [M<sup>+</sup>-H<sub>2</sub>O], 98 (36), 91 (31) [C<sub>7</sub>H<sub>7</sub><sup>+</sup>], 54 (100).

**HR-MS** (EI): [C<sub>16</sub>H<sub>12</sub>DNO<sub>4</sub><sup>+</sup>]: 284.0903 [M<sup>+</sup>-H<sub>2</sub>O], calc.: 284.0902.

**(1S\*,4R\*,5S\*,6S\*)-3-Oxo-2-phenyl-2-azabicyclo[2.2.2]oct-7-ene-5,6-dicarboxylic acid (9b)**



A mixture of 1-phenylpyridin-2(1*H*)-one<sup>[7]</sup> (7.80 g, 45.6 mmol, 1.0 eq.) and maleic anhydride (9.41 g, 91.2 mmol, 2.0 eq.) in PhCH<sub>3</sub> (57.0 mL) was gently refluxed for 2 d. The reaction mixture was concentrated to half of its volume under reduced pressure and CH<sub>2</sub>Cl<sub>2</sub> (250 mL) and water (50 mL) was added. The aqueous phase was basified by the addition of 1 M NaOH-solution and NaHCO<sub>3</sub>-solution (pH ≈ 10). The layers were separated completely and the aqueous phase was ex-

tracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 50$  mL). The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ . Filtration and removal of the solvent under reduced pressure provided a brown residue.

To the crude product  $\text{PhCH}_3$  (50 mL) and water (50 mL) was added and the resulting mixture was allowed to reflux with vigorous stirring for one hour. After cooling down to room temperature, EtOAc (150 mL) was added and the aqueous phase was basified by the addition of NaOH-solution (8 M,  $\text{pH} \approx 9$ ). The layers were separated, and the organic phase was extracted with NaOH-solution (1 M, 20 mL) and water (10 mL). The organic phase was washed successively with water (150 mL), aqueous  $\text{NaHCO}_3$ -solution (150 mL), brine (100 mL) and dried over  $\text{Na}_2\text{SO}_4$ . Filtration and removal of the solvent under reduced pressure provided remaining starting material (3.03 g, 17.7 mmol, 39%) as colorless, crystalline solid.

The combined aqueous layers were washed with EtOAc (100 mL) and acidified ( $\text{pH} \approx 1$ ) by adding concentrated hydrochloric acid (12 M). A white precipitate formed, which was purified by recrystallization from 1 M HCl-solution to give the diacid **9b** (1.10 g, 3.83 mmol, 8%) as a colorless powder.

**M.p.:**  $> 280$  °C (from 1 M HCl - decomposition).

**$^1\text{H-NMR}$**  ( $\text{DMSO-}d_6$ , 300 K, 500 MHz):

$\delta$  (ppm) = 12.28 (s, 2H,  $2 \times \text{COOH}$ ), 7.48-7.27 (m, 4H, H-2', H-3'), 7.26-7.10 (m, 1H, H-4'), 6.66 (ddd,  $^3J = 7.4$  Hz,  $^3J = 5.7$  Hz,  $^4J = 1.7$  Hz, 1H, H-7), 6.51 (ddd,  $^3J = 7.4$  Hz,  $^3J = 6.0$  Hz,  $^4J = 1.7$  Hz, 1H, H-8), 4.90 (ddd,  $^3J = 5.7$  Hz,  $^3J = 3.0$  Hz,  $^4J = 1.7$  Hz, 1H, H-1), 3.68 (dd,  $^3J = 10.5$  Hz,  $^3J = 3.0$  Hz, 1H, H-6), 3.59 (*virt. dt*,  $^3J = 6.0$  Hz,  $^3J \approx ^4J = 1.9$  Hz, 1H, H-4), 3.42 (dd,  $^3J = 10.5$  Hz,  $^3J = 2.2$  Hz, 1H, H-5).

**$^{13}\text{C-NMR}$**  ( $\text{DMSO-}d_6$ , 300 K, 126 MHz):

$\delta$  (ppm) = 171.9 (s, C-3), 171.4 (s, COOH), 170.5 (s, COOH), 139.8 (s, C-1'), 132.9 (d, C-7), 130.8 (d, C-8), 128.8 (d, 2C, C-3'), 125.5 (d, C-4'), 123.4 (d, 2C, C-2'), 58.2 (d, C-1), 48.7 (d, C-6), 47.8 (d, C-4), 42.9 (d, C-5).

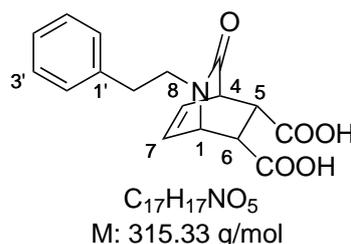
**IR** (ATR):

$\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 3059 (br, O-H), 1734 (s, HO-C=O), 1678 (s, N-C=O), 1494 (m), 1397 (m), 1158 (s), 1146 (s), 1108 (m), 1034 (m), 884 (m), 757 (s).

**MS** (EI, 70 eV):

$m/z$  (%) = 269 (25) [ $\text{M}^+ - \text{H}_2\text{O}$ ], 171 (18) [ $\text{M}^+ - \text{C}_4\text{H}_4\text{O}_4$ ], 119 (100) [ $\text{M}^+ - \text{C}_8\text{H}_8\text{O}_4$ ].

**HR-MS** (EI): [ $\text{C}_{15}\text{H}_{11}\text{NO}_4^+$ ]: 269.0681 [ $\text{M}^+ - \text{H}_2\text{O}$ ], calc.: 269.0681.

**(1S\*,4R\*,5S\*,6S\*)-3-Oxo-2-phenethyl-2-azabicyclo[2.2.2]oct-7-ene-5,6-dicarboxylic acid (9c)**

A mixture of 1-phenethylpyridin-2(1H)-one<sup>[8]</sup> (4.98 g, 25.0 mmol, 1.0 eq.) and maleic anhydride (4.90 g, 50.0 mmol, 2.0 eq.) in PhCH<sub>3</sub> (25.0 mL) was gently refluxed for 2 d. After cooling down to room temperature, water (10 mL) was added and the resulting mixture was allowed to reflux with vigorous stirring for two hours. After cooling down to room temperature, EtOAc (40 mL) was added and the aqueous phase was basified by the addition of 8 M (pH ≈ 12). The layers were separated, and the organic phase was extracted with NaOH-solution (1 M, 2 × 10 mL) and water (10 mL). The organic phase was washed successively with water (100 mL), aqueous NaHCO<sub>3</sub>-solution (50 mL), brine (50 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration and removal of the solvent under reduced pressure provided remaining starting material (2.90 g, 14.6 mmol, 58%) as colorless solid.

The combined aqueous layers were washed with EtOAc (50 mL) and acidified (pH ≈ 3) by adding concentrated hydrochloric acid (12 M). The aqueous layer was refluxed and stored over night in the refrigerator. The precipitate was collected by filtration to yield 7.07 g of a white solid, containing the product and maleic acid. Purification by flash chromatography (30 g SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH/HCOOH = 90:9.95:0.05) gave the diacid **9c** (2.08 g, 6.60 mmol, 26%) as a colorless solid. Further purification by recrystallization from water gave the diacid **9c** (1.91 g, 6.07 mmol, 24%) as colorless crystals.

**M.p.:** 169-171 °C (from H<sub>2</sub>O).

**TLC** (CH<sub>2</sub>Cl<sub>2</sub>/MeOH/HCOOH = 90:9.9:0.1): *R<sub>f</sub>* = 0.38 [UV].

**<sup>1</sup>H-NMR** (DMSO-*d*<sub>6</sub>, 300 K, 400 MHz):

δ (ppm) = 12.32 (s, 2H, 2 × COOH), 7.35-7.24 (m, 2H, H-3'), 7.24-7.13 (m, 3H, H-2', H-4'), 6.42 (ddd, <sup>3</sup>*J* = 7.4 Hz, <sup>3</sup>*J* = 5.3 Hz, <sup>4</sup>*J* = 1.6 Hz, 1H, H-7), 6.31 (ddd, <sup>3</sup>*J* = 7.4 Hz, <sup>3</sup>*J* = 6.1 Hz, <sup>4</sup>*J* = 1.7 Hz, 1H, H-8), 4.43 (ddd, <sup>3</sup>*J* = 5.3 Hz, <sup>3</sup>*J* = 3.0 Hz, <sup>4</sup>*J* = 1.7 Hz, 1H, H-1), 3.58-3.45 (m, 1H, NCHH), 3.39 (*virt. dt.*, <sup>3</sup>*J* = 6.1 Hz, <sup>3</sup>*J* ≈ <sup>4</sup>*J* = 1.9 Hz, 1H, H-4), 3.38-3.28 (m, 1H, NCHH), 3.21 (dd, <sup>3</sup>*J* = 10.5 Hz, <sup>3</sup>*J* = 3.0 Hz, 1H, H-6), 3.08 (dd, <sup>3</sup>*J* = 10.5 Hz, <sup>3</sup>*J* = 2.2 Hz, 1H, H-5), 2.81-2.56 (m, 2H, ArCH<sub>2</sub>).

**<sup>13</sup>C-NMR** (DMSO-*d*<sub>6</sub>, 300 K, 101 MHz):

$\delta$  (ppm) = 171.9 (s, COOH), 171.6 (s, COOH), 171.4 (s, C-3), 138.9 (s, C-1), 133.1 (d, C-7), 130.1 (d, C-8), 128.7 (d, 2C, C-2'), 128.3 (d, 2C, C-3'), 126.2 (d, C-4'), 55.5 (d, C-1), 48.7 (d, C-6), 47.1 (d, C-4), 45.3 (t, NCH<sub>2</sub>), 43.3 (d, C-5), 33.7 (t, ArCH<sub>2</sub>).

**IR** (ATR):

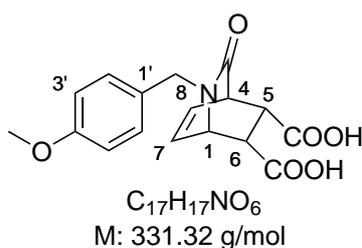
$\tilde{\nu}$  (cm<sup>-1</sup>) = 3098 (br, O–H), 2939 (m), 1732 (s, HO–C=O), 1650 (s, N–C=O), 1422 (m), 1335 (m), 1237 (s), 1175 (m), 1006 (m), 821 (m).

**MS** (EI, 70 eV):

$m/z$  (%) = 315 (3) [M<sup>+</sup>], 297 (5) [M<sup>+</sup>–H<sub>2</sub>O], 206 (17), 199 (7) [M<sup>+</sup>–C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>], 104 (100) [C<sub>8</sub>H<sub>8</sub><sup>+</sup>], 91 (14) [C<sub>7</sub>H<sub>7</sub><sup>+</sup>].

**HR-MS** (EI): [C<sub>17</sub>H<sub>17</sub>NO<sub>5</sub><sup>+</sup>]: 315.1068 [M<sup>+</sup>], calc.: 315.1101.

**(1S\*,4R\*,5S\*,6S\*)-2-(4-Methoxybenzyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene-5,6-dicarboxylic acid (9d)**



A mixture of 1-(4-methoxybenzyl)pyridin-2(1*H*)-one<sup>[5]</sup> (3.81 g, 17.7 mmol, 1.0 eq.) and maleic anhydride (3.47 g, 35.4 mmol, 2.0 eq.) in PhCH<sub>3</sub> (17.7 mL) was gently refluxed for 4 d. The reaction mixture was concentrated to yield a brown residue. To the crude product PhCH<sub>3</sub> (20 mL) and water (10 mL) was added and the resulting mixture was allowed to reflux with vigorous stirring for four hours. After cooling down to room temperature, EtOAc (40 mL) was added and the aqueous phase was basified by the addition of NaOH-solution (8 M, pH ≈ 12). The layers were separated, and the organic phase was extracted with NaOH-solution (1 M, 20 mL) and water (10 mL). The organic phase was washed successively with water (50 mL), aqueous NaHCO<sub>3</sub>-solution (50 mL), brine (100 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration and removal of the solvent under reduced pressure provided remaining starting material (1.83 g, 8.50 mmol, 48%) as a colorless solid.

The combined aqueous layers were washed with EtOAc (50 mL) and acidified (pH ≈ 1) by adding concentrated hydrochloric acid (12 M). The mixture was refluxed and stored over night in the refrigerator. The precipitate was collected by filtration to yield 3.39 g of a white solid. Purification by recrystallization from water gave the diacid **9d** (2.50 g, 7.55 mmol, 43%) as colorless crystals.

**M.p.:** 139-141 °C (from H<sub>2</sub>O).

**<sup>1</sup>H-NMR** (DMSO-*d*<sub>6</sub>, 300 K, 400 MHz):

δ (ppm) = 12.37 (s, 2H, 2 × COOH), 7.19-7.04 (m, 2H, H-2'), 6.98-6.84 (m, 2H, H-3'), 6.43-6.28 (m, 2H, H-7, H-8), 4.45 (d, <sup>2</sup>*J* = 14.7 Hz, 1H, CHH), 4.33 (virt. dt, <sup>3</sup>*J* = 4.8 Hz, <sup>3</sup>*J* ≈ <sup>4</sup>*J* = 2.3 Hz, 1H, H-1), 4.21 (d, <sup>2</sup>*J* = 14.7 Hz, 1H, CHH), 3.73 (s, 3H, OCH<sub>3</sub>), 3.51 (virt. dt, <sup>3</sup>*J* = 4.9 Hz, <sup>3</sup>*J* ≈ <sup>4</sup>*J* = 1.8 Hz, 1H, H-4), 3.27-3.14 (m, 2H, H-5, H-6).

**<sup>13</sup>C-NMR** (DMSO-*d*<sub>6</sub>, 300 K, 101 MHz):

δ (ppm) = 171.9 (s, COOH), 171.6 (s, COOH), 171.3 (s, C-3), 158.6 (s, C-4'), 132.9 (d, C-7), 130.3 (d, C-8), 129.2 (d, 2C, C-2'), 129.1 (s, C-1'), 114.0 (d, 2C, C-3'), 55.1 (d, C-1), 54.8 (q, OCH<sub>3</sub>), 48.7 (d, C-6), 47.2 (d, C-4), 46.2 (t, CH<sub>2</sub>), 43.5 (d, C-5).

**IR** (ATR):

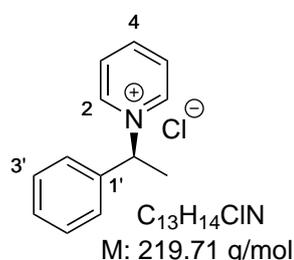
$\tilde{\nu}$  (cm<sup>-1</sup>) = 3190 (br, O-H), 2954 (w), 1730 (s, OH-C=O), 1703 (s, N-C=O), 1633 (s), 1611 (s), 1445 (m), 1353 (m), 1170 (m), 1033 (m), 852 (m), 828 (m).

**MS** (EI, 70 eV):

*m/z* (%) = 313 (32) [M<sup>+</sup>-H<sub>2</sub>O], 215 (12), 162 (27), 135 (24), 121 (100), 54 (31).

**HR-MS** (EI): [C<sub>17</sub>H<sub>15</sub>NO<sub>5</sub><sup>+</sup>]: 313.0945 [M<sup>+</sup>-H<sub>2</sub>O], calc.: 313.0938.

### (S)-1-(1-Phenylethyl)pyridin-1-ium chloride (S3)



According to a literature procedure,<sup>[9]</sup> to a stirred suspension of 1-(2,4-dinitrophenyl)pyridin-1-ium chloride<sup>[10]</sup> (20.0 g, 70.9 mmol, 1.0 eq.) in *n*-butanol (200 mL), (*S*)-1-phenylethan-1-amine (10.1 mL, 9.46 g, 78.0 mmol, 1.1 eq.) was added. The mixture was then refluxed for 24 h, and the crude mixture was concentrated. To the residue water (150 mL) was added and the precipitate filtered. The filtrate was washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 75 mL). The aqueous phase was concentrated under reduced pressure and the title compound **S3** (12.9 g, 58.5 mmol, 82%) obtained as yellow solid.

**<sup>1</sup>H-NMR** (DMSO-*d*<sub>6</sub>, 300 K, 500 MHz):

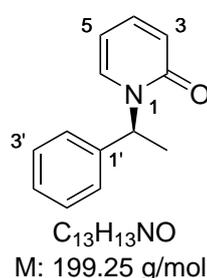
$\delta$  (ppm) = 9.33 (dt,  $^3J = 5.2$  Hz,  $^4J = 1.3$  Hz, 2H, H-2), 8.63 (tt,  $^3J = 7.7$  Hz,  $^4J = 1.3$  Hz, 1H, H-4), 8.19 (*virt.* t,  $^3J \approx ^3J = 7.1$  Hz, 2H, H-3), 7.61-7.56 (m, 2H, H-2'), 7.49-7.40 (m, 3H, H-3', H-4'), 6.32 (q,  $^3J = 7.0$  Hz, 1H, CHCH<sub>3</sub>), 2.06 (d,  $^3J = 7.0$  Hz, 3H, CHCH<sub>3</sub>).

<sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 300 K, 126 MHz):

$\delta$  (ppm) = 146.2 (d, C-4), 143.6 (d, 2C, C-2), 138.0 (s, C-1'), 129.2 (d, 2C, C-3'), 128.9 (d, C-4'), 128.6 (d, 2C, C-2'), 127.4 (d, 2C, C-3), 69.4 (d, CHCH<sub>3</sub>), 19.8 (q, CHCH<sub>3</sub>).

The analytical data obtained matched those reported in the literature.<sup>[9]</sup>

### (S)-1-(1-Phenylethyl)pyridin-2(1H)-on (S4)



According to a literature procedure,<sup>[11]</sup> a stirred solution of the pyridinium salt **S3** (12.9 g, 58.5 mmol, 1.0 eq.) in water (360 mL) was cooled to 5 °C and a solution of Potassium hexacyanoferrate(III) (212 g, 643 mmol, 11.0 eq.) in water (440 mL) was added dropwise over a period of 1 h. Then a solution of KOH (51.8 g, 924 mmol, 15.8 eq.) in water (145 mL) was added dropwise over 30 min. Toluene (600 mL) was added and the mixture was stirred at room temperature for 16 h. The layers were separated and the organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 150 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed *in vacuo*. The residue was purified by flash chromatography (150 g SiO<sub>2</sub>, Pn/CH<sub>2</sub>Cl<sub>2</sub>/EtOAc 1:1:0 → 0:1:0 → 0:8:2) to give the pyridone **S4** (7.73 g, 38.8 mmol, 66%, 97% *ee*) as a colorless solid.

**M.p.:** 79-81 °C.

**TLC** (Cy/EtOAc = 1:1): *R<sub>f</sub>* = 0.20 [UV].

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz):

$\delta$  (ppm) = 7.46-7.21 (m, 6H, PhH, H-4), 7.09 (ddd,  $^3J = 7.1$  Hz,  $^4J = 2.1$  Hz,  $^5J = 0.7$  Hz, 1H, H-6), 6.60 (ddd,  $^3J = 9.2$  Hz,  $^4J = 1.5$  Hz,  $^5J = 0.7$  Hz, 1H, H-3), 6.46 (q,  $^3J = 7.1$  Hz, 1H, CHCH<sub>3</sub>), 6.09 (*virt.* td,  $^3J \approx ^3J = 6.7$  Hz,  $^4J = 1.5$  Hz, 1H, H-5), 1.71 (d,  $^3J = 7.1$  Hz, 3H, CHCH<sub>3</sub>).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz):

$\delta$  (ppm) = 162.6 (s, C-2), 140.3 (s, C-1'), 138.9 (d, C-4), 134.4 (d, C-6), 128.9 (d, 2C, C-3'), 128.1

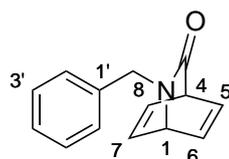
(d, C-4'), 127.6 (d, 2C, C-2'), 120.8 (d, C-3), 106.5 (d, C-5), 52.5 (d, CHCH<sub>3</sub>), 19.2 (q, CHCH<sub>3</sub>).

**Chiral HPLC:** (AS-H, *n*-heptane/*i*-propanol = 7:3, 1 mL/min,  $\lambda$  = 210 nm)

$t_R$  = 7.3 min [(*ent*)-**S4**], 14.1 min [**S4**].

The analytical data obtained matched those reported in the literature.<sup>[12]</sup>

### 2-Benzyl-2-azabicyclo[2.2.2]octa-5,7-dien-3-one (**1a**)



C<sub>14</sub>H<sub>13</sub>NO  
M: 211.26 g/mol

A solution of the diacid **9a** (6.20 g, 20.6 mmol, 1.0 eq.) in a pyridine/water-mixture (9:1, 300 mL) and NEt<sub>3</sub> (5.74 mL, 4.17 g, 41.2 mmol, 2.0 eq.) was electrolyzed at 30 V in an open water-cooled (25 °C) vessel for 25 h. The current diminished from 530 mA till 161 mA within that time. HCl (1 M, 200 mL) and EtOAc (400 mL) were added. The organic phase was separated and the aqueous phase was extracted with EtOAc (100 mL). The combined organic phases were washed with HCl (1 M, 5 × 100 mL) and water (200 mL), dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo* to give a dark residue. The azabarrelenone **1a** (1.74 g, 8.25 mmol, 40%) was obtained after purification by flash chromatography (250 g SiO<sub>2</sub>, Cy/EtOAc 8:2 → 1:1) as an oily solid. Further purification was achieved by recrystallization from Pn/Et<sub>2</sub>O to yield the title compound **1a** (1.47 g, 6.97 mmol, 34%) as colorless crystals.

**M.p.:** 57-59 °C (from Pn/Et<sub>2</sub>O).

**TLC** (Cy/EtOAc = 2:1):  $R_f$  = 0.34 [UV].

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 K, 500 MHz):

$\delta$  (ppm) = 7.38-7.29 (m, 2H, H-2'), 7.30-7.24 (m, 1H, H-4'), 7.16-7.07 (m, 2H, H-3'), 6.86 (ddd, <sup>3</sup> $J$  = 6.7 Hz, <sup>3</sup> $J$  = 5.8 Hz, <sup>4</sup> $J$  = 1.7 Hz, 2H, H-5, H-8), 6.63 (ddd, <sup>3</sup> $J$  = 6.7 Hz, <sup>3</sup> $J$  = 5.4 Hz, <sup>4</sup> $J$  = 1.7 Hz, 2H, H-6, H-7), 4.72 (tt, <sup>3</sup> $J$  = 5.4 Hz, <sup>4</sup> $J$  = 1.7 Hz, 1H, H-1), 4.48 (tt, <sup>3</sup> $J$  = 5.8 Hz, <sup>4</sup> $J$  = 1.7 Hz, 1H, H-4), 4.38 (s, 2H, CH<sub>2</sub>).

**<sup>13</sup>C-NMR** (CDCl<sub>3</sub>, 300 K, 126 MHz):

$\delta$  (ppm) = 172.7 (s, C-3), 137.0 (d, 2C, C-5, C-8), 136.6 (s, C-1'), 136.0 (d, 2C, C-6, C-7), 128.7 (d, 2C, C-2'), 128.2 (d, 2C, C-3'), 127.6 (d, C-4'), 57.2 (d, C-1), 54.6 (d, C-4), 49.2 (t, CH<sub>2</sub>).

**IR** (ATR):

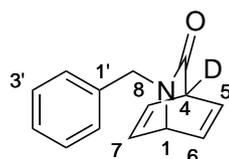
$\tilde{\nu}$  (cm<sup>-1</sup>) = 3087 (w, C–H), 3030 (w, C–H), 2919 (w, C–H), 1671 (s, N–C=O), 1581 (w, C=C).

**MS** (EI, 70 eV):

$m/z$  (%) = 133 (100) [M<sup>+</sup>–C<sub>6</sub>H<sub>6</sub>], 104 (55) [C<sub>7</sub>H<sub>6</sub>N<sup>+</sup>], 91 (75) [C<sub>7</sub>H<sub>7</sub><sup>+</sup>], 77 (34) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>], 51 (21).

**HR-MS** (EI): [C<sub>14</sub>H<sub>13</sub>NO<sup>+</sup>]: 211.0992 [M<sup>+</sup>], calc.: 211.0983.

### 2-Benzyl-2-azabicyclo[2.2.2]octa-5,7-dien-3-one-4-d (1a-d<sup>1</sup>)



C<sub>14</sub>H<sub>12</sub>DNO  
M: 212.27 g/mol

A solution of the diacid **9a-d<sup>1</sup>** (2.10 g, 6.96 mmol, 1.0 eq.) in a pyridine/water-mixture (9:1, 100 mL) and NEt<sub>3</sub> (1.70 mL, 1.23 g, 20.9 mmol, 3.0 eq.) was electrolyzed at 40 V in an open water-cooled (10 °C) vessel for 20 h. The current diminished from 390 mA till 90 mA within that time. Silica gel was added to the reaction mixture and the solvent removed *in vacuo*. A first purification by flash chromatography (40 g SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/Acetone 1:1) yielded a black tar. Further flash chromatographies (40 g SiO<sub>2</sub>, Hex/EtOAc 8:2 → 7:3; 40 g SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH 999:1 → 99:1) yield the title compound **1a-d<sup>1</sup>** (491 mg, 2.31 mmol, 33%, 85% D) as a colorless solid.

**M.p.:** 56-58 °C.

**TLC** (Cy/EtOAc = 2:1):  $R_f$  = 0.35 [UV].

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 K, 500 MHz):

$\delta$  (ppm) = 7.36-7.28 (m, 2H, H-2'), 7.29-7.24 (m, 1H, H-4'), 7.16-7.07 (m, 2H, H-3'), 6.85 (dd, <sup>3</sup> $J$  = 6.6 Hz, <sup>4</sup> $J$  = 1.8 Hz, 2H, H-5, H-8), 6.63 (ddd, <sup>3</sup> $J$  = 6.6 Hz, <sup>3</sup> $J$  = 5.4 Hz, <sup>4</sup> $J$  = 1.8 Hz, 2H, H-6, H-7), 4.72 (tt, <sup>3</sup> $J$  = 5.4 Hz, <sup>4</sup> $J$  = 1.8 Hz, 1H, H-1), 4.48 (tt, <sup>3</sup> $J$  = 5.8 Hz, <sup>4</sup> $J$  = 1.8 Hz, 0.15H, H-4), 4.38 (s, 2H, CH<sub>2</sub>).

**<sup>13</sup>C-NMR** (CDCl<sub>3</sub>, 300 K, 126 MHz):

$\delta$  (ppm) = 172.7 (C-3), 136.9 (d, 2C, C-5, C-8), 136.6 (s, C-1'), 136.0 (d, 2C, C-6, C-7), 128.7 (d, 2C, C-2'), 128.2 (d, 2C, C-3'), 127.6 (d, C-4'), 57.2 (d, C-1), 54.2 (t, <sup>1</sup> $J_{CD}$  = 22.7 Hz, C-4), 49.2 (t, CH<sub>2</sub>).

**IR** (ATR):

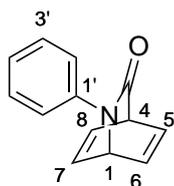
$\tilde{\nu}$  (cm<sup>-1</sup>) = 3067 (w, C–H), 1669 (s, N–C=O), 1496 (w), 1443 (w), 1418 (w), 1357 (w), 1226 (w), 950 (w), 764 (w), 701 (m).

**MS** (EI, 70 eV):

$m/z$  (%) = 133 (34) [ $M^+ - C_6H_5D$ ], 105 (21) [ $C_7H_7N^+$ ], 91 (49) [ $C_7H_7^+$ ], 79 (100) [ $C_6H_5D^+$ ], 51 (27).

**HR-MS** (EI): [ $C_{14}H_{12}DNO^+$ ]: 212.1046 [ $M^+$ ], calc.: 212.1054.

### 2-Phenyl-2-azabicyclo[2.2.2]octa-5,7-dien-3-one (**1b**)



$C_{13}H_{11}NO$   
M: 197.24 g/mol

A solution of the diacid **9b** (1.50 g, 5.22 mmol, 1.0 eq.) in a pyridine/water-mixture (9:1, 130 mL) and  $NEt_3$  (1.46 mL, 1.06 g, 10.4 mmol, 2.0 eq.) was electrolyzed at 35 V in an open water-cooled (10 °C) vessel for 23 h. The current diminished from 387 mA till 86 mA within that time. The solvent was removed *in vacuo* and EtOAc (400 mL) was added to the residue. The organic phase was washed with HCl (1 M, 5 × 100 mL) and water (150 mL), dried with anhydrous  $Na_2SO_4$ , and concentrated *in vacuo* to give a dark residue. A first purification by flash chromatography (40 g  $SiO_2$ , Hex/EtOAc 9:1 → 7:3) yields a yellow oily solid. Another purification by flash chromatography (40 g  $SiO_2$ ,  $CH_2Cl_2/MeOH$  99.5:0.5 → 97:3) yields the title compound **1b** (98.5 mg, 500  $\mu$ mol, 10%) as a yellow solid. Further purification was achieved by recrystallization from cyclohexane to yield the title compound **1b** (83.0 mg, 420  $\mu$ mol, 8%) as a colorless solid.

**M.p.:** 104-106 °C (from Cy).

**TLC** (Cy/EtOAc = 1:1):  $R_f$  = 0.40 [UV].

**$^1H$ -NMR** ( $CDCl_3$ , 300 K, 300 MHz):

$\delta$  (ppm) = 7.41-7.31 (m, 2H, H-3'), 7.25-7.12 (m, 3H, H-2', H-4'), 6.98 (ddd,  $^3J$  = 6.8 Hz,  $^3J$  = 5.7 Hz,  $^4J$  = 1.8 Hz, 2H, H-5, H-8), 6.90 (ddd,  $^3J$  = 6.8 Hz,  $^3J$  = 5.4,  $^4J$  = 1.8 Hz, 2H, H-6, H-7), 5.38 (tt,  $^3J$  = 5.4 Hz,  $^4J$  = 1.8 Hz, 1H, H-1), 4.53 (tt,  $^3J$  = 5.7 Hz,  $^4J$  = 1.8 Hz, 1H, H-4).

**$^{13}C$ -NMR** ( $CDCl_3$ , 300 K, 126 MHz):

$\delta$  (ppm) = 171.2 (s, C-3), 140.6 (s, C-1'), 137.2 (d, 2C, C-5, C-8), 135.9 (d, 2C, C-6, C-7), 129.1 (d, 2C, C-3'), 125.5 (d, C-4'), 122.5 (d, 2C, C-2'), 60.5 (d, C-1), 55.2 (d, C-4).

**IR** (ATR):

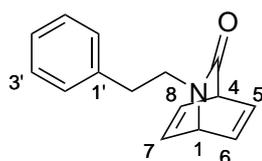
$\tilde{\nu}$  (cm<sup>-1</sup>) = 3070 (w, C–H), 1680 (s, N–C=O), 1493 (s), 1386 (m), 1262 (m), 1109 (w), 1090 (w), 768 (m), 755 (m).

**MS** (EI, 70 eV):

$m/z$  (%) = 119 (100) [M<sup>+</sup>–C<sub>6</sub>H<sub>6</sub>], 91 (53) [C<sub>7</sub>H<sub>7</sub><sup>+</sup>], 64 (23).

**HR-MS** (EI): [C<sub>13</sub>H<sub>11</sub>NO<sup>+</sup>]: 197.0830 [M<sup>+</sup>], calc.: 197.0835.

### 2-Phenethyl-2-azabicyclo[2.2.2]octa-5,7-dien-3-one (**1c**)



C<sub>15</sub>H<sub>15</sub>NO  
M: 225.29 g/mol

A solution of the diacid **9c** (1.75 g, 5.55 mmol, 1.0 eq.) in a pyridine/water-mixture (9:1, 130 mL) and NEt<sub>3</sub> (1.55 mL, 1.12 g, 11.1 mmol, 2.0 eq.) was electrolyzed at 35 V in an open water-cooled (10 °C) vessel for 21 h. The current diminished from 285 mA till 65 mA within that time. Silica gel was added to the reaction mixture and the solvent removed *in vacuo*. A first purification by flash chromatography (100 g SiO<sub>2</sub>, Cy/Acetone 1:1) yielded a black oil. Another purification by flash chromatography (50 g SiO<sub>2</sub>, Hex/EtOAc 8:2 → 1:2) yields the azabarrelenone **1c** (514 mg, 2.28 mmol, 41%) as a colorless solid. Further purification was achieved by recrystallization from Pn/Et<sub>2</sub>O to yield the title compound **1c** (352 mg, 1.56 mmol, 28%) as colorless crystals.

**M.p.:** 73-74 °C (from Pn/Et<sub>2</sub>O).

**TLC** (Cy/EtOAc = 1:1):  $R_f$  = 0.32 [UV].

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 K, 400 MHz):

$\delta$  (ppm) = 7.34-7.25 (m, 2H, H-2'), 7.25-7.16 (m, 3H, H-3', H-4'), 6.81 (ddd, <sup>3</sup> $J$  = 6.9 Hz, <sup>3</sup> $J$  = 5.8 Hz, <sup>4</sup> $J$  = 1.7 Hz, 2H, H-5, H-8), 6.61 (ddd, <sup>3</sup> $J$  = 6.9, <sup>3</sup> $J$  = 5.4 Hz, <sup>4</sup> $J$  = 1.7 Hz, 2H, H-6, H-7), 4.64 (tt, <sup>3</sup> $J$  = 5.4 Hz, <sup>4</sup> $J$  = 1.7 Hz, 1H, H-1), 4.37 (tt, <sup>3</sup> $J$  = 5.8 Hz, <sup>4</sup> $J$  = 1.7 Hz, 1H, H-4), 3.45 (dd, <sup>3</sup> $J$  = 7.9 Hz, <sup>3</sup> $J$  = 6.7 Hz, 2H, NCH<sub>2</sub>), 2.71 (*virt. t.*, <sup>3</sup> $J$   $\approx$  <sup>3</sup> $J$  = 7.3 Hz, 2H, ArCH<sub>2</sub>).

**<sup>13</sup>C-NMR** (CDCl<sub>3</sub>, 300 K, 101 MHz):

$\delta$  (ppm) = 173.1 (s, C-3), 139.0 (s, C-1'), 137.0 (d, 2C, C-5, C-8), 136.1 (d, 2C, C-6, C-7), 129.1 (d, 2C, C-3'), 128.6 (d, 2C, C-2'), 126.6 (d, C-4'), 58.8 (d, C-1), 54.6 (d, C-4), 47.5 (t, NCH<sub>2</sub>), 34.7 (t, ArCH<sub>2</sub>).

**IR** (ATR):

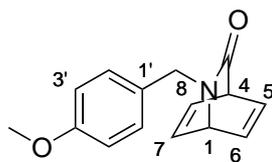
3066 (w, C–H), 2927 (w, C–H), 1664 (s, N–C=O), 1453 (m), 1224 (m), 1198 (m), 1085 (w), 997 (w), 785 (m), 693 (m).

**MS** (EI, 70 eV):

$m/z$  (%) = 147 (60)  $[M^+ - C_6H_6]$ , 91 (100)  $[C_7H_7^+]$ , 89 (7), 65 (21).

**HR-MS** (ESI):  $[C_{15}H_{16}NO^+]$ : 226.1227  $[M^+ + H]$ , calc.: 226.1226.

**2-(4-Methoxybenzyl)-2-azabicyclo[2.2.2]octa-5,7-dien-3-one (1d)**



$C_{15}H_{15}NO_2$   
M: 241.29 g/mol

A solution of the diacid **9d** (1.02 g, 3.08 mmol, 1.0 eq.) in a pyridine/water-mixture (9:1, 120 mL) and  $NEt_3$  (860  $\mu$ L, 620 mg, 6.16 mmol, 2.0 eq.) was electrolyzed at 35 V in an open water-cooled (10 °C) vessel for 21 h. The current diminished from 173 mA till 78 mA within that time. Silica gel was added to the reaction mixture and the solvent removed *in vacuo*. A first purification by flash chromatography (40 g  $SiO_2$ ,  $CH_2Cl_2$ /Acetone 1:1) yielded a black tar. Another purification by flash chromatography (50 g  $SiO_2$ , Hex/EtOAc 8:2  $\rightarrow$  1:2) yields the title compound **1d** (121 mg, 500  $\mu$ mol, 16%) as a colorless solid.

**M.p.:** 117-119 °C.

**TLC** (Cy/EtOAc = 1:1):  $R_f$  = 0.24 [UV].

**$^1H$ -NMR** ( $CDCl_3$ , 300 K, 400 MHz):

$\delta$  (ppm) = 7.08-7.01 (m, 2H, H-2'), 6.89-6.79 (m, 4H, H-3', H-5, H-8), 6.61 (ddd,  $^3J$  = 6.8 Hz,  $^3J$  = 5.4 Hz,  $^4J$  = 1.7 Hz, 2H, H-6, H-7), 4.71 (tt,  $^3J$  = 5.4 Hz,  $^4J$  = 1.7 Hz, 1H, H-1), 4.46 (tt,  $^3J$  = 5.8 Hz,  $^4J$  = 1.7 Hz, 1H, H-4), 4.31 (s, 2H,  $CH_2$ ), 3.80 (s, 3H,  $OCH_3$ ).

**$^{13}C$ -NMR** ( $CDCl_3$ , 300 K, 101 MHz):

$\delta$  (ppm) = 172.6 (s, C-3), 159.2 (s, C-4'), 137.0 (d, 2C, C-5, C-8), 136.0 (d, 2C, C-6, C-7), 129.6 (d, 2C, C-2'), 128.6 (s, C-1'), 114.1 (d, 2C, C-3'), 57.0 (d, C-1), 55.4 (q,  $OCH_3$ ), 54.6 (d, C-4), 48.6 (t,  $CH_2$ ).

**IR** (ATR):

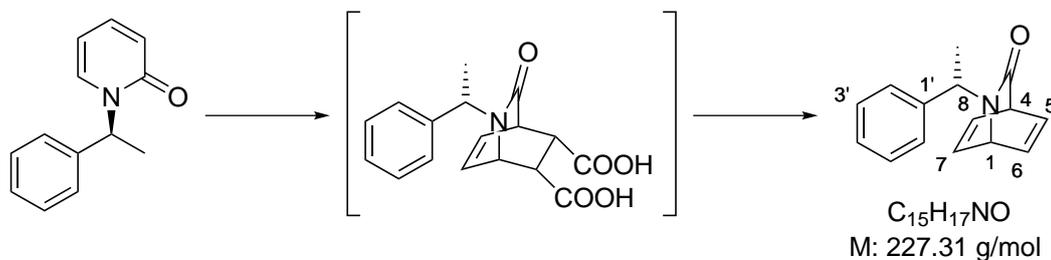
$\tilde{\nu}$  ( $cm^{-1}$ ) = 3057 (w), 2960 (w), 1663 (s, N–C=O), 1513 (m), 1444 (m), 1241 (s), 1031 (m), 939 (m), 816 (m).

**MS** (EI, 70 eV):

$m/z$  (%) = 163 (52) [ $M^+ - C_6H_6$ ], 121 (100) [ $M^+ - C_7H_6NO$ ], 91 (7), 77 (13).

**HR-MS** (EI): [ $C_{15}H_{15}NO_2^+$ ]: 241.1103 [ $M^+$ ], calc.: 241.1097.

### 2-[(S)-1-Phenylethyl]-2-azabicyclo[2.2.2]oct-5-en-3-on (**1e**)



#### *Diels-Alder-Reaction of S4 and maleic anhydride*

A mixture of **S4** (7.73 g, 38.8 mmol, 1.0 eq.) and maleic anhydride (7.61 g, 78.0 mmol, 2.0 eq.) in  $PhCH_3$  (48.5 mL) was gently refluxed for 2 d. The reaction mixture was concentrated to half of its volume under reduced pressure and  $CH_2Cl_2$  (60 mL) and water (30 mL) was added. The layers were separated as far as possible and the aqueous phase was basified by the addition of 4 M and 1 M NaOH-solution (pH  $\approx$  10) to solubilize colorless solid at the phase boundary. The layers were separated completely and the aqueous phase was extracted with  $CH_2Cl_2$  (3  $\times$  50 mL). The combined organic layers were dried over  $Na_2SO_4$ . Filtration and removal of the solvent under reduced pressure provided a brown residue.

To the crude product  $PhCH_3$  (30 mL) and water (10 mL) was added and the resulting mixture was allowed to reflux with vigorous stirring for three hours. After cooling down to room temperature, EtOAc (80 mL) was added and the aqueous phase was basified by the addition of NaOH-solution (8 M, pH  $\approx$  9). The layers were separated, and the organic phase was extracted with NaOH-solution (1 M, 40 mL). The organic phase was washed successively with water (200 mL), aqueous  $NaHCO_3$ -solution (200 mL), brine (100 mL) and dried over  $Na_2SO_4$ . Filtration and removal of the solvent under reduced pressure provided remaining starting material **S4** (3.66 g, 18.4 mmol, 47%) as a beige solid.

The combined aqueous layers were washed with EtOAc (50 mL) and acidified (pH  $\approx$  1) by adding concentrated hydrochloric acid (12 M). A white precipitate was collected by filtration to yield the diacid **9e** (4.64 g, 14.7 mmol, 38%) as colorless crystals.

#### *Electrolysis of the diacid 9e*

A solution of the diacid **9e** (4.50 g, 14.3 mmol, 1.0 eq.) in a pyridine/water-mixture (9:1, 142 mL) and  $\text{NEt}_3$  (3.98 mL, 2.89 g, 28.5 mmol, 2.0 eq.) was electrolyzed at 35 V in an open water-cooled (10 °C) vessel for 27 h. The current diminished from 540 mA till 95 mA within that time. HCl (1 M, 200 mL) and EtOAc (250 mL) were added. The organic phase was separated and the aqueous phase was extracted with EtOAc (100 mL). The combined organic phases were washed with HCl (1 M, 6 × 200 mL) and water (200 mL), dried with anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated *in vacuo* to give a dark residue. The azabarrelenone **1e** (1.51 g, 6.71 mmol, 47%, 99% *ee*) was obtained after purification by flash chromatography (140 g  $\text{SiO}_2$ , Hex/EtOAc 7:3 → 1:1) as a colorless solid.

**M.p.:** 79-81 °C.

**TLC** (Cy/EtOAc = 1:1):  $R_f = 0.41$  [UV].

**$^1\text{H-NMR}$**  ( $\text{CDCl}_3$ , 300 K, 500 MHz):

$\delta$  (ppm) = 7.41-7.27 (m, 3H, H-3', H-4'), 7.24-7.17 (m, 2H, H-2'), 6.89 (ddd,  $^3J = 7.0$  Hz,  $^3J = 5.9$  Hz,  $^4J = 1.7$  Hz, 1H, H-5\*/H-8\*), 6.81 (ddd,  $^3J = 7.0$  Hz,  $^3J = 5.9$  Hz,  $^4J = 1.7$  Hz, 1H, H-8\*/H-5\*), 6.72 (ddd,  $^3J = 7.0$  Hz,  $^3J = 5.4$  Hz,  $^4J = 1.8$  Hz, 1H, H-6\*/H-7\*), 6.43 (ddd,  $^3J = 7.0$  Hz,  $^3J = 5.4$  Hz,  $^4J = 1.8$  Hz, 1H, H-6\*/H-7\*), 5.38 (q,  $^3J = 7.0$  Hz, 1H, NCH), 4.64 (tt,  $^3J = 5.4$  Hz,  $^4J = 1.7$  Hz, 1H, H-1), 4.50 (tt,  $^3J = 5.9$  Hz,  $^4J = 1.8$  Hz, 1H, H-4), 1.43 (d,  $^3J = 7.0$  Hz, 3H,  $\text{CH}_3$ ).

**$^{13}\text{C-NMR}$**  ( $\text{CDCl}_3$ , 300 K, 126 MHz):

$\delta$  (ppm) = 171.9 (s, C-3), 140.1 (s, C-1'), 137.6 (d, C-5\*/C-8\*), 136.6 (d, C-8\*/C-5\*), 136.3 (d, C-6\*, C-7\*), 128.5 (d, C-3'), 127.5 (d, C-4'), 127.4 (d, C-2'), 54.7 (d, C-4), 53.2 (d, C-1), 50.1 (d, NCH), 15.9 (q,  $\text{CH}_3$ ).

\* The assignment is interchangeable.

**IR** (ATR):

$\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 3029 (w), 2974 (w), 1664 (s, N-C=O), 1622 (m, C=C), 1495 (w), 1405 (m), 1327 (m), 1206 (m), 1191 (m), 1033 (m), 873 (w), 791 (m).

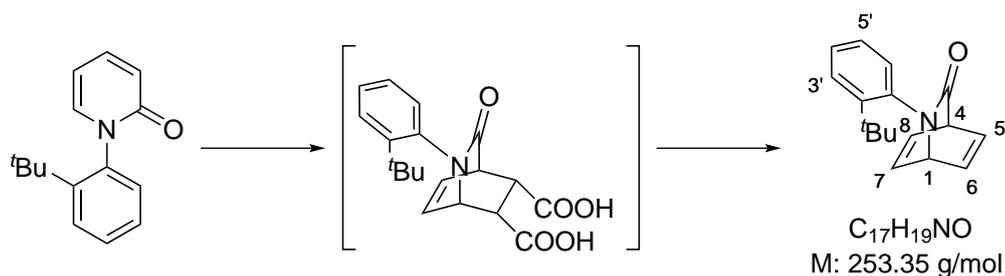
**MS** (EI, 70 eV):

$m/z$  (%) = 147 (47) [ $\text{M}^+ - \text{C}_6\text{H}_6$ ], 132 (100) [ $\text{M}^+ - \text{C}_7\text{H}_9$ ], 105 (27) [ $\text{C}_8\text{H}_9^+$ ], 77 (34) [ $\text{C}_6\text{H}_5^+$ ].

**HR-MS** (EI): [ $\text{C}_{15}\text{H}_{15}\text{NO}^+$ ]: 225.1156 [ $\text{M}^+$ ], calc.: 225.1148.

**Chiral HPLC:** (AD-H, *n*-heptane/*i*-propanol = 7:3, 1 mL/min,  $\lambda = 210$  nm)

$t_R = 8.0$  min [(*ent*)-**1e**], 12.6 min [**1e**].

2-[(*R*<sup>a</sup>)-2-(*tert*-Butyl)phenyl]-2-azabicyclo[2.2.2]octa-5,7-dien-3-one (**1f**)*Diels-Alder-Reaction of 1-[2-(tert-Butyl)phenyl]pyridin-2(1H)-one and maleic anhydride*

A mixture of 1-[2-(*tert*-Butyl)phenyl]pyridin-2(1*H*)-one<sup>[13]</sup> (6.58 g, 28.9 mmol, 1.0 eq.) and maleic anhydride (5.98 g, 57.9 mmol, 2.0 eq.) in PhCH<sub>3</sub> (36.2 mL) was gently refluxed for 2 d. The reaction mixture was concentrated to half of its volume under reduced pressure and CH<sub>2</sub>Cl<sub>2</sub> (80 mL) and water (40 mL) was added. The layers were separated as far as possible and the aqueous phase was basified by the addition of 4 M and 1 M NaOH-solution (pH ≈ 10) to solubilize colorless solid at the phase boundary. The layers were separated completely and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration and removal of the solvent under reduced pressure provided a brown residue.

To the crude product PhCH<sub>3</sub> (20 mL) and water (20 mL) was added and the resulting mixture was allowed to reflux with vigorous stirring for one hour. After cooling down to room temperature, EtOAc (60 mL) was added and the aqueous phase was basified by the addition of NaOH-solution (8 M, pH ≈ 8). The layers were separated, and the organic phase was extracted with NaOH-solution (1 M, 20 mL). The organic phase was washed successively with water (200 mL), aqueous NaHCO<sub>3</sub>-solution (150 mL), brine (100 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration and removal of the solvent under reduced pressure provided remaining starting material (4.84 g, 21.3 mmol, 74%) as a brown solid.

The combined aqueous layers were washed with EtOAc (50 mL) and acidified (pH ≈ 1) by adding concentrated hydrochloric acid (12 M). The formation of an dark oil at the bottom of the flask was observed and no precipitation occurred. The oil was isolated by decanting the supernatant fluid and dried under reduced pressure. The crude diacid **9f** (1.78 g, 5.18 mmol, 18%) was obtained as brown solid and used without further purification in the next step.

*Electrolysis of the diacid 9f*

A solution of the diacid **9f** (1.77 g, 5.14 mmol, 1.0 eq.) in a pyridine/water-mixture (9:1, 103 mL) and NEt<sub>3</sub> (1.43 mL, 1.04 g, 10.3 mmol, 2.0 eq.) was electrolyzed at 35 V in an open water-cooled

(10 °C) vessel for 22 h. The current diminished from 253 mA till 140 mA within that time. HCl (1 M, 200 mL) and EtOAc (150 mL) were added. The organic phase was separated and the aqueous phase was extracted with EtOAc (100 mL). The combined organic phases were washed with HCl (1 M, 5 × 200 mL) and water (200 mL), dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo* to give a dark residue. The azabarrelenone **1f** (219 mg, 860 μmol, 17%) was obtained after purification by flash chromatography (60 g SiO<sub>2</sub>, Hex/EtOAc 85:15 → 4:6) as a beige solid. Further purification was achieved by recrystallization from Pn/Et<sub>2</sub>O to yield the atropisomeric title compound **1f** (144 mg, 570 μmol, 11%) as colorless solid.

**M.p.:** 126-128 °C (from Pn/Et<sub>2</sub>O).

**TLC** (Cy/EtOAc = 2:1):  $R_f = 0.34$  [UV].

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 K, 500 MHz):

$\delta$  (ppm) = 7.46 (dd, <sup>3</sup> $J = 8.0$  Hz, <sup>4</sup> $J = 1.6$  Hz, 1H, H-3'), 7.30-7.23 (m, 1H, H-4'), 7.20 (*virt. td*, <sup>3</sup> $J \approx$  <sup>3</sup> $J = 7.6$  Hz, <sup>4</sup> $J = 1.6$  Hz, 1H, H-5'), 7.08 (*virt. td*, <sup>3</sup> $J \approx$  <sup>3</sup> $J = 6.2$  Hz, <sup>4</sup> $J = 1.8$  Hz, 1H, H-6\*/H-7\*), 7.02-6.93 (m, 3H, H-5, H-8, H-7\*/H-6\*), 6.82 (dd, <sup>3</sup> $J = 7.6$  Hz, <sup>4</sup> $J = 1.6$  Hz, 1H, H-6'), 4.87 (tt, <sup>3</sup> $J = 5.2$  Hz, <sup>4</sup> $J = 1.8$  Hz, 1H, H-1), 4.53 (tt, <sup>3</sup> $J = 5.7$  Hz, <sup>4</sup> $J = 1.8$  Hz, 1H, H-4), 1.32 (s, 9H, CH<sub>3</sub>).

**<sup>13</sup>C-NMR** (CDCl<sub>3</sub>, 300 K, 126 MHz):

$\delta$  (ppm) = 173.3 (s, C-3), 148.8 (s, C-2'), 141.5 (s, C-1'), 137.5 (d, C-6\*/C-7\*), 136.7 (d, C-5\*/C8\*), 136.5 (d, C-7\*/C-6\*), 135.7 (d, C-8\*/C5\*), 128.5 (d, C-4'), 127.72 (d, C-3'\*/C-5'\*), 127.69 (d, C-5'\*/C-3'\*), 127.0 (d, C-6'), 63.2 (d, C-1), 55.2 (d, C-4), 35.2 (s, C(CH<sub>3</sub>)<sub>3</sub>), 30.9 [q, C(CH<sub>3</sub>)<sub>3</sub>].

\* The assignment is interchangeable.

**IR** (ATR):

$\tilde{\nu}$  (cm<sup>-1</sup>) = 3069 (w), 3006 (w), 2958 (w), 1684 (s, N-C=O), 1618 (w, C=C), 1487 (m), 1441 (m), 1375 (m), 1241 (w), 1109 (w), 1052 (w), 774 (m).

**MS** (EI, 70 eV):

$m/z$  (%) = 175 (42) [M<sup>+</sup>-C<sub>6</sub>H<sub>6</sub>], 160 (100), 142 (39), 132 (35), 117 (16), 115 (16).

**HR-MS** (EI): [C<sub>17</sub>H<sub>19</sub>NO<sup>+</sup>]: 253.1451 [M<sup>+</sup>], calc.: 254.1461.

**Chiral HPLC:** (AD-H, *n*-heptane/*i*-propanol = 9:1, 1 mL/min,  $\lambda = 210$  nm)

$t_R = 7.6$  min, 9.2 min.

### 3 Di- $\pi$ -Methane Rearrangements of 2-Azabarrelenones

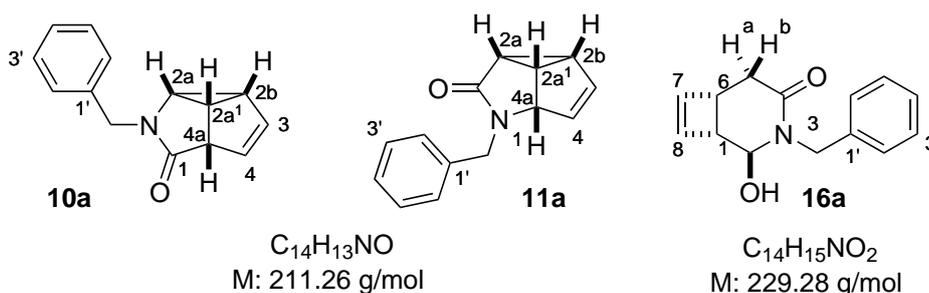
#### General procedure 1 (GP1): Intramolecular Di- $\pi$ -Methane Rearrangement

A solution of the corresponding 2-azabarrelenone (1.0 eq.) and 9*H*-xanthen-9-one (50 mol%) in anhydrous  $\alpha,\alpha,\alpha$ -trifluorotoluene (TFT,  $c = 12.0$  mmol/L) was degassed by purging with argon for 15 min in a ultrasonating bath. The solution was irradiated at 366 nm at room temperature and the solvent was removed *in vacuo*. The rearrangement products were obtained by flash chromatography.

**(2a*R*<sup>\*</sup>,2a'<sup>1</sup>*R*<sup>\*</sup>,2b*R*<sup>\*</sup>,4a*S*<sup>\*</sup>)-2-Benzyl-2a,2a'<sup>1</sup>,2b,4a-tetrahydro-2-azacyclopropa[cd]pentalen-1(2*H*)-one (10a),**

**(2a*R*<sup>\*</sup>,2a'<sup>1</sup>*S*<sup>\*</sup>,2b*R*<sup>\*</sup>,4a*S*<sup>\*</sup>)-1-Benzyl-2a,2a'<sup>1</sup>,2b,4a-tetrahydro-1-azacyclopropa[cd]pentalen-2(1*H*)-one (11a) and**

**(1*R*<sup>\*</sup>,2*S*<sup>\*</sup>,6*S*<sup>\*</sup>)-3-Benzyl-2-hydroxy-3-azabicyclo[4.2.0]oct-7-en-4-one (16a)**



According to **GP1** a solution of the azabarrelenone **1a** (100 mg, 473  $\mu$ mol, 1.0 eq.) and xanthenone (46.4 mg, 237  $\mu$ mol, 50 mol%) in TFT (39.4 mL,  $c = 12.0$  mmol/L) was irradiated for five hours. Purification by flash chromatography (30 g SiO<sub>2</sub>, Hex/EtOAc 8:2  $\rightarrow$  0:1) afforded the main product **10a** (53.3 mg, 252  $\mu$ mol, 53%) and the regioisomer **11a** (30.0 mg, 142  $\mu$ mol, 30%) as colorless, highly viscous resins. In a later fraction the side product **16a** (10.4 mg, 45.0  $\mu$ mol, 10%) was obtained as a colorless, highly viscous oil.

#### Background reaction

According to **GP1** a solution of the azabarrelenone **1a** (6.00 mg, 28.0  $\mu$ mol, 1.0 eq.) in TFT (2.40 mL,  $c = 12.0$  mmol/L) was irradiated for twelve hours. The solvent was removed under reduced pressure. The <sup>1</sup>H-NMR-spectrum of the crude product confirms no conversion of the azabarrelenone.

#### Data of **10a**:

**TLC** (Cy/EtOAc = 1:1):  $R_f = 0.40$  [UV].

**$^1\text{H-NMR}$**  ( $\text{CDCl}_3$ , 300 K, 500 MHz):

$\delta$  (ppm) = 7.35-7.24 (m, 3H, H-2', H-4'), 7.22-7.15 (m, 2H, H-3'), 5.58 (dd,  $^3J = 5.2$  Hz,  $^3J = 2.2$  Hz, 1H, H-4), 5.56 (dd,  $^3J = 5.2$  Hz,  $^3J = 2.5$  Hz, 1H, H-3), 4.40 (s, 2H,  $\text{CH}_2$ ), 3.64 (dd,  $^3J = 6.9$  Hz,  $^3J = 2.2$  Hz, 1H, H-4a), 3.30 (dd,  $^3J = 7.8$  Hz,  $^3J = 4.5$  Hz, 1H, H-2a), 2.66 (*virt. q.*,  $^3J \approx ^3J \approx ^3J = 7.0$  Hz, 1H, H-2a<sup>1</sup>), 2.23 (ddd,  $^3J = 6.7$  Hz,  $^3J = 4.5$  Hz,  $^3J = 2.5$  Hz, 1H, H-2b).

**$^{13}\text{C-NMR}$**  ( $\text{CDCl}_3$ , 300 K, 126 MHz):

$\delta$  (ppm) = 176.1 (s, C-1), 136.0 (s, C-1'), 133.6 (d, C-4), 128.5 (d, 2C, C-2'), 128.5 (d, 2C, C-3'), 127.9 (d, C-3), 127.6 (d, C-4'), 54.5 (d, C-4a), 47.6 (t,  $\text{CH}_2$ ), 43.8 (d, C-2a), 35.9 (d, C-2b), 33.6 (d, C-2a<sup>1</sup>).

**IR** (ATR):

$\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 3062 (w, C-H), 1678 (s, N-C=O), 1412 (w), 1248 (w), 1224 (w), 781 (w), 733 (w), 661 (w).

**MS** (EI, 70 eV):

$m/z$  (%) = 211 (68) [ $\text{M}^+$ ], 120 (12) [ $\text{M}^+ - \text{C}_7\text{H}_7$ ], 91 (100) [ $\text{C}_7\text{H}_7^+$ ], 65 (33).

**HR-MS** (EI): [ $\text{C}_{14}\text{H}_{13}\text{NO}^+$ ]: 211.0978 [ $\text{M}^+$ ], calc.: 211.0992.

*Data of 11a:*

**TLC** (Cy/EtOAc = 1:1):  $R_f = 0.26$  [ $\text{KMnO}_4$ ].

**$^1\text{H-NMR}$**  ( $\text{CDCl}_3$ , 300 K, 500 MHz):

$\delta$  (ppm) = 7.39-7.27 (m, 5H, H-2', H-3', H-4'), 5.99 (ddd,  $^3J = 5.4$  Hz,  $^3J = 2.4$  Hz,  $^4J = 1.2$  Hz, 1H, H-3), 5.87 (dd,  $^3J = 5.4$  Hz,  $^3J = 1.6$  Hz, 1H, H-4), 4.80 (d,  $^2J = 15.1$  Hz, 1H, CHH), 4.20 (*virt. dt.*,  $^3J = 6.1$  Hz,  $^3J \approx ^4J = 1.2$  Hz, 1H, H-4a), 3.76 (d,  $^2J = 15.1$  Hz, 1H, CHH), 2.95 (*virt. q.*,  $^3J \approx ^3J \approx ^3J = 6.2$  Hz, 1H, H-2a<sup>1</sup>), 2.55 (dd,  $^3J = 6.8$  Hz,  $^3J = 6.1$  Hz, 1H, H-2a), 2.51 (ddd,  $^3J = 6.8$  Hz,  $^3J = 5.8$  Hz,  $^3J = 2.4$  Hz, 1H, H-2b).

**$^{13}\text{C-NMR}$**  ( $\text{CDCl}_3$ , 300 K, 126 MHz):

$\delta$  (ppm) = 170.1 (s, C-2), 136.9 (s, C-1'), 134.8 (d, C-4), 131.2 (d, C-3), 128.8 (d, 2C, C-3'), 128.4 (d, 2C, C-2'), 127.7 (d, C-4'), 64.1 (d, C-4a), 45.6 (t,  $\text{CH}_2$ ), 38.3 (d, C-2a), 37.4 (d, C-2a<sup>1</sup>), 34.5 (d, C-2b).

**IR** (ATR):

$\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 2922 (w, C-H), 1677 (s, N-C=O), 1415 (w), 1357 (w), 1219 (w), 812 (w), 741 (w), 702 (w).

**MS** (EI, 70 eV):

$m/z$  (%) = 211 (100) [ $\text{M}^+$ ], 182 (10), 134 (17), 106 (32), 91 (97) [ $\text{C}_7\text{H}_7^+$ ], 78 (59), 65 (33).

**HR-MS** (EI): [ $\text{C}_{14}\text{H}_{13}\text{NO}^+$ ]: 211.0975 [ $\text{M}^+$ ], calc.: 211.0992.

**Data of 16a:****TLC** (EtOAc):  $R_f = 0.45$  [UV]. **$^1\text{H-NMR}$**  ( $\text{CDCl}_3$ , 300 K, 500 MHz):

$\delta$  (ppm) = 7.39-7.22 (m, 5H, H-2', H-3', H-4'), 6.14 (dd,  $^3J = 2.8$  Hz,  $^3J = 0.5$  Hz, 1H, H-7), 5.73 (dd,  $^3J = 2.8$  Hz,  $^3J = 0.7$  Hz, 1H, H-8), 5.04 (br. s, 1H, H-2), 4.68 (d,  $^2J = 14.8$  Hz 1H, NCHH), 4.62 (d,  $^2J = 14.8$  Hz, 1H, NCHH), 3.32 (ddd,  $^3J = 6.2$  Hz,  $^3J = 4.1$  Hz,  $^3J = 1.8$  Hz, 1H, H-6), 3.12 (dd,  $^3J = 4.1$  Hz,  $^3J = 2.1$  Hz, 1H, H-1), 2.84 (dd,  $^2J = 15.6$  Hz,  $^3J = 6.2$  Hz, 1H, H-5a), 2.59 (dd,  $^2J = 15.6$  Hz,  $^3J = 1.8$  Hz, 1H, H-5b), 1.73 (s, 1H, OH).

 **$^{13}\text{C-NMR}$**  ( $\text{CDCl}_3$ , 300 K, 126 MHz):

$\delta$  (ppm) = 170.6 (s, C-4), 141.0 (d, C-7), 137.8 (s, C-1'), 136.2 (d, C-8), 128.9 (d, 2C, C-3'), 128.6 (d, 2C, C-2'), 127.9 (d, C-4'), 81.5 (d, C-2), 49.4 (t,  $\text{NCH}_2$ ), 46.4 (d, C-1), 39.0 (d, C-6), 35.1 (t, C-5).

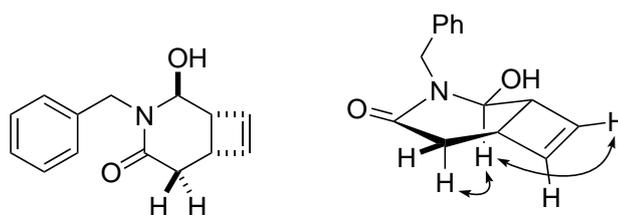
**IR** (ATR):

$\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 3323 (br, O-H), 3036 (w), 2927 (w), 1629 (s, N-C=O), 1454 (m), 1353 (m), 1247 (m), 1157 (m), 1050 (m), 943 (w), 761 (m).

**MS** (EI, 70 eV):

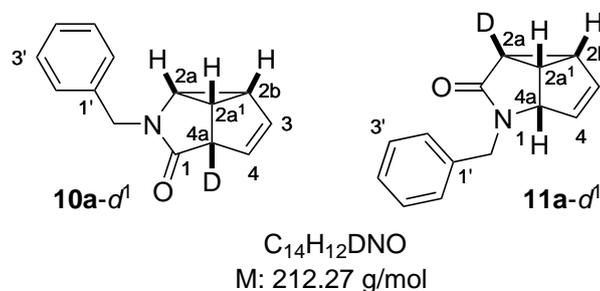
$m/z$  (%) = 211 (81) [ $\text{M}^+ - \text{H}_2\text{O}$ ], 182 (26), 154 (12), 91 (100) [ $\text{C}_7\text{H}_7^+$ ], 65 (28).

**HR-MS** (ESI): [ $\text{C}_{14}\text{H}_{15}\text{NO}_2^+$ ]: 230.1176 [ $\text{M}^+ + \text{H}$ ], calc.: 230.1175.

Significant NOE-contacts of the photoproduct **16a**:

(2aR\*,2a<sup>1</sup>R\*,2bR\*,4aS\*)-2-Benzyl-2a,2a<sup>1</sup>,2b,4a-tetrahydro-2-azacyclopropa[cd]pentalen-1(2H)-one-4a-d (10a-d<sup>1</sup>) and

(2aR\*,2a<sup>1</sup>S\*,2bR\*,4aS\*)-1-Benzyl-2a,2a<sup>1</sup>,2b,4a-tetrahydro-1-azacyclopropa[cd]pentalen-2(1H)-one-2a-d (11a-d<sup>1</sup>)



According to **GP1** a solution of the azabarrelenone **1a-d<sup>1</sup>** (50.6 mg, 240  $\mu$ mol, 1.0 eq.) and xanthone (23.5 mg, 120  $\mu$ mol, 50 mol%) in TFT (20.0 mL, c = 12.0 mmol/L) was irradiated for five hours. Purification by flash chromatography (30 g SiO<sub>2</sub>, Hex/EtOAc 8:2  $\rightarrow$  0:1) afforded the main product **10a-d<sup>1</sup>** (24.5 mg, 120  $\mu$ mol, 50%, 85% D) and the regioisomer **11a-d<sup>1</sup>** (13.5 mg, 64.0  $\mu$ mol, 27%, 85% D) as colorless, highly viscous resins.

Data of **10a-d<sup>1</sup>**:

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz):

$\delta$  (ppm) = 7.36-7.25 (m, 3H, H-2', H-4'), 7.22-7.17 (m, 2H, H-3'), 5.60 (d, <sup>3</sup>J = 5.2 Hz, 1H, H-4), 5.57 (dd, <sup>3</sup>J = 5.2 Hz, <sup>3</sup>J = 2.5 Hz, 1H, H-3), 4.42 (s, 2H, CH<sub>2</sub>), 3.66 (dd, <sup>3</sup>J = 6.8 Hz, <sup>3</sup>J = 2.2 Hz, 0.15H, H-4a), 3.32 (dd, <sup>3</sup>J = 7.8 Hz, <sup>3</sup>J = 4.5 Hz, 1H, H-2a), 2.67 (virt. t, <sup>3</sup>J  $\approx$  <sup>3</sup>J = 7.1 Hz, 1H, H-2a<sup>1</sup>), 2.25 (ddd, <sup>3</sup>J = 6.7 Hz, <sup>3</sup>J = 4.5 Hz, <sup>3</sup>J = 2.5 Hz, 1H, H-2b).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz):

176.1 (s, C-1), 135.9 (s, C-1'), 133.5 (d, C-4), 128.5 (d, 2C, C-2'), 128.5 (d, 2C, C-3'), 128.0 (d, C-3), 127.6 (d, C-4'), 54.1 (t, <sup>1</sup>J<sub>CD</sub> = 23.2 Hz, C-4a), 47.6 (t, CH<sub>2</sub>), 43.8 (d, C-2a), 35.9 (d, C-2b), 33.5 (d, C-2a<sup>1</sup>).

IR (ATR):

$\tilde{\nu}$  (cm<sup>-1</sup>) = 3062 (w, C-H), 2925 (w, C-H), 1681 (s, N-C=O), 1443 (w), 1248 (w), 1078 (w), 944 (w), 734 (w).

HR-MS (ESI): [C<sub>14</sub>H<sub>12</sub>DNO<sup>+</sup>]: 213.1133 [M<sup>+</sup>+H], calc.: 213.1133.

Data of **11a-d<sup>1</sup>**:

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 K, 500 MHz):

$\delta$  (ppm) = 7.39-7.32 (m, 3H, H-2'), 7.32-7.27 (m, 3H, H-3', H-4'), 5.99 (dd,  $^3J = 5.5$  Hz,  $^3J = 2.4$  Hz, 1H, H-3), 5.87 (dd,  $^3J = 5.5$  Hz,  $^3J = 1.5$  Hz, 1H, H-4), 4.80 (d,  $^2J = 15.2$  Hz, 1H, CHH), 4.20 (d,  $^3J = 6.1$  Hz, 1H, H-4a), 3.76 (d,  $^2J = 15.2$  Hz, 1H, CHH), 2.95 (*virt. t.*,  $^3J \approx ^3J = 6.0$  Hz, 1H, H-2a<sup>1</sup>), 2.55 (*virt. t.*,  $^3J \approx ^3J = 6.9$  Hz, 0.15H, H-2a), 2.51 (*virt. td.*,  $^3J \approx ^3J = 6.0$  Hz,  $^3J = 2.4$  Hz, 1H, H-2b).

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 300 K, 126 MHz):

$\delta$  (ppm) = 170.1 (s, C-2), 136.9 (s, C-1'), 134.8 (d, C-4), 131.2 (d, C-3), 128.8 (d, 2C, C-3'), 128.4 (d, 2C, C-2'), 127.7 (d, C-4'), 64.1 (d, C-4a), 45.6 (t,  $\text{CH}_2$ ), 38.0 (t,  $^1J_{\text{CD}} = 26.6$  Hz, C-2a), 37.4 (d, C-2a<sup>1</sup>), 34.4 (d, C-2b).

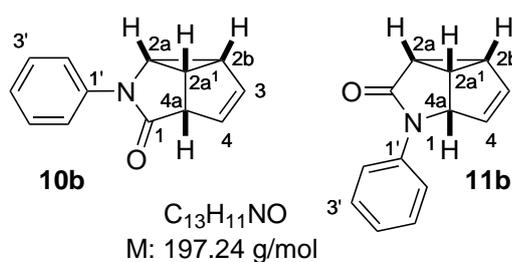
**IR** (ATR):

$\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 3062 (w, C-H), 2924 (w, C-H), 1673 (s, N-C=O), 1420 (w), 1358 (w), 1251 (w), 1080 (w), 818 (w), 702 (w).

**HR-MS** (ESI):  $[\text{C}_{14}\text{H}_{12}\text{DNO}^+]$ : 213.1133  $[\text{M}^+ + \text{H}]$ , calc.: 213.1133.

**(2aR\*,2a<sup>1</sup>R\*,2bR\*,4aS\*)-2-Phenyl-2a,2a<sup>1</sup>,2b,4a-tetrahydro-2-azacyclopropa[cd]pentalen-1(2H)-one (10b) and**

**(2aR\*,2a<sup>1</sup>S\*,2bR\*,4aS\*)-1-Phenyl-2a,2a<sup>1</sup>,2b,4a-tetrahydro-1-azacyclopropa[cd]pentalen-2(1H)-one (11b)**



According to **GP1** a solution of the azabarrelenone **1b** (23.7 mg, 120  $\mu\text{mol}$ , 1.0 eq.) and xanthone (11.8 mg, 60.0  $\mu\text{mol}$ , 50 mol%) in TFT (10.0 mL,  $c = 12.0$  mmol/L) was irradiated for eight hours. The clear solution turns into a yellow suspension after half of the reaction time. Purification by flash chromatography (15 g  $\text{SiO}_2$ , Hex/EtOAc 85:15  $\rightarrow$  7:3) afforded the main product **10b** (7.70 mg, 39.0  $\mu\text{mol}$ , 33%) and the regioisomer **11b** (7.50 mg, 38.0  $\mu\text{mol}$ , 32%) as colorless, highly viscous oils.

*Data of 10b:*

**TLC** (Cy/EtOAc = 2:1):  $R_f = 0.37$  [UV].

**$^1\text{H-NMR}$**  ( $\text{CDCl}_3$ , 300 K, 500 MHz):

$\delta$  (ppm) = 7.51-7.42 (m, 2H, H-2'), 7.33-7.23 (m, 2H, H-3'), 7.12-6.96 (m, 1H, H-4'), 5.79 (dd,  $^3J = 5.2$  Hz,  $^3J = 2.5$  Hz, 1H, H-3), 5.57 (dd,  $^3J = 5.2$  Hz,  $^3J = 2.5$  Hz, 1H, H-4), 3.72 (dd,  $^3J = 7.9$  Hz,  $^3J = 4.5$  Hz, 1H, H-2a), 3.69 (dd,  $^3J = 6.7$  Hz,  $^3J = 2.5$  Hz, 1H, H-4a), 2.73 (q,  $^3J \approx ^3J \approx ^3J = 7.0$  Hz, H-2a<sup>1</sup>), 2.52 (ddd,  $^3J = 6.8$  Hz,  $^3J = 4.5$  Hz,  $^3J = 2.5$  Hz, 1H, H-2b).

**$^{13}\text{C-NMR}$**  ( $\text{CDCl}_3$ , 300 K, 126 MHz):

$\delta$  (ppm) = 174.9 (s, C-1), 140.6 (s, C-1'), 133.9 (d, C-4), 129.0 (d, 2C, C-3'), 128.2 (d, C-3), 124.6 (d, C-4'), 119.7 (d, 2C, C-2'), 55.6 (d, C-4a), 44.9 (d, C-2a), 36.0 (d, C-2b), 32.4 (d, C-2a<sup>1</sup>).

**IR** (ATR):

$\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 3062 (w, C-H), 1691 (s, N-C=O), 1494 (s), 1382 (s), 1279 (s), 1219 (m), 1066 (m), 904 (w), 818 (m), 757 (s).

**MS** (EI, 70 eV):

$m/z$  (%) = 197 (74) [ $\text{M}^+$ ], 168 (42), 104 (100), 77 (57) [ $\text{C}_6\text{H}_5^+$ ].

**HR-MS** (EI): [ $\text{C}_{13}\text{H}_{11}\text{NO}^+$ ]: 197.0838 [ $\text{M}^+$ ], calc.: 197.0835.

*Data of 11b:*

**TLC** (Cy/EtOAc = 2:1):  $R_f = 0.23$  [UV].

**$^1\text{H-NMR}$**  ( $\text{CDCl}_3$ , 300 K, 500 MHz):

$\delta$  (ppm) = 7.55 (d,  $^3J = 8.1$  Hz, 2H, H-2'), 7.36 (virt. t,  $^3J \approx ^3J = 7.8$  Hz, 2H, H-3'), 7.14 (t,  $^3J = 7.4$  Hz, 1H, H-4'), 6.09 (dd,  $^3J = 5.4$  Hz,  $^3J = 2.4$  Hz, 1H, H-3), 6.00 (d,  $^3J = 5.4$  Hz, 1H, H-4), 4.96 (d,  $^3J = 6.3$  Hz, 1H, H-4a), 3.15 (virt. q,  $^3J \approx ^3J \approx ^3J = 6.2$  Hz, 1H), 2.68 (virt. t,  $^3J \approx ^3J = 6.9$  Hz, 1H, H-2a), 2.65-2.60 (m, 1H, H-2b).

**$^{13}\text{C-NMR}$**  ( $\text{CDCl}_3$ , 300 K, 126 MHz):

$\delta$  (ppm) = 168.9 (s, C-2), 138.5 (s, C-1'), 134.9 (d, C-4), 130.9 (d, C-3), 129.0 (d, 2C, C-3'), 124.6 (d, C-4'), 120.5 (d, 2C, C-2'), 66.9 (d, C-4a), 39.2 (d, C-2a), 36.3 (d, C-2a<sup>1</sup>), 35.2 (d, C-2b).

**IR** (ATR):

$\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 3062 (w, C-H), 1684 (s, N-C=O), 1596 (w), 1495 (m), 1371 (m), 1357 (m), 1118 (w), 827 (w), 754 (m), 692 (w).

**MS** (EI, 70 eV):

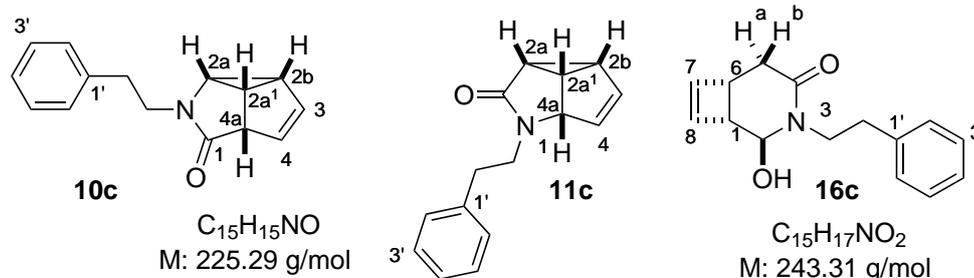
$m/z$  (%) = 197 (100) [ $\text{M}^+$ ], 168 (37), 156 (34), 119 (49), 104 (29), 91 (11), 77 (41) [ $\text{C}_6\text{H}_5^+$ ].

**HR-MS** (EI): [ $\text{C}_{13}\text{H}_{11}\text{NO}^+$ ]: 197.0836 [ $\text{M}^+$ ], calc.: 197.0835.

(2a*R*\*,2a<sup>1</sup>*R*\*,2b*R*\*,4a*S*\*)-2-Phenethyl-2a,2a<sup>1</sup>,2b,4a-tetrahydro-2-azacyclopropa[cd]pentalen-1(2*H*)-one (**10c**),

(2a*R*\*,2a<sup>1</sup>*S*\*,2b*R*\*,4a*S*\*)-1-Phenethyl-2a,2a<sup>1</sup>,2b,4a-tetrahydro-1-azacyclopropa[cd]pentalen-2(1*H*)-one (**11c**) and

(1*R*\*,2*S*\*,6*S*\*)-2-Hydroxy-3-phenethyl-3-azabicyclo[4.2.0]oct-7-en-4-one (**16c**)



According to **GP1** a solution of the azabarrelenone **1c** (54.1 mg, 24.0  $\mu$ mol, 1.0 eq.) and xanthone (23.5 mg, 120  $\mu$ mol, 50 mol%) in TFT (20.0 mL,  $c = 12.0$  mmol/L) was irradiated for 4.5 h. Purification by flash chromatography (31 g  $SiO_2$ , Hex/EtOAc 8:2  $\rightarrow$  0:1) afforded the main product **10c** (24.8 mg, 110  $\mu$ mol, 46%) and the regioisomer **11c** (10.4 mg, 46.0  $\mu$ mol, 19%) as colorless, highly viscous resins. In a later fraction the side product **16c** (10.3 mg, 42.0  $\mu$ mol, 18%) was obtained as a colorless, highly viscous oil.

#### Data of **10c**:

**TLC** (Cy/EtOAc = 1:1):  $R_f = 0.30$  [UV].

**<sup>1</sup>H-NMR** ( $CDCl_3$ , 300 K, 500 MHz):

$\delta$  (ppm) = 7.31-7.26 (m, 2H, H-3'), 7.23-7.17 (m, 3H, H-2', H-4'), 5.66 (dd,  $^3J = 5.2$  Hz,  $^3J = 2.5$  Hz, 1H, H-3), 5.60 (dd,  $^3J = 5.2$  Hz,  $^3J = 2.4$  Hz, 1H, H-4), 3.62 (dt,  $^2J = 13.6$  Hz,  $^3J = 7.9$  Hz, 1H, NCHH), 3.56 (dd,  $^3J = 6.8$  Hz,  $^3J = 2.4$  Hz, 1H, H-4a), 3.39 (dt,  $^2J = 13.6$  Hz,  $^3J = 7.5$  Hz, 1H, NCHH), 3.30 (dd,  $^3J = 7.8$  Hz,  $^3J = 4.5$  Hz, 1H, H-2a), 2.72 (*virt. t.*,  $^3J \approx ^3J = 7.7$  Hz, 2H,  $ArCH_2$ ), 2.66 (*virt. q.*,  $^3J \approx ^3J \approx ^3J = 7.0$  Hz, 1H, H-2a<sup>1</sup>), 2.31 (ddd,  $^3J = 6.8$  Hz,  $^3J = 4.5$  Hz,  $^3J = 2.5$  Hz, 1H, H-2b).

**<sup>13</sup>C-NMR** ( $CDCl_3$ , 300 K, 126 MHz):

$\delta$  (ppm) = 176.5 (s, C-1), 138.8 (s, C-1'), 134.4 (d, C-4), 128.8 (d, 2C, C-2'), 128.6 (d, 2C, C-3'), 128.0 (d, C-3), 126.5 (d, C-4'), 54.5 (d, C-4a), 44.7 (t, NCH<sub>2</sub>), 44.6 (d, C-2a), 36.1 (d, C-2b), 33.9 (d, C-2a<sup>1</sup>), 33.2 (t,  $ArCH_2$ ).

**IR** (ATR):

$\tilde{\nu}$  ( $cm^{-1}$ ) = 3028 (w, C-H), 2928 (w, C-H), 1676 (s, N-C=O), 1454 (m), 1355 (m), 1248 (m),

1225 (m), 1030 (w), 816 (m), 750 (m).

**MS** (EI, 70 eV):

$m/z$  (%) = 225 (44) [ $M^+$ ], 134 (12) [ $M^+ - C_7H_7$ ], 105 (100) [ $C_8H_9^+$ ], 91 (16) [ $C_7H_7^+$ ].

**HR-MS** (ESI): [ $C_{15}H_{16}NO^+$ ]: 226.1227 [ $M^+ + H$ ], calc.: 226.1226.

*Data of 11c:*

**TLC** (Cy/EtOAc = 1:1):  $R_f$  = 0.22 [UV].

**$^1H$ -NMR** ( $CDCl_3$ , 300 K, 500 MHz):

$\delta$  (ppm) = 7.34-7.27 (m, 2H, H-3'), 7.25-7.18 (m, 3H, H-2', H-4'), 5.95 (dd,  $^3J$  = 5.5 Hz,  $^3J$  = 1.4 Hz, 1H, H-3), 5.88 (dd,  $^3J$  = 5.5 Hz,  $^3J$  = 1.4 Hz, 1H, H-4), 4.17 (*virt. dt*,  $^3J$  = 6.3 Hz,  $^3J \approx ^4J$  = 1.4 Hz, 1H, H-4a), 3.78 (ddd,  $^2J$  = 14.6 Hz,  $^3J$  = 8.5 Hz,  $^3J$  = 6.0 Hz, 1H, NCHH), 2.94-2.88 (m, 2H, NCHH, H-2a<sup>1</sup>), 2.86 (dd,  $^3J$  = 8.5 Hz,  $^3J$  = 6.0 Hz, 2H, ArCH<sub>2</sub>), 2.56-2.39 (m, 2H, H-2a, H-2b).

**$^{13}C$ -NMR** ( $CDCl_3$ , 300 K, 126 MHz):

$\delta$  (ppm) = 170.1 (s, C-2), 139.2 (s, C-1'), 134.5 (d, C-4), 131.0 (d, C-3), 128.8 (d, 2C, C-3'), 128.7 (d, 2C, C-2'), 126.6 (d, C-4'), 65.3 (d, C-4a), 43.3 (t, NCH<sub>2</sub>), 38.2 (d, C-2a), 37.3 (d, C-2a<sup>1</sup>), 34.8 (t, ArCH<sub>2</sub>), 34.4 (d, C-2b).

**IR** (ATR):

$\tilde{\nu}$  ( $cm^{-1}$ ) = 3061 (w, C-H), 2926 (w, C-H), 1673 (s, N-C=O), 1454 (m), 1411 (w), 1222 (m), 1030 (w), 940 (w), 824 (m), 742 (m).

**MS** (EI, 70 eV):

$m/z$  (%) = 225 (83) [ $M^+$ ], 134 (100) [ $M^+ - C_7H_7$ ], 105 (11) [ $C_8H_9^+$ ], 91 (28) [ $C_7H_7^+$ ].

**HR-MS** (ESI): [ $C_{15}H_{16}NO^+$ ]: 226.1227 [ $M^+ + H$ ], calc.: 226.1226.

*Data of 16c:*

**TLC** (EtOAc):  $R_f$  = 0.36 [UV].

**$^1H$ -NMR** ( $CDCl_3$ , 300 K, 500 MHz):

$\delta$  (ppm) = 7.39-7.29 (m, 2H, H-2'), 7.29-7.21 (m, 3H, H-3', H-4'), 6.11 (d,  $^3J$  = 2.8 Hz, 1H, H-7), 5.85 (d,  $^3J$  = 2.8 Hz, 1H, H-8), 4.76 (d,  $^3J$  = 2.1 Hz, 1H, H-2), 3.87 (ddd,  $^2J$  = 13.4 Hz,  $^3J$  = 7.6 Hz,  $^3J$  = 4.9 Hz, 1H, NCHH), 3.45 (*virt. dt*,  $^2J$  = 13.4 Hz,  $^3J \approx ^3J$  = 7.8 Hz, 1H, NCHH), 3.29-3.22 (m, 1H, H-6), 3.08 (dd,  $^3J$  = 4.2 Hz,  $^3J$  = 2.1 Hz, 1H, H-1), 2.98 (*virt. dt*,  $^2J$  = 13.5 Hz,  $^3J \approx ^3J$  = 7.9 Hz, 1H, ArCHH), 2.80 (ddd,  $^2J$  = 13.5 Hz,  $^3J$  = 7.2 Hz,  $^3J$  = 4.9 Hz, 1H, ArCHH), 2.74 (dd,  $^2J$  = 15.4 Hz,  $^3J$  = 6.2 Hz, 1H, H-5a), 2.46 (dd,  $^2J$  = 15.4 Hz,  $^3J$  = 1.8 Hz, 1H, H-5b), 2.06 (s, 1H, OH).

**$^{13}C$ -NMR** ( $CDCl_3$ , 300 K, 126 MHz):

$\delta$  (ppm) = 170.6 (s, C-4), 141.0 (d, C-7), 139.5 (s, C-1'), 135.9 (d, C-8), 129.0 (d, 2C, C-3'), 128.9 (d, 2C, C-2'), 128.7 (d, C-4'), 83.7 (d, C-2), 50.3 (t, NCH<sub>2</sub>), 46.3 (d, C-1), 38.8 (d, C-6), 35.0 (t, C-5), 34.9 (t, ArCH<sub>2</sub>).

**IR** (ATR):

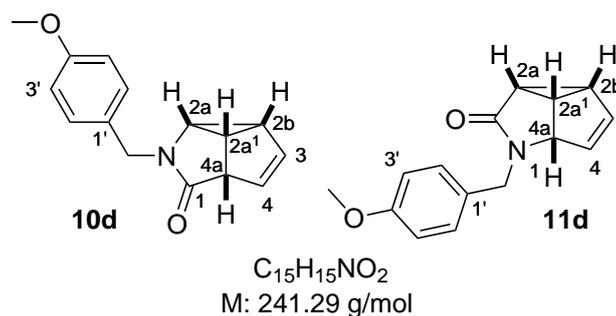
$\tilde{\nu}$  (cm<sup>-1</sup>) = 3334 (br, O–H), 3028 (w, C–H), 2928 (w), 1634 (s, N–C=O), 1478 (m), 1245 (m), 1149 (w), 1027 (m), 899 (w), 748 (m).

**MS** (EI, 70 eV):

$m/z$  (%) = 225 (100) [M<sup>+</sup>–H<sub>2</sub>O], 134 (93) [M<sup>+</sup>–C<sub>7</sub>H<sub>9</sub>O], 121 (21), 106 (53), 105 (56) [M<sup>+</sup>–C<sub>8</sub>H<sub>11</sub>O], 91 (20) [C<sub>7</sub>H<sub>7</sub><sup>+</sup>], 77 (54) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>].

**HR-MS** (ESI): [C<sub>15</sub>H<sub>18</sub>NO<sub>2</sub><sup>+</sup>]: 244.1333 [M<sup>+</sup>+H], calc.: 244.1332.

**(2aR\*,2a<sup>1</sup>R\*,2bR\*,4aS\*)-2-(4-Methoxybenzyl)-2a,2a<sup>1</sup>,2b,4a-tetrahydro-2-azacyclopropa[cd]pentalen-1(2H)-one (10d) and (2aR\*,2a<sup>1</sup>S\*,2bR\*,4aS\*)-1-(4-Methoxybenzyl)-2a,2a<sup>1</sup>,2b,4a-tetrahydro-1-azacyclopropa[cd]pentalen-2(1H)-one (11d)**



According to **GPI** a solution of the azabarrelenone **1d** (29.0 mg, 120  $\mu$ mol, 1.0 eq.) and xanthone (11.8 mg, 60.0  $\mu$ mol, 50 mol%) in TFT (10.0 mL,  $c$  = 12.0 mmol/L) was irradiated for three hours. Purification by flash chromatography (28 g SiO<sub>2</sub>, Hex/EtOAc 8:2  $\rightarrow$  3:7) afforded the main product **10d** (13.0 mg, 54.0  $\mu$ mol, 45%) and the regioisomer **11d** (7.1 mg, 29.0  $\mu$ mol, 25%) as colorless, highly viscous oils.

*Data of 10d:*

**TLC** (Cy/EtOAc = 1:1):  $R_f$  = 0.27 [UV].

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 K, 400 MHz):

$\delta$  (ppm) = 7.17-7.07 (m, 2H, H-2'), 6.88-6.79 (m, 2H, H-3'), 5.60-5.53 (m, 1H, H-4), 5.54 (dd, <sup>3</sup> $J$  = 5.1 Hz, <sup>3</sup> $J$  = 2.4 Hz, 1H, H-3), 4.33 (d, <sup>2</sup> $J$  = 14.6 Hz, 1H, CHH), 4.30 (d, <sup>2</sup> $J$  = 14.6 Hz, 1H, CHH),

3.79 (s, 3H, OCH<sub>3</sub>), 3.62 (dd,  $^3J = 6.8$  Hz,  $^3J = 2.1$  Hz, 1H, H-4a), 3.28 (dd,  $^3J = 7.7$  Hz,  $^3J = 4.6$  Hz, 1H, H-2a), 2.63 (*virt.* q,  $^3J \approx ^3J \approx ^3J = 7.1$  Hz, 1H, H-2a<sup>1</sup>), 2.22 (ddd,  $^3J = 7.0$  Hz,  $^3J = 4.6$  Hz,  $^3J = 2.4$  Hz, 1H, H-2b).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 101 MHz):

$\delta$  (ppm) = 175.9 (s, C-1), 159.1 (s, C-4'), 133.6 (d, C-4), 129.8 (d, 2C, C-2'), 128.0 (s, C-1'), 127.9 (d, C-3), 113.9 (d, 2C, C-3'), 55.4 (q, OCH<sub>3</sub>), 54.6 (d, C-4a), 47.0 (t, CH<sub>2</sub>), 43.7 (d, C-2a), 35.9 (d, C-2b), 33.5 (d, C-2a<sup>1</sup>).

IR (ATR):

$\tilde{\nu}$  (cm<sup>-1</sup>) = 3061 (w, C-H), 2929 (w, C-H), 1678 (s, N-C=O), 1513 (s), 1412 (m), 1303 (m), 1245 (s), 1176 (m), 1032 (m), 819 (m).

MS (EI, 70 eV):

$m/z$  (%) = 241 (23) [M<sup>+</sup>], 121 (100) [M<sup>+</sup>-C<sub>6</sub>H<sub>7</sub>NO], 91 (10) [C<sub>7</sub>H<sub>7</sub><sup>+</sup>], 78 (17), 77 (16) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>].

HR-MS (EI): [C<sub>15</sub>H<sub>15</sub>NO<sub>2</sub><sup>+</sup>]: 241.1115 [M<sup>+</sup>], calc.: 241.1097.

*Data of 11d:*

TLC (Cy/EtOAc = 1:1):  $R_f = 0.20$  [UV].

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 400 MHz):

$\delta$  (ppm) = 7.23-7.17 (m, 2H, H-2'), 6.91-6.85 (m, 2H, H-3'), 5.97 (ddd,  $^3J = 5.4$  Hz,  $^3J = 2.3$  Hz,  $^4J = 1.1$  Hz, 1H, H-3), 5.87-5.82 (m, 1H, H-4), 4.70 (d,  $^2J = 14.9$  Hz, 1H, CHH), 4.18 (*virt.* dt,  $^3J = 6.2$  Hz,  $^3J \approx ^4J = 1.4$  Hz, 1H, H-4a), 3.81 (s, 3H, OCH<sub>3</sub>), 3.73 (d,  $^2J = 14.9$  Hz, 1H, CHH), 2.93 (*virt.* q,  $^3J \approx ^3J \approx ^3J = 6.1$  Hz, 1H, H-2a<sup>1</sup>), 2.53 (ddd,  $^3J = 7.2$  Hz,  $^3J = 6.3$  Hz,  $^4J = 0.9$  Hz, 1H, H-2a), 2.51-2.47 (m, 1H, H-2b).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 101 MHz):

$\delta$  (ppm) = 170.0 (s, C-2), 159.2 (s, C-4'), 134.9 (d, C-4), 131.0 (d, C-3), 129.8 (d, 2C, C-2'), 128.9 (s, C-1'), 114.2 (d, 2C, C-3'), 64.0 (d, C-4a), 55.4 (q, OCH<sub>3</sub>), 45.1 (t, CH<sub>2</sub>), 38.3 (d, C-2a), 37.5 (d, C-2a<sup>1</sup>), 34.5 (d, C-2b).

IR (ATR):

$\tilde{\nu}$  (cm<sup>-1</sup>) = 3060 (w), 2925 (w), 1674 (s, N-C=O), 1512 (s), 1413 (m), 1303 (m), 1246 (s), 1176 (m), 1032 (m), 810 (m).

MS (EI, 70 eV):

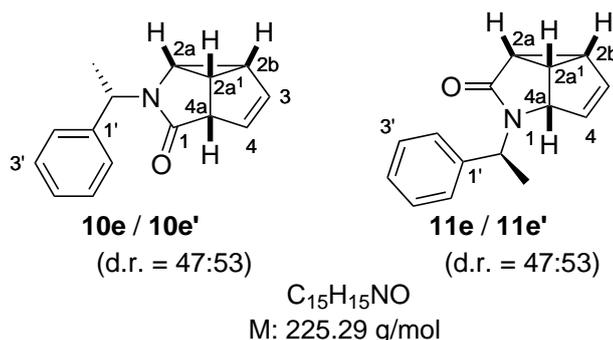
$m/z$  (%) = 241 (40) [M<sup>+</sup>], 136 (84), 121 (100) [M<sup>+</sup>-C<sub>6</sub>H<sub>7</sub>NO], 106 (75), 91 (12) [C<sub>7</sub>H<sub>7</sub><sup>+</sup>], 78 (35), 77 (24) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>].

HR-MS (EI): [C<sub>15</sub>H<sub>15</sub>NO<sub>2</sub><sup>+</sup>]: 241.1102 [M<sup>+</sup>], calc.: 241.1097.

(2a*R*\*,2a<sup>1</sup>*R*\*,2b*R*\*,4a*S*\*)-2-[(*S*)-1-Phenylethyl]-2a,2a<sup>1</sup>,2b,4a-tetrahydro-2-azacyclopropa[cd]pentalen-1(2*H*)-one (**10e**),

(2a*S*\*,2a<sup>1</sup>*S*\*,2b*S*\*,4a*R*\*)-2-[(*S*)-1-Phenylethyl]-2a,2a<sup>1</sup>,2b,4a-tetrahydro-2-azacyclopropa[cd]pentalen-1(2*H*)-one (**10e'**) and

(2a*R*\*,2a<sup>1</sup>*S*\*,2b*R*\*,4a*S*\*)-1-[(*S*)-1-phenylethyl]-2a,2a<sup>1</sup>,2b,4a-tetrahydro-1-azacyclopropa[cd]pentalen-2(1*H*)-one (**11e**, **11e'**)



According to **GPI** a solution of the azabarrelenone **1e** (53.1 mg, 236  $\mu$ mol, 1.0 eq.) and xanthone (23.1 mg, 118  $\mu$ mol, 50 mol%) in TFT (19.6 mL,  $c = 12.0$  mmol/L) was irradiated for six hours. Purification by flash chromatography (30 g  $SiO_2$ , Hex/EtOAc 8:2  $\rightarrow$  1:1) afforded the diastereomers **10e** (12.3 mg, 55.0  $\mu$ mol, 23%) and **10e'** (13.7 mg, 61.0  $\mu$ mol, 26%) as colorless, viscous oils (d.r. = 47:53). The diastereomers **11e** and **11e'** were obtained as a inseparable mixture (14.1 mg, 63.0  $\mu$ mol, 27%, d.r. = 47:53) as colorless, viscous oils.

*Data of the main product 10e:*

**TLC** (Cy/EtOAc = 2:1):  $R_f = 0.47$  [UV].

**<sup>1</sup>H-NMR** ( $CDCl_3$ , 300 K, 500 MHz):

$\delta$  (ppm) = 7.42-7.34 (m, 4H, H-2', H-3'), 7.32-7.27 (m, 1H, H-4'), 5.80 (dd,  $^3J = 5.2$  Hz,  $^3J = 2.5$  Hz, 1H, H-4), 5.66 (dd,  $^3J = 5.2$  Hz,  $^3J = 2.3$  Hz, 1H, H-3), 5.24 (q,  $^3J = 7.1$  Hz, 1H, NCHCH<sub>3</sub>), 3.65 (dd,  $^3J = 6.8$  Hz,  $^3J = 2.5$  Hz, 1H, H-4a), 3.12 (dd,  $^3J = 7.9$  Hz,  $^3J = 4.5$  Hz, 1H, H-2a), 2.59 (virt. q,  $^3J \approx ^3J \approx ^3J = 7.0$  Hz, 1H, H-2a<sup>1</sup>), 2.32 (ddd,  $^3J = 6.7$  Hz,  $^3J = 4.5$  Hz,  $^3J = 2.3$  Hz, 1H, H-2b), 1.29 (d,  $^3J = 7.1$  Hz, 3H, CH<sub>3</sub>).

**<sup>13</sup>C-NMR** ( $CDCl_3$ , 300 K, 126 MHz):

$\delta$  (ppm) = 175.7 (s, C-1), 141.0 (s, C-1'), 134.4 (d, C-3), 128.7 (d, 2C, C-3'), 127.8 (s, C-4), 127.6 (d, C-4'), 127.3 (d, 2C, C-2'), 54.9 (d, C-4a), 49.7 (d, NCHCH<sub>3</sub>), 40.6 (d, C-2a), 36.0 (d, C-2b), 33.0 (d, C-2a<sup>1</sup>), 13.9 (q, CH<sub>3</sub>).

**IR** (ATR):

$\tilde{\nu}$  (cm<sup>-1</sup>) = 3053 (w, C–H), 2977 (w, C–H), 1679 (s, N–C=O), 1495 (m), 1388 (m), 1249 (m), 1217 (w), 1106 (m), 820 (m).

**MS** (EI, 70 eV):

$m/z$  (%) = 225 (20) [M<sup>+</sup>], 121 (66) [M<sup>+</sup>–C<sub>8</sub>H<sub>8</sub>], 105 (100) [C<sub>8</sub>H<sub>9</sub><sup>+</sup>], 93 (17), 77 (25) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>].

**HR-MS** (EI): [C<sub>15</sub>H<sub>15</sub>NO<sup>+</sup>]: 225.1148 [M<sup>+</sup>], calc.: 225.1148.

*Data of the main product 10e'*:

**TLC** (Cy/EtOAc = 2:1):  $R_f$  = 0.36 [UV].

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 K, 500 MHz):

$\delta$  (ppm) = 7.30-7.25 (m, 2H, H-3'), 7.25-7.20 (m, 1H, H-4'), 7.14-7.10 (m, 2H, H-2'), 5.37 (dd, <sup>3</sup> $J$  = 5.1 Hz, <sup>3</sup> $J$  = 2.3 Hz, 1H, H-4), 5.24 (q, <sup>3</sup> $J$  = 7.2 Hz, 1H, NCHCH<sub>3</sub>), 5.20 (dd, <sup>3</sup> $J$  = 5.1 Hz, <sup>3</sup> $J$  = 2.6 Hz, 1H, H-3), 3.60 (dd, <sup>3</sup> $J$  = 6.8 Hz, <sup>3</sup> $J$  = 2.3 Hz, 1H, H-4a), 3.37 (dd, <sup>3</sup> $J$  = 7.8 Hz, <sup>3</sup> $J$  = 4.5 Hz, 1H, H-2a), 2.60 (*virt.* dt, <sup>3</sup> $J$  = 7.5 Hz, <sup>3</sup> $J$   $\approx$  <sup>3</sup> $J$  = 6.8 Hz, 1H, H-2a<sup>1</sup>), 2.07 (ddd, <sup>3</sup> $J$  = 6.8 Hz, <sup>3</sup> $J$  = 4.5 Hz, <sup>3</sup> $J$  = 2.6 Hz, 1H, H-2b), 1.64 (d, <sup>3</sup> $J$  = 7.2 Hz, 3H, CH<sub>3</sub>).

**<sup>13</sup>C-NMR** (CDCl<sub>3</sub>, 300 K, 126 MHz):

$\delta$  (ppm) = 174.9 (s, C-2), 138.6 (s, C-1'), 132.6 (d, C-4), 128.1 (d, 2C, C-3'), 127.5 (d, C-4'), 127.4 (d, C-3), 127.3 (d, 2C, C-2'), 54.7 (d, C-4a), 50.3 (d, NCHCH<sub>3</sub>), 40.3 (d, C-2a), 35.9 (d, C-2b), 33.0 (d, H-2a<sup>1</sup>), 17.6 (q, CH<sub>3</sub>).

**IR** (ATR):

$\tilde{\nu}$  (cm<sup>-1</sup>) = 3053 (w, C–H), 2977 (w, C–H), 1677 (s, N–C=O), 1453 (m), 1397 (m), 1251 (m), 1198 (m), 1108 (m), 940 (m), 820 (m).

**MS** (EI, 70 eV):

$m/z$  (%) = 225 (25) [M<sup>+</sup>], 121 (72) [M<sup>+</sup>–C<sub>8</sub>H<sub>8</sub>], 105 (100) [C<sub>8</sub>H<sub>9</sub><sup>+</sup>], 93 (20), 77 (29) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>].

**HR-MS** (EI): [C<sub>15</sub>H<sub>15</sub>NO<sup>+</sup>]: 225.1149 [M<sup>+</sup>], calc.: 225.1148.

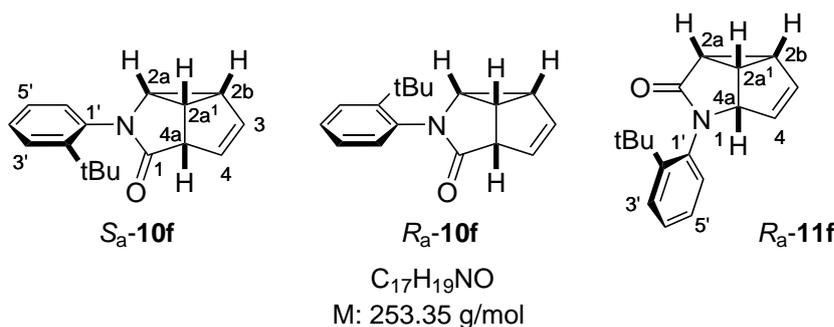
*Data of the mixture of regioisomers 11e and 11e'*:

**TLC** (Cy/EtOAc = 2:1):  $R_f$  = 0.23 [UV].

(2a*R*\*,2a<sup>1</sup>*R*\*,2b*R*\*,4a*S*\*)-2-[(*S*<sub>a</sub>)-2-(*tert*-Butyl)phenyl]-2a,2a<sup>1</sup>,2b,4a-tetrahydro-2-azacyclopropa[cd]pentalen-1(2*H*)-one (*S*<sub>a</sub>-10f),

(2a*R*\*,2a<sup>1</sup>*R*\*,2b*R*\*,4a*S*\*)-2-[(*R*<sub>a</sub>)-2-(*tert*-Butyl)phenyl]-2a,2a<sup>1</sup>,2b,4a-tetrahydro-2-azacyclopropa[cd]pentalen-1(2*H*)-one (*R*<sub>a</sub>-10f) and

(2a*R*\*,2a<sup>1</sup>*S*\*,2b*R*\*,4a*S*\*)-1-[(*R*<sub>a</sub>)-2-(*tert*-Butyl)phenyl]-2a,2a<sup>1</sup>,2b,4a-tetrahydro-1-azacyclopropa[cd]pentalen-2(1*H*)-one (*R*<sub>a</sub>-11f)



According to **GP1** a solution of the azabarrelenone **1f** (53.0 mg, 209  $\mu$ mol, 1.0 eq.) and xanthone (20.5 mg, 105  $\mu$ mol, 50 mol%) in TFT (17.4 mL, *c* = 12.0 mmol/L) was irradiated for seven hours. Purification by flash chromatography (30 g SiO<sub>2</sub>, Hex/EtOAc 8:2  $\rightarrow$  6:1) afforded the main product **10f** (37.7 mg, 149  $\mu$ mol, 71%) as an inseparable mixture of the diastereoisomers *S*<sub>a</sub>-**10f** and *R*<sub>a</sub>-**10f** (d.r. = 78/22) as colorless, highly viscous resin. The regioisomer *R*<sub>a</sub>-**11f** (8.30 mg, 33.0  $\mu$ mol, 16%) was obtained as colorless, viscous oil.

*Data of the major diastereoisomer S<sub>a</sub>-10f:*

**TLC** (Cy/EtOAc = 1:1): *R<sub>f</sub>* = 0.49 [UV].

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 K, 500 MHz):

$\delta$  (ppm) = 7.51 (dd, <sup>3</sup>*J* = 8.1 Hz, <sup>4</sup>*J* = 1.5 Hz, 1H, H-3'), 7.29-7.24 (m, 1H, H-4'), 7.19 (*virt.* td, <sup>3</sup>*J*  $\approx$  <sup>3</sup>*J* = 7.5 Hz, <sup>4</sup>*J* = 1.5 Hz, 1H, H-5'), 6.63 (dd, <sup>3</sup>*J* = 7.7 Hz, <sup>4</sup>*J* = 1.6 Hz, 1H, H-6'), 6.12 (dd, <sup>3</sup>*J* = 5.2 Hz, <sup>3</sup>*J* = 2.6 Hz, 1H, H-3), 5.72 (dd, <sup>3</sup>*J* = 5.2 Hz, <sup>3</sup>*J* = 2.4 Hz, 1H, H-4), 3.78 (dd, <sup>3</sup>*J* = 6.8 Hz, <sup>3</sup>*J* = 2.4 Hz, 1H, H-4a), 3.67 (dd, <sup>3</sup>*J* = 7.7 Hz, <sup>3</sup>*J* = 4.5 Hz, 1H, H-2a), 2.90 (q, <sup>3</sup>*J*  $\approx$  <sup>3</sup>*J* = 7.0 Hz, 1H, H-2a<sup>1</sup>), 2.34 (ddd, <sup>3</sup>*J* = 6.8 Hz, <sup>3</sup>*J* = 4.5 Hz, <sup>3</sup>*J* = 2.6 Hz, 1H, H-2b), 1.48 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (CDCl<sub>3</sub>, 300 K, 126 MHz):

$\delta$  (ppm) = 174.5 (s, C-1), 148.8 (s, C-2'), 136.9 (s, C-1'), 134.3 (d, C-4), 128.7 (d, C-3), 128.4 (d, C-4'), 128.3 (d, C-3'), 127.2 (d, C-5'), 126.8 (d, C-6'), 54.6 (d, C-4a), 49.6 (d, C-2a), 35.8 [s, C(CH<sub>3</sub>)<sub>3</sub>\*], 35.8 (d, C-2b\*), 33.9 (d, C-2a<sup>1</sup>), 32.0 [q, C(CH<sub>3</sub>)<sub>3</sub>].

\* The assignment is interchangeable.

**IR** (ATR):

$\tilde{\nu}$  (cm<sup>-1</sup>) = 3059 (w, C–H), 2960 (w, C–H), 2909 (w), 1694 (s, N–C=O), 1487 (m), 1441 (m), 1381 (w), 1363 (m), 1256 (m), 1141 (w), 1052 (w), 819 (w), 793 (m), 777 (m).

**MS** (EI, 70 eV):

$m/z$  (%) = 253 (83) [M<sup>+</sup>], 210 (29), 160 (100), 144 (22), 132 (15), 91 (50).

**HR-MS** (EI): [C<sub>17</sub>H<sub>19</sub>NO<sup>+</sup>]: 253.1458 [M<sup>+</sup>], calc.: 253.1461.

**Chiral HPLC**: (AD-H, *n*-heptane/*i*-propanol = 9:1, 1 mL/min,  $\lambda$  = 210 nm)

$t_R$  = 7.27 min, 10.7 min.

*Data of the minor diastereoisomer R<sub>a</sub>-10f:*

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 K, 500 MHz):

$\delta$  (ppm) = 7.45-7.41 (m, 1H, H-3'), 7.32-7.26 (m, 2H, H-5', H-6'), 7.21-7.17 (m, 1H, H-4'), 5.98 (dd, <sup>3</sup> $J$  = 5.2 Hz, <sup>3</sup> $J$  = 2.6 Hz, 1H, H-3), 5.74 (dd, <sup>3</sup> $J$  = 5.2 Hz, <sup>3</sup> $J$  = 2.3 Hz, 1H, H-4), 3.69 (dd, <sup>3</sup> $J$  = 6.9 Hz, <sup>3</sup> $J$  = 2.3 Hz, H-4a), 3.58 (dd, <sup>3</sup> $J$  = 7.7 Hz, <sup>3</sup> $J$  = 4.8 Hz, 1H, H-2a), 3.04 (*virt. q*, <sup>3</sup> $J$   $\approx$  <sup>3</sup> $J$  = 7.1 Hz, 1H, H-2a<sup>1</sup>), 2.50 (ddd, <sup>3</sup> $J$  = 7.0 Hz, <sup>3</sup> $J$  = 4.8 Hz, <sup>3</sup> $J$  = 2.6 Hz, 1H, H-2b), 1.20 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (CDCl<sub>3</sub>, 300 K, 126 MHz):

$\delta$  (ppm) = 181.0 (s, C-1), 149.1 (s, C-2'), 138.8 (s, C-1'), 132.1 (d, C-4'), 131.7 (d, C-4), 128.6 (d, C-3), 128.5 (d, C-5'), 127.8 (d, C-6'), 127.2 (d, C-4'), 54.8 (d, C-4a), 49.5 (d, C-2a), 37.1 (d, C-2a<sup>1</sup>), 36.4 (d, C-2b), 35.0 [s, C(CH<sub>3</sub>)<sub>3</sub>], 30.5 [q, C(CH<sub>3</sub>)<sub>3</sub>].

*Data of the regioisomer R<sub>a</sub>-11f:*

**TLC** (Cy/EtOAc = 2:1):  $R_f$  = 0.27 [UV].

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 K, 500 MHz):

$\delta$  (ppm) = 7.48 (dd, <sup>3</sup> $J$  = 8.1 Hz, <sup>4</sup> $J$  = 1.5 Hz, 1H, H-3'), 7.27 (ddd, <sup>3</sup> $J$  = 8.1 Hz, <sup>3</sup> $J$  = 7.3 Hz, <sup>4</sup> $J$  = 1.6 Hz, 1H, H-4'), 7.14 (*virt. td*, <sup>3</sup> $J$   $\approx$  <sup>3</sup> $J$  = 7.5 Hz, <sup>4</sup> $J$  = 1.5 Hz, 1H, H-5'), 6.89 (dd, <sup>3</sup> $J$  = 7.8 Hz, <sup>4</sup> $J$  = 1.6 Hz, 1H, H-6'), 6.16 (ddd, <sup>3</sup> $J$  = 5.4 Hz, <sup>3</sup> $J$  = 2.4 Hz, <sup>4</sup> $J$  = 1.0 Hz, 1H, H-3), 6.01 (ddd, <sup>3</sup> $J$  = 5.4 Hz, <sup>3</sup> $J$  = 1.8 Hz, <sup>4</sup> $J$  = 0.8 Hz, 1H, H-4), 4.60 (ddd, <sup>3</sup> $J$  = 6.2 Hz, 1.8, <sup>4</sup> $J$  = 1.0 Hz, 1H, H-4a), 3.21 (*virt. q*, <sup>3</sup> $J$   $\approx$  <sup>3</sup> $J$   $\approx$  <sup>3</sup> $J$  = 6.2 Hz, 1H, H-2a<sup>1</sup>), 2.62 (ddd, <sup>3</sup> $J$  = 7.7 Hz, <sup>3</sup> $J$  = 5.9 Hz, <sup>3</sup> $J$  = 2.4 Hz, 1H, H-2b), 2.58 (ddd, <sup>3</sup> $J$  = 7.7 Hz, <sup>3</sup> $J$  = 6.4 Hz, <sup>4</sup> $J$  = 0.8 Hz, 1H, H-2a), 1.44 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C-NMR** (CDCl<sub>3</sub>, 300 K, 126 MHz):

$\delta$  (ppm) = 171.3 (s, C-2), 149.1 (s, C-2'), 136.6 (s, C-1'), 135.9 (d, C-4), 132.3 (d, C-6'), 131.3 (d, C-3), 128.7 (d, C-4'), 128.1 (d, C-3'), 126.8 (d, C-5'), 69.8 (d, C-4a), 37.7 [s, C(CH<sub>3</sub>)<sub>3</sub>], 36.9 (d,

C-2a<sup>1</sup>), 35.8 (d, C-2a), 34.9 (d, C-2b), 31.7 [q, C(CH<sub>3</sub>)<sub>3</sub>].

**IR** (ATR):

$\tilde{\nu}$  (cm<sup>-1</sup>) = 3062 (w, C–H), 2960 (w, C–H), 2870 (w), 1689 (s, N–C=O), 1486 (m), 1441 (m), 1370 (m), 1101 (m), 828 (m), 761 (m), 749 (m).

**MS** (EI, 70 eV):

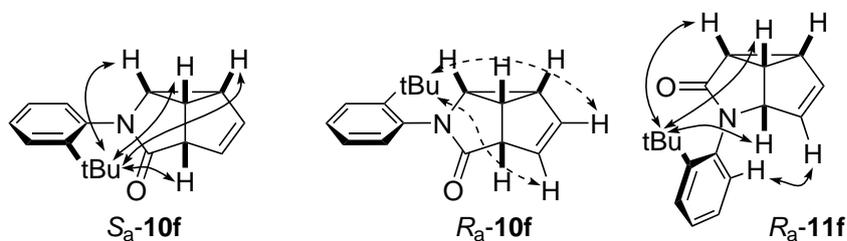
$m/z$  (%) = 253 (9) [M<sup>+</sup>], 196 (100) [M<sup>+</sup>–C<sub>4</sub>H<sub>9</sub>], 160 (20), 132 (32), 91 (14).

**HR-MS** (EI): [C<sub>17</sub>H<sub>19</sub>NO<sup>+</sup>]: 253.1457 [M<sup>+</sup>], calc.: 253.1461.

**Chiral HPLC**: (AD-H, *n*-heptane/*i*-propanol = 9:1, 1 mL/min,  $\lambda$  = 210 nm)

$t_R$  = 8.57 min, 9.95 min.

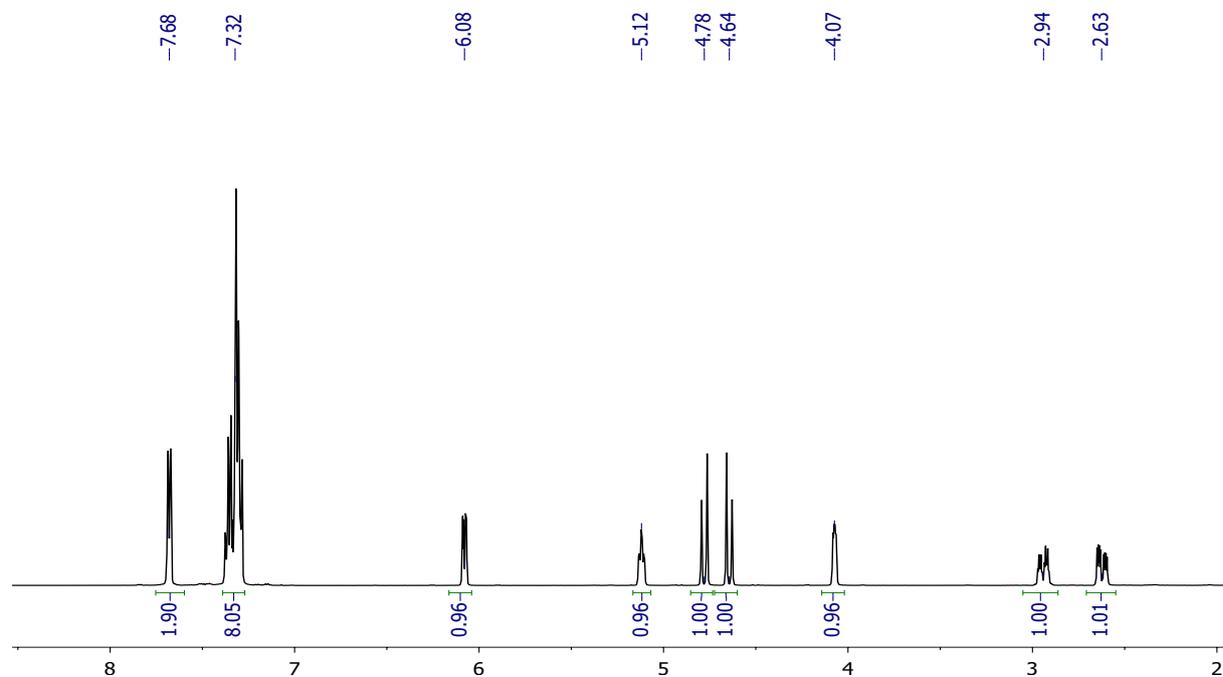
Significant NOE-contacts of the photoproducts *S*<sub>a</sub>-**10f**, *R*<sub>a</sub>-**10f** and *R*<sub>a</sub>-**11f**:



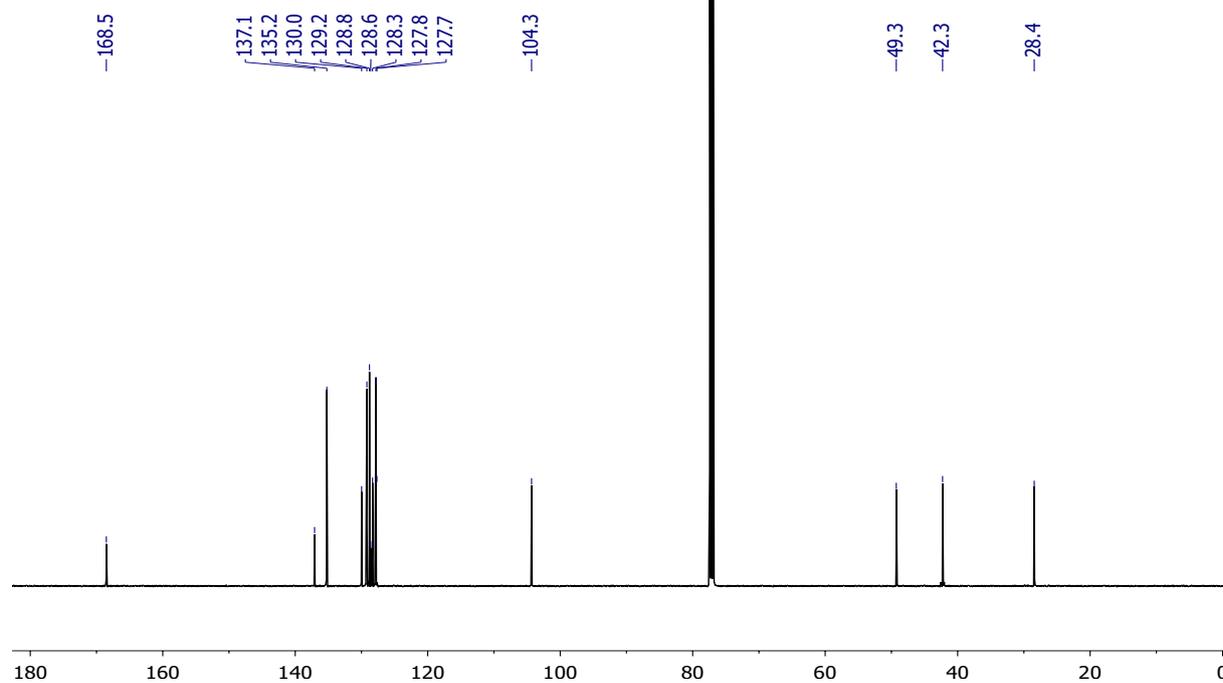
## 4 NMR-Spectra of New Compounds

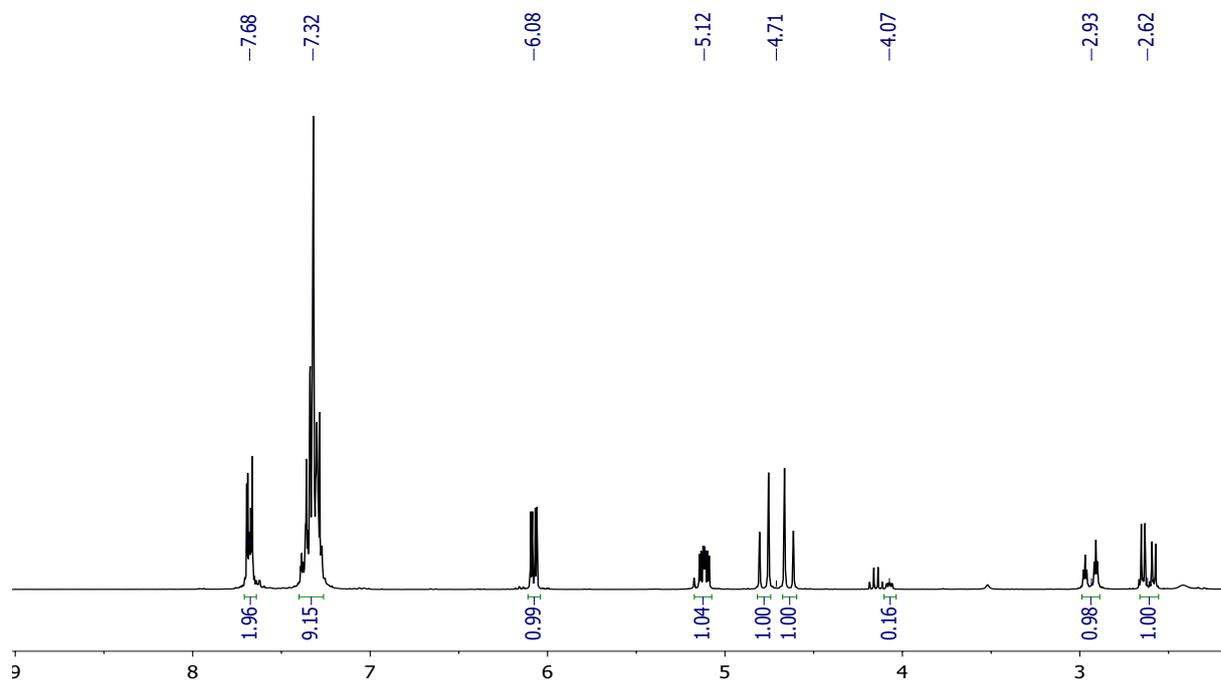
(*R*<sup>\*</sup>)-1-Benzyl-3-(phenylselanyl)-3,4-dihydropyridin-2(1*H*)-one (S1)

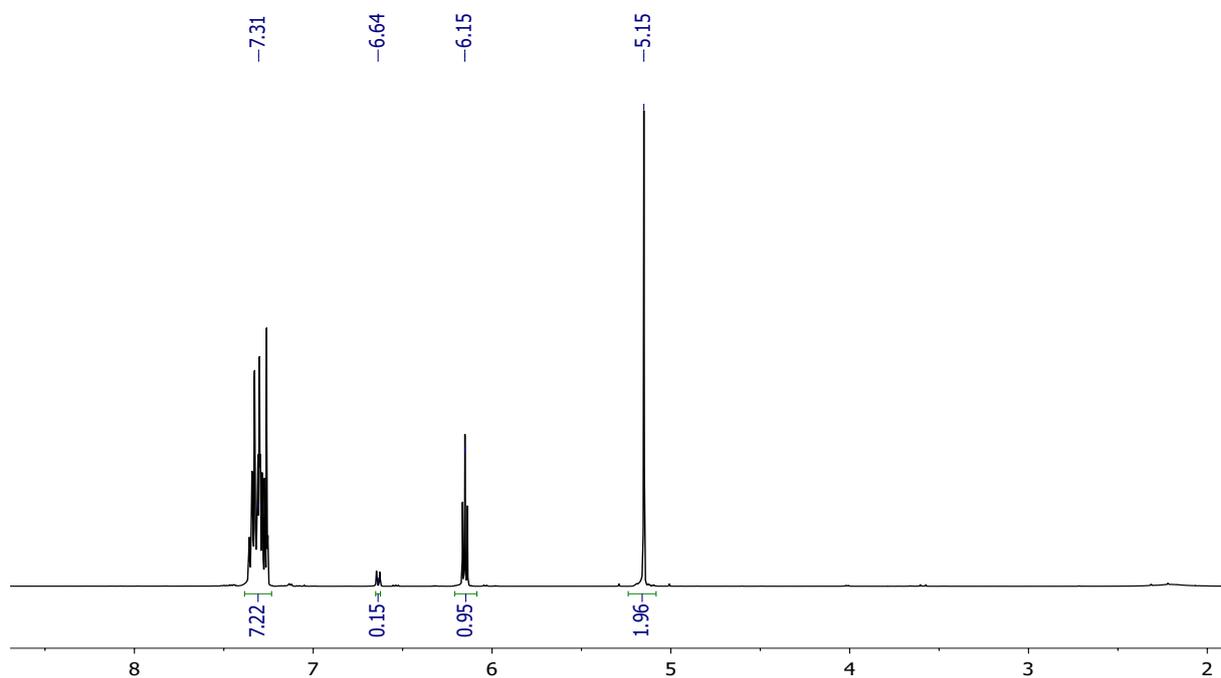
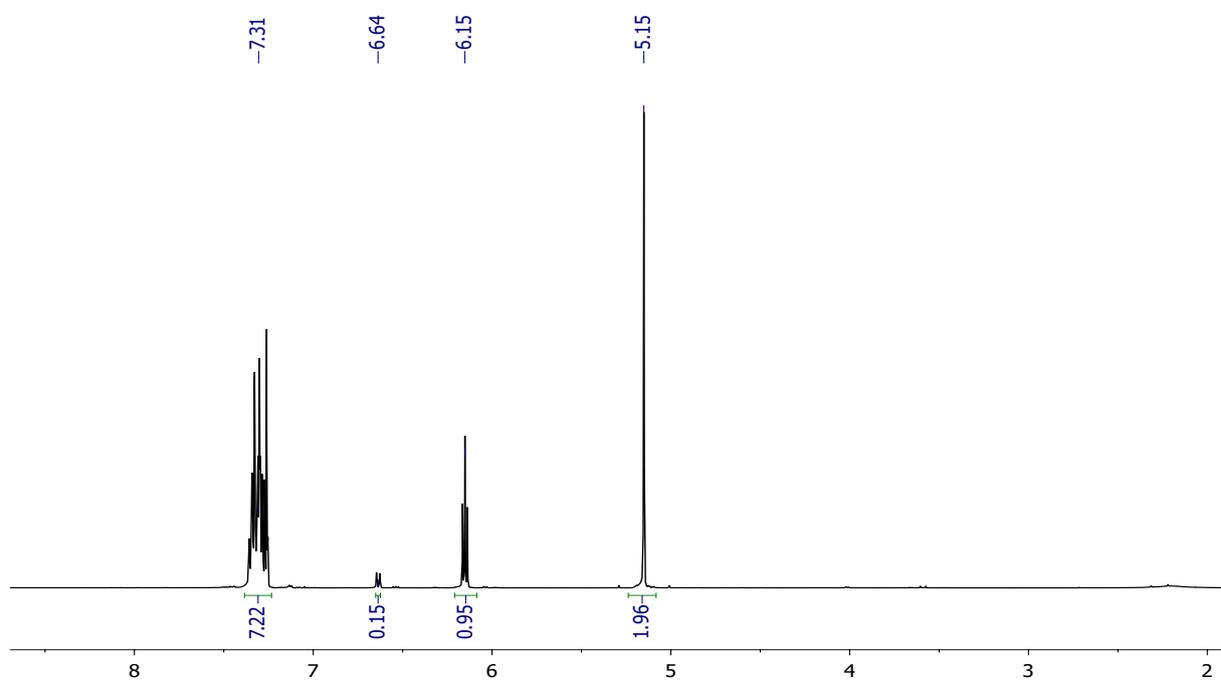
<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)

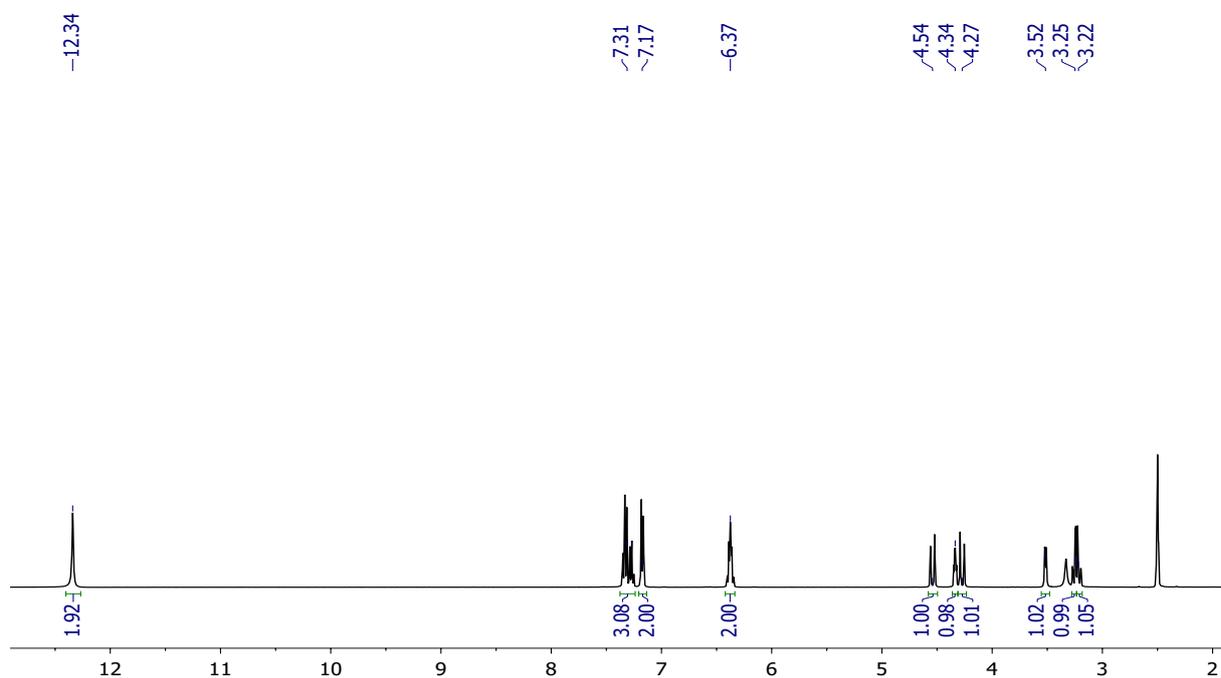
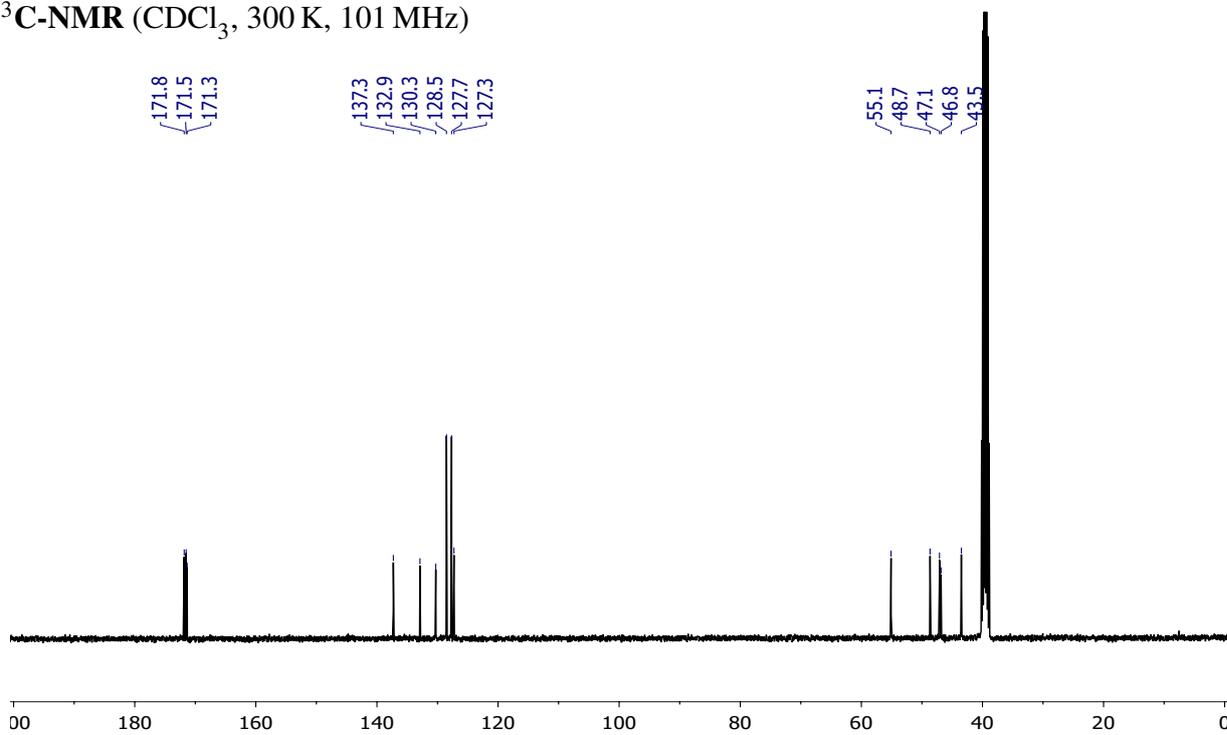


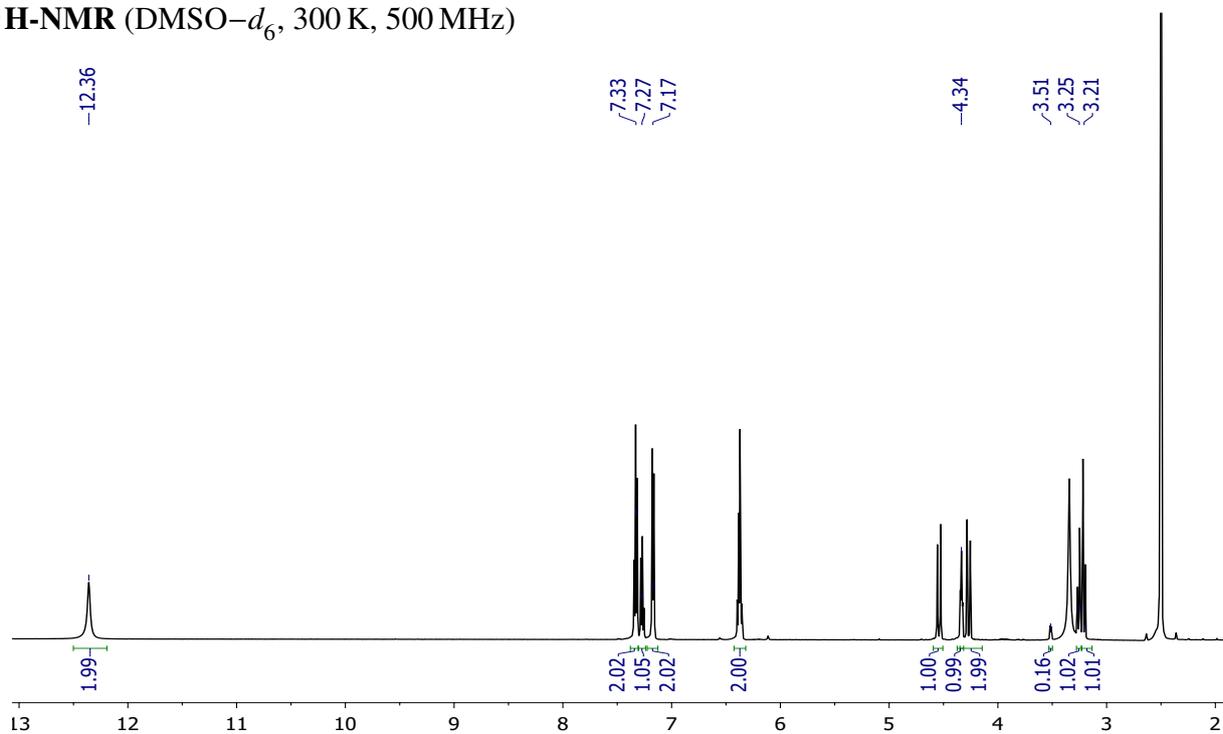
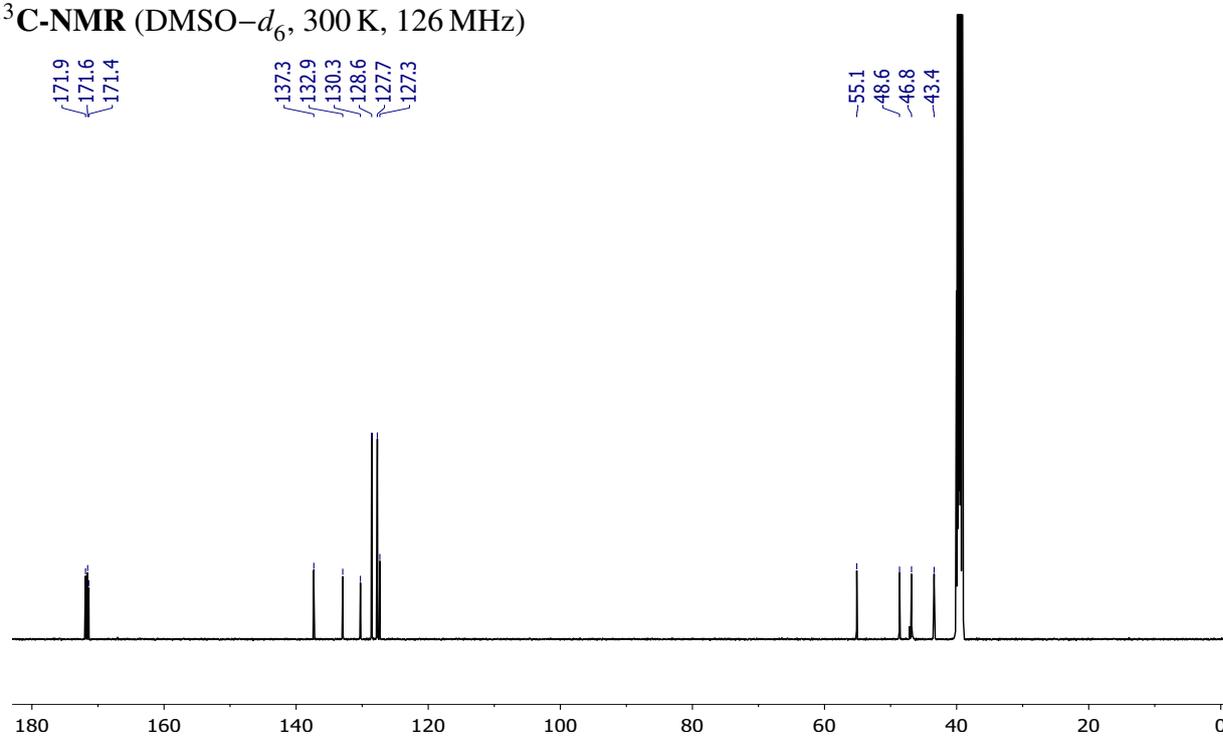
<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz)

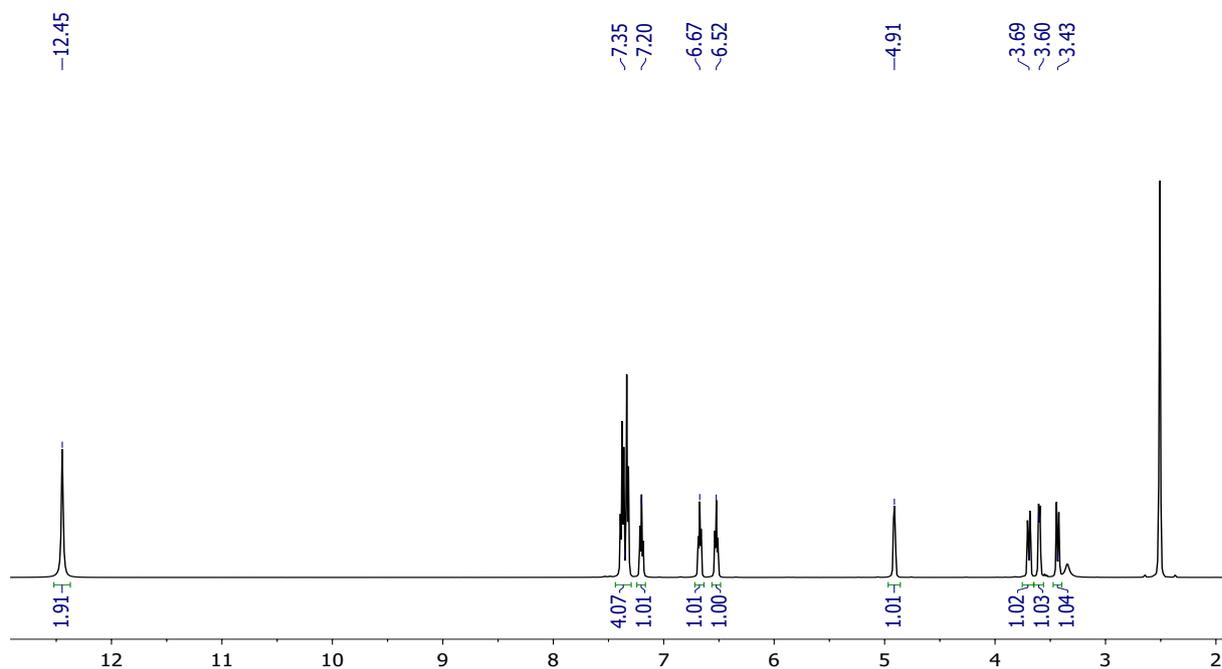
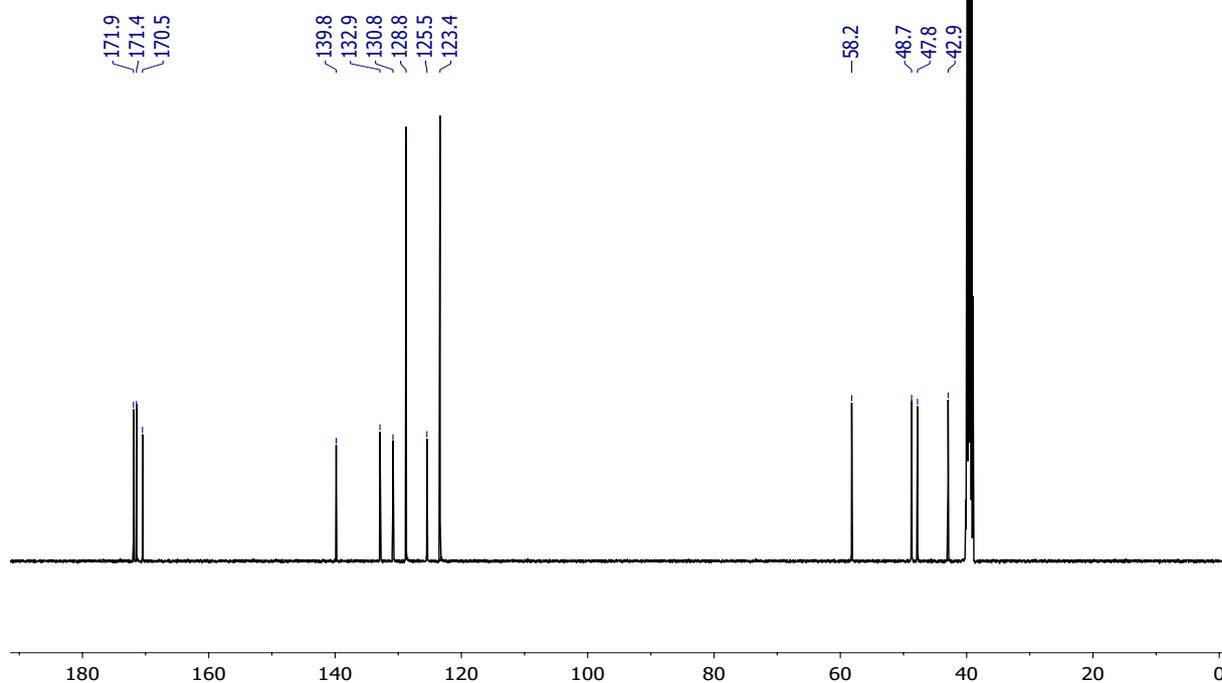


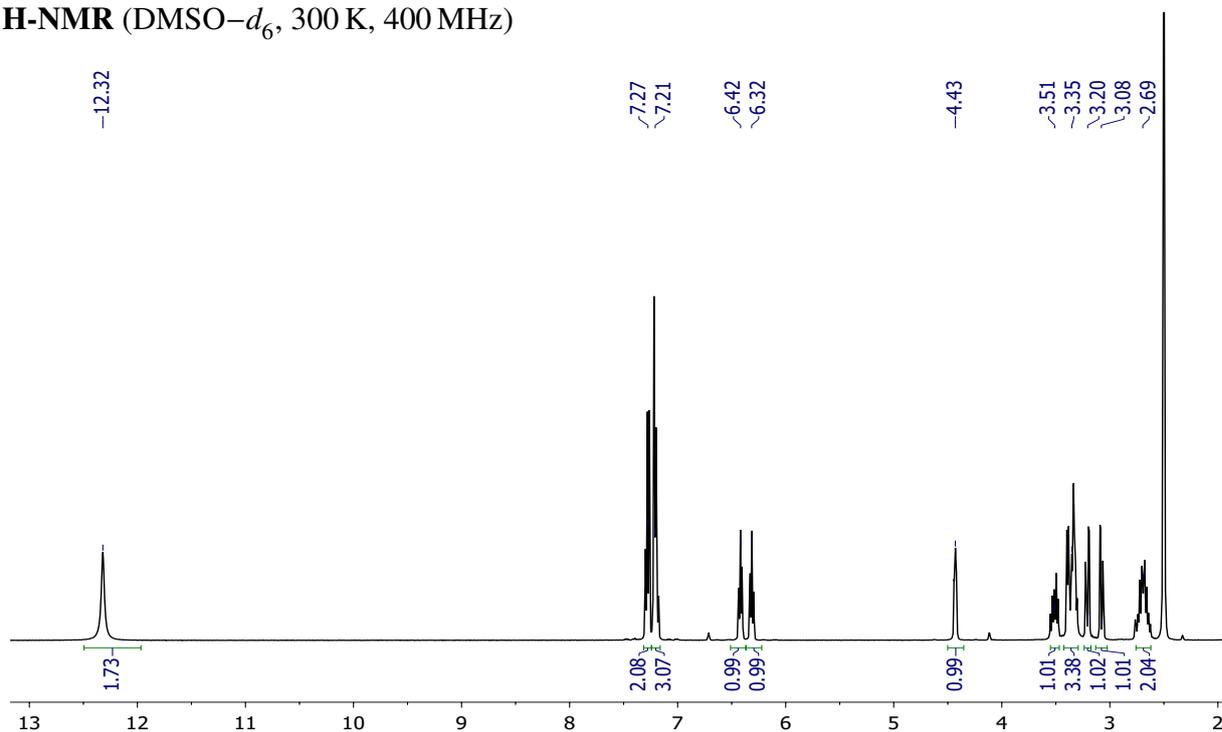
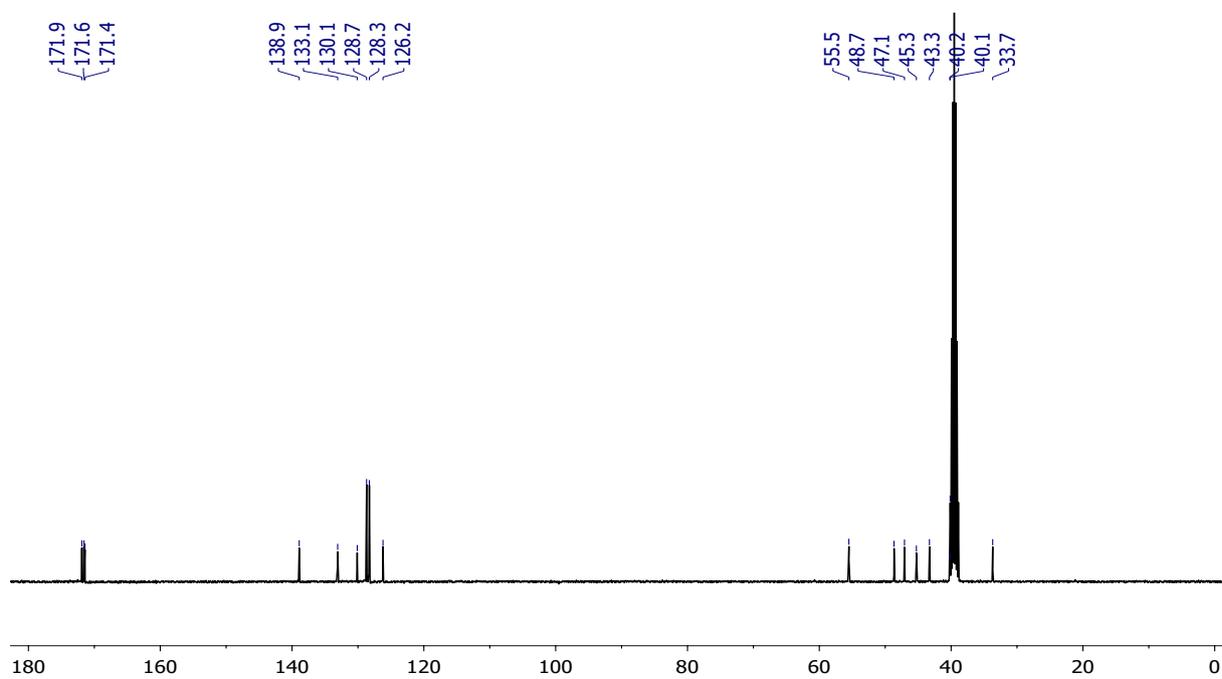
**(*R*<sup>\*</sup>)-1-Benzyl-3-(phenylselanyl)-3,4-dihydropyridin-2(1*H*)-one-3-d (S2)**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 300 MHz)

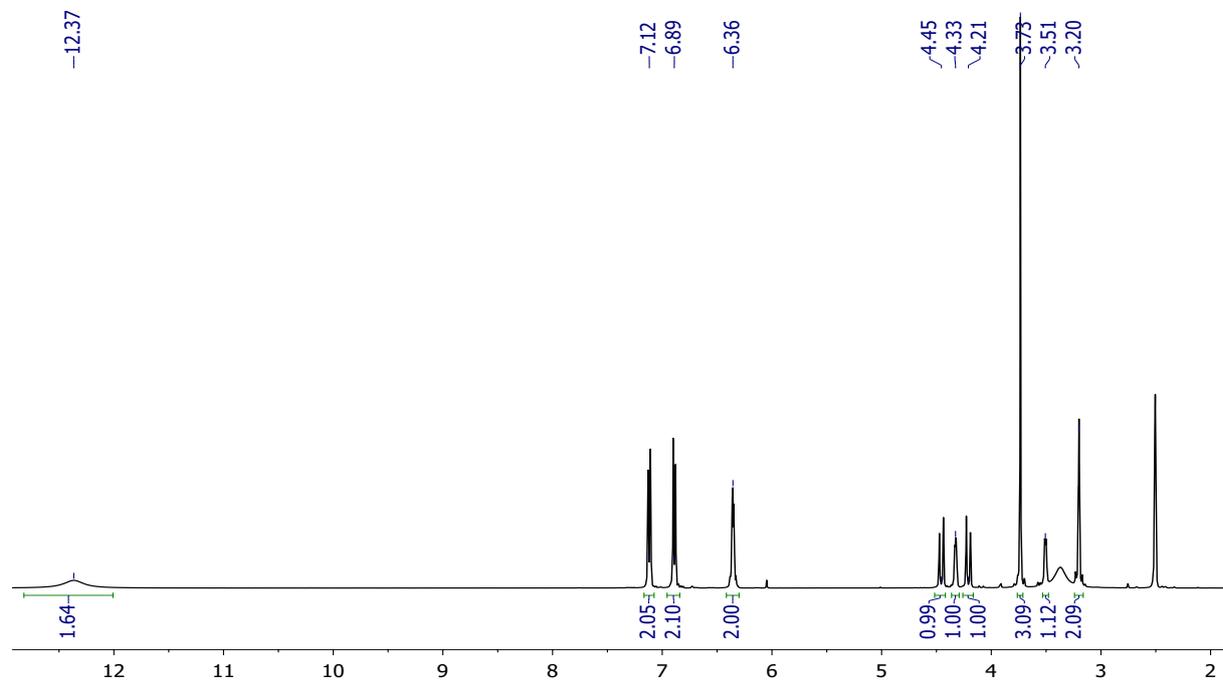
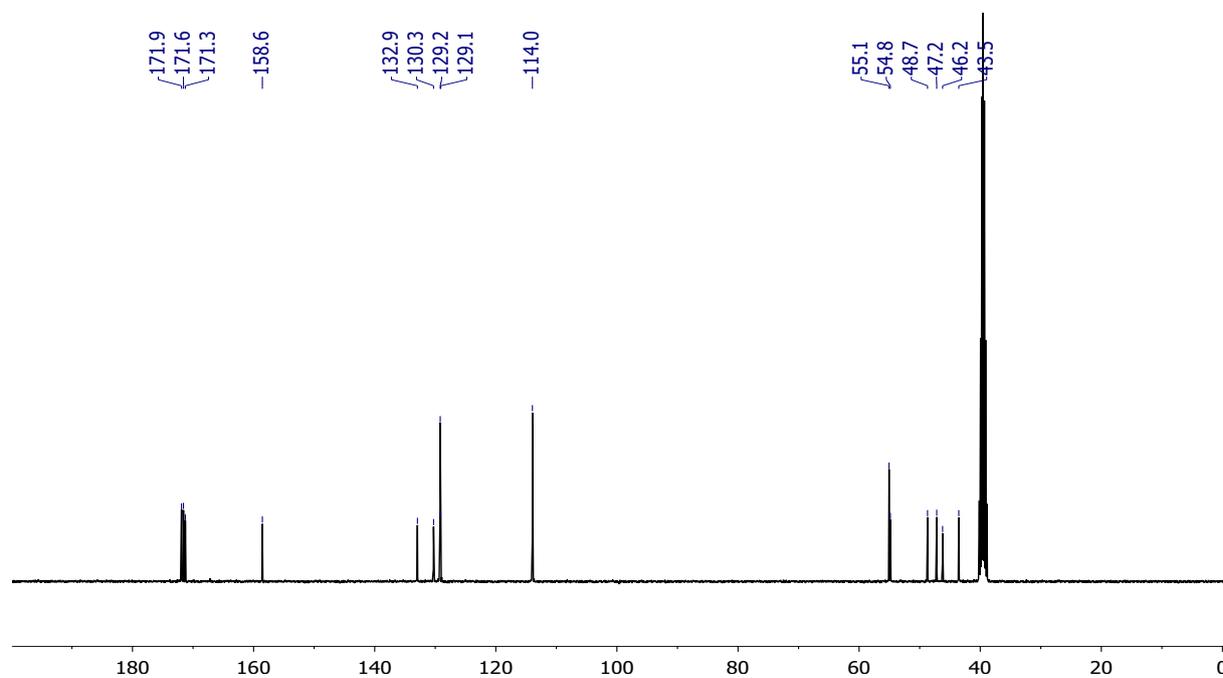
**1-Benzylpyridin-2(1H)-one-3-d (6a-d<sup>1</sup>)**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz)

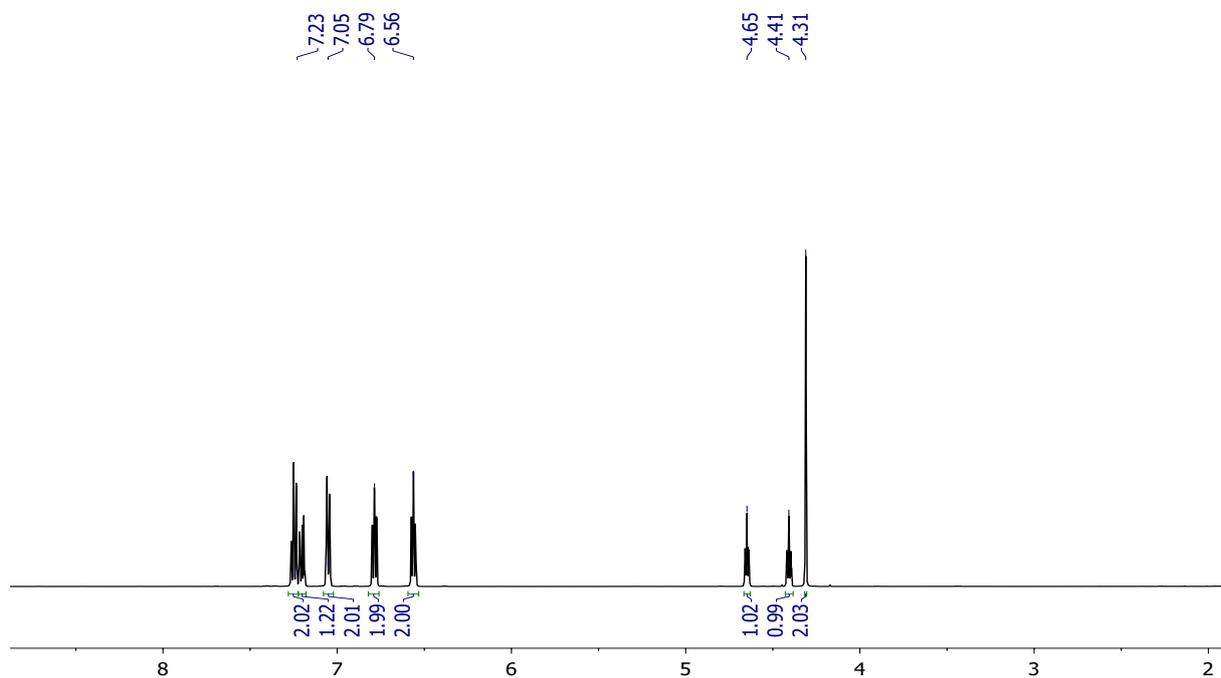
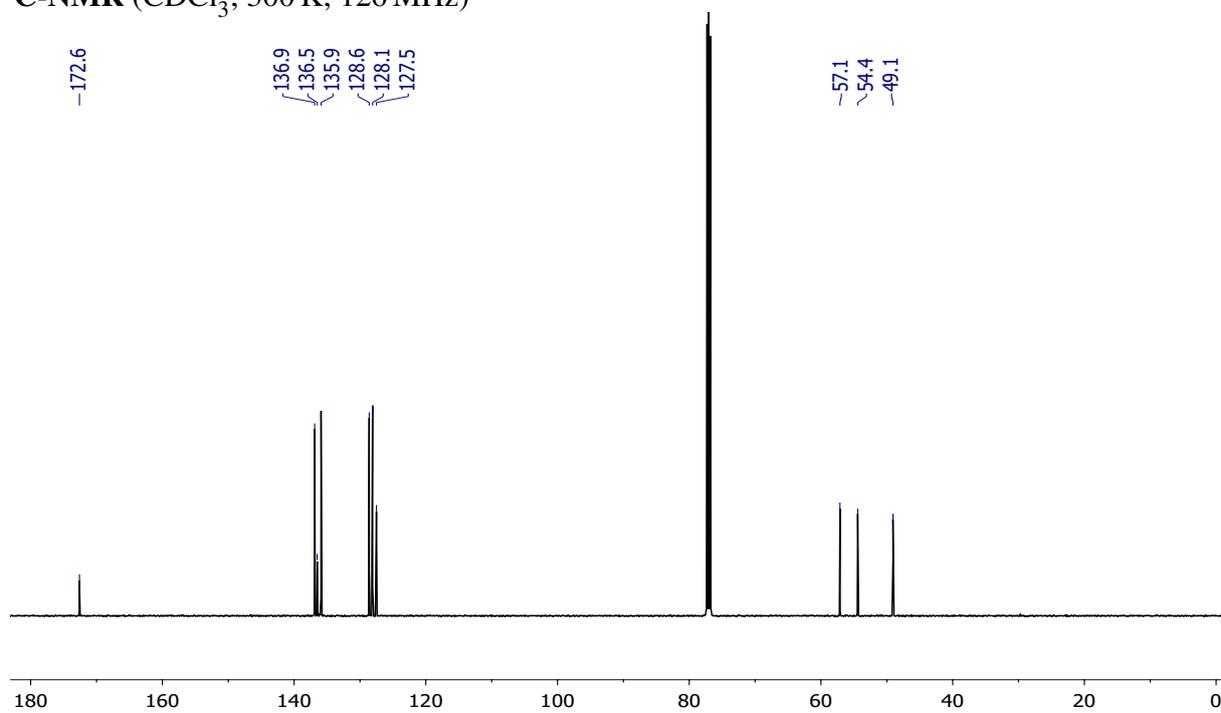
**(1S\*,4R\*,5S\*,6S\*)-2-Benzyl-3-oxo-2-azabicyclo[2.2.2]oct-7-ene-5,6-dicarboxylic acid (9a)**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 400 MHz)<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 101 MHz)

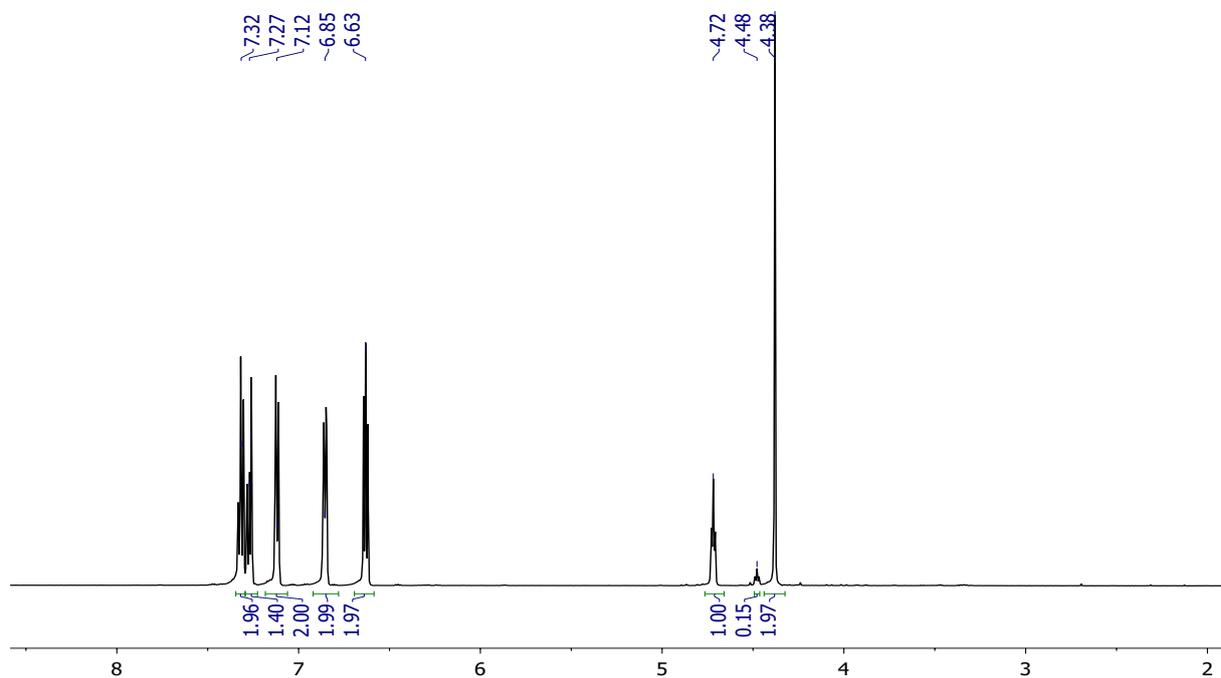
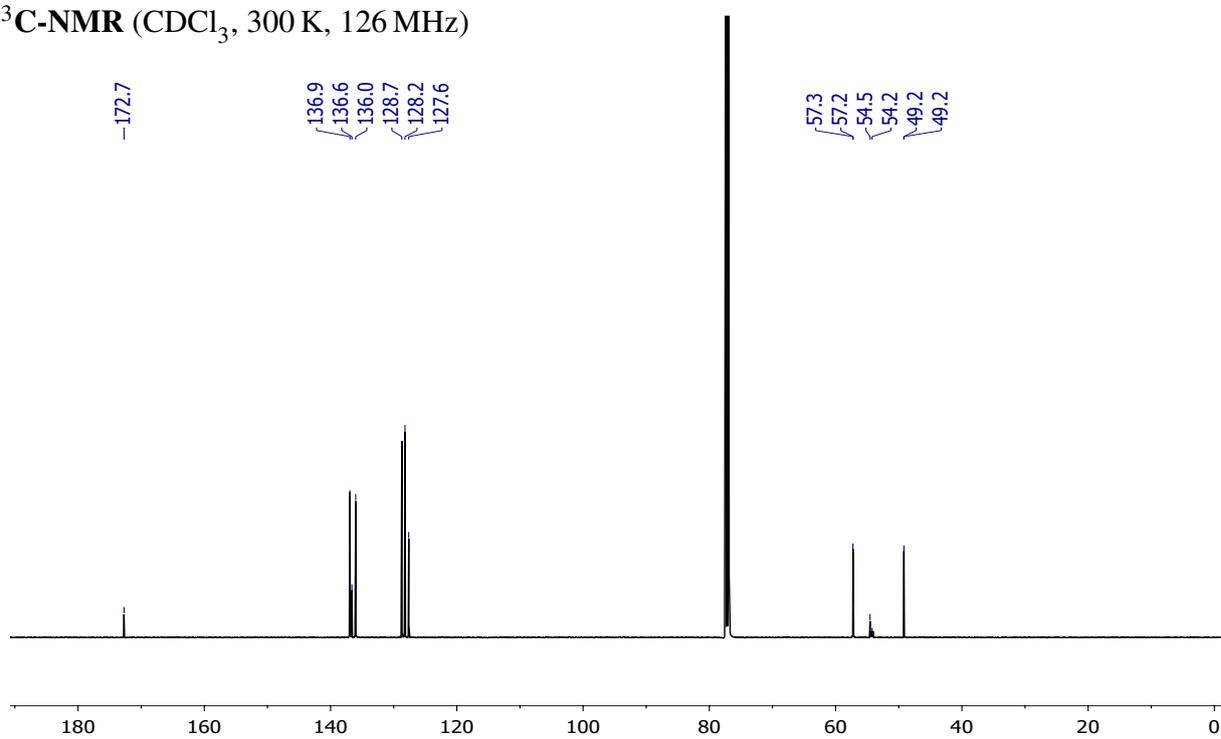
**(1*S*\*,4*R*\*,5*S*\*,6*S*\*)-2-Benzyl-3-oxo-2-azabicyclo[2.2.2]oct-7-ene-5,6-dicarboxylic-4-d acid (9a-*d*<sup>1</sup>)**<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 300 K, 500 MHz)<sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 300 K, 126 MHz)

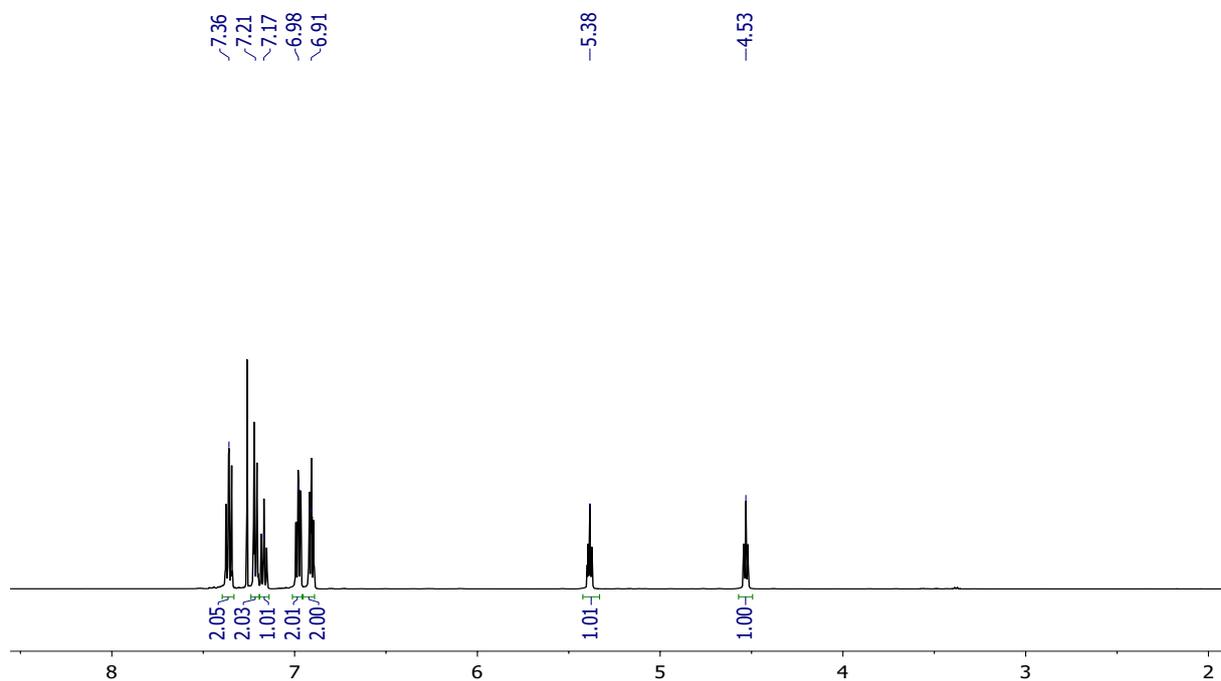
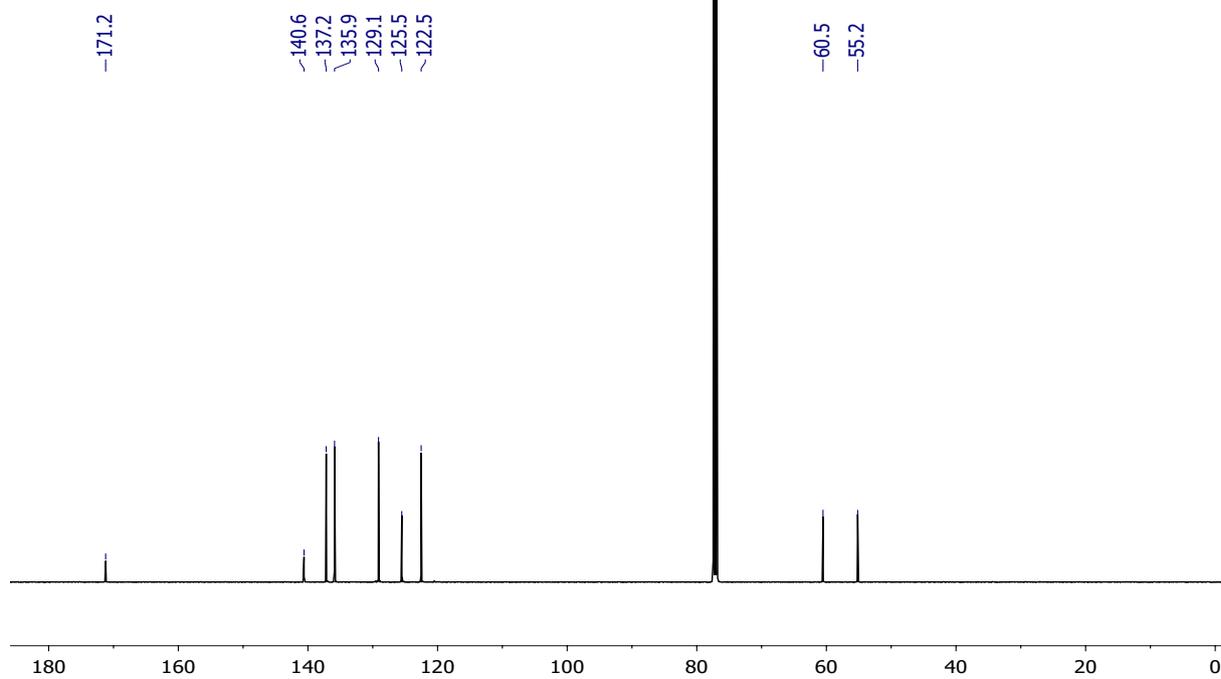
**(1*S*\*,4*R*\*,5*S*\*,6*S*\*)-3-Oxo-2-phenyl-2-azabicyclo[2.2.2]oct-7-ene-5,6-dicarboxylic acid (9b)**<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 300 K, 500 MHz)<sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 300 K, 126 MHz)

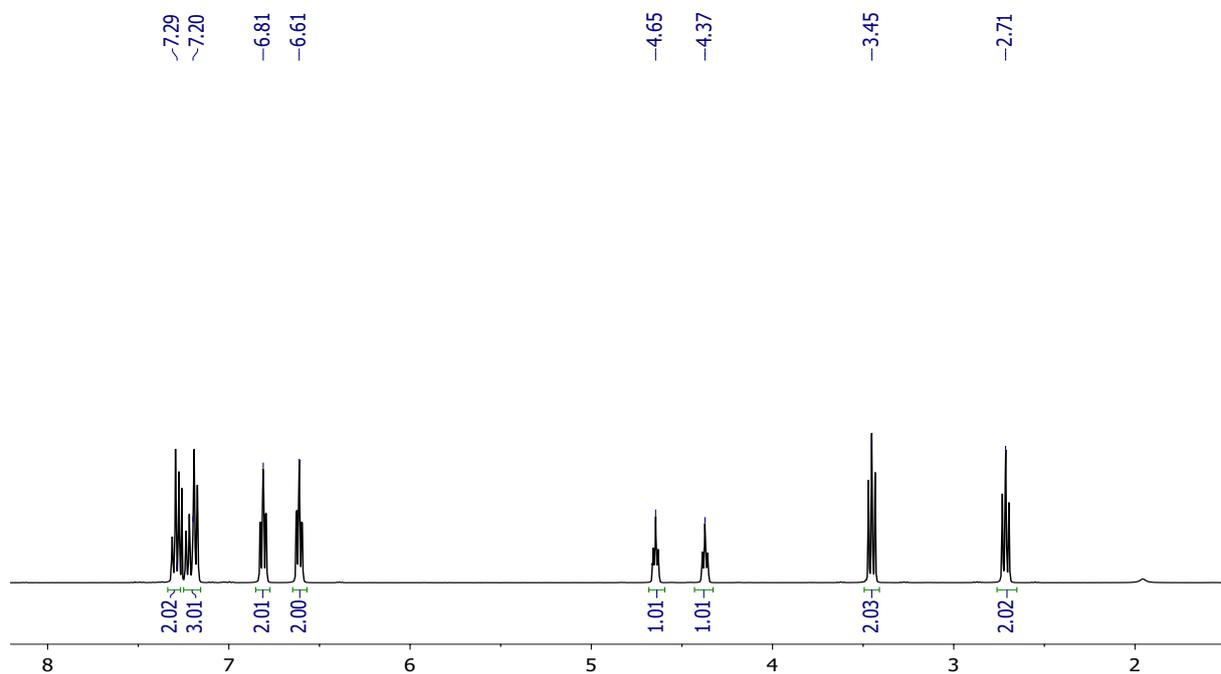
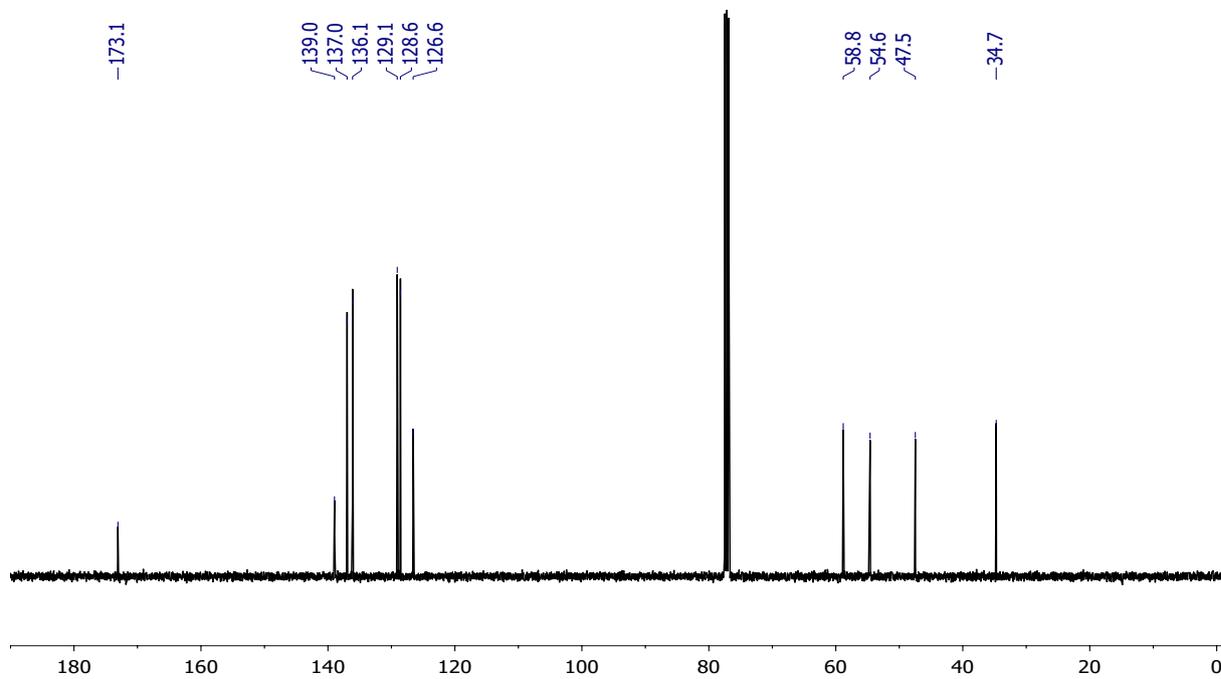
**(1S\*,4R\*,5S\*,6S\*)-3-Oxo-2-phenethyl-2-azabicyclo[2.2.2]oct-7-ene-5,6-dicarboxylic acid (9c)**<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 300 K, 400 MHz)<sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 300 K, 101 MHz)

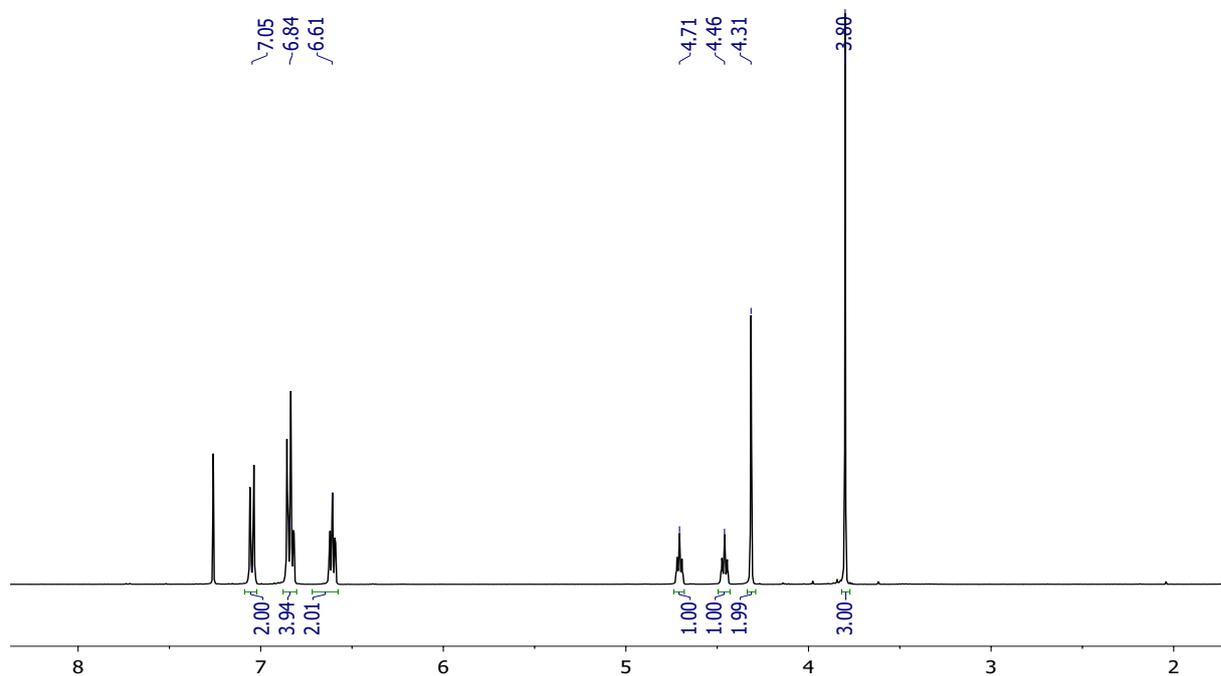
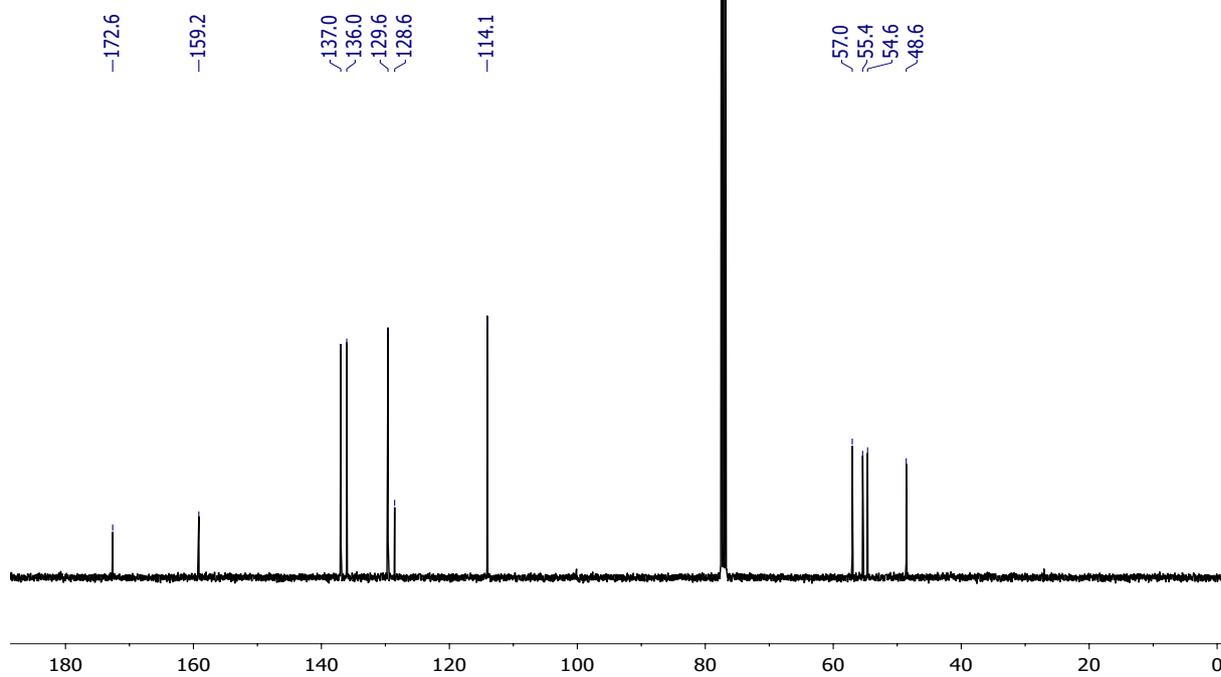
**(1*S*\*,4*R*\*,5*S*\*,6*S*\*)-2-(4-Methoxybenzyl)-3-oxo-2-azabicyclo[2.2.2]oct-7-ene-5,6-dicarboxylic acid (9d)****<sup>1</sup>H-NMR** (DMSO-*d*<sub>6</sub>, 300 K, 400 MHz)**<sup>13</sup>C-NMR** (DMSO-*d*<sub>6</sub>, 300 K, 101 MHz)

**2-Benzyl-2-azabicyclo[2.2.2]octa-5,7-dien-3-one (1a)**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz)

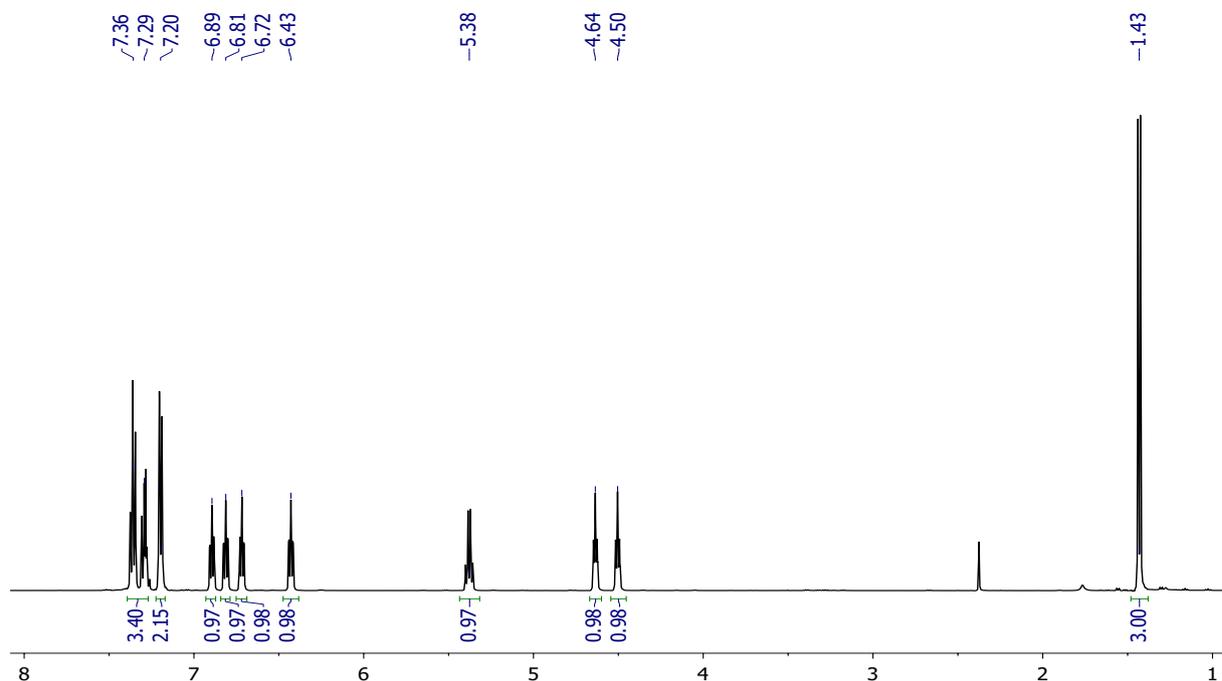
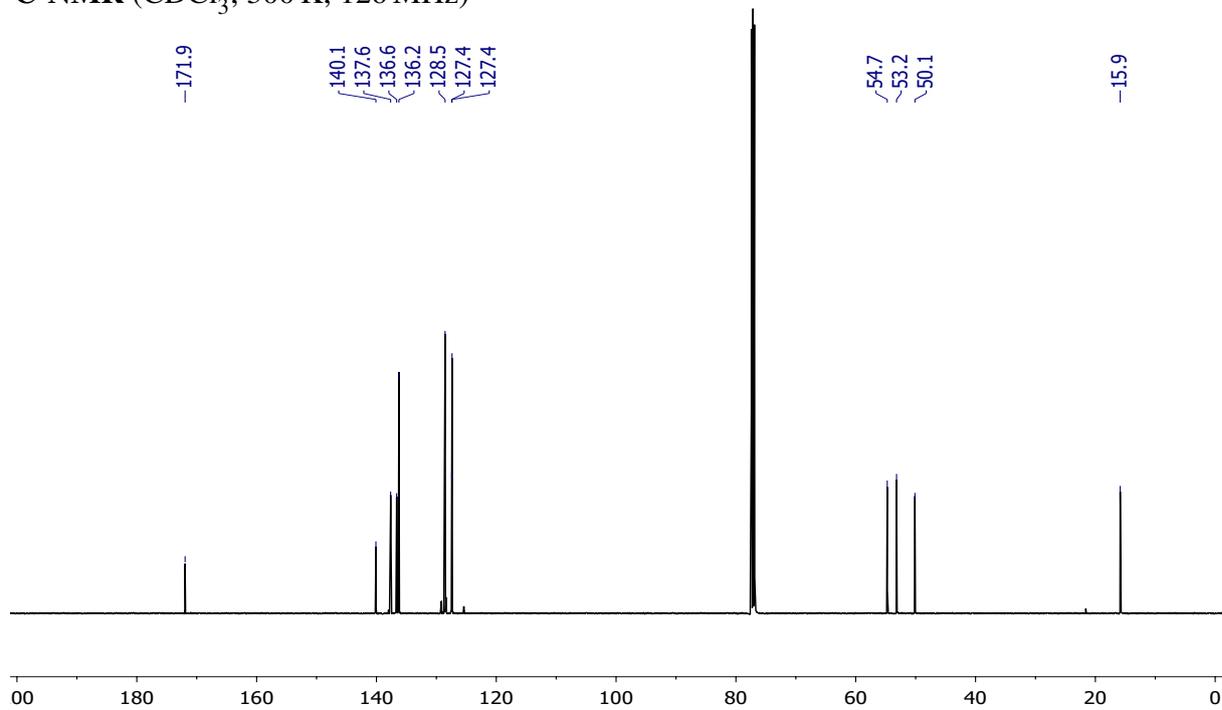
**2-Benzyl-2-azabicyclo[2.2.2]octa-5,7-dien-3-one-4-d (1a-d<sup>1</sup>)**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz)

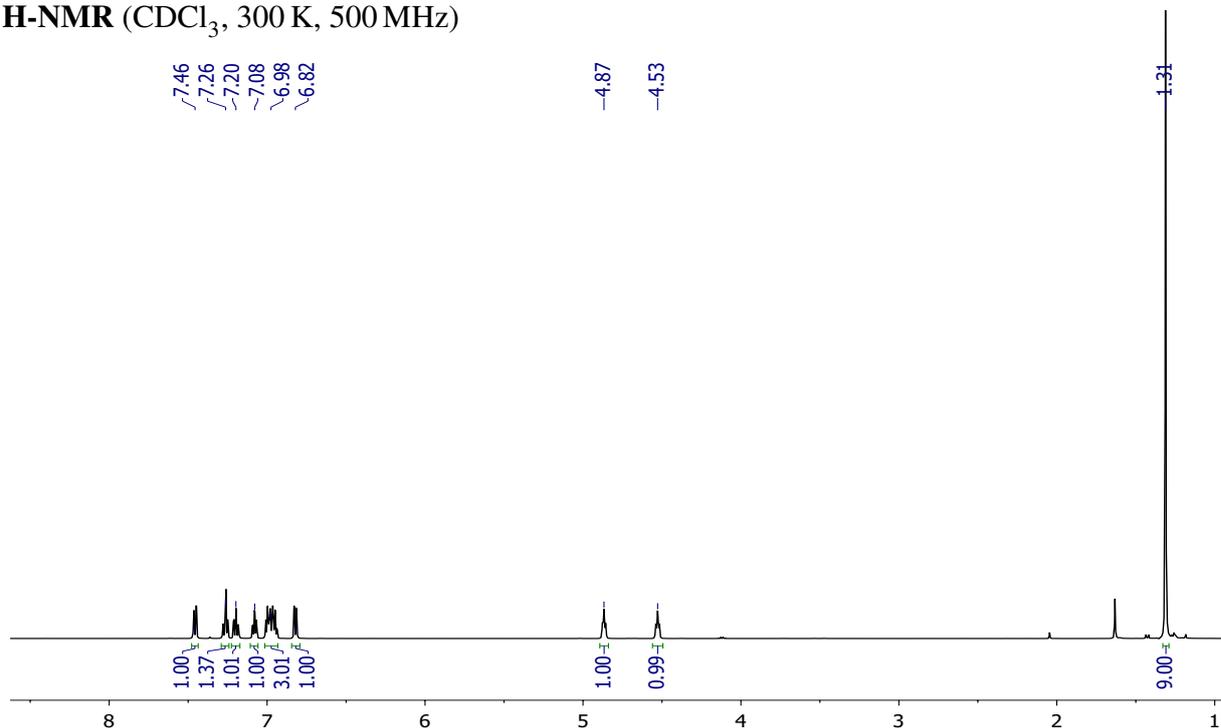
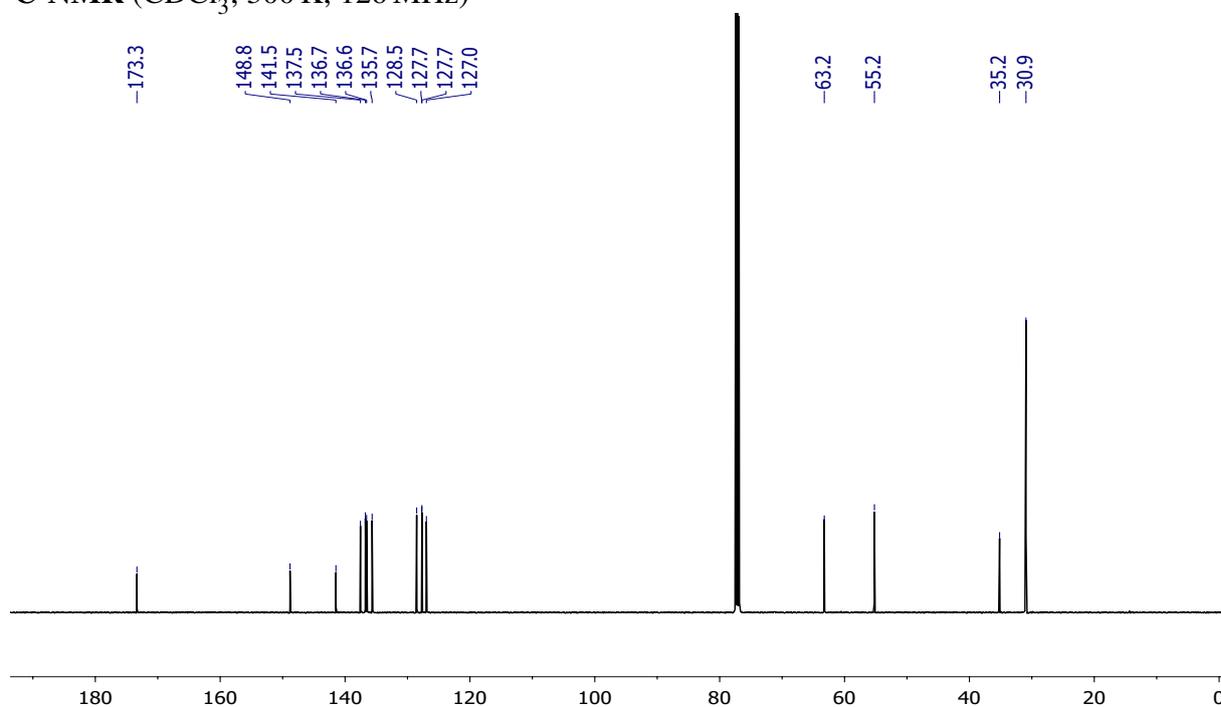
**2-Phenyl-2-azabicyclo[2.2.2]octa-5,7-dien-3-one (1b)**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz)

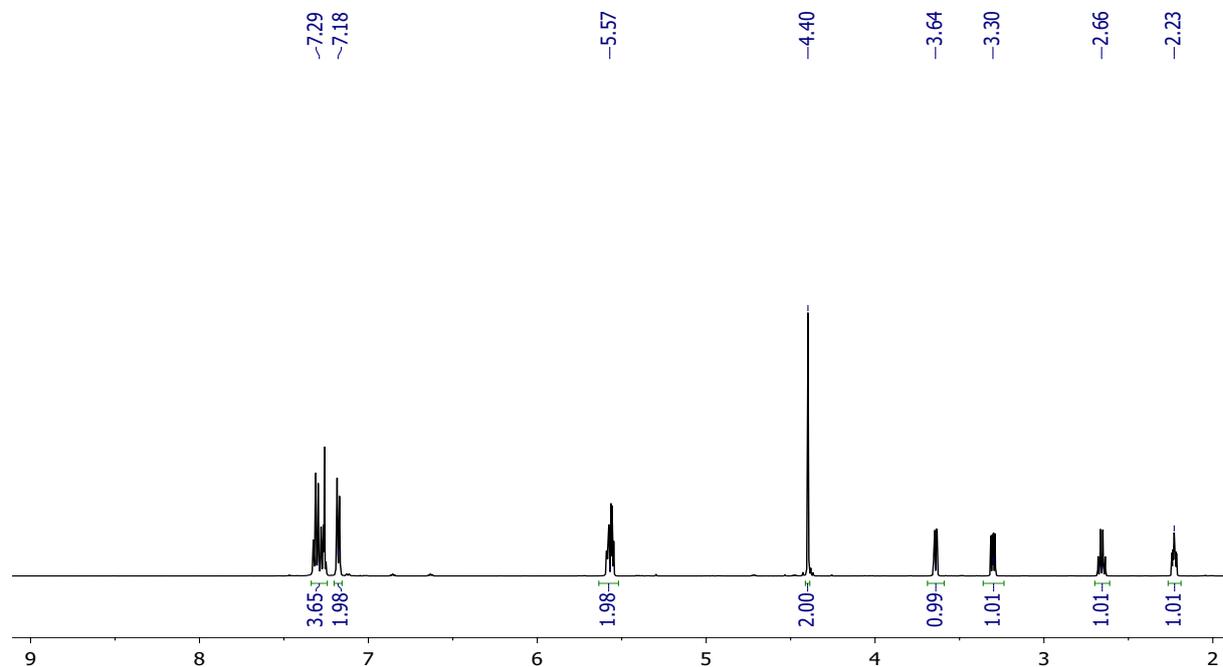
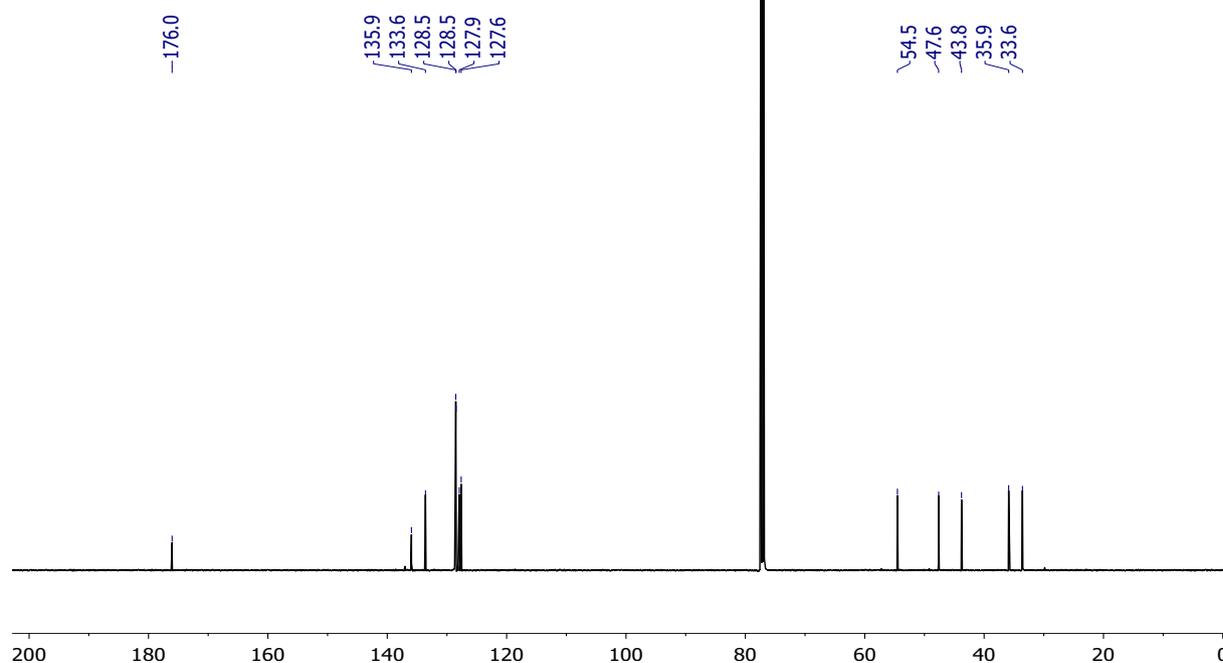
**2-Phenethyl-2-azabicyclo[2.2.2]octa-5,7-dien-3-one (1c)**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 400 MHz)<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 101 MHz)

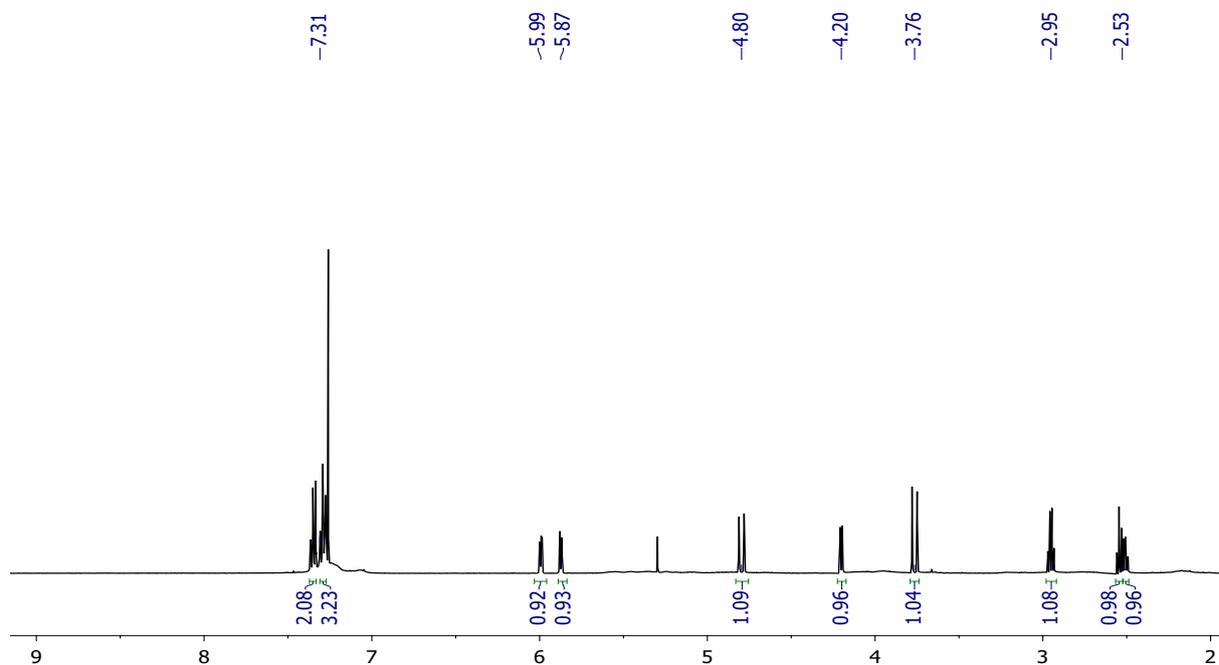
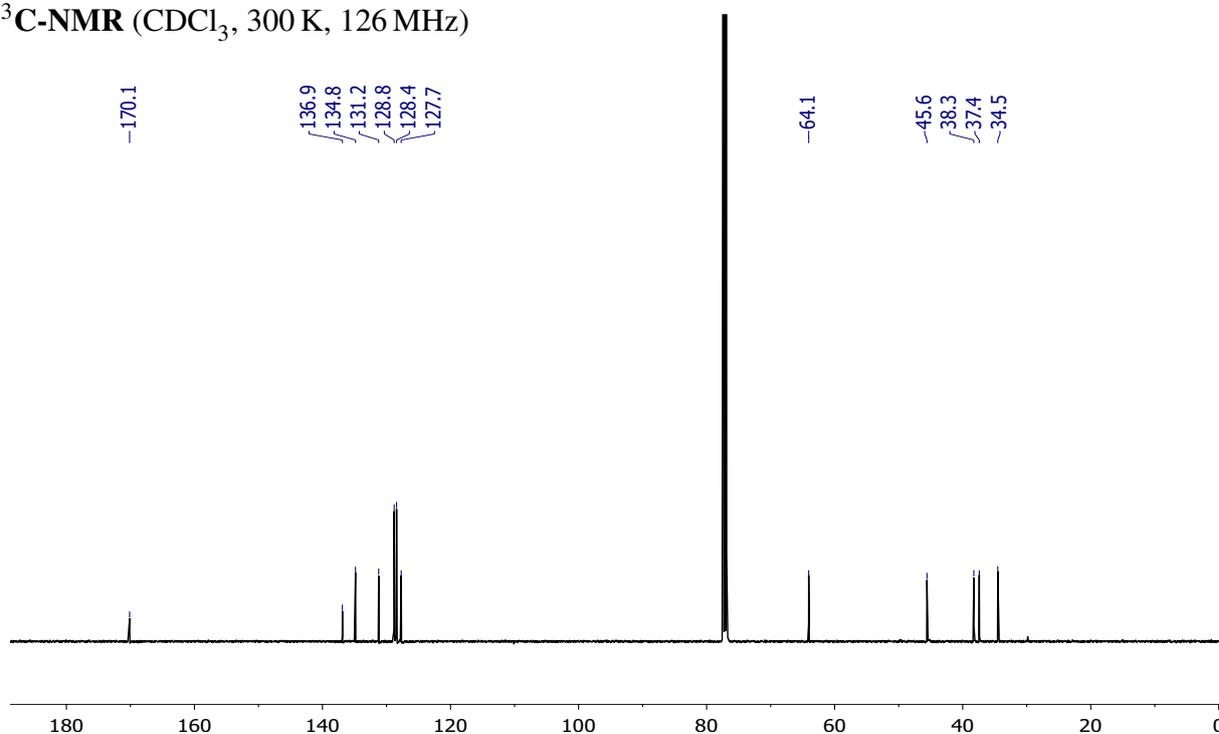
**2-(4-Methoxybenzyl)-2-azabicyclo[2.2.2]octa-5,7-dien-3-one (1d)**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 400 MHz)<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 101 MHz)

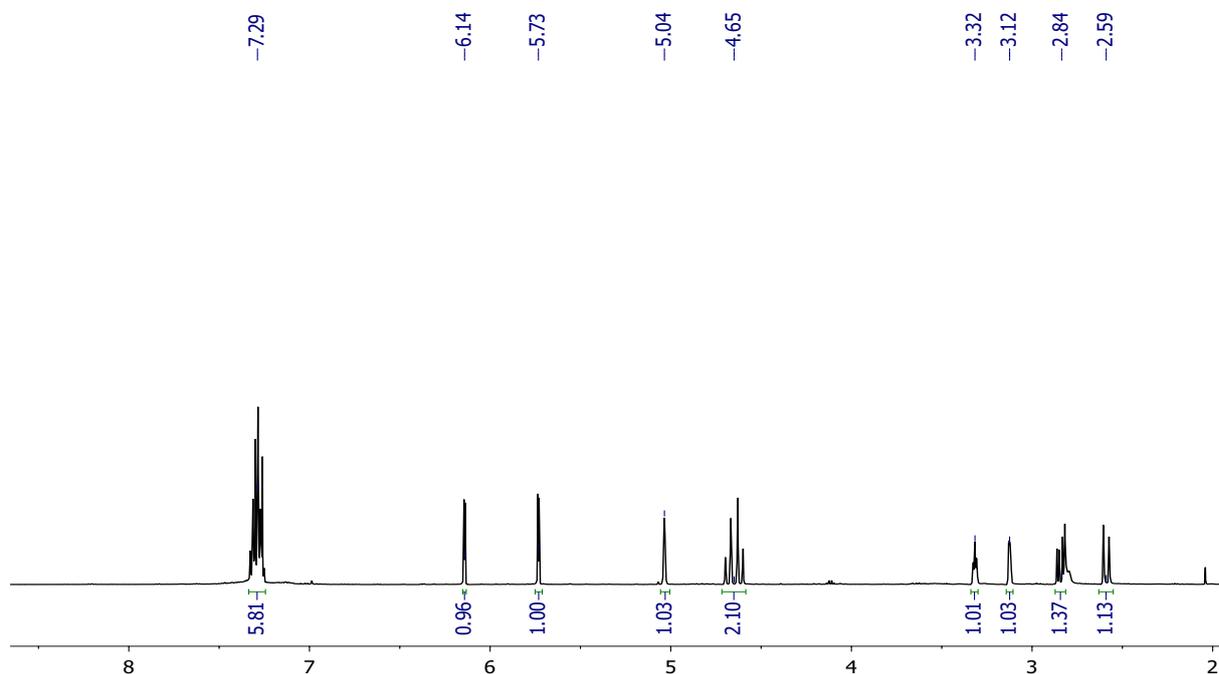
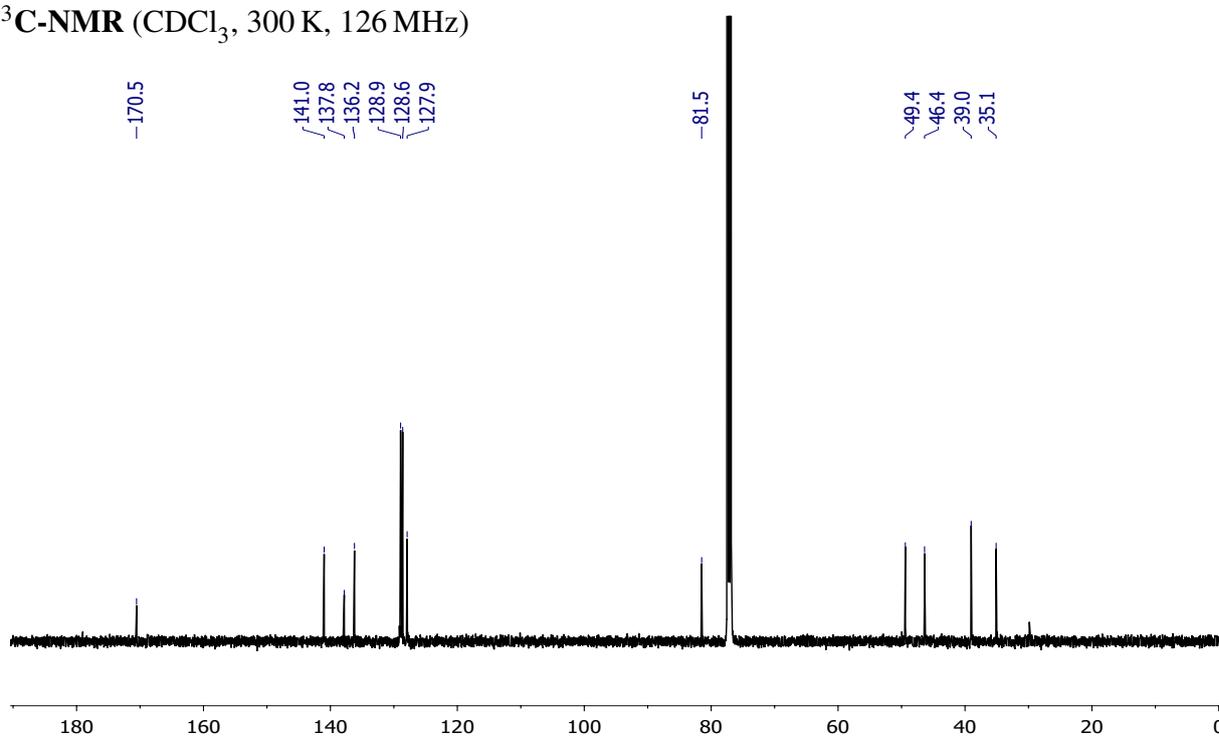
## 2-[(S)-1-Phenylethyl]-2-azabicyclo[2.2.2]oct-5-en-3-on (1e)

 $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 K, 500 MHz) $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 300 K, 126 MHz)

2-[(*R*<sup>a</sup>)-2-(*tert*-Butyl)phenyl]-2-azabicyclo[2.2.2]octa-5,7-dien-3-one (1f)<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz)

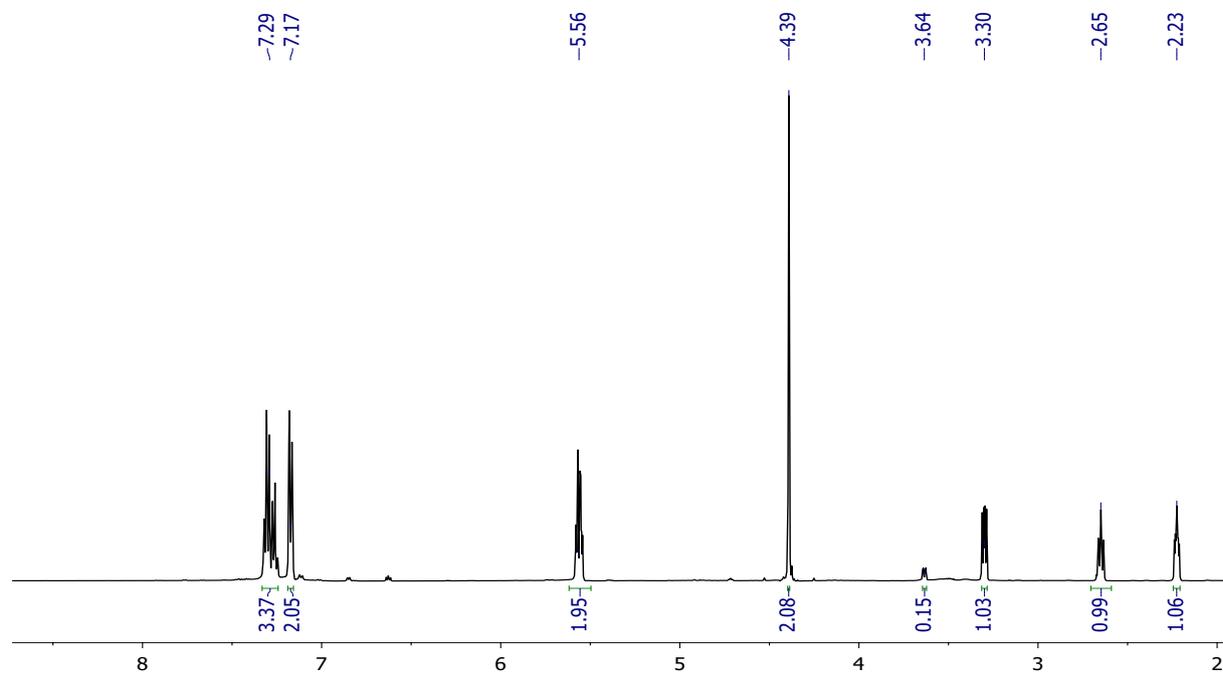
**(2aR\*,2a<sup>1</sup>R\*,2bR\*,4aS\*)-2-Benzyl-2a,2a<sup>1</sup>,2b,4a-tetrahydro-2-azacyclopropa[cd]pentalen-1(2H)-one (10a)****<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 K, 500 MHz)**<sup>13</sup>C-NMR** (CDCl<sub>3</sub>, 300 K, 126 MHz)

**(2aR\*,2a<sup>1</sup>S\*,2bR\*,4aS\*)-1-Benzyl-2a,2a<sup>1</sup>,2b,4a-tetrahydro-1-azacyclopropa[cd]pentalen-2(1H)-one (11a)**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz)

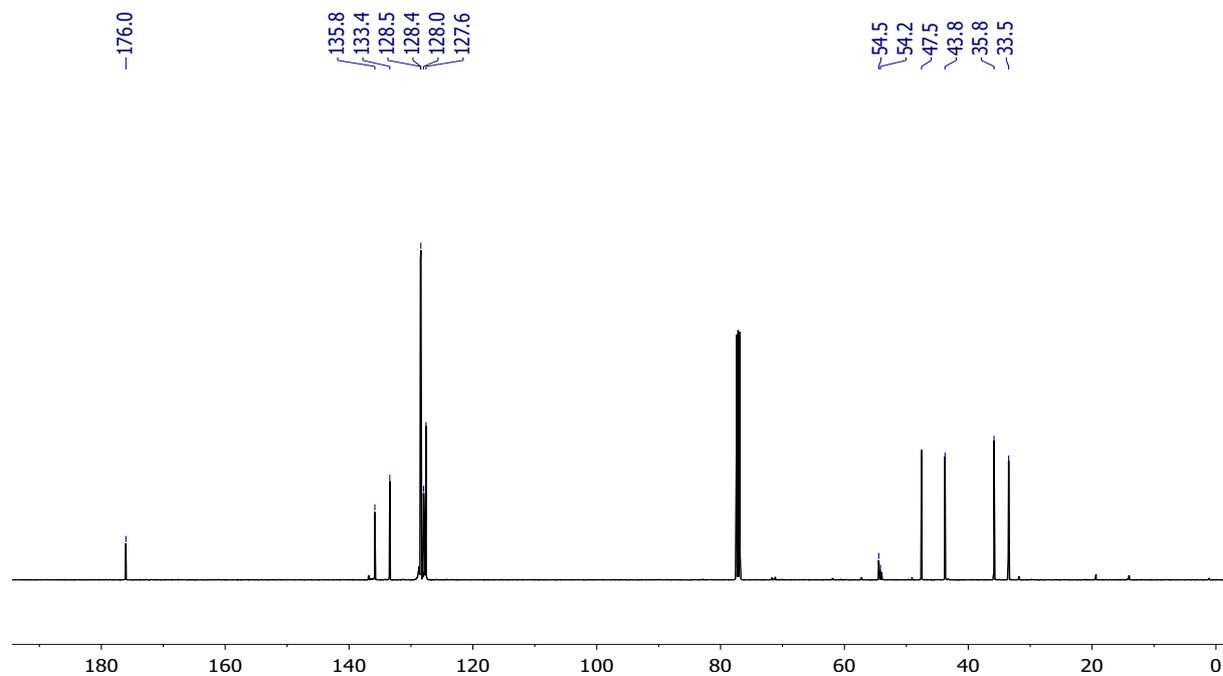
**(1*R*\*,2*S*\*,6*S*\*)-3-Benzyl-2-hydroxy-3-azabicyclo[4.2.0]oct-7-en-4-one (16a)**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz)

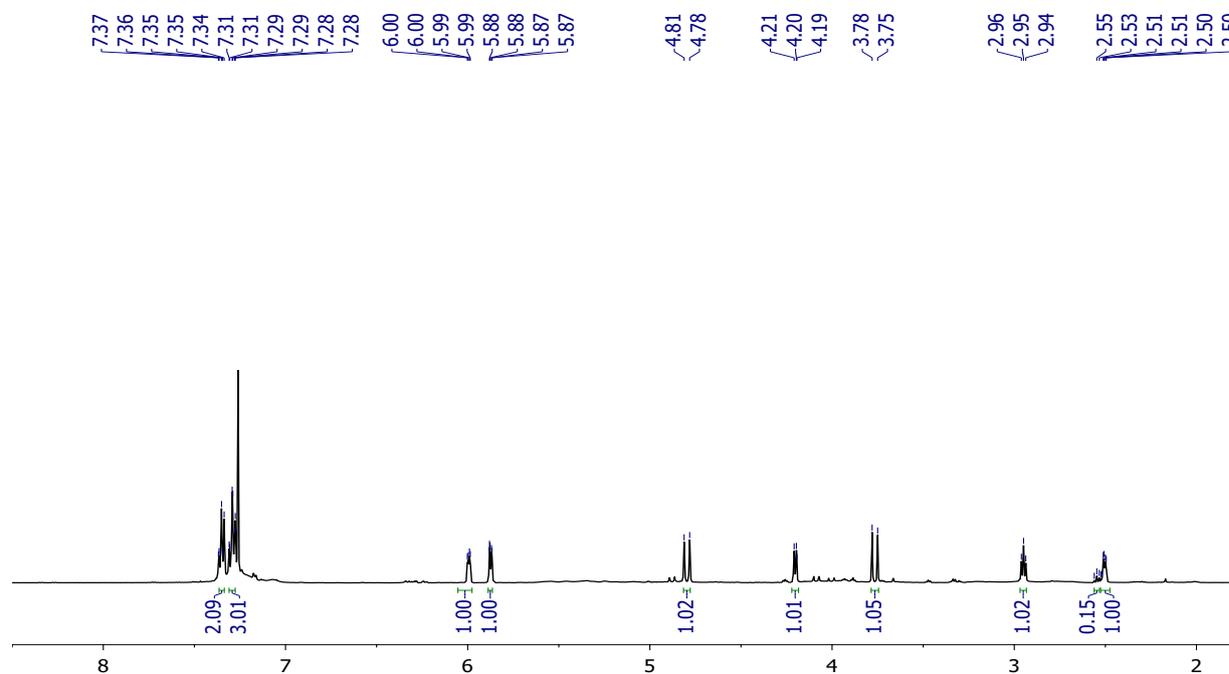
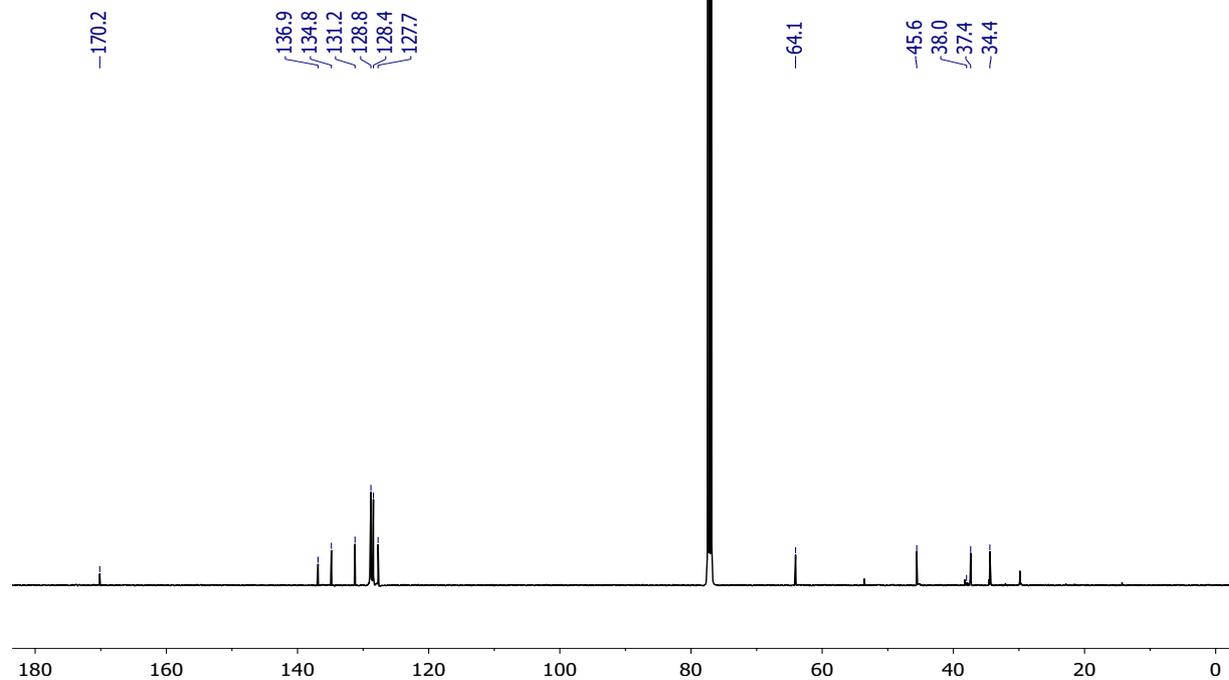
**(2aR\*,2a<sup>1</sup>R\*,2bR\*,4aS\*)-2-Benzyl-2a,2a<sup>1</sup>,2b,4a-tetrahydro-2-azacyclopropa[cd]pentalen-1(2H)-one-4a-d (10a-d<sup>1</sup>)**

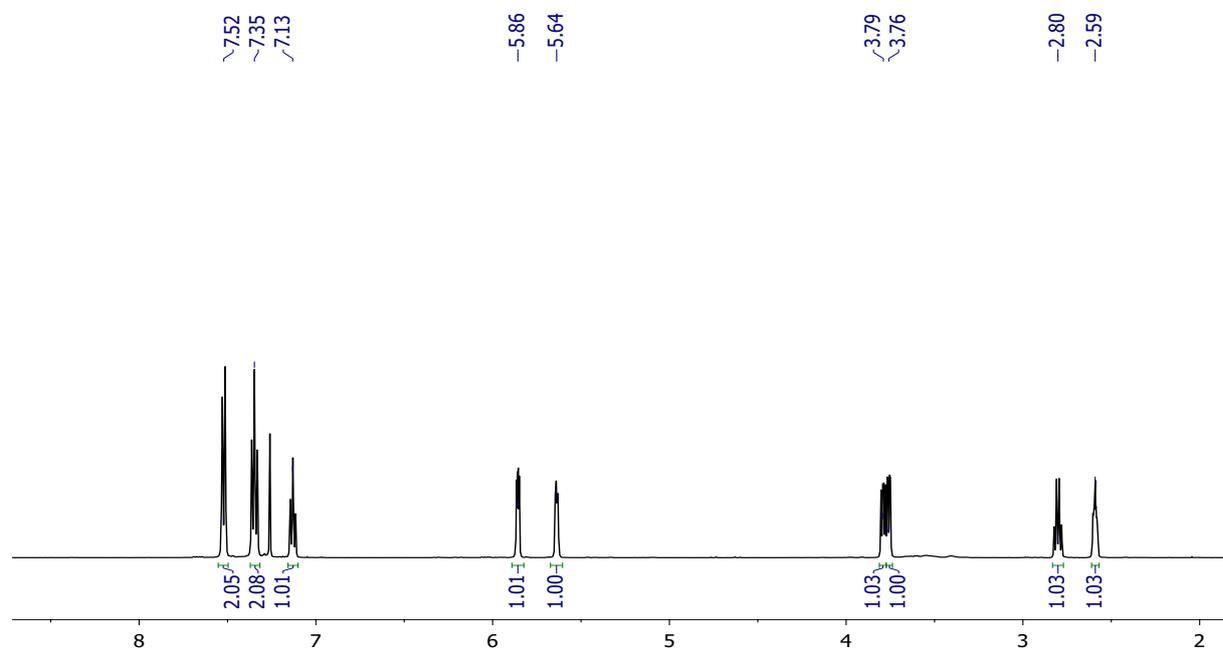
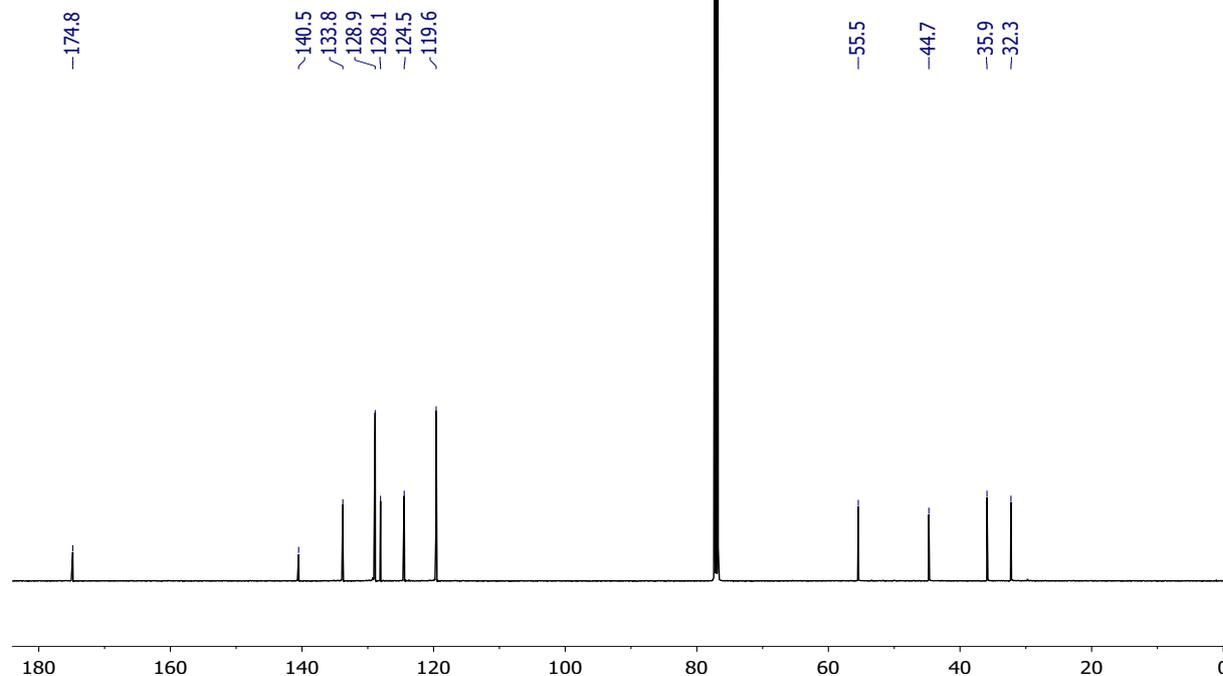
<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)

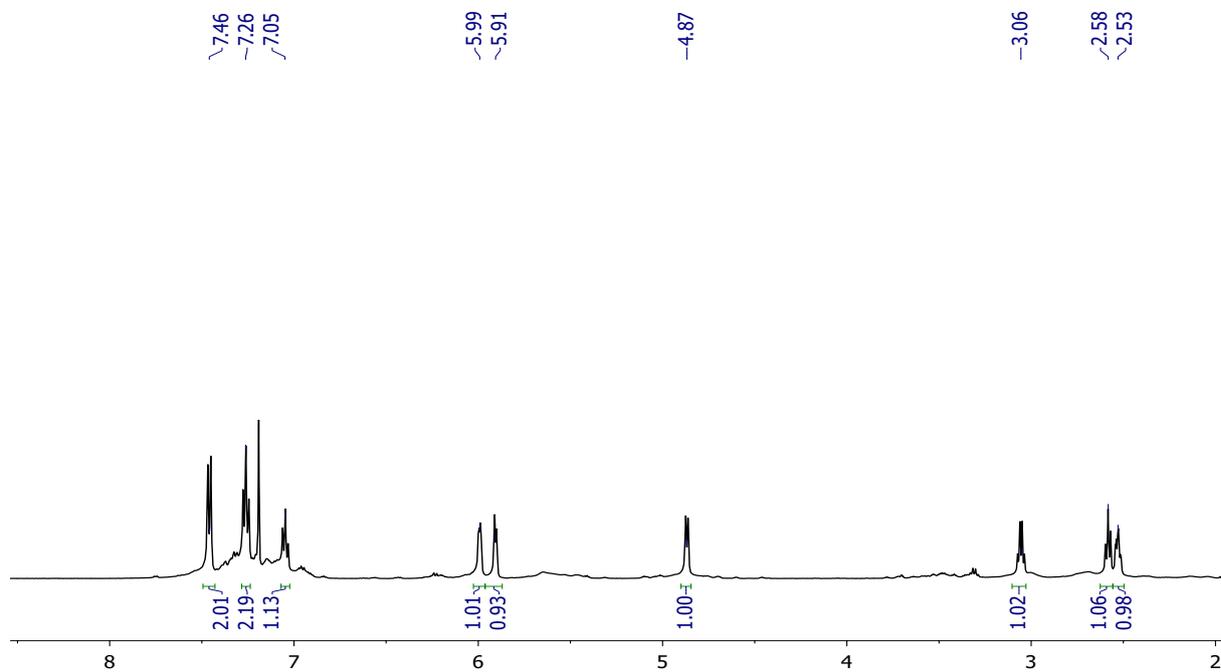
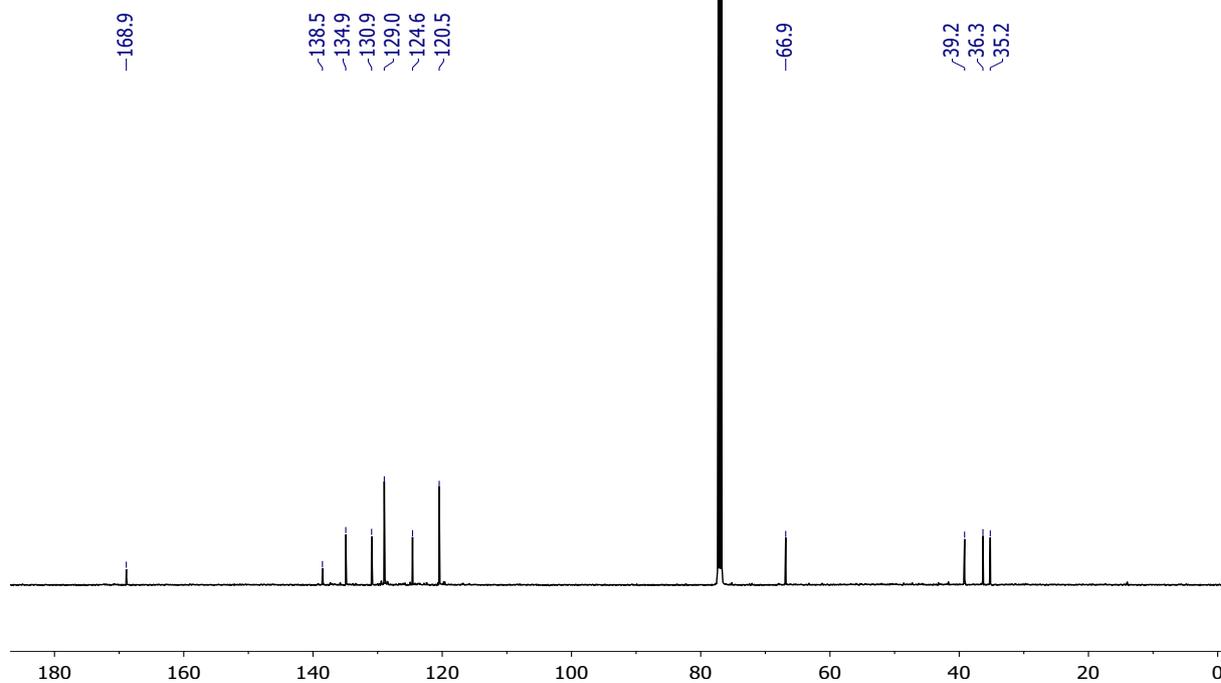


<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz)



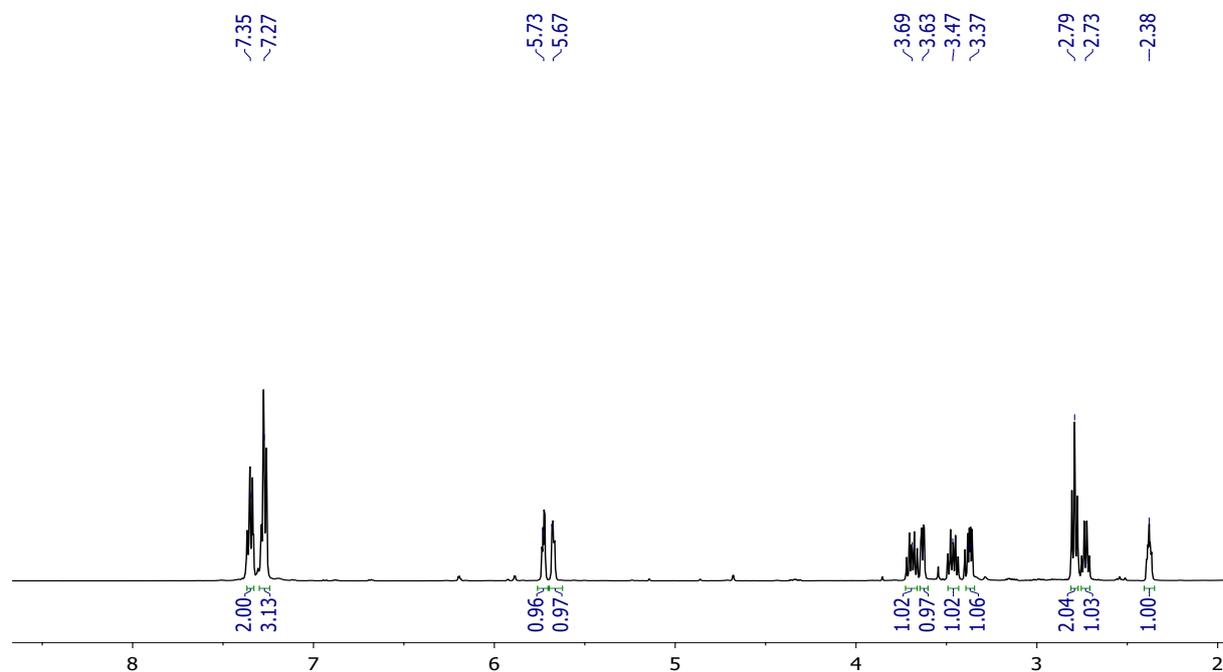
**(2aR\*,2a<sup>1</sup>S\*,2bR\*,4aS\*)-1-Benzyl-2a,2a<sup>1</sup>,2b,4a-tetrahydro-1-azacyclopropa[cd]pentalen-2(1H)-one-2a-d (11a-d<sup>1</sup>)****<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 K, 500 MHz)**<sup>13</sup>C-NMR** (CDCl<sub>3</sub>, 300 K, 126 MHz)

**(2aR\*,2a<sup>1</sup>R\*,2bR\*,4aS\*)-2-Phenyl-2a,2a<sup>1</sup>,2b,4a-tetrahydro-2-azacyclopropa[cd]pentalen-1(2H)-one (10b)**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz)

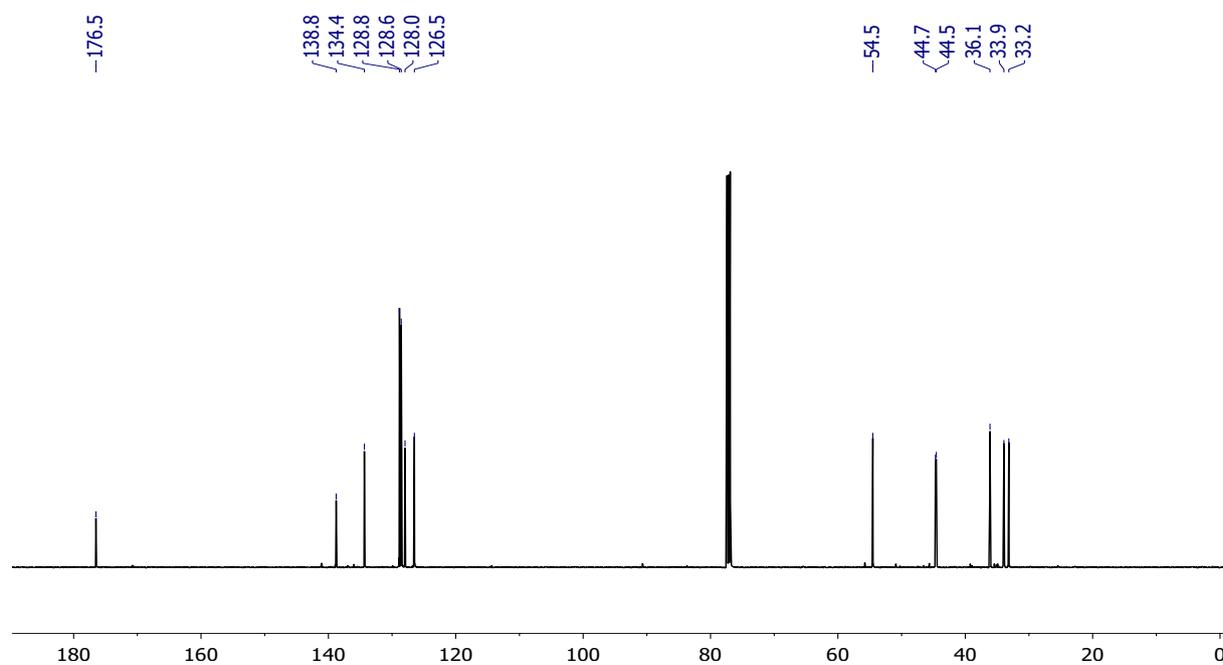
**(2aR\*,2a<sup>1</sup>S\*,2bR\*,4aS\*)-1-Phenyl-2a,2a<sup>1</sup>,2b,4a-tetrahydro-1-azacyclopropa[cd]pentalen-2(1H)-one (11b)**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz)

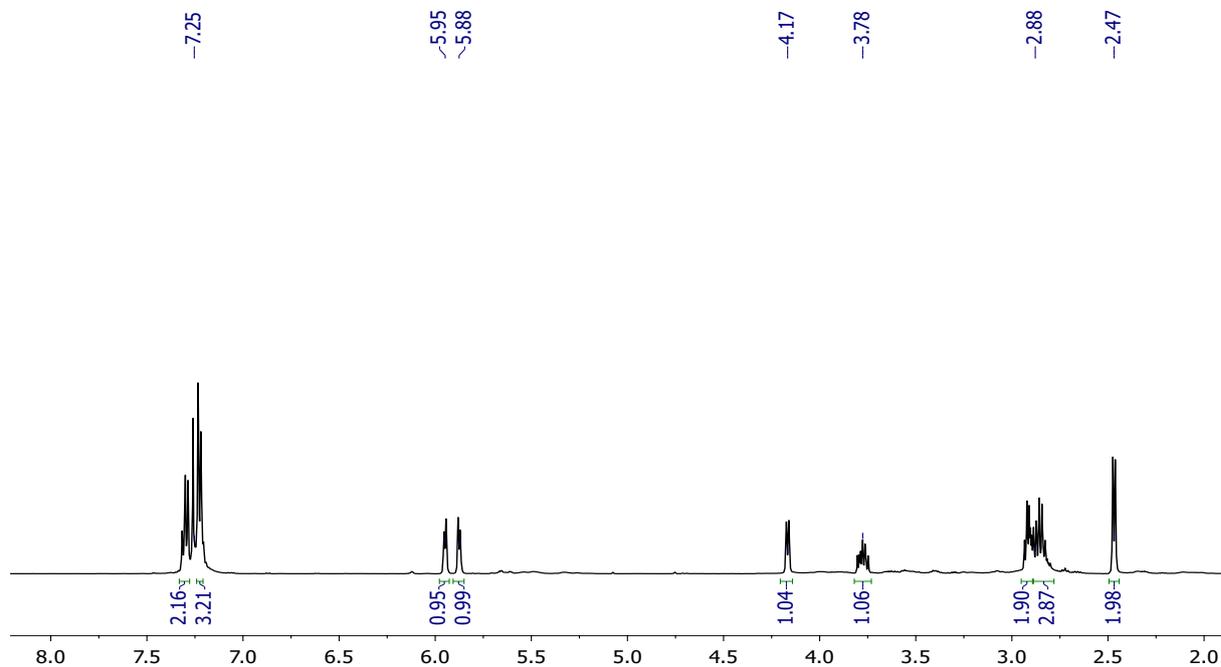
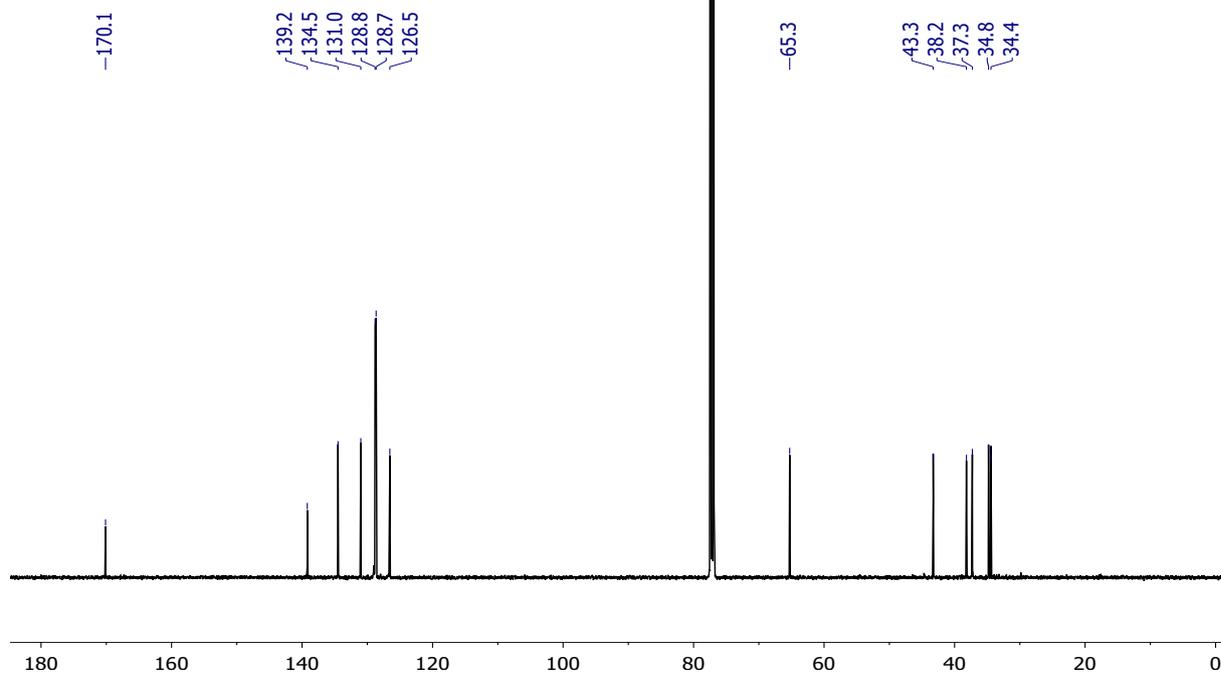
(2a*R*\*,2a<sup>1</sup>*R*\*,2b*R*\*,4a*S*\*)-2-Phenethyl-2a,2a<sup>1</sup>,2b,4a-tetrahydro-2-azacyclopropa[cd]pentalen-1(2*H*)-one (10c)

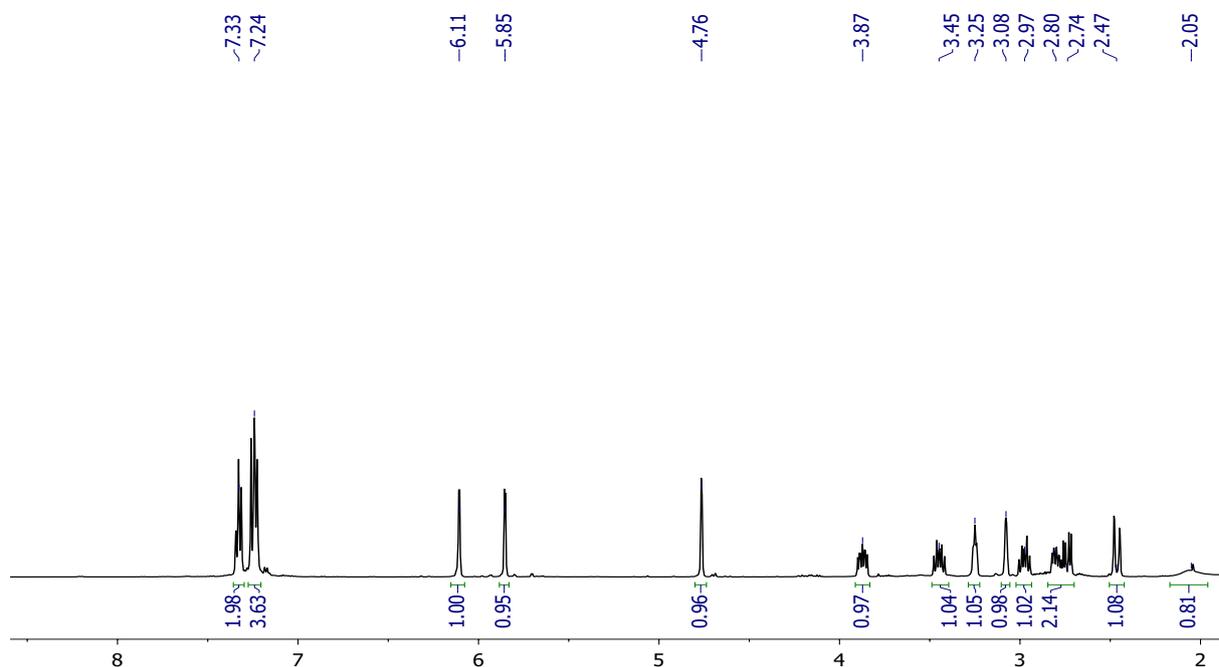
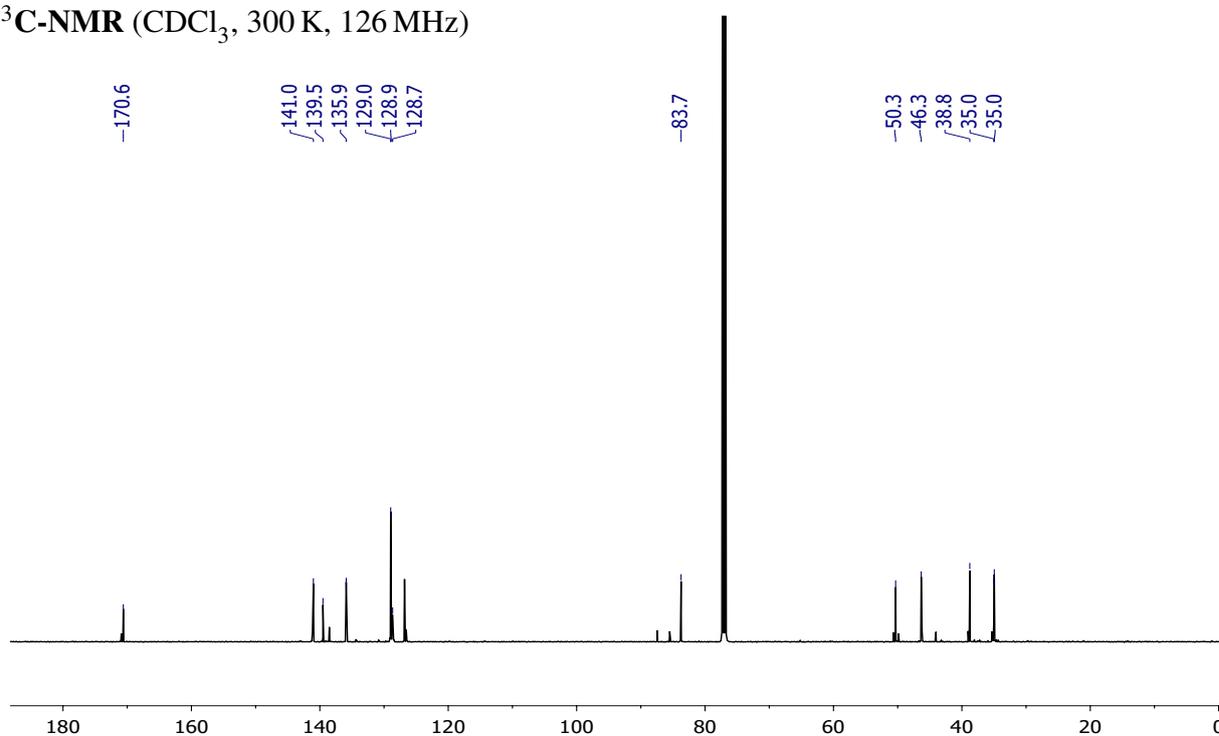
<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)



<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz)

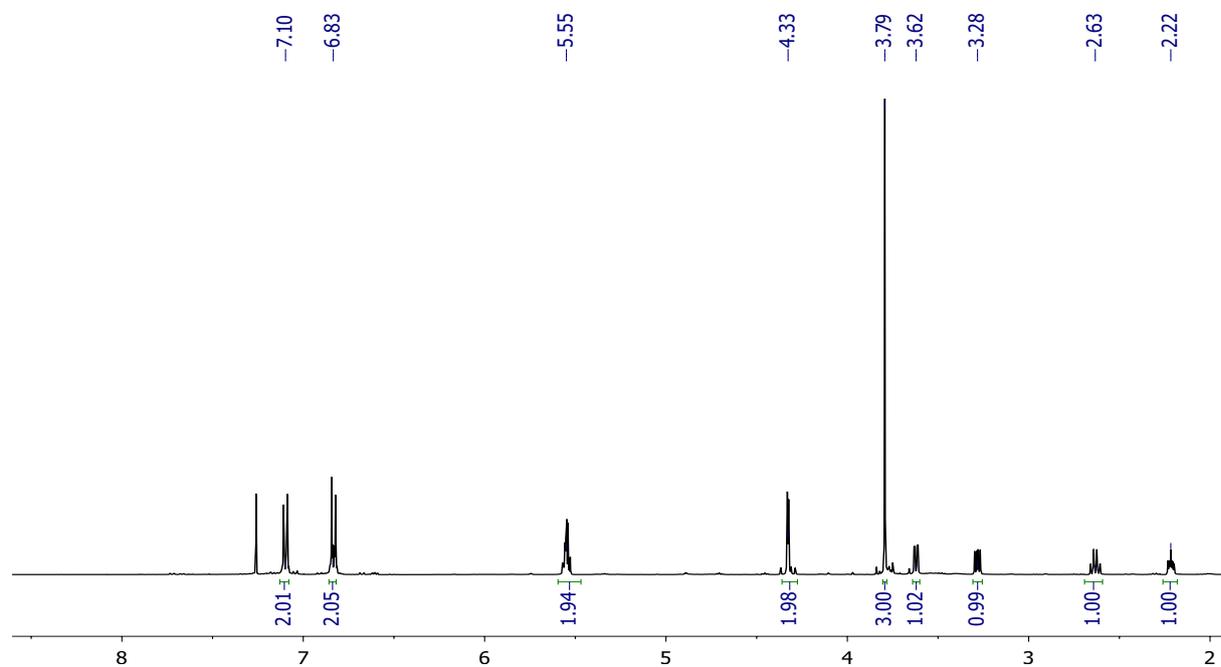


**(2aR\*,2a<sup>1</sup>S\*,2bR\*,4aS\*)-1-Phenethyl-2a,2a<sup>1</sup>,2b,4a-tetrahydro-1-azacyclopropa[cd]pentalen-2(1H)-one (11c)**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz)

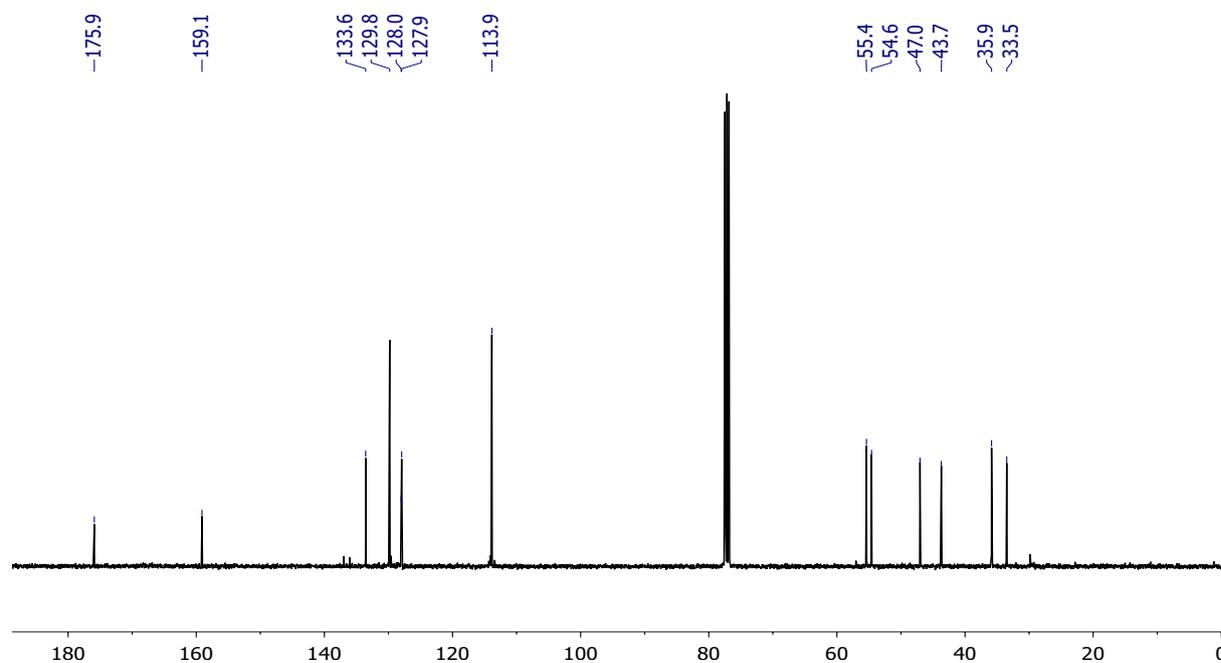
**(1*R*\*,2*S*\*,6*S*\*)-2-Hydroxy-3-phenethyl-3-azabicyclo[4.2.0]oct-7-en-4-one (16c)**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz)

**(2a*R*\*,2a<sup>1</sup>*R*\*,2b*R*\*,4a*S*\*)-2-(4-Methoxybenzyl)-2a,2a<sup>1</sup>,2b,4a-tetrahydro-2-azacyclopropa[cd]pentalen-1(2*H*)-one (10d)**

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 400 MHz)

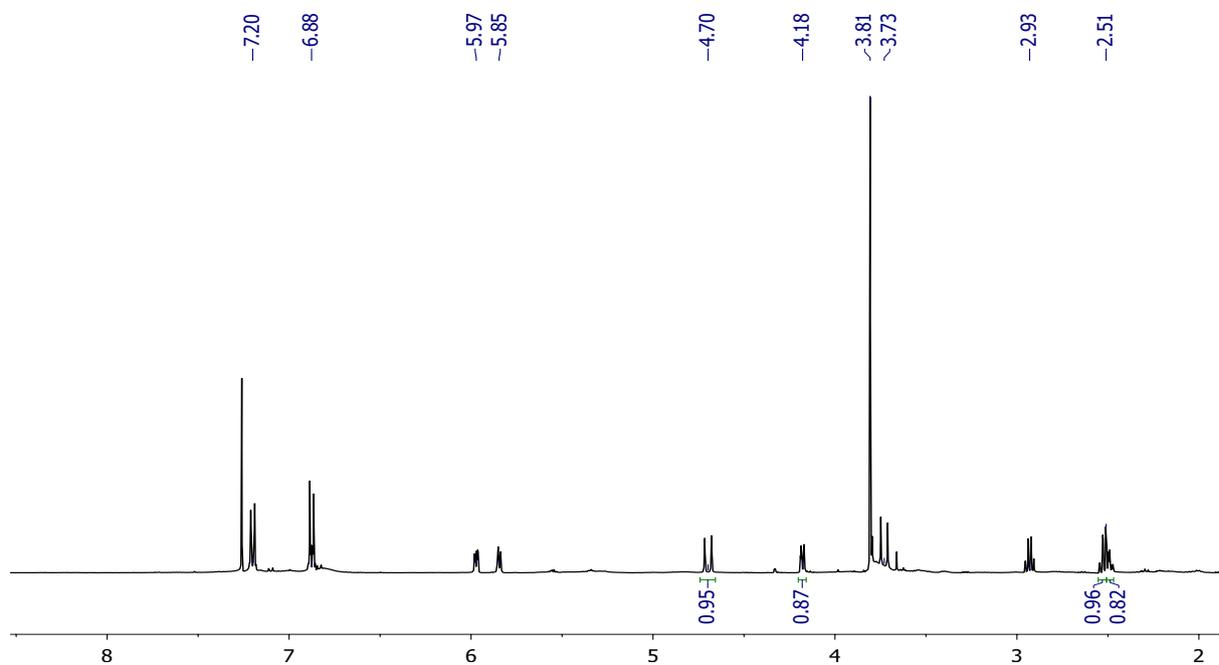


<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 101 MHz)

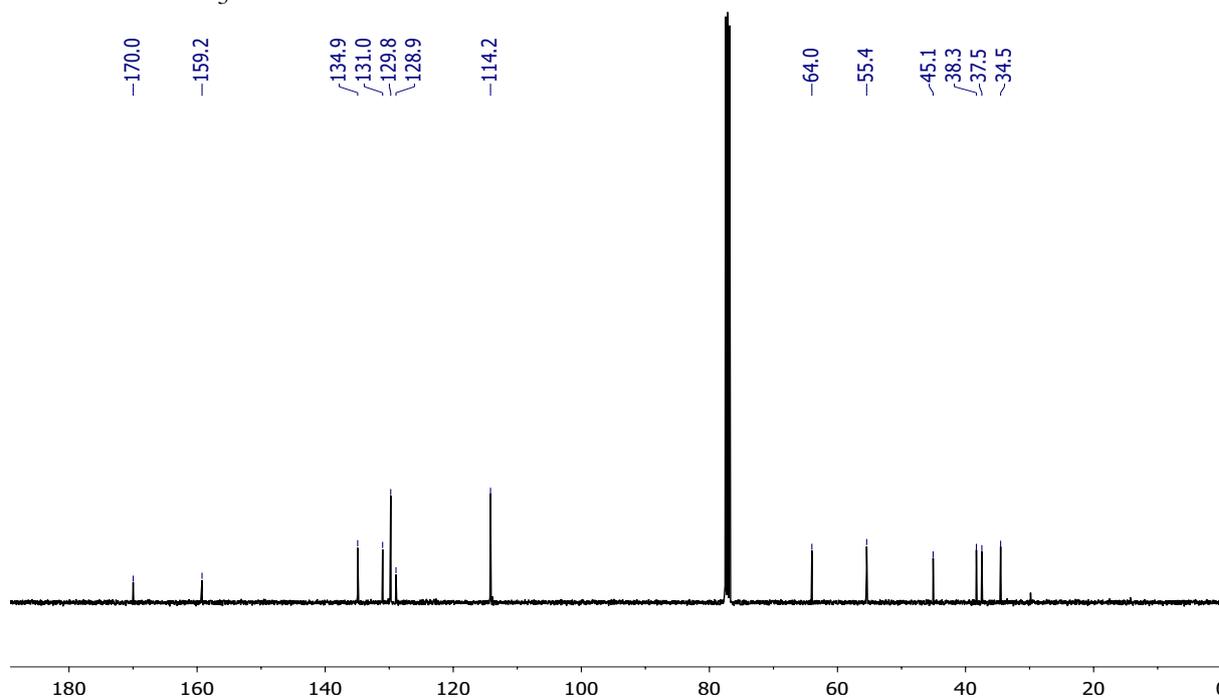


**(2a*R*\*,2a<sup>1</sup>*S*\*,2b*R*\*,4a*S*\*)-1-(4-Methoxybenzyl)-2a,2a<sup>1</sup>,2b,4a-tetrahydro-1-azacyclopropa[cd]pentalen-2(1*H*)-one (11d)**

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 400 MHz)

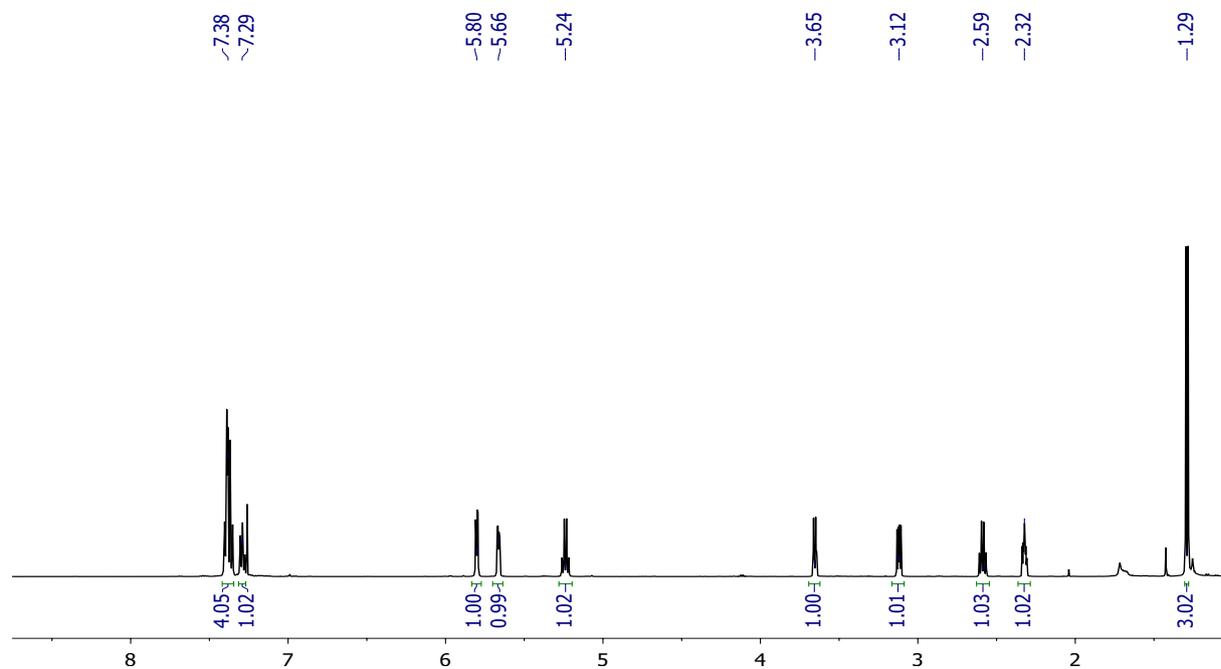


<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 101 MHz)

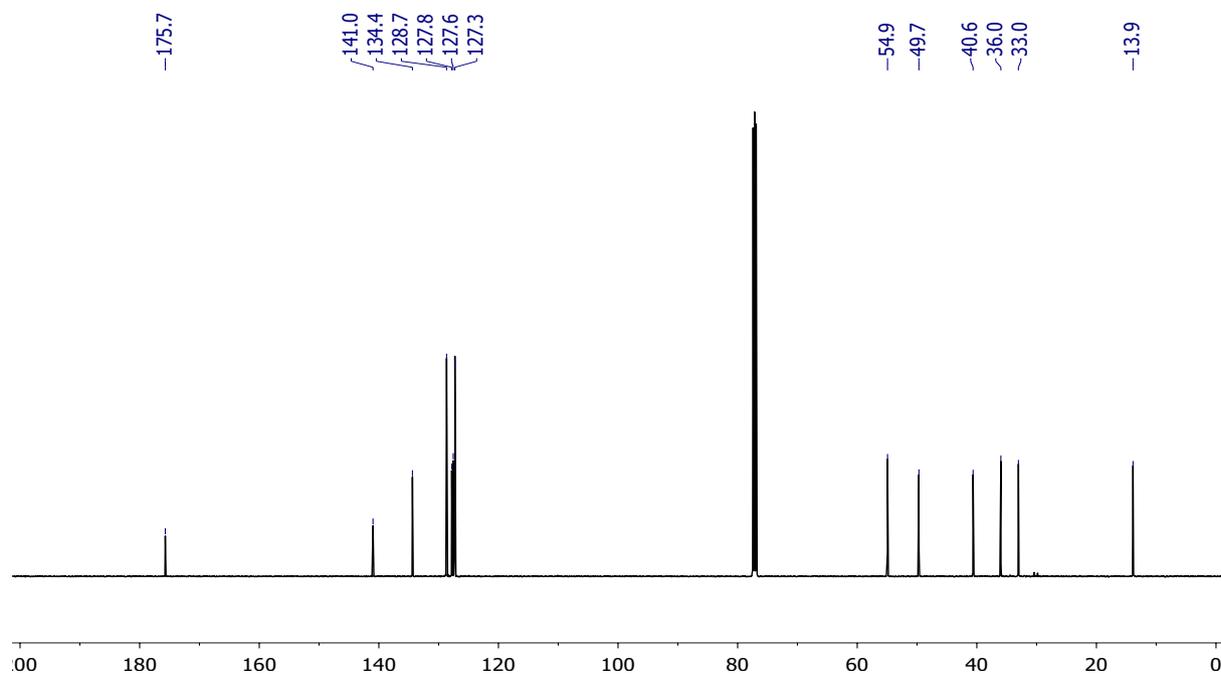


(2a*R*<sup>\*</sup>,2a<sup>1</sup>*R*<sup>\*</sup>,2b*R*<sup>\*</sup>,4a*S*<sup>\*</sup>)-2-[(*S*)-1-Phenylethyl]-2a,2a<sup>1</sup>,2b,4a-tetrahydro-2-azacyclopropa[*cd*]pentalen-1(2*H*)-one (10e)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)

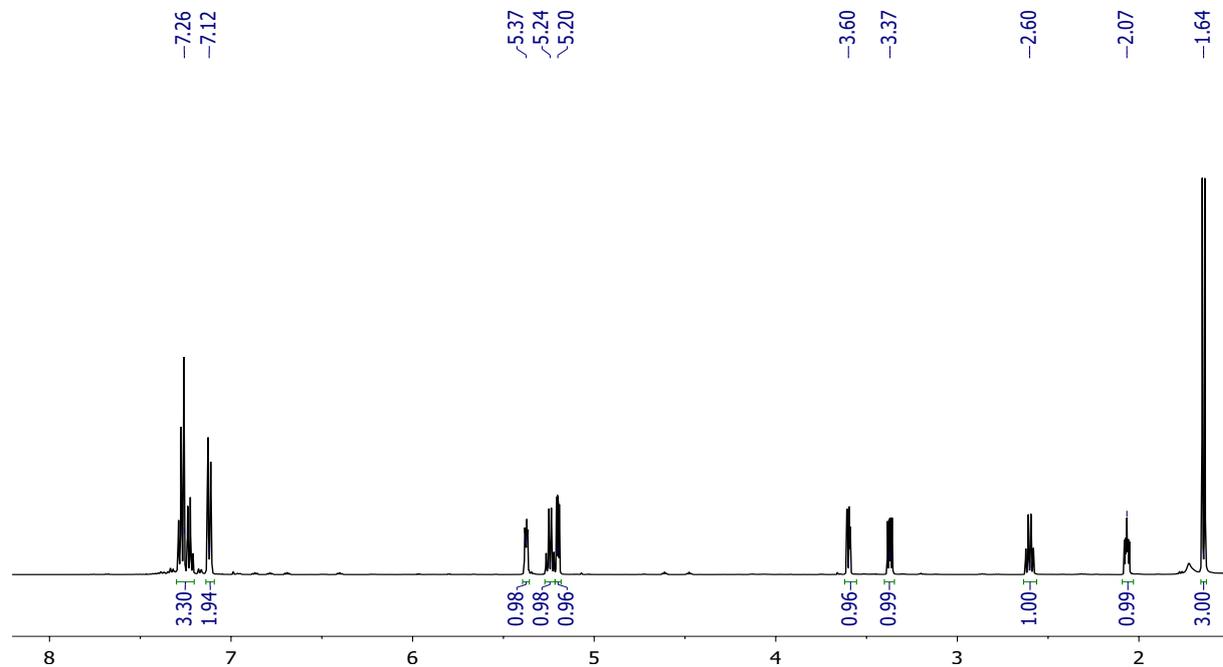


<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz)

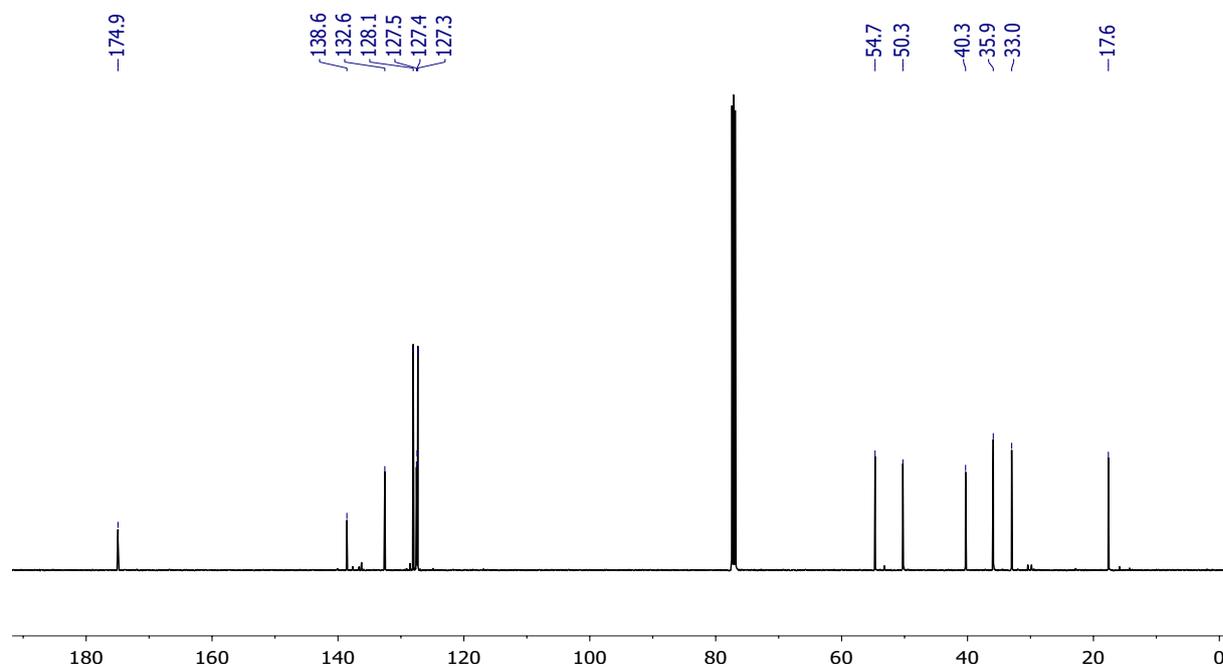


(2a*S*\*,2a<sup>1</sup>*S*\*,2b*S*\*,4a*R*\*)-2-[(*S*)-1-Phenylethyl]-2a,2a<sup>1</sup>,2b,4a-tetrahydro-2-azacyclopropa[cd]pentalen-1(2*H*)-one (10e')

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)

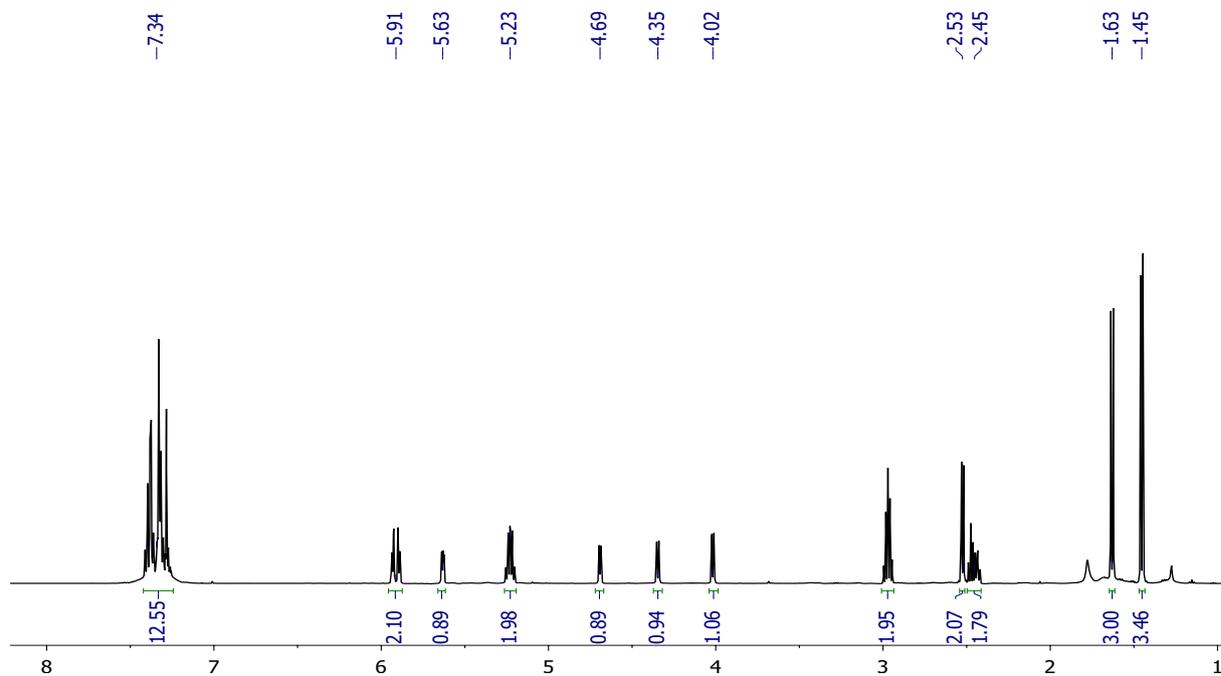


<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz)



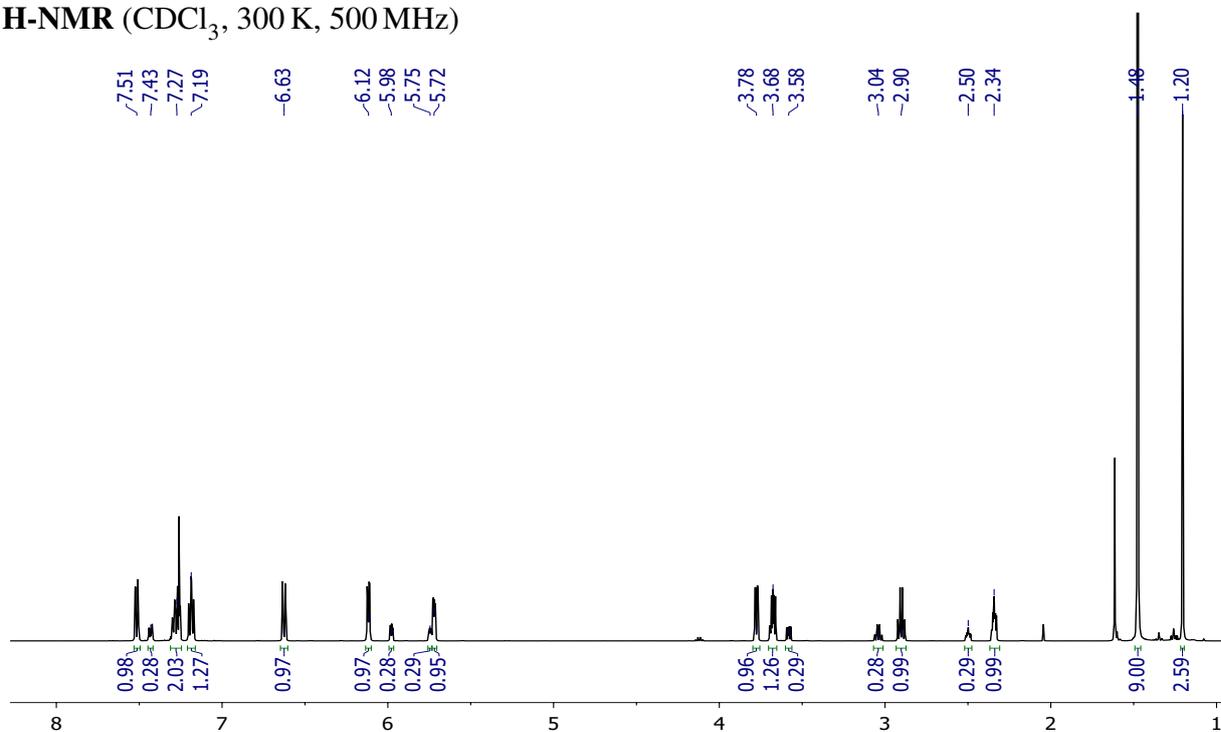
**(2aR\*,2a<sup>1</sup>S\*,2bR\*,4aS\*)-1-[(S)-1-phenylethyl]-2a,2a<sup>1</sup>,2b,4a-tetrahydro-1-azacyclopropa[cd]pentalen-2(1H)-one (11e, 11e')**

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)

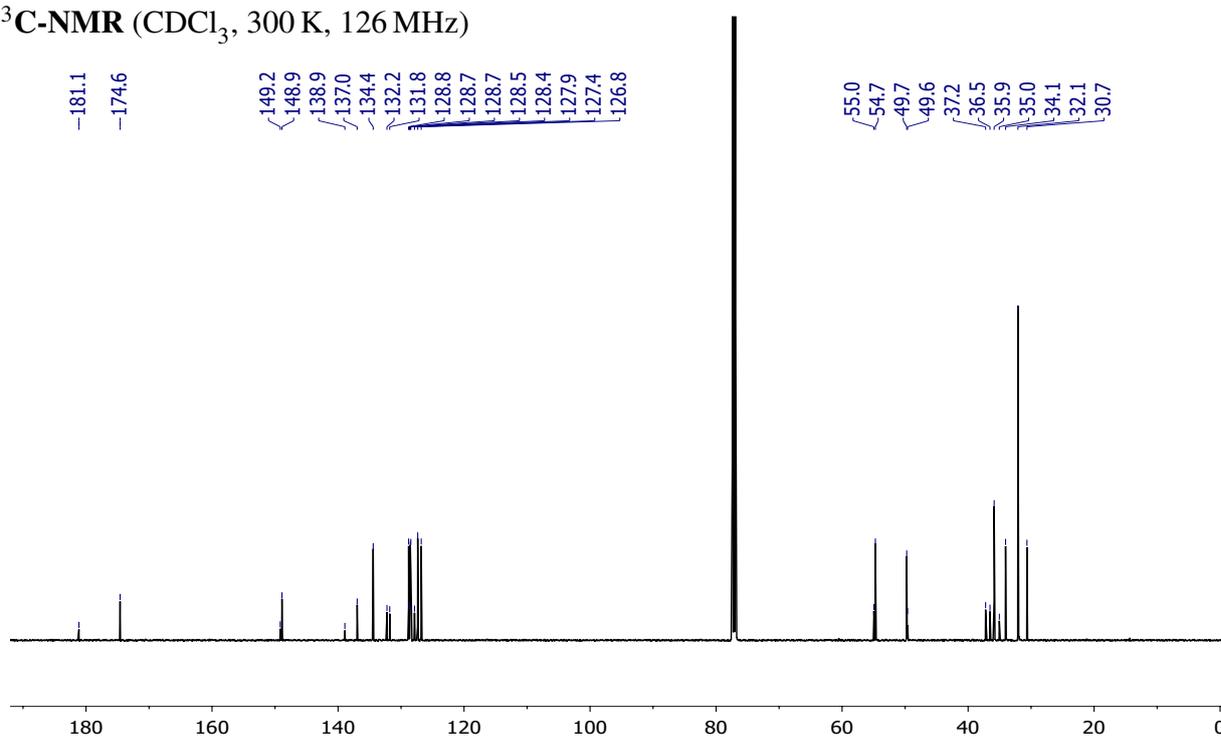


**(2aR\*,2a<sup>1</sup>R\*,2bR\*,4aS\*)-2-[(S<sub>a</sub>)-2-(tert-Butyl)phenyl]-2a,2a<sup>1</sup>,2b,4a-tetrahydro-2-azacyclopropa[cd]pentalen-1(2H)-one (S<sub>a</sub>-10f) and**  
**(2aR\*,2a<sup>1</sup>R\*,2bR\*,4aS\*)-2-[(R<sub>a</sub>)-2-(tert-Butyl)phenyl]-2a,2a<sup>1</sup>,2b,4a-tetrahydro-2-azacyclopropa[cd]pentalen-1(2H)-one (R<sub>a</sub>-10f)**

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)

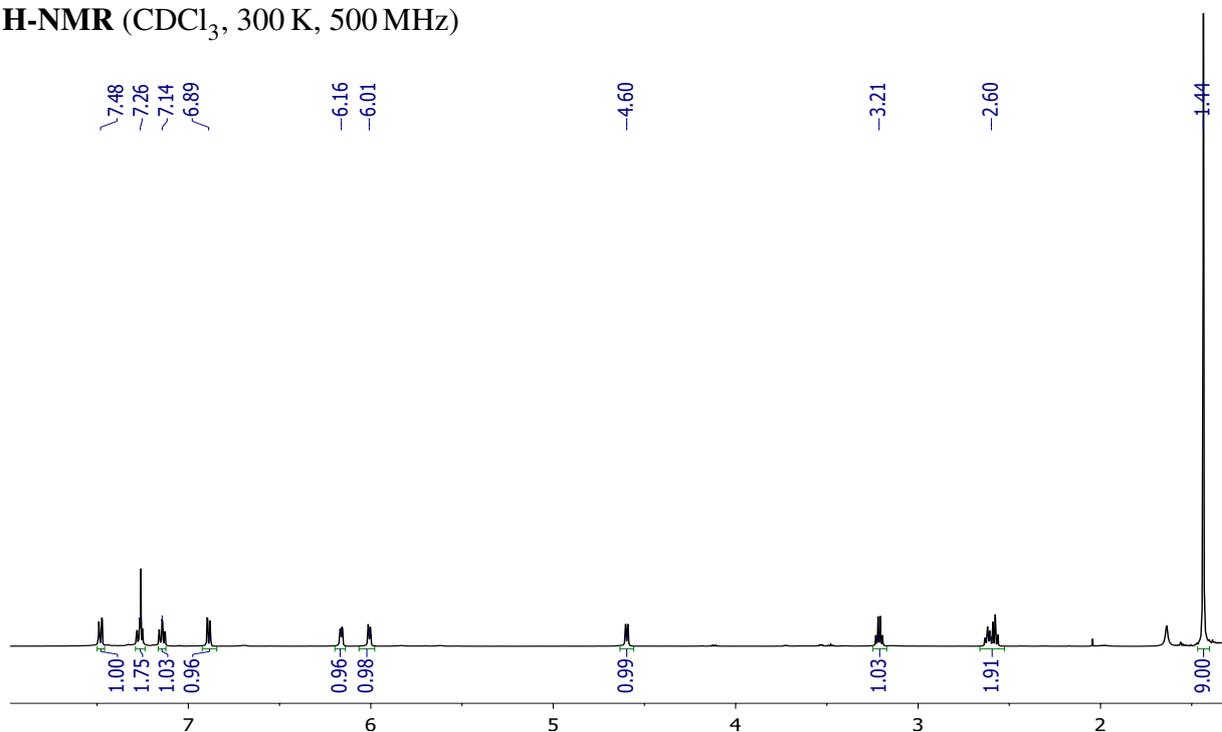


<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz)

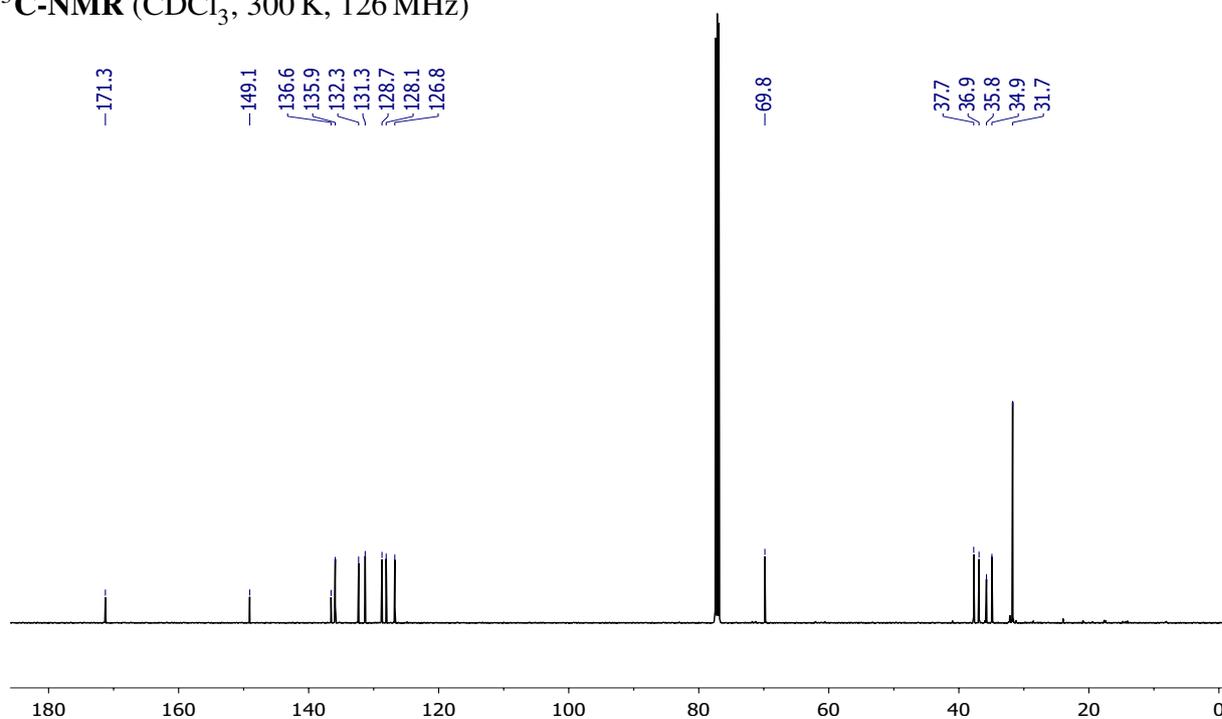


**(2a*R*<sup>\*</sup>,2a<sup>1</sup>*S*<sup>\*</sup>,2b*R*<sup>\*</sup>,4a*S*<sup>\*</sup>)-1-[(*R*<sub>a</sub>)-2-(*tert*-Butyl)phenyl]-2a,2a<sup>1</sup>,2b,4a-tetrahydro-1-azacyclopropa[cd]pentalen-2(1*H*)-one (*R*<sub>a</sub>-11f)**

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K, 500 MHz)



<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 K, 126 MHz)



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