Electronic Supplementary Information for:

Reversal of reaction type selectivity by Lewis acid coordination: the *ortho* photocycloaddition of 1- and 2-naphthaldehyde

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Inhalt

1. General information

All air and moisture sensitive reactions were carried out in flame-dried glassware under a positive pressure of dry argon (4.8, purity 99.998%) using standard *Schlenk* techniques.

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

For moisture sensitive reactions, tetrahydrofuran (THF) 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)

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.

benzene: *Sigma Aldrich*, 99.8%, anhydrous.

toluene: *Acros Organics*, 99.5% extra dry, over molecular sieves.

For photochemical reactions, dry dichloromethane and dry acetonitrile were degassed by four freeze-pump-thaw cycles and stored over activated molecular sieve (dichloromethane: 4 Å molecular sieve, acetonitrile: 3 Å molecular sieve). *n*-Hexane was distilled from CaH_2, degassed by four freeze-pump-thaw cycles and stored over 3 Å activated molecular sieves.

Olefins for Lewis acid catalysed photoreactions were prepared as follows: 2,3-Dimethyl-2-butene (≥ 99%, *Sigma Aldrich*) was degassed by four freeze-pump-thaw cycles and stored under argon before use. Cyclopentene (96 %, *Sigma Aldrich*) was distilled, filtered over activated, basic aluminium oxide, degassed by four freeze-pump-thaw cycles and stored under

argon prior to use. (*E*)- and (*Z*)-hex-3-ene [(*E*)-**17** >99.0%, *TCI*; (*Z*)-**17** >97.0%, *TCI*] were filtered over activated, basic aluminium oxide prior to use.

In the non-Lewis acid catalysed photoreactions 2,3-dimethyl-2-butene (98%, *Sigma Aldrich*) was distilled and used without further purification.

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 mixtures.

Photochemical experiments at 300 nm and 366 nm were carried out in flame-dried *Duran* tubes (diameter = 1 cm) in a positive geometry setup (cylindrical array of 16 UV-A lamps, *Rayonet* RPR-3000, λ_{max} = 300 nm or Fluorescent light tube, UV-A, λ_{max} = 366 nm) with the sample placed in the center of the illumination chamber.

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.[1] If necessary the *Schlenk* tubes were cooled to −40 °C or −78 °C by using an *Huber* TC100E immersion cooler with ethanol as coolant.

Ice/water (0 °C) or dry ice/ethanol (−78 °C) were used as cooling baths.

2. Analytical methods

Melting points (M.p.) were determined using a *Kofler* heating bar designed by *L. Kofler* (*Reichert*) without correction or using a *Büchi* M-510 melting point apparatus, with range quoted to the nearest whole number.

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 [$KMnO_4$] and/or cerium ammonium molybdate solution [CAM] followed by heat treatment.

> $KMnO_4$-staining solution: potassium permanganate (3.00 g), potassium carbonate (20.0 g) and 5% aqueous sodium hydroxide solution (5.00 mL) in water (300 mL).
>
> CAM-staining solution: cerium sulfate heptahydrate (1.00 g), ammonium molybdate (25.0 g), sulfuric acid (25.0 mL) in water (250 mL).

Infrared spectra (IR) were recorded on a *Perkin Elmer* Frontier Optica+SP10 spectrometer by ATR technique. The signal intensity is assigned using the following abbreviations: vs (very strong), s (strong), m (medium), w (weak).

Standard 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 proton signal of chloroform-d_1 (δ = 7.26 ppm) or dimethylsulfoxide-d_6 (δ = 2.50 ppm). ^{13}C NMR spectra were referenced to the ^{13}C-D triplet of $CDCl_3$ (δ = 77.16 ppm) or to the ^{13}C-D septet of DMSO-d_6 (δ = 39.5 ppm). Apparent multiplets which occur as a result of coupling constant equality between 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, m – multiplet. Assignment and multiplicity of the ^{13}C NMR signals were determined by two-dimensional NMR experiments (COSY, HSQC, HMBC, NOESY).

Low-temperature nuclear resonance spectra were recorded at 213 K (–60 °C) on a *Bruker* DRX400 spectrometer using Ptfe500-5-7 NMR-tubes (*Deutero*). ^{1}H NMR spectra were calibrated to the residual proton signal of methylene chloride-d_2 (δ = 5.30 ppm). ^{13}C NMR spectra were referenced to the ^{13}C-D quintet of CD_2Cl_2 (δ = 54.00 ppm).

Mass Spectroscopy (MS) and High Resolution Mass Spectroscopy (HRMS) was measured on a *Thermo Scientific* DFS-HRMS spectrometer (EI, 70 eV).

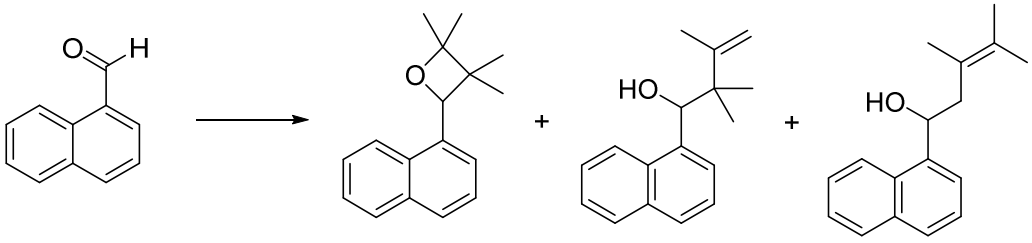
UV/Vis Spectroscopy was measured on a *Perkin Elmer* Lambda 35 UV/Vis spectrometer. Spectra were recorded using a *Hellma* precision cell made of quartz *Suprasil* with a pathway of 1 mm. Solvents and concentrations are given for each spectrum.

Luminescence Measurements were performed on Horiba Scientific FluoroMax-4 instrument (part number J810005 rev. C) to record emission spectra.

3. Experimental procedure

3.1 Photochemical carbonyl addition reactions

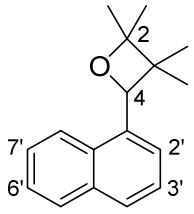
Irradiation of 1-Naphthaldehyde (1)



1 **5a** **6a** **7a**

A solution of 1-naphthaldehyde (**1**, 65.7 mg, 420 µmol, 1.00 eq.) in 2,3-dimethyl-2-butene (5.00 mL, 3.54 g, 42.1 mmol, 100 eq.) was irradiated at λ = 366 nm for 20 h. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica, P/EtOAc = 100/1 → 75/1 → 60/1). 35.1 mg of oxetane **5a** (146 µmol, 35%) were obtained as a colourless oil besides 13.3 mg of carbonyl addition product **6a** (55.3 µmol, 13%) as a colourless oil and 15.6 mg of carbonyl addition product **7a** (64.9 µmol, 15%) as a pale yellow oil.

2,2,3,3-Tetramethyl-4-(naphthalen-1'-yl)oxetane (5a)



5a

$C_{17}H_{20}O$
MW = 240.35

TLC: R_f = 0.69 (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3051 (w, sp^2-CH), 2964 (m, sp^3-CH), 2923 (m, sp^3-CH), 2870 (w, sp^3-CH), 1713 (m), 1371 (m, sp^3-CH), 1283 (w, C-O-C), 1146 (m, C-O-C), 800 (m, sp^2-CH), 781 (m, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.66 (s, 3 H, C-3-CH_3), 1.36 (s, 3 H, C-2-CH_3), 1.52 (s, 3 H, C-3-CH_3), 1.60 (s, 3 H, C-2-CH_3), 6.14 (d, ^4J = 1.1 Hz, 1 H, H-4), 7.45 – 7.49 (m, 2 H, H-6', H-7'), 7.54 (*virt.* t, $^3J \approx {}^3J$ = 7.6 Hz, 1 H, H-3'), 7.67 – 7.71 (m, 1 H, H-8'), 7.76 (d, ^3J = 8.1 Hz, 1 H, H-4'), 7.84 (*virt.* dt, ^3J = 7.1 Hz, $^4J \approx {}^4J$ = 1.2 Hz, 1 H, H-2'), 7.85 – 7.88 (m, 1 H, H-5').

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 19.6 (q, C-3-*C*H_3), 23.8 (q, C-3-*C*H_3), 25.5 (q, C-2-*C*H_3), 25.5 (q, C-2-*C*H_3), 44.0 (s, C-3), 85.0 (d, C-4), 85.4 (s, C-2), 123.1 (d, C-8'), 123.4 (d, C-2'), 125.5 (d, C-3'*), 125.8 (d, C-6'*), 125.8 (d, C-7'*), 127.3 (d, C-4'), 128.9 (d, C-5'), 130.6 (s, C-8'a), 133.3 (s, C-4'a), 137.1 (s, C-1').

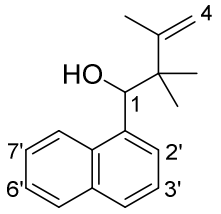
* assignment is interconvertible.

MS (EI, 70 eV): *m/z* (%) = 240 (2) $[M]^+$, 214 (3), 182 (6), 167 (13), 155 (19), 127 (18) $[M - C_7H_{13}O]^+$, 84 (100) $[C_6H_{12}]^+$, 69 (42), 42 (9).

HRMS (EI, 70 eV): calcd for $C_{17}H_{20}O$ $[M]^+$: 240.1509; found: 240.1509.

calcd for $C_{16}{}^{13}CH_{20}O$ $[M]^+$: 241.1542; found: 241.1541.

2,2,3-Trimethyl-1-(naphthalen-1'-yl)but-3-en-1-ol (6a)



$C_{17}H_{20}O$
MW = 240.35

6a

TLC: R_f = 0.56 (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3460 (m, OH), 3051 (w, sp^2-CH), 2973 (s, sp^3-CH), 2883 (w, sp^3-CH), 1632 (w), 1464 (w, sp^3-CH), 1376 (m, OH), 1163 (w), 1060 (m), 893 (w), 800 (m, sp^2-CH), 780 (s, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 0.89 (s, 3 H, C-2-CH_3), 1.12 (s, 3 H, C-2-CH_3), 2.01 (dd, ^4J = 1.4 Hz, ^4J = 0.7 Hz, 3 H, C-3-CH_3), 2.18 (*br* s, 1 H, OH), 5.08 – 5.09 (m, 1 H, *H*H-4), 5.10 (*virt.* quint, $^2J \approx {}^4J$ = 1.4 Hz, 1 H, H*H*-4), 5.67 (s, 1 H, H-1), 7.44 – 7.51 (m, 2 H, H-6', H-7')[#], 7.52 (*virt.* t, $^3J \approx {}^3J$ = 7.7 Hz, 1 H, H-3')[#], 7.74 (dd, ^3J = 7.7 Hz, ^4J = 1.3 Hz, 1 H, H-2'), 7.80 (d, ^3J = 8.1 Hz, 1 H, H-4'), 7.86 (dd, ^3J = 7.9 Hz, ^4J = 1.7 Hz, 1 H, H-5'), 8.18 (dd, ^3J = 8.6 Hz, ^4J = 1.4 Hz, 1 H, H-8').

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 20.3 (q, C-3-*C*H_3), 20.5 (q, C-2-*C*H_3), 25.2 (q, C-2-*C*H_3), 46.0 (s, C-2), 71.8 (d, C-1), 113.5 (t, C-4), 124.0 (d, C-8'), 125.1 (d, C-3'*), 125.2 (d, C-6'*), 125.6 (d, C-7'*), 126.6 (d, C-2'), 128.1 (d, C-4'), 129.0 (d, C-5'), 132.4 (s, C-8a'), 133.6 (s, C-4a'), 136.5 (s, C-1'), 151.2 (s, C-3).

[#] signals are partially overlapped.

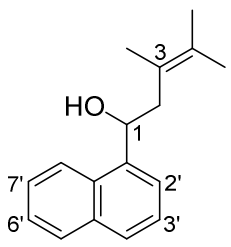
* assignment is interconvertible.

MS (EI, 70 eV): *m/z* (%) = 240 (3) $[M]^+$, 207 (2), 179 (2), 165 (4), 157 (98) $[M - C_6H_{11}]^+$, 129 (100), 84 (94) $[C_6H_{12}]^+$, 69 (27), 41 (10).

HRMS (EI, 70 eV): calcd for $C_{17}H_{20}O$ $[M]^+$: 240.1509; found: 240.1512.

calcd for $C_{16}{}^{13}CH_{20}O$ $[M]^+$: 241.1542; found: 241.1543.

3,4-Dimethyl-1-(naphthalen-1'-yl)pent-3-en-1-ol (7a)



$C_{17}H_{20}O$
MW = 240.35

7a

TLC: R_f = 0.44 (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3407 (m, OH), 3050 (w, sp^2-CH), 2974 (w, sp^3-CH), 2921 (m, sp^3-CH), 2859 (w, sp^3-CH), 1511 (w), 1443 (w, sp^3-CH), 1374 (m, OH), 1165 (m), 1017 (w), 799 (s, sp^2-CH), 777 (vs, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.74 (*br* s, 6 H, C-3-CH_3, C-4-CH_3), 1.81 (s, 3 H, C-4-CH_3), 2.18 (d, ^3J = 1.9 Hz, 1 H, OH), 2.50 (dd, ^2J = 13.9 Hz, ^3J = 3.9 Hz, 1 H, *H*H-2), 2.81 (dd, ^2J = 13.9 Hz, ^3J = 9.8 Hz, 1 H, H*H*-2), 5.58 (ddd, ^3J = 9.8 Hz, ^3J = 3.9 Hz, ^3J = 1.9 Hz, 1 H, H-1), 7.47 – 7.53 (m, 3 H, H-3', H-6', H-7'), 7.75 (*virt.* dt, ^3J = 7.1 Hz, $^4J \approx {}^4J$ = 1.0 Hz, 1 H, H-2'), 7.78 (d, ^3J = 8.2 Hz, 1 H, H-4'), 7.88 (dd, ^3J = 7.8 Hz, ^4J = 1.9 Hz, 1 H, H-5'), 8.13 (dd, ^3J = 8.7 Hz, ^4J = 1.3 Hz, 1 H, H-8').

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 18.8 (q, C-4-*C*H_3), 20.9 (q, C-3-*C*H_3*), 21.1 (q, C-4-*C*H_3*), 44.1 (t, C-2), 69.4 (d, C-1), 123.0 (d, C-2'), 123.1 (d, C-8'), 124.3 (s, C-3**), 125.5 (d, C-3'***), 125.7 (d, C-6'***), 126.0 (d, C-7'***), 127.9 (d, C-4'), 129.0 (d, C-5'), 129.5 (s, C-4**), 130.5 (s, C-8a'), 133.9 (s, C-4a'), 140.3 (s, C-1').

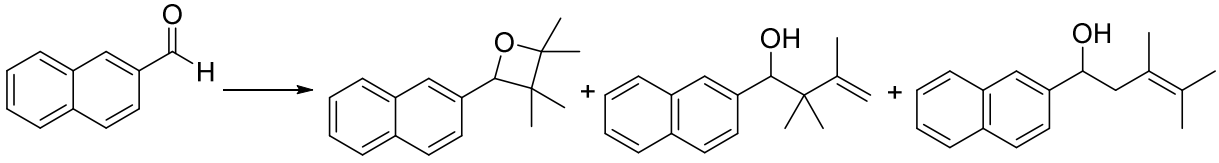
*, **,*** assignment is interconvertible.

MS (EI, 70 eV): *m/z* (%) = 240 (2) $[M]^+$, 222 (5), 207 (12), 192 (9), 165 (6), 157 (97) $[M - C_6H_{11}]^+$, 129 (100), 84 (93) $[C_6H_{12}]^+$, 69 (24), 55 (19).

HRMS (EI, 70 eV): calcd for $C_{17}H_{20}O$ $[M]^+$: 240.1509; found: 240.1510.

calcd for $C_{16}{}^{13}CH_{20}O$ $[M]^+$: 241.1542; found: 241.1543.

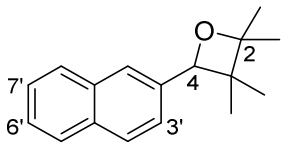
Irradiation of 2-Naphthaldehyde (2)



2 **5b** **6b** **7b**

A solution of 2-naphthaldehyde (**2**, 65.7 mg, 420 µmol, 1.00 eq.) in 2,3-dimethyl-2-butene (5.00 mL, 3.54 g, 42.1 mmol, 100 eq.) was irradiated at λ = 366 nm for 20 h. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica, P/Et_2O = 50/1 → 40/1 → 10/1). 35.3 mg of oxetane **5b** (147 µmol, 35%) were obtained as a colourless solid besides 23.3 mg of carbonyl addition product **6b** (96.9 µmol, 23%) as a colourless oil and 21.5 mg of carbonyl addition product **7b** (89.5 µmol, 21%) as a colourless oil.

2,2,3,3-Tetramethyl-4-(naphthalen-2'-yl)oxetane (5b)



$C_{17}H_{20}O$
MW = 240.35

5b

M.p.: 28 °C.

TLC: R_f = 0.78 (P/Et_2O = 4/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3057 (w, sp^2-CH), 2980 (s, sp^3-CH), 2924 (m, sp^3-CH), 2869 (w, sp^3-CH), 1714 (m), 1371 (m, sp^3-CH), 1284 (s, C-O-C), 1123 (vs, C-O-C), 779 (s, sp^2-CH), 759 (m, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.74 (s, 3 H, C-3-CH_3), 1.32 (s, 3 H, C-3-CH_3), 1.36 (s, 3 H, C-2-CH_3), 1.56 (s, 3 H, C-2-CH_3), 5.58 (s, 1 H, H-4), 7.29 (dd, ^3J = 8.4 Hz,

^4J = 1.6 Hz, 1 H, H-3'), 7.44 – 7.50 (m, 2 H, H-6', H-7'), 7.80 (d, ^3J = 8.4 Hz, 1 H, H-4'), 7.82 (*br* s, 1 H, H-1')[#], 7.82 – 7.87 (m, 2 H, H-5', H-8')[#].

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 20.2 (q, C-3-*C*H_3), 23.6 (q, C-3-*C*H_3), 25.3 (q, C-2-*C*H_3), 25.4 (q, C-2-*C*H_3), 44.0 (s, C-3), 85.7 (s, C-2), 87.0 (d, C-4), 123.7 (d, C-3'), 123.8 (d, C-1'), 125.6 (d, C-6'*), 126.1 (d, C-7'*), 127.6 (d, C-4'), 127.8 (d, C-5'**), 128.1 (d, C-8'**), 132.9 (s, C-4a'), 133.4 (s, C-8a'), 138.3 (s, C-2').

[#] signals are partially overlapped.

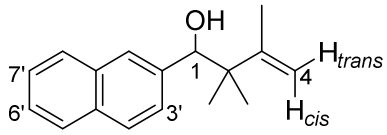
*, ** assignment is interconvertible.

MS (EI, 70 eV): *m/z* (%) = 240 (3) $[M]^+$, 182 (18), 167 (21), 156 (27) $[M - C_6H_{12}]^+$, 127 (28) $[M - C_7H_{13}O]^+$, 84 (100) $[C_6H_{12}]^+$, 69 (38).

HRMS (EI, 70 eV): calcd for $C_{17}H_{20}O$ $[M]^+$: 240.1509; found: 240.1514.

calcd for $C_{16}{}^{13}CH_{20}O$ $[M]^+$: 241.1542; found: 241.1545.

2,2,3-Trimethyl-1-(naphthalen-2'-yl)but-3-en-1-ol (6b)



$C_{17}H_{20}O$
MW = 240.35

6b

TLC: R_f = 0.61 (P/Et_2O = 4/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3458 (m, OH), 3057 (w, sp^2-CH), 2972 (vs, sp^3-CH), 2881 (w, sp^3-CH), 1633 (w), 1464 (w, sp^3-CH), 1376 (m, OH), 1122 (w), 1051 (m), 817 (s, sp^2-CH), 749 (m, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.00 (s, 3 H, C-2-CH_3), 1.05 (s, 3 H, C-2-CH_3), 1.92 (s, 3 H, C-3-CH_3), 2.20 (d, ^3J = 1.7 Hz, 1 H, OH), 4.81 (*br* s, 1 H, H-1), 5.01 (*br* s, 1 H, H-4$_{cis}$), 5.07 (*br* s, 1 H, H-4$_{trans}$), 7.45 – 7.48 (m, 2 H, H-6', H-7'), 7.50 (dd, ^3J = 8.6 Hz,

^4J = 1.8 Hz, 1 H, H-3'), 7.79 (d, ^3J = 8.6 Hz, 1 H, H-4')$^{\#}$, 7.80 (*br* s, 1 H, H-1')$^{\#}$, 7.83 – 7.85 (m, 2 H, H-5', H-8').

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 20.0 (q, C-3-*C*H_3), 20.3 (q, C-2-*C*H_3), 24.5 (q, C-2-*C*H_3), 45.0 (s, C-2), 77.6 (d, C-1), 113.6 (t, C-4), 125.8 (d, C-6'*), 126.0 (d, C-7'*), 126.4 (d, C-3'), 127.0 (d, 2 C, C-1', C-4'), 127.7 (d, C-5'**), 128.1 (d, C-8'**), 132.9 (s, C-4a'***), 133.0 (s, C-8a'***), 138.0 (s, C-2'), 150.8 (s, C-3).

$^{\#}$ signals are partially overlapped.

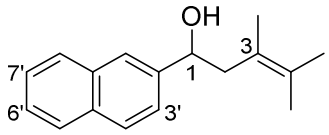
*, **, *** assignment is interconvertible.

MS (EI, 70 eV): *m/z* (%) = 240 (3) $[M]^+$, 207 (5), 165 (4), 157 (100) $[M - C_6H_{11}]^+$, 129 (89), 127 (50) $[M - C_7H_{13}O]^+$, 84 (72) $[C_6H_{12}]^+$, 69 (27).

HRMS (EI, 70 eV): calcd for $C_{17}H_{20}O$ $[M]^+$: 240.1509; found: 240.1510.

calcd for $C_{16}{}^{13}CH_{20}O$ $[M]^+$: 241.1542; found: 241.1546.

3,4-Dimethyl-1-(naphthalen-2'-yl)pent-3-en-1-ol (7b)



$C_{17}H_{20}O$
MW = 240.35

7a

TLC: R_f = 0.41 (P/Et_2O = 4/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3390 (m, OH), 3055 (w, sp^2-CH), 2981 (m, sp^3-CH), 2919 (s, sp^3-CH), 2859 (m, sp^3-CH), 1508 (w), 1442 (m, sp^3-CH), 1373 (m, OH), 1124 (m), 1020 (w), 818 (s, sp^2-CH), 746 (vs, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.71 (s, 3 H, CH_3), 1.72 (s, 3 H, CH_3), 1.74 (s, 3 H, CH_3), 2.12 (d, ^3J = 2.0 Hz, 1 H, OH), 2.37 (dd, ^2J = 13.6 Hz, ^3J = 4.6 Hz, 1 H, *H*H-2), 2.75 (dd, ^2J = 13.6 Hz, ^3J = 9.4 Hz, 1 H, H*H*-2), 4.96 (ddd, ^3J = 9.4 Hz, ^3J = 4.6 Hz,

^{3}J = 2.0 Hz, 1 H, H-1), 7.44 – 7.49 (m, 2 H, H-6', H-7'), 7.52 (dd, ^{3}J = 8.6 Hz, ^{4}J = 1.6 Hz, 1 H, H-3'), 7.82 – 7.85 (m, 4 H, H-1', H-4', H-5', H-8').

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 18.8 (q, CH_3), 20.8 (q, CH_3), 21.1 (q, CH_3), 45.1 (t, C-2), 72.7 (d, C-1), 123.9 (s, C-3), 124.2 (d, C-3'), 124.4 (d, C-1'*), 125.8 (d, C-6'**), 126.2 (d, C-7'**), 127.8 (d, C-4'*), 128.1 (d, C-5'*), 128.2 (d, C-8'*), 129.4 (s, C-4), 133.0 (s, C-4a'***), 133.5 (s, C-8a'***), 142.0 (s, C-2').

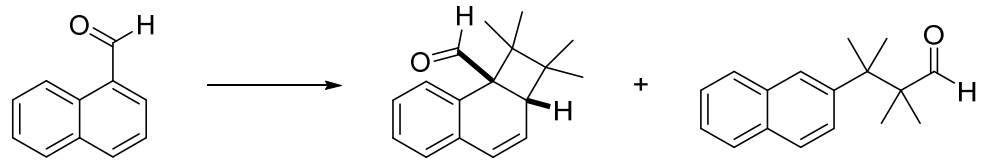
*, **, *** assignment is interconvertible.

MS (EI, 70 eV): *m/z* (%) = 240 (2) $[M]^+$, 222 (9), 207 (20), 192 (16), 156 (87) $[M - C_6H_{12}]^+$, 129 (93), 127 (100) $[M - C_7H_{13}O]^+$, 84 (79) $[C_6H_{12}]^+$, 69 (22), 49 (89).

HRMS (EI, 70 eV): calcd for $C_{17}H_{20}O$ $[M]^+$: 240.1509; found: 240.1509.

calcd for $C_{16}{}^{13}CH_{20}O$ $[M]^+$: 241.1542; found: 241.1544.

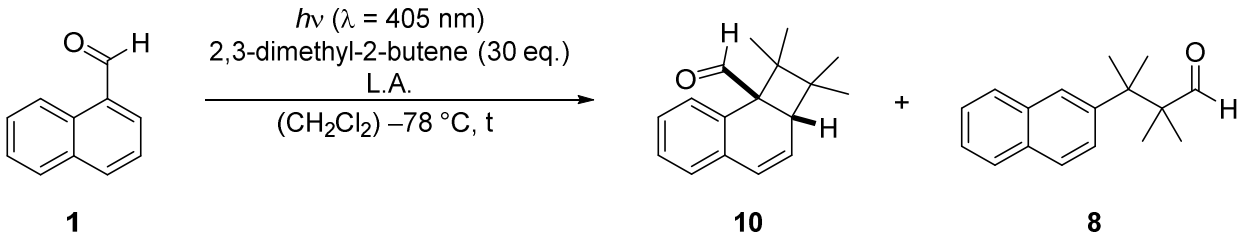
3.2 Lewis acid catalysed irradiation experiments of 1-naphthaldehyde



1 **10** **8**

Freshly distilled 1-naphthyldehyde (**1**, 15.6 mg, 100 µmol, 1.00 eq.) was dissolved in dichloromethane (5 mL) in a *Schlenk* tube and 2,3-dimethyl-2-butene (360 µL, 253 mg, 3.00 mmol, 30.0 eq.) was added. The solution was cooled to −78 °C and an aluminium bromide solution (25.0 µL, 1 M in CH_2Br_2, 25.0 µmol, 25.0 mol%) was added. The solution was irradiated at $\lambda = 405$ nm for six hours at −78 °C and the reaction was then quenched by the addition of triethylamine (100 µL). After warming to room temperature the crude product was loaded onto Celite and purified by column chromatography (silica, P/Et_2O = 20/1). 2.88 mg of the cycloaddition product **10** (12.0 µmol, 12%) were obtained as a colourless oil besides 10.3 mg of the rearrangement product **8** (42.9 mmol, 43%) as a colourless oil.

Other tested conditions are described in the following table.

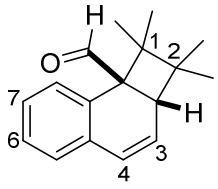


1 **10** **8**

entry	**L.A.**	**irradiation time**	**yield 10**	**yield 8**	**comment**
1	$AlBr_3$ (50 mol%)	6 h	14%	27%	**---**
2	$AlBr_3$ (25 mol%)	6 h	12%	43%	---
3	$AlBr_3$ (10 mol%)	16 h	n.d.	n.d.	complex mixture
4	$EtAlCl_2$ (25 mol%)	6 h	7%	37%	---
5[a]	$AlBr_3$ (50 mol%)	13 h	---	---	only sm, no product formation

[a] w/o light; n.d. = not determined.

1,1,2,2-Tetramethyl-2,2a-dihydrocyclobuta[*a*]naphthalene-8b(1*H*)-carbaldehyde (10)



$C_{17}H_{20}O$
MW = 240.35 g/mol

10

TLC: R_f = 0.62 (P/Et_2O = 10/1) [UV].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3026 (w, sp^2-CH), 2971 (w, sp^3-CH), 2922 (w, sp^3-CH), 2869 (w, sp^3-CH), 2730 (w), 1709 (m, C=O), 1487 (w), 1370 (w), 1199 (w), 1137 (w), 1039 (w), 873 (w), 791 (m, sp^2-CH), 775 (w).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 0.92 (s, 3 H, C-2-CH_3), 0.94 (s, 3 H, C-1-CH_3), 1.02 (s, 3 H, C-2-CH_3), 1.18 (s, 3 H, C-1-CH_3), 3.62 (d, ^3J = 5.6 Hz, 1 H, H-2a), 5.71 (dd, ^3J = 9.8 Hz, ^3J = 5.6 Hz, 1 H, H-3), 6.33 (d, ^3J = 9.8 Hz, 1 H, H-4), 7.03 (dd, ^3J = 6.9 Hz, ^4J = 2.0 Hz, 1 H, H-8), 7.13 (dd, ^3J = 6.9 Hz, ^4J = 1.9 Hz, 1 H, H-5), 7.19 (dd, ^3J = 7.4 Hz, ^3J = 6.9 Hz, 1 H, H-6), 7.20 (dd, ^3J = 7.4 Hz, ^3J = 6.9 Hz, 1 H, H-7), 9.63 (s, 1 H, CHO).

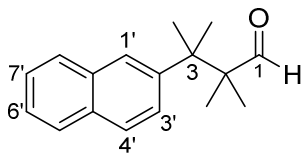
^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ [ppm] = 21.5 (q, C-2-*C*H_3), 22.0 (q, C-1-*C*H_3), 23.4 (q, C-1-*C*H_3), 24.7 (q, C-2-*C*H_3), 40.3 (d, C-2a), 45.0 (s, C-2), 51.8 (s, C-1), 57.3 (s, C-8b), 125.4 (d, C-3), 127.1 (d, C-7), 127.5 (d, C-6), 127.5 (d, C-4), 128.3 (d, C-8), 129.4 (d, C-5), 130.4 (s, C-8a), 134.5 (s, C-4a), 200.8 (d, CHO).

MS (EI, 70 eV): *m/z* (%) = 240 (2) $[M]^+$, 169 (13), 156 (23) $[C_{11}H_8O]^+$, 153 (9), 128 (79) $[C_{10}H_8]^+$, 84 (100) $[C_6H_{12}]^+$, 69 (64) $[C_5H_9]^+$.

HRMS (EI, 70 eV): calcd for $C_{17}H_{20}O$ $[M]^+$: 240.1509; found: 240.1511.

calcd for $C_{16}{}^{13}CH_{20}O$ $[M]^+$: 241.1542; found: 241.1547.

2,2,3-Trimethyl-3-(naphthalen-2'-yl)butanal (8)



$C_{17}H_{20}O$
MW = 240.35 g/mol

8

TLC: R_f = 0.53 (P/Et_2O = 10/1) [UV].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3058 (w, sp^2-CH), 2975 [m, sp^3-CH], 2926 (w, sp^3-CH), 2877 [w, sp^3-CH], 2717 (w), 1715 (m, C=O), 1631 (w), 1463 (m), 1200 (w), 1131 (m), 949 (m), 853 (m), 748 (m, sp^2-CH), 668 (m).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.05 (s, 6 H, C-2-CH_3), 1.53 (s, 6 H, C-3-CH_3), 7.44 – 7.51 (m, 3 H, H-3'*, H-6'*, H-7'*), 7.76 (d, ^4J = 2.1 Hz, 1 H, H-1'), 7.79 (d, ^3J = 8.7 Hz, 1 H, H-4'), 7.82 (dd, ^3J = 7.4 Hz, ^4J = 2.1 Hz, 1 H, H-8'*), 7.83 (dd, ^3J = 7.2 Hz, ^4J = 2.1 Hz, 1 H, H-5'*), 9.60 (s, 1 H, H-1).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 18.8 (q, 2 C, C-2-*C*H_3), 24.8 (q, 2 C, C-3-*C*H_3), 42.4 (s, C-3), 50.9 (s, C-2), 126.0 (d, C-7'*), 126.2 (d, C-6'*), 126.4 (d, C-3'*), 126.7 (d, C-1'), 127.1 (d, C-4'), 127.4 (d, C-8'*), 128.3 (d, C-5'*), 131.9 (s, C-4a'**), 132.9 (s, C-8a'**), 142.8 (s, C-2'), 207.6 (d, C-1).

*, ** assignment is interconvertible.

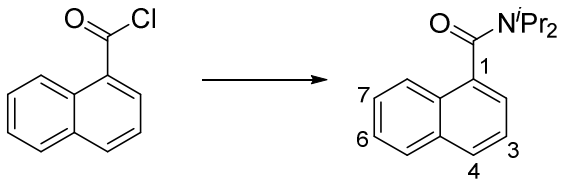
MS (EI, 70 eV): *m/z* (%) = 240 (1) $[M]^+$, 169 (100) $[C_{13}H_{13}]^+$, 153 (17), 141 (29), 128 (16) $[C_{10}H_8]^+$.

HRMS (EI, 70 eV): calcd for $C_{17}H_{20}O$ $[M]^+$: 240.1509; found: 240.1508.

calcd for $C_{16}{}^{13}CH_{20}O$ $[M]^+$: 241.1542; found: 241.1547.

Synthesis of deuterated 1-naphthaldehyde

***N,N*-Diisopropyl-1-naphthamide (S1)**



$C_{17}H_{21}NO$
MW = 255.36 g/mol

S1

To a solution of 1-naphthoylchloride (500 mg, 2.62 mmol, 1.00 eq.) in dichloromethane (11 mL) was added diisopropylamine (1.06 g, 10.5 mmol, 4.00 eq.) at 0 °C. After stirring at 0 °C for 90 minutes the solution was washed with 1 M aqueous HCl (2 × 20 mL) and brine (20 mL), dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was recrystallized from cyclohexane/ethyl acetate (10/1, 20 mL) and 670 mg of amide **S1** (2.62 mmol, *quant.*) were obtained as a colourless solid.

TLC: R_f = 0.37 (P/Et_2O = 1/1) [UV].

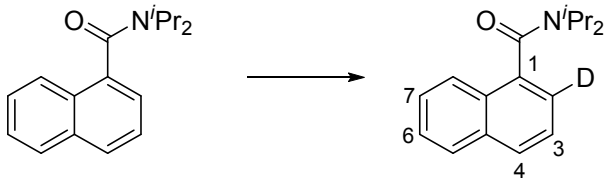
^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.04 [d, ^3J = 6.7 Hz, 3 H, N(CHCH_3CH$_3$)^{i}Pr], 1.08 [d, ^3J = 6.7 Hz, 3 H, N(CHCH$_3$CH_3)^{i}Pr], 1.66 [d, ^3J = 6.8 Hz, 3 H, N^{i}Pr(CHCH_3CH$_3$)], 1.73 [d, ^3J = 6.8 Hz, 3 H, N^{i}Pr(CHCH$_3$CH_3)], 3.60 [*virt.* sept, $^3J \approx {}^3J$ = 6.8 Hz, 1 H, N^{i}Pr(CHMe$_2$)], 3.63 [*virt.* sept, $^3J \approx {}^3J$ = 6.7 Hz, 1 H, N(CHMe$_2$)^{i}Pr], 7.32 (dd, ^3J = 7.0 Hz, ^4J = 1.1 Hz, 1 H, H-2), 7.46 (dd, ^3J = 8.5 Hz, ^3J = 7.0 Hz, 1 H, H-3), 7.47 – 7.53 (m, 2 H, H-6*, H-7*), 7.83 (d, ^3J = 8.5 Hz, 1 H, H-4), 7.79 – 7.90 (m, 2 H, H-5*, H-8*).

^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ [ppm] = 20.8 [q, N(CH*C*H$_3$CH$_3$)^{i}Pr], 20.8 [q, N^{i}Pr(CH*C*H$_3$CH$_3$)], 20.9 [q, N^{i}Pr(CHCH$_3$*C*H$_3$)], 21.0 [q, N(CHCH$_3$*C*H$_3$)^{i}Pr], 46.1 [d, N^{i}Pr(CHMe$_2$)], 51.2 [d, N(CHMe$_2$)^{i}Pr], 122.2 (d, C-2), 125.1 (d, C-6*), 125.4 (d, C-3), 126.4 (d, C-5*), 126.8 (d, C-8*), 128.3 (d, C-4*), 128.4 (d, C-7*), 129.7 (s, C-8a), 133.7 (s, C-4a**), 136.9 (s, C-1**), 170.2 (s, CON^{i}Pr$_2$).

*, ** assignment is interconvertible.

The analytical data obtained matched those reported in the literature.[2]

***N*,*N*-Diisopropyl-1-naphthamide-2-*d* (S2)**



S1 **S2**

$C_{17}H_{20}DNO$
MW = 256.37 g/mol

A solution of amide **S1** (50.0 mg, 196 µmol, 1.00 eq.) in tetrahydrofuran (1 mL) was added dropwise to a solution of *sec*-butyllithium (300 µL, 1.3 M in cyclohexane/hexane 92/8, 390 µmol, 2.00 eq.) and TMEDA (60.0 µL, 45.5 mg, 390 µmol, 2.00 eq.) in tetrahydrofuran (2 mL) at −78 °C. After stirring at this temperature for 15 minutes D_2O (300 µL, 333 mg, 16.6 mmol, 85.0 eq.) was added. The solution was warmed to room temperature followed by the addition of 1 M HCl (2 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with 1 M aqueous HCl (20 mL), water (20 mL) and brine (20 mL). After drying the combined organic layers over Na_2SO_4 and filtration, the solvent was removed under reduced pressure. Purification of the crude product by column chromatography (silica, P/Et_2O = 3/2) gave 44.5 mg of the deuterated amide **S2** (174 µmol, 89%, >98% D) as a colourless solid.

M.p.: 183 °C.

TLC: R_f = 0.37 (P/Et_2O = 1/1) [UV].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2962 (w, sp^3-CH), 2925 (w, sp^3-CH), 1619 (s, C=O), 1505 (w), 1370 [m, >C(CH$_3$)$_2$], 1321 (m, CH-N), 1208 (m), 1124 (m), 878 (m), 842 (m), 756 (m, sp^2-CH), 710 (m), 661 (w).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.04 [d, ^3J = 6.7 Hz, 3 H, N(CHCH_3CH$_3$)^{i}Pr], 1.08 [d, ^3J = 6.7 Hz, 3 H, N(CHCH$_3$CH_3)^{i}Pr], 1.66 [d, ^3J = 6.8 Hz, 3 H, N^{i}Pr(CHCH_3CH$_3$)], 1.73 [d, ^3J = 6.8 Hz, 3 H, N^{i}Pr(CHCH$_3$CH_3)], 3.60 [*virt.* sept, $^3J \approx {}^3J$ = 6.8 Hz, 1 H, N^{i}Pr(CHMe$_2$)], 3.63 [*virt.* sept, $^3J \approx {}^3J$ = 6.7 Hz, 1 H, N(CHMe$_2$)^{i}Pr], 7.44 – 7.48 (m, 1 H,

H-3), 7.47 – 7.53 (m, 2 H, H-6*, H-7*), 7.83 (d, ^{3}J = 8.5 Hz, 1 H, H-4), 7.79 – 7.90 (m, 2 H, H-5*, H-8*).

^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ [ppm] = 20.8 [q, N(CH*C*H$_3$CH$_3$)^{i}Pr], 20.8 [q, N^{i}Pr(CH*C*H$_3$CH$_3$)], 20.9 [q, N^{i}Pr(CHCH$_3$*C*H$_3$)], 21.0 [q, N(CHCH$_3$*C*H$_3$)^{i}Pr], 46.2 [d, N^{i}Pr(CHMe$_2$)], 51.2 [d, N(CHMe$_2$)^{i}Pr], 122.0 (t, ^{1}J = 24.6 Hz, C-2), 125.0 (d, C-6*), 125.3 (d, C-3), 126.5 (d, C-5*), 126.8 (d, C-8*), 128.3 (d, C-4*), 128.4 (d, C-7*), 129.7 (s, C-8a), 133.7 (s, C-4a**), 136.7 (s, C-1**), 170.3 (s, CON^{i}Pr$_2$).

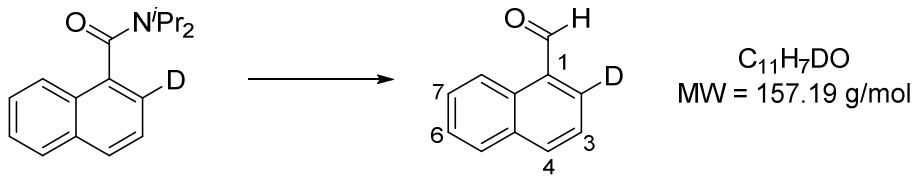
*, ** assignment is interconvertible.

MS (EI, 70 eV): *m/z* (%) = 256 (20) $[M]^+$, 213 (16) $[M - C_3H_8]^+$, 156 (100) $[M - N^{i}Pr_2]^+$, 128 (36) $[C_{10}H_6D]^+$, 84 (7), 49 (8).

HRMS (EI, 70 eV): calcd for $C_{17}H_{20}DNO$ $[M]^+$: 256.1680; found: 256.1677.

calcd for $C_{16}{}^{13}CH_{20}DNO$ $[M]^+$: 257.1714; found: 257.1713.

1-Naphthaldehyde-2-*d* (S3)



S2 **S3**

Ethyl trifluoromethanesulfonate (249 mg, 1.40 mmol, 1.50 eq.) was added to a solution of amide **S2** (239 mg, 930 µmol, 1.00 eq.) and 2,6-di-*tert*-butyl-4-methylpyridine (574 mg, 2.80 mmol, 3.00 eq.) in dichloromethane (6.5 mL). After stirring under reflux for three hours tetrahydrofuran (13 mL) was added, the solution was cooled to −78 °C and lithium tri-*tert*-butoxyaluminium hydride (1.70 mL, 1.1 M in THF, 1.86 mmol, 2.00 eq.) was added dropwise. Stirring was continued at this temperature for four hours followed by addition of saturated aqueous sodium potassium tartrate solution (6 mL). The mixture was allowed to warm to room temperature and the layers were separated. The aqueous layer was extracted with diethyl ether (3 × 20 mL) and the combined organic layers were washed with water (2 × 50 mL) and brine (2 × 50 mL), dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. Purification of the crude product by column chromatography (silica, P/Et_2O = 20/1) gave 118 mg of aldehyde **S3** (750 µmol, 81%, >98% D) as a pale yellow oil.

TLC: R_f = 0.32 (P/Et_2O = 10/1) [UV].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3054 (w, sp^2-CH), 2841 (w, sp^3-CH), 2723 (m, sp^3-CH), 1683 (s, C=O), 1620 (m), 1581 (m), 1505 (m), 1264 (w), 1111 (m), 957 (w), 752 (s, sp^2-CH), 711 (m), 695 (m).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 7.60 (ddd, ^3J = 8.2 Hz, ^3J = 6.9 Hz, ^4J = 1.2 Hz, 1 H, H-6), 7.64 (d, ^3J = 8.3 Hz, 1 H, H-3), 7.70 (ddd, ^3J = 8.5 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1 H, H-7), 7.93 (dd, ^3J = 8.2 Hz, ^4J = 1.5 Hz, 1 H, H-5), 8.11 (d, ^3J = 8.3 Hz, 1 H, H-4), 9.26 (d, ^3J = 8.5 Hz, 1 H, H-8), 10.41 (s, 1 H, CHO).

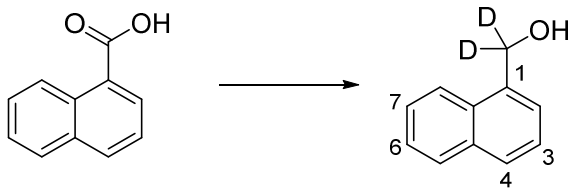
^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 124.9 (d, C-8), 125.0 (d, C-3), 127.1 (d, C-6), 128.6 (d, C-5), 129.2 (d, C-7), 130.6 (s, C-8a), 131.5 (s, C-1), 133.8 (s, C-4a), 135.5 (d, C-4), 136.5 (t, ^1J = 24.2 Hz, C-2), 193.7 (d, CHO).

MS (EI, 70 eV): *m/z* (%) = 157 (100) $[M]^+$, 128 (83) $[M - CHO]^+$, 116 (4), 102 (8), 78 (9).

HRMS (EI, 70 eV): calcd for $C_{11}H_7DO$ $[M]^+$: 157.0632; found: 157.0636.

calcd for $C_{10}{}^{13}CH_7DO$ $[M]^+$: 158.0666; found: 158.0670.

Naphthalen-1-ylmethan-d_2-ol (S4)



$C_{11}H_8D_2O$
MW = 160.21 g/mol

S4

A solution of 1-naphthoic acid (200 mg, 1.16 mmol, 1.00 eq.) in tetrahydrofuran (2 mL) was added to a suspension of lithium aluminium deuteride (48.8 mg, 1.16 mmol, 1.00 eq.) in tetrahydrofuran (2 mL) at 0 °C. The mixture was warmed to room temperature, stirred for 17 hours and then diluted with diethyl ether (5 mL). When no further gas evolution was observed, water (50 µL), 3 M aqueous NaOH solution (50 µL), again water (150 µL) and $MgSO_4$ were added. The mixture was filtered and the filtrate was washed with water (3 × 10 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. 183 mg of the deuterated alcohol **S4** (1.14 mmol, 98%, >99% D) were obtained as a colourless solid.

M.p.: 62 °C.

TLC: R_f = 0.81 (P/Et_2O = 2/3) [UV].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3376 (w, OH), 3306 (w, OH), 2962 (w, sp^3-CH), 1594 (w), 1508 (w), 1383 (w), 1260 (w, C-OH), 1057 (w), 868 (w), 797 (m), 765 (m, sp^2-CH), 698 (w).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.78 (s, 1 H, OH), 7.45 (dd, ^3J = 8.2 Hz, ^3J = 7.0 Hz, 1 H, H-3), 7.48 – 7.56 (m, 2 H, H-2, H-6), 7.56 (ddd, ^3J = 8.4 Hz, ^3J = 6.8 Hz, ^4J = 1.6 Hz, 1 H, H-7), 7.83 (d, ^3J = 8.2 Hz, 1 H, H-4), 7.89 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 1 H, H-5), 8.13 (d, ^3J = 8.4 Hz, 1 H, H-8).

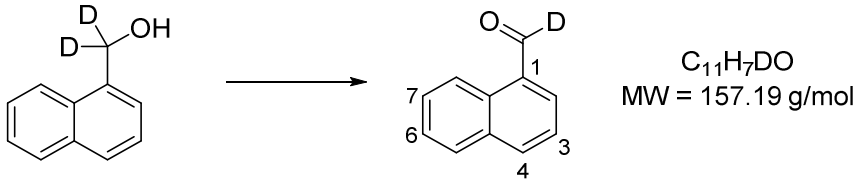
^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 63.2 (quint, ^1J = 21.9 Hz, CD_2OH), 123.8 (d, C-8), 125.5 (d, C-3), 125.5 (d, C-2), 126.0 (d, C-6), 126.5 (d, C-7), 128.7 (d, C-4), 128.8 (d, C-5), 131.4 (s, C-4a), 133.9 (s, C-8a), 136.3 (s, C-1).

MS (EI, 70 eV): *m/z* (%) = 160 (82) $[M]^+$, 143 (29) $[M - OH]^+$, 130 (100) $[C_{10}H_6D_2]^+$, 117 (11), 77 (5).

HRMS (EI, 70 eV): calcd for $C_{11}H_8D_2O$ $[M]^+$: 160.0852; found: 160.0845.

calcd for $C_{10}{}^{13}CH_8D_2O$ $[M]^+$: 161.0885; found: 161.0879.

1-Naphthaldehyde-α-*d* (S5)



S4 **S5**

To a solution of alcohol **S4** (50.0 mg, 310 µmol, 1.00 eq.) in dichloromethane (4 mL) was added manganese dioxide (543 mg, 6.24 mmol, 20.0 eq.) and the suspension was stirred for six days at room temperature. The mixture was filtered over Celite and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica, P/Et_2O = 10/1) and 35.4 mg of deuterated aldehyde **S5** (225 µmol, 72%, >99% D) were obtained as a pale yellow oil.

TLC: R_f = 0.32 (P/Et_2O = 10/1) [UV].

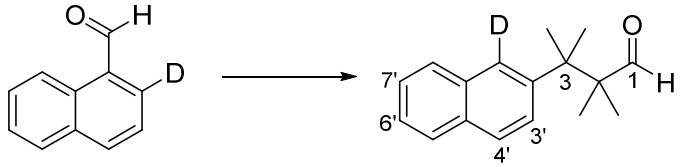
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 7.60 (ddd, ^3J = 8.2 Hz, ^3J = 6.9 Hz, ^4J = 1.2 Hz, 1 H, H-6), 7.64 (dd, ^3J = 8.3 Hz, ^3J = 7.1 Hz, 1 H, H-3), 7.70 (ddd, ^3J = 8.5 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1 H, H-7), 7.93 (dd, ^3J = 8.2 Hz, ^4J = 1.5 Hz, 1 H, H-5), 8.00 (dd, ^3J = 7.1 Hz, ^4J = 1.4 Hz, 1 H, H-2), 8.11 (d, ^3J = 8.3 Hz, 1 H, H-4), 9.26 (d, ^3J = 8.5 Hz, 1 H, H-8).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 125.0 (d, C-8), 125.0 (d, C-3), 127.1 (d, C-6), 128.6 (d, C-5), 129.2 (d, C-7), 130.7 (s, C-8a), 131.4 (t, ^2J = 3.7 Hz, C-1), 133.8 (s, C-4a), 135.5 (d, C-4), 136.8 (d, C-2), 193.4 (t, ^1J = 26.7 Hz, CDO).

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

Irradiation of deuterated compounds

2,2,3-Trimethyl-3-(naphthalen-2-yl-1-*d*)butanal (S6)



$C_{17}H_{19}DO$
MW = 241.35 g/mol

S3 **S6**

Deuterated aldehyde **S3** (15.7 mg, 100 µmol, 1.00 eq.) was dissolved in dichloromethane (5 mL) in a *Schlenk* tube and 2,3-dimethyl-2-butene (360 µL, 253 mg, 3.00 mmol, 30.0 eq.) was added. The solution was cooled to −78 °C and an aluminium bromide solution (25.0 µL, 1 M in CH_2Br_2, 25.0 mol%) was added. The solution was irradiated at $\lambda = 405$ nm for six hours at −78 °C followed by addition of triethylamine (100 µL). After warming to room temperature the crude product was loaded onto Celite and purified by column chromatography (silica, P/Et_2O = 20/1). 4.70 mg of the rearrangement product **S6** (19.4 µmol, 19%, >99% D) were obtained as a colourless oil.

TLC: $R_f = 0.53$ (P/Et_2O = 10/1) [UV].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3055 (w, sp^2-CH), 2976 (m, sp^3-CH), 2875 (w, sp^3-CH), 2847 (w), 1715 (m, C=O), 1504 (w), 1262 (w), 1018 (w), 886 (w), 753 (m, sp^2-CH), 707 (w).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.04 (s, 6 H, C-2-CH_3), 1.53 (s, 6 H, C-3-CH_3), 7.44 – 7.50 (m, 3 H, H-3'*, H-6'*, H-7'*), 7.78 (d, ^3J = 8.7 Hz, 1 H, H-4'), 7.82 (dd, ^3J = 7.6 Hz, ^4J = 2.1 Hz, 1 H, H-8'*), 7.83 (dd, ^3J = 7.5 Hz, ^4J = 2.1 Hz, 1 H, H-5'*), 9.60 (s, 1 H, H-1).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 18.8 (q, 2 C, C-2-*C*H_3), 24.8 (q, 2 C, C-3-*C*H_3), 42.4 (s, C-3), 50.9 (s, C-2), 126.0 (d, C-7'*), 126.2 (d, C-6'*), 126.4 (d, C-3'*), 126.7 (t, ^1J = 8.1 Hz, C-1'), 127.1 (d, C-4'), 127.4 (d, C-8'*), 128.2 (s, C-5'*), 131.9 (s, C-4a'**), 132.9 (s, C-8a'**), 142.7 (s, C-2'), 207.6 (d, C-1).

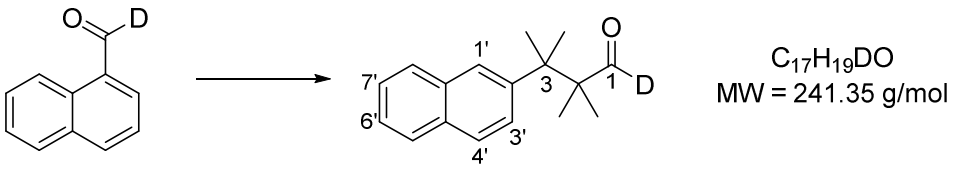
*, ** assignment is interconvertible.

MS (EI, 70 eV): *m/z* (%) = 241 (1) $[M]^+$, 211 (4) $[C_{16}H_{18}D]^+$, 170 (100) $[C_{13}H_{12}D]^+$, 154 (20) $[C_{12}H_8D]^+$, 142 (26) $[C_{11}H_8D]^+$, 129 (18) $[C_{10}H_7D]^+$.

HRMS (EI, 70 eV): calcd for $C_{17}H_{19}DO$ $[M]^+$: 241.1571; found: 241.1571.

calcd for $C_{16}{}^{13}CH_{19}DO$ $[M]^+$: 242.1605; found: 242.1606.

2,2,3-Trimethyl-3-(naphthalen-2'-yl)butanal-1-*d* (S7)



S5 **S7**

Deuterated aldehyde **S5** (15.7 mg, 100 µmol, 1.00 eq.) was dissolved in dichloromethane (5 mL) in a *Schlenk* tube and 2,3-dimethyl-2-butene (360 µL, 253 mg, 3.00 mmol, 30.0 eq.) was added. The solution was cooled to −78 °C and an aluminium bromide solution (25.0 µL, 1 M in CH_2Br_2, 25.0 mol%) was added. The solution was irradiated at $\lambda = 405$ nm for six hours at −78 °C followed by addition of triethylamine (100 µL). After warming to room temperature the crude product was loaded onto Celite and purified by column chromatography (silica, P/Et_2O = 20/1). 9.70 mg of the rearrangement product **S7** (40.2 µmol, 40%, >99% D) were obtained as a colourless oil.

TLC: $R_f = 0.53$ (P/Et_2O = 10/1) [UV].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3058 (w, sp^2-CH), 2975 (m, sp^3-CH), 2917 (m, sp^3-CH), 2875 (w), 2061 (w), 1709 (m, C=O), 1461 (m), 1083 (w), 894 (w), 730 (m, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.05 (s, 6 H, C-2-CH_3), 1.53 (s, 6 H, C-3-CH_3), 7.44 – 7.51 (m, 3 H, H-3'*, H-6'*, H-7'*), 7.76 (d, ^4J = 2.0 Hz, 1 H, H-1'), 7.79 (d, ^3J = 8.7 Hz, 1 H, H-4'), 7.82 (dd, ^3J = 7.4 Hz, ^4J = 2.2 Hz, 1 H, H-8'*), 7.83 (dd, ^3J = 7.6 Hz, ^4J = 2.1 Hz, 1 H, H-5'*).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 18.8 (q, 2 C, C-2-*C*H_3), 24.8 (q, 2 C, C-3-*C*H_3), 42.4 (s, C-3), 50.8 (t, C-2), 126.0 (d, C-7'*), 126.2 (d, C-6'*), 126.3 (d, C-3'*), 126.7 (d, C-1'), 127.1 (d, C-4'), 127.4 (d, C-8'*), 128.3 (d, C-5'*), 131.9 (s, C-4a'**), 132.9 (s, C-8a'**), 142.8 (s, C-2'), 207.2 (t, ^1J = 26.3 Hz, C-1).

*, ** assignment is interconvertible.

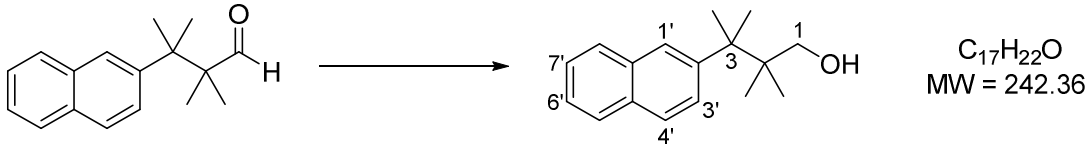
MS (EI, 70 eV): *m/z* (%) = 241 (1) $[M]^+$, 169 (100) $[C_{13}H_{13}]^+$, 153 (21) $[C_{12}H_9]^+$, 141 (30) $[C_{11}H_9]^+$, 129 (23) $[C_{10}H_7D]^+$.

HRMS (EI, 70 eV): calcd for $C_{17}H_{19}DO$ $[M]^+$: 241.1571; found: 241.1568.

calcd for $C_{16}{}^{13}CH_{19}DO$ $[M]^+$: 242.1605; found: 242.1603.

Reduction of rearrangement product 8

2,2,3-Trimethyl-3-(naphthalen-2'-yl)butan-1-ol (9)



8 **9**

A solution of aldehyde **8** (43.0 mg, 179 µmol, 1.00 eq.) in tetrahydrofuran (15 mL) was added dropwise to a suspension of lithium aluminium hydride (20.4 mg, 53.7 µmol, 3.00 eq.) in tetrahydrofuran (10 mL) at 0 °C. After one hour the mixture was diluted with diethyl ether (10 mL) at 0 °C to quench the excess of lithium aluminium hydride. When no further gas evolution was observed, water (100 µL), 10% aqueous NaOH solution (100 µL) and again water (300 µL) was added. After warming the mixture to room temperature it was vigorously stirred at this temperature for 15 minutes and then $MgSO_4$ was added. After filtration over Celite and washing with diethyl ether (20 mL) the solvent was removed under reduced pressure. Purification by column chromatography (silica, P/EtOAc = 20/1) gave 39.4 mg of alcohol **9** (163 µmol, 91%) as a colourless solid.

Single crystals were obtained by vapour diffusion using diethyl ether (solvent) and pentane (anti-solvent).

M.p.: 105 °C.

TLC: R_f = 0.21 (P/EtOAc = 10/1) [UV, $KMnO_4$,].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3367 (s, OH), 3057 (w, sp^2-CH), 2974 (vs, sp^3-CH), 1598 (w), 1505 (w), 1376 (m, OH), 1277 (w), 1132 (w), 1028 (s), 819 (s, sp^2-CH), 748 (s, sp^2-CH).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.94 (s, 6 H, C-2-CH_3), 1.50 (s, 6 H, C-3-CH_3), 3.45 (*br* s, 2 H, H-1), 7.40 – 7.49 (m, 2 H, H-6', H-7'), 7.58 (dd, ^3J = 8.8 Hz,

^4J = 2.0 Hz, 1 H, H-3'), 7.76 (d, ^3J = 8.8 Hz, 1 H, H-4'), 7.78 – 7.83 (m, 3 H, H-1', H-5', H-8').

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 20.9 (q, 2 C, C-2-*C*H_3), 25.1 (q, 2 C, C-3-*C*H_3), 40.9 (s, C-2), 42.6 (s, C-3), 69.7 (t, C-1), 125.7 (d, C-6'*), 125.9 (d, C-7'*), 126.7 (d, 2 C, C-1'**, C-4'), 127.0 (d, C-3'), 127.3 (d, C-5'**), 128.2 (d, C-8'**), 131.7 (s, C-4a'), 132.9 (s, C-8a'), 145.0 (s, C-2').

*, ** assignment is interconvertible.

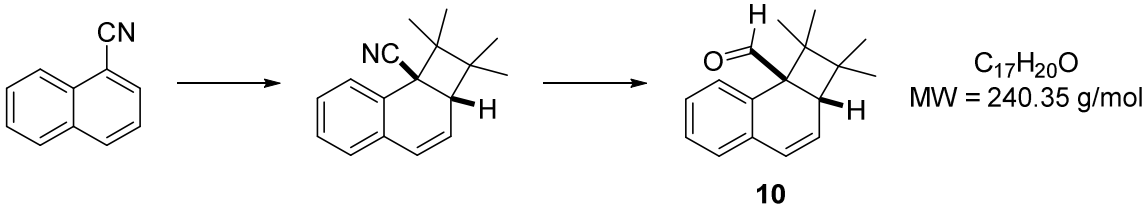
MS (EI, 70 eV): m/z (%) = 242 (2) $[M]^+$, 211 (2) $[M - CH_2OH]^+$, 195 (3), 169 (100) $[M - C(CH_3)_2CH_2OH]^+$, 155 (9), 141 (24), 129 (11), 55 (3).

HRMS (EI, 70 eV): calcd for $C_{17}H_{22}O$ $[M]^+$: 242.1665; found: 242.1671.

calcd for $C_{16}{}^{13}CH_{22}O$ $[M]^+$: 243.1699; found: 243.1704.

Independent synthesis of *ortho* photocycloaddition product 10

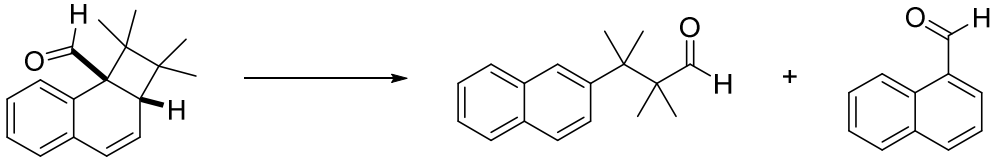
Irradiation of 1-naphthonitrile[4] and in situ reduction



10

2,3-Dimethyl-2-butene (3.04 mL, 2.16 g, 24.0 mmol, 30.0 eq.) was added to a solution of 1-naphthonitrile (120 mg, 800 µmol, 1.00 eq.) in benzene (40 mL). The solution was irradiated at $\lambda = 300$ nm for five hours followed by removal of the solvent under reduced pressure. The residue was dissolved in toluene (40 mL), the solution was cooled to −78 °C and a DIBAL-H solution (880 µL, 1 M in CH_2Cl_2, 880 µmol, 1.10 eq.) was added dropwise. The solution was stirred at this temperature for 75 minutes and the reaction was quenched by the addition of saturated aqueous NH_4Cl solution (20 mL). After warming to room temperature the mixture was filtered over Celite followed by washing the residue with diethyl ether (200 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with water (4 × 100 mL) and brine (2 × 100 mL), dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. Purification of the crude product by column chromatography (silica, P/Et_2O = 25/1) gave 55.8 mg of cyclobutane **10** (232 µmol, 29%) as a colourless oil.

Lewis acid catalysed rearrangement of *ortho* photocycloaddition product 10



10 **8** **1**

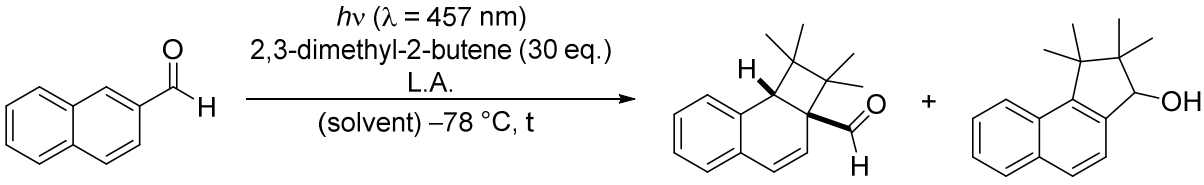
An aluminium bromide solution (25.0 µL, 1 M in CH_2Br_2, 25.0 mol%) was added to a solution of *ortho* photocycloaddition product **10** (22.8 mg, 94.9 µmol, 1.00 eq.) in dichloromethane (5 mL) at −78 °C. The mixture was stirred at this temperature for three hours and then poured into saturated $NaHCO_3$ solution (50 mL). The solution was extracted with dichloromethane (3× 30 mL) followed by washing the combined organic layers with water (50 mL) and brine (50 mL). The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica, P/Et_2O = 20/1). 14.6 mg of rearrangement product **8** (60.7 µmol, 64%) and 1.03 mg of 1-naphthaldehyde (**1**, 6.6 µmol, <10%) were obtained as colourless oils.

3.3 Lewis acid catalysed irradiation experiments of 2-naphthaldehyde

General Procedure 1: ortho photocycloaddition reaction on 2-naphthaldehyde (**2**)

2-Naphthaldehyde (**2**, 15.6 mg, 100 µmol, 1.00 eq.) was dissolved in the corresponding solvent (5 mL) in a *Schlenk* tube and the corresponding olefin (3.00 mmol, 30.0 eq.) was added. The solution was cooled to −78 °C (or −40 °C) followed by addition of Lewis acid (10.0 µmol, 10.0 mol% or 5.00 µmol, 5.00 mol%). The solution was irradiated at λ = 457 nm for the indicated irradiation time and the reaction was quenched by the addition of triethylamine (50 µL). After warming to room temperature the solvent was removed under reduced pressure and the crude product was purified by column chromatography.

Optimization of *ortho* photocycloaddition reaction between 2-naphthaldehyde (2) and 2,3-dimethyl-2-butene



2 **13** **14**

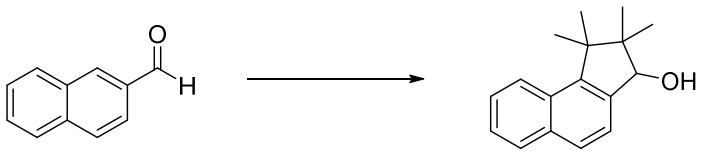
Described for entry 8: According to the General Procedure 1, a solution of 2-naphthaldehyde (**2**, 15.6 mg, 100 µmol, 1.00 eq.), 2,3-dimethyl-2-butene (360 µL, 253 mg, 3.00 mmol, 30.0 eq.) and aluminium bromide solution (50.0 µL, 100 mM in CH_2Br_2/CH_2Cl_2, 5.0 µmol, 5.0 mol%) in dichloromethane (5 mL) was irradiated at λ = 457 nm (LED045) for twelve hours. After removal of the solvent, the crude product was purified by column chromatography (silica, P/Et_2O = 100/1 → 75/1 → 25/1 → 5/1). 13.4 mg of *ortho* photocycloaddition product **13** (55.8 µmol, 56%) were obtained as a colourless solid besides 7.20 mg of secondary alcohol **14** (30.0 µmol, 30%) as a colourless oil.

Other tested conditions are described in the following table.

entry	L.A.	solvent	irradiation time	yield 13	rsm	comment
1[a]	$AlBr_3$ (10 mol%)	CH_2Cl_2	12 h	51%	21%	+ product **14**
2[a,b]	$AlBr_3$ (10 mol%)	MeCN	12 h	--	n.d.	crude ^{1}H-NMR: no product formation
3[a]	$AlBr_3$ (10 mol%)	n-hexane	12 h	--	n.d.	crude ^{1}H-NMR: no product formation
4[a]	$AlCl_3$ (10 mol%)	CH_2Cl_2	12 h	--	n.d.	crude ^{1}H-NMR: no product formation
5[a]	$EtAlCl_2$ (10 mol%)	CH_2Cl_2	24 h	49%	21%	+ product **14**
6[a]	BF_3*OEt_2 (10 mol%)	CH_2Cl_2	12 h	n.d.	n.d.	crude ^{1}H-NMR: traces of **13**
7[c]	$Sc(OTf)_3$ (10 mol%)	CH_2Cl_2	12 h	--	n.d.	crude ^{1}H-NMR: no product formation
8[c]	$AlBr_3$ (5 mol%)	CH_2Cl_2	12 h	56%	traces	+ product **14** (30%)
9[c]	$EtAlCl_2$ (5 mol%)	CH_2Cl_2	24 h	46%	16%	+ product **14** (23%)
10[d]	$AlBr_3$ (10 mol%)	CH_2Cl_2	24 h	--	94%	crude ^{1}H-NMR: no product formation

[a] λ = 457 nm, LED005; [b] temperature –40 °C, [c] λ = 457 nm, LED045; [d] w/o light; n.d. = not determined.

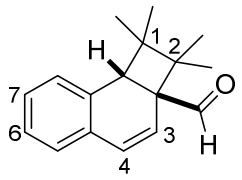
Optimized conditions for the generation of secondary alcohol 14 as the exclusive product



2 **14**

According to the General Procedure 1, a solution of 2-naphthaldehyde (**2**, 15.6 mg, 100 µmol, 1.00 eq.), 2,3-dimethyl-2-butene (360 µL, 253 mg, 3.00 mmol, 30.0 eq.) and aluminium bromide solution (50.0 µL, 100 mM in CH_2Br_2/CH_2Cl_2, 5.0 µmol, 5.0 mol%) in dichloromethane (5 mL) was irradiated at $\lambda = 457$ nm (LED045) for twelve hours. After warming to 0 °C the mixture was stirred for further twelve hours without irradiation at this temperature. The reaction was quenched by the addition of triethylamine (50 µL) followed by removal of the solvent under reduced pressure. Purification of the crude product by column chromatography (silica, $P/Et_2O = 15/1 \rightarrow 5/1$) gave 17.8 mg of secondary alcohol **14** (74.1 µmol, 74%) as a colourless oil.

(2a*SR*,8b*SR*)-1,1,2,2-Tetramethyl-1,8b-dihydrocyclobuta[*a*]naphthalene-2a(2*H*)-carbaldehyde (13)



13

$C_{17}H_{20}O$
MW = 240.35

M.p.: 92 °C.

TLC: R_f = 0.55 (P/Et_2O = 10/1) [UV, $KMnO_4$, CAM].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3018 (w, sp^2-CH), 2956 (s, sp^3-CH), 2926 (m, sp^3-CH), 2867 (w, sp^3-CH), 2805 (w, sp^3-CH), 1714 (vs, C=O), 1451 (m), 1370 (s), 1140 (w), 792 (vs, sp^2-CH), 767 (m, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 0.83 (s, 3 H, C-1-CH_3), 1.03 (s, 3 H, C-1-CH_3), 1.18 (s, 6 H, C-2-CH_3), 3.93 (s, 1 H, H-8b), 5.94 (dd, ^3J = 9.8 Hz, ^4J = 1.1 Hz, 1 H, H-3), 6.55 (d, ^3J = 9.8 Hz, 1 H, H-4), 6.93 (d, ^3J = 7.3 Hz, 1 H, H-8), 7.00 (dd, ^3J = 7.3 Hz, ^4J = 1.6 Hz, 1 H, H-5), 7.12 (*virt.* td, $^3J \approx {}^3J$ = 7.4 Hz, ^4J = 1.6 Hz, 1 H, H-6), 7.16 (*virt.* td, $^3J \approx {}^3J$ = 7.3 Hz, ^4J = 1.6 Hz, 1 H, H-7), 9.50 (s, 1 H, CHO).

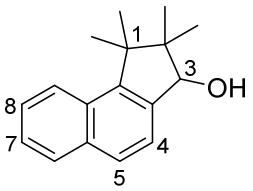
^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ [ppm] = 20.0 (q, C-2-*C*H_3), 22.0 (q, C-1-*C*H_3), 23.3 (q, C-2-*C*H_3), 25.2 (q, C-1-*C*H_3), 42.5 (d, C-8b), 45.1 (s, C-1), 51.6 (s, C-2), 56.7 (s, C-2a), 124.1 (d, C-3), 127.0 (d, C-6), 127.6 (d, C-5), 128.3 (d, C-8), 128.6 (d, C-7), 131.3 (d, C-4), 131.4 (s, C-8a), 132.0 (s, C-4a), 199.8 (d, CHO).

MS (EI, 70 eV): *m/z* (%) = 240 (3) $[M]^+$, 211 (18) $[M - CHO]^+$, 195 (8) $[M - C_3H_9]^+$, 155 (25), 128 (58), 84 (100) $[C_6H_{12}]^+$, 69 (52) $[C_5H_9]^+$, 41 (14).

HRMS (EI, 70 eV): calcd for $C_{17}H_{20}O$ $[M]^+$: 240.1509; found: 240.1506.

calcd for $C_{16}{}^{13}CH_{20}O$ $[M]^+$: 241.1542; found: 241.1545.

1,1,2,2-Tetramethyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-3-ol (14)



$C_{17}H_{20}O$
MW = 240.35

14

TLC: R_f = 0.08 (P/Et_2O = 10/1) [UV, $KMnO_4$, CAM].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3382 (m, OH), 3052 (w, sp^2-CH), 2968 (vs, sp^3-CH), 2871 (w, sp^3-CH), 1517 (w), 1464 (w, sp^3-CH), 1376 (m, OH), 1236 (w), 1077 (s), 814 (m, sp^2-CH), 764 (vs, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 0.91 (s, 3 H, C-2-CH_3), 1.11 (s, 3 H, C-2-CH_3), 1.36 (s, 3 H, C-1-CH_3), 1.57 (s, 3 H, C-1-CH_3), 1.71 (d, ^3J = 7.7 Hz, 1 H, OH), 4.90 (d, ^3J = 7.7 Hz, 1 H, H-3), 7.43 (ddd, ^3J = 8.1 Hz, ^3J = 6.8 Hz, ^4J = 1.4 Hz, 1 H, H-7), 7.47 (ddd, ^3J = 8.4 Hz, ^3J = 6.8 Hz, ^4J = 1.7 Hz, 1 H, H-8), 7.52 (d, ^3J = 8.2 Hz, 1 H, H-4), 7.76 (d, ^3J = 8.2 Hz, 1 H, H-5), 7.89 (d, ^3J = 8.1 Hz, 1 H, H-6), 8.22 (d, ^3J = 8.4 Hz, 1 H, H-9).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 17.6 (q, C-2-*C*H_3), 21.3 (q, C-2-*C*H_3), 24.9 (q, C-1-*C*H_3), 25.7 (q, C-1-*C*H_3), 48.6 (s, C-2*), 50.5 (s, C-1*), 82.7 (d, C-3), 122.1 (d, C-4), 124.3 (d, C-9), 125.0 (d, C-7), 125.8 (d, C-8), 128.1 (d, C-5), 129.6 (d, C-6), 130.4 (s, C-9a), 134.9 (s, C-5a), 140.1 (s, C-3a), 144.7 (s, C-9b).

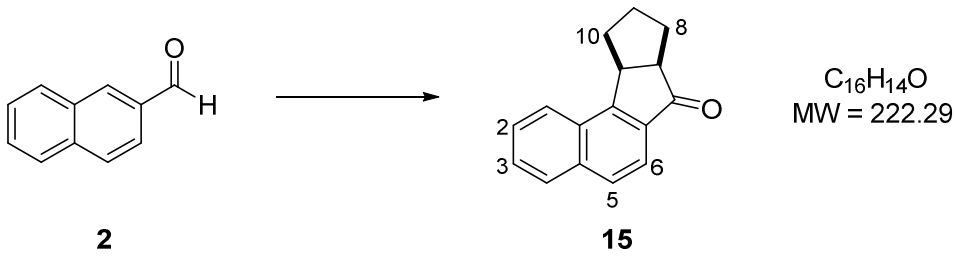
* assignment is interconvertible.

MS (EI, 70 eV): *m/z* (%) = 240 (34) $[M]^+$, 225 (100) $[M - CH_3]^+$, 207 (25), 192 (14), 165 (16), 141 (13), 128 (4) $[M - C_7H_{12}O]$, 115 (4), 57 (3).

HRMS (EI, 70 eV): calcd for $C_{17}H_{20}O$ $[M]^+$: 240.1509; found: 240.1507.

calcd for $C_{16}{}^{13}CH_{20}O$ $[M]^+$: 241.1542; found: 241.1542.

(7a*RS*,10a*SR*)-8,9,10,10a-Tetrahydropentaleno[1,2-*a*]naphthalen-7(7a*H*)-one (15)



2 **15**

According to the General Procedure 1, a solution of 2-naphthaldehyde (**2**, 15.6 mg, 100 µmol, 1.00 eq.), cyclopentene (275 µL, 204 mg, 3.00 mmol, 30.0 eq.) and aluminium bromide solution (50.0 µL, 100 mM in CH_2Br_2/CH_2Cl_2, 5.0 µmol, 5.0 mol%) in dichloromethane (5 mL) was irradiated at $\lambda = 457$ nm (LED045) for twelve hours. After addition of triethylamine (50 µL) the mixture was warmed to 0°C. A solution of *Dess-Martin* periodinane (42.4 mg, 100 µmol, 1.00 eq.) in dichloromethane (2 mL) was added and stirring was continued at 0 °C without irradiation for further six hours. The reaction was quenched by the addition of a saturated aqueous $Na_2S_2O_3$ solution (3 mL) and saturated aqueous $NaHCO_3$ solution (3 mL). The mixture was stirred for ten minutes followed by separation of the layers and extraction of the aqueous layer with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Purification of the crude product by column chromatography (silica, P/Et_2O = 75/1 → 50/1 → 25/1) gave 9.20 mg of ketone **15** (41.4 µmol, 41%) as a colourless solid.

M.p.: 83 °C.

TLC: R_f = 0.40 (P/EtOAc = 10/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3058 (w, sp^2-CH), 2952 (m, sp^3-CH), 2865 (m, sp^3-CH), 1696 (vs, C=O), 1623 (m), 1244 (m), 826 (m, sp^2-CH), 752 (s, sp^2-CH).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.20 – 1.29 (m, 1 H, *H*H-9), 1.66 – 1.71 (m, 1 H, H*H*-9), 1.88 – 2.00 (m, 2 H, *H*H-8, *H*H-10), 2.12 – 2.22 (m, 2 H, H*H*-8, H*H*-10), 3.23

(ddd, ^3J = 9.5 Hz, ^3J = 6.6 Hz, ^3J = 2.4 Hz, 1 H, H-7a), 4.21 (ddd, ^3J = 9.5 Hz, ^3J = 6.6 Hz, ^3J = 2.7 Hz, 1 H, H-10a), 7.63 – 7.69 (m, 2 H, H-2, H-3)[#], 7.69 (d, ^3J = 8.6 Hz, 1 H, H-6)[#], 7.80 (d, ^3J = 8.6 Hz, 1 H, H-5), 7.96 (d, ^3J = 7.9 Hz, 1 H, H-4), 8.16 (d, ^3J = 7.9 Hz, 1 H, H-1).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 25.5 (t, C-9), 30.1 (t, C-8), 32.2 (t, C-10), 42.7 (d, C-10a), 53.2 (d, C-7a), 119.3 (d, C-6), 125.4 (d, C-1), 127.0 (d, C-2*), 128.9 (d, C-5), 129.1 (d, C-3*), 129.3 (d, C-4*), 130.1 (s, C-10c), 135.1 (s, C-6a), 137.4 (s, C-4a), 159.3 (s, C-10b), 210.1 (s, CO).

[#] signals are partially overlapped.

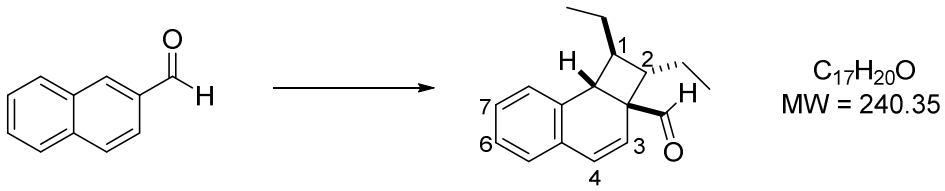
* assignment is interconvertible.

MS (EI, 70 eV): *m/z* (%) = 222 (100) $[M]^+$, 194 (61) $[M - CO]^+$, 179 (14), 165 (49), 152 (14), 127 (11), 95 (4), 57 (10).

HRMS (EI, 70 eV): calcd for $C_{16}H_{14}O$ $[M]^+$: 222.1039; found: 222.1041.

calcd for $C_{15}{}^{13}CH_{14}O$ $[M]^+$: 223.1073; found: 223.1077.

(1*SR*,2*SR*,2a*RS*,8b*SR*)-1,2-Diethyl-1,8b-dihydrocyclobuta[*a*]naphthalene-2a(2*H*)-carbaldehyde (18)



2 **18**

Using (*E*)-3-hexene as olefin:

According to the General Procedure 1, a solution of 2-naphthaldehyde (**2**, 15.6 mg, 100 µmol, 1.00 eq.), (*E*)-3-hexene (373 µL, 352 mg, 3.00 mmol, 30.0 eq.) and aluminium bromide solution (50.0 µL, 100 mM in CH_2Br_2/CH_2Cl_2, 5.0 µmol, 5.0 mol%) in dichloromethane (5 mL) was irradiated at λ = 457 nm (LED045) for twelve hours. After removal of the solvent, the crude product was purified by column chromatography (silica, P/Et_2O = 75/1 → 50/1). 15.0 mg of *ortho* photocycloaddition product **18** (62.4 µmol, 62%, 78% brsm, d.r. > 95/5) were obtained as a colourless oil besides 3.10 mg of recovered starting material **2** (19.8 µmol, 20%).

Using (*Z*)-3-hexene as olefin:

According to the General Procedure 1, a solution of 2-naphthaldehyde (**2**, 15.6 mg, 100 µmol, 1.00 eq.), (*Z*)-3-hexene (373 µL, 352 mg, 3.00 mmol, 30.0 eq.) and aluminium bromide solution (50.0 µL, 100 mM in CH_2Br_2/CH_2Cl_2, 5.0 µmol, 5.0 mol%) in dichloromethane (5 mL) was irradiated at λ = 457 nm (LED045) for twelve hours. After removal of the solvent, the crude product was purified by column chromatography (silica, P/Et_2O = 75/1 → 50/1). 9.30 mg of *ortho* photocycloaddition product **18** (38.7 µmol, 39%, 63% brsm, d.r. ≈ 90/10) were obtained as a colourless oil besides 5.90 mg of recovered starting material **2** (37.8 µmol, 38%).

TLC: R_f = 0.62 (P/Et_2O = 10/1) [UV, $KMnO_4$, CAM].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3021 (w, sp^2-CH), 2961 (s, sp^3-CH), 2924 (m, sp^3-CH), 2875 (w, sp^3-CH), 1715 (vs, C=O), 1459 (m), 1380 (w), 792 (s, sp^2-CH), 753 (w).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.88 (td, ^3J = 7.4 Hz, ^4J = 4.2 Hz, 6 H, CH_3), 1.47 – 1.65 (m, 4 H, CH_2), 2.11 (*virt.* tt, $^3J \approx {}^3J$ = 9.2 Hz, $^3J \approx {}^3J$ = 6.8 Hz, 1 H, H-1), 2.42 (*virt.* td, $^3J \approx {}^3J$ = 9.5 Hz, ^3J = 5.6 Hz, 1 H, H-2), 3.36 (dd, ^3J = 9.2 Hz, ^4J = 1.1 Hz, 1 H, H-8b), 5.87 (dd, ^3J = 10.0 Hz, ^4J = 1.1 Hz, 1 H, H-3), 6.71 (d, ^3J = 10.0 Hz, 1 H, H-4), 6.98 – 7.01 (m, 1 H, H-8), 7.06 (dd, ^3J = 5.5 Hz, ^4J = 3.4 Hz, 1 H, H-5), 7.12 – 7.16 (m, 2 H, H-6, H-7), 9.58 (s, 1 H, CHO).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 11.8 (q, CH_3), 13.1 (q, CH_3), 23.4 (t, CH_2), 27.9 (t, CH_2), 40.8 (d, C-8b), 49.0 (d, C-1), 53.9 (d, C-2), 54.1 (s, C-2a), 122.3 (d, C-3), 127.1 (d, C-8), 127.3 (d, C-6*), 127.8 (d, C-5), 128.4 (d, C-7*), 131.2 (s, C-4a), 131.7 (d, C-4), 134.6 (s, C-8a), 200.9 (d, CHO).

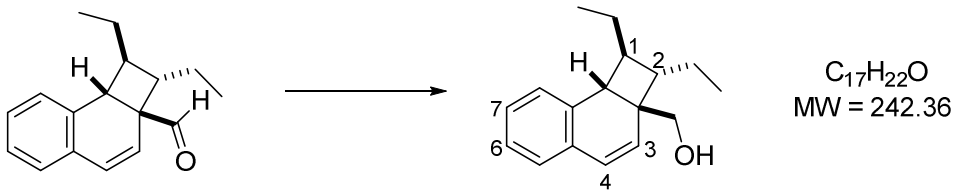
* assignment is interconvertible.

MS (EI, 70 eV): *m/z* (%) = 240 (4) $[M]^+$, 210 (9), 181 (24), 156 (100) $[M - C_6H_{12}]^+$, 127 (31) $[M - C_6H_{12} - CHO]$, 77 (4), 55 (5).

HRMS (EI, 70 eV): calcd for $C_{17}H_{20}O$ $[M]^+$: 240.1509; found: 240.1509.

calcd for $C_{16}{}^{13}CH_{20}O$ $[M]^+$: 241.1542; found: 241.1538.

[(1*SR*,2*SR*,2a*RS*,8b*SR*)-1,2-Diethyl-1,8b-dihydrocyclobuta[*a*]naphthalen-2a(2*H*)-yl]methanol (S8)



18 **S8**

A solution of aldehyde **18** (15.4 mg, 64.1 µmol, 1.00 eq.) in tetrahydrofuran (10 mL) was added dropwise to a suspension of lithium aluminium hydride (7.30 mg, 192 µmol, 3.00 eq.) in tetrahydrofuran (5 mL) at 0 °C. After 45 minutes the mixture was diluted with diethyl ether (10 mL) at 0 °C to quench the excess of lithium aluminium hydride. When no further gas evolution was observed, water (50 µL), 10% aqueous NaOH solution (50 µL) and water (150 µL) was added. After warming to room temperature the mixture was vigorously stirred at this temperature for 15 minutes and then $MgSO_4$ was added. After filtration of the suspension over Celite followed by washing the residue with diethyl ether (15 mL) the solvent was removed under reduced pressure. Purification by column chromatography (silica, P/EtOAc = 20/1) gave 13.6 mg of alcohol **S8** (56.1 µmol, 88%) as a colourless oil.

TLC: R_f = 0.31 (P/EtOAc = 10/1) [UV, CAM].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3365 (s, OH), 3018 (m, sp^2-CH), 2959 (vs, sp^3-CH), 2921 (vs, sp^3-CH), 2874 (s, sp^3-CH), 2855 (s, sp^3-CH), 1458 (m), 1378 (w), 1260 (w), 1038 (m), 791 (s, sp^2-CH), 747 (m).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 0.82 (t, ^3J = 7.4 Hz, 3 H, C-1-CH_3), 0.86 (t, ^3J = 7.5 Hz, 3 H, C-2-CH_3), 1.35 – 1.54 (m, 4H, CH_2), 1.72 (*virt.* tt, $^3J \approx {}^3J$ = 8.8 Hz, $^3J \approx {}^3J$ = 6.5 Hz, 1 H, H-1), 2.17 (*virt.* td, $^3J \approx {}^3J$ = 8.8 Hz, ^3J = 6.5 Hz, 1 H, H-2), 2.92 (d, ^3J = 8.8 Hz, 1 H, H-8b), 3.19 (dd, ^2J = 11.0 Hz, ^3J = 5.5 Hz, 1 H, C-2a-C*H*H), 3.26 (dd,

^{2}J = 11.0 Hz, ^{3}J = 5.6 Hz, 1 H, C-2a-CH*H*), 4.64 (*virt.* t, $^{3}J \approx {}^{3}J$ = 5.6 Hz, 1 H, OH), 5.65 (d, ^{3}J = 9.9 Hz, 1 H, H-3), 6.51 (d, ^{3}J = 9.9 Hz, 1 H, H-4), 6.95 (dd, ^{3}J = 5.4 Hz, ^{4}J = 3.3 Hz, 1 H, H-8), 7.02 (dd, ^{3}J = 5.5 Hz, ^{4}J = 3.4 Hz, 1 H, H-5), 7.06 – 7.09 (m, 2 H, H-6, H-7).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 11.9 (q, C-1-*C*H_3), 13.1 (q, C-2-*C*H_3), 23.2 (t, CH_2), 27.7 (t, CH_2), 41.8 (d, C-8b), 45.4 (s, C-2a), 48.5 (d, C-1), 50.1 (d, C-2), 66.8 (t, C-2a-*C*H_2), 126.3 (d, C-6*), 126.8 (d, C-5*), 127.2 (d, C-8*), 127.5 (d, C-7*), 128.2 (d, C-4), 129.4 (d, C-3), 131.7 (s, C-4a), 135.8 (s, C-8a).

* assignment is interconvertible.

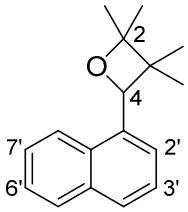
MS (EI, 70 eV): m/z (%) = 242 (2) $[M]^+$, 220 (4), 195 (3), 181 (7), 158 (100) $[M - C_6H_{12}]^+$, 144 (54), 129 (45), 115 (10).

HRMS (EI, 70 eV): calcd for $C_{17}H_{22}O$ $[M]^+$: 242.1665; found: 242.1666.

calcd for $C_{16}{}^{13}CH_{22}O$ $[M]^+$: 243.1699; found: 243.1699.

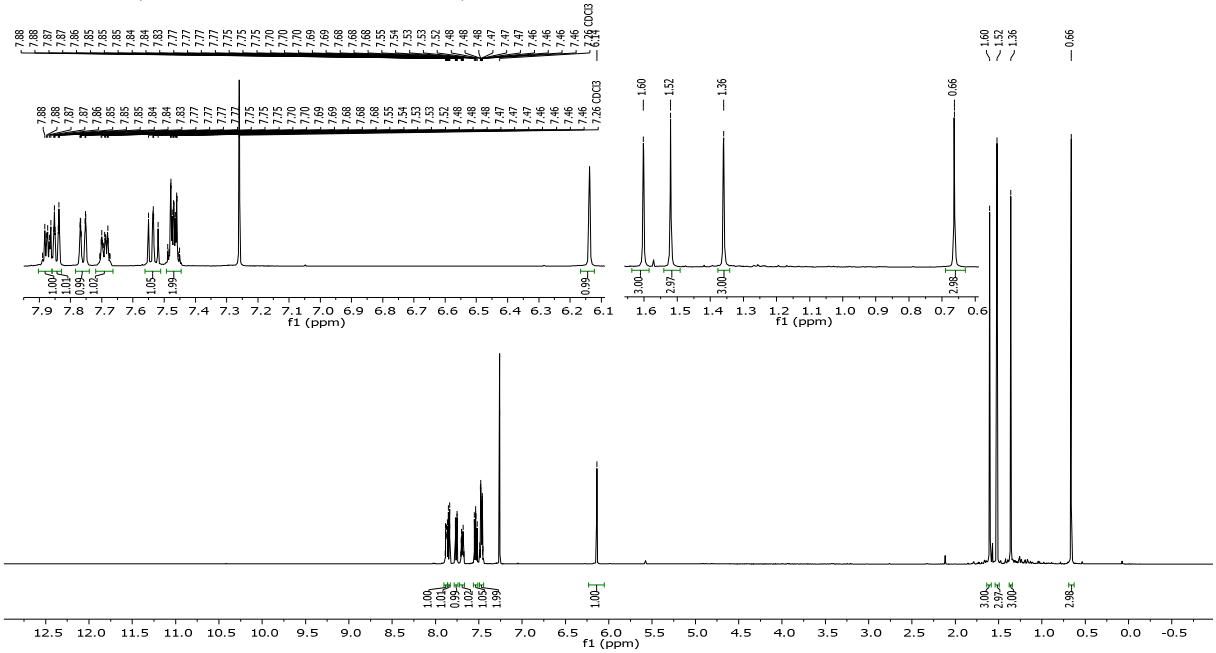
4. NMR spectra of new compounds

2,2,3,3-Tetramethyl-4-(naphthalen-1'-yl)oxetane (5a)

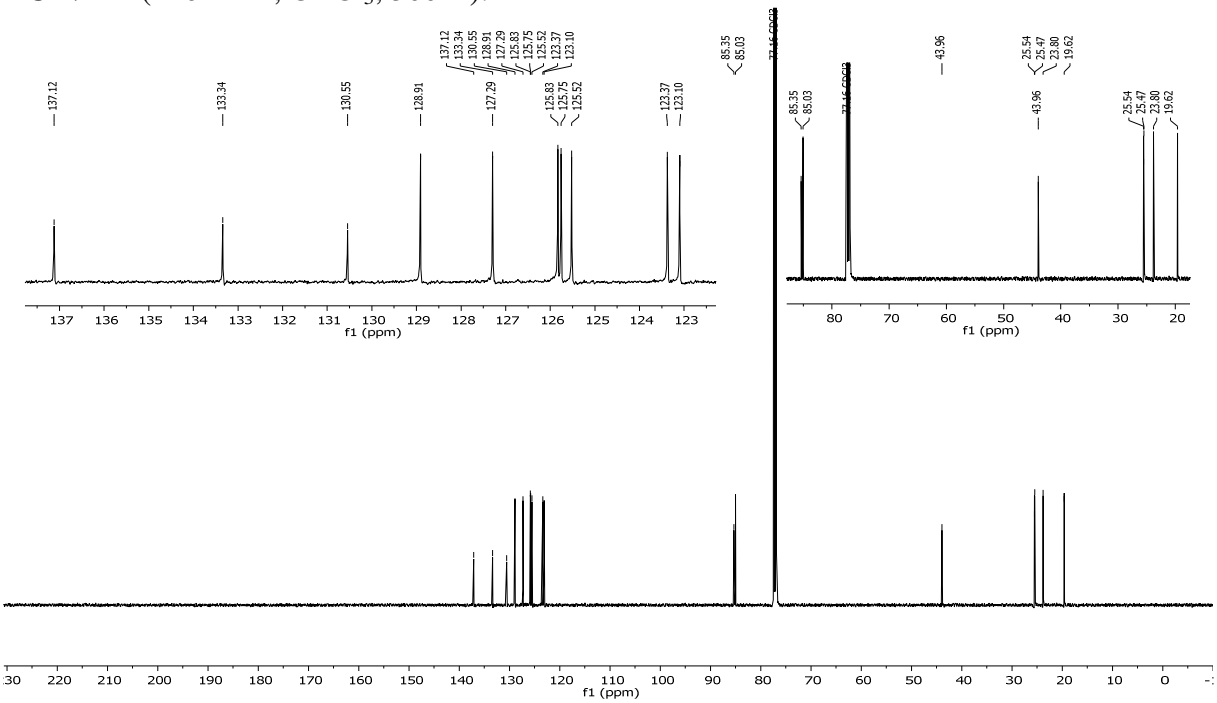


5a

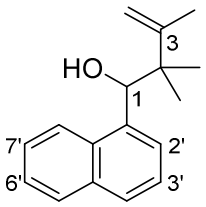
^{1}H NMR (500 MHz, $CDCl_3$, 300 K):



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

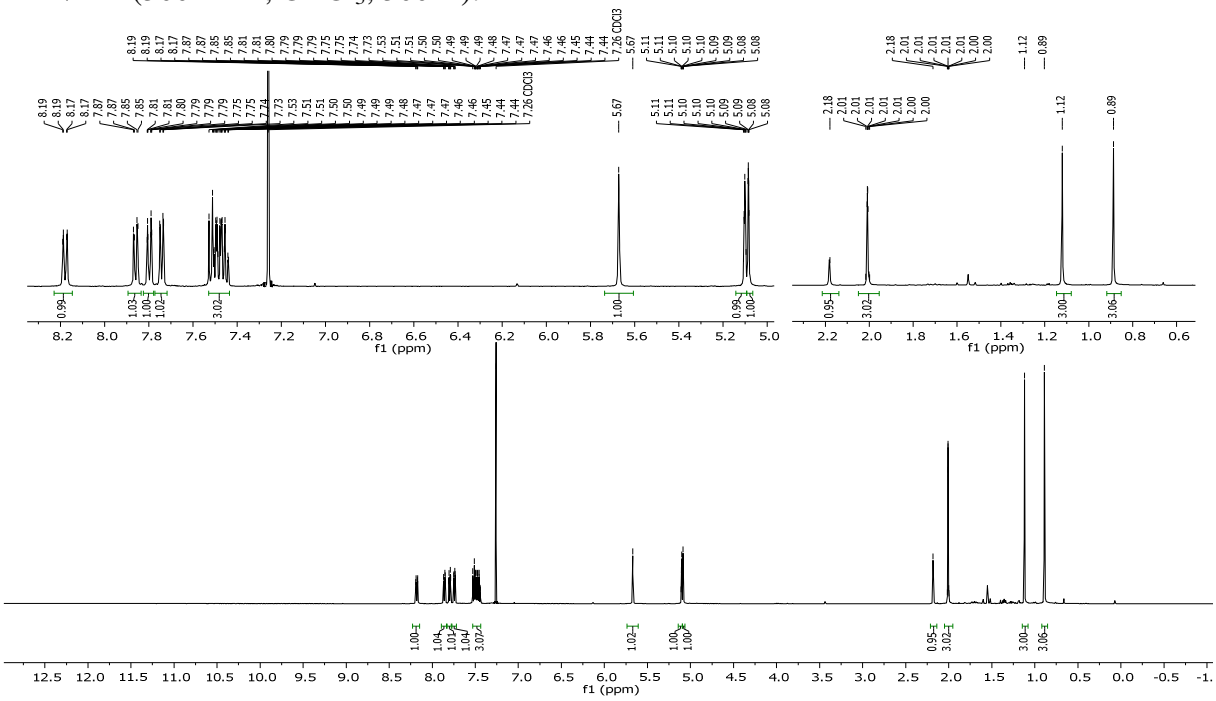


2,2,3-Trimethyl-1-(naphthalen-1'-yl)but-3-en-1-ol (6a)

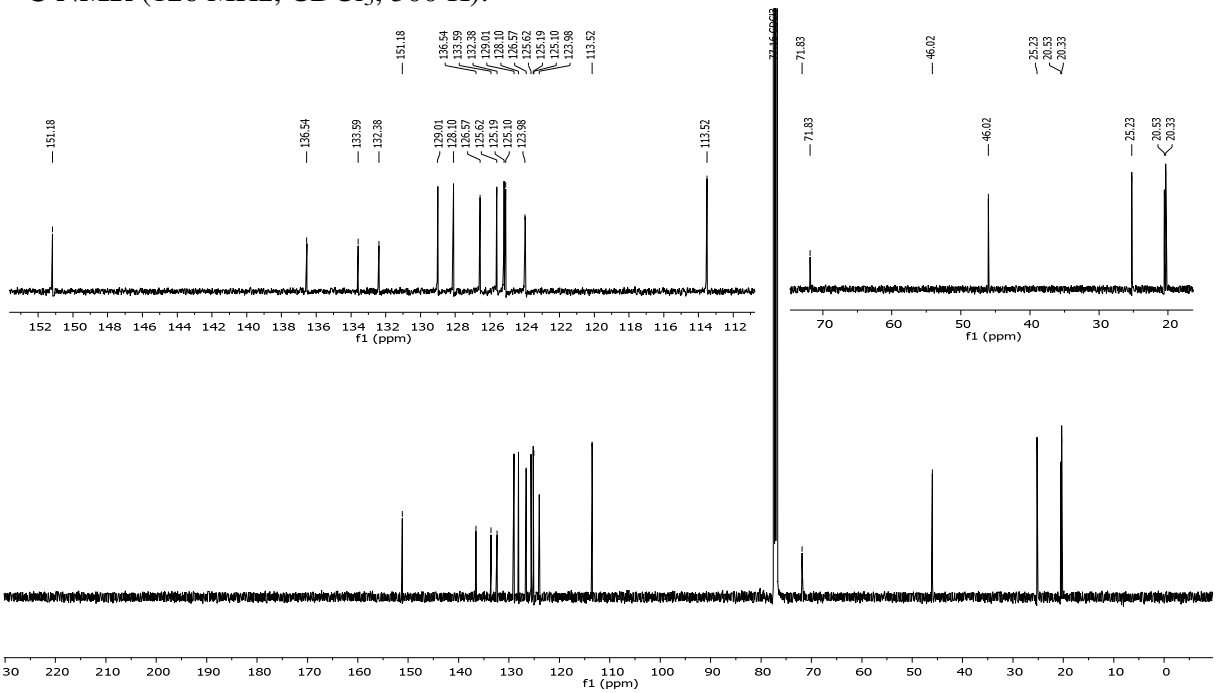


6a

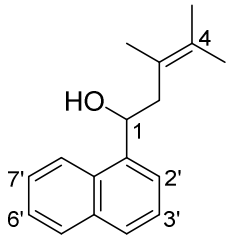
^{1}H NMR (500 MHz, $CDCl_3$, 300 K):



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

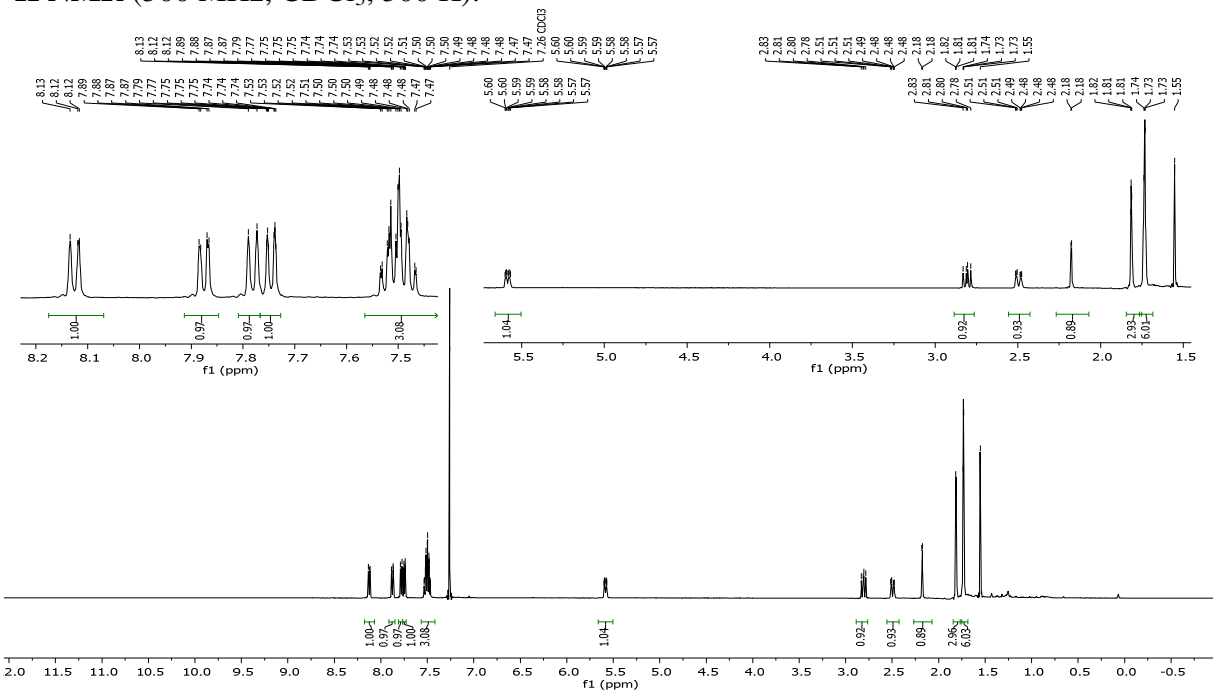


3,4-Dimethyl-1-(naphthalen-1'-yl)pent-3-en-1-ol (7a)

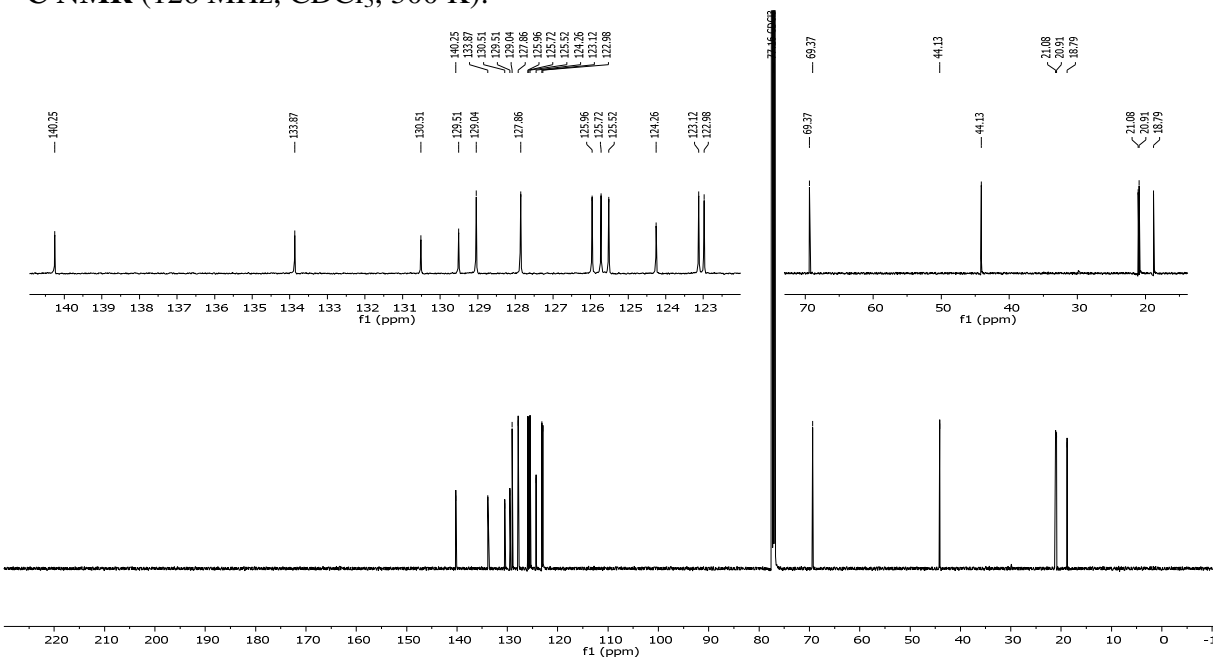


7a

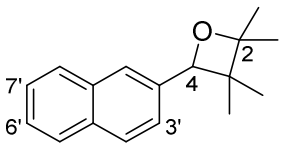
^{1}H NMR (500 MHz, $CDCl_3$, 300 K):



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

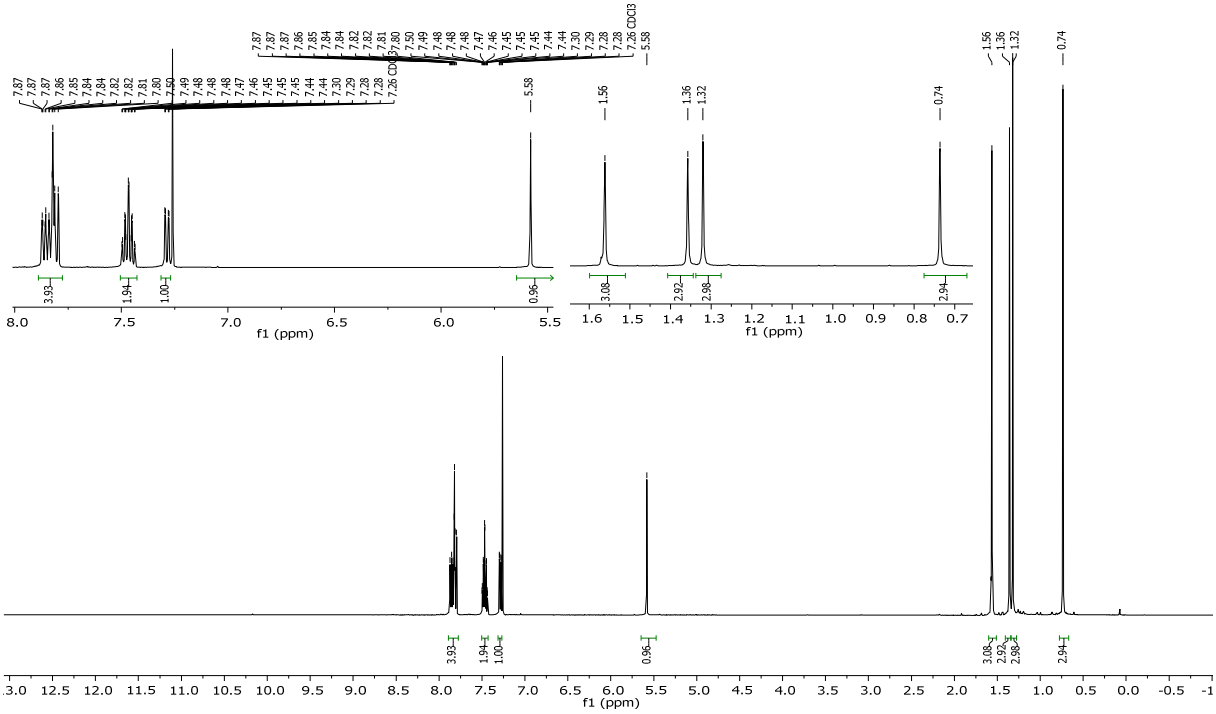


2,2,3,3-Tetramethyl-4-(naphthalen-2'-yl)oxetane (5b)

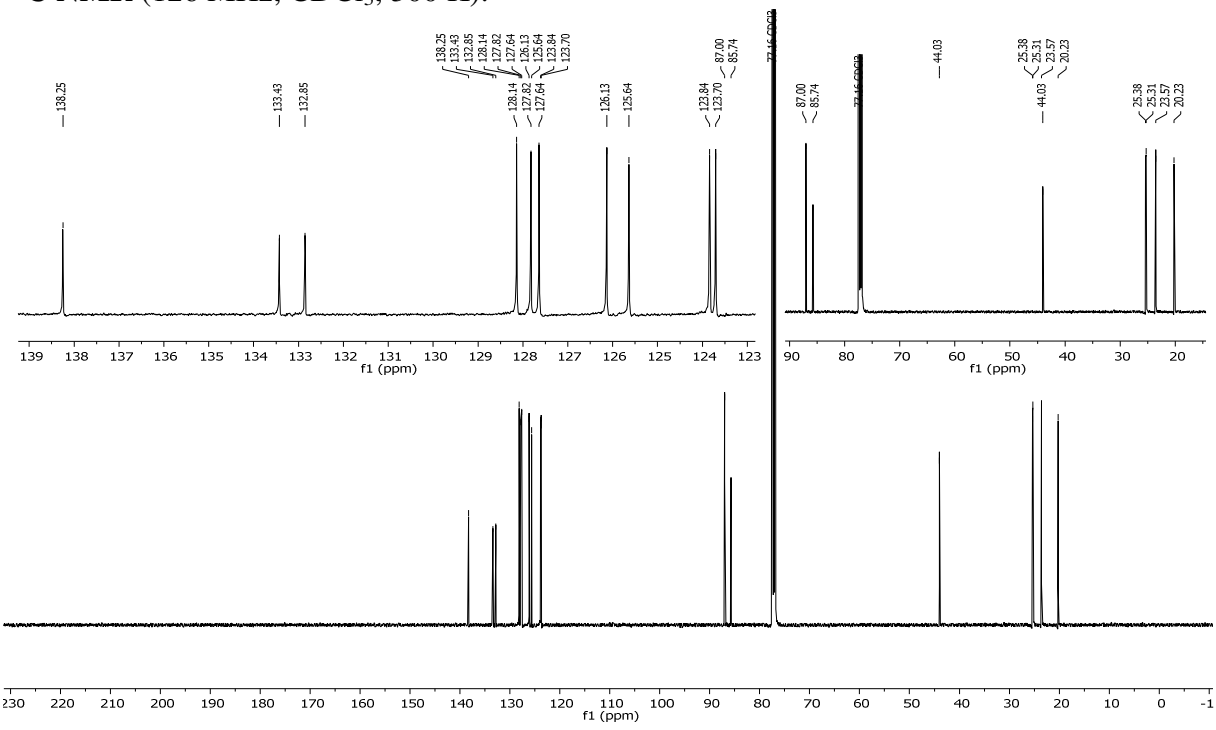


5b

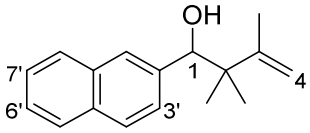
^{1}H NMR (500 MHz, $CDCl_3$, 300 K):



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

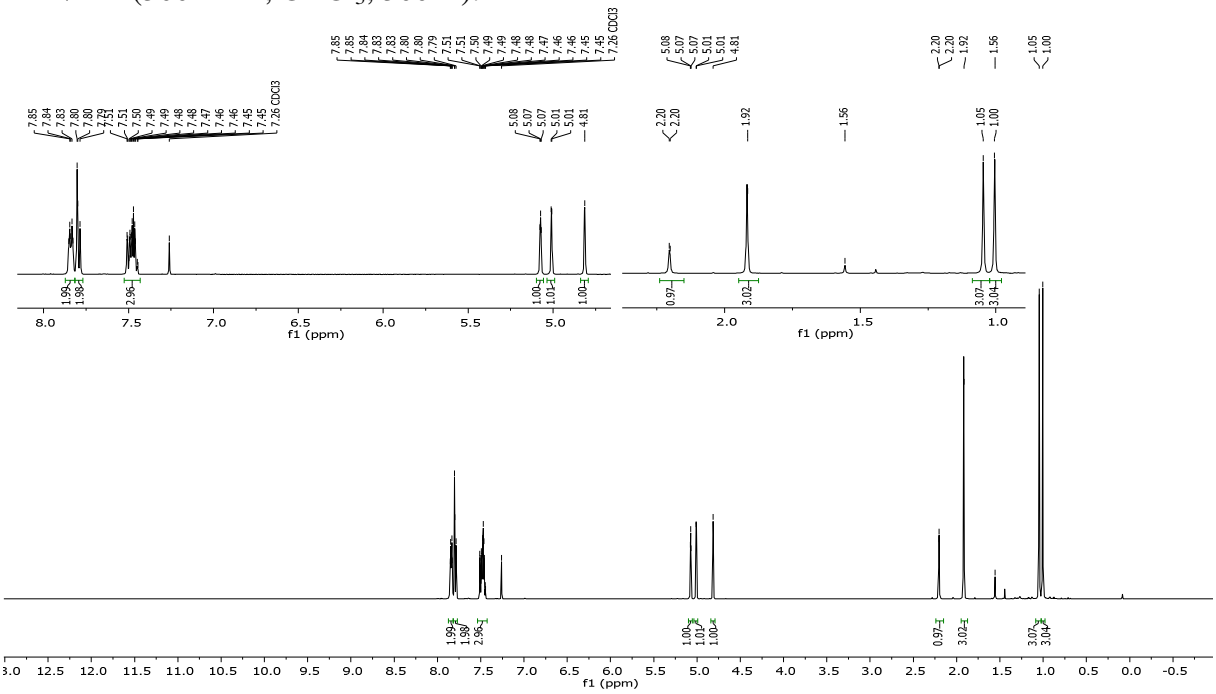


2,2,3-Trimethyl-1-(naphthalen-2'-yl)but-3-en-1-ol (6b)

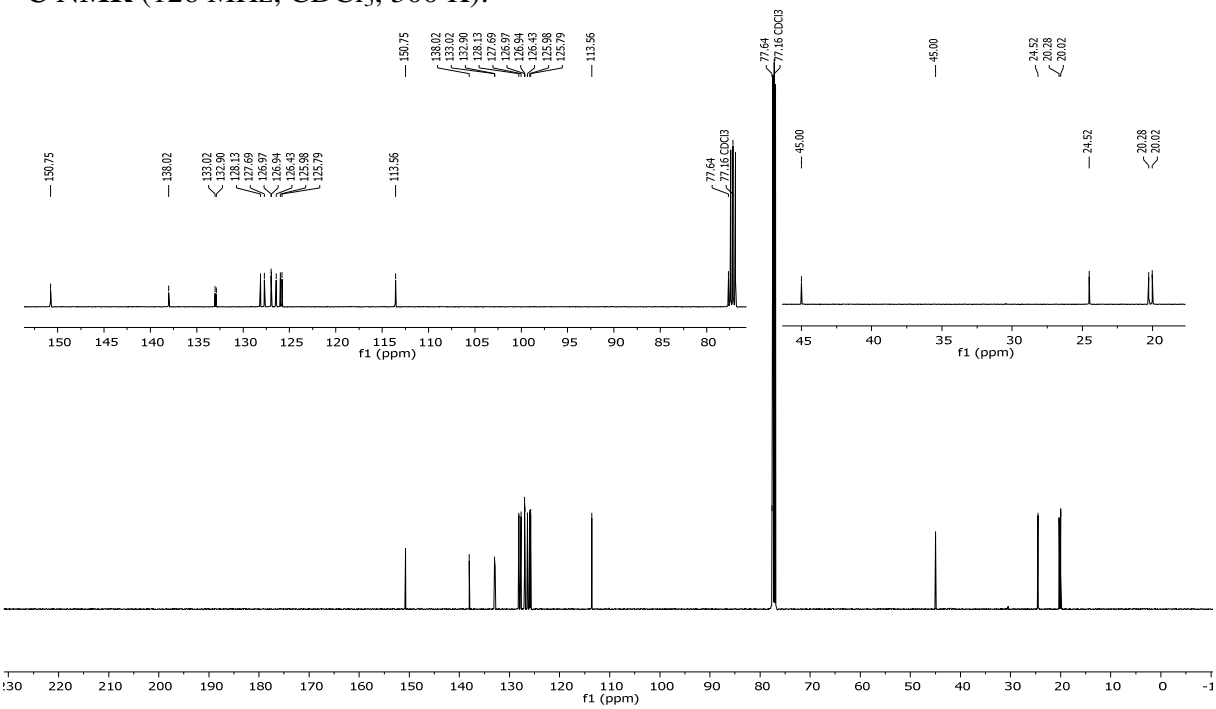


6b

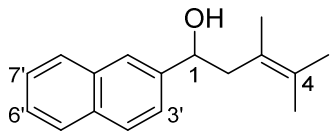
^{1}H NMR (500 MHz, $CDCl_3$, 300 K):



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

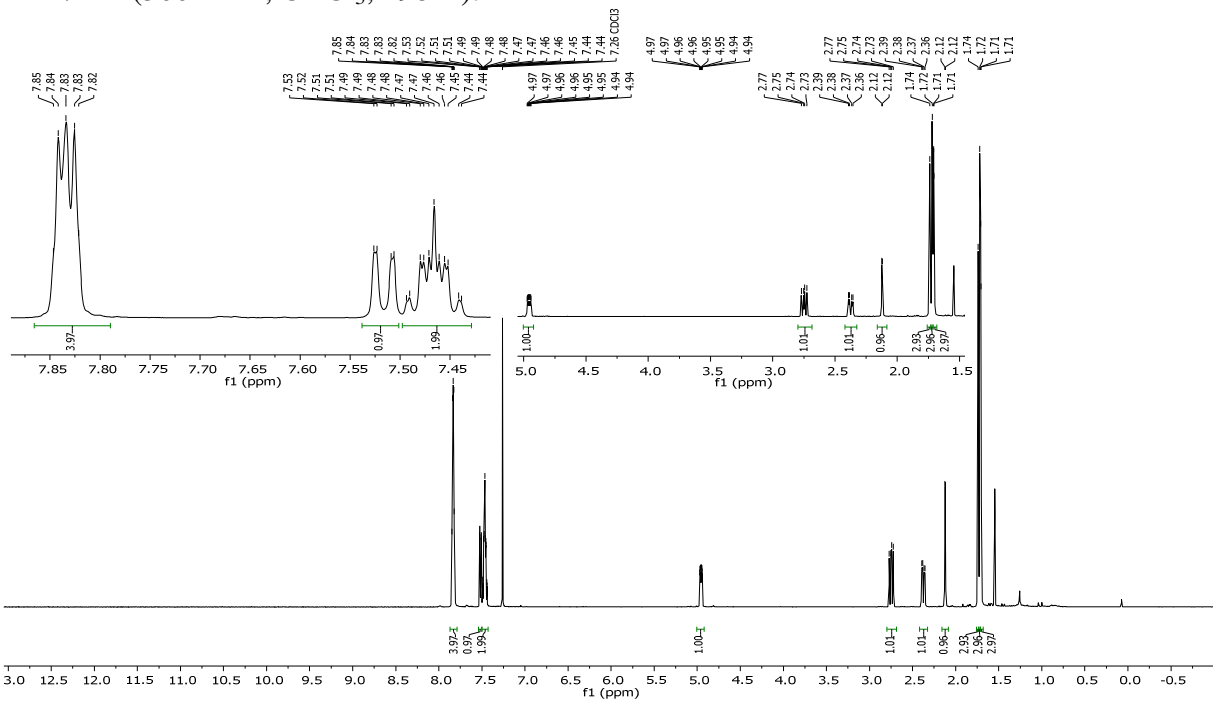


3,4-Dimethyl-1-(naphthalen-2'-yl)pent-3-en-1-ol (7b)

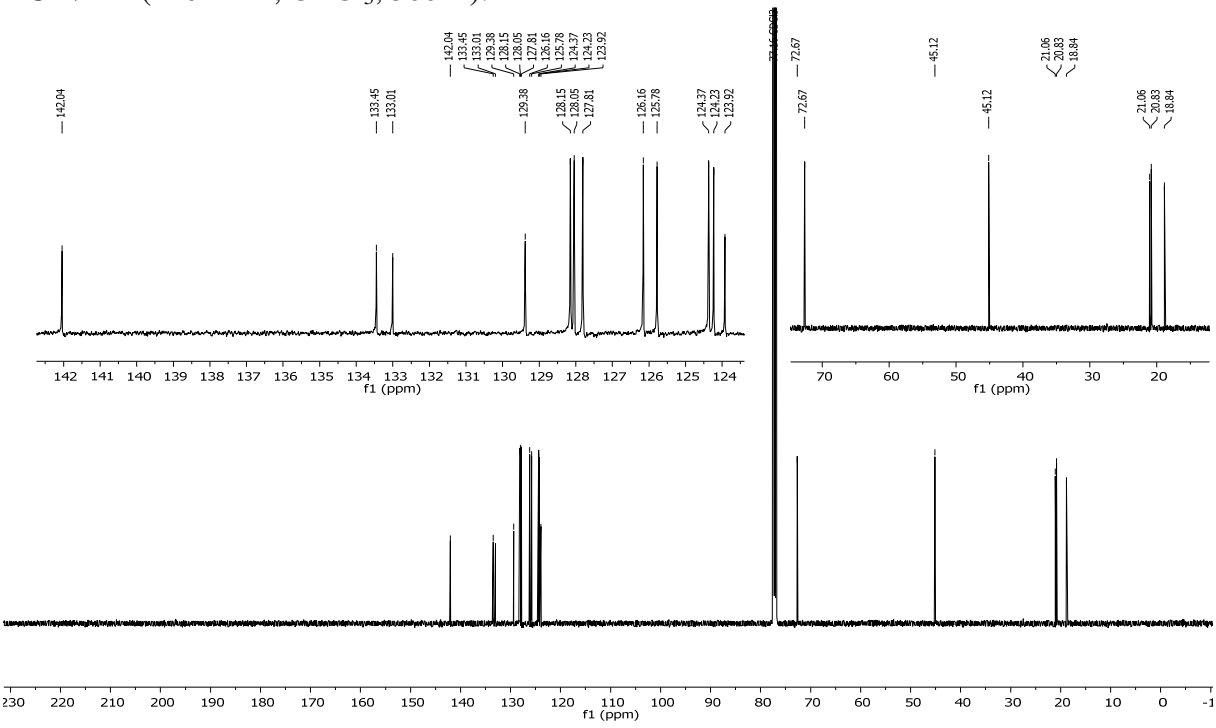


7a

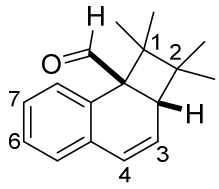
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



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

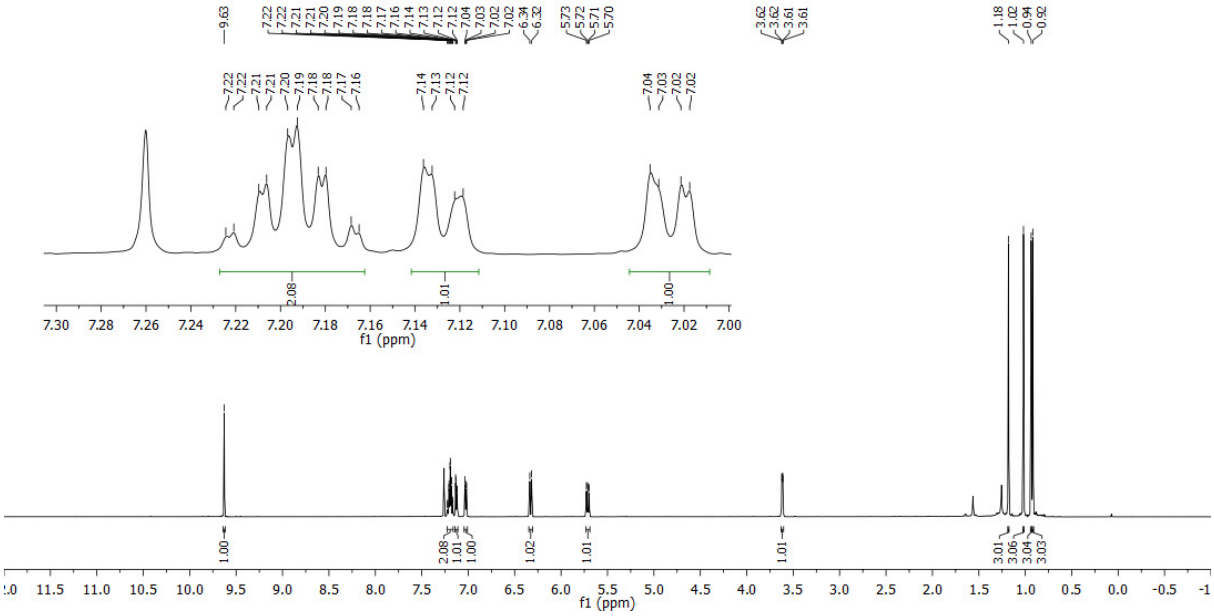


1,1,2,2-Tetramethyl-2,2a-dihydrocyclobuta[*a*]naphthalene-8b(1*H*)-carbaldehyde (10)

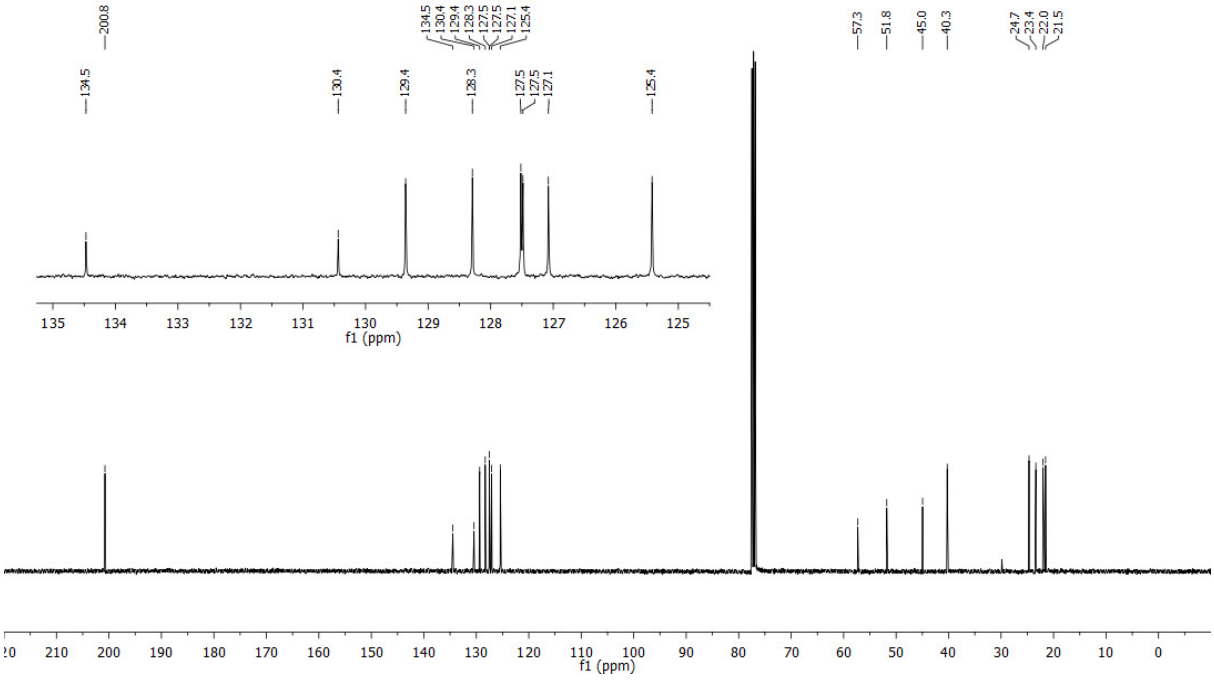


10

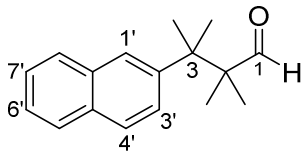
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

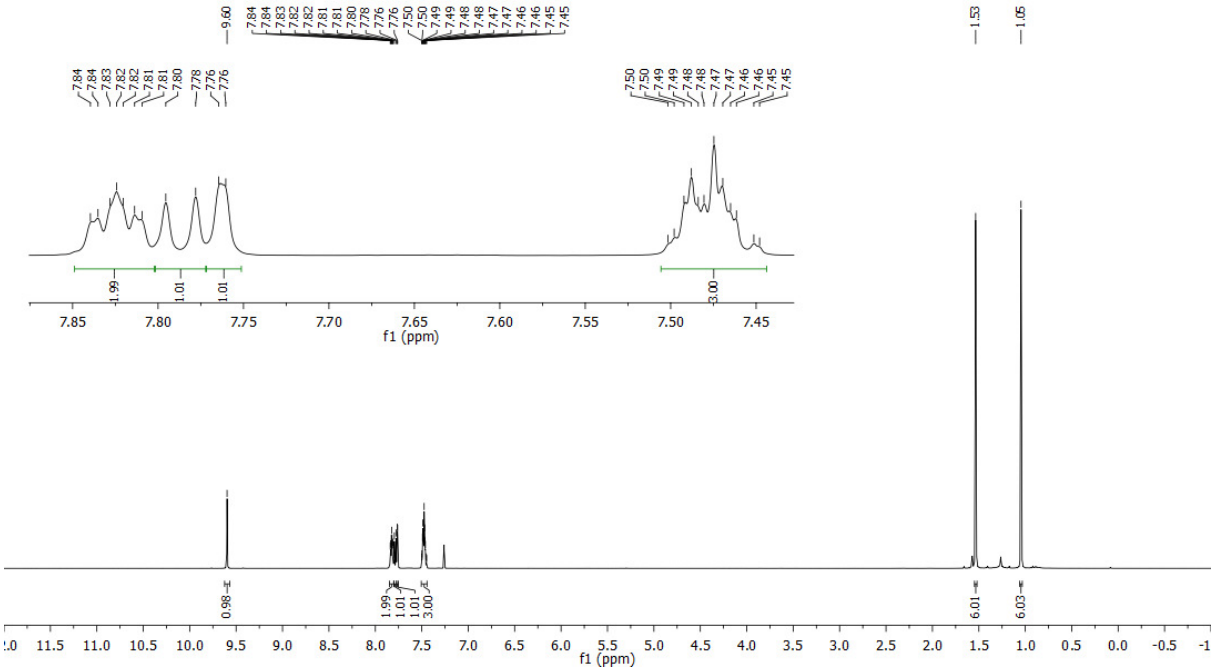


2,2,3-Trimethyl-3-(naphthalen-2'-yl)butanal (8)

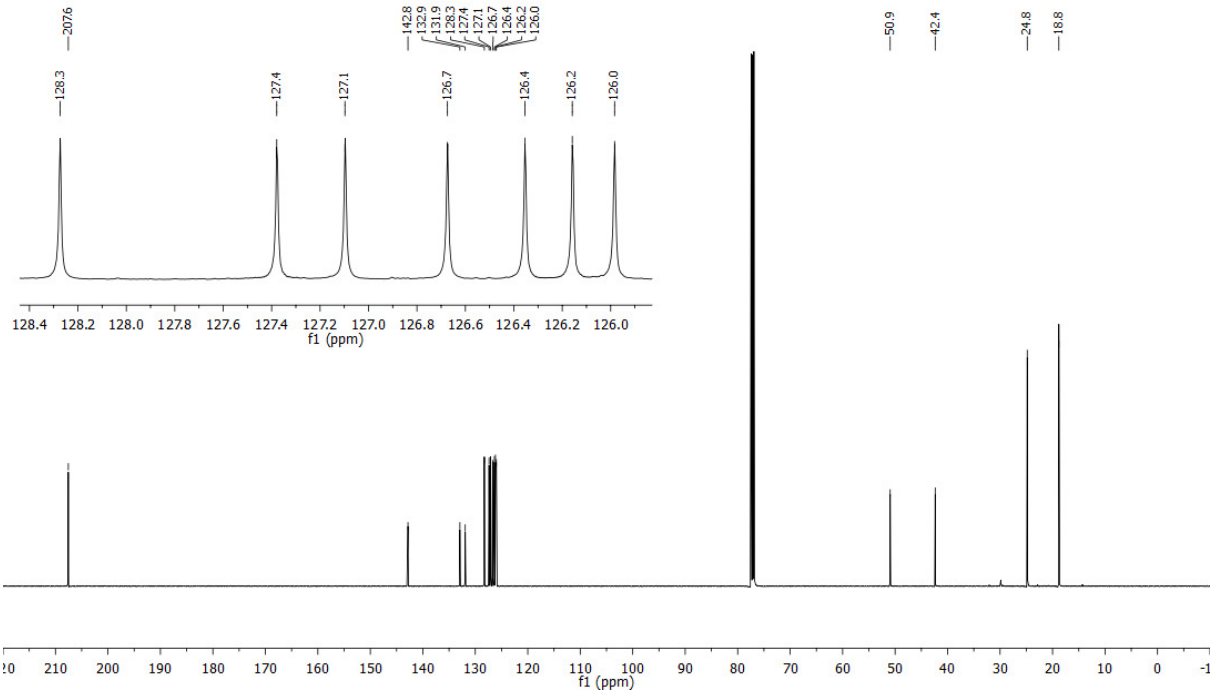


8

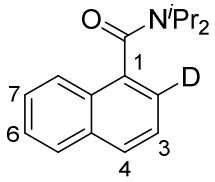
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

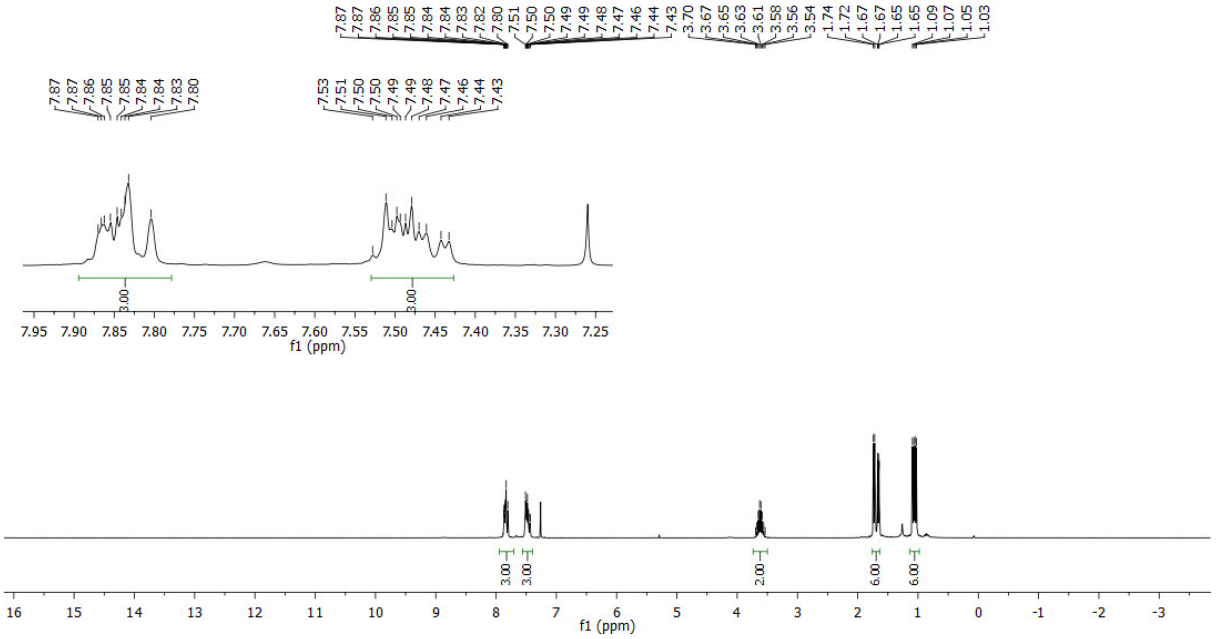


N,N-Diisopropyl-1-naphthamide-2-*d* (S2)

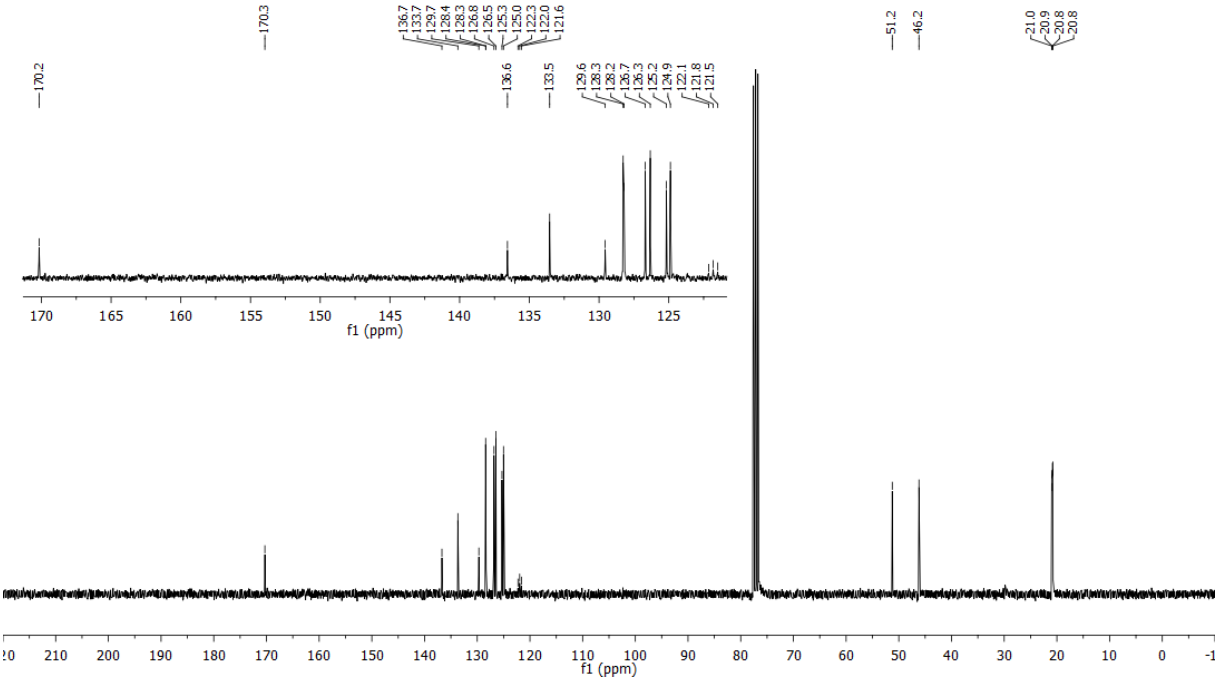


S2

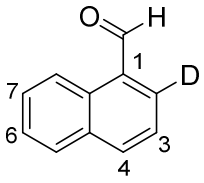
^{1}H NMR (300 MHz, $CDCl_3$, 298 K):



^{13}C NMR (75 MHz, $CDCl_3$, 298 K):

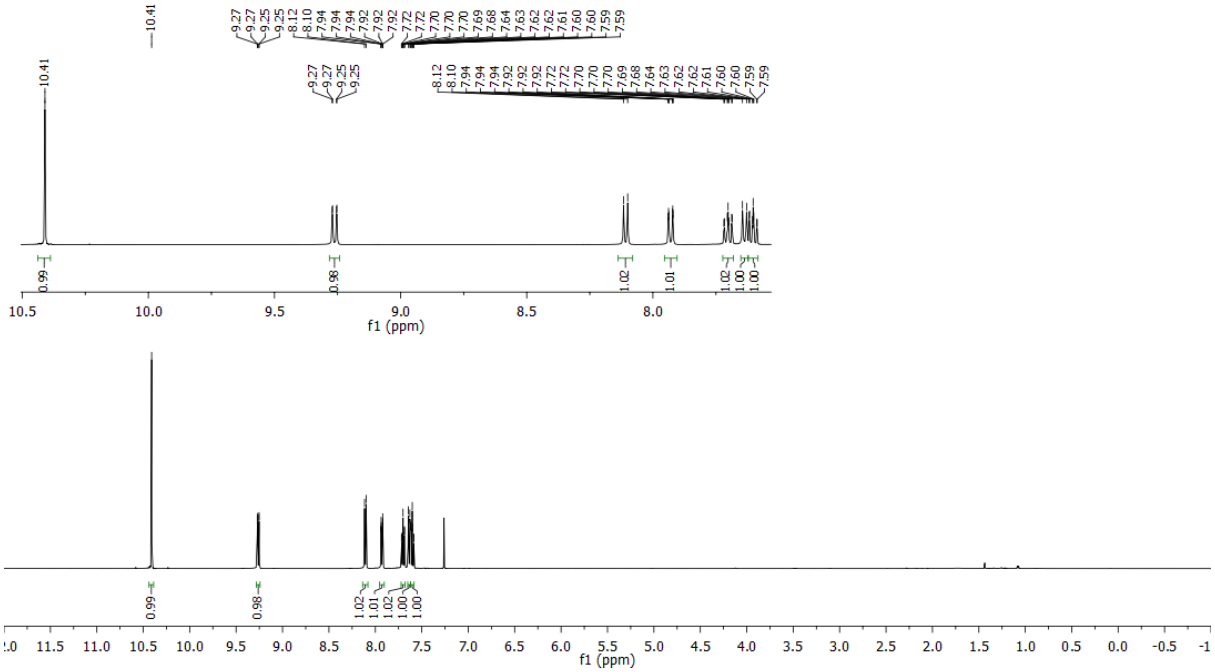


1-Naphthaldehyde-2-*d* (S3)

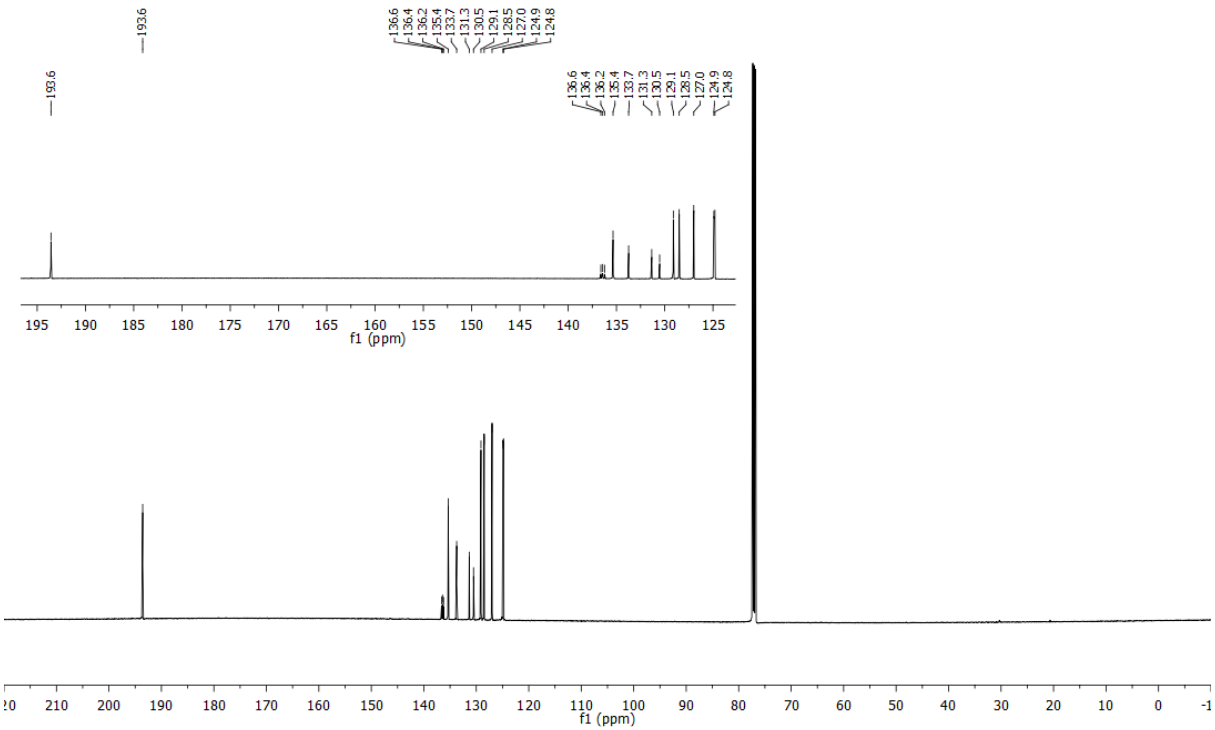


S3

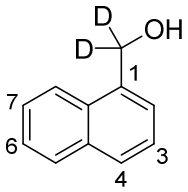
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

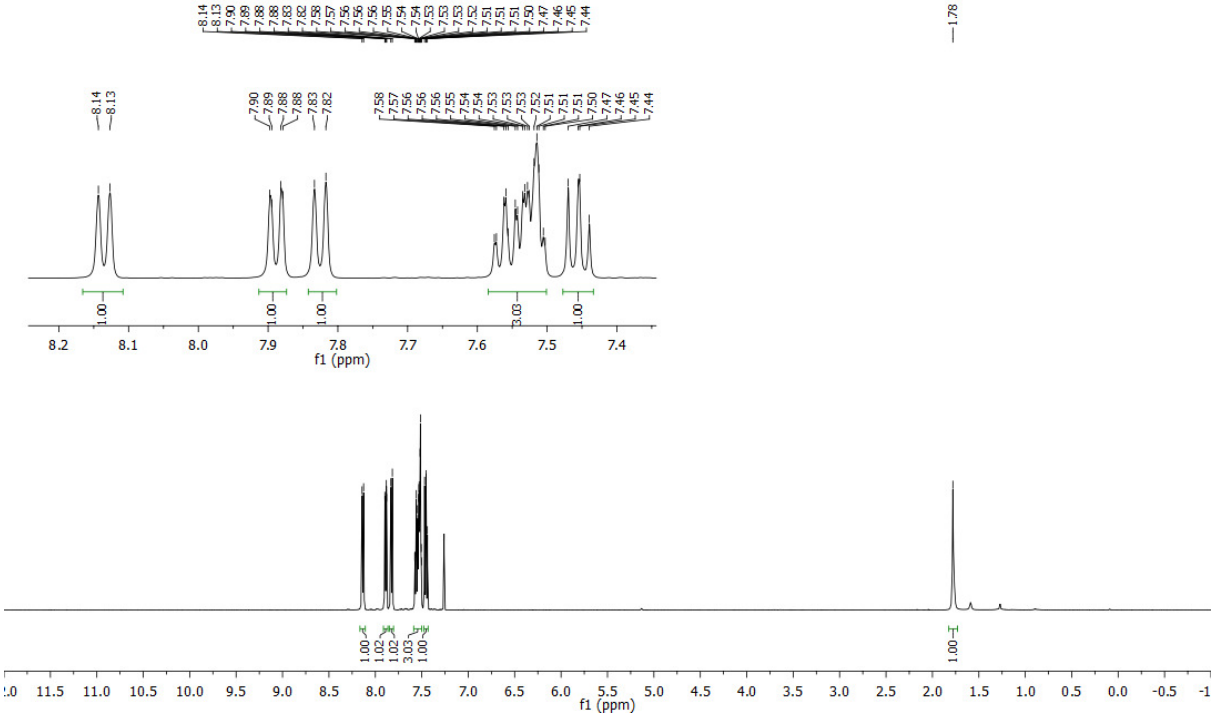


Naphthalen-1-ylmethan-d_2-ol (S4)

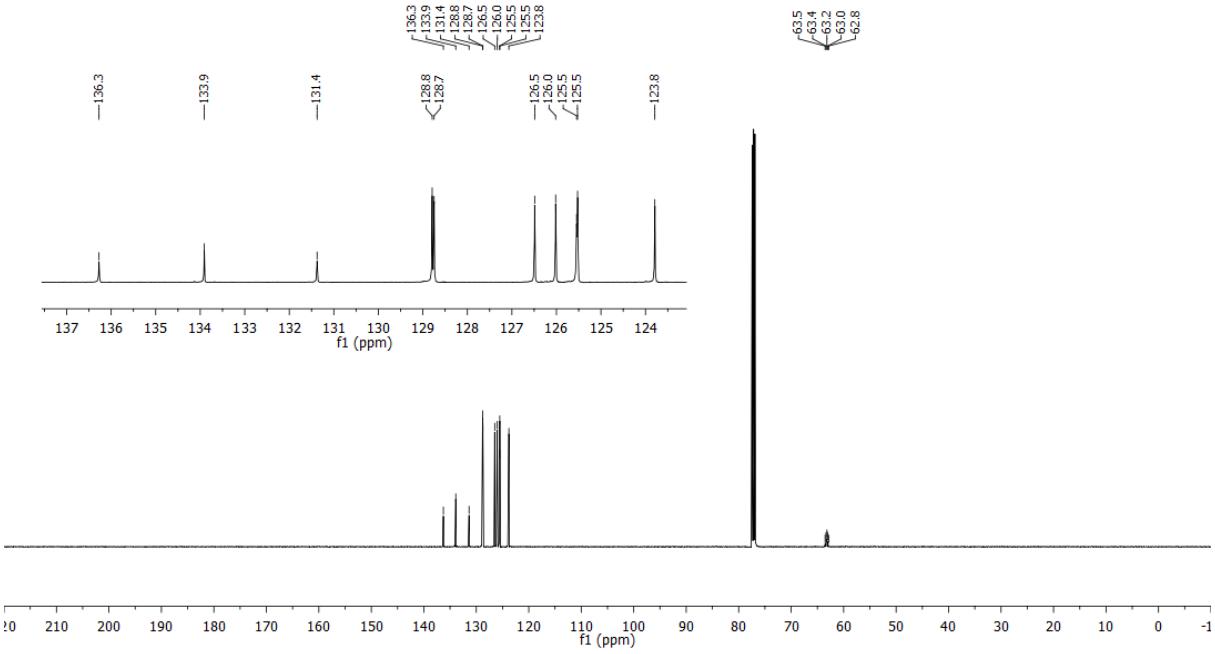


S4

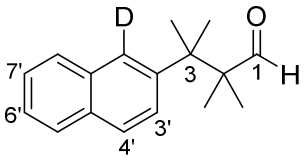
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

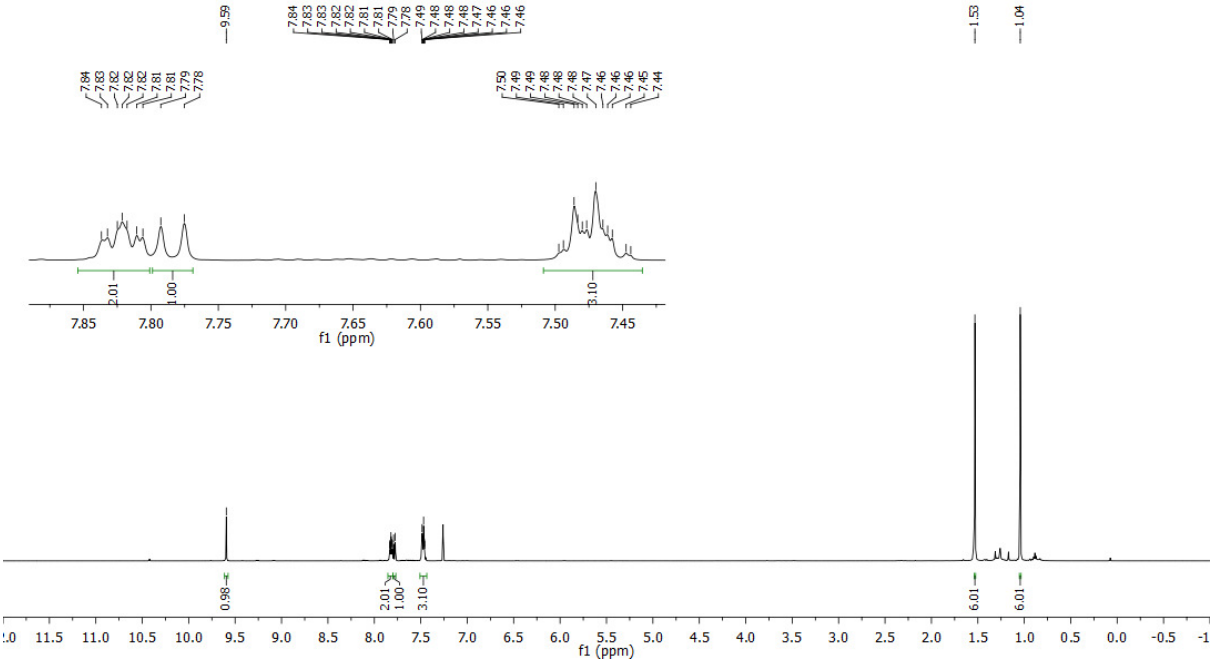


2,2,3-Trimethyl-3-(naphthalen-2-yl-1-*d*)butanal (S6)

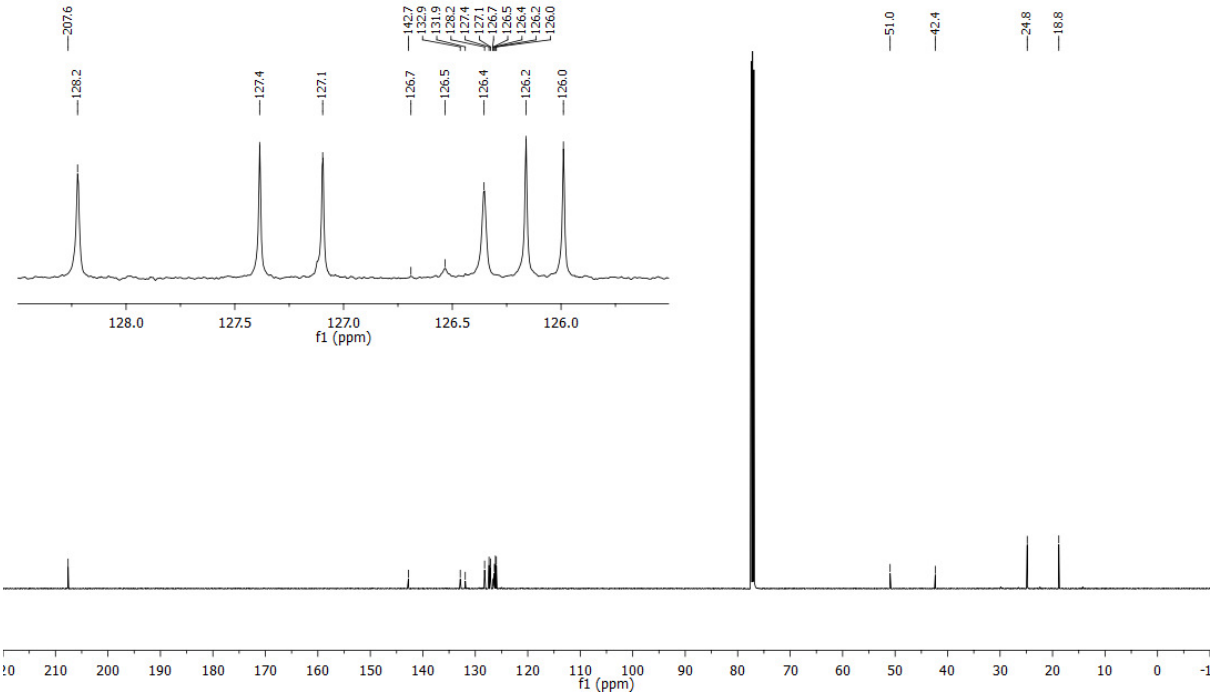


S6

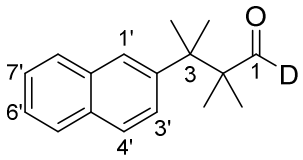
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

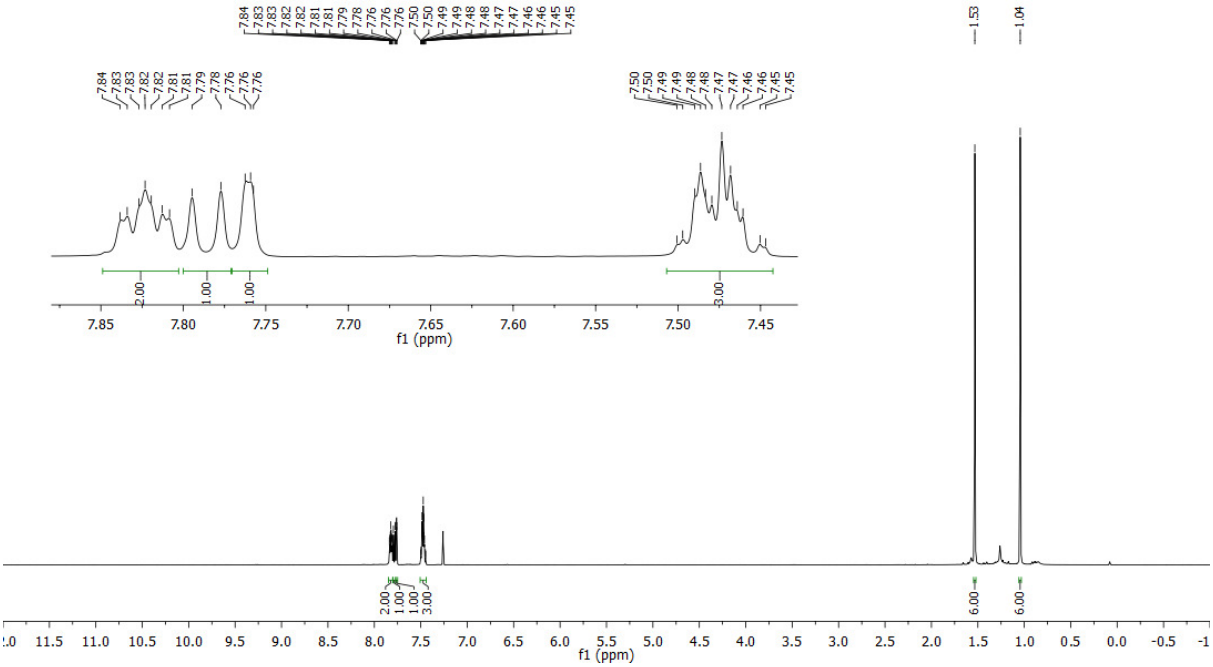


2,2,3-Trimethyl-3-(naphthalen-2-yl)butanal-1-*d* (S7)

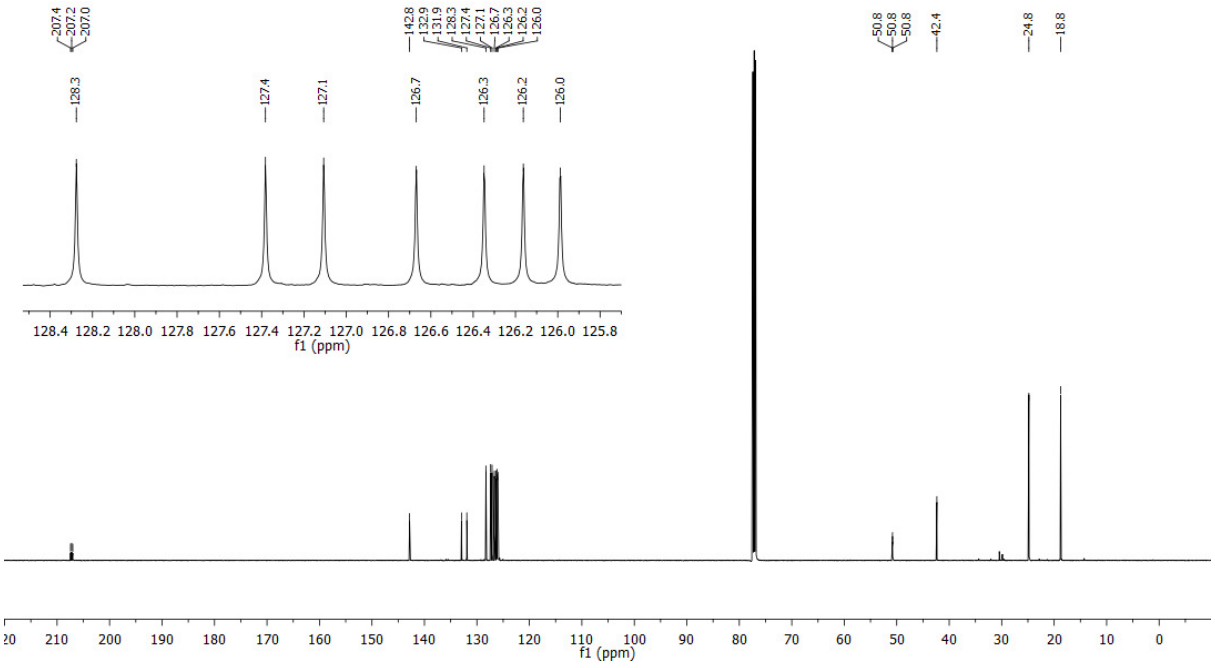


S7

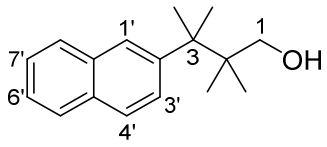
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

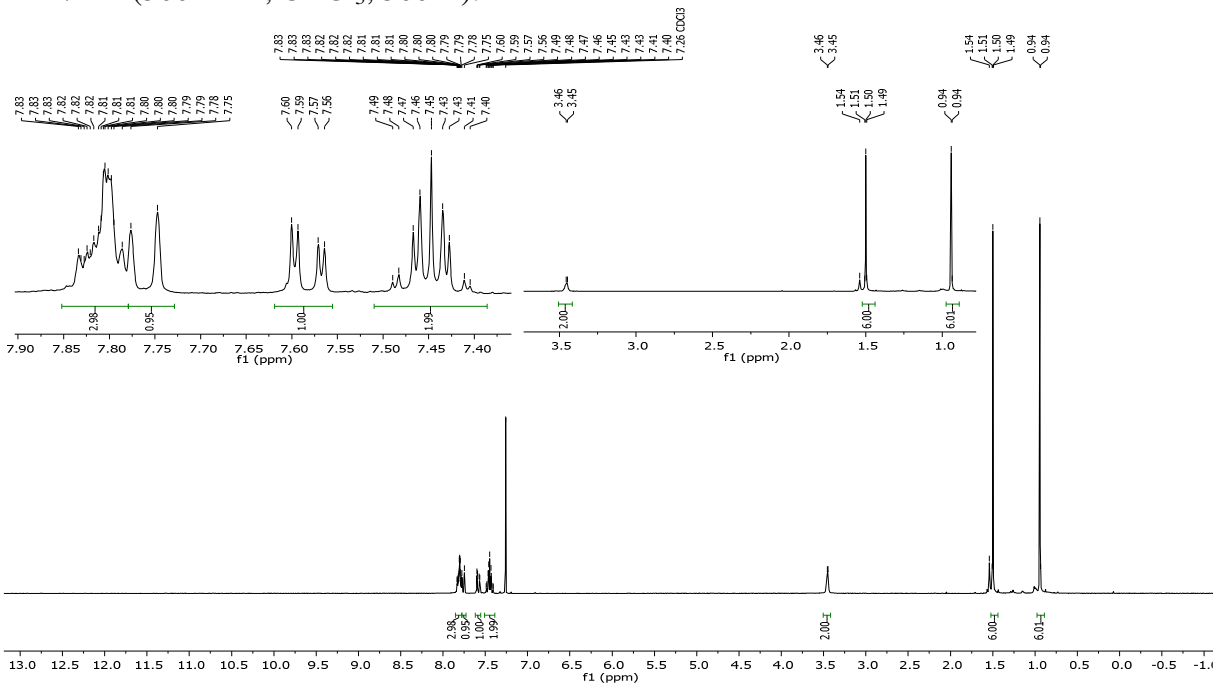


2,2,3-Trimethyl-3-(naphthalen-2'-yl)butan-1-ol (9)

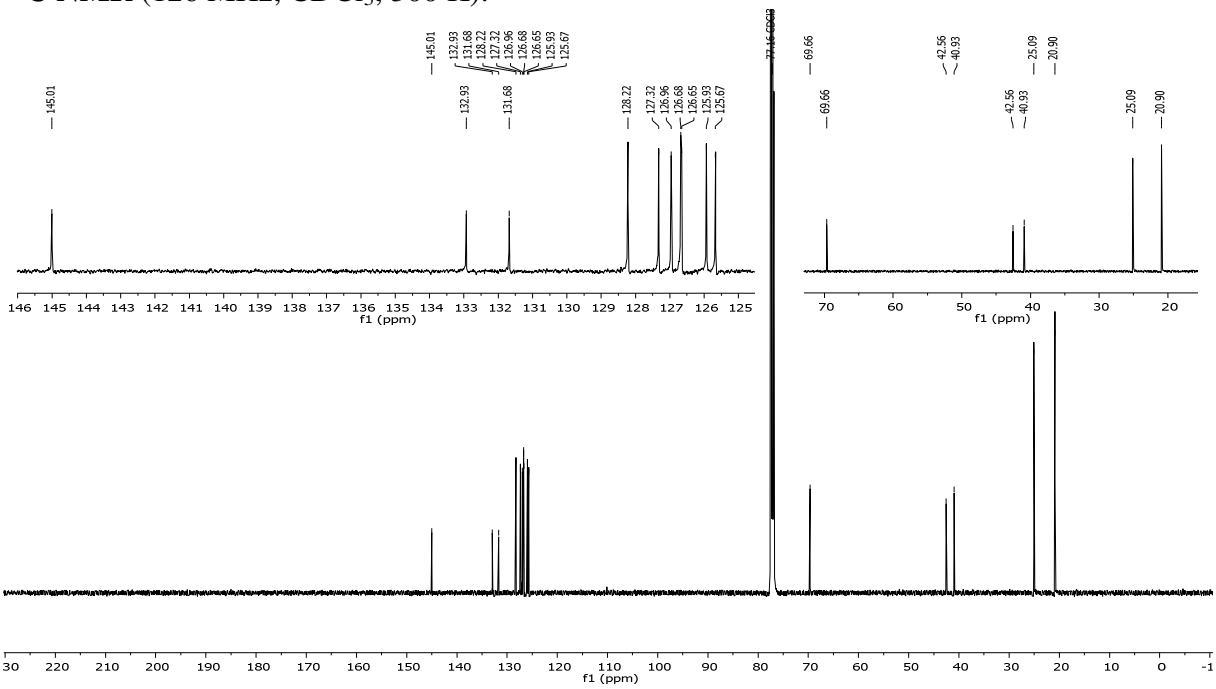


9

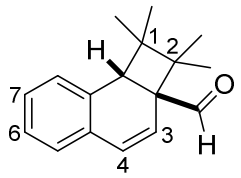
^{1}H NMR (300 MHz, $CDCl_3$, 300 K):



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

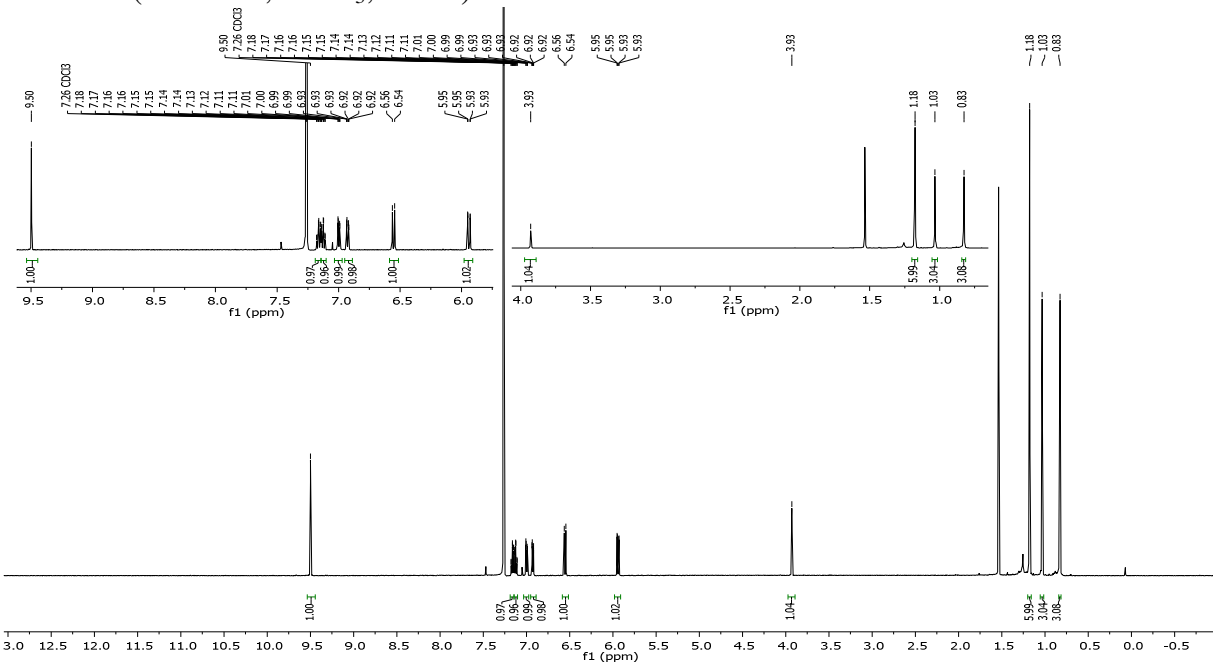


(2a*SR*,8b*SR*)-1,1,2,2-Tetramethyl-1,8b-dihydrocyclobuta[*a*]naphthalene-2a(2*H*)-carbaldehyde (13)

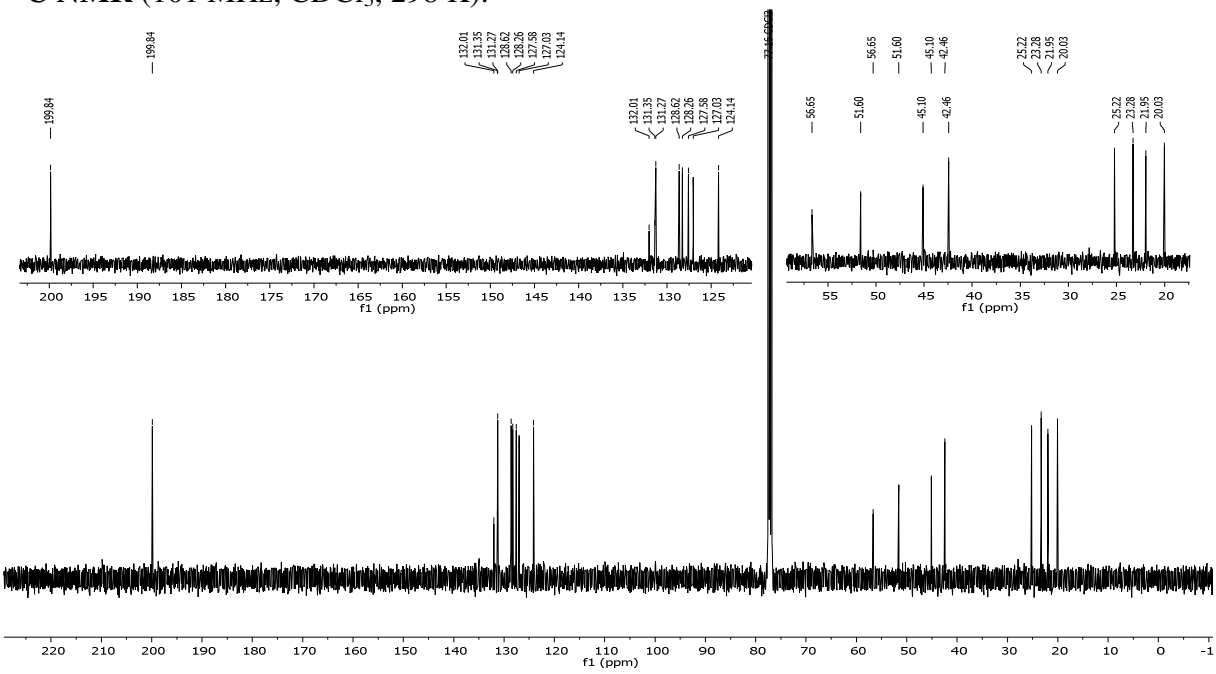


13

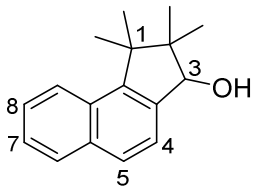
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



^{13}C NMR (101 MHz, $CDCl_3$, 298 K):

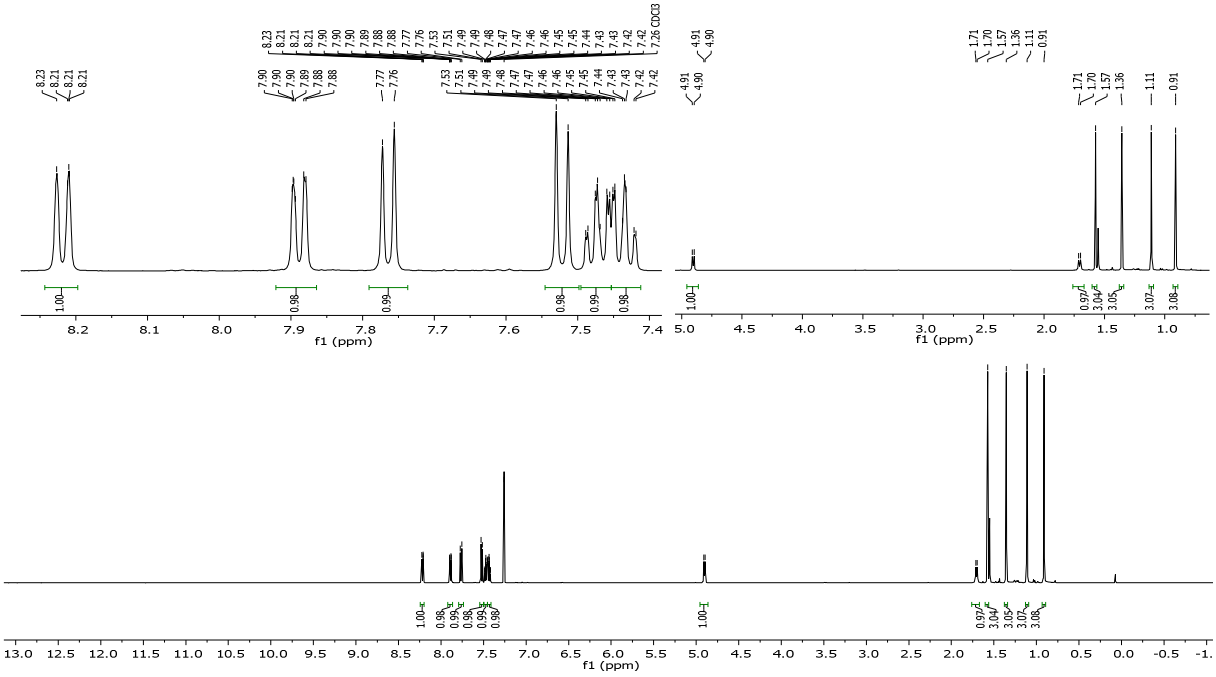


1,1,2,2-Tetramethyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-3-ol (14)

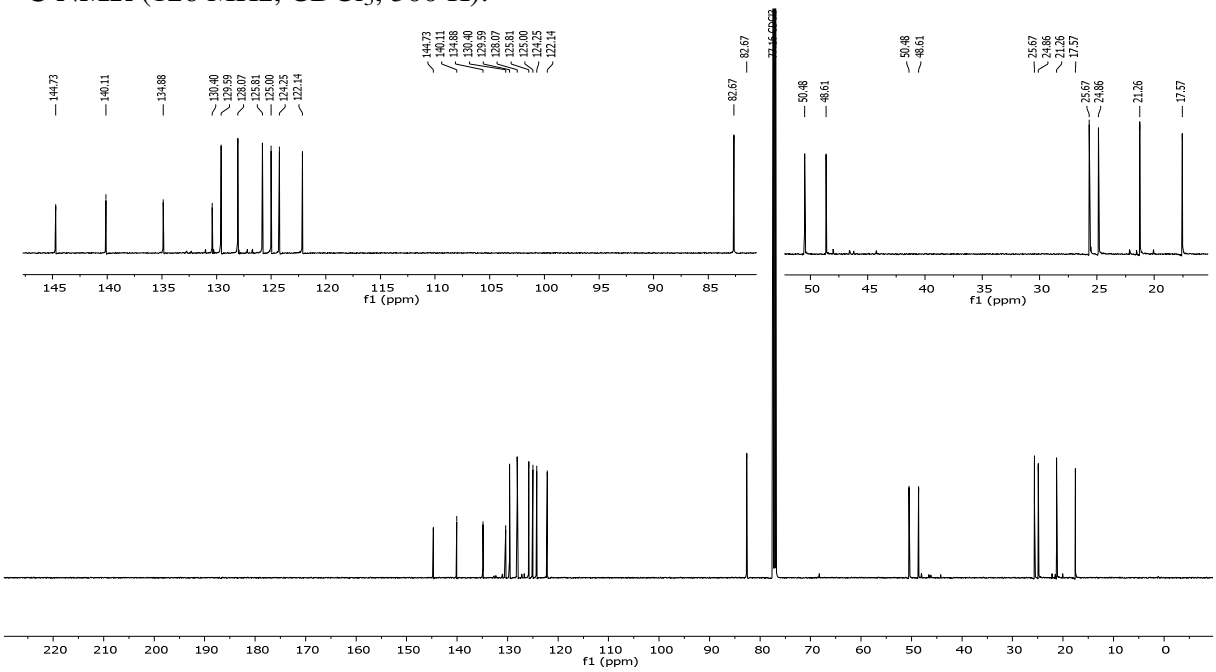


14

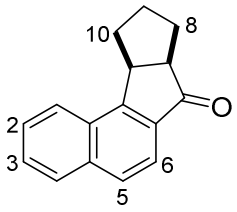
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



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



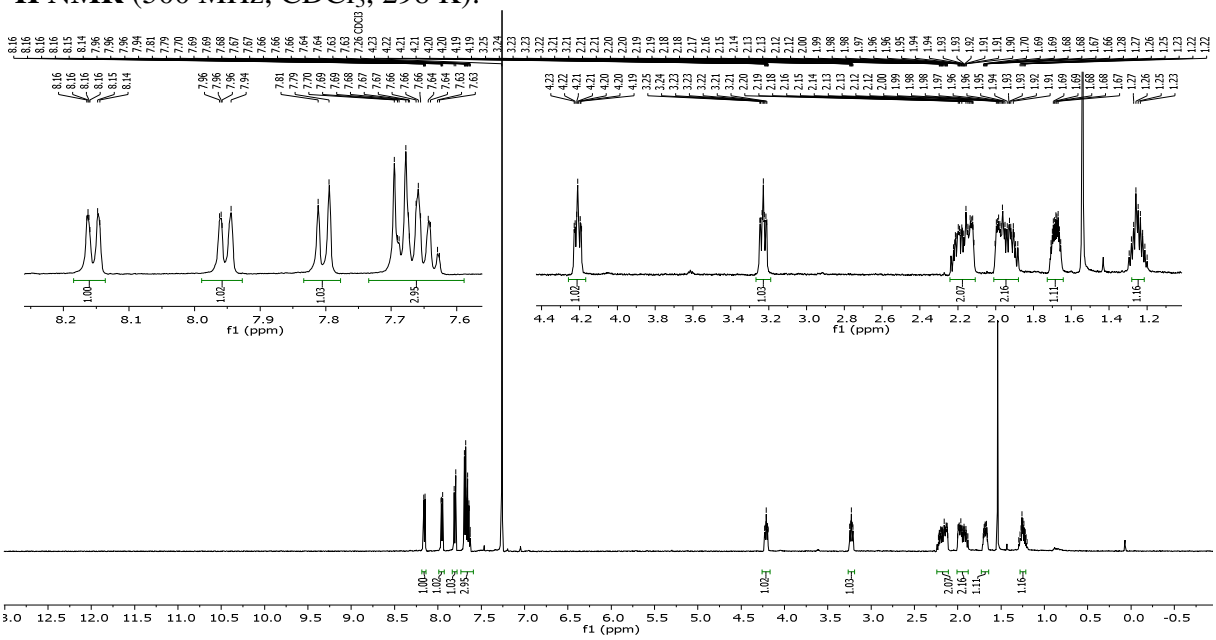
(7a*RS*,10a*SR*)-8,9,10,10a-Tetrahydropentaleno[1,2-*a*]naphthalen-7(7a*H*)-one (15)



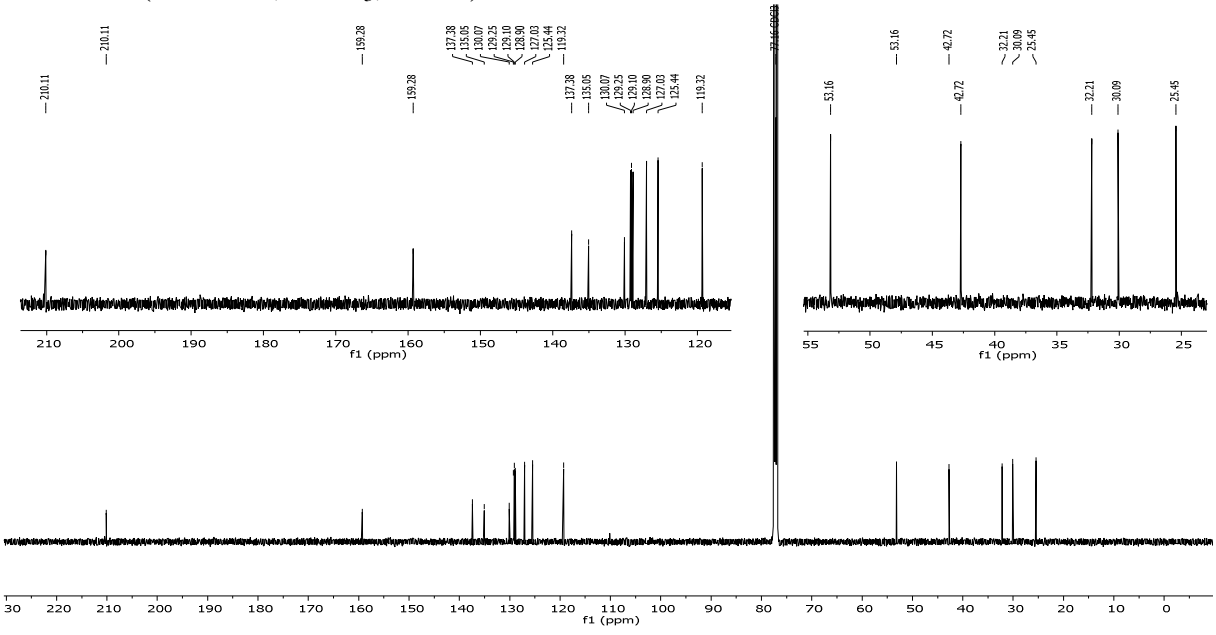
$C_{16}H_{14}O$
MW =222.29

15

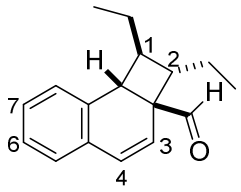
^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



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

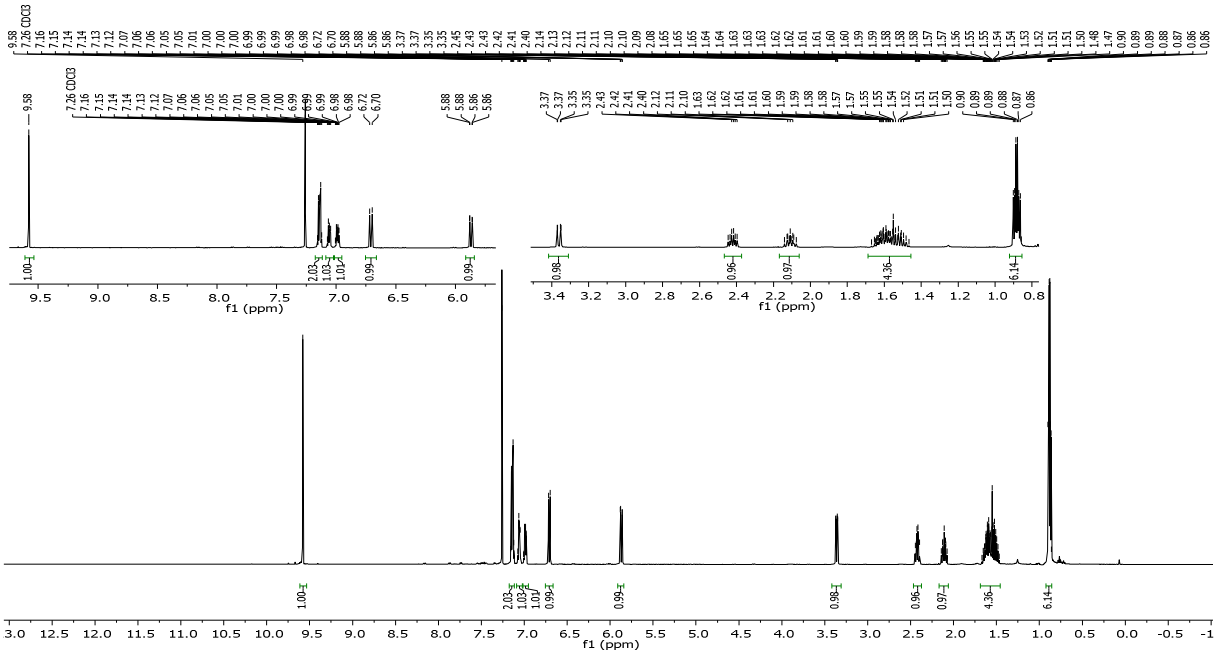


(1*SR*,2*SR*,2a*RS*,8b*SR*)-1,2-Diethyl-1,8b-dihydrocyclobuta[*a*]naphthalene-2a(2*H*)-carbaldehyde (18)

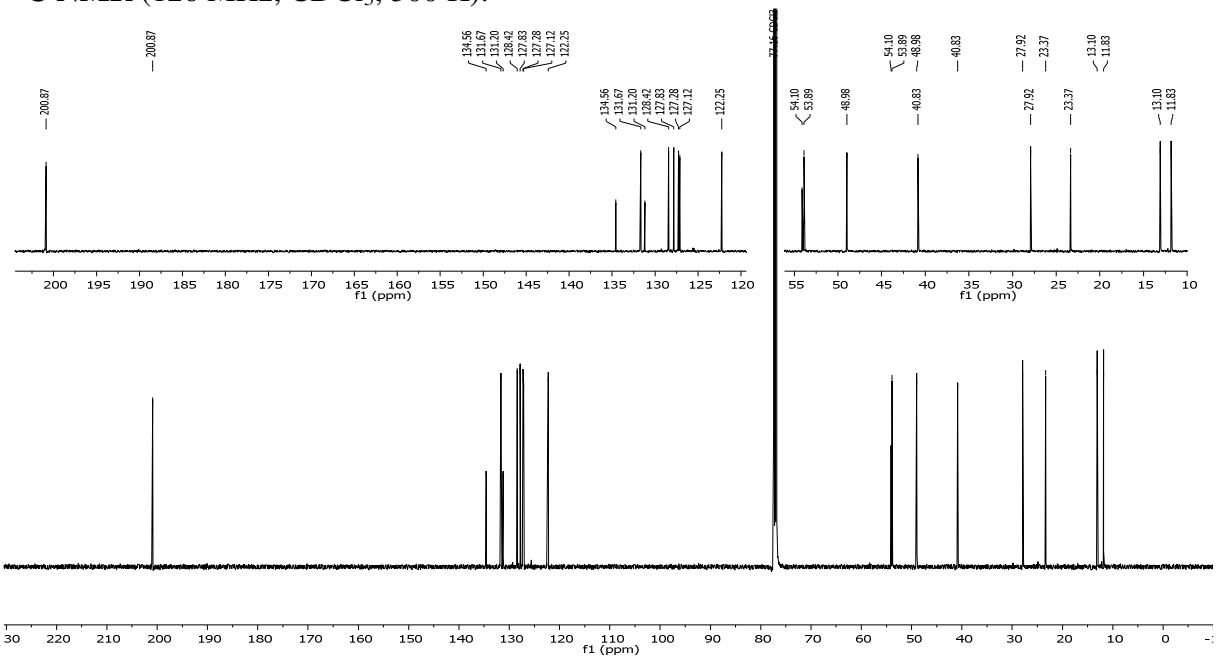


18

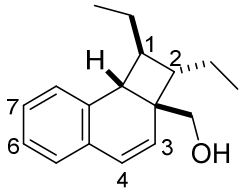
^{1}H NMR (500 MHz, $CDCl_3$, 300 K):



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

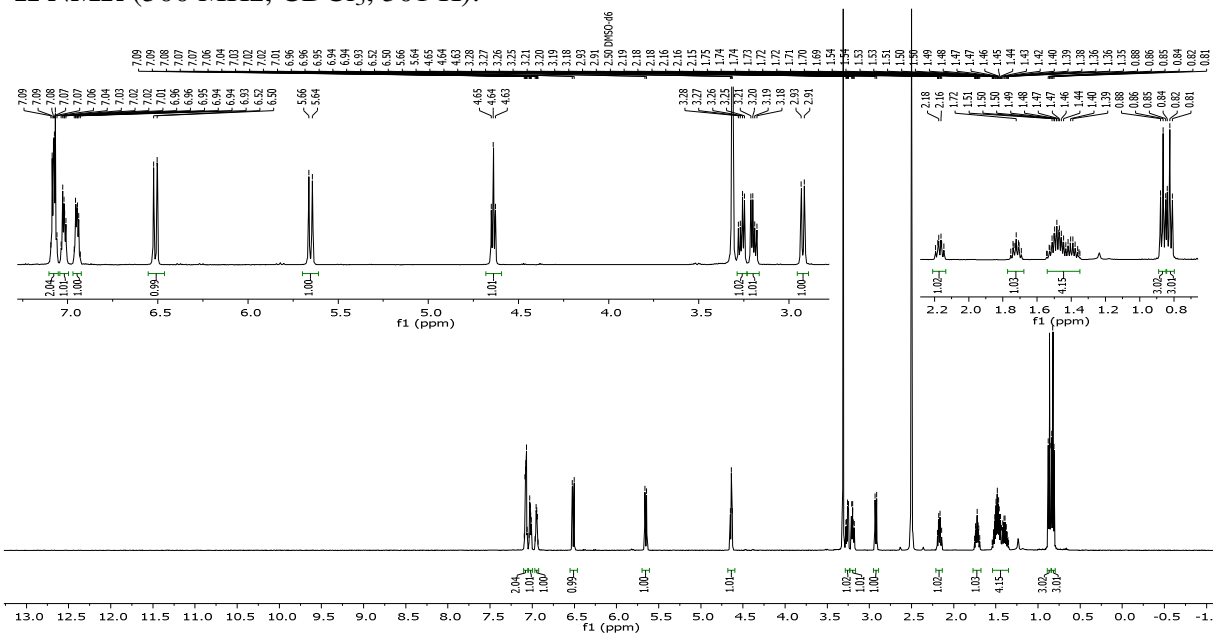


[(1*SR*,2*SR*,2a*RS*,8b*SR*)-1,2-Diethyl-1,8b-dihydrocyclobuta[*a*]naphthalen-2a(2*H*)-yl]methanol (S8)

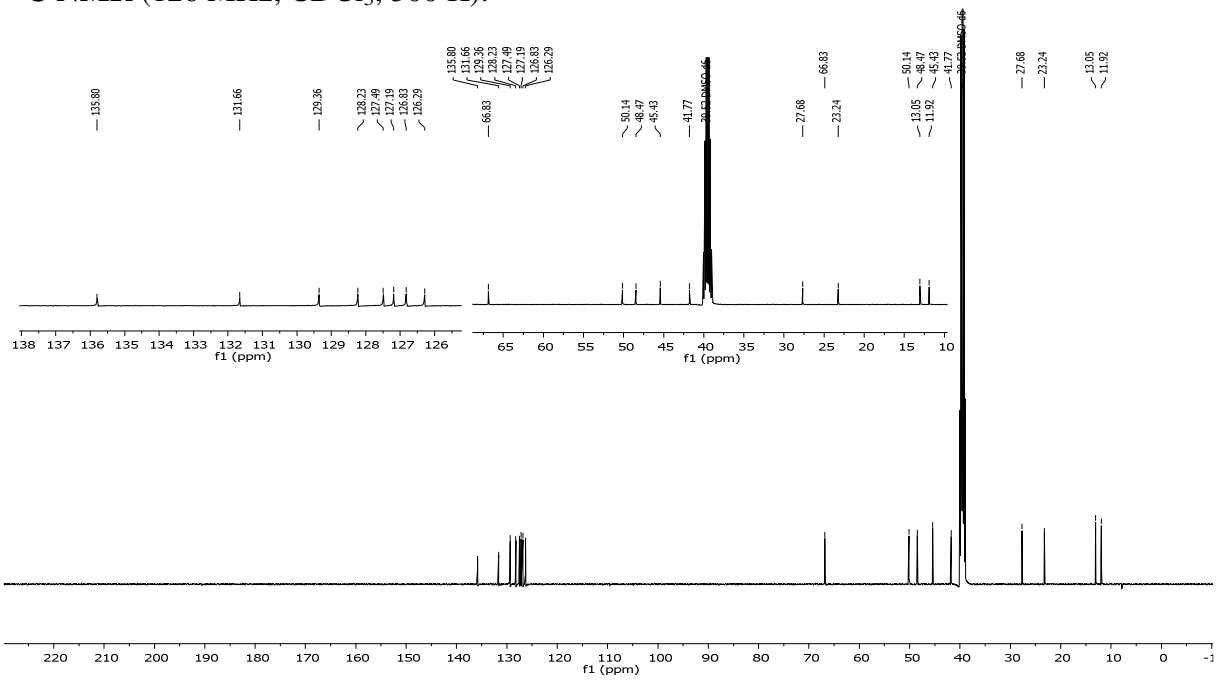


S8

^{1}H NMR (500 MHz, $CDCl_3$, 301 K):



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



Datasheets of fluorescent light sources

366 nm reactor

Lehrstuhl OC 1 - TUM

Datasheet FLT015 RPR-Set1-UV-A

Basic Information

Type	Fluorescent light tube
Description	Set1 (UV-A)
Manufacturer / Supplier	n/a / Rayonet
Order number / Date of purch.	n/a / n/a
Internal lot / serial number	Set1 / FLT015

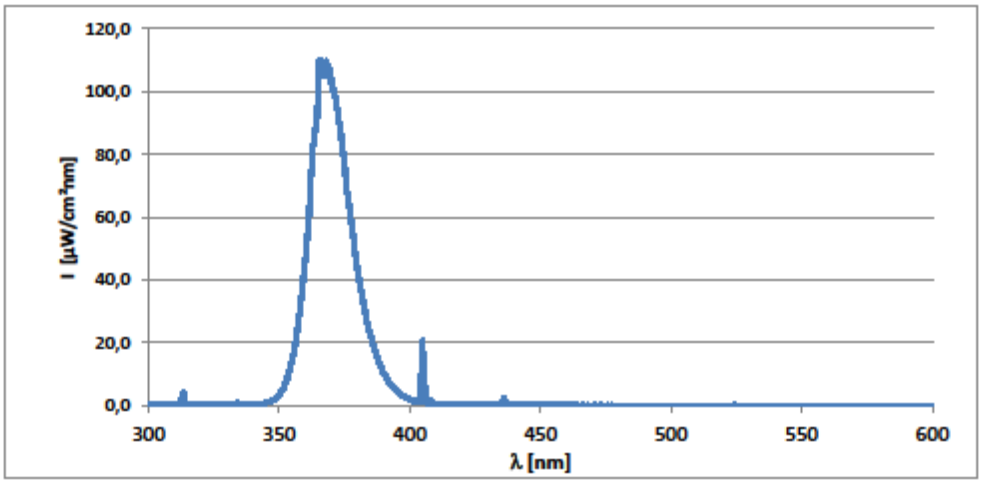
Specification Manufacturer

Type / size	T5 tube, G5 socket
Mechanical specification	16 mm diameter, 288 mm length
Electrical specification	8 W
Wavelength (range, typ.)	350 nm
Spectral width (FWHM)	~ 30 nm
Datasheet	

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.	365 nm	104 µW/mm²nm
Measured spectral width (FWHM)	18 nm	
Integral Reference intensity / range	2194 µW/cm²	300-450 nm

Spectrum



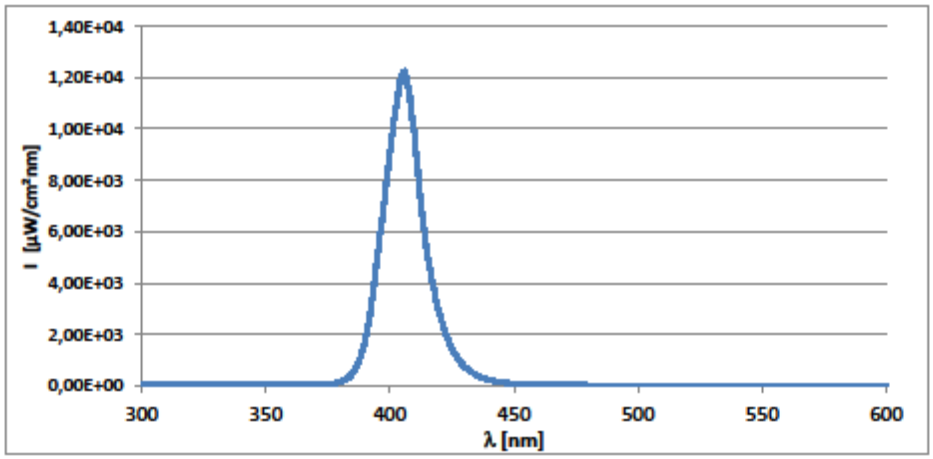
405 nm LED (LED037)

Lehrstuhl OC 1 - TUM

Datasheet LED037 — 405 / 10 W

Basic Information	**Ultra-High-Power Violet (405)**
Type	High-Power-LED
Description	
Manufacturer / Supplier	LED-Engine Mouser
Order number / Date of purch.	LZ4-40UA00-00U7 / 03/2016
Internal lot / serial number	2016-03 / LED037
Specification Manufacturer	
Type / size	quattro emitter / not spec.
Mechanical specification	
Electrical specification	700 mA @15 V
Wavelength (range, typ.)	
Spectral width (FWHM)	
Datasheet	LZ4-00UA-series.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 500 mA on a passive heat-sink at approx. 20 °C
Measured wavelength	405 nm
Measured spectral width	18 nm
Integral Reference intensity	247500 µW/cm² (360-480 nm @ 20 mm distance, 4 mmcosine corr.)

Spectrum



457 nm LED (LED005)

Lehrstuhl OC 1 - TUM

Datasheet LED005 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

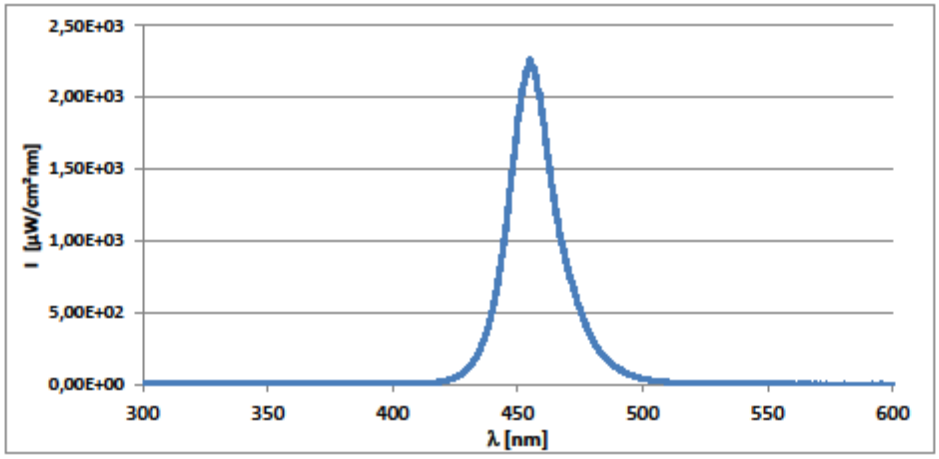
Specification Manufacturer

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



457 nm LED (LED045)

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 LED045 Av-455-5W

Basic Information

Type	High-Power-LED
Description	Avonec 455-460 nm / 5 W
Manufacturer / Supplier	n/a / Avonec
Order number / Date of purch.	n/a / 07/2016
Internal lot / serial number	2016-07 / LED045

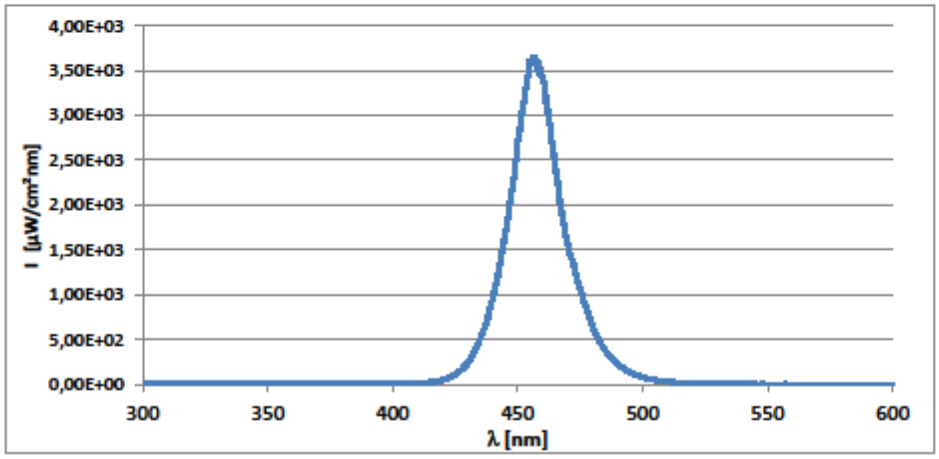
Specification Manufacturer

Type / size	dual emitter / 2 x ca. 1 x 1 mm
Mechanical specification	
Electrical specification	700 mA, UF 6.8 V
Wavelength (range, typ.)	455-460 nm, typ. n/a
Spectral width (FWHM)	n/a
Datasheet	n/a

Characterization

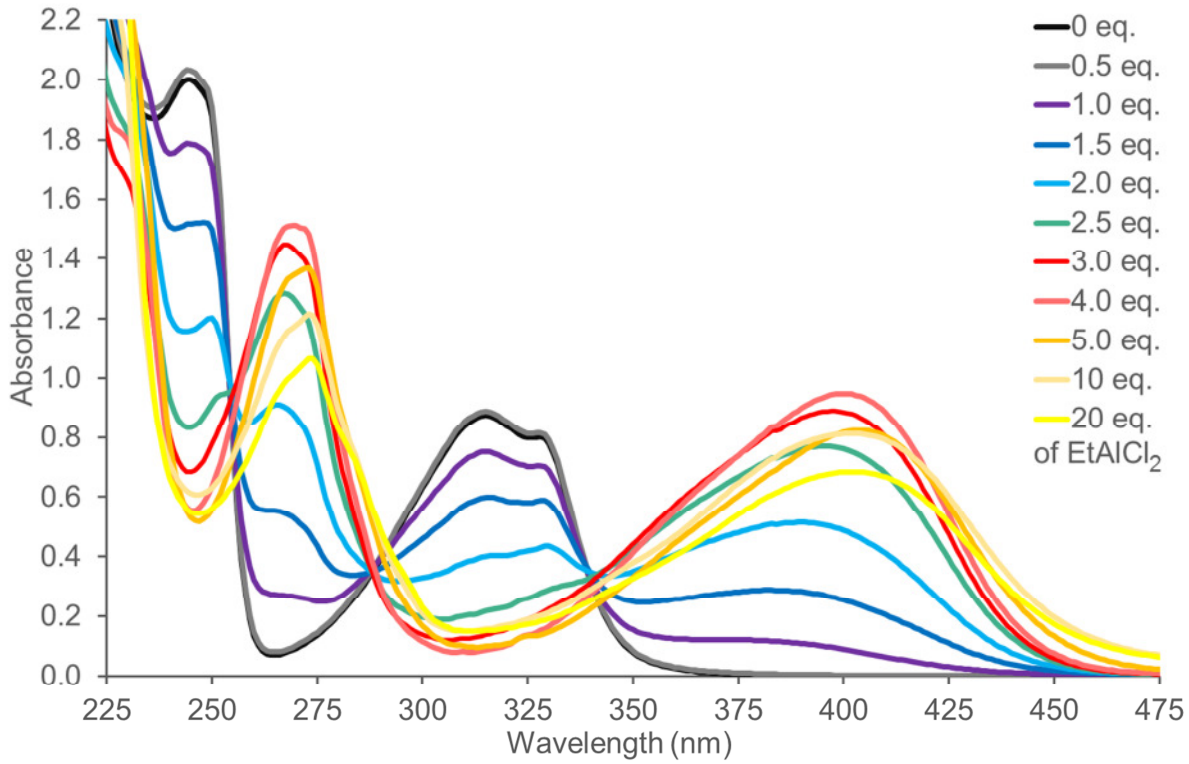
Description of measurement	Measured with Ocean-optics USB4000 spectrometer using a calibrated setup (cosine corrector/fibre). The distance between the emitting surface and the surface of the cosine corrector was 20 mm. The LED was operated at 700 mA on a passive heat-sink at approx. 20 °C
Measured wavelength	457 nm
Measured spectral width	22 nm
Integral Reference intensity	99250 µW/cm² (400-550 nm @ 20 mm distance, 4 mmcosine corr.)

Spectrum



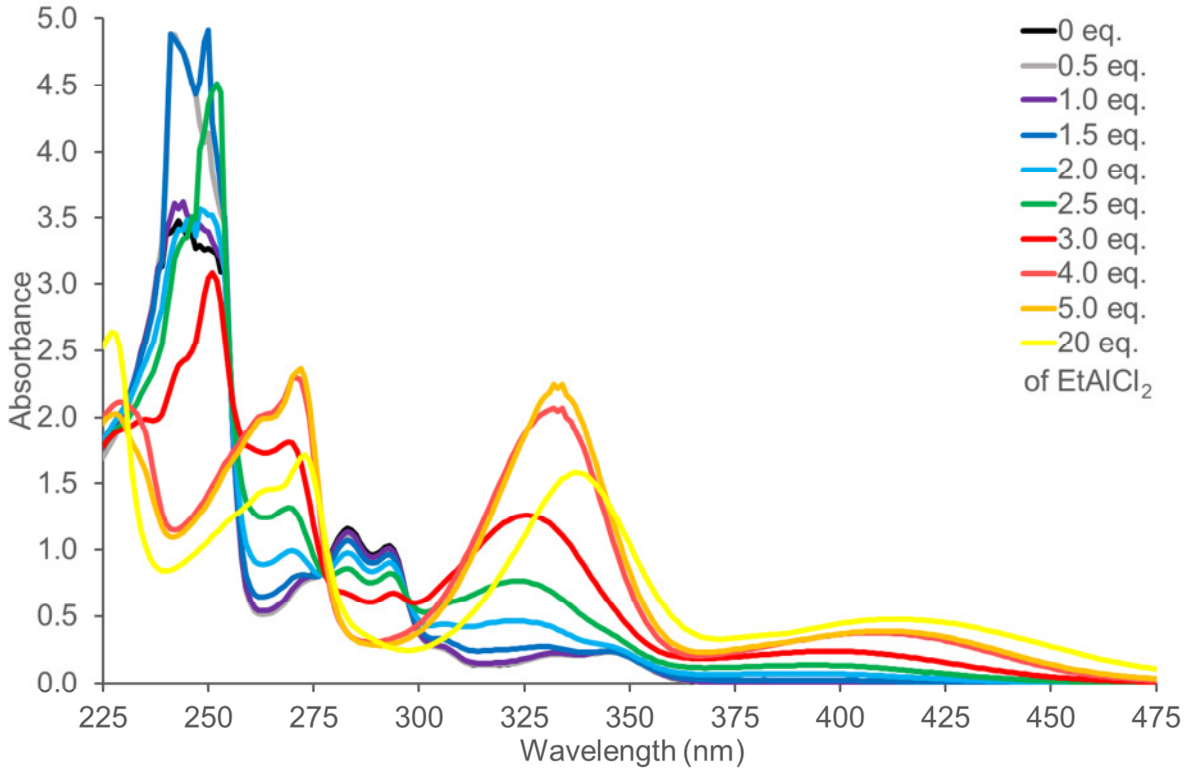
5. UV/Vis spectra

UV/Vis spectrum of 1-naphthaldehyde (1)



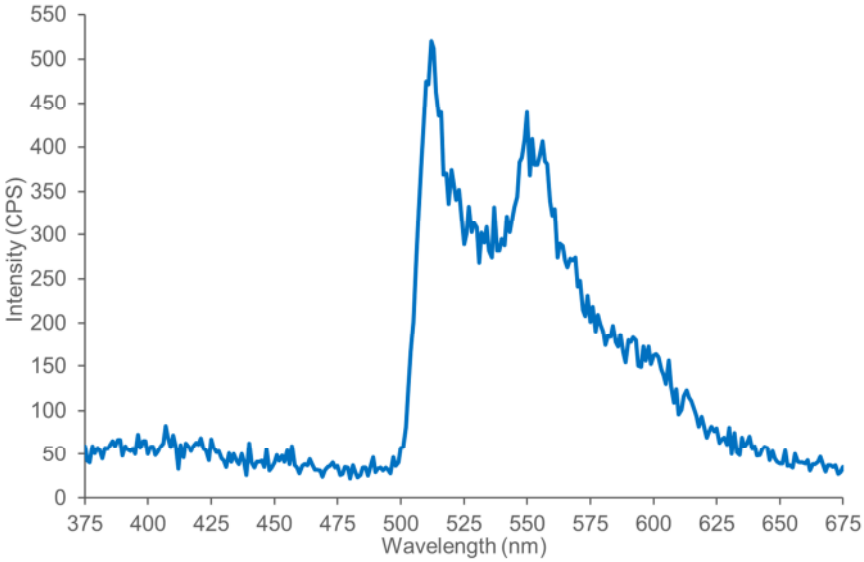
UV/Vis spectrum of 1-naphthaldehyde (**1**) in the absence of a Lewis acid (black line) and in the presence of variable equivalents of $EtAlCl_2$ (0.5 eq. – 20.0 eq.) in dichloromethane [c = 1 mM].

UV/Vis spectrum of 2-naphthaldehyde (2)

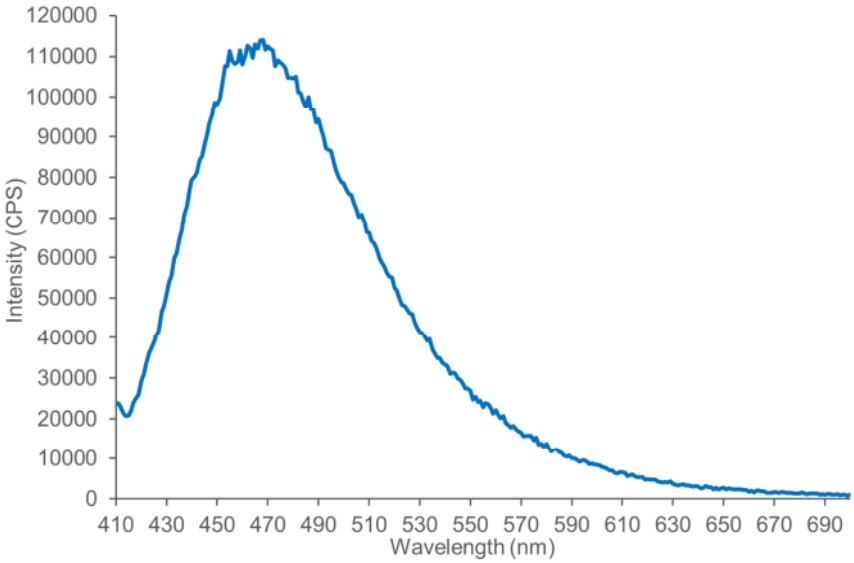


UV/Vis spectrum of 2-naphthaldehyde (**2**) in the absence of a Lewis acid (black line) and in the presence of variable equivalents of $EtAlCl_2$ (0.5 eq. – 20.0 eq.) in dichloromethane [c = 1 mM]. There are two isosbestic points at $\lambda = 278$ nm and $\lambda = 298$ nm (between 0 eq. – 3.0 eq. L.A.).

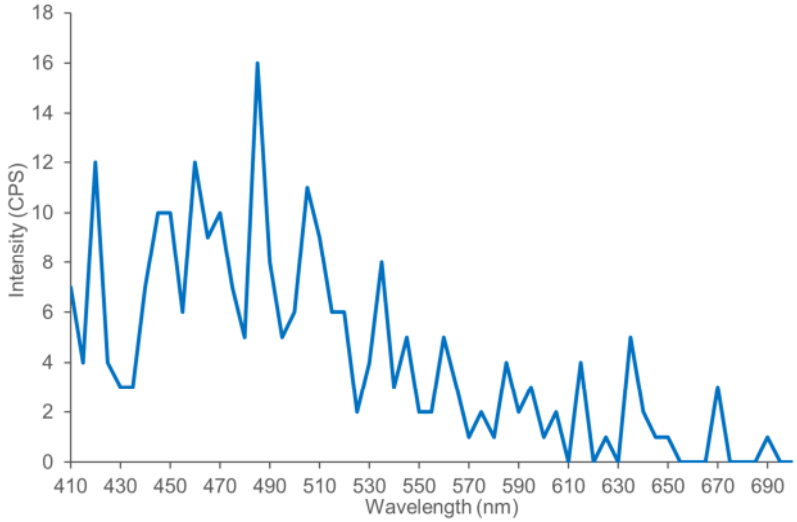
6. Luminescence measurements



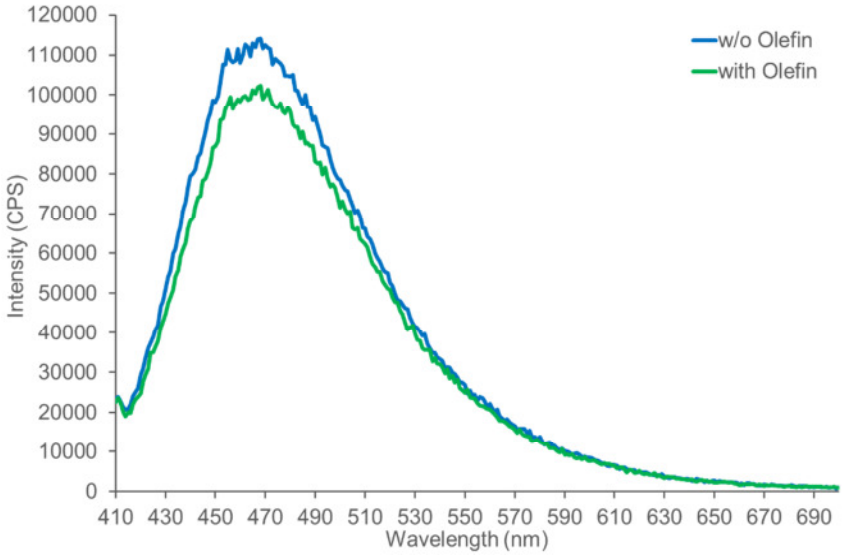
The emission spectrum of 1-naphthaldehyde (**1**, 100 µM in CH_2Cl_2) was measured at 77 K with a flash delay of 0.3 ms. We used 350 nm as the excitation wavelength and observed the emission spectrum from 375 – 675 nm. Both excitation and emission bandwidth was set to 5 nm.



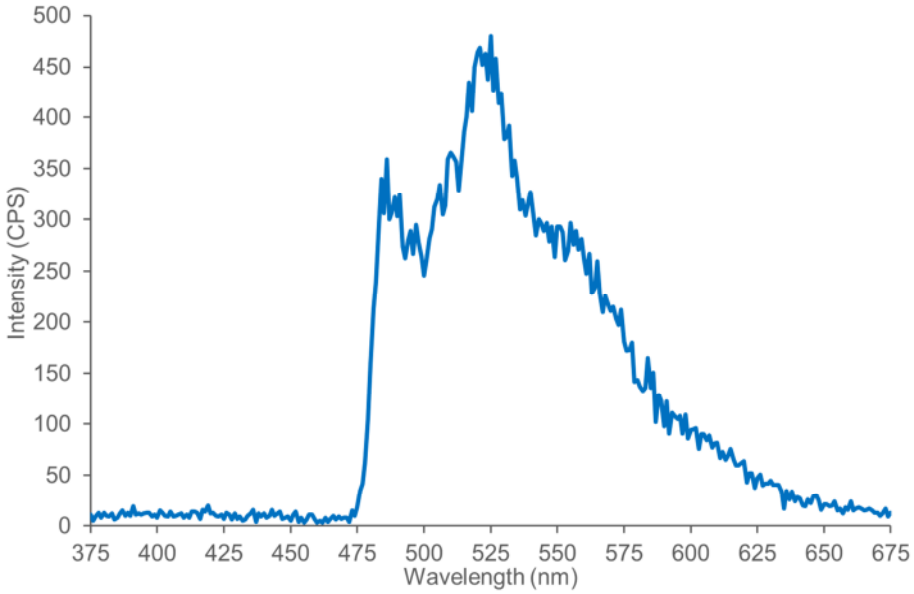
The emission spectrum of complex 1-naphthaldehyde·$AlEtCl_2$ (**1**·$AlEtCl_2$, 100 µM of **1** in CH_2Cl_2) was measured at RT in the presence of an excess of $EtAlCl_2$ (3.0 eq.). We used 400 nm as the excitation wavelength and observed the emission spectrum from 410 – 700 nm. Both excitation and emission bandwidth was set to 2 nm.



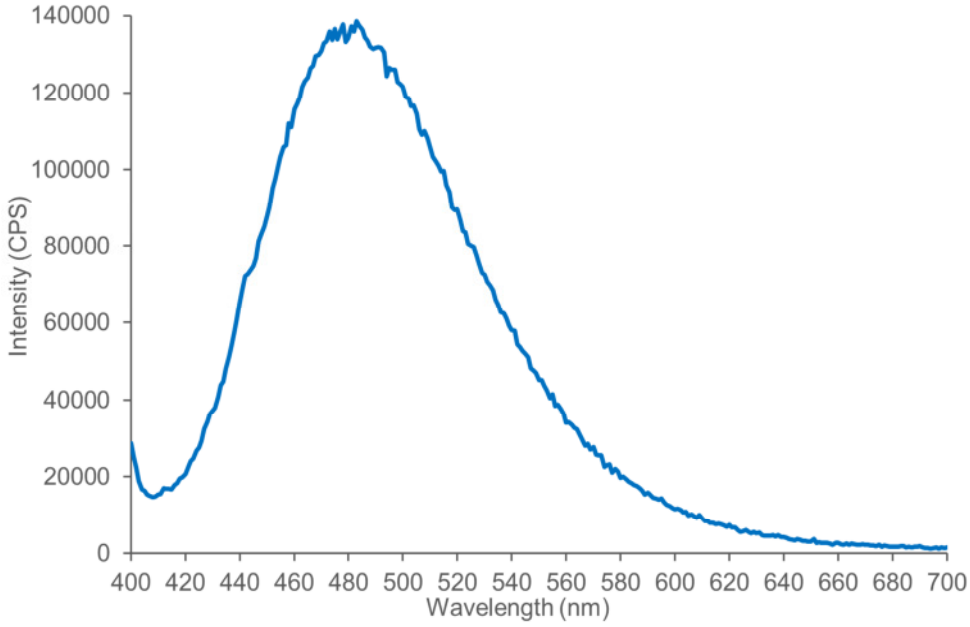
The emission spectrum of complex 1-naphthaldehyde·$AlEtCl_2$ (**1**·$AlEtCl_2$, 100 µM of **1** in CH_2Cl_2) was measured at 77 K with a flash delay of 0.8 ms in the presence of an excess of $EtAlCl_2$ (3.0 eq.). We used 400 nm as the excitation wavelength and observed the emission spectrum from 410 – 700 nm. Both excitation and emission bandwidth was set to 3 nm.



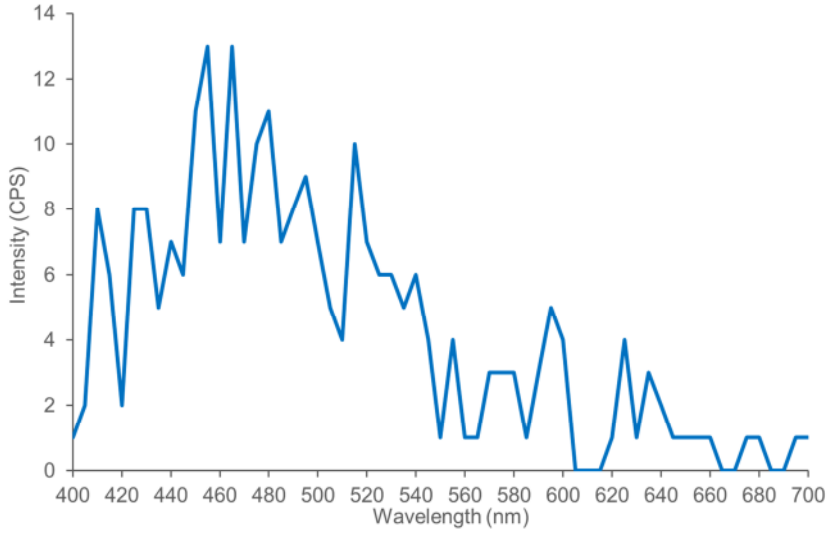
The emission spectrum of complex 1-naphthaldehyde·$AlEtCl_2$ (**1**·$AlEtCl_2$, 100 µM of **1** in CH_2Cl_2, blue line) was measured at RT in the presence of an excess of $EtAlCl_2$ (3.0 eq.). We used 400 nm as the excitation wavelength and observed the emission spectrum from 410 – 700 nm. Both excitation and emission bandwidth was set to 2 nm. The quenching experiment was performed by addition of 2,3-dimethyl-2-butene (ca. 1000 eq., green line) to the solution of **1** (100 µM of **1** in CH_2Cl_2) in the presence of an excess of $EtAlCl_2$ (3.0 eq.).



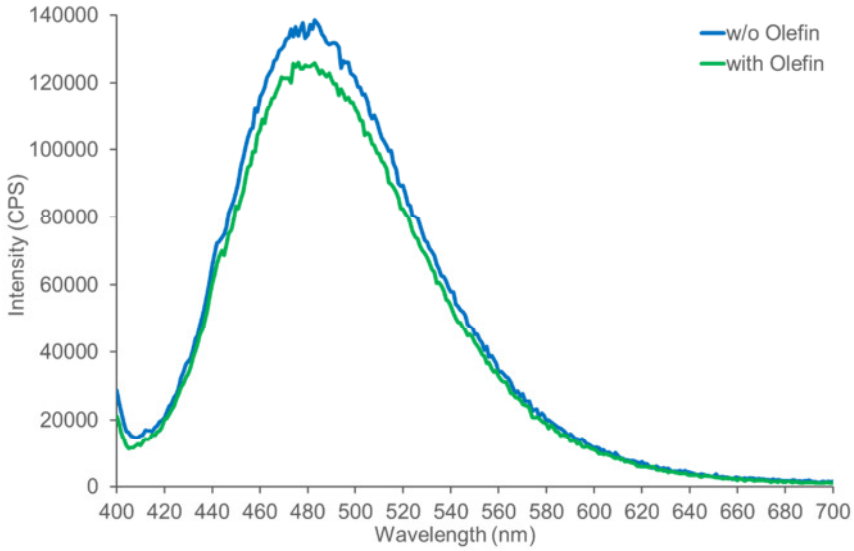
The emission spectrum of 2-naphthaldehyde (**2**, 100 µM in CH_2Cl_2) was measured at 77 K with a flash delay of 0.3 ms. We used 350 nm as the excitation wavelength and observed the emission spectrum from 375 – 675 nm. Both excitation and emission bandwidth was set to 3 nm.



The emission spectrum of complex 2-naphthaldehyde·$AlEtCl_2$ (**2**·$AlEtCl_2$, 100 µM of **2** in CH_2Cl_2) was measured at RT in the presence of an excess of $EtAlCl_2$ (3.0 eq.). We used 390 nm as the excitation wavelength and observed the emission spectrum from 400 – 700 nm. Both excitation and emission bandwidth was set to 2 nm.



The emission spectrum of complex 2-naphthaldehyde·$AlEtCl_2$ (**2**·$AlEtCl_2$, 100 µM of **2** in CH_2Cl_2) was measured at 77 K with a flash delay of 0.8 ms in the presence of an excess of $EtAlCl_2$ (3.0 eq.). We used 390 nm as the excitation wavelength and observed the emission spectrum from 400 – 700 nm. Both excitation and emission bandwidth was set to 3 nm.

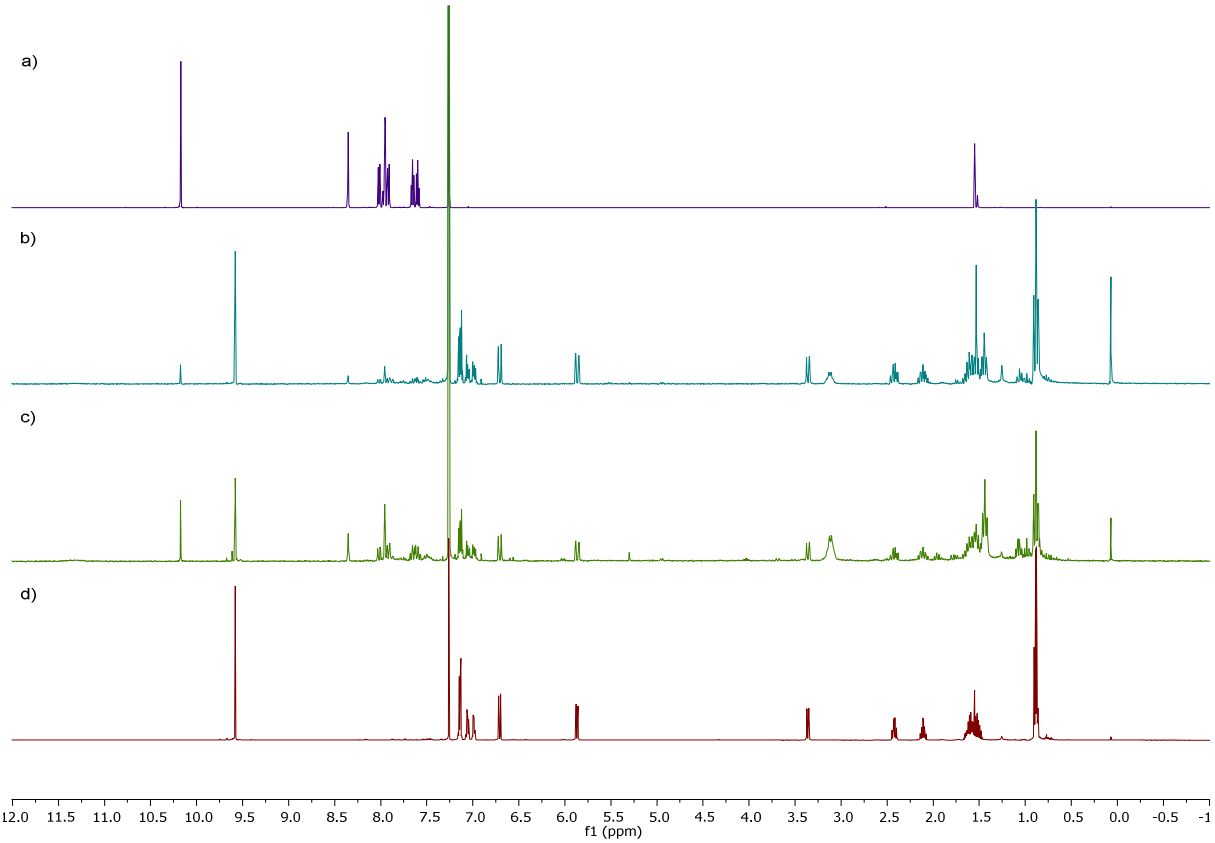


The emission spectrum of complex 2-naphthaldehyde·$AlEtCl_2$ (**2**·$AlEtCl_2$, 100 µM of **2** in CH_2Cl_2, blue line) was measured at RT in the presence of an excess of $EtAlCl_2$ (3.0 eq.). We used 390 nm as the excitation wavelength and observed the emission spectrum from 400 – 700 nm. Both excitation and emission bandwidth was set to 2 nm. The quenching experiment was performed by addition of 2,3-dimethyl-2-butene (ca. 1000 eq., green line) to the solution of **2** (100 µM of **2** in CH_2Cl_2) in the presence of an excess of $EtAlCl_2$ (3.0 eq.).

7. Stereoconvergent reaction of 2-naphthaldehyde and 3-hexene

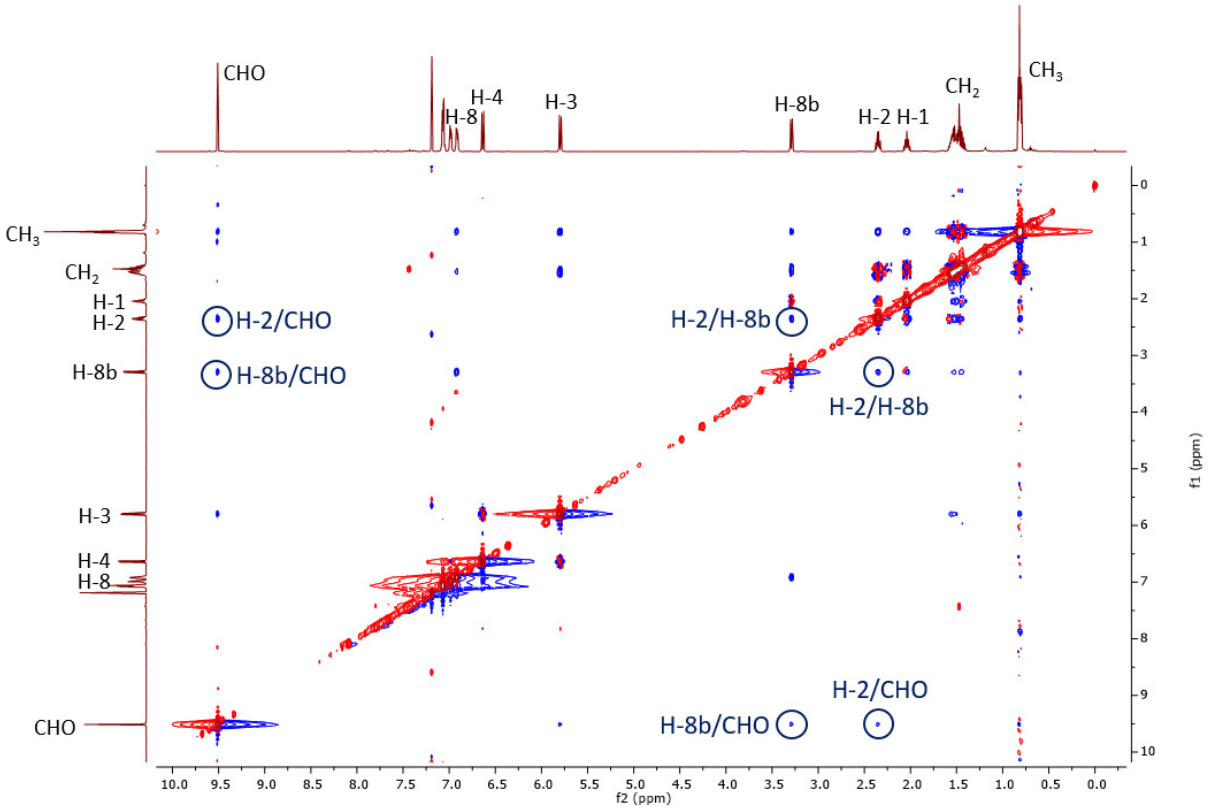
Photoreactions of aldehyde **2** and 3-hexene (**17**) were not stereospecific while both isomers [(*E*)-**17**, (*Z*)-**17**] delivered mainly a single product **18** (compare ^{1}H-NMR spectra b, c, d) besides starting material (compare ^{1}H-NMR spectra a, b, c,)

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

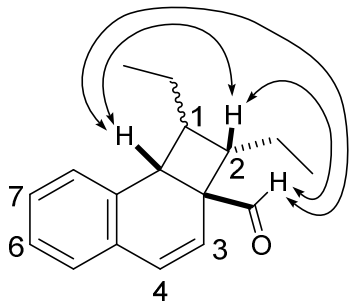


a) 2-naphthaldehyde; b) crude product: photoreaction of 2-naphthaldehyde (**2**) with (*E*)-3-hexene [(*E*)-**17**] as olefin (experimental details see S41); c) crude product: photoreaction of 2-naphthaldehyde (**2**) with (*Z*)-3-hexene [(*Z*)-**17**] as olefin (experimental details see S41); d) purified photoproduct **18**

NOESY experiment of *ortho* photocycloaddition product **18** [500 MHz (f2), 500 MHz (f1), $CDCl_3$, 299 K]:



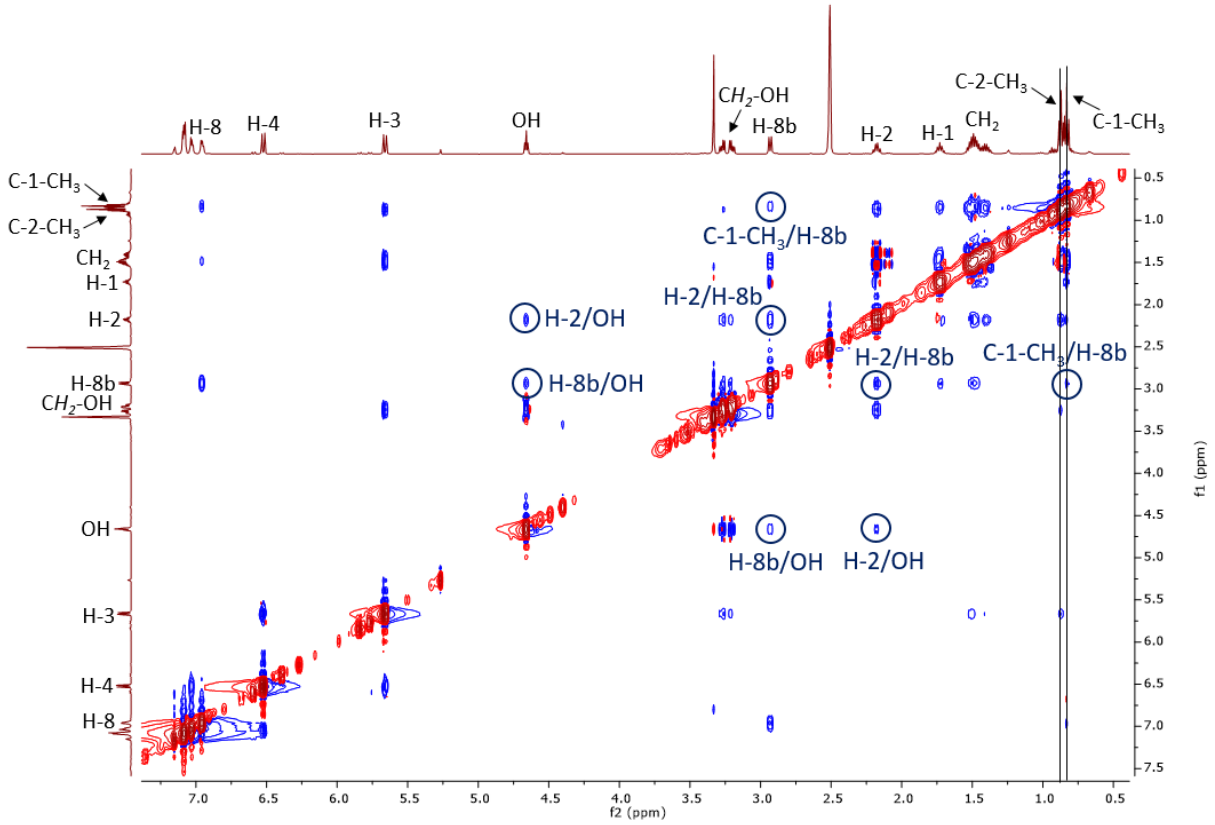
Important NOE-contacts are marked.



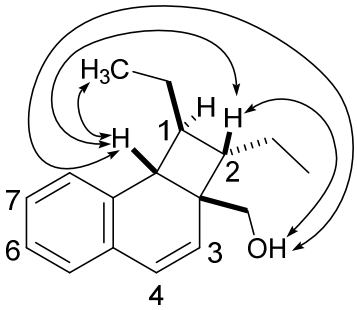
18

Relative configuration on C-1 not clear from this experiment.

NOESY experiment of alcohol **S8** [500 MHz (f2), 500 MHz (f1), DMSO-d_6, 298 K]:



Important NOE-contacts are marked.



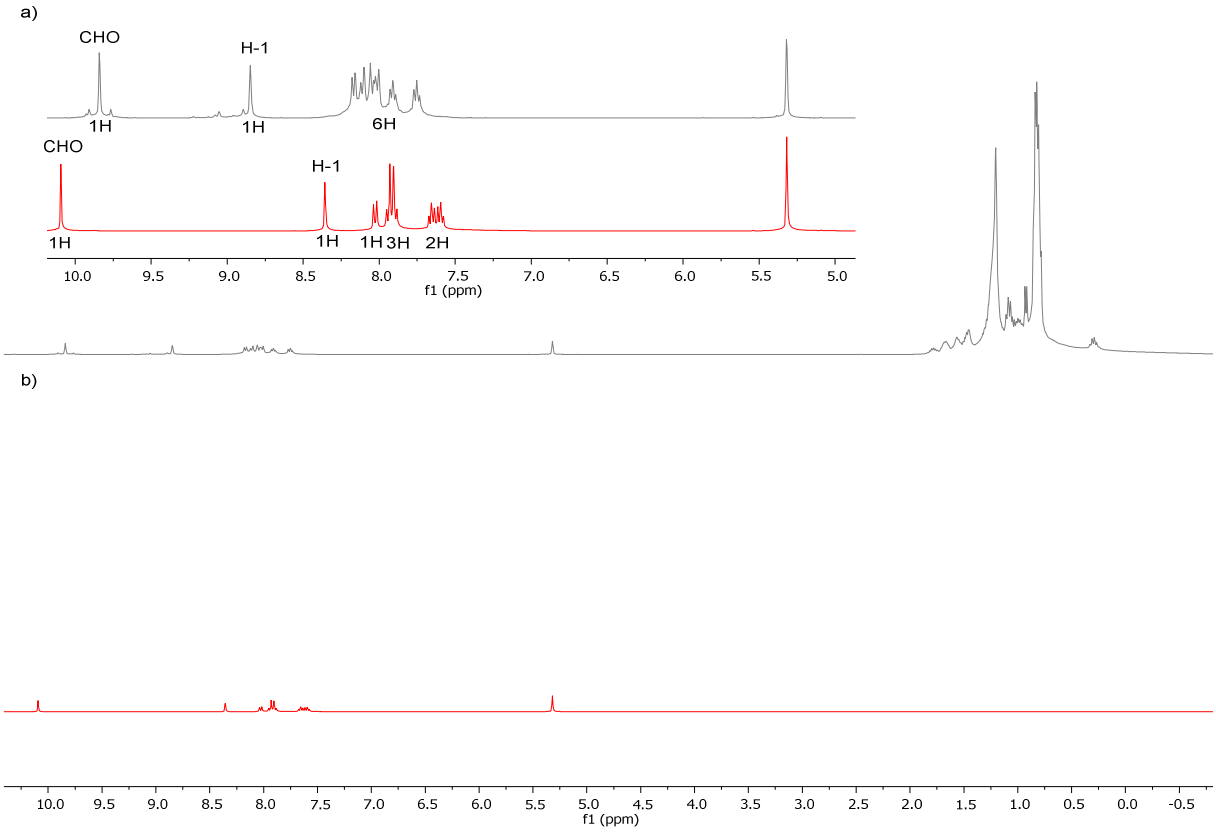
S8

With this experiment the relative configuration could be solved.

8. Low-temperature NMR experiments

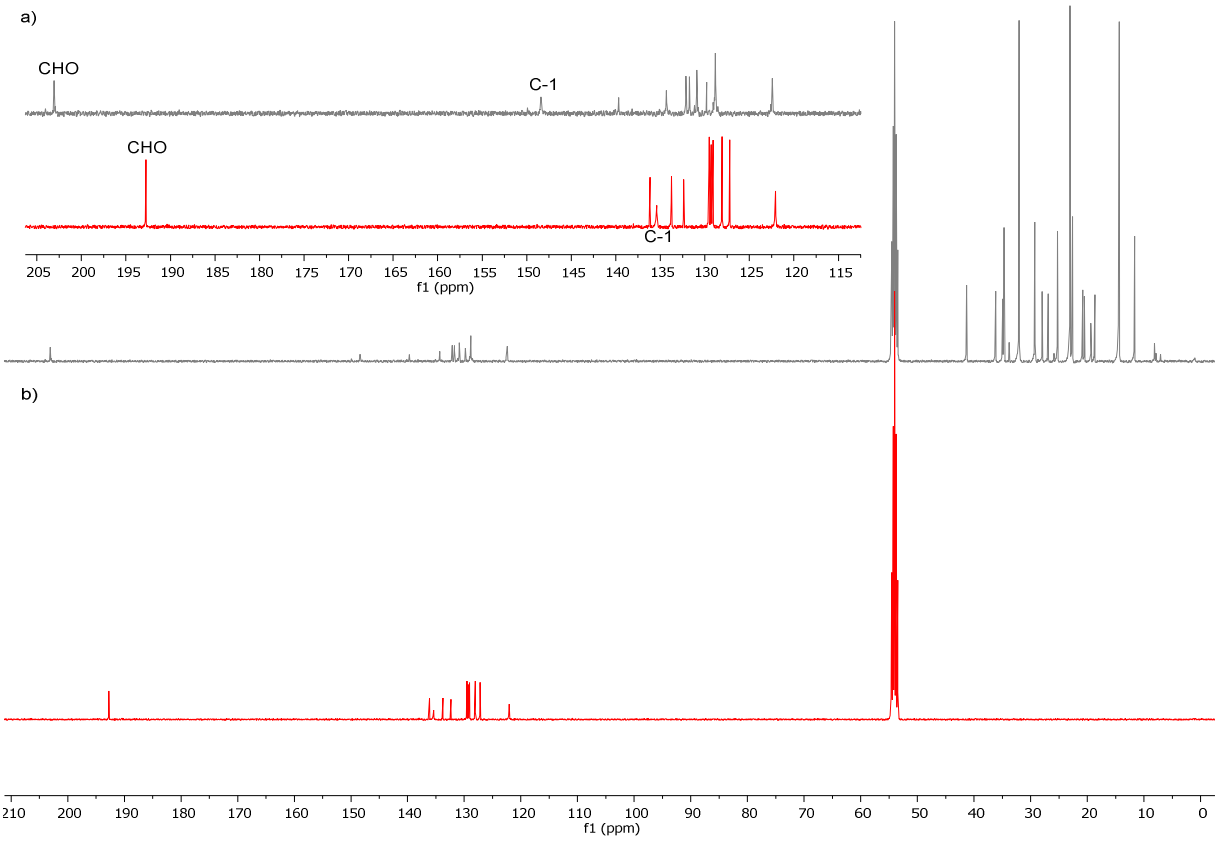
For low-temperature NMR experiments of 2-naphthaldehyde in presence of ethyl aluminium dichloride deuterated dichloromethane (CD_2Cl_2) was filtered over activated basic aluminium oxide and stored for 48 hours over 4 Å activated molecular sieves prior to use. A pre-heated Ptfe500-5-7 NMR-tube (from *Deutero*) was loaded with a 2-naphthaldehyde solution (**2**, 400 µL, 125 mM in CD_2Cl_2, 50 µmol, 1.00 eq.) under an argon counterflow and cooled to −78 °C. A pre-cooled ethyl aluminium dichloride solution (110 µL, 500 mM in *n*-hexane/CD_2Cl_2, 55 µmol, 1.10 eq.) was added. After careful shaking, an intense yellow solution is formed. ^{1}H- and ^{13}C-NMR spectra were recorded at 213 K (−60 °C) on a *Bruker* DRX400 spectrometer.

^{1}H NMR (400 MHz, CD_2Cl_2, 213 K):



a) 2-naphthaldehyde [98 mM] in presence of 1.1 eq. of $EtAlCl_2$ b) 2-naphthaldehyde [100 mM] in CD_2Cl_2; Assigned protons are marked.

^{13}C NMR (101 MHz, CD_2Cl_2, 213 K):

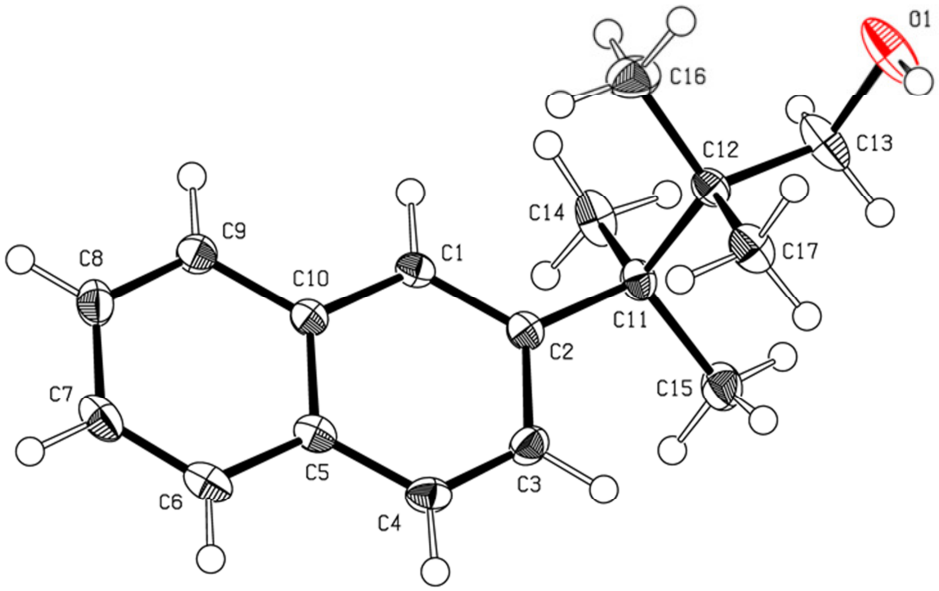


a) 2-naphthaldehyde [98 mM] in presence of 1.1 eq. of $EtAlCl_2$ b) 2-naphthaldehyde [100 mM] in CD_2Cl_2; Assigned carbons are marked.

9. X-ray crystallographic details

Data were collected on a single crystal x-ray diffractometer equipped with a CMOS detector (Bruker APEX III, κ-CMOS), an IMS microsource with MoK_α radiation (λ = 0.71073 Å) and a Helios optic using the APEX3 software package.[6] The measurement was performed on a single crystal coated with perfluorinated ether. The crystal was fixed on top of a kapton micro sampler and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were corrected for Lorentz and polarisation effects, scan speed, and background using SAINT.[7] Absorption correction, including odd and even ordered spherical harmonics was performed using SADABS.[8] Space group assignment was based upon systematic absences, E statistics, and successful refinement of the structure. The structure was solved using SHELXT with the aid of successive difference Fourier maps, and was refined against all data using SHELXL-2014 in conjunction with SHELXLE.[9-11] Hydrogen atoms were calculated in ideal positions as follows: Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{iso(H)} = 1.5 \cdot U_{eq(C)}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 Å and 0.95 Å, respectively, other C–H distances of 1.00 Å, all with $U_{iso(H)} = 1.2 \cdot U_{eq(C)}$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL weighting scheme.[9] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[12] The H atom on C13 is disordered over two positions, which were constrained at 50% occupancy each as required by the symmetry of the crystal. Images of the crystal structure were generated with PLATON.[13] CCDC 1937926 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Compound 9 (CCDC 1937926)



Diffractometer operator J. Jolliffe
scanspeed 5 s per frame
dx 34 mm
2882 frames measured in 9 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5
shutterless mode

Crystal data

$C_{17}H_{22}O$

M_r = 242.35	D_x = 1.163 Mg m^{-3}
Orthorhombic, *Pbcn*	Melting point: ? K
Hall symbol: -P 2n 2ab	Cu *K*α radiation, λ = 1.54178 Å
a = 31.0922 (6) Å	Cell parameters from 9953 reflections
b = 11.7199 (2) Å	θ = 4.0–70.1°
c = 7.5960 (1) Å	μ = 0.53 mm^{-1}
V = 2767.96 (8) Å^3	*T* = 100 K
Z = 8	Block, colourless
F(000) = 1056	0.30 × 0.30 × 0.11 mm

Data collection

Bruker Photon CMOS diffractometer	2622 independent reflections
Radiation source: IMS microsource	2269 reflections with $I > 2\sigma(I)$
Helios optic monochromator	R_{int} = 0.041
Detector resolution: 16 pixels mm^{-1}	θ_{max} = 70.1°, θ_{min} = 4.0°
phi– and ω–rotation scans	h = –37 37
Absorption correction: multi-scan *SADABS* 2016/2, Bruker	k = –14 14
T_{min} = 0.709, T_{max} = 0.753	l = –9 9
27664 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.041	H-atom parameters constrained
$wR(F^2)$ = 0.119	$W = 1/[\Sigma^2(FO^2) + (0.0747P)^2 + 0.8403P]$ WHERE $P = (FO^2 + 2FC^2)/3$
S = 1.02	$(\Delta/\sigma)_{max}$ = 0.001
2622 reflections	$\Delta\rho_{max}$ = 0.25 e Å^{-3}
168 parameters	$\Delta\rho_{min}$ = –0.25 e Å^{-3}
0 restraints	Extinction correction: none
2 constraints	Extinction coefficient: -
Primary atom site location: intrinsic phasing	

10. References

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