Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Evidence for Triplet Sensitization in the Visible-Light-Induced [2+2] Photocycloaddition of Eniminium Ions

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1. General Information

All reactions sensitive to air and moisture were carried out in flame-dried glassware under an argon atmosphere using standard Schlenk techniques.

Commercially available chemicals were used without further purification unless otherwise mentioned.

For moisture sensitive reactions tetrahydrofuran (THF), diethyl ether (Et_2O) and dichloromethane (CH_2Cl_2) were dried using a MBSPS 800 *MBraun* solvent purification system. The following columns were used:

THF: 2 × MB-KOL-M type 2 (3 Å molecular sieve)

Et_2O: 1 × MB-KOL-A type 2 (aluminium oxide), 1 × MB-KOL-M type 2 (3 Å molecular sieve)

CH_2Cl_2: 2 × MB-KOL-A type 2 (aluminium oxide)

The following dry solvents are commercially available and were used without further purification:

Acetonitrile: *Acros Organics*, 99.9% extra dry, over molecular sieves.

Ethanol: *Sigma-Aldrich*, puriss., 99.8% (stored over molecular sieves).

Toluene: *Acros Organics*, 99.8% extra dry, over molecular sieves.

For photochemical reactions, dry acetonitrile was used and degassed either by three freeze-pump-thaw cycles or by purging with argon in an ultrasonicating bath for 15 minutes prior to irradiation.

2,3-Dimethylbutadiene (*Alfa-Aesar*), isoprene (*Sigma-Aldrich*), 2-methylhex-1-en-3-yne (*Sigma-Aldrich*) and (3-methylbut-3-en-1-ynyl)-trimethylsilane (*Alfa-Aesar*) are commercially available and were distilled and degassed by three freeze-pump-thaw cycles prior to use. 1,3-Butadiene (2 M in THF, *TCI Europe*) was dried over 3 Å molecular sieves prior to use. Cinnamaldehyde (*Sigma-Aldrich*) was distilled prior to use. 3-Ethoxycyclohex-2-en-1-one (*Sigma-Aldrich*), 5,5-dimethyl-3-ethoxycyclohex-2-en-1-one (*Sigma-Aldrich*) and (*S*)-bis(3,5-bis(trifluoromethyl)phenyl)(pyrrolidin-2-yl)methanol (*Sigma-Aldrich*) are commercially available. 5-Bromo-2-methylpent-1-ene was prepared according to a literature known procedure.[1]

Technical solvents for column chromatography (pentane, diethyl ether, ethylacetate) were used after simple distillation.

Flash column chromatography was performed on silica 60 (*Merck*, 230-400 mesh) with the indicated eluent mixture.

Photochemical experiments using a LED were carried out in a Schlenk tube (diameter = 1 cm) with a polished quartz rod as an optical fiber, which was roughened by sandblasting at one end. The roughed end has to be completely submerged in the solvent during the reaction, in order to guarantee optimal and reproducible irradiation conditions.[2] Photochemical experiments at 366 nm and 420 nm were performed in Duran tubes (diameter = 1 cm) in an RPR-100 photochemical reactor (*Southern New England Ultra Violet Company*, Branford, CT, USA) equipped with 16 fluorescence lamps (λ = 420 nm: Luzchem LZC-420, 8 W; λ = 366 nm: Philips Lighting, Black Light Blue, 8 W).[3]

2. Analytical Methods

Thin Layer Chromatography (TLC) was performed on silica coated glass plates (*Merck*, silica 60 F254) with detection by UV-light (λ = 254 nm) and/or by staining with a potassium permanganate solution [$KMnO_4$] followed by heat treatment.

> $KMnO_4$-staining solution: 3.00 g potassium permanganate, 20.0 g potassium carbonate and 5.00 mL 5% sodium hydroxide solution in 300 mL water.

Infrared Spectra (IR) were recorded on a *Perkin Elmer* Frontier IR-FTR spectrometer by ATR technique. The signal intensity is assigned using the following abbreviations: s (strong), m (medium), w (weak).

Nuclear Magnetic Resonance-Spectra were recorded at room temperature either on a *Bruker* AVHD-300, AVHD-400, AVHD-500 or an AV-500 cryo. ^{1}H-NMR spectra were calibrated to the residual solvent signal of chloroform-d_1 (δ = 7.26 ppm) or acetonitrile-d_3 (δ = 1.94 ppm). ^{13}C-NMR spectra were calibrated to the ^{13}C-D triplet of $CDCl_3$ (δ = 77.16 ppm) or CD_3CN (δ = 118.26 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.*). Following abbreviations for single multiplicities were used: *br*.-broad, s-singlet, d-doublet, t-triplet, q-quartet, quint-quintet, sept-septet. Assignment and multiplicity of the ^{13}C-NMR signals were determined by two dimensional NMR experiments (COSY, HSQC, HMBC, NOESY). Protons oriented above the molecular plane are labeled as α and those oriented below as β.

Melting Points were determined using a Büchi M-565 melting point apparatus, with range quoted to the nearest whole number.

Mass Spectroscopy (MS) and High Resolution Mass Spectroscopy (HR-MS) was performed on a *Thermo Scientific* LTQ-FT Ultra (ESI) or a *Thermo Scientific* DFS-HRMS spectrometer (EI).

UV/Vis Spectroscopy was performed on a *Perkin Elmer* Lambda 35 UV/Vis spectrometer. Spectra were recorded using a *Hellma* precision cell made of quartz SUPRASIL® with a pathway of 1 mm. Solvents and concentrations are given for each spectrum.

Chiral Gas Chromatography (GC) was performed on an *Agilent* 7890 B gas chromatograph using a Cyclosil-B column (30 m, 0.25 mm, 0.25 µm) with a flame ionization detector. The temperature method is given for the corresponding compounds.

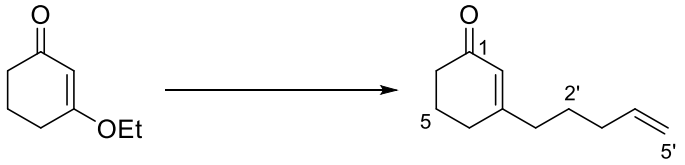
Electrochemical Measurements were performed on EmStat^{3+} potentiostat using a three-electrode cell equipped with glassy carbon working electrode, a platinum wire counter electrode and a $Ag/AgNO_3$ reference electrode.

Specific Rotation was determined using a Bellingham+Stanley ADP440+ polarimeter and is reported as follows: $[\alpha]_D^T$ (c in g per 100 mL solvent).

Luminescence Measurements were performed on Horiba Scientific FluoroMax-4 instrument (part number J810005 rev. C) using a SUPRASIL® quartz cuvette with a 1 mm light path to record emission spectra. Luminescent lifetimes were performed using a PL2250 Series laser from *Ekspla* equipped with a LeCroy waverunner 6030 oscilloscope 2.5 GS (4 ns in between two points) and H7732-10 Hamamatsu PMT (approximately 50 ns). All lifetime runs were averaged from 100 scans and all samples were purged with argon for 15 minutes to ensure no oxygen was present.

3. Synthetic Procedures and Analytical Data

3-(Pent-4-en-1-yl)cyclohex-2-en-1-one (1)



$C_{11}H_{16}O$
MW = 164.25 g/mol

To a suspension of 338 mg magnesium (13.3 mmol, 1.30 eq.) and catalytic amounts of iodine in 7 mL dry THF were added 1.27 mL 5-bromopent-1-ene (1.60 g, 10.7 mmol, 1.00 eq.) dropwise and stirred for 30 minutes at 40 °C. After cooling to room temperature a solution of 1.56 mL 3-ethoxycyclohex-2-en-1-one (1.50 g, 10.7 mmol, 1.00 eq.) in 5 mL dry THF was added dropwise and stirred for 1 hour at room temperature. After addition of 50 mL water, conc. HCl was added dropwise until the formed precipitate dissolved and the mixture was extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and the solvent was removed in vacuo. After column chromatography (silica, P/Et_2O = 4/1), 1.38 g enone **1** (8.40 mmol, 79%) were obtained as a colorless oil.

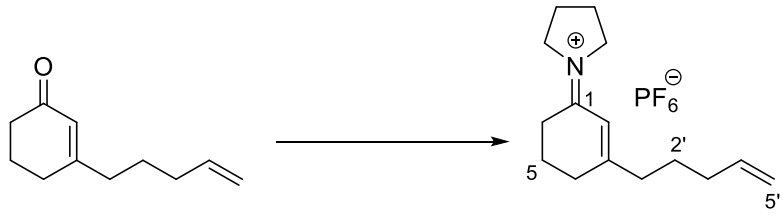
TLC: R_f = 0.29 (P/Et_2O = 4/1) [UV, $KMnO_4$].

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.61 (*virt*. quint, $^3J \approx {}^3J$ = 7.5 Hz, 2 H, C-2'-H_2), 1.99 (*virt*. quint, $^3J \approx {}^3J$ = 6.2 Hz, 2 H, C-5-H_2), 2.08 (*virt*. q, $^3J \approx {}^3J$ = 7.1 Hz, 2 H, C-3'-H_2), 2.22 (t, ^3J = 7.7 Hz, 2 H, C-1'-H_2), 2.28 (t, ^3J = 6.0 Hz, 2 H, C-4-H_2), 2.36 (t, ^3J = 6.7 Hz, 2 H, C-6-H_2), 4.97 - 5.05 (m, 2 H, C-5'-H_2), 5.78 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 1 H, C-4'-H), 5.88 (s, 1 H, C-2-H).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 22.9 (t, C-5-H_2), 26.2 (t, C-2'-H_2), 29.9 (t, C-4-H_2), 33.3 (t, C-3'-H_2), 37.5 (t, C-6-H_2), 37.5 (t, C-1'-H_2), 115.4 (t, C-5'-H_2), 126.0 (d, C-2-H), 138.0 (d, C-4'-H), 166.3 (s, C-3), 200.0 (s, C-1).

The analytical data obtained matched those reported in the literature.[3,4]

1-[3-(Pent-4-en-1-yl)cyclohex-2-en-1-ylidene]pyrrolidin-1-ium hexafluorophosphate (2)



$C_{15}H_{24}F_6NP$
MW = 363.33 g/mol

To a solution of 500 mg enone **1** (3.04 mmol, 1.00 eq.) and 250 µL pyrrolidine (216 mg, 3.04 mmol, 1.00 eq.) in 7.6 mL dry toluene were added 496 mg ammonium hexafluorophosphate (3.04 mmol, 1.00 eq.). The suspension was refluxed for 3 hours with continuous removal of the water formed (*Dean-Stark*). The mixture was cooled to 0 °C and the formed precipitate was collected by filtration and washed with dry diethyl ether. After recrystallization (EtOH) 629 mg iminium ion **2** (1.73 mmol, 57%) were obtained as a colorless solid.

M.p.: 95 ºC.

IR (ATR): $\tilde{\nu}$ = 2946 cm^{-1} (w, $C_{sp3}H$), 2884 (w, $C_{sp3}H$), 1625 (s, C=N), 1447 (m, $C_{sp3}H$), 1403 (m), 1383 (w), 820 (s), 756 (m).

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.66 (*virt.* quint, $^3J \approx {}^3J$ = 7.4 Hz, 2 H, C-2'-H_2), 2.01 (*virt.* quint, $^3J \approx {}^3J$ = 6.4 Hz, 2 H, C-5-H_2), 2.12 (*virt.* q, $^3J \approx {}^3J$ = 7.1 Hz, 2 H, C-3'-H_2), 2.17 - 2.21 (m, 4 H, NCH_2CH_2), 2.40 - 2.47 (m, 4 H, C-4-H_2, C-1'-H_2), 2.80 (t, ^3J = 6.6 Hz, 2 H, C-6-H_2), 3.89 - 3.93 (m, 4 H, NCH_2CH_2), 5.00 - 5.08 (m, 2 H, C-5'-H_2), 5.77 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 1 H, C-4'-H), 6.33 (s, 1 H, C-2-H).

^{13}C-NMR (76 MHz, $CDCl_3$, 298 K): δ (ppm) = 20.7 (t, C-5-H_2), 24.4 (t, NCH_2CH_2), 24.4 (t, NCH_2CH_2), 26.3 (t, C-2'-H_2), 29.7 (t, C-4-H_2)*, 29.8 (t, C-6-H_2)*, 33.2 (t, C-3'-H_2), 39.3 (t, C-1'-H_2), 52.4 (t, NCH_2CH_2), 52.8 (t, NCH_2CH_2), 116.0 (t, C-5'-H_2), 117.2 (d, C-2-H), 137.5 (d, C-4'-H), 173.4 (s, C-1), 177.9 (s, C-3).

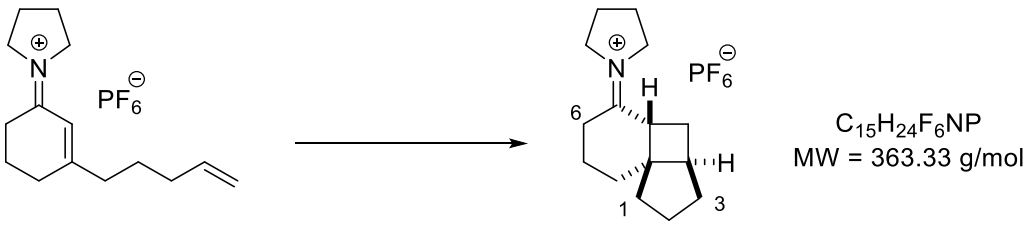
^{19}F-NMR (377 MHz, $CDCl_3$, 300 K): δ (ppm) = –73.8 (d, ^1J = 713 Hz, PF_6).

^{31}P-NMR (162 MHz, $CDCl_3$, 300 K): δ (ppm) = –144.7 (sept, ^1J = 713 Hz, PF_6).

* assignment is interconvertible.

HRMS (ESI): calc. $[M–PF_6]^+$: 218.1903; found: 218.1902.

1-(Octahydrocyclopenta[1,4]cyclobuta[1,2]benzen-5(6*H*)-ylidene)pyrrolidin-1-ium hexafluorophosphate (*rac*-3)



To a solution of 36.3 mg iminium ion **2** (100 µmol, 1.00 eq.) in 5 mL acetonitrile were added 2.50 mg **6** (2.50 µmol, 2.5 mol%.) and the solution was degassed for 15 minutes by purging with argon in an ultrasonicating bath. After irradiation (λ = 420 nm) at room temperature for 2 hours, the solvent was removed under reduced pressure. After recrystallization [EtOH/MeCN = 20/1 (V/V)], 27.2 mg iminium ion *rac*-**3** (74.9 µmol, 75%) were obtained as a colorless solid.

M.p.: 215 °C.

IR (ATR): $\tilde{\nu}$ = 2938 cm^{-1} (w, $C_{sp3}H$), 2858 (w, $C_{sp3}H$), 1648 (m, C=N), 1445 (m, $C_{sp3}H$), 1369 (w), 877 (w), 822 (s).

^{1}H-NMR (500 MHz, CD_3CN, 298 K): δ (ppm) = 1.37 (*virt.* td, $^{2}J \approx {}^{3}J$ = 12.8 Hz, ^{3}J = 6.5 Hz, 1 H, C-1-*H*H), 1.48 (ddd, ^{2}J = 13.7 Hz, ^{3}J = 11.1 Hz, ^{3}J = 5.2 Hz, 1 H, C-8-*H*H), 1.57 - 1.70 (m, 4 H, C-1-H*H*, C-6-*H*H, C-7-*H*H, C-8-H*H*), 1.86 (*virt.* dt, ^{2}J = 12.8 Hz, $^{3}J \approx {}^{3}J$ = 6.4 Hz, 1 H, C-2-*H*H), 1.91 - 2.18 (m, 9 H, 2 × NCH_2CH_2, C-2-H*H*, C-3-H_2, C-4-H_2), 2.42 - 2.53 (m, 2 H, C-3a-H, C-7-H*H*), 2.84 - 2.91 (m, 1 H, C-6-H*H*), 2.99 (t, ^{3}J = 9.3 Hz, 1 H, C-4a-H), 3.49 - 3.56 (m, 1 H, NCH_2CH_2), 3.63 - 3.80 (m, 3 H, NCH_2CH_2).

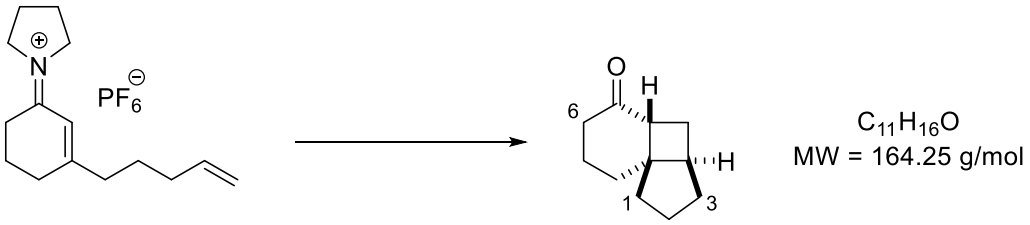
^{13}C-NMR (101 MHz, CD_3CN, 300 K): δ (ppm) = 19.6 (t, C-3-H_2), 24.8 (t, NCH_2CH_2), 24.9 (t, NCH_2CH_2), 25.4 (t, C-2-H_2), 26.8 (t, C-4-H_2), 31.8 (t, C-8-H_2), 33.2 (t, C-6-H_2), 33.7 (t, C-7-H_2), 39.4 (d, C-3a-H), 40.6 (t, C-1-H_2), 41.5 (d, C-4a-H), 48.7 (s, C-8a), 54.0 (t, NCH_2CH_2), 54.2 (t, NCH_2CH_2), 191.3 (s, C-5).

^{19}F-NMR (471 MHz, CD_3CN, 300 K) δ (ppm) = –73.4 (d, ^{1}J = 713 Hz, PF_6).

^{31}P-NMR (203 MHz, CD_3CN, 300 K) δ (ppm) = –144.7 (sept, ^{1}J = 713 Hz, PF_6).

HRMS (ESI): calc. $[M–PF_6]^+$: 218.1903; found: 218.1902.

Octahydrocyclopenta[1,4]cyclobuta[1,2]benzen-5(6*H*)-one (*rac*-4)



To a solution of 18.1 mg iminium ion **2** (49.8 µmol, 1.00 eq.) in 2.5 mL dry acetonitrile were added 865 µg **5** (1.25 µmol, 2.5 mol%) and the solution was degassed for 15 minutes by purging with argon in an ultrasonicating bath. After irradiation (λ = 433 nm) at room temperature for 2 hours, 3 M NaOH solution was added and the mixture was extracted with ethylacetate. The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. After column chromatography (silica, P/Et_2O = 10/1) 6.00 mg ketone *rac*-**4** (36.5 µmol, 73%) were obtained as a colourless oil.

TLC: R_f = 0.11 (P/Et_2O = 10/1) [$KMnO_4$].

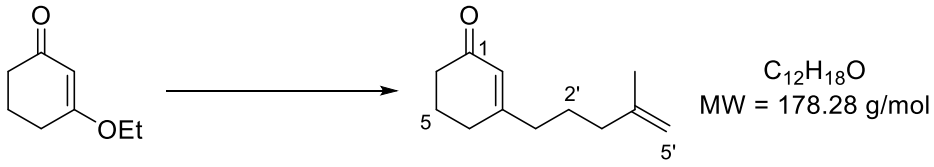
^{1}H-NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.34 (*virt.* td, $^2J \approx {}^3J$ = 12.5 Hz, ^3J = 6.9 Hz, 1 H, C-1-*H*H), 1.48 - 1.67 (m, 5 H, C-1-H*H*, C-3-H_2, C-8-H_2), 1.76 - 1.94 (m 3 H, C-2-H_2, C-4-*H*H), 1.94 - 2.10 (m, 3 H, C-4-H*H*, C-7-H_2), 2.11 - 2.23 (m, 1 H, C-6-*H*H), 2.40 (dt, ^3J = 10.1 Hz, ^3J = 5.9 Hz, 1 H, C-3a-H), 2.48 (dd, ^3J = 11.3 Hz, ^3J = 7.0 Hz, 1 H, C-4a-H), 2.57 (dt, ^2J = 17.5 Hz, ^3J = 3.6 Hz, 1 H, C-6-H*H*).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 21.3 (t, C-7-H_2), 25.1 (t, C-2-H_2), 26.9 (t, C-4-H_2), 32.9 (t, C-3-H_2)*, 33.1 (t, C-8-H_2)*, 39.6 (d, C-3a-H), 39.6 (t, C-6-H_2), 40.5 (t, C-1-H_2), 47.3 (d, C-4a-H), 50.1 (s, C-8a), 215.6 (s, C-5).

* assignment is interconvertible.

The analytical data obtained matched those reported in the literature.[3,5]

3-(4-Methylpent-4-en-1-yl)cyclohex-2-en-1-one (S1)



To a suspension of 338 mg magnesium (13.3 mmol, 1.30 eq.) and catalytic amounts of iodine in 7 mL dry THF were added 1.27 mL 5-bromo-2-methylpent-1-ene (1.74 g, 10.7 mmol, 1.00 eq.) dropwise and stirred for 30 minutes at 40 °C. After cooling to room temperature a solution of 1.56 mL 3-ethoxycyclohex-2-en-1-one (1.50 g, 10.7 mmol, 1.00 eq.) in 5 mL dry THF was added dropwise and stirred for 1 hour at room temperature. After addition of 50 mL water, conc. HCl was added dropwise until the formed precipitate dissolved and the mixture was extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and the solvent was removed in vacuo. After column chromatography (silica, P/Et_2O = 4/1), 1.90 g enone **S1** (7.81 mmol, 73%) were obtained as a colorless oil.

TLC: R_f = 0.39 (P/Et_2O = 1/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ = 3074 cm^{-1} (w, $C_{sp2}H$), 2936 (m, $C_{sp3}H$), 2868 (w, $C_{sp3}H$), 1666 (s, C=O), 1624 (s, C=C), 885 (s, C=C).

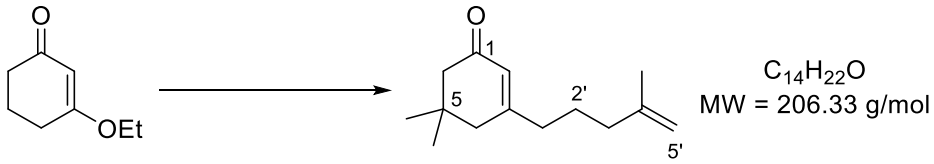
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.60 - 1.69 (m, 2 H, C-2'-H_2), 1.71 (t, ^4J = 1.1 Hz, 3 H, C-4'-CH_3), 1.96 - 2.02 (m, 4 H, C-5-H_2, C-3'-H_2), 2.18 - 2.23 (m, 2 H, C-1'-H_2), 2.26 - 2.31 (m, 2 H, C-4-H_2), 2.34 - 2.39 (m, 2 H, C-6-H_2), 4.68 (dq, ^2J = 2.2 Hz, ^4J = 1.0 Hz, 1 H, C-5'-*H*H), 4.73 - 4.75 (m, 1 H, C-5'-H*H*), 5.89 (*virt.* quint, $^4J \approx {}^4J$ = 1.4 Hz, 1 H, C-2-H).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 22.4 (q, C-4'-CH_3), 22.9 (t, C-5-H_2), 24.8 (t, C-2'-H_2), 29.9 (t, C-4-H_2), 37.3 (t, C-3'-H_2), 37.5 (t, C-6-H_2), 37.6 (t, C-1'-H_2), 110.7 (t, C-5'-H_2), 125.9 (d, C-2-H), 145.1 (s, C-4'), 166.5 (s, C-3), 200.1 (s, C-1).

MS (EI, 70 eV): *m*/*z* (%) = 178 (5) $[M]^+$, 163 (16) $[M–CH_3]^+$, 141 (23), 135 (29), 123 (100) $[M–C_4H_7]^+$, 110 (38) $[C_7H_{10}O]^+$, 94 (68) $[C_6H_6O]^+$, 82 (99) $[C_6H_{10}]^+$, 67 (40), 41 (37).

HRMS (EI, 70 eV): calc. ($C_{12}H_{18}O$): 178.1352; found: 178.1355.

5,5-Dimethyl-3-(pent-4-en-1-yl)-cyclohex-2-en-1-one (S2)



To a suspension of 338 mg magnesium (13.3 mmol, 1.30 eq.) and catalytic amounts of iodine in 7 mL dry THF were added 1.27 mL 5-bromo-2-methylpent-1-ene (1.80 g, 10.7 mmol, 1.00 eq.) dropwise and stirred for 30 minutes at 40 °C. After cooling to room temperature a solution of 1.56 mL 5,5-dimethyl-3-ethoxycyclohex-2-en-1-one (1.50 g, 10.7 mmol, 1.00 eq.) in 5 mL dry THF was added dropwise and stirred for 1 hour at room temperature. After addition of 50 mL water, conc. HCl was added dropwise until the formed precipitate dissolved and the mixture was extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and the solvent was removed in vacuo. After column chromatography (silica, P/Et_2O = 4/1), 860 mg enone **S2** (4.17 mmol, 39%) were obtained as a colorless oil.

TLC: R_f = 0.39 (P/Et_2O = 1/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ = 3074 cm^{-1} (w, $C_{sp2}H$), 2938 (m, $C_{sp3}H$), 2869 (w, $C_{sp3}H$), 1666 (s, C=O), 1628 (s, C=C), 886 (s, C=C).

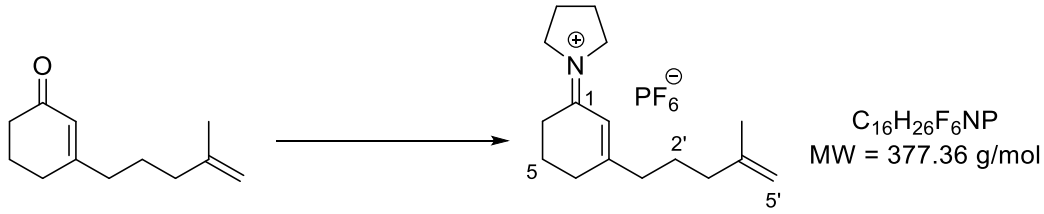
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.03 [s, 6 H, C-5-$(CH_3)_2$], 1.64 (*virt.* quint, $^3J \approx {}^3J$ = 7.8 Hz, 2 H, C-2'-H_2), 1.71 (s, 3 H, C-4'-CH_3), 2.03 (t, ^3J = 7.6 Hz, 2 H, C-3'-H_2), 2.15 - 2.19 (m, 4 H, C-4-H_2, C-1'-H_2), 2.21 (s, 2 H, C-6-H_2), 4.67 - 4.68 (m, 1 H, C-5'-*H*H), 4.73 - 4.74 (m, 1 H, C-5'-H*H*), 5.89 (*virt.* quint, $^4J \approx {}^4J$ = 1.4 Hz, 1 H, C-2-H).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 22.4 (q, C-4'-CH_3), 24.8 (t, C-2'-H_2), 28.4 (q, 2 × C-5-CH_3), 33.8 (s, C-5), 37.3 (t, C-3'-H_2), 37.6 (t, C-1'-H_2), 44.1 (t, C-4-H_2), 51.2 (t, C-6-H_2), 110.7 (t, C-5'-H_2), 124.9 (d, C-2-H), 145.1 (s, C-4'), 164.1 (s, C-3), 200.3 (s, C-1).

MS (EI, 70 eV): *m*/*z* (%) = 206 (30) $[M]^+$, 191 (26) $[M–CH_3]^+$, 163 (30), 151 (73), 138 (38), 107 (36), 94 (90) $[C_6H_6O]^+$, 82 (100) $[C_6H_{10}]^+$, 67 (19), 41 (25).

HRMS (EI, 70 eV): calc. ($C_{14}H_{22}O$): 206.1665; found: 206.1651.
calc. ($C_{13}{}^{13}CH_{22}O$): 207.1699; found: 207.1689.

1-[3-(4-Methylpent-4-en-1-yl)cyclohex-2-en-1-ylidene]pyrrolidin-1-ium hexafluorophosphate (8a)



To a solution of 164 mg enone **S1** (920 µmol, 1.00 eq.) and 75.0 µL pyrrolidine (65.0 mg, 920 µmol, 1.00 eq.) in 2 mL dry toluene were added 150 mg ammonium hexafluorophosphate (920 µmol, 1.00 eq.). The suspension was refluxed for 3 hours with continuous removal of the water formed (*Dean-Stark*). The solvent was evaporated under reduced pressure to afford a yellow solid. After washing the solid with cold ethanol, 164 mg iminium ion **8a** (435 µmol, 47%) were obtained as a white solid.

M.p.: 59 °C.

IR (ATR): $\tilde{\nu}$ = 2943 cm^{-1} (w, $C_{sp3}H$), 1623 (s, C=N), 1446 (w, $C_{sp3}H$), 1400 (w), 1350 (w), 824 (s).

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.66 - 1.73 (m, 2 H, C-2'-H_2), 1.72 (dd, ^{4}J = 1.3 Hz, ^{4}J = 0.9 Hz, 3 H, C-4'-CH_3), 2.00 (*virt.* quint, $^{3}J \approx {}^{3}J$ = 6.4 Hz, 2 H, C-5-H_2), 2.06 (t, ^{3}J = 7.3 Hz, 2 H, C-3'-H_2), 2.15 - 2.22 (m, 4 H, NCH_2CH_2), 2.37 - 2.42 (m, 2 H, C-1'-H_2), 2.44 (t, ^{3}J = 6.0 Hz, 2 H, C-4-H_2), 2.79 (t, ^{3}J = 6.6 Hz, 2 H, C-6-H_2), 3.87 - 3.94 (m, 4 H, NCH_2CH_2), 4.69 (dq, ^{2}J = 2.1 Hz, ^{4}J = 1.3 Hz, 1 H, C-5-*H*H), 4.75 - 4.76 (m, 1 H, C-5-H*H*), 6.34 (*virt.* quint, $^{4}J \approx {}^{4}J$ = 1.3 Hz, 1 H, C-2-H).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 20.7 (t, C-5-H_2), 22.3 (q, C-4'-CH_3), 24.4 (t, NCH_2CH_2), 24.4 (t, NCH_2CH_2), 24.9 (t, C-2'-H_2), 29.7 (t, C-4-H_2)*, 29.8 (t, C-6-H_2)*, 37.2 (t, C-3'-H_2) , 39.4 (t, C-1'-H_2), 52.4 (t, NCH_2CH_2), 52.8 (t, NCH_2CH_2), 111.2 (t, C-5'-H_2), 117.3 (d, C-2-H), 144.6 (s, C-4'), 173.5 (s, C-1), 178.0 (s, C-3).

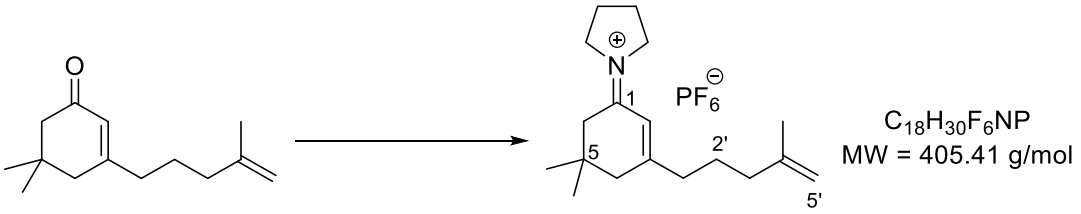
^{19}F-NMR (471 MHz, $CDCl_3$, 300 K): δ (ppm) = –73.6 (d, ^{1}J = 713 Hz, PF_6).

^{31}P-NMR (203 MHz, $CDCl_3$, 300 K): δ (ppm) = –144.7 (sept, ^{1}J = 713 Hz, PF_6).

* assignment is interconvertible.

HRMS (ESI): calc. $[M–PF_6]^+$: 232.2060; found: 232.2059.

1-[5,5-Dimethyl-3-(4-methylpent-4-en-1-yl)cyclohex-2-en-1-ylidene]pyrrolidin-1-ium hexafluorophosphate (8b)



To a solution of 119 mg enone **S2** (580 µmol, 1.00 eq.) and 47.0 µL pyrrolidine (41.0 mg, 580 µmol, 1.00 eq.) in 2 mL dry toluene were added 94.0 mg of ammonium hexafluorophosphate (580 µmol, 1.00 eq.). The suspension was refluxed for 3 hours with continuous removal of the water formed (*Dean-Stark*). The solvent was removed in vacuo to afford a yellow solid. After washing with diethyl ether, 62.0 mg iminium ion **8b** (153 µmol, 26%) were obtained as a white solid.

M.p.: 109 °C.

IR (ATR): $\tilde{\nu}$ = 2965 cm^{-1} (w, $C_{sp3}H$), 1629 (s, C=N), 1441 (w, $C_{sp3}H$), 1400 (w), 1357 (w), 826 (s).

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.09 [s, 6 H, C-5-$(CH_3)_2$], 1.68 (*virt.* quint, $^3J \approx {}^3J$ = 7.5 Hz, 2 H, C-2'-H_2), 1.72 (s, 3 H, C-4'-CH_3), 2.07 (t, ^3J = 7.4 Hz, 2 H, C-3'-H_2), 2.17 - 2.22 (m, 4 H, NCH_2CH_2), 2.35 (s, 2 H, C-4-H_2), 2.38 (t, ^3J = 7.7 Hz, 2 H, C-1'-H_2), 2.65 (s, 2 H, C-6-H_2), 3.84 - 4.01 (m, 4 H, NCH_2CH_2), 4.62 - 4.69 (m, 1 H, C-5'-*H*H), 4.74 - 4.76 (m, 1 H, C-5'-H*H*), 6.37 (s, 1 H, C-2-H).

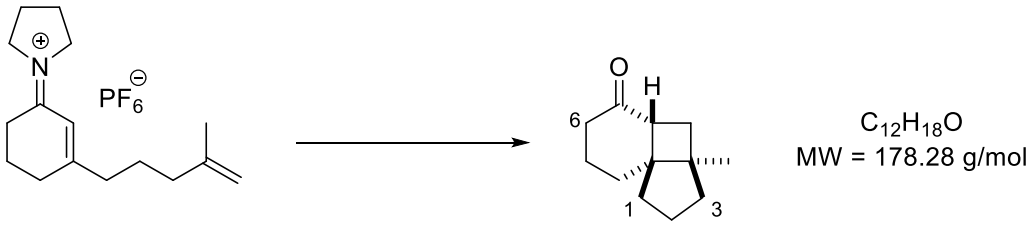
^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 22.3 (q, C-4'-CH_3), 24.4 (t, NCH_2CH_2), 24.5 (t, NCH_2CH_2), 24.8 (t, C-2'-H_2), 28.2 (q, 2 × C-5-CH_3), 32.7 (s, C-5), 37.2 (t, C-3'-H_2), 39.5 (t, C-1'-H_2), 43.0 (t, C-6-H_2), 44.0 (t, C-4-H_2), 52.7 (t, NCH_2CH_2), 53.0 (t, NCH_2CH_2), 111.2 (t, C-5'-H_2), 116.4 (d, C-2-H), 144.6 (s, C-4'), 173.2 (s, C-1), 176.2 (s, C-3).

^{19}F-NMR (471 MHz, $CDCl_3$, 300 K): δ (ppm) = –73.5 (d, ^1J = 713 Hz, PF_6).

^{31}P-NMR (203 MHz, $CDCl_3$, 300 K): δ (ppm) = –144.6 (sept, ^1J = 713 Hz, PF_6).

HRMS (ESI): calc. $[M–PF_6]^+$: 260.2373; found: 260.2372.

3a-Methyloctahydrocyclopenta[1,4]cyclobuta[1,2]benzen-5(6*H*)-one (*rac*-9a)



To a solution of 37.0 mg iminium ion **8a** (100 µmol, 1.00 eq.) in 5 mL dry acetonitrile were added 1.70 mg **5** (2.50 µmol, 2.50 mol%) and the solution was degassed for 15 minutes by purging with argon in an ultrasonicating bath. After irradiation (λ = 433 nm) at room temperature for 2 hours, 3 M NaOH solution was added and the mixture was extracted with ethylacetate. The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. After column chromatography (silica, P/Et_2O = 4/1), 12.7 mg ketone *rac*-**9a** (71.0 µmol, 71%) were obtained as a colourless oil.

TLC: R_f = 0.58 (P/Et_2O = 1/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ = 2933 cm^{-1} (s, $C_{sp3}H$), 2865 (m, $C_{sp3}H$), 2847 (m, $C_{sp3}H$), 1701 (s, C=O), 1442 (m, $C_{sp3}H$).

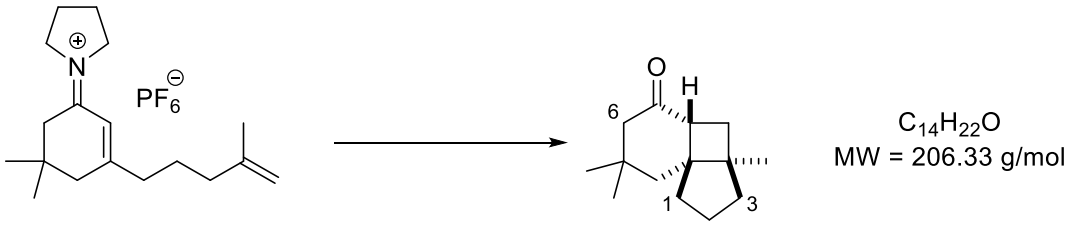
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.06 (s, 3 H, C-3a-CH_3), 1.29 - 1.36 (m, 1 H, C-3-*H*H), 1.36 - 1.42 (m, 1 H, C-1-*H*H), 1.45 (ddd, ^2J = 13.7 Hz, ^3J = 9.1 Hz, ^3J = 4.2 Hz, 1 H, C-8-*H*H), 1.57 - 1.63 (m, 1 H, C-3-H*H*), 1.71 - 1.83 (m, 4 H, C-1-H*H*, C-2-H_2, C-8-H*H*), 1.86 (ddd, ^2J = 12.7 Hz, ^3J = 7.2 Hz, ^4J = 1.4 Hz, 1 H, C-4-*H*H), 1.88 - 1.98 (m, 2 H, C-7-H_2), 2.01 (dd, ^2J = 12.7 Hz, ^3J = 11.0 Hz, 1 H, C-4-H*H*), 2.21 - 2.28 (m, 1 H, C-6-*H*H), 2.37 - 2.44 (m, 2 H, C-4a-H, C-6-H*H*).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 22.0 (t, C-7-H_2), 22.9 (q, C-3a-CH_3), 23.9 (t, C-2-H_2), 29.5 (t, C-8-H_2), 35.1 (t, C-4-H_2), 40.0 (t, C-6-H_2), 41.7 (t, C-1-H_2), 42.0 (t, C-3-H_2), 44.6 (s, C-3a), 45.3 (d, C-4a-H), 51.3 (s, C-8a), 216.5 (s, C-5).

MS (EI, 70 eV): *m*/*z* (%) = 178 (24) $[M]^+$, 163 (31) $[M–CH_3]^+$, 135 (62) $[C_9H_{11}O]^+$, 123 (90) $[C_8H_{11}O]^+$, 110 (56) $[C_7H_{10}O]^+$, 94 (100) $[C_6H_6O]^+$, 83 (68) $[C_6H_{10}]^+$, 67 (41), 55 (27).

HRMS (EI, 70 eV): calc. ($C_{12}H_{18}O$): 178.1352; found: 178.1357.

3a,7,7-Trimethyloctahydrocyclopenta[1,4]cyclobuta[1,2]benzen-5(6*H*)-one (*rac*-9b)



To a solution of 40.0 mg iminium ion **8b** (100 µmol, 1.00 eq.) in 5 mL dry acetonitrile were added 1.70 mg **5** (2.50 µmol, 2.50 mol%) and the solution was degassed for 15 minutes by purging with argon in an ultrasonicating bath. After irradiation (λ = 433 nm) at room temperature for 2 hours, 3 M NaOH solution was added and the mixture was extracted with ethylacetate. The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. After column chromatography (silica, P/Et_2O = 4/1) 15.7 mg ketone *rac*-**9b** (76.0 µmol, 76%) were obtained as a colourless oil.

TLC: R_f = 0.58 (P/Et_2O = 1/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ = 2945 (m, $C_{sp3}H$), 2866 (m, $C_{sp3}H$), 1698 (s, C=O), 1446 (m, $C_{sp3}H$).

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 0.90 (s, 3 H, C-7-CH_3), 1.01 (s, 3 H, C-3a-CH_3), 1.04 (s, 3 H, C-7-CH_3), 1.27 (dd, ^2J = 14.2 Hz, ^4J = 2.4 Hz, 1 H, C-8-*H*H), 1.30 - 1.34 (m, 1 H, C-3-*H*H), 1.39 (*virt.* td, $^2J \approx {}^3J$ = 12.3 Hz, ^3J = 7.0 Hz, 1 H, C-1-*H*H), 1.62 (dd, ^2J = 12.8 Hz, ^3J = 6.0 Hz, 1 H, C-3-H*H*), 1.69 - 1.82 (m, 3 H, C-4-*H*H, C-2-H_2), 1.91 (d, ^2J = 14.2 Hz, 1 H, C-8-*H*H), 1.96 (dd, ^2J = 12.7 Hz, ^3J = 5.7 Hz, 1 H, C-1-H*H*), 2.02 (dd, ^2J = 12.4 Hz, ^3J = 11.3 Hz, 1 H, C-4-H*H*), 2.12 (ddd, ^2J = 16.1 Hz, ^4J = 2.4 Hz, ^4J = 1.2 Hz, 1 H, C-6-*H*H), 2.21 (d, ^2J = 16.1 Hz, 1 H, C-6-H*H*), 2.36 (dd, ^3J = 11.1 Hz, ^3J = 7.8 Hz, 1 H, C-4a-H).

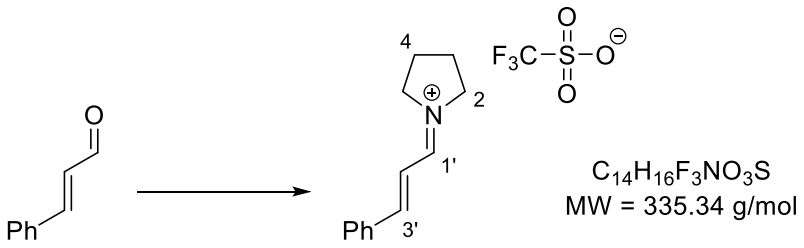
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 24.3 (q, C-3a-CH_3)*, 24.3 (t, C-2-H_2)*, 28.0 (q, C-7-CH_3), 31.8 (q, C-7-CH_3), 33.9 (s, C-7), 34.8 (t, C-4-H_2), 40.8 (t, C-3-H_2), 42.8 (t, C-8-H_2), 43.7 (d, C-4a-H), 44.0 (t, C-1-H_2), 45.4 (s, C-3a)**, 50.0 (s, C-8a)**, 52.7 (t, C-6-H_2), 216.2 (s, C-5).

*,** assignment is interconvertible.

MS (EI, 70 eV): *m*/*z* (%) = 206 (35) $[M]^+$, 191 (39) $[M–CH_3]^+$, 163 (50), 151 (67), 138 (47), 125 (42), 94 (100) $[C_6H_6O]^+$, 82 (78) $[C_6H_{10}]^+$, 67 (15), 41 (27).

HRMS (EI, 70 eV): calc. ($C_{14}H_{22}O$): 206.1665; found: 206.1648.
calc. ($C_{13}{}^{13}CH_{22}O$): 207.1699; found: 207.1681.

(*E*)-1-(3-Phenylallyliden)pyrrolidin-1-ium trifluoromethanesulfonate (11)



To a solution of 402 µL aldehyde **10** (456 mg, 3.45 mmol, 1.00 eq.) and 632 µL *N*-trimethylsilylpyrrolidine (519 mg, 3.62 mmol, 1.05 eq.) in 14 mL dry diethyl ether were added 656 µL TMSOTf (805 mg, 3.62 mmol, 1.05 eq.) dropwise. After 2 hours stirring at room temperature the solvent was removed by filtration and the solid was washed with dry diethyl ether (2 × 25 mL). After recrystallization (Et_2O/CH_2Cl_2), 765 mg iminium ion **11** (2.28 mmol, 66%) were obtained as pale yellow crystals.

M.p.: 121 °C.

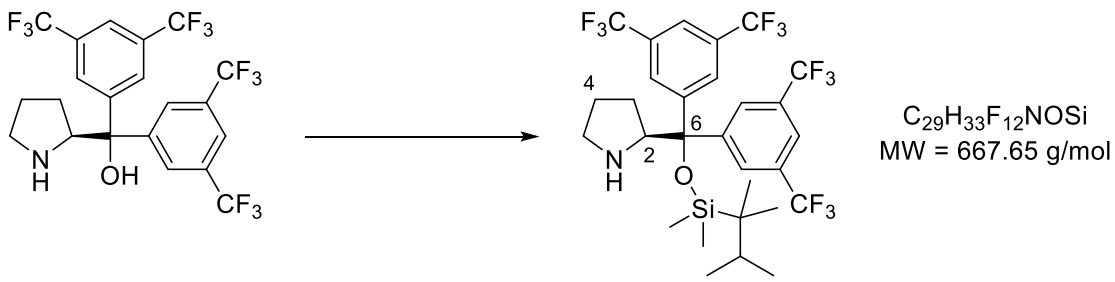
^{1}H-NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 2.02 (*virt.* quint, $^3J \approx {}^3J$ = 6.8 Hz, 2 H, C-3-H_2), 2.14 (*virt.* quint, $^3J \approx {}^3J$ = 6.8 Hz, 2 H, C-4-H_2), 4.00 (t, ^3J = 6.9 Hz, 2 H, C-5-H_2), 4.08 (t, ^3J = 6.9 Hz, 2 H, C-2-H_2), 7.08 (dd, ^3J = 15.3 Hz, ^3J = 10.5 Hz, 1 H, C-2'-H), 7.39 (*virt.* t, $^3J \approx {}^3J$ = 7.4 Hz, 2 H, C_{Ph}-H_{meta}), 7.47 (t, ^3J = 7.3 Hz, 1 H, C_{Ph}-H_{para}), 7.68 (d, ^3J = 7.3 Hz, 2 H, C_{Ph}-H_{ortho}), 7.90 (d, ^3J = 15.3 Hz, 1 H, C-3'-H), 8.80 (d, ^3J = 10.5 Hz, 1 H, C-1'-H).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 24.4 (t, C-3-H_2), 24.6 (t, C-4-H_2), 51.9 (t, C-5-H_2), 57.3 (t, C-2-H_2), 117.4 (d, C-2'-H), 120.9 (q, ^1J = 320 Hz, CF_3), 129.5 (d, 2 × C_{Ph}-H_{meta}), 130.5 (d, 2 × C_{Ph}-H_{ortho}), 133.5 (s, C_{Ph}), 133.7 (d, C_{Ph}-H_{para}), 161.1 (d, C-3'-H), 166.6 (d, C-1'-H).

^{19}F-NMR (377 MHz, CD_3CN, 300 K): δ (ppm) = –79.3.

The analytical data obtained matched those reported in the literature.[6]

(*S*)-2-{Bis[3,5-bis(trifluoromethyl)phenyl][((2,3-dimethylbutan-2-yl)dimethylsilyl)oxy]-methyl}pyrrolidine (S3)



To a solution of 478 mg (*S*)-bis(3,5-bis(trifluoromethyl)phenyl)(pyrrolidin-2-yl)methanol (909 µmol, 1.00 eq.) in 4.6 mL dry THF were added 109 mg NaH (60 wt% in mineral oil, 2.73 mmol, 3.00 eq.) portionwise. After 10 minutes of stirring, 377 µL chloro(2,3-dimethylbutan-2-yl)dimethylsilane (342 mg, 1.82 mmol, 2.00 eq.) were added dropwise. After 8 hours of stirring at room temperature the reaction mixture was poured onto ice and extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with 30 mL water, 30 mL brine, dried over Na_2SO_4, filtered and the solvent was removed in vacuo. Purification by column chromatography (silica, P/EtOAc = 50/1) gave 554 mg amine **S3** (830 µmol, 91%) as a colorless solid.

TLC: R_f = 0.50 (P/EtOAc = 9/1) [UV, $KMnO_4$].

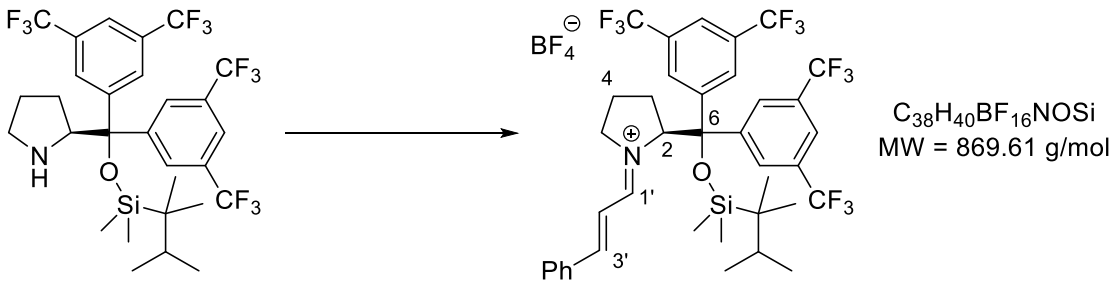
^{1}H-NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = –0.47 [s, 3 H, $Si(CH_3)_2$], –0.16 [s, 3 H, $Si(CH_3)_2$], 0.67 - 0.82 (m, 1 H, C-4-*H*H), 0.85 [d, ^3J = 10.1 Hz, 6 H, $SiC(CH_3)_2CH(CH_3)_2$], 0.92 [d, ^4J = 1.8 Hz, 3 H, $SiC(CH_3)_2)_2$], 0.93 [d, ^4J = 1.8 Hz, 3 H, $SiC(CH_3)_2$], 1.42 - 1.50 (m, 2 H, C-3-*H*H, C-4-H*H*), 1.68 - 1.90 [m, 2 H, C-3-H*H*, $SiC(CH_3)CH(CH_3)_2$], 2.42 - 2.49 (m, 1 H, C-5-*H*H), 2.87 (dt, ^2J = 10.0 Hz, ^3J = 7.0 Hz, 1 H, C-5-H*H*), 4.30 (dd, ^3J = 8.6 Hz, ^3J = 5.1 Hz, 1 H, C-2-H), 7.74 (s, 2 H, C_{Ar}-H_{ortho}), 7.85 (s, 2 H, C_{Ar}-H_{para}), 8.08 (s, 2 H, C_{Ar}-H_{ortho}).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = –0.82 [q, $Si(CH_3)_2$], –0.03 [q, $Si(CH_3)_2$], 18.6 [q, $SiC(CH_3)_2$], 18.7 [q, $SiC(CH_3)_2$], 20.2 [q, $SiC(CH_3)_2CH(CH_3)_2$], 20.4 [q, $SiC(CH_3)_2CH(CH_3)_2$], 25.5 (t, C-4-H_2), 25.8 [s, $SiC(CH_3)_2$], 28.1 (t, C-3-H_2), 33.9 [d, $SiC(CH_3)_2CH(CH_3)_2$], 47.4 (t, C-5-H_2), 63.7 (d, C-2-H), 83.1 (s, C-6), 121.6 (d, C_{Ar}-H_{para}), 122.0 (d, C_{Ar}-H_{para}), 123.3 (q, ^1J = 273 Hz, 2 × CF_3), 123.6 (q, ^1J = 273 Hz, 2 × CF_3), 129.4 (d, 4 × C_{Ar}-H_{ortho}), 130.5 (q, ^2J = 33.4 Hz, 2 × CCF_3), 131.6 (q, ^2J = 33.4 Hz, 2 × CCF_3), 146.1 (s, C_{Ar}), 147.8 (s, C_{Ar}).

^{19}F-NMR (471 MHz, $CDCl_3$, 300 K): δ (ppm) = –62.8 (s, 2 × CF_3), –62.9 (s, 2 × CF_3).

The analytical data obtained matched those reported in the literature.[7]

(*S*,*E*)-2-{Bis[3,5-bis(trifluoromethyl)phenyl][((2,3-dimethylbutan-2-yl)dimethylsilyl)-oxy]methyl}-1-[(*E*)-3-phenylallylidene]pyrrolidin-1-ium tetrafluoroborate (17)



A solution of 400 mg amine **S3** (599 µmol, 1.00 eq) in 6 mL dry *n*-pentane was cooled to 0 °C and 103 µL tetrafluoroboric acid diethyl ether complex (121 mg, 749 µmol, 1.25 eq.) were added dropwise. The reaction mixture was warmed to room temperature and after 3.5 hours of stirring, the precipitate was filtered, washed with dry *n*-pentane (3 × 5 mL) and dried in vacuo. A mixture of 200 mg of the obtained ammonium salt (265 µmol, 1.00 eq.), 100 mg 4 Å molecular sieves and 50.0 µL aldehyde **10** (52.5 mg, 397 µmol, 1.50 eq.) in 1.5 mL dry dichloromethane was refluxed for 6 hours. After cooling to room temperature the yellow solution was added dropwise to 40 mL dry *n*-pentane and cooled to –20 °C. The formed precipitate was filtered and washed with dry *n*-pentane (3 × 5 mL). The obtained solid was dissolved in 2 mL dry dichloromethane and added dropwise to 50 mL dry *n*-pentane and cooled to –20 °C. The formed precipitate was filtered, washed with dry *n*-pentane (3 × 5 mL) and dried in vacuo, which gave 83.2 mg iminium ion **17** (95.7 µmol, 36%) as a yellow solid.

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = –0.32 [s, 3 H, $Si(CH_3)_2$], –0.27 [s, 3 H, $Si(CH_3)_2$], 0.83 [s, 3 H, $SiC(CH_3)_2$], 0.88 - 0.92 [m, 9 H, $SiC(CH_3)_2$, $SiC(CH_3)_2CH(CH_3)_2$], 1.34 - 1.44 (m, 1 H, C-4-*H*H), 1.76 [*virt.* sept, $^{3}J \approx {}^{3}J$ = 6.4 Hz, 1 H, $SiC(CH_3)_2CH(CH_3)_2$], 1.84 - 1.94 (m, 1 H, C-4-H*H*), 2.05 - 2.13 (m, 1 H, C-3-*H*H), 2.34 (dt, ^{2}J = 14.5 Hz, ^{3}J = 8.6 Hz, 1 H, C-5-*H*H), 2.52 - 2.63 (m 1 H, C-3-H*H*), 3.93 (ddd, ^{2}J = 14.5 Hz, ^{3}J = 8.9 Hz, ^{3}J = 4.6 Hz, 1 H, C-5-H*H*), 5.56 (dd, ^{3}J = 9.2 Hz, ^{3}J = 4.1 Hz, 1 H, C-2-H), 7.12 (dd, ^{3}J = 15.3 Hz, ^{3}J = 10.7 Hz, 1 H, C-2'-H), 7.60 (*virt.* t, $^{3}J \approx {}^{3}J$ = 7.7 Hz, 2 H, C_{Ph}-H_{meta}), 7.70 (t, ^{3}J = 7.4 Hz, 1 H, C_{Ph}-H_{para}), 7.89 (d, ^{3}J = 7.7 Hz, 2 H, C_{Ph}-H_{ortho}), 7.97 (s, 2 H, C_{Ar}-H_{ortho}), 7.96 - 8.06 (m, 3 H, C-3'-H, C_{Ar}-H_{ortho}), 8.19 (s, 1 H, C_{Ar}-H_{para}), 8.22 (s, 1 H, C_{Ar}-H_{para}), 8.64 (d, ^{3}J = 10.7 Hz, 1 H, C-1'-H).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = –0.38 [q, $Si(CH_3)_2$], –0.33 [q, $Si(CH_3)_2$], 18.5 [q, $SiC(CH_3)_2CH(CH_3)_2$], 19.0 [q, $SiC(CH_3)_2CH(CH_3)_2$], 19.9 [q, $SiC(CH_3)_2$], 20.8 [q, $SiC(CH_3)_2$], 23.1 (t, C-4-H_2), 26.4 [s, $SiC(CH_3)_2$], 27.0 (t, C-3-H_2), 34.1 [d, $SiC(CH_3)_2CH(CH_3)_2$], 54.4 (t, C-5-H_2), 77.1 (d, C-2-H), 84.3 (s, C-6), 118.6 (d, C-2'-H), 124.1

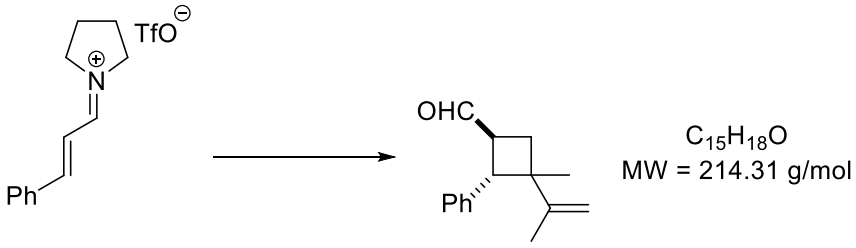
(q, ^1J = 272 Hz, 2 × CF_3), 124.2 (q, ^1J = 272 Hz, 2 × CF_3), 124.6 (d, C_{Ar}-H_{para}), 124.8 (d, C_{Ar}-H_{para}), 130.2 (d, 2 × C_{Ar}-H_{ortho}), 130.7 (d, 2 × C_{Ph}-H_{meta}), 131.8 (d, 2 × C_{Ar}-H_{ortho}, 2 × C_{Ph}-H_{ortho}), 132.5 (q, ^2J = 33.6 Hz, 2 × CCF_3), 132.9 (q, ^2J = 33.7 Hz, 2 × CCF_3), 134.3 (s, C_{Ph}), 135.7 (d, C_{Ph}-H_{para}), 142.2 (s, C_{Ar}), 142.6 (s, C_{Ar}), 164.4 (d, C-3'-H), 169.0 (d, C-1'-H).

^{19}F-NMR (471 MHz, $CDCl_3$, 300 K): δ (ppm) = –63.3 (s, 2 × CF_3), –63.4 (s, 2 × CF_3), –151.8 (s, BF_4).

The analytical data obtained matched those reported in the literature.[7]

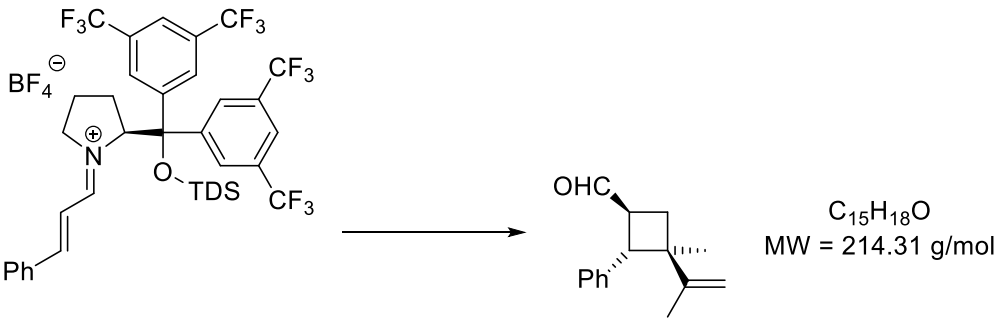
3-Methyl-2-phenyl-3-(prop-1-en-2-yl)cyclobutane-1-carbaldehyde (*rac*-12)

*[2+2]-photocycloaddition of iminium ion **11***



To a solution of 69.6 mg iminium ion **11** (208 µmol, 1.00 eq.) and 4.46 mg $Ru(bpy)_3(PF_6)_2$ (5.19 µmol, 2.5 mol%) in dry, degassed acetonitrile were added 467 µL 2,3-dimethylbutadiene (341 mg, 4.15 mmol, 20.0 eq.). After irradiation (λ = 457 nm) for 4 hours, 25 mL 3 M NaOH solution were added and the mixture was extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed with 25 mL 1 M HCl solution, 25 mL saturated $NaHCO_3$-solution, 25 mL brine and dried over Na_2SO_4, filtered and the solvent was removed in vacuo. After column chromatography (silica, P/Et_2O = 25/1) 30.8 mg aldehyde *rac*-**12** (144 µmol, 69%, d.r. = 87/13) were obtained as a colorless oil.

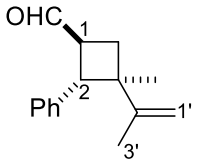
*Enantioselective [2+2]-photocycloaddition of chiral iminium ion **17***



A solution of 35.0 mg iminium ion **17** (40.3 µmol, 1.00 eq.) and 865 µg $Ru(bpy)_3(PF_6)_2$ (1.01 µmol, 2.5 mol%) in 2 mL dry, degassed acetonitrile was cooled to –40 °C and 91.6 µL

2,3-dimethylbutadiene (66.1 mg, 805 µmol, 20.0 eq.) were added. After irradiation (λ = 457 nm) at –40 °C for 3.5 hours the solution was warmed up to room temperature, 15 mL 3 M NaOH solution were added and the mixture was extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with 15 mL 1 M HCl solution, 15 mL saturated $NaHCO_3$-solution, 15 mL brine and dried over Na_2SO_4, filtered and the solvent was removed in vacuo. After column chromatography (silica, P/Et_2O = 25/1), 6.70 mg aldehyde **12a** (31.3 µmol, 78%, d.r. = 94/6, 88% *ee*) were obtained as a colorless oil.

Major Diastereoisomer



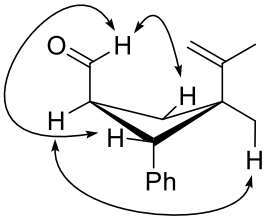
TLC: R_f = 0.39 (P/EtOAc = 9/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ = 3085 cm^{-1} (w, $C_{sp2}H$), 3062 (w, $C_{sp2}H$), 2964 (m, $C_{sp3}H$), 2926 (m, $C_{sp3}H$), 1718 (s, C=O), 1448 (m, $C_{sp3}H$), 1378 (m), 891 (m), 774 (m, $C_{sp2}H$), 699 (s, $C_{sp2}H$).

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.06 (s, 3 H, C-3-*C*H_3), 1.75 (*br*. s, 3 H, C-3'-H_3), 1.94 (dd, ^2J = 11.0 Hz, ^3J = 8.7 Hz, 1 H, C-4-H_β), 2.33 (dd, ^2J = 11.0 Hz, ^3J = 9.6 Hz, 1 H, C-4-H_α), 3.47 (*virt.* qd, $^3J \approx {}^3J$ = 9.6 Hz, ^3J = 2.5 Hz, 1 H, C-1-H), 3.89 (d, ^3J = 10.2 Hz, 1 H, C-2-H), 4.85 (*virt.* quint, $^2J \approx {}^4J$ = 1.4 Hz, 1 H, C-1'-*H*H), 4.89 (*br*. s, 1 H, C-1'-H*H*), 7.22 - 7.26 (m, 3 H, C_{Ph}-H_{ortho}, C_{Ph}-H_{para}), 7.30 - 7.34 (m, 2 H, C_{Ph}-H_{meta}), 9.80 (d, ^3J = 2.5 Hz, 1 H, CHO).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 18.9 (q, C-3'-H_3), 21.6 (q, C-3-*C*H_3), 31.5 (t, C-4-H_2), 44.8 (d, C-1-H), 46.1 (s, C-3), 47.7 (d, C-2-H), 109.1 (t, C-1'-H_2), 126.8 (d, C_{Ph}-H_{para}), 128.1 (d, 2 × C_{Ph}-H_{ortho}), 128.4 (d, 2 × C_{Ph}-H_{meta}), 139.2 (s, C_{Ph}), 152.4 (s, C-2'), 202.4 (d, CHO).

Important NOE-contacts



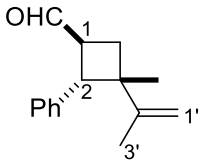
MS (EI, 70 eV): *m*/*z* (%) = 214 (3) $[M]^+$, 183 (19), 131 (74) $[C_9H_7O]^+$, 91 (27) $[C_7H_7]^+$, 82 (100), 77 (7) $[C_6H_5]^+$, 67 (67) $[C_5H_7]^+$.

HRMS (EI, 70 eV): calc. ($C_{15}H_{18}O$): 214.1352; found: 214.1344.
calc. ($C_{14}{}^{13}CH_{18}O$): 215.1386; found: 215.1377.

Chiral GC: t_{R1} = 95.8 min, t_{R2} = 96.0 min [60 °C (3 min), 125 °C (25 °C/min), 125 °C (90 min), 230 °C (15 °C/min), 230 °C (3 min)].

Specific Rotation: $[\alpha]_D^{25}$ = +76.0 (c = 0.5, $CHCl_3$) [88% *ee*].

Minor Diastereoisomer



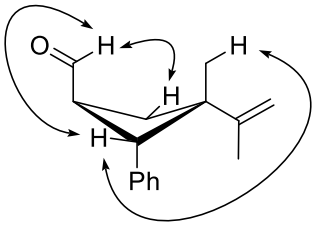
TLC: R_f = 0.41 (P/EtOAc = 9/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ = 3089 cm^{-1} (w, $C_{sp2}H$), 3062 (w, $C_{sp2}H$), 2959 (m, $C_{sp3}H$), 2925 (m, $C_{sp3}H$), 1719 (s, C=O), 1454 (m, $C_{sp3}H$), 1376 (m), 890 (m), 762 (m, $C_{sp2}H$), 698 (s, $C_{sp2}H$).

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.08 (*br*. s, 3 H, C-3'-H_3), 1.39 (s, 3 H, C-3-*C*H_3), 2.11 (dd, ^2J = 12.0 Hz, ^3J = 8.7 Hz, 1 H, C-4-H_α), 2.55 (dd, ^2J = 12.0 Hz, ^3J = 9.1 Hz, 1 H, C-4-H_β), 3.39 (*virt*. qd, $^3J \approx {}^3J$ = 9.0 Hz, ^3J = 2.0 Hz, 1 H, C-1-H), 3.51 (d, ^3J = 9.2 Hz, 1 H, C-2-H), 4.88 (*virt*. quint, $^2J \approx {}^4J$ = 1.4 Hz, 1 H, C-1'-*H*H), 4.91 (*br*. s, 1 H, C-1'-H*H*), 7.20 - 7.24 (m, 3 H, C_{Ph}-H_{ortho}, C_{Ph}-H_{para}), 7.26 - 7.30 (m, 2 H, C_{Ph}-H_{meta}), 9.80 (d, ^3J = 2.0 Hz, 1 H, CHO).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 20.3 (q, C-3'-H_3), 28.7 (q, C-3-*C*H_3), 30.6 (t, C-4-H_2), 45.9 (d, C-1-H), 47.7 (s, C-3), 52.0 (d, C-2-H), 111.2 (t, C-1'-H_2), 127.0 (d, C_{Ph}-H_{para}), 127.8 (d, 2 × C_{Ph}-H_{ortho}), 128.3 (d, 2 × C_{Ph}-H_{meta}), 136.7 (s, C_{Ph}), 147.5 (s, C-2'), 202.4 (d, CHO).

Important NOE-contacts

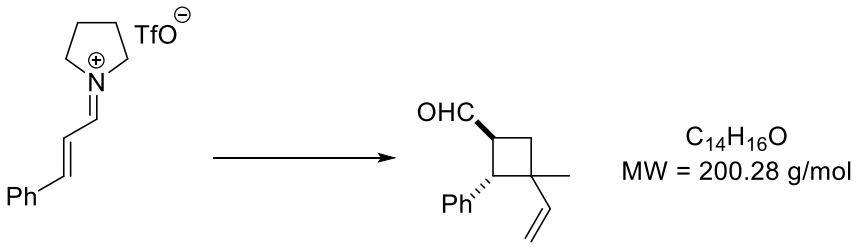


MS (EI, 70 eV): *m*/*z* (%) = 214 (6) $[M]^+$, 199 (8) $[M–CH_3]^+$, 183 (81), 172 (50), 131 (90) $[C_9H_7O]^+$, 115 (49), 91 (72) $[C_7H_7]^+$, 82 (100), 77 (53) $[C_6H_5]^+$, 67 (97) $[C_5H_7]^+$.

HRMS (EI, 70 eV): calc. ($C_{15}H_{18}O$): 214.1352; found: 214.1346.

calc. ($C_{14}{}^{13}CH_{18}O$): 215.1386; found: 215.1386.

3-Methyl-2-phenyl-3-vinylcyclobutane-1-carbaldehyde (*rac*-13)



To a solution of 69.6 mg iminium ion **11** (208 µmol, 1.00 eq.) and 4.46 mg $Ru(bpy)_3(PF_6)_2$ (5.19 µmol, 2.5 mol%) in 4.2 mL dry, degassed acetonitrile were added 416 µL isoprene (283 mg, 4.15 mmol, 20.0 eq.). After irradiation (λ = 457 nm) for 4 hours, 25 mL 3 M NaOH solution were added and the mixture was extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed with 25 mL brine and dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was filtered through a short pad of silica and after column chromatography (silica, P/Et_2O = 25/1) 27.1 mg aldehyde *rac*-**13** (135 µmol, 65%, d.r. = 75/25, r.r. = 90/10) were obtained as a colorless oil.

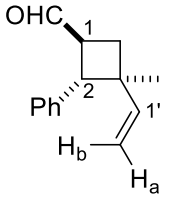
TLC: R_f = 0.35 (P/EtOAc = 9/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ = 3084 cm^{-1} (w, $C_{sp2}H$), 3062 (w, $C_{sp2}H$), 2963 (m, $C_{sp3}H$), 2865 (m, $C_{sp3}H$), 1718 (s, C=O), 1450 (m, $C_{sp3}H$), 1377 (m), 778 (m, $C_{sp2}H$), 699 (s, $C_{sp2}H$).

MS (EI, 70 eV): *m*/*z* (%) = 200 (1) $[M]^+$, 169 (8), 131 (100) $[C_9H_7O]^+$, 104 (19), 91 (13) $[C_7H_7]^+$, 77 (9) $[C_6H_5]^+$, 67 (11) $[C_5H_7]^+$.

HRMS (EI, 70 eV): calc. ($C_{14}H_{16}O$): 200.1196; found: 200.1196.
calc. ($C_{13}{}^{13}CH_{16}O$): 201.1229; found: 201.1226.

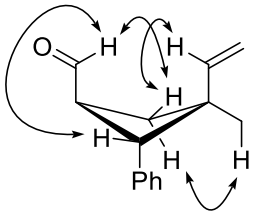
Major Diastereoisomer



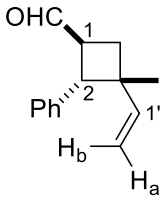
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 0.94 (s, 3 H, C-3-*C*H_3), 1.93 (dd, ^2J = 11.1 Hz, ^3J = 8.5 Hz, 1 H, C-4-H_β), 2.33 (*virt.* t, $^2J \approx {}^3J$ = 10.7 Hz, 1 H, C-4-H_α), 3.45 - 3.61 (m, 1 H, C-1-H), 3.73 (d, ^3J = 10.2 Hz, 1 H, C-2-H), 5.06 (dd, ^3J = 17.3 Hz, ^2J = 1.0 Hz, 1 H, C-2'-H_b), 5.07 (dd, ^3J = 10.7 Hz, ^2J = 1.0 Hz, 1 H, C-2'-H_a), 6.09 (dd, ^3J = 17.3 Hz, ^3J = 10.7 Hz, 1 H, C-1'-H), 7.11 - 7.16 (m, 2 H, C_{Ph}-H_{ortho}), 7.20 - 7.26 (m, 1 H, C_{Ph}-H_{para}), 7.28 - 7.34 (m, 2 H, C_{Ph}-H_{meta}), 9.82 (d, ^3J = 2.6 Hz, 1 H, CHO).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 20.4 (q, C-3-*C*H_3), 31.6 (t, C-4-H_2), 42.9 (s, C-3), 44.5 (d, C-1-H), 48.9 (d, C-2-H), 112.0 (t, C-2'-H_2), 126.8 (d, C_{Ph}-H_{para}), 127.2 (d, 2 × C_{Ph}-H_{ortho}), 128.4 (d, 2 × C_{Ph}-H_{meta}), 138.7 (s, C_{Ph}), 146.8 (d, C-1'-H), 202.3 (d, CHO).

Important NOE-contacts



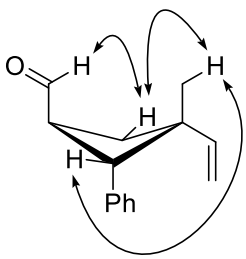
Minor Diastereoisomer



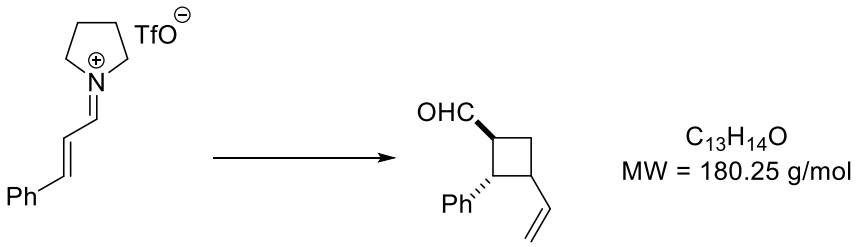
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.38 (s, 3 H, C-3-*C*H_3), 2.15 (dd, ^2J = 11.3 Hz, ^3J = 9.6 Hz, 1 H, C-4-$H_α$), 2.27 (dd, ^2J = 11.3 Hz, ^3J = 8.6 Hz, 1 H, C-4-$H_β$), 3.45 - 3.61 (m, 2 H, C-1-H, C-2-H), 4.98 (dd, ^3J = 10.8 Hz, ^2J = 1.2 Hz, 1 H, C-2'-H_a), 5.03 (dd, ^3J = 17.4 Hz, ^2J = 1.2 Hz, 1 H, C-2'-H_b), 5.58 (dd, ^3J = 17.4 Hz, ^3J = 10.8 Hz, 1 H, C-1'-H), 7.11 - 7.16 (m, 2 H, C_{Ph}-H_{ortho}), 7.20 - 7.26 (m, 1 H, C_{Ph}-H_{para}), 7.28 - 7.34 (m, 2 H, C_{Ph}-H_{meta}), 9.81 (d, ^3J = 2.3 Hz, 1 H, CHO).

^{13}C-NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 27.9 (q, C-3-*C*H_3), 30.5 (t, C-4-H_2), 44.2 (s, C-3), 45.1 (d, C-1-H), 51.8 (d, C-2-H), 112.8 (t, C-2'-H_2), 126.9 (d, C_{Ph}-H_{para}), 127.5 (d, 2 × C_{Ph}-H_{ortho}), 128.4 (d, 2 × C_{Ph}-H_{meta}), 138.5 (s, C_{Ph}), 142.0 (d, C-1'-H), 202.2 (d, CHO).

Important NOE-contacts



2-Phenyl-3-vinylcyclobutane-1-carbaldehyde (*rac*-14)



To a solution of 55.0 mg iminium ion **11** (164 µmol, 1.00 eq.) and 3.52 mg $Ru(bpy)_3(PF_6)_2$ (4.10 µmol, 2.5 mol%) in 3.3 mL dry, degassed acetonitrile were added 1.64 mL butadiene (2 M in THF, 3.28 mmol, 20.0 eq.). After irradiation (λ = 457 nm) for 4 hours, 25 mL 3 M NaOH solution were added and the mixture was extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed with 25 mL brine and dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was filtered through a short pad of silica and after column chromatography (silica, P/Et_2O = 30/1) 15.2 mg aldehyde *rac*-**14** (84.3 µmol, 50%, d.r. = 60/40) were obtained as a colorless oil.

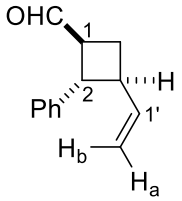
TLC: R_f = 0.35 (P/EtOAc = 9/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ = 3082 cm^{-1} (w, $C_{sp2}H$), 3063 (w, $C_{sp2}H$), 2980 (m, $C_{sp3}H$), 2811 (m, $C_{sp3}H$), 1716 (s, C=O), 1448 (m, $C_{sp3}H$), 1389 (m), 745 (m, $C_{sp2}H$), 699 (s, $C_{sp2}H$).

MS (EI, 70 eV): *m*/*z* (%) = 186 (1) $[M]^+$, 168 (4), 155 (5), 131 (74) $[C_9H_7O]^+$, 104 (27), 91 (11) $[C_7H_7]^+$, 77 (9) $[C_6H_5]^+$.

HRMS (EI, 70 eV): calc. ($C_{13}H_{14}O$): 186.1039; found: 186.1040.
calc. ($C_{14}{}^{13}CH_{18}O$): 187.1073; found: 187.1073.

Major Diastereoisomer

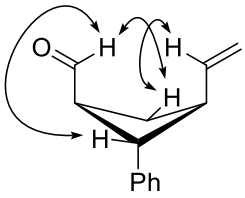


^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 2.10 (*virt.* q, $^2J \approx {}^3J$ = 10.1 Hz, 1 H, C-4-H_α), 2.35 (*virt.* dtd, ^2J = 11.0 Hz, $^3J \approx {}^3J$ = 8.2 Hz, ^4J = 0.9 Hz, 1 H, C-4-H_β), 3.06 (*virt.* tddt, $^3J \approx {}^3J$ = 9.4 Hz, ^3J = 8.0 Hz, ^3J = 6.7 Hz, $^4J \approx {}^4J$ = 1.2 Hz, 1 H, C-3-H), 3.23 (*virt.* tdd, $^3J \approx {}^3J$ = 10.0 Hz, ^3J = 8.3 Hz, ^3J = 2.2 Hz, 1 H, C-1-H), 3.54 (*virt.* t, $^3J \approx {}^3J$ = 9.6 Hz, 1 H, C-2-H), 5.06 (*virt.* dt, ^3J = 10.4 Hz, $^2J \approx {}^4J$ = 1.4 Hz, 1 H, C-2'-H_a), 5.10 (*virt.* dt, ^3J = 17.2 Hz, $^2J \approx {}^4J$ = 1.5 Hz, 1 H, C-2'-H_b), 5.97 (ddd, ^3J = 17.2 Hz, ^3J = 10.4 Hz, ^3J = 6.7 Hz, 1 H,

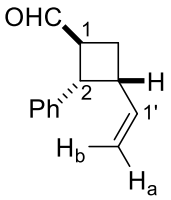
C-1'-H), 7.22 - 7.26 (m, 2 H, C_{Ph}-H_{ortho}), 7.30 - 7.36 (m, 3 H, C_{Ph}-H_{meta}, C_{Ph}-H_{para}), 9.80 (d, ^3J = 2.2 Hz, 1 H, CHO).

^{13}C-NMR (76 MHz, $CDCl_3$, 300 K): δ (ppm) = 25.7 (t, C-4-H_2), 42.7 (d, C-3-H), 47.1 (d, C-2-H), 49.4 (d, C-1-H), 115.0 (t, C-2'-H_2), 126.6 (d, 2 × C_{Ph}-H_{ortho}), 126.9 (d, C_{Ph}-H_{para}), 128.7 (d, 2 × C_{Ph}-H_{meta}), 140.3 (d, C-1'-H), 142.0 (s, C_{Ph}), 201.9 (d, CHO).

Important NOE-contacts



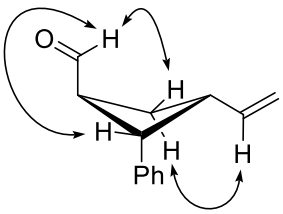
Minor Diastereoisomer



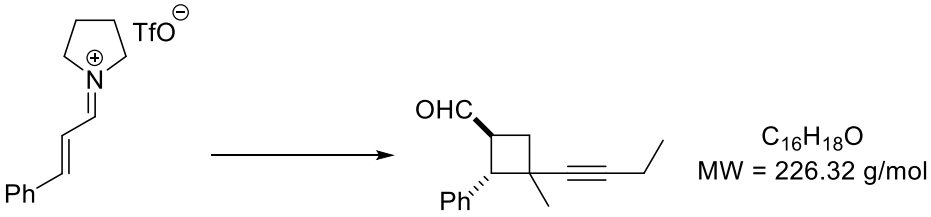
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 2.10 - 2.16 (m, 1 H, C-4-H_β), 2.58 (*virt.* dt, ^2J = 11.7 Hz, $^3J \approx {}^3J$ = 8.4 Hz, 1 H, C-4-H_α), 3.26 - 3.32 (m, 1 H, C-3-H), 3.61 (*virt.* qdd, $^3J \approx {}^3J$ = 9.0 Hz, ^3J = 2.1 Hz, ^4J = 1.2 Hz, 1 H, C-1-H), 4.03 (*virt.* t, $^3J \approx {}^3J$ = 9.1 Hz, 1 H, C-2-H), 4.97 (*virt.* dt, ^3J = 10.3 Hz, $^2J \approx {}^4J$ = 1.4 Hz, 1 H, C-2'-H_a), 5.03 (*virt.* dt, ^3J = 17.0 Hz, $^2J \approx {}^4J$ = 1.6 Hz, 1 H, C-2'-H_b), 5.64 (ddd, ^3J = 17.0 Hz, ^3J = 10.3 Hz, ^3J = 8.0 Hz, 1 H, C-1'-H), 7.14 - 7.17 (m, 2 H, C_{Ph}-H_{ortho}), 7.22 - 7.26 (m, 1 H, C_{Ph}-H_{para}), 7.30 - 7.35 (m, 2 H, C_{Ph}-H_{meta}), 9.87 (d, ^3J = 2.1 Hz, 1 H, CHO).

^{13}C-NMR (76 MHz, $CDCl_3$, 300 K): δ (ppm) = 24.5 (t, C-4-H_2), 40.7 (d, C-3-H), 43.9 (d, C-2-H), 48.1 (d, C-1-H), 115.7 (t, C-2'-H_2), 126.6 (d, C_{Ph}-H_{para}), 127.7 (d, 2 × C_{Ph}-H_{ortho}), 128.4 (d, 2 × C_{Ph}-H_{meta}), 138.3 (d, C-1'-H), 139.3 (s, C_{Ph}), 201.9 (d, CHO).

Important NOE-contacts



3-(But-1-yn-1-yl)-3-methyl-2-phenylcyclobutane-1-carbaldehyde (*rac*-15)



To a solution of 69.6 mg iminium ion **11** (208 µmol, 1.00 eq.) and 4.46 mg $Ru(bpy)_3(PF_6)_2$ (5.19 µmol, 2.5 mol%) in 4.2 mL dry, degassed acetonitrile were added 516 µL 2-methylhex-1-ene-3-yne (391 mg, 4.15 mmol, 20.0 eq.). After irradiation (λ = 457 nm) for 4 hours, 25 mL 3 M NaOH solution were added and the mixture was extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed with 25 mL brine and dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was filtered through a short pad of silica and after column chromatography (silica, P/Et_2O = 25/1) 36.6 mg aldehyde *rac*-**15** (162 µmol, 78%, d.r. = 80/20) were obtained as a colorless oil.

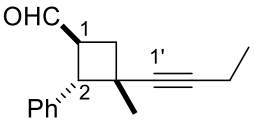
TLC: R_f = 0.35 (P/EtOAc = 9/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ = 3029 cm^{-1} (w, $C_{sp2}H$), 2974 (m, $C_{sp3}H$), 2934 (m, $C_{sp3}H$), 1717 (s, C=O), 1452 (m, $C_{sp3}H$), 1322 (m), 747 (m, $C_{sp2}H$), 697 (s, $C_{sp2}H$).

MS (EI, 70 eV): *m*/*z* (%) = 226 (1) $[M]^+$, 211 (7) $[M–CH_3]^+$, 197 (18) $[M–C_2H_5]^+$, 155 (15), 131 (63) $[C_9H_7O]^+$, 94 (82), 91 (18) $[C_7H_7]^+$, 79 (100), 77 (21) $[C_6H_5]^+$.

HRMS (EI, 70 eV): calc. ($C_{15}H_{18}O$): 226.1352; found: 226.1348.
calc. ($C_{14}{}^{13}CH_{18}O$): 227.1386; found: 227.1385.

Major Diastereoisomer



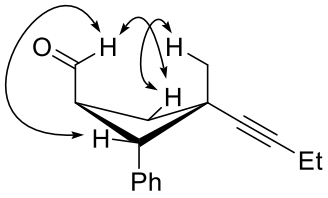
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 0.92 (t, ^3J = 7.5 Hz, 3 H, C-4'-H_3), 1.45 (s, 3 H, C-3-*C*H_3), 1.99 - 2.04 (m, 2 H, C-3'-H_2), 2.16 (dd, ^2J = 10.7 Hz, ^3J = 9.8 Hz, 1 H, C-4-H_α), 2.32 (dd, ^2J = 10.7 Hz, ^3J = 8.6 Hz, 1 H, C-4-H_β), 3.46 (d, ^3J = 10.2 Hz, 1 H, C-2-H), 3.64 (*virt*. tdd, $^3J \approx {}^3J$ = 10.4 Hz, ^3J = 8.6 Hz, ^3J = 2.1 Hz, 1 H, C-1-H), 7.22 - 7.29 (m, 3 H, C_{Ph}-H_{ortho}, C_{Ph}-H_{para}), 7.31 - 7.36 (m, 2 H, C_{Ph}-H_{meta}), 9.78 (d, ^3J = 2.1 Hz, 1 H, CHO).

^{13}C-NMR (76 MHz, $CDCl_3$, 300 K): δ (ppm) = 12.5 (t, C-3'-H_2), 14.2 (q, C-4'-H_3), 28.9 (q, C-3-*C*H_3), 34.4 (t, C-4-H_2), 38.1 (s, C-3), 46.3 (d, C-1-H), 52.3 (d, C-2-H), 82.9 (s, C-1'), 86.6

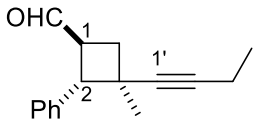
(s, C-2'), 127.1 (d, C_{Ph}-H_{para}), 127.9 (d, 2 × C_{Ph}-H_{ortho})*, 128.0 (d, 2 × C_{Ph}-H_{meta})*, 138.9 (s, C_{Ph}), 201.9 (d, CHO).

* assignment is interconvertible.

Important NOE-contacts



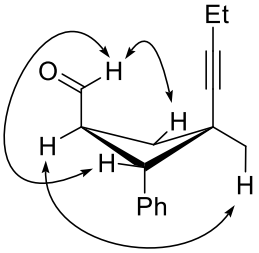
Minor Diastereoisomer



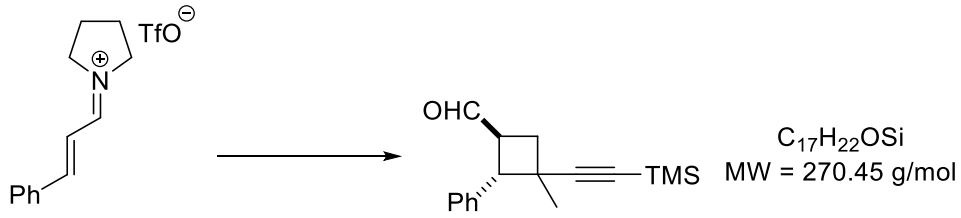
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.03 (s, 3 H, C-3-*C*H_3), 1.17 (t, ^{3}J = 7.5 Hz, 3 H, C-4'-H_3), 2.07 (dd, ^{2}J = 11.1 Hz, ^{3}J = 8.5 Hz, 1 H, C-4-H_β), 2.24 (q, ^{3}J = 7.5 Hz, 2 H, C-3'-H_2), 2.53 (*virt.* t, $^{2}J \approx {}^{3}J$ = 10.8 Hz, 1 H, C-4-H_α), 3.41 - 3.49 (m, 1 H, C-1-H), 3.99 (d, ^{3}J = 10.3 Hz, 1 H, C-2-H), 7.22 - 7.29 (m, 3 H, C_{Ph}-H_{ortho}, C_{Ph}-H_{para}), 7.31 - 7.36 (m, 2 H, C_{Ph}-H_{meta}), 9.81 (d, ^{3}J = 2.8 Hz, 1 H, CHO).

^{13}C-NMR (76 MHz, $CDCl_3$, 300 K): δ (ppm) = 12.7 (t, C-3'-H_2), 14.4 (q, C-4'-H_3), 22.8 (q, C-3-*C*H_3), 33.8 (t, C-4-H_2), 33.9 (s, C-3), 44.6 (d, C-1-H), 50.5 (d, C-2-H), 84.0 (s, C-2'), 86.2 (s, C-1'), 127.0 (d, C_{Ph}-H_{para}), 127.1 (d, 2 × C_{Ph}-H_{ortho}), 128.5 (d, 2 × C_{Ph}-H_{meta}), 138.1 (s, C_{Ph}), 201.7 (d, CHO).

Important NOE-contacts



3-Methyl-2-phenyl-3-[(3-trimethylsilyl)ethynyl]cyclobutane-1-carbaldehyde (*rac*-16)



To a solution of 69.6 mg iminium ion **11** (208 µmol, 1.00 eq.) and 4.46 mg $Ru(bpy)_3(PF_6)_2$ (5.19 µmol, 2.5 mol%) in 4.2 mL dry, degassed acetonitrile were added 738 µL (3-methylbut-3-en-1-ynyl)trimethylsilane (574 mg, 4.15 mmol, 20.0 eq.). After irradiation (λ = 457 nm) for 4 hours, 25 mL 3 M NaOH solution were added and the mixture was extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed with 25 mL brine and dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was filtered through a short pad of silica and after column chromatography (silica, P/Et_2O = 25/1) 41.5 mg aldehyde *rac*-**16** (153 µmol, 74%, d.r. = 76/24) were obtained as a colorless oil.

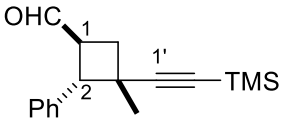
TLC: R_f = 0.33 (P/EtOAc = 9/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ = 3031 cm^{-1} (w, $C_{sp2}H$), 2962 (m, $C_{sp3}H$), 2899 (m, $C_{sp3}H$), 2163 (m, C_{sp}) 1719 (s, C=O), 1450 (m, $C_{sp3}H$), 1249 (s), 839 (s), 759 (m, $C_{sp2}H$), 696 (s, $C_{sp2}H$).

MS (EI, 70 eV): *m*/*z* (%) = 270 (1) $[M]^+$, 255 (11) $[M–CH_3]^+$, 199 (6), 138 (28), 131 (25) $[C_9H_7O]^+$, 123 (100), 73 (12).

HRMS (EI, 70 eV): calc. ($C_{17}H_{22}OSi$): 270.1434; found: 270.1422.

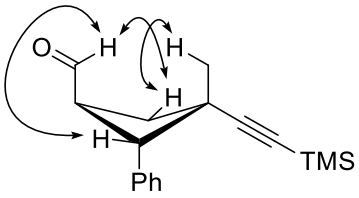
Major Diastereoisomer



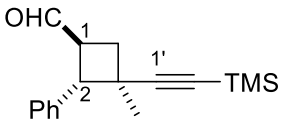
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 0.00 [s, 9 H, $Si(CH_3)_3$], 1.48 (s, 3 H, C-3-*C*H_3), 2.19 (dd, ^2J = 10.8 Hz, ^3J = 9.8 Hz, 1 H, C-4-H_α), 2.39 (dd, ^2J = 10.8 Hz, ^3J = 8.6 Hz, 1 H, C-4-H_β), 3.49 (d, ^3J = 10.3 Hz, 1 H, C-2-H), 3.68 (*virt.* tdd, $^3J \approx {}^3J$ = 9.6 Hz, ^3J = 8.6 Hz, ^3J = 2.0 Hz, 1 H, C-1-H), 7.22 - 7.30 (m, 3 H, C_{Ph}-H_{ortho}, C_{Ph}-H_{para}), 7.31 - 7.39 (m, 2 H, C_{Ph}-H_{meta}), 9.80 (d, ^3J = 2.0 Hz, 1 H, CHO).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = –0.03 (q, 3 × $SiCH_3$), 28.3 (q, C-3-*C*H_3), 34.1 (t, C-4-H_2), 38.8 (s, C-3), 46.1 (d, C-1-H), 52.3 (d, C-2-H), 88.9 (s, C-2'), 110.1 (s, C-1'), 127.2 (d, C_{Ph}-H_{para}), 127.9 (d, 2 × C_{Ph}-H_{ortho}), 128.1 (d, 2 × C_{Ph}-H_{meta}), 138.5 (s, C_{Ph}), 201.8 (d, CHO).

Important NOE-contacts



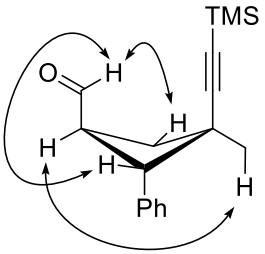
Minor Diastereoisomer



^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 0.21 [s, 9 H, $Si(CH_3)_3$], 1.06 (s, 3 H, C-3-*C*H_3), 2.10 (dd, ^{2}J = 11.1 Hz, ^{3}J = 8.5 Hz, 1 H, C-4-H_β), 2.59 (*virt.* t, $^{2}J \approx {}^{3}J$ = 10.7 Hz, 1 H, C-4-H_α), 3.46 - 3.52 (m, 1 H, C-1-H), 4.05 (d, ^{3}J = 10.3 Hz, 1 H, C-2-H), 7.22 - 7.30 (m, 3 H, C_{Ph}-H_{ortho}, C_{Ph}-H_{para}), 7.31 - 7.39 (m, 2 H, C_{Ph}-H_{meta}), 9.83 (d, ^{3}J = 2.6 Hz, 1 H, CHO).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 0.32 (q, 3 × $SiCH_3$), 22.3 (q, C-3-*C*H_3), 33.5 (t, C-4-H_2), 34.3 (s, C-3), 44.5 (d, C-1-H), 50.3 (d, C-2-H), 86.1 (s, C-2'), 112.9 (s, C-1'), 127.0 (d, 2 × C_{Ph}-H_{ortho}), 127.2 (d, C_{Ph}-H_{para}), 128.5 (d, 2 × C_{Ph}-H_{meta}), 137.7 (s, C_{Ph}), 201.6 (d, CHO).

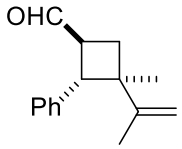
Important NOE-contacts



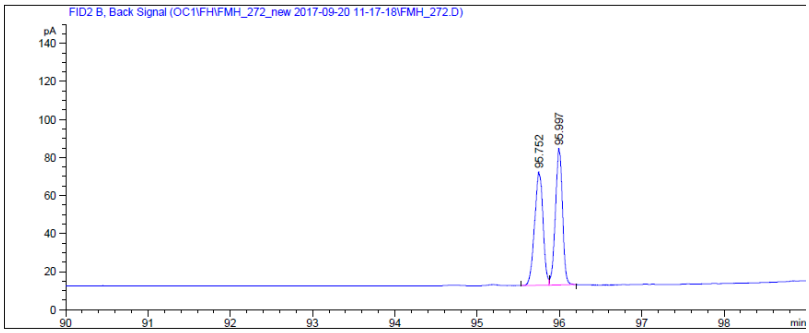
4. Additional Experiments for the Sensitization of Eniminium ion 11

#	sens. (mol%)	λ [nm]	t [h]	yield [%]	d.r.
1	benzil (50)	366	7	34	75/25
2	thioxanthone (20)	420	24	38	86/14
3	$Ru(bpz)_3(PF_6)_2$ (2.5)	457	4	73	87/13
4	Eosin Y (2.5)	512	4	-	-
5	-	457	4	-	-
6	$Ru(bpy)_3(PF_6)_2$	-	4	-	-

5. Chiral GC Trace of Aldehyde 12



Racemic product (major diastereomer)

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=====================================================================
                      Area Percent Report
=====================================================================

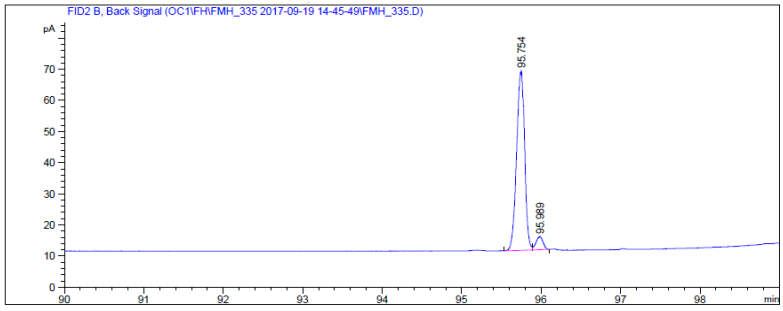
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: FID2 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  95.752 BV    0.0885  425.13300   59.83357 49.73861
   2  95.997 VBA   0.0763  429.60138   71.73585 50.26139

Totals :                  854.73438  131.56942
```

Enantioenriched product (major diastereoisomer, 88% *ee)*




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: FID2 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  95.754 BV    0.0916  405.93402   57.72308 93.97853
   2  95.989 VB    0.0772   26.00936    4.28353  6.02147

Totals :                  431.94338   62.00661
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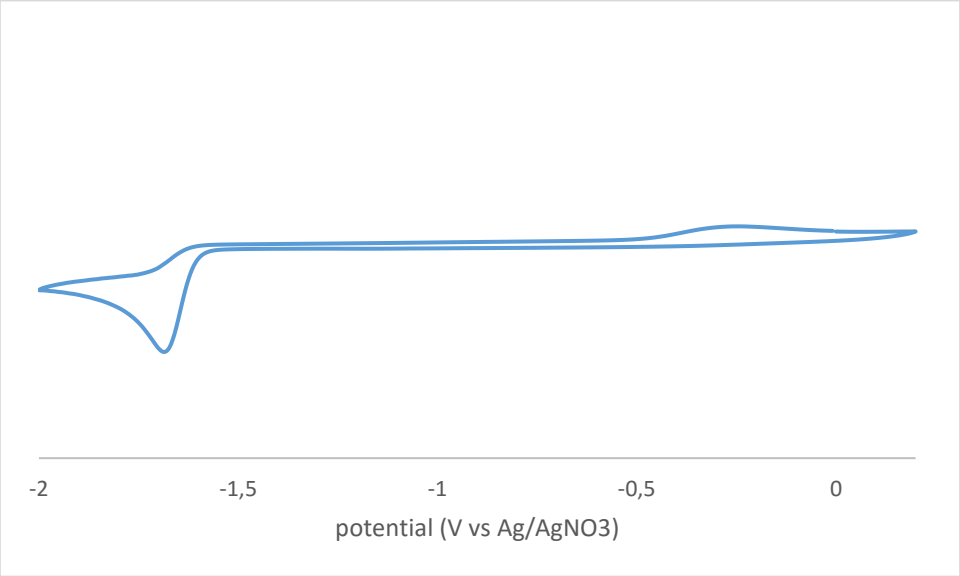
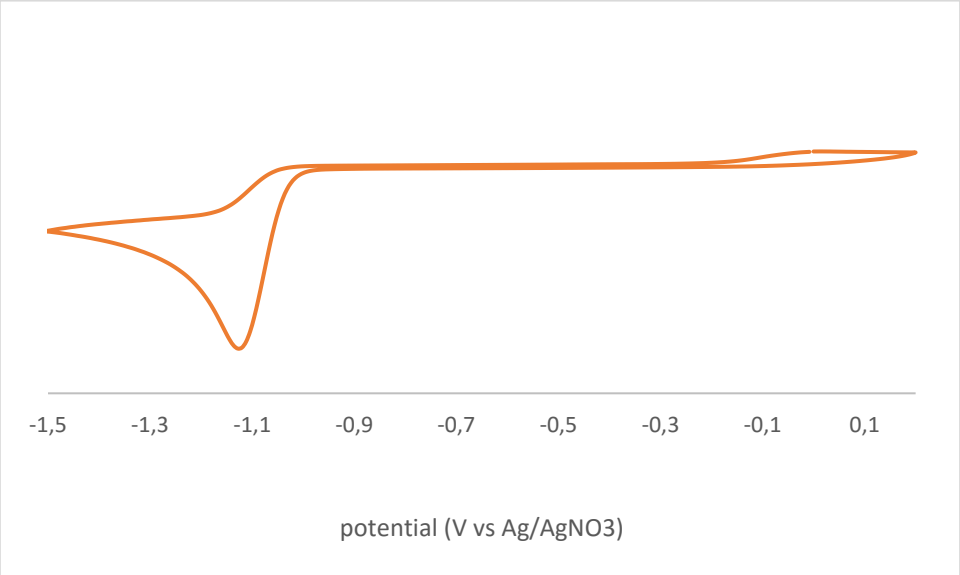
6. Cyclic Voltammetry



Cyclic voltammogram of iminium ion **2** [1.43 mM] in $TBAPF_6$ [0.1 M] in CH_3CN. Scan rate: 0.1 V/s, glassy carbon working electrode, platinum wire counter electrode, $Ag/AgNO_3$ [0.01 M] reference electrode, $E_{1/2}$ (**2**/**2**$^{-}$) = –1.69 V.



Cyclic voltammogram of iminium ion **11** [2.86 mM] in $TBAPF_6$ [0.1 M] in CH_3CN. Scan rate: 0.1 V/s, glassy carbon working electrode, platinum wire counter electrode, $Ag/AgNO_3$ reference electrode [0.01 M], $E_{1/2}$ (**11**/**11**$^{-}$) = –1.13 V.

7. Data Sheets of Light Sources

420 nm

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 FLT020 — LZC-420

Basic Information

Type	Fluorescent light tube
Description	Luzchem LZC-420
Manufacturer / Supplier	n/a / Luzchem
Order number / Date of purch.	n/a / 09/2015
Internal lot / serial number	2015-09 / FLT020

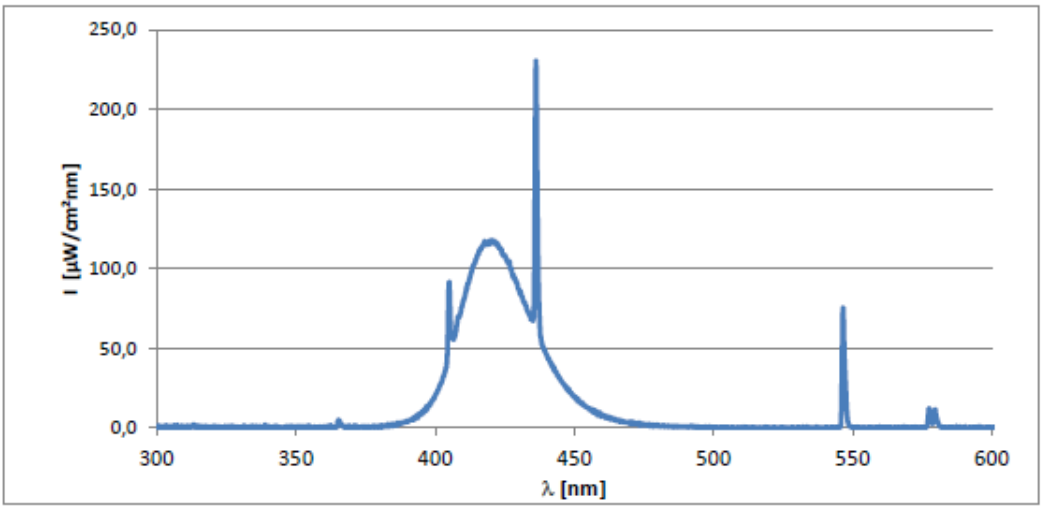
Specification Manufacturer

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

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.	
Measured dominant wavelength / Int.	421 nm	117 µW/mm²nm
Measured spectral width (FWHM)	31 nm	
Integral Reference intensity / range	4118 µW/cm²	350-500 nm

Spectrum



LED 433 nm

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 LED029 — Av-430-3W

Basic Information

Type	High-Power-LED
Description	Avonec 430-435 nm / 3 W
Manufacturer / Supplier	n/a / Avonec
Order number / Date of purch.	n/a / 01/2016
Internal lot / serial number	2016-01 / LED029

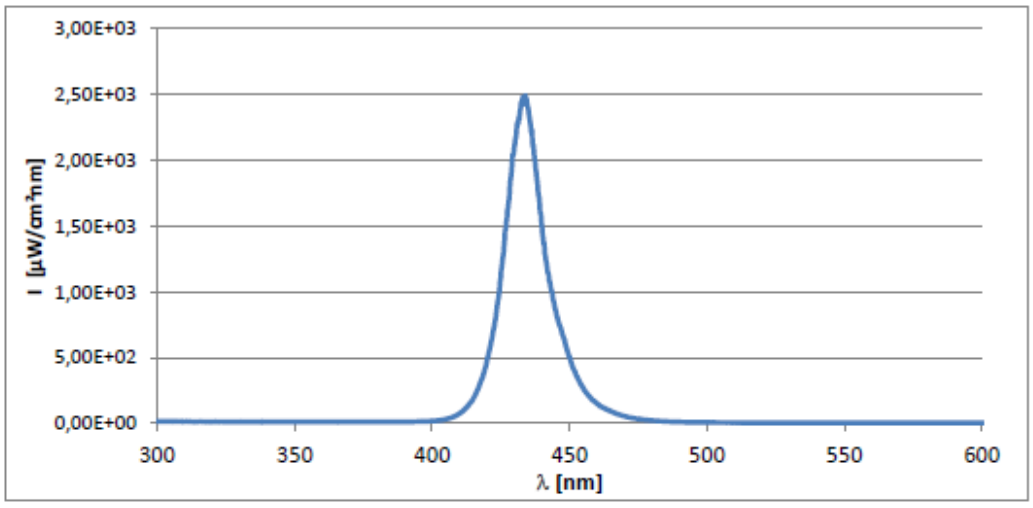
Specification Manufacturer

Type / size	single emitter / ca. 1 x 1 mm
Mechanical specification	
Electrical specification	700 mA, UF 3.7 V
Wavelength (range, typ.)	430-435 nm, typ. n/a
Spectral width (FWHM)	n/a
Datasheet	n/a

Characterization

Description of measurement	Measured with Ocean-optics USB4000 spectrometer using a calibrated setup (cosine corrector/fibre). The distance between the emitting surface and the surface of the cosine corrector was 20 mm. The LED was operated at 700 mA on a passive heat-sink at approx. 20 °C
Measured wavelength	433 nm
Measured spectral width	15 nm
Integral Reference intensity	50270 µW/cm² (350-550 nm @ 20 mm distance, 4 mmcosine corr.)

Spectrum



LED 457 nm

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 H2A3-H470

Basic Information

Type	High-Power-LED
Description	H2A3-H470
Manufacturer / Supplier	n/a / Roithner-Lasertechnik, Wien
Order number / Date of purch.	H2A3-H470 / 12/2011
Internal lot / serial number	2011-12 / LED005

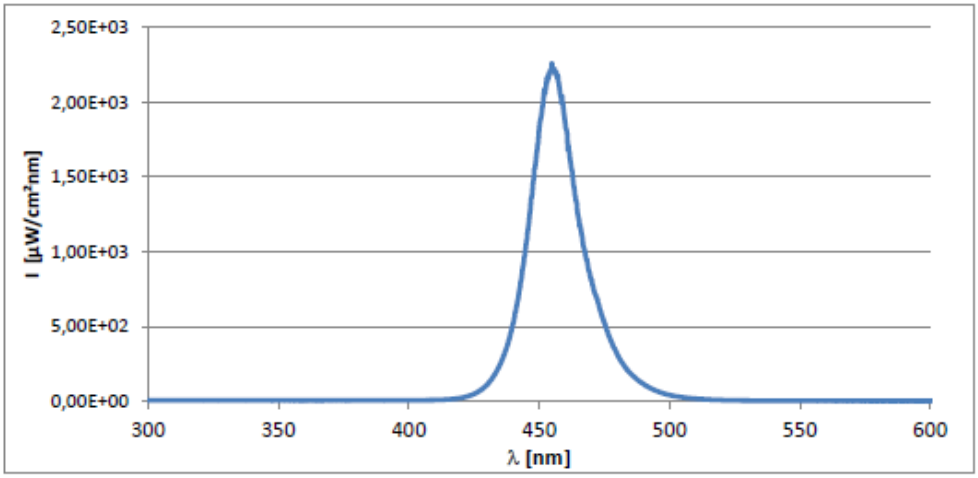
Specification Manufacturer

Type / size	single emitter / <1 x <1 mm
Mechanical specification	
Electrical specification	700 mA, UF~3.8 V
Wavelength (range, typ.)	not spec., typ. 470 nm
Spectral width (FWHM)	25 nm
Datasheet	H2A3H470.pdf (n. b. - datasheet is for H2A3H530!)

Characterization

Description of measurement	Measured with Ocean-optics USB4000 spectrometer using a calibrated setup (cosine corrector/fibre). The distance between the emitting surface and the surface of the cosine corrector was 20 mm. The LED was operated at 700 mA on a passive heat-sink at approx. 20 °C
Measured wavelength	457 nm
Measured spectral width	21 nm
Integral Reference intensity	56580 µW/cm² (400-550 nm @ 20 mm distance, 4 mmcosine corr.)

Spectrum



LED 512 nm

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 LED039 XPEGRN-Q2

Basic Information

Type	High-Power-LED
Description	Cree® XLamp® XP-E green
Manufacturer / Supplier	Cree / Conrad
Order number / Date of purch.	181826 - 62 / 03/2015
Internal lot / serial number	2016-03 / LED039

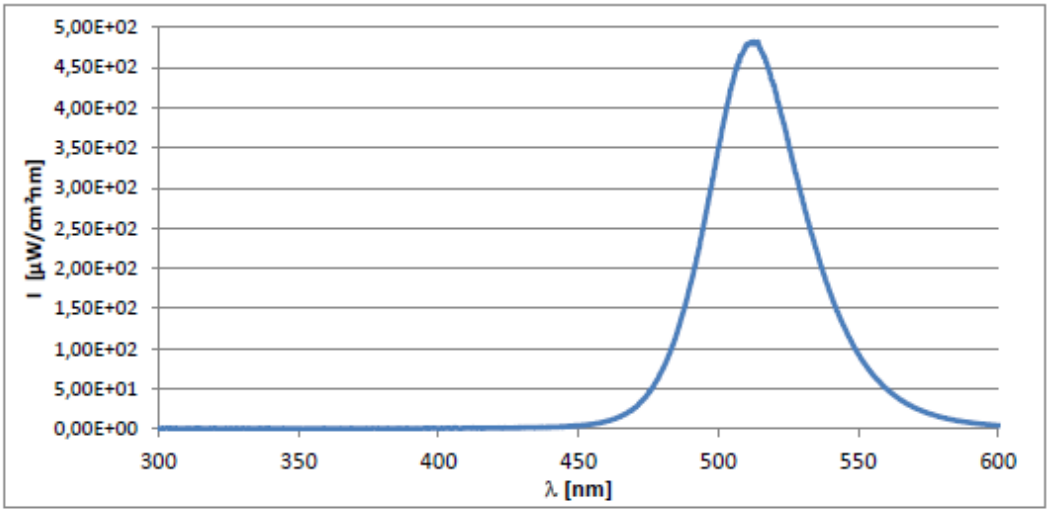
Specification Manufacturer

Type / size	single emitter / <1 x <1 mm
Mechanical specification	
Electrical specification	1000 mA, UF~3.8 V
Wavelength (range, typ.)	520 – 535 nm, typ. 520 nm
Spectral width (FWHM)	40 nm
Datasheet	XPEGRN-Q2.pdf

Characterization

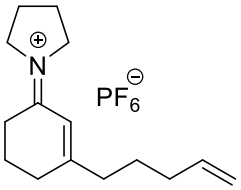
Description of measurement	Measured with Ocean-optics USB4000 spectrometer using a calibrated setup (cosine corrector/fibre). The distance between the emitting surface and the surface of the cosine corrector was 20 mm. The LED was operated at 700 mA on a passive heat-sink at approx. 20 °C
Measured wavelength	512 nm
Measured spectral width	38 nm
Integral Reference intensity	20915 µW/cm² (450-600 nm @ 20 mm distance, 4 mmcosine corr.)

Spectrum

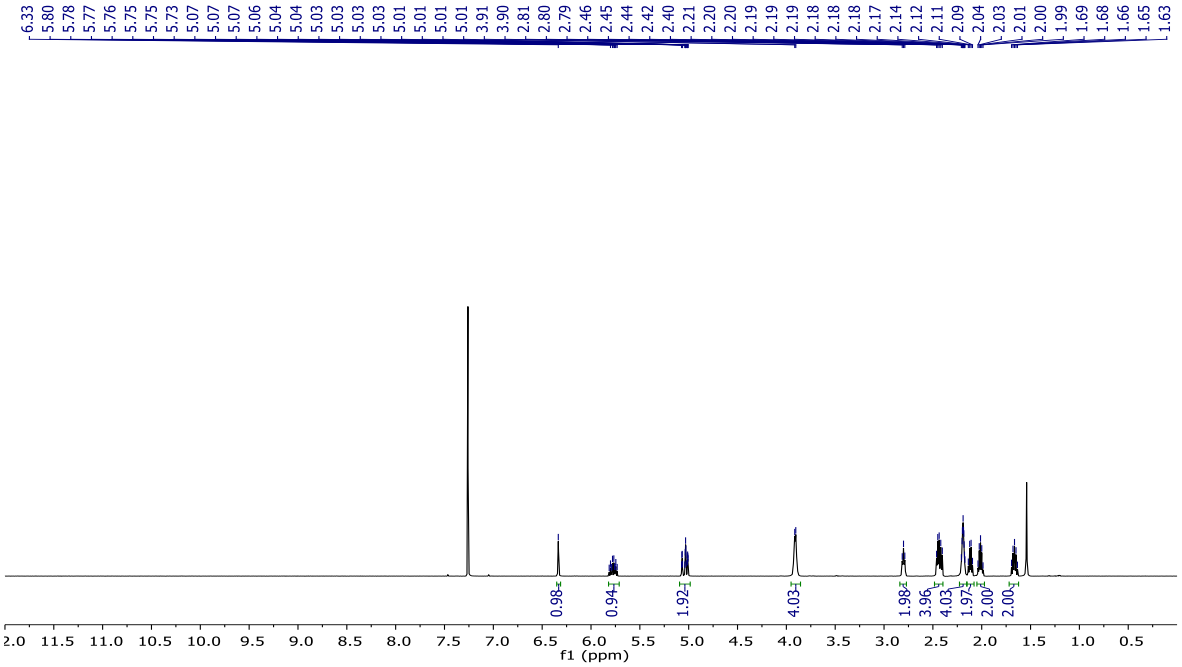


8. NMR-Spectra of New Compounds

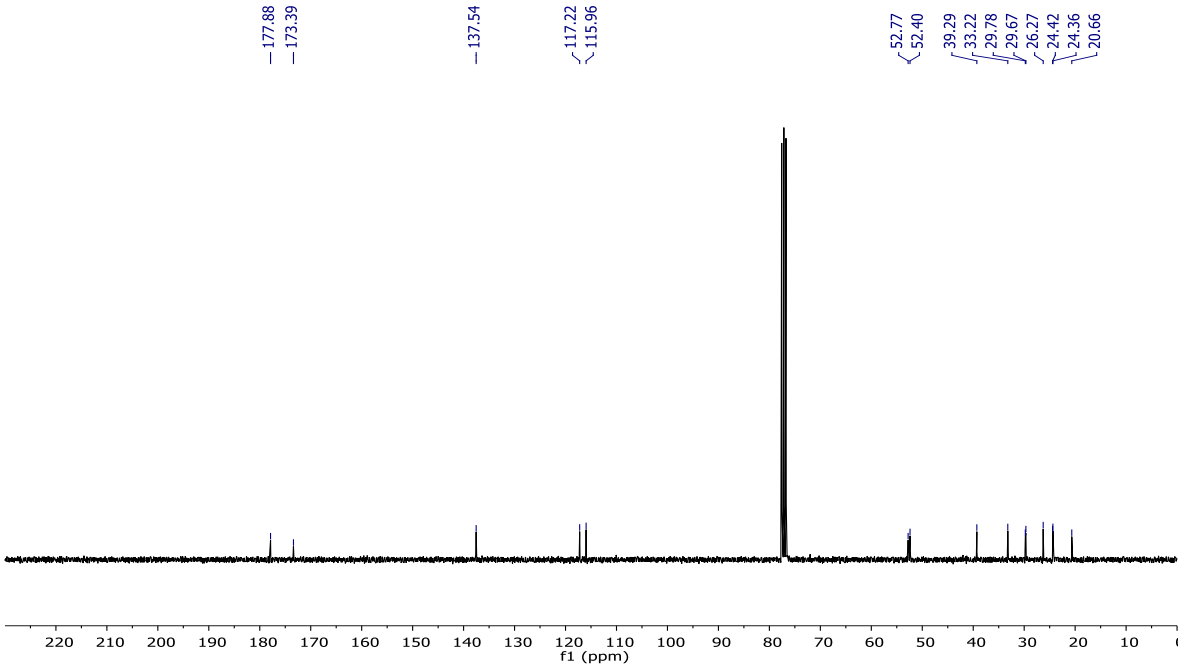
1-[3-(Pent-4-en-1-yl)cyclohex-2-en-1-ylidene]pyrrolidin-1-ium hexafluorophosphate (2)



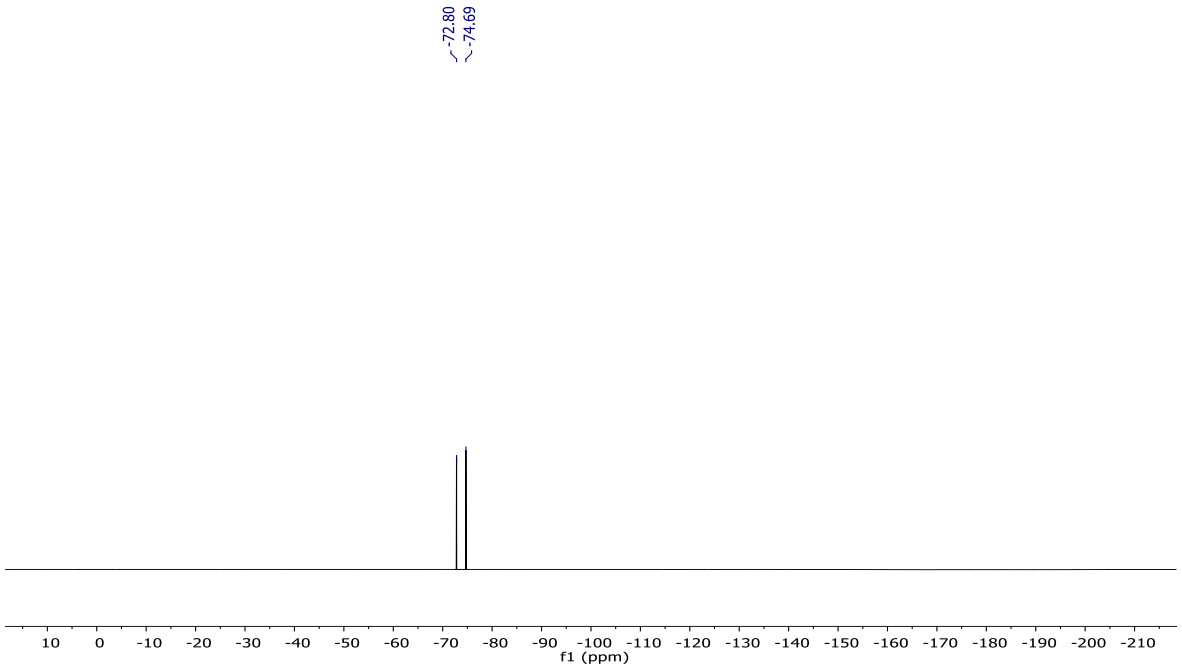
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K):



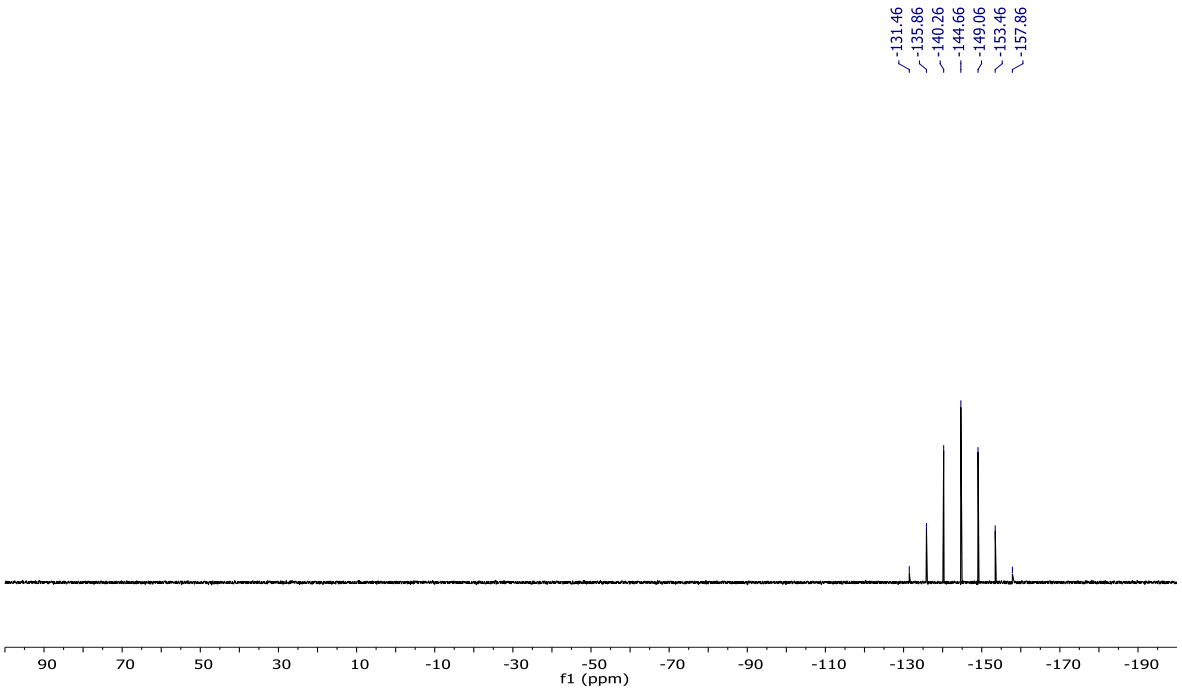
^{13}C-NMR (76 MHz, $CDCl_3$, 298 K):



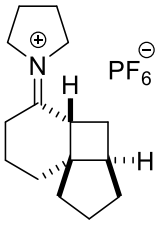
^{19}F-NMR (377 MHz, $CDCl_3$, 300 K):



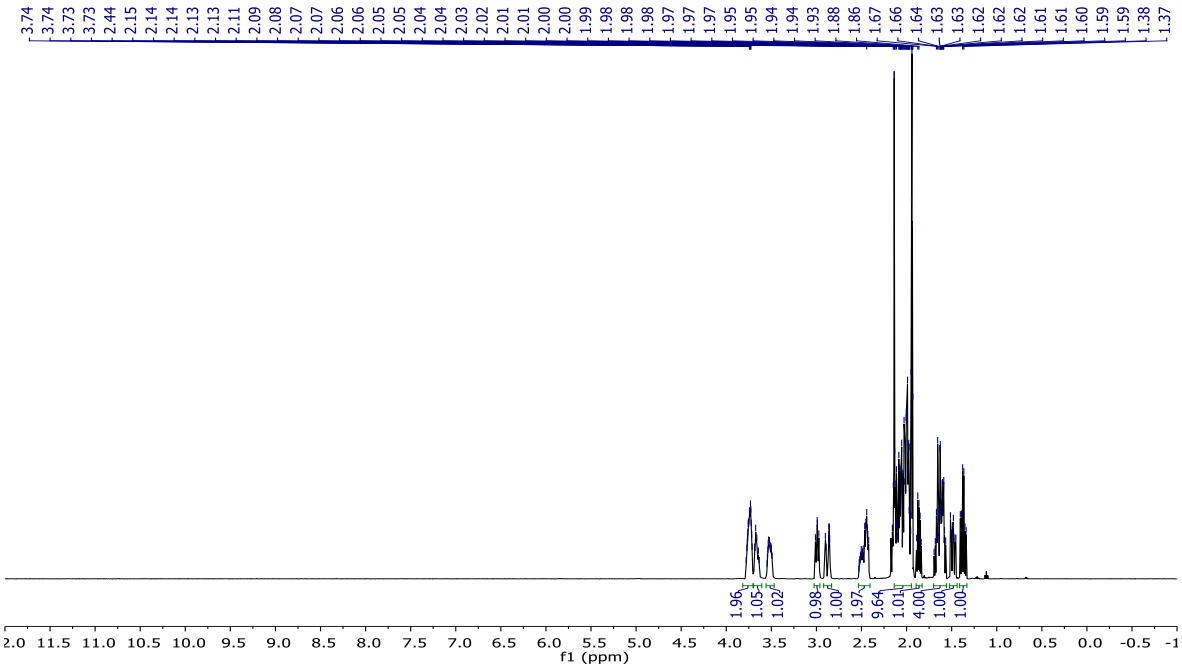
^{31}P-NMR (162 MHz, $CDCl_3$, 300 K):



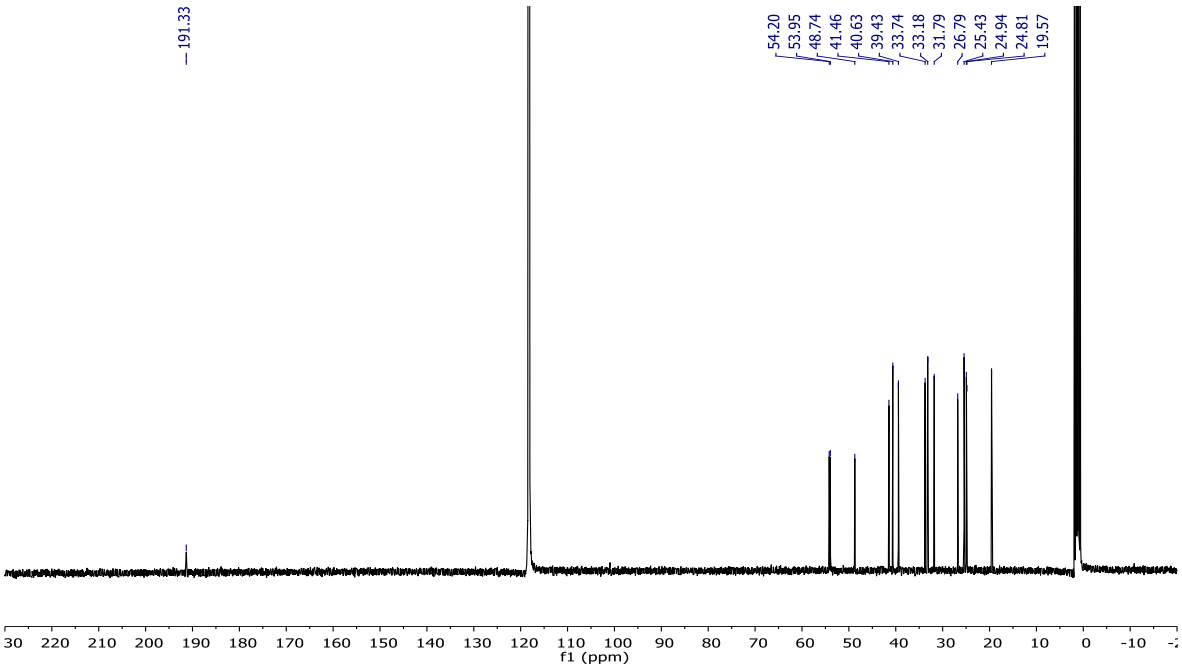
1-(Octahydrocyclopenta[1,4]cyclobuta[1,2]benzen-5(6*H*)-ylidene)pyrrolidin-1-ium hexafluorophosphate (*rac*-3)



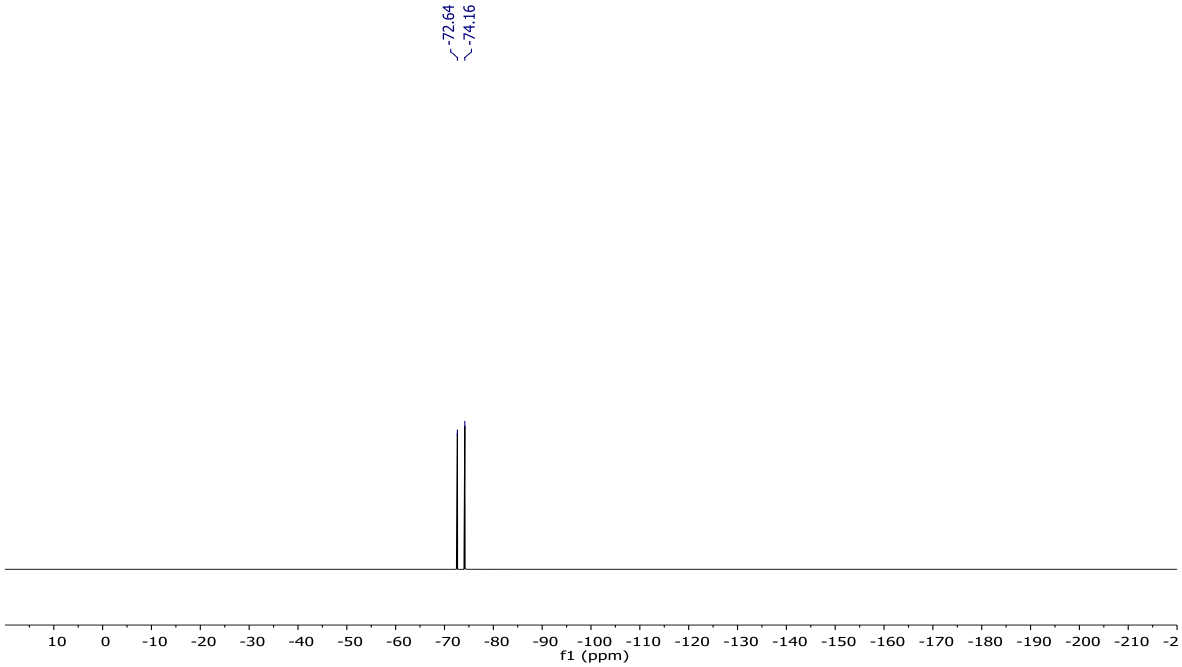
^{1}H-NMR (500 MHz, CD_3CN, 298 K):



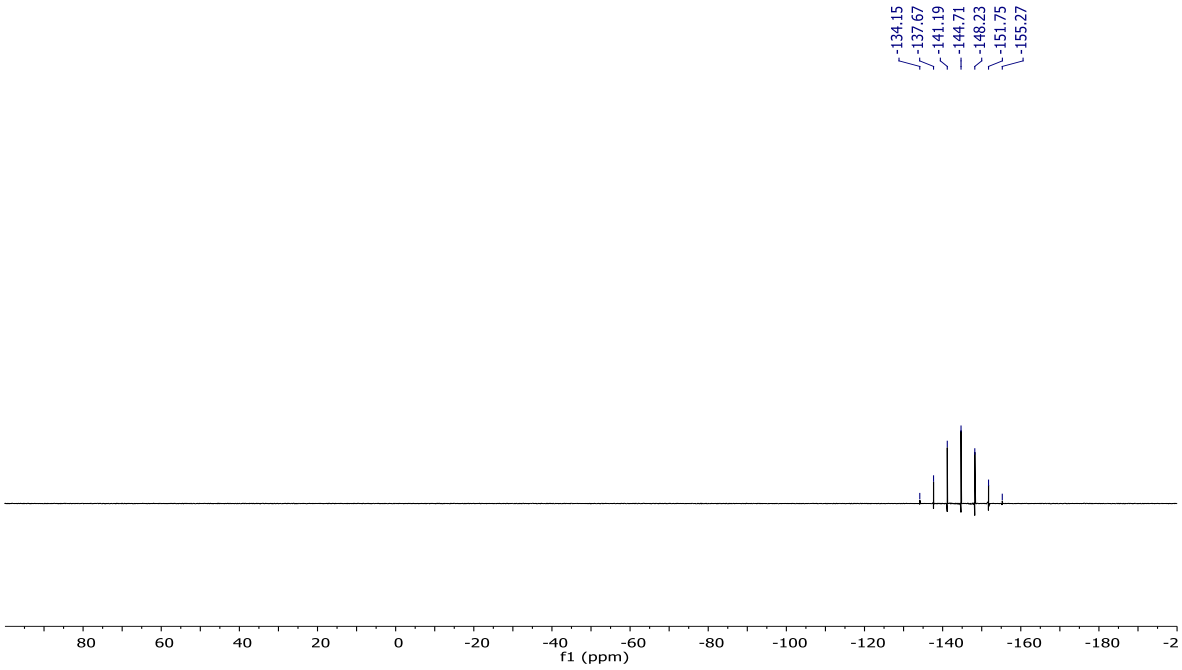
^{13}C-NMR (101 MHz, CD_3CN, 300 K):



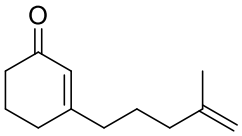
^{19}F-NMR (471 MHz, CD_3CN, 300 K):



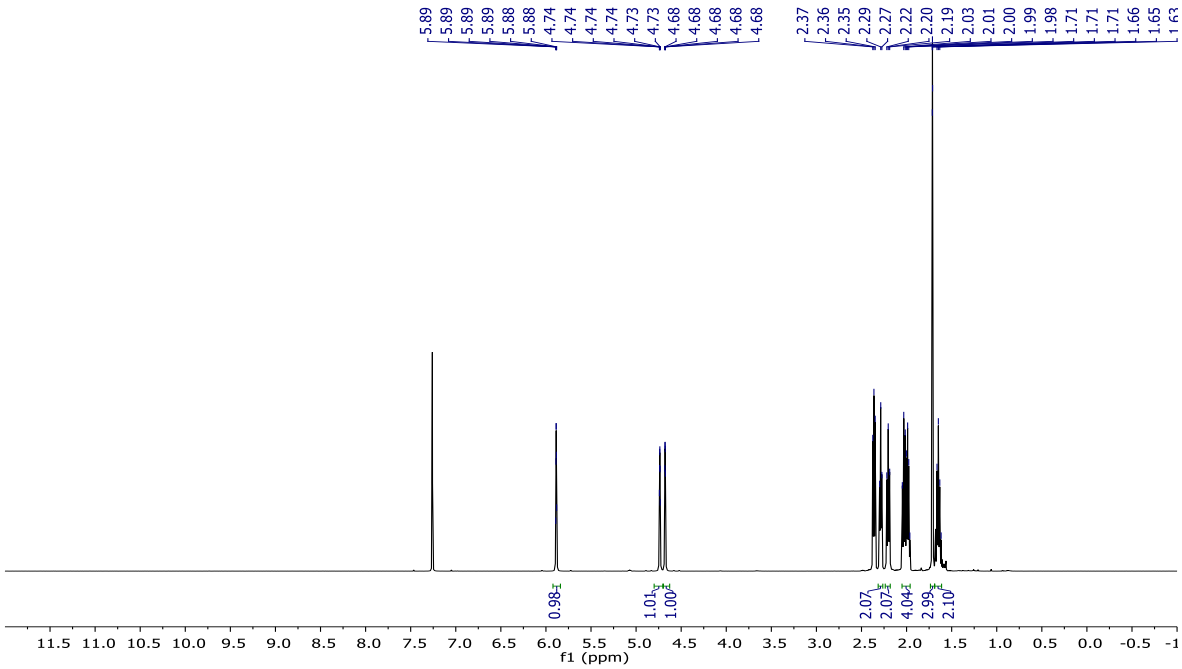
^{31}P-NMR (203 MHz, CD_3CN, 300 K):



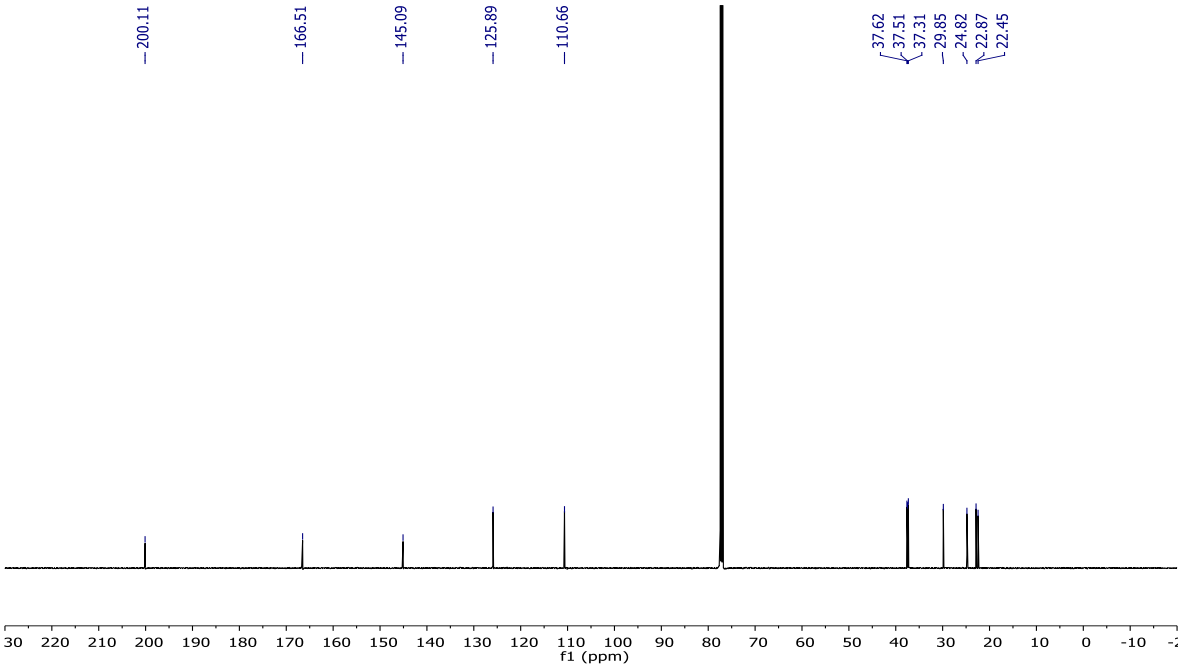
3-(4-Methylpent-4-en-1-yl)cyclohex-2-en-1-one (S1)



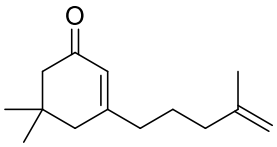
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K):



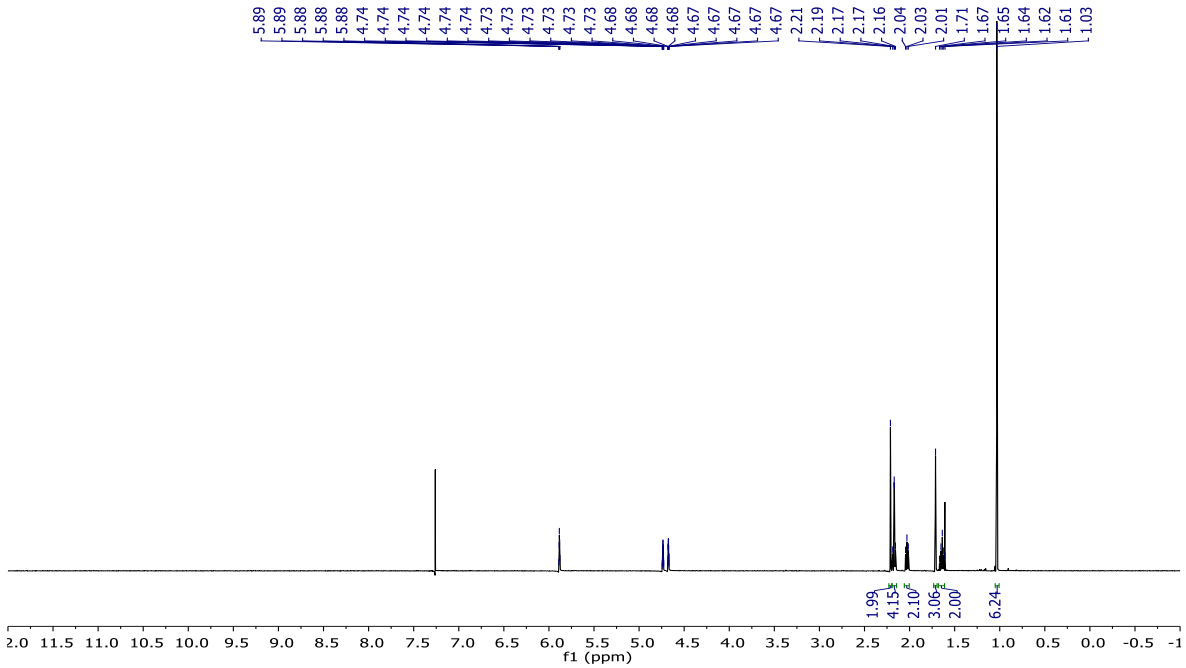
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K):



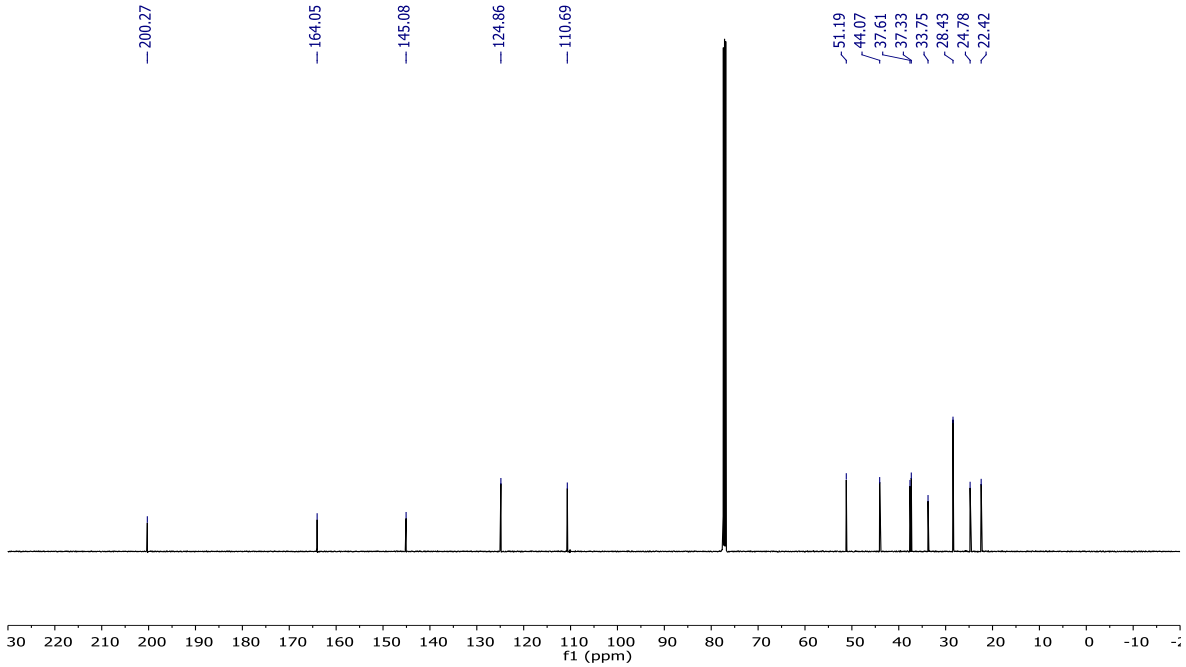
5,5-Dimethyl-3-(4-methylpent-4-en-1-yl)cyclohex-2-en-1-one (S2)



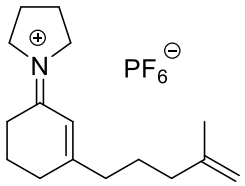
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K):



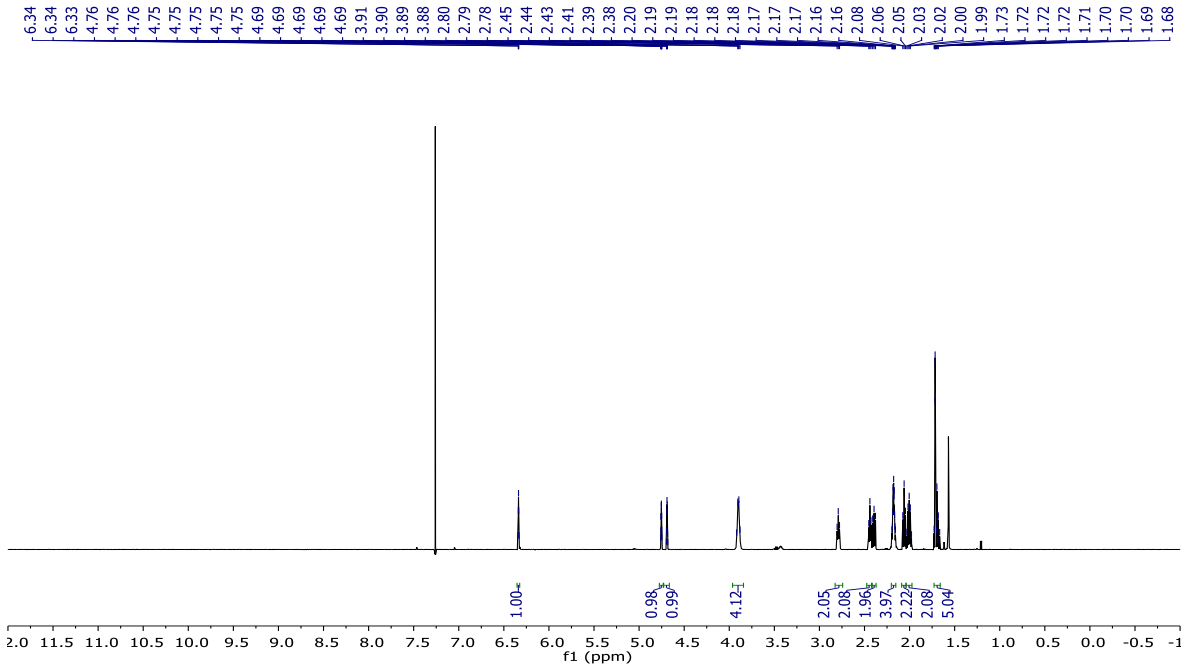
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K):



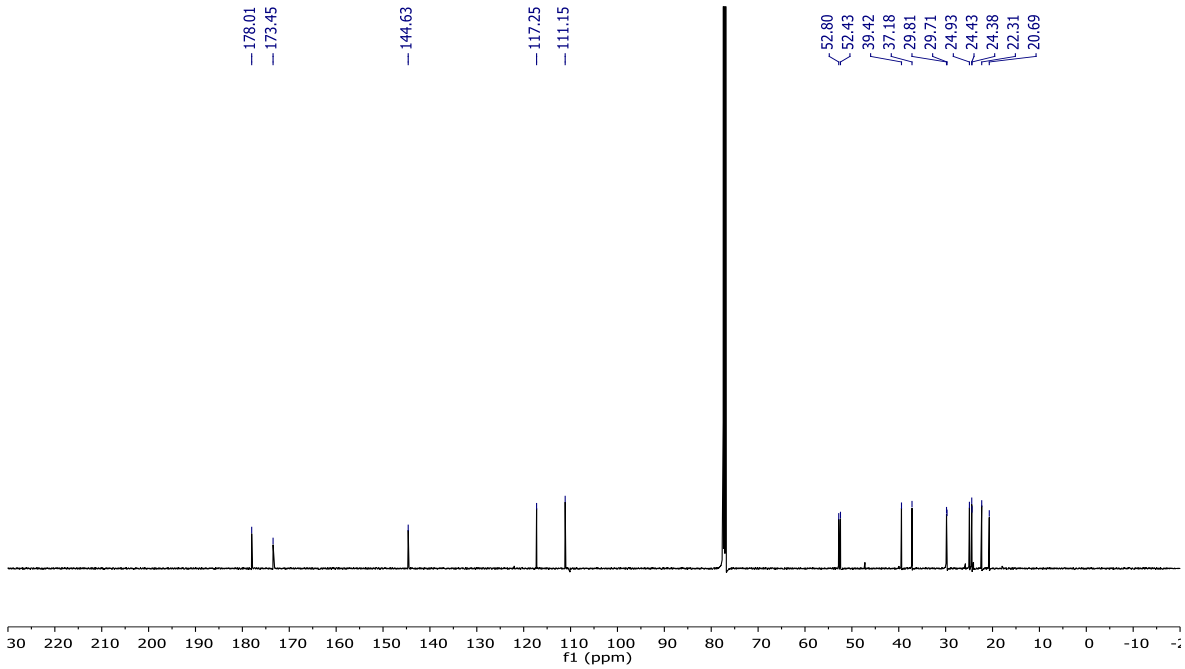
1-[3-(4-Methylpent-4-en-1-yl)cyclohex-2-en-1-ylidene]pyrrolidin-1-ium hexafluorophosphate (8a)



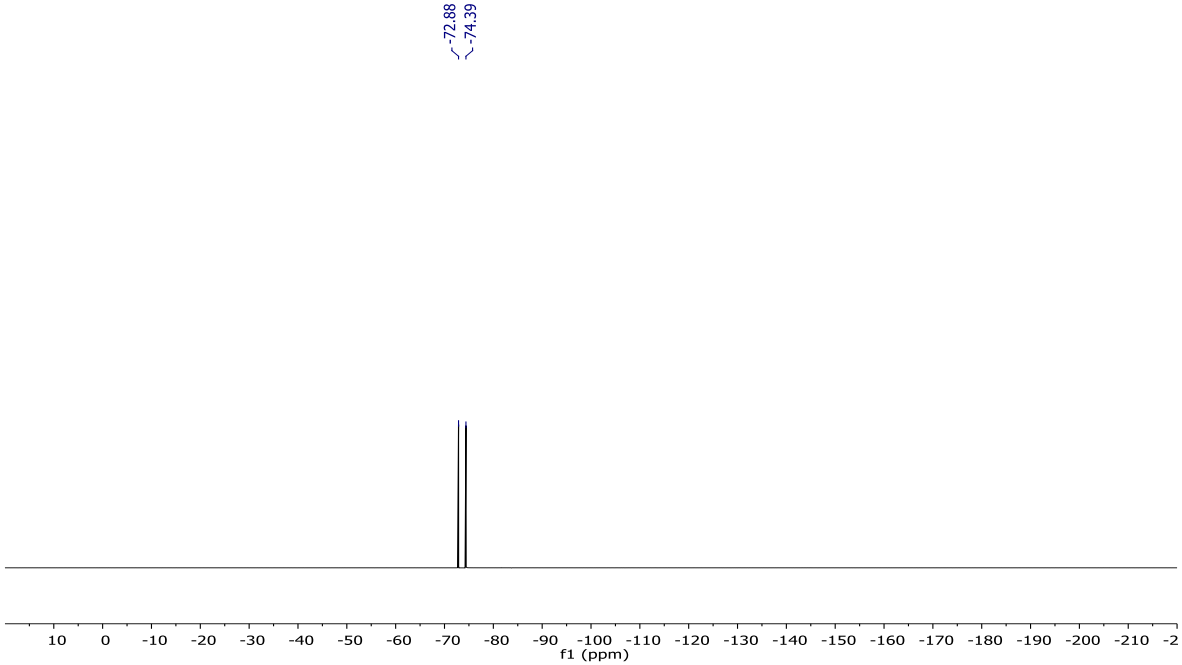
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K):



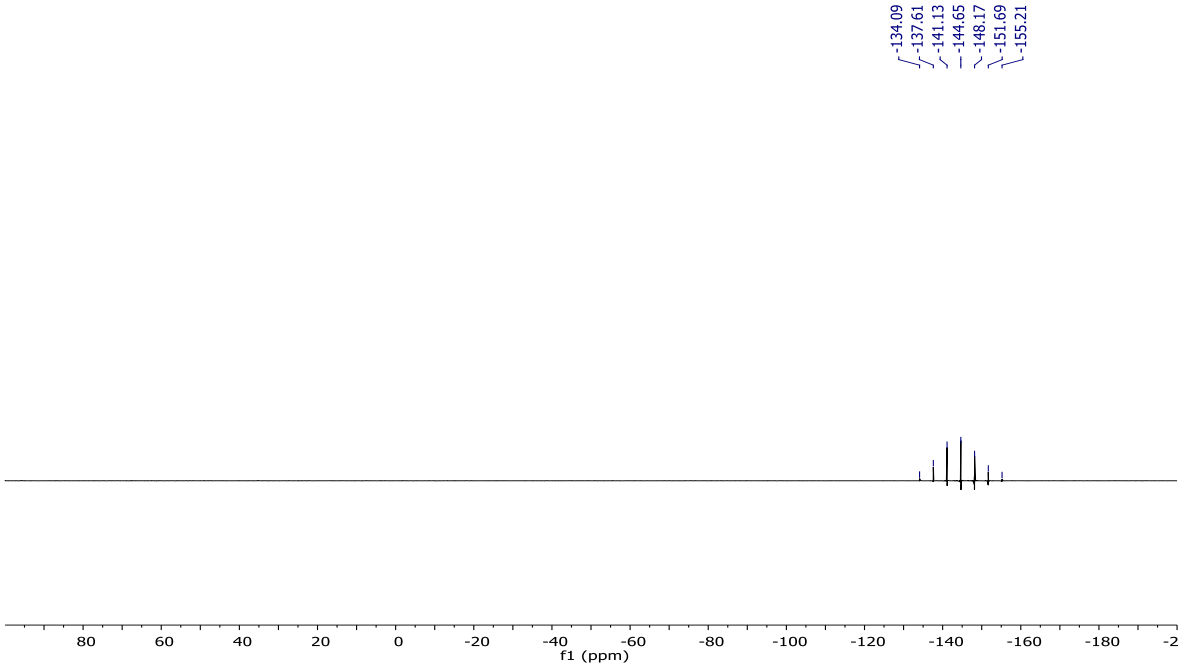
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K):



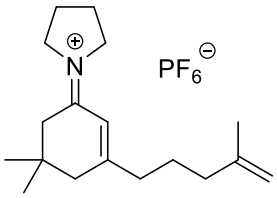
^{19}F-NMR (471 MHz, $CDCl_3$, 300 K):



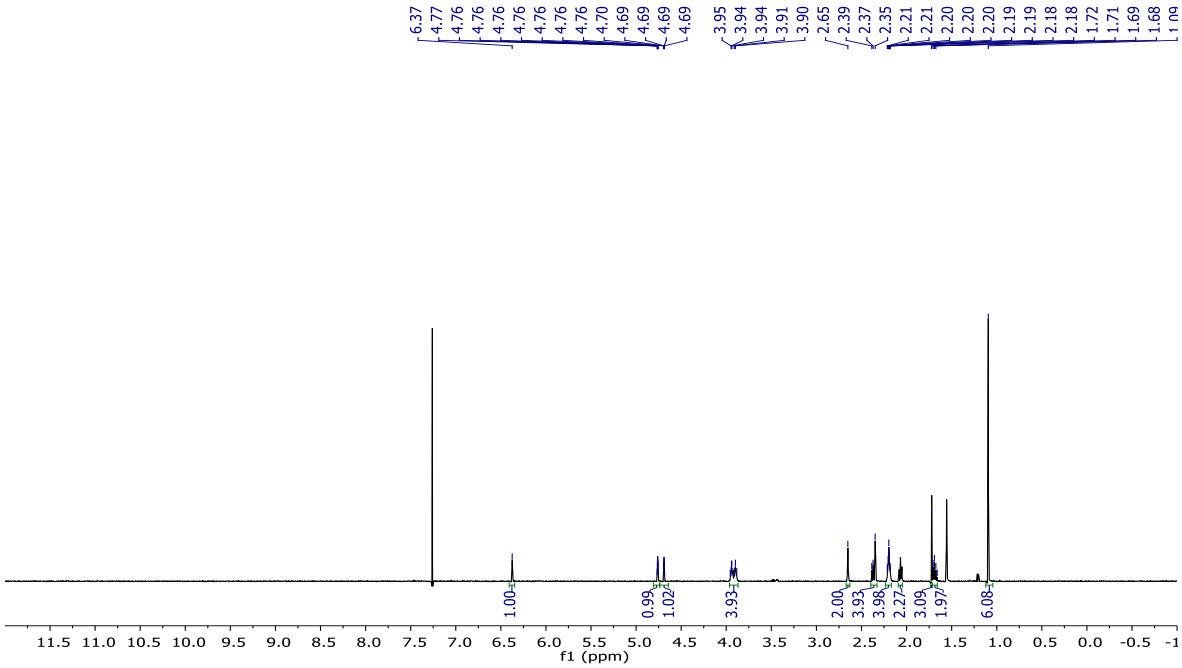
^{31}P-NMR (203 MHz, $CDCl_3$, 300 K):



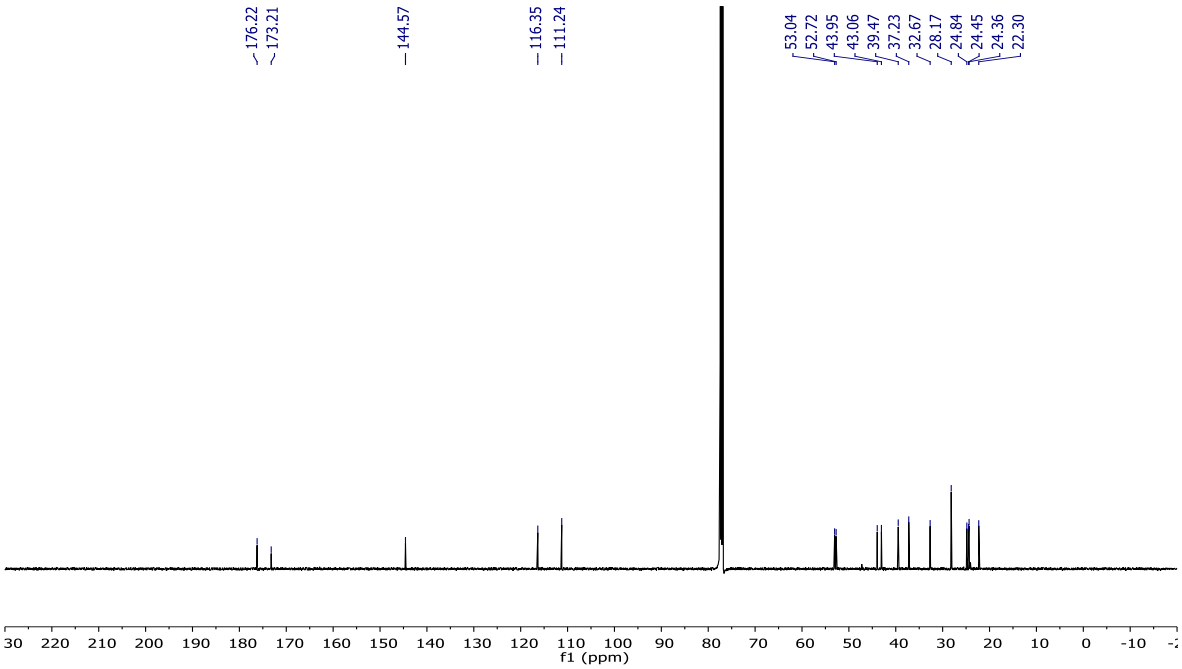
1-[5,5-Dimethyl-3-(4-ethylpent-4-en-1-yl)cyclohex-2-en-1-ylidene]pyrrolidin-1-ium hexafluorophosphate (8b)



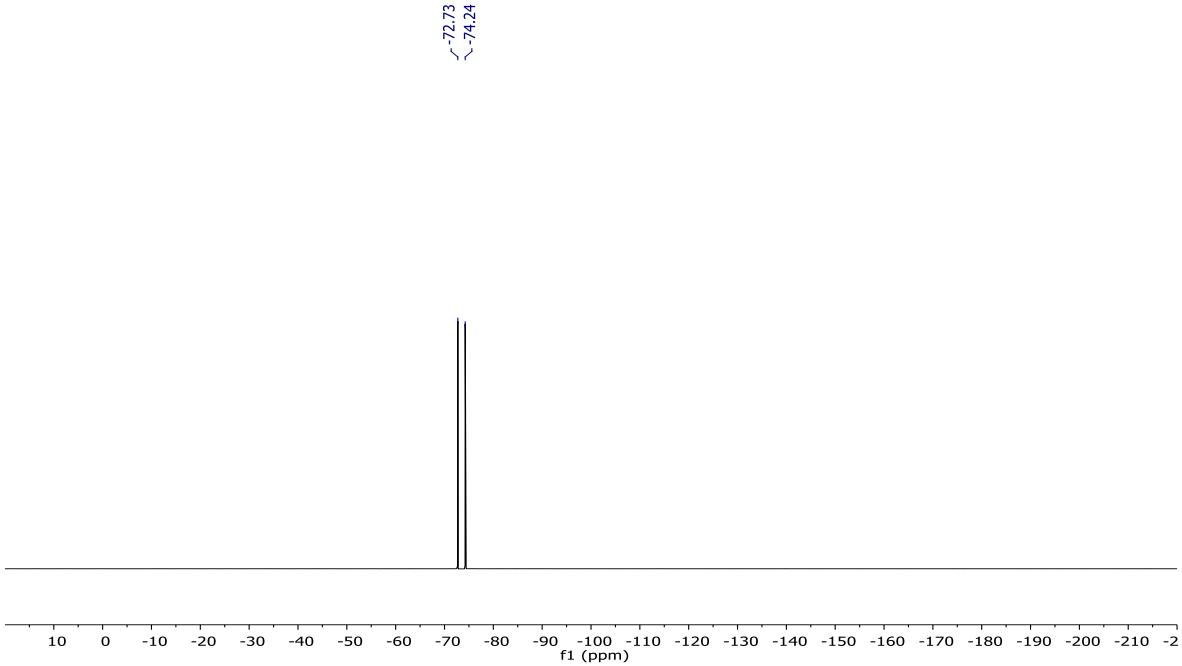
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K):



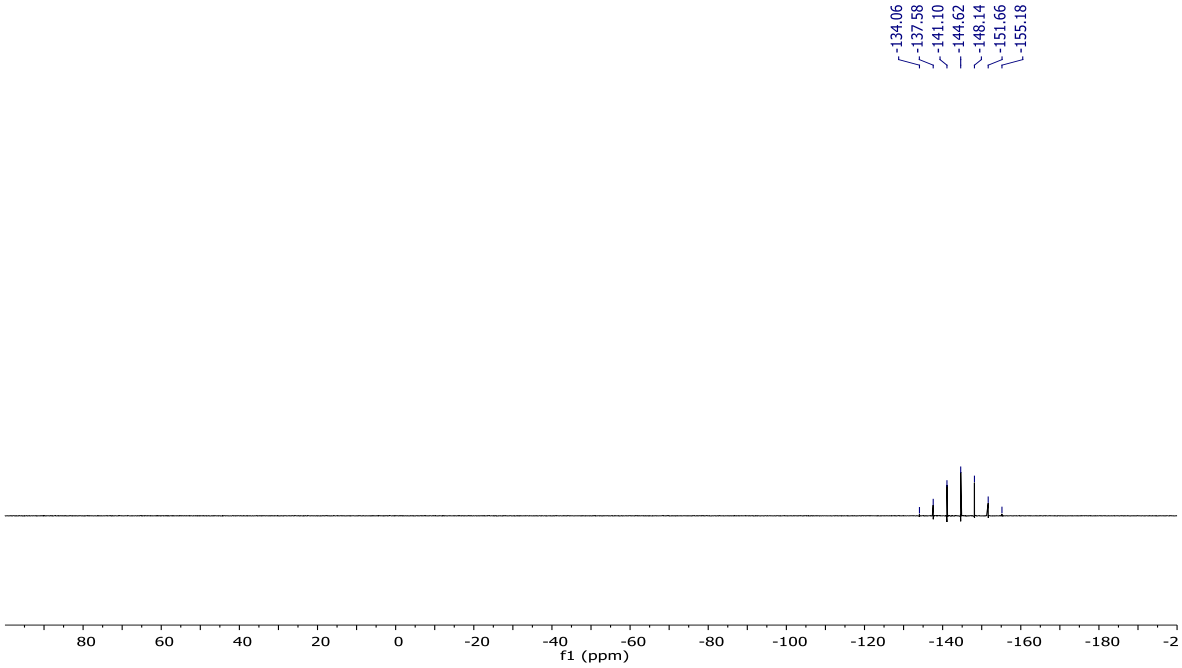
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K):



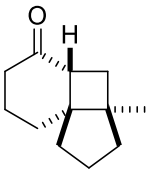
^{19}F-NMR (471 MHz, $CDCl_3$, 300 K):



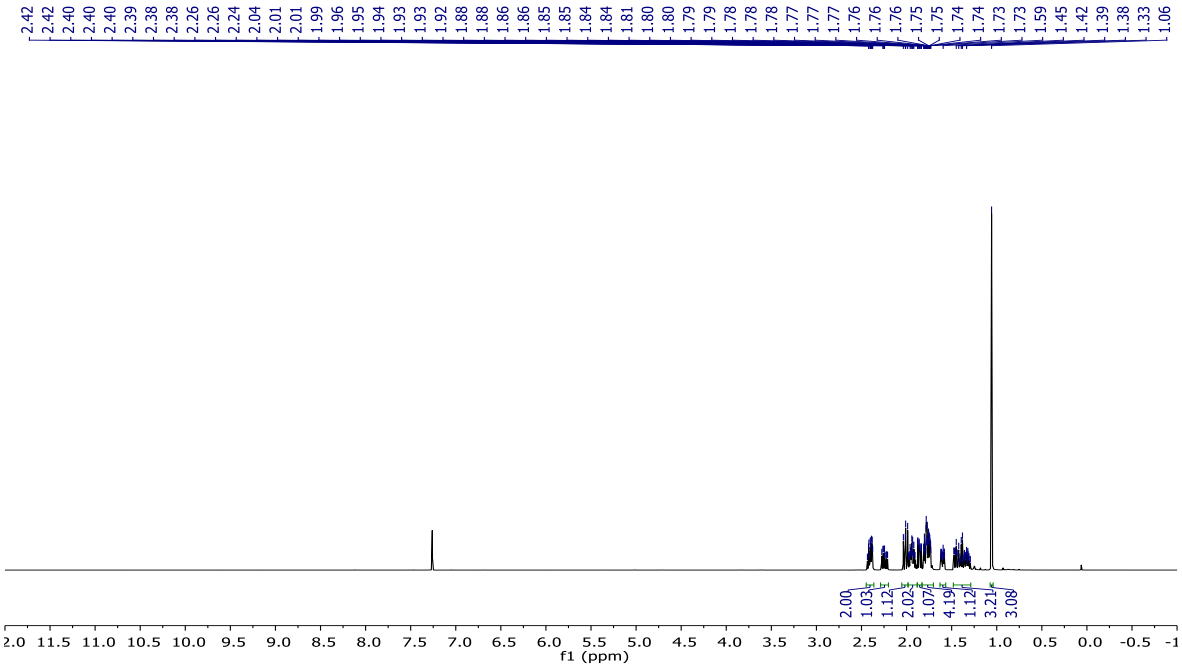
^{31}P-NMR (203 MHz, $CDCl_3$, 300 K):



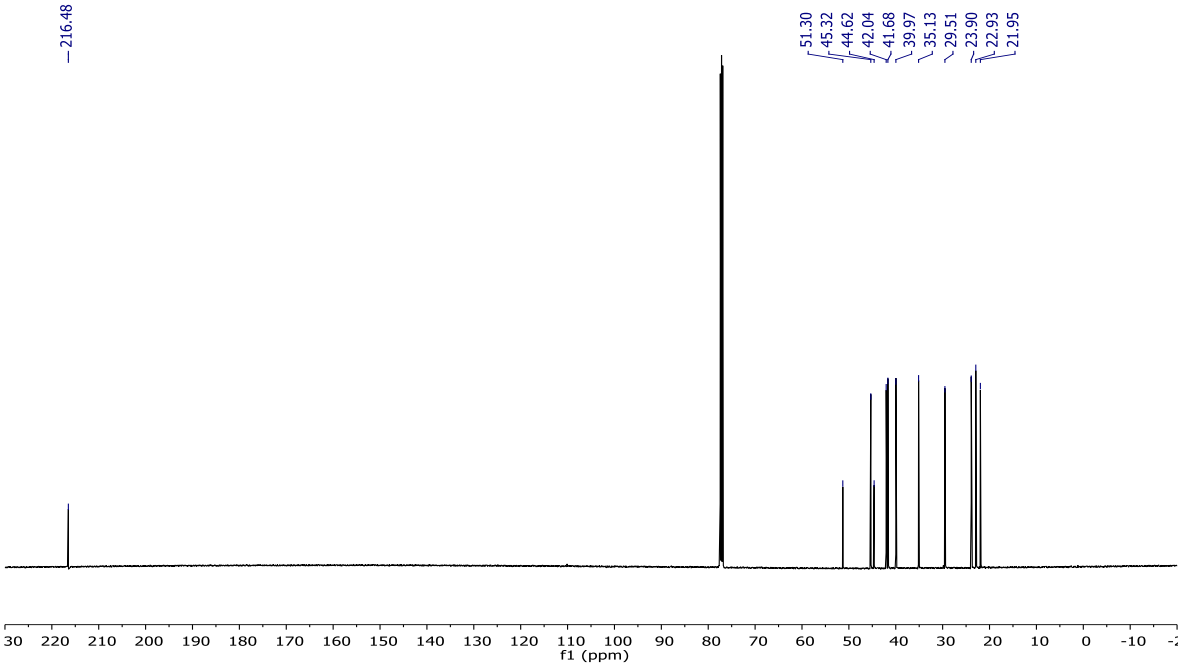
3a-Methyloctahydrocyclopenta[1,4]cyclobuta[1,2]benzen-5(6*H*)-one (*rac*-9a)



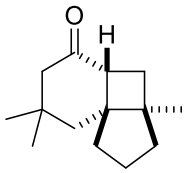
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K):



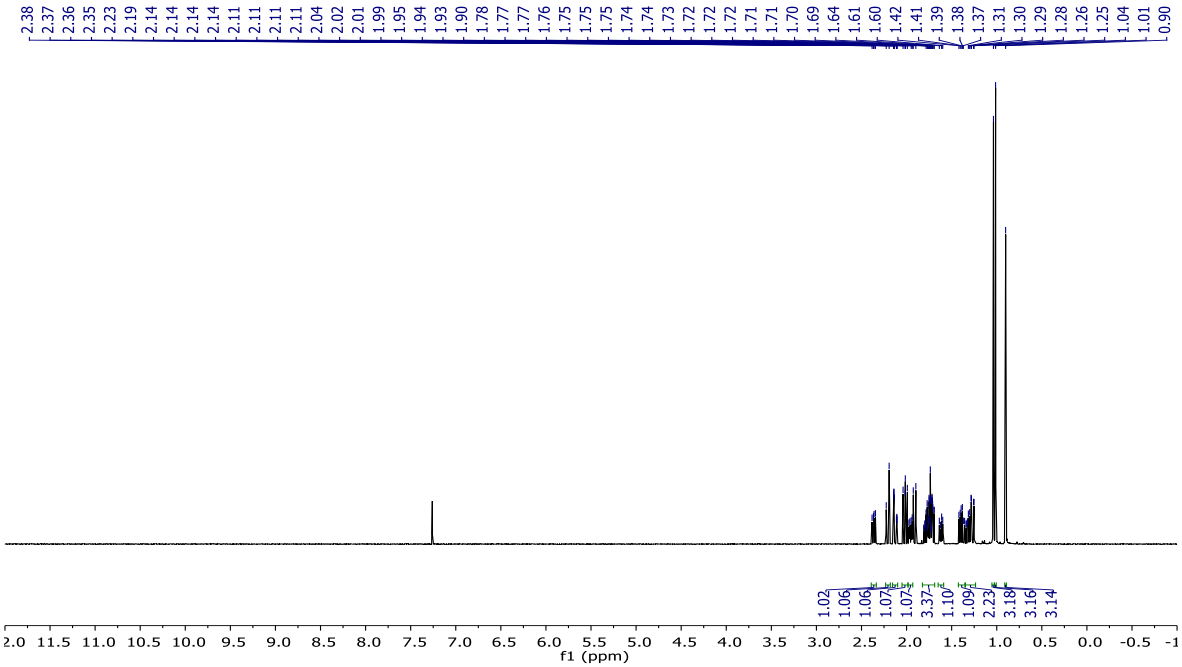
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K):



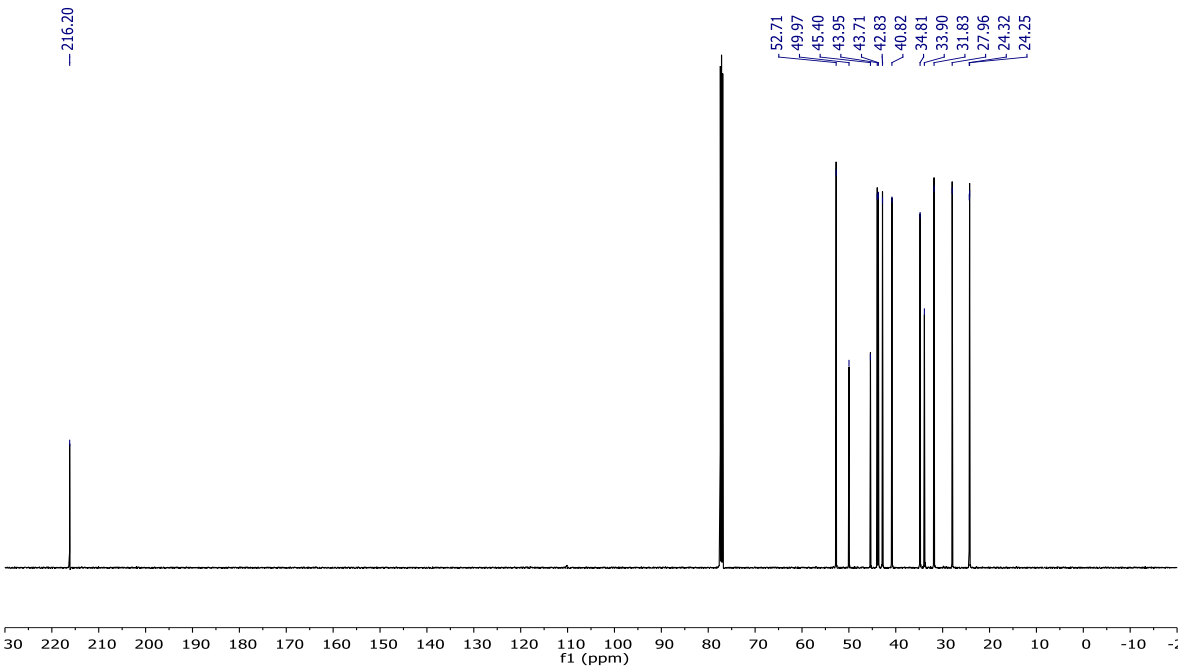
3a,7,7-Trimethyloctahydrocyclopenta[1,4]cyclobuta[1,2]benzen-5(6*H*)-one (*rac*-9b)



^{1}H-NMR (500 MHz, $CDCl_3$, 298 K):

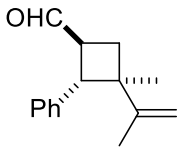


^{13}C-NMR (126 MHz, $CDCl_3$, 300 K):

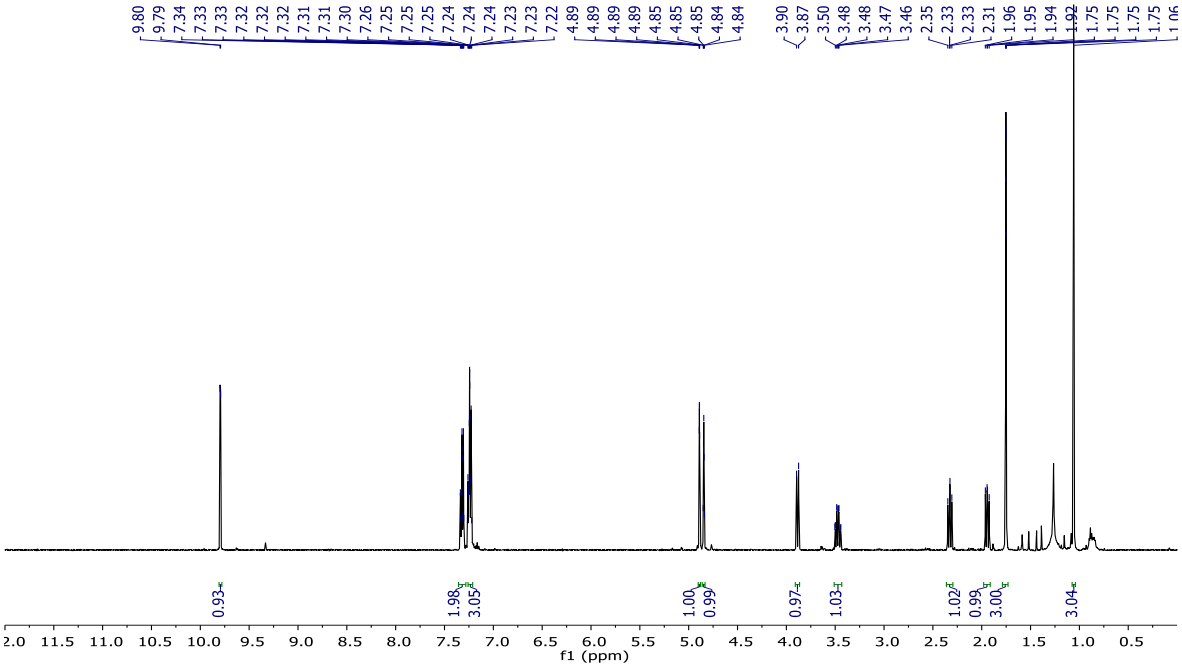


3-Methyl-2-phenyl-3-(prop-1-en-2-yl)cyclobutane-1-carbaldehyde (*rac*-12)

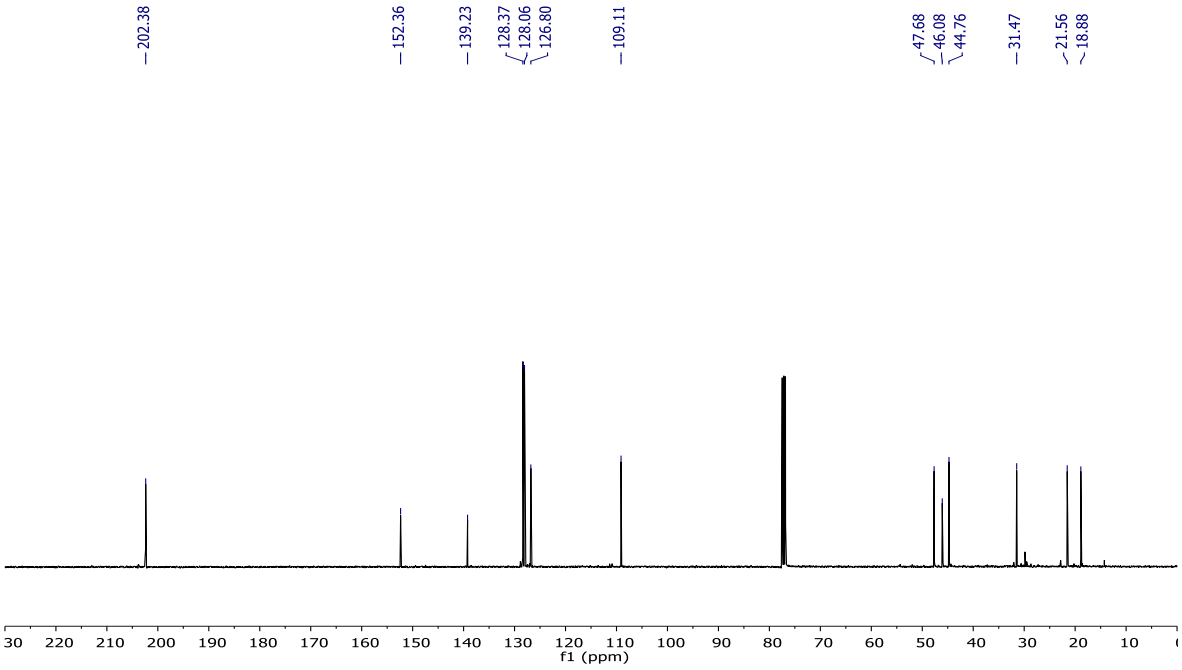
Major diastereoisomer



^{1}H-NMR (500 MHz, $CDCl_3$, 298 K):

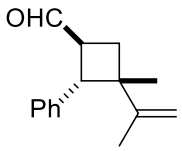


^{13}C-NMR (101 MHz, $CDCl_3$, 300 K):

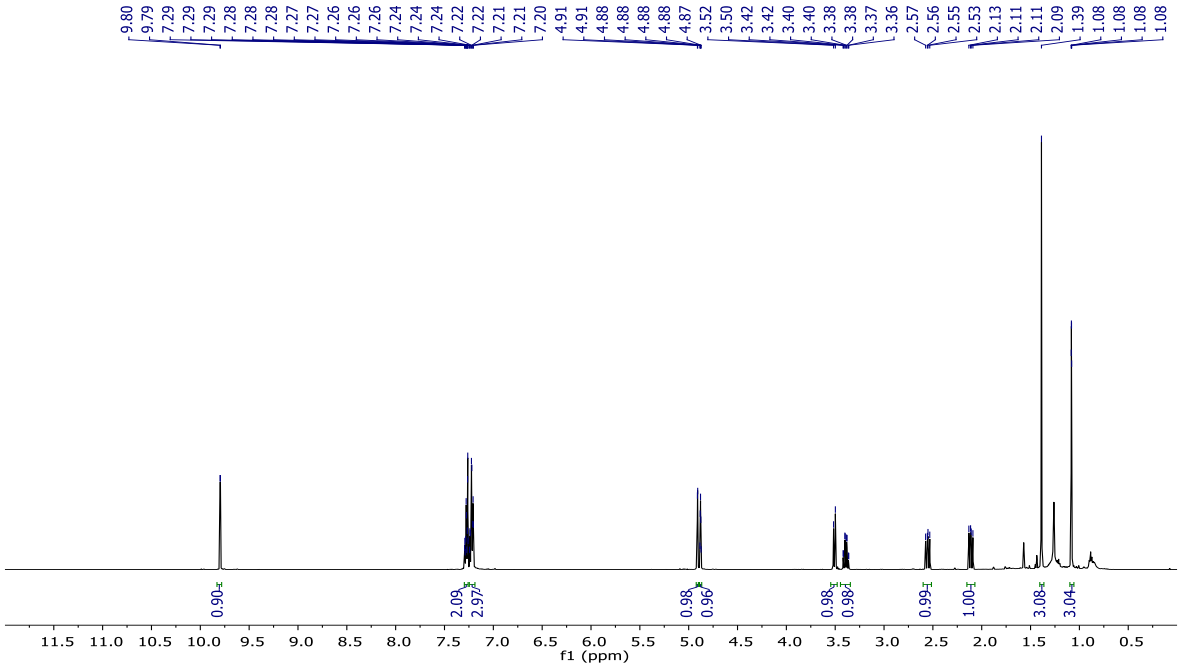


3-Methyl-2-phenyl-3-(prop-1-en-2-yl)cyclobutane-1-carbaldehyde (*rac*-12)

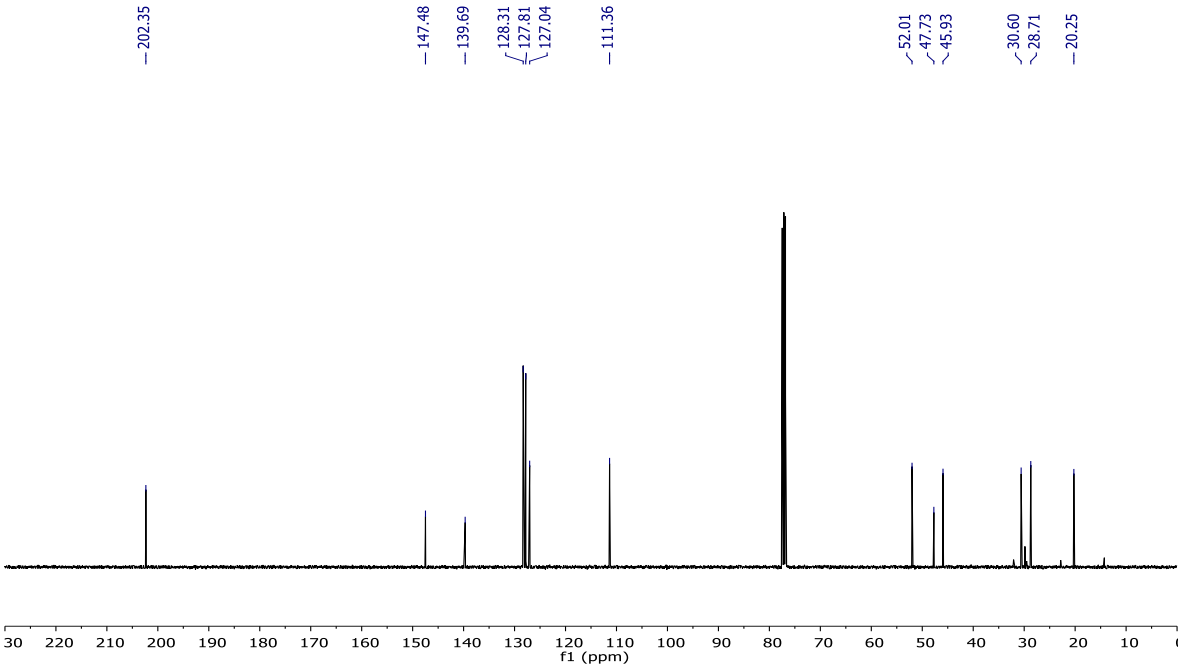
Minor diastereoisomer



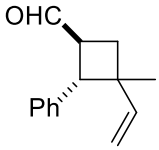
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K):



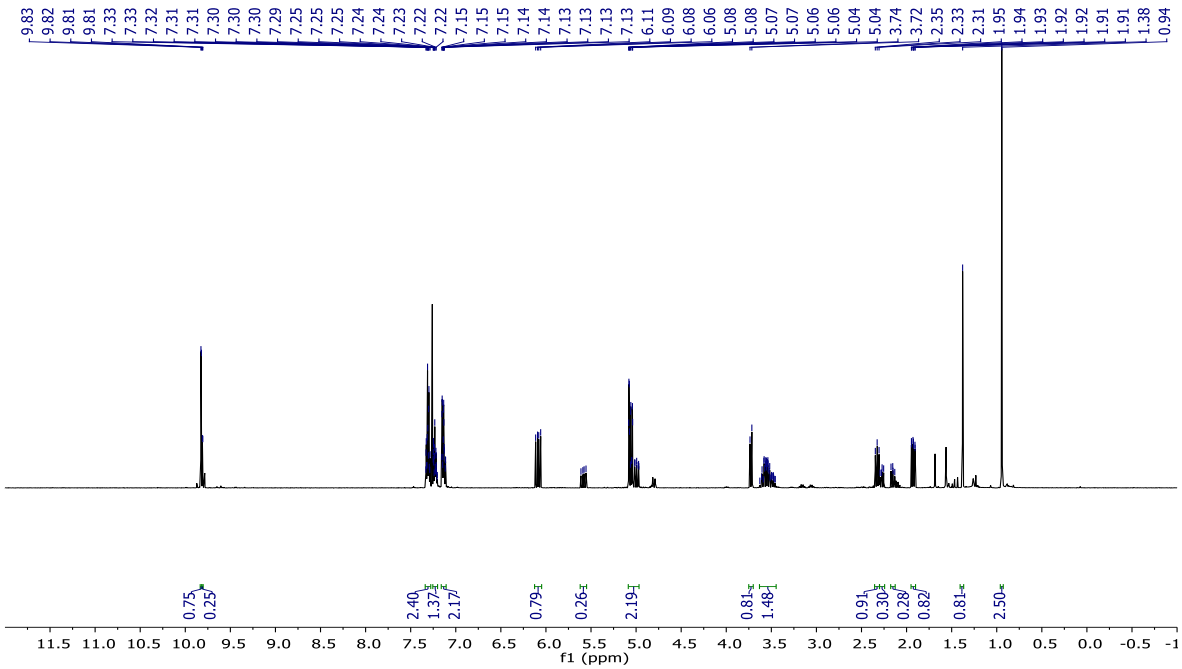
^{13}C-NMR (101 MHz, $CDCl_3$, 300 K):



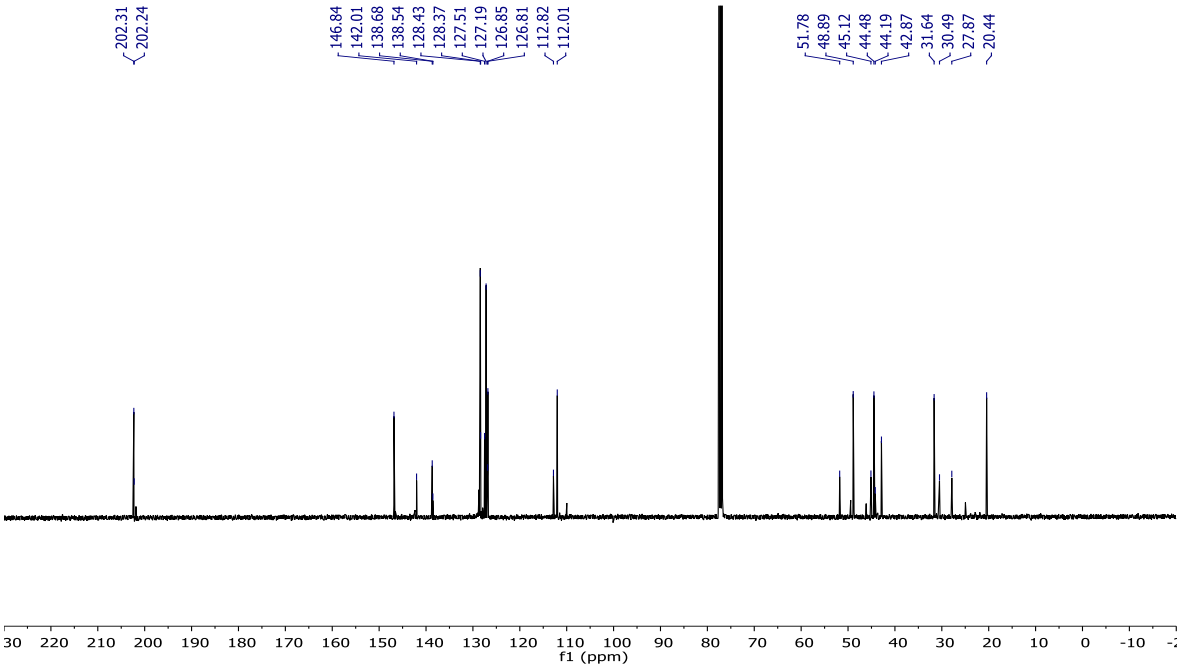
3-Methyl-2-phenyl-3-vinylcyclobutane-1-carbaldehyde (*rac*-13)



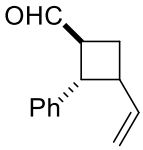
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K):



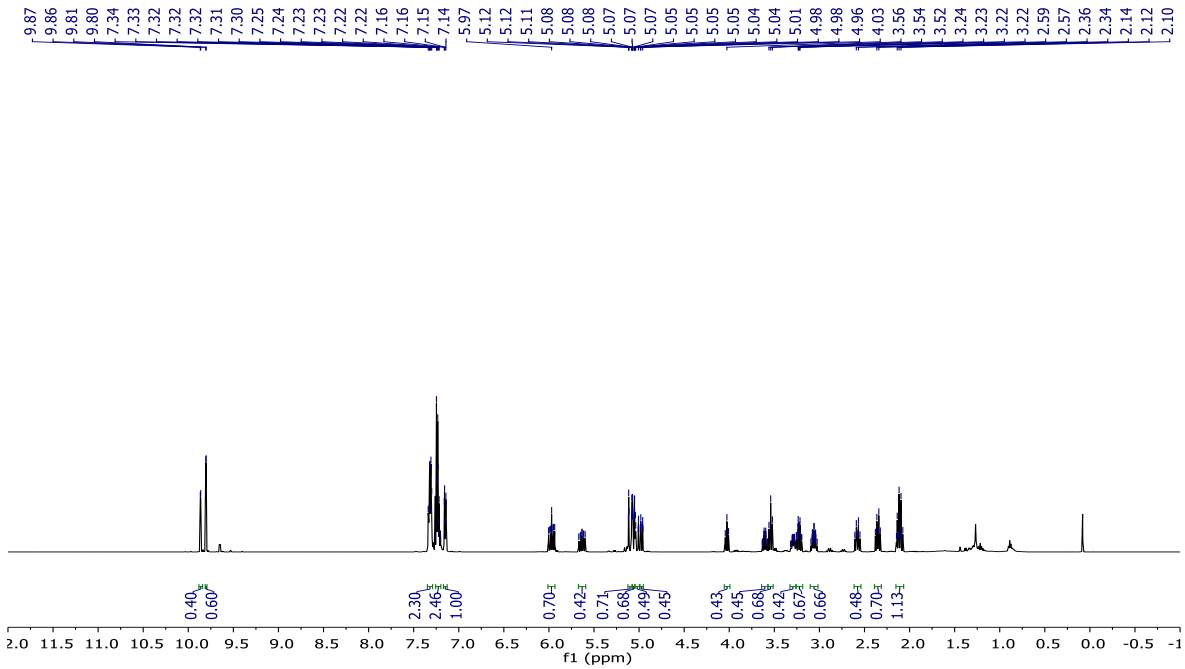
^{13}C-NMR (101 MHz, $CDCl_3$, 300 K):



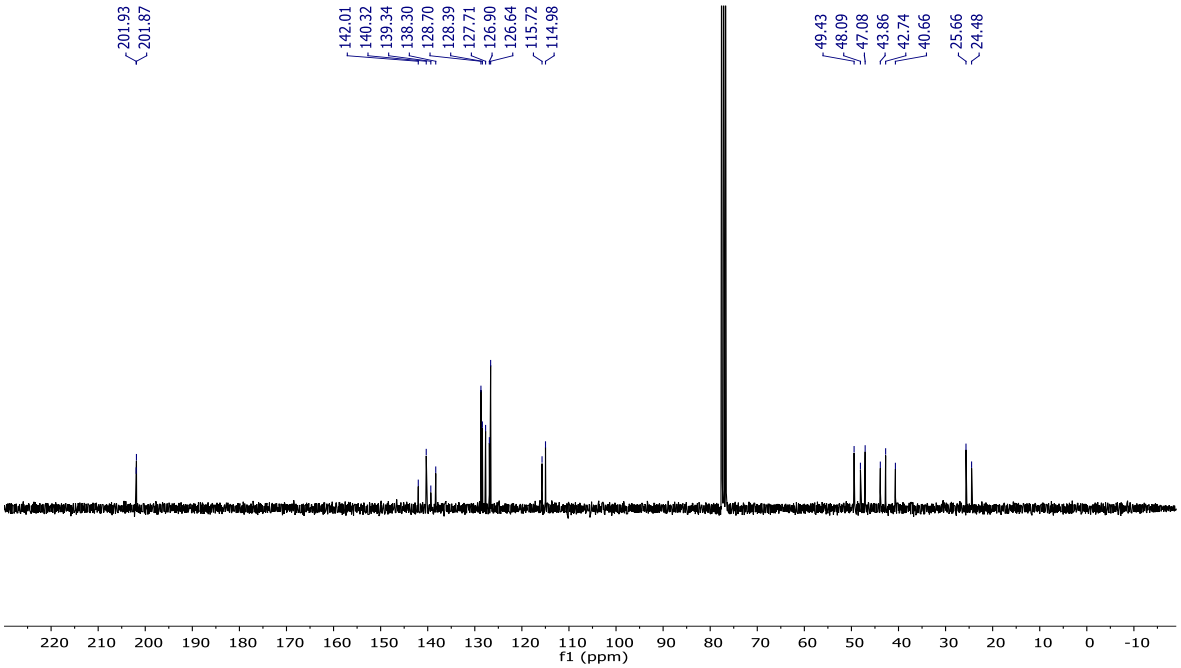
2-Phenyl-3-vinylcyclobutane-1-carbaldehyde (*rac*-14)



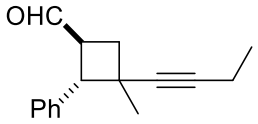
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K):



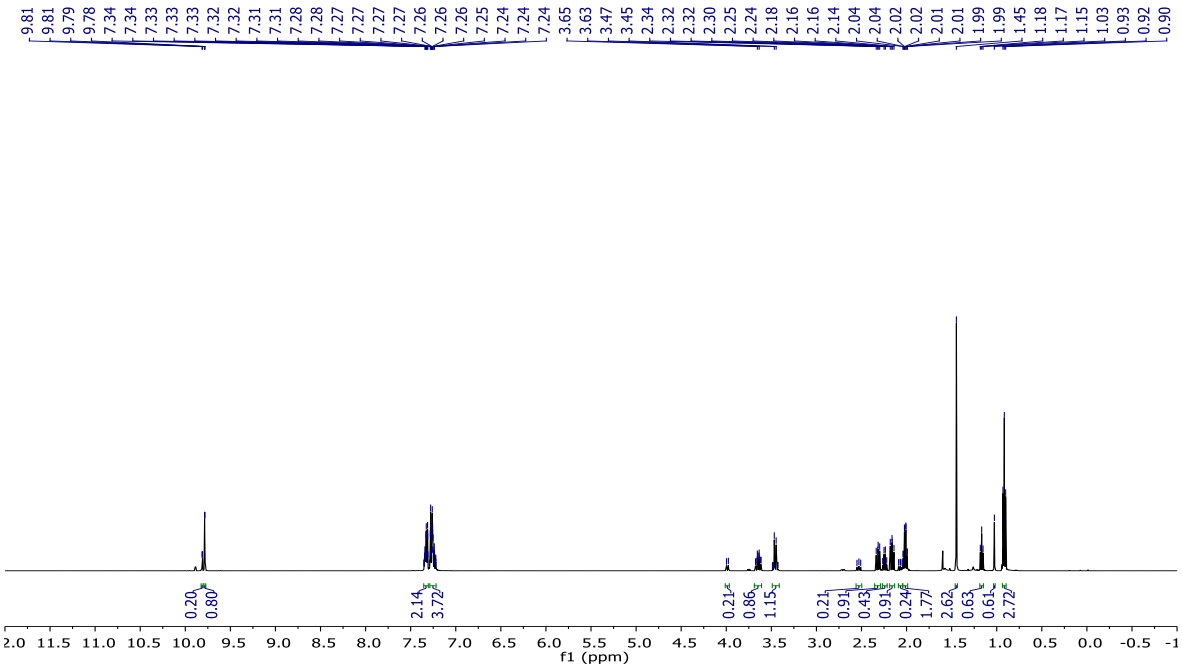
^{13}C-NMR (76 MHz, $CDCl_3$, 300 K):



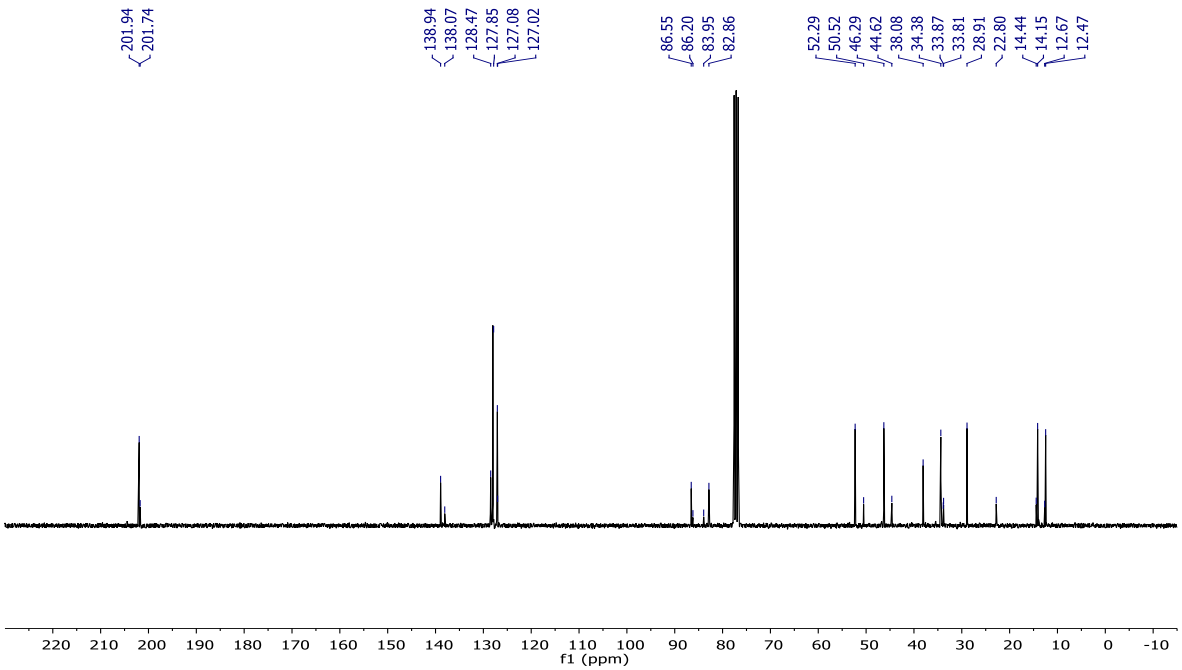
3-(But-1-yn-1-yl)-3-methyl-2-phenylcyclobutane-1-carbaldehyde (*rac*-15)



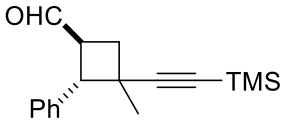
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K):



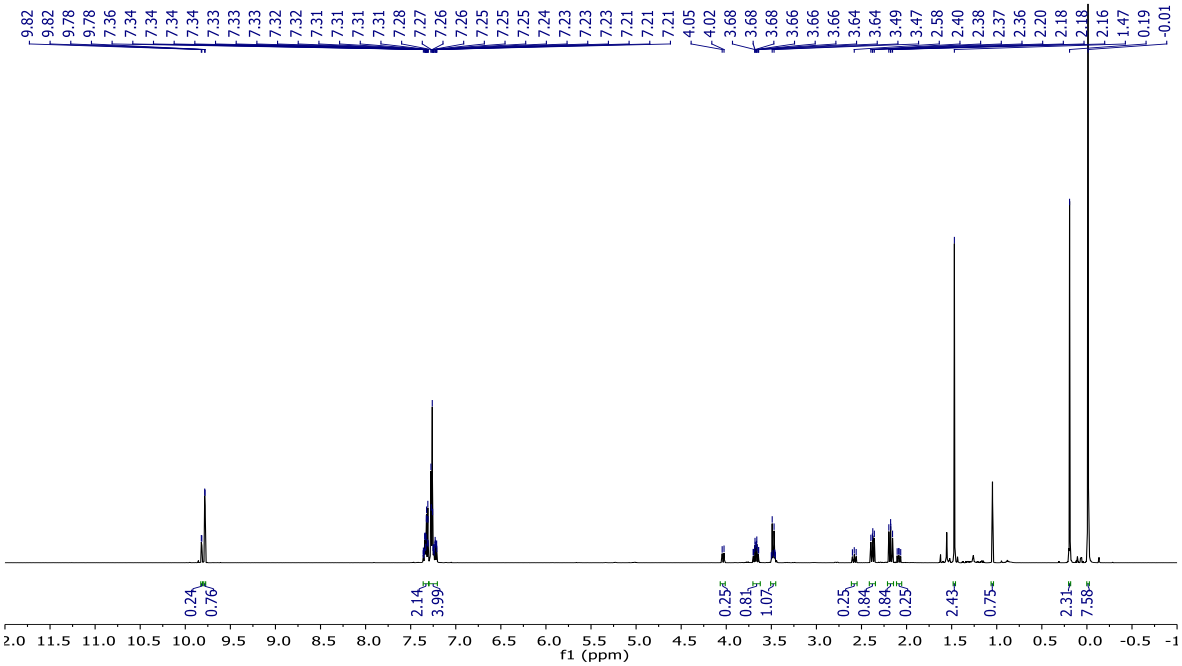
^{13}C-NMR (76 MHz, $CDCl_3$, 300 K):



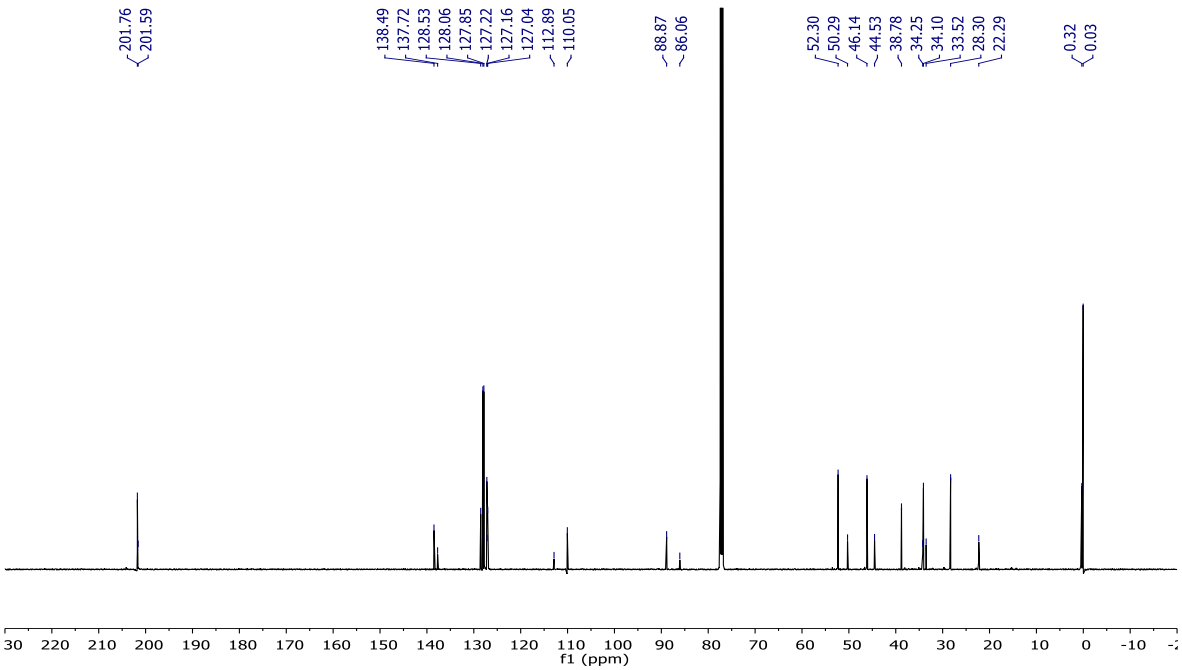
3-Methyl-2-phenyl-3-[(3-trimethylsilyl)ethynyl]cyclobutane-1-carbaldehyde (*rac*-16)



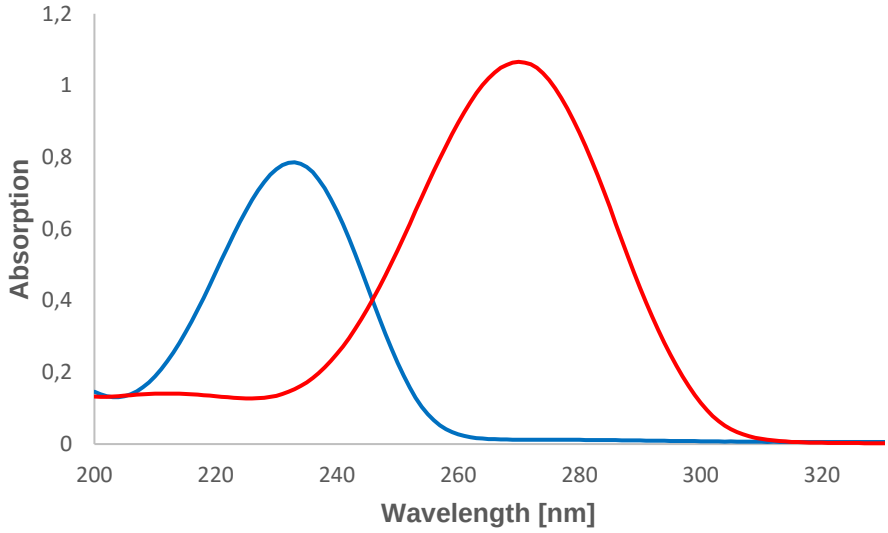
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K):



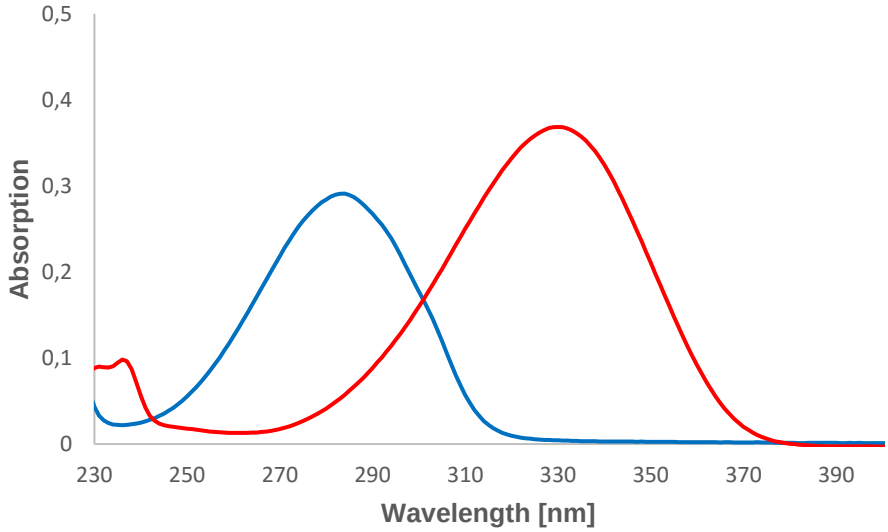
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K):



9. UV/Vis-Spectra

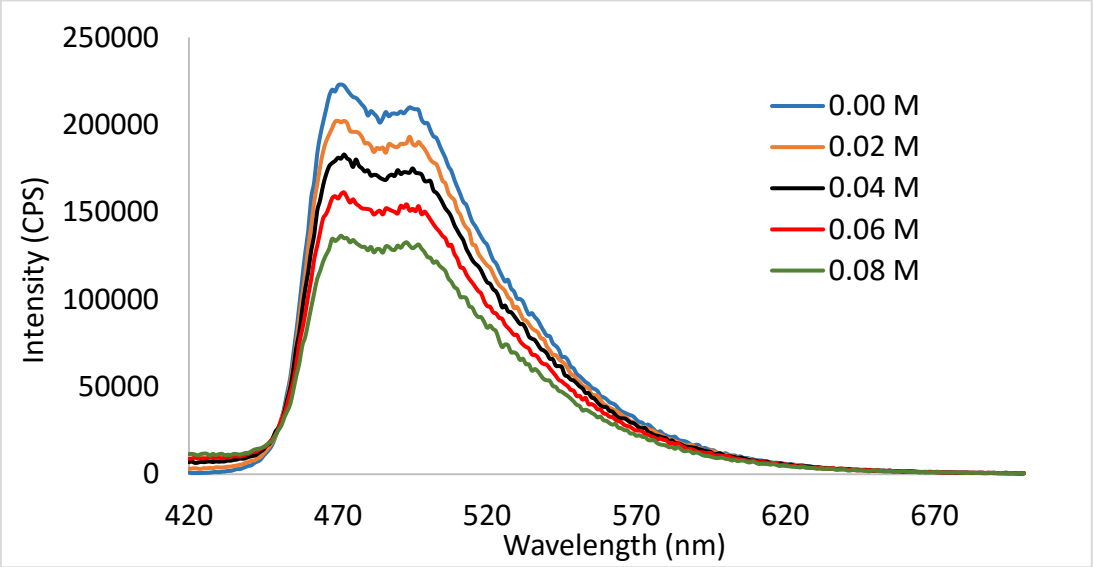


UV/Vis-spectra of enone **1** ($\varepsilon_{233\ nm}$ = 15650 L/mol^{-1}cm^{-1}, $\varepsilon_{320\ nm}$ = 70 L/mol^{-1}cm^{-1}) and eniminium ion **2** ($\varepsilon_{270\ nm}$ = 21320 L/mol^{-1}cm^{-1}) in MeCN [c = 0.5 mM].

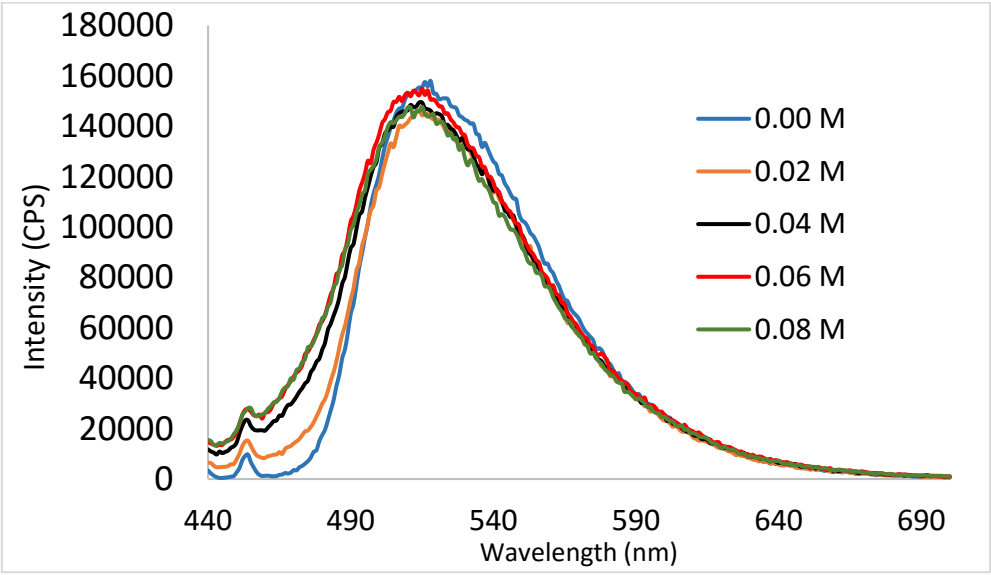


UV/Vis-spectra of aldehyde **10** ($\varepsilon_{284\ nm}$ = 29100 L/mol^{-1}cm^{-1}) and iminium ion **11**, ($\varepsilon_{330\ nm}$ = 36840 L/mol^{-1}cm^{-1}) in MeCN [c = 0.1 mM].

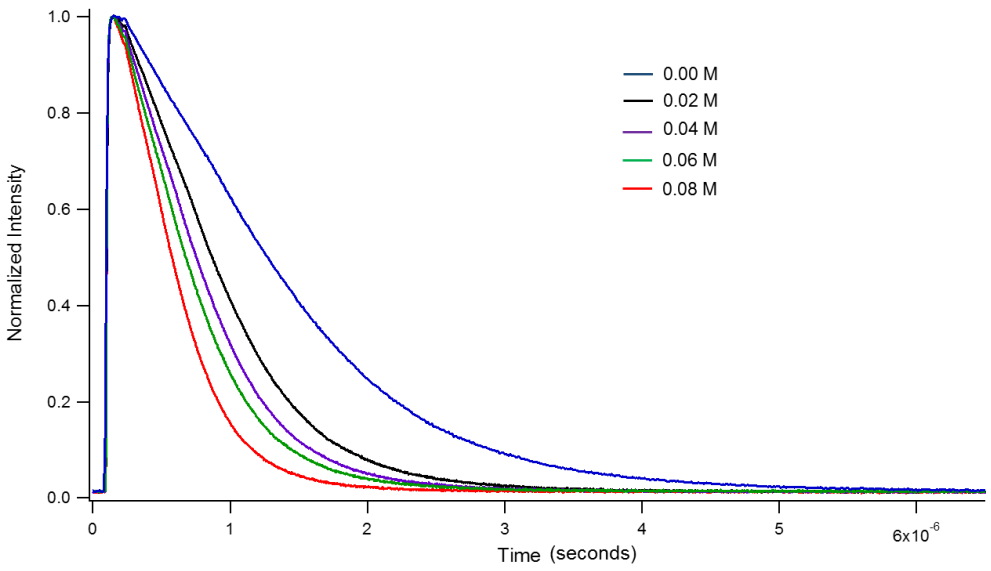
10. Luminescence Measurements



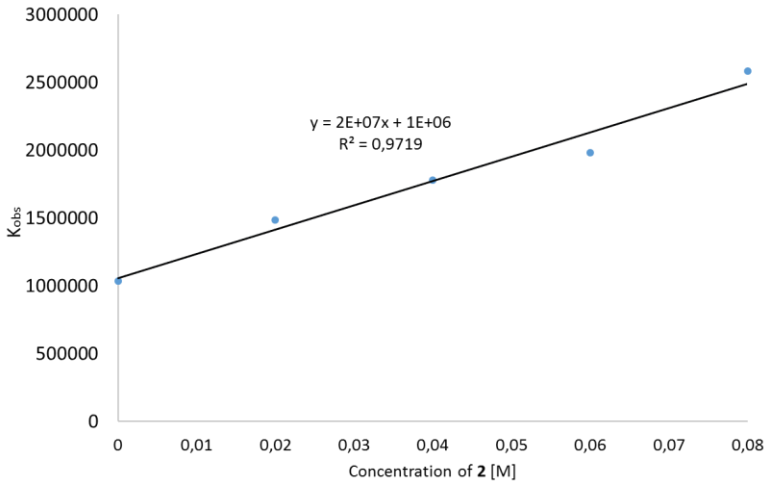
Emission spectra of [Ir(dF(CF_3)ppy)bpy] (PF_6) (**6**) with varying concentration of iminium ion **2**. A 10μM solution of **6** was prepared and arduously degassed for 30 minutes. For each run, 1.4 mL of the stock solution was placed in a cuvette with varying amounts (0.00 - 0.08 M) of the iminium ion added to the cuvette. We used 370 nm as the excitation wavelength and observed emission spectra from 420-700 nm. Both excitation and emission bandwidth was set to 1 nm for each sample.



Emission spectra of $Ir(ppy)_3$ was recorded using analogous conditions as that of [Ir(dF(CF_3)ppy)bpy] (PF_6) (**6**). We prepared a 10μM solution of $Ir(ppy)_3$ and used 400 nm as the excitation wavelength and observed emission spectra from 440-700 nm. Both excitation and emission bandwidth was set to 1 nm for each sample.



Kinetic lifetimes of FIrPic (**5**) with varying concentrations of iminium ion **2** using PL2250 Series laser from Ekspla equipped with a LeCroy waverunner 6030 oscilloscope 2.5 GS (4 ns in between two points) and H7732-10 Hamamatsu PMT (approximately 50 ns). Excitation wavelength was set to 380 nm and we detected all wavelengths (global) by placing a 410 nm filter in front of the PMT to record luminescent lifetimes. Each concentration point was averaged to 100 scans.



Kinetic plot using the following equation to reveal the dynamic quenching constant (*k*q):

$k_{obs} = 1/\tau^{o} + k_q c_q$

$k_q = 2 \times 10^7\ M^{-1}\ s^{-1}$ for FIrPic under our instrumental setup.

11. References

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[3] For emission spectra of the 366 nm lamps, see: C. Brenninger, A. Pöthig, T. Bach, *Angew. Chem. Int. Ed.* **2017**, *56*, 4337-4341.

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