Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information

Photocatalytic Carbanion Generation – Benzylation of Aliphatic Aldehydes to Secondary Alcohols

Karsten Donabauer, Mitasree Maity, Anna Lucia Berger, Gregory S. Huff, Stefano Crespi, Burkhard Koenig*

Institute of Organic Chemistry, Universitätsstraße 31, 93053 Regensburg, Germany

Table of contents

1. General information

Starting materials and reagents were purchased from commercial suppliers (Sigma Aldrich, Alfa Aesar, Acros, Fluka, TCI or VWR) and used without further purification. Solvents were used as p.a. grade or dried and distilled according to literature known procedures.[1] For automated flash column chromatography industrial grade of solvents was used. All reactions with oxygen- or moisture-sensitive reagents were carried out in glassware, which was dried before use by heating under vacuum. Dry nitrogen was used as inert gas atmosphere. Liquids were added *via* syringe, needle and septum techniques unless otherwise stated.

All NMR spectra were measured at room temperature using a Bruker Avance 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C, 282 MHz for ^{19}F) or a Bruker Avance 400 (400 MHz for ^{1}H, 101 MHz for ^{13}C, 376 MHz for ^{19}F)[2] NMR spectrometer. All chemical shifts are reported in δ-scale as parts per million [ppm] (multiplicity, coupling constant *J*, number of protons) relative to the solvent residual peaks as the internal standard.[3] Coupling constants *J* are given in Hertz [Hz]. Abbreviations used for signal multiplicity: ^{1}H-NMR: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, and m = multiplet;

^{13}C-NMR: (+) = primary/tertiary, (–) = secondary, (C_q) = quaternary carbon.

HRMS (high resolution mass spectra) and LRMS (low resolution mass spectra) were measured at the Central Analytical Laboratory of the University of Regensburg. These mass spectra were recorded on a Finnigan MAT 95, ThermoQuest Finnigan TSQ 7000, Finnigan MAT SSQ 710 A or an Agilent Q-TOF 6540 UHD instrument.

GC measurements were performed on a GC 7890 from Agilent Technologies. Data acquisition and evaluation was done with Agilent ChemStation Rev.C.01.04. GC/MS measurements were performed on a 7890A GC system from Agilent Technologies with an Agilent 5975 MSD Detector. Data acquisition and evaluation was done with MSD ChemStation E.02.02.1431. A capillary column HP-5MS/30 m x 0.25 mm/0.25 μM film and helium as carrier gas (flow rate of 1 mL/min) were used. The injector temperature (split injection: 40:1 split) was 280 °C, detection temperature 300 °C (FID). GC measurements were made and investigated *via* integration of the signal obtained. The GC oven temperature program was adjusted as follows: initial temperature 40 °C was kept for 3 minutes, the temperature was increased at a rate of 15 °C/min over a period of 16 minutes until 280 °C was reached and kept for 5 minutes, the temperature was again increased at a rate of 25 °C/min over a period of 48 seconds until the final temperature (300 °C) was reached and kept for 5 minutes. *n*-Decane was used as an internal standard.

Analytical TLC was performed on silica gel coated alumina plates (MN TLC sheets ALUGRAM® Xtra SIL G/UV_{254}). Visualization was done by UV light (254 or 366 nm). If necessary, potassium permanganate or ceric ammonium molybdate was used for chemical staining.

Purification by column chromatography was performed with silica gel 60 M (40-63 μm, 230-440 mesh, Merck) or with a pre-packed Biotage® Snap Ultra HP-Sphere™ 25 *u*m column on a Biotage® Isolera™ Spektra One device.

For irradiation with blue light OSRAM Oslon SSL 80 LDCQ7P-1U3U (blue, λ_{max} = 455 nm, I_{max} = 1000 mA, 1.12 W) was used. For irradiation with green light Cree XPEGRN L1 G4 Q4 (green, λ_{max} = 535 nm, I_{max} = 1000 mA, 1.12 W), and for irradiation with 400 nm Edison EDEV-SLC1-03 (λ_{max} = 400 nm, I_{max} = 700 mA, 400 mW) was used.

Fluorescence spectra were measured on a HORIBA FluoroMax®-4 Spectrofluorometer at room temperature. Gas tight 10 mm Hellma® quartz fluorescence cuvettes with a screw cap with PTFE-coated silicon septum were used. FluorEssence Version 3.5.1.20 was used as a software for measurement and analysis.

UV-Vis absorption spectroscopy was performed at 25 °C on a Varian Cary 100 Spectrometer with a 10 mm quartz cuvette.

Oxidation and reduction potentials given in the text are cited from literature reports. All potentials therein were determined in acetonitrile.

CCDC 1884950 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

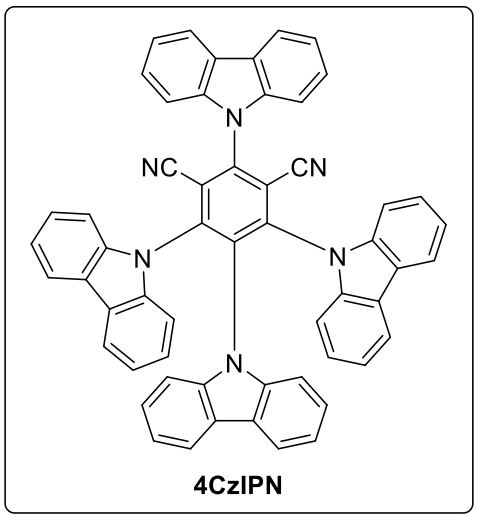
2. Synthetic procedures

2.1 Synthesis of photocatalysts

2,4,5,6-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN)[4]

The photocatalyst was synthesized using an adapted literature procedure.[4]

NaH (60% in paraffin oil, 800 mg, 20 mmol, 10 eq.) was added portionwise to a stirred solution of carbazole (1.67 g, 10 mmol, 5 eq.) in dry THF (40 mL). The reaction mixture was heated to 35 °C and stirred for 1 h before adding tetrafluoroisophthalonitrile (400 mg, 2 mmol, 1 eq.). The reaction mixture was stirred at 35 °C overnight for approx. 16 h, afterwards quenched by H_2O (2 mL) and concentrated *in vacuo*. The solid residue was washed with H_2O and EtOH to yield the crude product, which was purified by recrystallization from hexane/DCM to give 2,4,5,6-tetrakis(carbazol-9-yl)-4,6-dicyano-benzene (4CzIPN) as bright yellow powder (840 mg, 1.06 mmol, 53%).



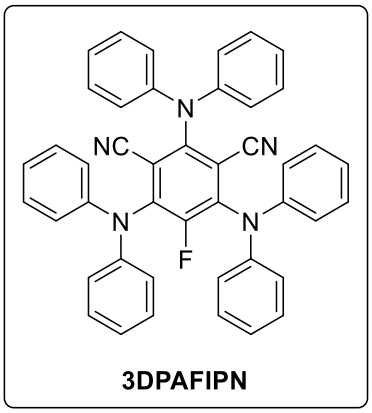
4CzIPN

^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 8.22 (d, *J* = 7.7 Hz, 2H), 7.75 – 7.67 (m, 8H), 7.52 – 7.47 (m, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.25 – 7.19 (m, 4H), 7.12 – 7.05 (m, 8H), 6.82 (t, *J* = 8.2 Hz, 4H), 6.63 (td, *J* = 7.6, 1.2 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 145.3, 144.7, 140.1, 138.3, 137.1, 134.9, 127.1, 125.9, 125.1, 124.9, 124.7, 124.0, 122.5, 122.1, 121.5, 121.1, 120.6, 119.8, 116.5, 111.8, 110.1, 109.6, 109.6.

2,4,6-Tris(diphenylamino)-5-fluoroisophthalonitrile (3DPAFIPN)[5]

The photocatalyst was synthesized analogous to 4CzIPN with diphenylamine (1.69 g, 10 mmol, 5 eq.) instead of carbazole. 2,4,6-Tris(diphenylamino)-5-fluoroisophthalonitrile (3DPAFIPN) (900 mg, 1.39 mmol, 70%) was obtained as bright yellow powder.



3DPAFIPN

^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.29 – 7.24 (m, 16H), 7.12-7.04 (m, 8H), 7.02 – 6.98 (m, 16H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 145.7, 145.4, 143.3, 143.1, 129.6, 129.5, 124.7, 124.2, 122.9, 122.8, 112.7, 109.0.

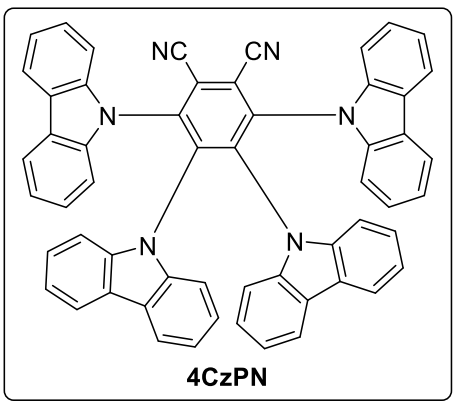
^{19}F-NMR (282 MHz, $CDCl_3$, δ_F): -121.81 (s).

Field desorption mass spectra (**FD-MS**) (m/z): $[M^+]$ ($C_{44}H_{30}FN_5^+$) calc. 647.25; observed 647.1977.

FD-MS revealed, that 4DPAFIPN[4] is present in smaller amount as well (m/z): $[M^+]$ ($C_{56}H_{40}N_6^+$) calc. 796.33; observed 796.2684. It may be the impurity visible in the NMR.

3,4,5,6-Tetra(carbazol-9-yl)phthalonitrile (4CzPN)[4]

The photocatalyst was synthesized using the adapted literature procedure analogous to 4CzIPN with tetrafluorophthalonitrile (400 mg, 2 mmol, 1 eq.) instead of tetrafluroisophthalonitrile. 3,4,5,6-Tetra(carbazol-9-yl)phthalonitrile (4CzPN) (584 mg, 0.74 mmol, 37%) was obtained as bright orange powder.



4CzPN

^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.89 – 7.86 (m, 4H), 7.72 – 7.68 (m, 4H), 7.38 (t, *J* = 7.4 Hz, 8H), 7.16 – 7.09 (m, 8H), 6.73 (t, *J* = 7.5 Hz, 4H), 6.59 (t, *J* = 8.2 Hz, 4H).

[Ir(dF-CF_3-ppy)$_2$(dtbpy)](PF_6)

The photocatalyst was synthesized according to a literature procedure.[6]

3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine

The photocatalyst was synthesized according to a literature procedure.[7]

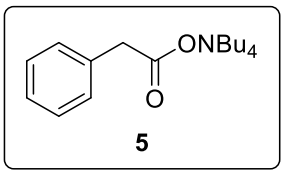
2.2 Synthesis of starting materials

Tetrabutylammonium phenylacetate (NBu_4PA) (5) solution

Tetrabutylammonium phenylacetate (**5**) was obtained using an adapted literature procedure.[8]

An NBu_4OH in H_2O solution (40 wt%, 1.3 mL, 2 mmol, 1eq.) and H_2O (2 mL) were added to phenylacetic acid (**1a**) (286 mg, 2.1 mmol, 1.05 eq.). The mixture was stirred for 2 h during which it became a clear solution. Subsequently, the water was removed by freeze drying for 2 d yielding the hygroscopic Tertbutylammonium phenylaetate salt (**5**). (A small amount for the NMR-analysis was taken at this point).

4 Å Molecular sieve was added to the residue followed by either dry DMF (27 mL) or dry DMA (27 mL) to obtain a 75 mM solution of **5**. The solution was allowed to stand for at least 1 d before further use.



5

^{1}H-NMR (300 MHz, d_7-DMF, δ_H): 7.34 – 7.29 (m, 2H), 7.21 – 7.14 (m, 2H), 7.09 – 7.03 (m, 1H), 3.45 – 3.37 (m, 8H), 3.30 (s, 2H), 1.81 – 1.68 (m, 8H), 1.45 – 1.32 (m, 8H), 0.96 (t, *J* = 7.3 Hz, 12H).

^{13}C-NMR (75 MHz, d_7-DMF, δ_C): 174.1 (C_q), 142.4 (C_q), 130.4 (+), 128.3 (+), 125.5 (+), 59.2 (–), 48.2 (–), 24.6 (–), 20.6 (–), 14.2 (+).

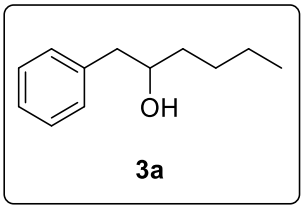
3. Photocatalytic benzylation of aldehydes

General procedure for the photocatalytic benzylation of aldehydes (General Procedure A)

A 5 mL crimp cap vial equipped with a magnetic stirring bar was loaded with 4CzIPN (5.9 mg, 7.5 µmol, 5 mol%), Cs_2CO_3 (48.9 mg, 150 µmol, 1 eq.), the corresponding carboxylic acid (150 µmol, 1 eq.), the corresponding aldehyde (450 µmol, 3 eq.) and DMA (2 mL). In doing so, all solid compounds were added before capping the vial, whereas all liquid compounds were added *via* syringe after setting the capped vial under inert conditions. The reaction mixture was degassed by four cycles of freeze-pump-thaw and subsequently stirred under light irradiation using a 455 nm (± 25 nm) LED for 16 h at 25 °C. Two reaction batches were combined and diluted with brine (15 mL), water (5 mL) and ethyl acetate (15 mL). The phases were separated and the water phase was extracted with ethyl acetate (3 x 8 mL). The combined organic phases were washed with H_2O/brine (1:1) (15 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by automated flash column chromatography (PE/EtOAc, 0-20% EtOAc). If necessary, the product was further purified by another automated flash column chromatography (DCM/MeOH, 1% MeOH), yielding the corresponding product.

If specified in the table, the corresponding decarboxylated side-product was isolated along the desired coupling product in the purification process or was quantified in a separate reaction batch by GC-FID analysis directly after the reaction with *n*-decane as internal standard.

1-Phenylhexan-2-ol (3a)[9]



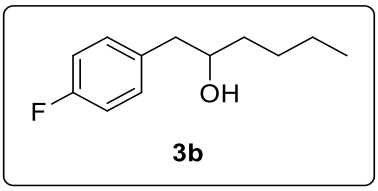
3a

^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.36 – 7.20 (m, 5H), 3.86 – 3.77 (m, 1H), 2.84 (dd, *J* = 13.5, 4.2 Hz, 1H), 2.65 (dd, *J* = 13.5, 8.4 Hz, 1H), 1.67-1.27 (m, 7H), 0.92 (t, *J* = 7.1 Hz, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 138.8 (C_q), 129.5 (+), 128.7 (+), 126.5 (+), 72.8 (+), 44.2 (–), 36.7 (–), 28.1 (–), 22.9 (–), 14.2 (+).

Yield: 63% (colorless liquid)

1-(4-Fluorophenyl)hexan-2-ol (3b)



3b

^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.20 – 7.13 (m 2H), 7.03 – 6.95 (m, 2H), 3.80 – 3.72 (m, 2H), 2.78 (dd, *J* = 13.7, 4.3 Hz, 1H), 2.61 (dd, *J* = 13.7, 8.2 Hz, 1H), 1.66 (s, 1H), 1.53-1.28 (m, 6H), 0.91 (t, *J* = 7.1 Hz, 3H).

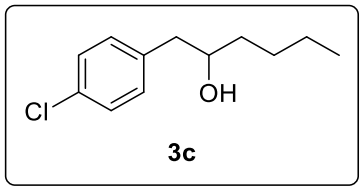
^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 161.7 (d, $^{1}J_{CF}$ = 244.2 Hz, C_q), 134.5 (d, $^{4}J_{CF}$ = 3.3 Hz, C_q), 130.9 (d, $^{3}J_{CF}$ = 7.8 Hz, +), 115.3 (d, $^{2}J_{CF}$ = 21.1 Hz, +), 72.8 (d, J_{CF} = 0.9 Hz, +), 43.2 (–), 36.6 (–), 28.0 (–), 22.8 (–), 14.2 (+).

^{19}F-NMR (282 MHz, $CDCl_3$, δ_F): -117.40 (s).

HRMS (EI) (m/z): [M^+] ($C_{12}H_{17}FO^+$) calc. 196.12579; observed 196.12558.

Yield: 62% (colorless, highly viscous oil)

1-(4-Chlorophenyl)hexan-2-ol (3c)



3c

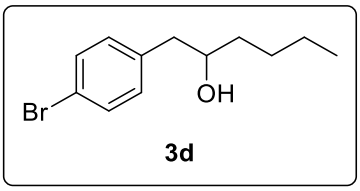
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.30 – 7.25 (m, 2H), 7.18 – 7.11 (m, 2H), 3.82-3.73 (m, 1H), 2.79 (dd, *J* = 13.7, 4.3 Hz, 1H), 2.62 (dd, *J* = 13.6, 8.3 Hz, 1H), 1.54 (s, 1H), 1.51 – 1.27 (m, 6H), 0.91 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 137.3 (C_q), 132.3 (C_q), 130.9 (+), 128.7 (+), 72.7 (+), 43.4 (–), 36.7 (–), 28.0 (–), 22.8 (–), 14.2 (+).

HRMS (APCI) (m/z): [MNH_4^+] ($C_{12}H_{21}ClNO^+$) calc.: 230.1306, found: 230.1325.

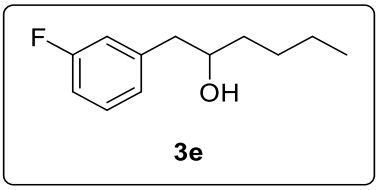
Yield: 53% (white solid)

1-(4-Bromophenyl)hexan-2-ol (3d)



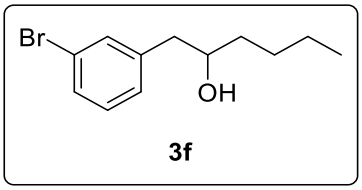
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.46 – 7.40 (m, 2H), 7.12 – 7.07 (m, 2H), 3.82 – 3.74 (m, 1H), 2.77 (dd, *J* = 13.6, 4.3 Hz, 1H), 2.61 (dd, *J* = 13.7, 8.3 Hz, 1H), 1.56 – 1.27 (m, 7H), 0.91 (t, *J* = 7.1 Hz, 2H).
^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 137.8 (C_q), 131.7 (+), 131.3 (+), 120.4 (C_q), 72.7 (+), 43.5 (–), 36.7 (–), 28.0 (–), 22.8 (–), 14.2 (+).
HRMS (APCI) (m/z): [MNH_4^+] ($C_{12}H_{21}ClNO^+$) calc.: 274.0801, found: 274.0805.
Yield: 32% (white solid)

1-(3-Fluorophenyl)hexan-2-ol (3e)



^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.31 – 7.23 (m, 2H), 7.02 – 6.89 (m, 3H), 3.86 – 3.77 (m, 1H), 2.82 (dd, *J* = 13.6, 4.2 Hz, 1H), 2.65 (dd, *J* = 13.6, 8.3 Hz, 1H), 1.58 – 1.30 (m, 7H), 0.91 (t, *J* = 7.1 Hz, 3H).
^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 163.0 (d, $^{1}J_{CF}$ = 245.8 Hz, C_q), 141.5 (d, $^{3}J_{CF}$ = 7.3 Hz, C_q), 130.0 (d, $^{3}J_{CF}$ = 8.4 Hz, +), 125.2 (d, $^{4}J_{CF}$ = 2.7 Hz, +), 116.4 (d, $^{2}J_{CF}$ = 20.9 Hz, +), 113.4 (d, $^{2}J_{CF}$ = 21.0 Hz, +), 72.6 (+), 43.9 (–), 36.7 (–), 28.0 (–), 22.8 (–), 14.2 (+).
^{19}F-NMR (282 MHz, $CDCl_3$, δ_F): -113.93 (s).
HRMS (APCI) (m/z): [MNH_4^+] ($C_{12}H_{21}FNO^+$) calc.: 214.1602, found: 214.1599.
Yield: 17% (colorless liquid)

1-(3-Bromophenyl)hexan-2-ol (3f)



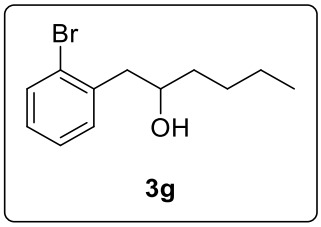
^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.40 – 7.34 (m, 2H), 7.20 – 7.13 (m, 2H), 3.84 – 3.77 (m, 1H), 2.79 (dd, *J* = 13.7, 4.1 Hz, 1H), 2.62 (dd, *J* = 13.7, 8.4 Hz, 1H), 1.53 – 1.31 (m, 7H), 0.92 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 141.3 (C_q), 132.5 (+), 130.2 (+), 129.7 (+), 128.2 (+), 122.7 (C_q), 72.6 (+), 43.8 (–), 36.8 (–), 28.0 (–), 22.8 (–), 14.2 (+).

HRMS (APCI) (m/z): [MNH_4^+] ($C_{12}H_{21}BrNO^+$) calc.: 274.0801, found: 274.0804.

Yield: 16% (colorless, highly viscous oil)

1-(2-Bromophenyl)hexan-2-ol (3g)



3g

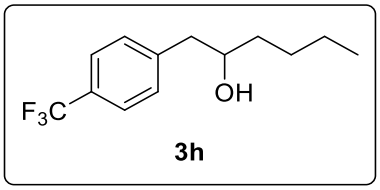
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.58 – 7.53 (m, 1H), 7.29 – 7.22 (m, 2H), 7.14 – 7.05 (m, 1H), 3.97 – 3.87 (m, 1H), 3.03 (dd, *J* = 13.6, 3.9 Hz, 1H), 2.74 (dd, *J* = 13.6, 8.7 Hz, 1H), 1.61 – 1.30 (m, 7H), 0.92 (t, *J* = 7.1 Hz, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 138.5 (C_q), 133.1 (+), 131.9 (+), 128.3 (+), 127.5 (+), 125.0 (C_q), 71.3 (+), 44.2 (–), 37.0 (–), 28.0 (–), 22.9 (–), 14.2 (+).

HRMS (EI) (m/z): [M^+] ($C_{12}H_{17}BrO^+$) calc.: 256.04573, found: 256.04613.

Yield: 43% (colorless, highly viscous oil)

1-(4-(Trifluoromethyl)phenyl)hexan-2-ol (3h)



3h

^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.56 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.89 – 3.79 (m, 1H), 2.87 (dd, *J* = 13.6, 4.2 Hz, 1H), 2.72 (dd, *J* = 13.6, 8.3 Hz, 1H), 1.55 – 1.30 (m, 7H), 0.92 (t, *J* = 7.2 Hz, 3H).

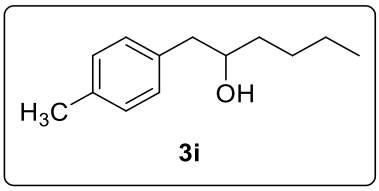
^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 143.1 (d, $^{5}J_{CF}$ = 1.5 Hz, C_q), 129.9 (+), 128.8 (d, $^{2}J_{CF}$ = 32.2 Hz, C_q), 125.5 (q, $^{3}J_{CF}$ = 3.7 Hz, +), 124.4 (d, $^{1}J_{CF}$ = 272.0 Hz, C_q), 72.6 (+), 43.9 (–), 36.9 (–), 28.0 (–), 22.8 (–), 14.2 (+).

^{19}F-NMR (282 MHz, $CDCl_3$, δ_F): -62.9 (s).

HRMS (APCI) (m/z): [MNH_4^+] ($C_{13}H_{21}F_3NO^+$) calc.: 264.1570, found: 264.1575.

Yield: 37% (white solid)

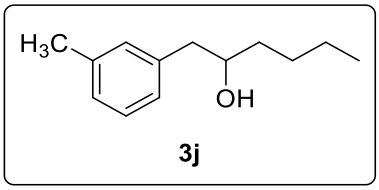
1-(*p*-Tolyl)hexan-2-ol (3i)



3i

^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.16 – 7.09 (m, 4 H), 3.83 – 3.75 (m, 1H), 2.81 (dd, *J* = 13.6, 4.2 Hz, 1H), 2.60 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.34 (s, 3H), 1.59 – 1.30 (m, 7H), 0.92 (t, *J* = 7.1 Hz, 3H).
^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 136.1 (C_q), 135.6 (C_q), 129.4 (+), 129.4 (+), 72.8 (+), 43.7 (–), 36.6 (–), 28.1(–), 22.9 (–), 21.2 (+), 14.2 (+).
HRMS (EI) (m/z): [M^+] ($C_{13}H_{20}O^+$) calc.: 192.15087, found: 192.15122.
Yield: 60% (colorless liquid)

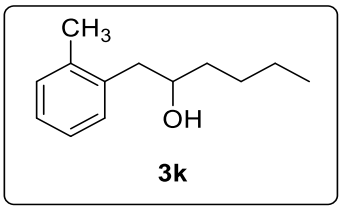
1-(*m*-Tolyl)hexan-2-ol (3j)



3j

^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.25 – 7.18 (m, 1H), 7.08 – 7.00 (m, 3H), 3.85 – 3.76 (m, 1H), 2.81 (dd, *J* = 13.5, 4.1 Hz, 1H), 2.60 (dd, *J* = 13.5, 8.5 Hz, 1H), 2.35 (s, 3H), 1.59 (s, 1H), 1.55 – 1.30 (m, 6H), 0.93 (t, *J* = 7.1 Hz, 2H).
^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 138.7 (C_q), 138.3 (C_q), 130.3 (+), 128.6 (+), 127.3 (+), 126.5 (+), 72.8 (+), 44.1 (–), 36.7 (–), 28.1 (–), 22.9 (–), 21.5 (+), 14.2 (+).
HRMS (EI) (m/z): [M^+] ($C_{13}H_{20}O^+$) calc.: 192.15087, found: 192.15049.
Yield: 68% (colorless liquid)

1-(*o*-Tolyl)hexan-2-ol (3k)



3k

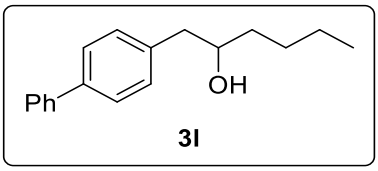
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.20 – 7.13 (m, 4H), 3.85-3.77 (m, 1H), 2.86 (dd, *J* = 13.7, 4.2 Hz, 1H), 2.67 (dd, *J* = 13.7, 8.8 Hz, 1H), 2.35 (s, 3H), 1.64 (s, 1H), 1.59 – 1.32 (m, 6H), 0.94 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 137.1 (C_q), 136.7 (C_q), 130.6 (+), 130.3 (+), 126.6 (+), 126.1 (+), 71.8 (+), 41.4 (–), 37.0 (–), 28.1 (–), 22.9 (–), 19.8 (+), 14.2 (+).

HRMS (EI) (m/z): [M^+] ($C_{13}H_{20}O^+$) calc.: 192.15087, found: 192.15057.

Yield: 54% (colorless liquid)

1-([1,1'-Biphenyl]-4-yl)hexan-2-ol (3l)[10]



3l

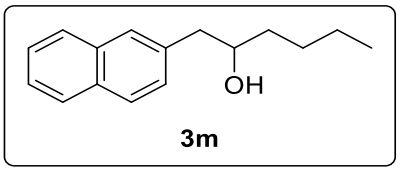
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.63 – 7.55 (m, 4H), 7.49 – 7.43 (m, 2H), 7.39 – 7.29 (m, 3H), 3.91 – 3.83 (m, 1H), 2.90 (dd, *J* = 13.6, 4.2 Hz, 1H), 2.71 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.68 (s, 1H), 1.61 – 1.35 (m, 6H), 0.96 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 141.0 (C_q), 139.4 (C_q), 137.9 (C_q), 130.0 (+), 128.9 (+), 127.3 (+), 127.2 (+), 127.1 (+), 72.8 (+), 43.8 (–), 36.7 (–), 28.1 (–), 22.9 (–), 14.2 (+).

HRMS (EI) (m/z): [M^+] ($C_{13}H_{20}O^+$) calc.: 254.16652, found: 254.16588.

Yield: 58% (white solid)

1-(Naphthalen-2-yl)hexan-2-ol (3m)



3m

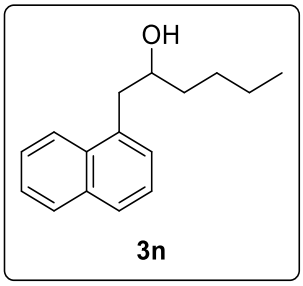
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.87 – 7.78 (m, 3H), 7.68 (s, 1H), 7.52 – 7.42 (m, 2H), 7.37 (dd, *J* = 8.4, 1.7 Hz, 1H), 3.96 – 3.87 (m, 1H), 3.01 (dd, *J* = 13.5, 4.2 Hz, 1H), 2.82 (dd, *J* = 13.5, 8.4 Hz, 1H), 1.65 – 1.29 (m, 7H), 0.94 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 136.3 (C_q), 133.7 (C_q), 132.4 (C_q), 128.3 (+), 128.0 (+), 127.9 (+), 127.8 (+), 127.6 (+), 126.2 (+), 125.6 (+), 72.7 (+), 44.3 (–), 36.7 (–), 28.1 (–), 22.9 (–), 14.3 (+).

HRMS (EI) (m/z): [M^+] ($C_{16}H_{20}O^+$) calc.: 228.15087, found: 228.15084.

Yield: 33% (colorless liquid)

1-(Naphthalen-1-yl)hexan-2-ol (3n)



3n

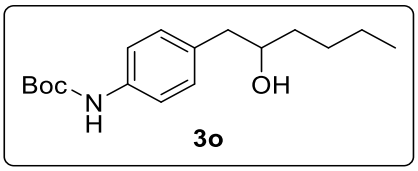
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 8.07 – 8.03 (m, 1H), 7.90 – 7.87 (m, 1H), 7.79 – 7.75 (m, 1H), 7.57 – 7.36 (m, 4H), 4.03 – 3.93 (m, 1H), 3.37 (dd, *J* = 13.8, 3.9 Hz, 1H), 3.05 (dd, *J* = 13.8, 8.7 Hz, 1H), 1.69 – 1.31 (m, 7H), 0.95 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 134.9 (C_q), 134.1 (C_q), 132.3 (C_q), 129.0 (+), 127.8 (+), 127.5 (+), 126.1 (+), 125.8 (+), 125.6 (+), 124.0 (+), 72.1 (+), 41.4 (–), 37.1 (–), 28.1 (–), 22.9 (–), 14.3 (+).

HRMS (EI) (m/z): [M^+] ($C_{16}H_{20}O^+$) calc.: 228.15087, found: 228.15109.

Yield: 56% (colorless liquid)

***tert*-Butyl (4-(2-hydroxyhexyl)phenyl)carbamte (3o)**



3o

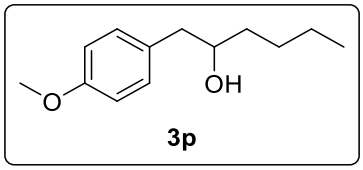
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.27 – 7.21 (m, 2H), 7.10 – 7.05 (m, 2H), 6.53 (s, 1H), 3.75 – 3.66 (m, 1H), 2.72 (dd, *J* = 13.6, 4.3 Hz, 1H), 2.53 (dd, *J* = 13.6, 8.3 Hz, 1H), 1.59 (s, 1H), 1.46 (s, 9H), 1.45 – 1.20 (m, 6H), 0.85 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 153.0 (C_q), 136.9 (C_q), 133.3 (C_q), 130.0 (+), 119.0 (+), 80.6 (C_q), 72.8 (+), 43.4 (–), 36.5 (–), 28.5 (+), 28.1 (–), 22.8 (–), 14.2 (+).

HRMS (ESI) (m/z): [MNH_4^+] ($C_{17}H_{31}N_2O_3^+$) calc.: 311.2329, found: 311.2331.

Yield: 48% (white solid)

1-(4-Methoxyphenyl)hexan-2-ol (3p)



3p

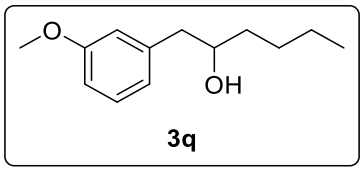
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.16 – 7.10 (m, 2H), 6.88 – 6.83 (m, 2H), 3.82 – 3.71 (m, 4H), 2.78 (dd, *J* = 13.7, 4.2 Hz, 1H), 2.58 (dd, *J* = 13.7, 8.4 Hz, 1H), 1.58 (s, 1H), 1.52 – 1.43 (m, 3H), 1.41 – 1.28 (m, 3H), 0.91 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 158.4 (C_q), 130.7 (C_q), 130.5 (+), 114.1 (+), 72.9 (+), 55.4 (+), 43.2 (–), 36.6 (–), 28.1 (–), 22.9 (–), 14.2 (+).

HRMS (APCI) (m/z): [MNH_4^+] ($C_{13}H_{24}NO_2^+$) calc.: 266.1802, found: 266.1804.

Yield: 13% (colorless liquid)

1-(3-Methoxyphenyl)hexan-2-ol (3q)[11]



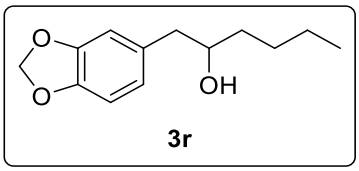
3q

^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.26 – 7.19 (m, 1H), 6.83 – 6.75 (m, 3H), 3.87 – 3.73 (m, 4H), 2.81 (dd, *J* = 13.5, 4.2 Hz, 1H), 2.62 (dd, *J* = 13.5, 8.4 Hz, 1H), 1.69 (d, *J* = 3.5 Hz, 1H), 1.55 – 1.30 (m, 6H), 0.92 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 159.8 (C_q), 140.4 (C_q), 129.6 (+), 121.8 (+), 115.2 (+), 111.8 (+), 72.7 (+), 55.2 (+), 44.2 (–), 36.6 (–), 28.0 (–), 22.8 (–), 14.2 (+).

Yield: 63% (colorless liquid)

1-(Benzo[d][1,3]dioxol-5-yl)hexan-2-ol (3r)



3r

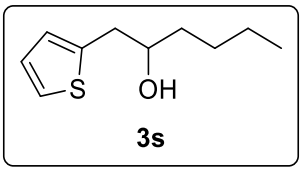
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 6.77 – 6.63 (m, 3H), 5.93 (s, 2H), 3.79 – 3.69 (m, 1H), 2.74 (dd, *J* = 13.7, 4.2 Hz, 1H), 2.54 (dd, *J* = 13.7, 8.4 Hz, 1H), 1.57 (s, 1H), 1.51 – 1.29 (m, 6H), 0.91 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 147.9 (C_q), 146.3 (C_q), 132.5 (C_q), 122.4 (+), 109.8 (+), 108.4 (+), 101.0 (–), 72.8 (+), 43.8 (–), 36.6 (–), 28.1 (–), 22.9 (–), 14.2 (+).

HRMS (EI) (m/z): [M^+] ($C_{13}H_{18}O_3^+$) calc.: 222.12505, found: 222.12541.

Yield: 35% (colorless liquid)

1-(Thiophen-2-yl)hexan-2-ol (3s)



3s

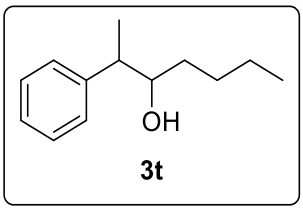
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.18 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.99 – 6.93 (m, 1H), 6.88 – 6.85 (m, 1H), 3.84 – 3.76 (m, 1H), 3.04 (ddd, *J* = 14.7, 4.0, 0.8 Hz, 1H), 2.88 (dd, *J* = 14.8, 8.0 Hz, 1H), 1.76 (s, 1H), 1.57 – 1.29 (m, 6H), 0.92 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 140.8 (C_q), 127.1 (+), 126.1 (+), 124.3 (+), 72.5 (+), 38.1 (–), 36.4 (–), 28.0 (–), 22.8 (–), 14.2 (+).

HRMS (EI) (m/z): [M^+] ($C_{10}H_{16}OS^+$) calc.: 184.09164, found: 184.09188.

Yield: 61% (colorless liquid)

2-Phenylheptan-3-ol (*syn*/*anti* diastereomeric mixture) (3t)[12]



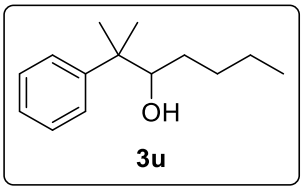
3t

^{1}H-NMR (diastereomeric mixture) (300 MHz, $CDCl_3$, δ_H): 7.36 – 7.19 (m, 5H), 3.70 – 3.62 (m, 1H), 2.83 – 2.71 (m, 1H), 1.59 – 1.24 (m, 10H), 0.95 – 0.84 (m, 3H).

^{13}C-NMR (diastereomeric mixture) (75 MHz, $CDCl_3$, δ_C): 144.8 (C_q), 143.7 (C_q), 128.7 (+), 128.6 (+), 128.3 (+), 127.9 (+), 126.8 (+), 126.5 (+), 76.3 (+), 76.2 (+), 46.2 (+), 45.7 (+), 34.5 (–), 34.3 (–), 28.4 (–), 28.0 (–), 22.9 (–), 22.8 (–), 18.1 (+), 15.5 (+), 14.3 (+), 14.2 (+).

Yield: 62% (colorless liquid)

2-Methyl-2phenylheptan-3-ol (3u)



3u

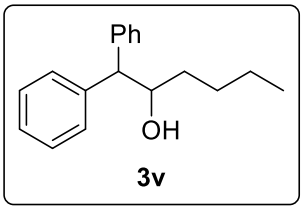
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.41 – 7.30 (m, 4H), 7.25 – 7.19 (m, 1H), 3.63 – 3.57 (m, 1H), 1.51 – 1.18 (m, 13H), 0.87 (t, J = 7.0 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 147.4 (C_q), 128.4 (+), 126.6 (+), 126. (+), 79.8 (+), 42.8 (C_q), 31.3 (–), 29.4 (–), 24.4 (+), 23.7 (+), 22.8 (–), 14.2 (+).

HRMS (APCI) (m/z): [MH^+–H_2O] ($C_{14}H_{21}^+$) calc.: 189.1638, found: 189.1642.

Yield: 57% (colorless liquid)

1,1-diphenylhexan-2-ol (3v)[10]



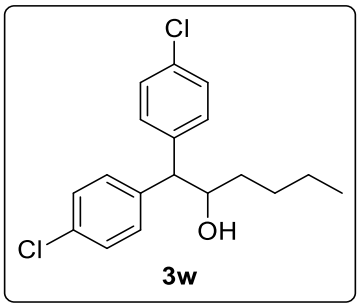
3v

^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.41 – 7.17 (m, 10H), 4.38 – 4.32 (m, 1H), 3.90 (d, J = 8.3 Hz, 1H), 1.58 (s, 1H), 1.54 – 1.22 (m, 6H), 0.87 (t, J = 7.2 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 142.7 (C_q), 141.7 (C_q), 129.0 (+), 128.9 (+), 128.7 (+), 128.4 (+), 127.0 (+), 126.6 (+), 73.9 (+), 58.9 (+), 34.9 (–), 28.2 (–), 22.8 (–), 14.2 (+).

Yield: 51% (colorless liquid)

1,1-Bis(4-chlorophenyl)hexan-2-ol (3w)



3w

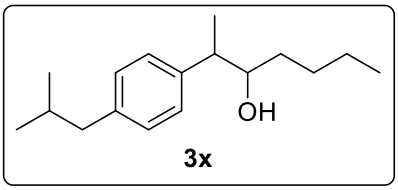
^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.30 – 7.18 (m, 8H), 4.29 – 4.22 (m, 1H), 3.86 (d, *J* = 7.5 Hz, 1H), 1.53 (s, 1H), 1.49 – 1.22 (m, 6H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ 140.8 (C_q), 139.6 (C_q), 132.9 (C_q), 132.6 (C_q), 130.4 (+), 129.7 (+), 129.0 (+), 129.0 (+), 73.7 (+), 57.1 (+), 35.1 (–), 28.1 (–), 22.7 (–), 14.2 (+).

HRMS (APCI) (m/z): [MNH_4^+] ($C_{18}H_{24}OCl_2N$) calc.: 340.1229, found: 340.1230.

Yield: 33% (colorless liquid)

2-(4-isobutylphenyl)heptan-3-ol (3x)



3x

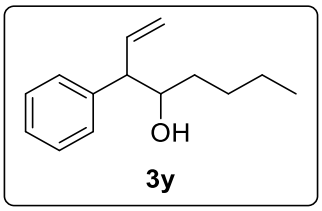
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.14 – 7.06 (m, 4H), 3.69 – 3.61 (m, 1H), 2.81 – 2.72 (m, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.85 (hept, *J* = 6.8 Hz, 1H), 1.46 – 1.36 (m, 3H), 1.32 – 1.24 (m, 6H), 0.92 – 0.86 (m, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 141.9 (C_q), 139.8 (C_q), 129.3 (+), 127.6 (+), 76.4 (+), 45.2 (+), 45.2 (–), 34.4 (–), 30.4 (+), 28.4 (–), 22.8 (–), 22.6 (+), 15.2 (+), 14.2 (+).

HRMS (APCI) (m/z): [MH^+ - H_2O] ($C_{17}H_{27}^+$) calc.: 231.2107, found: 231.2119.

Yield: 27% (colorless oil)

3-Phenyloct-1-en-4-ol (*syn*/*anti* diastereomeric mixture) (3y)[13]



Starting materials: (*E*)-4-phenylbut-3-enoic acid (*trans*-styrylacetic acid) and *n*-pentanal (**2a**).

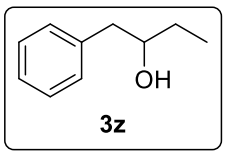
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.38 – 7.18 (m, 5H), 6.19 – 6.00 (m, 1H), 5.26 – 5.09 (m, 2H), 3.90 – 3.75 (m, 1H), 3.35 – 3.22 (m, 1H), 1.85 – 1.81 [1.66 – 1.63] (m, 1H), 1.53 – 1.21 (m, 6H), 0.94 – 0.82 (m, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 141.8 (C_q), 141.1 (C_q), 138.8 (+), 138.5 (+), 128.9 (+), 128.8 (+), 128.6 (+), 128.1 (+), 127.0 (+), 126.7 (+), 118.0 (–), 116.8 (–), 74.4 (+), 74.1 (+), 57.5 (+), 57.5 (+), 34.3 (–), 34.2 (–), 28.1 (–), 28.0 (–), 22.9 (–), 22.8 (–), 14.2 (+), 14.2 (+).

HRMS (APCI) (m/z): [MNH_4^+] ($C_{14}H_{24}ON^+$) calc.: 222.1853, found: 222.1852.

Yield: 35% (colorless liquid)

1-Phenylbutan-2-ol (3z)[14]

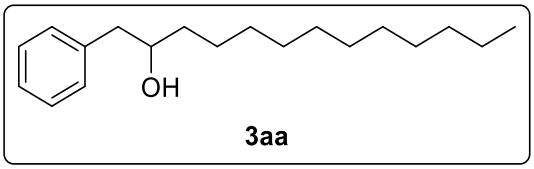


^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.35 – 7.29 (m, 2H), 7.26 – 7.20 (m, 3H), 3.79 – 3.72 (m, 1H), 2.84 (dd, *J* = 13.6, 4.3 Hz, 1H), 2.65 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.62 – 1.49 (m, 3H), 1.00 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 138.8 (C_q), 129.6 (+), 128.7 (+), 126.6 (+), 74.2 (+), 43.7 (–), 29.7 (–), 10.2 (+).

Yield: 41% (colorless liquid)

1-Phenyltridecan-2-ol (3aa)



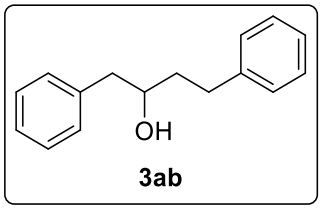
^{1}H-NMR (400 MHz, $CDCl_3$, δ_H) 7.35 – 7.29 (m, 2H), 7.26 – 7.21 (m, 3H), 3.85 – 3.78 (m, 1H), 2.84 (dd, *J* = 13.5, 4.3 Hz, 1H), 2.65 (dd, *J* = 13.5, 8.4 Hz, 1H), 1.75 – 1.61 (m, 1H), 1.54 – 1.49 (m, 2H), 1.34 – 1.26 (m, 18H), 0.90 (t, *J* = 6.8 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C) 138.8 (C_q), 129.5 (+), 128.6 (+), 126.5 (+), 72.8 (+), 44.2 (–), 37.0 (–), 32.1 (–), 29.8 (–), 29.8 (–), 29.8 (–), 29.5 (–), 25.9 (–), 22.8 (–), 14.3 (+).

HRMS (APCI) (m/z): [MNH_4^+] ($C_{19}H_{36}NO^+$) calc.: 294.2791, found: 294.2794.

Yield: 73% (brown solid)

1,4-Diphenylbutan-2-ol (3ab)[15]



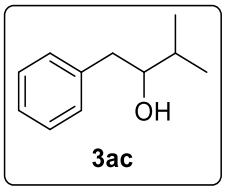
3ab

^{1}H-NMR (300 MHz, $CDCl_3$, δ_H) 7.38 – 7.21 (m, 10H), 3.91 – 3.82 (m, 1H), 2.94 – 2.83 (m, 2H), 2.80 – 2.67 (m, 2H), 1.92 – 1.82 (m, 2H), 1.66 (s, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C) 142.1 (C_q), 138.5 (C_q), 129.6 (+), 128.7 (+), 128.6 (+), 128.5 (+), 126.6 (+), 125.9 (+), 72.0 (+), 44.2 (–), 38.5 (–), 32.2 (–).

Yield: 72% (yellow solid)

3-Methyl-1-phenylbutan-2-ol (3ac)[14a, 16]



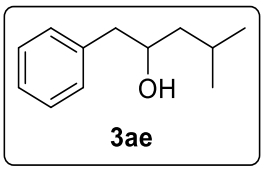
3ac

^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.35 – 7.29 (m, 2H), 7.26 – 7.21 (m, 3H), 3.63 – 3.56 (m, 1H), 2.86 (dd, *J* = 13.6, 3.5 Hz, 1H), 2.61 (dd, *J* = 13.6, 9.4 Hz, 1H), 1.81 – 1.72 (m, 1H), 1.46 (s, 1H), 1.01 (d, *J* = 6.8 Hz, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 139.3 (C_q), 129.5 (+), 128.7 (+), 126.5(+), 77.6 (+), 40.9 (–), 33.3 (+), 19.1 (+), 17.6 (+).

Yield: 25% (colorless liquid)

4-Methyl-1-phenylpentan-2-ol (3ae)[17]



3ae

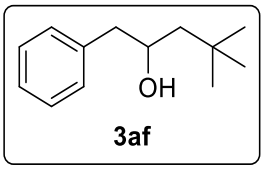
^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.35 – 7.30 (m, 2H), 7.26 – 7.21 (m, 3H), 3.90 (hept, *J* = 4.1 Hz, 1H), 2.82 (dd, *J* = 13.6, 4.1 Hz, 1H), 2.64 (dd, *J* = 13.5, 8.4 Hz, 1H), 1.89 – 1.79 (m, 1H), 1.57 (s, 1H), 1.51 – 1.44 (m, 1H), 1.35 – 1.28 (m, 1H), 0.94 (dd, *J* = 12.3, 6.6 Hz, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 138.8 (C_q), 129.6 (+), 128.7 (+), 126.6 (+), 70.8 (+), 46.2 (–), 44.7 (–), 24.8 (+), 23.6 (+), 22.2 (+).

HRMS (APCI) (m/z): [MNH_4^+] ($C_{12}H_{22}NO^+$) calc.: 196.1696, found: 196.1695.

Yield: 56% (colorless liquid)

4,4-Dimethyl-1-phenylpentan-2-ol (3af)[18]



3af

^{1}H-NMR (300 MHz, $CDCl_3$, δ_H) 7.36 – 7.29 (m, 2H), 7.27 – 7.20 (m, 3H), 4.01 – 3.92 (m, 1H), 2.78 (dd, *J* = 13.4, 4.5 Hz, 1H), 2.67 (dd, *J* = 13.4, 8.4 Hz, 1H), 1.50 – 1.43 (m, 3H), 0.97 (s, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C) 138.8 (C_q), 129.6 (+), 128.7 (+), 126.6 (+), 70.5 (+), 50.5 (–), 46.2 (–), 30.5 (C_q), 30.3 (+).

HRMS (APCI) (m/z): [MNH_4^+] ($C_{13}H_{24}NO^+$) calc.: 210.1852, found: 210.1850.

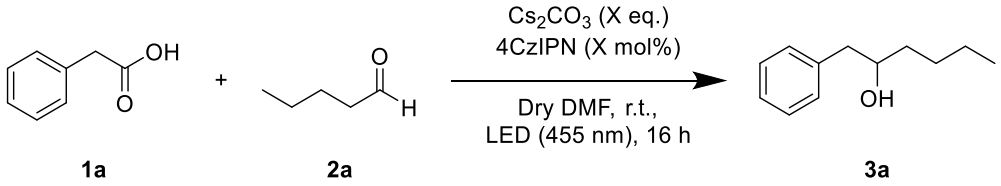
Yield: 41% (colorless liquid)

4. Detailed reaction optimization process

General procedure for the reaction optimization process (General Procedure B)

A 5 mL crimp cap vial equipped with a magnetic stirring bar was loaded with photocatalyst, base, phenylacetic acid (**1a**), *n*-pentanal (**2a**), solvent and if noted an additive in the amounts given in the corresponding tables. In doing so, all solid compounds were added before capping the vial, whereas all liquid compounds were added *via* syringe after setting the capped vial under inert conditions. The reaction mixture was degassed by four cycles of freeze-pump-thaw and subsequently stirred under light irradiation for the given time at 25 °C. Subsequently, an aliquot of the reaction mixture was submitted to GC-FID analysis to determine the product yield with *n*-decane as internal standard.

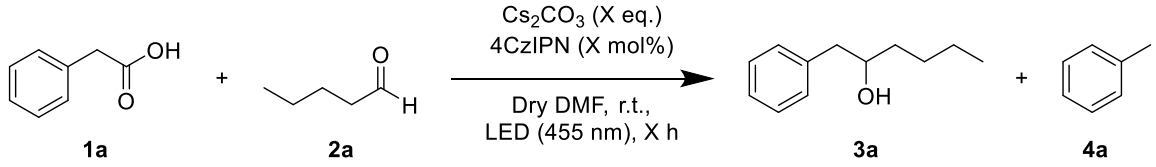
Table S1. Control experiments in absence of either Photocatalyst, light or base.[a]



Entry	Catalyst loading [mol%]	Pentanal	Cs_2CO_3 eq.	Yield **3a**[b] [%]
1	2	3	1	70
2	-	10	1	n.d.
3[c]	2	10	1	n.d.
4	2	10	-	n.d.

[a] Reactions were performed with phenylacetic acid (**1a**) (150 µmol, 1 eq.) in dry DMF (2 mL). [b] Determined by GC-FID analysis with *n*-decane as internal standard. [c] Reaction performed in absence of light.

Table S2. Optimization of reaction time, catalyst- and base loading.[a]

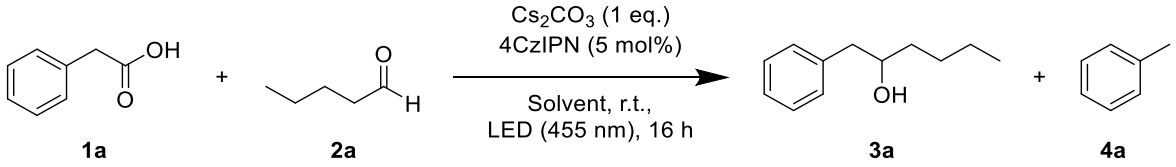


Entry	Catalyst loading [mol%]	Cs_2CO_3 equivalents	Time [h]	Yield[b] **3a** [%]	Yield[b] **4a** [%]
1	2	1	6	51	9
2	2	1	16	70	15
3	2	1	24	73	16

4	5	1	6	67	13
5	5	1	16	73	15
6	5	1	24	73	17
7	5	1.5	16	39	12
8	5	0.5	16	50	5

[a] Reactions were performed with phenylacetic acid (**1a**) (150 µmol, 1 eq.) and *n*-pentanal (**2a**) (450 µmol, 3 eq.) in dry DMF (2 mL). [b] Determined by GC-FID analysis with *n*-decane as internal standard.

Table S3. Solvent screening.[a]



1a **2a** **3a** **4a**

Entry	Solvent	Yield[b] **3a** [%]	Yield[b] **4a** [%]
1	Dry DMF	73	15
2	Dry DMA	75	11
3	Dry DCM	n.d.	n.d.
4	Dry EtOAc	n.d.	n.d.
5	Dry MeCN	20	20
6	Dry THF	Traces	n.d.
7	DMA	75	12
8	1,4-Dioxane	Traces	n.d.
9[c]	DMA	42	13

[a] Reactions were performed with phenylacetic acid (**1a**) (150 µmol, 1 eq.) and *n*-pentanal (**2a**) (450 µmol, 3 eq.) in 2 mL solvent. [b] Determined by GC-FID analysis with *n*-decane as internal standard. [c] Without prior freeze-pump-thaw degassing of reaction mixture before irradiation.

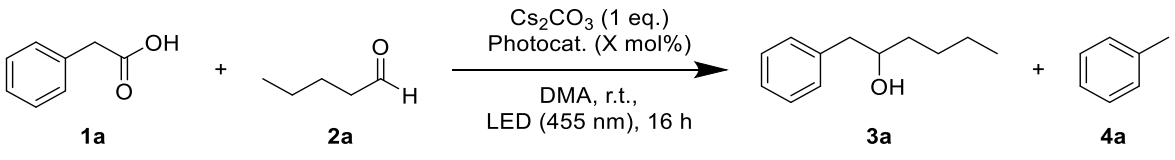
Table S4. Base screening.[a]

1a **2a** **3a** **4a**

Entry	Base (eq.)	Yield **3a**[b] [%]	Yield **4a**[b] [%]
1	Cs_2CO_3 (1)	75	12
2	K_2CO_3 (1)	68	18
3	Na_2CO_3 (1)	60	23
4	CsF (1)	65	16
5	CsF (1.5)	69	16
6	KOAc (1)	72	16
7	KOAc (1.5)	72	18
8	CF_3COOK (1.5)	7	Traces
9	CsOAc (1)	49	11
10	CsOAc (1.5)	46	11
11	NBu_4OAc (1.5)	61	12
12	DBU (1.5)	Traces	n.d.
13	Lutidin (1.5)	Traces	n.d.
14	Tetramethylguanidine (1.5)	7	3
15	2,2,6,6-Tetramethyl-piperidine (1.5)	Traces	n.d.

[a] Reactions were performed with phenylacetic acid (**1a**) (150 µmol, 1 eq.) and *n*-pentanal (**2a**) (450 µmol, 3 eq.) in DMA (2 mL). [b] Determined by GC-FID analysis with *n*-decane as internal standard.

Table S5. Photocatalyst screening.[a]



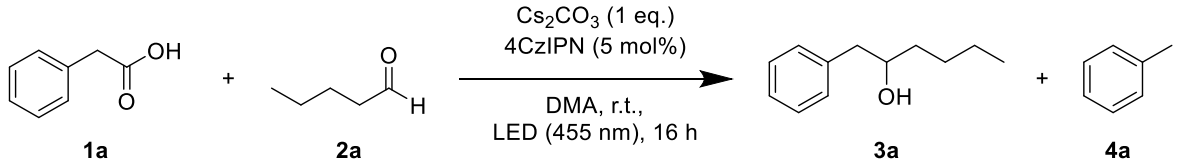
1a **2a** **3a** **4a**

Entry	Photocatalyst (Irradiation wavelength [nm], loading [mol%])	Yield[b] **3a** [%]	Yield[b] **4a** [%]
1	4CzIPN (455, 5)	75	12
2	4CzPN (455, 5)	55	10
3	3DPAFIPN (455, 5)	6	Traces
4	$[Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbpy)](PF_6)$ (455, 2)	4	5

5	3,7-Di(4-biphenyl) 1-naphthalene-10-phenoxazine (400, 5)	Traces	n.d.
6	Rhodamin-6G (455, 5)	n.d.	n.d.
7	Dicyanoanthracene (400, 5)	6	Traces
8	[Acr$^+$-Mes](ClO_4) (455, 5)	n.d.	n.d.
9	2,4,6-triphenylpyrylium (455, 5)	n.d.	n.d.
10	Eosin Y (535, 5)	n.d.	n.d.

[a] Reactions were performed with phenylacetic acid (**1a**) (150 µmol, 1 eq.) and *n*-pentanal (**2a**) (450 µmol, 3 eq.) in DMA (2 mL). [b] Determined by GC-FID analysis with *n*-decane as internal standard.

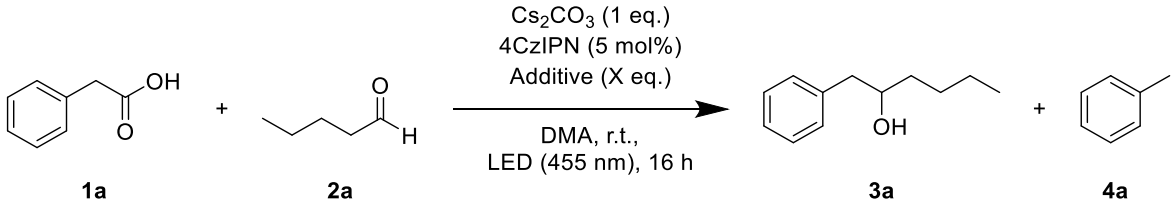
Table S6. Variation of the electrophile amount.[a]



Entry	**2a** (eq.)	Yield[b] **3a** [%]	Yield[b] **4a** [%]
1	1	50	31
2	2	67	17
3	3	75	12
4	5	78	7
5	10	79	3

[a] Reactions were performed with phenylacetic acid (**1a**) (150 µmol, 1 eq.) in DMA (2 mL). [b] Determined by GC-FID analysis with *n*-decane as internal standard.

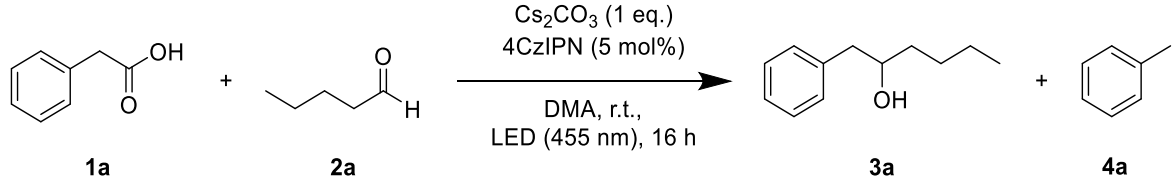
Table S7. Additive Screening.[a]



Entry	Additive (eq.)	Yield[b] **3a** [%]	Yield[b] **4a** [%]
1	H_2O (3)	34	55
2	$LiBF_4$ (1)	35	18
3	B_2pin_2 (1)	n.d.	n.d.
4	$Sc(OTf)_3$ (0.5)	Traces	Traces

[a] Reactions were performed with phenylacetic acid (**1a**) (150 µmol, 1 eq.) and *n*-pentanal (**2a**) (450 µmol, 3 eq.) in DMA (2 mL). [b] Determined by GC-FID analysis with *n*-decane as internal standard.

Table S8. Repetition of control experiments with optimized conditions.[a]



Entry	Catalyst loading [mol%]	Cs_2CO_3 equivalents	Yield[b] **3a** [%]	Yield[b] **4a** [%]
1	5	1	75	12
2	-	1	n.d.	n.d.
3[c]	5	1	n.d.	n.d.
4	5	-	n.d.	n.d.

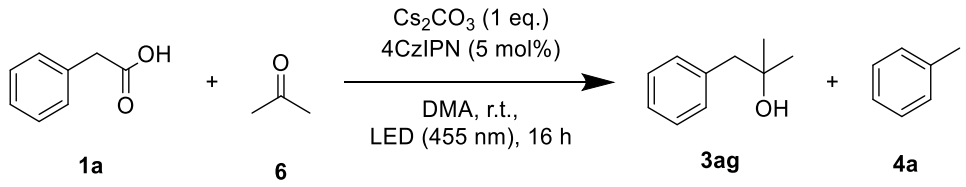
[a] Reactions were performed with phenylacetic acid (**1a**) (150 µmol, 1 eq.) and *n*-pentanal (**2a**) (150 µmol, 3 eq.) in DMA (2 mL). [b] Determined by GC-FID analysis with *n*-decane as internal standard. [c] Reaction performed in absence of light.

5. Photocatalytic benzylation of acetone and potassium benzyltrifluoroborate as carbanion precursor

Photocatalytic benzylation of acetone (6) with phenylacetic acid (1a) – GC-Yields

The GC-Yields of the photocatalytic benzylation of acetone (**6**) with phenylacetic acid (**1a**) were determined according to General Procedure B with acetone (**6**) instead of *n*-pentanal (**2a**)

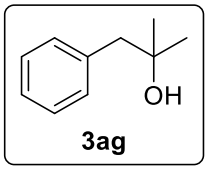
Table S9. Benzylation of acetone (**6**) with phenylacetic acid (**1a**).



Entry	Acetone equivalents	Yield[b] **3ag** [%]	Yield[b] **4a** [%]
1	3	4	77
2	10	13	70
3[c]	approx. 91 (1 mL)	39	49

[a] Reactions were performed with phenylacetic acid (**1a**) (150 µmol, 1 eq.) in DMA (2 mL). [b] Determined by GC-FID analysis with *n*-decane as internal standard. [c] Acetone/DMA (1:1) (2 mL) was used as solvent.

2-Methyl-1-phenylpropan-2-ol (3ag)[19]



2-Methyl-1-phenylpropan-2-ol (**3ag**) was synthesized according to General Procedure A with an acetone/DMA (1:1) (2 mL) mixture as solvent.

^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.35 – 7.19 (m, 5H), 2.77 (s, 2H), 1.23 (s, 6H).

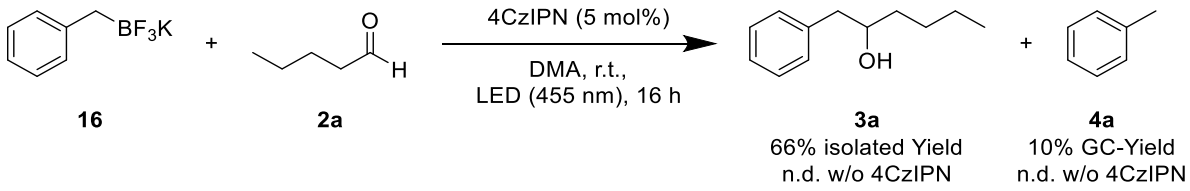
^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 137.9 (C_q), 130.6 (+), 128.3 (+), 126.6 (+), 70.9 (C_q), 49.9 (–), 29.3 (+).

Yield: 32% (colorless liquid)

Photocatalytic benzylation of *n*-pentanal (2a) with potassium benzyltrifluoroborate (16)

According to the proposed mechanism, every compound that bears a functional group in a benzylic position that can be oxidized by the excited photocatalyst leading to the formation of a benzyl radical should be a viable carbanion precursor. Hence, it was attempted to use benzyltrifluoroborate (**16**) as starting material. Furthermore, **16** does not hold a protic hydrogen and it was tested if the yield can thus be increased.

Indeed, benzylation product **3a** using *n*-pentanal (**2a**) and potassium benzyltrifluoroborate (**16**) as carbanion precursor could be isolated according to General Procedure A in absence of Cs_2CO_3 and with **16** instead of a carboxylic acid. Only a very small increase of yield in **3a** accompanied by a small decrease in toluene (**4a**) side product compared to carboxylic acids as starting material could be observed.

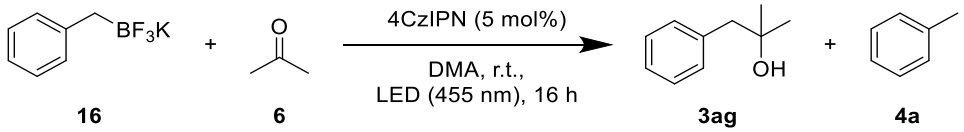


Scheme S1. Benzylation of *n*-pentanal (**2a**) with potassium benzyltrifluoroborate (**16**) as carbanion precursor.

Photocatalytic benzylation of acetone (6) with potassium benzyltrifluoroborate (16) – GC-Yields

The GC-Yields of the photocatalytic benzylation of acetone (**6**) with potassium benzyltrifluoroborate (**16**) were determined according to General Procedure B with **16** instead of phenylacteic acid (**1a**) and acetone (**6**) instead of *n*-pentanal (**2a**) in absence of Cs_2CO_3.

Table S10. Benzylation of acetone (**6**) with potassium benzyltrifluoroborate (**16**).[a]



Entry	Acetone equivalents	Yield[b] **3ag** [%]	Yield[b] **4a** [%]
1	3	6	67
2	10	13	56
3[c]	approx. 91 (1 mL)	43	43

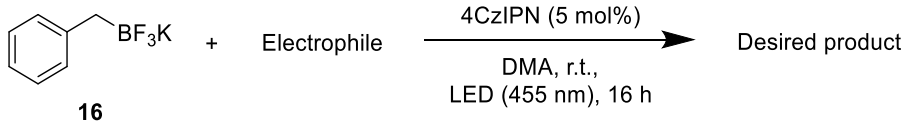
[a] Reactions were performed with potassium benzyltrifluoroborate (**16**) (150 µmol, 1 eq.) in DMA (2 mL). [b] Determined by GC-FID analysis with *n*-decane as internal standard. [c] Acetone/DMA (1:1) (2 mL) was used as solvent.

6. Attempted S_N2 reactions with potassium benzyltrifluoroborate as carbanion precursor

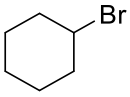
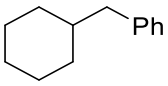
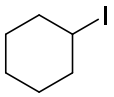
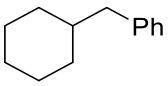
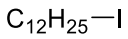
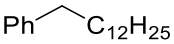
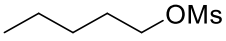
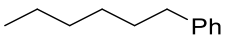
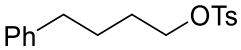
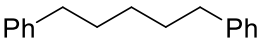
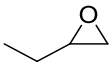
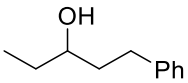
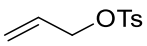
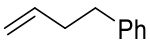
Attempted S_N2 reactions with potassium benzyltrifluoroborate (**16**) as carbanion precursor were performed according to General Procedure B in absence of Cs_2CO_3, with **16** instead of phenyl acetic acid (**1a**) and with the electrophile according to Table S11 instead of *n*-pentanal (**2a**). After the given reaction time, the mixture was submitted to GC-MS analysis.

16 was used instead of **1a** to avoid an esterification reaction with the carboxylate as direct electrophile.

Table S11. Attempted S_N2 reactions with potassium benzyltrifluoroborate (**16**) as carbanion precursor.[a]



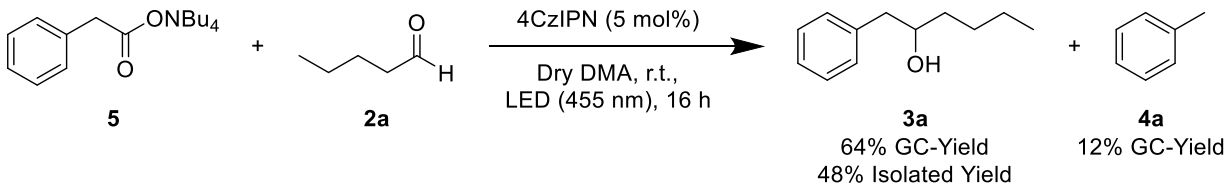
16

Entry	Electrophile	Desired product	Product Formation[b]
1	 **17**	 **18**	n.d.
2	 **19**	 **18**	Traces detected
3	 **20**	 **21**	Traces detected
4	 **22**[c]	 **23**	n.d.
5	 **24**[d]	 **25**	n.d.
6	 **26**	 **27**	n.d.
7	 **28**[e]	 **29**	Traces detected

[a] Reactions were performed with potassium benzyltrifluoroborate (**16**) (150 µmol, 1 eq.) and the corresponding electrophile (450 µmol, 3 eq.) in DMA (2 mL). [b] Determined by GC-MS analysis. [c] Starting material synthesized according to a literature procure.[20] [d] Starting material synthesized according to a literature procure.[21] [e] Starting material synthesized according to a literature procure.[22]

7. Mechanistic investigations

7.1 Photocatalytic benzylation with NBu_4PA (5) as carbanion precursor



Scheme S2. Benzylation of *n*-pentanal (**2a**) with NBu_4PA (**5**).

A 5 mL crimp cap vial equipped with a magnetic stirring bar was loaded with 4CzIPN (5.9 mg, 7.5 µmol, 5 mol%) and set under inert conditions. Subsequently, a solution of tetrabutylammonium phenylacetate (**5**) in dry DMA (75 mM, 2 mL, 150 µmol, 1 eq.) followed by *n*-pentanal (**2a**) (48 µL, 450 µmol, 3 eq.) were added *via* syringe. The reaction mixture was degassed by four cycles of freeze-pump-thaw and subsequently stirred under light irradiation using a 455 nm (± 25 nm) LED for 16 h at 25 °C.

One reaction batch was submitted to GC-FID analysis to determine the product GC-yield with *n*-decane as internal standard, while the desired product was isolated from two other batches.

For the isolation, the two combined reaction mixtures were diluted with brine (15 mL), water (5 mL) and ethyl acetate (15 mL). The phases were separated and the water phase was extracted with ethyl acetate (3 x 8 mL). The combined organic phases were washed with H_2O/brine (1:1) (15 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by automated flash column chromatography (PE/EtOAc, 0-15% EtOAc). 1-Phenylhexan-2-ol (**3a**) was obtained as colorless oil (25.8 mg, 145 µmol, 48%).

7.2 4CzIPN photo-degradation

UV-VIS online

During the course of the reaction, 4CzIPN is photo-degraded. This process was monitored by a UV-VIS online measurement. For this purpose, a sample containing 4CzIPN (37.5 µM) and NBu_4PA (**5**) (750 µM) in degassed dry DMA (100-fold dilution in respect to the reaction concentration) in a gas-tight fluorescence cuvette was irradiated using a 455 nm (± 25 nm) LED for 10 min at 25 °C, while recording UV-VIS spectra at defined times after start of the irradiation (Figure S1, right). As reference, the same measurement was repeated in absence of NBu_4PA (**5**) using an analogous sample containing only 4CzIPN (37.5 µM) (Figure S1, left). The data shows, that the photo-degradation of 4CzIPN is highly accelerated in the presence of NBu_4PA (**5**), indicating a photoreaction between 4CzIPN and the carboxylate.

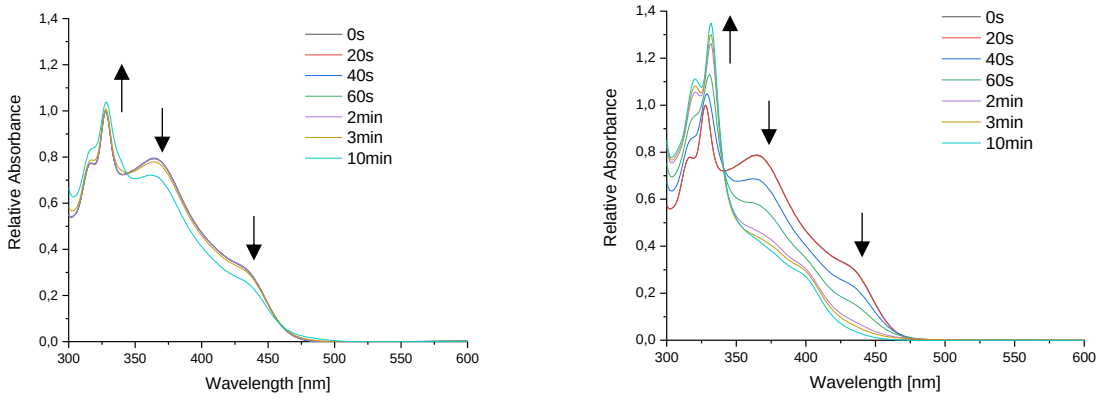
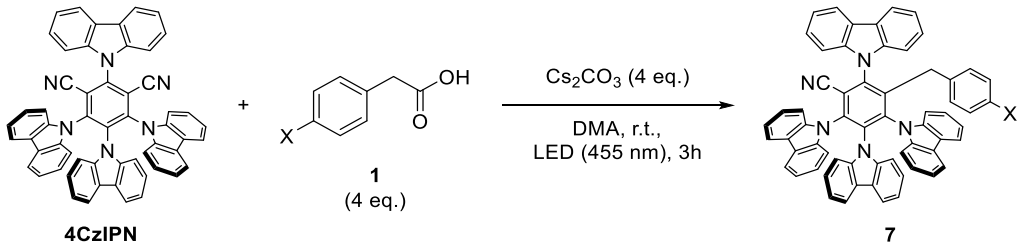


Figure S1. Left: UV-VIS online measurement of a sample containing 4CzIPN (37.5 µM) in degassed dry DMA. Right: UV-VIS online measurement of a sample containing 4CzIPN (37.5 µM) and NBu_4PA (**5**) (750 µM) in degassed dry DMA. Both spectra are normalized to the absorbance maxima of 4CzIPN at 328 nm before irradiation.

Procedure for 4CzIPN photo-conversion to 4CzBnBN

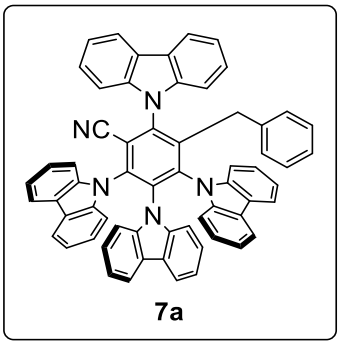


A 5 mL crimp cap vial equipped with a magnetic stirring bar was loaded with 4CzIPN (23.7 mg, 30 µmol, 1 eq.), Cs_2CO_3 (39.1 mg, 120 µmol, 4 eq.), the carboxylic acid (120 µmol, 4 eq.) and DMA (2 mL). In doing so, all solid compounds were added before capping the vial, whereas all liquid

compounds were added *via* syringe after setting the capped vial under inert conditions. The reaction mixture was degassed by three cycles of freeze-pump-thaw and subsequently stirred under light irradiation using a 455 nm (± 25 nm) LED for 3 h at 25 °C.

Two reaction batches were combined and diluted with brine (15 mL), water (5 mL) and ethyl acetate (15 mL). The phases were separated and the water phase was extracted with ethyl acetate (10 mL). The combined organic phases were washed with brine/H_2O (1:1) (4x10 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by automated flash column chromatography (PE/EtOAc, 10-20% EtOAc).

(2*r*,4*r*,5*r*,6*r*)-3-benzyl-2,4,5,6-tetra(9*H*-carbazol-9-yl)benzonitrile (4CzBnBN) (7a)



7a

Phenylacetic acid was used as carboxylic aid. The product was obtained as light yellow solid. Clear colorless/light yellow plate-shaped crystals could be obtained by recrystallization from PE/EA (8:2).

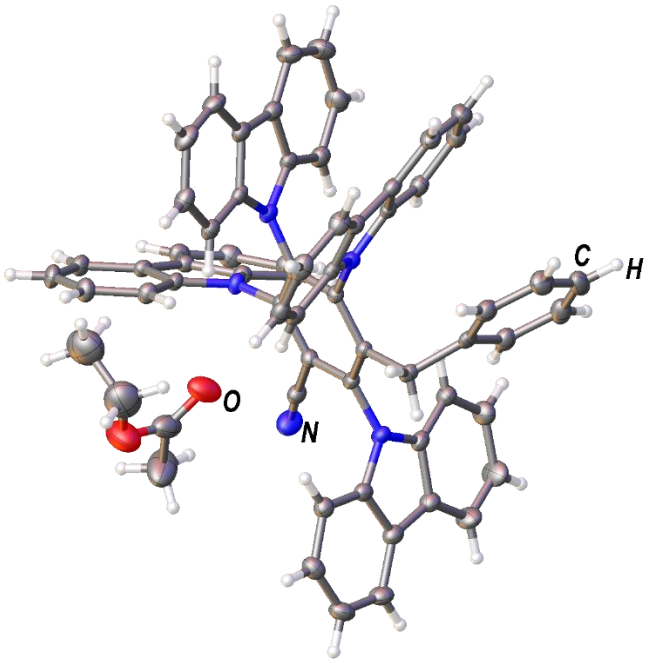
^{1}H-NMR (400 MHz, d_7-DMF, δ_H): 8.30 (d, *J* = 7.7 Hz, 2H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.88–7.75 (m, 8H), 7.64 (t, *J* = 8.1 Hz, 2H), 7.45–7.36 (m, 4H), 7.21–7.12 (m, 4H), 7.10–6.99 (m, 4H), 6.84–6.74 (m, 4H), 6.48 (t, *J* = 7.3 Hz, 1H), 6.41 (t, *J* = 7.3 Hz, 2H), 6.13 (d, *J* = 7.2 Hz, 2H), 3.72 (s, 2H).

^{13}C-NMR (101 MHz, d_7-DMF, δ_C): 146.6, 144.4, 142.9, 141.9, 141.6, 140.9, 140.4, 140.0, 139.2, 137.5, 128.4, 128.3, 127.8, 126.6, 126.5, 126.3, 125.3, 124.8, 124.6, 124.3, 124.1, 122.0, 121.8, 121.7, 121.4, 121.0, 120.9, 120.2, 119.5, 114.2, 113.0, 112.6, 112.4, 111.6

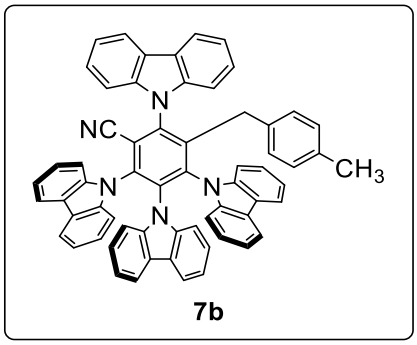
LRMS (FD-MS) (m/z): [M^+] ($C_{62}H_{39}N_5^+$) calc.: 853.32, found: 853.36.

Yield: 64%.

Crystal structure (CCDC 1884950)**:**



(2*r*,3*r*,4*r*,6*r*)-2,3,4,6-tetra(9H-carbazol-9-yl)-5-(4-methylbenzyl)benzonitrile (7b)



4-methylphenylactic acid was used as carboxylic aid. The product was obtained as light yellow solid.

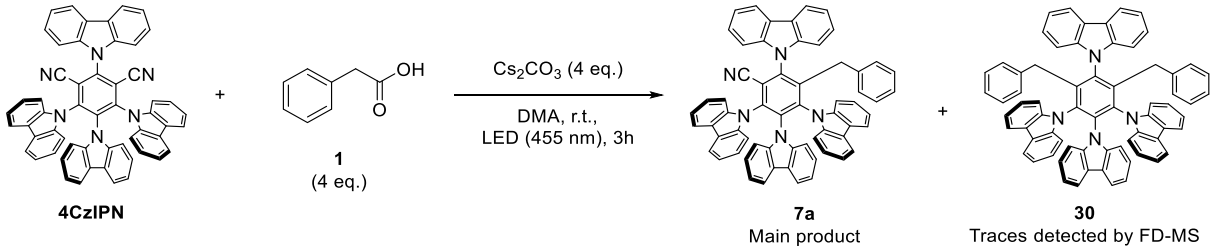
^{1}H-NMR (300 MHz, d_7-DMF, δ_H): 8.30 (d, *J* = 7.7 Hz, 2H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.94–7.75 (m, 10H), 7.64 (t, *J* = 8.2 Hz, 2H), 7.46–7.36 (m, 4H), 7.21–6.99 (m, 8H), 6.83–6.73 (m, 4H), 6.19 (d, *J* = 7.8 Hz, 2H), 5.95 (d, *J* = 8.0 Hz, 2H), 3.62 (s, 2H), 1.78 (s, 3H).

^{13}C-NMR (75 MHz, d_7-DMF, δ_C): 146.9, 144.3, 142.8, 141.8, 141.6, 140.9, 140.4, 140.1, 139.2, 136.0, 134.4, 129.1, 128.2, 127.7, 126.5, 126.2, 125.3, 124.8, 124.6, 124.4, 124.1, 122.0, 121.7, 121.3, 121.0, 120.9, 120.2, 119.4, 114.2, 113.0, 112.6, 112.4, 111.6, 20.9.

LRMS (FD-MS) (m/z): [M^+] ($C_{63}H_{41}N_5^+$) calc.: 867.34, found: 867.29.

Yield: 47%.

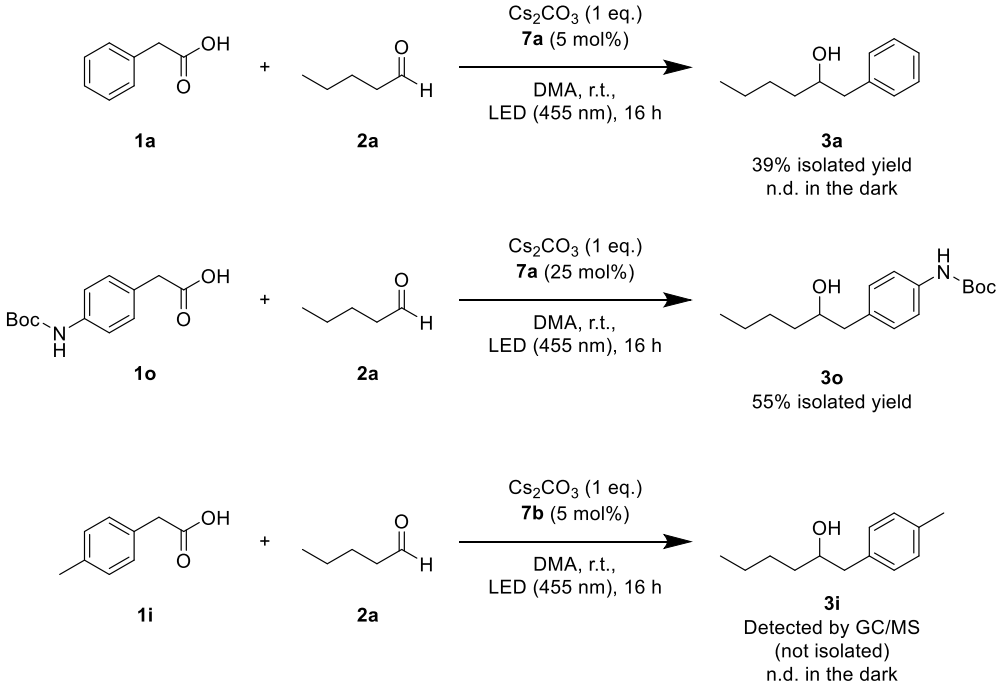
During the synthesis of **7a**, FD-MS analysis of the solid residue prior to column chromatography showed, that **7a** is the main product, while the degradation product from a two-fold cyanide elimination (**30**) is only generated in traces (Scheme S3).



Scheme S3. Cyanide elimination products of 4CzIPN with phenylacetic acid (**1a**).

4CzBnBN as photocatalyst

Compounds **7a** and **7b** could both be used as catalyst for the benzylation of aliphatic aldehydes, following General procedure A (Scheme S4). In accordance, the use of 4CzIPN derivatives with one cyano group and five electron donating groups was recently reported.[5]



Scheme S4. Benzylation of *n*-pentanal (**2a**) using **7a** (upper and middle) and **7b** (lower) as catalyst.

7a and **7b** are light yellow powders. The UV/VIS-spectra were measured. They shows a weak absorption within the range of the employed LED at the reaction concentration (Figure S2).

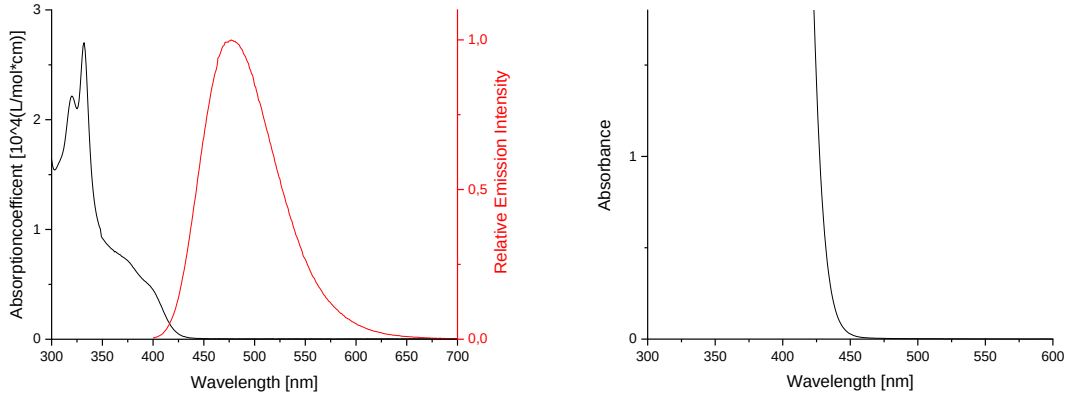


Figure S2. Left: UV/VIS absorption (black) and emission (red) spectrum of **7a** in dry DMA (37.5 µM). Right: UV/VIS absorption spectrum of **7a** in dry DMA at reaction concentration (3.75 mM).

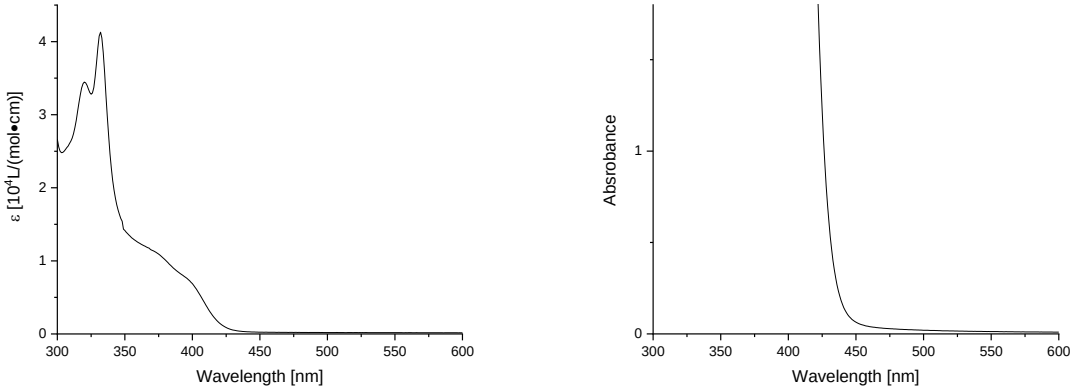


Figure S3. Left: UV/VIS absorption spectrum of **7b** in dry DMA (37.5 µM). Right: UV/VIS absorption spectrum of **7b** in dry DMA at reaction concentration (3.75 mM).

7.3 Cyclic voltammetry (CV) measurement

The CV measurement was performed with the three-electrode potentiostat galvanostat PGSTAT302N from Metrohm Autolab using a glassy carbon working electrode, a platinum wire counter electrode, a silver wire as a reference electrode and Tetrabutylammonium tetrafluoroborate (TBATFB) (0.1 M) as supporting electrolyte. The potentials were achieved relative to the Fc/Fc+ redox couple with ferrocene as internal standard.[23] The control of the measurement instrument, the acquisition and processing of the cyclic voltammetric data were performed with the software Metrohm Autolab NOVA 1.10.4. The measurement was carried out as follows: a 0.1 M solution of TBATFB in DMF was added to the measuring cell and the solution was degassed by argon purge for 5 min. After recording the baseline a solution of 4CzBnBN in DMF (0.01 M) was added and the solution was again degassed by a stream of argon for 5 min. The cyclic voltammogram was recorded with two scans. Afterwards ferrocene (2.20 mg, 12.0 µmol) was added to the solution which was again degassed by argon purge for 5 min and the final measurement was performed with three scans.

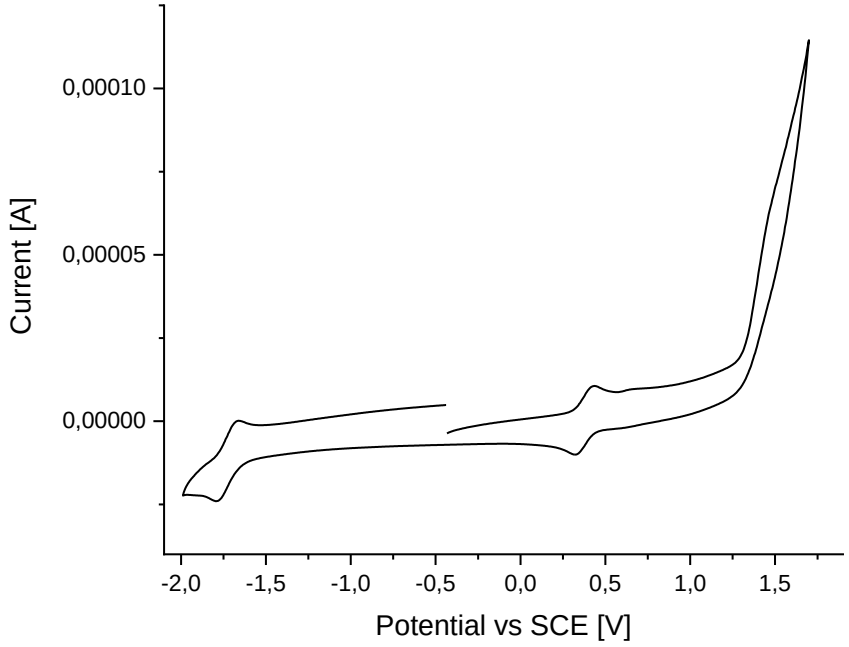


Figure S4. CV of 4CzBnBN (**7a**) in DMF. The reversible peak at 0.380 V refers to the added internal standard ferrocene. The measurement was conducted with TBATFB (0.1 M) as supporting electrolyte and a scan rate of 50 mV/s.

A ground state oxidation potential of $E_{1/2}$(4CzBnBN^{+}/4CzBnBN) = +1.48 V *vs* SCE and ground state reduction potential of $E_{1/2}$(4CzBnBN/4CzBnBN^{-}) = –1.72 V *vs* SCE in DMF could be determined. The emission maximum was measured to be 477 nm (in dry DMA). The excited state potentials were estimated from the crossing point of the normalized absorption and emission spectra (Figure S2). $E_{1/2}$(4CzBnBN^{+}/4CzBnBN*) = +1.21 V *vs* SCE and $E_{1/2}$(4CzBnBN*/4CzBnBN^{-}) = -1.45 V *vs* SCE.

7.4 Emission quenching studies

Emission quenching of 4CzIPN with NBu_4PA (5)

For the emission quenching experiment of 4CzIPN with NBu_4PA, a 15 µM solution of 4CzIPN in degassed dry DMF was prepared under nitrogen atmosphere in a gas-tight 10 mm quartz cuvette. The photocatalyst was irradiated at 435 nm and the change of the fluorescence emission upon addition of different amounts of quencher solution was measured (Figure S5). The quencher solution contained NBu_4PA (c = 67.5 mM, dry DMF) as quencher, as well as 4CzIPN (c = 15 µM) to exclude an emission decrease due to dilution.

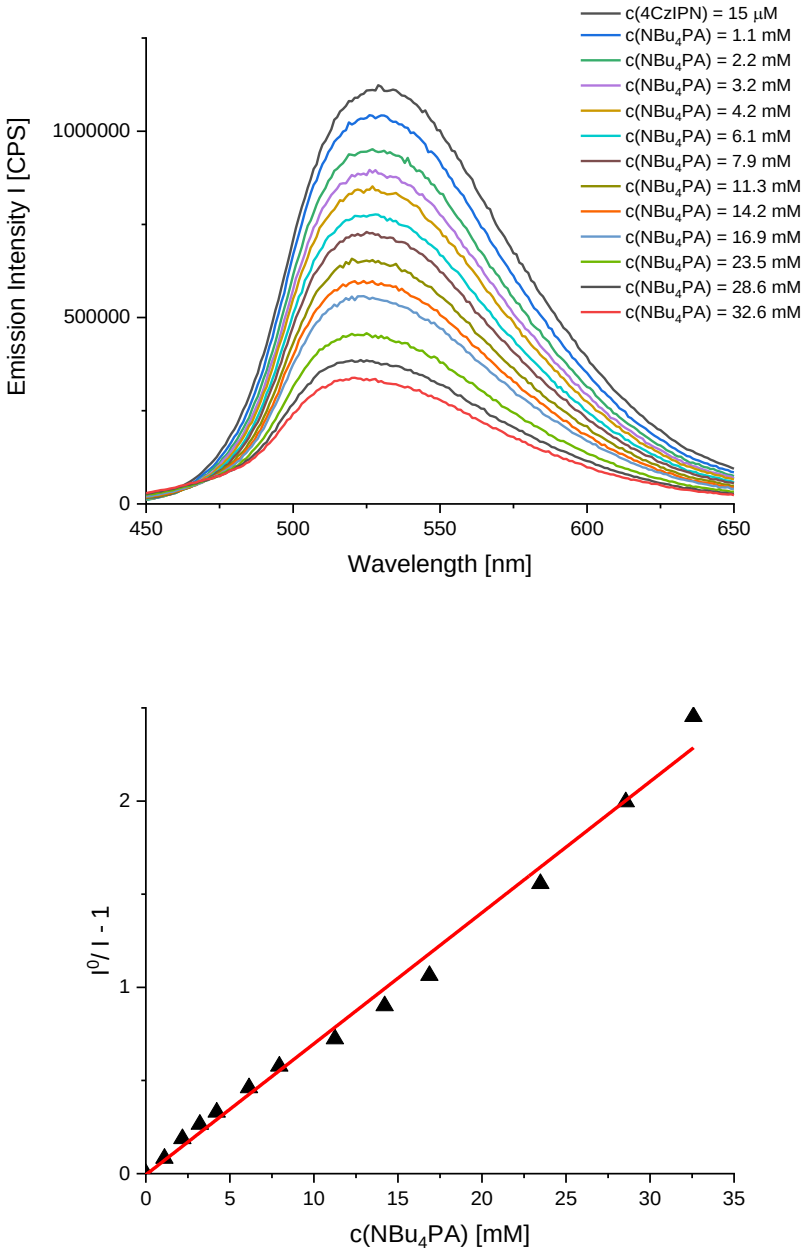


Figure S5. Upper: Emission quenching of 4CzIPN (15 µM in dry DMF) upon titration with NBu_4PA (**5**). Lower: Corresponding Stern-Volmer plot with a Stern-Volmer constant of K_{SV} = 70.3 μM^{-1}.

An efficient quenching of 4CzIPN upon the addition of NBu_4PA (**5**) could be observed (Figure S5). By plotting $I^0/I-1$ versus the quencher concentration, a Stern-Volmer constant of $K_{SV} = 70.3\ \mu M^{-1}$ was determined from the slope of the linear fit.

$$\frac{I^0}{I} - 1 = K_{SV} \cdot [Q]$$

(With I^0 being the fluorescence intensity at 535 nm in absence of the quencher, I the fluorescence intensity at 535 nm in presence of the quencher and [Q] the quencher concentration)

Emission quenching of 4CzIPN with *n*-pentanal (2a)

An 80 µM solution of 4CzIPN in DMA was prepared in a 10 mm quartz cuvette. The photocatalyst was irradiated with 435 nm and the change of the fluorescence emission upon addition of different amounts of quencher solution was measured. The quencher solution contained *n*-pentanal (**2a**) (c = 18.7 mM, DMA) as well as 4CzIPN (c = 80 µM). The Quenching experiment showed, that *n*-pentanal (**2a**) does not efficiently quench the excited state of 4CzIPN (Figure S6).

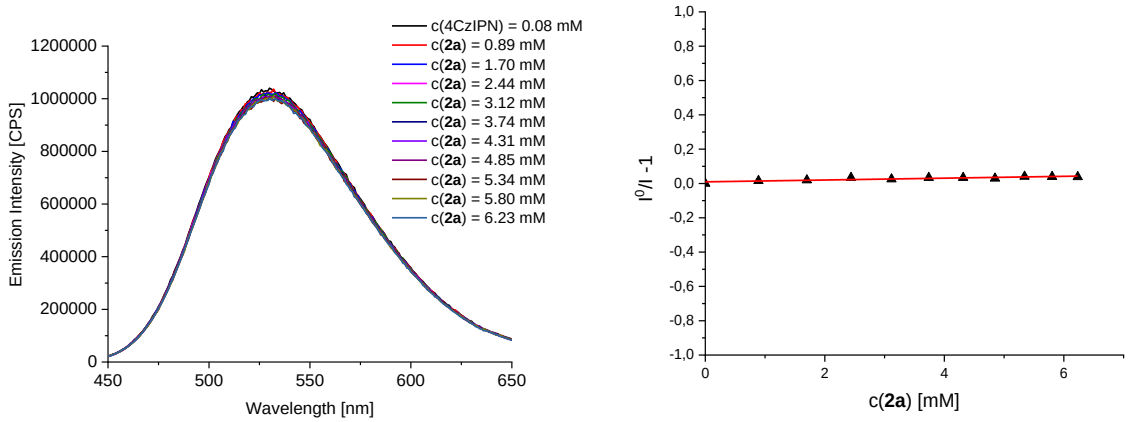


Figure S6. Upper: Emission quenching of 4CzIPN (80 µM in DMA) upon titration with *n*-pentanal (**2a**). Lower: Corresponding Stern-Volmer plot.

Emission quenching of 4CzBnBN (7a) with NBu_4PA (5)

For the emission quenching experiment of 4CzBnBN with NBu_4PA (**5**), a 37.5 µM solution of 4CzBnBN in degassed dry DMA was prepared under nitrogen atmosphere in a gas-tight 10 mm quartz cuvette. The photocatalyst was irradiated at 390 nm and the change of the fluorescence emission upon addition of different amounts of quencher solution was measured (Figure S7). The quencher solution contained NBu_4PA (c = 67.5 mM, dry DMA) as quencher, as well as 4CzBnBN (c = 37.5 µM) to exclude an emission decrease due to dilution. An efficient quenching of 4CzBnBN upon the addition of NBu_4PA (**5**) could be observed.

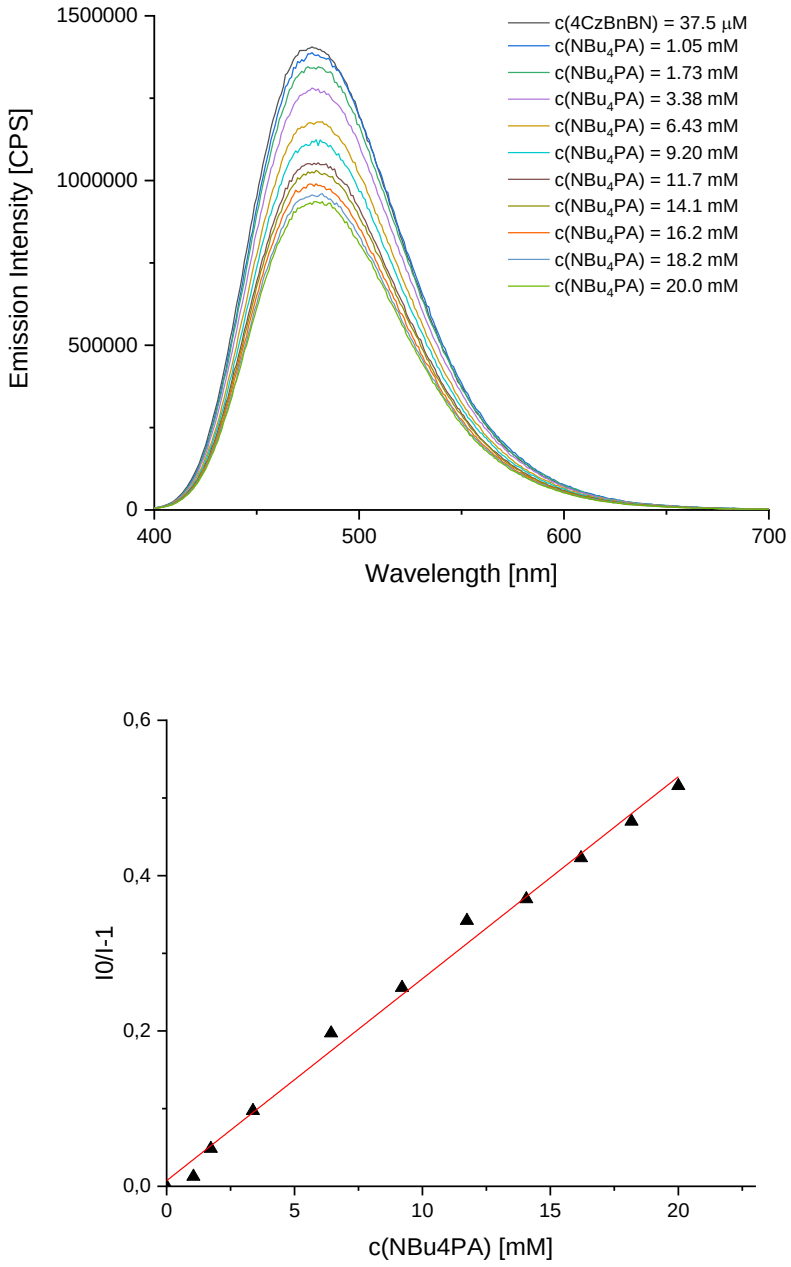


Figure S7. Upper: Emission quenching of 4CzBnBN (37.5 µM in dry DMA) upon titration with NBu_4PA (**5**). Lower: Corresponding Stern-Volmer plot with a Stern-Volmer constant of K_{SV} = 26.0 μM^{-1}.

7.5 *In situ* FT-IR measurements

FT-IR spectra were recorded on Varian Excalibur 3100 spectrometer using 1 cm^{-1} resolution. A solution of NBu_4PA (**5**) (75 mM), *n*-pentanal (75 mM) and 4CzBnBN (3.75 mM) in dry DMA (6 mL) was prepared and degassed by three cycles of freeze-pump-thaw. The sample was held in a septum-capped vial connected to a Harrick Scientific (Pleasantville, New York) DLC-S25 flow cell with a 56 µm path length and CaF_2 windows. The vial was irradiated from the bottom with a 455 nm (± 25 nm) LED and circulated to the flow cell with a peristaltic pump at a flow rate of 3 mL/min. Spectra were recorded at 5-minute intervals using the starting reaction mixture as a blank so that difference spectra were produced (Figure S8). The main features are the appearance of a dissolved CO_2 band at 2338 cm^{-1} and a negative aldehyde C=O stretch at 1722 cm^{-1}. Kinetic plots show saturation of the solution with CO_2 after about 3 hours. Complete loss of the aldehyde is apparent after about 10 hours.

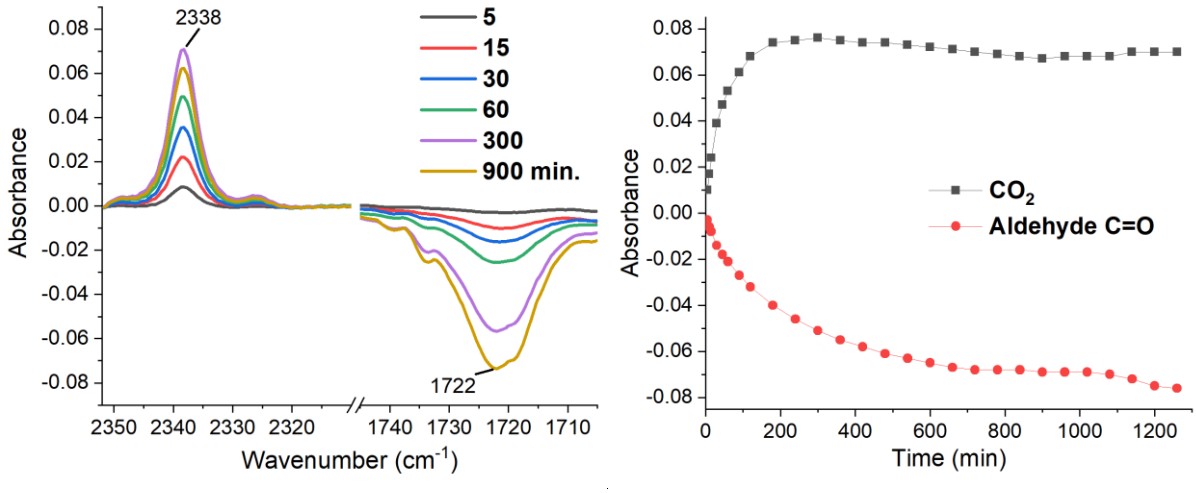
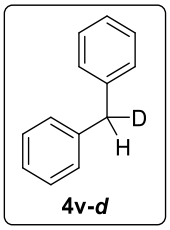


Figure S8. Left: FT-IR difference spectra of a solution containing NBu_4PA (**5**) (75 mM), n-pentanal (75 mM) and 4CzBnBN (3.75 mM) in degassed dry DMA (6 mL) irradiated using a 455 nm (± 25 nm) LED at defined periods of time after irradiation start. Right: Corresponding kinetic plot of the CO_2 band at 2338 cm^{-1} and aldehyde C=O stretch at 1722 cm^{-1}.

7.6 Deuterium labeling studies

Employing D_2O instead of an aldehyde as electrophile leads to the formation of the corresponding deuterated product.

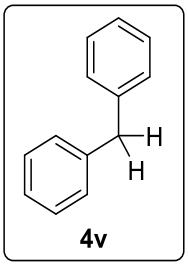
Diphenylmethane-*d*$_1$ (4v-*d*)[24]



4v-*d*

A 5 mL crimp cap vial equipped with a magnetic stirring bar was loaded with 4CzIPN (5.9 mg, 7.5 µmol, 5 mol%), Cs_2CO_3 (48.9 mg, 150 µmol, 1 eq.) and diphenylacetic acid (**1v**) (31.8 mg, 150 µmol, 1 eq.). The vial was set under inert conditions and dry DMF (2 mL) followed by D_2O (30 µL, 1.50 mmol, 10 eq.) were added *via* syringe. The reaction mixture was degassed by four cycles of freeze-pump-thaw and subsequently stirred under light irradiation using a 455 nm (± 25 nm) LED for 16 h at 25 °C.
The reaction mixture was diluted with brine (10 mL), water (5 mL) and ethyl acetate (10 mL). The phases were separated and the water phase was extracted with ethyl acetate (3 x 6 mL). The combined organic phases were washed with H_2O/brine (1:1) (3 x 10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by automated flash column chromatography (PE). Diphenylmethane-*d*$_1$ (**4v-*d***) (21.6 mg, 128 µmol, 85%, 81% deuterium incorporation) was obtained as colorless oil.
^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.35 – 7.17 (m, 10H), 4.00-3.96 (m, 1H).

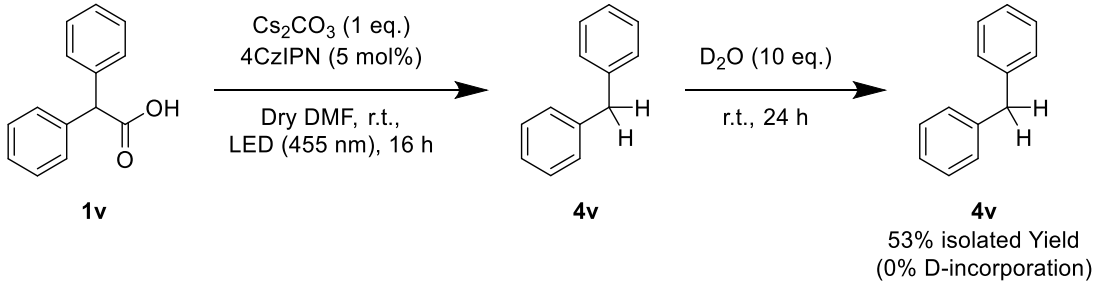
Diphenylmethane (4v)[25]



4v

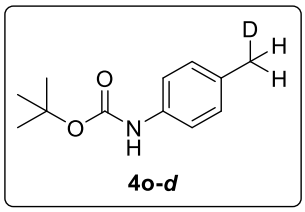
Following the same experimental procedure in absence of D_2O with d_7-DMF instead of dry DMF as solvent, diphenylmethane (**4v**) was obtained in 75% isolated yield with no deuterium incorporation.
^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.35 – 7.17 (m, 10H), 3.99 (s, 2H).

To exclude that **4v-*d*** is formed by an H/D-exchange between **4v** and D_2O in the presence of Cs_2CO_3, the reactive intermediate was generated in absence of D_2O to form **4v**. Subsequently, D_2O was added to the reaction mixture and it was stirred for further 24 h. **4v** was not deuterated (Scheme S5).



Scheme S5. Control experiment for the exclusion of an H/D-exchange between **4v** and D_2O in presence of Cs_2CO_3.

(4-Methylphenyl)carbamic acid *tert*-butyl ester-d_1 (4o-*d*)



A 5 mL crimp cap vial equipped with a magnetic stirring bar was loaded with 4CzIPN (5.9 mg, 7.5 µmol, 5 mol%), Cs_2CO_3 (48.9 mg, 150 µmol, 1 eq.) and 4-(*t*-Butyloxycarbonylamino)phenylacetic acid (**1o**) (37.7 mg, 150 µmol, 1 eq.). The vial was set under inert conditions and dry DMA (2 mL) followed by D_2O (30 µL, 1.50 mmol, 10 eq.) were added *via* syringe. The reaction mixture was degassed by four cycles of freeze-pump-thaw and subsequently stirred under light irradiation using a 455 nm (± 25 nm) LED for 16 h at 25 °C.

Two reaction batches were combined and diluted with brine (10 mL), water (5 mL) and ethyl acetate (10 mL). The phases were separated and the water phase was extracted with ethyl acetate (3 x 6 mL). The combined organic phases were washed with H_2O/brine (1:1) (3 x 10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by automated flash column chromatography (PE/EtOAc 0-20%). (4-Methylphenyl)carbamic acid *tert*-butyl ester-d_1 (**4o-*d***) (41.6 mg, 200 µmol, 67%, 84% deuterium incorporation) was obtained as white solid.

^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.24 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.5 Hz, 2H), 6.46 (s, 1H), 2.30-2.27 (m, 2H), 1.52 (s, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 153.0 (C_q), 135.8 (C_q), 132.6 (C_q), 129.6 (+), 118.8 (+), 80.4 (C_q), 28.5 (+), 20.8 (+, non-deuterated), 20.6 (t, J = 19.5 Hz, –).

HRMS (ESI) (m/z): [MH^+] ($C_{12}H_{16}DNO_2^+$) calc.: 209.1395, found: 209.1391.

7.7 NMR *in-situ* irradiation studies

A benzyl anion (**15**) is expected to show a highly upfield-shifted NMR-signal. It was attempted to detect its potential presence by measuring NMR-spectra while *in-situ* irradiating the reaction mixture in absence of electrophiles like aldehydes or water. Therefore, potassium benzyltrifluoroborate (**16**) (14.9 mg, 75 µmol, 1 eq.) and 4CzIPN (3 mg, 3.8 µmol, 5 mol%) were dissolved in 0.5 mL dry d_7-DMF and the solution was irradiated using a 455 nm LED while simultaneously measuring NMR-spectra at defined periods of time.

No new upfield-shifted peak after irradiation could be detected. However, the depletion of residual H_2O was observed, indicating the generation of a reactive anionic species.[26] Additionally, the generation of toluene and formation of 4CzBnBN could be detected (Figure S9).

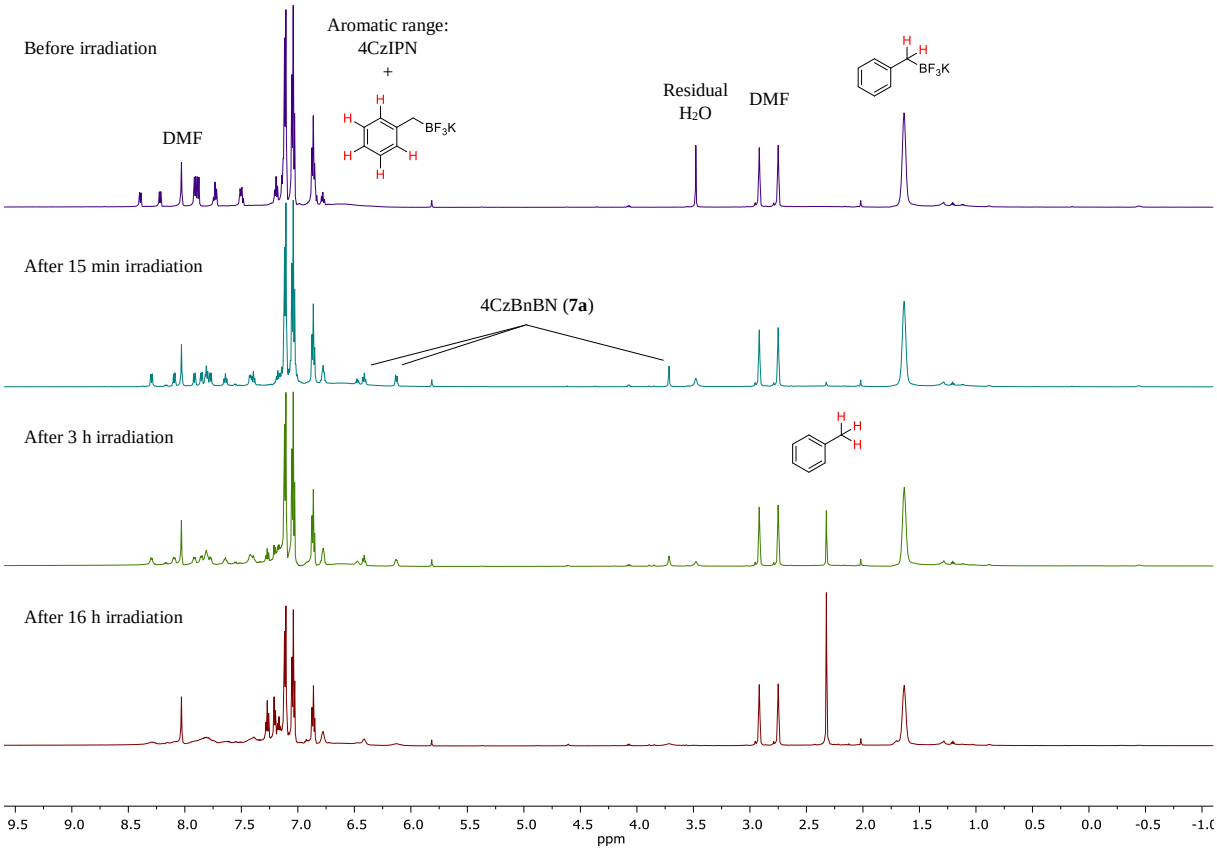


Figure S9. Measurement of NMR-spectra during irradiation of a mixture containing potassium benzyltrifluoroborate (**16**) (75 µmol, 1 eq.) and 4CzIPN (3.8 µmol, 5 mol%) in dry d_7-DMF (0.5 mL).

7.8 E1cb-elimination reactions

The proposed carbanion intermediate is expected to undergo an E1cb elimination in case a suitable leaving group is present. Thus, the styrene (**10**) formation of two benzylic carboxylic acids bearing different leaving groups in the homobenzylic position was monitored. Dry DMF instead of DMA was chosen as solvent, as the DMA peak covers the potential styrene peak in the GC-FID analysis. The formation of styrene (**10**) was confirmed by GC-FID retention time, GC-MS analysis and crude NMR.

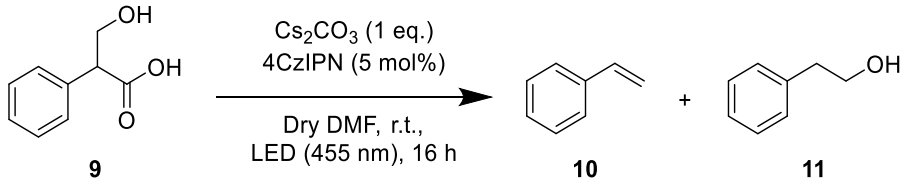
Photocatalytic E1cb-eliminiation of benzylic carboxylic acids bearing leaving groups in the homobenzylic position (General procedure C)

A 5 mL crimp cap vial equipped with a magnetic stirring bar was loaded with 4CzIPN (5.9 mg, 7.5 µmol, 5 mol%), Cs_2CO_3 (48.9 mg, 150 µmol, 1 eq.) and the carboxylic acid (150 µmol, 1 eq.). The vial was set under inert conditions and dry DMF (2 mL) was added *via* syringe. The reaction mixture was degassed by four cycles of freeze-pump-thaw and subsequently stirred under light irradiation using a 455 nm (± 25 nm) LED for 16 h at 25 °C. An aliquot of the reaction mixture was submitted to GC-FID analysis to quantify the product yields with *n*-decane as internal standard.

E1cb-elimination of tropic acid (9)

Tropic acid (**9**) was subjected to General procedure C.

Table S12. E1cb-elimination of tropic acid (**9**).[a]

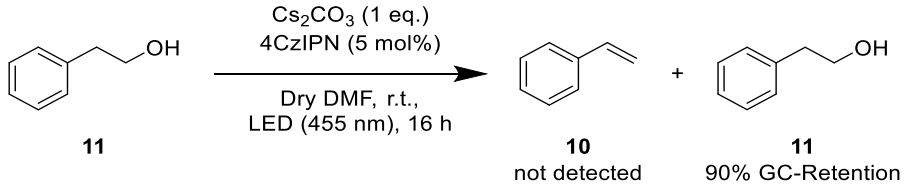


Entry	Photocatalyst	Base	Yield[b] **10** [%]	Yield[b] **11** [%]
1	Yes	Yes	23	33
2	No	Yes	n.d.	n.d.
3[c]	Yes	Yes	n.d.	n.d.
4	Yes	No	n.d.	n.d.

[a] Reactions were performed with tropic acid (**9**) (150 µmol, 1 eq.) in dry DMF (2 mL). [b] Determined by GC-FID analysis with *n*-decane as internal standard. [c] Reaction performed in absence of light.

Control experiment 2-phenylethanol (11) under reaction conditions

2-Phenylethanol (**11**) instead of tropic acid (**9**) was subjected to General Procedure C, to exclude a styrene (**10**) formation by a decarboxylation of **9** to **11** followed by an E2-elimination with Cs_2CO_3 (Scheme S6).

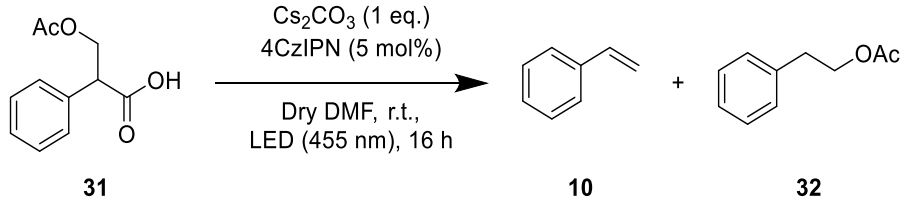


Scheme S6. Control experiment excluding the formation of styrene (**10**) by an E2-elimination of **11** in presence of Cs_2CO_3.

E1cb-elimination of acetyltropic acid (31)

Acetyltropic acid (**31**) was subjected to General procedure C.

Table S13. E1cb-elimination of acetyltropic acid (**31**).[a]

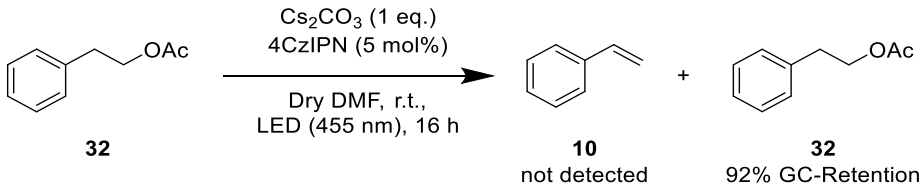


Entry	Photocatalyst	Base	Yield[b] **10** [%]	Yield[b] **32** [%]
1	Yes	Yes	72	n.d.
2	No	Yes	18	n.d.
3[c]	Yes	Yes	13	n.d.
4	Yes	No	9	n.d.

[a] Reactions were performed with tropic acid (**31**) (150 µmol, 1 eq.) in dry DMF (2 mL). [b] Determined by GC-FID analysis with *n*-decane as internal standard. [c] Reaction performed in absence of light.

Control experiment 2-phenylacetate (32) under reaction conditions

2-Phenylacetate (**32**) instead of acetyltropic acid (**31**) was subjected to General Procedure C, to exclude a styrene (**10**) formation by a decarboxylation of **31** to **32** followed by an E2-elimination with Cs_2CO_3 (Scheme S7).



Scheme S7. Control experiment excluding the formation of styrene (**10**) by an E2-elimination of **30** in presence of Cs_2CO_3.

Crude NMR of the E1cb-elimination of acetyltropic acid (31)

To verify the formation of styrene beyond GC-FID and GC-MS analysis, acetyltropic acid (**31**) was subjected to General Procedure C in d_7-DMF and the reaction solution was irradiated within the NMR tube. NMR-spectra before and after the irradiation were measured. The characteristic peaks of styrene can be observed in the ^{1}H-NMR of the reaction mixture after completed reaction (Figure S10).

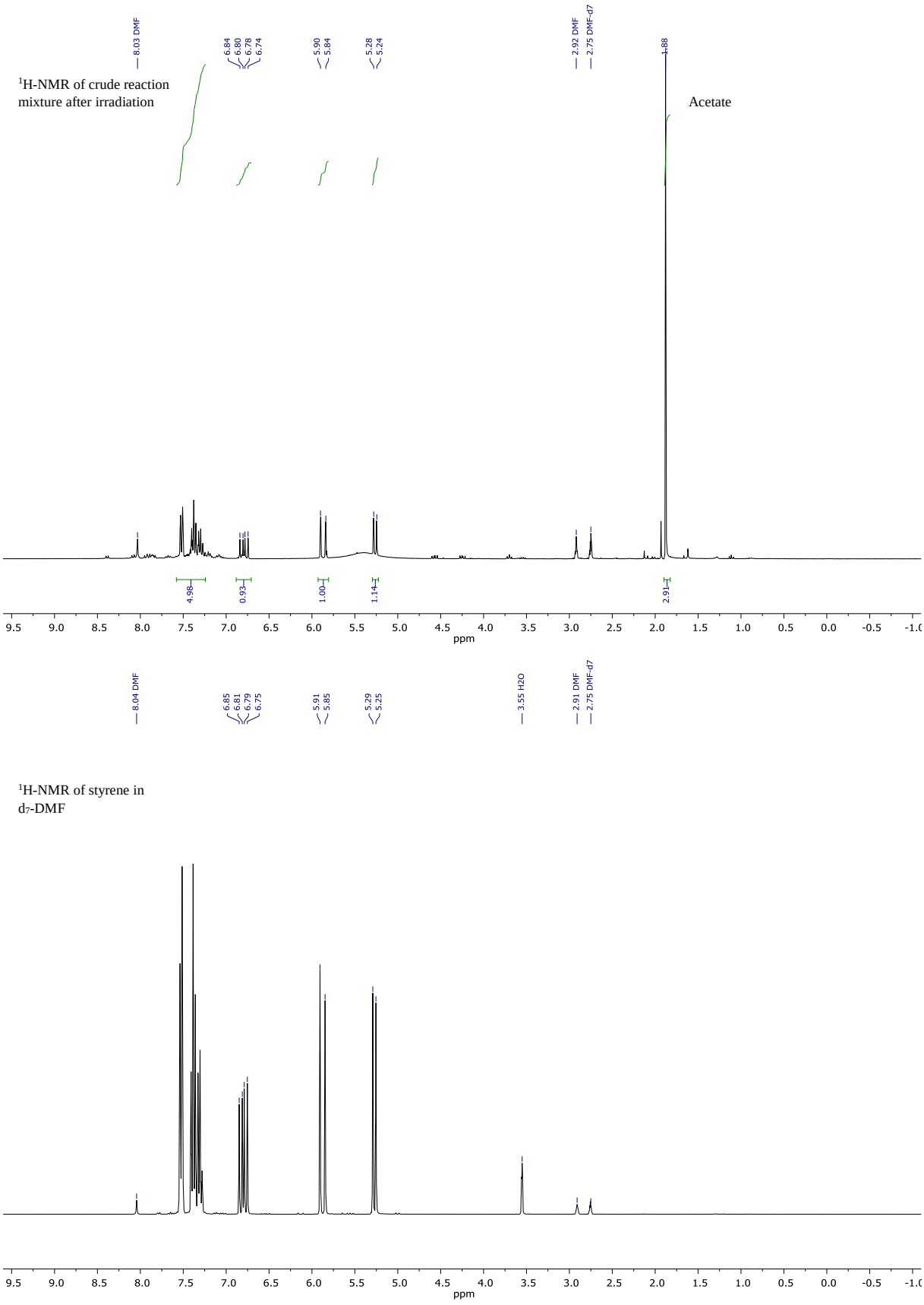
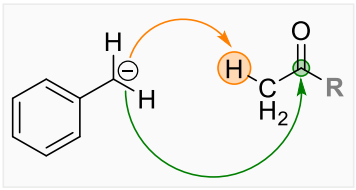


Figure S10. [1]H-NMR of crude reaction mixture of photocatalytic E1cb elimination of acetyltropic acid (**31**) to styrene (**10**) (upper) compared to [1]H-NMR of styrene (**10**) in d_7-DMF (lower).

7.9 DFT-calculations



R	$\Delta G_{CO}^{\ddagger}$	ΔG_{CO}	$\Delta G_{H}^{\ddagger}$	ΔG_{H}
	Kcal/mol			
H	6.2	-6.9	6.8	-17.7
CH_3	10.4	1.5	10.7	-12.1
NMe_2	19.5	11.1	15.4	-2.8

Figure S11. Calculated energy values for possible reaction pathways with 4CzIPN as photocatalyst.

DFT calculations were performed using Gaussian 09 Revision E.01.[27] All structures were optimized using the wB97X-D functional with the TZVP basis set. The SMD solvation model[28] for DMF was included in all the optimizations. DMF was used instead of DMA due to the similar dielectric constant. Frequency calculations confirmed that the optimized structures were local minima or transition states and were used to calculate Gibbs free energies. The saddle points were connected to the reagents and products *via* the Intrinsic Reaction Coordinate method.

The competition between the abstraction of the proton in α of the carbonyl and the C=O attack of the benzyl anion **15** was tested for aldehydes, ketones and the solvent (DMA). For the calculations, acetaldehyde was chosen as the prototypical member of the aldehyde class while acetone was selected for the ketones. The results of the analysis are reported in Figure S11.

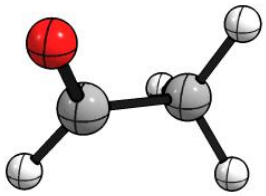
Interestingly, all the kinetic barriers are extremely low. Even the barrier of the acid-base reaction between **15** and DMA are compatible with a reaction extremely feasible at room temperature. Hence we can state that the reduction product (toluene) can confidently come both from the reaction of the benzyl anion with the H in α to the carbonyl of the solvent and of the one of the aldehyde/ketone. The acid-base reaction with the DMA is kinetically less favored, but it is equally feasible due to the higher concentration of the species.

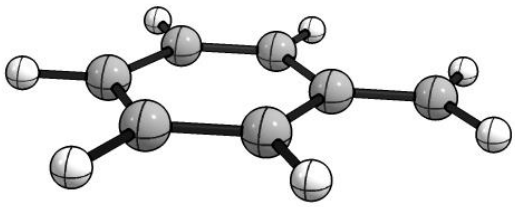
The energies and cartesian coordinates of the species analyzed are herein reported.

15 + acetaldehyde (H^+ abstraction): reagent

C	0.0371434505	2.0396221661	1.5674770206
H	-0.4788084362	1.8872708996	2.5101288245
H	0.0547957072	3.0440309903	1.1568191851
C	0.650995074	0.9819951888	0.9059473867
C	1.332047693	1.1357427676	-0.3527885488
C	0.6412002781	-0.3679248519	1.4044608695
C	1.9428516698	0.0812132877	-0.9982581799
H	1.3672362649	2.1250551122	-0.8010809675
C	1.2620780297	-1.4067060285	0.7421901973
H	0.133859765	-0.5677287626	2.3444368812
C	1.926446064	-1.216563459	-0.4743271734
H	2.4437495189	0.2692950846	-1.9441950486
H	1.2220726803	-2.4014956894	1.1777791601
H	2.4113957851	-2.038413275	-0.9864500689
C	-1.7770808914	-0.742053442	-1.1126856041
O	-2.5190921275	-1.66493574	-0.863037017
C	-2.2065579229	0.6789308765	-1.2430087672
H	-1.7755401081	1.2467389698	-0.408243494
H	-1.7903018301	1.1027638218	-2.1607570777
H	-3.292406704	0.7730505337	-1.2333748698
H	-0.6964009604	-0.9252594503	-1.2567807078

Energy= -424.86724
Zero-point correction= 0.170443 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.132256
Sum of electronic and zero-point Energies= -424.696797
Sum of electronic and thermal Energies= -424.685413
Sum of electronic and thermal Enthalpies= -424.684469
Sum of electronic and thermal Free Energies= -424.734984
G + ZVPE = -424.564541

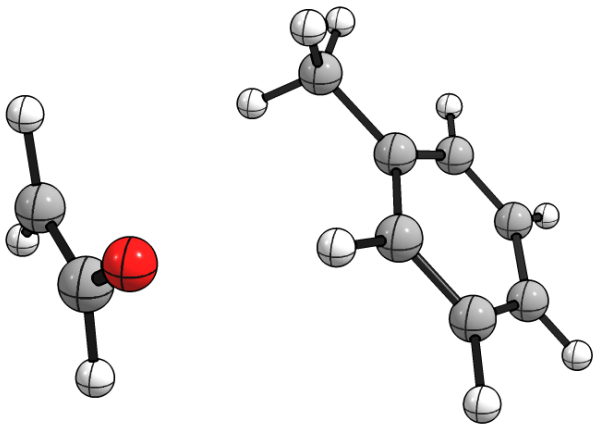




15 + acetaldehyde (H^+ abstraction): product

C	-0.1598240874	1.9221698929	0.5879016987
H	-0.7512183768	1.6671130112	1.4697765429
H	0.2805404222	2.908312311	0.7428828466
C	0.8968899017	0.8845104056	0.32706662
C	2.2164840724	1.247890884	0.0684542125
C	0.5665251486	-0.4727387461	0.3261153552
C	3.1869886137	0.2852649064	-0.185588766
H	2.4901651459	2.2978345224	0.0669669298
C	1.5348337762	-1.4346214697	0.0722484978
H	-0.4607171479	-0.7717871019	0.529175425
C	2.8493120856	-1.0609960685	-0.1848580639
H	4.2091556959	0.5888945896	-0.3810503091
H	1.2621204824	-2.4842092778	0.0773063635
H	3.6042941629	-1.8134547615	-0.3809037239
C	-2.965515025	-0.7819052011	-0.4682580711
O	-2.7035267626	-1.1593319155	0.7113309881
C	-3.456185647	0.4228656626	-0.9115060511
H	-0.8539325186	1.9882143899	-0.2546896166
H	-3.6294476383	0.5889306327	-1.970001751
H	-3.6894397865	1.226926767	-0.2168014382
H	-2.7723415174	-1.5162804333	-1.2884176893

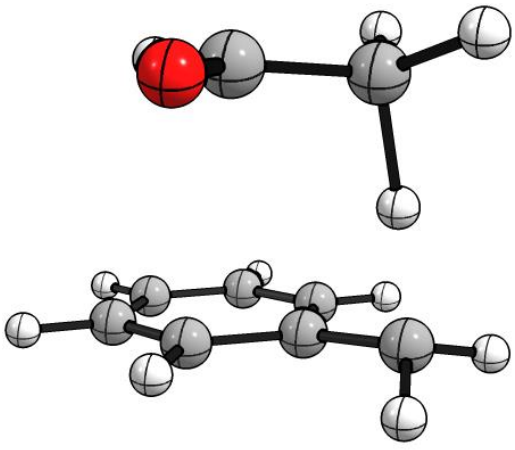
Energy= -424.8972188
Zero-point correction= 0.172281 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.132143
Sum of electronic and zero-point Energies= -424.724937
Sum of electronic and thermal Energies= -424.713522
Sum of electronic and thermal Enthalpies= -424.712578
Sum of electronic and thermal Free Energies= -424.765075
G + ZVPE = -424.592794



15 + acetaldehyde (H^+ abstraction): TS

C	-0.6039184283	2.4481481751	-0.4577577892
H	-0.2326765965	2.7045958318	-1.4502395933
H	-0.9989122122	3.3053671742	0.0877038944
C	-1.3528824303	1.2294764874	-0.3577869144
C	-2.2773777125	0.9904228069	0.6888675314
C	-1.0792852098	0.1260877504	-1.2015468709
C	-2.8918309393	-0.2376537855	0.8569791722
H	-2.5154669418	1.8017833068	1.3704246448
C	-1.7020666269	-1.1013635792	-1.0292076749
H	-0.3698235177	0.2533193009	-2.0132140982
C	-2.6153847868	-1.3035571409	0.0002131001
H	-3.5987971217	-0.3701620448	1.6698968353
H	-1.4640398156	-1.9153310531	-1.7067448529
H	-3.0998391232	-2.2634096581	0.1332961774
C	2.1493849698	0.3252760261	-0.1418938736
O	2.8280247766	0.4060392613	-1.1686519951
C	1.788299013	1.4076872913	0.7243909639
H	0.6925248919	1.9384661173	0.2048160734
H	1.4888738812	1.0988833812	1.726574977
H	2.4875615711	2.2456899419	0.7182985303
H	1.7001661689	-0.6576086211	0.1194772023

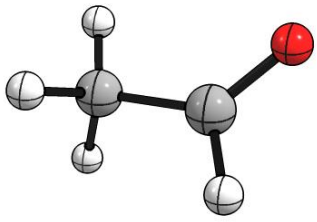
Energy= -424.8512799
Zero-point correction= 0.167382 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.130227
Sum of electronic and zero-point Energies= -424.683898
Sum of electronic and thermal Energies= -424.673899
Sum of electronic and thermal Enthalpies= -424.672955
Sum of electronic and thermal Free Energies= -424.721053
G + ZVPE = -424.553671

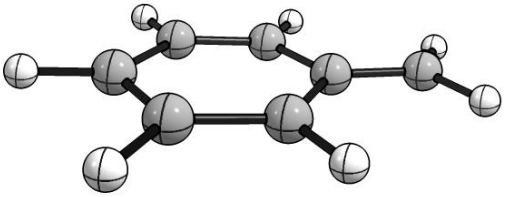


15 + acetaldehyde (C=O attack): reagent

C	-0.1886612606	0.4276492021	2.2426191649
H	-0.6523566777	-0.4079876983	2.7569666133
H	-0.3270212908	1.4195473228	2.6607163425
C	0.621611911	0.2243564516	1.1307608541
C	1.2747147212	1.2981312245	0.4304796962
C	0.8528663385	-1.0759355776	0.5598031023
C	2.0191845777	1.091640837	-0.7122094335
H	1.1535804648	2.3093402978	0.8093687516
C	1.6006381832	-1.257480708	-0.5850574212
H	0.4049634909	-1.9393049631	1.0441459929
C	2.1967171495	-0.184787899	-1.2573768926
H	2.4749660343	1.9490060003	-1.2001676031
H	1.7276079134	-2.2655767643	-0.9706423501
H	2.7817082411	-0.3378360427	-2.1559373924
C	-2.5441675875	-0.2695377174	-0.4434530868
O	-3.7183288067	-0.0998951778	-0.2070647531
H	-1.9721379985	-1.0357466556	0.1123299664
C	-1.7660085456	0.4817329553	-1.4693299755
H	-0.9413846362	1.0073261829	-0.9775824719
H	-1.3096957229	-0.229493747	-2.1643305244
H	-2.3969764992	1.1872894765	-2.0093695795

Energy= -424.867137
Zero-point correction= 0.170380 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.131174
Sum of electronic and zero-point Energies= -424.696757
Sum of electronic and thermal Energies= -424.685245
Sum of electronic and thermal Enthalpies= -424.684301
Sum of electronic and thermal Free Energies= -424.735962
G + ZVPE = -424.565582

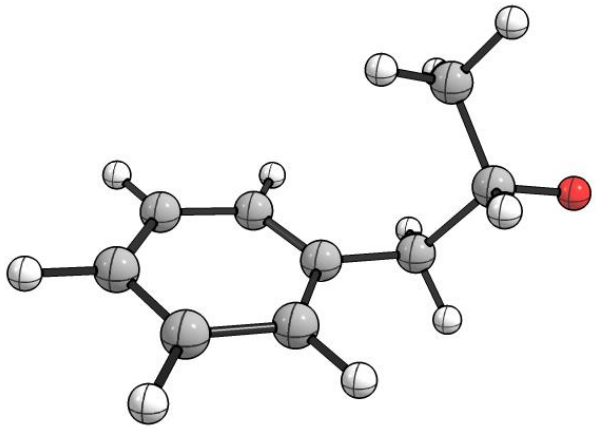




15 + acetaldehyde (C=O attack): product

C	-0.9698015879	0.2241330894	1.1041002958
H	-1.0780256088	-0.4439016272	1.9630670152
H	-1.1062026051	1.2499781857	1.4619233631
C	0.3889412581	0.0595209953	0.4930769536
C	1.1159567486	1.1533089014	0.0185400563
C	0.9405500882	-1.2123872995	0.3185162089
C	2.3448013717	0.9864157646	-0.6061170139
H	0.7093265734	2.1518441355	0.1412063747
C	2.1677913904	-1.386558609	-0.3083906256
H	0.3997800921	-2.0784886354	0.686001461
C	2.8759012731	-0.2865113622	-0.7759202163
H	2.8892375193	1.8535709067	-0.9628548432
H	2.5728353161	-2.3849357489	-0.4301362542
H	3.8344232238	-0.4189076411	-1.2640680419
C	-2.1904276406	-0.0984197761	0.1619697066
O	-3.3531720573	-0.0267497736	0.8138460055
H	-1.952168515	-1.1309713818	-0.2359001094
C	-2.1295217158	0.8235345001	-1.0786453263
H	-1.2132403774	0.7115269573	-1.6702881066
H	-2.9818635228	0.599497533	-1.7266981004
H	-2.2138642239	1.8712988858	-0.7656978027

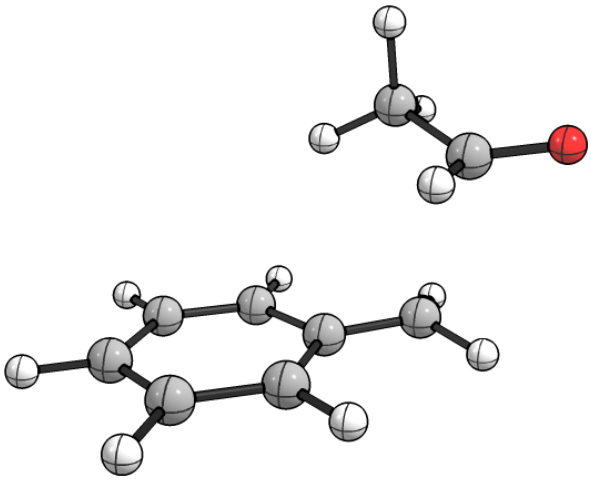
Energy= -424.8947076
Zero-point correction= 0.176442 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.141750
Sum of electronic and zero-point Energies= -424.718265
Sum of electronic and thermal Energies= -424.709192
Sum of electronic and thermal Enthalpies= -424.708247
Sum of electronic and thermal Free Energies= -424.752958
G + ZVPE = -424.576516



15 + acetaldehyde (C=O attack): TS

C	-1.2712815871	0.5606559034	1.5557947492
H	-1.6551094836	-0.2255368155	2.1964268242
H	-1.5837852967	1.5732324269	1.7925940643
C	-0.0802857286	0.3514532893	0.8425327701
C	0.6100191298	1.4059950581	0.1690408968
C	0.4686256133	-0.9519131856	0.6376726364
C	1.7344588252	1.1777266066	-0.6003467604
H	0.2401185051	2.4211769514	0.2805590521
C	1.5953915557	-1.1634179314	-0.1358309835
H	-0.011775661	-1.7985053336	1.1199361975
C	2.252762239	-0.108434693	-0.7707450773
H	2.2232087458	2.0205013892	-1.0804499259
H	1.9726848258	-2.1757170471	-0.248600206
H	3.1374599808	-0.2804942694	-1.3716344544
C	-3.0136040396	0.0305456589	-0.0221655472
O	-4.0704234753	-0.0835324994	0.5982035979
H	-2.3789345442	-0.855456346	-0.205217795
C	-2.7627895408	1.1822787786	-0.9610143213
H	-1.7026502704	1.2967808301	-1.1902976403
H	-3.2943080962	0.9789277247	-1.8986510325
H	-3.1558257871	2.1115297137	-0.5442264447

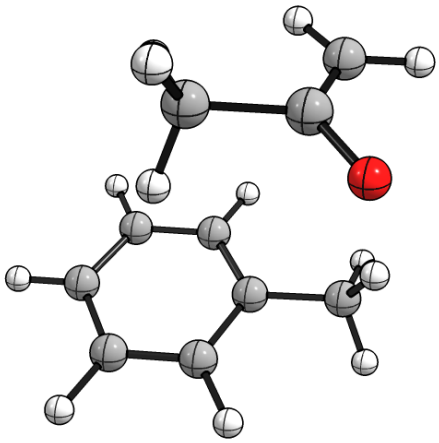
Energy= -424.8632841
Zero-point correction= 0.171791 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.135747
Sum of electronic and zero-point Energies= -424.691493
Sum of electronic and thermal Energies= -424.681635
Sum of electronic and thermal Enthalpies= -424.680691
Sum of electronic and thermal Free Energies= -424.727537
G + ZVPE = -424.555746



15 + acetone (H^+ abstraction): product

C	-0.0752531939	2.1395549532	0.8801034935
H	0.1836486033	2.5783818718	1.8462771802
H	-0.0548667175	2.927652181	0.1257456747
C	0.8586971529	1.0186412129	0.5227919569
C	1.2840703209	0.8253693421	-0.7900937941
C	1.2752495678	0.1048624205	1.4909716365
C	2.0947879551	-0.2502965009	-1.129804212
H	0.969139005	1.5233910364	-1.5581750729
C	2.0871298469	-0.9707081905	1.1576301798
H	0.9548073061	0.2380741497	2.519093074
C	2.4977892512	-1.1555081955	-0.1569716446
H	2.4103253262	-0.3825241729	-2.1584620537
H	2.3971538992	-1.6691520072	1.9265696979
H	3.1300021847	-1.9954947923	-0.4197840742
C	-2.2951468386	-0.2048130873	-0.5629666884
O	-2.7160383566	-0.0158561899	0.6191612936
C	-2.4435738985	0.6567248792	-1.6320562894
H	-1.0978161966	1.7512399352	0.9446493049
H	-2.0398160408	0.4232977623	-2.6113434943
H	-2.9642122061	1.6029685232	-1.5068422198
C	-1.5395733055	-1.5129931594	-0.8053535468
H	-2.1914456517	-2.3604577647	-0.5718780255
H	-1.1758636302	-1.6247476182	-1.8295758461
H	-0.6854773833	-1.5662315885	-0.1233775304

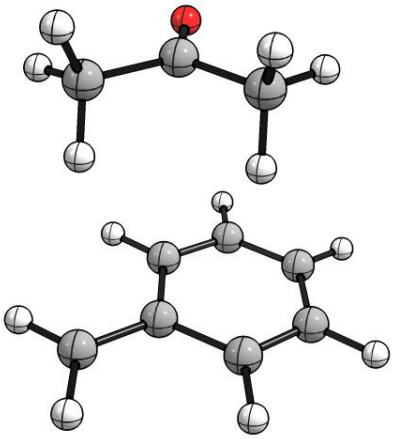
Energy= -464.2200049
Zero-point correction= 0.200937 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.161576
Sum of electronic and zero-point Energies= -464.019068
Sum of electronic and thermal Energies= -464.006793
Sum of electronic and thermal Enthalpies= -464.005849
Sum of electronic and thermal Free Energies= -464.058429
G + ZVPE = -463.857492



15 + acetone (H^+ abstraction): reagent

C	0.5951962749	2.6493868771	0.1976203463
H	-0.0609646863	2.9986422518	0.9883309335
H	0.8902397533	3.3605436108	-0.5673399387
C	1.0907989631	1.3495823339	0.1988381153
C	1.9861909057	0.8498420773	-0.811374022
C	0.7409456034	0.380297577	1.2032111935
C	2.4599420298	-0.4453893016	-0.8054653391
H	2.2944527379	1.523377139	-1.6065807356
C	1.2283677693	-0.9101252877	1.188145671
H	0.0636703468	0.6815974943	1.9977638163
C	2.0961105895	-1.3612314128	0.1882468954
H	3.1321596583	-0.7580878148	-1.6001786754
H	0.9192801963	-1.5924400848	1.9754801728
H	2.4734581274	-2.3764516791	0.1851111245
C	-2.1858368128	-0.9298520566	-0.2841539879
O	-2.5797431511	-1.7773131508	0.4909224113
C	-2.6072290685	0.5089544802	-0.1735311596
H	-1.7244285567	1.1473338974	-0.0629346573
H	-3.1060794076	0.8165318821	-1.0969092559
H	-3.2785782612	0.6518286228	0.6721035661
C	-1.2730304631	-1.2660314566	-1.4322098196
H	-1.8389067318	-1.1894686873	-2.365808942
H	-0.4526990551	-0.5471984223	-1.4917426544
H	-0.8802207615	-2.2765328892	-1.3312300586

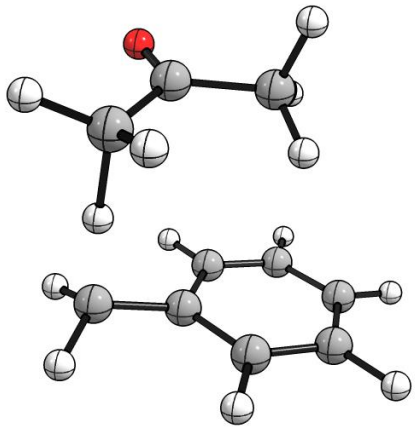
Energy= -464.1958901
Zero-point correction= 0.198781 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.158955
Sum of electronic and zero-point Energies= -463.997109
Sum of electronic and thermal Energies= -463.984427
Sum of electronic and thermal Enthalpies= -463.983483
Sum of electronic and thermal Free Energies= -464.036935
G + ZVPE = -463.838154



15 + acetone (H^+ abstraction): TS

C	-0.065038	2.208279	0.459612
H	-0.343235	2.474136	1.480392
H	0.115416	3.080203	-0.170695
C	0.881059	1.132606	0.328849
C	1.589752	0.908617	-0.874844
C	1.011826	0.130764	1.318433
C	2.353576	-0.22906	-1.07368
H	1.521828	1.649489	-1.665892
C	1.779349	-1.003739	1.115595
H	0.484283	0.254808	2.2595
C	2.455433	-1.205866	-0.085363
H	2.874509	-0.360906	-2.016654
H	1.844738	-1.748326	1.90251
H	3.050176	-2.097345	-0.244323
C	-2.294851	-0.473329	-0.155707
O	-2.938908	-0.734124	0.869131
C	-2.254623	0.829261	-0.765146
H	-1.254693	1.507412	-0.154495
H	-1.962193	0.842432	-1.815909
H	-3.131443	1.443865	-0.556783
C	-1.445714	-1.566526	-0.78754
H	-2.073531	-2.146471	-1.472279
H	-0.606881	-1.165165	-1.358518
H	-1.072331	-2.247182	-0.021149

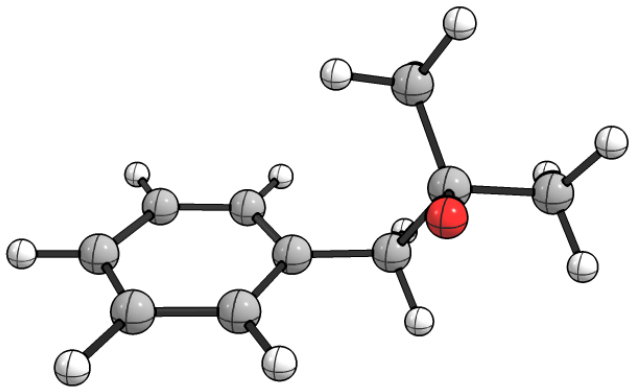
Energy= -464.1759247
Zero-point correction= 0.196069 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.158756
Sum of electronic and zero-point Energies= -463.979856
Sum of electronic and thermal Energies= -463.968778
Sum of electronic and thermal Enthalpies= -463.967834
Sum of electronic and thermal Free Energies= -464.017169
G + ZVPE = -463.821100



15 + acetone (C=O attack): product

C	-0.8928609531	0.6993394903	0.7955854668
H	-1.2696108829	0.314336109	1.7484007636
H	-0.8681179722	1.7925235552	0.8648966407
C	0.495047031	0.1914688395	0.5624288278
C	1.4926418087	1.0183824007	0.0429624217
C	0.8203389558	-1.1437027712	0.8143417068
C	2.7696137684	0.5350298191	-0.2161778425
H	1.2624108845	2.0587210358	-0.1637746561
C	2.0943333019	-1.632584535	0.5573183165
H	0.0477896983	-1.798390555	1.1965700567
C	3.0768411324	-0.794898198	0.0410897983
H	3.5256343941	1.200282382	-0.6183757027
H	2.3246954289	-2.672173022	0.7633227185
H	4.0723877921	-1.1756335042	-0.1562957006
C	-1.9461292048	0.2401593393	-0.2990522904
O	-2.0945759289	-1.0918183036	-0.3447354235
C	-3.267897549	0.9577943786	0.0916179346
H	-3.185453456	2.051379727	0.1334612867
H	-4.0443045492	0.701215462	-0.6364232114
H	-3.6003102201	0.6007907109	1.0718866705
C	-1.4958803826	0.8243922949	-1.665290565
H	-2.2594223769	0.59866068	-2.4169416619
H	-1.3391415379	1.9106388196	-1.6534947833
H	-0.5655171823	0.347714845	-1.9864917719

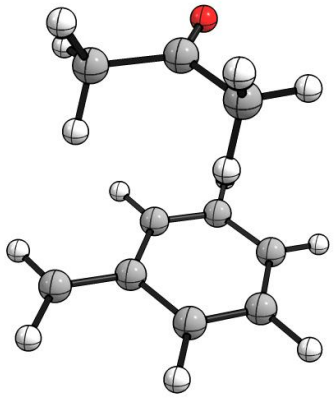
Energy= -464.2124778
Zero-point correction= 0.204793 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.169361
Sum of electronic and zero-point Energies= -464.007685
Sum of electronic and thermal Energies= -463.997445
Sum of electronic and thermal Enthalpies= -463.996501
Sum of electronic and thermal Free Energies= -464.043117
G + ZVPE = -463.838324



15 + acetone (C=O attack): reagent

C	-0.1856228449	1.8273236502	2.1148049162
H	-0.9377122286	1.4080890354	2.7754055052
H	-0.0332059981	2.9019774569	2.1356024693
C	0.5868209881	1.0088475103	1.2965625969
C	1.6022115311	1.5168748279	0.4121568722
C	0.429183085	-0.4205029285	1.2483803081
C	2.3513317768	0.6956351967	-0.4043110181
H	1.7781322478	2.5891287398	0.3906272714
C	1.1899934214	-1.2215504292	0.4223587214
H	-0.3255038488	-0.8785377424	1.8819763793
C	2.167520212	-0.6916863931	-0.4260484034
H	3.1015559184	1.1459565417	-1.0489051089
H	1.0140890077	-2.2938617476	0.4315340491
H	2.7574009552	-1.3281285265	-1.0741832049
C	-2.0708402181	-0.6788036084	-1.2200869489
O	-2.2364871988	-1.8687894214	-1.393368878
C	-2.8206433159	0.0796362081	-0.1586808477
H	-2.1550737994	0.7531162614	0.3885615632
H	-3.5742189352	0.7045013749	-0.6485247948
H	-3.3170336555	-0.6053802257	0.5277406648
C	-1.1347491369	0.1283495093	-2.0774007966
H	-1.7000319821	0.9080639275	-2.5958155158
H	-0.4005301203	0.6317229805	-1.4427274085
H	-0.6277458609	-0.5052691978	-2.8035323913

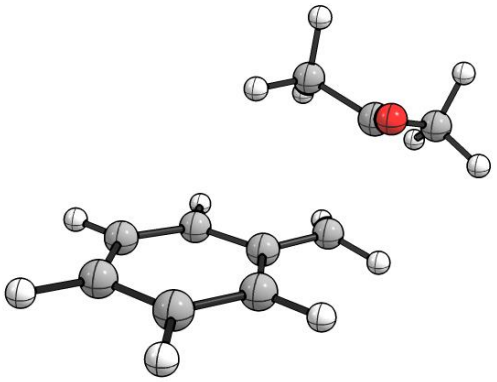
Energy= -464.195812
Zero-point correction= 0.197791 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.157330
Sum of electronic and zero-point Energies= -463.998021
Sum of electronic and thermal Energies= -463.985662
Sum of electronic and thermal Enthalpies= -463.984718
Sum of electronic and thermal Free Energies= -464.038482
G + ZVPE = -463.840691



15 + acetone (C=O attack): TS

C	-1.0947611727	1.064241857	0.9323372038
H	-1.698845713	0.5686161772	1.6856662254
H	-1.2022120695	2.1447768034	0.8822074614
C	0.1493935055	0.4979817885	0.5912467424
C	1.1383653397	1.2096238567	-0.1499596887
C	0.4629785491	-0.8649944983	0.8637219004
C	2.3178087657	0.6179928955	-0.5620316945
H	0.9541446579	2.2527159468	-0.3910141409
C	1.646485856	-1.4451673253	0.4441866992
H	-0.2526178407	-1.4591048882	1.4225225426
C	2.5972253426	-0.7195334098	-0.2749521573
H	3.0382164874	1.2099815524	-1.118969118
H	1.8372323282	-2.4873161444	0.6835583418
H	3.5248855771	-1.1781850678	-0.595668212
C	-2.518685014	0.2990474596	-0.7956782181
O	-2.4334332099	-0.9364285052	-0.8146143195
C	-3.7417809106	0.9494996023	-0.1699578432
H	-3.5906687308	2.0029809949	0.0657018669
H	-4.5673331179	0.8769820456	-0.8904648557
H	-4.0381451724	0.4131227998	0.7320148334
C	-1.8494497395	1.1044838802	-1.8911631596
H	-2.4177240646	0.9573465775	-2.8183466901
H	-1.8212323139	2.1727080812	-1.6729544637
H	-0.8331975495	0.7444055402	-2.0592730561

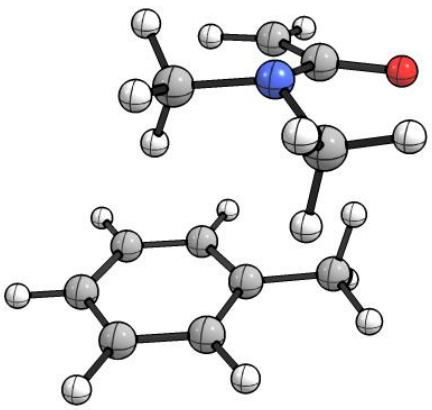
Energy= -464.18536
Zero-point correction= 0.199509 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.161701
Sum of electronic and zero-point Energies= -463.985851
Sum of electronic and thermal Energies= -463.974495
Sum of electronic and thermal Enthalpies= -463.973551
Sum of electronic and thermal Free Energies= -464.023659
G + ZVPE = -463.824150



15 + DMA (H^+ abstraction): product

C	-0.3086030857	2.1796188253	-0.7551228408
H	-0.3164794032	2.311419668	-1.8384929435
H	-0.5440886097	3.1407628275	-0.2920020268
C	-1.2859068166	1.1203125111	-0.3305247308
C	-1.6023915125	0.9484509348	1.01751095
C	-1.8737662837	0.263926373	-1.2583785264
C	-2.4738094697	-0.0510748231	1.4253182062
H	-1.1507736121	1.6017780741	1.7562180318
C	-2.7466665675	-0.7403709371	-0.8553947761
H	-1.6433403843	0.3812806527	-2.3117885499
C	-3.0496487752	-0.9024518535	0.4890118417
H	-2.702772573	-0.1673221085	2.4784011031
H	-3.190004008	-1.3959776545	-1.5961569949
H	-3.7304163338	-1.683468265	0.8066015383
C	2.3626395381	0.0993008783	0.5372929061
O	3.0161041353	1.0035275538	-0.0557204201
C	2.0755612866	0.0929585886	1.9020231629
H	0.7102192174	1.910492365	-0.4575694974
H	1.4577569652	-0.6476497744	2.3895918824
H	2.4559799449	0.9130515572	2.5003159849
N	1.9250842199	-0.9985465785	-0.2604159375
C	1.7812039216	-0.7699066999	-1.6818909839
H	1.9127521967	-1.7096867124	-2.2258522056
H	0.7934603117	-0.3633533825	-1.9472217305
H	2.5392593567	-0.0620702137	-2.0062744597
C	0.9761963606	-1.9452471389	0.2793911028
H	0.8360940799	-2.7577394585	-0.4367833977
H	1.3479397282	-2.3863353113	1.2056997612
H	-0.0099398278	-1.5012948979	0.4833095501

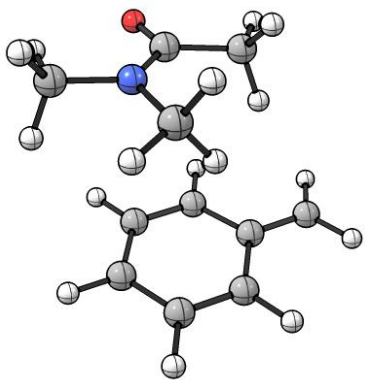
Energy= -558.8841059
Zero-point correction= 0.246235 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.204161
Sum of electronic and zero-point Energies= -558.637871
Sum of electronic and thermal Energies= -558.623630
Sum of electronic and thermal Enthalpies= -558.622686
Sum of electronic and thermal Free Energies= -558.679945
G + ZVPE = -558.433710



15 + DMA (H^+ abstraction): reagent

C	1.4107461985	2.8895062522	0.4454555983
H	0.7428976009	3.3065012375	1.1924150402
H	1.9040937851	3.57744978	-0.2337537653
C	1.6739407607	1.5239426717	0.4016669159
C	2.5701833896	0.9273200933	-0.553657173
C	1.0604701743	0.5801155125	1.2980353903
C	2.8023112822	-0.431534329	-0.6023005715
H	3.0745074855	1.5775628086	-1.2635294653
C	1.3074078609	-0.7746500615	1.2289884239
H	0.3653317542	0.9541514733	2.0447869422
C	2.1791582195	-1.3205677477	0.2803671228
H	3.4879538293	-0.81653096	-1.3525867471
H	0.7978731469	-1.4330231239	1.9275672095
H	2.3663302086	-2.3863475342	0.2336542055
C	-2.2699727489	-0.1965995934	0.1591906711
O	-2.916289695	-0.5469297202	1.1454803921
C	-2.156575431	1.2594953183	-0.222966436
H	-1.1224976538	1.6055754151	-0.1412295524
H	-2.4810526401	1.4313718036	-1.251184087
H	-2.7789266611	1.8432246598	0.4515521607
N	-1.627205571	-1.079342765	-0.6409660959
C	-1.6776859132	-2.4993398769	-0.3596326081
H	-2.1030167975	-3.0419400477	-1.2082321202
H	-0.6736546019	-2.8867021684	-0.165866519
H	-2.2977461719	-2.6664767391	0.5168247226
C	-0.8314162209	-0.6608651056	-1.7833798689
H	-0.2781674732	-1.5233804062	-2.1504002499
H	-1.4554380215	-0.2837009249	-2.5981261876
H	-0.106379095	0.1063660777	-1.5064333481

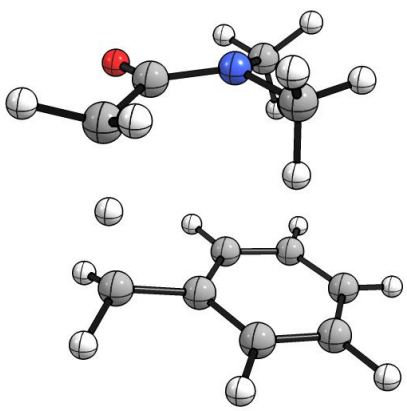
Energy= -558.8759995
Zero-point correction= 0.245515 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.201265
Sum of electronic and zero-point Energies= -558.630485
Sum of electronic and thermal Energies= -558.615162
Sum of electronic and thermal Enthalpies= -558.614217
Sum of electronic and thermal Free Energies= -558.674735
G + ZVPE = -558.429220



15 + DMA (H^+ abstraction): TS

C	0.5253599404	2.3289031967	0.6902301388
H	0.1732721752	2.496484489	1.7100694196
H	0.9212245551	3.2412896364	0.2399319794
C	1.3463173869	1.1538843582	0.517307484
C	2.2415716748	1.0165034976	-0.5680130505
C	1.1828312868	0.0107710751	1.332691086
C	2.9246766172	-0.1650815653	-0.8092762672
H	2.3968723238	1.8648015146	-1.2280272661
C	1.8660284047	-1.1682749088	1.0862253624
H	0.4932711007	0.0607045692	2.1700124336
C	2.7475995535	-1.2747685227	0.0127012962
H	3.605459211	-0.2218793129	-1.6526659172
H	1.7094177384	-2.019197352	1.7413846784
H	3.2809940955	-2.1982131047	-0.1782278444
C	-2.2511700321	0.3602588078	-0.0561735933
O	-2.8913628783	0.3413997419	1.0117287684
C	-1.8665729052	1.5984455474	-0.7027334093
H	-0.6911349974	1.9835654321	-0.042434172
H	-1.6245848573	1.560472526	-1.7623740402
H	-2.5607497028	2.4047248663	-0.4676822304
N	-1.8116908079	-0.8365576814	-0.6045412945
C	-1.8274947856	-2.0240657882	0.2216611312
H	-2.0117804288	-2.9065793882	-0.3951064569
H	-0.8716202982	-2.1651143714	0.7460610244
H	-2.6162676377	-1.9352252765	0.9637455561
C	-0.8913306537	-0.8694076222	-1.7236180945
H	-0.7422043542	-1.907408914	-2.0213401429
H	-1.2938403351	-0.3358762693	-2.5858697111
H	0.0878826104	-0.4407421805	-1.4769428682

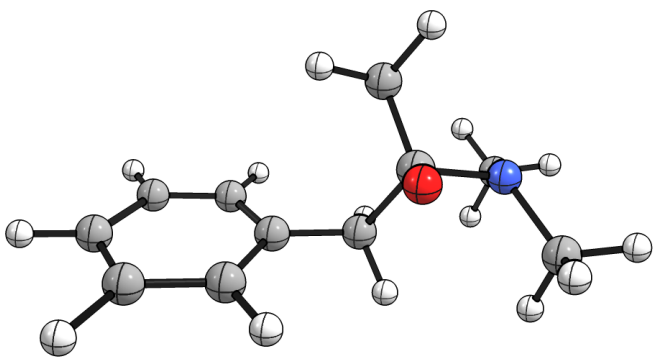
Energy= -558.8487253
Zero-point correction= 0.242210 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.201884
Sum of electronic and zero-point Energies= -558.606515
Sum of electronic and thermal Energies= -558.592889
Sum of electronic and thermal Enthalpies= -558.591945
Sum of electronic and thermal Free Energies= -558.646841
G + ZVPE = -558.404631



15 + DMA (C=O attack): product

C	0.4239863919	-0.0612798545	-0.7779996533
H	0.6779334926	-0.9863804838	-1.3026345364
H	0.6674435543	0.7743616174	-1.4399696138
C	-1.0446677822	-0.0363038099	-0.4940694942
C	-1.797518633	1.1256665108	-0.6733110775
C	-1.7018918006	-1.1703037014	-0.0092680679
C	-3.1556166707	1.1598999786	-0.3790459942
H	-1.3092288027	2.0193635997	-1.0488955947
C	-3.0577480064	-1.1422451068	0.285900692
H	-1.1227610094	-2.070072688	0.1548644552
C	-3.7933007943	0.0238738306	0.1017492778
H	-3.7160880751	2.0759224709	-0.5297543423
H	-3.5463583471	-2.0353597355	0.6599080713
H	-4.8532926234	0.0436901947	0.3274204333
C	1.3294938748	-0.0325971128	0.5287220009
O	1.0892202445	-1.0561643771	1.3264379851
C	1.1116748504	1.3235264947	1.2466811177
H	1.8444447536	1.4113762034	2.0536415142
H	1.1889781334	2.2089425865	0.6076169608
H	0.1146012367	1.3199529307	1.6919970705
N	2.7957252513	-0.038169687	0.062754618
C	3.2003690841	0.9614845796	-0.902918266
H	2.8671665121	1.9566105595	-0.6077714002
H	4.2939215605	0.9917383673	-0.9689111953
H	2.8267993605	0.7717711294	-1.9259566886
C	3.2304174159	-1.3467199186	-0.3689678525
H	2.897919661	-1.6076507233	-1.3926980369
H	4.3249763385	-1.4038593322	-0.3655593823
H	2.8266518287	-2.0861675227	0.3211289989

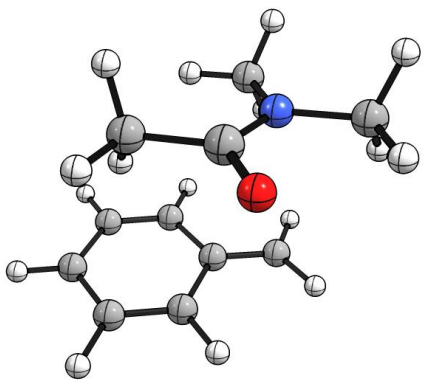
Energy= -558.8701278
Zero-point correction= 0.249650 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.210494
Sum of electronic and zero-point Energies= -558.620478
Sum of electronic and thermal Energies= -558.607577
Sum of electronic and thermal Enthalpies= -558.606633
Sum of electronic and thermal Free Energies= -558.659634
G + ZVPE = -558.409984



15 + DMA (C=O attack): reagent

C	-0.1214481693	-0.8688868804	-2.4224190948
H	0.1449926484	-1.9209512598	-2.4248790479
H	0.3445235923	-0.2275299186	-3.1635998773
C	-0.9697886491	-0.3458078976	-1.4534546471
C	-1.315888404	1.0502258525	-1.3809257768
C	-1.5841730865	-1.152298148	-0.4303425518
C	-2.1814891831	1.5506770702	-0.4299465353
H	-0.8806440948	1.7284740815	-2.1098947737
C	-2.4456548611	-0.6291392582	0.5096789133
H	-1.3560375117	-2.2145657837	-0.407196368
C	-2.7727466963	0.731826333	0.5380736767
H	-2.4032017188	2.6147322532	-0.4357768966
H	-2.875345232	-1.2976516839	1.2510174558
H	-3.4493264578	1.1349454431	1.2815361041
C	1.6201293638	-0.4138432545	1.3042475586
O	1.7362749373	-1.5508149862	1.7579410969
C	0.6894314866	0.5819700073	1.9569193504
H	1.2372912464	1.4479981055	2.3340200581
H	-0.0705699413	0.9359473561	1.2580586189
H	0.1976586577	0.0855046353	2.7902638262
N	2.3205808911	0.0008517993	0.2206654228
C	2.2318867714	1.317974517	-0.3752953009
H	1.5687598106	1.9707137049	0.1823682814
H	3.2239250398	1.7781821517	-0.4044893835
H	1.8591170751	1.2385579541	-1.4008083013
C	3.2126161521	-0.9102506692	-0.4659079125
H	2.9158631833	-1.0009976055	-1.5148031904
H	4.2415107196	-0.5401600915	-0.4248867219
H	3.1645164302	-1.8877348274	0.0049040161

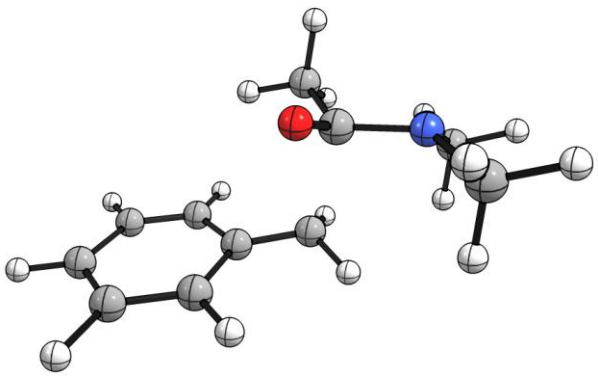
Energy= -558.8760453
Zero-point correction= 0.245525 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.202843
Sum of electronic and zero-point Energies= -558.630521
Sum of electronic and thermal Energies= -558.615447
Sum of electronic and thermal Enthalpies= -558.614503
Sum of electronic and thermal Free Energies= -558.673202
G + ZVPE = -558.427677



15 + DMA (C=O attack):TS

C	0.7962351019	-0.26007225	1.1788690135
H	1.2586529886	0.5697170474	1.7097659296
H	0.993607132	-1.2294843299	1.6323930798
C	-0.5302527819	-0.0419723075	0.7119281901
C	-1.4051348605	-1.1100213856	0.3813697372
C	-1.022817296	1.2591139927	0.4354860679
C	-2.6551402384	-0.8924969656	-0.1715439714
H	-1.0786288566	-2.1279514053	0.5735202167
C	-2.2765590679	1.4689255913	-0.1124433823
H	-0.3926203295	2.111735711	0.6659236741
C	-3.1136466187	0.3993191293	-0.4285460002
H	-3.2866831414	-1.7444343504	-0.4046975225
H	-2.6106188133	2.4850655561	-0.2995774892
H	-4.0939606912	0.5677647821	-0.8583478468
C	2.0471228495	-0.2094680354	-0.629497034
O	1.6161014559	0.7216283928	-1.3432738697
C	1.7439463201	-1.6320884263	-1.079710983
H	2.3434614396	-1.8515685019	-1.9713645668
H	1.9339843643	-2.4034668538	-0.3360788699
H	0.6922307538	-1.6784941772	-1.3599369506
N	3.3456488796	-0.0388970727	-0.0424503384
C	3.804270834	-0.9611820717	0.9740545402
H	3.6323736201	-1.995180956	0.6823140648
H	4.8811303835	-0.8348354576	1.1112513724
H	3.3205891161	-0.7939123433	1.9473135608
C	3.6886284755	1.3290406448	0.2778224086
H	3.1720899447	1.6904098383	1.1824469281
H	4.764365695	1.4022643656	0.4543637199
H	3.4164546112	1.980049669	-0.5493394987

Energy= -558.8501053
Zero-point correction= 0.246688 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.206845
Sum of electronic and zero-point Energies= -558.603418
Sum of electronic and thermal Energies= -558.590146
Sum of electronic and thermal Enthalpies= -558.589202
Sum of electronic and thermal Free Energies= -558.643261
G + ZVPE = -558.396573



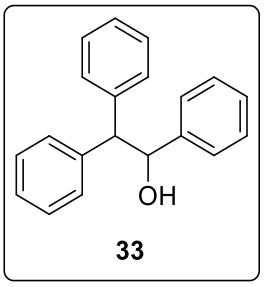
8. Photocatalytic benzylation of aromatic aldehydes

General procedure for the photocatalytic benzylation of aromatic aldehydes (General Procedure D)

A 5 mL crimp cap vial equipped with a magnetic stirring bar was loaded with 4CzIPN (2 mg, 2.5 µmol, 2.5 mol%), Cs_2CO_3 (48.9 mg, 150 µmol, 1.5 eq.) and the corresponding carboxylic acid (150 µmol, 1.5 eq.). The vial was set under inert conditions and dry DMF (2 mL) and the corresponding aldehyde or ketone (100 µmol, 1 eq.) were added *via* syringe. The reaction mixture was degassed by four cycles of freeze-pump-thaw and subsequently stirred under light irradiation using a 455 nm (± 25 nm) LED for 16 h at 25 °C.

Four reaction batches were combined and diluted with H_2O (10 mL) and EtOAc (10 mL). The phases were separated and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic phases were washed with 2 M HCl (15 mL) and subsequently dried over Na_2SO_4. The crude product was purified by automated flash column chromatography (PE/EtOAc, 0-20% EtOAc). If noted, the GC-yield was determined by GC-FID analysis using 1-naphthol as internal standard.

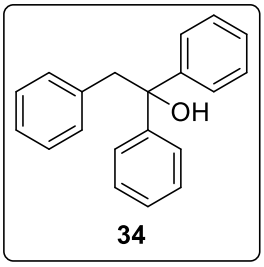
1,2,2-triphenylethan-1-ol (33)[10]



33

^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.45 – 7.05 (m. 15H), 5.41 (d, *J* = 8.8 Hz, 1H), 4.26 (d, *J* = 8.8, 1H).
^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 142.3, 141.6, 141.0, 129.1, 128.9, 128.7, 128.4, 128.2, 127.7, 127.1,127.0, 126.5, 77.0, 60.5.
Yield: 71%

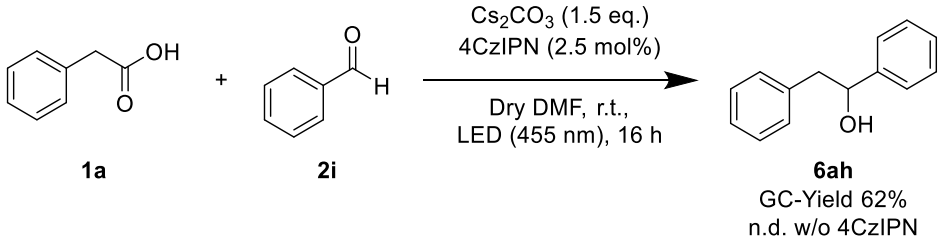
1,1,2-triphenylethan-1-ol (34)[29]



34

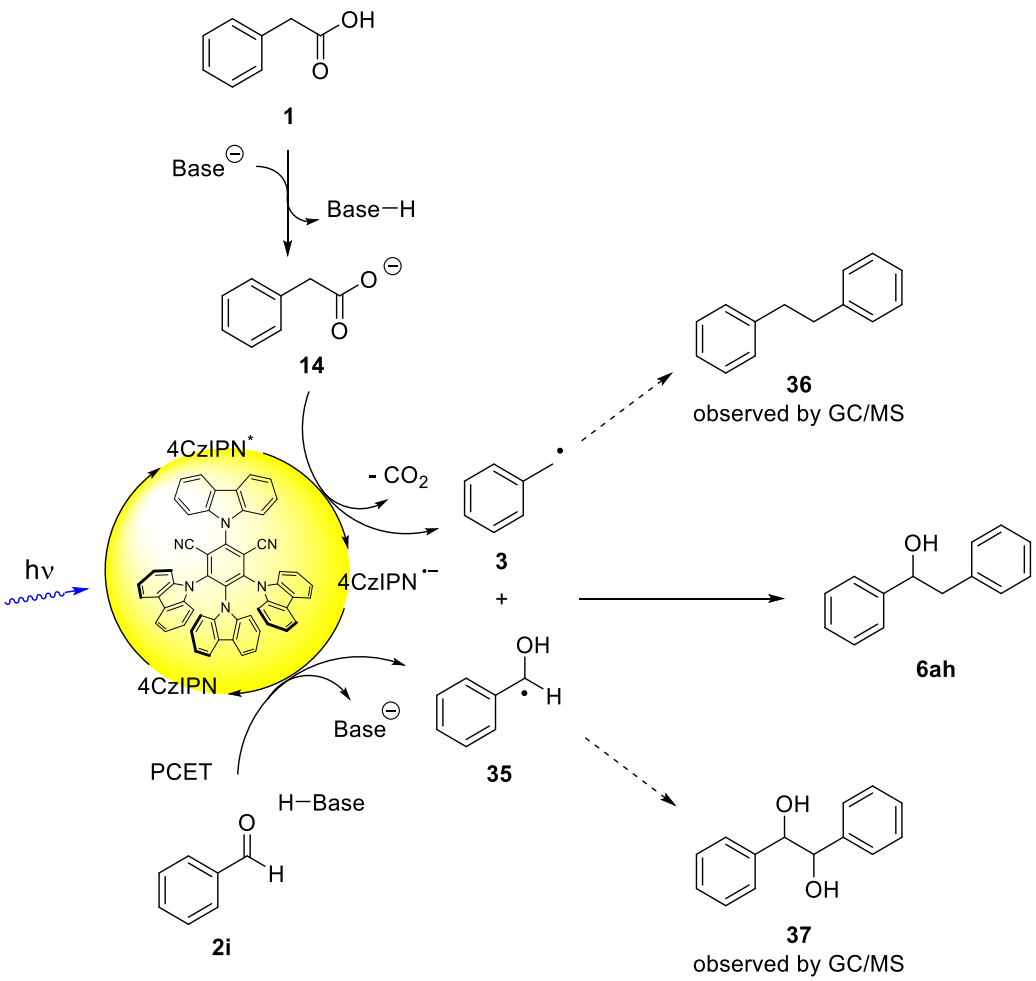
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.48 – 7.12 (m, 13H), 6.95 – 6.88 (m, 2H), 3.67 (s, 2H), 2.34 (s, 1H).
^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 146.7, 135.9, 131.0, 128.2, 128.2, 127.0, 126.9, 126.3, 78.0, 48.1.
Yield: 27%

1,2-Diphenylethan-1-ol (**6ah**) could be formed as well. Only the GC-yield was determined in this case (Scheme S8).



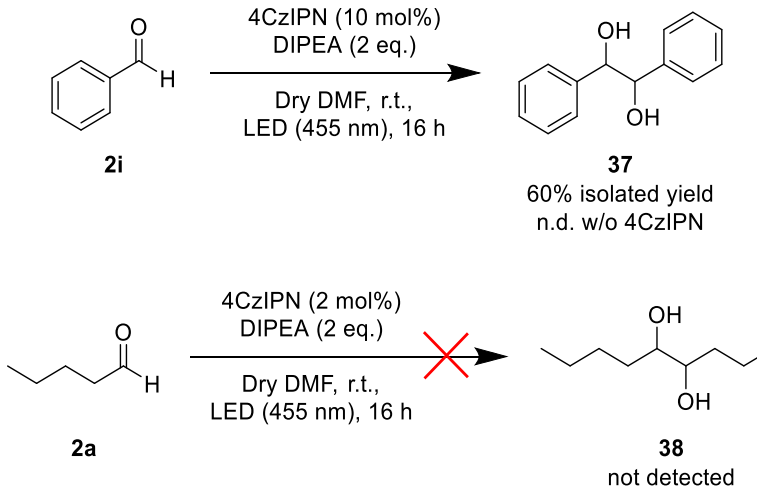
Scheme S8. Benzylation of benzyaldehyde (**2i**) with phenylacetic acid (**1a**).

Proposed mechanism for the photocatalytic benzylation of aromatic aldehydes



Scheme S9. Proposed mechanism for the benzylation of aromatic aldehydes.

When employing aromatic instead of aliphatic aldehydes, the corresponding coupling product can be formed as well, yet a radical-radical cross-coupling similar to our previously reported procedure[30] is the likely pathway (Scheme S9). Observations supporting a radical-radical cross-coupling mechanism are the formation of the corresponding homocoupling products **36** and **37** detected by GC/FID and GC/MS in several reactions in the brief optimization process. Furthermore, 4CzIPN is a viable photocatalyst for the pinacol homocoupling of benzaldehyde (**2i**) ($E_{1/2}^{red}$ = –1.93 V *vs* SCE[31]) with DIPEA as electron donor (Scheme S10, upper).[32] An analogous reaction is not possible with *n*-pentanal (**2a**) ($E_{1/2}^{red}$(3-methylbutanal **2g**) = –2.24 V *vs* SCE[31]) (Scheme S11, lower).

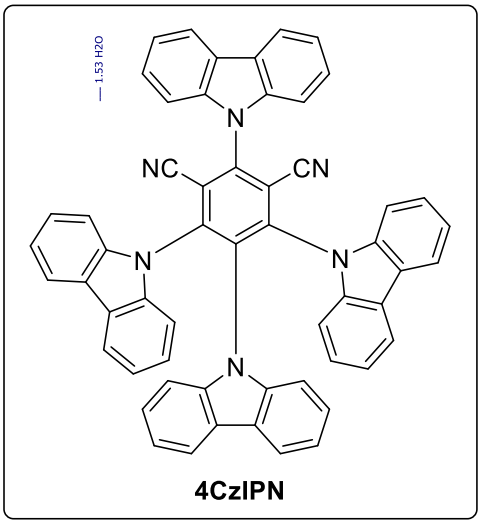


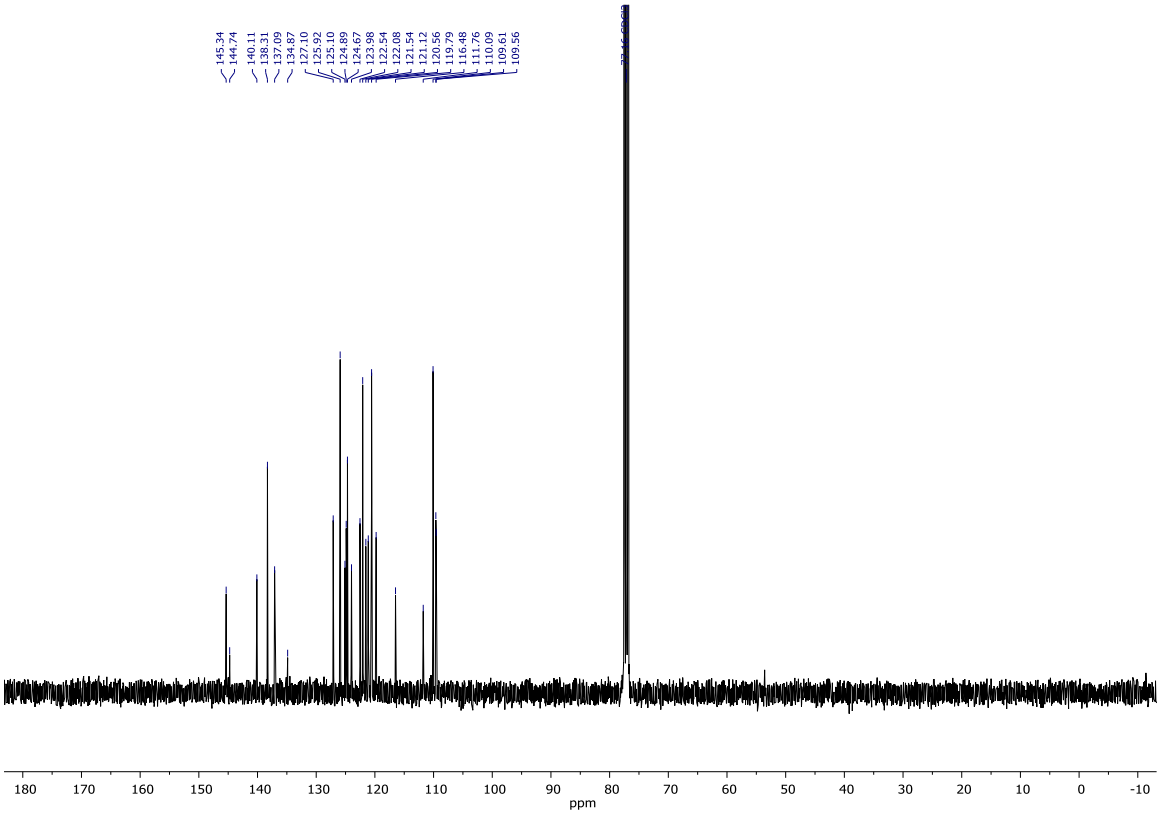
Scheme S10. Photocatalytic pinacol reaction with 4CzIPN as catalyst of benzaldehyde (**2i**) (upper) and *n*-pentanal (**2a**) (lower).

Thus aromatic aldehydes (or ketones) were not included in the substrate scope, although the corresponding products can be formed under the same conditions.

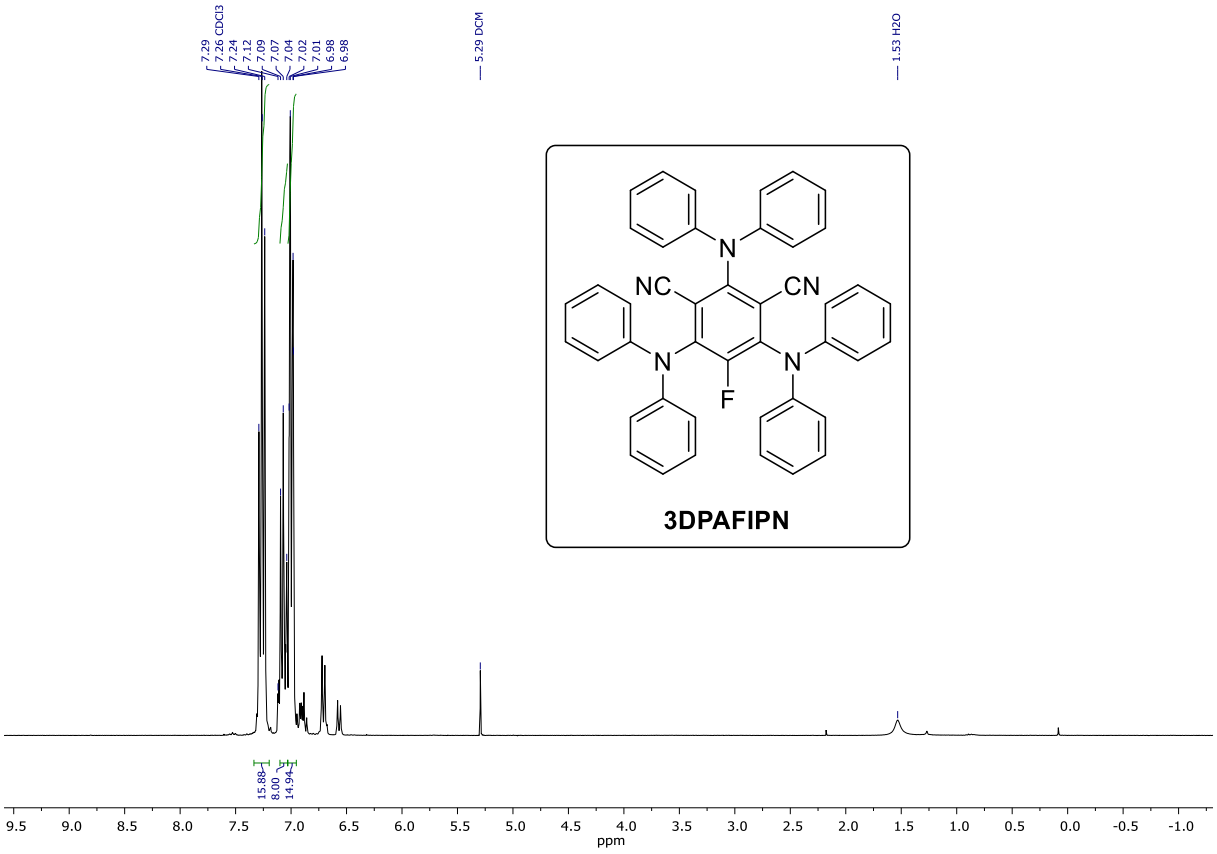
9. NMR-spectra

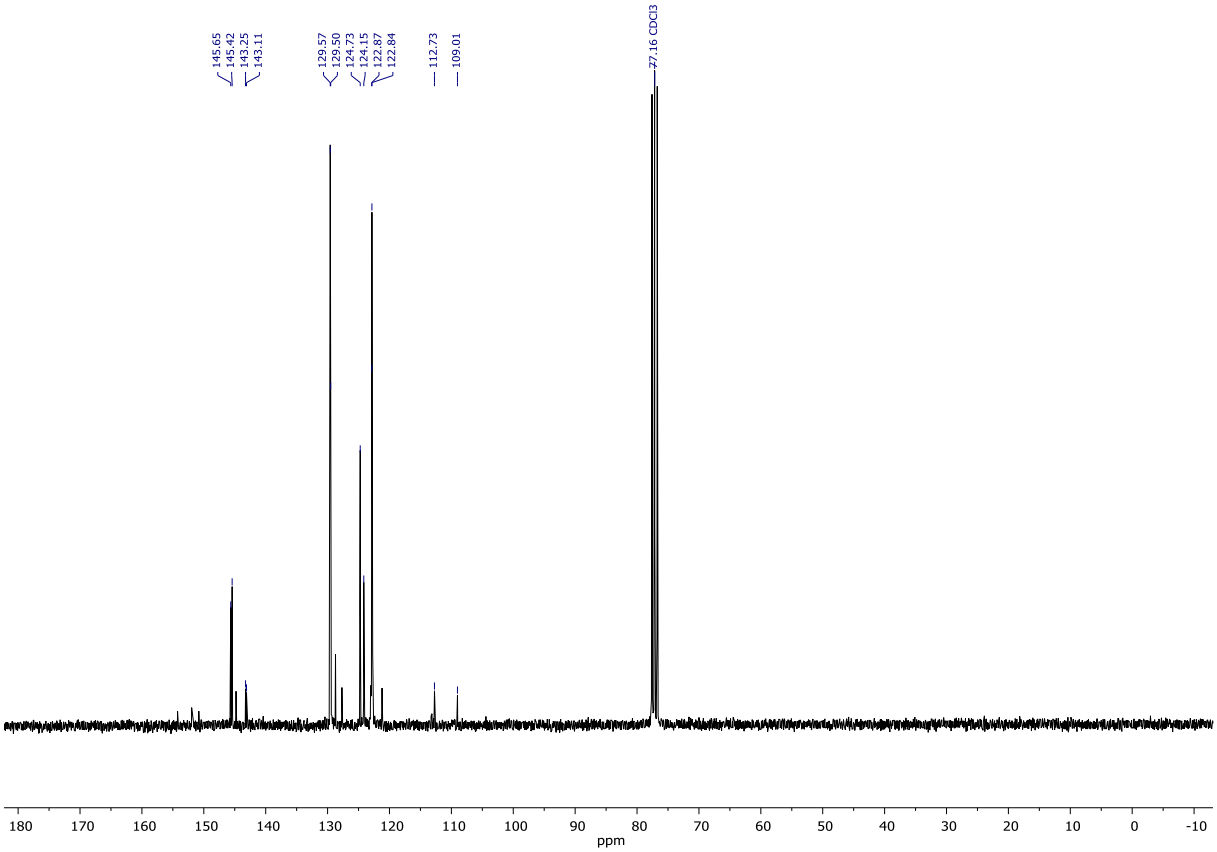
4CzIPN, ^{1}H- and ^{13}C-NMR ($CDCl_3$)

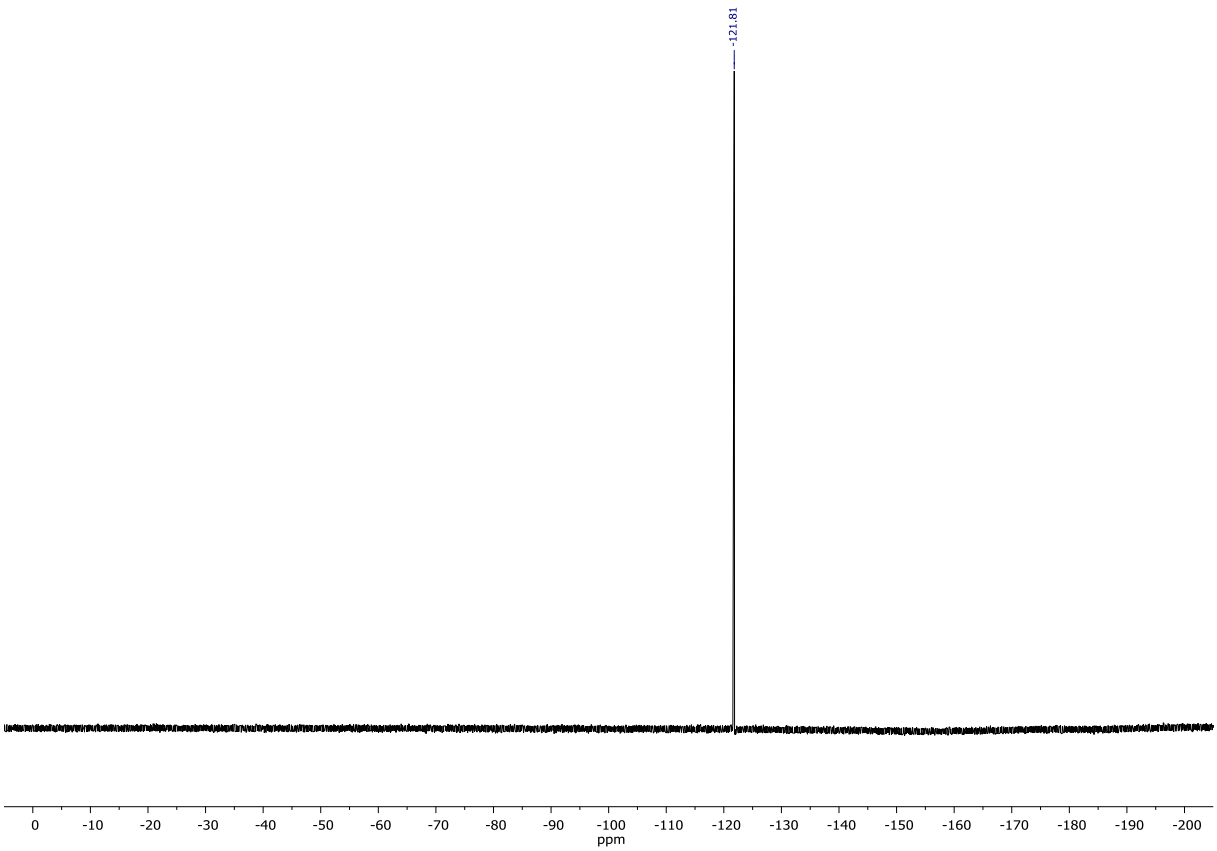




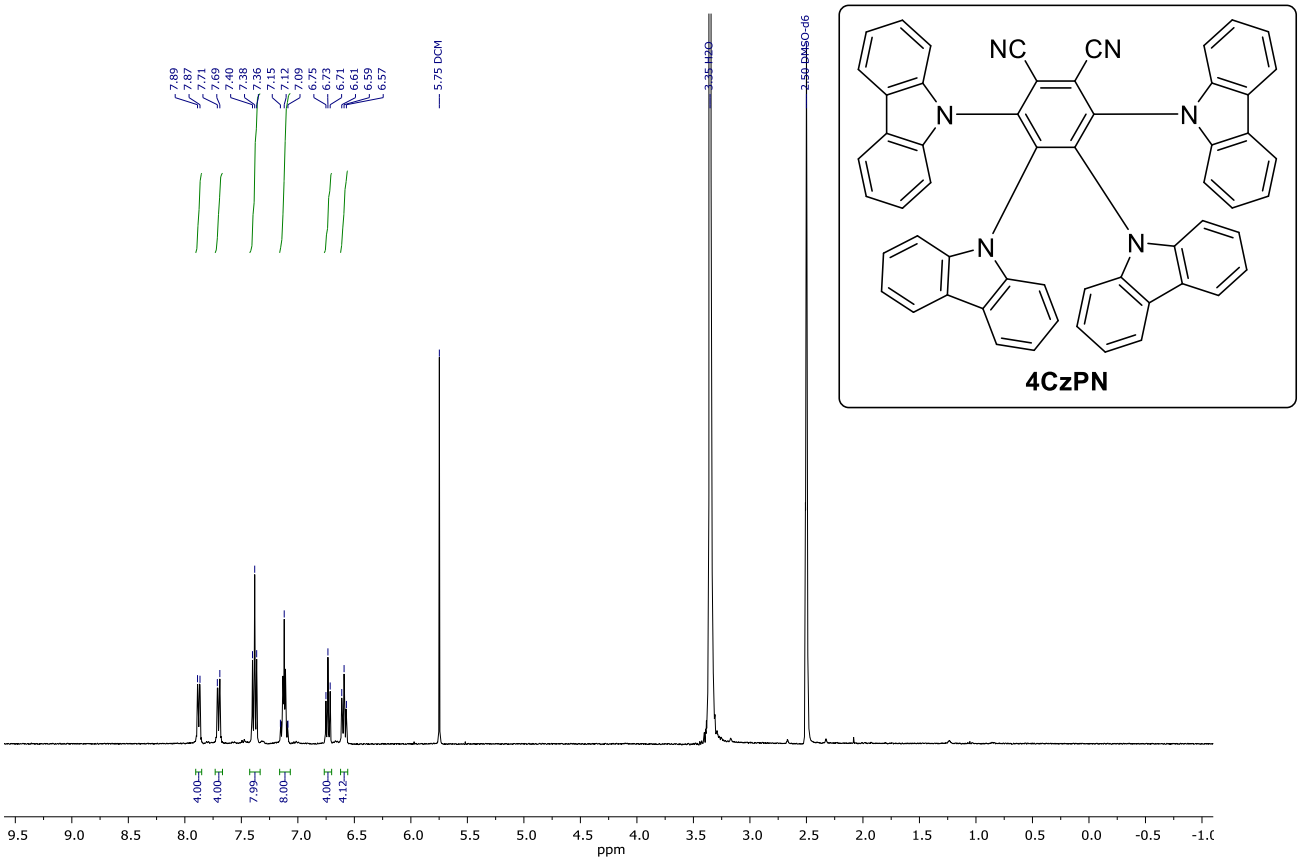
3DPAFIPN, ^{1}H-, ^{13}C-NMR and ^{19}F-NMR ($CDCl_3$)



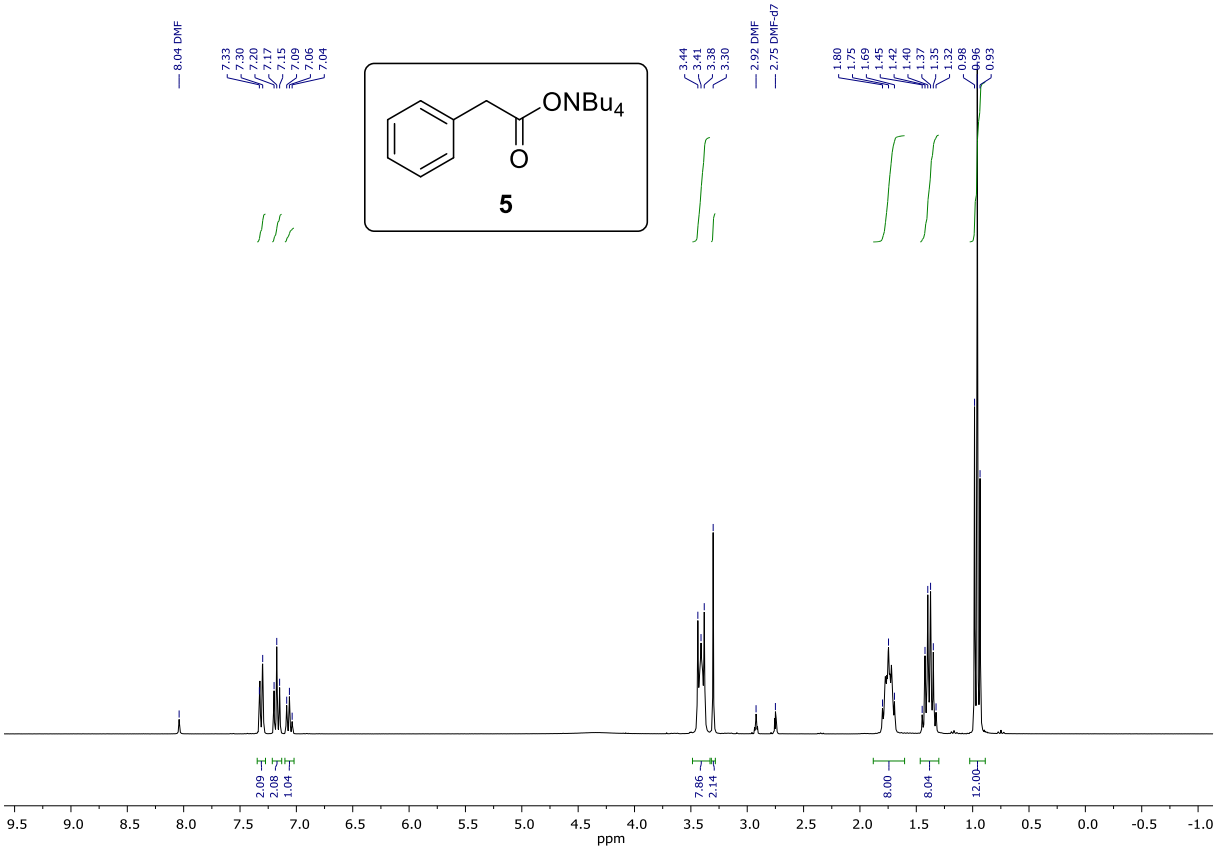


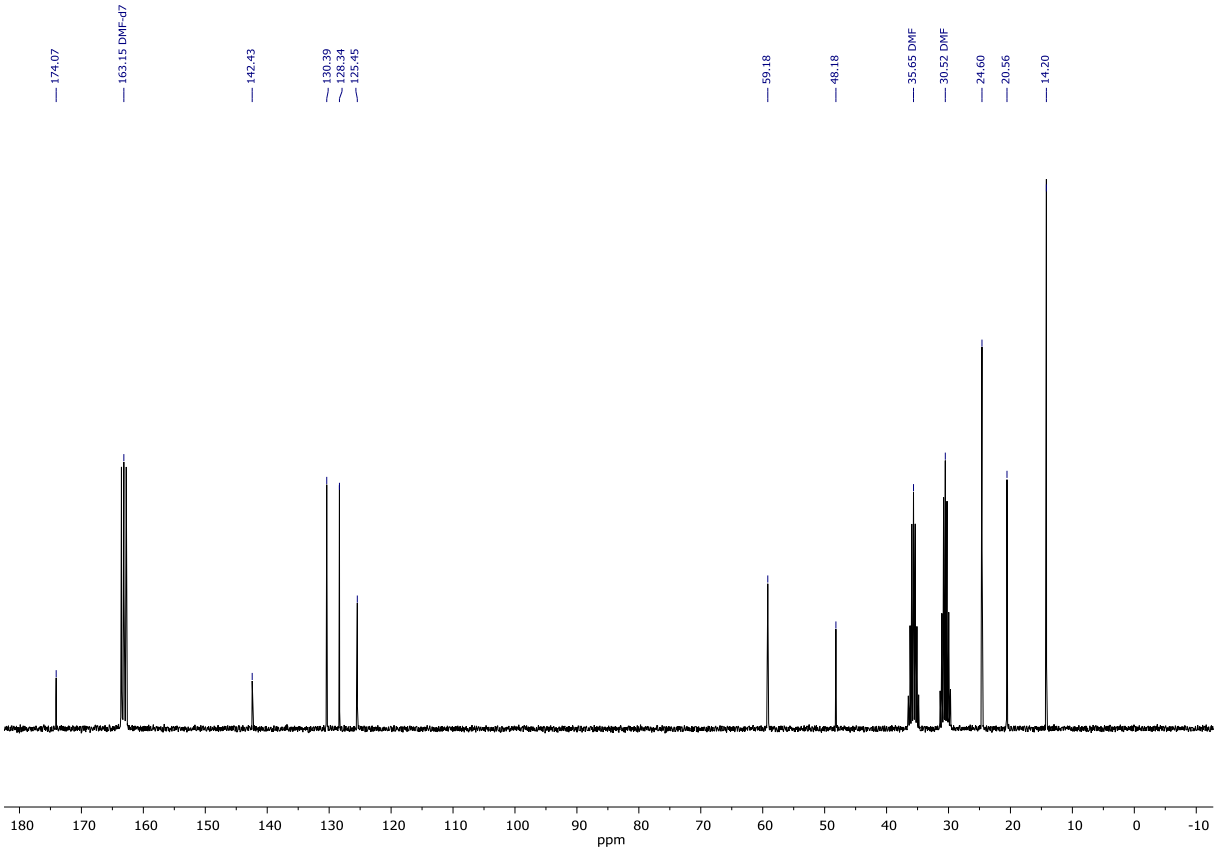

-121.81
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
ppm

4CzPN, ^{1}H-NMR (d_6-DMSO)

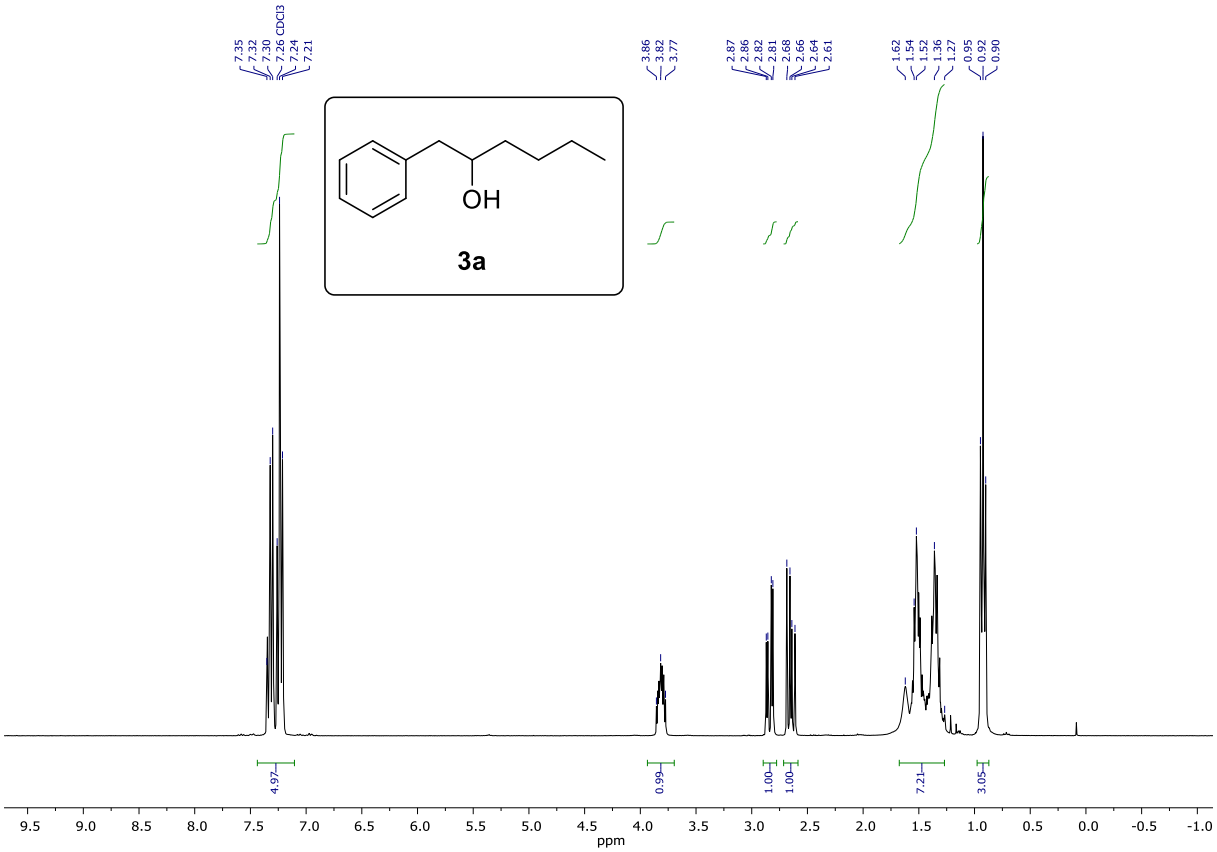


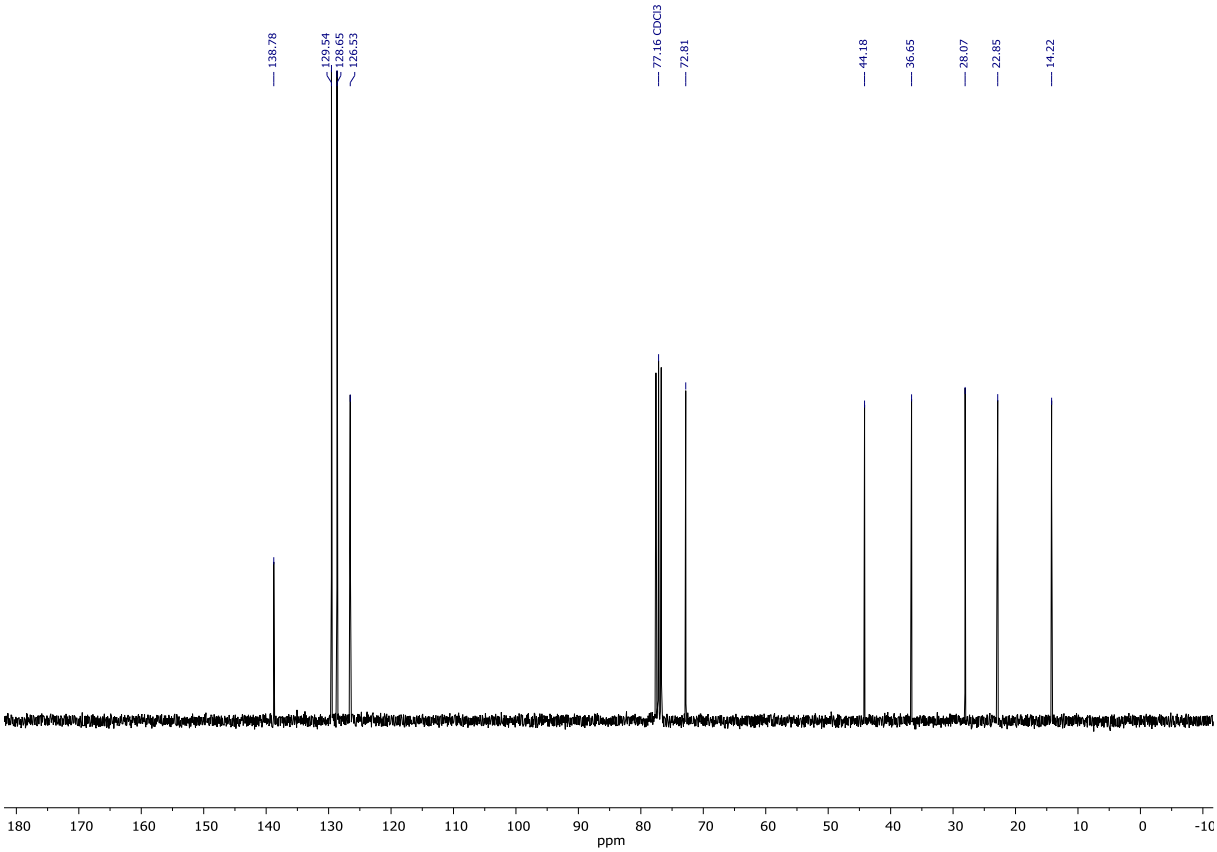
Compound **5**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



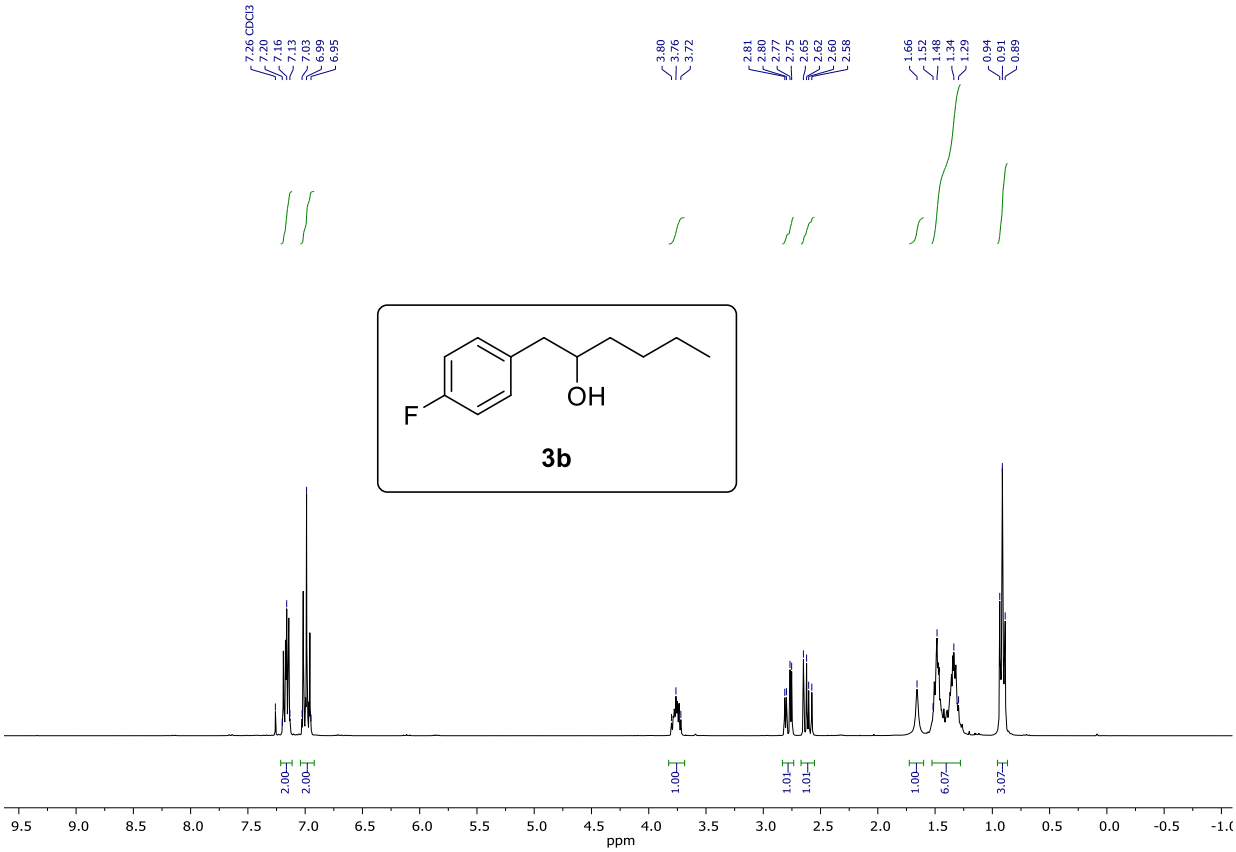


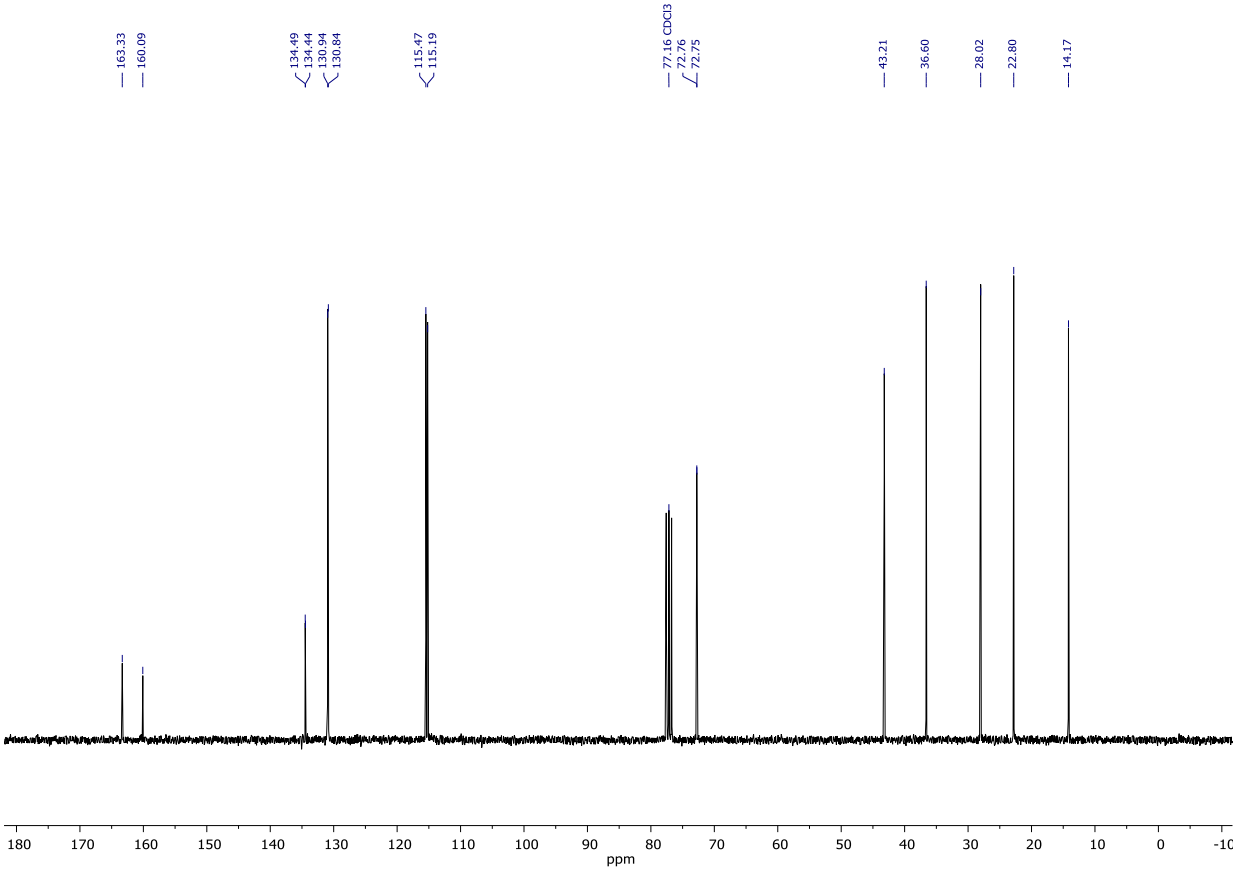
Compound **3a**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)

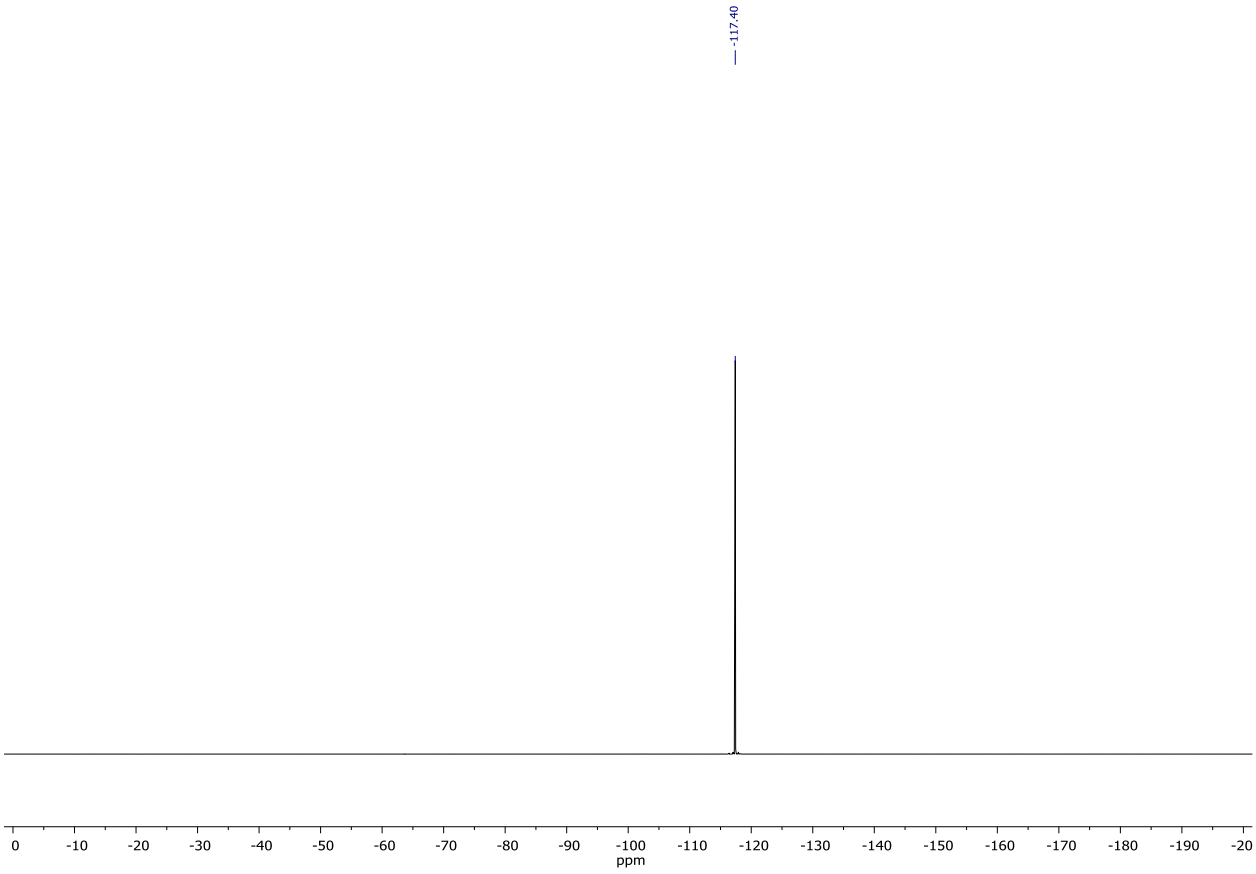




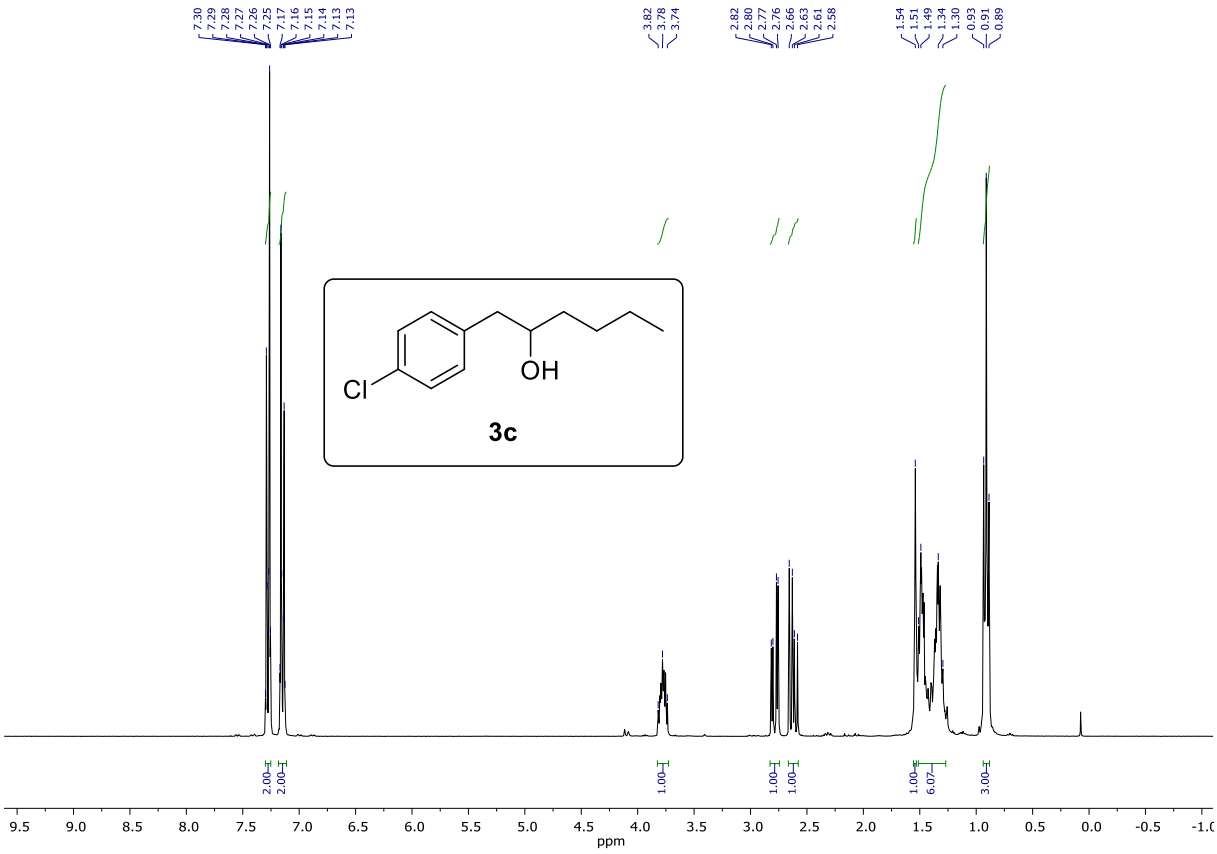
Compound **3b**, ^{1}H-, ^{13}C-NMR and ^{19}F-NMR ($CDCl_3$)

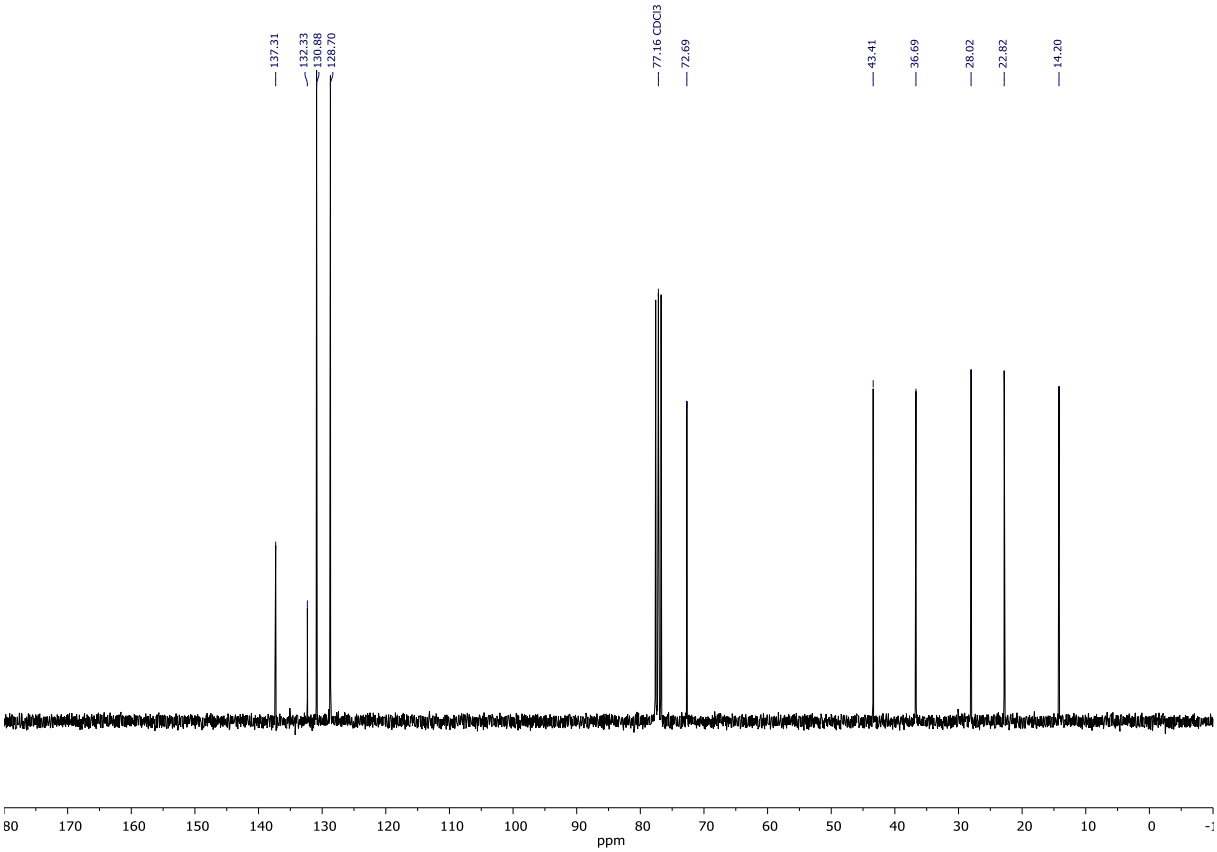




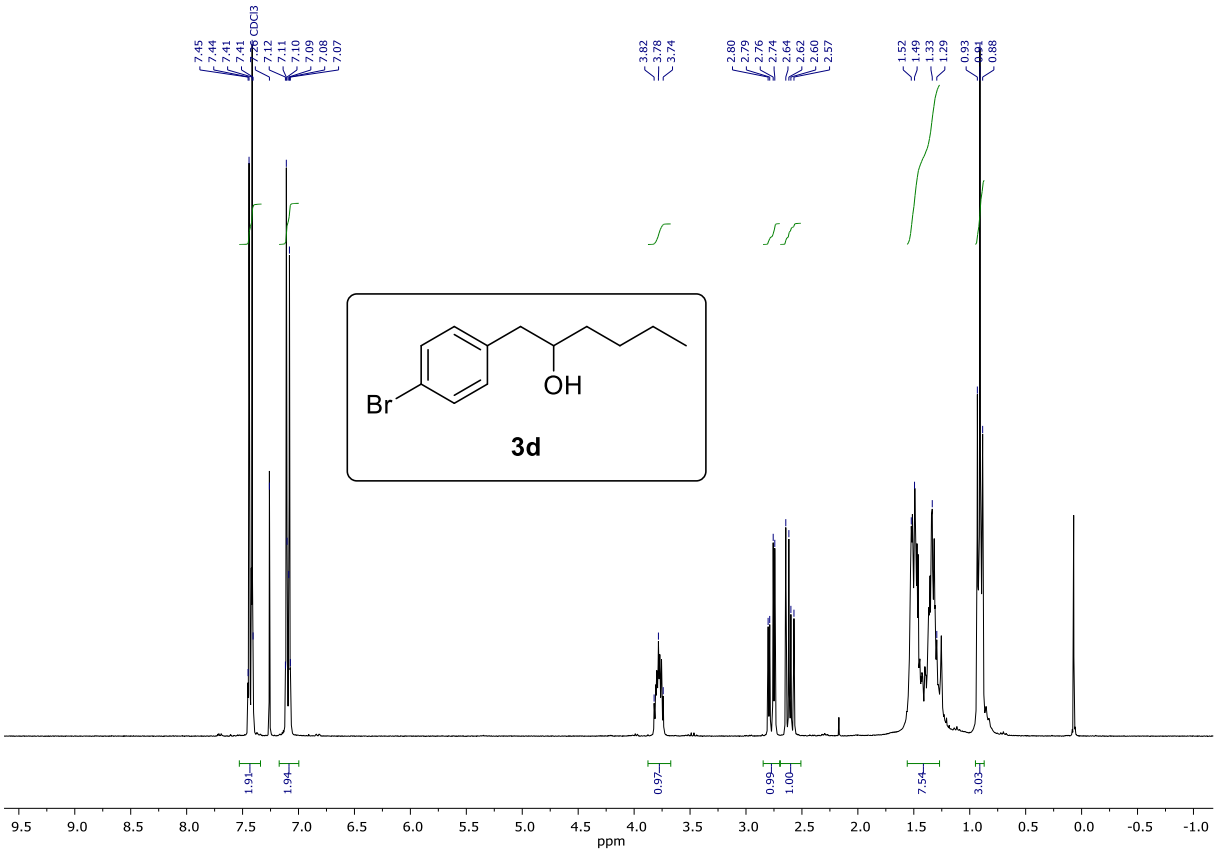

-117.40
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
ppm

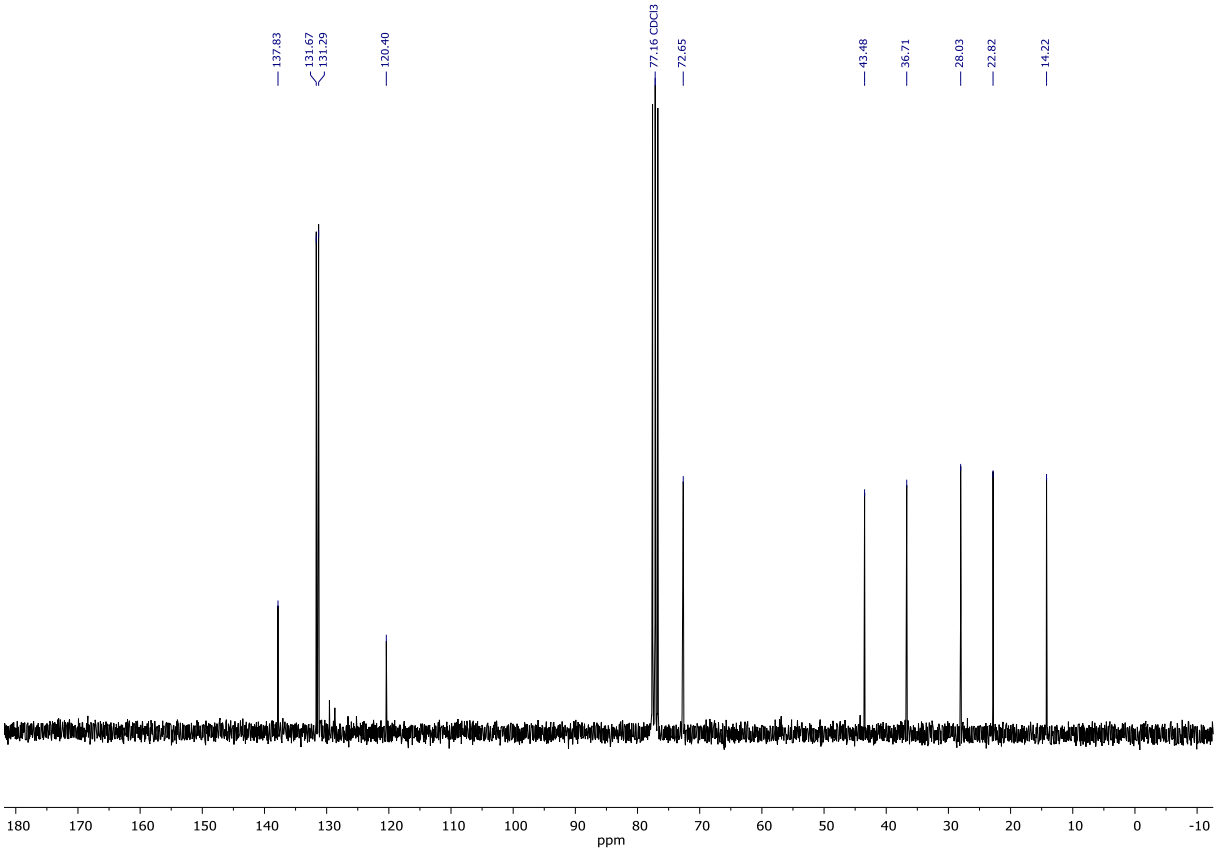
Compound **3c**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



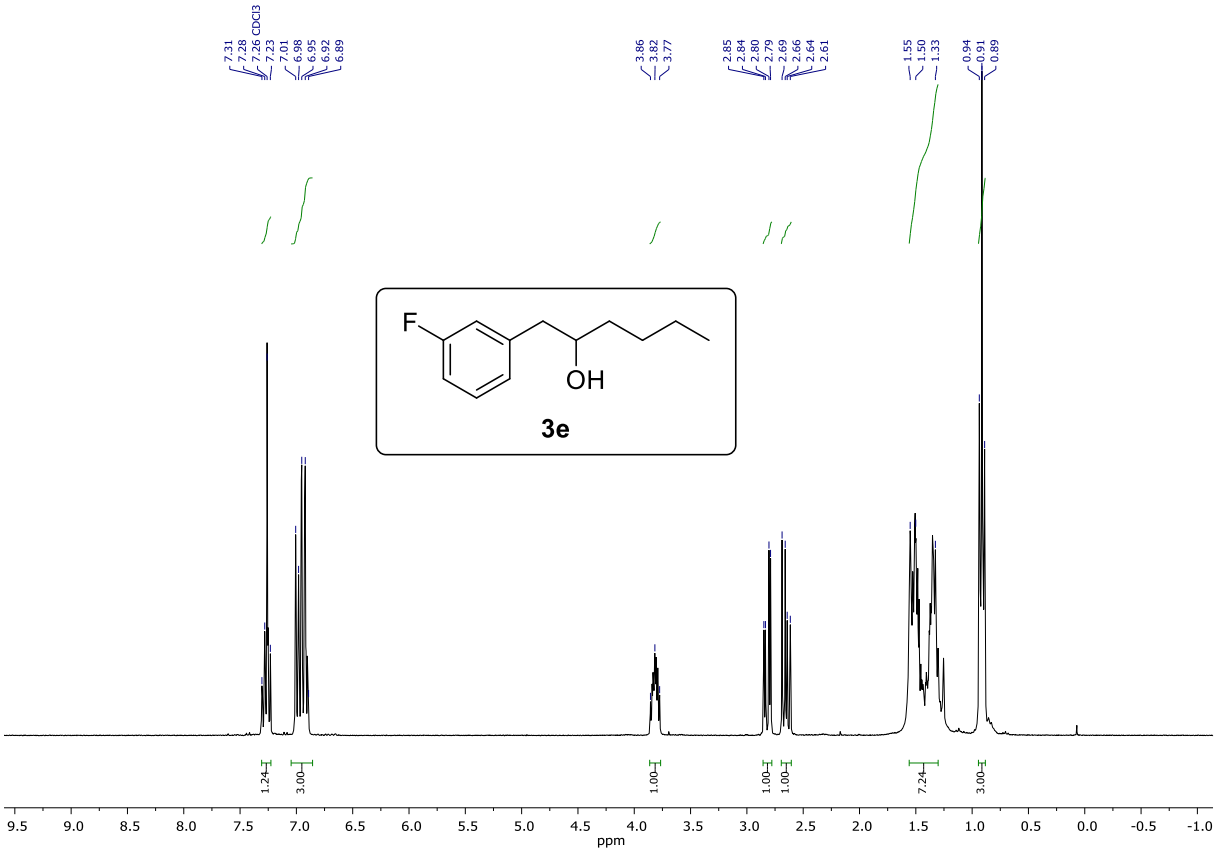


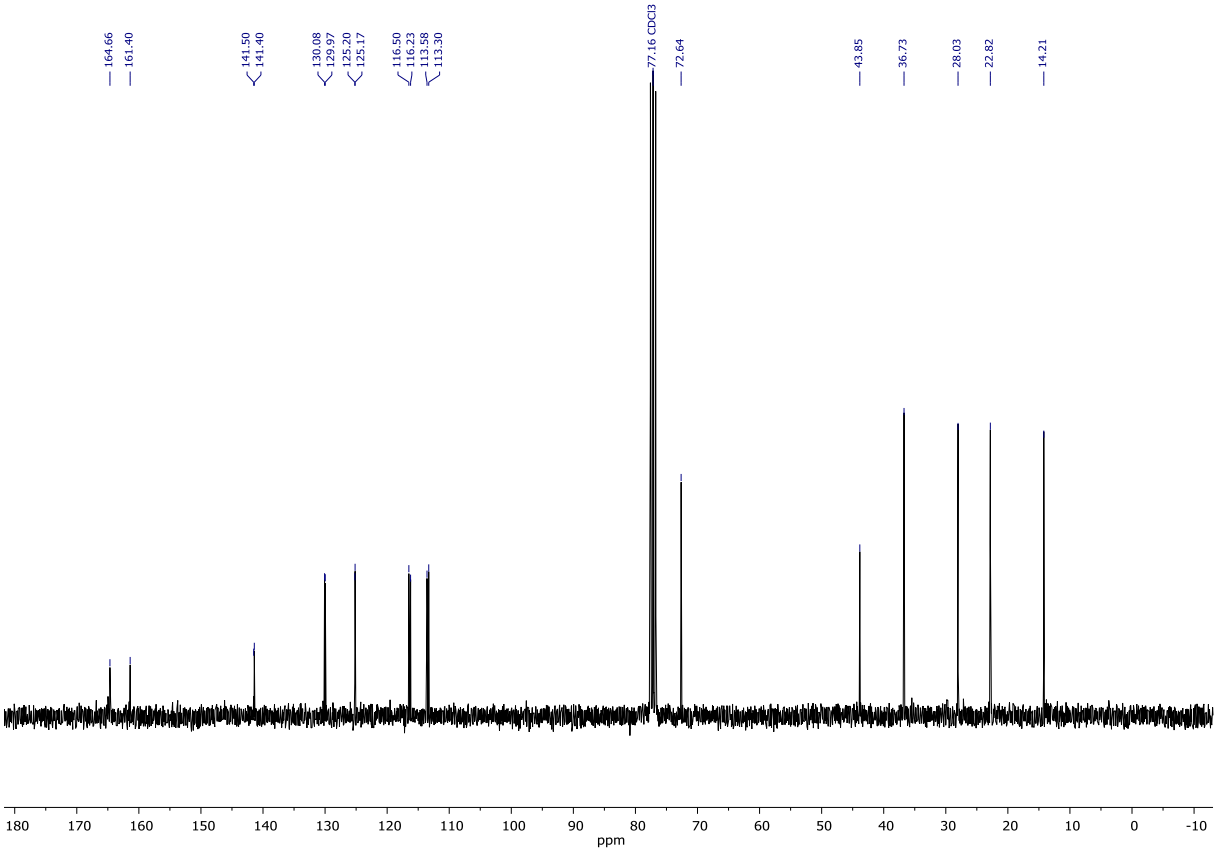
Compound **3d**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)

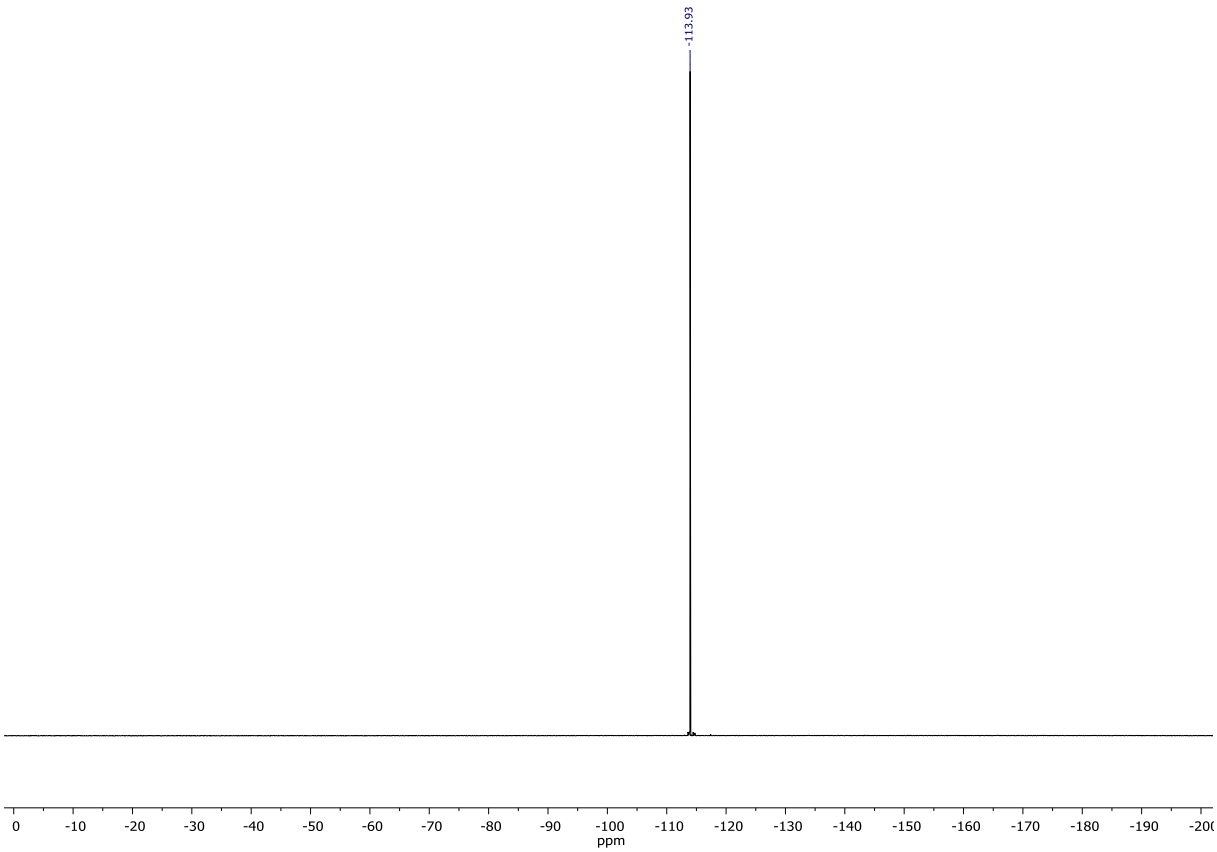




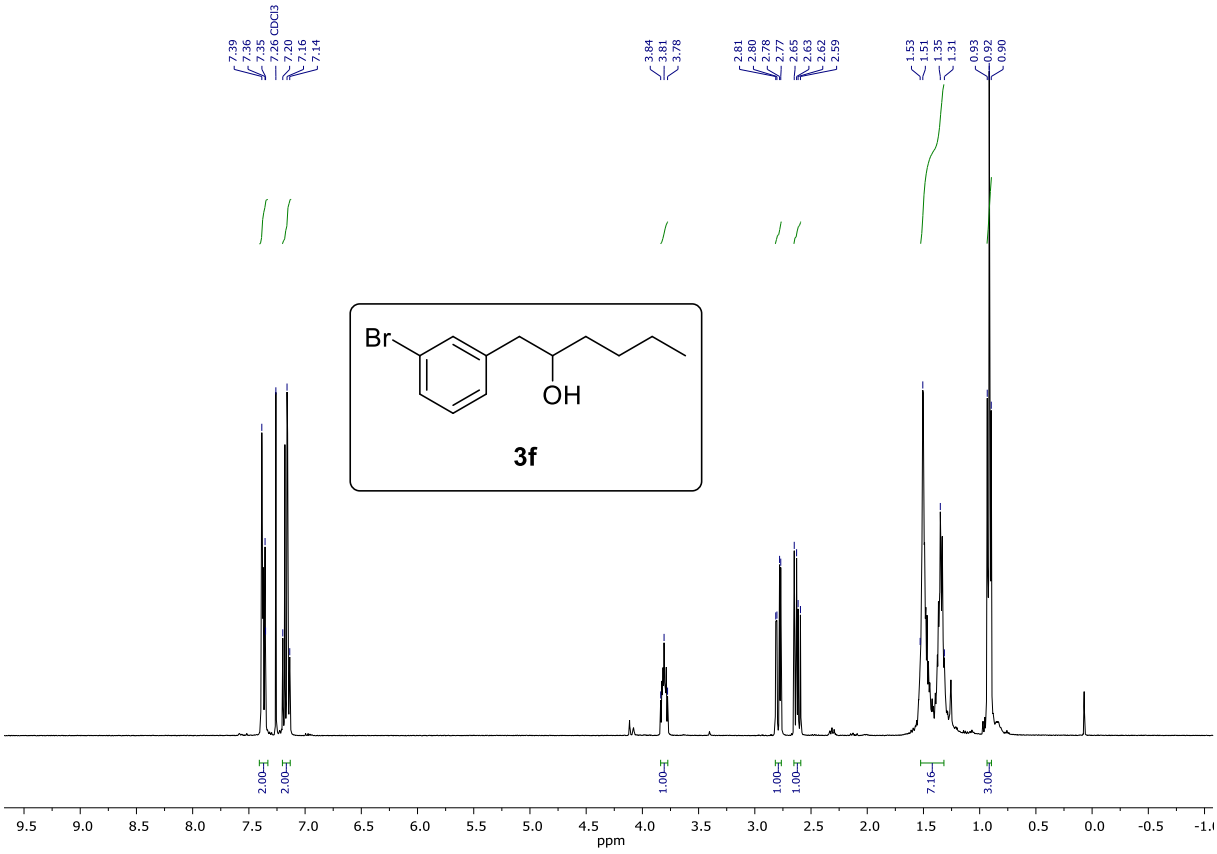
Compound **3e**, ^{1}H-, ^{13}C-NMR and ^{19}F-NMR ($CDCl_3$)

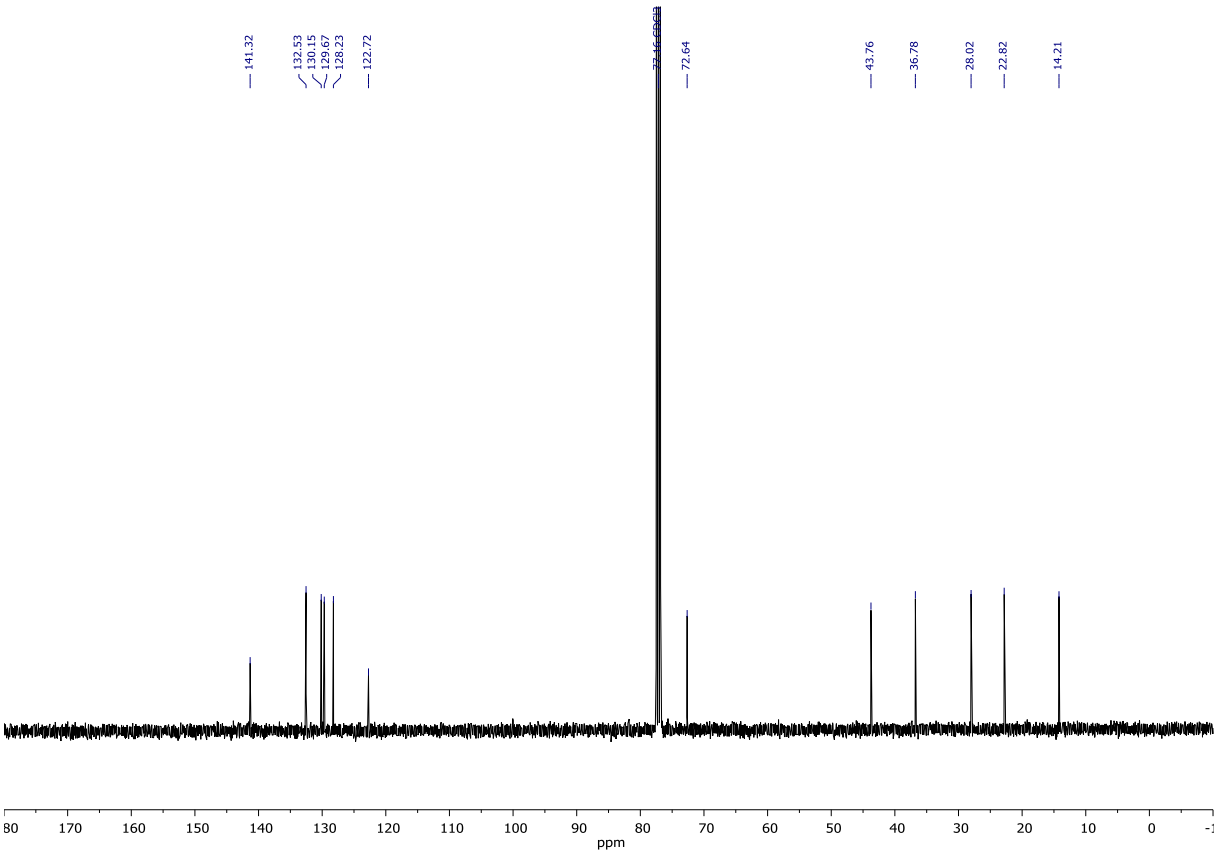




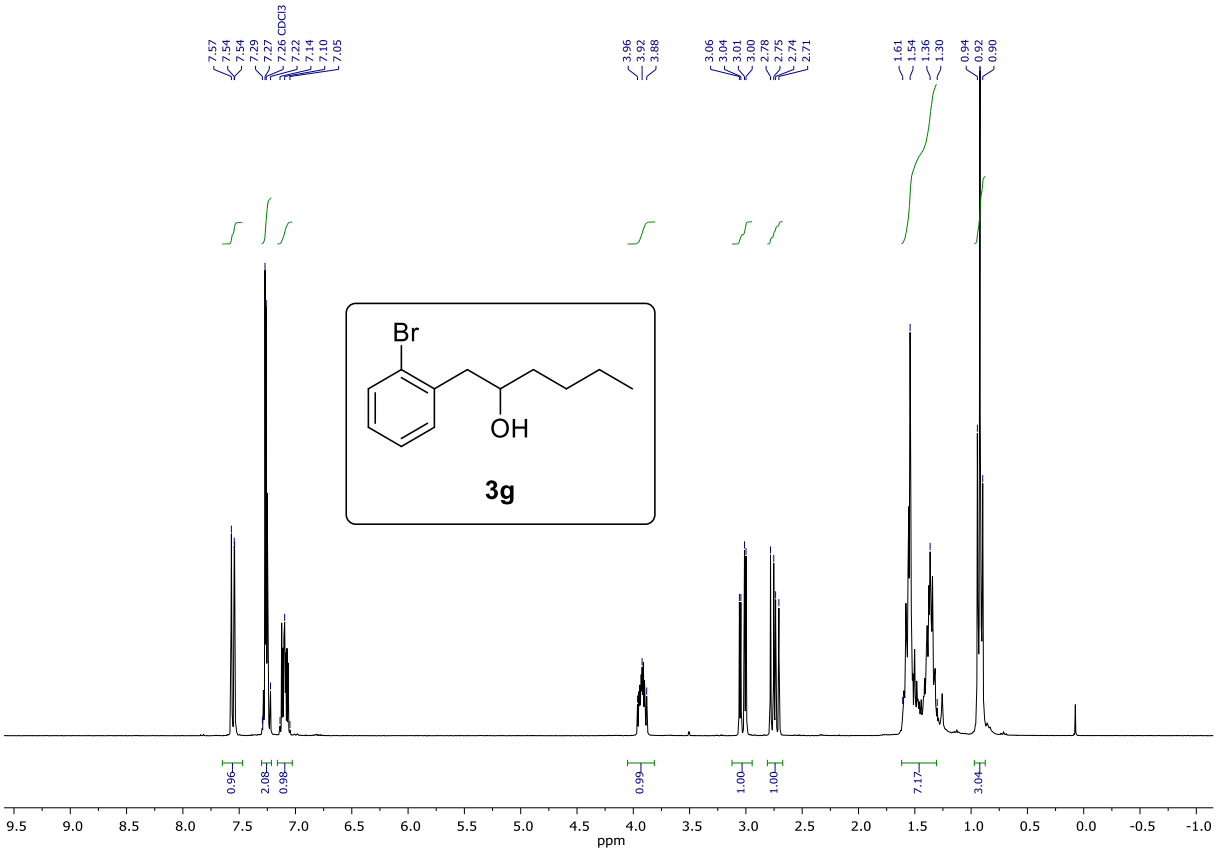

-113.93
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
ppm

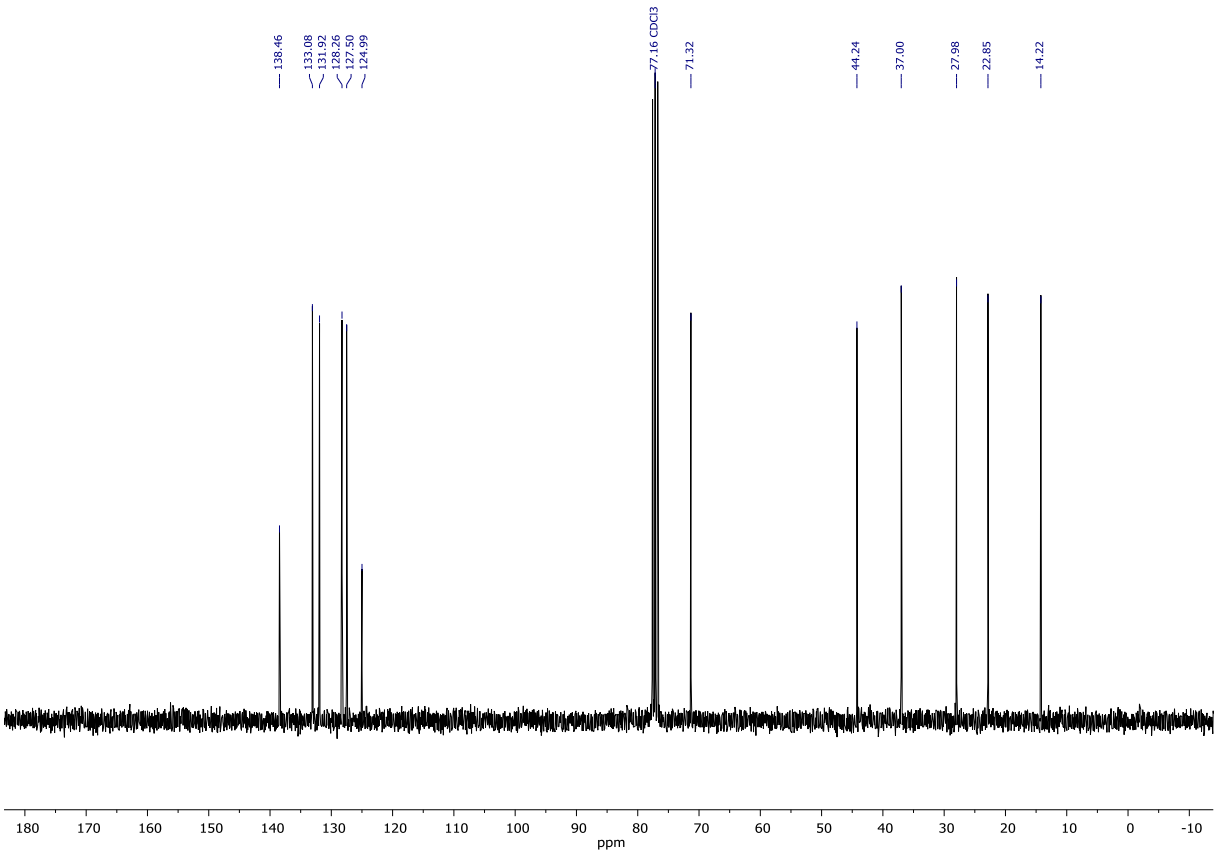
Compound **3f**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



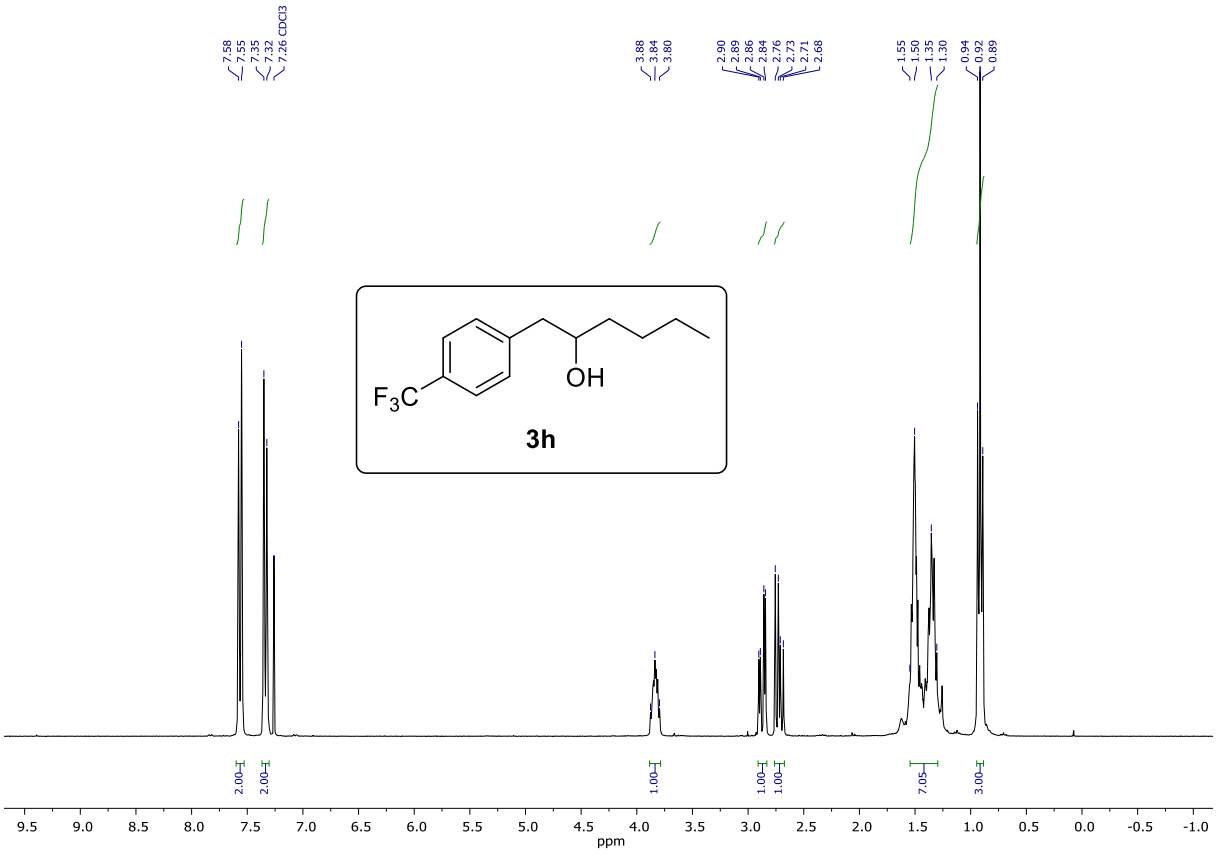


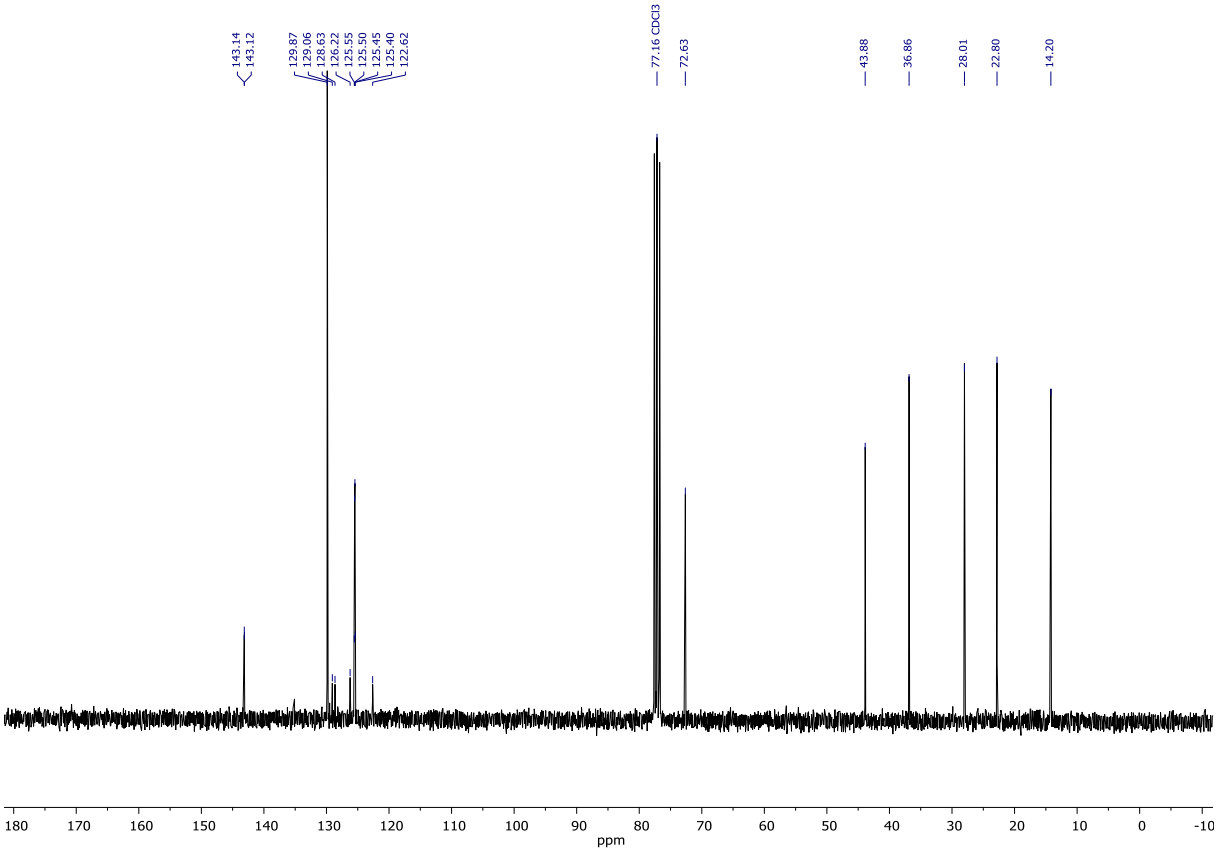
Compound **3g**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)

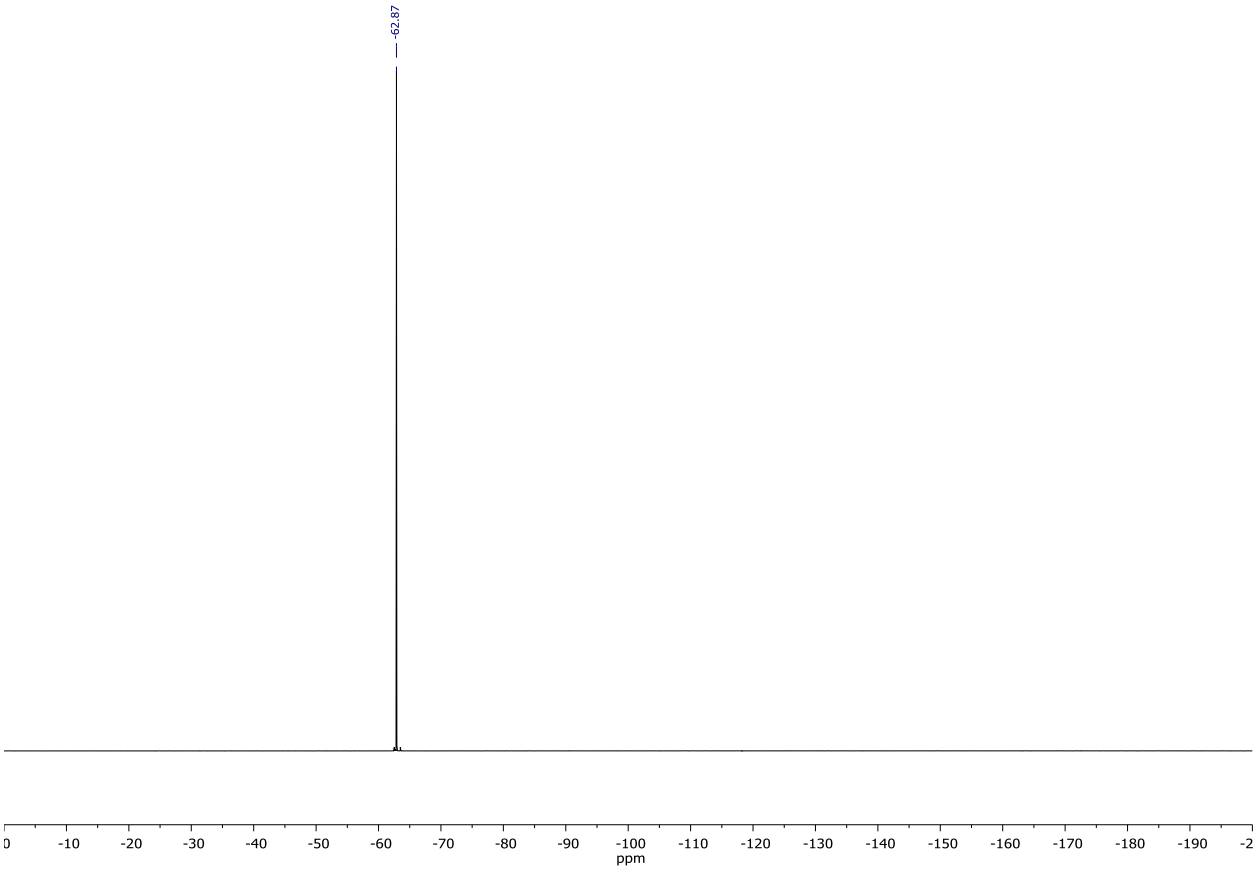




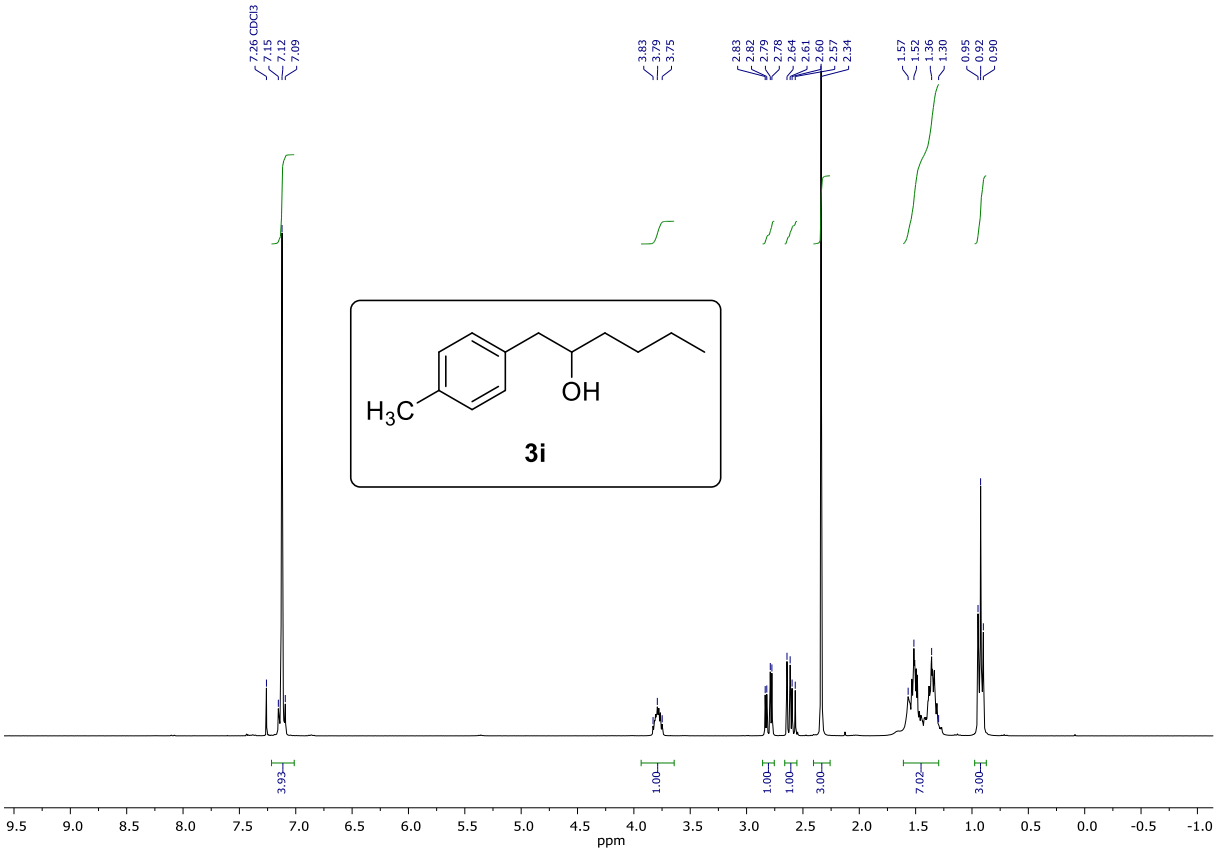
Compound **3h**, ^{1}H-, ^{13}C-NMR and ^{19}F-NMR ($CDCl_3$)

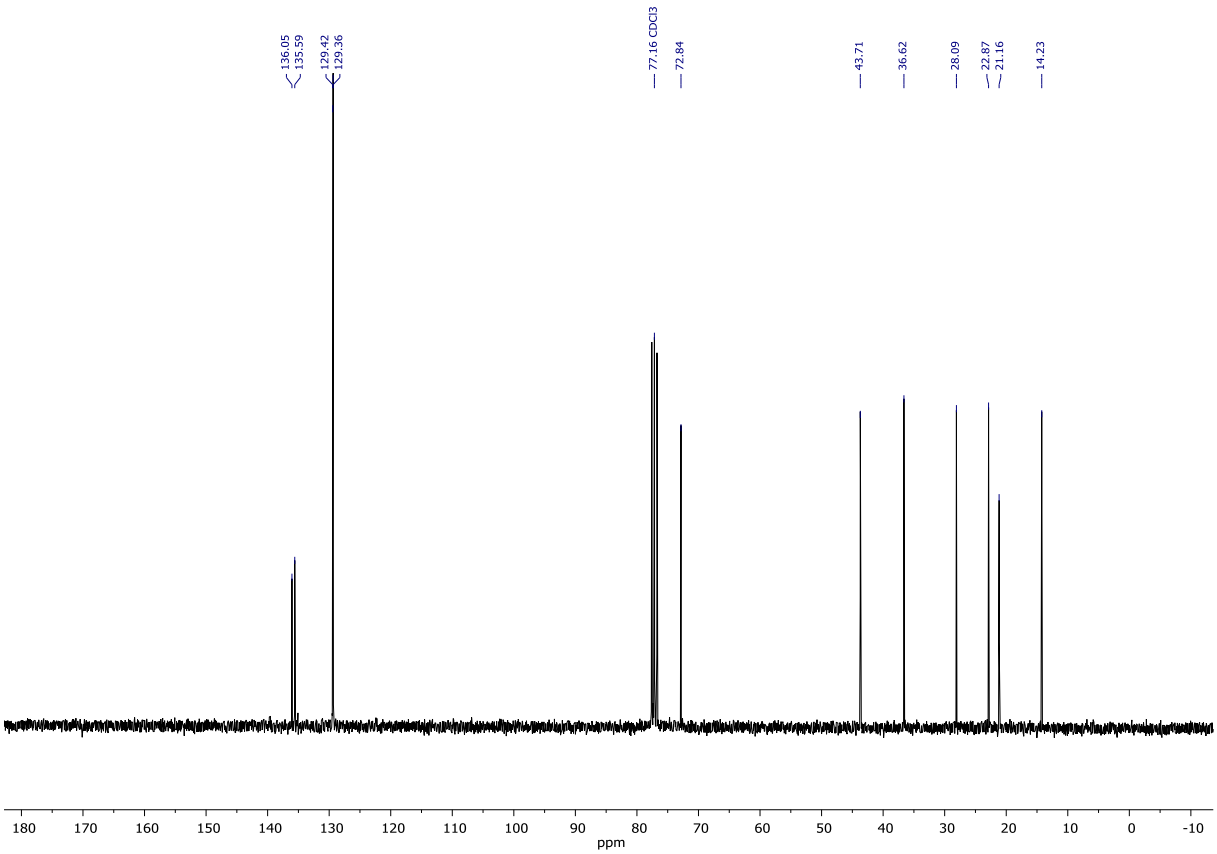




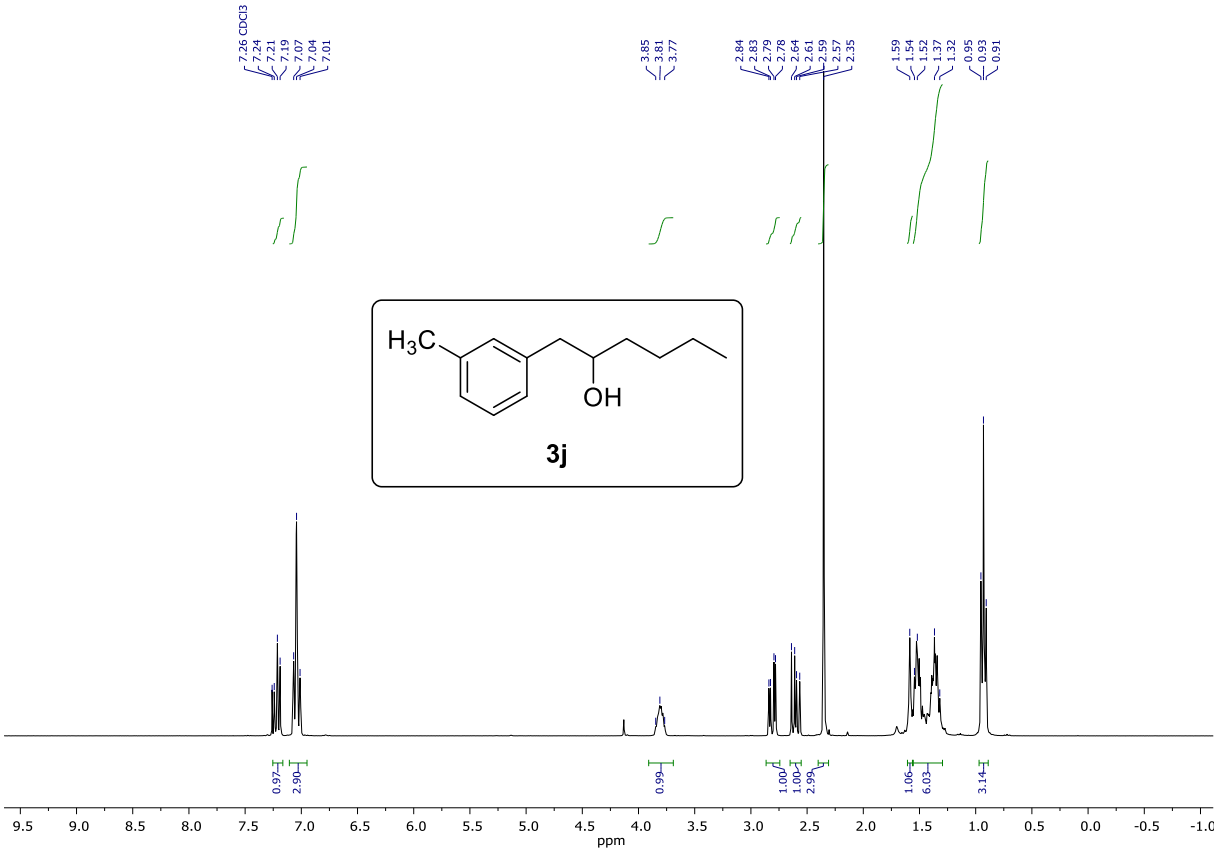

-62.87
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
ppm

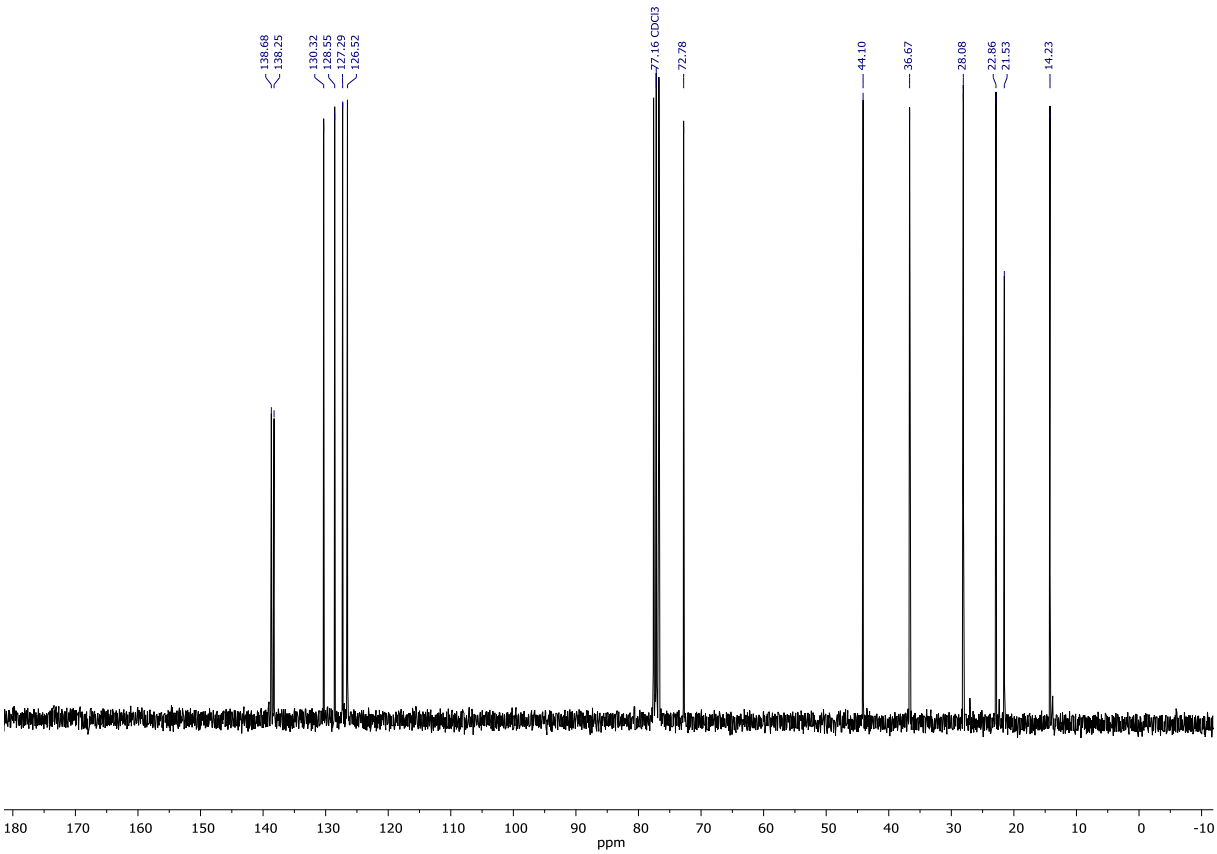
Compound **3i**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



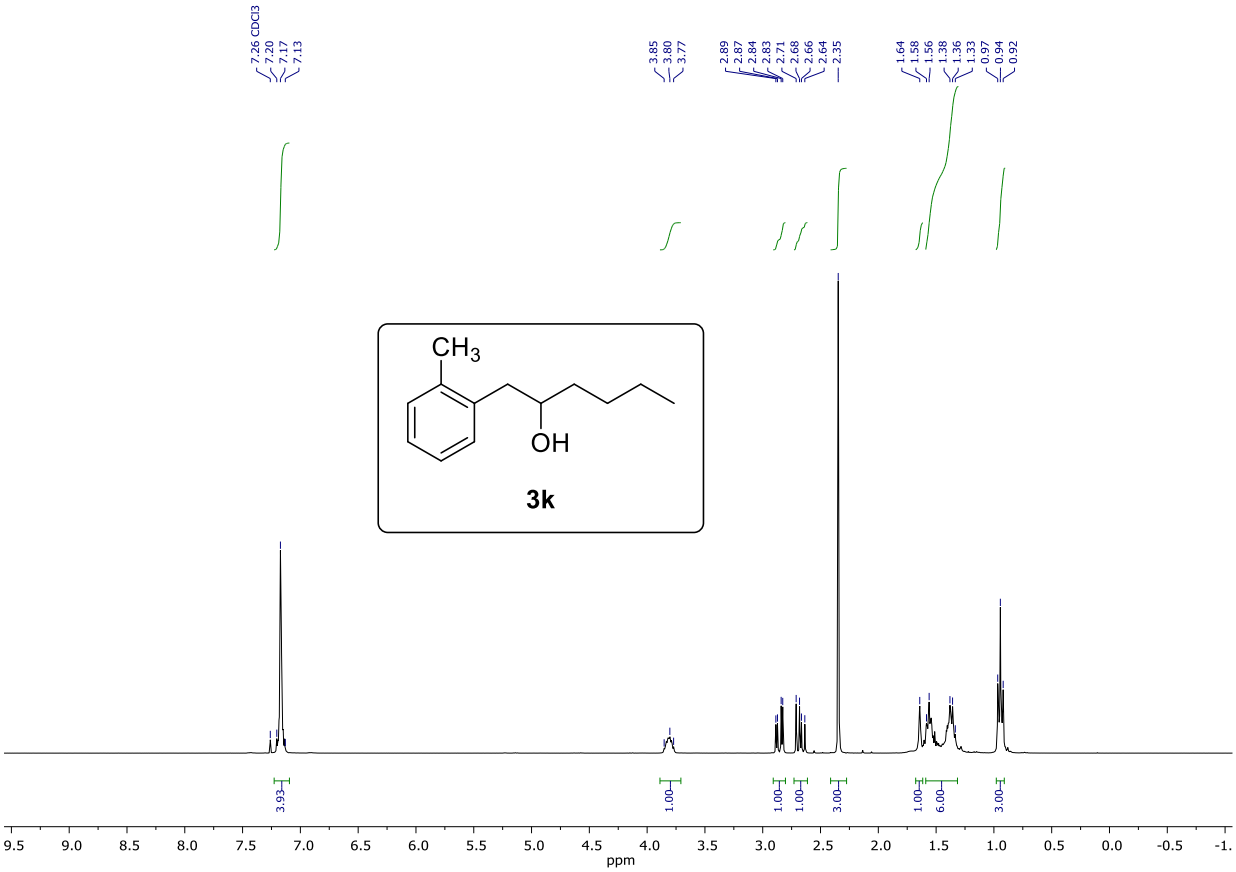


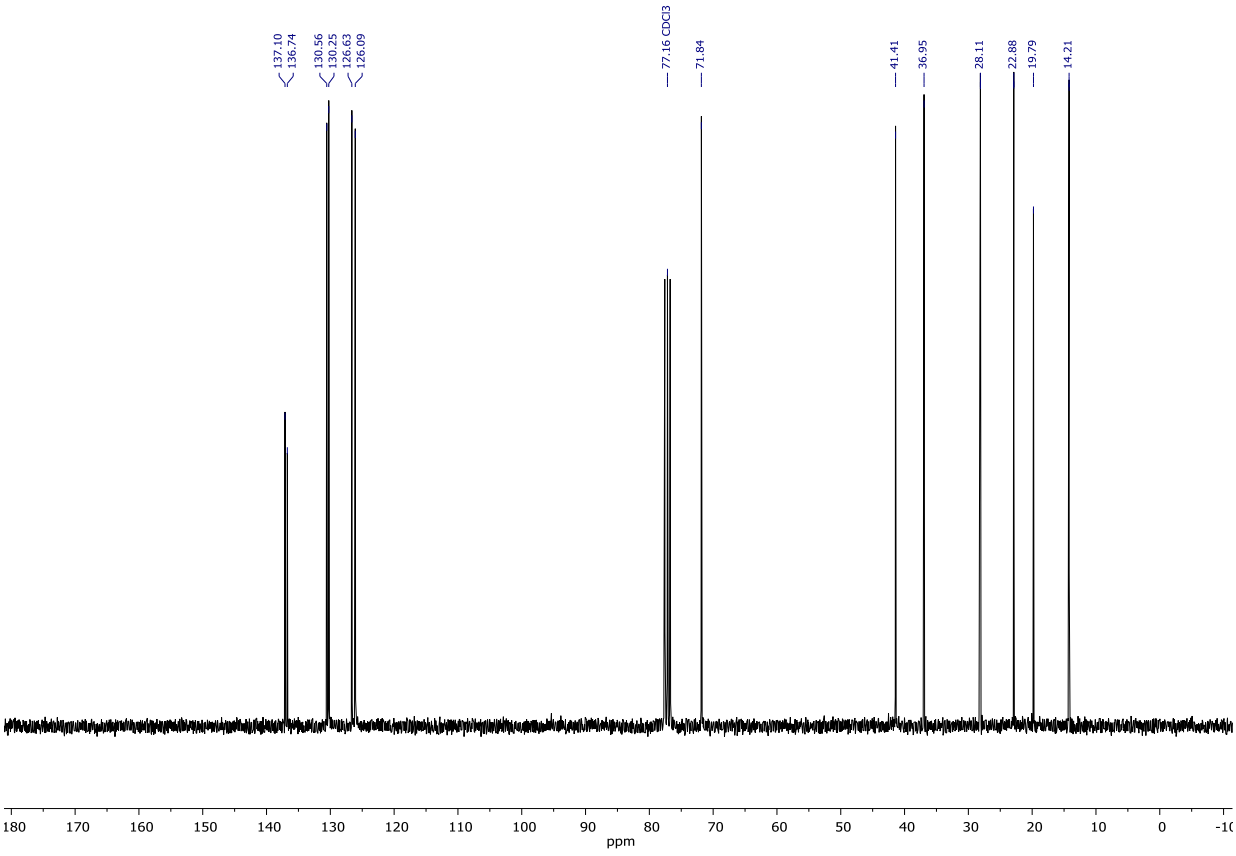
Compound **3j**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



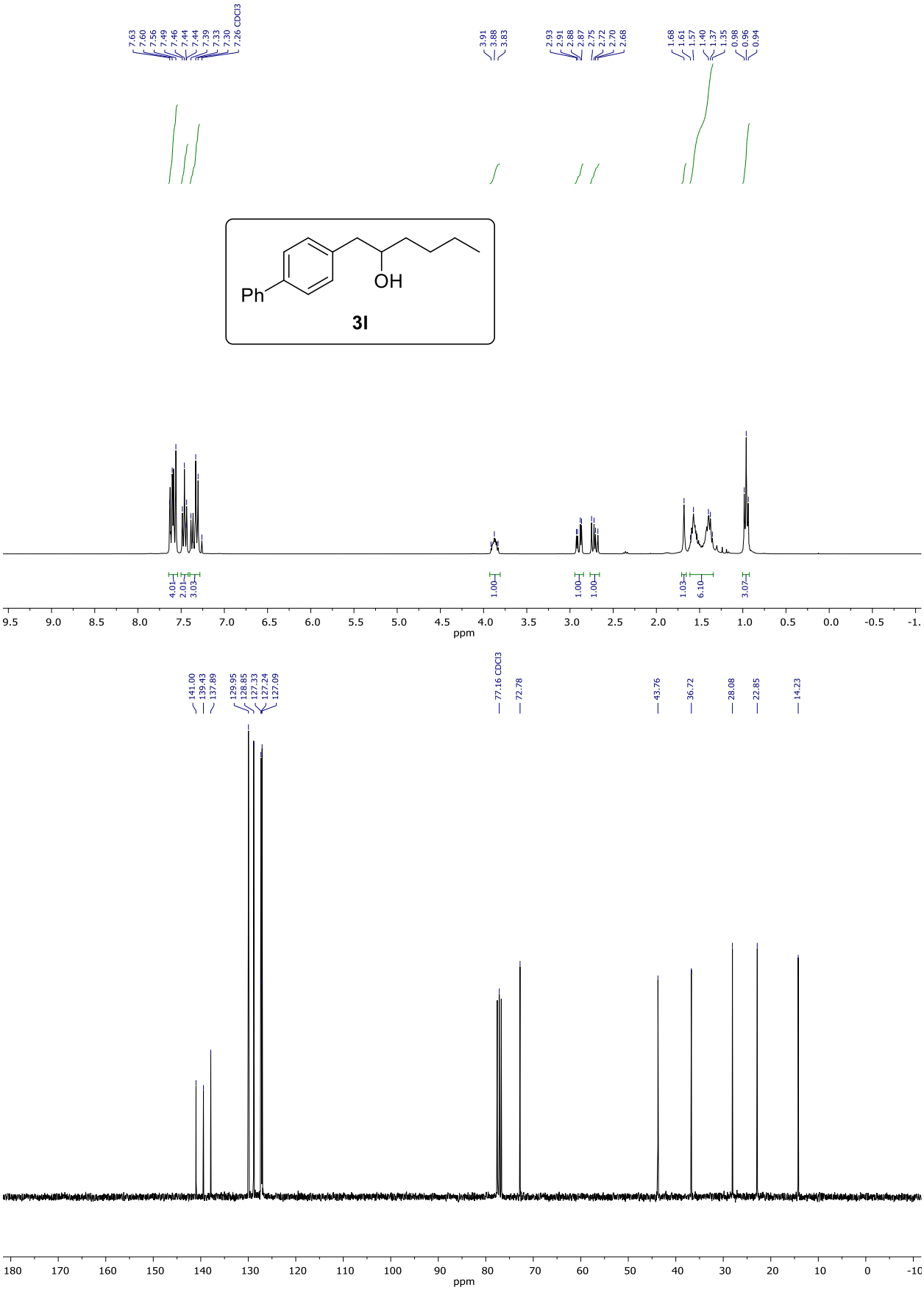


Compound **3k**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)

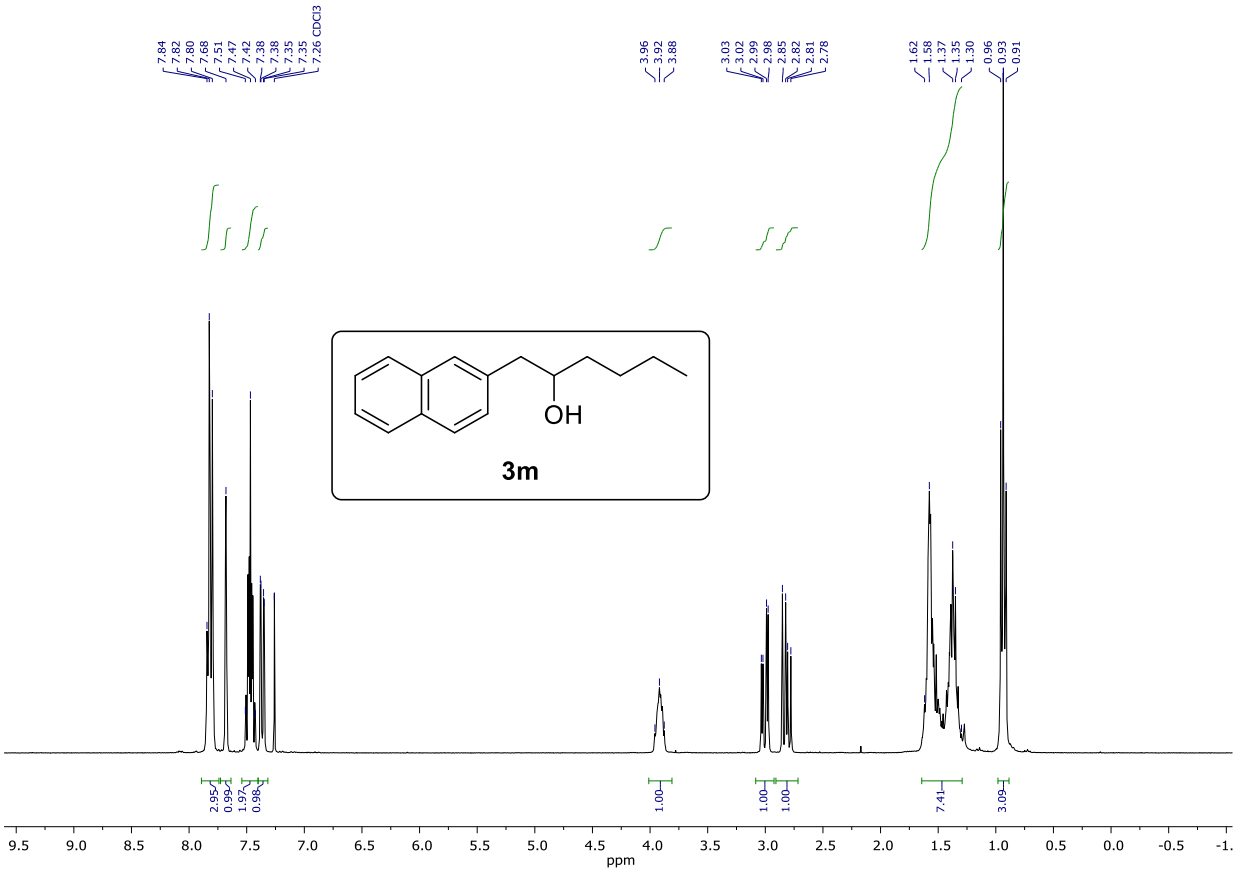


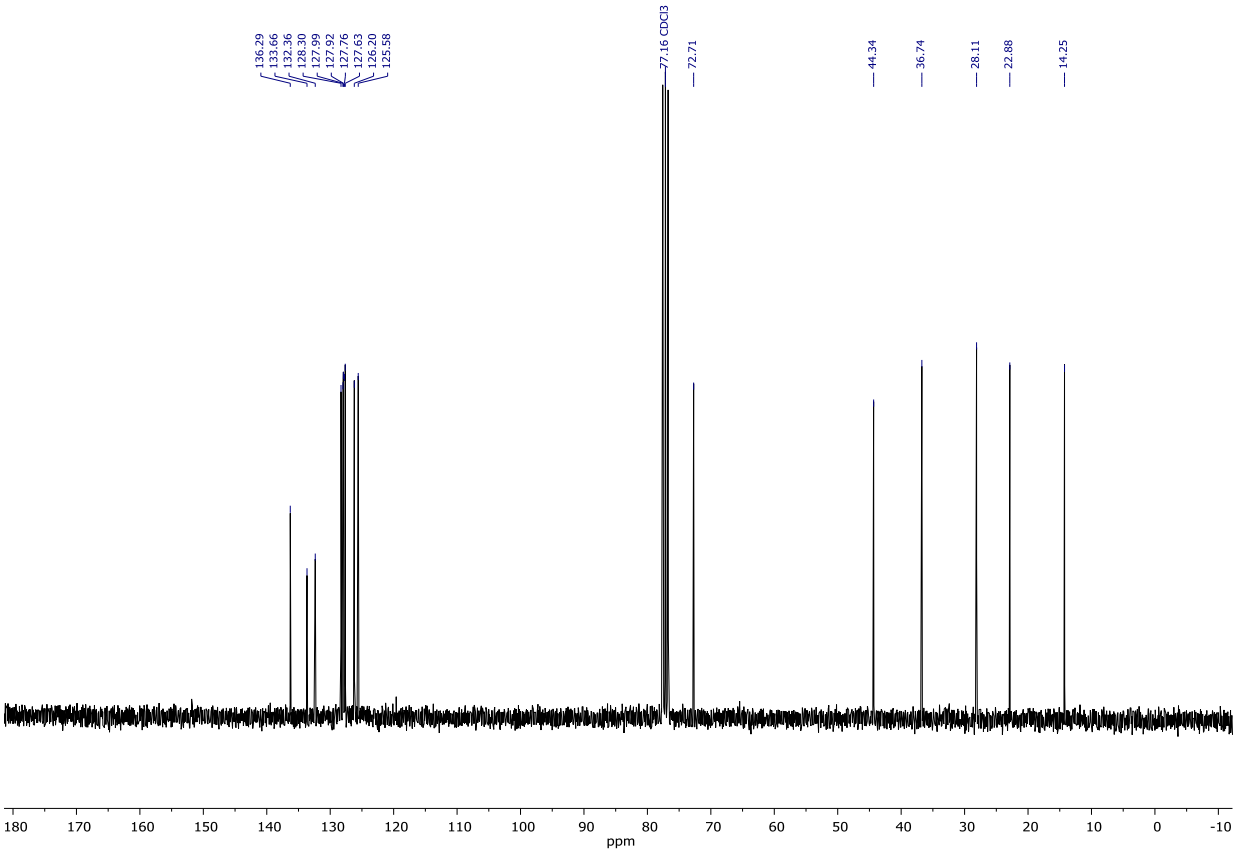


Compound **3l**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)

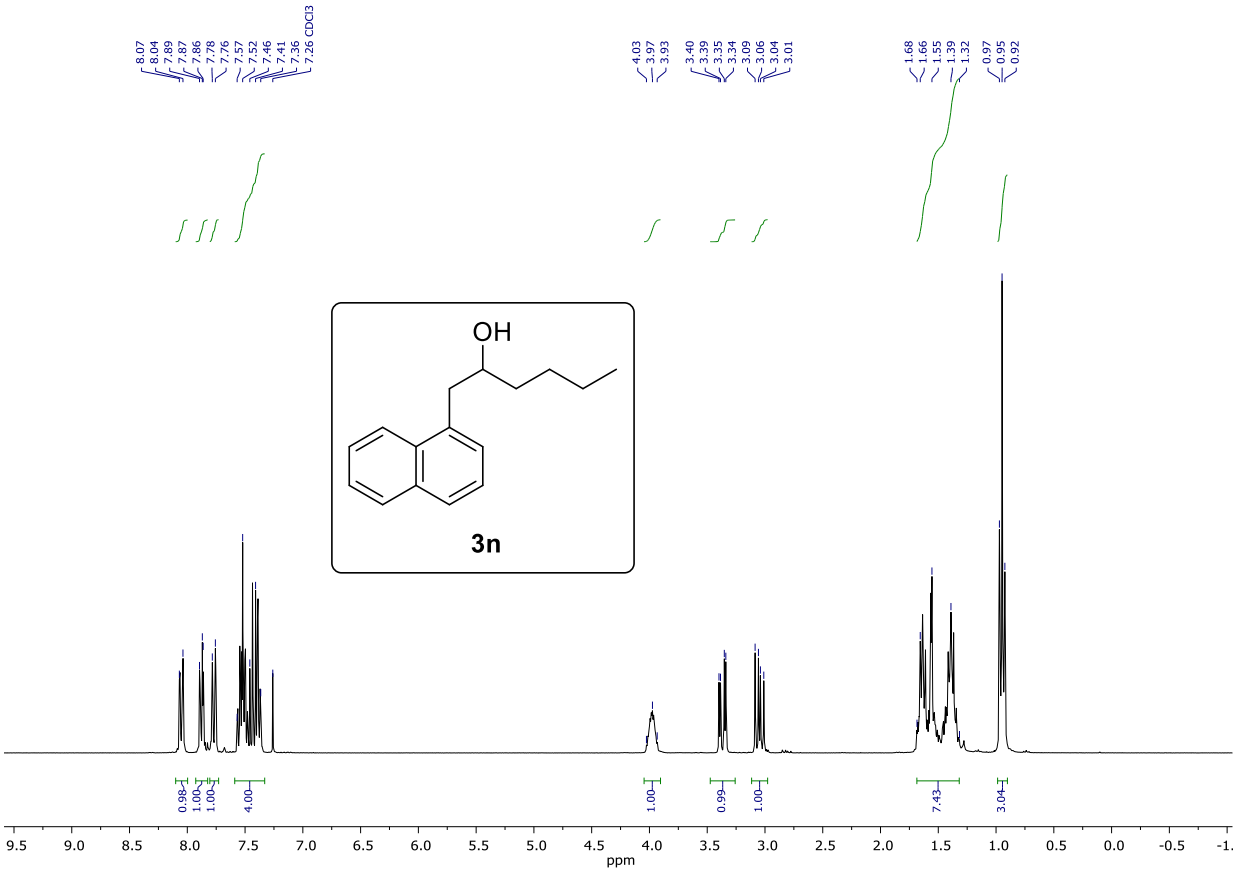


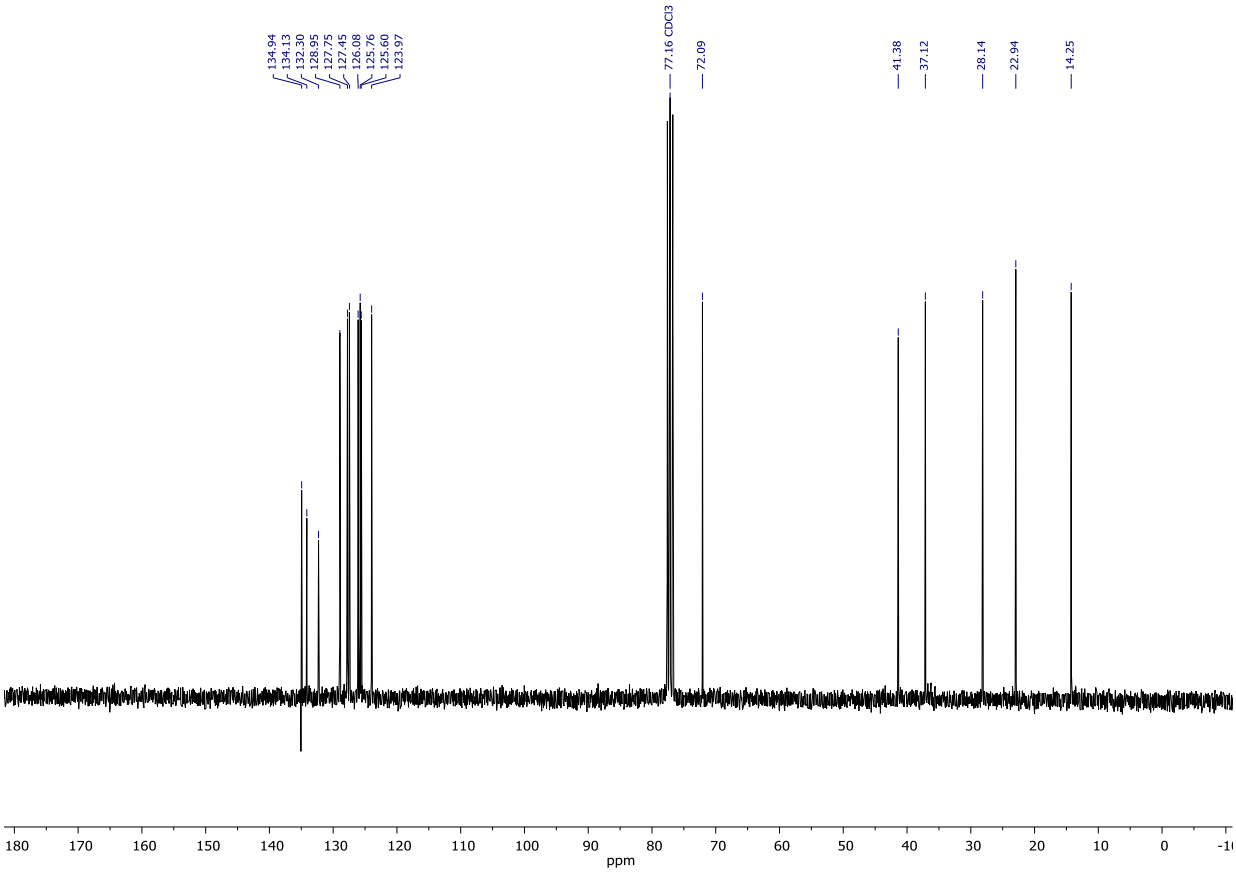
Compound **3m**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



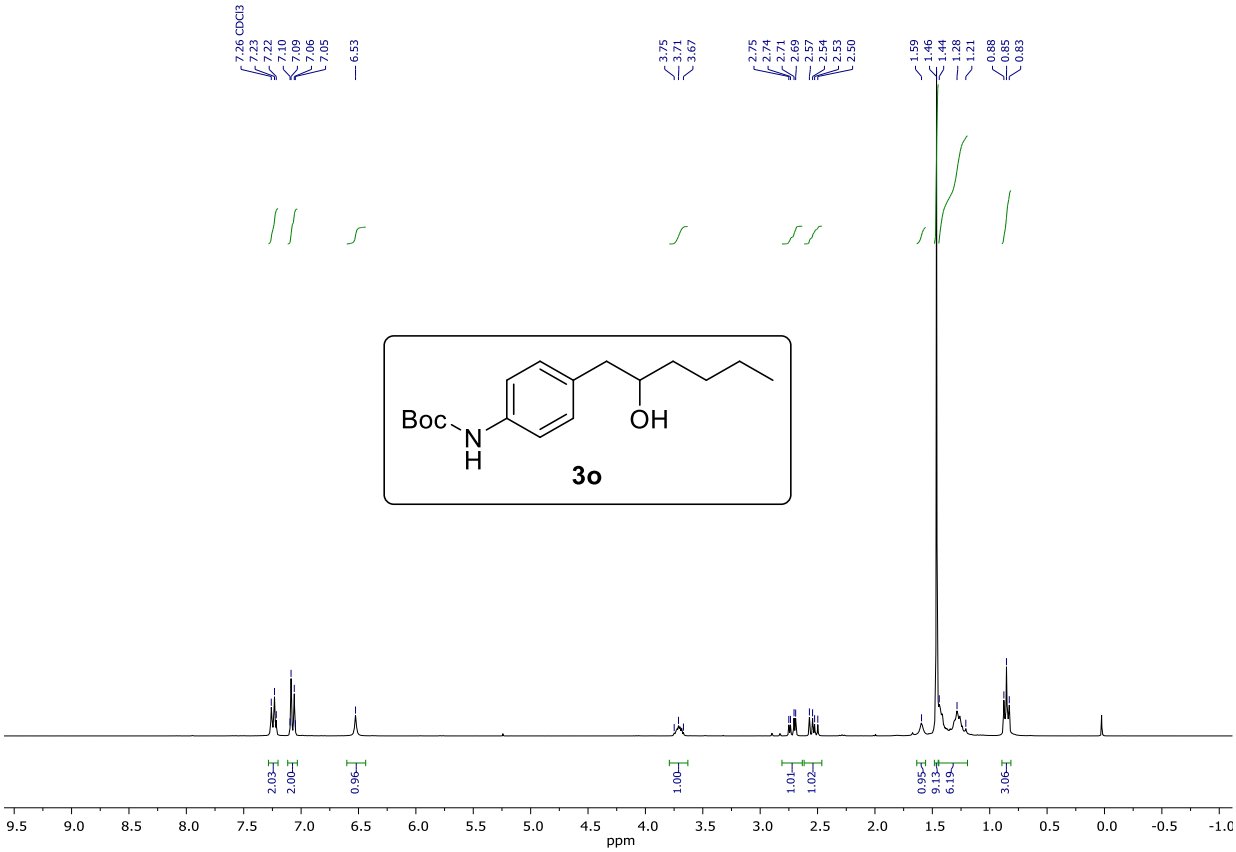


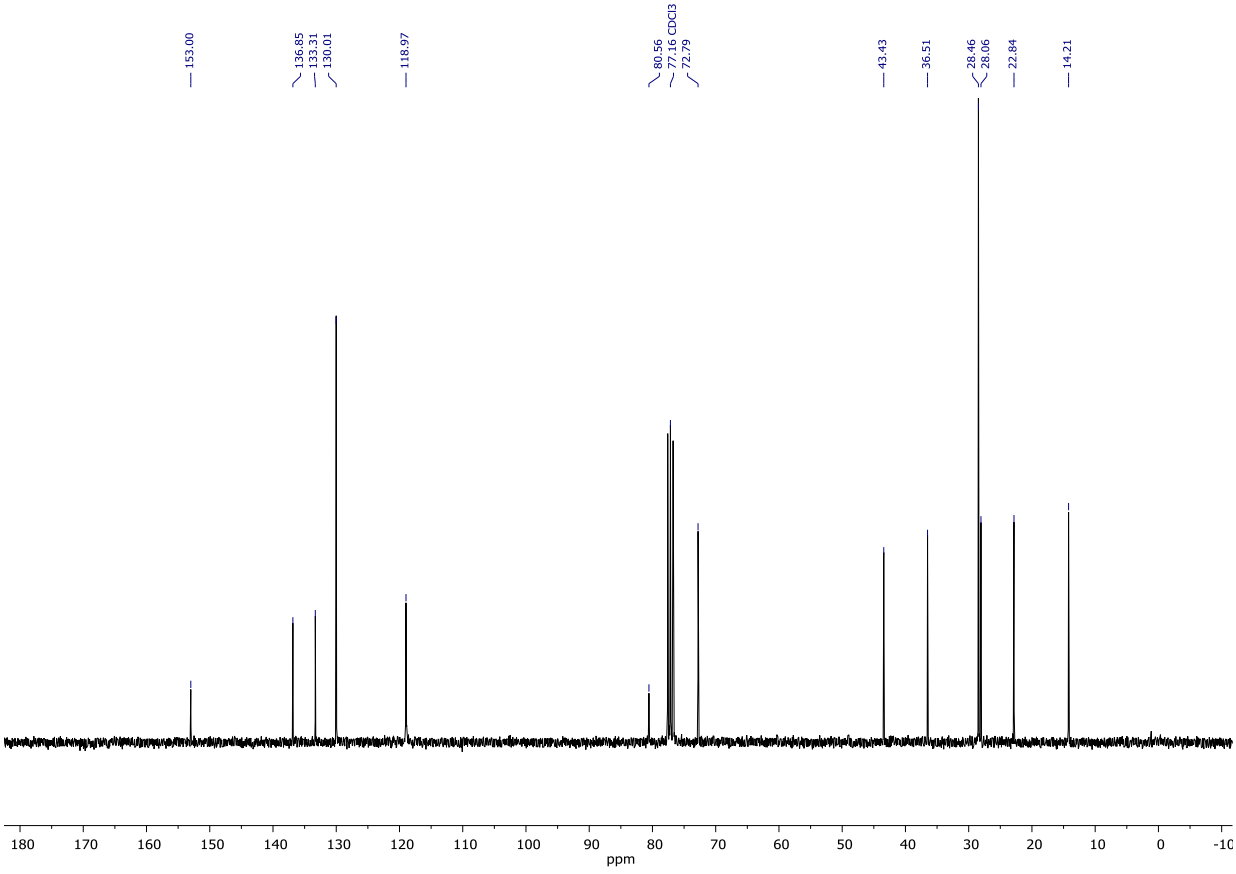
Compound **3n**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



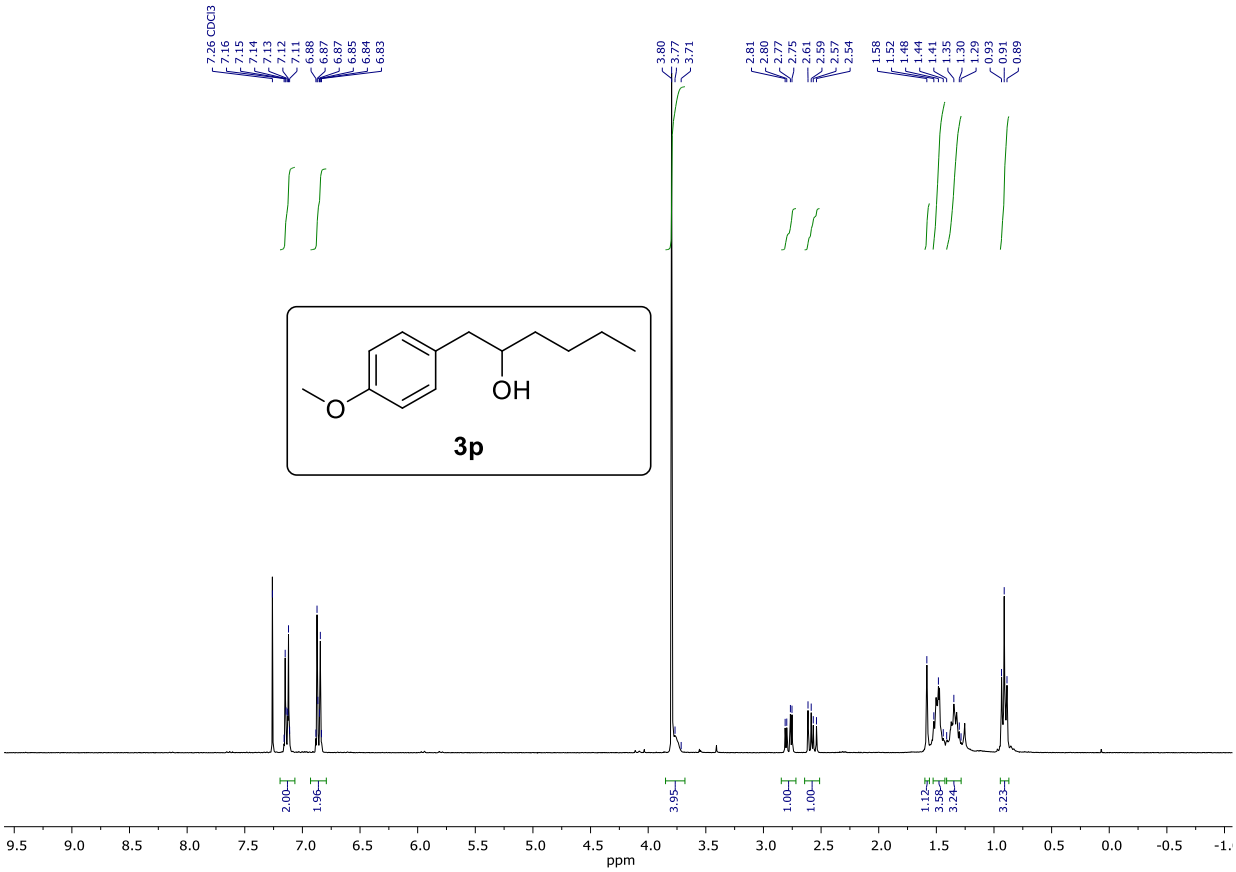


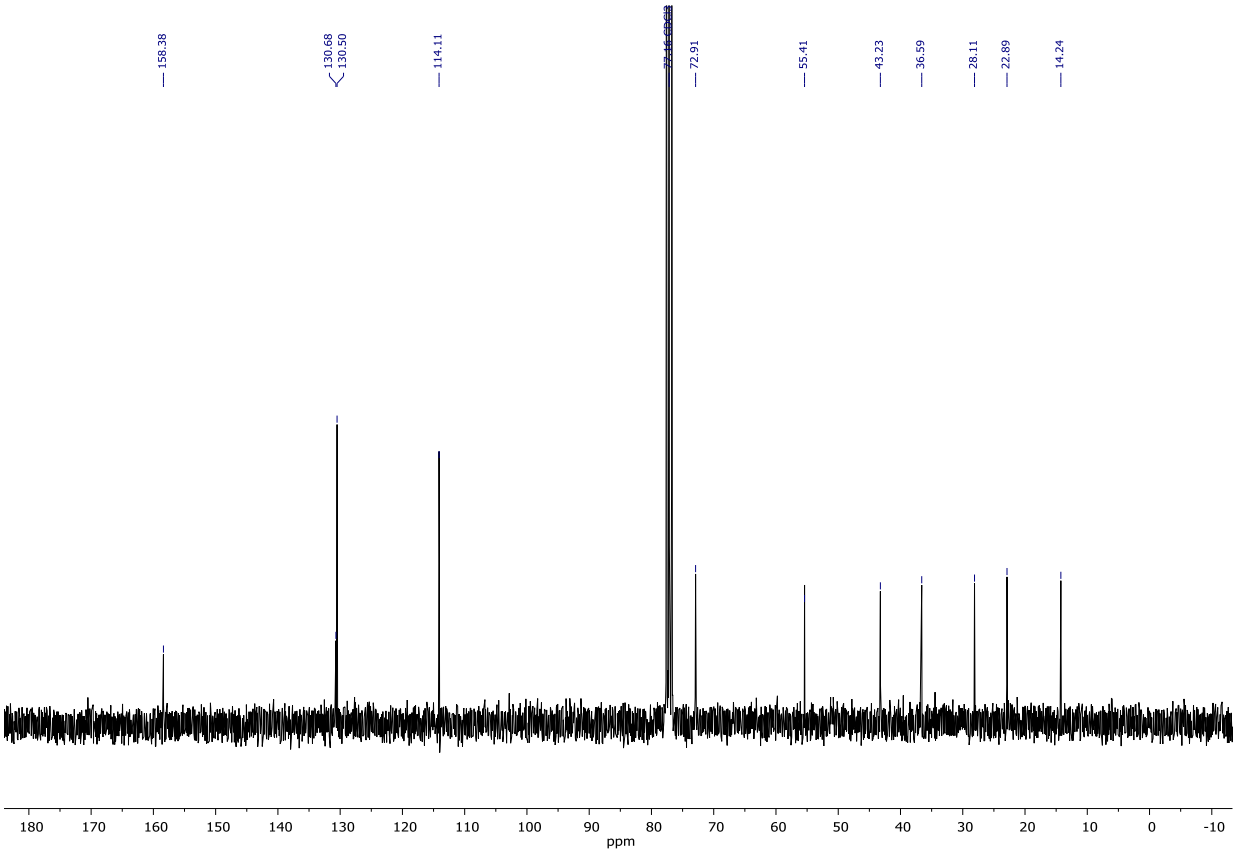
Compound **3o**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



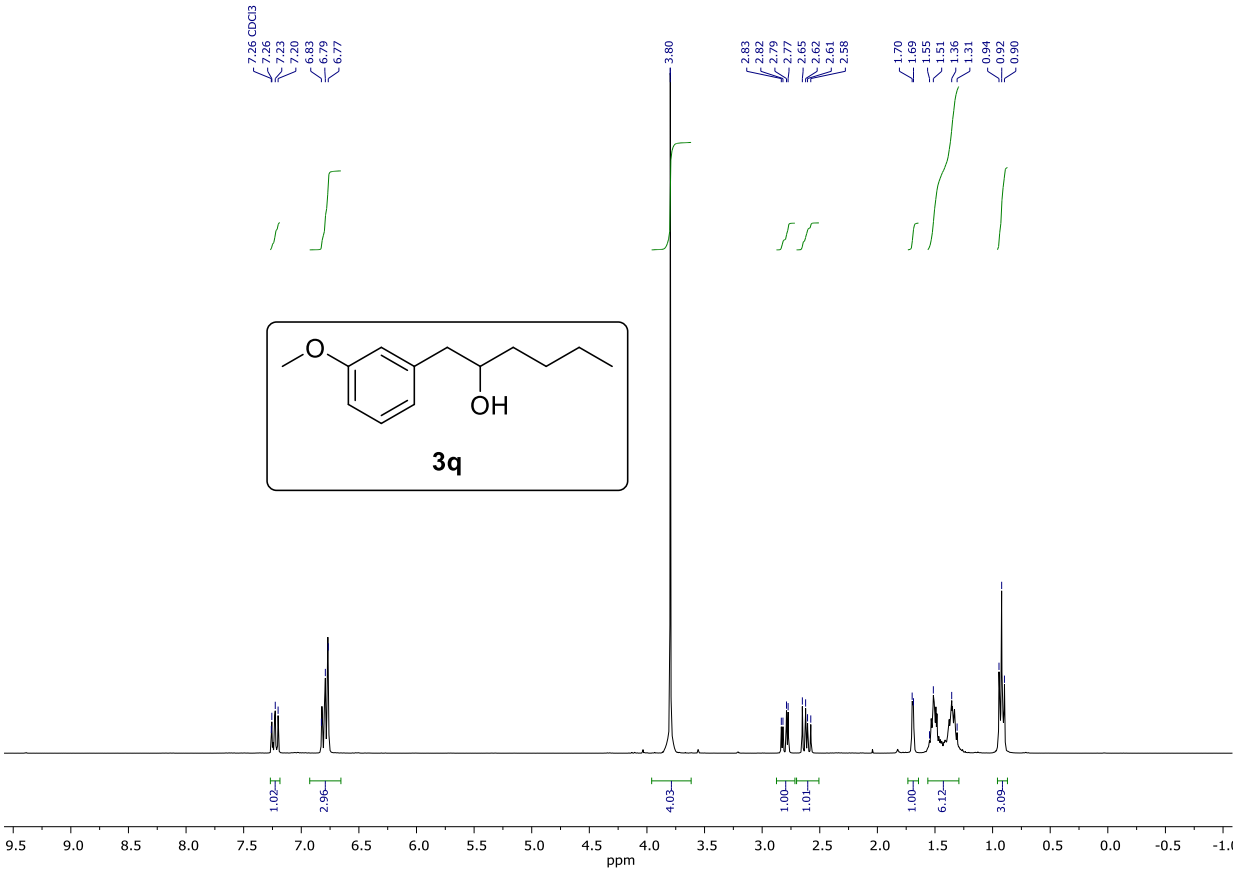


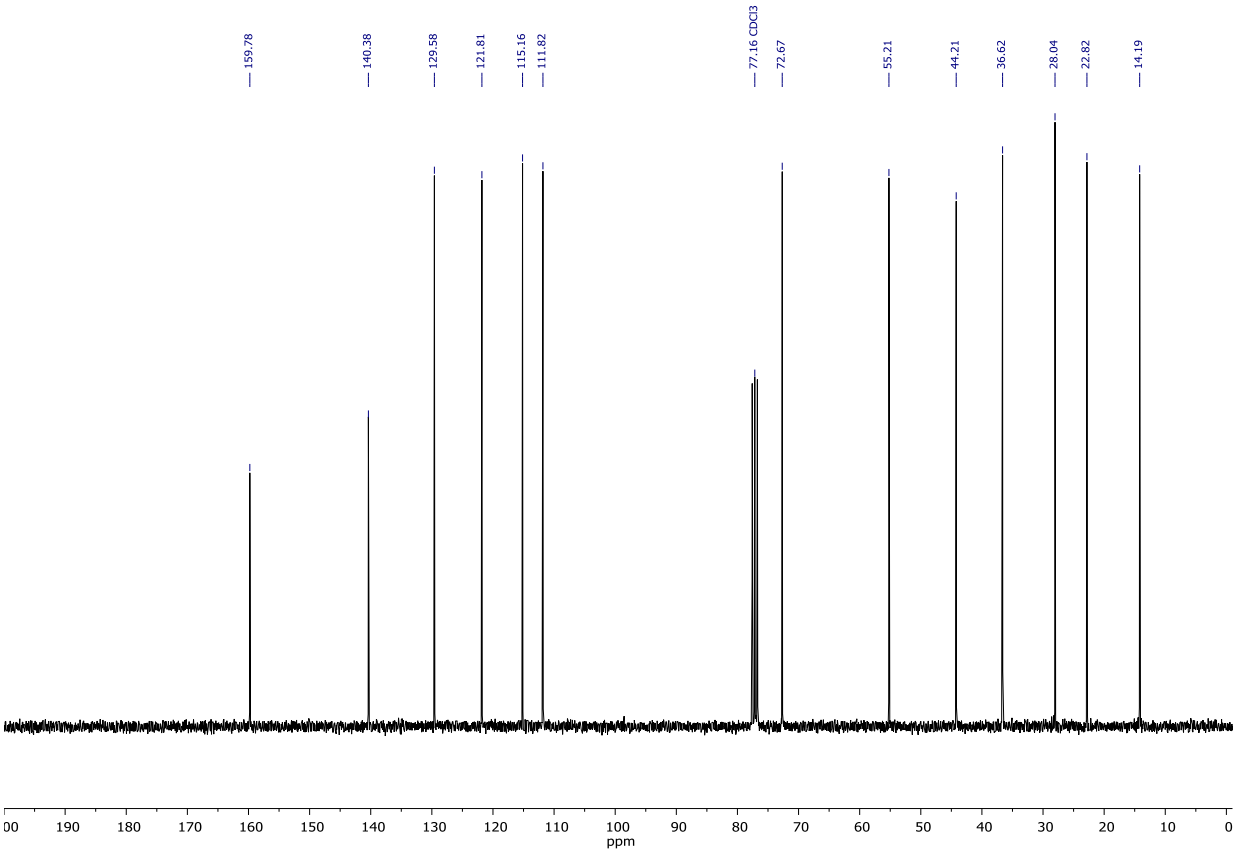
Compound **3p**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



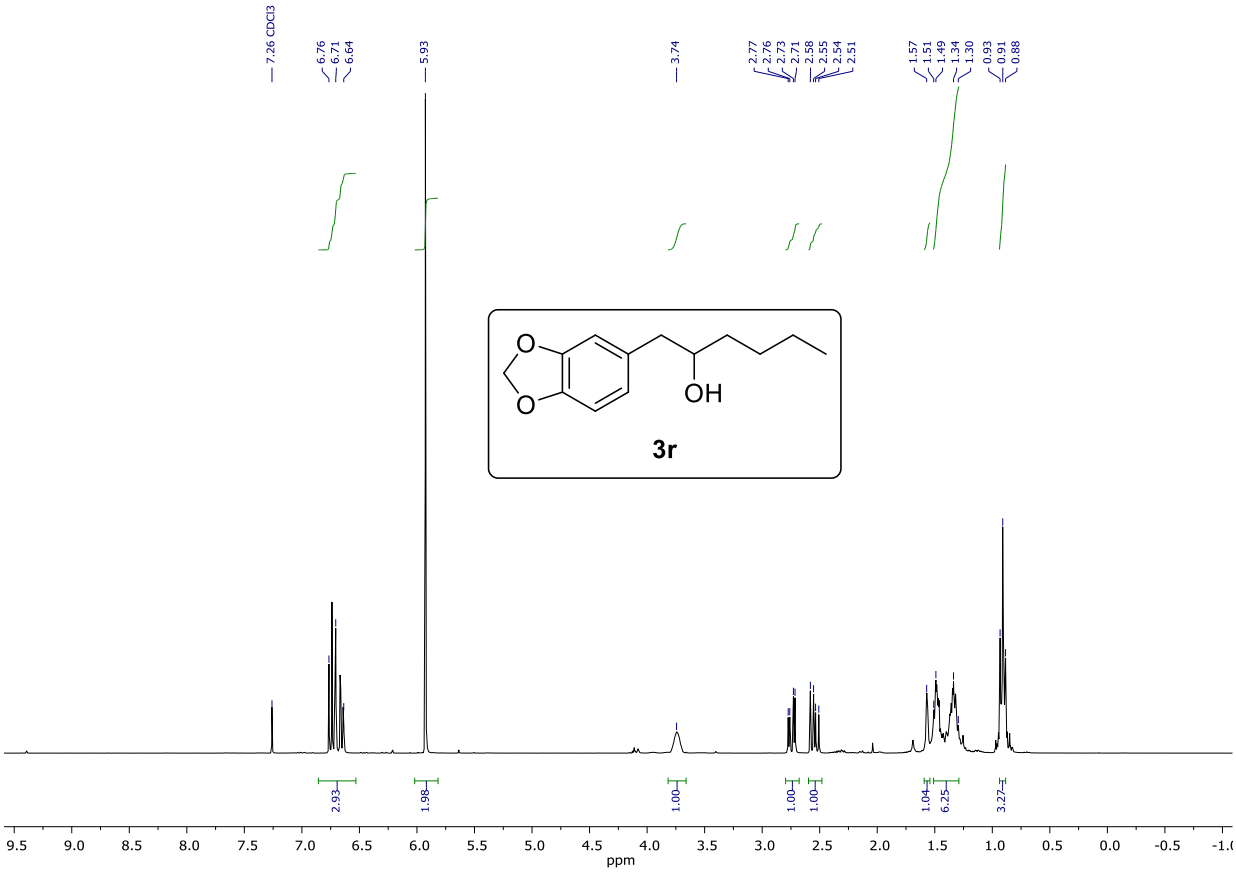


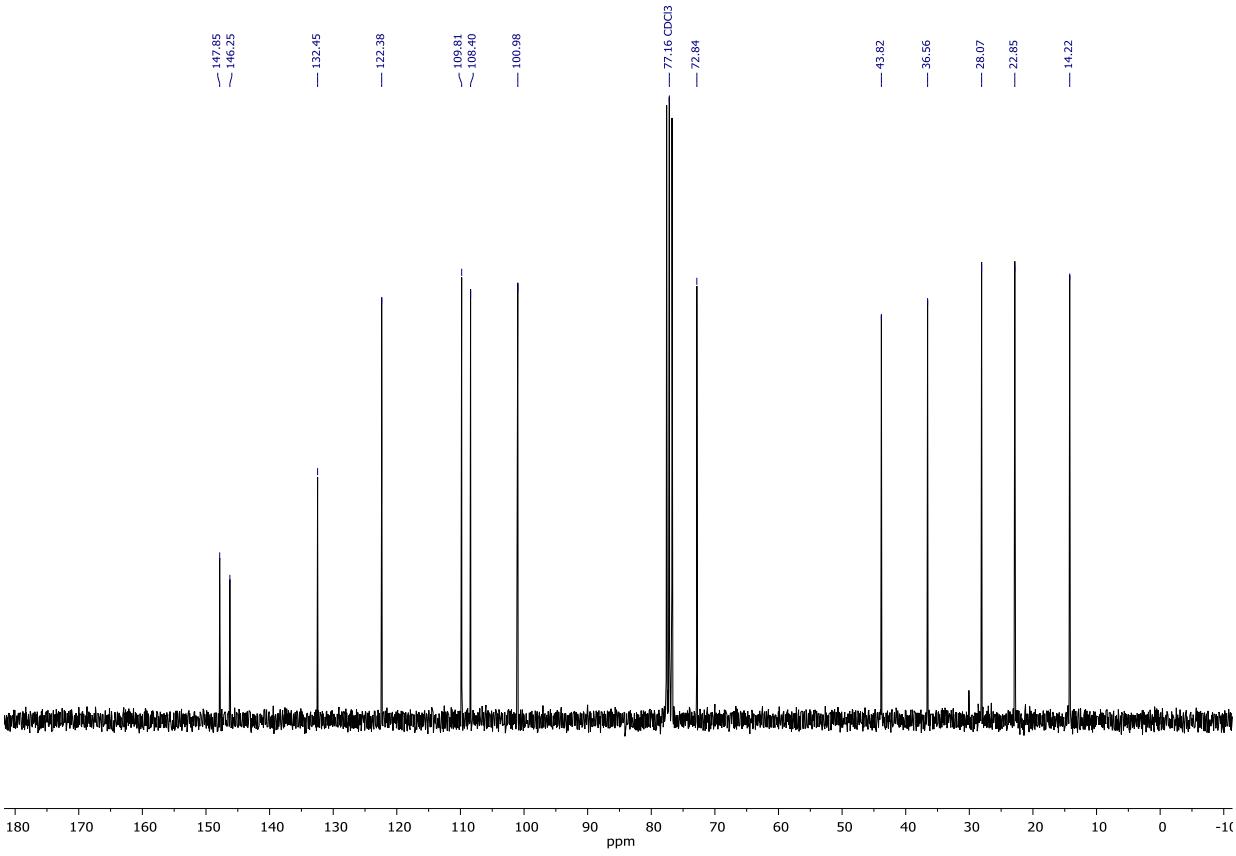
Compound **3q**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



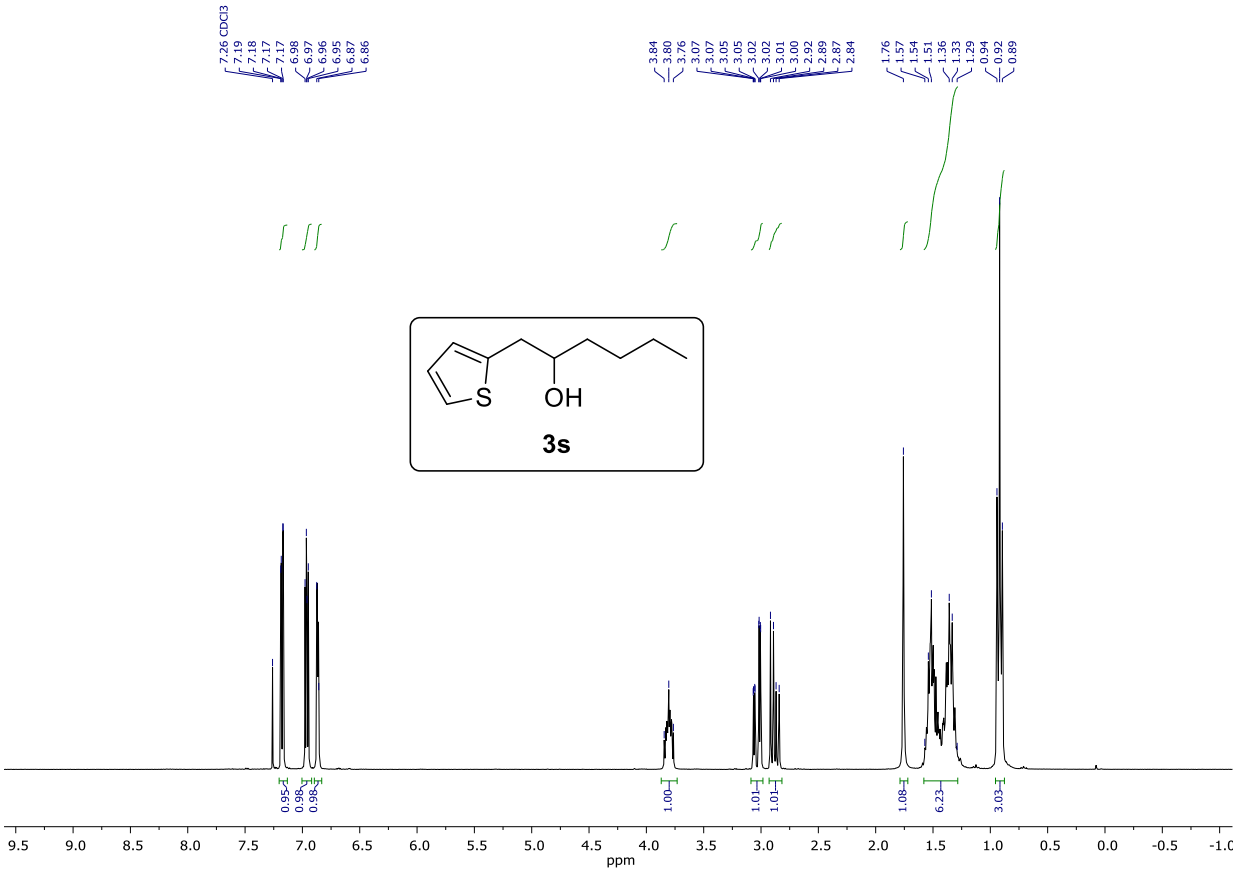


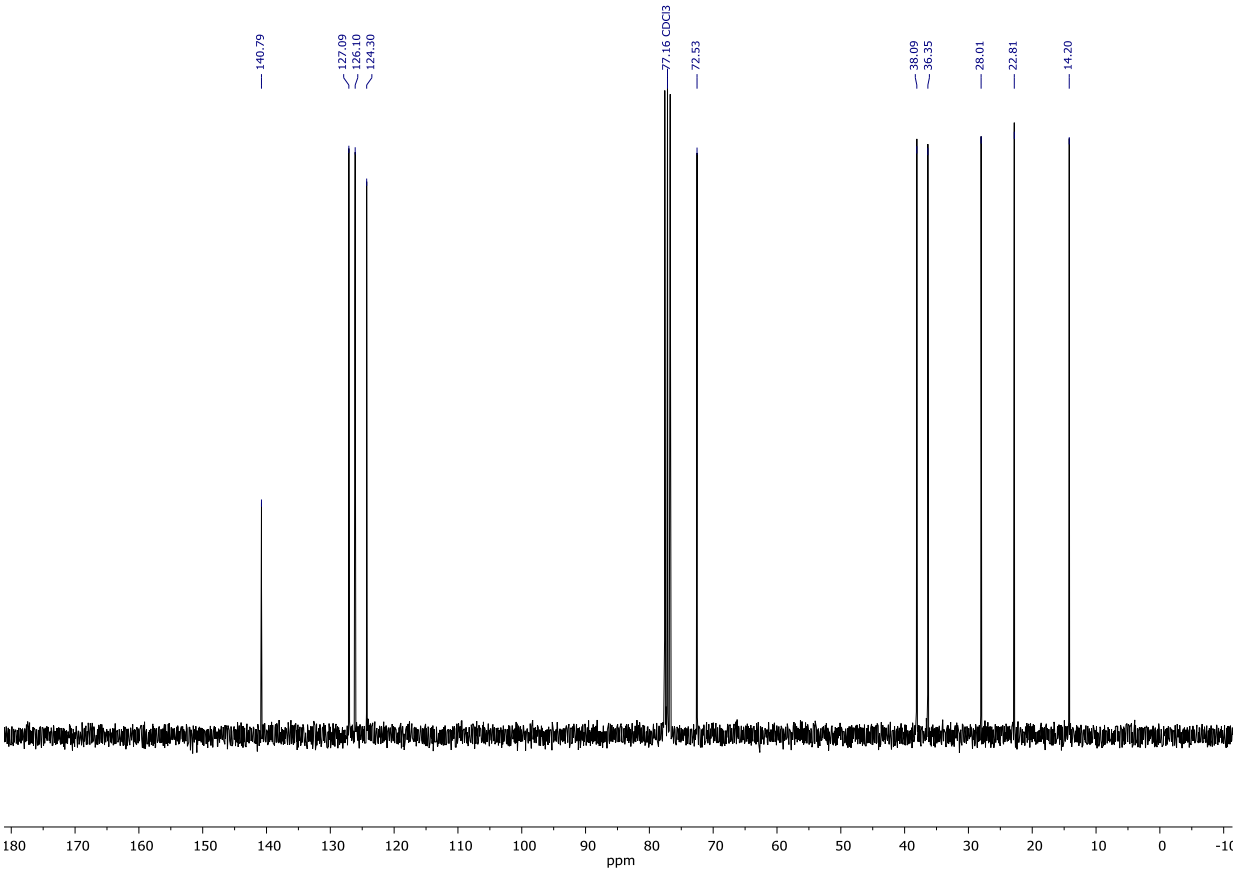
Compound **3r**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



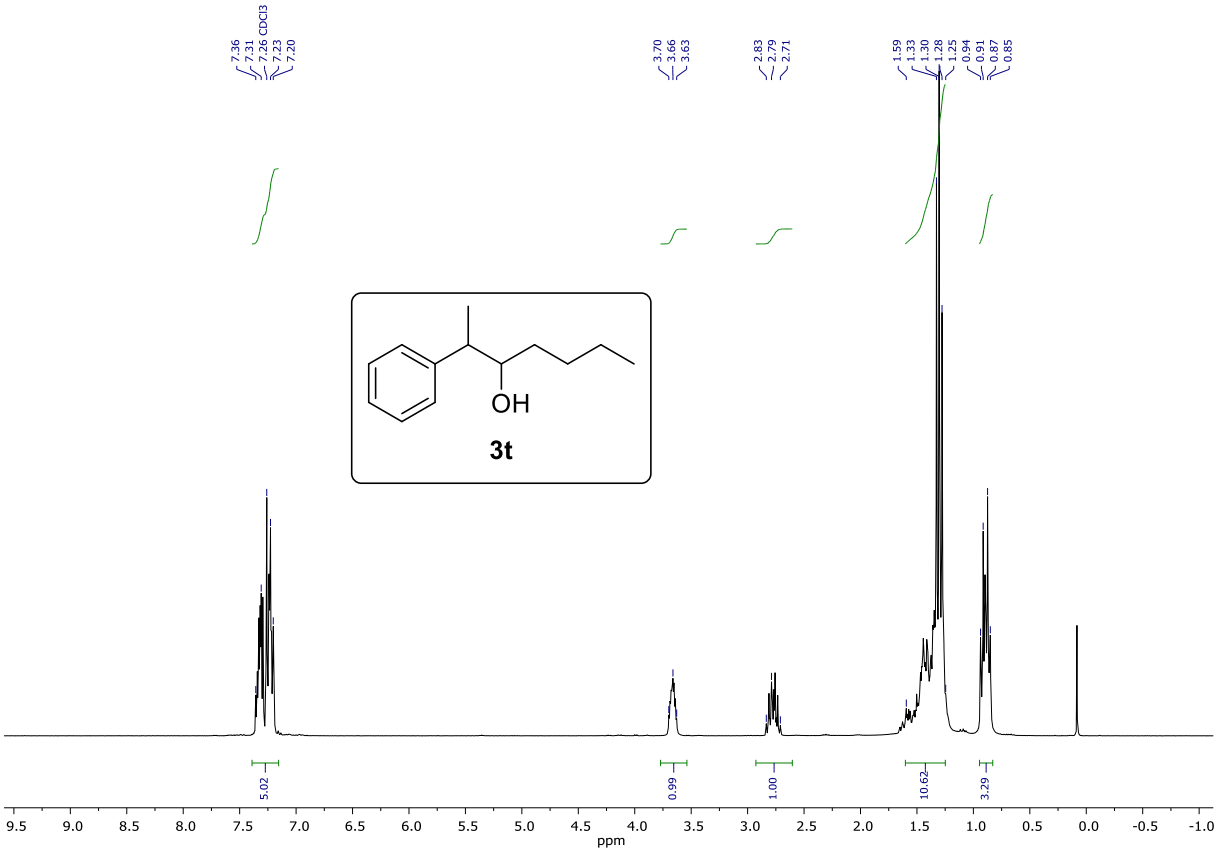


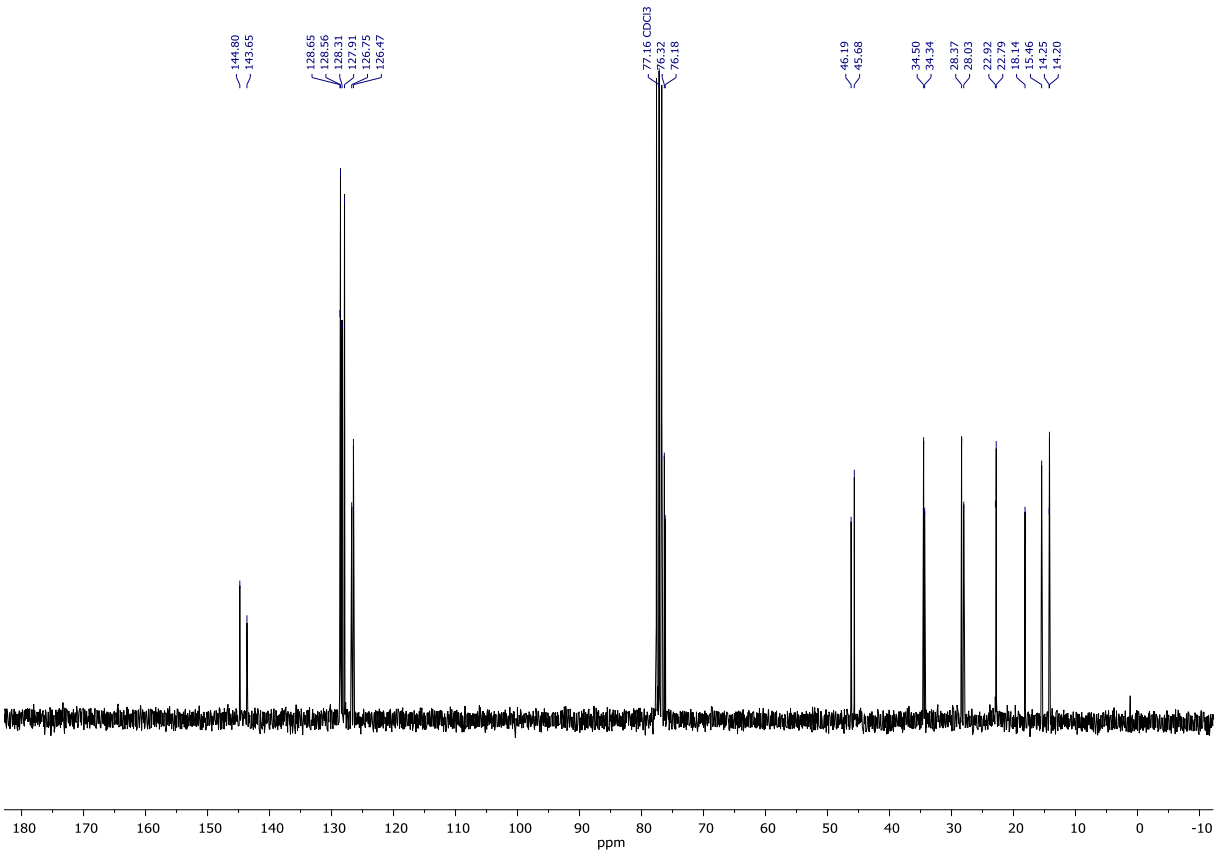
Compound **3s**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



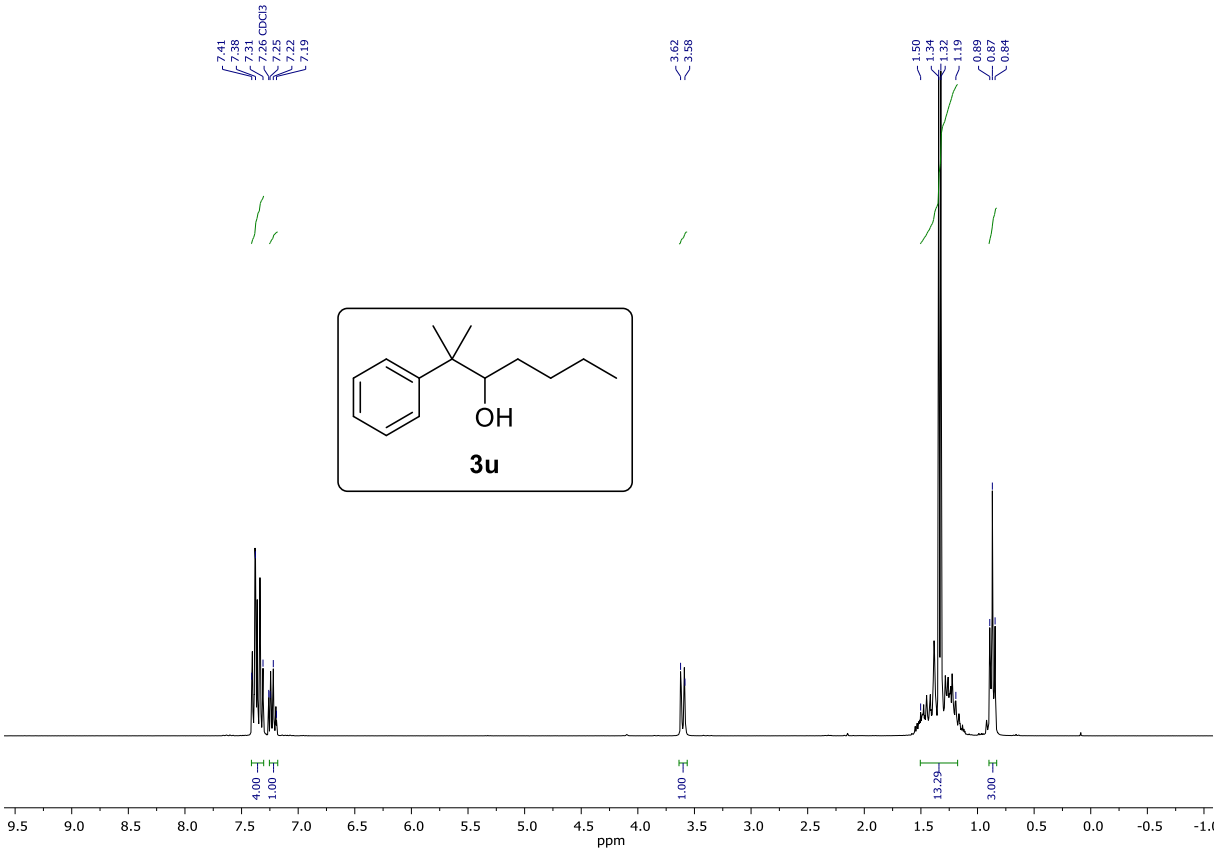


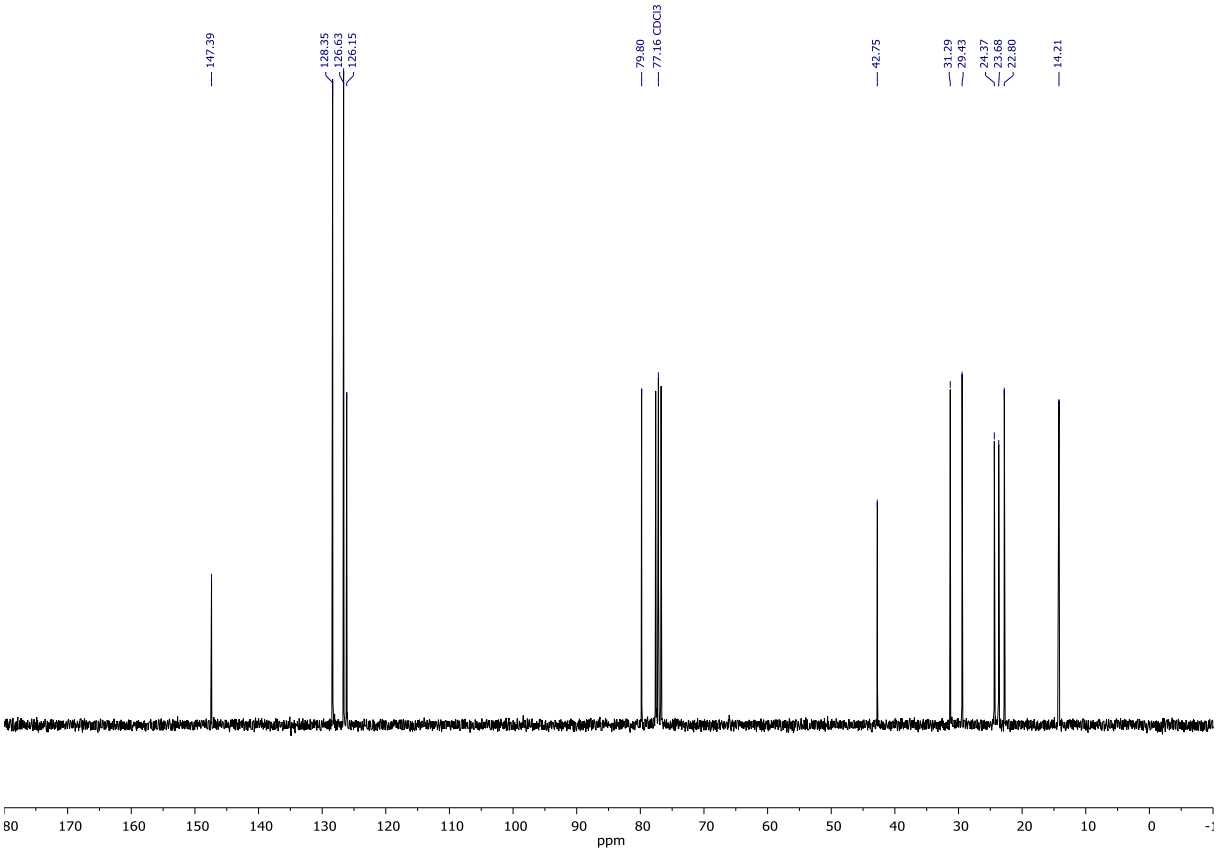
Compound **3t**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



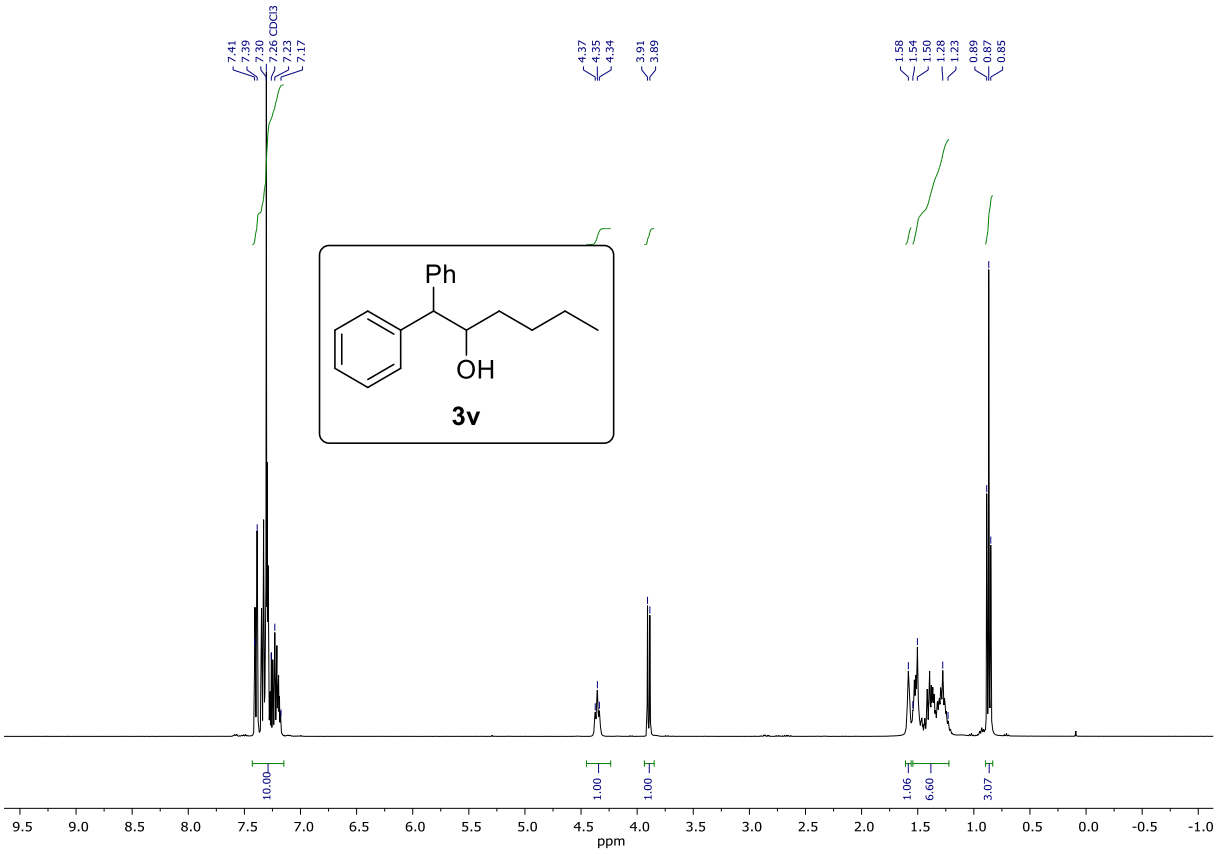


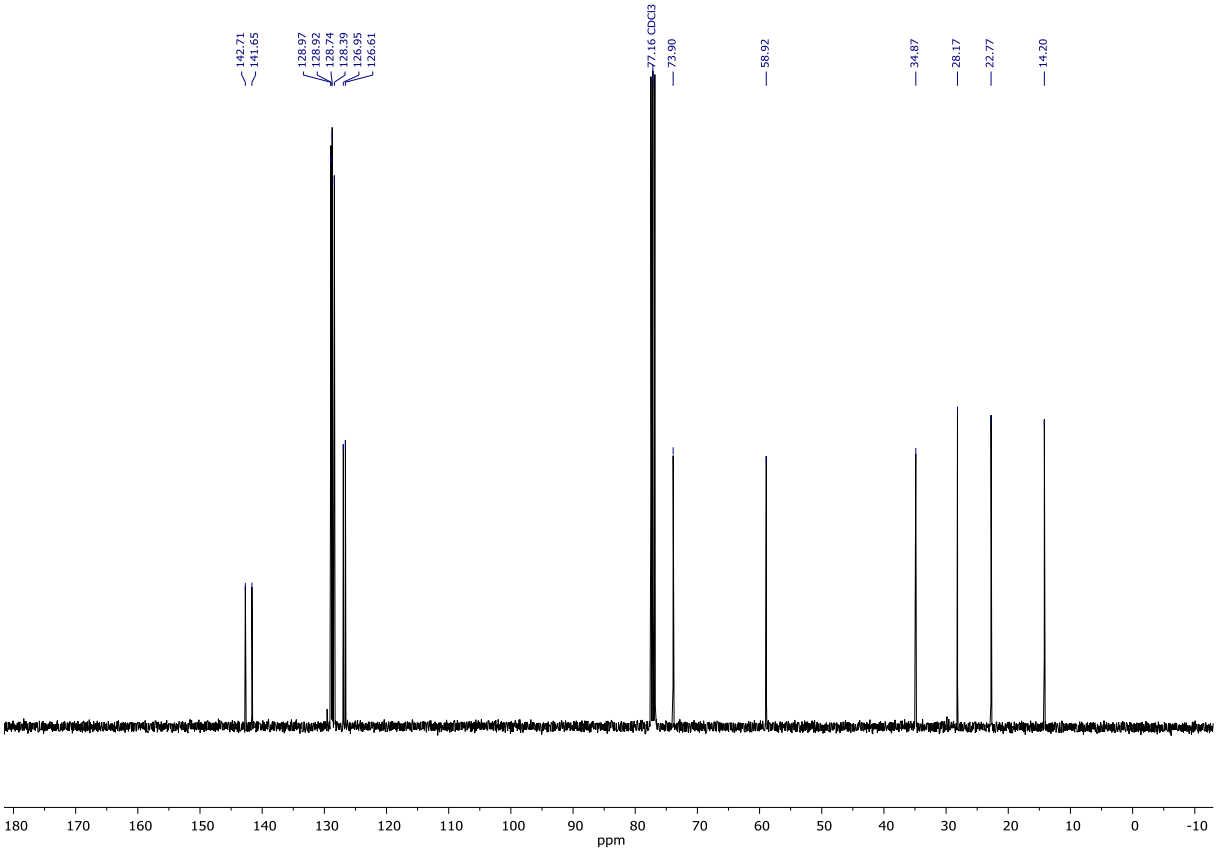
Compound **3u**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



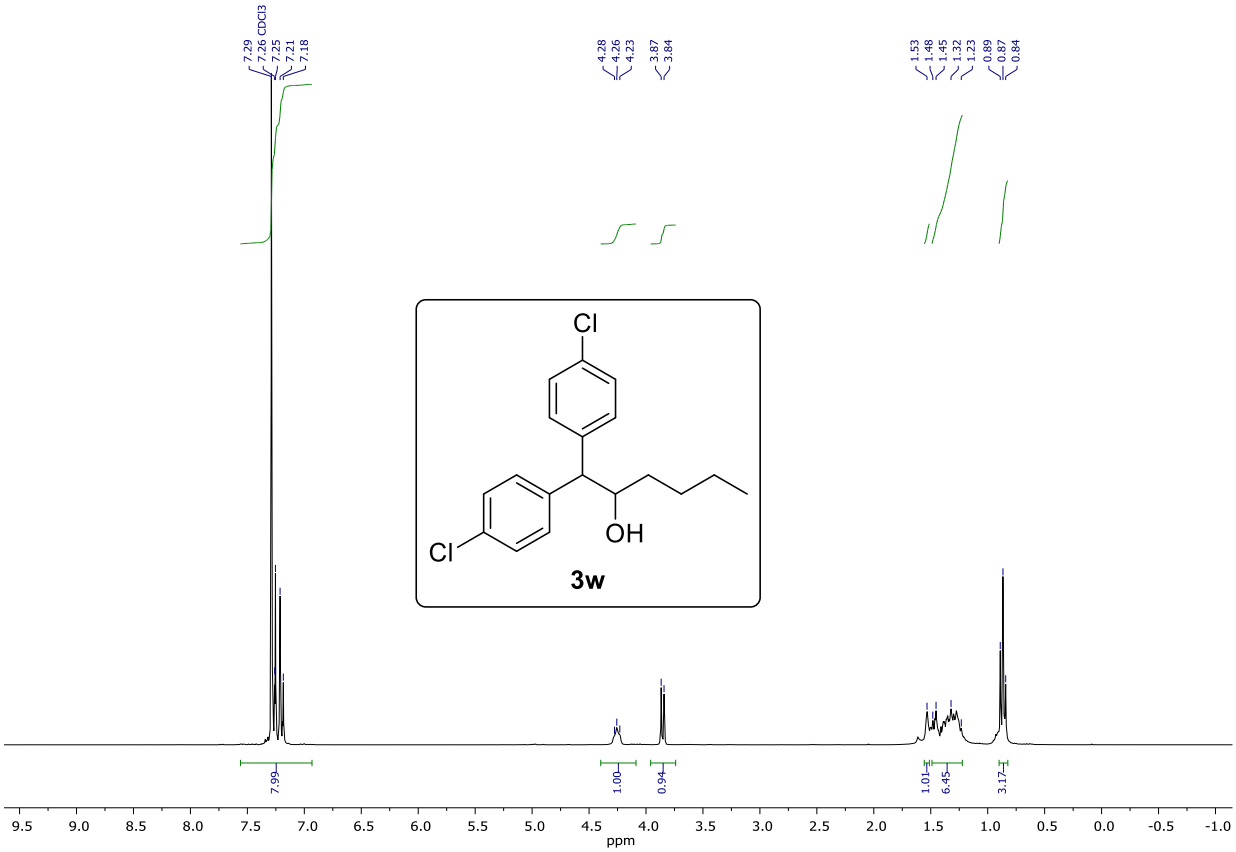


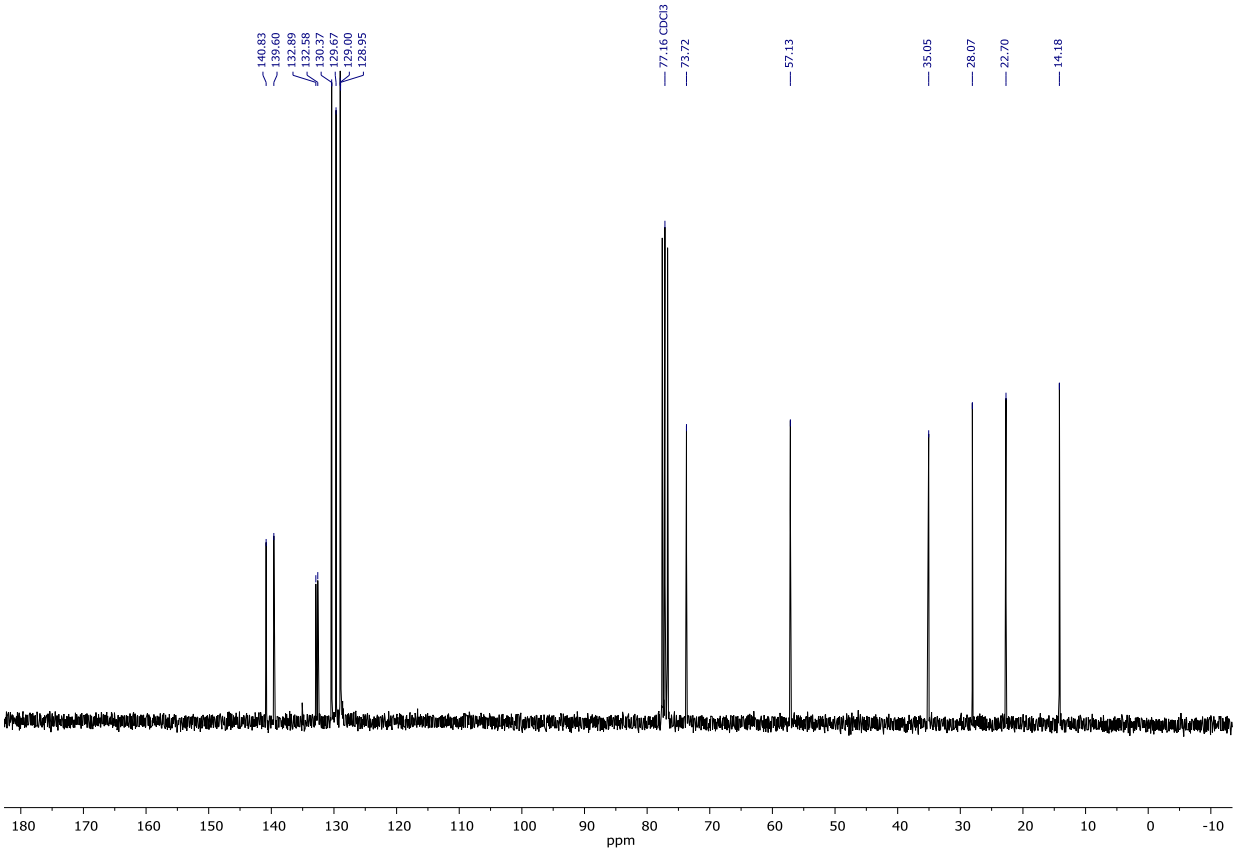
Compound **3v**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



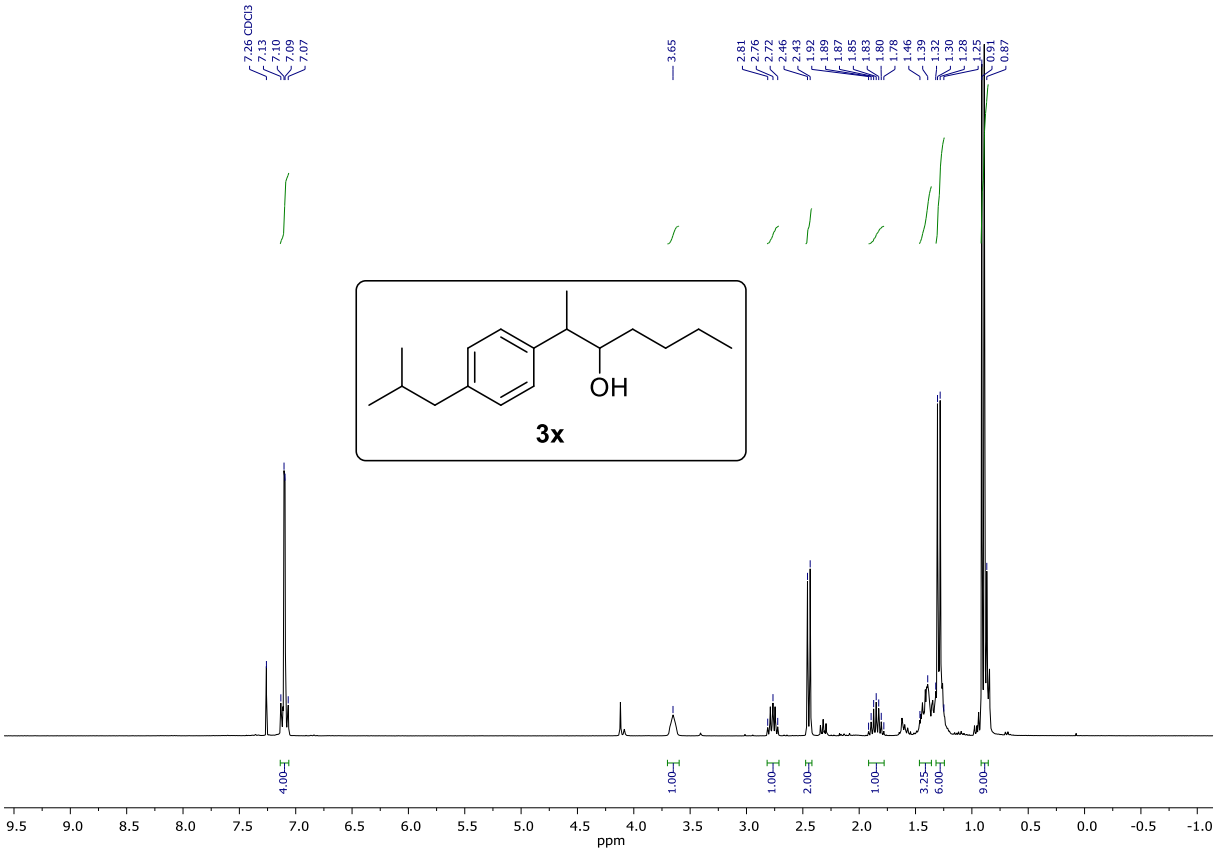


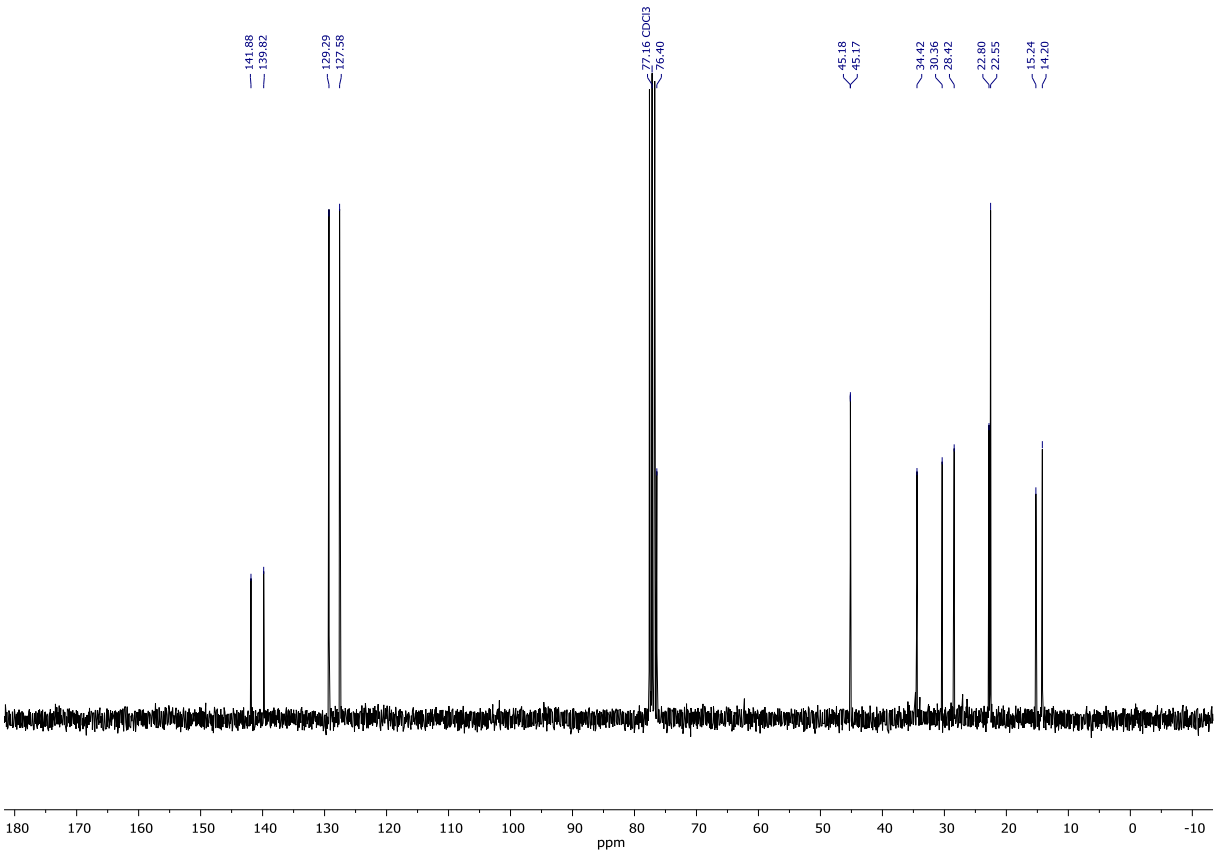
Compound **3w**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



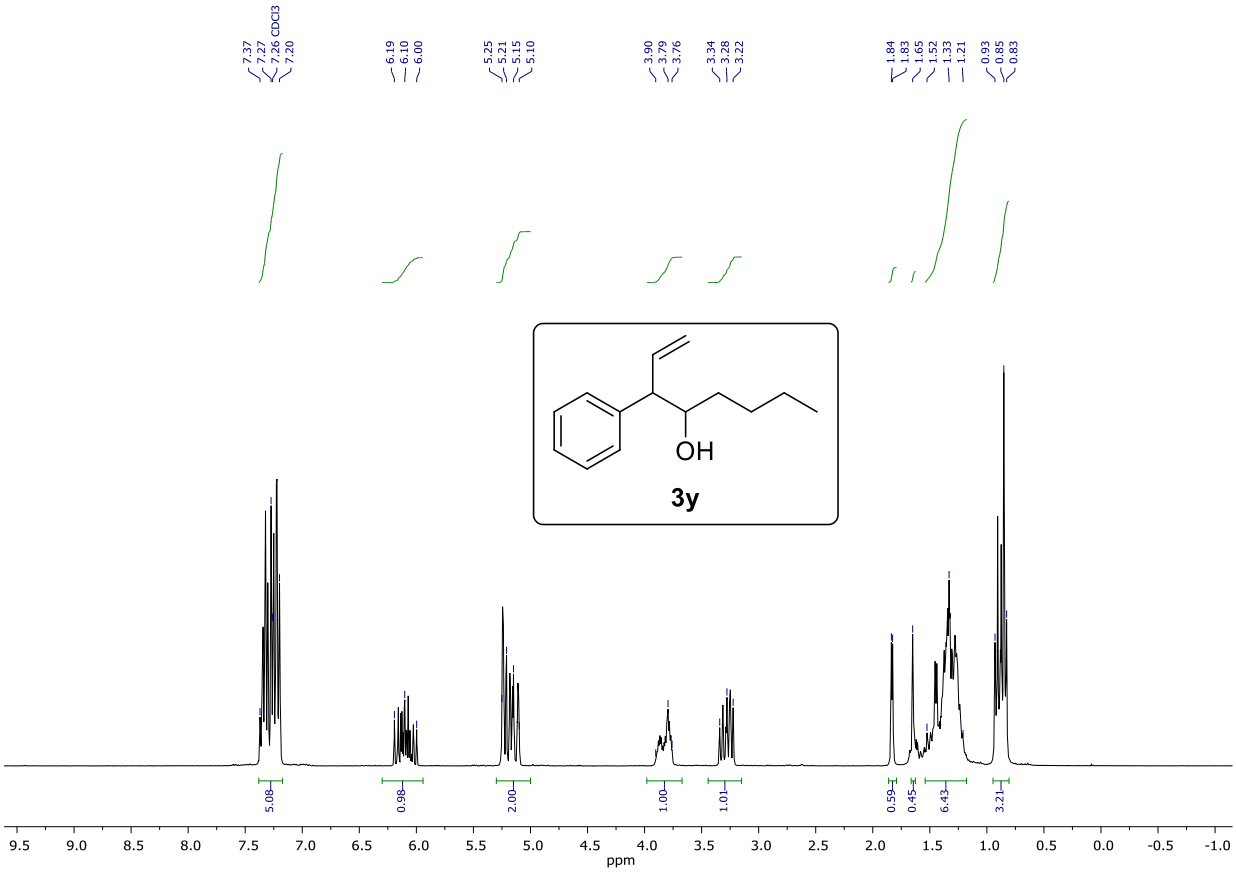


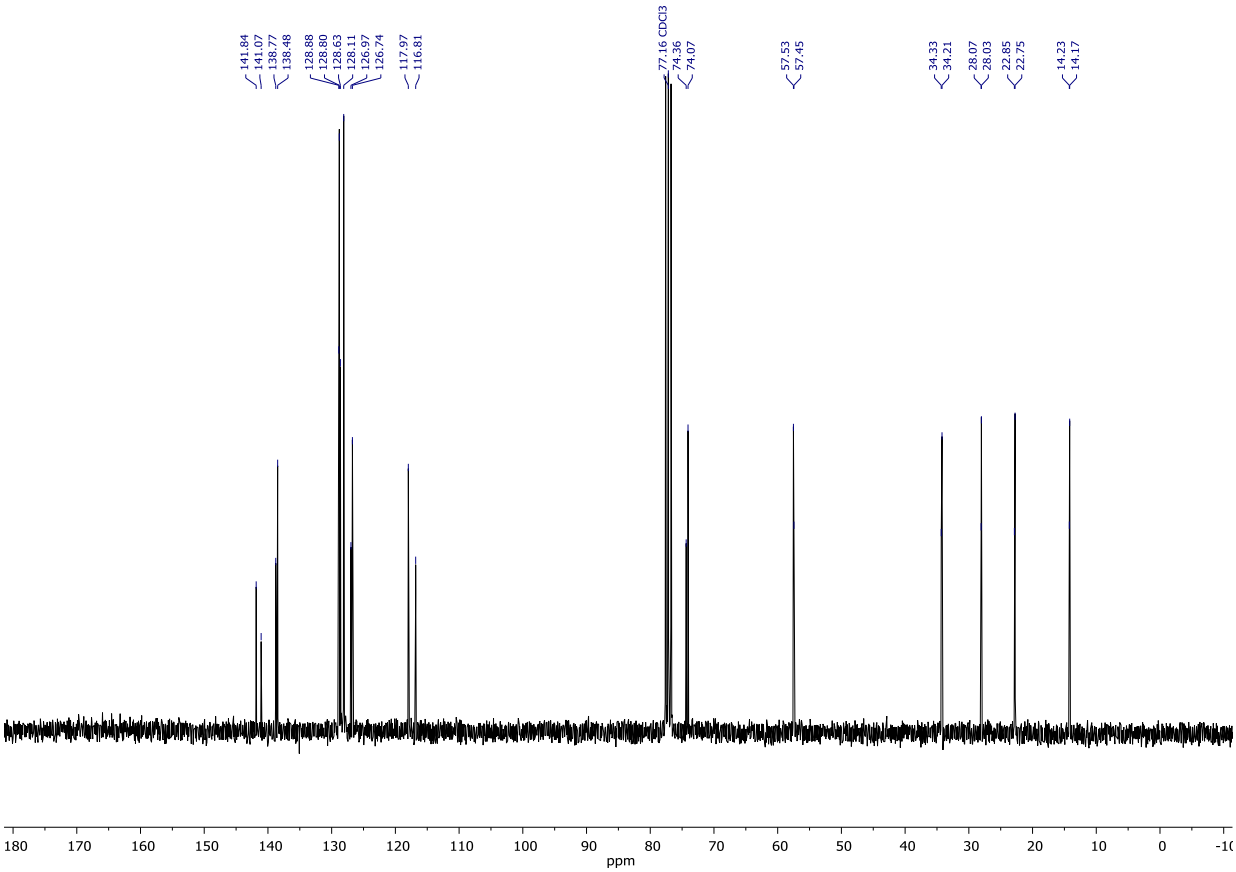
Compound **3x**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



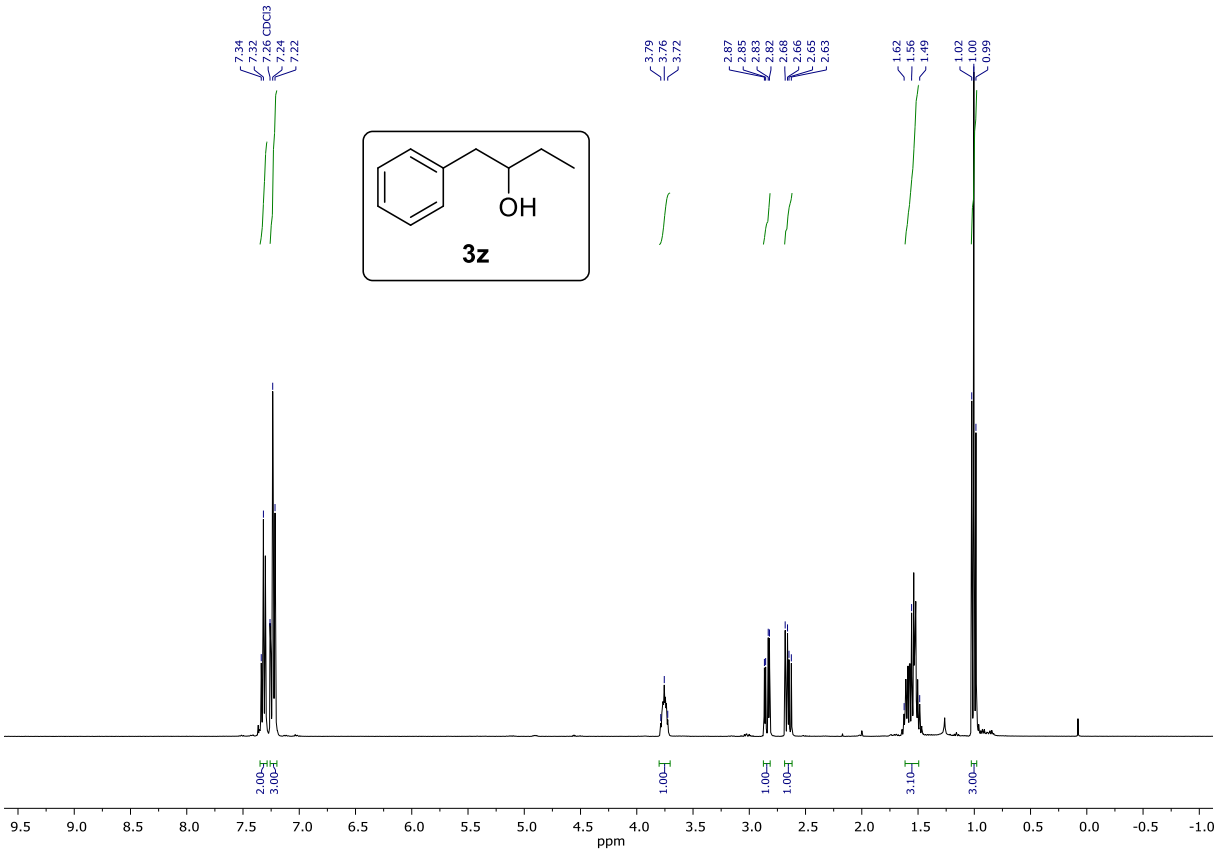


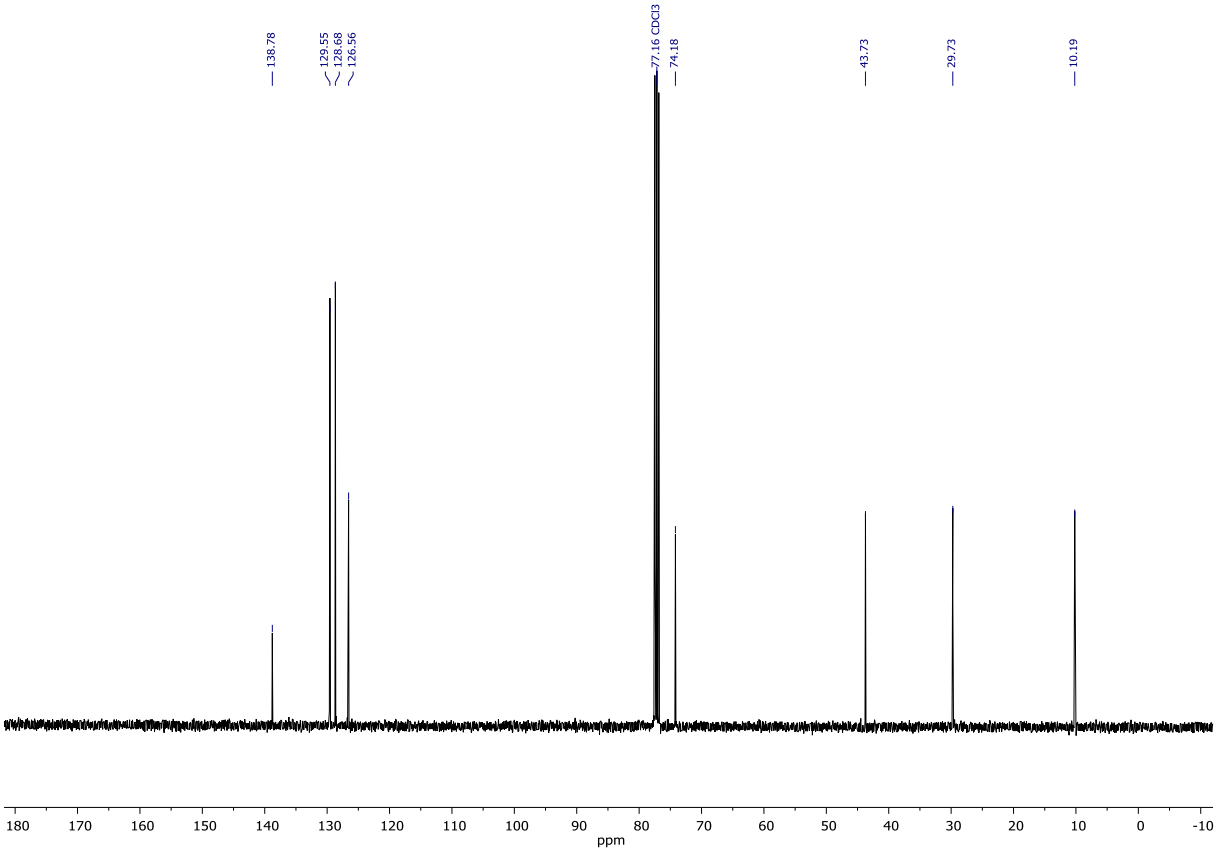
Compound **3y**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



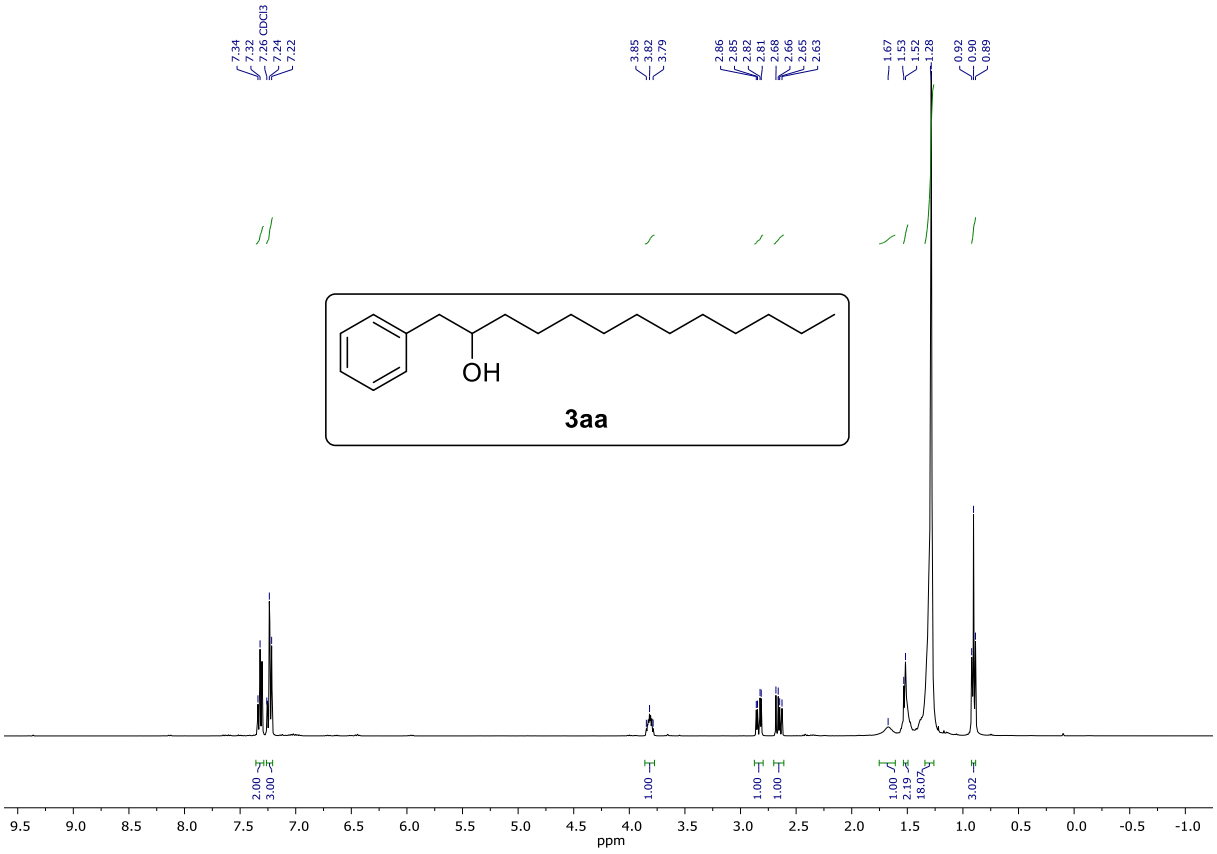


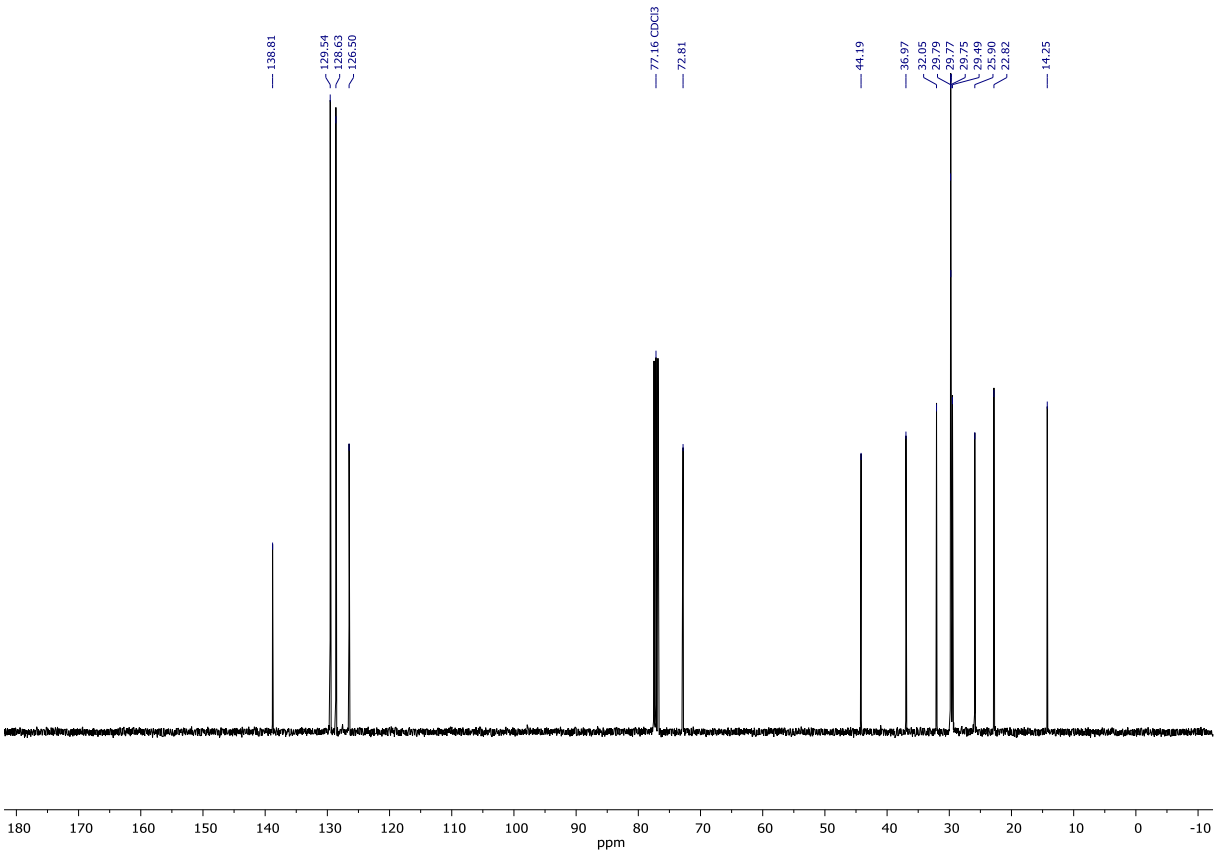
Compound **3z**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



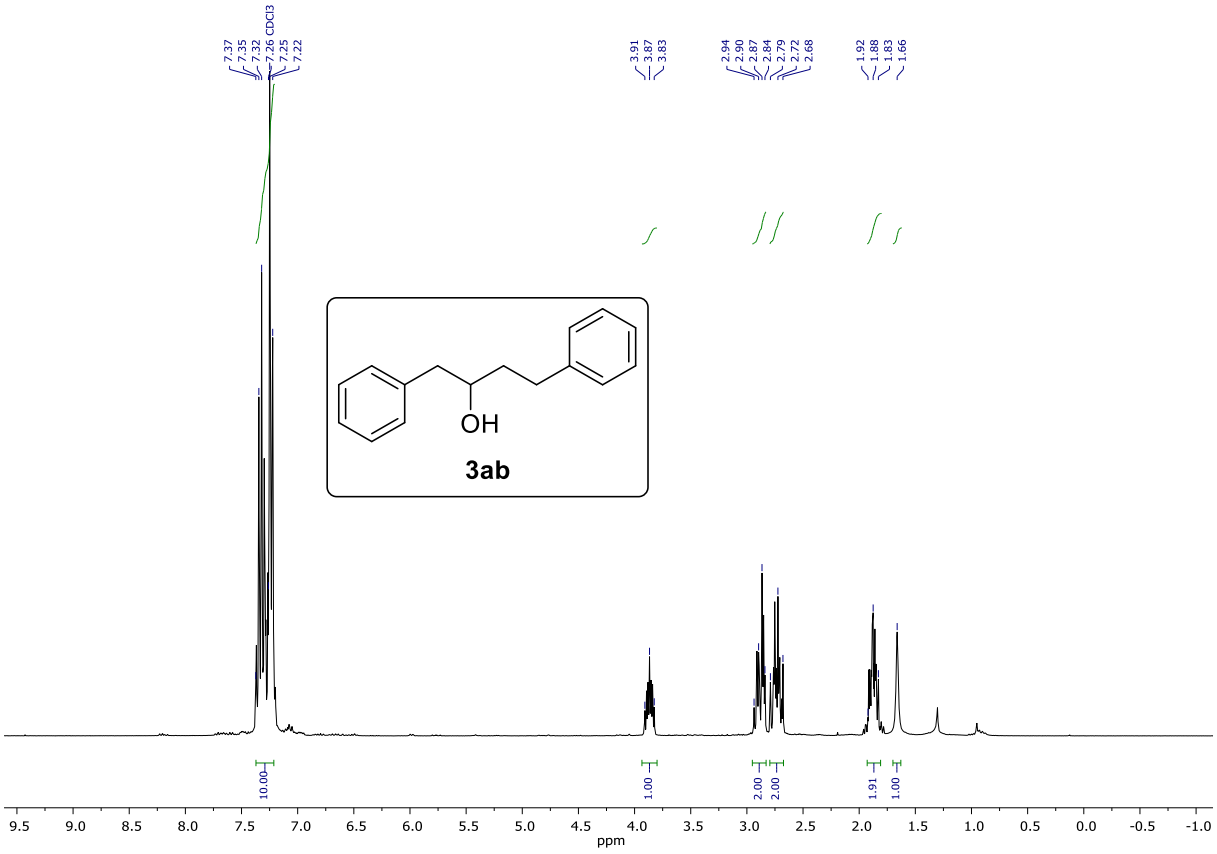


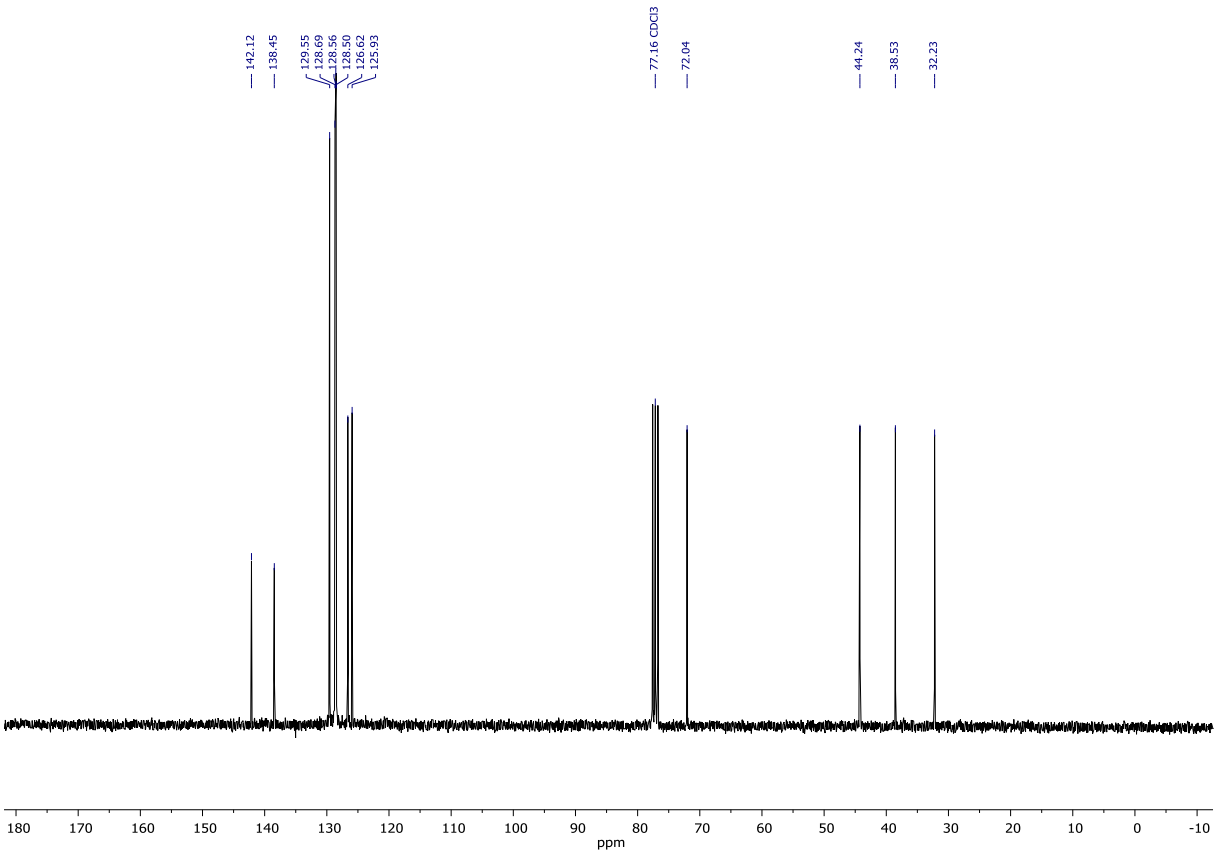
Compound **3aa**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



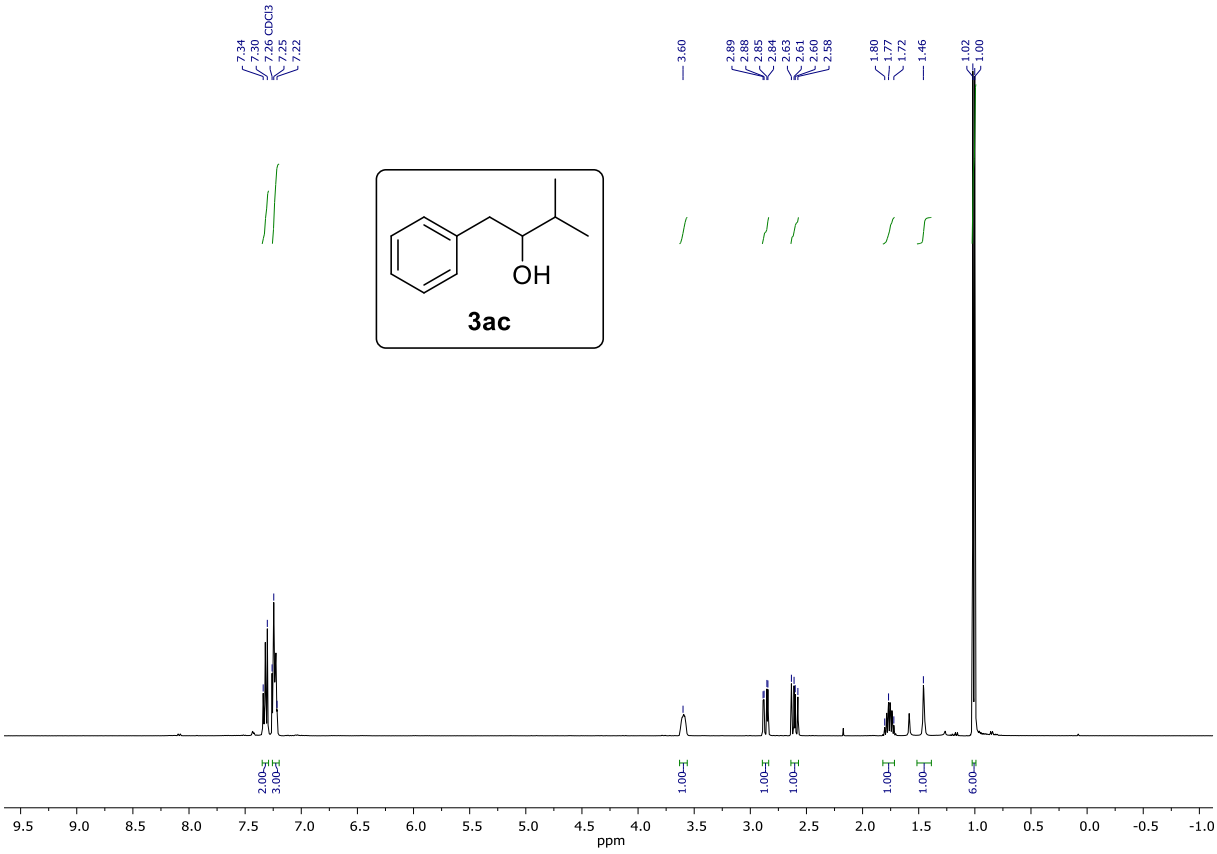


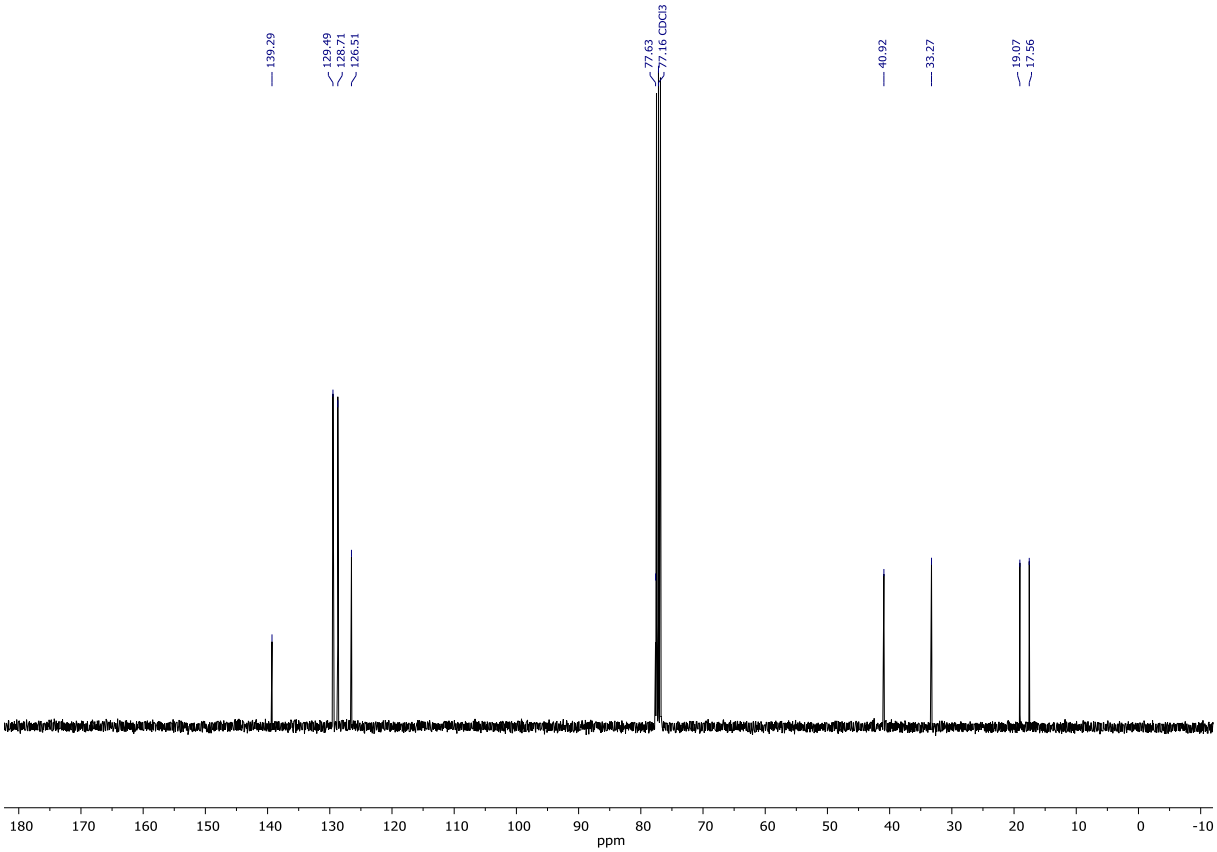
Compound **3ab**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



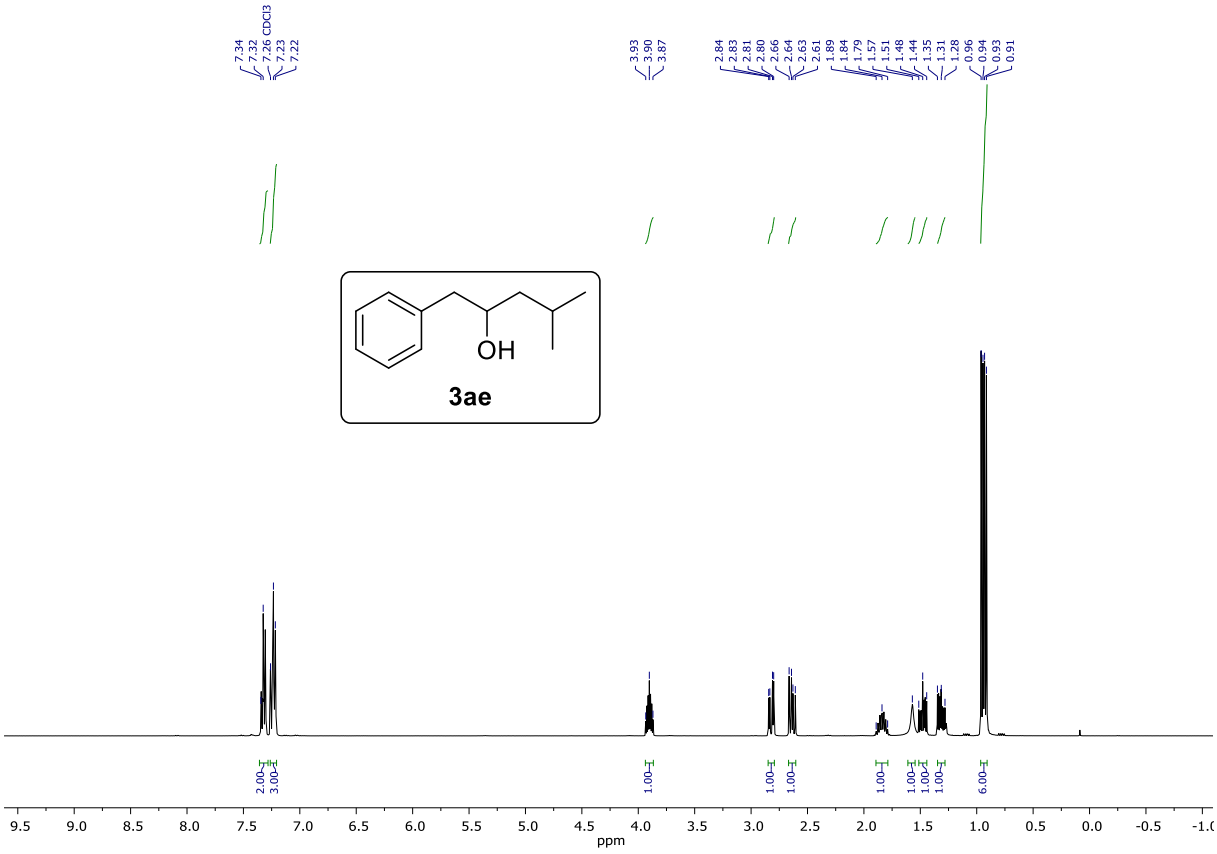


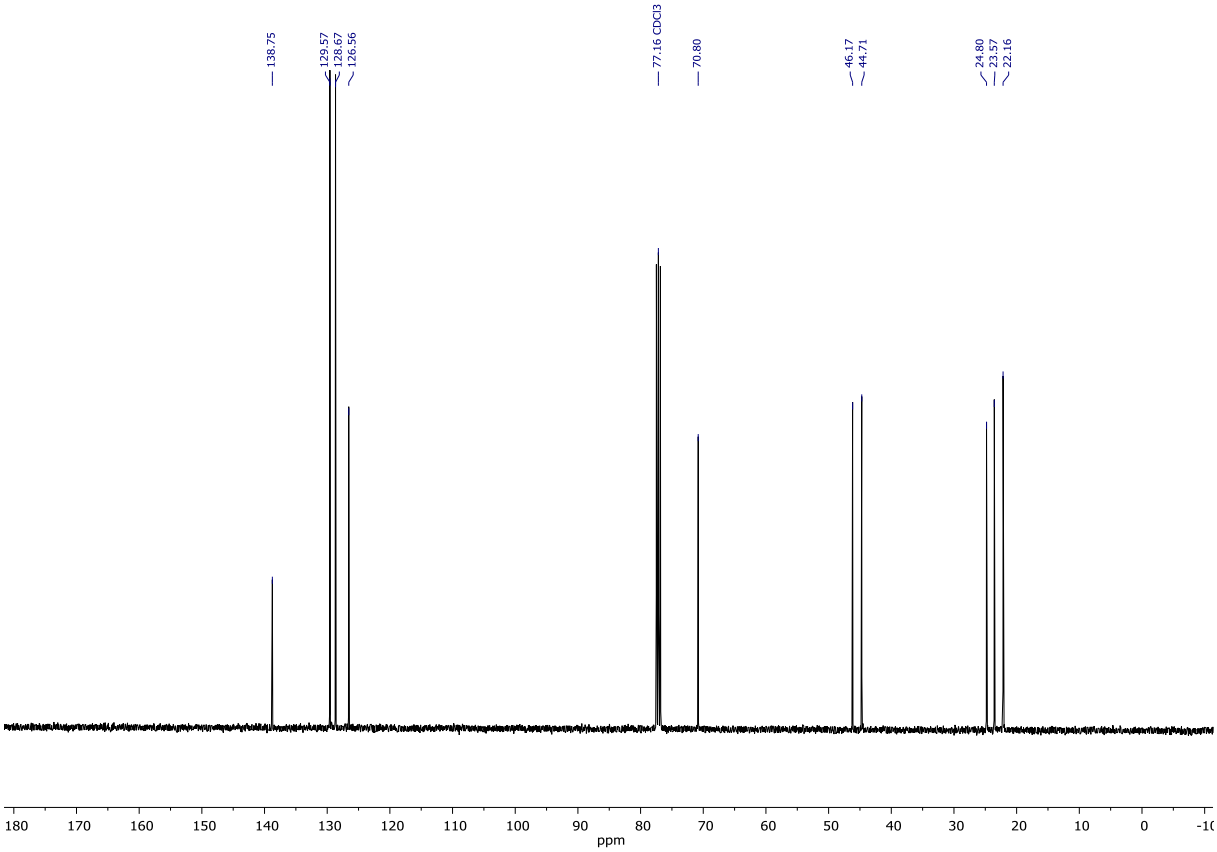
Compound **3ac**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



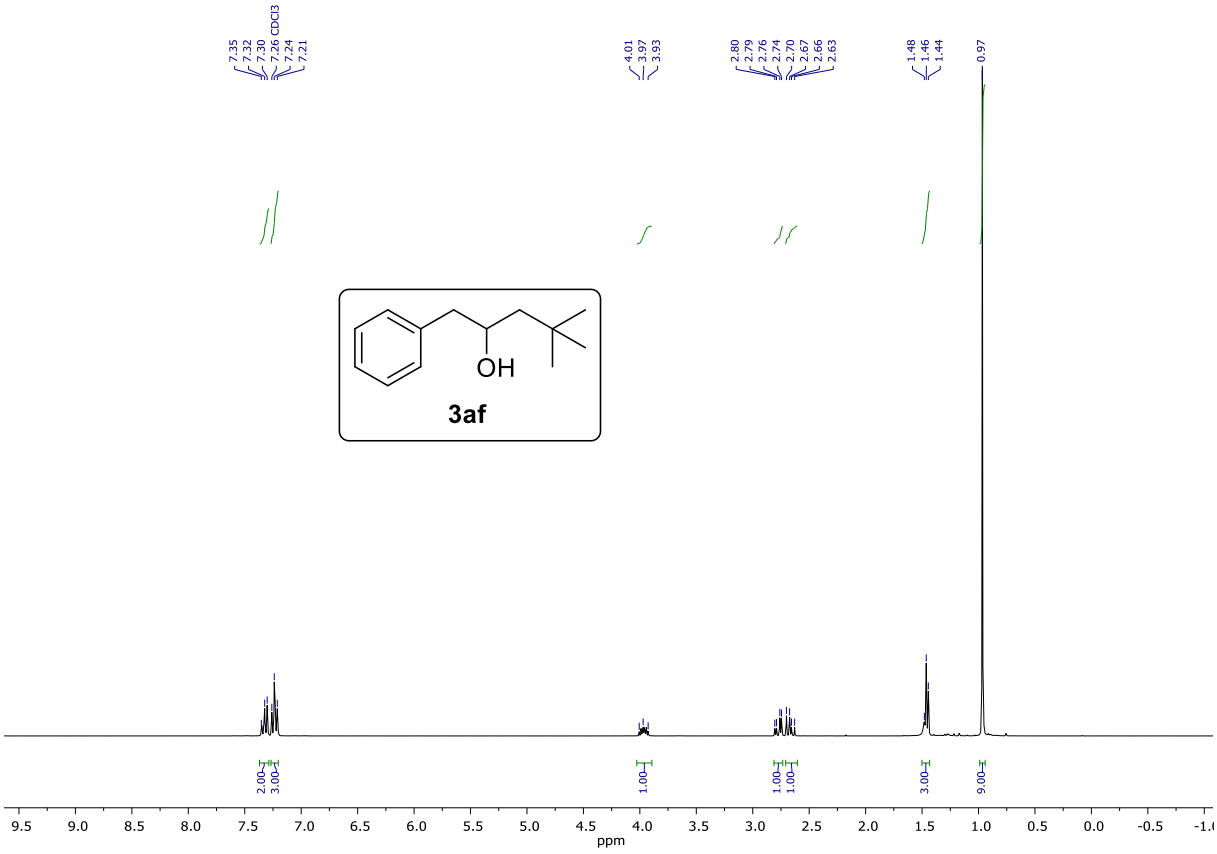


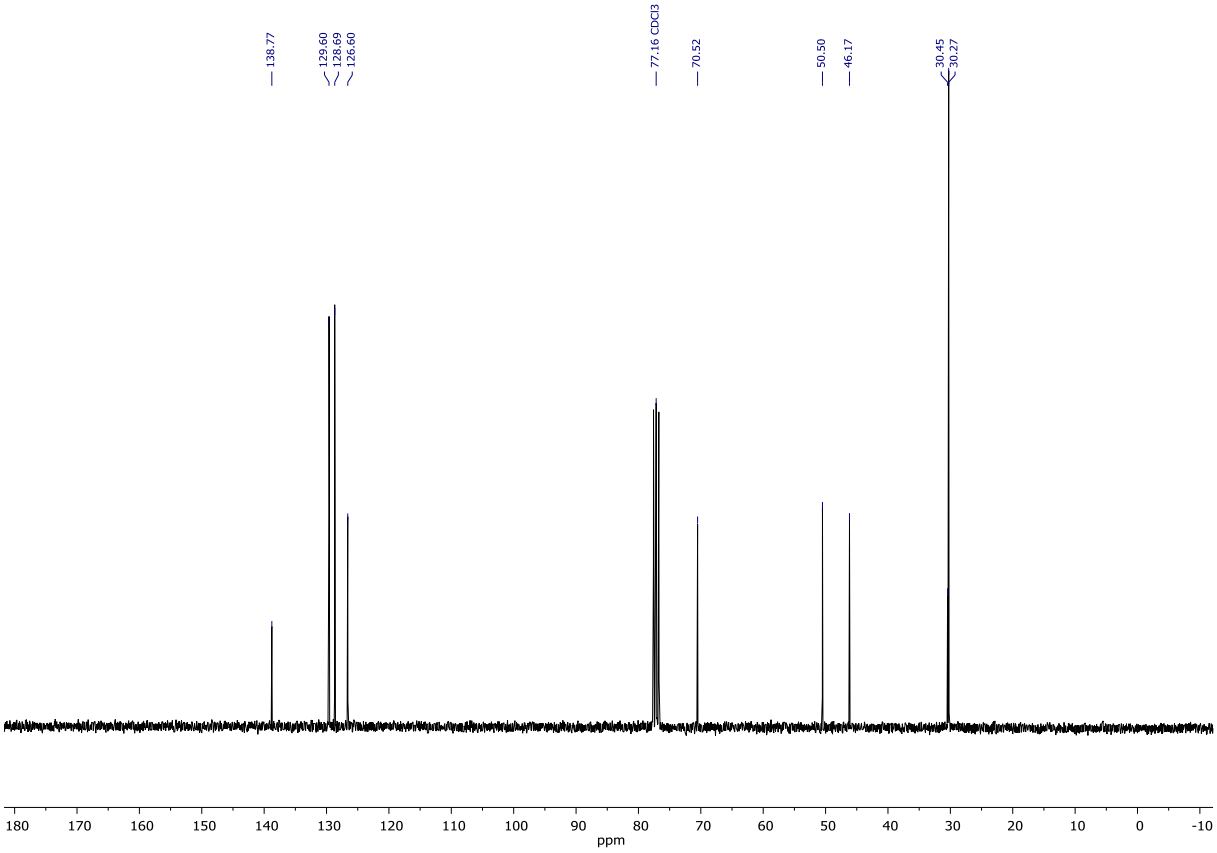
Compound **3ae**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



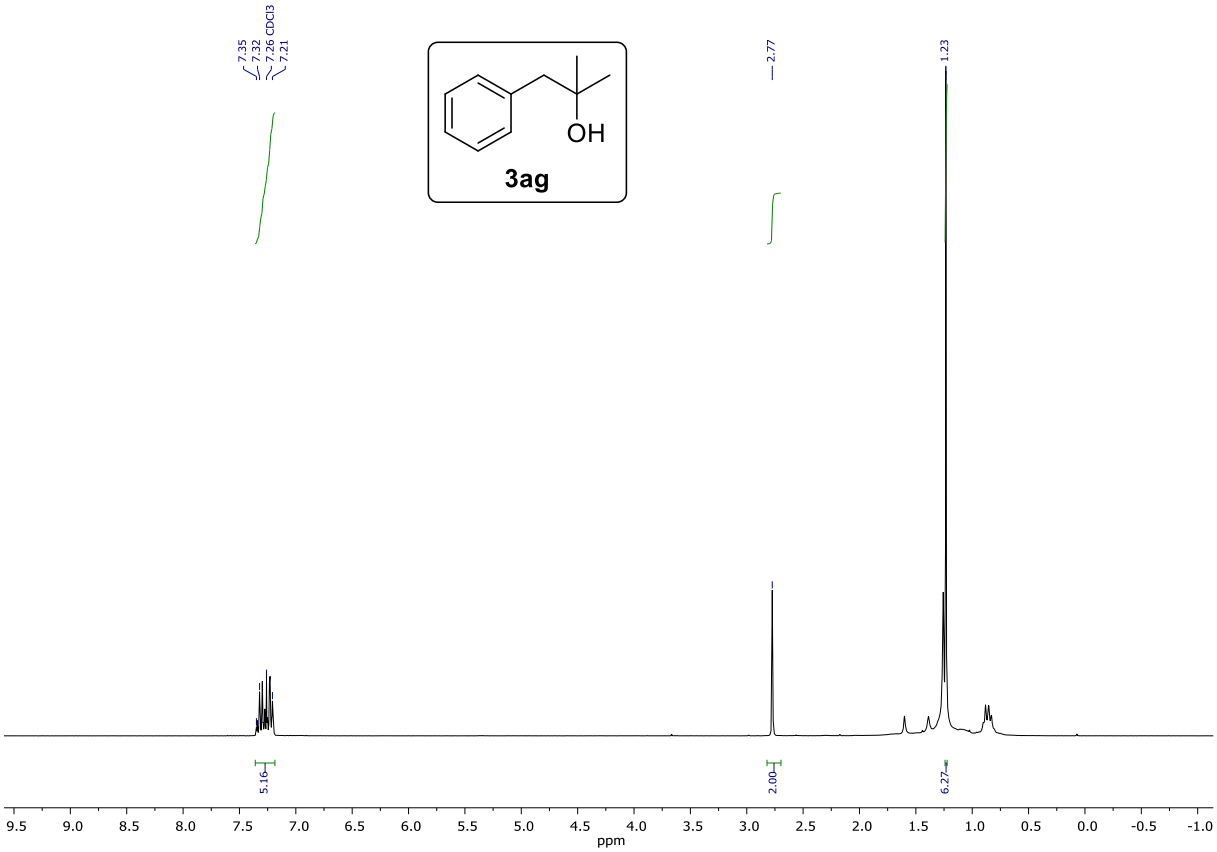


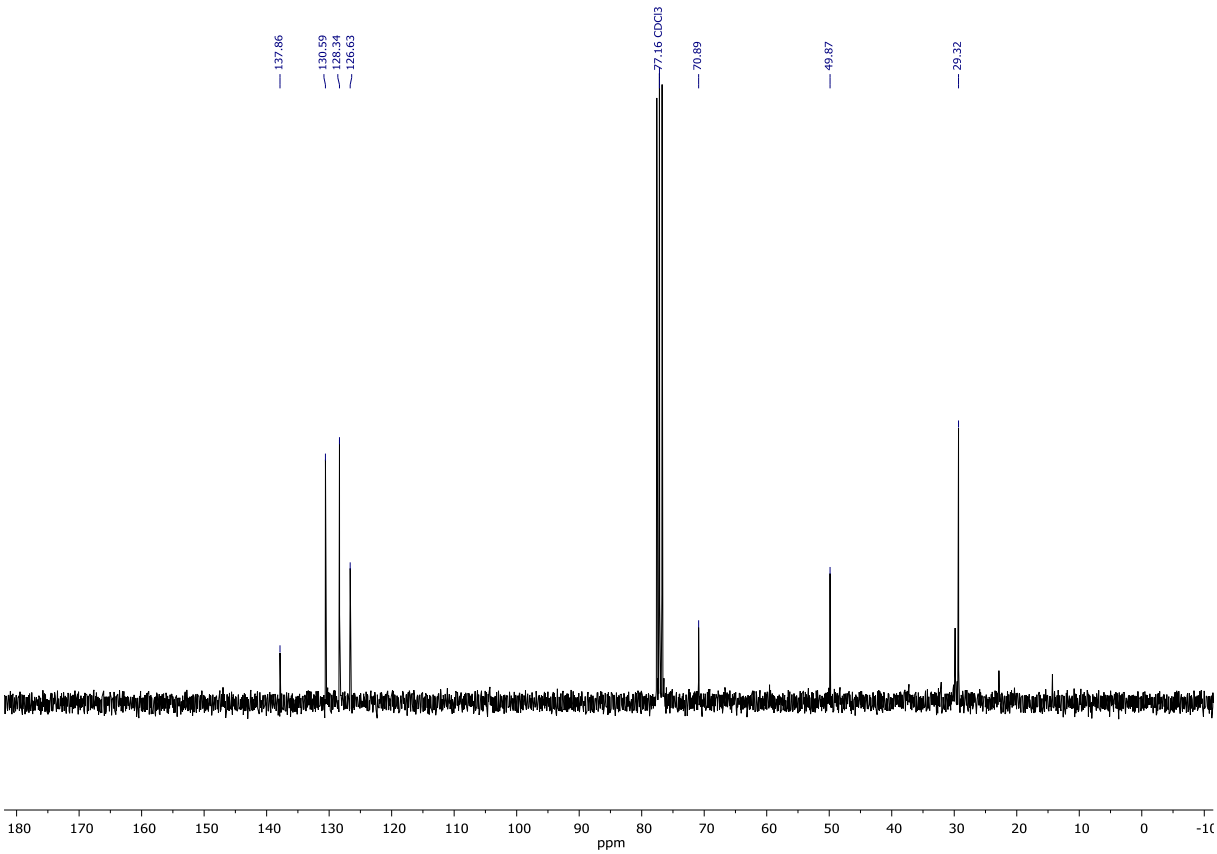
Compound **3af**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



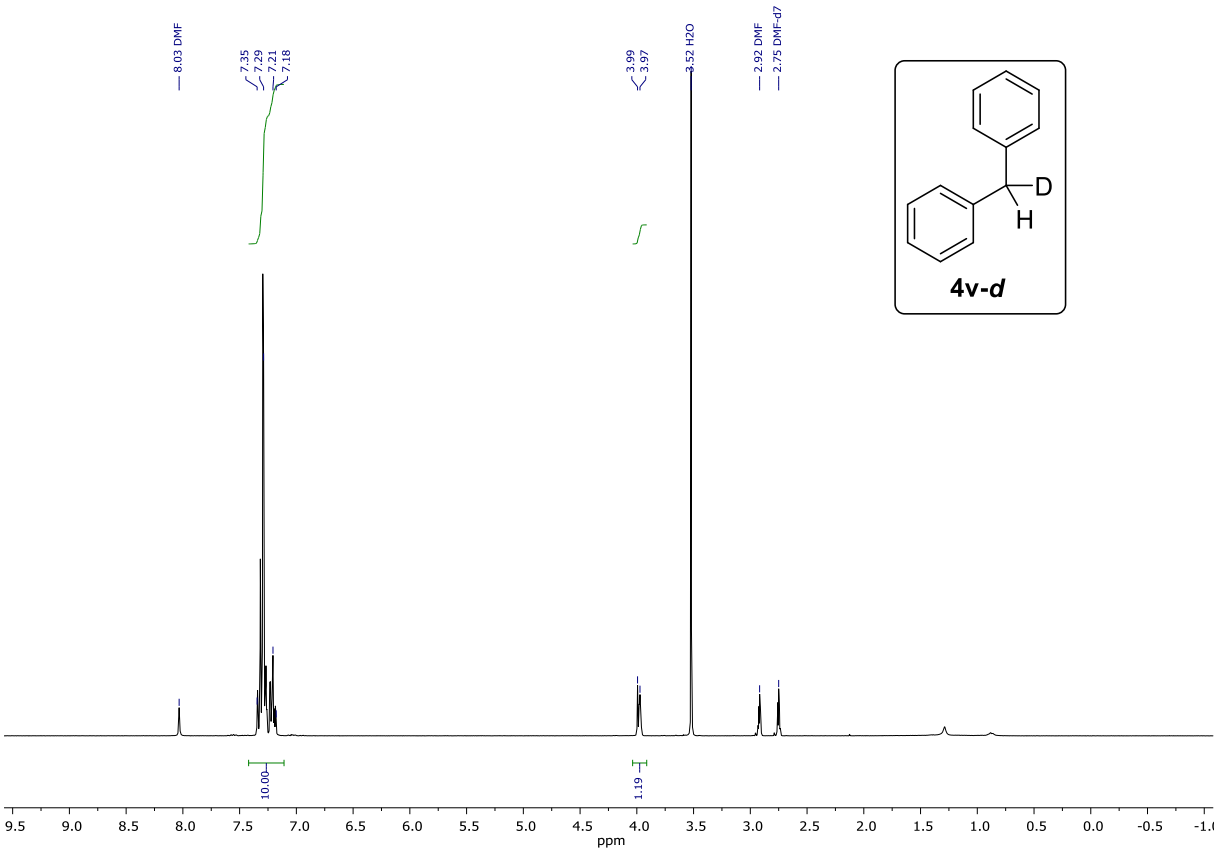


Compound **3ag**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)

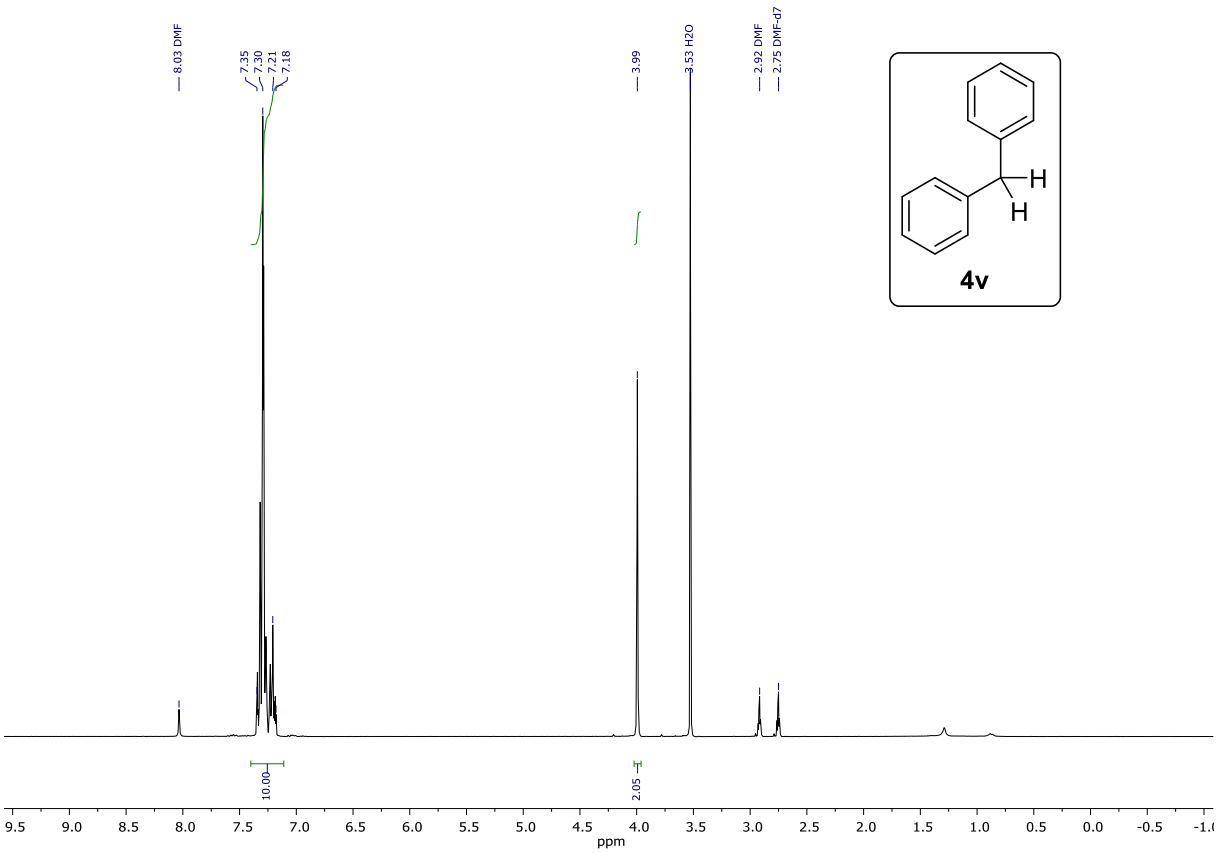




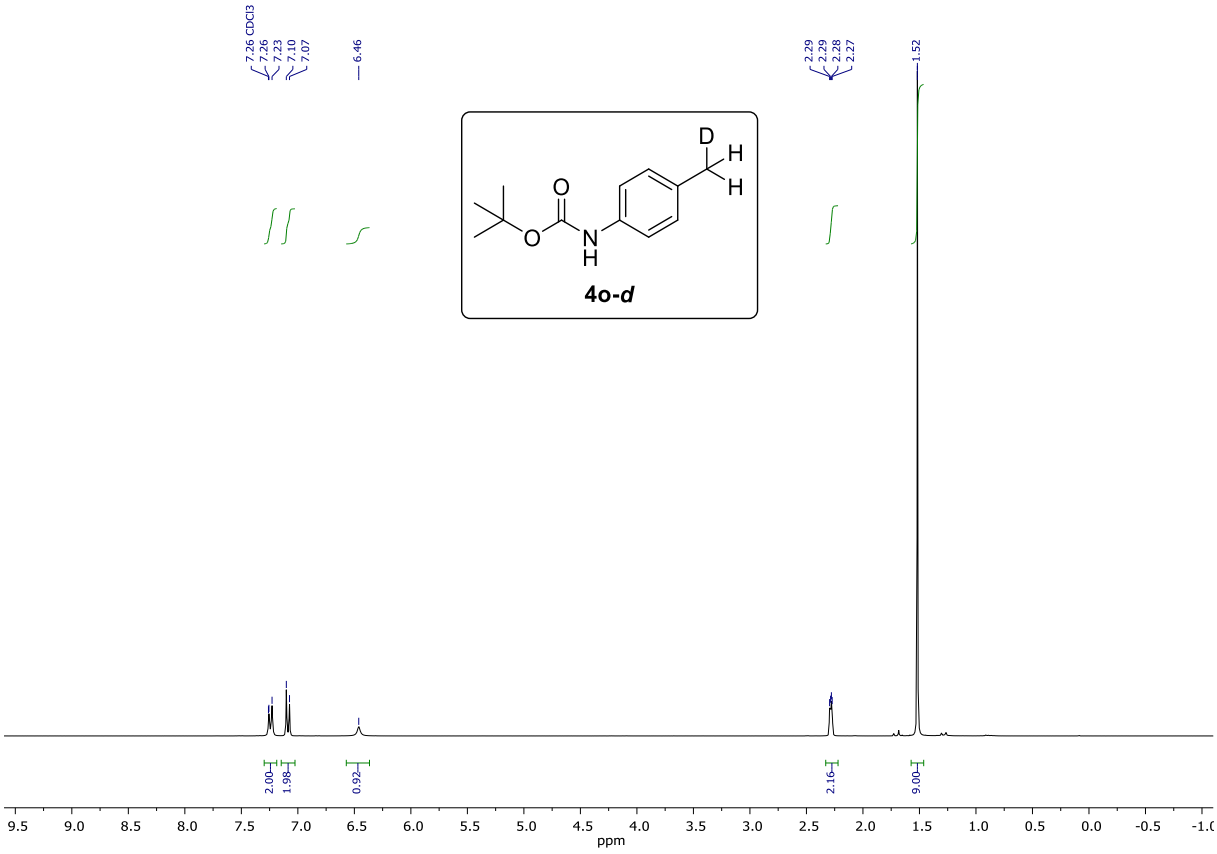
Compound **4v-*d***, ^{1}H-NMR (d_7-DMF)

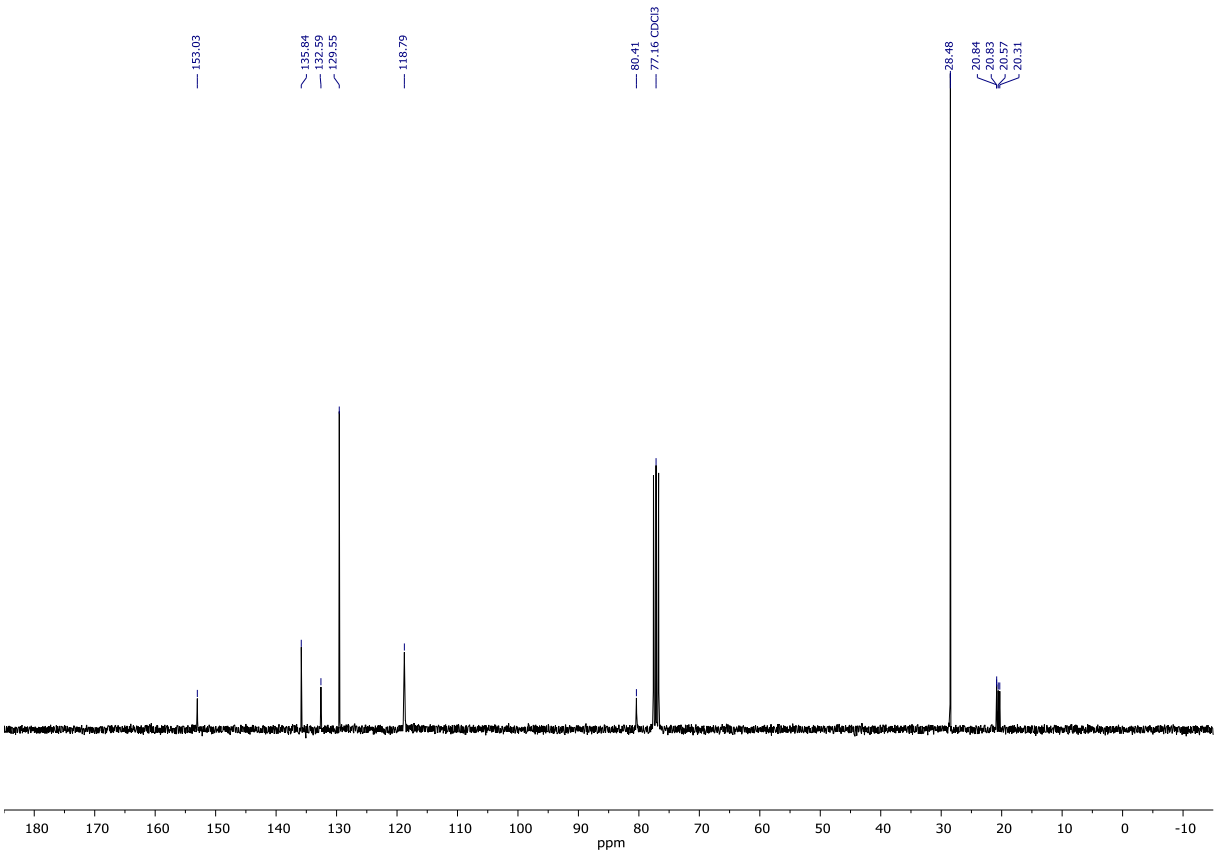


Compound **4v**, ^{1}H-NMR (d_7-DMF)

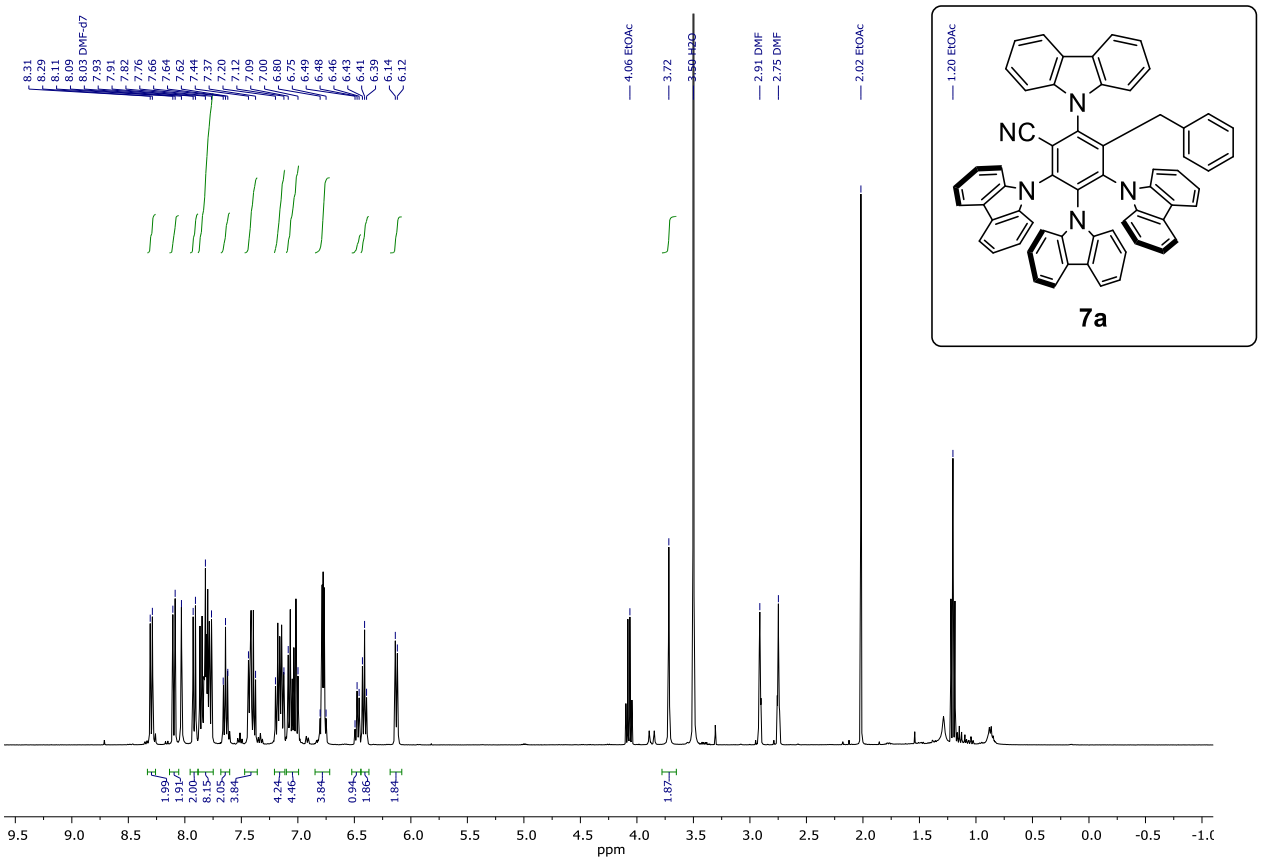


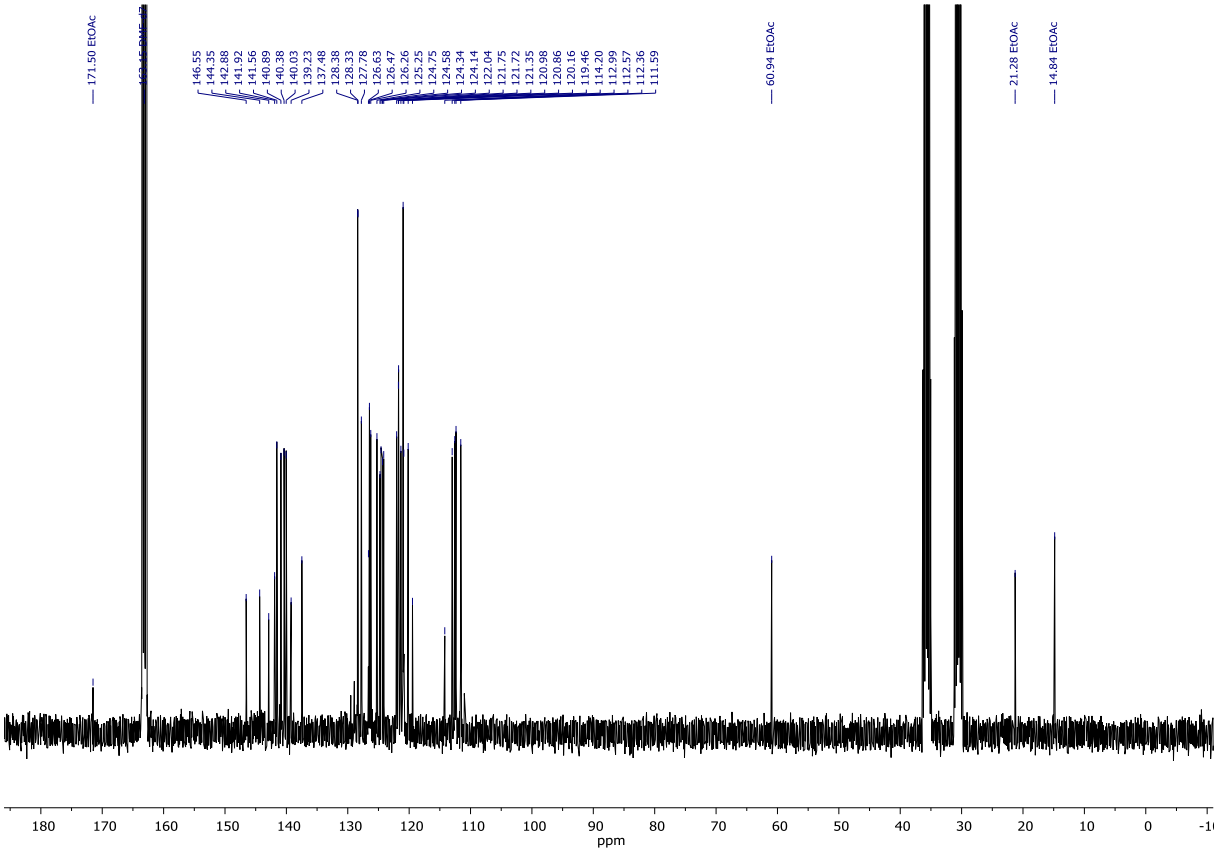
Compound **4o-*d***, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



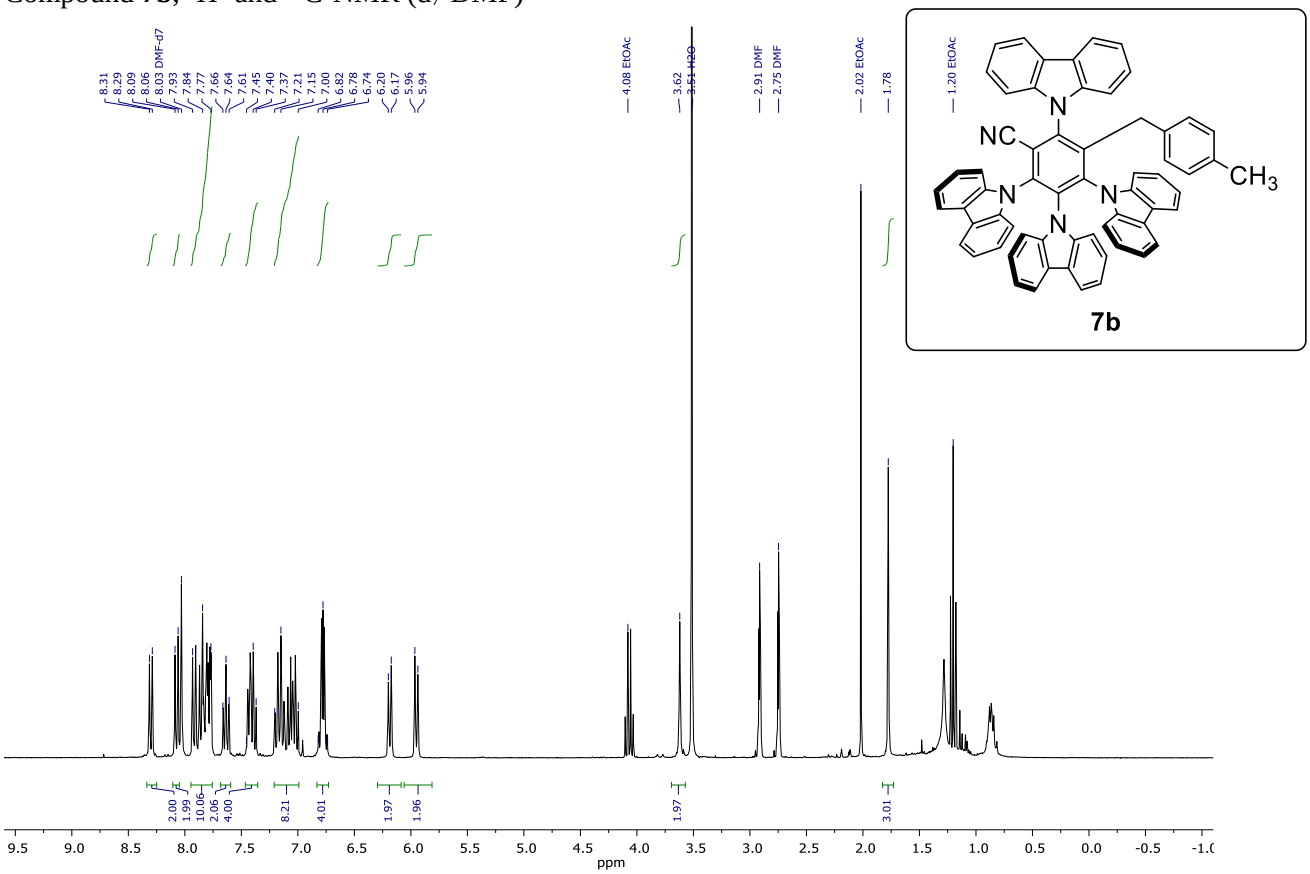


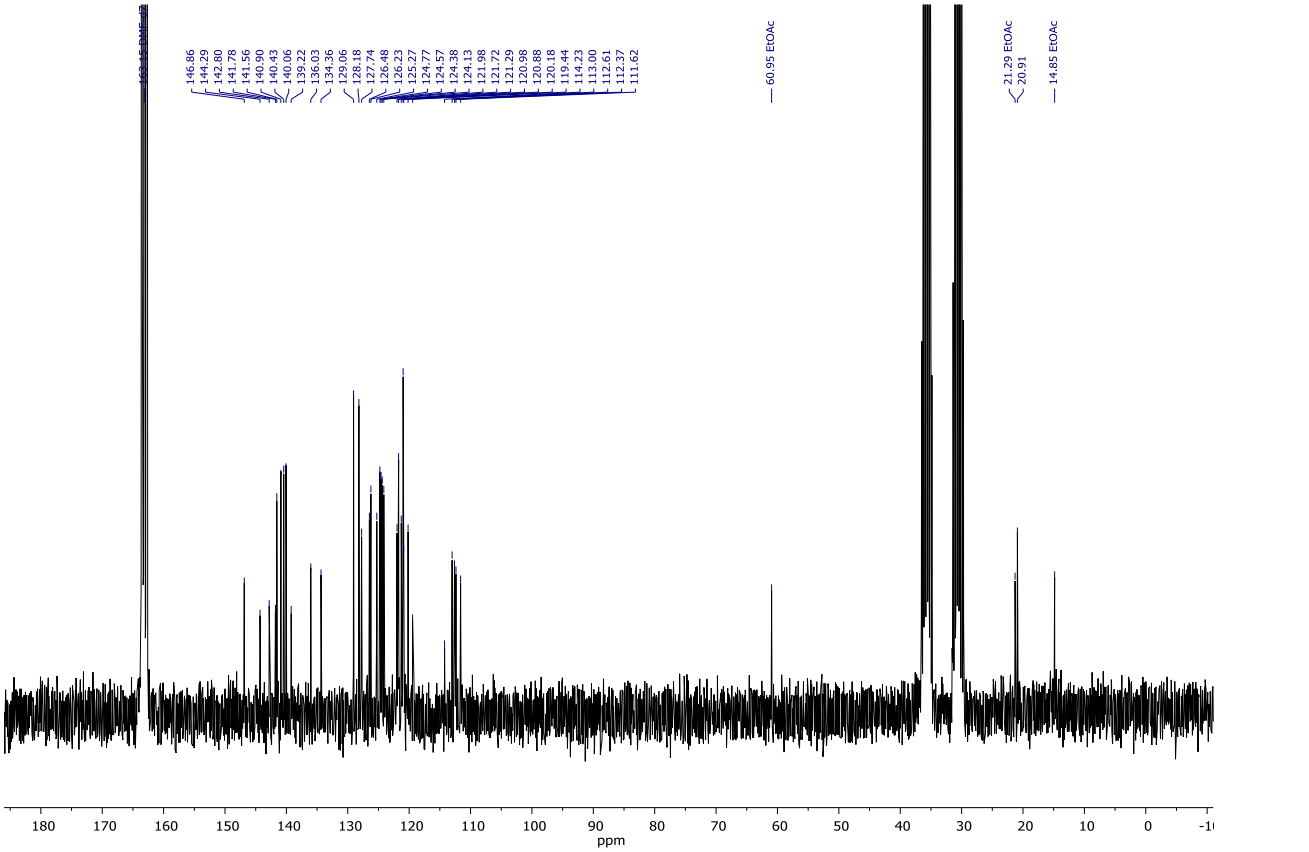
Compound **7a**, ^{1}H- and ^{13}C-NMR (d_7-DMF)



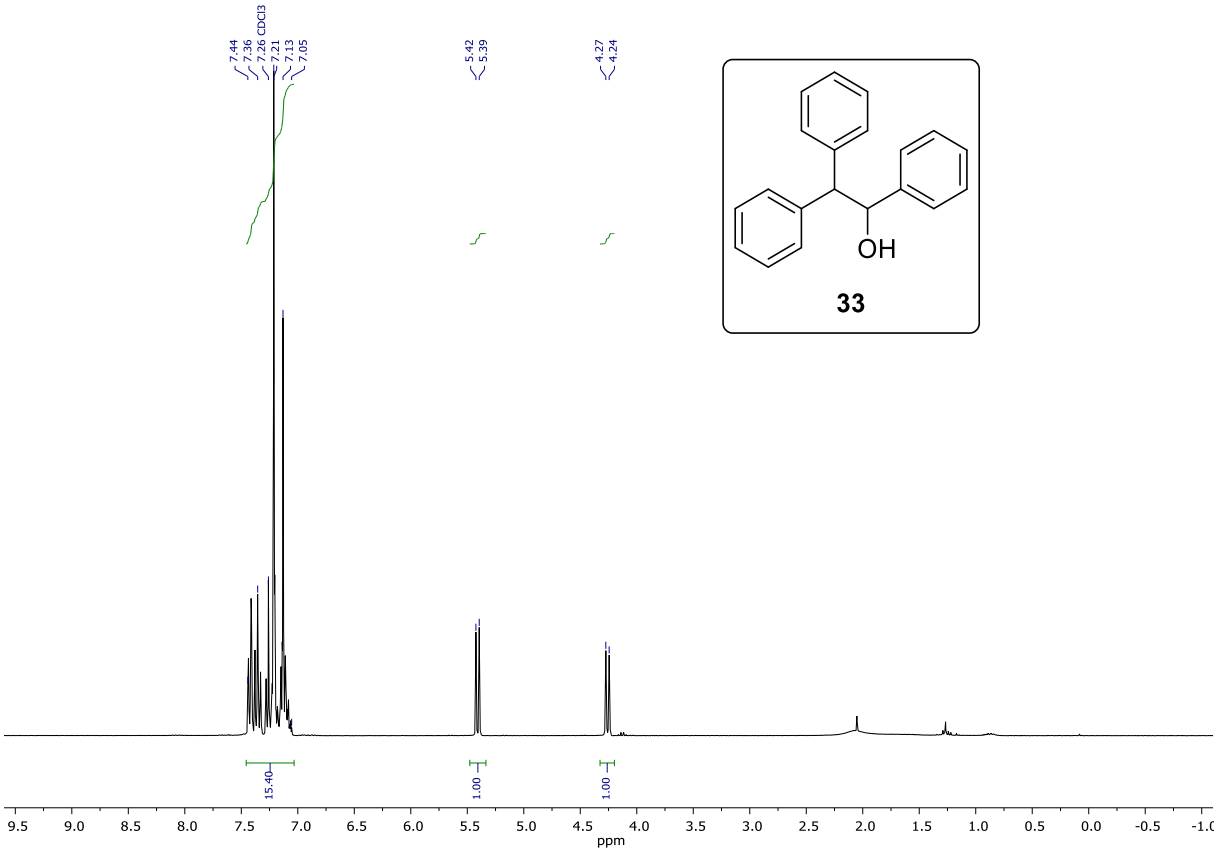


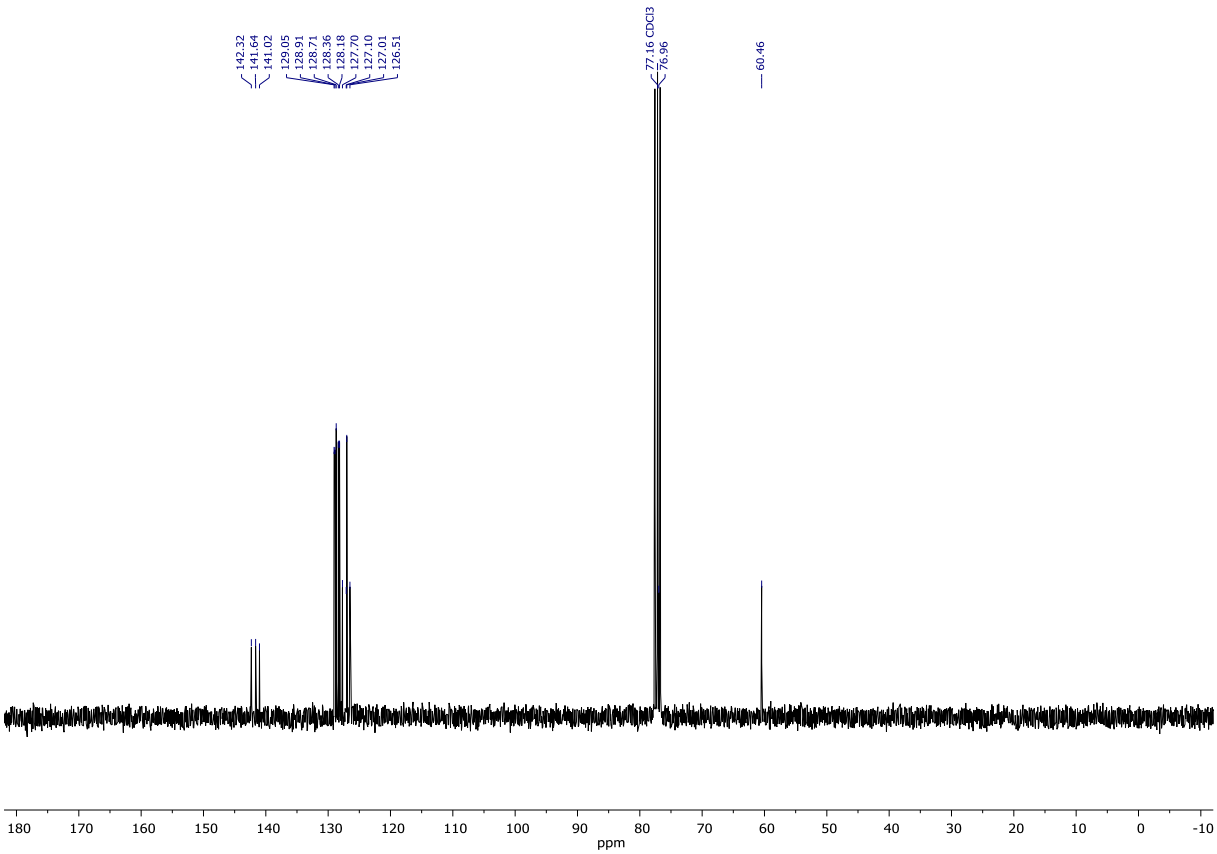
Compound **7b**, ^{1}H- and ^{13}C-NMR (d_7-DMF)



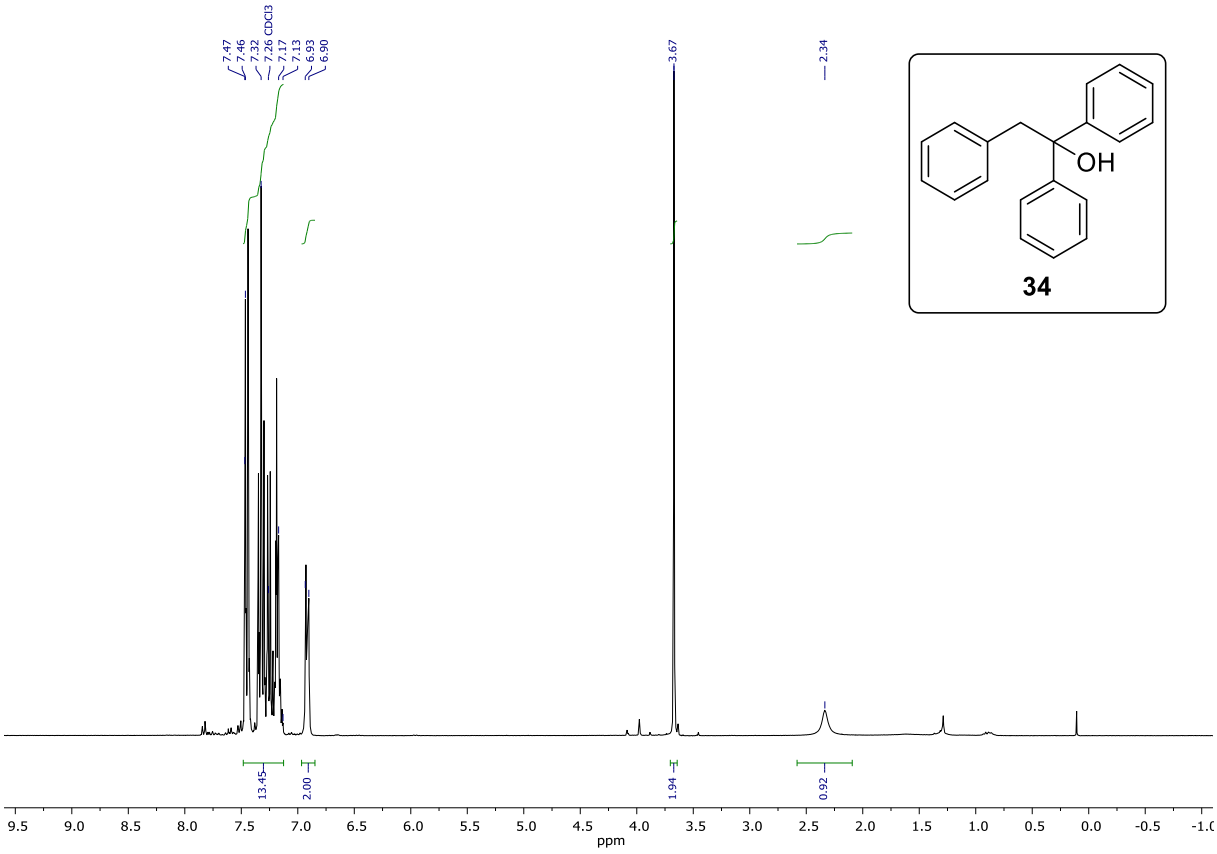


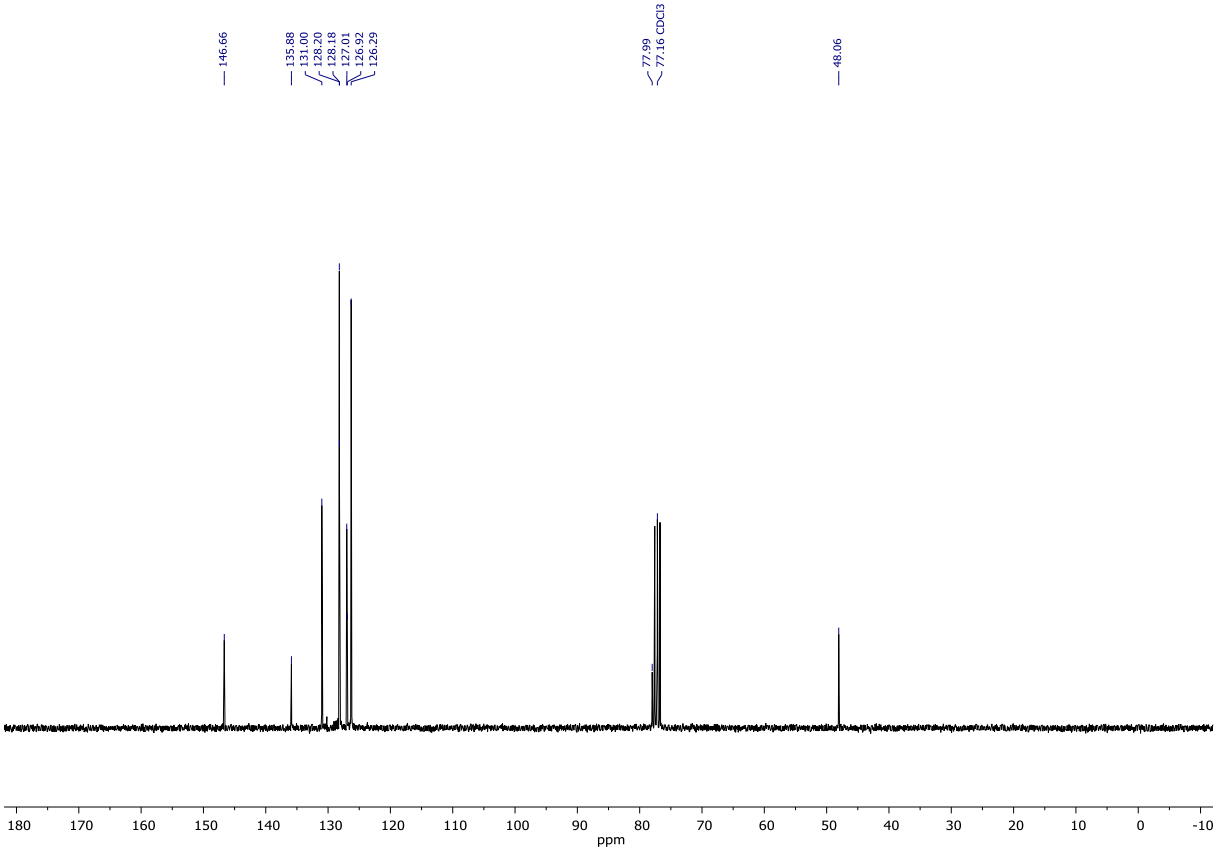
Compound **33**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)





Compound **34**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)





10. References

[1] S. Hünig, P. Kreitmeier, G. Märkl, J. Sauer, *Verlag Lehmanns* **2006**.

[2] R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow, P. Granger, *Magn. Reson. Chem.* **2002**, *40*, 489-505.

[3] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176-2179.

[4] J. Luo, J. Zhang, *ACS Catal.* **2016**, *6*, 873-877.

[5] E. Speckmeier, T. G. Fischer, K. Zeitler, *J. Am. Chem. Soc.* **2018**, *140*, 15353-15365.

[6] M. S. Lowry, J. I. Glodsmith, J. D. Slinker, R. Rohl, R. A. Pascal, G. G. Malliaras, S. Bernhard, *Chem. Mater.* **2005**, *17*, 5712-5719.

[7] R. M. Pearson, C. H. Lim, B. G. McCarthy, C. B. Musgrave, G. M. Miyake, *J. Am. Chem. Soc.* **2016**, *138*, 11399-11407.

[8] X. Dong, P. Hu, W. Shen, Z. Li, R. Liu, X. Liu, *Polymers* **2017**, *9*, 400.

[9] P. R. Blakemore, S. P. Marsden, H. D. Vater, *Org. Lett.* **2006**, *8*, 773-776.

[10] A. R. Katritzky, Y. Fang, *Heterocycles* **2000**, *53*, 1783.

[11] M. Das, D. F. O'Shea, *Tetrahedron* **2013**, *69*, 6448-6460.

[12] a) M. T. Reetz, S. Stanchev, H. Haning, *Tetrahedron* **1992**, *48*, 6813-6820; b) S.-i. Fukuzawa, K. Mutoh, T. Tsuchimoto, T. Hiyama, *J. Org. Chem.* **1996**, *61*, 5400-5405.

[13] D. Basavaiah, P. Dharma Rao, *Tetrahedron Asymm.* **1995**, *6*, 789-800.

[14] a) S. Zushi, Y. Kodama, Y. Fukuda, K. Nishihata, M. Nishio, M. Hirota, J. Uzawa, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2113-2119; b) R. D. Rieke, R. M. Wehmeyer, T.-C. Wu, G. W. Ebert, *Tetrahedron* **1989**, *45*, 443-454.

[15] M. Chierchia, C. Law, J. P. Morken, *Angew. Chem. Int. Ed.* **2017**, *56*, 11870-11874.

[16] A. Rioz-Martinez, G. de Gonzalo, D. E. Torres Pazmino, M. W. Fraaije, V. Gotor, *J. Org. Chem.* **2010**, *75*, 2073-2076.

[17] B. Bennetau, J. Dunogues, *Tetrahedron Lett.* **1983**, *24*, 4217-4218.

[18] G. Zweifel, R. Fisher, A. Horng, *Synthesis* **2002**, *1973*, 37-38.

[19] A. Fernandez-Mateos, S. Encinas Madrazo, P. Herrero Teijon, R. Rubio Gonzalez, *J. Org. Chem.* **2009**, *74*, 3913-3918.

[20] M. Blesic, M. Swadzba-Kwasny, T. Belhocine, H. Q. Gunaratne, J. N. Lopes, M. F. Gomes, A. A. Padua, K. R. Seddon, L. P. Rebelo, *Phys. Chem. Chem. Phys.* **2009**, *11*, 8939-8948.

[21] Y. Liu, J. Cornella, R. Martin, *J. Am. Chem. Soc.* **2014**, *136*, 11212-11215.

[22] W. Xu, T. Li, G. Li, Y. Wu, T. Miyashita, *J. Photochem. Photobiol. A: Chem.* **2011**, *219*, 50-57.

[23] V. V. Pavlishchuk, A. W. Addison, *Inorg. Chim. Acta* **2000**, *298*, 97-102.

[24] T. Kurita, F. Aoki, T. Mizumoto, T. Maejima, H. Esaki, T. Maegawa, Y. Monguchi, H. Sajiki, *Chemistry* **2008**, *14*, 3371-3379.

[25] M. Pena-Lopez, M. Ayan-Varela, L. A. Sarandeses, J. Perez Sestelo, *Chemistry* **2010**, *16*, 9905-9909.

[26] K. Takahashi, M. Takaki, R. Asami, *Org. Magn. Reson.* **1971**, *3*, 539-543.

[27] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, Z. G., J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian, Inc., Wallingford CT* **2013**.

[28] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378-6396.

[29] T. Taniguchi, H. Zaimoku, H. Ishibashi, *Chemistry* **2011**, *17*, 4307-4312.

[30] A. L. Berger, K. Donabauer, B. König, *Chem. Sci.* **2018**, *9*, 7230-7235.

[31] D. Nicewicz, H. Roth, N. Romero, *Synlett* **2015**, *27*, 714-723.
[32] M. Nakajima, E. Fava, S. Loescher, Z. Jiang, M. Rueping, *Angew. Chem. Int. Ed.* **2015**, *54*, 8828-8832.