Supporting Information

Photocatalytic Barbier Reaction – Visible-Light induced Allylation and Benzylation of Aldehydes and Ketones

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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).

The mass spectrometrical measurements were performed at the Central Analytical Laboratory of the University of Regensburg. All 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. 1-Naphthol 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, vanillin 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) 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.

CV measurements were 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 TBATFB 0.1 M as supporting electrolyte. The potentials were achieved relative to the Fc/Fc+ redox couple with ferrocene as internal standard.[4] 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 measurements were carried out as follows: a 0.1 M solution of TBATFB in acetonitrile was added to the measuring cell and the solution was degassed by argon purge for 5 min. After recording the baseline the electroactive compound was added (0.01 M) and the solution was again degassed a stream of argon for 5 min. The cyclic voltammogram was recorded with one to three 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.

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.

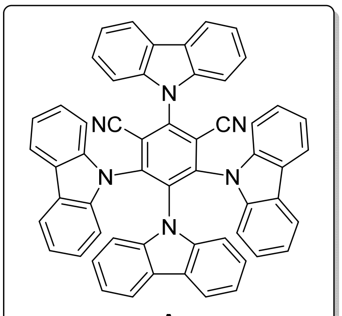
2. General procedures

1.1. Synthesis of photocatalysts

2,4,5,6-Tetra(carbazole-9-yl)isophthalonitrile (4CzIPN, A)

The photocatalysts were synthesized according to a literature procedure.[5]

Under a nitrogen atmosphere, carbazole (1.67 g, 10 mmol, 5 eq.) was dissolved in dry THF (40 ml) at room temperature. Sodium hydride (60 % in paraffin oil, 0.6 g, 15 mmol, 6 eq.) was slowly added and the reaction mixture was stirred for 30 minutes at room temperature. Tetrafluoroisophthalonitrile or tetrafluorophthalonitrile (0.4 g, 2 mmol, 1 eq.) was added and the reaction was heated to 40 °C. After 12 h, the reaction mixture was quenched with water (2 ml), concentrated under vacuum and washed with water and EtOH. After recrystallization from hexane/DCM, the desired products were obtained.



A

^{1}H NMR (400 MHz, CDCl$_3$, δ_H) 8.22 (d, *J* = 7.7 Hz, 2H), 7.78 – 7.65 (m, 8H), 7.52 – 7.47 (m, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.25 – 7.18 (m, 4H), 7.16 – 7.00 (m, 8H), 6.82 (td, *J* = 8.2, 1.1 Hz, 4H), 6.63 (td, *J* = 7.6, 1.2 Hz, 2H).

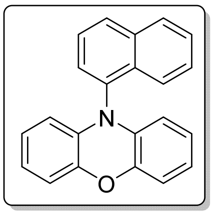
^{13}C NMR (101 MHz, CDCl$_3$, δ_C) 145.3 (C$_q$), 144.7 (C$_q$), 140.1 (C$_q$), 138.3 (C$_q$), 137.1 (C$_q$), 134.9 (C$_q$), 127.1 (+), 125.9 (+), 125.1 (C$_q$), 124.9 (C$_q$), 124.7 (+), 124.0, 122.5 (+), 122.1 (+), 121.5 (+), 121.1 (+), 120.6 (+), 119.8 (+), 116.5 (C$_q$), 111.8 (C$_q$), 110.1 (+), 109.6 (+), 109.6 (+).

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

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

1-Naphthalene-10-phenoxazine[6b]

A flame dried schlenk flask was equipped with phenoxazine (2.0 g, 10.9 mmol, 1 eq.), NaO^{t}Bu (2.1 g, 21,8 mmol, 2 eq.), RuPhos (131.2 mg, 0.32 mmol. 3 mol%), RuPhos precat (229.5 mg, 0.32 mmol, 3 mol%), 1-bromonaphthalene (3.1 ml, 21.8 mmol, 2 eq.) and 12 ml dry dioxane. The reaction mixture was stirred at 130 °C for 48 h. After cooling to room temperature DCM (20 ml) was added and the solution was washed with water (3 x 20 ml), brine (1 x 20 ml) and dried over $MgSO_4$. After removing the solvents under reduced pressure, the crude product was obtained. It was purified by recrystallization from DCM. After recrystallization, the solution was layered with hexane at –25 °C and the product was obtained as a light yellow powder.



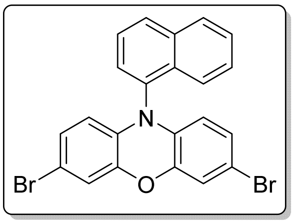
^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 8.08 (d, *J* = 8.4 Hz, 1H), 8.02 – 7.94 (m, 2H), 7.68 – 7.60 (m, 1H), 7.59 – 7.52 (m, 2H), 7.51 – 7.44 (m, 1H), 6.78 – 6.69 (m, 2H), 6.63 (t, *J* = 7.6 Hz, 2H), 6.49 (dt, *J* = 7.7, 1.5 Hz, 2H), 5.70 (dd, *J* = 8.0, 1.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, δ_C) 144.1 (C_q), 135.7 (C_q), 135.2 (C_q), 134.4 (C_q), 131.5 (C_q), 129.3 (+), 129.1 (+), 128.9 (+), 127.4 (+), 127.0 (+), 126.9 (+), 123.5 (+), 123.5 (+), 121.4 (+), 115.5 (+), 113.5 (+).

Yield: 78%

3,7-Dibromo 1-naphthalene-10-phenoxazine

In a flask which was covered in aluminum foil to block out light, 1-naphthalene-10-phenoxazine (1.6 g, 5.2 mmol, 1 eq.) was dissolved in 160 ml chloroform. 160 ml of glacial acetic acid was added to the solution. *N*-Bromosuccinimide (1.9 mg, 10.6 mmol, 2.1 eq.) was added to the stirred reaction mixture in small portions in the dark. After stirring at room temperature for 2 h, the solvents were removed under reduced pressure. The solid residue was dissolved in chloroform, washed with water (3 x 20 ml), brine (1 x 20 ml) and dried with $MgSO_4$ and the product was collected as a brown powder.



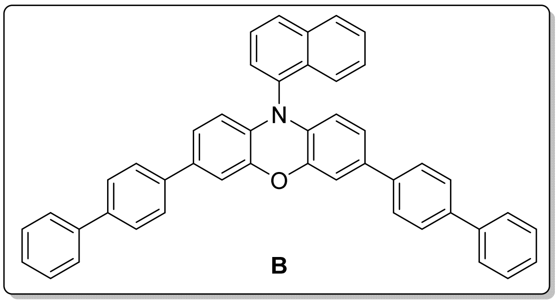
^{1}H NMR (400 MHz, Benzene-*d*$_6$, δ_H) δ 7.82 (d, *J* = 8.3 Hz, 1H), 7.57 (dd, *J* = 18.9, 8.1 Hz, 2H), 7.21 – 7.18 (m, 1H), 7.15 – 7.10 (m, 2H), 6.90 (dd, *J* = 7.3, 1.2 Hz, 1H), 6.84 (d, *J* = 2.2 Hz, 2H), 6.36 (dd, *J* = 8.5, 2.2 Hz, 2H), 5.31 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR (101 MHz, Benzene-*d*$_6$, δ_C) 144.6 (C_q), 135.9 (C_q), 134.6 (C_q), 133.4 (C_q), 131.2 (C_q), 129.6 (+), 129.1 (+), 128.8 (+), 127.3 (+), 127.0 (+), 126.9 (+), 123.2 (+), 119.1 (+), 114.(+), 113.4 (+), 110.4 (C_q).

Yield: 77%

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

In a flame dried schlenk flask 3,7-dibromo 1-naphthalene-10-phenoxazine (1.1 g, 2.2 mmol, 1 eq.) and 4-biphenylboronic acid (1.9 g, 9.7 mmol, 4 eq.) were dissolved in 90 ml THF. 27 ml of a 2 M solution of K_2CO_3 in water was added to the solution and the reaction mixture was stirred at 80 °C for 20 minutes. After that, a solution of palladium tetrakis(triphenylphosphine) (420 mg, 0.4 mmol, 15 mol%) in 90 ml THF was added and the mixture was refluxed at 100 °C for 24 h. After cooling to room temperature, the solvents were removed under reduced pressure. The solid residue was dissolved in DCM, washed with water (2 x 20 ml), brine (1 x 20 ml) and dried with $MgSO_4$. The crude product was purified by recrystallization in DCM/Methanol and the product was obtained as a light tan powder.



B

^{1}H NMR (400 MHz, DMSO-*d*$_6$, δ_H) 8.18 (dd, *J* = 14.5, 8.0 Hz, 2H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.81 – 7.76 (m, 2H), 7.72 – 7.7 (m, 14H), 7.46 (t, *J* = 7.8 Hz, 4H), 7.38 – 7.33 (m, 2H), 7.21 (d, *J* = 2.1 Hz, 2H), 6.98 (dd, *J* = 8.4, 2.1 Hz, 2H), 5.73 (d, *J* = 8.3 Hz, 2H).

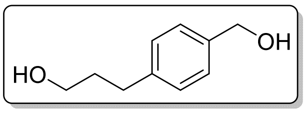
Yield: 80%

1.2. Synthesis of starting materials

3-(4-(Hydroxymethyl)phenyl)propan-1-ol[7]

The substrate was synthesized according to a literature procedure.[8]

Lithium aluminium hydride (2.4 g, 61.8 mmol, 6 eq) was added to a solution of 4-(2-carboxethyl)benzoic acid (2 g, 10.3 mmol, 1 eq) in 120 mL anhydrous THF. The reaction mixture was stirred at room temperature for 3 h and quenched by addition of aqueous KOH (80 mL, 5 wt%). The resulting solution was extracted with ethyl acetate. The organic layer was and washed twice with brine, dried over $MgSO_4$ and the solvent was removed in vacuum. The crude product was purified by automated flash column chromatography (PE/EtOAc 1:1) to provide the desired product as a colorless oil.



^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.30 – 7.26 (m, 2H), 7.21 – 7.17 (m, 2H), 4.65 (s, 2H), 3.66 (t, J = 6.4 Hz, 2H), 2.73 – 2.68 (m, 2H), 1.92 – 1.84 (m, 2H), 1.69 (s, 2H).

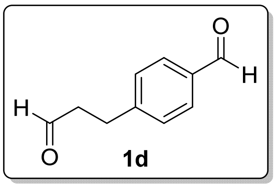
^{13}C NMR (101 MHz, $CDCl_3$, δ_C) 141.5 (C_q), 138.6 (C_q), 128.8 (+), 127.4 (+), 65.3 (–), 62.3 (–), 34.3 (–), 31.9 (–).

Yield: 64%

4-(3-Oxopropyl)benzaldehyde[9]

The substrate was synthesized according to a literature procedure.[10]

Pyridinium chlorochromate (1.8 g, 8.58 mmol, 3 eq.) was added to a solution of 3-(4-(hydroxymethyl)phenyl) propan-1-ol (1 g, 2.86 mmol, 1 eq.) in THF (30ml) and stirred at 75 °C for 16 h. After cooling, the solution was filtered and evaporated. The product was purified by automated flash column chromatography (DCM/MeOH, 20:1) to give compound **1d**.



1d

^{1}H NMR (300 MHz, $CDCl_3$, δ_H) 9.81 (s, 1H), 9.70 – 9.64 (m, 1H), 7.68 – 7.63 (m, 2H), 7.26 – 7.19 (m, 2H), 2.91 – 2.85 (m, 2H), 2.76 – 2.64 (m, 2H).

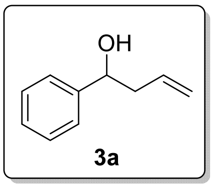
^{13}C NMR (75 MHz, $CDCl_3$, δ_C) 200.8 (+), 191.9 (+), 147.8 (C_q), 134.7 (C_q), 130.1 (+), 129.0 (+), 44.6 (–), 28.1 (–).

1.3. General procedure for the photocatalytic allylation of aldehydes and ketones

A 5 mL crimp cap vial was equipped with the aldehyde/ketone **1** (0.2 mmol, 1 equiv.), an allyl or benzyl bromide **2** (0.4 mmol, 2 equiv.), DIPEA (200 µl, 1.2 mmol, 6 equiv.), $LiBF_4$ (28.1 mg, 0.3 mmol, 1.5 eq.) the photocatalyst (5 mol%) and a stirring bar. After adding the solvent (2 mL DMA) via syringe, the vessel was capped and degassed by three cycles of freeze pump thaw. The reaction mixture was stirred and irradiated using a 400 nm (± 10 nm) LED for 2 – 6 h at 25 °C. The progress could be monitored by TLC, GC analysis and GC-MS analysis.

The reaction mixture was diluted with water (10 ml), extracted with ethyl acetate (3 x 20 ml), washed with brine (1 x 20 ml) and dried over Na_2SO_4. The crude product was obtained by removing the solvents under reduced pressure. Purification was performed by automated flash column chromatography (PE/EtOAc, 0-20% EtOAc or DCM/MeOH,0-5% MeOH) yielding the corresponding product **3**.

1-Phenyl-3-buten-1-ol (3a)[11]



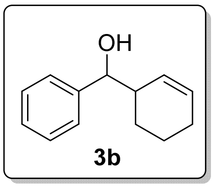
3a

^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.40 – 7.32 (m, 4H), 7.31 – 7.24 (m, 1H), 5.88 – 5.74 (m, 1H), 5.21 – 5.11 (m, 2H), 4.74 (dd, *J* = 7.6, 5.4 Hz, 1H), 2.58 – 2.45 (m, 2H), 2.07 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, δ_C) 144.0 (C_q), 134.6 (+), 128.5 (+), 127.7 (+), 125.9 (+), 118.5 (–), 73.4 (+), 43.9 (–).

Yield: 44%

Cyclohex-2-enyl(phenyl)methanol (3b)[12]



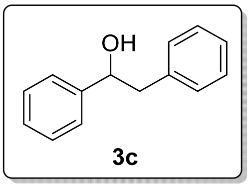
3b

^{1}H NMR (300 MHz, CDCl$_3$, δ_H) 7.39 – 7.26 (m, 10H), 5.85 (s, 2H), 5.84 – 5.77 (m, 1H), 5.44 – 5.34 (m, 1H), 4.58 (d, *J* = 6.6 Hz, 1H), 4.46 (d, *J* = 7.0 Hz, 1H), 2.57 – 2.42 (m, 2H), 2.02 – 1.96 (m, 5H), 1.80 – 1.69 (m, 3H), 1.57 – 1.44 (m, 4H), 1.37 – 1.23 (m, 2H).

^{13}C NMR (75 MHz, CDCl$_3$, δ_C) 143.6 (C$_q$), 143.0 (C$_q$), 130.5 (+), 129.9 (+), 128.4 (+), 128.3 (+), 128.1 (+), 127.5 (+), 127.5 (+), 127.2 (+), 126.6 (+), 126.4 (+), 78.1 (+), 77.49 (+), 43.1 (+), 42.9 (+), 26.4 (–), 25.4 (–), 25.3 (–), 24.0 (–), 21.6 (–), 21.2 (–).

Yield: 58 % (mixture syn/anti 1:1)

1,2-Diphenylethanol (3c)[13]



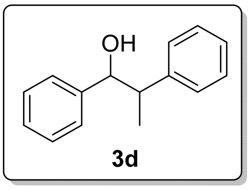
3c

^{1}H NMR (400 MHz, DMSO-d_6, δ_H) 7.34 – 7.12 (m, 10H), 5.26 (s, 1H), 4.80 – 4.69 (m, 1H), 2.94 – 2.82 (m, 2H).

^{13}C NMR (101 MHz, DMSO-d_6, δ_C) 145.7 (C$_q$), 139.1 (C$_q$), 129.5 (+), 127.8 (+), 127.8 (+), 126.7 (+), 126.0 (+), 125.8 (+), 73.7 (+), 45.7 (–).

Yield: 31 %

1,2-Diphenyl-1-propanol (3d)[14]



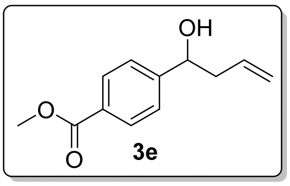
3d

^{1}H NMR (400 MHz, CDCl$_3$, δ_H) 7.41 – 7.13 (m, 20H), 4.82 (d, *J* = 5.7 Hz, 1H), 4.67 (d, *J* = 8.7 Hz, 1H), 3.17 – 3.09 (m, 1H), 3.08 – 2.98 (m, 1H), 1.93 (s, 1H), 1.90 (s, 1H), 1.33 (d, *J* = 7.0 Hz, 3H), 1.10 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$, δ_C) 143.7 (C$_q$), 143.5 (C$_q$), 143.0 (C$_q$), 142.7 (C$_q$), 128.8 (+), 128.4 (+), 128.4 (+), 128.2 (+), 128.2 (+), 128.1 (+), 127.9 (+), 127.3 (+), 127.1 (+), 127.0 (+), 126.6 (+), 126.4 (+), 79.8 (+), 78.8 (+), 48.3 (+), 47.3 (+), 18.5 (+), 15.1 (+).

Yield: 37 % (mixture syn/anti 1:1)

Methyl 4-(1-hydroxybut-3-en-1-yl)benzoate (3e)[15]



3e

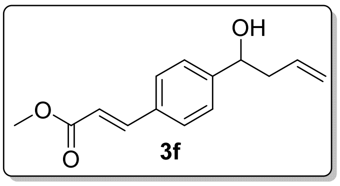
^{1}H NMR (300 MHz, CDCl$_3$, δ_H) 8.05 – 7.96 (m, 2H), 7.45 – 7.39 (m, 2H), 5.87 – 5.70 (m, 1H), 5.20 – 5.12 (m, 2H), 4.80 (dd, J = 7.8, 4.9 Hz, 1H), 3.90 (s, 3H), 2.58 – 2.41 (m, 2H), 2.18 (s, 1H).

^{13}C NMR (75 MHz, CDCl$_3$, δ_C) 167.1 (C$_q$), 149.1 (C$_q$), 133.9 (+), 129.9 (+), 129.4 (C$_q$), 125.9 (+), 119.2 (–), 72.9 (+), 52.2 (+), 44.0 (–).

HRMS (APCI) (m/z): [MH$^+$] (C$_{12}$H$_{15}$O$_3$$^+$) calc.: 207.1016, found: 207.1018.

Yield: 33%

Methyl 3-(4-(1-hydroxybut-3-en-1-yl)phenyl)acrylate (3f)[16]



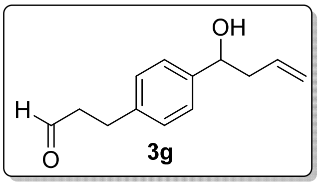
^{1}H NMR (400 MHz, DMSO-*d*$_6$, δ_H) 7.56 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 6.99 (d, J = 12.7 Hz, 1H), 5.98 (d, J = 12.7 Hz, 1H), 5.82 – 5.71 (m, 1H), 5.31 (d, J = 4.5 Hz, 1H), 5.03 – 4.95 (m, 2H), 4.60 (q, J = 6.0 Hz, 1H), 3.65 (s, 3H), 2.40 – 2.33 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$, δ_C) 166.3 (C$_q$), 146.8 (C$_q$), 142.4 (+), 135.4 (+), 132.9 (C$_q$), 129.5 (+), 125.6 (+), 118.6 (+), 116.8 (–), 71.9 (+), 51.2 (+), 43.5 (–).

HRMS (ESI) (m/z): [MH$^+$] ($C_{19}H_{20}ClO_4^+$) calc.: 233.1172, found: 233.1175.

Yield: 19%

3-(4-(1-hydroxybut-3-en-1-yl)phenyl)propanal (3g)



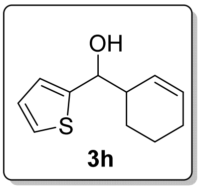
^{1}H NMR (400 MHz, CDCl$_3$, δ_H) 9.81 (t, J = 1.4 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.21 – 7.14 (m, 2H), 5.87 – 5.73 (m, 1H), 5.19 – 5.11 (m, 2H), 4.70 (dd, J = 7.5, 5.4 Hz, 1H), 2.99 – 2.90 (m, 2H), 2.82 – 2.69 (m, 2H), 2.53 – 2.42 (m, 2H), 2.09 (s, 1H).

^{13}C NMR (101 MHz, CDCl$_3$, δ_C) 201.7 (+), 142.1 (C$_q$), 139.7 (C$_q$), 134.6 (+), 128.5 (+), 126.2 (+), 118.5 (–), 73.2 (+), 45.3 (–), 43.9 (–), 27.9 (–).

HRMS (APCI) (m/z): [MNH$_4^+$] ($C_{13}H_{20}NO_2^+$) calc.: 222.1489, found: 222.1493.

Yield: 30%

Cyclohex-2-enylthiophen-2-ylmethanol (3h)[17]



3h

anti-product (R,S / S,R)

^{1}H NMR (400 MHz, CDCl$_3$, δ_H) 7.29 – 7.26 (m, 1H), 7.03 – 6.94 (m, 2H), 5.88 – 5.80 (m, 1H), 5.51 – 5.43 (m, 1H), 4.83 (d, *J* = 6.9 Hz, 1H), 2.61 – 2.53 (m, 1H), 2.06 – 1.96 (m, 3H), 1.90 – 1.73 (m, 2H), 1.59 – 1.50 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$, δ_C) 146.9 (C$_q$), 130.7 (+), 127.5 (+), 126.6 (+), 124.8 (+), 124.6 (+), 73.9 (+), 43.6 (+), 25.4 (–), 24.6 (–), 21.2 (–).

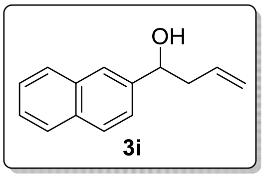
syn-product (R,R / S,S)

^{1}H NMR (400 MHz, CDCl$_3$, δ_H) 7.26 – 7.24 (m, 1H), 7.00 – 6.95 (m, 2H), 5.94 – 5.86 (m, 1H), 5.86 – 5.80 (m, 1H), 4.74 (d, *J* = 6.6 Hz, 1H), 2.61 – 2.50 (m, 1H), 2.04 – 1.98 (m, 2H), 1.79 – 1.69 (m, 1H), 1.66 – 1.48 (m, 3H), 1.42 – 1.32 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$ δ_C) 147.9 (C$_q$), 130.7 (+), 126.7 (+), 126.6 (+), 124.6 (+), 124.1 (+), 74.3 (+), 43.5 (+), 26.2 (–), 25.4 (–), 21.5 (–).

Yield: 32 % (mixture syn/anti 1:1)

1-(2-Naphthyl)-3buten-1-ol (3i)[18]



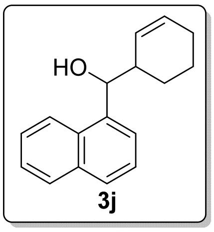
3i

^{1}H NMR (400 MHz, CDCl$_3$, δ_H) 7.88 – 7.79 (m, 4H), 7.53 – 7.44 (m, 3H), 5.91 – 5.78 (m, 1H), 5.24 – 5.12 (m, 2H), 4.91 (dd, *J* = 7.6, 5.3 Hz, 1H), 2.69 – 2.53 (m, 2H), 2.20 (s, 1H).

^{13}C NMR (101 MHz, CDCl$_3$, δ_C) 141.4 (C$_q$), 134.5 (+), 133.4 (C$_q$), 133.1 (C$_q$), 128.3 (+), 128.1 (+), 127.8 (+), 126.3 (+), 125.9 (+), 124.6 (+), 124.1 (+), 118.7 (–), 73.5 (+), 43.9 (–).

Yield: 48%

Cyclohex-2-enyl(1-naphthyl)methanol (3j)[19]



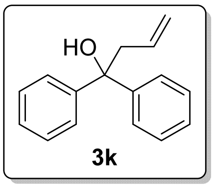
3j

^{1}H NMR (400 MHz, DMSO-*d$_6$*, δ_H) 8.28 – 8.22 (m, 1H), 8.22 – 8.15 (m, 1H), 7.96 – 7.88 (m, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.65 – 7.59 (m, 2H), 7.56 – 7.43 (m, 6H), 5.90 (dq, *J* = 10.3, 2.2 Hz, 1H), 5.77 – 5.67 (m, 1H), 5.66 – 5.56 (m, 1H), 5.42 (d, *J* = 4.3 Hz, 1H), 5.33 (d, *J* = 4.3 Hz, 1H), 5.29 (dq, *J* = 10.2, 2.3 Hz, 1H), 5.20 (dd, J = 6.7, 4.3 Hz, 1H), 5.03 (dd, J = 7.0, 4.3 Hz, 1H), 2.62 – 2.51 (m, 2H), 1.99 – 1.83 (m, 4H), 1.76 – 1.57 (m, 4H), 1.44 – 1.27 (m, 4H).

^{13}C NMR (101 MHz, DMSO-*d$_6$*, δ_C) 140.4 (C_q), 140.3 (C_q), 133.4 (C_q), 133.3 (C_q), 130.5 (+), 129.5 (+), 128.7 (+), 128.6 (+), 128.5 (+), 127.9 (+), 127.4 (+), 127.1 (+), 127.0 (+), 125.6 (+), 125.6 (+), 125.3 (+), 125.2 (+), 125.2 (+), 125.2 (+), 124.3 (+), 124.3 (+), 123.9 (+), 123.8 (+), 73.4 (+), 72.3 (+), 42.2 (+), 42.2 (+), 26.4 (–), 24.8 (–), 24.8 (–), 24.2 (–), 21.5 (–), 20.9 (–).

Yield: 48% (mixture syn/anti 1:1)

1,1-Diphenylbut-3-en-1-ol (3k)[20]



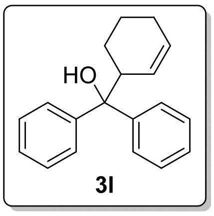
3k

^{1}H NMR (300 MHz, CDCl$_3$, δ_H) 7.54 – 7.46 (m, 4H), 7.38 – 7.32 (m, 4H), 7.29 – 7.22 (m, 2H), 5.80 – 5.62 (m, 1H), 5.34 – 5.17 (m, 2H), 3.13 (dt, *J* = 7.2, 1.2 Hz, 2H), 2.64 (s, 1H).

^{13}C NMR (75 MHz, CDCl$_3$, δ_C) 146.6 (C_q), 133.5 (+), 128.3 (+), 126.9 (+), 126.1 (+), 120.6 (–), 77.0 (C_q), 46.8 (–).

Yield: 75 %

Cyclohex-2-en-1-yldiphenylmethanol (3l)[21]



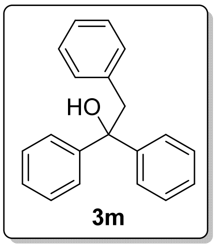
3l

^{1}H NMR (300 MHz, $CDCl_3$, δ_H) 7.71 – 7.61 (m, 2H), 7.58 – 7.50 (m, 2H), 7.42 – 7.28 (m, 4H), 7.28 – 7.16 (m, 2H), 6.06 – 5.96 (m, 1H), 5.60 – 5.51 (m, 1H), 3.60 – 3.43 (m, 1H), 2.30 (s, 1H), 2.12 – 2.00 (m, 2H), 1.88 – 1.77 (m, 1H), 1.64 – 1.47 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, δ_C) 146.9 (C_q), 145.6 (C_q), 133.8 (+), 128.4 (+), 128.1 (+), 126.6 (+), 126.5 (+), 126.3 (+), 126.1 (+), 125.5 (+), 79.4 (C_q), 43.8 (+), 25.4 (–), 23.9 (–), 22.1 (–).

Yield: 76 %

1,1,2-Triphenylethan-1-ol (3m)[22]



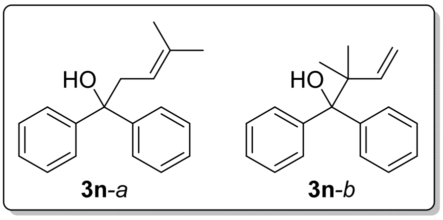
3m

^{1}H NMR (300 MHz, $CDCl_3$, δ_H) 7.49 – 7.42 (m, 4H), 7.36 – 7.29 (m, 4H), 7.29 – 7.22 (m, 2H), 7.22 – 7.14 (m, 3H), 6.97 – 6.87 (m, 2H), 3.68 (s, 2H), 2.34 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$, δ_C) 146.7 (C_q), 135.9 (C_q), 131.0 (+), 128.2 (+), 128.2 (+), 127.0 (+), 126.9 (+), 126.3 (+), 78.0 (C_q), 48.1 (–).

Yield: 33 %

4-Methyl-1,1-diphenylpent-3-en-1-ol & 2,2-dimethyl-1,1-diphenylbut-3-en-1-ol (3n)[20, 23]



3n-*a*   **3n**-*b*

3n-*a*:

^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.51 – 7.46 (m, 4H), 7.37 – 7.30 (m, 4H), 7.26 – 7.21 (m, 2H), 5.12 – 5.04 (m, 1H), 3.05 (d, *J* = 7.4 Hz, 2H), 2.59 (s, 1H), 1.71 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, δ_C) 147.1 (C_q), 138.1 (C_q), 128.2 (+), 126.8 (+), 126.1 (+), 118.5 (+), 77.8 (C_q), 40.9 (–), 26.3 (+), 18.4. (+)

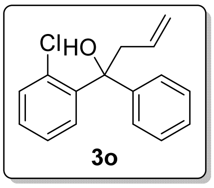
3n-*b*:

^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.58 – 7.52 (m, 4H), 7.29 – 7.20 (m, 6H), 6.19 (dd, J = 17.6, 10.9 Hz, 1H), 5.26 – 5.10 (m, 2H), 2.46 (s, 1H), 1.19 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, δ_C) 146.5 (+), 145.7 (C_q), 128.6 (+), 127.4 (+), 126.8 (+), 112.8 (–), 81.8 (C_q), 45.6 (C_q), 24.4 (+).

Yield: 77 % (**3n**-*a*/**3n**-*b* = 2.6:1)

1-(2-Chlorophenyl)-1-phenylbut-3-en-1-ol (3o)



3o

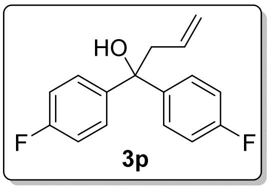
^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.80 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.33 – 7.17 (m, 8H), 5.74 – 5.61 (m, 1H), 5.16 – 5.03 (m, 2H), 3.41 (ddt, *J* = 14.1, 6.7, 1.3 Hz, 1H), 3.13 (s, 1H), 3.01 (ddt, *J* = 14.1, 7.2, 1.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, δ_C) 145.7 (C_q), 142.7 (C_q), 133.7 (+), 132.5 (C_q), 131.5 (+), 128.9 (+), 128.8 (+), 128.1 (+), 127.2 (+), 126.6 (+), 126.3 (+), 119.1 (–), 77.7 (C_q), 44.7 (–).

HRMS (APCI) (m/z): $[M + NH_4]^+$ ($C_{16}H_{19}ClNO^+$) calc.: 276.1150, found: 276.1150.

Yield: 41 %

1,1-Bis(4-fluorophenyl)but-3-en-1-ol (3p)[20]



3p

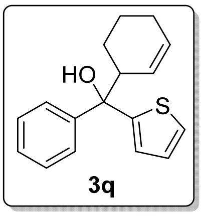
^{1}H NMR (400 MHz, CDCl$_3$, δ_H) 7.43 – 7.37 (m, 4H), 7.06 – 6.96 (m, 4H), 5.71 – 5.59 (m, 1H), 5.28 – 5.19 (m, 2H), 3.04 (dt, J_{CF} = 7.2, 1.1 Hz, 2H), 2.59 (s, 1H).

^{13}C NMR (101 MHz, CDCl$_3$, δ_C) 161.9 (d, $^1J_{CF}$ = 245.9 Hz, C$_q$), 142.3 (d, $^4J_{CF}$ = 3.1 Hz, C$_q$), 133.0 (+), 127.8 (d, $^3J_{CF}$ = 8.1 Hz, +), 121.1 (–), 115.1 (d, $^2J_{CF}$ = 21.3 Hz, +),76.4 (C$_q$), 47.0 (–).

^{19}F NMR (376 MHz, CDCl$_3$, δ_F) -116.4 (s).

Yield: 66 %

Cyclohex-2-en-1-yl(phenyl)(thiophen-2-yl)methanol (3q)



3q

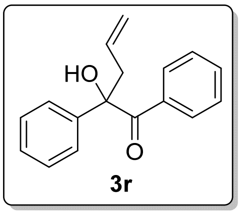
^{1}H NMR (400 MHz, CDCl$_3$, δ_H) 7.68 – 7.62 (m, 2H), 7.58 – 7.53 (m, 2H), 7.35 (ddd, J = 17.6, 8.4, 7.0 Hz, 4H), 7.29 – 7.15 (m, 4H), 7.12 (dd, J = 3.6, 1.2 Hz, 1H), 6.99 (dd, J = 5.1, 3.6 Hz, 1H), 6.96 – 6.90 (m, 2H), 6.09 – 6.00 (m, 1H), 5.97 – 5.89 (m, 1H), 5.67 (dq, J = 10.3, 2.3 Hz, 1H), 5.44 – 5.35 (m, 1H), 3.41 – 3.32 (m, 1H), 3.32 – 3.23 (m, 1H), 2.65 (s, 1H), 2.44 (s, 1H), 2.06 – 1.97 (m, 4H), 1.88 – 1.68 (m, 3H), 1.63 – 1.46 (m, 3H), 1.44 – 1.36 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$, δ_C) 153.3 (C$_q$), 151.2 (C$_q$), 146.0 (C$_q$), 144.7 (C$_q$), 134.4 (+), 133.3 (+), 128.3 (+), 128.1 (+), 127.0 (+), 126.9 (+), 126.7 (+), 126.3 (+), 126.1 (+), 125.7 (+), 125.3 (+), 124.5 (+), 124.0 (+), 123.3 (+), 123.0 (+), 79.4 (C$_q$), 79.1 (C$_q$), 46.4 (+), 46.4 (+), 25.3 (–), 25.3 (–), 24.1 (–), 24.0 (–), 22.0 (–), 21.9 (–).

HRMS (APCI) (m/z): [MH$^+$ - H$_2$O] (C$_{17}$H$_{17}$S$^+$) calc.: 253.1045, found: 253.1045.

Yield: 57 % (mixture syn/anti 1:1)

2-Hydroxy-1,2-diphenylpent-4-en-1-one (3r)[24]



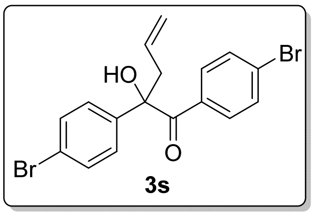
3r

^{1}H NMR (400 MHz, DMSO-*d*$_6$, δ_H) 7.96 – 7.89 (m, 2H), 7.50 – 7.41 (m, 3H), 7.34 (q, *J* = 7.4 Hz, 4H), 7.26 – 7.18 (m, 1H), 6.47 (s, 1H), 5.70 – 5.56 (m, 1H), 4.94 (d, *J* = 1.3 Hz, 1H), 4.93 – 4.88 (m, 1H), 2.93 – 2.77 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$, δ_C) 200.1 (C$_q$), 142.1 (C$_q$), 135.0 (C$_q$), 133.5 (+), 132.3 (+), 130.2 (+), 128.3 (+), 127.8 (+), 127.0 (+), 124.8 (+), 118.1 (–), 82.0 (C$_q$), 45.0 (–).

Yield: 65 %

1,2-Bis(4-bromophenyl)-2-hydroxypent-4-en-1-one (3s)[25]



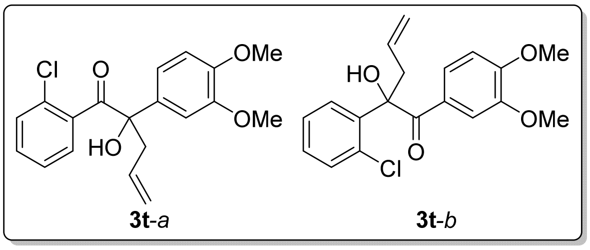
3s

^{1}H NMR (300 MHz, CDCl$_3$, δ_H) 7.71 – 7.63 (m, 2H), 7.54 – 7.42 (m, 4H), 7.39 – 7.32 (m, 2H), 5.81 – 5.59 (m, 1H), 5.23 – 5.02 (m, 2H), 3.84 (s, 1H), 3.10 (ddt, *J* = 13.7, 7.3, 1.0 Hz, 1H), 2.82 (ddt, *J* = 13.7, 7.1, 1.2 Hz, 1H).

^{13}C NMR (75 MHz, CDCl$_3$, δ_C) 199.0 (C$_q$), 140.7 (C$_q$), 133.1 (C$_q$), 132.2 (+), 132.0 (+), 131.9 (+), 131.6 (+), 128.4 (C$_q$), 127.2 (+), 122.4 (C$_q$), 121.5 (–), 81.3 (C$_q$), 44.7 (–).

Yield: 28 %

1-(2-Chlorophenyl)-2-(3,4-dimethoxyphenyl)-2-hydroxypent-4-en-1-one (3t-*a*) and 2-(2-chlorophenyl)-1-(3,4-dimethoxyphenyl)-2-hydroxypent-4-en-1-one (3t-*b*)



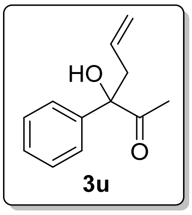
^{1}H NMR (400 MHz, CDCl$_3$, δ_H) 7.88 (dd, J = 7.9, 1.4 Hz, 1H), 7.40 – 7.31 (m, 3H), 7.30 – 7.23 (m, 4H), 7.06 (td, J = 7.6, 1.2 Hz, 1H), 7.03 – 6.97 (m, 3H), 6.86 – 6.80 (m, 1H), 6.68 – 6.62 (m, 2H), 5.87 – 5.66 (m, 2H), 5.24 – 5.17 (m, 3H), 5.10 – 5.04 (m, 1H), 5.00 – 4.91 (m, 1H), 4.76 (s, 1H), 3.87 (s, 4H), 3.83 (s, 3H), 3.81 (s, 4H), 3.69 (s, 3H), 3.56 (s, 1H), 3.21 – 3.10 (m, 2H), 3.08 – 2.98 (m, 1H), 2.89 – 2.81 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$, δ_C) 204.6 (C$_q$), 197.4 (C$_q$), 153.3 (C$_q$), 149.0 (C$_q$), 148.8 (C$_q$), 148.5 (C$_q$), 140.7 (C$_q$), 137.5 (C$_q$), 133.9 (C$_q$), 132.3 (+), 131.9 (+), 131.5 (+), 131.1 (C$_q$), 130.8 (+), 129.9 (+), 129.5 (+), 128.1 (+), 127.4 (+), 127.0 (+), 126.6 (C$_q$), 125.9 (+), 124.3 (+), 120.8 (–), 119.7 (–), 118.6 (+), 112.1 (+), 111.0 (+), 110.0 (+), 109.3 (+), 82.4 (–), 79.8 (–), 56.0 (+), 55.9 (+), 55.9 (+), 55.8 (+), 43.9 (–), 43.2 (–).

HRMS (ESI) (m/z): [MH$^+$] ($C_{19}H_{20}ClO_4^+$) calc.: 347.1045, found: 347.1052.

Yield: 57 % (**3t**-*a*/**3t**-*b* = 1:1.3)

3-Hydroxy-3-phenylhex-5-en-2-one (3u)[26]

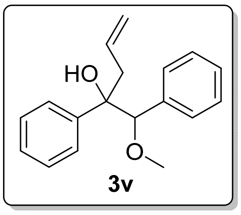


^{1}H NMR (400 MHz, CDCl$_3$, δ_H) 7.51 – 7.45 (m, 2H), 7.41 – 7.34 (m, 2H), 7.34 – 7.28 (m, 1H), 5.82 – 5.69 (m, 1H), 5.26 – 5.14 (m, 2H), 4.24 (s, 1H), 3.04 – 2.88 (m, 2H), 2.09 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$, δ_C) 208.9 (C$_q$), 140.6 (C$_q$), 132.3 (+), 128.8 (+), 128.2 (+), 126.1 (+), 119.8 (–), 82.3 (C$_q$), 41.6 (–), 24.2 (+).

Yield: 12 %

1-Methoxy-1,2-diphenylpent-4-en-2-ol (3v)



^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.30 – 7.21 (m, 3H), 7.20 – 7.10 (m, 5H), 7.03 – 6.94 (m, 2H), 5.70 – 5.50 (m, 1H), 5.15 – 4.95 (m, 2H), 4.30 – 4.28 (2 x s, 1H), 3.26 – 3.22 (2 x s, 3H), 2.92 – 2.82 (m, 2H), 2.73 – 2.51 (m, 1H).

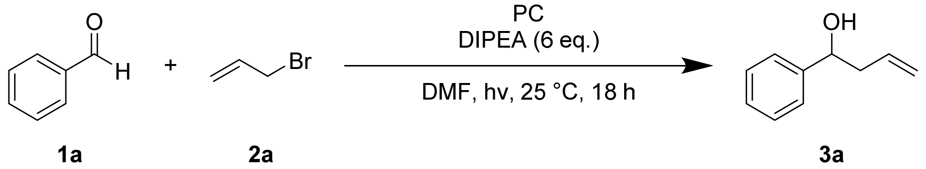
^{13}C NMR (101 MHz, $CDCl_3$, δ_C) 142.7 (C_q), 142.2 (C_q), 136.9 (C_q), 136.8 (C_q), 133.9 (+), 133.7 (+), 128.8 (+), 128.7 (+), 128.0 (+), 127.7 (+), 127.7 (+), 127.5 (+), 127.5 (+), 127.0 (+), 126.9 (+), 126.7 (+), 126.6 (+), 118.7 (–), 118.6 (–), 90.6 (+), 89.8 (+), 78.3 (C_q), 78.3 (C_q), 57.6 (+), 57.6 (+), 42.9 (–), 41.1 (–).

Yield: 36 % (mixture syn/anti 1:1)

3. Detailed optimization of the reaction conditions

3.1. Screening of different photocatalysts

Table 1 – Optimization of the reaction conditions: screening of different photocatalysts [a]

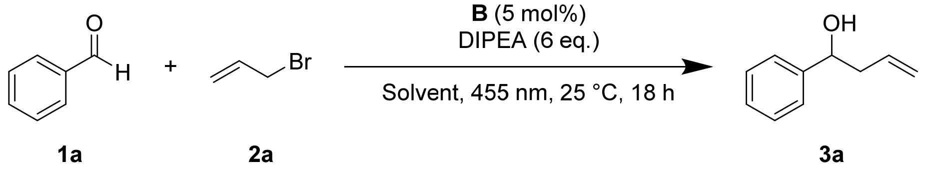


Entry	Photocatalyst (mol%, hν [nm])	Yield[b] [%]
1	4CzIPN (5, 455)	22
2[c]	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (2, 455)	21
3	**D** (5, 400)	48
4	Eosin Y (5, 535)	0
5	Fluorescein (5, 535)	0
6	$[Ru(bpy)_3]Cl_2$ (5, 455)	0
7	Rhodamine 6G	0

[a] The reactions were performed using 1 eq. of **1a** and 2 eq. of **2a**. [b] Determined by GC analysis with 1-Naphthol as an internal standard, [c] DMA was used as a solvent instead of DMF.

3.2. Screening of different solvents

Table 2 – Optimization of the reaction conditions: screening of different solvents[a]



Entry	Solvent	Yield[b] [%]
1	DMF (dry)	38
2	MeCN (dry)	24
3	EtOH	24
4	DCE (dry)	19

5	Toluene (dry)	0
6	DMSO	34
7	THF	7
8	DMA	54

[a] The reactions were performed using 1 eq. of **1a** and 1 eq of **2a**. in 2 mL of degassed solvent under nitrogen[b] Determined by GC analysis with 1-Naphthol as an internal standard.

3.3. Screening of different additives

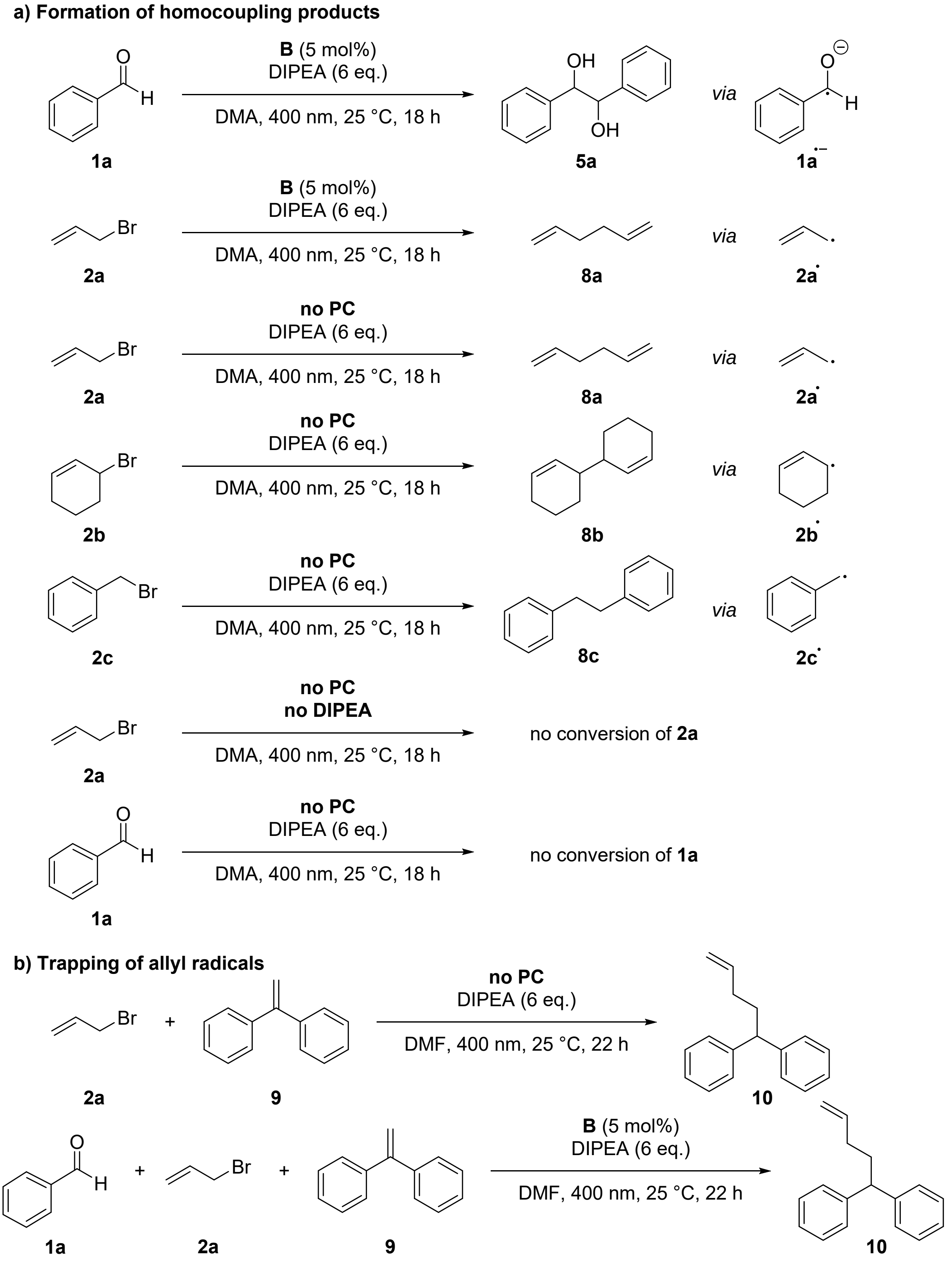
Table 3 – Optimization of the reaction conditions: screening of different additives[a]

Entry	**Electron donor (eq.)**	**Additive (eq.)**	**Yield[b] [%]**
1	DIPEA (6)	–	38
2	TEA (6)	–	0
3	TBA (2)	–	16
4	Hantzsch ester (2)	K_2CO_3 (1)	25
5	DIPEA (6)	$LiBF_4$ (1)	43
6[c, d]	DIPEA (6)	$LiBF_4$ (1.5)	64
7[c, d]	DIPEA (6)	Li_2CO_3 (1)	56
8[c, d]	DIPEA (6)	LiCl (1.5)	0
9[c, d]	DIPEA (6)	Thiophenol (1)	51
10[c, d]	DIPEA (6)	$LiBF_4$ (0.5)	43
11[c, d]	DIPEA (3)	$LiBF_4$ (1.5)	39
12[c, d]	DIPEA (6)	$La(OTf)_3$ (1)	0
13[c, d]	DIPEA (6)	B_2pin_2 (1)	0

[a] The reactions were performed using 1 eq. of **1a** and 1 eq. of **2a** in 2 mL of degassed solvent under nitrogen [b] Determined by GC analysis with 1-Naphthol as an internal standard, [c] DMA was used as a solvent instead of DMF, [d] reaction performed at 400 nm.

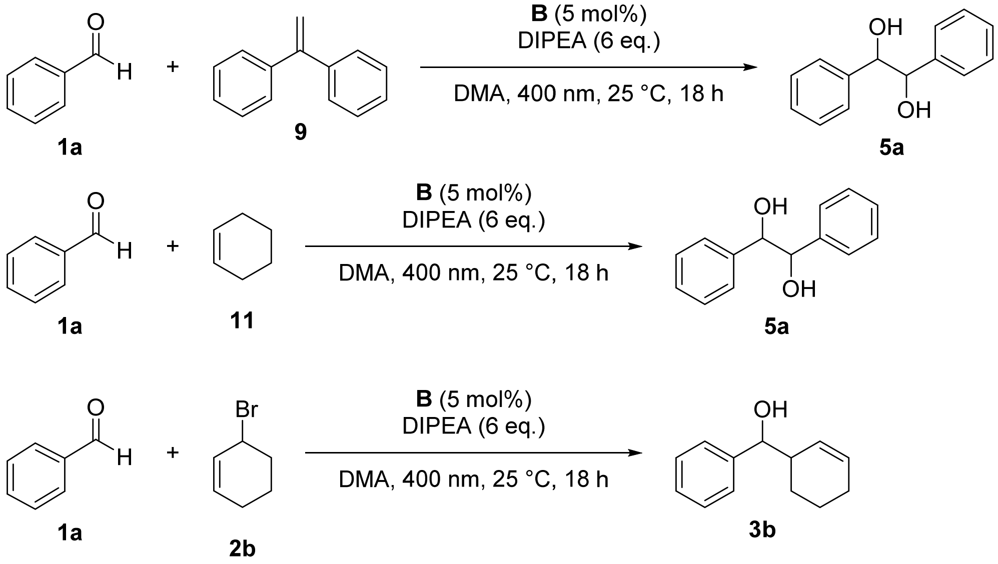
4. Mechanistic investigations

4.1. Control reactions

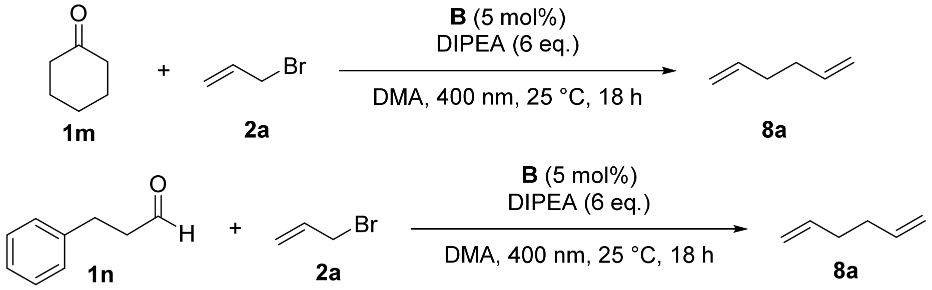


Scheme 1 – Control reactions for the formation of ketyl- and allyl-/benzyl radicals

a) Control reactions for the trapping of ketyl radicals with alkenes



b) Control reactions for the trapping of allyl radicals with carbonyls



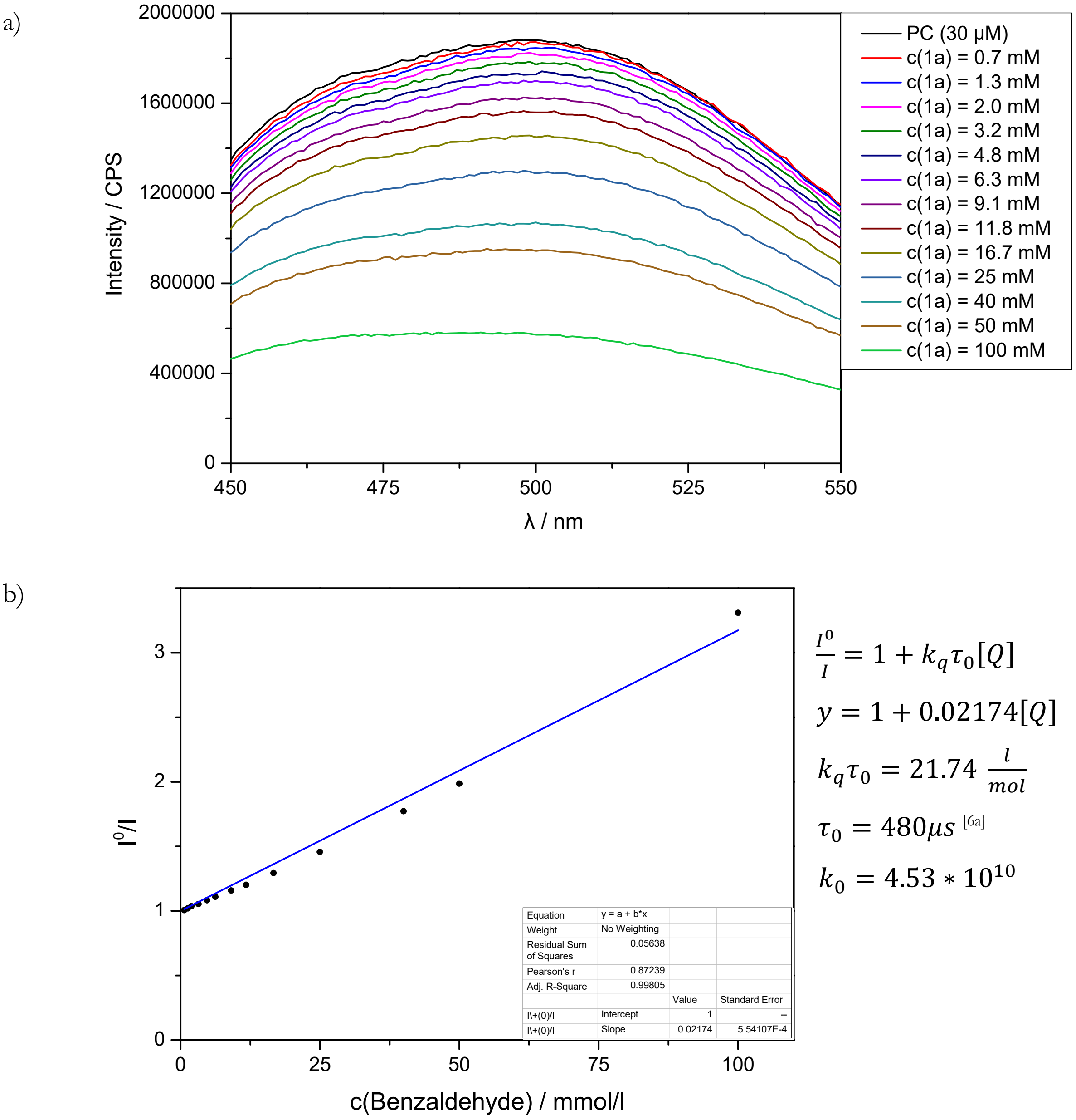
Scheme 2 – Control experiments for radical-radical cross-coupling.

All control experiments were performed with 1 eq. of **1** (0.2 mmol), 2 eq. of **2** (0.4 mmol), 5 mol% photocatalyst **B**, 6 eq. DIPEA (1.2 mmol) in 2 mL degassed solvent (DMA or DMF) under nitrogen. In radical trapping experiments, 10 eq. of 1,1-diphenylethylene **9** were added. The reactions were irradiated with 400 nm at 25 °C. The reaction mixtures were analyzed with GC and GC-MS.

4.2. Fluorescence quenching experiments

For fluorescence quenching experiments, a 30 μM solution of the photocatalyst **D** in degassed DMF was prepared under nitrogen atmosphere in a gas-tight 10 mm quartz cuvette. The photocatalyst was irradiated with 390 nm and the change of the fluorescence emission upon addition of different potential quenchers was recorded.

Benzaldehyde **1a**:



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.05638		
Pearson's r	0.87239		
Adj. R-Square	0.99805		
		Value	Standard Error
I\+(0)/I	Intercept	1	--
I\+(0)/I	Slope	0.02174	5.54107E-4

$$\frac{I^0}{I} = 1 + k_q\tau_0[Q]$$

$$y = 1 + 0.02174[Q]$$

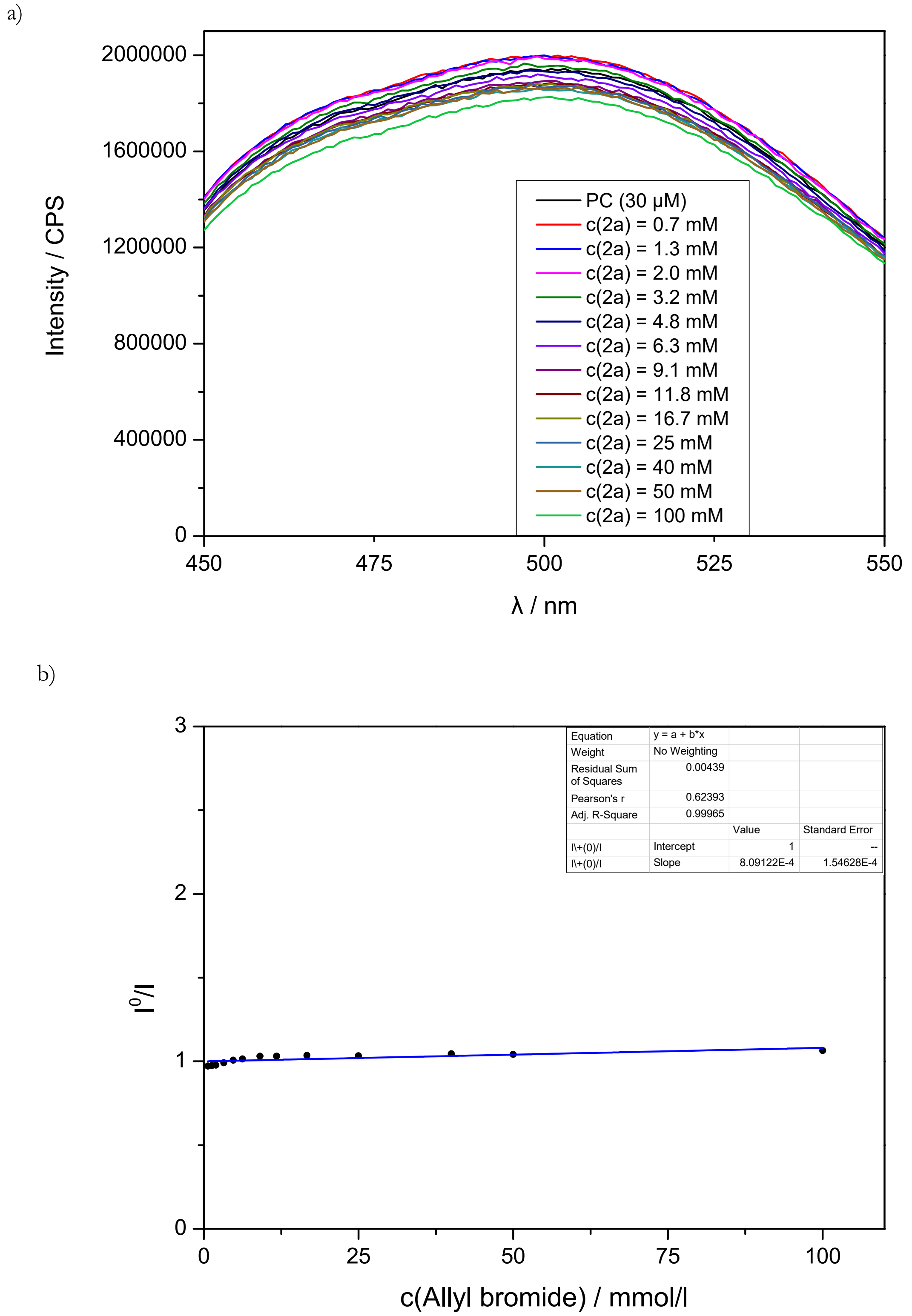
$$k_q\tau_0 = 21.74\ \frac{l}{mol}$$

$$\tau_0 = 480\mu s$$ [6a]

$$k_0 = 4.53 * 10^{10}$$

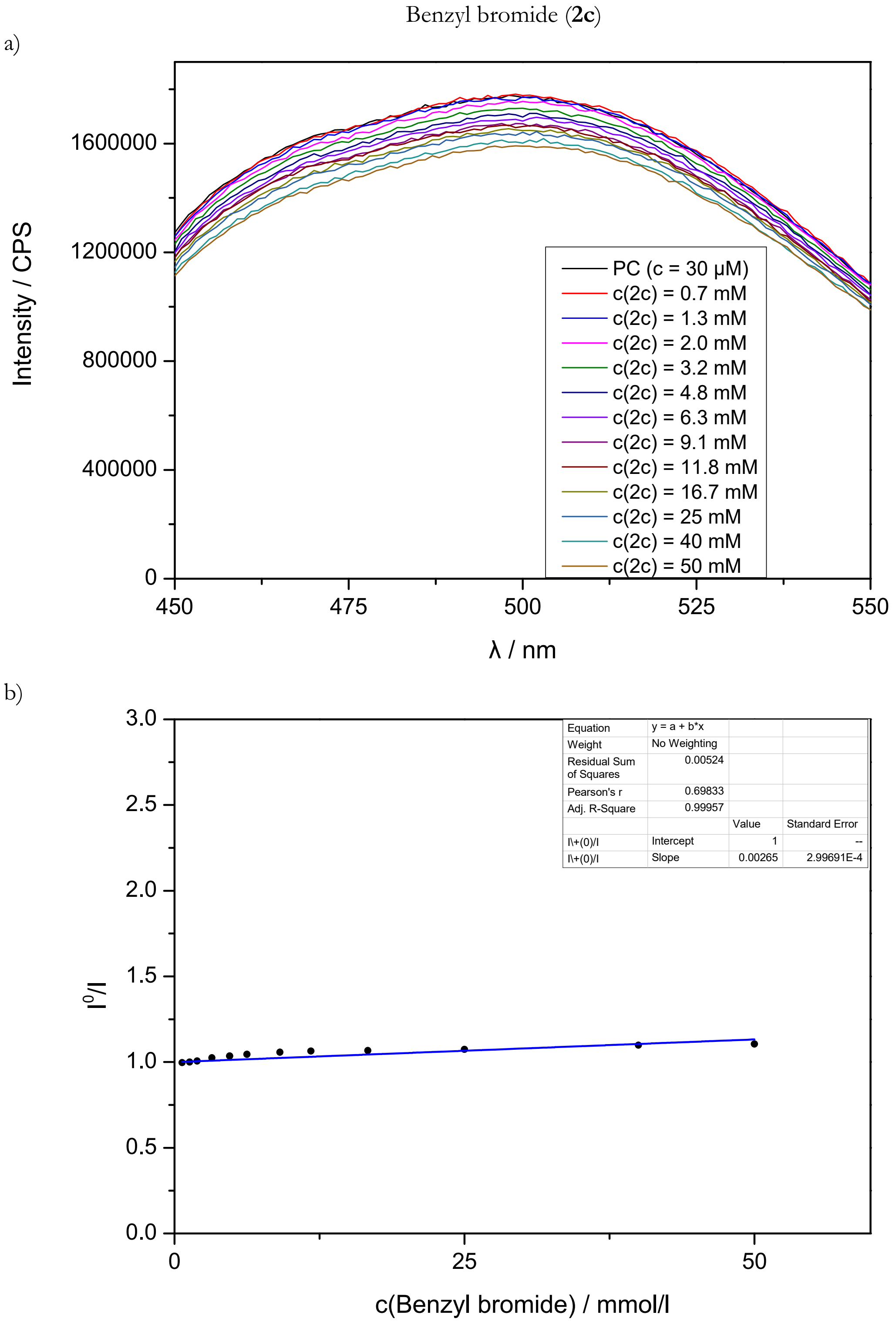
Figure 1 – a) Fluorescence quenching of **D** (30 μM in DMF) upon titration with **1a**, b) corresponding Stern-Volmer plot.

Allyl bromide **2a**:



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.00439		
Pearson's r	0.62393		
Adj. R-Square	0.99965		
		Value	Standard Error
I\+(0)/I	Intercept	1	--
I\+(0)/I	Slope	8.09122E-4	1.54628E-4

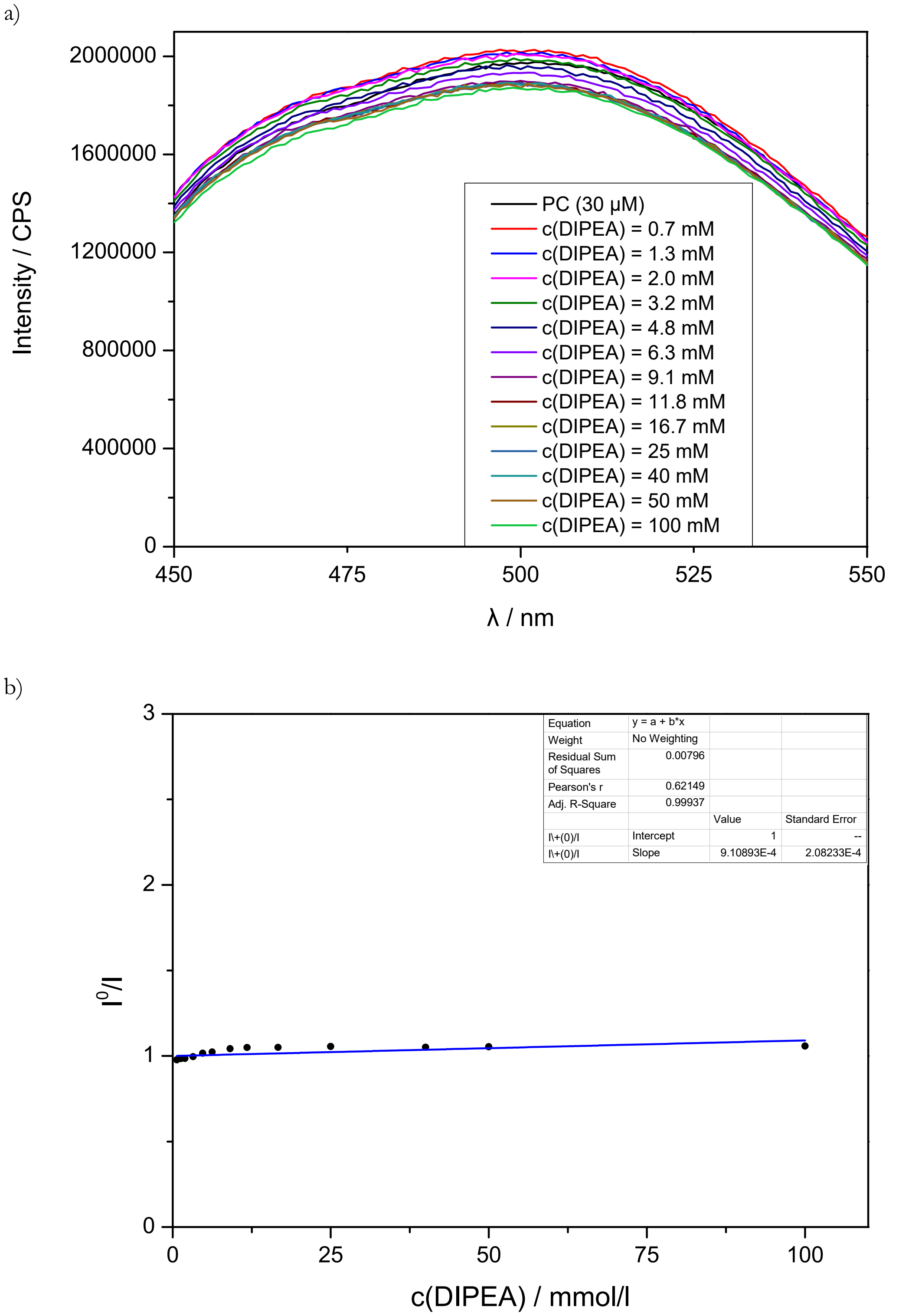
Figure 2 – a) Fluorescence quenching of **D** (30 μM in DMF) upon titration with **2a**, b) corresponding Stern-Volmer plot.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.00524		
Pearson's r	0.69833		
Adj. R-Square	0.99957		
		Value	Standard Error
I\+(0)/I	Intercept	1	--
I\+(0)/I	Slope	0.00265	2.99691E-4

Figure 3 – Fluorescence quenching of **D** (30 µM in DMF) upon titration with **2c**, b) corresponding Stern-Volmer plot.

DIPEA:



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.00796		
Pearson's r	0.62149		
Adj. R-Square	0.99937		
		Value	Standard Error
I\+(0)/I	Intercept	1	--
I\+(0)/I	Slope	9.10893E-4	2.08233E-4

Figure 4 – a) Fluorescence quenching of **D** (30 µM in DMF) upon titration with DIPEA, b) corresponding Stern-Volmer plot.

The fluorescence titration experiments show an effective quenching of the emission of photocatalyst **D** after the addition of benzaldehyde (**1a**) (Figure 1). This indicates that an electron transfer from the excited state of the photocatalyst to **1a** takes place upon irradiation which leads to the formation of the ketyl radical anion **1a**$^{\bullet-}$ and the oxidized form of the photocatalyst PC$^{\bullet+}$. Ally bromide (**2a**), benzyl bromide (**2c**) and DIPEA did not quench the emission of the **D**, so there seems to be no interaction between the excited state of the photocatalyst and **2a**, **2c** or DIPEA (Figure 2 – 4).

4.3. Cyclic voltammetry measurements

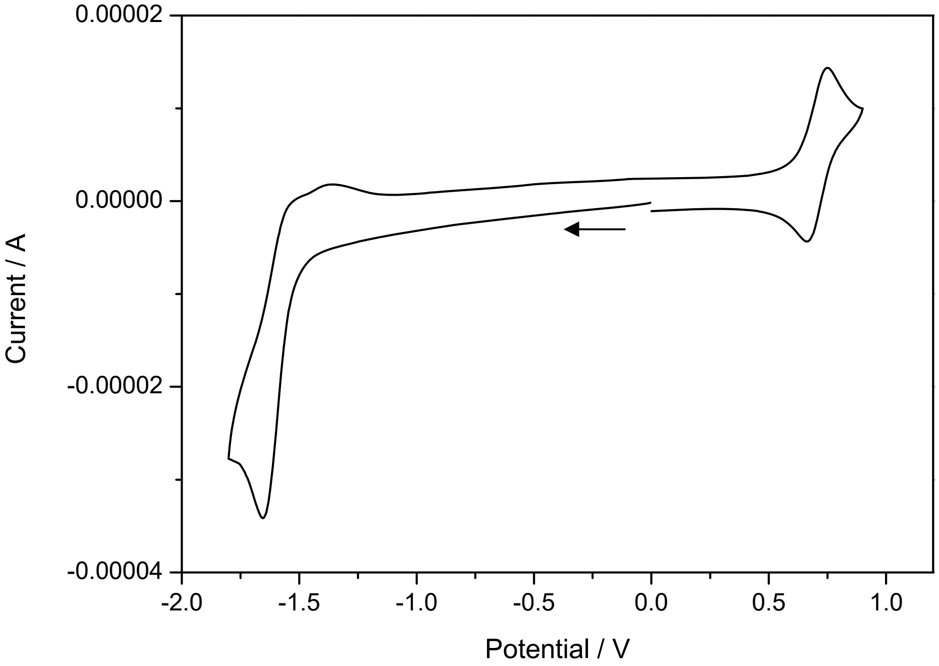


Figure 5 – Cyclic voltammogram of benzaldehyde (**1a**) in DMF under argon (scan direction indicated by black arrow). The peak at -1.65 V shows the reduction of **1a** and corresponds to a potential of -2.0 V *vs* SCE; the reversible peaks at 0.66 and 0.75 V correspond to ferrocene, which was used as an internal standard. The measurement was performed with a scan rate of 50 mV/s and with TBATFB (0.1 M) as supporting electrolyte.

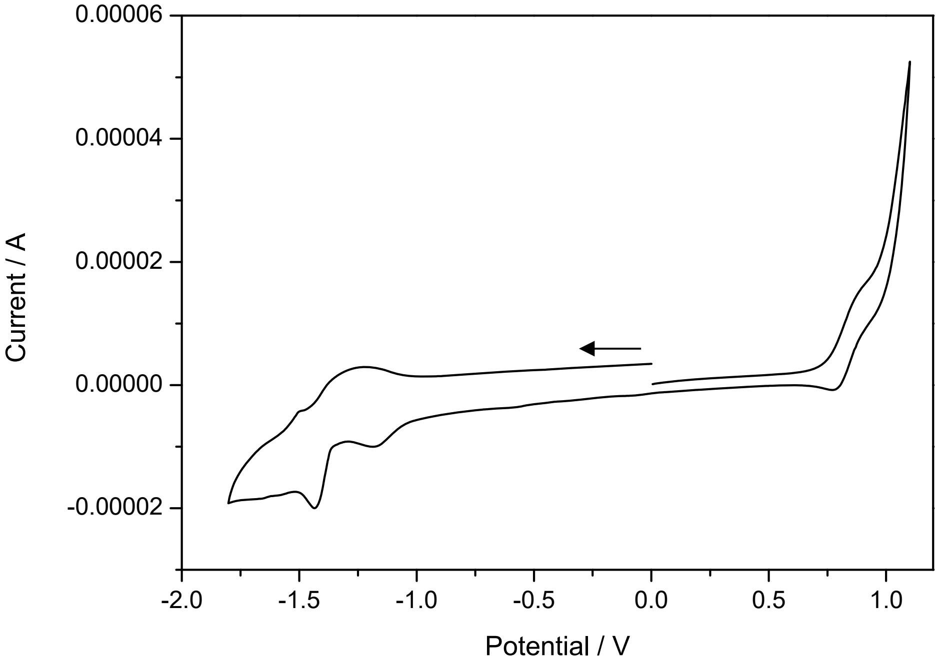


Figure 6 – Cyclic voltammogram of a mixture of benzaldehyde (**1a**, 1 eq.), DIPEA (6 eq.) and $LiBF_4$ (1.5 eq.) in DMF under argon (scan direction indicated by black arrow). The peak at -1.43 V shows the reduction of **1a** and corresponds to a potential of -1.88 V *vs* SCE; the reversible peaks at 0.79 and 0.87 V correspond to ferrocene, which was used as an internal standard. The measurement was performed with a scan rate of 50 mV/s and with TBATFB (0.1 M) as supporting electrolyte.

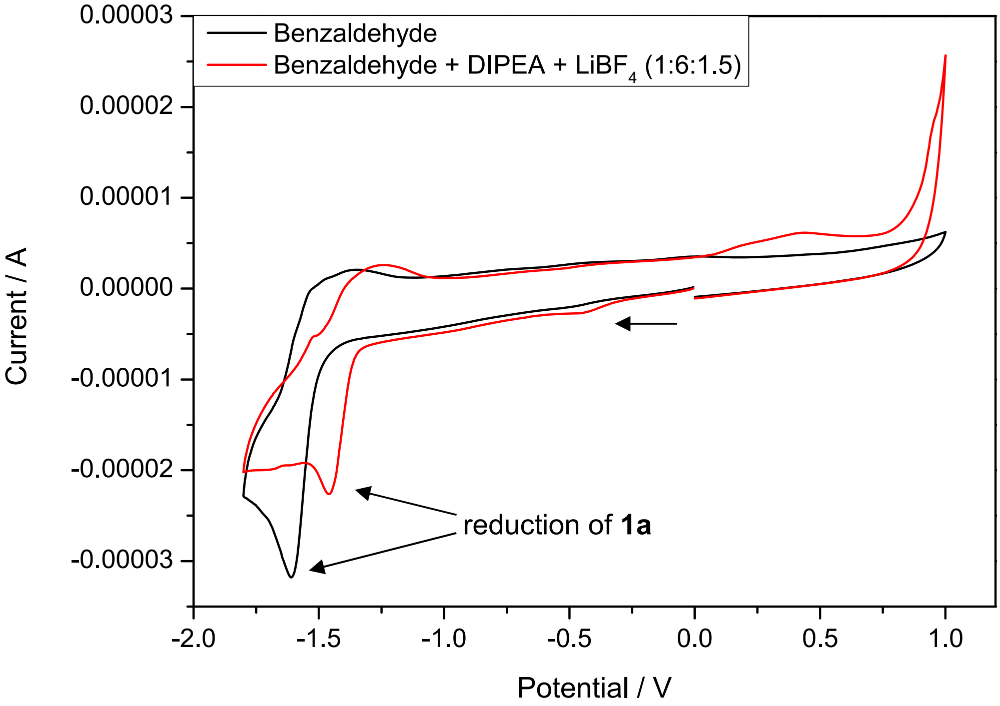


Figure 7 – Cyclic voltammograms of benzaldehyde (**1a**, black) and mixture of **1a** (1 eq.), DIPEA (6 eq.) and $LiBF_4$ (1.5 eq.) (red) under argon (scan direction indicated by black arrow). The peak that corresponds to the reduction of **1a** is shifted to lower potentials upon addition of DIPEA and $LiBF_4$. The measurement was performed with a scan rate of 50 mV/s and with TBATFB (0.1 M) as supporting electrolyte.

4.4. UV/Vis measurements

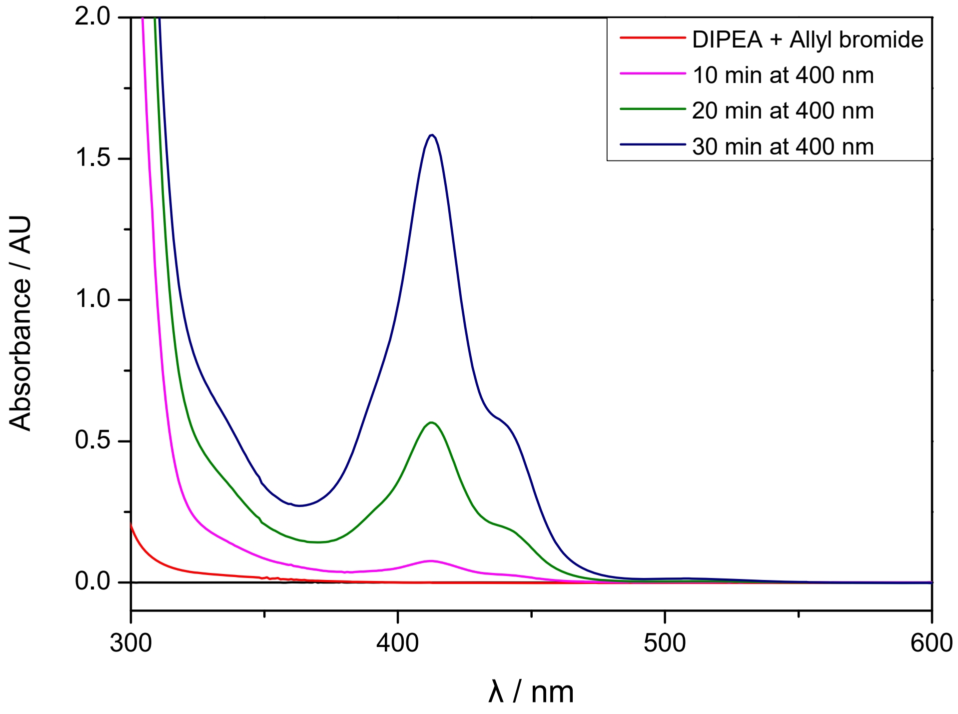


Figure 8 – UV/Vis absorption spectra of allyl bromide (**2a**, 1 eq., 0.4 mmol) and DIPEA (3 eq., 1.2 mmol) in DMA before irradiation and after 10, 20 and 30 minutes of 400 nm irradiation.

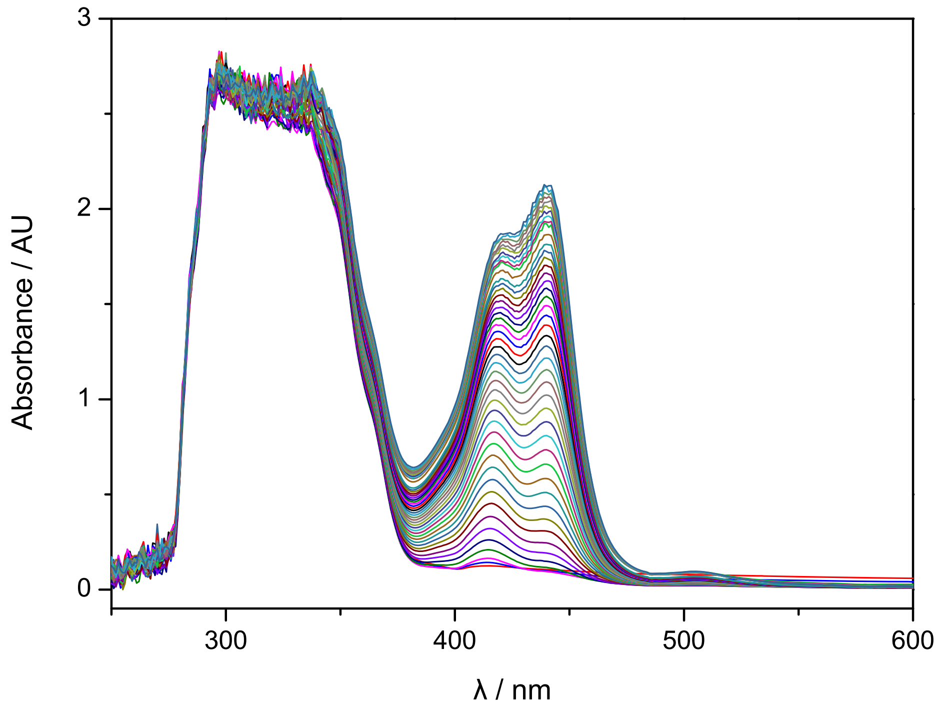


Figure 9 – On-line UV/Vis measurements of a mixture of benzaldehyde (**1a**, 1 eq., 0.2 mmol), allyl bromide (**2a**, 2 eq., 0.4 mmol), DIPEA (6 eq., 1.2 mmol) and $LiBF_4$ (1.5 eq., 0.3 mmol) in DMA (2 mL). The reaction mixture was irradiated for 22 h with 400 nm light, a UV/Vis spectrum was recorded every 30 minutes.

4.5. Quantum yield determination

The quantum yield was measured using a quantum yield determination setup determined by our group and the group of Riedle:[27] Thorlabs DT 25/M or DT S25M translation stages (horizontal and vertical), photographic lens with f = 50 mm, magnetic stirrer (Faulhaber motor 1524B024S R with 14:1 gear), PS19Q power sensor from Coherent, adjustable power supply (Basetech BT-153-0-15 V/DC 0-3 A 45 W), PowerMax software.

A reaction mixture of **1a** (20.33 µl, 0.2 mmol, 1 eq.), **2a** (34.62 µl, 0.2 mmol, 2 eq.), DIPEA (0.2 ml, 1.2 mmol, 6 eq.) and $LiBF_4$ (28.1 mg, 0.3 mmol, 1.5 eq.) and photocatalyst **B** (6.1 mg, 5 mol%) in 2 ml DMA was degassed with three cycles freeze pump thaw and transferred into a gas tight 10 mm Hellma® quartz fluorescence cuvette with a stirring bar under nitrogen atmosphere. A cuvette with solvent (DMA, 2 ml) and a stirring bar was placed in the beam of a 400 nm LED and the transmitted power (P_{ref} = 72 mW) was determined by a calibrated photodiode horizontal to the cuvette. The cuvette containing the reaction mixture was placed in the beam of the LED and the transmitted power P_{sample} was measured analogously. The sample was irradiated and the transmitted power as well as the yield of the photocatalytic reaction were recorded after different times (Table 4). These values enabled the determination of the quantum yield according to the following equation **E1**:

$$\emptyset = \frac{N_{product}}{N_{ph}} = \frac{N_A * n_{product}}{\frac{E_{light}}{E_{ph}}} = \frac{N_A * n_{product}}{\frac{E_{absorbed} * t}{\frac{h * c}{\lambda}}} = \frac{h * c * N_A * n_{product}}{\lambda * \left(P_{ref} - P_{sample}\right) * t} \quad \mathbf{(E1)}$$

where Φ is the quantum yield, $N_{product}$ is the number of product molecules generated during the reaction, N_{ph} is the number of absorbed photons, N_A is Avogadro's constant, $n_{product}$ is the the amount of product generated in mol, E_{light} is the energy of absorbed light in Joules, E_{ph} is the energy of a single photon, $P_{absorbed}$ is the radiant power absorbed in Watts, t is the irradiation time in seconds, h is the Planck's constant in J*s, c is the speed of light in m s^{-1}, λ is the wavelength of the irradiation source (400 nm), P_{ref} is the radiant power transmitted by a the blank sample containing only the solvent and P_{sample} is the radiant power transmitted by the cuvette containing the reaction mixture.

After one hour of irradiation, the yield of the reaction was 34 %, and P_{sample} was 50 µW, which corresponds to a quantum yield of **Φ = 7.6%**

4.6. NMR-experiments

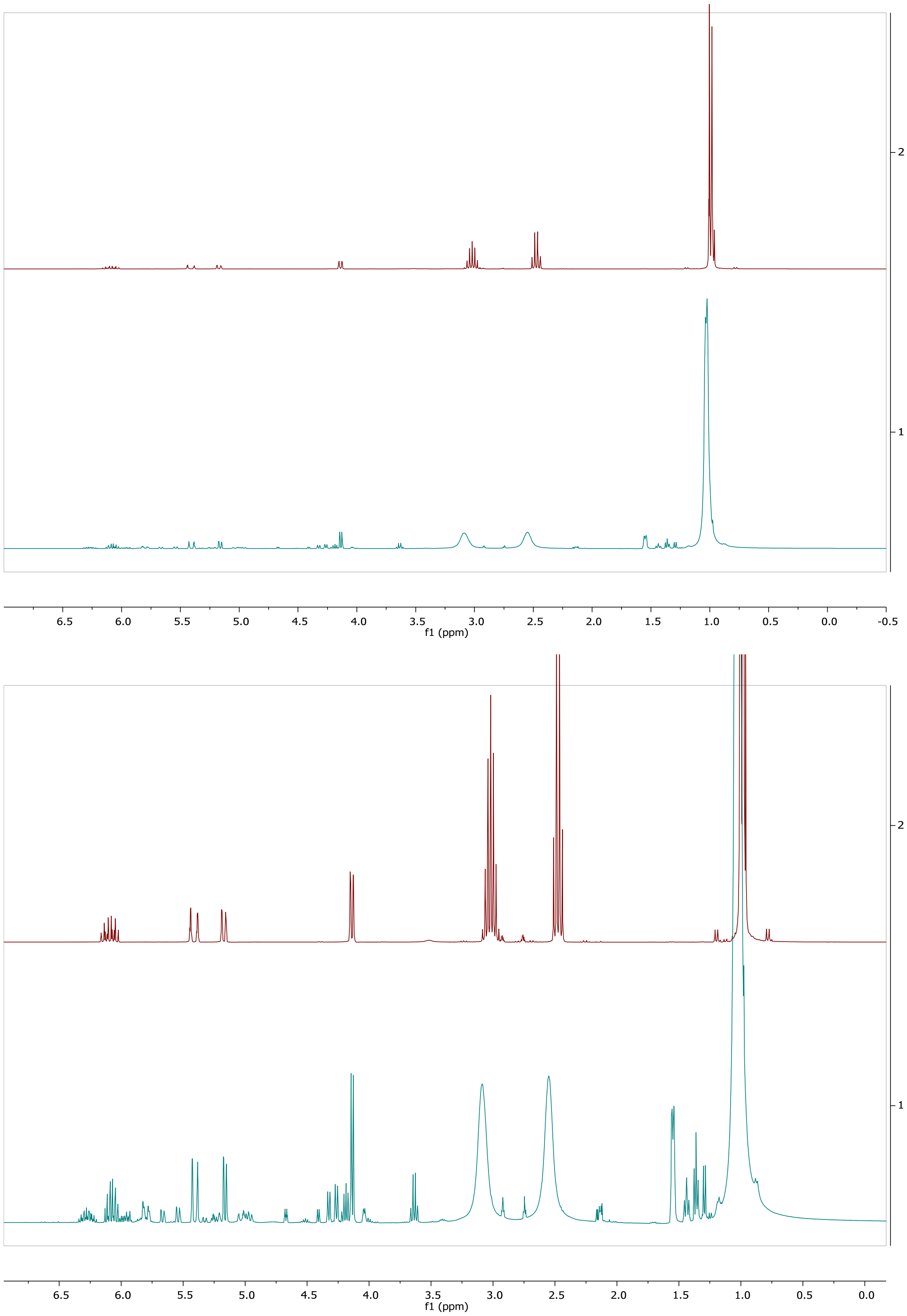
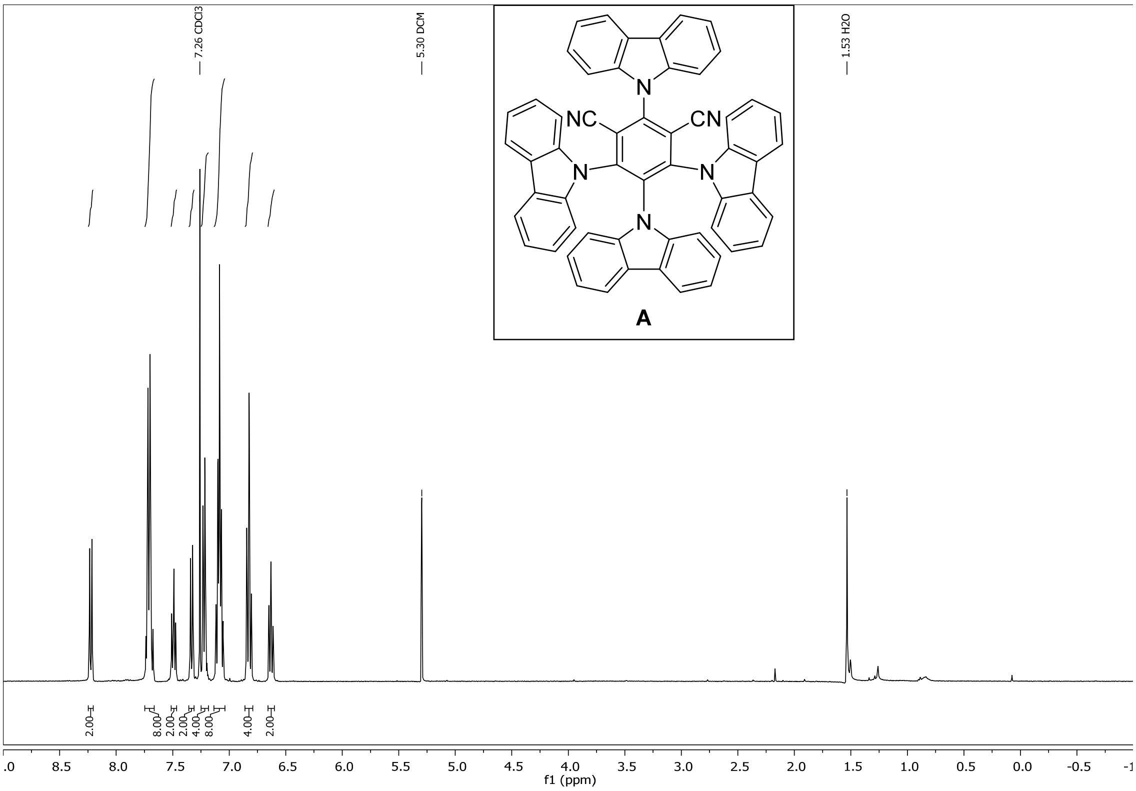
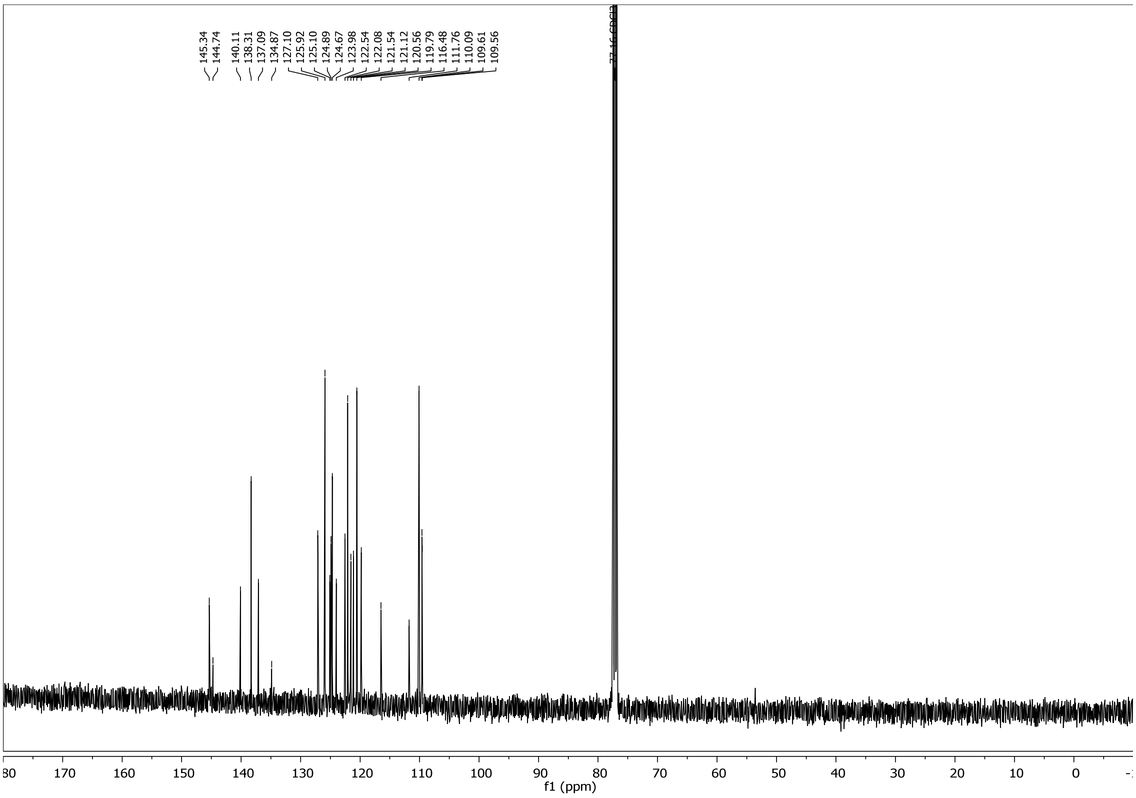


Figure 10 – ^{1}H-NMR-spectra of allyl bromide (**2a**, 1 eq.) and DIPEA (3 eq.) in DMF-*d*$_7$ before (red) and after (blue) 22 h of 400 nm irradiation. While the allyl bromide signals remain unchanged, the signals of DIPEA (1.03, 2.55 and 3.09 ppm) show a broadening, which indicates the formation of radicals or ionic species in the reaction mixture upon irradiation.

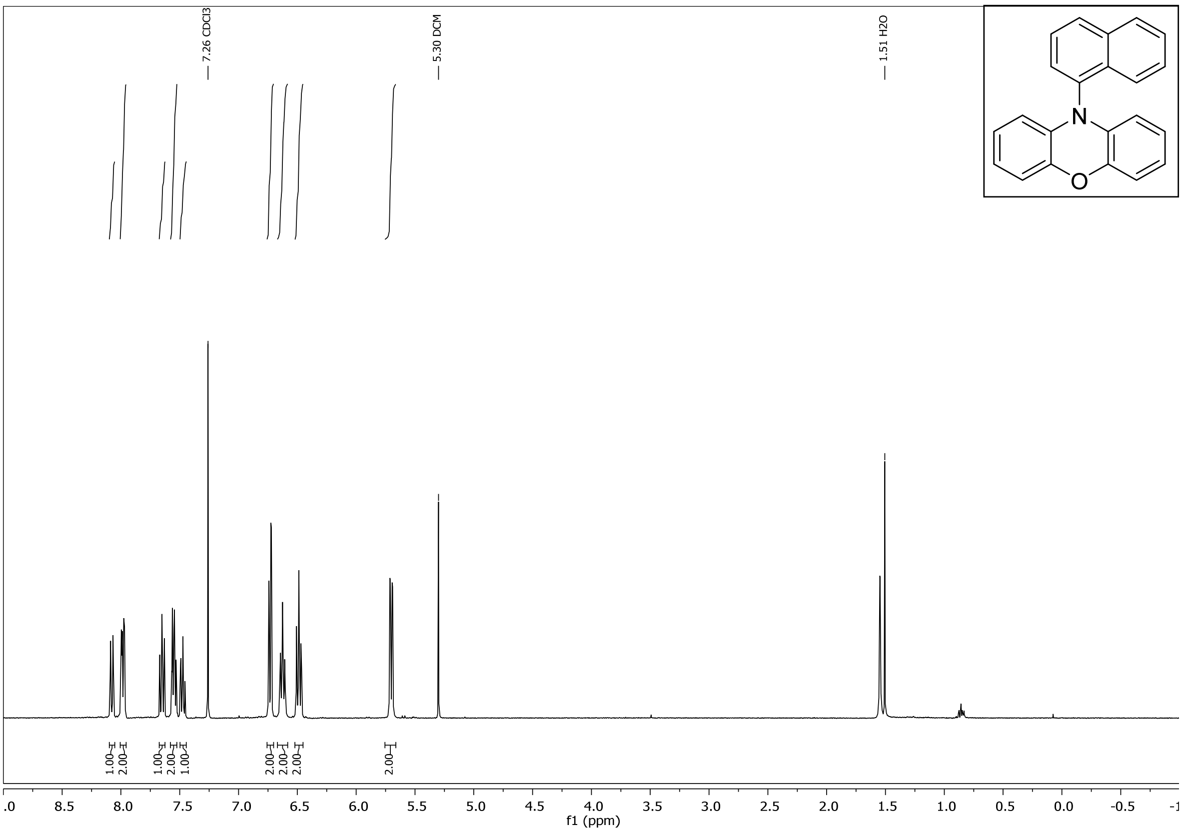
5. NMR-spectra

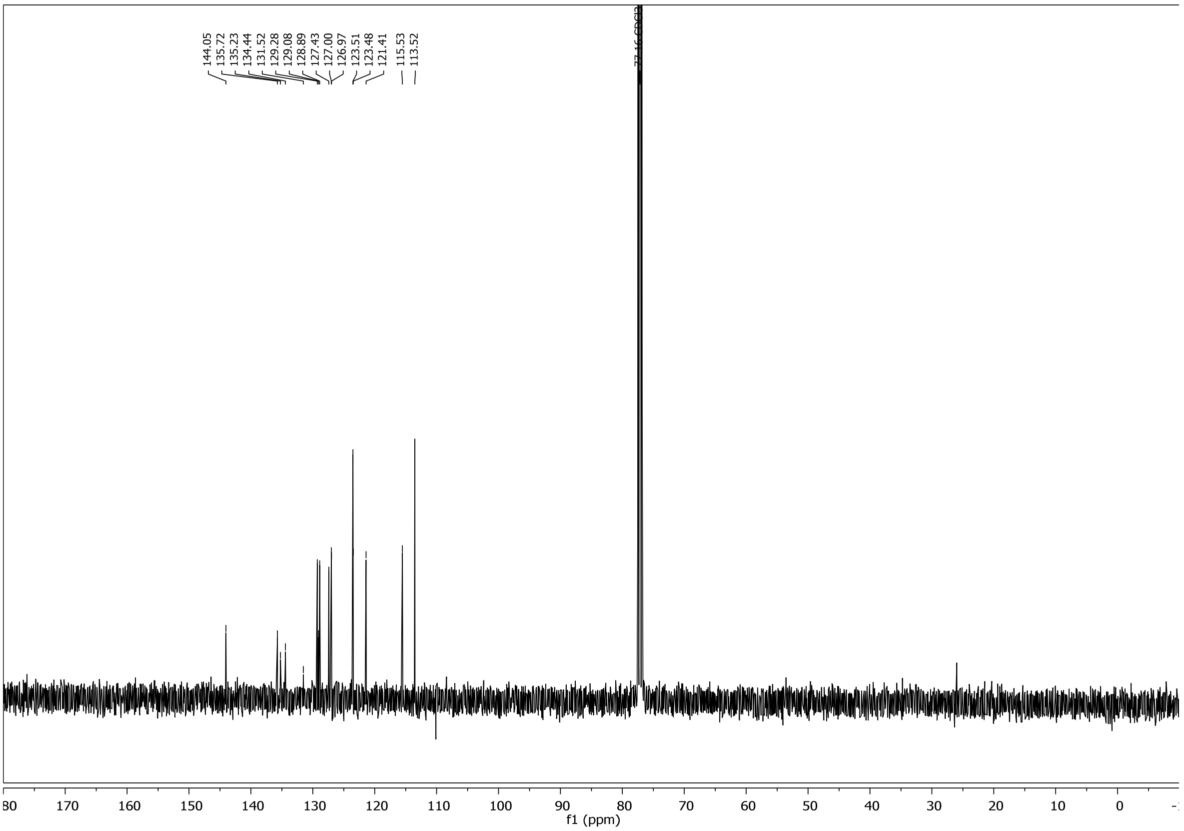
Compound **A**, ^{1}H- and ^{13}C-NMR (CDCl$_3$)



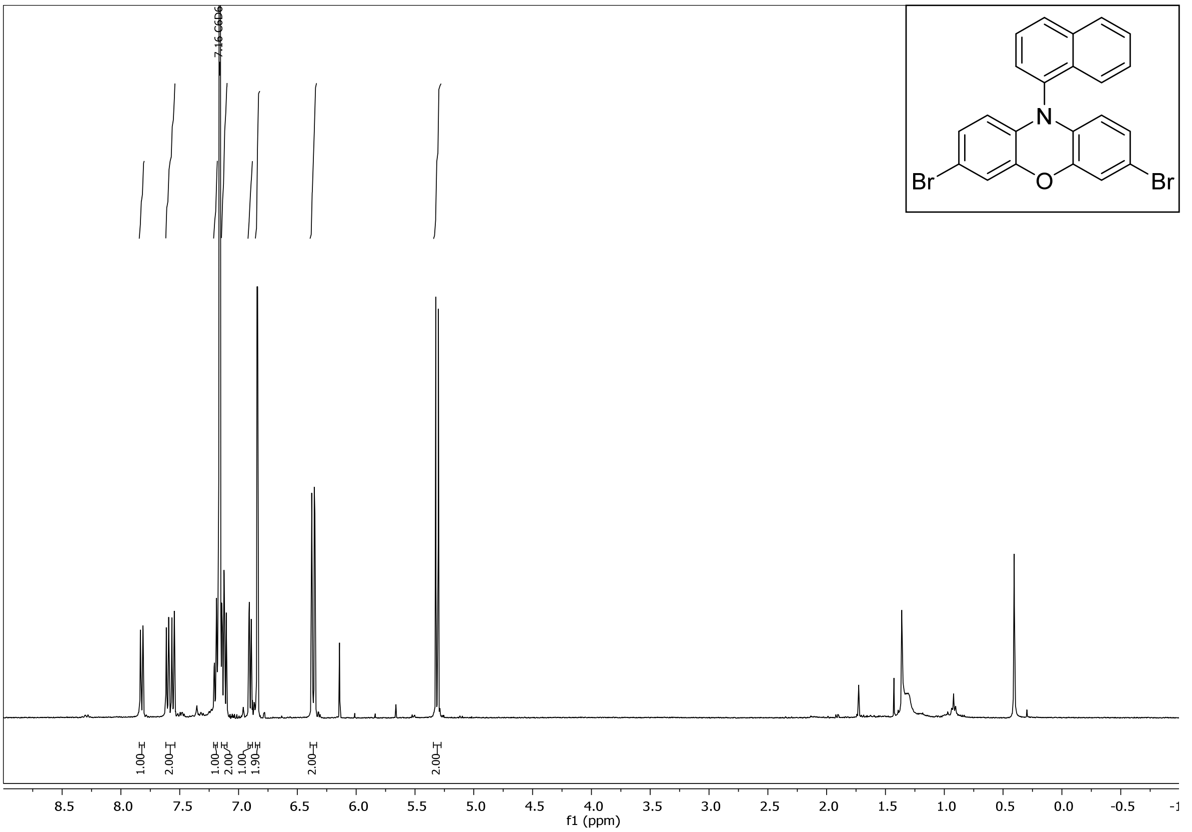


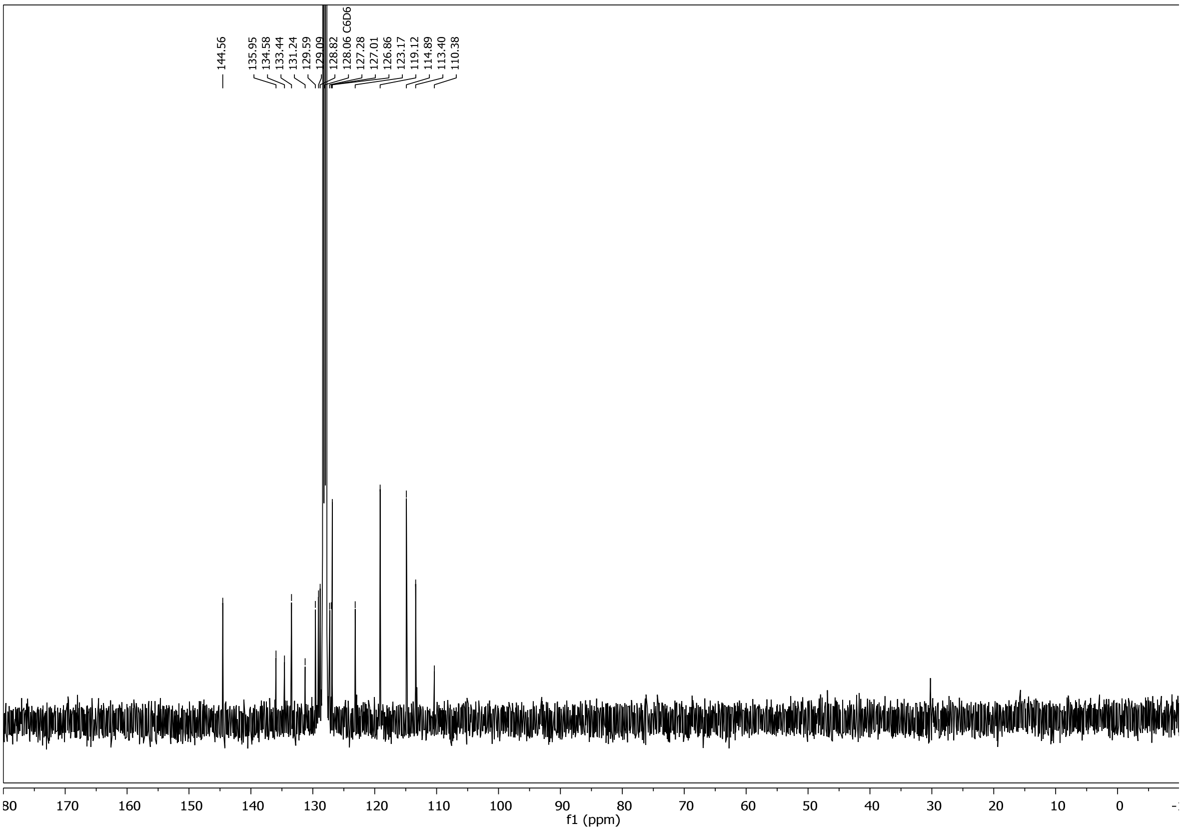
1-Naphthalene-10-phenoxazine, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



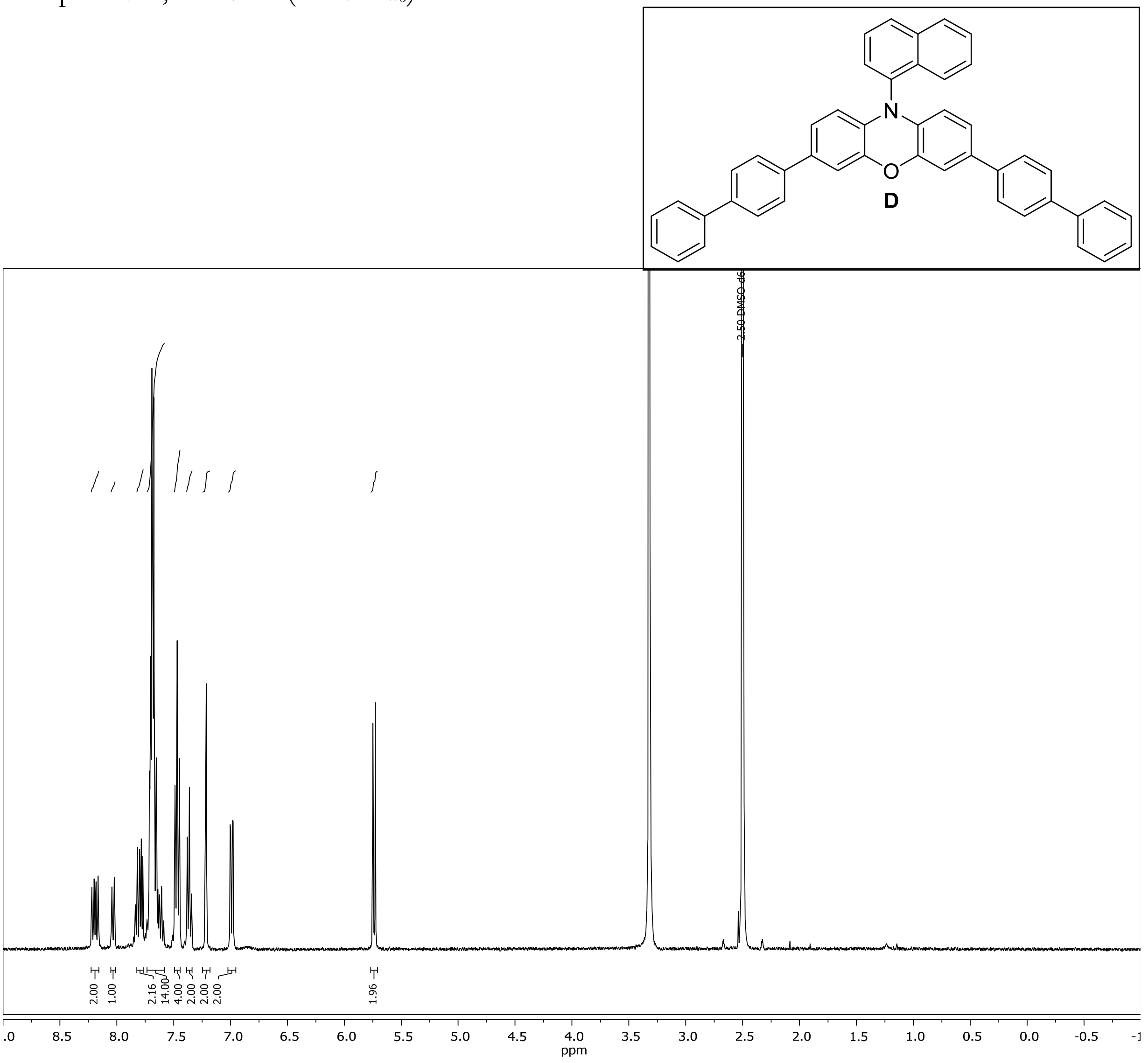


3,7-Dibromo 1-naphthalene-10-phenoxazine, ^{1}H- and ^{13}C-NMR (C_6D_6)

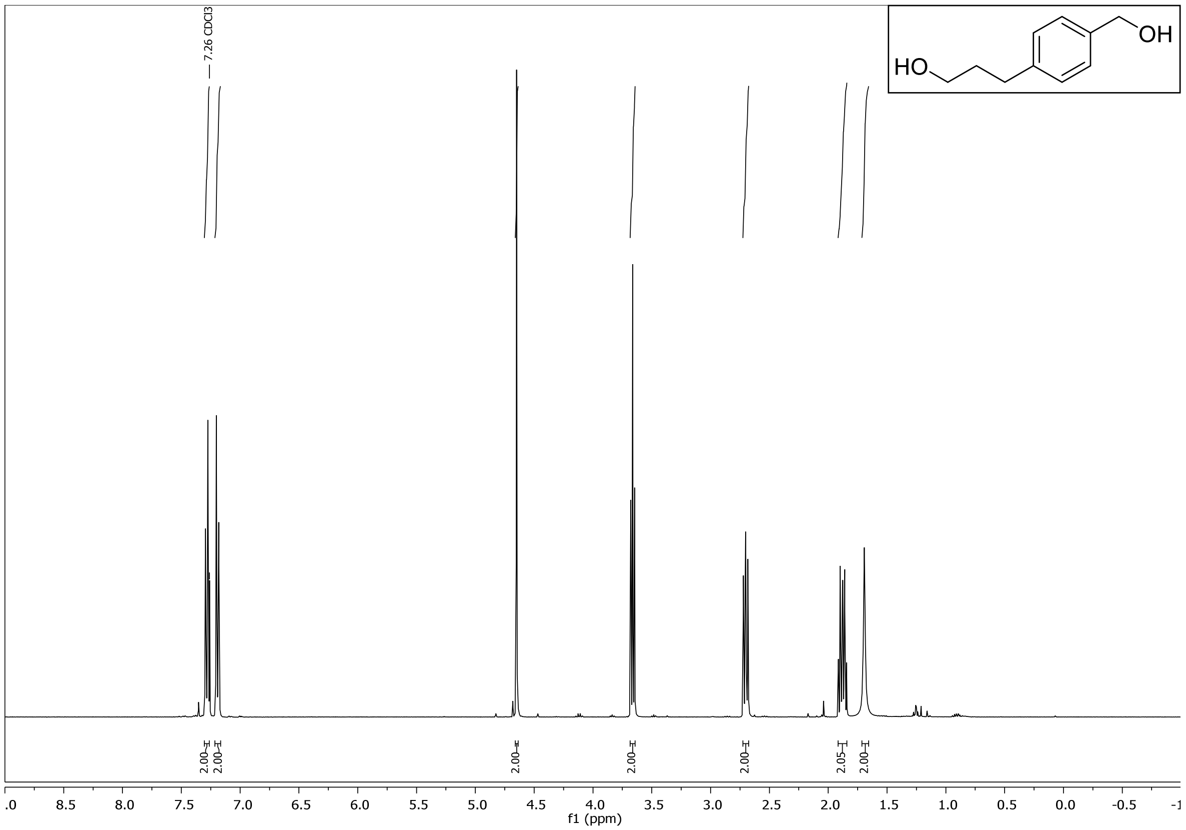


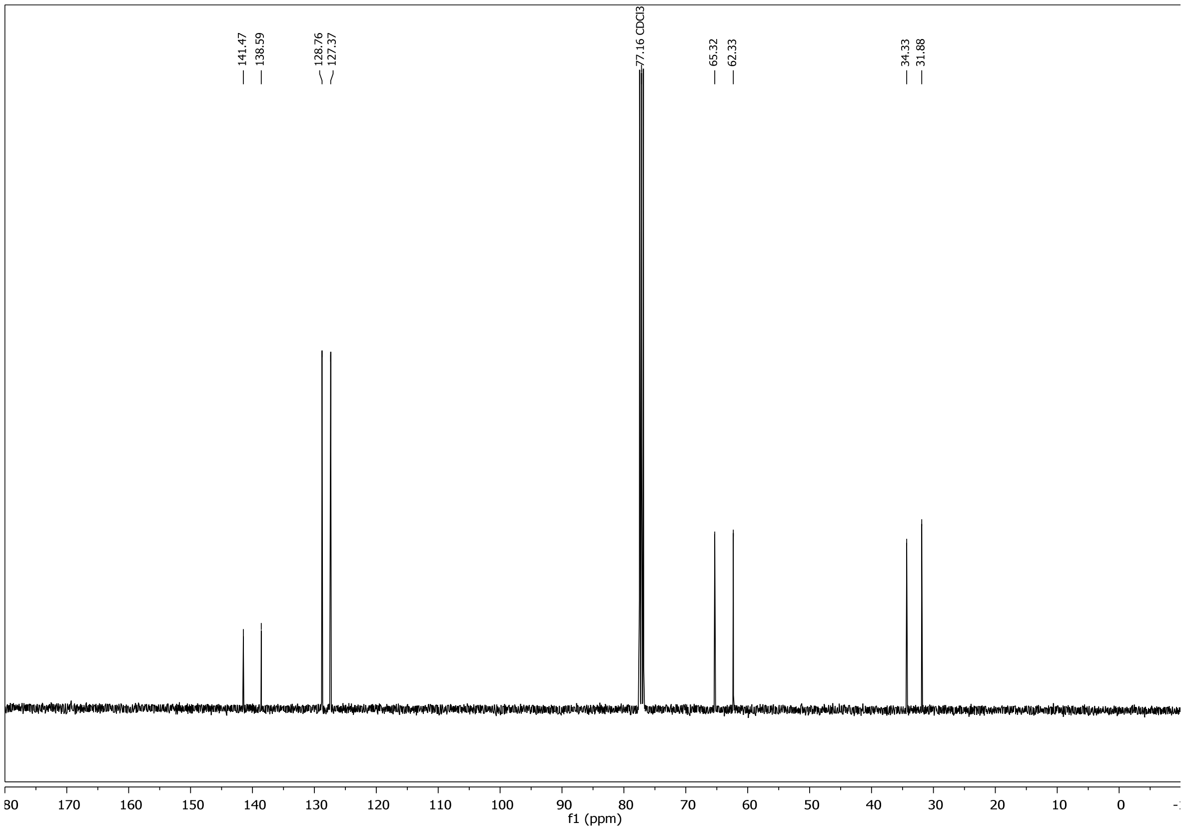


Compound **D**, ^{1}H-NMR (DMSO-d_6)

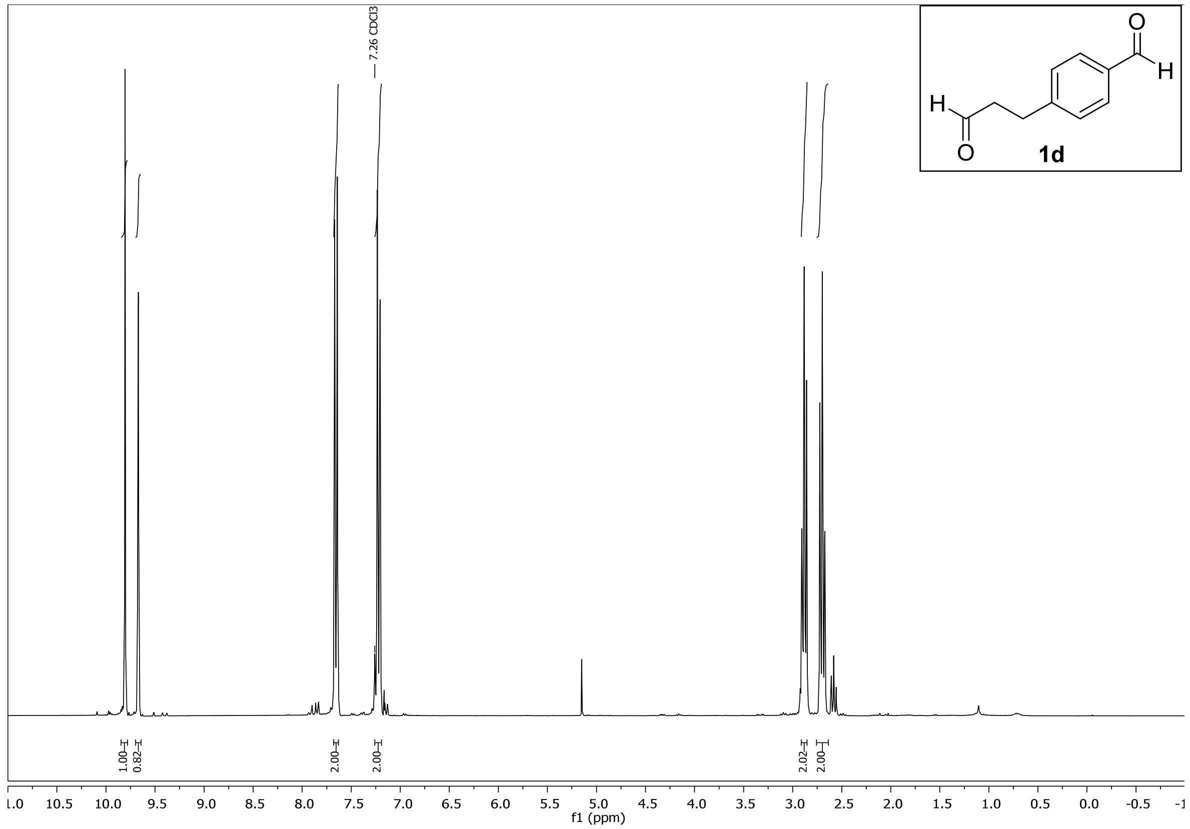


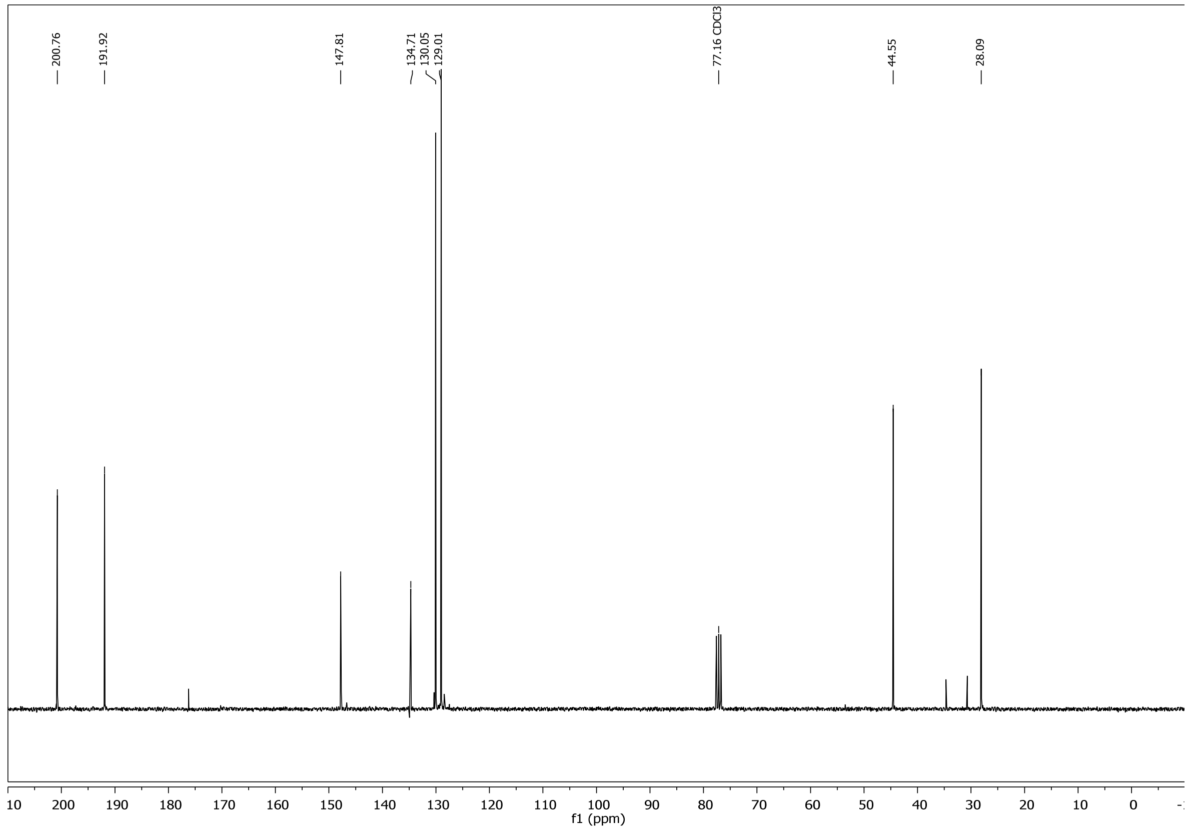
3-(4-(Hydroxymethyl)phenyl)propan-1-ol, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



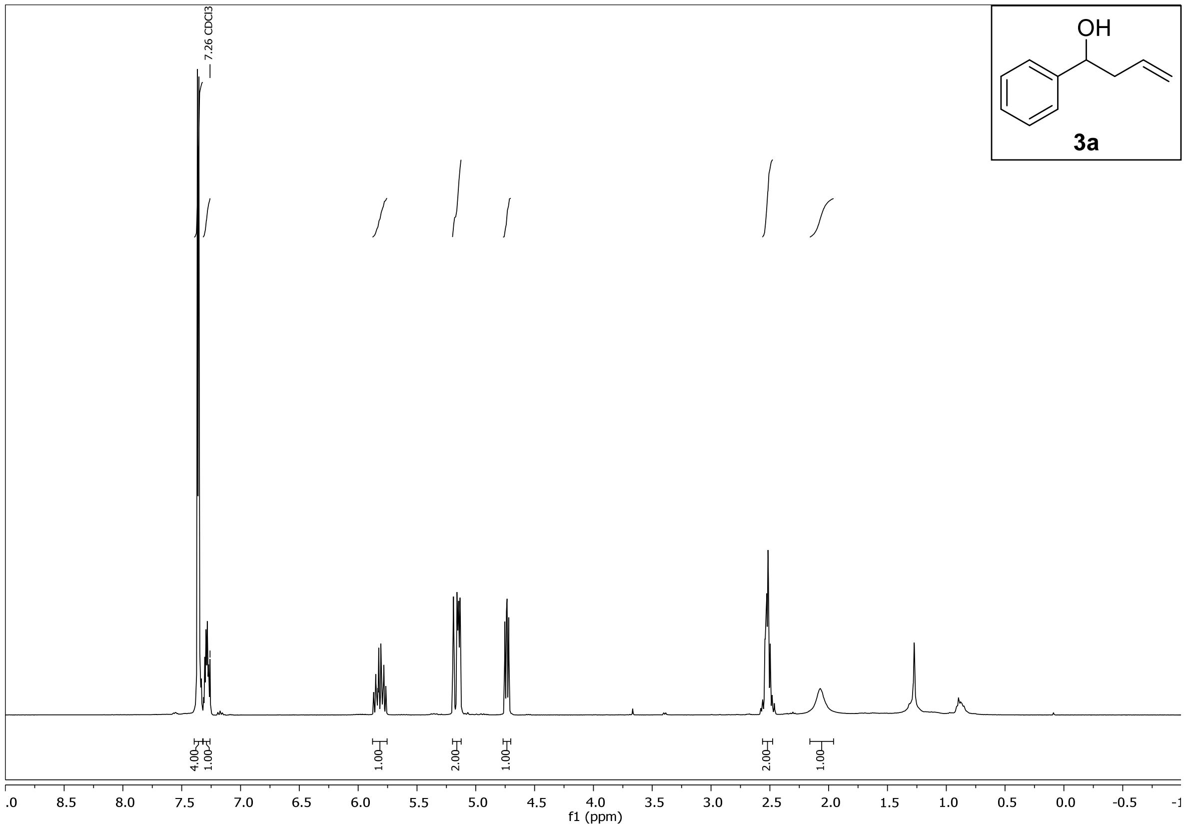


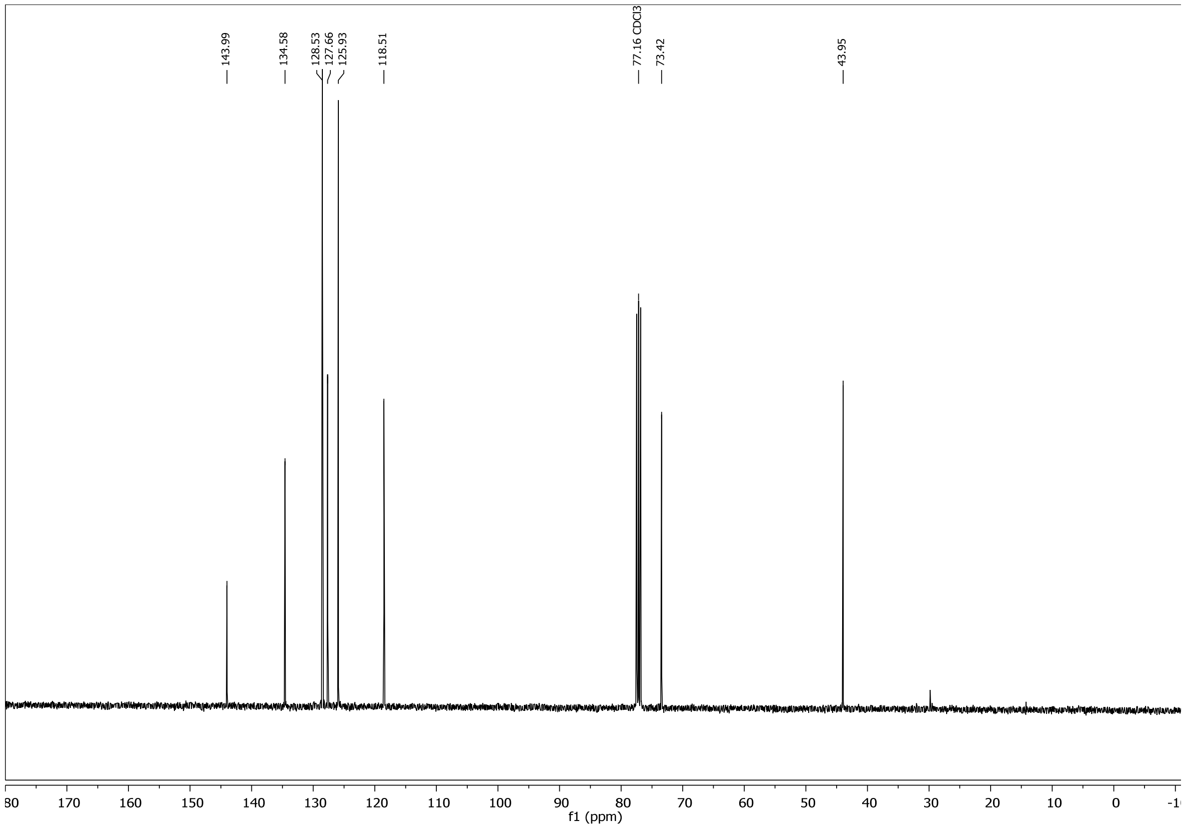
Compound **1d**, ^{1}H- and ^{13}C-NMR (CDCl$_3$)



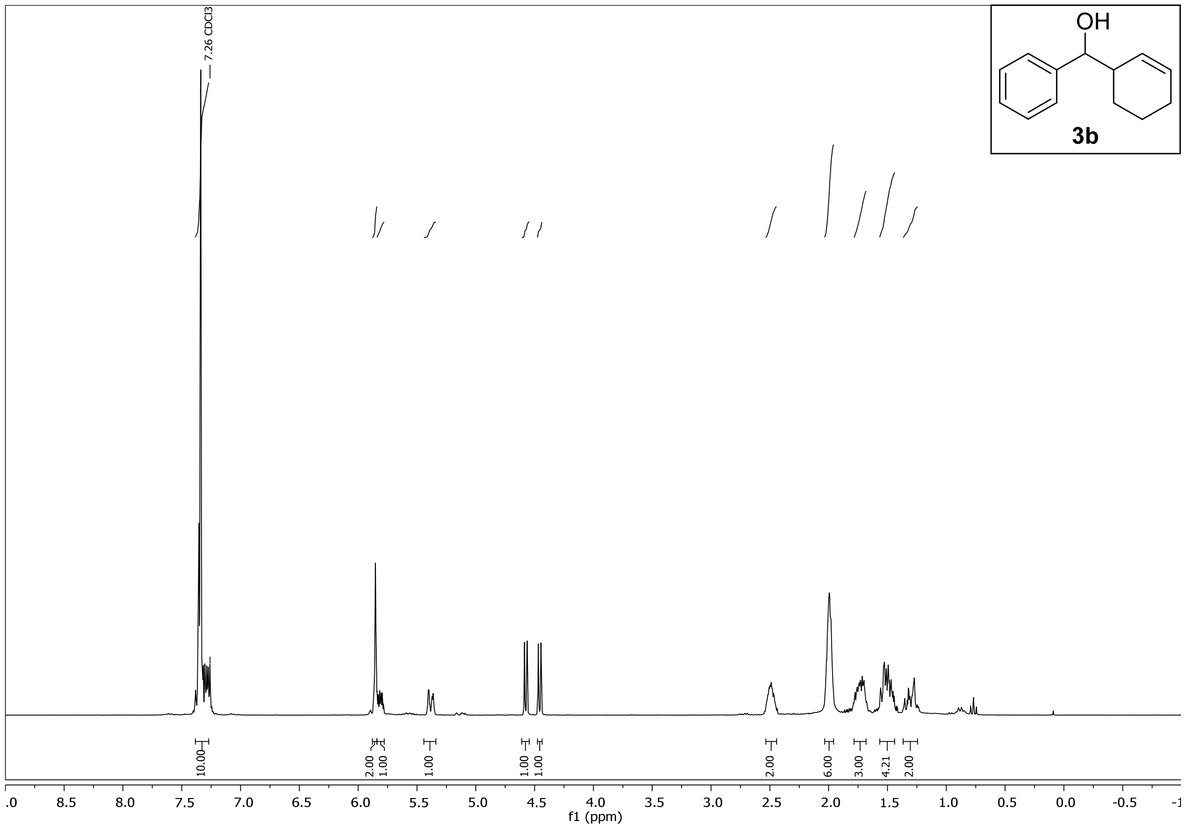


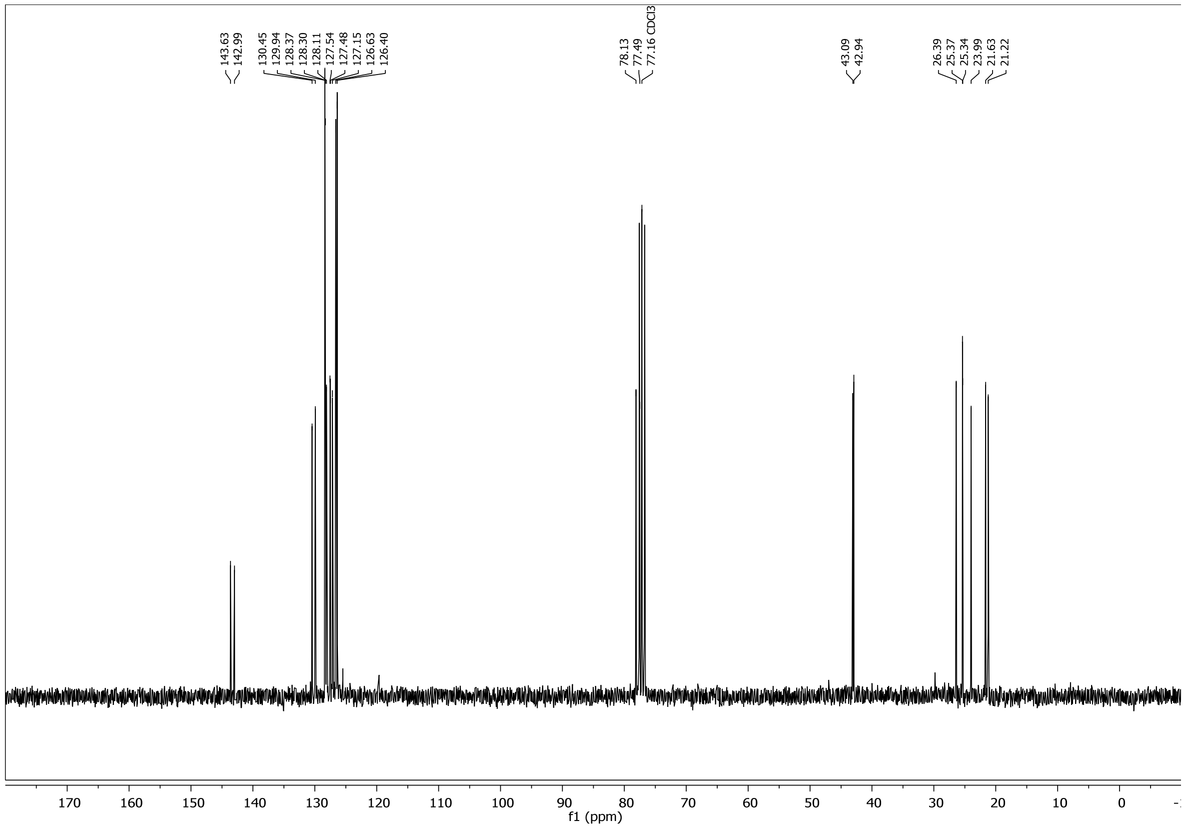
Compound **3a**, ^{1}H- and ^{13}C-NMR (CDCl$_3$)



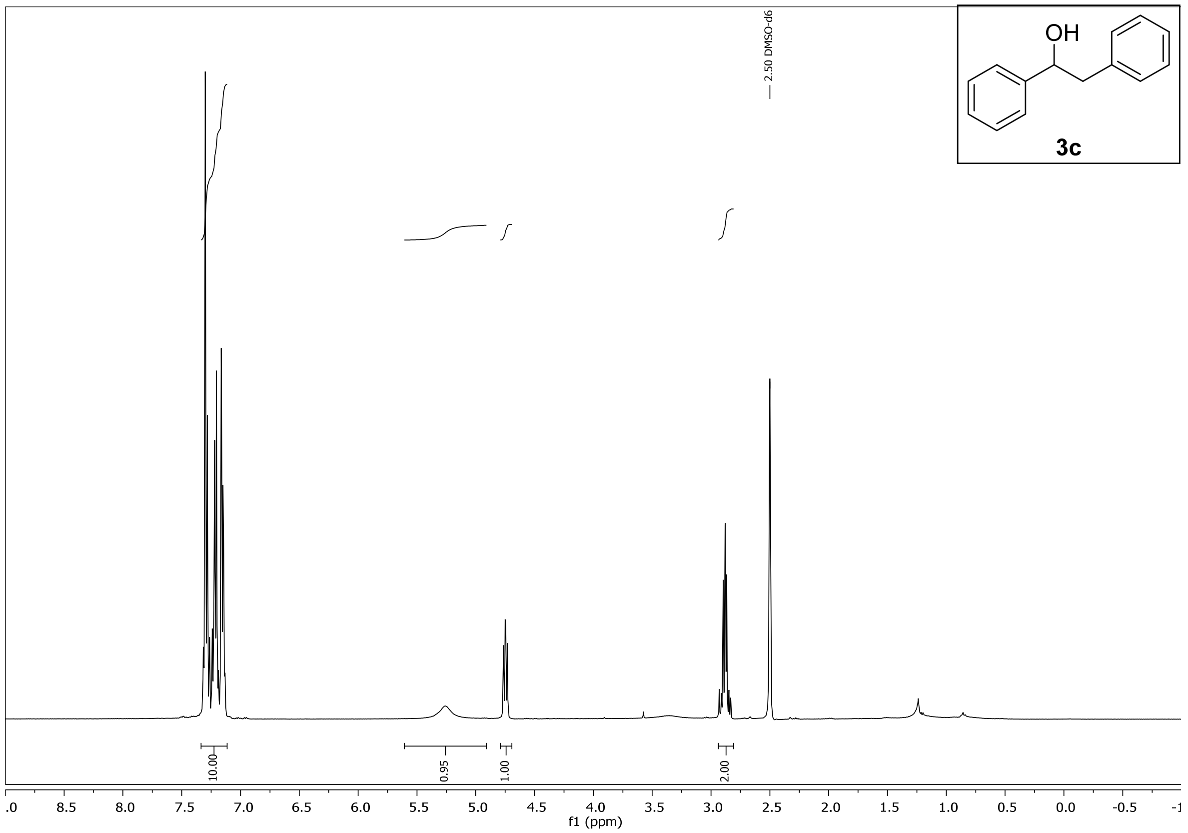


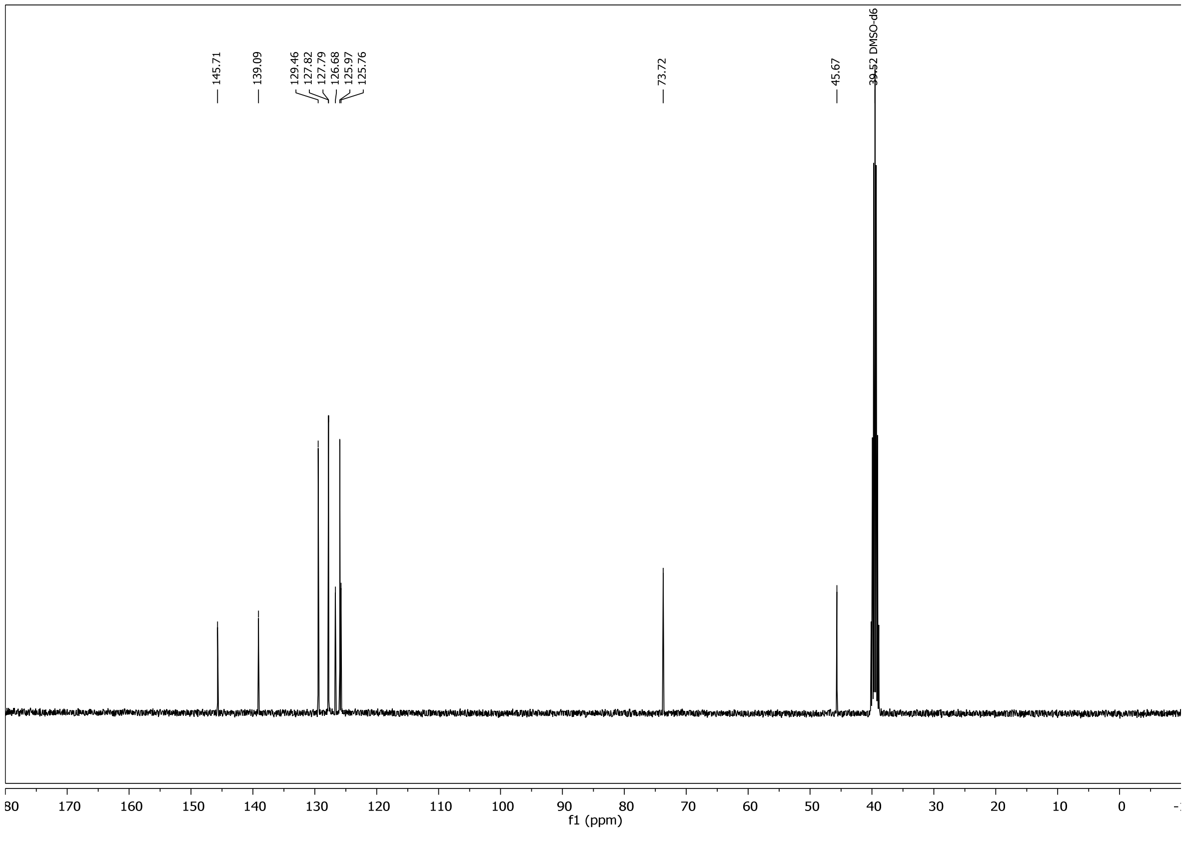
Compound **3b**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



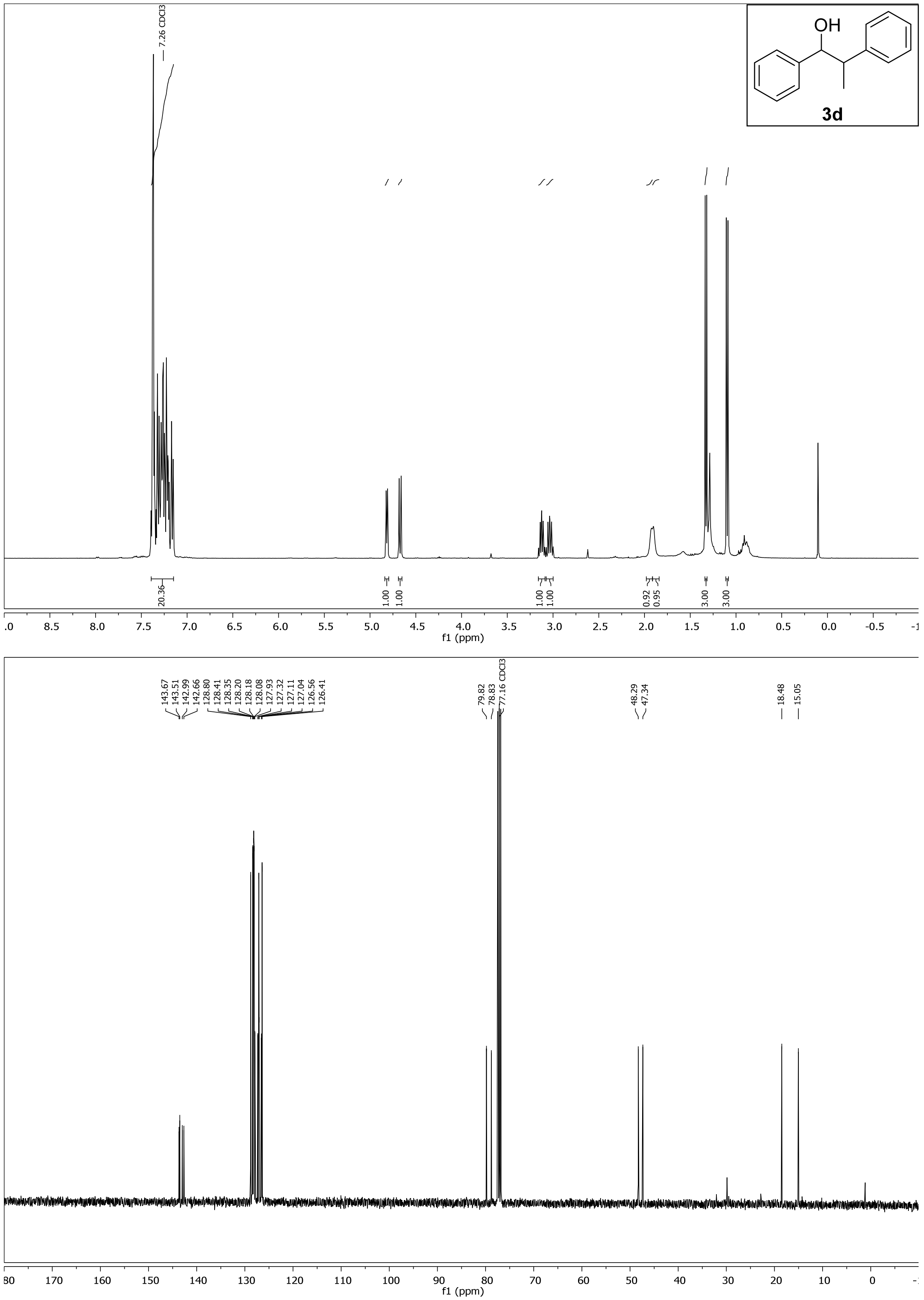


Compound **3c**, ^{1}H- and ^{13}C-NMR (DMSO-d_6)

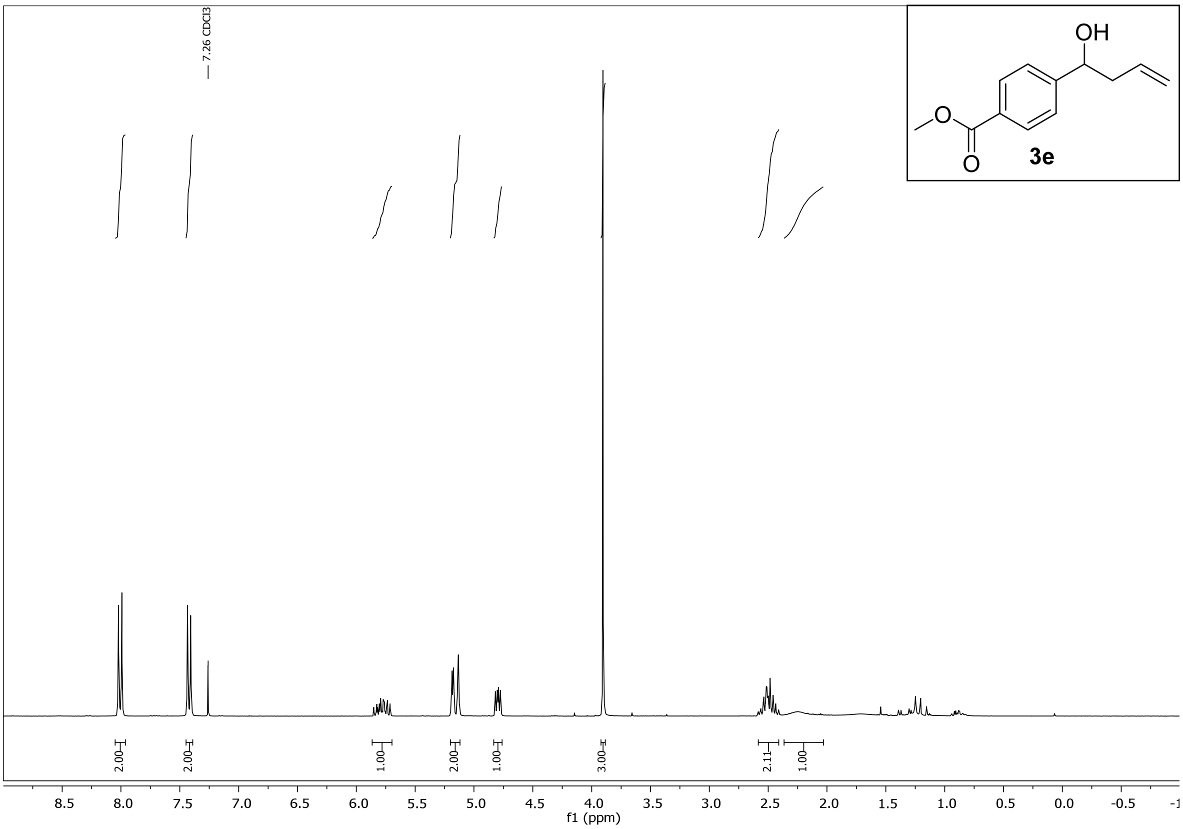


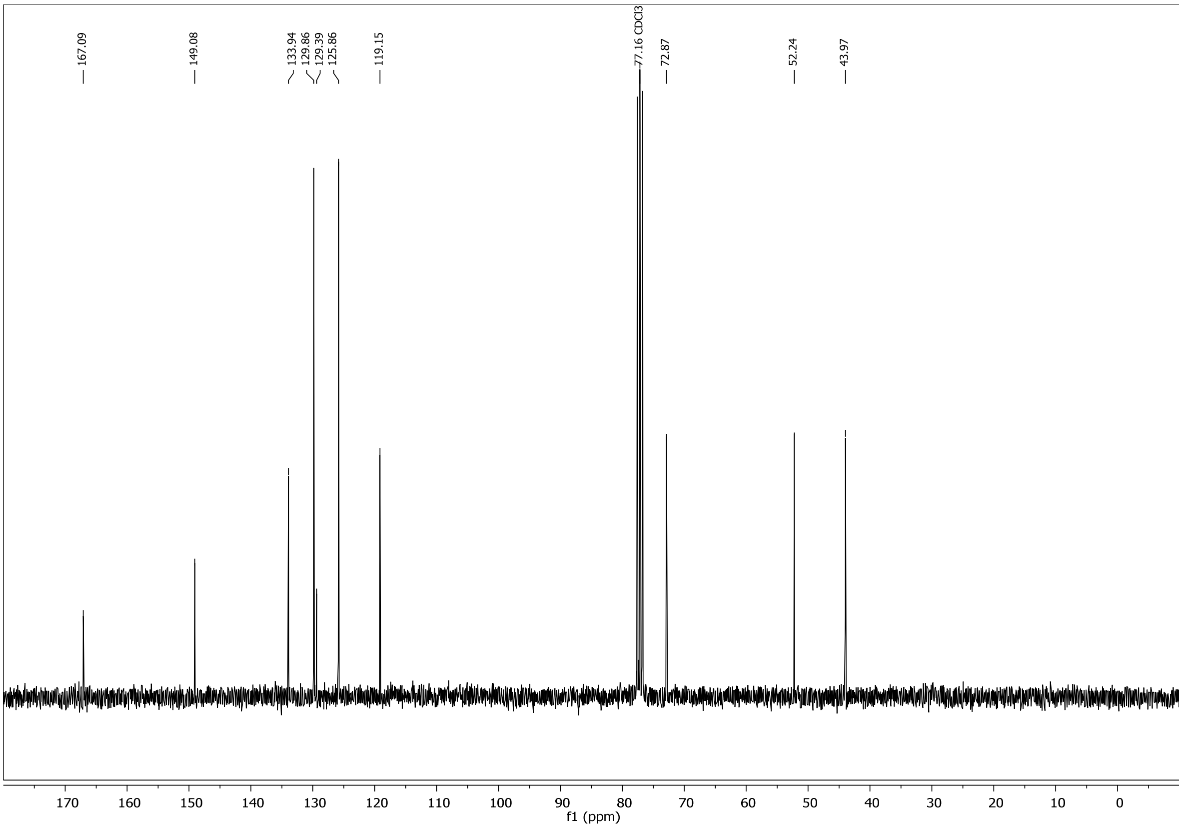


Compound **3d**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)

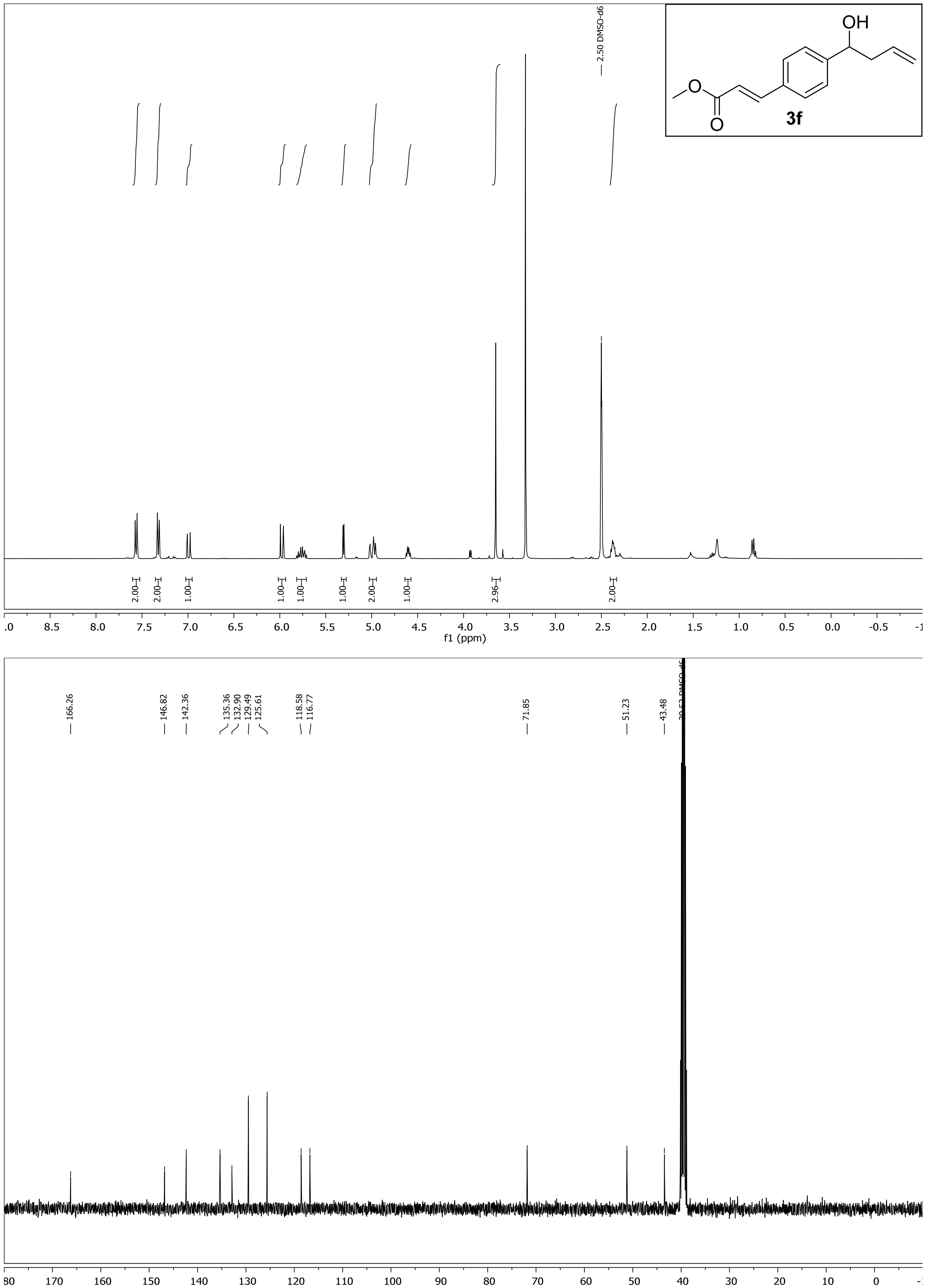


Compound **3e**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)

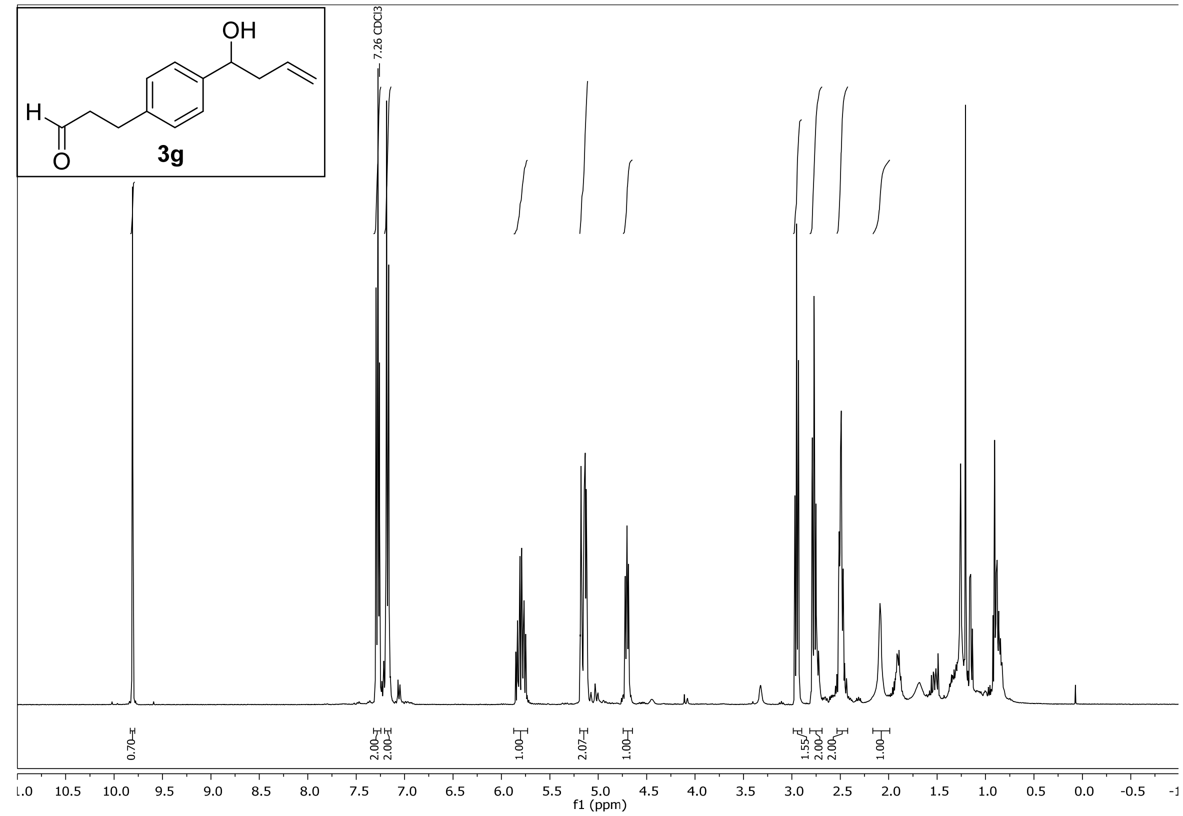




Compound **3f**, ^{1}H- and ^{13}C-NMR (DMSO-d_6)



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



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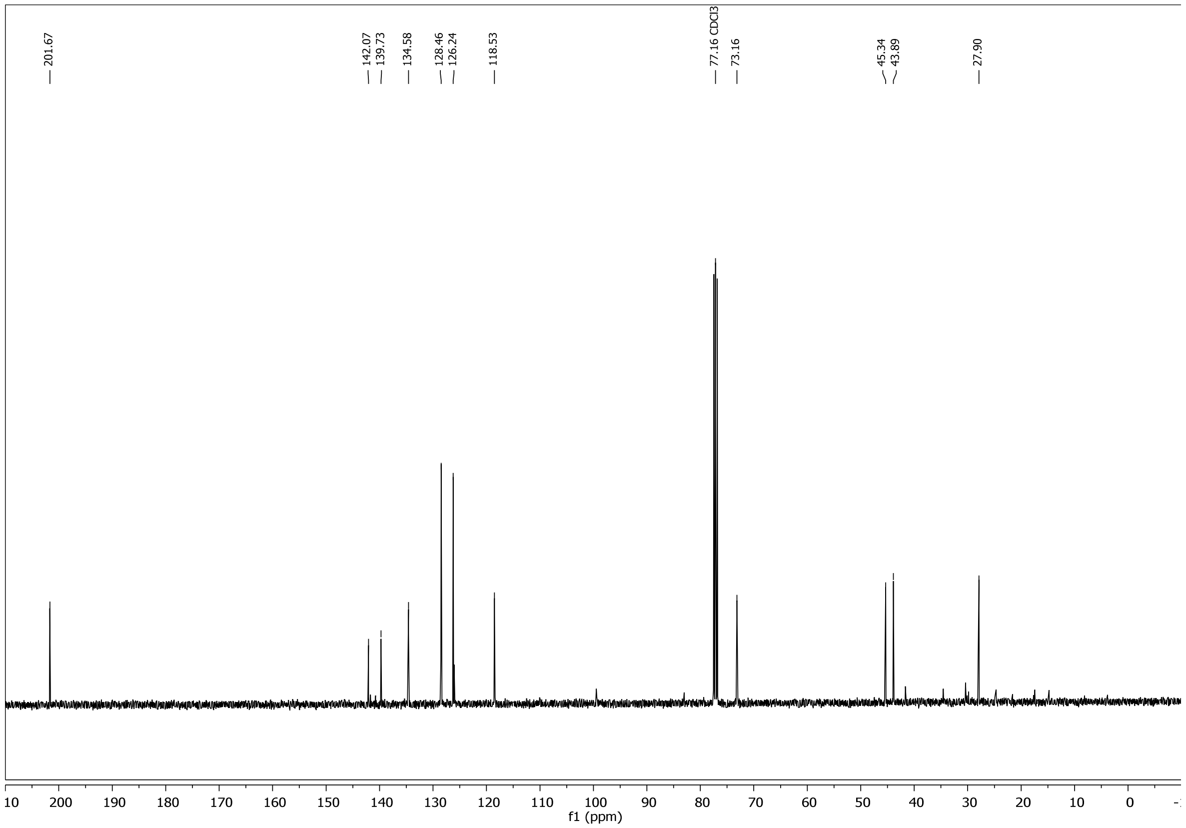
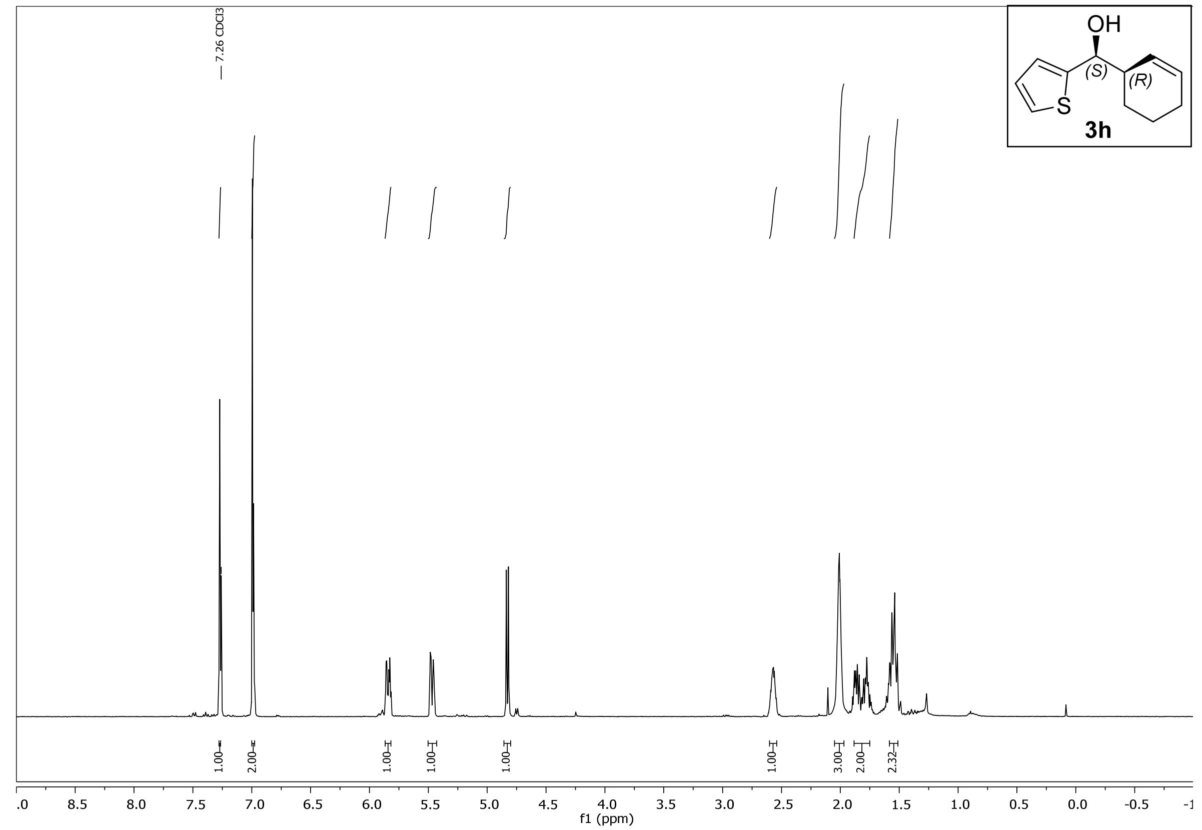
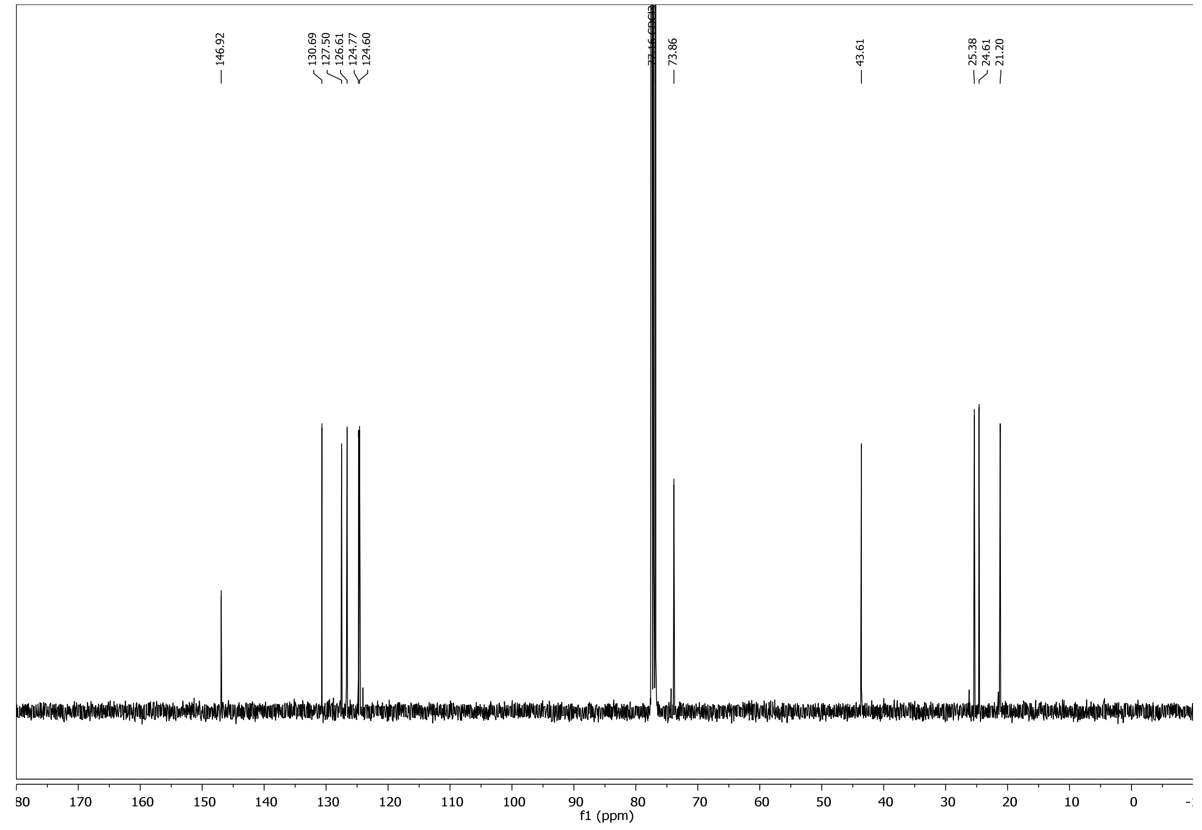
[1] NMR-studies revealed, that the product is degrading during purification. Hence, no clean NMR of the product could be obtained. The additional signals between 0.5 and 2.2 ppm correspond to degradation products.

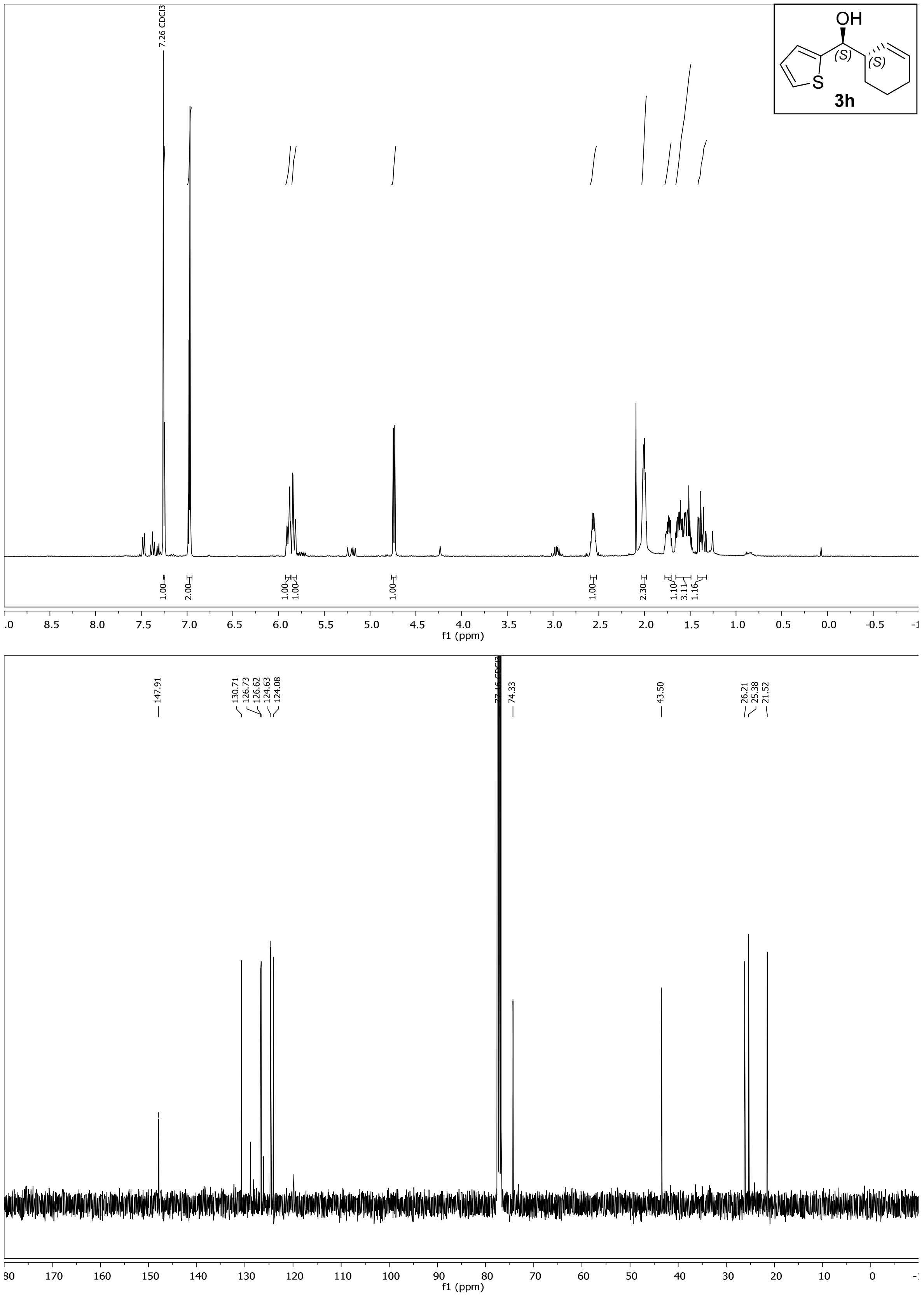

201.67
142.07
139.73
134.58
128.46
126.24
118.53
77.16 CDCl3
73.16
45.34
43.89
27.90
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

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

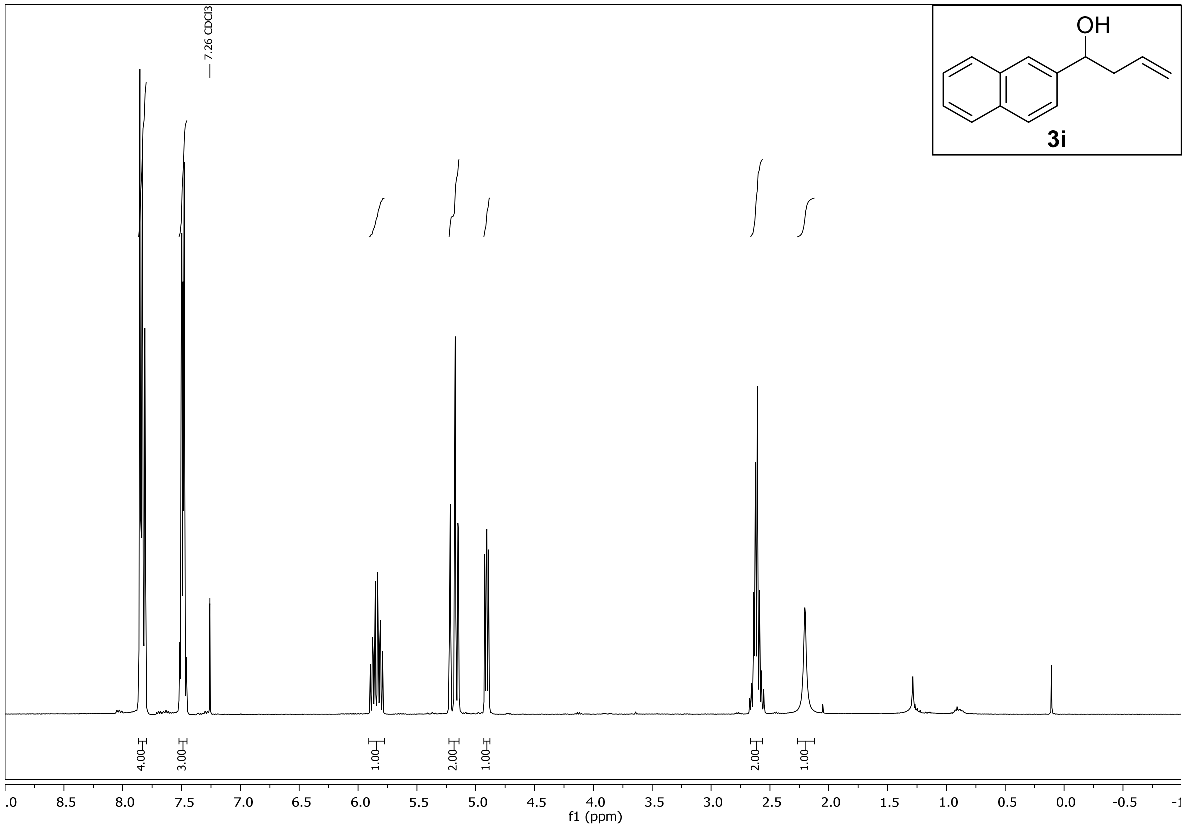


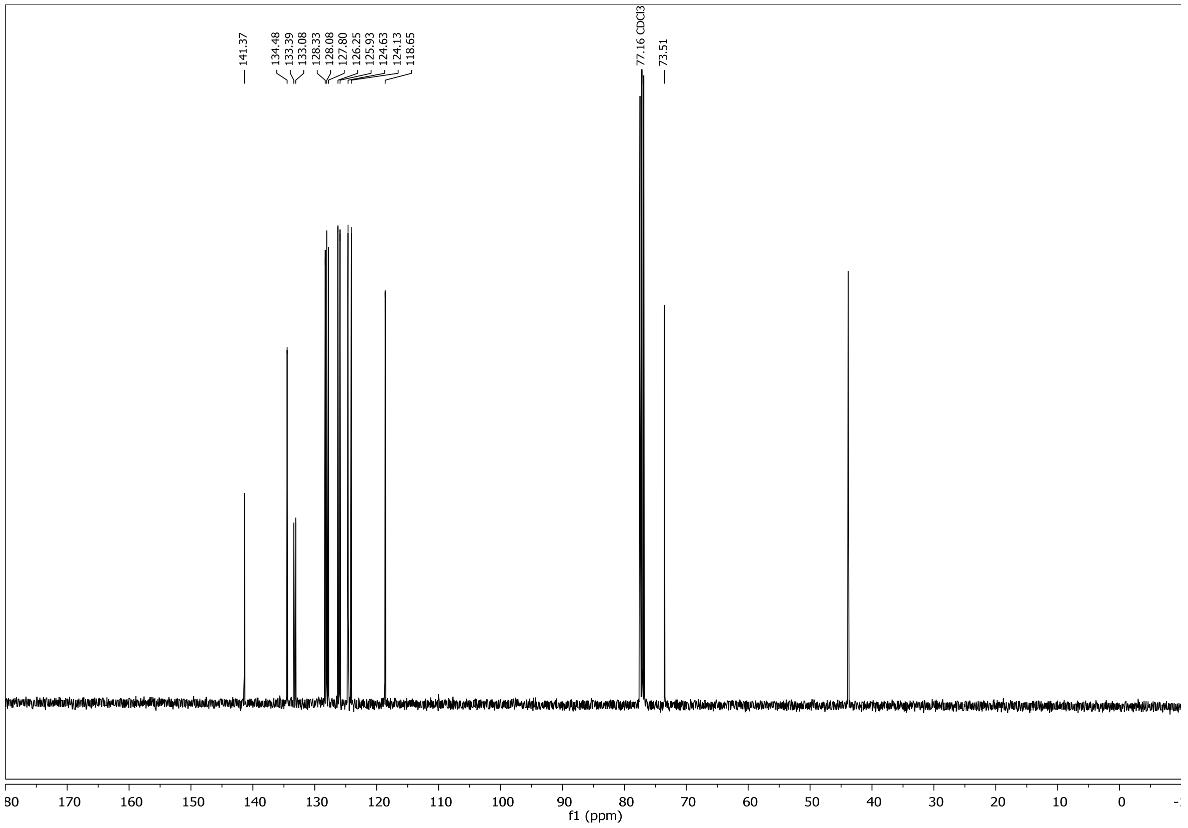


Compound **3h** syn, ^{1}H- and ^{13}C-NMR (CDCl$_3$)

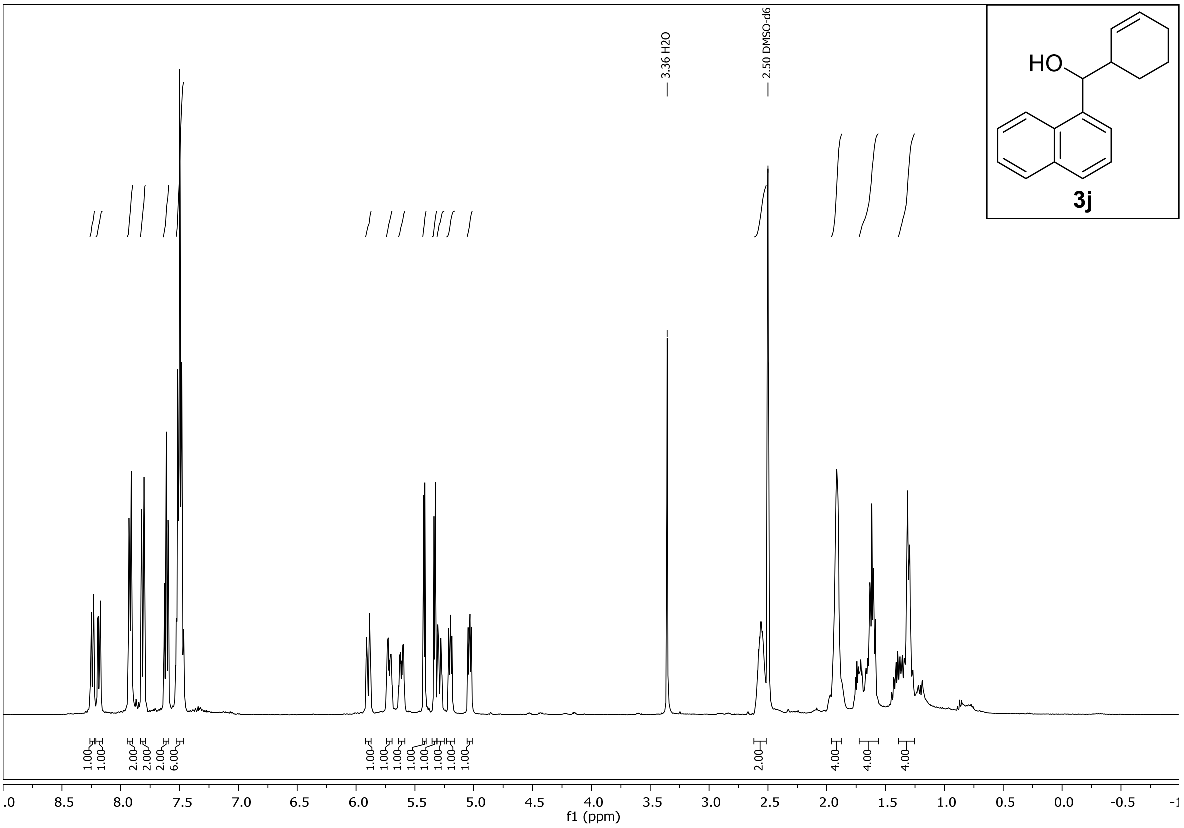


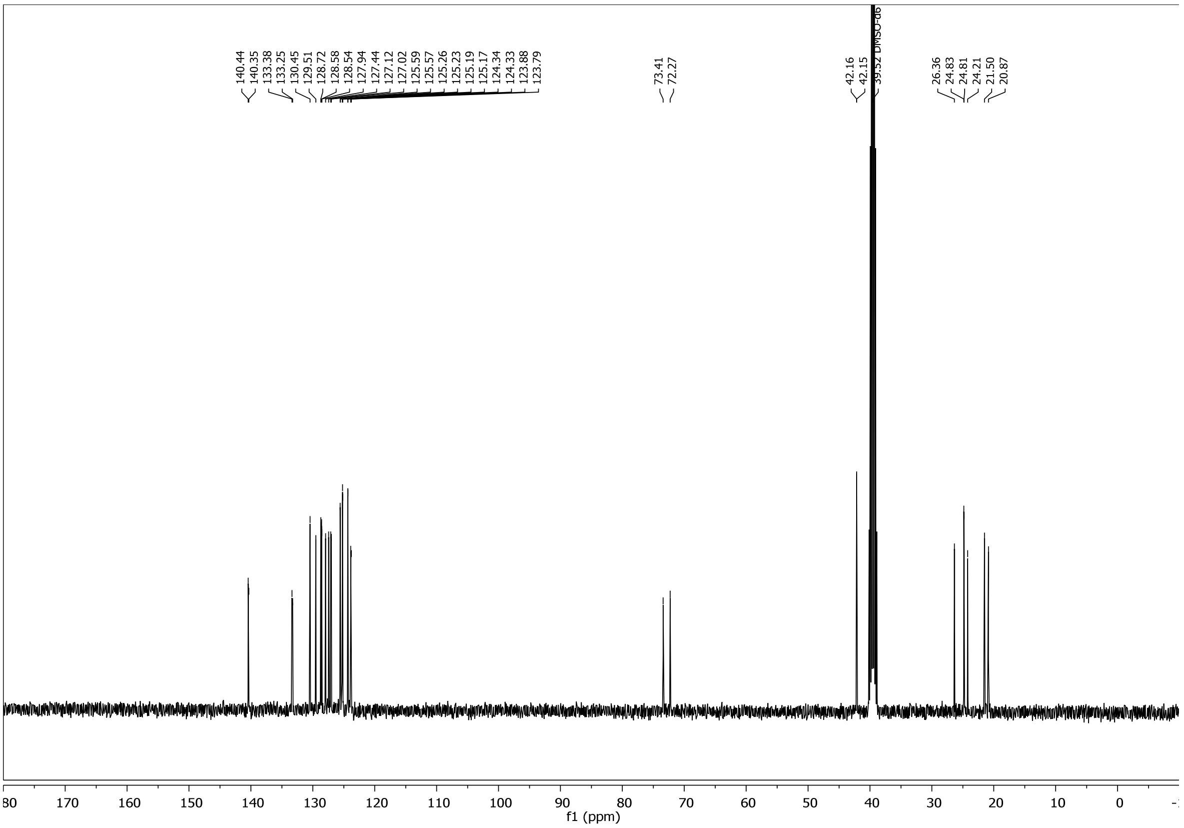
Compound **3i**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



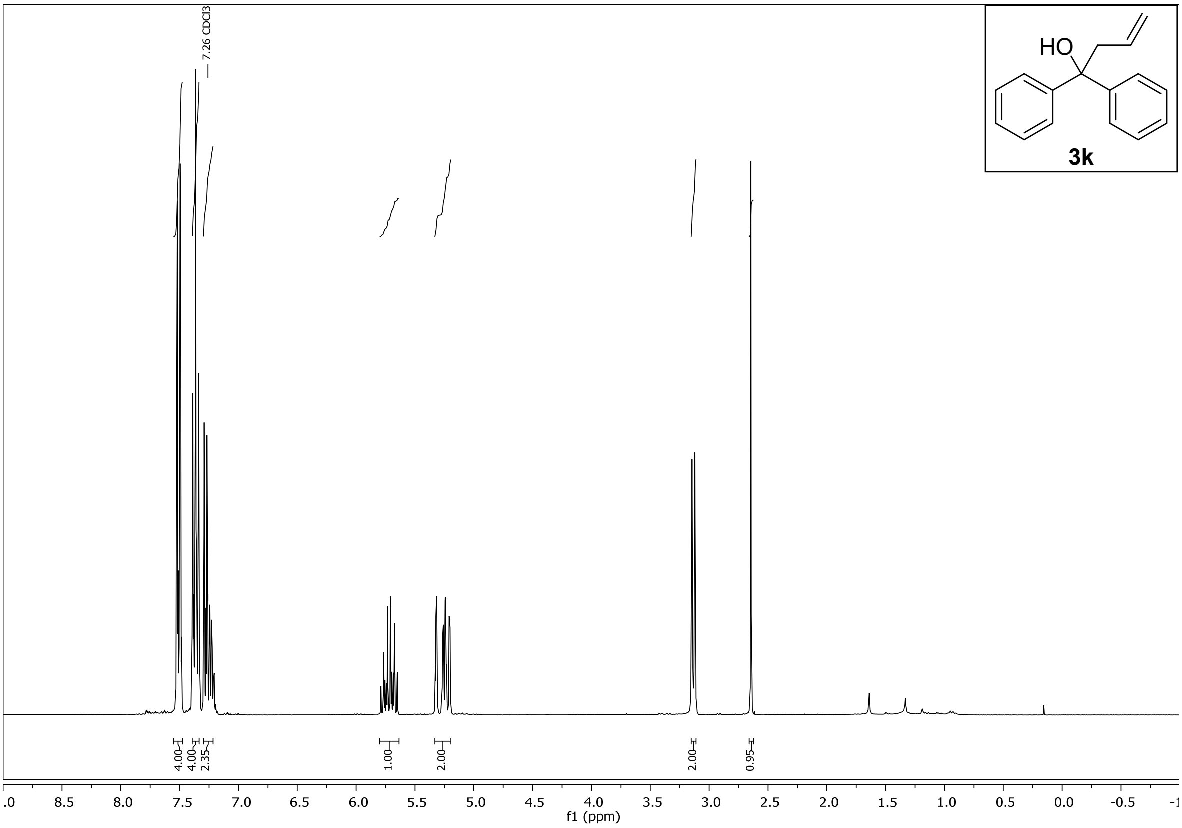


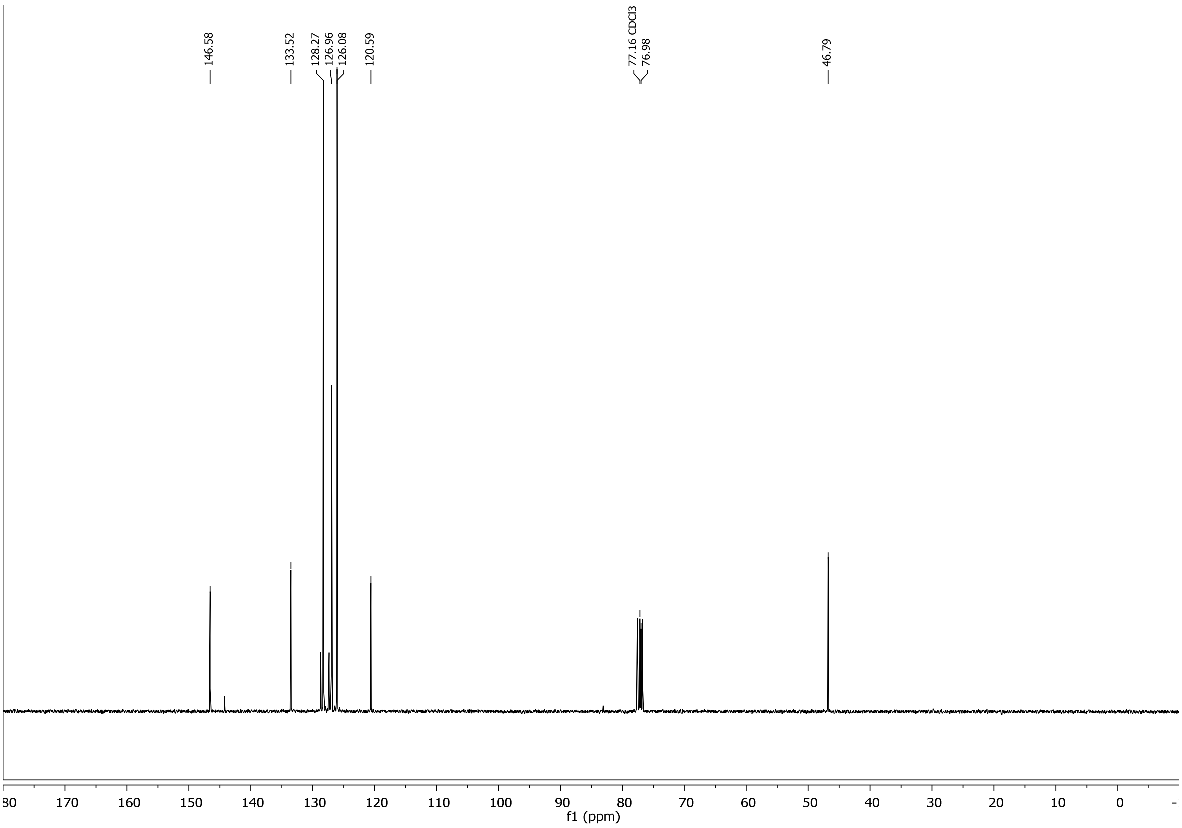
Compound **3j**, ^{1}H- and ^{13}C-NMR (DMSO-d_6)



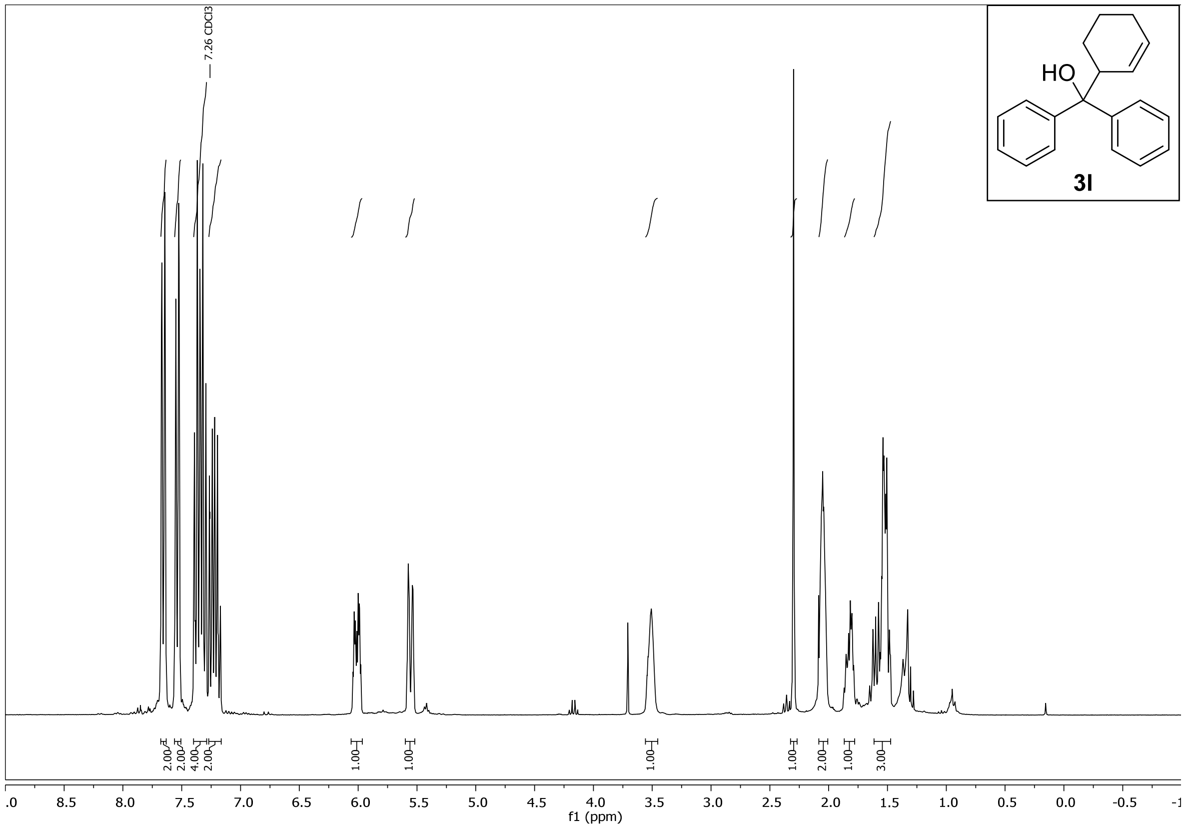


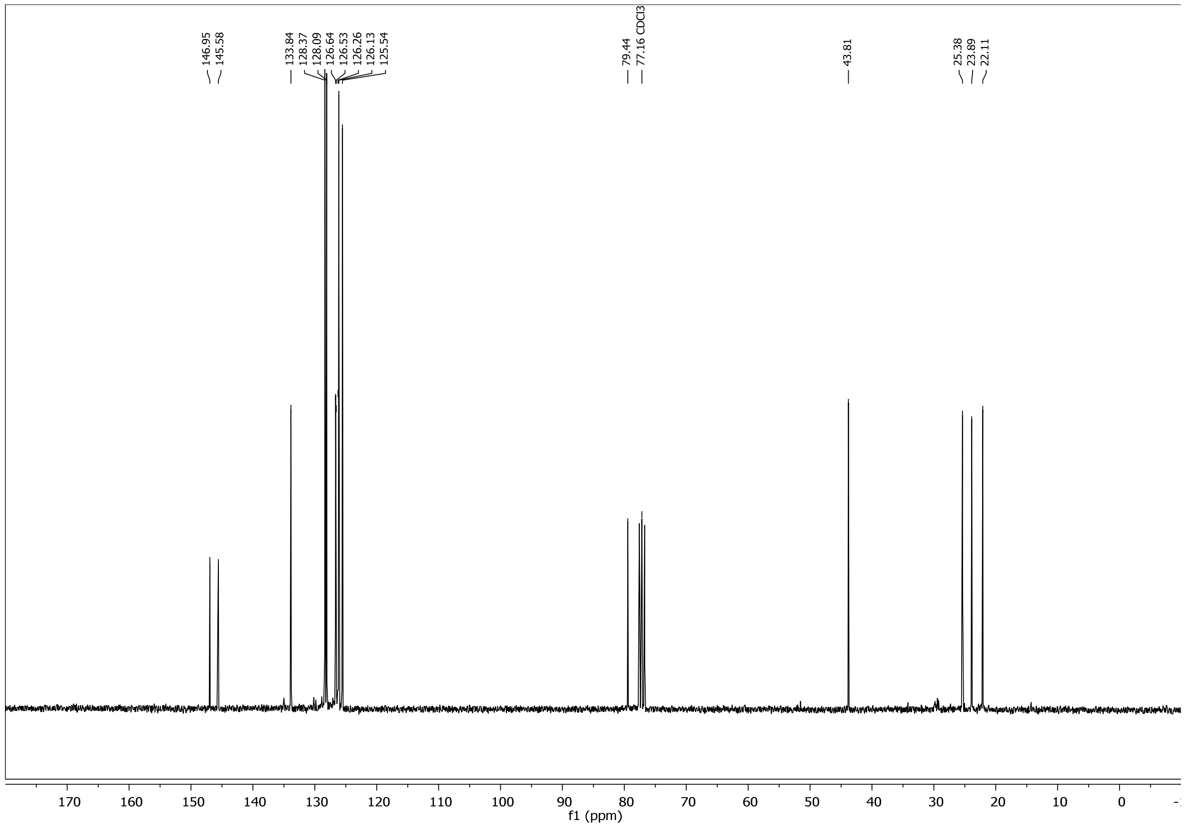
Compound **3k**, ^{1}H- and ^{13}C-NMR (CDCl$_3$)



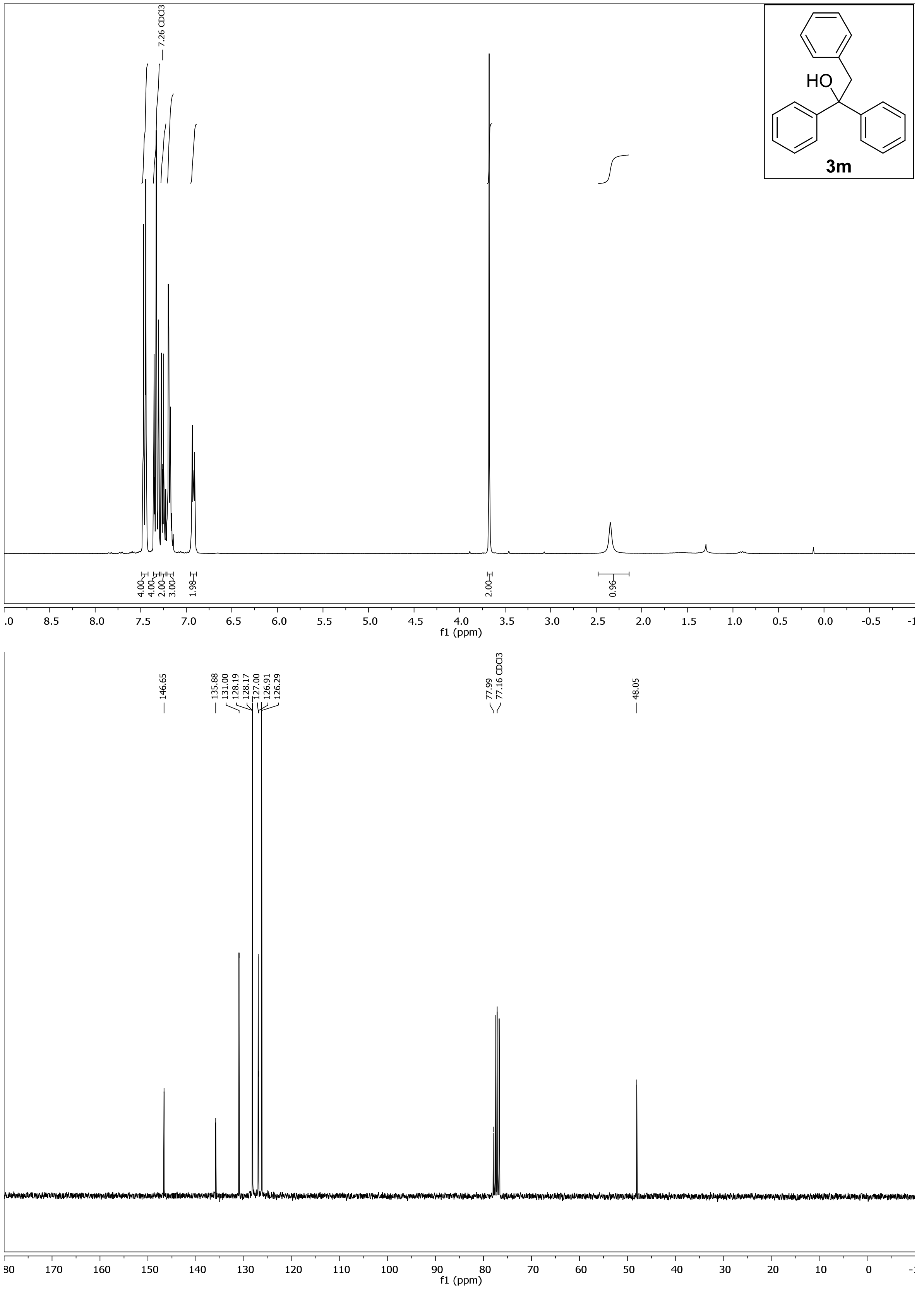


Compound **3l**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)

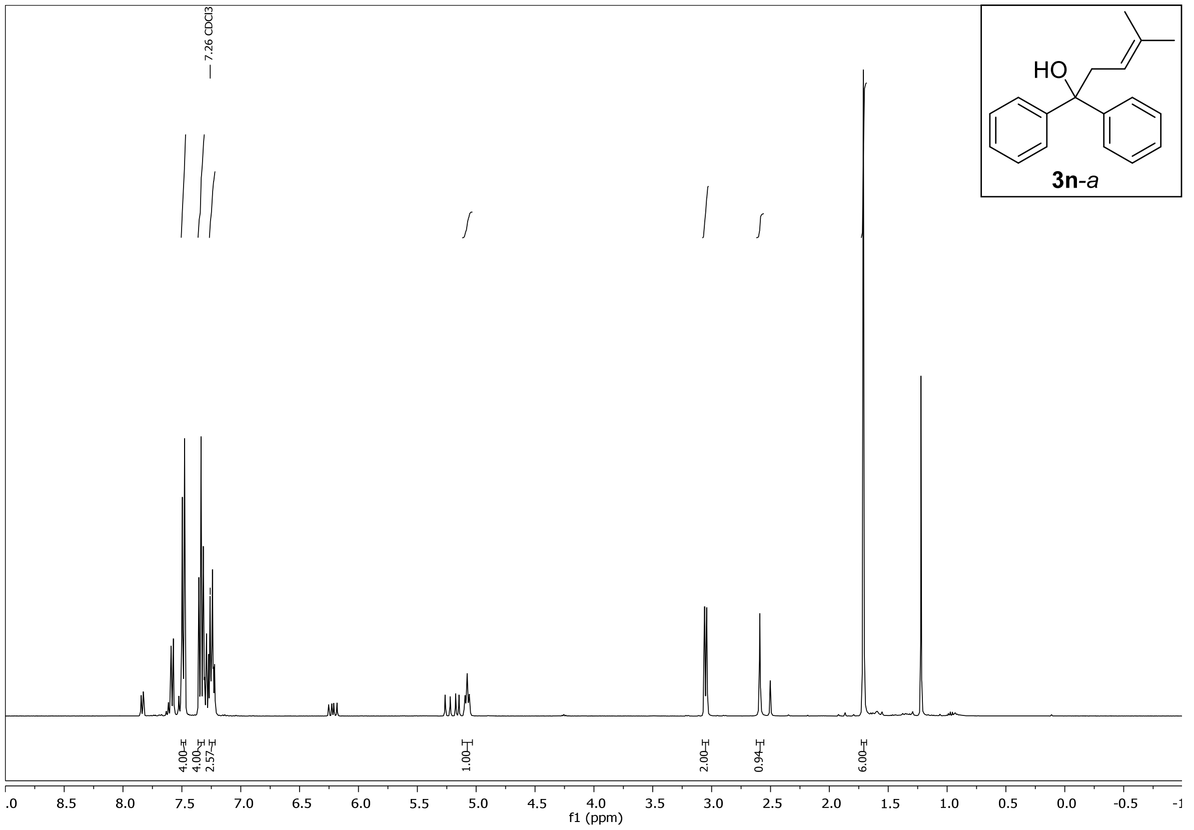


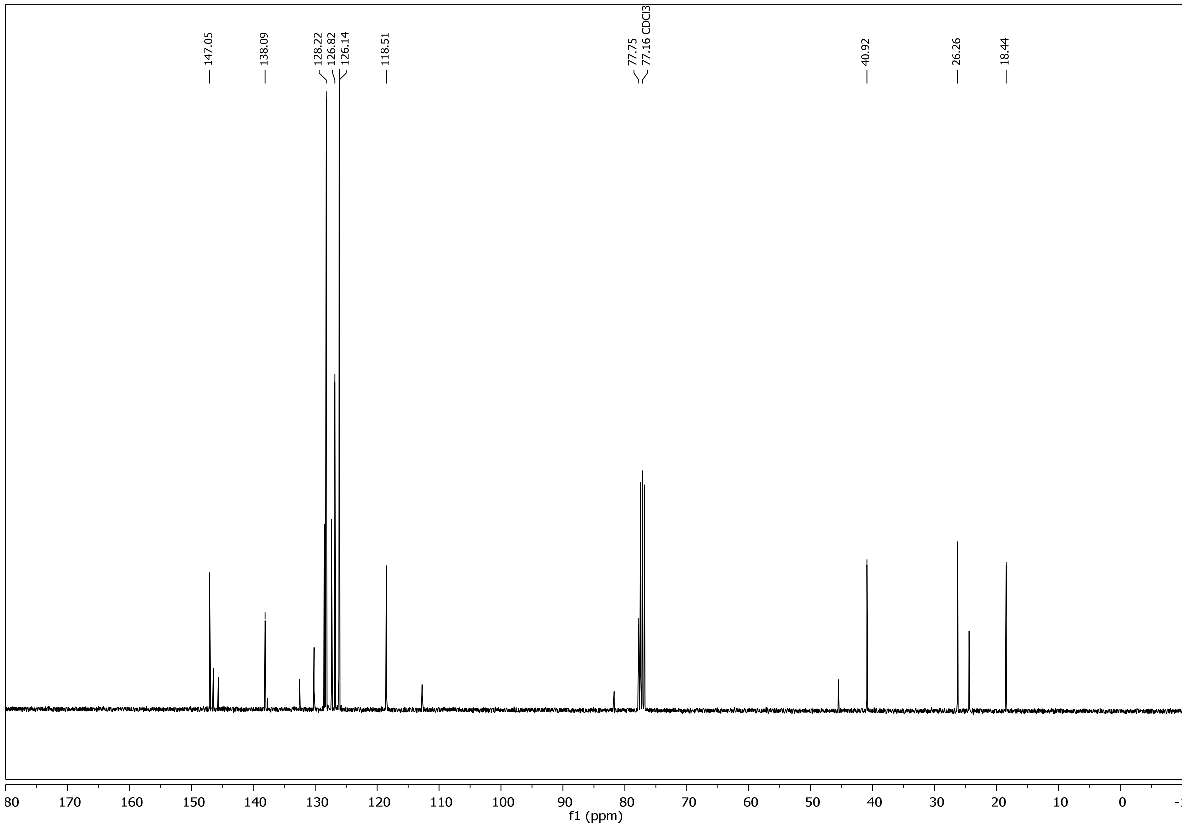


Compound **3m**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)

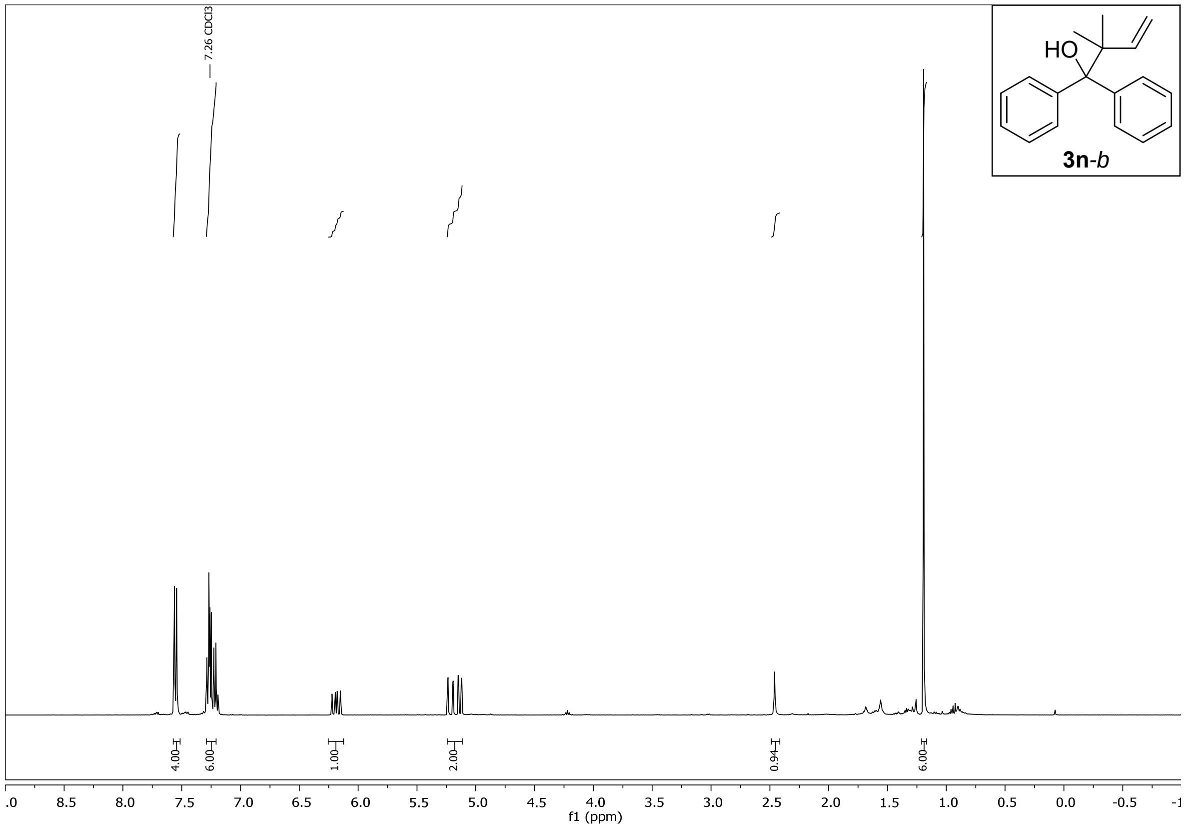


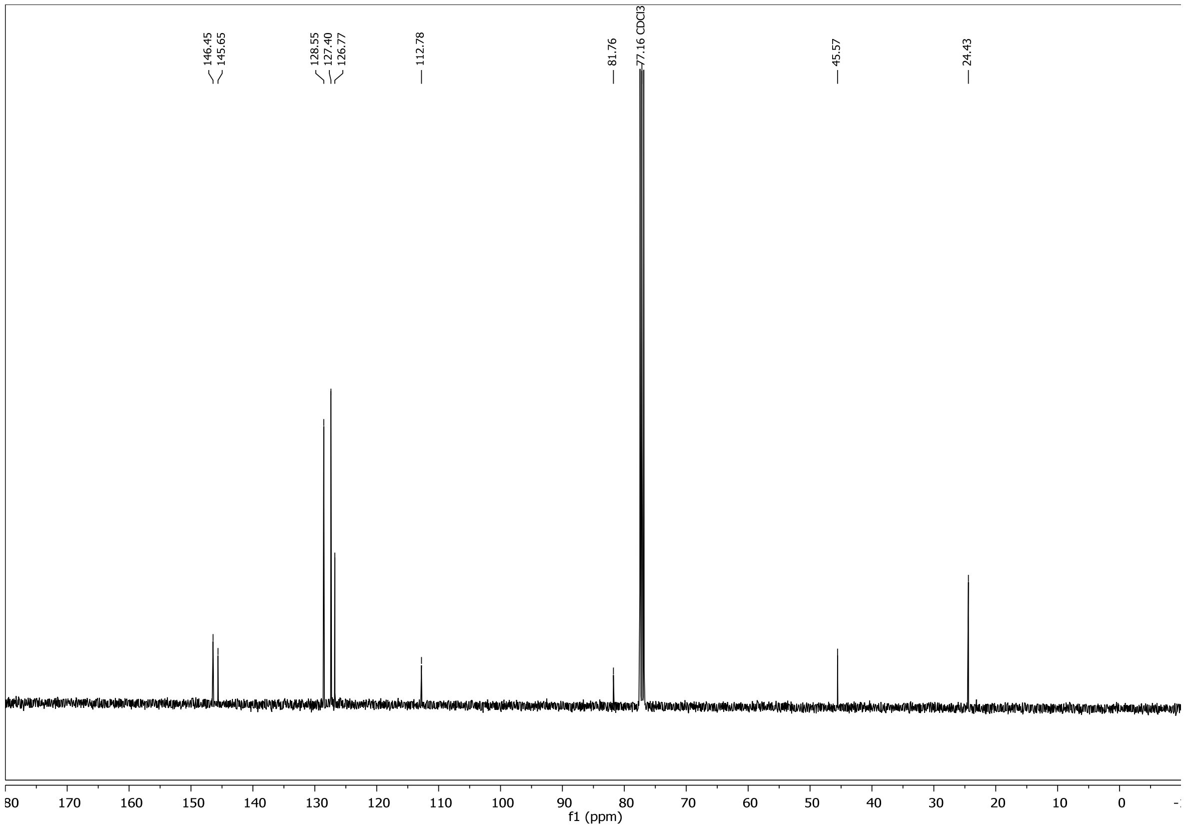
Compound **3n**-*a*, ^{1}H- and ^{13}C-NMR (CDCl$_3$)



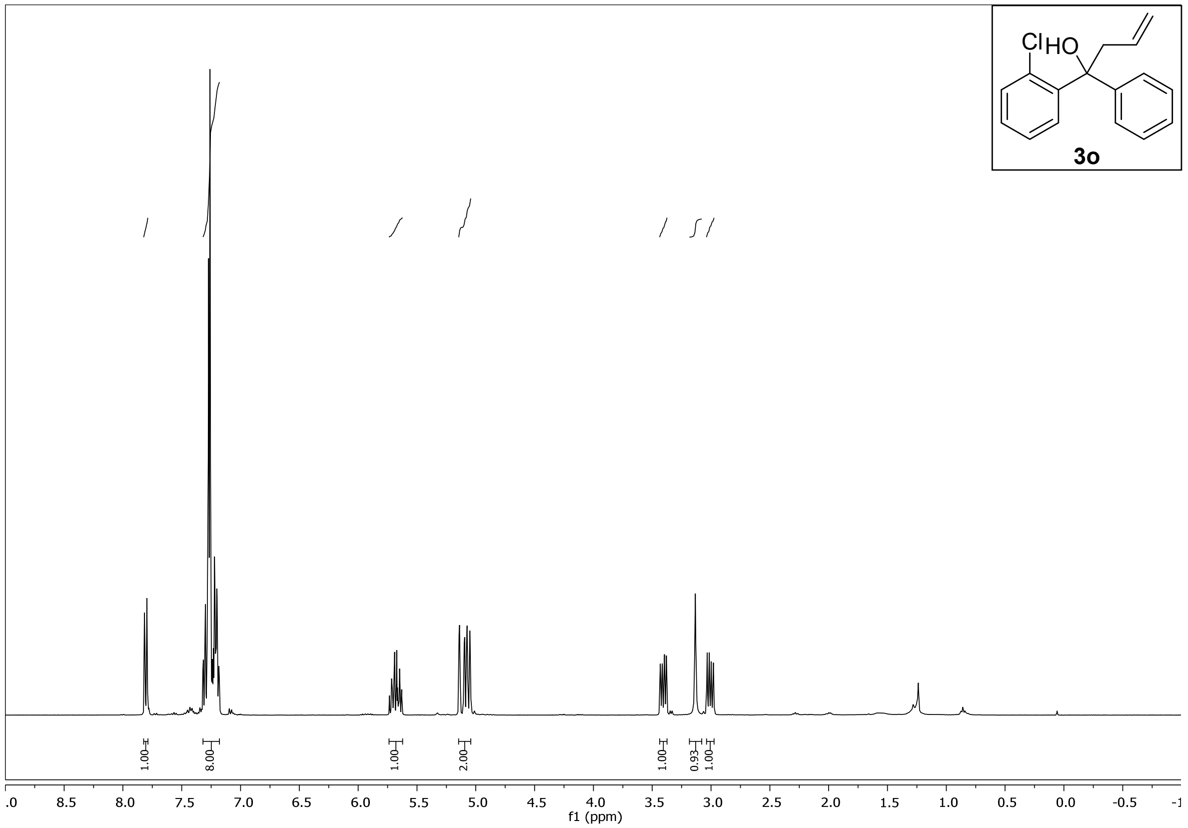


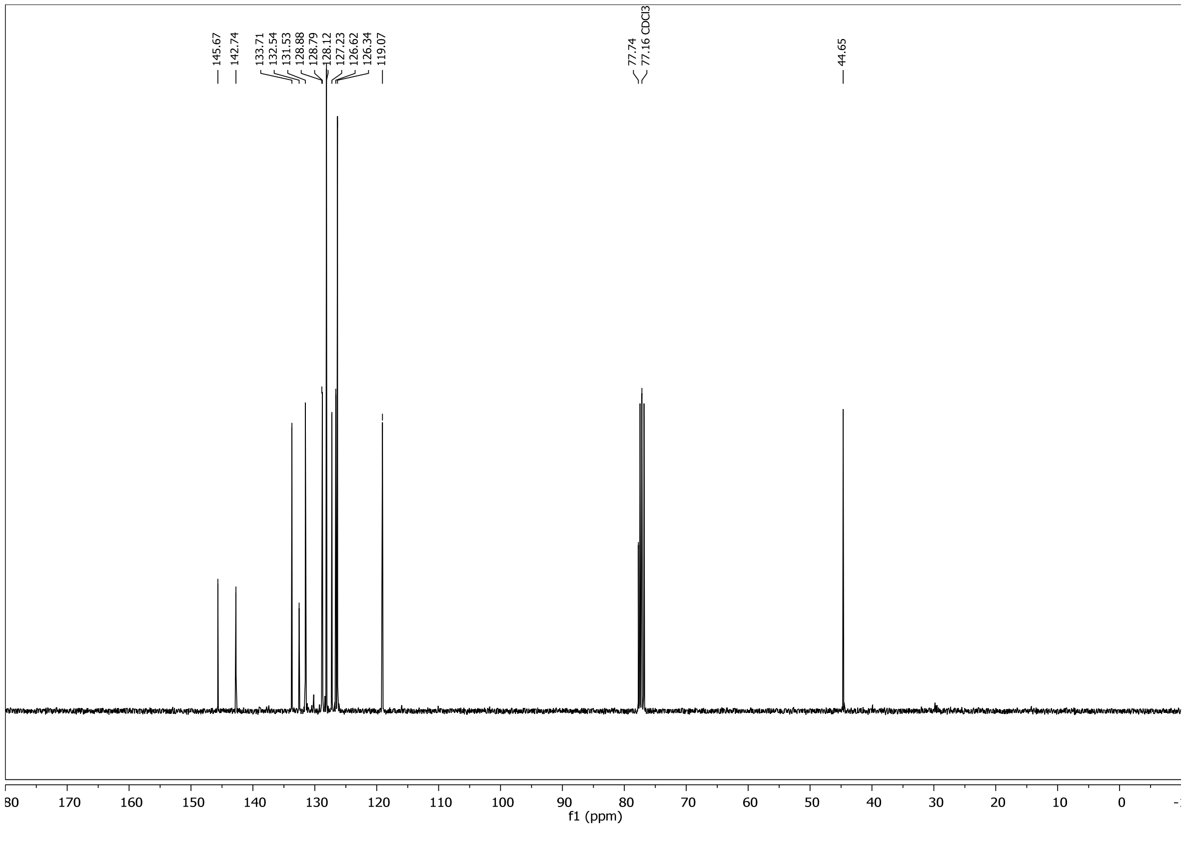
Compound **3n**-*b*, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



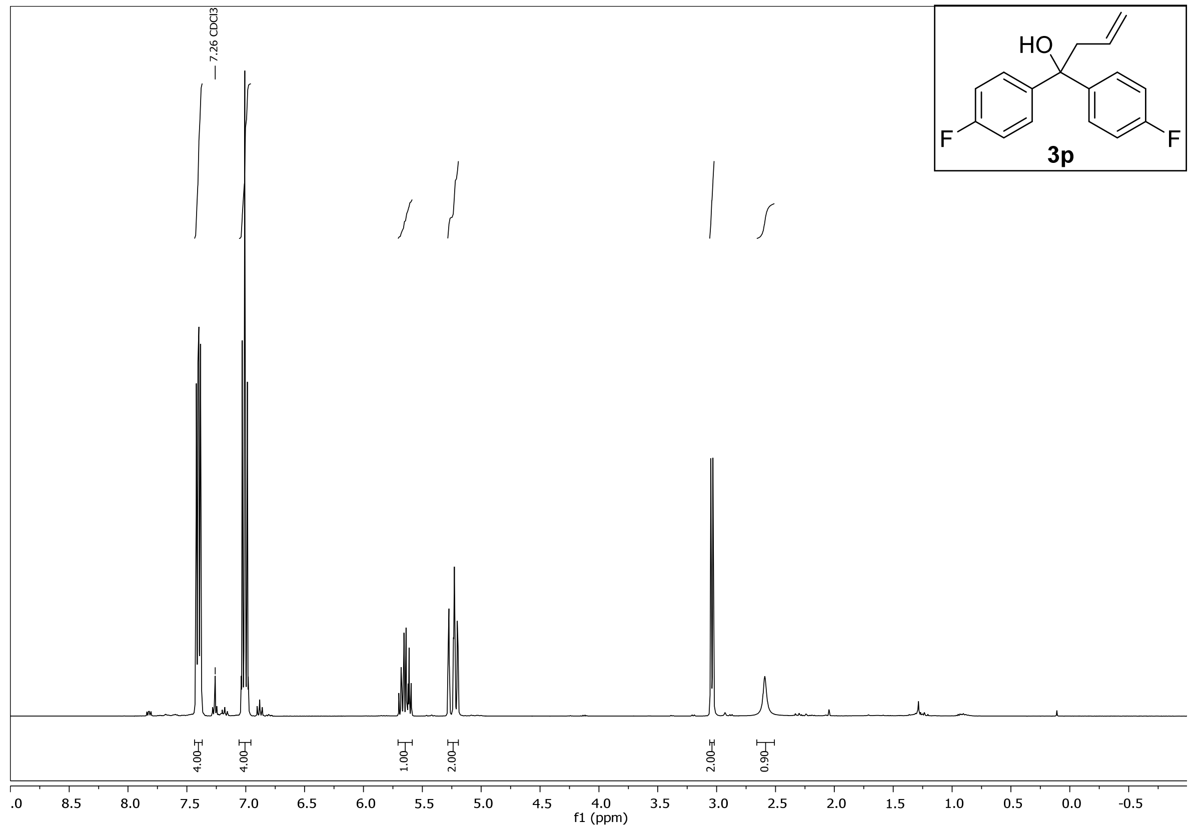


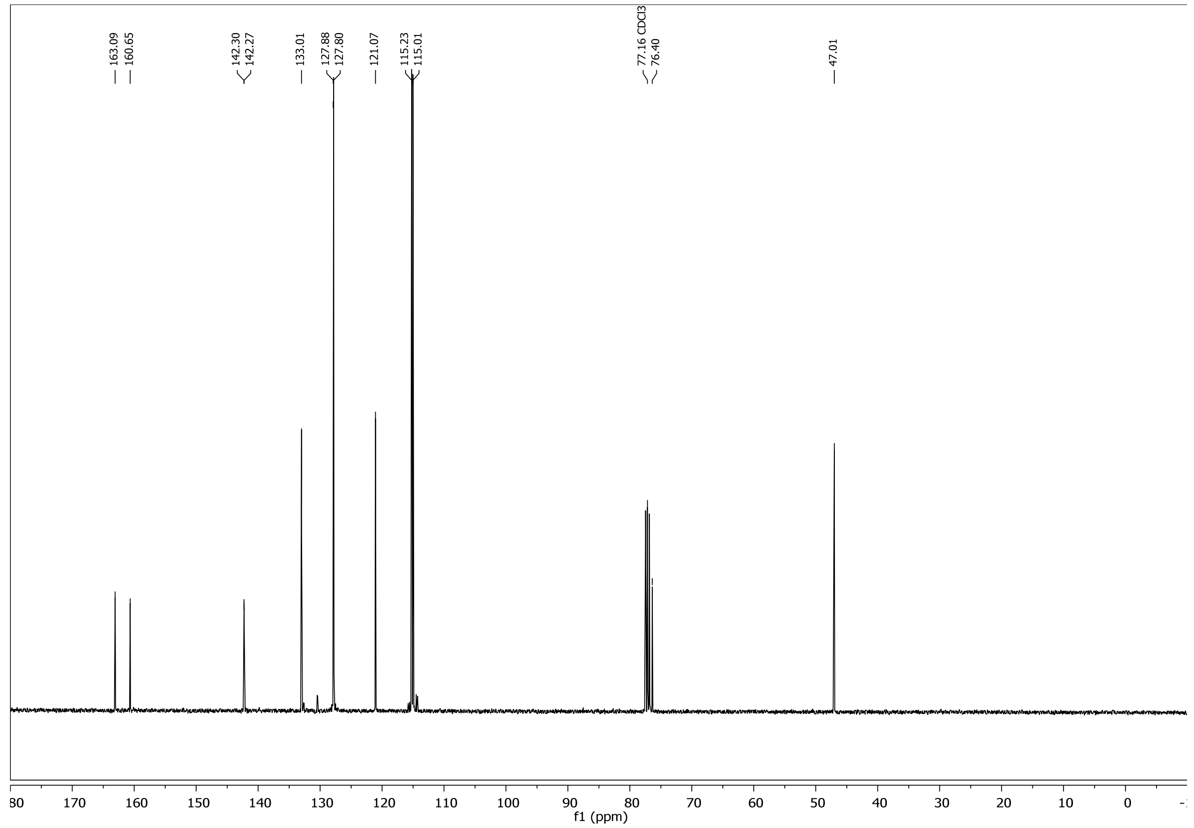
Compound **3o**, ^{1}H- and ^{13}C-NMR (CDCl$_3$)

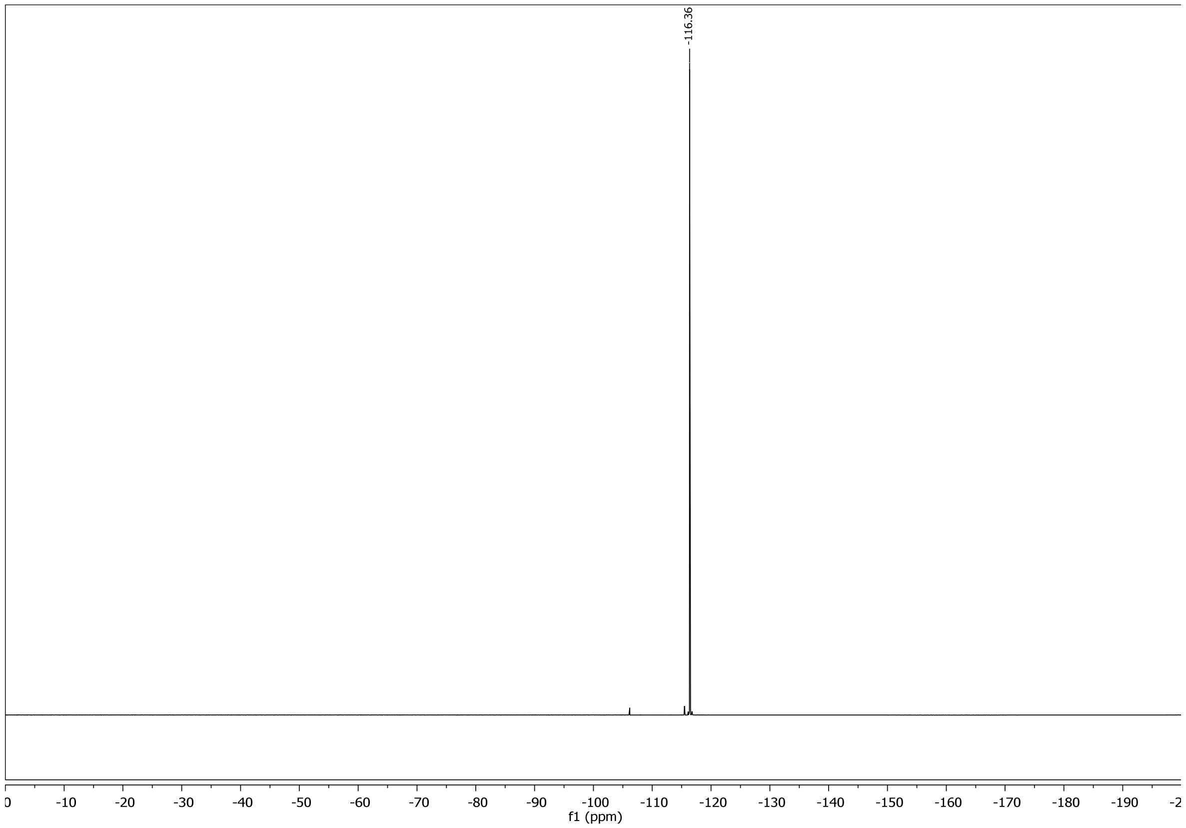




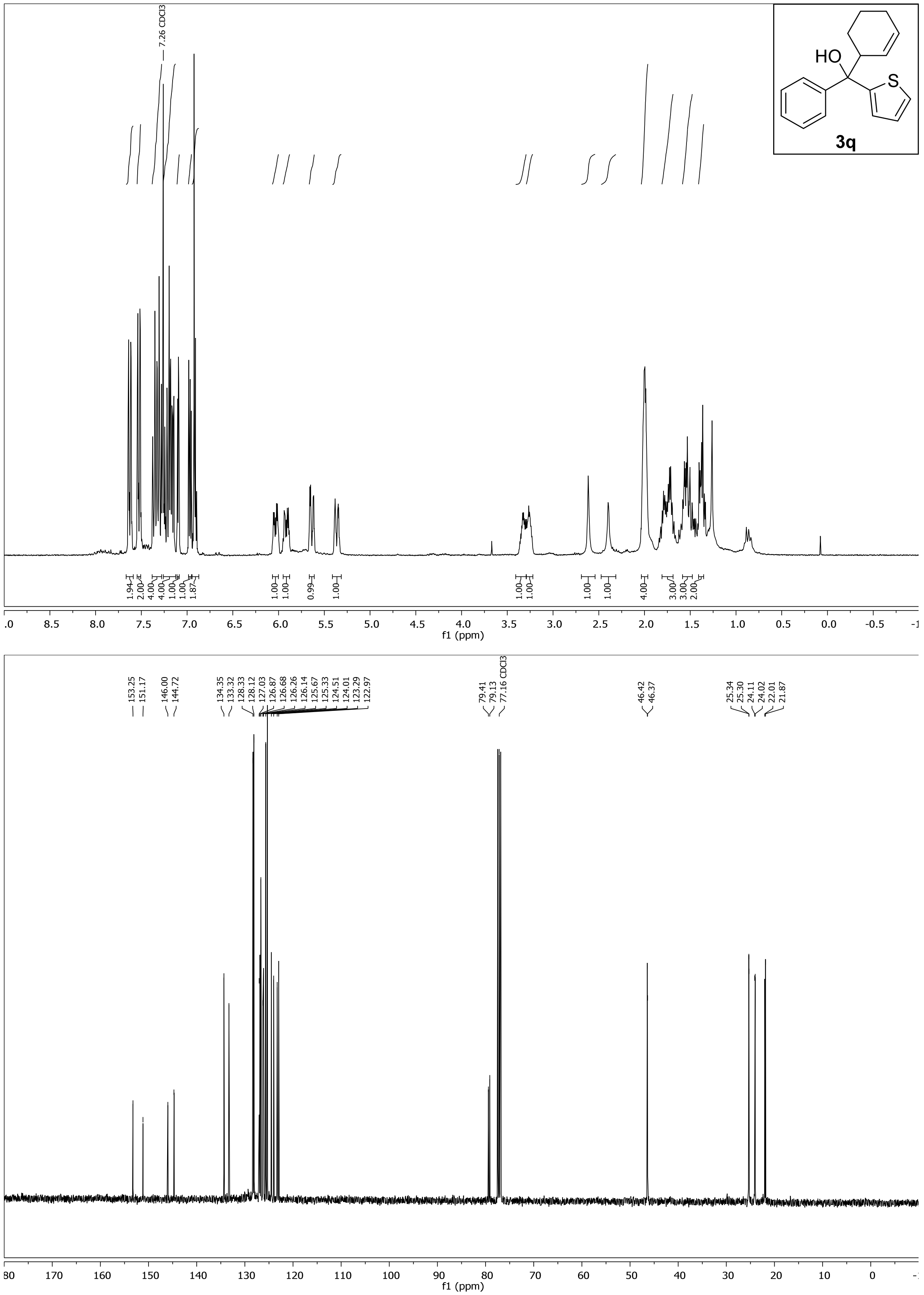
Compound **3p**, ^{1}H-, ^{13}C and ^{19}F-NMR (CDCl$_3$)



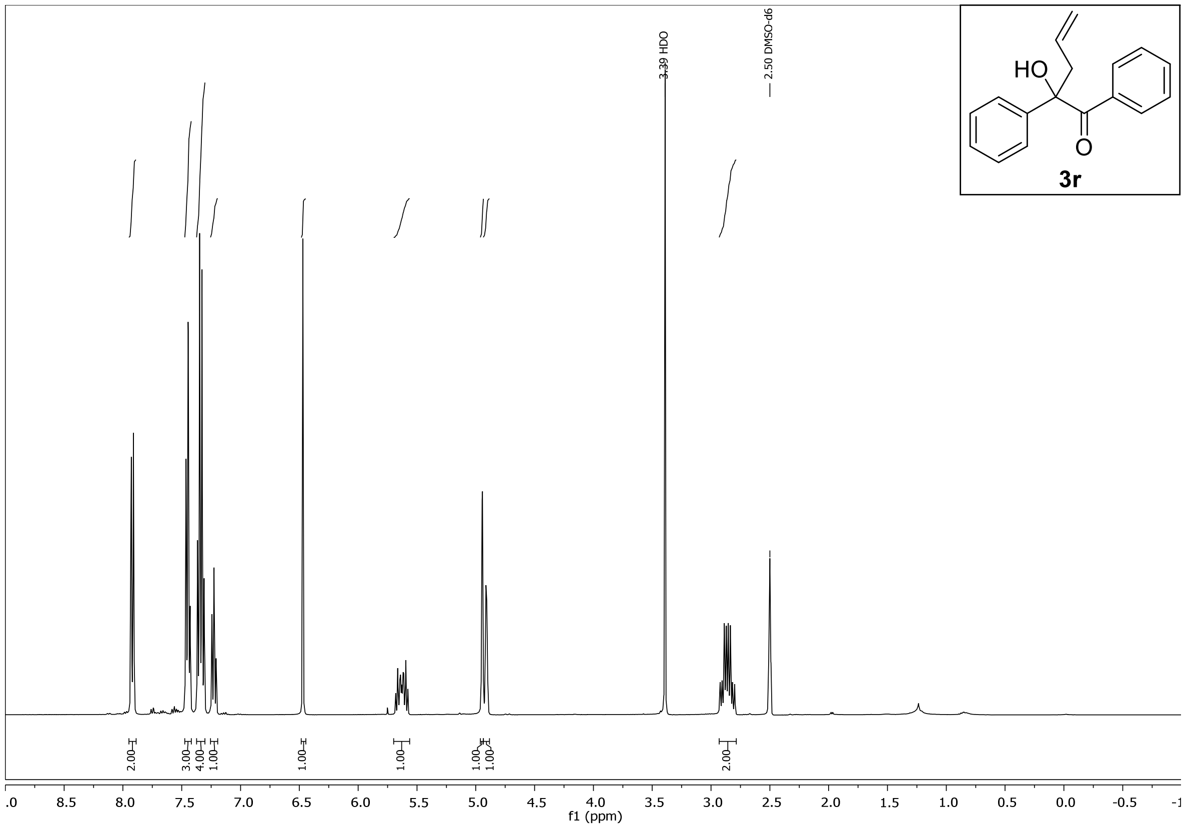


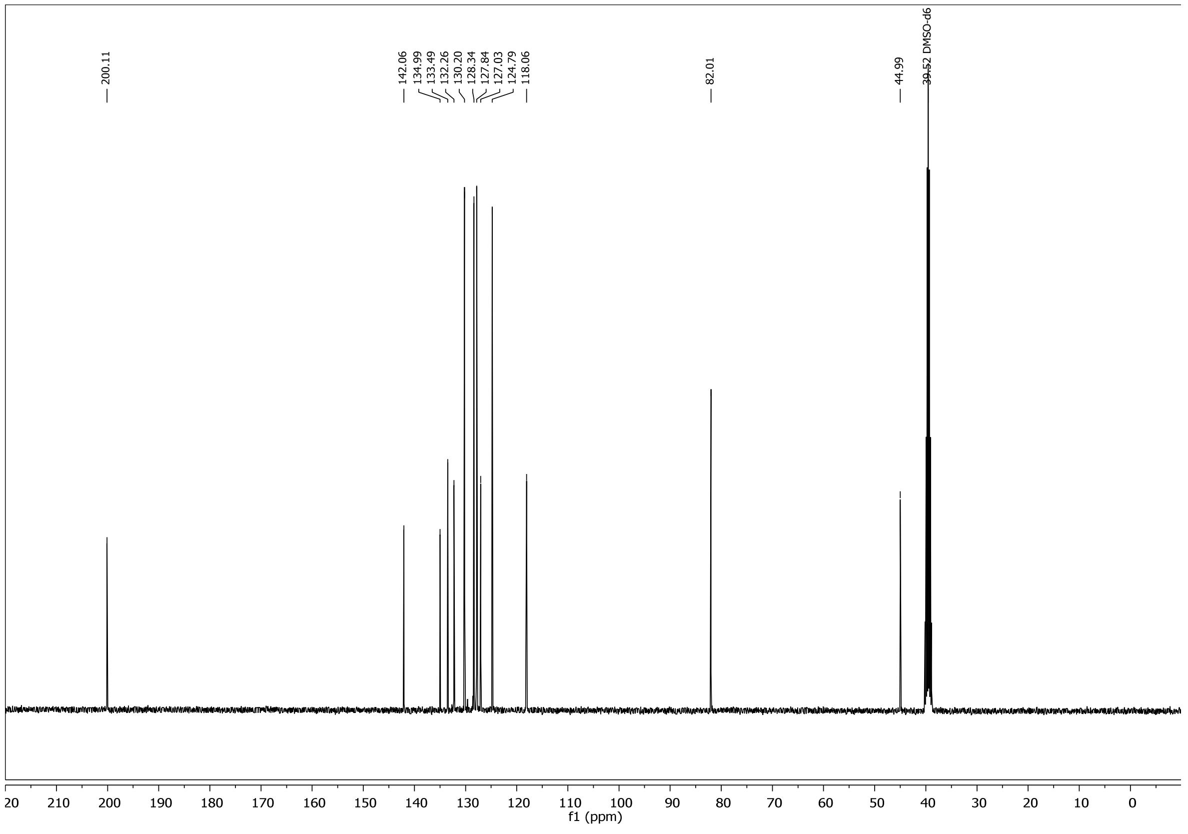

-116.36
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

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

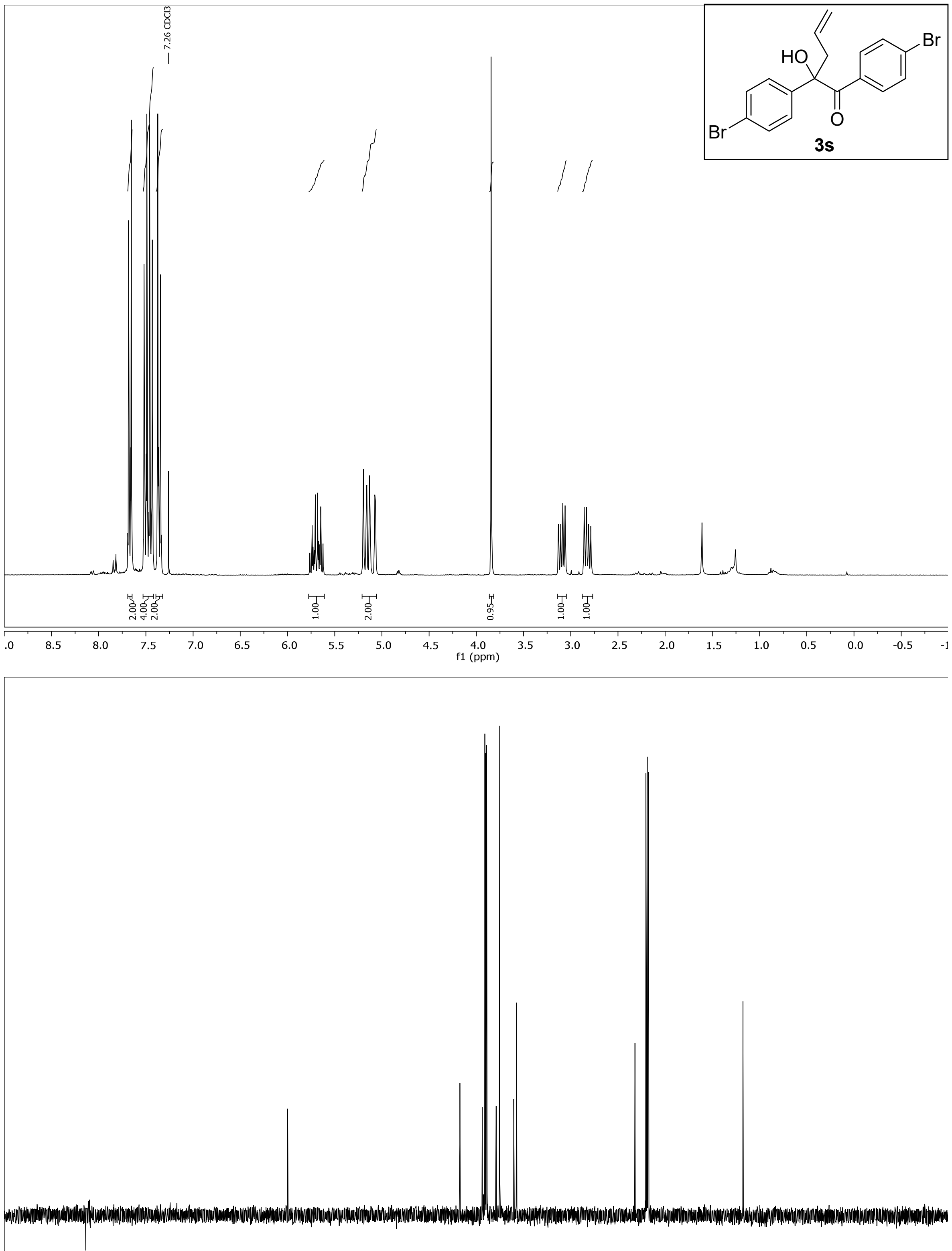


Compound **3r**, ^{1}H- and ^{13}C-NMR (DMSO-d_6)

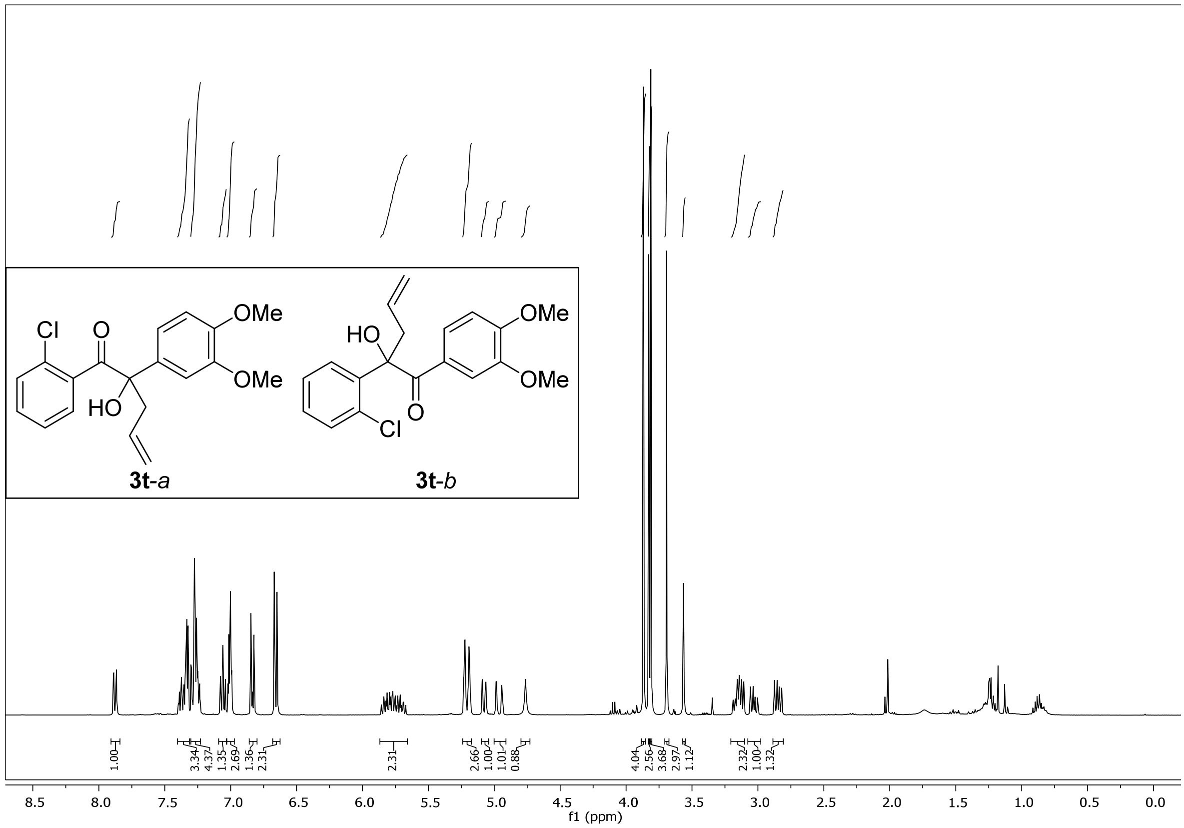


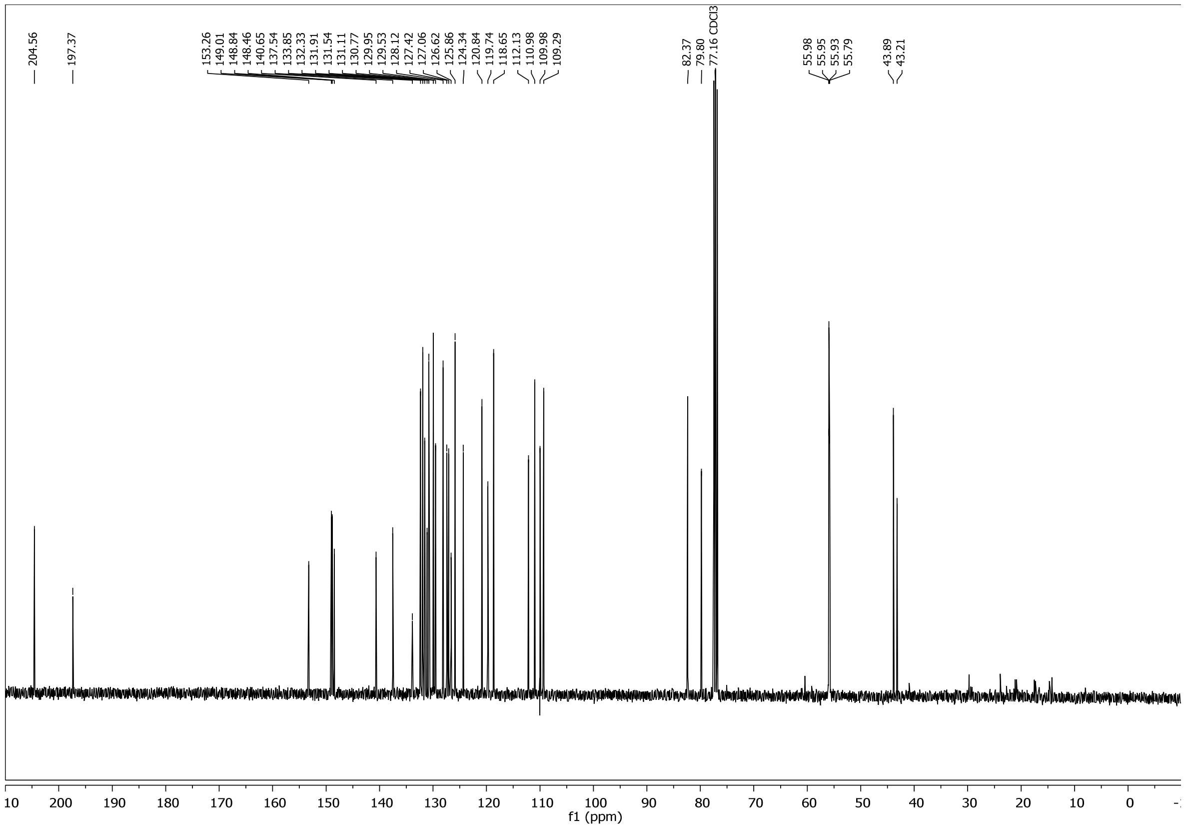


Compound **3s**, ^{1}H- and ^{13}C-NMR (CDCl$_3$)

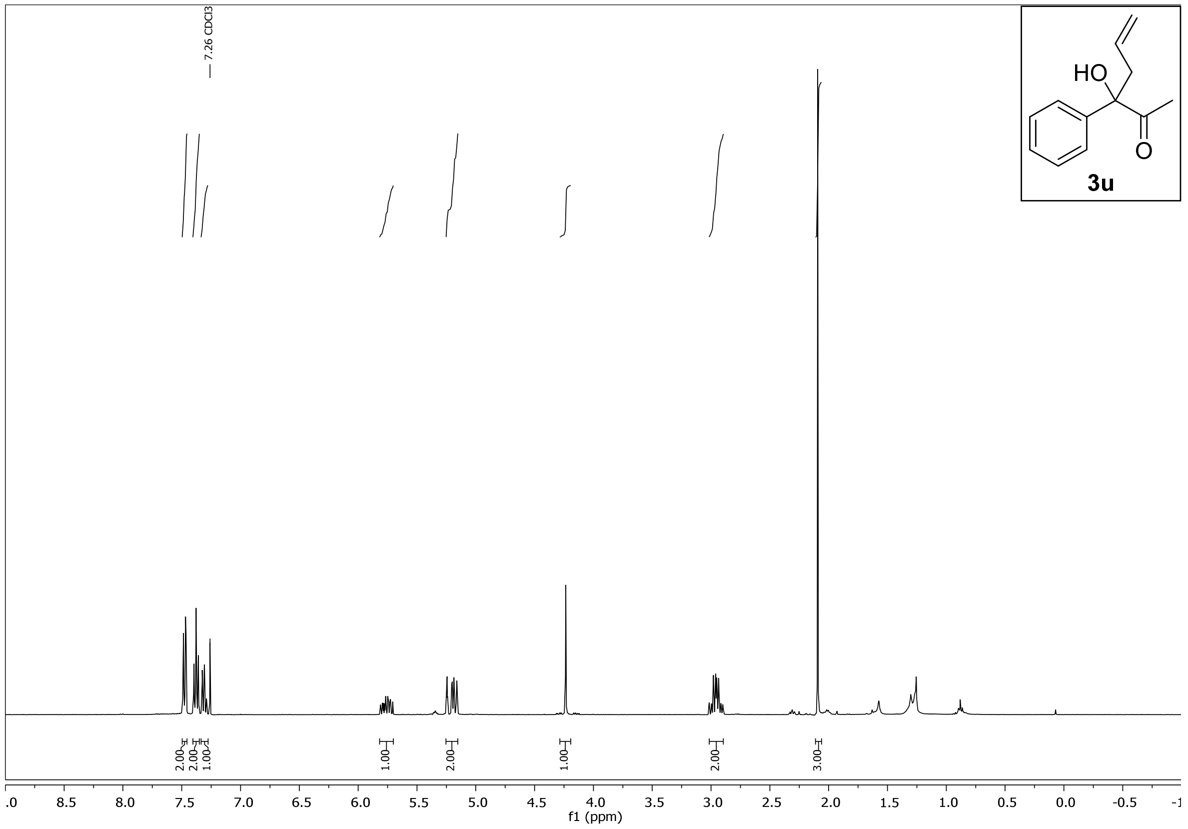


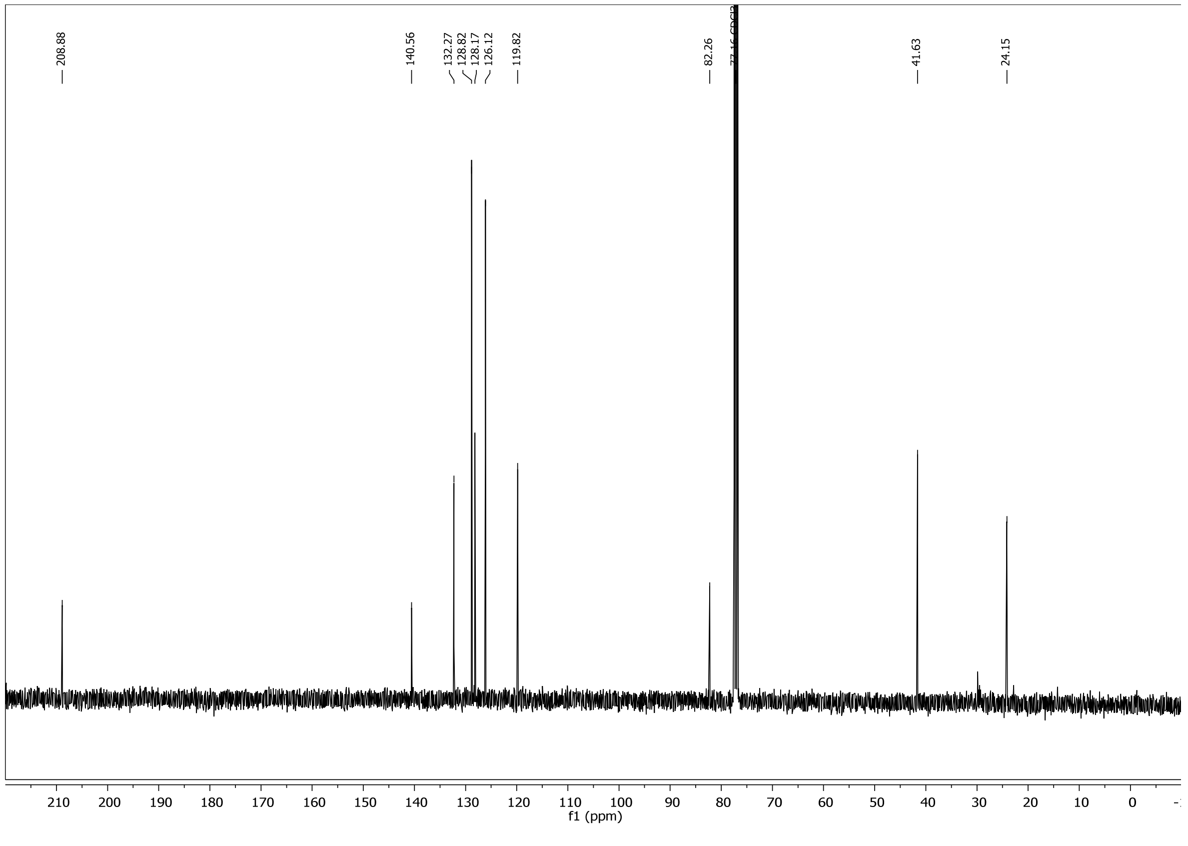
Compound **3t**-*a* and compound **3t**-*b*, ^{1}H- and ^{13}C-NMR ($CDCl_3$)



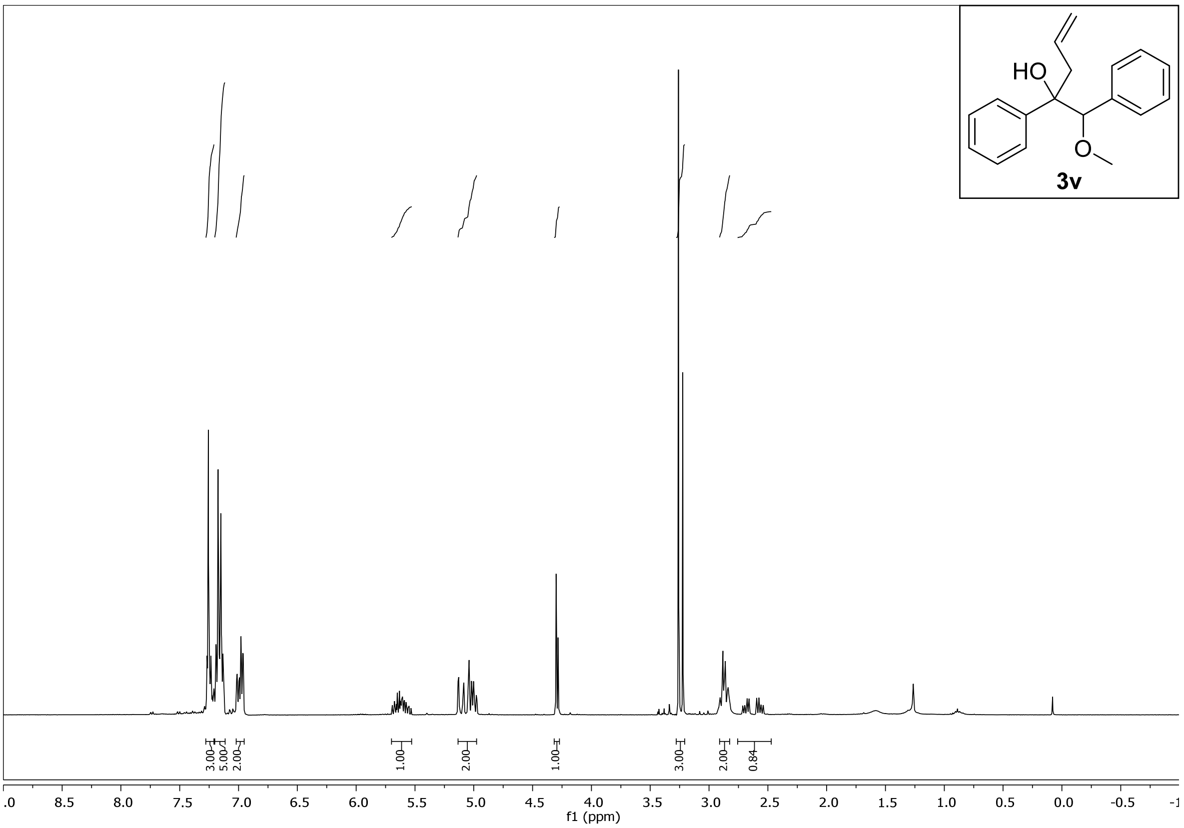


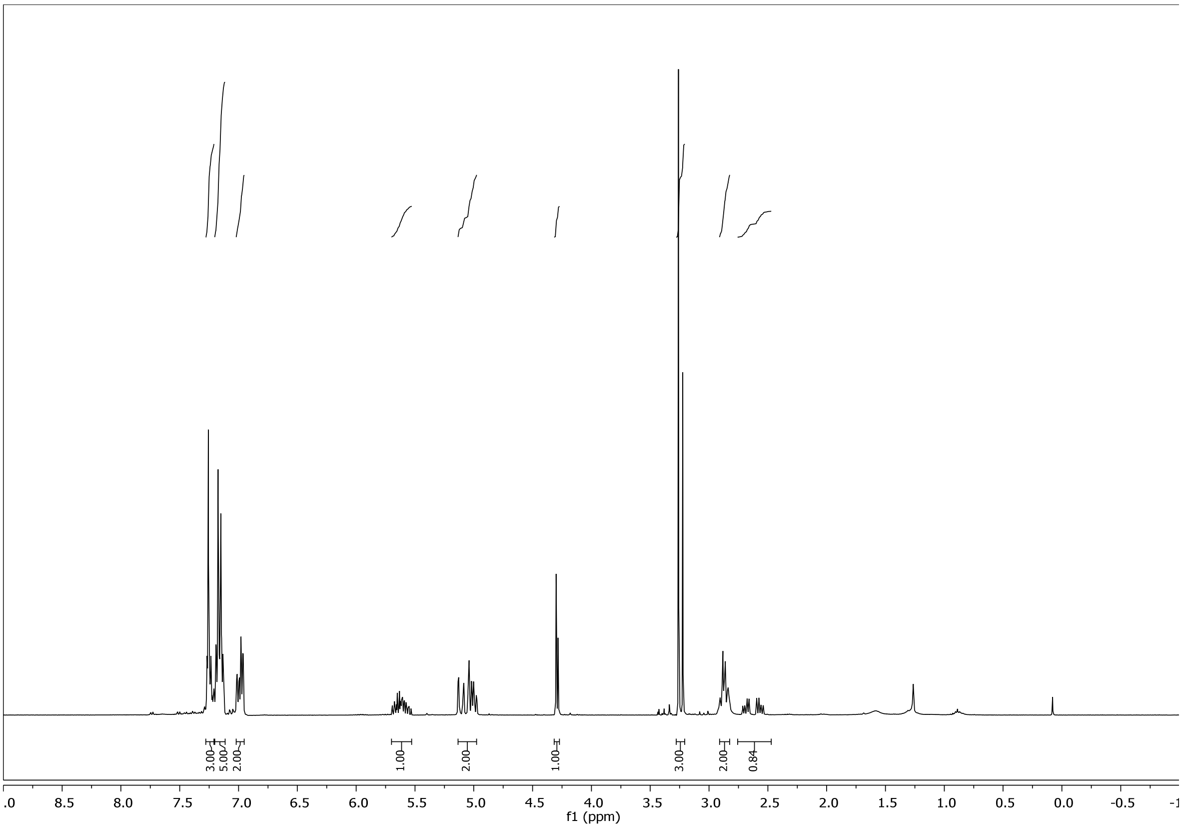
Compound **3u**, ^{1}H- and ^{13}C-NMR ($CDCl_3$)





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





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